Electronic Supplementary information

Palladium(II) catalysed cascade strategy for the synthesis of dibenzo[5,6:7,8]cycloocta[1,2-*b*]indol-10-ols/-10(15*H*)-ones: easy access to 1,3,5,7-cyclooctatetraenes (COTs)

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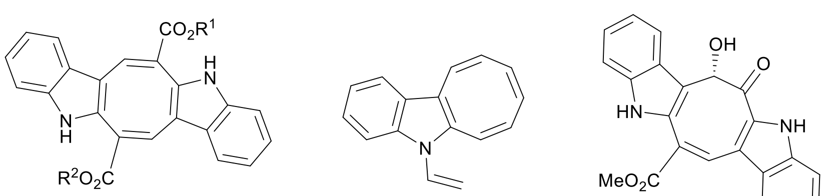
1. General Information:

All solvents were distilled prior to use. Petroleum ether refers to fraction boiling in the range 60−80 °C. Dichloromethane (DCM) was dried over phosphorous pentaoxide, distilled, and stored over 3 Å molecular sieves in a sealed container. 1,4-Dioxane was distilled over sodium and benzophenone. Commercial grade dry DMF (Dimethylformamide), NMA (N-Methylacetamide) were used as a solvent. All the reactions were carried out under an argon atmosphere and anhydrous conditions unless otherwise noted. Analytical thin-layer chromatography (TLC) was performed on silica gel 60 F_{254} aluminum TLC sheets. Visualization of the developed chromatogram was performed by UV absorbance. For purification, column chromatography was performed using 100−200 mesh silica gel. ^{1}H and ^{13}C NMR spectra were recorded on 400 or 600 MHz spectrometer using tetramethylsilane (TMS) as internal standard. Chemical shifts (δ) are given from TMS (δ = 0.00) in parts per million (ppm) with reference to the residual nuclei of the deuterated solvent used [$CDCl_3$: ^{1}H NMR δ = 7.26 ppm (s); ^{13}C NMR δ = 77.0 ppm]. Coupling constants (*J*) are expressed in Hertz (Hz), and spin multiplicities are given as s (singlet), d (doublet), dd (double doublet), t (triplet), td (triple doublet), q (quartet), m (multiplet), and br (broad). All ^{13}C NMR spectra were obtained with complete proton decoupling. Mass spectra were performed using ESI-TOF or EI mode.

2. Structure of natural products 1-3 reported in manuscript:



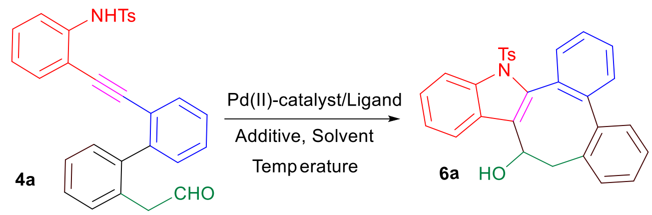
1a : R^1= R^2= Me (caulerpin)
1b : R^1= Me, R^2 = H
1c : R^1= R^2= H

2 (jolynamine)

3 (racemosin C)

Figure S1. Natural products **1**-**3** containing COT or 2,4,6-cyclooctatrien-1-one

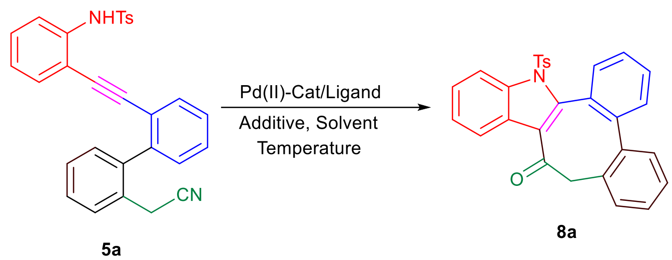
3. Table S1. Optimisation of the reaction conditions for the product 6a[a]



Entry	Catalyst	Ligand	Additive	Solvent	Temp. (°C)	Time (h)	Yield (%) 6a
1[b]	$Pd(OAc)_2$	bpy	D-CSA	1,4-dioxane	100	8	27
2	$Pd(OAc)_2$bpy	---	D-CSA	1,4-dioxane	100	5	trace
3[b]	$Pd(OAc)_2$	bpy	*p*-TsOH.H_2O	1,4-dioxane	100	8	40
4	$Pd(OAc)_2$	bpy	*p*-TsOH.H_2O	NMA	100	5.5	nr
5	$Pd(OAc)_2$	bpy	*p*-TsOH.H_2O	THF	reflux	6	nr
6[c]	$Pd(OAc)_2$bpy	---	*p*-TsOH.H_2O	1,4-dioxane	100	7	21
7	$Pd(OAc)_2$bpy	---	$MeSO_3H$	1,4-dioxane	100	6	trace
8	$Pd(OAc)_2$bpy	---	Triflic Acid	1,4-dioxane	100	5	16
9	$Pd(OAc)_2$bpy	---	$PhCO_2H$	1,4-dioxane	100	4.5	47
10	$Pd(OAc)_2$bpy	---	2,3-Naphthalenedicarboxylic acid	1,4-dioxane	100	6	nr
11	$Pd(OAc)_2$bpy	---	AcOH	1,4-dioxane	100	6	36
12[d]	$Pd(OAc)_2$bpy	---	AcOH	1,4-dioxane	100	3.5	73
13[de]	$Pd(OAc)_2$bpy	---	AcOH	1,4-dioxane	100	4.2	70
14[df]	$PdCl_2$	bpy	AcOH	1,4-dioxane	100	12	nr
15[df]	$Pd(MeCN)_4(BF_4)_2$	bpy	AcOH	1,4-dioxane	100	6	nr
16[df]	$Pd(MeCN)_2Cl_2$	bpy	AcOH	1,4-dioxane	100	6	nr

[a]Reaction conditions: **4a** (0.086 mmol), catalyst (6 mol%), ligand (6 mol%), and additive (2 equiv.) in solvent (1 mL) heated at 100 °C (except entry 5). [b]Starting material recovered (40% in the case of entry 1 and 28% in the case of entry 3). [c]Cyclooctatetraene derivative **7a** (20%) formed along with **6a**. [d]AcOH (10%, v/v) in 1,4-dioxane. [e]5 mol% palladium catalyst. [f]Multiple other spots (TLC) were formed which were not characterised, nr:no reaction.

4. Table S2. Optimisation of reaction conditions for the synthesis of dibenzo[5,6:7,8]cycloocta[1,2-*b*]indol-10(15*H*)-one 8a[a]



Entry	Catalyst	Ligand	Additive	Solvent	Temp.(°C)	Time (h)	Yield (%) **8a**
1[b]	Pd(OAc)₂bpy	----	AcOH	1,4-dioxane	100	10	50
2	Pd(OAc)₂bpy	----	*p*-TsOH.H₂O	1,4-dioxane	100	4.5	75
3	Pd(OAc)₂bpy	----	D-CSA	1,4-dioxane	100	6	87
4[c]	Pd(OAc)₂bpy	----	D-CSA	THF	Reflux	22	48
5	Pd(OAc)₂bpy	----	*p*-TsOH.H₂O	THF	Reflux	17	86
6	Pd(OAc)₂bpy	----	*p*-TsOH.H₂O	NMA	100	4.5	88
7	**Pd(OAc)₂bpy**	**----**	**D-CSA**	**NMA**	**100**	**5.2**	**92**
8[d]	Pd(OAc)₂bpy	----	D-CSA	NMA	100	7	73
9[e]	Pd(OAc)₂	bpy	D-CSA	NMA	100	6.5	84

[a]Reaction conditions: **5a** (0.14 mmol), Catalyst (6 mol %) and D-CSA (2 equiv.) was heated at 100 °C (except entries 4 and 5) in solvent (1.5 mL) under argon. [b]AcOH (10%, v/v) in 1,4-dioxane.[c]55% Starting material Recovered. [d] D-CSA used 1.5 equiv. [e]Catalyst and Ligand used are 5 and 6 mol % respectively.

Initially, we allowed the reaction of **5a** under the optimized reaction conditions for **4a**; to our disappointment, the desire product 2,4,6-cyclooctatrien-1-one **8a** was formed in 50% yield only (Table S2, entry 1). But replacing the additive AcOH either by *p*-TsOH.H_2O or D-CSA improved the reaction considerably by delivering the product **8a** with higher yields (75-87%) and reducing the reaction time (i.e, 4.5-6 h) (Table S2, entries 2 & 3). A change in the solvent from 1,4-dioxane to THF necessitated the use of longer reaction time (17-22 h); though the yield of the product **8a** was found to be very good (86%) upon employment of *p*-TsOH.H_2O as an additive (Table S2, entries 4 and 5). While carrying out the reaction in polar solvent (NMA) and using *p*-TsOH.H_2O as an additive improved the efficiency of the reaction by reducing the reaction time considerably (Table S2, entry 6). Furthermore, to our pleasure, switching to D-CSA acid as an additive proved to be still better by improving the yield of **8a** to 92% (Table S2, entry 7). But reducing the amount of additive (1.5 equiv instead of 2.0 equiv) or changing the catalytic system (i.e., $Pd(OAc)_2$/bpy) made the reaction sluggish and diminished the yield of product (Table S2, entry 8 and 9).

From this study, the best result was obtained when the reaction of **5a** was carried out at 100 °C in NMA using $Pd(OAc)_2bpy$ (6 mol%), D-CSA (2.0 equiv) as catalyst and additive, respectively leading to the generation of desired dibenzo[5,6:7,8]cycloocta[1,2-*b*]indol-10(15*H*)-one **8a** with excellent yield (92%).

5. X-Ray crystallographic information of products 6a, 6l, 7a, 8a and 8f

Single crystal of products **6a**, **6l, 7a, 8a and 8f** were obtained through slow evaporation (at room temperature) of a solution in dichloromethane-petroleum ether or ethyl acetate-petroleum ether. A single crystal of **6a, 6l, 7a, 8a and 8f** were attached to a glass fiber with epoxy glue and transferred to a X-ray diffractometer, equipped with a graphite-monochromator. Diffraction data of products **6a, 6l, 7a, 8a and 8f** were measured with MoKα radiation (λ = 1.54178 Å) at 100 K. The structure was solved by direct methods using the SHELXS-97 program.[1] Refinements were carried out with a full matrix least squares method against F 2 using SHELXL-97.[2] The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. The important crystal data and ORTEP diagram (drawn at 50% probability level) of product **6a, 6l, 7a, 8a and 8f** are given below.

Table S3: Important crystal data of product **(6a)**

Empirical formula	$C_{29} H_{23} N O_3 S$
Formula weight	1016.01
Temperature	100 K
Wavelength	1.54178
Crystal system	Monoclinic
Space group	P 1 21/n 1
Unit cell dimensions	a = 8.3459(3) Å α = 90.00°
	b = 31.8448(10) Å β = 92.018(2)
	c = 18.0413(6) Å γ = 90.00°
Volume	4791.9(3) $Å^3$
Z	4
Density (calculated)	1.408 g/cm^3
Absorption coefficient (Mu)	2.498 mm^{-1}
F(000)	2120.0
Theta range for data collection	2.775° to 66.672°
Index ranges	-9<=h<=6, -37<=k<=37, -21<=l<=21
Reflection collected	88704
Independent reflections	8465 [R(int) = 0.1452]
Completeness to theta= 25.44°	99.9 %
Absorption correction	multi-scan
Max. and min. transmission	0.972 and 0.850
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8465 /0/645
Goodness-of-fit on F^2	1.222
Final R indices [I>2sigma(I)]	R1 = 0.0876, wR2 = 0.1861
R indices (all data)	R1 = 0.0949, wR2 = 0.1904
Largest diff. peak and hole	0.469 & -0.452e.A^{-3}

The single crystal of the product **6a** was obtained by slow evaporation of the solvent when the compound was dissolved in minimum volume of Petroleum ether/ dichoromethane mixture. The crystal data of product **6a** has already been deposited at Cambridge Crystallographic Data Centre. The CCDC reference number is **2034270**.

Table S4: Important crystal data of product **(6l)**

Empirical formula	$C_{30} H_{25} N O_4 S$
Formula weight	1079.24
Temperature	100 K
Wavelength	1.54178
Crystal system	triclinic
Space group	P -1
Unit cell dimensions	a = 8.748(3) Å α = 97.243(9)°
	b = 14.050(5) Å β = 100.218(5)°
	c = 22.585(8) Å γ = 97.968(9)°
Volume	2673.0(16) Å^3
Z	2
Density (calculated)	1.341 g/cm^3
Absorption coefficient (Mu)	1.430 mm^{-1}
F(000)	1136.0
Theta range for data collection	2.012° to 62.501°
Index ranges	-10<=h<=10, -16<=k<=16, -25<=l<=25
Reflection collected	63419
Independent reflections	8479 [R(int) = 0.1163]
Completeness to theta= 25.44°	99.6 %
Absorption correction	multi-scan
Max. and min. transmission	0.972 and 0.850
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8479 /0/712
Goodness-of-fit on F^2	1.079
Final R indices [I>2sigma(I)]	R1 = 0.0680, wR2 = 0.1607
R indices (all data)	R1 = 0.0768, wR2 = 0.1666
Largest diff. peak and hole	0.586 & -0.377 e.A^{-3}

The single crystal of the product **6l** was obtained by slow evaporation of the solvent when the compound was dissolved in minimum volume of Petroleum ether/ ethyl acetate mixture. The crystal data of product **6l** has already been deposited at Cambridge Crystallographic Data Centre. The CCDC reference number is **2034271**.

Table S5: Important crystal data of product **(7a)**

Empirical formula	$C_{29} H_{21} N O_2 S$
Formula weight	447.53
Temperature	116 K
Wavelength	1.54178
Crystal system	triclinic
Space group	P -1
Unit cell dimensions	a = 8.5406(7) Å α = 89.172(4)°
	b = 10.0271(8) Å β = 79.068(4)°
	c = 13.9349(11) Å γ = 66.547(3)°
Volume	1072.43(15) $Å^3$
Z	2
Density (calculated)	1.386 g/cm^3
Absorption coefficient (Mu)	1.561 mm^{-1}
F(000)	468.0
Theta range for data collection	5.839° to 66.825°
Index ranges	-10<=h<=9, -11<=k<=11, -16<=l<=16
Reflection collected	11582
Independent reflections	3659 [R(int) = 0.0746]
Completeness to theta= 25.44°	96.2 %
Absorption correction	multi-scan
Max. and min. transmission	0.753 and 0.473
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3659 /0/ 299
Goodness-of-fit on F^2	1.058
Final R indices [I>2sigma(I)]	R1 = 0.0713, wR2 = 0.1868
R indices (all data)	R1 = 0.0745, wR2 = 0.1905
Largest diff. peak and hole	0.425 & -0.770 $e.A^{-3}$

The single crystal of the product **7a** was obtained by slow evaporation of the solvent when the compound was dissolved in minimum volume of Petroleum ether/ dichoromethane mixture. The crystal data of product **7a** has already been deposited at Cambridge Crystallographic Data Centre. The CCDC reference number is **2034272**.

Table S6: Important crystal data of product **(8a)**

Empirical formula	$C_{29} H_{21} N O_3 S$
Formula weight	463.53
Temperature	100 K
Wavelength	1.54178
Crystal system	monoclinic
Space group	C 1 2/c 1
Unit cell dimensions	a = 17.1953(3) Å α = 90°
	b = 11.2998(3) Å β = 99.631(1)°
	c = 23.4679(5) Å γ = 90°
Volume	4495.62(17) $Å^3$
Z	8
Density (calculated)	1.370 g/cm^3
Absorption coefficient (Mu)	1.544 mm^{-1}
F(000)	1936.0
Theta range for data collection	3.821° to 66.632°
Index ranges	-20<=h<=20, -13<=k<=13, -27<=l<=27
Reflection collected	86526
Independent reflections	3971 [R(int) = 0.0792]
Completeness to theta= 25.44°	99.7 %
Absorption correction	multi-scan
Max. and min. transmission	0.972 and 0.850
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3971 /0/308
Goodness-of-fit on F^2	1.120
Final R indices [I>2sigma(I)]	R1 = 0.0394, wR2 = 0.0958
R indices (all data)	R1 = 0.0399, wR2 = 0.0962
Largest diff. peak and hole	0.314 & -0.528 e.A^{-3}

The single crystal of the product **8a** was obtained by slow evaporation of the solvent when the compound was dissolved in minimum volume of Petroleum ether/ dichoromethane mixture. The crystal data of product **8a** has already been deposited at Cambridge Crystallographic Data Centre. The CCDC reference number is **2034273**.

Table S7: Important crystal data of product **(8f)**

Empirical formula	$C_{30} H_{23} N O_4 S$
Formula weight	493.55
Temperature	102 K
Wavelength	1.54178
Crystal system	monoclinic
Space group	P 1 21/c 1
Unit cell dimensions	a = 12.6739(9)Å α = 90°
	b = 16.317(3)Å β = 109.725(12)°
	c = 12.1213(13)Å γ = 90°
Volume	2359.6 (5)$Å^3$
Z	4
Density (calculated)	1.389 g/cm^3
Absorption coefficient (Mu)	1.538 mm^{-1}
F(000)	1032.0
Theta range for data collection	4.73° to 72.464°
Index ranges	-15<=h<=15, -19<=k<=20, -14<=l<=14
Reflection collected	35390
Independent reflections	4631 [R(int) 0.0629]
Completeness to theta= 25.44°	99.2 %
Absorption correction	multi-scan
Max. and min. transmission	0.754 and 0.656
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4631 /0/ 327
Goodness-of-fit on F^2	1.079
Final R indices [I>2sigma(I)]	R1 = 0.0480, wR2 = 0.1155
R indices (all data)	R1 = 0.0506, wR2 = 0.1174
Largest diff. peak and hole	0.352 & -0.557 e.A^{-3}

The single crystal of the product **8f** was obtained by slow evaporation of the solvent when the compound was dissolved in minimum volume of Petroleum ether/ ethyl acetate mixture. The crystal data of product **8f** has already been deposited at Cambridge Crystallographic Data Centre. The CCDC reference number is **2034274**.

