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Table of Content

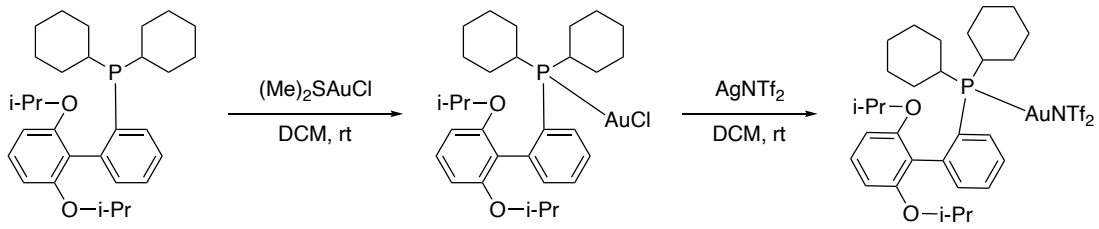
I. General Methods and Materials

All of the reactions dealing with air and/or moisture-sensitive compounds were carried out under an atmosphere of argon using oven/flame-dried glassware and standard syringe/septa techniques. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. Tetrahydrofuran (THF), toluene, 1,4- dioxane, dichloromethane (DCM) was used directly from solvent purification system. Other anhydride solvents were purchased from Acros Organic in AcroSeal glass bottle (extra dry over molecular sieve) and used directly.

^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and ^{11}B NMR spectra were recorded on Bruker Avance NEO-600 MHz, NEO-400 MHz spectrometers. Chemical shifts were reported relative to internal tetramethyl-silane (δ 0.00 ppm) or $CDCl_3$ (δ 7.26 ppm) or DMSO-d6 (δ 2.50 ppm) for ^{1}H and $CDCl_3$(δ 77.00 ppm), DMSO-d6 (δ 40.00 ppm) for ^{13}C. Flash column chromatography was performed on 230-430 mesh silica gel. Analytical thin layer chromatography was performed with pre-coated glass baked plates (250μ) and visualized by fluorescence and by charring after treatment with potassium permanganate stain. HRMS were recorded on Agilent 7890A GC/QTOF spectrometer and an Agilent 6520 Q-TOF spectrometer in the mass-spec facility in the University of South Florida. The UV-vis and fluorescence experiments were recorded at room temperature using a HORIBA FLUOROMAX-4C-L. PL decay curves were recorded on an Edinburgh FS5 spectrophotometer. The X-ray diffraction data was measured on Bruker D8 Venture PHOTON 100 CMOS system.

II. General Procedures

2.1 General procedure for synthesis of RuphosAuNTf$_2$



To a 25 mL round bottom flask with RuPhos (933.3 mg, 2 mmol) was added Me_2SAuCl (589.1 mg, 2 mmol) and DCM (10 mL) under N_2. The reaction mixture was stirred in the dark at rt for 2 h. The reaction mixture was filtered with celite and washed with DCM. The filtrate was evaporated under reduced pressure in a rt water bath to get the crude product. Then the crude product was recrystallized with DCM and hexane to get the RuPhosAuCl as a white solid.

To a 25 mL round bottom flask with RuPhosAuCl (699.1 mg, 1 mmol) was added $AgNTf_2$(388.0 mg, 1 mmol) and DCM (5 mL) under N_2. The reaction mixture was stirred in the dark at rt for 2 h. The reaction mixture was filtered with celite and washed with DCM. The filtrate was evaporated under reduced pressure in a rt water bath to get the crude product. Then the crude product was recrystallized with DCM and hexane to get the RuPhosAuNTf$_2$.

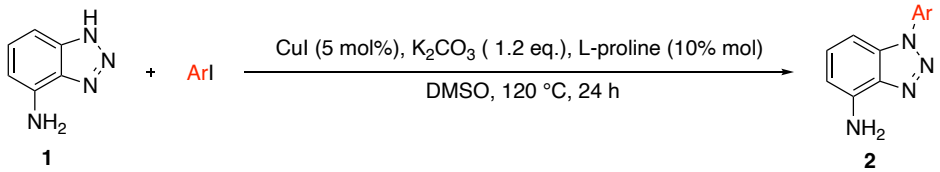
2.2 General procedure for Synthesis of 4-Nitrobenzotriazole

Benzotriazole (90.0 g, 0.75 mol) is dissolved in small parts in concentrated sulfuric acid (300.0 ml, 96%). Nitric acid (54.0 ml, 65%, at 30 °C) is added dropwise to the cooled solution. After adding the whole amount of acid, the reaction mixture is heated to 60°C for 1 h and poured onto cold water. The light-yellow precipitate is filtered, dried, and recrystallized from acetic acid, yield 109.0 g (89%).

2.3 General procedure for Synthesis of 4-amine-benzotriazole

To a solution of 4-nitrobenzotriazole (5.0 g, 30.5 mmol) in methanol (120.0 ml) was added 10% Pd/C (0.33 g) under a hydrogen gas atmosphere overnight. The reaction mixture was filtered through celite and the filtrate concentrated in vacuo, to give the product as the orange solid (3.5g, 86%) without further purification.

2.4 General procedure for Synthesis of 1-Aryl-4-amine-benzotriazoles

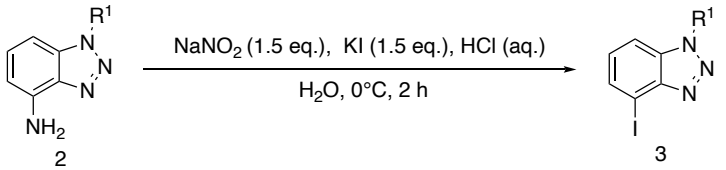


1 **2**

A flame-dried Schlenk test tube with a magnetic stirring bar was charged with CuI (0.095 g, 0.05 mmol), L-proline (1.45 g, 0.1 mmol), K_2CO_3 (1.65 g, 1.2 mmol), 4-amine-benzotriazoles **1** (5.0 mmol, 1.0 equiv.), aryl halide (6.0 mmol, 1.2 eq) and DMSO (20 mL) under N_2. The system was then evacuated three times and back filled with N_2. The reaction mixture was stirred for 30 min at

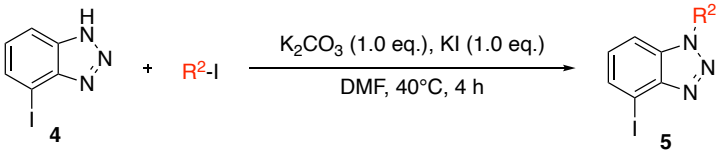
room temperature, and then heated at 120 ºC for 24 h. The resulting mixture was cooled to ambient temperature, diluted with 20-30 mL of ethyl acetate, filtered through a plug of silica gel, and washed with 50-100 mL of ethyl acetate. The filtrate was concentrated, and the resulting residue was purified by column chromatography on silica gel to provide the desired product **2**.

2.5 General procedure for Synthesis of 4-iodo-benzotriazole derivatives



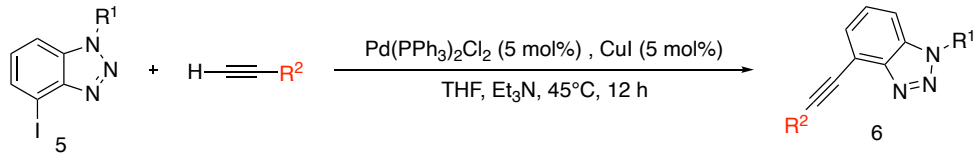
A mixture of 4-amine-benzotriazole derivatives **2** (5.0 mmol, 1.0 equiv.), aqueous HCl (37%, 1.0 mL) and water (1.0 mL) in the 200ml flask was cooled to 0°C. A solution of $NaNO_2$ (7.5 mmol, 1.5 equiv.) in water (1.0 mL) was added dropwise and stirred for 10 min. The resulting diazonium salt was slowly treated with a solution of KI (7.5 mmol, 1.5 equiv.) in water (1.0 mL). The resulting brown foamy mixture was stirred for 2 hours at room temperature. The reaction was diluted with water (20.0 mL) and neutralized by slow addition of aqueous $Na_2S_2O_3$. The mixture was extracted with dichloromethane (10.0 mL x 3). The combined organic layer was dried over $MgSO_4$, filtered and evaporated in vacuo. The residue was purified by silica gel column chromatography to give the product **3**.

2.6 General procedure for the Synthesis of 1-methyl substituted-4-iodo-benzotriazoles



To a 25 mL dry flask was added 4-iodo-benzotriazole (1.0 mmol, 1.0 equiv.), Dimethylformamide (5.0 mL), potassium carbonate (1.0 mmol, 1.0 equiv.), Potassium iodide (1.0 mmol, 1.0 equiv.), and methyl substituted bromide (1.1 mmol, 1.1 equiv.) successively. The reaction mixture was stirred for 4 hours at 40 ºC. After cooling down to room temperature, the mixture was diluted with EtOAc (10.0 mL) and water (10.0 mL). The layers were separated; then the aqueous phase was extracted with EtOAc (2 X 10 mL). The combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography.

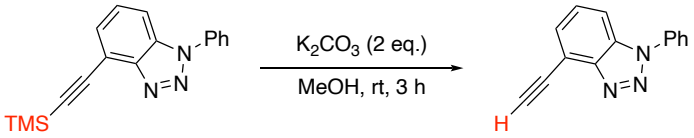
2.7 General procedure for the Sonogashira Coupling



Under argon protection, to a solution of compound 4-iodo-benzotriaozles derivatives (1.0 mmol, 1.0 equiv.), terminal alkyne (1.2 equiv.), $Pd(PPh_3)_2Cl_2$ (35.0 mg, 0.05 mmol), copper iodide (9.5 mg, 0.05 mmol) and 4-iodo-benzotriaozles derivatives **5** (1.0 mmol, 1.0 equiv.) in THF (5.0 mL) was added Et_3N (4.0 mmol, 4.0 equiv.). The reaction was stirred at 50 ºC and monitored by TLC

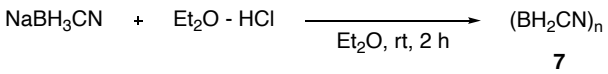
to establish completion. The reaction mixture was partitioned between water and EtOAc and the organic layer collected then dried over $MgSO_4$, filtered and concentrated. The product **6** was purified by column chromatography.

2.8 General procedure for the Synthesis of terminal alkyne



The TMS-benzotriazole substrates (298.0 mg, 1.0 equiv.), K_2CO_3 (276.0 mg, 2.0 equiv.) were dissolved in 10.0 mL MeOH. The reaction mixture was stirred at room temperature for 3 h. Upon completion, the reaction was filtered through celite and the filtrate was evaporated under reduced pressure and purified through silica column.

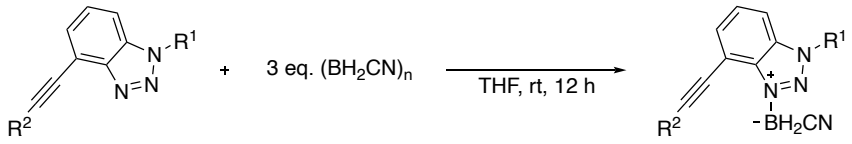
2.9 General procedure for the Synthesis of polymeric cyano-borane solution



7

To a 15.0 ml diethyl ether solution of $NaBH_3CN$ (376.5 mg, 6.0 mmol, 1.0 equiv.) was slowly added 3.0 ml Et_2O-HCl solution (2 M, 1.0 equiv.). (Caution: large amount of gas generated). The reaction mixture was stirred at room temperature for 2 hours. The solid precipitates were removed by filtering through a plug of celite and the filtrate was concentrated in vacuo to give polymeric cyanoborane complex ($(BH_2CN)_n$) in trace amount of Et_2O. (Caution: the dry $(BH_2CN)_n$ is solid and will cause serious exploration). The resulting sluggish mixture was dissolved in anhydrous THF (3.0 mL) as the cyano borane reagent **7** (2 M in THF) to use immediately.

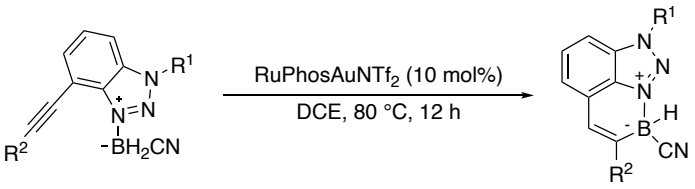
2.10 General procedure for the Synthesis of cyano-amino-borane benzotriazole derivatives



6 **7** **8**

To a solution of internal alkyne benzotriazoles (2.0 mmol, 1.0 equiv.) in anhydrous tetrahydrofuran (20.0 mL, 0.2 M), add 3.0 equiv. of $(BH_2CN)_n$. The reaction mixture was stirred at rt for 12 hours and monitored by TLC. Upon completion, the solvent was removed under reduced pressure and the residue was purified by a quick flash chromatography on silica gel to give **8**.

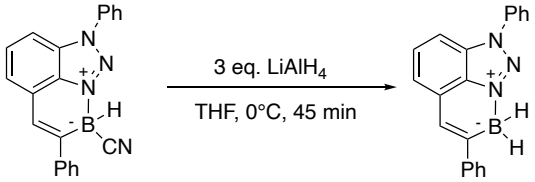
2.11 General Procedure for the Au(I) catalyzed alkyne hydroboration.



8 **9**

To a solution of **8** (0.2 mmol, 1.0 equiv.) in 1,2-dichloroethane (2.0 mL, 0.1 M), was added RuhosAuNTf$_2$ (17.0 mg, 10 mol %). The reaction mixture was stirred at 80 ℃ for 12 hours and monitored by TLC. Upon completion, the reaction mixture was concentrated via rotary evaporation and purified via flash column chromatography give **9** as solid.

2.12 General Procedure for lithium aluminum hydride ($LiAlH_4$) reduction of 3a.



3a **4a**

To a solution of 3a (0.5 mmol, 1.0 equiv.) in tetrahydrofuran (12.0 mL, 0.04 M) at 0 ℃, LiAlH4 was added (38.0 mg, 1.0 mmol, 2.0 equiv.). The reaction mixture was stirred at 0 ℃ for 15 min and warmed to RT and stirred for 30 min, then the second portion of $LiAlH_4$ was added (19.0 mg, 0.05 mmol, 1.0 equiv.). The reaction was monitored by TLC. Upon completion, solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel to give **4a** as yellow solid.

2.13 General Procedure for trifluoromethylacetoxylation 4c.

3a **4c**

A solution of **3a** (0.5 mmol, 1.0 equiv.) in 10.0 mL freshly distilled dichloromethane was cooled to 0 ℃. To this solution was added TFA (1.5 mmol, 3.0 equiv.) dropwise. The reaction stirred at 0 ℃ until complete conversion (monitored by TLC 3:1 Hexanes/ Ethyl Acetate), solvent was removed via rotary evaporation. The resulting crude product was then purified using silica gel column chromatography to give **4c** a yellow solid.

2.14 General procedure for 9 BBN hydroboration

Alkyne modified N-heterocycles (1mmol) and 9-BBN (131 mg, 1mmol) in either toluene or benzene (15 mL) were stirred at room temperature for 10 hours. The reaction is monitored by TLC.

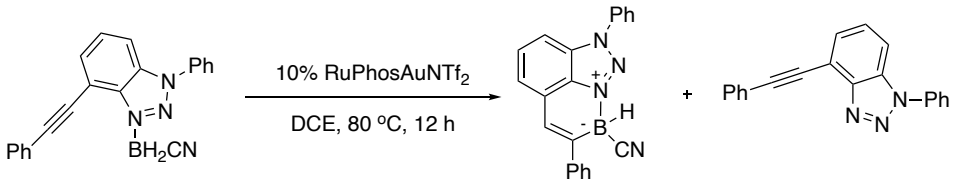
2.15 General Procedure for stability test.

a) stable in HCl: A solution of **3a** (1mmol) in 2 ml MeOH and added 1ml of 1N HCl. The reaction was stirred at rt for 24 hours. The compound was filtered and confirmed by NMR without decomposed.

b) stable in NaOH: A solution of **3a** in 2 ml MeOH and added 1ml of 1N NaOH (aq). The reaction was stirred at rt for 24 hours. The compound was filtered and confirmed by NMR without decomposed.

c) stable at 100 °C: A solution of **3a** (1mmol) in 2 ml DMF and stirred at 100 °C for 24 hours. The reaction mixture was partitioned between water and DCM, the organic layer collected then dried over $MgSO_4$, filtered and concentrated. The compound was confirmed by NMR without decomposed.

III. Extended Optimization

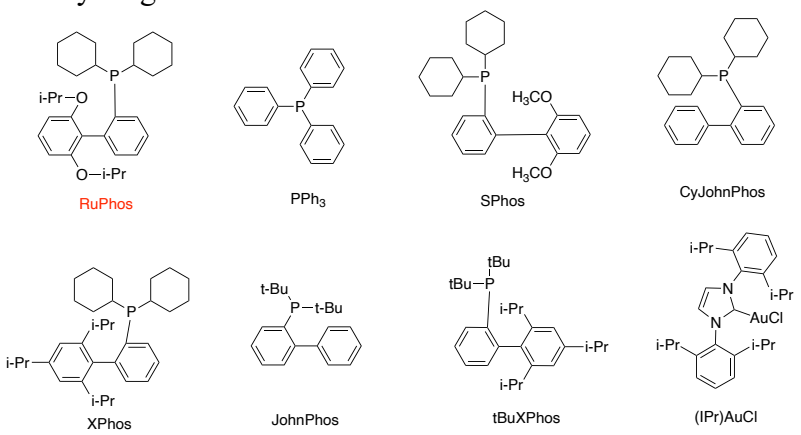


1e-CAB **3a** **1e**

Entry	Variation from "standard conditions"	conv. (%)	**3a** (%)	**1e** (%)
1	none	100	87	<5
2	PPh_3AuNTf_2	<5	n.d.	n.d.
3	$IPrAuNTf_2$	70	20	38
4	$JohnPhosAuNTf_2$	80	45	24
5	$(ArO)_3PAuNTf_2$	52	10	35
6	$SPhosAuNTf_2$	95	78	10
7	$CyJohn\ PhosAuNTf_2$	85	50	27
8	$tBuXPhosAuNTf_2$	72	40	25
9	PPh_3AuOTf	40	20	12
10	RuPhosAu(TA-H)OTf	43	8	30
11	RuPhosAu(TA-H)OTf + $Cu(OTf)_2$	20	<5	n.d.
12	CH_3CN (80 ℃) as solvent	89	71	17
13	CH_2Cl_2 (40 ℃) as solvent	20	n.d.	n.d.
14	Toluene (80 ℃)as solvent	50	34	8
15	DMF (80 ℃) as solvent	85	69	10
16	rt	20	<5	n.d.
17	60 °C	80	56	15
18	AgOTf, $Cu(OTf)_2$, $Zn(OTf)_2$, $Zr(OTf)_2$	<10%	trace	trace

[a] Conditions: **1e-CAB** (0.1 mmol), Au cat. (0.01 mmol), DCE (2 mL), 80 °C, 12 h. [b] ^1H NMR yields using 1,3,5-tribromobenzene as an internal standard (isolated yields). [c] isolated yield.

Structures of Gold catalyst ligand:



IV. ORTEP Drawing for Crystal Structures

Single-Crystal X-Ray Diffraction

X-ray diffraction data were measured on Bruker D8 Venture PHOTON II CPAD diffractometer equipped with a Cu Kα INCOATEC ImuS micro-focus source (λ = 1.54178 Å). Indexing was performed using APEX3 [1] (Difference Vectors method). Data integration and reduction were performed using SaintPlus [2]. Absorption correction was performed by multi-scan method implemented in SADABS [3]. Space groups were determined using XPREP implemented in APEX3 [1]. Structure was solved using SHELXT [4] and refined using SHELXL-2018 [5] (fullmatrix least-squares on F2) through OLEX2 interface program [6]. **3d**: Disordered -CF_3 group was refined with restraints. **3l**: Disordered thiophene group was refined with restraints. Crystal data and refinement conditions are shown in Tables **1 - 12**.

[1] Bruker (2019). APEX3 Bruker AXS Inc., Madison, Wisconsin, USA.
[2] Bruker (2019) SAINT V8.35A. Data Reduction Software.
[3] Sheldrick, G. M. (1996). SADABS. Program for Empirical Absorption Correction. University of Gottingen, Germany.
[4] XT, G.M. Sheldrick, Acta Cryst. (2015). A71, 3-8 [5] XL, Sheldrick, G. M. (2008). Acta Cryst. A64, 112-122.
[6] Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H., OLEX2: A complete structure solution, refinement and analysis program (2009). J. Appl. Cryst., 42, 339341

Table 1 Crystal data and structure refinement for Q-CAB.	
Identification code	**Q-CAB**
Empirical formula	$C_{10}H_9BN_2$
Formula weight	168.00
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.8712(2)
b/Å	11.4894(3)
c/Å	9.7181(2)
α/°	90
β/°	114.9734(7)
γ/°	90
Volume/Å^3	897.91(4)
Z	4
ρ_{calc}g/cm^3	1.243
μ/mm^{-1}	0.576
F(000)	352.0
Crystal size/mm^3	0.26 × 0.2 × 0.1
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	11.002 to 159.898
Index ranges	$-11 \leq h \leq 11$, $-14 \leq k \leq 13$, $-12 \leq l \leq 12$
Reflections collected	13328
Independent reflections	1922 [R_{int} = 0.0289, R_{sigma} = 0.0210]
Data/restraints/parameters	1922/0/126
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0324, wR_2 = 0.0847
Final R indexes [all data]	R_1 = 0.0336, wR_2 = 0.0858
Largest diff. peak/hole / e Å^{-3}	0.21/-0.20

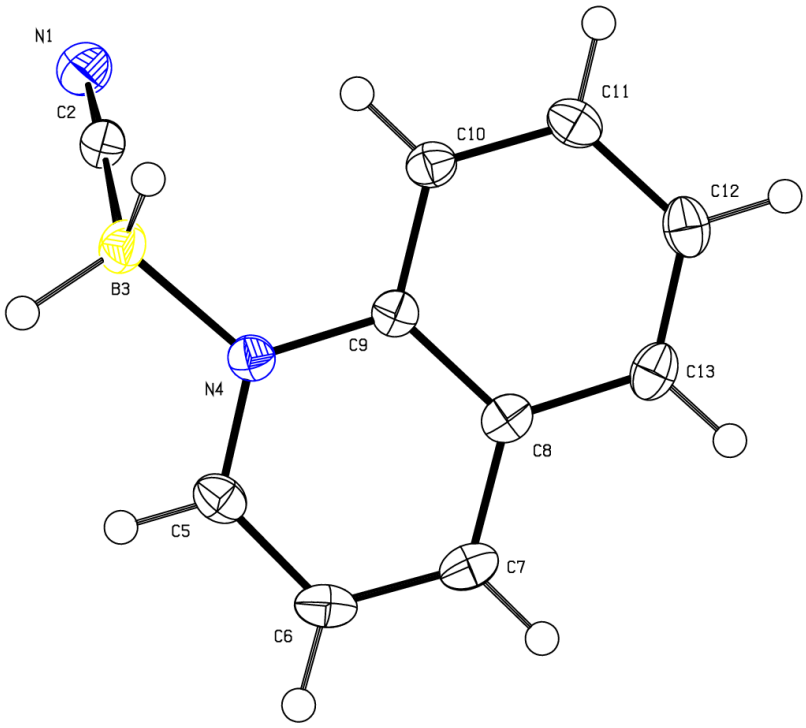


Fig.1. Ellipsoid plot **Q-CAB** Anisotropic displacement parameters were drawn at 50% probability level. CCDC: 2113561

Identification code	**3a-S4**
Empirical formula	$C_{21}H_{15}BN_4$
Formula weight	334.18
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	9.6002(3)
b/Å	9.8523(3)
c/Å	10.4405(3)
α/°	112.050(2)
β/°	100.947(2)
γ/°	100.116(2)
Volume/Å^3	864.90(5)
Z	2
ρ_{calc}g/cm^3	1.283
μ/mm^{-1}	0.608
F(000)	348.0
Crystal size/mm^3	0.52 × 0.32 × 0.05
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	9.522 to 157.746
Index ranges	$-12 \leq h \leq 11$, $-12 \leq k \leq 12$, $-13 \leq l \leq 13$
Reflections collected	3671
Independent reflections	3671 [R_{int} = 0.1189, R_{sigma} = 0.0433]
Data/restraints/parameters	3671/0/243
Goodness-of-fit on F^2	1.075
Final R indexes [I>=2σ (I)]	R_1 = 0.0525, wR_2 = 0.1438
Final R indexes [all data]	R_1 = 0.0583, wR_2 = 0.1488
Largest diff. peak/hole / e Å^{-3}	0.27/-0.35

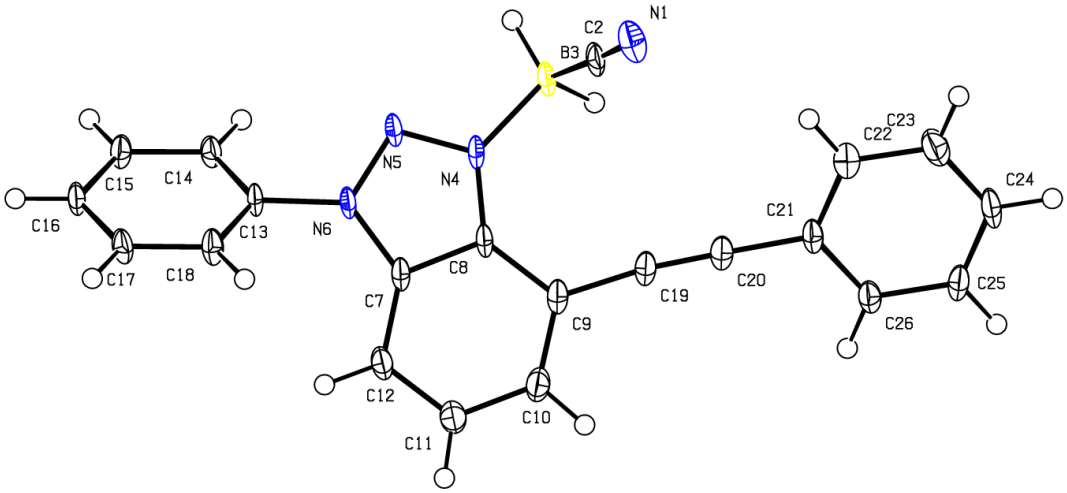


Fig.2. Ellipsoid plot of **3a-S4**. Anisotropic displacement parameters were drawn at 50% probability level. CCDC: 2113563

Identification code	**3a**
Empirical formula	$C_{22}H_{17}BCl_2N_4$
Moiety formula	$C_{21}H_{15}BN_4$, CH_2Cl_2
Formula weight	419.10
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	7.6707(2)
b/Å	8.6999(3)
c/Å	15.3408(5)
α/°	95.9950(10)
β/°	100.5720(10)
γ/°	91.4500(10)
Volume/Å^3	999.84(5)
Z	2
ρ_{calc}g/cm^3	1.392
μ/mm^{-1}	3.041
F(000)	432.0
Crystal size/mm^3	0.2 × 0.12 × 0.06
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	5.896 to 160.048
Index ranges	$-9 \leq h \leq 9$, $-11 \leq k \leq 10$, $-19 \leq l \leq 19$
Reflections collected	20096
Independent reflections	4231 [R_{int} = 0.0369, R_{sigma} = 0.0288]
Data/restraints/parameters	4231/0/266
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0335, wR_2 = 0.0862
Final R indexes [all data]	R_1 = 0.0363, wR_2 = 0.0884
Largest diff. peak/hole / e Å^{-3}	0.30/-0.34

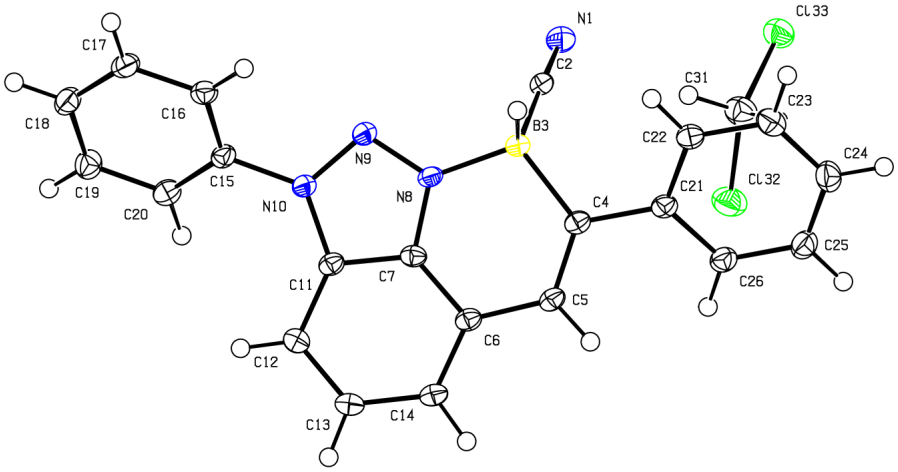


Fig.3. Ellipsoid plot of **3a**. Anisotropic displacement parameters were drawn at 50% probability level. CCDC: 2113568

Table 4 Crystal data and structure refinement for 3d.	
Identification code	**3d**
Empirical formula	$C_{22}H_{14}BF_3N_4$
Formula weight	402.18
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	8.8691(2)
b/Å	9.7159(2)
c/Å	11.5592(3)
α/°	87.7510(10)
β/°	85.0020(10)
γ/°	66.2210(10)
Volume/Å^3	908.04(4)
Z	2
ρ_{calc}g/cm^3	1.471
μ/mm^{-1}	0.928
F(000)	412.0
Crystal size/mm^3	0.09 × 0.08 × 0.04
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.678 to 159.804
Index ranges	$-10 \leq h \leq 11$, $-12 \leq k \leq 11$, $-14 \leq l \leq 14$
Reflections collected	14117
Independent reflections	3798 [R_{int} = 0.0299, R_{sigma} = 0.0254]
Data/restraints/parameters	3798/66/303
Goodness-of-fit on F^2	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0370, wR_2 = 0.0974
Final R indexes [all data]	R_1 = 0.0425, wR_2 = 0.1023
Largest diff. peak/hole / e Å^{-3}	0.25/-0.27

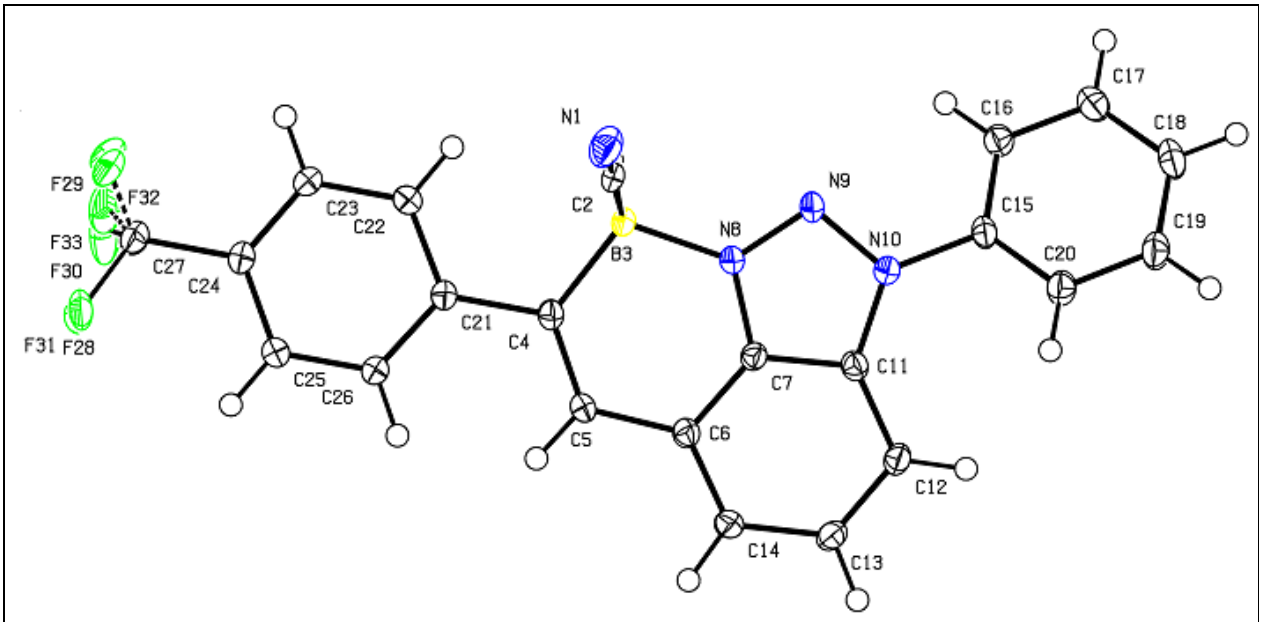


Fig.4. Ellipsoid plot of **3d**. Anisotropic displacement parameters were drawn at 50% probability level. CCDC: 2113569

Table 5 Crystal data and structure refinement for 3g.	
Identification code	**3g**
Empirical formula	$C_{22}H_{17}BN_4O$
Formula weight	364.20
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	9.69490(10)
b/Å	9.99890(10)
c/Å	10.3454(2)
α/°	74.2200(8)
β/°	68.3124(6)
γ/°	89.2819(7)
Volume/Å^3	892.41(2)
Z	2
ρ_{calc}g/cm^3	1.355
μ/mm^{-1}	0.678
F(000)	380.0
Crystal size/mm^3	0.14 × 0.12 × 0.02
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	9.236 to 160.07
Index ranges	-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -13 ≤ l ≤ 13
Reflections collected	20032
Independent reflections	3786 [R_{int} = 0.0379, R_{sigma} = 0.0241]
Data/restraints/parameters	3786/0/258
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0386, wR_2 = 0.0950
Final R indexes [all data]	R_1 = 0.0467, wR_2 = 0.1014
Largest diff. peak/hole / e Å^{-3}	0.28/-0.27

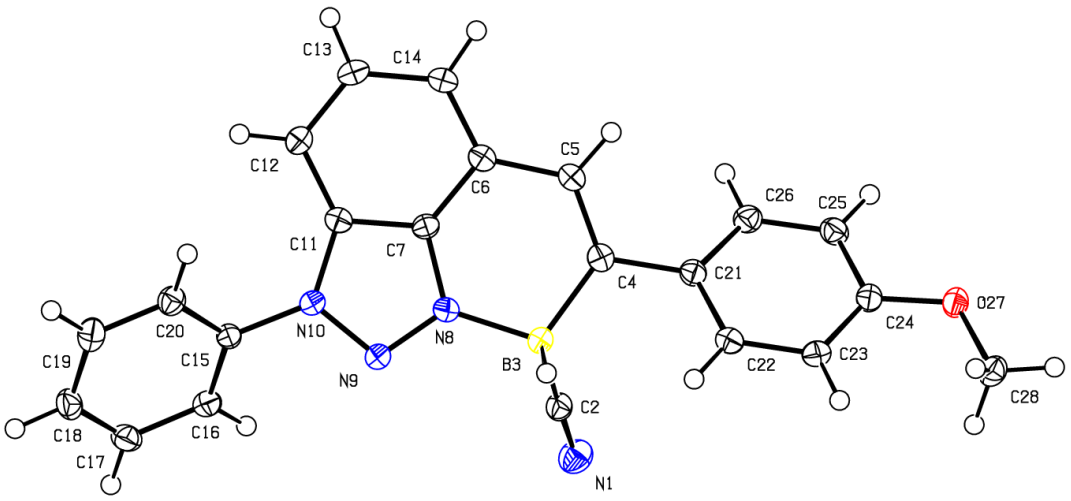


Fig.5. Ellipsoid plot of **3g**. Anisotropic displacement parameters were drawn at 50% probability level. CCDC: 2113566

Table 6 Crystal data and structure refinement for 3k.	
Identification code	**3k**
Empirical formula	$C_{23}H_{19}BN_4O_2$
Formula weight	394.23
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.0625(3)
b/Å	11.3405(3)
c/Å	15.4611(4)
α/°	90
β/°	94.428(2)
γ/°	90
Volume/Å^3	1933.87(9)
Z	4
ρ_{calc}g/cm^3	1.354
μ/mm^{-1}	0.708
F(000)	824.0
Crystal size/mm^3	0.14 × 0.12 × 0.04
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	9.492 to 159.776
Index ranges	$-14 \leq h \leq 13$, $-13 \leq k \leq 14$, $-19 \leq l \leq 19$
Reflections collected	23442
Independent reflections	4097 [R_{int} = 0.0785, R_{sigma} = 0.0579]
Data/restraints/parameters	4097/0/277
Goodness-of-fit on F^2	1.021
Final R indexes [I>=2σ (I)]	R_1 = 0.0518, wR_2 = 0.1234
Final R indexes [all data]	R_1 = 0.0766, wR_2 = 0.1377
Largest diff. peak/hole / e Å^{-3}	0.23/-0.31

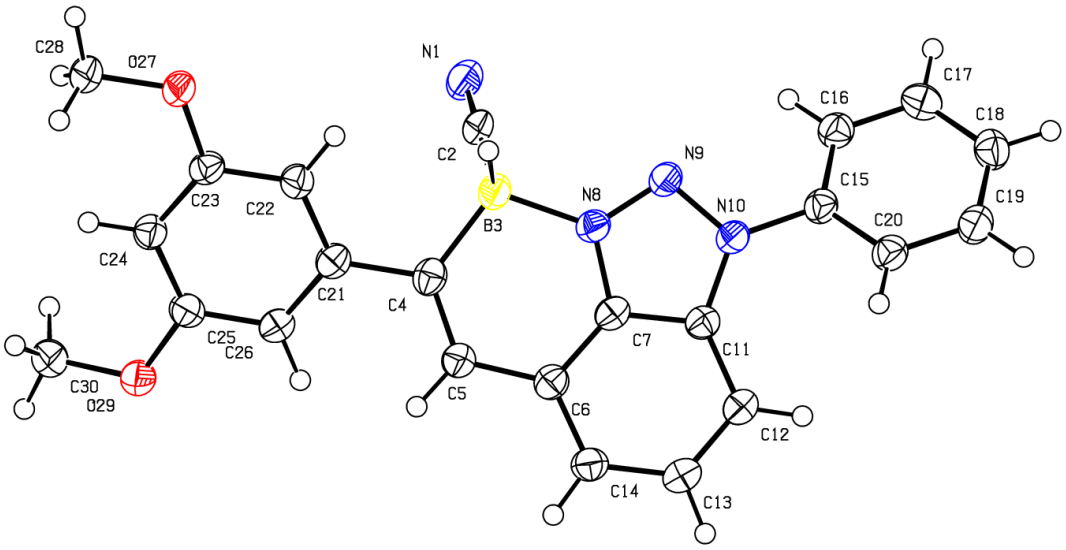


Fig.6. Ellipsoid plot of **3k.** Anisotropic displacement parameters were drawn at 50% probability level. CCDC: 2114086

Table 7 Crystal data and structure refinement for 3l.	
Identification code	**3l**
Empirical formula	$C_{20}H_{14}BCl_3N_4S$
Moiety formula	$C_{19}H_{13}BN_4S$, $CHCl_3$
Formula weight	459.57
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	9.5849(6)
b/Å	9.6966(6)
c/Å	12.5042(7)
α/°	102.614(2)
β/°	92.073(2)
γ/°	115.981(2)
Volume/Å^3	1007.91(11)
Z	2
ρ_{calc}g/cm^3	1.514
μ/mm^{-1}	5.205
F(000)	468.0
Crystal size/mm^3	0.16 × 0.09 × 0.04
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.328 to 160.708
Index ranges	$-12 \leq h \leq 12$, $-12 \leq k \leq 12$, $-15 \leq l \leq 15$
Reflections collected	20495
Independent reflections	4261 [R_{int} = 0.0294, R_{sigma} = 0.0231]
Data/restraints/parameters	4261/67/300
Goodness-of-fit on F^2	1.078
Final R indexes [I>=2σ (I)]	R_1 = 0.0259, wR_2 = 0.0654
Final R indexes [all data]	R_1 = 0.0271, wR_2 = 0.0663
Largest diff. peak/hole / e Å^{-3}	0.29/-0.30

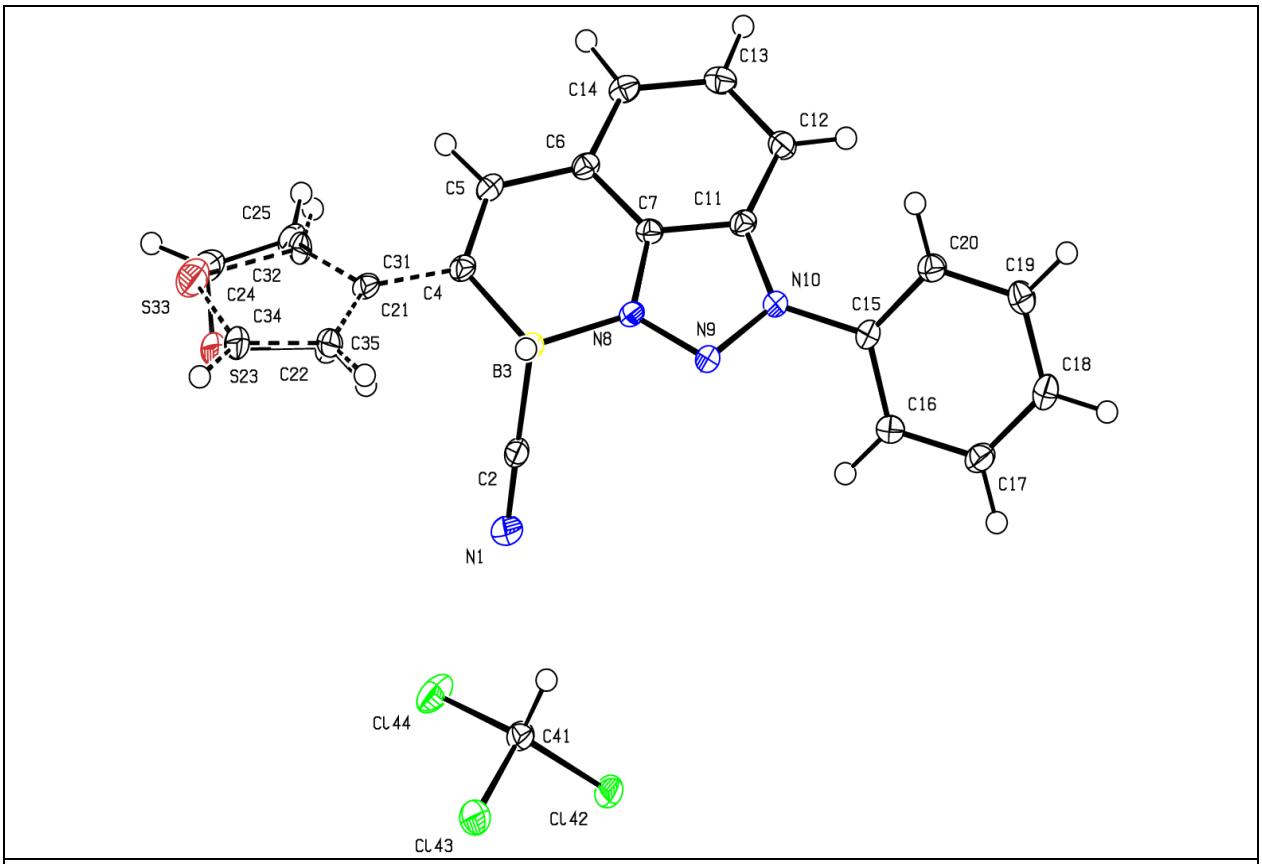


Fig.7. Ellipsoid plot of **3l**. Anisotropic displacement parameters were drawn at 50% probability level. CCDC: 2113571

b

Table 8 Crystal data and structure refinement for 3p.	
Identification code	**3p**
Empirical formula	$C_{15}H_{11}BN_4$
Formula weight	258.09
Temperature/K	100.0
Crystal system	orthorhombic
Space group	$Pca2_1$
a/Å	15.4138(4)
b/Å	5.27510(10)
c/Å	15.4456(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1255.87(6)
Z	4
ρ_{calc}g/cm^3	1.365
μ/mm^{-1}	0.665
F(000)	536.0
Crystal size/mm^3	0.23 × 0.14 × 0.09
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	11.458 to 159.478
Index ranges	$-19 \leq h \leq 19$, $-6 \leq k \leq 6$, $-17 \leq l \leq 18$
Reflections collected	23198
Independent reflections	2636 [R_{int} = 0.0805, R_{sigma} = 0.0405]
Data/restraints/parameters	2636/1/185
Goodness-of-fit on F^2	1.086
Final R indexes [I>=2σ (I)]	R_1 = 0.0405, wR_2 = 0.0907
Final R indexes [all data]	R_1 = 0.0477, wR_2 = 0.0946
Largest diff. peak/hole / e Å^{-3}	0.18/-0.21
Flack parameter	0.0(3)

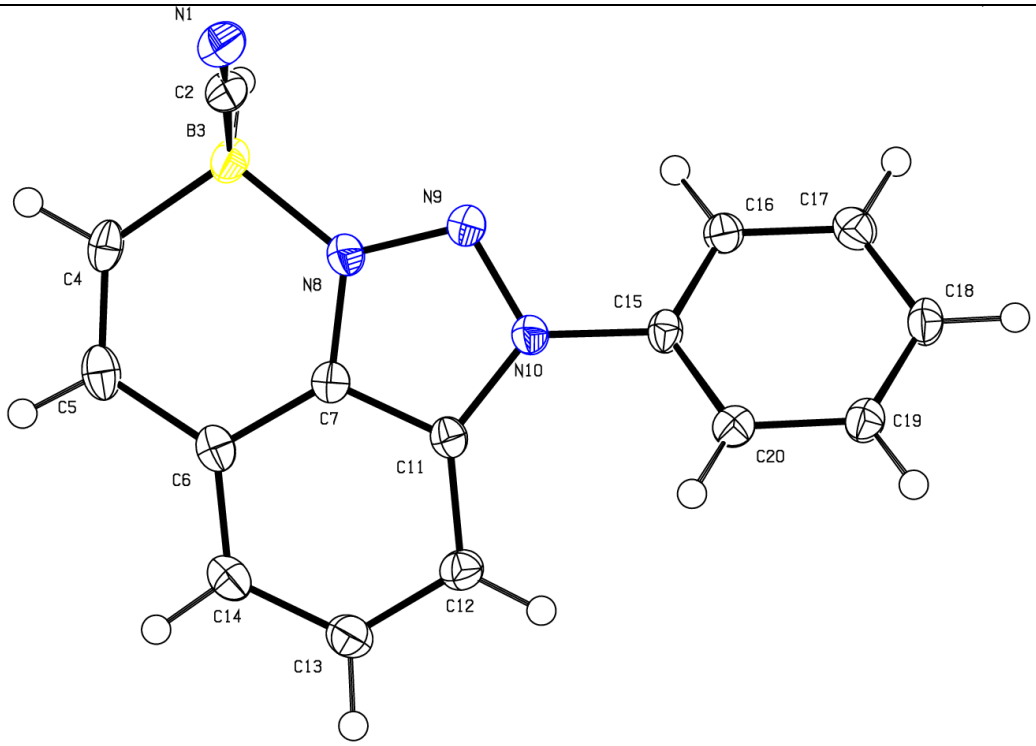


Fig.8. Ellipsoid plot of **3p**. Anisotropic displacement parameters were drawn at 50% probability level. CCDC: 2113565

Table 9 Crystal data and structure refinement for 3s.	
Identification code	**3s**
Empirical formula	$C_{22}H_{17}BN_4$
Formula weight	348.20
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	7.1974(2)
b/Å	14.8004(5)
c/Å	16.7357(5)
α/°	90
β/°	100.3030(10)
γ/°	90
Volume/Å^3	1754.01(9)
Z	4
ρ_{calc}g/cm^3	1.319
μ/mm^{-1}	0.621
F(000)	728.0
Crystal size/mm^3	0.47 × 0.16 × 0.07
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.032 to 160.286
Index ranges	$-9 \leq h \leq 9$, $-18 \leq k \leq 18$, $-21 \leq l \leq 21$
Reflections collected	29054
Independent reflections	3773 [R_{int} = 0.0512, R_{sigma} = 0.0333]
Data/restraints/parameters	3773/0/248
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0438, wR_2 = 0.1120
Final R indexes [all data]	R_1 = 0.0450, wR_2 = 0.1133
Largest diff. peak/hole / e Å^{-3}	0.29/-0.30

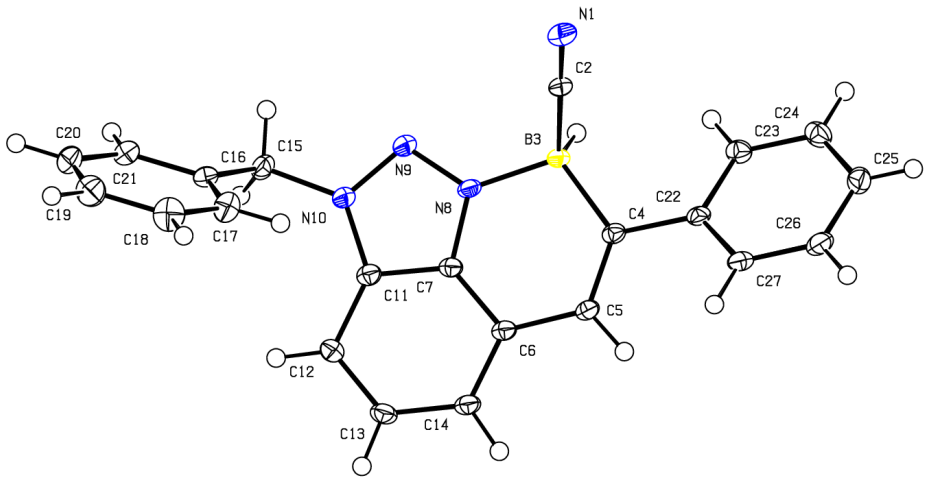


Fig.9. Ellipsoid plot of **3s.** Anisotropic displacement parameters were drawn at 50% probability level. CCDC: 2113567

Table 10 Crystal data and structure refinement for 4a.	
Identification code	**4a**
Empirical formula	$C_{20}H_{16}BN_3$
Formula weight	309.17
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	6.7975(2)
b/Å	8.0452(2)
c/Å	29.5872(7)
α/°	90
β/°	95.7970(10)
γ/°	90
Volume/Å^3	1609.77(7)
Z	4
ρ_{calc}g/cm^3	1.276
μ/mm^{-1}	0.589
F(000)	648.0
Crystal size/mm^3	0.22 × 0.09 × 0.03
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.004 to 159.708
Index ranges	$-8 \leq h \leq 8$, $-9 \leq k \leq 10$, $-36 \leq l \leq 37$
Reflections collected	23744
Independent reflections	3446 [R_{int} = 0.0485, R_{sigma} = 0.0252]
Data/restraints/parameters	3446/0/225
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0394, wR_2 = 0.0938
Final R indexes [all data]	R_1 = 0.0483, wR_2 = 0.1000
Largest diff. peak/hole / e Å^{-3}	0.21/-0.24

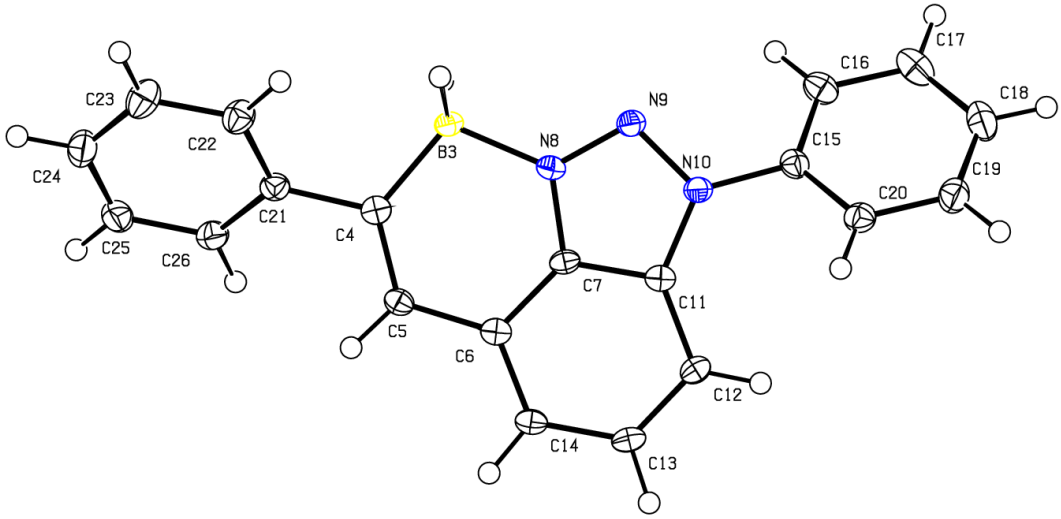


Fig.10. Ellipsoid plot of **4a**. Anisotropic displacement parameters were drawn at 50% probability level. CCDC: 2113570

Table 11 Crystal data and structure refinement for 4c.	
Identification code	**4c**
Empirical formula	$C_{24}H_{14}BF_6N_3O_4$
Formula weight	533.19
Temperature/K	100.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.8628(5)
b/Å	19.2303(8)
c/Å	11.1122(4)
α/°	90
β/°	114.593(2)
γ/°	90
Volume/Å^3	2305.02(16)
Z	4
ρ_{calc}g/cm^3	1.536
μ/mm^{-1}	1.203
F(000)	1080.0
Crystal size/mm^3	0.4 × 0.2 × 0.1
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.196 to 160.45
Index ranges	$0 \leq h \leq 14$, $-24 \leq k \leq 0$, $-14 \leq l \leq 12$
Reflections collected	4921
Independent reflections	4921 [R_{int} = 0.0412, R_{sigma} = 0.0141]
Data/restraints/parameters	4921/0/343
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0350, wR_2 = 0.0845
Final R indexes [all data]	R_1 = 0.0375, wR_2 = 0.0864
Largest diff. peak/hole / e Å^{-3}	0.32/-0.29

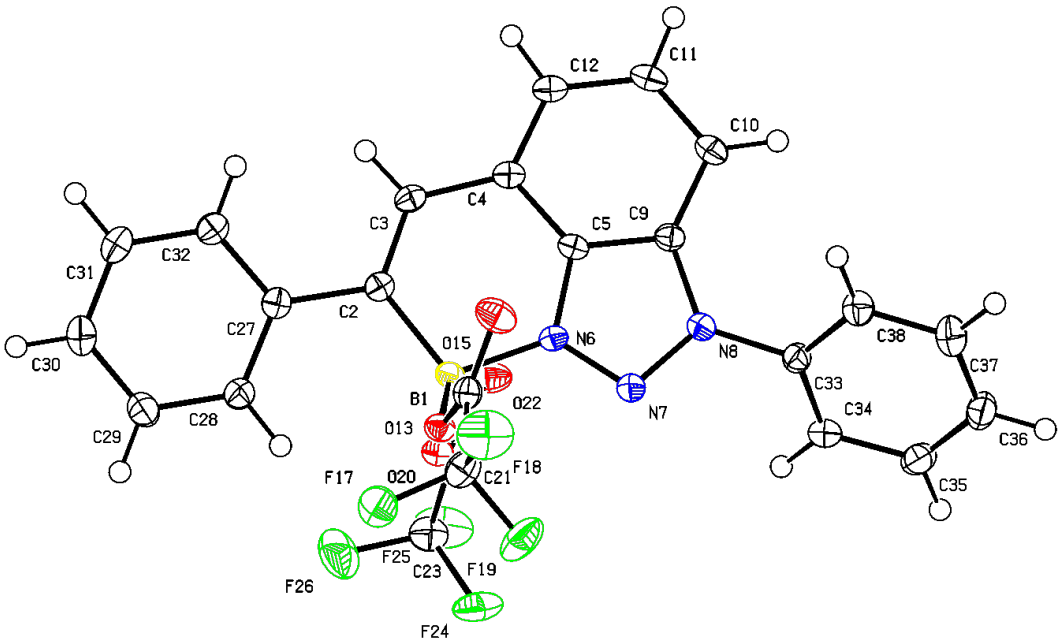


Fig.11. Ellipsoid plot of **4c**. Anisotropic displacement parameters were drawn at 50% probability level. CCDC:2114505

Table 12 Crystal data and structure refinement for 4e.	
Identification code	**4e**
Empirical formula	$C_{34}H_{30}B_2N_8O_2$
Formula weight	604.28
Temperature/K	100.0
Crystal system	orthorhombic
Space group	Pbca
a/Å	15.0807(2)
b/Å	9.70710(10)
c/Å	19.4956(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2853.96(6)
Z	4
ρ_{calc}g/cm^3	1.406
μ/mm^{-1}	0.722
F(000)	1264.0
Crystal size/mm^3	0.13 × 0.08 × 0.03
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	9.072 to 160.314
Index ranges	$-19 \leq h \leq 19$, $-12 \leq k \leq 12$, $-24 \leq l \leq 24$
Reflections collected	52062
Independent reflections	3101 [R_{int} = 0.0967, R_{sigma} = 0.0265]
Data/restraints/parameters	3101/0/220
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0370, wR_2 = 0.0819
Final R indexes [all data]	R_1 = 0.0476, wR_2 = 0.0879
Largest diff. peak/hole / e Å^{-3}	0.29/-0.20

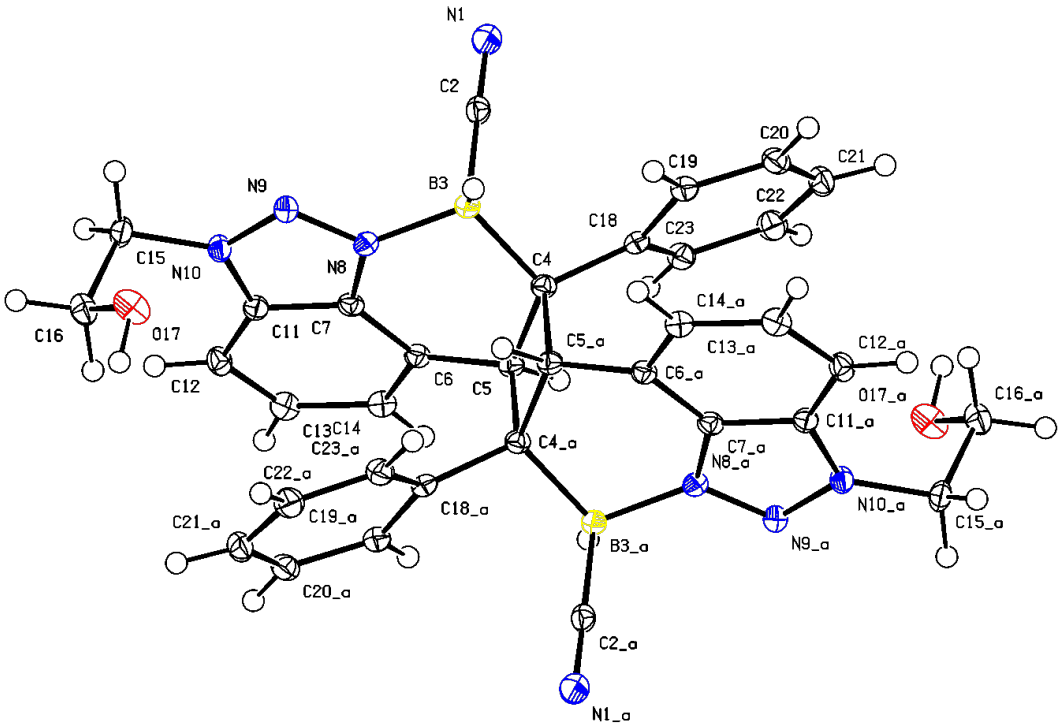


Fig.12. Ellipsoid plot of **4e**. Anisotropic displacement parameters were drawn at 50% probability level. The molecule is located on inversion center a≡1-x,1-y,1-z
CCDC: 2114265

V. Photophysical Properties

5.1 Summary of Photophysical data for compound 3a-3v in DCM at 1.0 x 10^{-5} M.

Compd.	$\lambda_{max(abs)}$ (nm)	$\lambda_{max(em)}$ (nm)	$\varepsilon(M^{-1}m^{-1})$	SS[a][cm^{-1} (nm)]	Φ_{Fl}
3a	287, 375	511	5525	234	18
3b	268, 370	501	3506	227	26
3c	290, 361	483	1233	247	14
3d	287, 380	485	5682	207	23
3e	283, 379	493	1224	203	5
3f	291, 396	527	4008	247	14
3g	294, 405	561	1697	274	17
3h	285, 389	512	5397	234	21
3i	294, 380	509	2521	239	28
3j	284, 382	517	2921	247	21
3k	287, 387	518	4531	240	20
3l	291, 403	535	3756	253	15
3m	298, 414	554	2807	270	27
3n	294, 399	551	2102	268	8
3o	265, 375	483	5606	215	16
3p	249,360	465	2552	200	10
3q	334, 444	539	2248	237	2
3r	284, 384	501	4961	221	20
3s	284,375	484	3379	205	2
3t	281,374	480	4876	173	5
3u	273, 328	497	2349	214	14
3v	263, 354	483	2291	193	12

Absorption maximum λ_{max} in CH_2Cl_2 (c = 1.0×10^{-5} mol L^{-1}); Emission maxima λ_{em} and quantum yields under air Φair in CH_2Cl_2 (c = 1.0×10^{-5} mol L^{-1}).

5.2 The UV-vis absorption spectra of 3a-3v.

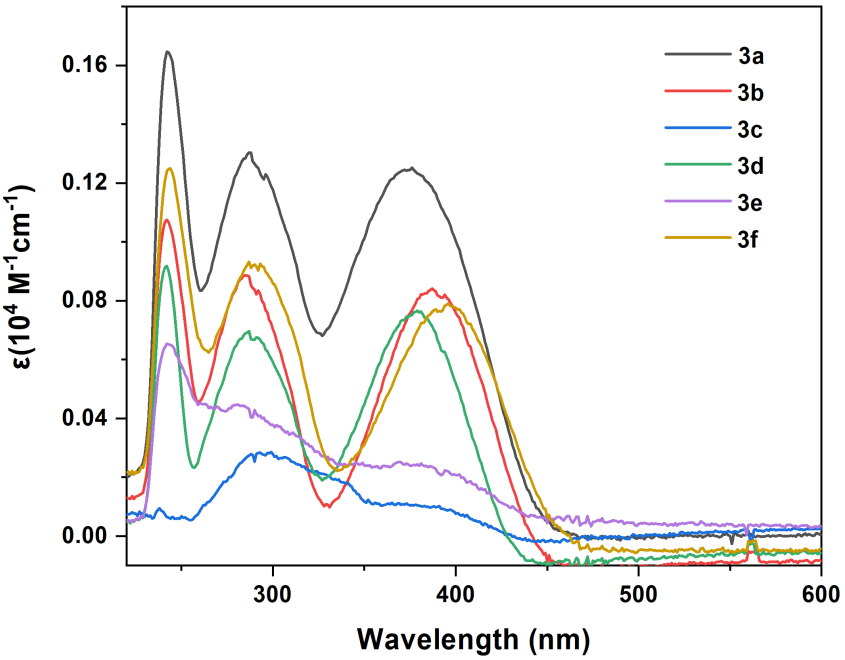


Fig. S13. UV-vis absorption spectra of compound **3a-3f**. Concentration: 100 μmol/L in DCM.

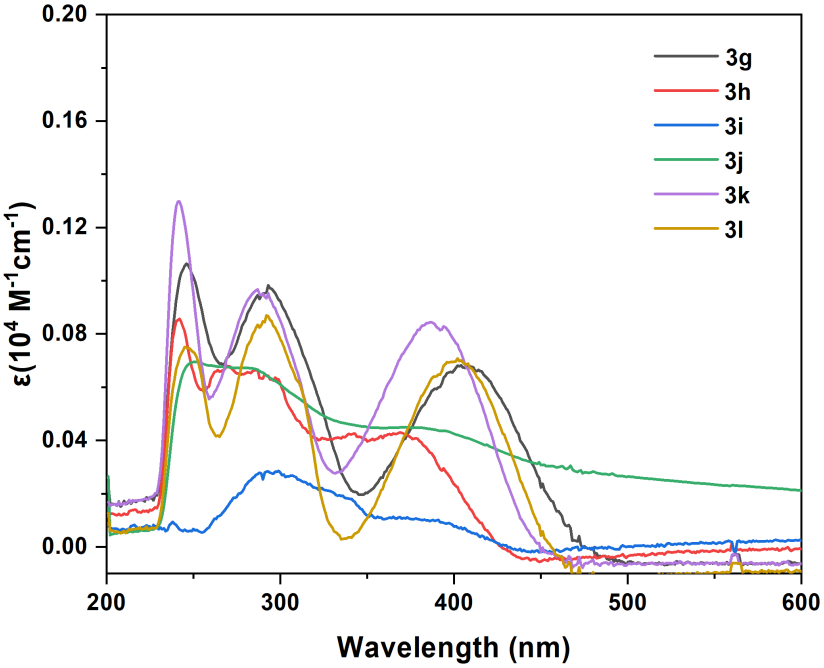


Fig. S14. UV-vis absorption spectra of compound **3g-3l**. Concentration: 100 μmol/L in DCM.

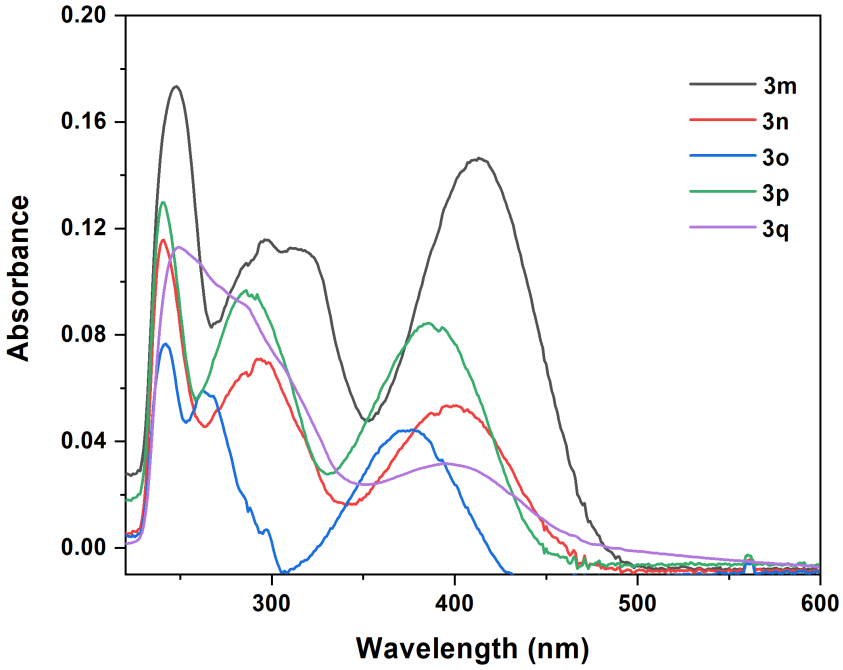


Fig. S15. UV-vis absorption spectra of compound **3m-3q**. Concentration: 100 μmol/L in DCM.

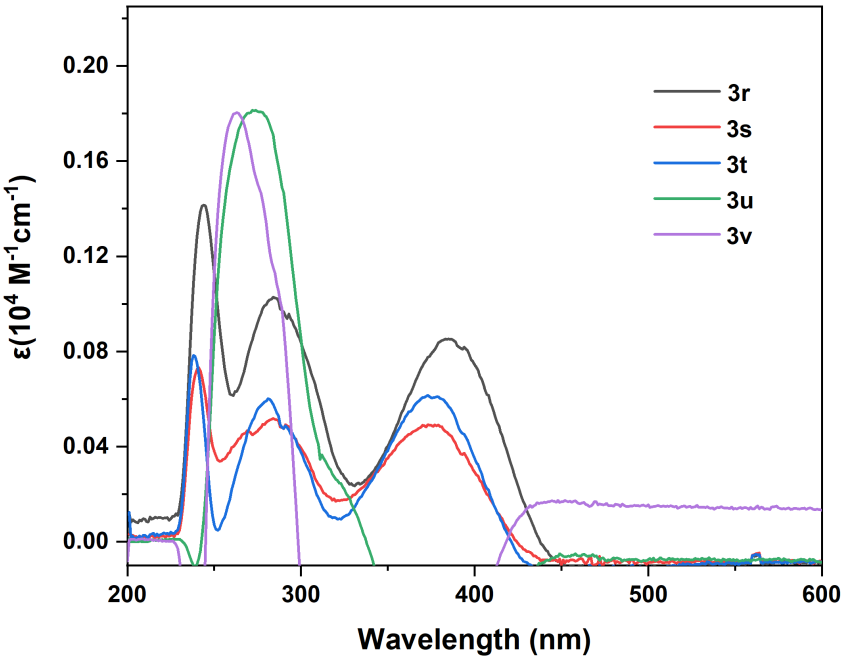


Fig. S16. UV-vis absorption spectra of compound **3r-3v**. Concentration: 100 μmol/L in DCM.

5.3 The Emission of 3a-3v in DCM solution

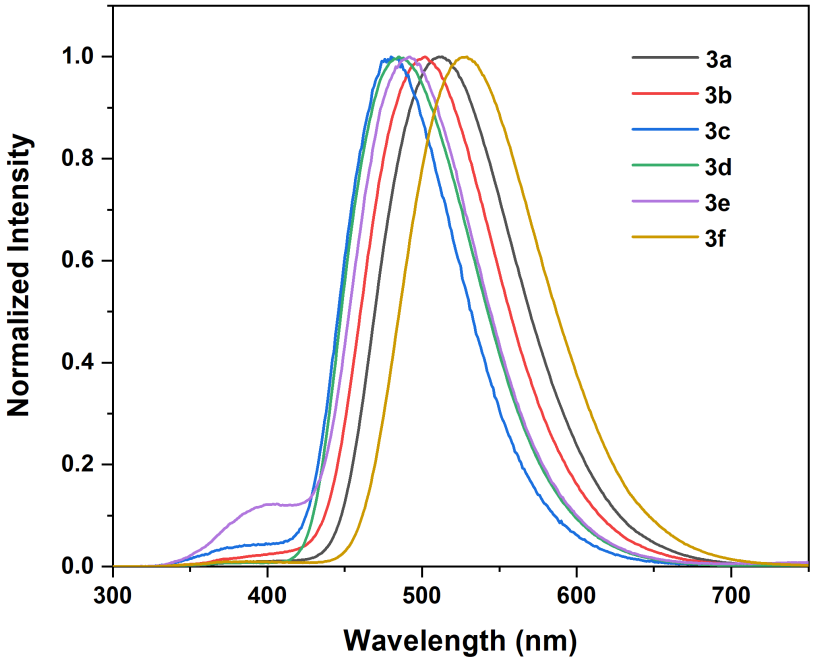


Fig. S17. Fluorescence emission of compound **3a-3f**. Concentration: 100 μmol/L in DCM.

