Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Efficient synthesis of benzo[c]cinnolines and azoarenes via dual C−N coupling of phthalhydrazide and trivalent halogen reagents

Yanyan Yang, Rongrong Xie, Yiwen Wang, Peiyan Zhu, Jinhua Wang, Shiqing Li*

**Guangxi Key Laboratory of Electrochemical and Magneto-Chemical Functional Materials, College of Chemistry and Bioengineering, Guilin University of Technology, 12 Jian Gan Road, Guilin, 541004, China, E-mail: lisq@glut.edu.cn*

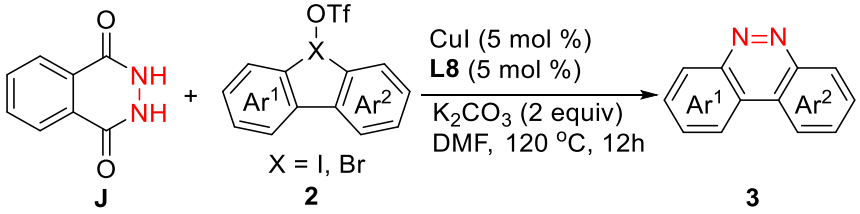
Table of contents

1. General remarks

NMR spectra were obtained on a BRUKER Ascend500. The ^{1}H NMR (500 MHz) chemical shifts were measured relative to $CDCl_3$ or DMSO-d_6 as the internal reference ($CDCl_3$: δ = 7.26 ppm; DMSO-d_6: δ = 2.50 ppm). The ^{13}C NMR (125 MHz) chemical shifts were given using $CDCl_3$ or DMSO-d_6 the internal standard ($CDCl_3$: δ = 77.16 ppm; DMSO-d_6: δ = 39.52 ppm). Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br s (broad singlet). High-resolution mass spectra (HR-MS) were obtained with a BRUKER solanX 70 FT-MS (ESI^+) at Shiyanjia lab (www.Shiyanjia.com). Melting points were determined with SGW® X-4 and are uncorrected. UV-vis spectra were recorded by a Perkin Elmer LAMBDA 365.

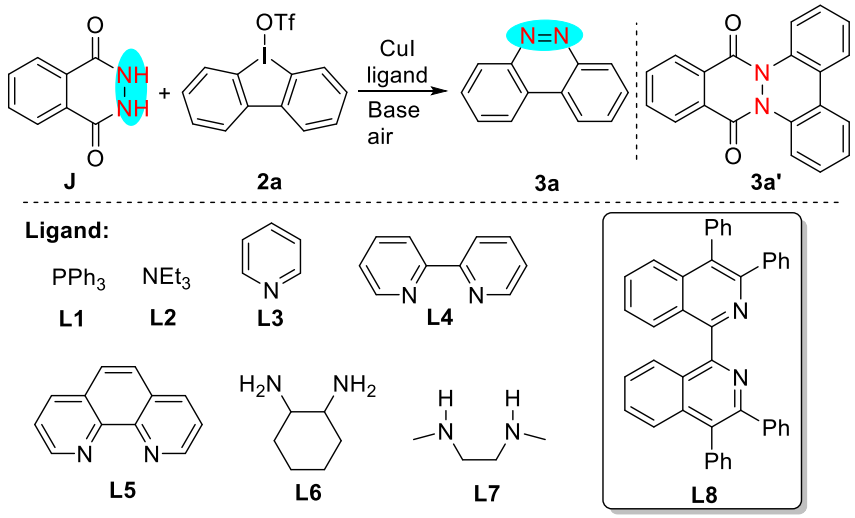
Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. All reaction mixtures were heated with oil bath. CuI, $Cu(OAc)_2$, $Cu(MeCN)_4BF_4$, NaOH, NEt_3, K_3PO_4, K_2CO_3, PPh_3, pyridine, 2,2′-bipyridine, 1,10-phenanthroline, (1*S*,2*S*)-cyclohexane-1,2-diamine, *N*,*N*′-dimethylethylenediamine, *N*,*N*-dimethylformamide, hydrazines **A**-**I** were purchased from Beijing Innochem Chemical Engineering Reagent (China) Co., Ltd. $TsOH\cdot H_2O$ and *m*-CPBA (purity of 75%) were purchased from Adamas-beta Ltd. Cyclic iodoniums,[1a-c] cyclic bromoniums,[1d] linear iodoniums,[2a-c] *N*-aryl phthalic hydrazides,[3] 3,3′,4,4′-Tetraphenyl-1,1′-biisoquinoline[4] were prepared according to the literature procedures.

2. General procedure for the synthesis of benzo[*c*]cinnolines from cyclic iodoniums/bromoniums



To a dry Schlenck tube with a magnetic stir bar was added phthalhydrazide **J** (0.2 mmol, 1 equiv, 32.4 mg), a cyclic iodonium or bromonium **2** (0.25mmol), CuI (1.9 mg, 5 mol %), 3,3',4,4'-tetraphenyl-1,1′-biisoquinoline (**L8**, 5 mol %), K_2CO_3 (0.4 mmol, 2 equiv, 55.2 mg) and DMF (1 mL). The mixture was stirred at 120 °C for 12 h under air. After the reaction was completed, the solvent was removed under reduced pressure, and the residue was purified by a silica gel column, eluting with petroleum ether/EtOAc (50/1→10/1, v/v) to afford corresponding benzo[*c*]cinnolines **3**.

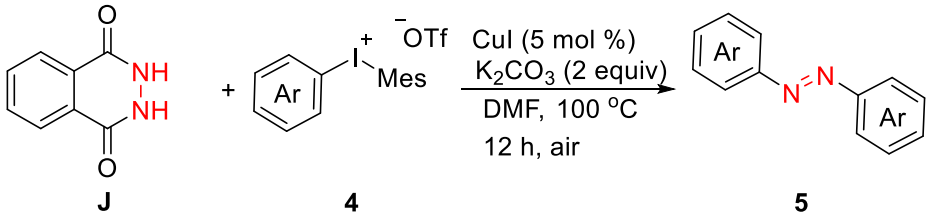
Table S1. Optimization of the reaction condition for the synthesis of benzo[c]cinnolines.[a]



Entry	CuI (mol %)	Ligand (mol %)	Base (2 equiv)	Yield (%)[b] (**3a:3a′**)
1	5	none	K_2CO_3	67:0
2	none	none	K_2CO_3	ND
3	5	**L1** (10)	K_2CO_3	89:0
4	5	**L2** (10)	K_2CO_3	90:0
5	5	**L3** (10)	K_2CO_3	85:0
6	5	**L4** (5)	K_2CO_3	90:0
7	5	**L4** (5)	none	ND
8	5	**L5** (5)	K_2CO_3	92:0
9	5	**L6** (5)	K_2CO_3	95:0
10	5	**L7** (5)	K_2CO_3	52:33
11	**5**	**L8 (5)**	**K_2CO_3**	**99:0**
12	1	**L8** (1)	K_2CO_3	75:0
13	5	**L8** (5)	Cs_2CO_3	68:0
14	5	**L8** (5)	DBU	20:80
15	5	**L8** (5)	NEt_3	trace:45

[a]Reaction conditions: **J** (0.2 mmol, 1 equiv), **2a** (0.25 mmol, 1.25 equiv), CuI (5 mol %), **L8** (5 mol %), and K_2CO_3 (0.4 mmol, 2 equiv) were stirred in DMF (1 mL) at 120 °C for 12 h under air, [b]Isolated yields.

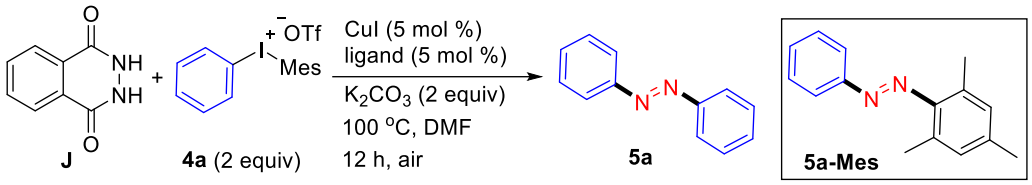
3. General procedure for the synthesis of symmetrical azobenzenes



To a dry Schleck tube with a magnetic stir bar was added phthalhydrazide **J** (0.2 mmol, 1 equiv, 32.4 mg), a linear iodonium **4** (0.4 mmol, 2 equiv), CuI (1.9 mg, 5 mol %), K_2CO_3 (0.4 mmol, 2 equiv, 55.2

mg) and DMF (1 mL). The mixture was placed in a dark environment and stirred at 100 °C for 12 h under air. After the reaction was completed, the solvent was removed under reduced pressure, and the residue was purified by a silica gel column, eluting with petroleum ether/EtOAc (100/1→50/1, v/v) to afford corresponding symmetrical azobenzenes **5**.

Table S2. Optimization of the reaction conditions of the synthesis of azoarenes.[a]

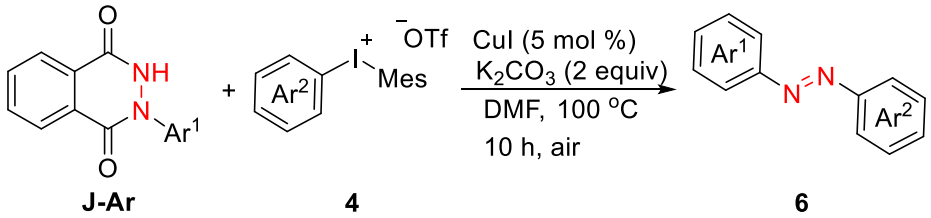


Entry	**4a**	Ligand	Yield of **5a** (%)[b]
1	1 equiv	**L8**	30
2	2 equiv	**L8**	92
3	2 equiv	-	95

[a]Reaction conditions: **J** (0.2 mmol, 1 equiv), **4a** (0.4 mmol, 2 equiv), CuI (1.9 mg, 5 mol%), K_2CO_3 (0.4 mmol, 85 mg, 2 equiv) and DMF (1 mL) were stirred at 100 °C for 10 h under air. [b]Isolated yield.

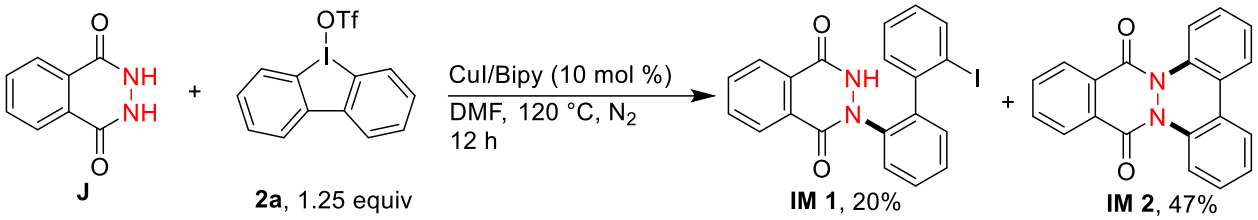
The reaction of phthalhydrazide and [Ph-I-Mes]OTf **4a** gave azobenzene **5a** in only 30% yield (Table S1, entry 1). The yield of **5a** increased to 92% when increasing the usage of **4a** to 2 equiv (Table S1, entry 2). Moving the ligand away gave 3a in the highest yield of 95% (Table S1, entry 3). In all of these tests, azo compound **5a-Mes** was not detected.

4. General procedure for the synthesis of unsymmetrical azobenzenes



To a dry Schlenck tube with a magnetic stir bar was added *N*-aryl phthalhydrazide **J-Ar** (0.2 mmol, 1 equiv), a linear iodonium **4** (0.2 mmol, 1 equiv), CuI (1.9 mg, 5 mol%), K_2CO_3 (0.4 mmol, 2 equiv, 55.2 mg) and DMF (1 mL). The mixture was placed in a dark environment and stirred at 100 °C for 10 h under air. After the reaction was completed, the solvent was removed under reduced pressure, and the residue was purified by a silica gel column, eluting with petroleum ether/EtOAc (100/1→50/1, v/v) to afford corresponding unsymmetrical azobenzenes **6**.

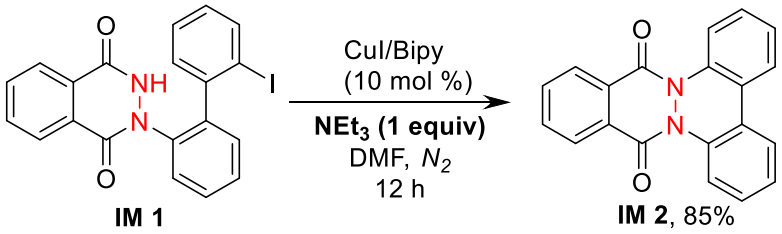
5. Mechanistic study



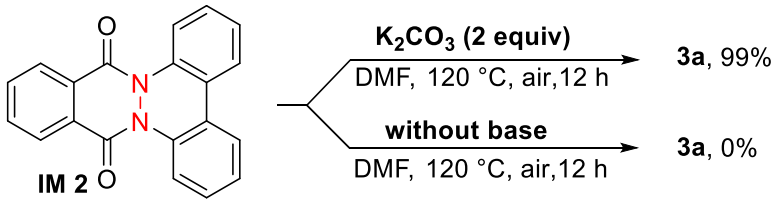
Synthesis of IM 1 and IM2: A mixture of phthalic hydrazide **J** (32.4 mg, 0.2 mmol), cyclic iodonium **2a** (107 mg, 0.25 mmol, 1.25 equiv), CuI (3.8 mg, 10 mol%), 2,2′-bipyridine (3.1 mg, 10 mol%) and DMF (1 mL) was reacted at 120 °C for 12 h under N_2 atmosphere. The reaction was cooled to room temperature before DMF was removed under reduced pressure. The residue was purified by a silica gel column, eluting with petroleum ether/EtOAc (50/1→20/1→5/1, v/v) to afford **IM 1** as a white solid (17.6 mg, 20% yield) and **3a'** as a yellow solid (29 mg, 47% yield).

2-(2'-iodo-[1,1'-biphenyl]-2-yl)-2,3-dihydrophthalazine-1,4-dione (IM 1). White solid (12 mg, 20%). M.p.: 177–179 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.94 (s, 1H), 8.29 (d, J = 8.0 Hz, 1H), 7.97 (d, J = 7.5 Hz, 1H), 7.80–7.73 (m, 3H), 7.53 (t, J = 7.5 Hz, 1H), 7.40–7.37 (m, 2H), 7.32 (d, J = 7.5 Hz, 1H), 7.20 (d, J = 7.5 Hz, 1H), 7.15 (t, J = 7.5 Hz, 1H), 6.80 (t, J = 7.5 Hz, 1H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 159.7, 151.5, 150.3, 142.5, 139.0, 137.3, 133.7, 132.4, 131.5, 130.5, 129.7, 129.2, 128.8. 127.8, 126.9, 125.9, 124.9, 124.1, 122.5, 99.8 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{20}H_{14}IN_2O_2^+$ $(M + H)^+$ 441.0094, found 441.0091.

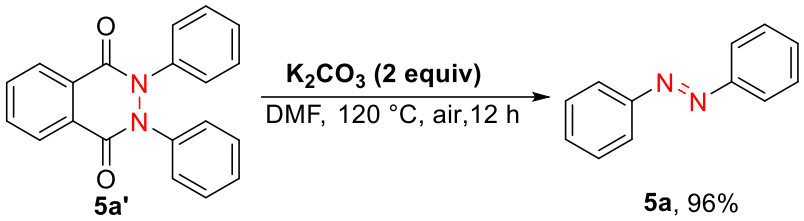
benzo[*c*]phthalazino[2,3-*a*]cinnoline-10,15-dione (IM 2). A yellow solid (29 mg, 47%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.44–8.42 (m, 2H), 792–7.90 (m, 4H), 7.80–7.78 (m, 2H), 7.36–7.33 (m, 4H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 158.2, 136.6, 134.3, 129.8, 128.7, 128.5, 127.0, 125.1, 123.8, 120.2 ppm. The data are consistent with the literature.[5]



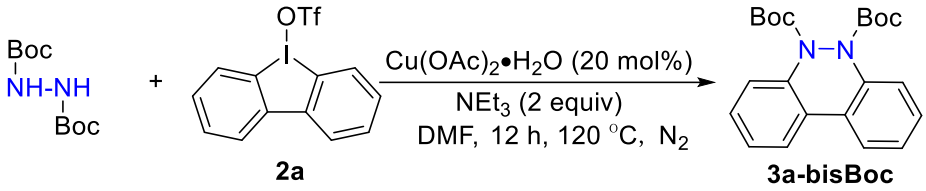
Transforming IM 1 to IM2: A mixture of **IM 1** (44 mg, 0.1 mmol), CuI (1.9 mg, 10 mol%), 2,2′-bipyridine (1.6 mg, 10 mol%), NEt_3 (14 μL, 0.1 mmol, 1 equiv) and DMF (0.5 mL) was reacted at 120 °C for 12 h under N_2 atmosphere. The reaction was cooled to room temperature before DMF was removed under reduced pressure. The residue was purified by a silica gel column, eluting with petroleum ether/EtOAc (50/1→20/1, v/v) to afford **IM2** as a yellow solid (26.5 mg, 85% yield).



Deprotection/oxidation under copper-free conditions: The solution of **IM2** (31 mg, 0.1 mmol, 1 equiv) with or without K_2CO_3 (27.6 mg, 0.2 mmol, 2equiv) in DMF (0.5 mL) was reacted at 120 °C for 12 h under air. **3a** was isolated in 99% yield in the presence of K_2CO_3, while **3a** was not detected by TLC in the absence of K_2CO_3.

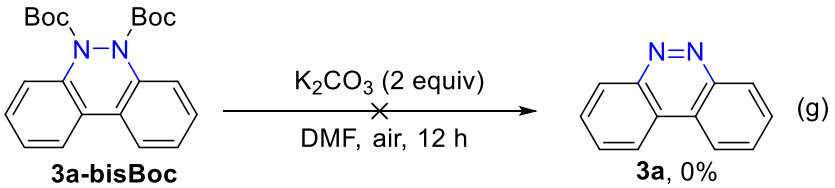


Transforming 5a' to 5a under the standard conditions: A mixture of **5a'** which was prepared according to our previous work[6] (31 mg, 0.1 mmol), CuI (1.9 mg, 10 mol%), K_2CO_3 (0.2 mmol, 27.6 mg, 2 equiv) and DMF (0.5 mL) was reacted at 120 °C for 12 h under air. After then DMF was removed under reduced pressure and the residue was purified by a silica gel column, eluting with petroleum ether/EtOAc (50/1→20/1, v/v) to afford **3a** (17.2 mg, 96% yield).



Synthesis of 3a-bisBoc: A mixture of bis-Boc hydrazine (23.2·mg, 0.1 mmol), cyclic iodonium **2a** (53.5·mg, 0.125 mmol), $Cu(OAc)_2$•H_2O (4.0 mg, 20 mo1%), NEt_3 (20.2 mg, 2 equiv), and DMF (0.5 mL) was reacted at120 ºC for 12 h under air. After then DMF was removed under reduced pressure and the residue was purified by a silica gel column, eluting with petroleum ether/EtOAc (50/1→10/1, v/v) to afford **3a-bisBoc** as a white solid (15 mg, 39% yield).

di-*tert*-butyl benzo[*c*]cinnoline-5,6-dicarboxylate(3a-bisBoc): White solid. M.p.: 131–133 ºC. **^{1}H NMR (500 MHz, $CDCl_3$)**: δ = 7.76 (d, J = 8.0 Hz, 2H), 7.27 (br s, 2H), 7.37 (t, J = 7.5 Hz, 2H), 7.31 (td, J = 7.5 Hz, 1.0 Hz, 2H), 1.48 (s, 18H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 128.0, 126.7, 126.3, 124.2, 123.5, 110.9, 82.2, 28.3 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{22}H_{26}N_2O_4^+$ $(M+H)^+$ 383.1965, found 383.1964.



Deprotection of 3a-bisBoc: The solution of **3a-bisBoc** (38 mg, 0.1 mmol) with K_2CO_3 (27.6 mg, 2 equiv) in DMF (0.5 mL) was reacted at 120 °C for 12 h under air. **3a** was not detected by TLC.

6. Studies on deprotection

Deprotection in different solvents:

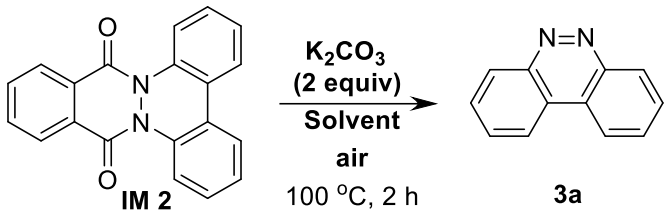


Table S3. Deprotection in different solvents.[a]

Entry	Solvent	Yield of **3a** (%)[b]
1	HOAc	0
2	PhCl	0
3	DCE	0
4	THF	20
5	MeCN	38
6	MeOH	100
7	DMSO	100
8	DMF	100
9	H_2O	0

[a]Reaction conditions: **IM 2** (0.1 mmol), K_2CO_3 (2 equiv) and solvent (1 mL) were stirred at 100 °C for 2 h under air.
[b]Isolated yield.

Deprotection with different bases:

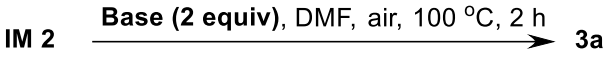
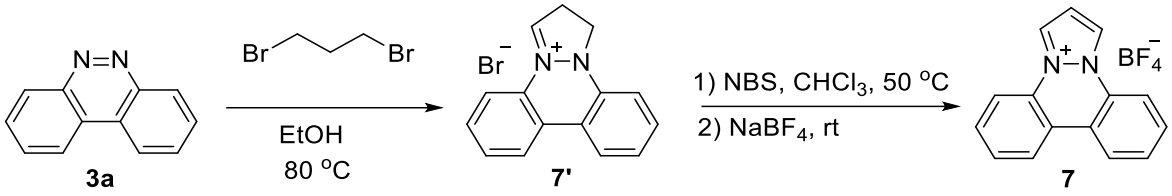


Table S4. Deprotection with different bases.[a]

Entry	Solvent	Yield of **3a** (%)[b]
1	$NaHCO_3$	12
2	NEt_3	0
3	NaOAc	21
4	K_2CO_3	100
5	Cs_2CO_3	100
6	DBU	100
7	K_3PO_4	46
8	NaOH	100
9	KO^tBu	100

[a]Reaction conditions: **IM 2** (0.1 mmol), base (2 equiv) and DMF (1 mL) were stirred at 100 °C for 2 h under air.
[b]Isolated yield.

7. Derivatization reactions



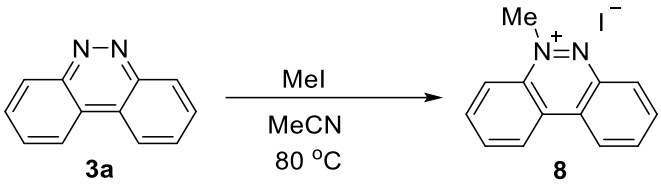
3a **7'** **7**

Compounds **7′** and **7** were prepared according to the modified procedure of reference:[6]

Synthesis of 7′: A mixture of benzo[*c*]cinnoline **3a** (74 mg, 0.4 mmol) and 1,3- dibromopropane (399.8 g, 2 mmol, 5 equiv) in EtOH (1 ml) was reacted at 80 °C for 24 h. Filtration of the cooled mixture yielded **7′** as red solid (84 mg, 70% yield) without further purification for next step.

Synthesis of 7: To a solution of bromide salt **7′** (60 mg, 0.2 mmol) in $CHCl_3$ (1 mL) was added N-bromosuccinimide (46.3 mg, 0.26 mmol, 1.3 equiv). The mixture was reacted at 50 °C for 3 h. Then $NaBF_4$ (110 mg, 5 equiv) was added and strired at room temperature for 10 h. After the anion was completely exchanged, MeOH (10 mL) was added and the mixture was filtered through a celite pad. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (100-200 mesh), eluting with CH_2Cl_2/MeOH (50/1→10/1, v/v) to provide **7** as a white solid (52 mg, 85% yield).

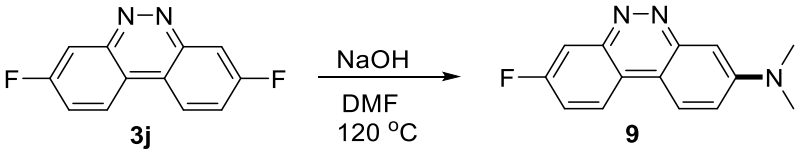
Benzo[*c*]pyrazolo[1,2-*a*]cinnolin-4-ium tetrafluoroborate (7): White solid. M.p.: > 240 ºC. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ = 9.93 (t, *J* = 3.5 Hz, 2H), 8.72 (t, *J* = 7.5 Hz, 2H), 8.54 (t, *J* = 6.5 Hz, 2H), 7.91–7.88 (m, 2H), 7.84–7.81 (m, 2H), 7.75–7.74 (m, 1H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 131.0, 130.0, 129. 6, 129.1, 124.4, 118.8, 116.6, 110.6 ppm. **^{19}F NMR (471 MHz, DMSO-*d*$_6$):** δ = -148.23 (s), -148.28 (s) ppm. **HRMS (ESI) *m/z*:** calcd for $C_{15}H_{11}N_2^+$ ([M−BF_4^-]$^+$) 219.0917, found 219.0918.



3a **8**

A mixture of **3a** (36 mg, 0.2 mmol), MeI (56.8 mg, 0.4 mmol, 2 equiv) and MeCN (1 mL) was stirred at 80 °C for 2 h. After the reaction was completed, the solvent was removed under reduced pressure, and the residue was purified by a silica gel column, eluting with CH_2Cl_2/MeOH (50/1→20/1, v/v) to afford salt **8** as yellow solid (58 mg, 90% yield).

5-Methylbenzo[*c*]cinnolin-5-ium iodide (8): Yellow solid. M.p.: 227–229 ºC. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ = 9.39 (d, *J* = 8.0 Hz, 1H), 9.33 (d, *J* = 8.5 Hz, 1H), 9.02 (d, *J* = 9.0 Hz, 1H), 8.88 (d, *J* = 8.5 Hz, 1H), 8.59 (t, *J* = 7.5 Hz, 1H), 8.47 (t, *J* = 7.5 Hz, 1H), 8.42–8.37 (m, 2H), 5.27 (s, 3H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 143.2, 140.0, 138.1, 135.7, 134.3, 133.8, 132.5, 128.8, 126.7, 124.8, 123.6, 121.8, 52.9 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{13}H_{11}N_2^+$ ([M−I^-]$^+$) 195.0917, found 195.0920.



3j **9**

Synthesis of 9: A solution of benzo[*c*]cinnoline **3j** (43.2 mg, 0.2 mmol) and NaOH (20 mg, 0.5 mmol, 2.5 equiv) in DMF (1 mL) was reacted at 120 °C for 4 h. DMF was removed under reduced pressure and the residue was purified by column chromatography on silica gel, eluting with petroleum ether/EtOAc (5/1→1/1, v/v) to afford **9** as orange solid (30 mg, 63%).

8-Fluoro-*N*,*N*-dimethylbenzo[*c*]cinnolin-3-amine (9): Orange solid. M.p.: 177–179 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.40–8.36 (m, 1H), 8.32–8.30 (m, 1H), 8.24 (dt, J = 9.0 Hz, 2.5 Hz, 1H), 7.80–7.78 (m, 1H), 7.58–7.54 (m, 1H), 7.45–7.42 (m, 1H), 3.18 (s, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 161.2 (d, $J_{C\text{-}F}$ = 246.9 Hz), 150.9, 147.5, 145.0 (d, $J_{C\text{-}F}$ = 10.0 Hz), 123.1 (d, $J_{C\text{-}F}$ = 8.8 Hz), 122.0, 121.4 (d, $J_{C\text{-}F}$ = 24.6 Hz), 120.3, 118.7, 115.0 (d, $J_{C\text{-}F}$ = 20.6 Hz), 111.7, 109.0, 40.6 ppm. **^{19}F NMR (471 MHz, $CDCl_3$):** δ = -112.56 (s) ppm. **HRMS (ESI) *m/z*:** calcd for $C_{14}H_{13}FN_3^+$ $(M+H)^+$ 242.1088, found 242.1087.

UV-vis absorption spectrum of 9:

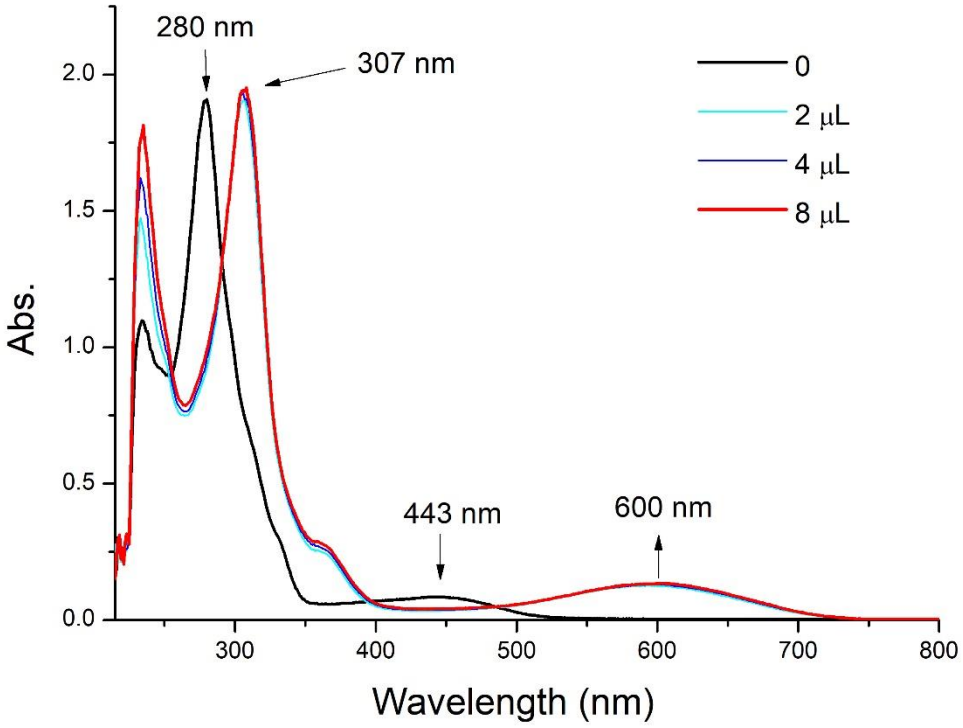
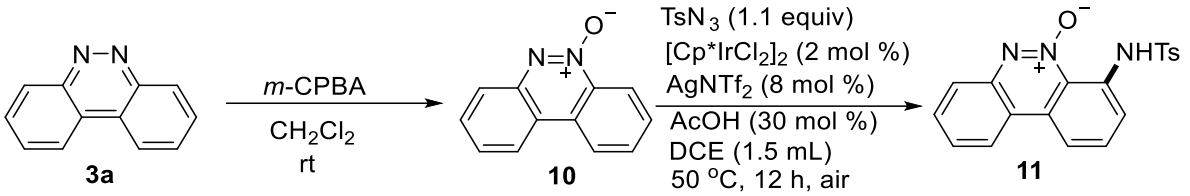


Figure S1. *UV-vis absorption spectrum of* ***9*** *in CH_2Cl_2 (0.1 mM)*

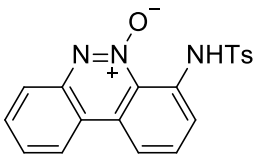


Synthesis of 10: To a solution of benzo[*c*]cinnoline **3a** (72 mg, 0.4 mmol) in CH_2Cl_2 (5 mL) was added *m*-chloroperoxybenzoic acid (*m*-CPBA, purity of 75%, 230.1 mg, 2.5 equiv) and the mixture was reacted at room temperature for 4 h. Then the mixture was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel, eluting with CH_2Cl_2/MeOH (100/1→50/1, v/v) to afford desired *N*-oxide **10** as yellow solid (57 mg, 72% yield).

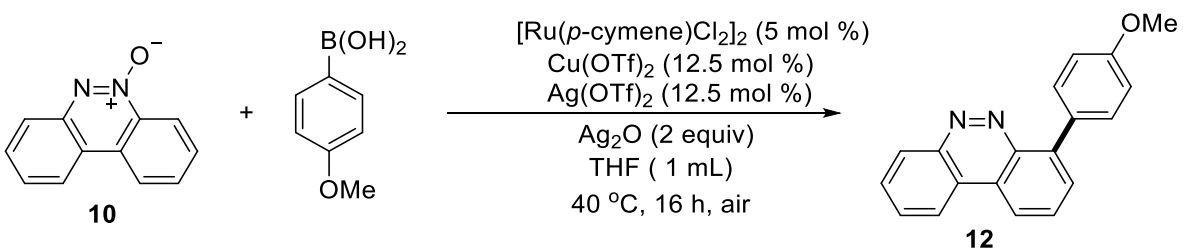
Benzo[*c*]cinnoline 5-oxide (10): Yellow solid. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.84 (d, J = 8.5 Hz, 1H), 8.50 (d, J = 8.5 Hz, 1H), 8.37 (d, J = 8.0 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.94 (t, J = 7.5 Hz, 1H), 7.81 (t, J = 7.5 Hz, 1H), 7.76 (t, J = 7.5 Hz, 1H), 7.70 (t, J = 7.5 Hz, 1H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 142.6, 132.8, 130.7, 130.3, 130.2, 129.1, 128.9, 128.4, 126.7, 122.6, 121. 4, 118.5 ppm. The NMR data are consistent with the literature.[7]

Synthesis of 11: To a dry Schlenk tube with a magnetic stir bar was added *N*-oxide **14** (39.2 mg, 0.2 mmol), azide (43.3 mg, 0.22 mmol, 1.1 equiv), $[IrCp^*Cl_2]_2$ (3.2 mg, 0.004 mmol, 2 mol%), $AgNTf_2$ (6.2 mg, 0.016 mmol, 8 mol%), AcOH (3.6 mg, 0.06 mmol, 30 mol%) and 1,2-dichloroethane (1 mL) under air. The reaction mixture was stirred at 50 °C for 12 h before filtered through a pad of celite and then washed with CH_2Cl_2 (10 mL × 3). Organic solvents were concentrated under reduced pressure and the residue was purified by chromatography on silica gel, eluting with petroleum ether/EtOAc (5/1, v/v) to afford **11**.

4-(4-methylphenylsulfonamido)benzo[*c*]cinnoline 5-oxide (11)



Yellow solid (45 mg, 62% yield). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 12.96 (s, 1H), 8.28 (d, J = 8.0 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.97 (d, J = 8.5 Hz, 1H), 7.85 (d, J = 7.0 Hz, 2H), 7.77 (t, J = 7.5 Hz, 2H), 7.72 (t, J = 7.5 Hz, 1H), 7.21 (d, J = 7.5 Hz, 2H), 2.32 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 144.4, 141.8, 136.4, 134.9, 133.3, 131.4, 131.2, 130.4, 129.9, 127.6, 126.9, 121.9, 118.9, 118.7, 116.3, 21.7 ppm. The NMR data are consistent with the literature.[8]

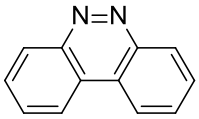


Synthesis of 12: To a dry Schlenk tube with a magnetic stir bar was added *N*-oxide **14** (39.2 mg, 0.2 mmol), (4-methoxyphenyl)boronic acid (91.2mg, 0.6 mmol, 3 equiv), [Ru(*p*-cymene)Cl_2]$_2$ (6 mg, 5 mol%), Cu(OTf)$_2$ (9 mg, 12.5 mol%), Ag(OTf)$_2$ (6.4 mg, 12.5 mol%), Ag_2O (93 mg, 0.4 mmol, 2 equiv) and THF (1 mL) under air. The reaction mixture was stirred at 40 °C for 16 h before filtered through a pad of celite and then washed with CH_2Cl_2 (10 mL × 3). Organic solvents were concentrated under reduced pressure and the residue was purified by chromatography on silica gel, eluting with petroleum ether/EtOAc (100/1-20/1, v/v) to afford **12**.

4-(4-methoxyphenyl)benzo[*c*]cinnoline (12): Yellow solid (23 mg, 40% yield). M.p.: 183–185 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.27 – 8.22 (m, 3H), 7.89 (t, *J* = 7.0 Hz, 1H), 7.85 – 7.78 (m, 5H), 7.10 (d, *J* = 8.5 Hz, 2H), 3.93 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 159.7, 143.4, 142.2, 140.8, 132.3, 131.0, 130.8, 130.6, 130.2, 130.0, 129.2, 128.4, 113.8, 55.5 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{19}H_{14}N_2NaO_2^+$ $(M + Na)^+$ 309.0999, found 309.1003.

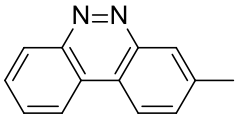
8. Experimental data for the described substances

benzo[*c*]cinnoline (3a and 3s)[7]



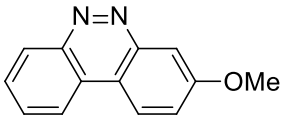
White solid (**3a**: 36 mg, 99% yield; **3s**: 35 mg, 95% yield), purification via a silica (100–200 meshes) gel column (petroleum ether/EtOAc = 20/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.78–8.76 (m, 2H), 8.61–8.59 (m, 2H), 7.95–7.91 (m, 4H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 145.4, 131.8, 131.4, 129.5, 121.6, 121.2 ppm. The NMR data are consistent with the literature.[9]

3-methylbenzo[*c*]cinnoline (3b)



Light yellow solid (31 mg, 85% yield), purification via a silica (100–200 meshes) gel column (petroleum ether/EtOAc = 20/1, v/v). M. p.: 122–124 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.71–8.70 (m, 1H), 8.50 (br, 2H), 8.44–8.41 (m, 1H), 7.88–7.83 (m, 2H), 7.72–7.70 (m, 1H), 2.66 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 145.7, 145.3, 139.8, 133.6, 131.6, 131.3, 130.5, 128.9, 121.4, 121.3, 121.2, 118.9, 21.8 ppm. The NMR data are consistent with the literature.[7]

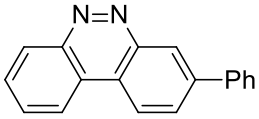
3-methoxybenzo[*c*]cinnoline (3c)



White solid (38 mg, 90% yield), purification via a silica (100–200 meshes) gel column (petroleum ether/EtOAc = 20/1, v/v). M. p.: 153–155 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.72 (d, *J* = 8.0 Hz, 1H), 8.50 (t, *J* = 7.5 Hz, 2H), 8.11 (s, 1H), 7.90–7.82 (m, 2H), 7.56 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H), 4.08 (s, 3H) ppm. **^{13}C NMR (125 MHz,**

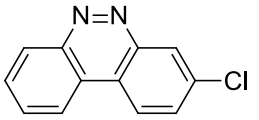
$CDCl_3$): δ = 160.6, 147.0, 145.2, 134.5, 131.9, 131.4, 128.5, 124.1, 122.9, 121.2, 115. 8, 109.5, 56.0 ppm. The NMR data are consistent with the literature.[7]

3-phenylbenzo[*c*]cinnoline (3d)



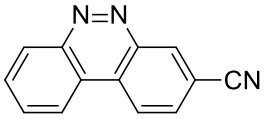
White solid (33 mg, 63% yield), purification via a silica (100–200 meshes) gel column (petroleum ether/EtOAc = 20/1, v/v). M. p.: 137–139 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.93 (s, 1H), 8.73–8.70 (m, 1H), 8.57–8.49 (m, 2H), 8.11 (t, *J* = 7.3 Hz, 1H), 7.89–7.85 (m, 2H), 7.81–7.79 (m, 2H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.45 (t, *J* = 7.0 Hz, 1H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 145.8, 145.4, 142.2, 139.5, 131.7, 131.4, 130.8, 129.3, 128.9, 128.4, 127.5, 122.1, 121.5, 120.8, 119.9 ppm. The NMR data are consistent with the literature.[10]

3-chlorobenzo[*c*]cinnoline (3e)



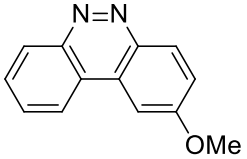
White solid (28 mg, 64% yield), purification via a silica (100–200 meshes) gel column (petroleum ether/EtOAc = 20/1, v/v). M. p.: 140–142 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.76–8.72 (m, 2H), 8.53–8.50 (m, 2H), 7.95–7.92 (m, 2H), 7.85 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 145.6, 145.5, 135.2, 132.5, 132.3, 131.6, 130.4, 129.8, 123.3, 121.4, 120.5, 119.6 ppm. The NMR data are consistent with the literature.[11]

benzo[*c*]cinnoline-3-carbonitrile (3f)



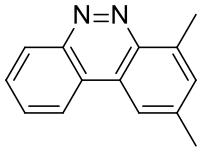
White solid (41 mg, 99% yield), purification via a silica (100–200 meshes) gel column (petroleum ether/EtOAc = 20/1, v/v). M. p.: 197–199 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 9.11 (s, 1H), 8.84 (d, *J* = 8.5 Hz, 1H), 8.70 (d, *J* = 8.5 Hz, 1H), 8.61 (d, *J* = 8.5 Hz, 1H), 8.09–8.02 (m, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 146.0, 144.0, 136.8, 132.8, 132.6, 131.9, 131.3, 124.0, 123.4, 121.9, 119.6, 117.9, 113.0 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{13}H_8N_3^+$ $(M + H)^+$ 206.0713, found 206.0716.

2-methoxybenzo[*c*]cinnoline (3g)



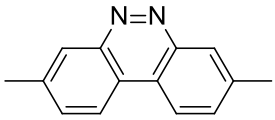
White solid (36 mg, 86% yield), purification via a silica (100–200 meshes) gel column (petroleum ether/EtOAc = 20/1, v/v). M. p.: 141–143 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.67 (d, *J* = 7.5 Hz, 1H), 8.61 (d, *J* = 9.0 Hz, 1H), 8.45 (d, *J* = 7.0 Hz, 1H), 7.88–7.83 (m, 2H), 7.75 (s, 1H), 7.46 (dd, *J* = 9.0 Hz, 2.0 Hz, 1H), 4.05 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 162.0, 145.2, 142.1, 133.3, 131.1, 130.9, 129.4, 123.3, 121.5, 121.1, 120.4, 100.6, 56.0 ppm. The NMR data are consistent with the literature.[12]

2,4-dimethylbenzo[*c*]cinnoline (3h)



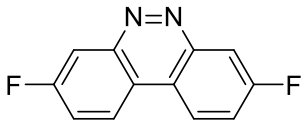
White solid (32 mg, 76% yield), purification via a silica (100–200 meshes) gel column (petroleum ether/EtOAc = 20/1, v/v). M. p.: 120–122 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.69–8.67 (m, 1H), 8.51–8.49 (m, 1H), 8.13 (s, 1H), 7.86–7.83 (m, 2H), 7.49 (s, 1H), 3.10 (s, 3H), 2.60 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 145.1, 143.0, 142.3, 139.6, 132.0, 131.1, 131.0, 129.0, 121.7, 121.2, 121.1, 118.5, 22.5, 18.1 ppm. The NMR data are consistent with the literature.[11]

3,8-dimethylbenzo[*c*]cinnoline (3i)



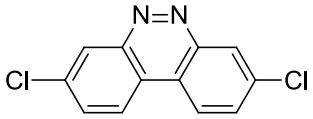
White solid (38 mg, 91% yield), purification via a silica (100–200 meshes) gel column (petroleum ether/EtOAc = 20/1, v/v). M.p.: 145–147 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.49 (s, 2H), 8.42 (dd, J = 8.5 Hz, 3.5 Hz, 2H), 7.71 (d, J = 8.5 Hz, 2H), 2.67 (s, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 145.6, 139.3, 133.6, 130.4, 121.2, 119.1, 21.8 ppm. The NMR data are consistent with the literature.[13]

3,8-difluorobenzo[*c*]cinnoline(3j)



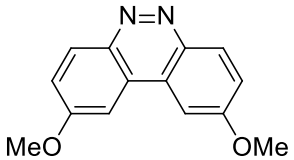
White solid (18 mg, 42% yield), purification via a silica (100–200 meshes) gel column (petroleum ether/EtOAc = 20/1, v/v). M.p.: 165–167 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.57–8.55 (m, 2H), 8.40 (d, J = 8.0 Hz, 2H), 7.72 (t, J = 8.5 Hz, 2H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 162.3 (d, $J_{C\text{-}F}$ = 250.4 Hz), 161.1 (d, $J_{C\text{-}F}$ = 11.1 Hz), 123.7 (d, $J_{C\text{-}F}$ = 9.6 Hz), 122.5 (d, $J_{C\text{-}F}$ = 24.8 Hz), 117.4, 115.5 (d, $J_{C\text{-}F}$ = 20.3 Hz) ppm. **^{19}F NMR (471 MHz, $CDCl_3$):** δ = -109.14 (s) ppm. The NMR data are consistent with the literature.[14]

3,8-dichlorobenzo[*c*]cinnoline (3k)



White solid (32 mg, 64% yield), purification via a silica (100–200 meshes) gel column (petroleum ether/EtOAc = 20/1, v/v). M.p.: 143–145 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.73 (s, 2H), 8.47 (d, J = 8.0 Hz, 2H), 7.88 (d, J = 7.5 Hz, 2H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 145.7, 135.6, 133.0, 130.6, 123.1, 119.0 ppm. The NMR data are consistent with the literature.[13]

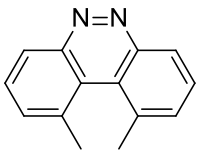
2,9-dimethoxybenzo[*c*]cinnoline (3l)



Gray solid (40 mg, 83% yield), purification via a silica (100–200 meshes) gel column (petroleum ether/EtOAc = 10/1, v/v). M.p.: 156–158 ºC. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.56 (d, J = 9.0 Hz, 2H), 7.64 (d, J = 2.0 Hz, 2H), 7.64 (dd,

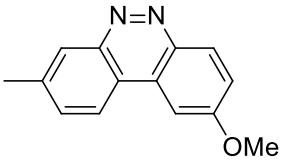
J = 9.0 Hz, 2.5 Hz, 2H), 4.06 (s, 6H) ppm. **^{13}C NMR (125 MHz, CDCl$_3$):** δ = 161.4, 141.9, 133.0, 123.1, 120.4, 100.7, 56.0 ppm. The NMR data are consistent with the literature.[15]

1,10-dimethylbenzo[*c*]cinnoline (3m)



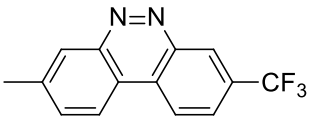
White solid (27 mg, 65% yield), purification via a silica (100–200 meshes) gel column (petroleum ether/EtOAc = 20/1, v/v). M.p.: 120–123 ºC. **^{1}H NMR (500 MHz, CDCl$_3$):** δ = 8.56 (d, *J* = 8.0 Hz, 2H), 7.83 (t, *J* = 7.5 Hz, 2H), 7.74 (d, *J* = 7.5 Hz, 2H), 2.65 (s, 6H) ppm. **^{13}C NMR (125 MHz, CDCl$_3$):** δ = 146.5, 134.5, 133.8, 128.5, 127.8, 121.2, 22.6 ppm. The NMR data are consistent with the literature.[15]

2-methoxy-8-methylbenzo[*c*]cinnoline (3n)



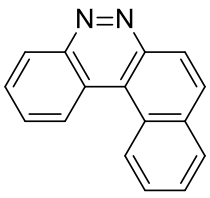
White solid (28 mg, 62% yield), purification via a silica (100–200 meshes) gel column (petroleum ether/EtOAc = 20/1, v/v). **^{1}H NMR (500 MHz, CDCl$_3$):** δ = 8.58–8.55 (m, 1H), 8.42 (s, 1H), 8.30 (t, *J* = 7.5 Hz, 1H), 7.69–7.63 (m, 2H), 7.43–7.40 (m, 1H), 4.04 (s, 3H), 2.65 (s, 3H) ppm. **^{13}C NMR (125 MHz, CDCl$_3$):** δ = 161.9, 145.4, 142.0, 139.8, 133.2, 132.9, 130.1, 123.3, 121.3, 120.0, 118.9, 100.4, 56.0, 21.8 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{14}H_{13}N_2O^+$ $(M + H)^+$ 225.1022, found 225.1021.

3-methyl-8-(trifluoromethyl)benzo[*c*]cinnoline (3o)



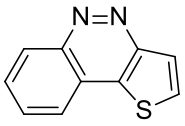
White solid (26 mg, 50% yield), purification via a silica (100–200 meshes) gel column (petroleum ether/EtOAc = 20/1, v/v). M.p.: 148–150 ºC. **^{1}H NMR (500 MHz, CDCl$_3$):** δ = 8.99 (s, 1H), 8.64–8.61 (m, 1H), 8.55 (s, 1H), 8.47–8.45 (m, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.80 (d, *J* = 8.5 Hz, 1H), 2.71 (s, 3H) ppm. **^{13}C NMR (125 MHz, CDCl$_3$):** δ = 146.2, 144.1, 141.4, 134.4, 130.9 (q, $J_{C\text{-}F}$ = 33.3 Hz), 130.8, 129.1 (q, $J_{C\text{-}F}$ = 3.9 Hz), 127.2 (q, $J_{C\text{-}F}$ = 3.0 Hz), 123.8 (q, $J_{C\text{-}F}$ = 271.1 Hz), 123.4, 122.9, 121.6, 117.8, 21.9 ppm. **^{19}F NMR (471 MHz, CDCl$_3$):** δ = -62.46 (s) ppm. **HRMS (ESI) *m/z*:** calcd for $C_{14}H_{10}F_3N_2^+$ $(M + H)^+$ 263.0791, found 263.0794.

dibenzo[*c*,*f*]cinnoline (3p)



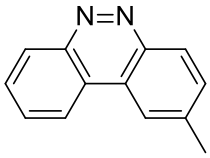
White solid (21 mg, 46% yield), purification via a silica (100–200 meshes) gel column (petroleum ether/EtOAc = 20/1, v/v). M.p.: 165–167 ºC. **^{1}H NMR (500 MHz, CDCl$_3$):** δ = 9.25–9.23 (m, 1H), 9.16 (d, *J* = 8.0 Hz, 1H), 8.90 (d, *J* = 3.0 Hz, 1H), 8.65 (d, *J* = 9.0 Hz, 1H), 8.21 (d, *J* = 9.0 Hz, 1H), 8.16–8.14 (m, 1H), 8.04–7.98 (m, 2H), 7.87–7.83 (m, 2H) ppm. **^{13}C NMR (125 MHz, CDCl$_3$):** 147.5, 145.0, 135.1, 131.9, 131.5, 131.0, 129.4, 129.1, 129.0, 128.5, 127.8, 127.6, 125.7, 122.0, 119.5.ppm. The NMR data are consistent with the literature.[16]

thieno[3,2-*c*]cinnoline (3q)



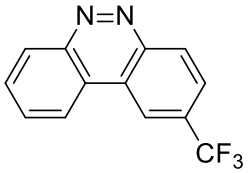
White solid (25 mg, 68% yield), purification via a silica (100–200 meshes) gel column (petroleum ether/EtOAc = 20/1, v/v). M.p.: 124–126 ºC. **^{1}H NMR (500 MHz, CDCl$_3$):** δ = 8.72–8.70 (m, 1H), 8.12–8.09 (m, 2H), 7.85–7.83 (m, 2H), 7.78 (d, J = 5.5 Hz, 1H) ppm. **^{13}C NMR (125 MHz, CDCl$_3$):** δ = 155.0, 145.2, 132.8, 131.7, 131.1, 129.4, 128.6, 125.9, 122.9, 122.5 ppm. The NMR data are consistent with the literature.[17]

2-methylbenzo[*c*]cinnoline (3t)



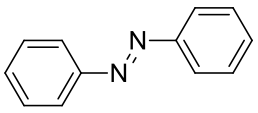
White solid (30 mg, 78% yield), purification via a silica (100–200 meshes) gel column (petroleum ether/EtOAc = 20/1, v/v). M.p.: 115–117 ºC. **^{1}H NMR (500 MHz, CDCl$_3$):** δ = 8.73–8.73 (m, 1H), 8.63 (d, J = 8.5 Hz, 1H), 8.57–8.56 (m, 1H), 8.35 (s, 1H), 7.90–7.88 (m, 2H), 7.72 (d, J = 8.5 Hz, 1H), 2.70 (s, 3H) ppm. **^{13}C NMR (125 MHz, CDCl$_3$):** δ = 145.5, 144.4, 142.5, 131.4, 131.3 (2C), 131.2, 129.2, 121.5, 121.1, 121.0, 120.8, 22.6 ppm. The NMR data are consistent with the literature.[18]

2-(trifluoromethyl)benzo[*c*]cinnoline (3u)



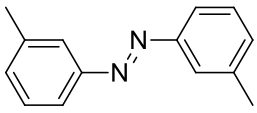
White solid (20 mg, 40% yield), purification via a silica (100–200 meshes) gel column (petroleum ether/EtOAc = 20/1, v/v). M.p.: 112–114 ºC. **^{1}H NMR (500 MHz, CDCl$_3$):** δ = 8.91–8.89 (m, 2H), 8.84–8.83 (m, 1H), 8.65–8.63 (m, 1H), 8.11 (d, J = 8.5 Hz, 1H), 8.02–8.01 (m, 2H) ppm. **^{13}C NMR (125 MHz, CDCl$_3$):** δ = 145.9, 145.5, 133.1, 132.8, 132.6, 131.9, 130.4, 125.5 (q, $J_{C\text{-}F}$ = 3.3 Hz), 123.8 (q, $J_{C\text{-}F}$ = 271.5 Hz), 121.6, 120.8, 120.4, 119.9 (q, $J_{C\text{-}F}$ = 4.0 Hz) ppm. **^{19}F NMR (471 MHz, CDCl3):** δ = -62.44 (s) ppm. **HRMS (ESI) *m/z*:** calcd for $C_{13}H_8N_2F_3^+$ $(M + H)^+$ 249.0634, found 249.0635.