6. **ORTEP Diagrams of the products 6a, 6l, 7a, 8a and 8f :**

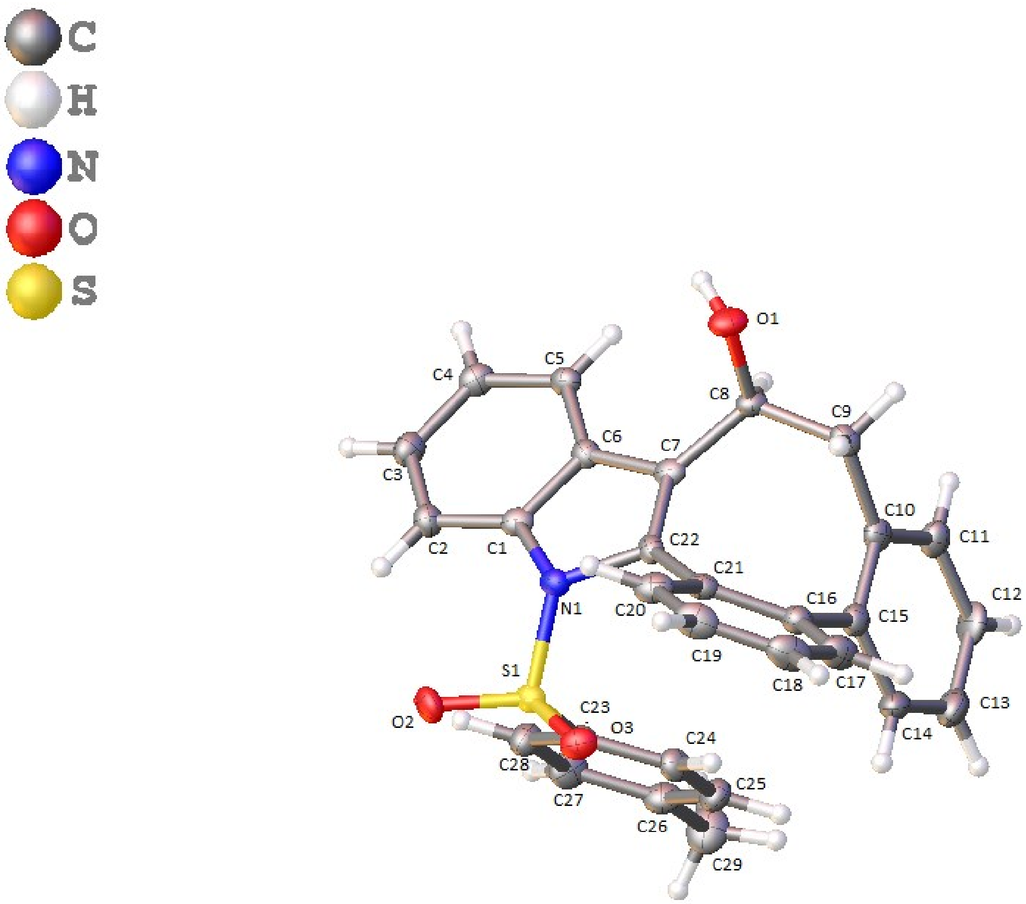


Figure S2. ORTEP Diagram (thermal ellipsoid plot) of Product **6a** (drawn at 50% probability level)

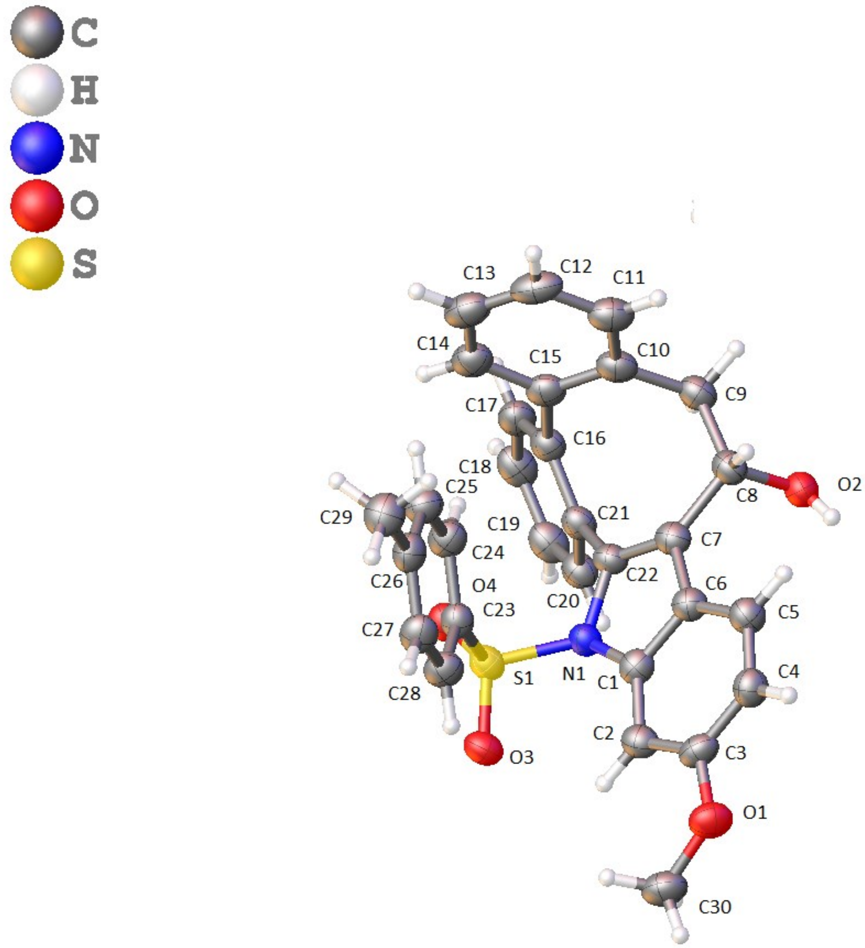


Figure S3. ORTEP Diagram (thermal ellipsoid plot) of Product **6l** (drawn at 50% probability level)

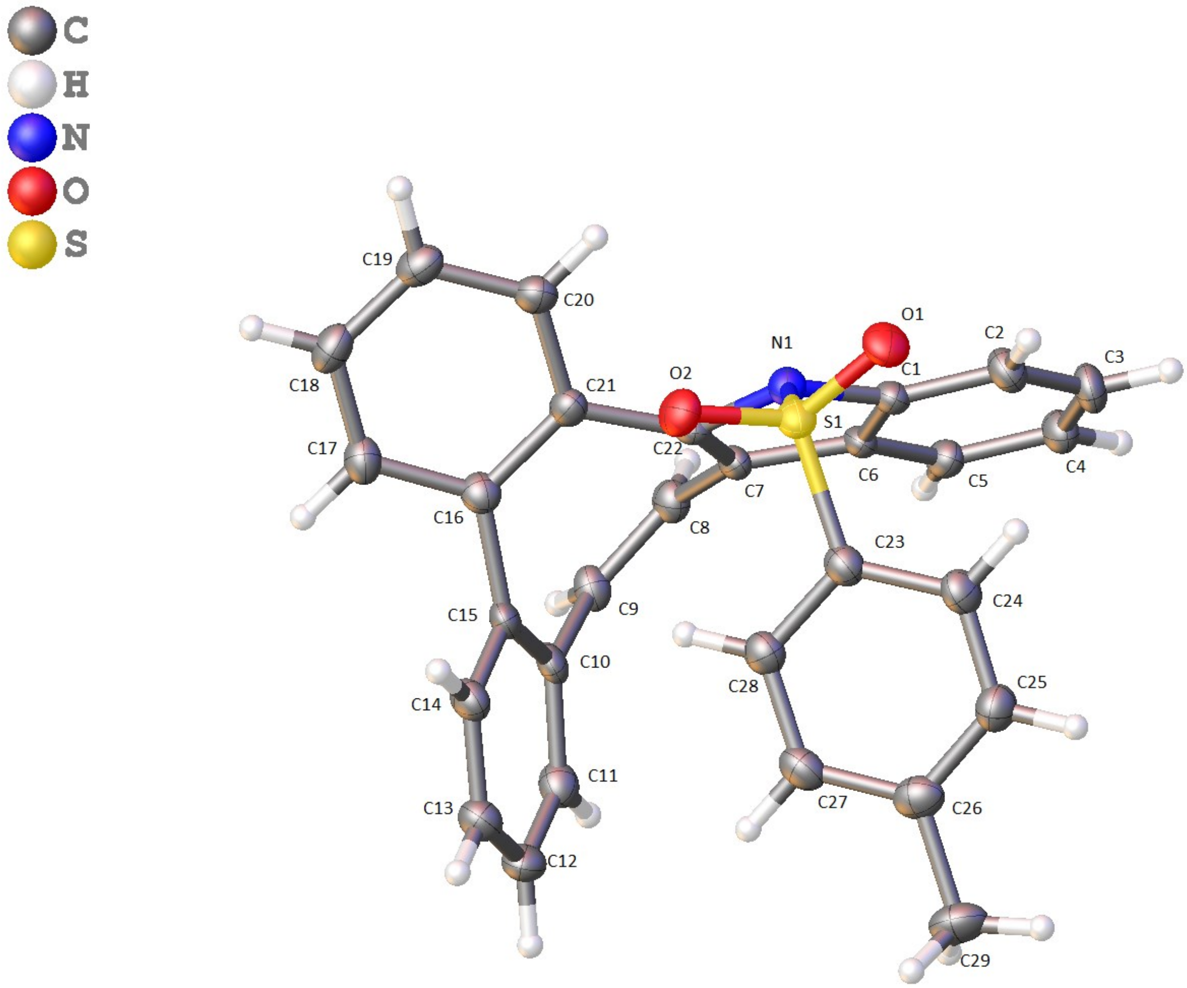


Figure S4. ORTEP Diagram (thermal ellipsoid plot) of Product **7a** (drawn at 50% probability level)

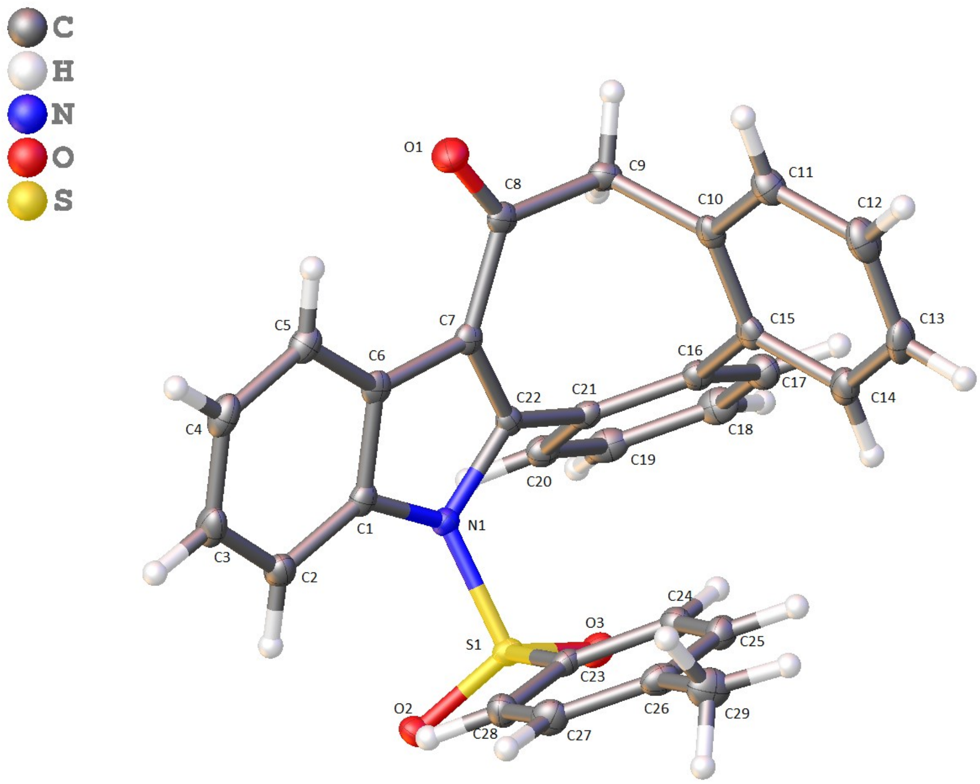


Figure S5. ORTEP Diagram (thermal ellipsoid plot) of Product **8a** (drawn at 50% probability level)

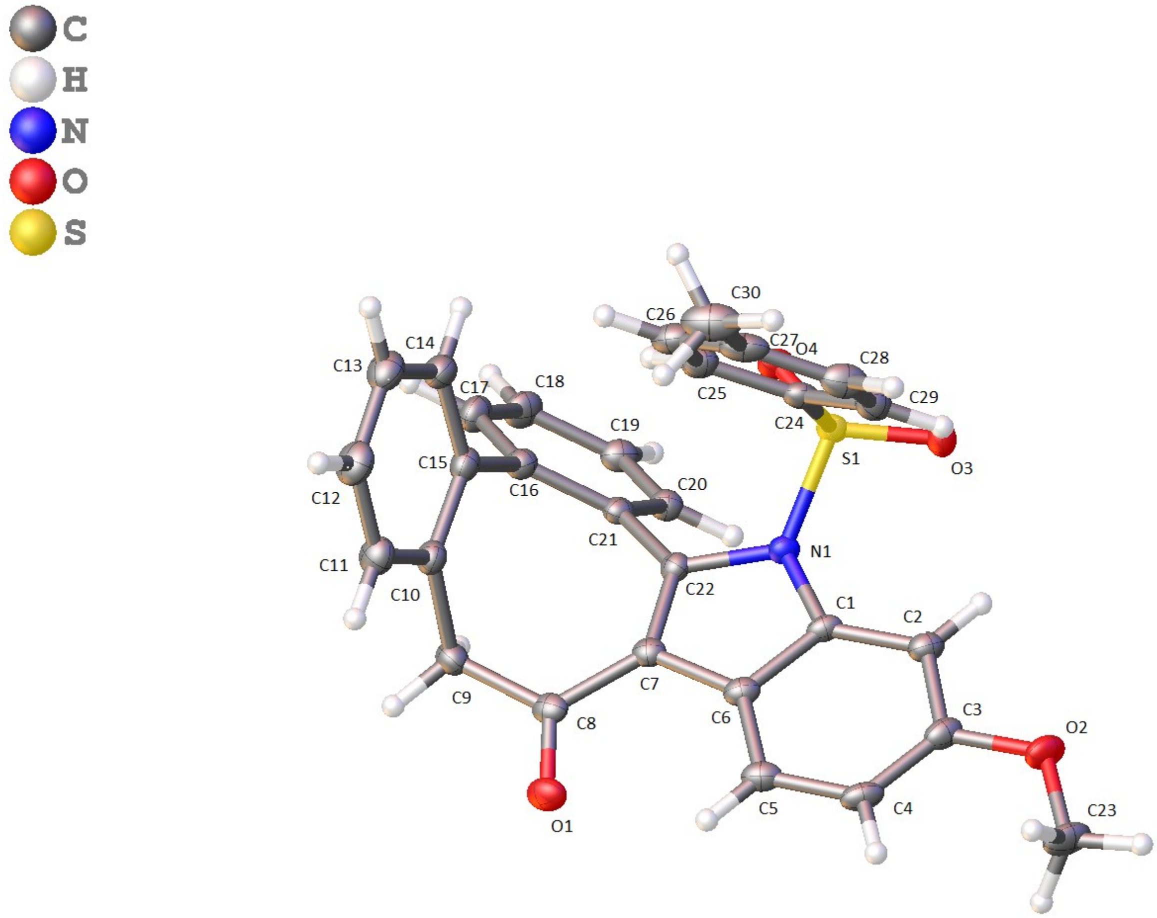
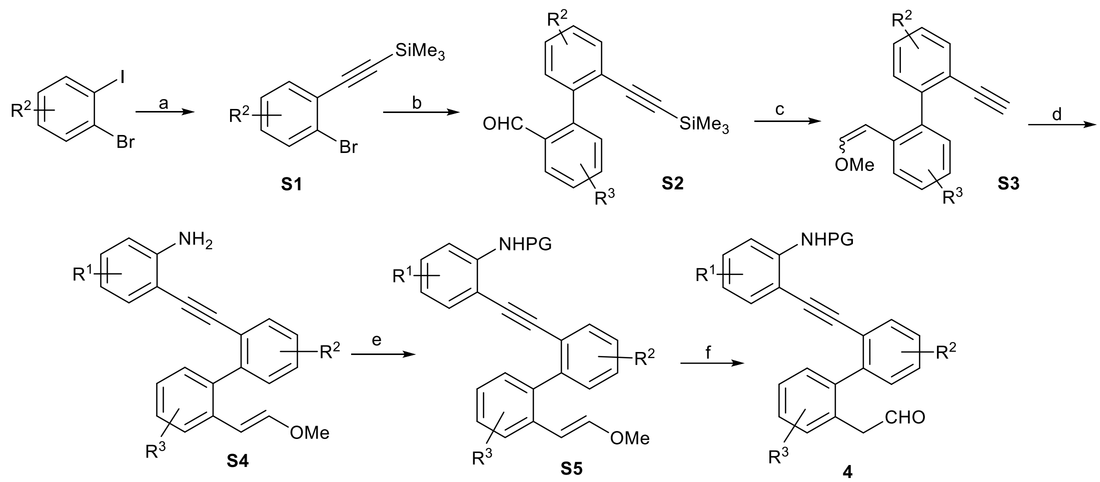


Figure S6. ORTEP Diagram (thermal ellipsoid plot) of product **8f** (drawn at 50% probability level)

7. Schematic representation and procedure for preparation of starting material 4:



Scheme S1. Reagents and Conditions: (a) Trimethylsilyl acetylene, $PdCl_2(PPh_3)_2$, CuI, Et_3N, DMF ,0 °C-rt, 1.5-2.5 h, 92-94%; (b) 2-Formylbenzeneboronic acid, $Pd(OAc)_2$, dppf, K_2CO_3, DME, 80°C, overnight, 50-80%; (c) (i) K_2CO_3, MeOH, rt, overnight, 92-95%, (ii) (Methoxymethyl)triphenylphosphonium chloride, NaHDMS (2M), THF, 0 °C-rt, 1-1.5 h, 78-82%; (d) 2-iodoaniline derivative, $PdCl_2(PPh_3)_2$, CuI, Et_3N, DMF ,0 °C-rt, 5-15 h, 72-88%; (e) TsCl/ NsCl, pyridine, DCM, 0 °C- rt, 12-24 h, 66-85%; (f) *p*-TsOH.H_2O, acetone, 0 °C-rt, 3.5-5.5 h, 49-91%.

The desired starting material **4** was prepared in few steps starting from 2-bromoiodobenzene derivatives. In the first step silylated derivative of 2-bromoiodobenze **S1** was obtained via "*Sonogashira reaction".* The silylated compound formed was then allowed to undergo "*Suzuki coupling*" with 2-formylbenzeneboronic acid derivatives to form **S2**[3] which on desilylation[3] followed by Wittig reaction delivered the masked aldehyde **S3** derivatives. **S3** was then underwent "*Sonogashira coupling"* with 2-iodoaniline derivatives to form **S4** derivatives. Later, the amine group of **S4** was protected (tosylated/ nosylated) to form **S5** and finally our desired starting material **4** was formed by demasking aldehyde group of **S5** using *p*-TsOH.H_2O.

<u>*Synthesis of silylated derivatives* **S1**</u> :

To a well stirred solution of commercially available 2-bromoiodobenzene derivatives (7.12 mmol, 1 equiv) in mixture of solvents (i.e., Et_3N : DMF= 1.5 : 1, 4.5 mL), $PdCl_2(PPh_3)_2$ (49.9 mg, 0.071 mmol, 1 mol %) was added. The reaction mixture was then cooled to 0 °C and trimethylsilylacetylene (1.11 ml, 7.83 mmol, 1.1 equiv) was added dropwise followed by the addition of CuI (27.0 mg, 0.142 mmol, 2 mol %,). After stirring few minutes at 0 °C, the temperature of the reaction was allowed to rise to rt and stirring was continued for 1.5-2.5 h. Upon completion of reaction (TLC), solvent was removed under reduced pressure and extracted with ethyl acetate (3x 50 mL); the combined organic extracts were washed with brine (25 mL) and dried over anhydrous Na_2SO_4 and concentrated *in vaccuo*. The crude product was then purified by silica gel (100-200 mesh) column chromatography eluting with petroleum ether to obtain a silylated acetylenic intermediate **S1** (92-94% yield).