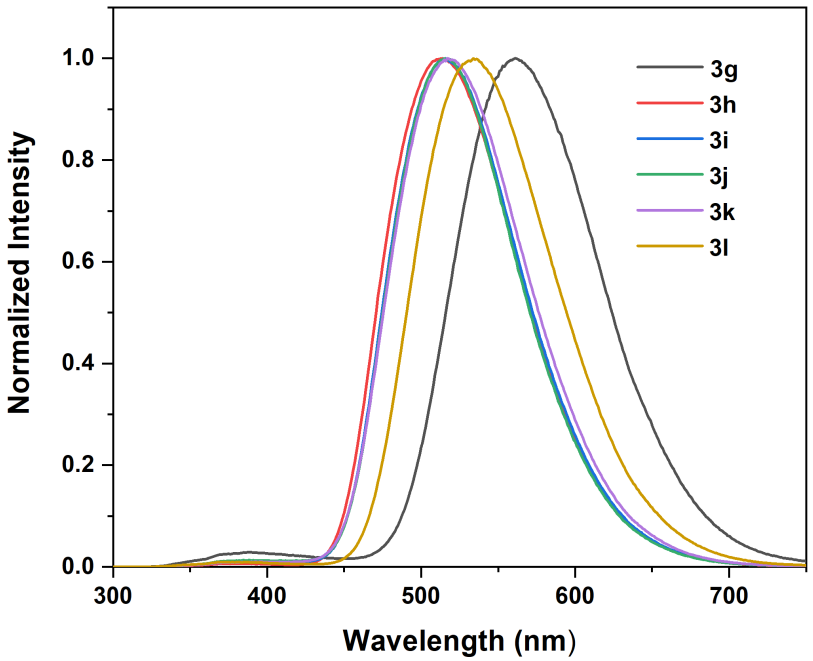


Fig. S18. Fluorescence emission of compound **3g-3l**. Concentration: 100 μmol/L in DCM.

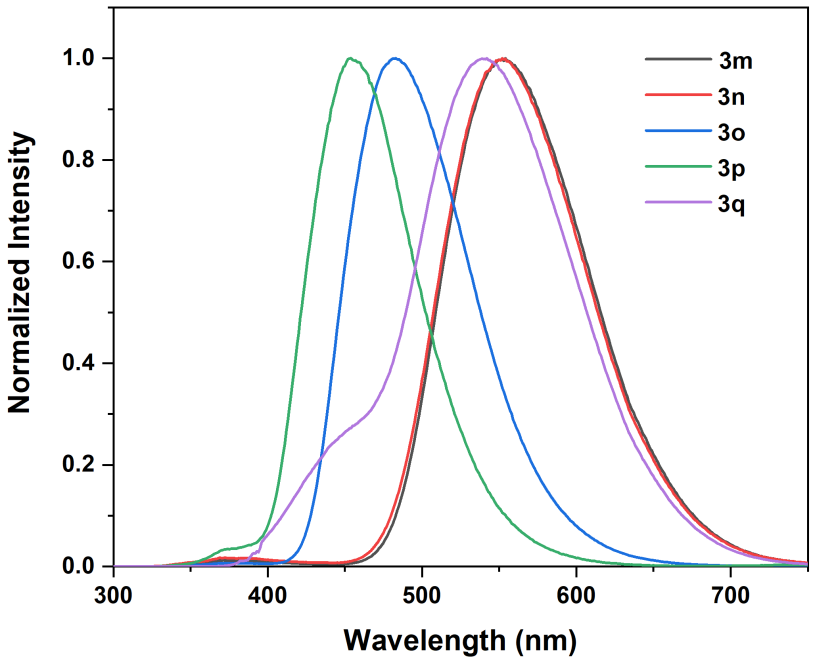


Fig. S19. Fluorescence emission of compound **3m-3q**. Concentration: 100 μmol/L in DCM.

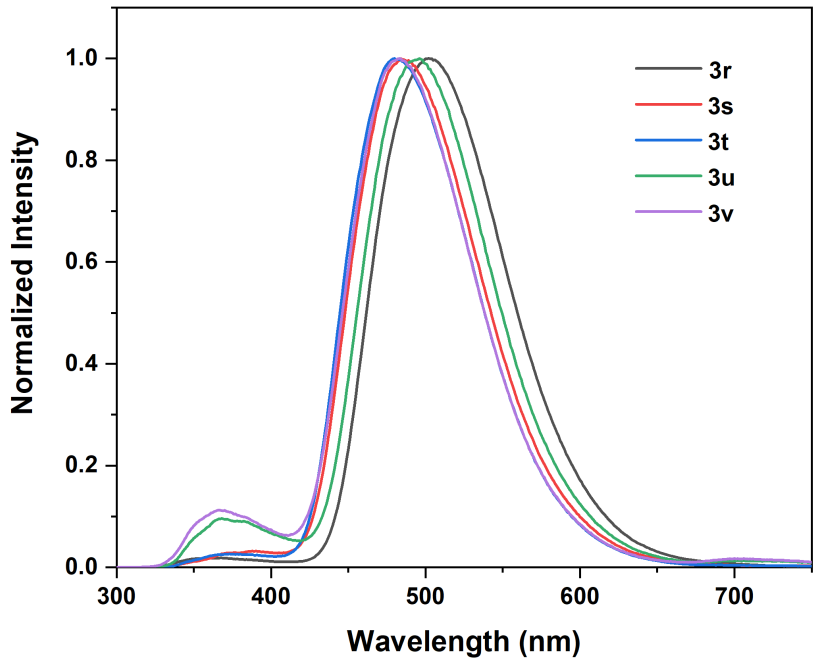


Fig. S20. Fluorescence emission of compound **3r-3v**. Concentration: 100 μmol/L in DCM.

5.3 The transient decay of 3a in DCM solution at 10^{-5}M.

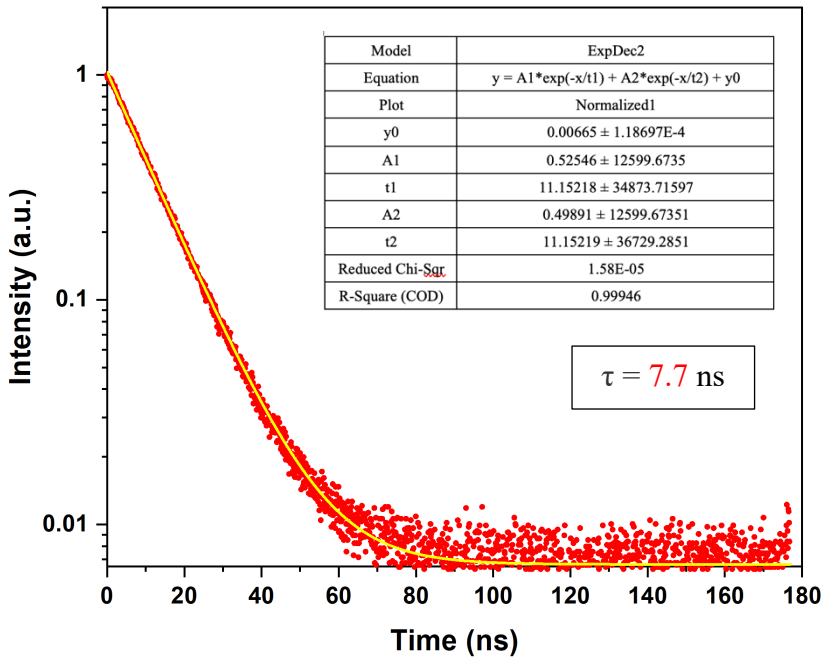


Fig. S21. Transient decay spectrum of **3a** (298 K, CH_2Cl_2, c = 1.0×10^{-5} mol L^{-1}, without delay).

III. Computational Details

All the calculations in this study were performed using the Gaussian 16 program package [1]. The All the geometries were optimized at the PBE0 [2] /6-31G(d, p) level, and the solvent effect was utilized the polarizable continuum model using integral equation formalism model (IEFPCM) in dichloroethane solvent. [3] All the optimized stationary points had been identified as minima (zero imaginary frequencies via the vibrational analysis. Furthermore, TD-DFT study at the same level within the adiabatic approximation to predict the excitation energies was conducted (nstates=100).

1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian16, Gaussian, Inc., Wallingford, CT, 2016.
2. C. Adamo and V. Barone, "Toward reliable density functional methods without adjustable parameters: The PBE0 model," J. Chem. Phys., 110 (1999) 6158-69.
3. (a) F. Furche and R. Ahlrichs, J. Chem. Phys., 2002, 117, 7433-7447; (b) G. Scalmani, M. J. Frisch, J. Chem. Phys. 2006, 124, 094107:1-15.

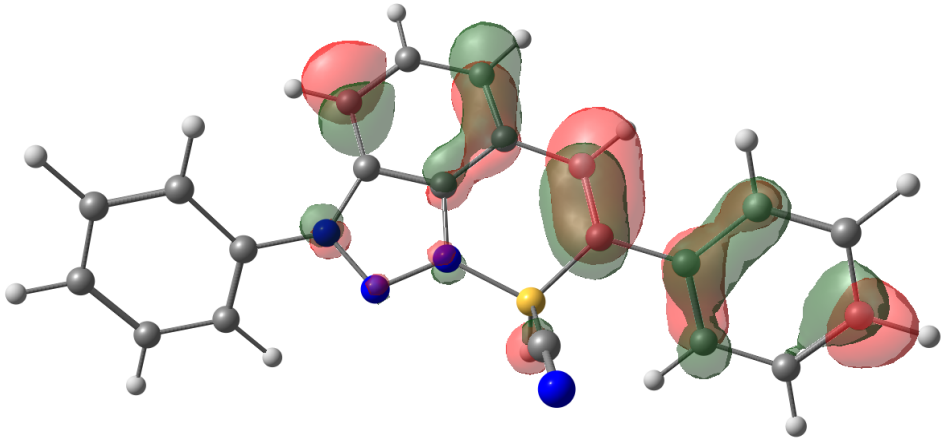
Supporting information

1. The calculated absorption from the output file.

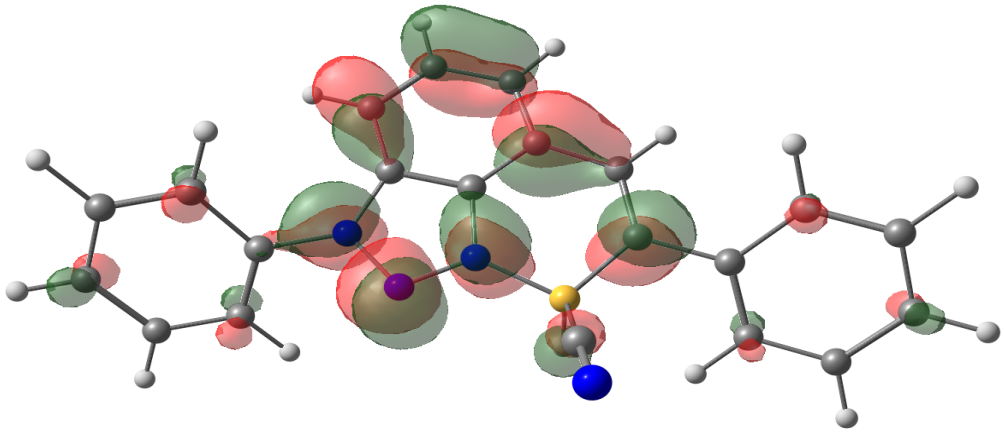
Excited State 1: Singlet-A 3.0709 eV 403.73 nm f=0.4452 <S**2>=0.000
87 -> 88 0.70252
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -1051.82954910
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 4.1670 eV 297.54 nm f=0.1961 <S**2>=0.000
82 -> 88 -0.11623
85 -> 88 -0.32952
86 -> 88 0.17596
87 -> 89 0.57860
Excited State 3: Singlet-A 4.2085 eV 294.60 nm f=0.1961 <S**2>=0.000
85 -> 88 -0.36268
86 -> 88 0.48235
87 -> 89 -0.33685

2. The orbitals of HOMO and LUMO



MO87(HOMO)



MO88(LUMO)

3. The calculated fluorescence from the output file.

Excited State 1: Singlet-A 2.3771 eV 521.57 nm f=0.5401 <S**2>=0.000
87 -> 88 0.70477
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -1051.84415859
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.6033 eV 344.08 nm f=0.5443 <S**2>=0.000
87 -> 89 0.69420

Excited State 3: Singlet-A 3.7226 eV 333.05 nm f=0.1079 <S**2>=0.000
86 -> 88 0.69888

4. Coordination for the **3a**

3a(S0)

C	-1.78054	1.17781	-0.06163
C	-0.40708	0.96831	-0.09165
C	0.56974	1.97372	-0.11301
C	0.04672	3.26103	-0.10634
C	-1.34973	3.49250	-0.08953
C	-2.29850	2.48264	-0.06946
H	0.71889	4.11353	-0.12117
H	-1.69550	4.52155	-0.09702
H	-3.36031	2.69382	-0.07179
N	-0.20079	-0.36901	-0.12393
N	-1.32824	-1.01419	-0.10827
N	-2.29230	-0.09887	-0.06998
C	1.95631	1.55796	-0.14736
C	2.31557	0.24693	-0.16234
H	2.70535	2.34661	-0.18396
B	1.24971	-0.97894	-0.20152
H	1.32304	-1.60403	-1.23916
C	3.75257	-0.09990	-0.16384
C	4.21669	-1.24807	-0.82575
C	4.69650	0.69717	0.50605
C	5.57035	-1.56740	-0.84506
H	3.50930	-1.88522	-1.34688
C	6.04817	0.37469	0.49250
H	4.35945	1.56327	1.06832
C	6.49323	-0.75744	-0.18798
H	5.90474	-2.45487	-1.37485
H	6.75602	1.00339	1.02534
H	7.54921	-1.01130	-0.19651
C	-3.65307	-0.51458	-0.06287
C	-4.04293	-1.57240	-0.88047
C	-4.56009	0.14377	0.76355
C	-5.37297	-1.97570	-0.86419
H	-3.31326	-2.06178	-1.51616
C	-5.89042	-0.26278	0.75648
H	-4.22801	0.94162	1.41941
C	-6.29761	-1.32004	-0.05339
H	-5.68809	-2.79960	-1.49629
H	-6.60545	0.24198	1.39794
H	-7.33615	-1.63546	-0.05114
C	1.44417	-1.98262	1.01064
N	1.59646	-2.73378	1.88505

E= -1051.94240

Temp= 298.15

E+ZPE= -1051.62412
G= -1051.67372
S= 147.498
Frequencies:
24 42 43 53 65 73 92 120 176 191 207 219 256 274 283 323 346
383 393 418 418 429 472 492 499 543 564 583 611 616 623 630 635
648 684 709 714 721 747 760 778 785 786 807 810 857 860 866 897
910 926 945 947 970 991 994 1001 1012 1017 1021 1021 1059 1064 1078
1083 1092 1115 1117 1120 1136 1182 1187 1200 1205 1208 1244 1256 1307
1310 1329 1355 1363 1384 1390 1404 1414 1436 1462 1490 1504 1508 1539 1554
1570 1623 1651 1670 1677 1678 1686 1705 2347 2489 3193 3207 3214 3223
3225 3226 3231 3234 3237 3238 3241 3248 3253 3269

3a(S1)

C	-1.76737	1.16384	0.06455
C	-0.39494	0.94260	0.03908
C	0.57263	1.96231	0.08548
C	0.06461	3.28349	0.16579
C	-1.30421	3.51975	0.17802
C	-2.25153	2.47450	0.11615
H	0.75932	4.11695	0.20821
H	-1.66695	4.54042	0.22784
H	-3.30977	2.70330	0.09059
N	-0.17360	-0.37106	-0.10019
N	-1.32616	-1.05906	-0.15779
N	-2.30564	-0.10735	-0.04791
C	1.93007	1.56797	0.00729
C	2.31983	0.22357	-0.11156
H	2.67186	2.36221	-0.00014
B	1.23865	-0.99144	-0.19104
H	1.33623	-1.61766	-1.23422
C	3.73156	-0.08076	-0.18648
C	4.15603	-1.36087	-0.62867
C	4.74261	0.84611	0.18831
C	5.49821	-1.68387	-0.71248
H	3.41050	-2.08687	-0.93140
C	6.08164	0.51339	0.11445
H	4.47180	1.82113	0.57763
C	6.46945	-0.75034	-0.34178
H	5.79595	-2.66521	-1.06809
H	6.83358	1.23439	0.41923
H	7.52279	-1.00634	-0.40326
C	-3.64691	-0.50518	-0.10559
C	-3.98335	-1.68358	-0.78504
C	-4.64032	0.25210	0.52665
C	-5.31190	-2.08120	-0.84375

H -3.20145 -2.26307 -1.26177
C -5.96602 -0.15674 0.44770
H -4.37751 1.12582 1.11181
C -6.31136 -1.31989 -0.23786
H -5.56899 -2.99209 -1.37612
H -6.73161 0.43222 0.94360
H -7.34847 -1.63519 -0.29208
C 1.44659 -2.02787 1.00793
N 1.61127 -2.79350 1.86817
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Temp= 298.15
E+ZPE= -1051.52864
G= -1051.57843
S= 148.710
Frequencies:
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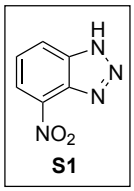
366 386 402 417 421 448 481 499 511 533 547 574 586 606 616 619
626 643 679 705 714 727 743 759 773 777 790 803 840 843 848 892
904 918 925 952 961 965 987 995 1007 1007 1014 1019 1055 1059 1071
1075 1089 1106 1116 1125 1130 1157 1182 1186 1198 1208 1216 1236 1270
1300 1313 1347 1354 1366 1391 1401 1403 1432 1475 1481 1494 1509 1530 1537
1543 1580 1610 1622 1653 1657 1672 1678 2339 2426 3213 3218 3222 3226 3229
3230 3239 3240 3246 3248 3250 3255 3257 3266

VI. Compounds Characterization

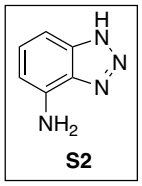
4-nitro-1H-benzo[d][1,2,3]triazole (S1)



S1

S1 was prepared following the General Procedure **2.1** as light yellow solid. Yield: 85% **^{1}H NMR** (600 MHz, DMSO-d_6) δ 8.61 (d, J = 8.2 Hz, 1H), 8.50 – 8.37 (m, 1H), 7.66 (t, J = 8.0 Hz, 1H).**^{13}C NMR** (151 MHz, DMSO-d_6) δ 146.94, 133.56, 127.35, 127.27, 124.27, 124.18. **HRMS** m/z (ESI) calcd. for $C_6H_5N_4O_2^+$ $(M+H)^+$ 165.0413, found 165.0418.

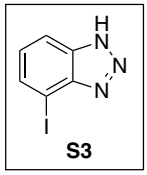
1H-benzo[d][1,2,3]triazol-4-amine (S2)



S2

S2 was prepared following the General Procedure **2.2** in HOAc salt formation as yellow solid. Yield: 87%
^{1}H NMR (600 MHz, DMSO-d_6) δ 7.13 (t, J = 7.8 Hz, 1H), 6.82 (d, J = 8.1 Hz, 1H), 6.40 (d, J = 7.5 Hz, 1H), 5.91 (s, 2H). **^{13}C NMR** (151 MHz, DMSO-d6) δ 139.73, 136.41, 134.49, 128.58, 104.67, 98.21. **HRMS** m/z (ESI) calcd. for $C_6H_7N_4^+$ $(M+H)^+$ 135.0671, found 135.0676.

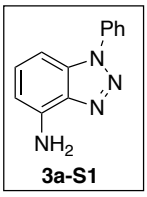
4-iodo-1H-benzo[d][1,2,3]triazole (S3)



S3

S3 was prepared following the General Procedure **2.4** and purified by column chromatography as yellow solid. Yield: 68%
^{1}H NMR (600 MHz, Acetone-d6) δ 7.89 (d, J = 7.3 Hz, 1H), 7.53 – 6.88 (m, 1H). **^{13}C NMR** (151 MHz, Acetone-d_6) δ 143.83, 134.38, 127.74, 114.14, 80.80. **HRMS** m/z (ESI) calcd. for $C_6H_4IN_3^+$ $(M+H)^+$ 245.9528, found 245.9524.

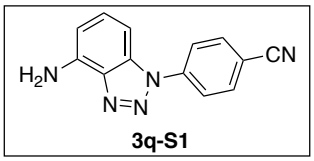
1-phenyl-1H-benzo[d][1,2,3]triazol-4-amine (3a-S1)



3a-S1

3a-S1 was prepared following the General Procedure **2.3** and purified by column chromatography as yellow solid. Yield: 58%
^{1}H NMR (600 MHz, Chloroform-d) δ 7.79 – 7.74 (m, 2H), 7.62 – 7.53 (m, 2H), 7.47 – 7.41 (m, 1H), 7.29 – 7.23 (m, 1H), 6.99 (dd, J = 8.5, 4.1 Hz, 1H), 6.53 (dd, J = 7.6, 1.8 Hz, 1H), 4.89 (d, J = 17.1 Hz, 2H).**^{13}C NMR** (151 MHz, Chloroform-d) δ 139.41, 137.39, 137.34, 133.57, 129.82, 129.75, 128.35, 122.70, 105.97, 98.69.**HRMS** m/z (ESI) calcd. for $C_{12}H_{11}N_4^+$ $(M+H)^+$ 211.0984, found 211.0996.

4-(4-amino-1H-benzo[d][1,2,3]triazol-1-yl)benzonitrile (3q-S1)

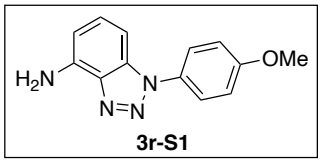


3q-S1

3q-S1 was prepared following the General Procedure **2.3** and purified by column chromatography as yellow solid. Yield: 50%
^{1}H NMR (600 MHz, Chloroform-d) δ 8.07 – 7.97 (m, 2H), 7.95 – 7.88 (m, 2H), 7.38 (q, J = 8.6, 7.9 Hz, 1H), 7.06 (d, J = 8.2 Hz, 1H), 6.61 (d, J = 7.6 Hz, 1H), 4.82 (s, 2H). **^{13}C NMR** (151 MHz, Chloroform-d) δ 140.91, 139.72, 137.40, 133.87,

132.95, 130.73, 122.22, 118.04, 111.59, 106.66, 98.38. **HRMS** m/z (ESI) calcd. for $C_{13}H_{10}N_5^+$ $(M+H)^+$ 236.0936, found 236.0955.

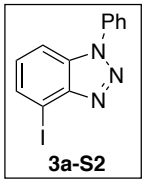
1-(4-methoxyphenyl)-1H-benzo[d][1,2,3]triazol-4-amine (3r-S1)



3r-S1

3r-S1 was prepared following the General Procedure **2.3** and purified by column chromatography as yellow solid. Yield: 55%
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.71 – 7.63 (m, 2H), 7.30 – 7.27 (m, 1H), 7.13 – 7.05 (m, 2H), 6.98 – 6.93 (m, 1H), 6.57 – 6.52 (m, 1H), 4.77 (s, 2H), 3.90 (s, 3H).**^{13}C NMR** (151 MHz, Chloroform-*d*) δ 159.59, 139.15, 137.18, 133.86, 130.38, 129.55, 124.47, 114.85, 105.71, 98.71, 55.68. **HRMS** m/z (ESI) calcd. for $C_{13}H_{13}N_4O^+$ $(M+H)^+$ 241.1089, found 241.1102.

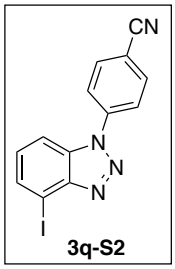
1-phenyl-1H-benzo[d][1,2,3]triazol-4-amine (3a-S2)



3a-S2

3a-S2 was prepared following the General Procedure **2.4** and purified by column chromatography as yellow solid. Yield: 56%
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.86 (dd, *J* = 7.4, 0.8 Hz, 1H), 7.78 – 7.73 (m, 2H), 7.70 (dd, *J* = 8.3, 0.8 Hz, 1H), 7.66 – 7.60 (m, 2H), 7.57 – 7.51 (m, 1H), 7.29 (dd, *J* = 8.3, 7.3 Hz, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 148.05, 136.87, 134.00, 132.13, 130.00, 129.46, 129.12, 123.17, 110.44, 85.83. **HRMS** m/z (ESI) calcd. for $C_{12}H_9IN_3^+$ $(M+H)^+$ 321.9841, found 321.9855.

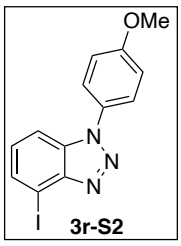
4-(4-iodo-1H-benzo[d][1,2,3]triazol-1-yl)benzonitrile (3q-S2)



3q-S2

3q-S2 was prepared following the General Procedure **2.4** and purified by column chromatography as yellow solid. Yield: 52%
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.00 – 7.97 (m, 2H), 7.96 – 7.91 (m, 3H), 7.75 (dd, *J* = 8.3, 0.8 Hz, 1H), 7.37 (dd, *J* = 8.3, 7.4 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 148.45, 140.31, 134.68, 134.10, 131.54, 130.28, 122.89, 117.78, 112.56, 110.06, 86.45. **HRMS** m/z (ESI) calcd. for $C_{13}H_8IN_4^+$ $(M+H)^+$ 346.9794, found 346.9802

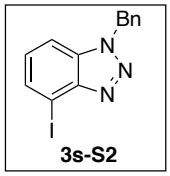
4-iodo-1-(4-methoxyphenyl)-1H-benzo[d][1,2,3]triazole (3r-S2)



3r-S2

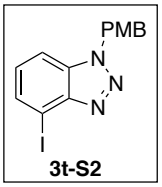
3r-S2 was prepared following the General Procedure **2.4** and purified by column chromatography as yellow solid. Yield: 54%
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 7.3 Hz, 1H), 7.62 (dd, *J* = 8.5, 5.1 Hz, 3H), 7.30 – 7.25 (m, 1H), 7.14 – 7.06 (m, 2H), 3.91 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 160.12, 147.84, 133.82, 132.45, 130.43, 129.83, 129.22, 124.88, 115.06, 110.34, 85.70, 55.72. **HRMS** m/z (ESI) calcd. for $C_{13}H_{10}IN_3O^+$ $(M+H)^+$ 351.9947, found 351.9947.

1-benzyl-4-iodo-1H-benzo[d][1,2,3]triazole (3s-S2)



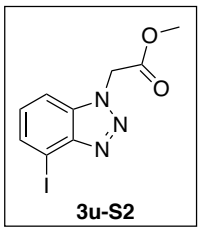
3s-S2 was prepared following the General Procedure **2.5** and purified by column chromatography as yellow solid. Yield: 60%
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 7.3 Hz, 1H), 7.39 – 7.23 (m, 7H), 7.17 – 7.11 (m, 1H), 5.84 (s, 2H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 147.98, 134.33, 133.53, 132.45, 129.09, 128.65, 127.57, 109.85, 85.63, 52.85. **HRMS** m/z (ESI) calcd. for $C_{13}H_{11}IN_3^+$ $(M+H)^+$ 335.9998, found 336.0012.

4-iodo-1-(4-methoxybenzyl)-1H-benzo[d][1,2,3]triazole (3t-S2)



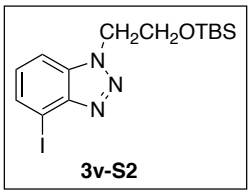
3t-S2 was prepared following the General Procedure **2.5** and purified by column chromatography as yellow solid. Yield:62%
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 7.3 Hz, 1H), 7.30 (dd, *J* = 8.3, 0.7 Hz, 1H), 7.25 – 7.19 (m, 2H), 7.11 (dd, *J* = 8.3, 7.3 Hz, 1H), 6.88 – 6.81 (m, 2H), 5.75 (s, 2H), 3.77 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 159.79, 147.97, 133.45, 132.33, 129.11, 128.54, 126.32, 114.42, 109.98, 85.54, 55.33, 52.49. **HRMS** m/z (ESI) calcd. for $C_{14}H_{13}IN_3O^+$ $(M+H)^+$ 366.0103, found 366.0098.

methyl 2-(4-iodo-1H-benzo[d][1,2,3]triazol-1-yl)acetate (3u-S2)



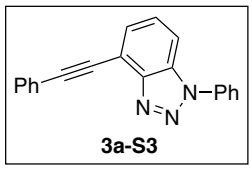
3u-S2 was prepared following the General Procedure **2.5** and purified by column chromatography as yellow solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 7.3 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 1H), 7.34 – 7.17 (m, 1H), 5.43 (s, 2H), 3.79 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 166.53, 147.68, 133.44 (d, *J* = 103.4 Hz), 129.22, 109.35, 85.75, 51.23 (d, *J* = 566.5 Hz). **HRMS** m/z (ESI) calcd. for $C_9H_9IN_3O_2^+$ $(M+H)^+$ 317.9739, found 317.9739.

1-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-4-iodo-1*H*-benzo[*d*][1,2,3]triazole (3v-S2)



3v-S2 was prepared following the General Procedure **2.5** and purified by column chromatography as yellow solid. Yield: 52%
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.03 – 7.90 (m, 1H), 7.85 – 7.74 (m, 1H), 7.40 (ddd, *J* = 11.8, 9.9, 6.9 Hz, 1H), 4.93 (dtt, *J* = 7.1, 5.0, 2.3 Hz, 2H), 4.44 – 4.16 (m, 2H), 1.16 – 0.74 (m, 12H), 0.21 – -0.17 (m, 5H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 147.40, 133.81, 133.33, 128.26, 110.67, 85.03, 62.67, 51.29, 25.67, 18.06, -5.73. **HRMS** m/z (ESI) calcd. for $C_{14}H_{23}IN_3OSi^+$ $(M+H)^+$ 404.0655, found 404.0680.

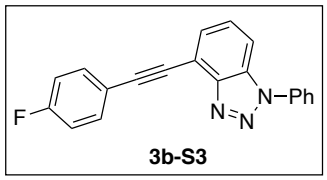
1-phenyl-4-(phenylethynyl)-1H-benzo[d][1,2,3]triazole (3a-S3)



3a-S3

3a-S3 was prepared following the General Procedure **2.6** and purified by column chromatography as yellow solid. **^{1}H NMR (**600 MHz, Chloroform-*d*) δ 7.82 – 7.77 (m, 2H), 7.76 – 7.67 (m, 3H), 7.64 (td, *J* = 7.4, 1.6 Hz, 3H), 7.59 – 7.51 (m, 2H), 7.40 (qd, *J* = 4.7, 1.4 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 146.45, 136.85, 132.59, 132.09, 129.93, 128.93, 128.85, 128.38, 128.26, 128.03, 123.12, 122.86, 115.99, 110.46, 95.88, 84.75. **HRMS** m/z (ESI) calcd. for $C_{20}H_{14}N_3^+$ $(M+H)^+$ 296.1188, found 296.1196

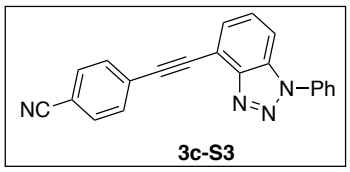
4-((4-fluorophenyl)ethynyl)-1-phenyl-1H-benzo[d][1,2,3]triazole (3b-S3)



3b-S3

3b-S3 was prepared following the General Procedure **2.6** and purified by column chromatography as yellow solid.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.8 Hz, 2H), 7.75 – 7.66 (m, 3H), 7.66 – 7.57 (m, 3H), 7.52 (td, *J* = 7.6, 3.5 Hz, 2H), 7.09 (t, *J* = 8.5 Hz, 2H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 146.42, 136.83, 134.07, 134.01, 132.59, 129.93, 128.95, 128.18, 128.02, 123.11, 118.99, 115.80, 115.65, 110.54, 94.74, 84.47. **^{19}F NMR** (564 MHz, Chloroform-*d*) δ -110.00. **HRMS** m/z (ESI) calcd. for $C_{20}H_{14}FN_3^+$ $(M+H)^+$ 314.1094, found 314.1103.

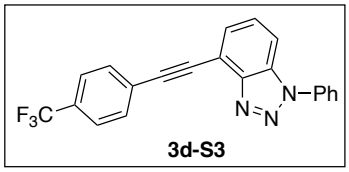
4-((1-phenyl-1*H*-benzo[*d*][1,2,3]triazol-4-yl)ethynyl)benzonitrile (3c-S3)



3c-S3

3c-S3 was prepared following the General Procedure **2.6** and purified by column chromatography as yellow solid.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 (ddd, *J* = 8.5, 6.8, 1.0 Hz, 5H), 7.70 – 7.67 (m, 2H), 7.66 – 7.62 (m, 3H), 7.57 – 7.53 (m, 2H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 146.37, 136.71, 132.63, 132.53, 132.09, 129.99, 129.10, 128.65, 128.02, 127.75, 123.14, 118.49, 114.83, 112.06, 111.46, 93.71, 88.88. **HRMS** m/z (ESI) calcd. for $C_{21}H_{13}N_4^+$ $(M+H)^+$ 321.1140, found 321.1146.

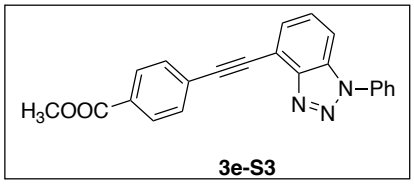
1-phenyl-4-((4-(trifluoromethyl)phenyl)ethynyl)-1H-benzo[d][1,2,3]triazole (3d-S3)



3d-S3

3d-S3 was prepared following the General Procedure **2.6** and purified by column chromatography as yellow solid.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.85 – 7.74 (m, 5H), 7.70 – 7.62 (m, 5H), 7.58 – 7.53 (m, 2H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 146.40, 136.74, 132.61, 132.30, 129.99, 129.06, 128.59, 128.04, 126.64, 125.35, 125.33, 123.15, 115.18, 111.14, 94.13, 86.94. **^{19}F NMR** (564 MHz, Chloroform-*d*) δ -62.77. **HRMS** m/z (ESI) calcd. for $C_{21}H_{13}F_3N_3^+$ $(M+H)^+$ 364.1062, found 364.1065.

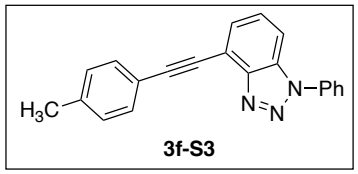
methyl 4-((1-phenyl-1*H*-benzo[*d*][1,2,3]triazol-4-yl)ethynyl)benzoate (3e-S3)



3e-S3

3e-S3 was prepared following the General Procedure **2.6** and purified by column chromatography as yellow solid.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.10 – 8.05 (m, 2H), 7.77 (tdd, *J* = 11.3, 7.8, 1.1 Hz, 5H), 7.64 (dd, *J* = 8.4, 7.4 Hz, 3H), 7.58 – 7.53 (m, 2H), 3.95 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 166.56, 146.41, 136.78, 135.12, 132.62, 131.99, 130.00, 129.54, 129.02, 128.51, 128.03, 127.50, 123.14, 115.37, 111.03, 94.83, 87.49, 52.29. **HRMS** m/z (ESI) calcd. for $C_{22}H_{16}N_3O_2^+$ $(M+H)^+$ 354.1243, found 354.1244.

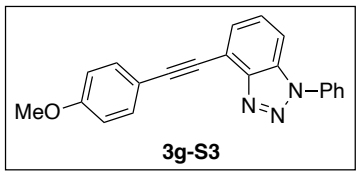
1-phenyl-4-(p-tolylethynyl)-1H-benzo[d][1,2,3]triazole (3f-S3)



3f-S3

3f-S3 was prepared following the General Procedure **2.6** and purified by column chromatography as yellow solid.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.81 – 7.76 (m, 2H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.66 – 7.56 (m, 5H), 7.52 (qd, *J* = 6.8, 2.8 Hz, 2H), 7.20 (d, *J* = 7.6 Hz, 2H), 2.39 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 146.45, 139.07, 136.89, 132.58, 132.00, 129.91, 129.16, 128.88, 128.12, 128.01, 123.11, 119.79, 116.24, 110.22, 96.20, 84.17, 21.63. **HRMS** m/z (ESI) calcd. for $C_{21}H_{16}N_3^+$ $(M+H)^+$ 310.1344, found 310.1362 .

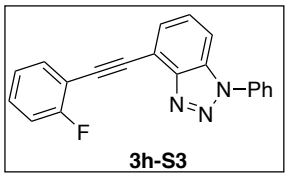
4-((4-methoxyphenyl)ethynyl)-1-phenyl-1H-benzo[d][1,2,3]triazole (3g-S3)



3g-S3

3g-S3 was prepared following the General Procedure **2.6** and purified by column chromatography as yellow solid.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.81 – 7.76 (m, 2H), 7.70 – 7.56 (m, 6H), 7.57 – 7.47 (m, 2H), 6.97 – 6.88 (m, 2H), 3.85 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 160.09, 146.42, 136.91, 133.64, 132.58, 129.91, 128.87, 128.03, 127.94, 123.11, 116.39, 114.97, 114.05, 110.02, 96.13, 83.62, 55.35. **HRMS** m/z (ESI) calcd. for $C_{21}H_{16}N_3O^+$ $(M+H)^+$ 326.1293, found 326.1308.

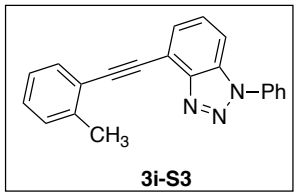
4-((2-fluorophenyl)ethynyl)-1-phenyl-1H-benzo[d][1,2,3]triazole (3h-S3)



3h-S3

3h-S3 was prepared following the General Procedure **2.6** and purified by column chromatography as yellow solid.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.82 – 7.76 (m, 2H), 7.75 – 7.69 (m, 2H), 7.69 – 7.59 (m, 3H), 7.57 – 7.49 (m, 2H), 7.37 (tdd, *J* = 7.4, 5.2, 1.8 Hz, 1H), 7.22 – 7.10 (m, 2H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 162.84, 146.39, 136.83, 133.94, 132.59, 130.61, 129.93, 128.95, 128.47, 127.99, 124.01, 123.13, 115.57, 111.65, 110.83, 89.33. **^{19}F NMR** (564 MHz, Chloroform-*d*) δ -108.86. **HRMS** m/z (ESI) calcd. for $C_{20}H_{13}FN_3^+$ $(M+H)^+$ 314.1094, found 314.1103.

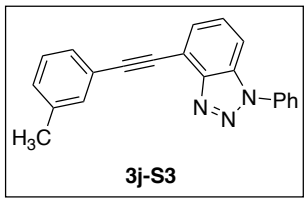
1-phenyl-4-(o-tolylethynyl)-1H-benzo[d][1,2,3]triazole (3i-S3)



3i-S3

3i-S3 was prepared following the General Procedure **2.6** and purified by column chromatography as yellow solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 7.9 Hz, 2H), 7.74 – 7.58 (m, 5H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 4.3 Hz, 2H), 7.21 (dt, *J* = 8.6, 4.2 Hz, 1H), 2.68 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.55, 140.91, 136.92, 132.59, 132.27, 129.93, 129.55, 128.88, 128.02, 127.94, 125.59, 123.07, 122.66, 116.30, 110.31, 94.96, 88.61, 20.96. **HRMS** m/z (ESI) calcd. for $C_{21}H_{16}N_3^+$ $(M+H)^+$ 310.1344, found 310.1361.

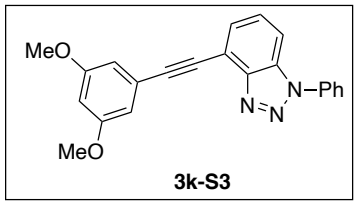
4-((3-methoxyphenyl)ethynyl)-1-phenyl-1H-benzo[d][1,2,3]triazole (3j-S3)



3j-S3

3j-S3 was prepared following the General Procedure **2.6** and purified by column chromatography as yellow solid.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.82 – 7.75 (m, 1H), 7.69 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.66 – 7.58 (m, 2H), 7.57 – 7.53 (m, 1H), 7.51 (ddd, *J* = 8.3, 7.3, 2.8 Hz, 1H), 7.33 – 7.23 (m, 1H), 7.23 – 7.10 (m, 0H), 2.38 (s, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.48, 138.07, 136.89, 132.71, 129.92, 129.75, 129.14, 128.91, 128.27, 128.18, 128.01, 123.14, 122.64, 116.15, 110.33, 96.16, 84.39, 21.25. **HRMS** m/z (ESI) calcd. for $C_{21}H_{16}N_3^+$ $(M+H)^+$ 310.1344, found 310.1360.

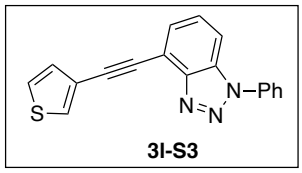
4-((3,5-dimethoxyphenyl)ethynyl)-1-phenyl-1H-benzo[d][1,2,3]triazole (3k-S3)



3k-S3

3k-S3 was prepared following the General Procedure **2.6** and purified by column chromatography as yellow solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 – 7.74 (m, 2H), 7.71 – 7.67 (m, 1H), 7.64 – 7.58 (m, 3H), 7.55 – 7.48 (m, 2H), 6.86 (d, *J* = 2.3 Hz, 2H), 6.51 (t, *J* = 2.3 Hz, 1H), 3.82 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 160.55, 146.40, 136.81, 134.01, 132.56, 129.93, 128.94, 128.41, 128.04, 124.11, 123.07, 110.58, 109.73, 102.65, 95.86, 84.29, 55.55. **HRMS** m/z (ESI) calcd. for $C_{22}H_{18}N_3O_2^+$ $(M+H)^+$ 356.1399, found 356.1406.

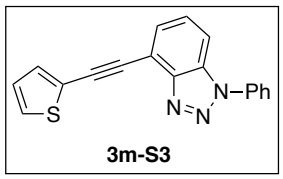
1-phenyl-4-(thiophen-3-ylethynyl)-1H-benzo[d][1,2,3]triazole (3l-S3)



3l-S3

3l-S3 was prepared following the General Procedure **2.6** and purified by column chromatography as yellow solid.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.80 – 7.75 (m, 2H), 7.73 – 7.68 (m, 2H), 7.65 – 7.59 (m, 3H), 7.55 – 7.49 (m, 2H), 7.37 – 7.32 (m, 2H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 146.41, 136.86, 132.59, 130.16, 129.93, 129.90, 128.93, 128.14, 128.01, 125.41, 123.13, 121.95, 115.98, 110.37, 91.04, 84.32. **HRMS** m/z (ESI) calcd. for $C_{18}H_{12}N_3S^+$ $(M+H)^+$ 302.0752, found 302.0769.

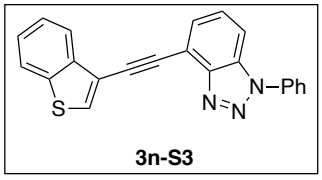
1-phenyl-4-(thiophen-2-ylethynyl)-1*H*-benzo[*d*][1,2,3]triazole (3m-S3)



3m-S3

3m-S3 was prepared following the General Procedure **2.6** and purified by column chromatography as yellow solid.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 1H), 7.65 – 7.58 (m, 3H), 7.52 (td, *J* = 7.5, 4.7 Hz, 2H), 7.49 – 7q(m, 1H), 7.37 (dd, *J* = 5.2, 1.1 Hz, 1H), 7.06 (dd, *J* = 5.1, 3.6 Hz, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 146.17, 136.83, 133.10, 132.60, 129.93, 128.95, 128.20, 128.07, 128.02, 127.24, 123.13, 122.81, 115.65, 110.55, 89.10, 88.51. **HRMS** m/z (ESI) calcd. for $C_{18}H_{12}N_3S^+$ $(M+H)^+$ 302.0752, found 302.0769.

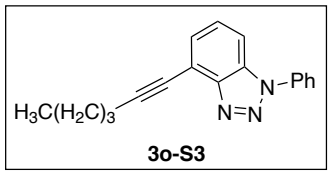
4-(benzo[*b*]thiophen-3-ylethynyl)-1-phenyl-1*H*-benzo[*d*][1,2,3]triazole (3n-S3)



3n-S3

3n-S3 was prepared following the General Procedure **2.6** and purified by column chromatography as yellow solid.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.30 – 8.23 (m, 1H), 7.88 – 7.81 (m, 2H), 7.78 – 7.69 (m, 2H), 7.64 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.60 (dd, *J* = 7.1, 2.1 Hz, 1H), 7.55 (td, *J* = 8.2, 7.7, 2.0 Hz, 2H), 7.52 – 7.42 (m, 3H), 7.43 – 7.36 (m, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 146.45, 139.24, 138.79, 136.81, 132.51, 131.02, 129.92, 128.88, 128.09, 125.27, 125.04, 123.47, 122.94, 122.60, 118.11, 115.72, 110.60, 89.63, 87.50. **HRMS** m/z (ESI) calcd. for $C_{22}H_{14}N_3S^+$ $(M+H)^+$ 352.0908, found 352.0922.

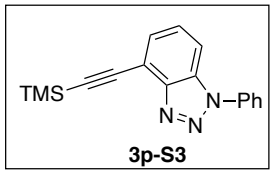
4-(hex-1-yn-1-yl)-1-phenyl-1H-benzo[d][1,2,3]triazole (3o-S3)



3o-S3

3o-S3 was prepared following the General Procedure **2.6** and purified by column chromatography as yellow solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 – 7.71 (m, 2H), 7.65 – 7.54 (m, 3H), 7.52 – 7.41 (m, 3H), 2.60 (t, *J* = 7.1 Hz, 2H), 1.72 (q, *J* = 7.3 Hz, 2H), 1.56 (q, *J* = 7.3 Hz, 2H), 0.98 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 146.80, 136.90, 132.46, 129.87, 128.81, 128.03, 127.96, 123.06, 116.81, 109.66, 97.81, 75.97, 30.72, 22.15, 19.66, 13.71. **HRMS** m/z (ESI) calcd. for $C_{18}H_{18}N_3^+$ $(M+H)^+$ 276.1501, found 276.1504.

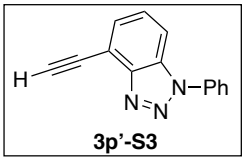
1-phenyl-4-((trimethylsilyl)ethynyl)-1*H*-benzo[*d*][1,2,3]triazole (3p-S3)



3p-S3

3p-S3 was prepared following the General Procedure **2.6** and purified by column chromatography as yellow solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.71 – 7.67 (m, 1H), 7.61 (t, *J* = 7.8 Hz, 2H), 7.58 – 7.45 (m, 3H), 0.35 (s, 9H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.56, 136.85, 132.50, 129.94, 128.98, 128.94, 127.88, 123.12, 115.79, 110.77, 101.76, 99.71, -0.00. **HRMS** m/z (ESI) calcd. for $C_{17}H_{18}N_3Si^+$ $(M+H)^+$ 292.1270, found 292.1263.

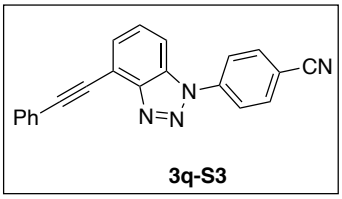
4-ethynyl-1-phenyl-1H-benzo[d][1,2,3]triazole (3p'-S3)



3p'-S3

3p'-S3 was prepared following the General Procedure **2.7** and purified by column chromatography as yellow solid. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.77 – 7.70 (m, 3H), 7.64 – 7.56 (m, 3H), 7.54 – 7.46 (m, 2H), 3.59 (d, *J* = 1.8 Hz, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 146.82, 136.68, 132.46, 129.95, 129.04, 128.96, 127.92, 123.14, 114.56, 111.28, 83.81, 78.76. **HRMS** m/z (ESI) calcd. for $C_{14}H_{10}N_3^+$ $(M+H)^+$ 220.0875, found 220.0878.

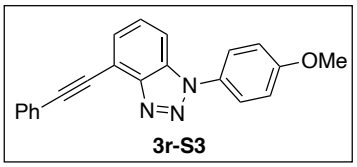
4-(4-(phenylethynyl)-1H-benzo[d][1,2,3]triazol-1-yl)benzonitrile (3q-S3)



3q-S3

3q-S3 was prepared following the General Procedure **2.6** and purified by column chromatography as yellow solid.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.03 – 7.97 (m, 2H), 7.95 – 7.90 (m, 2H), 7.76 – 7.72 (m, 1H), 7.71 – 7.65 (m, 2H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.58 (dd, *J* = 8.3, 7.3 Hz, 1H), 7.40 (tt, *J* = 3.4, 1.8 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 146.76, 140.27, 134.01, 132.07, 131.92, 129.07, 128.89, 128.70, 128.44, 122.75, 122.55, 117.84, 116.60, 112.27, 110.04, 96.47, 84.33. **HRMS** m/z (ESI) calcd. for $C_{21}H_{13}N_4^+$ $(M+H)^+$ 321.1140, found 321.1140.

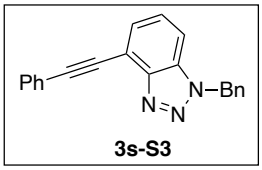
1-(4-methoxyphenyl)-4-(phenylethynyl)-1H-benzo[d][1,2,3]triazole (3r-S3)



3r-S3

3r-S3 was prepared following the General Procedure **2.6** and purified by column chromatography as yellow solid.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.73 – 7.69 (m, 2H), 7.69 – 7.60 (m, 4H), 7.51 (dd, *J* = 8.3, 7.2 Hz, 1H), 7.42 – 7.37 (m, 3H), 7.14 – 7.10 (m, 2H), 3.91 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ .99, 146.22, 132.90, 132.10, 129.79, 128.82, 128.38, 128.16, 127.81, 124.85, 122.88, 115.82, 115.01, 110.39, 95.76, 84.80, 55.72. **HRMS** m/z (ESI) calcd. for $C_{21}H_{16}N_3O^+$ $(M+H)^+$ 326.1293, found 326.1291.

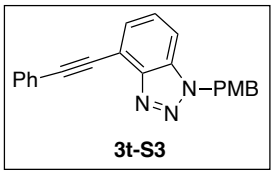
1-benzyl-4-(phenylethynyl)-1H-benzo[d][1,2,3]triazole (3s-S3)



3s-S3

3s-S3 was prepared following the General Procedure **2.6** and purified by column chromatography as yellow solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.53 (dd, *J* = 7.1, 1.1 Hz, 1H), 7.43 – 7.28 (m, 8H), 7.28 – 7.23 (m, 2H), 5.87 (s, 2H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 146.32, 134.60, 132.98, 132.06, 129.05, 128.77, 128.55, 128.35, 127.87, 127.52, 127.21, 122.90, 115.70, 109.91, 95.65, 84.77, 52.48. **HRMS** m/z (ESI) calcd. for $C_{21}H_{16}N_3^+$ $(M+H)^+$ 310.1344, found 310.1352.

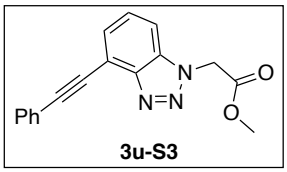
1-(4-methoxybenzyl)-4-(phenylethynyl)-1H-benzo[d][1,2,3]triazole (3t-S3)



3t-S3

3t-S3 was prepared following the General Procedure **2.6** and purified by column chromatography as yellow solid.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.70 – 7.63 (m, 2H), 7.53 – 7.49 (m, 1H), 7.41 – 7.33 (m, 4H), 7.30 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.24 – 7.19 (m, 2H), 6.87 – 6.82 (m, 2H), 5.79 (d, *J* = 2.0 Hz, 2H), 3.83 – 3.68 (m, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 159.74, 146.35, 132.87, 132.06, 129.05, 128.75, 128.34, 127.82, 127.10, 126.60, 122.92, 115.64, 114.39, 110.01, 95.59, 84.80, 55.31, 52.13. **HRMS** m/z (ESI) calcd. for $C_{22}H_{18}N_3O^+$ $(M+H)^+$ 340.1450, found 340.1464.

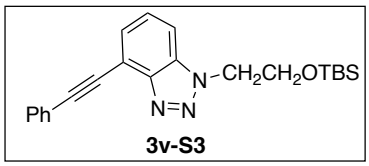
methyl 2-(4-(phenylethynyl)-1H-benzo[d][1,2,3]triazol-1-yl)acetate (3u-S3)



3u-S3

3u-S3 was prepared following the General Procedure **2.6** and purified by column chromatography as yellow solid.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.69 – 7.64 (m, 2H), 7.56 (dd, *J* = 7.0, 1.1 Hz, 1H), 7.47 (dd, *J* = 8.3, 7.0 Hz, 1H), 7.43 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.40 – 7.34 (m, 3H), 5.43 (s, 2H), 3.75 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 166.72, 145.94, 133.59, 132.03, 128.84, 128.37, 128.07, 127.76, 122.80, 115.80, 109.43, 95.70, 84.70, 53.01, 49.04. **HRMS** m/z (ESI) calcd. for $C_{17}H_{14}N_3O2^+$ $(M+H)^+$ 292.1086, found 292.1100 .

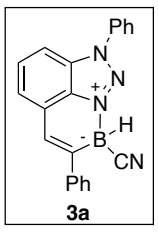
1-(2-((tert-butyldimethylsilyl)oxy)ethyl)-4-(phenylethynyl)-1H-benzo[d][1,2,3]triazole (3v-S3)



3v-S3

3v-S3 was prepared following the General Procedure **2.6** and purified by column chromatography as yellow solid.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93 – 7.85 (m, 2H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.74 (d, *J* = 7.1 Hz, 1H), 7.68 – 7.61 (m, 1H), 7.61 – 7.52 (m, 3H), 4.96 (t, *J* = 5.2 Hz, 2H), 4.30 (t, *J* = 5.2 Hz, 2H), 1.26 – 0.58 (m, 9H), 0.50 – 0.00 (m, 6H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 145.74 (d, *J* = 18.5 Hz), 134.32, 132.03, 128.70, 128.33, 127.83, 127.04, 126.79, 123.76, 122.95, 119.65, 115.12, 110.83, 110.40, 95.22, 85.03, 62.70 (d, *J* = 13.8 Hz), 50.91, 25.68 (d, *J* = 3.4 Hz), 18.07, -5.74. **HRMS** m/z (ESI) calcd. for $C_{22}H_{28}N_3OSi^+$ $(M+H)^+$ 378.2002, found 378.2002.

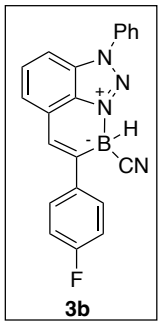
1,4-diphenyl-1,2,2aλ4-triaza-3-boraacenaphthylene-3(1H)-carbonitrile (3a)



3a

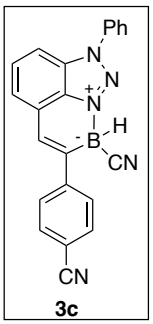
3a was prepared following the General Procedure **2.10** and purified by column chromatography as yellow solid.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.89 – 7.85 (m, 1H), 7.77 – 7.64 (m, 3H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.44 – 7.39 (m, 1H), 7.36 – 7.31 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.95, 136.06, 135.48, 132.92, 132.28, 130.97, 130.46, 129.99, 128.00, 126.99, 123.19, 122.68, 121.45, 108.05. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ -16.15. **HRMS** m/z (ESI) calcd. for $C_{21}H_{16}BN_4^+$ $(M+H)^+$ 335.1468, found 335.1472 .

4-(4-fluorophenyl)-1-phenyl-1,2,2aλ4-triaza-3-boraacenaphthylene-3(1H)-carbonitrile (3b)



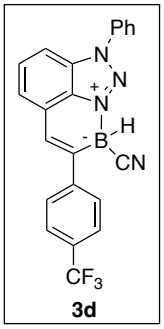
3b was prepared following the General Procedure **2.10** and purified by column chromatography as yellow solid.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.8 Hz, 2H), 7.75 – 7.65 (m, 3H), 7.65 – 7.56 (m, 3H), 7.52 (td, *J* = 7.6, 3.5 Hz, 2H), 7.09 (t, *J* = 8.5 Hz, 2H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 162.88 (d, *J* = 250.4 Hz), 146.42, 136.83, 134.07, 134.01, 132.59, 129.93, 128.95, 128.18, 128.02, 123.11, 118.99, 115.80, 115.65, 110.54, 94.74, 84.47. **^{19}F NMR** (564 MHz, Chloroform-*d*) δ -110.00. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ -16.34. **HRMS** m/z (ESI) calcd. for $C_{21}H_{15}BFN_4^+$ $(M+H)^+$ 353.1374, found 353.1387.

4-(4-cyanophenyl)-1-phenyl-1,2,2aλ4-triaza-3-boraacenaphthylene-3(1H)-carbonitrile (3c)



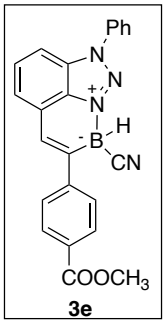
3c was prepared following the General Procedure **2.10** and purified by column chromatography as yellow solid. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.88 (d, J = 7.4 Hz, 2H), 7.81 (d, J = 8.1 Hz, 2H), 7.71 (t, J = 9.1 Hz, 6H), 7.59 (d, J = 8.6 Hz, 1H), 7.40 (d, J = 7.1 Hz, 1H), 7.15 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.74, 135.31, 132.95, 132.32, 131.22, 130.57, 129.06, 127.63, 123.72, 123.60, 123.24, 119.26, 111.08, 109.16. **^{11}B NMR** (128 MHz, Chloroform-d) δ -16.20. **HRMS** m/z (ESI) calcd. for $C_{22}H_{15}BN_5^+$ $(M+H)^+$ 360.1421, found 360.1428

1-phenyl-4-(4-(trifluoromethyl)phenyl)-1,2,2aλ4-triaza-3-boraacenaphthylene-3(1H)-carbonitrile (3d)



3d was prepared following the General Procedure **2.10** and purified by column chromatography.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.79 (dd, *J* = 7.4, 1.9 Hz, 2H), 7.73 (t, *J* = 8.4 Hz, 2H), 7.68 – 7.55 (m, 6H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.35 – 7.24 (m, 1H), 7.09 – 6.92 (m, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 146.64, 136.06, 135.37, 132.94, 132.31, 131.12, 130.52, 129.35, 128.97, 127.23, 125.38, 123.86, 123.18, 111.94, 108.8. **^{19}F NMR** (564 MHz, Chloroform-*d*) δ -62.42. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ -16.30. **HRMS** m/z (ESI) calcd. for $C_{22}H_{15}BF_3N_4^+$ $(M+H)^+$ 403.1342, found 403.1346.

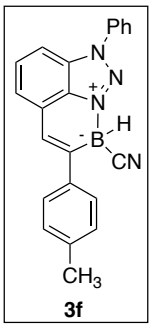
methyl 4-(3-cyano-1-phenyl-1,3-dihydro-1,2,2aλ4-triaza-3-boraacenaphthylen-4-yl)benzoate (3e)



3e

3e was prepared following the General Procedure **2.10** and purified by column chromatography.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.10 – 8.05 (m, 2H), 7.90 – 7.85 (m, 2H), 7.81 – 7.76 (m, 2H), 7.75 – 7.67 (m, 4H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.38 (d, *J* = 7.0 Hz, 1H), 7.19 – 7.16 (m, 1H), 3.94 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 167.13, 147.69, 136.10, 135.42, 132.91, 132.32, 131.09, 130.51, 129.81, 129.30, 126.97, 123.23, 122.95, 108.63, 52.06. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ -17.32. **HRMS** m/z (ESI) calcd. for $C_{23}H_{17}BN_4NaO_2^+$ $(M+Na)^+$ 415.1342, found 415.1348.

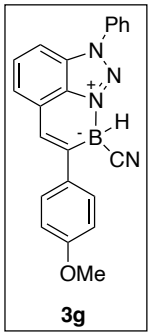
1-phenyl-4-(p-tolyl)-1,2,2aλ4-triaza-3-boraacenaphthylene-3(1H)-carbonitrile (3f)



3f

3f was prepared following the General Procedure **2.10** and purified by column chromatography.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.85 (dd, *J* = 7.5, 1.9 Hz, 2H), 7.72 – 7.61 (m, 6H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.29 (d, *J* = 7.1 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 2H), 7.14 – 7.08 (m, 1H), 2.38 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 139.96, 137.93, 136.04, 135.52, 132.92, 132.27, 130.93, 130.44, 130.18, 129.21, 126.89, 123.18, 122.46, 120.61, 107.77, 21.28. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ -16.23. **HRMS** m/z (ESI) calcd. for $C_{22}H_{18}BN_4^+$ $(M+H)^+$ 349.1625, found 349.1629.

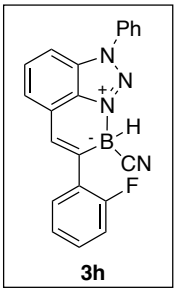
4-(4-methoxyphenyl)-1-phenyl-1,2,2aλ4-triaza-3-boraacenaphthylene-3(1H)-carbonitrile (3g)



3g

3g was prepared following the General Procedure **2.10** and purified by column chromatography.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.90 – 7.82 (m, 2H), 7.77 – 7.58 (m, 6H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.29 (d, *J* = 7.1 Hz, 1H), 7.10 (s, 1H), 6.96 (d, *J* = 8.2 Hz, 2H), 3.85 (d, *J* = 1.3 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 159.75, 135.95, 135.53, 135.22, 132.94, 132.27, 130.91, 130.43, 130.26, 128.27, 123.17, 122.28, 119.66, 113.90, 107.54, 55.35. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ -16.50. **HRMS** m/z (ESI) calcd. for $C_{22}H_{18}BN_4O^+$ $(M+H)^+$ 365.1574, found 365.1578.

4-(2-fluorophenyl)-1-phenyl-1,2,2aλ4-triaza-3-boraacenaphthylene-3(1H)-carbonitrile (3h)

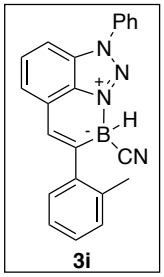


3h

3h was prepared following the General Procedure **2.10** and purified by column chromatography.
^{1}H NMR ((600 MHz, Chloroform-*d*) δ 7.88 – 7.83 (m, 2H), 7.73 – 7.62 (m, 5H), 7.53 (d, *J* = 8.6 Hz, 1H), 7.31 (d, *J* = 7.0 Hz, 1H), 7.26 (ddd, *J* = 13.1, 6.1, 1.8 Hz, 2H), 7.19 (td, *J* = 7.5, 1.3 Hz, 1H), 7.15 – 7.09 (m, 2H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 159.75 (d, *J* = 247.8 Hz), 135.90, 135.42, 132.89, 132.28, 131.02, 130.49, 130.31, 129.63, 128.64, 128.58, 125.17, 125.12, 124.04, 123.18, 123.02,

116.05, 115.89, 108.53. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ -16.11. **HRMS** m/z (ESI) calcd. for $C_{21}H_{15}BFN_4^+$ $(M+H)^+$ 353.1374, found 353.1376.

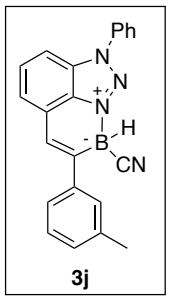
1-phenyl-4-(o-tolyl)-1,2,2aλ4-triaza-3-boraacenaphthylene-3(1H)-carbonitrile (3i)



3i

3i was prepared following the General Procedure **2.10** and purified by column chromatography as yellow solid
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.86 – 7.81 (m, 2H), 7.72 – 7.61 (m, 4H), 7.52 (dd, *J* = 8.8, 2.7 Hz, 1H), 7.29 (dt, *J* = 7.4, 1.8 Hz, 1H), 7.27 – 7.14 (m, 4H), 6.68 (d, *J* = 1.9 Hz, 1H), 2.39 (d, *J* = 3.0 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 144.10, 136.04, 135.43, 134.26, 132.94, 132.36, 131.01, 130.49, 130.15, 129.79, 127.86, 126.50, 125.33, 123.50, 123.16, 122.51, 108.34, 20.12. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ -15.86. **HRMS** m/z (ESI) calcd. for $C_{22}H_{18}BN_4^+$ $(M+H)^+$ 349.1625, found 349.1622.

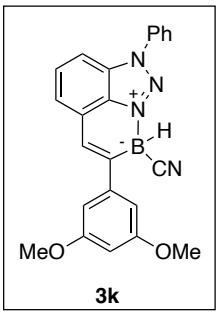
1-phenyl-4-(m-tolyl)-1,2,2aλ4-triaza-3-boraacenaphthylene-3(1H)-carbonitrile (3j)



3j

3j was prepared following the General Procedure **2.10** and purified by column chromatography.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.89 – 7.84 (m, 2H), 7.73 – 7.63 (m, 5H), 7.55 (dd, *J* = 4.6, 2.3 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.15 (d, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 1.7 Hz, 1H), 2.42 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 142.99, 137.87, 136.08, 135.51, 132.91, 132.29, 130.95, 130.45, 130.12, 128.83, 128.36, 127.63, 124.19, 123.20, 122.57, 121.34, 107.91, 21.63. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ -16.49. **HRMS** m/z (ESI) calcd. for $C_{22}H_{18}BN_4^+$ $(M+H)^+$ 349.1625, found 349.1622.

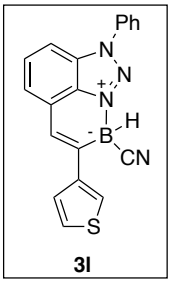
4-(3,5-dimethoxyphenyl)-1-phenyl-1,2,2aλ4-triaza-3-boraacenaphthylene-3(1H)-carbonitrile (3k)



3k

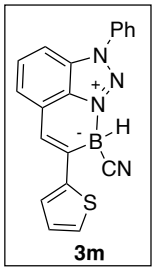
3k was prepared following the General Procedure **2.10** and purified by column chromatography.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.88 – 7.85 (m, 2H), 7.73 – 7.64 (m, 4H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.32 (d, *J* = 7.1 Hz, 1H), 7.11 (d, *J* = 1.6 Hz, 1H), 6.90 (d, *J* = 2.3 Hz, 2H), 6.47 (t, *J* = 2.2 Hz, 1H), 3.86 (s, 6H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 160.71, 145.30, 136.08, 135.45, 132.92, 132.25, 130.98, 130.46, 129.77, 123.16, 122.82, 121.86, 108.22, 105.17, 100.36, 55.42. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ -16.50. **HRMS** m/z (ESI) calcd. for $C_{23}H_{20}BN_4O_2^+$ $(M+H)^+$ 395.1679 , found 395.1678.

1-phenyl-4-(thiophen-3-yl)-1,2,2aλ^4-triaza-3-boraacenaphthylene-3(1*H*)-carbonitrile (3l)



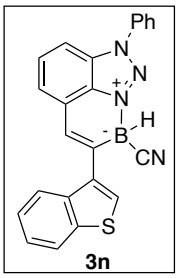
3l was prepared following the General Procedure **2.10** and purified by column chromatography.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.90 – 7.83 (m, 2H), 7.78 (dd, *J* = 2.9, 1.3 Hz, 1H), 7.74 – 7.62 (m, 4H), 7.54 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.34 (dd, *J* = 5.0, 2.9 Hz, 1H), 7.31 (d, *J* = 7.1 Hz, 1H), 7.24 – 7.17 (m, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 143.73, 135.91, 135.49, 132.91, 132.29, 130.97, 130.45, 130.16, 125.47, 125.25, 124.24, 123.21, 122.54, 119.90, 107.76. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ -16.50. **HRMS** m/z (ESI) calcd. for $C_{19}H_{14}BN_4S^+$ $(M+H)^+$ 341.1032, found 341.1031.

1-phenyl-4-(thiophen-2-yl)-1,2,2aλ^4-triaza-3-boraacenaphthylene-3(1H)-carbonitrile (3m)



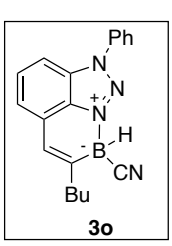
3m was prepared following the General Procedure **2.10** and purified by column chromatography.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.87 (dd, *J* = 7.5, 1.8 Hz, 2H), 7.78 (dd, *J* = 2.9, 1.3 Hz, 1H), 7.73 – 7.69 (m, 2H), 7.69 – 7.67 (m, 1H), 7.64 (dd, *J* = 8.6, 7.1 Hz, 1H), 7.54 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.35 (dd, *J* = 5.1, 2.9 Hz, 1H), 7.31 (d, *J* = 7.1 Hz, 1H), 7.21 (d, *J* = 1.5 Hz, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 142.70, 134.87, 134.45, 131.87, 131.26, 129.94, 129.42, 129.14, 124.44, 124.22, 123.20, 122.18, 121.50, 118.86, 106.72. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ -16.57. **HRMS** m/z (ESI) calcd. for $C_{19}H_{14}BN_4S^+$ $(M+H)^+$ 341.1032, found 341.1034.

4-(benzo[b]thiophen-3-yl)-1-phenyl-1,2,2aλ4-triaza-3-boraacenaphthylene-3(1H)-carbonitrile (3n)



3n was prepared following the General Procedure **2.10** and purified by column chromatography.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 – 8.08 (m, 1H), 7.90 (dd, *J* = 9.8, 7.9 Hz, 3H), 7.79 (s, 1H), 7.70 (dt, *J* = 18.4, 7.4 Hz, 4H), 7.54 (d, *J* = 8.6 Hz, 1H), 7.38 (ddd, *J* = 16.8, 12.1, 7.1 Hz, 3H), 7.24 (s, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 140.92, 139.25, 137.89, 135.47, 132.92, 132.40, 131.03, 130.50, 129.94, 124.70, 124.18, 124.05, 123.56, 123.24, 123.13, 122.98, 122.67, 108.17. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ -16.12. **HRMS** m/z (ESI) calcd. for $C_{23}H_{15}BN_4NaS^+$ $(M+Na)^+$ 413.1008, found 413.1010.

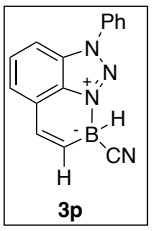
4-butyl-1-phenyl-1,2,2aλ4-triaza-3-boraacenaphthylene-3(1H)-carbonitrile (3o)



3o was prepared following the General Procedure **2.10** and purified by column chromatography.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.84 – 7.80 (m, 2H), 7.71 – 7.67 (m, 2H), 7.67 – 7.63 (m, 1H), 7.59 (dd, *J* = 8.6, 7.1 Hz, 1H), 7.42 (d, *J* = 8.6 Hz, 1H), 7.15 (d, *J* = 7.1 Hz, 1H), 6.65 (d, *J* = 1.8 Hz, 1H), 2.61 – 2.44 (m, 2H), 1.66 – 1.59 (m, 2H), 1.48 – 1.36 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (**151 MHz,

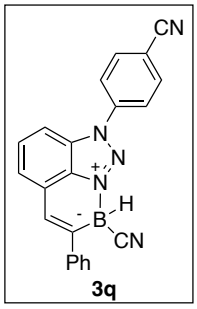
Chloroform-*d*) δ 136.18, 135.54, 132.88, 132.22, 130.82, 130.60, 130.39, 123.13, 121.26, 119.70, 107.12, 37.61, 30.84, 22.79, 14.11. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ -16.03. **HRMS** m/z (ESI) calcd. for $C_{19}H_{20}BN_4^+$ $(M+H)^+$ 315.1781, found 315.1781.

