Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2021

Supporting Information

Sustainable Passerini-tetrazole Three Component Reaction (PT-3CR): Selective Synthesis of Oxaborol-tetrazoles

Akansha Singh[†±] and Ravindra Kumar[*,†±]

[†]*Division of Medicinal and Process Chemistry, CSIR-Central Drug Research Institute, Lucknow-226031, U.P., India*
[±]*Chemical Sciences Division, Academy of Scientific & Innovative Research (AcSIR), Ghaziabad-201002, India*

E-mail: ravindra.kumar1@cdri.res.in

TABLE OF CONTENTS **PAGE**

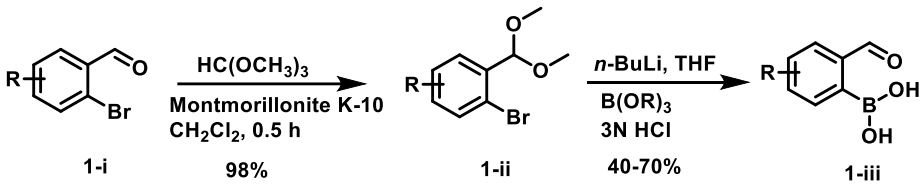
[1] General

^{1}H, ^{13}C and ^{19}F nuclear magnetic resonance spectra were recorded on Bruker Avance III 300, 400 and 500 MHz spectrometer at 25 °C. NMRs of the products were generally measured in $CDCl_3$, however, insoluble compounds were measured in a mixture of $CDCl_3$ and MeOH-D_4 (*ca* 8:2). The chemical shifts in ^{1}H NMR and $^{13}C\{1H\}$ NMR spectra are reported in parts per million (ppm) and are referenced to the residual solvent signal as the internal standard; ^{1}H NMR spectra ($CHCl_3$ δ 7.26 ppm) and ^{13}C ($CDCl_3$ δ 77.16). The residual solvent peaks appeared as multiplets at (CD_3OD/partial protonated; δ 3.88-3.22 ppm) and ^{13}C (CD_3OD δ 48.3-47.0) in the spectrum of products measured in a mixture of $CDCl_3$ and MeOH-D_4 (*ca* 8:2). ^{1}H Coupling constants (*J*) are quoted in Hz. Splitting patterns are denoted as "s" for singlet; "d" for doublet; "t" for triplet; "q" for quartet; "sext" for sextet; "sept" for septet; "m"for multiplet, "br" for broad; "dt" for doublet of triplets; "td" for triplet of doublets, and "app" for apparent. High Resolution Mass Spectra (HRMS) were recorded on Q-TOF mass spectrometer at SAIF department in CSIR-CDRI, Lucknow, India. Reactions were performed using round bottom flask or Schlenk tube. Temperature mentioned for any reaction is corresponding to the oil bath temperature. Column chromatography was done in 60-120 Å or 100-200 Å mesh silica gel of Merck Company. Hexane was distilled for purification in column chromatography. THF and toluene were distilled from sodium benzophenone ketyl and other solvents were distilled under standard procedures. Reagents and starting materials were used as received from company or synthesized with the

procedures that reported in literature. Chiral thiourea and squaramide catalysts were prepared by following the literature reports.[S1,2]

[2] Preparation of starting materials (1):

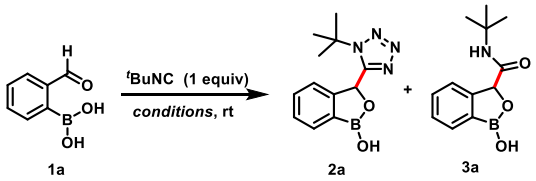
The general reaction procedure for the preparation of various substituted 2-formylphenylboronic acids were followed the method reported previously.[S3-6]



To a mixture of montmorillonite K-10 (2.0 g) and 2-bromobenzaldehyde (1.0 g, 5.02 mmol) in dichloromethane (10 mL) was added dropwise a solution of trimethyl orthoformate (2.20 mL, 20.0 mmol) at room temperature and the resulting mixture was stirred for 0.5 h. After filtration and complete evaporation of dichloromethane, acetals (**1-ii**) were obtained as pale yellow oil, which were employed for the next step without further purification.[S7]

To the solution of acetal (**1-ii**, 1.31 mmol) in dry THF was added *n*-butyllithium (2.0 N in cyclohexane, 0.72 mL, 1.1 equiv.) added drop wise at −78 °C. The reaction mixture was stirred at the same temperature for an hour and quenched with trimethoxyborate (0.18 mL, 1.57 mmol) followed by stirring for another an hour. The cooling bath was removed and quenched with 3M HCl to pH = 3 while temperature rose to 5 °C. The aqueous layer was separated and extracted with Et_2O (3 × 10 mL). The organic layers were combined and the volatile materials was removed. The solid residue products were simply washed/crystalized with hexane to give **1-(iii)** in crystalline pure in 40-70% yields.

[3] Optimization of reaction conditions[a]



run	X (equiv.)	solvent	time (h)	yield (%)[b]		
				2a	3a	rsm (1a)
1	$TMSN_3$ (1.0)	MeOH	12	71	7	nd
2	$TMSN_3$ (1.5)	MeOH	8	94 (96)[c]	nd	nd
3[d]	$TMSN_3$ (1.5)	MeOH	6	94	nd	nd
4	NaN_3 (1.5)	MeOH	6	76	nd	nd
5	$TMSN_3$ (1.5)	ACN	16	17	nd	6
6	$TMSN_3$ (1.5)	CH_2Cl_2	16	25	6	22
7	$TMSN_3$ (1.5)	$CHCl_3$	16	20	7	9
8	$TMSN_3$ (1.5)	THF	16	25	<5	10
9	$TMSN_3$ (1.5)	dioxane	16	23	26	18
10	$TMSN_3$ (1.5)	Toluene	16	17	18	32
11	$TMSN_3$ (1.5)	HFIP	16	26	24	4
12	$TMSN_3$ (1.5)	H_2O	8	26	24	4
13	$TMSN_3$ (1.5)	MeOH:H_2O	24	28	16	nd
14	$TMSN_3$ (1.5)	neat	1.0	96	nd	nd
15	$TMSN_3$ (1.0)	neat	1.5	85	10	trace
16	$TMSN_3$ (1.1)	neat	1.5	96 (94)[e]	nd	nd
17	$TMSN_3$ (1.1)	MeOH	10	80	<5	nd

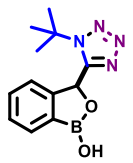
[a]Reaction was carried out at 0.1 mmol scale in 1.5 mL solvent. [b]yields were calculated by ^1H NMR using 2-methoxybenzene/mesitylene. [c]NMR tube experiment in CD_3OD. [d]4Å M.S. was used. [e]Isolated yield is mentioned. nd = not detected in ^1H NMR. rsm = remaining starting material (**1a**).

General experimental procedure for optimization study (Table 1): To a reaction vial, 2-formylphenylboronic acid (**1a**; 0.1 mmol, 1.0 equiv.) and $TMSN_3$ (1.0-1.5 equiv.) in specified solvent(s) (1.5 mL) or in neat was added 2-methoxynapthalene (internal standard; 0.05 mmol). After 5 minutes of stirring, isocyanide (0.5 mmol, 1.0 equiv) was added [for neat reactions; reaction mixture becomes homogenous solution after addition of isocyanide]. The progress of reaction was monitored by TLC with respect to 2-formylphenylboronic acid [under UV, PMA and $KMnO_4$, DNP staining agent]. The desired product and 2-formylphenylboronic acid have almost same Rf but development pattern under UV is different and can be differentiated under various staining agents. After the completion of reaction (**1**) as monitored on TLC, solvent was evaporated and aliquot was submitted for NMR analysis to check NMR yields [for neat reaction: product precipitate out with the progress of reactions and solid residue was submitted for NMR analysis in $CDCl_3$].
It was also noted that disappearance of any characteristic odor of isocyanide and appearance of fruity odor indicated the completion of reactions.

[4] Synthesis and spectral data for oxaborol-tetrazoles (2)

General Procedure for substrate scope (2): General Procedure for the synthesis of oxaborol-tetrazoles (**2**) compounds were followed the optimal neat reaction conditions (run 16, Table 1), as described below.
To a reaction vial, substituted 2-formylphenylboronic acid (**1**; 0.5 mmol, 1.0 equiv.) and $TMSN_3$ (0.55 mmol, 1.1 equiv.) were added. Isocyanide (0.5 mmol, 1.0 equiv) was added after five minutes, which turned the reaction mixture homogenous. After the completion of reaction, the product precipitated out. It was then applied to high vacuum to remove volatile impurities (and/or wash with hexane, if anything remained unreacted) to receive pure benzoxaborol-tetrazole products (**2)** in excellent yields, as specified separately for each cases. Structures of these products were confirmed by NMR/HRMS spectral analyses and single crystal X-ray crystallography for **2a**. Yields were calculated after the removal of all impurities (if any), ascertained by NMRs.

3-(1-(*tert*-Butyl)-1H-tetrazol-5-yl)benzo[c][1,2]oxaborol-1(3H)-ol (2a): General procedure was followed with 2-formylphenylboronic acid (**1a**; 75 mg, 0.5 mmol), $TMSN_3$ (73 µL, 0.55 mmol) and *tert*-butylisocyanide (56 µL, 0.5 mmol) at room temperature for 1.5 h to furnish **2a** (121 mg, 0.47 mmol) as a white solid.

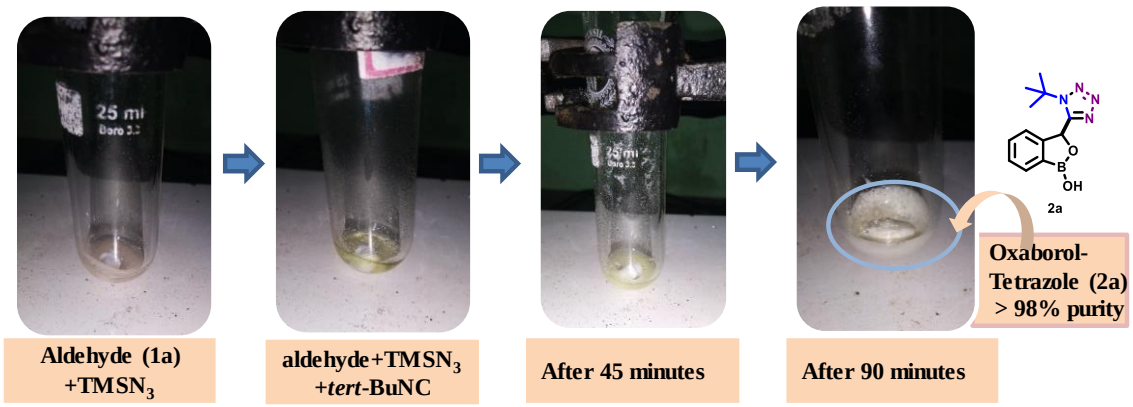


2a

Yield = 94%
R_f = 0.57 (50% EtOAc in hexane).

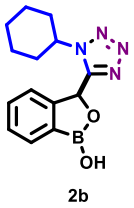
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 7.4 Hz, 1H), 7.60–7.56 (m, 1H), 7.47 (dd, *J* = 7.4, 7.3 Hz, 1H), 7.42 (dd, *J* = 7.0, 0.8 Hz, 1H), 6.59 (s, 1H), 5.08 (bs, 1H), 1.90 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$+CD_3OD): δ 153.2, 151.2, 131.3, 130.4, 128.5, 123.1, 72.7, 62.7, 29.7.
HRMS (ESI+): *m/z*: [M + H]+ calculated for $C_{16}H_{26}N_2O$: 259.1366, found 259.1361.

Gram scale synthesis of 2a: General procedure was followed with 2-formylphenylboronic acid (**1a**; 0.75 g, 5.0 mmol), $TMSN_3$ (0.73 mL, 5.5 mmol) and *tert*-butylisocyanide (0.56 mL, 5.0 mmol) at room temperature for 1.5 h to furnish **2a** as a white solid in 98% yield (1.26 g, 4.9 mmol). It was applied to high vacuum to remove volatile impurities [See Pictorial representation of progress of reaction and separation of desired product **2a**].



Pictorial representation of progress of reaction for the synthesis of 2a

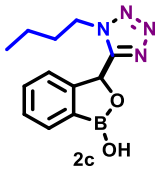
3-(1-Cyclohexyl-1H-tetrazol-5-yl)benzo[c][1,2]oxaborol-1(3H)-ol (2b): General procedure was followed with **1a** (75 mg, 0.5 mmol), $TMSN_3$ (73 µL, 0.55 mmol) and cyclohexyl isocyanide (62 µL, 0.5 mmol) at room temperature for 1.5 h to furnish **2b** (122 mg, 0.43 mmol) as a semi solid. Solid needed to be washed with hexane (2x5mL) to remove grease impurity.



Yield = 86%.
R_f = 0.67 (50% EtOAc in Hexane).

^{1}H (300 MHz, $CDCl_3$+CD_3OD): δ 7.81 (d, *J* = 6.8 Hz, 1H), 7.55−7.44 (m, 2H), 7.32 (d, *J* = 7.2 Hz, 1H), 6.63 (s, 1H), 4.14−4.04 (m, 1H), 2.05−1.97 (m, 2H), 1.83−1.66 (m, 4H), 1.35−1.22 (m, 2H), 1.22−1.06 (m, 2H) (labile B-O*H* proton probably exchanged with deuterium in CD_3OD).
^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3, 150.6, 131.7, 130.7, 128.8, 122.4, 73.1, 58.9, 32.7, 32.5, 25.2, 25.1, 24.6.
HRMS (ESI+): *m/z*: [M + H]+ calculated for $C_{14}H_{18}BN_4O_2$: 285.1523, found 285.1520.

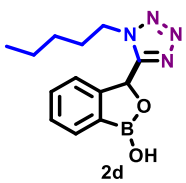
3-(1-Butyl-1H-tetrazol-5-yl)benzo[c][1,2]oxaborol-1(3H)-ol (2c): General procedure was followed with (2-formylphenyl)boronic acid (**1a**; 75 mg, 0.5 mmol), $TMSN_3$ (73µl, 0.55 mmol) and *n*-butyl isocyanide (52.3 µL, 0.5 mmol) at room temperature for 1.5 h to furnish **2c** (110 mg, 0.42 mmol) as a semi solid. Solid needed to be washed with hexane (2x5mL) to remove grease impurity.



Yield = 85%.
R_f = 0.63 (50% EtOAc in Hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 7.2 Hz, 1H), 7.57−7.51 (m, 1H), 7.49 (dd, *J* = 7.2, 7.4 Hz, 1H), 7.41 (dd, *J* = 6.8, 0.8 Hz, 1H), 6.67 (s, 1H), 5.36 (s, 1H), 4.20−4.08 (m, 2H), 1.74−1.67 (m, 2H), 1.22−1.19 (m, 2H), 0.83 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 152.7, 151.3, 132.2, 131.0, 129.1, 122.7, 73.5, 48.1, 31.5, 19.5, 13.3.
HRMS (ESI+): *m/z*: [M + H]+ calculated for $C_{12}H_{16}BN_4O_2$: 259.1366, found 259.1364.

3-(1-Pentyl-1H-tetrazol-5-yl)benzo[c][1,2]oxaborol-1(3H)-ol (2d): General procedure was followed with (2-formylphenyl)boronic acid (**1a**; 75 mg, 0.5 mmol), $TMSN_3$ (73 µl, 0.55 mmol) and *n*-pentyl isocyanide (63 µL, 0.5 mmol) at room temperature for 1.5 h to furnish **2d** (120 mg, 0.44 mmol) as a semi solid. Solid needed to be washed with hexane (2x5mL) to remove grease impurity.

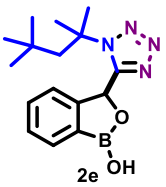


Yield = 89%.
R_f = 0.7 (50% EtOAc in Hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 7.2 Hz, 1H), 7.58−7.54 (m, 1H), 7.49 (dd, *J* = 7.2, 7.3 Hz, 1H),

7.40 (dd, J = 6.9, 0.7 Hz, 1H), 6.67 (s, 1H), 5.41 (s, 1H), 4.16−4.11 (m, 2H), 1.76−1.64 (m, 2H), 1.20−1.11 (m, 4H), 0.82 (t, J = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 152.8, 151.2, 132.2, 131.1, 129.0, 122.7, 73.5, 48.4, 29.2, 28.3, 21.9, 13.7.
HRMS (ESI+): *m/z*: [M + H]+ calculated for $C_{13}H_{18}BN_4O_2$: 273.1523, found 273.1518.

3-(1-(2,4,4-Trimethylpentan-2-yl)-1H-tetrazol-5-yl)benzo[c][1,2]oxaborol-1(3H)-ol (2e): General procedure was followed with (2-formylphenyl)boronic acid (**1a**; 75 mg, 0.5 mmol), $TMSN_3$ (73 µL, 0.55 mmol) and 1,1,3,3-Tetramethylbutyl isocyanide (87.7 µL, 0.5 mmol) at room temperature for 1.5 h to furnish **2e** (151 mg, 0.49 mmol) as a white solid.

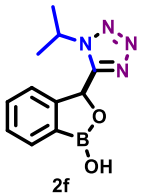


2e

Yield = 98%.
R_f = 0.66 (50% EtOAc in Hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 7.4 Hz, 1H), 7.57−7.53 (m, 1H), 7.46 (dd, J = 7.4, 7.3 Hz, 1H), 7.33 (dd, J = 6.9, 0.7 Hz, 1H), 6.63 (s, 1H), 5.30 (s, 1H), 2.27−2.08 (m, 2H), 1.97 (d, J = 3.1 Hz, 6H), 0.85 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$+CD_3OD): δ 153.8, 151.4, 131.4, 130.5, 128.5, 122.7, 72.8, 66.1, 53.8, 31.6, 30.4, 30.2.
HRMS (ESI+): *m/z*: [M + H]+ calculated for $C_{16}H_{24}BN_4O_2$: 315.1992, found 315.1985.

3-(1-Isopropyl-1H-tetrazol-5-yl)benzo[c][1,2]oxaborol-1(3H)-ol (2f): General procedure was followed with **1a** (75 mg, 0.5 mmol), $TMSN_3$ (73 µL, 0.55 mmol) and *iso*propyl isocyanide (47.1 µL, 0.5 mmol) at room temperature for 1.5 h to furnish **2f** (110 mg, 0.45 mmol) as a white solid. Solid needed to be washed with hexane (2x5mL) to remove grease impurity.

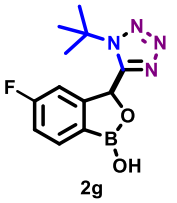


2f

Yield = 90%.
R_f = 0.45 (50% EtOAc in Hexane).

^{1}H NMR (400 MHz, $CDCl_3$+CD_3OD): δ 7.66 (d, J = 6.0 Hz, 1H), 7.42−7.33 (m, 2H), 7.19 (d, J = 7.4 Hz, 1H), 6.49 (s, 1H), 4.48−4.41 (m, 1H), 1.50 (d, J = 6.0 Hz, 3H), 1.19 (d, J = 6.0 Hz, 3H) (labile B-O*H* proton probably exchanged with deuterium in CD_3OD).
^{13}C NMR (100 MHz, $CDCl_3$): δ 152.0, 151.1, 132.0, 131.1, 128.9, 122.6, 73.2, 51.9, 22.6, 22.3.
HRMS (ESI+): *m/z*: [M + H]+ calculated for $C_{11}H_{14}BN_4O2$: 245.1210, found 245.1207.

3-(1-(*tert*-Butyl)-1H-tetrazol-5-yl)-5-fluorobenzo[c][1,2]oxaborol-1(3H)-ol (2g): General procedure was followed with (4-fluoro-2-formylphenyl)boronic acid (**1b**; 55 mg, 0.33 mmol), $TMSN_3$ (47.8 µL, 0.36 mmol) and *tert*-butyl isocyanide (36.8 µL, 0.33 mmol) at room temperature for 1.5 h to furnish **2g** (86 mg, 0.32 mmol) as a white solid.

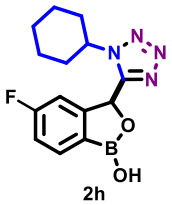


2g

Yield = 96%.
R_f = 0.41 (50% EtOAc in Hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (dd, J = 7.9, 5.6 Hz, 1H), 7.18−7.09 (m, 2H), 6.53 (s, 1H), 1.89 (s, 9H) (labile B-O*H* proton probably exchanged with deuterium in CD_3OD).
^{13}C NMR (100 MHz, $CDCl_3$+CD_3OD): δ 164.97 (d, J^1 = 249.2 Hz), 153.7 (d, J^3 = 8.7 Hz), 152.9, 132.5, 132.4, 116.5 (d, J^2 = 22.0 Hz), 110.6 (d, J^2 = 22.8 Hz), 72.3, 62.9, 29.8.
^{19}F (376 MHz, $CDCl_3$+CD_3OD): δ -106.9.
HRMS (ESI *m/z*: [M + H]+ calculated for $C_{12}H_{15}BFN_4O_2$: 277.1272, found 277.1272.

3-(1-Cyclohexyl-1H-tetrazol-5-yl)-5-fluorobenzo[c][1,2]oxaborol-1(3H)-ol (2h): General procedure was followed with (4-fluoro-2-formylphenyl)boronic acid (**1b**; 55 mg, 0.33 mmol), $TMSN_3$ (47.8 µL, 0.36 mmol) and cyclohexyl isocyanide (40.9 µL, 0.33 mmol) at room temperature for 1.5 h to furnish **2h** (91 mg, 0.30 mmol) as a semi solid.

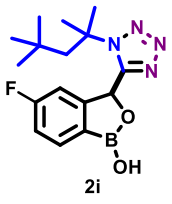


2h

Yield = 90%.
R_f = 0.56 (50% EtOAc in Hexane).

^{1}H (400 MHz, $CDCl_3$+CD_3OD): δ 7.64 (dd, *J* = 7.4, 6.0 Hz, 1H), 7.05 (dd, *J* = 8.6, 6.0 Hz, 1H), 6.99 (d, *J* = 8.1 Hz, 1H), 6.44 (s, 1H), 4.18–4.12 (m, 1H), 1.98–1.88 (m, 2H), 1.84–1.73 (m, 2H), 1.62–1.49 (m, 4H), 1.06–1.03 (m, 2H) (labile B-O*H* proton probably exchanged with deuterium in CD_3OD).
^{13}C NMR (100 MHz, $CDCl_3$): δ 164.8 (d, J^1= 251 Hz), 152.5, 132.5, 132.4, 116.4 (d, J^2 = 19.5 Hz), 109.7 (d, J^2 = 23.7 Hz), 72.4, 58.8, 32.7, 30.7, 25.1, 24.6, 24.1.
^{19}F (376 MHz, $CDCl_3$+CD_3OD): δ -106.2.
HRMS (ESI+): *m/z*: [M + H]+ calculated for $C_{14}H_{17}BFN_4O_2$: 303.1429, found 303.1428.

5-Fluoro-3-(1-(2,4,4-trimethylpentan-2-yl)-1H-tetrazol-5-yl)benzo[c][1,2]oxaborol-1(3H)-ol (2i): General procedure was followed with (4-fluoro-2-formylphenyl)boronic acid (**1b**; 55 mg, 0.33 mmol), TMSN3 (47.8 µl, 0.36 mmol) and 1,1,3,3 tetramethyl butyl isocyanide (57.9 µl, 0.33 mmol) at room temperature for 1.5h to furnish **2i** (105 mg, 0.32 mmol) as a white solid.

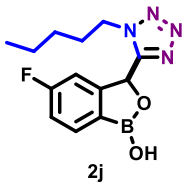


2i

Yield = 96%
Rf = 0.44 (50% EtOAc in Hexane).

^{1}H NMR (400 MHz, $CDCl_3$+CD_3OD): δ 7.76–7.66 (m, 1H), 7.18–7.12 (m, 1H), 7.03–6.99 (m, 1H), 6.57 (d, *J* = 4.2 Hz, 1H), 2.27–2.07 (m, 2H), 1.97 (m, 6H), 0.86 (s, 9H). (B-OH proton is labile shows deutration exchange in CD_3OD).
^{13}C NMR (100 MHz, $CDCl_3$+CD_3OD): δ 165.05 (d, J^1 = 250.0 Hz), 154.0, 153.2, 132.5, 132.4, 116.6 (d, J^2 = 22.0 Hz), 110.3 (d, J^2 = 22.2 Hz), 72.4, 66.2, 53.9, 31.6, 30.4, 30.2, 30.1.
^{19}F (282 MHz, $CDCl_3$+CD_3OD): δ -107.2.
HRMS (ESI+): *m/z*: $[M + H]^+$ calculated for $C_{16}H_{23}BFN_4O_2$: 333.1898, found 333.1894.

5-Fluoro-3-(1-pentyl-1H-tetrazol-5-yl)benzo[*c*][1,2]oxaborol-1(3H)-ol (2j): General procedure was followed with (4-fluoro-2-formylphenyl)boronic acid (**1b**; 55mg, 0.33 mmol), $TMSN_3$ (47.8 µL, 0.36 mmol) and *n*-pentyl isocyanide (41.5µL, 0.33 mmol) at room temperature for 1.5 h to furnish **2j** (91 mg, 0.30 mmol) as a semi solid.

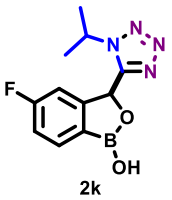


2j

Yield = 90%.
R_f = 0.47 (50% EtOAc in Hexane).

^{1}H NMR (300 MHz, $CDCl_3$+CD_3OD): δ 7.70–7.66 (m, 1H), 7.08 (dd, *J* = 7.6, 2.0 Hz, 1H), 6.98 (d, *J* = 8.5 Hz, 1H), 6.49 (s, 1H), 4.25–4.08 (m, 2H), 1.76–1.57 (m, 2H), 1.25–1.20 (m, 2H), 1.15–1.11 (m, 2H), 0.85 (t, *J* = 6.7 Hz, 3H) (labile B-O*H* proton probably exchanged with deuterium in CD_3OD).
^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4 (d, J^1 = 250.0 Hz), 153.8, 152.4, 133.1, 116.9, 110.2 (d, J^2 = 24.4 Hz), 72.8, 48.5, 29.3, 28.4, 21.9, 13.7.
^{19}F (282 MHz, $CDCl_3$+CD_3OD): δ -106.7.
HRMS (ESI+):*m/z*: [M + H]+ calculated for $C_{13}H_{17}BFN_4O_2$: 291.1429, found 291.1425.

3-(1-Butyl-1H-tetrazol-5-yl)-5-fluorobenzo[c][1,2]oxaborol-1(3H)-ol (2k): General procedure was followed with (4-fluoro-2-formylphenyl)boronic acid (**1b**; 55 mg, 0.33 mmol), TMSN3 (47.8 µL, 0.36 mmol) and *iso*propyl isocyanide (31.1 µL, 0.33 mmol) at room temperature for 1.5h to furnish **2k** (81 mg, 0.31 mmol) as a white solid. Solid needed to be washed with hexane (2x5mL) to remove grease impurity.

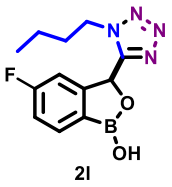


2k

Yield = 94%.
R_f = 0.38 (50% EtOAc in Hexane).

^{1}H NMR (300 MHz, $CDCl_3$+CD_3OD): δ 7.81−7.77 (m, 1H), 7.21–7.17 (m, 1H), 7.14–7.11 (m, 1H), 6.57 (s, 1H), 6.09 (br s, 1H), 4.69−4.55 (m, 1H), 1.62 (d, *J* = 6.6 Hz, 3H), 1.38 (d, *J* = 6.6 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$+CD_3OD): δ 165.3 (d, J^1 = 251.0 Hz), 153.3 (d, J^3 = 9.0 Hz), 151.7, 132.9, 132.8, 116.9 (d, J^2 = 22.8 Hz), 110.2 (d, J^2 = 22.8 Hz), 72.7, 52.0, 22.4, 22.3.
^{19}F (282 MHz, $CDCl_3$+CD_3OD): δ -105.9.
HRMS (ESI+): *m/z*: [M + H]+ calculated for $C_{11}H_{13}BFN_4O_2$: 263.1116, found 263.1112.

3-(1-Butyl-1H-tetrazol-5-yl)-5-fluorobenzo[c][1,2]oxaborol-1(3H)-ol (2l): General procedure was followed with (4-fluoro-2-formylphenyl)boronic acid (**1b**; 55 mg, 0.33 mmol), TMSN3 (47.8 µl, 0.36 mmol) and *n*-butyl isocyanide (34.5 µl, 0.33 mmol) at room temperature for 1.5h to furnish **2l** (83 mg, 0.30 mmol) as a semi solid.

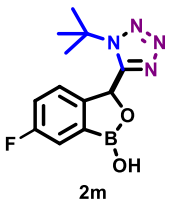


2l

Yield = 91%.
R_f = 0.51 (50% EtOAc in Hexane).

^{1}H NMR (300 MHz, $CDCl_3$+CD_3OD): δ 7.70 (dd, *J* = 7.3, 6.1 Hz, 1H), 7.13−7.02 (m, 2H), 6.51 (s, 1H), 4.26−4.11 (m, 2H), 1.78−1.57 (m, 2H), 1.24−1.17 (m, 2H), 0.80 (t, *J* = 7.2 Hz, 3H) (labile B-O*H* proton probably exchanged with deuterium in CD_3OD).
^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5 (d, J^1 = 250.3 Hz), 153.8, 152.4, 133.1, 117.1 (d, J^2 = 22 Hz), 110.3 (d, J^2 = 25.4 Hz), 72.9, 48.2, 31.6, 19.5, 13.3.
^{19}F (282 MHz, $CDCl_3$+CD_3OD): δ -105.8.
HRMS (ESI+): *m/z*: [M + H]+ calculated for $C_{12}H_{15}BFN_4O_2$: 277.1272, found 277.1262.

3-(1-(*tert*-Butyl)-1H-tetrazol-5-yl)-6-fluorobenzo[c][1,2]oxaborol-1(3H)-ol (2m): General procedure was followed with (5-fluoro-2-formylphenyl)boronic acid (**1c**; 60 mg, 0.36 mmol), $TMSN_3$ (52.2 µl, 0.39 mmol) and *tert*-butyl isocyanide (40.6 µl, 0.36 mmol) at room temperature for 1.5h to furnish **2m** (97 mg, 0.35 mmol) as a white solid.



2m

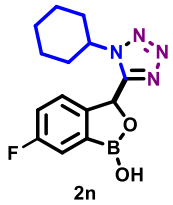
Yield = 98%.
R_f = 0.45 (50% EtOAc in Hexane).

^{1}H NMR (300 MHz, $CDCl_3$+CD_3OD): δ 7.42–7.40 (m, 2H), 7.29–7.24 (m, 1H), 6.57 (s, 1H), 1.92 (s, 9H) (labile B-O*H* proton probably exchanged with deuterium in CD_3OD).
^{1}H NMR (400 MHz, CD_3OD): δ 7.39–7.36 (m, 1H), 7.29–7.24 (dd, (d, *J* = 8.0, 2.3 Hz, 1H), 7.24–7.19 (m, 1H), 6.73 (s, 1H), 1.87 (s, 9H) (labile B-O*H* proton probably exchanged with deuterium in CD_3OD).

^{13}C NMR (100 MHz, $CDCl_3$+CD_3OD): δ 163.1 (d, J^1 = 247 Hz), 153.1, 146.6, 125.1, 119.1 (d, J^2 = 24.8 Hz), 116.3 (d, J^2 = 20.8 Hz), 72.5, 62.8, 29.9.
^{13}C NMR (100 MHz, CD_3OD): δ 164.4 (d, J^1 = 244 Hz), 155.0, 148.4, 126.9 (d, J^3 = 8.0 Hz), 119.6 (d, J^2 = 24.0 Hz), 116.8 (d, J^2 = 20.0 Hz), 73.4, 64.3, 30.2.

^{19}F (282 MHz, $CDCl_3$+CD_3OD): δ -114.0
HRMS (ESI+): *m/z*: [M + H]+ calculated for $C_{12}H_{15}BFN_4O_2$: 277.1272, found 277.1267.

3-(1-Cyclohexyl-1H-tetrazol-5-yl)-6-fluorobenzo[c][1,2]oxaborol-1(3H)-ol (2n): General procedure was followed with (5-fluoro-2-formylphenyl)boronic acid (**1c**; 60mg, 0.36 mmol), $TMSN_3$ (52.2µl, 0.39 mmol) and cyclohexyl isocyanide (44.7µl, 0.36mmol) at room temperature for 1.5h to furnish **2n** (96 mg, 0.32 mmol) as a semi solid.



2n

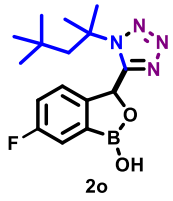
Yield = 88%.
R_f = 0.56 (50% EtOAc in Hexane).

^{1}H NMR (300 MHz, $CDCl_3$+CD_3OD): δ 7.35 (dd, *J* = 7.8, 2.4 Hz, 1H), 7.30−7.26 (m, 1H), 7.19−7.13 (m, 1H), 6.50 (s, 1H), 4.14−4.02 (m, 1H), 2.01−1.85 (m, 4H), 1.80−1.71 (m, 2H), 1.66−1.55 (m, 2H), 1.31−1.18 (m, 2H) (labile B-O*H* proton probably exchanged with deuterium in CD_3OD).
^{1}H NMR (400 MHz, CD_3OD): δ 7.36−7.31 (m, 2H), 7.23−7.18 (m, 1H), 6.60 (s, 1H), 4.47−4.39 (m, 1H), 2.11−1.88 (m, 4H), 1.79−1.67 (m, 4H), 1.45−1.34 (m, 2H) (labile B-O*H* proton probably exchanged with deuterium in CD_3OD).

^{13}C NMR (100 MHz, $CDCl_3$+CD_3OD): δ 163.2 (d, J^1 = 248.4 Hz), 152.6, 145.4, 124.2, 123.6, 118.6, 116.4 (d, J^2 = 20.0 Hz), 72.5, 58.8, 32.7, 30.6, 25.2, 24.5, 24.0.
^{13}C NMR (100 MHz, CD_3OD): δ 164.6 (d, J^1 = 244.0 Hz), 154.4, 147.3, 126.2 (d, J^3 = 9.0 Hz), 119.7 (d, J^2 = 24.0 Hz), 117.1 (d, J^2 = 21.0 Hz), 73.2, 60.0, 34.2, 33.7, 26.3, 26.2, 26.0.

^{19}F (376 MHz, $CDCl_3$+CD_3OD): δ -112.9.
HRMS (ESI+): *m/z*: [M + H]+ calculated for $C_{14}H_{17}BFN_4O_2$: 303.1429, found 303.1426.

6-Fluoro-3-(1-(2,4,4-trimethylpentan-2-yl)-1H-tetrazol-5-yl)benzo[c][1,2]oxaborol-1(3H)-ol (2o): General procedure was followed with (5-fluoro-2-formylphenyl)boronic acid (**1c**; 60 mg, 0.36 mmol), $TMSN_3$ (52.2 µl, 0.39 mmol) and 1,1,3,3 tetramethyl butyl isocyanide (63.1 µl, 0.36 mmol) at room temperature for 1.5h to furnish **2o** (115 mg, 0.34 mmol) as a white solid.

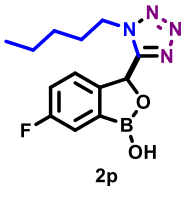


2o

Yield = 96%.
R_f = 0.44 (50% EtOAc in Hexane).

^{1}H NMR (400 MHz, $CDCl_3$+CD_3OD): δ 7.40 (d, *J* = 6.6 Hz, 1H), 7.31−7.30 (m, 1H), 7.24−7.21 (m, 1H), 6.59 (s, 1H), 2.28−2.07 (m, 2H), 1.98 (s, 6H), 0.85 (s, 9H) (labile B-O*H* proton probably exchanged with deuterium in CD_3OD).
^{13}C NMR (100 MHz, $CDCl_3$): δ 163.1 (d, J^1 = 246.1 Hz), 153.4, 147.0, 125.0, 124.9, 119.2 (d, J^2 = 23.6 Hz), 116.4 (d, J^2 = 20.8 Hz), 72.7, 66.0, 54.0, 31.8, 30.6, 30.5, 30.3.
^{19}F (376 MHz, $CDCl_3$+CD_3OD): δ -113.8
HRMS (ESI+):*m/z*: [M + H]+calculated for $C_{16}H_{23}BFN_4O_2$: 333.1898, found 333.1897.

6-Fluoro-3-(1-pentyl-1H-tetrazol-5-yl)benzo[c][1,2]oxaborol-1(3H)-ol (2p): General procedure was followed with (5-fluoro-2-formylphenyl)boronic acid (**1c**; 60 mg, 0.36 mmol), $TMSN_3$ (52.2 µl, 0.39 mmol) and *n*-pentyl isocyanide (45.3 µl, 0.36 mmol) at room temperature for 1.5h to furnish **2p** (99 mg, 0.34 mmol) as a semi solid.

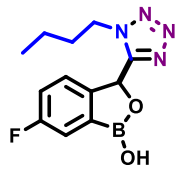


2p

Yield = 95%
R_f = 0.48 (50% EtOAc in Hexane).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47−7.40 (m, 2H), 7.26 (s, 1H), 6.59 (s, 1H), 4.22 (t, *J* = 7.2 Hz, 2H), 1.77−1.68 (m, 4H), 1.23−1.19 (m, 2H), 0.84 (t, *J* = 6.6 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$+CD_3OD): δ 163.3 (d, J^1 = 249.2 Hz), 152.6, 146.1, 124.6, 124.6, 119.6 (d, J^2 = 25.2 Hz), 116.6 (d, J^2 = 21.4 Hz), 73.1, 48.3, 29.3, 28.3, 21.9, 13.5.
^{19}F (282 MHz, $CDCl_3$+CD_3OD): δ -113.8.
HRMS (ESI+): *m/z*: [M + H]+calculated for $C_{13}H_{17}BFN_4O_2$: 291.1429, found 291.1419.

3-(1-Butyl-1H-tetrazol-5-yl)-6-fluorobenzo[c][1,2]oxaborol-1(3H)-ol (2q): General procedure was followed with (5-fluoro-2-formylphenyl)boronic acid (**1c**; 60 mg, 0.36 mmol), $TMSN_3$ (52.2 µl, 0.39 mmol) and *n*-butyl isocyanide (37.6 µl, 0.36 mmol) at room temperature for 1.5h to furnish **2q** (91 mg, 0.32 mmol) as a semi solid.

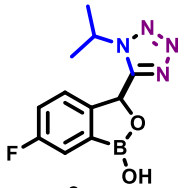


2q

Yield = 91%.
R_f = 0.5 (50% EtOAc in Hexane).

^{1}H NMR (300 MHz, $CDCl_3$+CD_3OD): δ 7.45 (dd, *J* = 7.8, 2.4 Hz, 1H), 7.42−7.39 (m, 1H), 7.26 (m, 1H), 6.60 (s, 1H), 4.33−4.16 (m, 2H), 1.85−1.64 (m, 2H), 1.33−1.26 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H). (B-OH proton is labile shows deutration exchange in CD_3OD).
^{13}C NMR (100 MHz, $CDCl_3$+CD_3OD): δ 163.3 (d, J^1 = 244.2 Hz), 152.6, 146.1, 124.7, 124.6, 119.6 (d, J^2 = 21.4 Hz), 116.7 (d, J^2 = 20 Hz), 73.0, 48.1, 31.5, 19.5, 13.2.
^{19}F (376 MHz, $CDCl_3$+CD_3OD): δ -101.2.
HRMS (ESI+): *m/z*: [M + H]+ calculated for $C_{12}H_{15}BFN_4O_2$: 277.1272, found 277.1264.

6-Fluoro-3-(1-isopropyl-1H-tetrazol-5-yl)benzo[c][1,2]oxaborol-1(3H)-ol (2r): General procedure was followed with (5-fluoro-2-formylphenyl)boronic acid (**1c**; 60 mg, 0.36 mmol), $TMSN_3$ (52.2 µl, 0.39 mmol) and *iso*propyl isocyanide (33.9 µl, 0.36 mmol) at room temperature for 1.5h to furnish **2r** (99 mg, 0.34 mmol) as a white solid. Solid needed to be washed with hexane (2x5mL) to remove grease impurity.

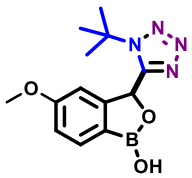


2r

Yield = 94%.
R_f = 0.38 (50% EtOAc in Hexane).

^{1}H NMR (300 MHz, $CDCl_3$+CD_3OD): δ 7.30 (dd, *J* = 7.7, 2.0 Hz, 1H), 7.28−7.24 (m, 1H), 7.16−7.10 (m, 1H), 6.45 (s, 1H), 4.59−4.48 (m, 1H), 1.52 (d, *J* = 6.7 Hz, 3H), 1.29 (d, *J* = 6.6 Hz, 3H) (labile B-O*H* proton probably exchanged with deuterium in CD_3OD).
^{13}C NMR (100 MHz, $CDCl_3$): δ 163.8 (d, J^1 = 246.8 Hz), 151.9, 146.5, 124.7, 124.7, 119.8 (d, J^2 = 24.4 Hz), 117.0 (d, J^2 = 21.0 Hz), 72.8, 52.0, 22.6, 22.4.
^{19}F (282 MHz, $CDCl_3$+CD_3OD): δ -112.9.
HRMS (ESI+): *m/z*: [M + H]+ calculated for $C_{11}H_{13}BFN_4O_2$: 263.1116, found 263.1108.

3-(1-(*tert*-Butyl)-1H-tetrazol-5-yl)-5-methoxybenzo[c][1,2]oxaborol-1(3H)-ol (2s): General procedure was followed with (2-formyl-4-methoxyphenyl)boronic acid (**1d**; 90 mg, 0.5 mmol), $TMSN_3$ (73 µl, 0.55 mmol) and *tert*-butyl isocyanide (56.4 µl, 0.5 mmol) at room temperature for 3h to furnish **2s** (142 mg, 0.49 mmol) as a white solid. Solid needed to be washed with hexane (2x5mL) to remove grease impurity.

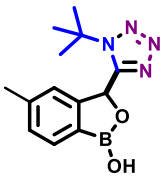


2s

Yield = 98%.
R_f = 0.39(50% EtOAc in Hexane).

^{1}H NMR (400 MHz, $CDCl_3$+CD_3OD): δ 7.53 (d, *J* = 8.2 Hz, 1H), 6.87 (dd, *J* = 8.2, 1.5 Hz, 1H), 6.73 (s, 1H), 6.41 (s, 1H), 3.90 (s, 3H), 1.76 (s, 9H) (labile B-O*H* proton probably exchanged with deuterium in CD_3OD).
^{13}C NMR (100 MHz, $CDCl_3$+CD_3OD): δ 162.5, 153.8, 153.4, 131.8, 116.0, 107.8, 72.5, 62.7, 55.3, 29.8.
HRMS (ESI+): *m/z*: [M + H]+ calculated for $C_{13}H_{18}BN_4O_3$: 289.1472, found 289.1466.

3-(1-(*tert*-Butyl)-1H-tetrazol-5-yl)-6-methylbenzo[c][1,2]oxaborol-1(3H)-ol (2t): General procedure was followed with (2-formyl-4-methylphenyl)boronic acid (**1e**; 50 mg, 0.3 mmol), $TMSN_3$ (44.5 µl, 0.33 mmol) and *tert*-butyl isocyanide (33.8 µl, 0.5 mmol) at room temperature for 3h to furnish **2t** (69 mg, 0.25 mmol) as a white solid. Solid needed to be washed with hexane (2x5mL) to remove grease impurity.

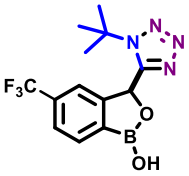


2t

Yield = 84%.
R_f = 0.62 (50% EtOAc in Hexane).

^{1}H NMR (400 MHz, $CDCl_3$+CD_3OD): δ 7.47 (d, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 6.98 (s, 1H), 6.40 (s, 1H), 2.23 (s, 3H), 1.73 (s, 9H) (labile B-O*H* proton probably exchanged with deuterium in CD_3OD).
^{13}C NMR (100 MHz, $CDCl_3$+CD_3OD): δ 153.4, 151.9, 142.0, 130.4, 129.9, 123.7, 72.7, 62.6, 30.0, 21.8.
HRMS (ESI+): *m/z*: [M + H]+ calculated for $C_{13}H_{18}BN_4O_2$: 273.1523, found 273.1514.

3-(1-(*tert*-Butyl)-1H-tetrazol-5-yl)-5-(trifluoromethyl)benzo[c][1,2]oxaborol-1(3H)-ol (2u): General procedure was followed with (2-formyl-4-trifluoromethylphenyl)boronic acid (**1f**; 66 mg, 0.3 mmol), $TMSN_3$ (43.8 µl, 0.33 mmol) and tert-butyl isocyanide (33.8 µl, 0.5 mmol) at room temperature for 1.5h to furnish **2u** (84 mg, 0.26 mmol) as a white solid. Solid needed to be washed with hexane (2x5mL) to remove grease impurity.

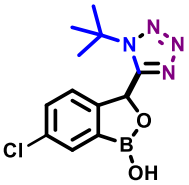


2u

Yield = 86%.
R_f = 0.3 (50% EtOAc in Hexane).

^{1}H NMR (300 MHz, $CDCl_3$+CD_3OD): δ 7.82 (d, *J* = 7.7 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.60 (s, 1H), 6.56 (s, 1H), 1.85 (s, 9H) (labile B-O*H* proton probably exchanged with deuterium in CD_3OD).
^{13}C NMR (100 MHz, $CDCl_3$+CD_3OD): δ 152.6, 151.5, 131.2, 125.6, 120.5, 72.7, 63.0, 29.9.
^{19}F (282 MHz, $CDCl_3$+CD_3OD): δ -62.8
HRMS (ESI+): *m/z*: [M + H]+ calculated for $C_{13}H_{15}BF_3N_4O_2$: 327.1240, found 327.1232.

3-(1-(*tert*-Butyl)-1H-tetrazol-5-yl)-6-chlorobenzo[c][1,2]oxaborol-1(3H)-ol (2v): General procedure was followed with (2-formyl-5-chlorophenyl)boronic acid (**1g**; 92 mg, 0.5 mmol), $TMSN_3$ (73 µl, 0.55 mmol) and *tert*-butyl isocyanide (56.3 µl, 0.5 mmol) at room temperature for 3h to furnish **2v** (137 mg, 0.47 mmol) as a white solid. Solid needed to be washed with hexane (2x5mL) to remove grease impurity.

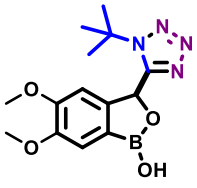


2v

Yield = 94%.
R_f = 0.44 (50% EtOAc in Hexane).

^{1}H NMR (300 MHz, $CDCl_3$+CD_3OD): δ 7.60 (s, 1H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 6.46 (s, 1H), 1.82 (s, 9H) (labile B-O*H* proton probably exchanged with deuterium in CD_3OD).
^{13}C NMR (100 MHz, $CDCl_3$+CD_3OD): δ 134.9, 131.5, 130.3, 130.2, 129.8, 124.8, 123.5, 72.5, 62.9, 29.7.
HRMS (ESI+): *m/z*: [M + H]+ calculated for $C_{12}H_{15}BClN_4O_2$: 293.0977, found 293.0970.

3-(1-(*tert*-Butyl)-1H-tetrazol-5-yl)-5,6-dimethoxybenzo[c][1,2]oxaborol-1(3H)-ol (2w): General procedure was followed with (2-formyl-4,5-dimethoxyphenyl)boronic acid (**1h**; 105 mg, 0.5 mmol), $TMSN_3$ (73 µl, 0.55 mmol) and *tert*-butyl isocyanide (56.3 µl, 0.5 mmol) at room temperature for 3h to furnish **2w** (137 mg, 0.43 mmol) as a white semi solid. Solid needed to be washed with hexane (2x5mL) to remove grease impurity.



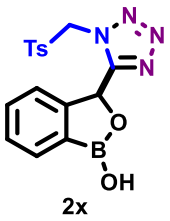
2w

Yield = 87%.
R_f = 0.39 (50% EtOAc in Hexane).

^{1}H NMR (400 MHz, $CDCl_3$+CD_3OD): δ 7.09 (s, 1H), 6.79 (s, 1H), 6.42 (s, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 1.81 (s, 9H) (labile B-O*H* proton probably exchanged with deuterium in CD_3OD).

^{13}C NMR (100 MHz, $CDCl_3$+CD_3OD): δ 156.4, 153.9, 149.2, 115.0, 109.7, 76.6, 66.8, 59.8, 33.8.
HRMS (ESI+): *m/z*: [M - H]- calculated for $C_{14}H_{18}BN_4O_4$: 317.1421, found 317.1432.

3-(1-(Tosylmethyl)-1H-tetrazol-5-yl)benzo[c][1,2]oxaborol-1(3H)-ol (2x): General procedure was followed with (2-formylphenyl)boronic acid (**1a**; 75 mg, 0.5 mmol), $TMSN_3$ (73 µl, 0.55 mmol) and p-Toluenesulfonylmethyl isocyanide (97.6 mg, 0.5 mmol) at room temperature for 16h to furnish **2x** (167 mg, 0.45 mmol) as a white solid. Solid needed to be washed with chloroform (2x5mL) to get free solid.

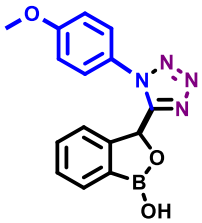


2x

Yield = 90%.
R_f = 0.64 (50% EtOAc in Hexane).

^{1}H NMR (300 MHz, $CDCl_3$+CD_3OD): δ 7.70−7.66 (m, 2H), 7.51 (dd, *J* = 8.3, 7.8 Hz, 1H), 7.45−7.35 (m, 3H), 7.26−7.24 (m, 2H), 6.55 (s, 1H), 5.89 (s, 2H), 2.35 (s, 3H) (labile B-O*H* proton probably exchanged with deuterium in CD_3OD).
^{13}C NMR (100 MHz, $CDCl_3$+CD_3OD): δ 154.7, 150.2, 146.9, 132.3, 131.7, 130.6, 130.4, 128.9, 128.8, 123.5, 73.7, 65.8, 21.6.
HRMS (ESI+): *m/z*: [M + H]+ calculated for $C_{16}H_{16}BN_4O_4S$: 371.0985, found 371.0977.

3-(1-(4-Methoxyphenyl)-1H-tetrazol-5-yl)benzo[c][1,2]oxaborol-1(3H)-ol (2y): General procedure was followed with (2-formylphenyl)boronic acid (**1a**; 75 mg, 0.5 mmol), $TMSN_3$ (98 µl, 0.75 mmol) and 4-Methoxyisocyanide (80 mg, 0.6 mmol) at room temperature for 12h. The crude product was purified by column chromatography, eluted with 2% MeOH in DCM to get pure **2y** (126 mg, 0.41 mmol) as a brown semi solid.

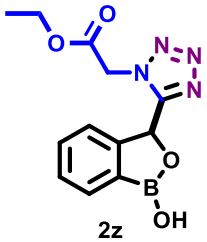


2y

Yield = 82%.
R_f = 0.69 (10% MeOH in $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (d, *J* = 7.3 Hz, 1H), 7.50−7.47 (m, 1H), 7.40−7.37 (m, 1H), 7.26−7.24 (m, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 7.0 Hz, 2H), 6.57 (s, 1H), 3.83 (s, 3H) (labile B-O*H* proton probably exchanged with deuterium in CD_3OD).
^{13}C NMR (125 MHz, $CDCl_3$): δ 161.1, 131.8, 130.7, 128.8, 127.2, 126.1, 122.2, 114.5, 72.9, 55.7.
HRMS (ESI+): *m/z*: [M + H]+ calculated for $C_{15}H_{14}BN_4O_3$: 309.1159, found 309.1175.

Ethyl-2-(5-(1-hydroxy-1,3-dihydrobenzo[c][1,2]oxaborol-3-yl)-1H-tetrazol-1-yl)acetate (2z): General procedure was followed with (2-formylphenyl)boronic acid (**1a**; 75 mg, 0.5 mmol), $TMSN_3$ (78.9µl, 0.6 mmol) and Ethyl isocyanoacetate (60.1 µl, 0.55 mmol) at room temperature for 12h. The crude product was purified by column chromatography, eluted with 1.5% MeOH in DCM to get pure **2z** (116 mg, 0.4 mmol) as a green fluorescent semi solid.

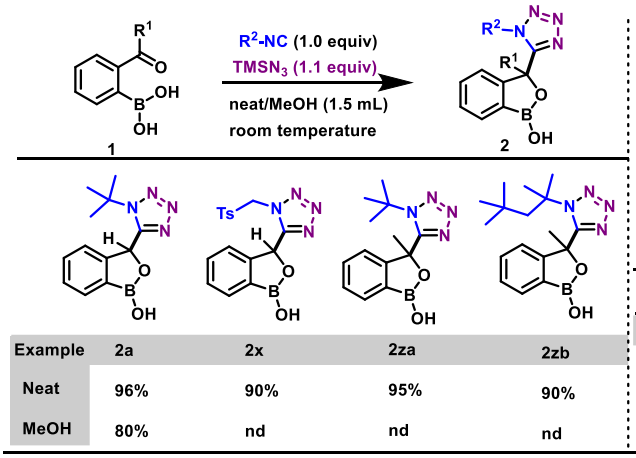


2z

Yield = 80%.
R_f = 0.57 (10% MeOH in $CHCl_3$).

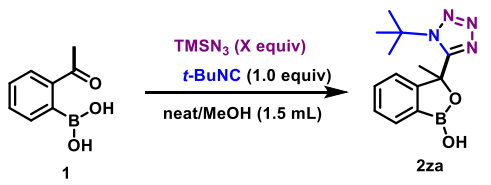
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, *J* = 7.3 Hz, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.58−7.55 (m, 1H), 7.45−7.42 (m, 1H), 6.82 (br s, 1H), 6.60 (s, 1H), 5.29 (d, *J* = 17.5 Hz, 1H), 5.17 (d, *J* = 17.5 Hz, 1H), 4.18−4.03 (m, 1H), 1.16 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 165.6, 153.7, 150.9, 132.2, 130.7, 129.0, 123.5, 74.1, 62.8, 49.4, 13.8.
HRMS (ESI+): *m/z*: [M + H]+ calculated for $C_{12}H_{14}BN_4O_4$: 289.1108, found 289.1109.

[5] Comparative study under solvent and solvent-free conditions



Example	2a	2x	2za	2zb
Neat	96%	90%	95%	90%
MeOH	80%	nd	nd	nd

Further detailed study on 2-acetylphenylboronic acid

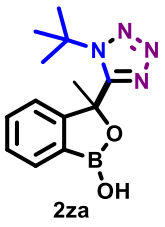


run	X (equiv)	condition	temp (°C)	time (h)	yield (%)
1	1.1	Neat	rt	12	95
2	4.0	Neat	rt	4	95
3	1.5	MeOH	rt	36	nd
4	1.5	MeOH	50 °C	18	<90[b]
5	4.0	meOH	50 °C	8	<90[b]

[a]Reaction was carried out at 0.1 mmol scale. Isolated yields were noted. [b]NMR yield. Reaction was sluggish & product "2za" couldn't be purified.

Neat conditions: 2za-2zb (90-95% isolated yield).
In Methanol: It was noted that products **2x-za** was not formed at room temperature (see table above). At 50-70 °C, Reaction was sluggish (1.5 eq. $TMSN_3$, <90% NMR yield at 24 h). products couldn't be isolated to pure form.

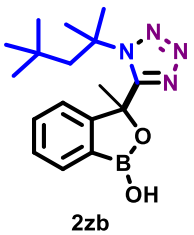
3-(1-(*tert*-Butyl)-1H-tetrazol-5-yl)-3-methylbenzo[c][1,2]oxaborol-1(3H)-ol (2za): General procedure was followed with (2-acetylphenyl)boronic acid (**1g**; 50 mg, 0.3 mmol), $TMSN_3$ (159.2 µl, 1.2 mmol) and *tert*-butyl isocyanide (33.8 µl, 0.3mmol) at room temperature for 4h to furnish **2za** (77 mg, 0.28 mmol) as a white solid.



Yield = 95%
R_f = 0.48 (50% EtOAc in Hexane).

^{1}H NMR (400 MHz, CD_3OD): δ 7.62−7.58 (m, 2H), 7.43 (ddd, *J* = 7.8, 7.6, 1.3 Hz, 1H), 7.31 (m, 1H), 1.89 (s, 3H), 1.62 (s, 9H) (labile B-O*H* proton probably exchanged with deuterium in CD_3OD).
^{13}C NMR (100 MHz, CD_3OD): δ 158.3, 156.8, 131.4, 130.1, 128.3, 123.3, 82.7, 63.5, 32.0, 29.4.
HRMS (ESI+): *m/z*: [M - H]+ calculated for $C_{13}H_{16}BN_4O_2$: 271.1366, found 271.1370.

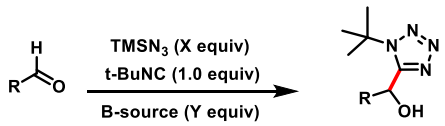
3-Methyl-3-(1-(2,4,4-trimethylpentan-2-yl)-1H-tetrazol-5-yl)benzo[c][1,2]oxaborol-1(3H)-ol (2zb): General procedure was followed with (2-acetylphenyl)boronic acid (**1g**; 50mg, 0.3 mmol), $TMSN_3$ (159.2µl, 1.2 mmol) and 1,1,3,3-Tetramethylbutyl isocyanide (52.6 µl, 0.3mmol) at room temperature for 4h to furnish **2zb** (88 mg, 0.27 mmol) as a colorless oil.



Yield = 90%.
R_f = 0.50 (50% EtOAc in Hexane).

^{1}H NMR (300 MHz, CD_3OD): δ 7.72 (d, *J* = 7.7 Hz, 2H), 7.55 (m, 1H), 7.42 (m, 1H), 2.04 (d, *J* = 1.3 Hz, 2H), 2.02 (s, 3H), 1.94 (s, 3H), 1.72 (s, 3H), 0.54 (s, 9H) (labile B-O*H* proton probably exchanged with deuterium in CD_3OD).
^{13}C NMR (100 MHz, CD_3OD): δ 162.1, 161.3, 135.6, 134.1, 132.3, 127.1, 87.1, 70.7, 55.8, 36.6, 34.9, 34.6, 33.9, 33.4.
HRMS (ESI+): *m/z*: [M - H]+ calculated for $C_{17}H_{24}BN_4O_2$: 327.1992, found 327.1999.

[6] Intermolecular reactions: Optimization of reaction conditions

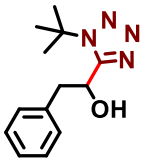


run	R	X (equiv.)	additive (Y equiv)	solvent		time (h)	yield (5a, %)[b]	rsm (4a)
1	Ph	1.5	$B(OH)_3$ (1.0)	MeOH	rt	36	-	>90
2	Ph	1.5	$B(OH)_3$(1.0)	MeOH	50 °C	18	39	11
3	Ph	1.5	$B(OH)_3$ (1.0)	-	rt	18	18	39
4	Ph	4.0	$B(OH)_3$(1.0)	-	rt	18	19	48
5	$PhCH_2$	1.5	$B(OH)_3$ (0.20)	-	rt	18	20	48
6	$PhCH_2$	1.5	$B(OH)_3$(1.0)	-	rt	18	33	29
7	$PhCH_2$	1.5	$B(OH)_3$ (2.0)	-	rt	18	24	16
8	$PhCH_2$	2.0	$B(OH)_3$(1.0)	-	rt	18	51	-
9	$PhCH_2$	4.0	$B(OH)_3$ (1.0)	-	rt	2	70	-
10	$PhCH_2$	1.5	$PhB(OH)_2$ (1.0)	-	rt	2	41	-
11	$PhCH_2$	1.5	$B(OMe)_3$ (1.0)	-	50 °C	18	-	>90

[a]Reaction was carried out with 0.1 mmol scale. [b]NMR yields were calculated using 2-methoxy-napthalene/mesitylene as internal standard

General Procedure for intermolecular reactions (entry 9): To the reaction vial, aldehyde (0.5 mmol, 1.0 equiv.) and $TMSN_3$ (2.0 mmol, 4.0 equiv.) were added and waited till it becomes homogeneous solution. Boric acid (0.5 mmol, 1.0 equiv.) was then added followed by an isocyanide (0.5 mmol, 1.0 equiv.). The reaction mixture was left on stirring at room temperature under neat conditions at room temperature. After the completion of reaction, product precipitated out and completion of aldehyde was monitored by TLC and the precipitate was diluted with EtOAc and washed with water/brine to remove boric acid. The organic layer was dried over Na_2SO_4, filtered and concentrated to receive tetrazoles **5** in pure form as a white solid.

1-(1-(*tert*-Butyl)-1H-tetrazol-5-yl)-2-phenylethanol (5a): General procedure was followed with phenylacetaldehyde (100 mg, 0.83 mmol), $TMSN_3$ (442 µl, 3.33 mmol), boric acid (51.3 mg, 0.83 mmol) and *tert*-butylisocyanide (93.8 µl, 0.83 mmol) for 4 h to afford **5a** (143 mg, 0.58 mmol) as a white solid.

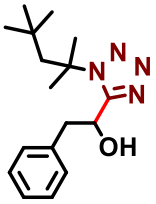


5a

Yield = 70%
R_f = 0.7 (30% EtOAc in Hexane)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31−7.27 (m, 1H), 7.25−7.22 (m, 2H), 7.19−7.16 (m, 2H), 5.29−5.22 (m, 1H), 3.56−3.41 (m, 2H), 2.94 (d, *J* = 8.7 Hz, 1H), 1.62 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 155.9, 136.0, 129.6, 128.8, 127.2, 66.8, 61.8, 43.3, 29.9.
HRMS (ESI+): *m/z*: $[M + H]^+$ calculated for $C_{13}H_{19}N_4O$: 247.1559, found 247.1554.

2-Phenyl-1-(1-(2,4,4-trimethylpentan-2-yl)-1H-tetrazol-5-yl)ethanol (5b): General procedure was followed with phenylacetaldehyde (100 mg, 0.83 mmol), $TMSN_3$ (442 µl, 3.33 mmol), boric acid (51.3mg, 0.83mmol) and 1,1,3,3-tetramethylbutylisocyanide (145.5 µl, 0.83 mmol) for 4 h to afford **5b** (181 mg, 0.60 mmol) as a white solid.



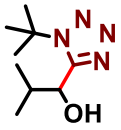
5b

Yield = 72%.
R_f = 0.72 (30% EtOAc in Hexane).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27−7.19 (m, 5H), 5.31−5.23 (m, 1H), 3.56−3.42 (m, 2H), 2.92 (br s, 1H), 1.99−1.80 (m, 2H), 1.79 (s, 3H), 1.58 (s, 3H), 0.70 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 156.1, 136.0, 129.7, 128.8, 127.2, 67.1, 65.2, 53.9, 43.3, 31.6, 30.5, 30.3, 30.2.
HRMS (ESI+): *m/z*: [M + H]+ calculated for $C_{17}H_{27}N_4O$: 303.2185, found 303.2179.

1-(1-(*tert*-Butyl)-1H-tetrazol-5-yl)-2-methylpropan-1-ol (5c): General procedure was followed with isobutyraldehyde (79 mg, 0.83 mmol), $TMSN_3$ (578.6 µl, 4.36 mmol), boric acid (67 mg, 1.0 mmol), and *tert*-butyl isocyanide (122.9 µl, 1.09 mmol) for 4 h to afford **5c** (130 mg, 2.8 mmol) as white solid.

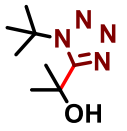


5c

Yield = 65%.
R_f = 0.57 (10% EtOAc in Hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.71 (dd, *J* = 10.0, 8.3 Hz, 1H), 2.70 (d, *J* = 12.0 Hz, 1H), 2.52−2.40 (m, 1H), 1.78 (s, 9H), 1.17 (d, *J* = 6.6 Hz, 3H), 0.88 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 156.3, 70.9, 61.6, 34.2, 30.3, 19.5, 18.0.
HRMS (ESI+): *m/z*: [M + H]+ calculated for $C_9H_{19}N_4O$: 199.1559, found 199.1553.

1-(1-(*tert*-Butyl)-1H-tetrazol-5-yl)-2-methylpropan-1-ol (5d): General procedure was followed with acetone (78 mg, 1.34 mmol), $TMSN_3$ (711.4µl, 5.36 mmol), boric acid (82.8mg, 1.0 mmol) and *tert*-butyl isocyanide (151.11 µl, 1.34 mmol) for 4 h to afford **5d** (148 mg, 0.8 mmol) as a white solid.

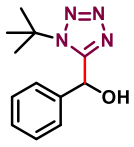


5d

Yield = 60%.
R_f = 0.56 (10% EtOAc in Hexane developed in $KMnO_4$).

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.48 (br s, 1H), 1.83 (s, 9H), 1.82 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 70.6, 63.7, 32.4, 30.6.
HRMS (ESI+): *m/z*: [M + H]+ calculated for $C_8H_{17}N_4O$: 185.1402, found 185.1390.

(1-(*tert*-Butyl)-1H-tetrazol-5-yl)(phenyl)methanol (5e): General procedure was followed with benzaldehyde (100 mg, 0.94 mmol), $TMSN_3$ (187.1 µl, 1.41 mmol), boric acid (58 mg, 0.94 mmol) and *tert*-butyl isocyanide (106.1 µl, 0.94 mmol) at room temperature for 18h. The crude product was purified by column chromatography, eluted with 22% EtOAc in hexane to get pure **5e** (40 mg, 0.18 mmol) as a white solid. The spectral data matched with the reported one.[S8]



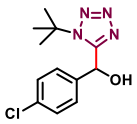
5e

Yield = 19%
R_f = 0.61 (50% EtOAc in Hexane)

Note: When identical set of reaction was conducted in methanol (1.5 mL) at 50 °C for 18h, yield of **5e** was improved to 39%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37−7.35 (m, 3H), 7.29−7.27 (m, 2H), 6.25 (d, *J* = 7.8 Hz, 1H), 3.90 (d, *J* = 8.3, 1 Hz, 1H), 1.62 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8, 139.2, 129.0, 127.2, 68.6, 62.0, 29.9.
HRMS (ESI+): *m/z*: [M + H]+ calculated for $C_{12}H_{17}N_4O$: 233.1402, found 233.1395.

