Electronic Supplementary Material (ESI) for ChemComm.

Synthesis of Complex Aryl MIDA Boronates by Rh-Catalyzed [2+2+2] Cycloaddition

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Supporting Information

Contents

1. General

Reagents and solvents were obtained from commercial suppliers and were not purified further unless specified. Purification (where specified) was performed following the standard procedures.[1] Dry solvents (THF, CH_2Cl_2) were provided by a PureSolv SPS-400-5 solvent purification system.

Reactions were carried out in standard borosilicate glassware or 2 mL microwave vials with septum caps. Glassware was either flame-dried under vacuum or allowed to dry in a 180 ºC oven for 24 h before use and then sparged with nitrogen. Room temperature was approximately 18 °C. Reactions at high temperature were heated using a DrySyn metal heating baths or a silicone oil bath. Reactions at 0 °C were performed using and ice/water bath, −5 °C reaction temperatures were achieved with ice/brine mixture, and −78 °C was using dry ice/acetone baths. Degassing was performed by the freeze-pump-thaw technique over three cycles. Additions over times greater than 1 h were performed using either a kdScientific 200 or a World Precision Instruments Aladdin-220 syringe pump.

TLC was carried out using Merck aluminium-backed silica plates coated with F_{254} fluorescent indicator, analysed under UV light and developed using aqueous $KMnO_4$ or ethanolic vanillin solutions, where appropriate. Flash column chromatography performed using silica gel (40-62 μm, Fluorochem).

^{1}H, ^{13}C (DEPTQ) and ^{19}F NMR spectra were recorded by either a Bruker AVII 400 (BBFO probe) or AVIII-HD 500 (and AVIII 500 with BBFO+ and Prodigy BBFO probes, respectively) at 400-101-376 MHz or at 500-126-377 MHz, respectively. ^{11}B NMR spectra were recorded on a Bruker AV300 spectrometer at 128 MHz. All spectra were recorded at room temperature with the deuterated solvents used as a lock for spectra and internal reference (*d*-chloroform: ^{1}H, 7.26 ppm; ^{13}C, 77.16 ppm; d_6-acetone: ^{1}H, 2.05 ppm, ^{13}C, 29.8 ppm; d_6-dimethylsulfoxide: ^{1}H 2.50 ppm, ^{13}C 39.5 ppm; d_3-acetonitrile: ^{1}H 1.94 ppm, ^{13}C 1.3 ppm). For ^{11}B NMR, samples were externally referenced to $F_3B{\bullet}OEt_2$ in $CDCl_3$. NMR spectra are reported as follows: chemical shift/ppm (multiplicity, coupling constant(s), number of nuclei, assignment). Multiplicity given as br (broad), s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), h (hextet), m (multiplet), and combinations thereof. Throughout, ^{13}C signals adjacent to boron were not observed. Signals which overlap with one another are described as multiplets. ^{11}B NMRs are often contaminated by BF_4 ion, leading to intense signal at ~0 ppm, this signal dominates spectra but integrates to very small area compared to product signal due to both the sharpness of the BF_4 and the broadness of the BMIDA signals. Note that restricted rotation around the C–B axis led to signal broadening. Where impurities are present in NMR spectra, they are assigned a grey chemical shift marker. The NMR solvents are assigned with a red chemical shift marker. IR spectra were recorded using a Shimadzu IT Affinity-1 Fourier transform IR spectrophotometer with a Specac Quest ATR (diamond puck). The spectra were recorded as specified in the procedure as films (using CH_2Cl_2), as solids or as neat liquids. Transmittance is recorded with maximal absorption wavenumbers given as cm^{-1}. Mass spectra were recorded on a Bruker micrOTOF benchtop ESI with either positive or negative electrospray ionisation or EI using a Thermo Mat 900XP, Double Focusing Hi-resolution mass spectrometer. The number of decimal places is determined by the accuracy of the machine (i.e., both 4 and 5 digits given).

2. General Procedures and Synthesis of Starting Materials

Synthetic procedures of alkyne BMIDA starting materials to produce **3**–**8**, **10**, **11**, **13** can be found in the literature.[2,3] Preparations of the following molecules can be found in corresponding references:

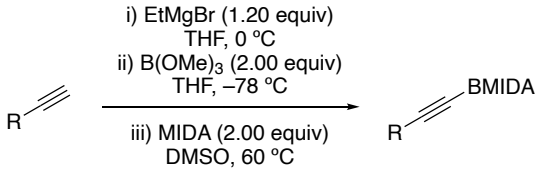
5-(prop-2-yn-1-yloxy)benzo[*d*][1,3]dioxole[4]

(but-3-yn-1-yloxy)(*tert*-butyl)dimethylsilane[5]

N,*N*-dibenzylbut-3-yn-1-amine[6]

Syntheses of diyne starting materials for products are reported in the corresponding references **3**–**17**,[7] **18**,[1] **19**,[8] **20**,[7] **21**,[9] **22**,[11] **26**.[12] Diynes for **23**, **24**, and **25** are commercially available.

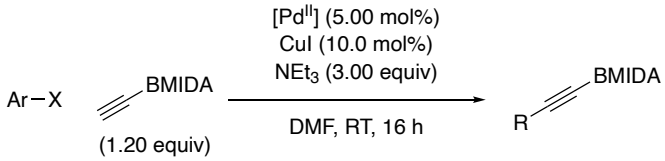
General procedure A: Synthesis of alkyne BMIDA through metalation-borylation.



A flame-dried flask was charged with the relevant alkyne (1.00 equiv) and dissolved in dry THF (750 mM) under nitrogen and the solution was cooled to 0 ºC. EtMgBr solution (~3.00 M in Et_2O, 1.20 equiv) was added dropwise and the mixture was allowed to stir for 10 mins before allowing to warm to RT. Another flame-dried flask was

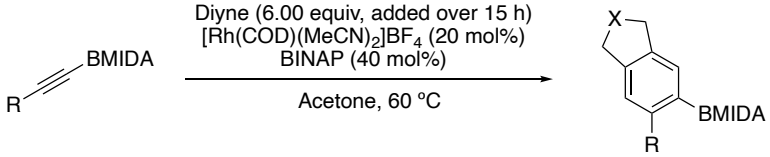
charged with $B(OMe)_3$ (2.00 equiv) in dry THF (1.50 M) under nitrogen and cooled to −78 ºC. The metallated alkyne solution was added dropwise to the trimethylborate solution then the solution was stirred at −78 ºC for 1 h before allowing to warm to RT over 2 h. MIDA acid (2.00 equiv) and DMSO (1.00 mL/mmol alkyne) were added, and volatiles were removed *via* rotary evaporation. DMSO was then removed *via* high vacuum distillation and after cooling to RT, brine:H_2O (1:1, ~7 mL/mmol alkyne) was added. The mixture was extracted with EtOAc:acetone (3:2, ~7 mL/mmol alkyne) twice. The combined organic extracts were washed with H_2O, dried over Na_2SO_4, filtered, and concentrated *in vacuo* to yield the crude product which was purified *via* recrystallisation or flash column chromatography to yield the desired product.

General procedure B: Synthesis of alkyne BMIDA through Sonogashira coupling



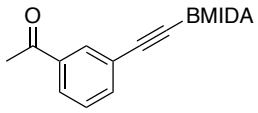
An oven-dried microwave vial was charged with acetylene BMIDA (1.20 equiv), [Pd^{II}] complex (either $Pd(PPh_3)_2Cl_2$ or $Pd(dppf)Cl_2$, 5.00 mol%), and CuI (10.0 mol%). After evacuating and backfilling with nitrogen, DMF (200 mM) was added followed by NEt_3 (3.00 equiv) and the aryl halide (1.00 equiv). The mixture was allowed to stir at RT for 16 h before undergoing work up. See individual compounds for work up procedures.

General procedure C: [2+2+2] Cycloaddition of diynes and internal borylated alkynes



An oven dried microwave vial was charged with the relevant alkyne BMIDA (1.00 equiv), $[Rh(COD)(MeCN)_2]BF_4$ (20.0 mol%), and BINAP (40.0 mol%). The vial was then sealed, evacuated, and backfilled with nitrogen. Acetone (100 mM/2) was added, and the solution was heated to 60 ºC. A separate flask was charged with the diyne (6.00 equiv) and acetone (100 mM/2), this solution was added over 15 h using syringe pump addition. Once addition was complete, the mixture was allowed to stir for a further 1 h before allowing to cool to RT. The mixture was then filtered through celite and concentrated *in vacuo* to yield the crude product, which was purified by flash column chromatography.

2-((3-acetylphenyl)ethynyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (S5)



Prepared according to **General Procedure B** from 3-bromoacetophenone (55.0 µL, 418 µmol, 1.20 equiv) and acetylene BMIDA (63.0 mg, 347 mmol, 1.00 equiv) using $Pd(dppf)Cl_2$. Work up procedure was dilution of reaction mixture with acetone, filtering through celite, and concentrating *in vacuo* to yield the crude which was purified by flash column chromatography (silica, 0–10% MeCN in CH_2Cl_2) to yield the desired product as a white solid (95.0 mg, 91%)

^{1}H NMR (500 MHz, Acetone-d_6) δ_H 8.08 (td, J = 1.77, 0.58 Hz, 1H), 8.00 (ddd, J = 7.87, 1.79, 1.15 Hz, 1H), 7.74 (dt, J = 7.72, 1.48 Hz, 1H), 7.55 (td, J = 7.75, 0.63 Hz, 1H), 4.37 (d, J = 16.95 Hz, 2H), 4.22 (d, J = 16.93 Hz, 2H), 3.37 (s, 3H), 2.62 (s, 3H).

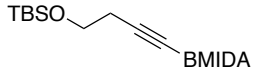
^{13}C NMR (126 MHz, Acetone-d_6) δ_C 196.5, 167.7, 137.5, 135.7, 131.3, 128.9, 128.3, 123.6, 98.6, 61.5, 47.7, 25.9.

^{11}B NMR (96 MHz, Acetone-d_6) δ_B 6.6.

IR (ATR, solid): 1767, 1682, 1275, 1223, 1098, 1069, 1024, 1009, 993, 959 cm^{-1}.

HRMS (ESI): Calculated for 300.1038 m/z, found 300.1035 m/z $[C_{15}H_{14}BNO_5+H]^+$.

2-(4-((*tert*-butyldimethylsilyl)oxy)but-1-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (S9)



Prepared according to **General Procedure A** from (but-3-yn-1-yloxy)(*tert*-butyl)dimethylsilane (13.8 g, 75 mmol, 1.0 equiv.). Purified by flash column chromatography (silica, 0-25% MeCN in CH_2Cl_2) to give the desired product as a white solid (8.14 g, 32%).

^{1}H NMR (500 MHz, Acetone-d_6) δ_H 4.25 (d, J = 16.87 Hz, 2H), 4.05 (d, J = 16.98 Hz, 2H), 3.77 (t, J = 6.96 Hz, 2H), 3.21 (s, 3H), 2.44 (t, J = 6.97 Hz, 2H), 0.91 (s, 9H), 0.09 (s, 6H).

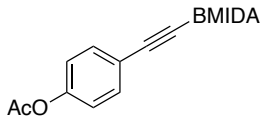
^{13}C NMR (126 MHz, Acetone-d_6) δ_C 167.7, 98.7, 61.7, 61.3, 47.4, 25.4, 23.5, 17.9, -6.0.

^{11}B NMR (96 MHz, Acetone-d_6) δ_B 6.0.

IR: (ATR, solid): 2955, 2930, 2857, 2208, 1759, 1462, 1337, 1252, 1024 cm^{-1}.

HRMS (ESI): Calculated for 362.1581 *m*/*z*, found 362.1560 *m*/*z* $[C_{15}H_{26}BNO_5Si+Na]^+$.

4-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)ethynyl)phenyl acetate (S12)



Prepared according to **General Procedure B** from 4-iodophenyl acetate (262 mg, 1.00 mmol, 1.00 equiv) using $[Pd(PPh_3)_2]Cl_2$. Work up procedure was dilution of reaction mixture with EtOAc followed by three washings with 10% aqueous LiCl. The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo* to yield the crude product which was purified *via* trituration with Et_2O to yield the desired product as a beige solid (244 mg, 77%).

^{1}H NMR (500 MHz, Acetone-d_6) δ_H 7.61 – 7.51 (m, 2H), 7.19 – 7.11 (m, 2H), 4.35 (d, J = 16.95 Hz, 2H), 4.20 (d, J = 16.90 Hz, 2H), 3.34 (s, 3H), 2.28 (s, 3H).

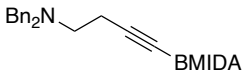
^{13}C NMR (126 MHz, Acetone-d_6) δ_C 168.6, 167.7, 151.2, 132.8, 122.1, 120.5, 99.3, 61.5, 47.6, 20.1.

^{11}B NMR (96 MHz, Acetone-d_6) δ_B 6.7.

IR (ATR, solid): 1769, 1290, 1181, 1022, 472, 422 cm^{-1}.

HRMS (ESI): Calculated for 316.0987 *m*/*z*, found 316.0990 *m*/*z* $[C_{15}H_{14}BNO_6+H]^+$.

2-(4-(dibenzylamino)but-1-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (S14)



Prepared according to a modified **General Procedure A:** flame-dried 25 mL Schlenk flask was charged with *N*,*N*-dibenzyl-3-butyn-1-amine (623 mg, 2.50 mmol, 1.00 equiv) and the flask was evacuated and re-filled with N_2 three times. Anhydrous THF (5.00 mL) was added and the mixture was cooled to −5 °C in an ice/brine bath. To this was added, dropwise, EtMgBr (2.36 M in Et_2O, 1.11 mL, 2.63 mmol, 1.05 equiv). After complete addition, the resultant suspension was stirred for a further 30 minutes at −5 °C before being gradually warmed to RT and stirring for a further 1 h. In a separate flame-dried 50 mL flask, $B(OMe)_3$ (360 µL, 3.23 mmol, 1.29 equiv) was dissolved in anhydrous THF (5.0 mL) and cooled to −78 °C. The metalated alkyne solution was added to this solution dropwise and the resulting solution was stirred at −78 °C for 45 minutes. The mixture was then allowed to warm to RT and stirred for a further 1 hour. After this point, ethereal HCl (2.00 M in Et_2O, 3.75 mL, 7.50 mmol, 3.00 equiv) was added dropwise followed by the addition of anhydrous DMF (7.00 mL). The volatiles were removed *in vacuo* and the remaining DMF solution was transferred to an oven-dried microwave vial then MIDA anhydride (968 mg, 7.50 mmol, 3.00 equiv) and H_2O (47.0 µL, 2.60 mmol, 1.00 equiv) were added. The vial was sealed and the mixture was stirred at 70 ºC for 1.5 h then allowed to cool to RT. 10% aqueous LiCl (10 mL) was added followed by EtOAc:acetone (3:2, 10.0 mL), the pH of the aqueous phase was adjusted to 7 by the addition of saturated aqueous $NaHCO_3$ solution, and the biphasic system was extracted with EtOAc:acetone (3:2, 3 × ~20 mL). The combined organic fractions were washed with three further portions of 10% aqueous LiCl (3 × ~10 mL) then the organic phase

was dried over Na_2SO_4, filtered, and concentrated *in vacuo* to yield the crude which was purified by flash column chromatography (silica, 0–20% MeCN in CH_2Cl_2) to yield the desired product as a white solid (730 mg, 72%).

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ_H 7.47 – 7.35 (d, J = 7.2 Hz, 4H), 7.32 (t, J = 7.4 Hz, 4H), 7.28 – 7.20 (m, 2H), 3.94 (d, J = 17.0 Hz, 2H), 3.78 (d, J = 17.0 Hz, 2H), 3.60 (s, 4H), 2.92 (s, 3H), 2.63 (t, J = 7.2 Hz, 2H), 2.43 (t, J = 7.2 Hz, 2H).

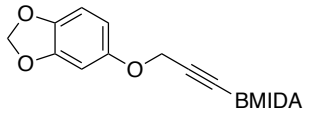
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ_C 168.8, 140.7, 129.7, 129.2, 127.9, 101.0 62.2, 58.5, 52.7, 48.5, 18.3.

^{11}B NMR (96 MHz, Acetonitrile-d_3) δ_B 6.1.

IR: (ATR, film): 2205, 1763, 1452, 1281, 1165, 1028, 988, 735, 698 cm^{-1}

HRMS (ESI): Calculated for 427.1800 *m/z*, found 427.1798 *m/z* $[C_{23}H_{25}BN_2O_4+Na]^+$.

2-(3-(benzo[*d*][1,3]dioxol-5-yloxy)prop-1-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (S15)



Prepared according to **General Procedure A** from 5-(prop-2-yn-1-yloxy)benzo[*d*][1,3]dioxole (705 mg, 4.00 mmol, 1.00 equiv.). Purified by flash column chromatography (silica, 10–20% MeCN in CH_2Cl_2) followed by recrystallisation from EtOAc:Acetone to yield the desired product as a white solid (331 mg, 25%).

^{1}H NMR (500 MHz, DMSO-d_6) δ_H 6.82 (d, J = 8.53 Hz, 1H), 6.69 (d, J = 2.50 Hz, 1H), 6.44 (dd, J = 8.52, 2.55 Hz, 1H), 5.97 (s, 2H), 4.74 (s, 2H), 4.27 (d, J = 17.18 Hz, 2H), 4.06 (d, J = 17.15 Hz, 2H), 2.93 (s, 3H).

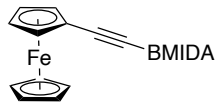
^{13}C NMR (126 MHz, DMSO-d_6) δ_C 169.1, 153.1, 148.3, 142.1, 108.4, 106.9, 101.6, 98.7, 96.0, 61.9, 57.3, 48.3.

^{11}B NMR (96 MHz, DMSO-d_6) δ_B 5.8.

IR (ATR, solid): 1761, 1487, 1284, 1268, 1180, 1132, 1030, 1011, 988, 870, 775 cm^{-1}.

HRMS (ESI): Calculated for 354.0756 *m/z*, found 354.0755 *m/z* $[C_{15}H_{14}BNO_7+Na]^+$.

2-(1-ferrocenylethynyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (S16)



Prepared according to **General Procedure A** from ethynlferrocene (840 mg, 4.00 mmol, 1.00 equiv.). Purified by flash column chromatography (silica, 0–30% MeCN in CH_2Cl_2) to give the desired product as a red solid (750 mg, 51%).

^{1}H NMR (500 MHz, DMSO-d_6) δ_H 4.50 (t, J = 1.86 Hz, 2H), 4.31 – 4.27 (m, 4H), 4.24 (s, 5H), 4.12 (d, J = 17.15 Hz, 2H), 3.05 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d_6) δ_C 169.2, 99.1, 71.7, 70.2, 69.3, 64.8, 62.0, 48.4.

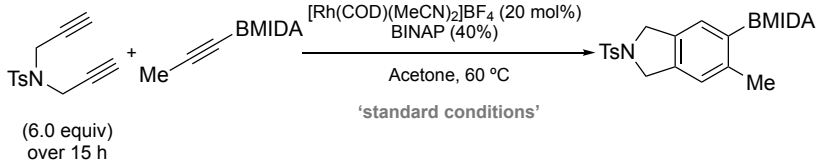
^{11}B NMR (96 MHz, DMSO-d_6) δ_B 6.5.

IR (ATR, solid): 2187, 1765, 1452, 1072, 1001 cm^{-1}.

HRMS (ESI): Calculated for 365.0522 *m/z*, found 365.0516 *m/z* $[C_{17}H_{16}BFeNO_4]^+$.

3. Optimization Data

Table 1: Selected optimization data.[2]

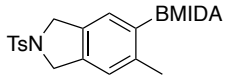


Entry	Deviation from Standard Conditions	Yield (%)[a]
1	--	75
2	10 mol% Rh, 20 mol% ligand	39
3	PPh_3 as ligand	<5
4	dppp as ligand	10
5	$[Rh(COD)Cl]_2$ (10 mol%)	NR
6	[Ru(COD)Cp*]Cl	<5
7	RT	32
8	80 °C	70
9	Diyne added at outset (no slow addition)	22

[a]Yields determined by quantitative NMR spectroscopy against internal standard (1,4-dinitrobenzene). NR = [2+2+2] reaction not observed.

4. Product Characterisation Data

6-methyl-2-(6-methyl-2-tosylisoindolin-5-yl)-1,3,6,2-dioxazaborocane-4,8-dione (3)



Prepared according to **General Procedure C** from 6-methyl-2-(prop-1-yn-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (19.5 mg, 100 µmol, 1.00 equiv.) and 4-methyl-*N*,*N*-di(prop-2-yn-1-yl)benzenesulfonamide (148 mg, 600 µmol, 6.00 equiv.). Purified by flash column chromatography (silica, 0–10% MeCN in CH_2Cl_2) to yield the desired product as a white powder (32.3 mg, 73%).

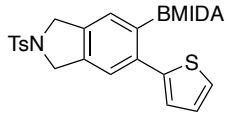
^{1}H NMR (500 MHz, Acetone-d_6) δ_H 7.85 – 7.76 (m, 2H), 7.48 – 7.41 (m, 2H), 7.34 (s, 1H), 7.07 (s, 1H), 4.57 (s, 4H), 4.35 (d, J = 17.16 Hz, 2H), 4.15 (d, J = 17.13 Hz, 2H), 2.74 (s, 3H), 2.40 (m, 6H).

^{13}C NMR (101 MHz, Acetone-d_6) δ_C 169.3, 144.6, 143.0, 138.4, 134.9, 134.2, 130.8, 129.1, 128.6, 125.9, 63.6, 54.5, 54.4, 48.3, 23.1, 21.4.

^{11}B NMR (96 MHz, Acetonitrile-d_3) δ_B 12.2.

Spectral data consistent with the literature.[2]

6-methyl-2-(6-(thiophen-2-yl)-2-tosylisoindolin-5-yl)-1,3,6,2-dioxazaborocane-4,8-dione (4)



Prepared according to **General Procedure C** from 6-methyl-2-(thiophen-2-ylethynyl)-1,3,6,2-dioxazaborocane-4,8-dione (26.3 mg, 100 µmol, 1.00 equiv.) and 4-methyl-*N*,*N*-di(prop-2-yn-1-yl)benzenesulfonamide (148 mg, 600 µmol, 6.00 equiv.). Purified by flash column chromatography (silica, 0–15% MeCN in CH_2Cl_2) to yield the desired product as a white powder (25.3 mg, 50%).

^{1}H NMR (500 MHz, Acetone-d_6) δ_H 7.83 – 7.77 (m, 2H), 7.67 (s, 1H), 7.45 – 7.40 (m, 3H), 7.18 (s, 1H), 7.01 (dd, J = 3.51, 1.18 Hz, 1H), 6.96 (dd, J = 5.14, 3.49 Hz, 1H), 4.68 – 4.61 (m, 4H), 4.10 (d, J = 16.96 Hz, 2H), 3.53 (d, J = 16.93 Hz, 2H), 2.66 (s, 3H), 2.39 (s, 3H).

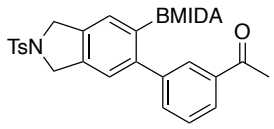
^{13}C NMR (126 MHz, Acetone-d_6) δ_C 167.7, 143.8, 143.5, 139.0, 137.3, 136.0, 133.8, 129.9, 128.9, 128.5, 127.7, 127.2, 126.6, 125.7, 62.7, 53.6, 53.5, 47.6, 20.5.

^{11}B NMR (96 MHz, Acetone-d_6) δ_B 11.9.

IR (ATR, film): 1769, 1705, 1339, 1161, 1096, 1030, 1005, 667, 575, 546 cm^{-1}.

HRMS (ESI): Calculated for 511.1163 *m*/*z*, found 511.1168 *m*/*z* $[C_{24}H_{23}BN_2O_6S_2+H]^+$.

2-(6-(3-acetylphenyl)-2-tosylisoindolin-5-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (5)



Prepared according to **General Procedure C** from 2-((3-acetylphenyl)ethynyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (26.3 mg, 100 µmol, 1.00 equiv.) and 4-methyl-*N*,*N*-di(prop-2-yn-1-yl)benzenesulfonamide (148 mg, 600 µmol, 6.00 equiv.). Purified by flash column chromatography (silica, 0–15% MeCN in CH_2Cl_2) to yield the desired product as a white powder (25.3 mg, 50%).

^{1}H NMR (500 MHz, Acetone-d_6) δ_H 7.93 – 7.88 (m, 2H), 7.86 – 7.82 (m, 2H), 7.68 (s, 1H), 7.54 (dt, *J* = 7.61, 1.46 Hz, 1H), 7.51 – 7.44 (m, 3H), 7.08 (d, *J* = 0.96 Hz, 1H), 4.70 (d, *J* = 2.27 Hz, 2H), 4.66 (m, 2H), 4.06 (brd, *J* = 16.73 Hz, 2H), 3.75 – 3.21 (m, 2H), 2.62 (s, 3H), 2.60 (s, 3H), 2.43 (s, 3H).

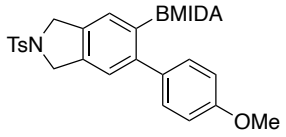
^{13}C NMR (126 MHz, Acetone-d_6) δ_C 197.1, 167.5, 146.7, 143.8, 143.5, 137.4, 136.6, 135.3, 133.9, 133.8, 130.1, 129.9, 128.7, 128.2, 127.8, 126.3, 125.2, 62.5, 53.6, 53.6, 47.6, 26.0, 20.5.

^{11}B NMR (96 MHz, Acetone-d_6) δ_B 11.8.

IR (ATR, film): 1763, 1682, 1339, 1289, 1250, 1184, 1161, 1121, 1096, 1055, 1030, 667, 575, 548 cm^{-1}.

HRMS (ESI): Calculated for 569.1524 *m*/*z*, found 569.1507 *m*/*z* $[C_{28}H_{27}BN_2O_7S+Na]^+$.

2-(6-(4-methoxyphenyl)-2-tosylisoindolin-5-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (6)



Prepared according to **General Procedure C** from 2-((4-methoxyphenyl)ethynyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (28.7 mg, 100 µmol, 1.00 equiv.) and 4-methyl-*N*,*N*-di(prop-2-yn-1-yl)benzenesulfonamide (148 mg, 600 µmol, 6.00 equiv.). Purified by flash column chromatography (silica, 0–10% MeCN in CH_2Cl_2) to yield the desired product as a white powder (54.1 mg, >99%).

^{1}H NMR (500 MHz, Acetone-d_6) δ_H 7.84 – 7.79 (m, 2H), 7.64 (s, 1H), 7.43 (m, 2H), 7.22 – 7.17 (m, 2H), 7.01 – 6.98 (m, 1H), 6.89 – 6.84 (m, 2H), 4.66 – 4.63 (m, 2H), 4.62 – 4.60 (m, 2H), 4.00 (d, *J* = 16.86 Hz, 2H), 3.79 (s, 3H), 3.39 (d, *J* = 16.85 Hz, 2H), 2.58 (s, 3H), 2.40 (s, 3H).

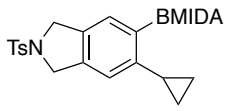
^{13}C NMR (126 MHz, Acetone-d_6) δ_C 167.6, 158.8, 147.3, 143.7, 137.1, 135.4, 134.6, 133.8, 130.9, 129.9, 128.5, 127.8, 125.4, 113.4, 62.6, 54.7, 53.6, 53.6, 47.4, 20.5.

^{11}B NMR (96 MHz, Acetone-d_6) δ_B 12.2.

IR (ATR, film): 1763, 1707, 1339, 1223, 1161, 1094, 1028, 667, 548, 530 cm^{-1}.

HRMS (ESI): Calculated for 535.1705 *m*/*z*, found 535.1710 *m*/*z* $[C_{27}H_{27}BN_2O_7S+H]^+$.

2-(6-cyclopropyl-2-tosylisoindolin-5-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (7)



Prepared according to **General Procedure C** from 2-(cyclopropylethynyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (22.1 mg, 100 µmol, 1.00 equiv.) and 4-methyl-*N*,*N*-di(prop-2-yn-1-yl)benzenesulfonamide (148 mg, 600

μmol, 6.00 equiv.). Purified by flash column chromatography (silica, 0–10% MeCN in CH_2Cl_2) to yield the desired product as a white powder (30.4 mg, 65%).

^{1}H NMR (500 MHz, Acetone-d_6) δ_H 7.80 – 7.76 (m, 2H), 7.43 – 7.39 (m, 2H), 7.34 (s, 1H), 6.85 (s, 1H), 4.54 (appq, J = 2.48 Hz, 4H), 4.34 (d, J = 17.18 Hz, 2H), 4.13 (d, J = 17.18 Hz, 2H), 2.81 (s, 3H), 2.38 (s, 3H), 2.31 (tt, J = 8.44, 5.39 Hz, 1H), 0.94 – 0.89 (m, 2H), 0.70 – 0.64 (m, 2H).

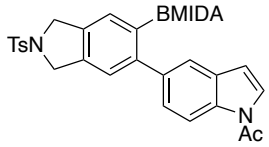
^{13}C NMR (126 MHz, Acetone-d_6) δ_C 169.3, 148.5, 144.5, 138.6, 134.8, 133.8, 130.7, 129.0, 128.6, 118.9, 63.5, 54.6, 54.3, 48.4, 21.4, 15.4, 9.9.

^{11}B NMR (128 MHz, Acetone-d_6) δ_B 12.5.

IR (ATR, film): 1763, 1707, 1339, 1190, 1161, 1096, 1053, 1026, 667, 550 cm^{-1}.

HRMS (ESI): Calculated for 469.1599 m/z, found 469.1603 m/z $[C_{23}H_{25}BN_2O_6S+H]^+$.

2-(6-(1-acetyl-1*H*-indol-5-yl)-2-tosylisoindolin-5-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (8)



Prepared according to **General Procedure C** 2-((1-acetyl-1*H*-indol-5-yl)ethynyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (33.8 mg, 100 μmol, 1.00 equiv.) and 4-methyl-*N*,*N*-di(prop-2-yn-1-yl)benzenesulfonamide (148 mg, 600 μmol, 6.00 equiv.). Purified by flash column chromatography (silica, 0–15% MeCN in CH_2Cl_2) to yield the desired product as a brown solid (52.0 mg, 89%).

^{1}H NMR (500 MHz, Acetone-d_6) δ_H 8.36 (d, J = 8.44 Hz, 1H), 7.87 – 7.80 (m, 2H), 7.76 (d, J = 3.76 Hz, 1H), 7.69 (s, 1H), 7.52 (dd, J = 1.84, 0.69 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.24 (dd, J = 8.44, 1.82 Hz, 1H), 7.06 (s, 1H), 6.66 (dd, J = 3.74, 0.74 Hz, 1H), 4.68 (s, 2H), 4.65 (m, 2H), 3.96 (brm, 2H), 3.60 – 3.10 (brm, 2H), 2.69 (s, 3H), 2.63 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (126 MHz, Acetone-d_6) δ_C 169.0, 167.6, 147.8, 143.8, 138.5, 137.1, 134.7, 134.4, 133.8, 130.3, 129.9, 128.5, 127.8, 127.1, 126.4, 125.7, 122.3, 115.6, 108.6, 62.6, 53.6, 53.6, 47.5, 23.1, 20.6.

^{11}B NMR (96 MHz, Acetone d_6) δ_B 11.7.

IR (ATR, film): 2363, 1767, 1706, 1331, 1161, 1026, 667 cm^{-1}.

HRMS (ESI): Calculated for 608.1633 m/z, found 608.1633 m/z $[C_{30}H_{28}BN_3O_7S+Na]^+$.

2-(6-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-2-tosylisoindolin-5-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (9)

Prepared according to **General Procedure C** from 2-(4-((*tert*-butyldimethylsilyl)oxy)but-1-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (33.9 mg, 100 μmol, 1.00 equiv.) and 4-methyl-*N*,*N*-di(prop-2-yn-1-yl)benzenesulfonamide (148 mg, 600 μmol, 6.00 equiv.). Purified by flash column chromatography (silica, 0–15% MeCN in CH_2Cl_2) to yield the desired product as a white solid (30.6 mg, 52%).

^{1}H NMR (500 MHz, Acetonitrile-d_3) δ_H 7.75 (d, J = 8.33 Hz, 2H), 7.40 – 7.35 (m, 2H), 7.23 (s, 1H), 7.11 (s, 1H), 4.58 (s, 2H), 4.55 (s, 2H), 4.06 (d, J = 17.20 Hz, 2H), 3.89 (d, J = 17.22 Hz, 2H), 3.78 (t, J = 6.56 Hz, 2H), 2.80 (t, J = 6.57 Hz, 2H), 2.47 (s, 3H), 2.39 (s, 3H), 0.82 (s, 9H), -0.07 (s, 6H).

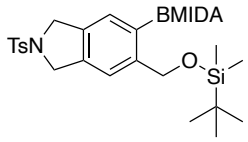
^{13}C NMR (126 MHz, Acetonitrile-d_3) δ_C 168.4, 144.1, 143.6, 137.2, 133.9, 133.4, 129.9, 128.1, 127.6, 125.6, 64.4, 62.3, 53.6, 53.6, 47.4, 38.8, 25.3, 20.5, 17.9, –6.2.

^{11}B NMR (96 MHz, Acetonitrile-d_3) δ_B 12.1.

IR (ATR, film): 1763, 1709, 1163, 1034, 835, 667, 550, 530 cm^{-1}.

HRMS (ESI): Calculated for 587.2413 m/z, found 587.2418 m/z $[C_{28}H_{39}BN_2O_7SSi+H]^+$.

2-(6-(((*tert*-butyldimethylsilyl)oxy)methyl)-2-tosylisoindolin-5-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (10)



Prepared according to **General Procedure C** from 2-(3-((*tert*-butyldimethylsilyl)oxy)prop-1-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (32.5 mg, 100 µmol, 1.00 equiv.) and 4-methyl-*N*,*N*-di(prop-2-yn-1-yl)benzenesulfonamide (148 mg, 600 µmol, 6.00 equiv.). Purified by flash column chromatography (silica, 0–15% MeCN in CH_2Cl_2) to yield the desired product as a white solid (11.3 mg, 20%).

^{1}H NMR (500 MHz, Acetonitrile-d_3) δ_H 7.77 – 7.73 (m, 2H), 7.39 – 7.35 (m, 2H), 7.31 (s, 1H), 7.28 (s, 1H), 4.78 (s, 2H), 4.61 – 4.58 (m, 4H), 4.08 (d, J = 17.21 Hz, 2H), 3.93 (d, J = 17.22 Hz, 2H), 2.48 (s, 3H), 2.38 (s, 3H), 0.92 (s, 9H), 0.11 (s, 6H).

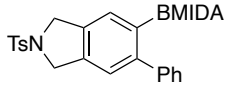
^{13}C NMR (126 MHz, Acetonitrile-d_3) δ_C 168.5, 144.8, 144.1, 137.7, 135.1, 133.5, 129.8, 128.4, 127.6, 122.9, 65.2, 62.8, 53.7, 53.6, 48.3, 25.5, 20.5, 18.3, -6.0.

^{11}B NMR (96 MHz, Acetonitrile-d_3) δ_B 12.1.

IR (ATR, film): 1767, 1341, 1163, 1098, 1045, 837, 667 cm^{-1}.

HRMS (ESI): Calculated for 573.2257 *m*/*z*, found 573.2276 *m*/*z* $[C_{27}H_{37}BN_2O_7SSi+H]^+$.

6-methyl-2-(6-phenyl-2-tosylisoindolin-5-yl)-1,3,6,2-dioxazaborocane-4,8-dione (11)



Prepared according to **General Procedure C** from 6-methyl-2-(phenylethynyl)-1,3,6,2-dioxazaborocane-4,8-dione (25.7 mg, 100 µmol, 1.00 equiv.) and 4-methyl-*N*,*N*-di(prop-2-yn-1-yl)benzenesulfonamide (148 mg, 600 µmol, 6.00 equiv.). Purified by flash column chromatography (silica, 0–20% MeCN in CH_2Cl_2) to yield the desired product as a pale-yellow solid (44.5 mg, 88%).

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ_H 7.77 (d, J = 8.24 Hz, 2H), 7.58 (s, 1H), 7.41 – 7.38 (m, 2H), 7.36 – 7.30 (m, 3H), 7.24 – 7.18 (m, 2H), 6.96 (d, J = 1.01 Hz, 1H), 4.65 (m, 2H), 4.65 – 4.58 (m, 2H), 3.76 (d, J = 16.94 Hz, 2H), 3.29 (d, J = 17.03 Hz, 2H), 2.40 (m, 6H).

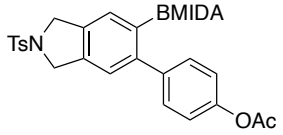
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ_C 167.8, 147.4, 144.2, 143.2, 137.2, 135.0, 133.5, 129.9, 129.6, 128.4, 127.9, 127.6, 127.0, 125.1, 62.5, 53.6, 53.6, 47.6, 17.8.

^{11}B NMR (128 MHz, Acetonitrile-d_3) δ_B 11.3.

IR (ATR, film): 1761, 1709, 1337, 1290, 1161, 1096, 1030, 665, 548, 530 cm^{-1}.

HRMS (ESI): Calculated for 505.1599 *m*/*z*, found 505.1604 *m*/*z* $[C_{26}H_{26}BN_2O_6S+H]^+$.

4-(6-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-2-tosylisoindolin-5-yl)phenyl acetate (12)



Prepared according to **General Procedure C** from 4-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)ethynyl)phenyl acetate (31.5 mg, 100 µmol, 1.00 equiv.) and 4-methyl-*N*,*N*-di(prop-2-yn-1-yl)benzenesulfonamide (148 mg, 600 µmol, 6.00 equiv.). Purified by flash column chromatography (silica, 0–15% MeCN in CH_2Cl_2) to yield the desired product as a pale-yellow solid (10.9 mg, 19%).

^{1}H NMR (500 MHz, Acetone-d_6) δ_H 7.87 – 7.81 (m, 2H), 7.66 (s, 1H), 7.49 – 7.43 (m, 2H), 7.34 – 7.28 (m, 2H), 7.09 – 7.03 (m, 3H), 4.70 – 4.66 (m, 2H), 4.66 – 4.63 (m, 2H), 4.04 (d, J = 16.95 Hz, 2H), 3.46 (d, J = 16.92 Hz, 2H), 2.61 (s, 3H), 2.42 (s, 3H), 2.28 (s, 3H).

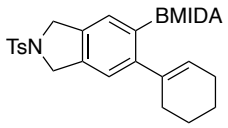
^{13}C NMR (126 MHz, Acetone-d_6) δ_C 168.7, 167.5, 150.0, 146.7, 143.8, 140.7, 137.2, 135.0, 133.8, 130.8, 129.9, 128.6, 127.8, 125.3, 121.2, 62.6, 53.6, 53.6, 47.5, 20.5, 20.1.

^{11}B NMR (96 MHz, Acetone-d_6) δ_B 12.2.

IR (ATR, film): 1749, 1707, 1339, 1221, 1194, 1161, 1096, 667, 586, 559, 542 cm^{-1}.

HRMS (ESI): Calculated for 585.14734 *m*/*z*, found 585.14532 *m*/*z* $[C_{28}H_{27}BN_2O_8S+Na]^+$.

2-(6-(cyclohex-1-en-1-yl)-2-tosylisoindolin-5-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (13)



Prepared according to **General Procedure C** from 2-(cyclohex-1-en-1-ylethynyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (31.5 mg, 100 µmol, 1.00 equiv.) and 4-methyl-*N*,*N*-di(prop-2-yn-1-yl)benzenesulfonamide (148 mg, 600 µmol, 6.00 equiv.). Purified by flash column chromatography (silica, 0–15% MeCN in CH_2Cl_2) followed by recrystallisation (Acetone-CH_2Cl_2-hexane) to yield the desired product as a pale-yellow solid (10.9 mg, 19%).

^{1}H NMR (500 MHz, Acetonitrile-d_3) δ_H 7.85 – 7.73 (m, 2H), 7.41 – 7.35 (m, 3H), 6.86 (s, 1H), 5.38 – 5.30 (m, 1H), 4.62 – 4.55 (m, 4H), 4.01 (d, J = 17.14 Hz, 2H), 3.81 (brd, J = 17.51 Hz, 2H), 2.44 (s, 3H), 2.40 (s, 3H), 2.02 (s, 2H), 1.79 – 1.69 (m, 2H), 1.64 (m, 2H). One remaining CH_2 at around 2.20 ppm overlaps with residual water in NMR solvent.

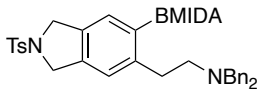
^{13}C NMR (126 MHz, Acetone-d_6) δ_C 168.5*, 150.1, 143.7, 143.5, 137.1, 133.9, 133.9, 129.8, 128.2, 127.7, 123.4, 123.3, 62.8, 53.6, 53.4, 48.3, 25.0, 25.0, 22.2, 21.4, 20.5. Peak assigned through HMBC as desired peak broadened into baseline.

^{11}B NMR (96 MHz, Acetone-d_6) δ_B 12.3.

IR (ATR, film): 1773, 1341, 1161, 1034, 669, 411 cm^{-1}.

HRMS (ESI): Calculated for 531.17316 *m*/*z*, found 531.17177 *m*/*z* $[C_{26}H_{29}BN_2O_6S+Na]^+$.

2-(6-(2-(dibenzylamino)ethyl)-2-tosylisoindolin-5-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (14)



Prepared according to **General Procedure C** from 2-(4-(dibenzylamino)but-1-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (404 mg, 1.00 mmol, 1.00 equiv.) and 4-methyl-*N*,*N*-di(prop-2-yn-1-yl)benzenesulfonamide (1.48 mg, 6.00 mmol, 6.00 equiv.). Purified by flash column chromatography (silica, 0–15% MeCN in CH_2Cl_2) to yield the desired product as a brown solid (413 mg, 63%).

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ_H ^{1}H NMR (500 MHz, Acetonitrile-d_3) δ 7.78 – 7.74 (m, 2H), 7.39 – 7.35 (m, 2H), 7.34 – 7.31 (m, 4H), 7.29 – 7.25 (m, 4H), 7.25 – 7.20 (m, 2H), 7.16 (s, 1H), 6.93 (s, 1H), 4.56 (s, 2H), 4.52 (d, J = 2.08 Hz, 2H), 4.02 (d, J = 17.21 Hz, 2H), 3.82 (d, J = 17.20 Hz, 2H), 3.64 (s, 4H), 2.85 (dd, J = 8.82, 6.11 Hz, 2H), 2.65 – 2.59 (m, 2H), 2.37 (s, 3H), 2.34 (s, 3H).

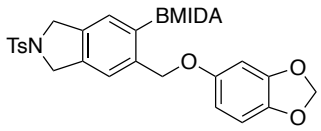
^{13}C NMR (126 MHz, Acetonitrile-d_3) δ_C 168.41, 145.2, 144.1, 139.9, 137.4, 133.7, 133.4, 129.9, 128.7, 128.1, 128.1, 127.6, 126.8, 124.8, 117.4, 62.2, 57.7, 56.0, 53.6, 53.5, 47.1, 32.8, 20.5.

^{11}B NMR (96 MHz, Acetonitrile-d_3) δ_B 12.7.

IR (ATR, film): 1763, 1618, 1341, 1161, 1096, 1028, 702, 667, 548, 409, 401 cm^{-1}.

HRMS (ESI): Calculated for 674.24666 *m*/*z*, found 674.24452 *m*/*z* $[C_{36}H_{38}BN_3O_6S+Na]^+$.

2-(6-((benzo[*d*][1,3]dioxol-5-yloxy)methyl)-2-tosylisoindolin-5-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (15)



Prepared according to **General Procedure C** from the 2-(3-(benzo[*d*][1,3]dioxol-5-yloxy)prop-1-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (33.1 mg, 100 µmol, 1.00 equiv.) and 4-methyl-*N*,*N*-di(prop-2-yn-1-yl)benzenesulfonamide (148 mg, 600 µmol, 6.00 equiv.). Purified by flash column chromatography (silica, 0–10% MeCN in CH_2Cl_2) to yield the desired product as an off-white solid (31.9 mg, 55%).

^{1}H NMR (500 MHz, Acetone-d_6) δ_H 7.85 – 7.79 (m, 2H), 7.49 (s, 1H), 7.45 – 7.41 (m, 3H), 6.74 (d, J = 8.45 Hz, 1H), 6.59 (d, J = 2.56 Hz, 1H), 6.44 (dd, J = 8.50, 2.55 Hz, 1H), 5.95 (s, 2H), 5.11 (s, 2H), 4.66 – 4.65 (m, 2H), 4.64 (s, 2H), 4.36 (d, J = 17.19 Hz, 2H), 4.14 (d, J = 17.19 Hz, 2H), 2.83 (s, 3H), 2.40 (s, 3H).

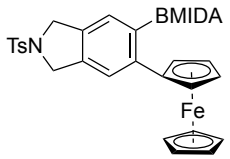
^{13}C NMR (126 MHz, Acetone-d_6) δ_C 168.1, 154.2, 148.3, 143.7, 141.9, 140.8, 137.6, 136.0, 133.9, 129.8, 128.9, 127.7, 124.5, 107.9, 105.9, 101.2, 97.7, 71.2, 63.2, 53.6, 53.5, 48.7, 20.5.

^{11}B NMR (96 MHz, Acetone-d_6) δ_B 12.5.

IR (ATR, film): 1763, 1487, 1341, 1184, 1161, 1096, 1034, 667, 548 cm^{-1}.

HRMS (ESI): Calculated for 493.15751 *m*/*z*, found 493.11013 *m*/*z* $[C_{23}H_{27}BN_2O_6S+Na]^+$.

6-methyl-2-(6-ferrocenyl-2-tosylisoindolin-5-yl)-1,3,6,2-dioxazaborocane-4,8-dione (16)



Prepared according to **General Procedure C** from the 6-methyl-2-(ferrocenyl)-1,3,6,2-dioxazaborocane-4,8-dione (36.5 mg, 100 µmol, 1.00 equiv.) and 4-methyl-*N*,*N*-di(prop-2-yn-1-yl)benzenesulfonamide (148 mg, 600 µmol, 6.00 equiv.). Purified by flash column chromatography (silica, 0–5% MeCN in CH_2Cl_2) followed by recrystallisation (CH_2Cl_2-Et_2O-hexane) to yield the desired product as a red-brown solid (24.0 mg, 39%). ^{1}H NMR (500 MHz, Acetone-d_6) δ_H 8.09 (s, 1H), 7.87 – 7.83 (m, 2H), 7.52 (s, 1H), 7.49 – 7.45 (m, 2H), 4.74 – 4.69 (m, 2H), 4.65 – 4.59 (m, 2H), 4.49 (t, J = 1.82 Hz, 2H), 4.25 – 4.18 (m, 7H), 4.01 (d, J = 16.79 Hz, 2H), 3.39 (d, J = 16.85 Hz, 2H), 2.43 (s, 3H), 2.37 (s, 3H).