Synthesis of the acetylenic derivatives **S2**[3] **:**

A mixture of $Pd(OAc)_2$ (118.7 mg, 0.531 mmol, 8 mol %), DPPF [1,1'-Ferrocenediyl-bis(diphenylphosphine)] (440.6 mg, 0.795 mmol, 12 mol %) and K_2CO_3 (2743.6 mg, 19.88 mmol, 3 equiv) were stirred in DME (30 mL) for 30 min. Then **S1** (6.63 mmol, 1 equiv) and 2-formylbenzeneboronic acid (1491.1 mg, 9.94 mmol, 1.5 equiv) were sequentially added to the solution and the resulting mixture was heated at 80 ^{o}C for overnight. Upon completion of reaction (TLC), the mixture was extracted with ethyl acetate (3x 60 mL); the combined organic extracts were washed with brine (22 mL) and dried over anhydrous Na_2SO_4 and concentrated *in vaccuo*. The crude product was then purified by silica gel (100-200 mesh) column chromatography eluting with 2-4% ethyl acetate-petroleum ether (v/v) to obtain the acetylenic derivatives **S2** (50-80% yield).

Synthesis of **S3** *derivatives :*

To a well stirred solution of the acetylenic derivatives **S2** (2.52 mmol, 1 equiv), K_2CO_3 (1042.4 mg, 7.55 mmol, 3 equiv) was added in MeOH (5 mL) and stirring was continued for overnight. After completion of reaction (TLC), the mixture was extracted with ethyl acetate (3 x 40 mL); the combined organic extracts were washed with brine (20 mL) and dried over anhydrous Na_2SO_4 and concentrated *in vaccuo*. The crude product was then purified by silica gel (100-200 mesh) column chromatography eluting with 4-5% ethyl acetate-petroleum ether (v/v) to obtain the desilyated acetylinic aldehyde derivatives[3] (92-95% yield).

Then a suspension of (Methoxymethyl)triphenylphosphonium chloride (1603.7 mg, 4.69 mmol, 2.1 equiv) in THF (1.0 mL) was cooled using ice-salt mixture (temperature around -5 to -10 ^{o}C) and to it, 2M NaHDMS in THF (2.34 mL, 2.1 equiv) was added dropwise and the colour of the solution changed from white to red to dark brown. The solution was allowed to stirred for 30 min at the same temperature, after which the desilylated acetylinic aldehyde derivatives of **S2** (2.23 mmol, 1 equiv) dissolved in dry THF (0.4 mL) was added dropwise to the solution at the same temp.; after stirring for 15 min, the solution was then stirred at rt for 1-1.5 h. After completion of reaction (TLC), the mixture was extracted with ethyl acetate (3x 25 mL); the combined organic extracts were washed with brine (25 mL) and dried over anhydrous Na_2SO_4 and concentrated *in vaccuo*. The crude product was then purified by silica gel (100-200 mesh) column chromatography eluting with 2-3% ethyl acetate-petroleum ether (v/v) to obtain the **S3** derivatives (78-82% yield).

Synthesis of Amine derivatives ***S4*** *:*

To a well stirred solution of 2-iodoaniline derivatives (1.32 mmol, 1 equiv) in mixture of solvents (i.e., Et_3N : DMF = 2 : 1, 1.5 mL), $PdCl_2(PPh_3)_2$ (37.1 mg, 0.053 mmol, 4 mol %) was added. The reaction mixture was then cooled to 0 ^oC and **S3** derivative (1.72 mmol, 1.3 equiv) was added dropwise followed by the addition of CuI (20.1 mg, 0.106 mmol, 8 mol %). After stirring few minutes at 0 ^oC, the temperature of the reaction was allowed to rise to room temperature and stirring was continued for 5-15 h. Upon completion of reaction (TLC), solvent was removed under reduced pressure and extracted with ethyl acetate (3 x 20 mL); the combined organic extracts were washed with brine (15 mL) and dried over anhydrous Na_2SO_4 and concentrated *in vaccuo*. The crude product was then purified by silica gel (100-200 mesh) column chromatography eluting with 10-24% ethyl acetate-petroleum ether (v/v) to obtain **S4** derivatives (72-88% yield).

Synthesis of N-protected amine derivatives ***S5*** *:*

To a well stirred solution of amine derivative **S4** (0.92 mmol, 1 equiv) in dry DCM (3 mL) at 0 ^oC was added pyridine (186.03 µL, 2.31 mmol, 2.5 equiv) dropwise. Thereafter, TsCl or NsCl (2.49 mmol, 2.7 equiv) was added portion-wise at the same temperature and whole reaction mixture was allowed to stir at rt for 12-24 h. Upon completion of the reaction (TLC), solvent was removed in *vaccuo* and then extracted with DCM (3x 25 mL); the combined organic extracts were washed with brine (15 mL) and dried over anhydrous Na_2SO_4 and concentrated *in vaccuo*. Then the crude product was purified by silica gel (100-200 mesh) column chromatography eluting with 12-30% ethyl acetate-petroleum ether (v/v) to obtain the pure tosylated/nosylated product **S5** in 66-85% yield.

Synthesis of Final Substrates ***4****:*

To a well-stirred and ice-cooled solution of **S5** (0.625 mmol, 1 equiv) in dry acetone *p*-TsOH.H_2O (190.0 mg, 1.00 mmol, 1.6 equiv) was added portion-wise and the whole reaction mixture was then allowed to stir at rt for another 3.5-5.5 h until completion of reaction (TLC). Next, the reaction mixture was neutralized with dilute sodium bicarbonate solution and extracted with DCM (3 x 20 mL), dried over anhydrous Na_2SO_4 and concentrated *in vaccuo.* The resulting crude product was purified by silica gel (100-200 mesh) column chromatography eluting with 10-27% ethyl acetate in petroleum ether (v/v) to afford the desired starting material **4** in (49-91%) yield.

8. Spectral data of compounds 4a-4q :

*4-Methyl-N-(2-((2'-(2-oxoethyl)-[1,1'-biphenyl]-2-yl)ethynyl)phenyl)benzenesulfonamide (**4a**)*:

Yellow gummy liquid (223.8 mg, 77%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 9.55 (t, J = 2.0 Hz, 1H, -CHO), 7.58-7.55 (m, 1H, Ar-H), 7.53 (d, J = 8.4 Hz, 2H, Ar-H), 7.49-7.46 (m, 3H, Ar-H), 7.43 (td, J = 6.9, 1.8 Hz, 2H, Ar-H), 7.38-7.34 (m, 2H, Ar-H), 7.29-7.26 (m, 1H, Ar-H), 7.21-7.17 (m, 1H, Ar-H), 7.13 (d, J = 8.0 Hz, 2H, Ar-H), 7.04 (dd, J = 7.8, 1.4 Hz, 1H, Ar-H), 6.94 (td, J = 7.5, 1.1 Hz, 1H, Ar-H), 6.63 (s, 1H, -N$\underline{H}$Ts), 3.64 (dd, J = 17.0, 1.8 Hz, 1H, H_a of -CH_2-), 3.56 (dd, J = 16.8, 2.0 Hz, 1H, H_b of -CH_2-), 2.33 (s, 3H, -$SO_2PhC\underline{H_3}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz) δ_C 199.3 (-CHO), 143.8 (Ar-C), 143.0 (Ar-C), 141.1 (Ar-C), 137.3 (Ar-C), 136.0 (Ar-C) , 132.1 (Ar-C), 130.7 (Ar-C), 130.4 (Ar-C), 130.2 (Ar-C), 129.8 (Ar-C), 129.5 (Ar-C), 129.4 (3C, Ar-C), 129.0 (Ar-C), 128.7 (Ar-C), 127.8 (Ar-C), 127.7 (Ar-C), 127.2 (2C, Ar-C), 124.2 (Ar-C), 121.9 (Ar-C), 119.9 (Ar-C), 114.0 (Ar-C), 94.9 (-$\underline{C}$≡C-), 87.4 (-C≡$\underline{C}$-), 48.2 (-CH_2-), 21.5 (-$SO_2Ph\underline{C}H_3$); High-resolution mass spectrometry (HRMS) (ESI) m/z calcd for $C_{29}H_{23}NNaO_3S$ [M + Na]$^+$ 488.1296, found 488.1297.

*4-Nitro-N-(2-((2'-(2-oxoethyl)-[1,1'-biphenyl]-2-yl)ethynyl)phenyl)benzenesulfonamide (**4b**) :*

Yellow gummy liquid (235.6 mg, 76%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 9.54 (t, J = 1.6 Hz, 1H, -CHO), 8.12 (d, J = 8.8 Hz, 2H, Ar-H), 7.73 (d, J = 8.8 Hz, 2H, Ar-H), 7.51-7.39 (m, 6H, Ar-H), 7.37-7.34 (m, 2H, Ar-H), 7.30-7.23 (m, 2H, Ar-H), 7.11 (dd, J = 8.0, 1.6 Hz, 1H, Ar-H), 7.04 (td, J = 7.5, 0.9 Hz, 1H, Ar-H), 6.67 (s, 1H, -N$\underline{H}$Ts), 3.65 (dd, J = 17.4, 1.8 Hz, 1H, H_a of -CH_2-), 3.57 (dd, J = 17.2, 1.6 Hz, 1H, H_b of -CH_2-); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 199.1 (-CHO), 150.2 (Ar-C), 144.6 (Ar-C), 143.1 (Ar-C), 141.1 (Ar-C), 136.2 (Ar-C), 132.4 (Ar-C), 132.1 (Ar-C), 131.0 (Ar-C), 130.6 (Ar-C), 130.2 (Ar-C), 129.9 (Ar-C), 129.8 (Ar-C), 129.4 (Ar-C), 128.9 (Ar-C), 128.6 (2C, Ar-C), 128.0 (Ar-C), 127.9 (Ar-C), 125.6 (Ar-C), 124.0 (2C, Ar-C), 121.7 (Ar-C), 121.6 (Ar-C), 115.4 (Ar-C), 95.2 (-$\underline{C}$≡C-), 87.1 (-C≡$\underline{C}$-), 48.3 (-CH_2-); HRMS (ESI) m/z calcd for $C_{28}H_{20}N_2NaO_5S$ [M + Na]$^+$ 519.0991, found 519.0973.

*N-(4-Fluoro-2-((2'-(2-oxoethyl)-[1,1'-biphenyl]-2-yl)ethynyl)phenyl)-4-methylbenzenesulfonamide (**4c**)* **:**

Yellow gummy liquid (256.6 mg, 85%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 9.54 (t, J = 1.8 Hz, 1H, -CHO), 7.54-7.52 (m, 1H, Ar-H), 7.49-7.45 (m, 5H, Ar-H), 7.44-7.39 (m, 2H, Ar-H), 7.36-7.33 (m, 2H, Ar-H), 7.29-7.27 (m, 1H, Ar-H), 7.11 (d, J = 8.0 Hz, 2H, Ar-H), 6.94-6.89 (m, 1H, Ar-H), 6.71 (dd, J = 8.6, 3.0 Hz, 1H, Ar-H), 6.45 (s, 1H, -N$\underline{H}$Ts), 3.62 (dd, J = 17.0, 1.8 Hz, 1H, H_a of -CH_2-), 3.54 (dd, J = 17, 1.8 Hz, 1H, H_b of -CH_2-), 2.33 (s, 3H, -$SO_2PhC\underline{H_3}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 199.2 (-CHO), 159.2 (d, $J_{C\text{-}F}$ = 244.1 Hz, Ar-C), 144.0 (Ar-C), 143.4 (Ar-C), 141.0 (Ar-C), 135.8 (Ar-C), 133.6 (d, $J_{C\text{-}F}$ = 2.4 Hz, Ar-C), 132.2 (Ar-C), 130.9 (Ar-C), 130.5 (Ar-C), 130.3 (Ar-C), 129.9 (Ar-C), 129.6 (2C, Ar-C), 129.4 (Ar-C), 128.9 (Ar-C), 127.92 (Ar-C), 127.91 (Ar-C), 127.3 (2C, Ar-C), 123.2 (d, $J_{C\text{-}F}$ = 8.7 Hz, Ar-C), 121.6 (Ar-C), 118.4 (d, $J_{C\text{-}F}$ = 24.1 Hz, Ar-C), 116.9 (d, $J_{C\text{-}F}$ = 22.6 Hz, Ar-C), 116.6 (d, $J_{C\text{-}F}$ = 9.9 Hz, Ar-C), 95.5 (-$\underline{C}$≡C-), 86.6 (-C≡$\underline{C}$-), 48.3 (-CH_2-), 21.6 (-$SO_2Ph\underline{C}H_3$); HRMS (ESI) m/z calcd for $C_{29}H_{22}FNNaO_3S$ [M + Na]$^+$ 506.1202, found 506.1201.

*N-(4-Chloro-2-((2'-(2-oxoethyl)-[1,1'-biphenyl]-2-yl)ethynyl)phenyl)-4-methylbenzenesulfonamide (**4d**)* **:**

Yellow solid (265.1 mg, 85%), mp 56-58 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 9.55 (s, 1H, -CHO), 7.56-7.54 (m, 1H, Ar-H), 7.51-7.47 (m, 4H, Ar-H), 7.46-7.40 (m, 3H, Ar-H), 7.37-7.34 (m, 2H, Ar-H), 7.29-7.27 (m, 1H, Ar-

H), 7.15-7.13 (m, 3H, Ar-H), 7.01 (d, *J* = 2.4 Hz, 1H, Ar-H), 6.59 (s, 1H, -N<u>H</u>Ts), 3.64 (d, *J* = 17.2 Hz, 1H, H_a of $-CH_2-$), 3.55 (d, *J* = 17.2 Hz, 1H, H_b of $-CH_2-$), 2.34 (s, 3H, $-SO_2PhC\underline{H_3}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 199.2 (-CHO), 144.2 (Ar-C), 143.4 (Ar-C), 141.0 (Ar-C), 136.1 (Ar-C), 135.8 (Ar-C), 132.2 (Ar-C), 131.6 (Ar-C), 131.0 (Ar-C), 130.5 (Ar-C), 130.2 (Ar-C), 129.9 (Ar-C) , 129.7 (2C, Ar-C), 129.68 (Ar-C), 129.66 (Ar-C), 129.4 (Ar-C), 128.9 (Ar-C), 128.0 (Ar-C), 127.9 (Ar-C), 127.3 (2C, Ar-C), 121.6 (Ar-C), 121.4 (Ar-C), 115.7 (Ar-C), 96.0 (-<u>C</u>≡C-), 86.3 (-C≡<u>C</u>-), 48.3 ($-CH_2-$), 21.6 ($-SO_2Ph\underline{C}H_3$); HRMS (ESI) m/z calcd for $C_{29}H_{22}ClNNaO_3S$ [M + Na]$^+$ 522.0907, found 522.0903.

*4-Methyl-N-(2-((2'-(2-oxoethyl)-[1,1'-biphenyl]-2-yl)ethynyl)-4-(trifluoromethyl)phenyl)-benzenesulfonamide (**4e**):*

Yellow gummy liquid (209.9 mg, 63%); ^1H NMR ($CDCl_3$, 400 MHz) δ_H 9.56 (t, *J* = 1.6 Hz, 1H, -CHO), 7.62-7.58 (m, 3H, Ar-H), 7.52 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.49-7.47 (m, 2H, Ar-H), 7.46-7.44 (m, 1H, Ar-H), 7.43-7.35 (m, 4H, Ar-H), 7.33-7.32 (m, 1H, Ar-H), 7.30-7.28 (m, 1H, Ar-H), 7.20 (d, *J* = 8.0 Hz, 2H, Ar-H), 6.98 (s, 1H, -N<u>H</u>Ts), 3.69 (dd, *J* = 17.0, 1.4 Hz, 1H, H_a of $-CH_2-$), 3.59 (dd, *J* = 17.2, 1.4 Hz, 1H, H_b of $-CH_2-$), 2.36 (s, 3H, $-SO_2PhC\underline{H_3}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 199.1 (-CHO), 144.5 (Ar-C), 143.5 (Ar-C), 141.1 (Ar-C), 140.4-140.3 (m, Ar-C), 135.8 (Ar-C), 132.3 (Ar-C), 131.1 (Ar-C), 130.5 (Ar-C), 130.2 (Ar-C), 129.9 (Ar-C), 129.8 (2C, Ar-C), 129.53 (Ar-C), 129.5 (q, J_{C-F} = 3.8 Hz, Ar-C), 128.9 (Ar-C), 128.0 (Ar-C), 127.9 (Ar-C), 127.3 (2C, Ar-C), 126.3 (q, J_{C-F} = 3.7 Hz, Ar-C), 125.9 (q, J_{C-F} = 33.2 Hz, Ar-C), 123.5 (q, J_{C-F} = 262.6 Hz, Ar-C), 121.5 (Ar-C), 118.3 (Ar-C), 113.4 (Ar-C), 96.5 (-<u>C</u>≡C-), 86.1 (-C≡<u>C</u>-), 48.4 ($-CH_2-$), 21.6 ($-SO_2Ph\underline{C}H_3$); HRMS (ESI) m/z calcd for $C_{30}H_{22}F_3NNaO_3S$ [M + Na]$^+$ 556.1170, found 556.1166.

*4-Methyl-N-(4-methyl-2-((2'-(2-oxoethyl)-[1,1'-biphenyl]-2-yl)ethynyl)phenyl)benzenesulfonamide (**4f**)* :

Yellow gummy liquid (227.5 mg, 76%); ^1H NMR ($CDCl_3$, 400 MHz) δ_H 9.54 (t, *J* = 1.8 Hz, 1H, -CHO), 7.54-7.45 (m, 5H, Ar-H), 7.42 (td, *J* = 7.0, 1.7 Hz, 2H, Ar-H), 7.38-7.34 (m, 3H, Ar-H), 7.28-7.26 (m, 1H, Ar-H), 7.10 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.00 (d, *J* = 9.6 Hz, 1H, Ar-H), 6.84 (s, 1H, Ar-H/ -N<u>H</u>Ts), 6.45 (s, 1H, -N<u>H</u>Ts/ Ar-H), 3.65-3.53 (m, 2H, $-CH_2-$), 2.32 (s, 3H, $-SO_2PhC\underline{H_3}$), 2.18 (s, 3H, $-CH_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 199.5 (-CHO), 143.8 (Ar-C), 143.1 (Ar-C), 141.3 (Ar-C), 136.1 (Ar-C), 134.9 (Ar-C), 134.3 (Ar-C), 132.4 (Ar-C), 132.1 (Ar-C), 130.8 (Ar-C), 130.6 (Ar-C), 130.5 (Ar-C), 130.3 (Ar-C), 129.9 (Ar-C), 129.5 (2C, Ar-C), 129.0 (Ar-C), 128.8 (Ar-C), 127.9 (Ar-C), 127.8 (Ar-C), 127.3 (2C, Ar-C), 122.1 (Ar-C), 120.8 (Ar-C), 114.4 (Ar-C), 94.5 (-<u>C</u>≡C-), 87.8 (-C≡<u>C</u>-), 48.3 ($-CH_2-$), 21.6 ($-SO_2Ph\underline{C}H_3$), 20.6 ($-CH_3$); HRMS (ESI) m/z calcd for $C_{30}H_{25}NNaO_3S$ [M + Na]$^+$ 502.1453, found 502.1451.