(1-(*tert*-Butyl)-1H-tetrazol-5-yl)(4-chlorophenyl)methanol (5f): General procedure was followed with 4-chlorobenzaldehyde (100 mg, 0.71 mmol), $TMSN_3$ (373.5 µl, 2.84 mmol), boric acid (44 mg, 0.71 mmol) and *tert*-butyl isocyanide (8.0 µl, 0.71 mmol) at rt for 16h. The crude product was purified by column chromatography, eluted with 22% EtOAc in hexane to get pure **5f** (56 mg, 0.21 mmol) as a semi solid.



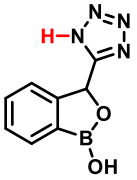
5f

Yield = 30%
R_f = 0.61 (50% EtOAc in Hexane)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35−7.32 (m, 2H), 7.24−7.22 (m, 2H), 6.26 (s, 1H), 4.36 (br s, 1H), 1.64 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 155.5, 137.8, 134.9, 129.1, 128.5 67.7, 62.2, 30.0.
HRMS (ESI+): *m/z*: [M + H]+ calculated for $C_{12}H_{16}ClN_4O$: 267.1013, found 267.1027.

[7] Synthetic utilities of benzoxaboroles

3-(1H-Tetrazol-5-yl)benzo[c][1,2]oxaborol-1(3H)-ol (7): In a reaction vial, a mixture of **2a** (80 mg, 0.3 mmol), 12 N HCl (1.0 mL) and 1,4-dioxane (0.5 mL) was heated with stirring at 75 °C for 12 h. The mixture was then extracted with EtOAc (3×15 mL). The combined organic layers were washed with brine and dried over Na_2SO_4, filtered and concentrated. The solid residue was washed with chloroform (2x5mL) to get pure as a white solid in 90% yield (55 mg, 0.27 mmol).



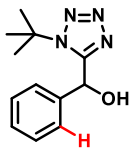
7

Note: For **2e (cleavage of *N*-tetramethylpropane group)**; 6 N HCl (1.0 mL) was used instead of 12 N HCl, gave the desired free tetrazole **7** in 92% yield.

Yield = 90% (92% for **2e**)
R_f = 0.8 (10% MeOH in $CHCl_3$)

^{1}H NMR (300 MHz, $CDCl_3$+CD_3OD): δ 7.77 (d, *J* = 7.2 Hz, 1H), 7.52 (m, 2H), 7.46−7.43 (m, 1H), 6.60 (br s, 1H) (labile B-O*H* proton probably exchanged with deuterium in CD_3OD).
^{13}C NMR (125 MHz, $CDCl_3$+CD_3OD): δ 151.9, 131.8, 130.6, 128.6, 122.4, 74.2.
HRMS (ESI-): *m/z*: [M - H]+calculated for $C_8H_6BN_4O_2$: 201.0584, found 201.0590.

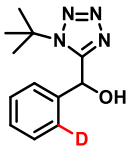
(1-(*tert*-Butyl)-1H-tetrazol-5-yl)(phenyl)methanol (5e): In a round bottom flask, a mixture of **2a** (36 mg, 0.14 mmol), $AgNO_3$ (2.4 mg, 0.014 mmol) and Et_3N (6 µL, 0.042 mmol) in 2 mL solvent (EtOH : H_2O = 1:1) was allowed to stir for 2 hours. After the completion of reaction, 10 mL water was added and the mixture was extracted with dichloromethane (3×15 mL). The combined organic layers were washed with brine water and dried over Na_2SO_4, filtered and concentrated. The crude product was purified by column chromatography, eluted with 22% EtOAc in hexane to get protonated product compound **5e** as a white solid (25 mg, 0.11 mmol).[S9]



5e

Yield = 75%
R_f = 0.61 (50% EtOAc in Hexane)

(1-(*tert*-Butyl)-1H-tetrazol-5-yl)(*o*-(D)phenyl)methanol (8): In a Schlenk reaction vial, a mixture of **2a** (80.0 mg, 0.3 mmol), K_3PO_4 (131.6 mg, 2 mmol) and Ag_2CO_3 (8.27 mg, 0.03 mmol) was degassed under vacuum and backfilled with nitrogen and the process repeated for three times. A degassed mixture of D_2O (0.5 mL) and dry 1,4-dioxane (0.5 ml) was then added to the reaction vial and the resulting solution was stirred at 60 °C for 6 h. The reaction mixture was then filtered through celite and extracted with dichloromethane (3×15 mL). The combined organic layers were washed with brine water and dried over Na_2SO_4, filtered and concentrated to get **8** (56 mg, 0.24 mmol) as a white solid.

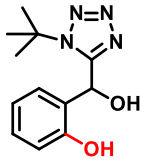


8

Yield = 82%
R_f = 0.54 (30% EtOAc in Hexane)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38−7.35 (m, 3H), 7.30−7.27 (m, 1H), 6.25 (s, 1H), 3.84 (br s, 1H), 1.62 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$+CD_3OD): δ 156.2, 139.3, 128.7, 128.5, 128.5, 126.7, 67.3, 62.3, 29.8.
HRMS (ESI+): *m/z*: [M + H]+ calculated for $C_{12}H_{16}DN_4O$: 234.1465, found 234.1457.

2-((1-(*tert*-Butyl)-1H-tetrazol-5-yl)(hydroxy)methyl)phenol (9): In a 5 mL round bottom flask, compound **2a** (39 mg, 0.15 mmol) was dissolved in 2 mL ethyl acetate. After 5 min, saturated aqueous Na_2CO_3 solution (1 mL) was added followed by addition of aqueous H_2O_2 (0.15 mL; 35% by volume). The reaction mixture stirred further for 30 minutes at room temperature. After completion of the reaction, it was quenched with $Na_2S_2O_3$ and $NaHCO_3$ solution (1:5) and further stirred for 5-10 minutes. The organic layer was extracted with EtOAc (10 mL x 3) and dried over anhydrous Na_2SO_4 and the residue was purified by column chromatography on silica gel using 35% EtOAc in hexanes as an eluent to give the corresponding product **9** (27 mg, 0.11 mmol) as a white solid.[S10]

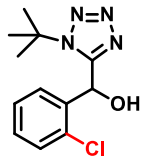


9

Yield = 73%
R_f = 0.58 (50% EtOAc in Hexane)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (br s, 1H), 7.17 (m, 1H), 6.93 (dd, *J* = 8.1, 0.9 Hz, 1H), 6.88 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.81 (m, 1H), 6.40 (s, 1H), 4.79 (br s, 1H), 1.73 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8, 154.6, 130.4, 128.0, 125.0, 120.5, 118.1, 65.9, 62.5, 29.9.
HRMS (ESI+): *m/z*: [M + H]+ calculated for $C_{12}H_{17}N_4O_2$: 249.1352, found 249.1341.

(1-(*tert*-Butyl)-1H-tetrazol-5-yl)(2-chlorophenyl)methanol (10): A Schlenk tube was charged with **2a** (50.0 mg, 0.19 mmol), NCS (25.8 mg, 0.19 mmol) and copper(I)chloride (19.2 mg, 0.19 mmol). The tube was degassed under vacuum and backfilled with nitrogen and the process was repeated for three times. A degassed mixture of water (0.20 µL, 1.16 mmol) and dry acetonitrile (3 mL) was added to the reaction tube and the resulting solution was stirred at 80 °C for 22 h. The reaction was cooled to an ambient temperature, diluted with Et_2O (15 mL) and sequentially washed with 1N aq. HCl (10 mL), 1 N aq. NaOH (10 mL) and brine (10 mL). The organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure and further purified by chromatography using Hexane / EtOAc (100 / 22) to afford desired product **10** (36 mg, 0.134 mmol) as a white solid.[S11]

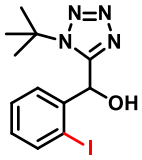


10

Yield = 70%.
R_f = 0.65 (50% EtOAc in Hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43−7.41 (m, 1H), 7.39−7.37 (m, 1H), 7.33−7.30 (m, 2H), 6.59 (s, 1H), 3.93 (bs, 1H), 1.71 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 136.9, 132.8, 130.2, 129.9, 128.4, 127.5, 64.9, 62.3, 29.8.
HRMS (ESI+): *m/z*: [M + H]+ calculated for : $C_{12}H_{16}ClN_4O$ 267.1013, found 267.1008.

(1-(*tert*-Butyl)-1H-tetrazol-5-yl)(2-iodophenyl)methanol (11): A mixture of compound **2a** (26 mg, 1 mmol) $Cu(NO_3)_2 \cdot 3H_2O$ (1.2 mg, 0.05 mmol) and I_2 (25.3 mg, 1 mmol) in acetonitrile (1 mL) was stirred at room temperature for 6 h. After the completion of reaction, 10 mL water was added and extracted with dichloromethane (3×15 mL). The combined organic layers were washed with aqueous sodium hyposulfite, dried over Na_2SO_4, filtered and concentrated. The crude product was purified by column chromatography using 21% EtOAc in hexane to afford iodinated product **11** (29 mg, 0.082 mmol) as a white solid.[S12]



11

Yield = 82%.
R_f = 0.66 (50% EtOAc in Hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (dd, *J* = 6.8, 1.1 Hz, 1H), 7.36 (dd, *J* = 7.0, 7.3 Hz, 1H), 7.25 (d, *J* = 7.5, 1H), 7.06 (dd, *J* = 7.7, 7.4, 1H), 6.40 (br s, 1H), 3.97 (br s, 1H), 1.71 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 141.5, 140.0, 130.7, 128.9, 128.4, 99.2, 77.2, 62.5, 29.9.
HRMS (ESI+): *m/z*: [M + H]+ calculated for $C_{12}H_{16}IN_4O$: 359.0369, found 359.0360.

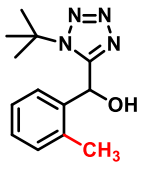
[1,1'-Biphenyl]-2-yl(1-(tert-butyl)-1H-tetrazol-5-yl)methanol (12): To a solution of iodobenzene (130.3 µL, 1.16 mmol) in dimethoxyethane (3 mL) was added the compound **2a** (50 mg, 0.194 mmol) and dissolved in a minimal amount of ethanol (1.0 mL), followed by added a solution of Na_2CO_3 (164 µl, 1.55 mmol, 2M solution in deionized water). $Pd(dba)_2$ (13.8 mg, 0.024 mmol) was then added and the solution was heated at reflux temperature for overnight. The reaction mixture was then cooled to room temperature and filtered through celite. The filtrate was concentrated and the residue was diluted in ether and washed with brine, dried over Na_2SO_4, filtered and concentrated. Purification of the crude product by column chromatography (100:20 hexane / ethyl acetate) afforded the biaryl compound **12** (54 mg, 0.174 mmol) as a pale yellow solid.

12

Yield = 90%.
R_f = 0.75 (50% EtOAc in Hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (m, 4H), 7.41 (dd, *J* = 6.6, 1.9 Hz, 2H), 7.34 (dd, *J* = 6.8, 1.8 Hz, 2H), 7.34-7.33 (m, 1H), 6.11 (s, 1H), 3.93 (br s, 1H), 1.31 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 155.9, 141.6, 139.8, 136.6, 130.6, 129.5, 129.1, 128.5, 128.3, 127.8, 127.5, 127.3, 65.3, 61.8, 29.4.
HRMS (ESI+): *m/z*: [M + H]+calculated for $C_{18}H_{21}N_4O$: 309.1715, found 309.1710.

(1-(*tert*-Butyl)-1H-tetrazol-5-yl)(o-tolyl)methanol (13): In a reaction vial containing compound **2a** (80 mg, 0.31 mmol), K_3PO_4 (131.6 mg, 1.5 equiv.) and P(*o*-tol)$_3$ (8.49 mg, 0.09) was degassed under vacuum and backfilled with nitrogen and the process was repeated for three times. MeI (29.1 µL, 1.5 equiv.) and $Pd(OAc)_2$ (2.0 mg, 0.03 equiv.) were then added under nitrogen flow. A degassed mixture of solvent [water (11.16 µL, 1.5 equiv.) and dry THF (3.5 mL)] was added and the resulting solution was stirred at room temperature for 16 h. The reaction mixture was then filtered through celite. The filtrate was concentrated and the residue was diluted in ether and washed with brine, dried (MgSO4), filtered and concentrated. Purification of the crude product is done by column chromatography using hexane / ethyl acetate (100:20) to afford the methylated product **13** (36 mg, 0.134 mmol) as viscous liquid.[S13]



13

Yield = 65%
R_f = 0.72 (50% EtOAc in Hexane)

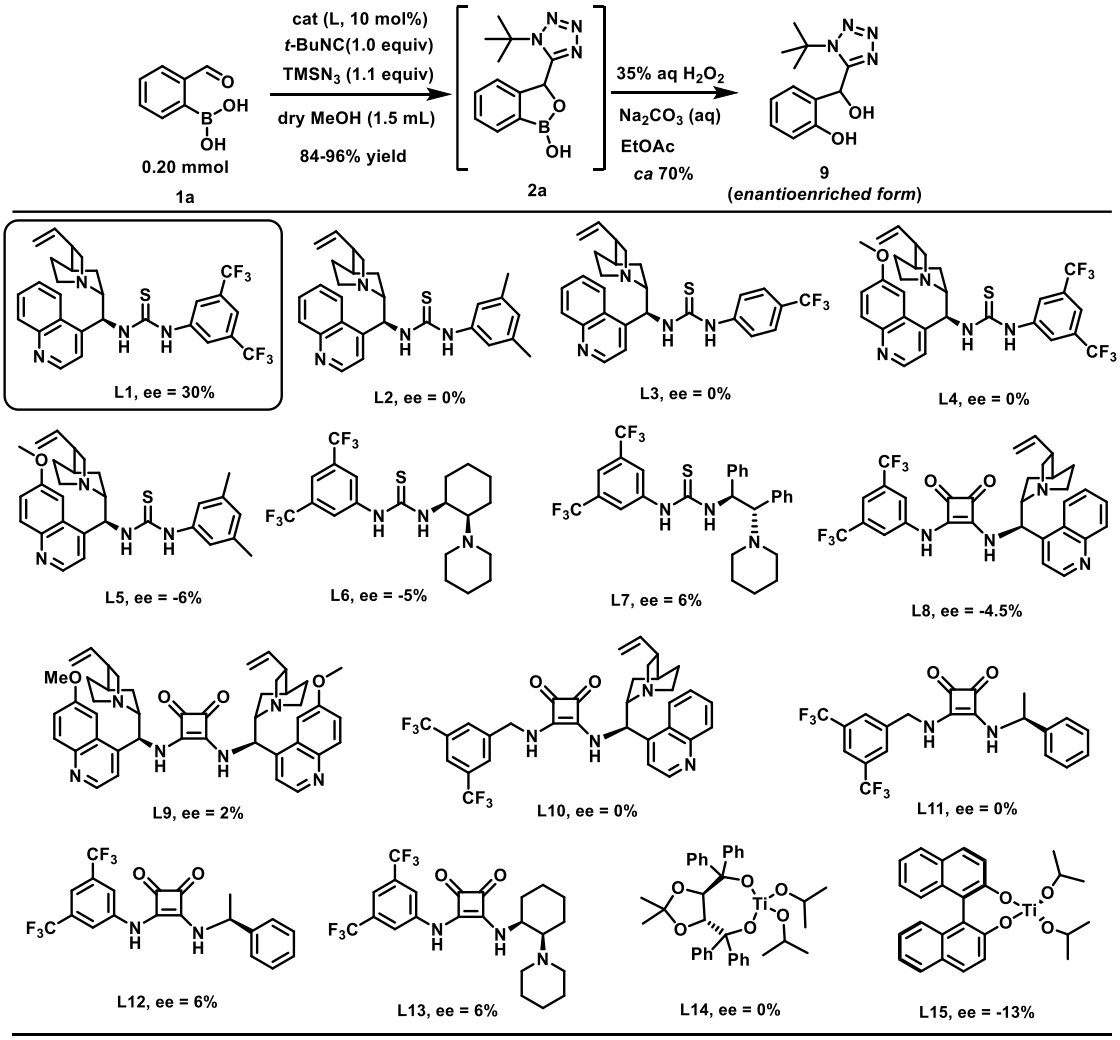
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26 (m, 2H), 7.14-7.11 (m, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 6.36 (br s, 1H), 3.63 (br s, 1H), 2.49 (s, 3H), 1.58 (s, 9H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 155.6, 137.5, 136.3, 131.3, 129.3, 126.7, 126.6, 66.2, 62.0, 29.7, 19.0.
HRMS (ESI+): *m/z*: [M + H]+calculated for $C_{13}H_{19}N_4O$: 247.1559, found 247.1554.

[8] Preliminary study on asymmetric synthesis

General Procedure for chiral catalyst study (Scheme S1): Slightly modified procedure was employed. To a mixture of 2-formylphenylboronic acid (**1a**; 30 mg, 0.2 mmol) and chiral catalysts (**L1-15**; 10 mol%) in dry methanol (2 mL), $TMSN_3$ (29.1 µL, 0.22 mmol) and *tert*-butylisocyanide (22.5 µL, 0.2 mmol) were sequentially added under nitrogen atmosphere at room temperature and run it to complete the reaction (*ca* 6 h) to furnish **2a** as a white solid in 84-96% yields.

Note: BINOL and TADDOL-titanate complex (**L14** and **L15**; 10 mol%) was generated in-situ by mixing diol and $Ti(O^iPr)_4$ (1:1) in dry methanol at 0 °C. After 10 min. of stirring (it turned to yellow color, probably due to titan-ate complex formation), 2-formylphenylboronic acid (**1a**; 30 mg, 0.2 mmol), $TMSN_3$ (29.1 µL, 0.22 mmol), *tert*-butylisocyanide (22.5 µL, 0.2 mmol) were sequentially added and allowed to stir at 0 °C to rt for 6-8 h.

The product **2a** was directly converted into product **9** (for the measurement of enantioselectivity) under oxidative deborylation conditions as used previously.



Scheme S1. Screening of chiral catalysts: Enantioselectivity in **2a** was measured after converting it (after 100% conversion of **1a**) into corresponding oxidation product **9** by HPLC using chiral stationary phase.

Experimental procedure: In a 5 mL round bottom flask, compound **2a** (39 mg, 0.15 mmol) was dissolved in 2 mL ethyl acetate. After 5 min, saturated aqueous Na_2CO_3 solution (1 mL) was added followed by addition of aqueous H_2O_2 (0.15 mL; 33-35% by volume). The reaction mixture stirred further for 30 minutes at room temperature. After completion of the reaction, it was quenched with $Na_2S_2O_3$ and $NaHCO_3$ aqueous

solution (1:5) and further stirred for 5-10 minutes. The organic layer was extracted with EtOAc (10 mL x 3) and dried over anhydrous Na_2SO_4 and concentrated to get enentioenriched diols (**9**). Enantiomeric excess (ee) was determined by HPLC analysis using Daicel Chiralpak **ID** column (IPA/*n*-Hexane 1:10, flow rate 1.0 mL/min, λ = 230 nm, t_{R1} = 18.9 min., t_{R2} = 25.2 min).

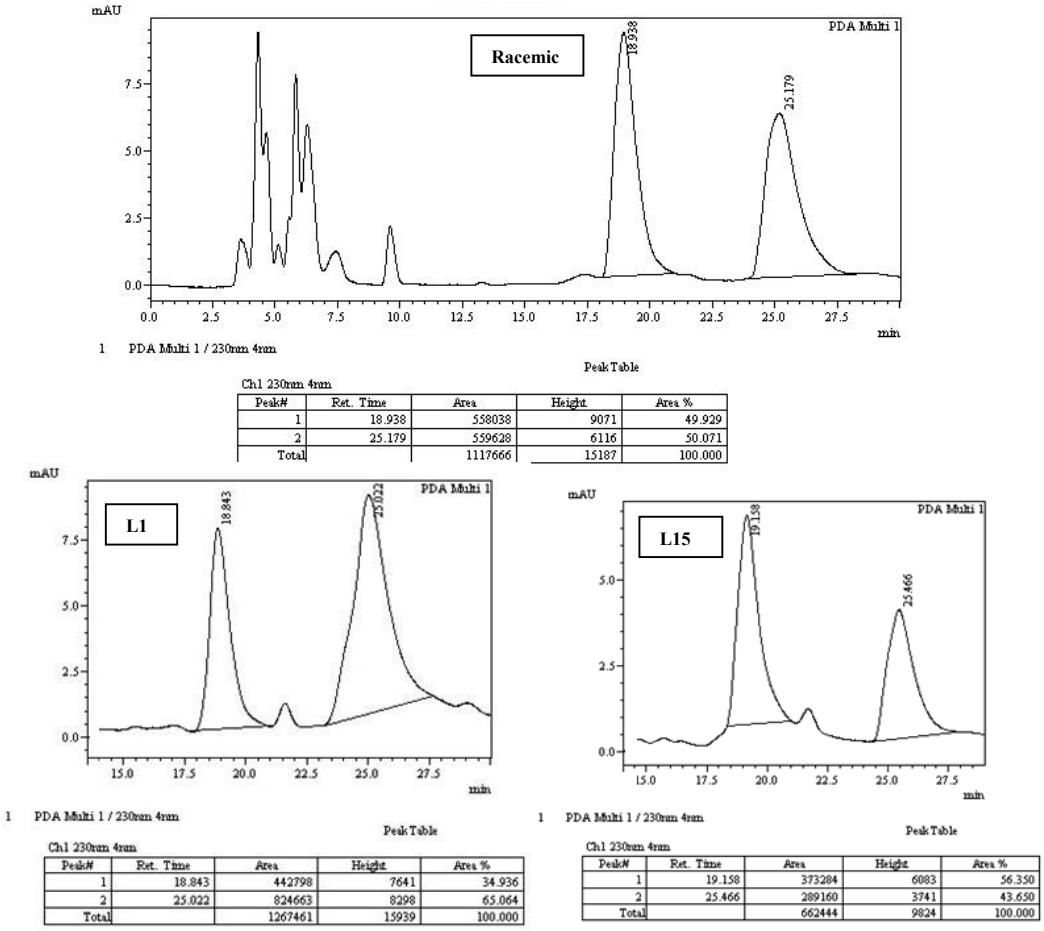


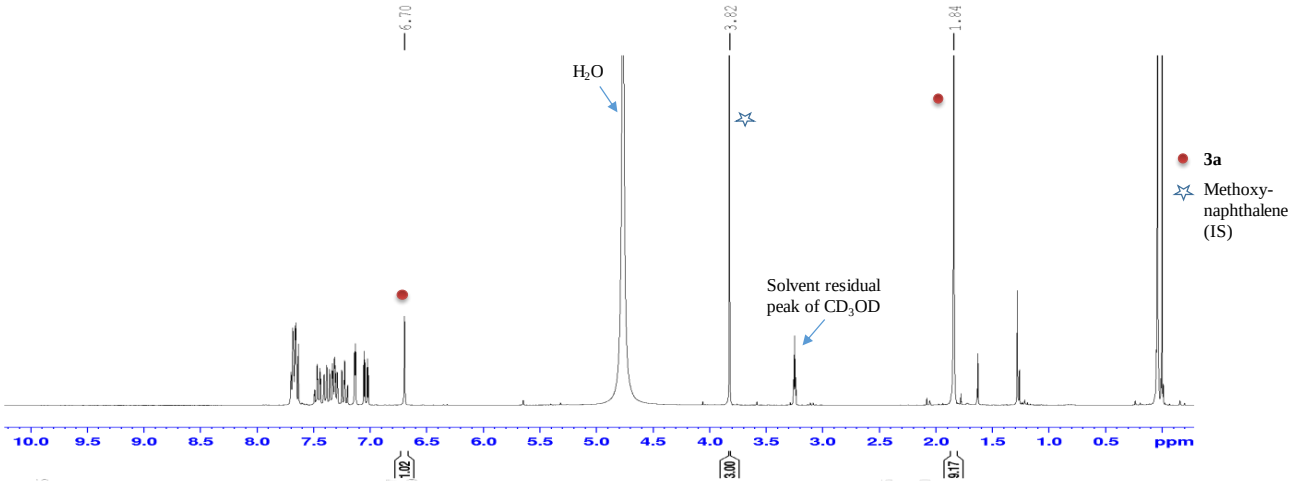
Figure S1. Chiral separation by using HPLC

[9] References:

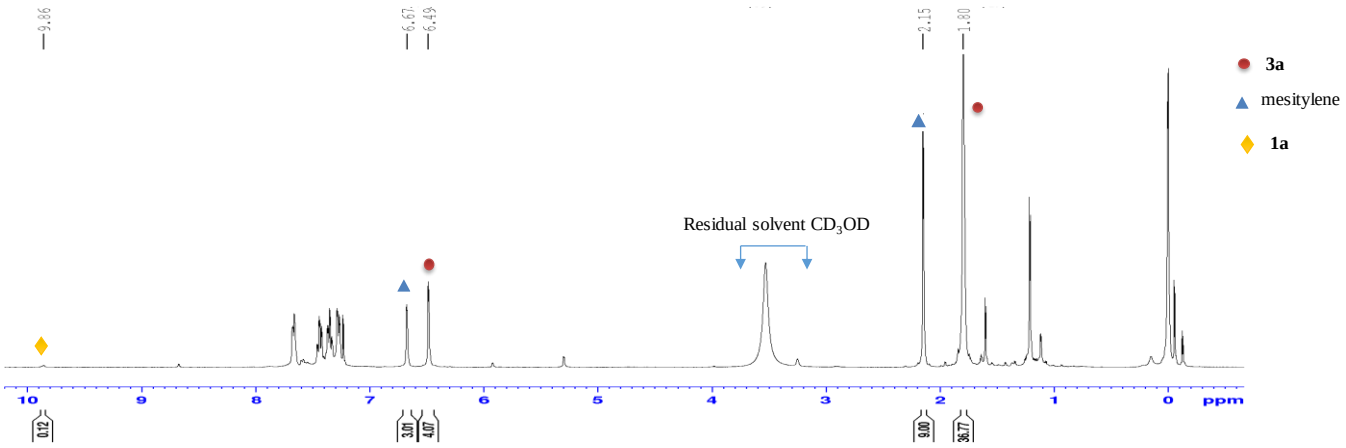
S1. (a) Cassani, C.; Martín-Rapún, R.; Arceo, E.; Bravo, F.; Melchiorre, P. *Nat. Protocols*, **2013**, *8*, 325 (b) Manna, M. S.; Kumar, V.; Mukherjee, S. *Chem. Commun.* **2012**, *48*, 5193.
S2. (a) Yang, W.; Du, D.-M. *Org. Lett.* **2010**, *12*, 5450. (b) Yang, W.; Du, D.-M. *Adv. Synth. Cat.* **2011**, *353*, 1241.
S3. Adamczyk-Woźniak, A.; Gozdalik, J. T.; Wieczorek, D.; Madura, I. D.; Kaczorowska, E.; Brzezińska, E.; Sporzyński, A.; Lipok, J. *Molecules* **2020**, *25*, 799.
S4. Stegbauer, S.; Jandl, C.; Bach, T. *Angew. Chem., Int. Ed.* **2018**, ***57***,14593.
S5. Liu, C.; Liu, C. Y.; Zhang, Y.-K.; Zhou, Y. PCT Int. Appl. (2020), WO 2020264581 A1 Dec 30, 2020.
S6. Kim, Y. H.; Lee, H.; Kim, Y. J.; Kim, B. T.; Heo, J.-N. *J. Org. Chem.* **2008**, *73*, 495-501.
S7. Hoshimoto, Y; Yabuki, H.; Kumar R.; Suzuki, H.; Ohashi, M.; Ogoshi, S. J. Am. Chem. Soc. 2014, *136*, 48, 16752–16755
S8. Chandgude, A. L.; Dömling, A. *Green Chem.* **2016**, *18*, 3718-3721.
S9. Hazra, G.; Maity, S.; Bhowmick, S.; Ghorai, P. ***Chem. Sci.*, 2017, 8,** 3026-3030.
S10. Li, R. D.; Murugan, A.; Falck, R. J. *J. Am. Chem. Soc.*, **2008**, ***130***, 46.
S11. Wu, H.; Hynes, J. Org. Lett. 2010, *12*, 6, 1192–1195.
S12. Zhang, G.; Lv, G.; Li, L.; Chen, F. Cheng, J. *Tetrahedron lett*. **2011**, *52*, 1993-1995.
S13. Haydl, M. A.; Hartwig, F. J. *Org. Lett.* **2019,** *21***,** 5, 1337-1341.

[10] NMR and mass spectra:

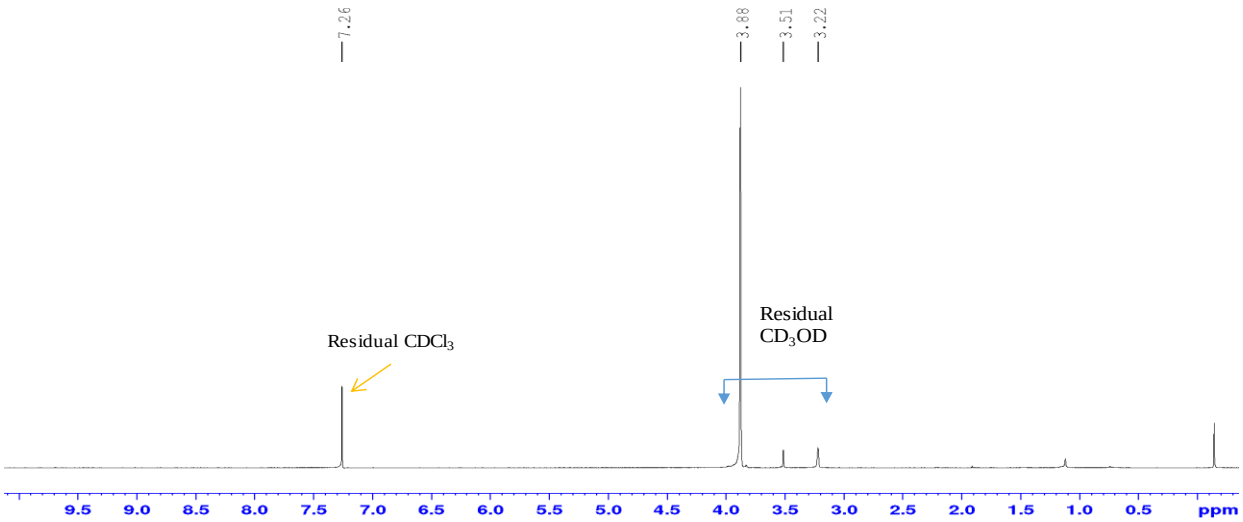
A. Entry 2 (Table 1, NMR tube experiment: ^{1}H NMR (400 MHz, **CD_3OD**)) [**1a** = 0.053 mmol, IS (2-methoxynaphthalene) = 0.05 mmol, **2a** = 0.051 mmol; 96% yield]



B. Entry 16 (Table 1, Neat reaction in 1h): ^{1}H NMR of crude reaction mixture (400 MHz, **$CDCl_3$+CD_3OD**) [**1a** = 0.48 mmol, Internal Standard (mesitylene) = 0.108 mmol, 2a = 0.44 mmol; **2a** = 92%, **1a** (rsm) = 2.7%]



C. Blank NMR of $CDCl_3$+CD_3OD (400 MHz)



Openlynx Report -
Sample: 713
File:ESMS21I20JAN10
Description:AS-26NEAT

Vial:1:A,10
Date:20-Jan-2021

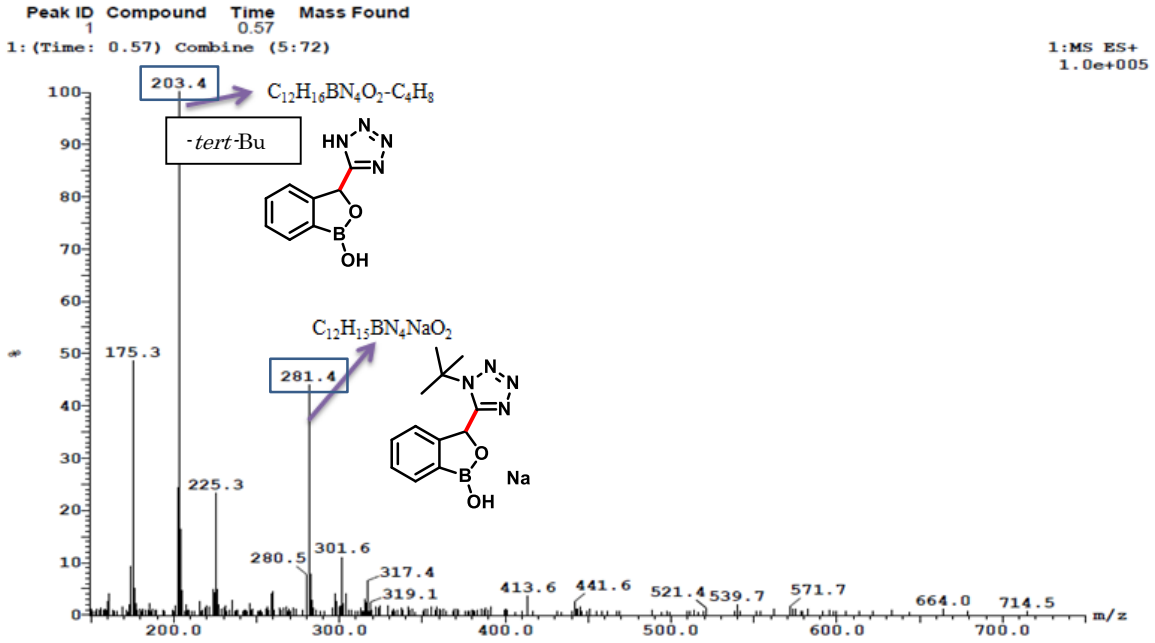
ID:ESMS21I20JAN10
Time:11:58:49

Printed: Wed Jan 20 14:02:53 2021

Sample Report:

ESMS of Crude mass (Entry 16, Table 1)

Sample 713 Vial 1:A,10 ID ESMS21I20JAN10 File ESMS21I20JAN10 Date 20-Jan-2021 Time 11:58:49 Description AS-26NEAT



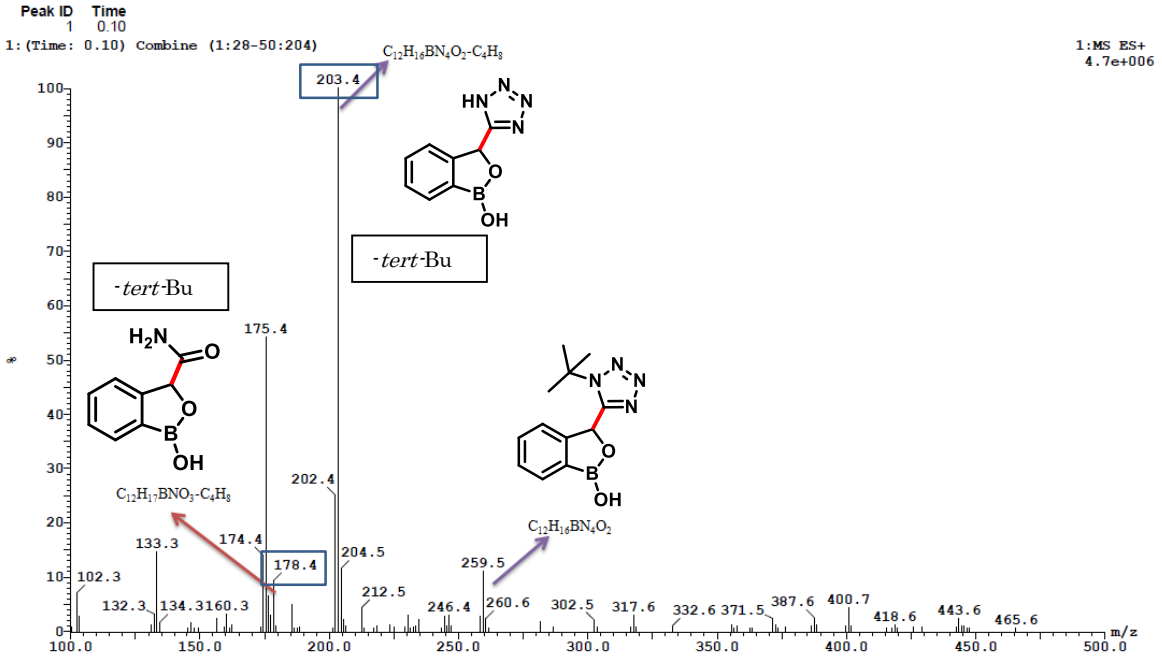
Openlynx Report SAIF, CSIR-CDRI, LUCKNOW
Sample: 102
File:ESMS21I31MAY17
Description:AS-1013

Vial:1:B,5
Date:31-May-2021

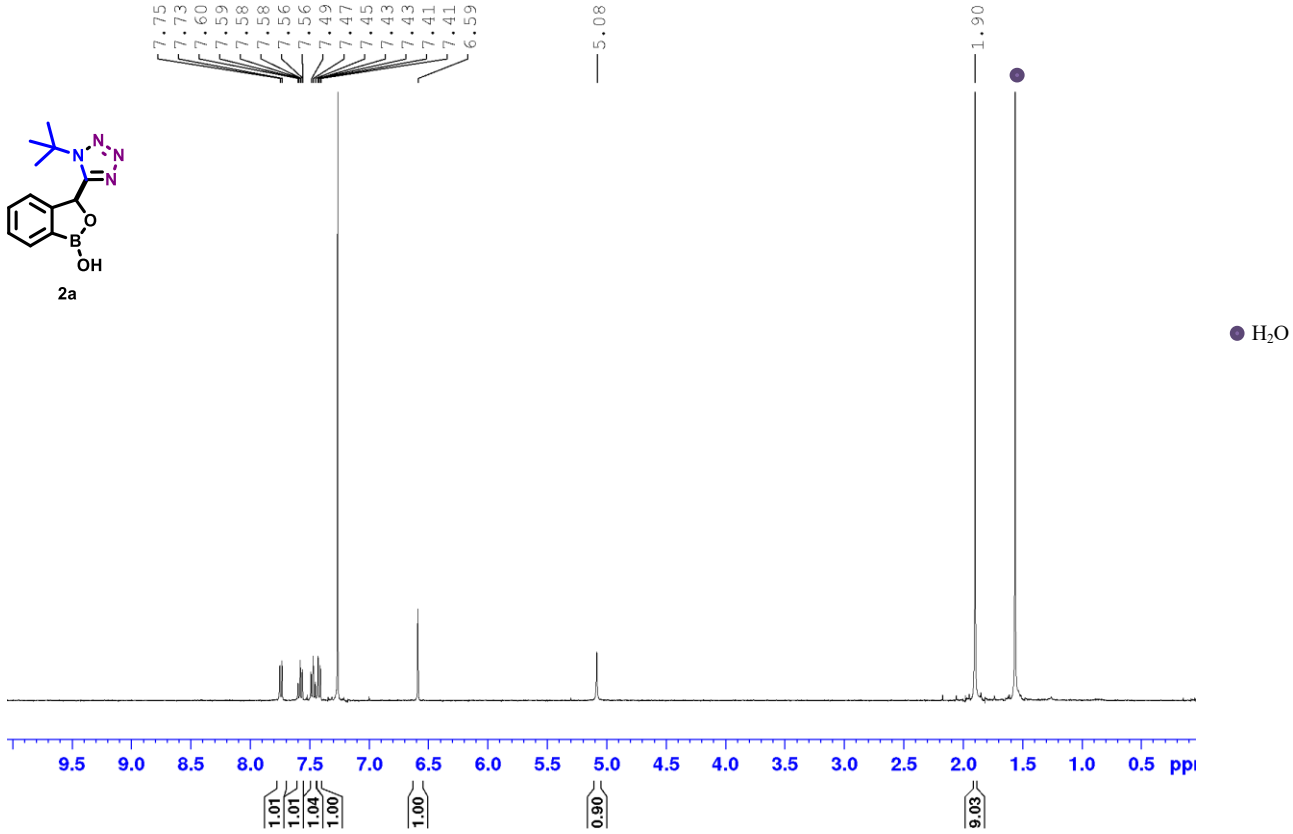
ID:ESMS21I31MAY17
Time:11:26:29

Printed: Mon May 31 13:16:53 2021

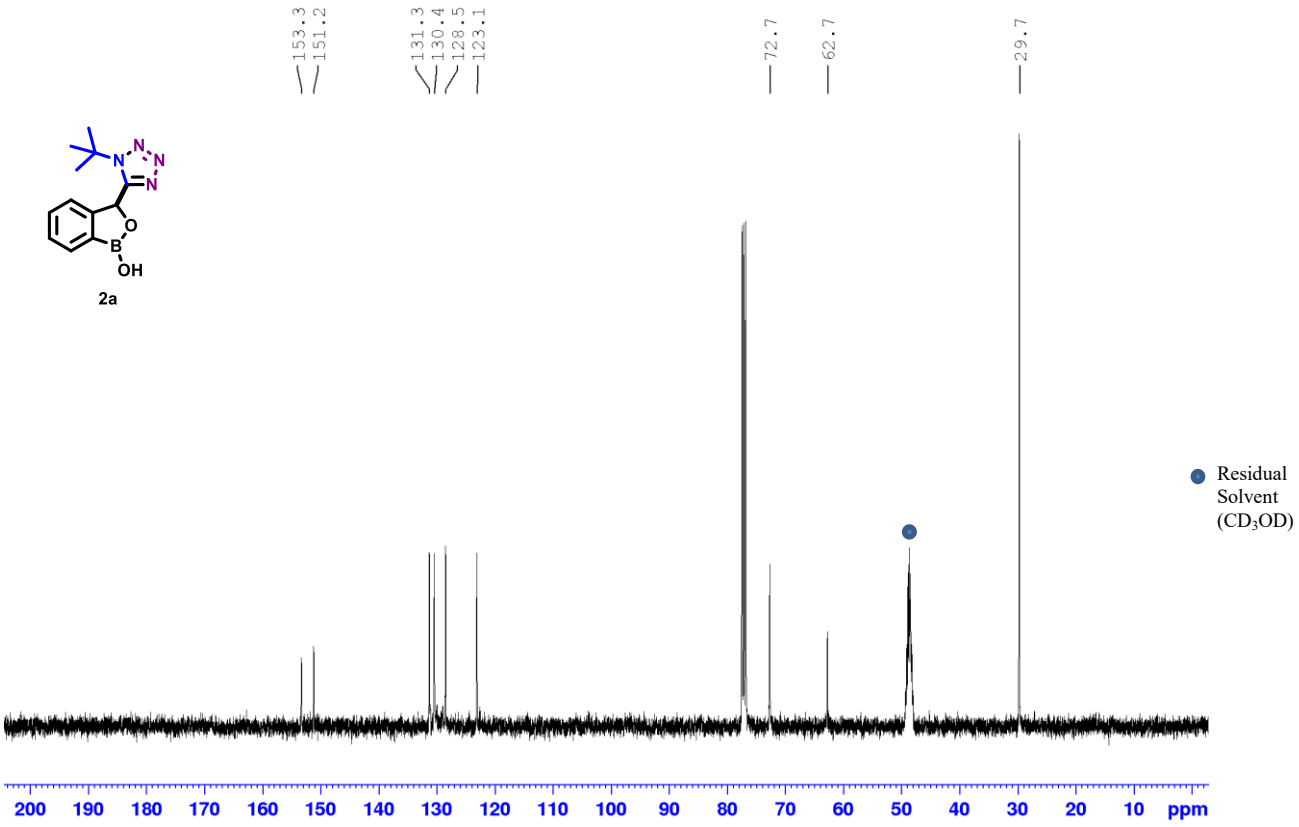
ESMS of Crude mass (Entry 15, Table 1)

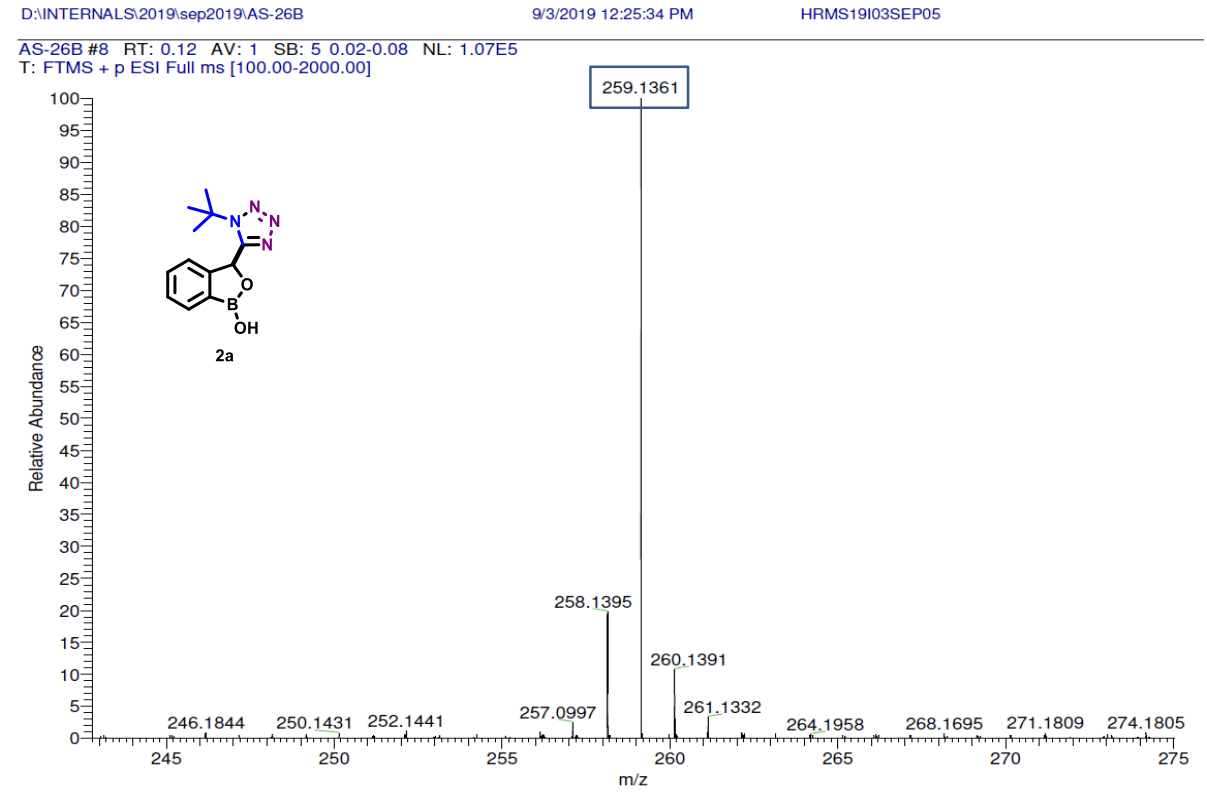


^{1}H NMR (400 MHz, $CDCl_3$):

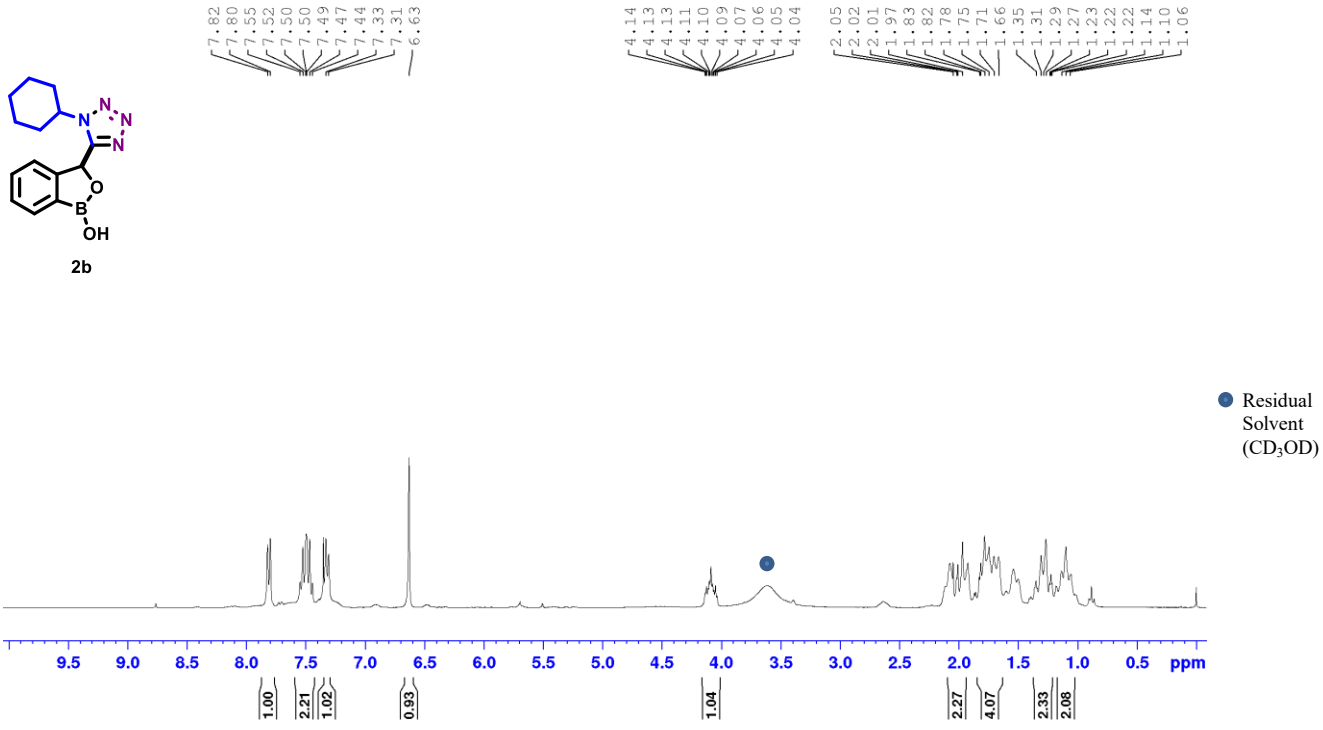


^{13}C NMR (100 MHz, $CDCl_3$ + CD_3OD):

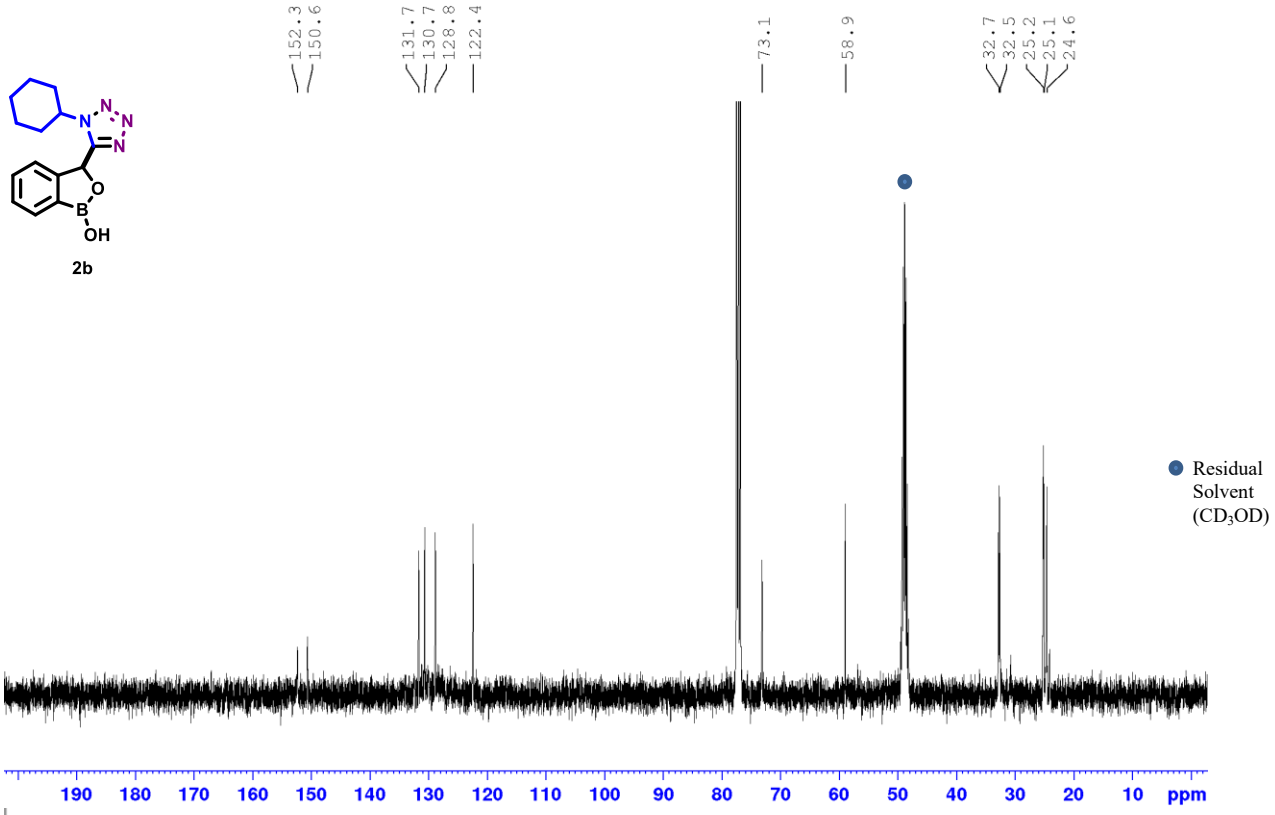


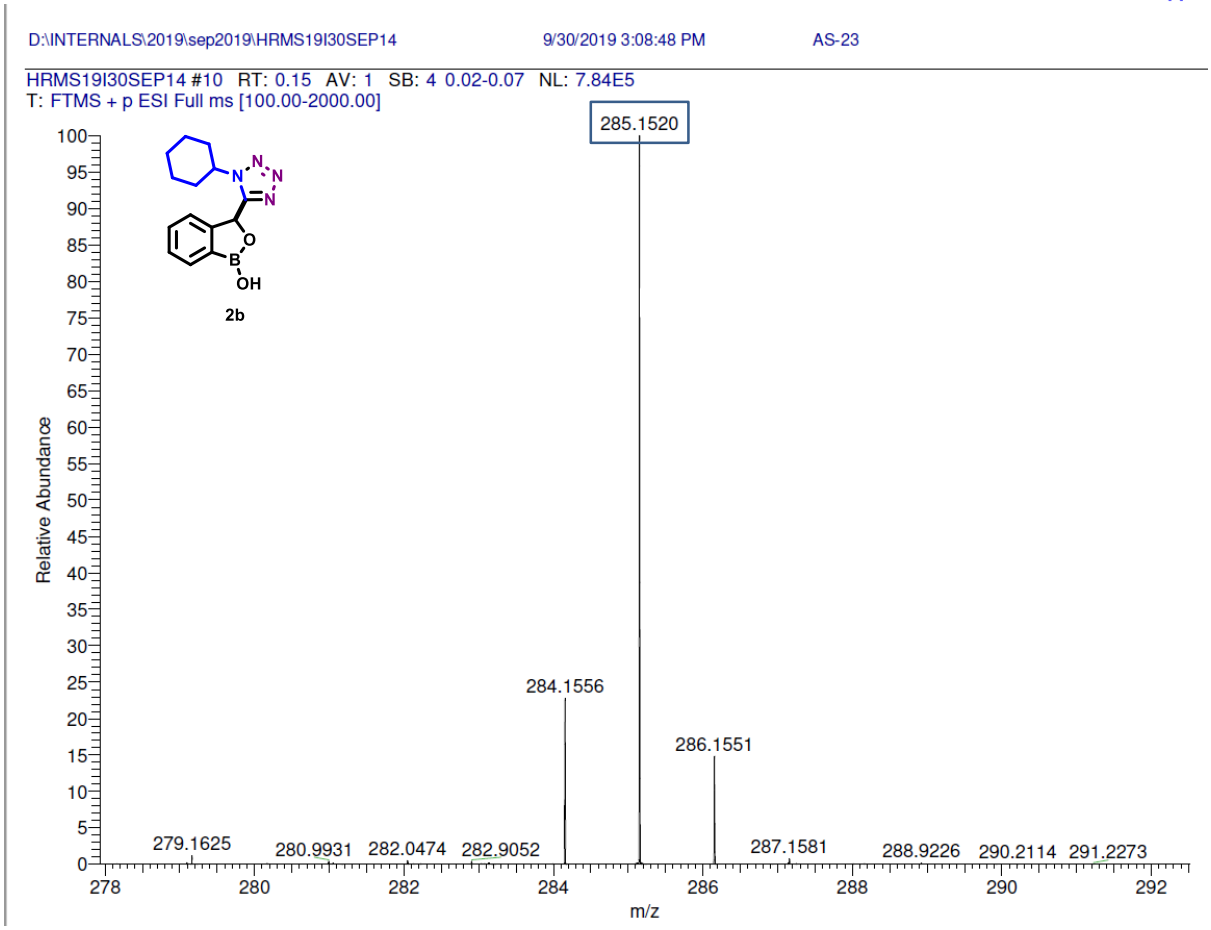


^{1}H (300 MHz, CDCl$_3$+CD$_3$OD):

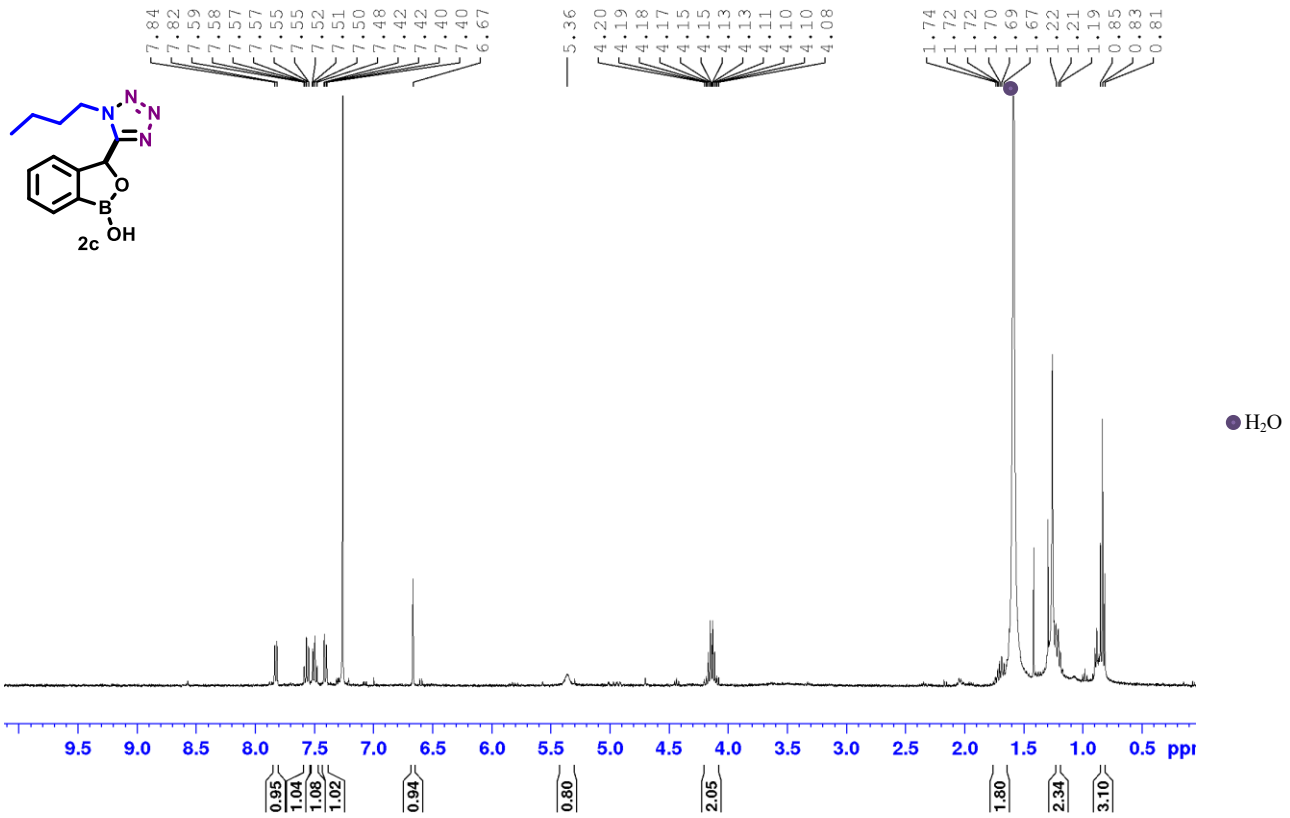


^{13}C NMR (100 MHz, $CDCl_3$):

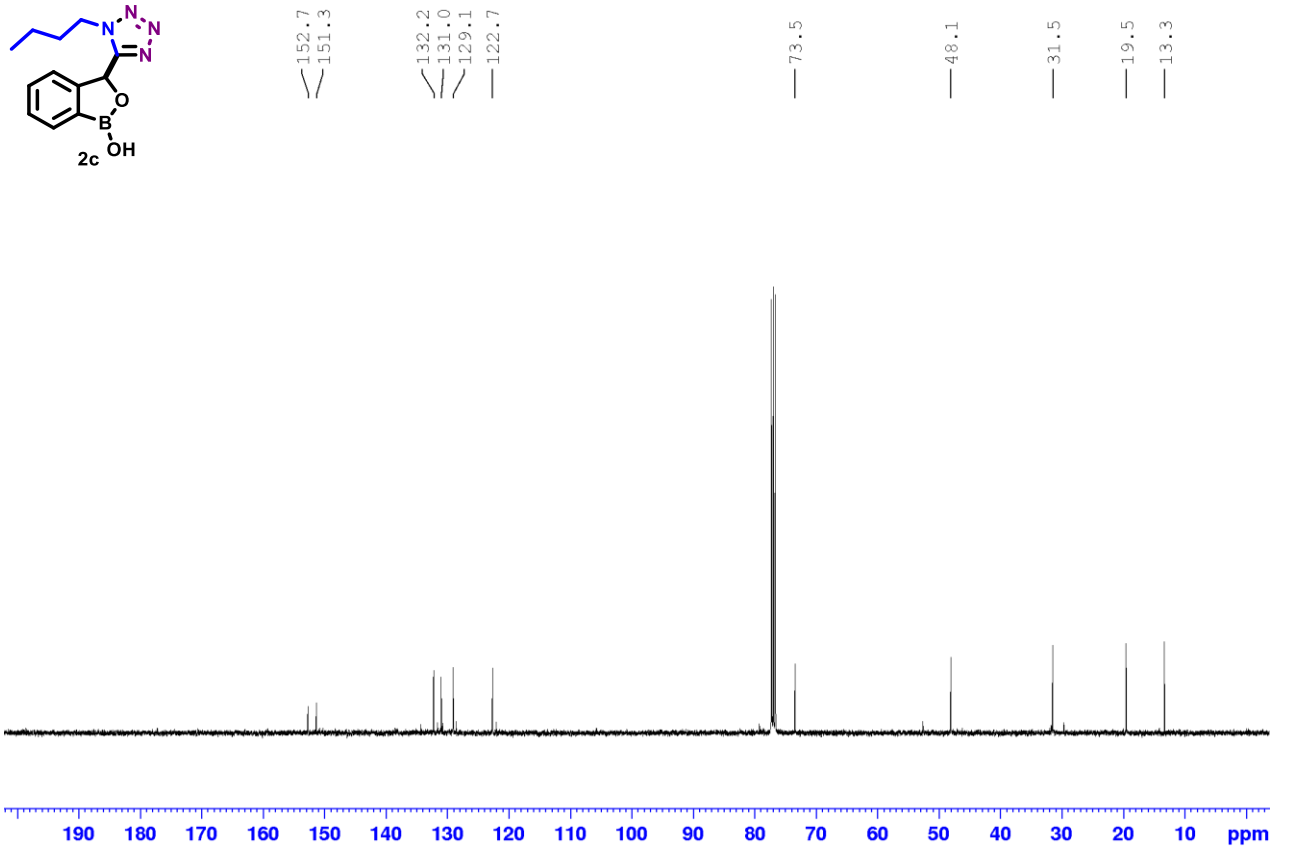


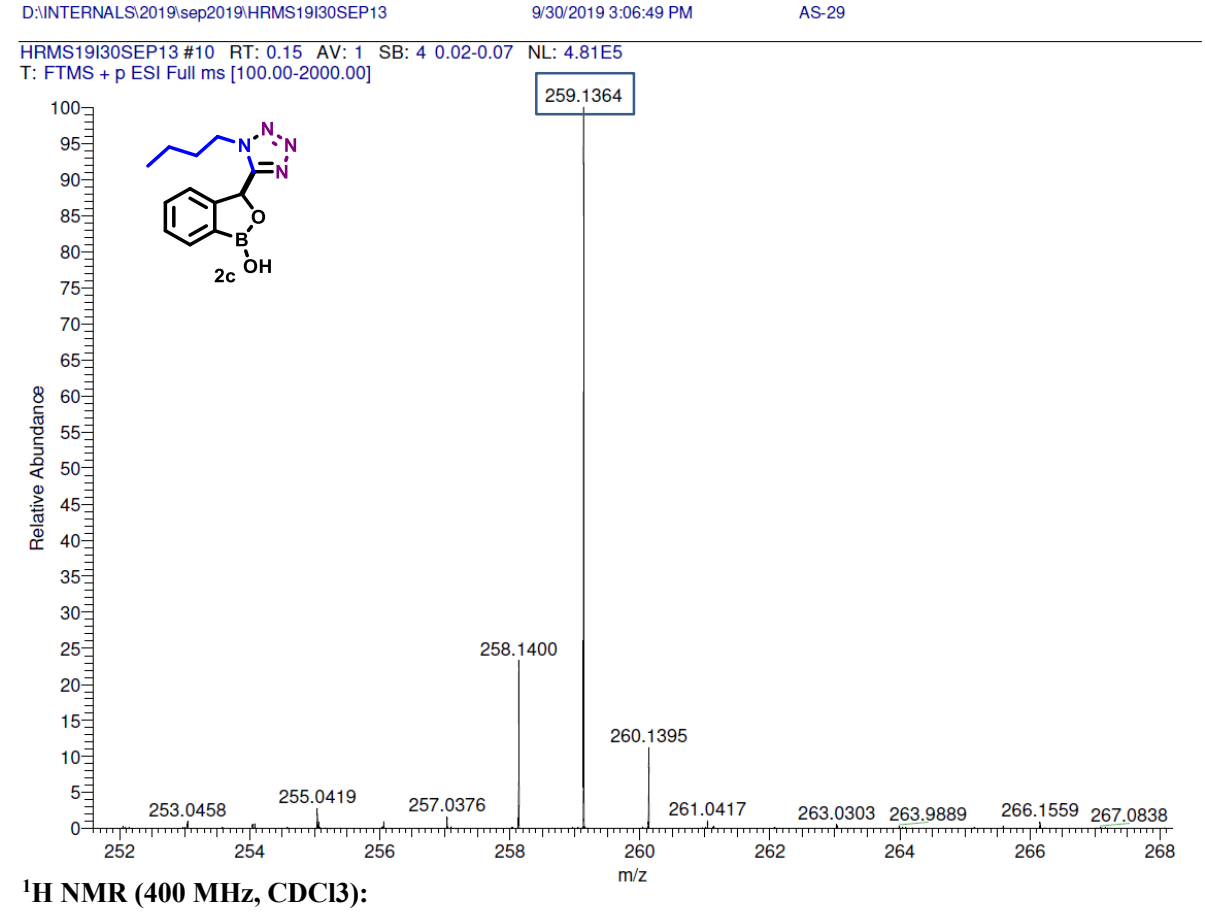


^{1}H NMR (400 MHz, $CDCl_3$):