1-phenyl-1,2,2aλ^4-triaza-3-boraacenaphthylene-3(1*H*)-carbonitrile (3p)



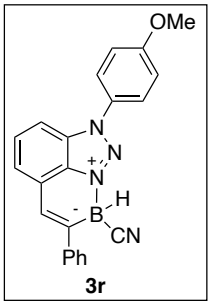
3p was prepared following the General Procedure **2.10** and purified by column chromatography as yellow solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 7.4 Hz, 2H), 7.73 – 7.66 (m, 3H), 7.63 (t, *J* = 7.7 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 1H), 6.91 (d, *J* = 12.3 Hz, 1H), 6.77 (dd, *J* = 12.1, 2.9 Hz, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 136.61, 135.41, 132.66, 132.38, 130.96, 130.45, 130.27, 129.92, 124.60, 123.23, 122.43, 108.45. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ -16.38. **HRMS** m/z (ESI) calcd. for $C_{15}H_{12}BN_4^+$ $(M+H)^+$ 259.1155, found 259.1155

1-(4-cyanophenyl)-4-phenyl-1,2,2aλ4-triaza-3-boraacenaphthylene-3(1H)-carbonitrile (3q)



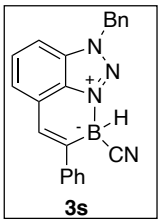
3q was prepared following the General Procedure **2.10** and purified by column chromatography as yellow solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 – 8.00 (m, 4H), 7.77 – 7.69 (m, 3H), 7.53 (d, *J* = 8.6 Hz, 1H), 7.44 – 7.31 (m, 4H), 7.14 (d, *J* = 1.6 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.59, 138.65, 136.27, 134.46, 133.92, 132.06, 130.56, 128.54, 128.25, 126.99, 123.50, 123.15, 121.20, 117.02, 114.93, 107.45. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ -16.23. **HRMS** m/z (ESI) calcd. for $C_{22}H_{15}BN_5^+$ $(M+H)^+$ 360.1421, found 360.1420.

1-(4-methoxyphenyl)-4-phenyl-1,2,2aλ4-triaza-3-boraacenaphthylene-3(1H)-carbonitrile (3r)



3r was prepared following the General Procedure **2.10** and purified by column chromatography as yellow solid.
^{1}H NMR (600 MHz, DMSO-d_6) δ 7.82 – 7.73 (m, 2H), 7.62 (dd, *J* = 8.5, 6.9 Hz, 1H), 7.59 – 7.52 (m, 3H), 7.40 (d, *J* = 6.9 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.17 – 7.12 (m, 3H), 3.76 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 161.43, 154.36, 143.12, 135.36, 133.21, 133.14, 131.77, 128.96, 128.29, 128.18, 126.99, 126.10, 123.80, 122.66, 115.85, 110.50, 56.31. **^{11}B NMR** (128 MHz, DMSO-d_6) δ -16.39. **HRMS** m/z (ESI) calcd. For $C_{22}H_{18}BN_4O^+$ $(M+H)^+$ 365.1574, found 365.1578.

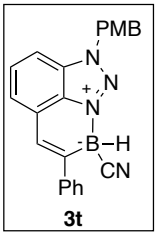
1-benzyl-4-phenyl-1,2,2aλ4-triaza-3-boraacenaphthylene-3(1H)-carbonitrile (3s)



3s was prepared following the General Procedure **2.10** and purified by column chromatography as yellow solid.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.73 – 7.68 (m, 2H), 7.47 (dd, *J* = 8.6, 7.1 Hz, 1H), 7.46 – 7.37 (m, 7H), 7.35 – 7.26 (m, 1H), 7.21 (d, *J* = 7.1 Hz, 1H), 7.09 – 7.04 (m, 2H), 5.92 (d, *J* = 15.0 Hz, 1H), 5.88 (d, *J* = 15.0 Hz, 1H), 4.23 (s, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 143.07, 136.04, 132.60, 132.07, 131.91, 129.73, 129.57,

128.44, 128.34, 127.92, 126.95, 122.26, 121.50, 107.38, 54.97. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ -16.27. **HRMS** m/z (ESI) calcd. for $C_{22}H_{18}BN_4^+$ $(M+H)^+$ 349.1625, found 349.1616.

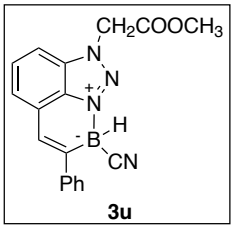
1-(4-methoxybenzyl)-4-phenyl-1,2,2aλ4-triaza-3-boraacenaphthylene-3(1H)-carbonitrile (3t)



3t

3t was prepared following the General Procedure **2.10** and purified by column chromatography as yellow solid.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.73 – 7.65 (m, 2H), 7.43 (dd, *J* = 8.6, 7.1 Hz, 1H), 7.40 – 7.32 (m, 4H), 7.32 – 7.28 (m, 1H), 7.18 (d, *J* = 7.1 Hz, 1H), 7.09 – 7.01 (m, 2H), 6.94 – 6.90 (m, 2H), 5.85 – 5.77 (m, 2H), 3.80 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 160.56, 143.08, 135.99, 132.47, 131.91, 130.02, 129.59, 128.43, 127.89, 126.93, 123.84, 122.23, 121.54, 114.87, 107.62, 55.42, 54.66. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ -16.30. **HRMS** m/z (ESI) calcd. for $C_{23}H_{20}BN_4O^+$ $(M+H)^+$ 379.1730, found 379.1730.

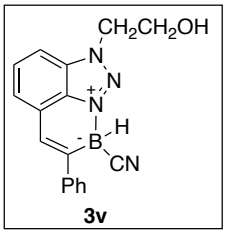
methyl 2-(3-cyano-4-phenyl-1,2,2aλ4-triaza-3-boraacenaphthylen-1(3H)-yl)acetate (3u)



3u

3u was prepared following the General Procedure **2.10** and purified by column chromatography as yellow solid.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.74 – 7.67 (m, 2H), 7.61 (dd, *J* = 8.5, 7.1 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.34 – 7.30 (m, 1H), 7.30 – 7.23 (m, 3H), 7.08 (d, *J* = 1.7 Hz, 1H), 5.52 (q, *J* = 17.6 Hz, 2H), 3.87 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.82, 142.95, 135.85, 133.48, 132.75, 129.91, 128.46, 127.99, 126.96, 122.46, 121.43, 106.92, 53.74, 50.81. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ -16.75. **HRMS** m/z (ESI) calcd. for $C_{18}H_{16}BN_4O_2^+$ $(M+H)^+$ 331.1366, found 331.1371.

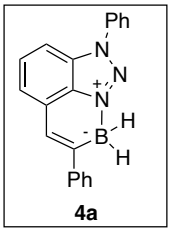
1-(2-hydroxyethyl)-4-phenyl-1,2,2aλ4-triaza-3-boraacenaphthylene-3(1H)-carbonitrile (3v)



3v

3v was prepared following the General Procedure **2.10** and purified by column chromatography as yellow solid.
^{1}H NMR (400 MHz, DMSO-d_6) δ 7.83 (d, *J* = 8.6 Hz, 1H), 7.75 – 7.71 (m, 1H), 7.70 – 7.64 (m, 2H), 7.48 (d, *J* = 7.0 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 7.3 Hz, 1H), 7.26 (s, 1H), 5.20 (t, *J* = 5.7 Hz, 1H), 5.04 – 4.97 (m, 2H), 3.98 (q, *J* = 5.3 Hz, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 143.27, 134.19, 131.97, 128.93, 128.19, 127.74, 126.96, 123.39, 122.72, 110.92, 60.00, 54.16. **^{11}B NMR** (128 MHz, DMSO-d_6) δ -17.46. **HRMS** m/z (ESI) calcd. for $C_{17}H_{15}BN_4NaO^+$ $(M+Na)^+$ 325.1237, found 325.1235.

1,4-diphenyl-1,3-dihydro-1,2,2aλ4-triaza-3-boraacenaphthylene (4a)

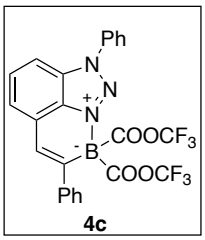


4a

4a was prepared following the General Procedure **2.11** and purified by column chromatography as yellow solid.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.85 – 7.81 (m, 2H), 7.76 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.67 – 7.64 (m, 2H), 7.62 – 7.58 (m, 1H), 7.56 – 7.53 (m, 1H), 7.41 – 7.35 (m, 3H), 7.32 – 7.27 (m, 1H), 7.18 (d, *J* = 7.1 Hz, 1H), 7.08 (d, *J* = 1.7 Hz, 1H). **^{13}C**

NMR (151 MHz, Chloroform-*d*) δ 144.88, 136.48 (d, *J* = 140.8 Hz), 133.37 – 131.42 (m), 130.17 (d, *J* = 16.1 Hz), 128.20, 127.39, 126.59, 122.89, 120.67, 119.27, 106.43. **^{11}B NMR (**128 MHz, Chloroform-*d*) δ -13.25. **HRMS** m/z (ESI) calcd. for $C_{20}H_{17}BN_3^+$ $(M+H)^+$ 310.1516, found 350.1511.

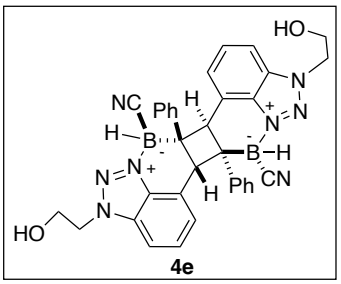
bis(trifluoromethyl) 1,4-diphenyl-1,2,2aλ4-triaza-3λ4-boraacenaphthylene-3,3(1H)-dicarboxylate (4c)



4c

4c was prepared following the General Procedure **2.12** and purified by column chromatography as yellow solid.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.88 – 7.82 (m, 2H), 7.77 (dd, *J* = 8.6, 7.1 Hz, 1H), 7.72 (q, *J* = 7.6, 7.0 Hz, 3H), 7.69 – 7.64 (m, 3H), 7.61 (d, *J* = 7.1 Hz, 1H), 7.48 (s, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 157.24, 156.96, 140.20, 136.79, 135.17, 132.75, 132.05, 131.57, 130.58, 128.52, 128.06, 127.82, 127.40, 127.13, 125.42, 123.55, 109.43. **^{19}F NMR** (564 MHz, Chloroform-*d*) δ -76.23. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 2.74. **HRMS** m/z (ESI) calcd. for $C_{24}H_{15}BF_6N_3O_4^+$ $(M+H)^+$ 534.1060, found 534.1061.

4e

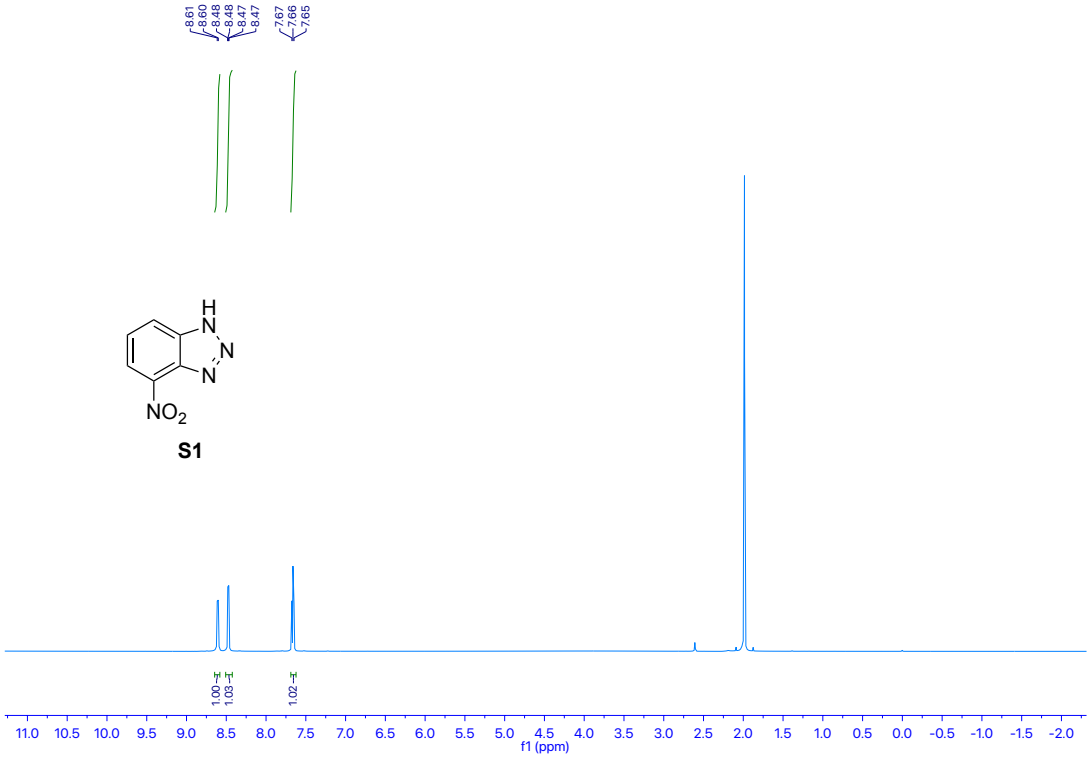


4e

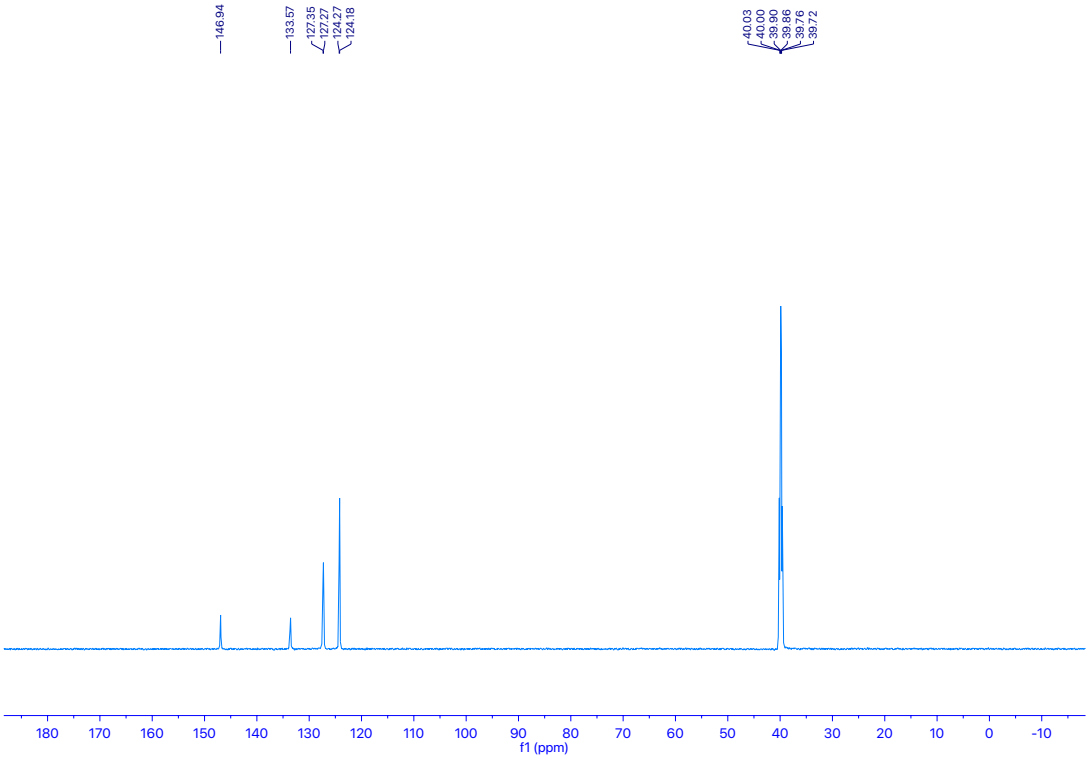
4e was prepared after column chromatography (1:1 ratio of hexane and EA, 10days 100% conversion) as yellow solid.
^{1}H NMR (600 MHz, DMSO-d_6) δ 7.90 (dd, *J* = 7.8, 5.1 Hz, 2H), 7.80 (dd, *J* = 8.5, 7.2 Hz, 1H), 6.86 (t, *J* = 7.6 Hz, 2H), 6.84 – 6.79 (m, 2H), 6.74 (s, 1H), 5.16 (t, *J* = 5.2 Hz, 1H), 4.91 (t, *J* = 5.2 Hz, 2H), 4.59 (s, 1H), 3.90 (dt, *J* = 23.5, 6.2 Hz, 2H). **^{13}C NMR** (151 MHz, DMSO-d_6) δ 147.69, 137.29, 134.09, 132.04, 130.78, 130.67, 128.84, 127.69, 127.15, 123.89, 110.98, 59.69, 53.91, 49.54, 47.14. **^{11}B NMR** (128 MHz, Chloroform-d) δ -22.85. **HRMS** m/z (ESI) calcd. for $C_{34}H_{31}B_2N_8O_2^+$ $(M+H)^+$ 605.2756, found 605.2760.

V. NMR Spectra

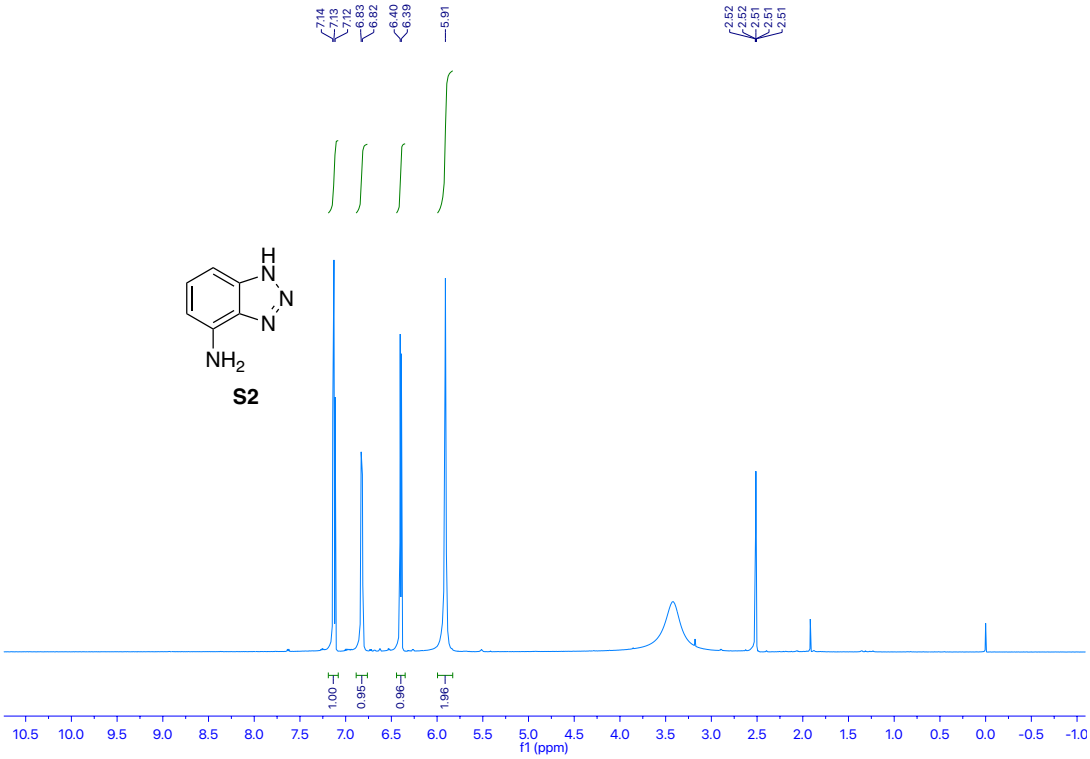
Compound S1, ^{1}H NMR (600 MHz, DMSO)



Compound S1, ^{13}C-NMR (151 M Hz, DMSO)

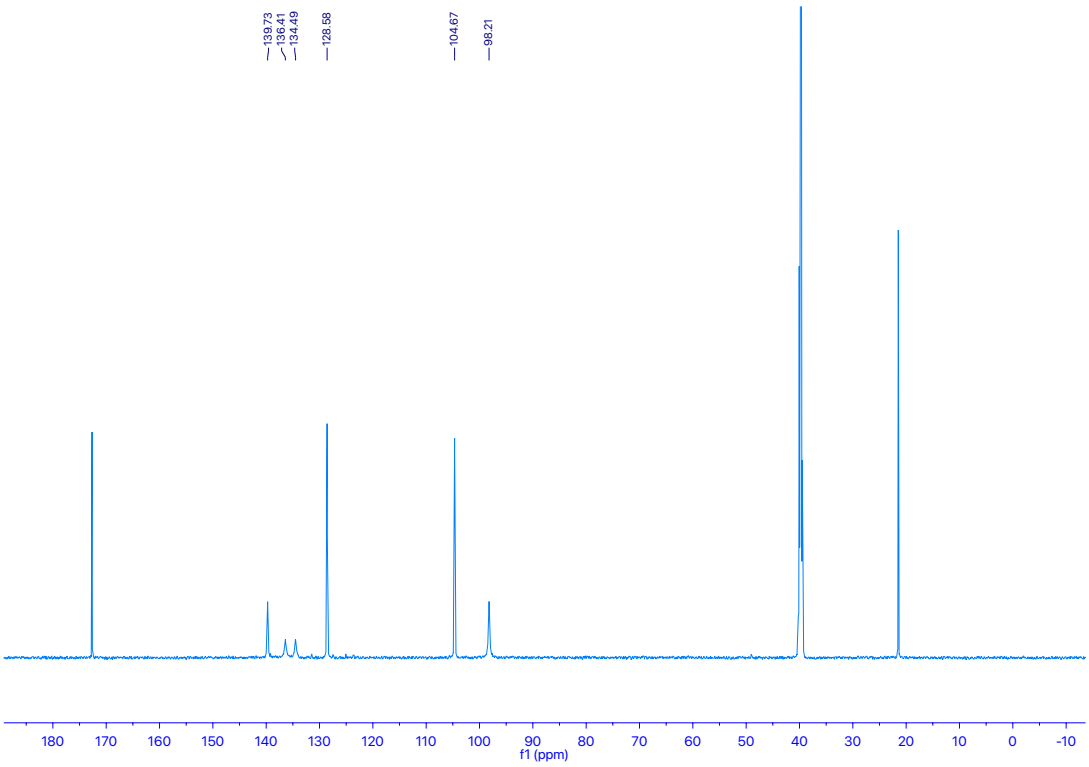


Compound S2, ^{1}H NMR (600 MHz, DMSO)

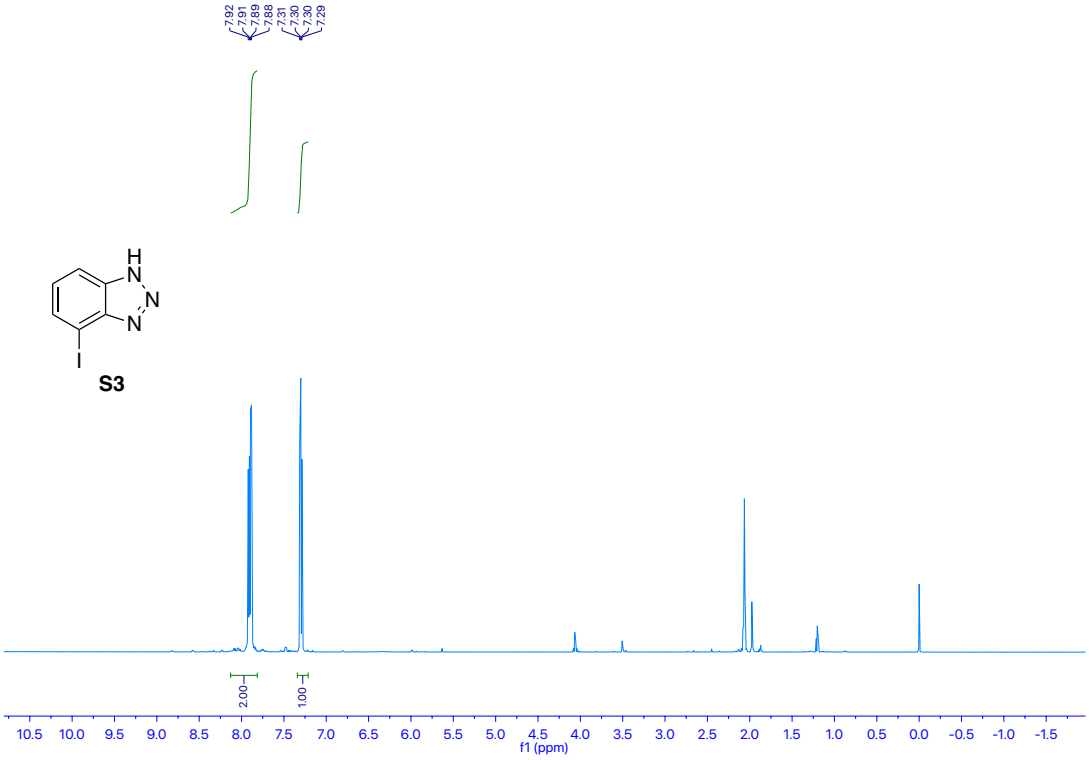


S2

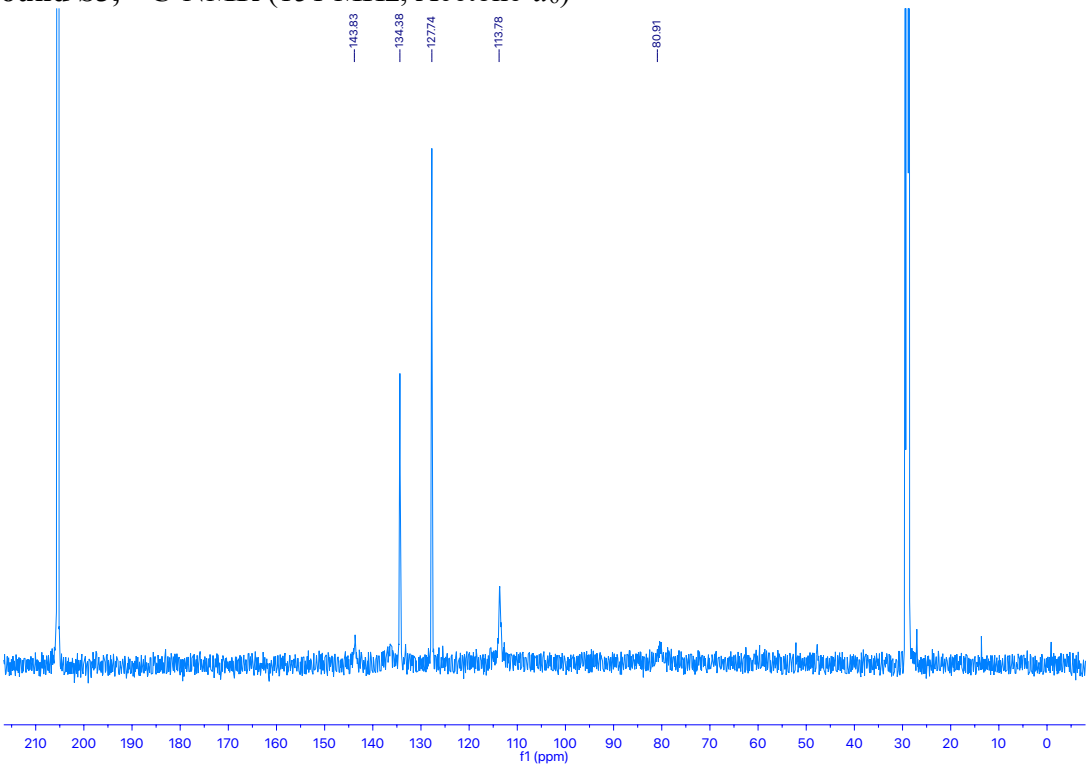
Compound S2, ^{13}C-NMR (151 MHz, DMSO)



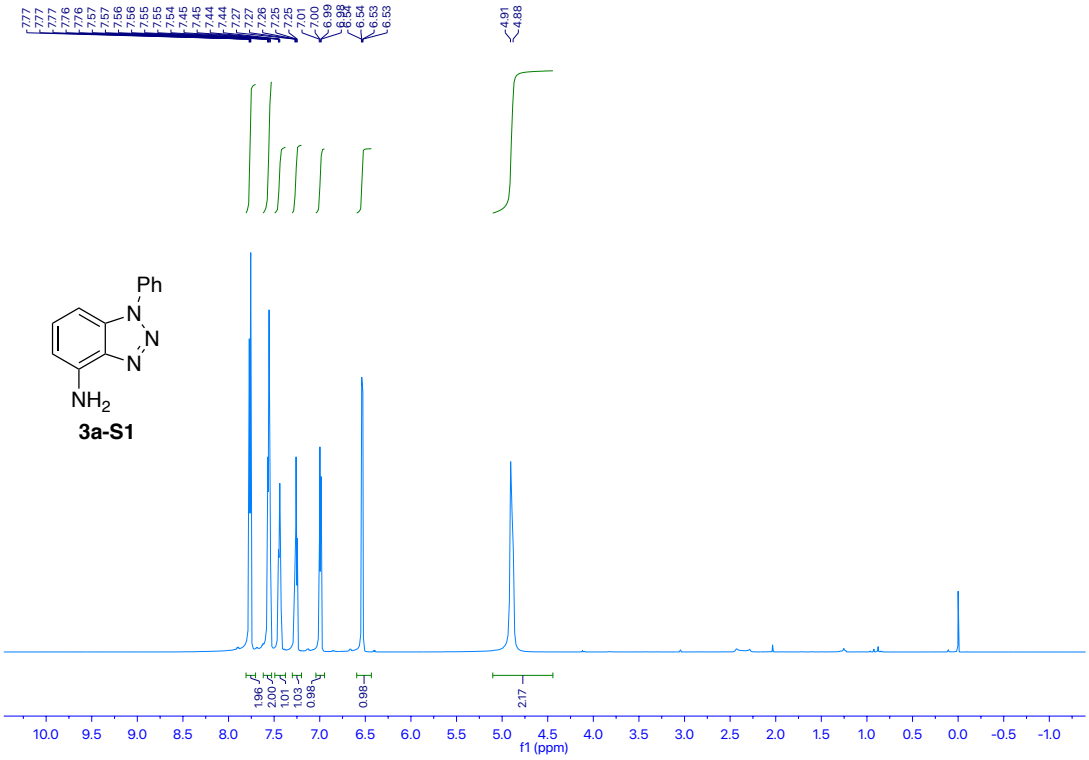
Compound S3, ^{1}H NMR (600 MHz, Acetone-d_6)



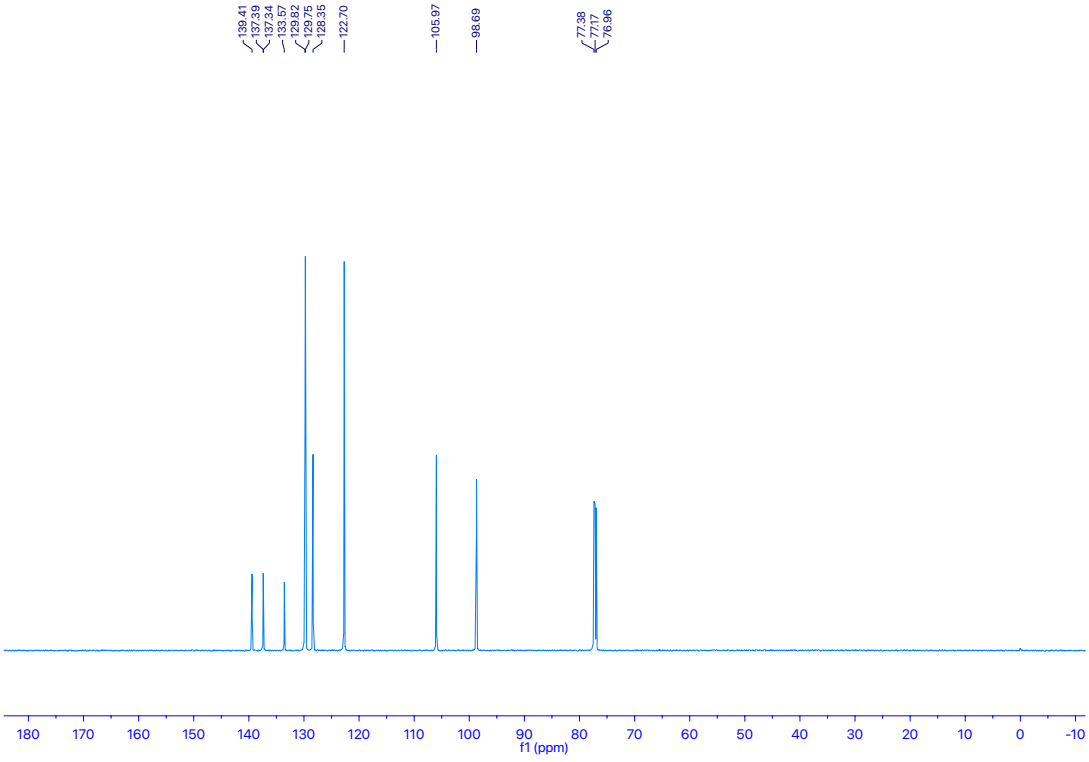
Compound S3, ^{13}C-NMR (151 MHz, Acetone-d_6)



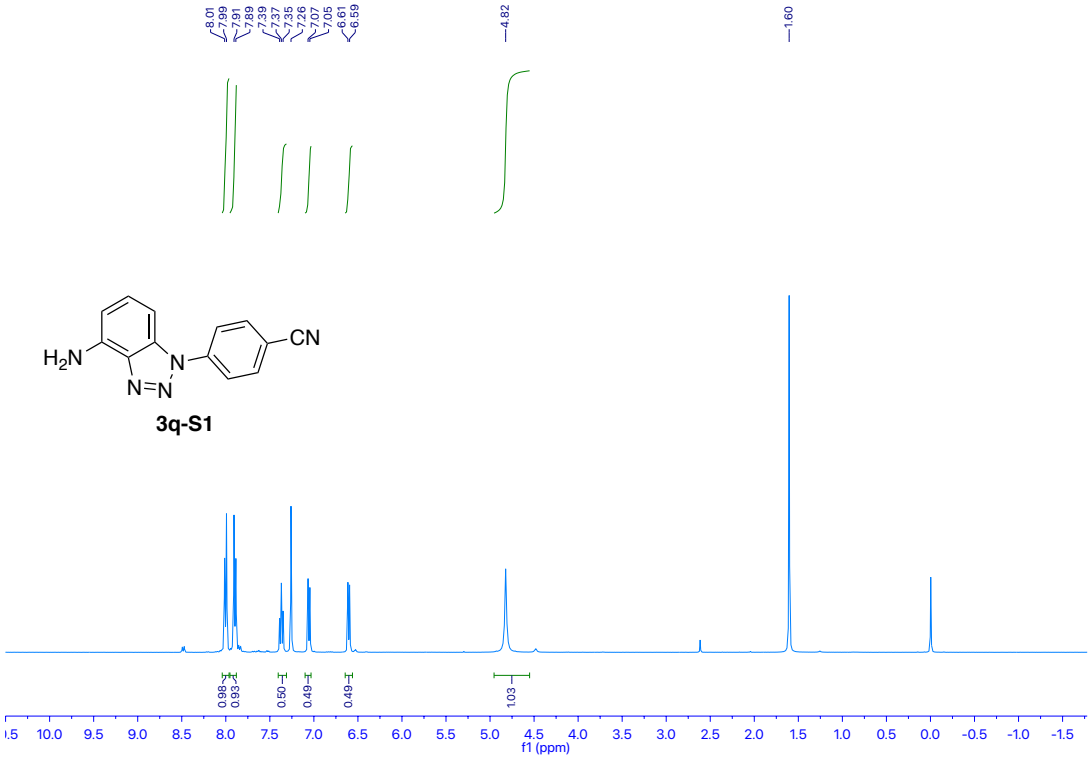
Compound 3a-S1, ^{1}H NMR (600 MHz, $CDCl_3$)



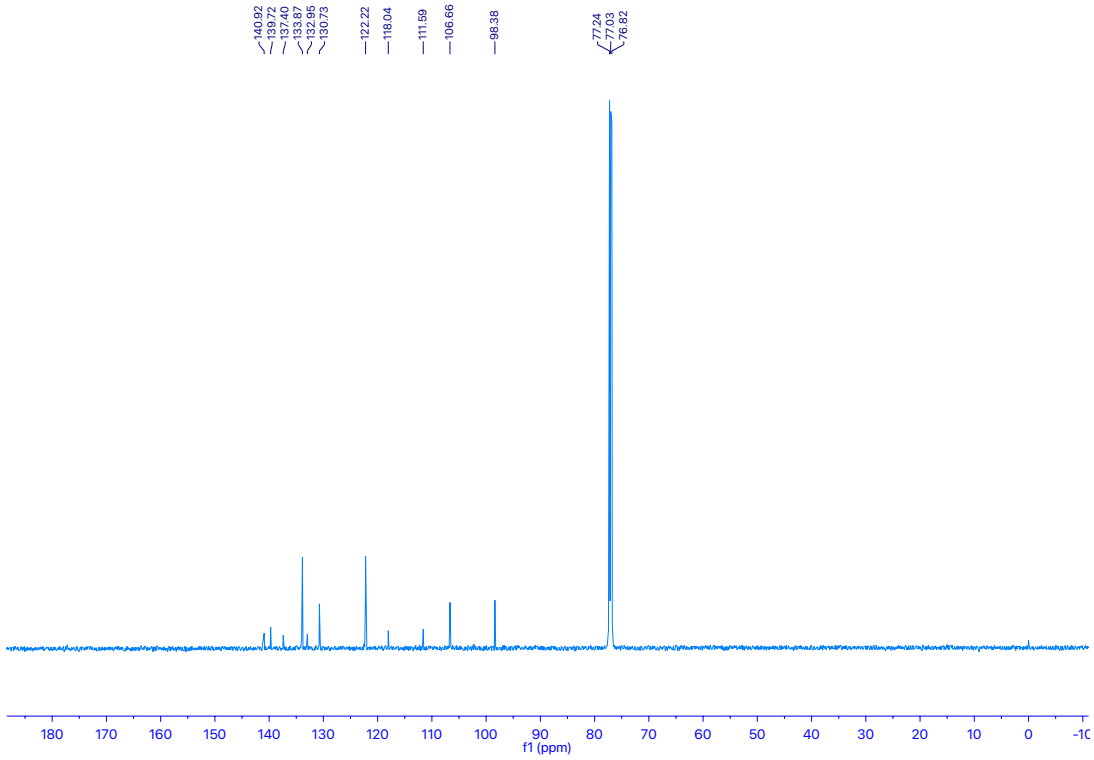
Compound 3a-S1, ^{13}C-NMR (151 MHz, $CDCl_3$)



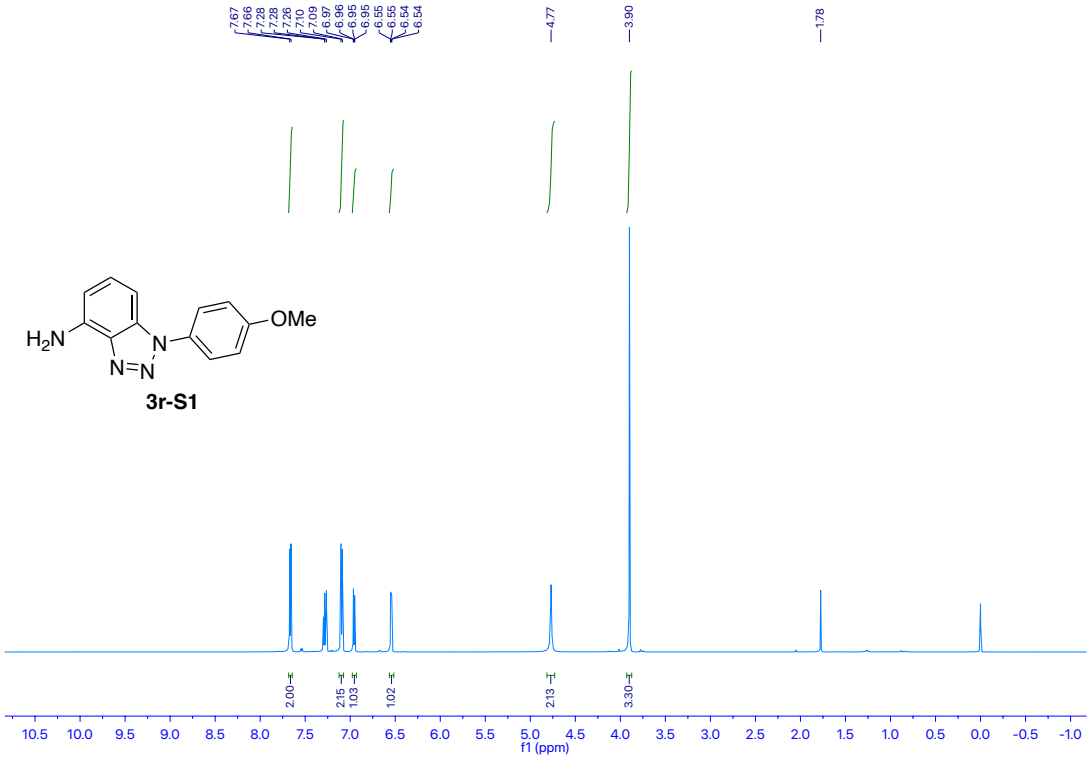
Compound 3q-S1, ^{1}H NMR (600 MHz, $CDCl_3$)



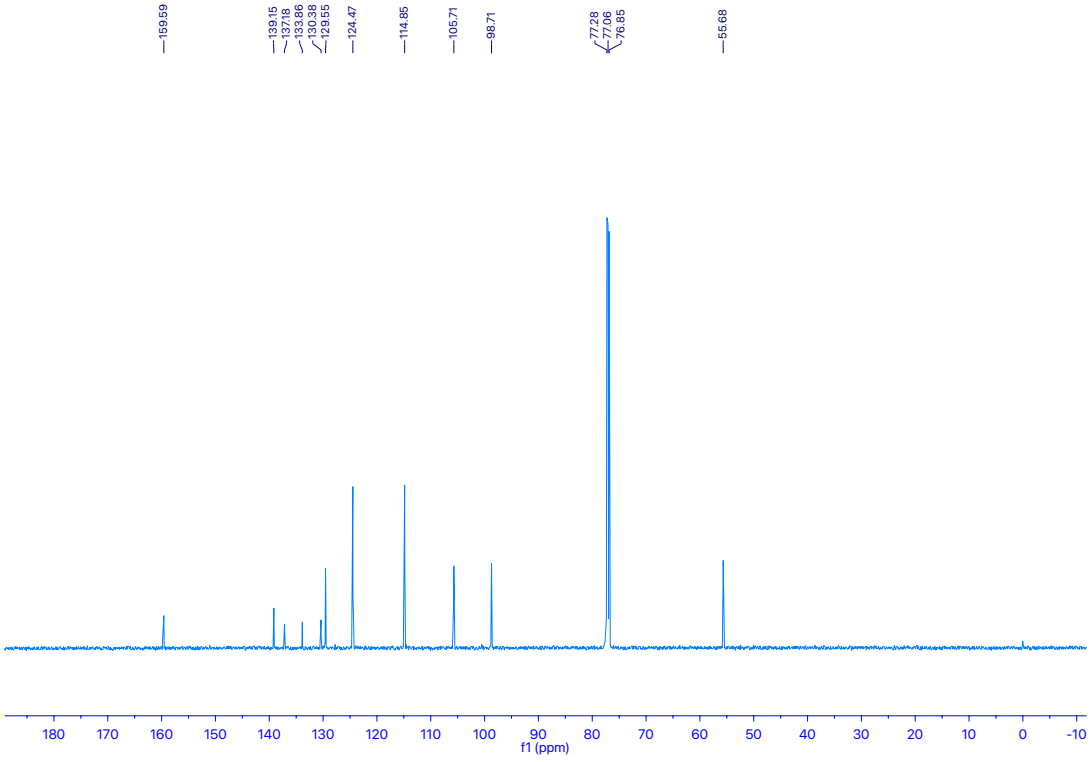
Compound 3q-S1, ^{13}C-NMR (151 MHz, $CDCl_3$)



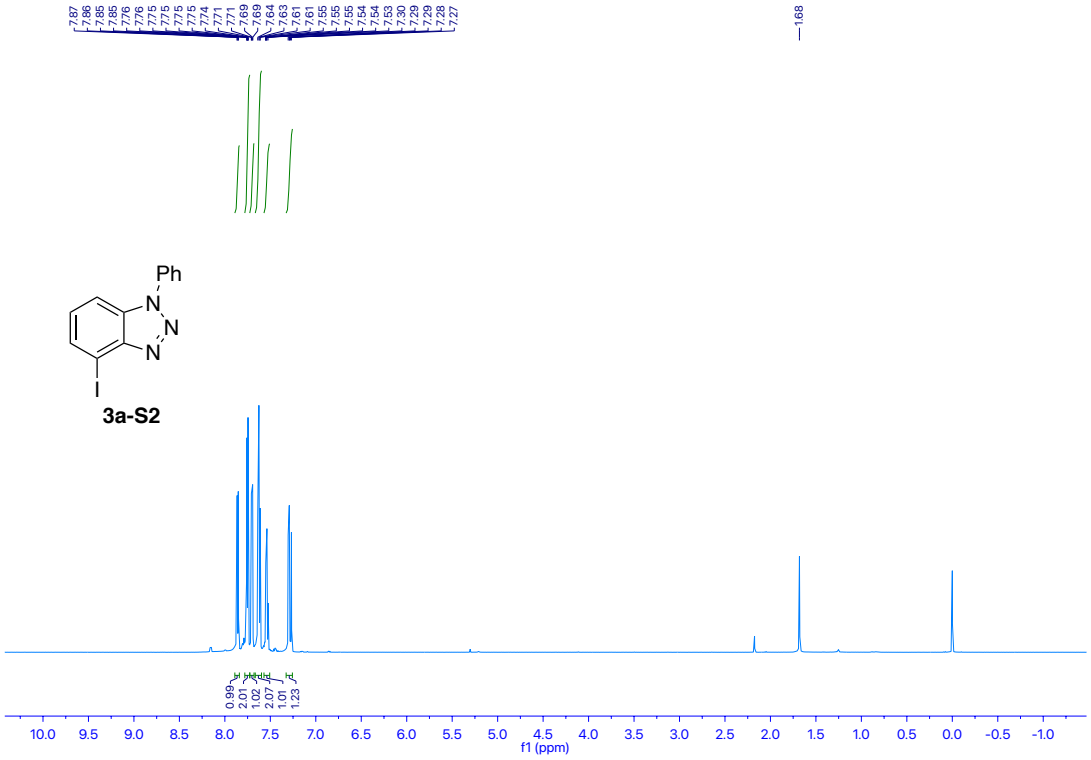
Compound 3r-S1, ^{1}H NMR (600 MHz, $CDCl_3$)



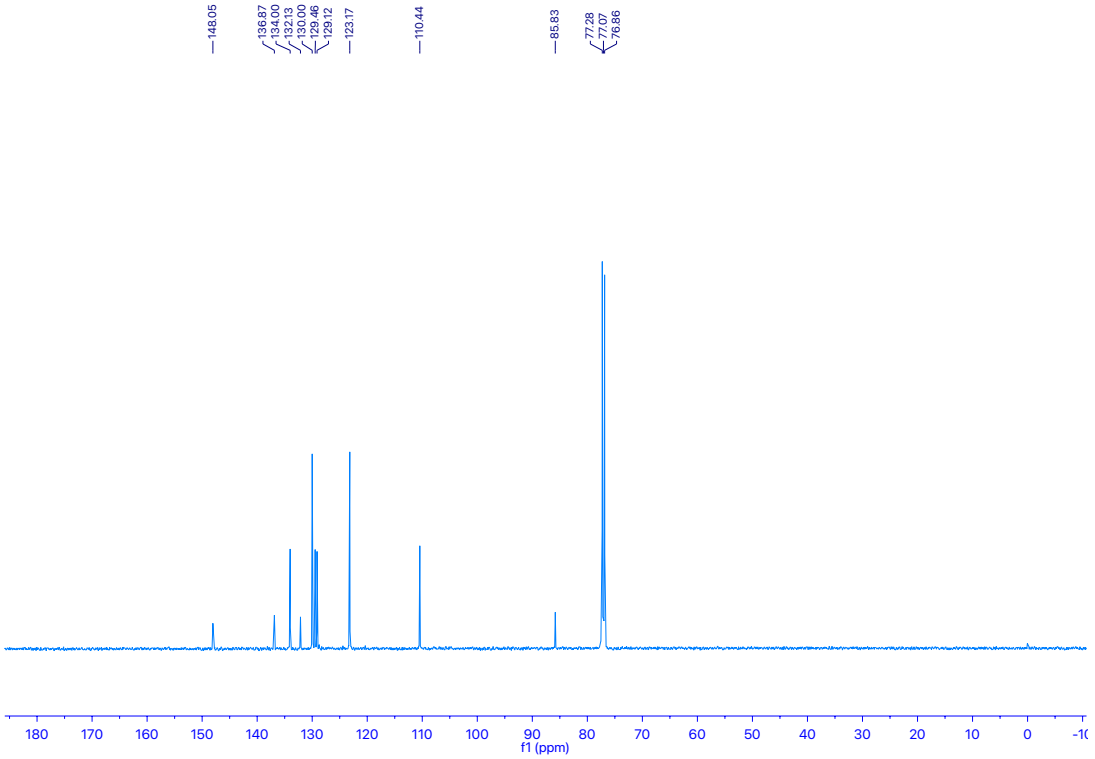
Compound 3r-S1, ^{13}C-NMR (151 MHz, $CDCl_3$)



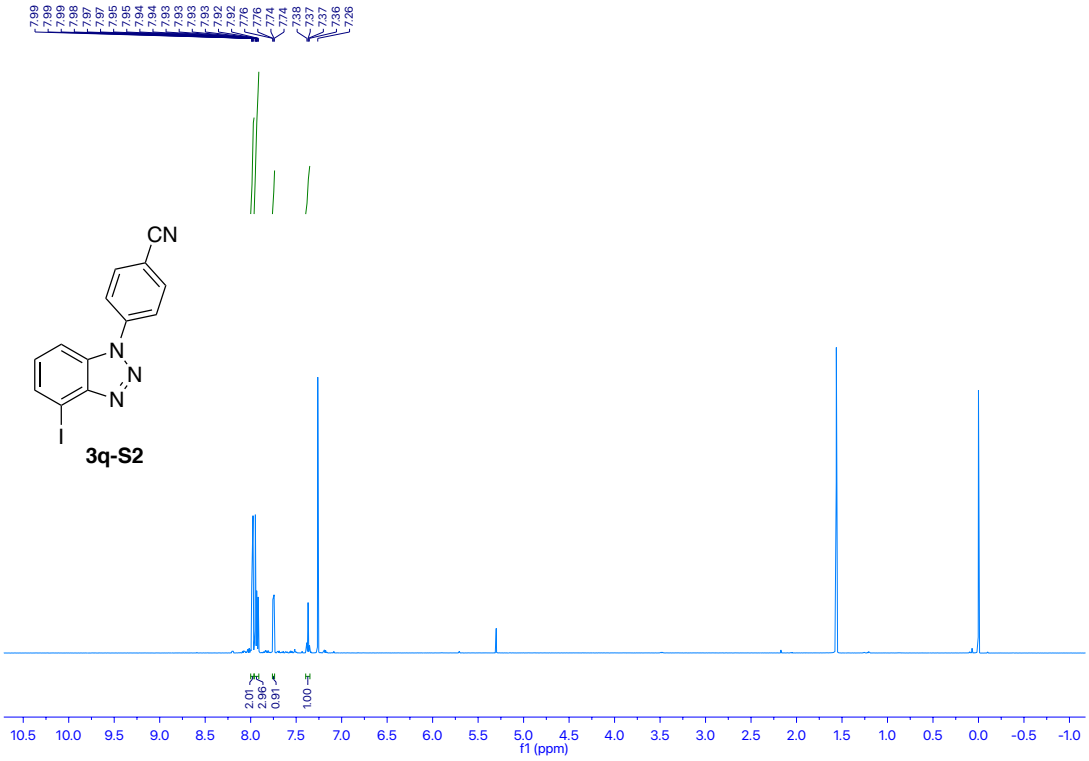
Compound 3a-S2, ^{1}H NMR (600 MHz, $CDCl_3$)



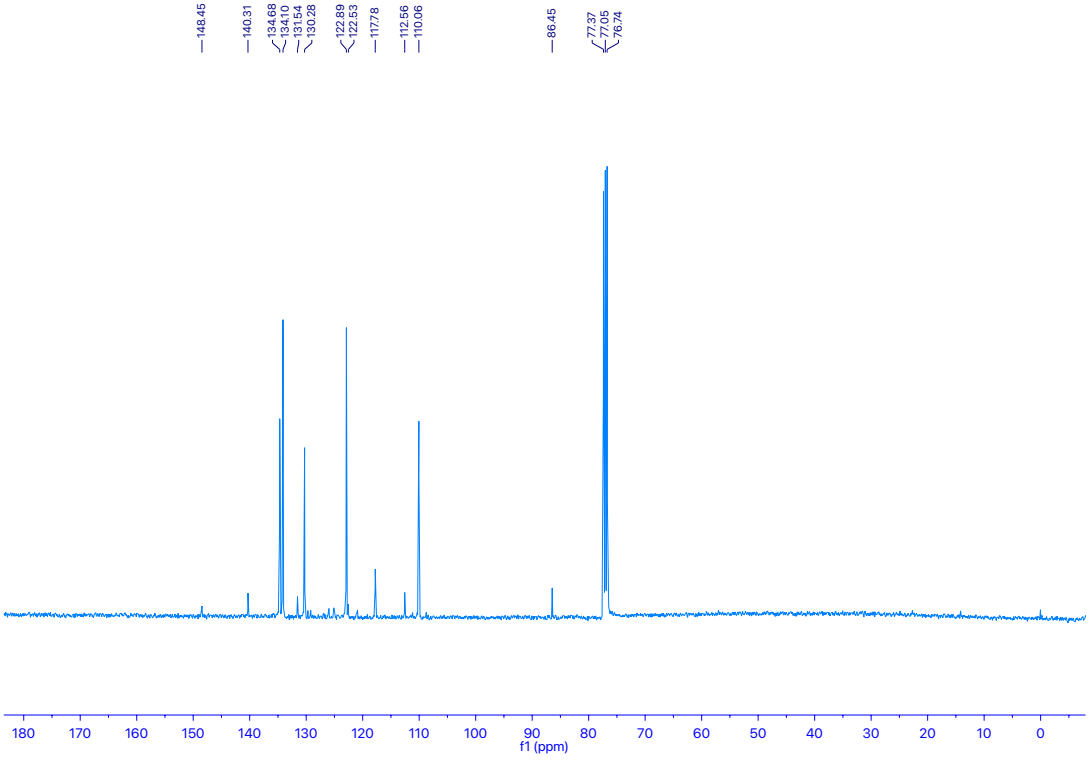
Compound 3a-S2, ^{13}C-NMR (151 MHz, $CDCl_3$)



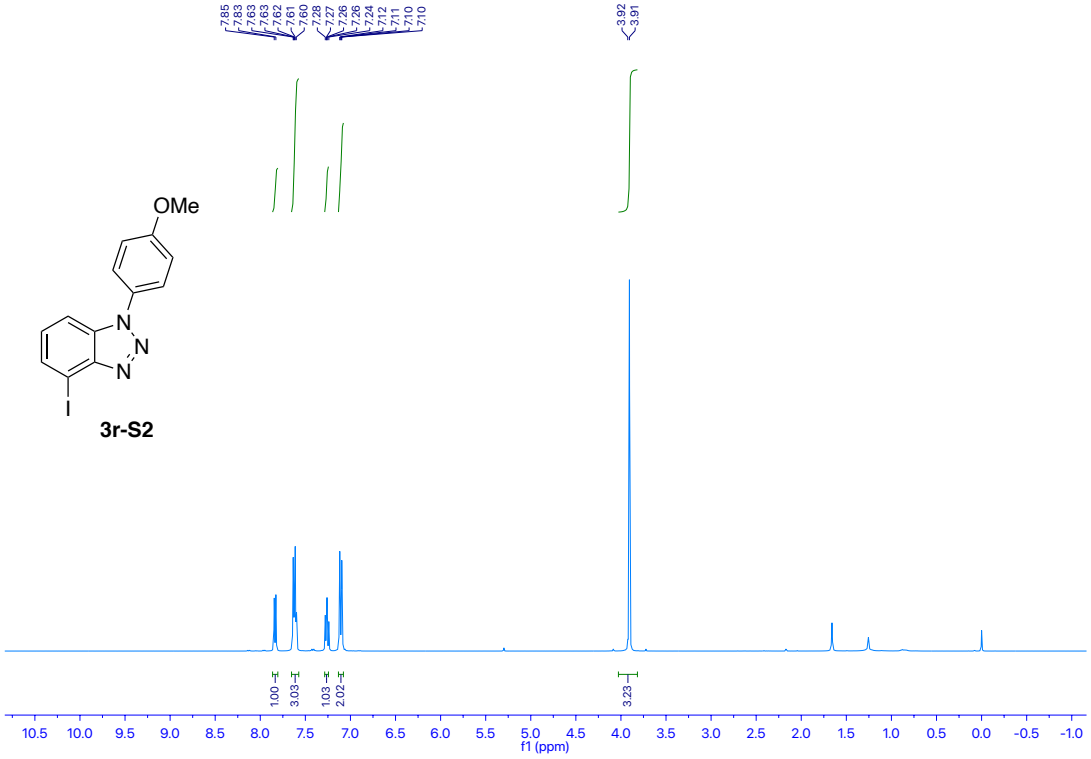
Compound 3q-S2, ^{1}H NMR (600 MHz, $CDCl_3$)



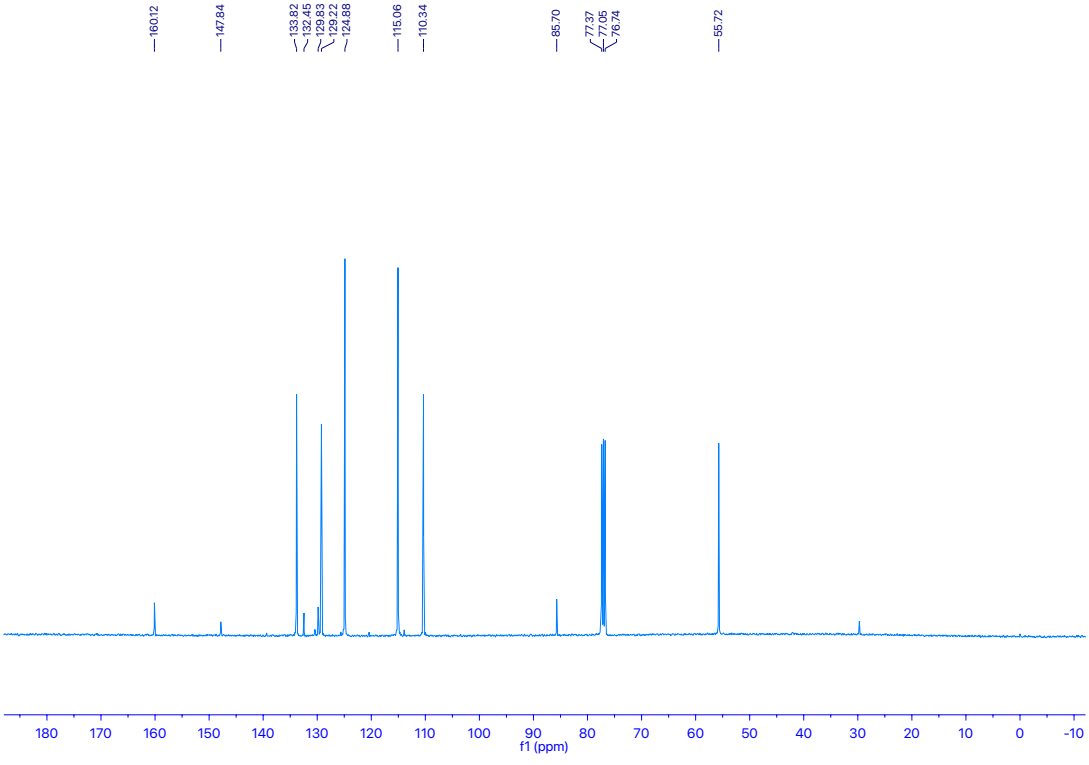
Compound 3q-S2, ^{13}C-NMR (151 MHz, $CDCl_3$)



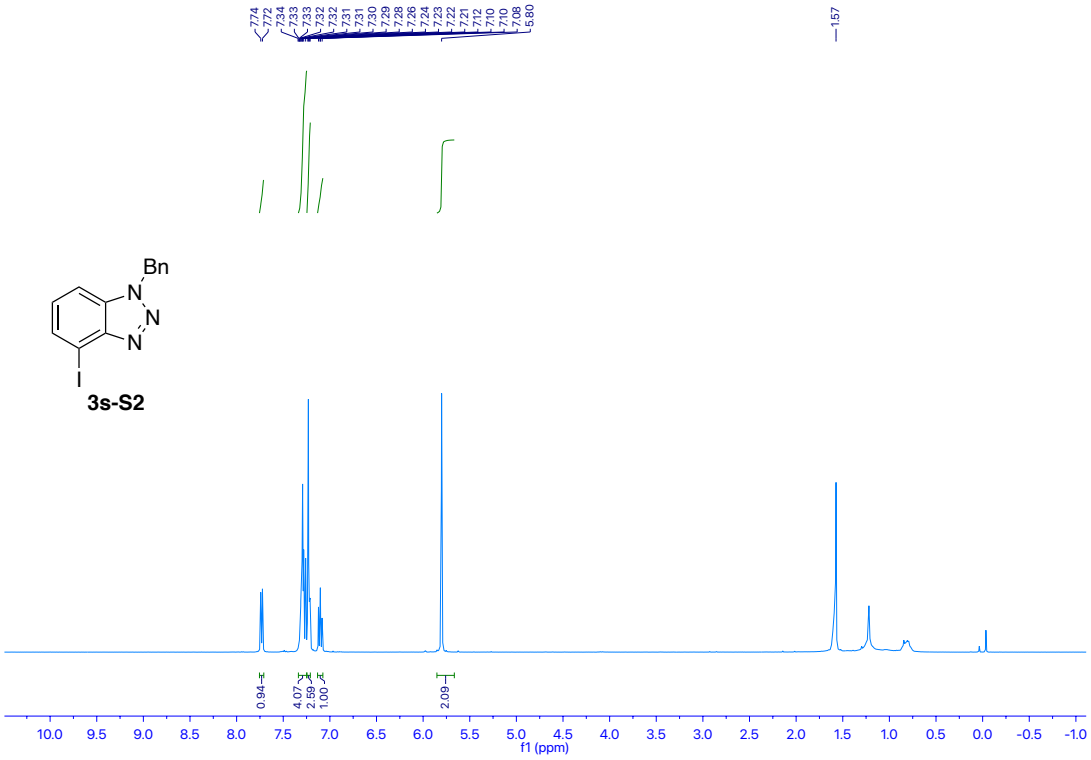
Compound 3r-S2, ^{1}H NMR (400 MHz, $CDCl_3$)



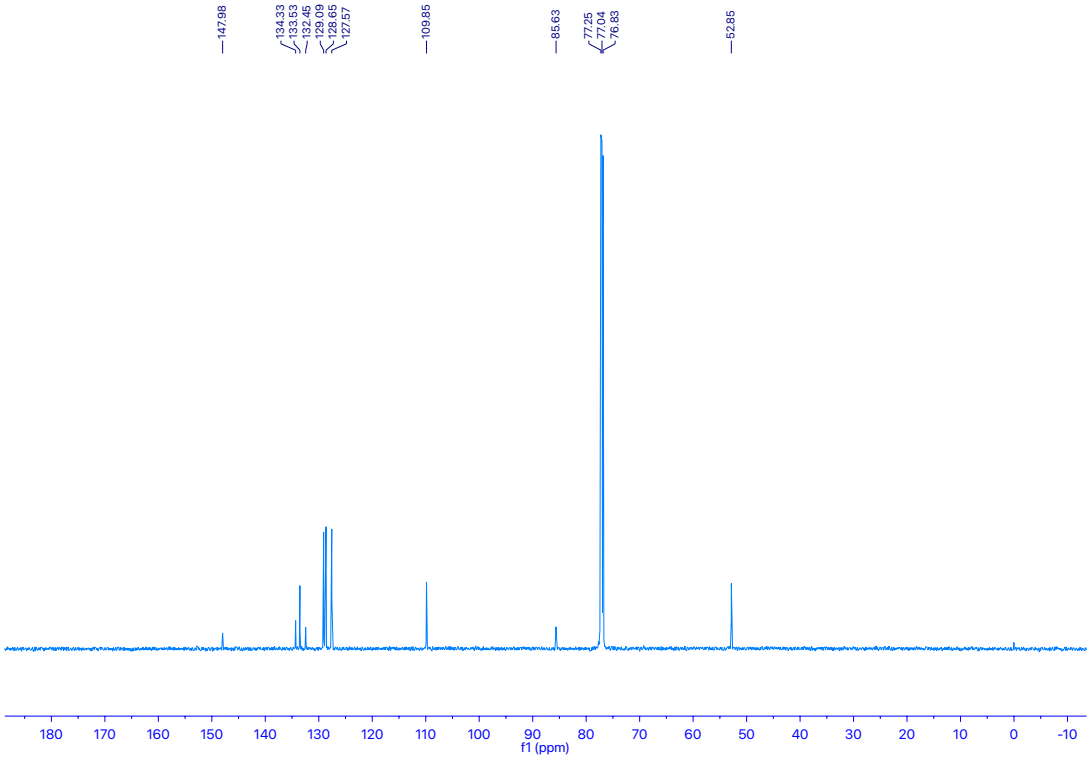
Compound 3r-S2, ^{13}C-NMR (151 MHz, $CDCl_3$)



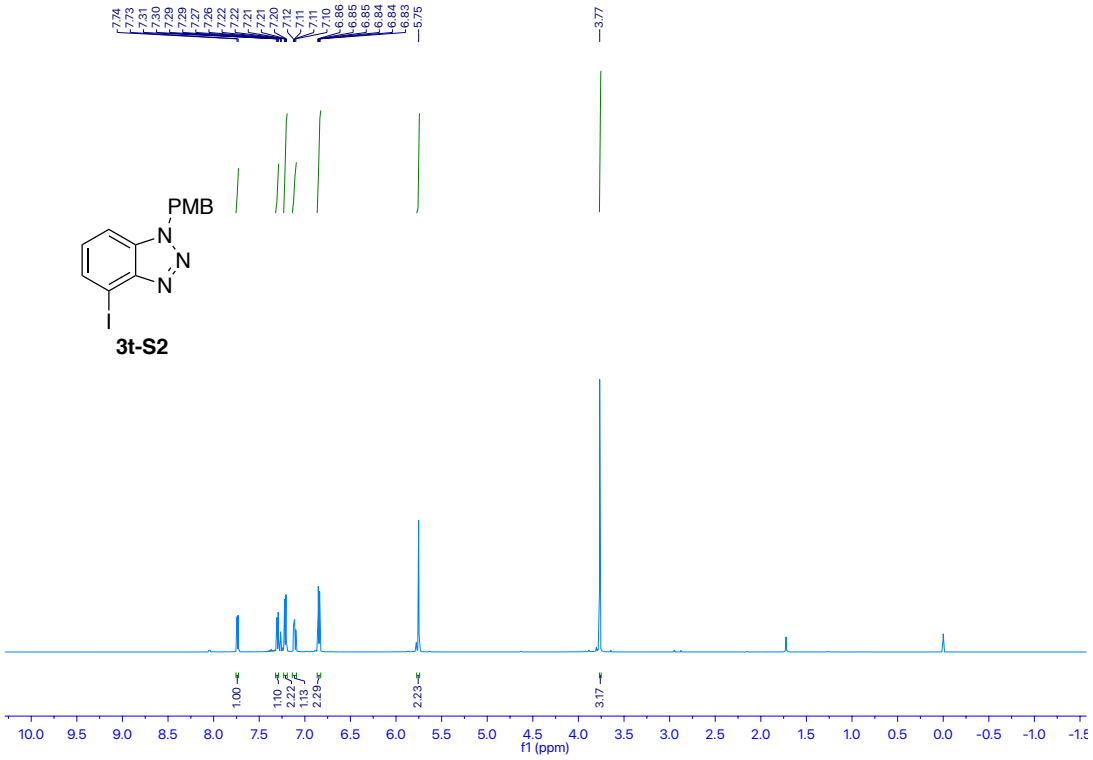
Compound 3s-S2, ^{1}H NMR (400MHz, $CDCl_3$)



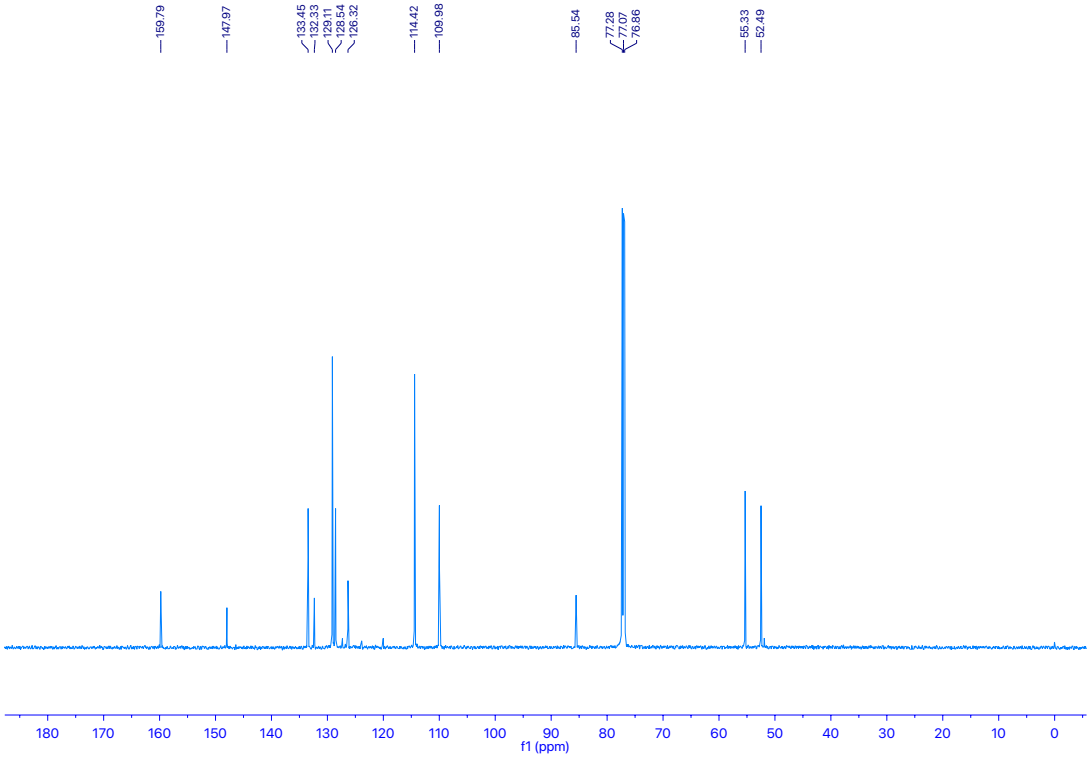
Compound 3s-S2, ^{13}C-NMR (151 MHz, $CDCl_3$)