*Methyl 4-(4-methylphenylsulfonamido)-3-((2'-(2-oxoethyl)-[1,1'-biphenyl]-2-yl)ethynyl)benzoate (**4g**)* :

Yellow solid (170.0 mg, 52%), mp 64-66 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ_H 9.56 (t, *J* = 1.8 Hz, 1H, -CHO), 7.82-7.79 (m, 2H, Ar-H), 7.63-7.60 (m, 1H, Ar-H), 7.57 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.49-7.42 (m, 5H, Ar-H), 7.40-7.36 (m, 2H, Ar-H), 7.29-7.27 (m, 1H, Ar-H), 7.17 (d, *J* = 8.0 Hz, 2H, Ar-H), 6.98 (s, 1H, -N<u>H</u>Ts), 3.85 (s, 3H, $-CO_2CH_3$), 3.69 (dd, *J* = 17.2, 1.6 Hz, 1H, H_a of $-CH_2-$), 3.60 (dd, *J* = 17.0, 2.0 Hz, 1H, H_b of $-CH_2-$), 2.35 (s, 3H,$-SO_2PhC\underline{H_3}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 199.2 (-CHO), 165.8 ($-\underline{C}O_2CH_3$), 144.4 (Ar-C), 143.3 (Ar-C), 141.3 (Ar-C), 141.1 (Ar-C), 135.8 (Ar-C), 133.9 (Ar-C), 132.4 (Ar-C), 131.1 (Ar-C), 130.8 (Ar-C), 130.4 (Ar-C), 130.2 (Ar-C), 129.9 (Ar-C), 129.8 (2C, Ar-C), 129.4 (Ar-C), 128.9 (Ar-C), 128.0 (Ar-C), 127.9 (Ar-C), 127.4 (2C, Ar-C), 125.5 (Ar-C), 121.7 (Ar-C), 117.6 (Ar-C), 112.9 (Ar-C), 96.0 (-<u>C</u>≡C-), 86.4 (-C≡<u>C</u>-), 52.3 (-$CO_2\underline{C}H_3$), 48.4 (-CH_2-), 21.6 (-$SO_2Ph\underline{C}H_3$); HRMS (ESI) m/z calcd for $C_{31}H_{25}NNaO_5S$ [M + Na]$^+$ 546.1351, found 546.1332.

*N-(4-Methoxy-2-((2'-(2-oxoethyl)-[1,1'-biphenyl]-2-yl)ethynyl)phenyl)-4-methylbenzenesulfonamide (**4h**)* **:**

Yellow gummy liquid (241.3 mg, 78%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 9.52 (t, *J* = 2.0 Hz, 1H, -CHO), 7.50-7.40 (m, 8H, Ar-H), 7.36-7.32 (m, 2H, Ar-H), 7.28-7.26 (m, 1H, Ar-H), 7.07 (d, *J* = 8.0 Hz, 2H, Ar-H), 6.78 (dd, *J* = 9.0, 3.0 Hz, 1H, Ar-H), 6.48 (d, *J* = 3.2 Hz, 1H, Ar-H), 6.23 (s, 1H, -N$\underline{H}$Ts), 3.69 (s, 3H, -OCH_3), 3.59 (dd, *J* = 17.0, 1.8 Hz, 1H, H_a of -CH_2-), 3.52 (dd, *J* = 17.2, 2.0 Hz, 1H, H_b of -CH_2-), 2.31 (s, 3H, -$SO_2PhC\underline{H_3}$); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 199.4 (-CHO), 156.7 (Ar-C), 143.7 (Ar-C), 143.3 (Ar-C), 141.2 (Ar-C), 136.0 (Ar-C), 131.9 (Ar-C), 130.7 (Ar-C), 130.6 (Ar-C), 130.4 (Ar-C), 130.3 (Ar-C), 129.9 (Ar-C), 129.4 (2C, Ar-C), 129.1 (Ar-C), 128.8 (Ar-C), 127.9 (Ar-C), 127.8 (Ar-C), 127.3 (2C, Ar-C), 124.0 (Ar-C), 122.0 (Ar-C), 116.7 (Ar-C), 116.2 (Ar-C), 116.1 (Ar-C), 94.3 (-$\underline{C}$≡C-), 87.9 (-C≡$\underline{C}$-), 55.5 (-OCH_3), 48.2 (-CH_2-), 21.6 (-$SO_2Ph\underline{C}H_3$); HRMS (ESI) m/z calcd for $C_{30}H_{25}NNaO_4S$ [M + Na]$^+$ 518.1402, found 518.1404.

*N-(5-Fluoro-2-((2'-(2-oxoethyl)-[1,1'-biphenyl]-2-yl)ethynyl)phenyl)-4-methylbenzenesulfonamide (**4i**) :*

Yellow gummy liquid (226.4 mg, 75%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 9.55 (t, *J* = 2.0 Hz, 1H, -CHO), 7.58-7.56 (m, 3H, Ar-H), 7.48-7.46 (m, 2H, Ar-H), 7.43 (td, *J* = 7.2, 1.9 Hz, 2H, Ar-H), 7.37-7.34 (m, 2H, Ar-H), 7.28-7.26 (m, 1H, Ar-H), 7.23-7.20 (m, 1H, Ar-H), 7.18 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.05-7.02 (m, 1H, Ar-H), 6.78 (s, 1H, -N$\underline{H}$Ts), 6.64 (td, *J* = 8.4, 2.4 Hz, 1H, Ar-H), 3.66 (dd, *J* = 17.2, 1.6 Hz, 1H, H_a of -CH_2-), 3.57 (dd, *J* = 17.2, 2.0 Hz, 1H, H_b of -CH_2-), 2.36 (s, 3H, -$SO_2PhC\underline{H_3}$); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 199.3 (-CHO), 162.9 (d, J_{C-F} = 248.9 Hz, Ar-C), 144.3 (Ar-C), 143.1 (Ar-C), 141.2 (Ar-C), 139.2 (d, J_{C-F} = 11.4 Hz, Ar-C), 135.8 (Ar-C), 133.6 (d, J_{C-F} = 9.7 Hz, Ar-C), 132.2 (Ar-C), 130.9 (Ar-C), 130.5 (Ar-C), 130.2 (Ar-C), 129.9 (Ar-C), 129.7 (2C, Ar-C), 129.1 (Ar-C), 128.8 (Ar-C), 127.92 (Ar-C), 127.90 (Ar-C), 127.3 (2C, Ar-C), 121.9 (Ar-C), 111.4 (d, J_{C-F} = 22.4 Hz, Ar-C), 109.3 (d, J_{C-F} = 3.4 Hz, Ar-C), 106.8 (d, J_{C-F} = 27.6 Hz, Ar-C), 86.52 (-$\underline{C}$≡C-), 86.51 (-C≡$\underline{C}$-), 48.3 (-CH_2-), 21.6 (-$SO_2Ph\underline{C}H_3$); HRMS (ESI) m/z calcd for $C_{29}H_{23}FNO_3S$ [M + H]$^+$ 484.1383, found 484.1387.

*4-Methyl-N-(5-methyl-2-((2'-(2-oxoethyl)-[1,1'-biphenyl]-2-yl)ethynyl)phenyl)benzenesulfonamide (**4j**)* **:**

Yellow gummy liquid (269.4 mg, 90%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 9.54 (t, *J* = 1.8 Hz, 1H, -CHO), 7.56-7.51 (m, 3H, Ar-H), 7.48-7.45 (m, 2H, Ar-H), 7.44-7.40 (m, 2H, Ar-H), 7.37-7.33 (m, 2H, Ar-H), 7.30 (s, 1H, Ar-H), 7.28-7.26 (m, 1H, Ar-H), 7.13 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.93 (d, *J* = 7.6 Hz, 1H, Ar-H), 6.77 (d, *J* = 8.0 Hz, 1H, Ar-H), 6.56 (s, 1H, -N$\underline{H}$Ts), 3.62 (dd, *J* = 17.0, 1.8 Hz, 1H, H_a of -CH_2-), 3.56 (dd, *J* = 17.0,1.8 Hz, 1H, H_b of -CH_2-), 2.33 (s, 3H, -$SO_2PhC\underline{H_3}$), 2.27 (s, 3H, -CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 199.5 (-CHO), 143.9 (Ar-C), 143.1 (Ar-C), 141.3 (Ar-C), 140.3 (Ar-C), 137.3 (Ar-C), 136.2 (Ar-C), 132.0 (Ar-C), 131.9 (Ar-C), 130.8 (Ar-C), 130.6 (Ar-C), 130.3 (Ar-C), 129.9 (Ar-C), 129.5 (2C, Ar-C), 128.9 (Ar-C), 128.7 (Ar-C), 127.9 (Ar-C), 127.8 (Ar-C), 127.3 (2C, Ar-C), 125.4 (Ar-C), 122.2 (Ar-C), 120.9 (Ar-C), 111.3 (Ar-C), 94.4 (-$\underline{C}$≡C-), 87.8 (-C≡$\underline{C}$-), 48.3 (-CH_2-), 21.8 (-CH_3/ $SO_2Ph\underline{C}H_3$), 21.6 ($SO_2Ph\underline{C}H_3$/-CH_3); HRMS (ESI) m/z calcd for $C_{30}H_{25}NNaO_3S$ [M + Na]$^+$ 502.1453, found 502.1452.

*Methyl 3-(4-methylphenylsulfonamido)-4-((2'-(2-oxoethyl)-[1,1'-biphenyl]-2-yl)ethynyl)benzoate (**4k**)* :

Yellow gummy liquid (258.2 mg, 79%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 9.54 (t, *J* = 2.0 Hz, 1H, -CHO), 8.11 (s, 1H, Ar-H), 7.61 (dd, *J* = 8.0, 1.6 Hz, 1H, Ar-H), 7.59-7.55 (m, 3H, Ar-H), 7.48-7.40 (m, 4H, Ar-H), 7.37-7.34 (m, 2H, Ar-H), 7.29-7.27 (m, 1H, Ar-H), 7.14 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.10 (d, *J* = 8.0 Hz, 1H, Ar-H), 6.72 (s, 1H, -N<u>H</u>Ts), 3.88 (s, 3H, $-CO_2CH_3$), 3.65 (dd, *J* = 17.0, 1.8 Hz, 1H, H_a of $-CH_2-$), 3.56 (dd, *J* = 17.2, 1.6 Hz, 1H, H_b of $-CH_2-$), 2.33 (s, 3H, $-SO_2PhC\underline{H_3}$); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 199.2 (-CHO), 166.0 ($-\underline{C}O_2CH_3$), 144.2 (Ar-C), 143.4 (Ar-C), 141.0 (Ar-C), 137.6 (Ar-C), 135.9 (Ar-C), 132.3 (Ar-C), 132.1 (Ar-C), 131.0 (Ar-C), 130.9 (Ar-C), 130.5 (Ar-C), 130.2 (Ar-C), 130.0 (Ar-C), 129.7 (2C, Ar-C), 129.6 (Ar-C), 128.9 (Ar-C), 127.95 (Ar-C), 127.92 (Ar-C), 127.4 (2C, Ar-C), 125.1 (Ar-C), 121.6 (Ar-C), 120.6 (Ar-C), 118.2 (Ar-C), 97.6 (-<u>C</u>≡C-), 86.9 (-C≡<u>C</u>-), 52.5 ($-CO_2\underline{C}H_3$), 48.3 ($-CH_2-$), 21.6 ($-SO_2Ph\underline{C}H_3$); HRMS (ESI) m/z calcd for $C_{31}H_{25}NNaO_5S$ $[M + Na]^+$ 546.1351, found 546.1356.

*N-(5-Methoxy-2-((2'-(2-oxoethyl)-[1,1'-biphenyl]-2-yl)ethynyl)phenyl)-4-methylbenzenesulfonamide (**4l**)* :

Yellow gummy liquid (151.6 mg, 49%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 9.54 (t, *J* = 1.8 Hz, 1H, -CHO), 7.56-7.54 (m, 3H, Ar-H), 7.48-7.43 (m, 2H, Ar-H), 7.42-7.39 (m, 2H, Ar-H), 7.38-7.34 (m, 2H, Ar-H), 7.27-7.25 (m, 1H, Ar-H), 7.15 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.03 (d, *J* = 2.8 Hz, 1H, Ar-H), 6.95 (d, *J* = 8.8 Hz, 1H, Ar-H), 6.65 (s, 1H, -N<u>H</u>Ts), 6.49 (dd, *J* = 8.6, 2.6 Hz, 1H, Ar-H), 3.75 (s, 3H, $-OCH_3$), 3.63 (dd, *J* = 17.0, 1.8 Hz, 1H, H_a of $-CH_2-$), 3.57 (dd, *J* = 17.0 , 1.8 Hz, 1H, H_b of $-CH_2-$), 2.34 (s, 3H, $-SO_2PhC\underline{H_3}$); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 199.5 (-CHO), 160.6 (Ar-C), 144.0 (Ar-C), 142.9 (Ar-C), 141.4 (Ar-C), 138.9 (Ar-C), 136.0 (Ar-C), 133.2 (Ar-C), 132.0 (Ar-C), 130.8 (Ar-C), 130.6 (Ar-C), 130.3 (Ar-C), 129.9 (Ar-C), 129.6 (3C, Ar-C), 128.7 (Ar-C), 127.9 (Ar-C), 127.8 (Ar-C), 127.4 (2C, Ar-C), 122.4 (Ar-C), 110.9 (Ar-C), 106.0 (Ar-C), 105.1 (Ar-C), 93.9 (-<u>C</u>≡C-), 87.6 (-C≡<u>C</u>-), 55.5 ($-OCH_3$), 48.3 ($-CH_2-$), 21.6 ($-SO_2Ph\underline{C}H_3$); HRMS (ESI) m/z calcd for $C_{30}H_{26}NO_4S$ $[M + H]^+$ 496.1583, found 496.1584.

*Methyl 4-((5-methoxy-2'-(2-oxoethyl)-[1,1'-biphenyl]-2-yl)ethynyl)-3-(4-methylphenylsulfonamido)benzoate (**4m**):*

Yellow gummy liquid (314.5 mg, 91%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 9.58 (t, *J* = 1.8 Hz, 1H, -CHO), 8.09 (s, 1H, Ar-H), 7.59 (dd, *J* = 8.0, 1.6 Hz, 1H, Ar-H), 7.55 (d, *J* = 8.0, 2H, Ar-H), 7.51-7.45 (m, 3H, Ar-H), 7.38-7.34 (m, 2H, Ar-H), 7.14 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.06 (d, *J* = 8.0 Hz, 1H, Ar-H), 6.95 (dd, *J* = 8.6, 2.6 Hz, 1H, Ar-H), 6.81 (d, *J* = 2.4 Hz, 1H, Ar-H), 6.67 (s, 1H, -N<u>H</u>Ts), 3.88 (s, 3H, $-CO_2CH_3$/$-OCH_3$), 3.86 (s, 3H, $-OCH_3$/$-CO_2CH_3$), 3.67 (dd, *J* = 17.0, 1.8 Hz, 1H, H_a of $-CH_2-$), 3.58 (dd, *J* = 17.0, 1.8 Hz, 1H, H_b of $-CH_2-$), 2.33 (s, 3H, $-SO_2PhC\underline{H_3}$); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 199.3 (-CHO), 166.0 ($-\underline{C}O_2CH_3$), 160.4 (Ar-C), 145.2 (Ar-C), 144.1 (Ar-C), 140.9 (Ar-C), 137.3 (Ar-C), 135.9 (Ar-C), 133.8 (Ar-C), 131.8 (Ar-C), 130.9 (Ar-C), 130.5 (Ar-C), 130.4 (Ar-C), 130.1 (Ar-C), 129.6 (2C, Ar-C), 128.9 (Ar-C), 127.9 (Ar-C), 127.4 (2C, Ar-C), 125.2 (Ar-C), 120.5 (Ar-C), 118.7 (Ar-C), 115.4 (Ar-C), 114.0 (Ar-C), 113.6 (Ar-C), 97.9 (-<u>C</u>≡C-), 85.6 (-C≡<u>C</u>-), 55.6 ($-CO_2\underline{C}H_3$/$-OCH_3$), 52.5 ($-OCH_3$/$-CO_2\underline{C}H_3$), 48.3 ($-CH_2-$), 21.6 ($-SO_2Ph\underline{C}H_3$); HRMS (ESI) m/z calcd for $C_{32}H_{27}NNaO_6S$ $[M + Na]^+$ 576.1457, found 576.1453.

*N-(2-((5-Methoxy-2'-(2-oxoethyl)-[1,1'-biphenyl]-2-yl)ethynyl)phenyl)-4-methylbenzenesulfonamide (**4n**)* **:**

Yellow gummy liquid (259.9 mg, 84%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 9.58 (t, *J* = 2.0 Hz, 1H, -CHO), 7.52 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.50-7.44 (m, 4H, Ar-H), 7.38-7.33 (m, 2H, Ar-H), 7.18-7.17 (m, 1H, Ar-H), 7.13 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.02 (dd, *J* = 7.8, 1.4 Hz, 1H, Ar-H), 6.96-6.91 (m, 2H, Ar-H), 6.80 (d, *J* = 2.8 Hz, 1H, Ar-H), 6.62 (s, 1H, -N<u>H</u>Ts), 3.85 (s, 3H, $-OCH_3$), 3.66 (dd, *J* = 17.0, 1.8 Hz, 1H, H_a of $-CH_2-$), 3.58 (dd, *J* = 16.8, 2.0 Hz, 1H, H_b of $-CH_2-$), 2.33 (s, 3H, $-SO_2PhC\underline{H_3}$); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 199.5 (-CHO), 160.0 (Ar-C), 144.9 (Ar-C), 143.9 (Ar-C), 141.2 (Ar-C), 137.2 (Ar-C), 136.1 (Ar-C), 133.6 (Ar-C), 131.9 (Ar-C), 130.8 (Ar-C), 130.5 (Ar-C), 130.1 (Ar-C), 129.5 (2C, Ar-C), 129.2 (Ar-C), 128.8 (Ar-C), 127.9 (Ar-C), 127.3 (2C, Ar-C), 124.3 (Ar-C), 119.9 (Ar-C), 115.3 (Ar-C), 114.5 (Ar-C), 114.1 (Ar-C), 114.0 (Ar-C), 95.2 (-<u>C</u>≡C-), 86.0 (-C≡<u>C</u>-), 55.6 ($-OCH_3$), 48.3 ($-CH_2-$), 21.6 ($-SO_2Ph\underline{C}H_3$); HRMS (ESI) m/z calcd for $C_{30}H_{25}NNaO_4S$ $[M + Na]^+$ 518.1402, found 518.1405.