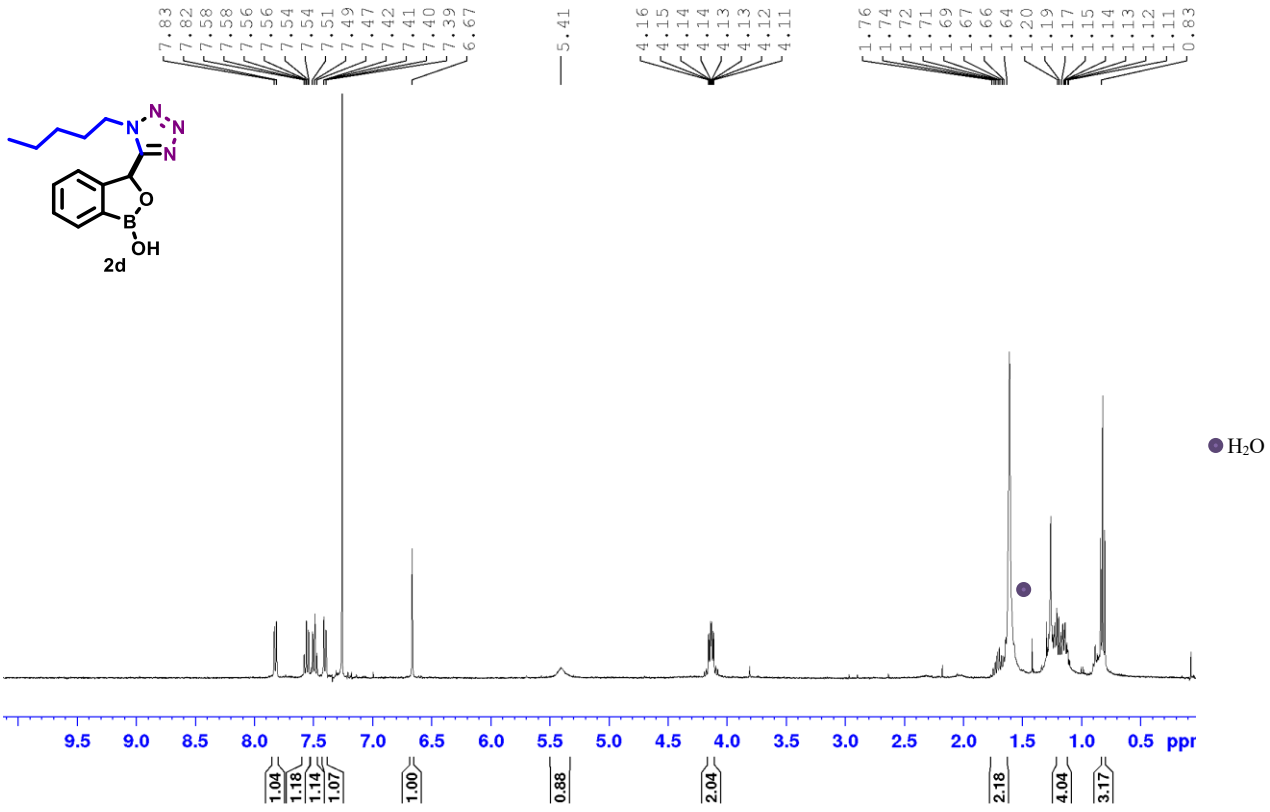


^{13}C NMR (100 MHz, $CDCl_3$):

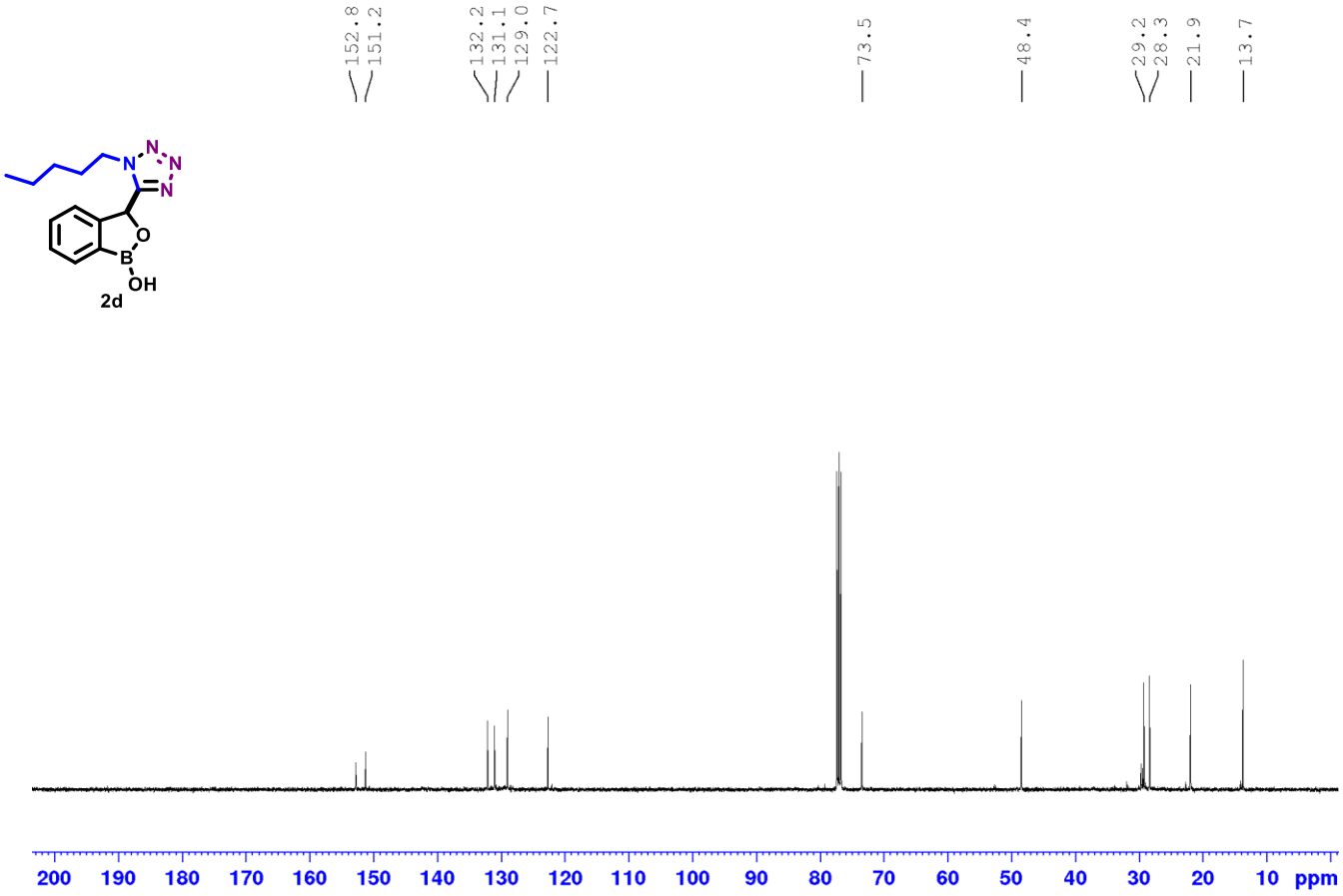


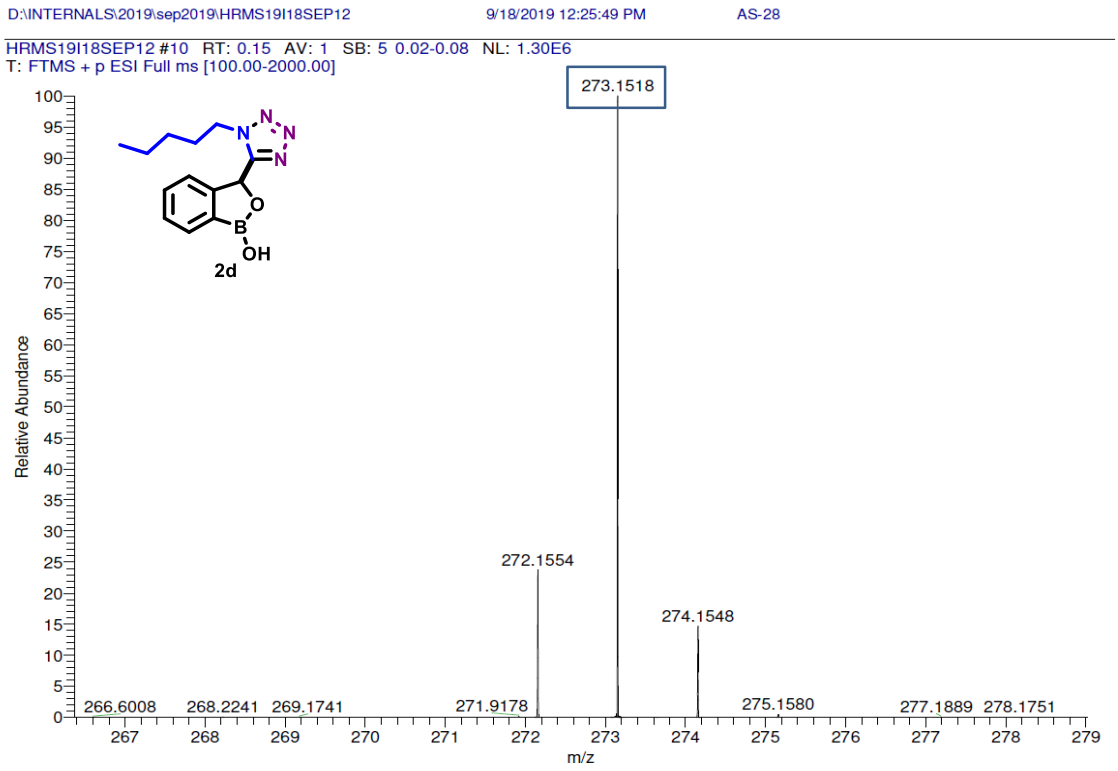


^{1}H NMR (400 MHz, CDCl3):

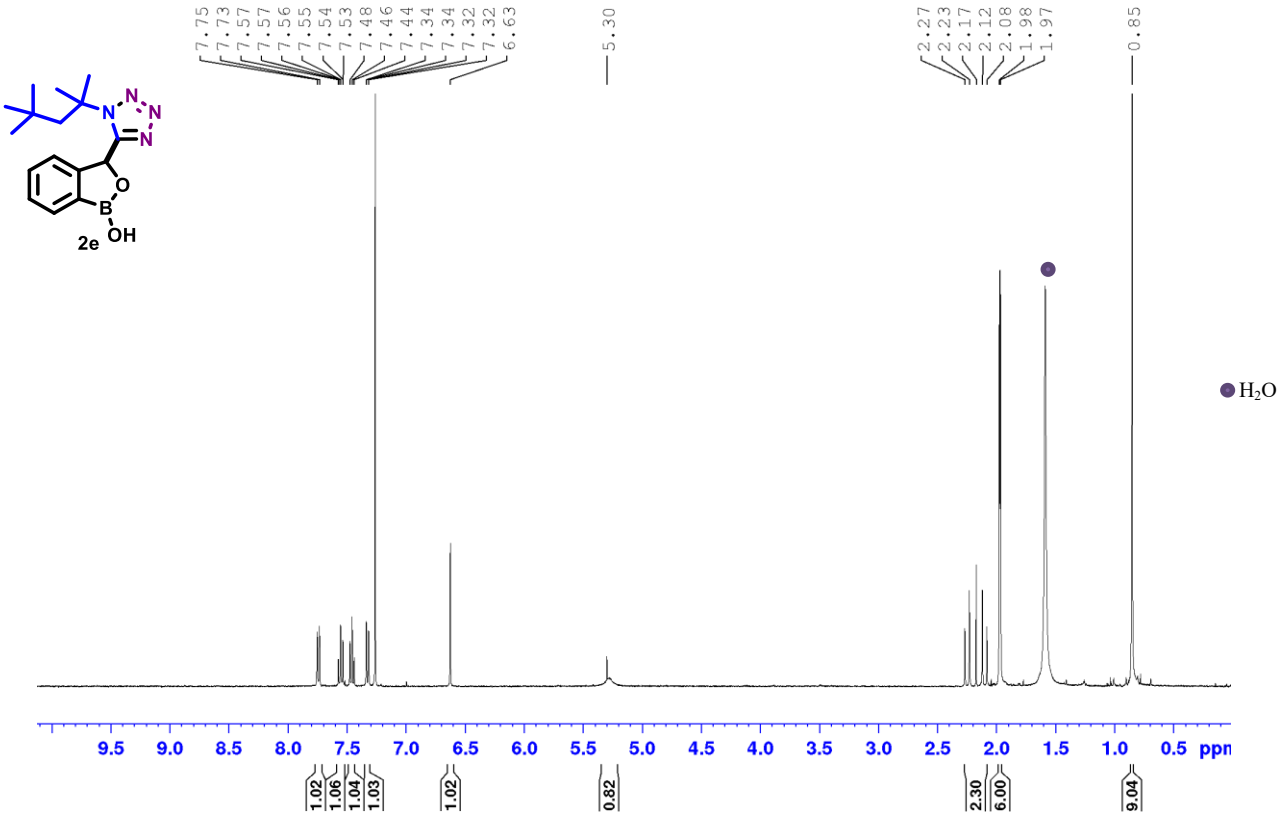


^{13}C NMR (100 MHz, $CDCl_3$):

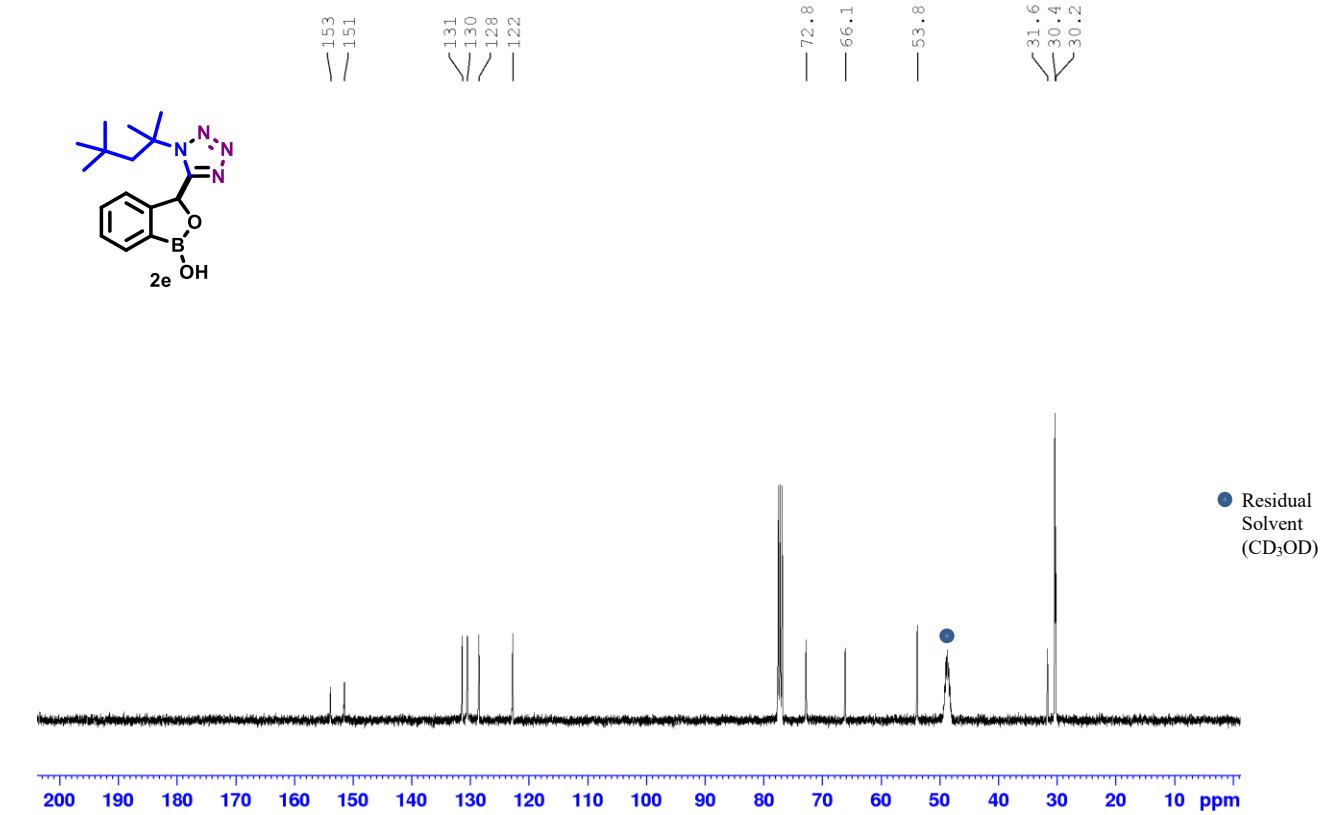


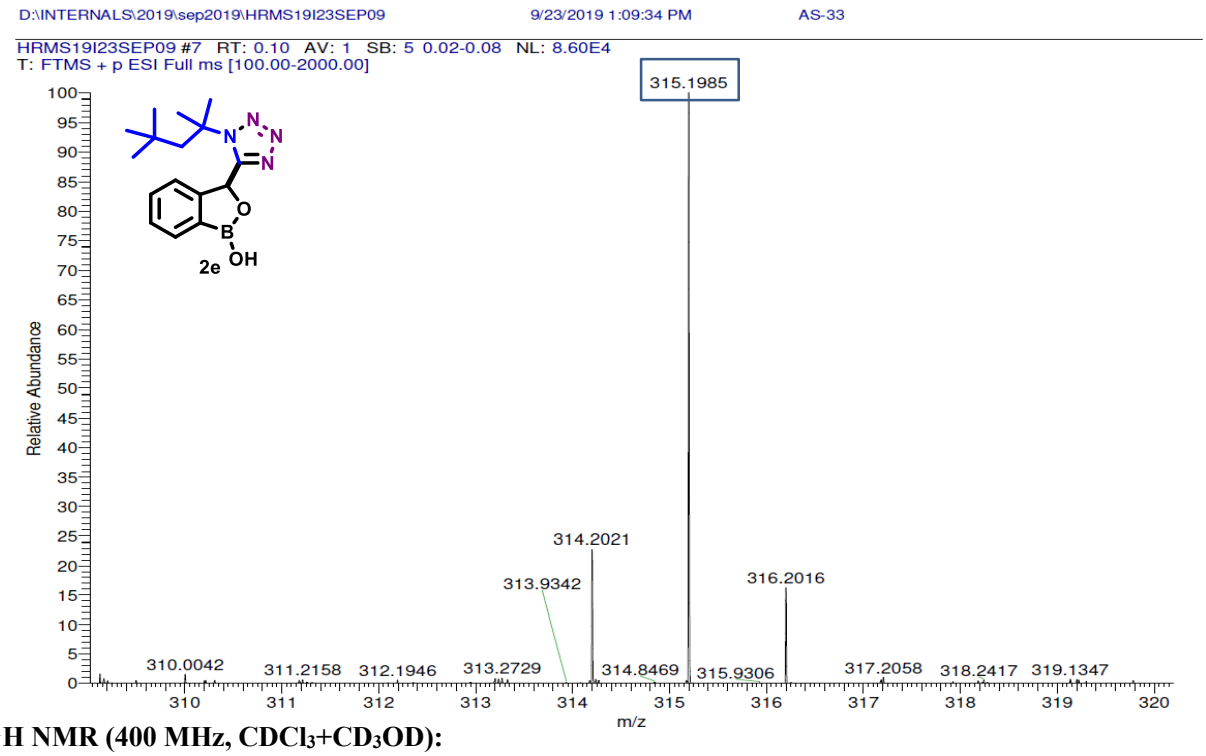


^{1}H NMR (400 MHz, $CDCl_3$):

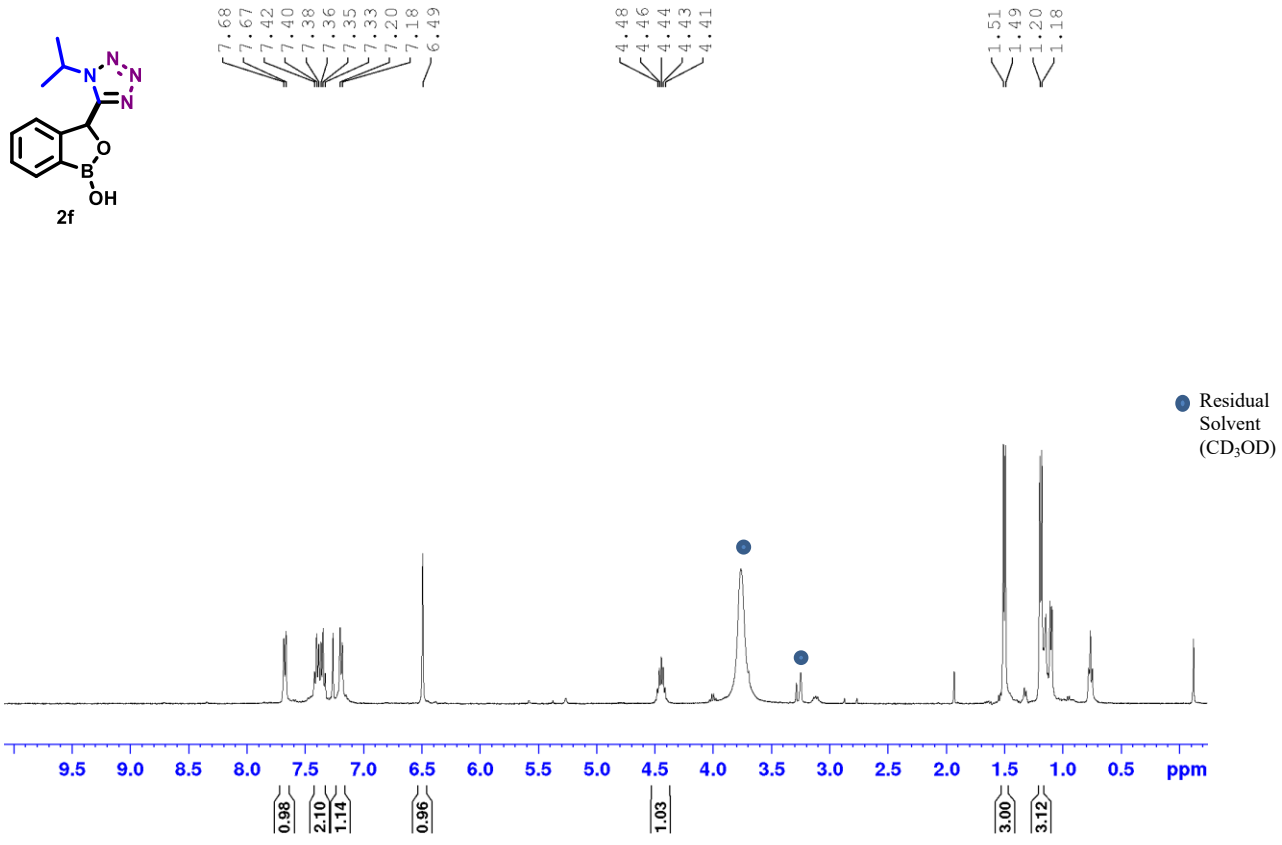


^{13}C NMR (100 MHz, $CDCl_3$+CD_3OD):

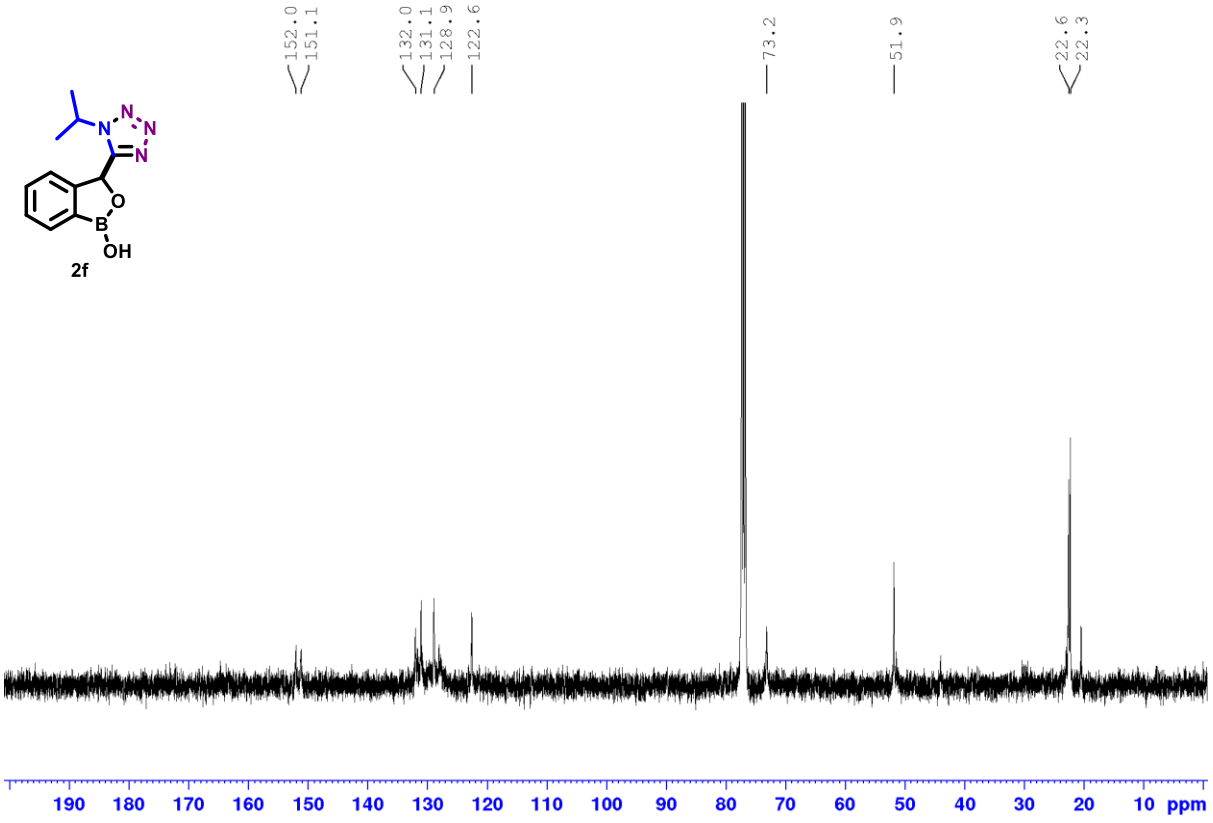


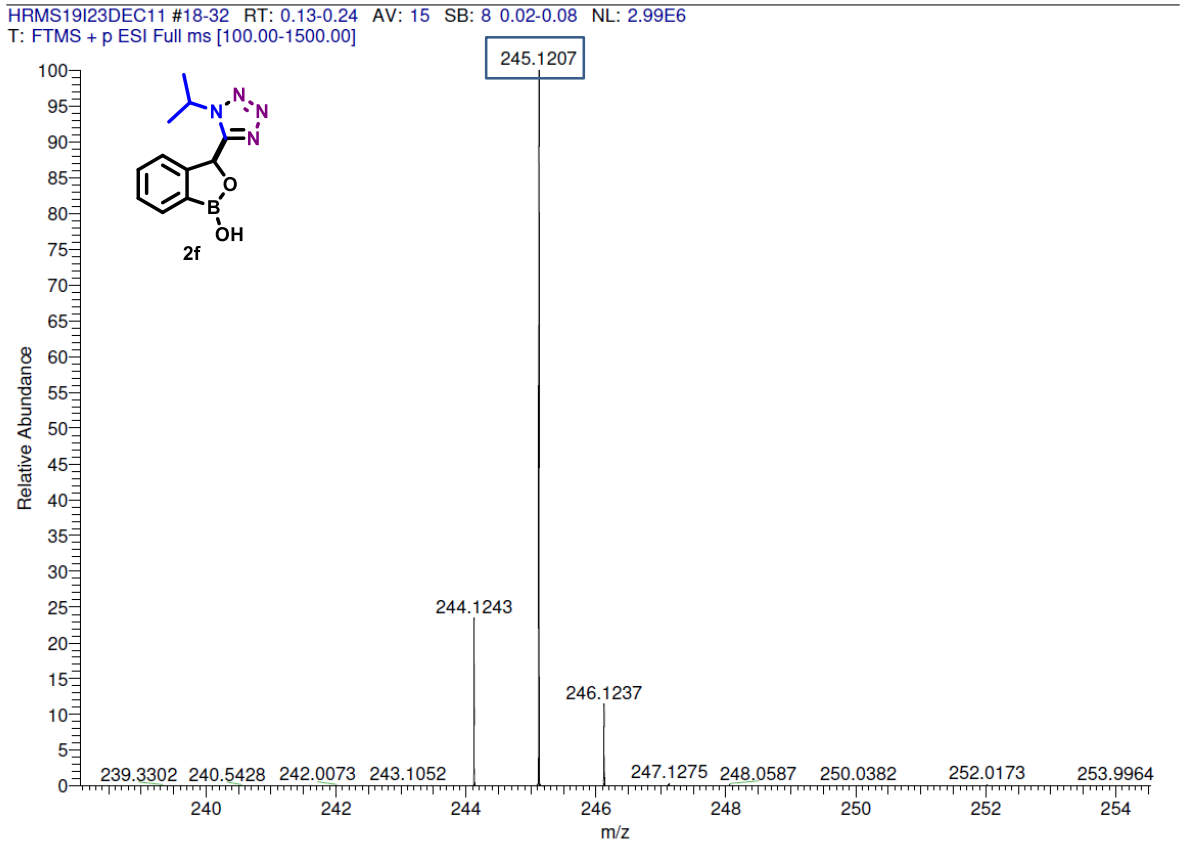


^{1}H NMR (400 MHz, $CDCl_3$+CD_3OD):

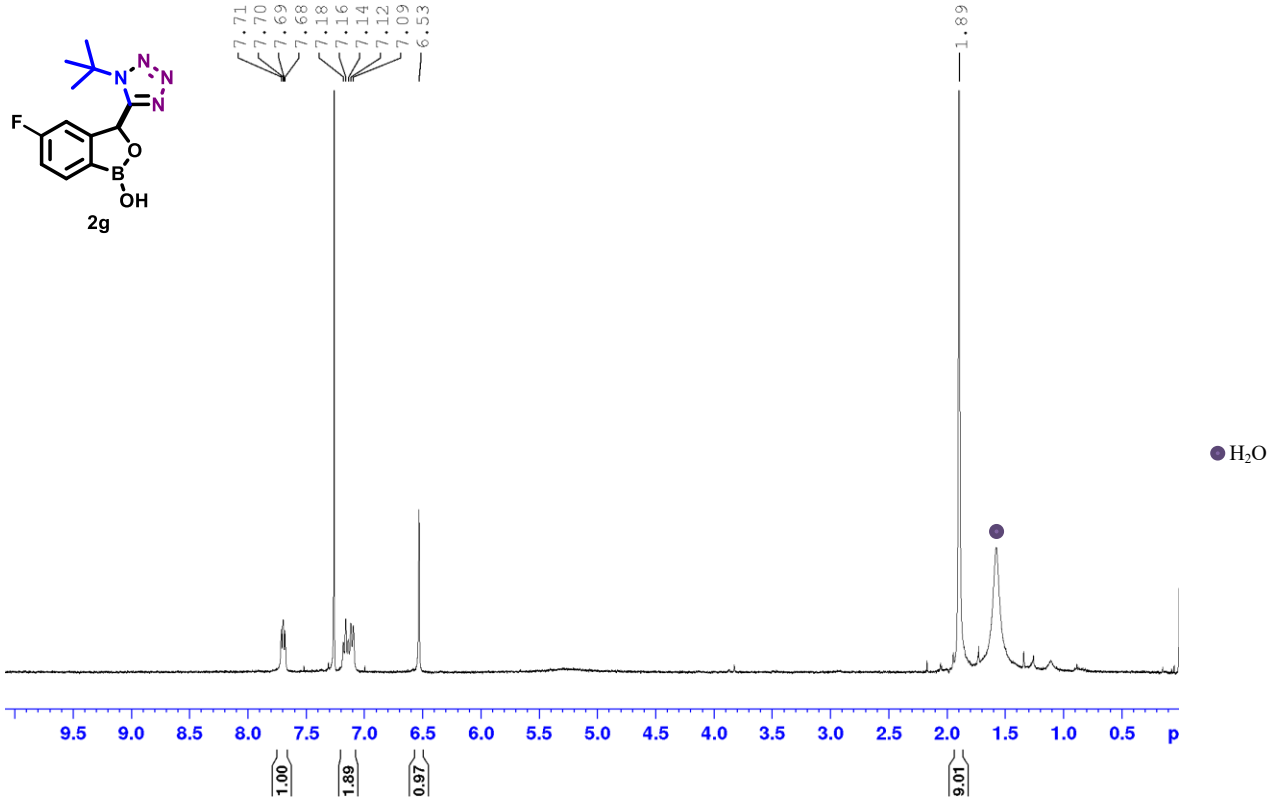


^{13}C NMR (100 MHz, $CDCl_3$):

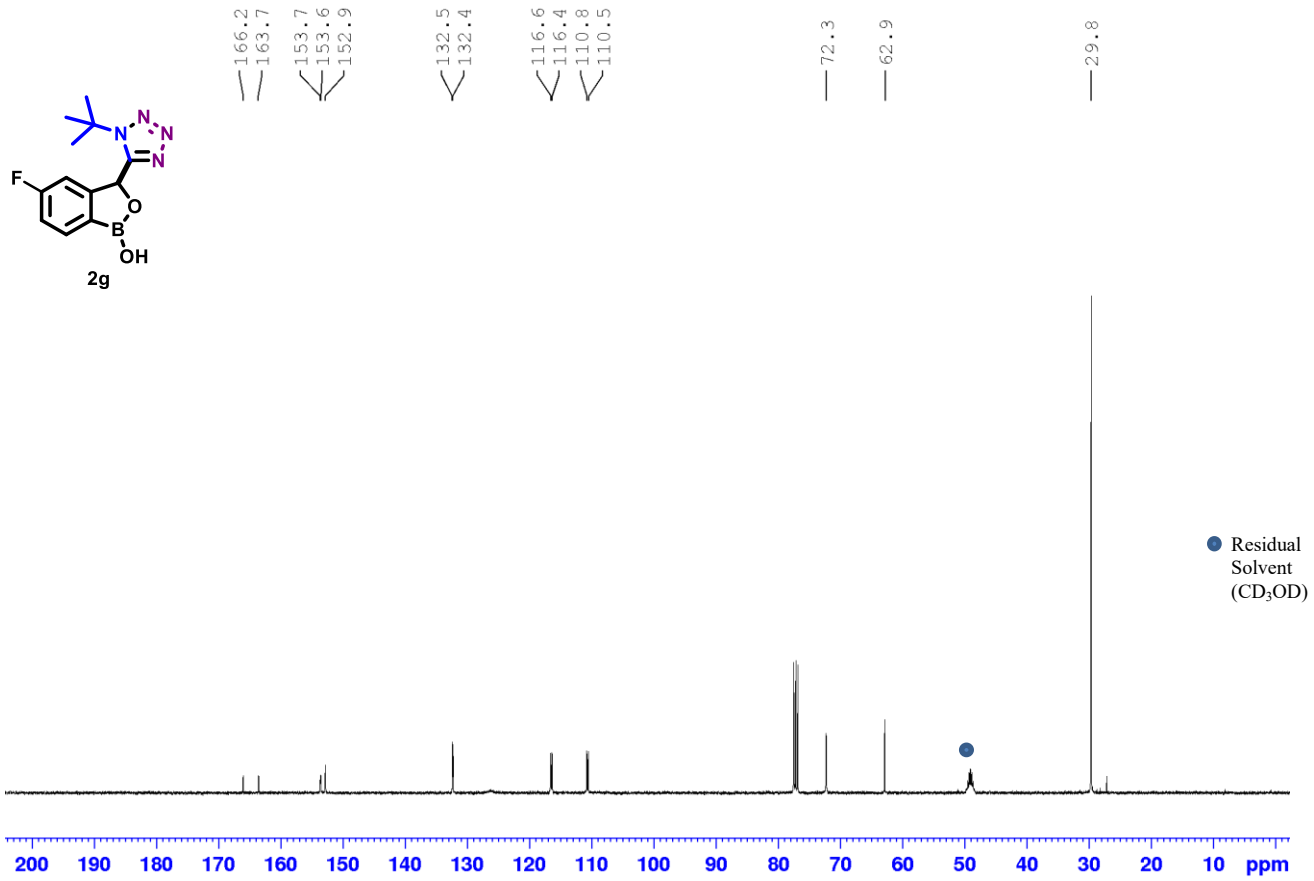




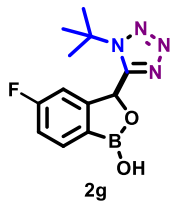
^{1}H NMR (400 MHz, $CDCl_3$):



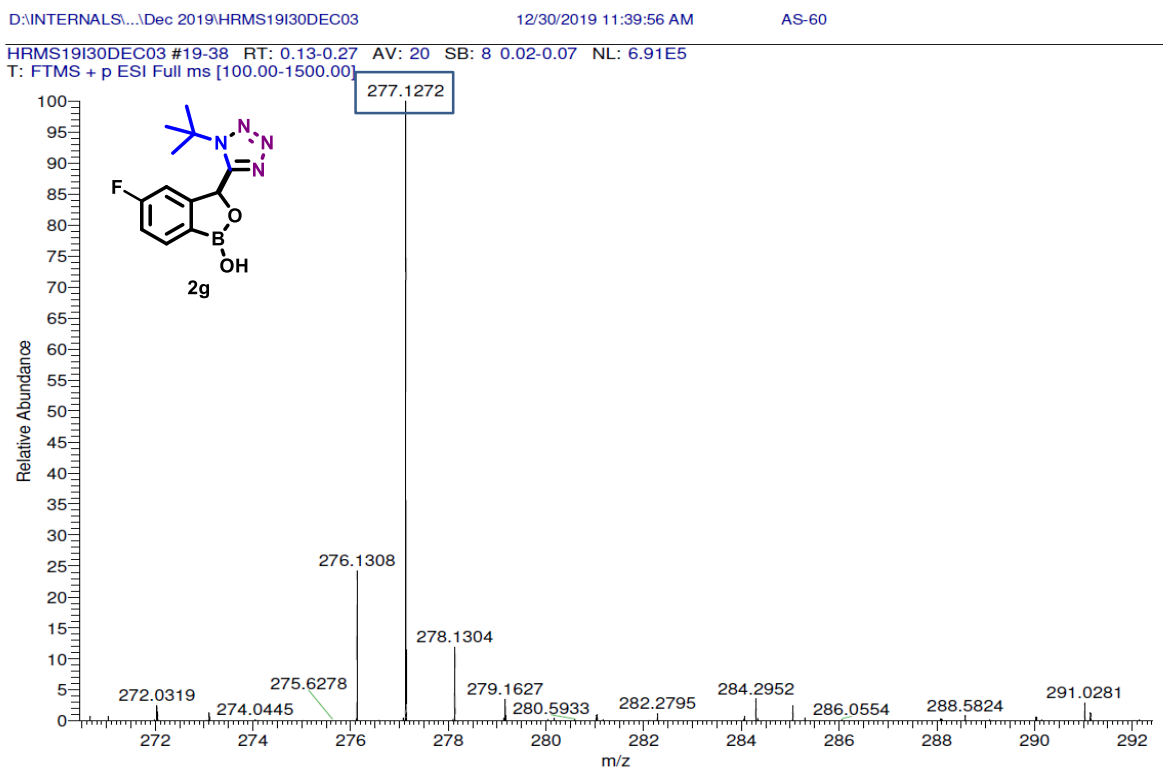
^{13}C NMR (100 MHz, $CDCl_3$+CD_3OD):



^{19}F (376 MHz, $CDCl_3$+CD_3OD):

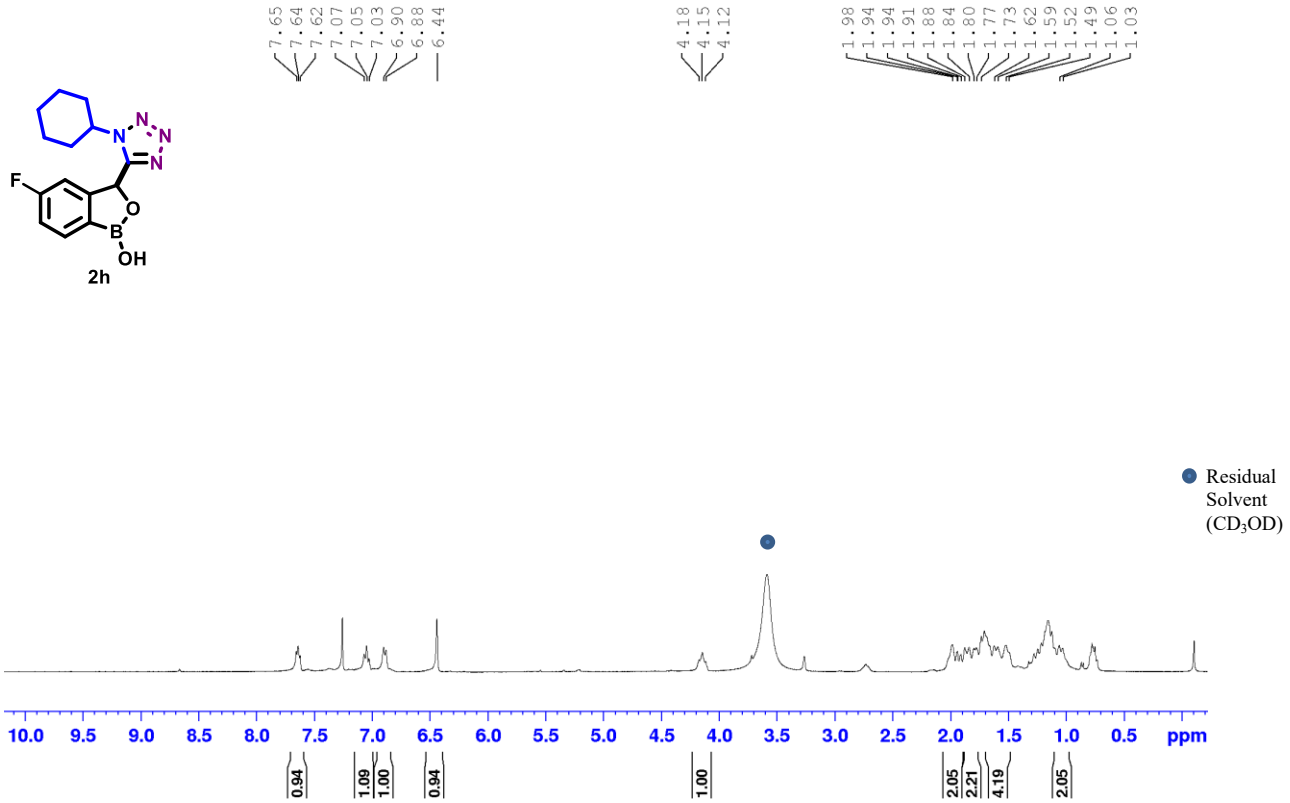


2g

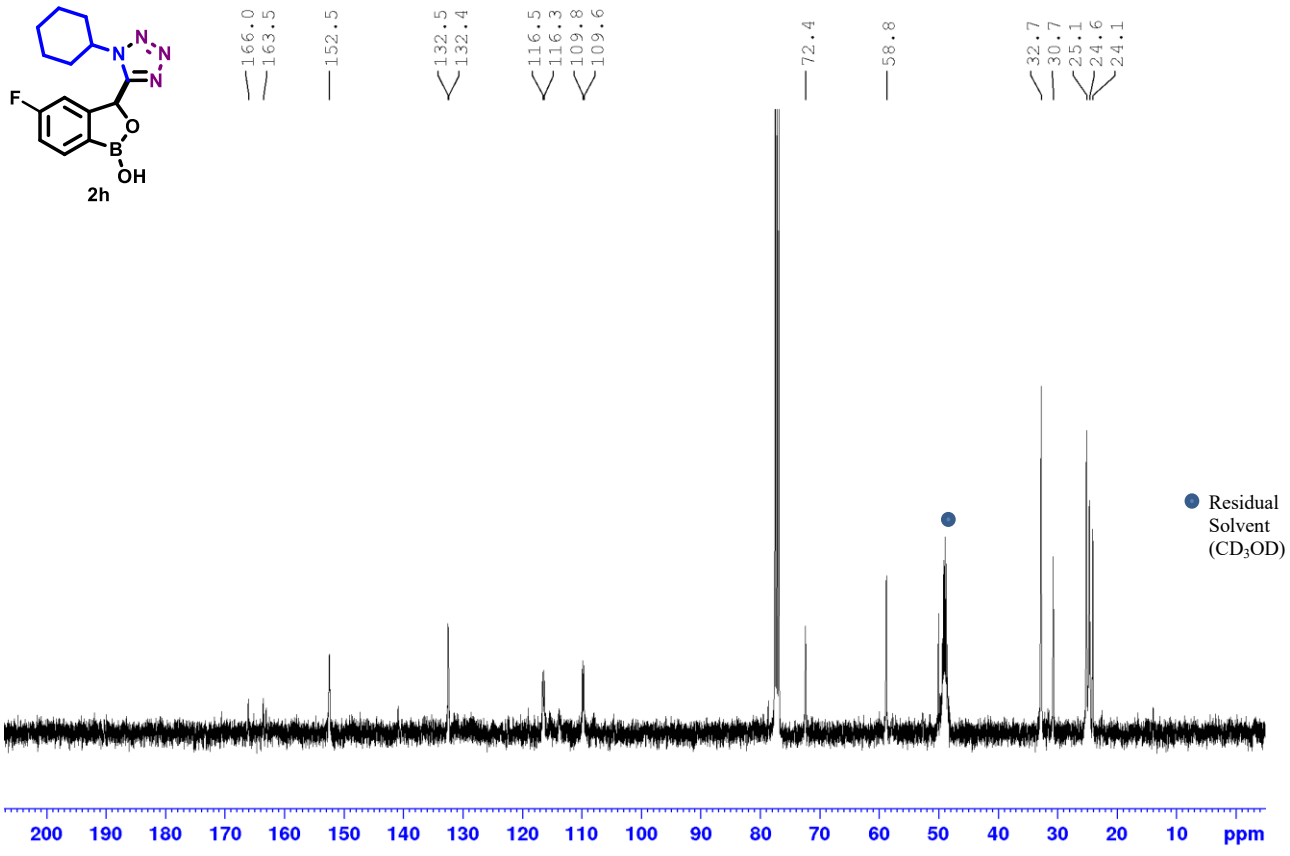


2g

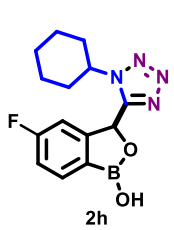
^{1}H (400 MHz, $CDCl_3$+CD_3OD):



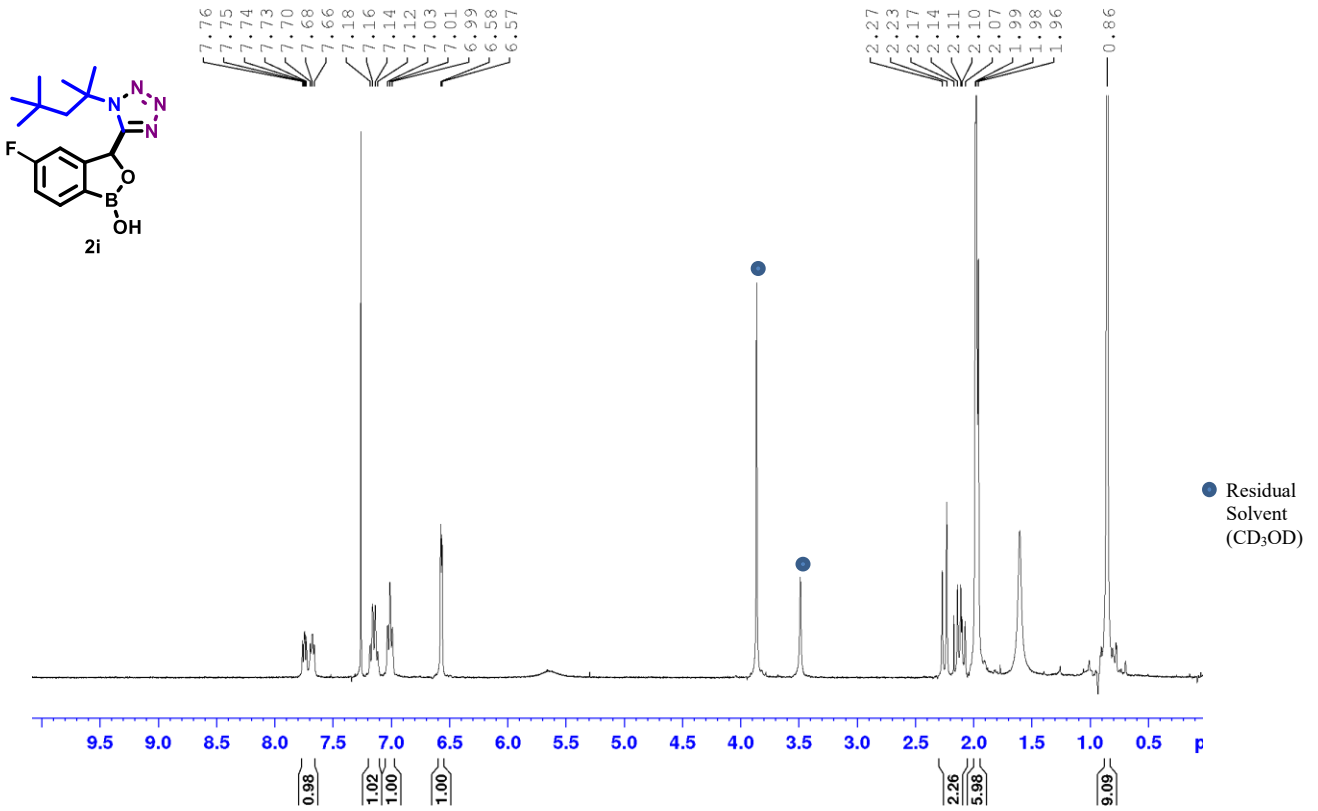
^{13}C NMR (100 MHz, $CDCl_3$):



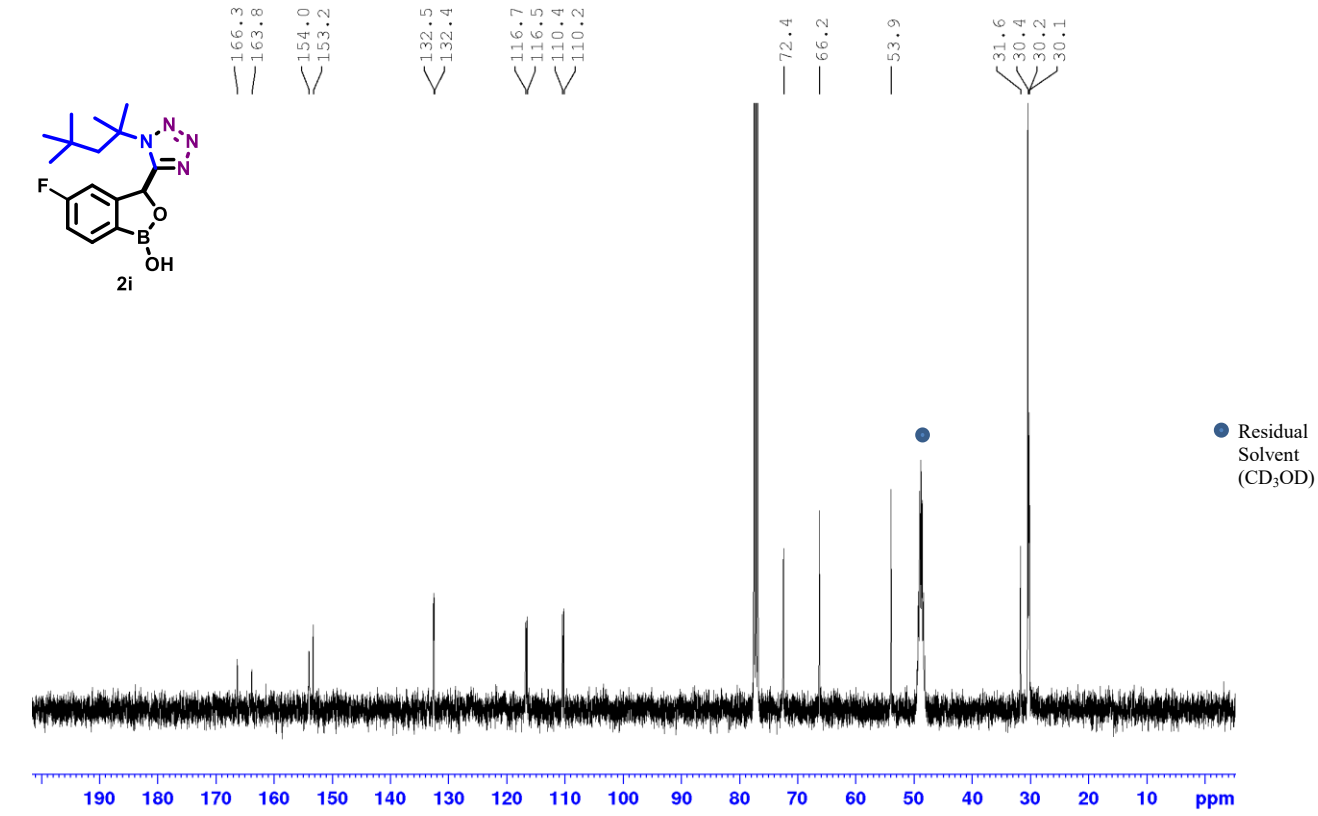
^{19}F (376 MHz, CDCl3+CD3OD):



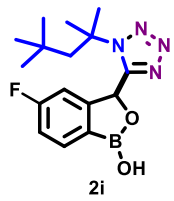
^{1}H NMR (400 MHz, $CDCl_3$+CD_3OD):



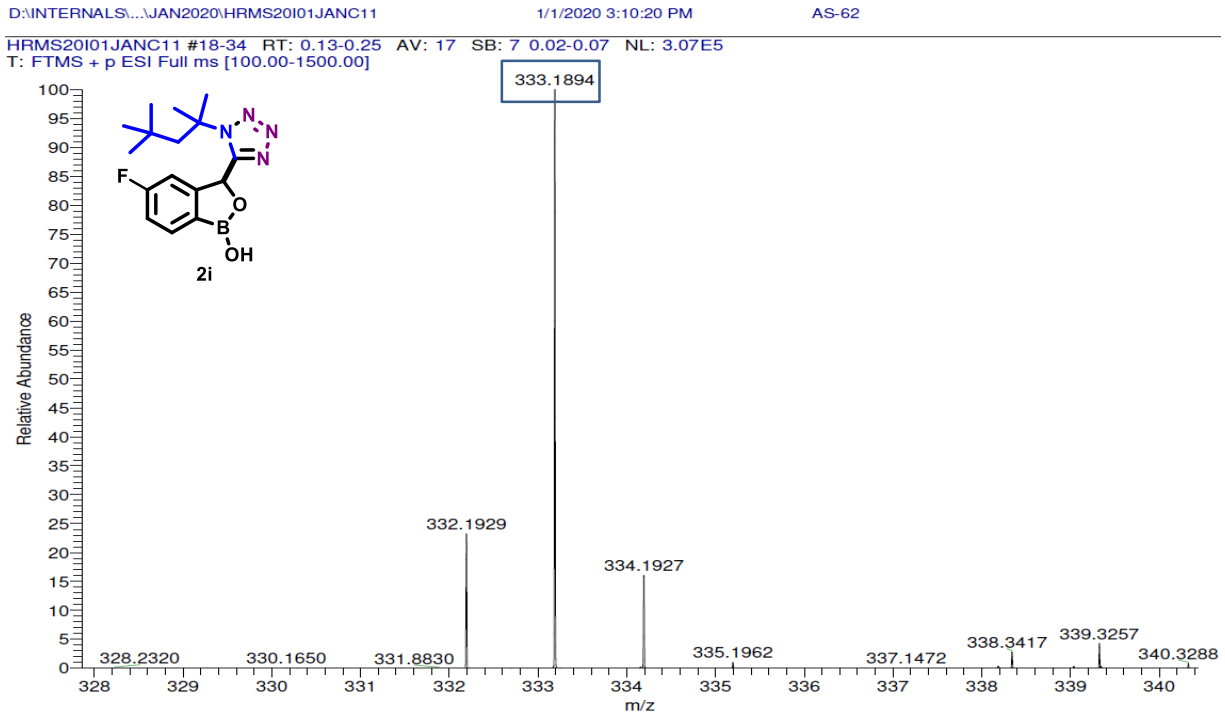
^{13}C NMR (100 MHz, $CDCl_3$+CD_3OD):



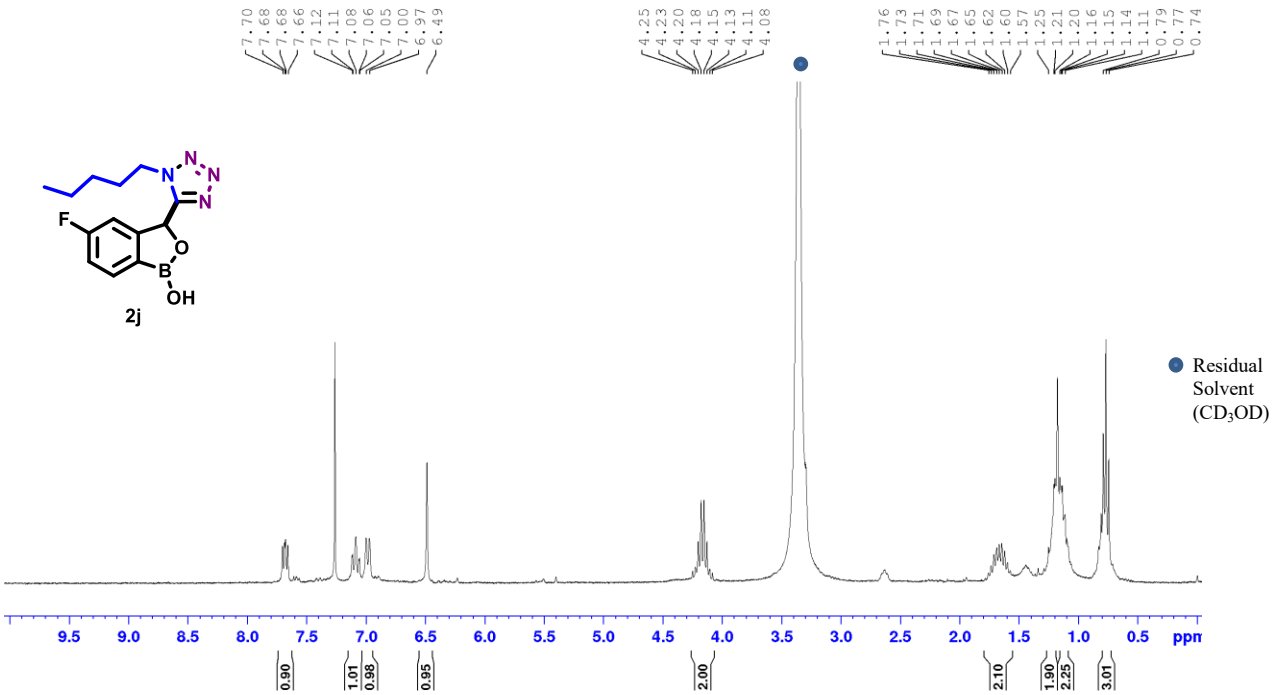
^{19}F (282 MHz, $CDCl_3$+CD_3OD):



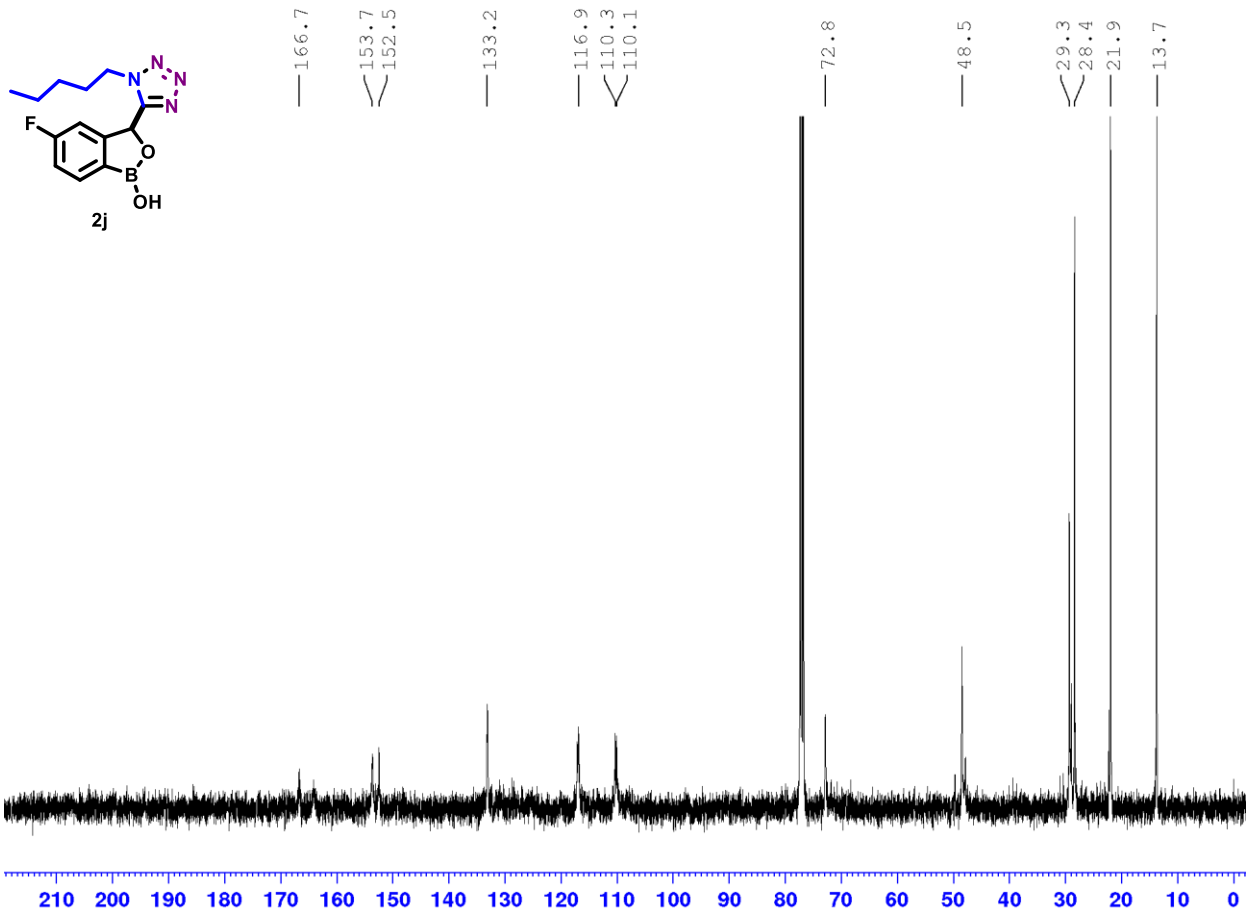
2i



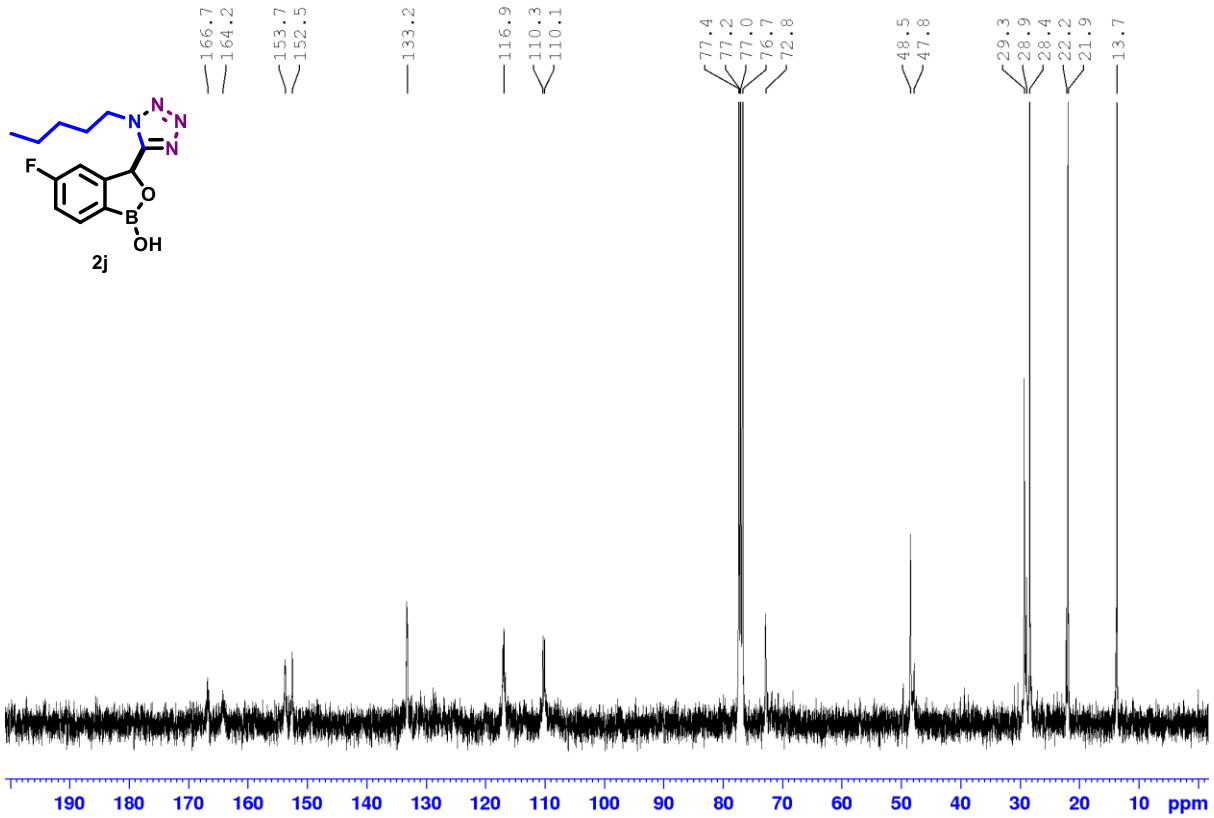
^{1}H NMR (300 MHz, $CDCl_3$+CD_3OD):