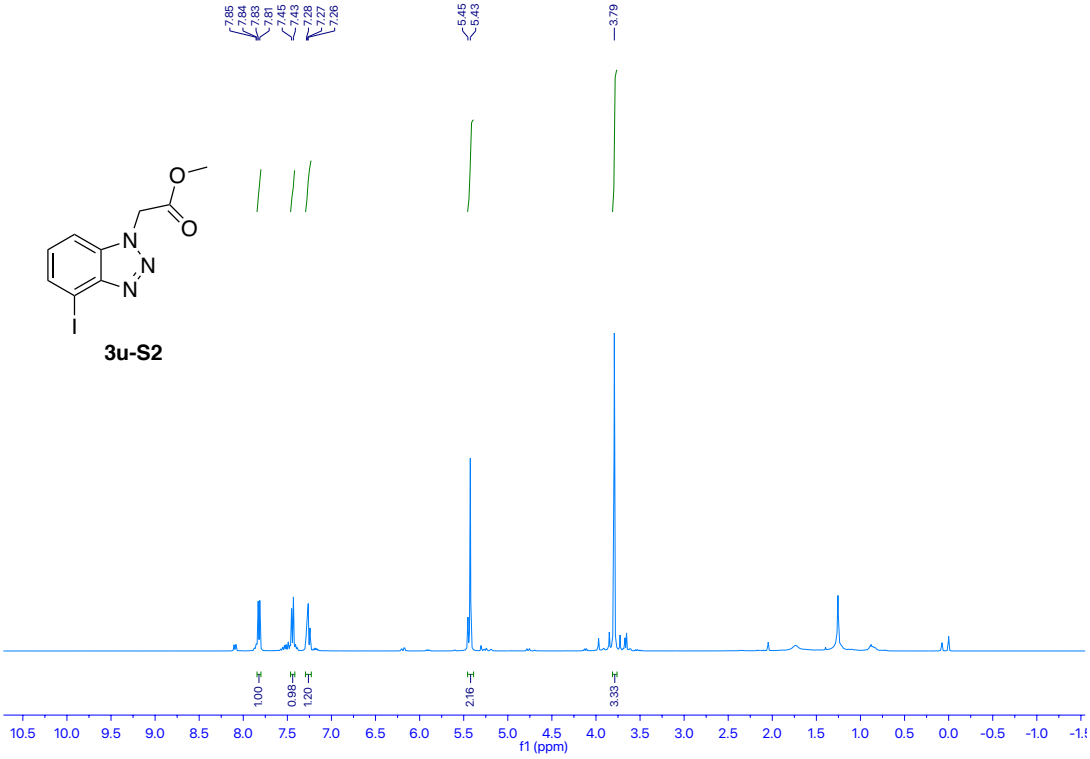
Compound 3t-S2, ^{1}H NMR (600 MHz, $CDCl_3$)



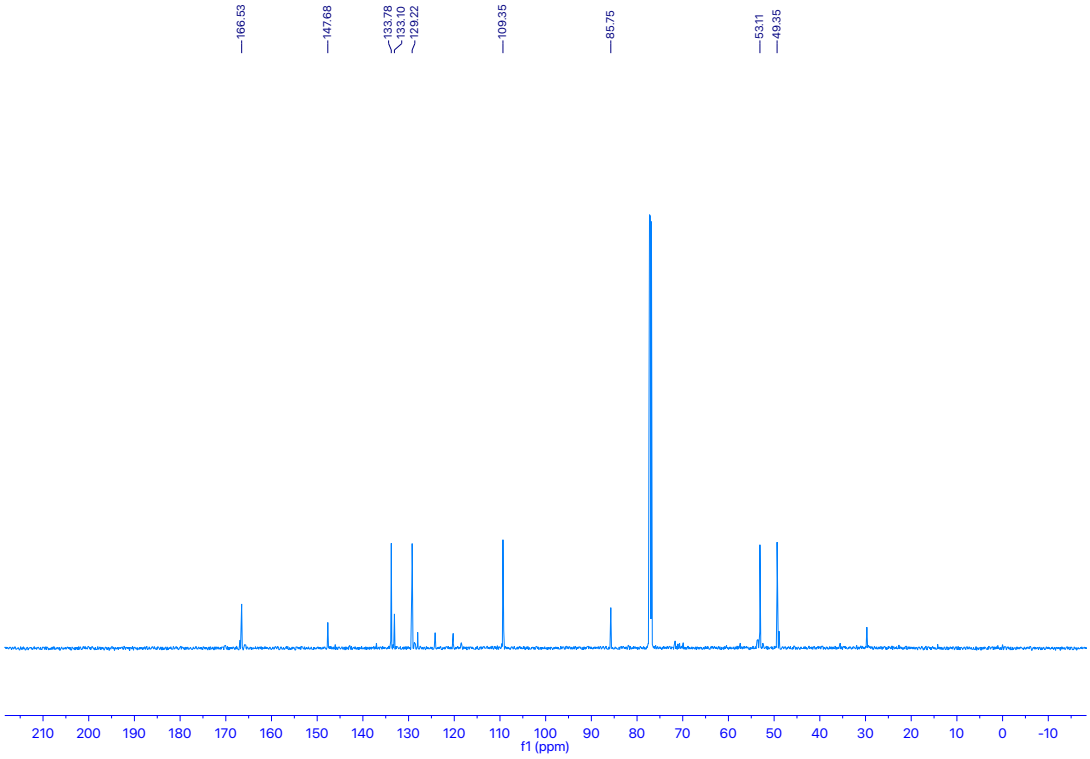
Compound 3t-S2,^{13}C-NMR (151 MHz, $CDCl_3$)



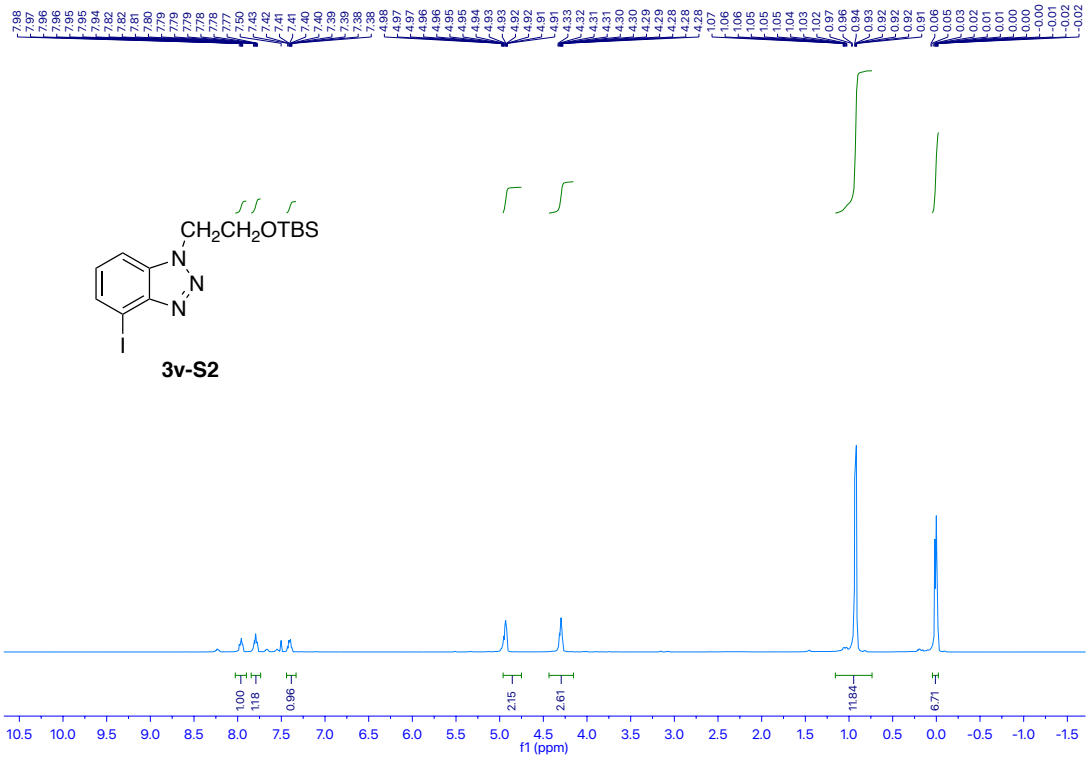
Compound 3u-S2, ^{1}H NMR (400 MHz, $CDCl_3$)



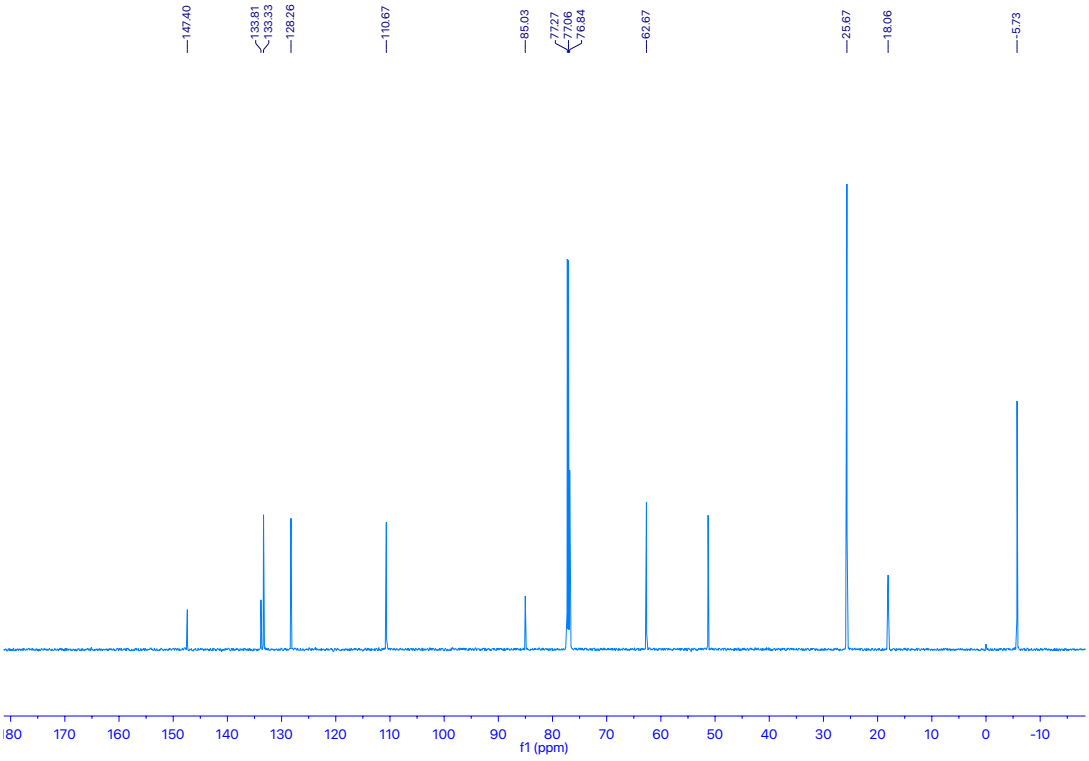
Compound 3u-S2,^{13}C-NMR (151 MHz, $CDCl_3$)



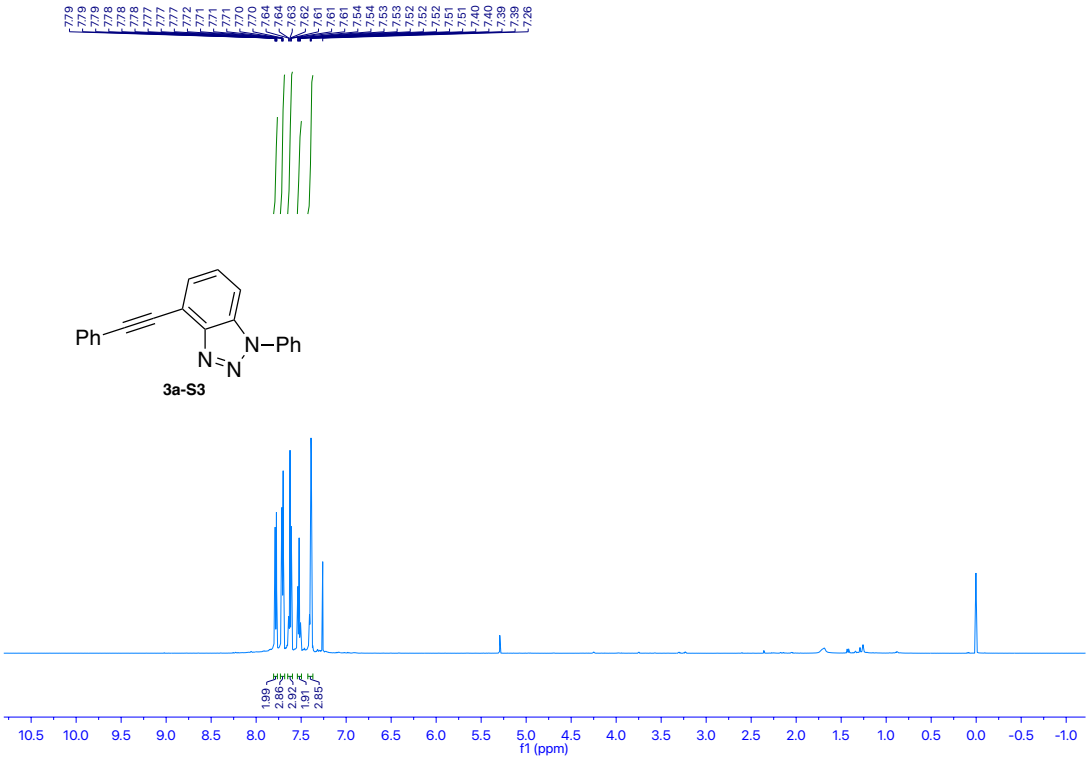
Compound 3v-S2, ^{1}H NMR (600 MHz, $CDCl_3$)



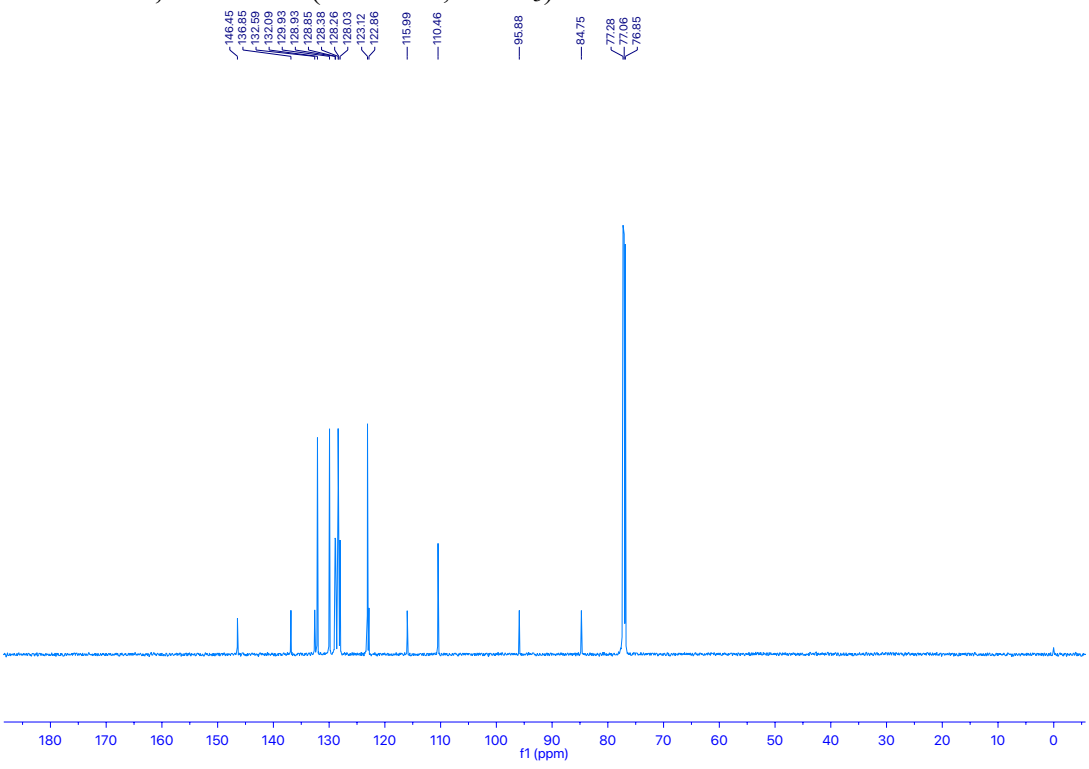
Compound 3v-S2,^{13}C-NMR (151 MHz, $CDCl_3$)



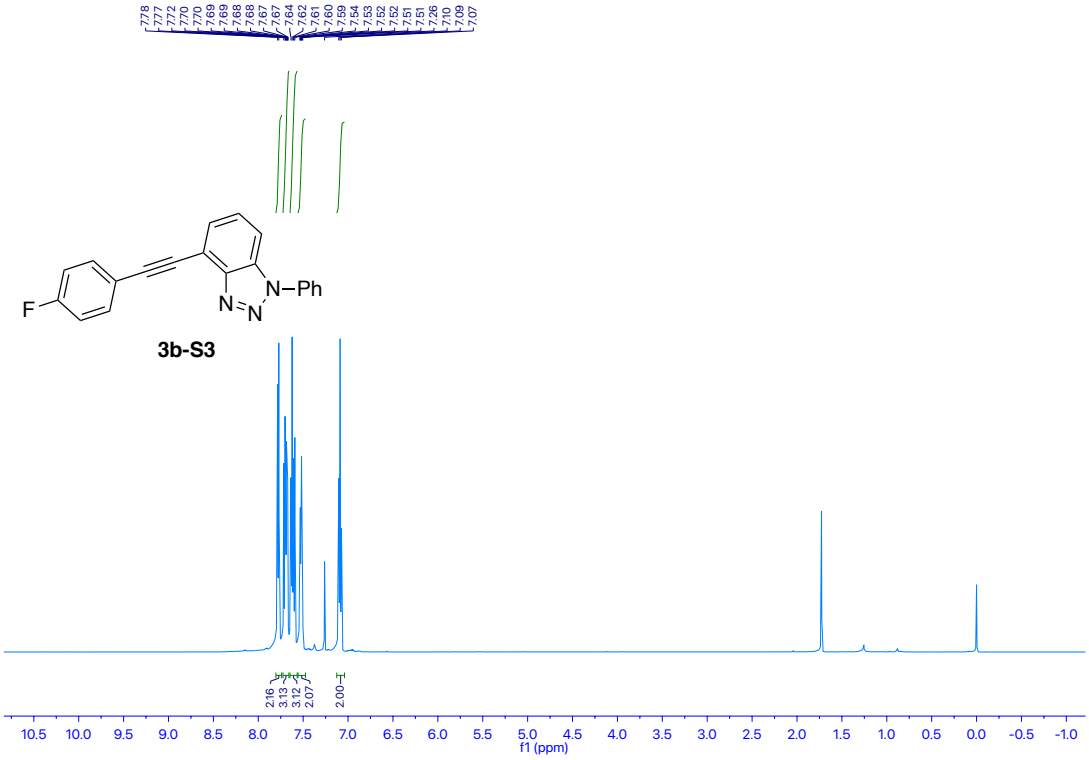
Compound 3a-S3, ^{1}H NMR (600 MHz, $CDCl_3$)



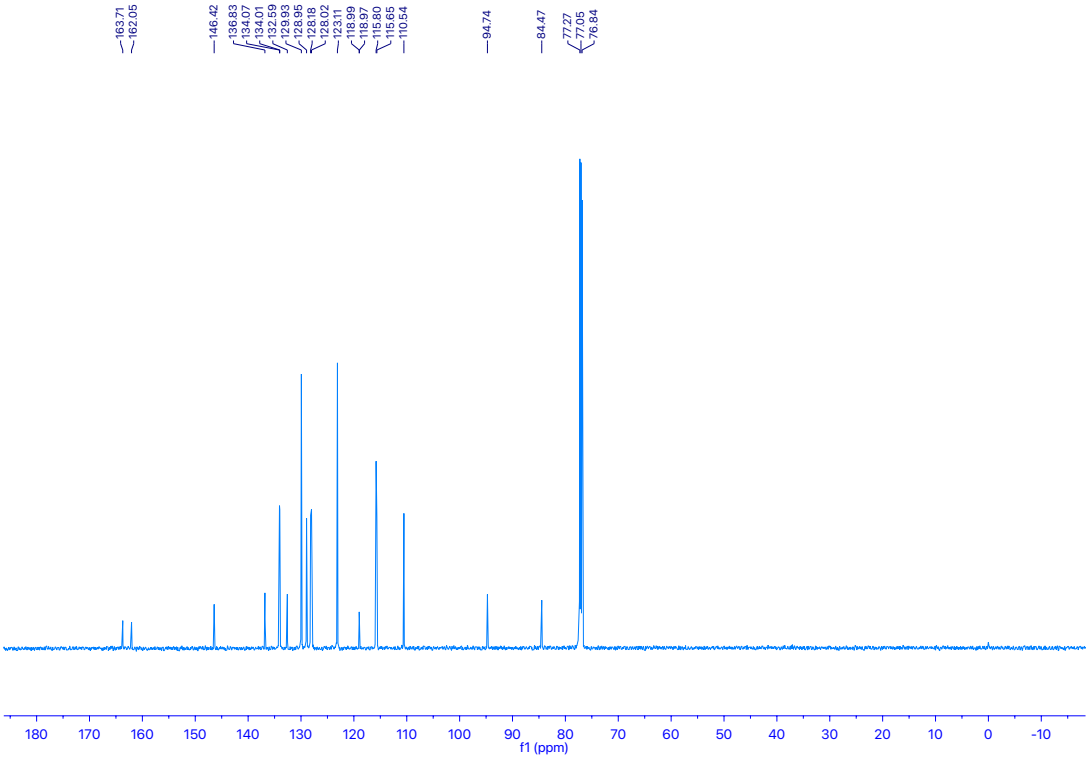
Compound 3a-S3, ^{13}C-NMR (151 MHz, $CDCl_3$)



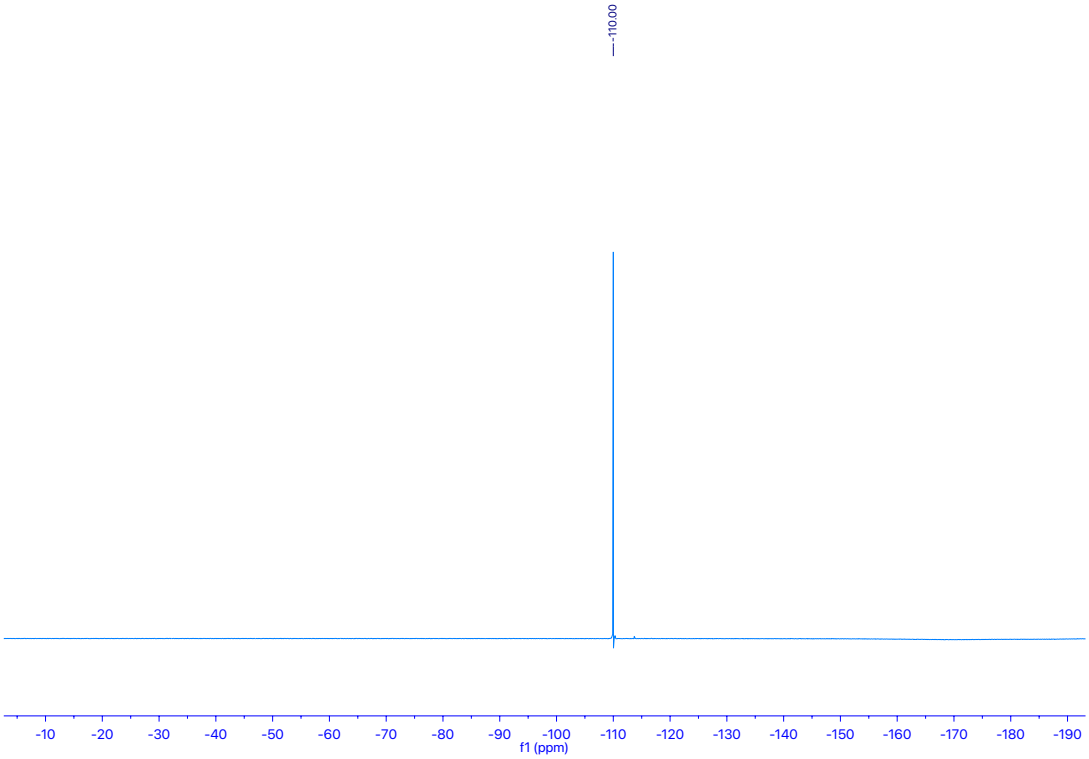
Compound 3b-S3, ^{1}H NMR (600 MHz, $CDCl_3$).



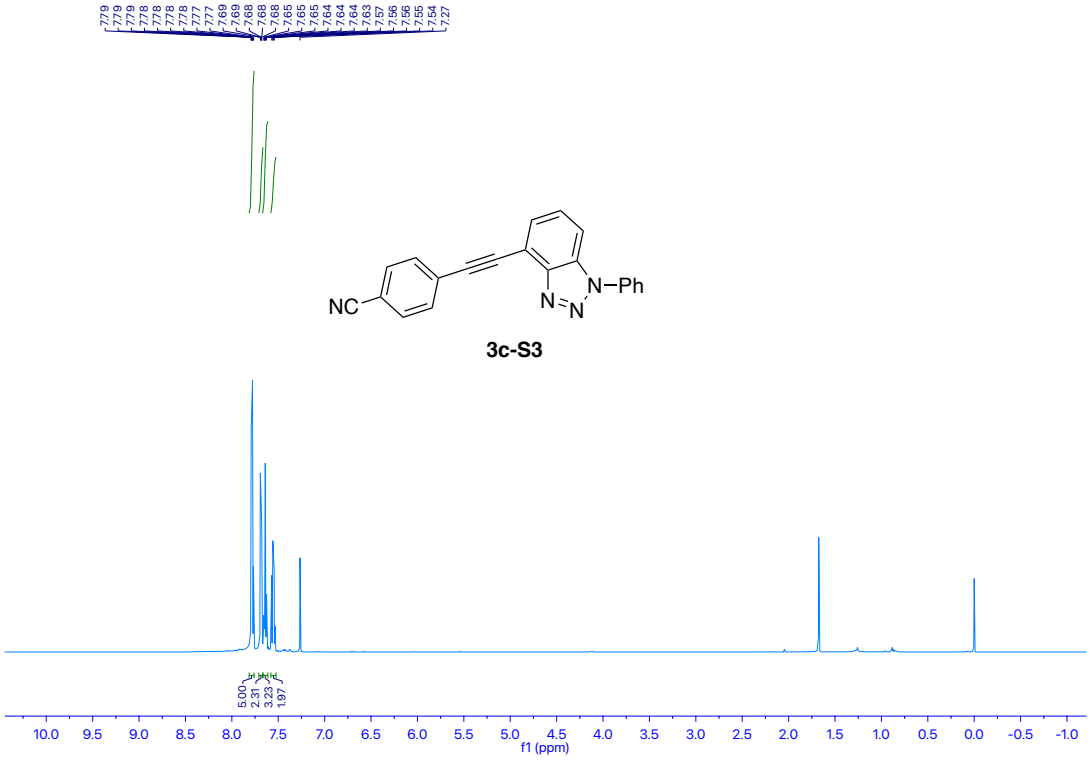
Compound 3b-S3, ^{13}C-NMR (151 MHz, $CDCl_3$)



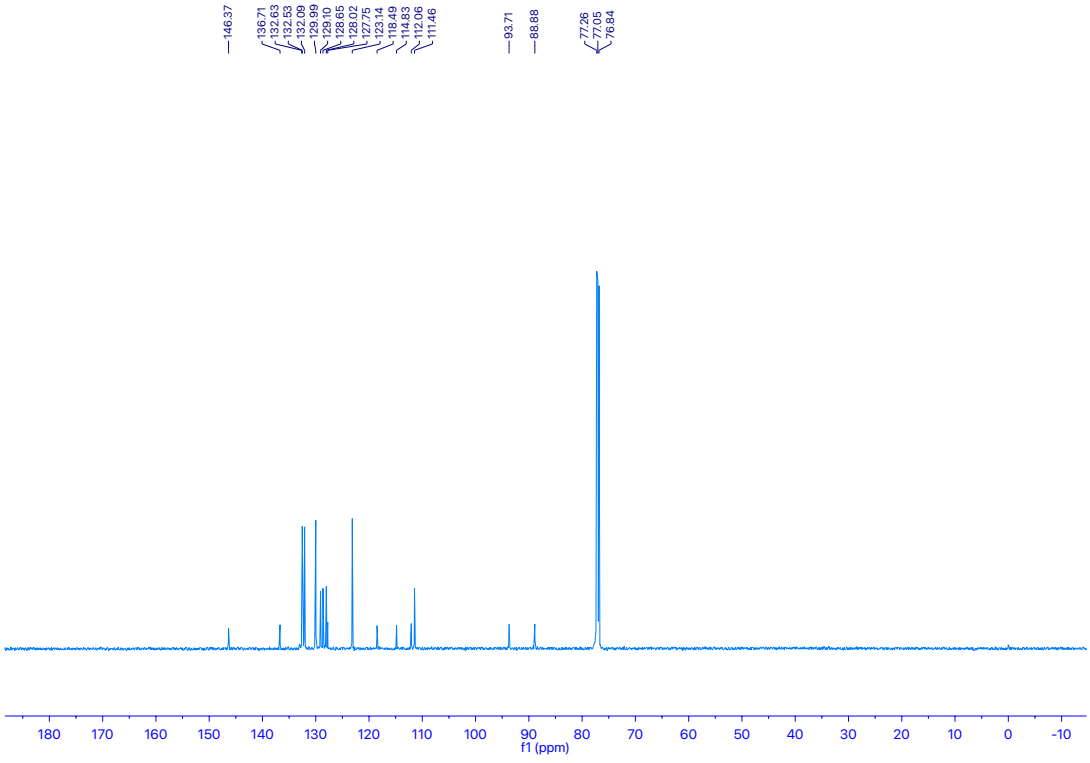
Compound 3b-S3, ^{19}F-NMR (564 MHz, $CDCl_3$).



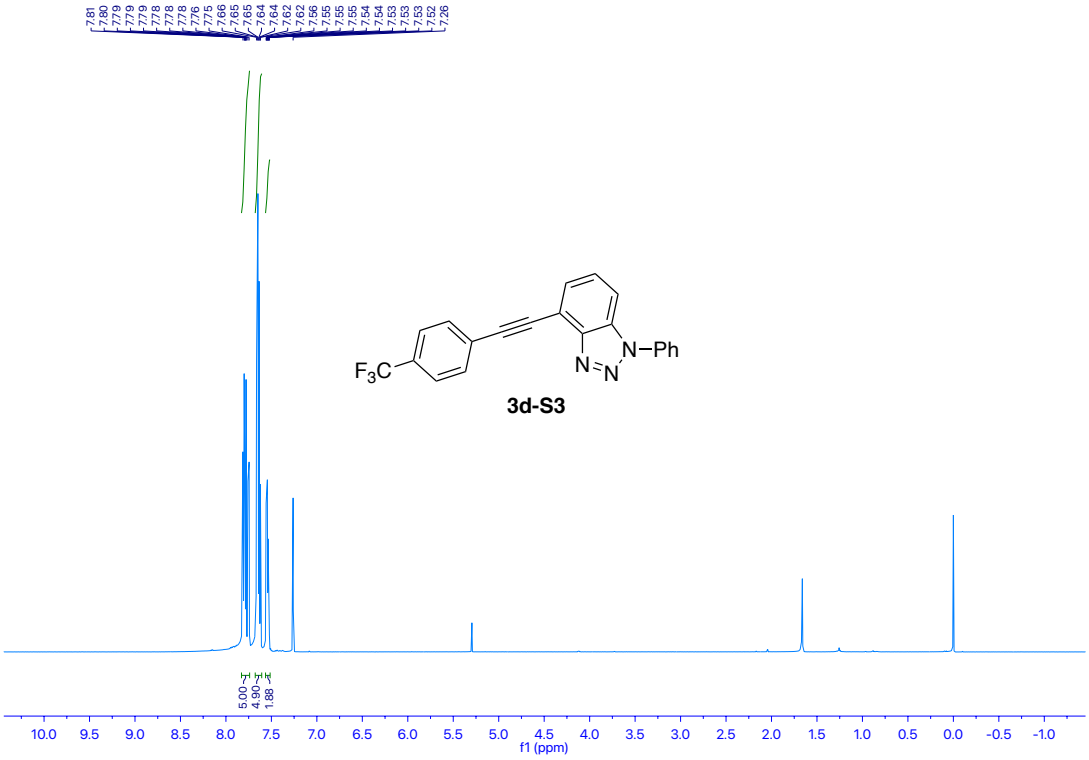
Compound 3c-S3, ^{1}H NMR (600 MHz, $CDCl_3$)



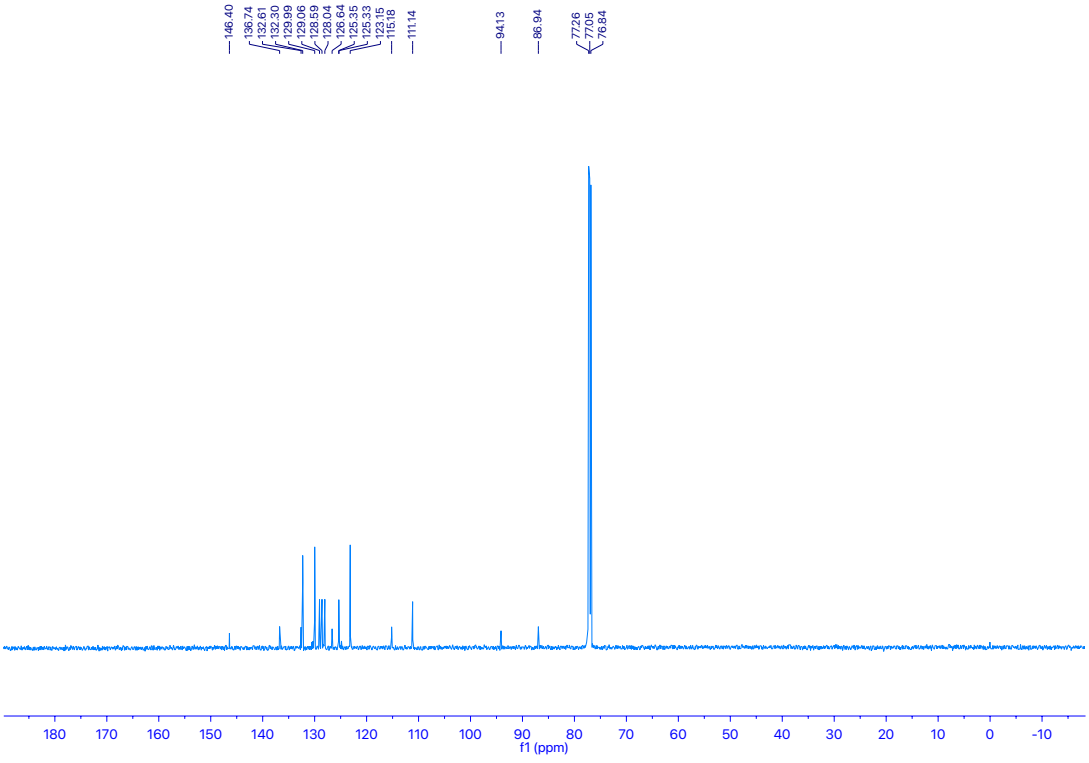
Compound 3c-S3, ^{13}C-NMR (151 MHz, $CDCl_3$)



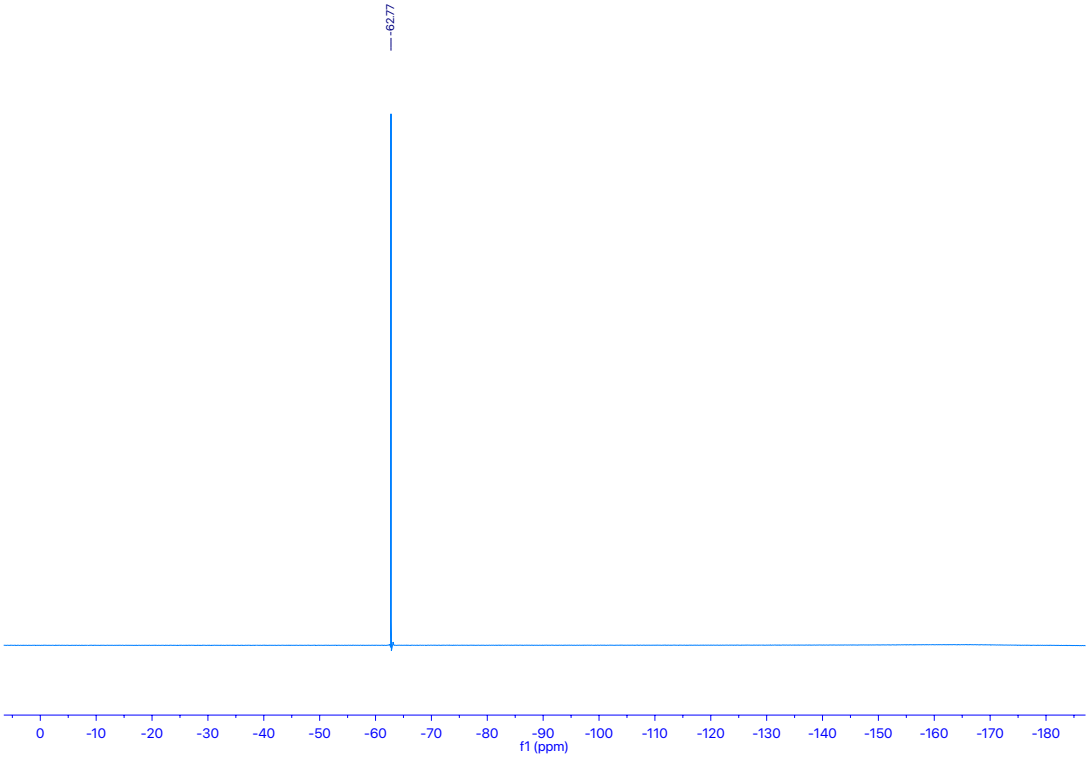
Compound 3d-S3, ^{1}H-NMR (600 MHz, $CDCl_3$)



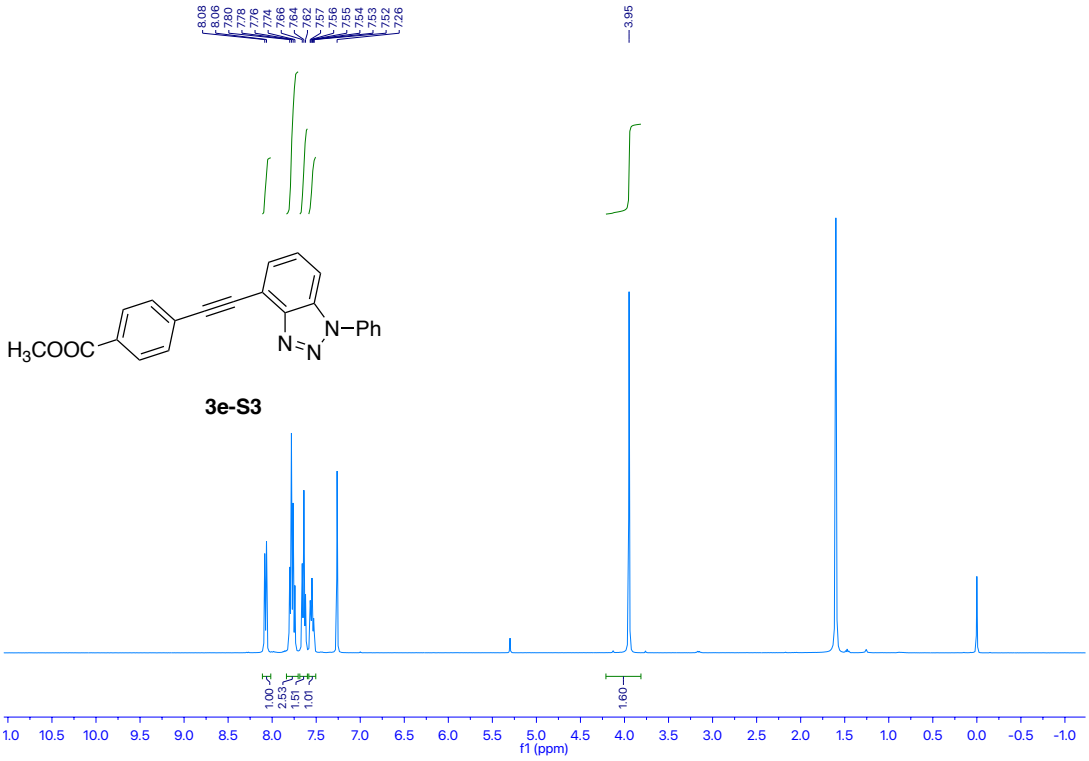
Compound 3d-S3,^{13}C-NMR (151 MHz, $CDCl_3$)



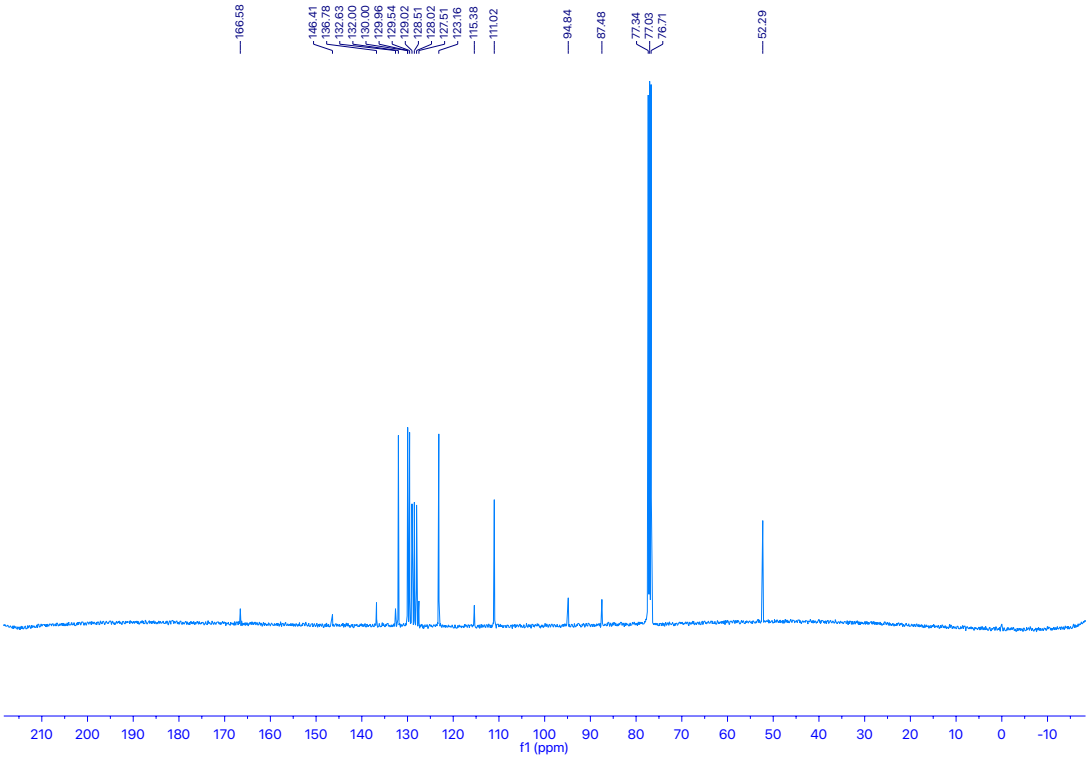
Compound 3d-S3,^{19}F-NMR (564MHz, $CDCl_3$)



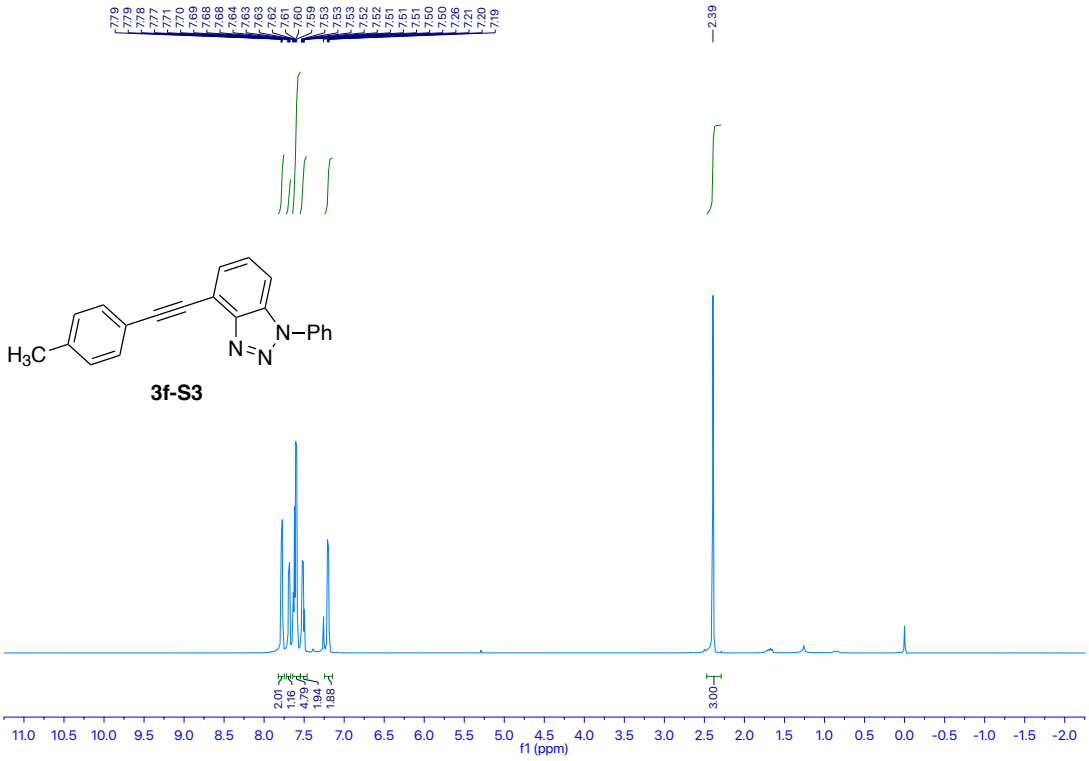
Compound 3e-S3, ^{1}H NMR (600 MHz, $CDCl_3$)



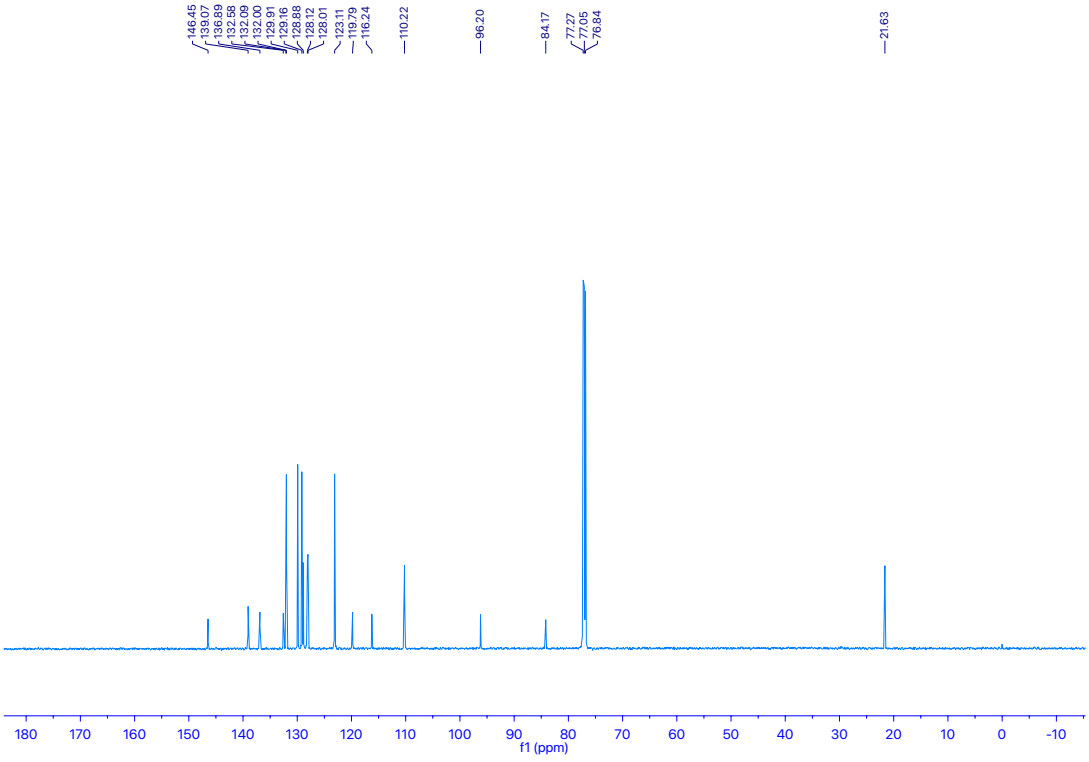
Compound 3e-S3,^{13}C-NMR (151 MHz, $CDCl_3$)



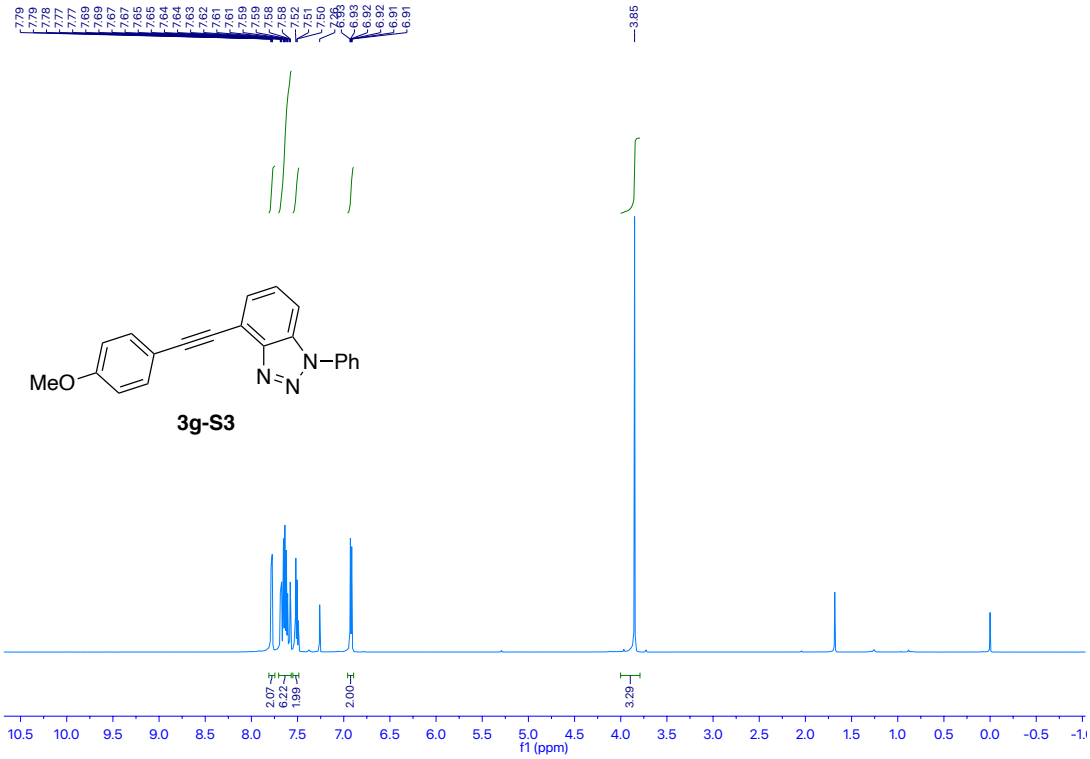
Compound 3f-S3, ^{1}H NMR (600 MHz, $CDCl_3$)



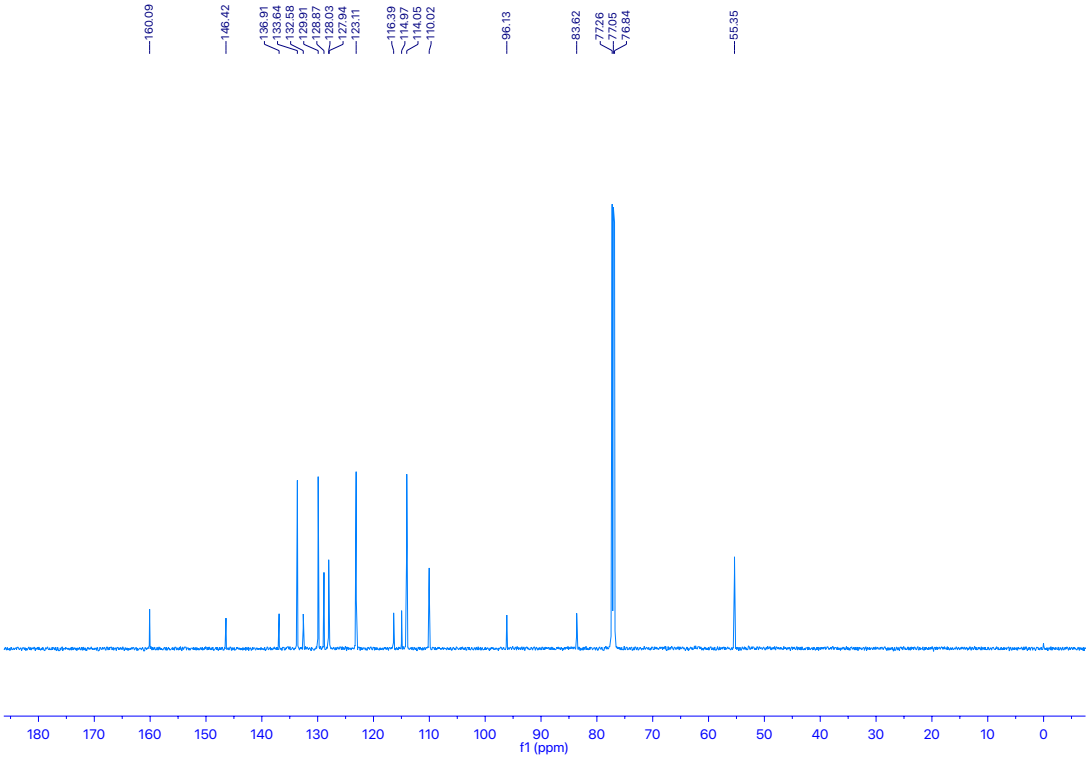
Compound 3f-S3, ^{13}C-NMR (151 MHz, $CDCl_3$)



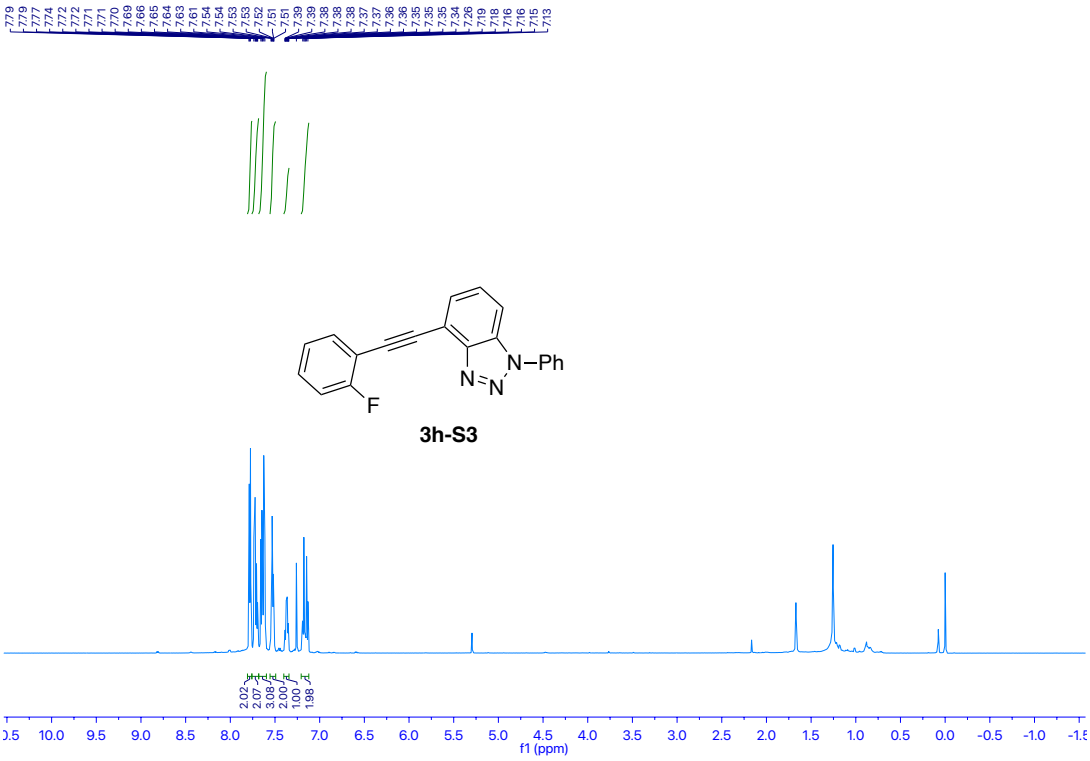
Compound 3g-S3, ^{1}H NMR (600 MHz, $CDCl_3$)



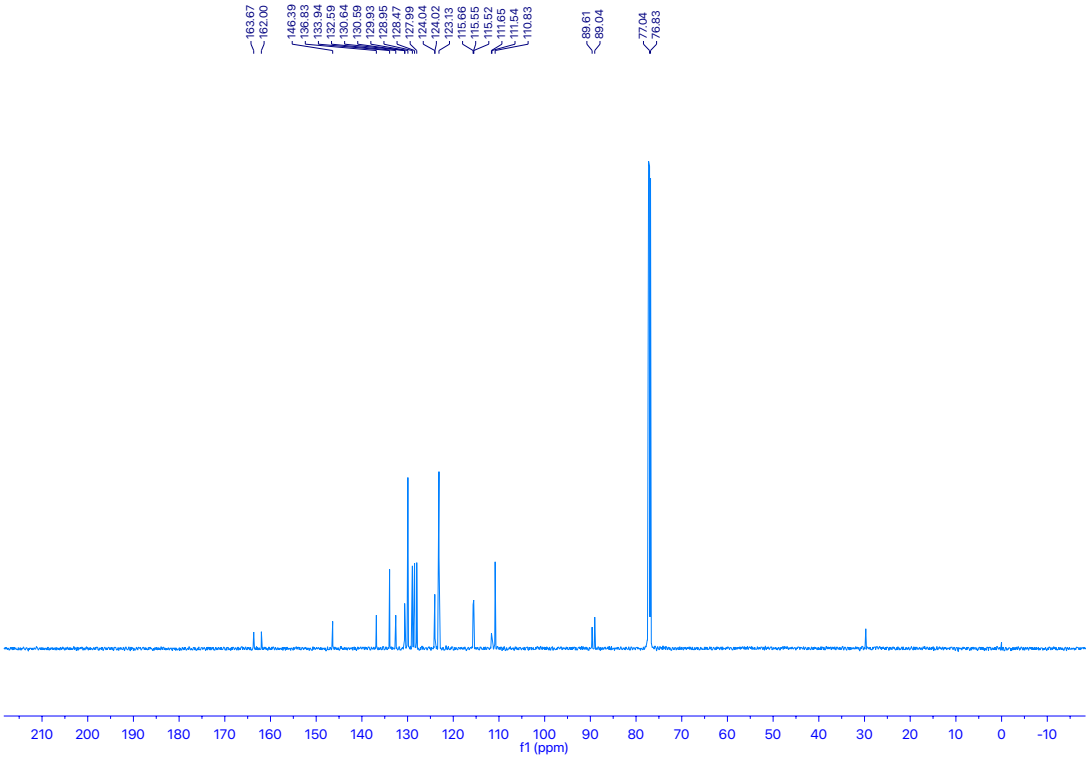
Compound 3g-S3, ^{13}C-NMR (151 MHz, $CDCl_3$)



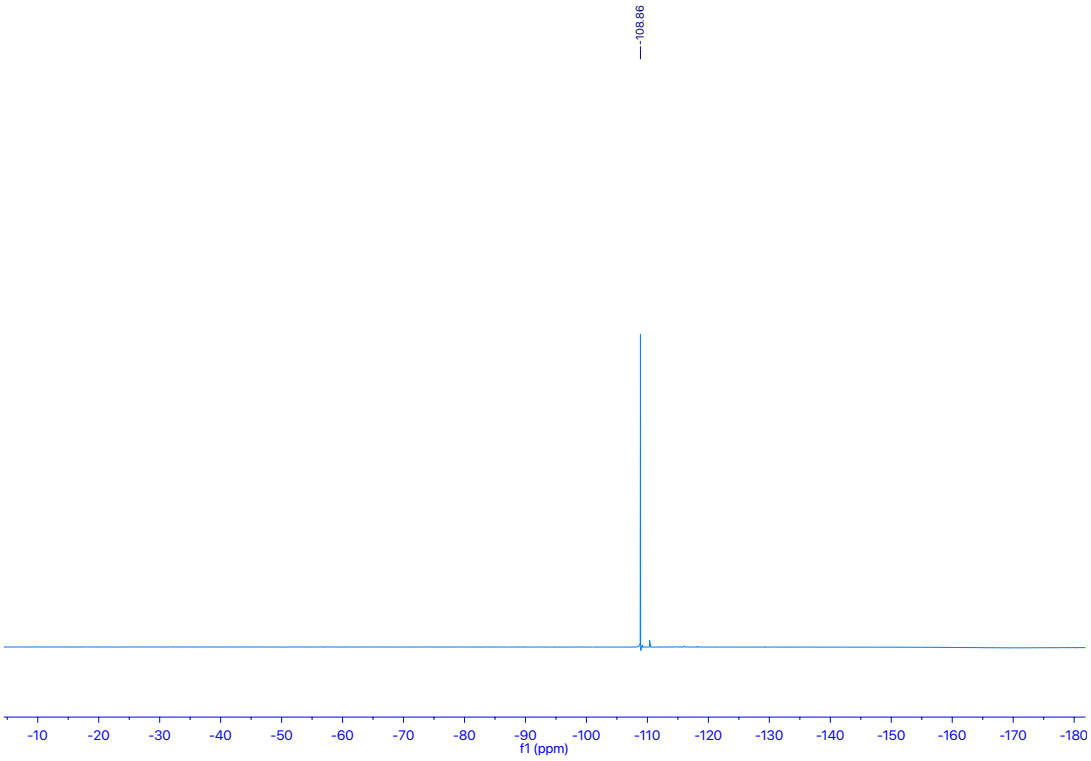
Compound 3h-S3, ^{1}H NMR (600 MHz, $CDCl_3$)



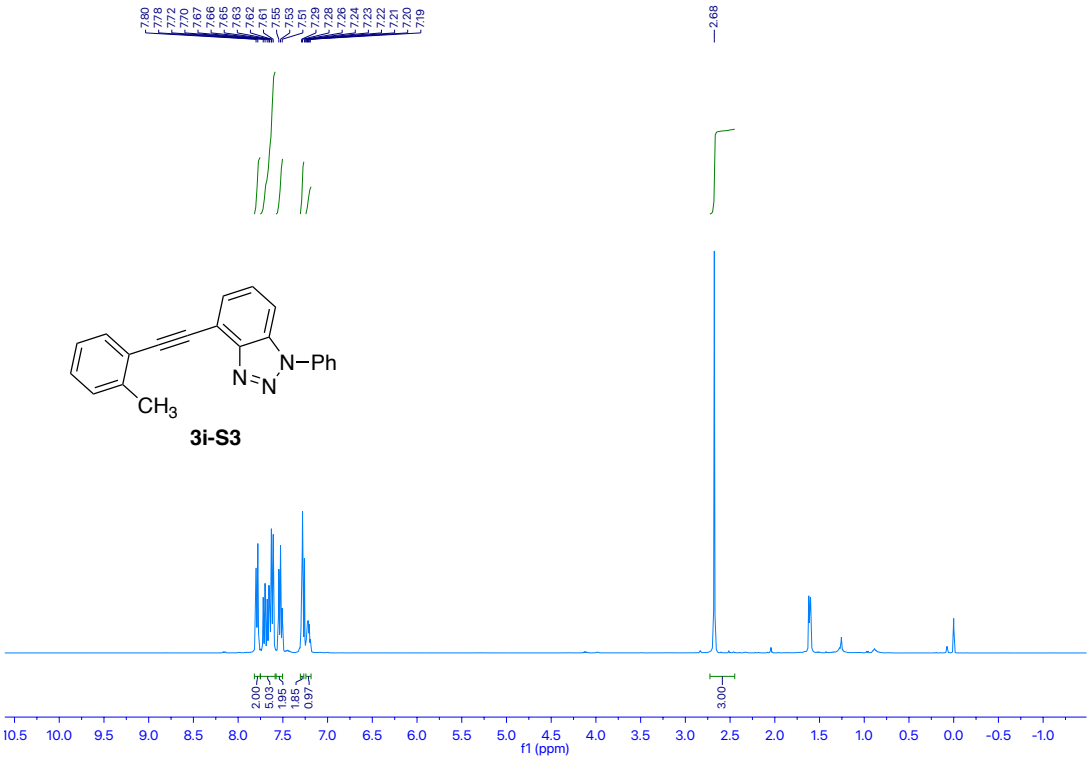
Compound 3h-S3, ^{13}C-NMR (151 MHz, $CDCl_3$))



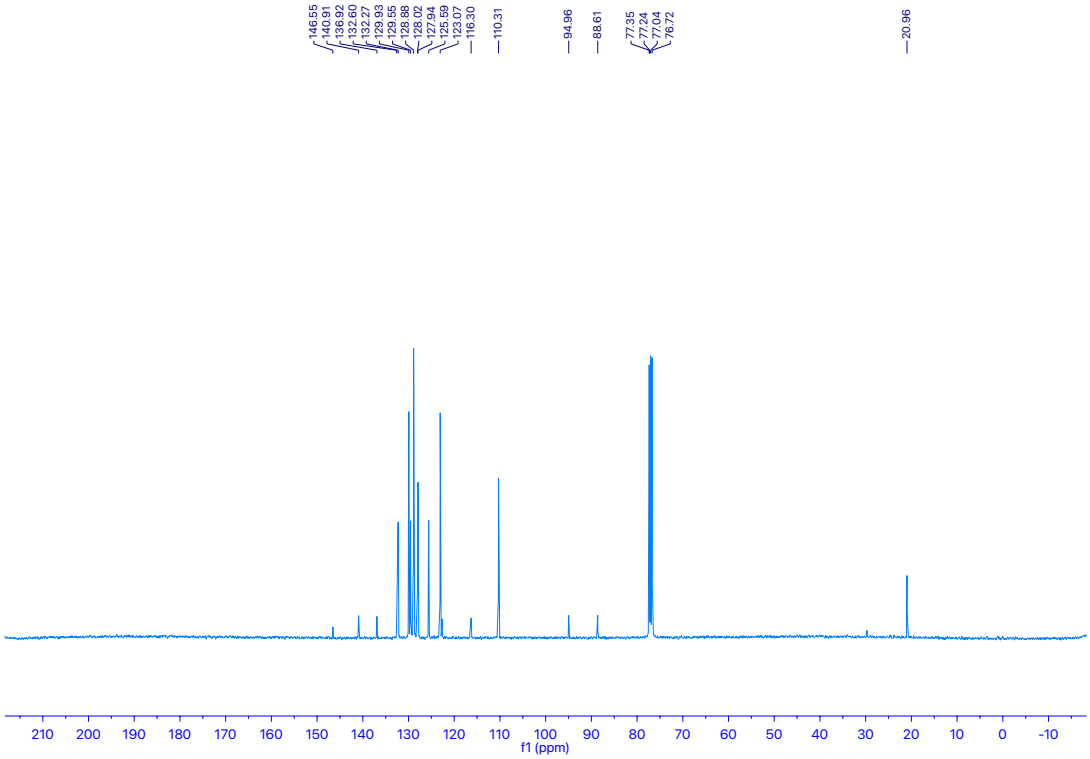
Compound 3h-S3, ^{19}F-NMR (564 MHz, $CDCl_3$)



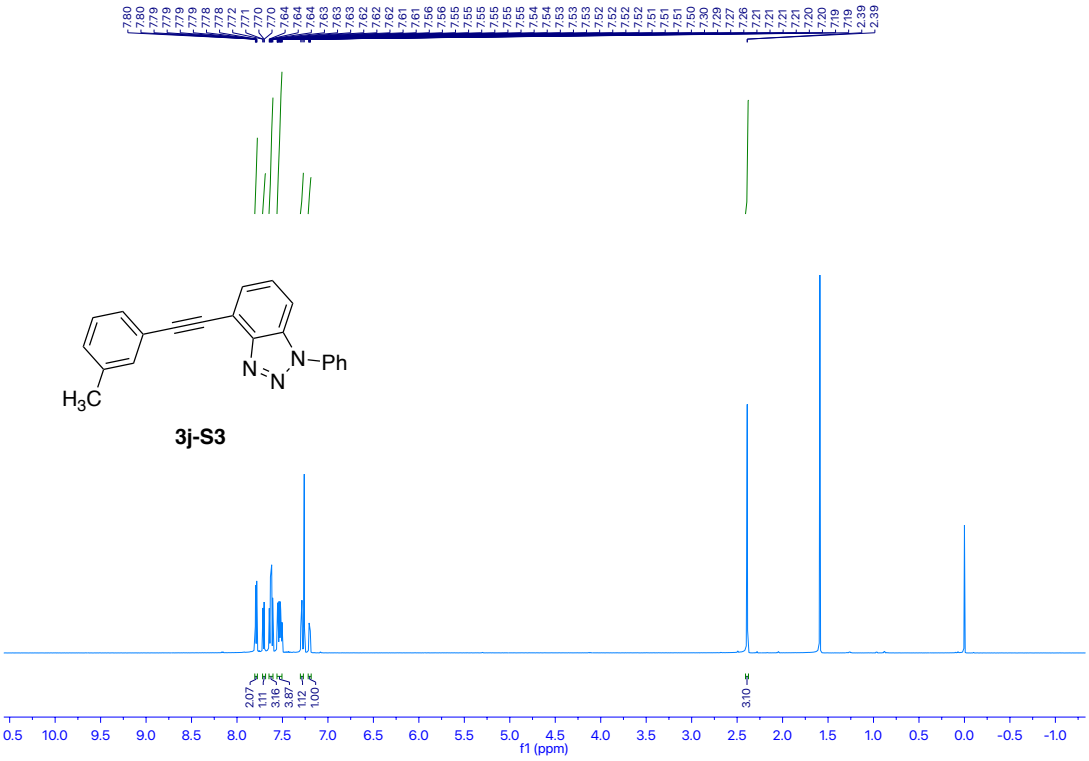
Compound 3i-S3, ^{1}H NMR (400 MHz, $CDCl_3$).