*4-Methyl-N-(2-((4-methyl-2'-(2-oxoethyl)-[1,1'-biphenyl]-2-yl)ethynyl)phenyl)benzenesulfonamide (**4o**)* **:**

Yellow gummy liquid (152.7 mg, 51%); ^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 9.54 (s, 1H, -CHO), 7.53 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.48-7.44 (m, 3H, Ar-H), 7.38 (s, 1H, Ar-H), 7.36-7.34 (m, 2H, Ar-H), 7.26-7.24 (m, 1H, Ar-H), 7.20-7.15 (m, 2H, Ar-H), 7.13 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.03 (d, *J* = 7.2 Hz, 1H, Ar-H), 6.94 (t, *J* = 7.5 Hz, 1H, Ar-H), 6.65 (s, 1H, -N<u>H</u>Ts), 3.63 (d, *J* = 16.8 Hz, 1H, H_a of $-CH_2-$), 3.57 (d, *J* = 16.8 Hz, 1H, H_b of $-CH_2-$), 2.44 (s, 3H, $-CH_3$), 2.34 (s, 3H, $-SO_2PhC\underline{H_3}$); ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz) δ_C 199.5 (-CHO), 143.8 (Ar-C), 141.1 (Ar-C), 140.2 (Ar-C), 137.6 (Ar-C), 137.3 (Ar-C), 136.0 (Ar-C), 132.5 (Ar-C), 132.1 (Ar-C), 130.7 (Ar-C), 130.6 (Ar-C), 130.3 (Ar-C), 129.9 (Ar-C), 129.7 (Ar-C), 129.5 (2C, Ar-C), 128.5 (Ar-C), 127.8 (Ar-C), 127.2 (2C, Ar-C), 124.2 (Ar-C), 121.6 (Ar-C), 119.8 (Ar-C), 114.0 (Ar-C), 95.2 (-<u>C</u>≡C-), 86.9 (-C≡<u>C</u>-), 48.2 ($-CH_2-$), 21.5 ($-SO_2Ph\underline{C}H_3/-CH_3$), 21.0 ($-CH_3/-SO_2Ph\underline{C}H_3$); HRMS (ESI) m/z calcd for $C_{30}H_{26}NO_3S$ $[M + H]^+$ 480.1633, found 480.1638.

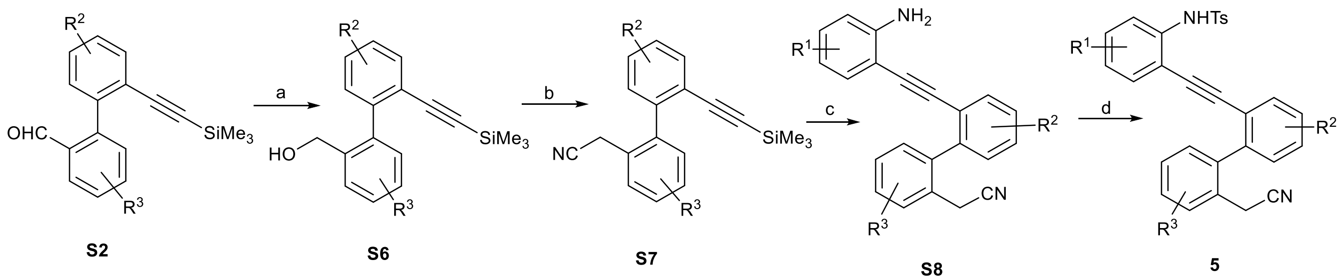
*Methyl 4-((4-methyl-2'-(2-oxoethyl)-[1,1'-biphenyl]-2-yl)ethynyl)-3-(4-methylphenylsulfonamido)benzoate (**4p**) :*

Yellow solid (292.0 mg, 87%), mp 66-68 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 9.54 (t, *J* = 1.8 Hz, 1H, -CHO), 8.10 (d, *J* = 1.2 Hz, 1H, Ar-H), 7.61 (dd, *J* = 8.0, 1.6 Hz, 1H, Ar-H), 7.56 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.47-7.44 (m, 2H, Ar-H), 7.40-7.39 (m, 1H, Ar-H), 7.36-7.32 (m, 2H, Ar-H), 7.29-7.26 (m, 1H, Ar-H), 7.17-7.14 (m, 3H, Ar-H), 7.09 (d, *J* = 8.0 Hz, 1H, Ar-H), 6.71 (s, 1H, -N<u>H</u>Ts), 3.89 (s, 3H, $-CO_2C\underline{H_3}$), 3.65 (dd, *J* = 16.8, 1.6 Hz, 1H, H_a of $-CH_2-$), 3.56 (dd, *J* = 17.0, 1.8 Hz, 1H, H_b of $-CH_2-$), 2.44 (s, 3H, $-CH_3$), 2.34 (s, 3H, $-SO_2PhC\underline{H_3}$); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 199.4 (-CHO), 166.0 ($-\underline{C}O_2CH_3$), 144.1 (Ar-C), 141.0 (Ar-C), 140.6 (Ar-C), 137.8 (Ar-C), 137.5 (Ar-C), 135.9 (Ar-C), 132.8 (Ar-C), 132.1 (Ar-C), 130.9 (Ar-C), 130.6 (Ar-C), 130.5 (Ar-C), 130.4 (Ar-C), 129.8 (Ar-C), 129.7 (2C, Ar-C), 128.8 (Ar-C), 127.9 (Ar-C), 127.4 (2C, Ar-C), 125.1 (Ar-C), 121.3 (Ar-C), 120.5 (Ar-C), 118.2 (Ar-C), 100.0 (Ar-C), 97.9 (-<u>C</u>≡C-), 86.5 (-C≡<u>C</u>-), 52.5 ($-CO_2\underline{C}H_3$), 48.3 ($-CH_2-$), 21.6 ($-CH_3/-SO_2Ph\underline{C}H_3$), 21.1 ($-SO_2Ph\underline{C}H_3$ $/-CH_3$); HRMS (ESI) m/z calcd for $C_{32}H_{27}NNaO_5S$ $[M + Na]^+$ 560.1508, found 560.1511.

*N-(2-((4'-Methoxy-2'-(2-oxoethyl)-[1,1'-biphenyl]-2-yl)ethynyl)phenyl)-4-methylbenzenesulfonamide(**4q**)* **:**

Yellow gummy liquid (204.2 mg, 66%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 9.54 (t, *J* = 1.8 Hz, 1H, -CHO), 7.57-7.55 (m, 1H, Ar-H), 7.52 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.46 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.40 (td, *J* = 7.6, 1.9 Hz, 2H, Ar-H), 7.30 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.26-7.24 (m, 1H, Ar-H), 7.21-7.17 (m, 1H, Ar-H), 7.15-7.12 (m, 3H, Ar-H), 7.03 (dd, *J* = 8.4, 2.4 Hz, 1H, Ar-H), 6.96 (td, *J* = 7.6, 0.8 Hz, 1H, Ar-H), 6.89 (d, *J* = 2.8 Hz, 1H, Ar-H), 6.65 (s, 1H, -N<u>H</u>Ts), 3.87 (s, 3H, $-OCH_3$), 3.61 (dd, *J* = 16.8, 1.6 Hz, 1H, H_a of $-CH_2$-), 3.55 (dd, *J* = 16.8, 1.6 Hz, 1H, H_b of $-CH_2$-), 2.33 (s, 3H, $-SO_2PhC\underline{H_3}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 199.3 (-CHO), 159.7 (Ar-C), 143.9 (Ar-C), 142.9 (Ar-C), 137.5 (Ar-C), 136.2 (Ar-C), 133.5 (Ar-C), 132.3 (Ar-C), 132.2 (Ar-C), 131.8 (Ar-C), 131.3 (Ar-C), 130.4 (Ar-C), 129.6 (2C, Ar-C), 129.5 (Ar-C), 129.1 (Ar-C), 127.7 (Ar-C), 127.3 (2C, Ar-C), 124.2 (Ar-C), 122.4 (Ar-C), 119.7 (Ar-C), 116.4 (Ar-C), 113.9 (Ar-C), 113.3 (Ar-C), 95.3 (-<u>C</u>≡C-), 87.3 (-C≡<u>C</u>-), 55.5 ($-OCH_3$), 48.5 ($-CH_2$-), 21.6 ($-SO_2Ph\underline{C}H_3$); HRMS (ESI) m/z calcd for $C_{30}H_{26}NO_4S$ $[M + H]^+$ 496.1583, found 496.1584.

9. Schematic representation and procedure for preparation of starting material 5 :



Scheme S2. Reagents and Conditions: (a) $NaBH_4$, MeOH, 0 °C, 0.5-0.6 h, 88-92%; (b) (i) MsCl, Et_3N, DCM, 0 °C-rt, 1.5-2.5 h; (ii) NaCN, DMF, rt, 2.5-3.0 h, 45-55%, (c) (i) K_2CO_3, MeOH, rt, 1.5-3.0 h, 70-80%; (ii) 2-iodoaniline derivatives, $PdCl_2(PPh_3)_2$, CuI, Et_3N, DMF ,0 °C-rt, 10-18 h, 70-85%; (d) TsCl, pyridine, DCM, 0 °C- rt, 15-28 h, 35-98%.

<u>*Synthesis of Silylated alcohol derivatives* **S6** *:*</u>

To a well-stirred and ice-cooled solution of **S2** (mentioned in the General Synthesis of derivatives **S2**) (2.52 mmol, 1 equiv) in dry methanol (4 mL) was added $NaBH_4$ (191.4 mg, 5.03 mmol, 2 equiv) portion-wise and the whole reaction mixture was then allowed to stir at 0 °C for 0.5-0.6 h until completion of reaction (TLC). Next, the reaction mixture was diluted with water and extracted with DCM (3 x 40 mL), dried over anhydrous Na_2SO_4 and concentrated *in vaccuo.* The resulting crude product was purified by silica gel (100-200 mesh) column chromatography eluting with 3-6% ethyl acetate in petroleum ether (v/v) to afford the desired silylated alcohol derivatives **S6** in (88-92%) yield.

<u>*Synthesis of cyano derivatives* **S7** *:*</u>

To a well-stirred and ice cooled solution of the silylated alcohol derivatives **S6** (2.21 mmol, 1 equiv) in dry DCM (7 mL) was added Et_3N (528.04 µL, 3.76 mmol, 1.7 equiv) dropwise and the stirring was continued for 5 min at the same temperature. Methanesulfonyl chloride (252.43 µL, 3.32 mmol, 1.5

equiv) was then added dropwise at 0 °C, and after 30 mins the temperature of the reaction was increased upto rt with continuation of the stirring. After completion of reaction 1.5-2.5 h (TLC), the reaction was quenched with water (20 mL) and extracted with DCM (3 × 20 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated in *vaccuo* to obtain a crude product of silylated mesyl-alcohol derivatives. The crude product (without purification) (0.29 mmol, 1 equiv) was dissolved in dry DMF (1.2 mL) (7 batches of reaction was set up with 0.29 mmol of crude) and treated with NaCN (62.0 mg, 1.24 mmol, 4.2 equiv), and the mixture was stirred at rt for 2.5-3.0 h. After completion of reaction (TLC) of each batch, reaction mixture was diluted with water and the combined reaction mixtures was extracted with DCM (3 × 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in *vaccuo*. The resulting crude mixture was subjected to silica gel (100−200 mesh) column chromatography and eluted with 1-2% ethyl acetate in petroleum ether (v/v) to afford the silylated acetylenic intermediates **S7** in 45-55% yield.

Synthesis of amine derivatives **S8** *:*

K_2CO_3 (385.4 mg, 2.79 mmol, 3 equiv) was added to a well stirred solution of the aforesaid intermediate **S7** (0.93 mmol, 1 equiv) in MeOH (5 mL) and stirred for 1.5-3.0 h. After completion of reaction (TLC), the mixture was extracted with ethyl acetate (3 x 25 mL); the combined organic extracts were washed with brine (25 mL) and dried over anhydrous Na_2SO_4 and concentrated *in vaccuo*. The crude product was then purified by silica gel (100-200 mesh) column chromatography eluting with 4-5% ethyl acetate-petroleum ether (v/v) to obtain the desilylated acetylenic derivatives in 70-80% yield.

Next, To a well stirred solution of 2-iodoaniline derivatives (0.64 mmol, 1 equiv) in a mixture of solvents (i.e., Et_3N : DMF = 2:1, 0.9 mL), $PdCl_2(PPh_3)_2$ (13.4 mg, 0.019 mmol, 3 mol %) was added. The reaction mixture was then cooled to 0 °C and the desilylated acetylenic derivative (0.70 mmol, 1.1 equiv) was added dropwise followed by the addition of CuI (7.3 mg, 0.038 mmol, 6 mol %,). After stirring few minutes at 0 °C, the temperature of the reaction was allowed to rise to rt and stirring was continued for 10-18 h. Upon completion of reaction (TLC), solvent was removed under reduced pressure and extracted with ethyl acetate (3x 25 mL); the combined organic extracts were washed with brine (15 mL) and dried over anhydrous Na_2SO_4 and concentrated *in vaccuo*. The crude product was then purified by silica gel (100-200 mesh) column chromatography eluting with 10-27% ethyl acetate-petroleum ether (v/v) to obtain the amine derivatives **S8** in 70-85% yield.

Synthesis of the Final Substrates **5***:*

To a well stirred solution of amine derivative **S8** (0.454 mmol, 1 equiv) in dry DCM (2.5 mL) at 0 °C was added pyridine (146.6 µL, 1.82 mmol, 4 equiv) dropwise. Thereafter, TsCl (431.8 mg, 2.27 mmol, 5 equiv) was added portion-wise at the same temperature and whole reaction mixture was allowed to stir at rt for 15-28 h. Upon completion of the reaction (TLC), solvent was removed in *vaccuo* and then extracted with ethyl acetate (3x 30 mL); the combined organic extracts were washed with brine (15 mL) and dried over anhydrous Na_2SO_4 and concentrated *in vaccuo*. Then the crude product was purified by silica gel (100-200 mesh) column chromatography eluting with 10-32% ethyl acetate-petroleum ether (v/v) to obtain the pure Final Substrates **5** in 35-98% yield.

10. Spectral data of compounds 5a-5i :

*N-(2-((2'-(Cyanomethyl)-[1,1'-biphenyl]-2-yl)ethynyl)phenyl)-4-methylbenzenesulfonamide (**5a**) :*

White solid (146.8 mg, 70%), mp 132-134 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.61-7.59 (m, 2H, Ar-H), 7.53 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.52-7.44 (m, 5H, Ar-H), 7.36-7.33 (m, 2H, Ar-H), 7.22-7.18 (m, 1H, Ar-H), 7.14 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.02 (dd, *J* = 7.6, 1.6 Hz, 1H, Ar-H), 6.95 (td, *J* = 7.5, 0.9 Hz, 1H, Ar-H), 6.55 (s, 1H, -N$\underline{H}$Ts), 3.63 (d, *J* = 18.4 Hz, 1H, H_a of -CH_2-), 3.49 (d, *J* = 18.4 Hz, 1H, H_b of -CH_2-), 2.34 (s, 3H, -$SO_2PhC\underline{H_3}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 144.0 (Ar-C), 142.1 (Ar-C), 140.1 (Ar-C), 137.4 (Ar-C), 136.1 (Ar-C), 132.3 (Ar-C), 132.2 (Ar-C), 130.4 (Ar-C), 129.8 (Ar-C), 129.7 (Ar-C), 129.6 (2C, Ar-C), 129.5 (Ar-C), 129.1 (Ar-C), 129.0 (Ar-C), 128.7 (Ar-C), 128.4 (Ar-C), 128.3 (Ar-C), 127.3 (2C, Ar-C), 124.5 (Ar-C), 121.9 (Ar-C), 120.1 (Ar-C), 118.0 (Ar-C), 113.9 (Ar-C), 94.5 (-$\underline{C}$≡C-), 87.6 (-C≡$\underline{C}$-), 21.8 (-CH_2-), 21.6 (-$SO_2Ph\underline{C}H_3$); HRMS (ESI) m/z calcd for $C_{29}H_{22}N_2NaO_2S$ $[M + Na]^+$ 485.1300, found 485.1303.

*N-(2-((2'-(Cyanomethyl)-[1,1'-biphenyl]-2-yl)ethynyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (**5b**)* **:**

Pale white gummy liquid (102.7 mg, 46%); ^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 7.59 (d, *J* = 7.2 Hz, 1H, Ar-H), 7.53-7.49 (m, 4H, Ar-H), 7.47-7.44 (m, 3H, Ar-H), 7.40 (d, *J* = 9.0 Hz, 1H, Ar-H), 7.34 (t, *J* = 7.2 Hz, 2H, Ar-H), 7.09 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.80 (dd, *J* = 9.0, 3.0 Hz, 1H, Ar-H), 6.46 (d, *J* = 3.0 Hz, 1H, Ar-H), 6.19 (s, 1H, -N$\underline{H}$Ts), 3.70 (s, 3H, -OCH_3), 3.58 (d, *J* = 18.6 Hz, 1H, H_a of -CH_2-), 3.46 (d, *J* = 18.6 Hz, 1H, H_b of -CH_2-), 2.32 (s, 3H, -$SO_2PhC\underline{H_3}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz) δ_C 156.7 (Ar-C), 143.6 (Ar-C), 142.1(Ar-C), 140.0 (Ar-C), 135.9 (Ar-C), 132.0 (Ar-C), 130.3 (Ar-C), 130.2 (Ar-C), 129.6 (Ar-C), 129.4 (Ar-C), 129.3 (2C, Ar-C), 129.0 (Ar-C), 128.7 (Ar-C), 128.5 (Ar-C), 128.4 (Ar-C), 128.1 (Ar-C), 127.2 (2C, Ar-C), 124.0 (Ar-C), 121.7 (Ar-C), 117.9 (Ar-C), 116.5 (Ar-C), 116.2 (Ar-C), 116.1 (Ar-C), 93.6 (-$\underline{C}$≡C-), 87.8 (-C≡$\underline{C}$-), 55.4 (-OCH_3), 21.7 (-CH_2-), 21.5 (-$SO_2Ph\underline{C}H_3$); HRMS (ESI) m/z calcd for $C_{30}H_{24}N_2NaO_3S$ $[M + Na]^+$ 515.1405, found 515.1421.

*N-(2-((2'-(Cyanomethyl)-[1,1'-biphenyl]-2-yl)ethynyl)-4-methylphenyl)-4-methylbenzenesulfonamide(**5c**)* **:**

Pale yellow gummy liquid (207.4 mg, 96%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.61-7.55 (m, 2H, Ar-H), 7.53-7.43 (m, 6H, Ar-H), 7.38-7.33 (m, 3H, Ar-H), 7.12 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.02 (dd, *J* = 8.4, 2.0 Hz, 1H, Ar-H), 6.82 (d, *J* = 2.0 Hz, 1H, Ar-H), 6.36 (s, 1H, -N$\underline{H}$Ts), 3.62 (d, *J* = 18.4 Hz, 1H, H_a of -CH_2-), 3.48 (d, *J* = 18.4 Hz, 1H, H_b of -CH_2-), 2.33 (s, 3H, -$SO_2PhC\underline{H_3}$), 2.19 (s, 3H, -CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 143.8 (Ar-C), 142.1 (Ar-C), 140.2 (Ar-C), 136.1 (Ar-C), 134.9 (Ar-C), 134.5 (Ar-C), 132.4 (Ar-C), 132.2 (Ar-C), 130.7 (Ar-C), 130.4 (Ar-C), 129.7 (Ar-C), 129.5 (2C, Ar-C), 129.4 (Ar-C), 129.1 (Ar-C), 128.9 (Ar-C), 128.7 (Ar-C), 128.4 (Ar-C), 128.2 (Ar-C), 127.3 (2C, Ar-C), 122.0 (Ar-C), 120.8 (Ar-C), 118.0 (Ar-C), 114.2 (Ar-C), 94.0 (-C≡C-), 87.9 (-C≡C-), 21.8 ($-CH_2-$), 21.6 ($-SO_2PhCH_3$), 20.6 ($-CH_3$); HRMS (ESI) m/z calcd for $C_{30}H_{24}N_2NaO_2S$ $[M + Na]^+$ 499.1456, found 499.1454.