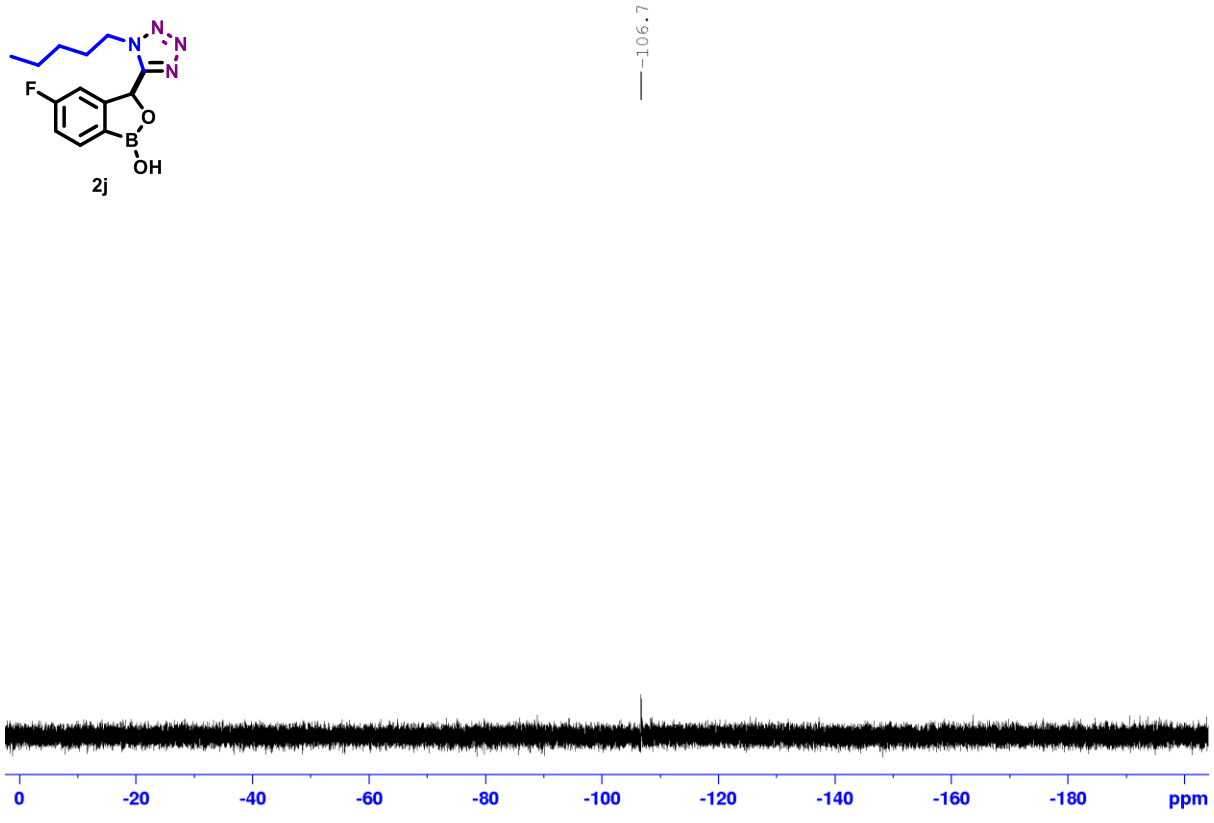
^{13}C NMR (100 MHz, $CDCl_3$):

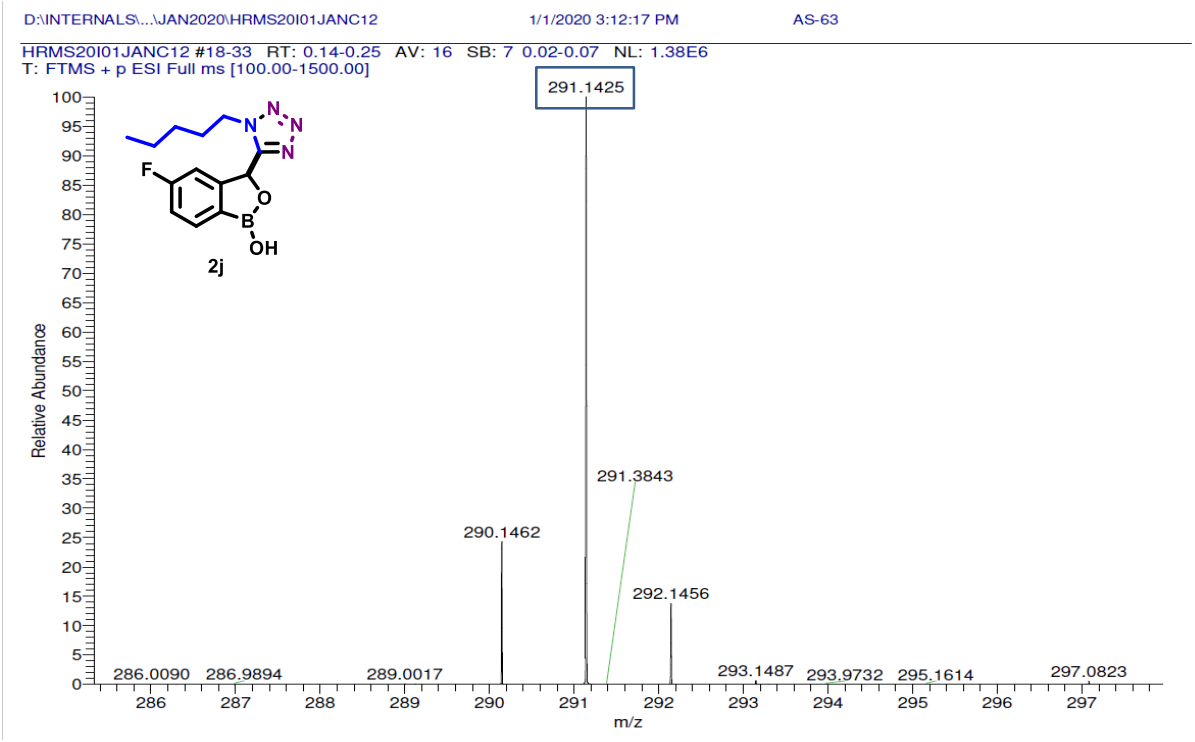


^{13}C NMR (100 MHz, $CDCl_3$):

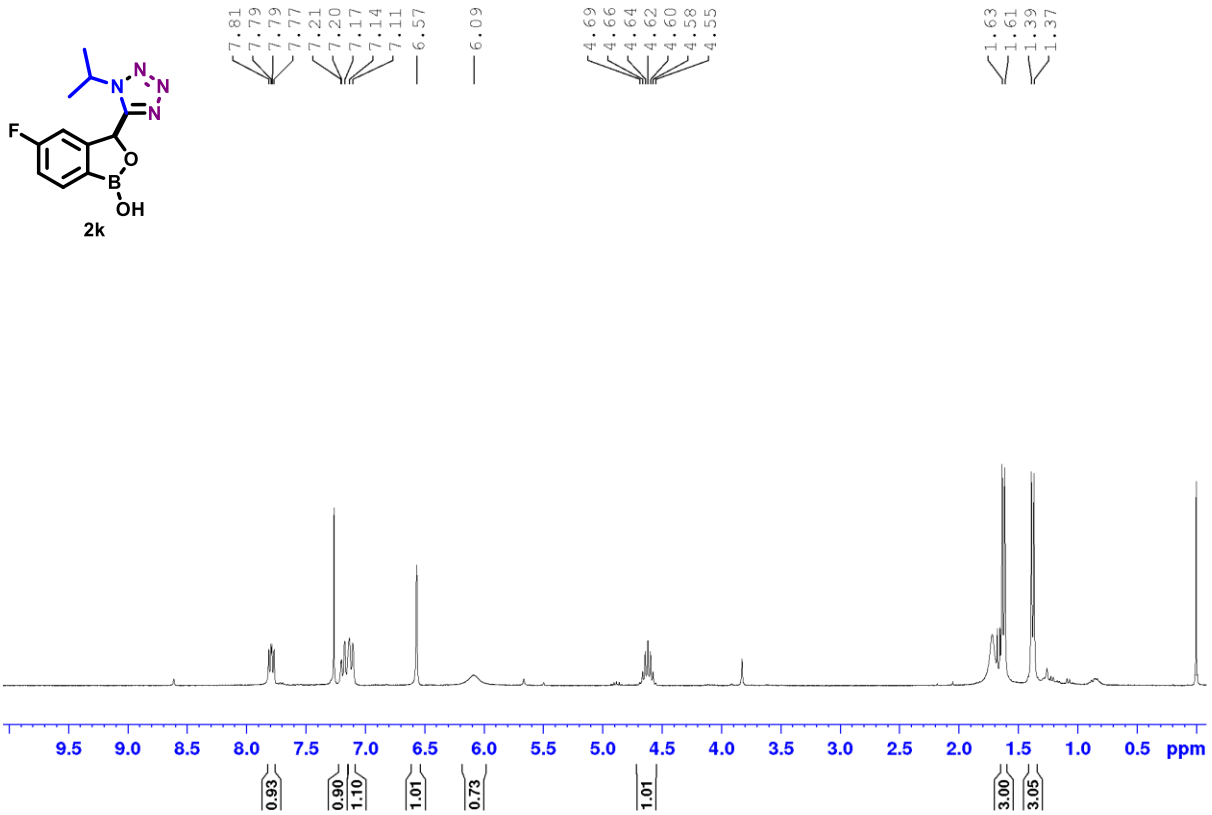


^{19}F (282 MHz, $CDCl_3$+CD_3OD):

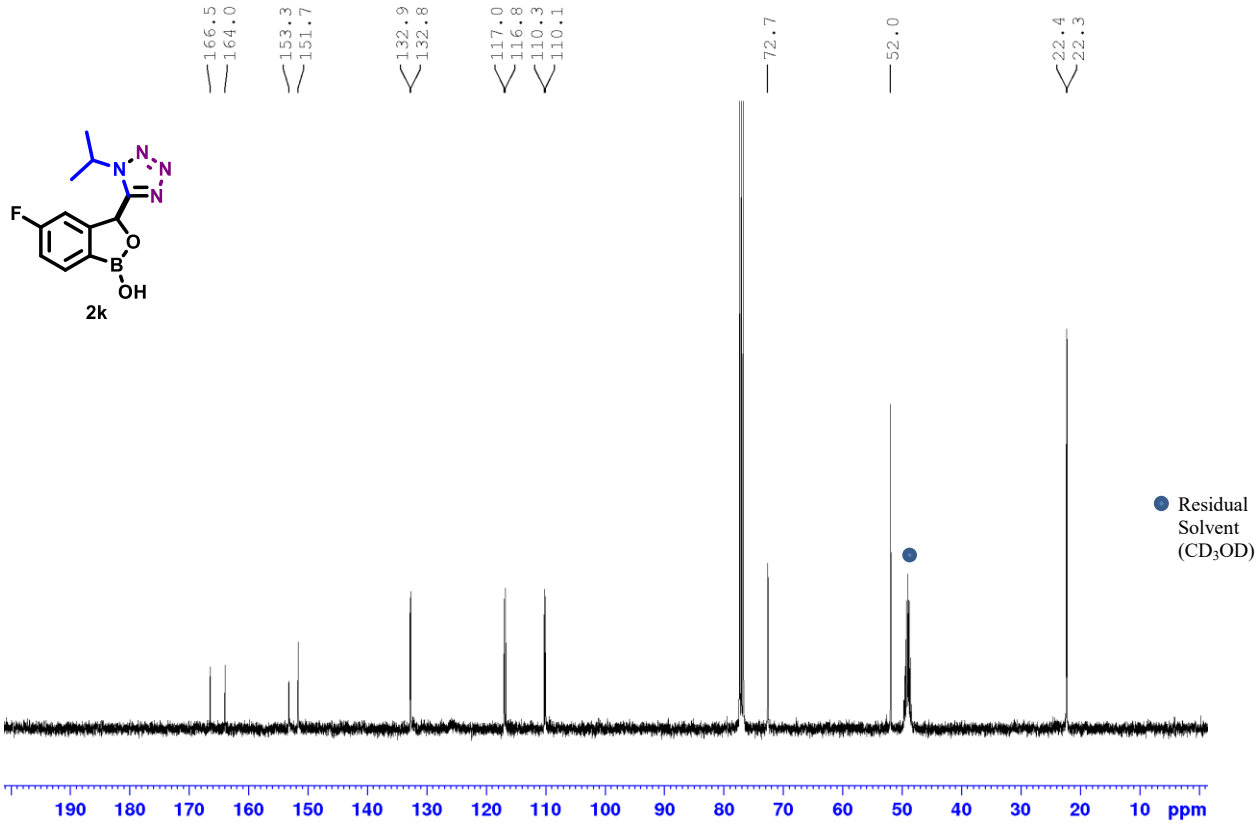




^{1}H NMR (300 MHz, $CDCl_3$+CD_3OD):

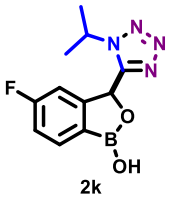


^{13}C NMR (100 MHz, $CDCl_3$+CD_3OD):

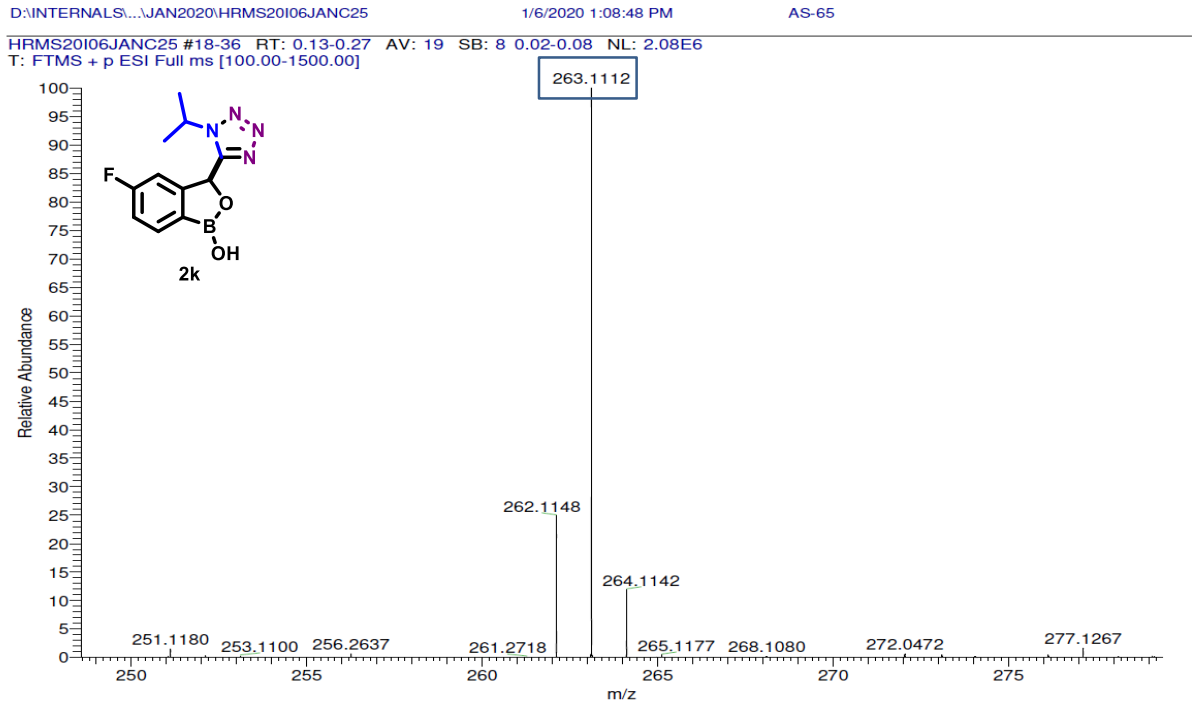


2k

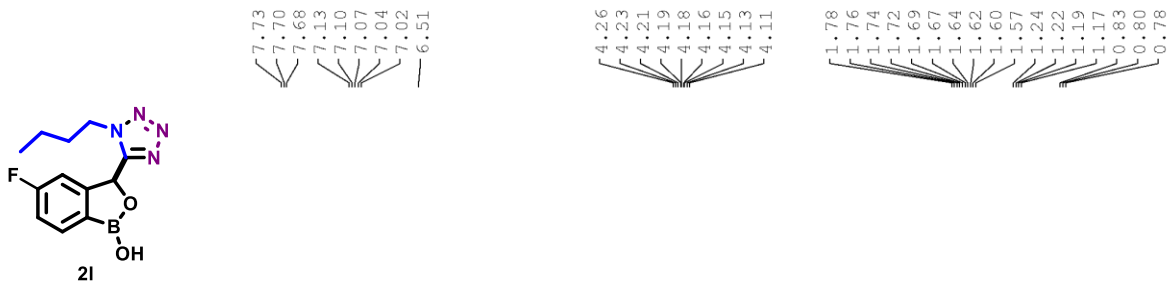
^{19}F (282 MHz, $CDCl_3$+CD_3OD):

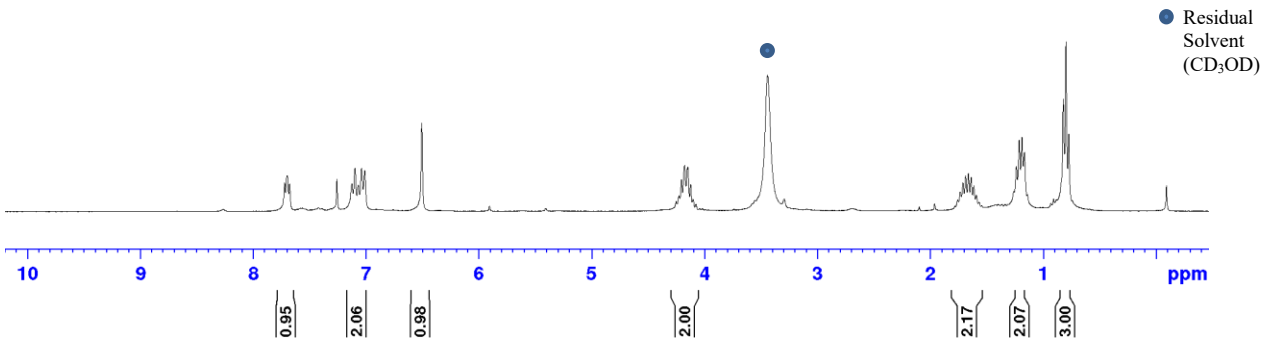


2k

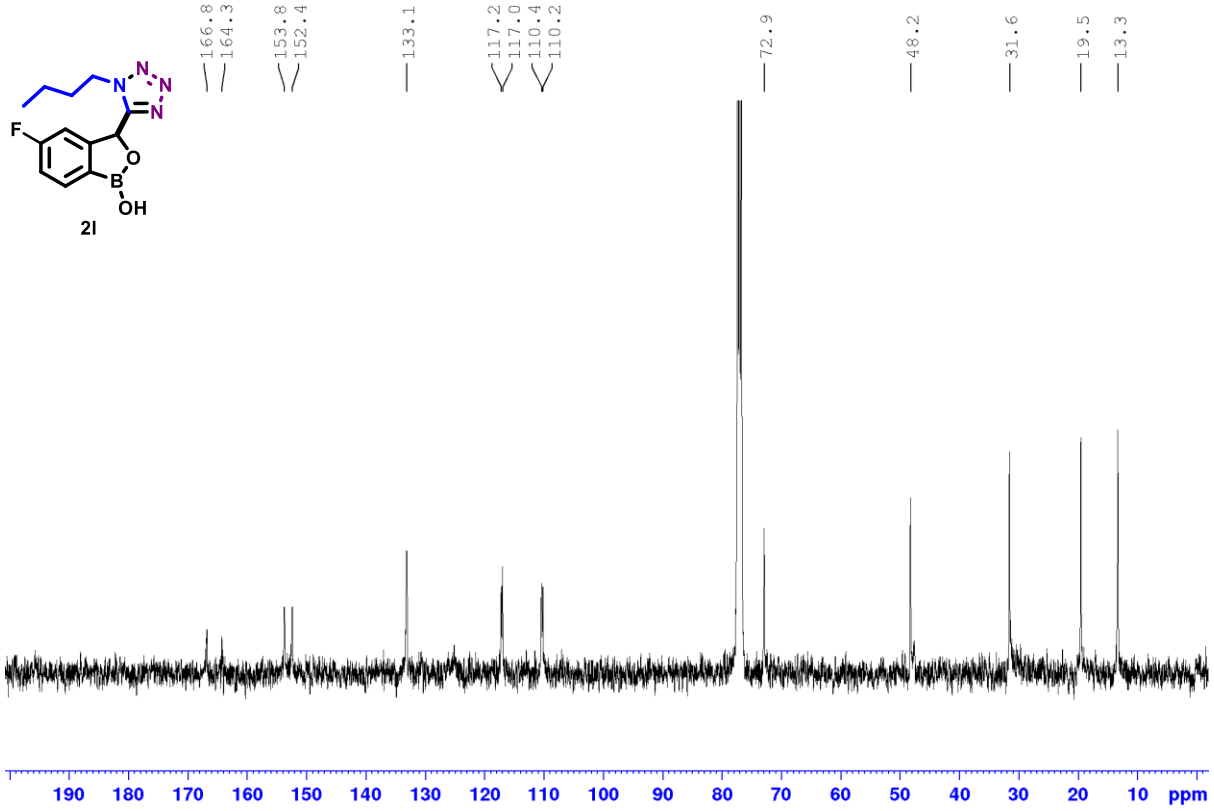


^{1}H NMR (300 MHz, $CDCl_3$+CD_3OD):

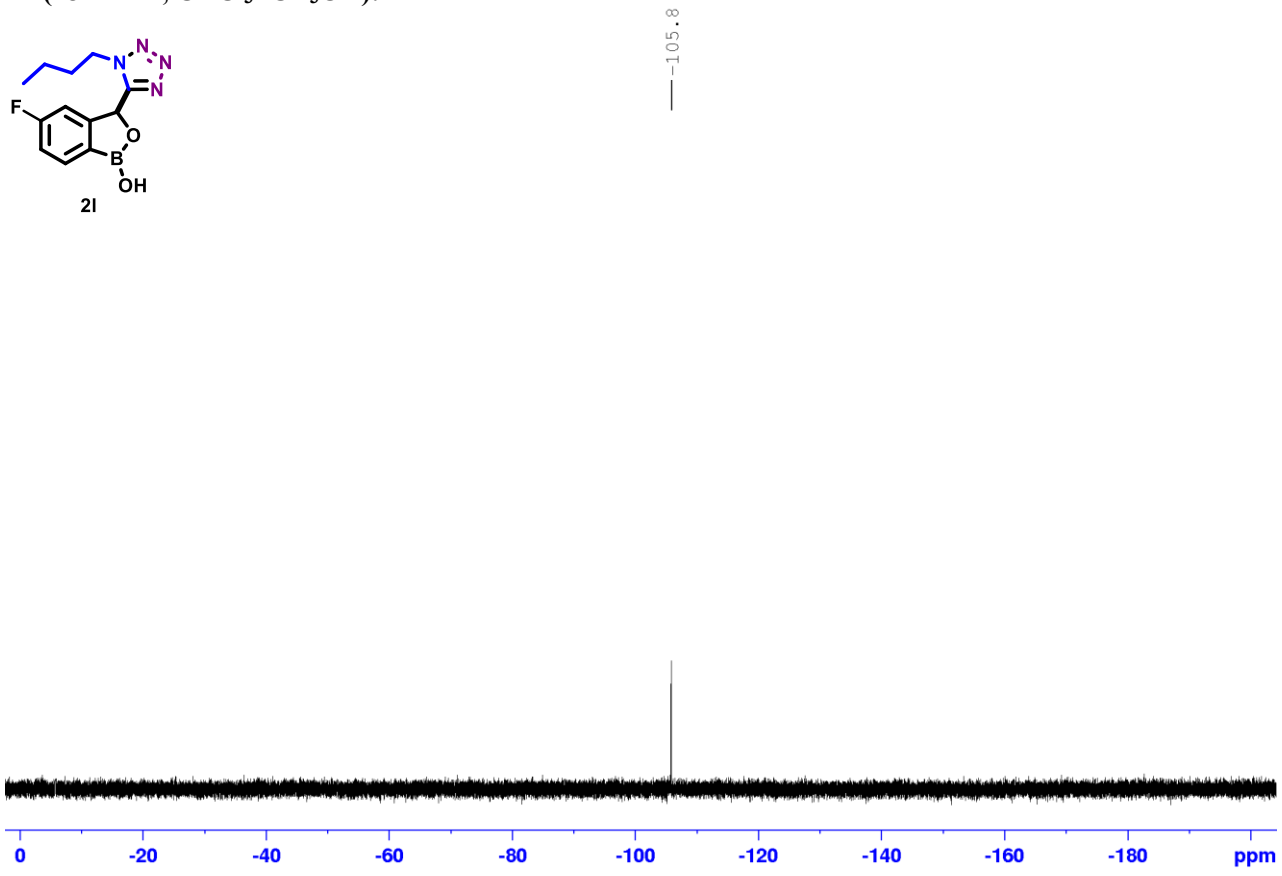


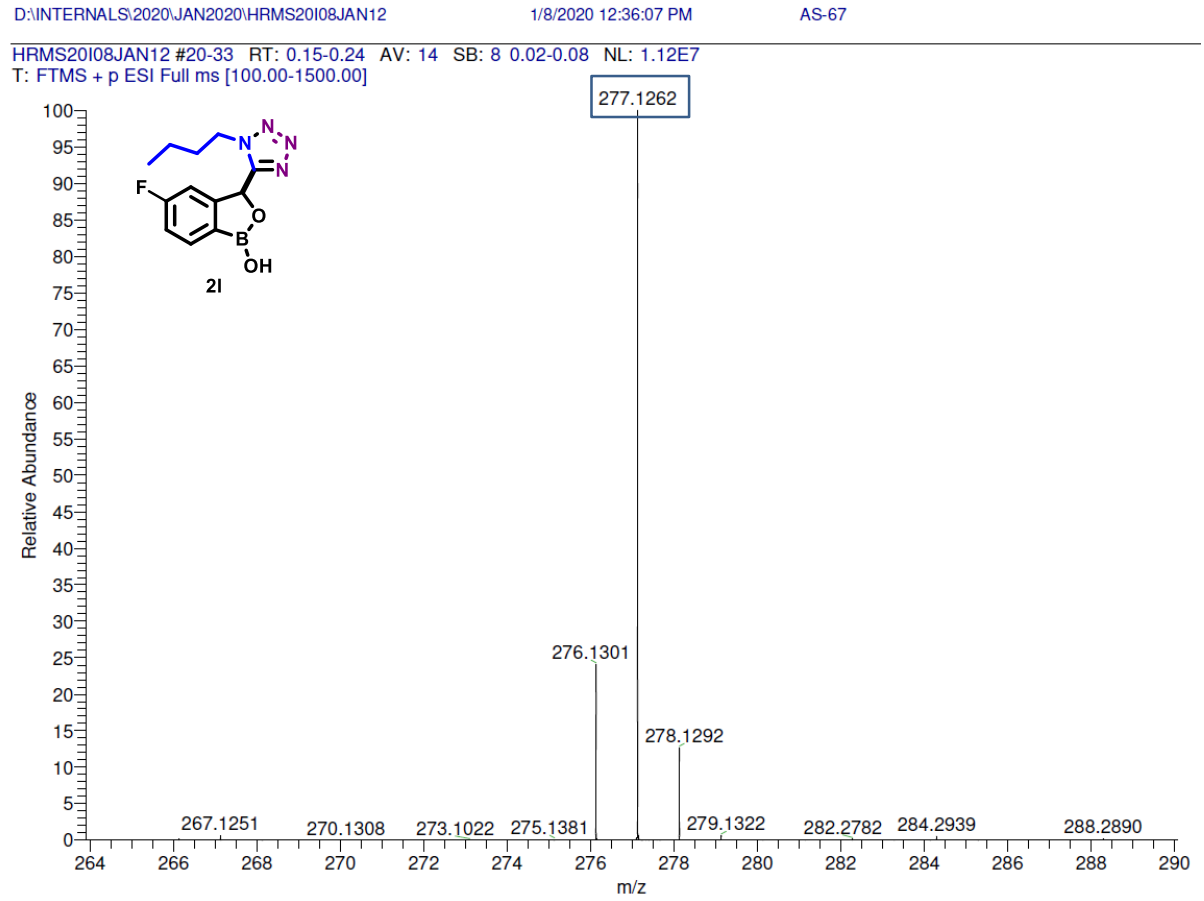


^{13}C NMR (100 MHz, $CDCl_3$):

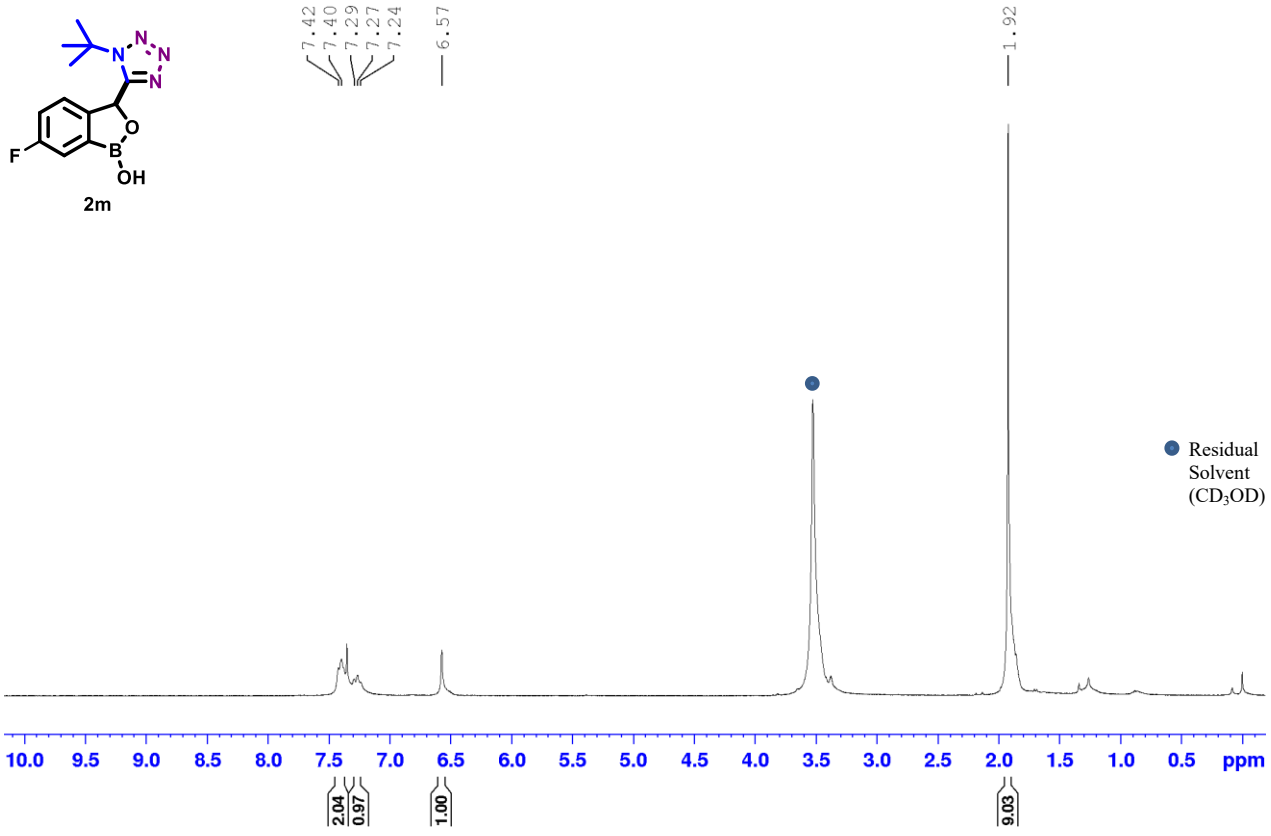


^{19}F (282 MHz, $CDCl_3$+CD_3OD):

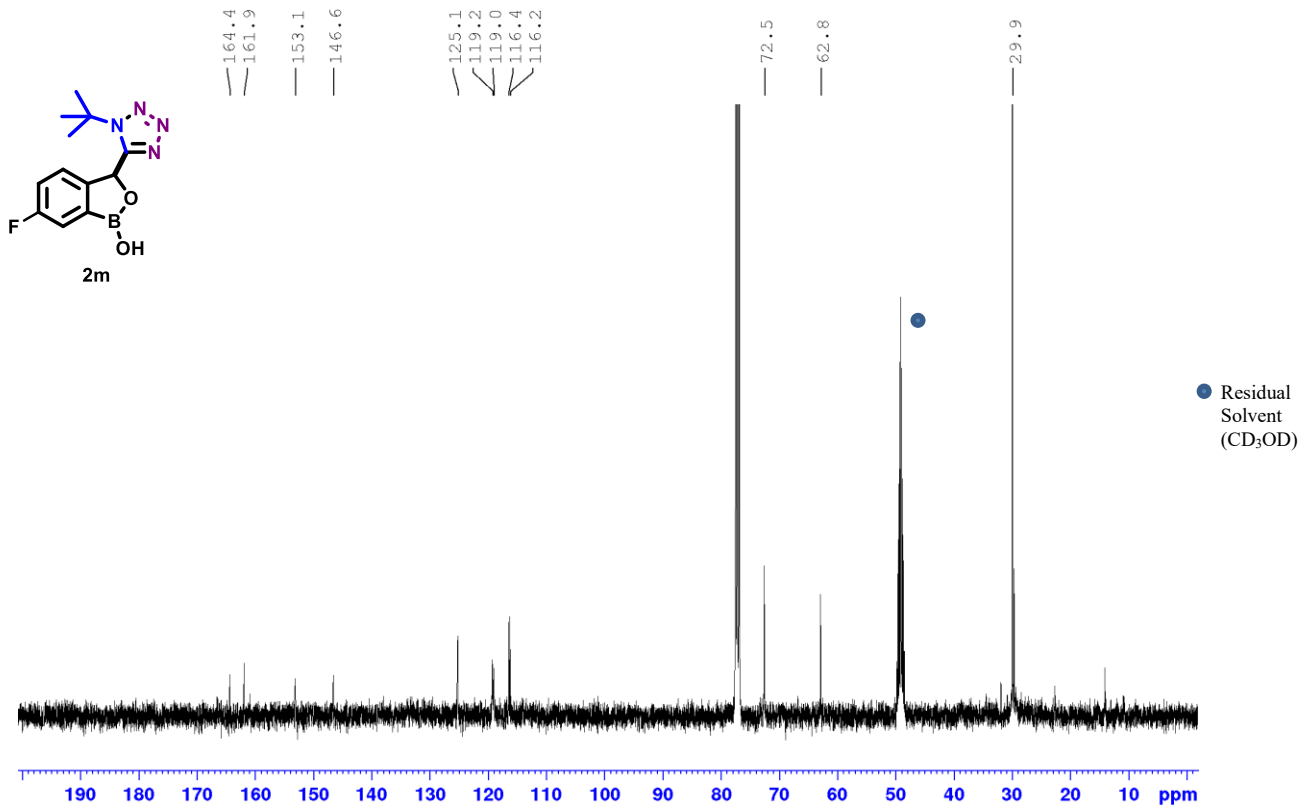




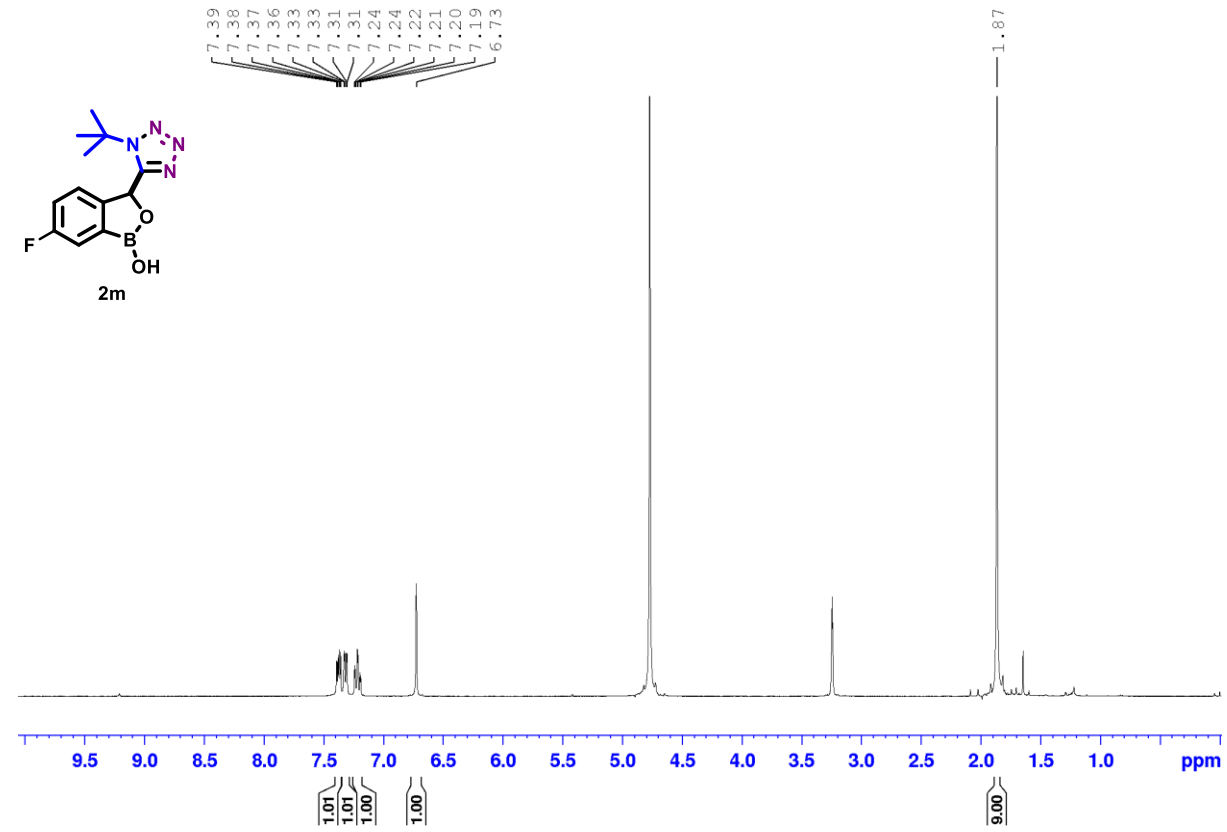
^{1}H NMR (300 MHz, $CDCl_3$+CD_3OD):



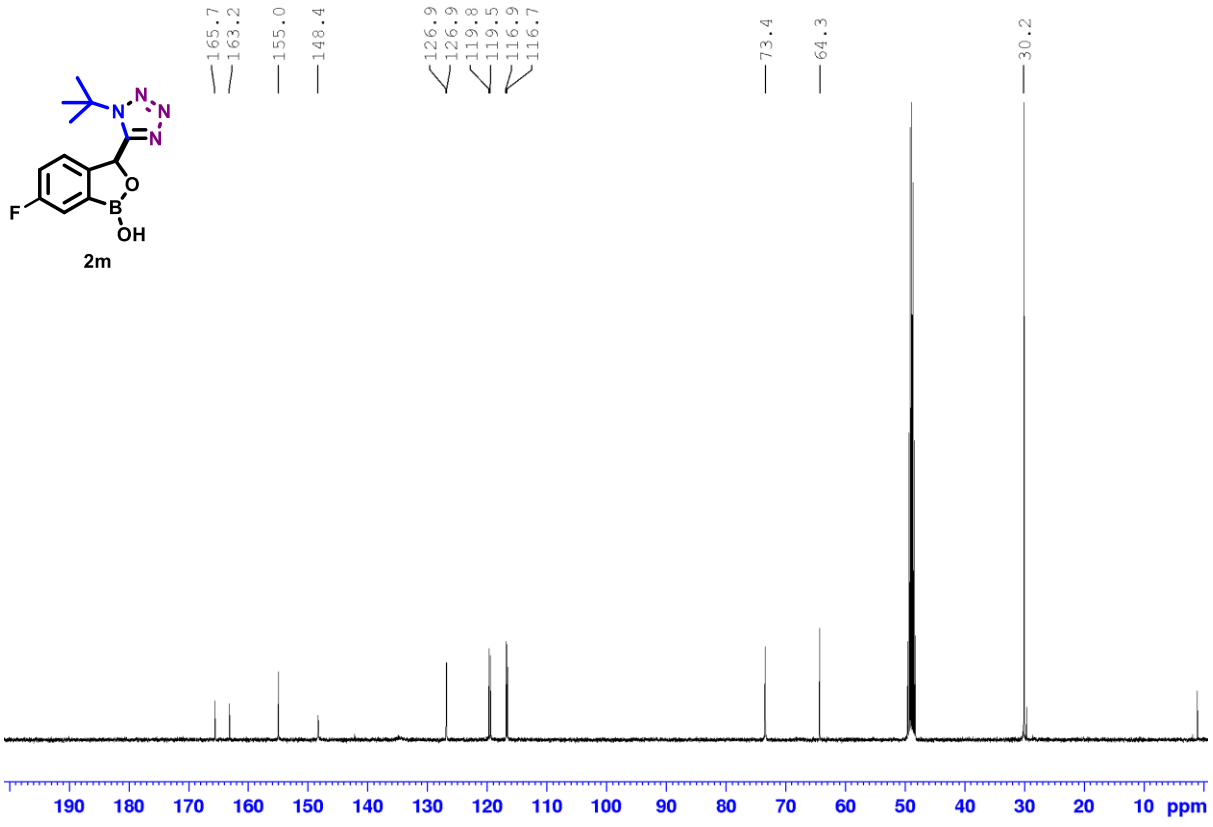
^{13}C NMR (100 MHz, $CDCl_3$+CD_3OD):



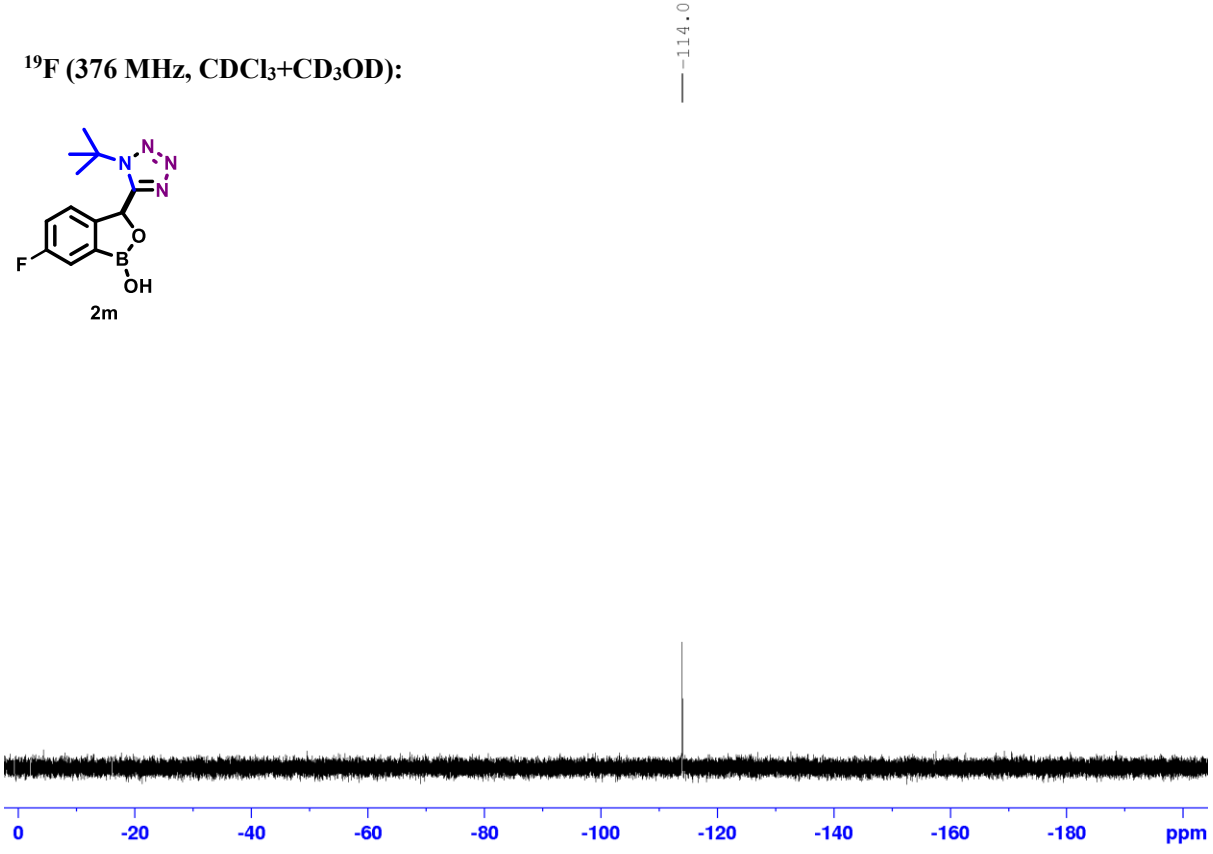
^{1}H NMR (400 MHz, CD_3OD):

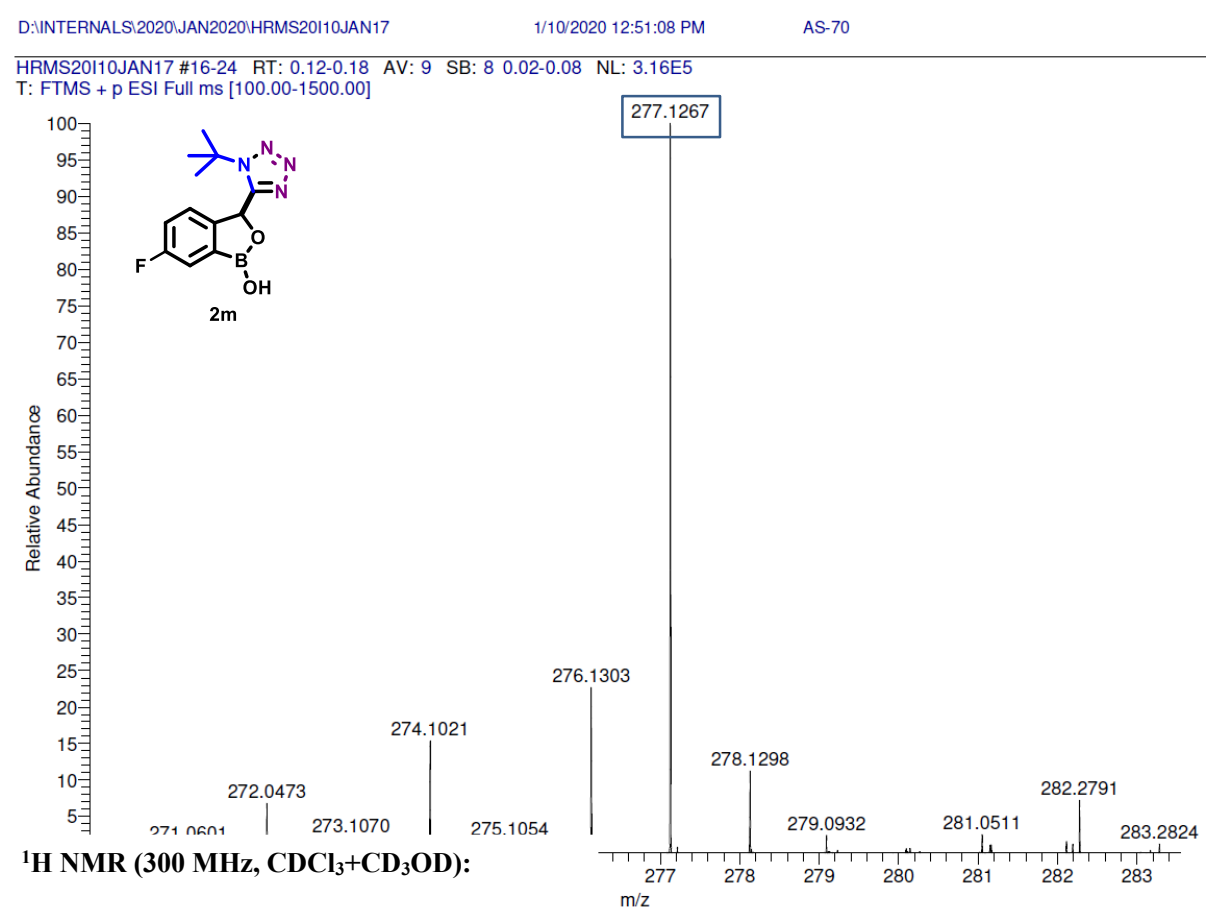


^{13}C NMR (100 MHz, CD_3OD):

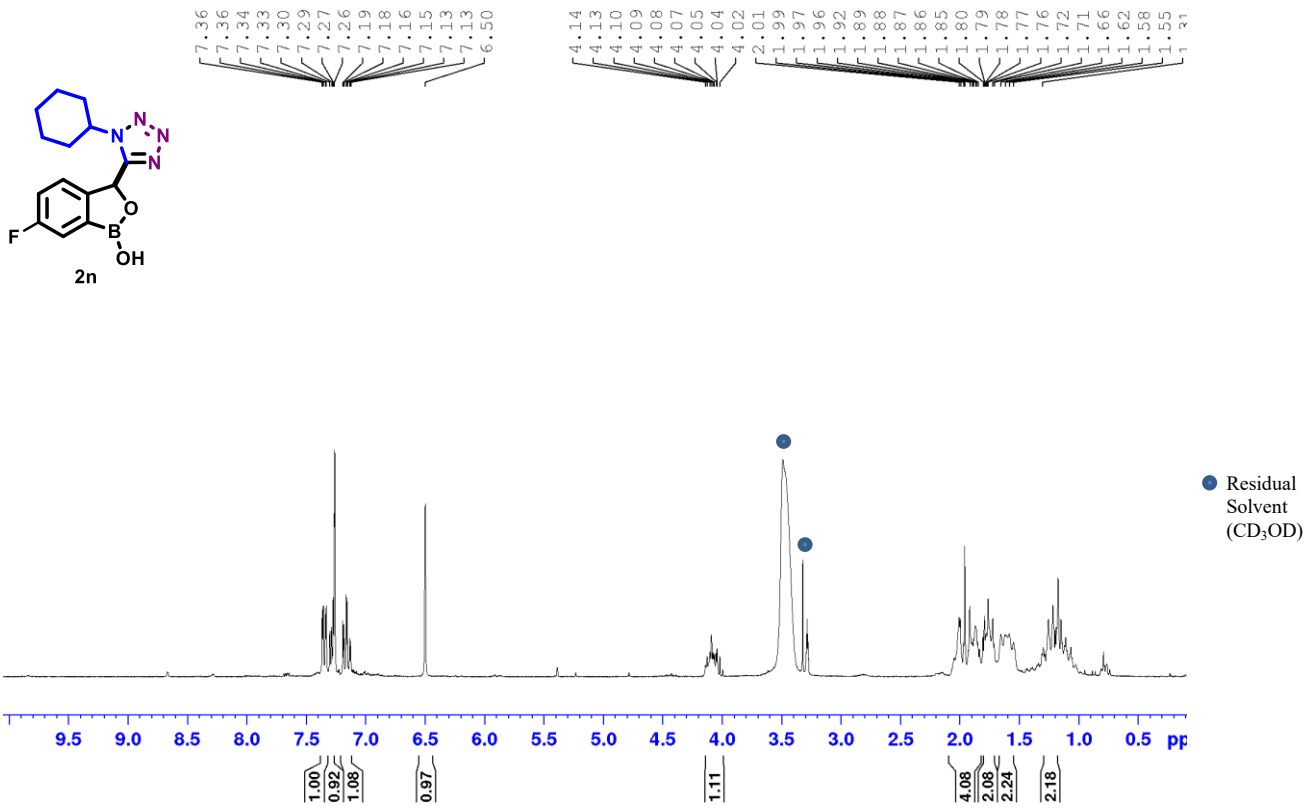


^{19}F (376 MHz, $CDCl_3$+CD_3OD):

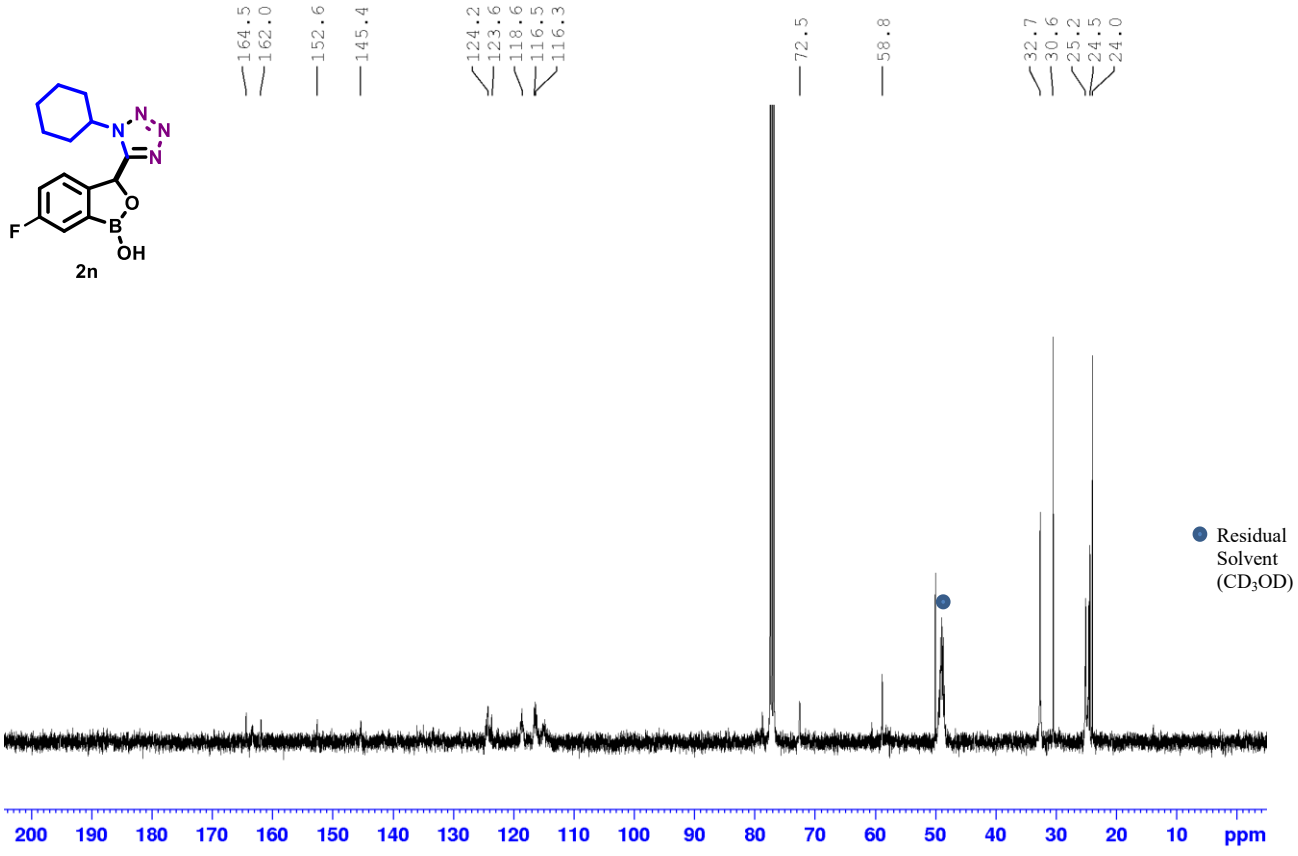




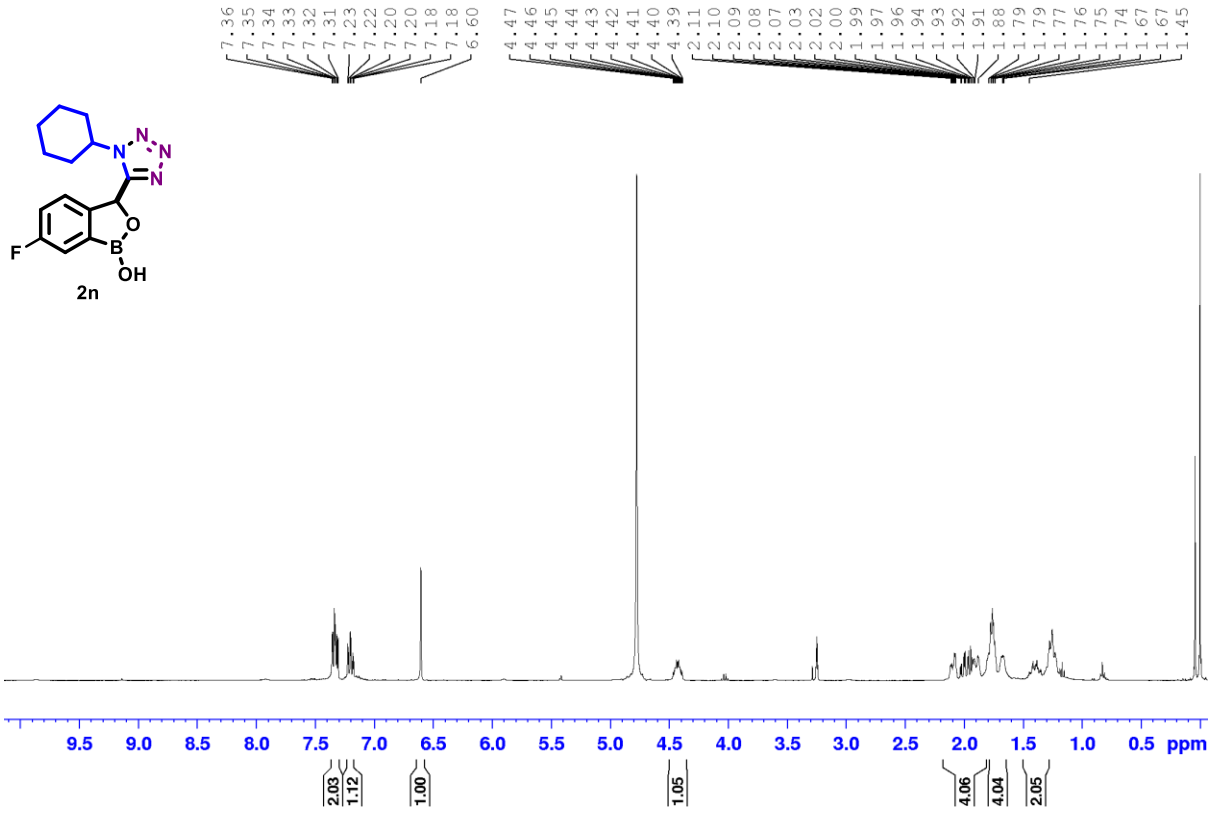
^{1}H NMR (300 MHz, $CDCl_3$+CD_3OD):



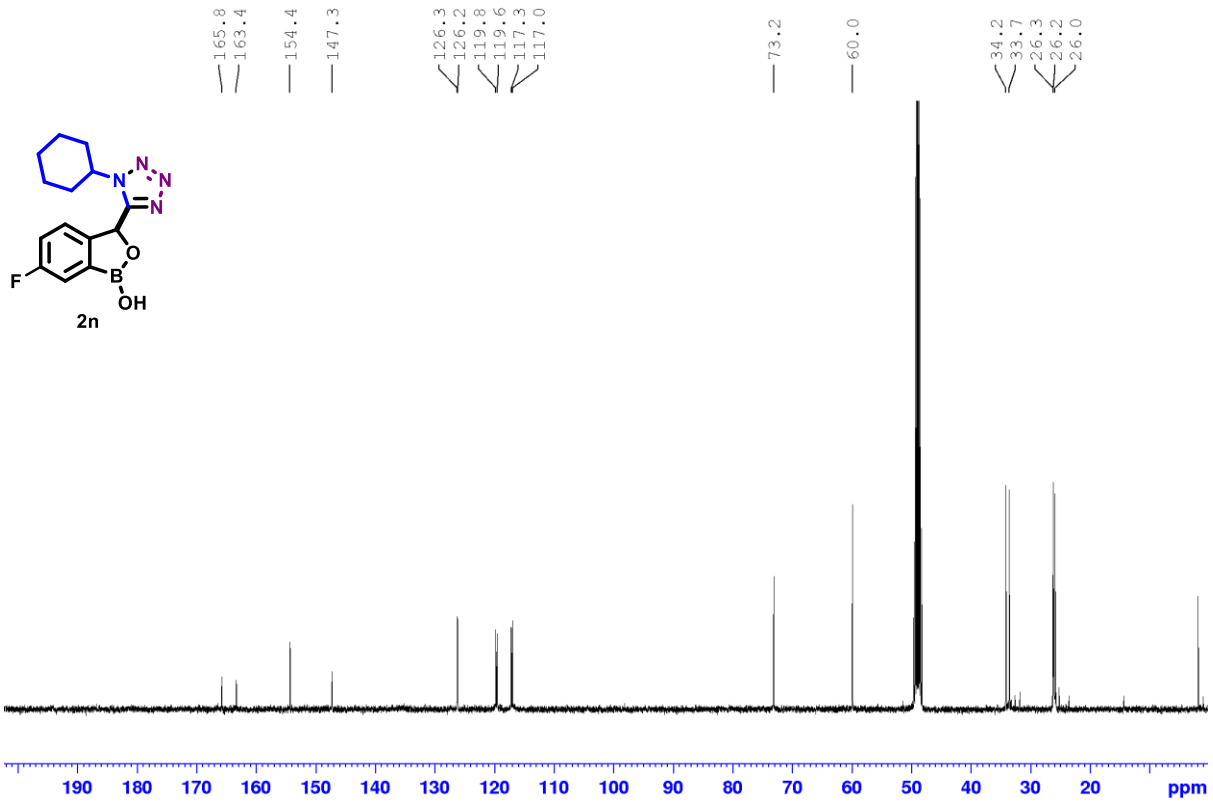
^{13}C NMR (100 MHz, $CDCl_3$+CD_3OD):



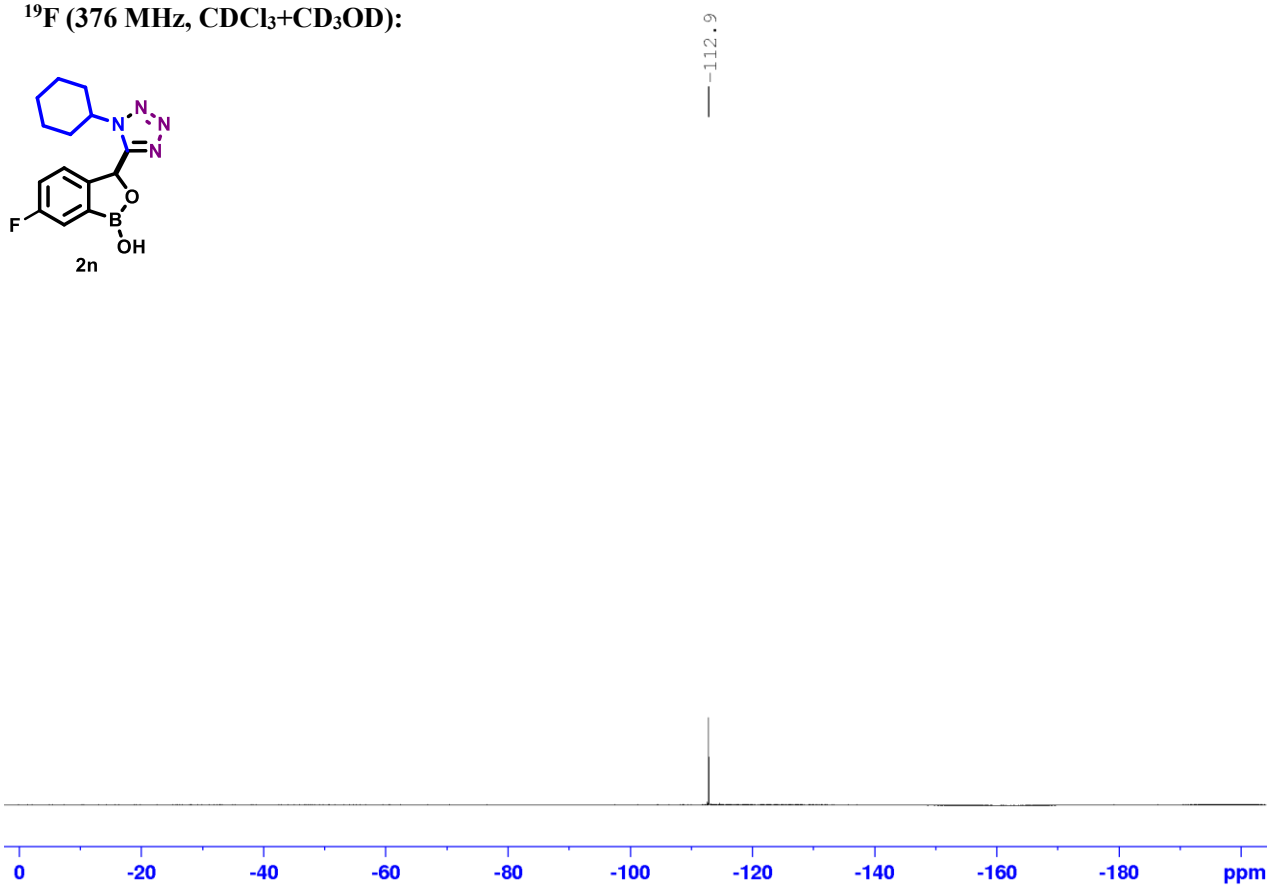
^{1}H NMR (400 MHz, CD_3OD):