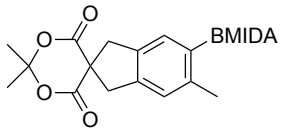
^{13}C NMR (126 MHz, Acetone-d_6) δ_C 167.8, 143.7, 142.8, 137.0, 134.2, 133.9, 129.8, 128.1, 127.9, 127.8, 92.6, 72.0, 69.5, 67.5, 62.9, 53.7, 53.6, 47.1, 20.5.

^{11}B NMR (96 MHz, Acetone-d_6) δ_B 12.0.

IR (ATR, film): 1763, 1339, 1292, 1277, 1161, 1098, 1055, 1028, 829, 667, 581, 548, 407 cm^{-1}.

HRMS (ESI): Calculated for 612.11833 *m*/*z*, found 612.11615 *m*/*z* $[C_{30}H_{29}BFeN_2O_6S]^+$.

2-(5-methyl-2',2'-dimethyl-4',6'-dioxo-1,3-dihydrospiro[indene-2,5'-[1,3]dioxan]-6-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (17)



Prepared according to **General Procedure C** from the 6-methyl-2-(prop-1-yn-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (19.5 mg, 100 µmol, 1.00 equiv.) 2,2-dimethyl-5,5-di(prop-2-yn-1-yl)-1,3-dioxane-4,6-dione (132 mg, 600 µmol, 6.00 equiv.). Purified by flash column chromatography (silica, 0–15% MeCN in CH_2Cl_2) to yield the desired product as a white solid (29.9 mg, 72%).

^{1}H NMR (500 MHz, Acetonitrile-d_3) δ_H 7.29 (s, 1H), 7.09 (s, 1H), 4.09 (d, J = 17.22 Hz, 2H), 3.93 (d, J = 17.24 Hz, 2H), 3.68 (d, J = 4.53 Hz, 4H), 2.57 (s, 3H), 2.40 (s, 3H), 1.84 – 1.79 (m, 6H).

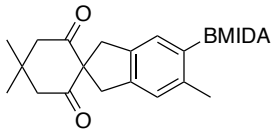
^{13}C NMR (126 MHz, Acetonitrile-d_3) δ_C 170.5, 168.6, 141.7, 141.3, 136.5, 129.5, 126.5, 105.4, 62.5, 52.3, 47.4, 45.2, 44.9, 28.1, 28.1, 22.0.

^{11}B NMR (96 MHz, Acetonitrile-d_3) δ_B 12.6.

IR (ATR, film): 1763, 1736, 1300, 1299, 1098, 1036, 953, 855 cm^{-1}.

HRMS (ESI): Calculated for 438.1331 *m/z*, found 438.1329 *m/z* $[C_{20}H_{22}BNO_8+Na]^+$.

6-methyl-2-(4,4,5'-trimethyl-2,6-dioxo-1',3'-dihydrospiro[cyclohexane-1,2'-inden]-6'-yl)-1,3,6,2-dioxazaborocane-4,8-dione (18)



Prepared according to **General Procedure C** from 6-methyl-2-(prop-1-yn-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (19.5 mg, 100 µmol, 1.00 equiv.)and 5,5-dimethyl-2,2-di(prop-2-yn-1-yl)cyclohexane-1,3-dione (130 mg, 600 µmol, 6.00 equiv.). Purified by flash column chromatography (silica, 0–5% MeCN in CH_2Cl_2) to yield the desired product as a white solid (12.3 mg, 30%).

^{1}H NMR (500 MHz, Acetonitrile-d_3) δ_H 7.20 (s, 1H), 7.03 (s, 1H), 4.07 (d, J = 17.20 Hz, 2H), 3.89 (d, J = 17.18 Hz, 2H), 3.41 (appd, J = 5.12 Hz, 4H), 2.79 (d, J = 14.28 Hz, 2H), 2.68 (d, J = 14.25 Hz, 2H), 2.54 (s, 3H), 2.36 (s, 3H), 1.04 (s, 3H), 0.98 (s, 3H).

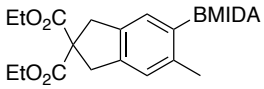
^{13}C NMR (126 MHz, Acetonitrile-d_3) δ_C 207.2, 168.6, 141.9, 141.2, 136.7, 129.7, 126.8, 71.0, 62.5, 54.2, 50.8, 47.4, 39.0, 37.3, 30.1, 27.6, 27.0, 22.0.

^{11}B NMR (96 MHz, Acetonitrile-d_3) δ_B 12.1.

IR (ATR, film): 1763, 1692, 1030, 434, 426, 411 cm^{-1}.

HRMS (ESI): Calculated for 434.17454 *m/z*, found 434.17349 *m/z* $[C_{22}H_{26}BNO_6+Na]^+$.

diethyl 5-methyl-6-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (19)



Prepared according to **General Procedure C** from 6-methyl-2-(prop-1-yn-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (19.5 mg, 100 µmol, 1.00 equiv.) and diethyl 2,2-di(prop-2-yn-1-yl)malonate (142 mg, 600 µmol, 6.00 equiv.). Purified by flash column chromatography (silica, 0–10% MeCN in CH_2Cl_2) to yield the desired product as an off-white solid (9.06 mg, 21%).

^{1}H NMR (500 MHz, Acetonitrile-d_3) δ_H 7.26 (s, 1H), 7.06 (s, 1H), 4.18 (q, J = 7.11 Hz, 4H), 4.08 (d, J = 17.22 Hz, 2H), 3.92 (d, J = 17.24 Hz, 2H), 3.52 (s, 4H), 2.54 (s, 3H), 2.37 (s, 3H), 1.23 (t, J = 7.10 Hz, 6H).

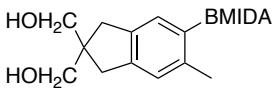
^{13}C NMR (126 MHz, Acetonitrile-d_3) δ_C 171.6, 168.6, 141.7, 141.2, 137.2, 129.7, 126.8, 62.6, 61.6, 60.0, 47.5, 40.0, 39.8, 22.0, 13.3.

^{11}B NMR (96 MHz, Acetonitrile-d_3) δ_B 12.6.

IR (ATR, film): 1724, 1275, 1233, 1179, 1069, 1051, 1028, 1011, 993, 978, 851 cm^{-1}.

HRMS (ESI): Calculated for 454.16437 *m/z*, found 454.16287 *m/z* $[C_{21}H_{26}BNO_8+Na]^+$.

2-(2,2-bis(hydroxymethyl)-6-methyl-2,3-dihydro-1*H*-inden-5-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (20)



Prepared according to **General Procedure C** from 6-methyl-2-(prop-1-yn-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (19.5 mg, 100 µmol, 1.00 equiv.) and 2,2-di(prop-2-yn-1-yl)propane-1,3-diol (91.3 mg, 600 µmol, 6.00 equiv.).

Purified by flash column chromatography (silica, 0–100% MeCN in CH_2Cl_2) to yield the desired product as an off-white solid (19.3 mg, 56%).

^{1}H NMR (500 MHz, Acetonitrile-d_3) δ_H 7.21 (s, 1H), 7.02 (s, 1H), 4.07 (d, J = 17.16 Hz, 2H), 3.91 (d, J = 17.17 Hz, 2H), 3.53 (d, J = 5.41 Hz, 4H), 2.99 (t, J = 5.41 Hz, 2H), 2.74 (d, J = 7.76 Hz, 4H), 2.55 (s, 3H), 2.36 (s, 3H).

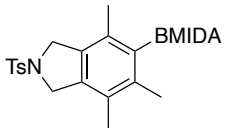
^{13}C NMR (126 MHz, Acetonitrile-d_3) δ_C 168.6, 144.0, 140.3, 139.4, 130.3, 127.5, 66.4, 62.5, 49.4, 47.4, 37.7, 37.4, 22.0.

^{11}B NMR (96 MHz, Acetonitrile-d_3) δ_B 12.3.

IR (ATR, film): 3404, 1763, 1744, 1703, 1026 cm^{-1}.

HRMS (ESI): Calculated for 370.14324 m/z, found 370.14223 m/z $[C_{17}H_{22}BNO_6+Na]^+$.

6-methyl-2-(4,6,7-trimethyl-2-tosylisoindolin-5-yl)-1,3,6,2-dioxazaborocane-4,8-dione (21)



Prepared according to **General Procedure C** from the propyne BMIDA ester (19.5 mg, 100 µmol, 1.00 equiv.) and *N*,*N*-di(but-2-yn-1-yl)-4-methylbenzenesulfonamide (165 mg, 600 µmol, 6.00 equiv.). Purified by flash column chromatography (silica, 0–15% MeCN in CH_2Cl_2) to yield the desired product as an off-white solid (13.3 mg, 28%).

^{1}H NMR (500 MHz, Acetonitrile-d_3) δ_H 7.80 (d, J = 8.30 Hz, 2H), 7.44 – 7.38 (m, 2H), 4.64 – 4.57 (m, 4H), 4.12 (d, J = 17.61 Hz, 2H), 4.01 (d, J = 17.61 Hz, 2H), 2.67 (s, 3H), 2.41 (s, 3H), 2.17 (s, 3H), 2.11 (s, 3H), 2.09 (s, 3H).

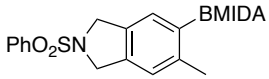
^{13}C NMR (126 MHz, Acetonitrile-d_3) δ_C 168.6, 144.1, 142.2, 136.1, 135.5, 133.5, 133.5, 129.9, 129.1, 127.6, 64.3, 54.5, 54.2, 48.8, 20.5, 20.0, 19.4, 16.0.

^{11}B NMR (96 MHz, Acetonitrile-d_3) δ_B 13.1.

IR (ATR, film): 1763, 1705, 1335, 1161, 1098, 667, 548, 409 cm^{-1}.

HRMS (ESI): Calculated for 493.15751 m/z, found 493.15793 m/z $[C_{23}H_{27}BN_2O_6S+Na]^+$.

6-methyl-2-(6-methyl-2-(phenylsulfonyl)isoindolin-5-yl)-1,3,6,2-dioxazaborocane-4,8-dione (22)



Prepared according to **General Procedure C** from 6-methyl-2-(prop-1-yn-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (19.5 mg, 100 µmol, 1.00 equiv.) and *N*,*N*-di(prop-2-yn-1-yl)benzenesulfonamide (140 mg, 600 µmol, 6.00 equiv.). Purified by flash column chromatography (silica, 0–20% MeCN in CH_2Cl_2) to yield the desired product as an off-white solid (41.2 mg, 96%).

^{1}H NMR (500 MHz, Acetone-d_6) δ_H 7.96 – 7.90 (m, 2H), 7.69 – 7.60 (m, 3H), 7.35 (s, 1H), 7.07 (s, 1H), 4.63 – 4.56 (m, 4H), 4.36 (d, J = 17.18 Hz, 2H), 4.15 (d, J = 17.17 Hz, 2H), 2.73 (s, 3H), 2.40 (s, 3H).

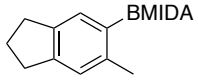
^{13}C NMR (126 MHz, Acetone-d_6) δ_C 168.4, 142.1, 137.4, 136.9, 133.2, 132.9, 129.3, 128.2, 127.6, 124.9, 62.6, 53.6, 53.5, 47.4, 22.2.

^{11}B NMR (96 MHz, Acetone-d_6) δ_B 12.3.

IR (ATR, film): 1763, 1339, 1296, 1165, 1098, 1032, 720, 608, 575 cm^{-1}.

HRMS (ESI): Calculated for 429.1286 m/z, found 429.1290 m/z $[C_{20}H_{21}BN_2O_6S+H]^+$.

6-methyl-2-(6-methyl-2,3-dihydro-1*H*-inden-5-yl)-1,3,6,2-dioxazaborocane-4,8-dione (23)



Prepared according to **General Procedure C** from 6-methyl-2-(prop-1-yn-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (19.5 mg, 100 µmol, 1.00 equiv.) and 1,6-heptadiyne (55.3 mg, 600 µmol, 6.00 equiv.). Purified by flash column chromatography (silica, 0–1% MeCN in CH_2Cl_2) followed by crystallisation form CH_2Cl_2:hexane:Et_2O to yield the desired product as an off-white solid (7.5 mg, 26%).

^{1}H NMR (500 MHz, Acetone-d_6) δ_H 7.31 (s, 1H), 7.02 (s, 1H), 4.33 (d, J = 17.10 Hz, 2H), 4.13 (d, J = 17.14 Hz, 2H), 2.82 (s, 4H), 2.75 (s, 3H), 2.38 (s, 3H), 2.03 – 1.97 (m, 2H).

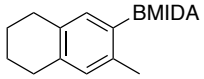
^{13}C NMR (126 MHz, Acetone-d_6) δ_C 168.5, 145.1, 140.6, 140.0, 129.7, 127.0, 62.6, 47.3, 32.4, 32.1, 25.1, 22.1.

^{11}B NMR (96 MHz, Acetone-d_6) δ_B 12.6.

IR (ATR, film): 3348, 1751m 1086, 1044, 880 cm^{-1}.

HRMS (ESI): Calculated for 288.1402 m/z, found 288.1398 m/z $[C_{15}H_{18}BNO_4+H]^+$.

6-methyl-2-(3-methyl-5,6,7,8-tetrahydronaphthalen-2-yl)-1,3,6,2-dioxazaborocane-4,8-dione (24)



Prepared according to **General Procedure C** from 6-methyl-2-(prop-1-yn-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (19.5 mg, 100 µmol, 1.00 equiv.) and 1,7-octadiyne (63.7 mg, 600 µmol, 6.00 equiv.). Purified by flash column chromatography (silica, 0–5% MeCN in CH_2Cl_2) followed by crystallisation form CH_2Cl_2:hexane:Et_2O to yield the desired product as an off-white solid (4.7 mg, 16%).

^{1}H NMR (500 MHz, Acetone-d_6) δ_H 7.15 (s, 1H), 6.85 (s, 1H), 4.34 (d, J = 17.15 Hz, 2H), 4.14 (d, J = 17.18 Hz, 2H), 2.77 (s, 3H), 2.75 – 2.64 (m, 4H), 2.35 (s, 3H), 1.77 (p, J = 3.22 Hz, 4H).

^{13}C NMR (126 MHz, Acetone-d_6) δ_C 168.5, 138.9, 137.6, 135.0, 133.3, 131.5, 62.5, 47.3, 28.8, 28.8, 23.4*, 23.2*, 21.7.

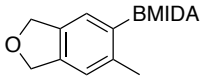
^{11}B NMR (96 MHz, Acetonitrile-d_3) δ_B 12.5.

IR (ATR, film): 1763, 1298, 1238, 1105, 1032, 993, 702, 540 cm^{-1}.

HRMS (ESI): Calculated for 302.1558 m/z, found 302.1568 m/z $[C_{16}H_{20}BNO_4+H]^+$.

*Overlap with solvent signal, presence confirmed by ^{1}H ^{13}C HSQC analysis.

6-methyl-2-(6-methyl-1,3-dihydroisobenzofuran-5-yl)-1,3,6,2-dioxazaborocane-4,8-dione (25)



Prepared according to **General Procedure C** from 6-methyl-2-(prop-1-yn-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (195 mg, 1.00 mmol, 1.00 equiv.) and propargyl ether (565 mg, 6.00 mmol, 6.00 equiv.). Purified by flash column chromatography (silica, 0–20% MeCN in CH_2Cl_2) followed by recrystallisation from CH_2Cl_2 and Et_2O to yield the desired product as an off-white solid (253 mg, 88%).

^{1}H NMR (500 MHz, Acetonitrile-d_3) δ_H 7.34 (s, 1H), 7.13 (s, 1H), 5.09 – 4.98 (m, 4H), 4.10 (d, J = 17.24 Hz, 2H), 3.93 (d, J = 17.21 Hz, 2H), 2.56 (s, 3H), 2.42 (s, 3H).

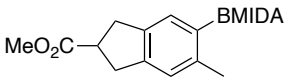
^{13}C NMR (126 MHz, Acetonitrile-d_3) δ_C 168.6, 141.6, 141.0, 136.6, 132.7, 126.5, 123.5, 72.8, 72.8, 62.6, 47.5, 22.1.

^{11}B NMR (96 MHz, Acetonitrile-d_3) δ_B 12.0.

IR (ATR, film): 1753, 1300, 1099, 1084, 1030, 856 cm^{-1}.

HRMS (ESI): Calculated for 290.1194 m/z, found 290.1202 m/z $[C_{14}H_{16}BNO_5+H]^+$.

methyl 5-methyl-6-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-2,3-dihydro-1*H*-indene-2-carboxylate (26)



Prepared according to **General Procedure C** from 6-methyl-2-(prop-1-yn-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (19.5 mg, 100 µmol, 1.00 equiv.) and methyl 2-(prop-2-yn-1-yl)pent-4-ynoate (90.1 mg, 600 µmol, 6.00 equiv.). Purified by flash column chromatography (silica, 0–15% MeCN in CH_2Cl_2) to yield the desired product as a yellow solid (22.2 mg, 64%).

^{1}H NMR (500 MHz, Acetonitrile-d_3) δ_H 7.27 (s, 1H), 7.06 (s, 1H), 4.24 – 4.03 (m, 2H), 3.92 (d, J = 17.23 Hz, 2H), 3.68 (s, 3H), 3.35 (appp, J = 8.12 Hz, 1H), 3.23 – 3.11 (m, 4H), 2.55 (s, 3H), 2.37 (s, 3H).

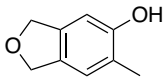
^{13}C NMR (126 MHz, Acetonitrile-d_3) δ_C 175.7, 168.7, 168.7, 143.3, 140.8, 138.8, 129.8, 127.0, 62.5, 62.5, 51.4, 47.5, 43.0, 35.8, 35.6, 22.1.

^{11}B NMR (96 MHz, Acetonitrile-d_3) δ_B 12.2.

IR (ATR, film): 1765, 1452, 1339, 1296, 1209, 1028, 849, 411 cm^{-1}.

HRMS (ESI): Calculated for 368.12759 *m*/*z*, found 368.12724 *m*/*z* $[C_{17}H_{20}BNO_6+Na]^+$.

6-methyl-1,3-dihydroisobenzofuran-5-ol (27)



A flask was charged with **25** (28.9 mg, 100 µmol, 1.00 equiv.) and THF (400 µL, 250 mM). K_3PO_4 (63.7 mg, 300 µmol, 3.00 equiv.) and H_2O_2 (30% in H_2O, 100 µL, 980 µmol, 9.80 equiv.) were added and the mixture was allowed to stir at RT for 16 h. The mixture was then quenched by the addition of sodium metabisulfite and then suspended between water and ethyl acetate. The aqueous layer was extracted with ethyl acetate (3 × 10 mL) and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo* to yield the crude product which was purified by flash column chromatography (silica, 0–100% CH_2Cl_2 in hexane) to yield the desired product as a white powder (11.8 mg, 79%).

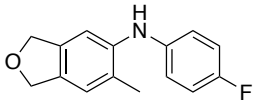
^{1}H NMR (500 MHz, Chloroform-*d*) δ_H 6.98 (s, 1H), 6.65 (s, 1H), 5.08 – 4.98 (m, 4H), 2.25 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 153.6, 138.2, 131.0, 123.2, 116.2, 107.5, 73.5, 73.4, 16.1.

IR (ATR, film): 3318, 2922, 1302, 1260, 1225, 1030, 893, 851 cm^{-1}.

HRMS (ESI): Calculated for 173.05730 *m*/*z*, found 173.05678 *m*/*z* $[C_9H_{10}O_2+Na]^+$.

***N*-(4-fluorophenyl)-6-methyl-1,3-dihydroisobenzofuran-5-amine (28)**



An oven-dried microwave vial was charged with **25** (28.9 mg, 100 µmol, 1.00 equiv.), $Cu(OAc)_2$ (23.6 mg, 130 µmol, 1.30 equiv.) and DMAP (15.9 mg, 130 µmol, 1.30 equiv.). The vial was capped and MeCN (200 µL, 500 mM) followed by 4-fluoroaniline (20.0 µL, 208 µmol, 2.08 equiv.). The mixture was heated to 80 ºC to stir for 36 h before allowing to cool, filtering through celite and diluting with CH_2Cl_2 and 10% aqueous ammonia. The mixture was extracted with CH_2Cl_2 (3 × 10 mL) and the organic layers were combined, dried over Na_2SO_4, filtered, and concentrated *in vacuo* to yield the crude product. This was purified by flash column chromatography (silica, 0–5% EtOAc in hexane) to yield the desired product as a yellow solid (8.0 mg, 33%)

^{1}H NMR (500 MHz, Chloroform-*d*) δ_H 7.09 (s, 1H), 7.04 – 6.93 (m, 5H), 5.29 (brs, 1H), 5.08 (m, 2H), 5.05 (m, 2H), 2.28 (s, 3H).

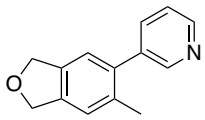
^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 157.9 (d, $^1J_{CF}$ = 239.8 Hz), 139.8 (d, $^4J_{CF}$ = 2.1 Hz), 138.0, 132.1, 126.7, 123.2, 120.2 (d, $^3J_{CF}$ = 7.7 Hz), 116.0 (d, $^2J_{CF}$ = 22.4 Hz), 109.9, 73.6, 73.4, 18.1.

^{19}F NMR (471 MHz, Chloroform-*d*) δ_F –122.58 (m).

IR (ATR, film): 1505, 1362, 1310, 1211, 1042, 895, 828, 783, 503, 488, 432 cm^{-1}.

HRMS (ESI): Calculated for 244.11322 *m*/*z*, found 244.11245 *m*/*z* $[C_{15}H_{14}FNO+H]^+$.

3-(6-methyl-1,3-dihydroisobenzofuran-5-yl)pyridine (29)



An oven dried microwave vial was charged with **25** (28.9 mg, 100 µmol, 1.00 equiv.), [Pd(dppf)]Cl_2 (2.9 mg, 4.00 µmol, 4.00 mol%) and K_3PO_4 (63.7 mg, 300 µmol, 3.00 equiv.). The vial was capped, evacuated and backfilled with nitrogen and then 3-bromopyridine (15.0 µL, 154 µmol, 1.54 equiv.), water (25.0 µL, 302 µmol, 3.02 equiv.) and THF (400 µL, 250 mM) were added. The mixture was heated to 90 ºC to stir for 24 h before cooling to RT and diluting with EtOAc and water. The aqueous layer was extracted with EtOAc (3 × 10 mL) and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo* to yield the crude product which was purified by flash column chromatography (silica, 1:99 NEt_3:hexane – 1:20:79 NEt_3:EtOAc:hexane) to yield the desired product as a white solid (10.2 mg, 48%).

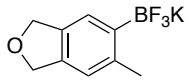
^{1}H NMR (500 MHz, Chloroform-*d*) δ_H 8.65 (brm 2H), 7.67 (dt, *J* = 7.91, 1.61 Hz, 1H), 7.40 (t, *J* = 6.23 Hz, 1H), 7.21 (s, 1H), 7.11 (s, 1H), 5.16 (m, 4H), 2.29 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 150.0, 148.2, 139.3, 137.6, 137.4, 137.2, 136.5, 134.9, 123.2, 122.9, 122.3, 73.4, 73.4, 20.5.

IR (ATR, film): 2922, 2853, 1765, 1472, 1454, 1404, 1364, 1049, 1011, 901, 872, 812, 718 cm^{-1}.

HRMS (ESI): Calculated for 212.10699 *m*/*z*, found 212.10626 *m*/*z* $[C_{14}H_{13}NO+H]^+$.

trifluoro(6-methyl-1,3-dihydroisobenzofuran-5-yl)-λ4-borane, potassium salt (30)



A flask was charged with **25** (28.9 mg, 100 µmol, 1.00 equiv.) and methanol (4.00 mL, 25.0 mM). KHF_2 (4.5 M in H_2O, 90.0 µL, 405 µmol, 4.05 equiv.) was added and the solution was heated to 70 ºC for 2 h. After cooling to RT, the solvent was removed *in vacuo* and the mixture was suspended in hot acetone then filtered. The filtrate was reconcentrated *in vacuo* and the crude product was recrystallised from acetone and hexane to yield the desired product as a white crystalline solid (19.3 mg, 80%)

^{1}H NMR (500 MHz, Acetone-d_6) δ_H 7.38 (s, 1H), 6.83 (s, 1H), 4.91 (m, 4H), 2.43 (s, 3H).

^{13}C NMR (126 MHz, Acetone-d_6) δ_C 140.3, 135.9, 133.9, 124.0, 120.4, 73.1, 73.0, 21.3.

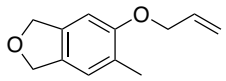
^{11}B NMR (96 MHz, Acetone-d_6) δ_B 3.6 (q, *J* = 59.2 Hz).

^{19}F NMR (471 MHz, Acetone-d_6) δ_F –140.66 (m).

IR (ATR, film): 1404, 1194, 1171, 1076, 1044, 1036, 1001, 953, 934, 918, 901, 887, 858, 610 cm^{-1}.

HRMS (ESI): Calculated for 201.0699 *m*/*z*, found 201.0700 *m*/*z* $[C_9H_9BF_3]^-$.

5-(allyloxy)-6-methyl-1,3-dihydroisobenzofuran (31)



An oven dried microwave vial was charged with **25** (28.9 mg, 100 µmol, 1.00 equiv.), $Cu(OAc)_2$ (23.6 mg, 130 µmol, 1.30 equiv.) and DMAP (15.9 mg, 130 µmol, 1.30 equiv.). The vial was capped and MeCN (200 µL, 500 mM) followed by allyl alcohol (14.0 µL, 206 µmol, 2.06 equiv.) were added. The mixture was heated to 80 ºC to stir for 36 h before allowing to cool, filtering through celite and diluting with CH_2Cl_2 and 10% aqueous ammonia. The mixture was extracted with CH_2Cl_2 (3 × 10 mL) and the organic layers were combined, dried over Na_2SO_4, filtered and concentrated *in vacuo* to yield the crude product. This was purified by flash column chromatography (silica, 0–3% EtOAc in hexane) to yield the desired product as a white solid (7.5 mg, 39%).

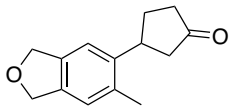
^{1}H NMR (500 MHz, Chloroform-*d*) δ_H 7.03 (s, 1H), 6.71 (s, 1H), 6.10 (ddt, *J* = 17.29, 10.32, 4.99 Hz, 1H), 5.46 (dq, *J* = 17.31, 1.70 Hz, 1H), 5.35 – 5.29 (m, 1H), 5.10 – 5.08 (m, 2H), 5.08 – 5.06 (m, 2H), 4.56 (dt, *J* = 5.03, 1.67 Hz, 2H), 2.28 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 156.5, 137.5, 133.5, 130.5, 126.4, 122.8, 117.1, 104.1, 73.8, 73.5, 69.0, 16.6.

IR (ATR, film): 2924, 2853, 1497, 1281, 1206, 1049, 419 cm^{-1}.

HRMS (ESI): Calculated for 189.0910 *m*/*z*, found 189.0912 *m*/*z* $[C_{12}H_{14}O_2-H]^+$.

3-(6-methyl-1,3-dihydroisobenzofuran-5-yl)cyclopentan-1-one (32)



An oven dried microwave vial was charged with **25** (28.9 mg, 100 µmol, 1.00 equiv.), K_3PO_4 (42.5 mg, 200 µmol, 2.00 equiv.) and $[Rh(COD)(NCMe)_2]BF_4$ (1.90 mg, 5.00 µmol, 5.00 mol%) then capped, evacuated and backfilled with nitrogen. Toluene (900 µL), H_2O (150 µL) and 2-cyclopenten-1-one (17.0 µL, 203 µmol, 2.03 equiv.) were added and the mixture was heated to 100 ºC for 24 h. The reaction flask was allowed to cool before adding saturated aqueous $NaHCO_3$. The mixture was extracted with EtOAc (3 × 10 mL) and the combined organic layers were dried over Na_2SO_4, filtered and concentrated *in vacuo* to yield the crude product which was purified by flash column chromatography (silica, 0–20% EtOAc in hexane) to yield the product as a white solid (9.2 mg, 43%)

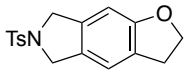
^{1}H NMR (500 MHz, Chloroform-*d*) δ_H 7.12 (s, 1H), 7.10 (s, 1H), 5.11 – 5.06 (m, 4H), 3.69 – 3.60 (m, 1H), 2.71 – 2.65 (m, 1H), 2.55 – 2.47 (m, 1H), 2.45 – 2.25 (m, 6H), 2.07 – 1.98 (m, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 218.5, 140.3, 137.5, 137.2, 135.2, 123.0, 117.3, 73.5, 73.4, 45.5, 38.5, 38.3, 30.2, 19.9.

IR (ATR, film): 2853, 1736, 1153, 1040, 901, 866, 419 cm^{-1}.

HRMS (ESI): Calculated for 239.10425 *m*/*z*, found 239.10349 *m*/*z* $[C_{14}H_{16}O_2+Na]^+$.

6-tosyl-3,5,6,7-tetrahydro-2*H*-furo[2,3-*f*]isoindole (33)



A flask was charged with **10** (58.7 mg, 100 µmol, 1.00 equiv.) and THF (500 µL, 200 mM). Pyridine-HF (70% HF, 100 µL, 1.11 mmol, 11.1 equiv.) was added and the mixture was allowed to stir for 1 h at RT. One drop of water was then added followed by the addition of excess $NaHCO_3$. Excess Na_2SO_4 was added, and the mixture was suspended in acetone then filtered. The filtrated was concentrated *in vacuo* then transferred to an oven-dried microwave vial with $Cu(OAc)_2$ (23.6 mg, 130 µmol, 1.30 equiv.) and DMAP (15.9 mg, 130 µmol, 1.30 equiv.). The vial was capped and MeCN (200 µL, 500 mM) was added then the mixture was heated to 80 ºC to stir for 24 h before allowing to cool, filtering through celite and diluting with CH_2Cl_2 and 10% aqueous ammonia. The mixture was extracted with CH_2Cl_2 (3 × 10 mL) and the organic layers were combined, dried over Na_2SO_4, filtered, and concentrated *in vacuo* to yield the crude product. This was purified by flash column chromatography (silica, 0–3% EtOAc in hexane) to yield the desired product as a white solid (23.3 mg, 74%).

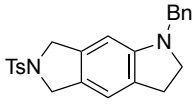
^{1}H NMR (500 MHz, Chloroform-*d*) δ_H 7.78 (d, *J* = 8.16 Hz, 2H), 7.33 (d, *J* = 8.02 Hz, 2H), 6.97 (s, 1H), 6.57 (s, 1H), 4.63 – 4.51 (m, 6H), 3.16 (t, *J* = 8.63 Hz, 2H), 2.42 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 160.2, 143.5, 135.9, 134.0, 129.8, 127.7, 127.6, 127.3, 118.9, 103.5, 71.7, 53.7, 53.3, 29.5, 21.5.

IR (ATR, film): 1339, 1161, 1096, 1059, 665, 602, 550 cm^{-1}.

HRMS (ESI): Calculated for 338.08214 *m*/*z*, found 338.08115 *m*/*z* $[C_{17}H_{17}NO_3S+Na]^+$.

1-benzyl-6-tosyl-1,2,3,5,6,7-hexahydropyrrolo[3,4-*f*]indole (34)



An oven-dried microwave vial was charged with **15** (65.2 mg, 100 μmol, 1.00 equiv.) and palladium on carbon (10%, 10.6 mg, 10.0 μmol, 10.0 mol%) before sealing, evacuating, and backfilling with nitrogen. A hydrogen balloon was then added followed by dioxane (500 μL, 200 mM) and acetic acid (120 μL, 2.09 mmol, 20.9 equiv.). The mixture was heated to 80 ºC and stirred under an atmosphere of hydrogen for 16 h before allowing to cool to RT, diluting with acetone, filtering through celite and concentrating *in vacuo* to yield the crude. This was transferred to another oven-dried microwave vial and $Cu(OAc)_2$ (26.0 mg, 130 μmol, 1.30 equiv.) and DMAP (15.9 mg, 130 μmol, 1.30 equiv.) were added. The vial was sealed and MeCN (200 μL, 500 mM) was added, and the mixture was heated to 80 ºC to stir for 24 h. After this period, the mixture was cooled to RT and diluted with CH_2Cl_2. This was filtered through celite, and 10% aqueous ammonia solution was added. This was extracted with CH_2Cl_2 (3 × 10 mL) and the organic layers were combined, dried over Na_2SO_4, filtered, and concentrated *in vacuo* to yield the crude product which was purified by flash column chromatography (silica, 0–20% EtOAc in hexane) to yield the desired product as a pale-yellow solid (3.3 mg, 8%).

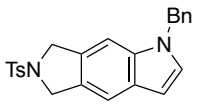
^{1}H NMR (500 MHz, Chloroform-*d*) δ_H 7.80 – 7.74 (m, 2H), 7.40 – 7.30 (m, 7H), 6.87 (s, 1H), 6.24 (s, 1H), 4.52 (m, 4H), 4.21 (s, 2H), 3.34 (t, J = 8.25 Hz, 2H), 2.93 (t, J = 8.24 Hz, 2H), 2.42 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 152.8, 143.5, 138.0, 135.1, 133.8, 130.6, 129.7, 128.6, 127.7, 127.6, 127.3, 124.6, 118.6, 100.6, 54.0, 54.0, 53.5, 53.5, 28.2, 21.5.

IR (ATR, film): 2922, 2361, 1344, 1161, 1096, 667, 550, 405 cm^{-1}.

HRMS (ESI): Calculated for 404.1559 *m*/*z*, found 404.1551 *m*/*z* $[C_{24}H_{24}N_2O_2S]^+$.

1-benzyl-6-tosyl-1,5,6,7-tetrahydropyrrolo[3,4-*f*]indole (35)



Prepared from same procedure as **34**. Purified by flash column chromatography (silica, 0–20% EtOAc in hexane) to yield the desired product as a yellow solid (15.6 mg, 38%).

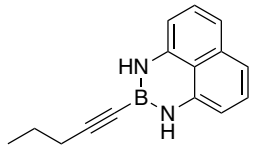
^{1}H NMR (500 MHz, Chloroform-*d*) δ_H 7.79 – 7.73 (m, 2H), 7.39 – 7.38 (m, 1H), 7.32 – 7.23 (m, 5H), 7.12 (d, J = 3.21 Hz, 1H), 7.06 – 7.03 (m, 2H), 7.02 – 7.00 (m, 1H), 6.48 (dd, J = 3.18, 0.84 Hz, 1H), 5.29 – 5.25 (m, 2fH), 4.68 – 4.66 (m, 2H), 4.66 – 4.63 (m, 2H), 2.38 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 143.5, 137.2, 136.2, 133.6, 130.3, 129.7, 129.3, 128.9, 128.9, 127.8, 127.7, 127.7, 126.6, 114.4, 103.5, 101.5, 53.6, 53.3, 50.2, 21.5.

IR (ATR, film): 2922, 1716, 1341, 1161, 1096, 667 cm^{-1}.

HRMS (ESI): Calculated for 425.12942 *m*/*z*, found 425.12839 *m*/*z* $[C_{24}H_{22}N_2O_2S+Na]^+$.

2-(pent-1-yn-1-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (36)



Prepared according to a modified **General Procedure A:** flame-dried flask was charged with 1-pentyne (300 μL, 3.04 mmol, 1.00 equiv) and THF (10.0 mL, ~300 mM) and cooled to −78 ºC. *n*-Butyllithium solution (2.27 M in hexane, 1.80 mL, 4.08 mmol, 1.34 equiv) was added dropwise and the resulting solution was allowed to stir for 1 h. Triisopropylborate (700 μL, 3.04 mmol, 1.00 equiv) was added and the mixture was stirred at −78 ºC for a further 2 h. HCl (2.0 M in Et_2O, 1.60 mL, 3.20 mmol, 1.05 equiv) was added and the solution was allowed to come up to RT to stir for 0.5 h. The magnetic stirrer was removed and the mixture was concentrated *in vacuo* and the resulting solution was suspended in MTBE (~ 10 mL) and then filtered through celite. The mixture was reconcentrated *in vacuo* to yield the crude diisopropyl boronic ester which was dissolved in PhMe (15.0 mL, ~200 mM) and 1,8-diaminonaphthalene (481 mg, 3.04 mmol, 1.00 equiv). The mixture was then stirred at 120 ºC for 1 h before concentrating *in vacuo* to yield the crude product which was purified by flash column chromatography (silica, 0–5% EtOAc in hexane) to yield the desired product as a white solid (320.2 mg, 42%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ_H 7.10 (dd, *J* = 8.31, 7.25 Hz, 2H), 7.03 (dd, *J* = 8.32, 1.02 Hz, 2H), 6.30 (dd, *J* = 7.26, 1.04 Hz, 2H), 5.88 – 5.73 (m, 2H), 2.30 (t, *J* = 7.07 Hz, 2H), 1.62 (h, *J* = 7.24 Hz, 2H), 1.06 (t, *J* = 7.38 Hz, 3H).

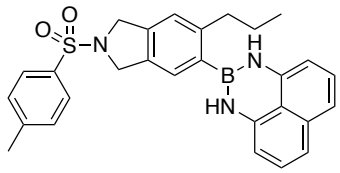
^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 140.8, 136.3, 127.5, 119.8, 117.8, 105.7, 78.7, 21.9, 21.6, 13.6.

^{11}B NMR (96 MHz, Chloroform-*d*) δ_B 21.9.

IR: (ATR, film): 3385, 2201, 1597, 1506, 1406, 1371, 1329, 1196, 1071, 820, 764, 658 cm^{-1}

HRMS (ESI): Calculated for 235.1401 *m*/*z*, found 245.1402 *m*/*z* $[C_{15}H_{15}BN_2+H]^+$.

2-(6-propyl-2-tosylisoindolin-5-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (37)



Prepared according to **General Procedure C** from 2-(pent-1-yn-1-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (25.0 mg, 100 µmol, 1.00 equiv.) and 4-methyl-*N*,*N*-di(prop-2-yn-1-yl)benzenesulfonamide (148 mg, 600 µmol, 6.00 equiv.). Purified by flash column chromatography (silica, 0–30% Et_2O in hexane) to yield the desired product as a white solid (25.7 mg, 53%).

^{1}H NMR (500 MHz, Acetonitrile-d_3) δ_H 7.27 (s, 1H), 7.06 (s, 1H), 4.24 – 4.03 (m, 2H), 3.92 (d, *J* = 17.23 Hz, 2H), 3.68 (s, 3H), 3.35 (app p, *J* = 8.12 Hz, 1H), 3.23 – 3.11 (m, 4H), 2.55 (s, 3H), 2.37 (s, 3H).

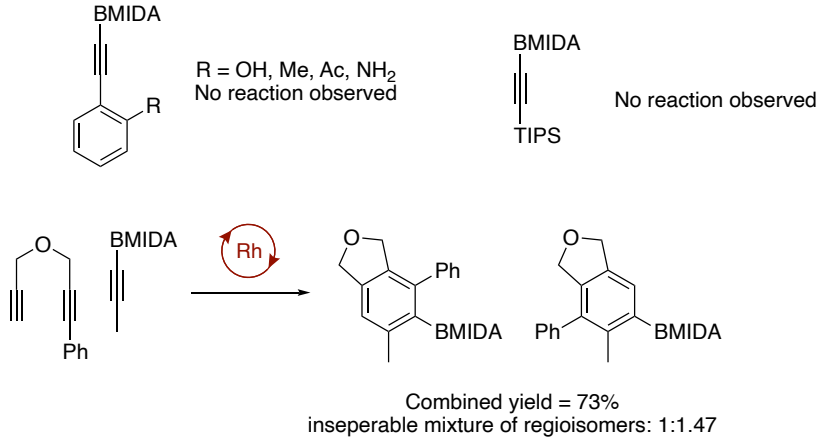
^{13}C NMR (126 MHz, Acetonitrile-d_3) δ_C 175.7, 168.7, 168.7, 143.3, 140.8, 138.8, 129.8, 127.0, 62.5, 62.5, 51.4, 47.5, 43.0, 35.8, 35.6, 22.1.

^{11}B NMR (96 MHz, Acetonitrile-d_3) δ_B 12.2.

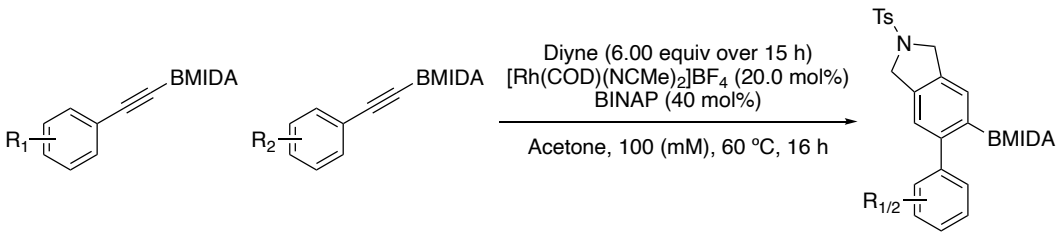
IR (ATR, film): 1597, 1512, 1416, 1398, 1327, 1319, 1159, 1096, 820, 768, 667, 548 cm^{-1}.

HRMS (ESI): Calculated for 481.1990 *m*/*z*, found 481.2003 *m*/*z* $[C_{28}H_{28}BN_3O_2S]^+$.

Failed examples



5. General Procedure for Electronic Competition Experiments



An oven-dried microwave vial was charged with the relevant BMIDA alkyne (50.0 µmol, 0.50 equiv) and its competing partner BMIDA alkyne (50.0 µmol, 0.50 equiv). $[Rh(COD)(NCMe)_2]BF_4$ (7.6 mg, 20.0 µmol, 20.0 mol%), and BINAP (24.9 mg, 40.0 µmol, 40.0 mol%) were added and the vial was capped, evacuated and backfilled with nitrogen. Acetone (0.5 mL) was added to the vial and then heated to 60 ºC. A separate flask was charged with 4-methyl-*N*,*N*-di(prop-2-yn-1-yl)benzenesulfonamide (148 mg, 600 µmol, 6.00 equiv) and acetone (0.5 mL) was added. The diyne solution was added *via* syringe pump over 15 h and the final solution was stirred for 1 h before allowing to cool to RT, filtering through celite and concentrating *in vacuo* to yield the crude mixture. 1,4-dinitrobenzene (4.8 mg, 25.0 µmol, 0.25 equiv) added and d_6-acetone was added until the mixture was homogeneous, then a sample was taken for quantitative NMR analysis to determine the product ratio.

Table 1: Electronic competition experiments results[12]

Entry	R_1	R_2	$\sigma(R_1)$	$\sigma(R2)$	$\Delta\sigma$	NMR yield (R_1)	NMR yield (R_2)	Ratio (R_1/R_2)
1	H	4-OMe	0	-0.27	0.27	38	39	0.9744
2	4-OAc	H	0.31	0	0.31	26	29	0.8966
3	4-OAc	4-OMe	0.31	-0.27	0.58	37	39	0.9487
4	3-Ac	H	0.38	0	0.38	12	15	0.8000
5	3-Ac	4-OMe	0.38	-0.27	0.65	15	16	0.9375
6	3-Ac	4-OAc	0.38	0.31	0.07	53	58	0.9138

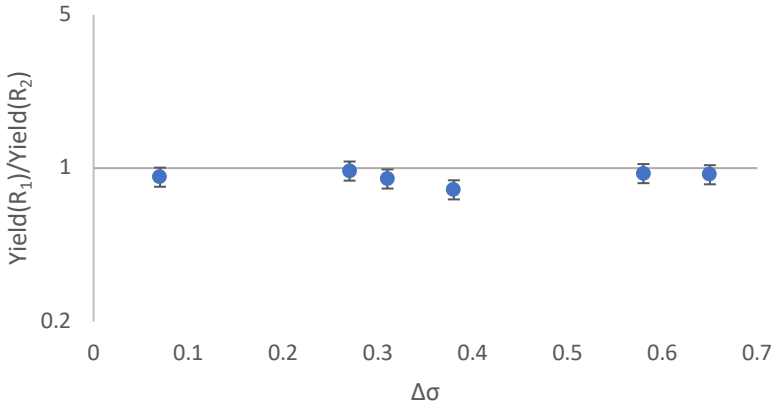
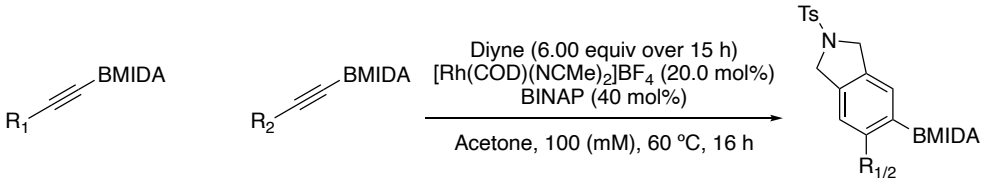


Figure 1: Electronic competition experiments results.

6. General Procedure for Steric Competition Experiments



An oven-dried microwave vial was charged with the relevant BMIDA alkyne (50.0 µmol, 0.50 equiv) and its competing partner BMIDA alkyne (50.0 µmol, 0.5 equiv). $[Rh(COD)(NCMe)_2]BF_4$ (7.6 mg, 20.0 µmol, 20.0 mol%), and BINAP (24.9 mg, 40.0 µmol, 40.0 mol%) were added and the vial was capped, evacuated, and backfilled with nitrogen. Acetone (0.5 mL) was added to the vial and then heated to 60 ºC. A separate flask was charged with 4-methyl-*N*,*N*-di(prop-2-yn-1-yl)benzenesulfonamide (148 mg, 600 µmol, 6.00 equiv) and acetone (0.5 mL) was added. The diyne solution was added *via* syringe pump over 15 h and the final solution was stirred for 1 h before allowing to cool to RT, filtering through celite and concentrating *in vacuo* to yield the crude mixture. 1,4-dinitrobenzene (4.8 mg, 25.0 µmol, 0.25 equiv) was added and d_6-acetone was added until the mixture was homogeneous, then a sample was taken for quantitative NMR analysis to determine the product ratio.

Table 2: Steric competition experiments results[13–16]

Entry	R_1	R_2	$A(R_1)$	$A(R_2)$	ΔA	NMR yield (R_1)	NMR yield (R_2)	Ratio (R_1/R_2)
1	Me	*c*-Pr	1.7	2.15	0.45	37	31	1.19354839
2	Me	Ph	1.7	3	1.3	50	20	2.5
3	*c*-Pr	Ph	2.15	3	0.85	46	27	1.7037037
4	Me	*n*-Pr	1.7	1.8	0.1	39	30	1.3
5	*n*-Pr	*c*-Pr	1.8	2.15	0.35	30	21	1.42857143
6	*n*-Pr	Ph	1.8	3	1.2	24	16	1.5

Assumed A(*c*-Pr) = A(*i*-Pr) = 2.15; A(*n*-Pr) = A(Et) = 1.8.