*Methyl 3-((2'-(cyanomethyl)-[1,1'-biphenyl]-2-yl)ethynyl)-4-(4-methylphenylsulfonamido)benzoate (**5d**)* **:**

Pale white solid (186.5 mg, 79%), mp 62-64 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 7.82 (dd, *J* = 9.0, 1.8 Hz, 1H, Ar-H), 7.77 (s, 1H, Ar-H), 7.65 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.62 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.58 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.55-7.50 (m, 3H, Ar-H), 7.49-7.45 (m, 2H, Ar-H), 7.38-7.35 (m, 2H, Ar-H), 7.19 (d, *J* = 7.8 Hz, 2H, Ar-H), 6.80 (s, 1H, -NHTs), 3.86 (s, 3H, $-CO_2CH_3$), 3.64 (d, *J* = 18.6 Hz, 1H, H_a of $-CH_2-$), 3.52 (d, *J* = 18.6 Hz, 1H, H_b of $-CH_2-$), 2.36 (s, 3H, $-SO_2PhCH_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz) δ_C 165.6 ($-CO_2CH_3$), 144.4 (Ar-C), 142.1 (Ar-C), 141.1 (Ar-C), 139.9 (Ar-C), 135.6 (Ar-C), 133.8 (Ar-C), 132.4 (Ar-C), 130.9 (Ar-C), 130.2 (Ar-C), 129.7 (2C, Ar-C), 129.66 (Ar-C), 129.64 (Ar-C), 129.2 (Ar-C), 129.1 (Ar-C), 128.7 (Ar-C), 128.3 (Ar-C), 128.2 (Ar-C), 127.2 (2C, Ar-C), 125.5 (Ar-C), 121.4 (Ar-C), 117.8 (Ar-C), 117.5 (Ar-C), 112.6 (Ar-C), 95.4 (-C≡C-), 86.4 (-C≡C-), 52.2 ($-CO_2CH_3$), 21.8 ($-CH_2-$), 21.5 ($-SO_2PhCH_3$); HRMS (ESI) m/z calcd for $C_{31}H_{25}N_2O_4S$ $[M + H]^+$ 521.1535, found 521.1533.

*N-(4-Chloro-2-((2'-(cyanomethyl)-[1,1'-biphenyl]-2-yl)ethynyl)phenyl)-4-methylbenzenesulfonamide (**5e**)* **:**

Yellow gummy liquid (184.6 mg, 82%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.61-7.46 (m, 8H, Ar-H), 7.40 (d, *J* = 8.8 Hz, 1H, Ar- H), 7.37-7.33 (m, 2H, Ar- H), 7.17-7.14 (m, 3H, Ar- H), 6.99 (d, *J* = 2.4 Hz, 1H, Ar- H), 6.45 (s, 1H, -NHTs), 3.59 (d, *J* = 18.0 Hz, 1H, H_a of $-CH_2-$), 3.48 (d, *J* = 18.0 Hz, 1H, H_b of $-CH_2-$), 2.35 (s, 3H, $-SO_2PhCH_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 144.3 (Ar-C), 142.3 (Ar-C), 140.0 (Ar-C), 136.0 (Ar-C), 135.8 (Ar-C), 132.4 (Ar-C), 131.7 (Ar-C), 130.3 (Ar-C), 129.9 (Ar-C), 129.81 (Ar-C), 129.80 (Ar-C), 129.77 (Ar-C), 129.73 (2C, Ar-C), 129.3 (Ar-C), 129.2 (Ar-C), 128.8 (Ar-C), 128.4 (Ar-C), 128.3 (Ar-C), 127.3 (2C, Ar-C), 121.5 (Ar-C), 121.4 (Ar-C), 117.9 (Ar-C), 115.6 (Ar-C), 95.5 (-C≡C-), 86.4 (-C≡C-), 21.9 ($-CH_2-$), 21.6 ($-SO_2PhCH_3$); HRMS (ESI) m/z calcd for $C_{29}H_{21}ClN_2NaO_2S$ $[M + Na]^+$ 519.0910, found 519.0918.

*N-(2-((2'-(Cyanomethyl)-[1,1'-biphenyl]-2-yl)ethynyl)-5-methoxyphenyl)-4-methylbenzenesulfonamide (**5f**):*

Pale white gummy liquid (218.9 mg, 98%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.60-7.57 (m, 2H, Ar-H), 7.55 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.51-7.42 (m, 4H, Ar-H), 7.35-7.31 (m, 2H, Ar-H), 7.15 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.02 (d, *J* = 2.4 Hz, 1H, Ar-H), 6.93 (d, *J* = 8.8 Hz, 1H, Ar-H), 6.56 (s, 1H, -NHTs), 6.49 (dd, *J* = 8.6, 2.6 Hz, 1H, Ar-H), 3.74 (s, 3H, $-OCH_3$), 3.63 (d, *J* = 18.4 Hz, 1H, H_a of $-CH_2-$), 3.49 (d, *J* = 18.4 Hz, 1H, H_b of $-CH_2-$), 2.35 (s, 3H, $-SO_2PhCH_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 160.7 (Ar-C), 144.1 (Ar-C), 141.8 (Ar-C), 140.3 (Ar-C), 138.8 (Ar-C), 136.0 (Ar-C), 133.2 (Ar-C), 132.1 (Ar-C), 130.3 (Ar-C), 129.7 (Ar-C), 129.6 (2C, Ar-C), 129.1 (Ar-C), 128.9 (Ar-C), 128.7 (Ar-C), 128.4 (Ar-C), 128.2 (Ar-C), 127.3 (2C, Ar-C), 122.2 (Ar-C), 118.1 (Ar-C), 111.0 (Ar-C), 105.8 (Ar-C), 105.2 (Ar-C), 100.0 (Ar-C), 93.4 (-C≡C-), 87.7 (-C≡C-), 55.5 ($-OCH_3$), 21.8 ($-CH_2-$), 21.6 ($-SO_2PhCH_3$); HRMS (ESI) m/z calcd for $C_{30}H_{24}N_2NaO_3S$ $[M + Na]^+$ 515.1405, found 515.1422.

*Methyl 4-((2'-(cyanomethyl)-[1,1'-biphenyl]-2-yl)ethynyl)-3-(4-methylphenylsulfonamido)benzoate (**5g**)* **:**

Pale white solid (224.3 mg, 95%), mp 122-124 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.09 (s, 1H, Ar-H), 7.63-7.59 (m, 3H, Ar-H), 7.56 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.54-7.45 (m, 4H, Ar-H), 7.36-7.33 (m, 2H, Ar-H), 7.16 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.08 (d, *J* = 8.4 Hz, 1H, Ar-H), 6.59 (s, 1H, -NHTs), 3.89 (s, 3H, $-CO_2CH_3$), 3.60 (d, *J* = 18.4 Hz, 1H, H_a of $-CH_2-$), 3.49 (d, *J* = 18.4 Hz, 1H, H_b of $-CH_2-$), 2.34 (s, 3H, $-SO_2PhCH_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 165.9 ($-CO_2CH_3$), 144.3 (Ar-C), 142.3 (Ar-C), 140.0 (Ar-C), 137.5 (Ar-C), 135.9 (Ar-C), 132.5 (Ar-C), 132.1 (Ar-C), 131.1 (Ar-C), 130.3 (Ar-C), 129.9 (Ar-C), 129.8 (Ar-C), 129.7 (2C, Ar-C), 129.3 (Ar-C), 129.1 (Ar-C), 128.7 (Ar-C), 128.4 (Ar-C), 128.3 (Ar-C), 127.4 (2C, Ar-C), 125.3 (Ar-C), 121.4 (Ar-C), 120.6 (Ar-C), 118.1 (Ar-C), 117.9 (Ar-C), 97.0 (-C≡C-), 87.0 (-C≡C-), 52.5 ($-CO_2CH_3$), 21.9 ($-CH_2-$), 21.6 ($-SO_2PhCH_3$); HRMS (ESI) m/z calcd for $C_{31}H_{24}N_2NaO_4S$ $[M + Na]^+$ 543.1354, found 543.1379.

*N-(2-((2'-(Cyanomethyl)-5-methoxy-[1,1'-biphenyl]-2-yl)ethynyl)phenyl)-4-methylbenzenesulfonamide (**5h**) :*

Pale yellow solid (127.3 mg, 57%), mp 118-120 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ_H 7.60-7.58 (m, 1H, Ar-H), 7.53-7.47 (m, 5H, Ar-H), 7.44 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.36-7.34 (m, 1H, Ar-H), 7.19-7.17 (m, 1H, Ar-H), 7.14 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.01-6.92 (m, 3H, Ar-H), 6.87 (d, *J* = 2.8 Hz, 1H, Ar-H), 6.55 (s, 1H, -NHTs), 3.89 (s, 3H, $-OCH_3$), 3.65 (d, *J* = 18.4 Hz, 1H, H_a of $-CH_2-$), 3.51 (d, *J* = 18.4 Hz, 1H, H_b of $-CH_2-$), 2.34 (s, 3H, $-SO_2PhCH_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 160.3 (Ar-C), 144.0 (Ar-C), 143.8 (Ar-C), 140.1 (Ar-C), 137.2 (Ar-C), 136.1 (Ar-C), 133.8 (Ar-C), 131.9 (Ar-C), 130.2 (Ar-C), 129.6 (2C, Ar-C), 129.4 (Ar-C), 129.2 (Ar-C), 129.0 (Ar-C), 128.7 (Ar-C), 128.4 (Ar-C), 127.3 (2C, Ar-C), 124.4 (Ar-C), 120.0 (Ar-C), 118.1 (Ar-C), 115.1 (Ar-C), 114.4 (Ar-C), 114.3 (Ar-C), 113.9 (Ar-C), 94.7 (-C≡C-), 86.1 (-C≡C-), 55.7 ($-OCH_3$), 21.8 ($-CH_2-$), 21.6 ($-SO_2PhCH_3$); HRMS (ESI) m/z calcd for $C_{30}H_{25}N_2O_3S$ $[M + H]^+$ 493.1586, found 493.1583.

*N-(3-((2'-(Cyanomethyl)-[1,1'-biphenyl]-2-yl)ethynyl)pyridin-2-yl)-4-methylbenzenesulfonamide (**5i**)* : White solid (73.6 mg, 35%), 70-72 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ_H 8.06 (d, *J* = 4.0 Hz, 1H, Ar-H), 7.95 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.70-7.68 (m, 1H, Ar-H), 7.62-7.60 (m, 1H, Ar-H), 7.53-7.44 (m, 4H, Ar-H), 7.39-7.33 (m, 3H, Ar-H), 7.28-7.26 (m, 2H, Ar-H), 6.80-6.77 (m, 1H, Ar-H), 3.67 (d, *J* = 18.4 Hz, 1H, $-H_a$ of CH_2-), 3.53 (d, *J* = 18.0 Hz, 1H, H_b of $-CH_2-$), 2.40 (s, 3H, $-SO_2PhCH_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 150.9 (Ar-C), 144.0 (Ar-C), 142.3 (Ar-C), 140.6 (Ar-C), 140.1 (Ar-C), 132.6 (Ar-C), 130.4 (Ar-C), 129.8 (Ar-C), 129.7(Ar-C), 129.3 (Ar-C), 129.2 (2C, Ar-C), 129.1 (Ar-C), 128.7 (Ar-C), 128.42 (Ar-C), 128.41 (Ar-C), 128.40 (Ar-C) 128.3 (Ar-C), 121.6 (Ar-C), 118.1 (Ar-C), 96.2 (-C≡C-), 85.9 (-C≡C-), 21.9 ($-CH_2-$) 21.7 ($-SO_2PhCH_3$); HRMS (ESI) m/z calcd for $C_{28}H_{22}N_3O_2S$ $[M + H]^+$ 464.1433, found 464.1435.

11. General procedure for the synthesis of products 6 :

To a well-stirred solution of $Pd(OAc)_2$bpy (1.96 mg, 0.005 mmol, 6 mol %) in 1,4-dioxane (0.5 mL) was added AcOH (0.1 mL) and the resulting mixture was heated at 100 °C under argon atmosphere. Next, the starting material **4** (0.086 mmol, 1 equiv) dissolved in dry 1,4-dioxane (0.5 mL) was added dropwise to the reaction mixture and it was then stirred at the same temp. for another 2.5-6.0 h. Upon completion of reaction (TLC), the reaction mixture was neutralized by dropwise addition of dilute aqueous sodium bicarbonate solution and extracted with ethyl acetate (3 x 15 mL). The combined organic extracts were washed with brine (5 mL), dried over anhydrous Na_2SO_4 and concentrated *in vaccuo.* The resulting crude product was purified by silica gel (100-200 mesh) column chromatography eluting with 15-28% ethyl acetate in petroleum ether (v/v) to afford the desired product **6** in (59-94%) yield.

12. Spectral Data of Products 6a-6q :

*15-Tosyl-10,15-dihydro-9H-dibenzo[5,6:7,8]cycloocta[1,2-b]indol-10-ol (**6a**)*:

White solid (29.2 mg, 73%), mp 128-130 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.08-8.05 (m, 1H, Ar-H), 7.72 (dd, *J* = 7.8, 1.4 Hz, 1H, Ar-H), 7.57-7.45 (m, 3H, Ar-H), 7.43-7.38 (m, 2H, Ar-H), 7.32-7.20 (m, 5H, Ar-H), 6.98 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.76 (d, *J* = 8.4 Hz, 2H, Ar-H), 5.26 (dd, *J* = 12.0, 6.4 Hz, 1H, -C<u>H</u>OH), 3.16 (dd, J = 12.8, 6.4 Hz, 1H, H_a of -CH_2-), 2.94 (t, *J* = 12.4 Hz, 1H, H_b of -CH_2-), 2.18 (s, 3H, -SO_2PhC<u>H_3</u>); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 144.1 (Ar-C), 141.4 (Ar-C), 139.4 (Ar-C), 137.6 (Ar-C), 137.1 (Ar-C), 135.7 (Ar-C), 134.3 (Ar-C), 134.0 (Ar-C), 130.7 (Ar-C), 130.5 (Ar-C), 129.5 (Ar-C), 129.1 (3C, Ar-C), 129.0 (Ar-C), 128.5 (Ar-C), 127.9 (Ar-C), 126.6 (2C, Ar-C), 126.5 (Ar-C), 126.2 (Ar-C), 125.3 (Ar-C), 124.3 (Ar-C), 123.6 (Ar-C), 119.2 (Ar-C), 116.2 (Ar-C), 68.7 (-CHOH), 39.3 (-CH_2-), 21.5 (-SO_2Ph<u>C</u>H_3); HRMS (ESI) m/z calcd for $C_{29}H_{23}NNaO_3S$ $[M+Na]^+$ 488.1296 , found 488.1298.

*15-((4-Nitrophenyl)sulfonyl)-10,15-dihydro-9H-dibenzo[5,6:7,8]cycloocta[1,2-b]indol-10-ol (**6b**)*:

Yellow solid (26.9 mg, 63%), mp >250 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.04-8.02 (m, 1H, Ar-H), 7.75-7.73 (m, 3H, Ar-H), 7.59-7.51 (m, 3H, Ar-H), 7.48-7.44 (m, 2H, Ar-H), 7.39-7.35 (m, 2H, Ar-H), 7.34-7.28 (m, 2H, Ar-H), 7.27-7.26 (m, 1H, Ar-H), 7.21-7.18 (m, 2H, Ar-H), 5.25 (dd, *J* = 12.0, 6.4 Hz, 1H, -C<u>H</u>OH), 3.19 (dd, *J* = 12.6, 6.2 Hz, 1H, H_a of -CH_2-), 2.96 (t, *J* = 12.2 Hz, 1H, H_b of -CH_2-); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 141.7 (Ar-C), 141.2 (Ar-C), 139.1 (Ar-C), 137.3 (Ar-C), 137.1 (Ar-C), 135.6 (Ar-C), 134.0 (Ar-C), 130.9 (Ar-C), 130.4 (Ar-C), 129.7 (Ar-C), 129.4 (Ar-C), 129.0 (Ar-C), 128.9 (Ar-C), 128.4 (Ar-C), 127.8 (2C, Ar-C), 126.9 (Ar-C), 126.4 (Ar-C), 126.0 (Ar-C), 125.24 (Ar-C), 125.23 (Ar-C), 123.6 (3C, Ar-C), 119.8 (Ar-C), 116.3 (Ar-C), 68.6 (-CHOH), 39.2 (-CH_2-); HRMS $(EI)^+$ m/z calcd for $C_{28}H_{20}N_2O_5S$ $[M]^+$ 496.1093 , found 496.1085.

12-Fluoro-15-tosyl-10,15-dihydro-9H-dibenzo[5,6:7,8]cycloocta[1,2-b]indol-10-ol (***6c***) :

Pale yellow solid (29.9 mg, 72%), mp > 250°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.02-7.99 (m, 1H, Ar-H), 7.71 (dd, *J* = 7.6, 1.6 Hz, 1H, Ar-H), 7.54 (td, *J* = 7.5, 1.5 Hz, 1H, Ar-H), 7.49 (td, *J* = 7.6, 1.6 Hz, 1H, Ar-H), 7.43-7.39 (m, 2H, Ar-H), 7.33-7.29 (m, 3H, Ar-H), 7.21 (dd, *J* = 8.4, 2.4 Hz, 1H, Ar-H), 6.99-6.94 (m, 3H, Ar-H), 6.77 (d, *J* = 8.0 Hz, 2H, Ar-H), 5.16 (dd, *J* = 11.8, 6.2 Hz, 1H, -C<u>H</u>OH), 3.15 (dd, *J* = 12.6, 6.2 Hz, 1H, H_a of -CH_2-), 2.93 (t, *J* = 12.2 Hz, 1H, H_b of -CH_2-), 2.19 (s, 3H, -SO_2PhC<u>H_3</u>); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 159.5 (d, J_{C-F} = 238.3 Hz, Ar-C), 144.3 (Ar-C), 141.2 (Ar-C), 139.3 (Ar-C), 137.5 (Ar-C), 136.9 (Ar-C), 134.0 (2C, Ar-C), 130.4 (Ar-C), 129.5 (Ar-C), 129.2 (Ar-C), 129.1 (3C, Ar-C), 128.5 (Ar-C), 128.1 (Ar-C), 126.6 (Ar-C), 126.5 (2C, Ar-C), 126.3 (Ar-C), 123.5 (d, J_{C-F} = 4.1 Hz, Ar-C), 117.4 (d, J_{C-F} = 9.0 Hz, Ar-C), 113.1 (d, J_{C-F} = 25.0 Hz, Ar-C), 105.1 (d, J_{C-F} = 24.1 Hz, Ar-C), 68.8 (-CHOH), 39.3 (-CH_2-), 21.5 (-SO_2Ph<u>C</u>H_3); ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = −118.0 (s, 1F); HRMS (ESI) m/z calcd for $C_{29}H_{23}FNO_3S$ $[M + H]^+$ 484.1383, found 484.1387.