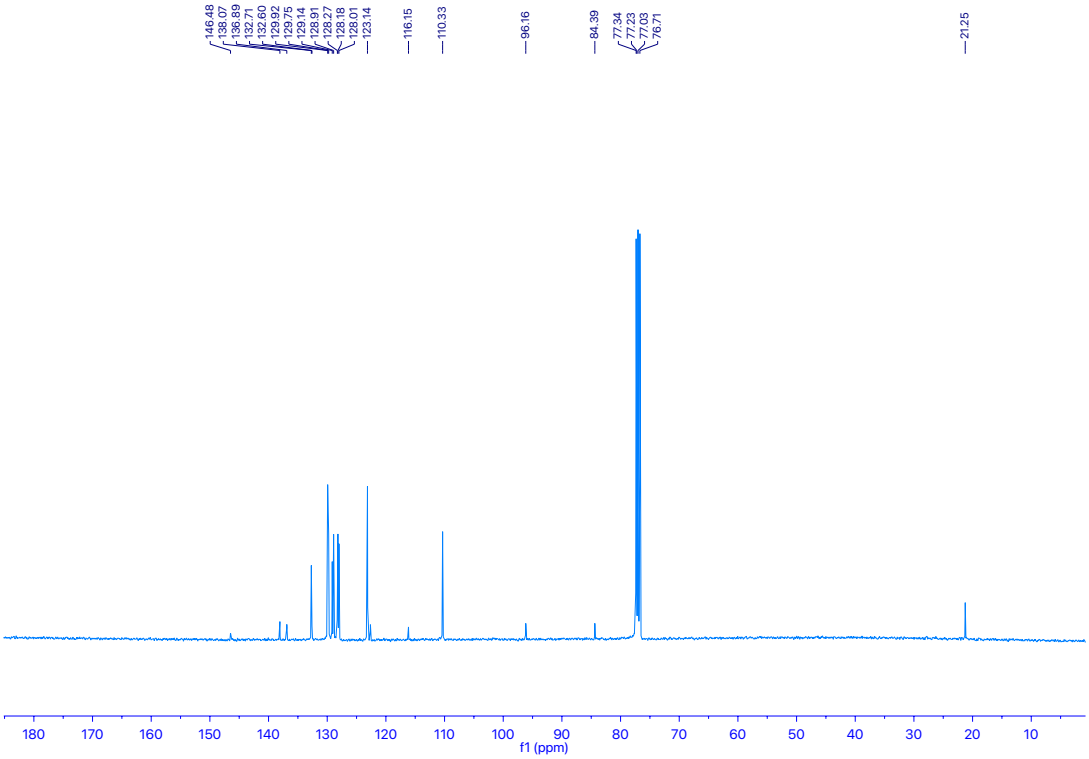
Compound 3i-S3, ^{13}C-NMR (101 MHz, $CDCl_3$)



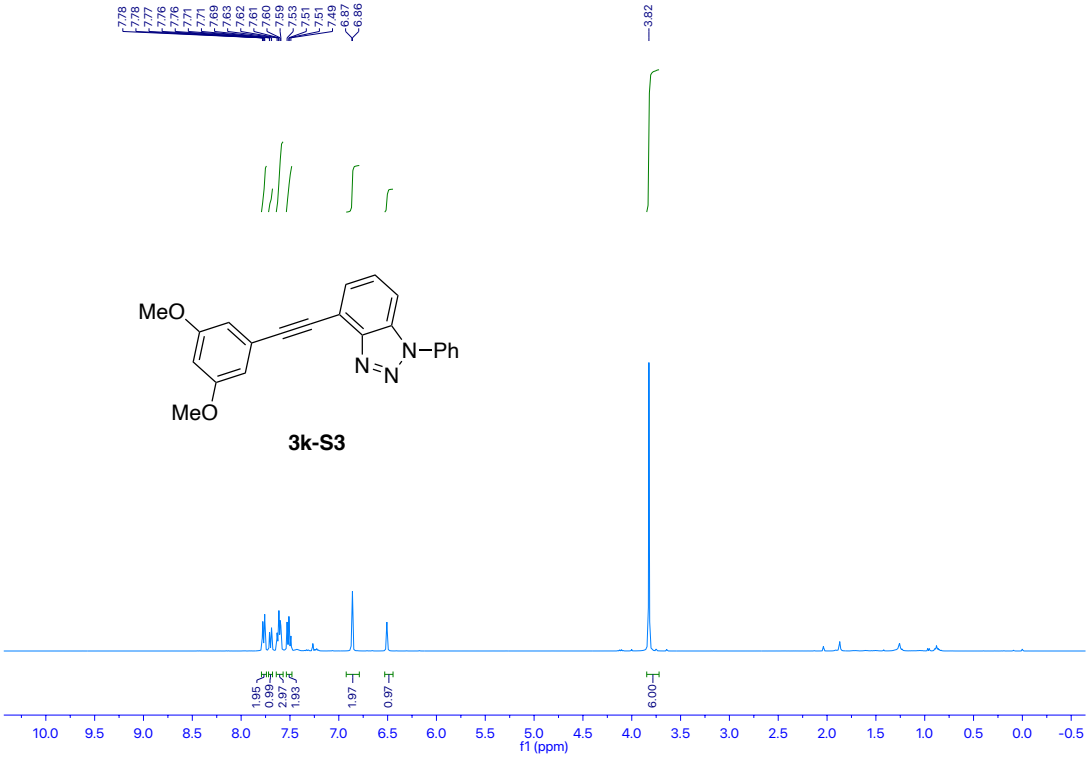
Compound 3j-S3, ^{1}H NMR (600 MHz, $CDCl_3$).



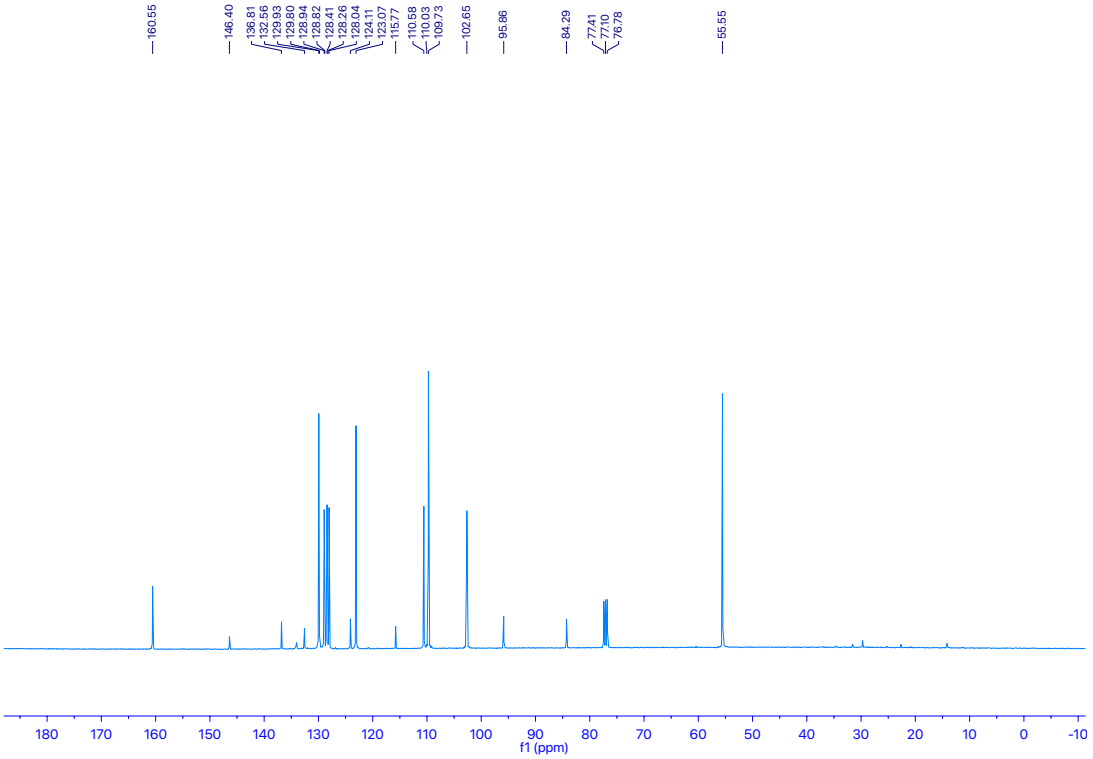
Compound 3j-S3, ^{13}C-NMR (101 MHz, $CDCl_3$)



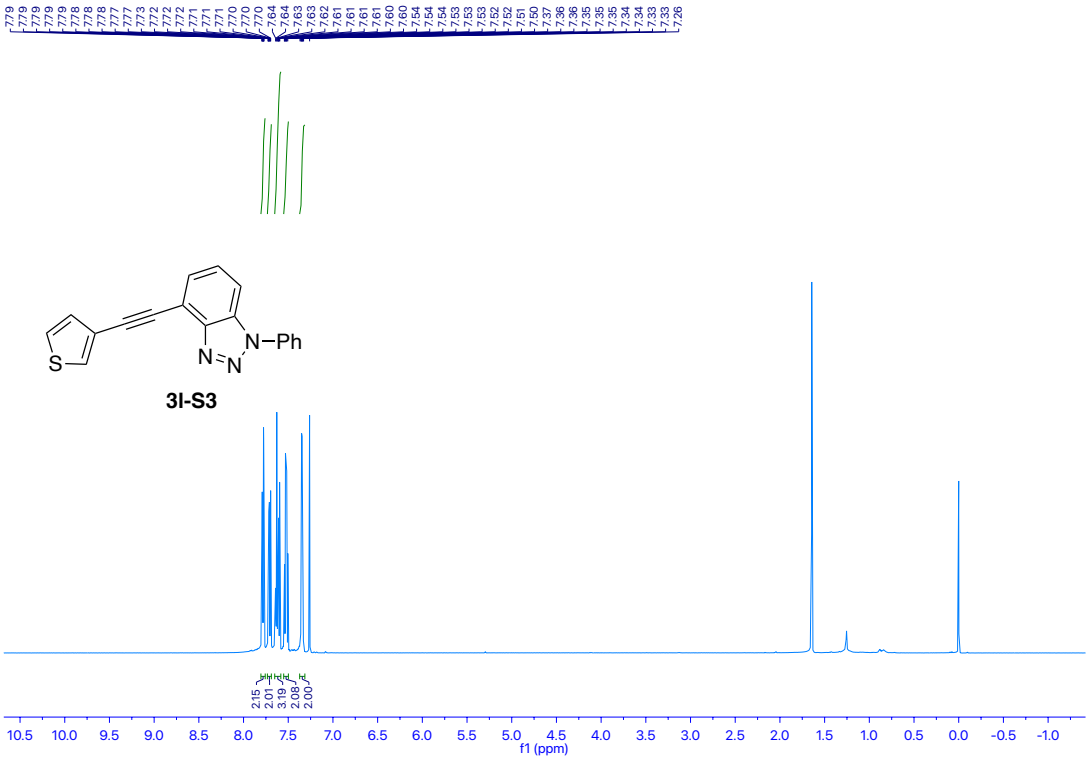
Compound 3k-S3, ^{1}H NMR (400 MHz, $CDCl_3$).



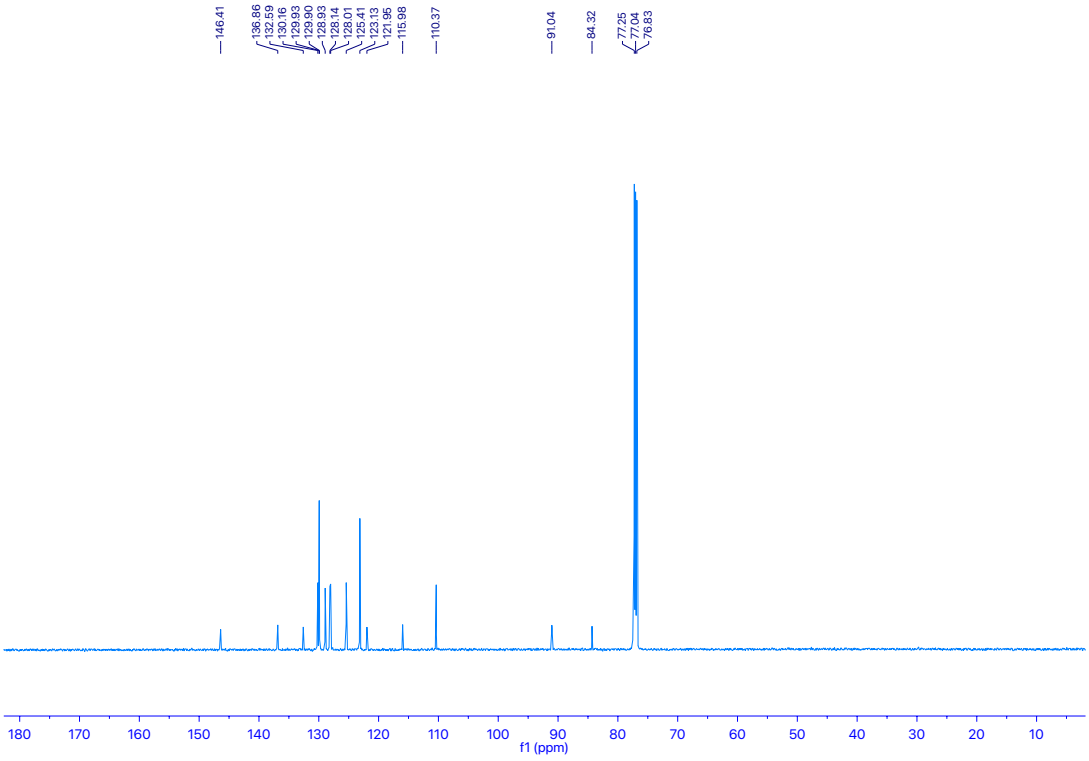
Compound 3k-S3, ^{13}C-NMR (101 MHz, $CDCl_3$)



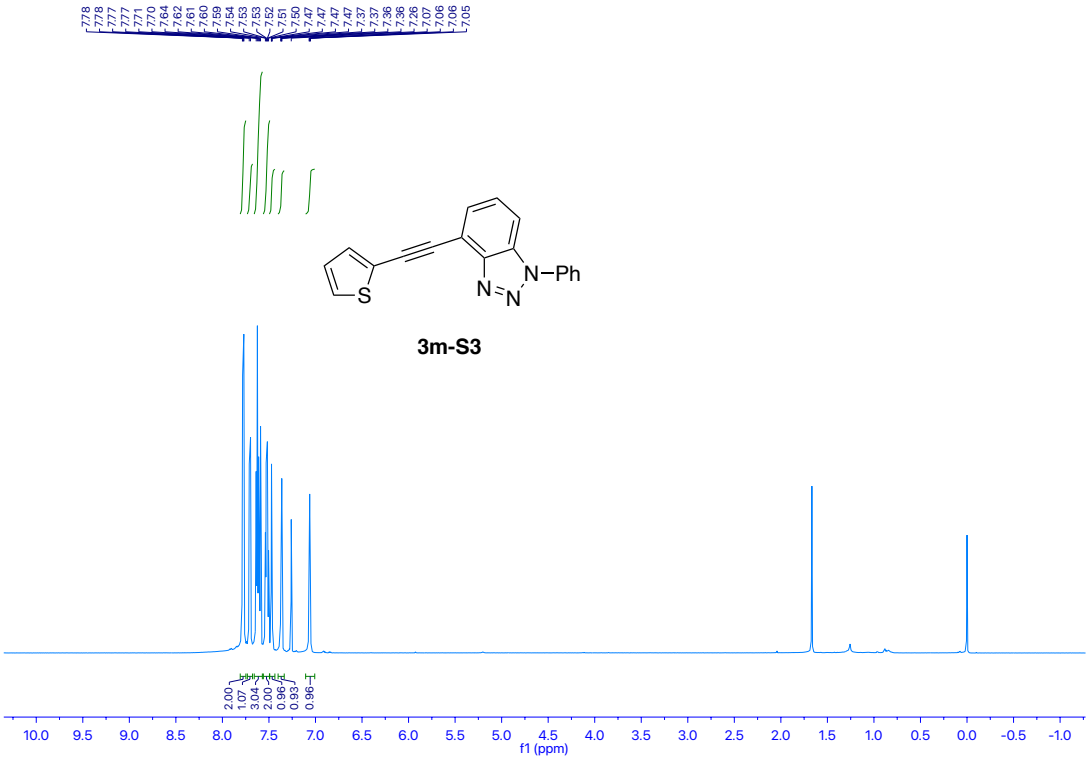
Compound 3l-S3, ^{1}H NMR (600 MHz, $CDCl_3$)



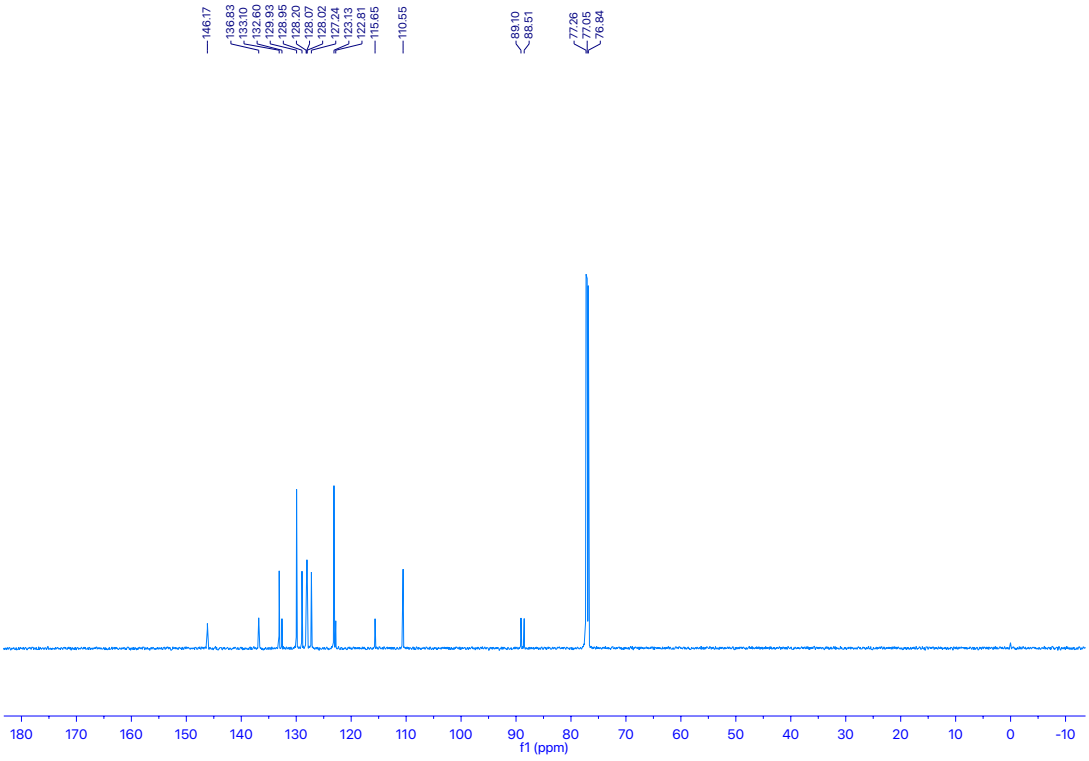
Compound 3l-S3, ^{13}C-NMR (151 MHz, $CDCl_3$)



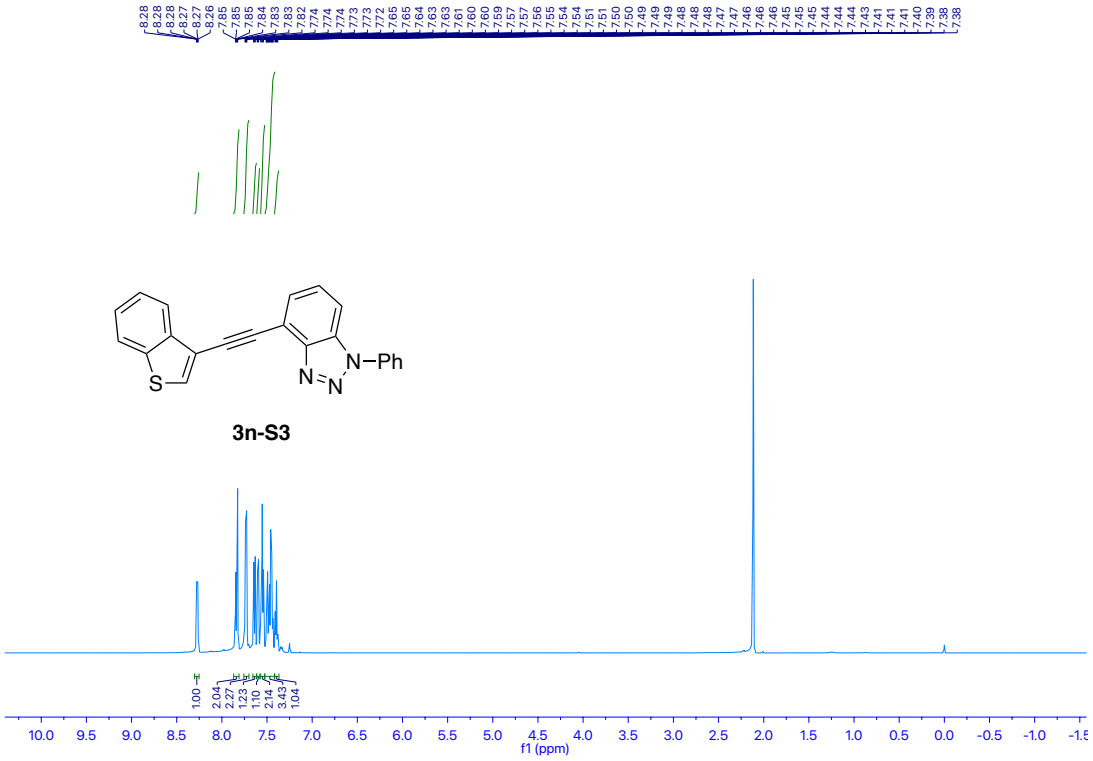
Compound 3m-S3, ^{1}H NMR (600 MHz, $CDCl_3$)



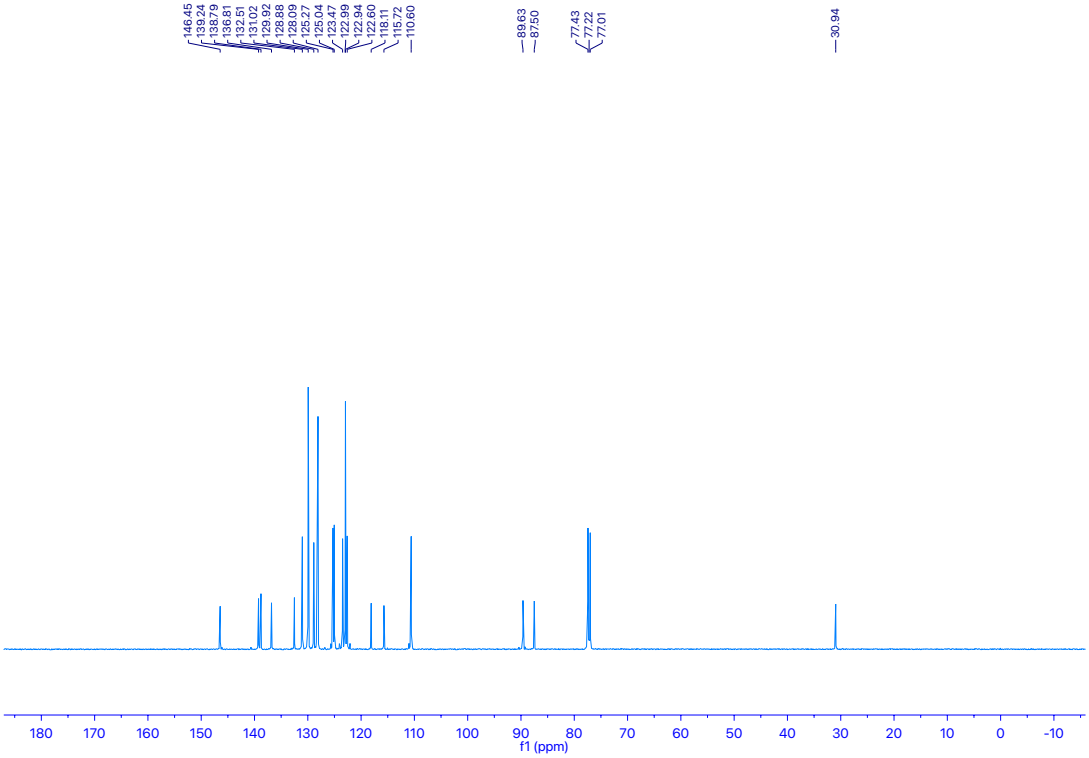
Compound 3m-S3, ^{13}C-NMR (151 MHz, $CDCl_3$)



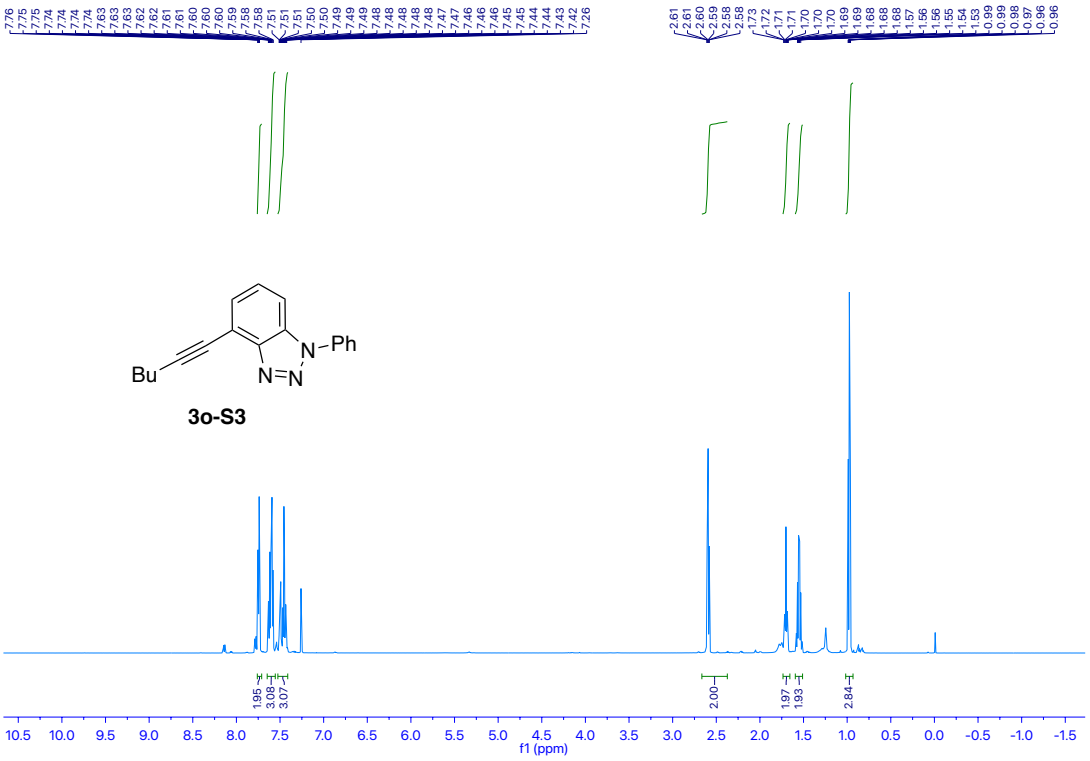
Compound 3n-S3, ^{1}H NMR (600 MHz, $CDCl_3$)



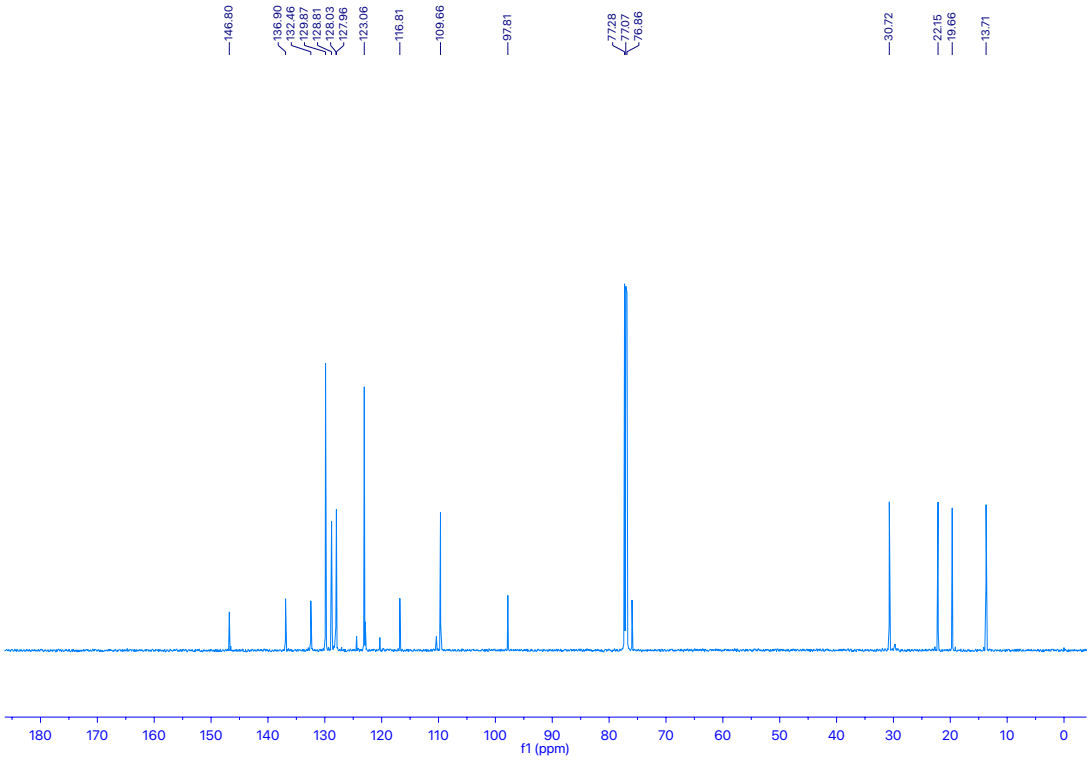
Compound 3n-S3, ^{13}C-NMR (151 MHz, $CDCl_3$)



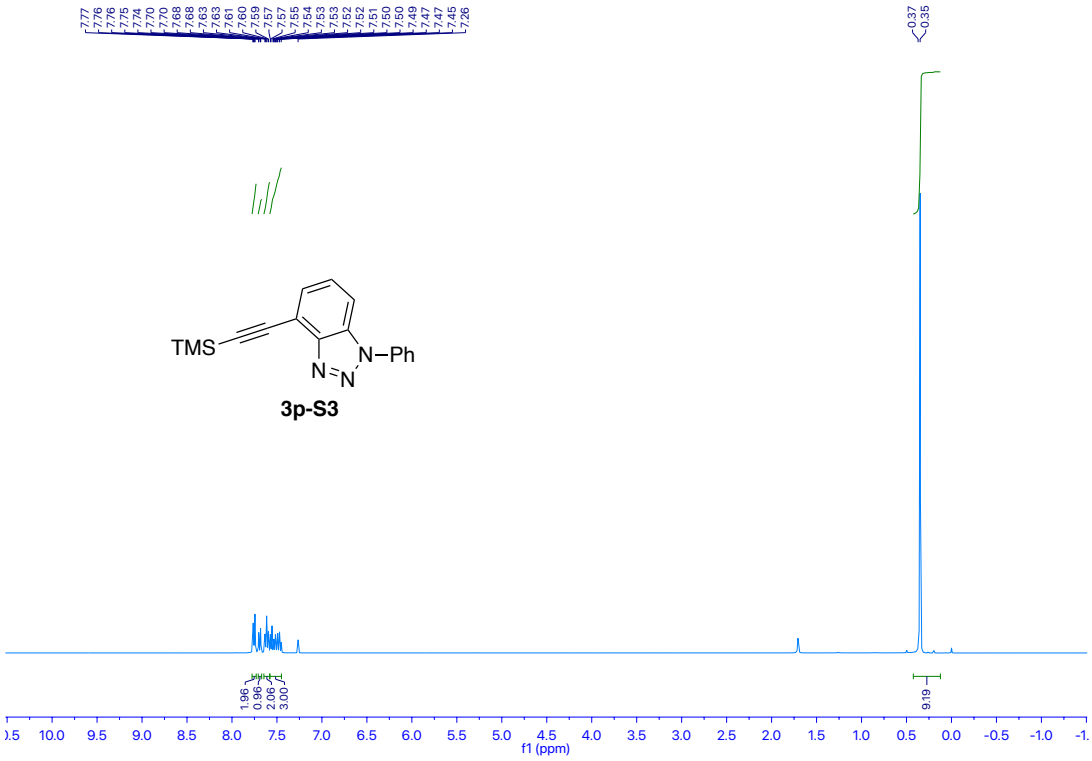
Compound 3o-S3, ^{1}H NMR (400 MHz, $CDCl_3$)



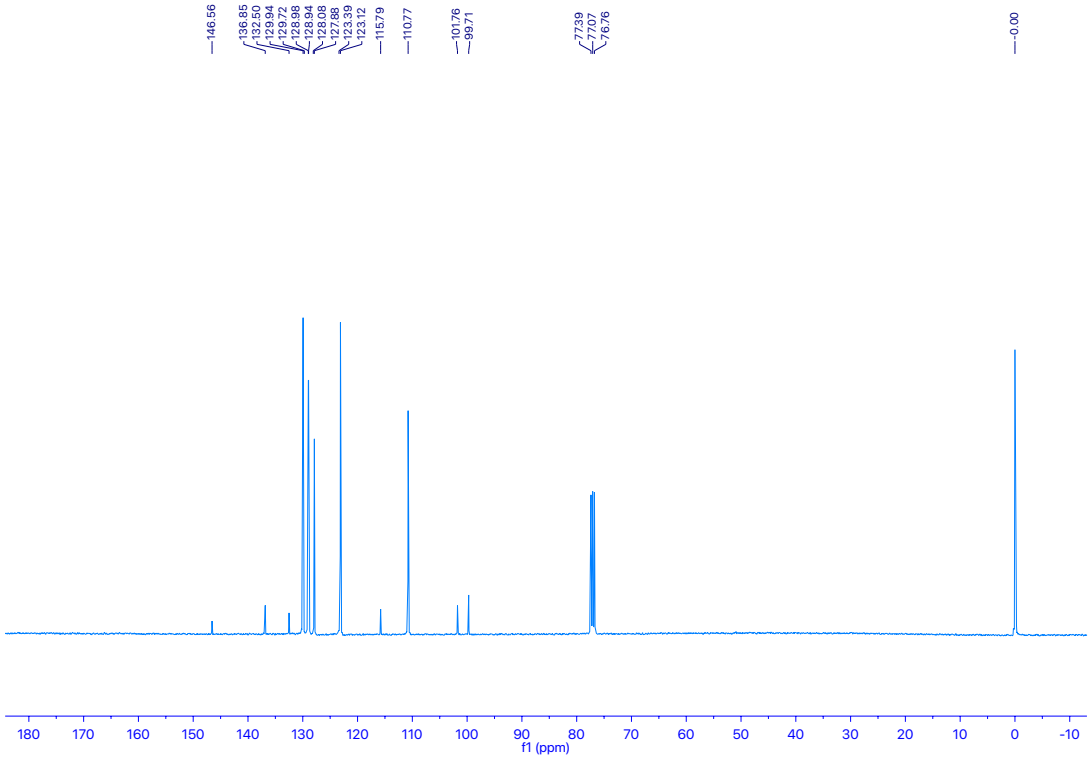
Compound 3o-S3, ^{13}C-NMR (151 MHz, $CDCl_3$)



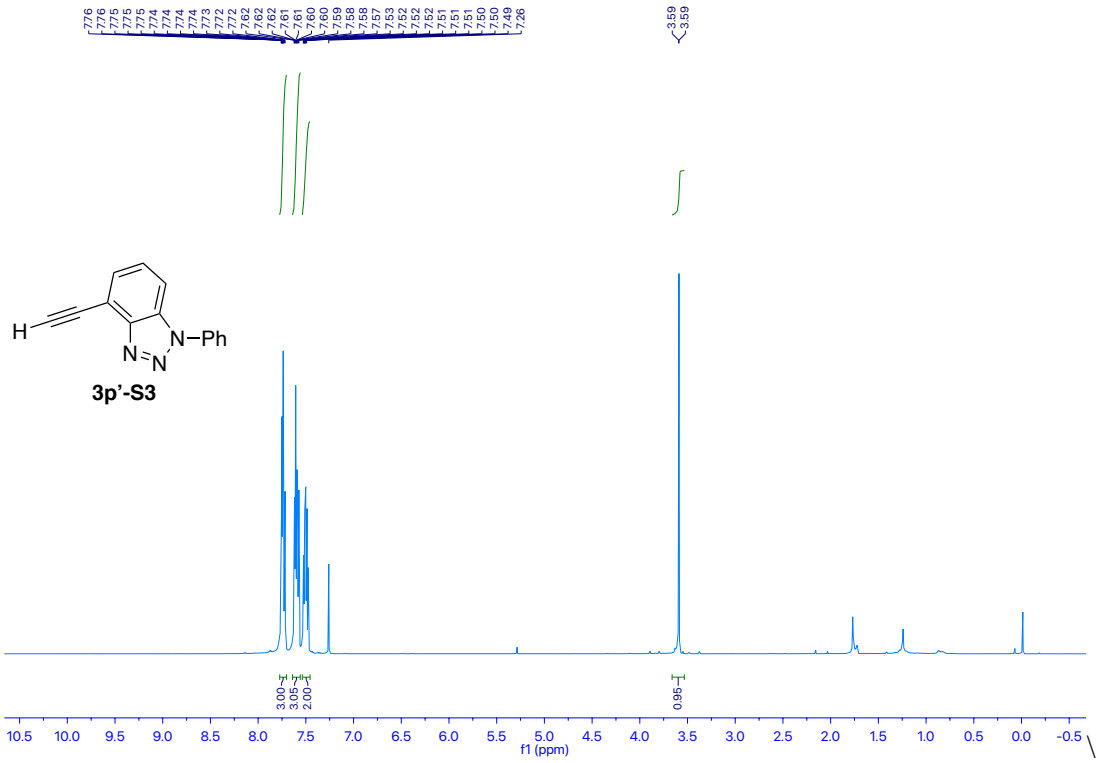
Compound 3p-S3, ^{1}H NMR (400 MHz, $CDCl_3$)



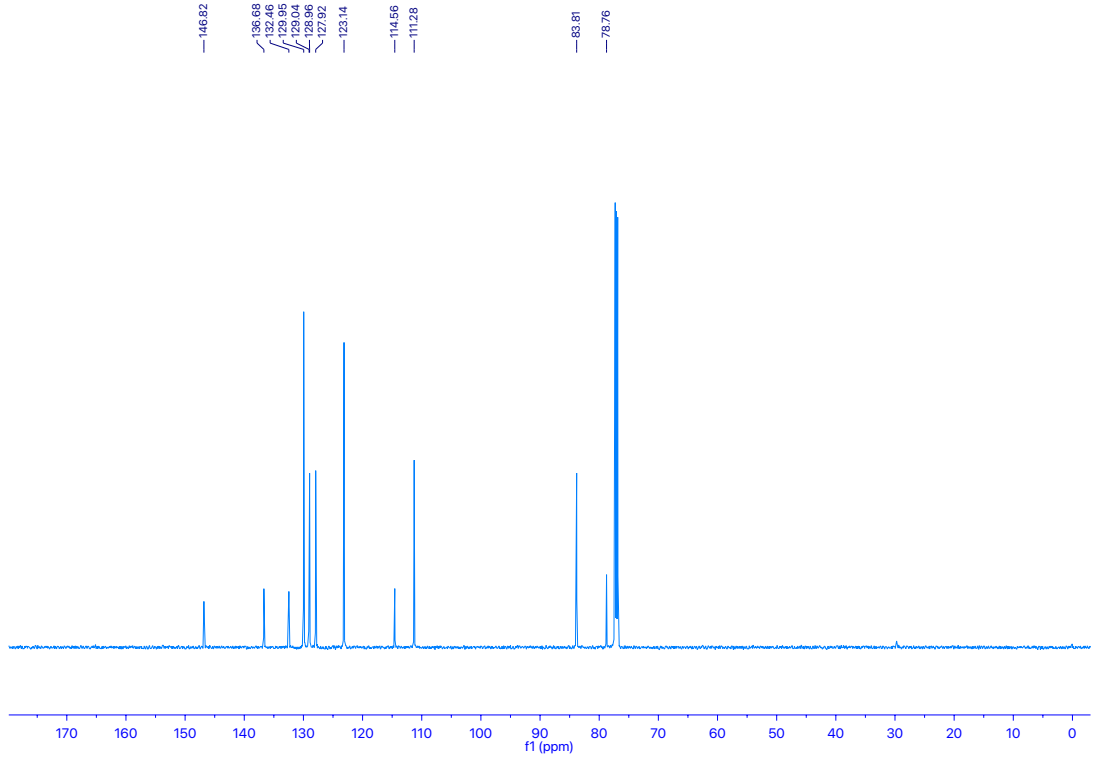
Compound 3p-S3, ^{13}C-NMR (101 MHz, $CDCl_3$)



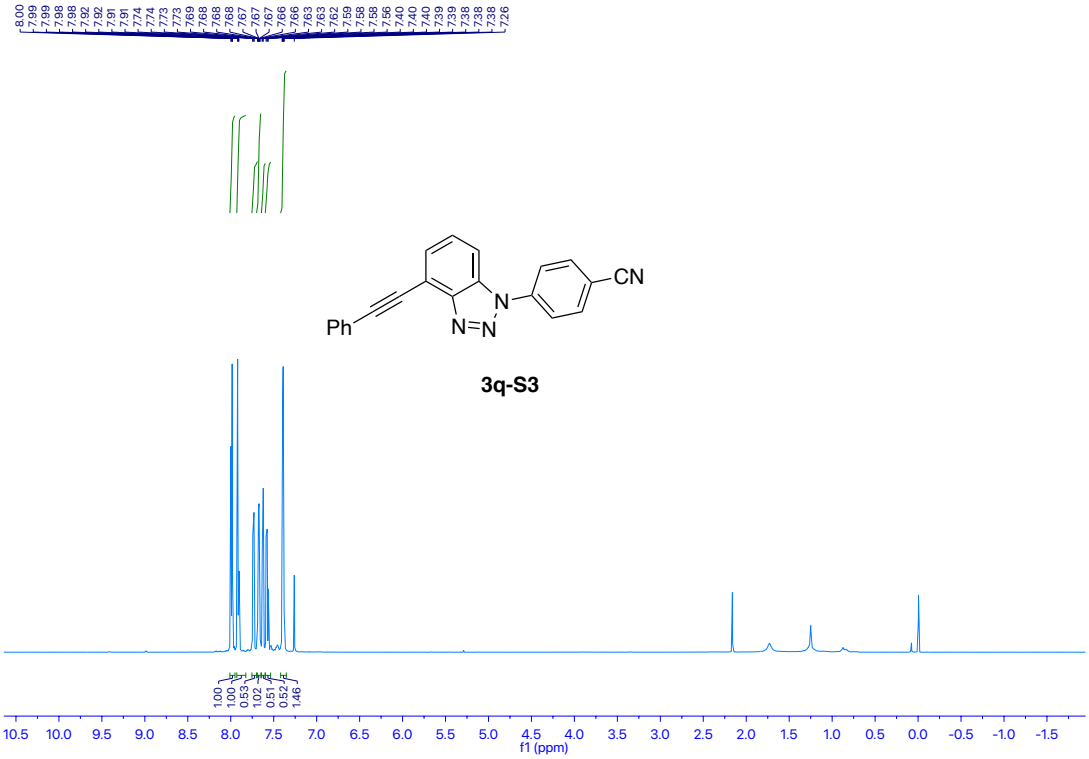
Compound 3p'-S3, ^{1}H NMR (600 MHz, $CDCl_3$)



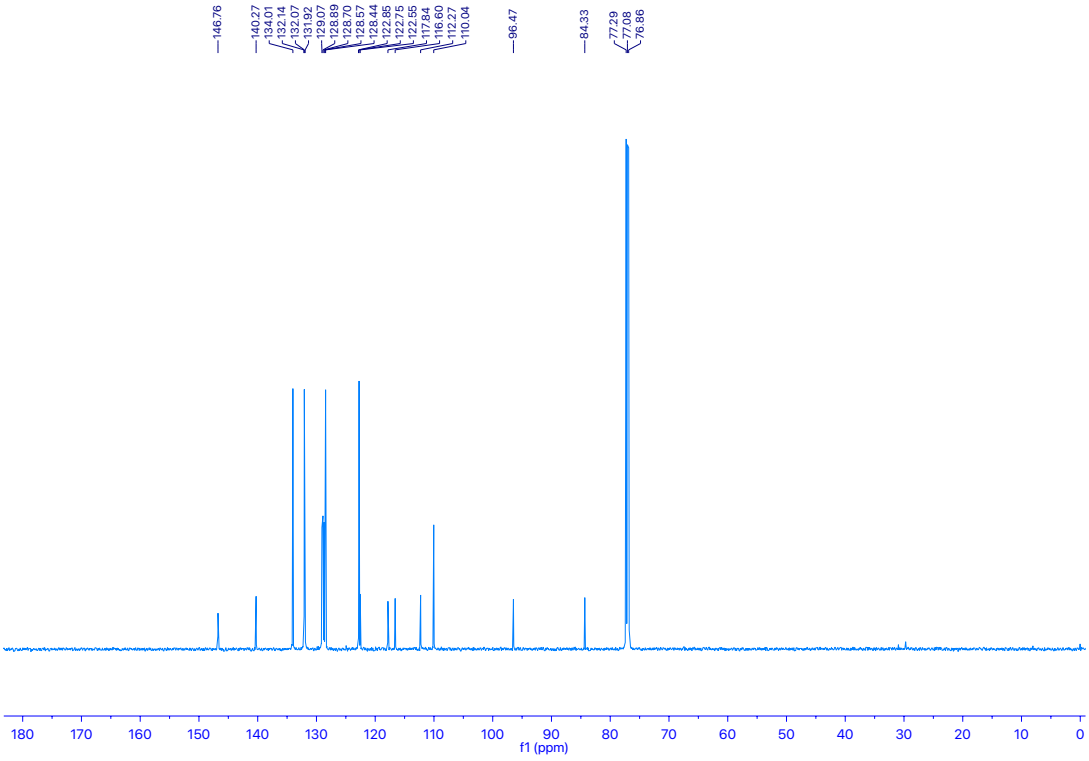
Compound 3p'-S3, ^{13}C-NMR (151 MHz, CDCl3)



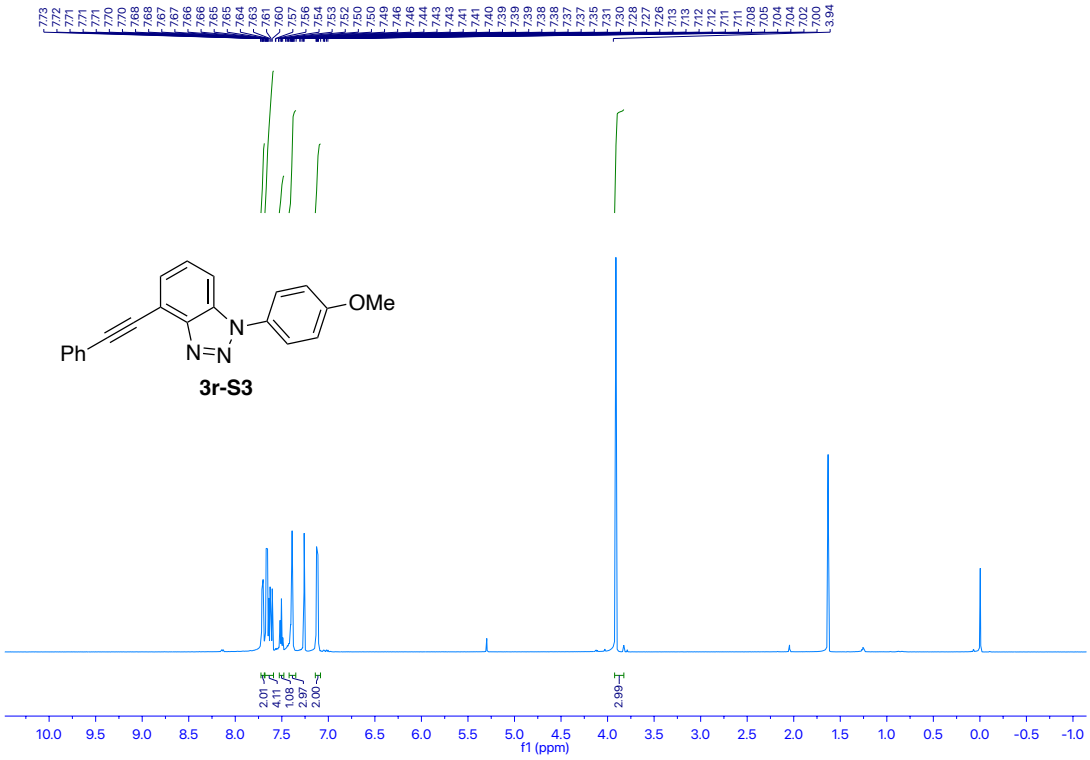
Compound 3q-S3, ^{1}H NMR (600 MHz, $CDCl_3$)



Compound 3q-S3, ^{13}C-NMR (151 MHz, $CDCl_3$)



Compound 3r-S3, ^{1}H NMR (600 MHz, $CDCl_3$)



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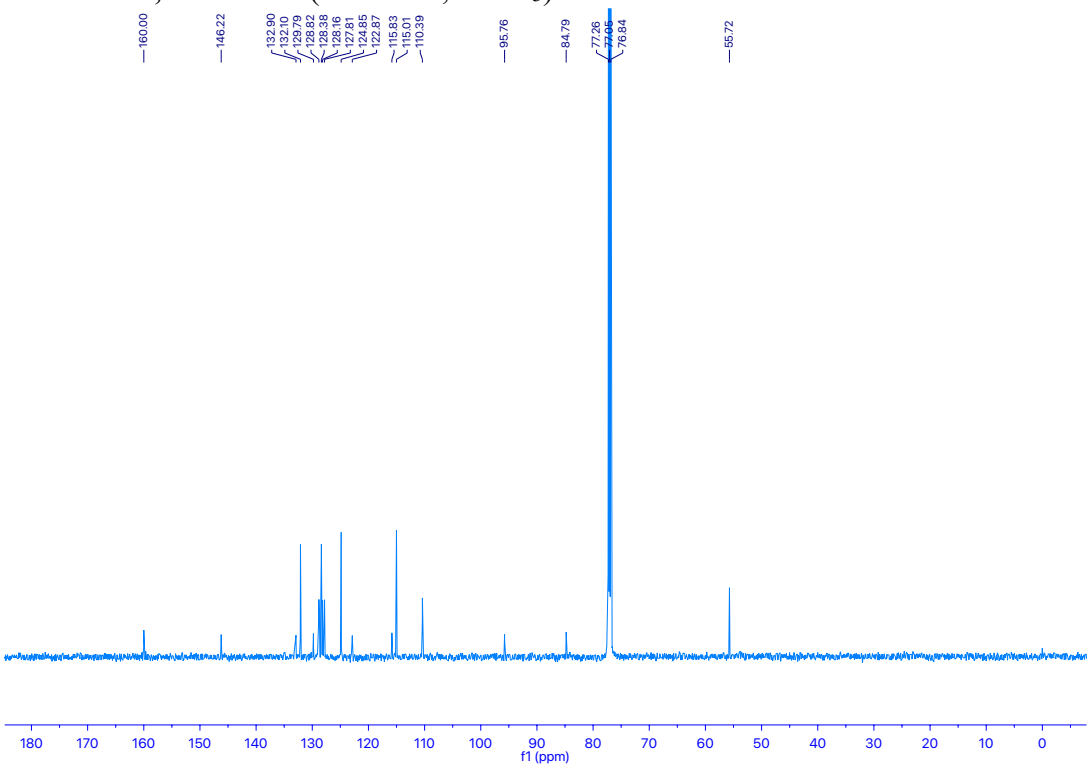
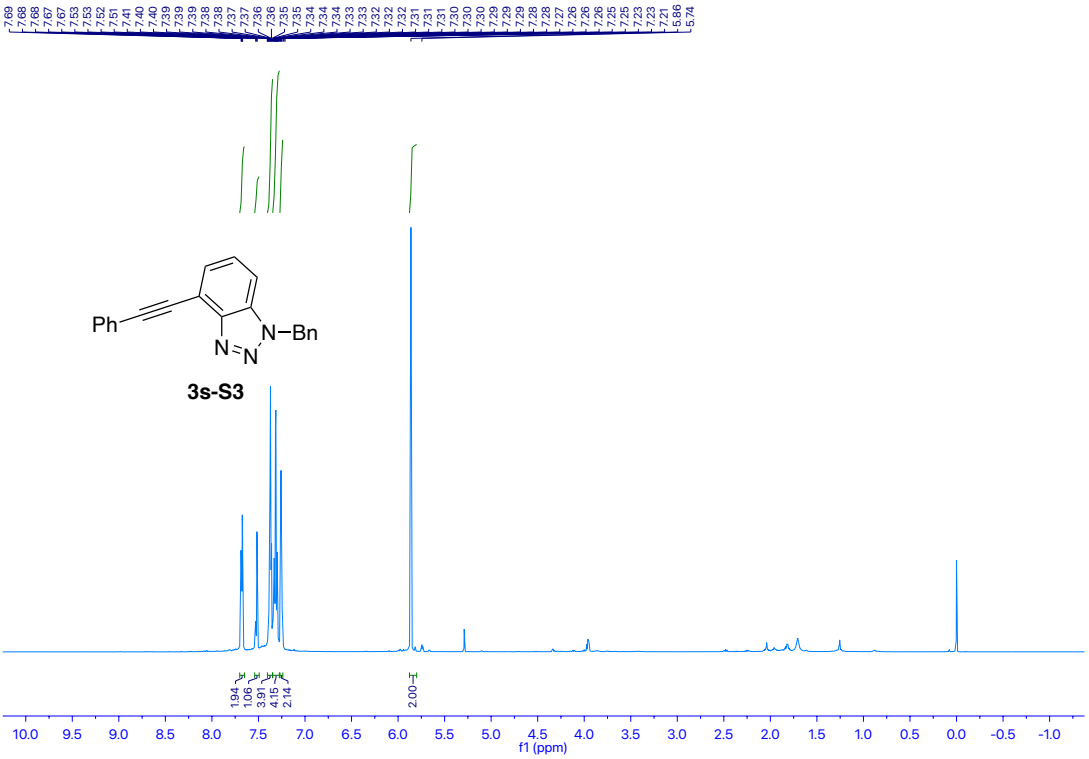
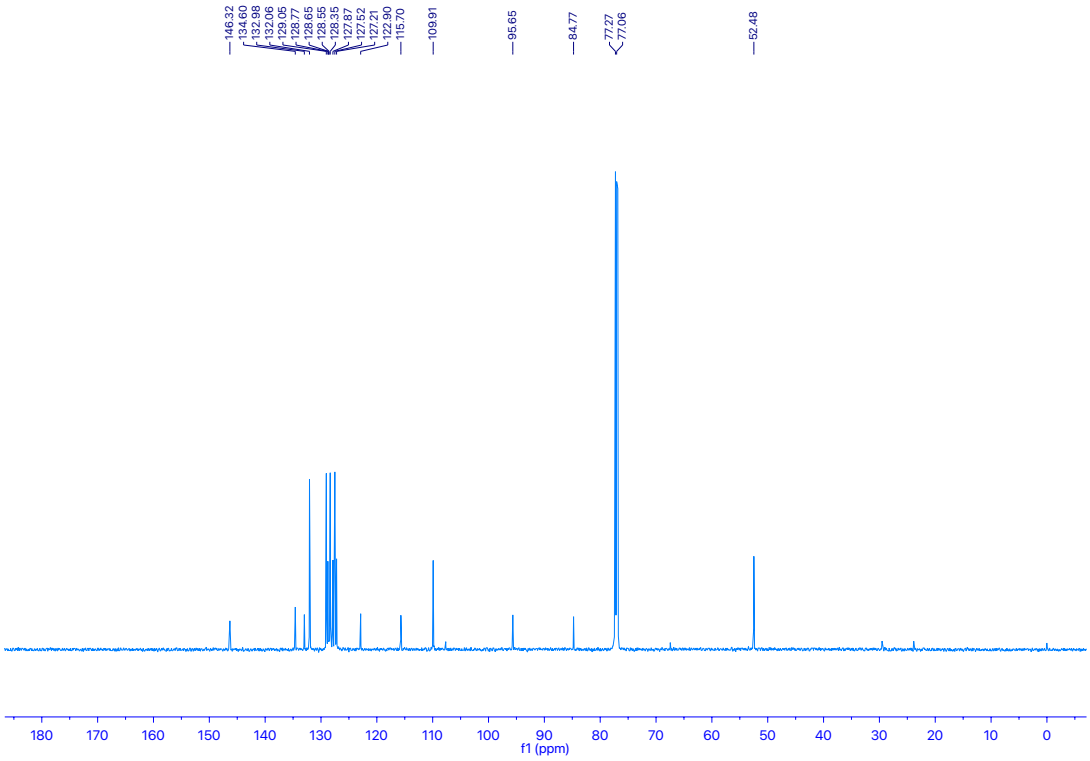
Compound 3r-S3, ^{13}C-NMR (151 MHz, $CDCl_3$)



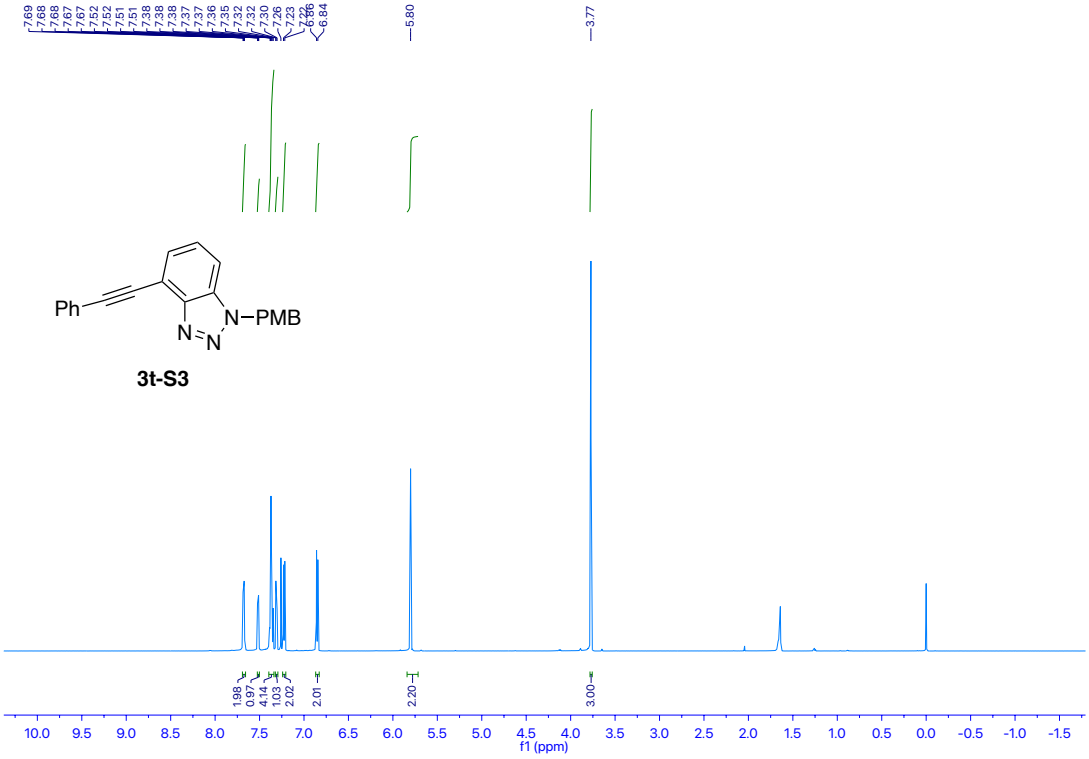
Compound 3s-S3, ^{1}H NMR (400 MHz, $CDCl_3$)



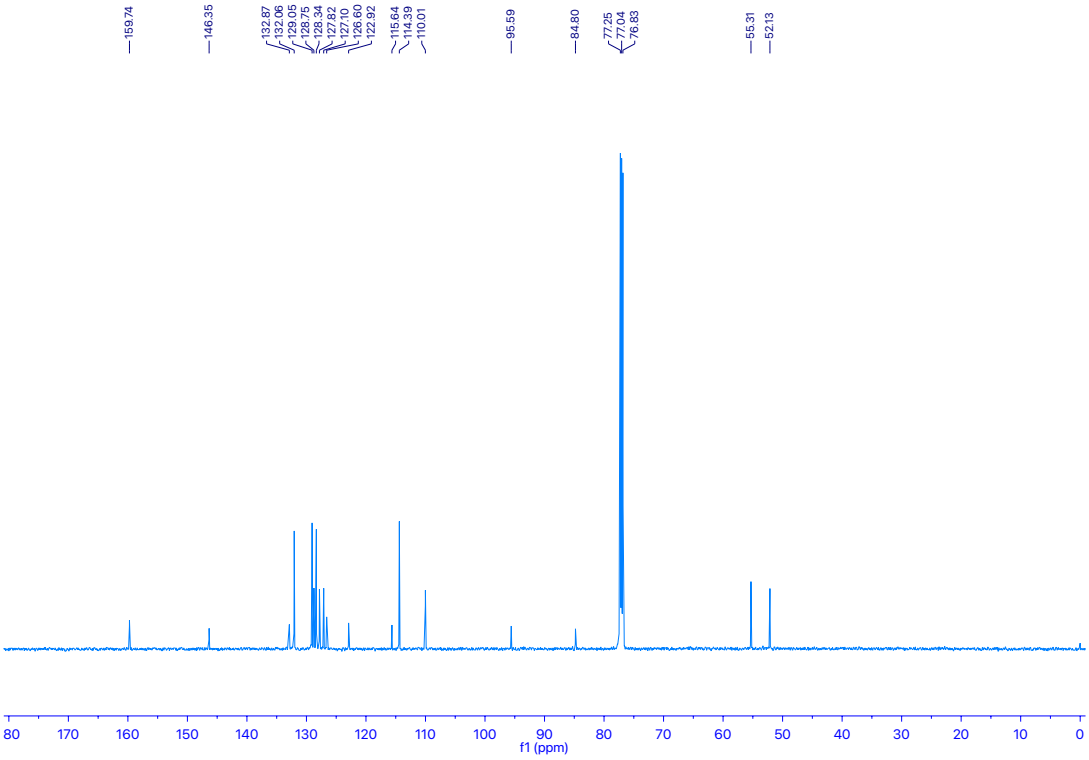
Compound 3s-S3, ^{13}C-NMR (151 MHz, $CDCl_3$)



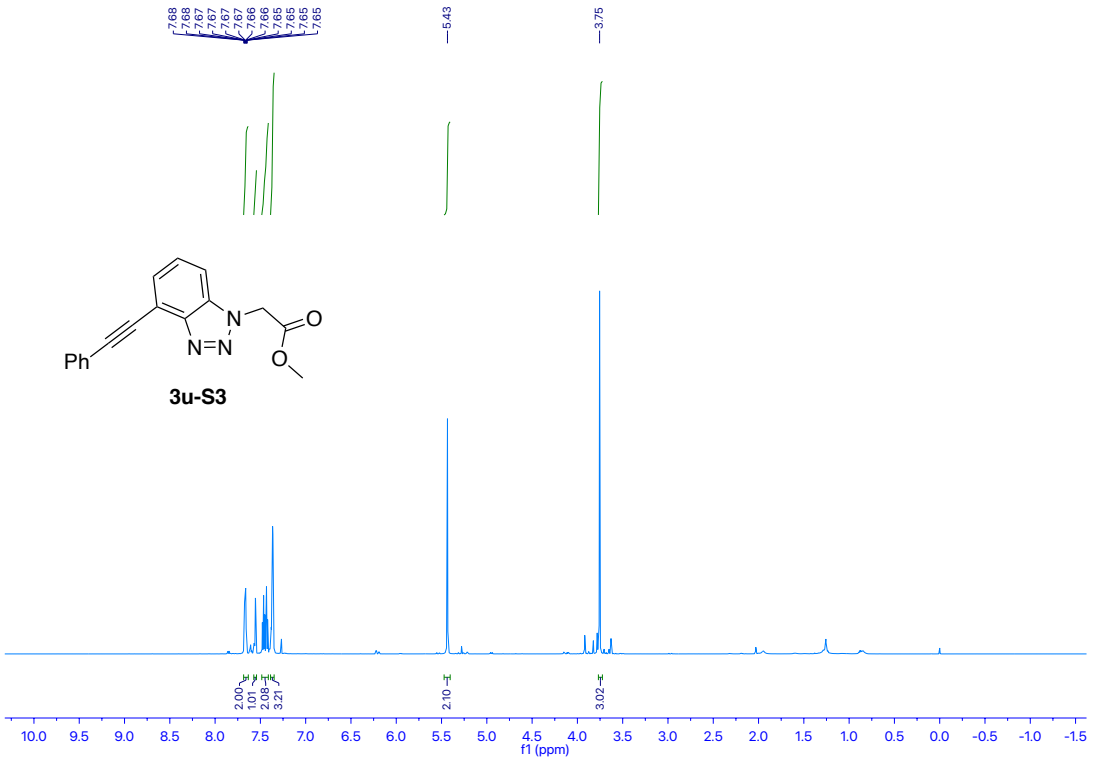
Compound 3t-S3, ^{1}H NMR (600 MHz, $CDCl_3$)



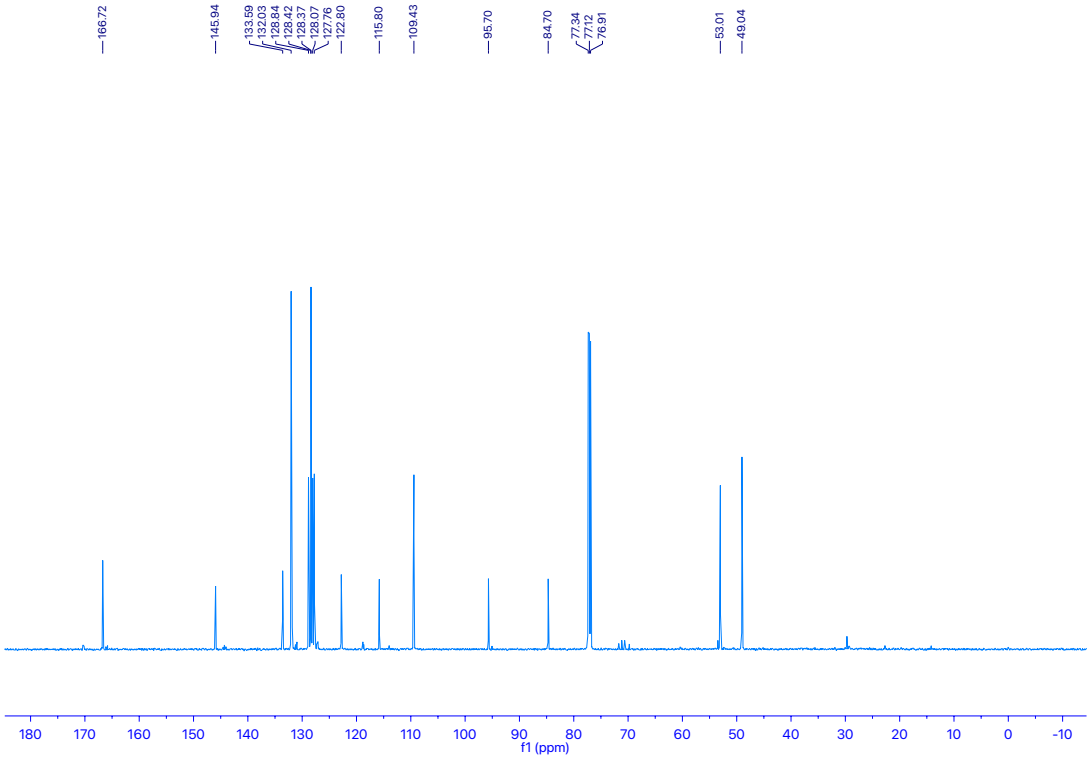
Compound 3t-S3, ^{13}C-NMR (151 MHz, $CDCl_3$)



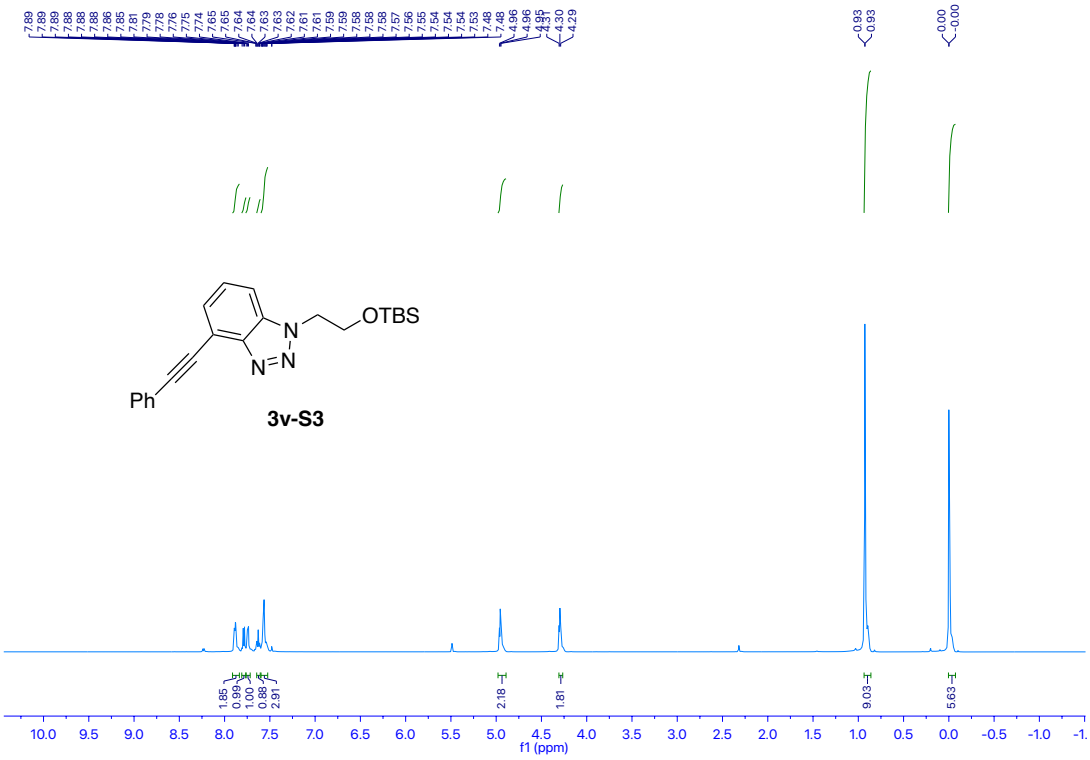
Compound 3u-S3, ^{1}H NMR (600 MHz, $CDCl_3$)