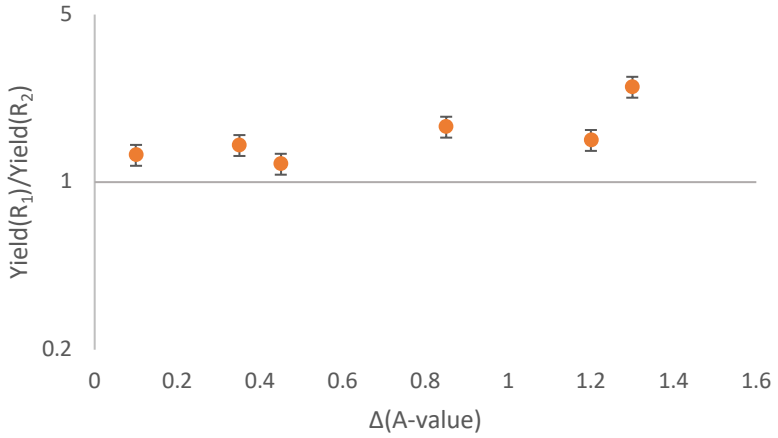


Figure 2: Steric competition experiments results.

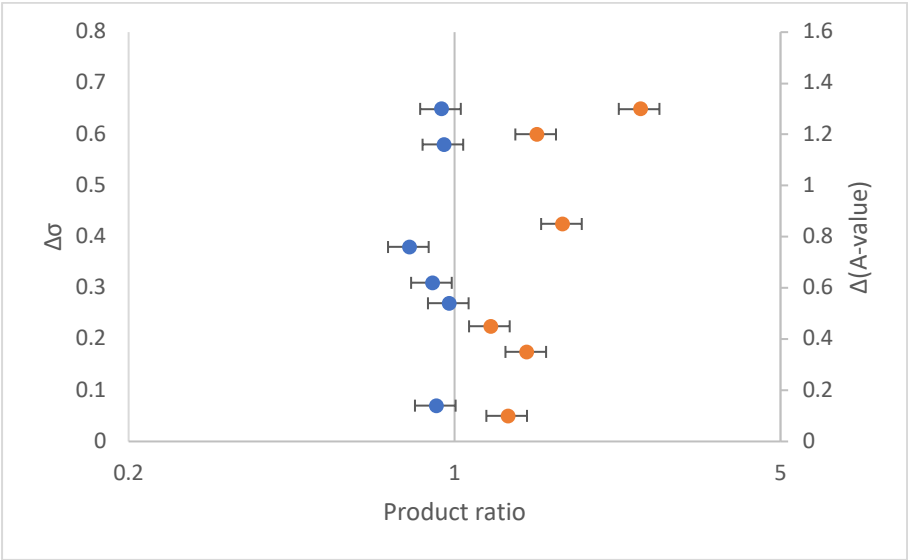


Figure 3: Combined data results from **Figures 1** and **2**.

7. X-ray Diffraction Data

X-ray diffraction data for compound **18** were collected at 173 K using a Rigaku MM-007HF High Brilliance RA generator/confocal optics with XtaLAB P200 diffractometer [Cu Kα radiation (λ = 1.54187 Å)]. Data for compounds **25** and **33** were collected at 173 K using a Rigaku FR-X Ultrahigh Brilliance Microfocus RA generator/confocal optics with XtaLAB P200 diffractometer [Mo Kα radiation (λ = 0.71075 Å)]. Intensity data for all compounds were collected using ω steps accumulating area detector images spanning at least a hemisphere of reciprocal space. Data were collected using CrystalClear[17] or CrysAlisPro[18] and processed (including correction for Lorentz, polarization and absorption) using CrysAlisPro. The structure was solved by direct (SIR2011[19]) or dual-space (SHELXT[20]) methods and refined by full-matrix least-squares against F^2 (SHELXL-2013[21]). Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using a riding model. The structure of **33** showed disorder in the orientation of the tricyclic ring system which was modelled over two sites with occupancies of 0.55:0.45. Restraints to bond distances and to thermal motion were used for the disordered atoms. All calculations were performed using the Olex2[22] interface. Selected crystallographic data are presented in Table S#. Deposition numbers 2181492-2181494 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Table 2: Selected crystallographic data.

	18	**25**	**33**
formula	$C_{22}H_{26}BNO_6$	$C_{17}H_{22}BNO_6$	$C_{17}H_{17}NO_3S$
fw	411.25	347.16	315.37
crystal description	Colourless plate	Colourless prism	Colourless plate
crystal size [mm^3]	0.15×0.04×0.01	0.07×0.04×0.02	0.30×0.24×0.03
space group	*Pc*	$P2_1/c$	$P2_1/c$
a [Å]	15.3311(2)	13.1060(4)	15.1250(4)
b [Å]	10.06926(11)	9.9589(3)	7.7985(2)
c [Å]	13.62417(19)	13.1775(5)	12.6248(3)
β [°]	101.3120(13)	91.771(4)	95.692(2)
vol [Å]^3	2062.35(5)	1719.14(10)	1481.78(7)
Z	4	4	4
ρ (calc) [g/cm^3]	1.324	1.341	1.414
μ [mm^{-1}]	0.782	0.100	0.231
F(000)	872	736	664
reflections collected	29685	11853	19815
independent reflections (R_{int})	7388 (0.0267)	3951 (0.0257)	3514 (0.0405)
parameters, restraints	549, 2	230, 0	300, 380
GOF on F^2	1.061	1.034	0.0986
R_1 [$I > 2\sigma(I)$]	0.0430	0.0402	0.0393
wR_2 (all data)	0.1224	0.1031	0.1017
largest diff. peak/hole [e/Å^3]	0.498, -0.184	0.295, -0.164	0.299, -0.339
Flack parameter	-0.04(7)	-	-

8. References

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9. Spectra

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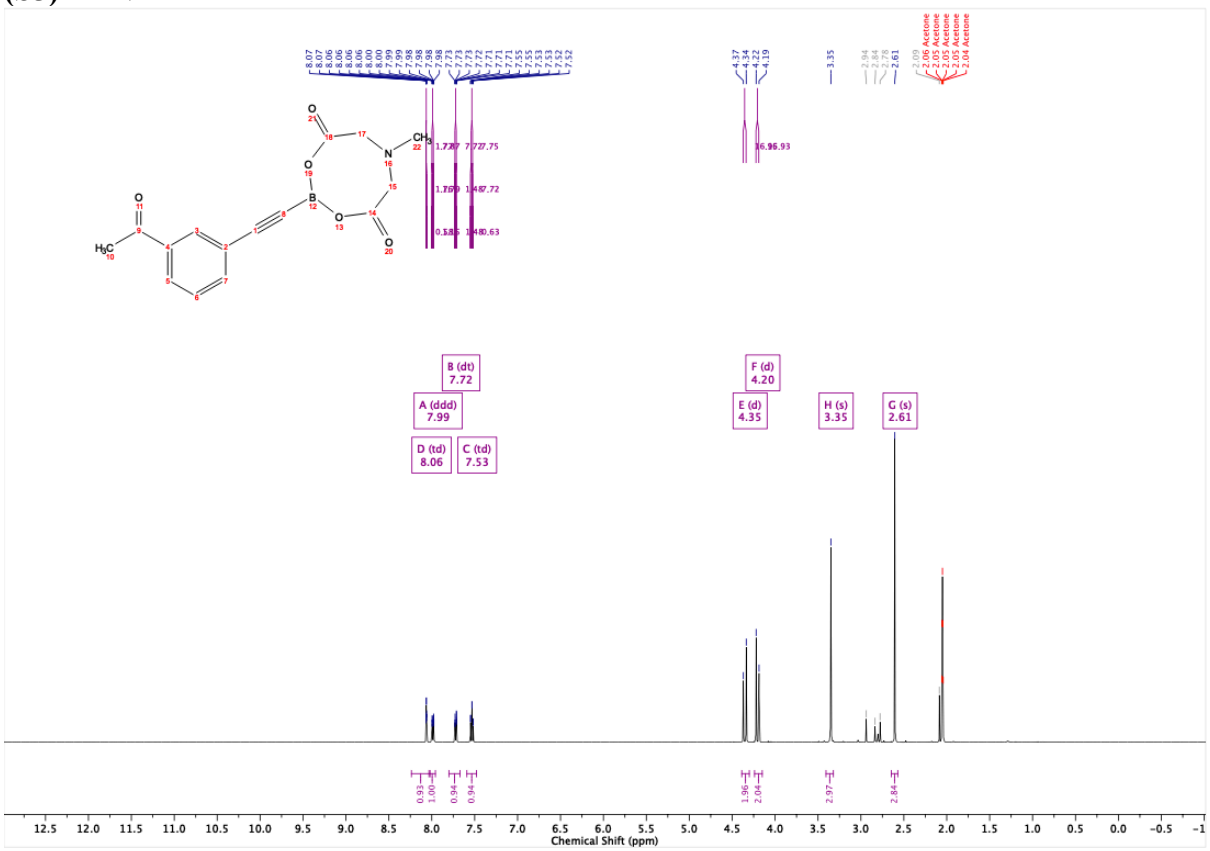

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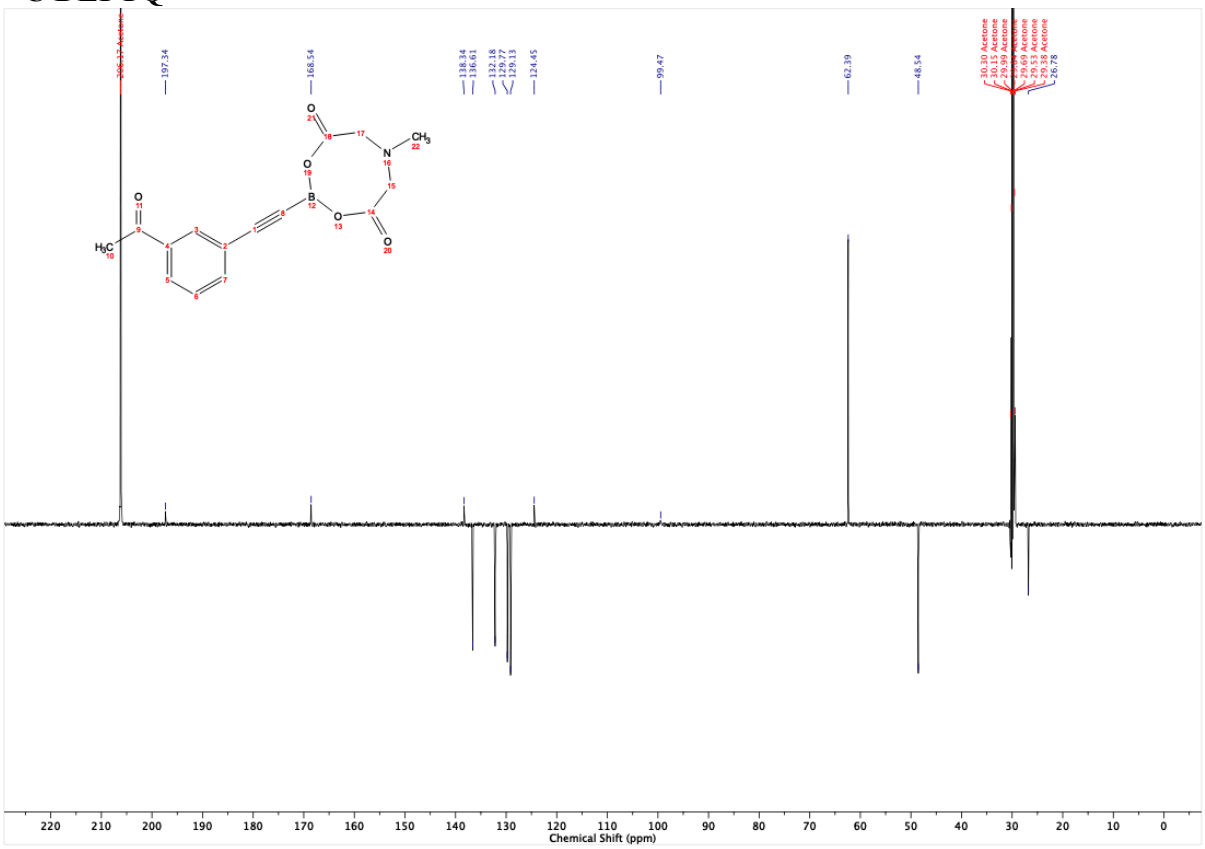

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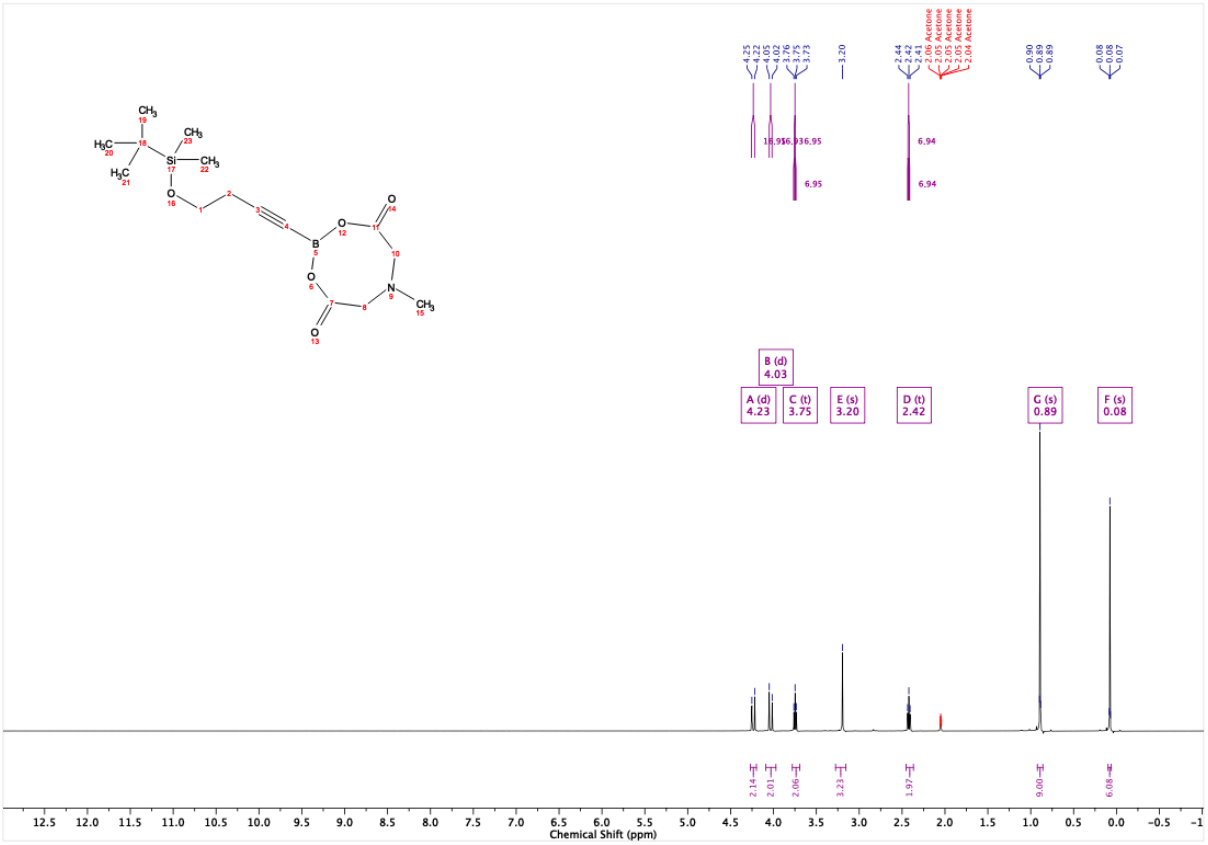
B (d)
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A (d)
4.23
C (t)
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E (s)
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D (t)
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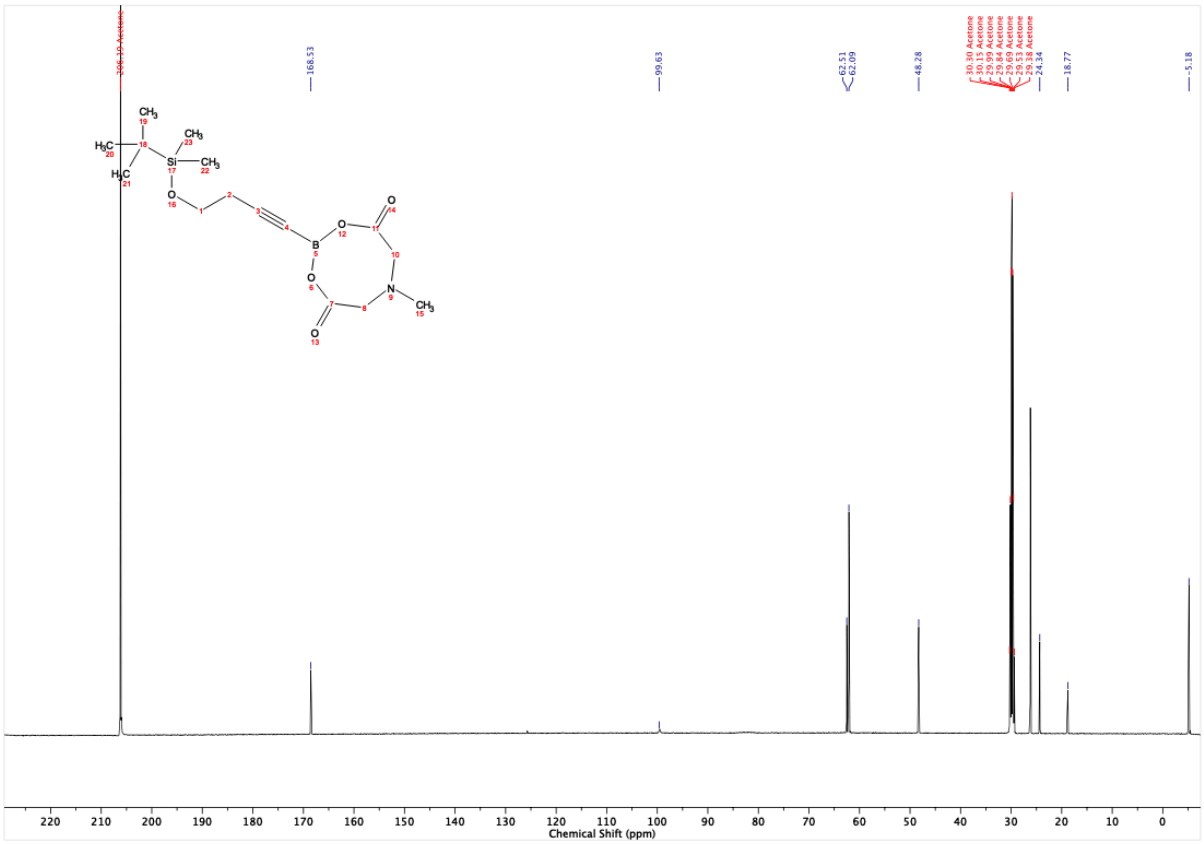
G (s)
0.89
F (s)
0.08
Chemical Shift (ppm)

^{13}C


Chemical Shift (ppm)

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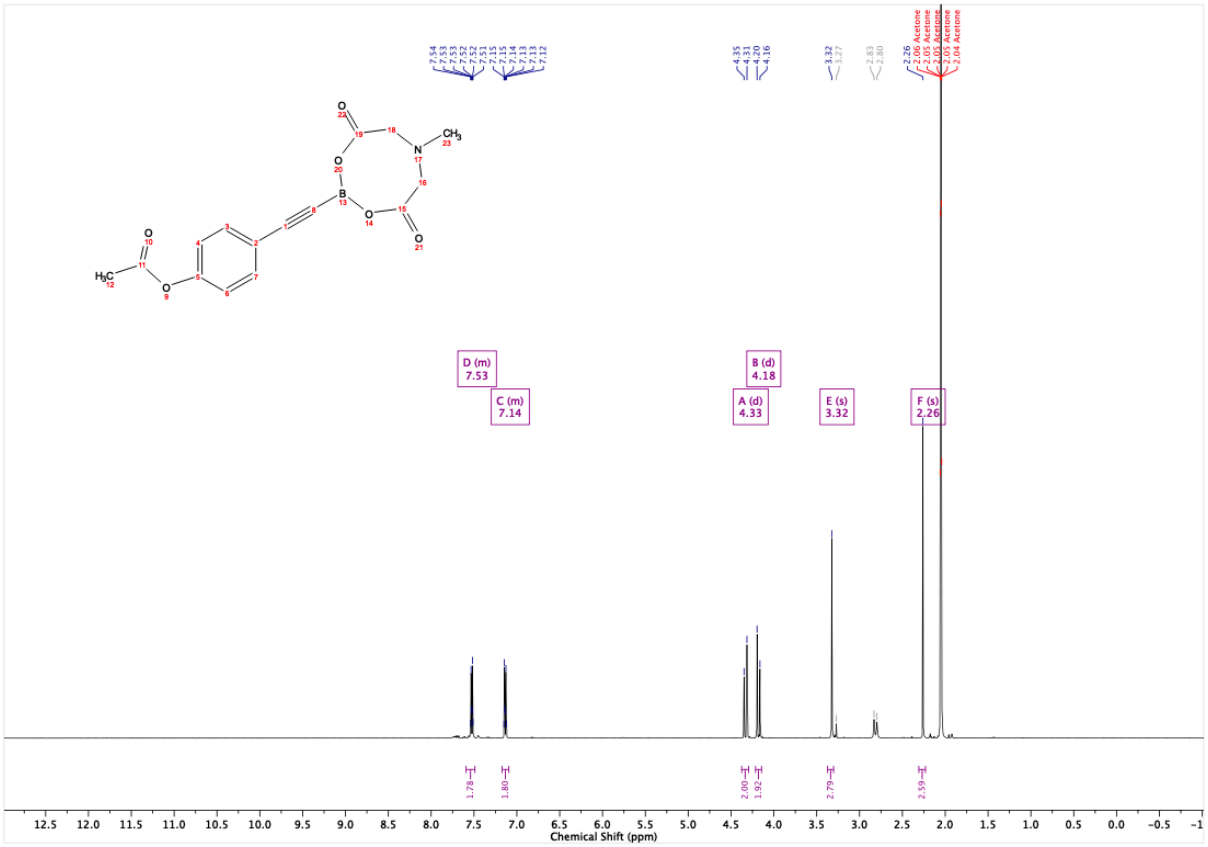

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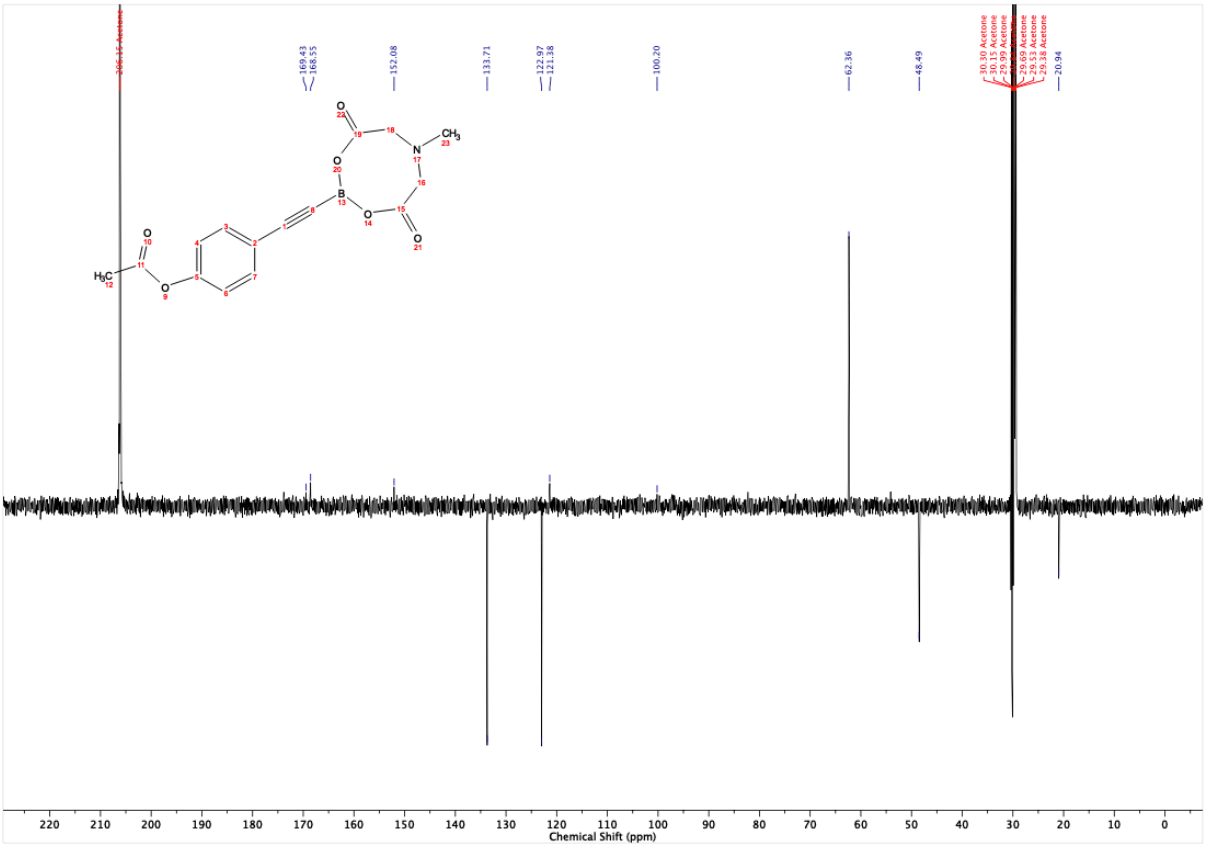

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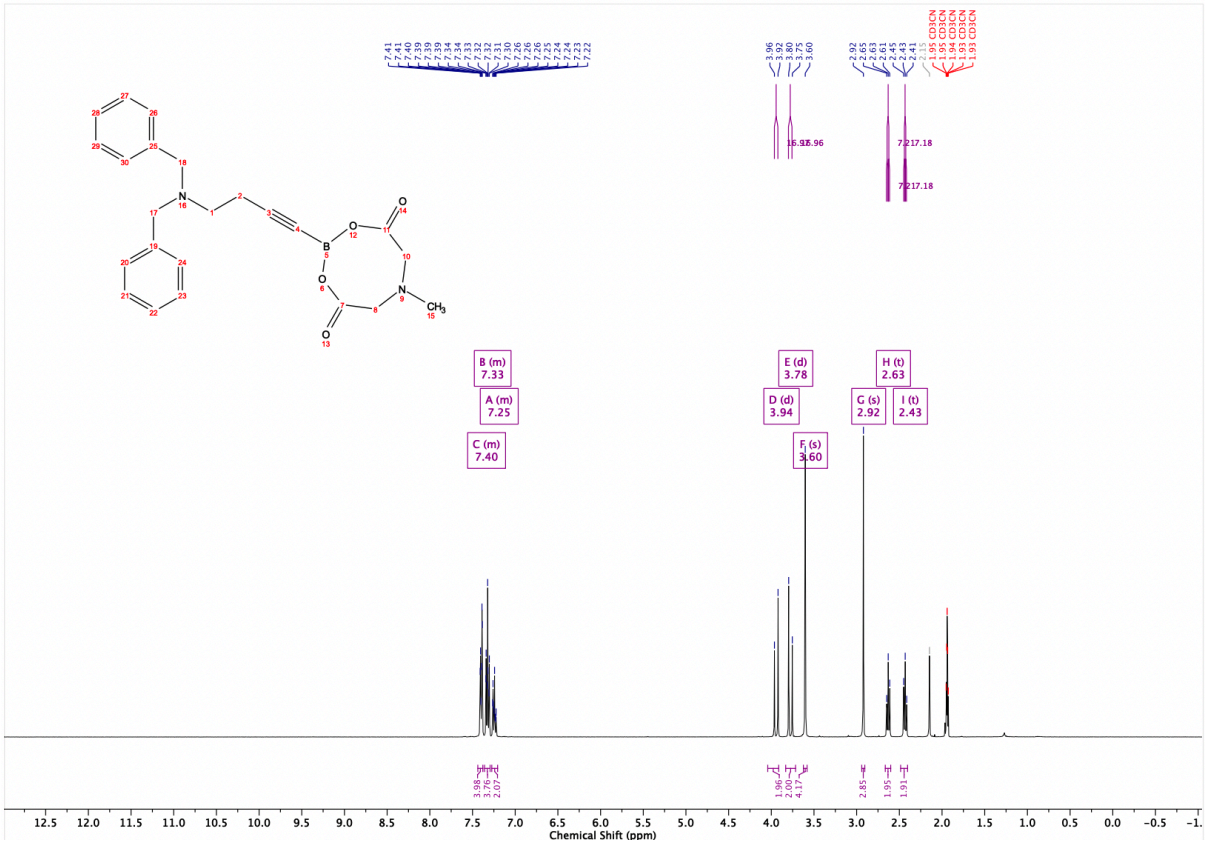

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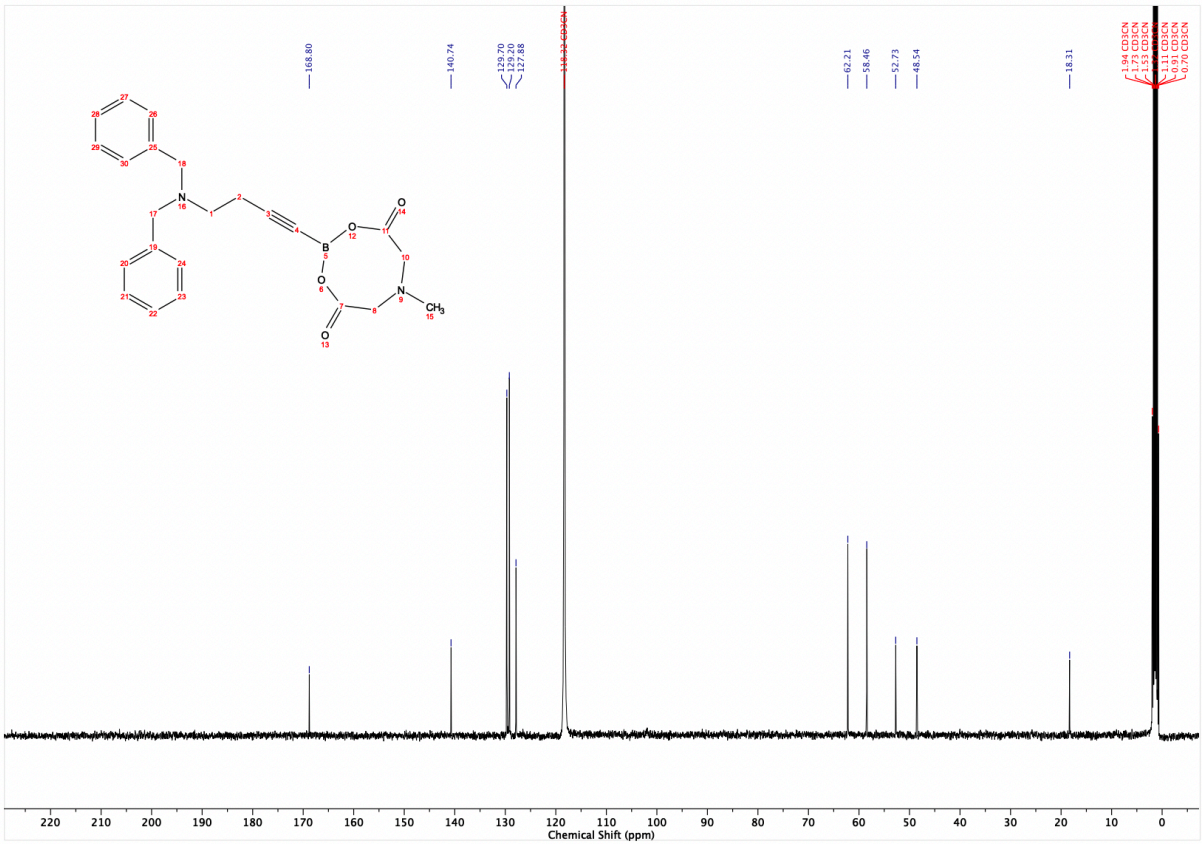

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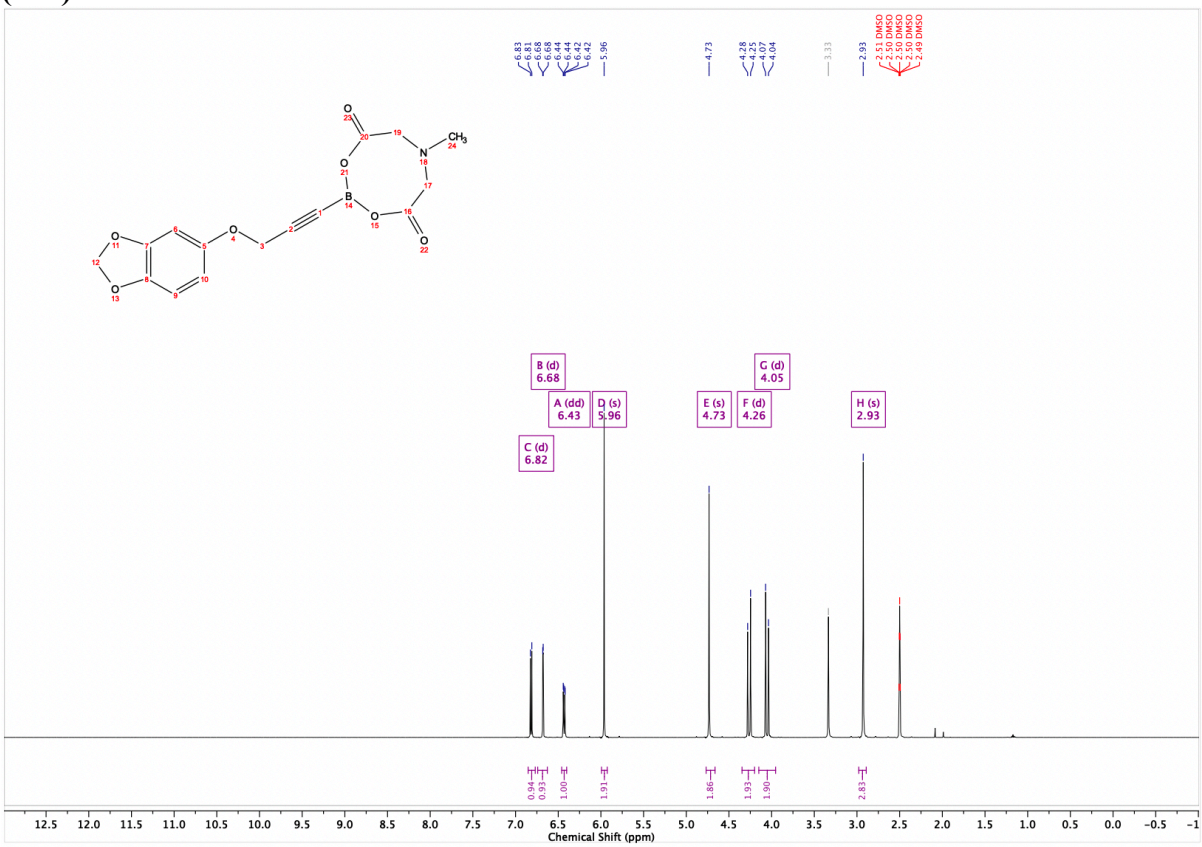

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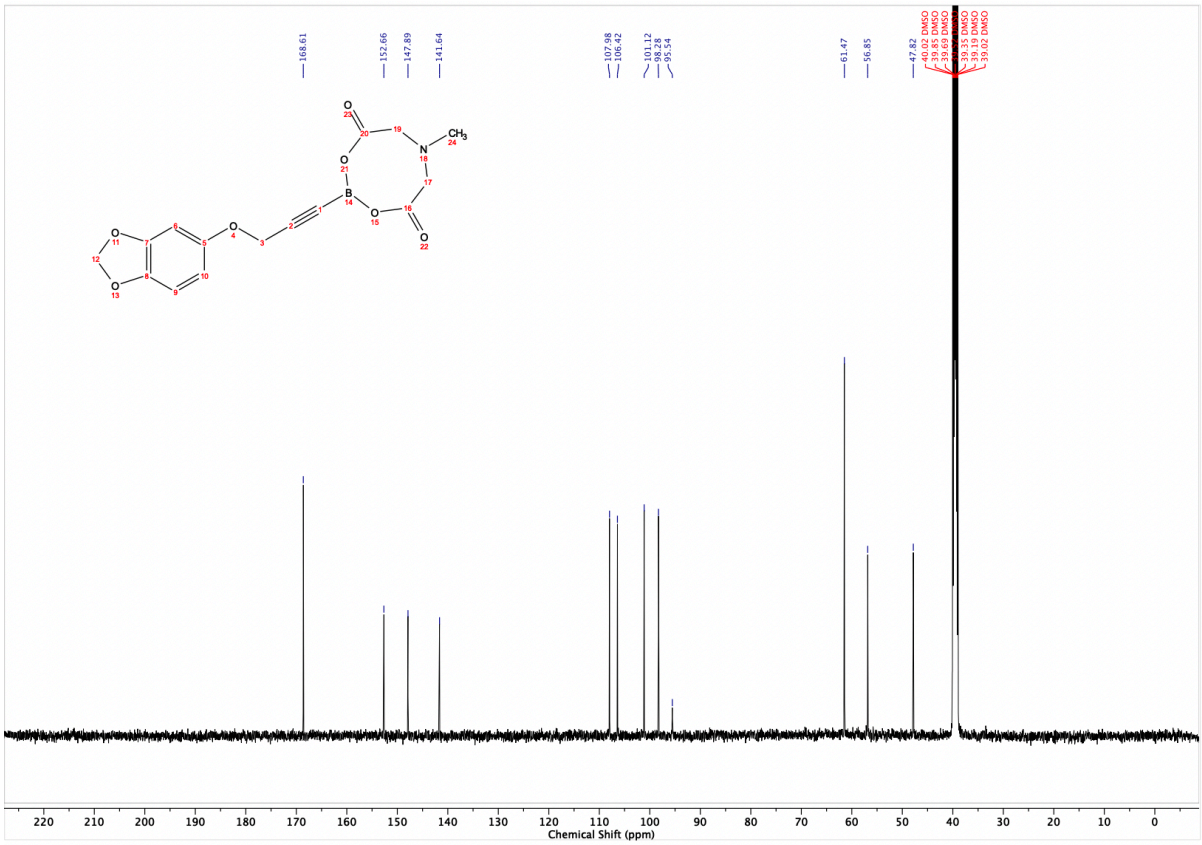

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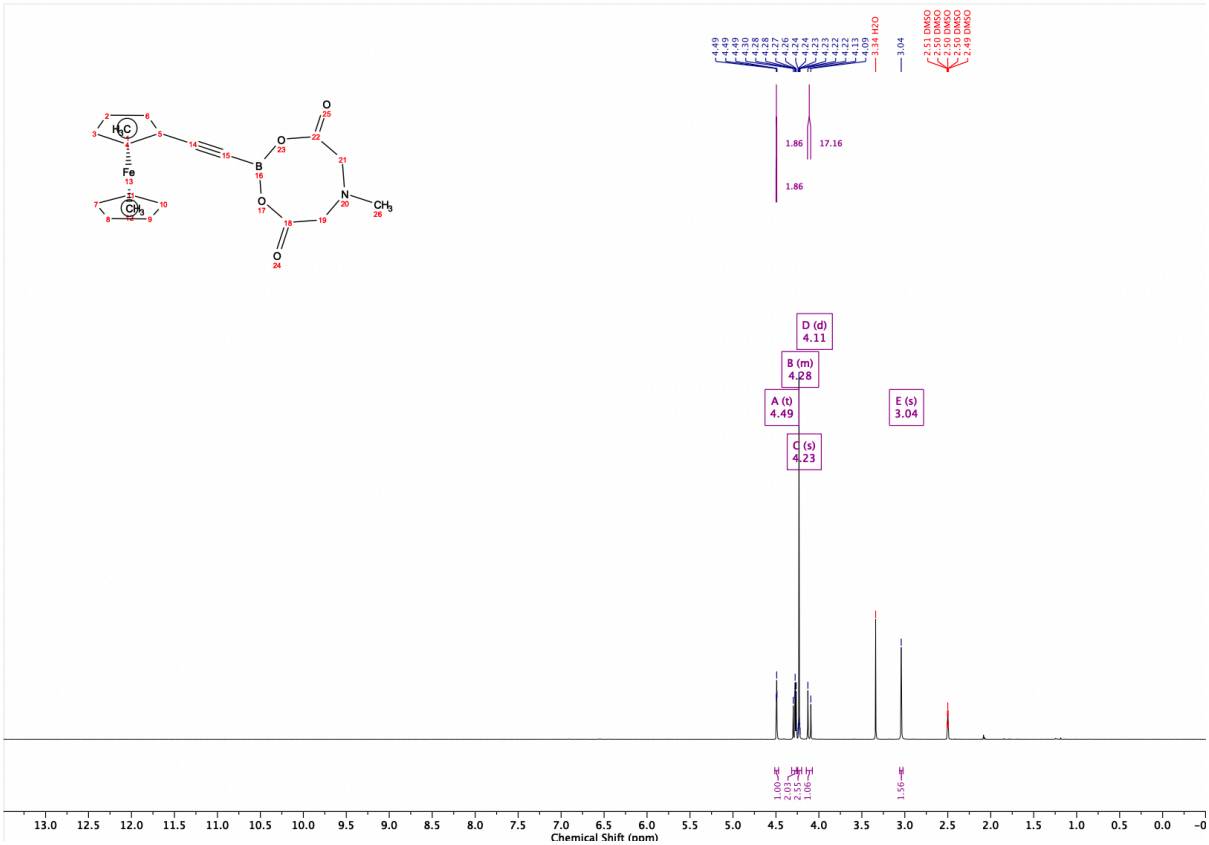

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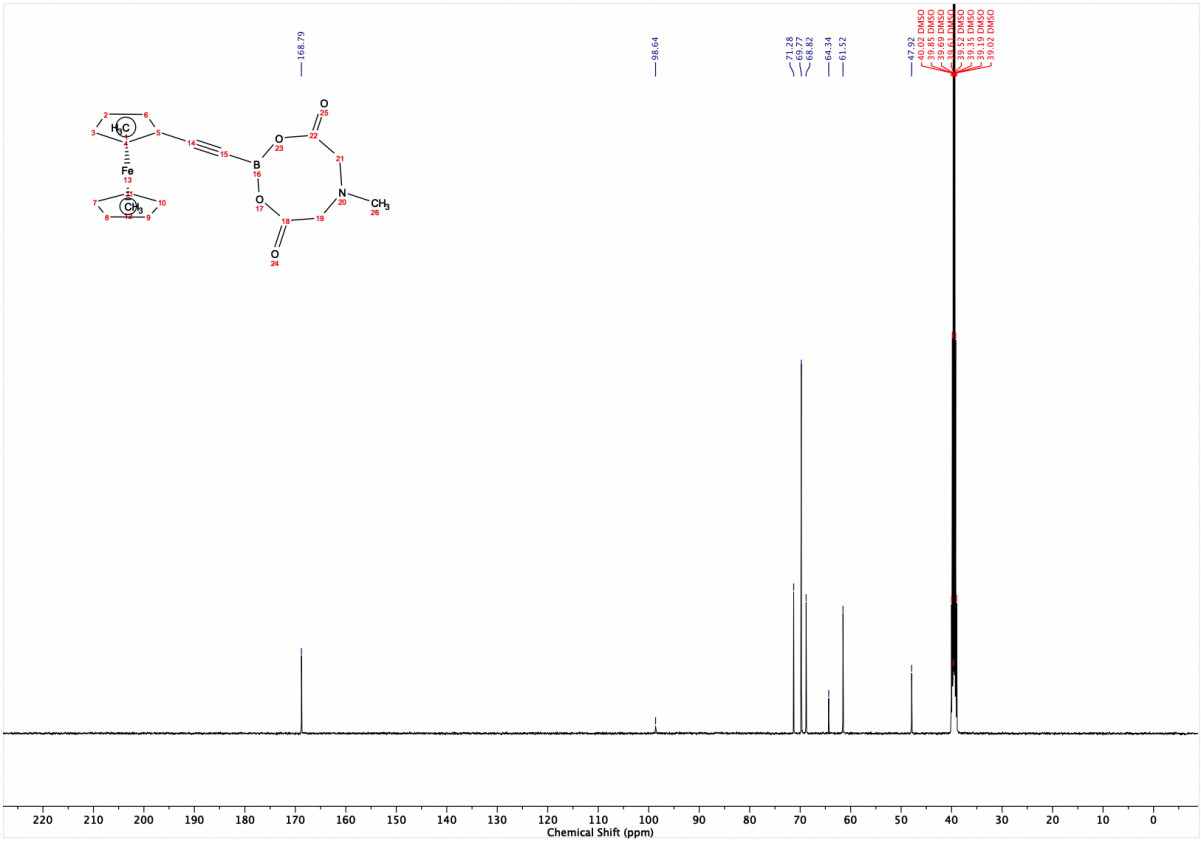