(*E*)-1,2-diphenyldiazene (5a)



Orange solid (34 mg, 95% yield), purification via a silica (100–200 meshes) gel column (petroleum ether/EtOAc = 100/1, v/v). **^{1}H NMR (500 MHz, CDCl$_3$):** δ = 7.99–7.97 (m, 4H), 7.56–7.53 (m, 4H), 7.51–7.48 (m, 2H) ppm. **^{13}C NMR (125 MHz, CDCl$_3$):** δ = 152.8, 131.1, 129.2, 123.0 ppm. The NMR data are consistent with the literature.[19]

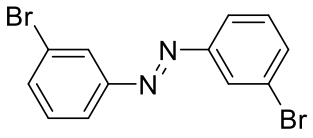
(*E*)-1,2-di-*m*-tolyldiazene (5b)



Orange solid (39 mg, 94% yield, *E/Z* = 15:1), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 100/1, v/v). **^{1}H NMR (500 MHz, CDCl$_3$, major):** δ = 7.75–7.74 (m, 4H), 7.42 (t, J = 7.5 Hz, 2H), 7.30 (d, J = 7.5

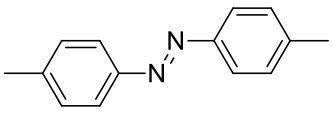
Hz, 2H), 2.47 (s, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$, major):** δ = 153.0, 139.1, 131.8, 129.0, 123.0, 120.6, 21.5 ppm. The NMR data are consistent with the literature.[19]

(*E*)-1,2-bis(3-bromophenyl)diazene (5c)



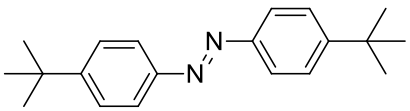
Orange solid (62 mg, 91% yield), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 100/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.05 (s, 2H), 7.88 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.0 Hz, 2H), 7.41 (t, J = 8.0 Hz, 2H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 153.3, 134.3, 130.7, 124.9, 123.4, 123.3 ppm. The NMR data are consistent with the literature.[20]

(*E*)-1,2-di-*p*-tolyldiazene (5d)



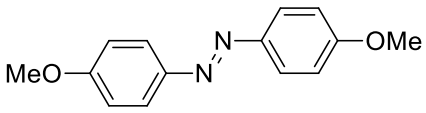
Orange solid (40 mg, 96% yield), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 100/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.82 (d, J = 8.5 Hz, 4H), 7.31 (d, J = 8.0 Hz, 4H), 2.44 (s, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 151.0, 141.3, 129.8, 122.9, 21.6 ppm. The NMR data are consistent with the literature.[19]

(*E*)-1,2-bis(4-(*tert*-butyl)phenyl)diazene (5e)



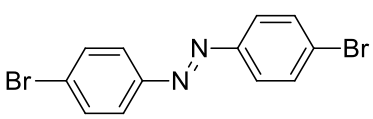
Orange solid (58 mg, 98% yield), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 100/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.84 (d, J = 8.5 Hz, 4H), 7.53 (d, J = 8.5 Hz, 4H), 1.38 (s, 18H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 154.4, 150.9, 126.1, 122.6, 35.1, 31.4 ppm. The NMR data are consistent with the literature.[21]

(*E*)-1,2-bis(4-methoxyphenyl)diazene (5f)



Orange solid (47 mg, 98% yield), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 50/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.88 (d, J = 8.5 Hz, 4H), 7.01 (d, J = 9.0 Hz, 4H), 3.89 (s, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 161.7, 147.2, 124.5, 114.3, 55.7 ppm. The NMR data are consistent with the literature.[19]

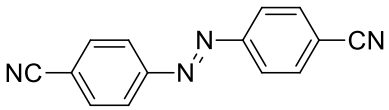
(*E*)-1,2-bis(4-bromophenyl)diazene (5g)



Orange solid (64 mg, 94% yield), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 100/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.79 (d, J = 8.5 Hz, 4H), 7.65 (d, J = 9.0 Hz, 4H) ppm.

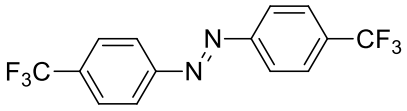
^{13}C NMR (125 MHz, $CDCl_3$): δ = 151.3, 132.6, 124.6, 122.3 ppm. The NMR data are consistent with the literature.[19]

(*E*)-1,2-bis(4-bromophenyl)diazene (5h)



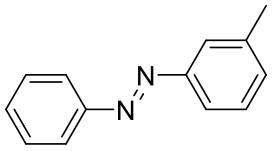
Orange solid (42 mg, 91% yield), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 20/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.03 (d, J = 8.5 Hz, 4H), 7.85 (d, J = 9.0 Hz, 4H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 154.1, 133.5, 123.9, 118.3, 115.3 ppm. The NMR data are consistent with the literature.[19]

(*E*)-1,2-bis(4-(trifluoromethyl)phenyl)diazene (5i)



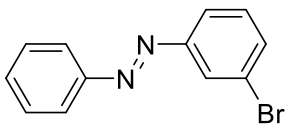
Orange solid (63 mg, 97% yield), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 50/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.04 (d, J = 8.0 Hz, 4H), 7.81 (d, J = 8.0 Hz, 4H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 154.2, 133.1 (q, $J_{C\text{-}F}$ = 32.4 Hz), 126.6 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.5, 123.9 (q, $J_{C\text{-}F}$ = 270.8 Hz) ppm. The NMR data are consistent with the literature.[19]

(*E*)-1-phenyl-2-(*m*-tolyl)diazene (6ab)



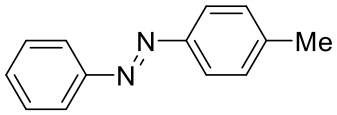
Orange solid (35 mg, 90% yield), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 100/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.92 (d, J = 7.5 Hz, 2H), 7.74–7.73 (m, 2H), 7.52 (t, J =7.5 Hz, 2H), 7.47 (t, J =7.5 Hz, 1H), 7.41 (t, J = 7.5 Hz, 1H), 7.30 (d, J = 7.5 Hz, 1H), 2.47 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 152.9, 152.9, 139.1, 131.9, 131.0, 129.2, 129.1, 123.1, 123.0, 120.7, 21.5. ppm. The NMR data are consistent with the literature.[21]

(*E*)-1-(3-bromophenyl)-2-phenyldiazene (6ac)



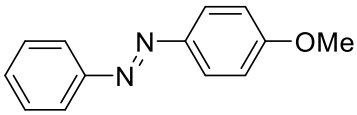
Orange solid (45 mg, 86% yield), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 100/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.07 (d, J = 2.0 Hz, 1H), 7.94–7.92 (m, 2H), 7.90–7.88 (m, 1H), 7.61–7.59 (m, 1H), 7.55–7.49 (m, 3H), 7.40 (t, J = 8.0 Hz, 1H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 153.7, 152.5, 133.7, 131.7, 130.6, 129.3, 124.8, 123.3, 123.2, 123.1 ppm. The NMR data are consistent with the literature.[21]

(*E*)-1-phenyl-2-(*p*-tolyl)diazene (6ad)



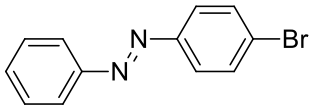
Orange solid (35 mg, 90% yield), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 100/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.92 (d, *J* = 7.5 Hz, 2H), 7.85 (d, *J* = 8.5 Hz, 2H), 7.52 (t, *J* = 7.0 Hz, 2H), 7.47 (t, *J* = 7.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 2.45 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 152.9, 150.9, 141.7, 130.8, 129.9, 129.2, 123.0, 122.9, 21.6 ppm. The NMR data are consistent with the literature.[21]

(*E*)-1-(4-methoxyphenyl)-2-phenyldiazene (6af)



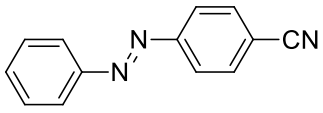
Orange solid (28 mg, 67% yield), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 50/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.94 (d, *J* = 9.0 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 7.0 Hz, 2H), 7.44 (t, *J* = 7.0 Hz, 1H), 7.03 (d, *J* = 9.0 Hz, 2H), 3.90 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 162.2, 152.9, 147.2, 130.5, 129.2, 124.9, 122.7, 114.3, 55.7 ppm. The NMR data are consistent with the literature.[21]

(*E*)-1-(4-bromophenyl)-2-phenyldiazene (6ag)



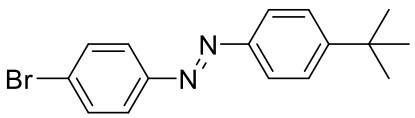
Orange solid (48 mg, 92% yield), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 100/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.92 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 8.5 Hz, 2H), 7.65 (d, *J* = 9.0 Hz, 2H), 7.54–7.47 (m, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 152.6, 151.5, 132.5, 131.5, 129.3, 125.5, 124.5, 123.1, ppm. The NMR data are consistent with the literature.[21]

(*E*)-4-(phenyldiazenyl)benzonitrile (6ah)



Orange solid (39 mg, 95% yield), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 30/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.99 (d, *J* = 8.5 Hz, 2H), 7.97–7.95 (m, 2H), 7.82 (d, *J* = 8.5 Hz, 2H), 7.56–7.54 (m, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 154.7, 152.5, 133.4, 132.4, 129.4, 123.5, 123.5, 118.6, 114.1 ppm. The NMR data are consistent with the literature.[22]

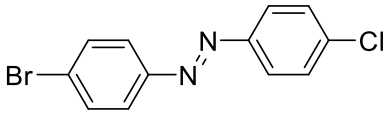
(*E*)-1-(4-bromophenyl)-2-(4-(*tert*-butyl)phenyl)diazene (6ge)



Orange solid (61 mg, 97% yield), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 100/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.85 (d, *J* = 8.5 Hz, 2H), 7.79 (d, *J* = 9.0 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 9.0 Hz, 2H), 1.38 (s, 9H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):**

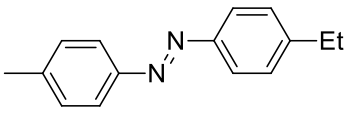
δ = 155.2, 151.7, 150.6, 132.4, 126.2, 125.1, 124.4, 122.8, 35.2, 31.4 ppm. The NMR data are consistent with the literature.[22]

(*E*)-1-(4-bromophenyl)-2-(4-chlorophenyl)diazene (6gi)



Orange solid (58 mg, 99% yield), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 100/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.87 (d, J = 8.5 Hz, 2H), 7.79 (d, J = 8.5 Hz, 2H), 7.65 (d, J = 9.0 Hz, 2H), 7.49 (d, J = 9.0 Hz, 2H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 132.6, 129.6, 124.6, 124.4 ppm. The NMR data are consistent with the literature.[23]

(*E*)-1-(4-ethylphenyl)-2-(*p*-tolyl)diazene (6kd)



Orange solid (following procedure B, 43 mg, 95% yield), purification via a silica (200–300 meshes) gel column (petroleum ether/EtOAc = 100/1, v/v). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.86–7.82 (m, 4H), 7.35–7.31 (m, 4H), 2.74 (q, J = 7.5 Hz, 2H), 2.44 (s, 3H), 1.30 (td, J = 7.5 Hz, 1.0 Hz, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 151.2, 151.0, 147.6, 141.3, 129.8, 128.6, 122.9, 122.9, 29.0, 21.6, 15.6 ppm. The NMR data are consistent with the literature.[22]

8. References

[1] (a) Z. Liu, D. Zhu, B. Luo, N. Zhang, Q. Liu, Y. Hu, R. Pi, P. Huang and S. Wen, Mild Cu(I)-catalyzed cascade reaction of cyclic diaryliodoniums, sodium azide, and alkynes: Efficient synthesis of triazolophenanthridines, *Org. Lett*., 2014, **16**, 5600–5603; (b) D. Zhu, Y. Wu, B. Wu, B. Luo, A. Ganesan, F.-H. Wu, R. Pi, P. Huang and S. Wen, Three-component Pd/Cu-catalyzed cascade reactions of cyclic iodoniums, alkynes, and boronic acids: An approach to methylidenefluorenes, *Org. Lett.,* 2014, **16**, 2350−2353; (c) B. Wu and N. Yoshikai, Conversion of 2-iodobiaryls into 2,2′-diiodobiaryls via oxidation-iodination sequences: A versatile route to ladder-type heterofluorenes, *Angew. Chem., Int. Ed.*, 2015, **54**, 8736–8739; (d) M. Lanzi, Q. Dherbassy and J. Wencel-Delord, Cyclic diaryl λ^3-bromanes as original aryne precursors, *Angew. Chem., Int. Ed*., 2021, **60**, 14852–14857.

[2] (a) M. Bielawski, M. Zhu and B. Olofssona, Efficient and General One-Pot Synthesis of Diaryliodonium Triflates: Optimization, Scope and Limitations, *Adv. Synth. Catal*., 2007, **349**, 2610–2618; (b) M. Reitti, P. Villo and B. Olofsson, One-Pot C−H Functionalization of Arenes by Diaryliodonium Salts, *Angew.Chem., Int. Ed*., 2016, **55**, 8928–8932.

[3] S. Mayakrishnan, Y. Arun, C. Balachandran, N. Emi, D. Muralidharana and P. T. Perumal, Synthesis of cinnolines via Rh(iii)-catalysed dehydrogenative C–H/N–H functionalization: aggregation induced emission and cell imaging, *Org. Biomol. Chem.*, 2016, **14**, 1958–1968.

[4] S. Li, H. Lv, R. Xie, Y. Yu, X. Ye and X. Kong, The C-H Activation/Bidirecting Group Strategy for Selective Direct Synthesis of Diverse 1,1′-Biisoquinolines, *Org. Lett.*, 2020, **22,** 4207−4212.

[5] R. Xie, H. Lv, X. Ye and X. Kong, S. Li, Cu-Catalyzed tandem N-arylation of phthalhydrazides with cyclic iodoniums to yield dihydrobenzo[c]cinnolines, *Org. Biomol. Chem.*, 2020, **18**, 4824–4830.

[6] D. G. Farnum, R. J. Alaimo and J. M. Dunston, Synthesis of azaindenes. The benzo[c]pyrazolo-[1,2-a]cinnolinium cation, a novel heteroaromatic cation, *J. Org. Chem.*, 1967, **32**, 1130−1134.

[7] A. Slevin, T. Koolmeister and M. Scobie, A versatile synthesis of diverse 3,4-fused cinnolines via the base-catalysed condensation of 2-amino-2′ -nitrobiaryls, *Chem. Commun.*, 2007, 2506−2508.

[8] H. Hwang, J. Kim, J. Jeong and S. Chang, Regioselective introduction of heteroatoms at the C-8 position of quinoline N-oxides: Remote C–H activation using N-oxide as a stepping stone. *J. Am. Chem. Soc.*, 2014, **136**, 10770−10776.

[9] D. S. Lee, T. Chatterjee, J. Ban, H. Rhee and E. J. Cho, *ChemistrySelect* 2018, **3**, 2092–2095.

[10] N.C. Jamieson and G.E Lewis, Photochemical reactions of azo compounds. IX. Further studies related to the photochemical reactions of bisazo compounds, *Aust. J. Chem.*, 1967, **20**, 321−336.

[11] G.M Badger, R.J Drewer and G.E Lewis, Photochemical reactions of azo compounds. III. Photochemical cyclodehydrogenations of substituted azobenzenes, *Aust. J. Chem.*, 1964, **17**, 1036–1049.

[12] M. Ramanathan and S. T. Liu, Preparation of Substituted Phenanthridines from the Coupling of Aryldiazonium Salts with Nitriles: A Metal Free Approach, *J. Org. Chem.*, 2015, **80**, 5329–5336.

[13] H. R. Bjørsvik, R. R. González, and L. Liguori, Investigations of a Novel Process to the Framework of Benzo[c]cinnoline, *J. Org. Chem.*, 2004, **69**,7720−7727.

[14] E. Kiliç and E. Tüzün, Synthesis of Fluorobenzo[c]Cinnolines, *Synthetic Communications*, 1992, **22**, 545−551.

[15] H. Fischer and F. A. Neugebauer, Radical cations and anions of benzo[c]cinnolines: an electron spin resonance study, *J . Chem. Soc. Perkin Trans.*, II., 1989, 727−730.

[16] Y. Takeda, M. Okazakib and S. Minakata, Oxidative skeletal rearrangement of 1,1′ -binaphthalene-2,2′ -diamines (BINAMs) via C‐C bond cleavage and nitrogen migration: a versatile synthesis of U-shaped azaacenes, *Chem. Commun.*,2014, **50**, 10291–10294.

[17] J. W. Barton, D. J. Lapham and D. J. Rowe, Intramolecular diazo coupling of 2-aminophenylthiophenes. The formation of isomeric thieno[*c*]cinnolines, *J . Chem. Soc. Perkin Trans.*, I, 1985, 131–134.

[18] G.M Badger, R.J Drewer and G.E Lewis, Photochemical Reactions of Azo Compounds. II. Photochemical Cyclodehydrogenations of Methyl- and Dimethylazobenzenes, *Aust. J. Chem.*, 1963, **16**, 1042−1047.

[19] N. Sakai, S. Asama, S. Anai and T. Konakahara, One-pot preparation of azobenzenes from nitrobenzenes by the combination of an indium-catalyzed reductive coupling and a subsequent oxidation, *Tetrahedron*, 2014, **70**, 2027–2033.

[20] X. Wang, X. Wang, C. Xia and L. Wu, Visible-light-promoted oxidative dehydrogenation of hydrazobenzenes and transfer hydrogenation of azobenzenes, *Green Chem.*, 2019, **21**, 4189–4193.

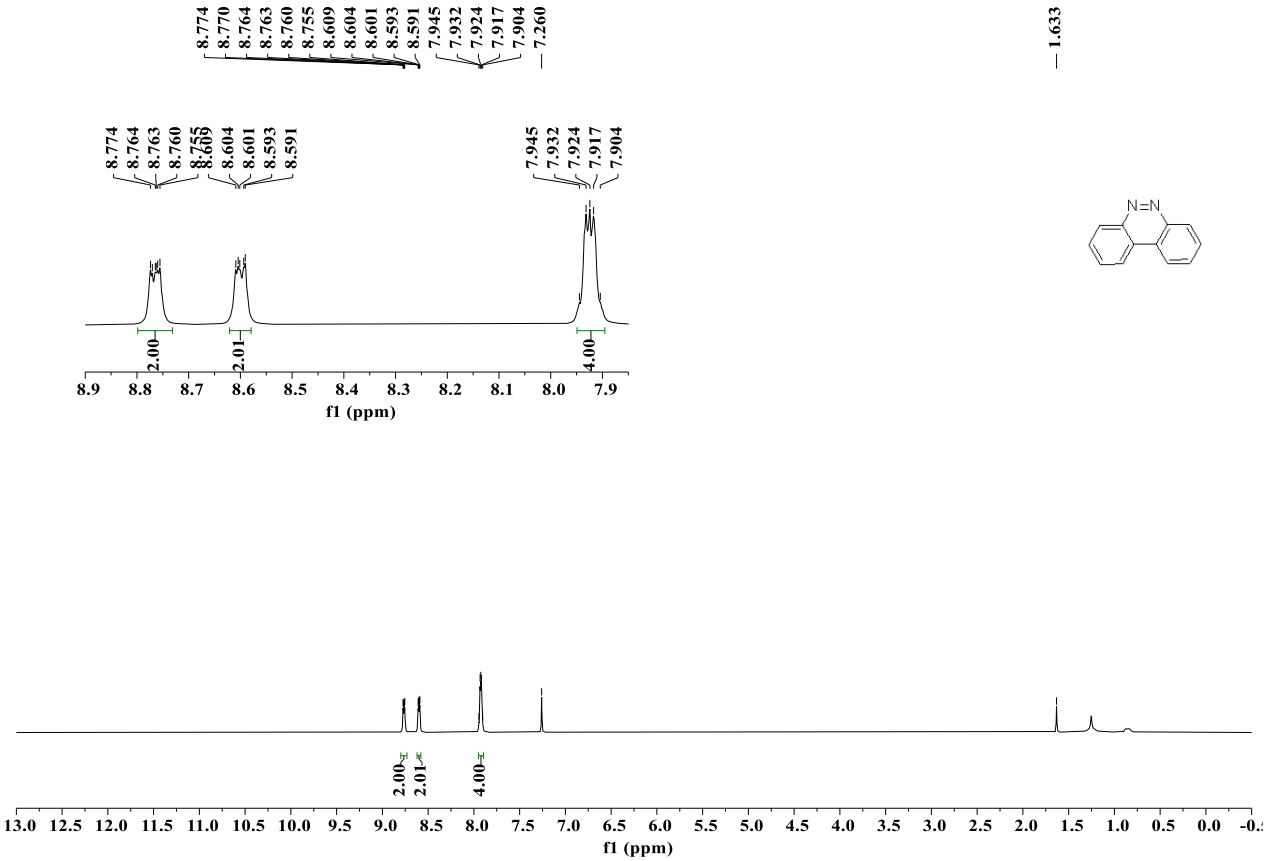
[21] H. Lv, R. D. Laishram, Y. Yang, J. Li, D. Xu,Y. Zhan, Y. Luo, Z. Su, S. More and B. Fan, TEMPO catalyzed oxidative dehydrogenation of hydrazobenzenes to azobenzenes, *Org. Biomol. Chem.*, 2020, **18**, 3471–3474.

[22] Y. Wang, R. Xie, L. Huang, Y.-N. Tian, S. Lv, X. Kong and S. Li, Divergent synthesis of unsymmetrical azobenzenes via Cu-catalyzed C–N coupling, *Org. Chem. Front.*, 2021, **8**, 5962–5967.

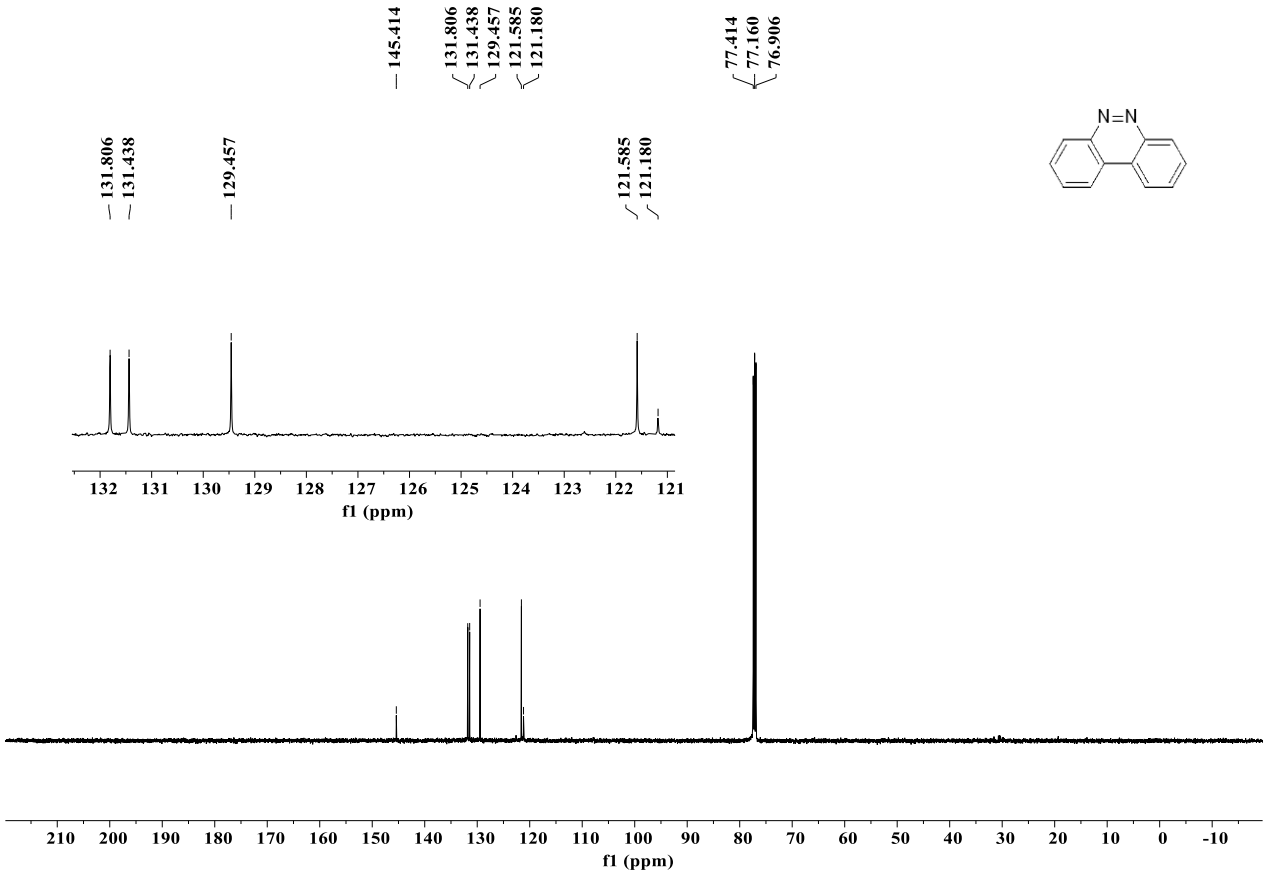
[23] J. Wang, J. He, C. Zhi, B. Luo, X. Li, Y. Pan, X. Cao and H. Gu, Highly efficient synthesis of azos catalyzed by the common metal copper (0) through oxidative coupling reactions, *RSC Adv.*, 2014, **4**, 16607–16611.