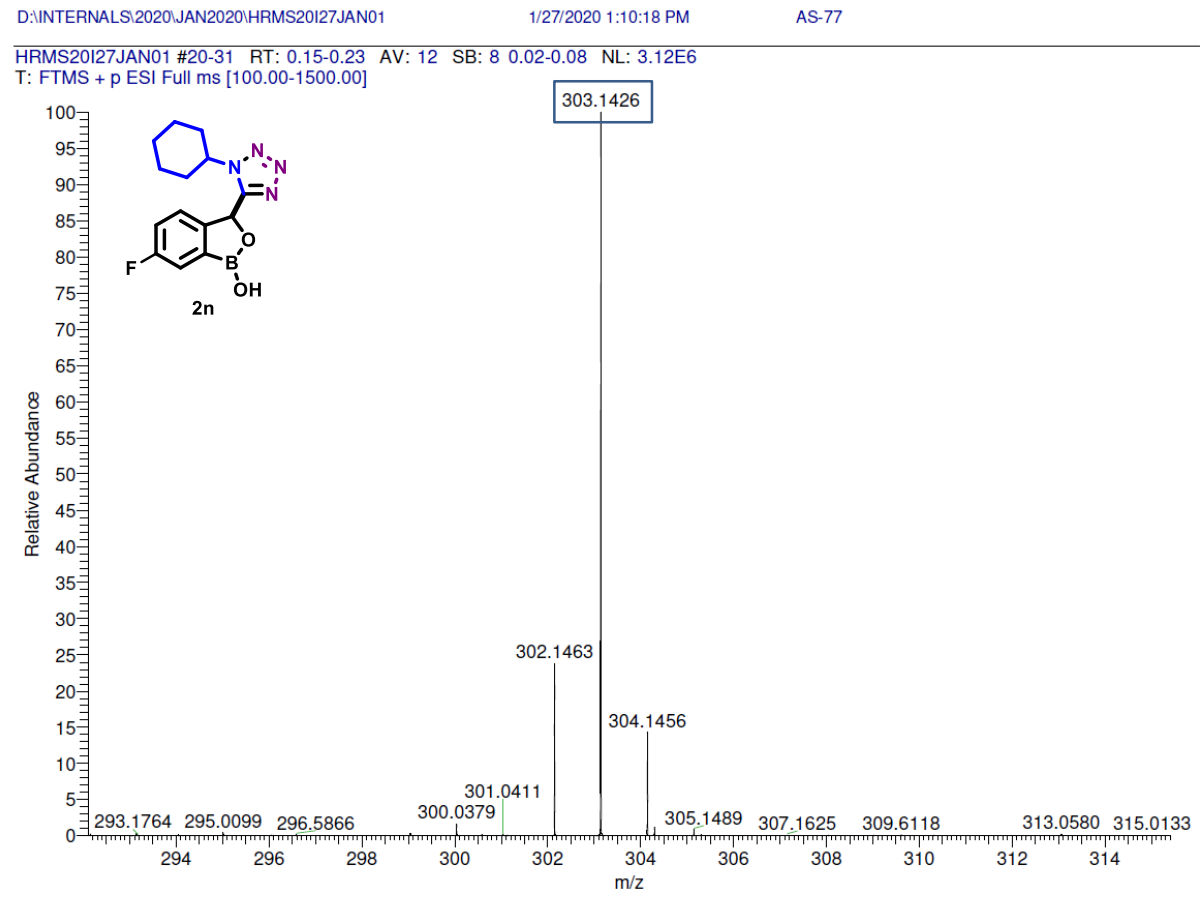


^{13}C NMR (100 MHz, CD_3OD):

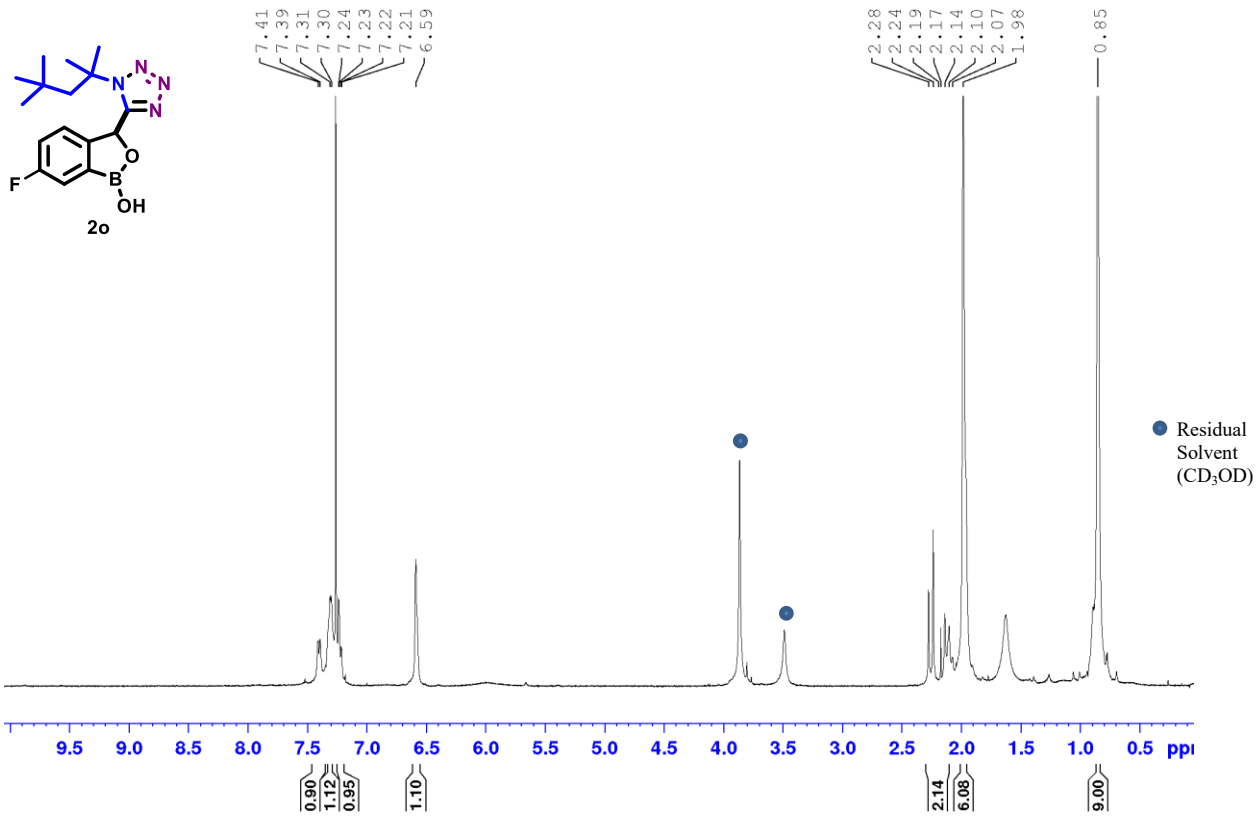


^{19}F (376 MHz, $CDCl_3$+CD_3OD):

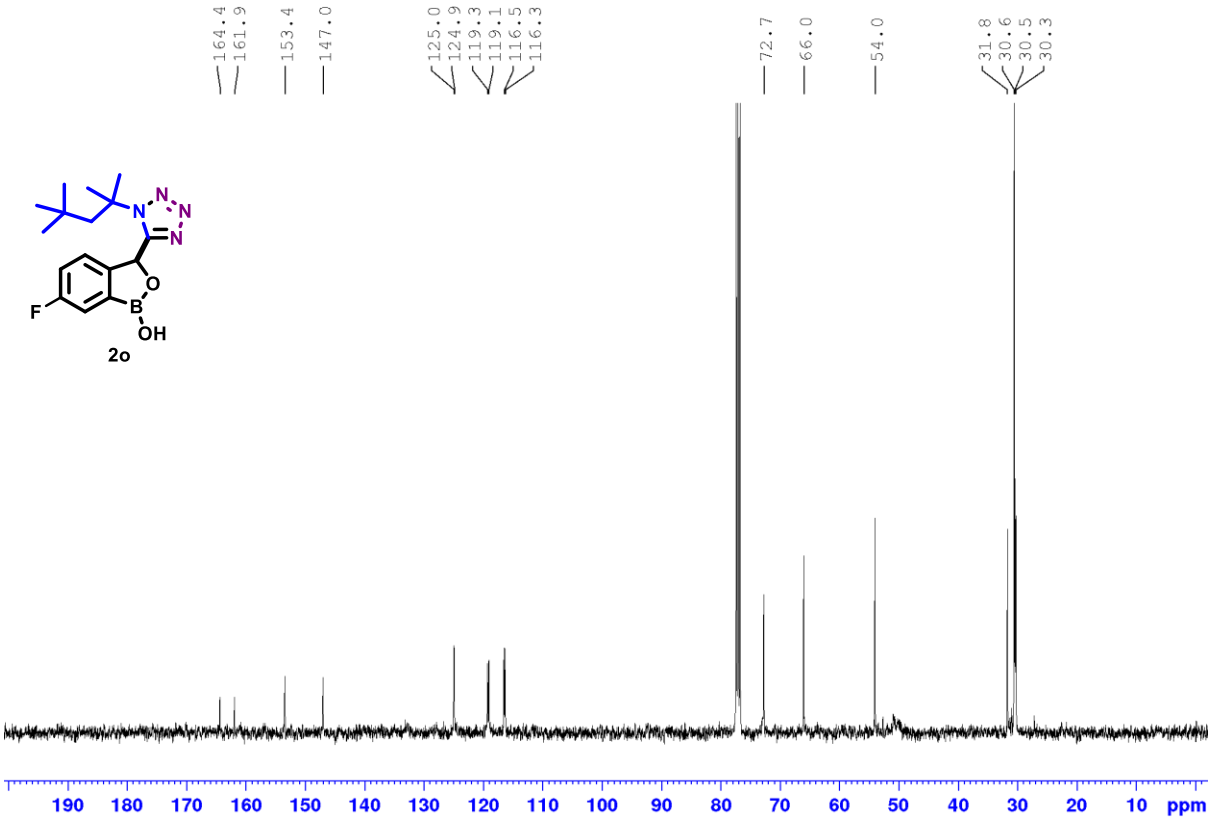




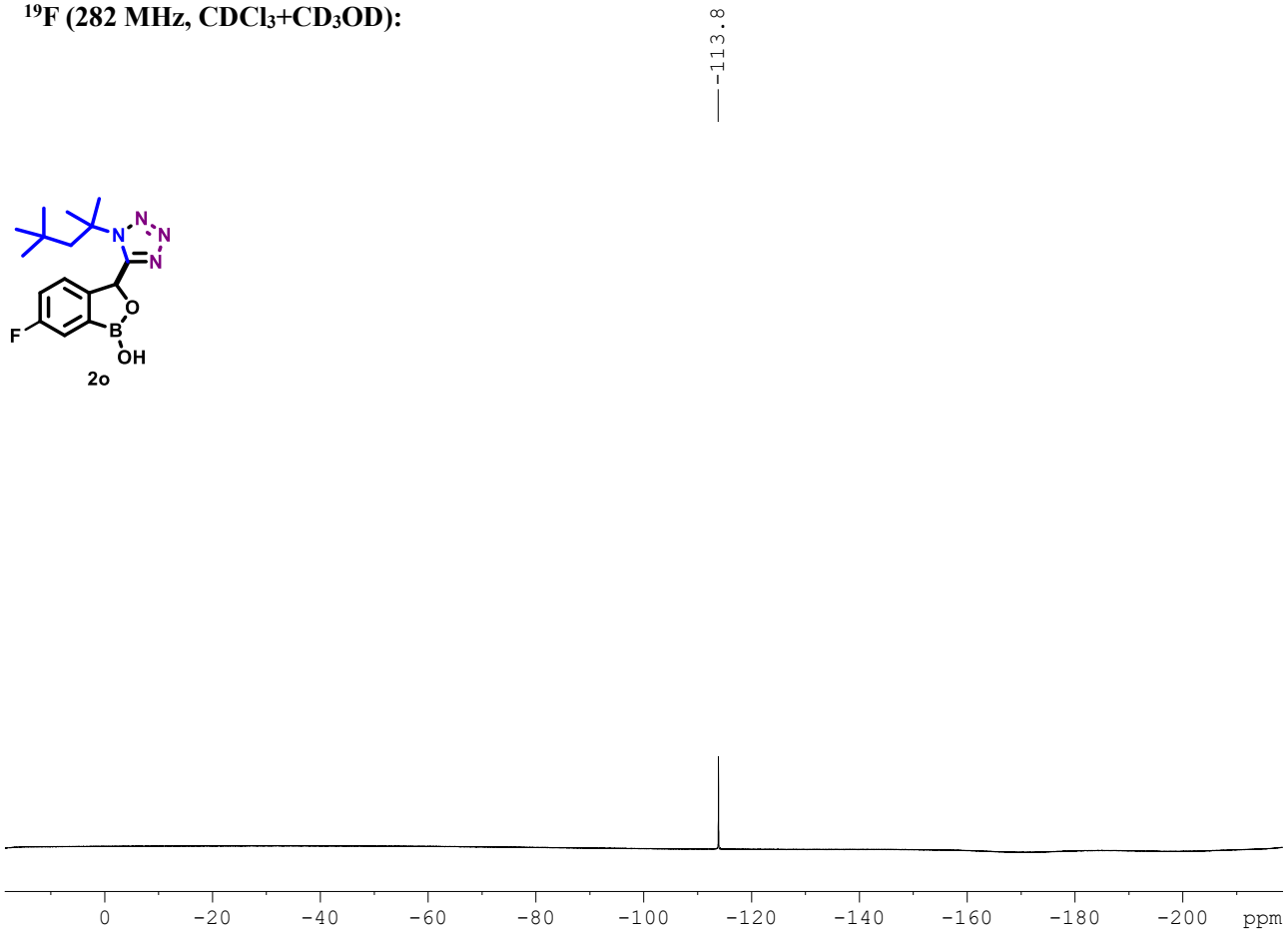
^{1}H NMR (400 MHz, $CDCl_3$+CD_3OD):

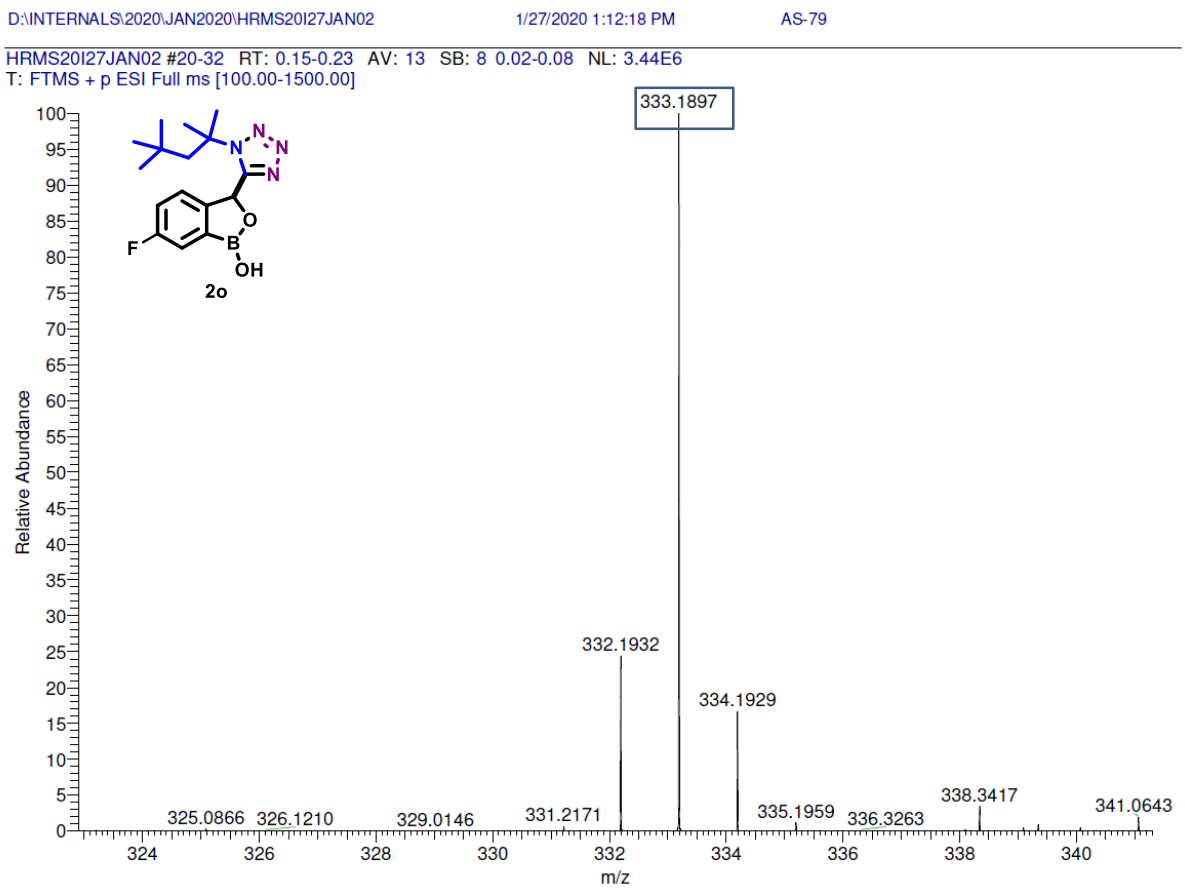


^{13}C NMR (100 MHz, $CDCl_3$):

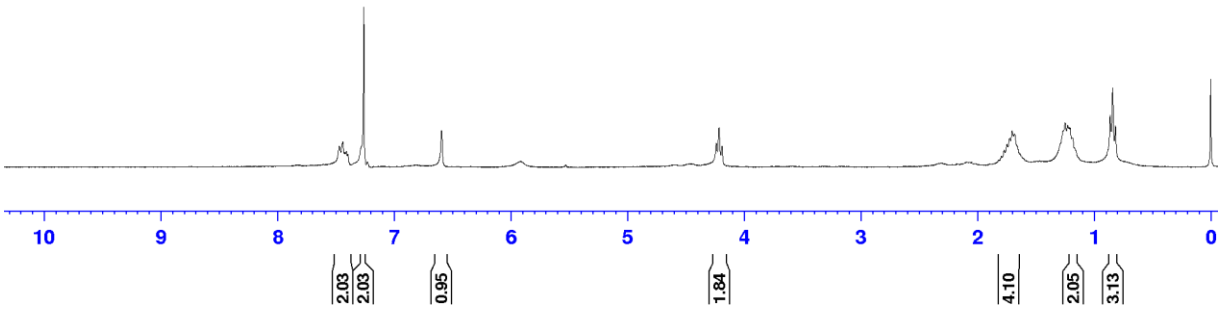


^{19}F (282 MHz, $CDCl_3$+CD_3OD):

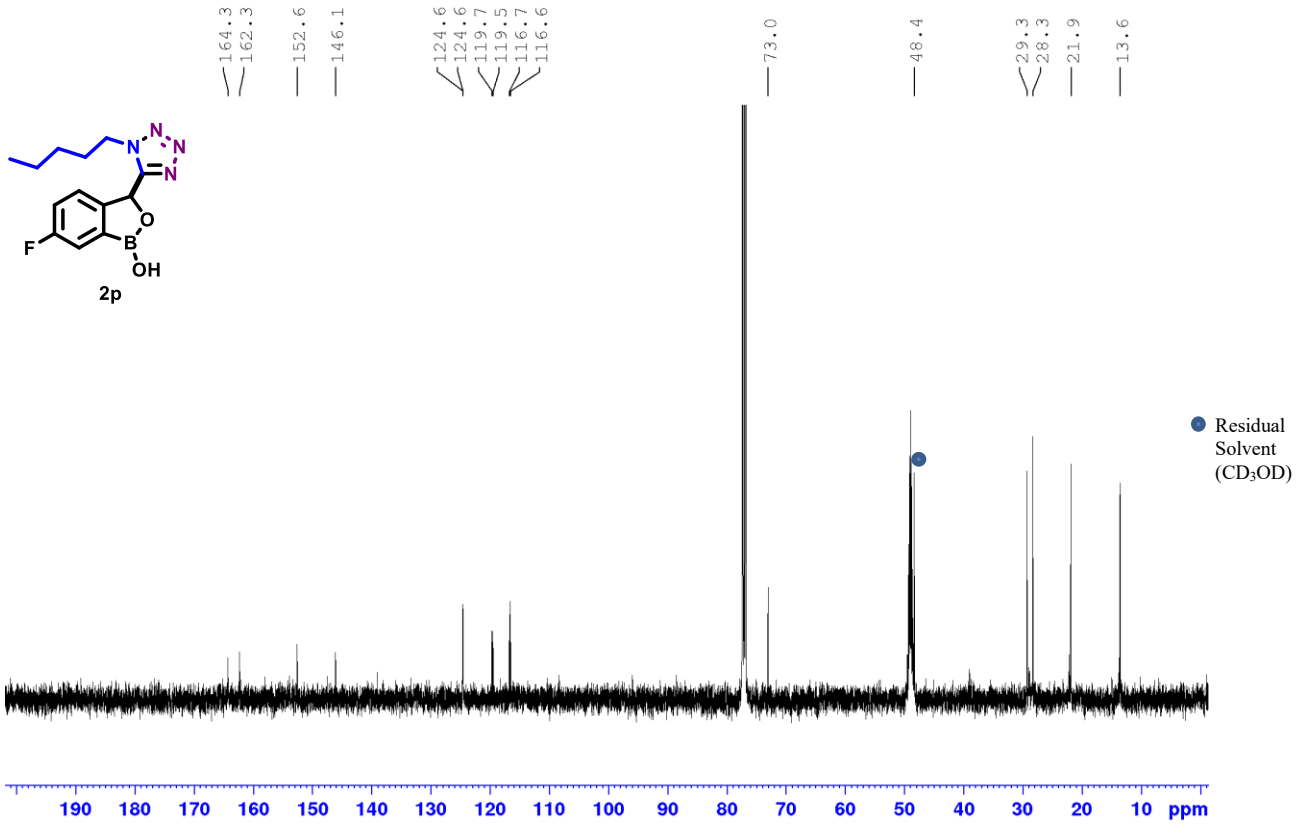




^{1}H NMR (300 MHz, $CDCl_3$):

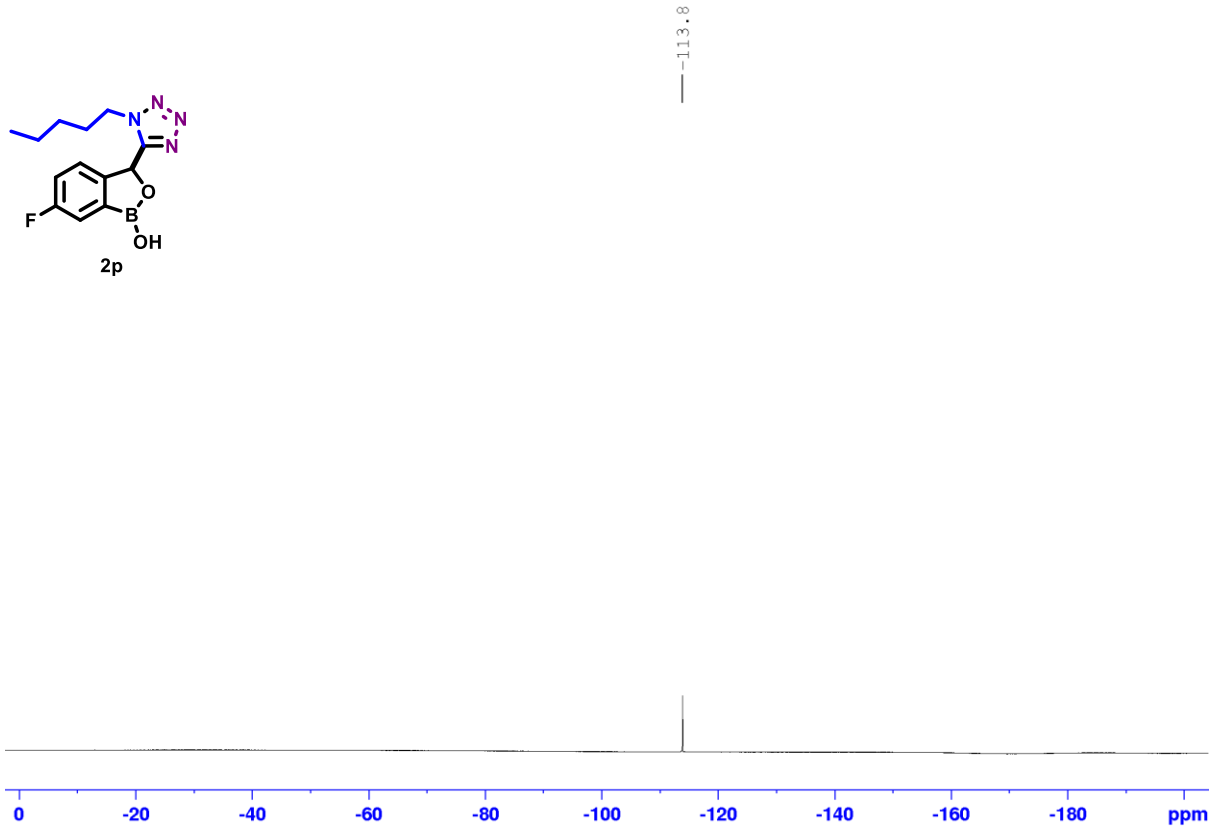


^{13}C NMR (125 MHz, $CDCl_3$+CD_3OD):



2p

^{19}F (282 MHz, $CDCl_3$+CD_3OD):

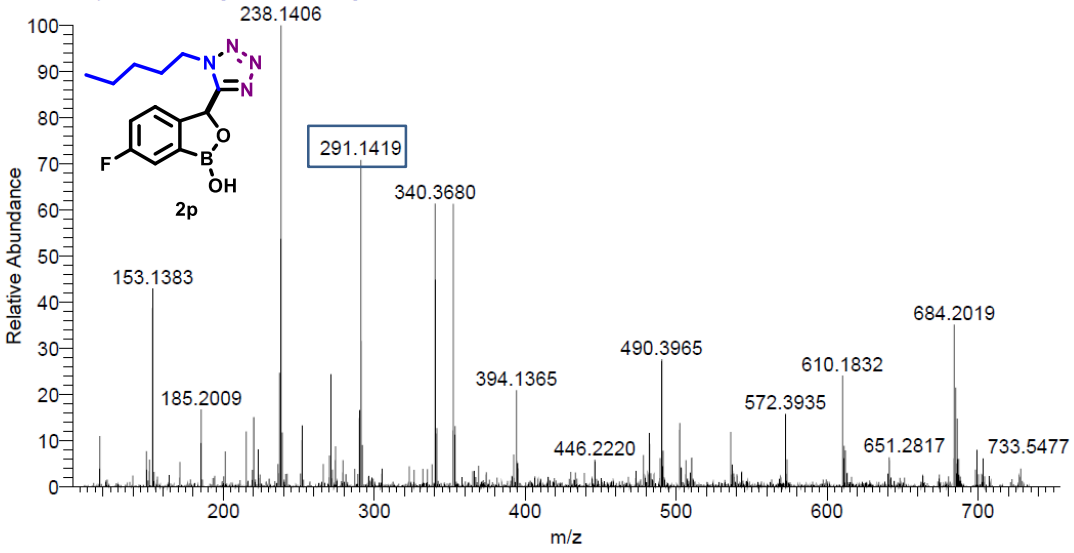


2p

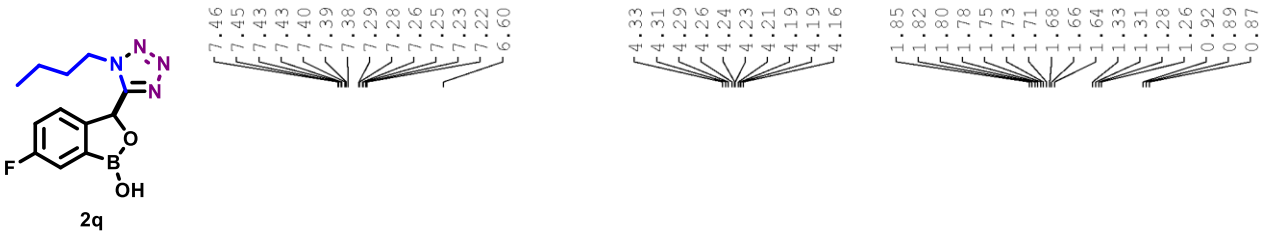
SAIF [HRMS Report]

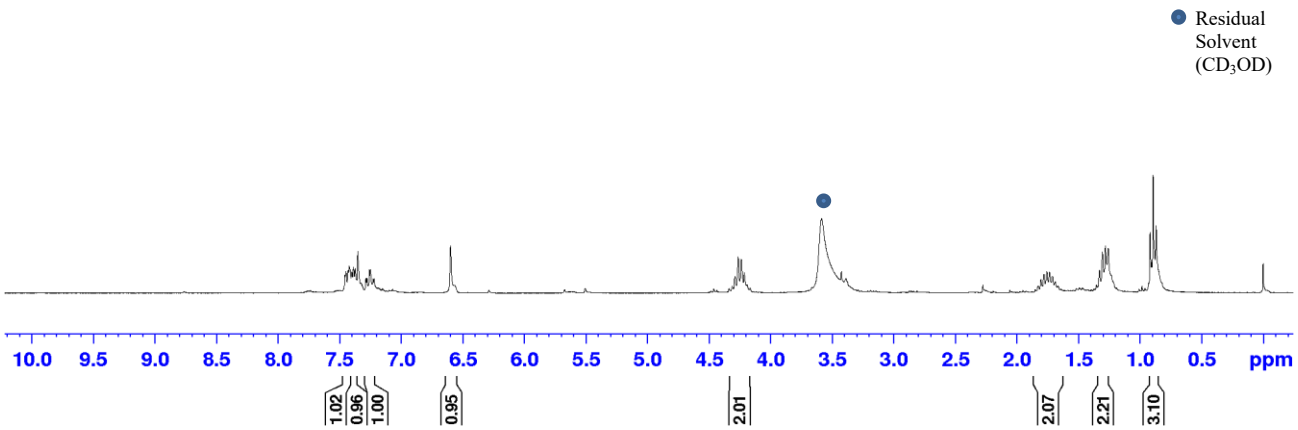
Data File:	HRMS20I02JUL20	Original Data Path:	D:\INTERNAL NEW\2020\June 2020
Sample ID:	AS-80	Sample Name:	
Acquisition Date:	07/02/20 11:26:54 AM	Run Time(min):	0.00
Vial:	CStk1-01:20	Injection Volume(µl):	1.00

HRMS20I02JUL20 #12-24 RT: 0.11-0.21 AV: 13 SB: 1 0.01 NL: 1.62E5
T: FTMS + p ESI Full ms [100.00-750.00]

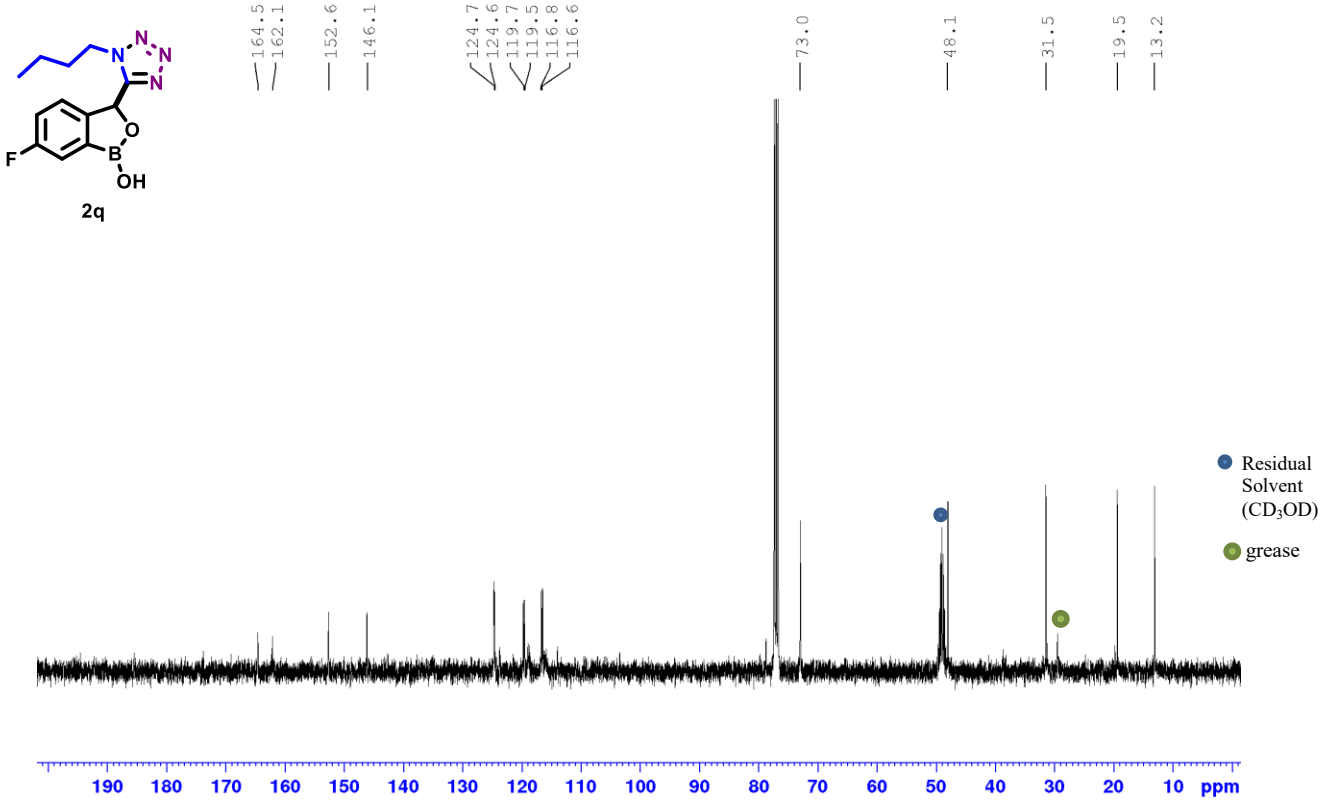


^{1}H NMR (300 MHz, $CDCl_3$+CD_3OD):



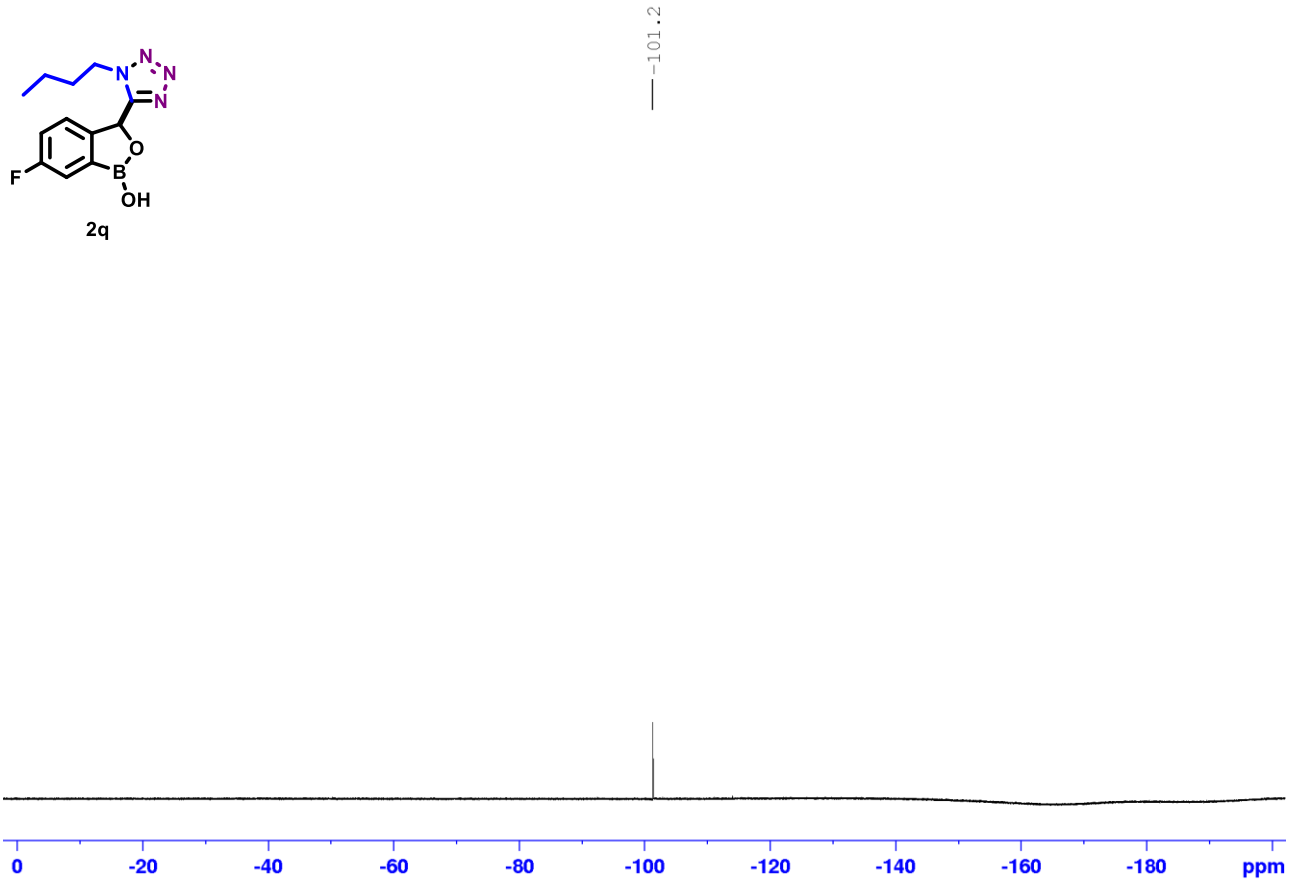


^{13}C NMR (100 MHz, $CDCl_3$+CD_3OD):



2q

^{19}F (376 MHz, $CDCl_3$+CD_3OD):

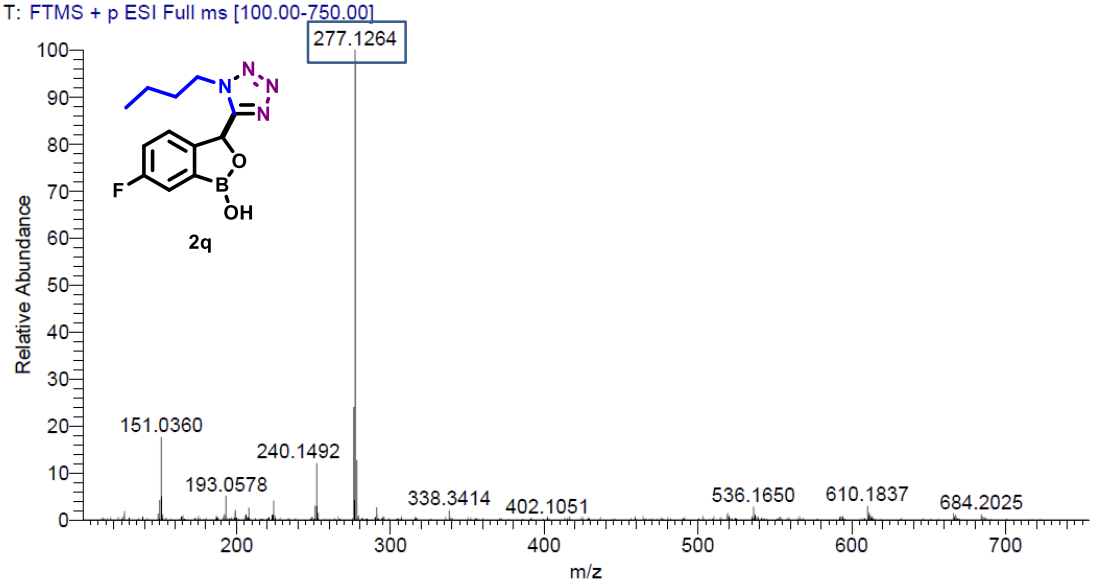


2q

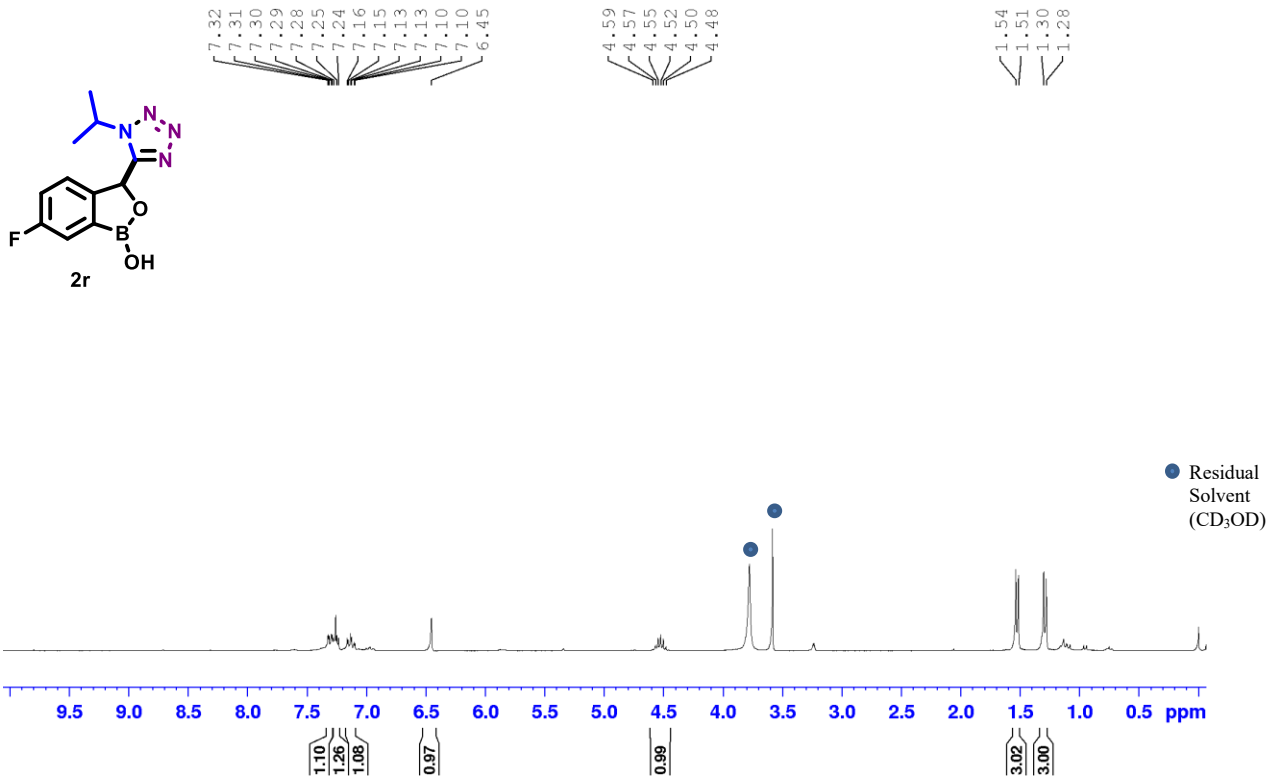
SAIF [HRMS Report]

Data File:	HRMS20I12MAY07	Original Data Path:	D:\INTERNALS\2020\May 2020
Sample ID:	AS-81	Sample Name:	
Acquisition Date:	05/12/20 12:02:50 PM	Run Time(min):	0.00
Vial:	CStk1-01:7	Injection Volume(µl):	1.00

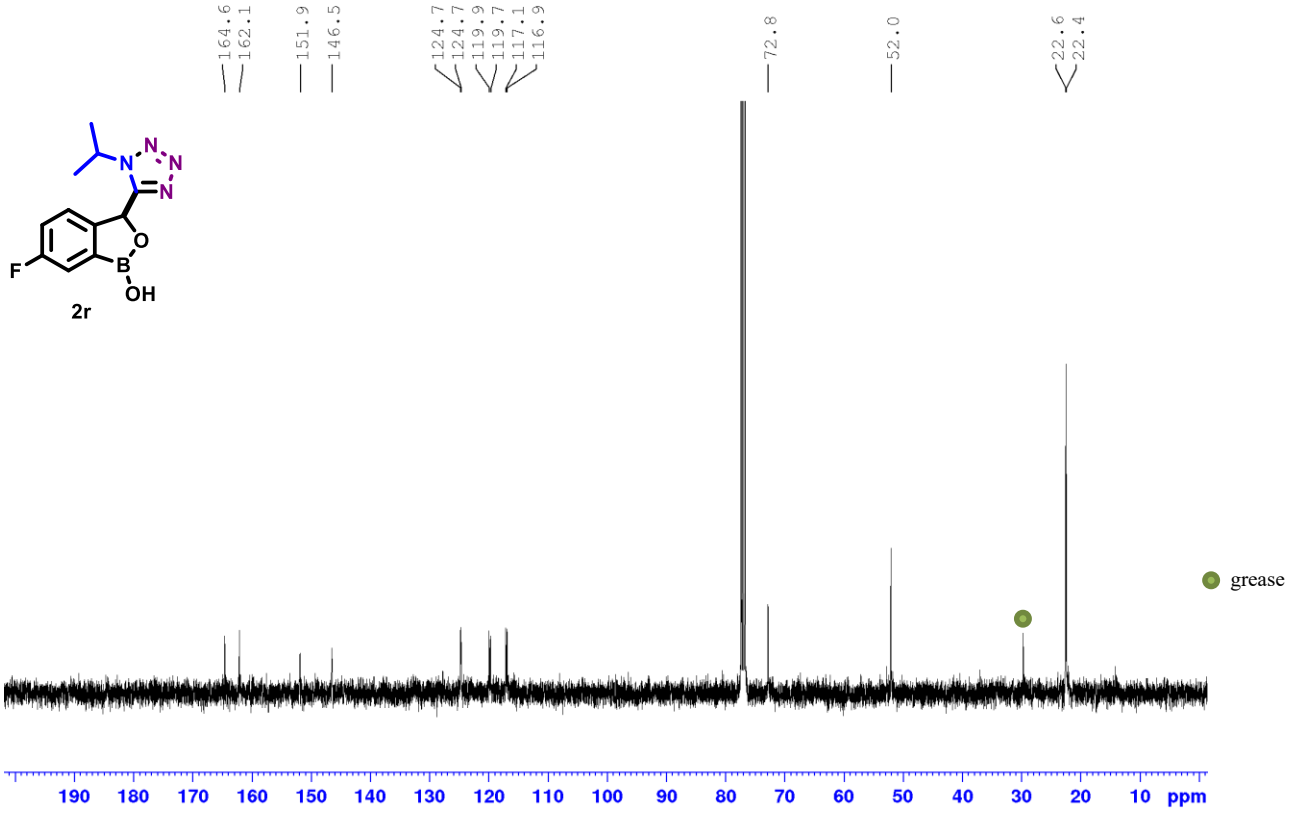
HRMS20I12MAY07 #14-27 RT: 0.11-0.21 AV: 14 SB: 1 0.01 NL: 6.31E6
T: FTMS + p ESI Full ms [100.00-750.00]



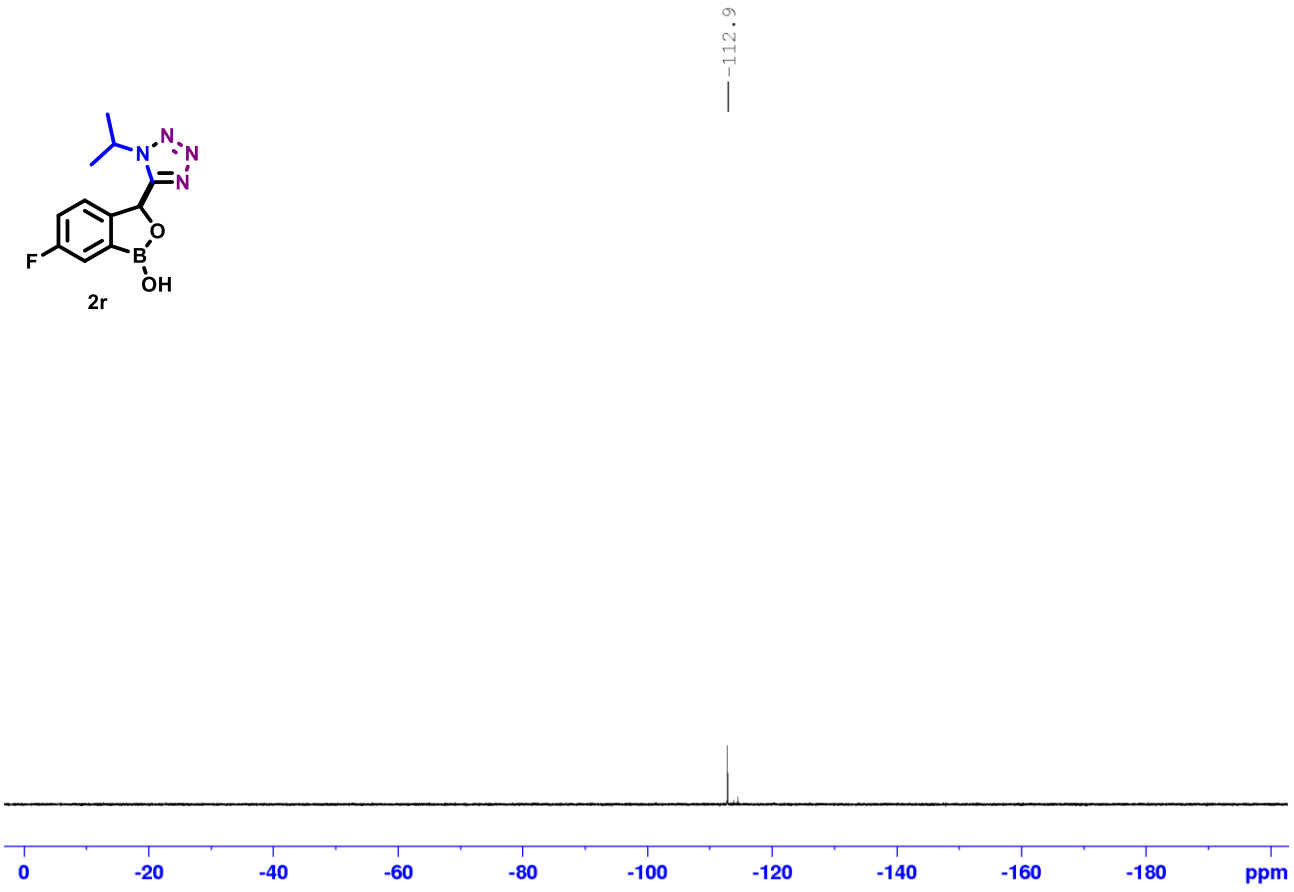
^{1}H NMR (300 MHz, $CDCl_3$+CD_3OD):



^{13}C NMR (100 MHz, $CDCl_3$):



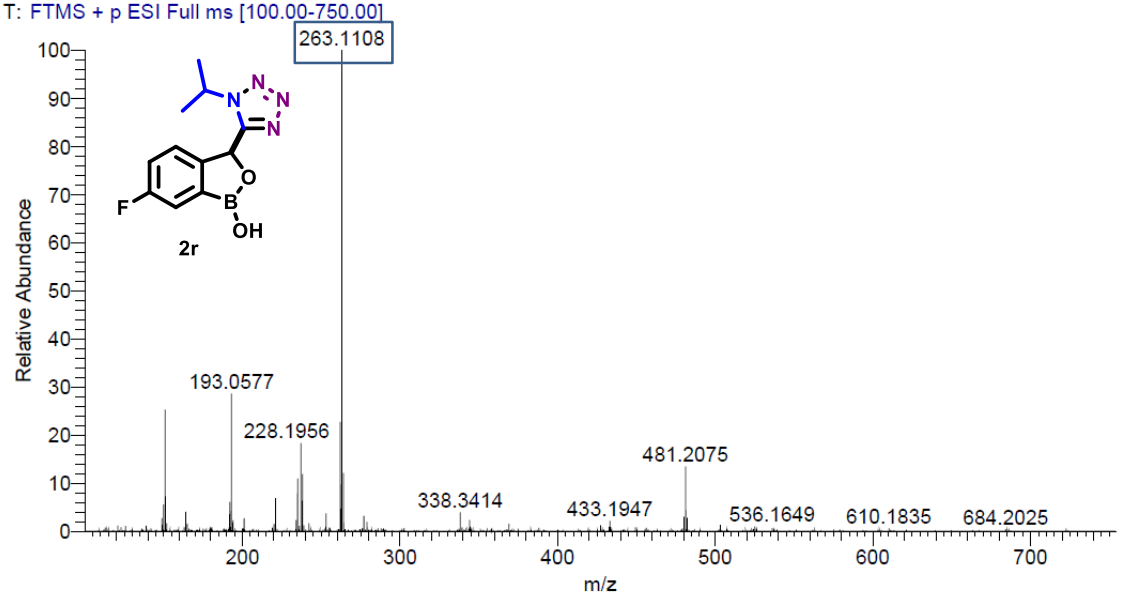
^{19}F (282 MHz, $CDCl_3$+CD_3OD):



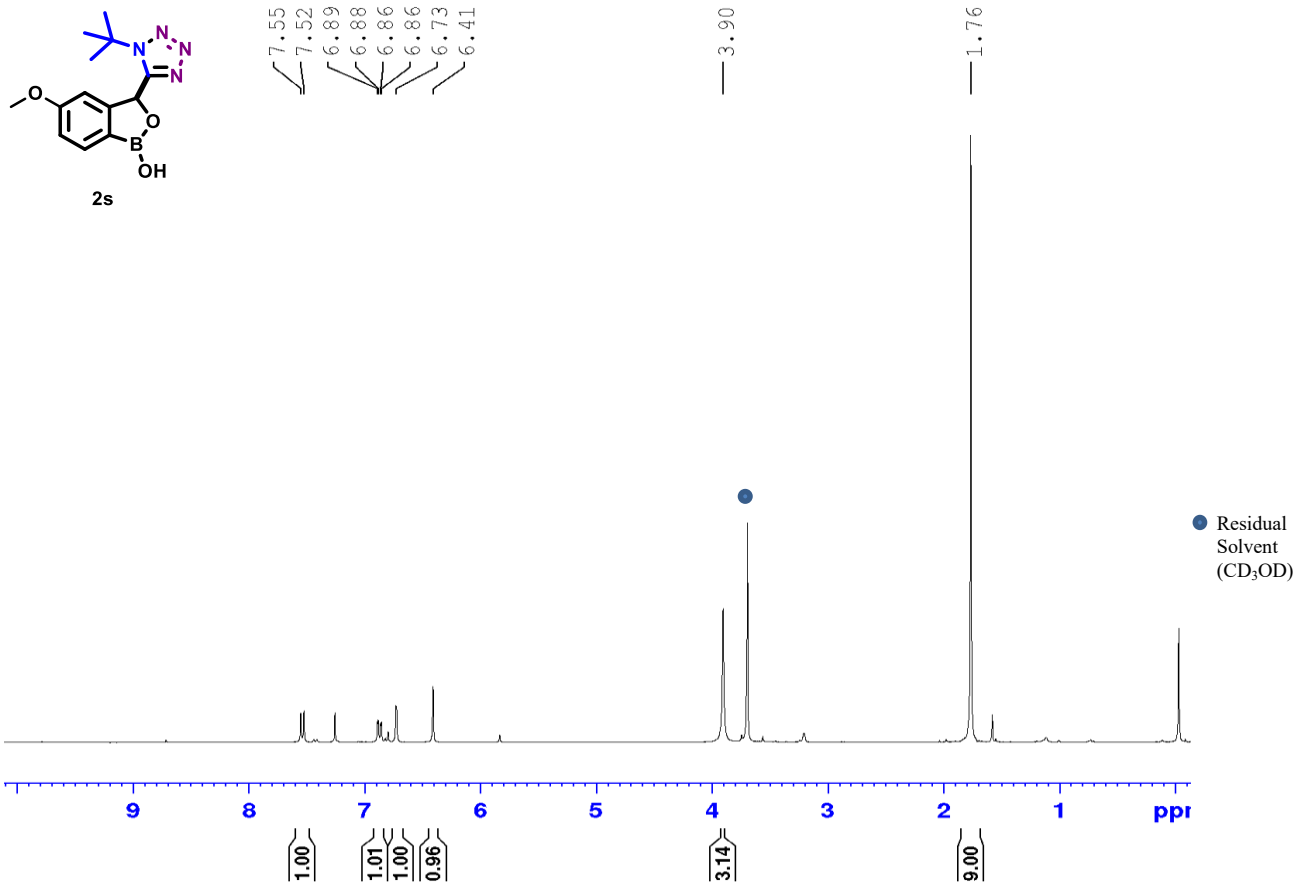
SAIF [HRMS Report]

Data File:	HRMS20I12MAY09	Original Data Path:	D:\INTERNALS\2020\May 2020
Sample ID:	AS-82	Sample Name:	
Acquisition Date:	05/12/20 12:06:47 PM	Run Time(min):	0.00
Vial:	CStk1-01:9	Injection Volume(µl):	1.00

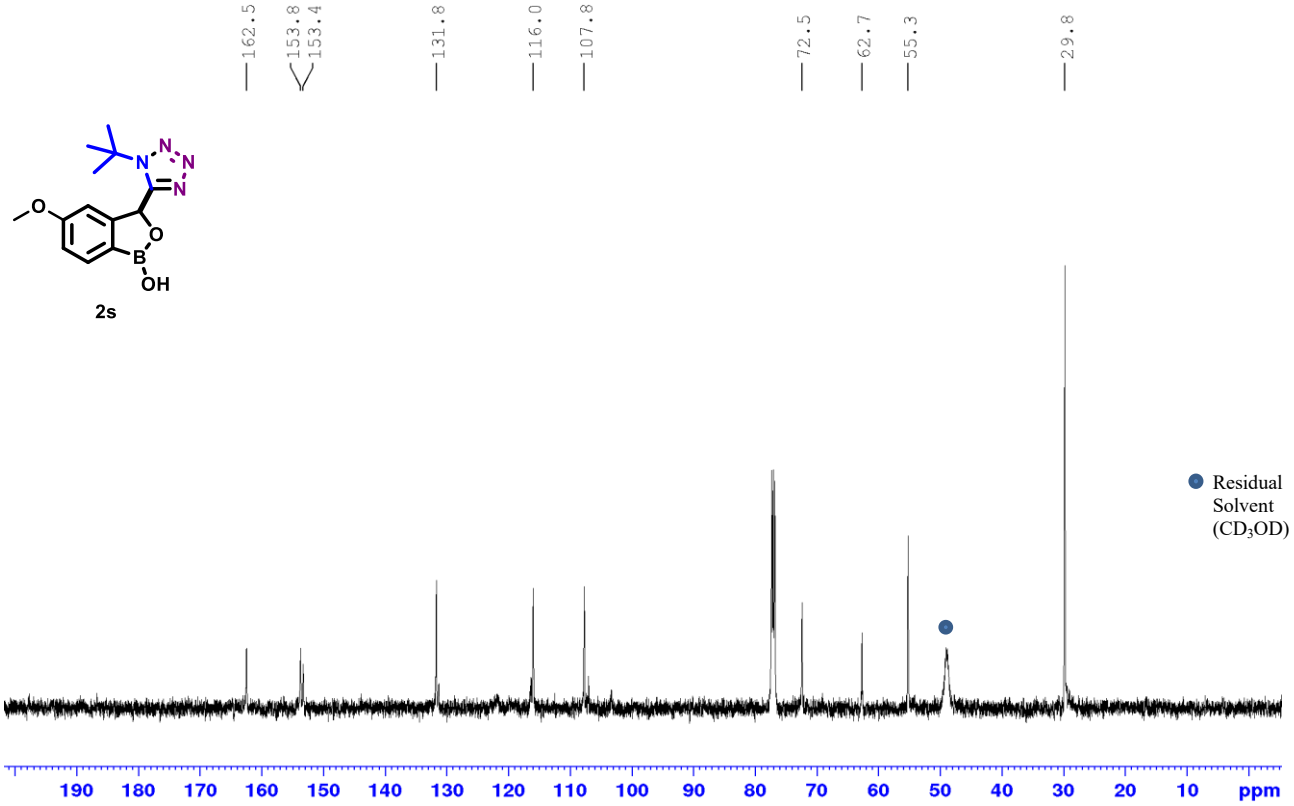
HRMS20I12MAY09 #14-27 RT: 0.11-0.21 AV: 14 SB: 1 0.01 NL: 4.24E6
T: FTMS + p ESI Full ms [100.00-750.00]



^{1}H NMR (400 MHz, $CDCl_3$+CD_3OD):



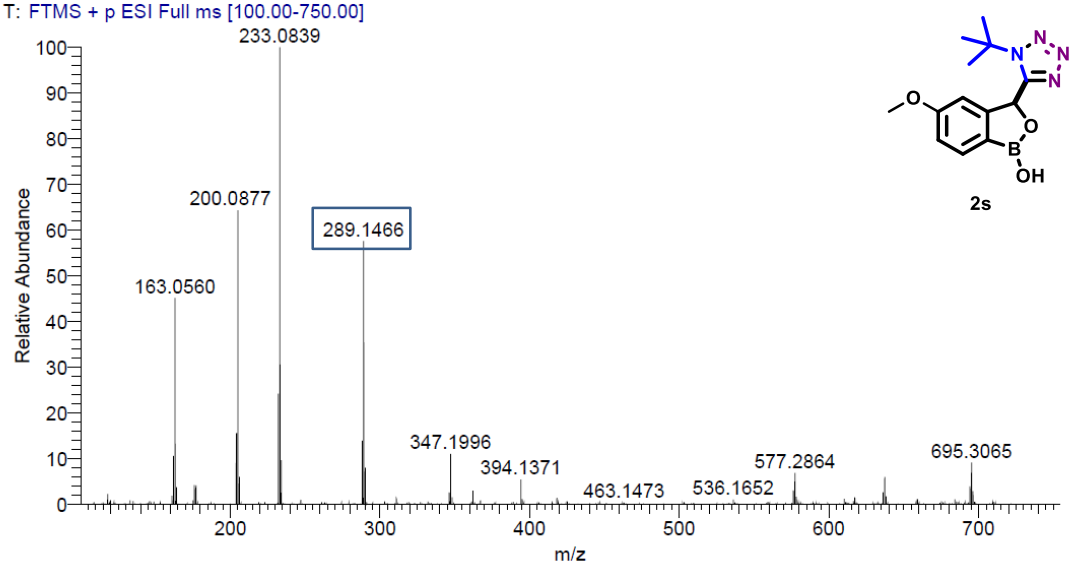
^{13}C NMR (100 MHz, $CDCl_3$+CD_3OD):



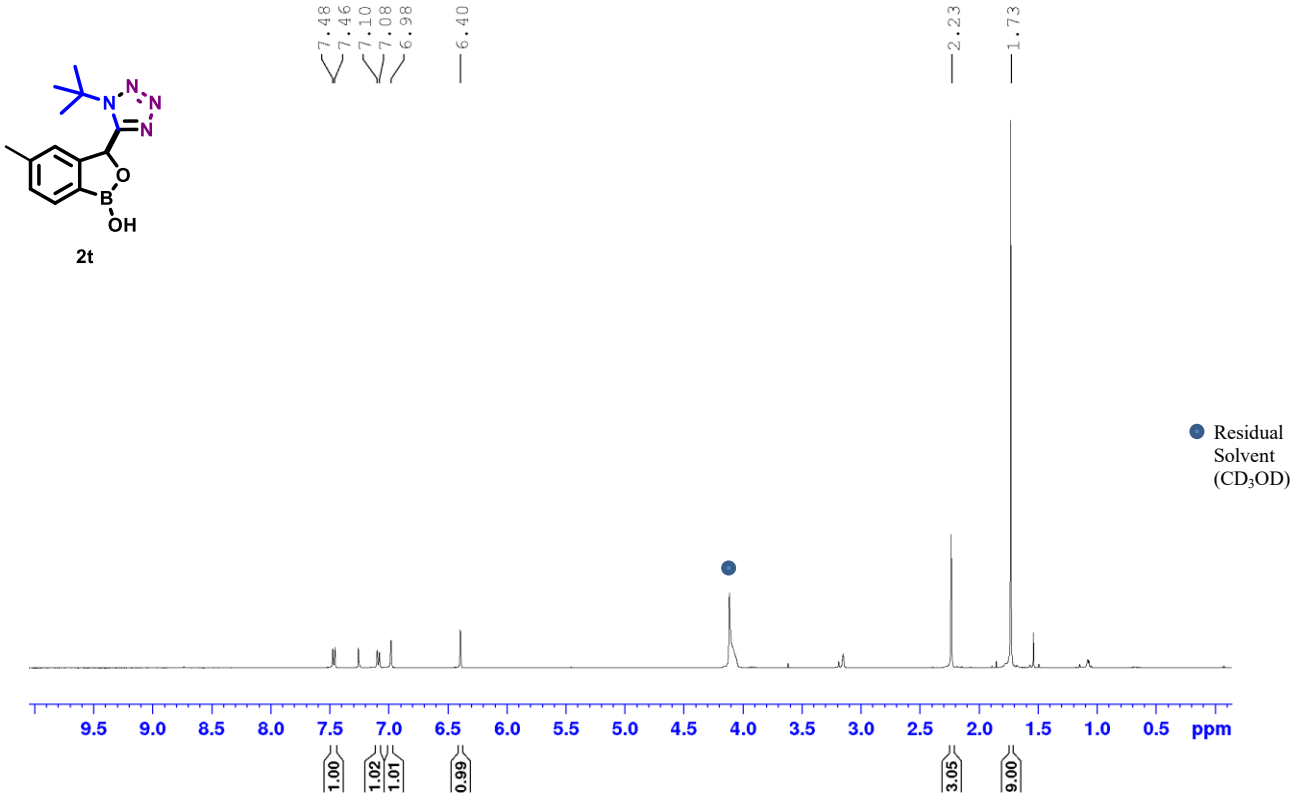
SAIF [HRMS Report]