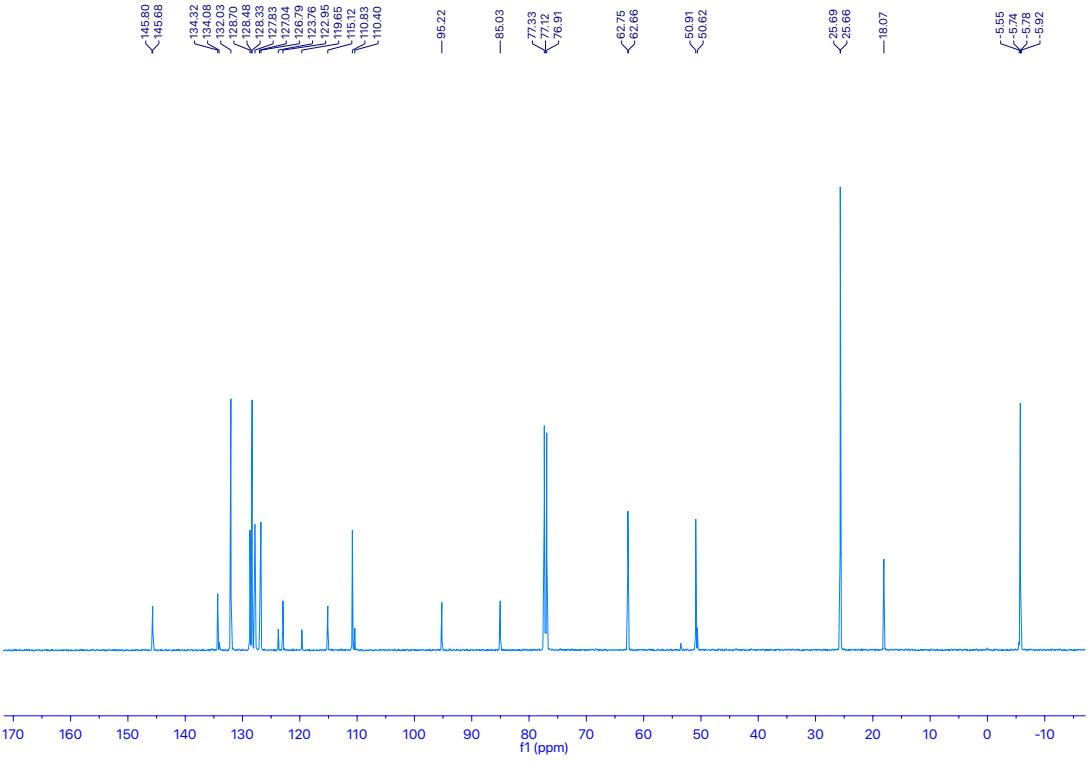
Compound 3u-S3, ^{13}C-NMR (151 MHz, $CDCl_3$)



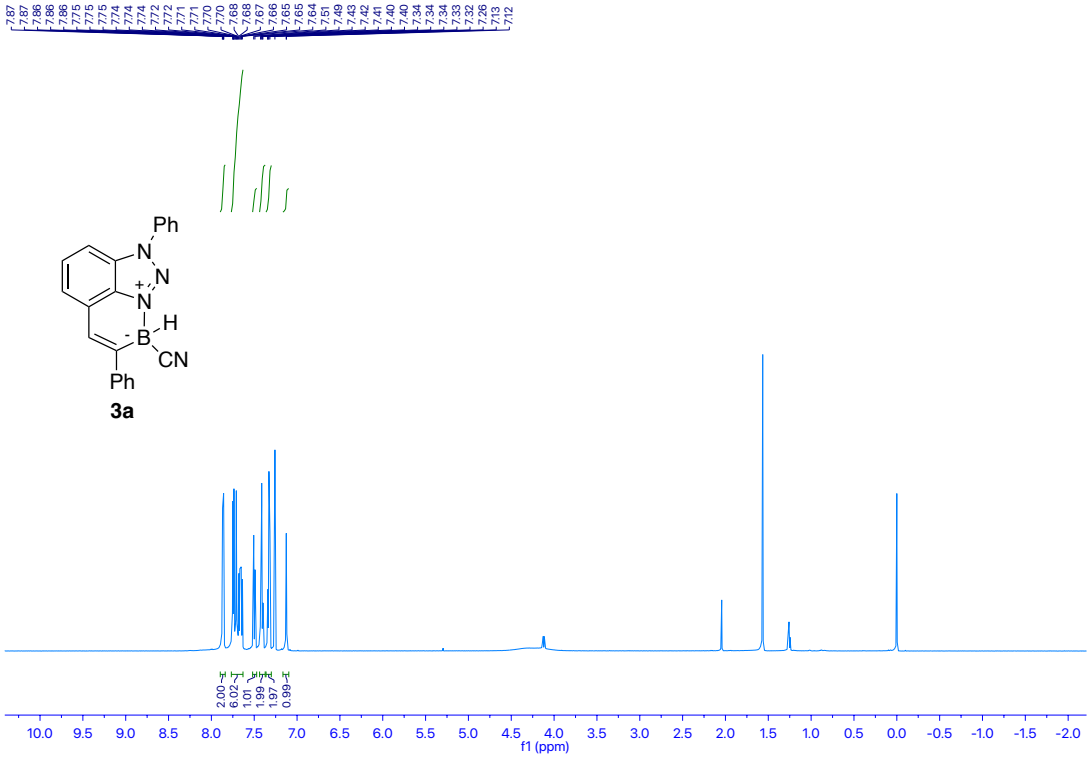
Compound 3v-S3, ^{1}H NMR (600 MHz, $CDCl_3$)



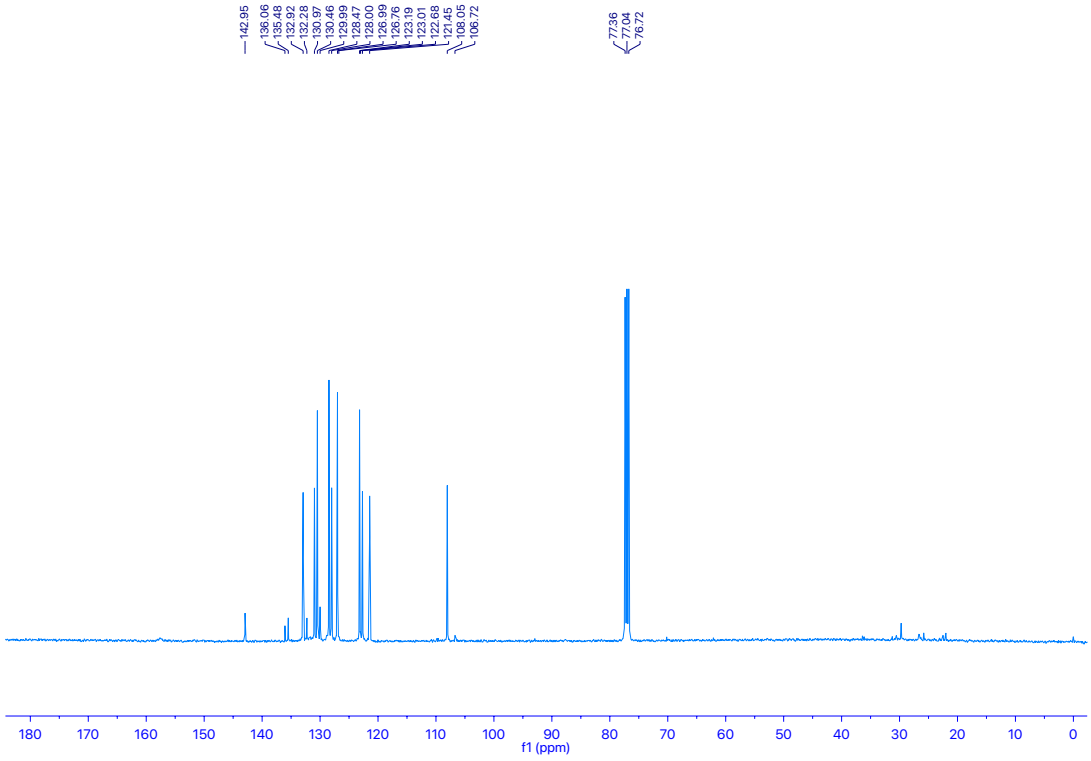
Compound 3v-S3, ^{13}C-NMR (151 MHz, $CDCl_3$)



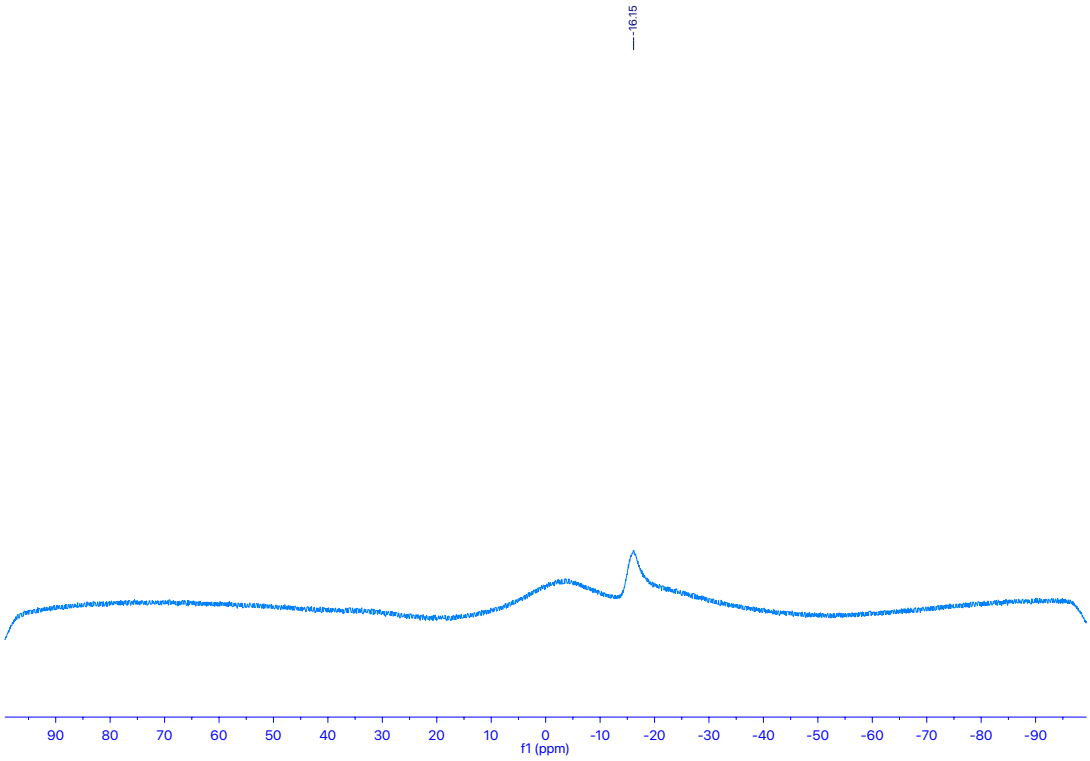
Compound 3a, ^{1}H NMR (600 MHz, $CDCl_3$)



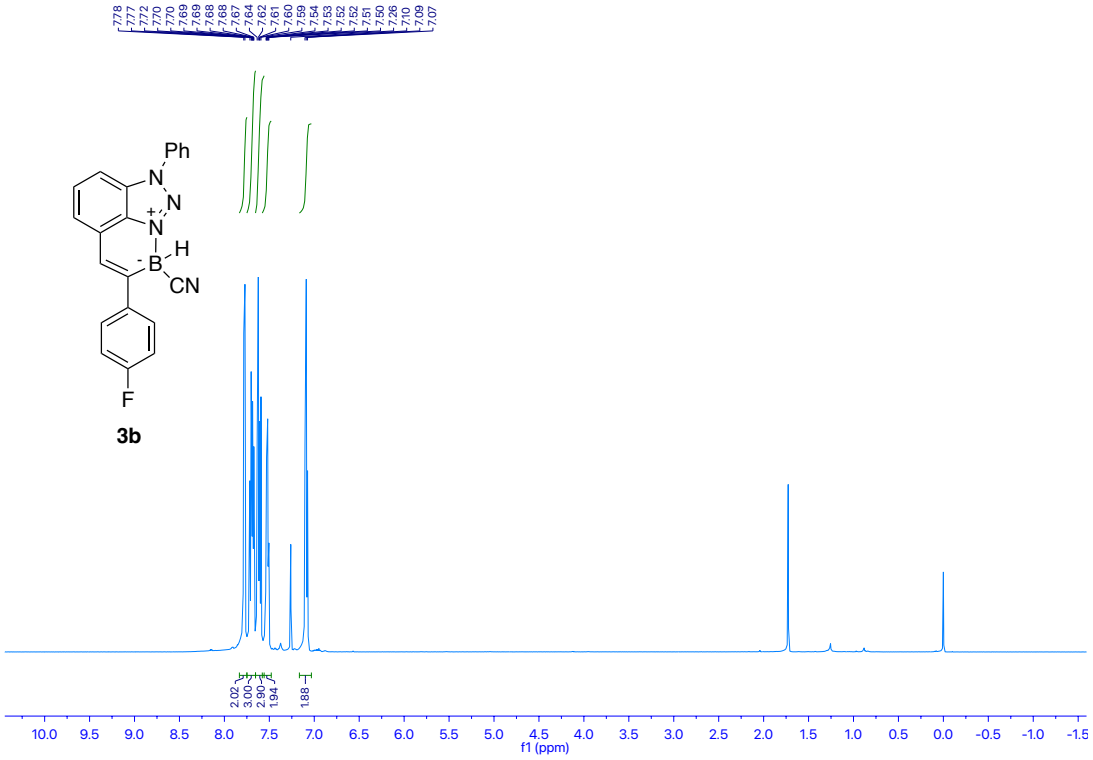
Compound 3a, ^{13}C-NMR (151 MHz, $CDCl_3$)



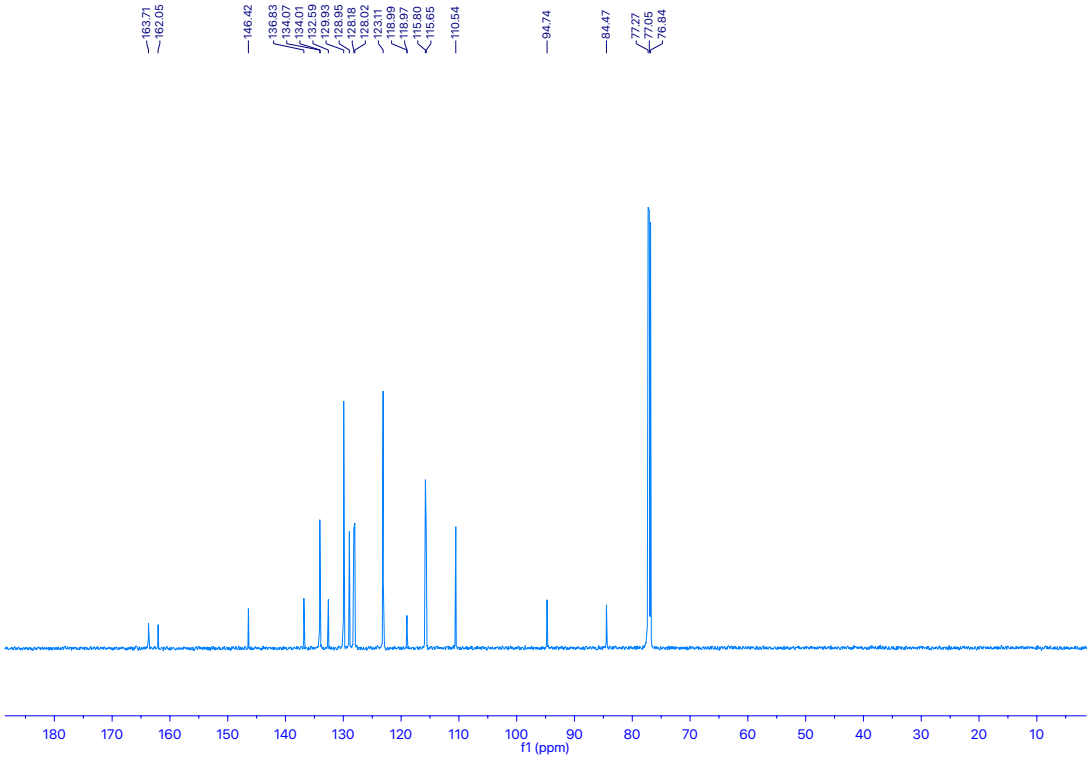
Compound 3a, ^{11}B NMR (128 MHz, $CDCl_3$)



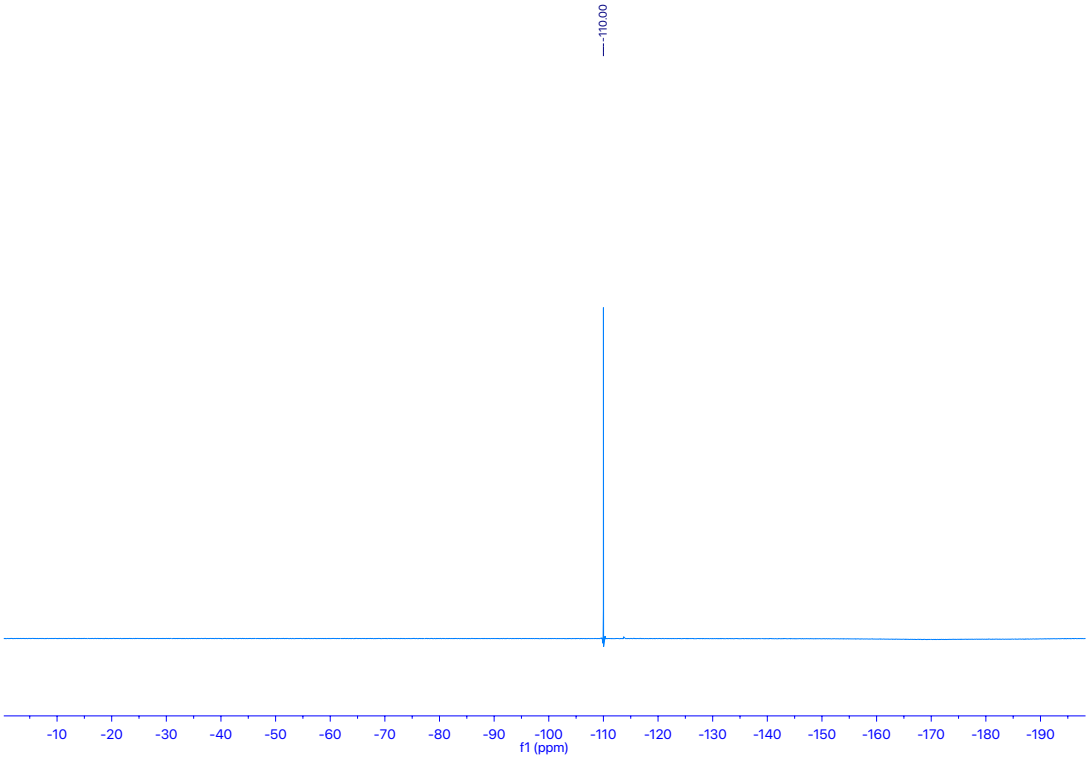
Compound 3b, ^{1}H NMR (600 MHz, $CDCl_3$)



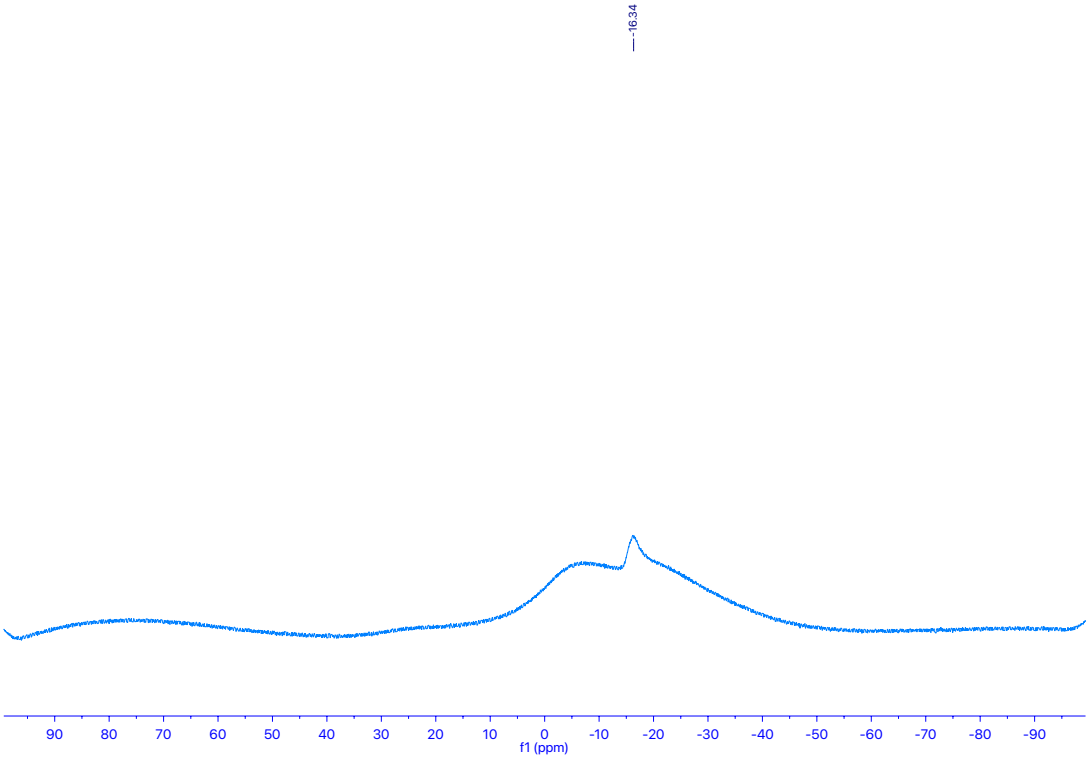
Compound 3b, ^{13}C-NMR (151 MHz, $CDCl_3$)



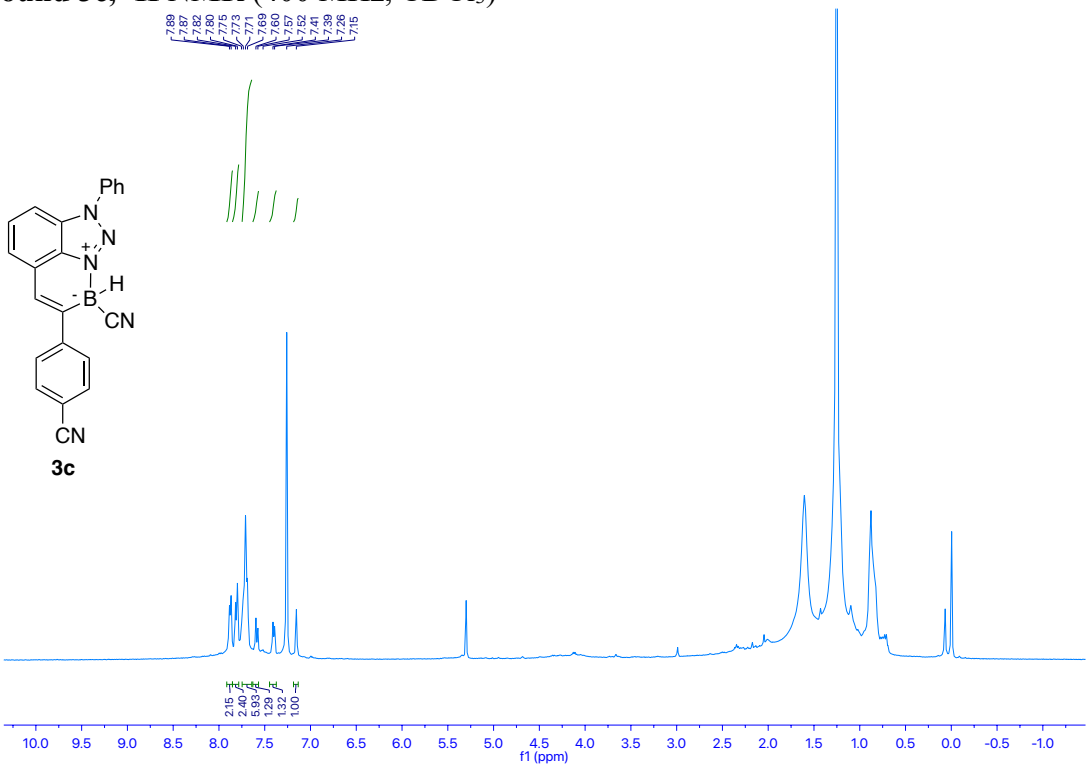
Compound 3b, ^{19}F-NMR (564 MHz, $CDCl_3$)



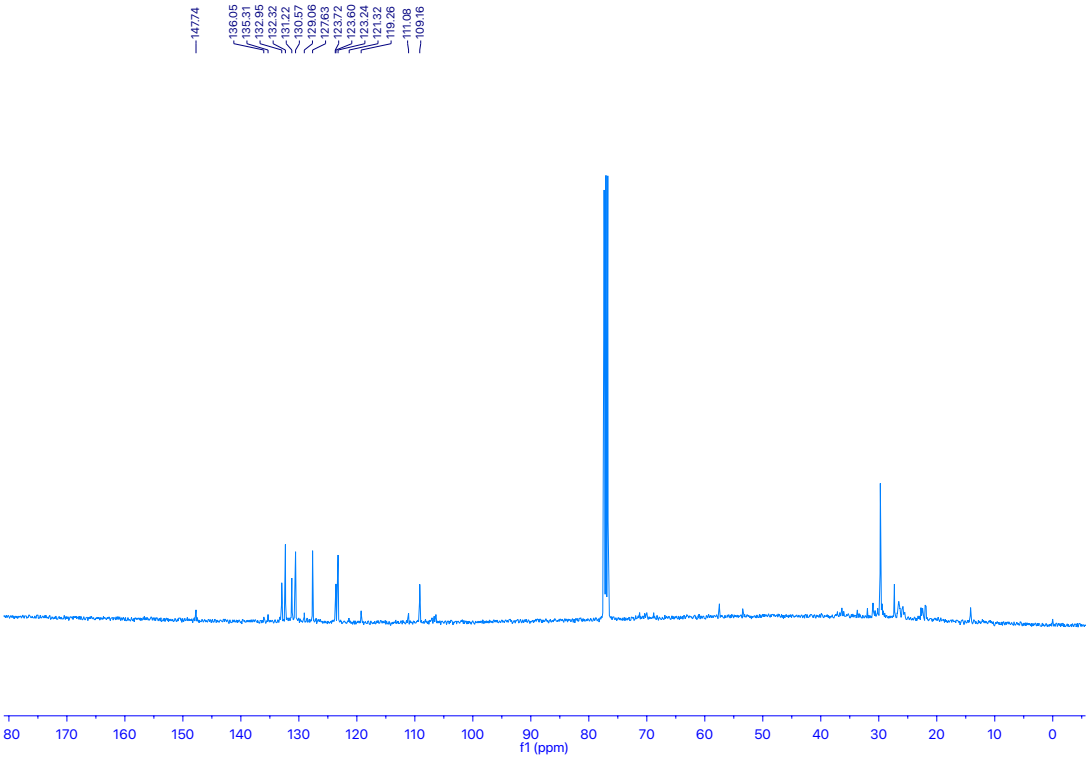
Compound 3b, ^{11}B NMR (128 MHz, $CDCl_3$)



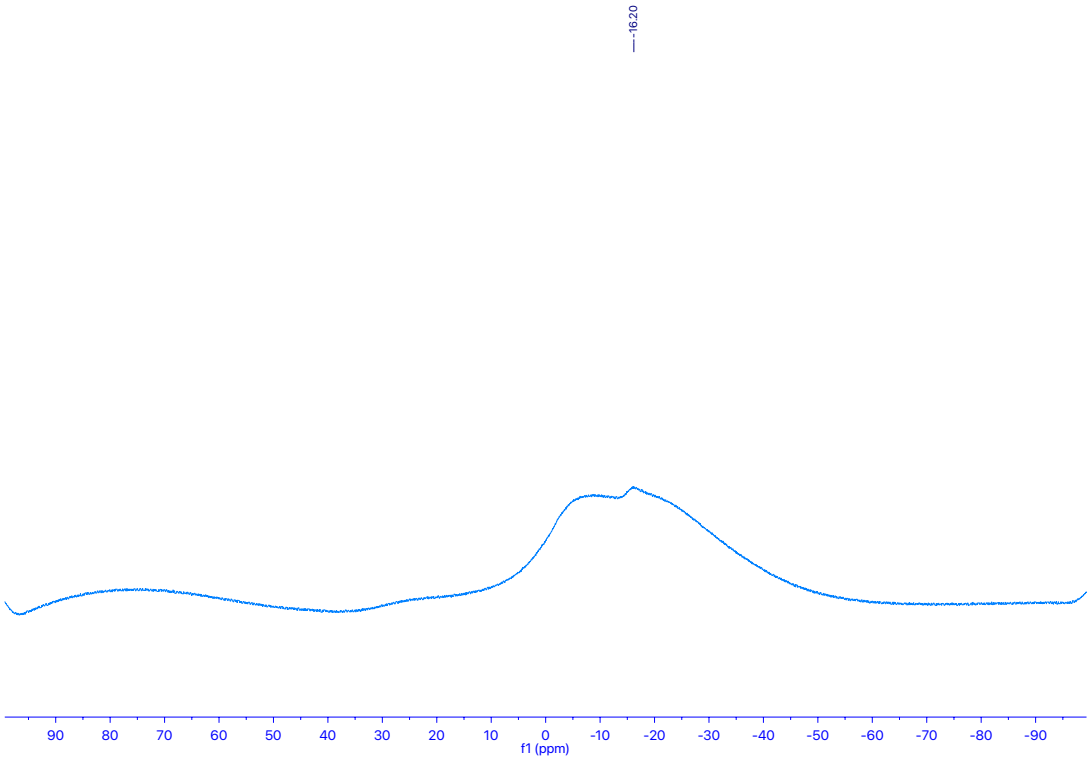
Compound 3c, ^{1}H NMR (400 MHz, $CDCl_3$)



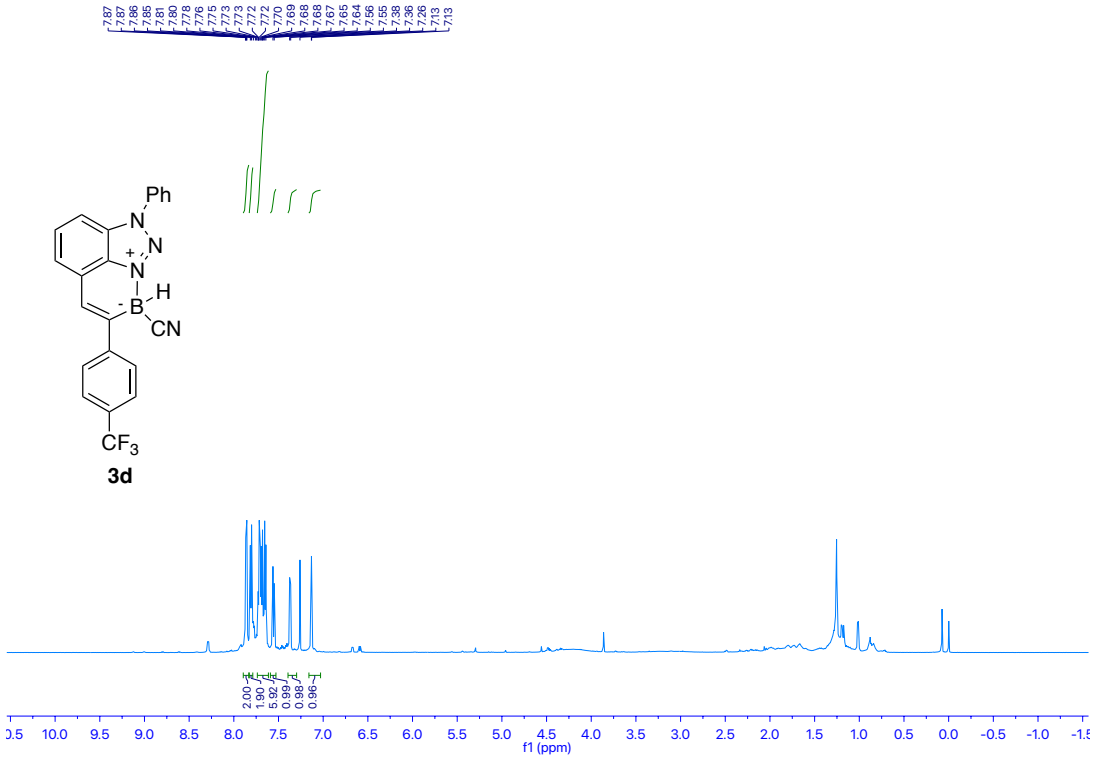
Compound 3c, ^{13}C-NMR (101 MHz, $CDCl_3$)



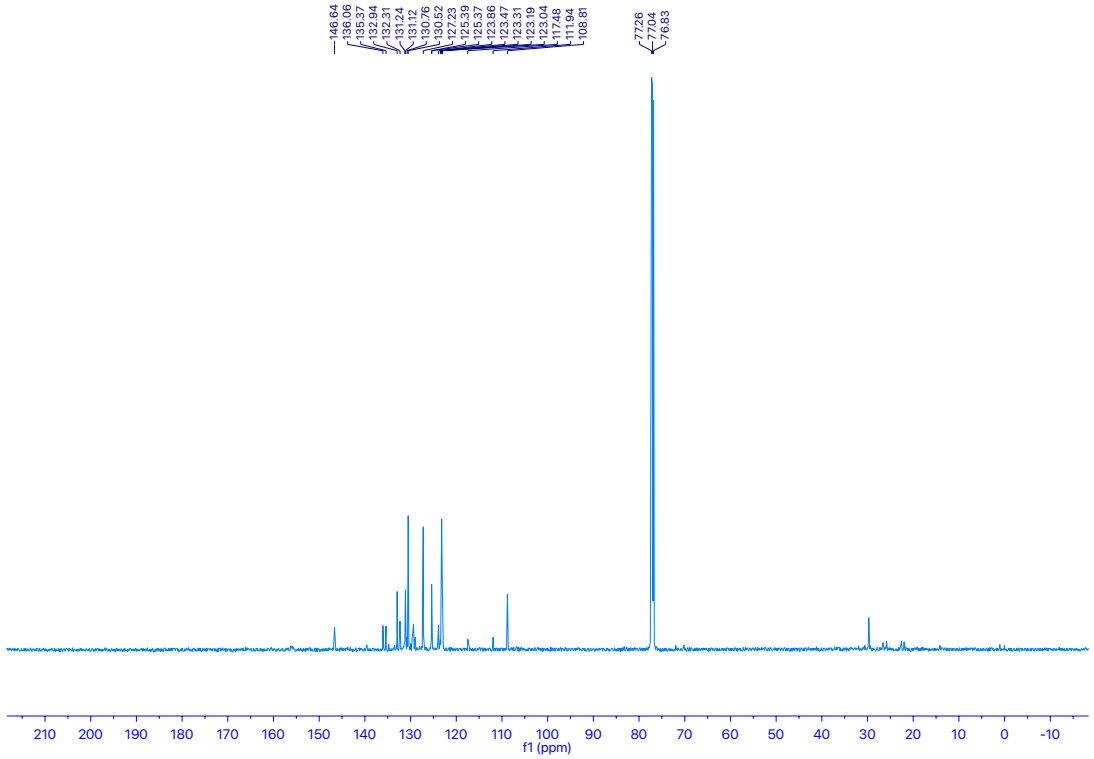
Compound 3c, ^{11}B NMR (128 MHz, $CDCl_3$)



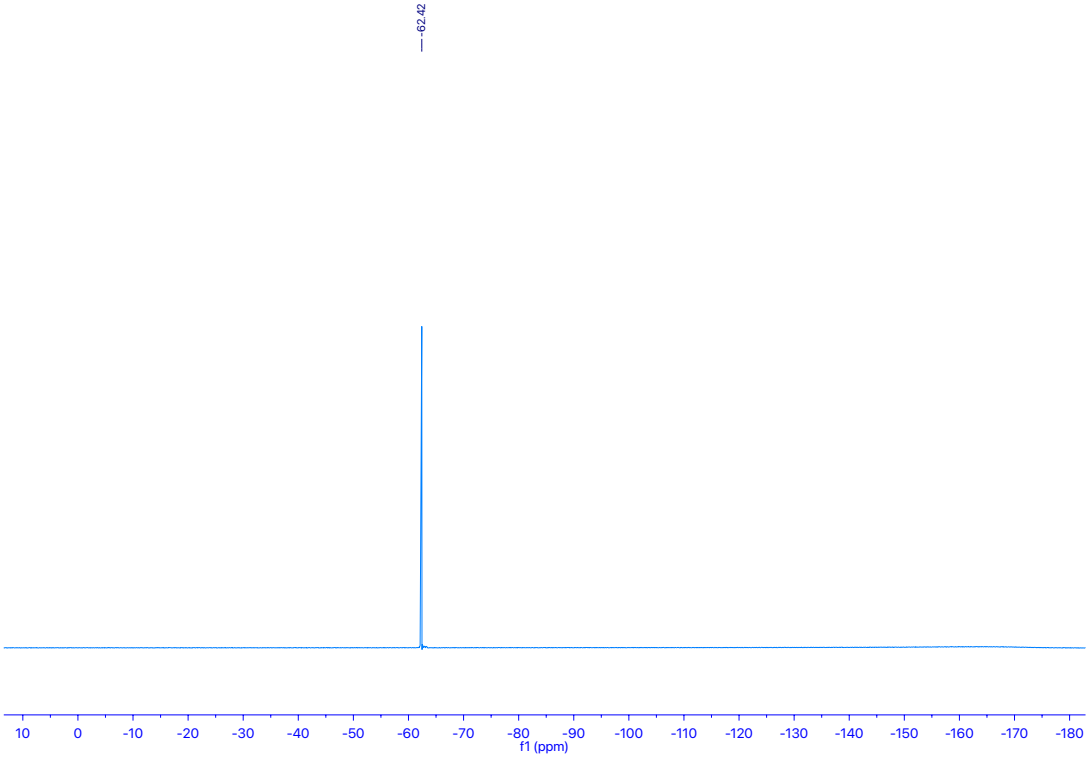
Compound 3d, ^{1}H NMR (600 MHz, $CDCl_3$).



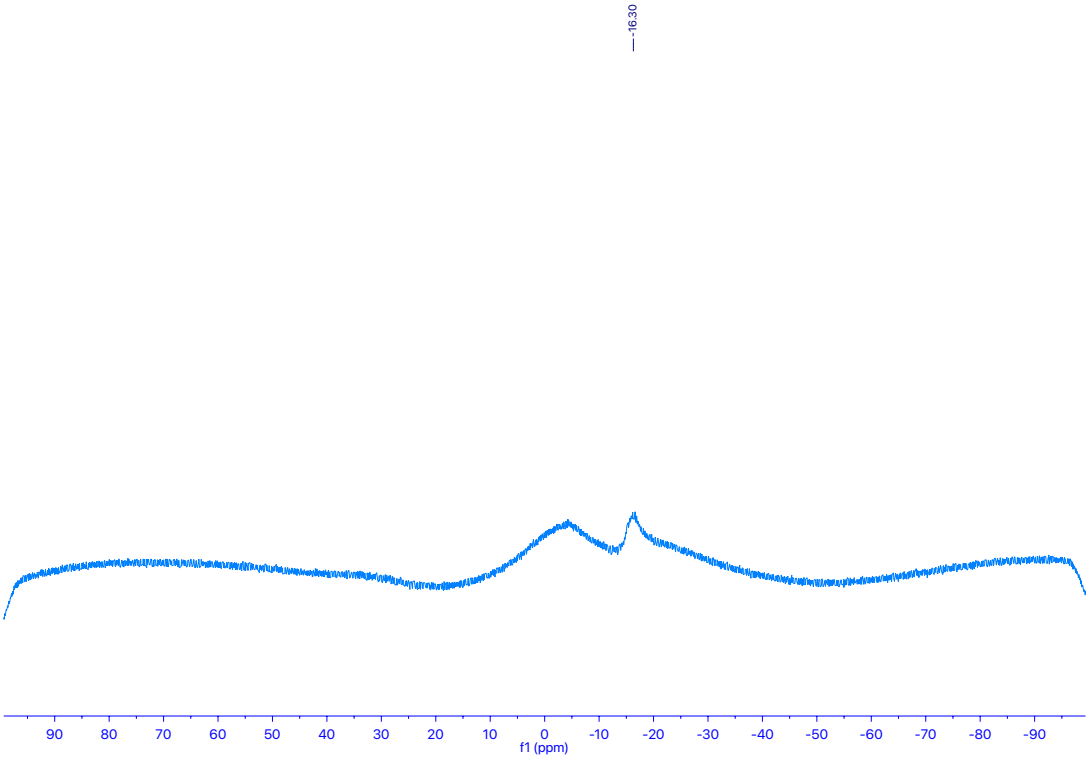
Compound 3d, ^{13}C-NMR (151 MHz, $CDCl_3$)



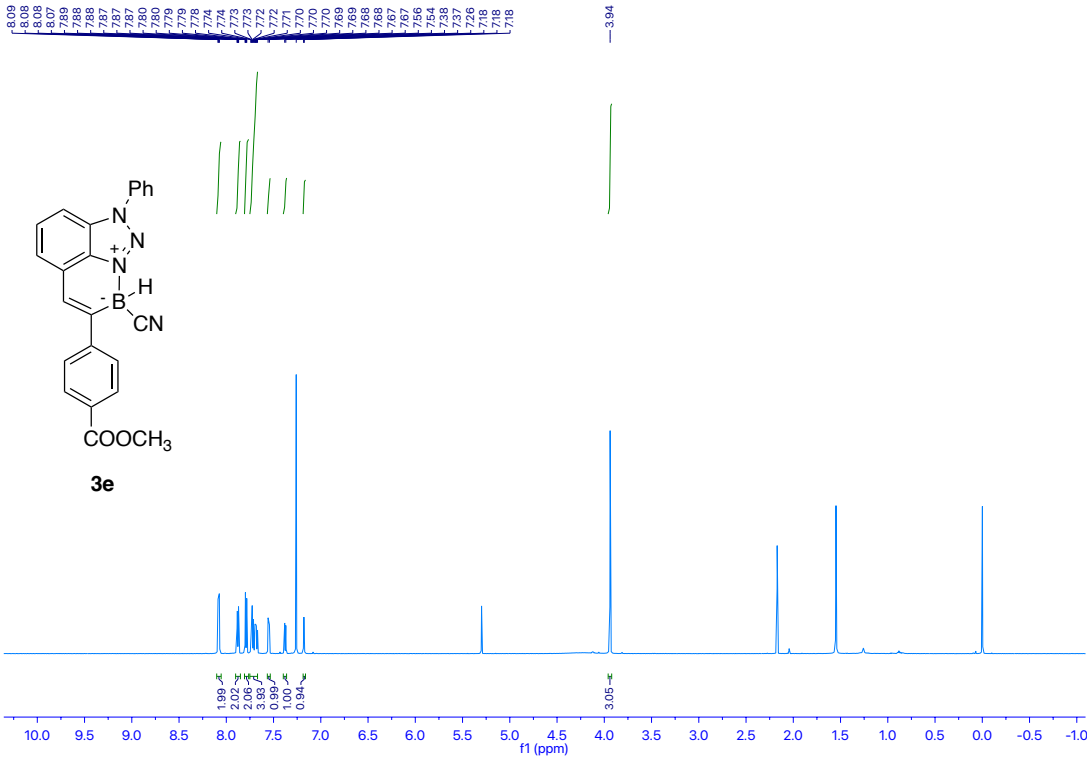
Compound 3d, ^{19}F-NMR (151 MHz, $CDCl_3$)



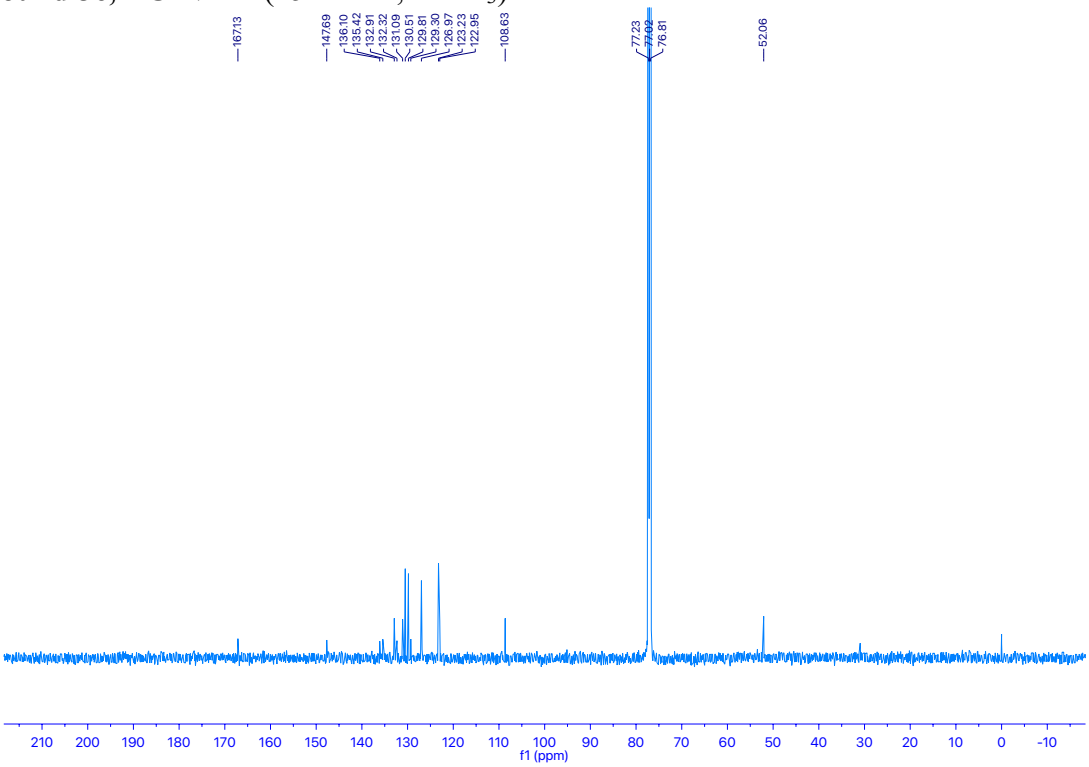
Compound 3d, ^{11}B NMR (128 MHz, $CDCl_3$)



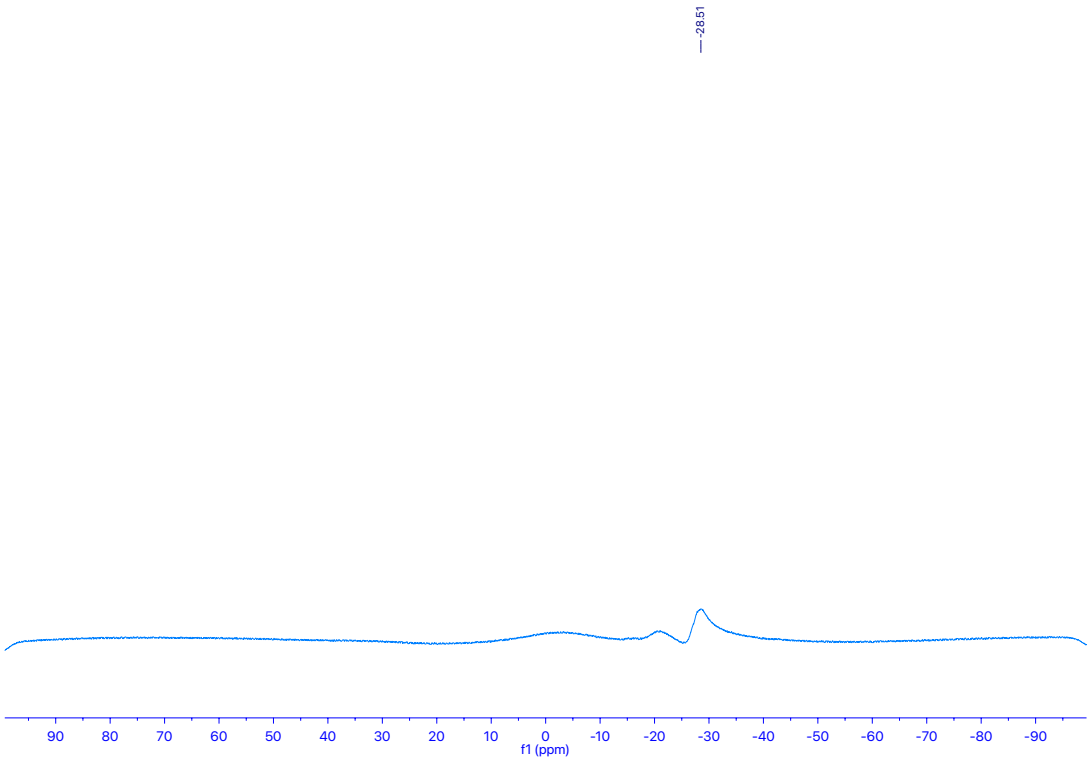
Compound 3e, ^{1}H NMR (600 MHz, $CDCl_3$)



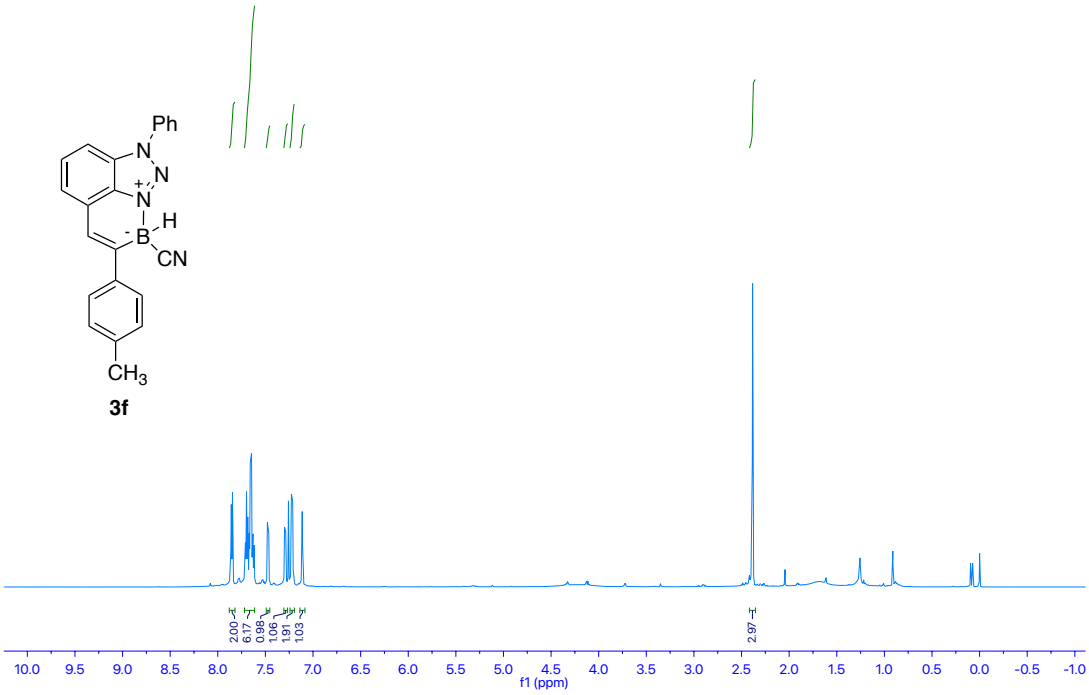
Compound 3e, ^{13}C-NMR (151 MHz, $CDCl_3$)



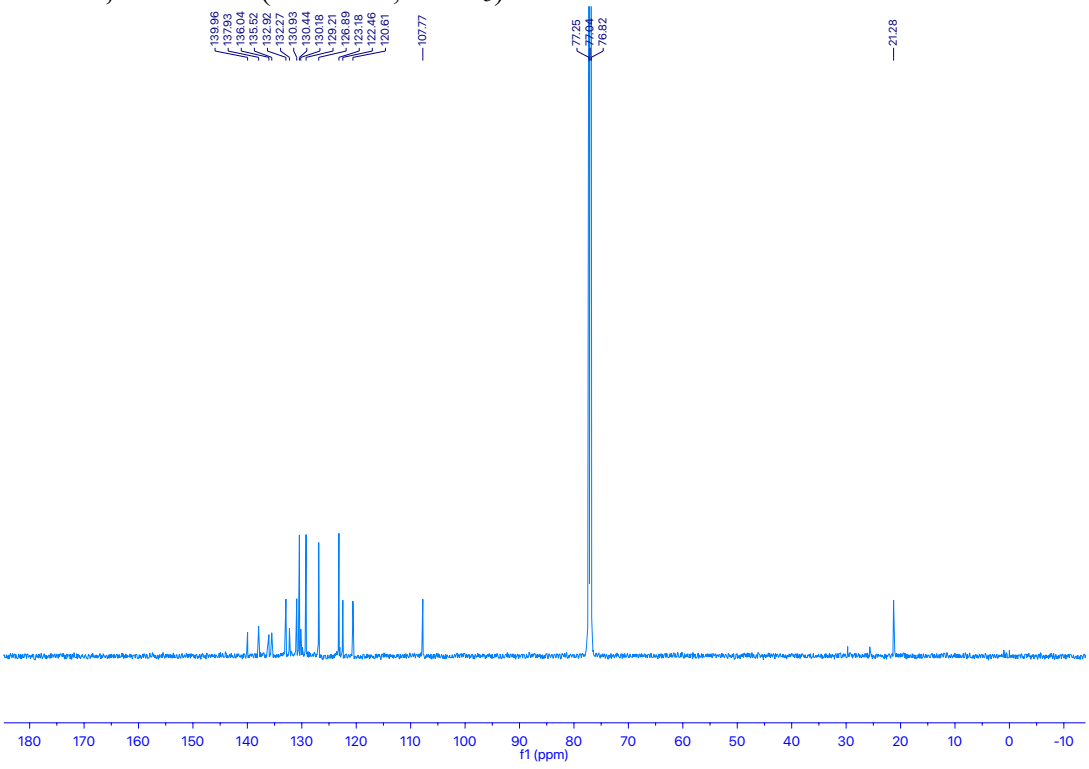
Compound 3e, ^{11}B NMR (128 MHz, $CDCl_3$)



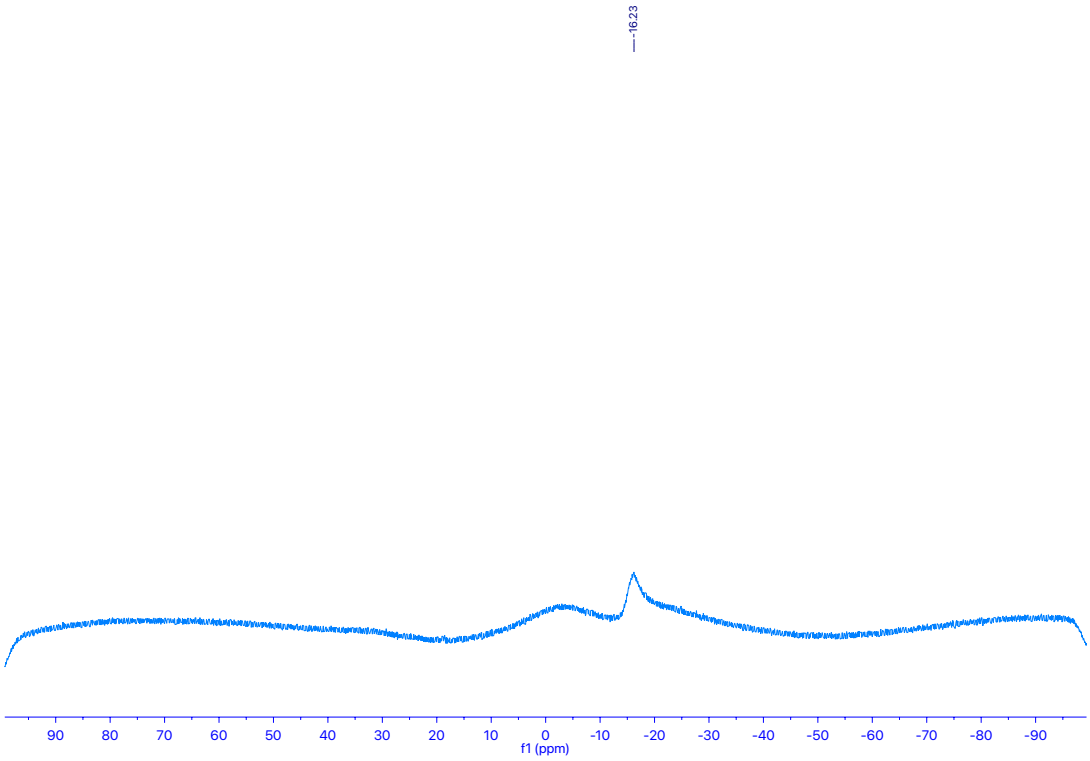
Compound 3f, ^{1}H NMR (600 MHz, $CDCl_3$).



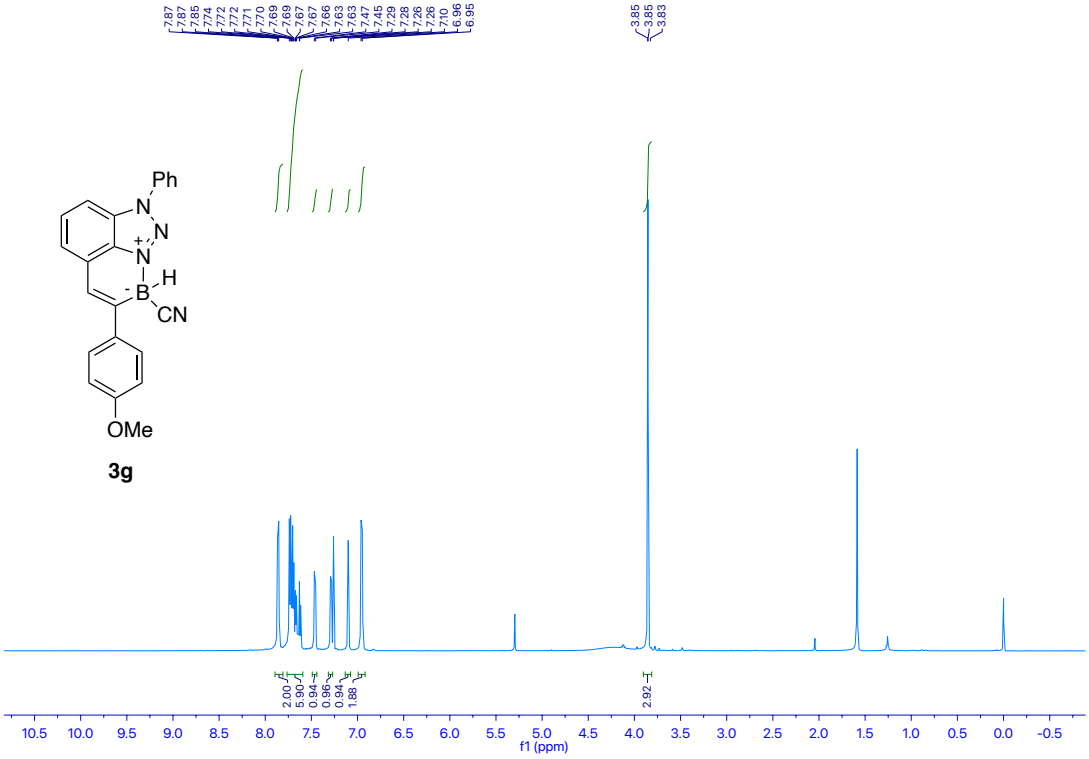
Compound 3f, ^{13}C-NMR (151 MHz, $CDCl_3$)



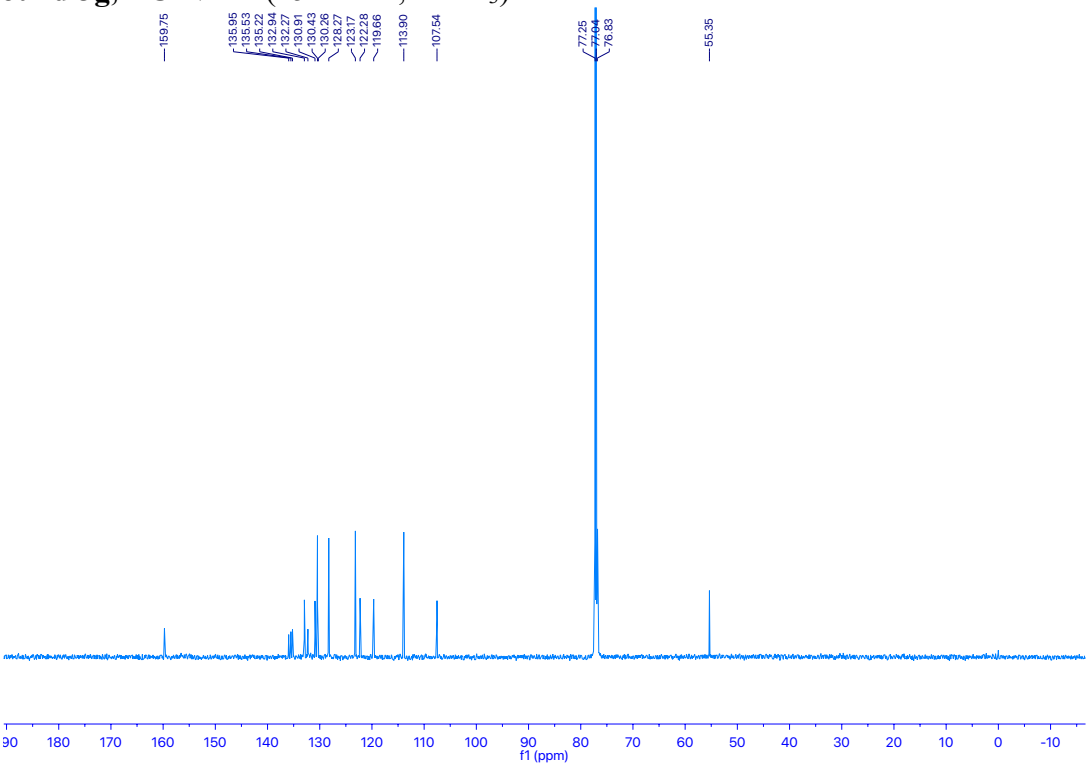
Compound 3f, ^{11}B NMR (128 MHz, $CDCl_3$)



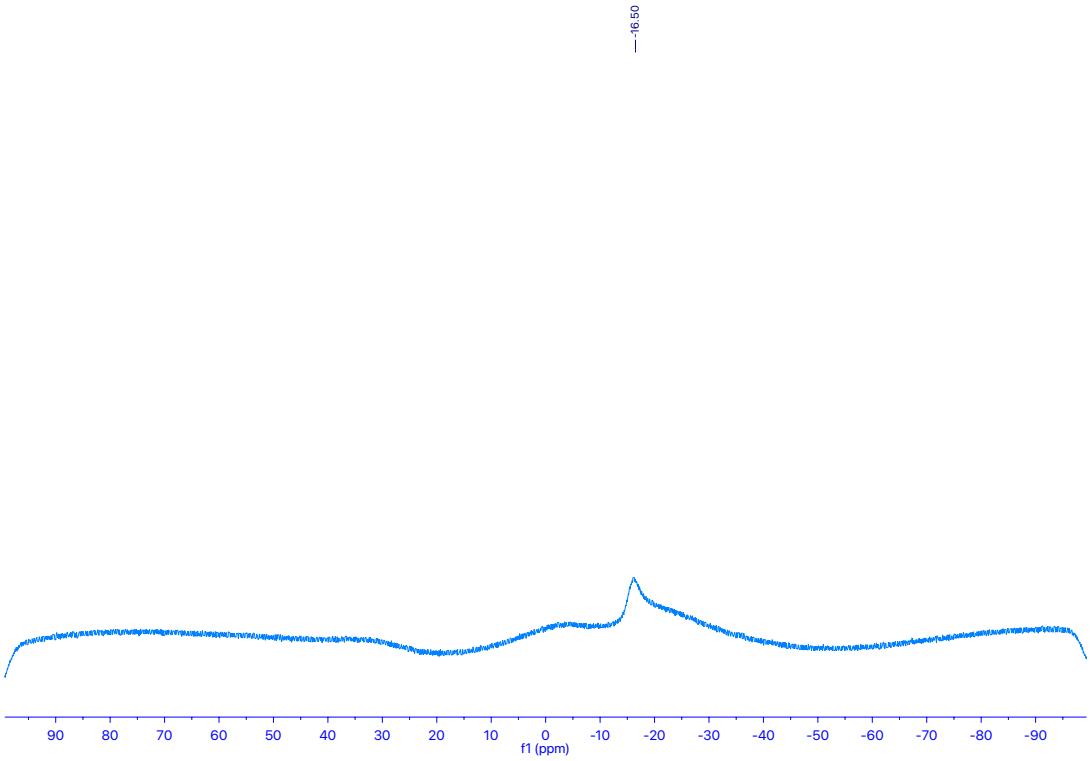
Compound 3g, ^{1}H NMR (600 MHz, $CDCl_3$**).**



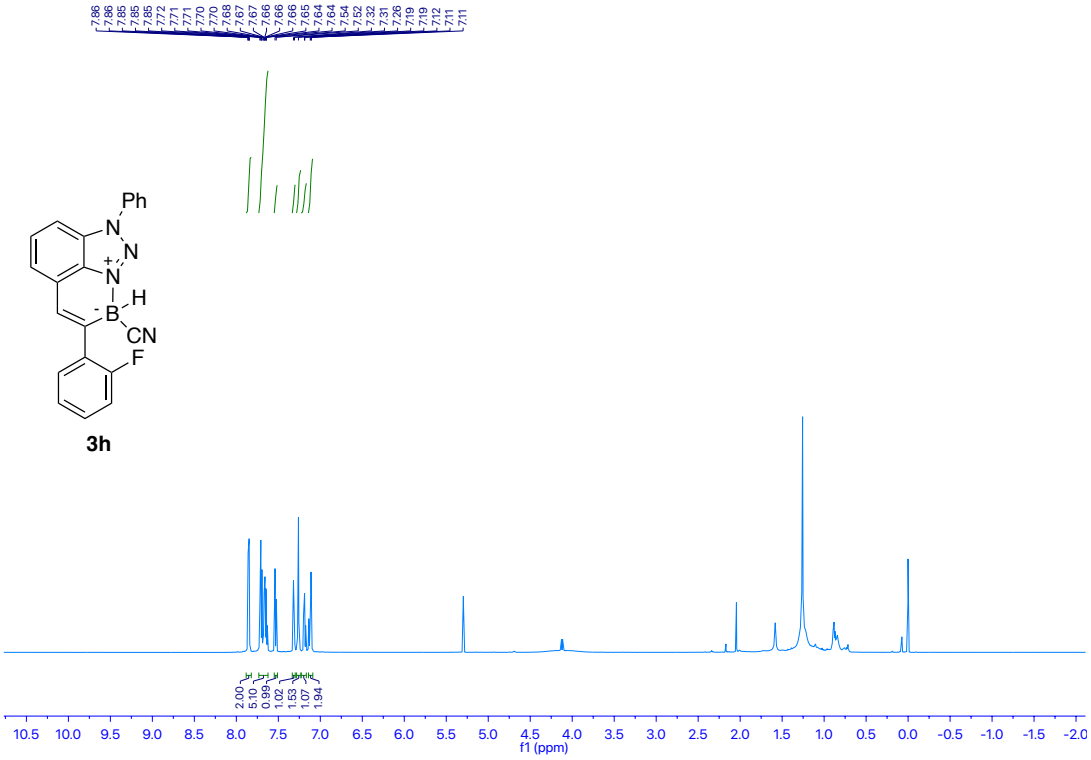
Compound 3g, ^{13}C-NMR (151 MHz, $CDCl_3$)



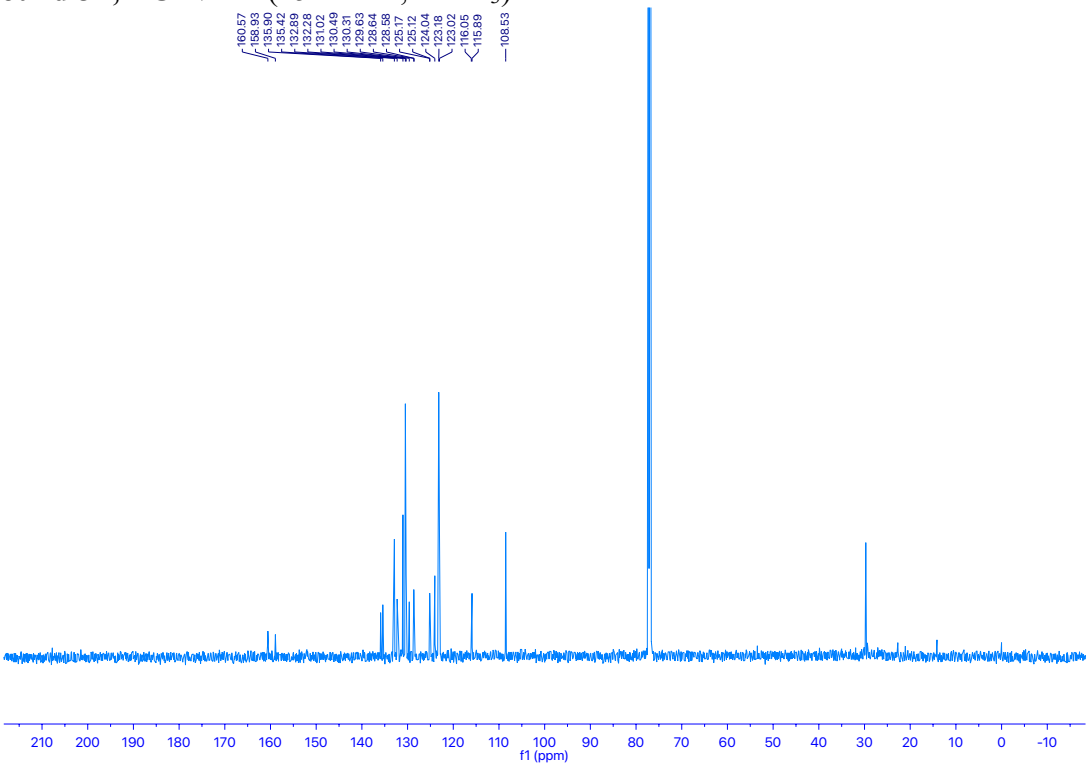
Compound 3g, ^{11}B NMR (128 MHz, $CDCl_3$)



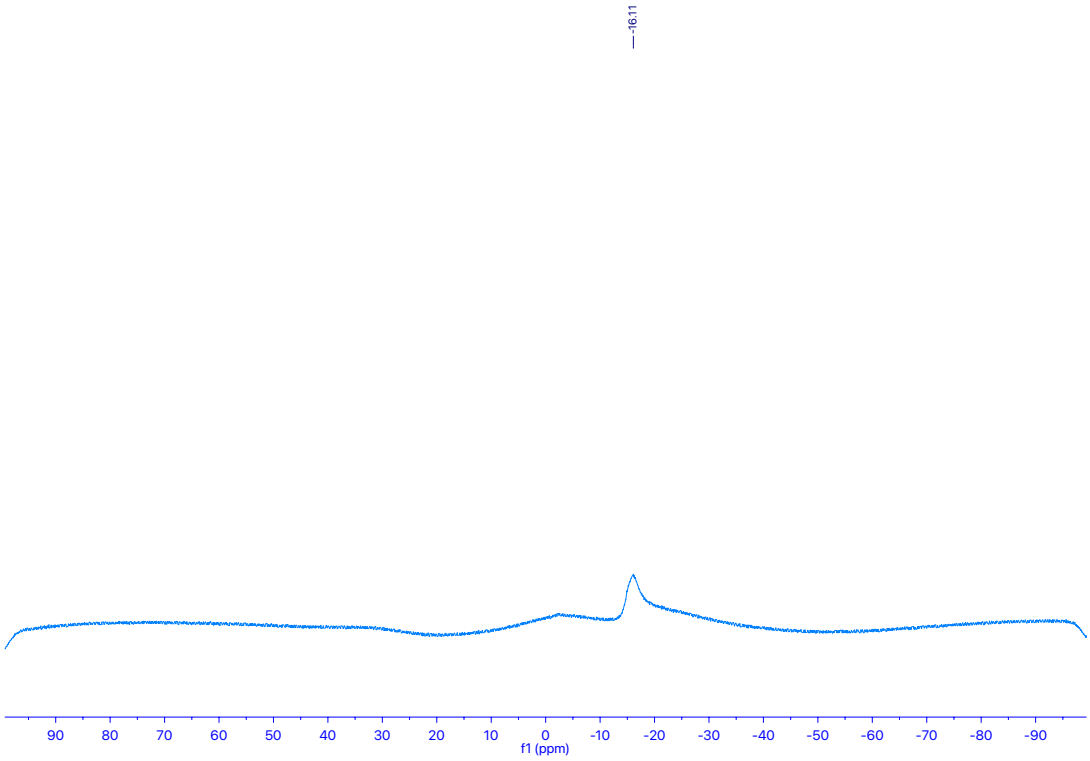
Compound 3h, ^{1}H NMR (600 MHz, $CDCl_3$).