9. Copies of ^{1}H, ^{13}C and ^{19}F NMR spectra

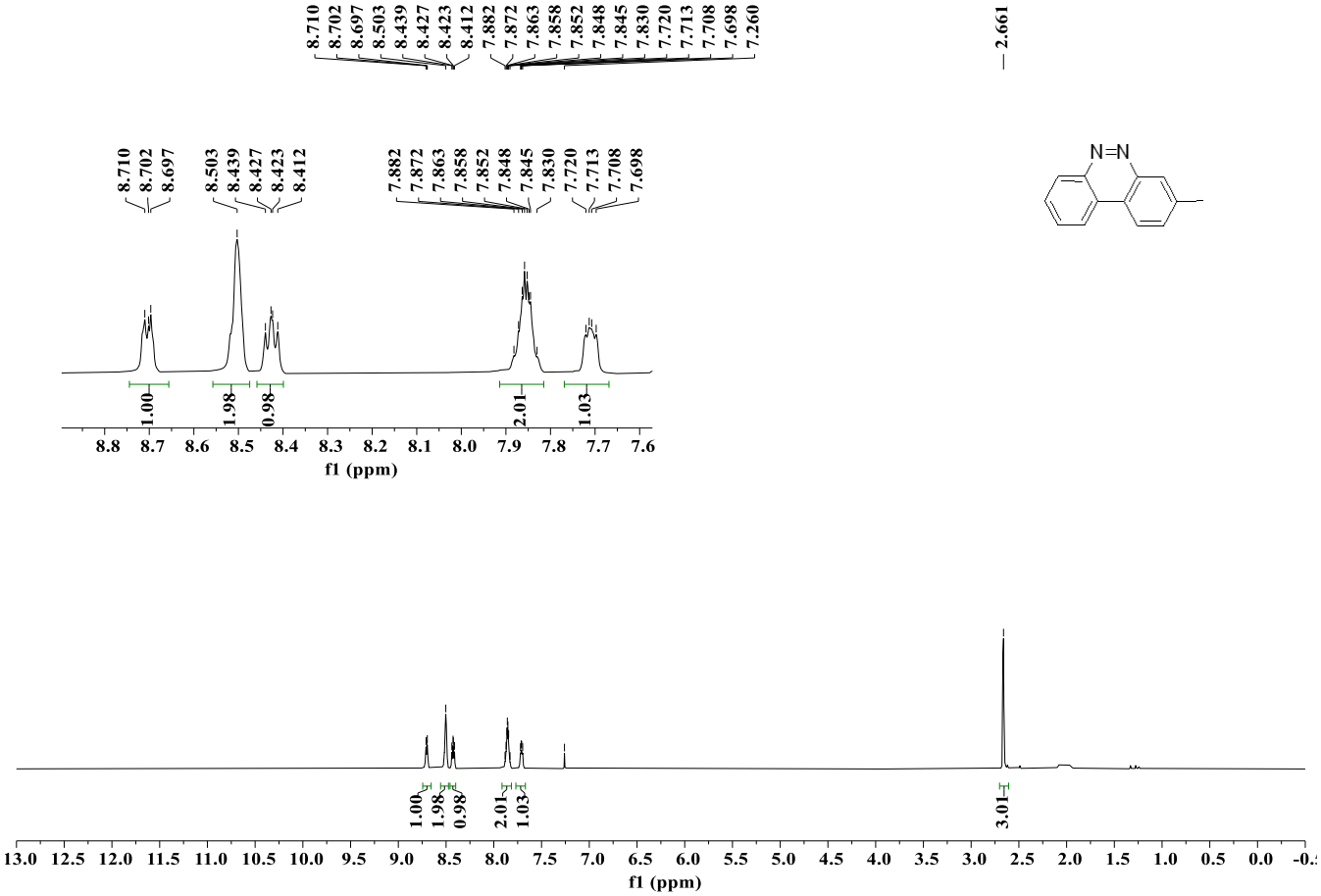
^{1}H NMR (500 MHz, $CDCl_3$) of 3a



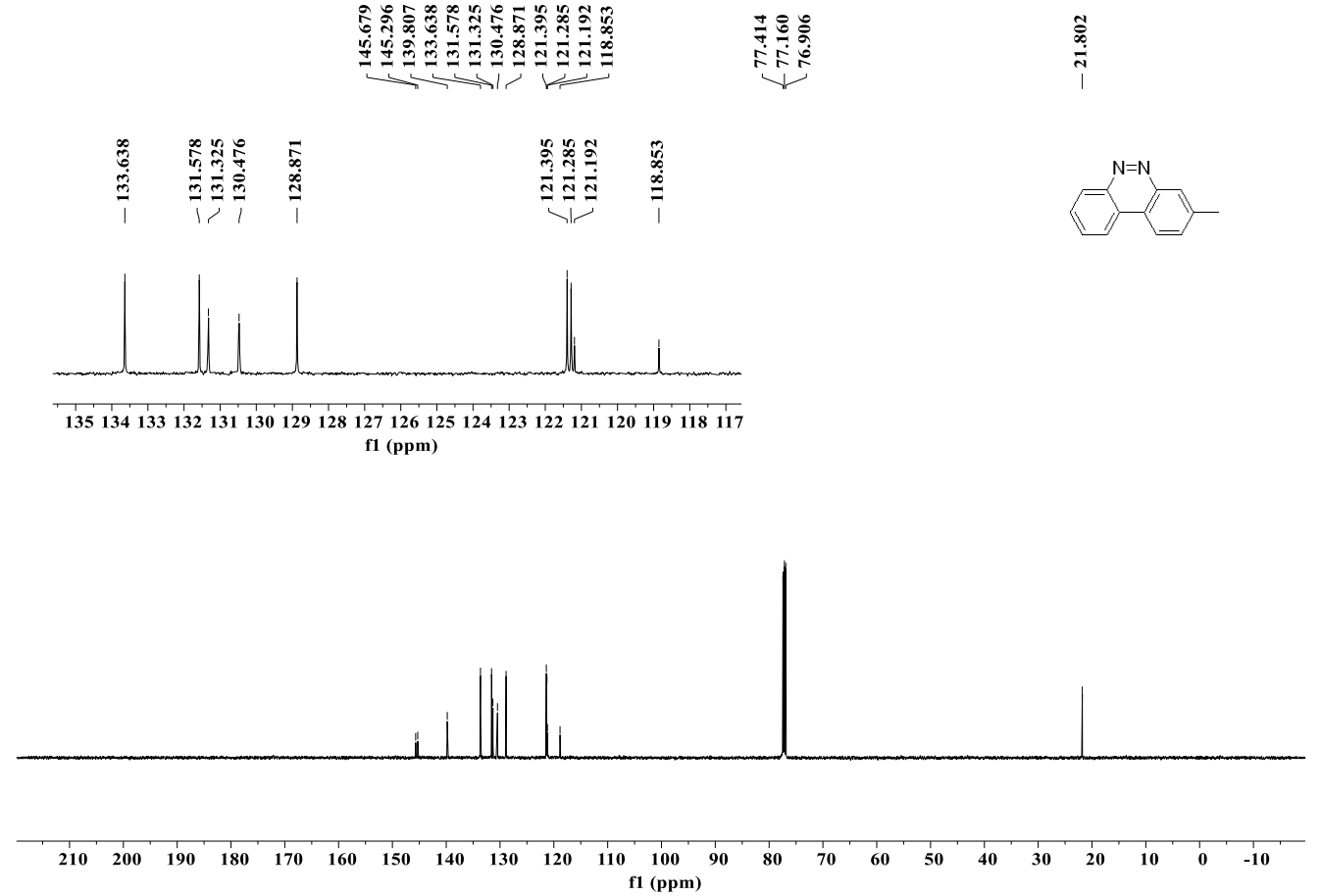
^{13}C NMR (125MHz, $CDCl_3$) of 3a



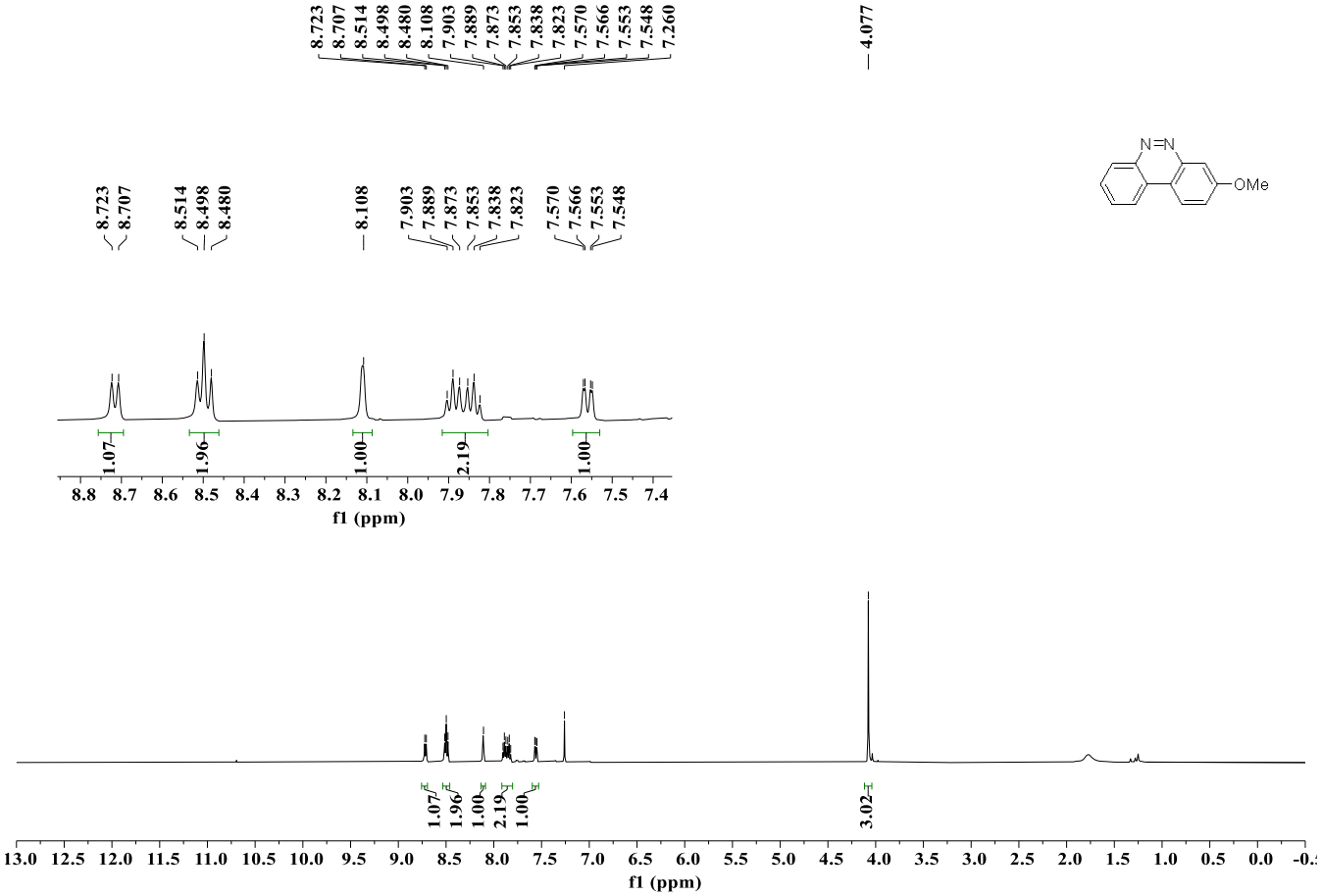
^{1}H NMR (500 MHz, $CDCl_3$) of 3b



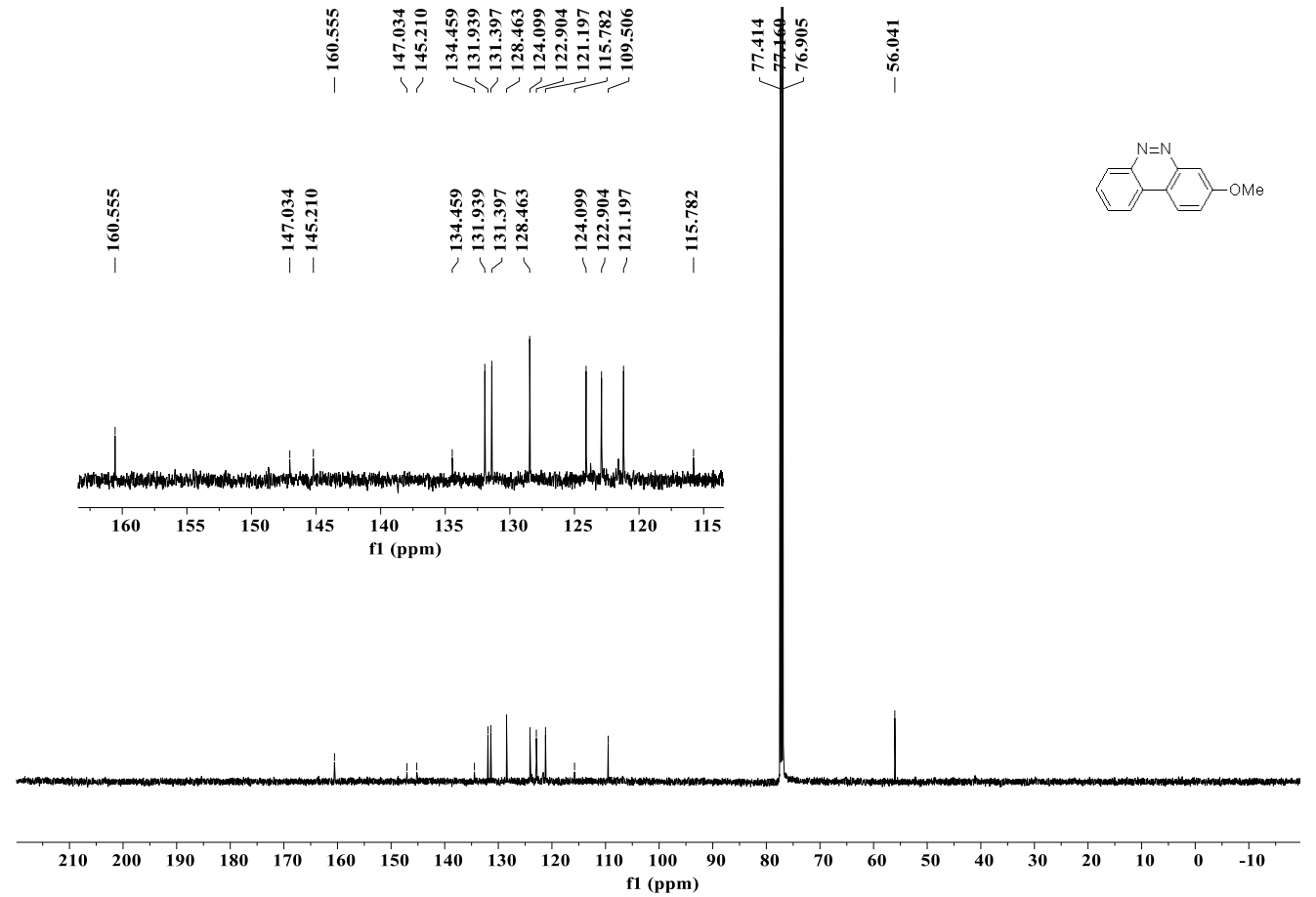
^{13}C NMR (125 MHz, $CDCl_3$) of 3b



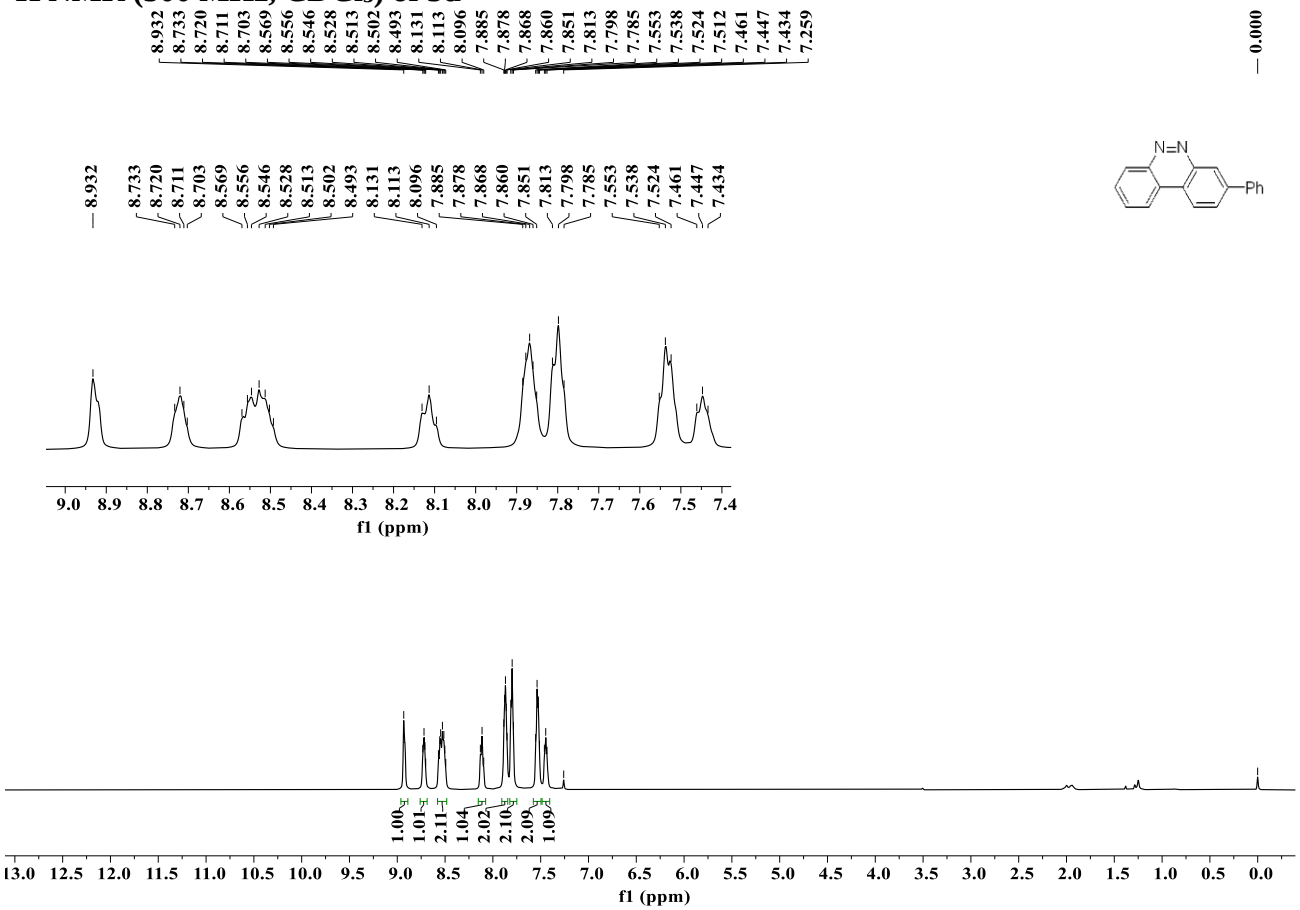
^{1}H NMR (500 MHz, $CDCl_3$) of 3c



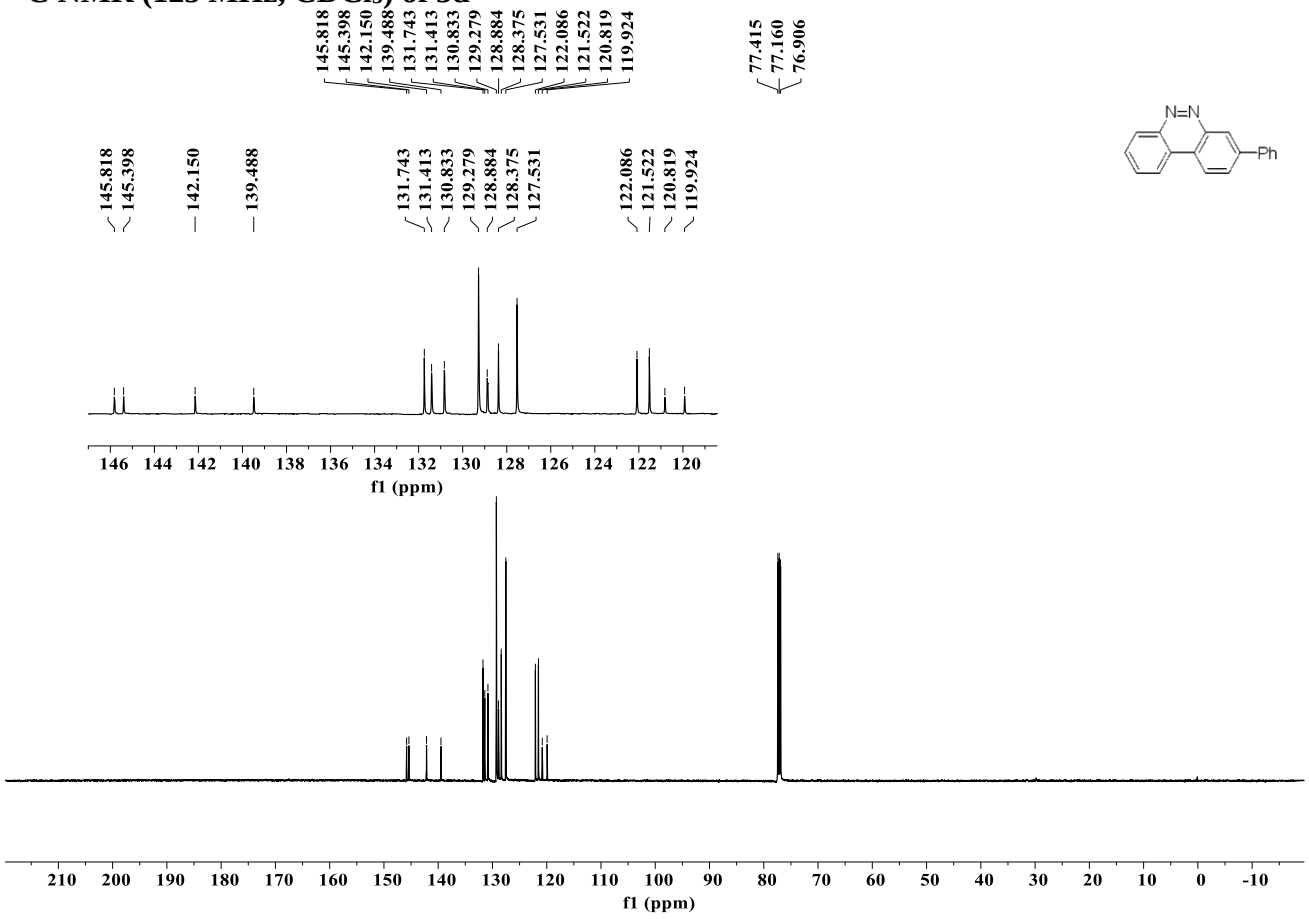
^{13}C NMR (125 MHz, $CDCl_3$) of 3c



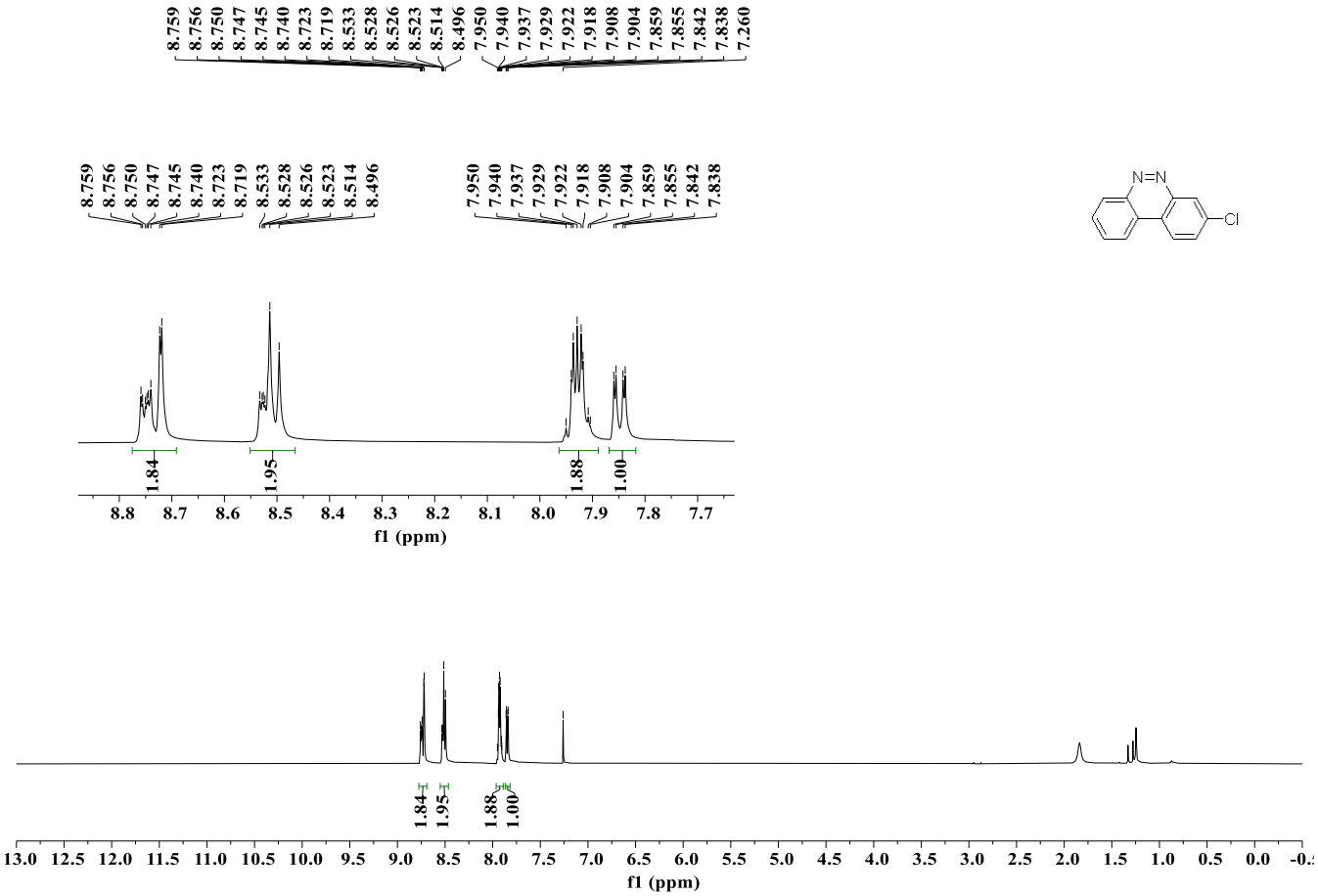
^{1}H NMR (500 MHz, $CDCl_3$) of 3d



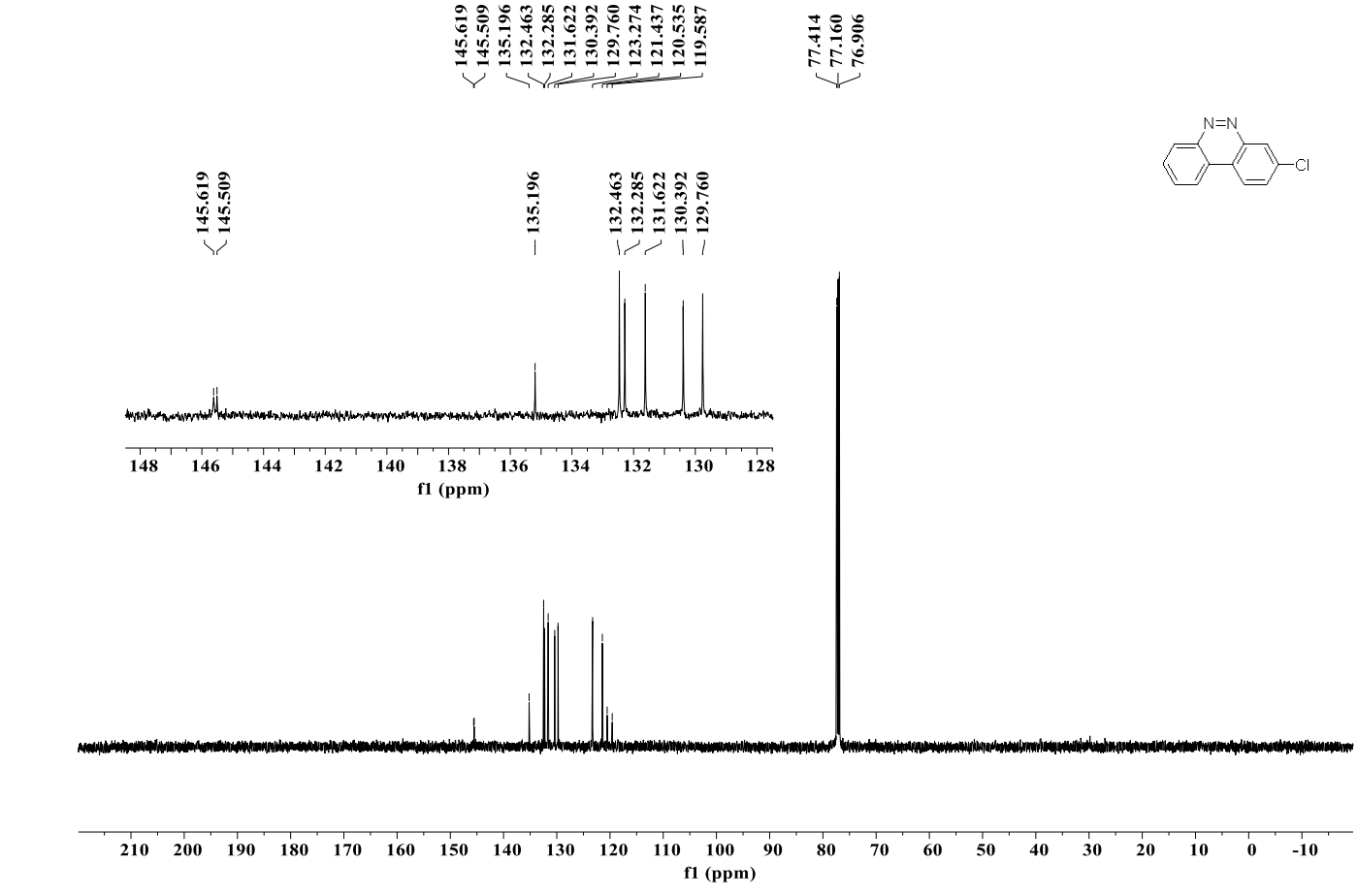
^{13}C NMR (125 MHz, $CDCl_3$) of 3d



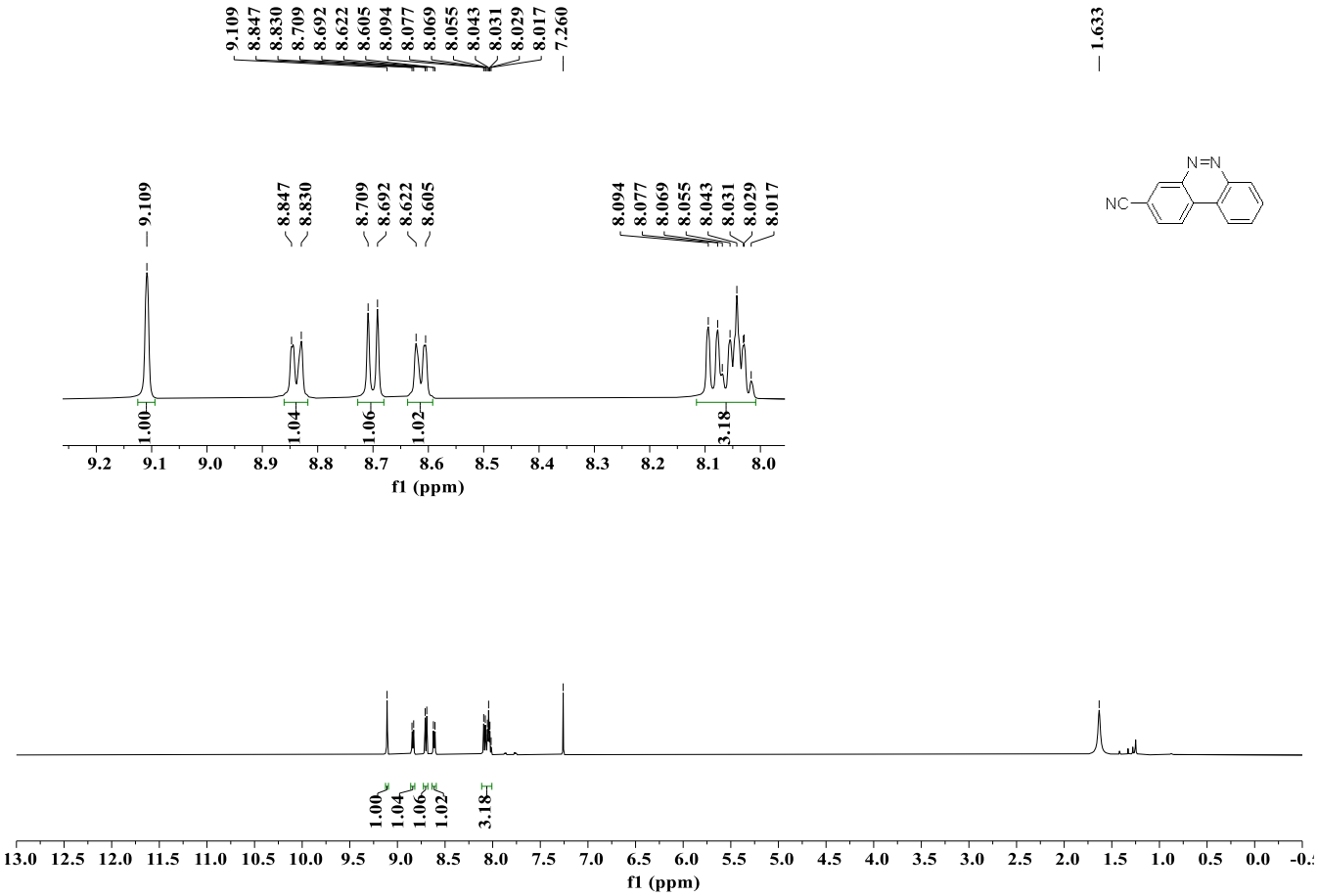
^{1}H NMR (500 MHz, $CDCl_3$) of 3e



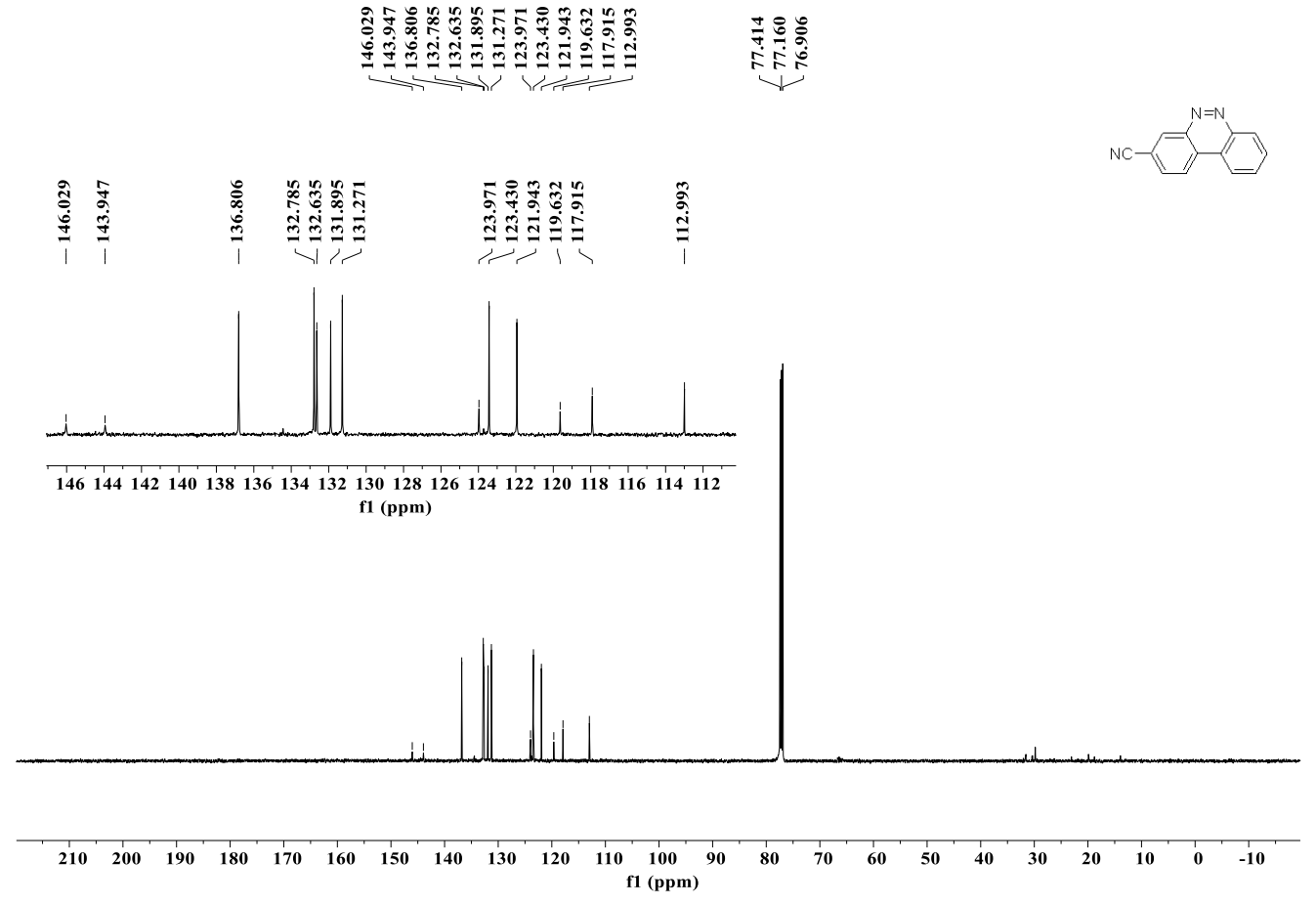
^{13}C NMR (125 MHz, $CDCl_3$) of 3e



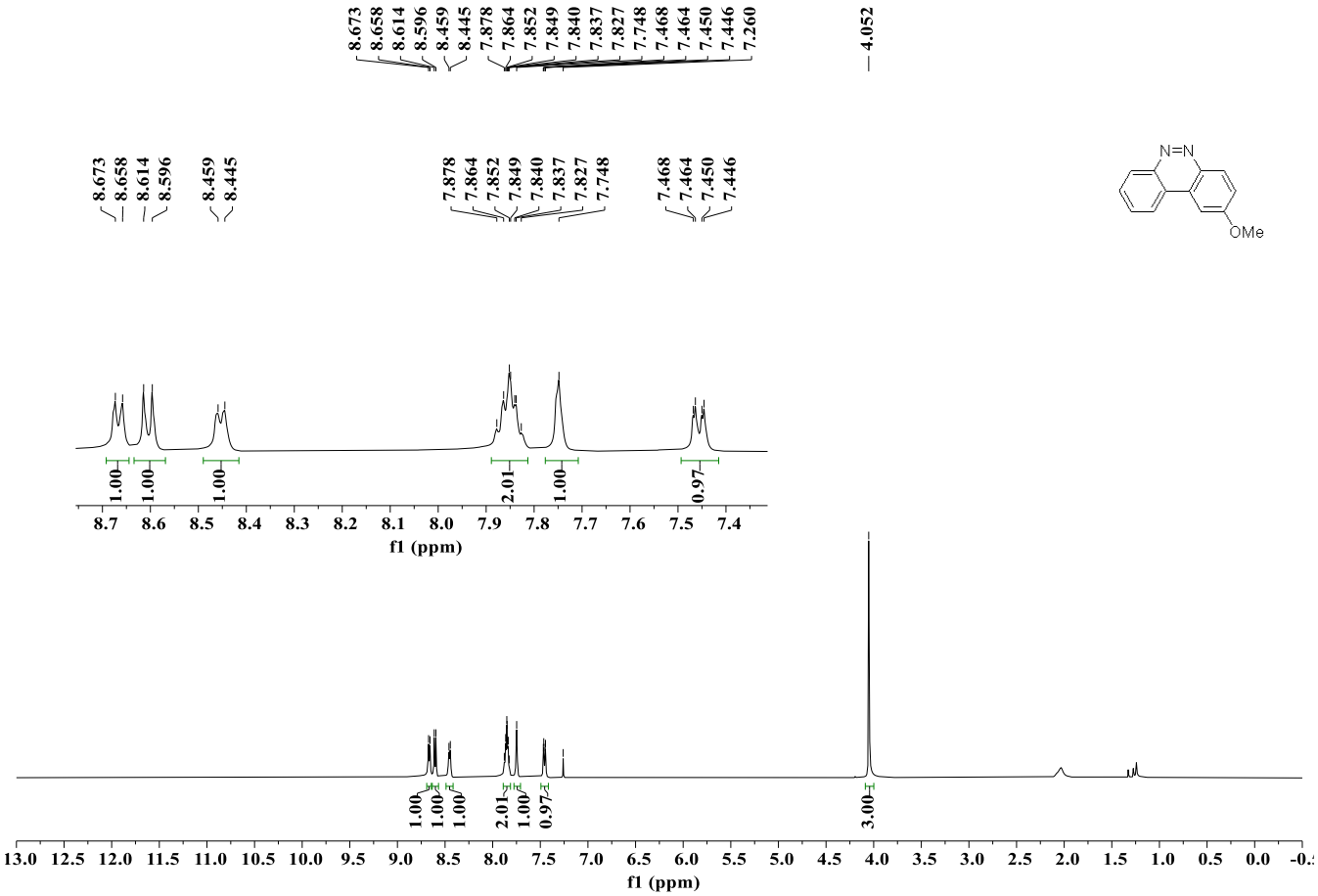
^{1}H NMR (500 MHz, $CDCl_3$) of 3f



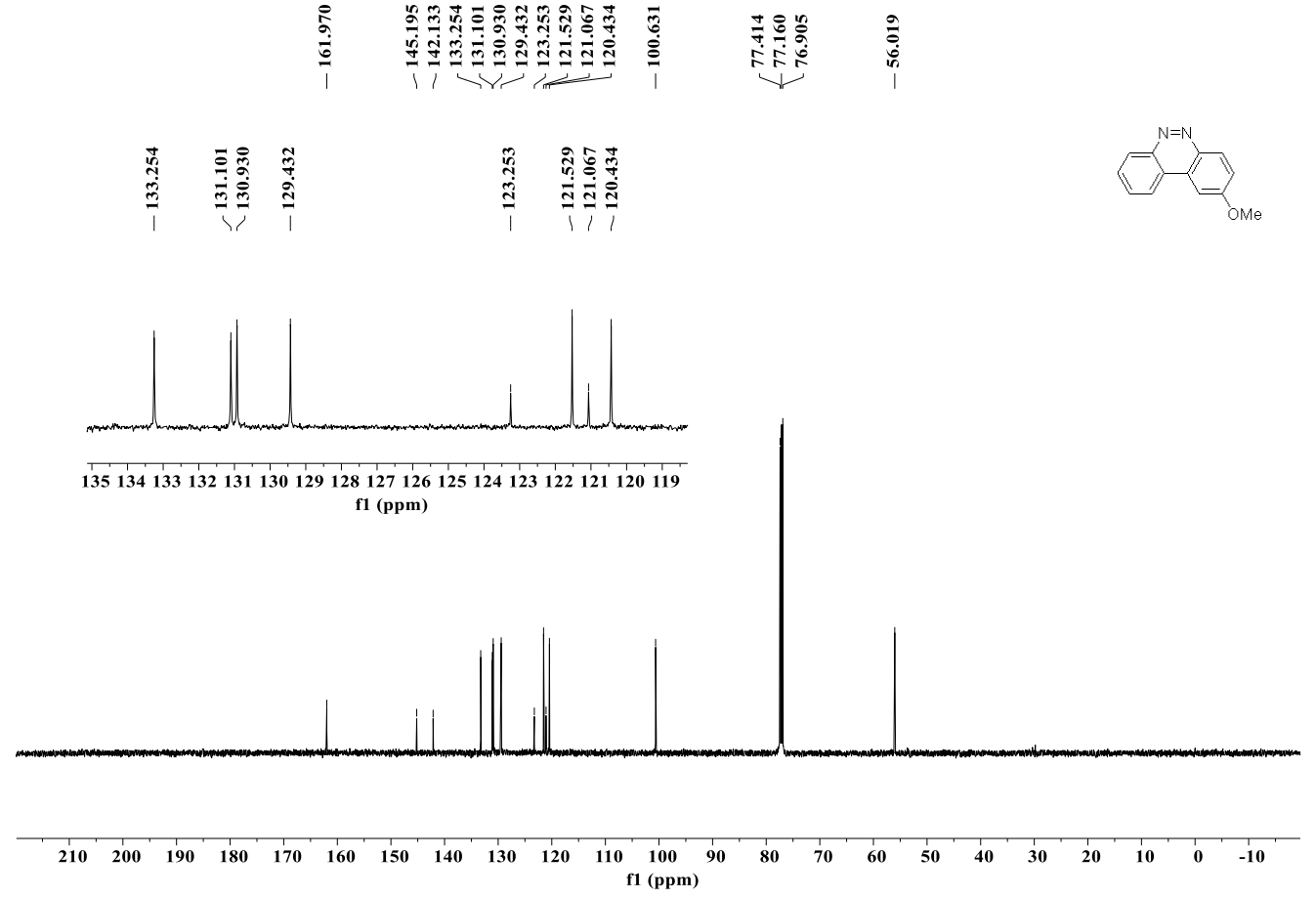
^{13}C NMR (125 MHz, $CDCl_3$) of 3f



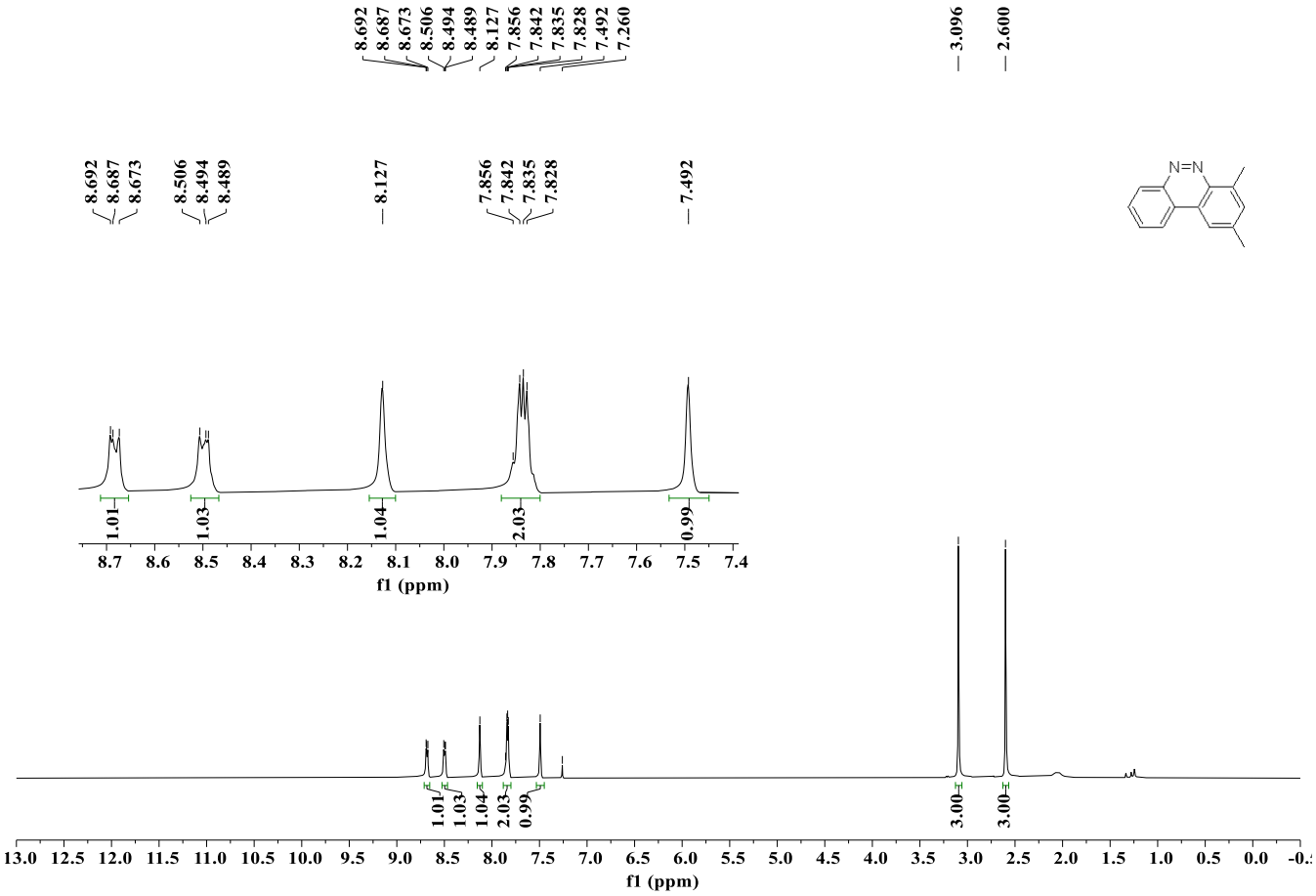
^{1}H NMR (500 MHz, $CDCl_3$) of 3g



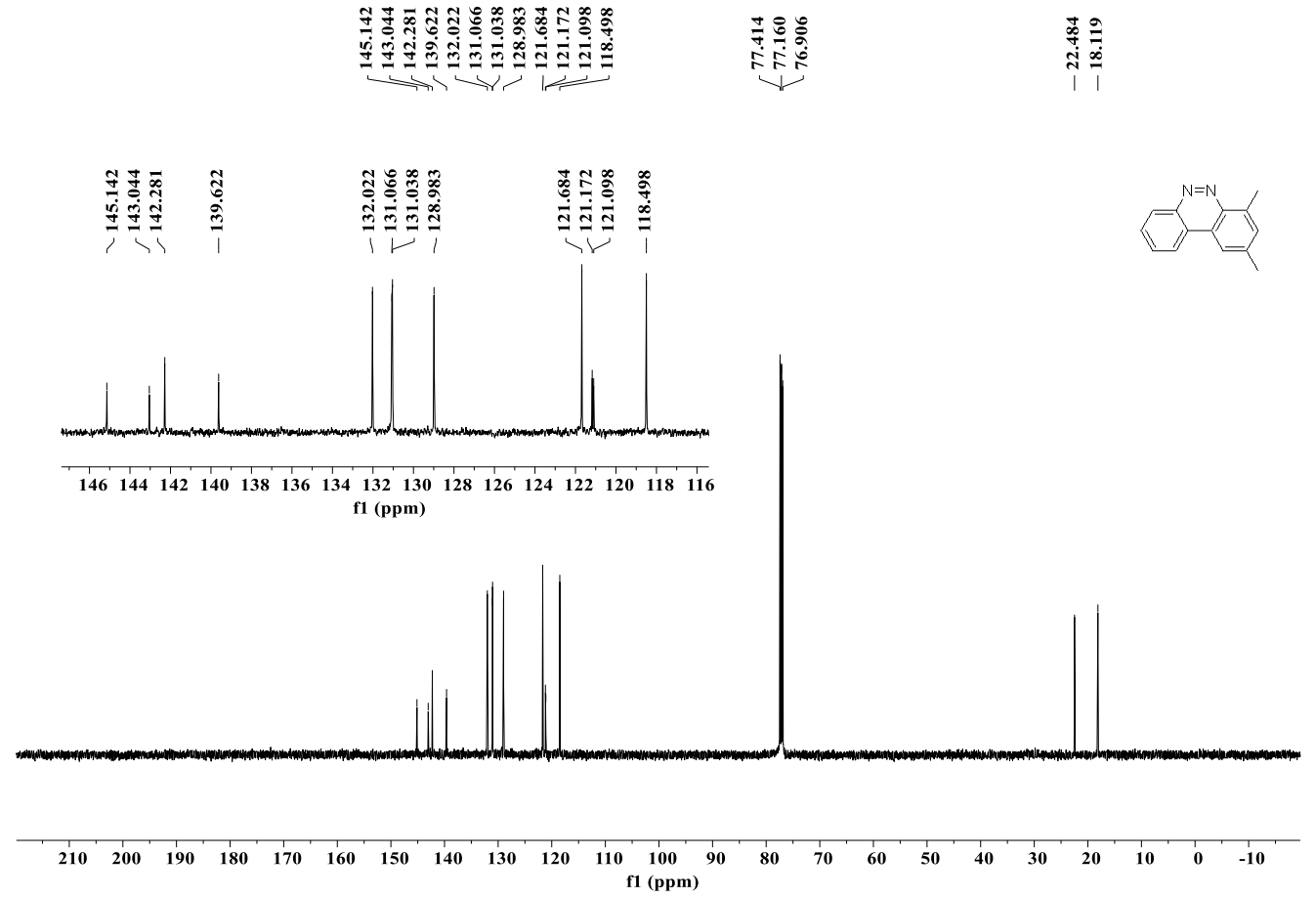
^{13}C NMR (125 MHz, $CDCl_3$) of 3g



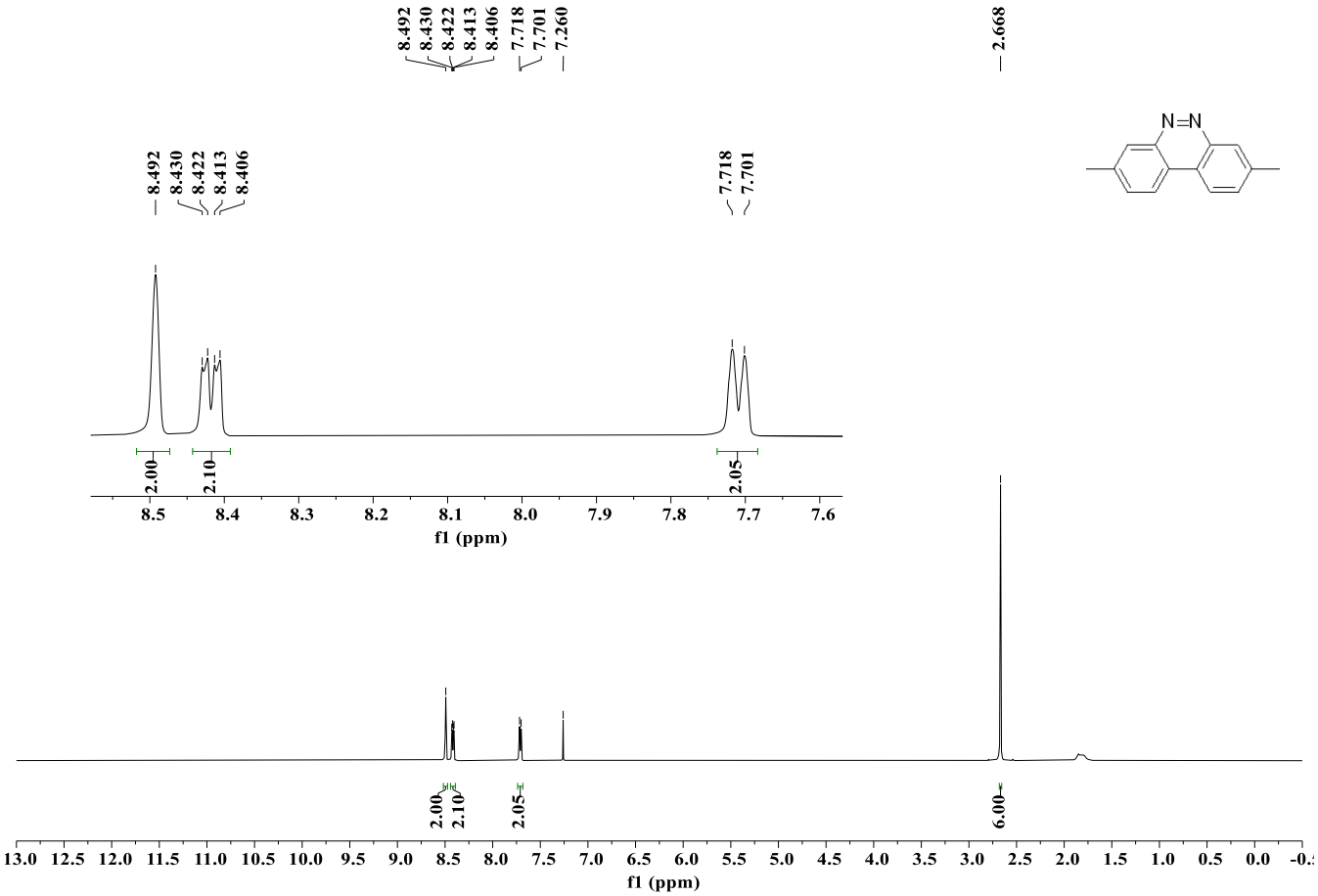
^{1}H NMR (500 MHz, $CDCl_3$) of 3h



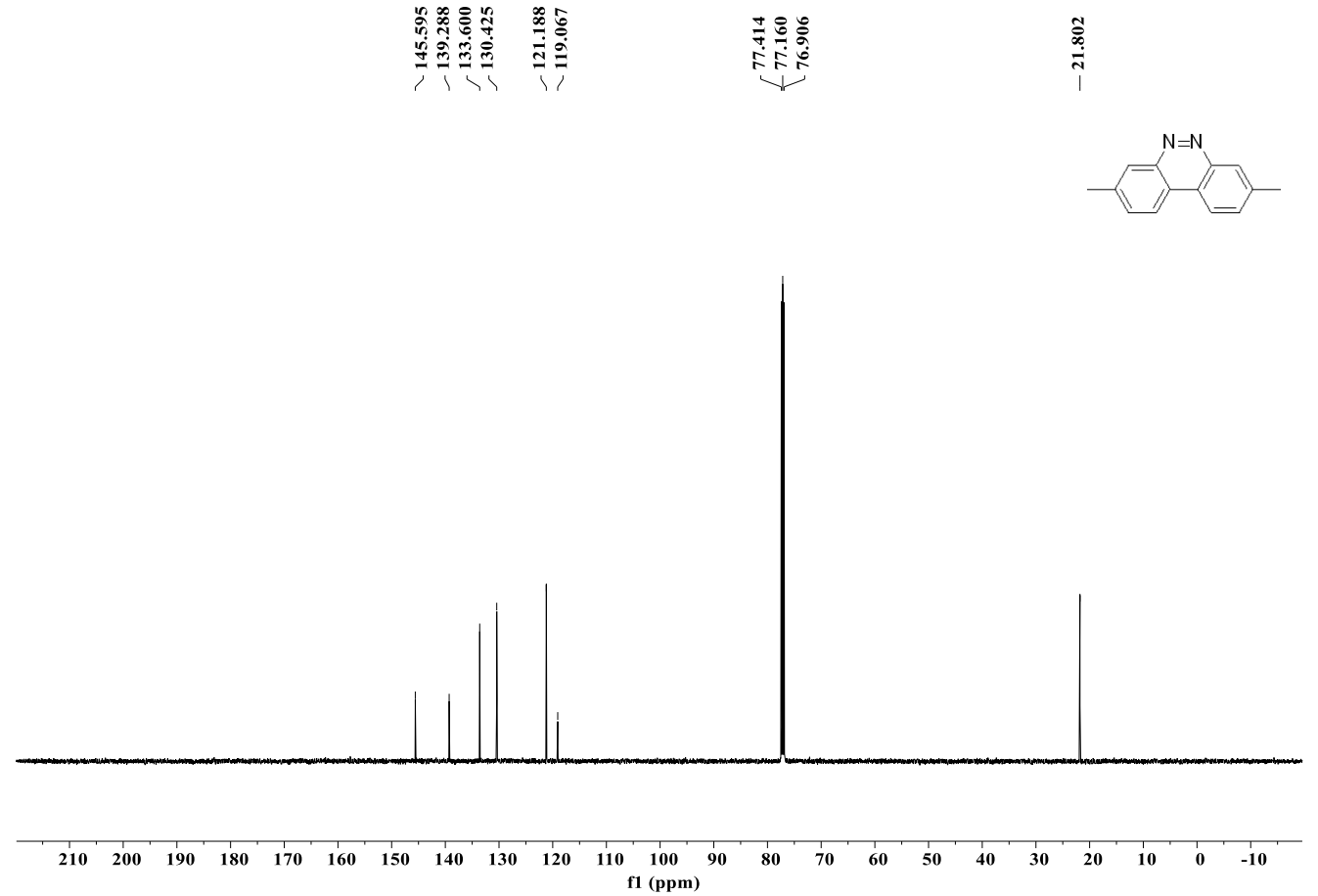