Data File:	HRMS20I02JUL18	Original Data Path:	D:\INTERNAL NEW\2020\June 2020
Sample ID:	AS-103	Sample Name:	
Acquisition Date:	07/02/20 11:22:57 AM	Run Time(min):	0.00
Vial:	CStk1-01:18	Injection Volume(µl):	1.00

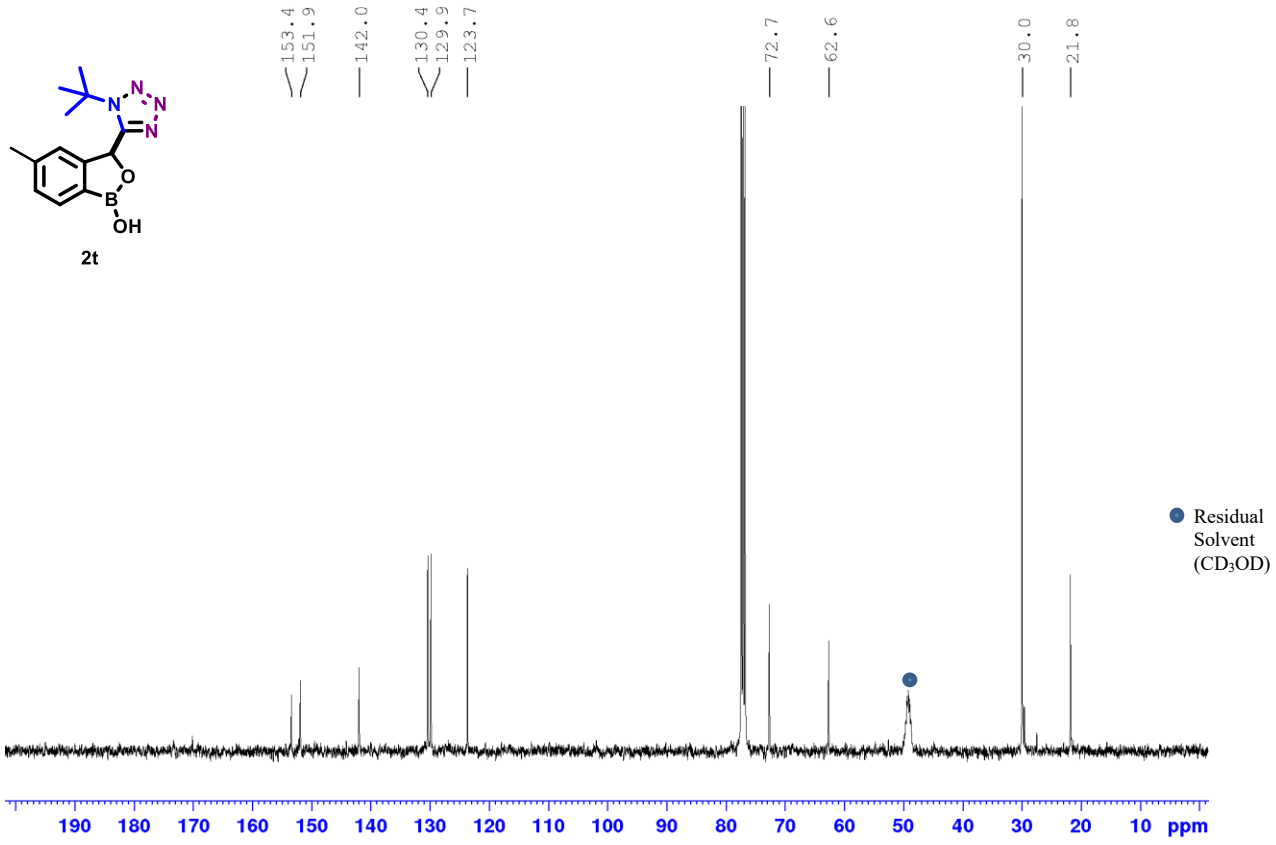
HRMS20I02JUL18 #12-25 RT: 0.11-0.21 AV: 14 SB: 1 0.01 NL: 2.29E6
T: FTMS + p ESI Full ms [100.00-750.00]



^{1}H NMR (400 MHz, $CDCl_3$+CD_3OD):



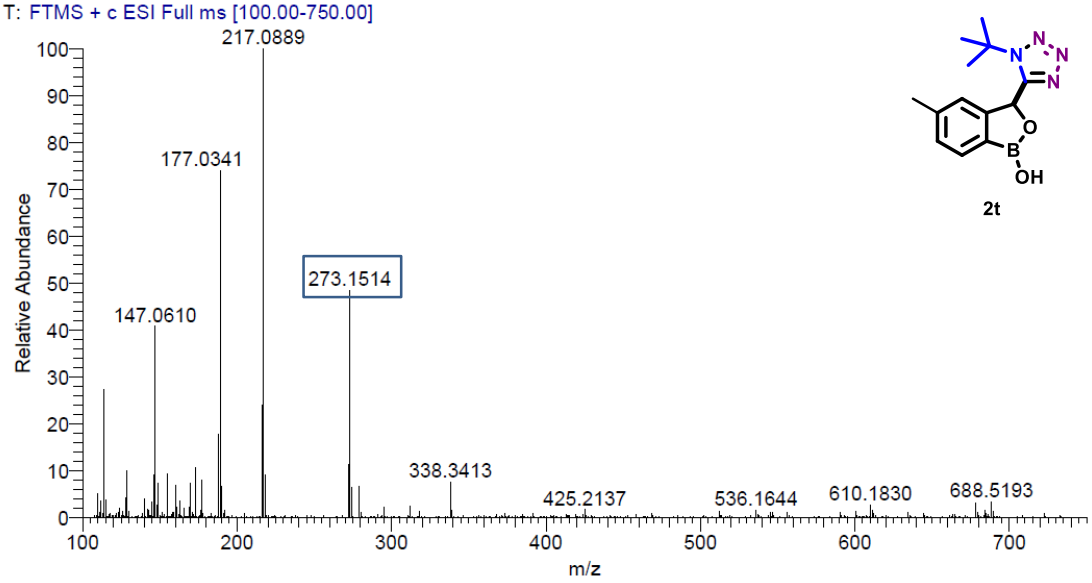
^{13}C NMR (100 MHz, $CDCl_3$+CD_3OD):



SAIF [HRMS Report]

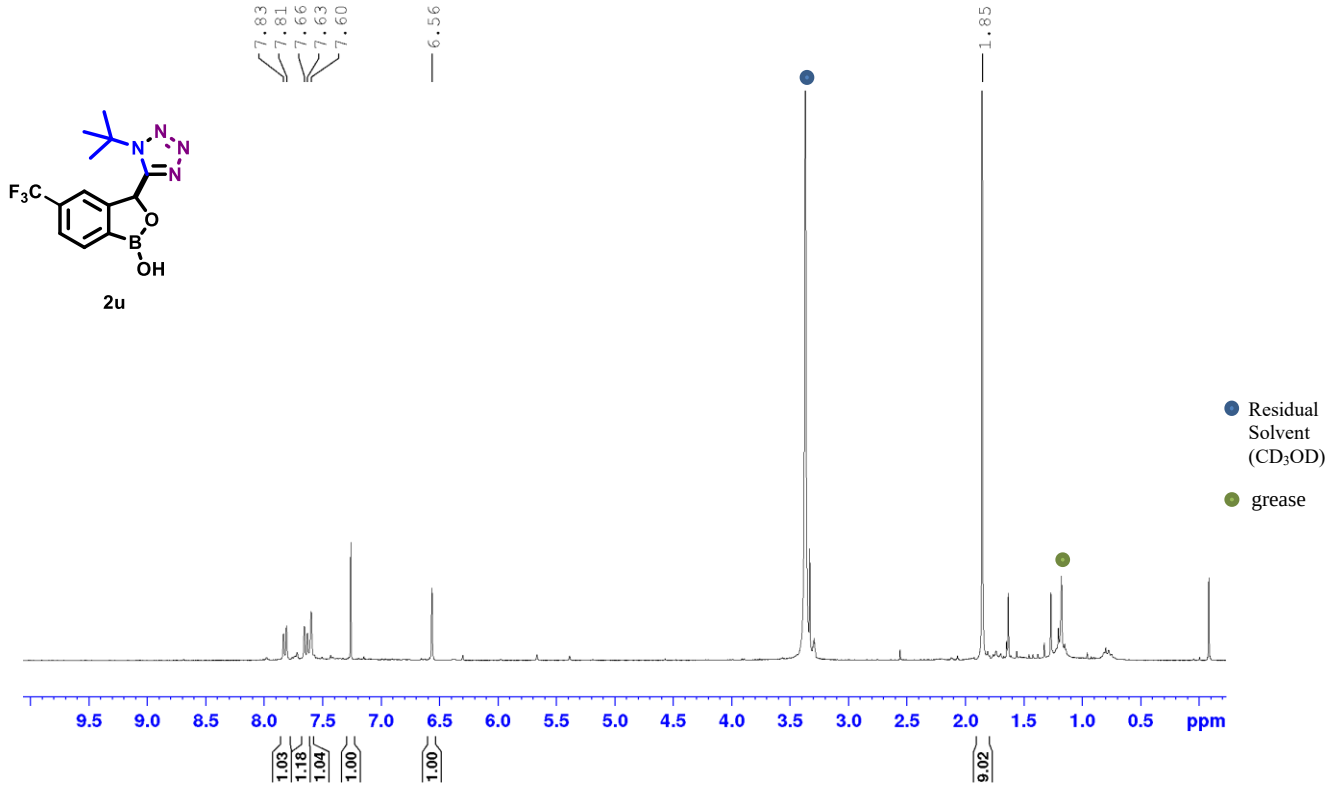
Data File:	HRMS20I29DEC24	Original Data Path:	D:\INTERNAL NEW\2020\DEC 2020
Sample ID:	AS-228	Sample Name:	
Acquisition Date:	12/29/20 12:32:21 PM	Run Time(min):	0.00
Vial:	CStk1-01:24	Injection Volume(µl):	1.00

HRMS20I29DEC24 #30-60 RT: 0.25-0.50 AV: 31 SB: 1 0.01 NL: 4.54E5
T: FTMS + c ESI Full ms [100.00-750.00]



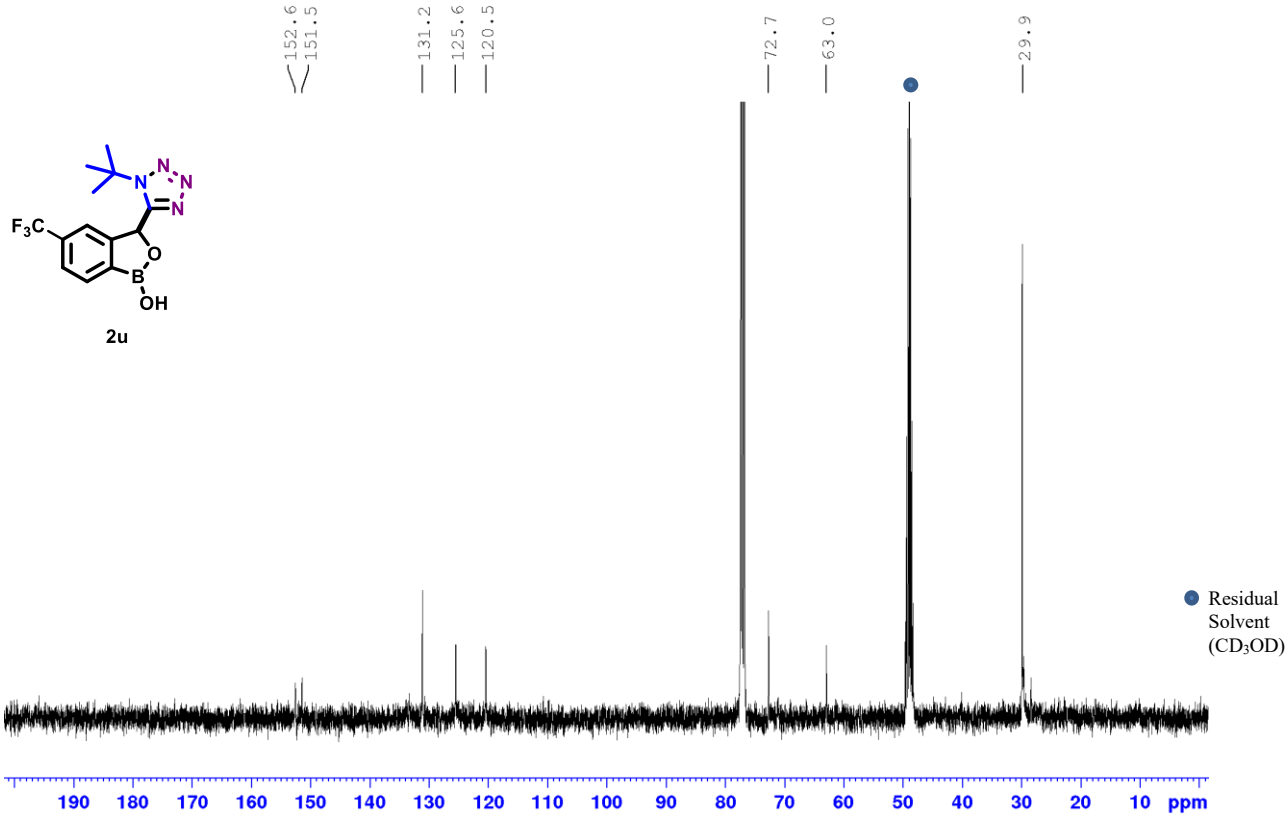
2t

^{1}H NMR (300 MHz, $CDCl_3$+CD_3OD):

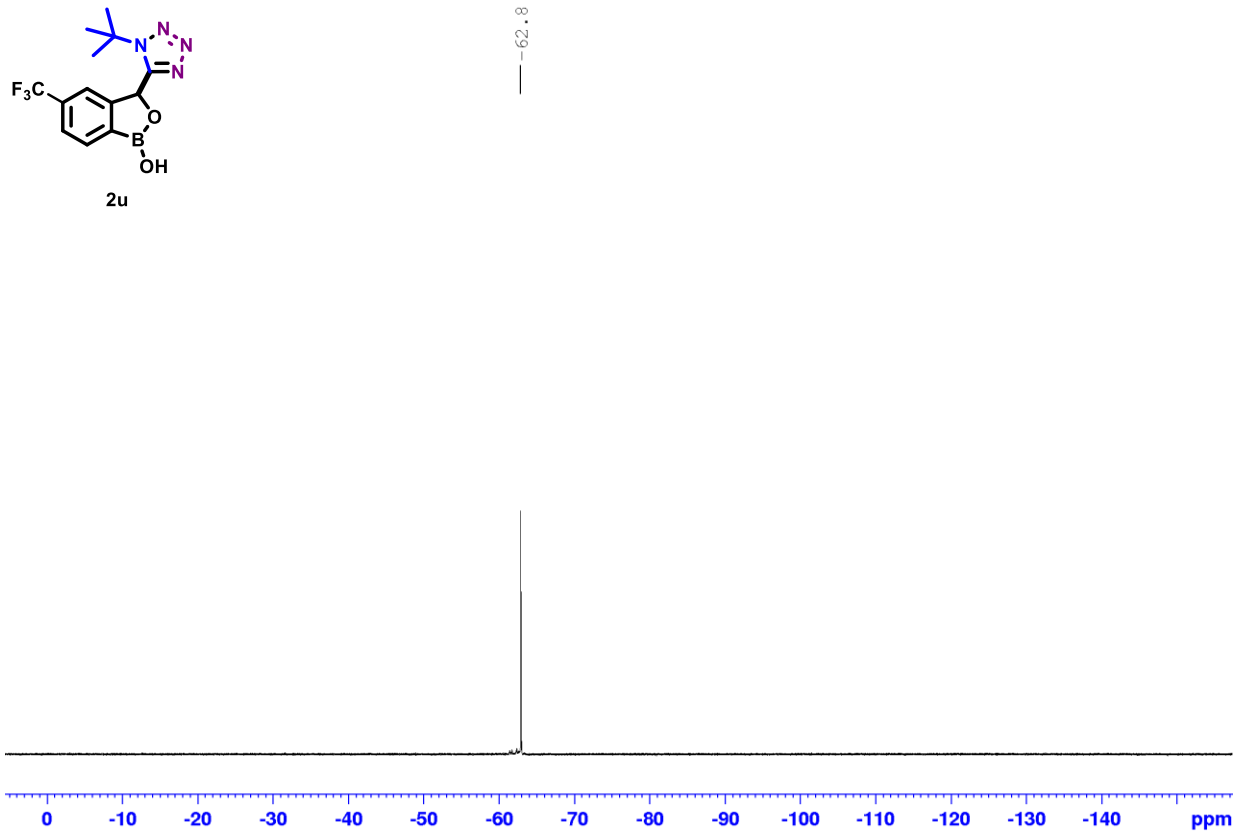


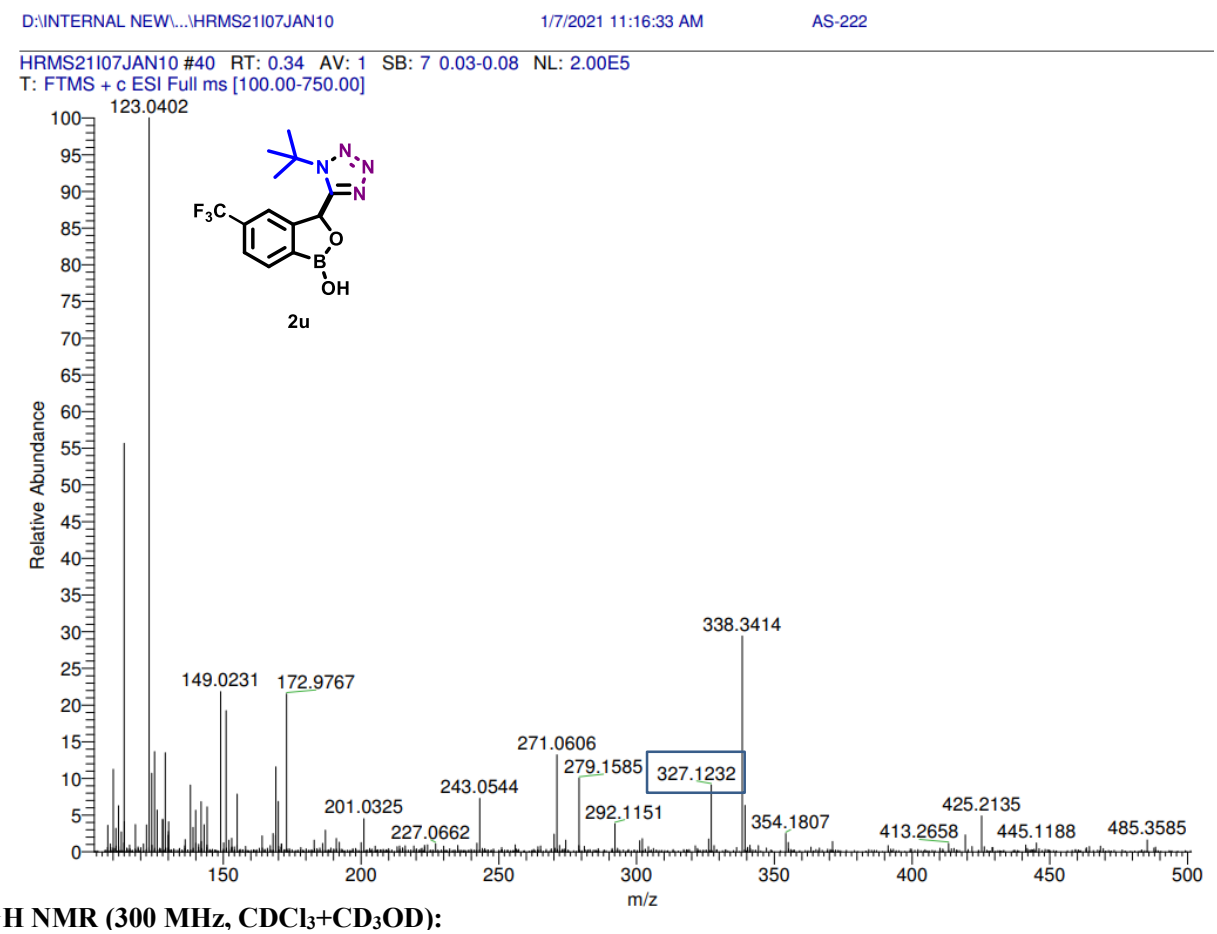
2u

^{13}C NMR (100 MHz, $CDCl_3$+CD_3OD):

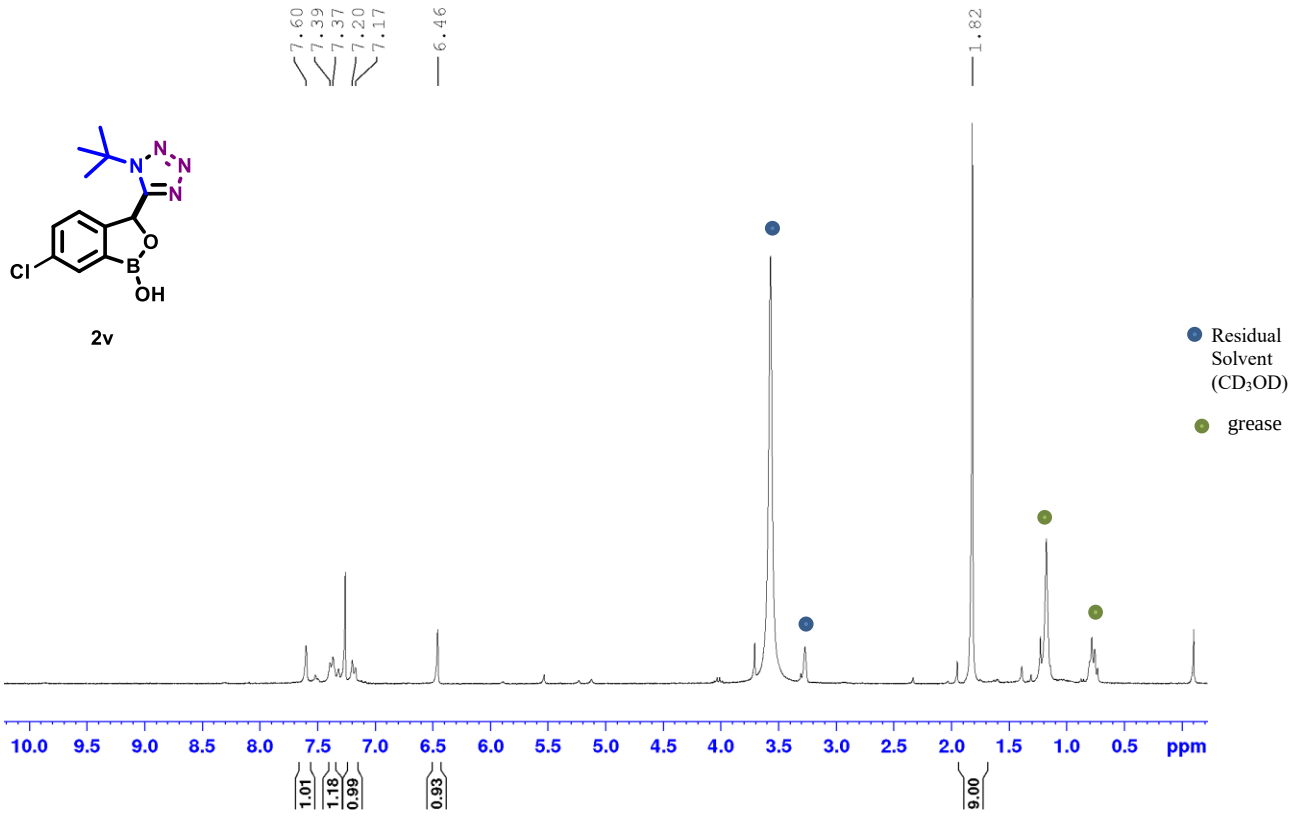


^{19}F (282 MHz, $CDCl_3$+CD_3OD):

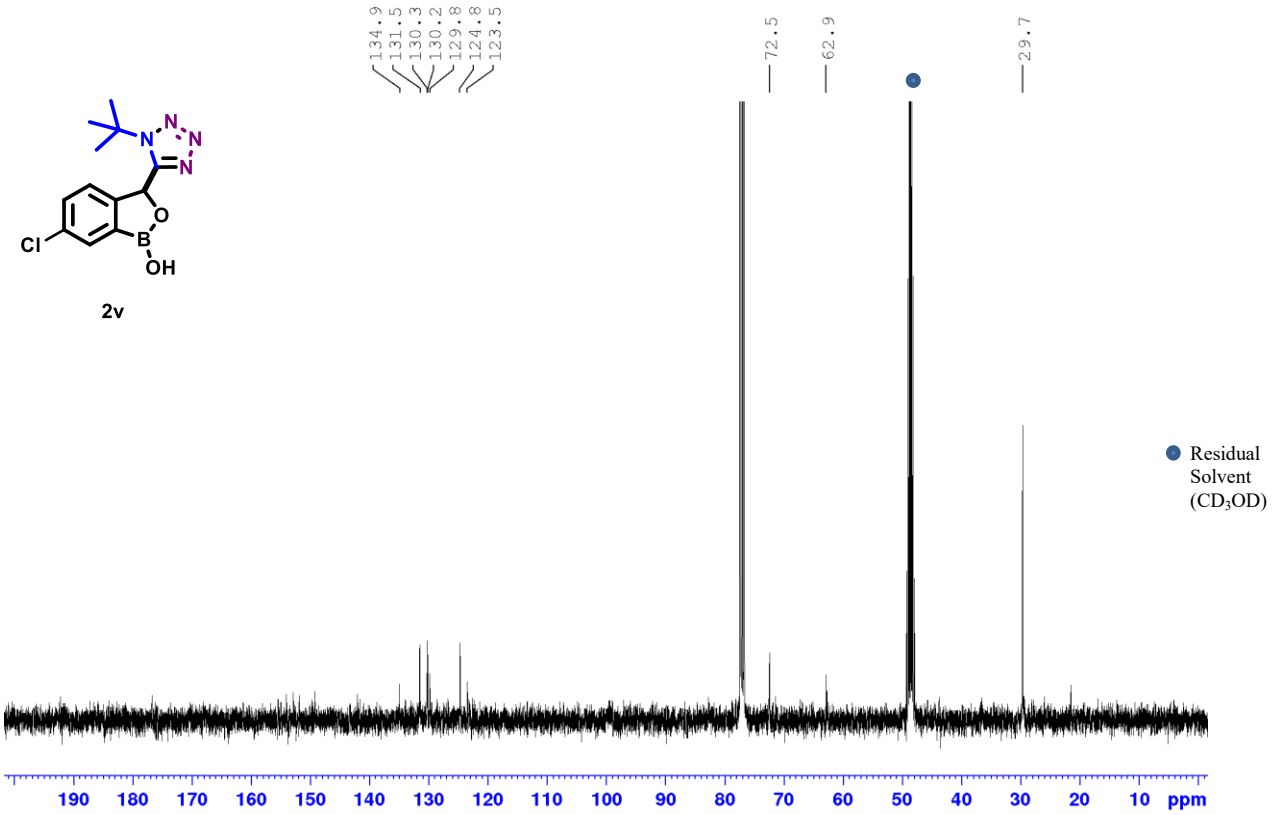




^{1}H NMR (300 MHz, $CDCl_3$+CD_3OD):



^{13}C NMR (100 MHz, $CDCl_3$+CD_3OD):

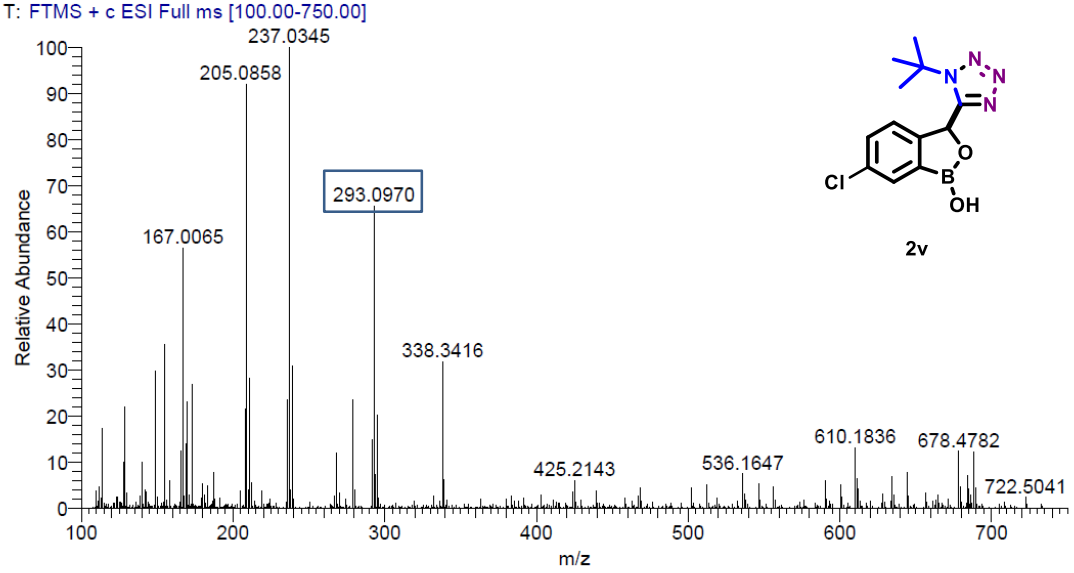


2v

SAIF [HRMS Report]

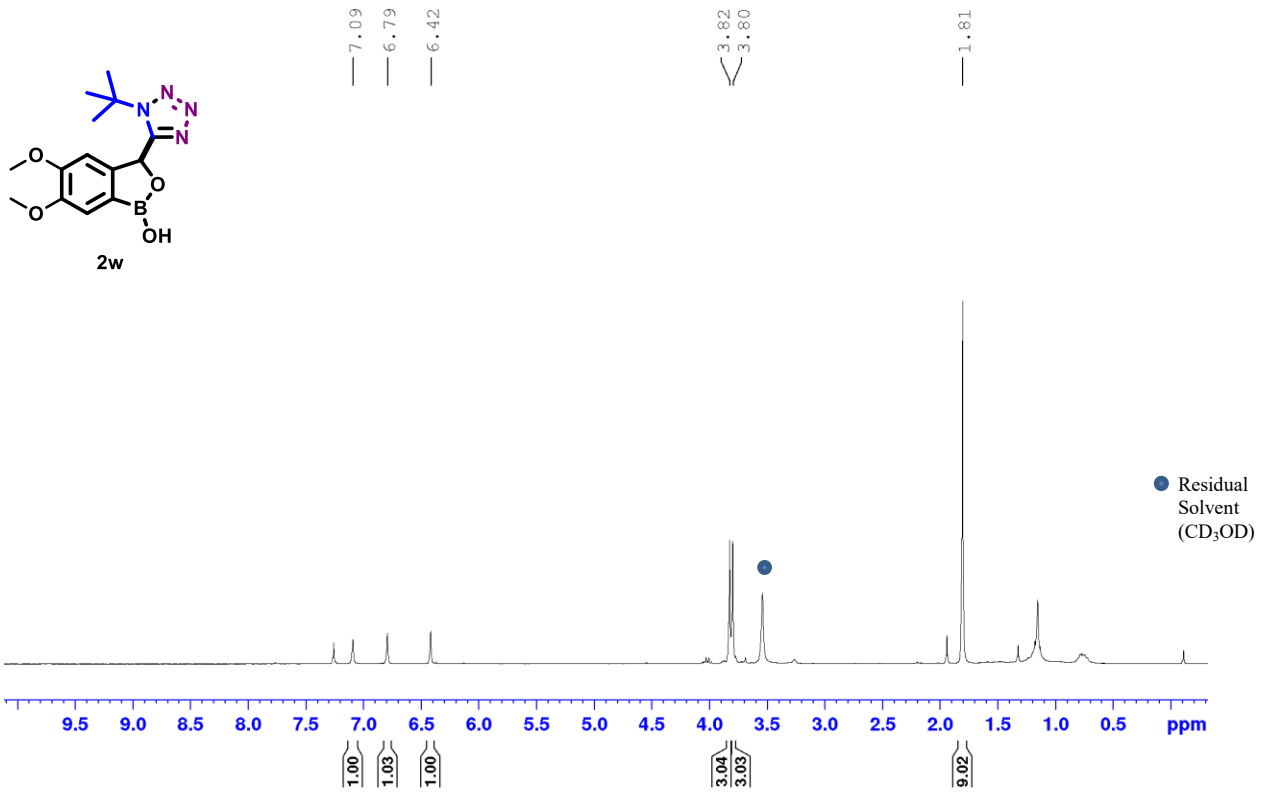
Data File:	HRMS20I23DEC21	Original Data Path:	D:\INTERNAL NEW\2020\DEC 2020
Sample ID:	AS-221	Sample Name:	
Acquisition Date:	12/23/20 11:35:38 AM	Run Time(min):	0.00
Vial:	CStk1-01:21	Injection Volume(µl):	1.00

HRMS20I23DEC21 #30-60 RT: 0.25-0.50 AV: 31 SB: 1 0.01 NL: 1.63E5
T: FTMS + c ESI Full ms [100.00-750.00]

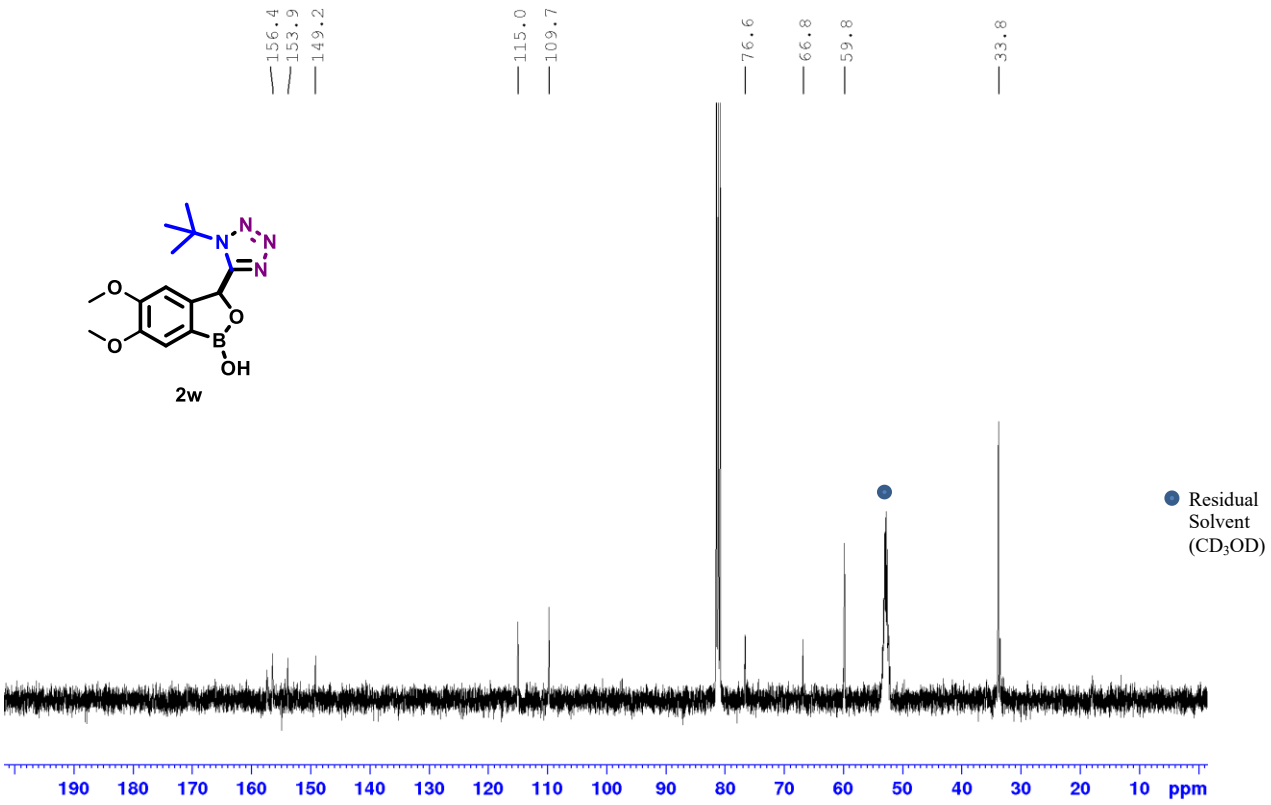


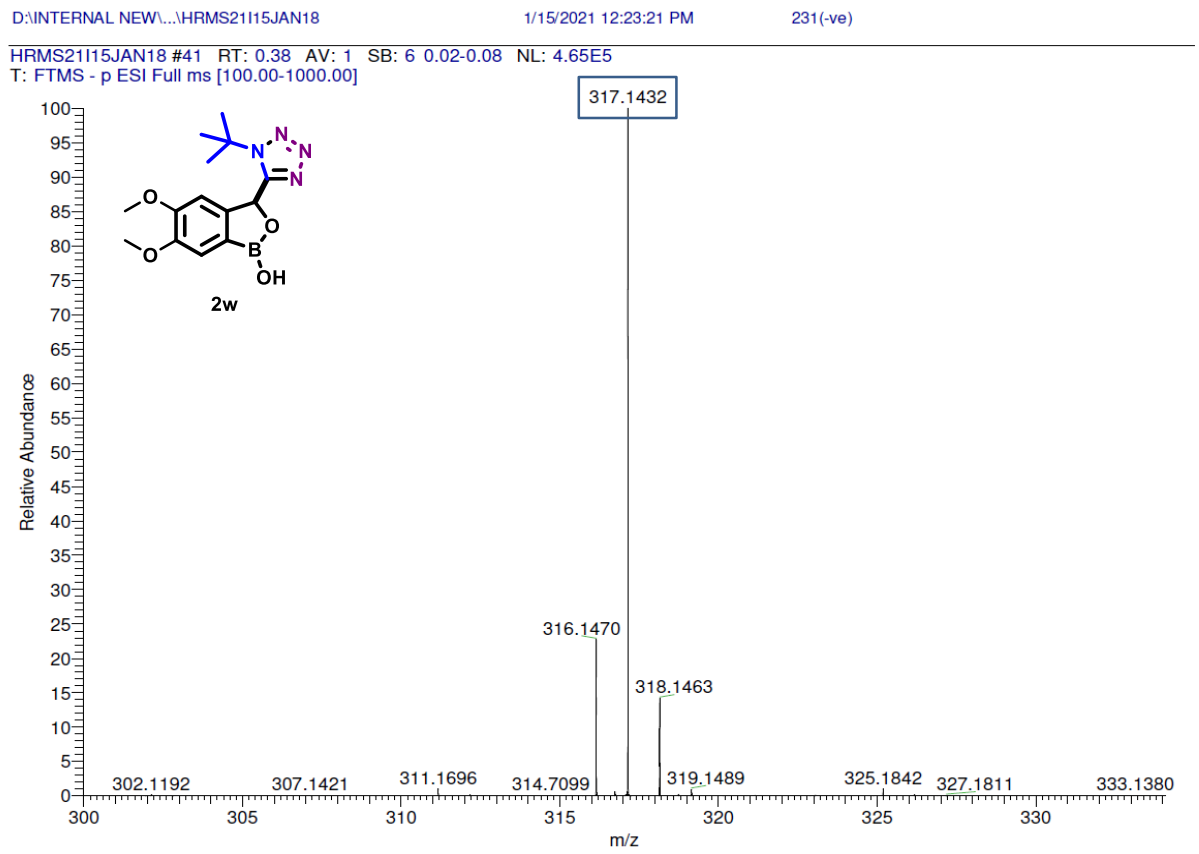
2v

^{1}H NMR (400 MHz, $CDCl_3$+CD_3OD):

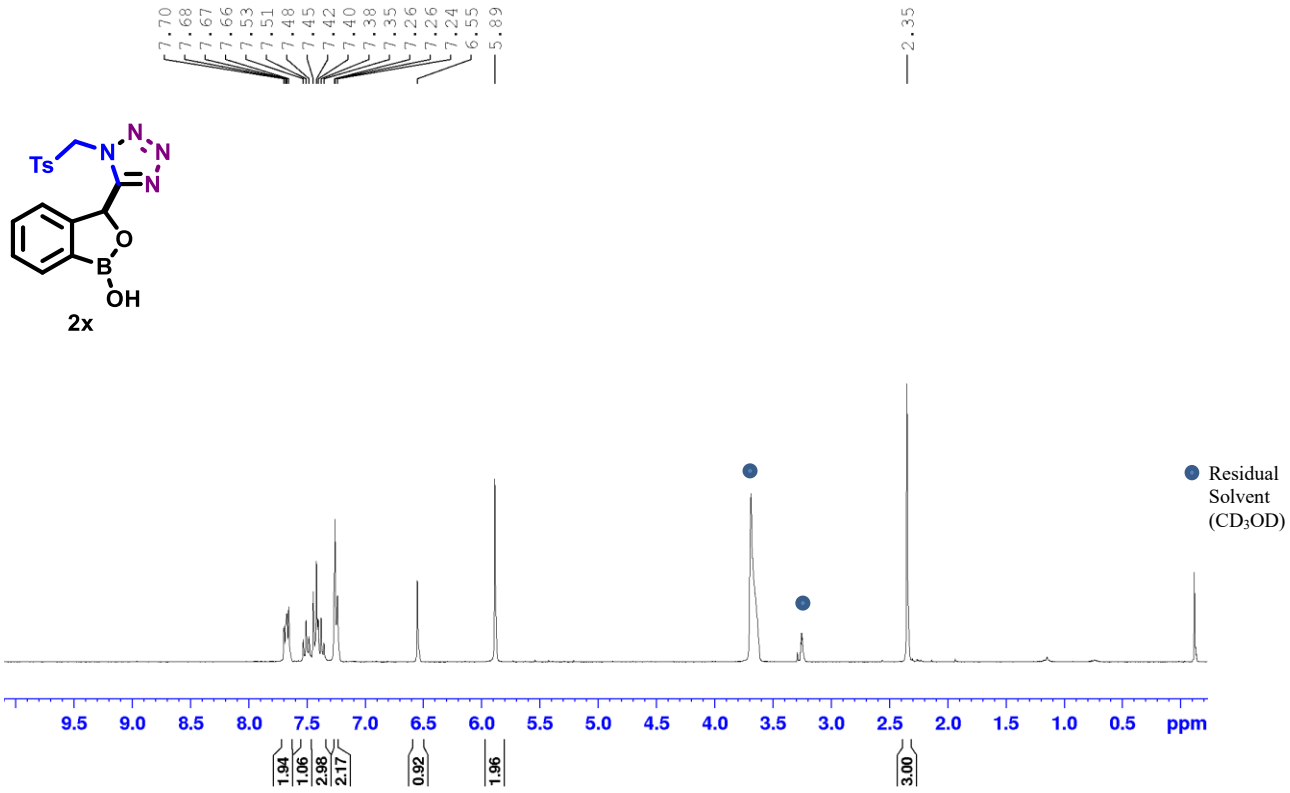


^{13}C NMR (100 MHz, $CDCl_3$+CD_3OD):

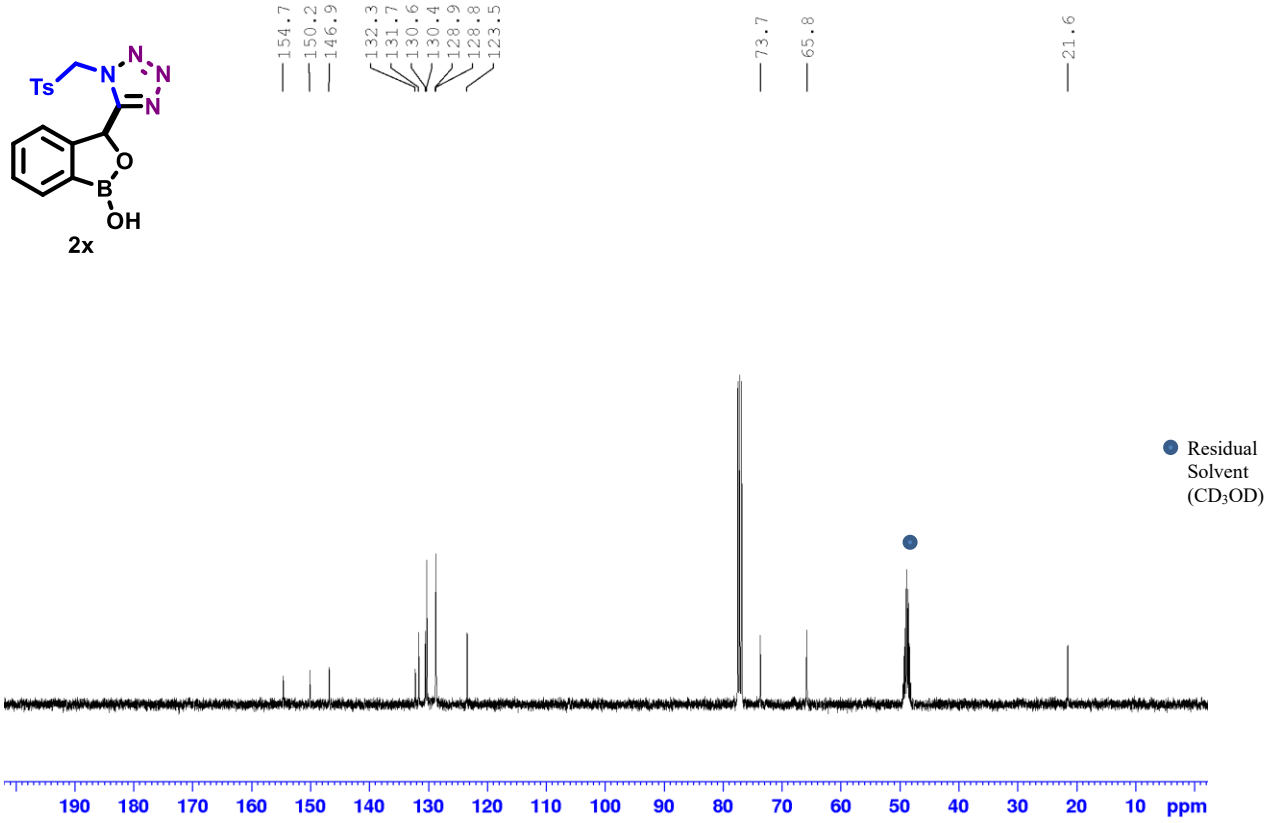


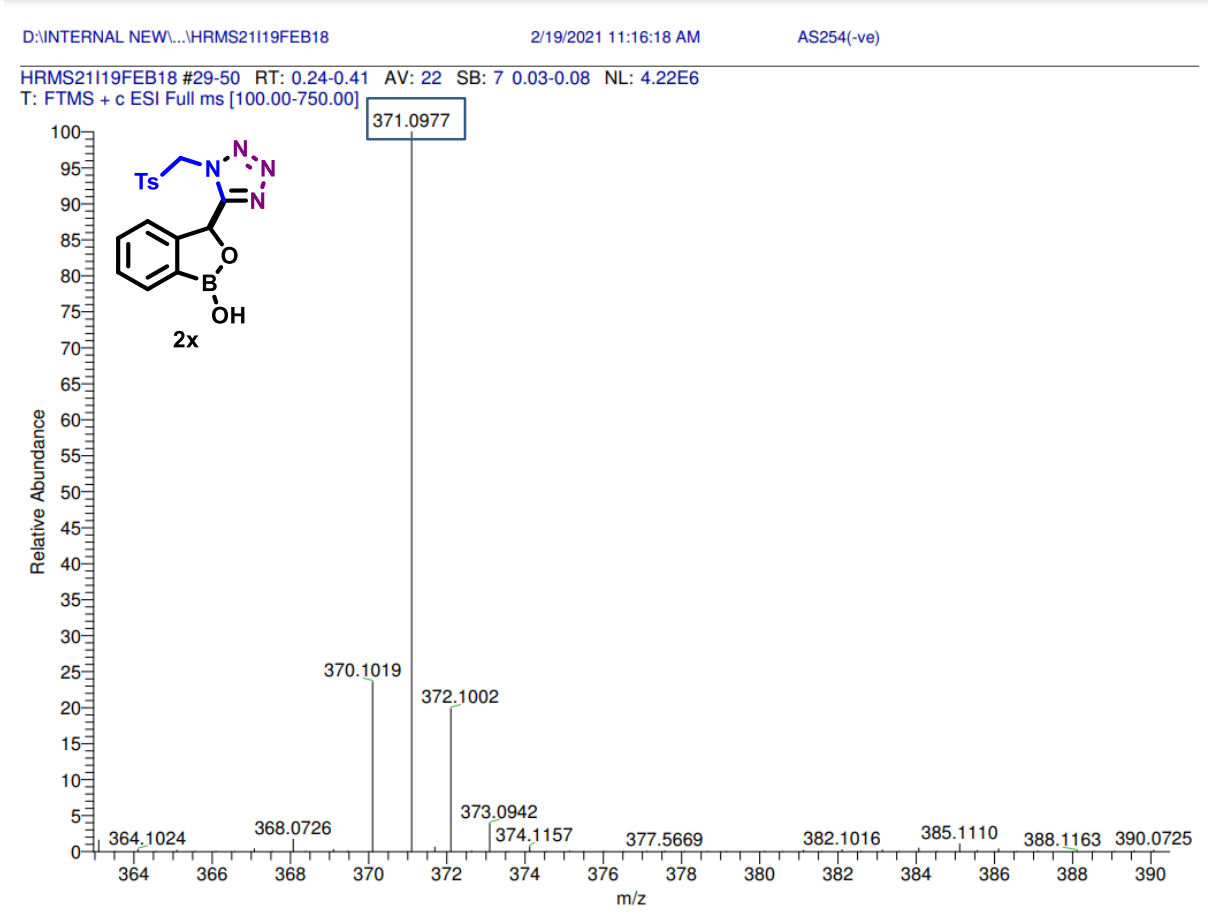


^{1}H NMR (300 MHz, $CDCl_3$+CD_3OD):

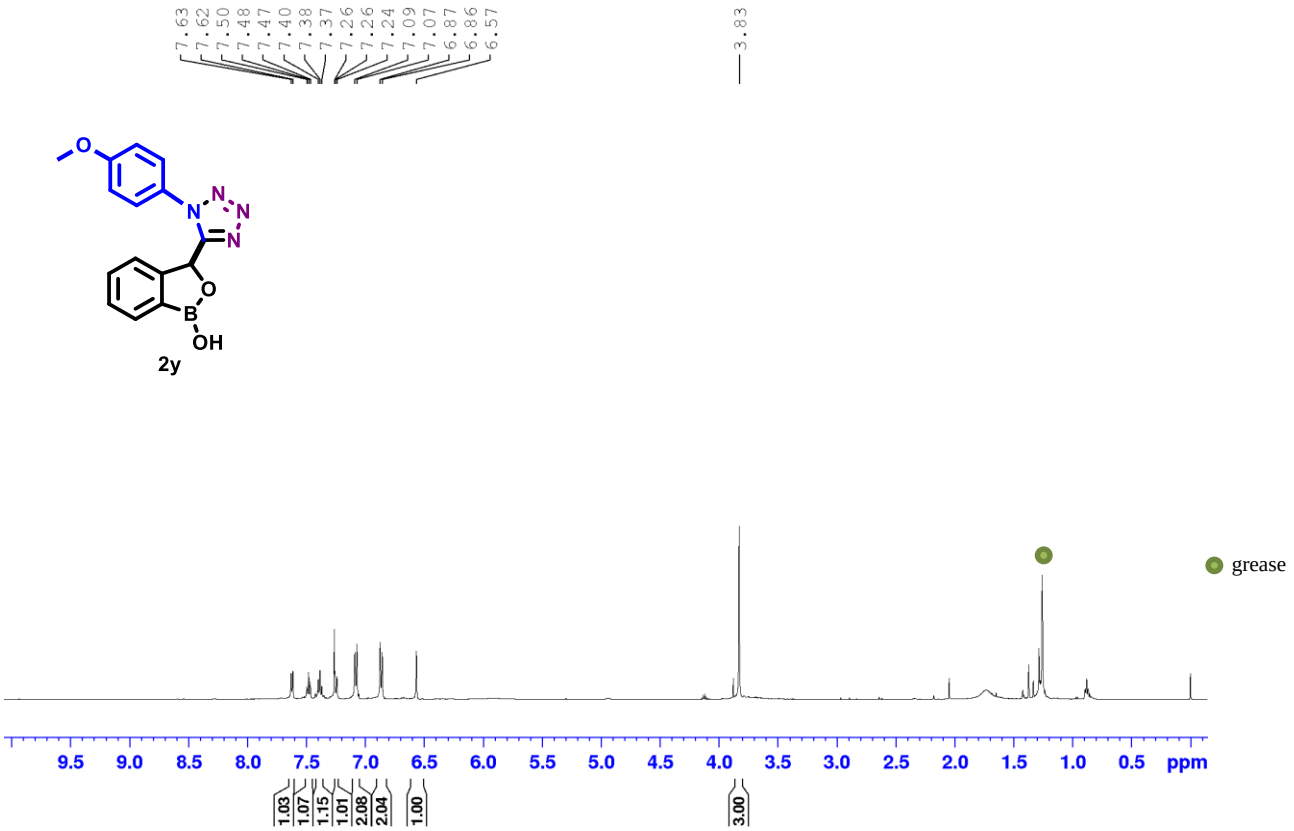


^{13}C NMR (100 MHz, $CDCl_3$+CD_3OD):

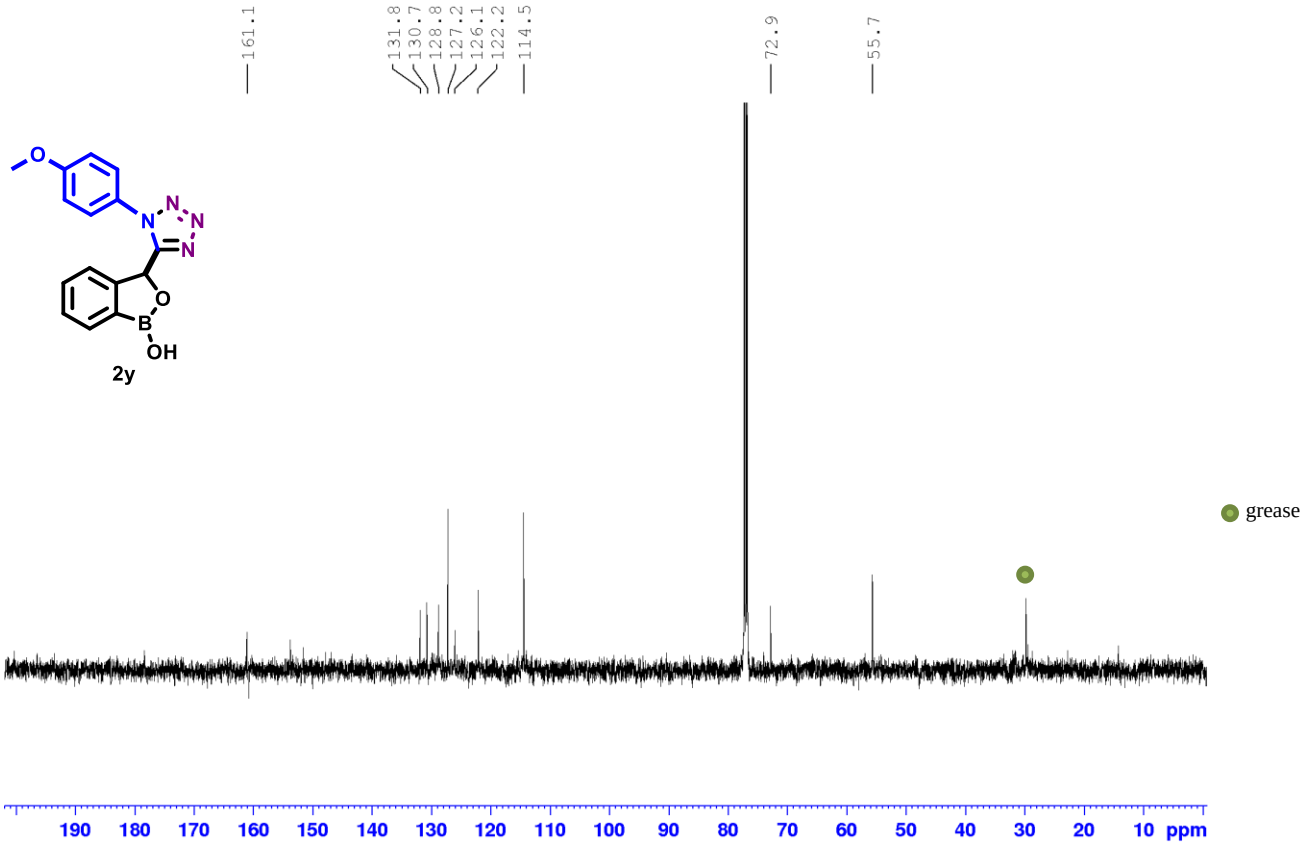


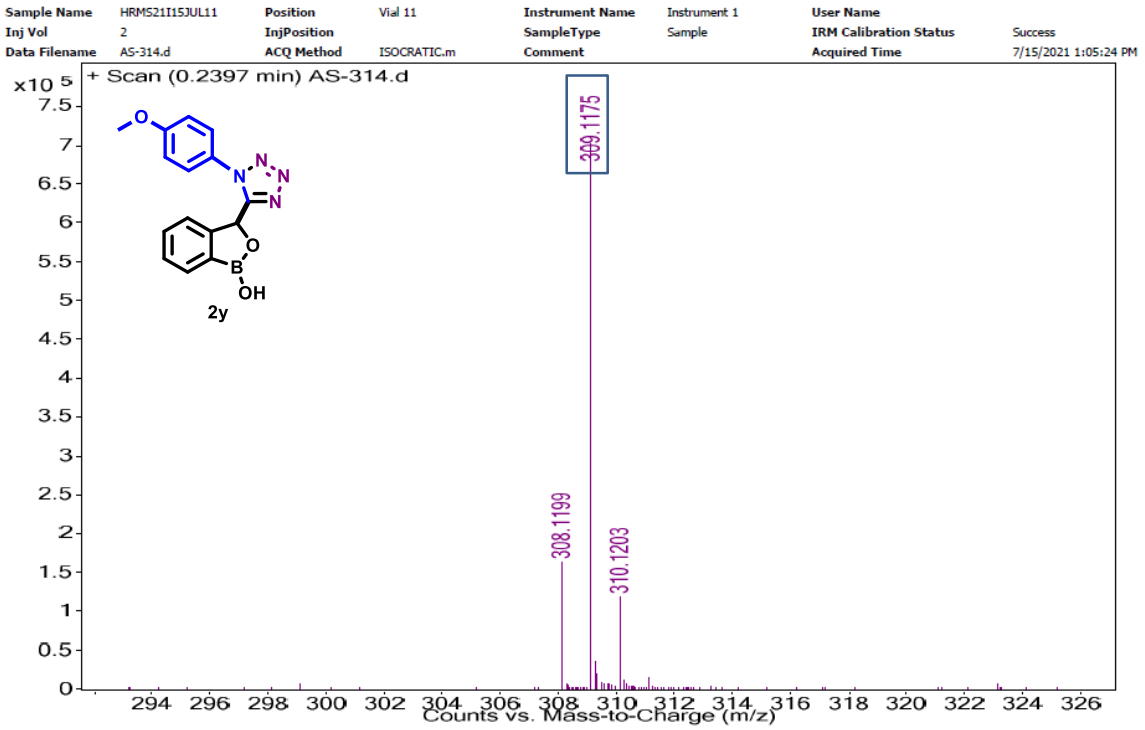


^{1}H NMR (500 MHz, $CDCl_3$):

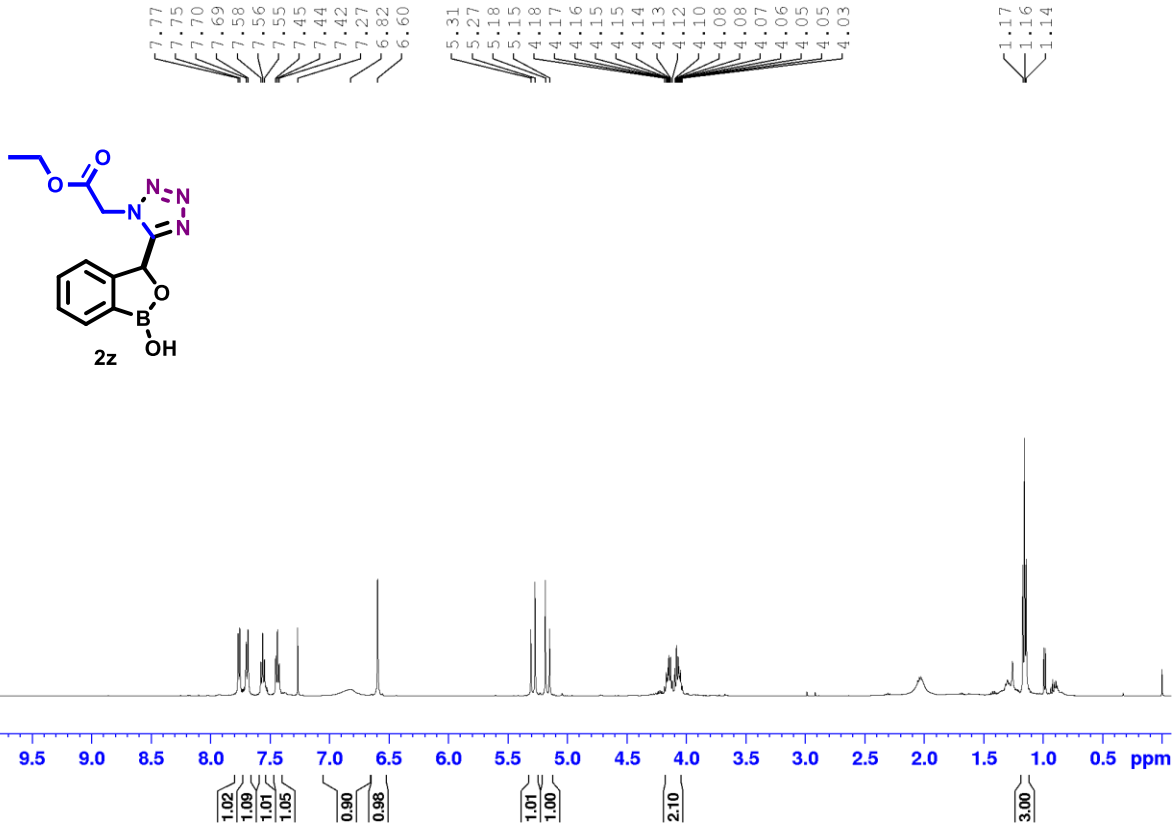


^{13}C NMR (125 MHz, $CDCl_3$):

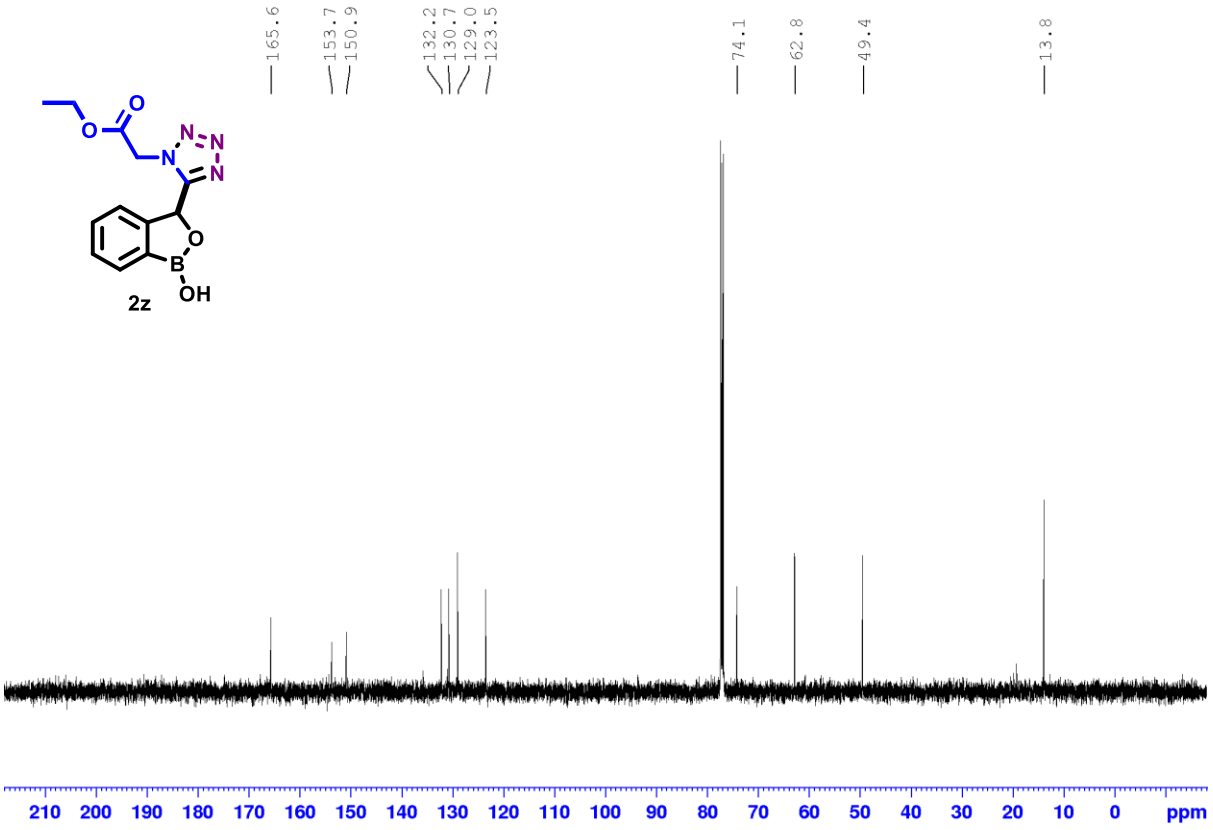


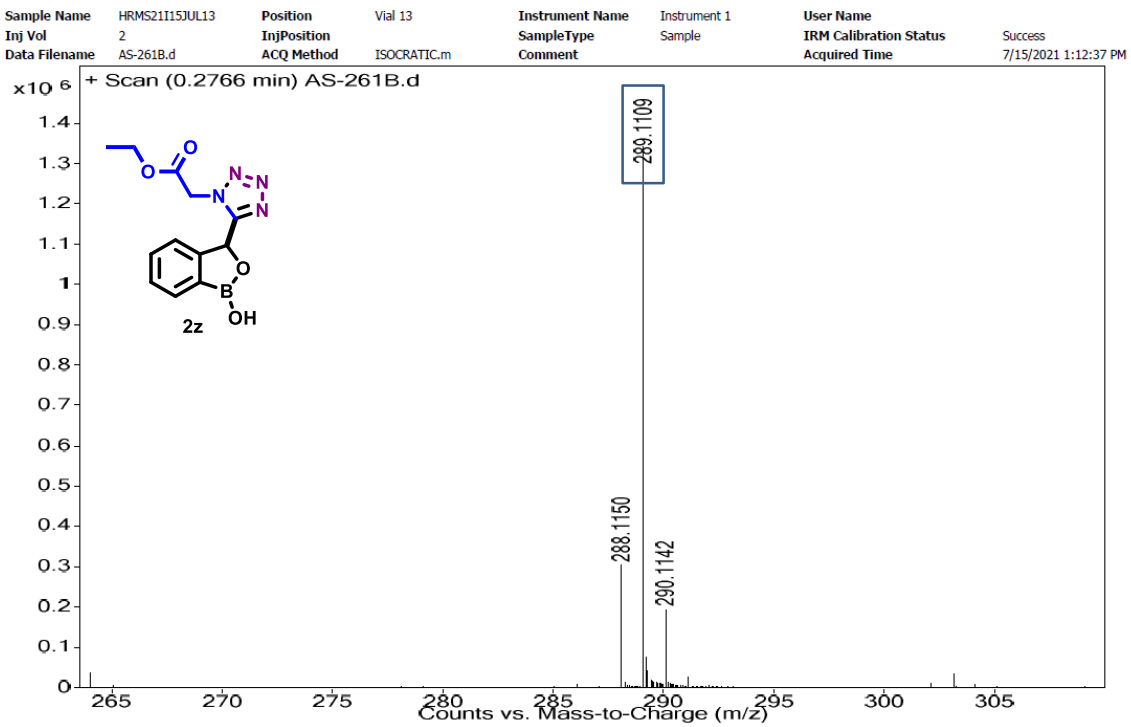


^{1}H NMR (500 MHz, $CDCl_3$):