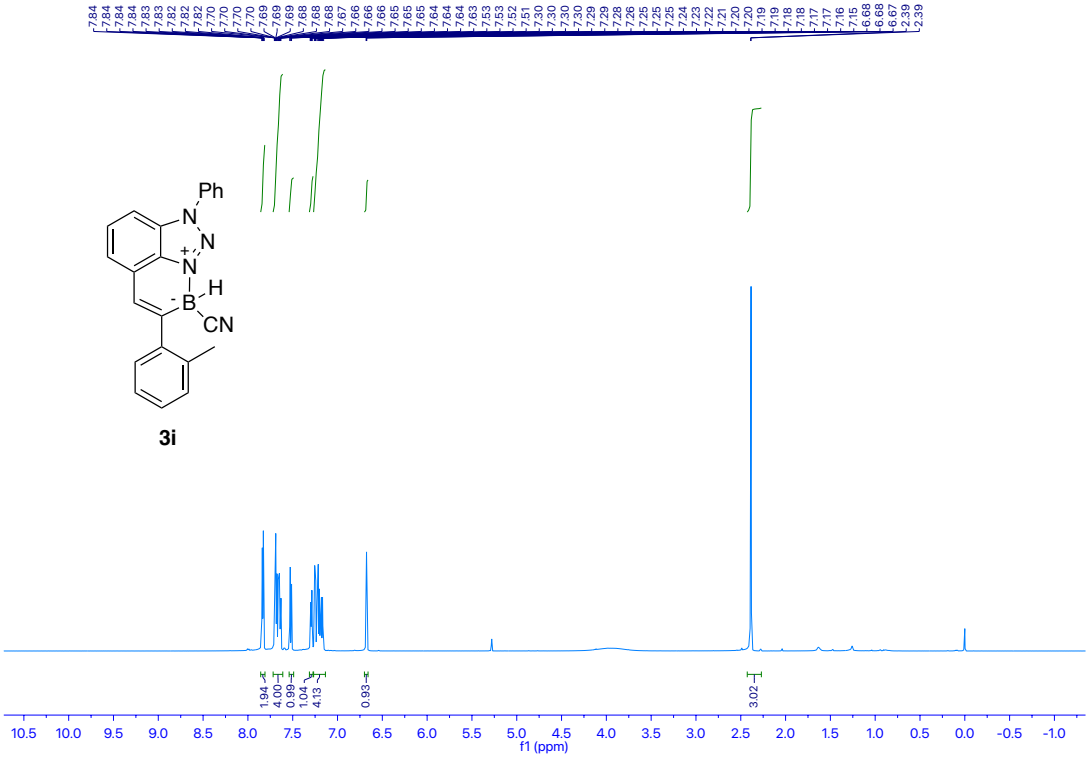
Compound 3h, ^{13}C-NMR (151 MHz, $CDCl_3$)



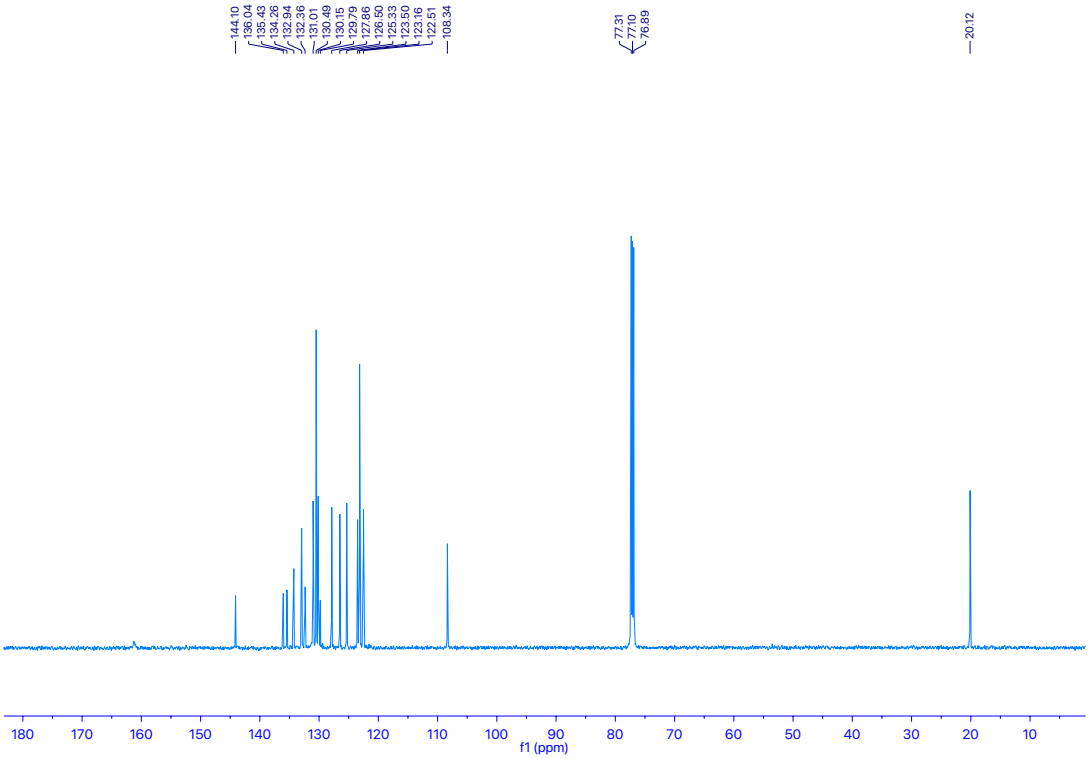
Compound 3h, ^{11}B NMR (128 MHz, $CDCl_3$)



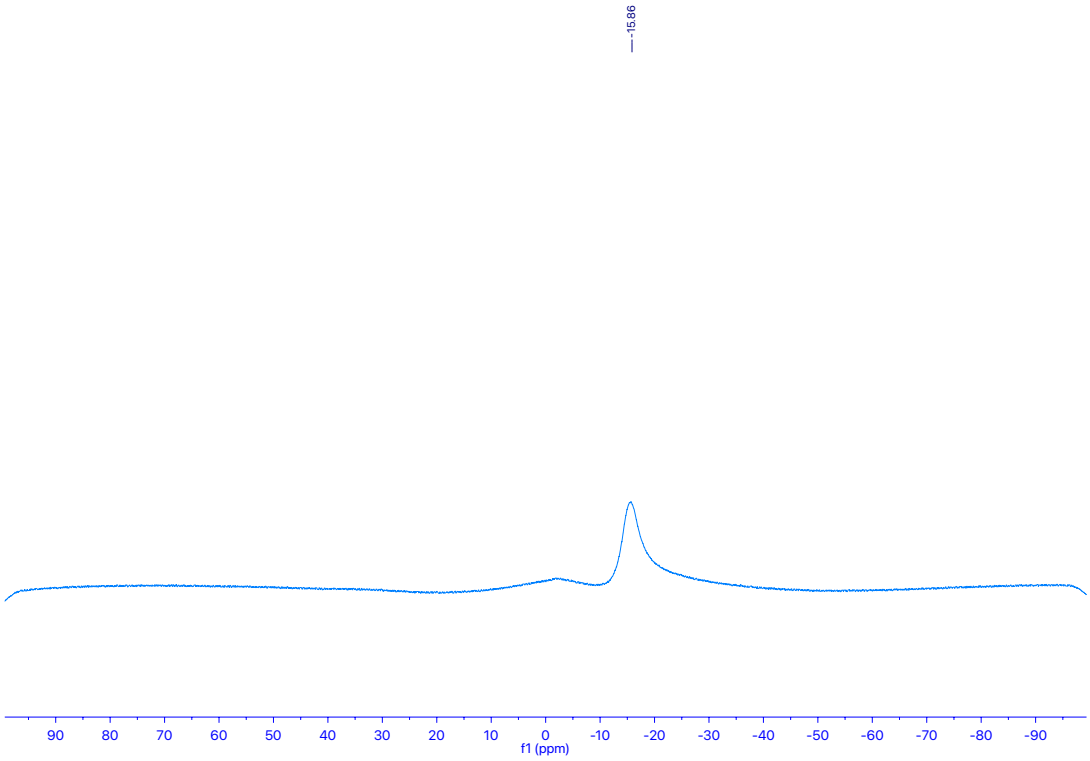
Compound 3i, ^{1}H NMR (600 MHz, $CDCl_3$)



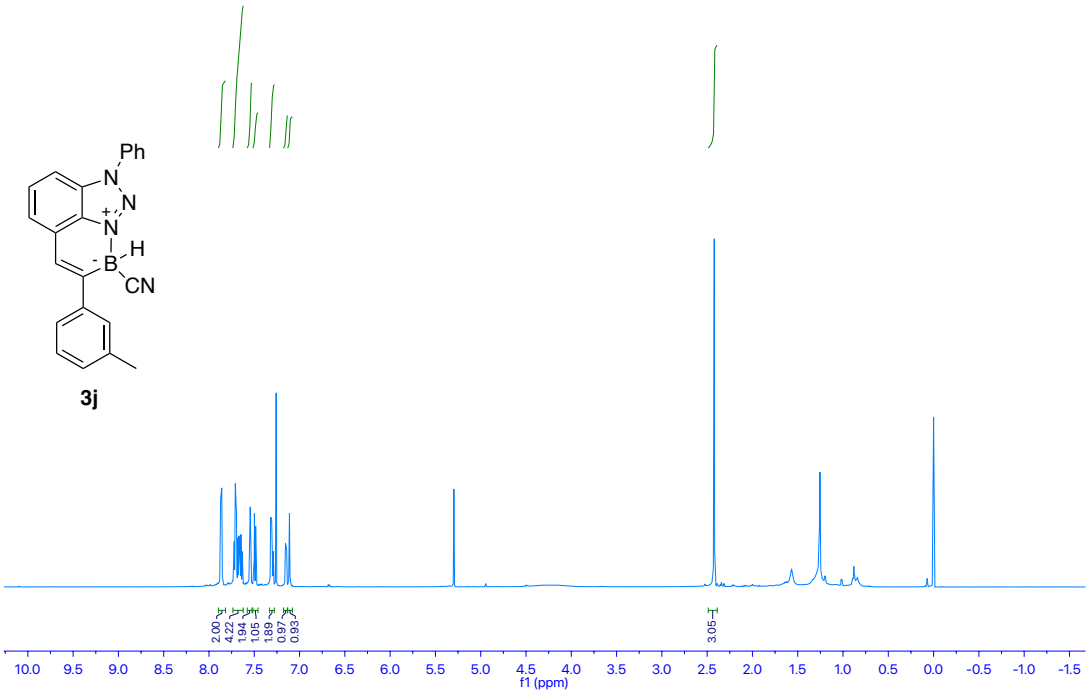
Compound 3i, ^{13}C-NMR (101 MHz, $CDCl_3$)



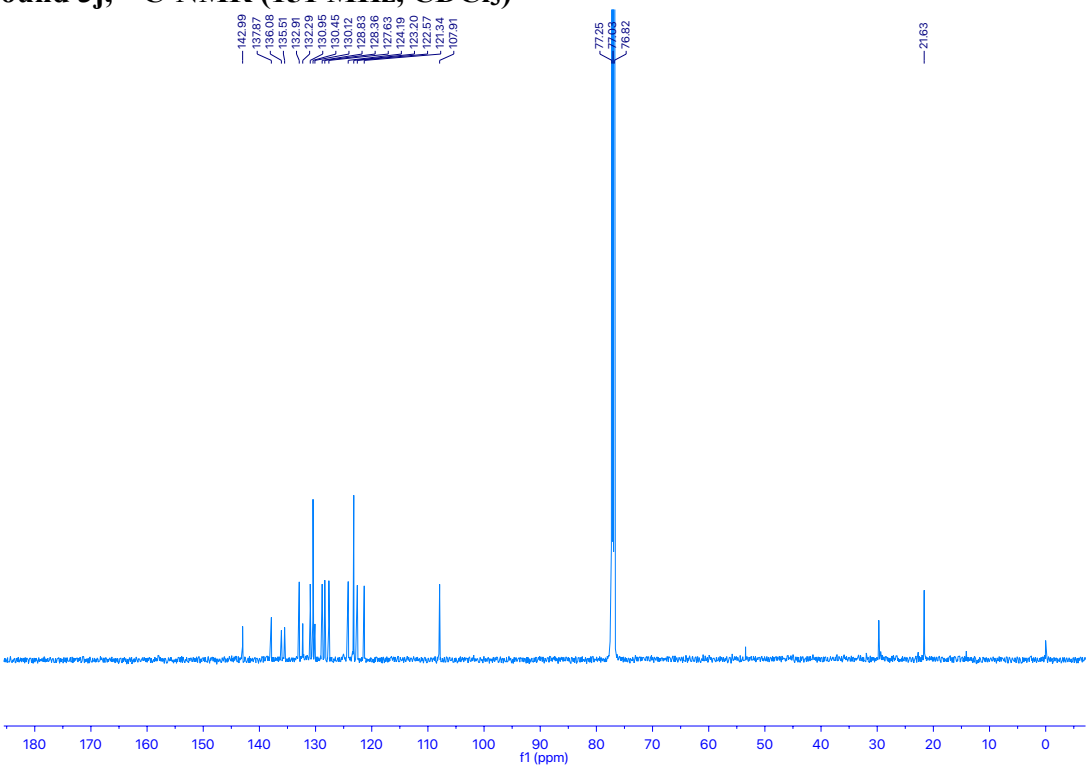
Compound 3i, ^{11}B NMR (128 MHz, $CDCl_3$)



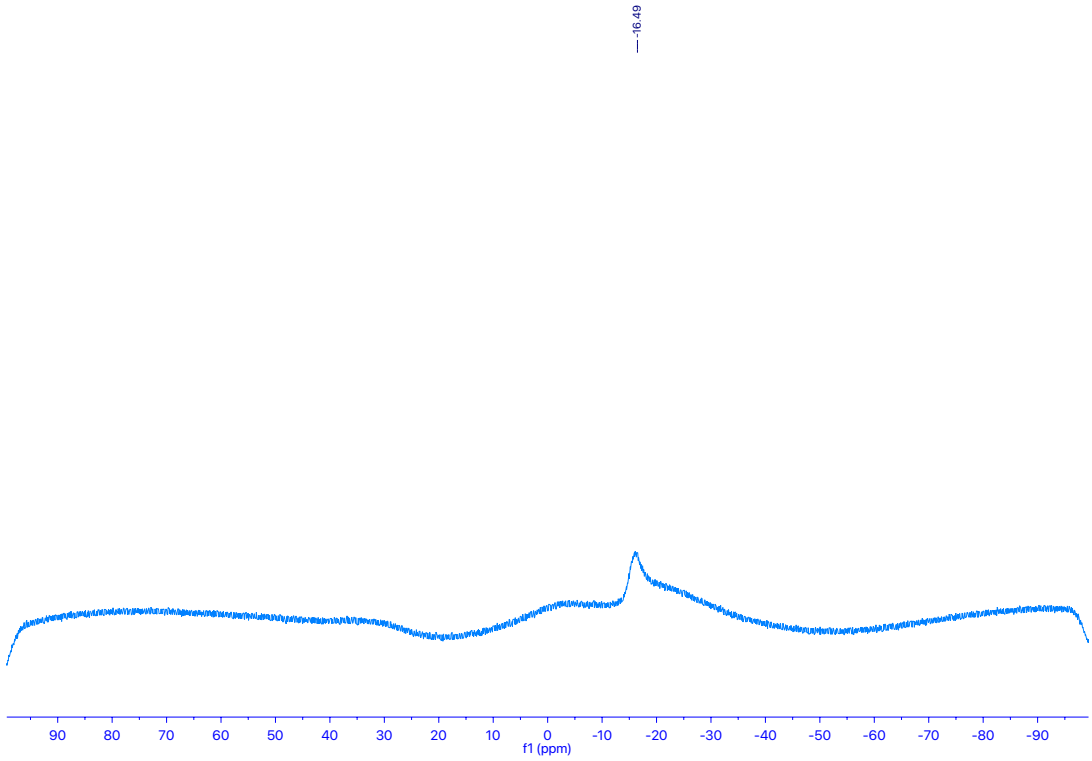
Compound 3j, ^{1}H NMR (600 MHz, $CDCl_3$)



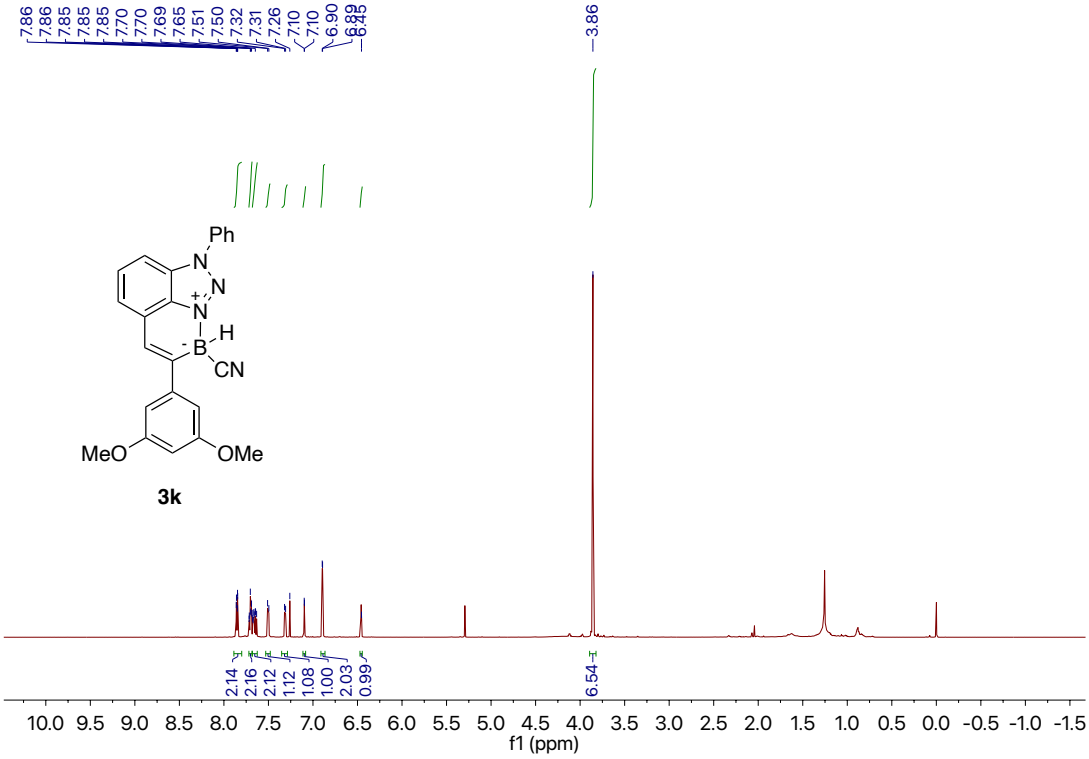
Compound 3j, ^{13}C-NMR (151 MHz, $CDCl_3$)



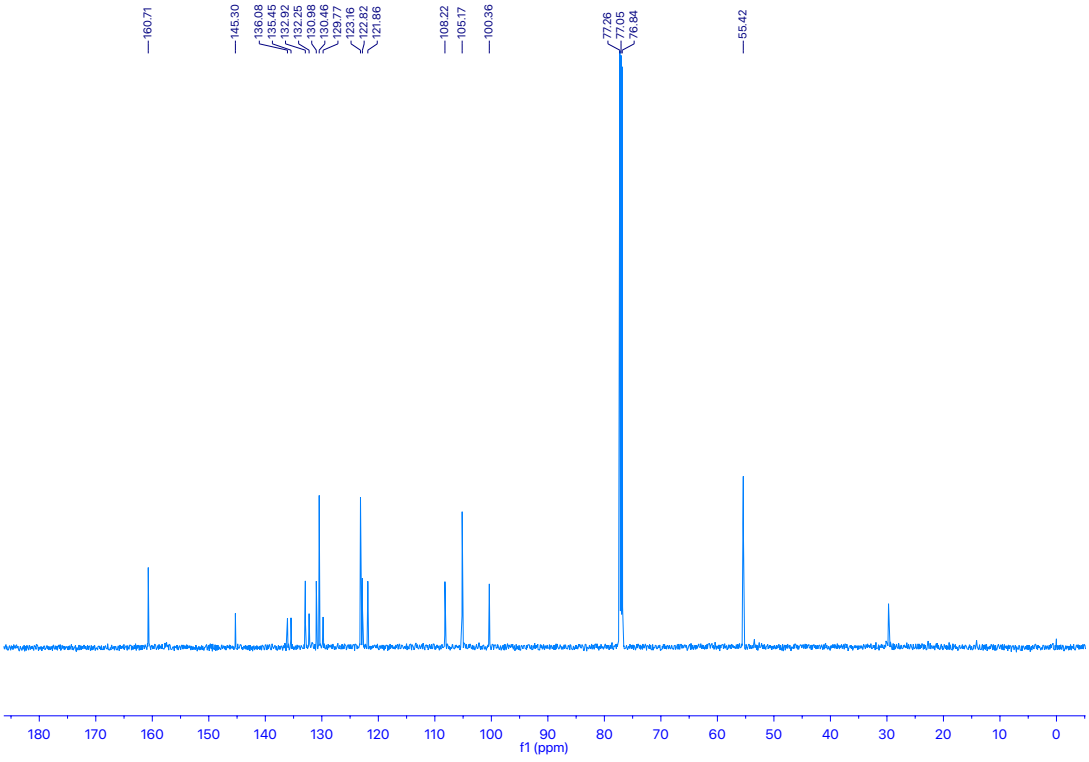
Compound 3j, ^{11}B NMR (128 MHz, $CDCl_3$)



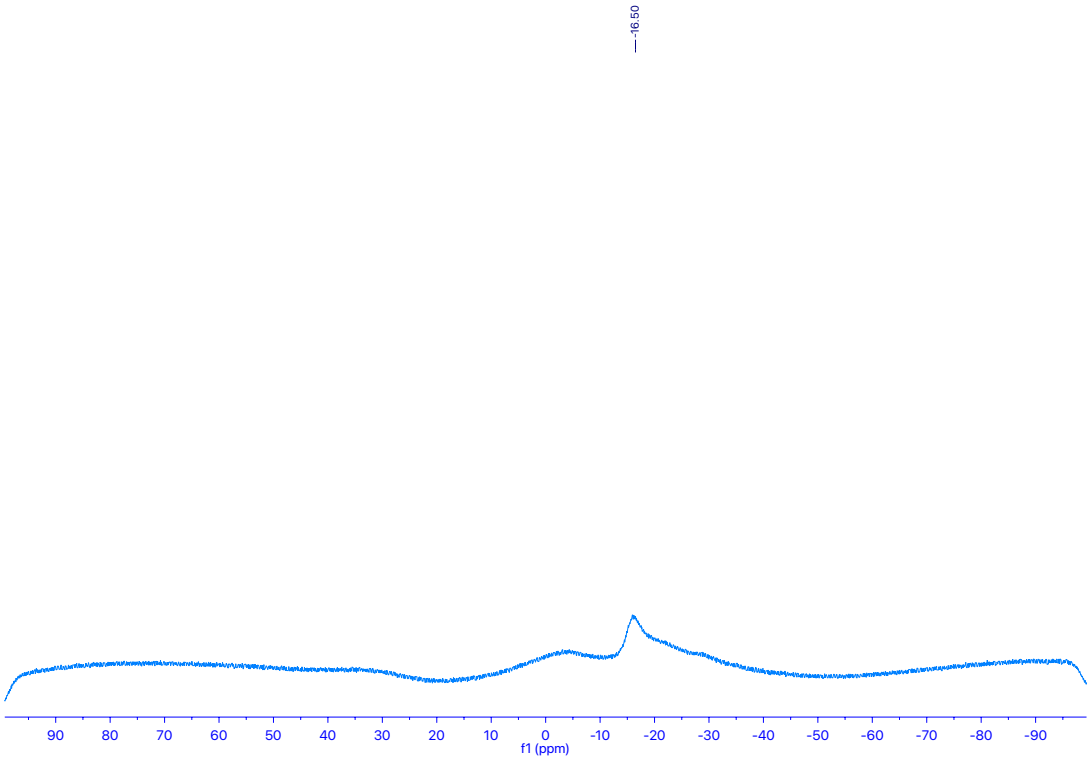
Compound 3k, ^{1}H NMR (600 MHz, $CDCl_3$)



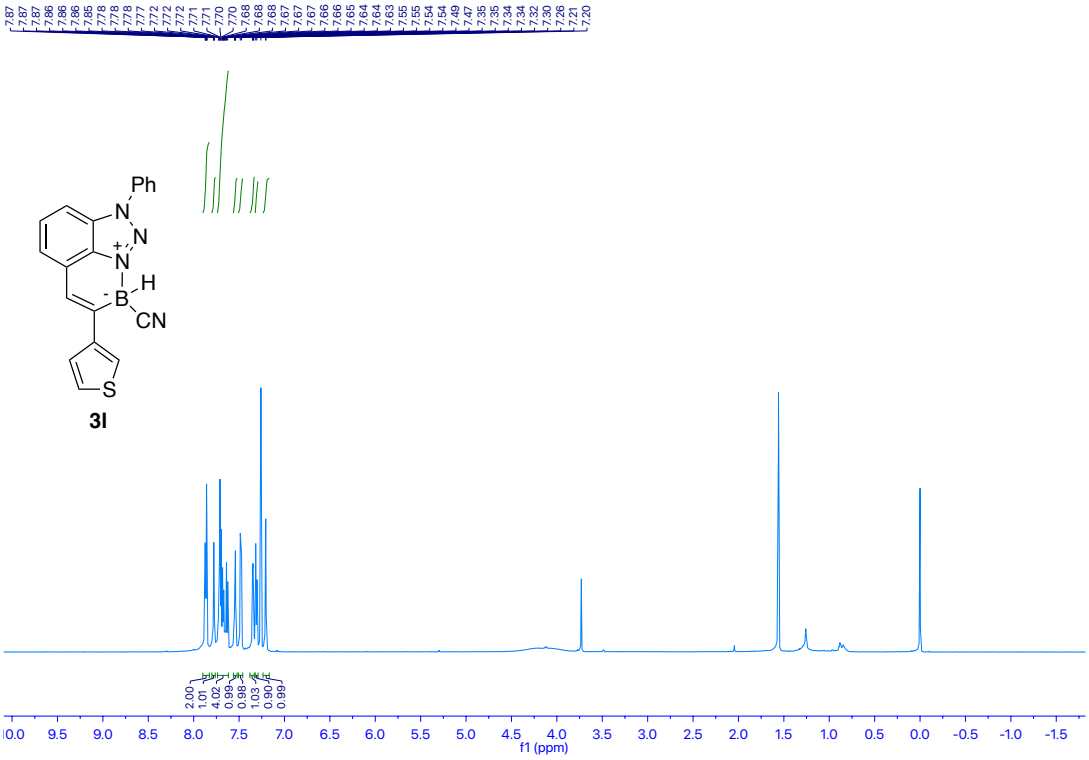
Compound 3k, ^{13}C-NMR (101 MHz, $CDCl_3$)



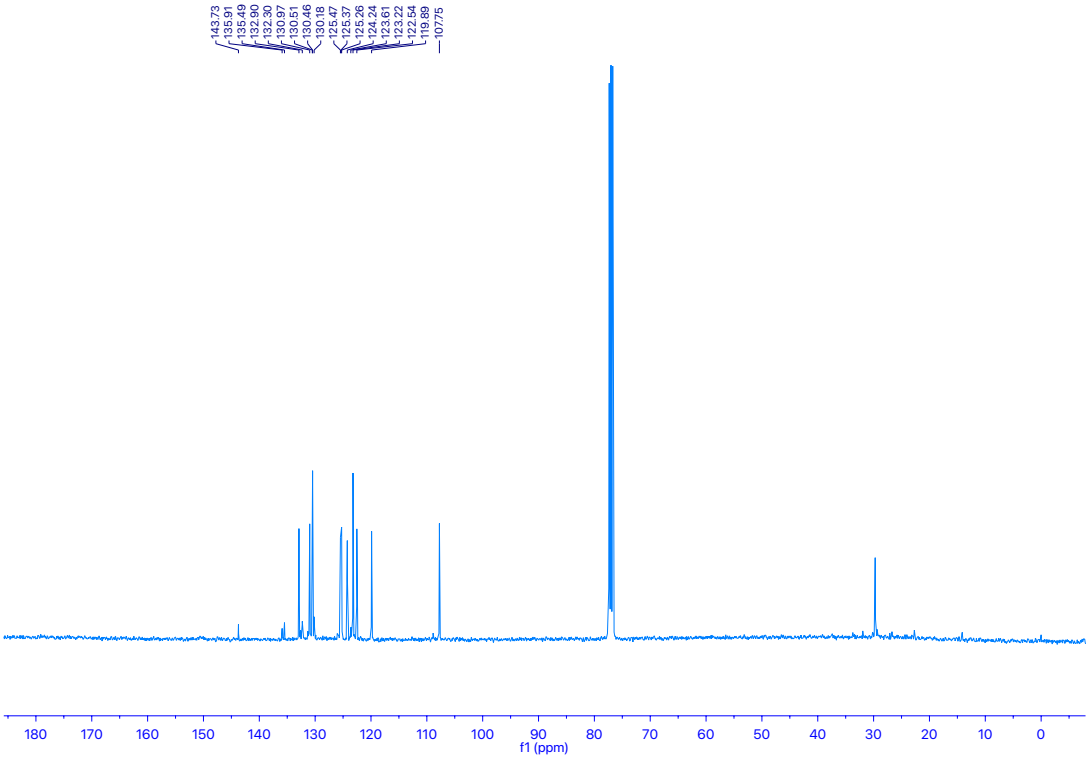
Compound 3k, ^{11}B NMR (128 MHz, $CDCl_3$)



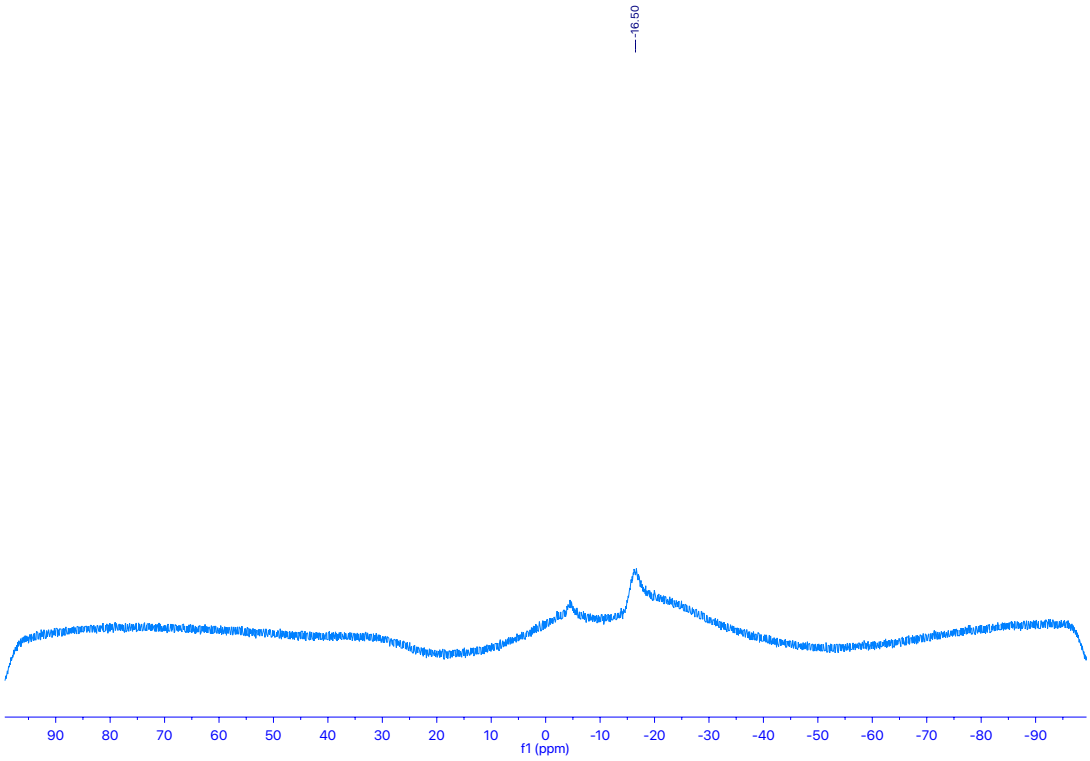
Compound 3l, ^{1}H NMR (600 MHz, $CDCl_3$)



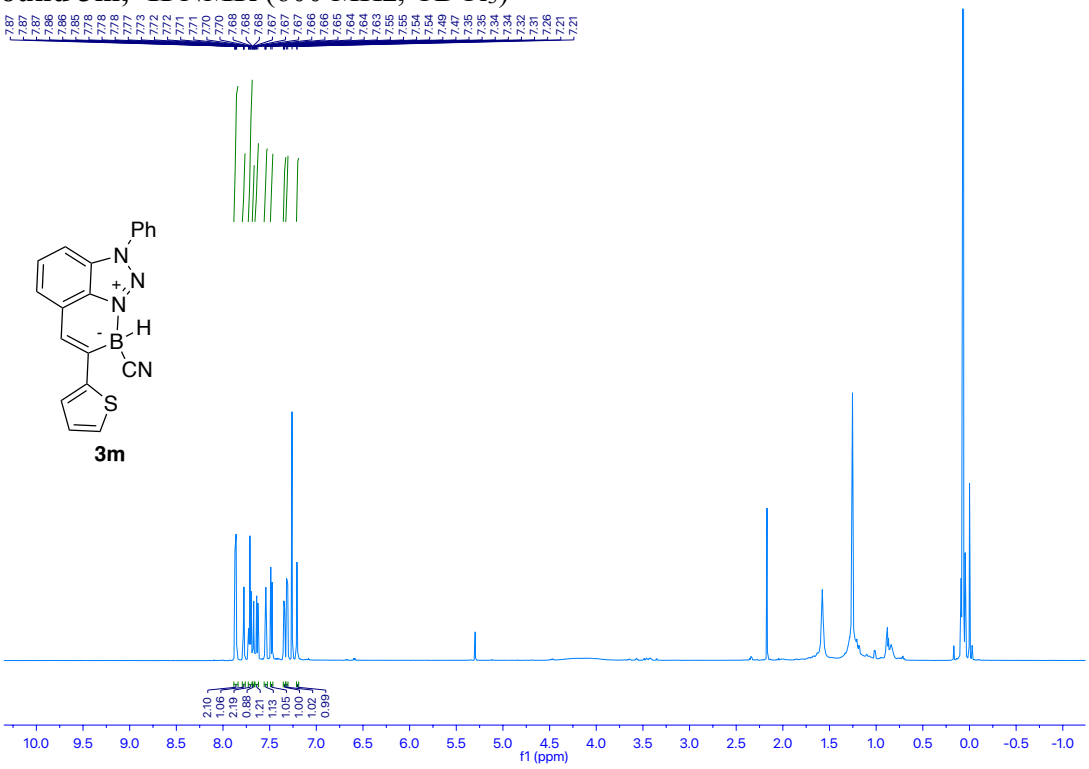
Compound 3l, ^{13}C-NMR (151 MHz, $CDCl_3$)



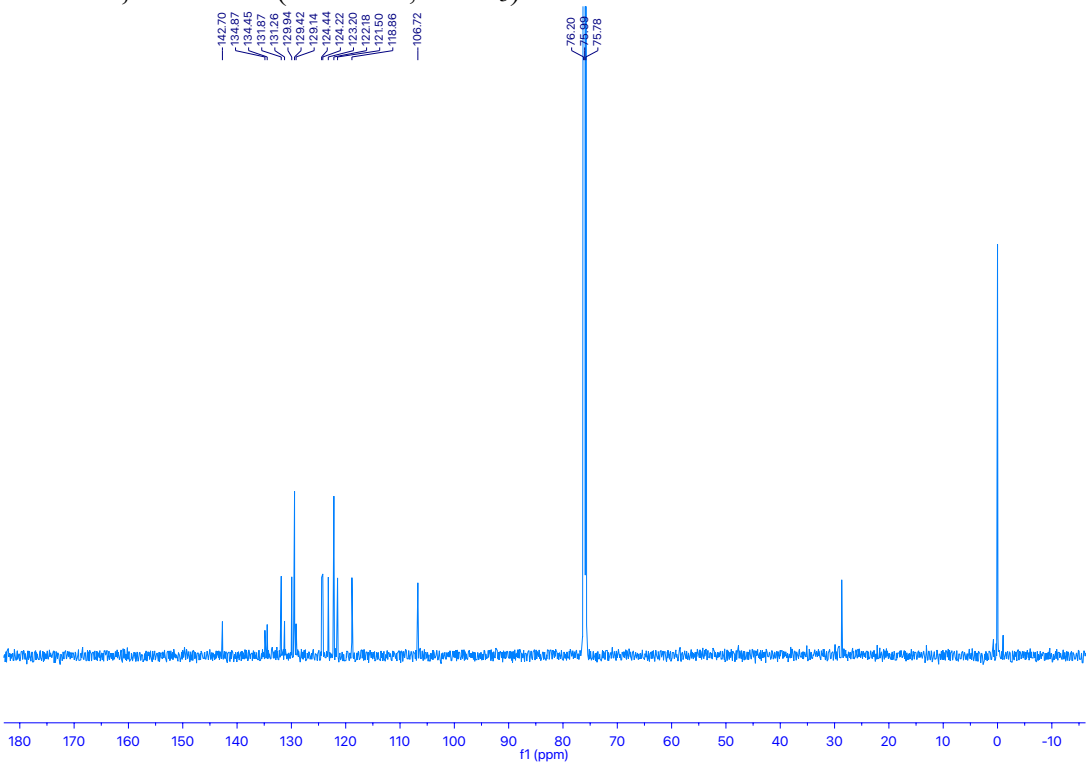
Compound 3l, ^{11}B NMR (128 MHz, $CDCl_3$)



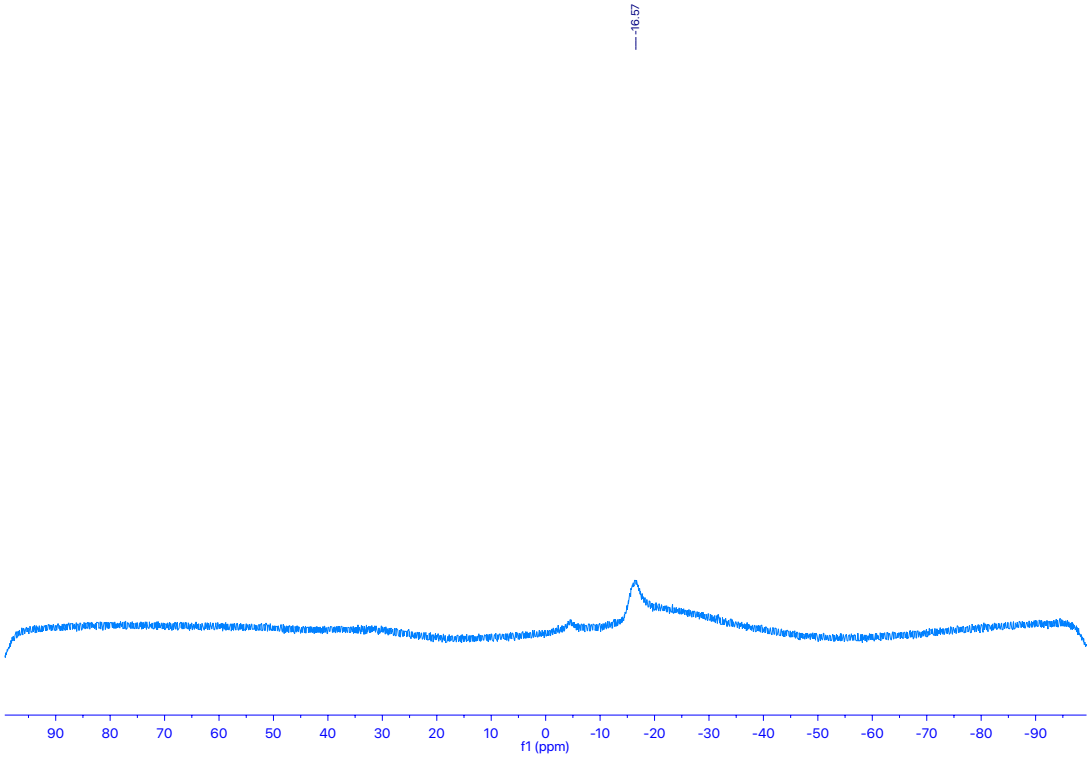
Compound 3m, ^{1}H NMR (600 MHz, $CDCl_3$)



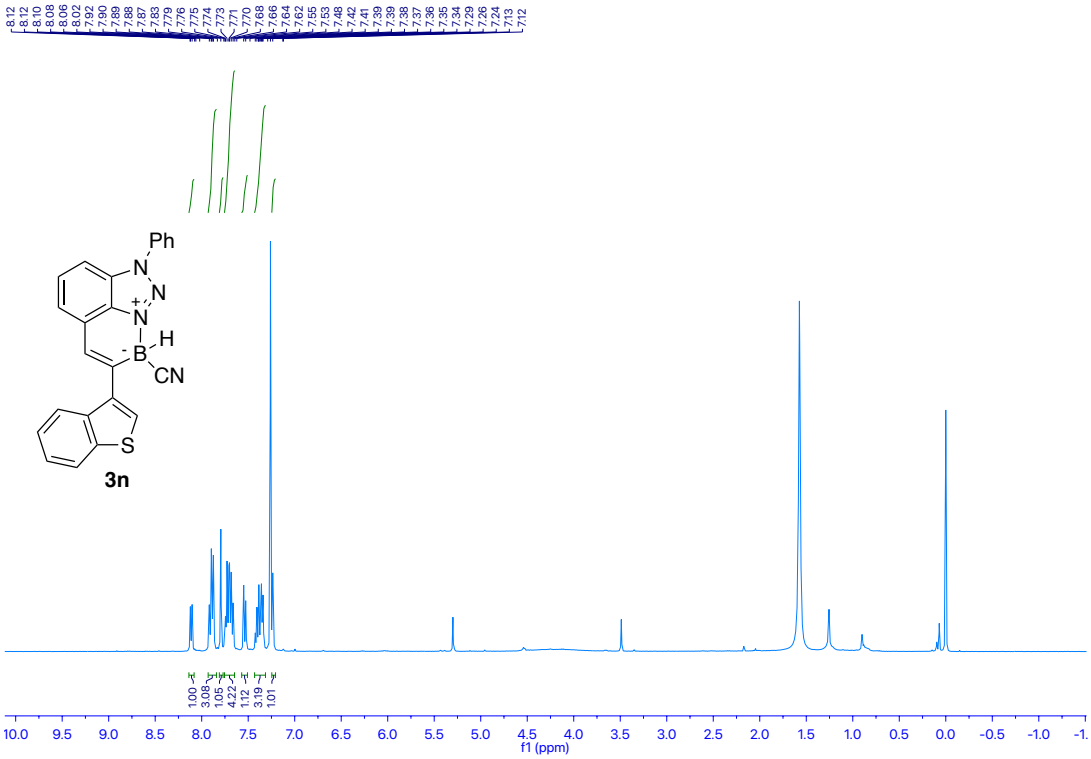
Compound 3m, ^{13}C-NMR (151 MHz, $CDCl_3$)



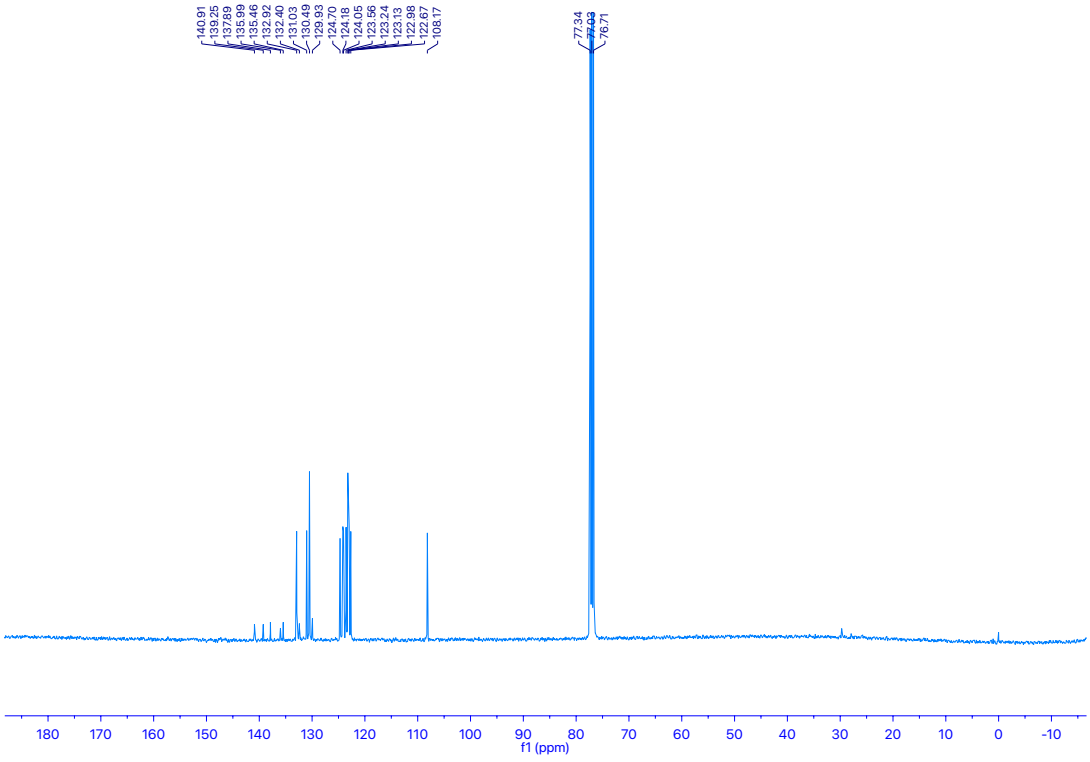
Compound 3m, ^{11}B NMR (128 MHz, $CDCl_3$)



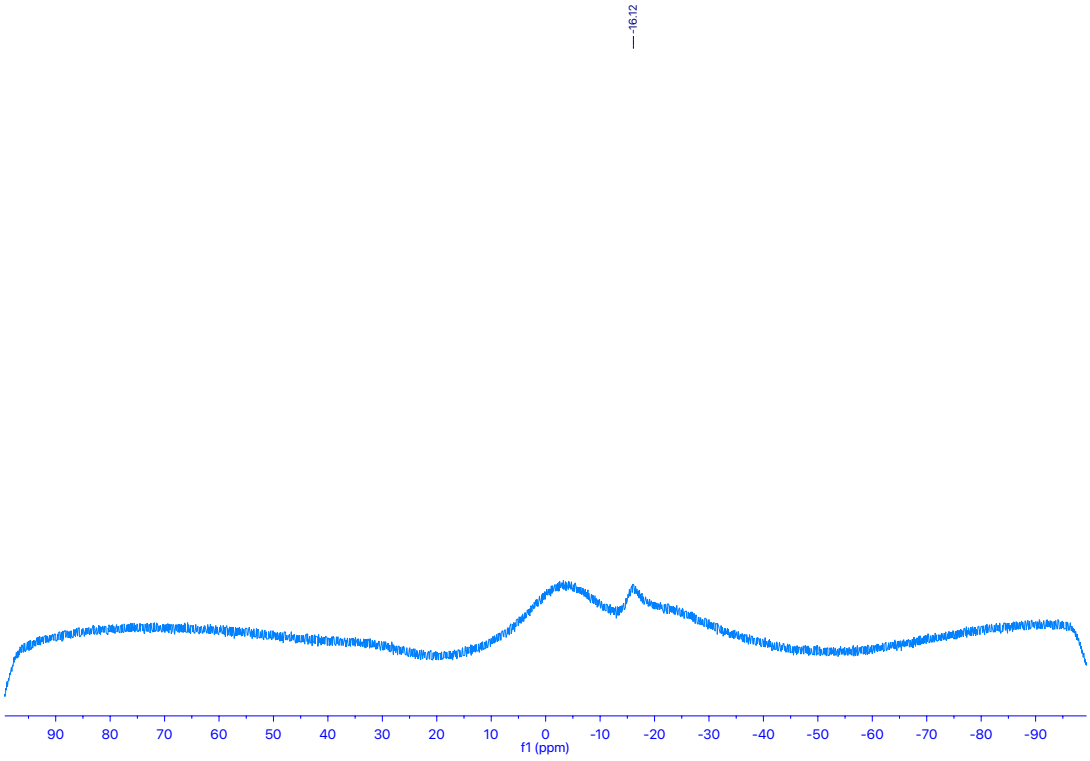
Compound 3n, ^{1}H NMR (400 MHz, $CDCl_3$)



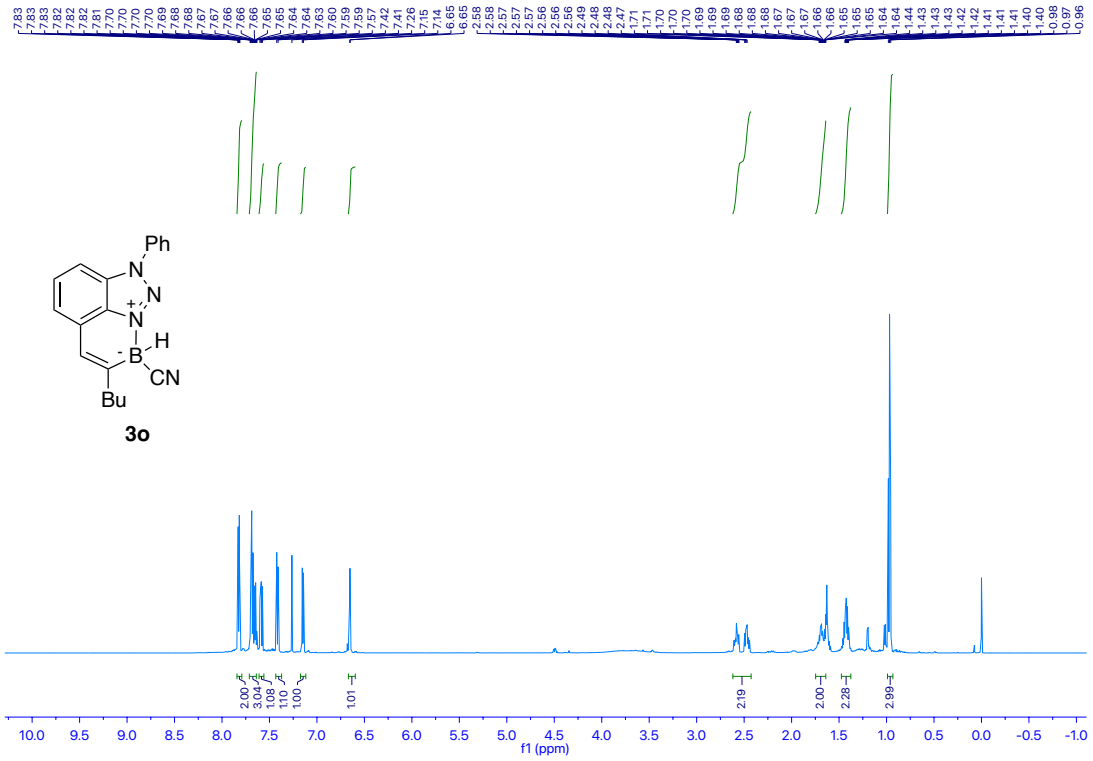
Compound 3n, ^{13}C-NMR (101MHz, $CDCl_3$)



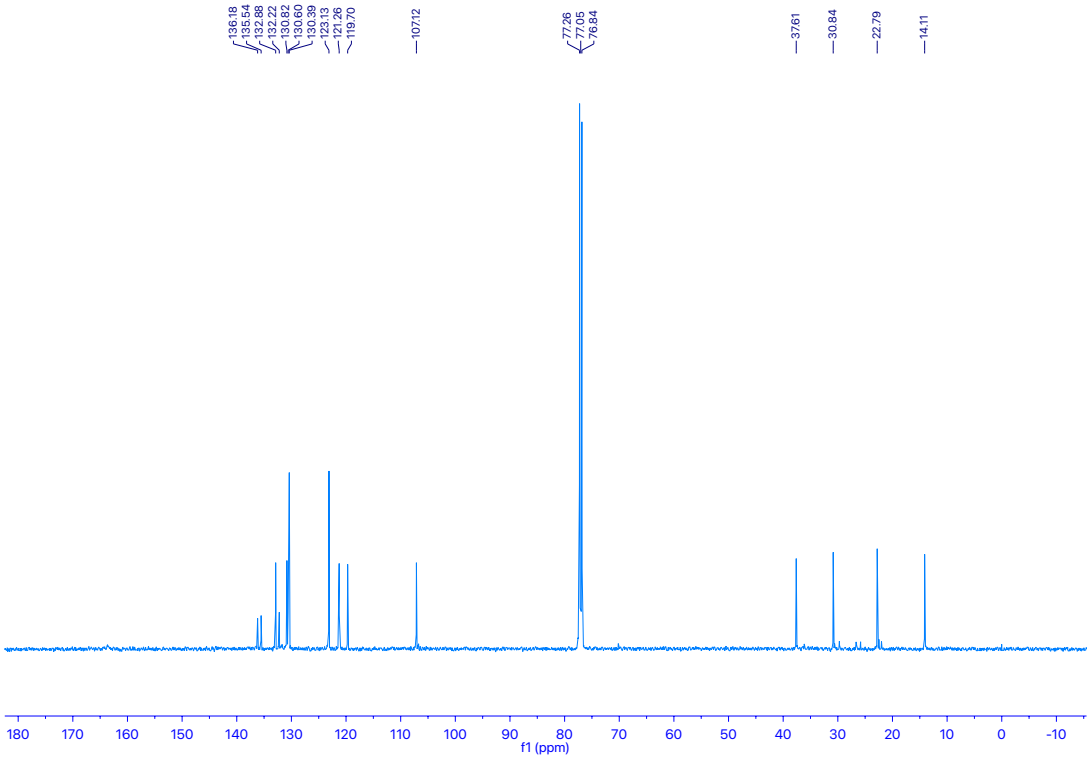
Compound 3n, ^{11}B NMR (128 MHz, $CDCl_3$)



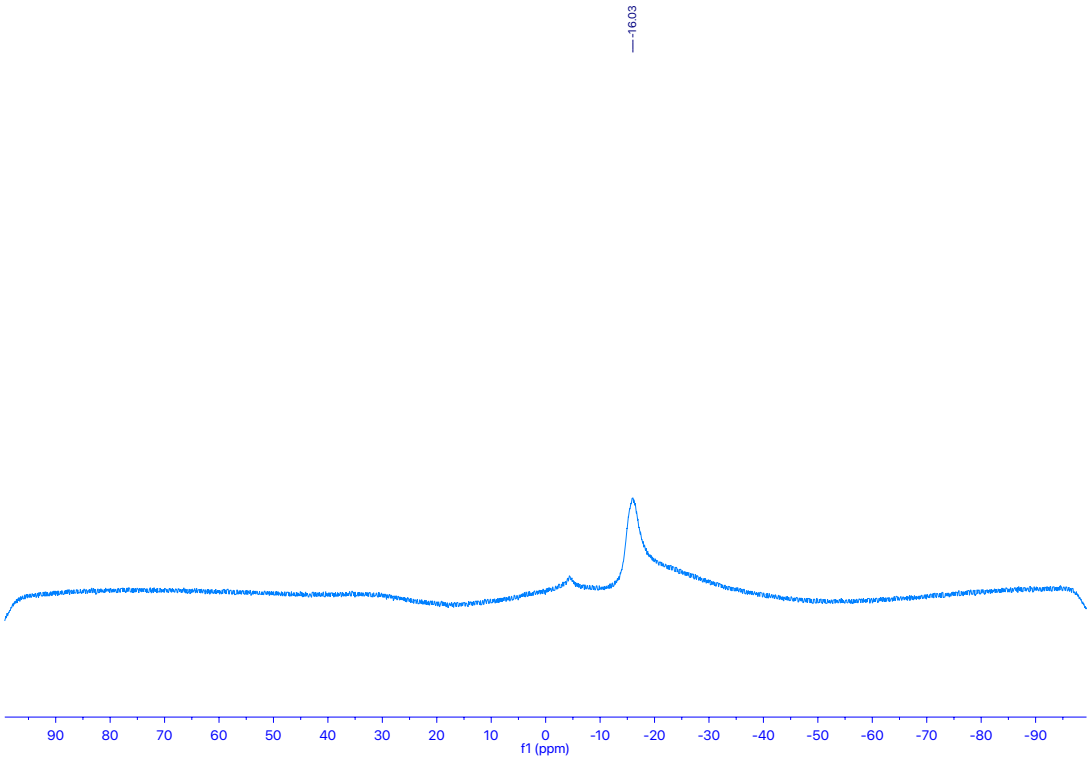
Compound 3o, ^{1}H NMR (600 MHz, $CDCl_3$).



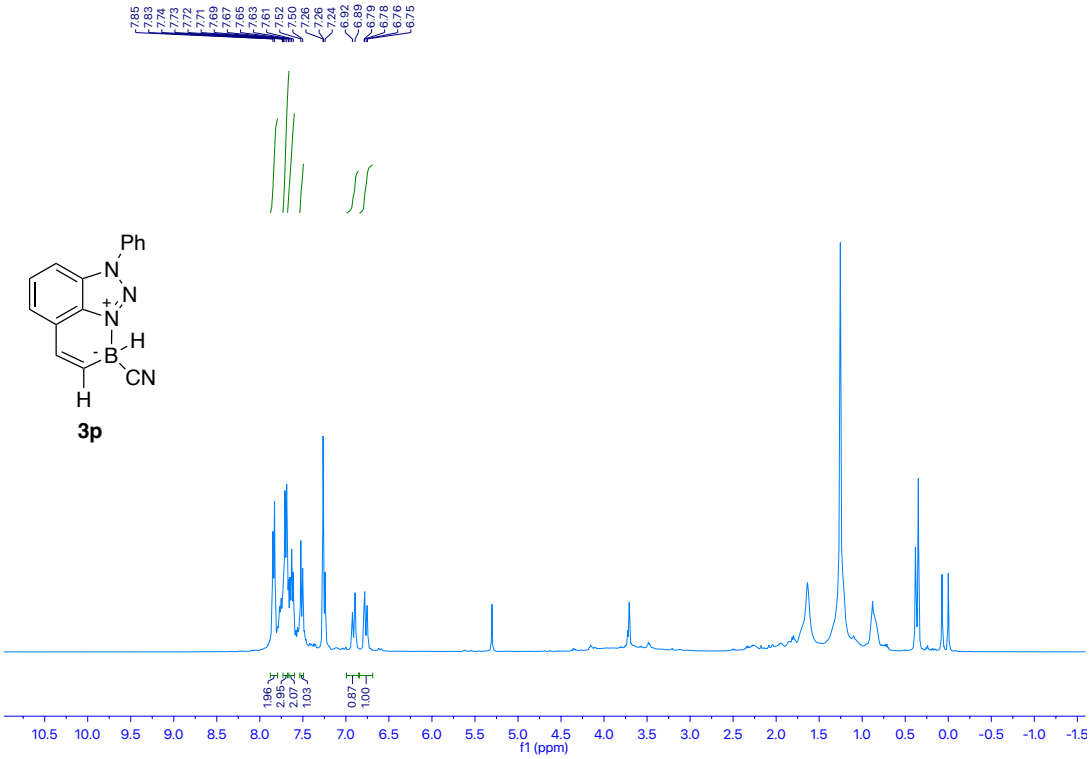
Compound 3o, ^{13}C-NMR (151 MHz, $CDCl_3$)



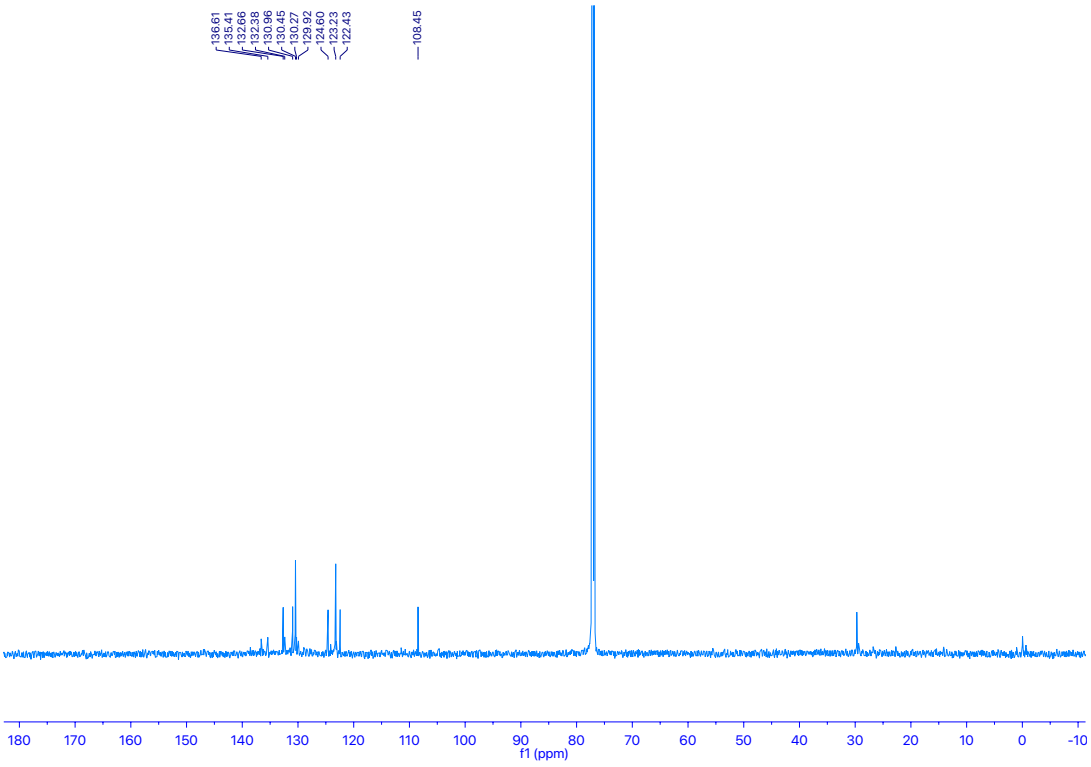
Compound 3o, ^{11}B NMR (128 MHz, $CDCl_3$)



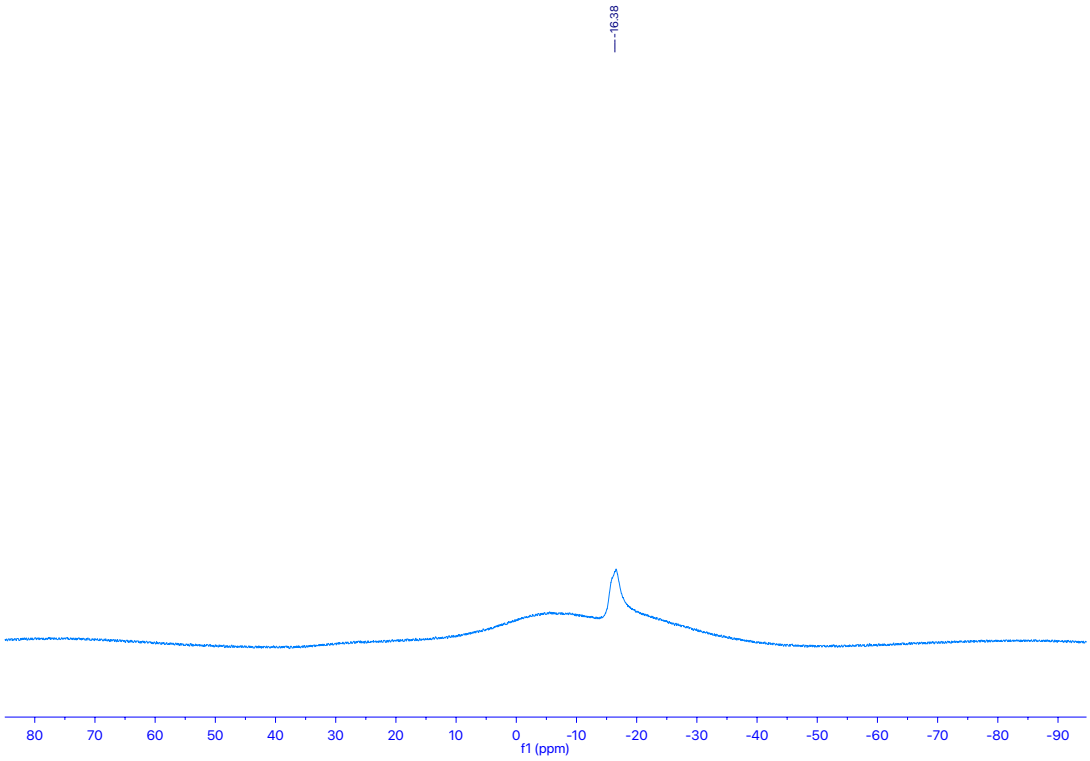
Compound 3p, ^{1}H NMR (400 MHz, $CDCl_3$).