^{13}C NMR (125 MHz, $CDCl_3$) of 3h



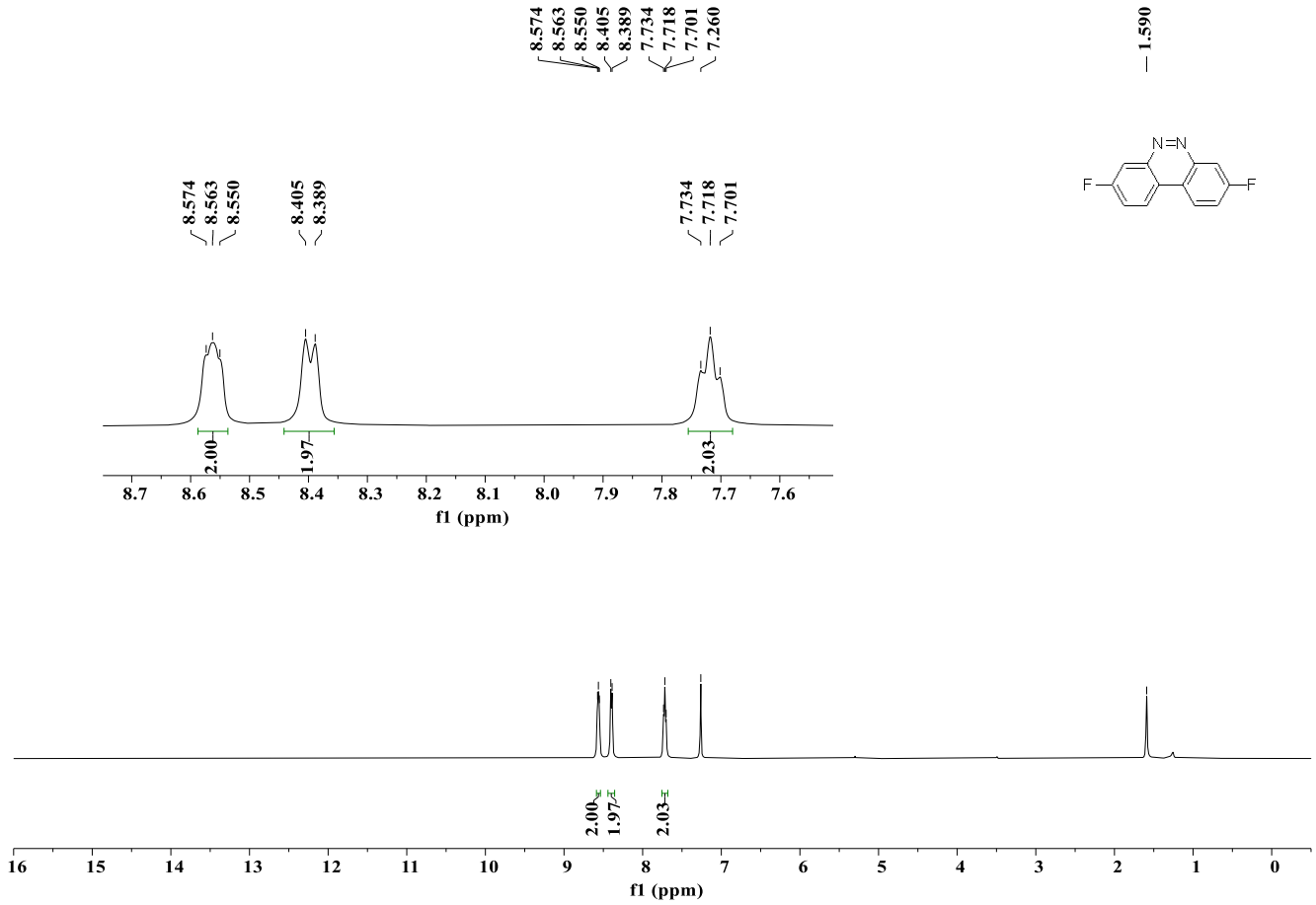
^{1}H NMR (500 MHz, $CDCl_3$) of 3i



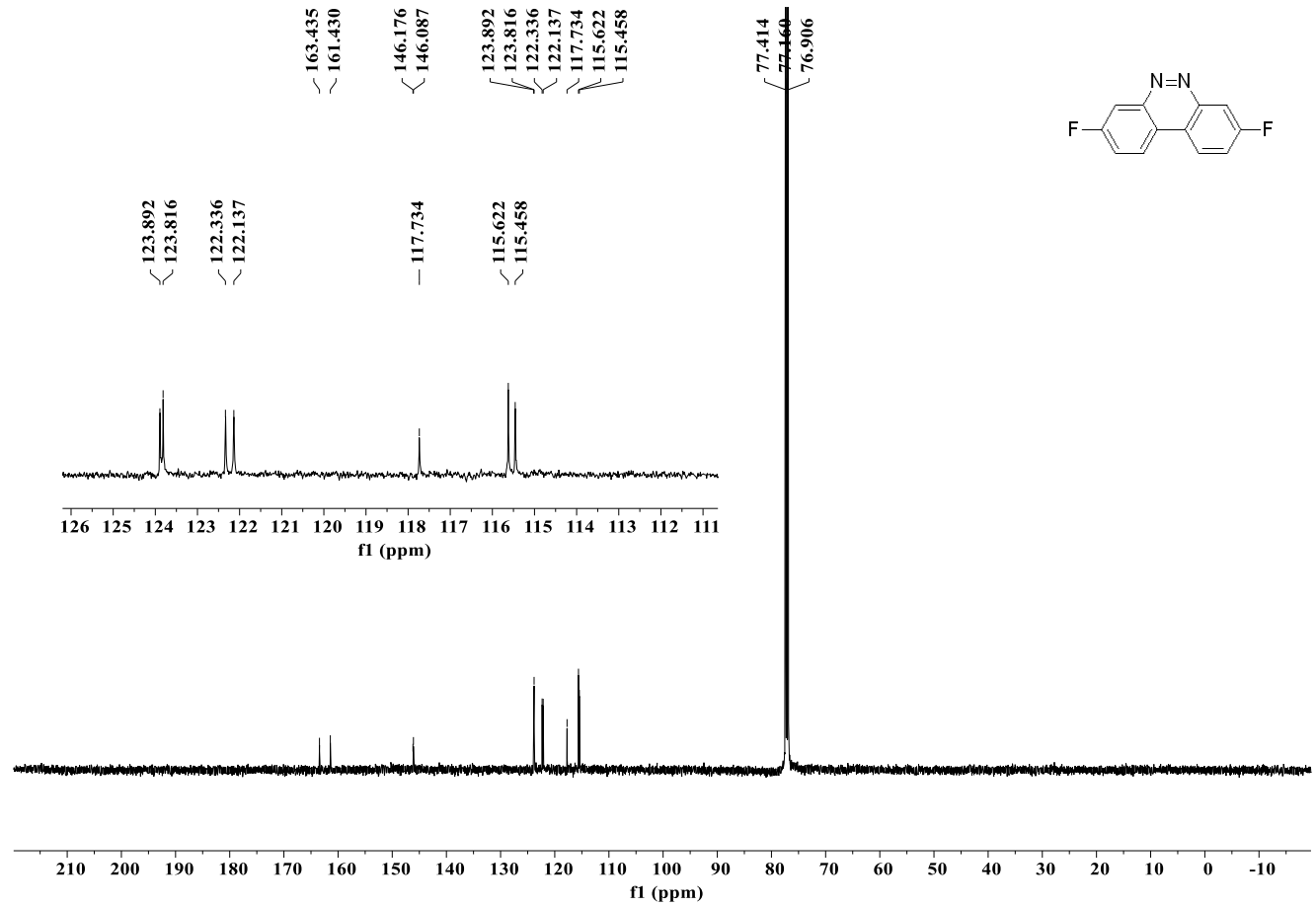
^{13}C NMR (125 MHz, $CDCl_3$) of 3i



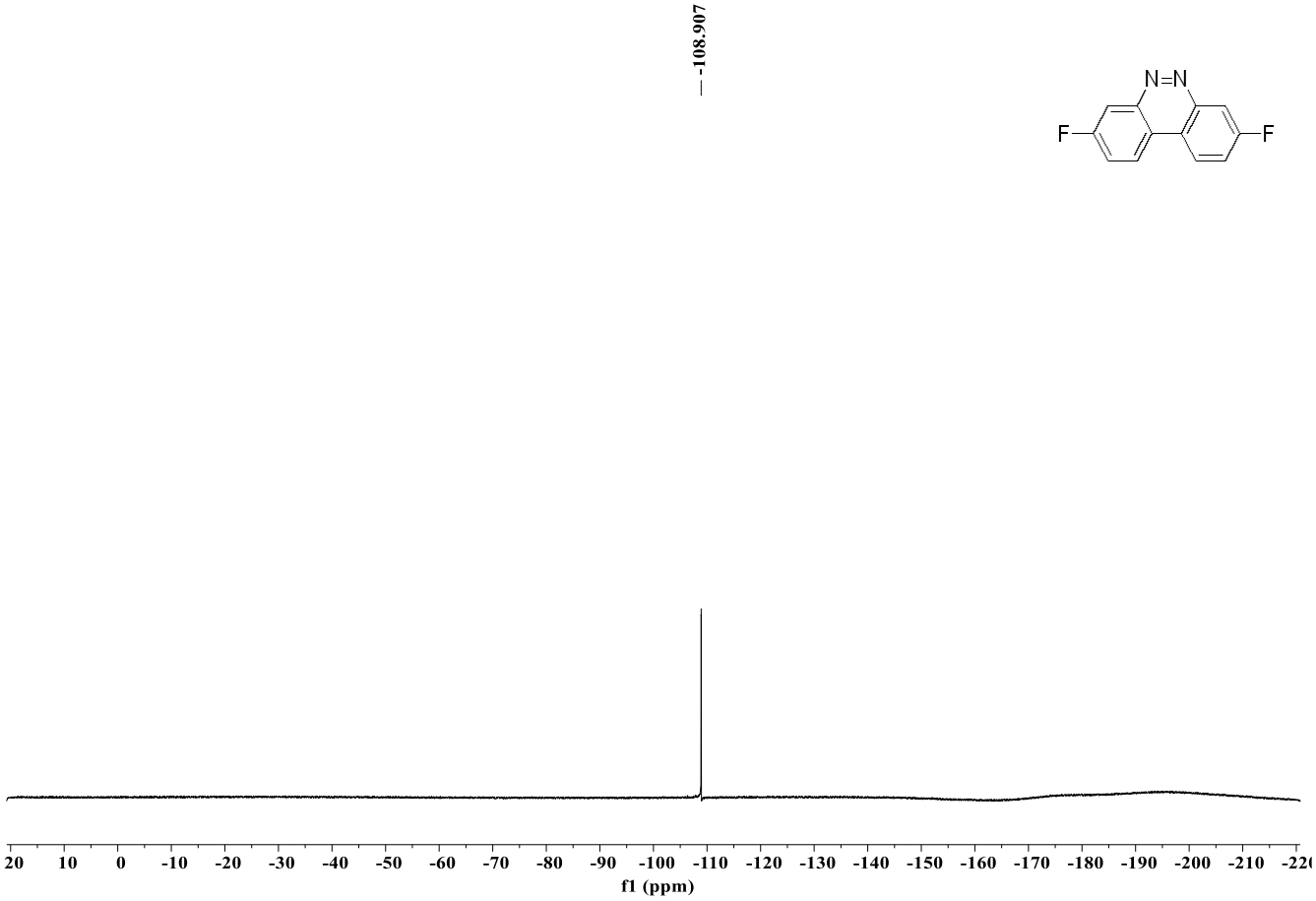
^{1}H NMR (500 MHz, $CDCl_3$) of 3j



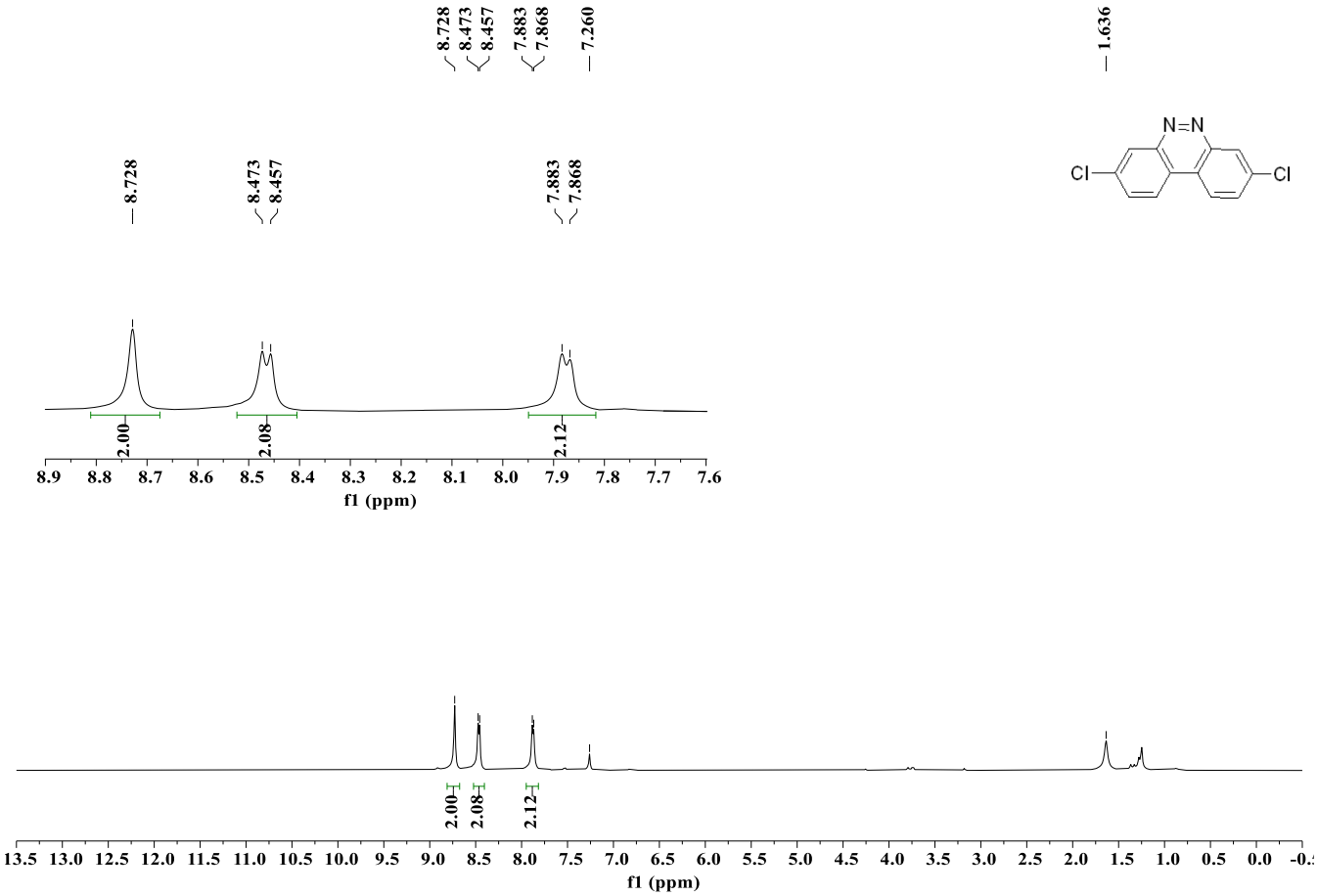
^{13}C NMR (125 MHz, $CDCl_3$) of 3j



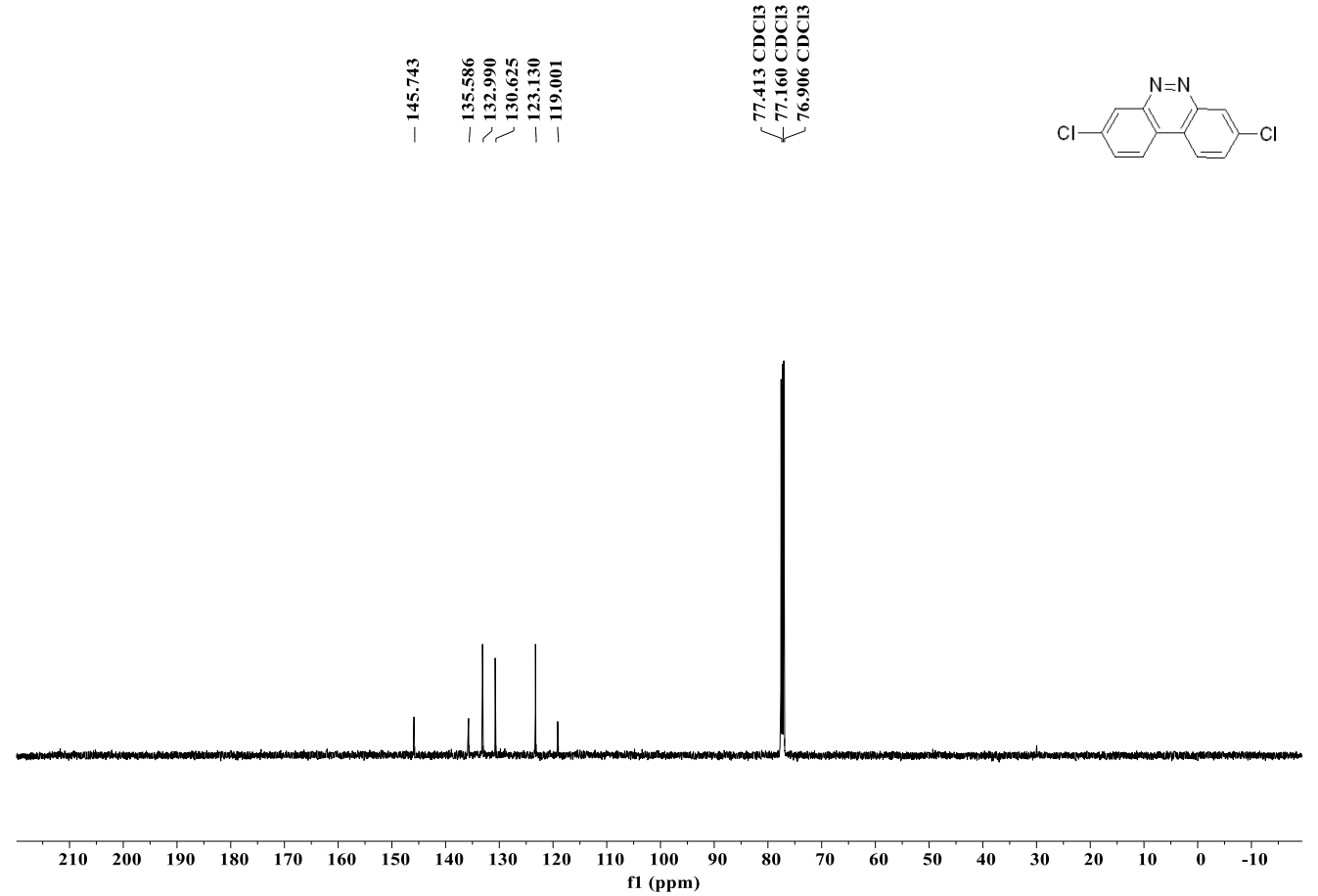
^{19}F NMR (471 MHz, $CDCl_3$) of 3j



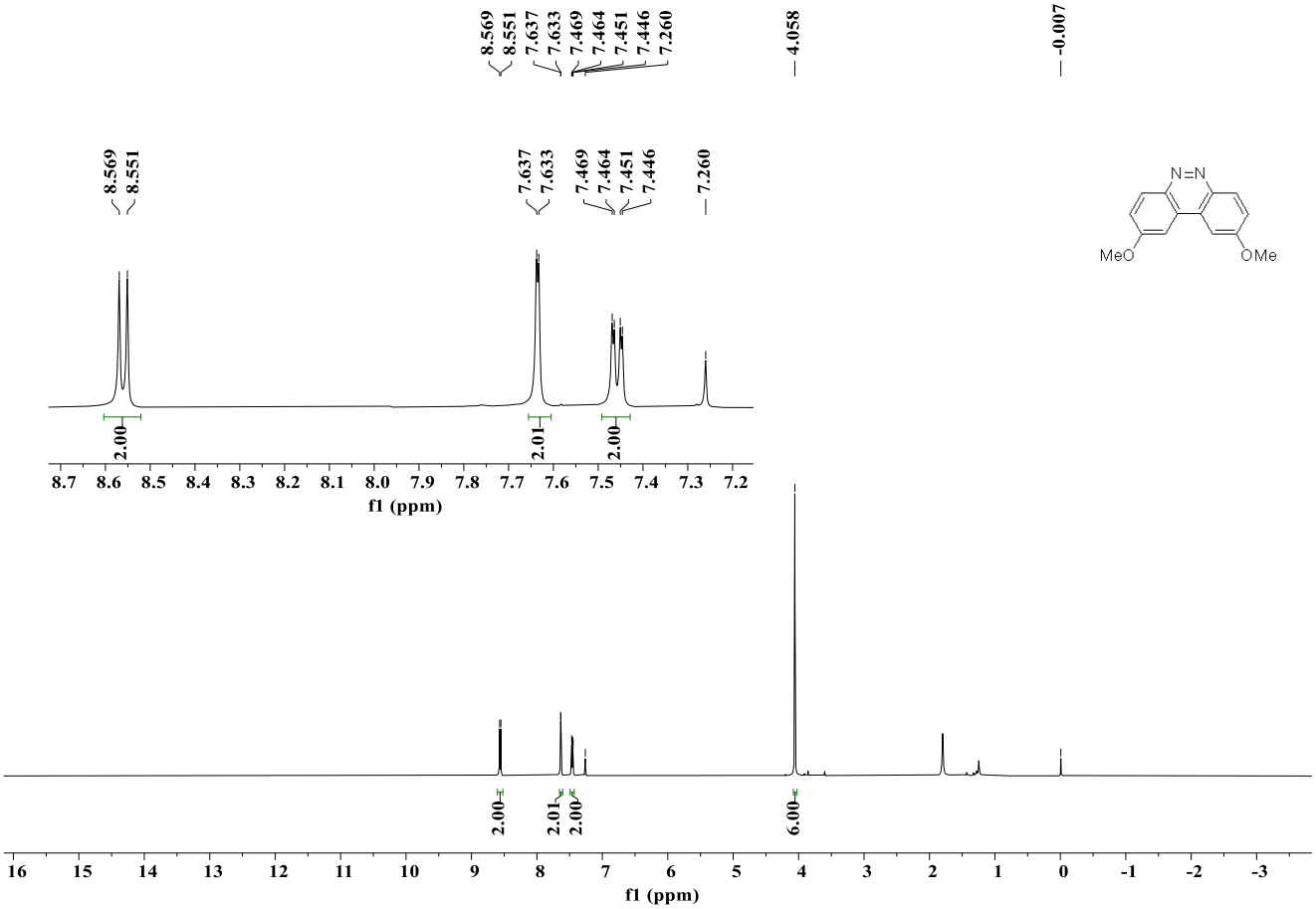
^{1}H NMR (500 MHz, $CDCl_3$) of 3k



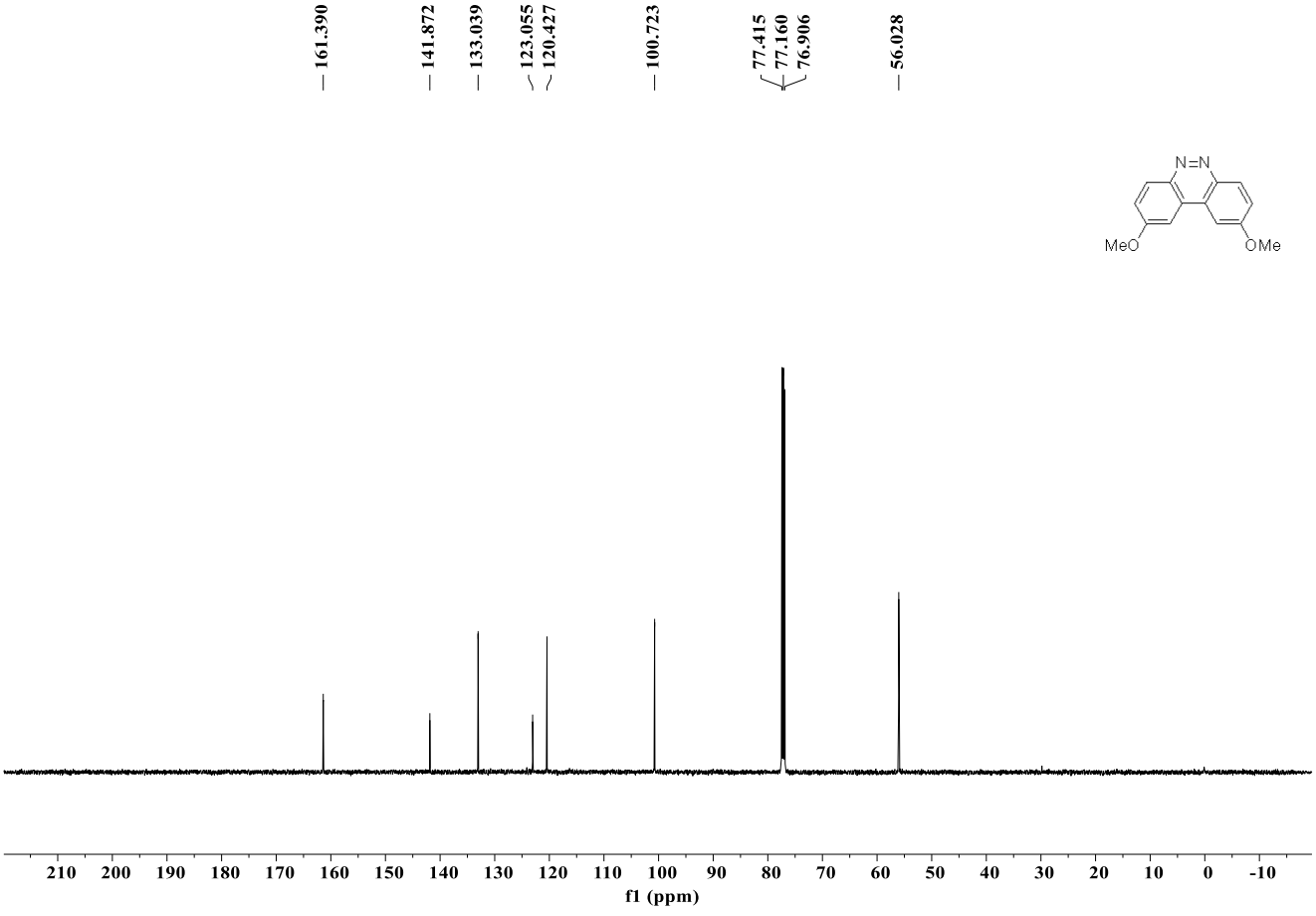
^{13}C NMR (125 MHz, $CDCl_3$) of 3k



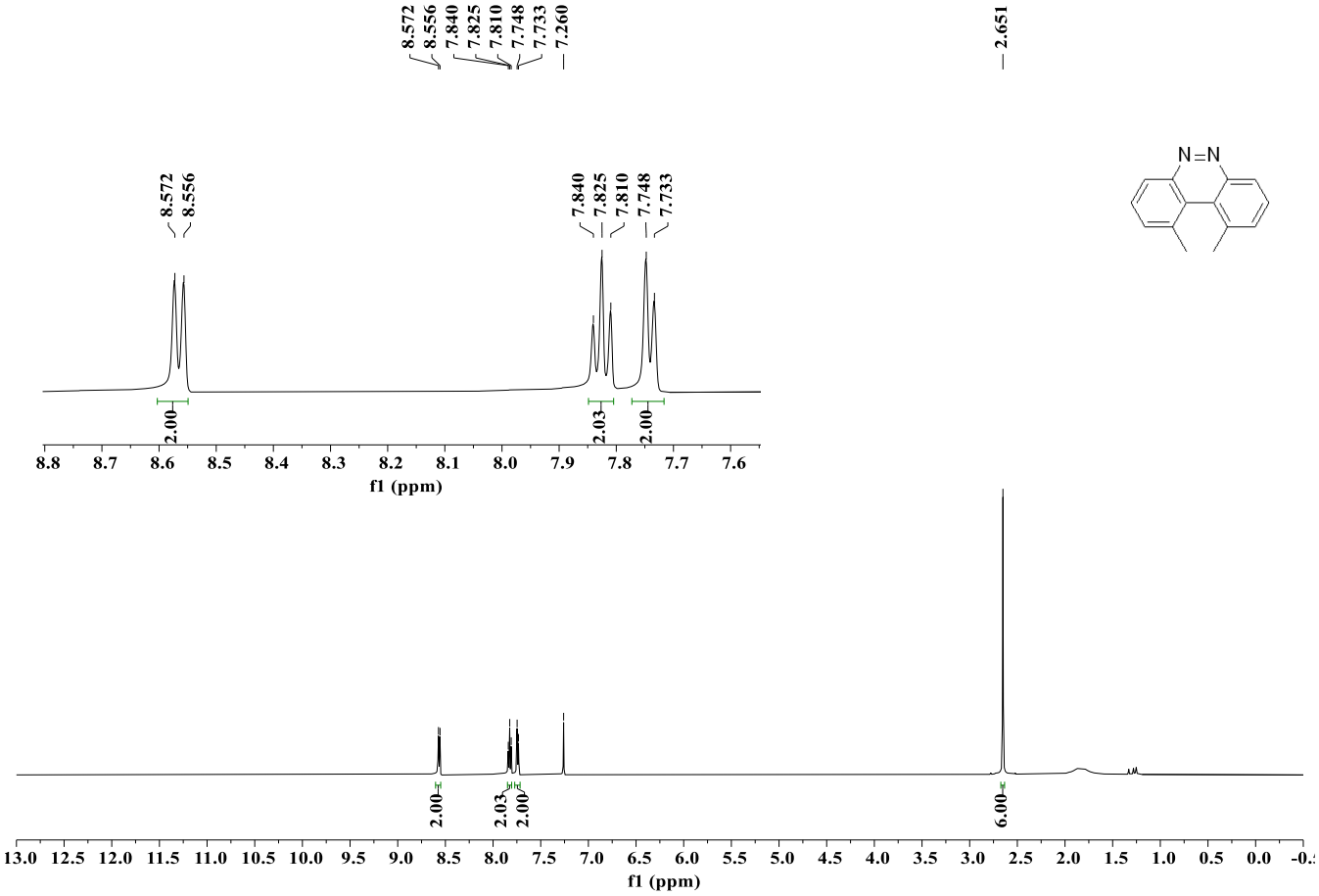
^{1}H NMR (500 MHz, $CDCl_3$) of 3l



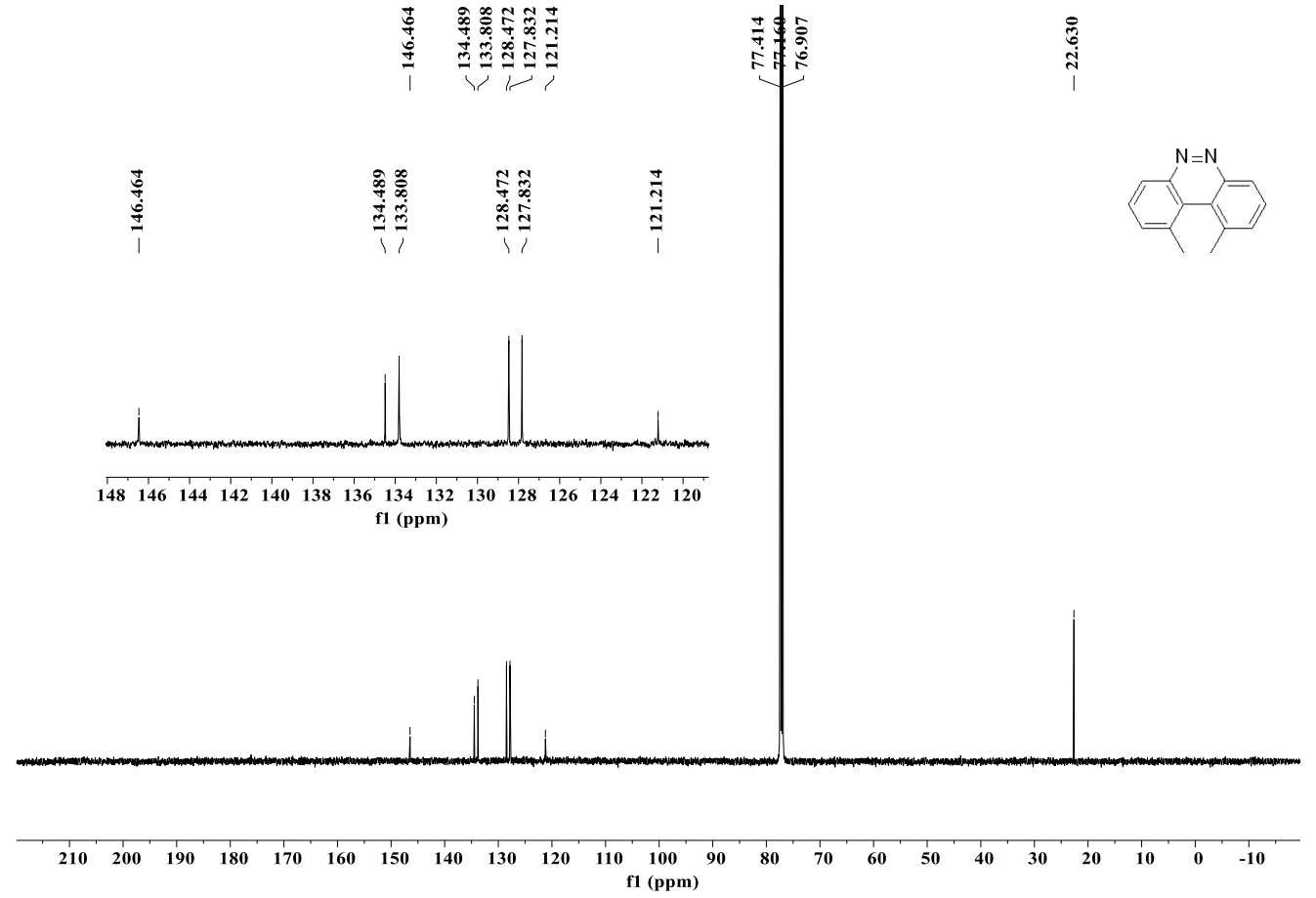
^{13}C NMR (125 MHz, $CDCl_3$) of 3l



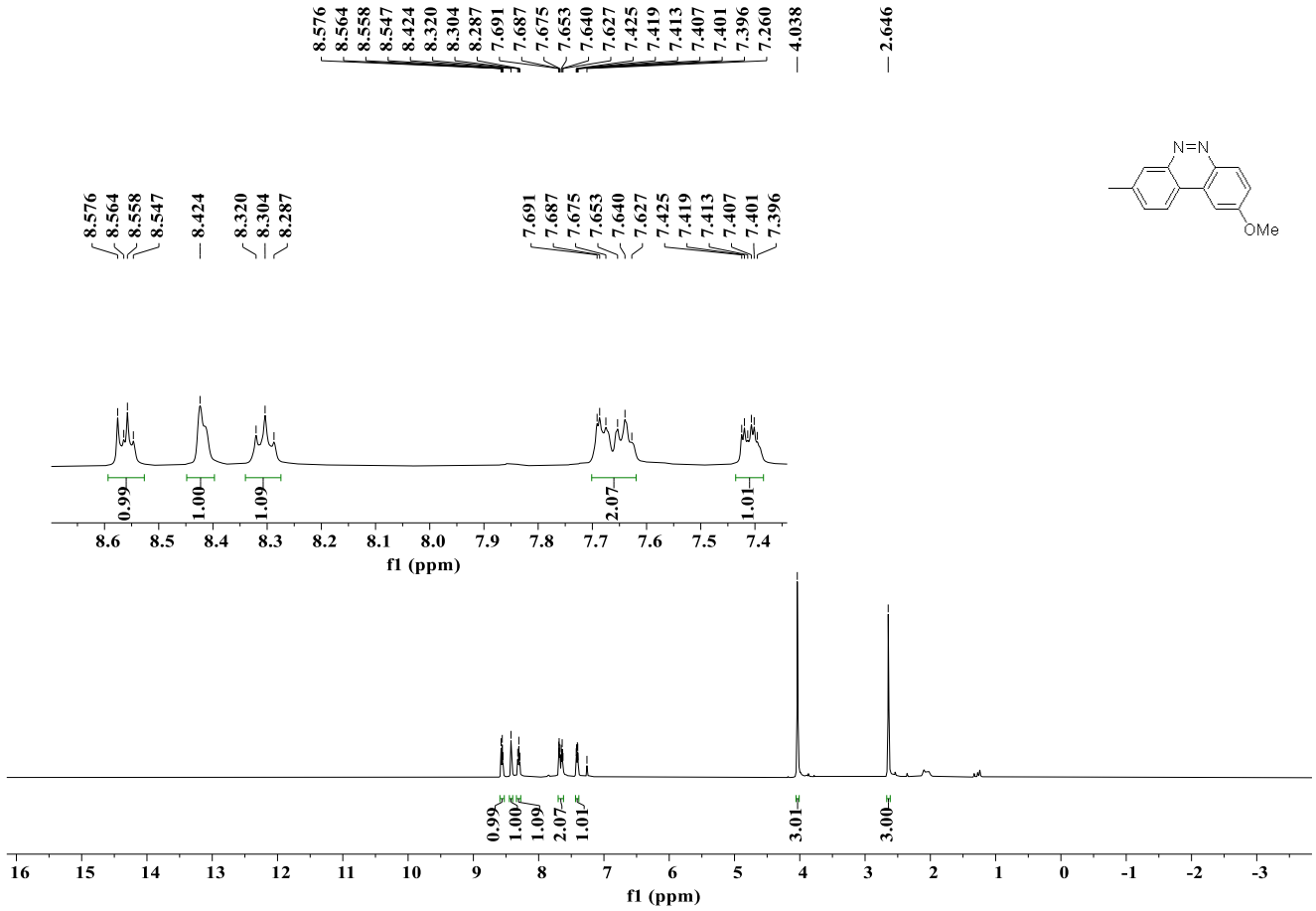
^{1}H NMR (500 MHz, $CDCl_3$) of 3m



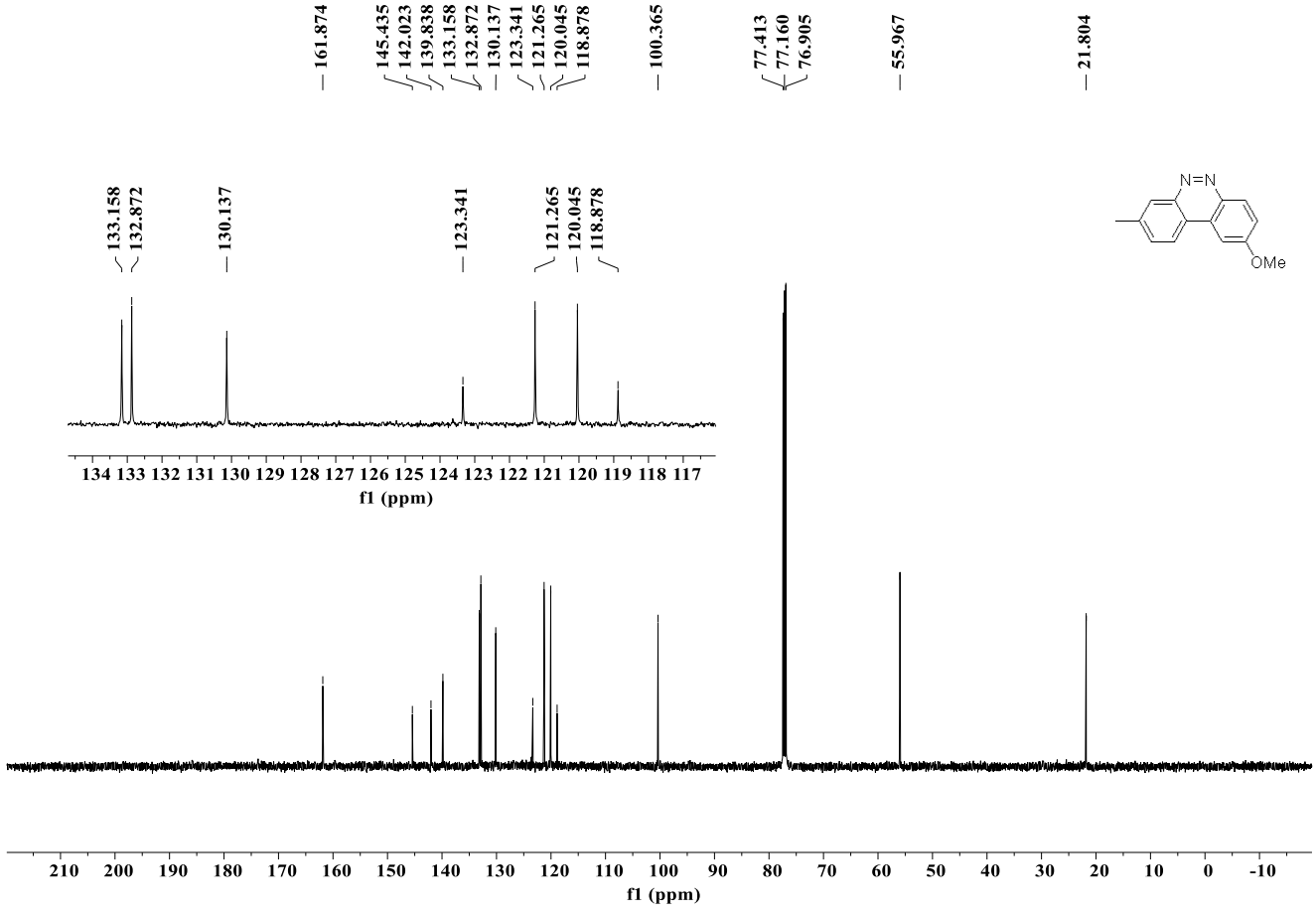
^{13}C NMR (125 MHz, $CDCl_3$) of 3m



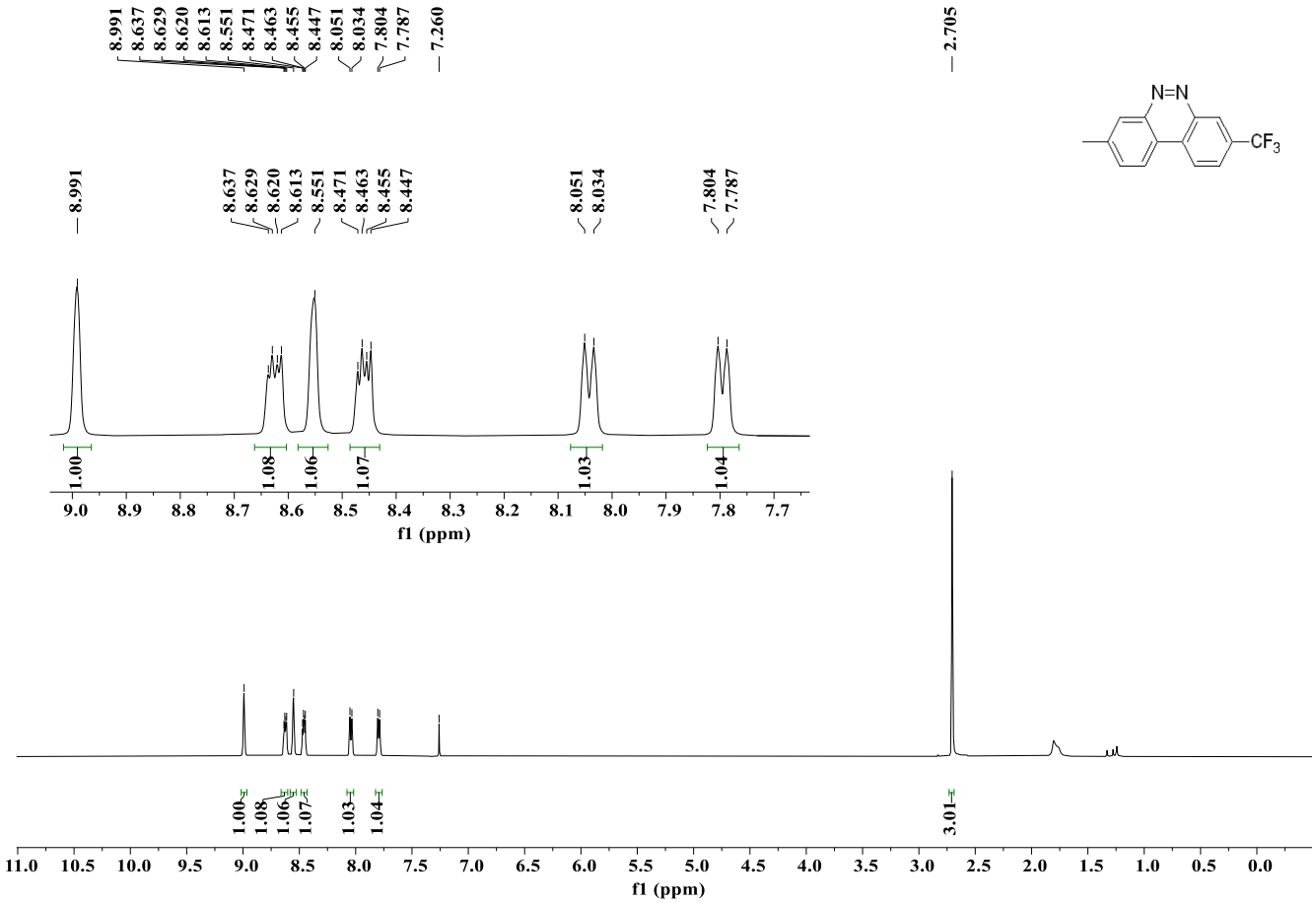
^{1}H NMR (500 MHz, $CDCl_3$) of 3n



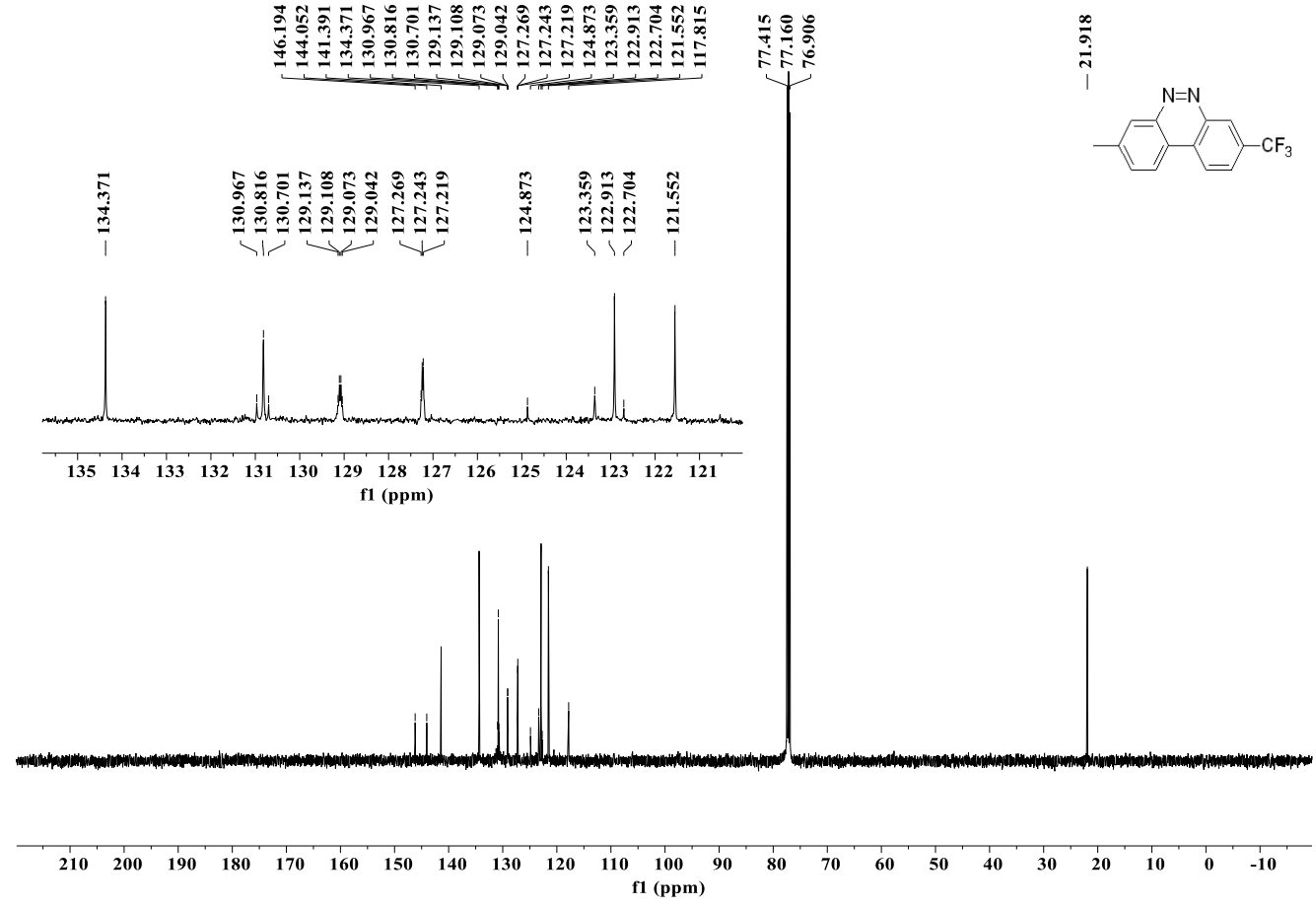
^{13}C NMR (125 MHz, $CDCl_3$) of 3n



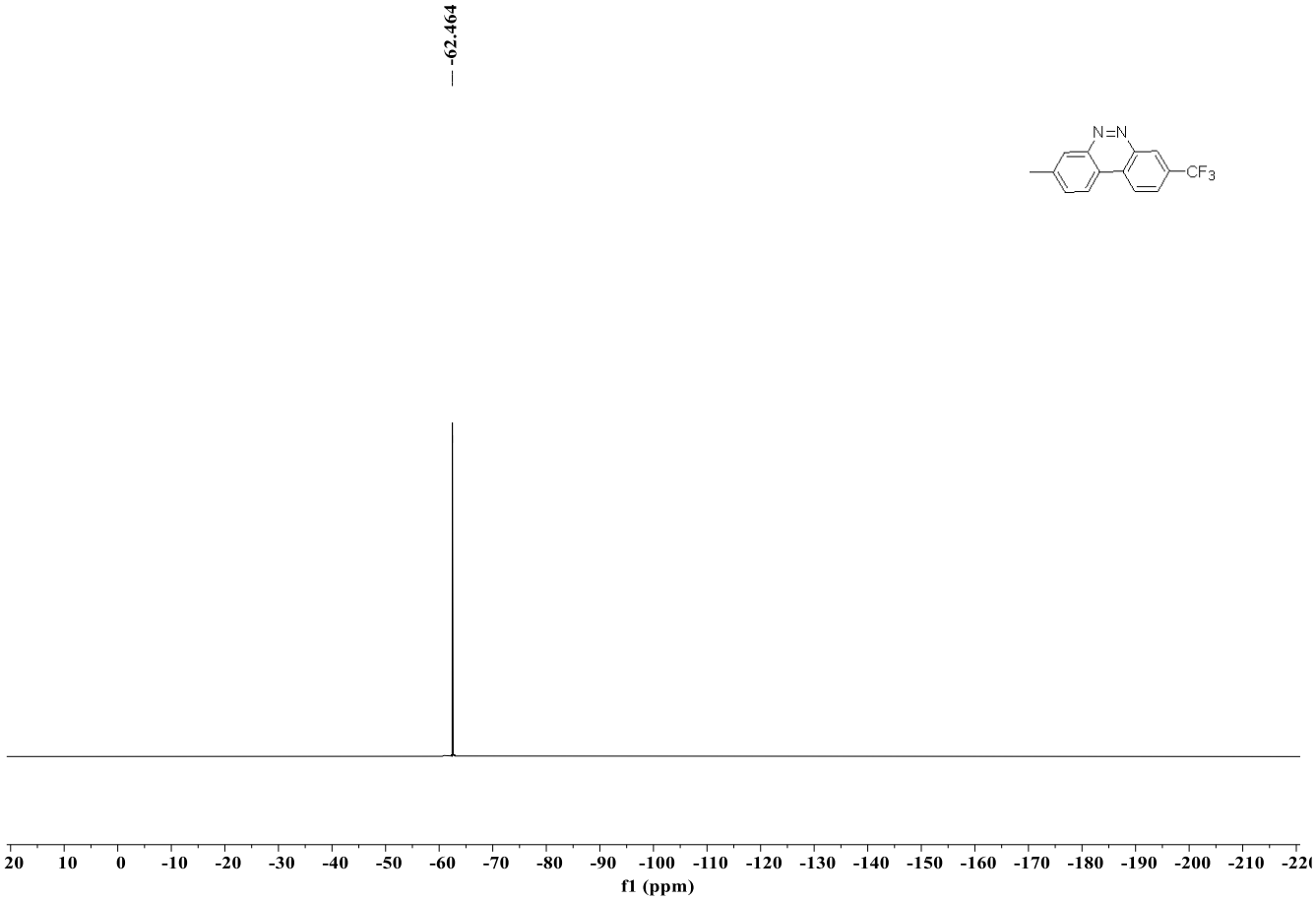
^{1}H NMR (500 MHz, $CDCl_3$) of 3o



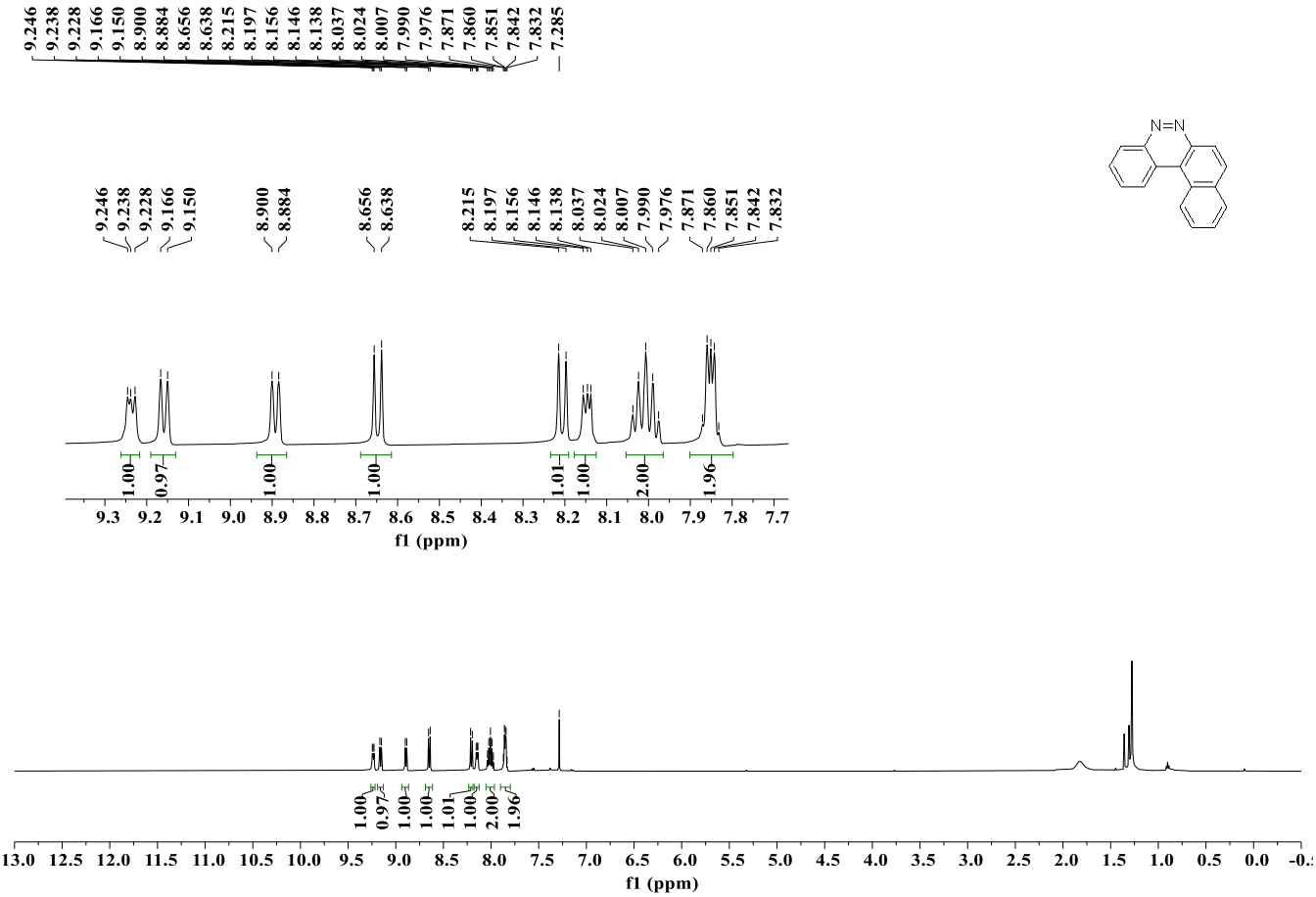
^{13}C NMR (125 MHz, $CDCl_3$) of 3o



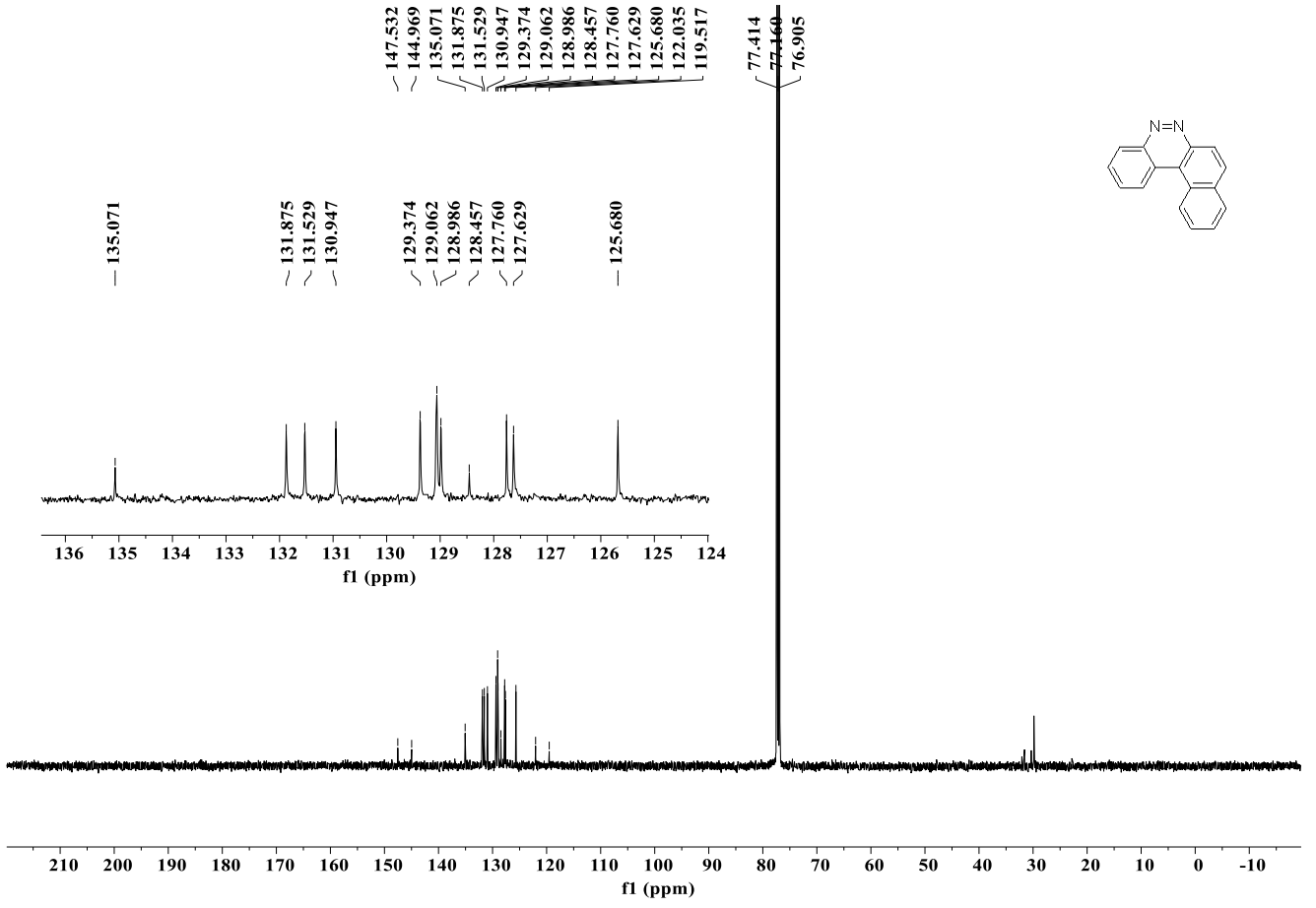