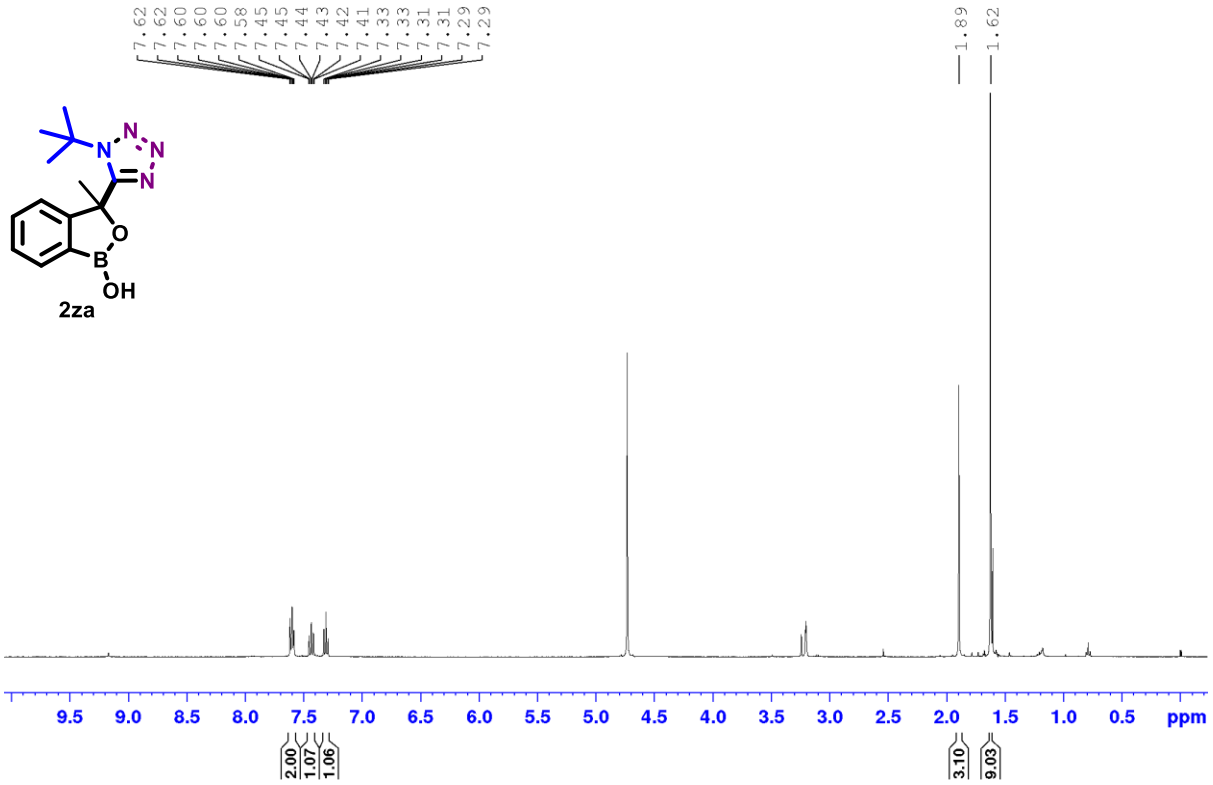


^{13}C NMR (125 MHz, $CDCl_3$):

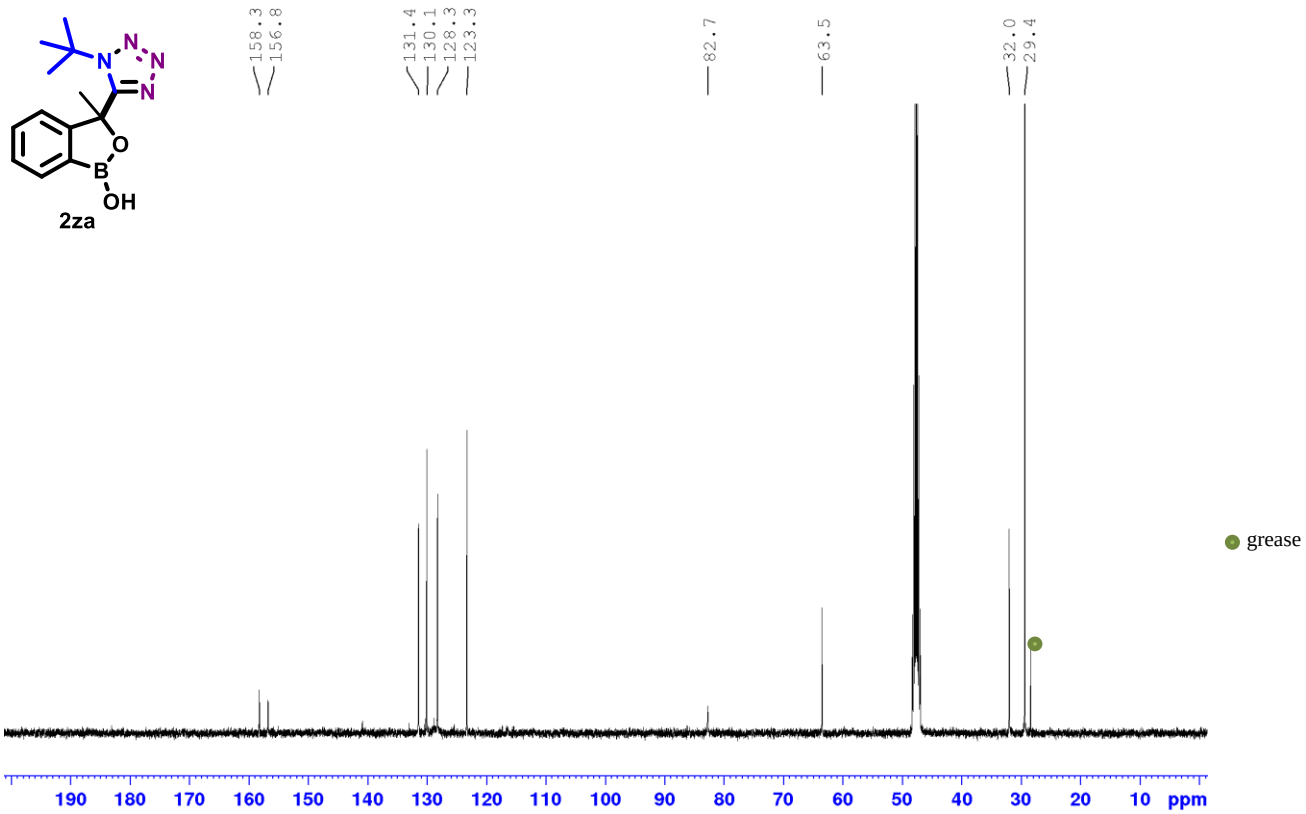


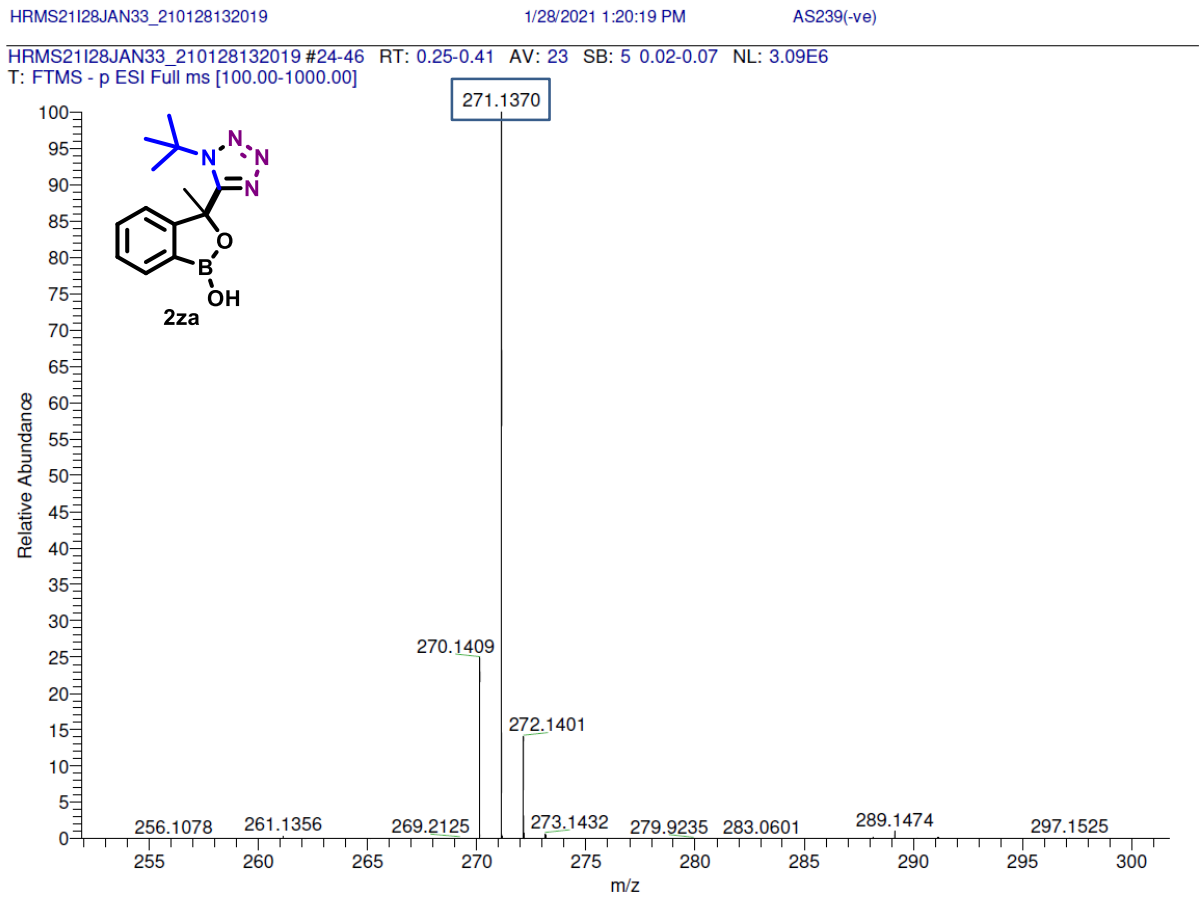


^{1}H NMR (400 MHz, CD_3OD):

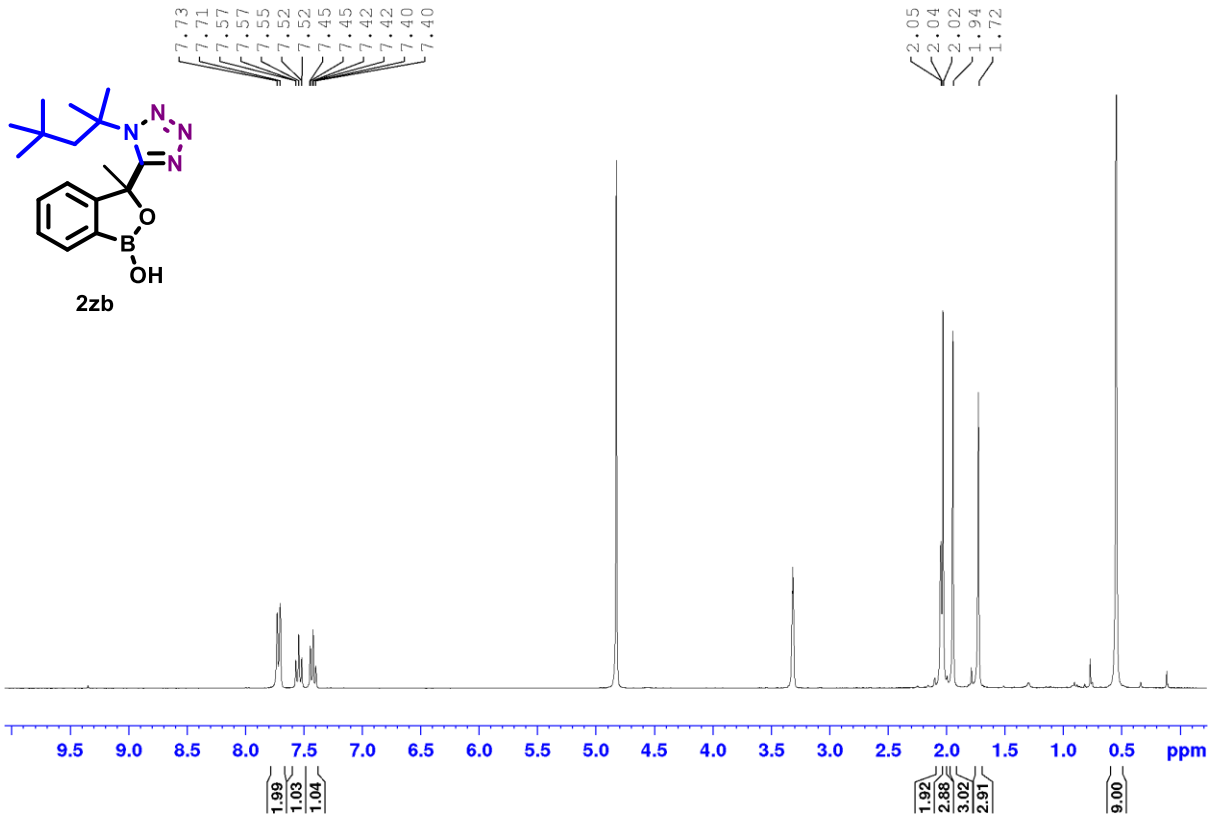


^{13}C NMR (100 MHz, CD_3OD):

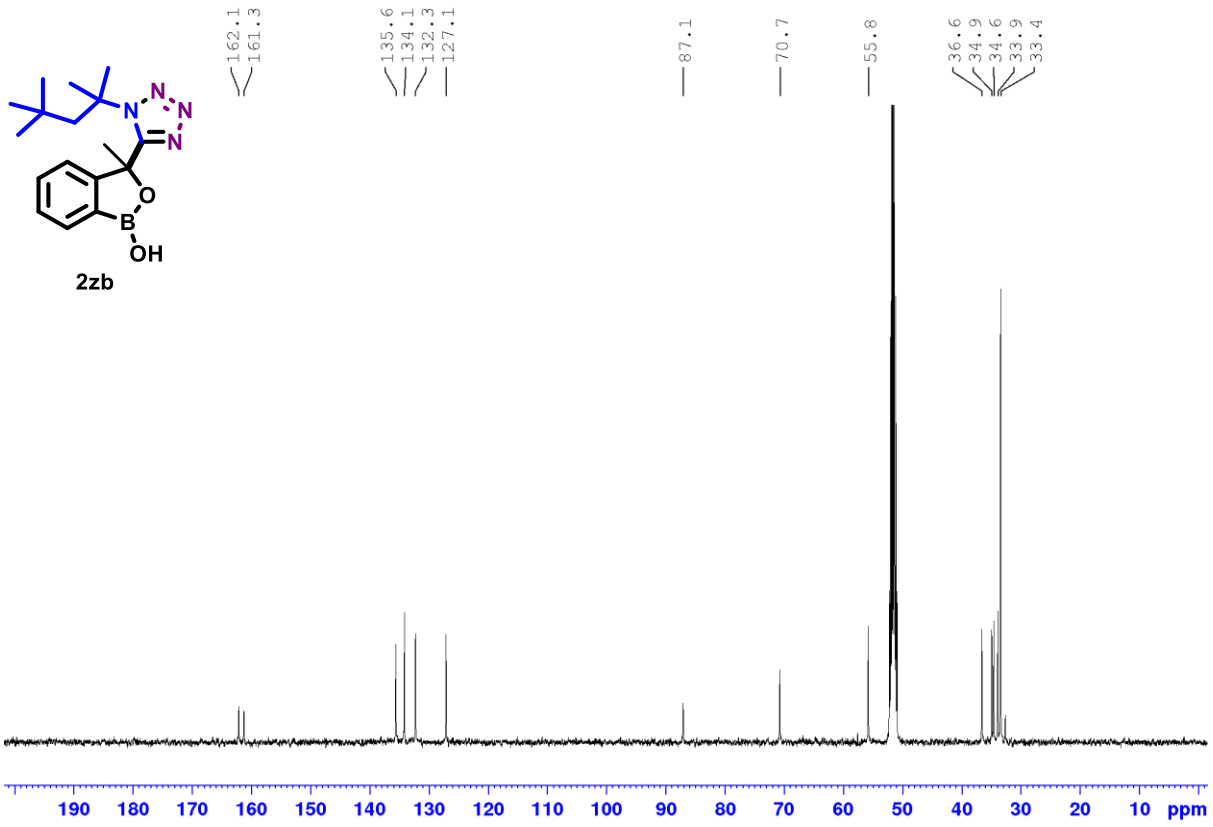




^{1}H NMR (300 MHz, CD_3OD):



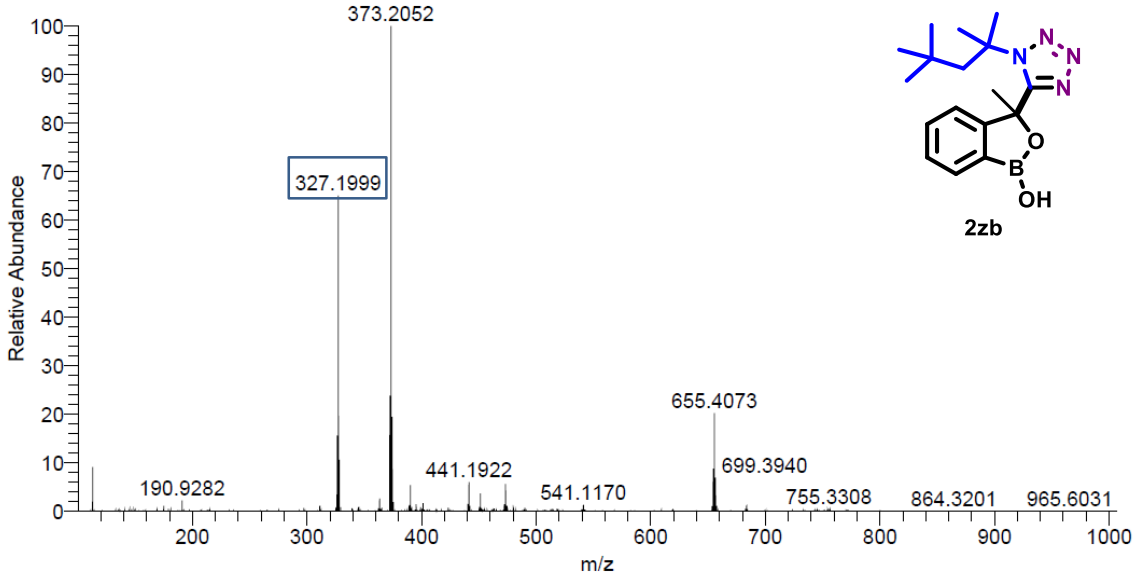
^{13}C NMR (100 MHz, CD_3OD):



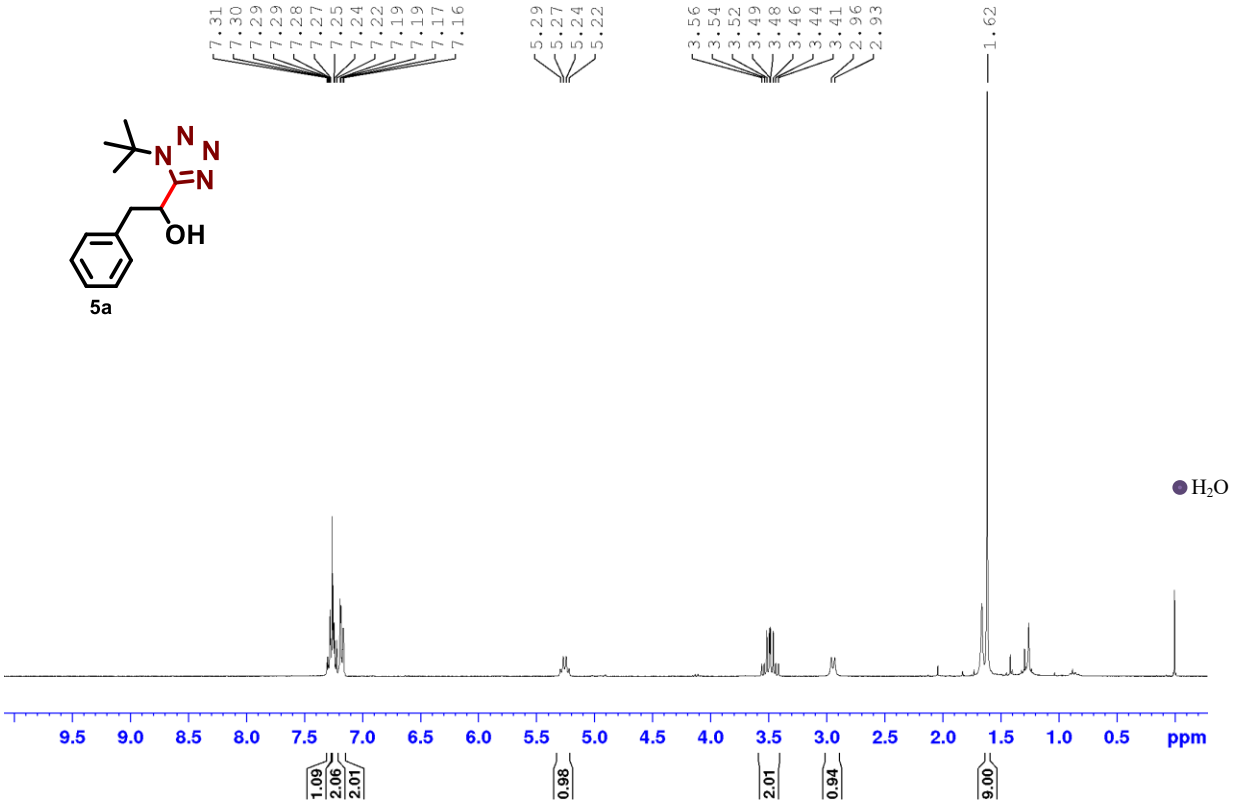
SAIF [HRMS Report]

Data File:	HRMS21I20JAN16	Original Data Path:	D:\INTERNAL NEW\2021\Jan 2021
Sample ID:	AS243(-ve)	Sample Name:	
Acquisition Date:	01/20/21 12:23:59 PM	Run Time(min):	0.00
Vial:	CStk1-01:16	Injection Volume(µl):	1.00

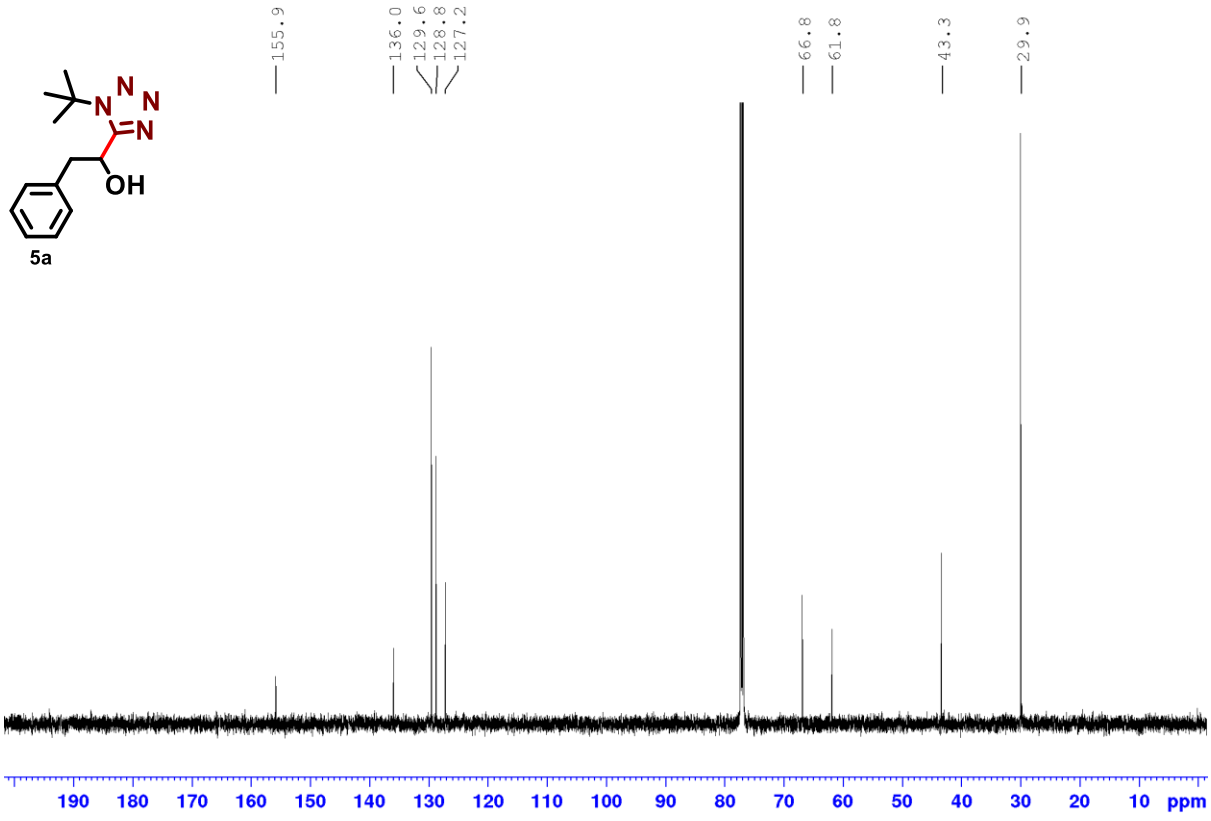
HRMS21I20JAN16 #25-57 RT: 0.25-0.50 AV: 33 SB: 1 0.01 NL: 1.26E6
T: FTMS - p ESI Full ms [100.00-1000.00]

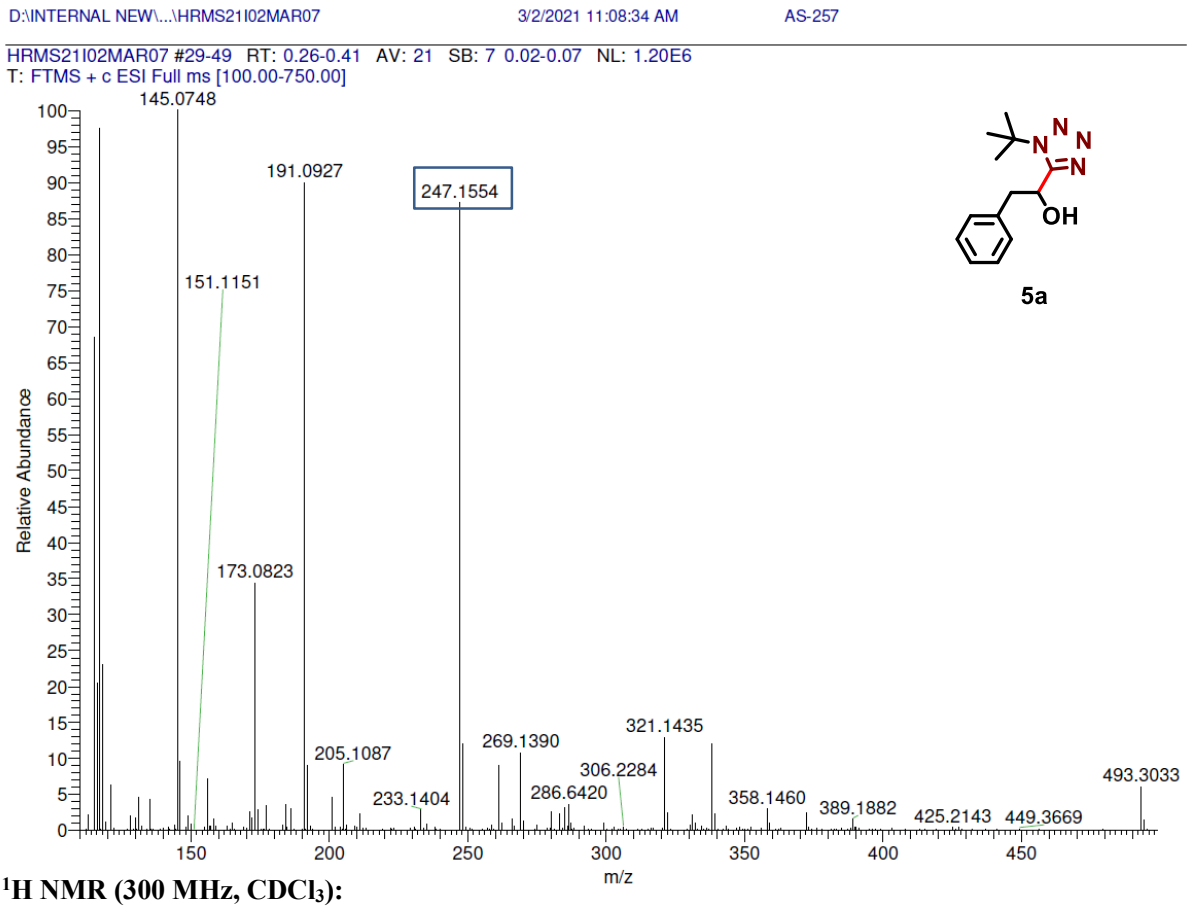


^{1}H NMR (300 MHz, $CDCl_3$):

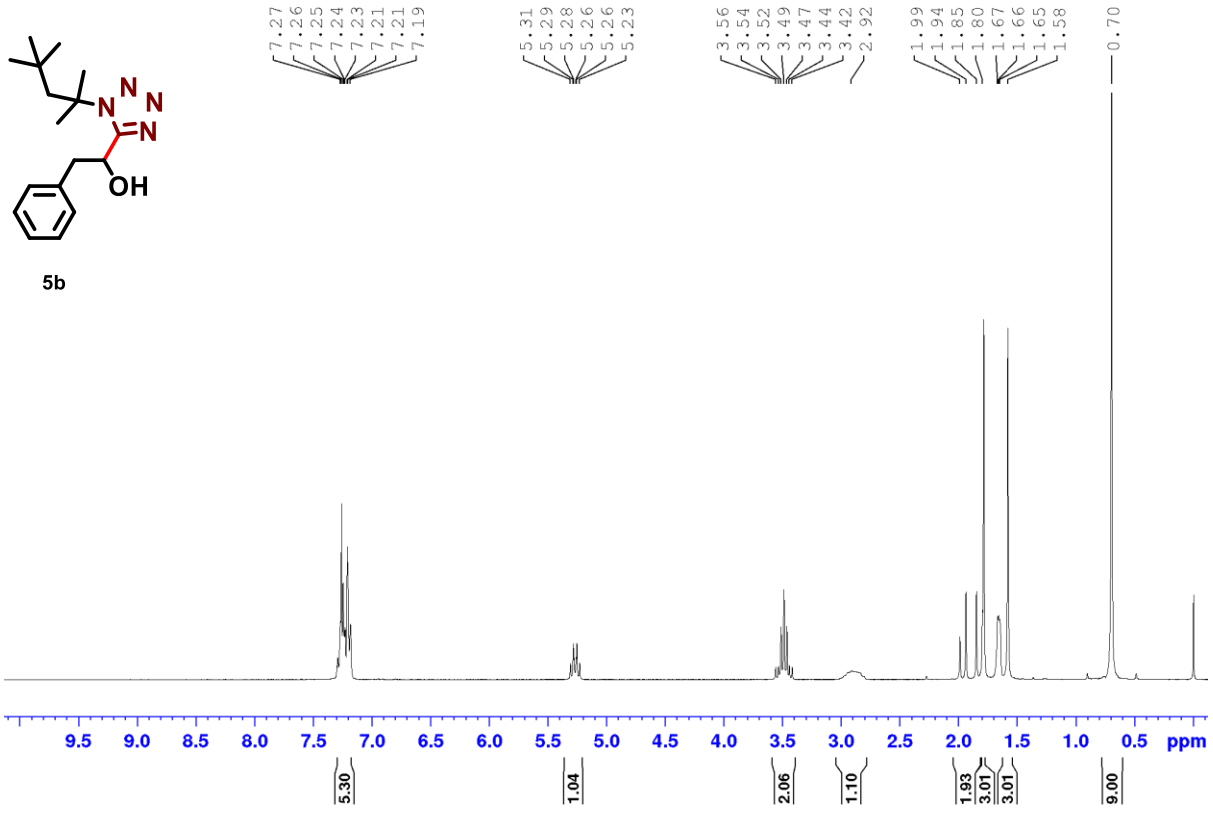


^{13}C NMR (100 MHz, $CDCl_3$):

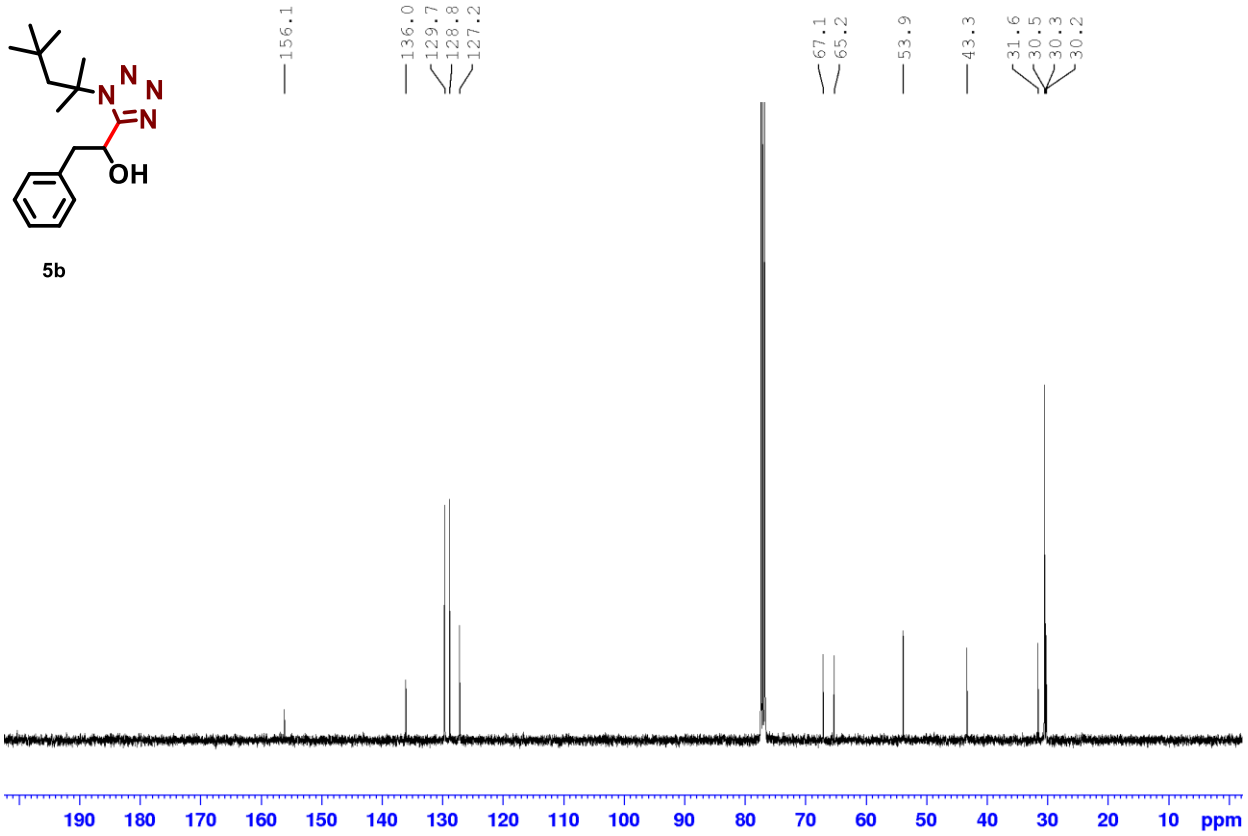




^{1}H NMR (300 MHz, $CDCl_3$):



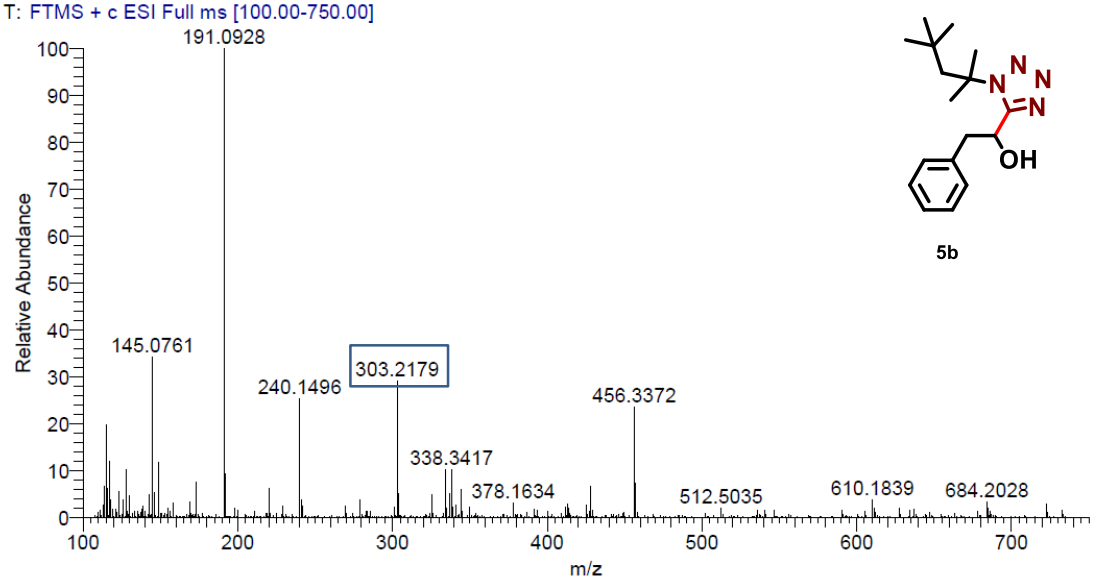
^{13}C NMR (125 MHz, $CDCl_3$):



SAIF [HRMS Report]

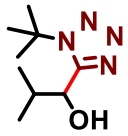
Data File:	HRMS21I25MAR19	Original Data Path:	D:\INTERNAL NEW\2021\Mar 2021
Sample ID:	AS-259	Sample Name:	
Acquisition Date:	03/25/21 11:59:01 AM	Run Time(min):	0.00
Vial:	CStk1-01:19	Injection Volume(µl):	1.00

HRMS21I25MAR19 #32-65 RT: 0.25-0.50 AV: 34 SB: 1 0.01 NL: 5.75E5
T: FTMS + c ESI Full ms [100.00-750.00]



5b

^{1}H NMR (400 MHz, $CDCl_3$):



5c

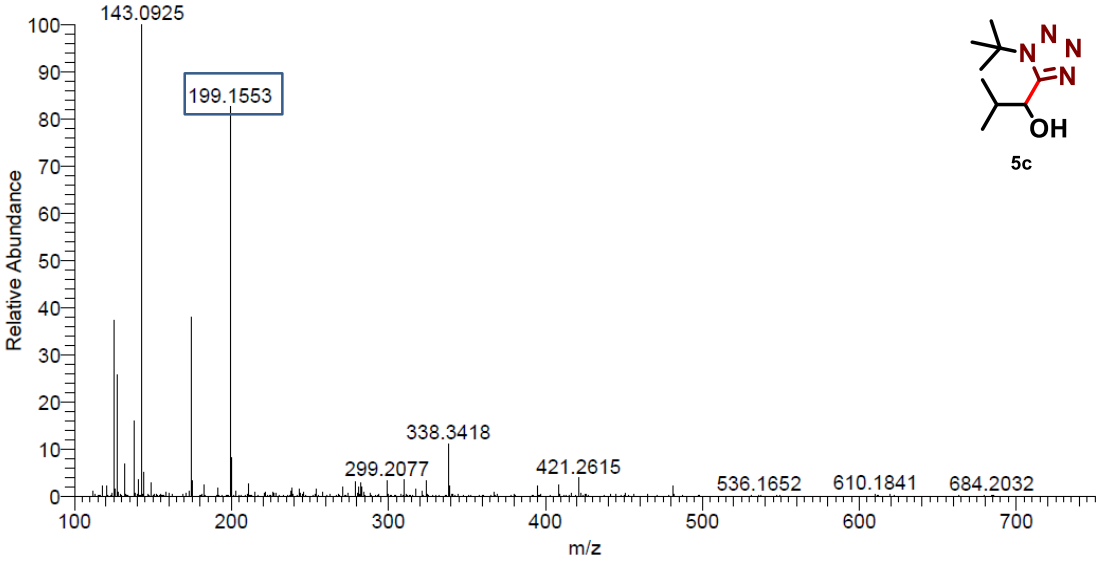
^{13}C NMR (125 MHz, $CDCl_3$):

5c

SAIF [HRMS Report]

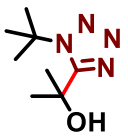
Data File:	HRMS21I02MAR06	Original Data Path:	D:\INTERNAL NEW\2021\Mar 2021
Sample ID:	AS-268	Sample Name:	
Acquisition Date:	03/02/21 11:06:37 AM	Run Time(min):	0.00
Vial:	CStk1-01:6	Injection Volume(µl):	1.00

HRMS21I02MAR06 #29-60 RT: 0.25-0.50 AV: 32 SB: 1 0.01 NL: 1.24E6
T: FTMS + c ESI Full ms [100.00-750.00]



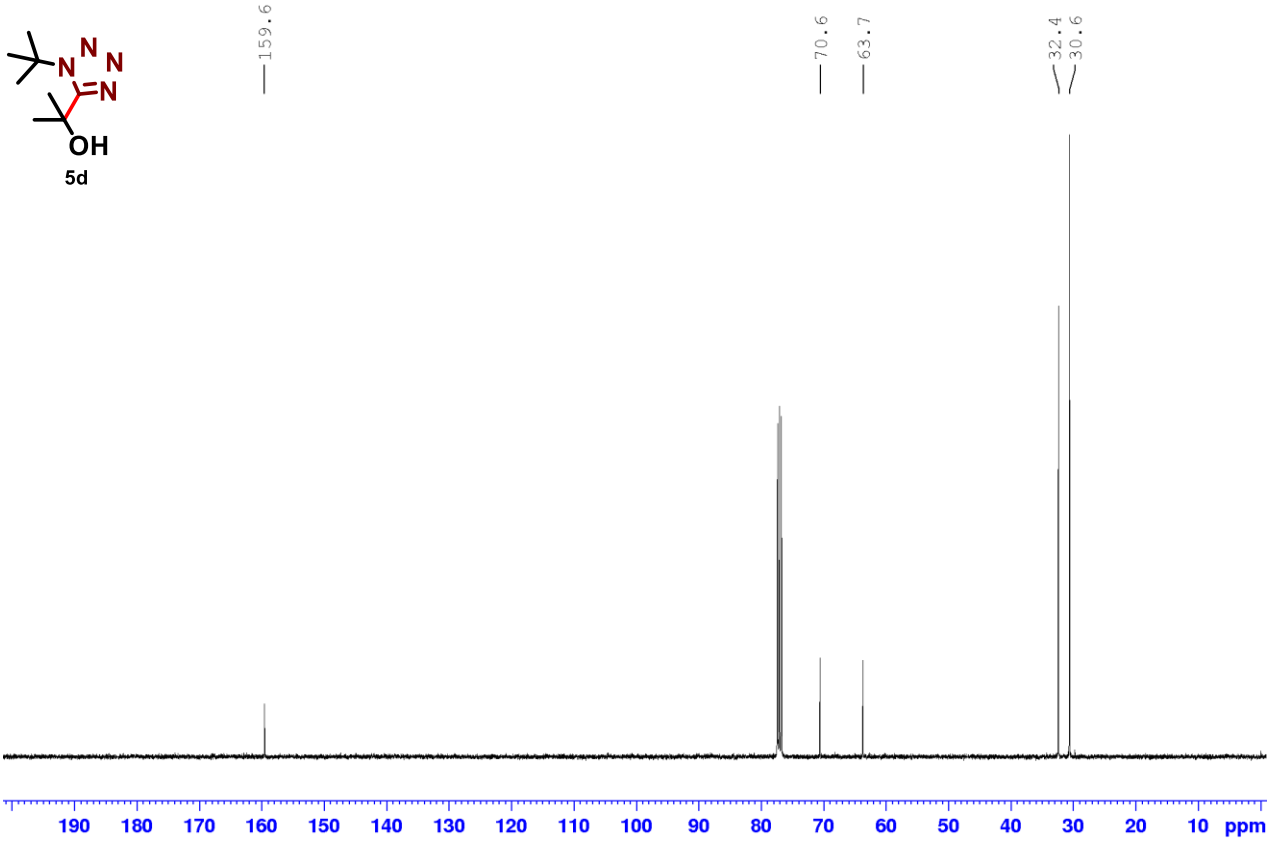
5c

^{1}H NMR (300 MHz, $CDCl_3$):



5d

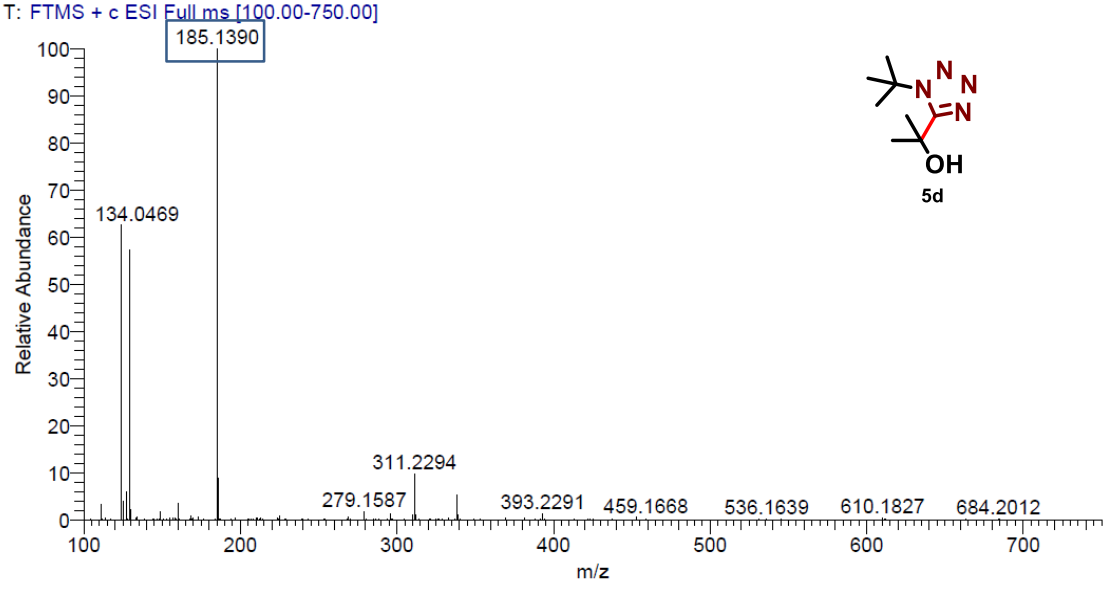
^{13}C NMR (100 MHz, $CDCl_3$):



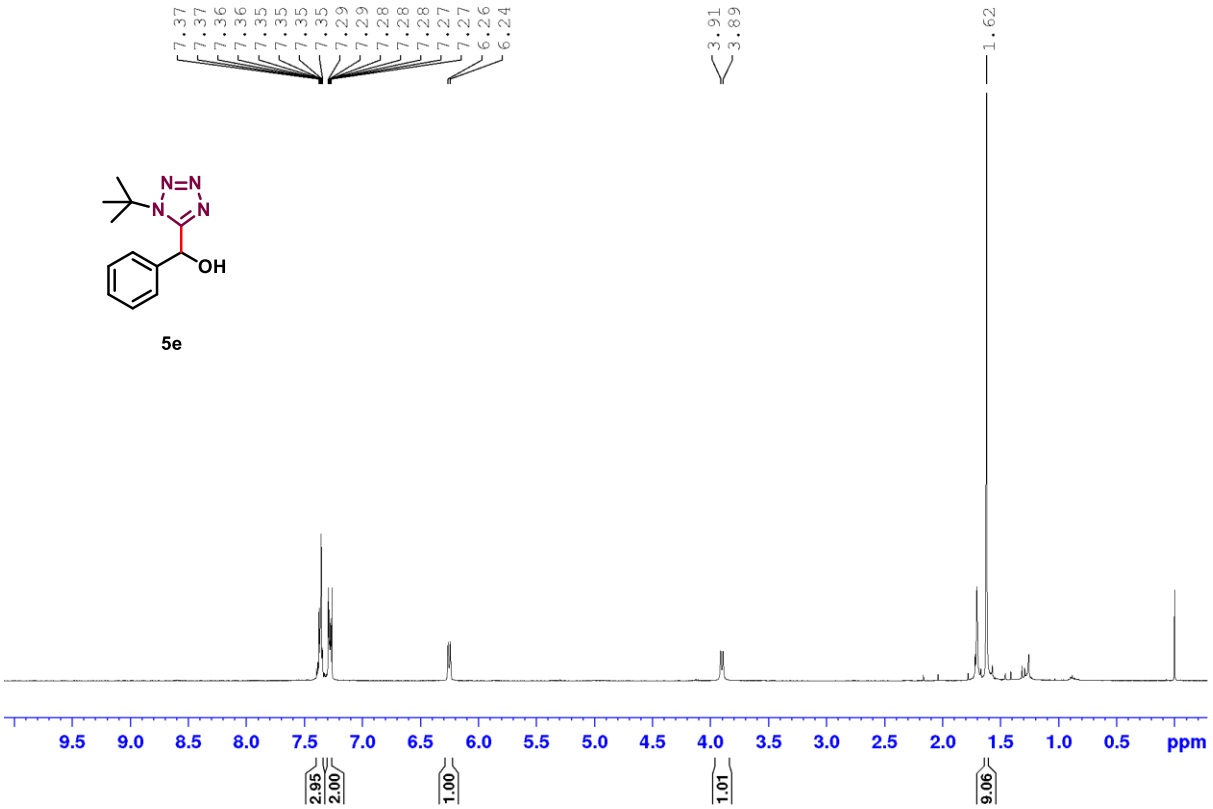
SAIF [HRMS Report]

Data File:	HRMS21I04MAR06	Original Data Path:	D:\INTERNAL NEW\2021\Mar 2021
Sample ID:	AS-271	Sample Name:	
Acquisition Date:	03/04/21 11:26:22 AM	Run Time(min):	0.00
Vial:	CStk1-01:6	Injection Volume(µl):	1.00

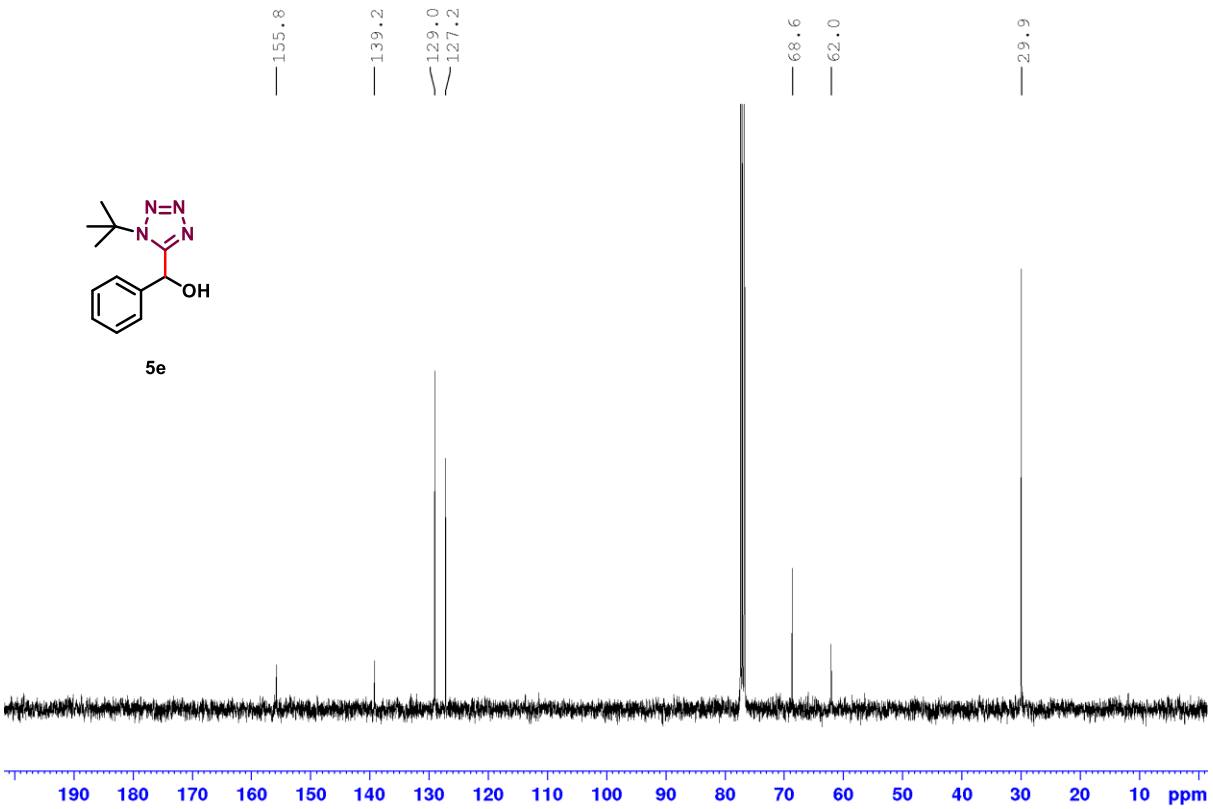
HRMS21I04MAR06 #28-58 RT: 0.25-0.50 AV: 31 SB: 1 0.01 NL: 1.34E6
T: FTMS + c ESI Full ms [100.00-750.00]



^{1}H NMR (400 MHz, $CDCl_3$):



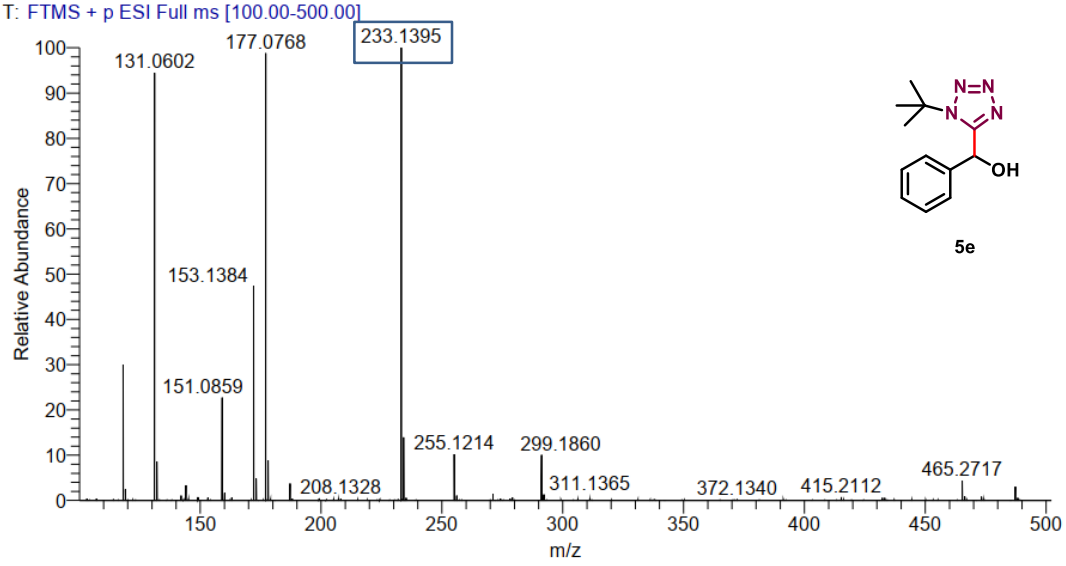
^{13}C NMR (100 MHz, $CDCl_3$):



SAIF [HRMS Report]

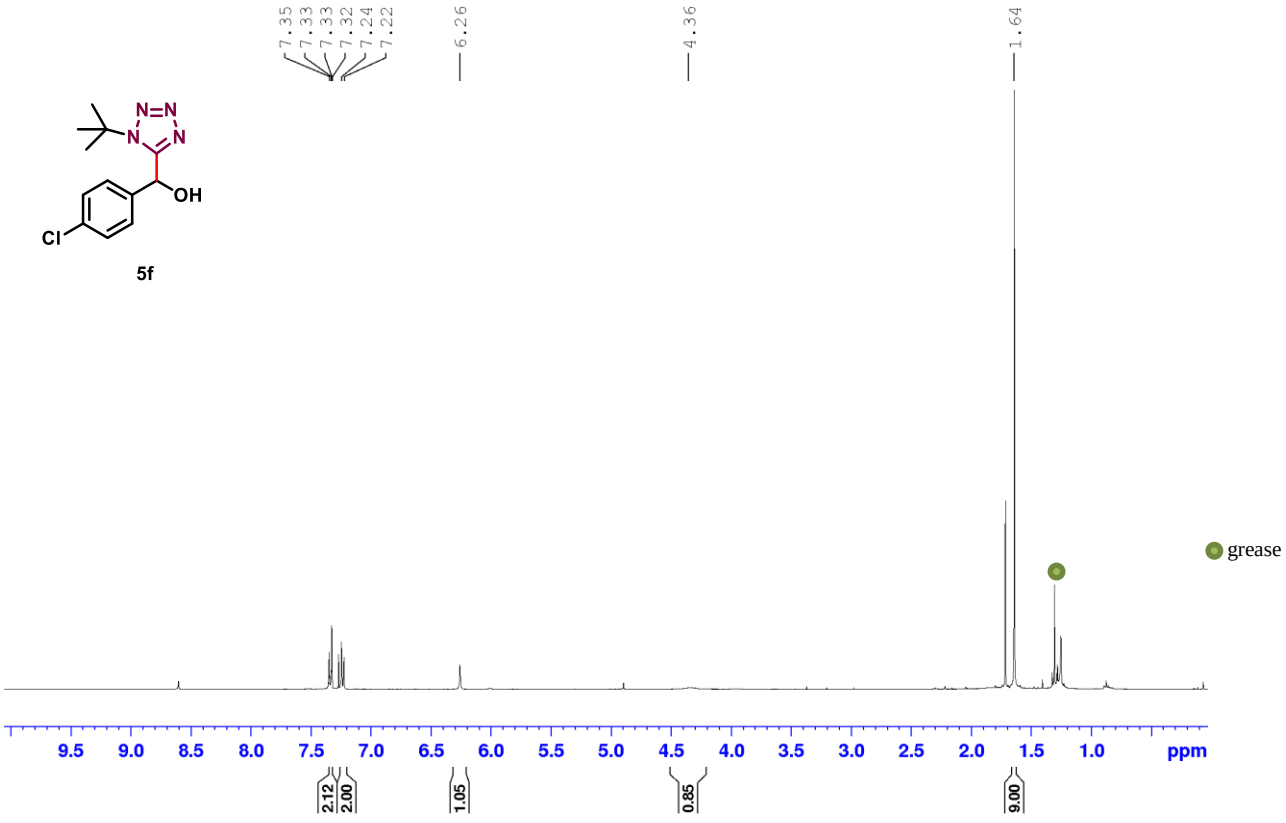
Data File:	HRMS20I09JUL15	Original Data Path:	D:\INTERNAL NEW\2020\July 2020
Sample ID:	AS-128	Sample Name:	
Acquisition Date:	07/09/20 11:05:42 AM	Run Time(min):	0.00
Vial:	CStk1-01:15	Injection Volume(µl):	1.00

HRMS20I09JUL15 #12-23 RT: 0.12-0.21 AV: 12 SB: 1 0.01 NL: 1.21E6
T: FTMS + p ESI Full ms [100.00-500.00]



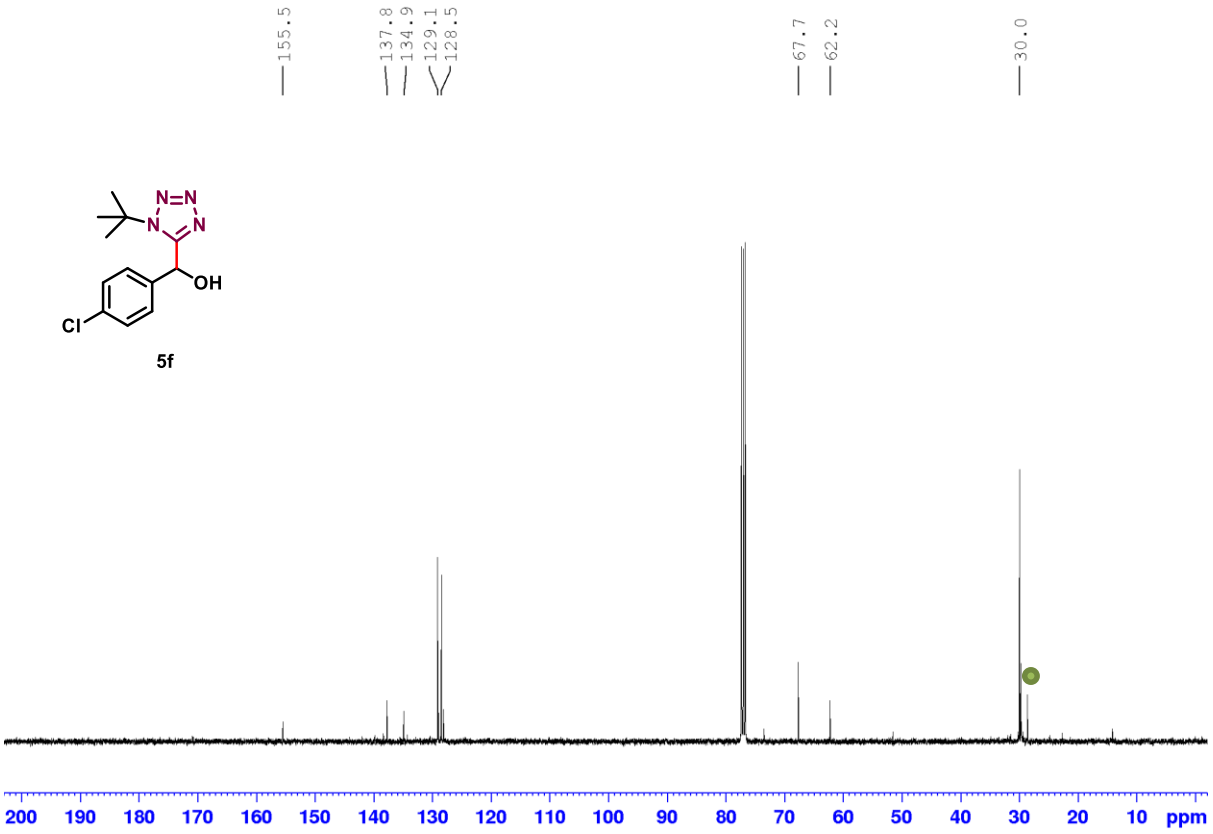
5e

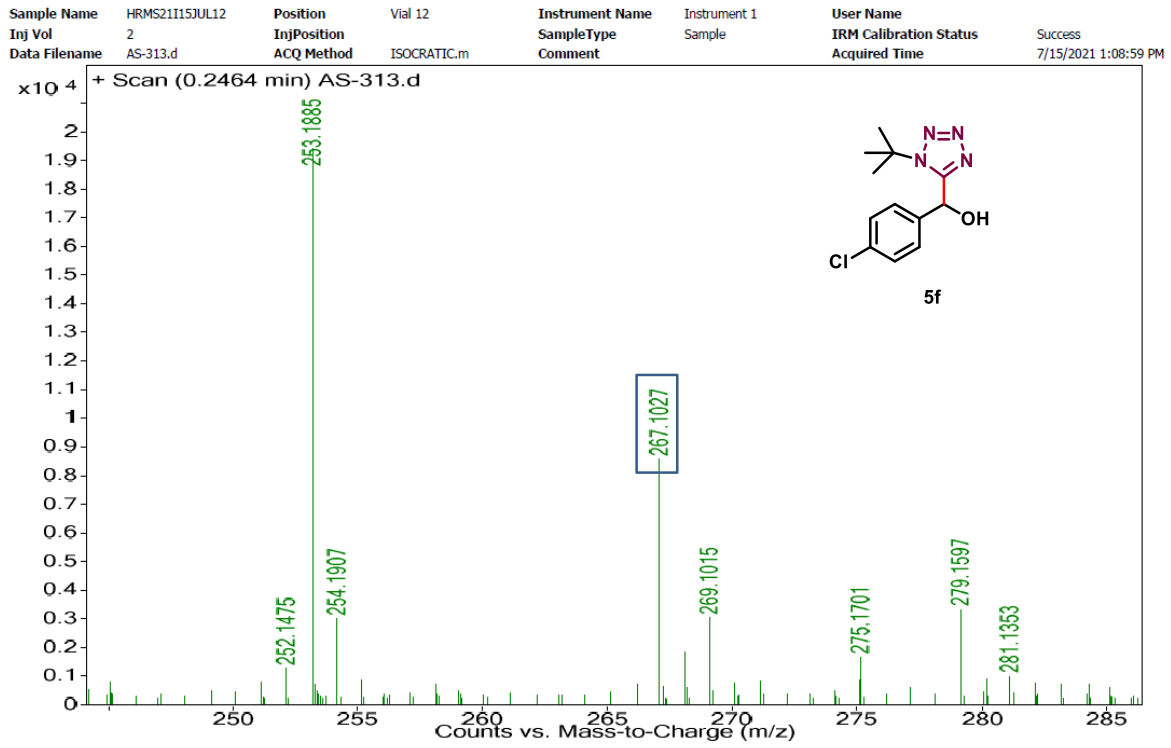
^{1}H NMR (400 MHz, $CDCl_3$):