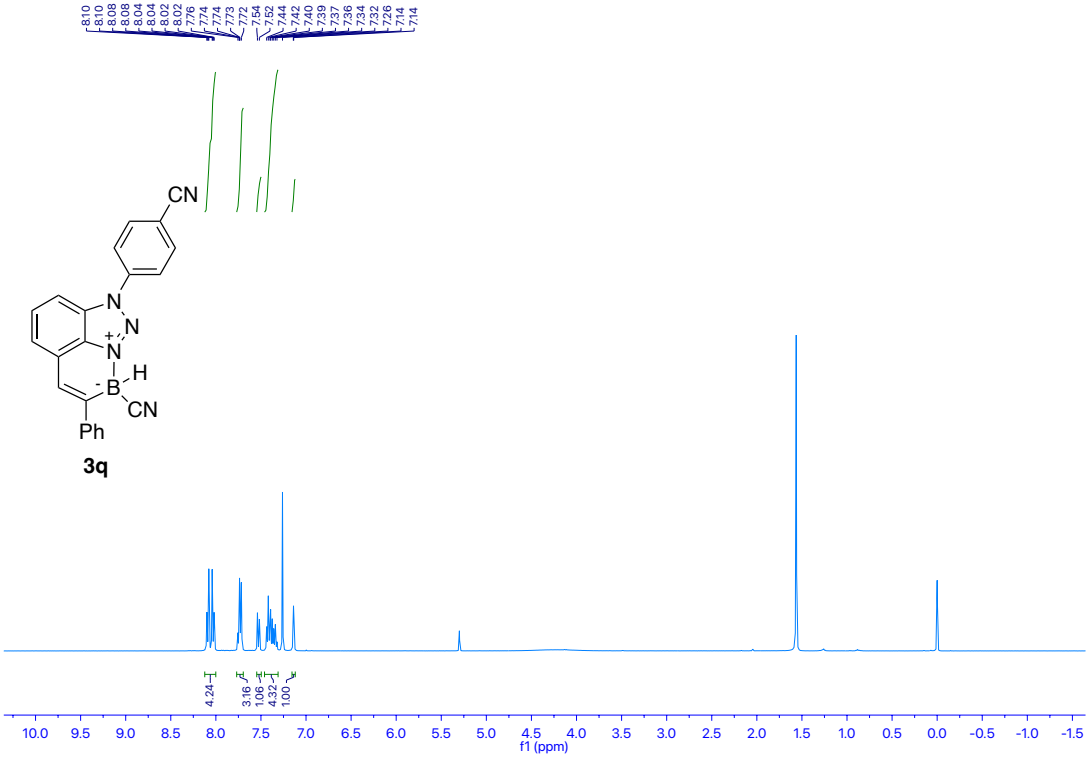
Compound 3p, ^{13}C-NMR (151 MHz, CDCl3)



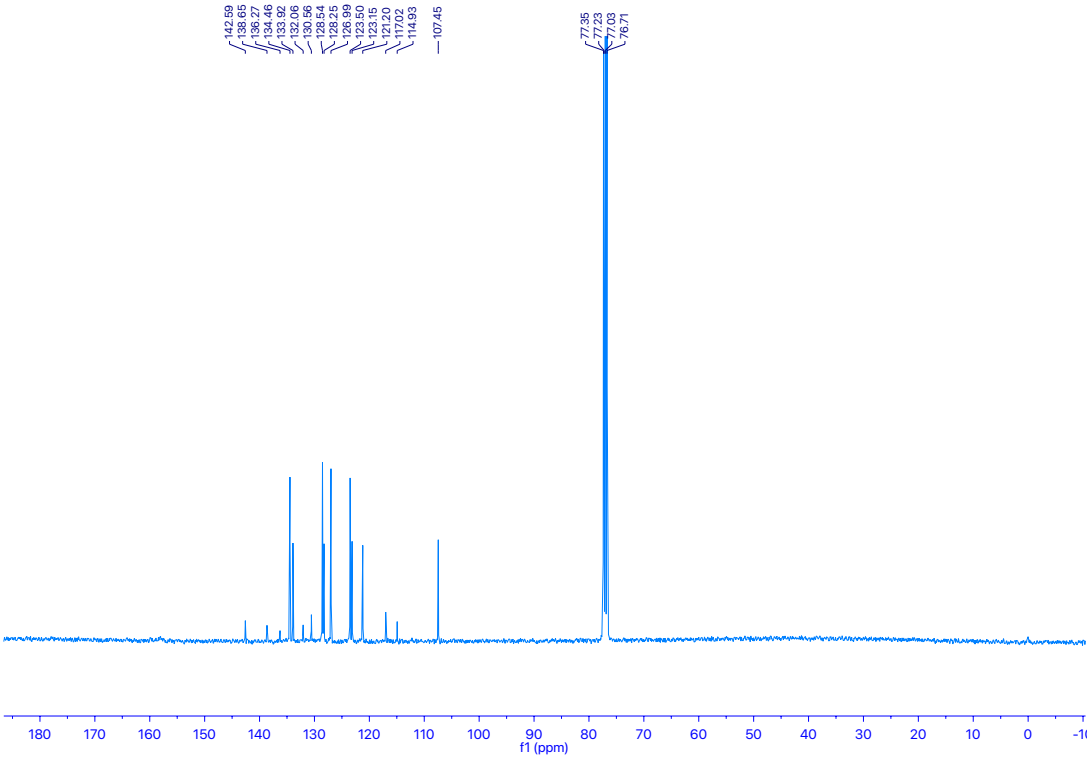
Compound 3p, ^{11}B NMR (128 MHz, $CDCl_3$)



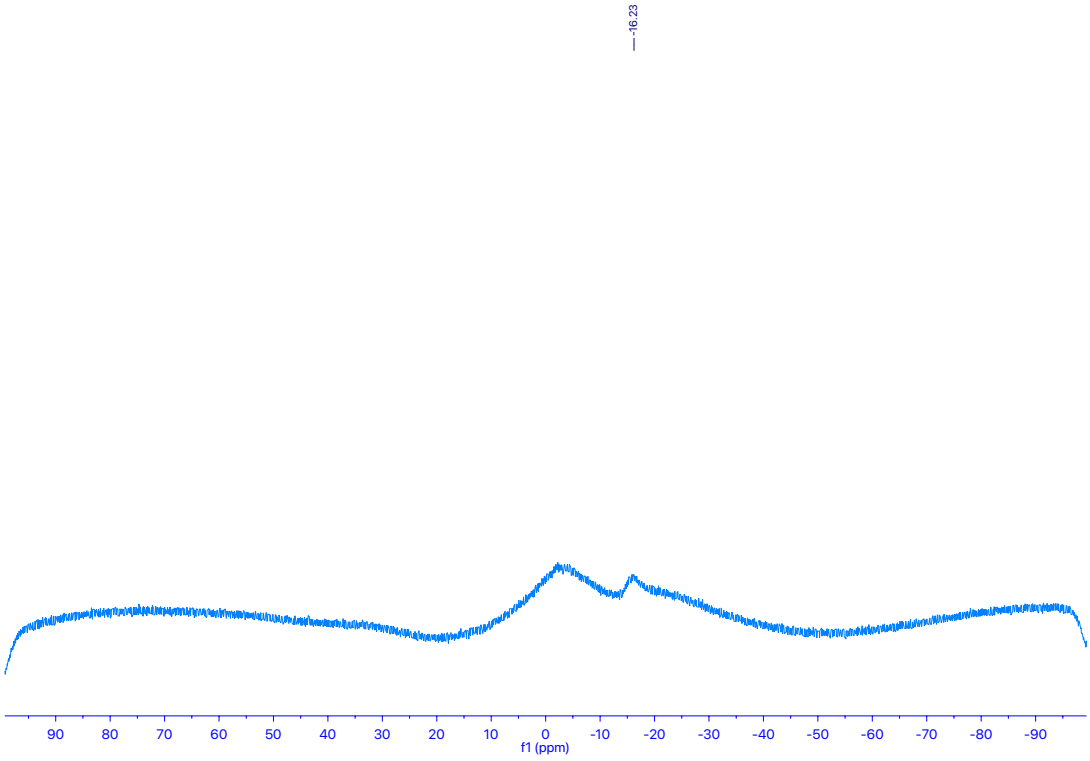
Compound 3q, ^{1}H NMR (400 MHz, $CDCl_3$)



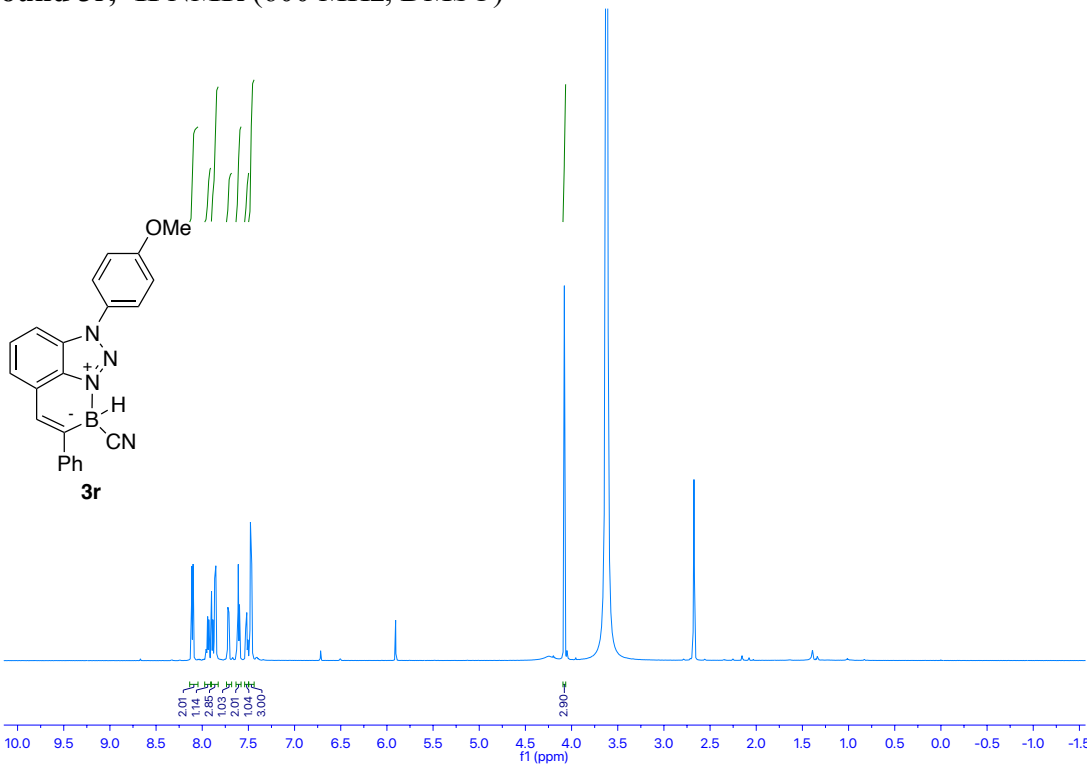
Compound 3q, ^{13}C-NMR (101 MHz, $CDCl_3$)



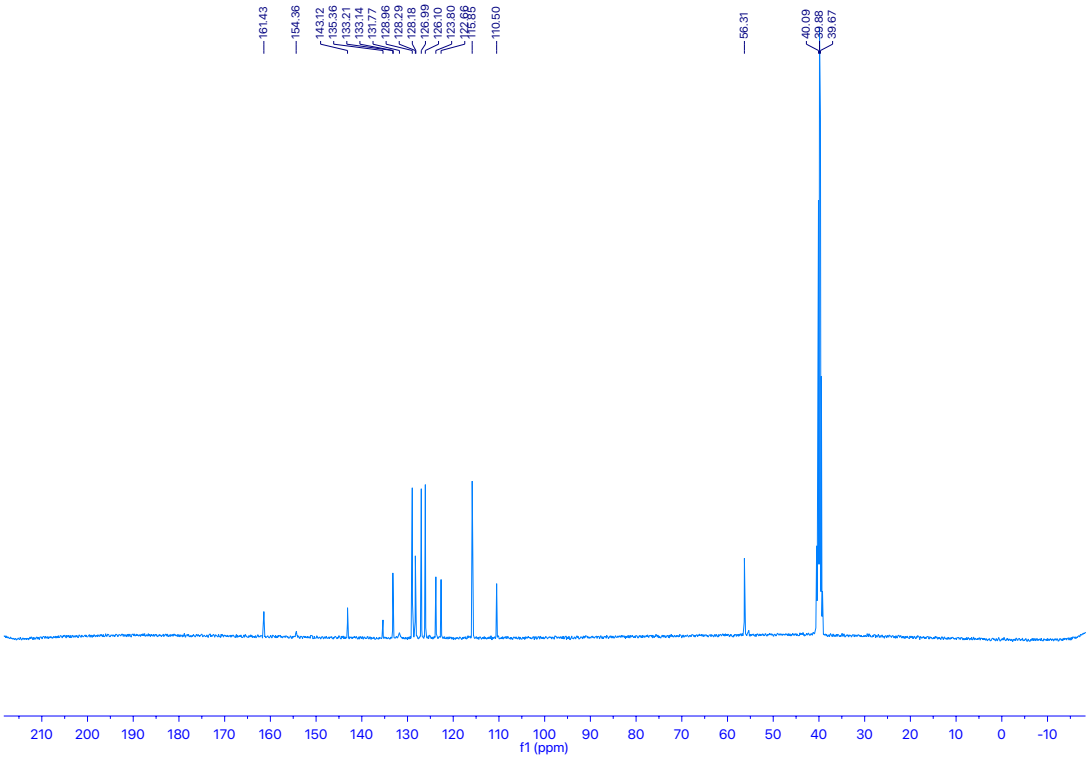
Compound 3q, ^{11}B NMR (128 MHz, $CDCl_3$)



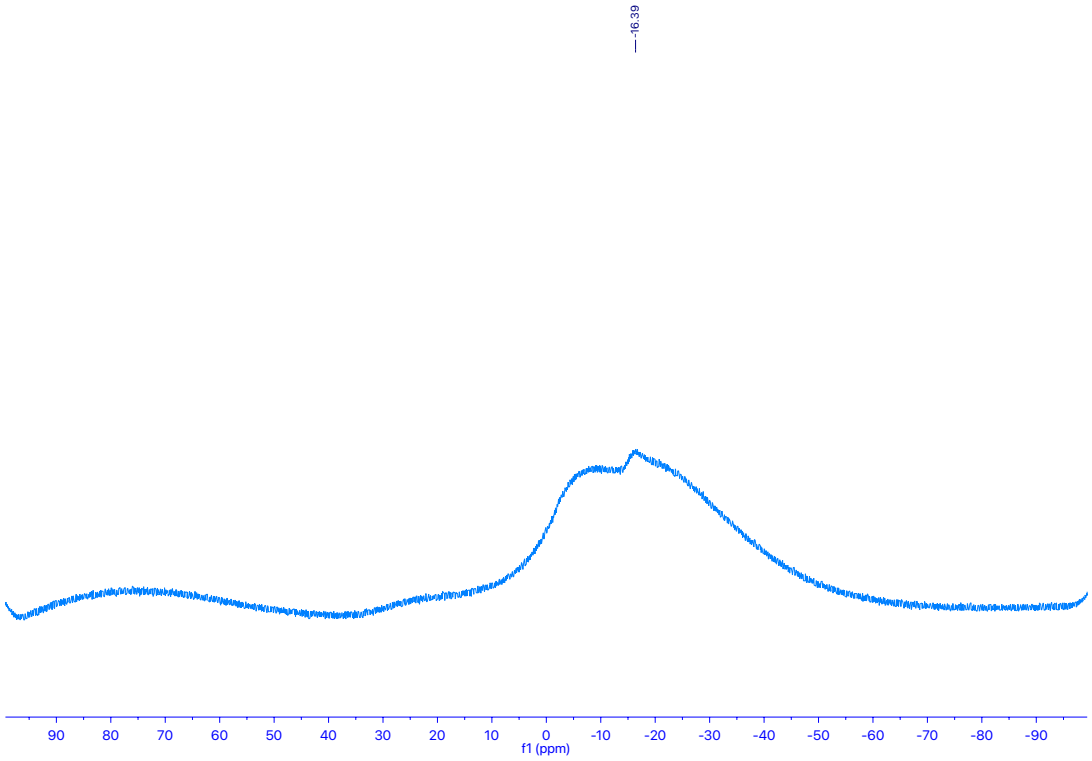
Compound 3r, ^{1}H NMR (600 MHz, DMSO)



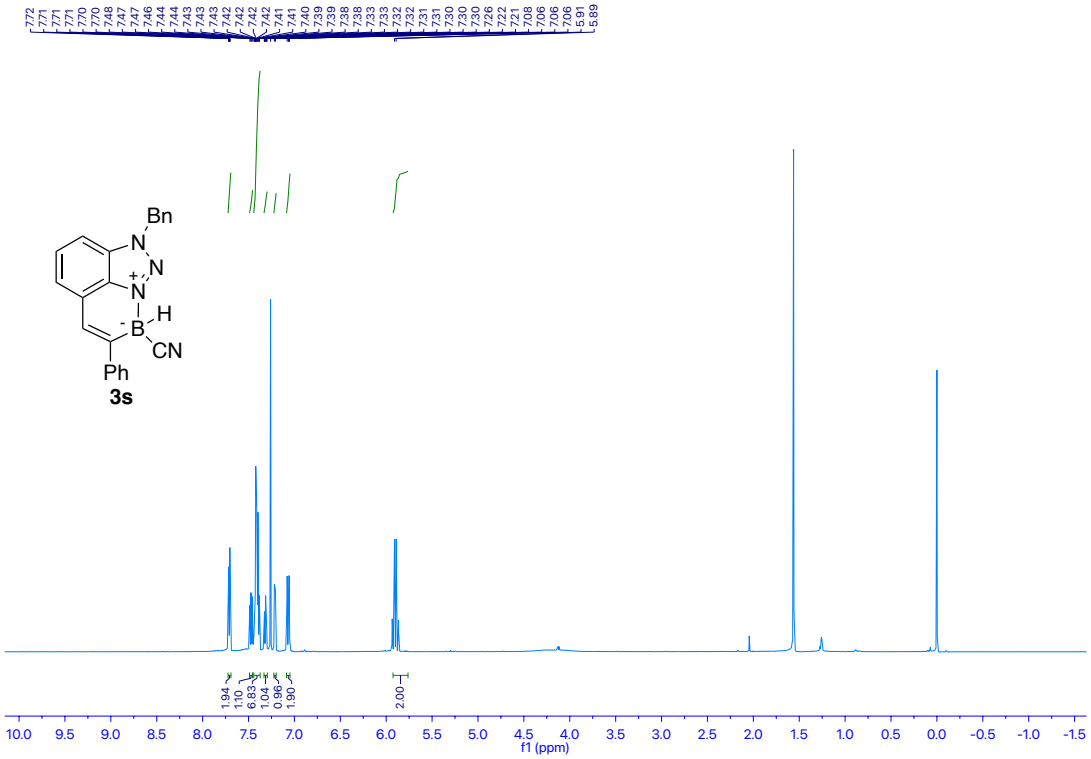
Compound 3r, ^{13}C-NMR (101 MHz, DMSO)



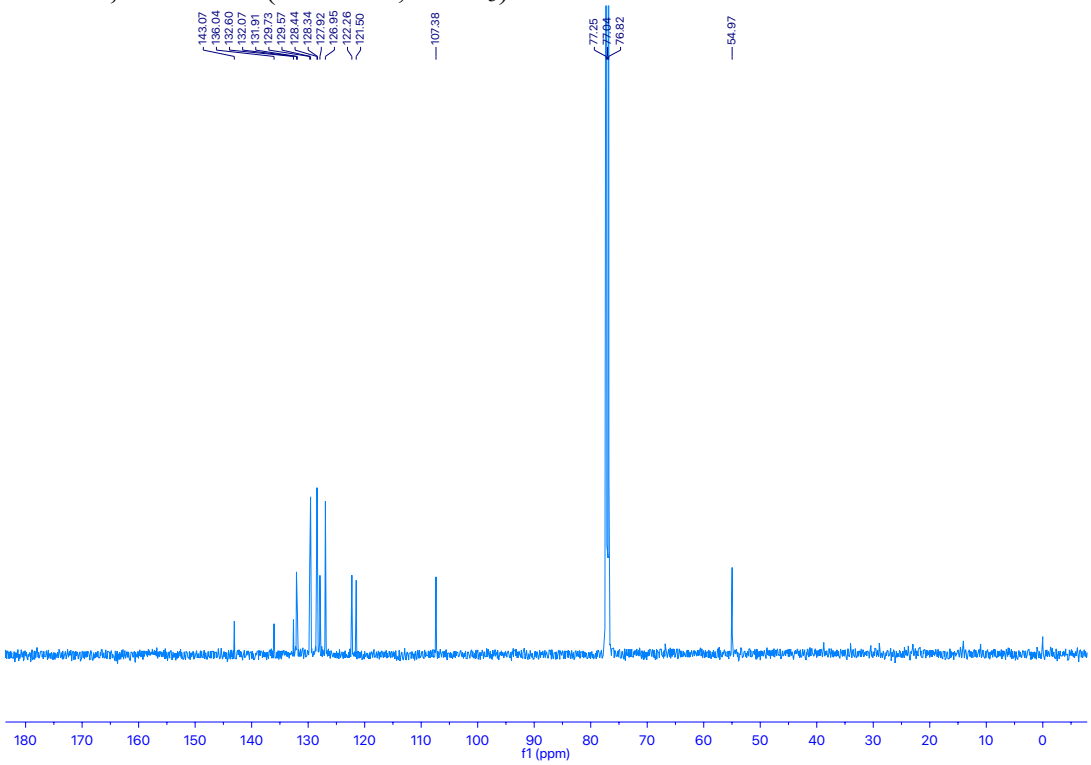
Compound 3r, ^{11}B NMR (128 MHz, DMSO)



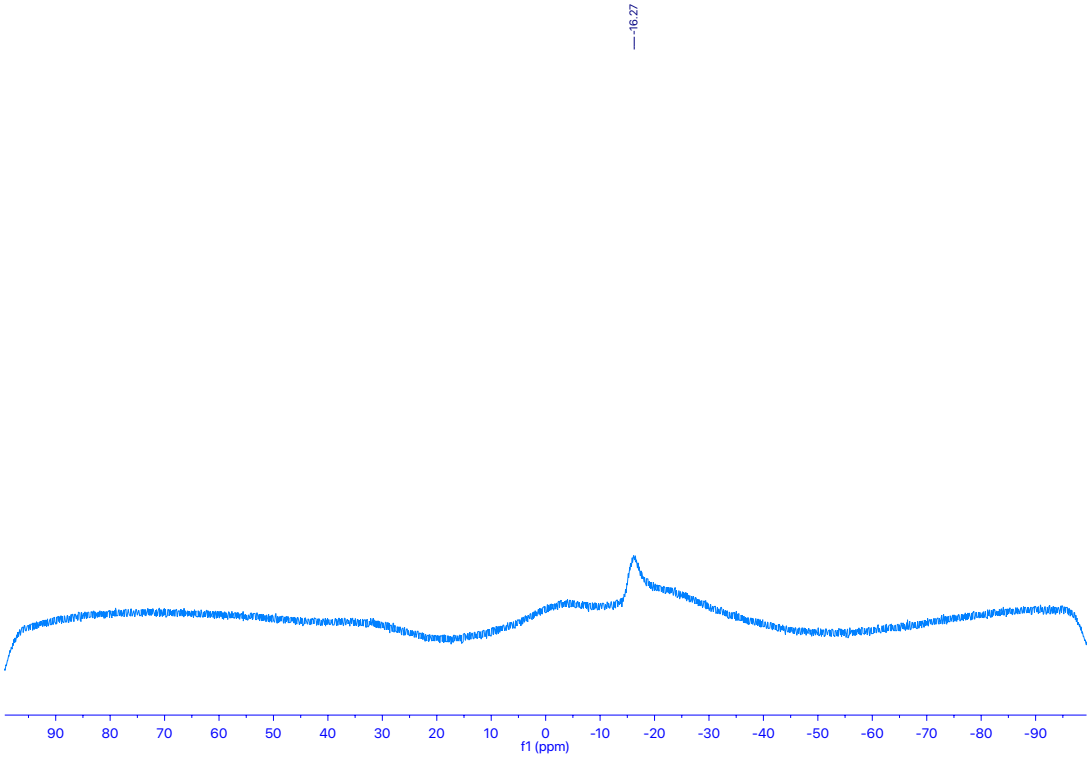
Compound 3s, ^{1}H NMR (600 MHz, $CDCl_3$).



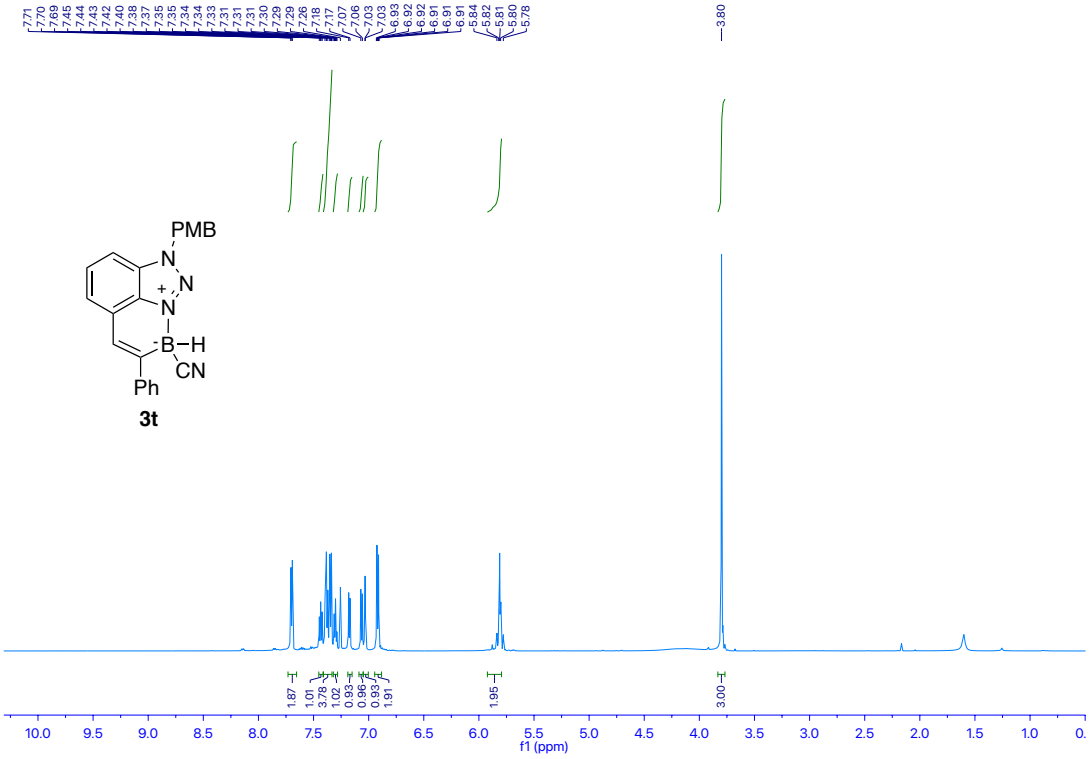
Compound 3s, ^{13}C-NMR (151 MHz, $CDCl_3$)



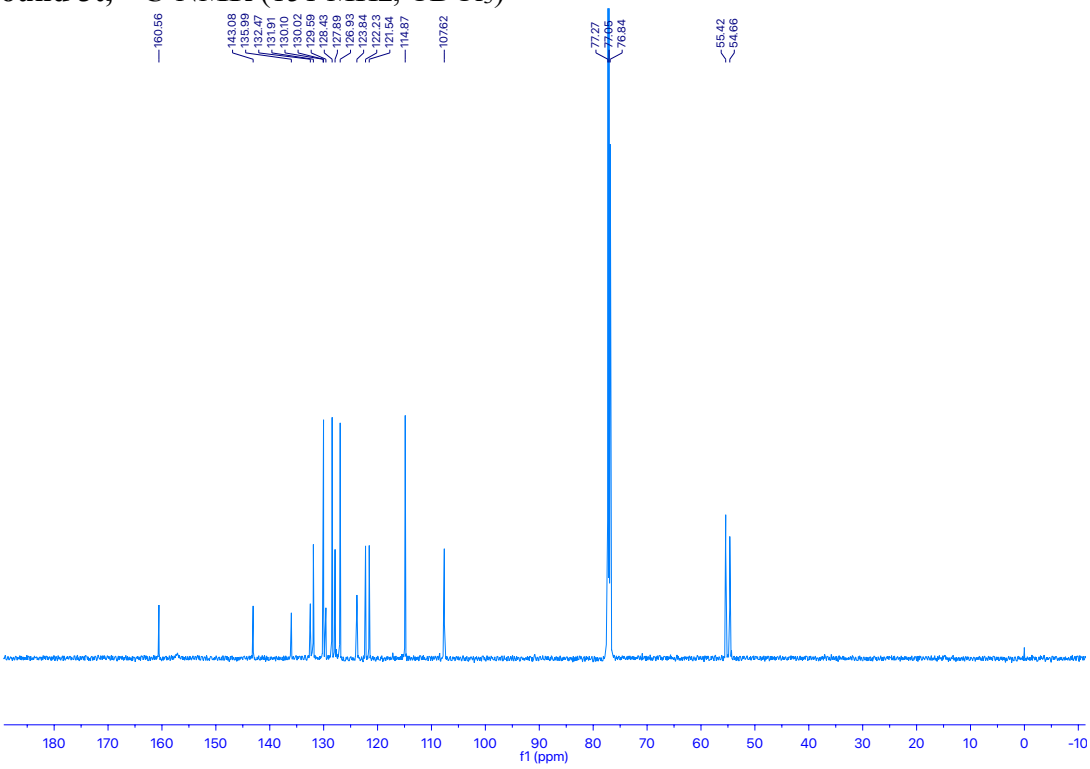
Compound 3s, ^{11}B NMR (128 MHz, $CDCl_3$)



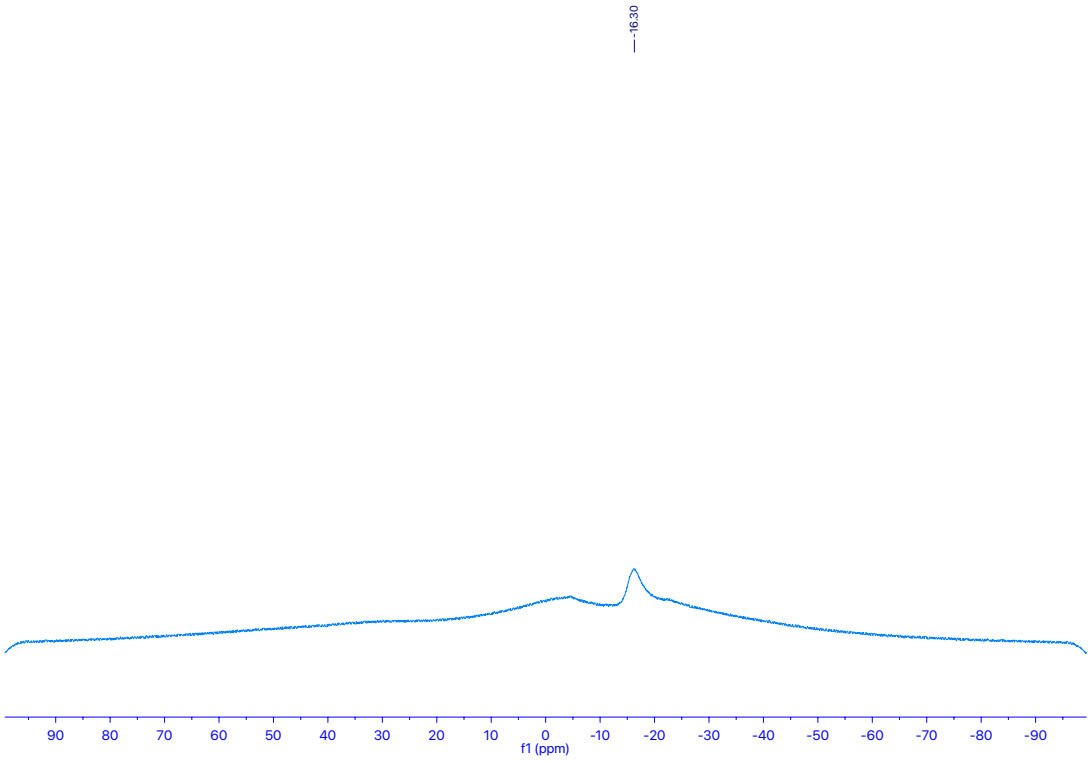
Compound 3t, ^{1}H NMR (600 MHz, $CDCl_3$)



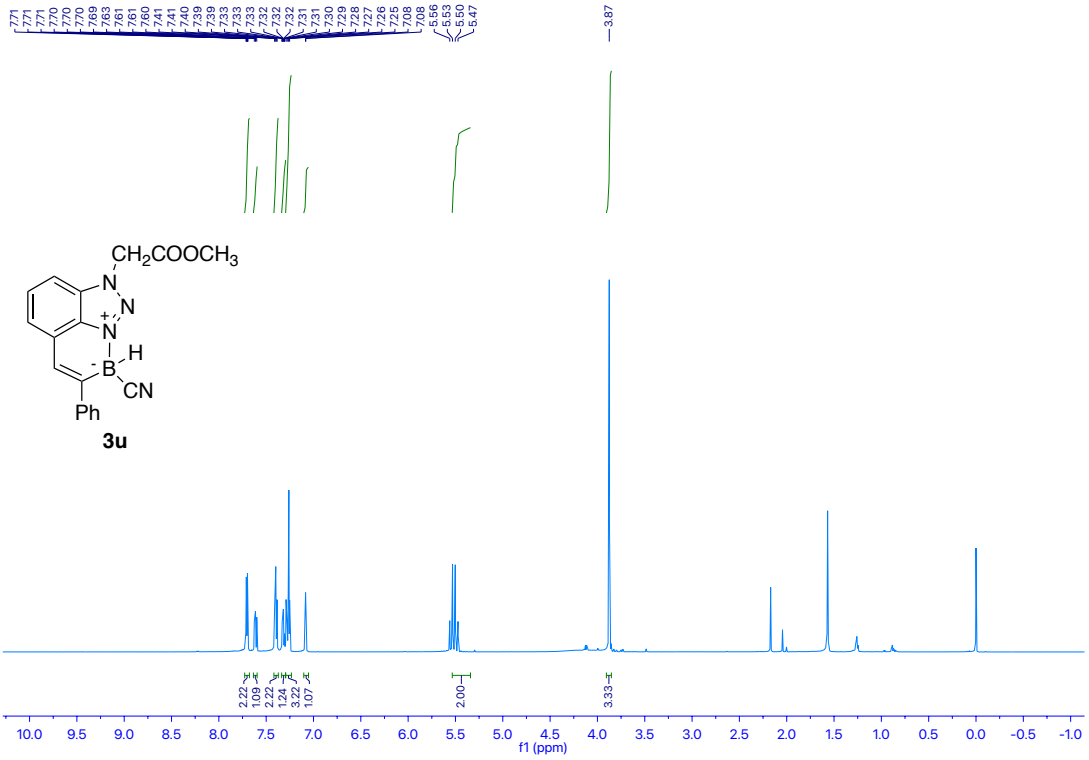
Compound 3t, ^{13}C-NMR (151 MHz, $CDCl_3$)



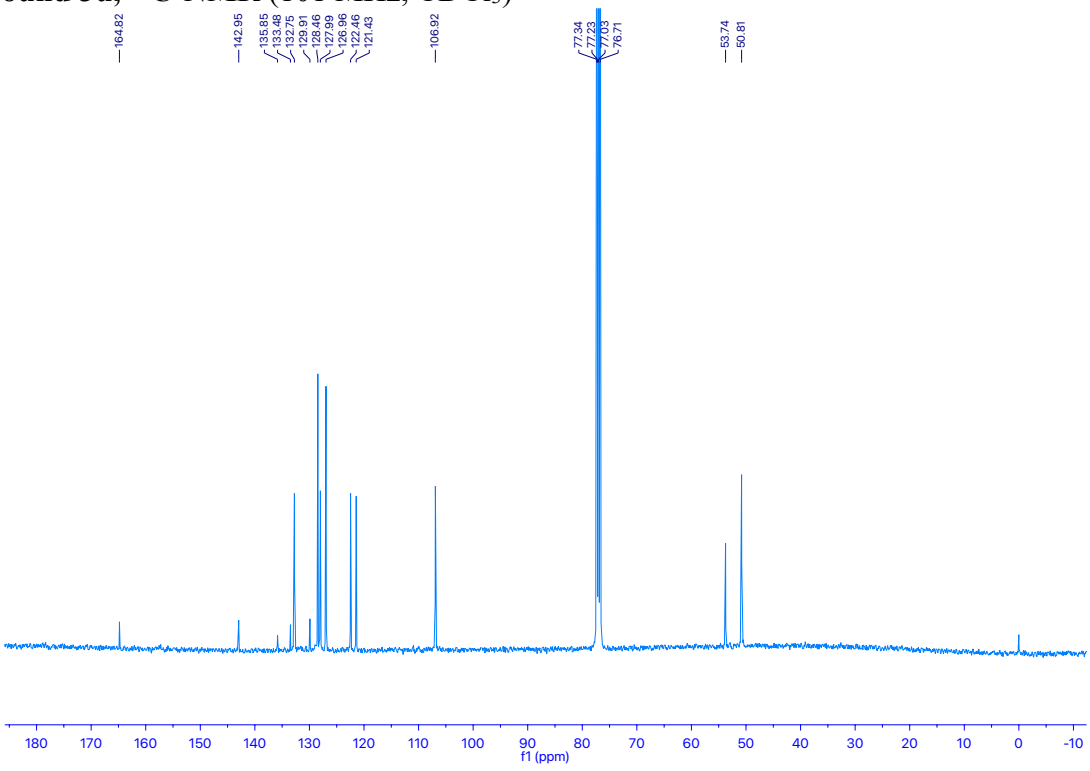
Compound 3t, ^{11}B NMR (128 MHz, $CDCl_3$)



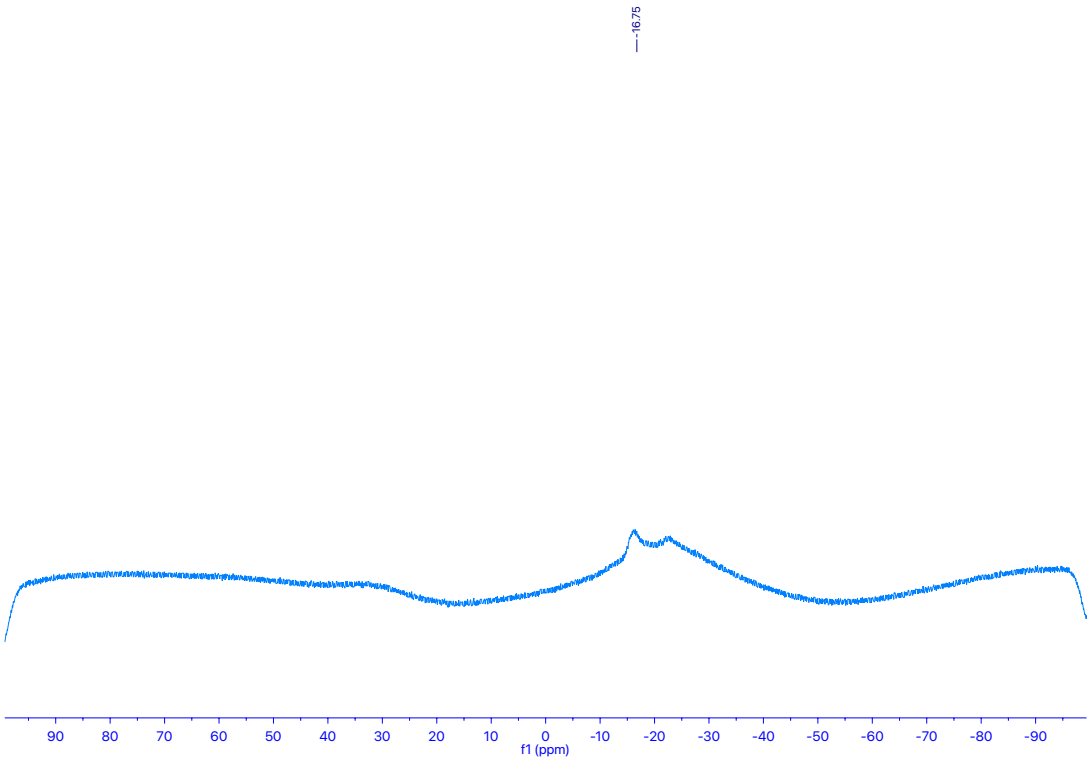
Compound 3u, ^{1}H NMR (600 MHz, $CDCl_3$)



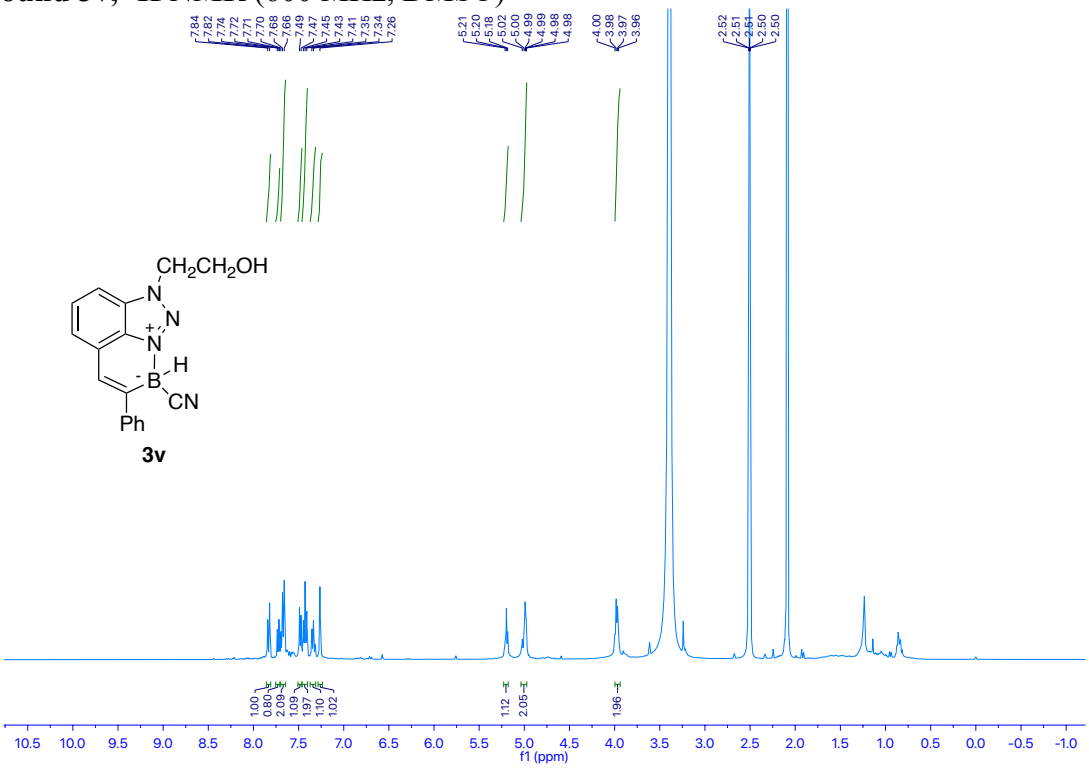
Compound 3u, ^{13}C-NMR (101 MHz, $CDCl_3$)



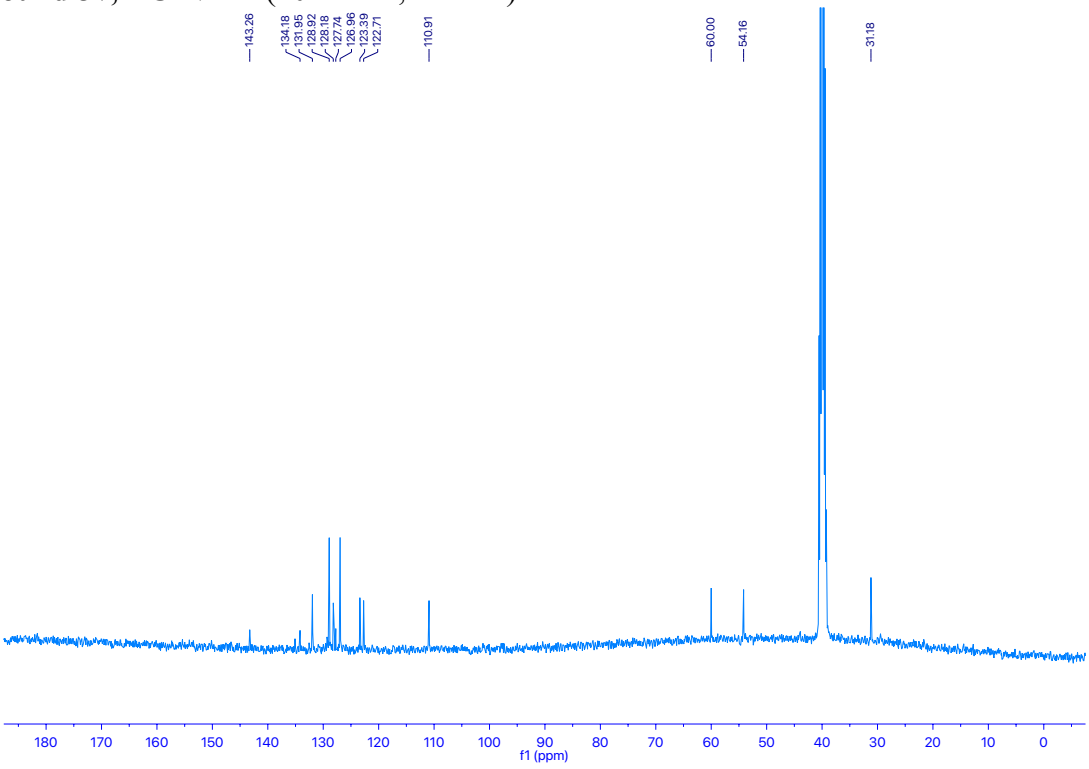
Compound 3u, ^{11}B NMR (128 MHz, $CDCl_3$)



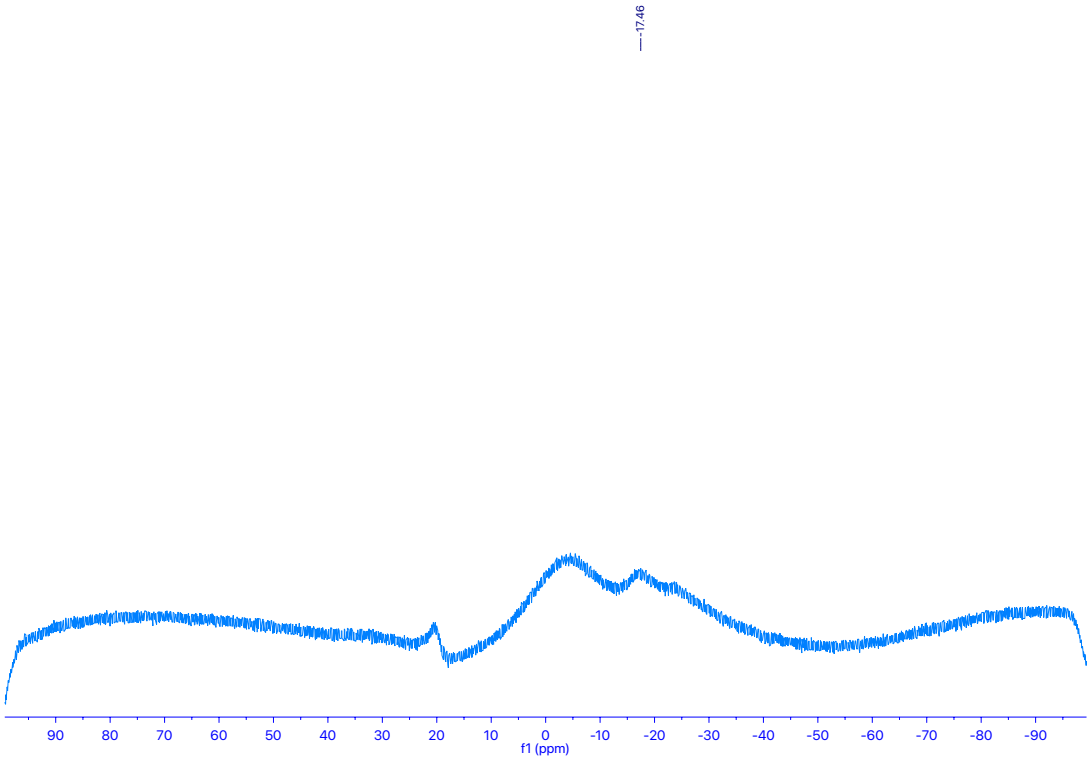
Compound 3v, ^{1}H NMR (600 MHz, DMSO)



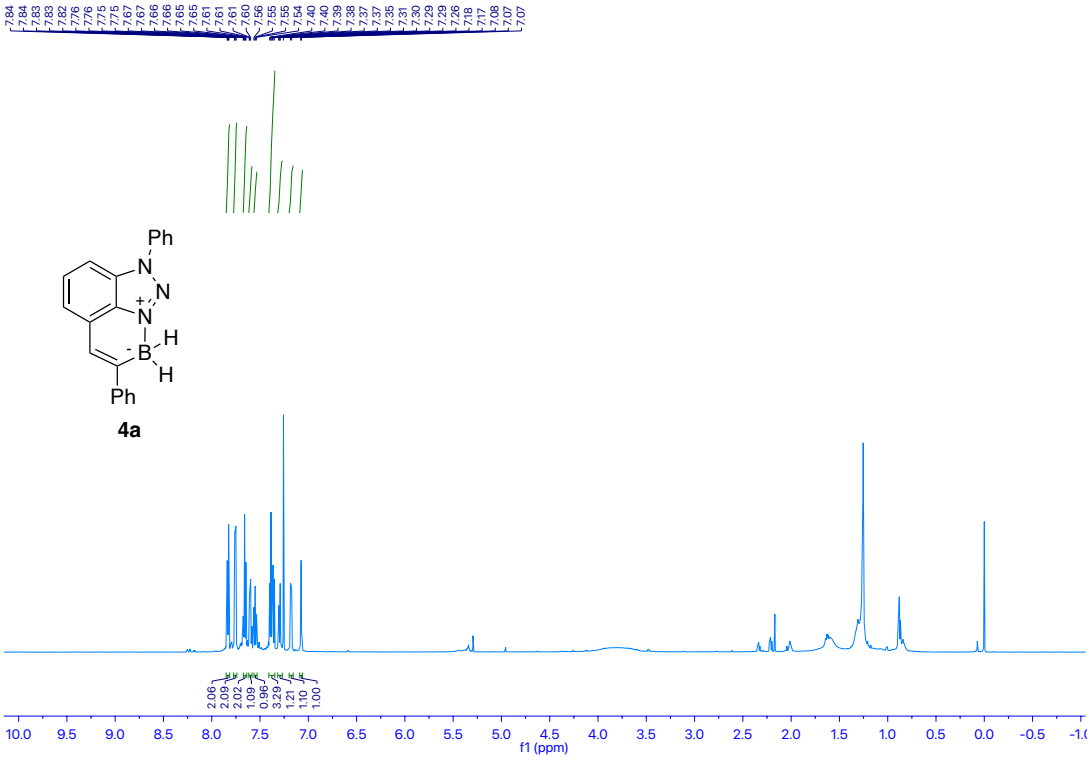
Compound 3v, ^{13}C-NMR (101 MHz, DMSO)



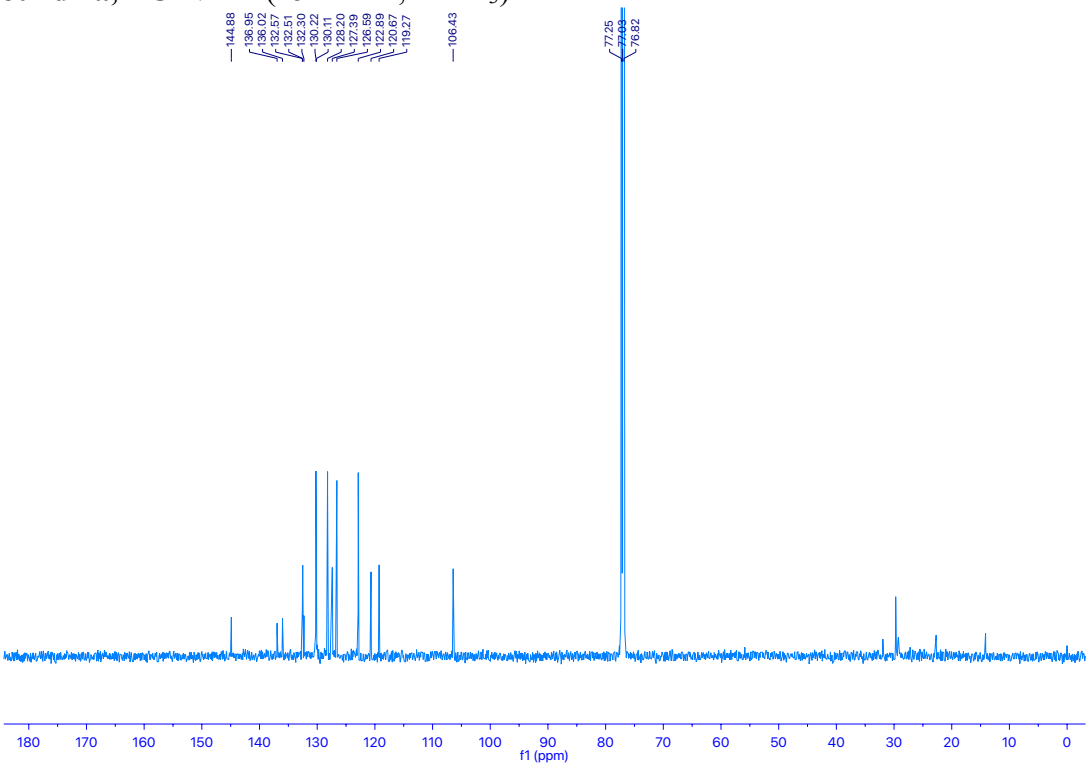
Compound 3v, ^{11}B NMR (128 MHz, DMSO)



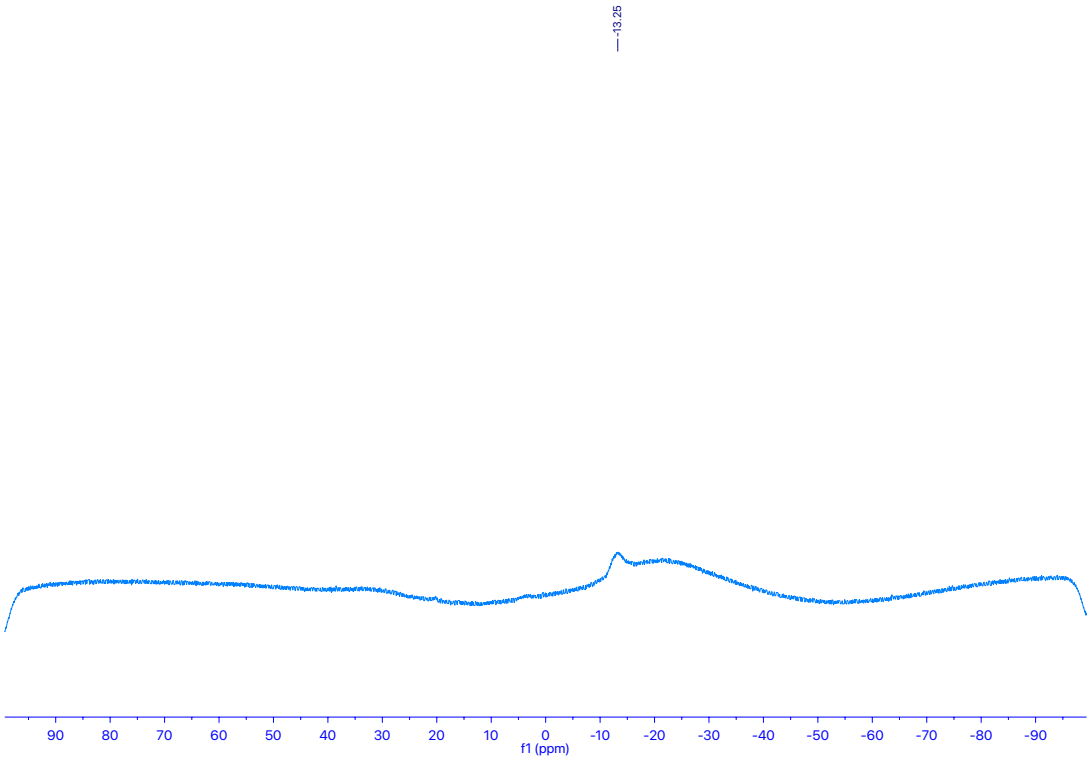
Compound 4a, ^{1}H NMR (600 MHz, $CDCl_3$).



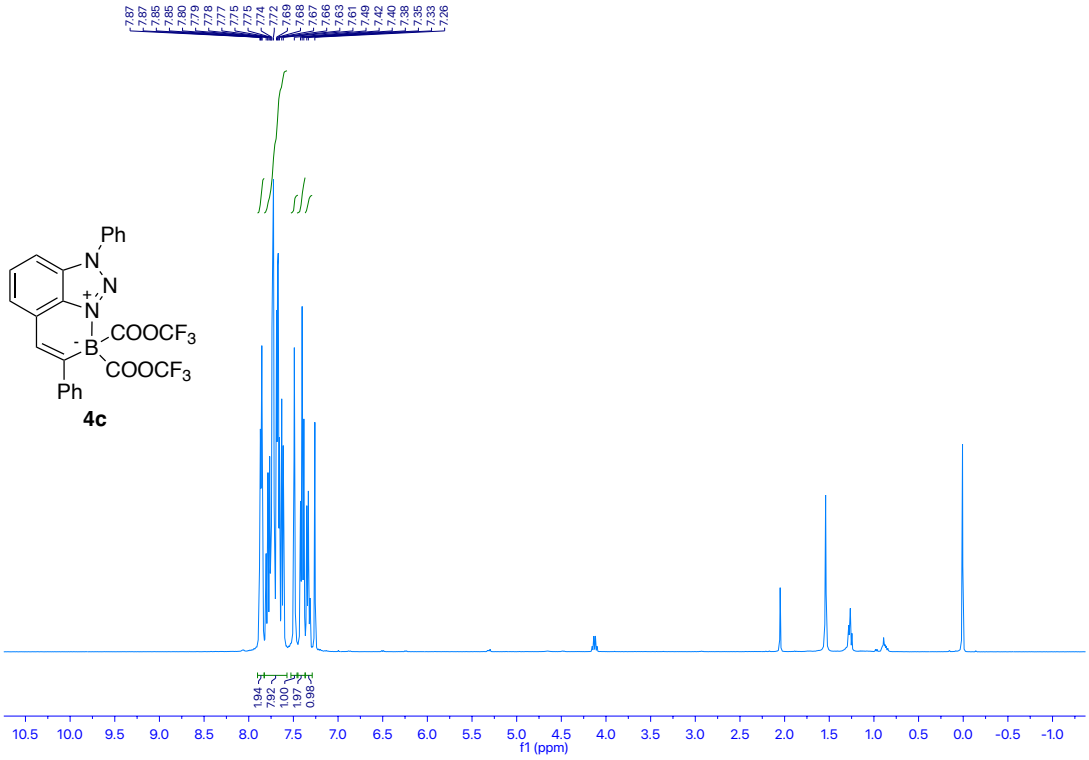
Compound 4a, ^{13}C-NMR (151 MHz, $CDCl_3$)



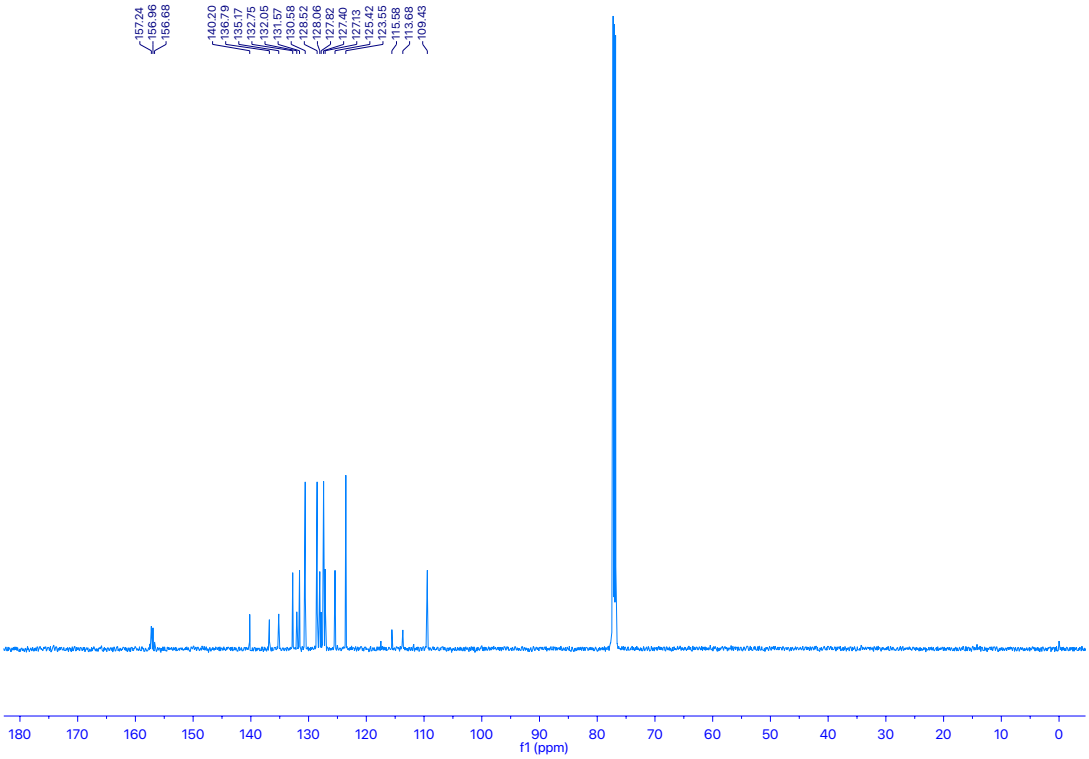
Compound 4a, ^{11}B NMR (128 MHz, $CDCl_3$)



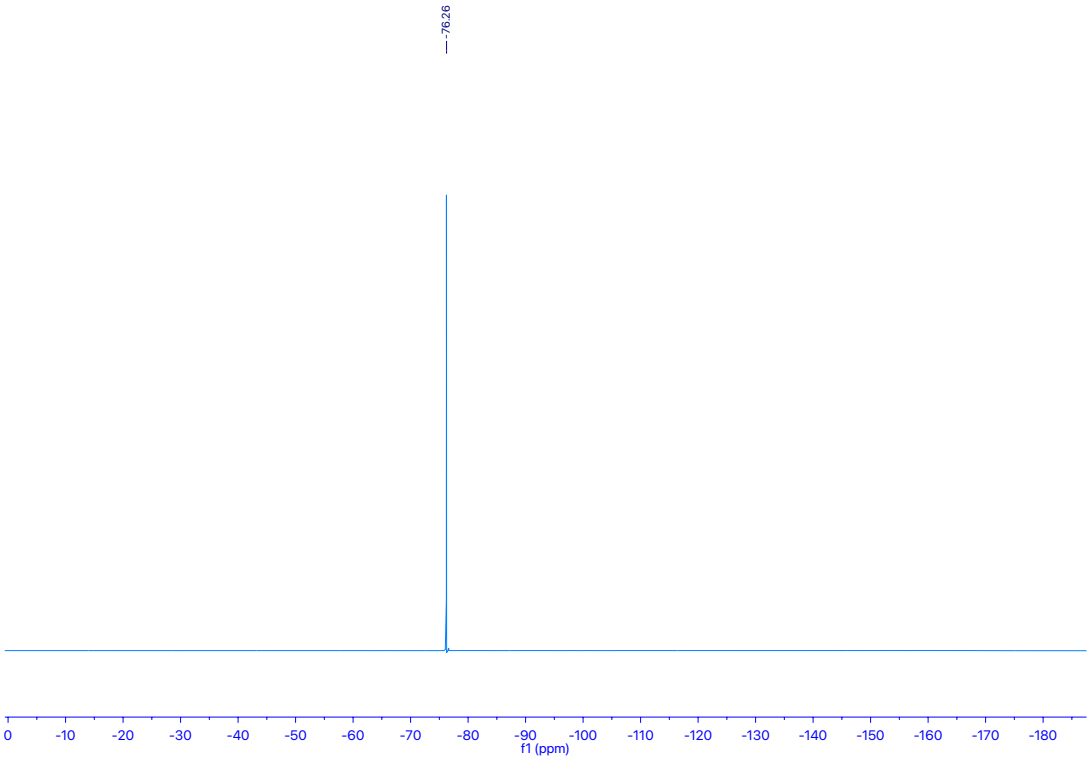
Compound 4c, ^{1}H NMR (600 MHz, $CDCl_3$).



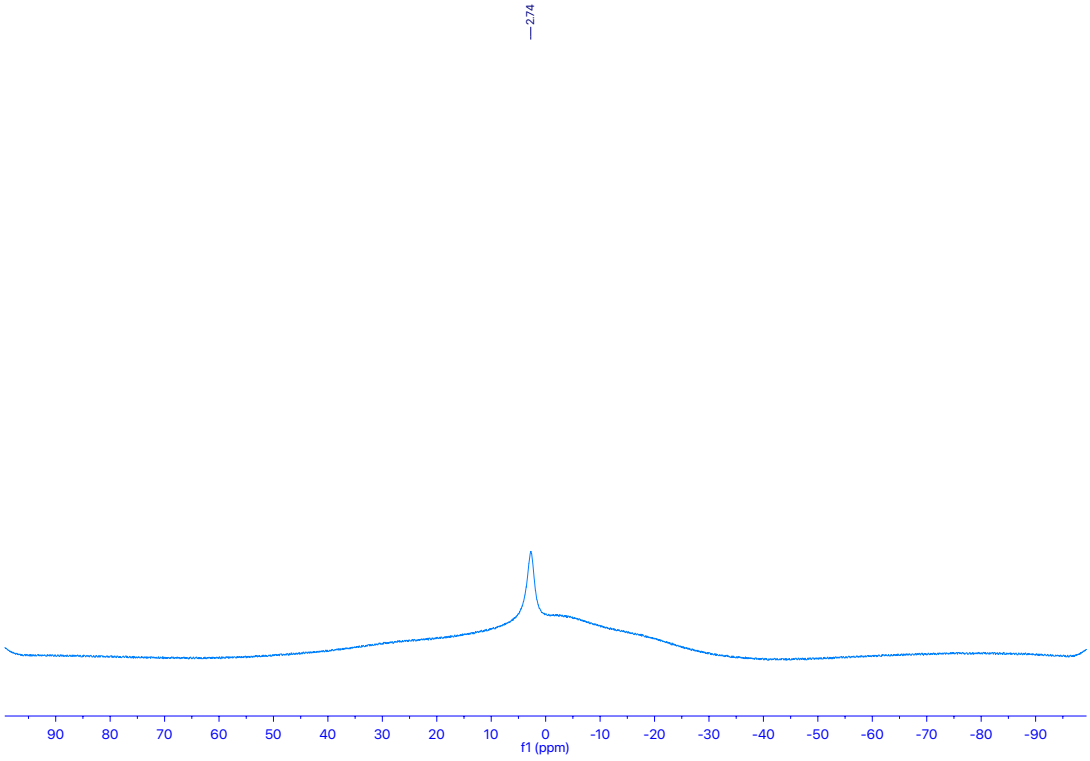
Compound 4c, ^{13}C-NMR (151 MHz, $CDCl_3$)



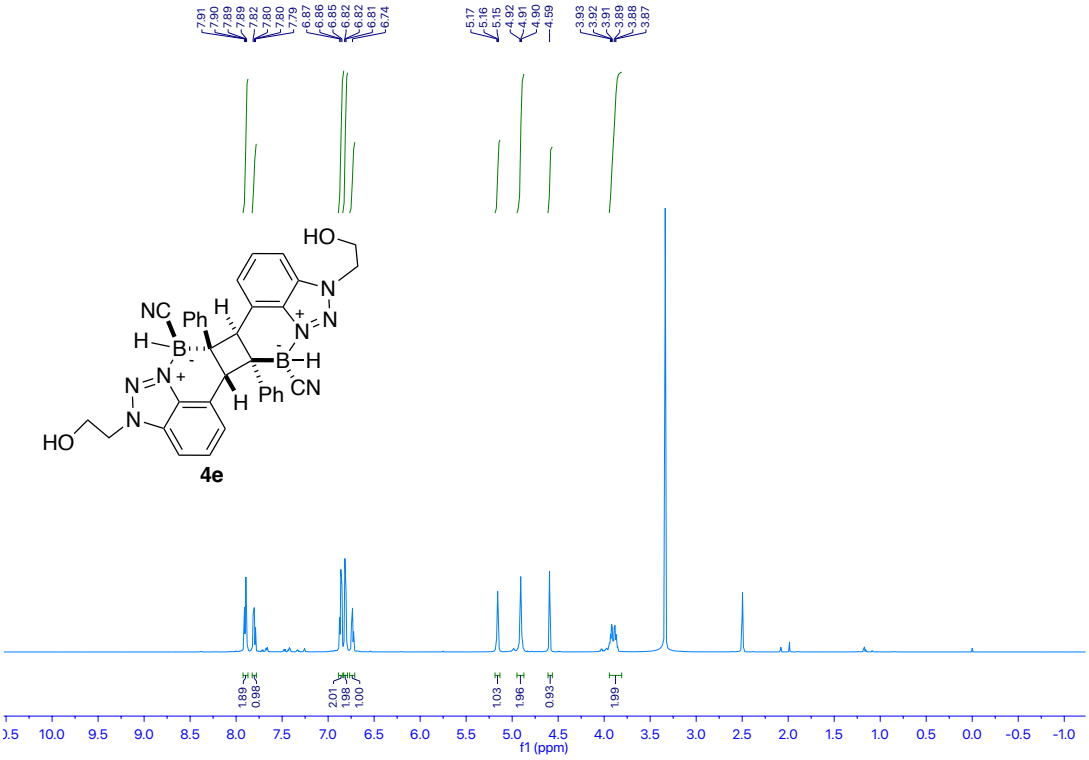
Compound 4c, ^{19}F-NMR (564 MHz, $CDCl_3$)



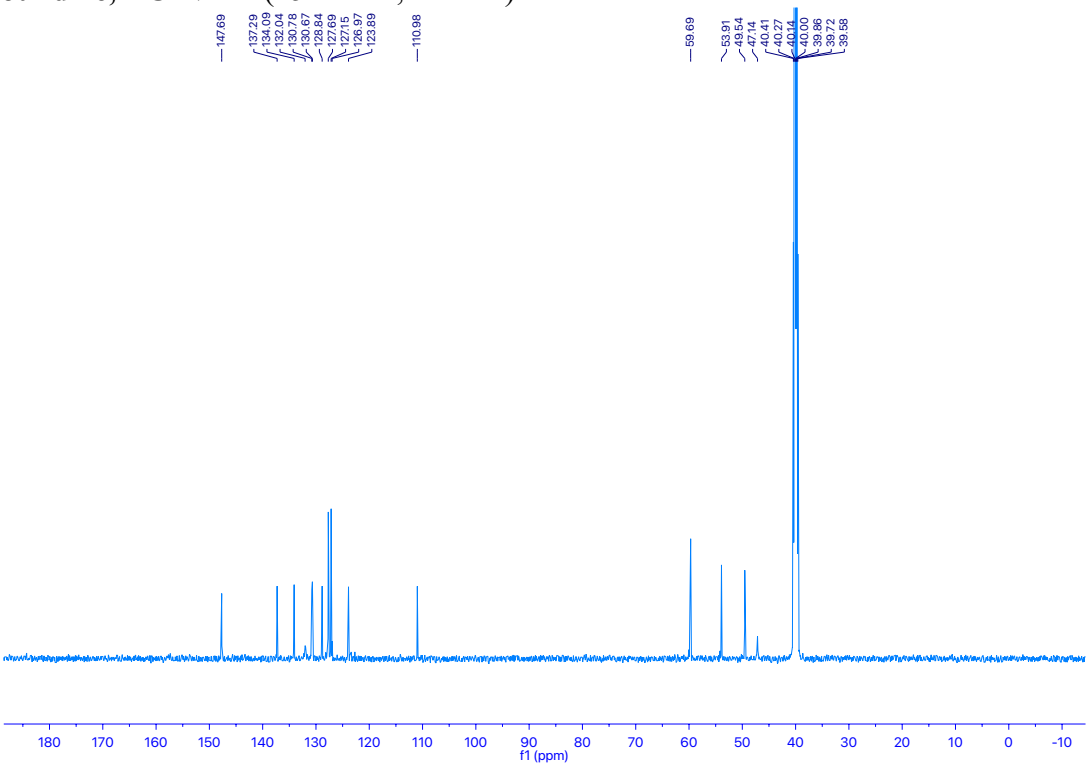
Compound 4c, ^{11}B NMR (128 MHz, $CDCl_3$)



Compound 4e, ^{1}H NMR (600 MHz, DMSO).



Compound 4e, ^{13}C-NMR (151 MHz, DMSO)



Compound 4e, ^{11}B NMR (128 MHz, DMSO)