^{19}F NMR (471 MHz, $CDCl_3$) of 3o



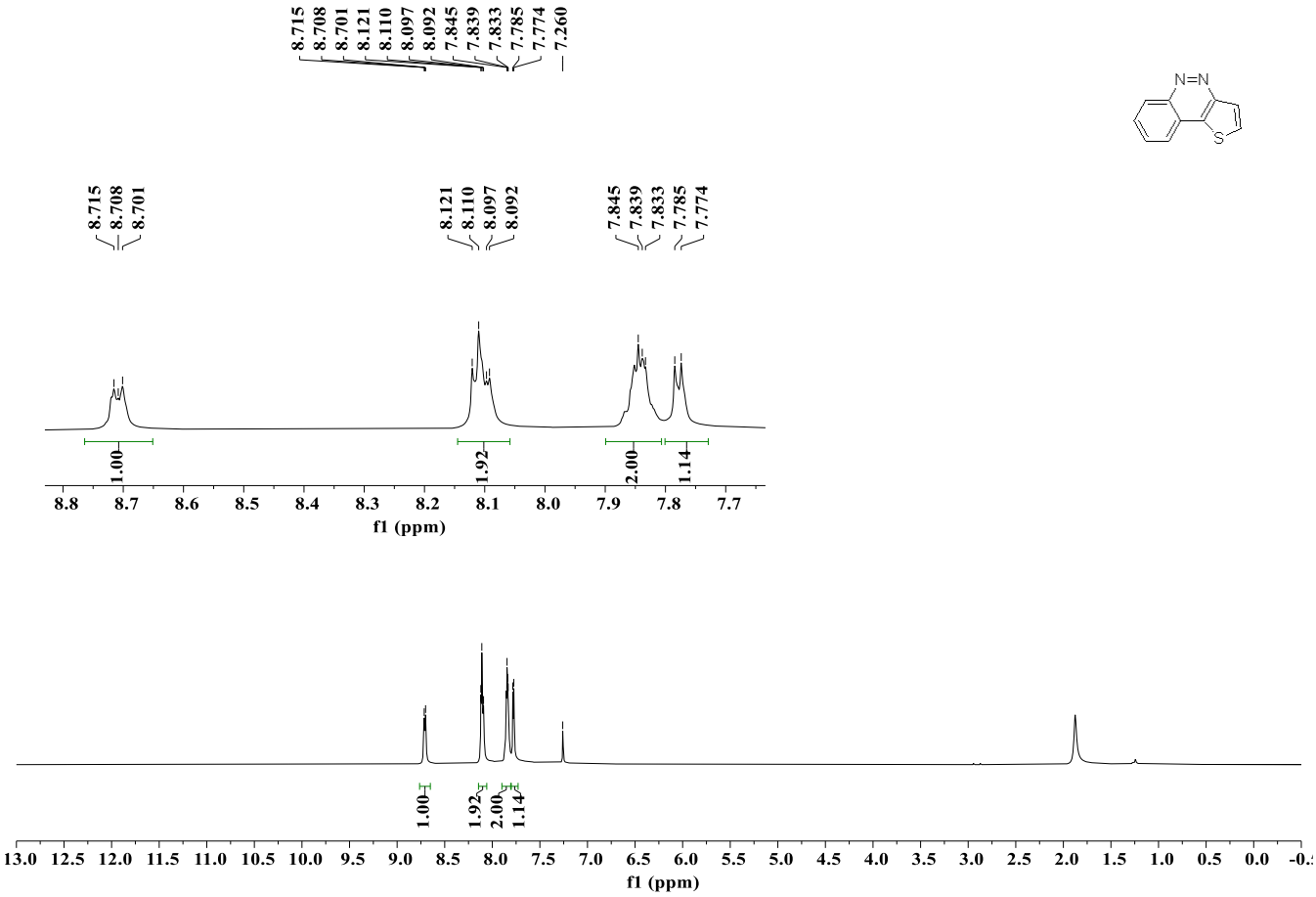
^{1}H NMR (500 MHz, $CDCl_3$) of 3p



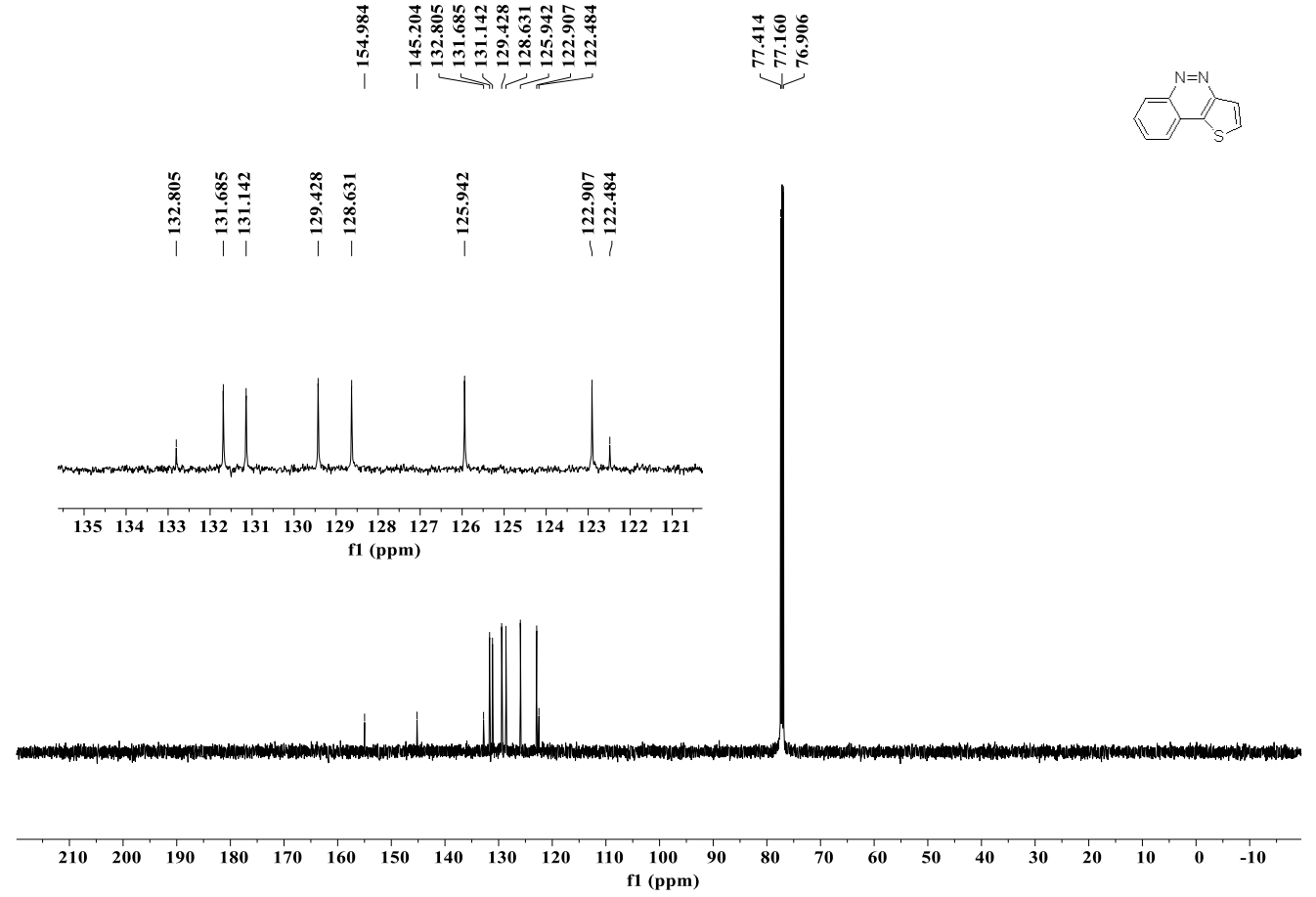
^{13}C NMR (125 MHz, $CDCl_3$) of 3p



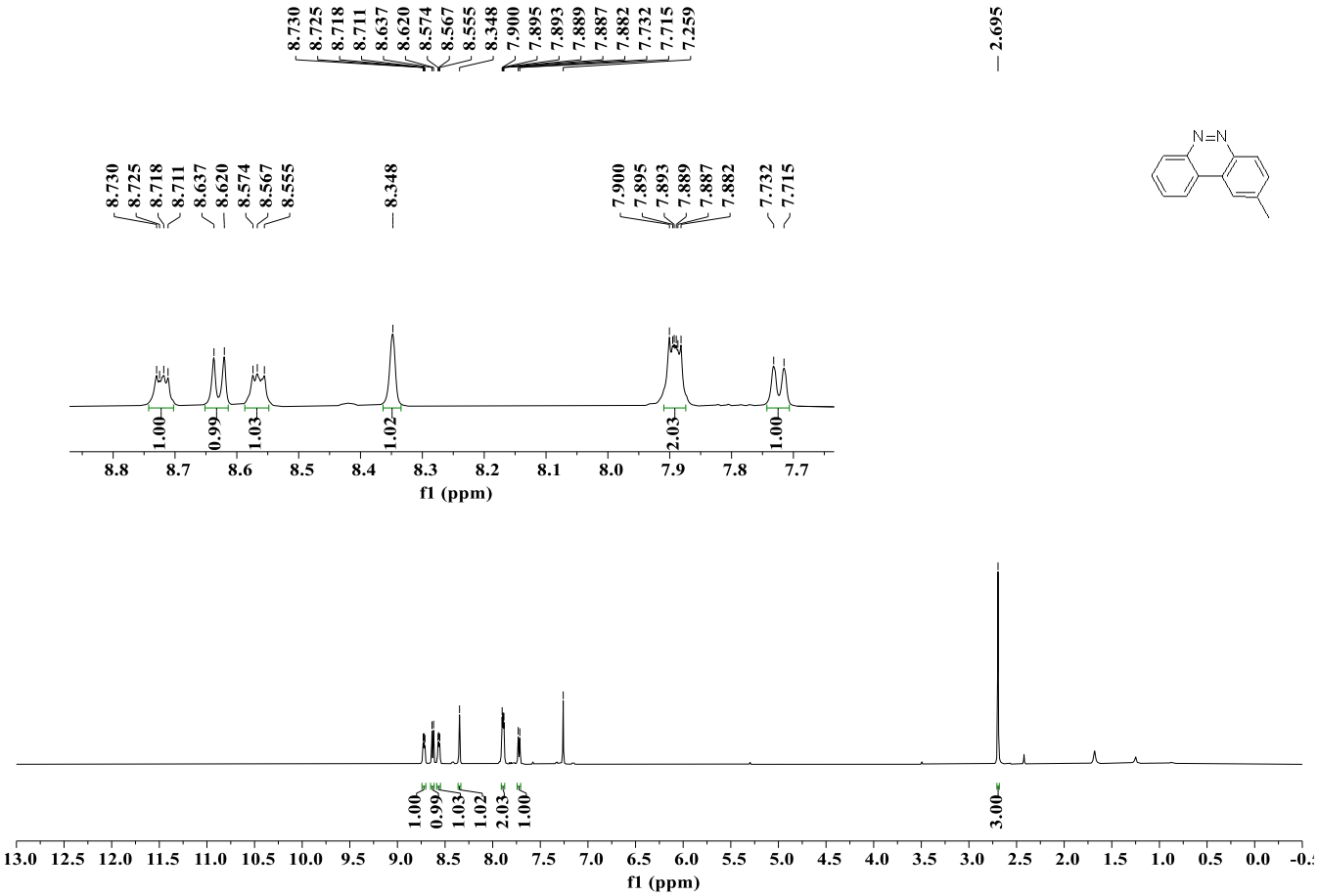
^{1}H NMR (500 MHz, $CDCl_3$) of 3q



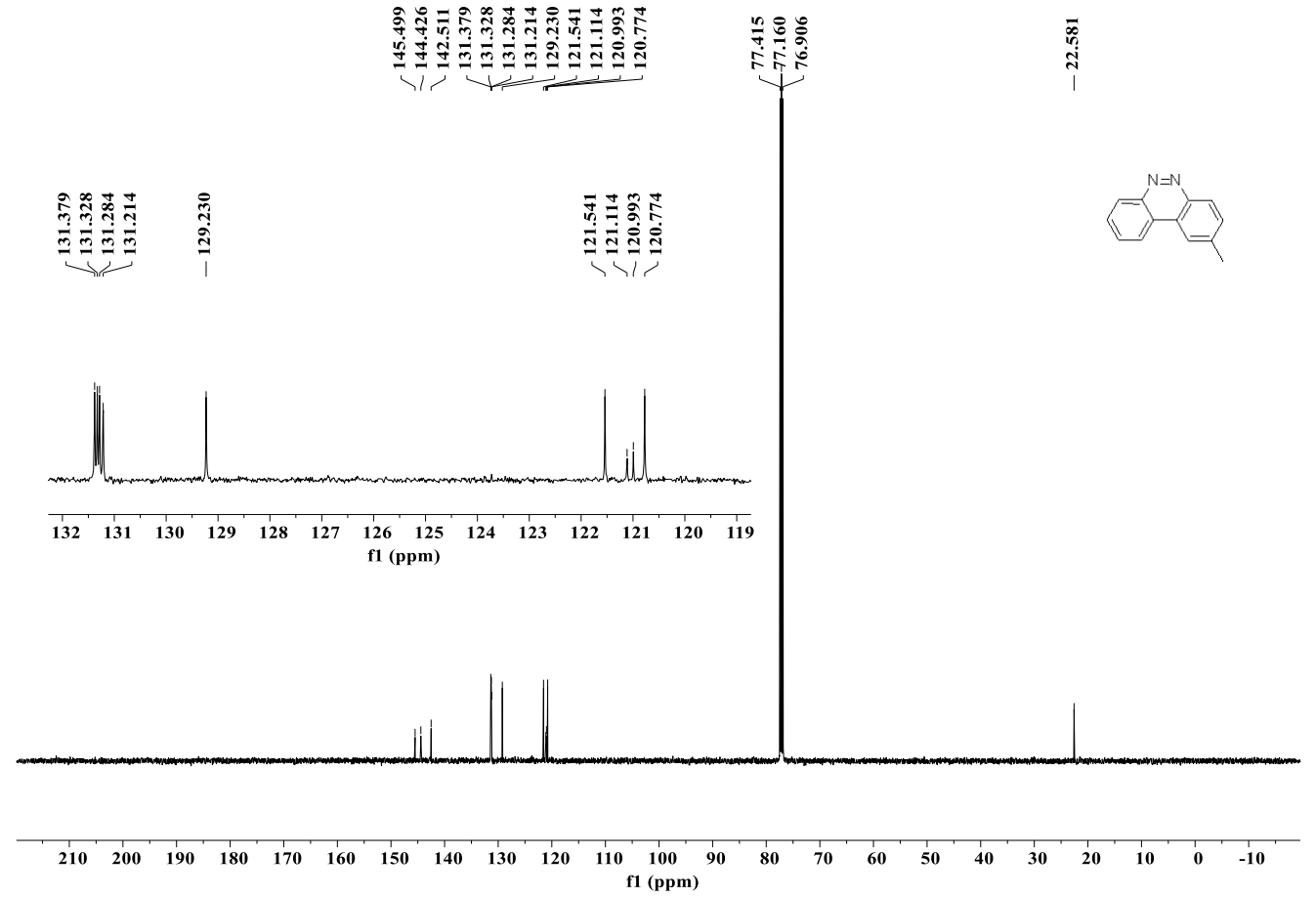
^{13}C NMR (125 MHz, $CDCl_3$) of 3q



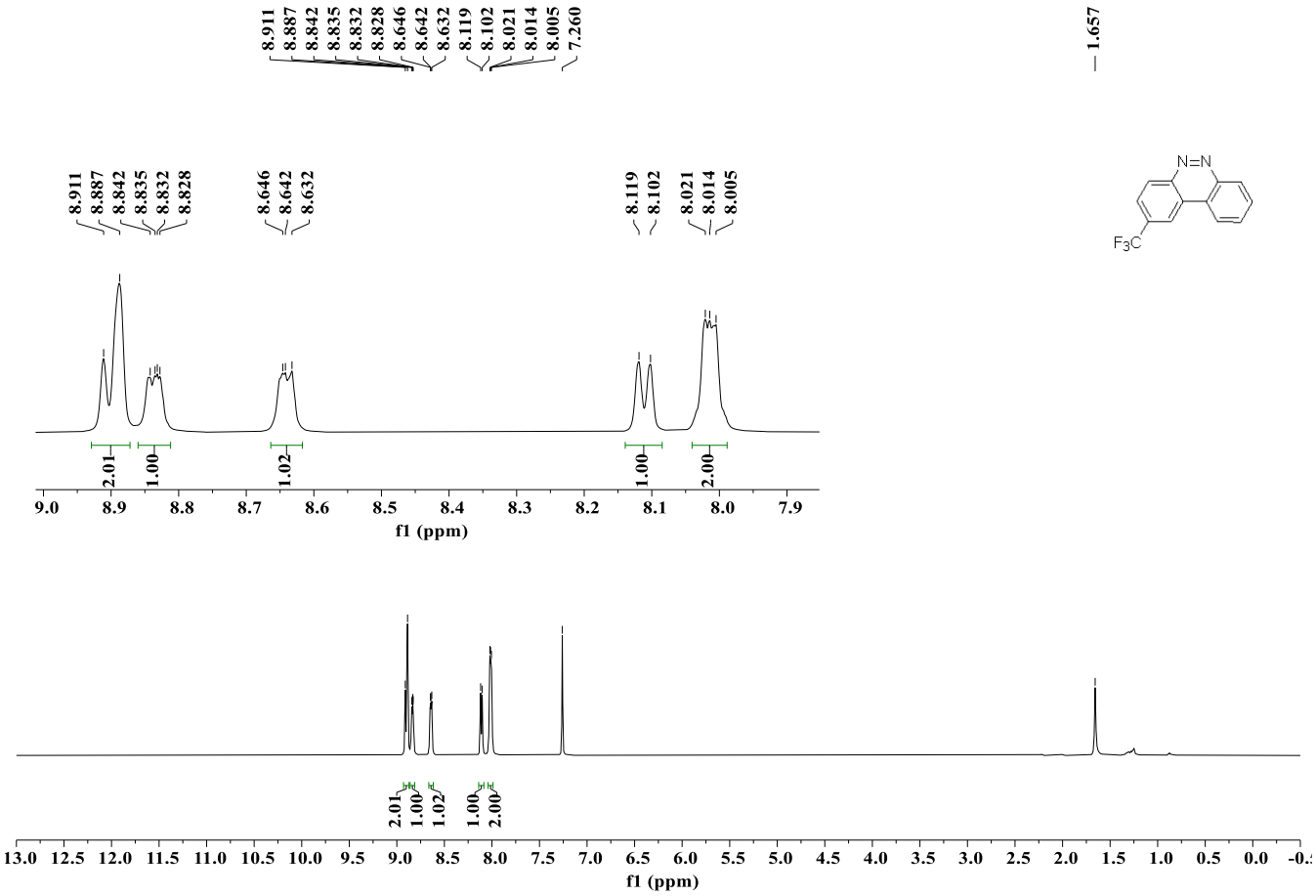
^{1}H NMR (500 MHz, $CDCl_3$) of 3t



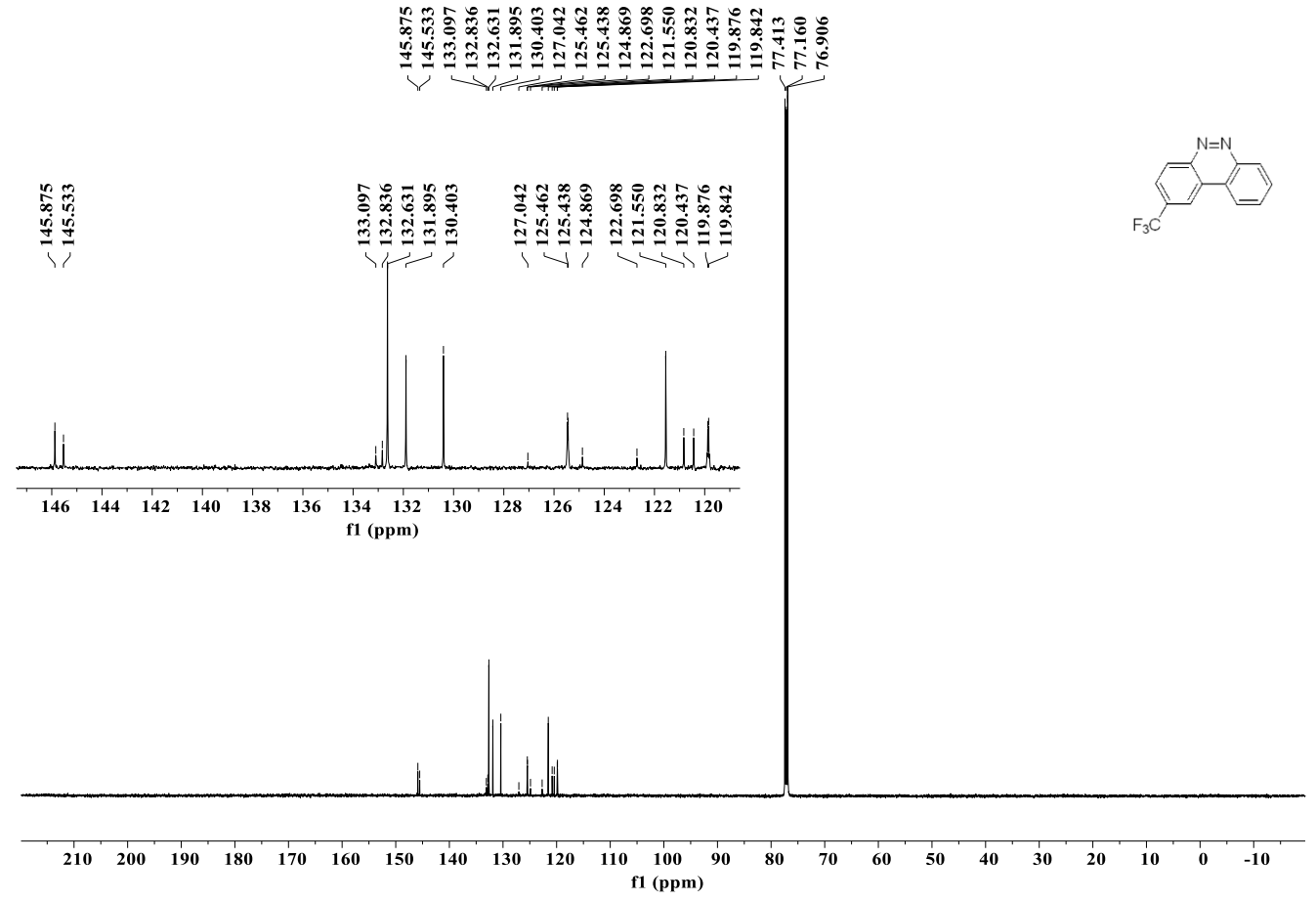
^{13}C NMR (125 MHz, $CDCl_3$) of 3t



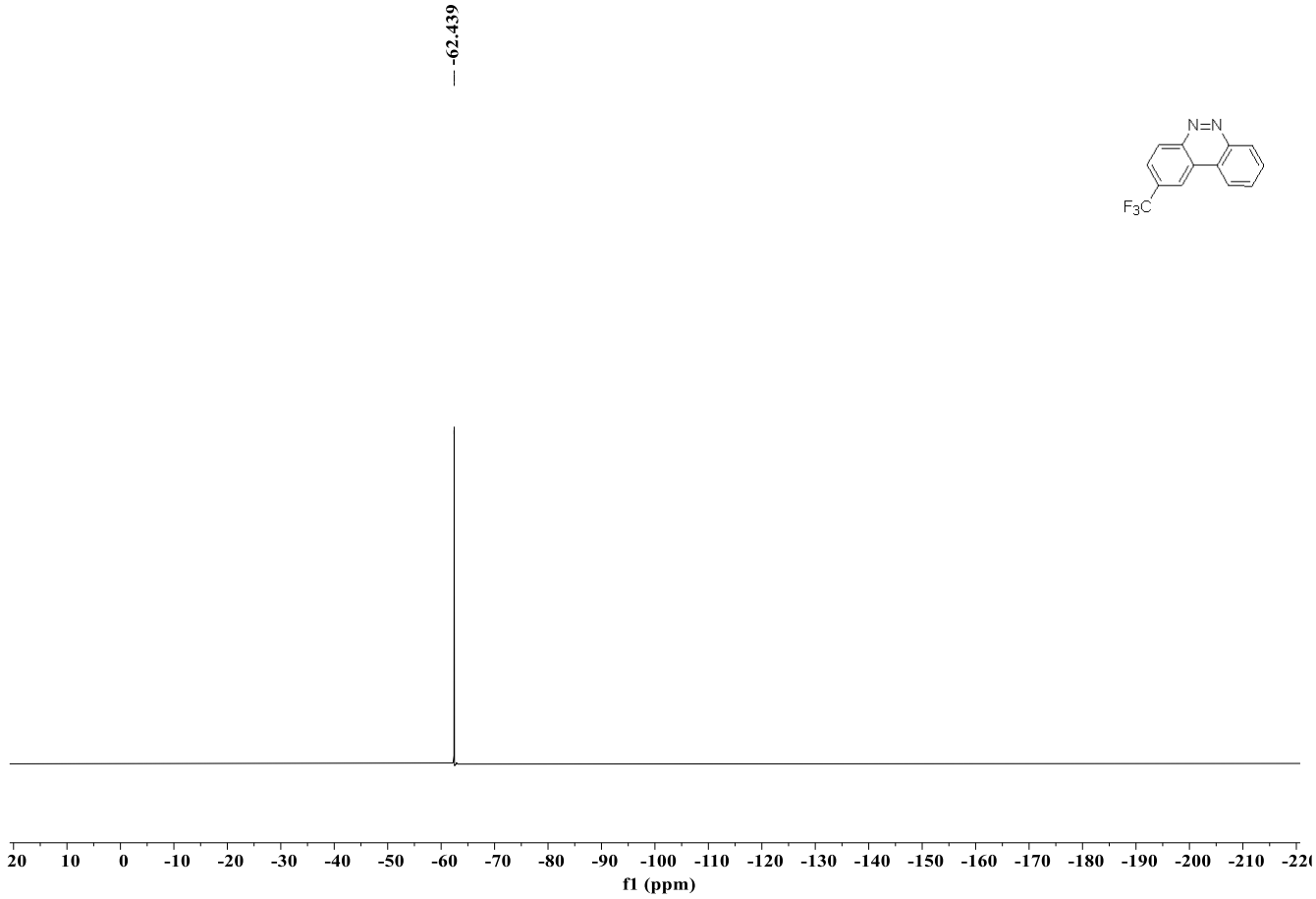
^{1}H NMR (500 MHz, $CDCl_3$) of 3u



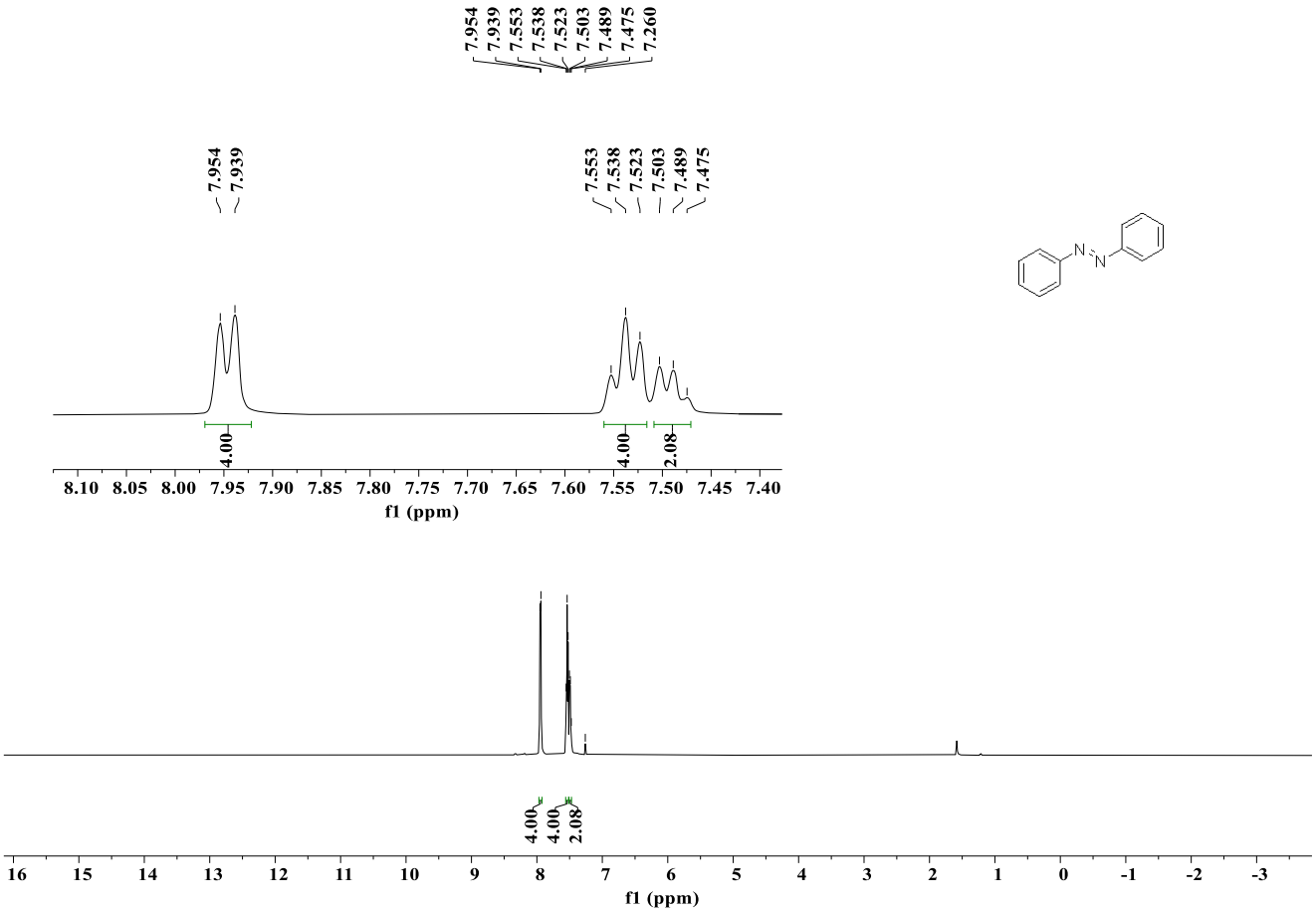
^{13}C NMR (125 MHz, $CDCl_3$) of 3u



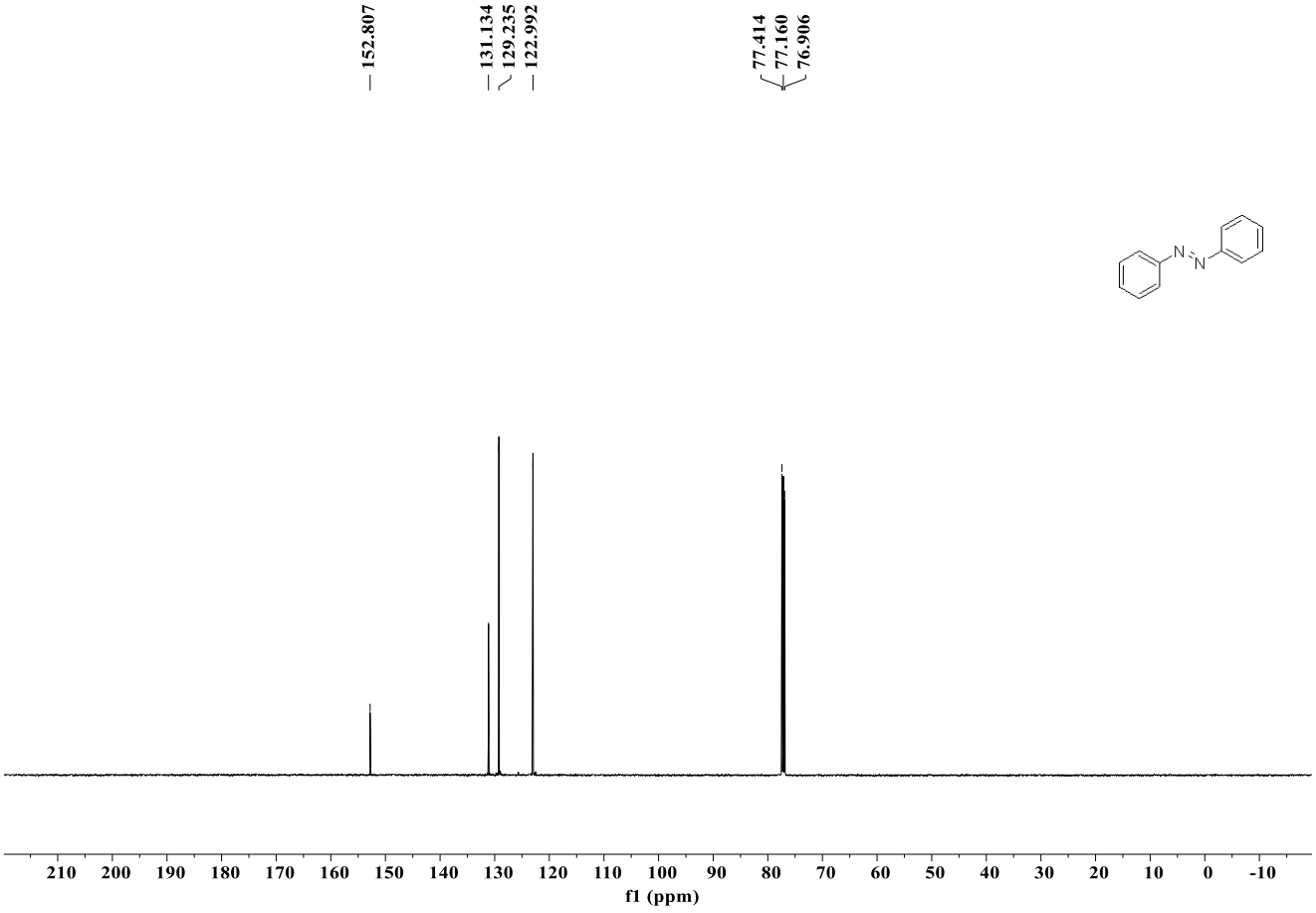
^{19}F NMR (471 MHz, $CDCl_3$) of 3u



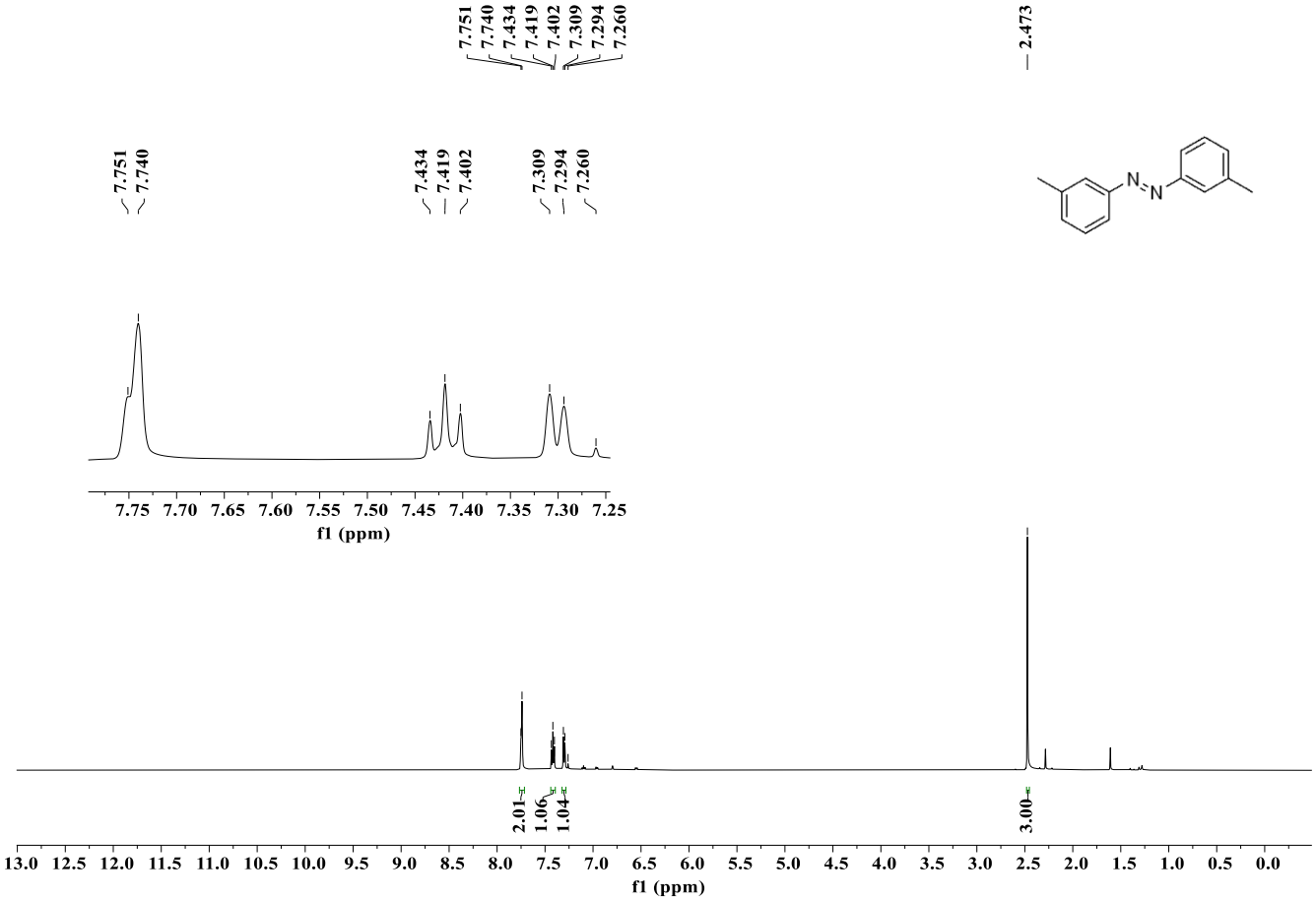
^{1}H NMR (500 MHz, $CDCl_3$) of 5a



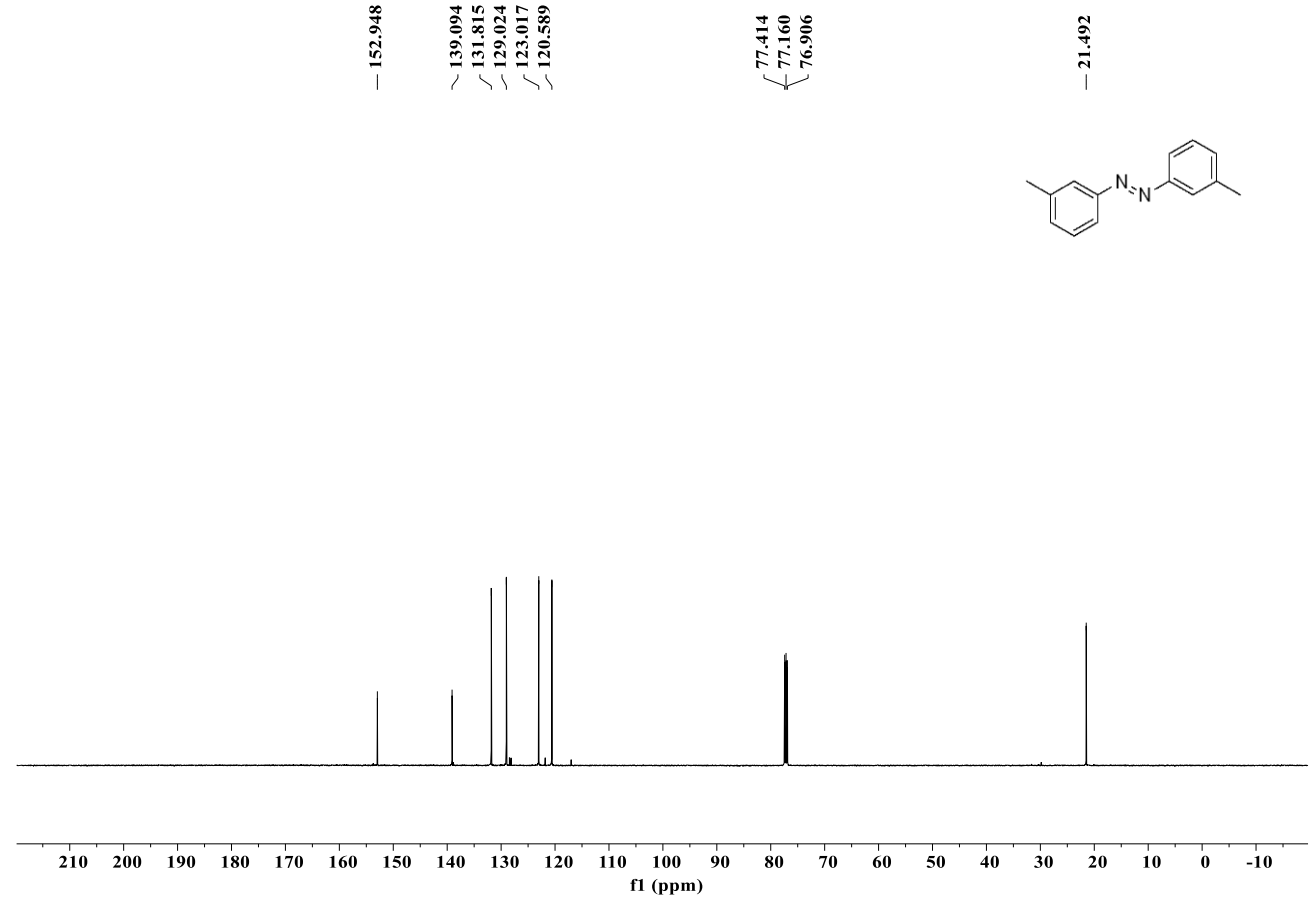
^{13}C NMR (125 MHz, $CDCl_3$) of 5a



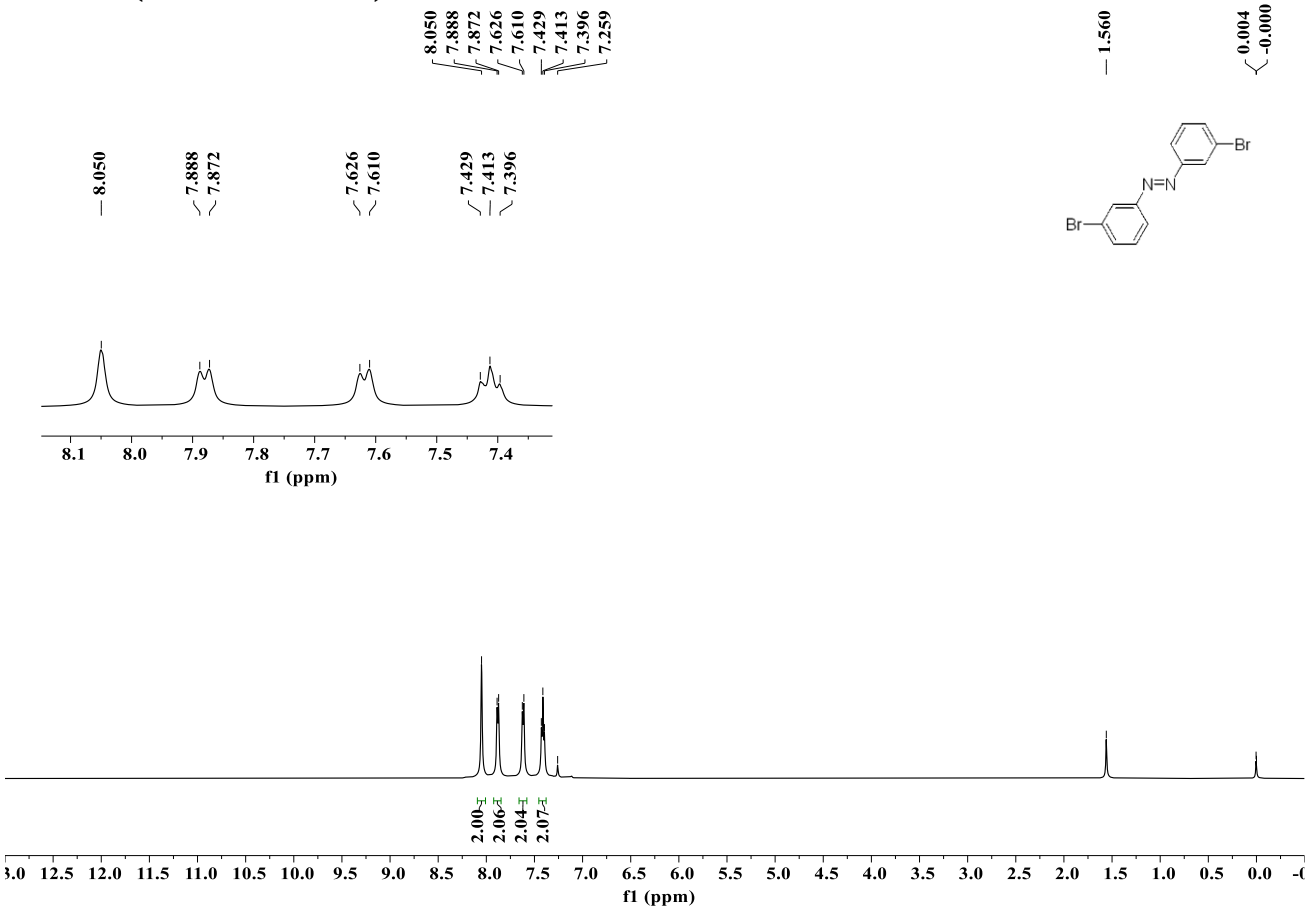
^{1}H NMR (500 MHz, $CDCl_3$) of 5b



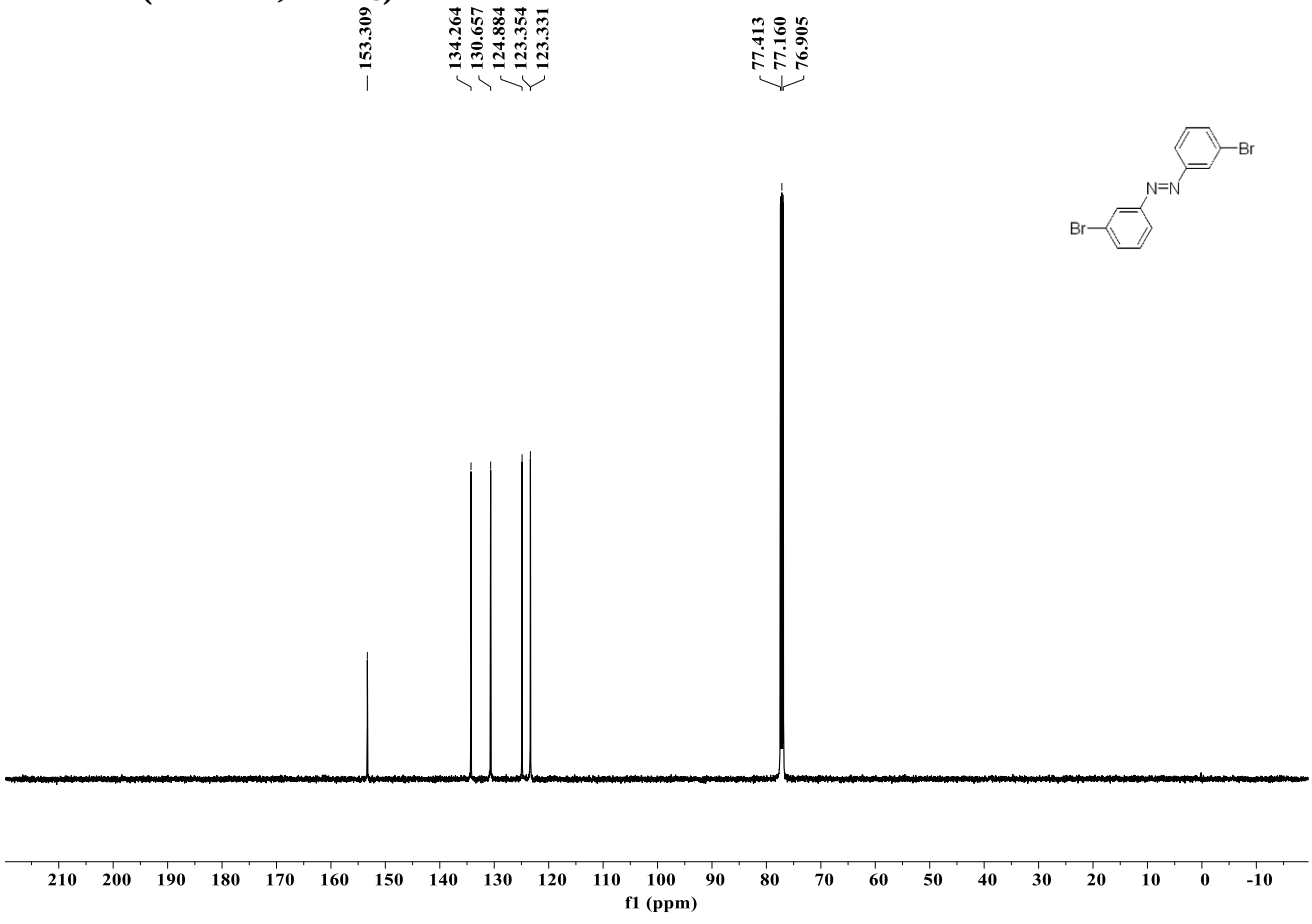
^{13}C NMR (125 MHz, $CDCl_3$) of 5b



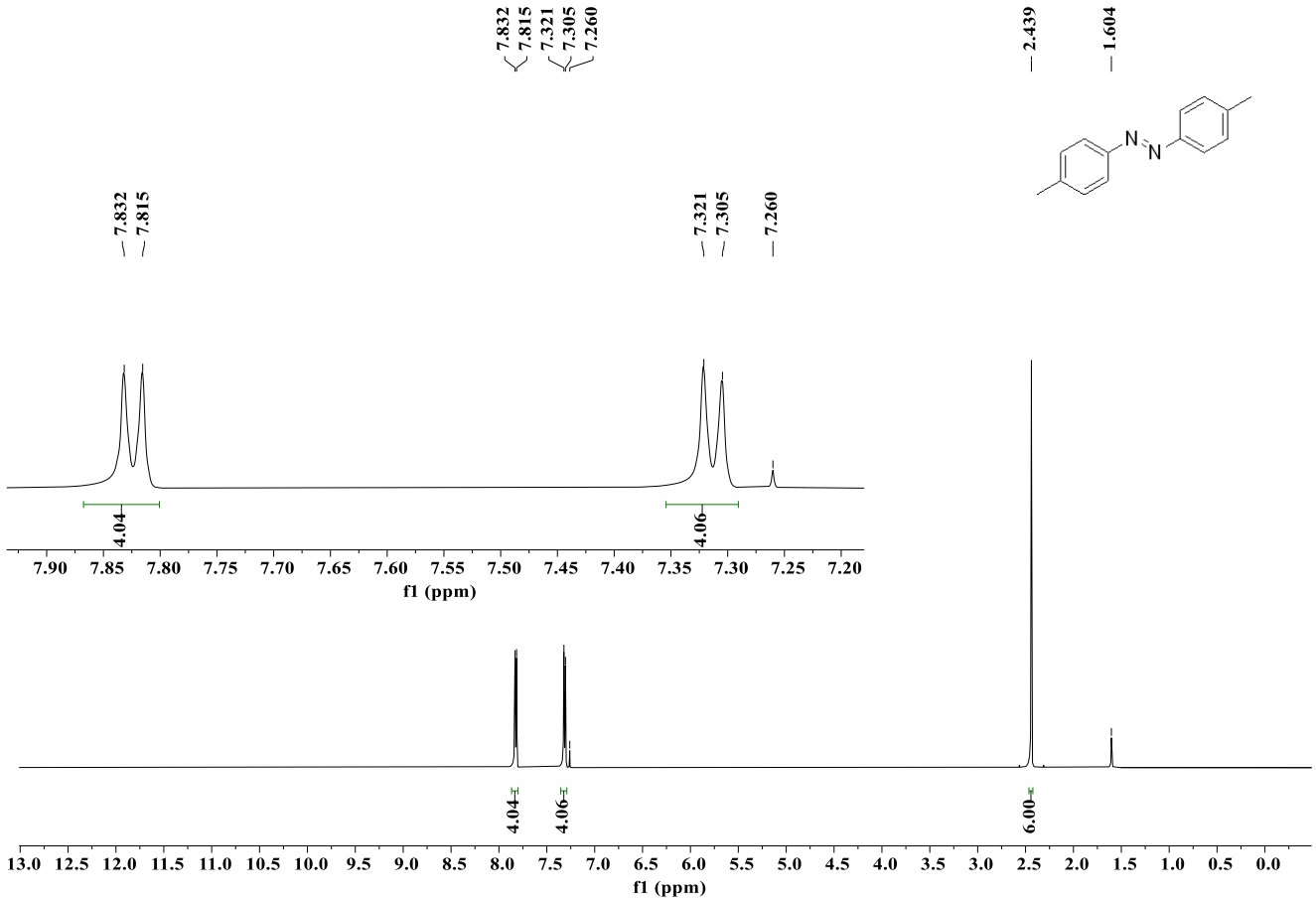
^{1}H NMR (500 MHz, $CDCl_3$) of 5c



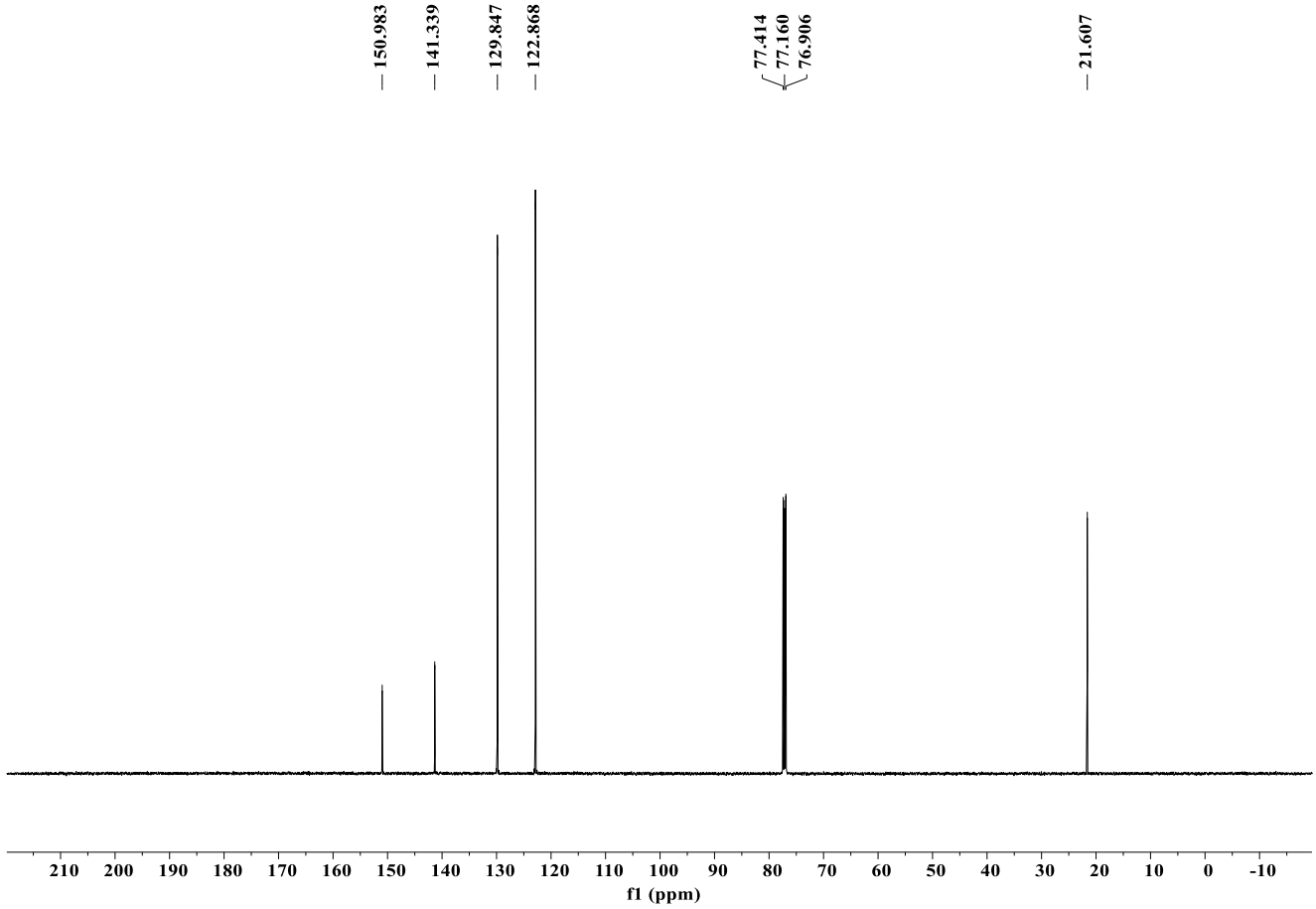
^{13}C NMR (125 MHz, $CDCl_3$) of 5c



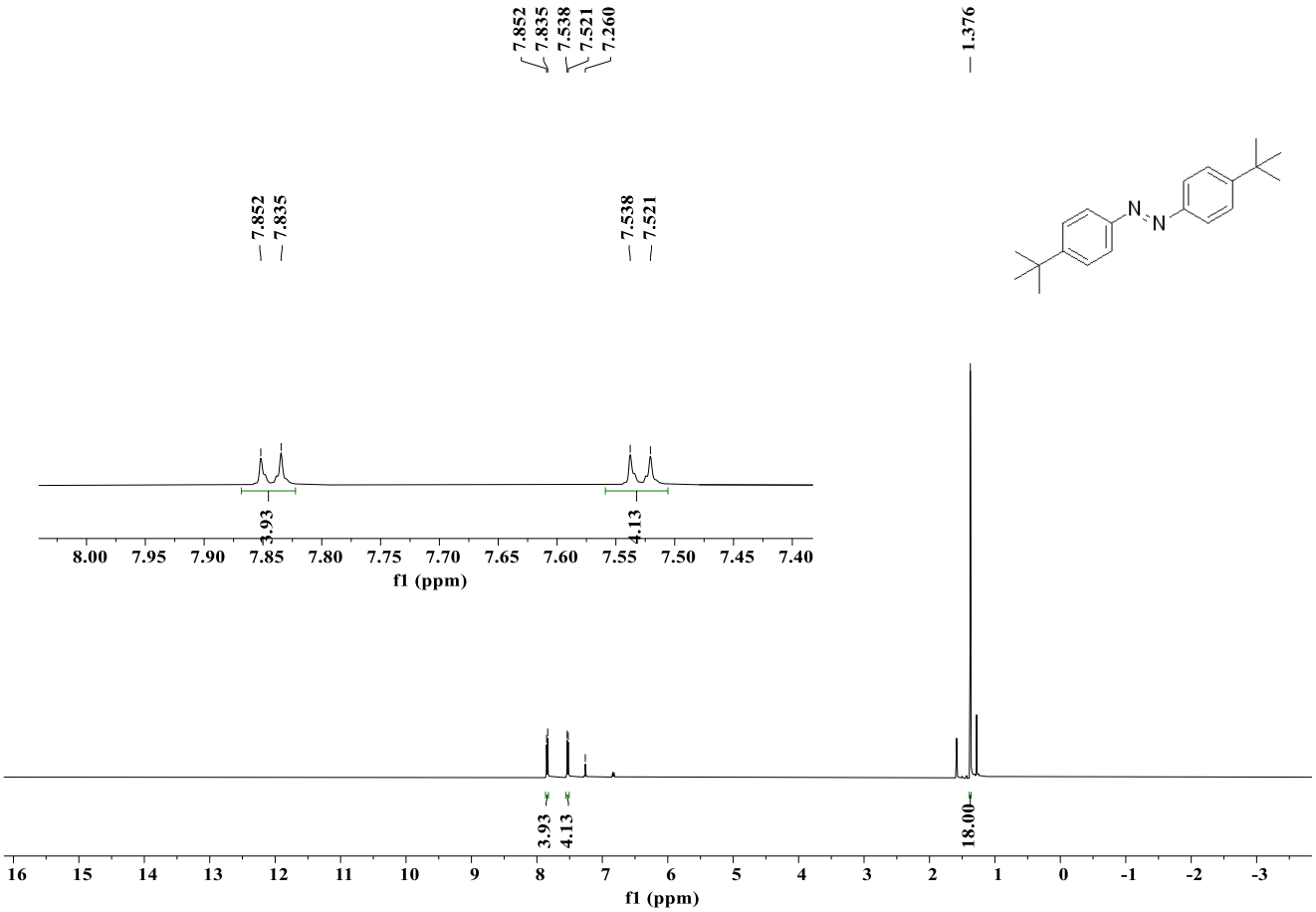