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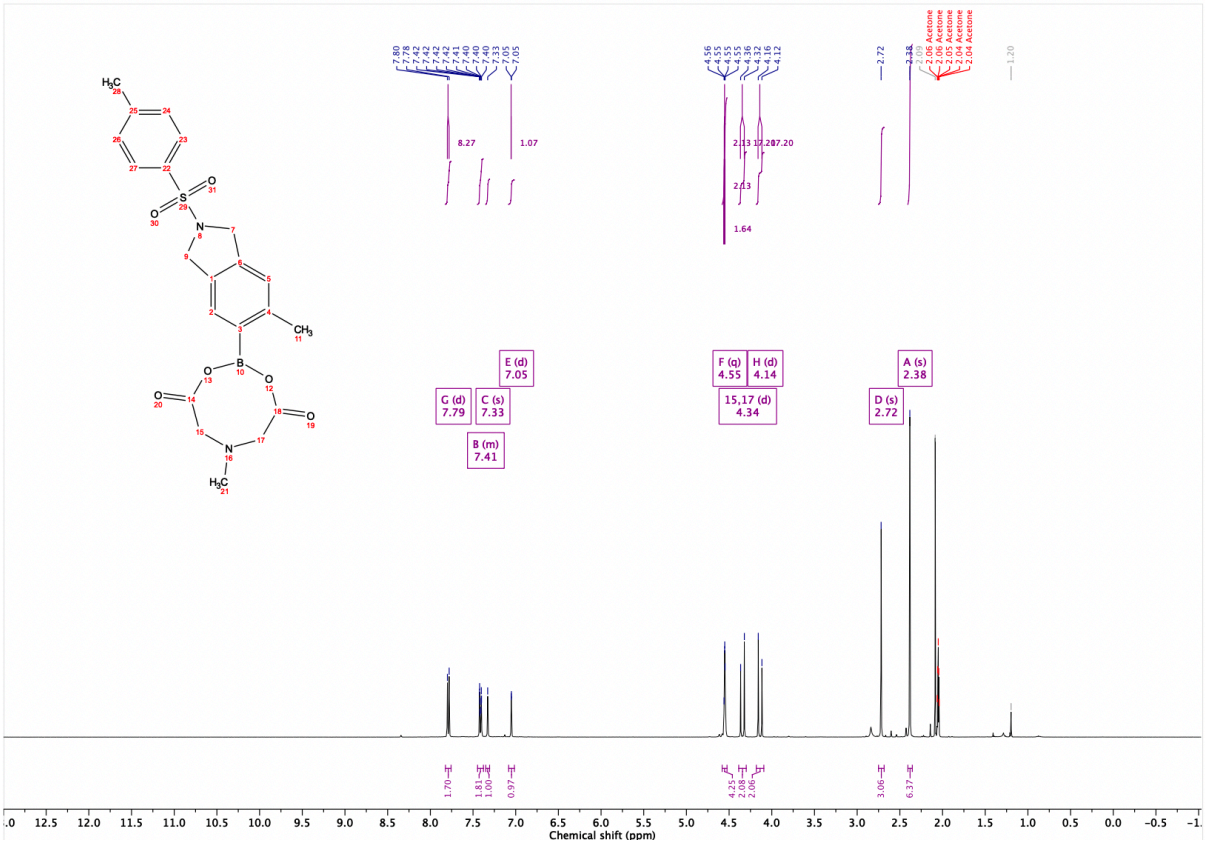

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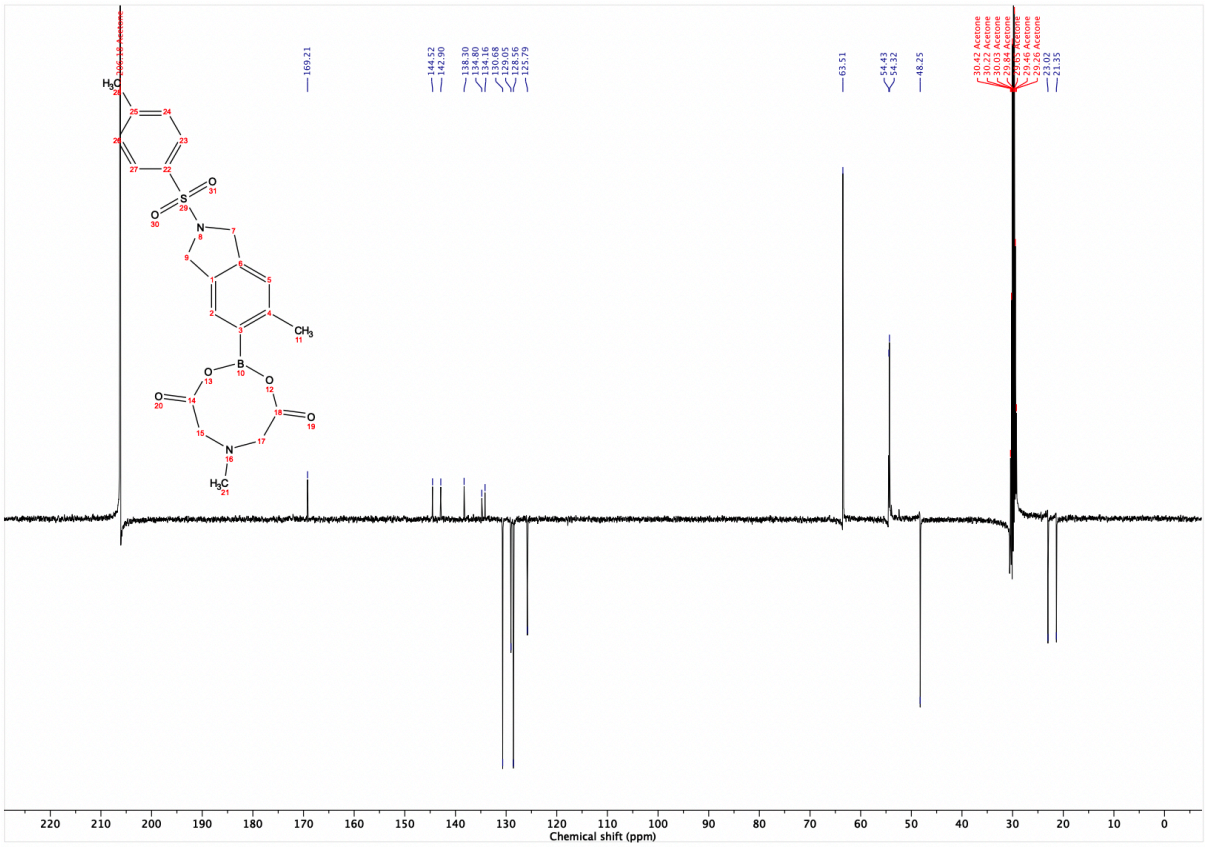

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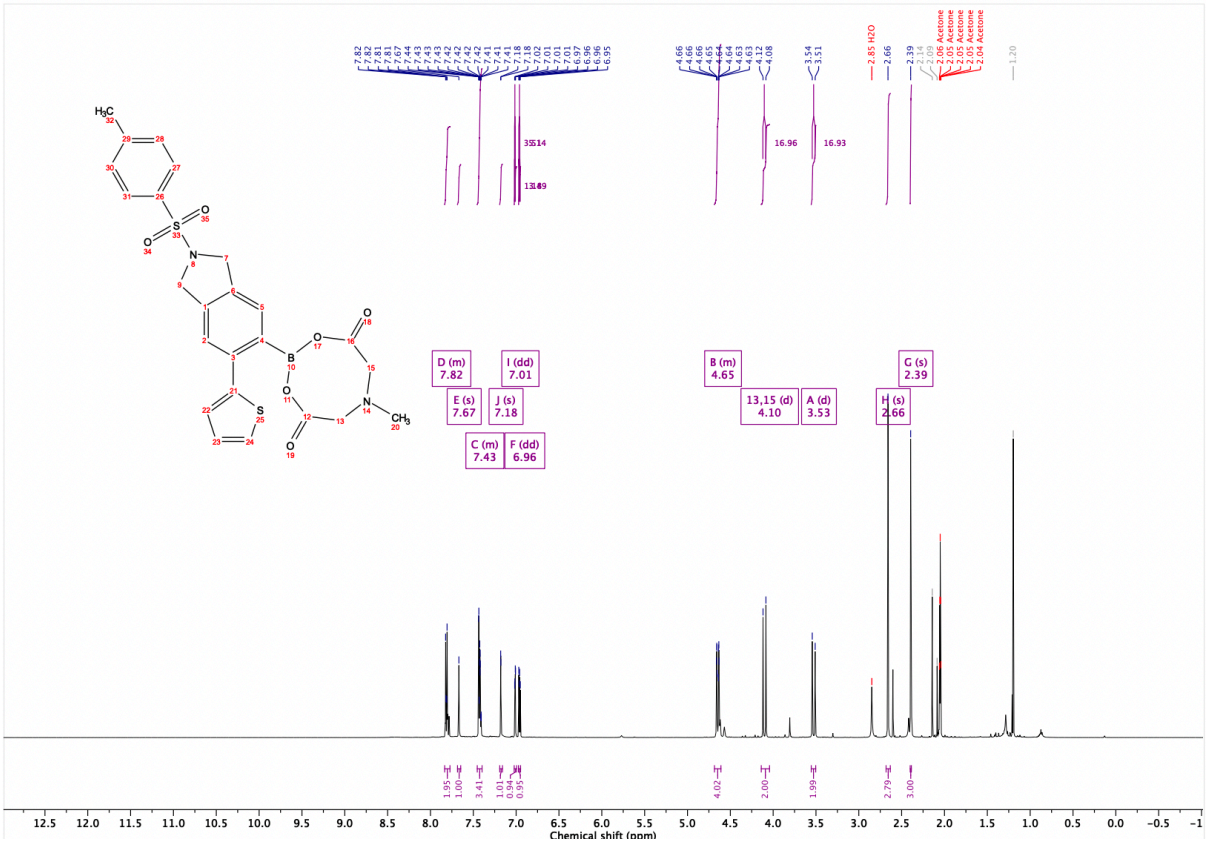

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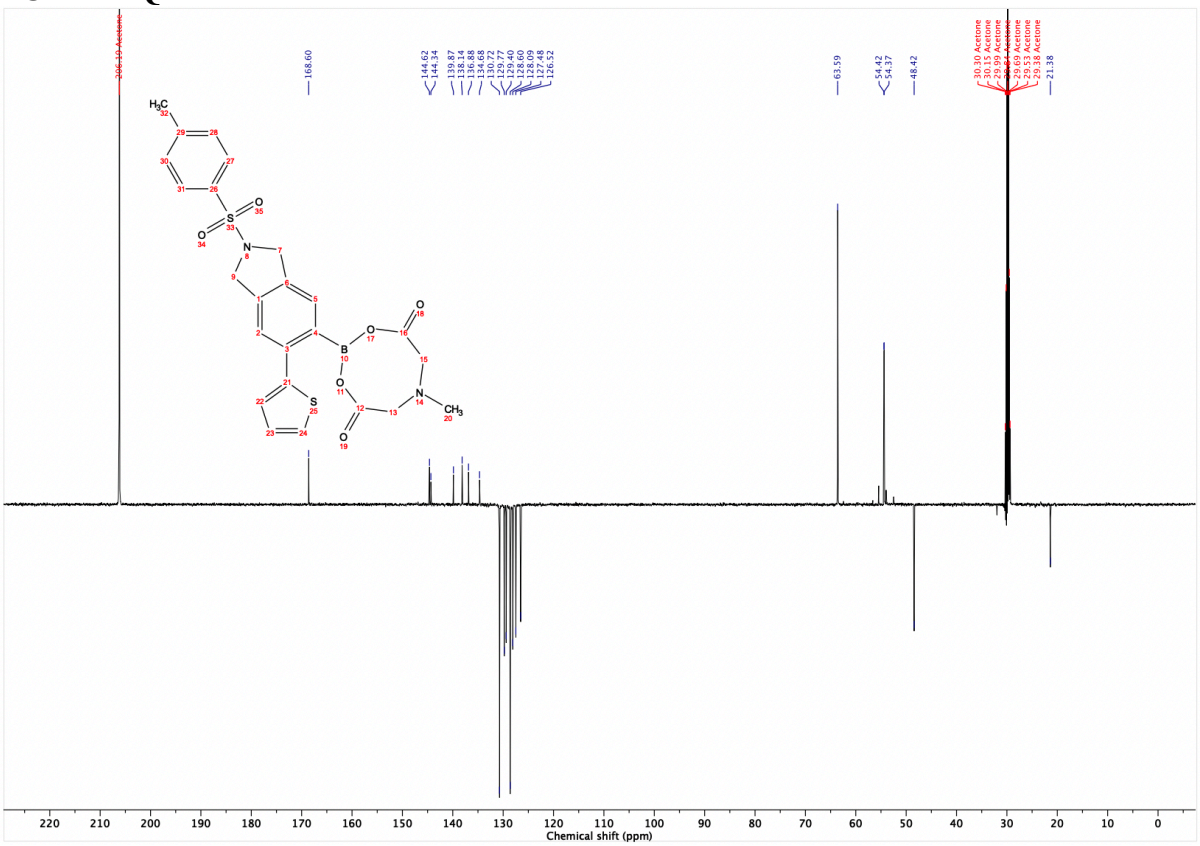

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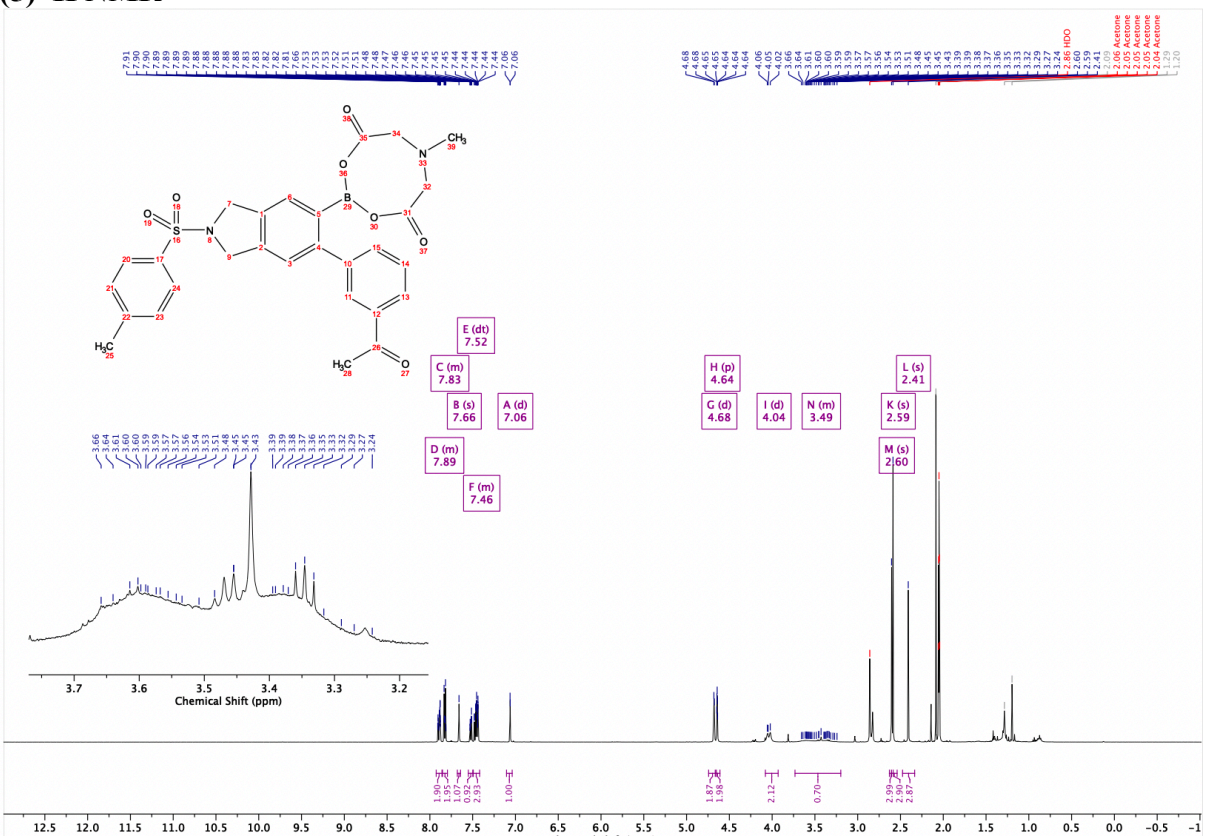

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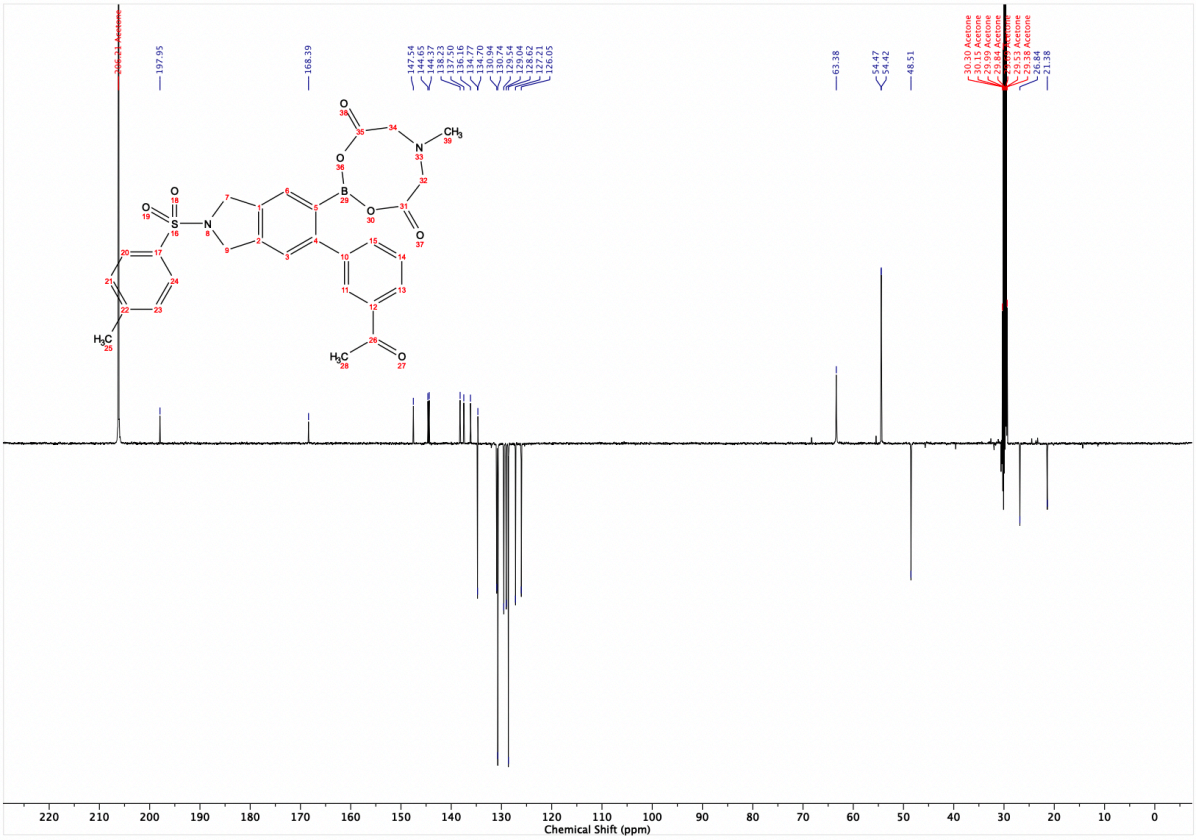

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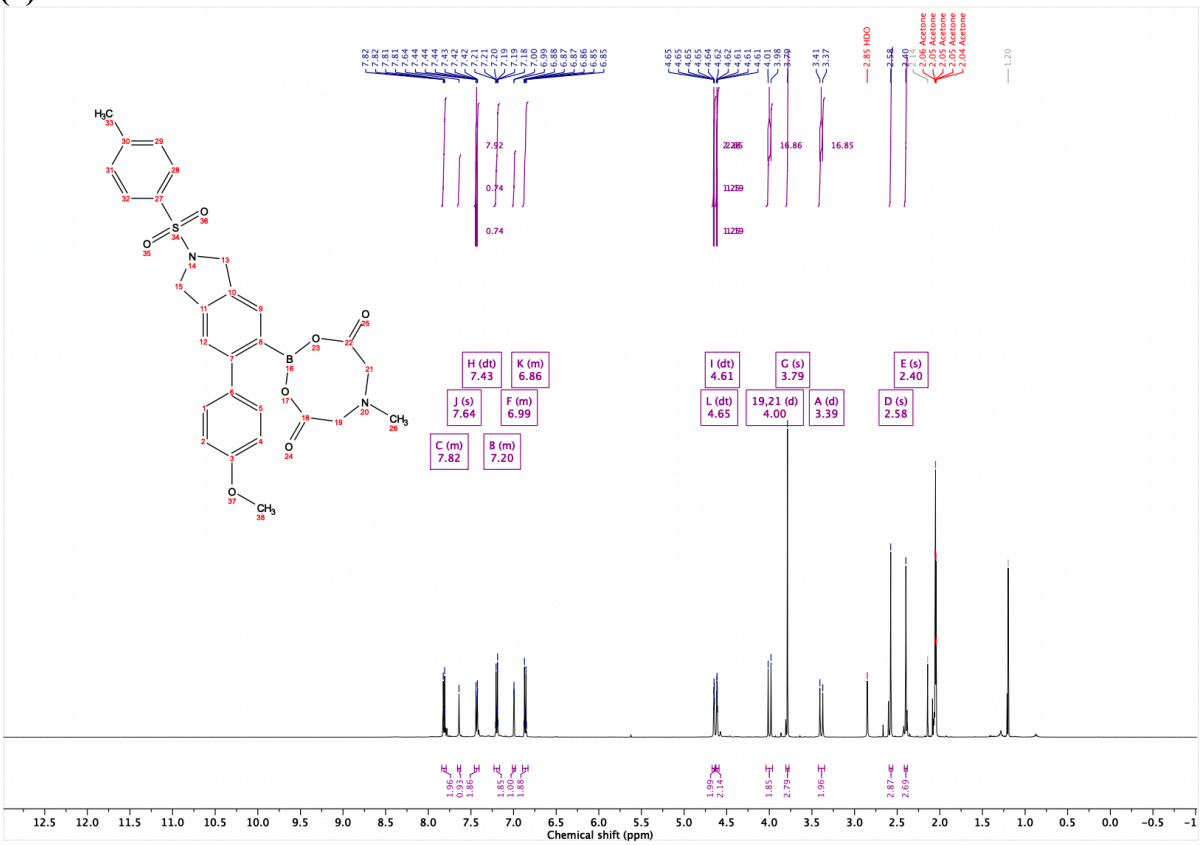

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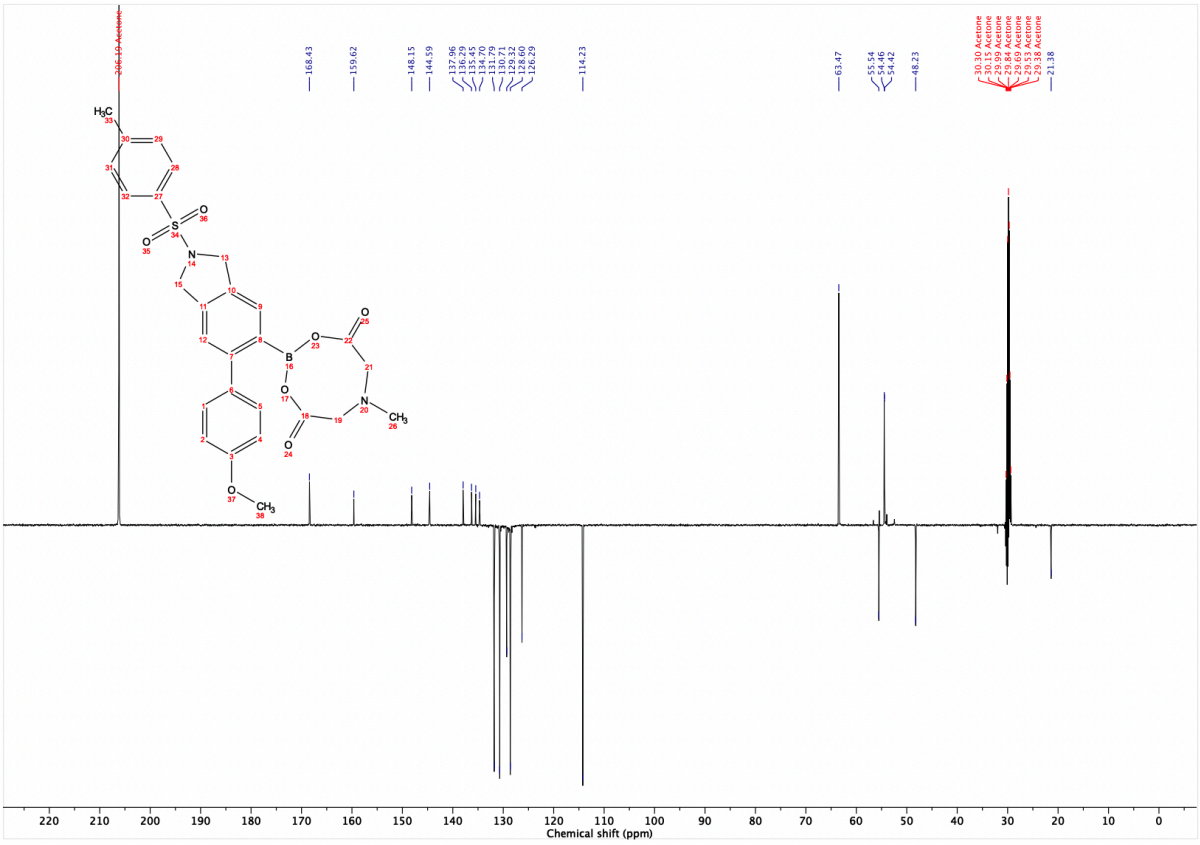
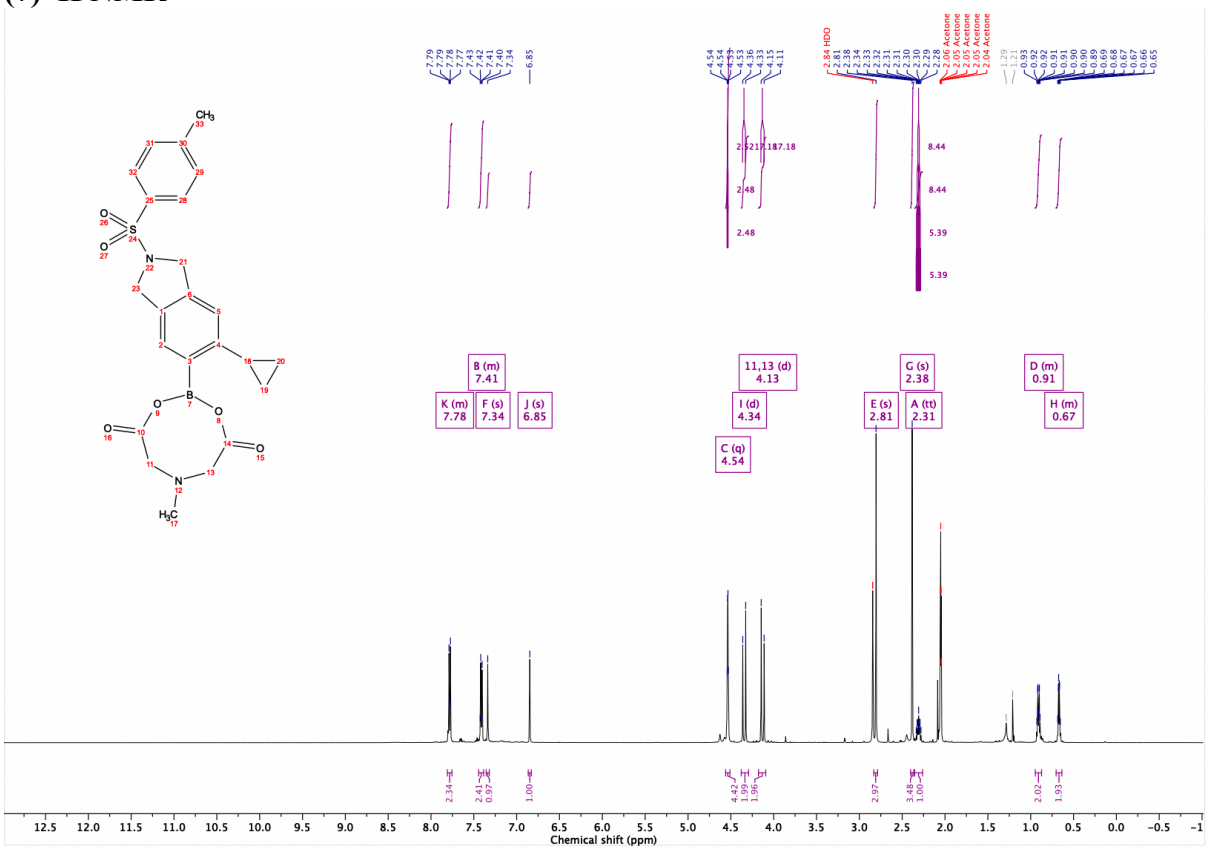


(7) ^{1}H NMR



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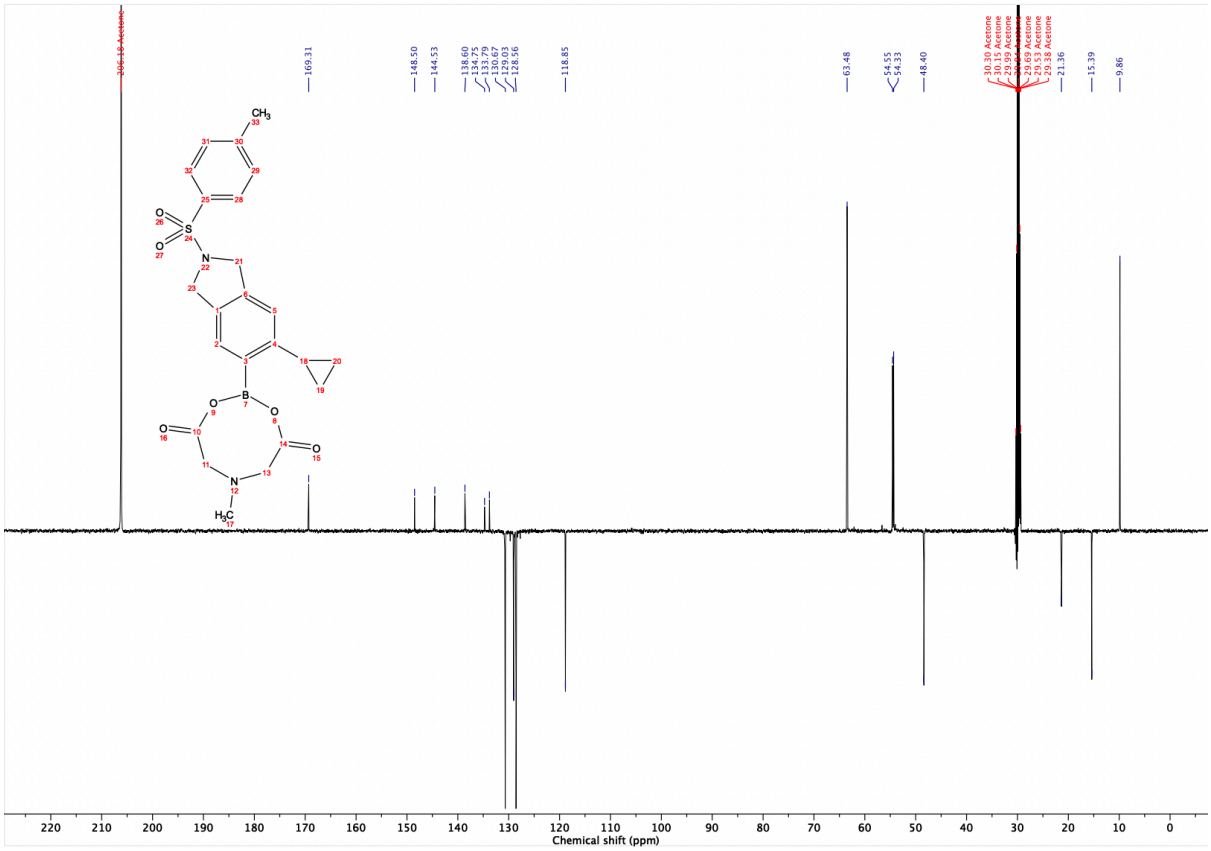

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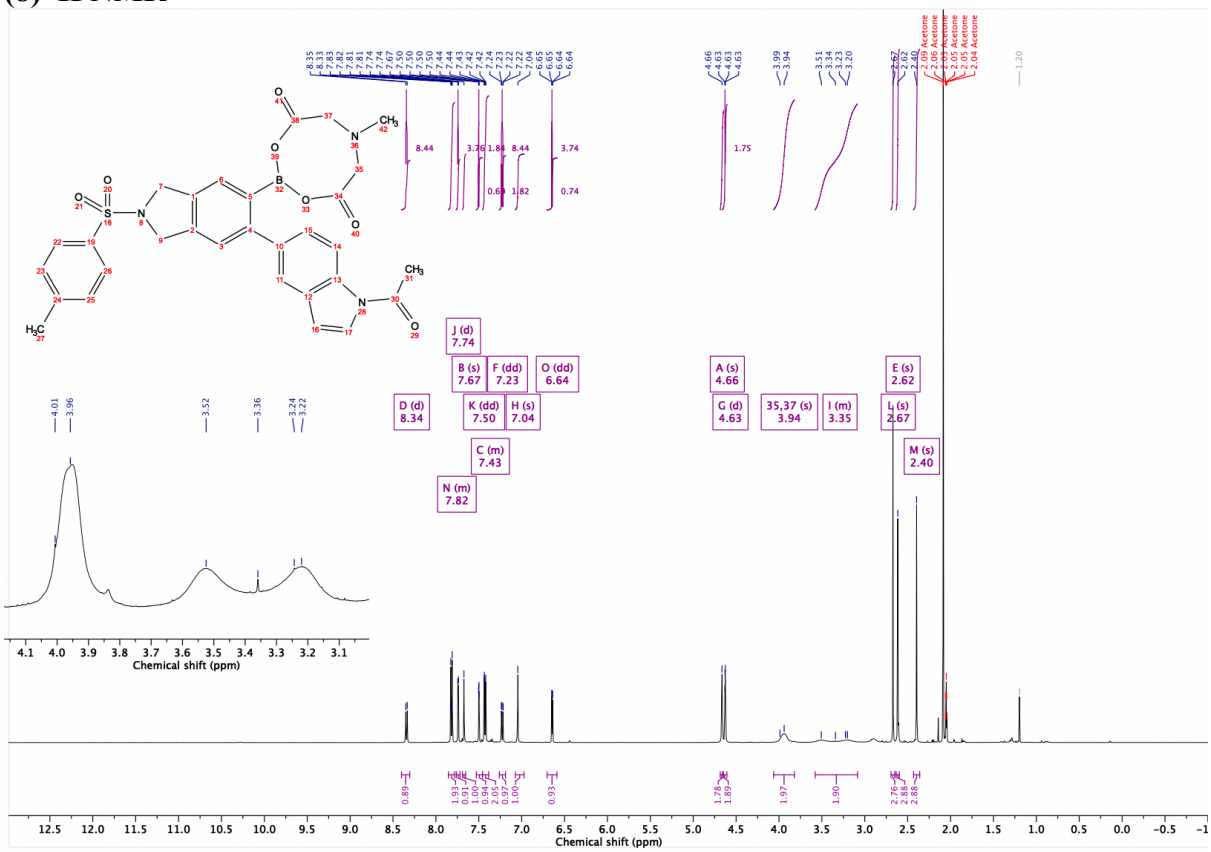

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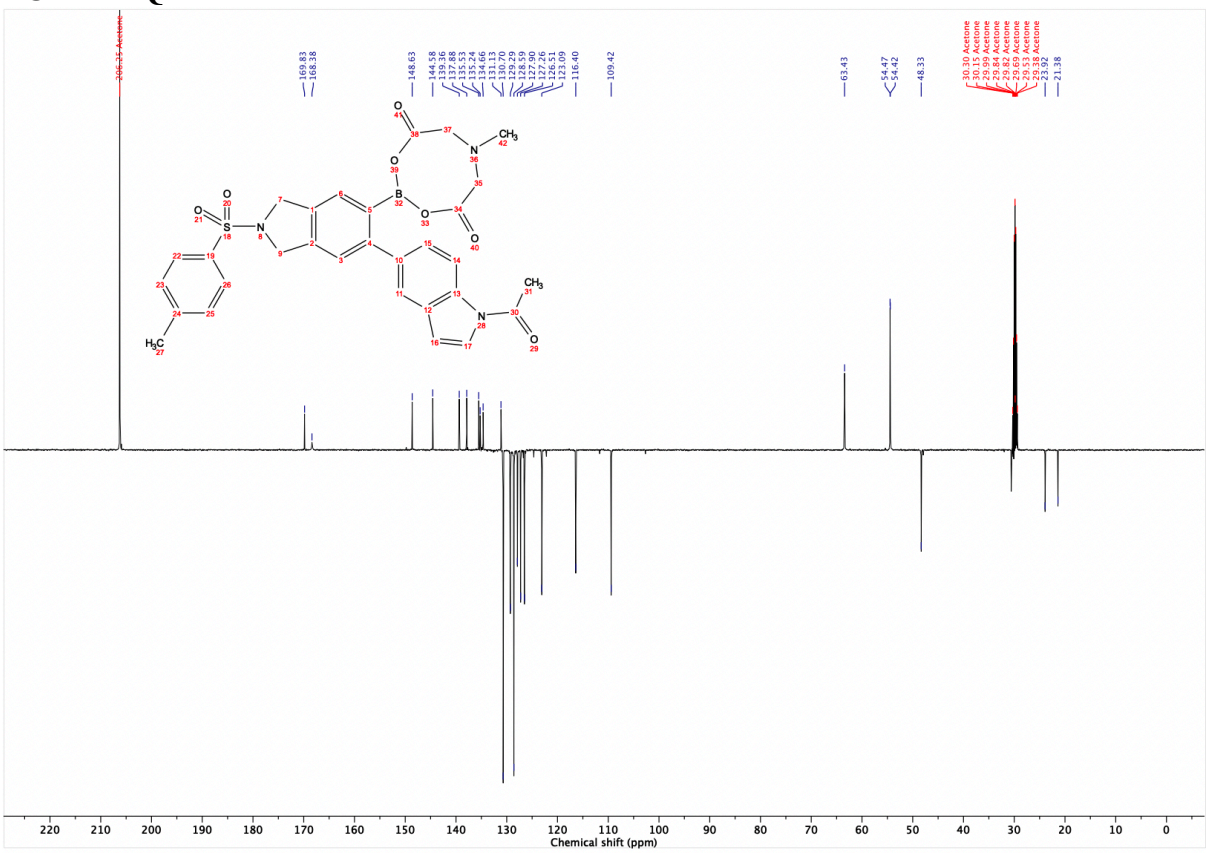
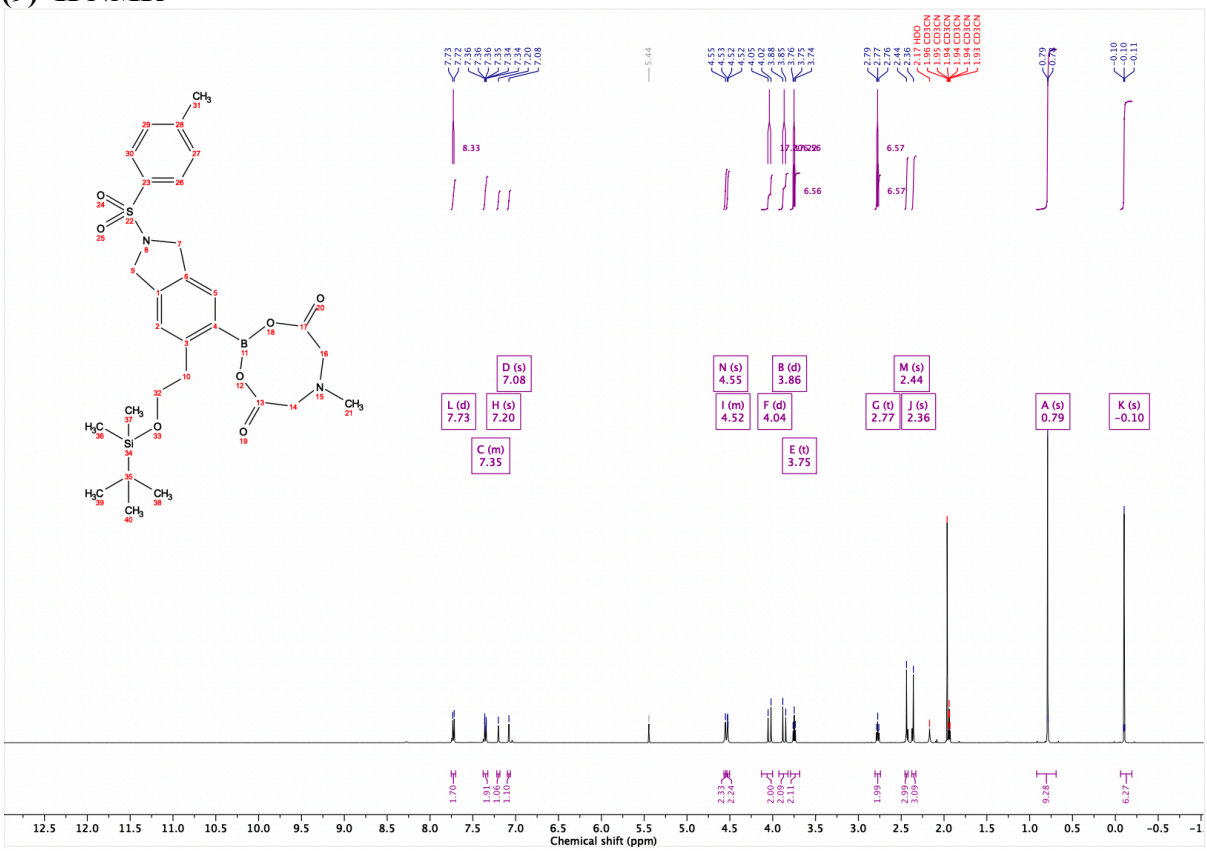


(9) ^{1}H NMR



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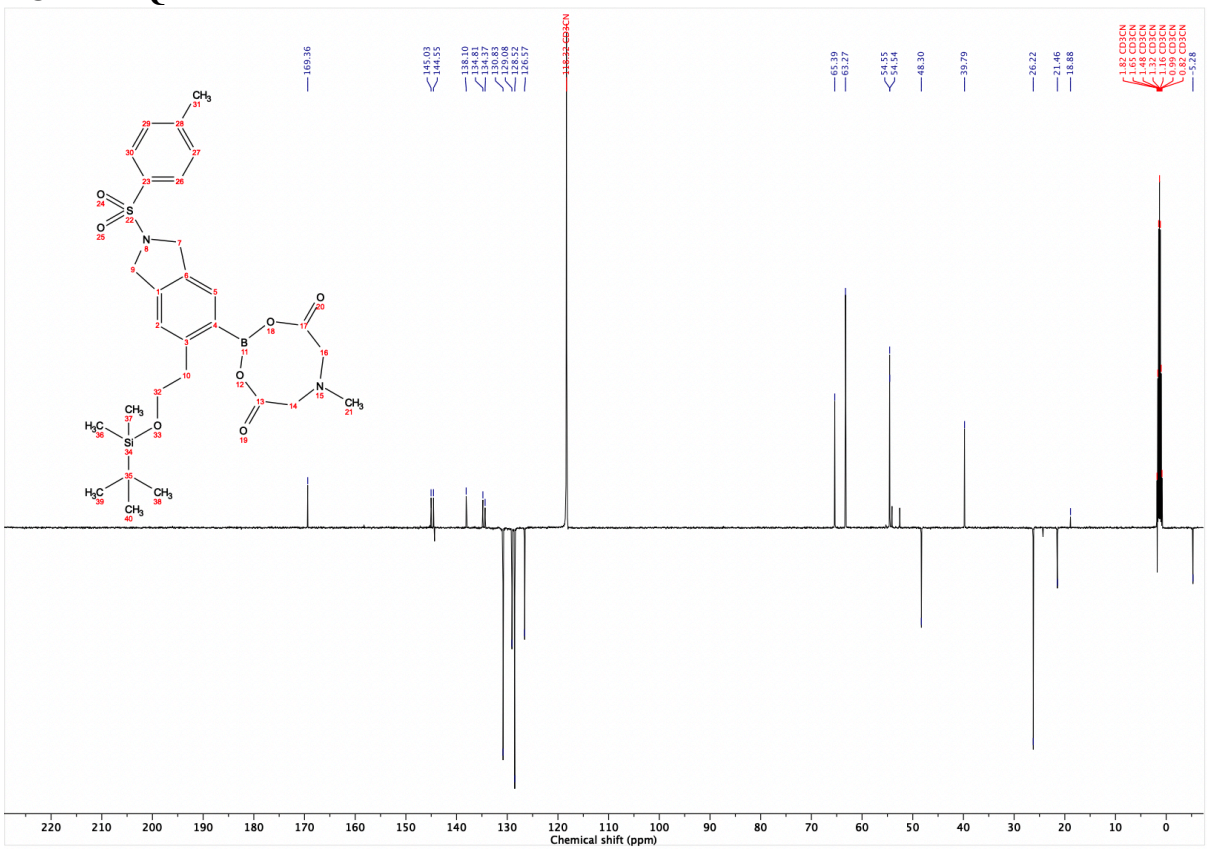
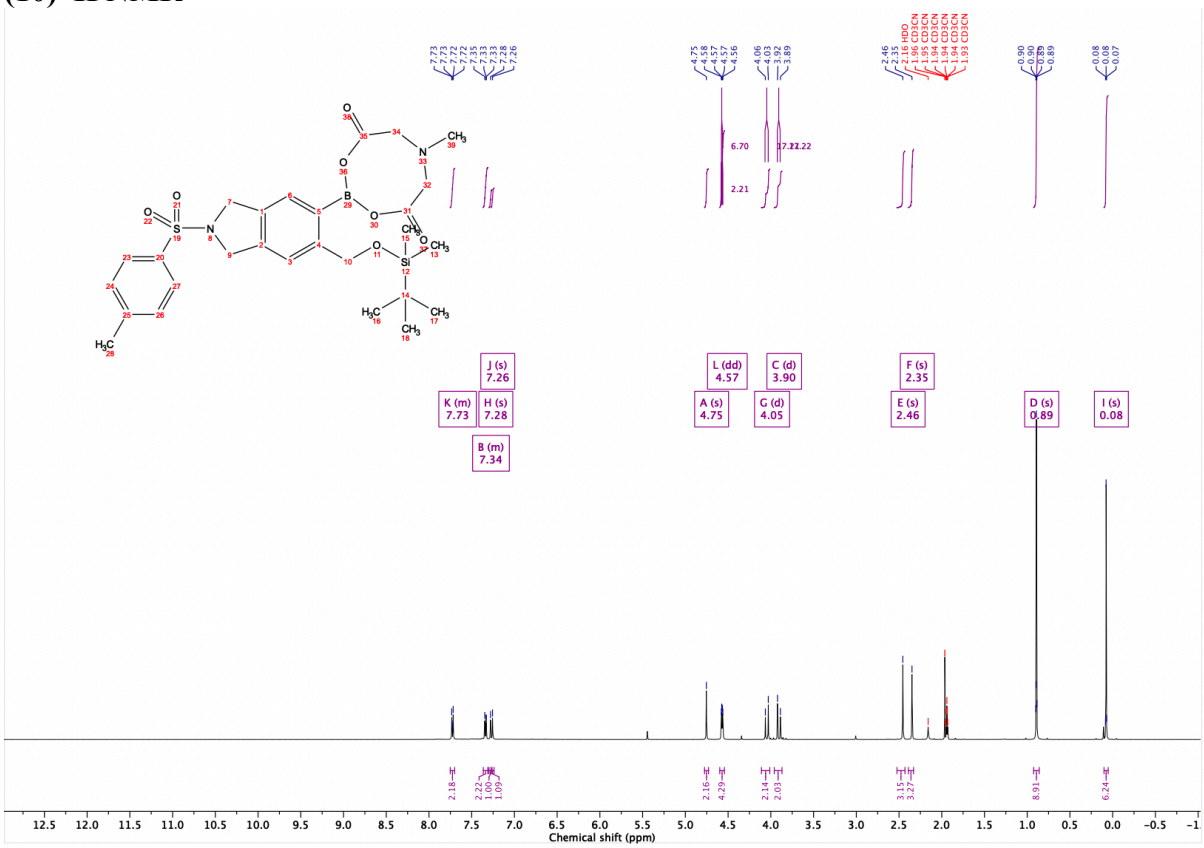
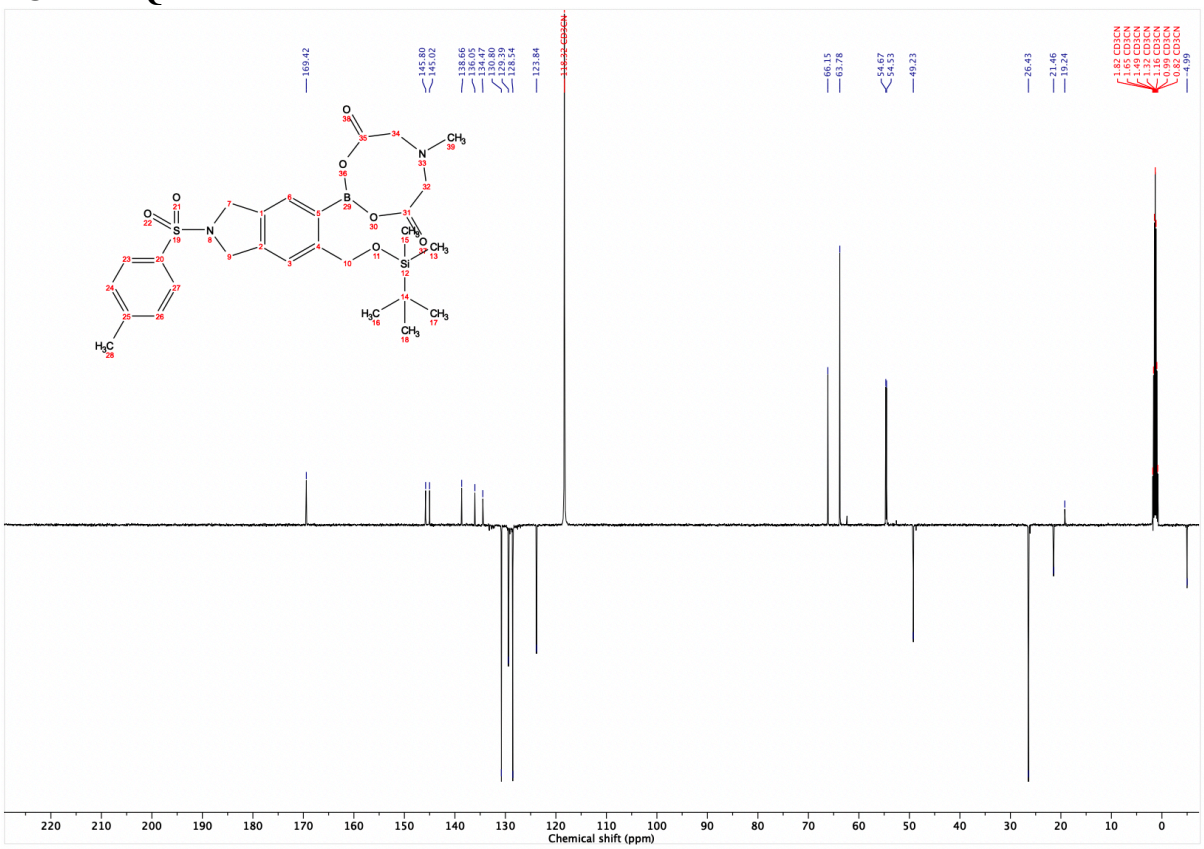