*12-Chloro-15-tosyl-10,15-dihydro-9H-dibenzo[5,6:7,8]cycloocta[1,2-b]indol-10-ol (**6d**)* **:**

Yellow solid (34.8 mg, 81%), mp 170-172 °C; ^{1}H NMR (CDCl$_3$, 400 MHz) δ_H 7.97 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.70 (d, *J* = 7.6 Hz, 1H, Ar-H), 7.55-7.45 (m, 3H, Ar-H), 7.40-7.38 (m, 2H, Ar-H), 7.32-7.26 (m, 3H, Ar-H), 7.18 (dd, *J* = 8.8, 2.0 Hz, 1H, Ar-H), 6.95 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.78 (d, *J* = 8.4 Hz, 2H, Ar-H), 5.18 (dd, *J* = 11.8, 6.2 Hz, 1H, -C<u>H</u>OH), 3.14 (dd, *J* = 12.8, 6.4 Hz, 1H, H$_a$ of -CH$_2$-), 2.91 (t, *J* = 12.2 Hz, 1H, H$_b$ of -CH$_2$-), 2.20 (s, 3H, -SO$_2$PhC<u>H$_3$</u>); ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz) δ_C 144.4 (Ar-C), 141.2 (Ar-C), 139.4 (Ar-C), 137.1 (Ar-C), 136.9 (Ar-C), 135.9 (Ar-C), 134.1 (Ar-C), 134.0 (Ar-C), 131.9 (Ar-C), 130.2 (Ar-C), 130.1 (Ar-C), 129.5 (Ar-C), 129.25 (Ar-C), 129.21 (2C, Ar-C), 129.1 (Ar-C), 128.5 (Ar-C), 128.1 (Ar-C), 126.6 (Ar-C), 126.5 (2C, Ar-C), 126.3 (Ar-C), 125.4 (Ar-C), 122.9 (Ar-C), 119.1 (Ar-C), 117.3 (Ar-C), 68.6 (-CHOH), 39.3 (-CH$_2$-), 21.5 (-SO$_2$Ph<u>C</u>H$_3$); HRMS (ESI) m/z calcd for $C_{29}H_{22}ClNNaO_3S$ [M + Na]$^+$ 522.0907, found 522.0898.

*15-Tosyl-12-(trifluoromethyl)-10,15-dihydro-9H-dibenzo[5,6:7,8]cycloocta[1,2-b]indol-10-ol (**6e**)* **:**

White solid (35.7 mg, 78%), mp 138-140 °C; ^{1}H NMR (CDCl$_3$, 400 MHz) δ_H 8.17 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.86 (s, 1H, Ar-H), 7.68 (dd, *J* = 7.6, 1.2 Hz, 1H, Ar-H), 7.55 (td, *J* = 7.5, 1.5 Hz, 1H, Ar-H), 7.50-7.46 (m, 2H, Ar-H), 7.40-7.35 (m, 2H, Ar-H), 7.32-7.28 (m, 3H, Ar-H), 7.00 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.82 (d, *J* = 8.8 Hz, 2H, Ar-H), 5.27 (dd, *J* = 12.0, 6.4 Hz, 1H, -C<u>H</u>OH), 3.17 (dd, *J* = 12.6, 6.2 Hz, 1H, H$_a$ of -CH$_2$-), 2.93 (t, *J* = 12.2 Hz, 1H, H$_b$ of -CH$_2$-), 2.21 (s, 3H, -SO$_2$PhC<u>H$_3$</u>); ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz) δ_C 144.7 (Ar-C), 141.1 (Ar-C), 139.5 (Ar-C), 139.1 (q, J_{C-F} = 1.6 Hz, Ar-C), 137.3 (Ar-C), 136.9 (Ar-C), 134.3 (Ar-C), 133.9 (Ar-C), 131.1 (q, J_{C-F} = 286.6 Hz, Ar-C), 130.3 (Ar-C), 129.9 (Ar-C), 129.5 (Ar-C), 129.4 (Ar-C), 129.3 (2C, Ar-C), 129.0 (Ar-C), 128.6 (Ar-C), 128.1 (Ar-C), 126.61 (Ar-C), 126.60 (3C, Ar-C), 126.5 (d, J_{C-F} = 32.3 Hz, Ar-C), 123.1 (Ar-C), 121.9 (q, J_{C-F} = 3.4 Hz, Ar-C), 116.9 (q, J_{C-F} = 4.3 Hz, Ar-C), 116.4 (Ar-C), 68.5 (-CHOH), 39.4 (-CH$_2$-), 21.5 (-SO$_2$Ph<u>C</u>H$_3$); ^{19}F{^{1}H} NMR (376 MHz, CDCl$_3$) δ = −61.2 (s, 3F); HRMS (ESI) m/z calcd for $C_{30}H_{22}F_3NNaO_3S$ [M + Na]$^+$ 556.1170, found 556.1174.

*12-Methyl-15-tosyl-10,15-dihydro-9H-dibenzo[5,6:7,8]cycloocta[1,2-b]indol-10-ol (**6f**)* **:**

Pale yellow solid (30.9 mg, 75%), mp 160-162 °C; ^{1}H NMR (CDCl$_3$, 400 MHz) δ_H 7.93 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.73-7.71 (m, 1H, Ar-H), 7.54-7.45 (m, 2H, Ar-H), 7.42-7.35 (m, 3H, Ar-H), 7.31-7.29 (m, 3H, Ar-H), 7.08-7.06 (m, 1H, Ar-H), 6.97 (d, *J* = 8.0 Hz, 2H, Ar-H), 6.76 (d, *J* = 8.0 Hz, 2H, Ar-H), 5.23 (dd, *J* = 11.8, 6.2 Hz, 1H, -C<u>H</u>OH), 3.15 (dd, *J* = 12.6, 6.2 Hz, 1H, H$_a$ of -CH$_2$-), 2.93 (t, *J* = 12.2 Hz, 1H, H$_b$ of -CH$_2$-), 2.37 (s, 3H, -CH$_3$), 2.18 (s, 3H, -SO$_2$PhC<u>H$_3$</u>); ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz) δ_C 144.0 (Ar-C), 141.4 (Ar-C), 139.3 (Ar-C), 137.1 (Ar-C), 135.7 (Ar-C), 134.3 (Ar-C), 134.1 (Ar-C), 134.0 (Ar-C), 130.8 (Ar-C), 130.6 (Ar-C), 129.4 (Ar-C), 129.1 (Ar-C), 129.0 (2C, Ar-C), 128.9 (Ar-C), 128.5 (Ar-C), 127.9 (Ar-C), 126.7 (Ar-C), 126.6 (3C, Ar-C), 126.5 (Ar-C), 126.2 (Ar-C), 123.4 (Ar-C), 119.1 (Ar-C), 115.9 (Ar-C), 68.7 (-CHOH), 39.3 (-CH$_2$-), 21.5 (-CH$_3$/-SO$_2$Ph<u>C</u>H$_3$), 21.4 (-SO$_2$Ph<u>C</u>H$_3$/-CH$_3$); HRMS (ESI) m/z calcd for $C_{30}H_{25}NNaO_3S$ [M + Na]$^+$ 502.1453, found 502.1443.

*Methyl 10-hydroxy-15-tosyl-10,15-dihydro-9H-dibenzo[5,6:7,8]cycloocta[1,2-b]indole-12-carboxylate (**6g**):*

White solid (28.8 mg, 64%), mp 246-248 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.27-8.26 (m, 1H, Ar-H), 8.08 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.92 (dd, *J* = 8.8, 1.6 Hz, 1H, Ar-H), 7.70 (dd, *J* = 7.6, 1.2 Hz, 1H, Ar-H), 7.53 (td, *J* = 7.4, 1.5 Hz, 1H, Ar-H), 7.47 (td, *J* = 7.6, 1.6 Hz, 1H, Ar-H), 7.40-7.36 (m, 2H, Ar-H), 7.31-7.28 (m, 3H, Ar-H), 6.97 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.78 (d, *J* = 8.0 Hz, 2H, Ar-H), 5.31 (dd, *J* = 12.0, 6.4 Hz, 1H, -C<u>H</u>OH), 3.89 (s, 3H, $-CO_2CH_3$), 3.17 (dd, *J* = 12.6, 6.2 Hz, 1H, H_a of $-CH_2-$), 2.94 (t, *J* = 12.2 Hz, 1H, H_b of $-CH_2-$), 2.19 (s, 3H, $-SO_2PhC\underline{H_3}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 167.1 ($-\underline{C}O_2CH_3$), 144.5 (Ar-C), 141.2 (Ar-C), 140.2 (Ar-C), 139.5 (Ar-C), 137.1 (Ar-C), 137.0 (Ar-C), 134.2 (Ar-C), 133.9 (Ar-C), 130.4 (Ar-C), 130.2 (Ar-C), 129.5 (Ar-C), 129.3 (Ar-C), 129.2 (2C, Ar-C), 129.0 (Ar-C), 128.6 (Ar-C), 128.1 (Ar-C), 126.6 (2C, Ar-C), 126.5 (Ar-C), 126.4 (Ar-C), 126.3 (Ar-C), 126.2 (Ar-C), 123.5 (Ar-C), 121.3 (Ar-C), 115.9 (Ar-C), 68.4 (-CHOH), 52.2 ($-CO_2\underline{C}H_3$), 39.3 ($-CH_2-$), 21.5 ($-SO_2Ph\underline{C}H_3$); HRMS (ESI) m/z calcd for $C_{31}H_{25}NNaO_5S$ $[M + Na]^+$ 546.1351, found 546.1353.

*12-Methoxy-15-tosyl-10,15-dihydro-9H-dibenzo[5,6:7,8]cycloocta[1,2-b]indol-10-ol (**6h**)* **:**

Pale yellow solid (28.1 mg, 66%), mp 168-170 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.94 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.73-7.71 (m, 1H, Ar-H), 7.54-7.47 (m, 2H, Ar-H), 7.45-7.38 (m, 2H, Ar-H), 7.32-7.29 (m, 3H, Ar-H), 6.98 (d, *J* = 2.4 Hz, 1H, Ar-H), 6.96 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.85 (dd, *J* = 9.2, 2.8 Hz, 1H, Ar-H), 6.75 (d, *J* = 8.0 Hz, 2H, Ar-H), 5.20 (dd, *J* = 12.0, 6.4 Hz, 1H, -C<u>H</u>OH), 3.80 (s, 3H, $-OCH_3$), 3.15 (dd, *J* = 12.4, 6.4 Hz, 1H, H_a of $-CH_2-$), 2.94 (t, *J* = 12.2 Hz, 1H, H_b of $-CH_2-$), 2.17 (s, 3H, $-SO_2PhC\underline{H_3}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 157.1 (Ar-C), 144.0 (Ar-C), 141.4 (Ar-C), 139.2 (Ar-C), 137.1 (Ar-C), 136.5 (Ar-C), 134.2 (Ar-C), 134.1 (Ar-C), 132.0 (Ar-C), 131.6 (Ar-C), 130.7 (Ar-C), 129.5 (Ar-C), 129.1 (Ar-C), 129.0 (2C, Ar-C), 128.9 (Ar-C), 128.5 (Ar-C), 128.0 (Ar-C), 126.6 (2C, Ar-C), 126.5 (Ar-C), 126.2 (Ar-C), 123.7 (Ar-C) , 117.2 (Ar-C), 114.1 (Ar-C), 101.6 (Ar-C), 68.8 (-CHOH), 55.7 ($-OCH_3$), 39.3 ($-CH_2-$), 21.5 ($-SO_2Ph\underline{C}H_3$); HRMS (ESI) m/z calcd for $C_{30}H_{25}NNaO_4S$ $[M + Na]^+$ 518.1402 , found 518.1416.

*13-Fluoro-15-tosyl-10,15-dihydro-9H-dibenzo[5,6:7,8]cycloocta[1,2-b]indol-10-ol (**6i**)* **:**

White solid (33.6 mg, 81%), mp 244-246 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.81 (dd, *J* = 10.2, 2.2 Hz, 1H, Ar-H), 7.71-7.68 (m, 1H, Ar-H), 7.54-7.45 (m, 3H, Ar-H), 7.40-7.37 (m, 2H, Ar-H), 7.33-7.27 (m, 3H, Ar-H), 7.00-6.95 (m, 3H, Ar-H), 6.80 (d, *J* = 8.0 Hz, 2H, Ar-H), 5.20 (dd, *J* = 11.8, 6.2 Hz, 1H, -C<u>H</u>OH), 3.14 (dd, *J* = 12.6, 6.2 Hz, 1H, H_a of $-CH_2-$), 2.91 (t, *J* = 12.2 Hz, 1H, H_b of $-CH_2-$), 2.20 (s, 3H, $-SO_2PhC\underline{H_3}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 161.2 (d, J_{C-F} = 241.1 Hz, Ar-C), 144.4 (Ar-C), 141.3 (Ar-C), 139.3 (Ar-C), 137.9 (d, J_{C-F} = 12.4 Hz, Ar-C), 137.0 (Ar-C), 135.9 (d, J_{C-F} = 4.1 Hz, Ar-C), 134.1 (Ar-C), 134.0 (Ar-C), 130.3 (Ar-C), 129.5 (Ar-C), 129.2 (2C, Ar-C), 129.1 (Ar-C), 129.0 (Ar-C), 128.5 (Ar-C), 128.0 (Ar-C), 126.7 (d, J_{C-F} = 6.0 Hz, Ar-C) 126.6 (2C, Ar-C), 126.5 (Ar-C), 126.3 (Ar-C), 123.1 (Ar-C), 120.1 (d, J_{C-F} = 9.7 Hz, Ar-C), 112.5 (d, J_{C-F} = 24.0 Hz, Ar-C), 103.7 (d, J_{C-F} = 28.5 Hz, Ar-C), 68.6 (-CHOH), 39.3 ($-CH_2-$), 21.5 ($-SO_2Ph\underline{C}H_3$); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ = −115.2 (s, 1F); HRMS (ESI) m/z calcd for $C_{29}H_{22}FNNaO_3S$ $[M + Na]^+$ 506.1202, found 506.1216.

*13-Methyl-15-tosyl-10,15-dihydro-9H-dibenzo[5,6:7,8]cycloocta[1,2-b]indol-10-ol (**6j**):*

Pale yellow solid (28.0 mg, 68%), mp 148-150 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.88 (s, 1H, Ar-H), 7.71-7.69 (m, 1H, Ar-H), 7.53-7.36 (m, 5H, Ar-H), 7.30-7.27 (m, 3H, Ar-H), 7.05 (d, *J* = 8.0 Hz, 1H, Ar-H), 6.96 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.77 (d, *J* = 8.4 Hz, 2H, Ar-H), 5.23 (dd, *J* = 12.0, 6.4 Hz, 1H, -C$\underline{H}$OH), 3.15 (dd, *J* = 12.6, 6.4 Hz, 1H, H_a of -CH_2-), 2.92 (t, *J* = 12.2 Hz, 1H, H_b of -CH_2-), 2.43 (s, 3H, -C$\underline{H}_3$), 2.18 (s, 3H, -SO_2PhC$\underline{H}_3$); ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz) δ_C 143.9 (Ar-C), 141.3 (Ar-C), 139.2 (Ar-C), 137.9 (Ar-C), 137.0 (Ar-C), 135.4 (Ar-C), 134.8 (Ar-C), 134.3 (Ar-C), 133.9 (Ar-C), 130.7 (Ar-C), 129.3 (Ar-C), 128.9 (3C, Ar-C), 128.7 (Ar-C), 128.4 (Ar-C), 128.1 (Ar-C), 127.8 (Ar-C), 126.4 (2C, Ar-C), 126.3 (Ar-C), 126.1 (Ar-C), 125.5 (Ar-C), 123.5 (Ar-C), 118.6 (Ar-C), 116.3 (Ar-C), 68.6 (-CHOH), 39.1 (-CH_2-), 21.9 (-SO_2Ph$\underline{C}H_3$/-CH_3), 21.4 (-CH_3/-SO_2Ph$\underline{C}H_3$); HRMS (ESI) m/z calcd for $C_{30}H_{25}NNaO_3S$ [M + Na]$^+$ 502.1453, found 502.1456.

*Methyl 10-hydroxy-15-tosyl-10,15-dihydro-9H-dibenzo[5,6:7,8]cycloocta[1,2-b]indole-13-carboxylate (**6k**) :*

White solid (27.0 mg, 60%), mp 188-190 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.75 (s, 1H, Ar-H), 7.91 (dd, *J* = 8.4, 1.2 Hz, 1H, Ar-H), 7.70 (dd, *J* = 7.8, 1.4 Hz, 1H, Ar-H), 7.59 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.55 (td, *J* = 7.5, 1.4 Hz, 1H, Ar-H), 7.48 (td, *J* = 7.5, 1.3 Hz, 1H, Ar-H), 7.41-7.38 (m, 2H, Ar-H), 7.32-7.29 (m, 3H, Ar-H), 7.00 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.78 (d, *J* = 8.0 Hz, 2H, Ar-H), 5.26 (m, 1H, -C$\underline{H}$OH), 3.94 (s, 3H, -CO_2CH_3), 3.16 (dd, *J* = 12.6, 6.2 Hz, 1H, H_a of -CH_2-), 2.94 (t, *J* = 12.2 Hz, 1H, H_b of -CH_2-), 2.19 (s, 3H, -SO_2PhC$\underline{H}_3$); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 167.2 (-$\underline{C}O_2CH_3$), 144.4 (Ar-C), 141.1 (Ar-C), 139.4 (Ar-C), 138.7 (Ar-C), 137.0 (Ar-C), 136.9 (Ar-C), 134.24 (Ar-C), 134.21 (Ar-C), 134.0 (Ar-C), 130.2 (Ar-C), 129.5 (Ar-C), 129.4 (Ar-C), 129.2 (2C, Ar-C), 129.0 (Ar-C), 128.6 (Ar-C), 128.1 (Ar-C), 127.0 (Ar-C), 126.7 (2C, (Ar-C), 126.6 (Ar-C), 126.3 (Ar-C), 125.4 (Ar-C), 123.3 (Ar-C), 119.0 (Ar-C), 117.8 (Ar-C), 68.6 (-CHOH), 52.3 (-$CO_2\underline{C}H_3$), 39.3 (-CH_2-), 21.5 (-SO_2Ph$\underline{C}H_3$); HRMS (ESI) m/z calcd for $C_{31}H_{26}NO_5S$ [M + H]$^+$ 524.1532, found 524.1529.

*13-Methoxy-15-tosyl-10,15-dihydro-9H-dibenzo[5,6:7,8]cycloocta[1,2-b]indol-10-ol (**6l**):*

Pale yellow solid (29.8 mg, 70%), mp 172-174 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.72-7.70 (m, 1H, Ar-H), 7.61-7.60 (m, 1H, Ar-H), 7.52-7.46 (m, 2H, Ar-H), 7.45-7.37 (m, 3H, Ar-H), 7.32-7.29 (m, 3H, Ar-H), 6.96 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.84 (dd, *J* = 8.6, 2.2 Hz, 1H, Ar-H), 6.76 (d, *J* = 8.0 Hz, 2H, Ar-H), 5.20 (dd, *J* = 12.0, 6.4 Hz, 1H, -C$\underline{H}$OH), 3.83 (s, 3H, -OCH_3), 3.14 (dd, *J* = 12.4, 6.4 Hz, 1H, H_a of -CH_2-), 2.92 (t, *J* = 12.2 Hz, 1H, H_b of -CH_2-), 2.18 (s, 3H, -SO_2PhC$\underline{H}_3$); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 158.4 (Ar-C), 144.1 (Ar-C), 141.5 (Ar-C), 139.2 (Ar-C), 138.7 (Ar-C), 137.2 (Ar-C), 134.3 (Ar-C), 134.2 (Ar-C), 134.0 (Ar-C), 130.9 (Ar-C), 129.4 (Ar-C), 129.1 (Ar-C), 129.0 (2C, Ar-C), 128.7 (Ar-C), 128.5 (Ar-C), 127.9 (Ar-C), 126.52 (2C, Ar-C), 126.51 (Ar-C), 126.2 (Ar-C), 124.3 (Ar-C), 123.6 (Ar-C), 119.8 (Ar-C), 113.4 (Ar-C), 100.6 (Ar-C), 68.8 (-CHOH), 55.9 (-OCH_3), 39.3 (-CH_2-), 21.5 (-SO_2Ph$\underline{C}H_3$); HRMS (ESI) m/z calcd for $C_{30}H_{25}NNaO_4S$ [M + Na]$^+$ 518.1402, found 518.1400.