^{1}H NMR (500 MHz, $CDCl_3$) of 5d



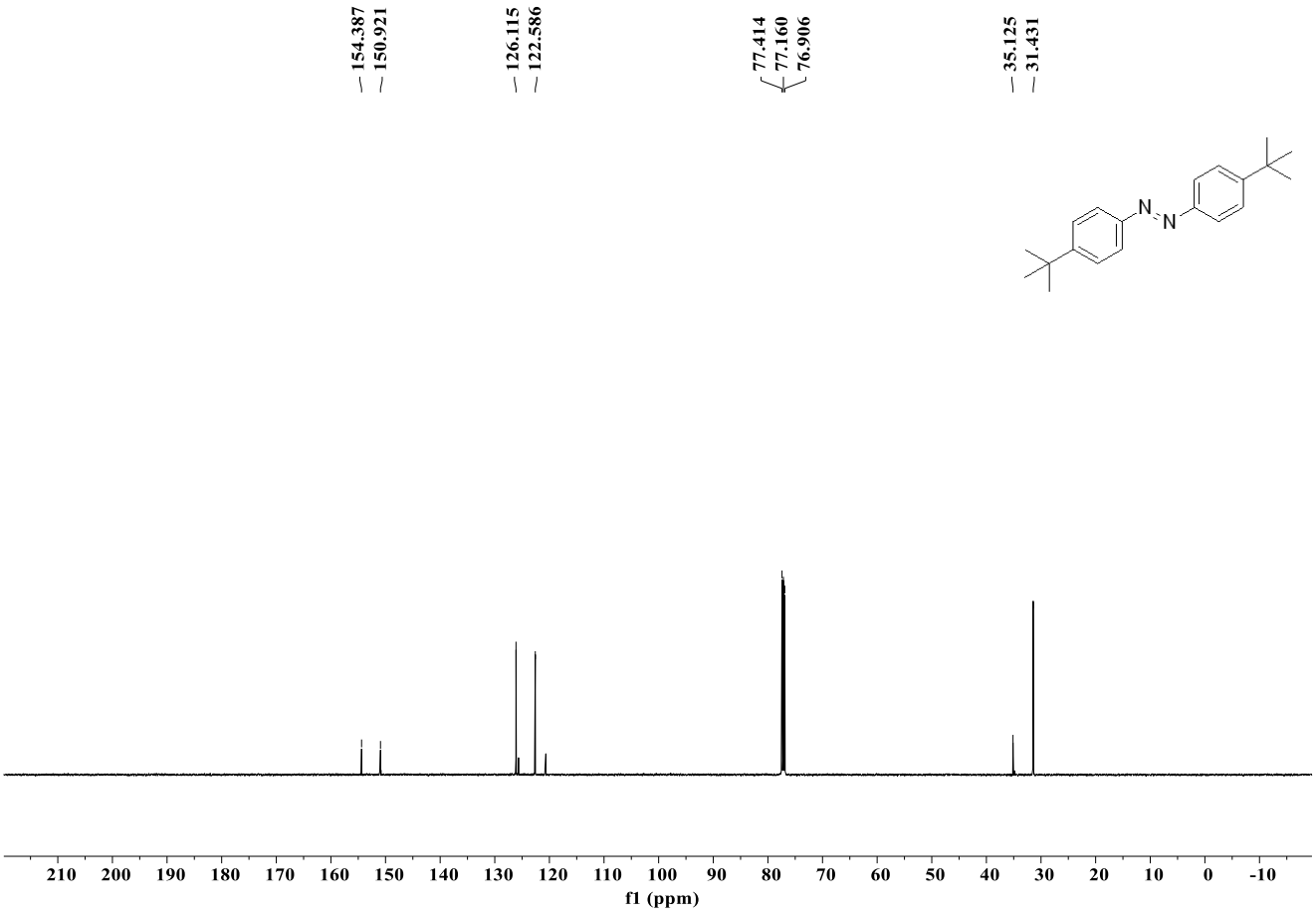
^{13}C NMR (125 MHz, $CDCl_3$) of 5d



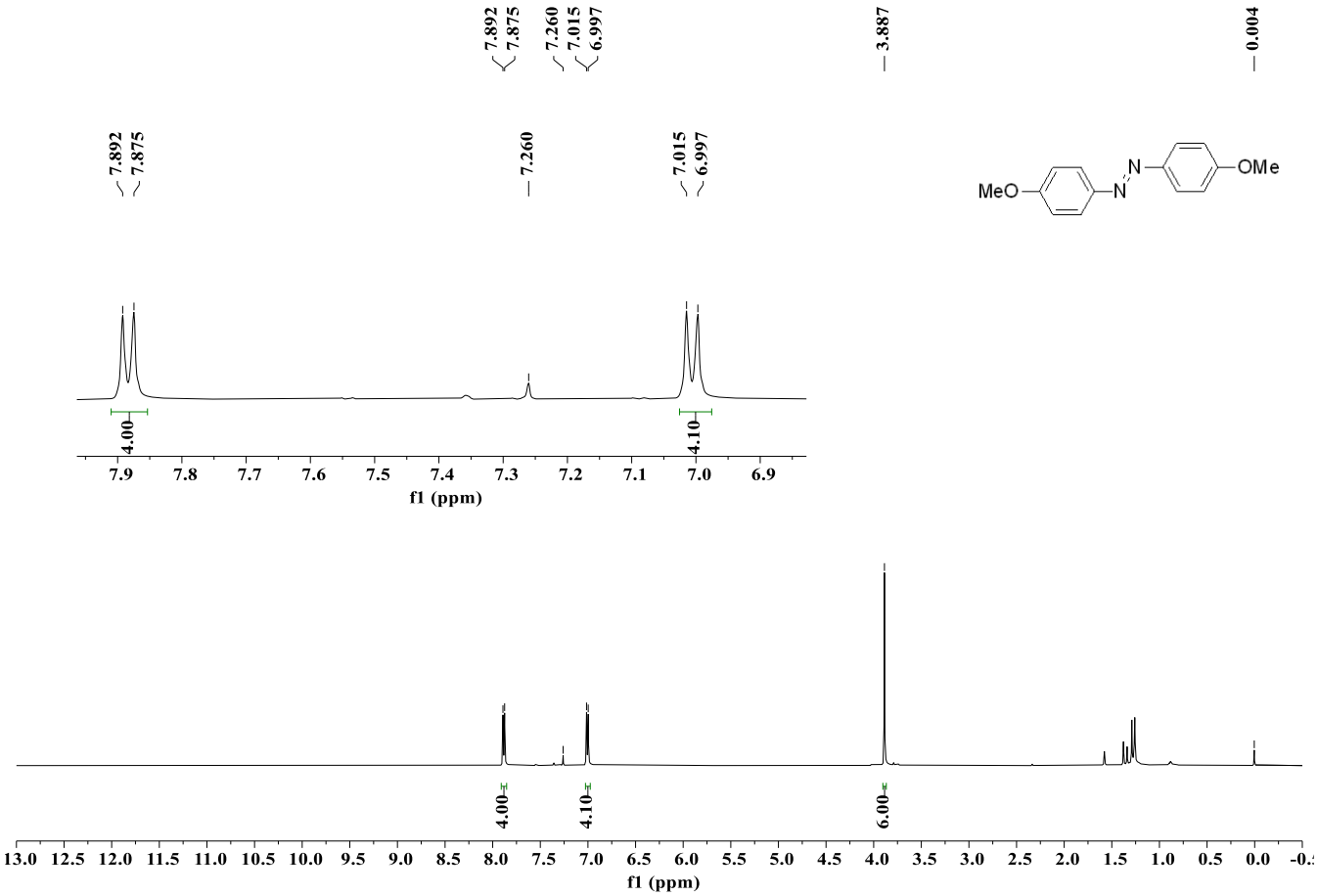
^{1}H NMR (500 MHz, $CDCl_3$) of 5e



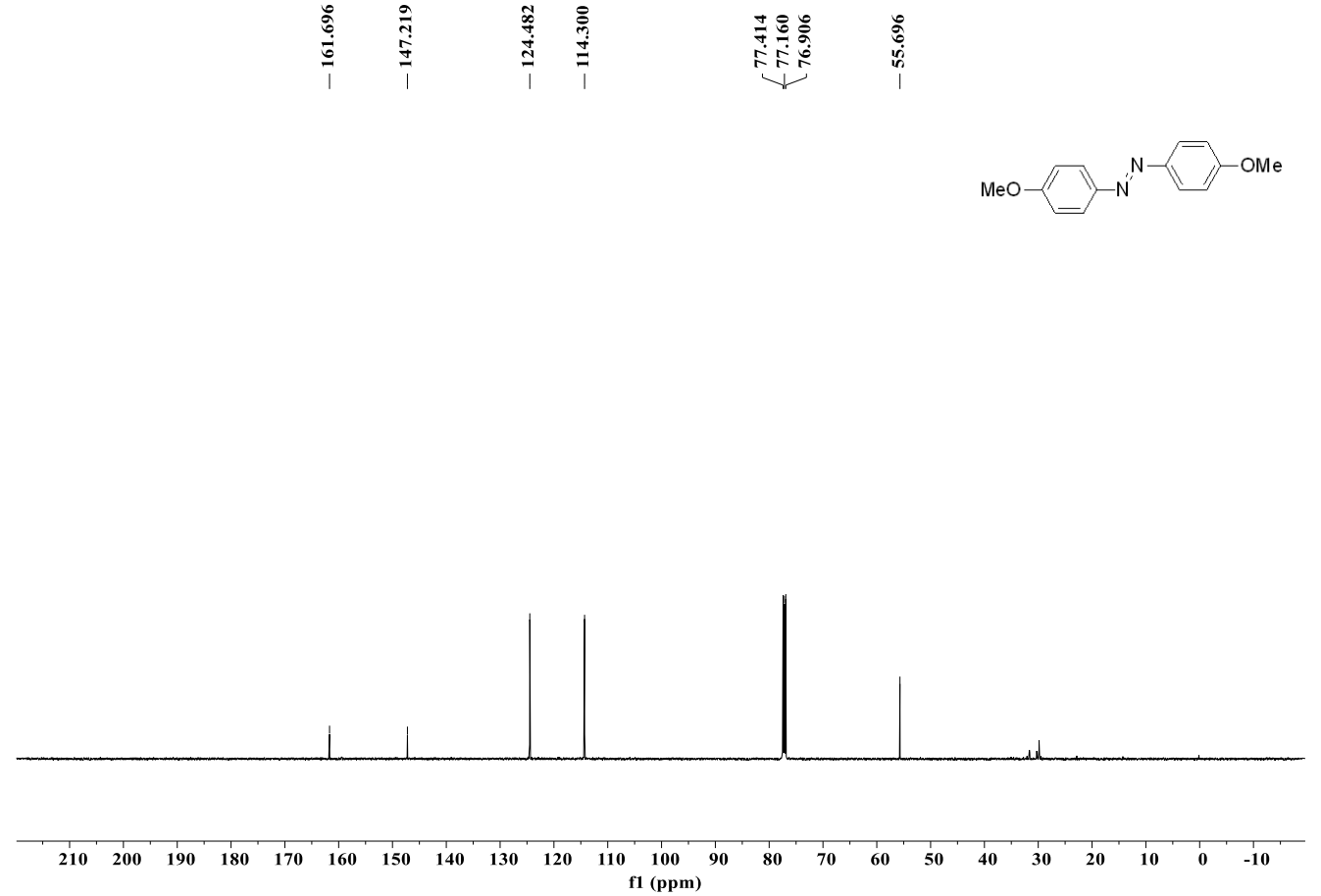
^{13}C NMR (125 MHz, $CDCl_3$) of 5e



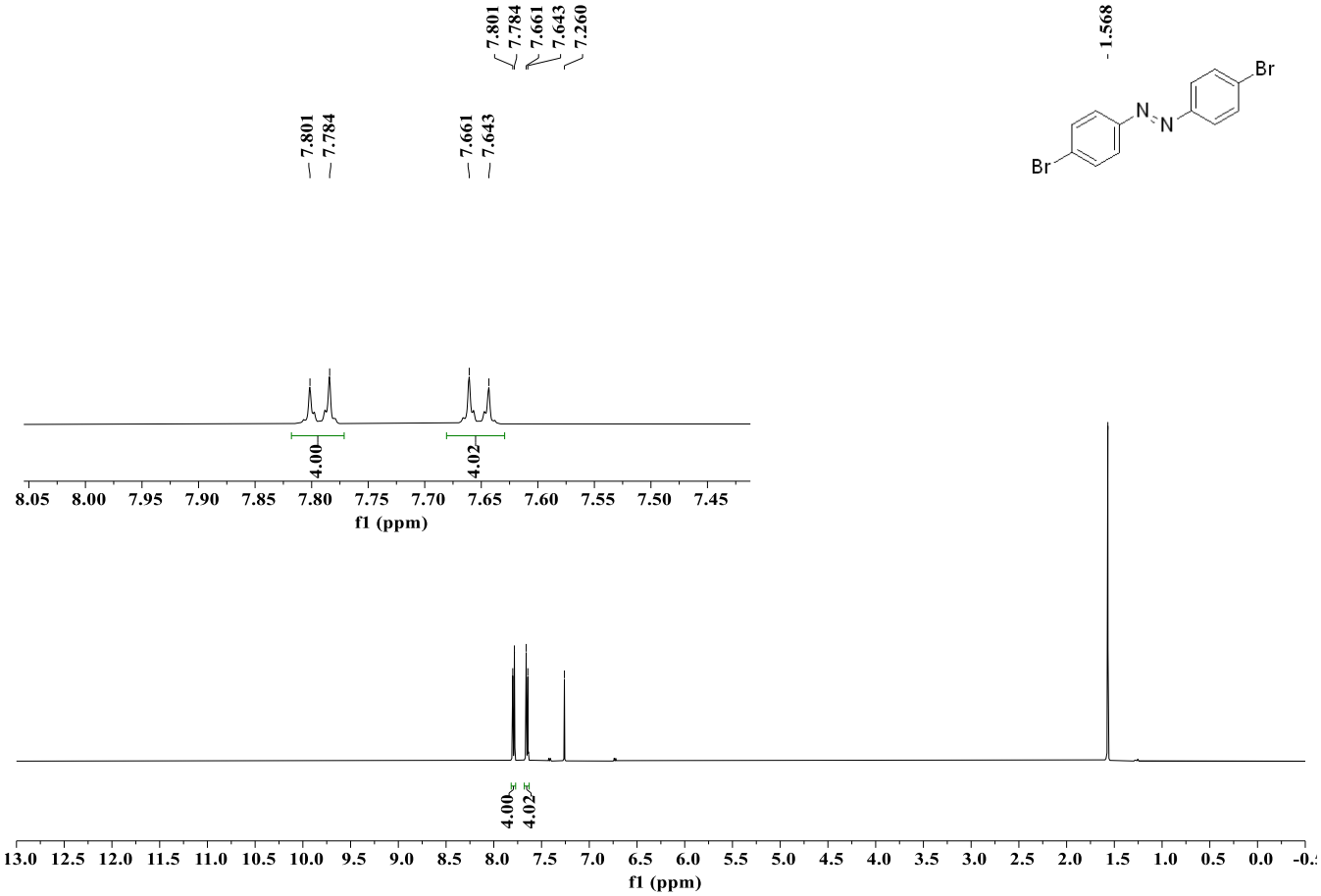
^{1}H NMR (500 MHz, $CDCl_3$) of 5f



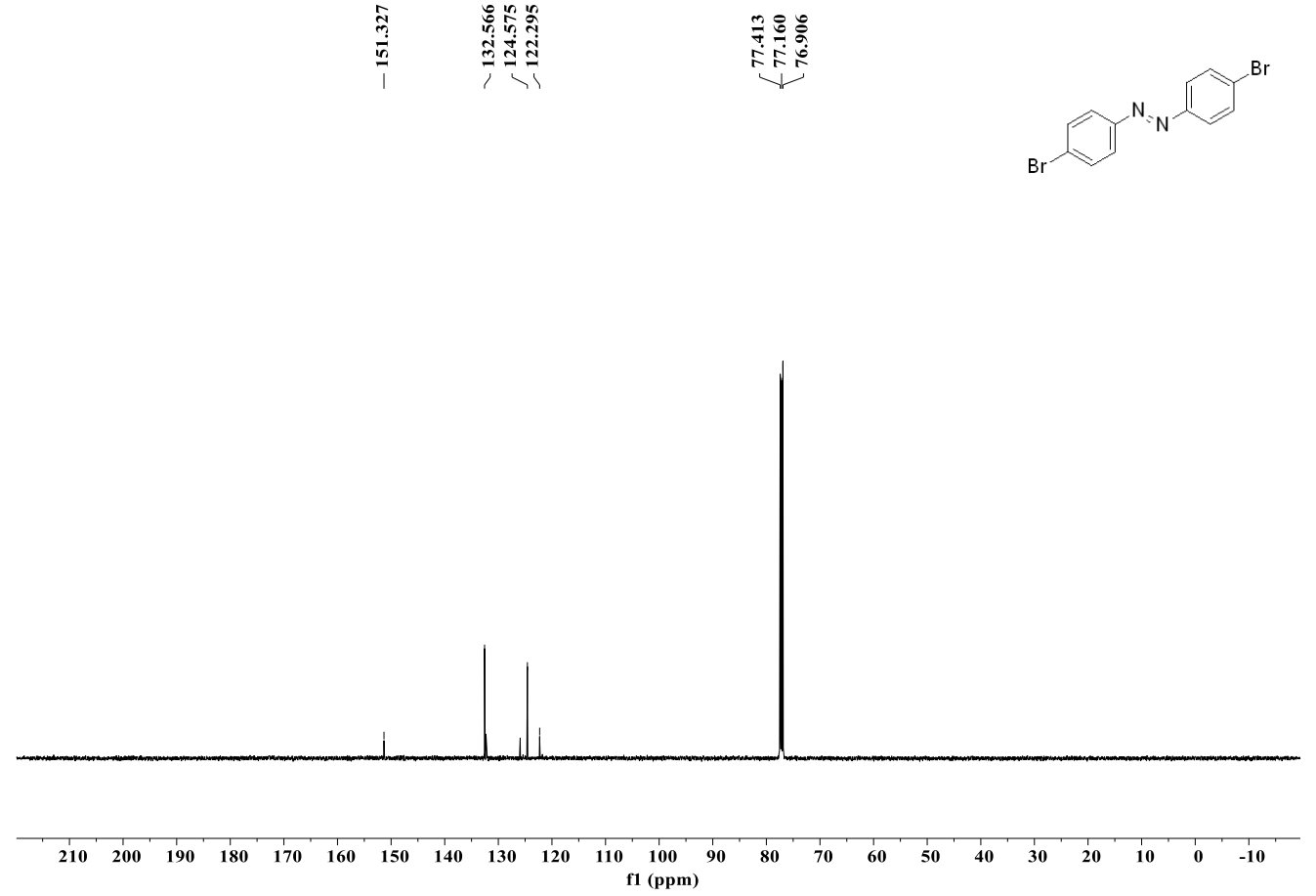
^{13}C NMR (125 MHz, $CDCl_3$) of 5f



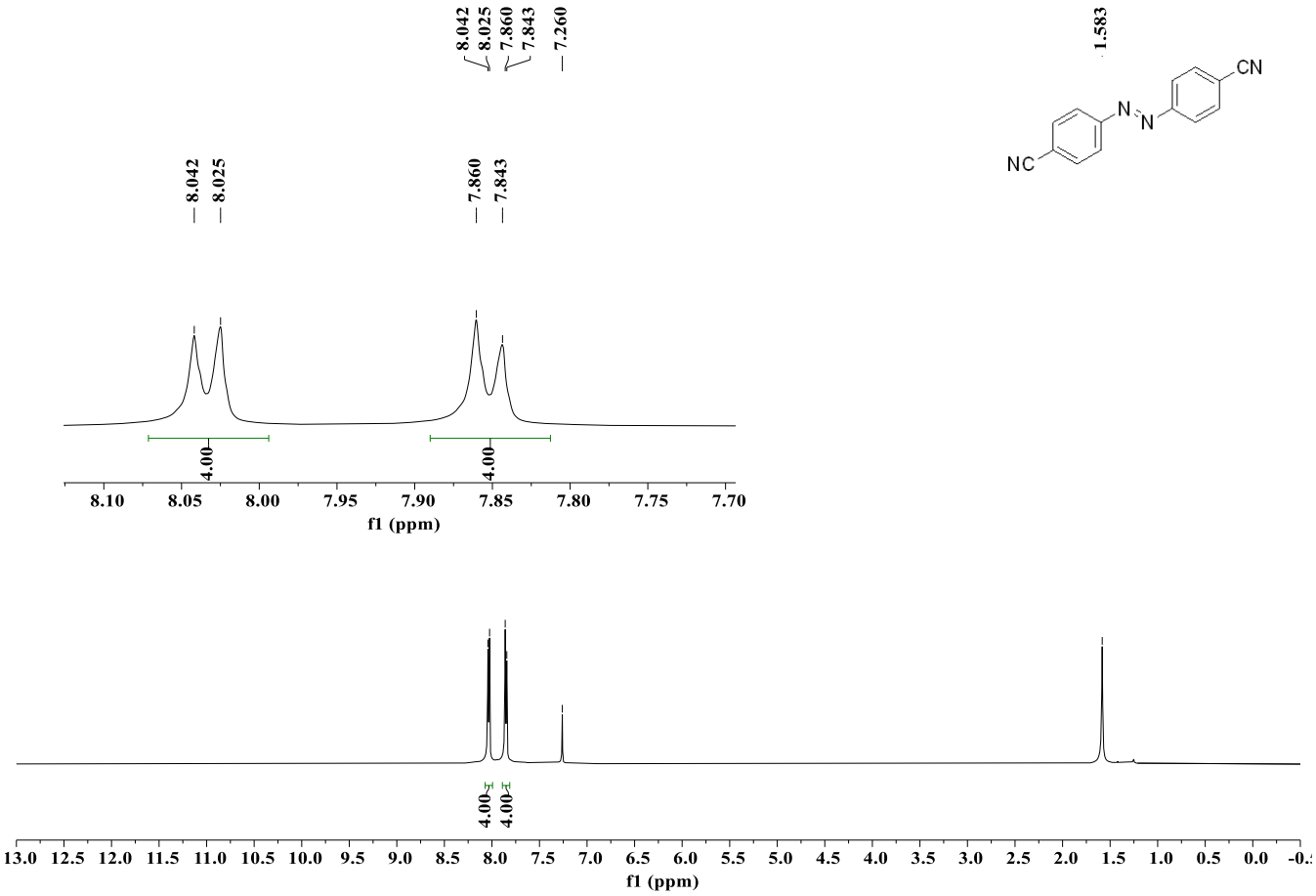
^{1}H NMR (500 MHz, $CDCl_3$) of 5g



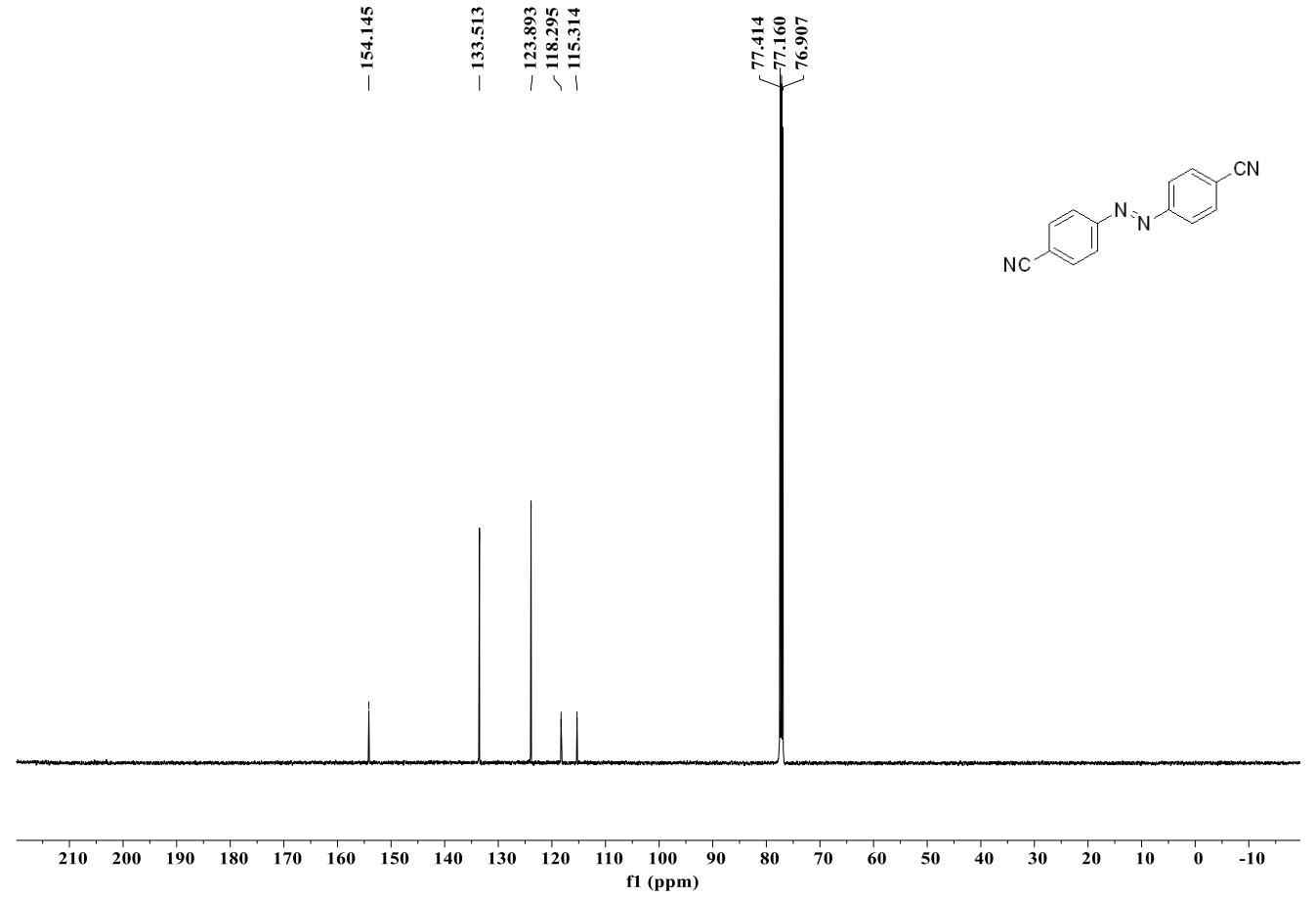
^{13}C NMR (125 MHz, $CDCl_3$) of 5g



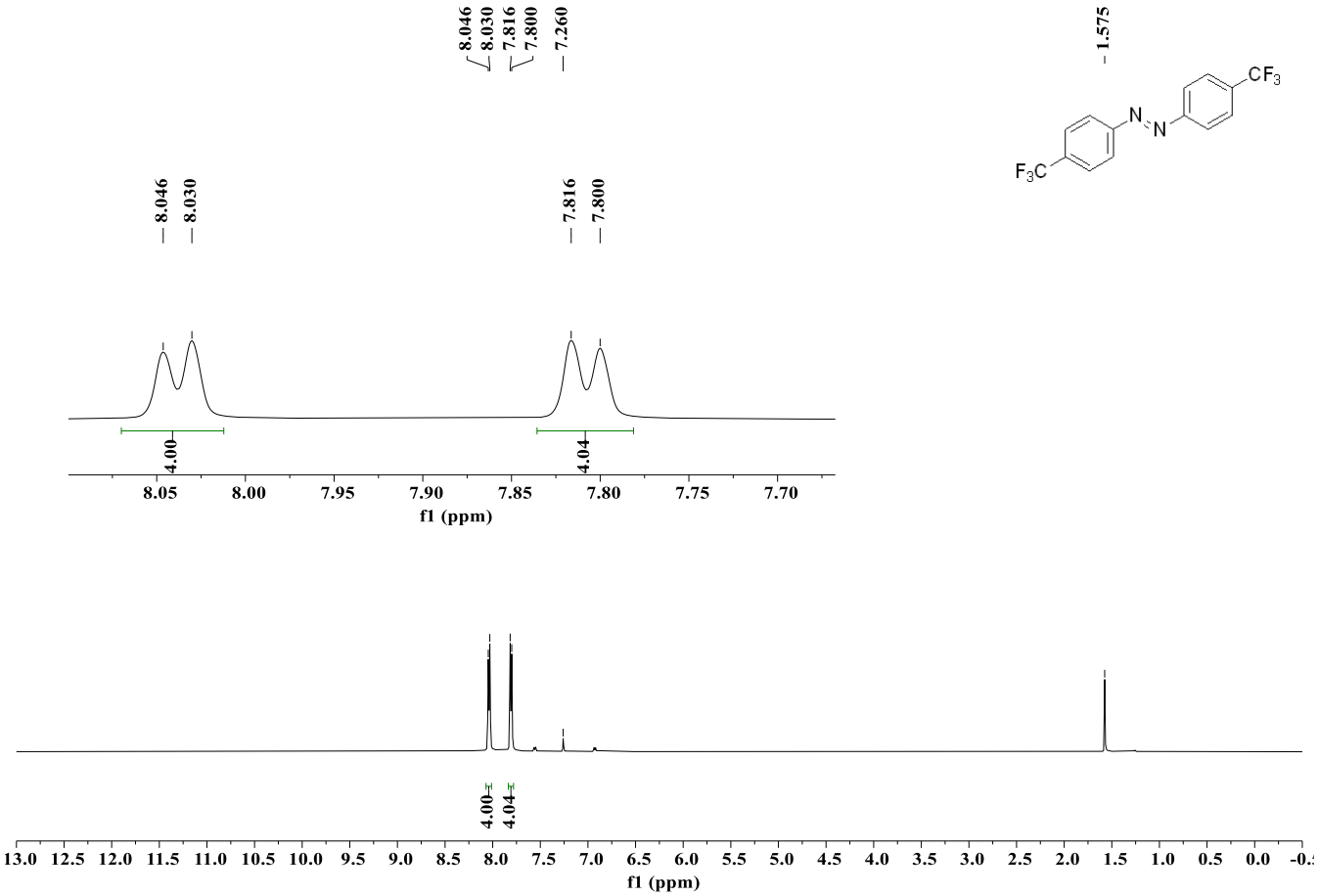
^{1}H NMR (500 MHz, $CDCl_3$) of 5h



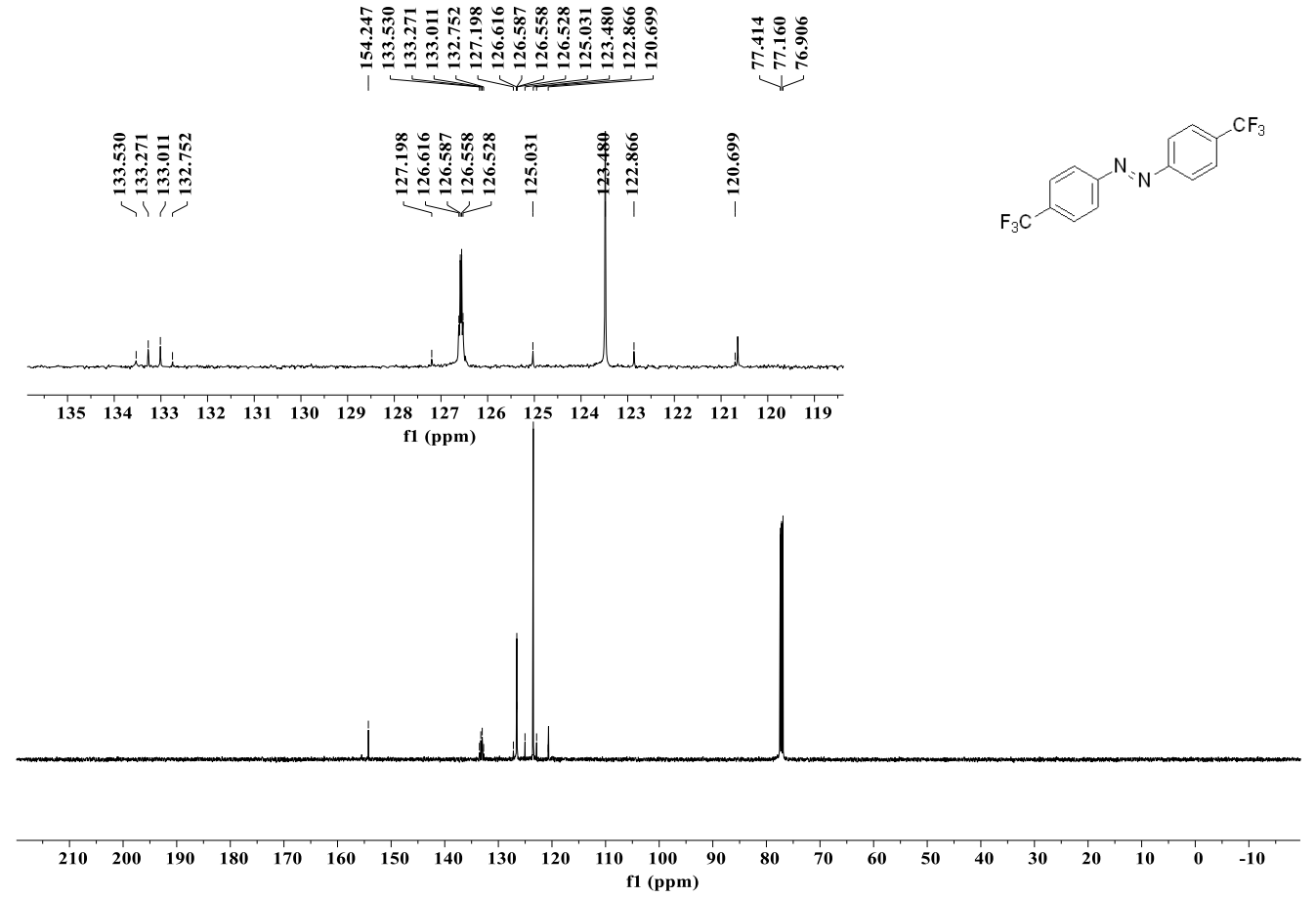
^{13}C NMR (125 MHz, $CDCl_3$) of 5h



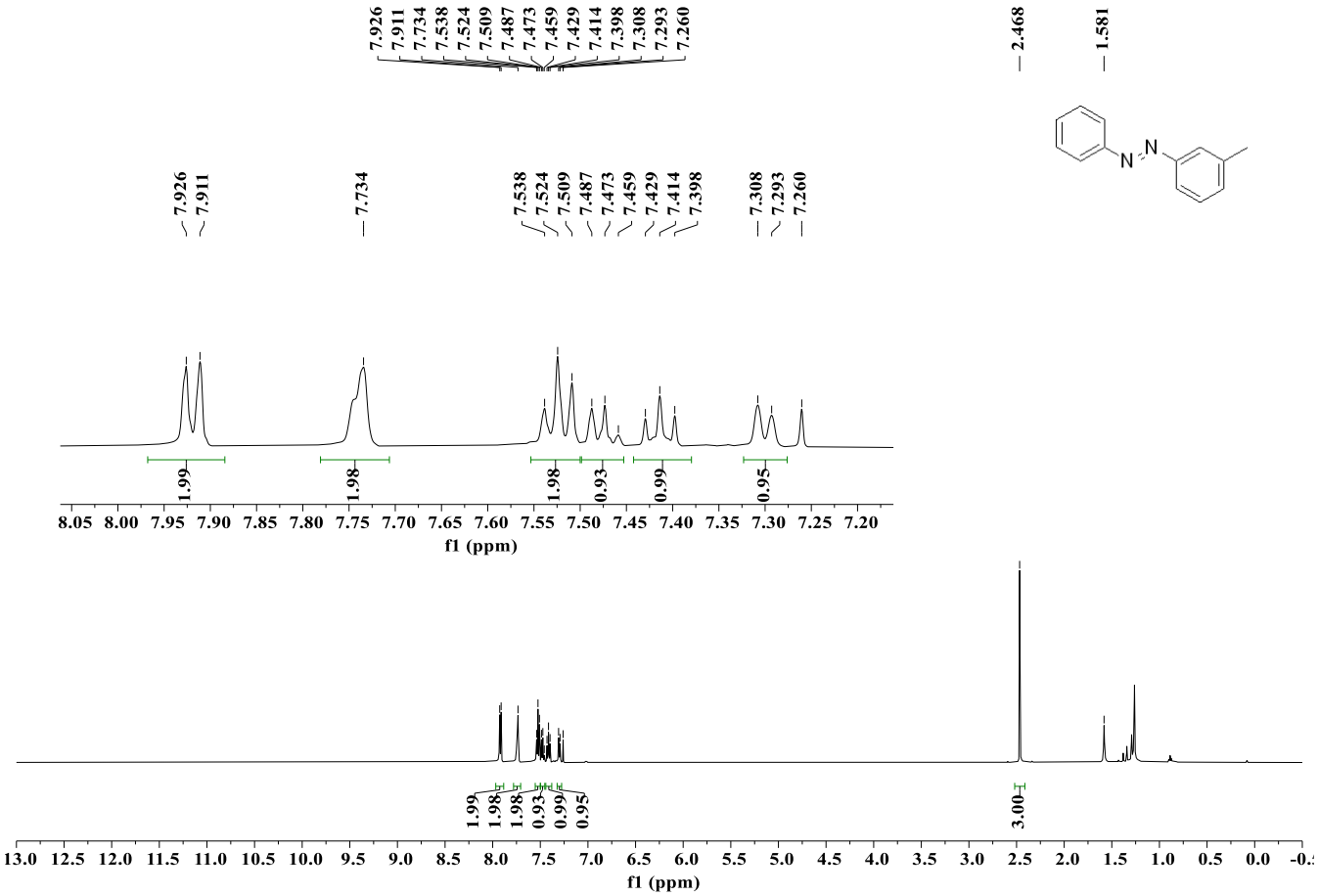
^{1}H NMR (500 MHz, $CDCl_3$) of 5i



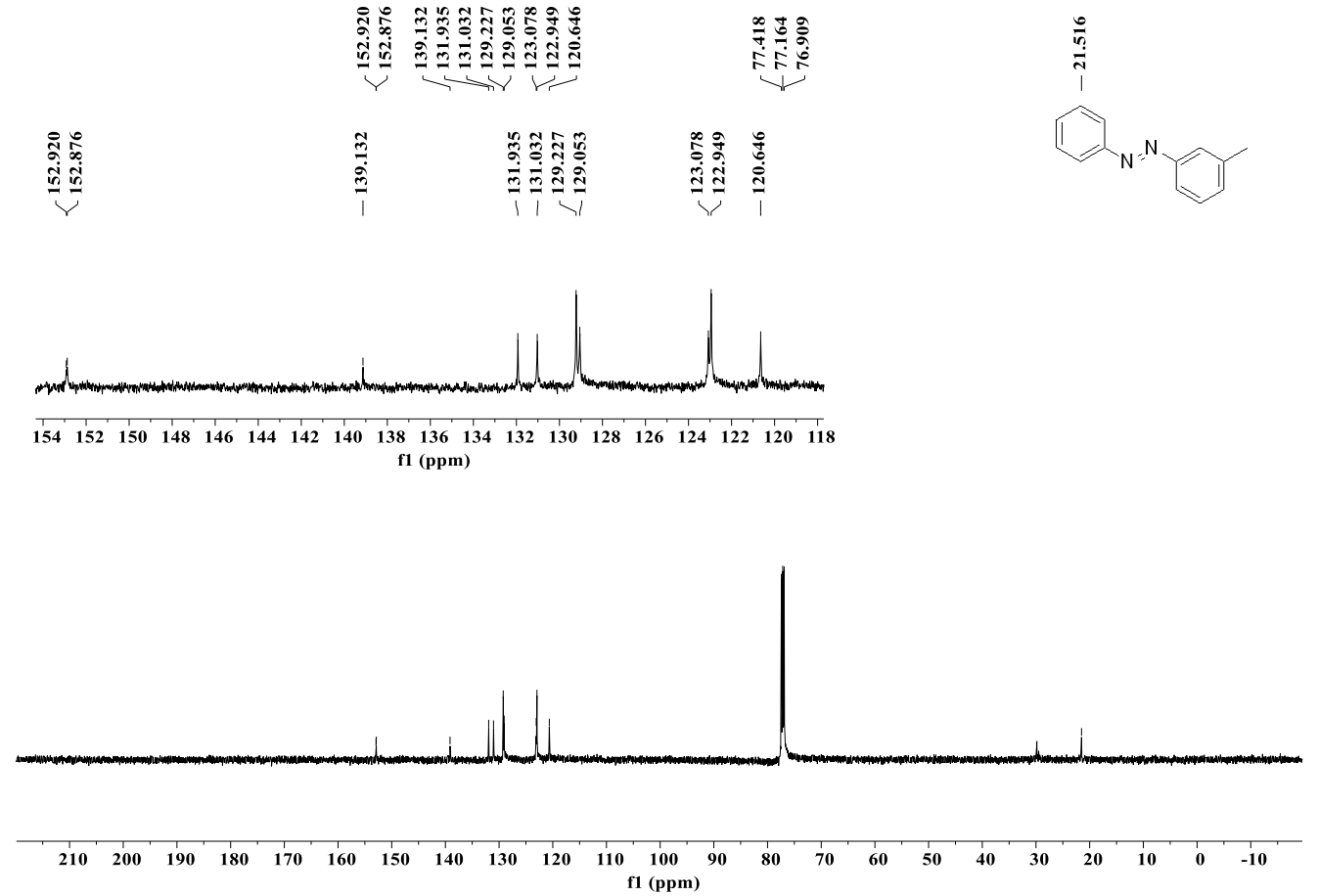
^{13}C NMR (125 MHz, $CDCl_3$) of 5i



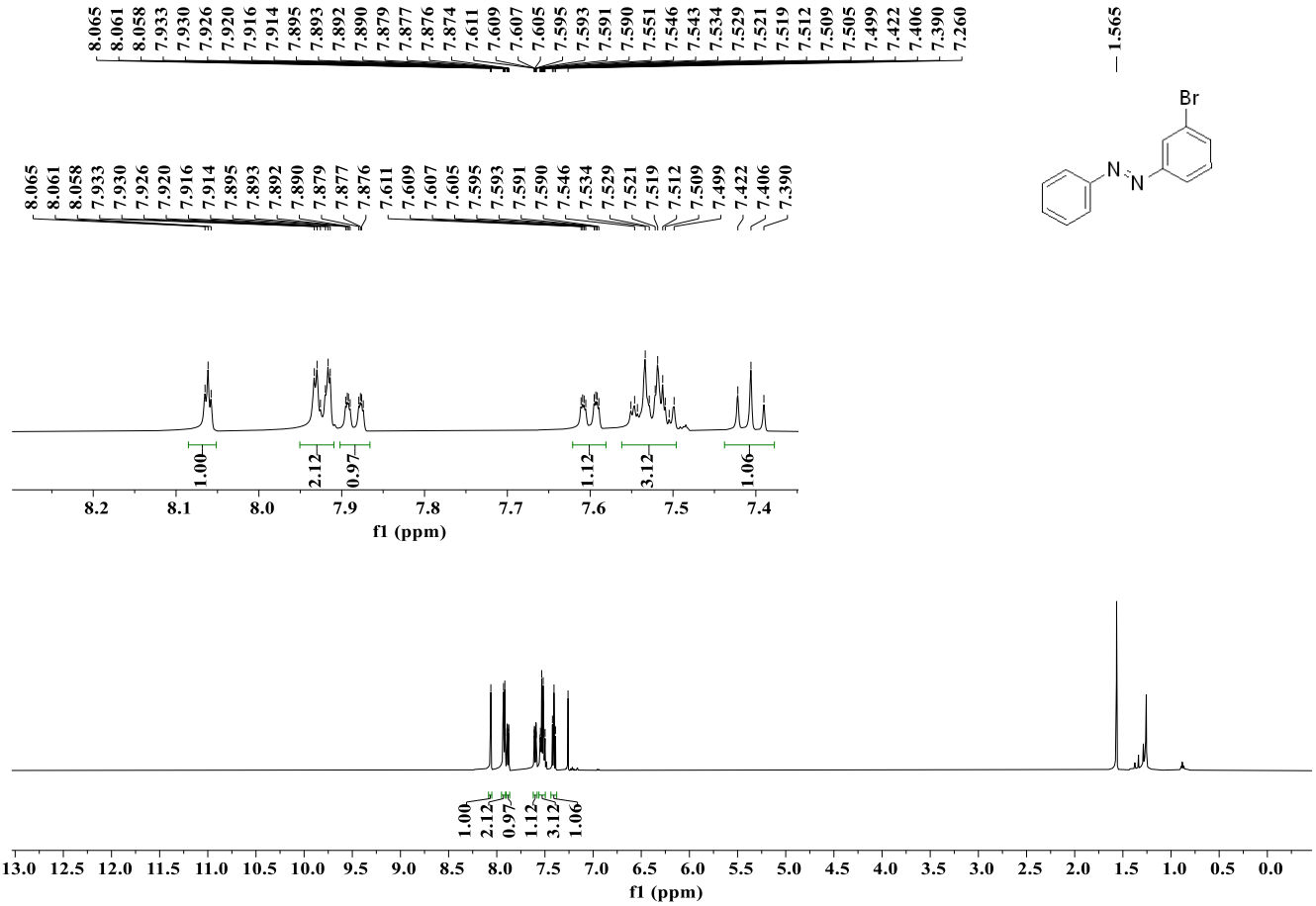
^{1}H NMR (500 MHz, $CDCl_3$) of 6ab



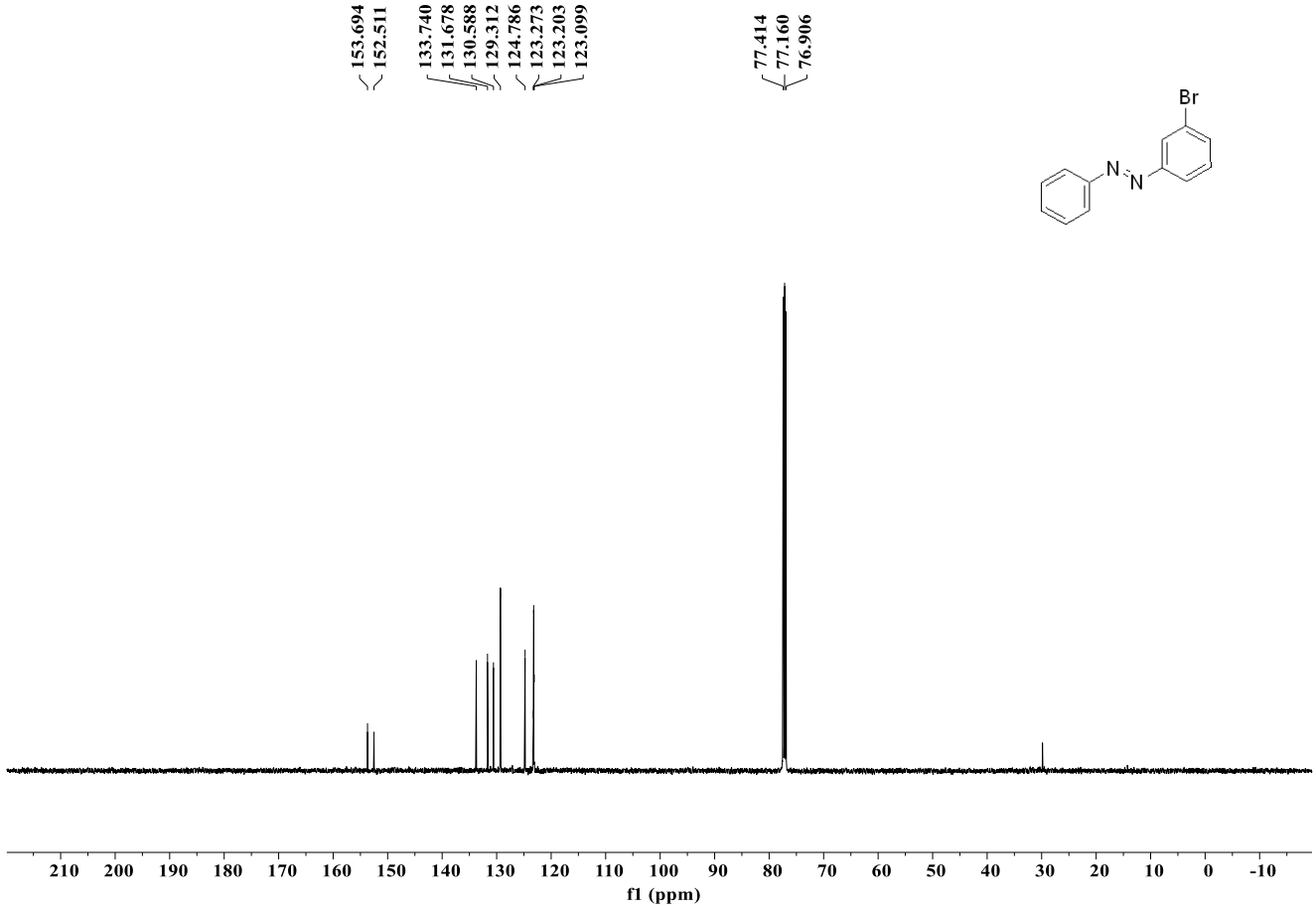
^{13}C NMR (125 MHz, $CDCl_3$) of 6ab



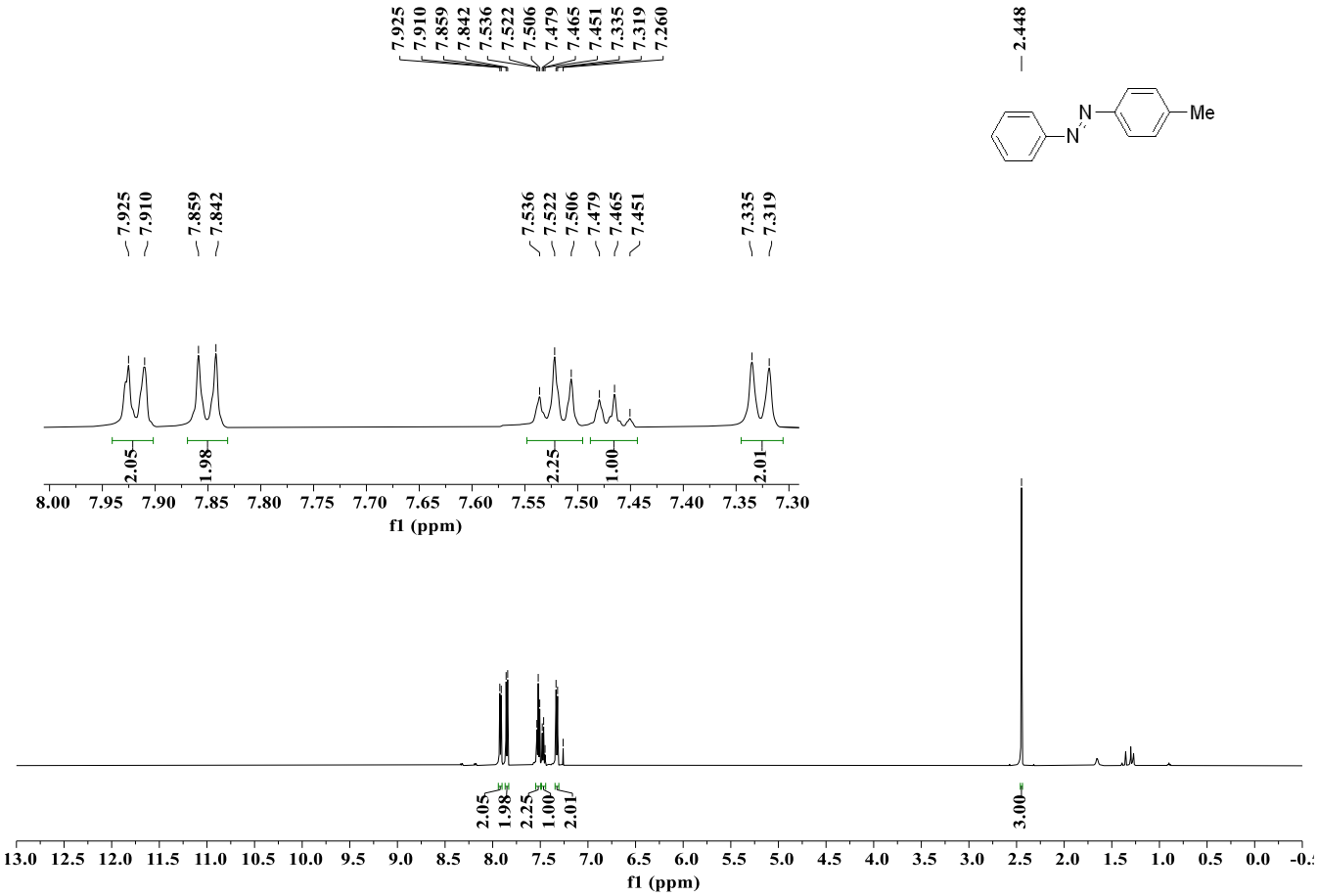
^{1}H NMR (500 MHz, $CDCl_3$) of 6ac



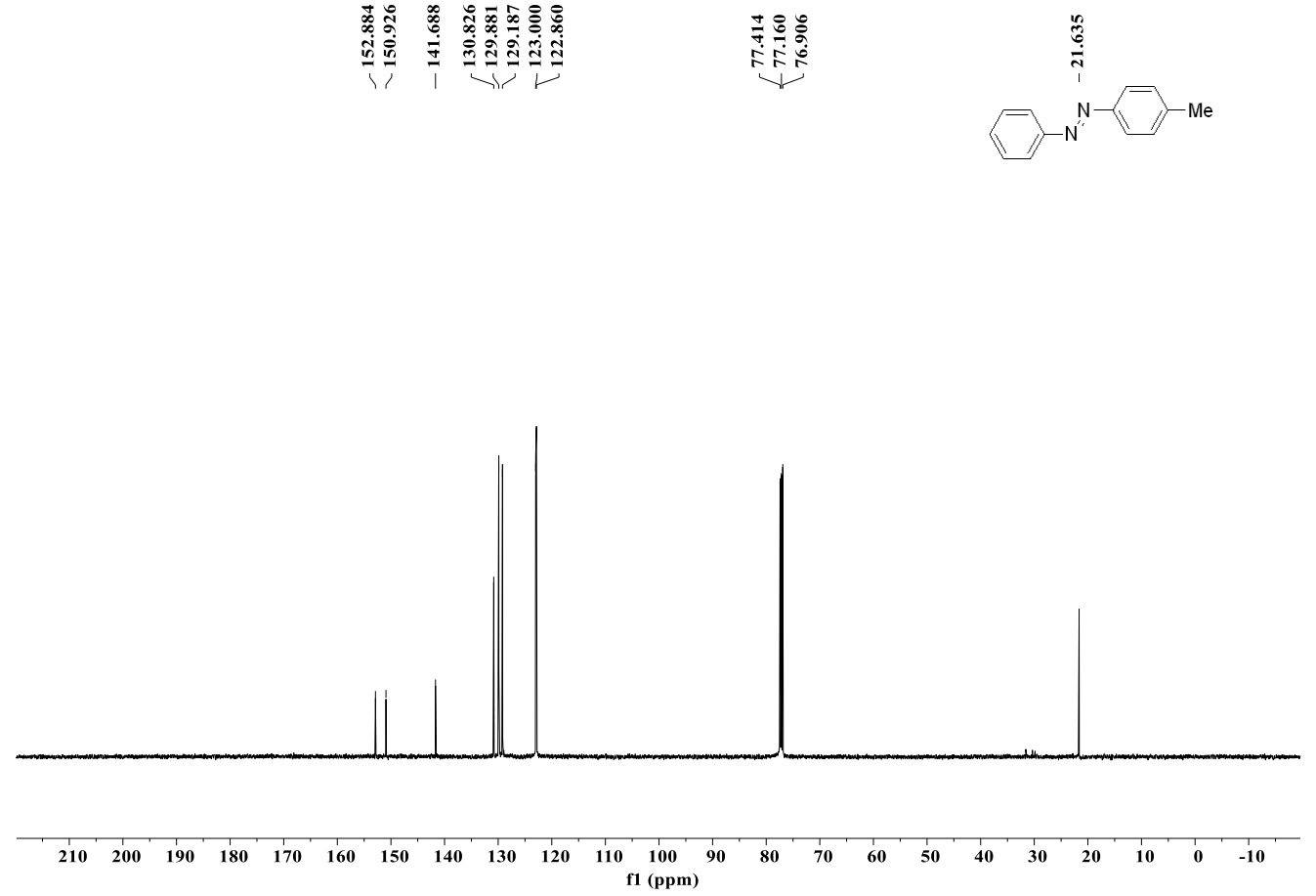
^{13}C NMR (125 MHz, $CDCl_3$) of 6ac



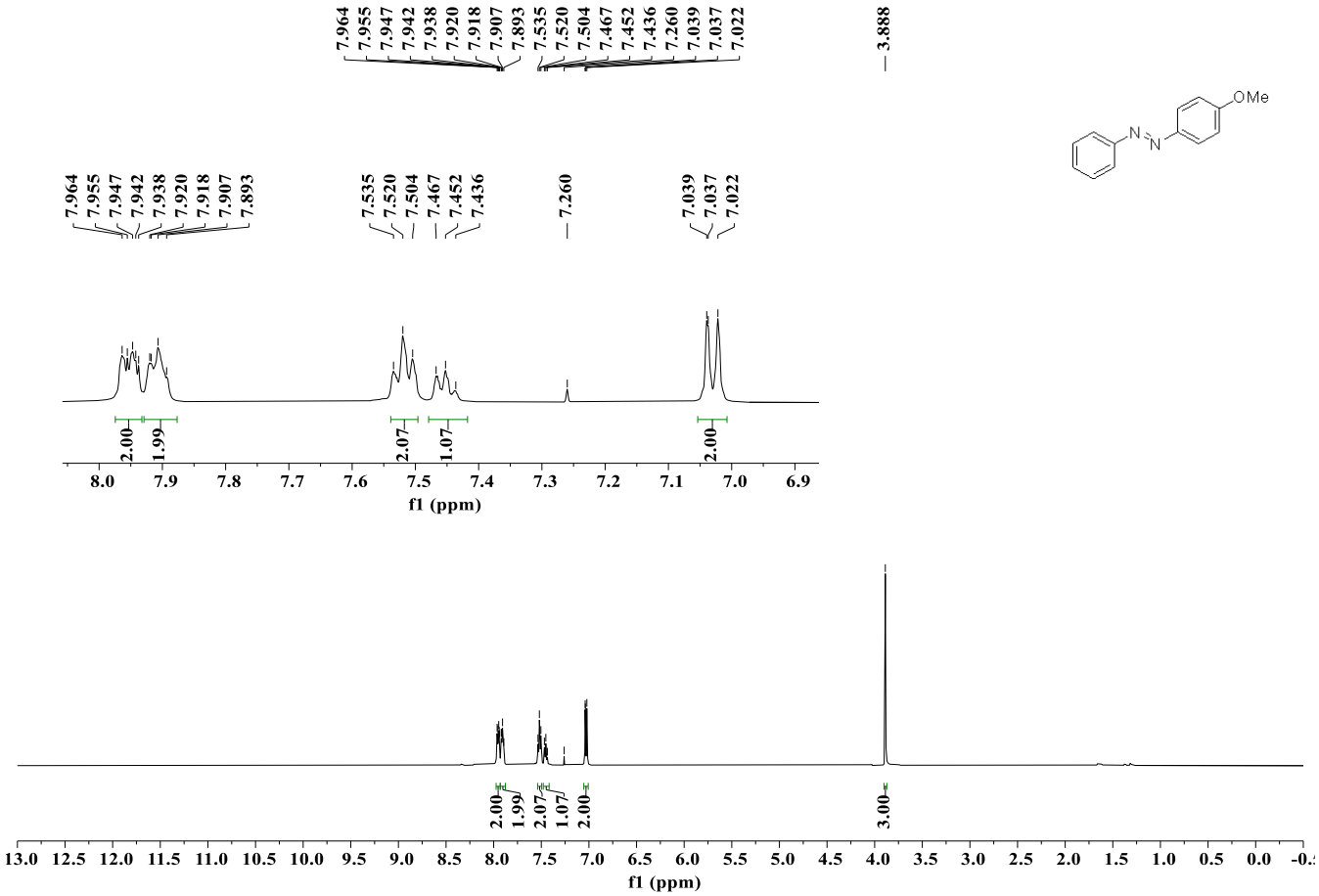