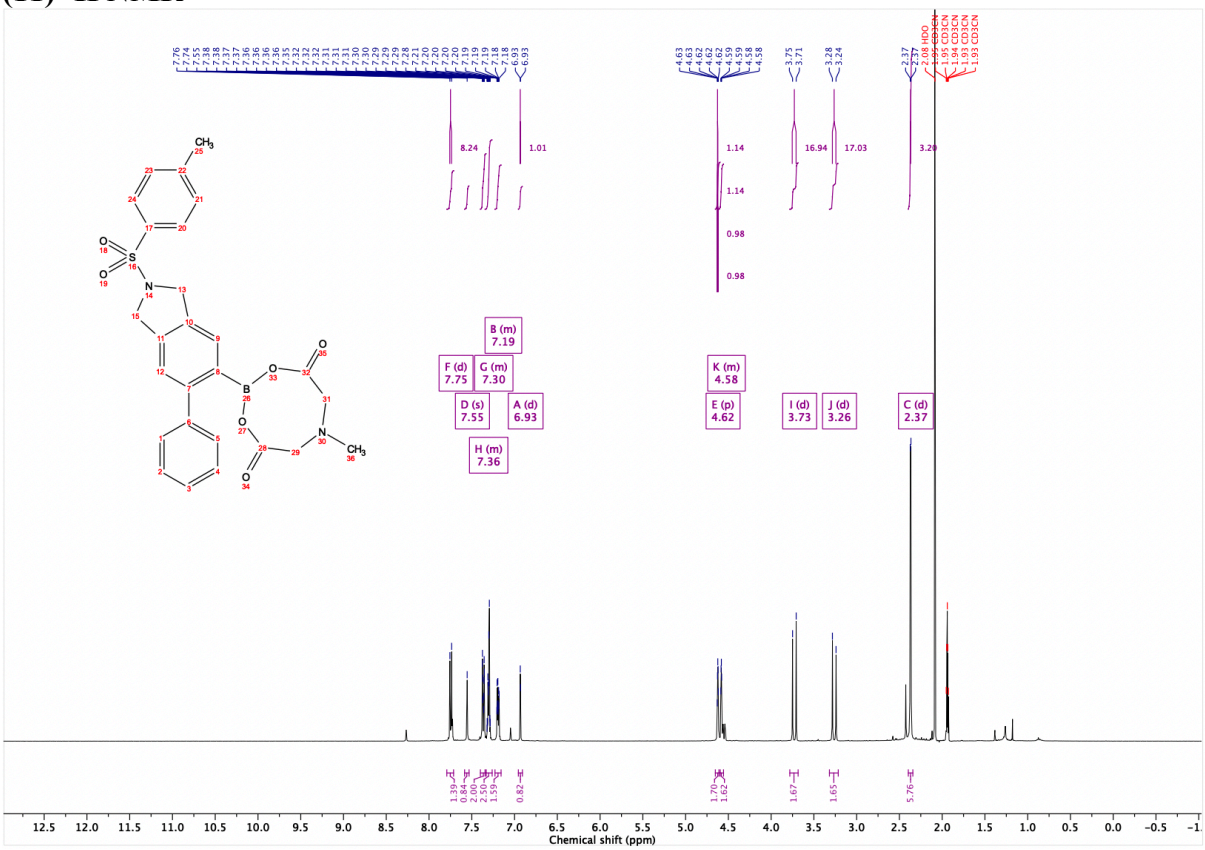
(10) ^{1}H NMR



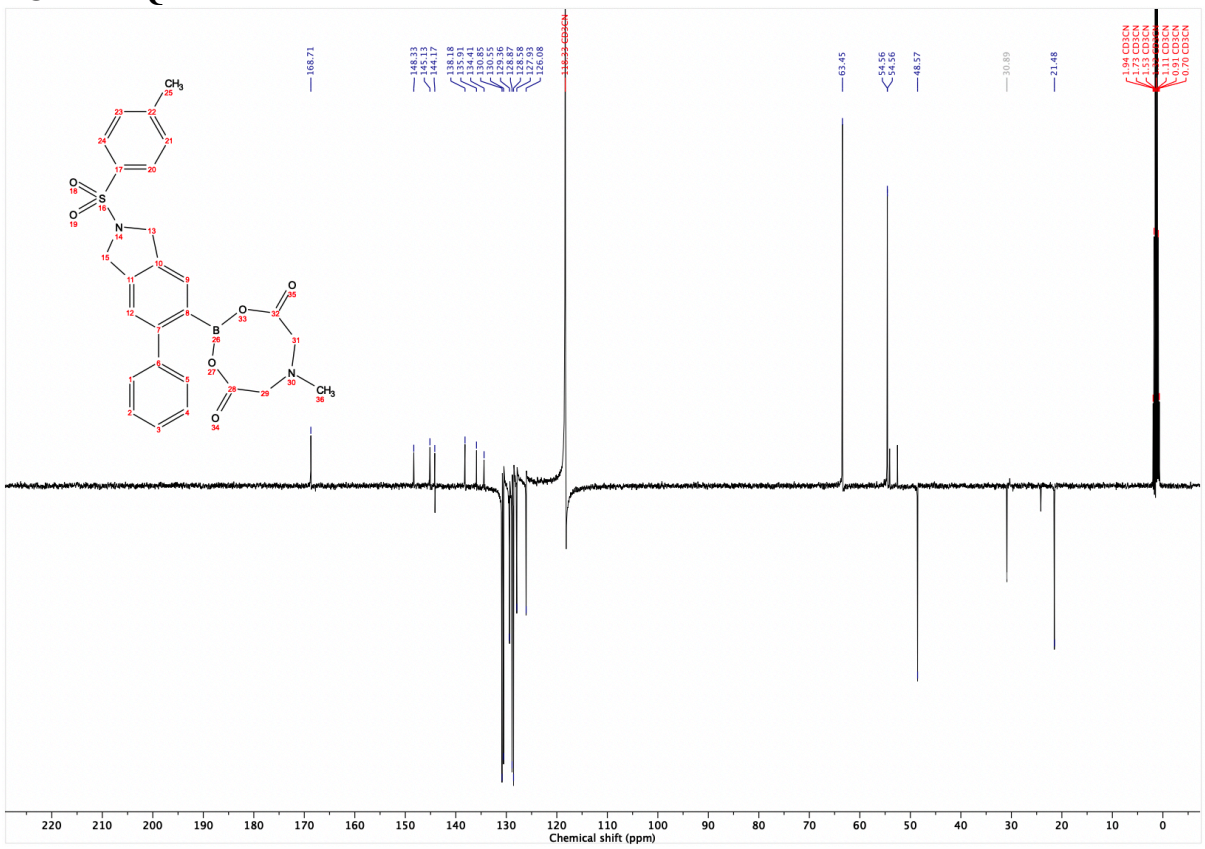
^{13}C DEPTQ



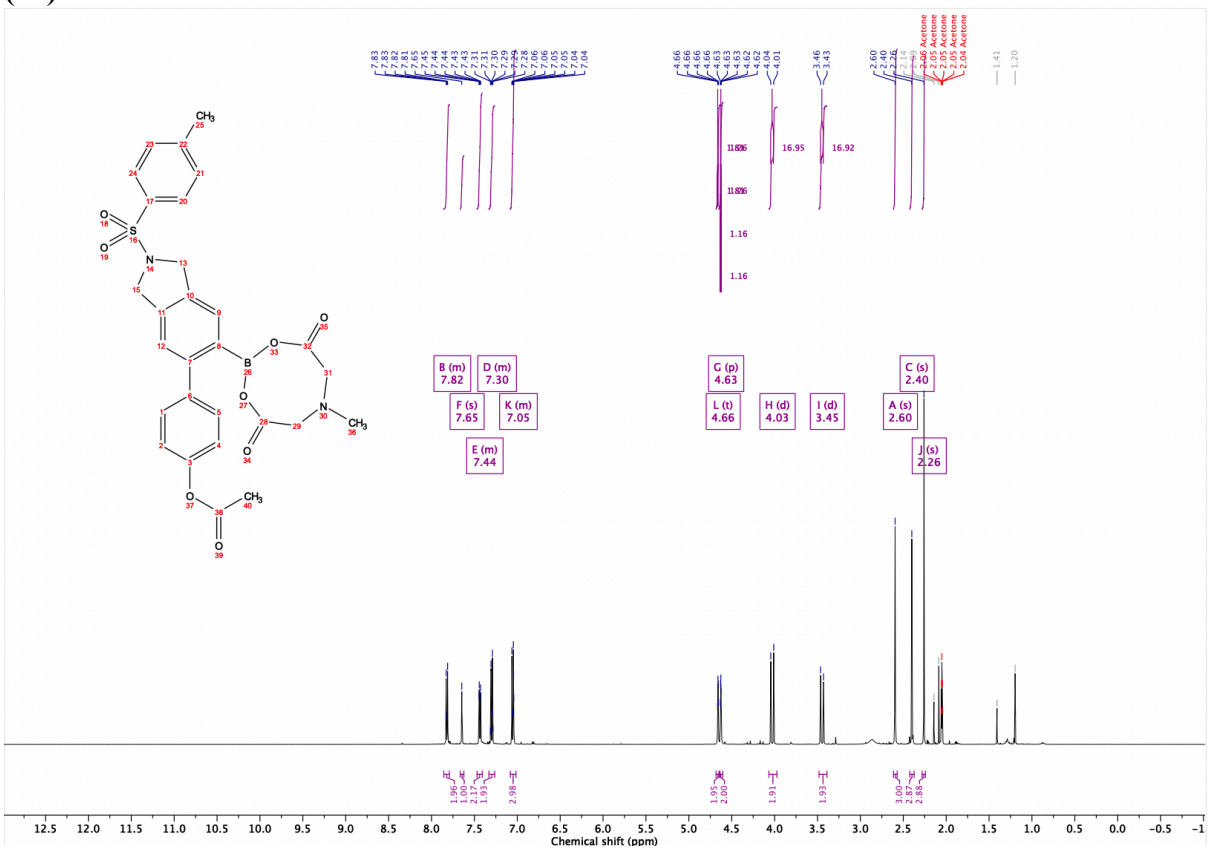
(11) ^{1}H NMR



^{13}C DEPTQ



(12) ^{1}H NMR



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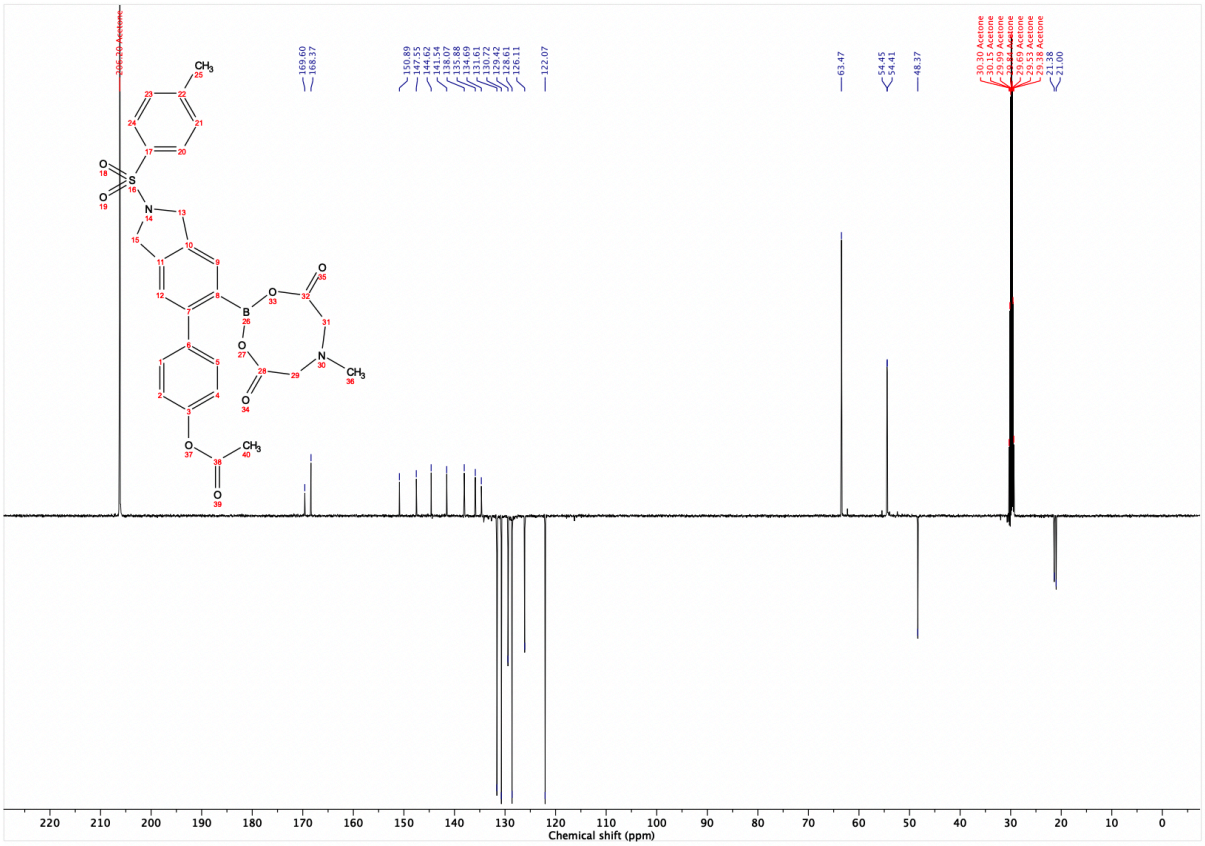
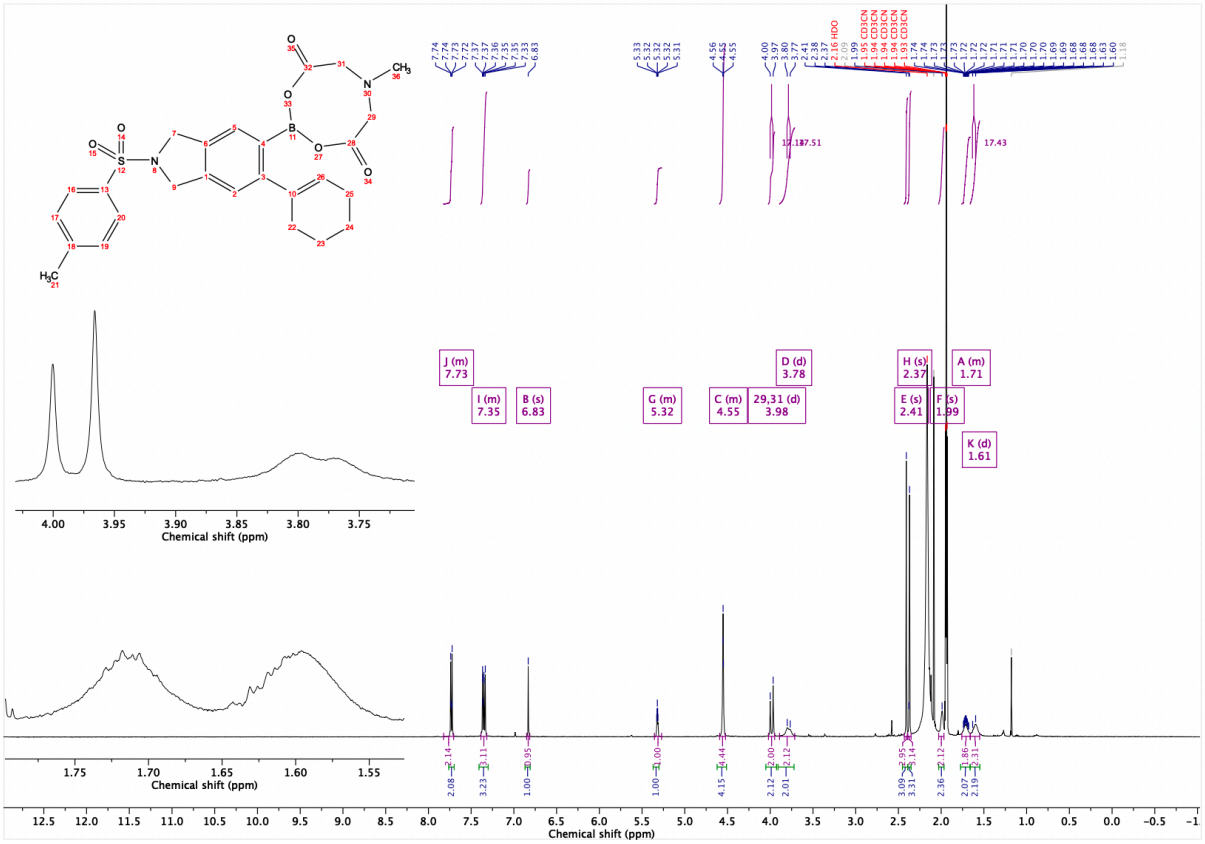
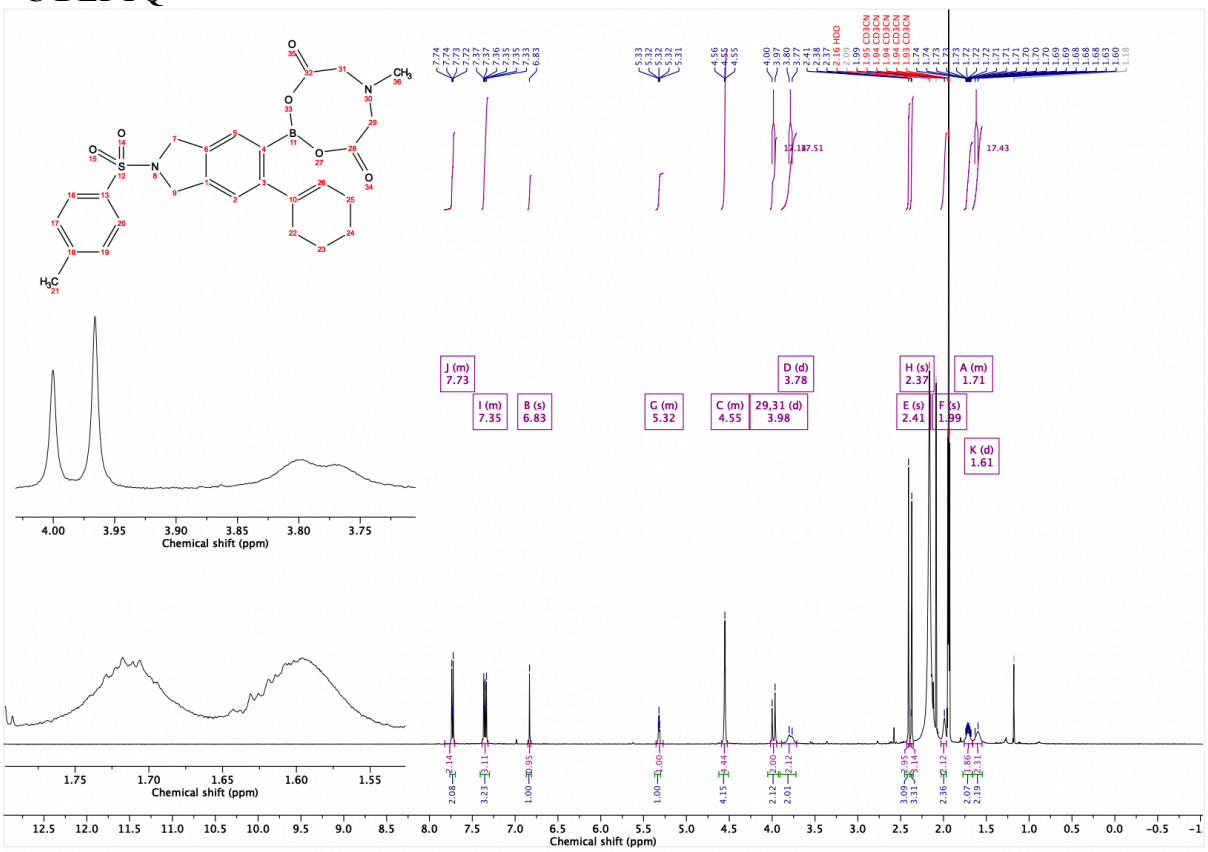