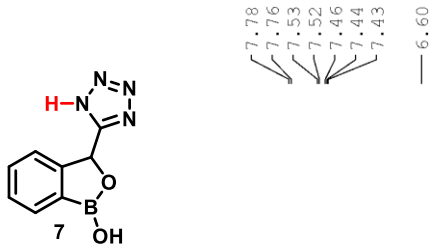
5f

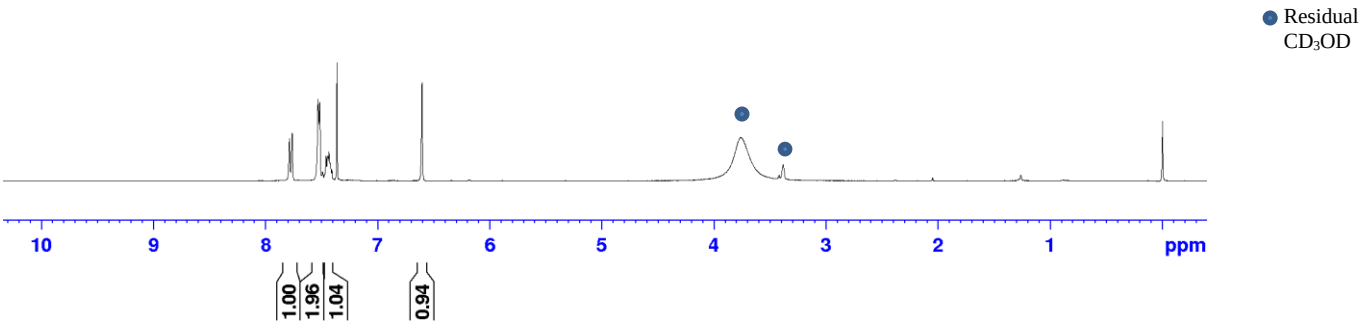
^{13}C NMR (100 MHz, $CDCl_3$):



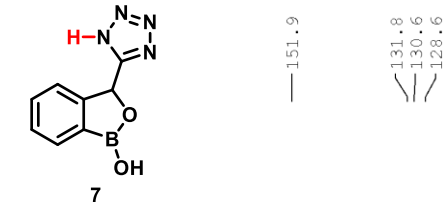


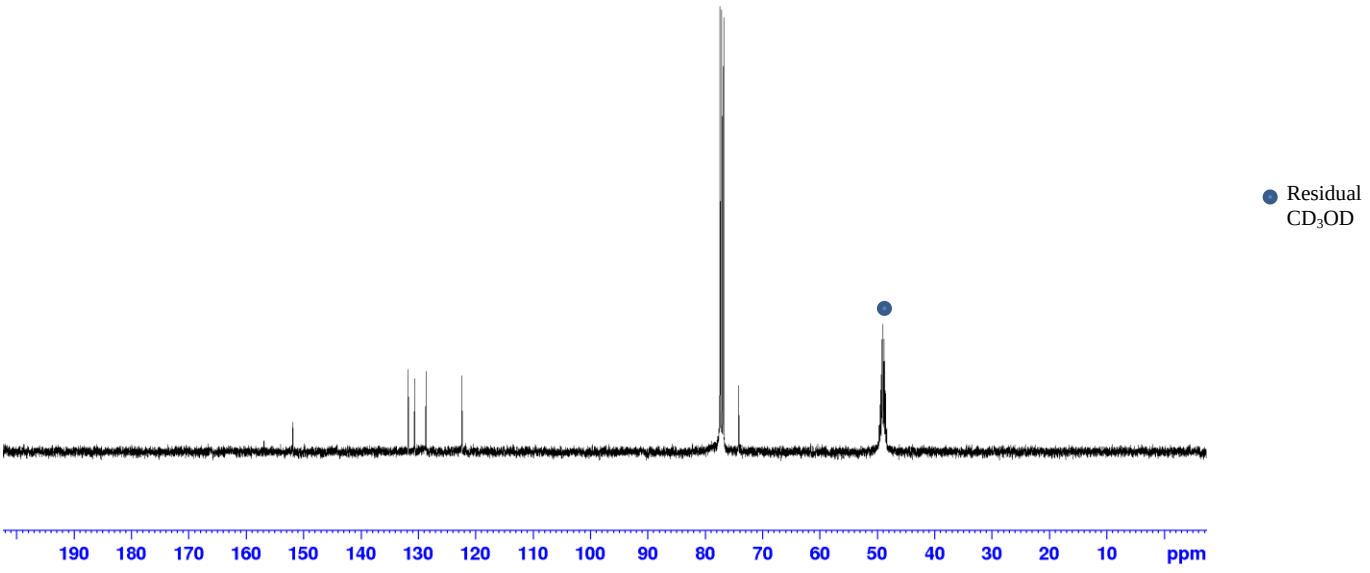
^{1}H NMR (300 MHz, $CDCl_3$+CD_3OD):

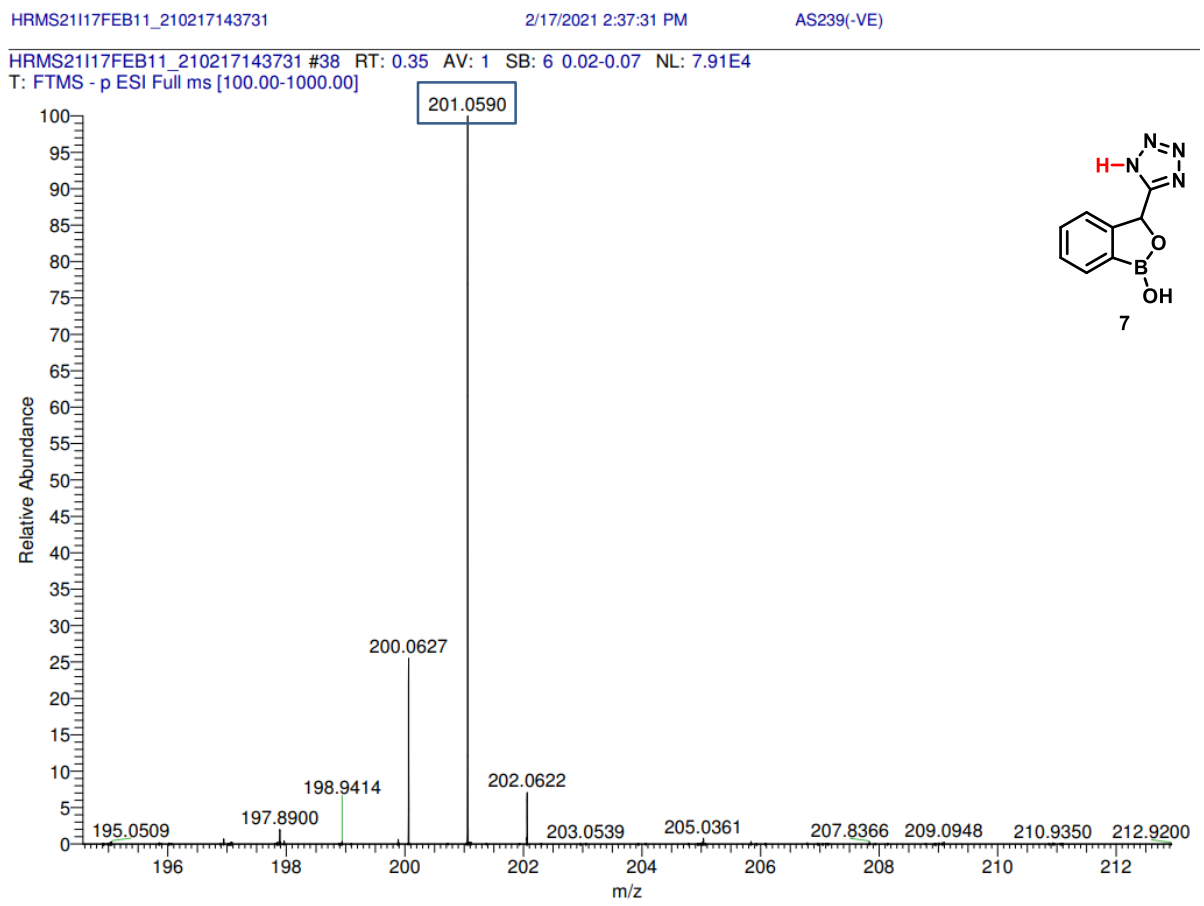




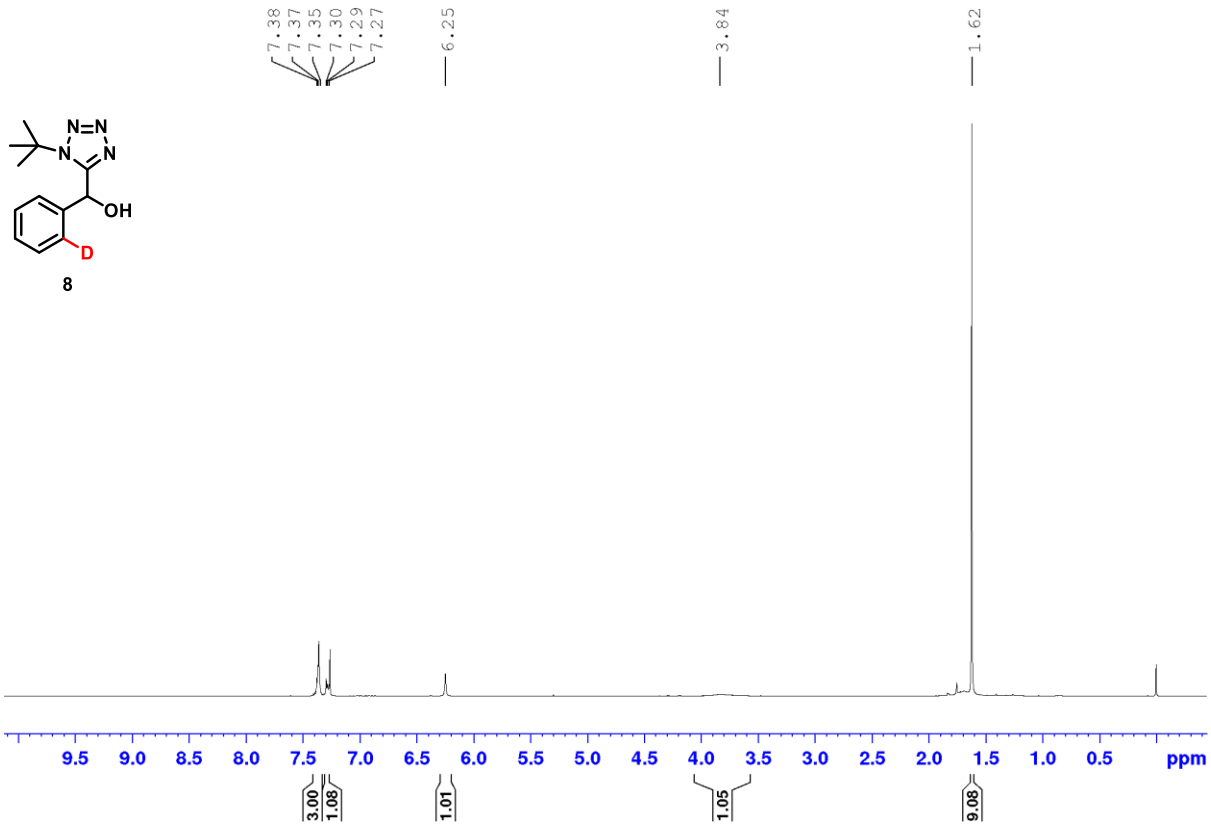
^{13}C NMR (125 MHz, $CDCl_3$+CD_3OD):



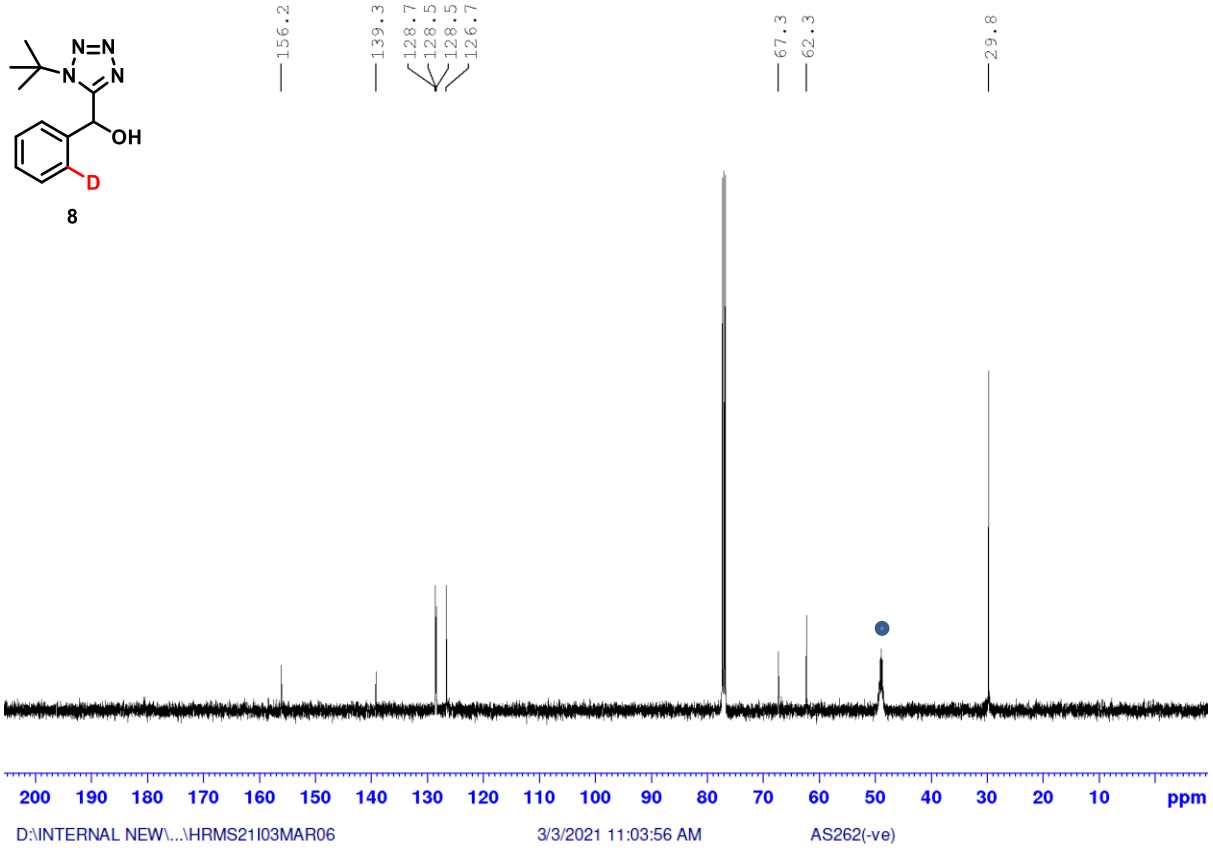


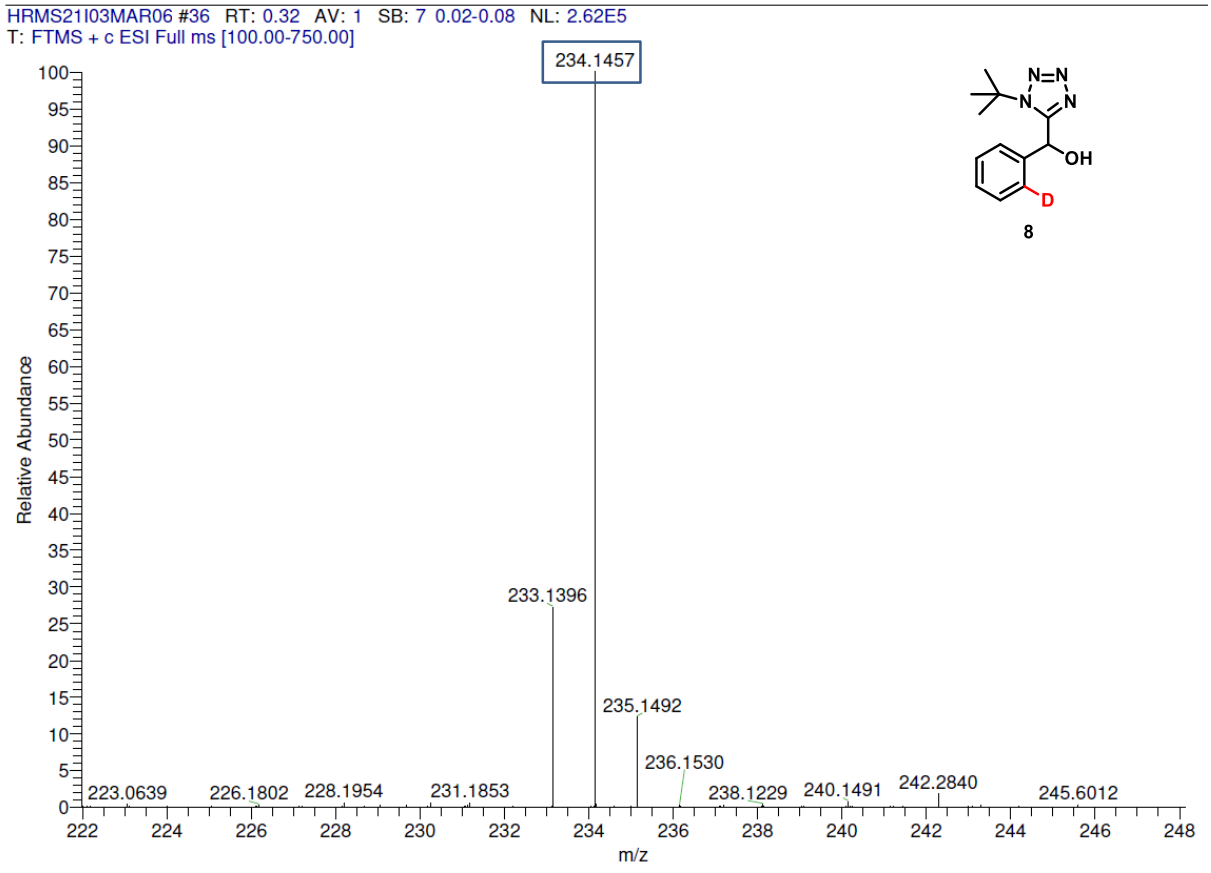


^{1}H NMR (300 MHz, $CDCl_3$):

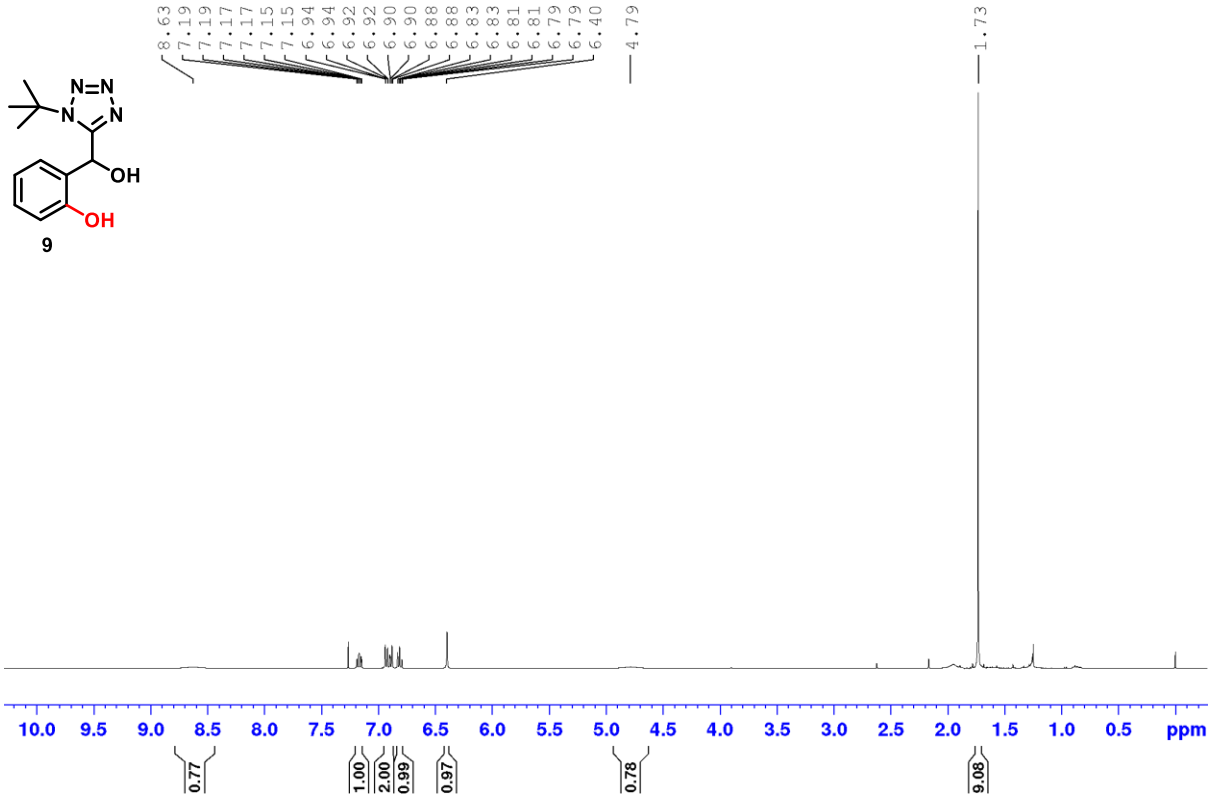


^{13}C NMR (100 MHz, CDCl3):

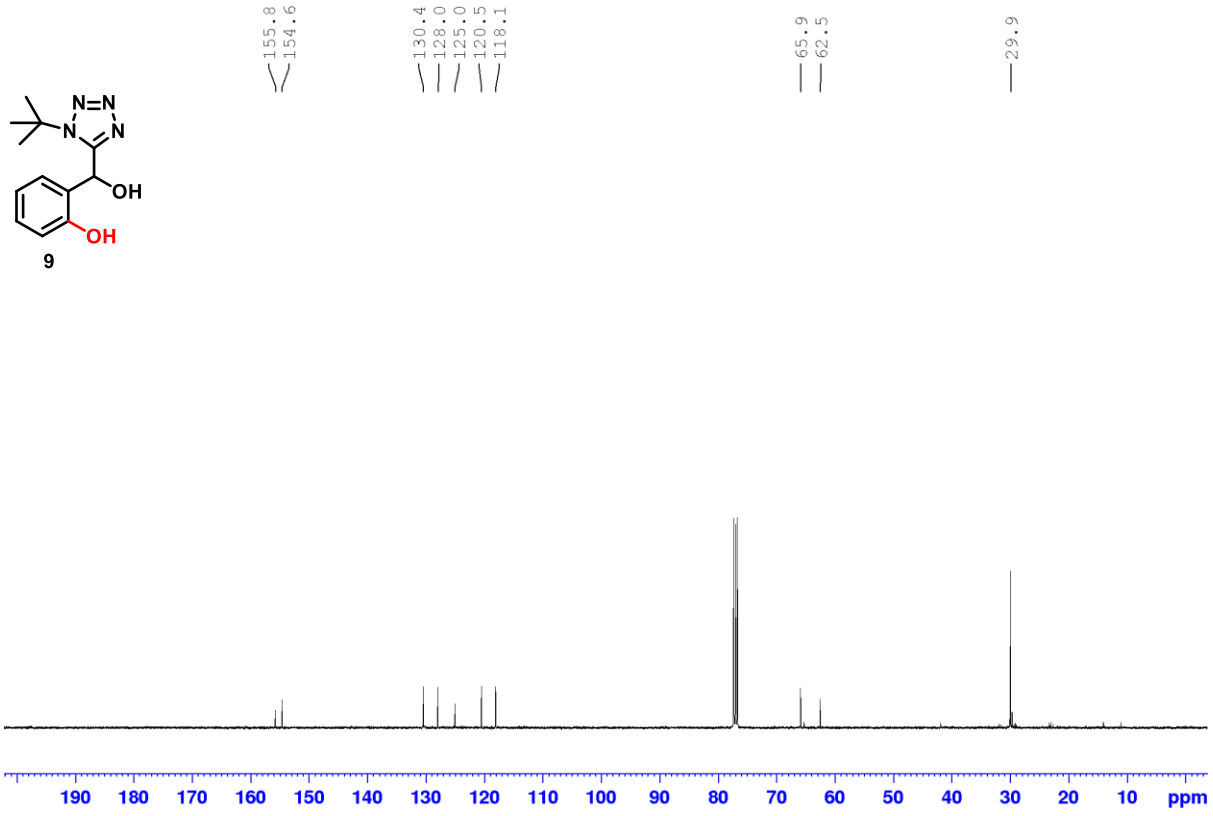




^{1}H NMR (400 MHz, $CDCl_3$):



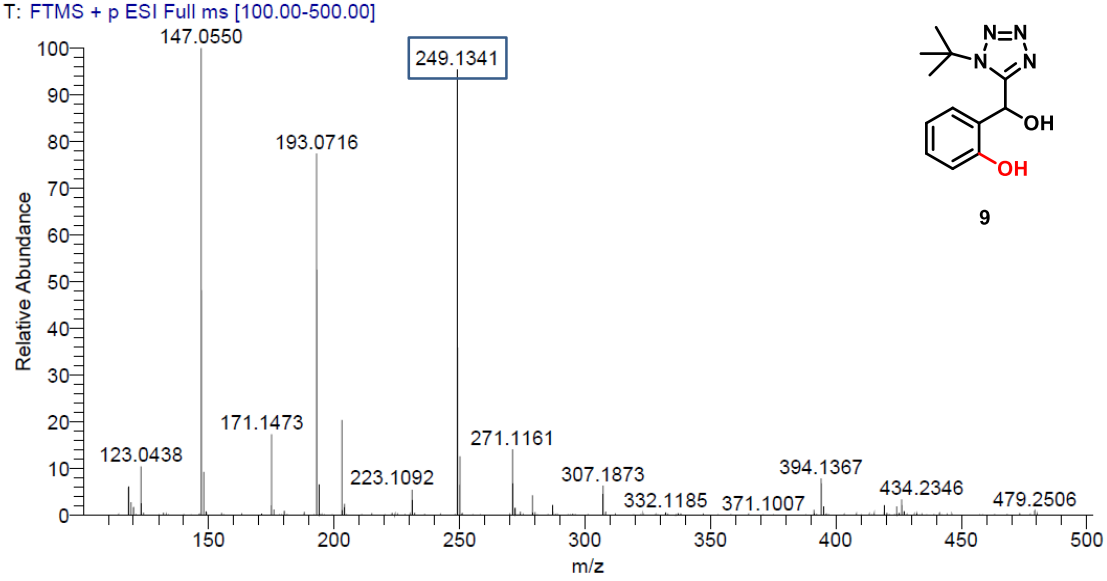
^{13}C NMR (100 MHz, $CDCl_3$):



SAIF [HRMS Report]

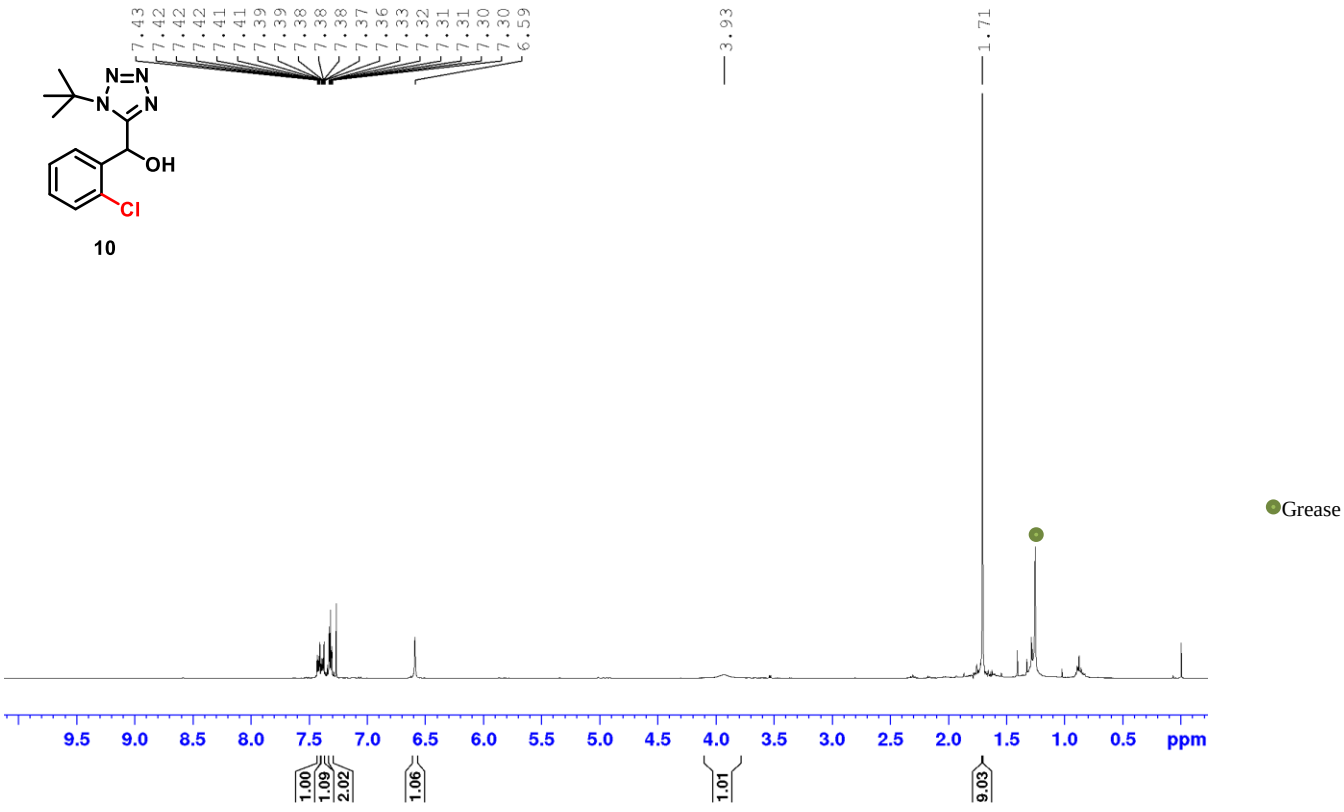
Data File:	HRMS20I02JUL21	Original Data Path:	D:\INTERNAL NEW\2020\June 2020
Sample ID:	AS-85	Sample Name:	
Acquisition Date:	07/02/20 11:28:53 AM	Run Time(min):	0.00
Vial:	CStk1-01:21	Injection Volume(µl):	1.00

HRMS20I02JUL21 #12-24 RT: 0.11-0.21 AV: 13 SB: 1 0.01 NL: 1.66E6
T: FTMS + p ESI Full ms [100.00-500.00]



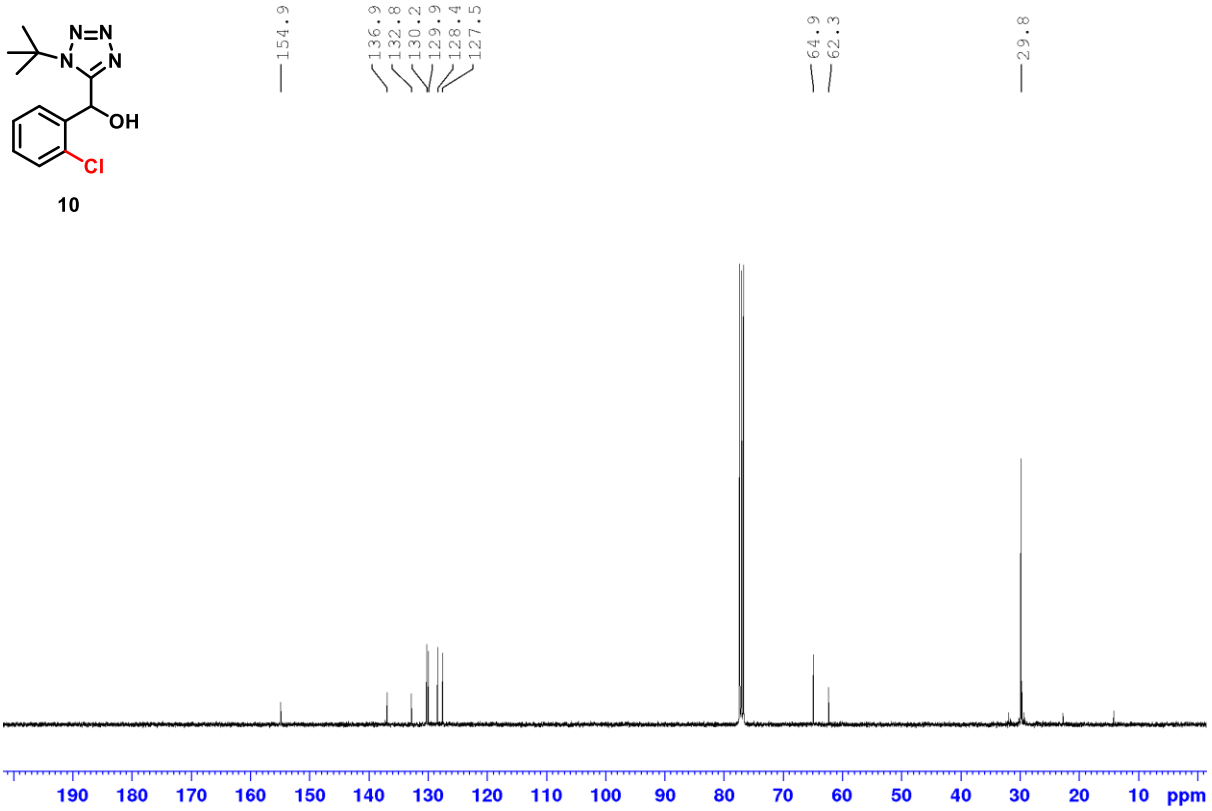
9

^{1}H NMR (400 MHz, $CDCl_3$):



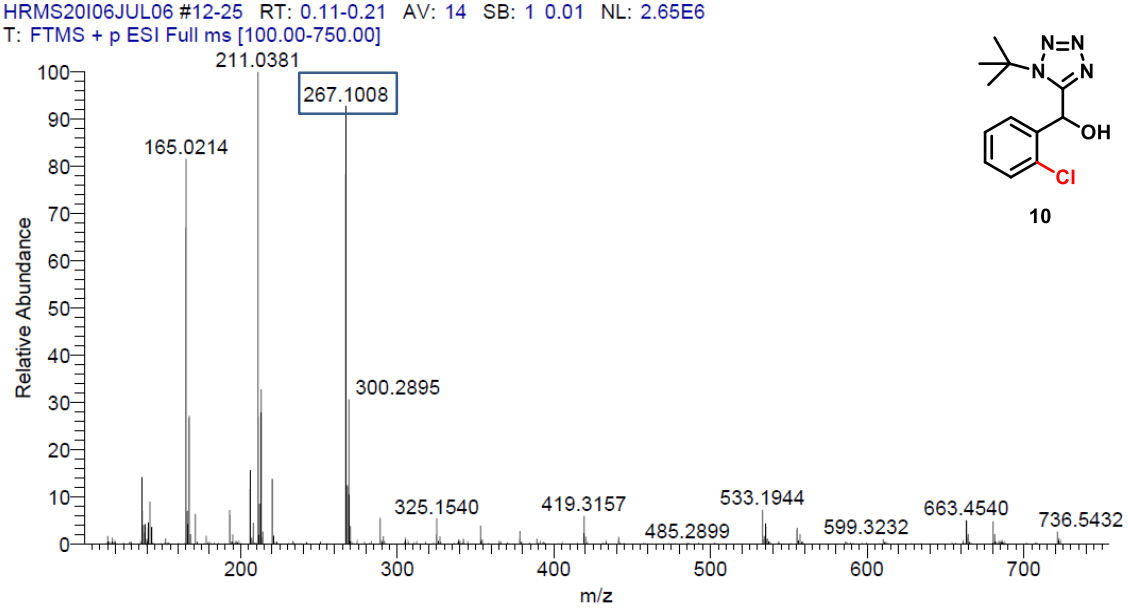
10

^{13}C NMR (100 MHz, $CDCl_3$):

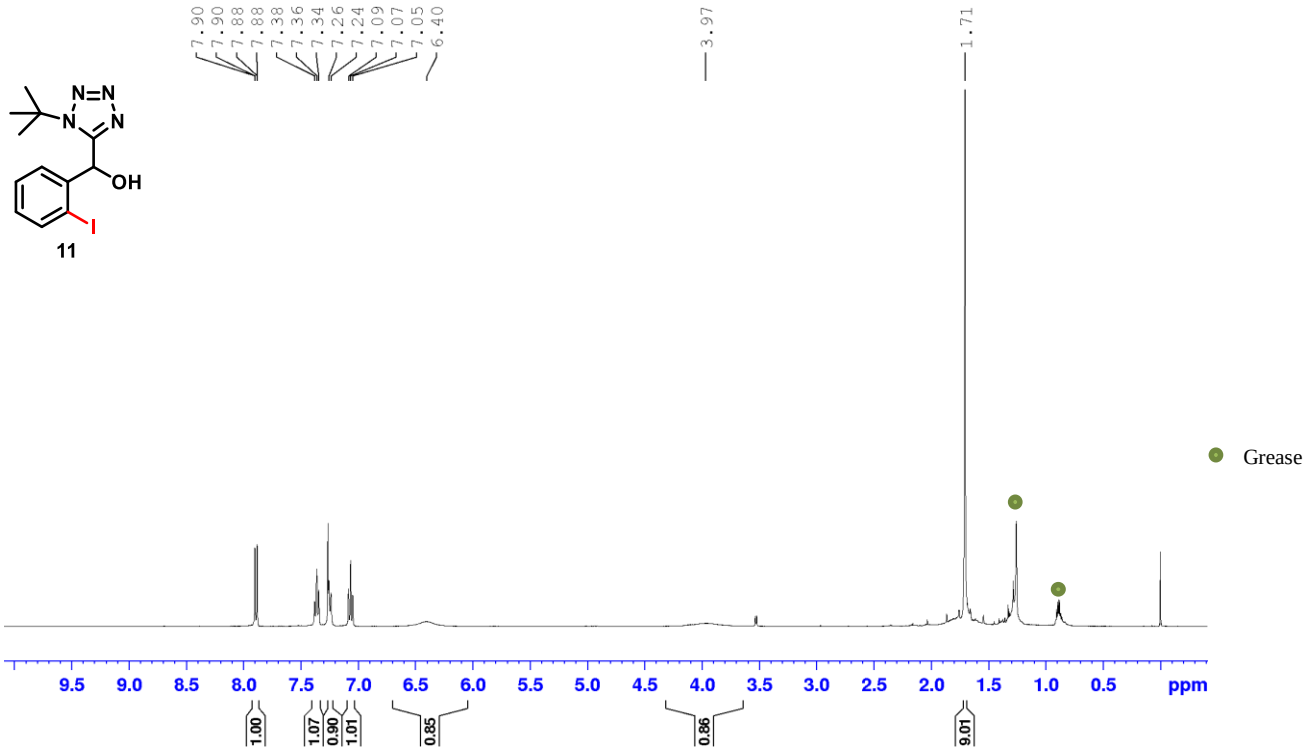


SAIF [HRMS Report]

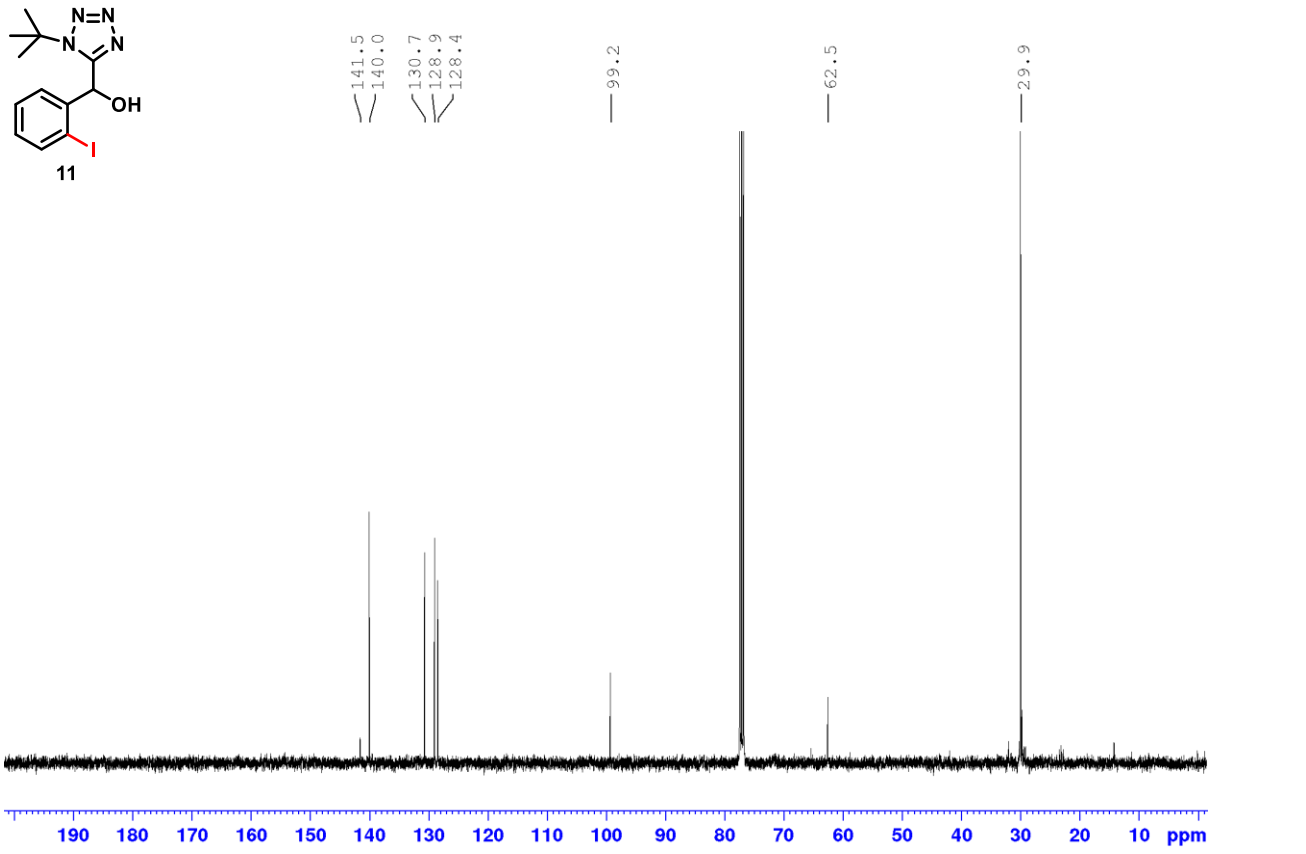
Data File:	HRMS20I06JUL06	Original Data Path:	D:\INTERNAL NEW\2020\July 2020
Sample ID:	as-114	Sample Name:	
Acquisition Date:	07/06/20 12:07:18 PM	Run Time(min):	0.00
Vial:	CStk1-01:6	Injection Volume(µl):	1.00



^{1}H NMR (400 MHz, $CDCl_3$):



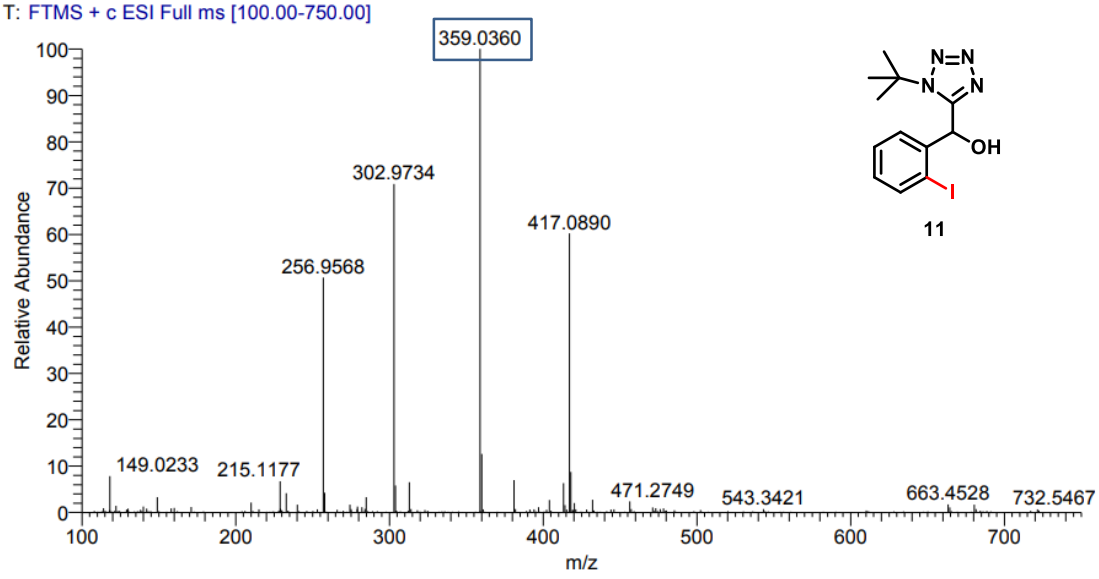
^{13}C NMR (100 MHz, $CDCl_3$):



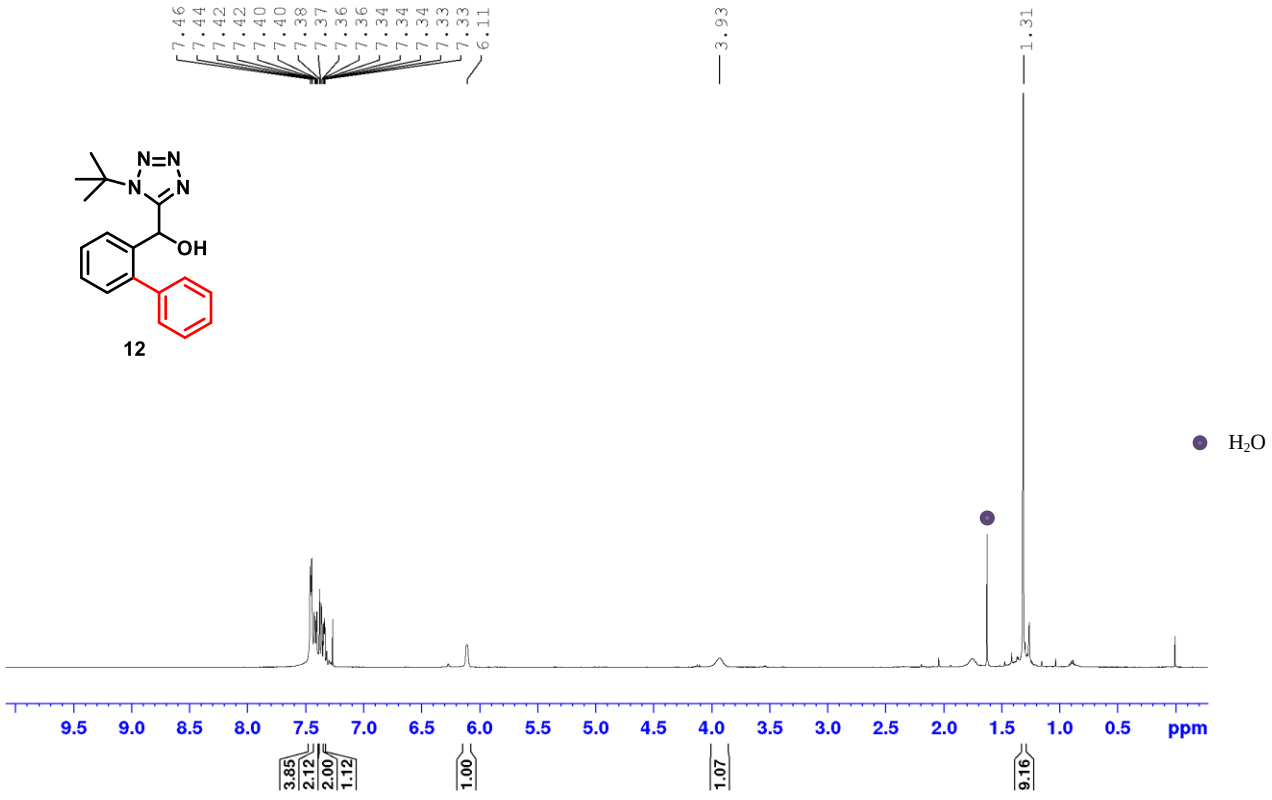
SAIF [HRMS Report]

Data File:	HRMS20I20JUL08	Original Data Path:	D:\INTERNAL NEW\2020\July 2020
Sample ID:	as-134	Sample Name:	
Acquisition Date:	07/20/20 11:45:17 AM	Run Time(min):	0.00
Vial:	CStk1-01:8	Injection Volume(µl):	1.00

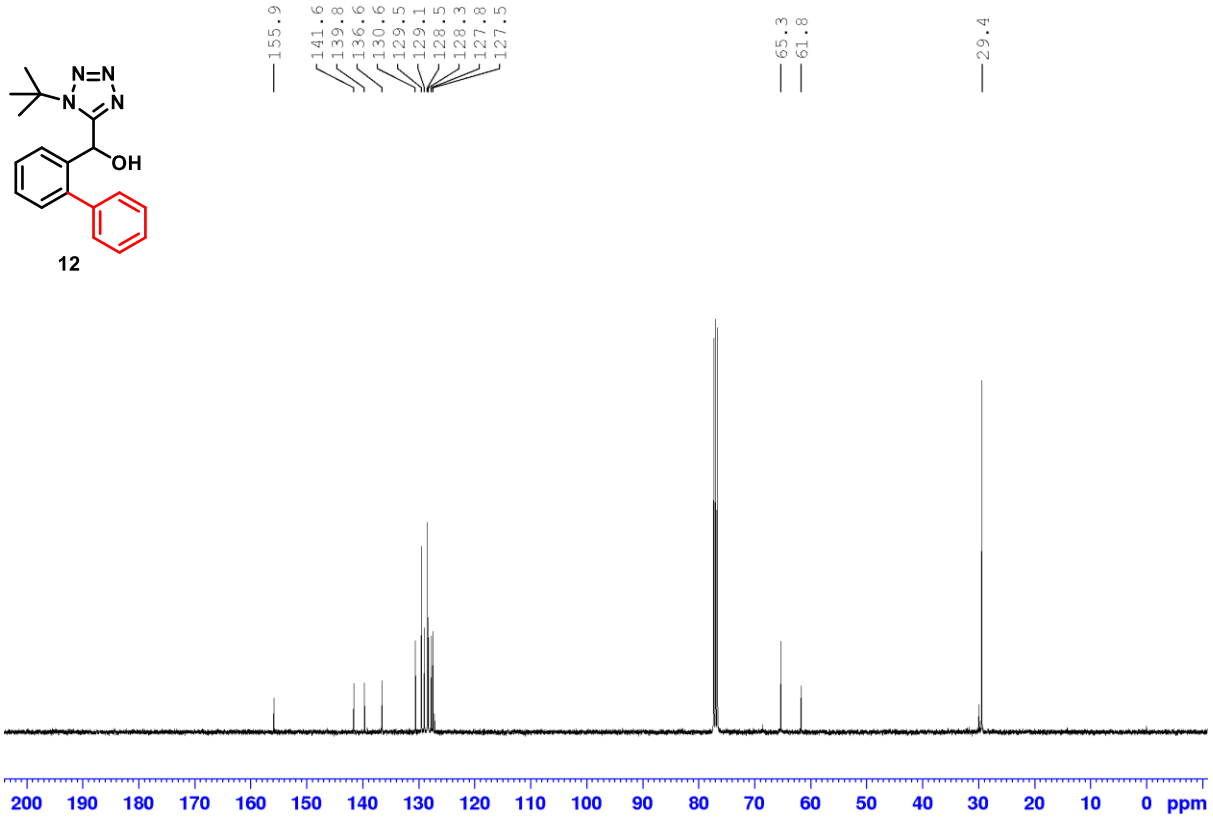
HRMS20I20JUL08 #12-23 RT: 0.11-0.21 AV: 12 SB: 1 0.01 NL: 5.06E5
T: FTMS + c ESI Full ms [100.00-750.00]



^{1}H NMR (400 MHz, $CDCl_3$):



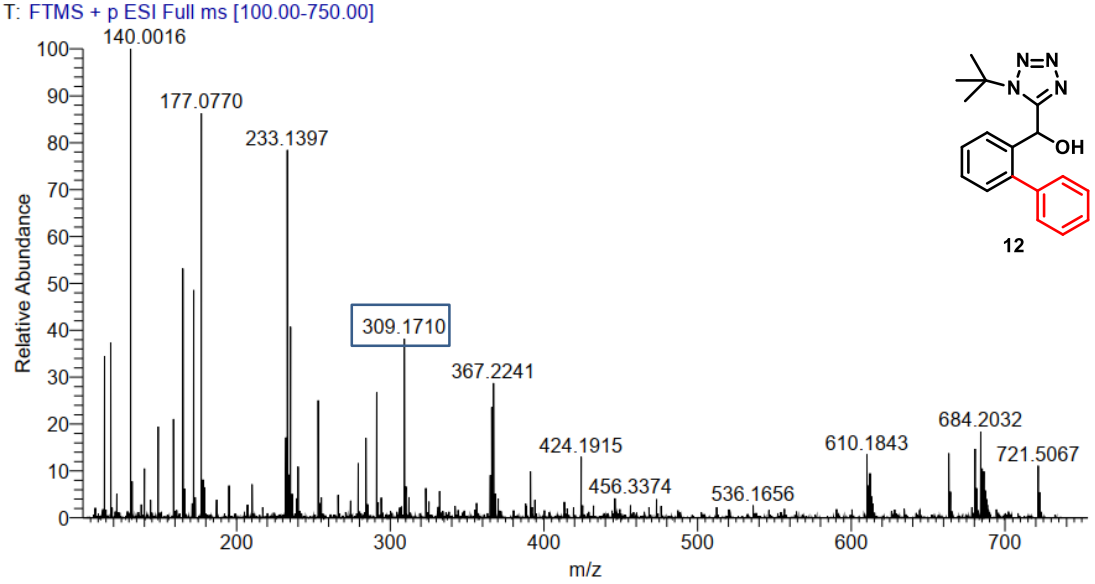
^{13}C NMR (100 MHz, $CDCl_3$):



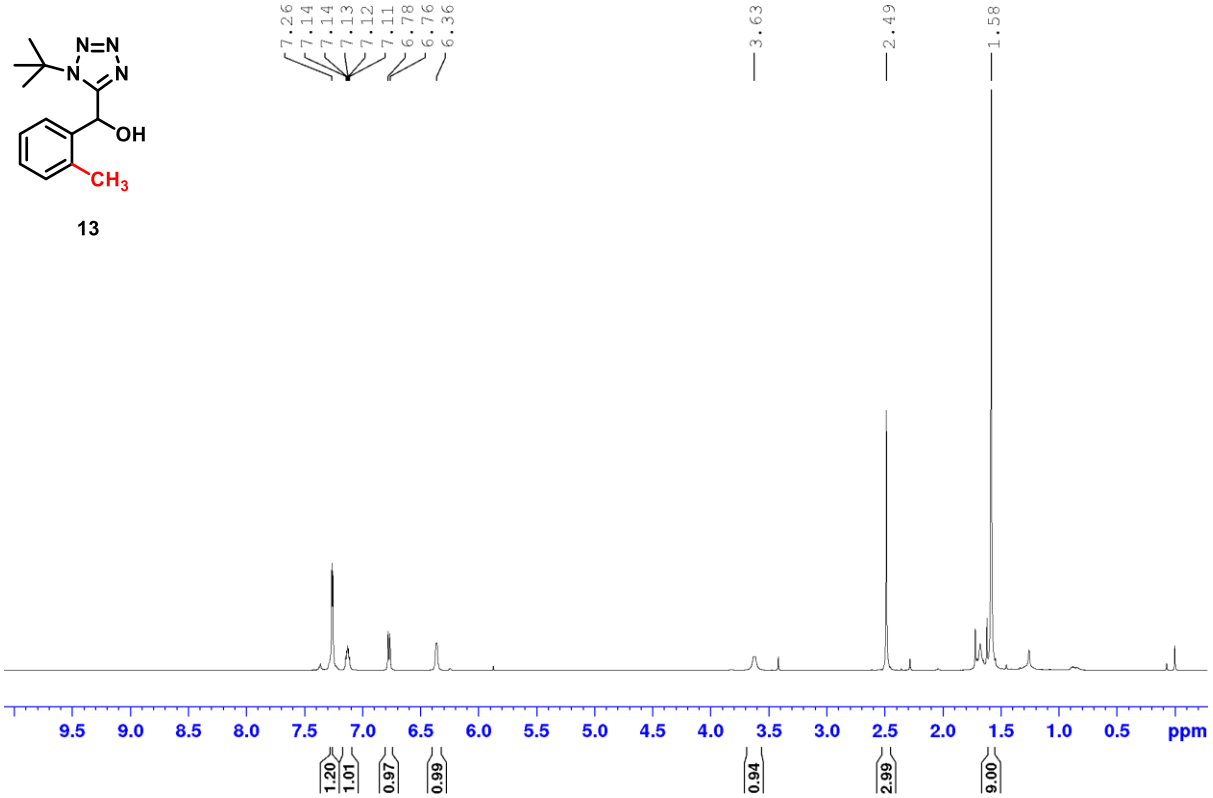
SAIF [HRMS Report]

Data File:	HRMS20I07JUL09	Original Data Path:	D:\INTERNAL NEW\2020\July 2020
Sample ID:	AS-IODO	Sample Name:	
Acquisition Date:	07/07/20 11:31:11 AM	Run Time(min):	0.00
Vial:	CStk1-01:9	Injection Volume(µl):	1.00

HRMS20I07JUL09 #13-25 RT: 0.11-0.21 AV: 13 SB: 1 0.01 NL: 1.80E5
T: FTMS + p ESI Full ms [100.00-750.00]

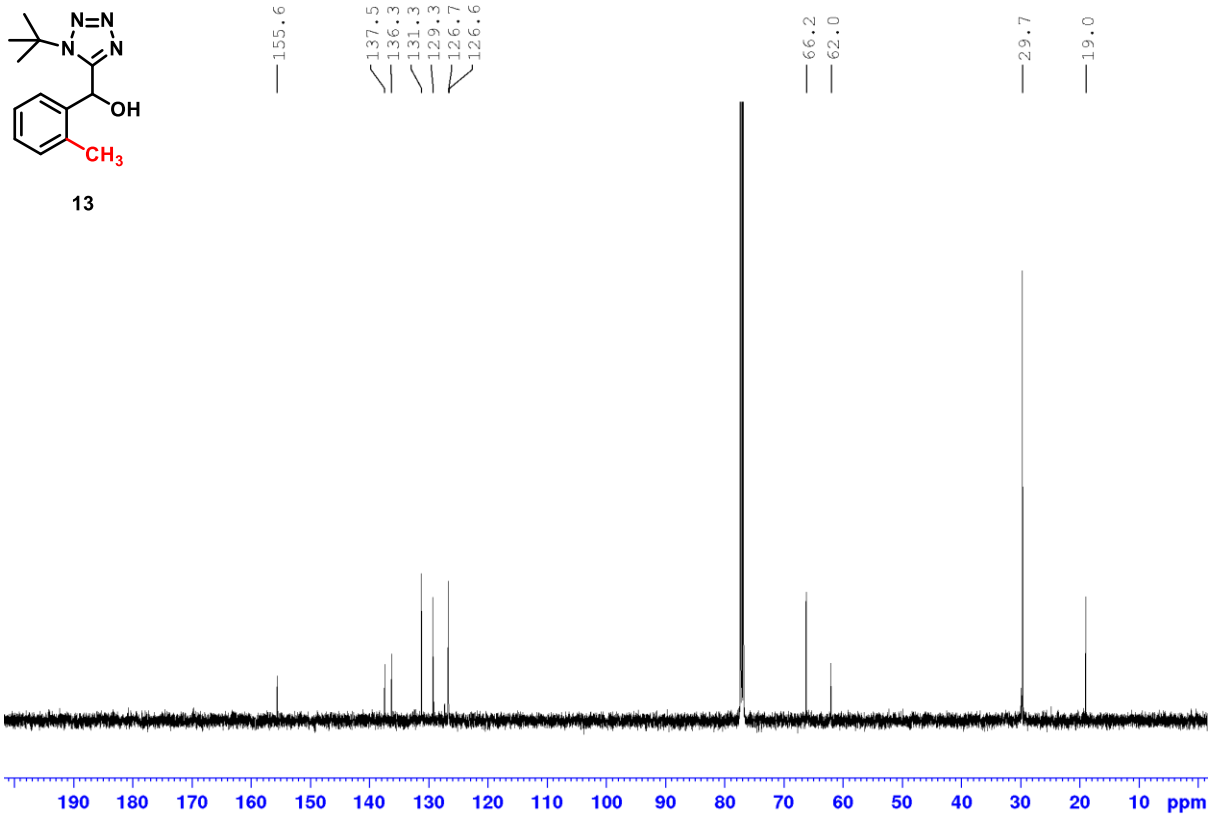


^{1}H NMR (500 MHz, $CDCl_3$):

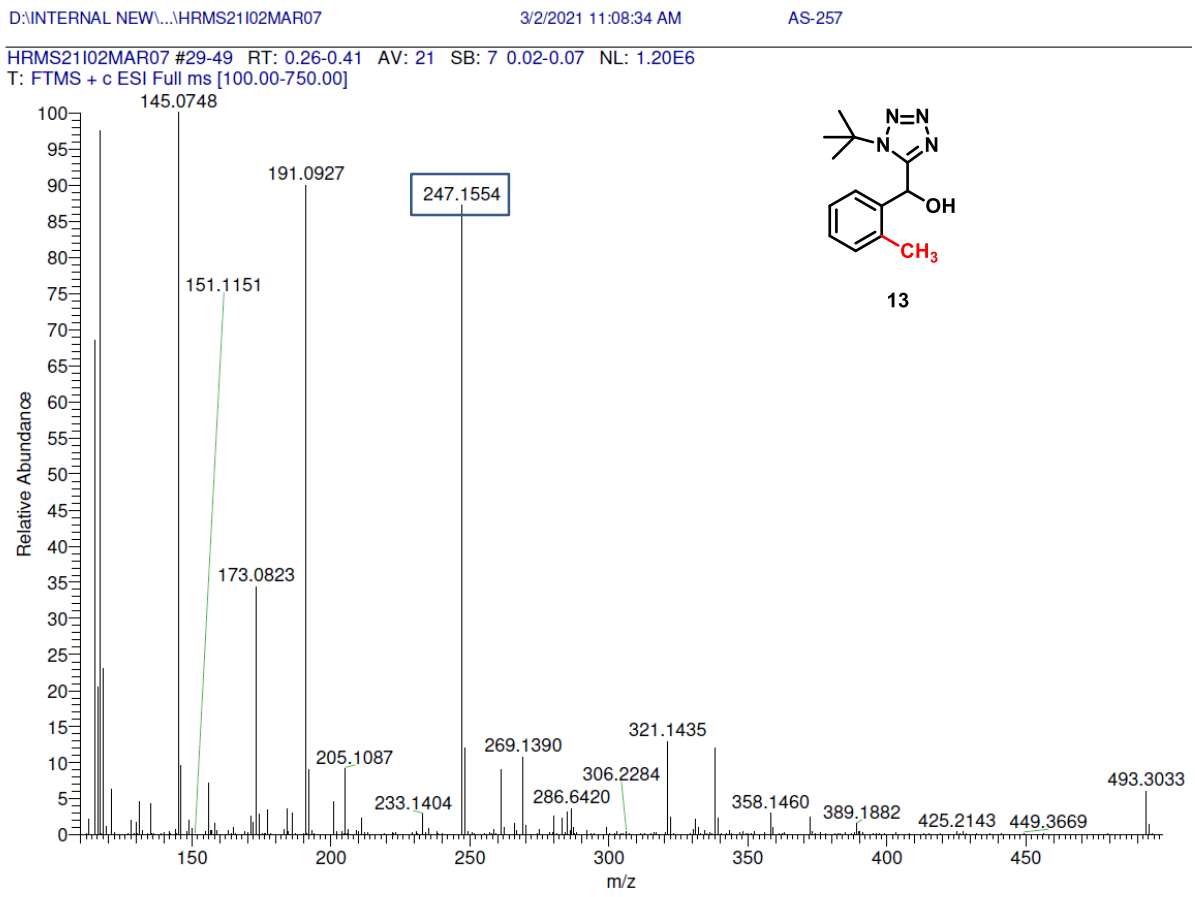


13

^{13}C NMR (125 MHz, $CDCl_3$):



13


D:\INTERNAL NEW\...\HRMS21I02MAR07
3/2/2021 11:08:34 AM
AS-257
HRMS21I02MAR07 #29-49 RT: 0.26-0.41 AV: 21 SB: 7 0.02-0.07 NL: 1.20E6
T: FTMS + c ESI Full ms [100.00-750.00]
145.0748
191.0927
247.1554
151.1151
173.0823
205.1087
233.1404
269.1390
286.6420
306.2284
321.1435
358.1460
389.1882
425.2143
449.3669
493.3033
Relative Abundance
m/z
N=N
N
N
OH
CH3
13