^{1}H NMR (500 MHz, $CDCl_3$) of 6ad



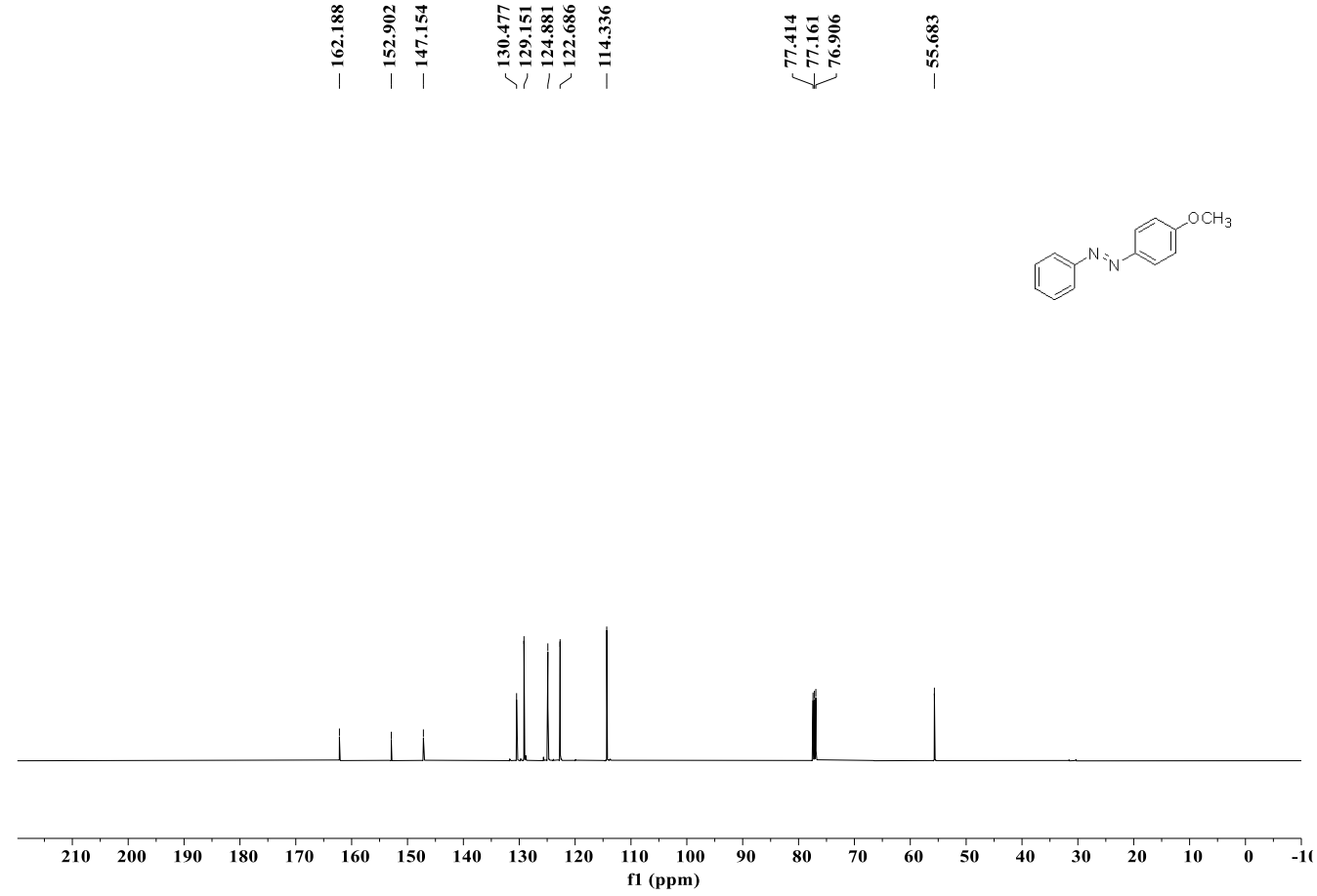
^{13}C NMR (125 MHz, $CDCl_3$) of 6ad



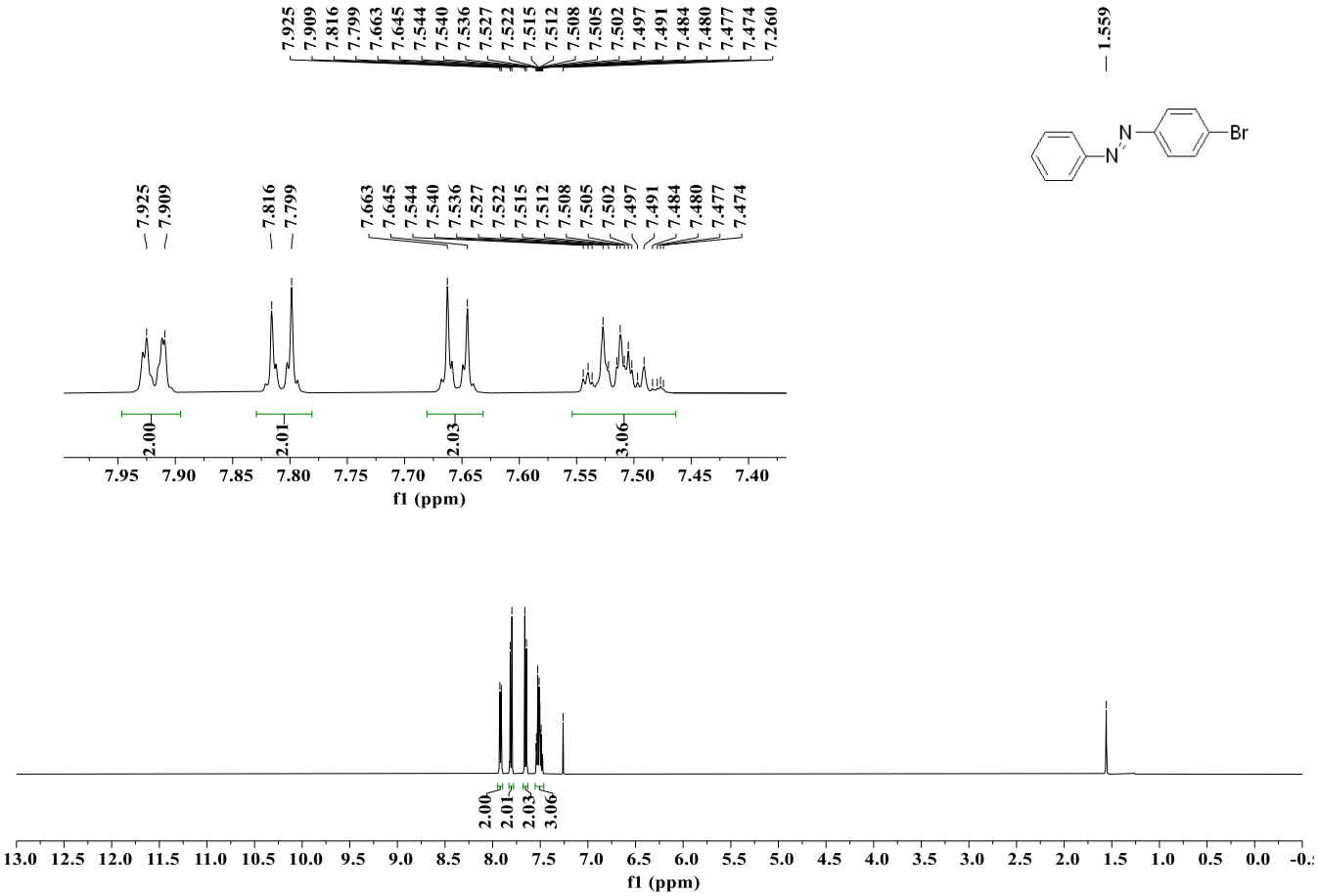
^{1}H NMR (500 MHz, $CDCl_3$) of 6af



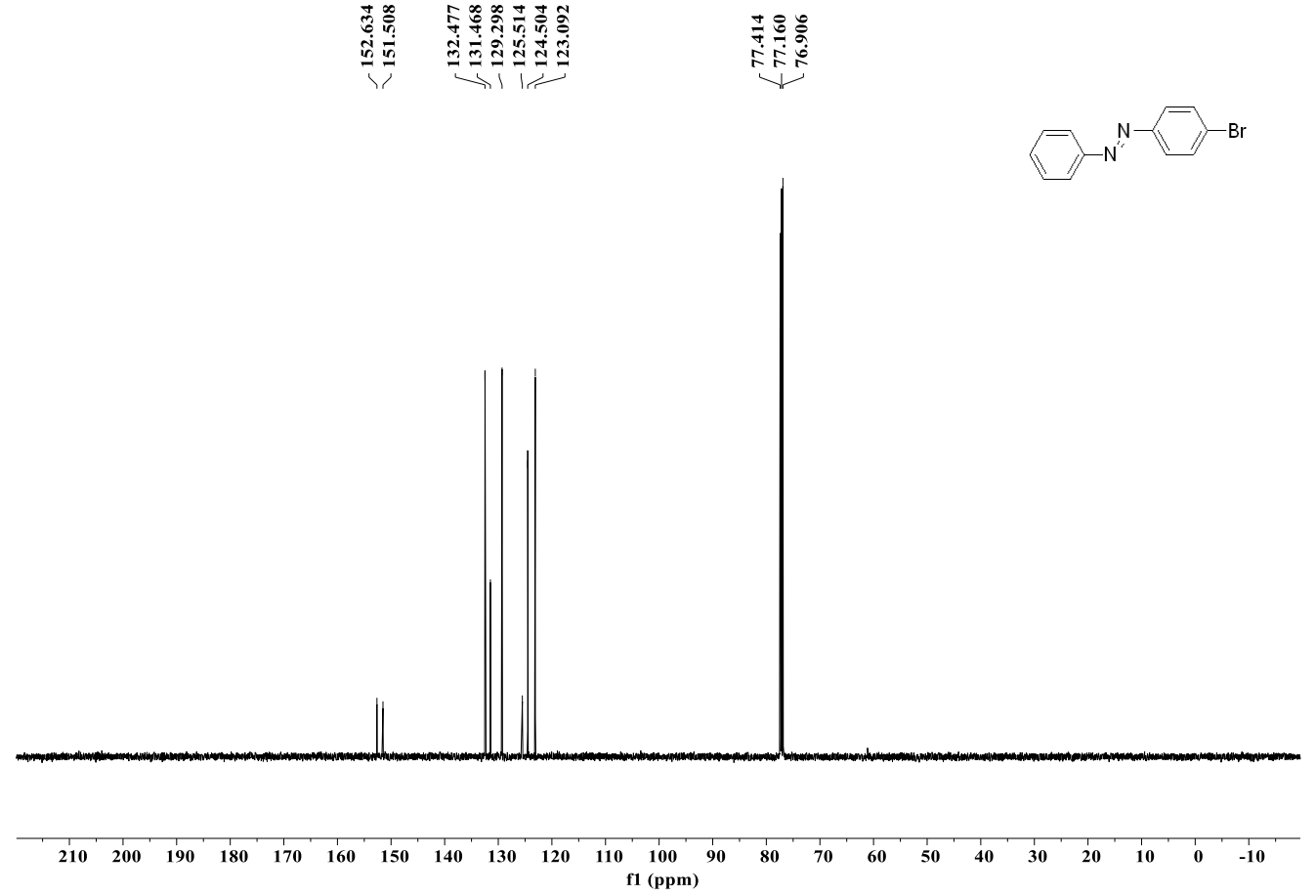
^{13}C NMR (125 MHz, $CDCl_3$) of 6af



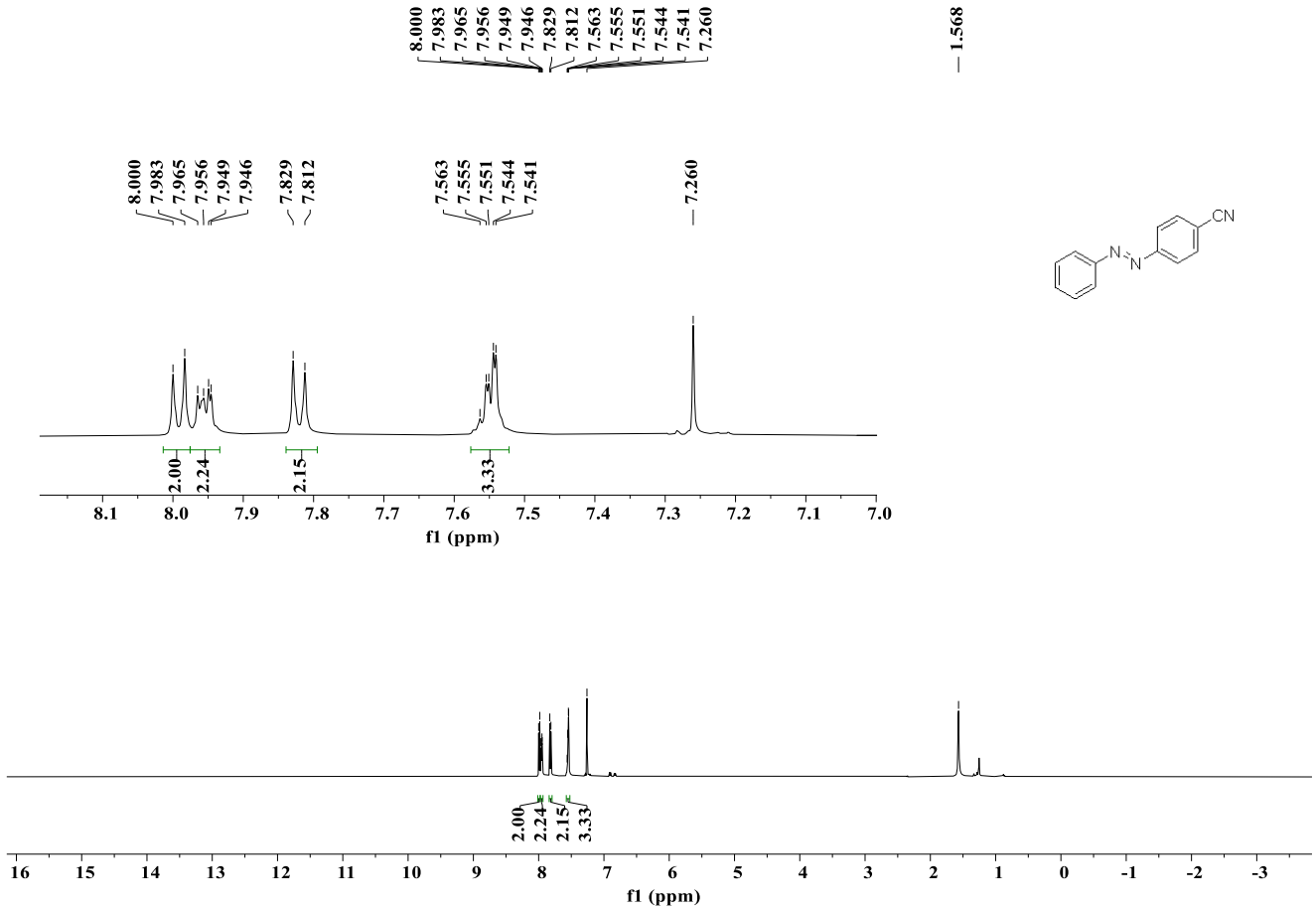
^{1}H NMR (500 MHz, $CDCl_3$) of 6ag



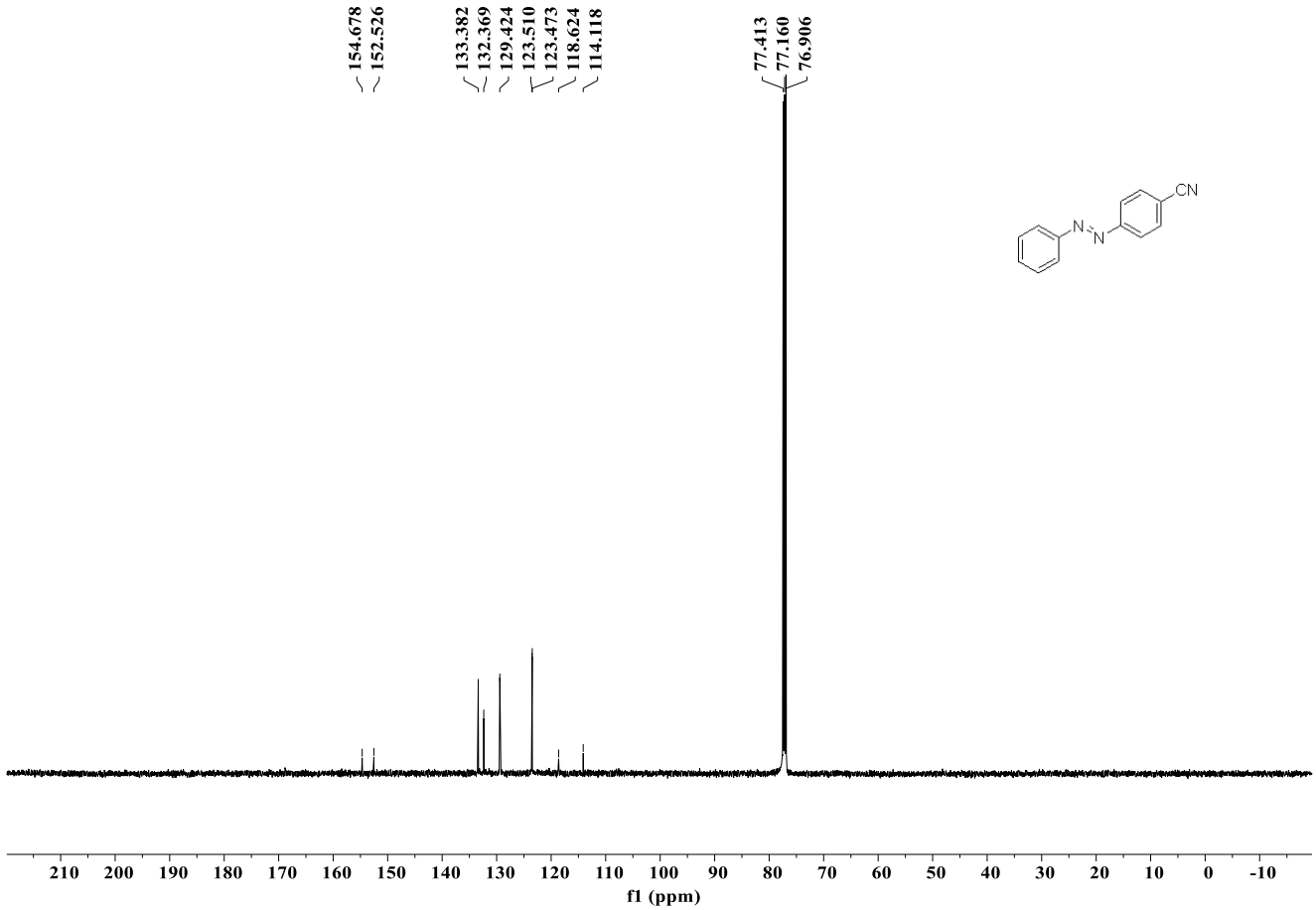
^{13}C NMR (125 MHz, $CDCl_3$) of 6ag



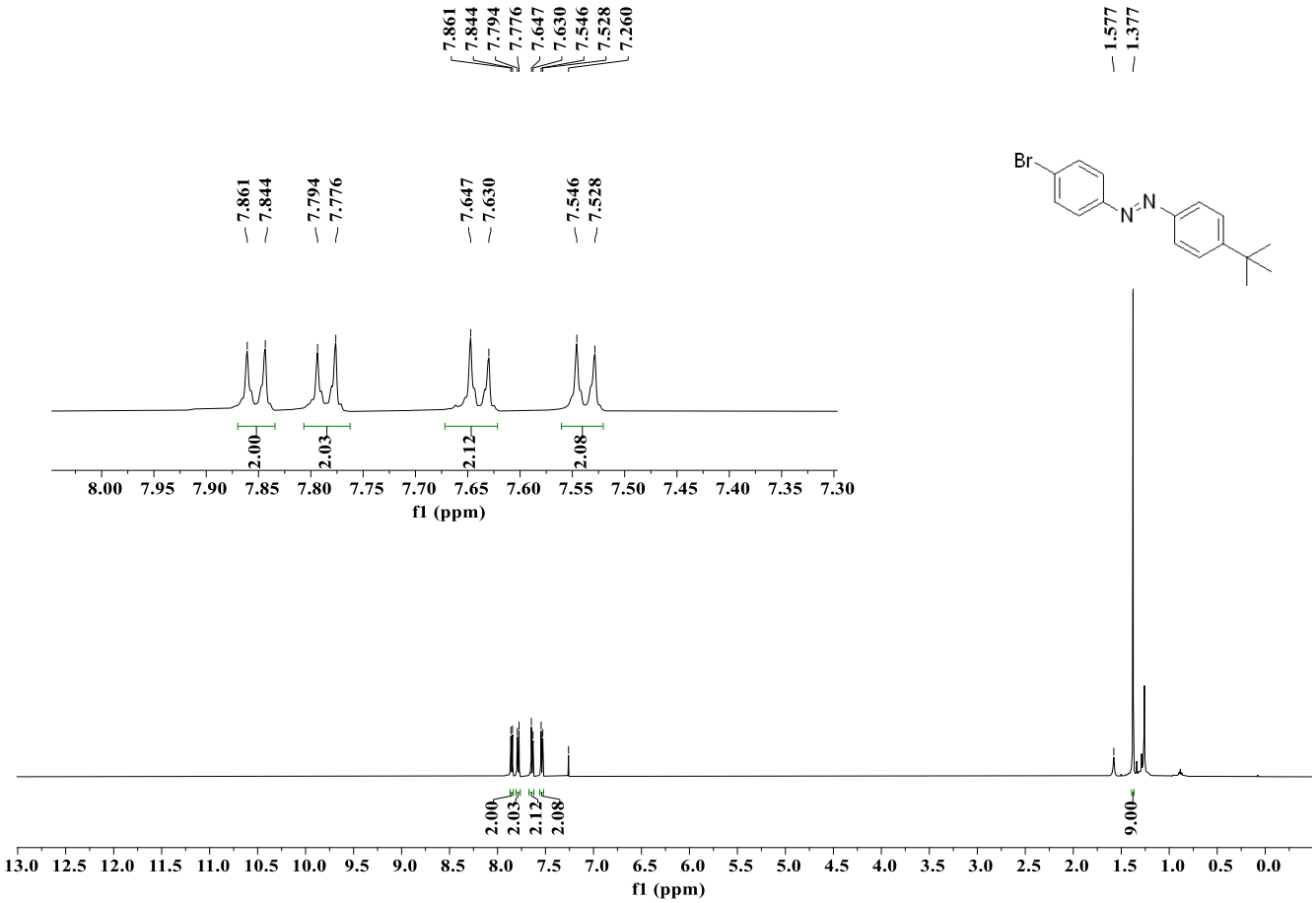
^{1}H NMR (500 MHz, $CDCl_3$) of 6ah



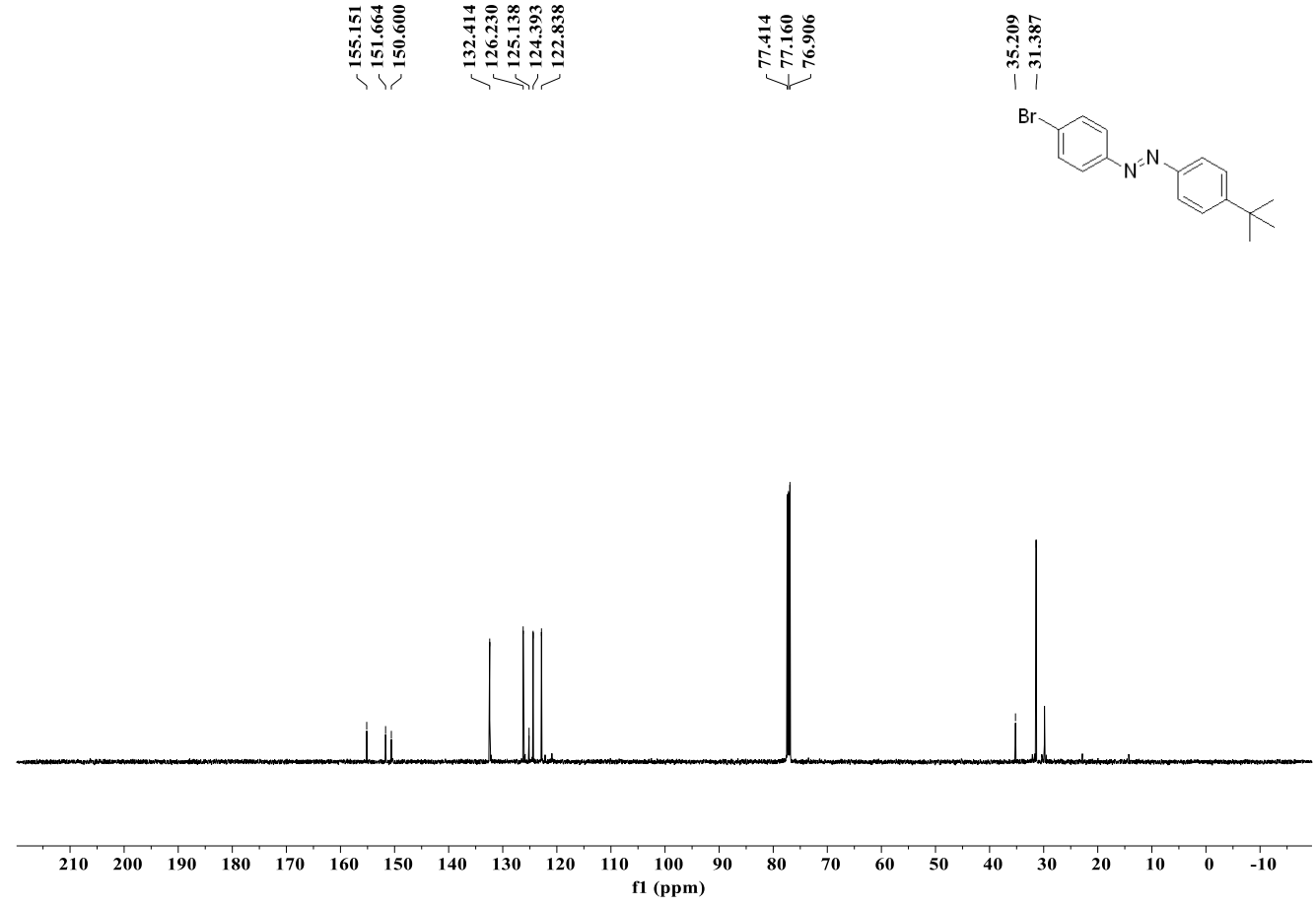
^{13}C NMR (125 MHz, $CDCl_3$) of 6ah



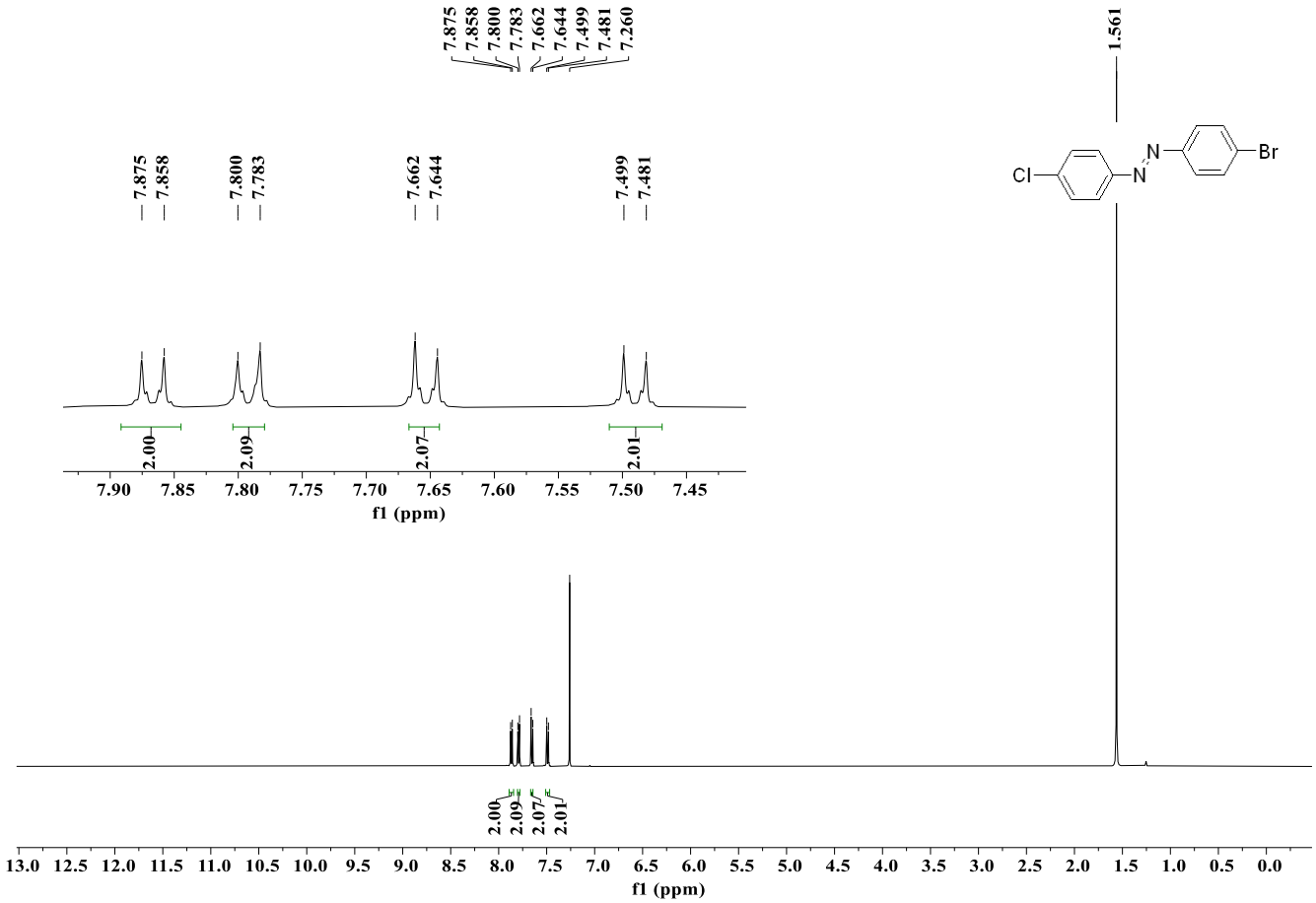
^{1}H NMR (500 MHz, $CDCl_3$) of 6ge



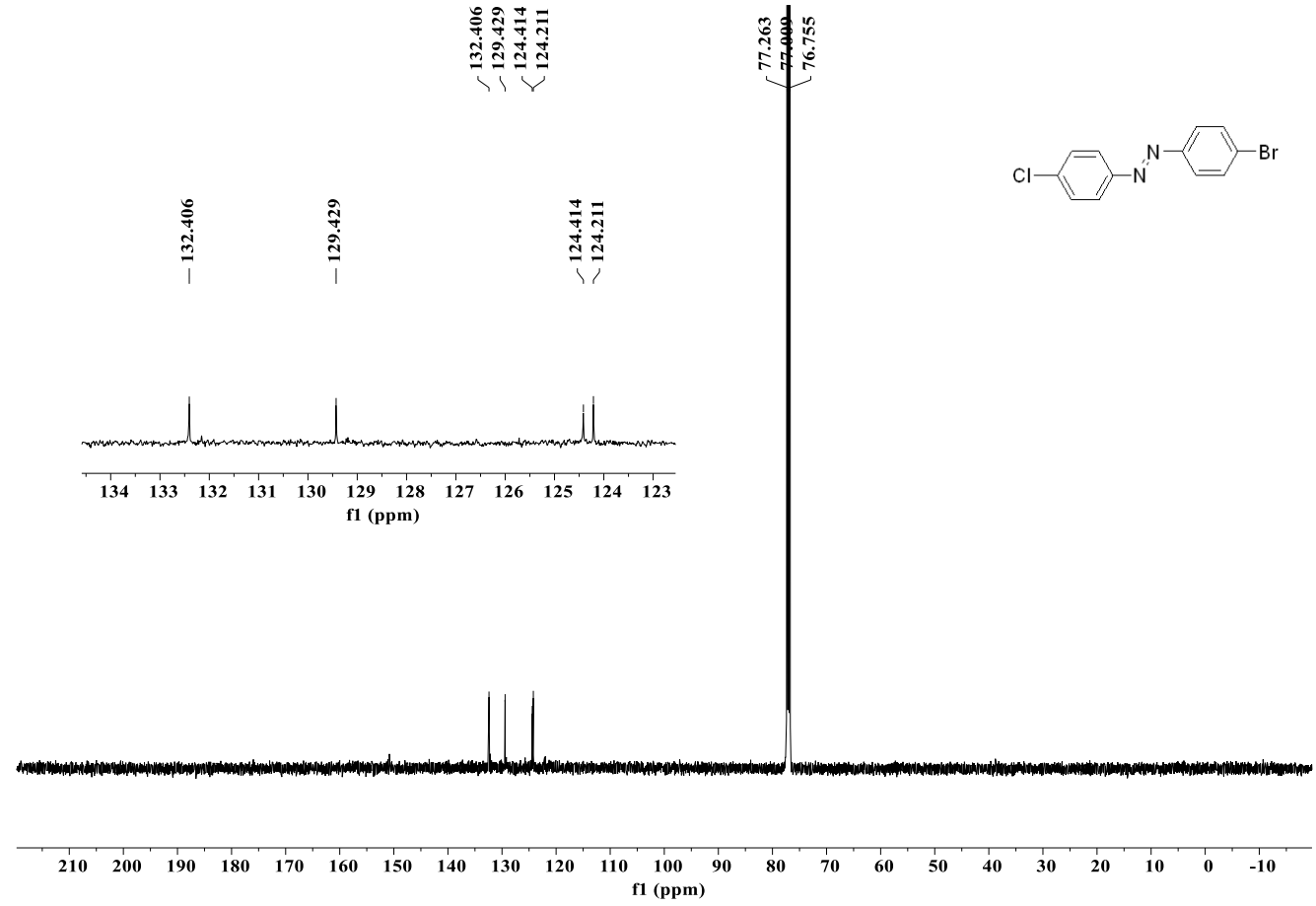
^{13}C NMR (125 MHz, $CDCl_3$) of 6ge



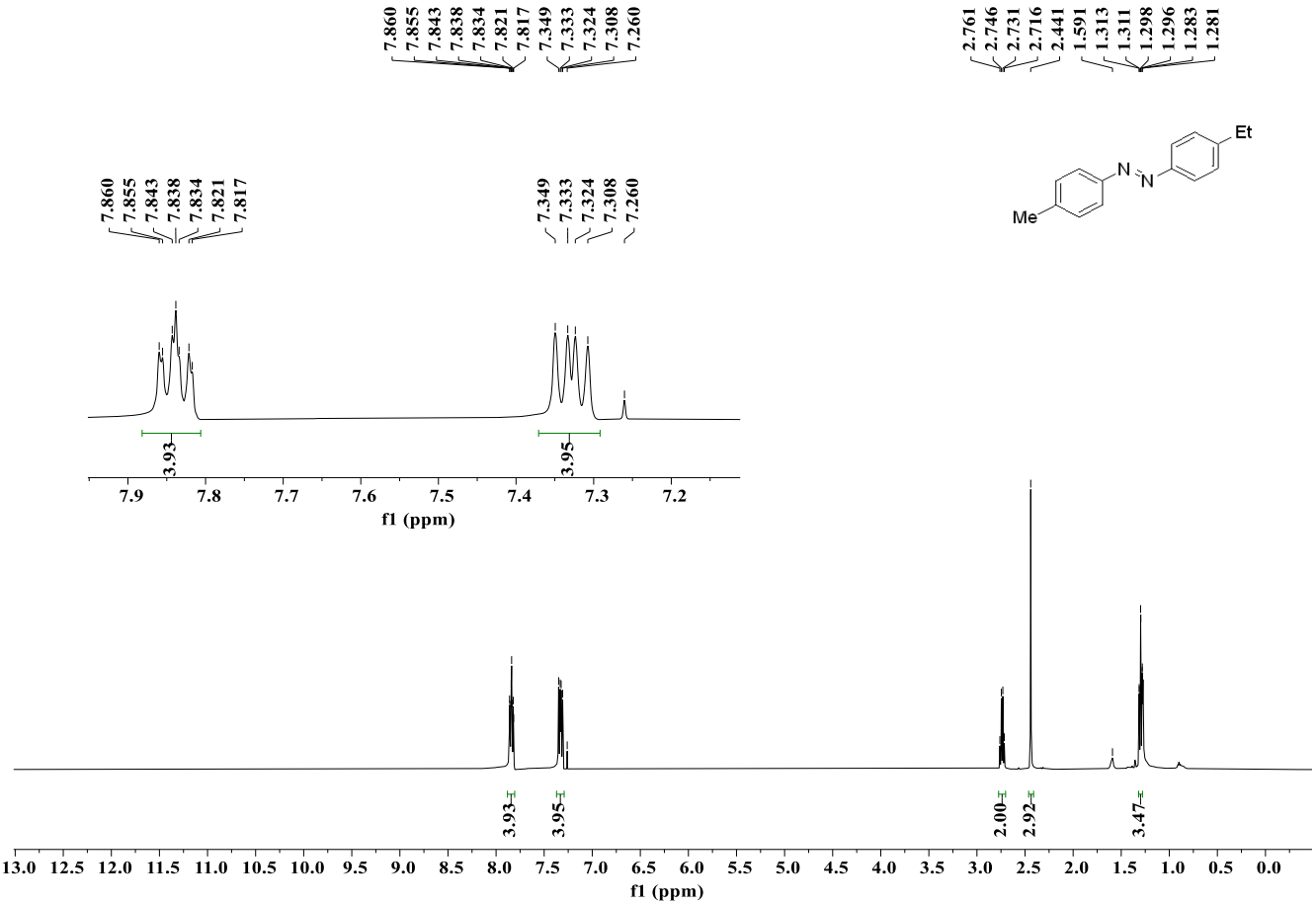
^{1}H NMR (500 MHz, $CDCl_3$) of 6gi



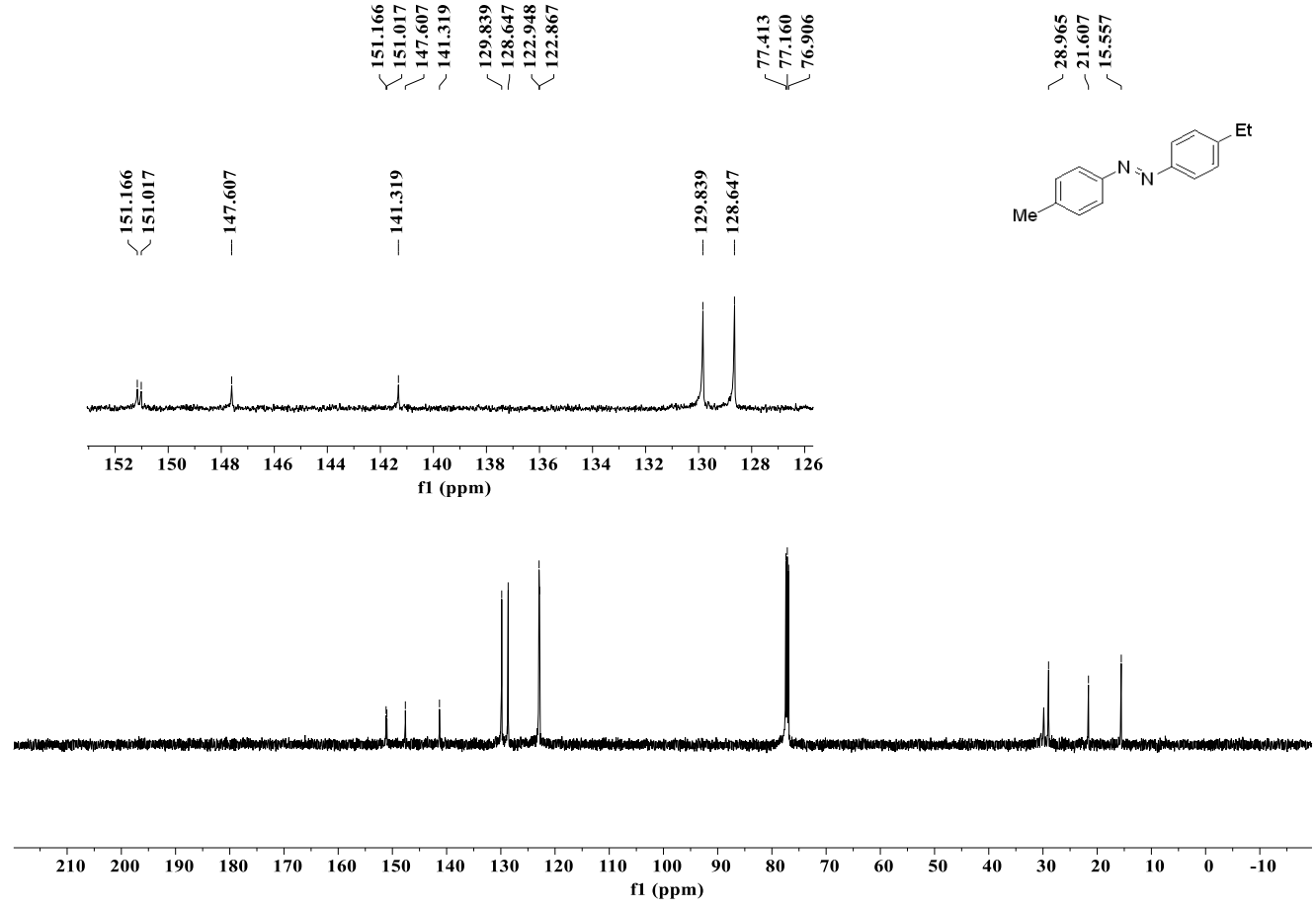
^{13}C NMR (125 MHz, $CDCl_3$) of 6gi



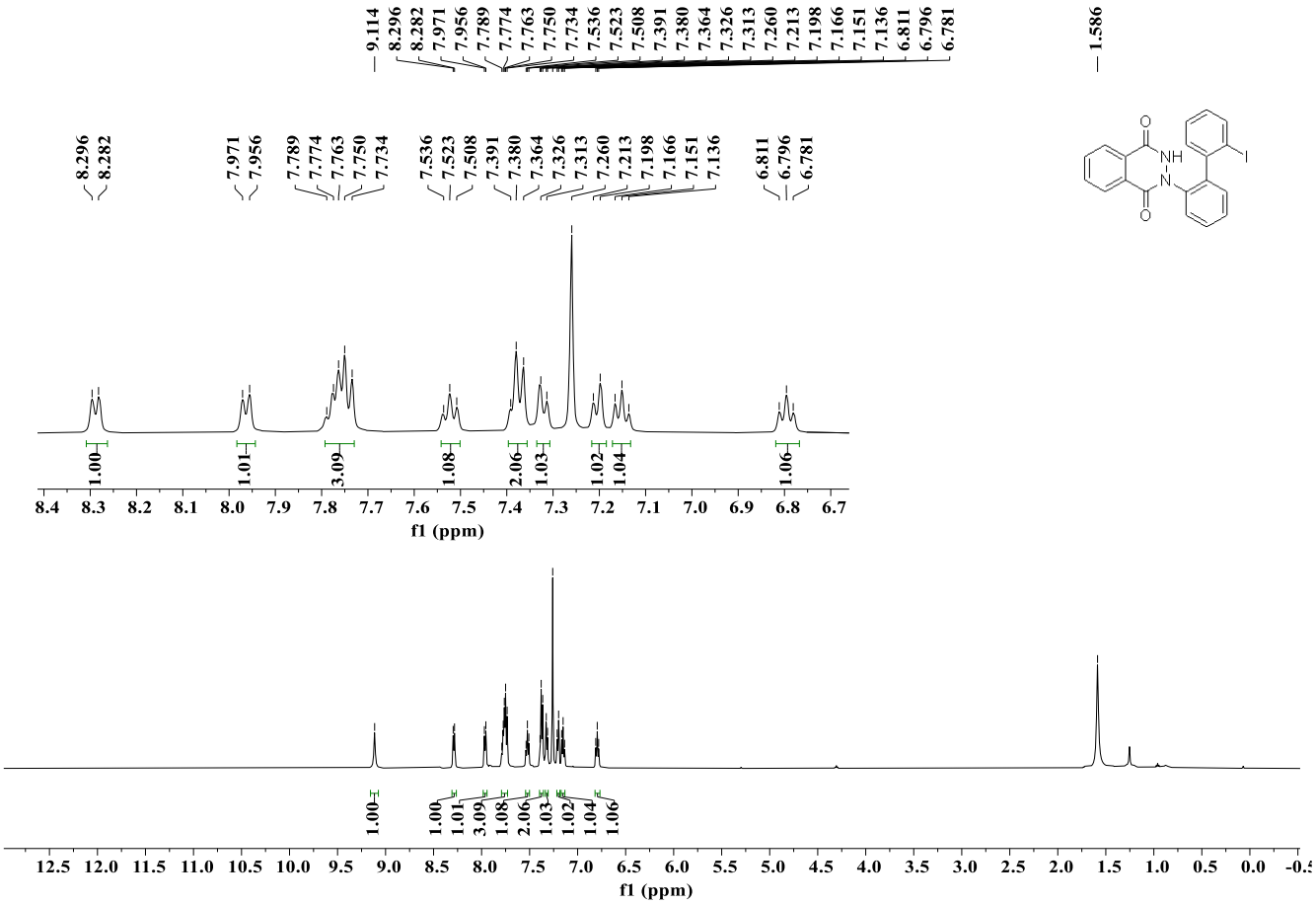
^{1}H NMR (500 MHz, $CDCl_3$) of 6kd



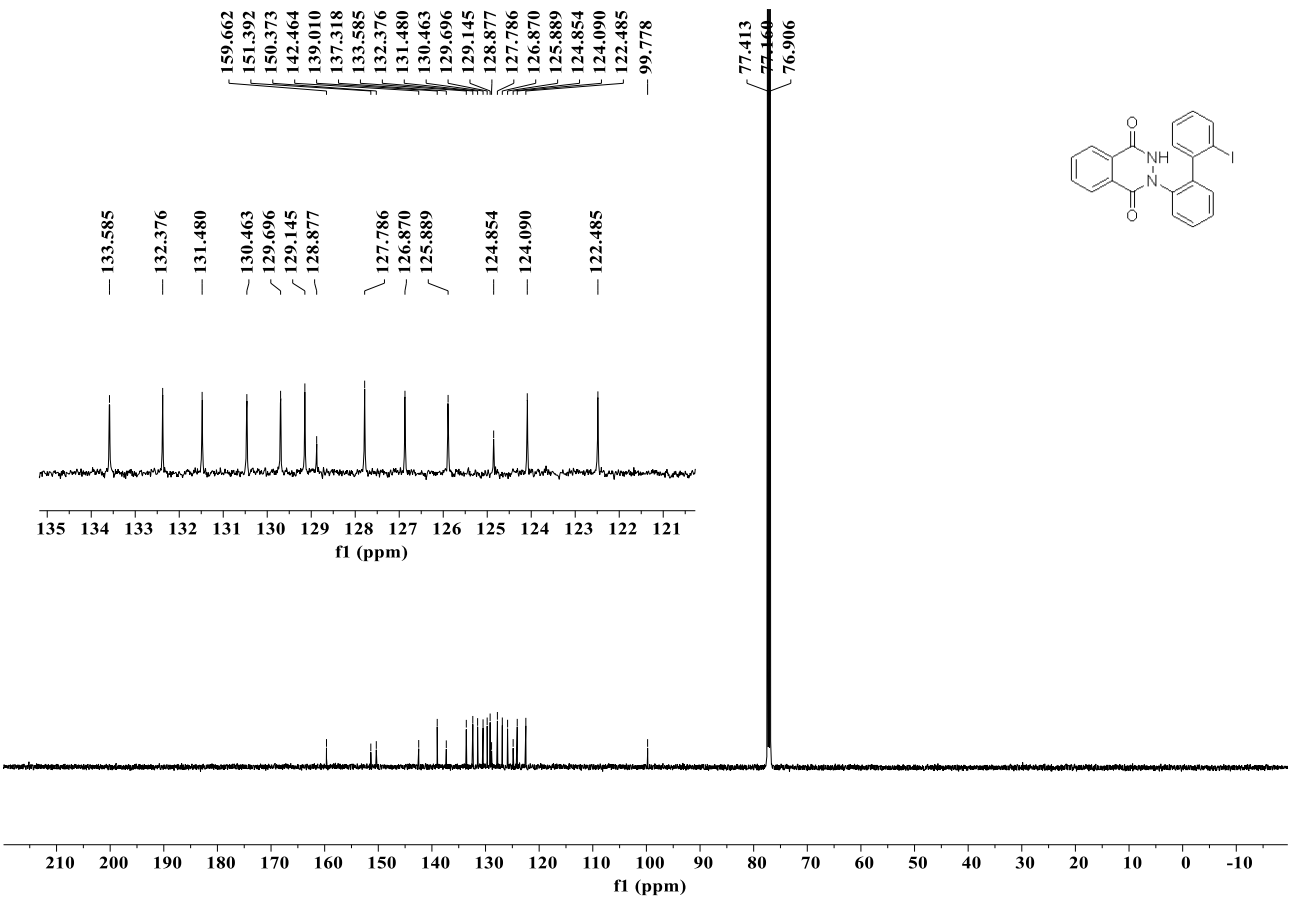
^{13}C NMR (125 MHz, $CDCl_3$) of 6kd



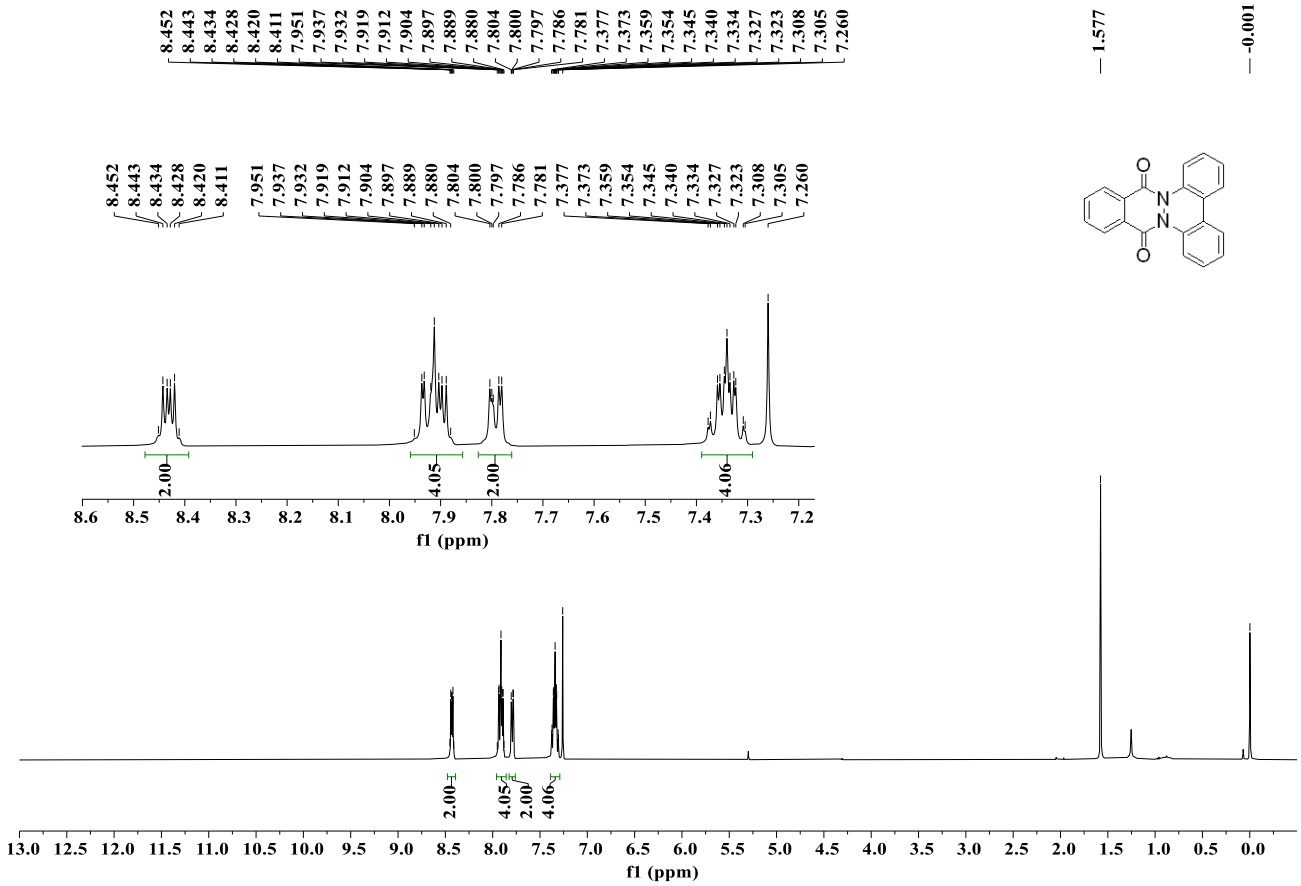
^{1}H NMR (500 MHz, $CDCl_3$) of IM1



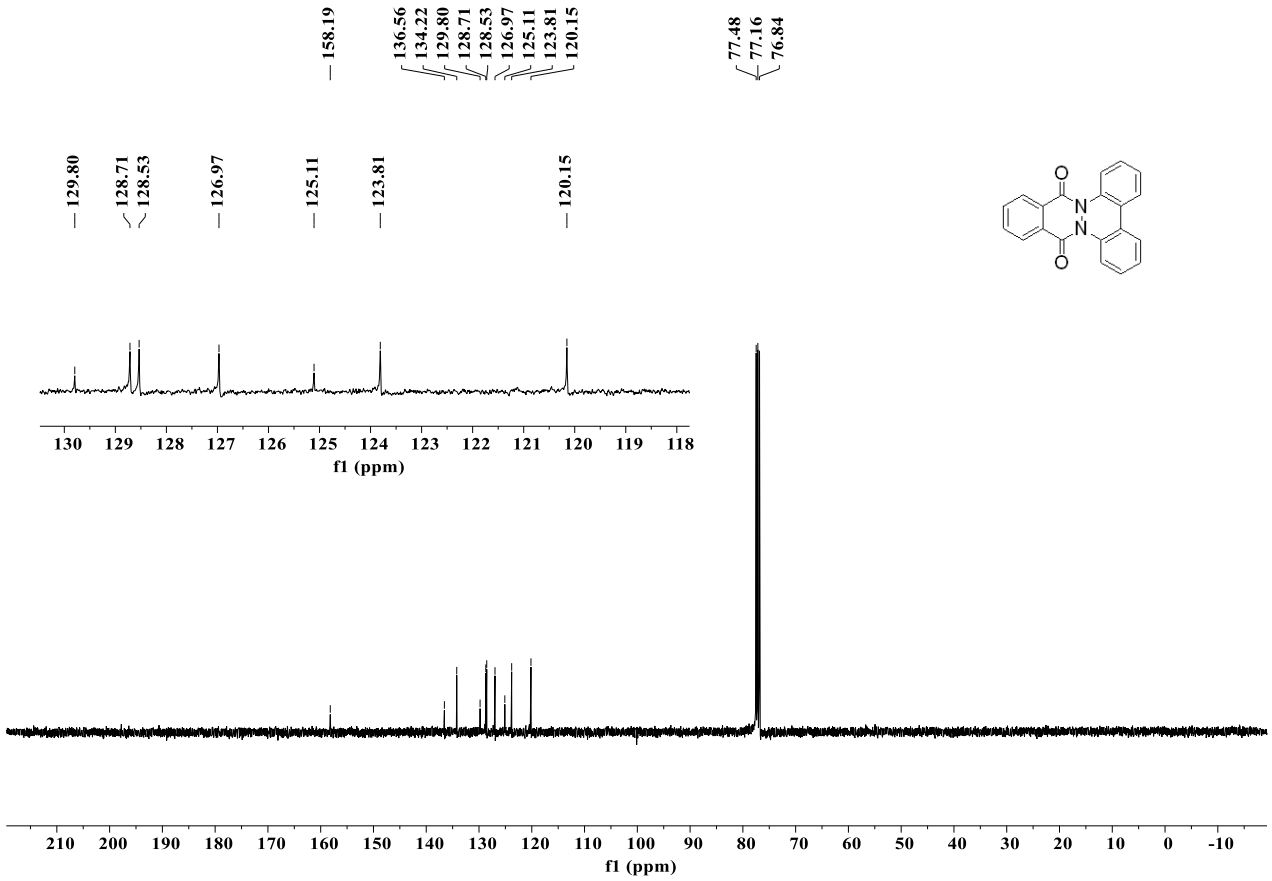
^{13}C NMR (125 MHz, $CDCl_3$) of IM 1



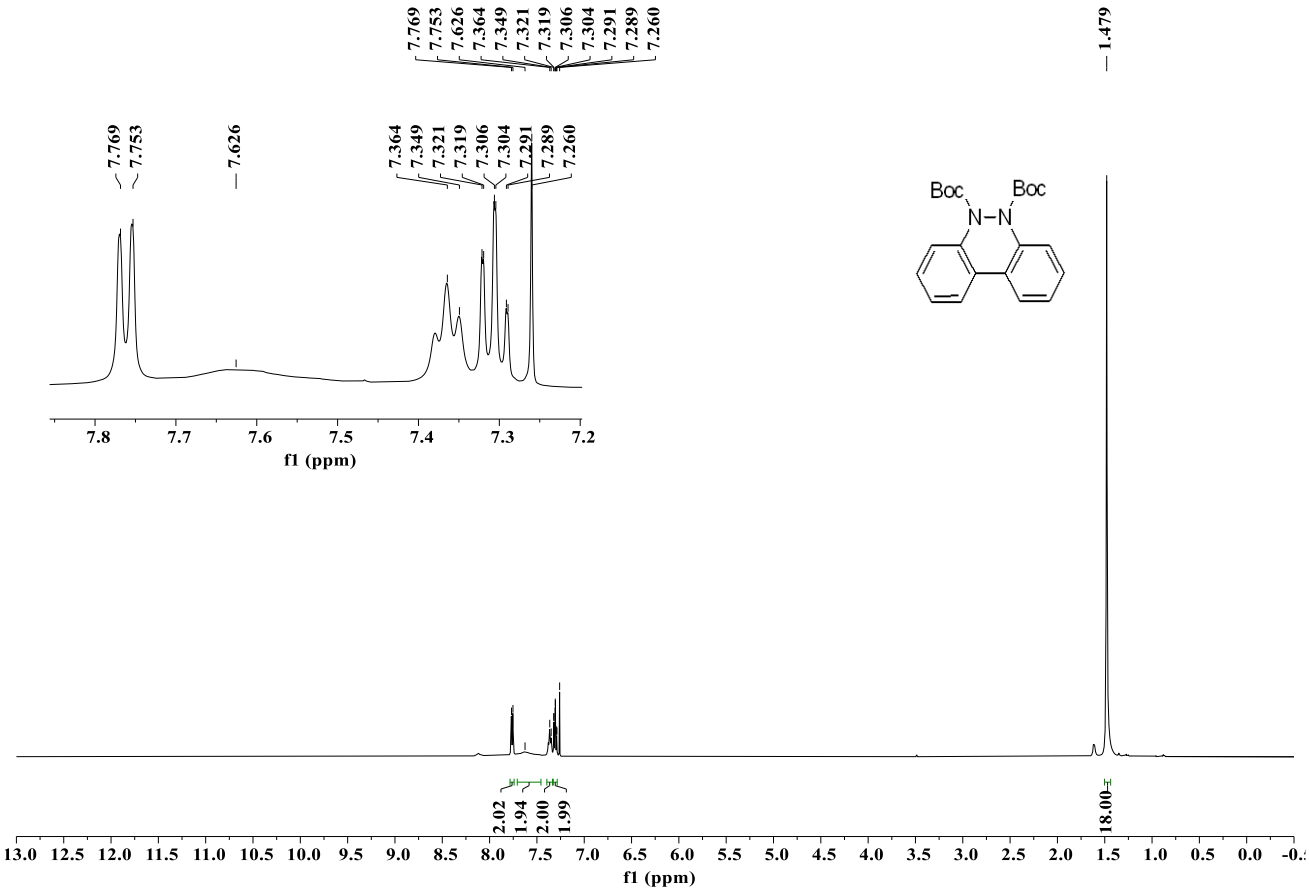