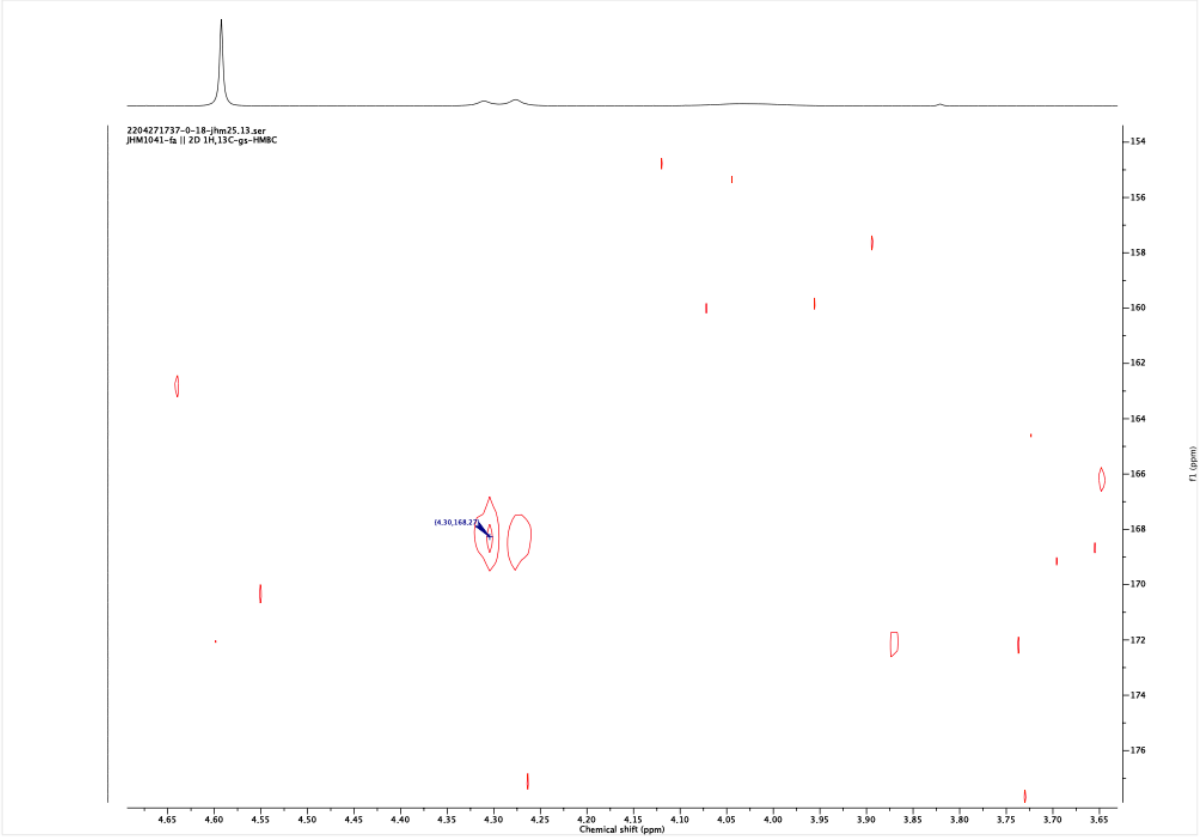
(13) ^{1}H NMR



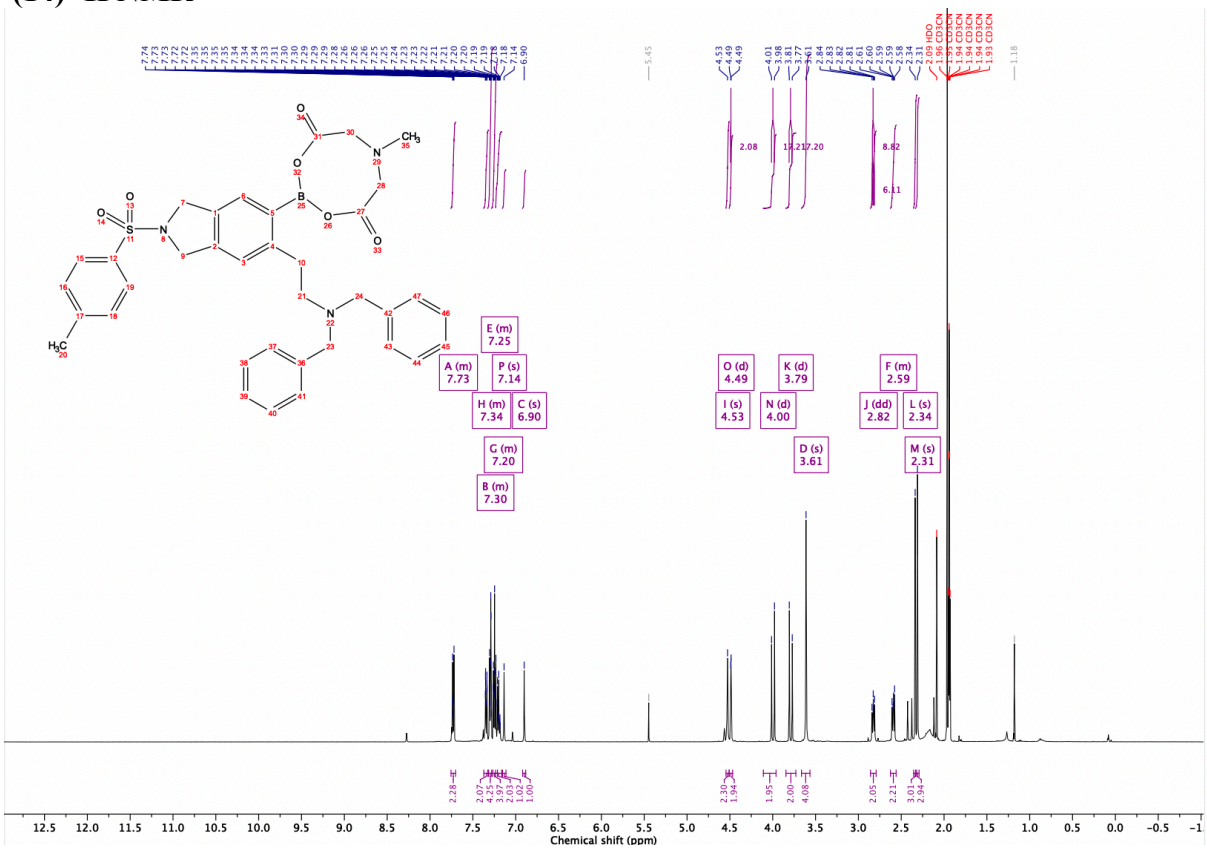
^{13}C DEPTQ



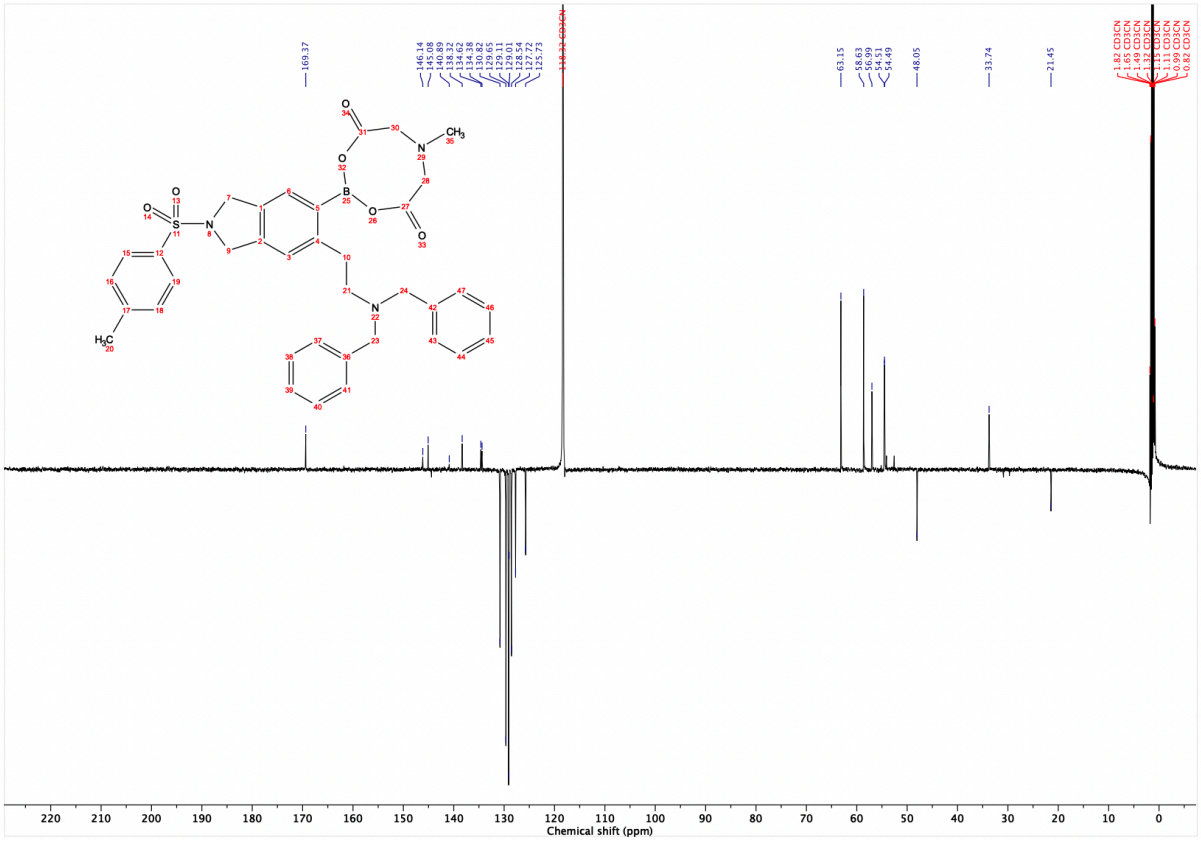
^{1}H-^{13}C HMBC



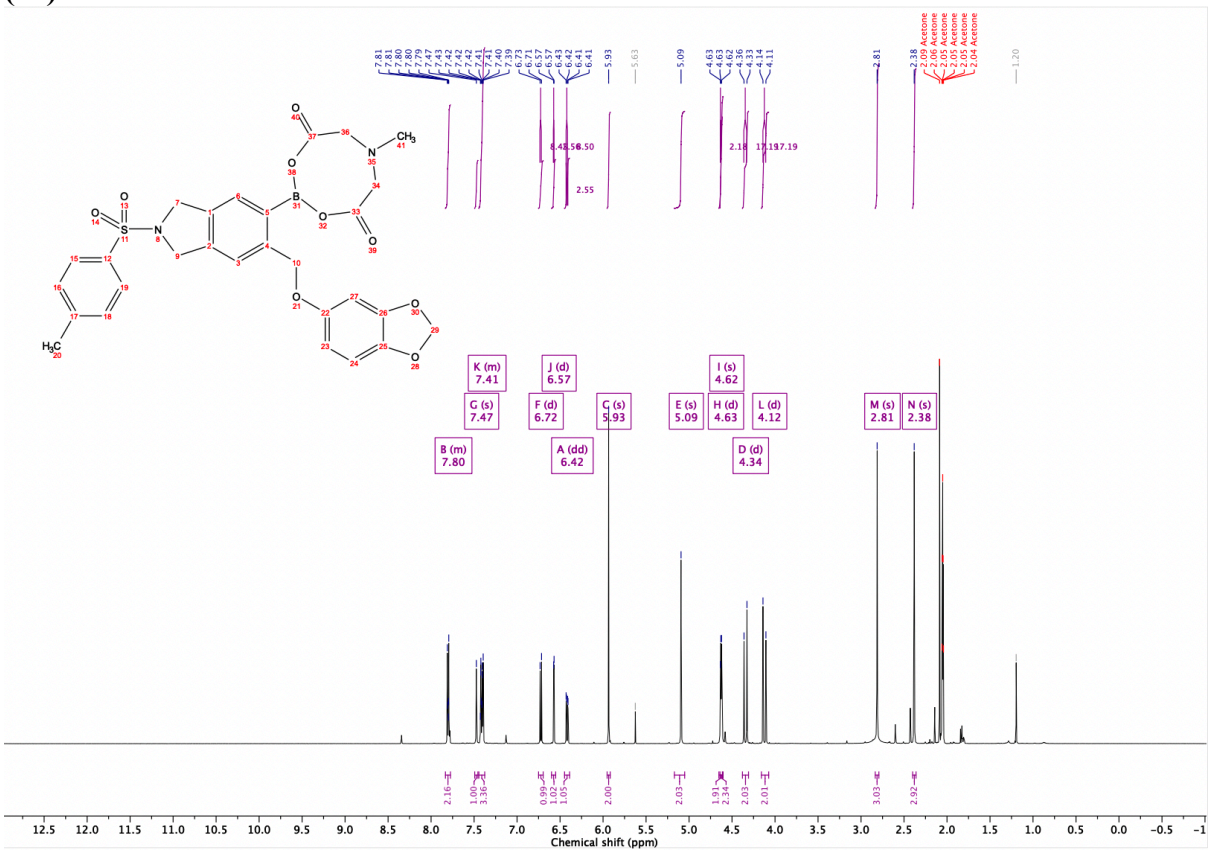
(14) ^{1}H NMR



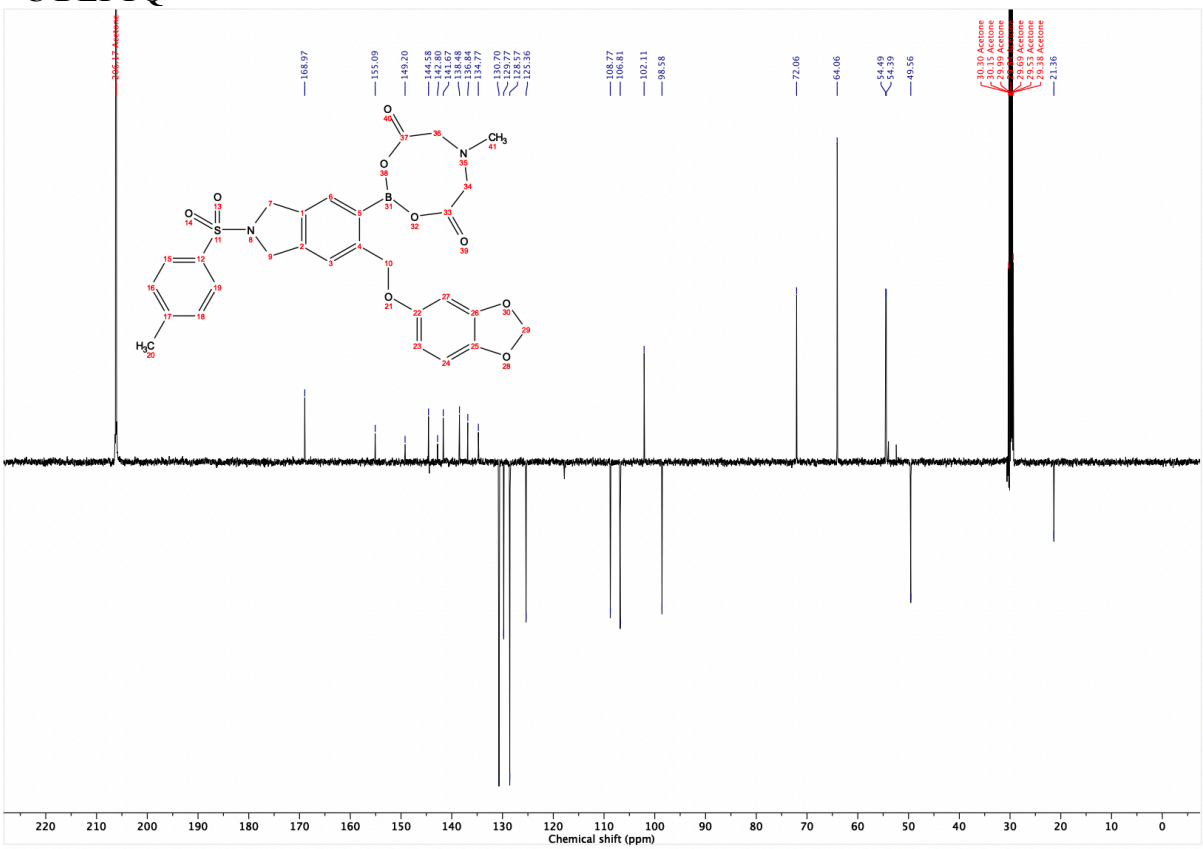
^{13}C DEPTQ



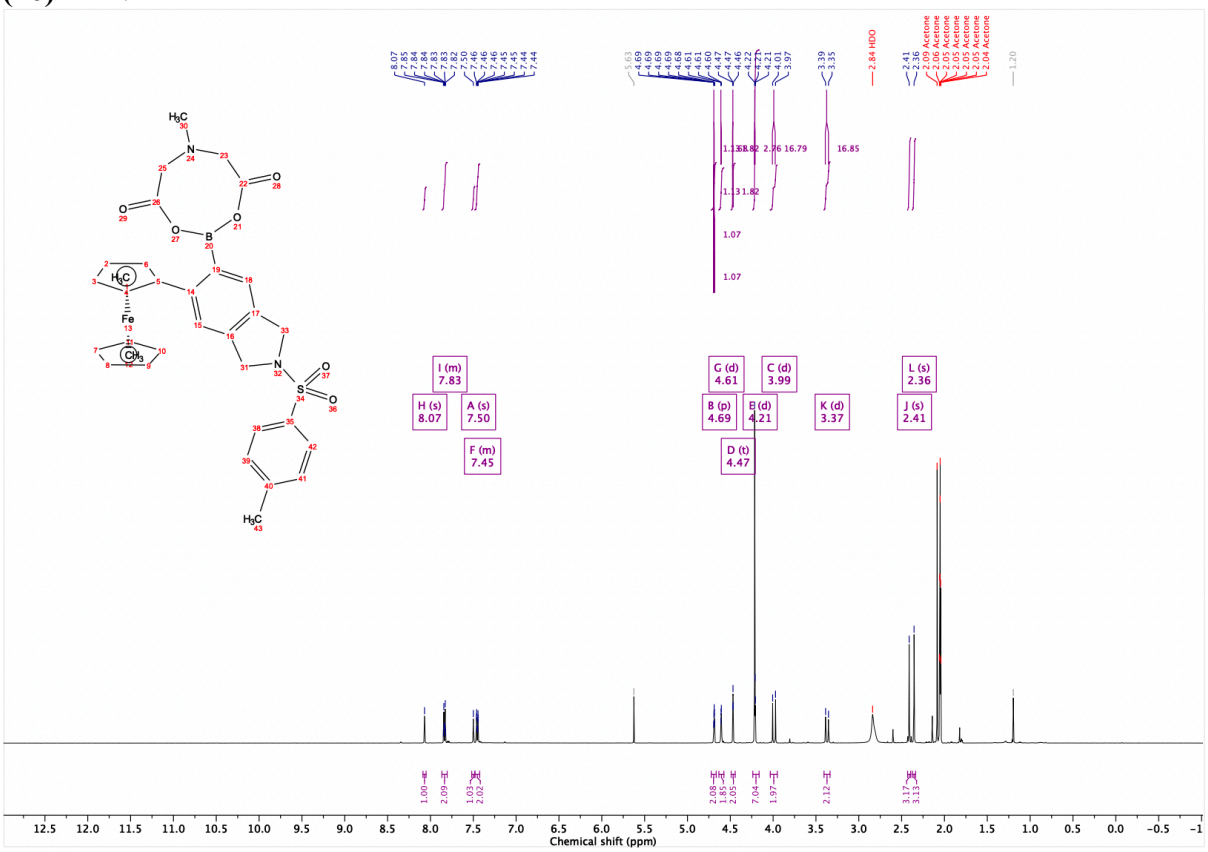
(15) ^{1}H NMR



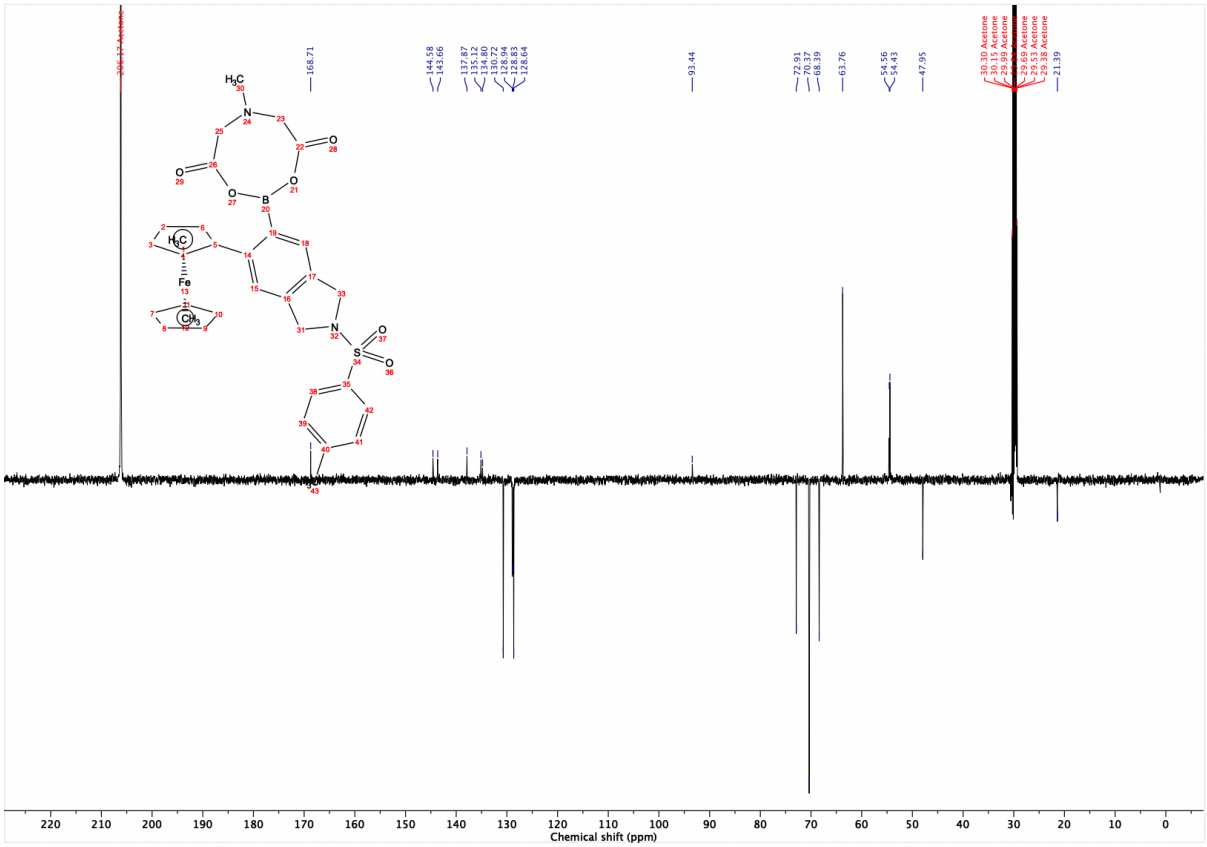
^{13}C DEPTQ



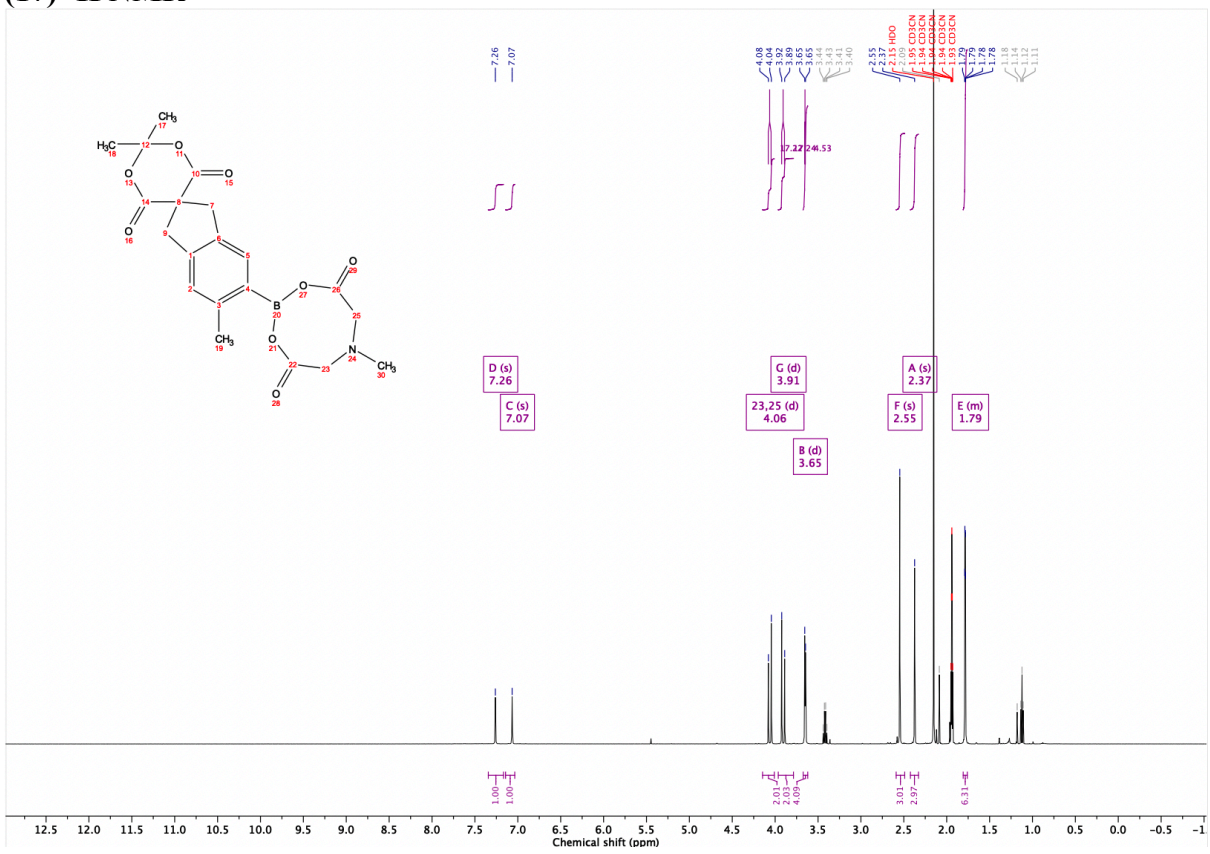
(16) ^{1}H NMR



^{13}C DEPTQ



(17) ^{1}H NMR



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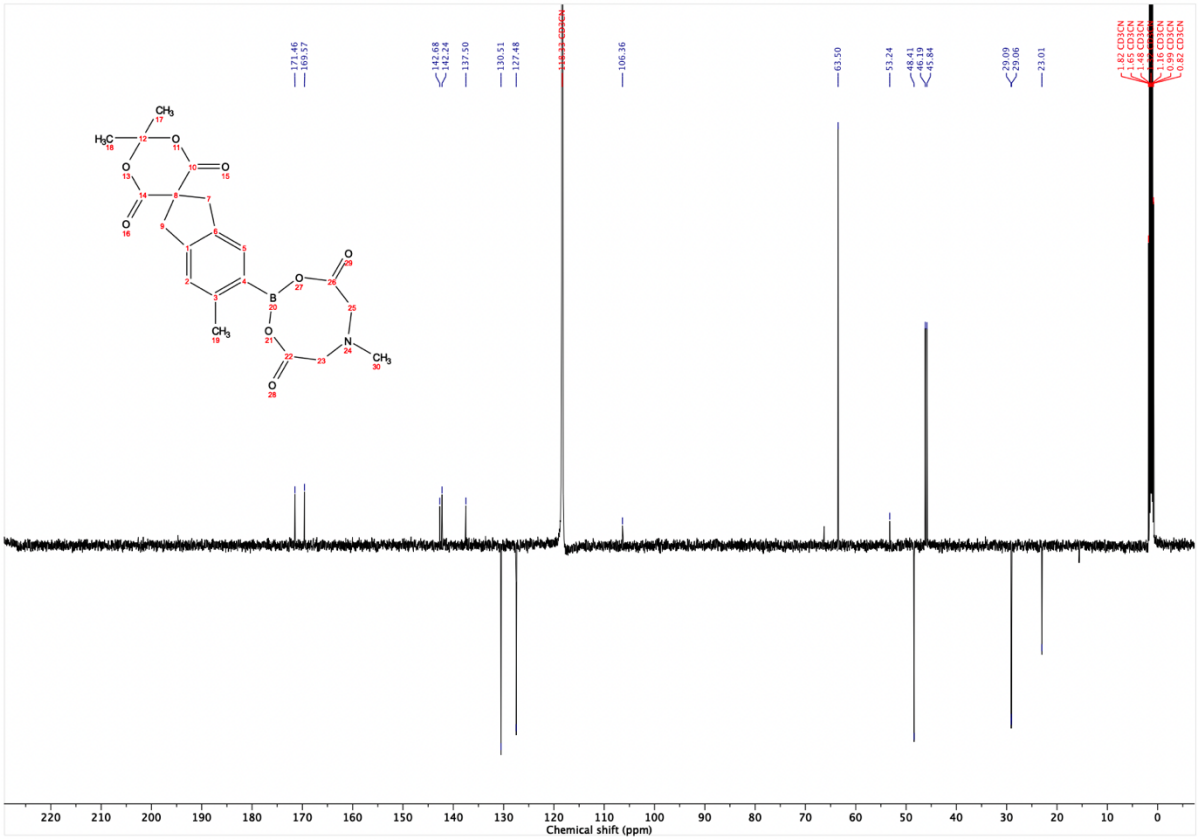
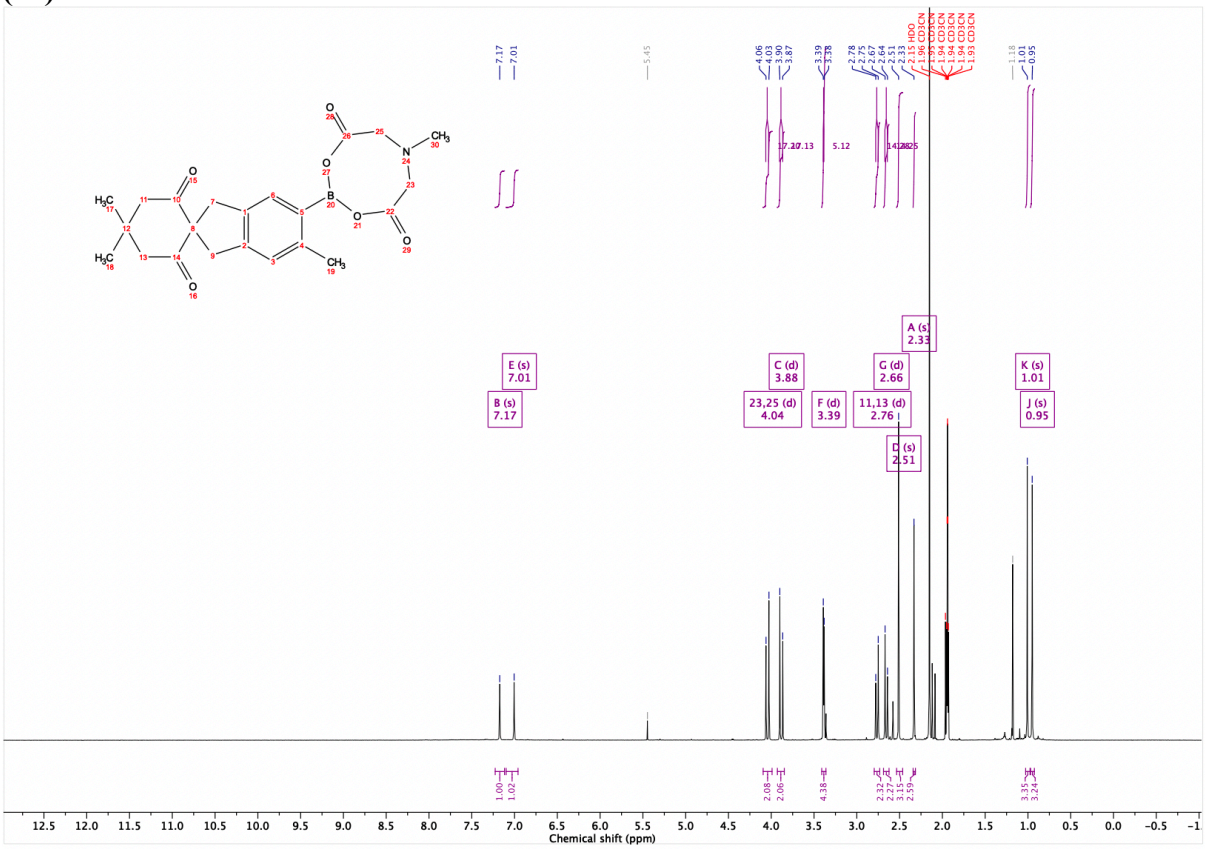


(18) ^{1}H NMR



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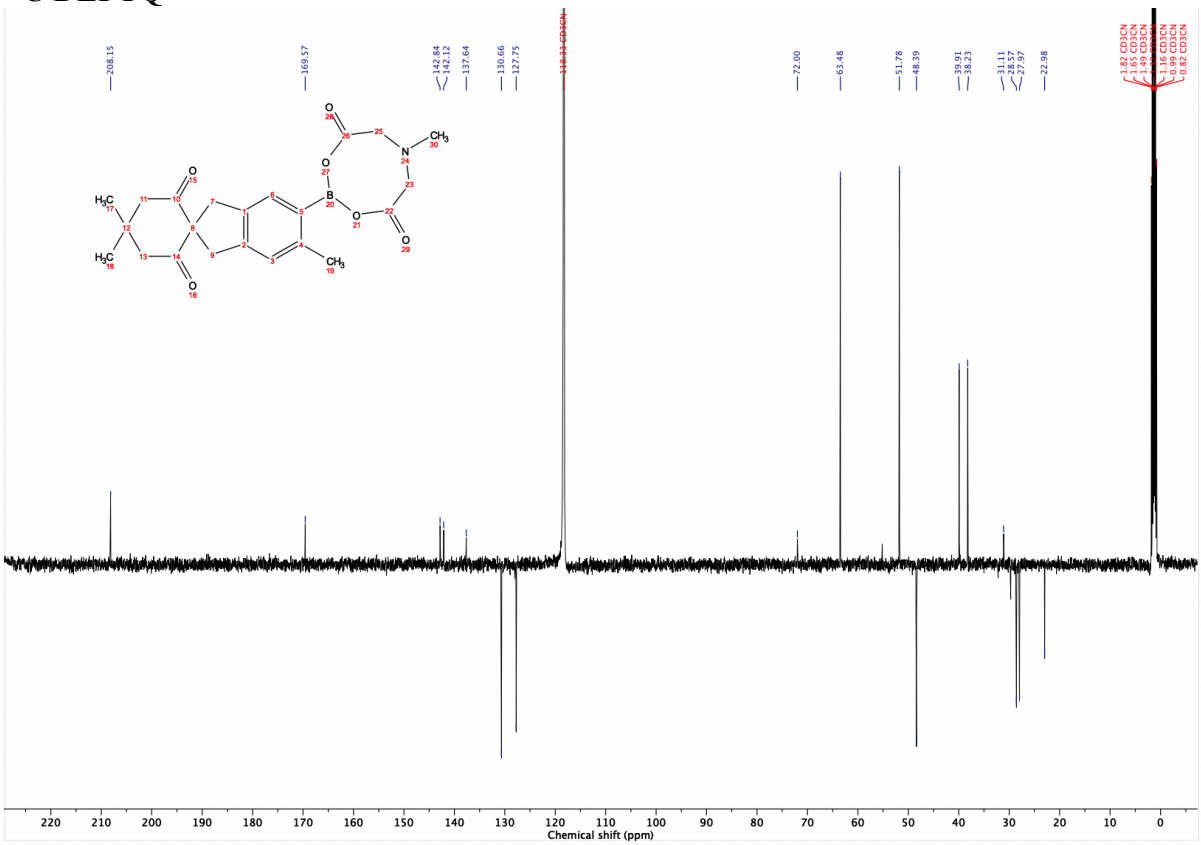
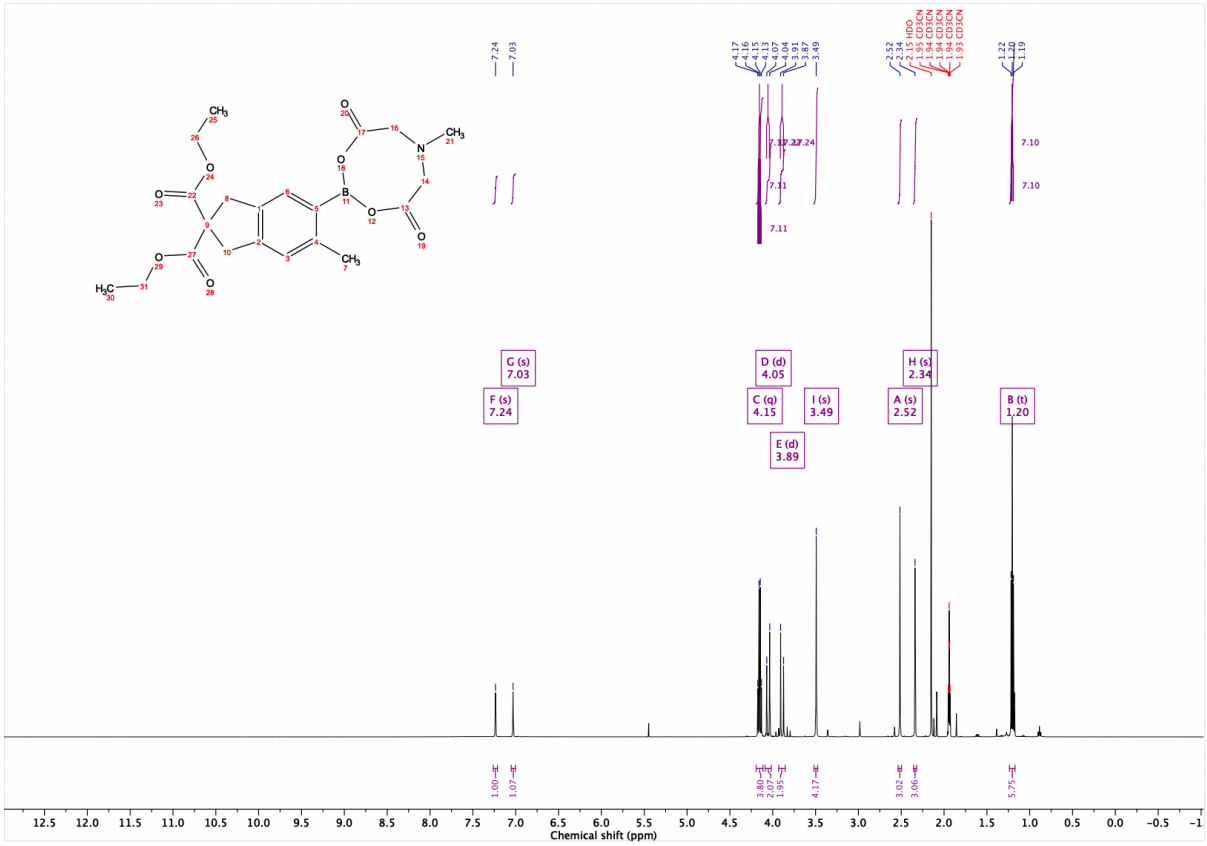


(19) ^{1}H NMR



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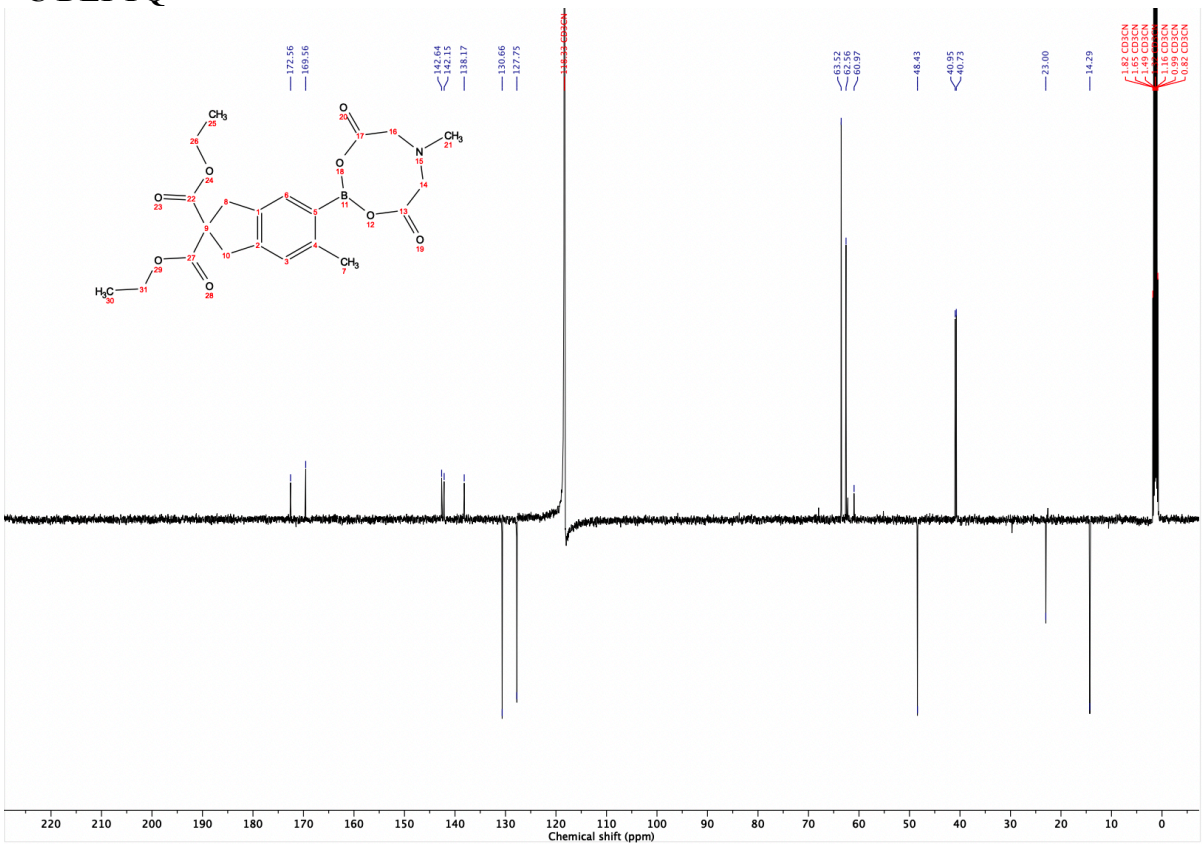
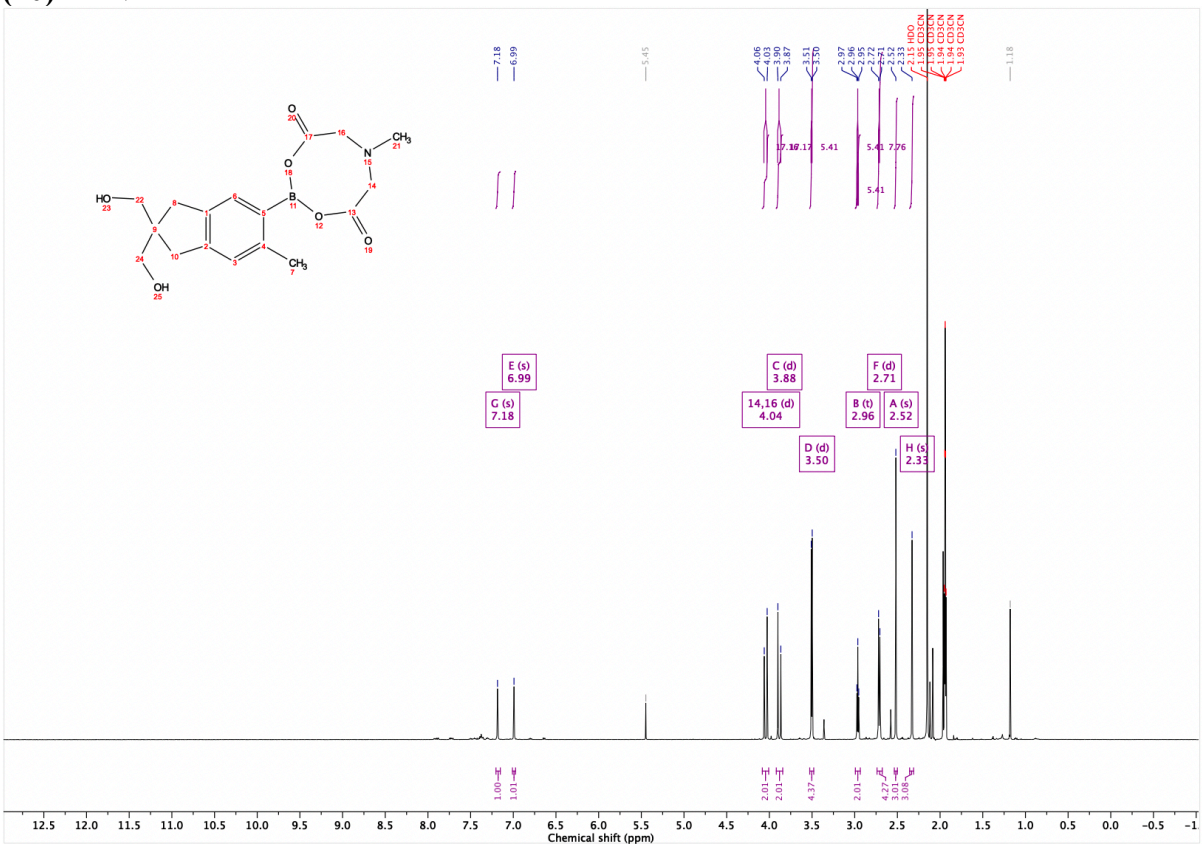
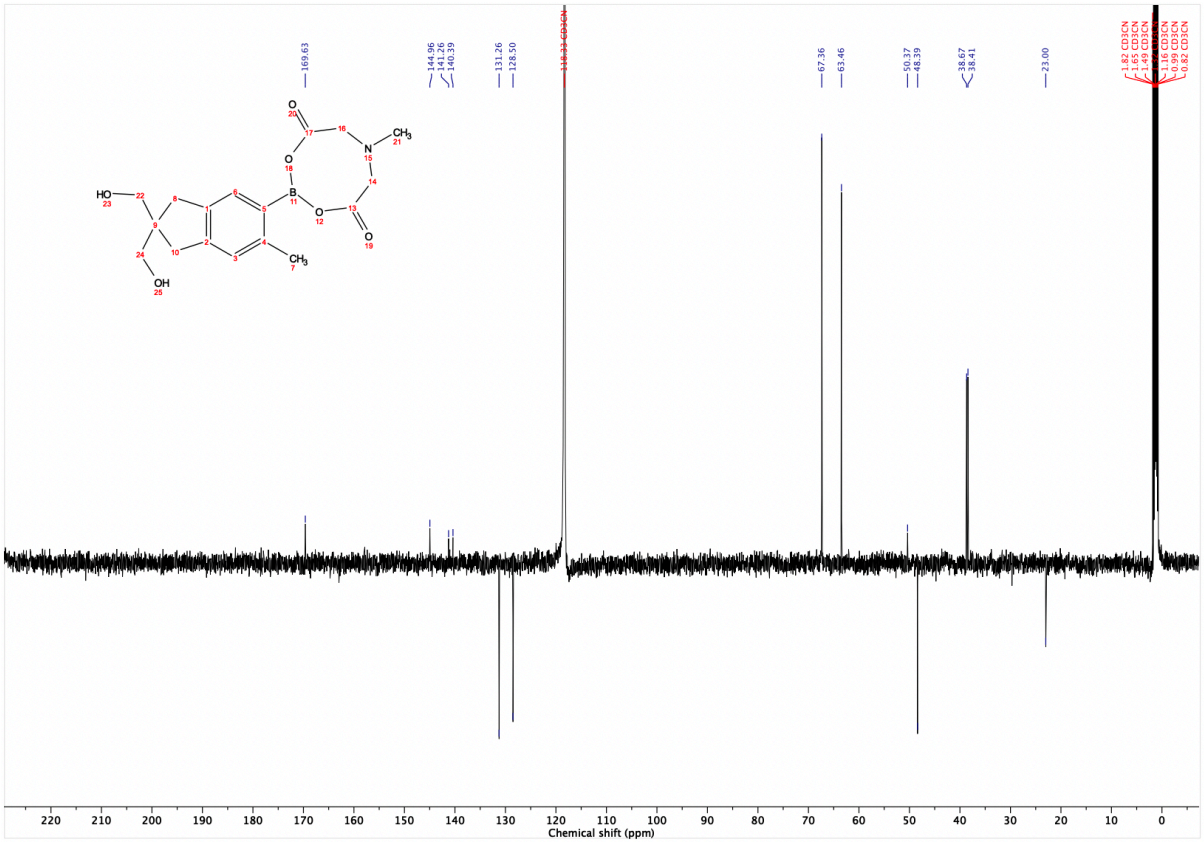


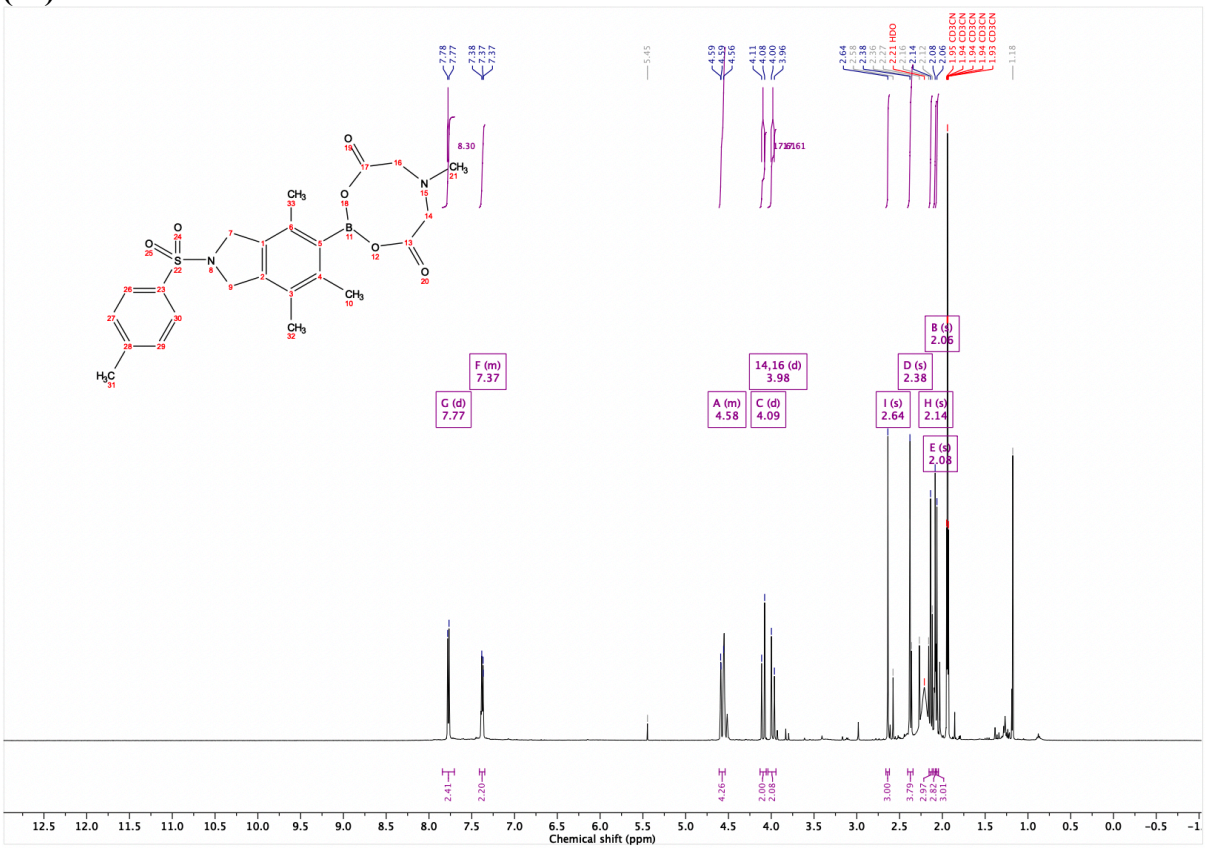
(20) ^{1}H NMR



^{13}C DEPTQ



(21) ^{1}H NMR



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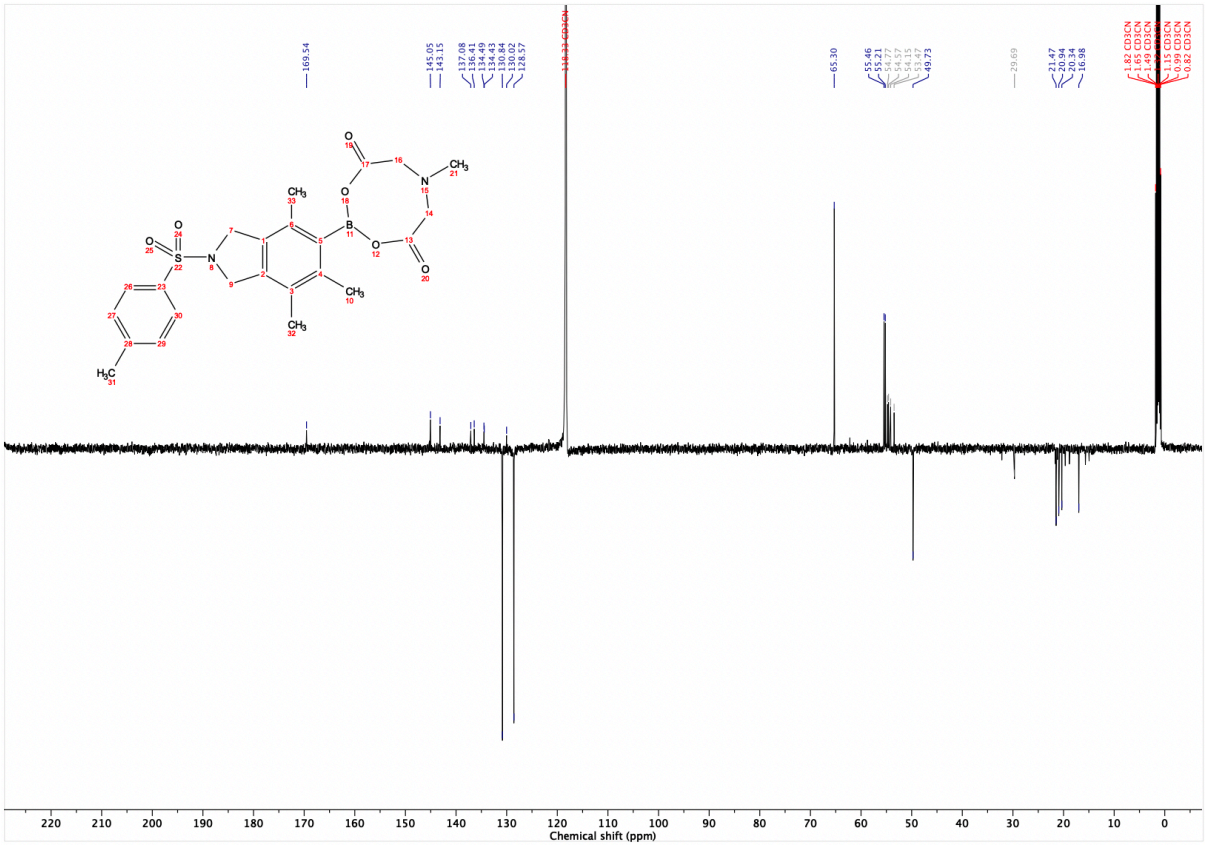
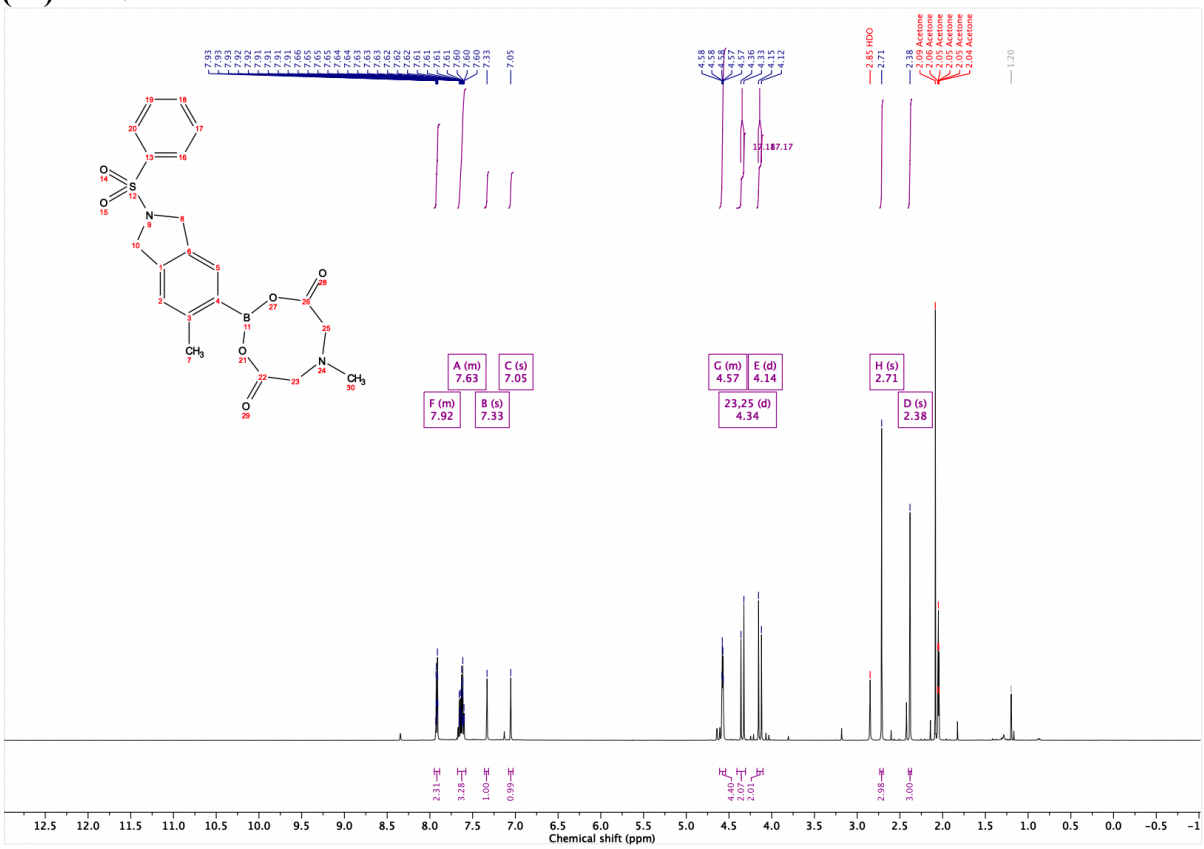


(22) ^{1}H NMR



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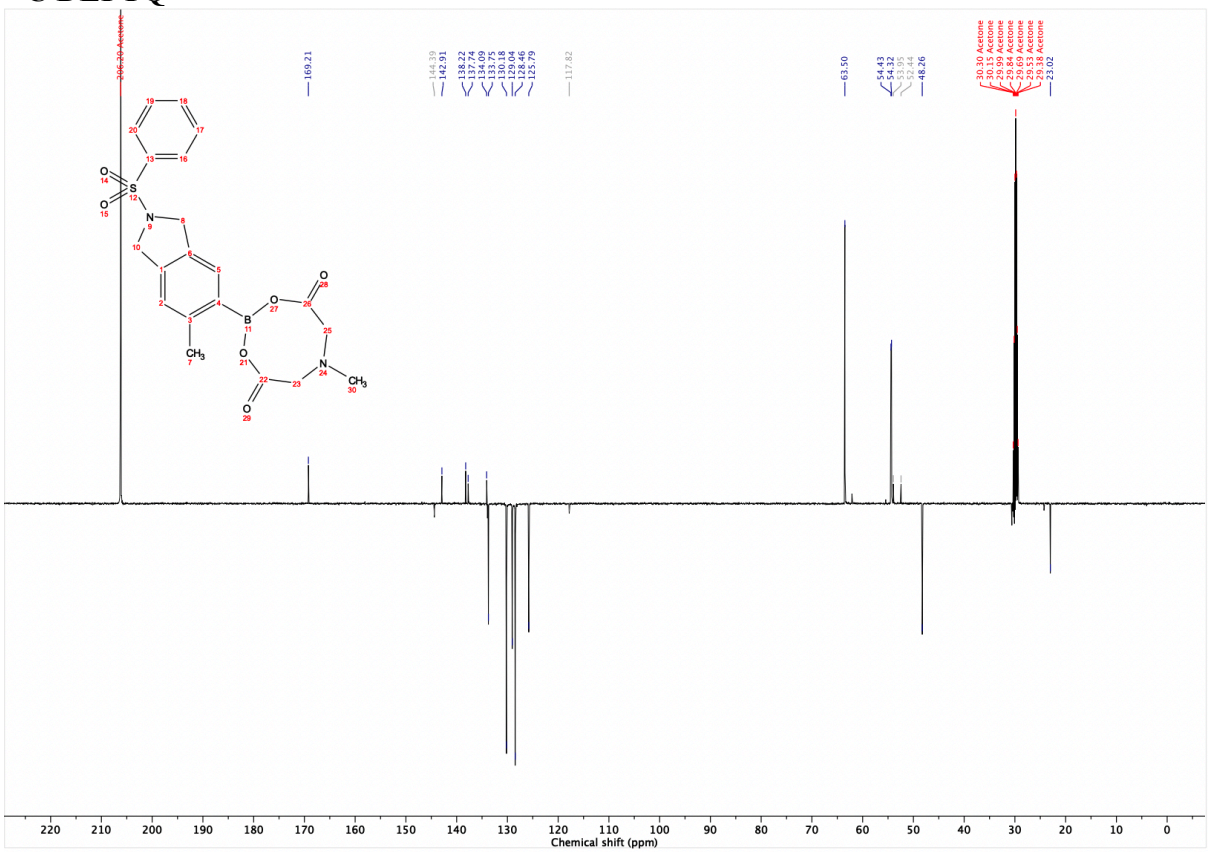
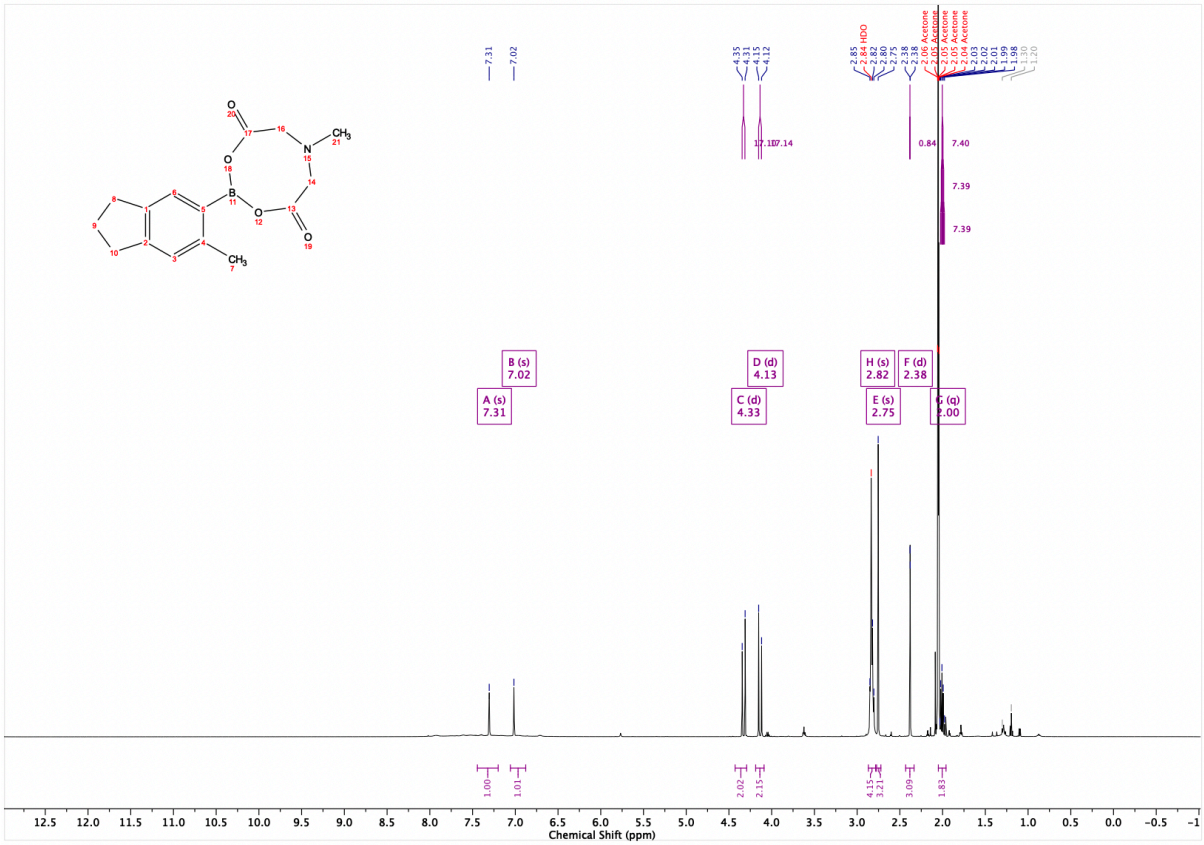


(23) ^{1}H NMR



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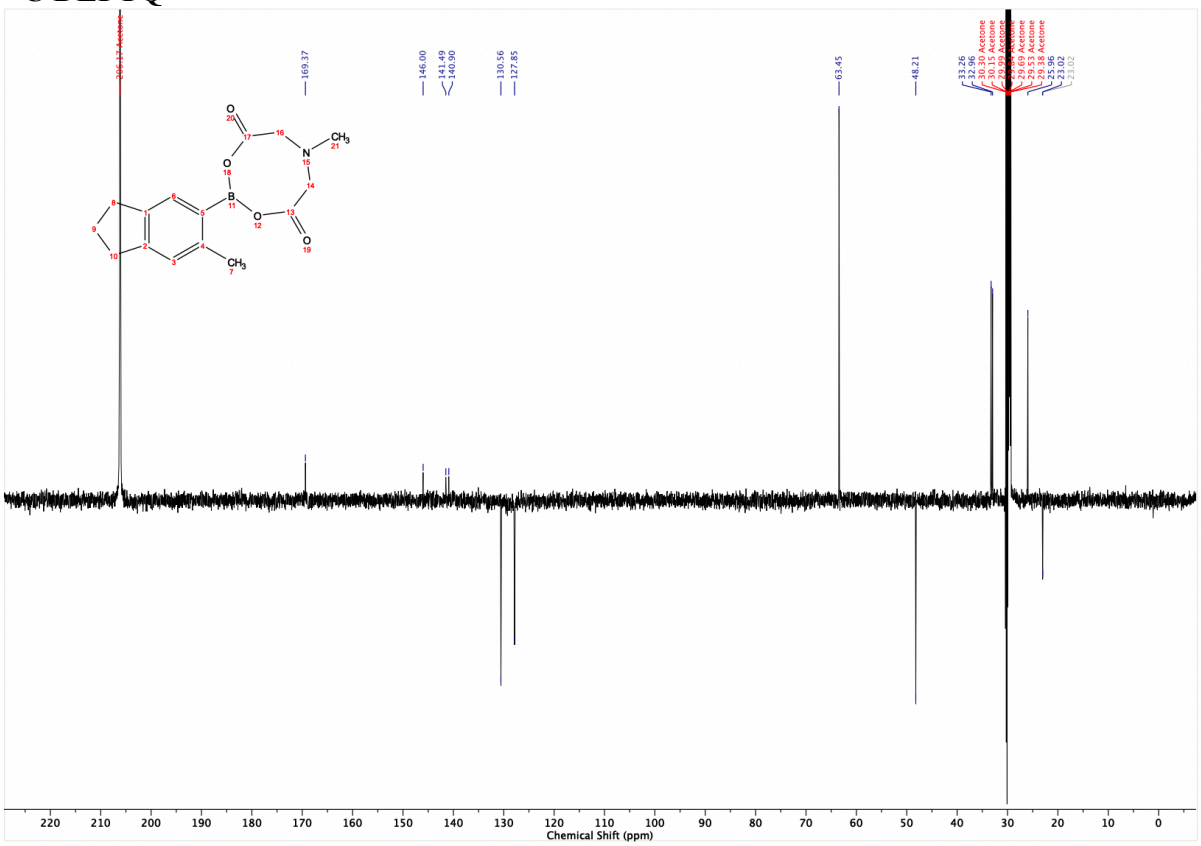
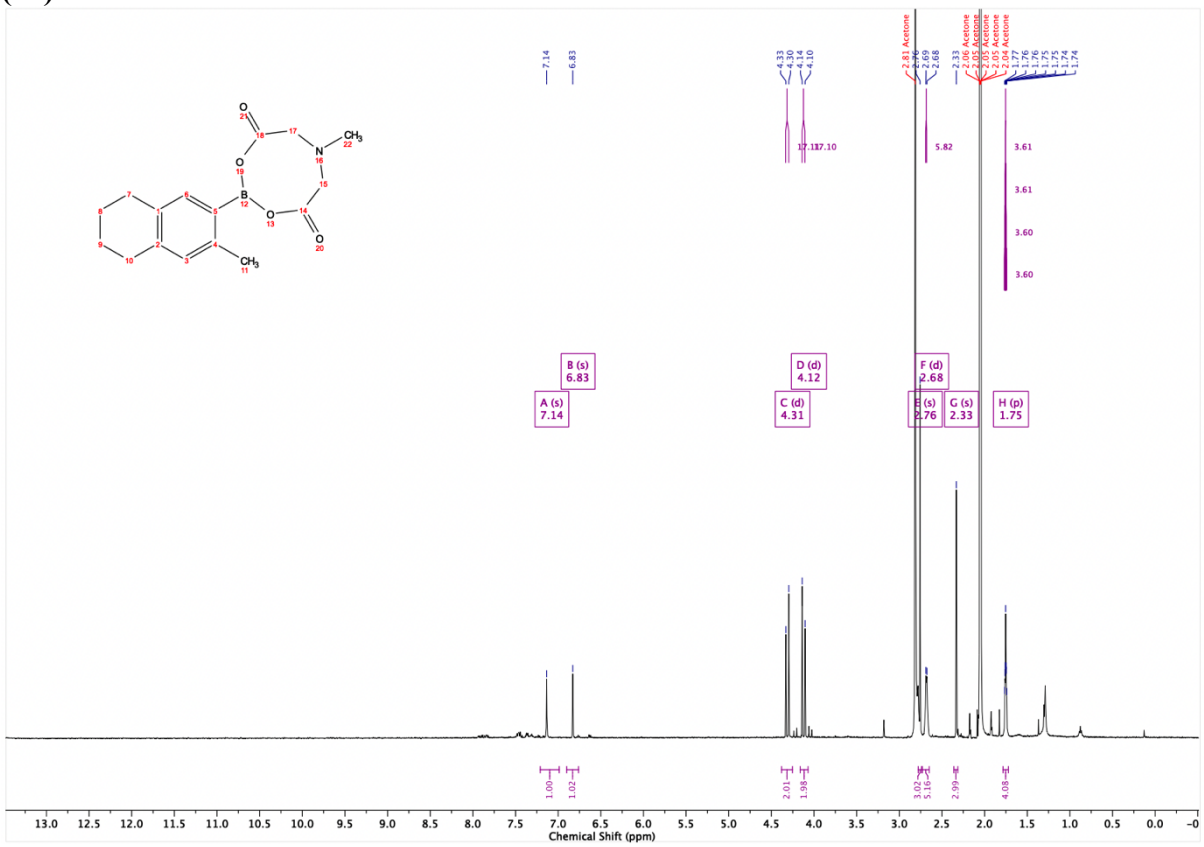