^{1}H NMR (500 MHz, $CDCl_3$) of IM2



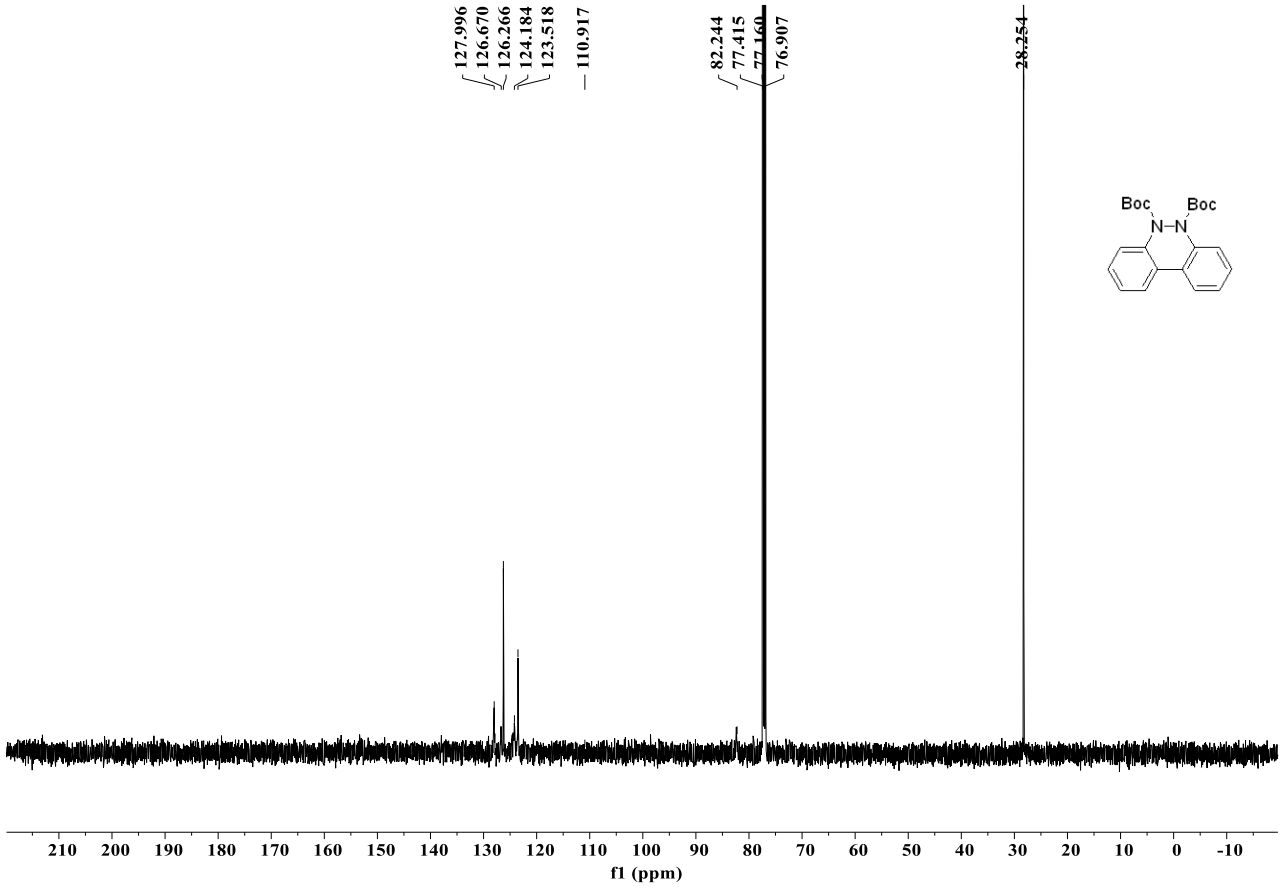
^{13}C NMR (125 MHz, $CDCl_3$) of IM 2



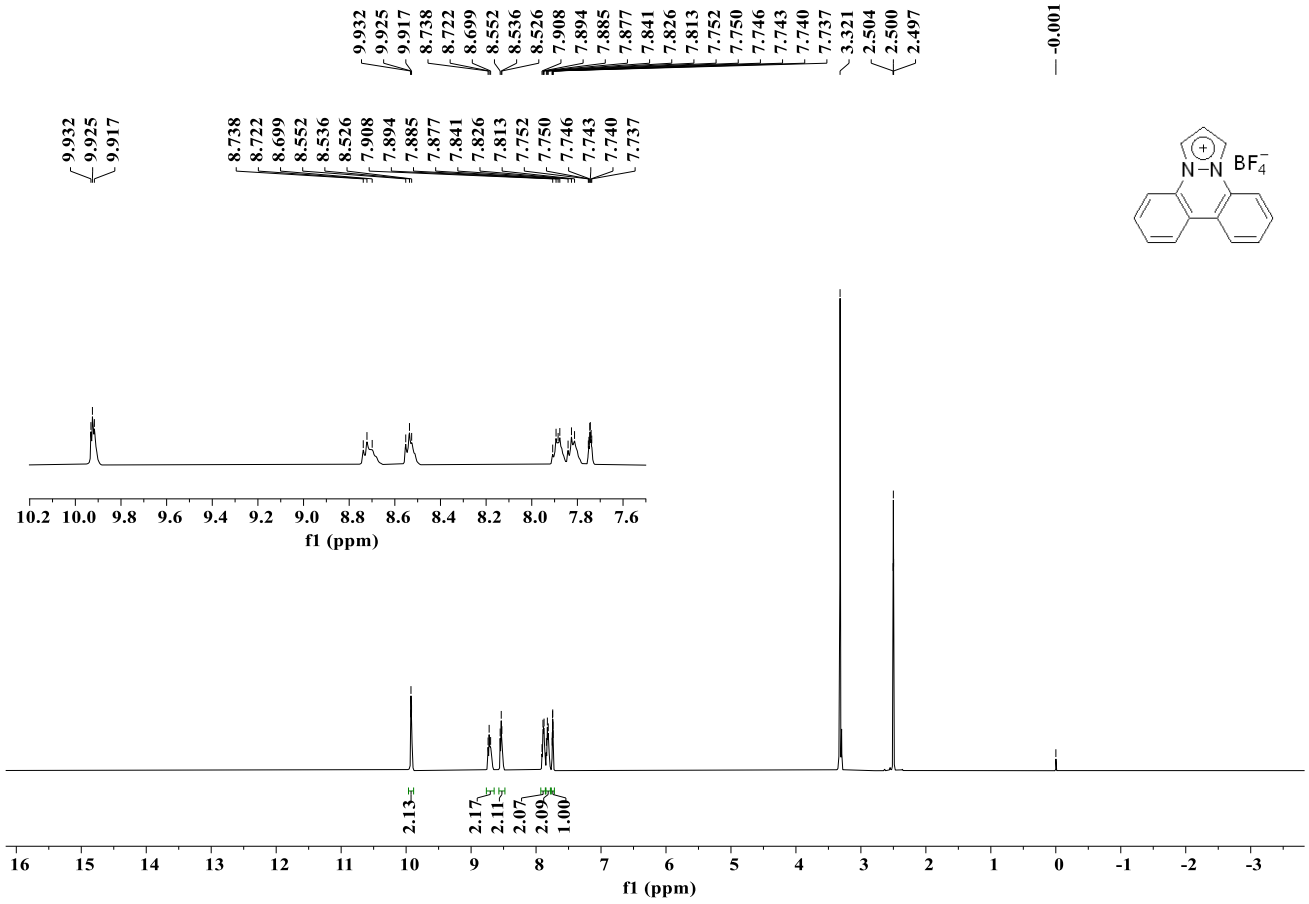
^{1}H NMR (500 MHz, $CDCl_3$) of 3a-bisBoc



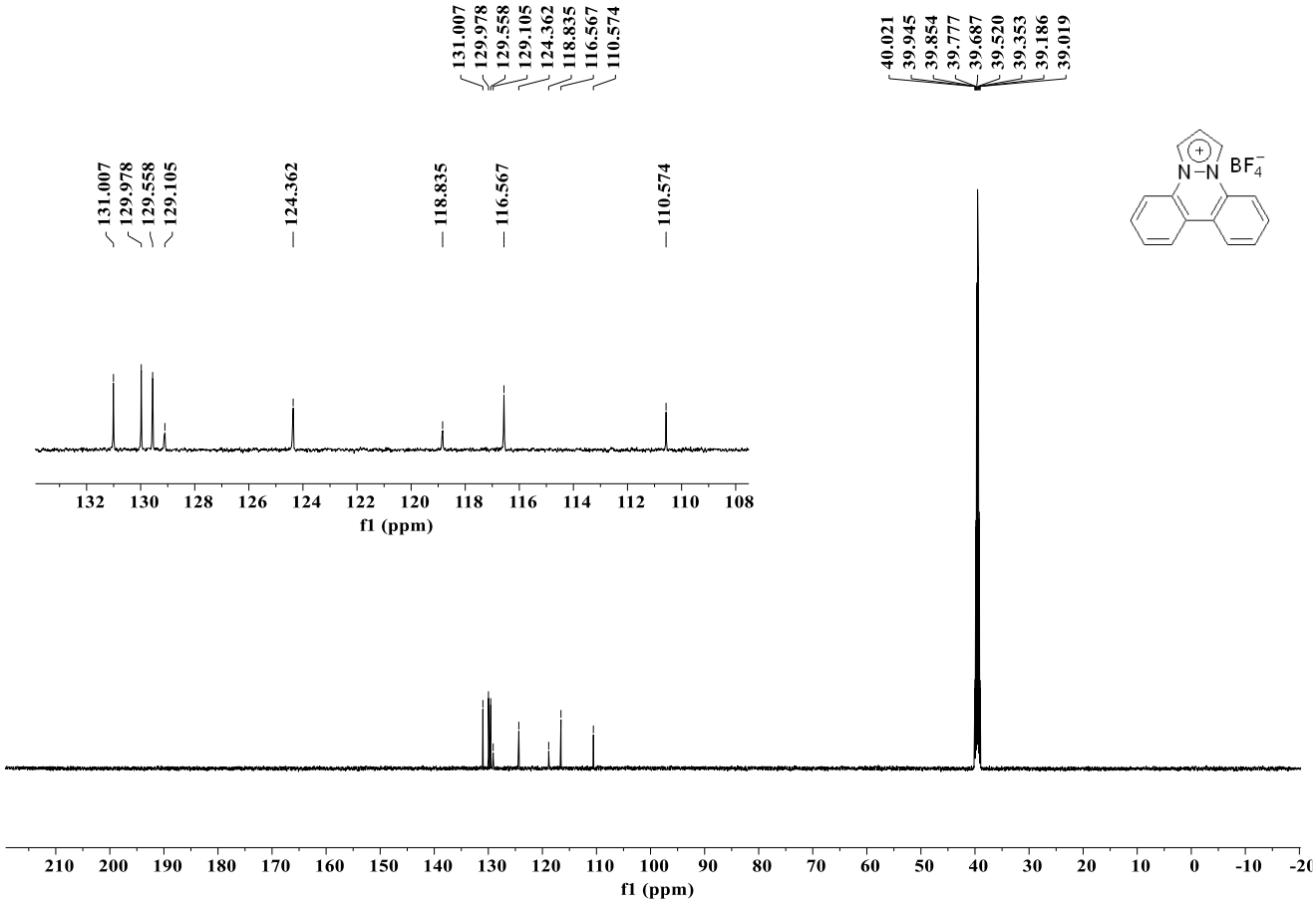
^{13}C NMR (125 MHz, $CDCl_3$) of 3a-bisBoc



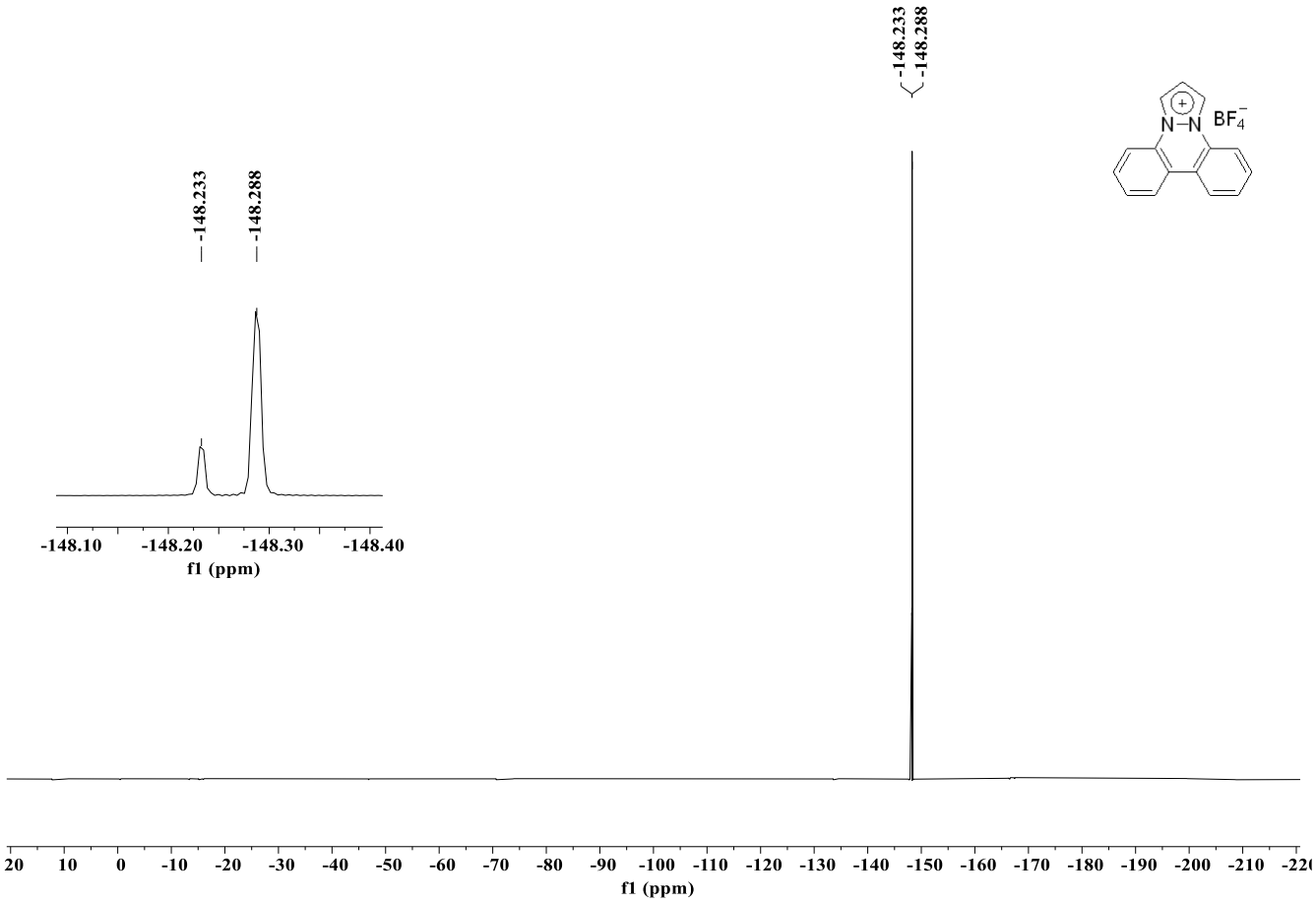
^{1}H NMR (500 MHz, DMSO-d_6) of 7



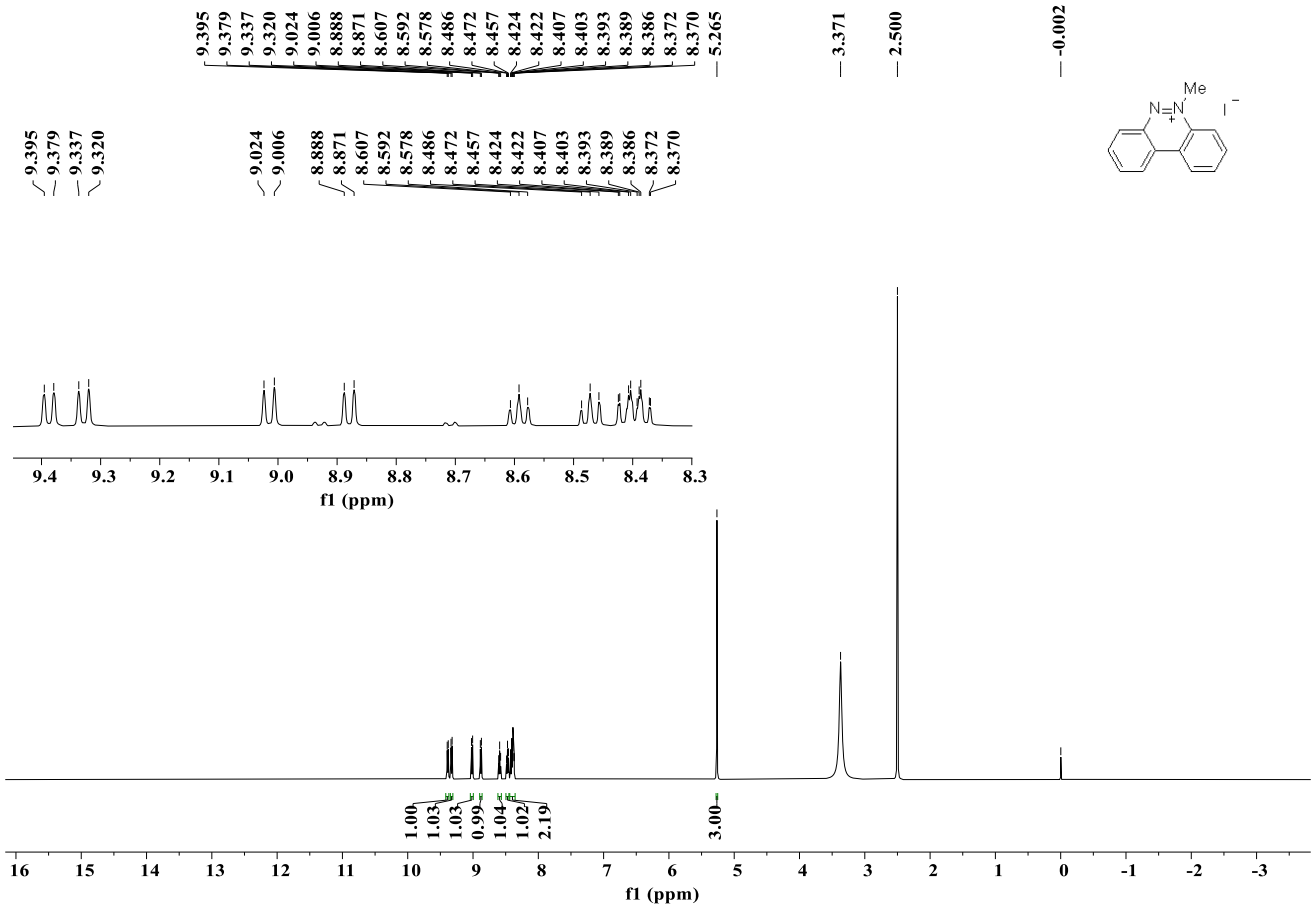
^{13}C NMR (125 MHz, DMSO-d_6) of 7



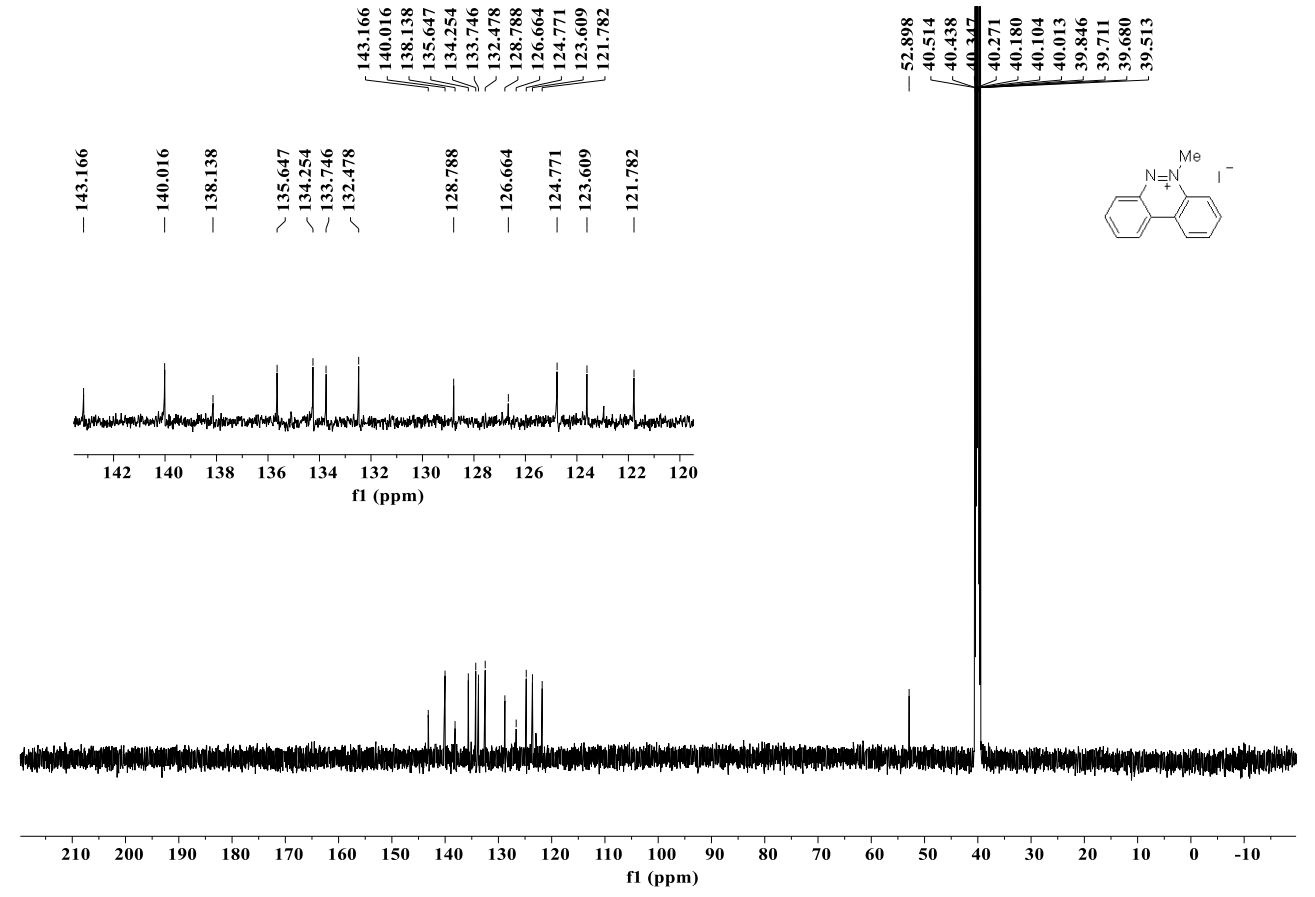
^{19}F NMR (471 MHz, DMSO-d_6) of 7



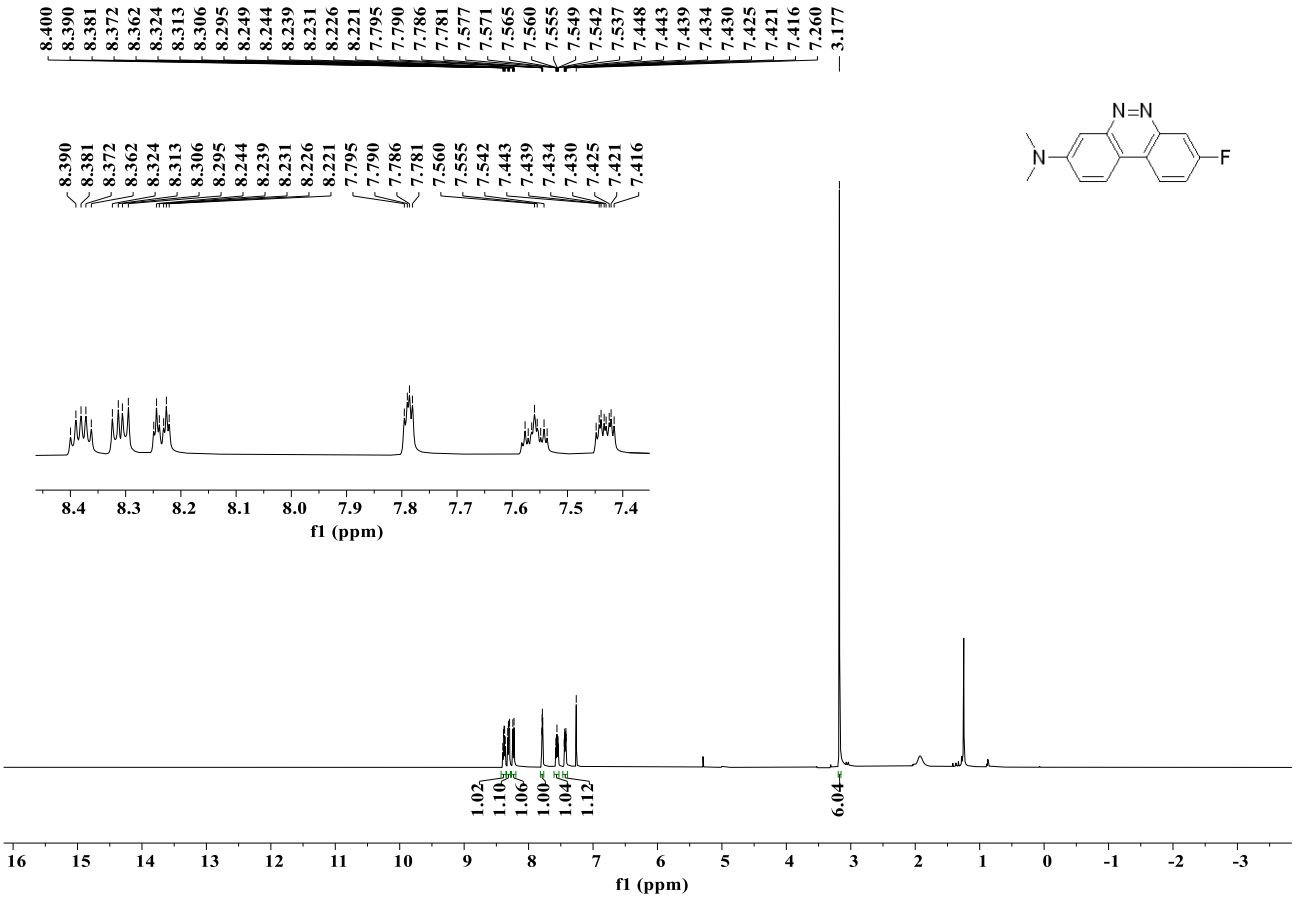
^{1}H NMR (500 MHz, DMSO-d_6) of 8



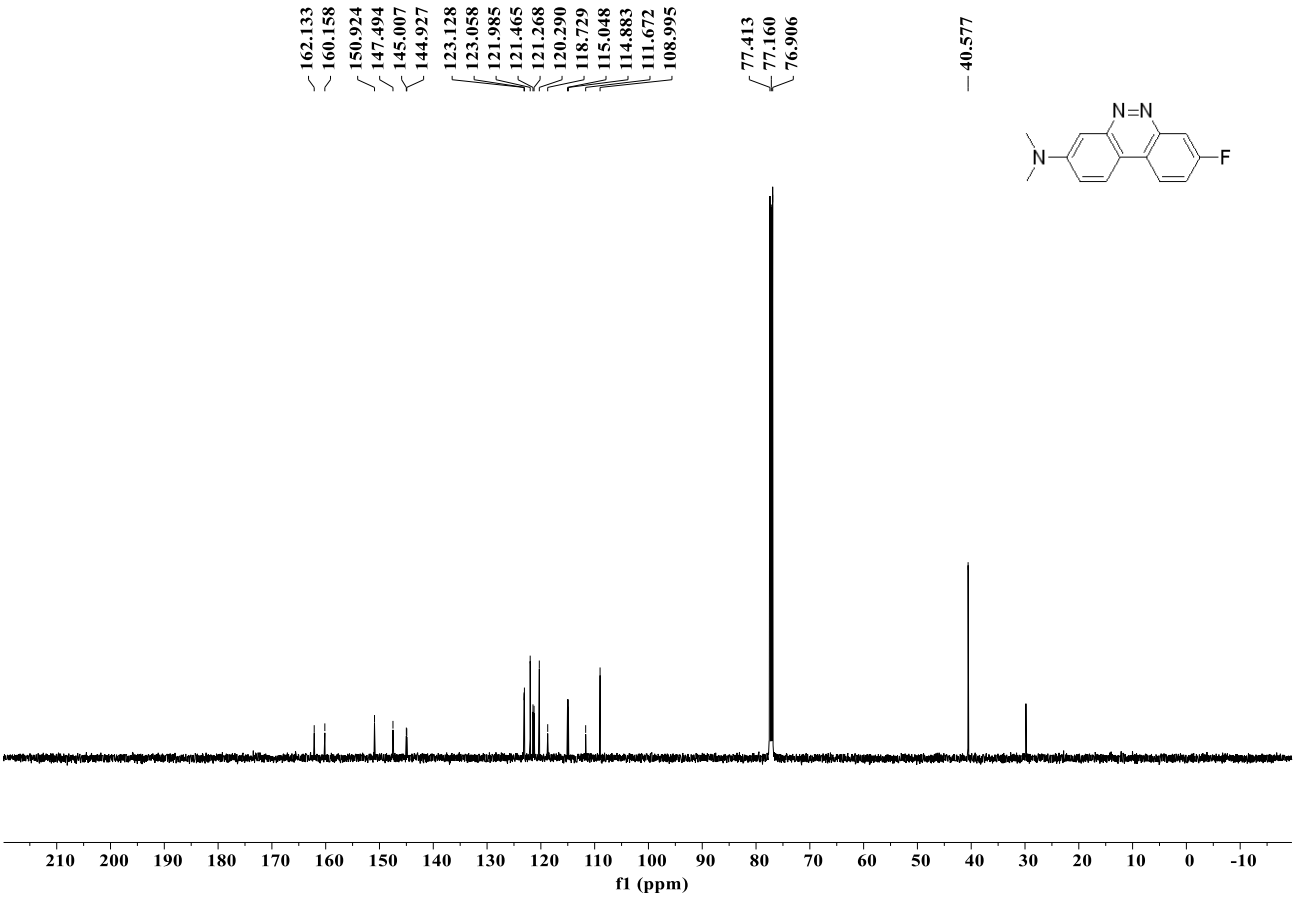
^{13}C NMR (125 MHz, DMSO-d_6) of 8



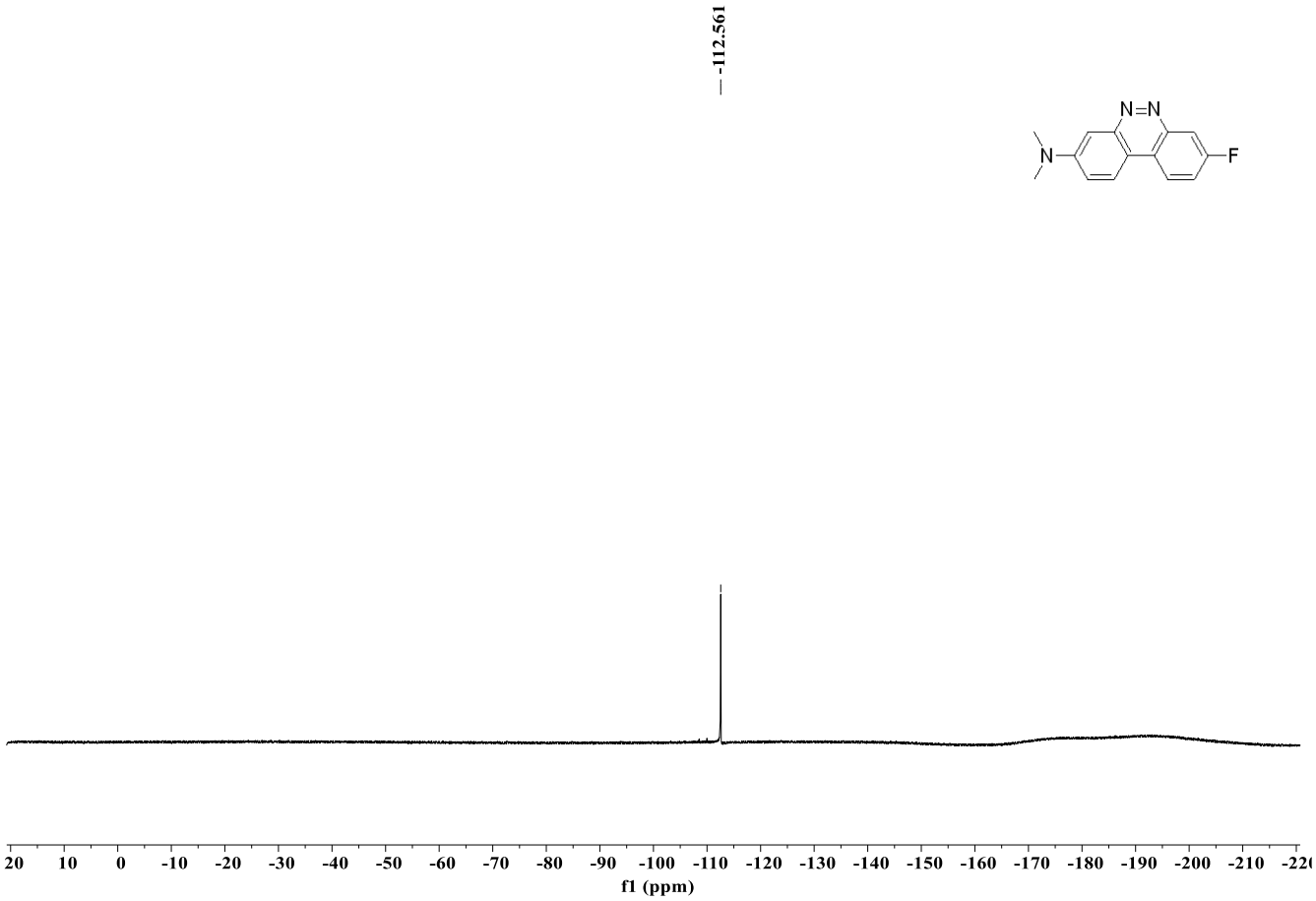
^{1}H NMR (500 MHz, $CDCl_3$) of 9



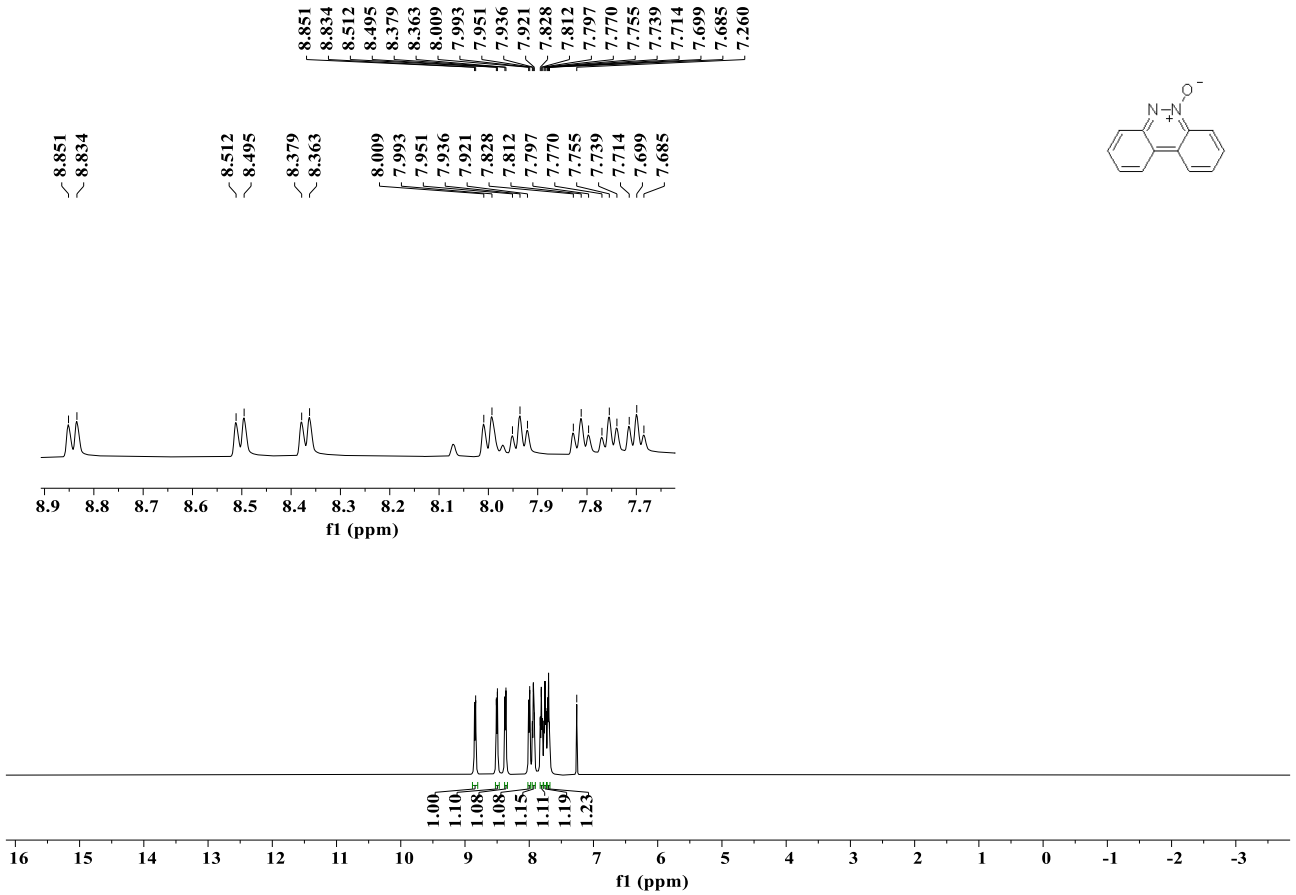
^{13}C NMR (125 MHz, $CDCl_3$) of 9



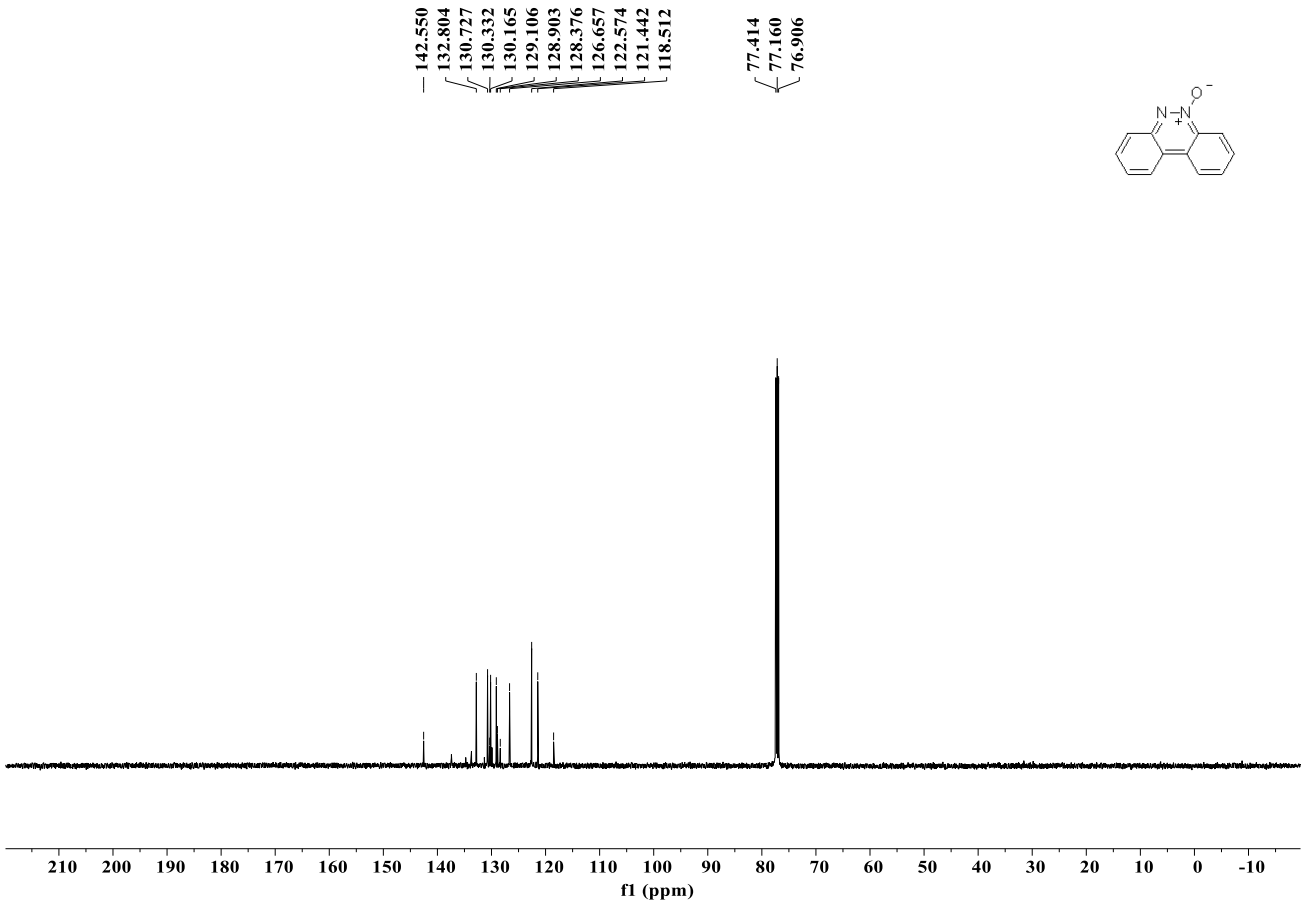
^{19}F NMR (471 MHz, $CDCl_3$) of 9



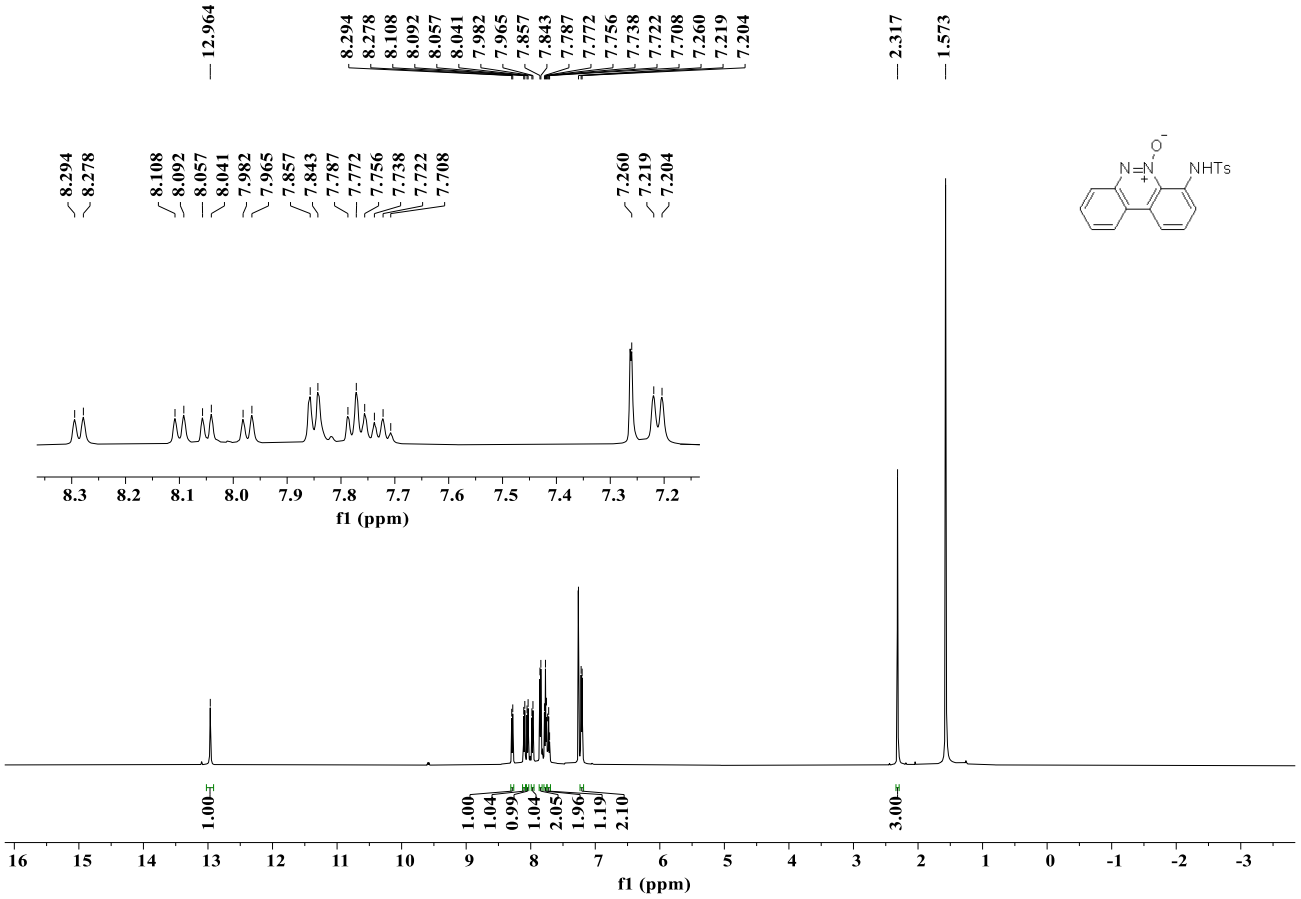
^{1}H NMR (500 MHz, $CDCl_3$) of 10



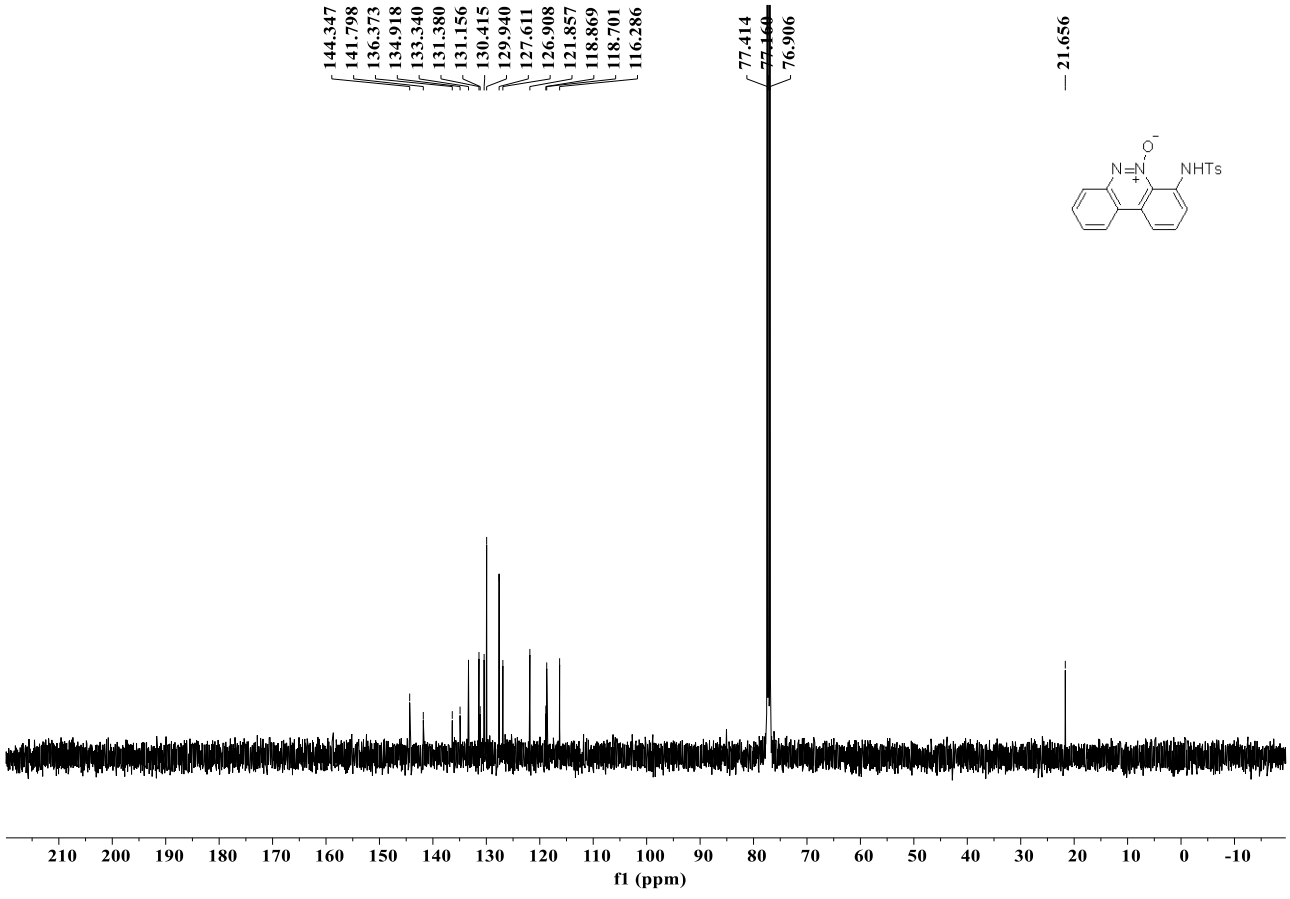
^{13}C NMR (125 MHz, $CDCl_3$) of 10



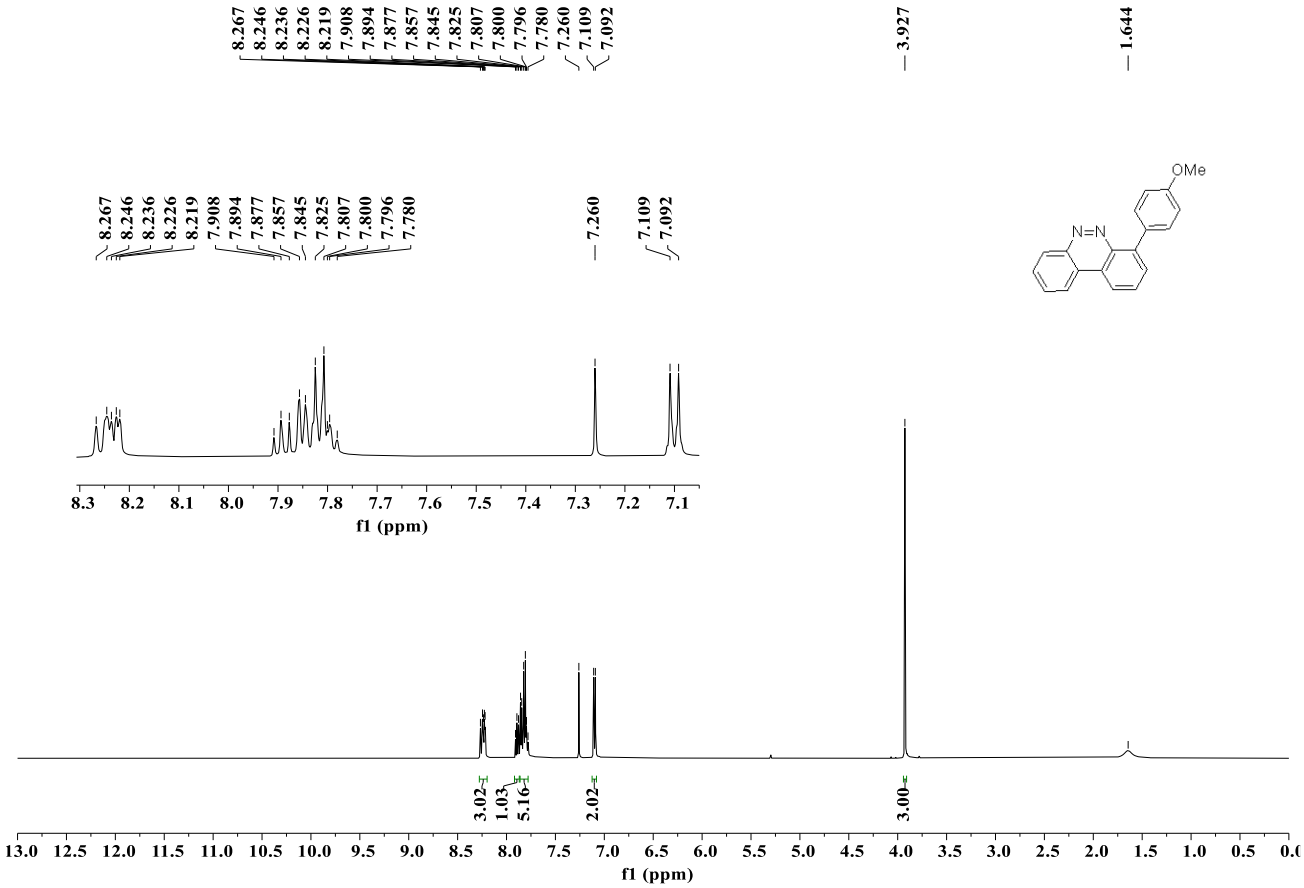
^{1}H NMR (500 MHz, $CDCl_3$) of 11



^{13}C NMR (125 MHz, $CDCl_3$) of 11



^{1}H NMR (500 MHz, $CDCl_3$) of 12



^{13}C NMR (125 MHz, $CDCl_3$) of 12