(24) ^{1}H NMR



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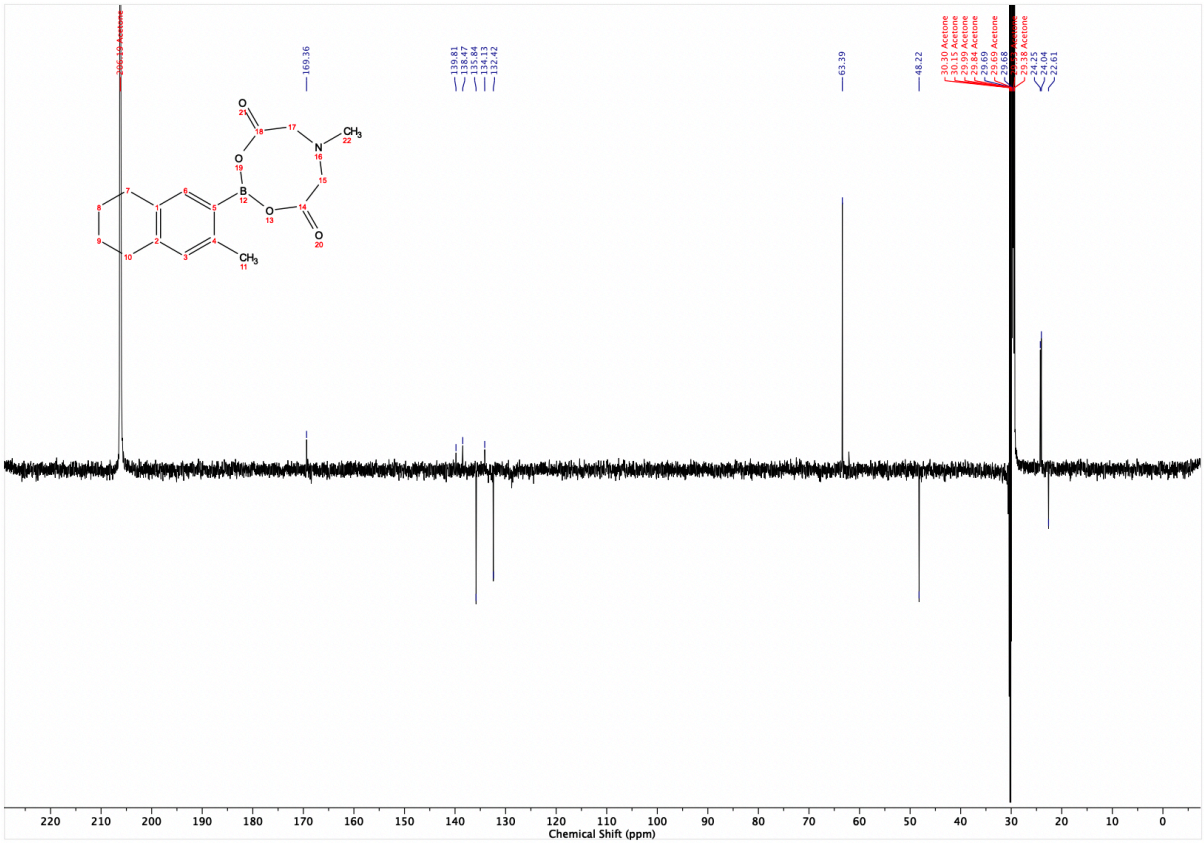
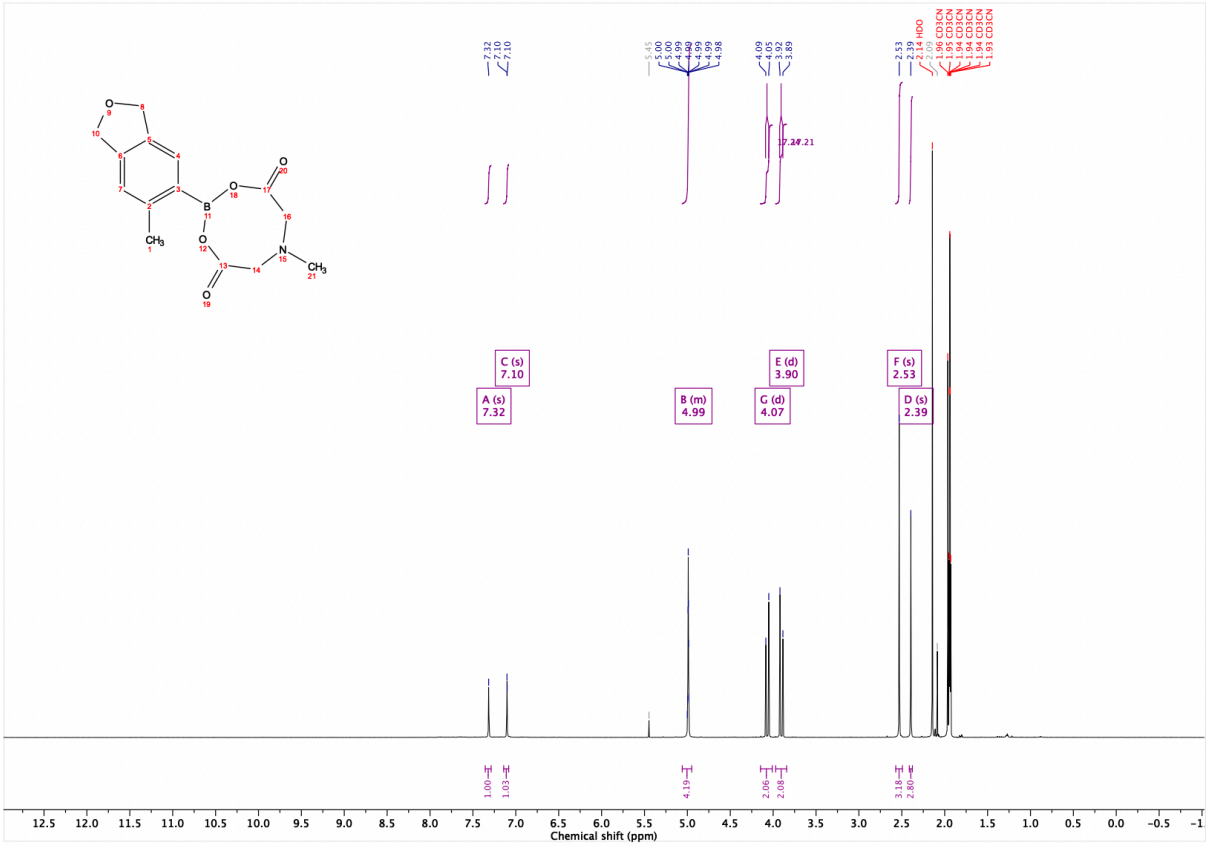


(25) ^{1}H NMR



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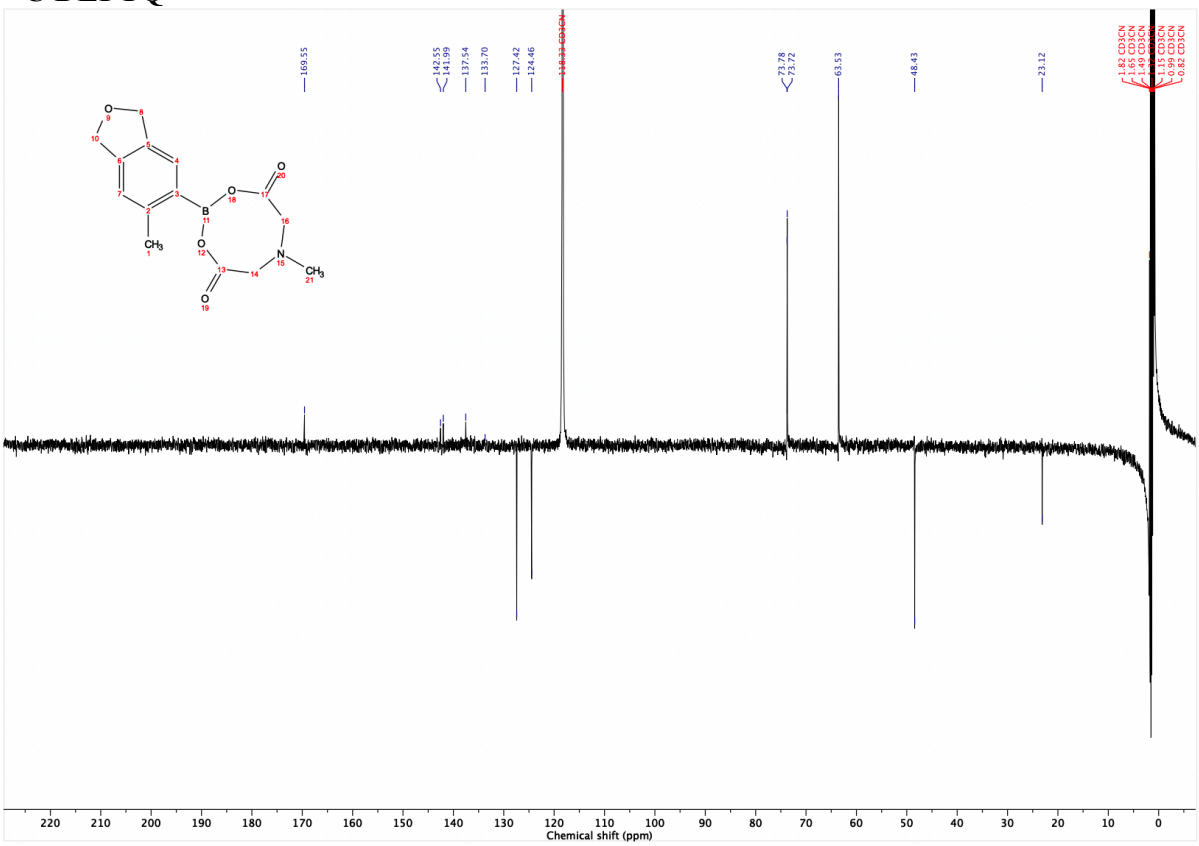
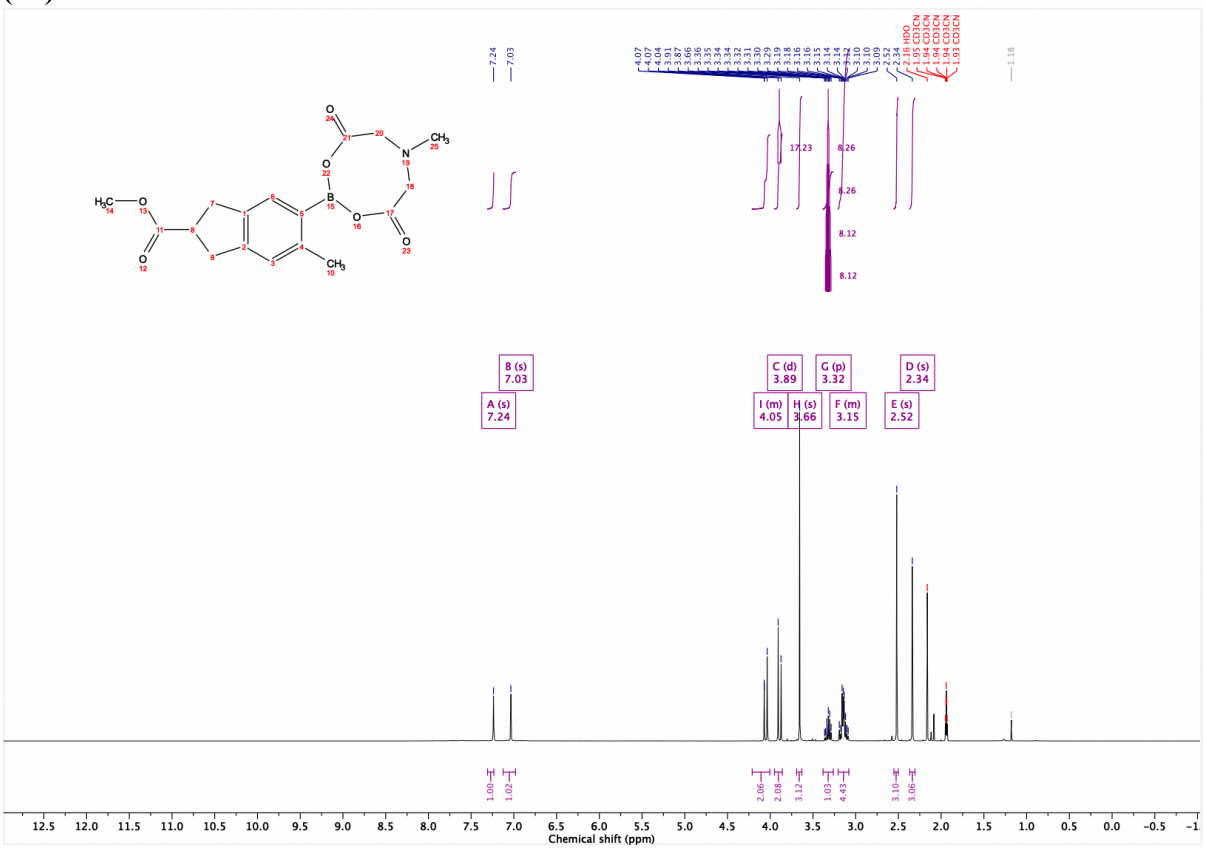


(26) ^{1}H NMR



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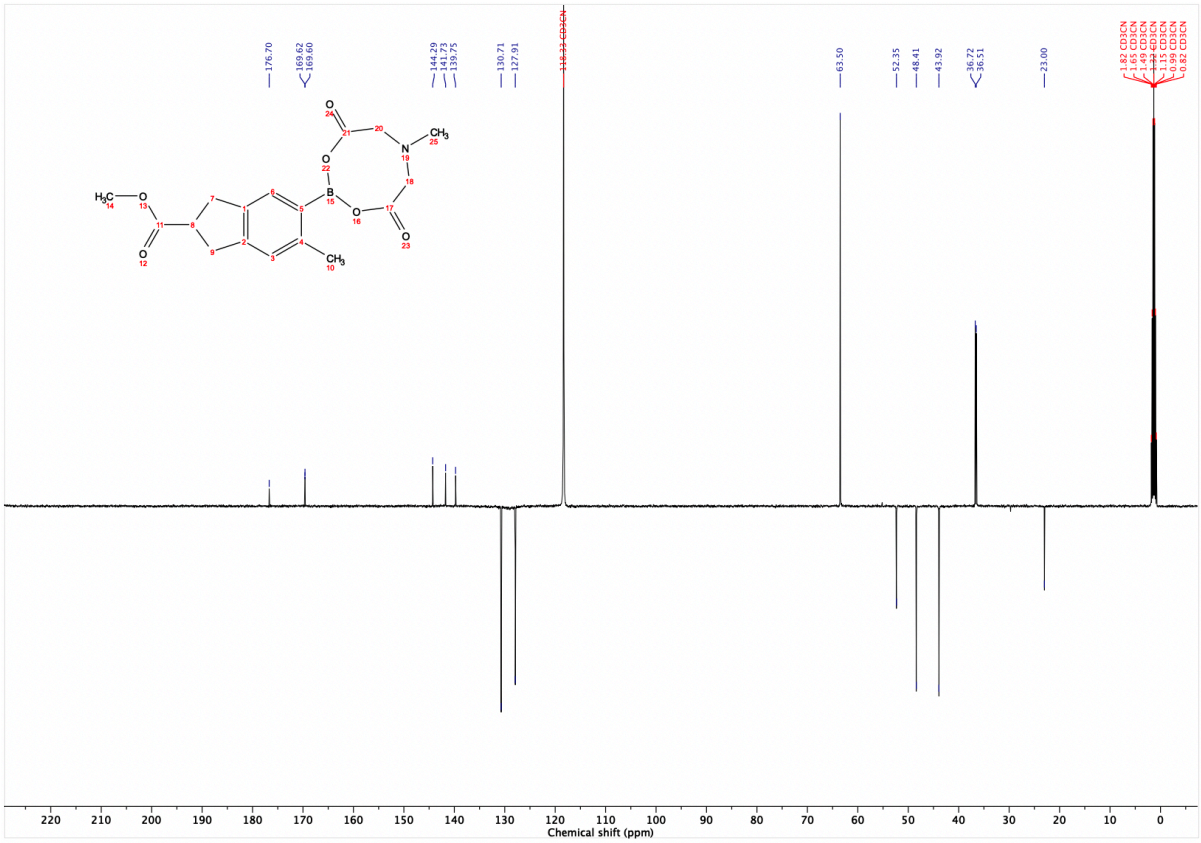
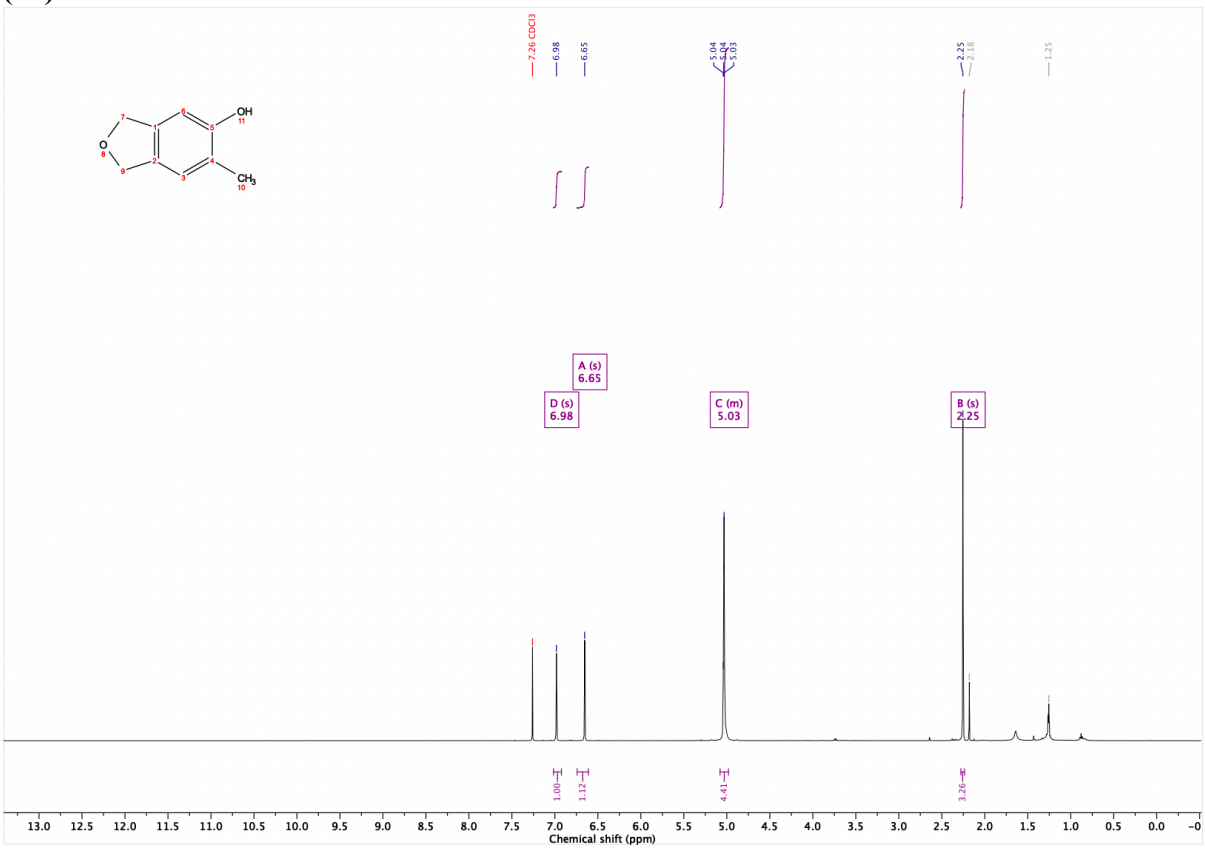


(27) ^{1}H NMR



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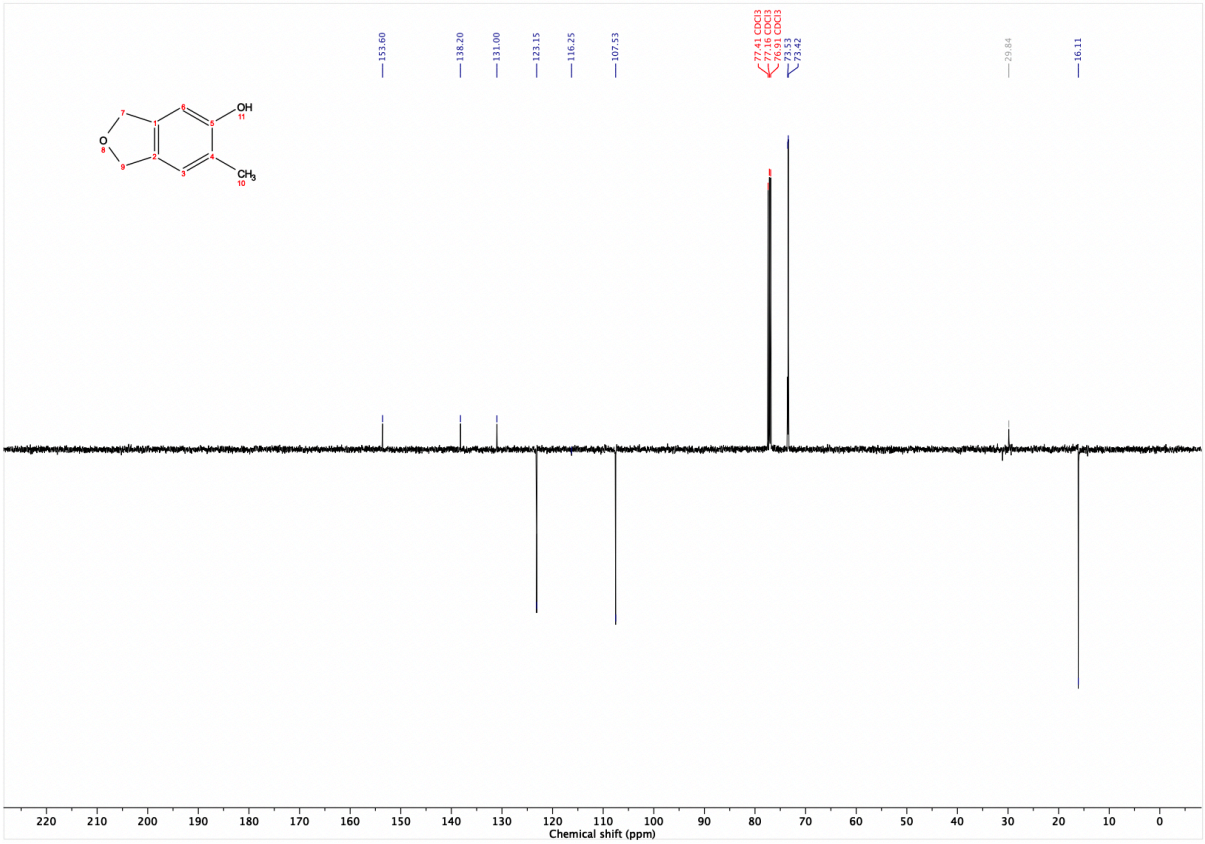
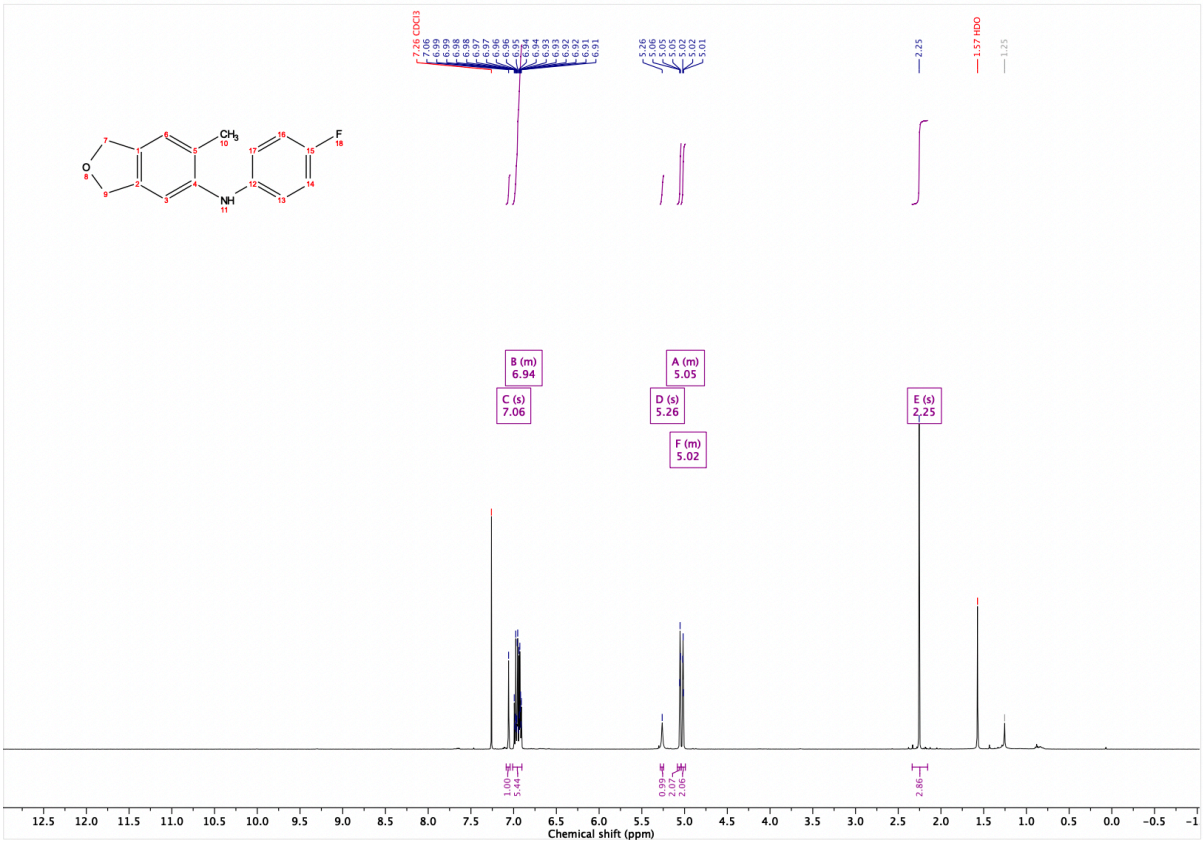


(28) ^{1}H NMR



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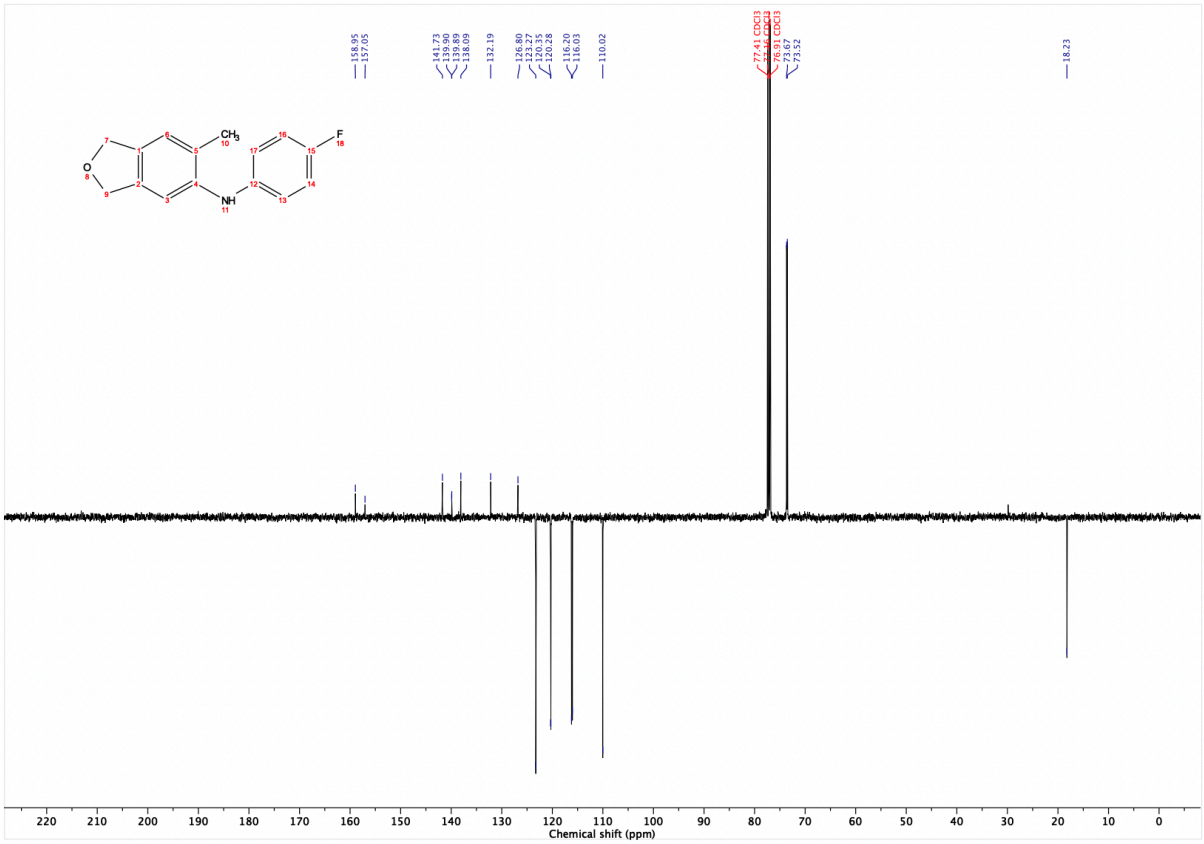
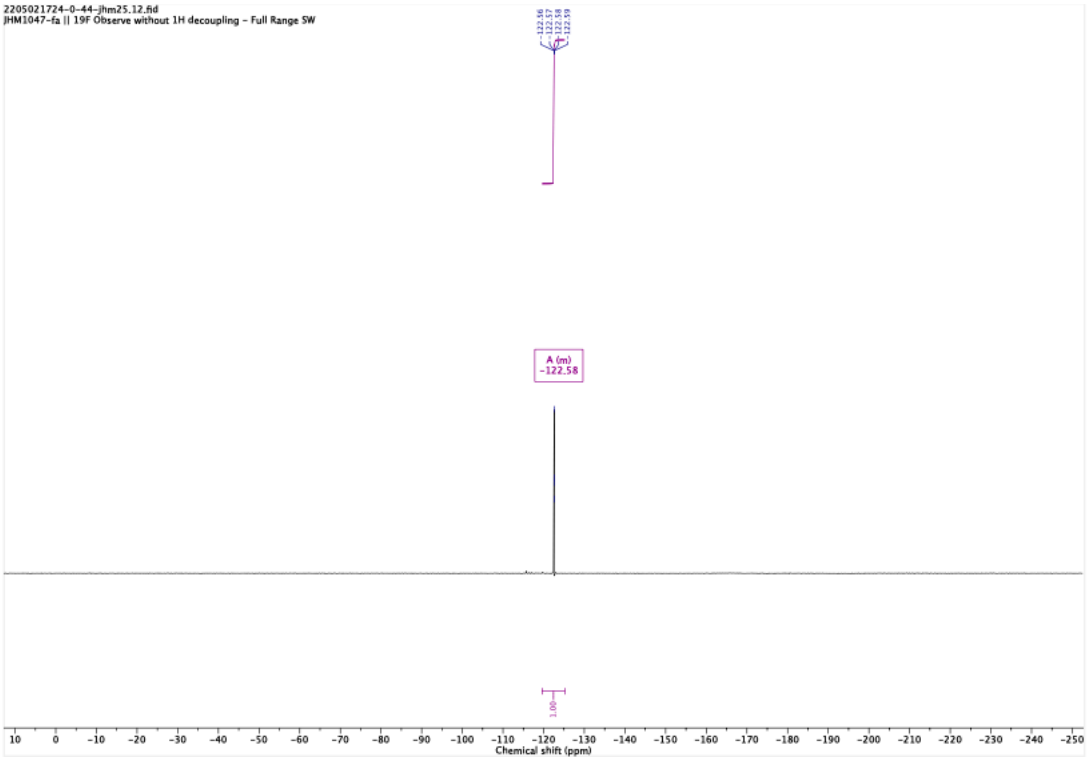
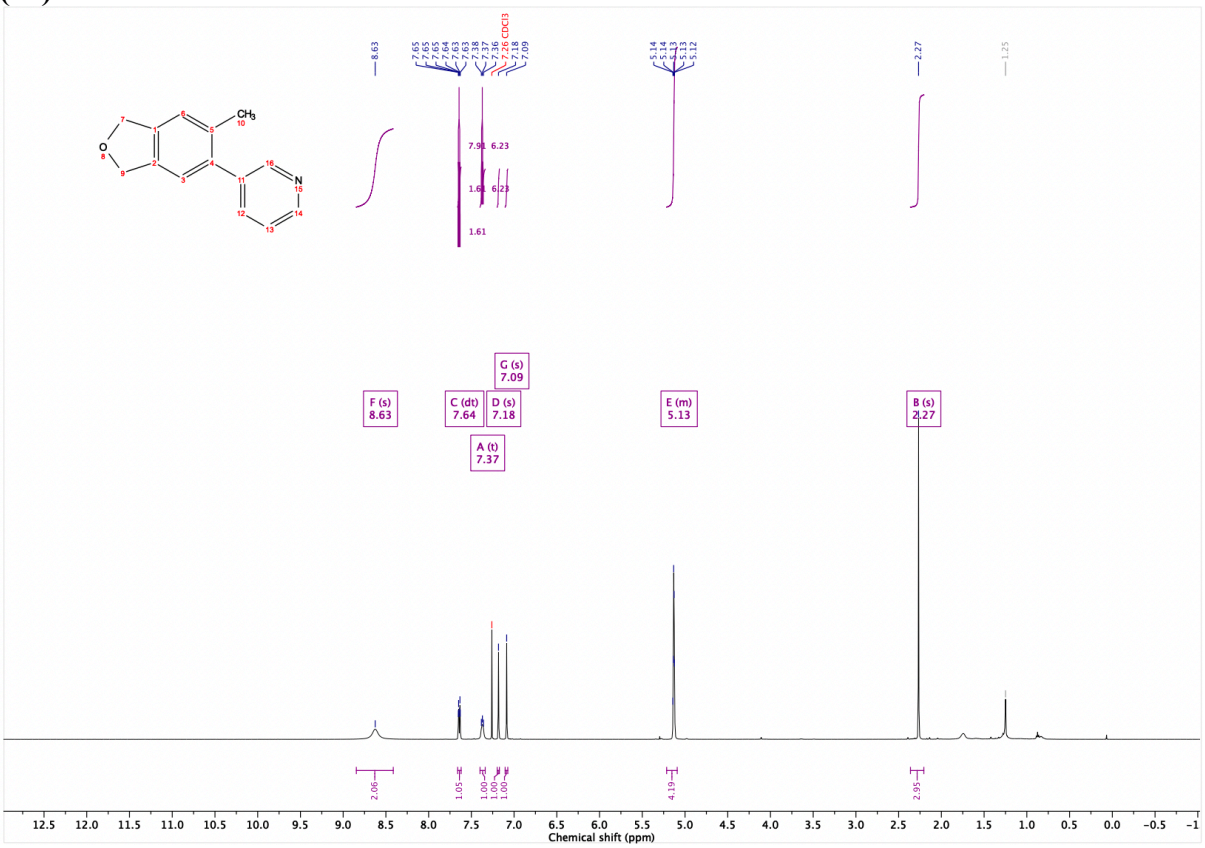


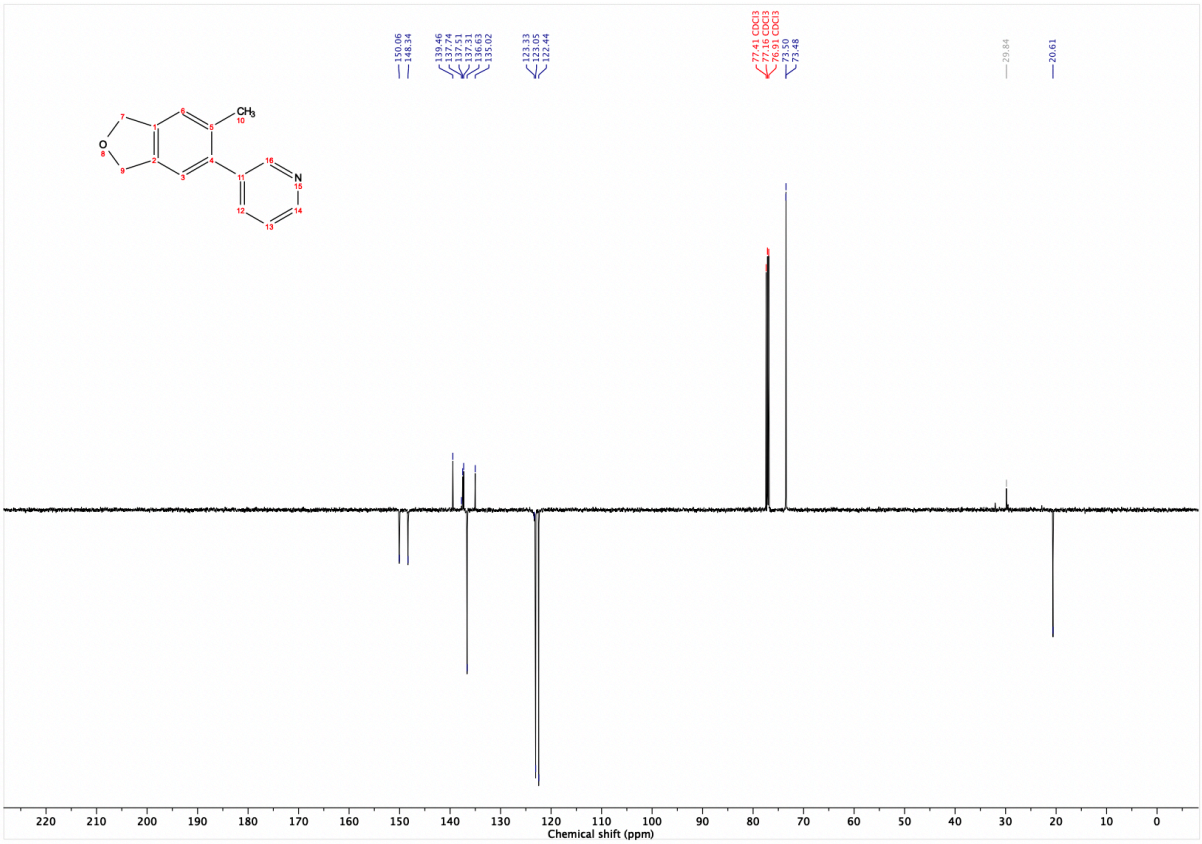
^{19}F



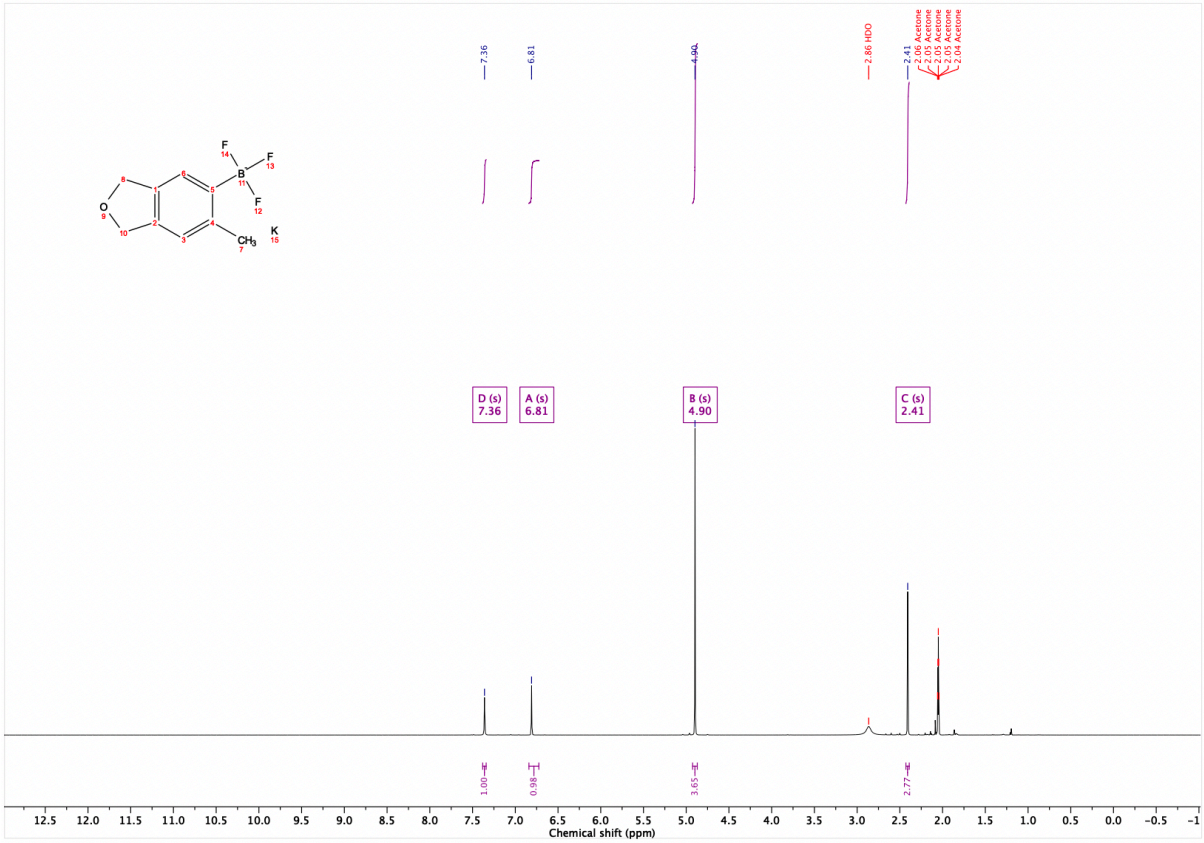
(29) ^{1}H NMR



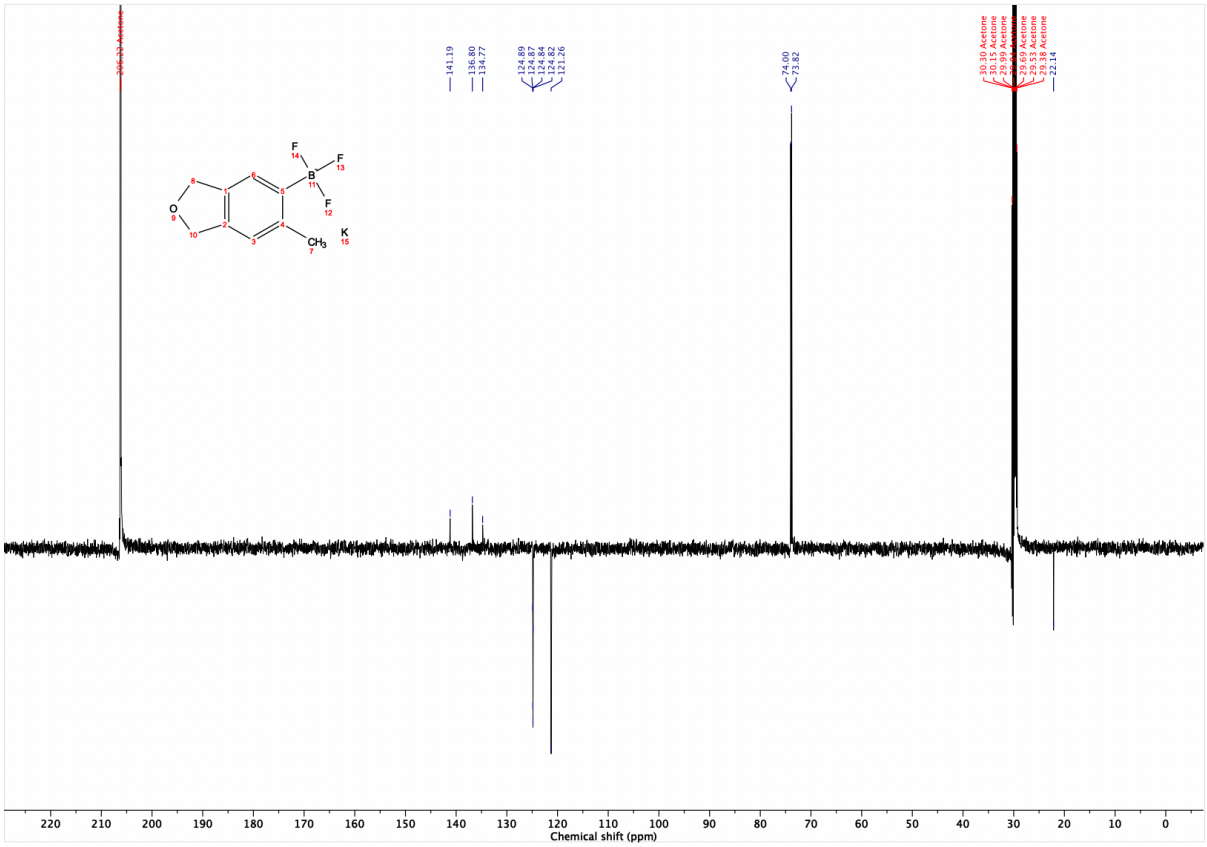
^{13}C DEPTQ



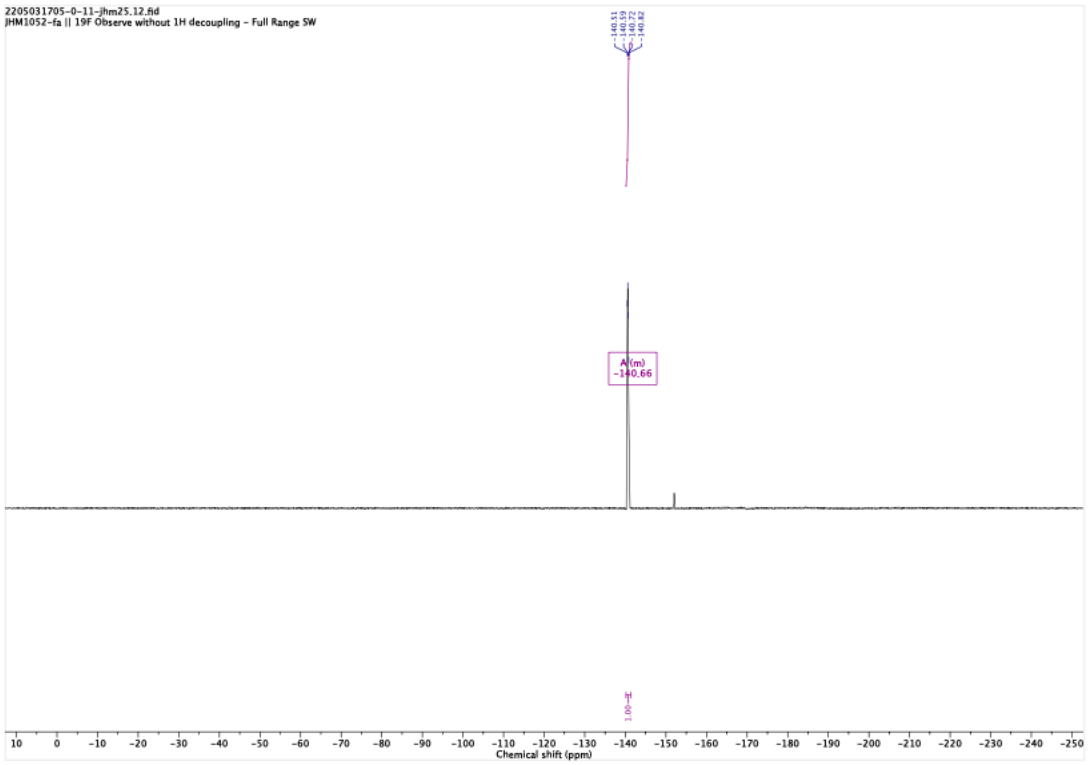
(30) ^{1}H NMR



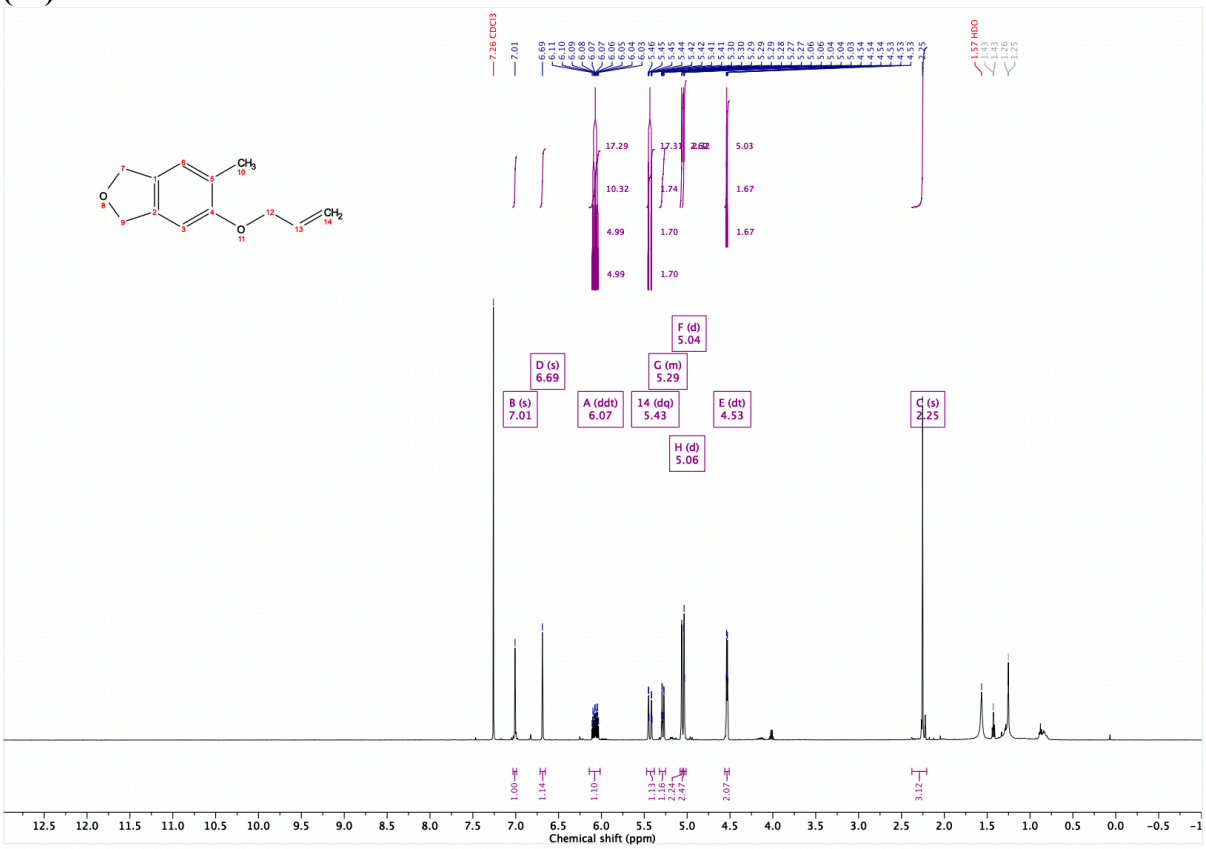
^{13}C DEPTQ



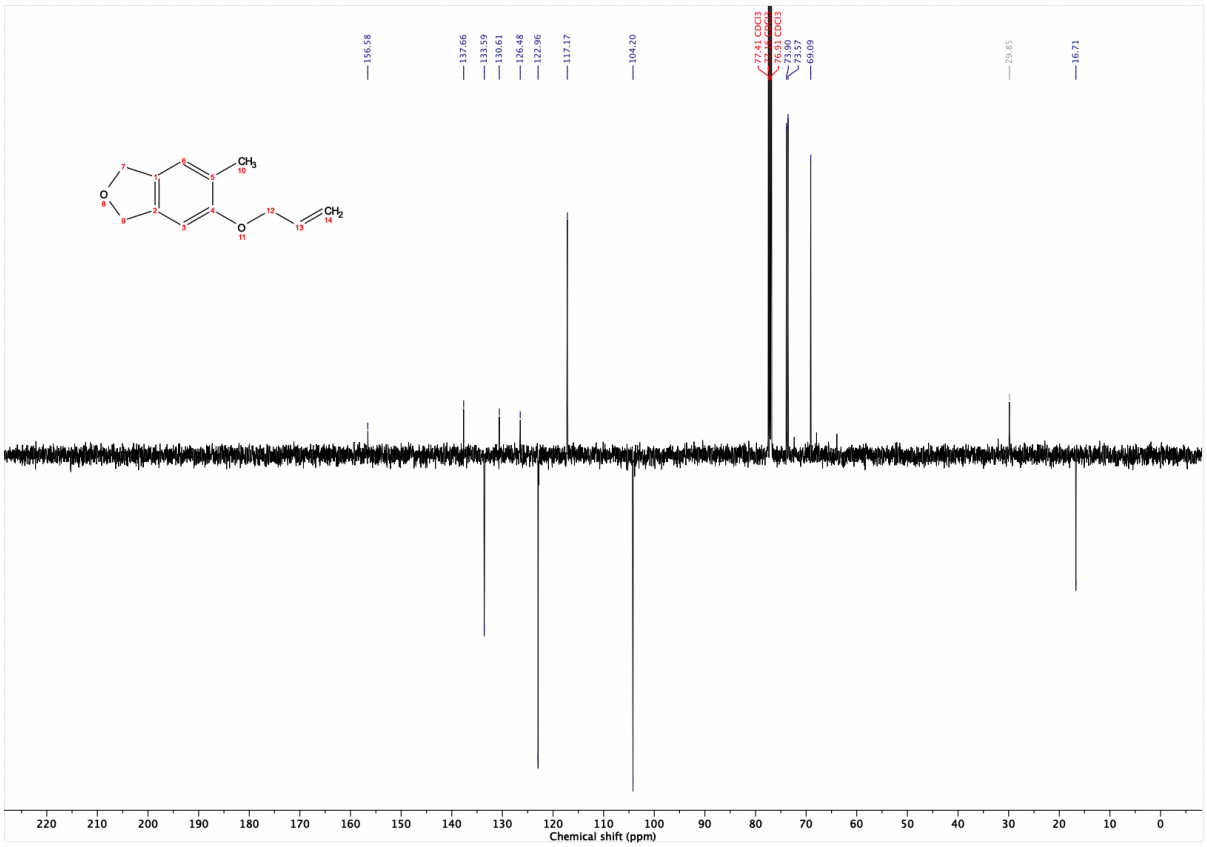
^{19}F


2205031705-0-11-jhm25_12.fid
JHM1052-fa || 19F Observe without 1H decoupling - Full Range SW
A(m)
-140.66
Chemical shift (ppm)

(31) ^{1}H NMR

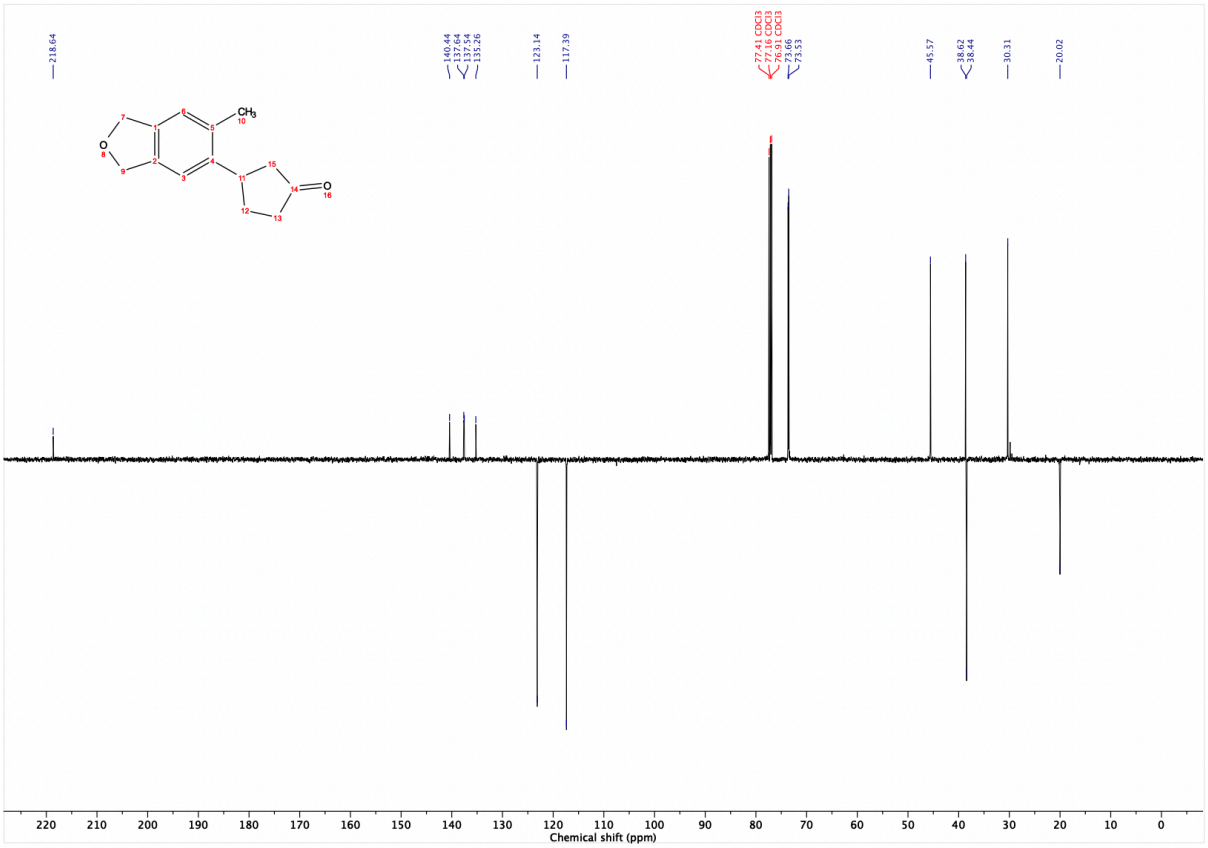

7.26 CDCl3
1.57 HDO
B (s)
7.01
D (s)
6.69
A (ddt)
6.07
14 (dq)
5.43
G (m)
5.29
F (d)
5.04
H (d)
5.06
E (dt)
4.53
C (s)
2.25
Chemical shift (ppm)

^{13}C DEPTQ

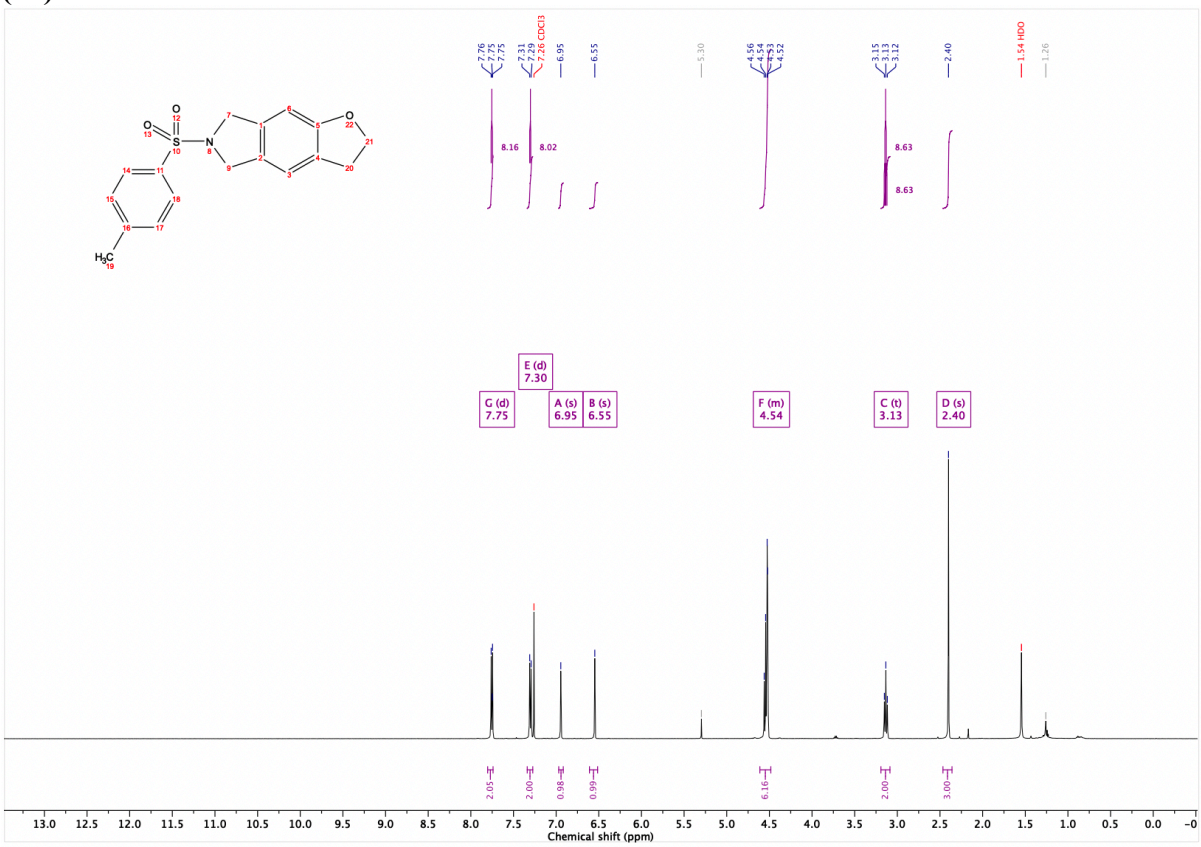


(32) ^{1}H NMR

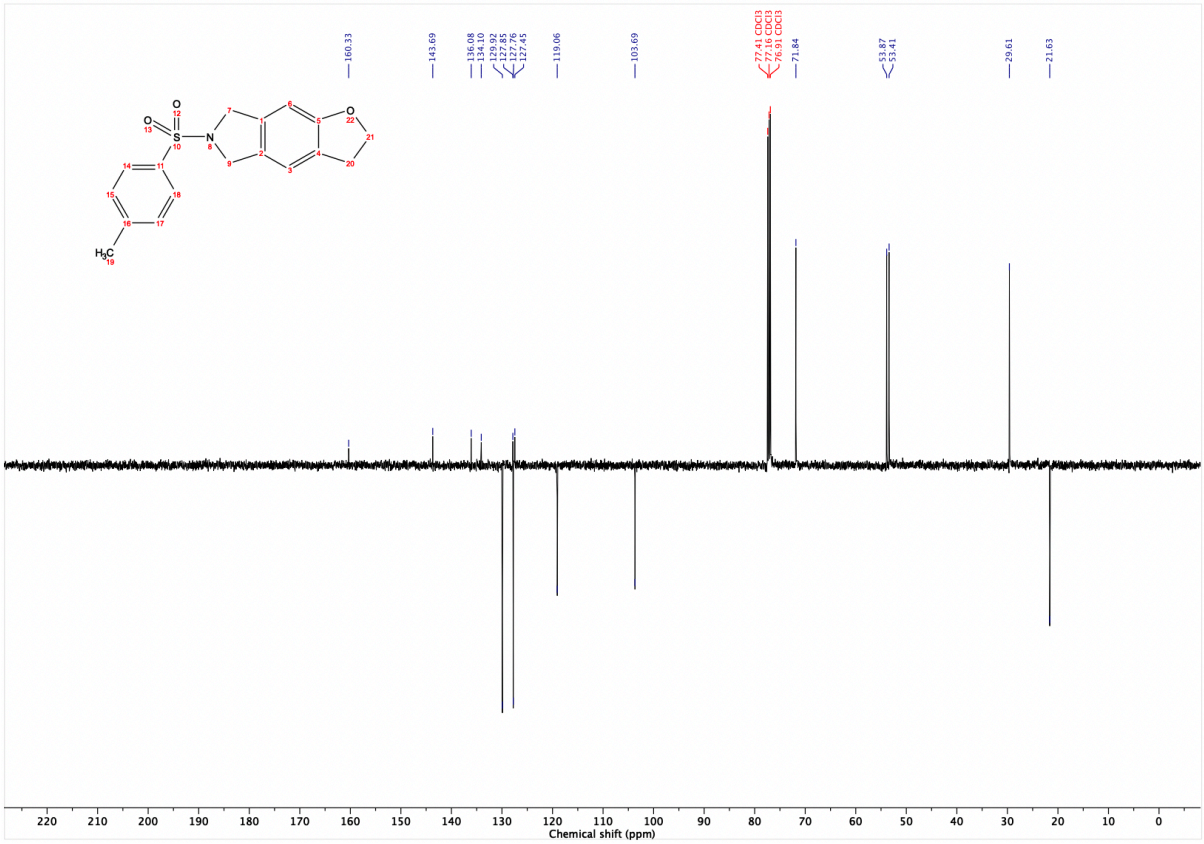
^{13}C DEPTQ



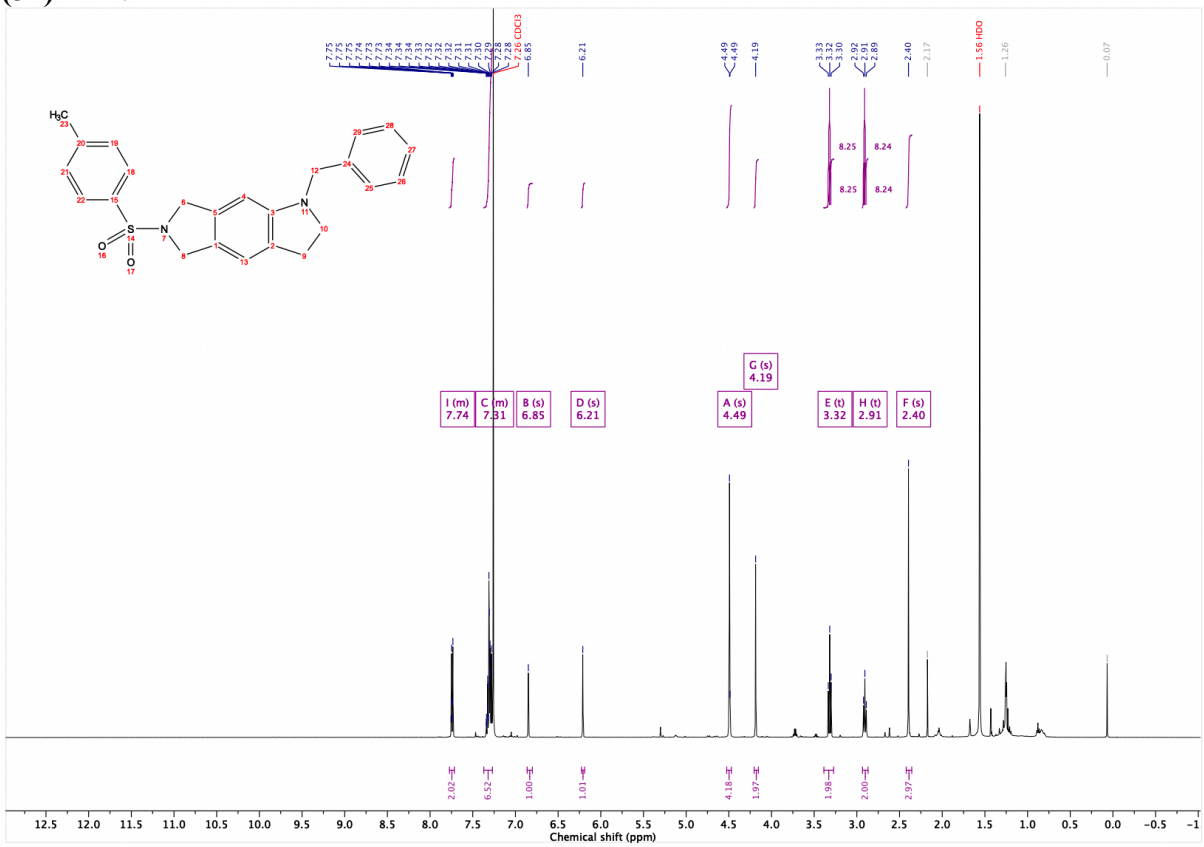
(33) ^{1}H NMR



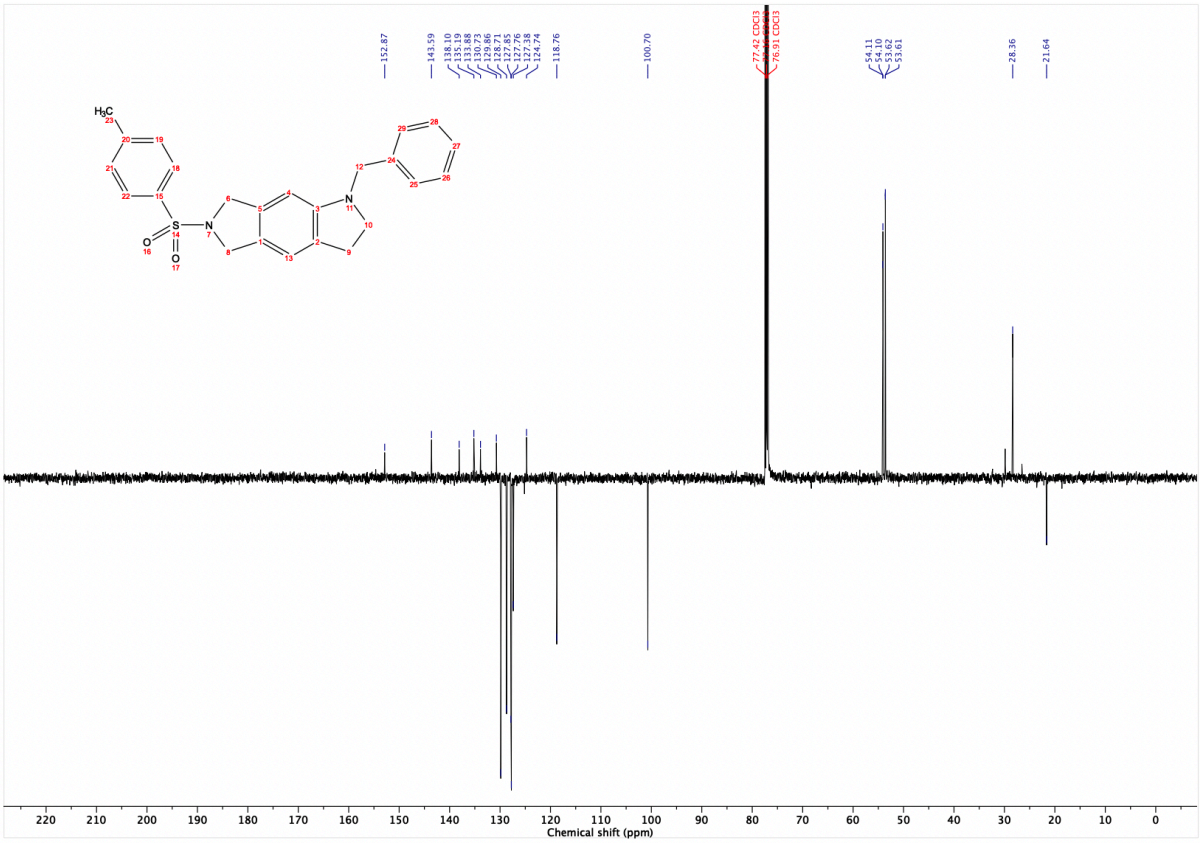
^{13}C DEPTQ



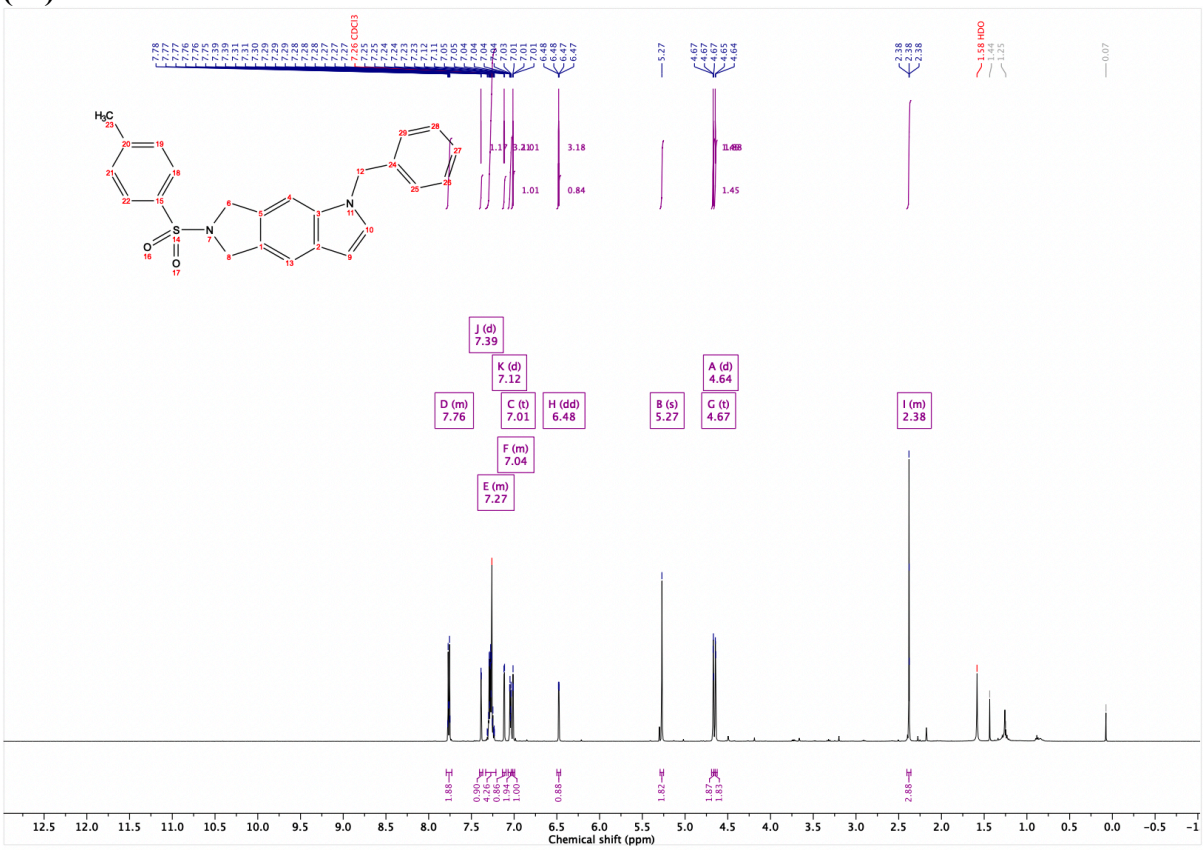
(34) ^{1}H NMR



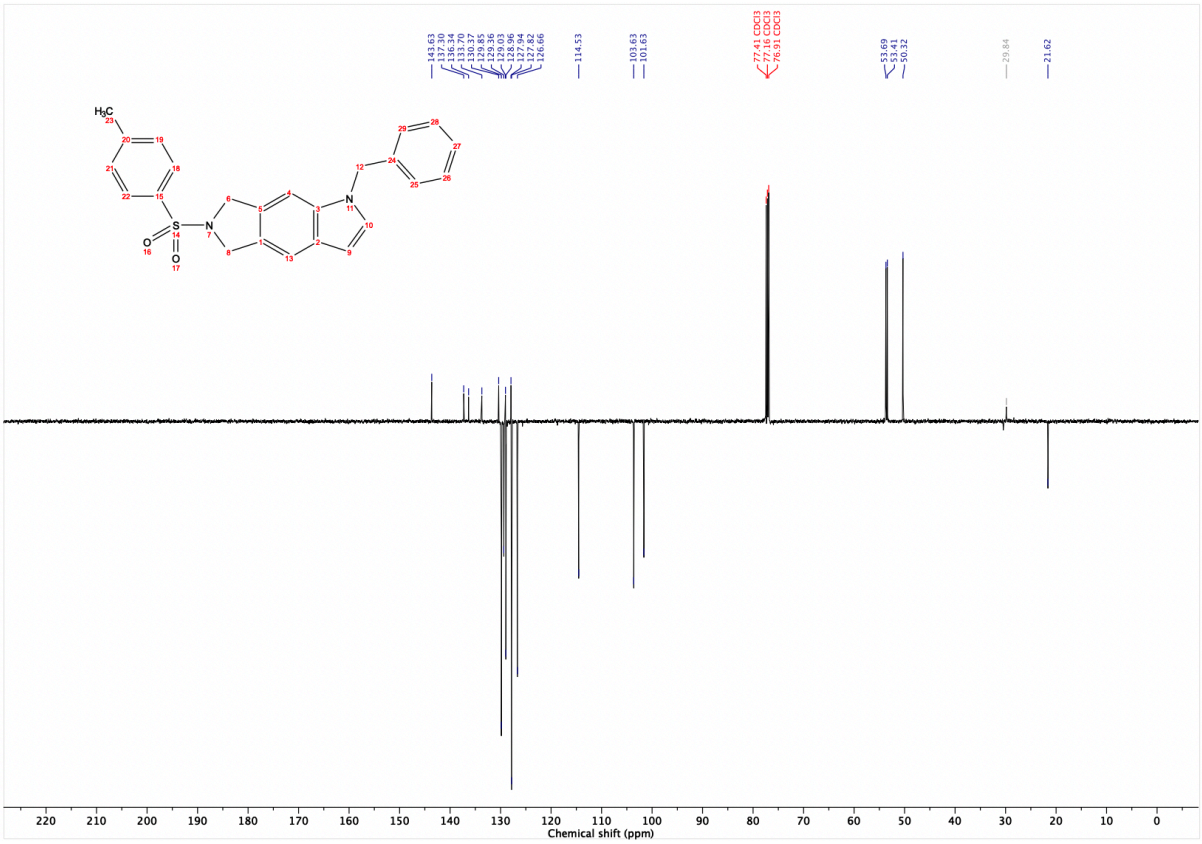
^{13}C DEPTQ



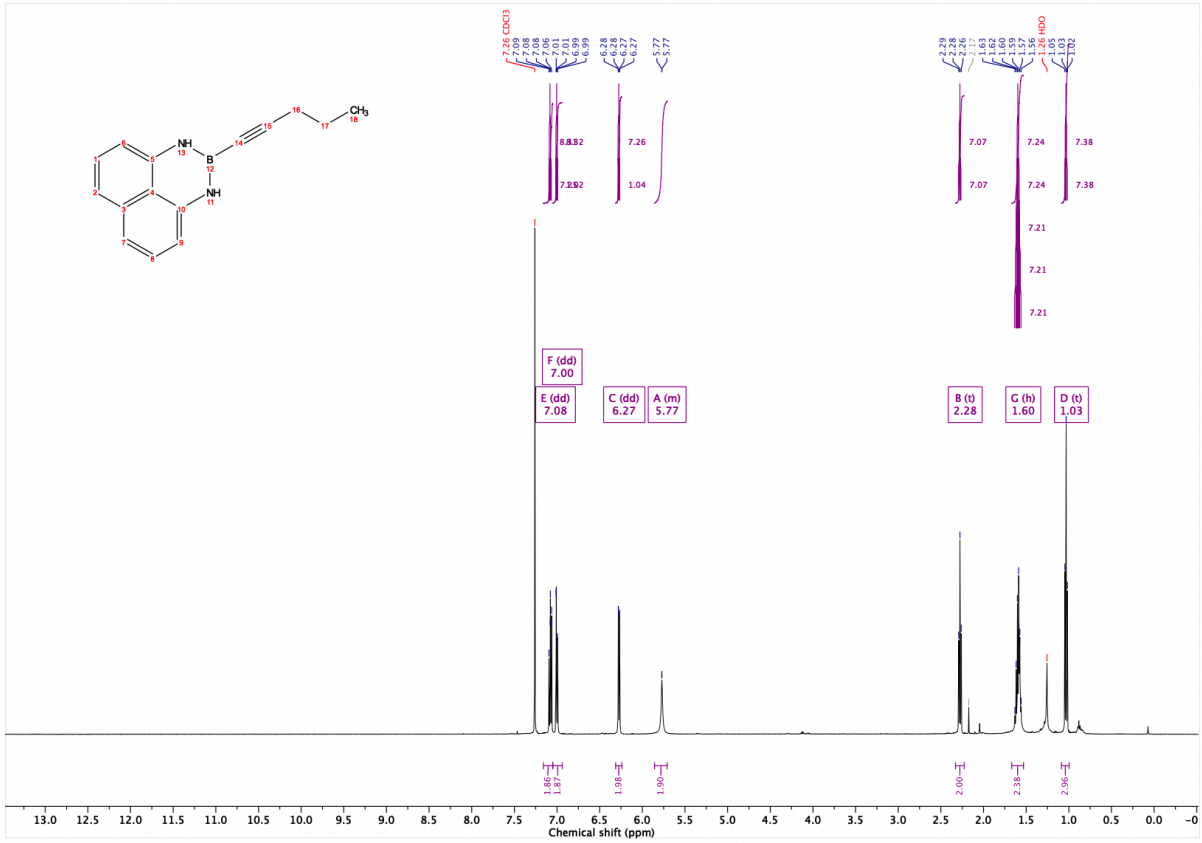
(35) ^{1}H NMR



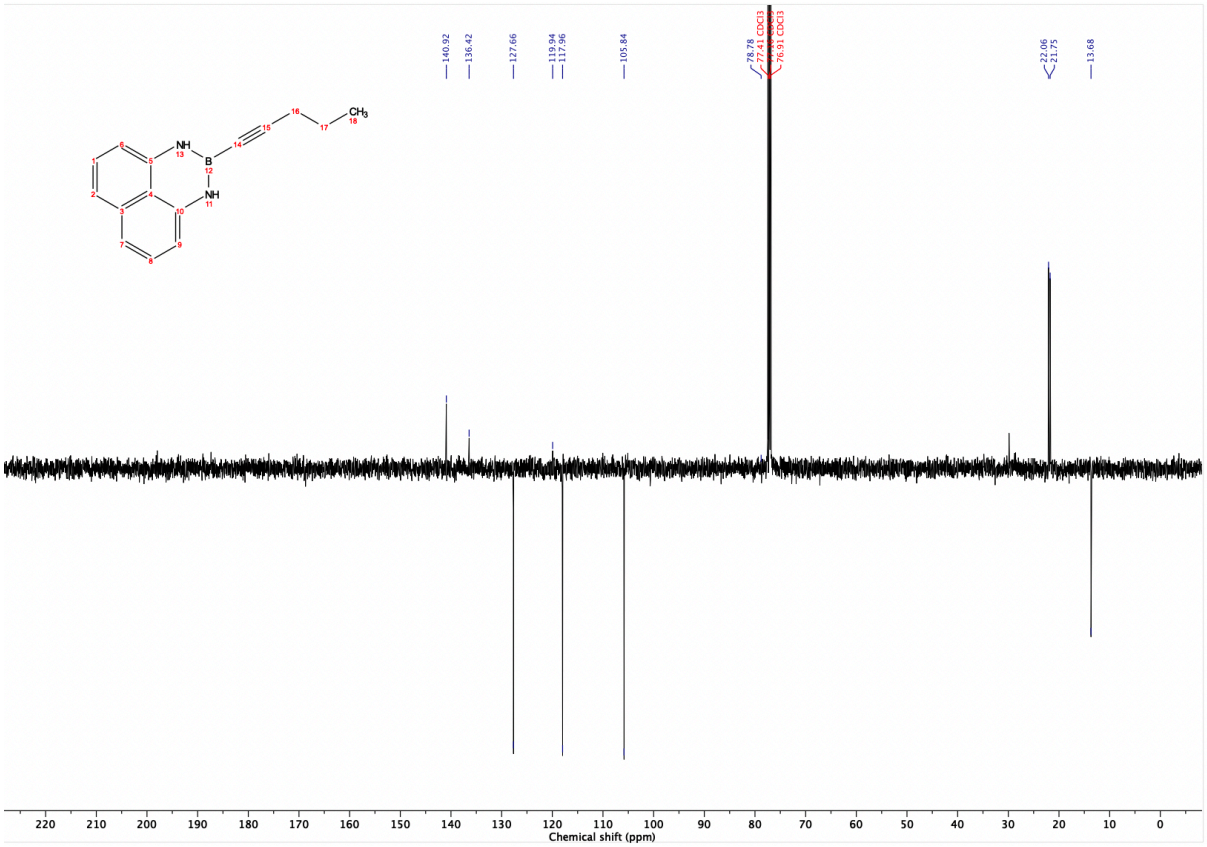
^{13}C DEPTQ



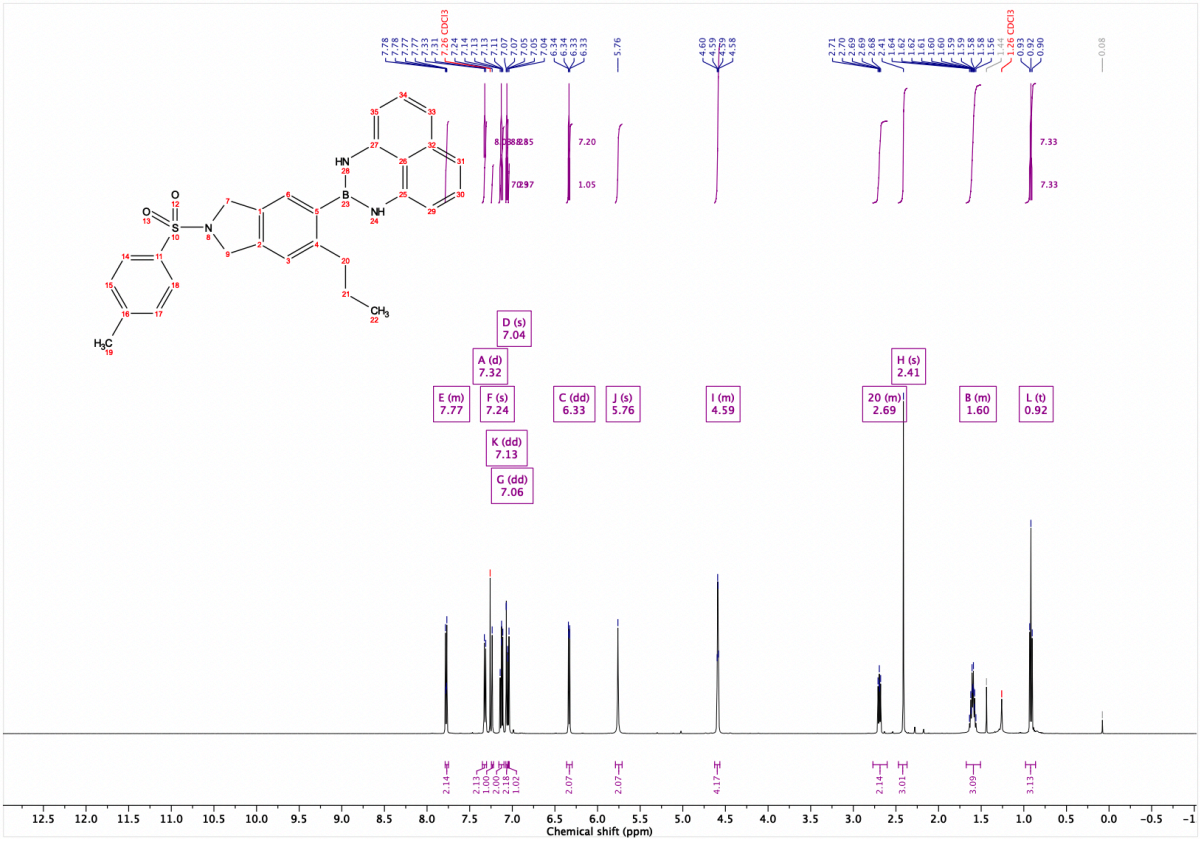
(36) ^{1}H



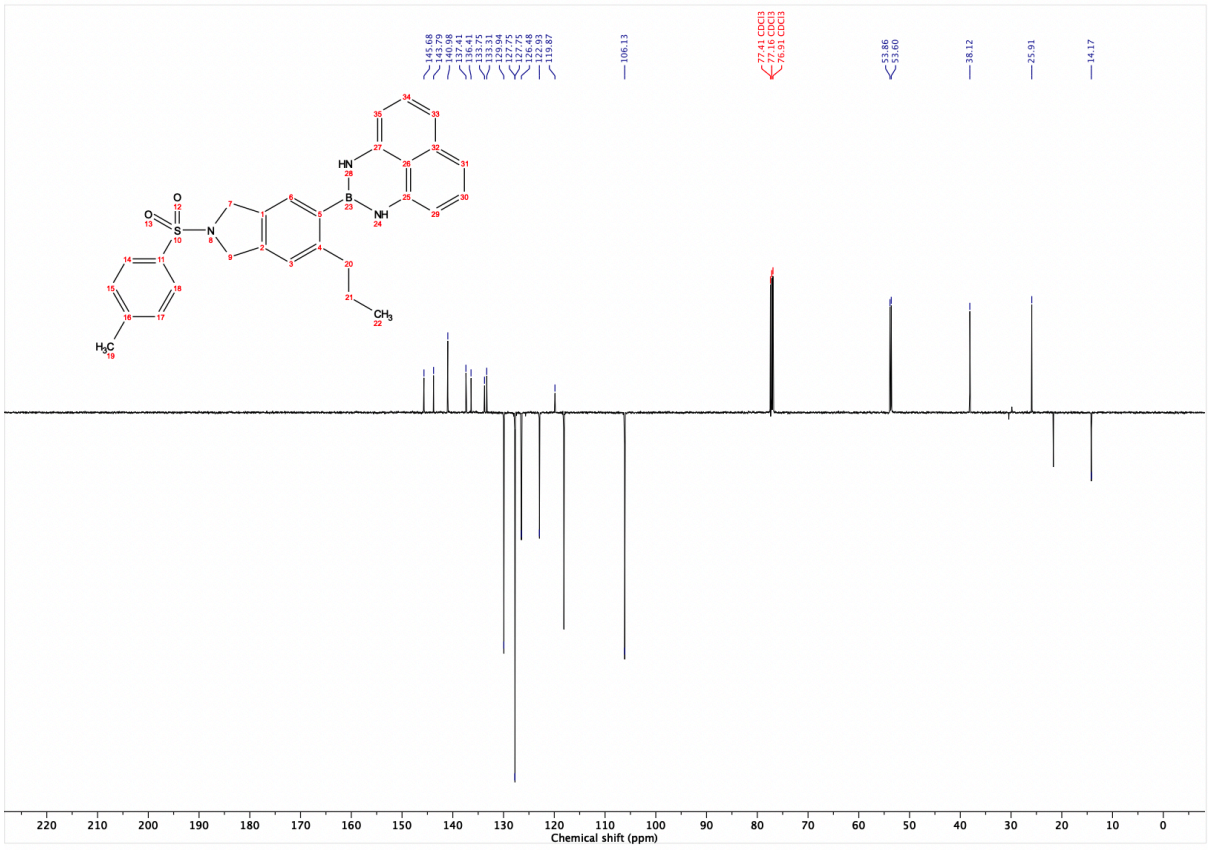
^{13}C DEPTQ



(37) ^{1}H



^{13}C DEPTQ


145.68
143.29
140.98
137.41
136.41
133.75
133.31
129.94
127.75
127.75
126.48
123.83
119.87
106.13
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
53.86
53.60
38.12
25.91
14.17
Chemical shift (ppm)