*Methyl 10-hydroxy-3-methoxy-15-tosyl-10,15-dihydro-9H-dibenzo[5,6:7,8]cycloocta[1,2-b]indole-13-carboxylate (**6m**):*

White solid (44.7 mg, 94%), mp 142-144 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.74 (s, 1H, Ar-H), 7.89 (dd, *J* = 8.4, 1.2 Hz, 1H, Ar-H), 7.61 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.56 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.37-7.34 (m, 1H, Ar-H), 7.30-7.27 (m, 3H, Ar-H), 7.03-6.98 (m, 3H, Ar-H), 6.88 (d, *J* = 2.8 Hz, 1H, Ar-H), 6.78 (d, *J* = 8.0 Hz, 2H, Ar-H), 5.23 (dd, *J* = 11.8, 6.2 Hz, 1H, -C<u>H</u>OH), 3.93 (s, 3H,-CO_2CH_3/ -OCH_3), 3.90 (s, 3H, -OCH_3/ -CO_2CH_3), 3.15 (dd, *J* = 12.6, 6.2 Hz, 1H, H_a of -CH_2-), 2.97 (t, *J* = 12.2 Hz, 1H, H_b of -CH_2-), 2.18 (s, 3H, -SO_2PhC<u>H</u>$_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 167.3 (<u>C</u>O_2CH_3), 160.2 (Ar-C), 144.4 (Ar-C), 141.1 (Ar-C), 140.9 (Ar-C), 138.9 (Ar-C), 136.9 (Ar-C), 136.8 (Ar-C), 135.5 (Ar-C), 134.4 (Ar-C), 134.3 (Ar-C), 129.2 (2C, Ar-C), 128.9 (Ar-C), 128.6 (Ar-C), 128.1 (Ar-C), 126.7 (Ar-C), 126.6 (2C, Ar-C), 126.3 (Ar-C), 125.4 (Ar-C), 122.8 (Ar-C), 122.5 (Ar-C), 118.9 (Ar-C), 117.8 (Ar-C), 114.7 (Ar-C), 112.5 (Ar-C), 68.6 (-CHOH), 55.5 (-CO_2<u>C</u>H_3/-OCH_3), 52.3 (-OCH_3/ -CO_2<u>C</u>H_3), 39.3 (-CH_2-), 21.5 (-SO_2Ph<u>C</u>H_3); HRMS (ESI) m/z calcd for $C_{32}H_{27}NNaO_6S$ $[M + Na]^+$ 576.1457, found 576.1459.

*3-Methoxy-15-tosyl-10,15-dihydro-9H-dibenzo[5,6:7,8]cycloocta[1,2-b]indol-10-ol (**6n**):*

White solid (34.5 mg, 81%), mp 178-180 ºC; ^1H NMR ($CDCl_3$, 600 MHz) δ_H 8.07 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.64 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.55 (d, *J* = 7.2 Hz, 1H, Ar-H), 7.39-7.38 (m, 1H, Ar-H), 7.29-7.21 (m, 5H, Ar-H), 7.03 (dd, *J* = 8.4, 2.4 Hz, 1H, Ar-H), 6.98 (d, *J* = 7.8 Hz, 2H, Ar-H), 6.89 (d, *J* = 2.4 Hz, 1H, Ar-H), 6.77 (d, *J* = 7.8 Hz, 2H, Ar-H), 5.24 (dd, J = 11.7, 6.3 Hz, 1H, -C<u>H</u>OH), 3.91 (s, 3H, -OCH_3), 3.16 (dd, *J* = 12.6, 6.0 Hz, 1H, H_a of -CH_2-), 2.98 (t, *J* = 12.0 Hz, 1H, H_b of -CH_2-), 2.18 (s, 3H, -SO_2PhC<u>H</u>$_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz) δ_C 159.7 (Ar-C) , 143.9 (Ar-C), 141.2 (Ar-C), 140.7 (Ar-C), 137.3 (Ar-C), 136.9 (Ar-C), 135.7 (Ar-C), 135.4 (Ar-C), 134.3 (Ar-C), 130.5 (Ar-C), 128.9 (2C, Ar-C), 128.8 (Ar-C), 128.4 (Ar-C), 127.9 (Ar-C), 126.5 (2C, Ar-C), 126.1 (Ar-C), 125.0 (Ar-C), 124.1 (Ar-C), 122.9 (Ar-C), 122.8 (Ar-C), 118.9 (Ar-C), 116.2 (Ar-C), 114.5 (Ar-C), 112.3 (Ar-C), 68.6 (-CHOH), 55.3 (-OCH_3), 39.2 (-CH_2-), 21.4 (-SO_2Ph<u>C</u>H_3); HRMS (ESI) m/z calcd for $C_{30}H_{25}NNaO_4S$ $[M + Na]^+$ 518.1402, found 518.1401.

*2-Methyl-15-tosyl-10,15-dihydro-9H-dibenzo[5,6:7,8]cycloocta[1,2-b]indol-10-ol (**6o**)* **:**

White solid (24.3 mg, 59%), mp 172-174 ºC; ^1H NMR ($CDCl_3$, 400 MHz) δ_H 8.08-8.06 (m, 1H, Ar-H), 7.56-7.54 (m, 1H, Ar-H), 7.47 (s, 1H, Ar-H), 7.42-7.39 (m, 1H, Ar-H), 7.34-7.20 (m, 7H, Ar-H), 7.00 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.77 (d, *J* = 8.4 Hz, 2H, Ar-H), 5.25 (dd, *J* = 11.6, 6.4 Hz, 1H, -C<u>H</u>OH), 3.15 (dd, *J* = 12.4, 6.4 Hz, 1H, H_a of -CH_2-), 2.95 (t, *J* = 12.2 Hz, 1H, H_b of -CH_2-), 2.45 (s, 3H, -CH_3), 2.18 (s, 3H, -SO_2PhC<u>H</u>$_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 144.0 (Ar-C), 141.4 (Ar-C), 137.6 (Ar-C), 137.1 (Ar-C), 136.6 (Ar-C), 136.1 (Ar-C), 135.9 (Ar-C), 134.5 (2C, Ar-C), 130.5 (Ar-C), 130.4 (Ar-C), 129.8 (Ar-C), 129.3 (Ar-C), 129.1 (Ar-C), 129.0 (2C, Ar-C), 128.5 (Ar-C), 127.7 (Ar-C), 126.6 (2C, Ar-C), 126.2 (Ar-C), 125.2 (Ar-C), 124.2 (Ar-C), 123.4 (Ar-C), 119.1 (Ar-C), 116.2 (Ar-C), 68.7 (-CHOH), 39.4 (-CH_2-) , 21.5 (-SO_2Ph<u>C</u>H_3/-CH_3), 21.2 (-CH_3/-SO_2Ph<u>C</u>H_3); HRMS (ESI) m/z calcd for $C_{30}H_{25}NNaO_3S$ $[M + Na]^+$ 502.1453, found 502.1470.

*Methyl 10-hydroxy-2-methyl-15-tosyl-10,15-dihydro-9H-dibenzo[5,6:7,8]cycloocta[1,2-b]indole-13-carboxylate (**6p**) :*

White solid (36.0 mg, 78%), mp 142-144 ºC; ^1H NMR ($CDCl_3$, 400 MHz) δ_H 8.75 (s, 1H, Ar-H), 7.91 (dd, *J* = 8.2, 1.4 Hz, 1H, Ar-H), 7.58 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.45 (s, 1H, Ar-H), 7.40-7.27 (m, 6H, Ar-H), 7.03 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.80 (d, *J* = 8.4 Hz, 2H, Ar-H), 5.25 (dd, *J* = 12.0, 6.4 Hz, 1H, -C<u>H</u>OH), 3.94 (s, 3H, -CO_2CH_3), 3.15 (dd, *J* = 12.6, 6.2 Hz, 1H, H_a of -CH_2-), 2.94 (t, *J* = 12.2 Hz, 1H, H_b of -CH_2-), 2.45 (s, 3H, -CH_3), 2.19 (s, 3H, -SO_2PhC<u>H</u>$_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 167.3 (<u>C</u>O_2CH_3), 144.4 (Ar-C), 141.2 (Ar-C), 138.9 (Ar-C), 137.0 (Ar-C), 136.9 (Ar-C), 136.7 (Ar-C), 136.2 (Ar-C), 134.4 (Ar-C), 134.3 (Ar-C), 130.2 (Ar-

C), 129.9 (Ar-C), 129.4 (Ar-C), 129.2 (3C, Ar-C), 129.1 (Ar-C), 128.5 (Ar-C), 127.9 (Ar-C), 126.9 (Ar-C), 126.7 (2C, Ar-C), 126.3 (Ar-C), 125.4 (Ar-C), 123.1 (Ar-C), 118.9 (Ar-C), 117.8 (Ar-C), 68.6 (-CHOH), 52.3 (-$CO_2\underline{C}H_3$), 39.4 (-CH_2-), 21.5 (-$SO_2Ph\underline{C}H_3$ /-CH_3), 21.2 (-CH_3/-$SO_2Ph\underline{C}H_3$); HRMS (ESI) m/z calcd for $C_{32}H_{27}NNaO_5S$ $[M+Na]^+$ 560.1508, found 560.1505.

*7-Methoxy-15-tosyl-10,15-dihydro-9H-dibenzo[5,6:7,8]cycloocta[1,2-b]indol-10-ol (**6q**)* **:**

White solid (26.0 mg, 61%), mp 166-168 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ_H 8.09-8.07 (m, 1H, Ar-H), 7.69 (dd, *J* = 7.6, 1.2 Hz, 1H, Ar-H), 7.58-7.56 (m, 1H, Ar-H), 7.50 (td, *J* = 7.4, 1.3 Hz, 1H, Ar-H), 7.44 (td, *J* = 7.6, 1.6 Hz, 1H, Ar-H), 7.37-7.22 (m, 4H, Ar-H), 7.01 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.85-6.79 (m, 4H, Ar-H), 5.26 (dd, *J* = 11.8, 6.2 Hz, 1H, -C$\underline{H}$OH), 3.83 (s, 3H, -OCH_3), 3.11 (dd, *J* = 12.4, 6.4 Hz, 1H, H_a of -CH_2-), 2.91 (t, *J* = 12.2 Hz, 1H, H_b of -CH_2-), 2.19 (s, 3H, -$SO_2PhC\underline{H_3}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 159.3 (Ar-C), 144.1 (Ar-C), 139.1 (Ar-C), 138.4 (Ar-C), 137.5 (Ar-C), 135.8 (Ar-C), 134.4 (Ar-C), 134.1 (Ar-C), 133.9 (Ar-C), 130.7 (Ar-C), 130.5 (Ar-C), 130.0 (Ar-C), 129.6 (Ar-C), 129.1 (2C, Ar-C), 128.9 (Ar-C), 126.6 (2C, Ar-C), 126.2 (Ar-C), 125.3 (Ar-C), 124.2 (Ar-C), 123.5 (Ar-C), 119.1 (Ar-C), 116.2 (Ar-C), 113.6 (Ar-C), 111.9 (Ar-C), 68.6 (-CHOH), 55.4 (-OCH_3), 39.6 (-CH_2-), 21.5 (-$SO_2Ph\underline{C}H_3$); HRMS (ESI) m/z calcd for $C_{30}H_{25}NNaO_4S$ $[M + Na]^+$ 518.1402, found 518.1401.

13. General procedure for the synthesis of products 7:

To a well-stirred solution of **6** (0.062 mmol, 1 equiv) in dry 1,4-dioxane (1.0 mL) was added *p*-TsOH.H_2O (35.6 mg, 0.186 mmol, 3 equiv). The resulting mixture was refluxed for 4.0-5.5 h under argon atmosphere. Upon completion of reaction (TLC), the reaction mixture was neutralized by dropwise addition of dilute aqueous sodium bicarbonate solution and extracted with ethyl acetate (3 x 10 mL). The combined organic extracts were washed with brine (5 mL), dried over anhydrous Na_2SO_4 and concentrated *in vaccuo.* The resulting crude product was purified by silica gel (100-200 mesh) column chromatography eluting with 5-15 % ethyl acetate in petroleum ether (v/v) to afford the desired product **7** in (60-98%) yield.

14. Spectral data of products 7a-7j :

*(Z)-15-Tosyl-15H-dibenzo[5,6:7,8]cycloocta[1,2-b]indole (**7a**)* **:**

Pale yellow solid (27.2 mg, 98%), mp >250 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ_H 8.10 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.54-7.52 (m, 1H, Ar-H), 7.48-7.27 (m, 7H, Ar-H), 7.24-7.20 (m, 2H, Ar-H), 7.18-7.15 (m, 2H, Ar-H), 7.06 (d, *J* = 8.0 Hz, 1H, Ar-H), 6.97 (d, *J* = 11.6 Hz, 1H, =CH), 6.73 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.62 (d, *J* = 11.6 Hz, 1H, =CH), 2.15 (s, 3H, -$SO_2PhC\underline{H_3}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 144.2 (Ar-C), 142.3 (Ar-C), 141.9 (Ar-C), 137.9 (Ar-C), 137.86 (Ar-C), 137.81 (Ar-C), 136.2 (Ar-C), 133.7 (Ar-C), 133.0 (Ar-C), 132.8 (Ar-C), 131.4 (Ar-C), 130.6 (Ar-C), 130.1 (Ar-C), 129.0 (2C, Ar-C), 128.9 (Ar-C), 128.8 (Ar-C), 127.2 (Ar-C), 126.9 (2C, Ar-C), 126.7 (Ar-C), 126.3 (Ar-C), 125.2 (Ar-C), 124.3 (Ar-C), 124.2 (Ar-C), 123.7 (Ar-C), 119.3 (Ar-C), 116.0 (Ar-C), 21.5 (-$SO_2Ph\underline{C}H_3$); HRMS (ESI) m/z calcd for $C_{29}H_{21}NNaO_2S$ $[M+Na]^+$ 470.1191, found 470.1196.

*(Z)-13-Fluoro-15-tosyl-15H-dibenzo[5,6:7,8]cycloocta[1,2-b]indole (**7b**)* **:**

White solid (28.2 mg, 98%), mp 244-246 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.85 (dd, *J* = 10.0, 2.0 Hz, 1H, Ar-H), 7.53-7.38 (m, 4H, Ar-H), 7.34-7.21 (m, 4H, Ar-H), 7.17 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.07 (d, *J* = 7.6 Hz, 1H, Ar-H), 6.98-6.93 (m, 2H, Ar-H and =CH), 6.77 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.57 (d, *J* = 11.6 Hz, 1H, =CH), 2.18 (s, 3H, -$SO_2PhC\underline{H}_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 161.3 (d, $J_{C\text{-}F}$ = 241.2 Hz, Ar-C), 144.5 (Ar-C), 142.2 (Ar-C), 141.9 (Ar-C), 138.2 (d, $J_{C\text{-}F}$ = 12.5 Hz, Ar-C), 138.0 (Ar-C), 137.8 (Ar-C), 136.5 (Ar-C), 133.6 (Ar-C), 132.8 (Ar-C), 132.7 (Ar-C), 131.4 (Ar-C), 130.6 (Ar-C), 129.2 (2C, Ar-C), 128.9 (Ar-C), 128.8 (Ar-C), 127.3 (Ar-C), 126.9 (Ar-C), 126.8 (2C, Ar-C), 126.35 (Ar-C), 126.34 (Ar-C), 123.7 (d, $J_{C\text{-}F}$ = 1.3 Hz, Ar-C), 123.3 (Ar-C), 120.1 (d, $J_{C\text{-}F}$ = 9.8 Hz, Ar-C), 112.4 (d, $J_{C\text{-}F}$ = 24.1 Hz, Ar-C), 103.6 (d, $J_{C\text{-}F}$ = 28.5 Hz, Ar-C), 21.5 (-$SO_2Ph\underline{C}H_3$); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ = −115.3 (s, 1F); HRMS (ESI) m/z calcd for $C_{29}H_{21}FNO_2S$ [M + H]$^+$ 466.1277, found 466.1278.

*(Z)-Methyl 15-tosyl-15H-dibenzo[5,6:7,8]cycloocta[1,2-b]indole-13-carboxylate (**7c**):*

White solid (29.7 mg, 95%), mp 218-220 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.79 (s, 1H, Ar-H), 7.91 (dd, *J* = 8.2, 1.4 Hz, 1H, Ar-H), 7.54-7.28 (m, 7H, Ar-H), 7.25-7.23 (m, 1H, Ar-H), 7.17 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.08 (d, *J* = 7.2 Hz, 1H, Ar-H), 6.99 (d, *J* = 11.6 Hz, 1H, =CH), 6.76 (d, *J* = 8.0 Hz, 2H, Ar-H), 6.61 (d, *J* = 11.2 Hz, 1H, =CH), 3.96 (s, 3H, -CO_2CH_3), 2.16 (s, 3H, -$SO_2PhC\underline{H}_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 167.3 (-$\underline{C}O_2CH_3$), 144.6 (Ar-C), 142.0 (Ar-C), 141.9 (Ar-C), 140.9 (Ar-C), 137.5 (Ar-C), 137.3 (Ar-C), 136.7 (Ar-C), 133.7 (Ar-C), 133.6 (Ar-C), 132.8 (Ar-C), 132.4 (Ar-C), 131.4 (Ar-C), 130.7 (Ar-C), 129.2 (2C, Ar-C), 129.1 (Ar-C), 128.9 (Ar-C), 127.3 (Ar-C), 127.0 (Ar-C), 126.9 (2C, Ar-C), 126.8 (Ar-C), 126.4 (Ar-C), 125.5 (Ar-C), 123.8 (Ar-C), 123.1 (Ar-C), 119.1 (Ar-C), 117.6 (Ar-C), 52.3 (-$CO_2\underline{C}H_3$), 21.5 (-$SO_2Ph\underline{C}H_3$); HRMS (ESI) m/z calcd for $C_{31}H_{24}NO_4S$ [M + H]$^+$ 506.1426, found 506.1427.

*(Z)-13-Methoxy-15-tosyl-15H-dibenzo[5,6:7,8]cycloocta[1,2-b]indole (**7d**)* **:**

White solid (25.4 mg, 86%), mp 226-228 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.67-7.66 (m, 1H, Ar-H), 7.54-7.52 (m, 1H, Ar-H), 7.47-7.38 (m, 3H, Ar-H), 7.34-7.28 (m, 2H, Ar-H), 7.23-7.19 (m, 2H, Ar-H), 7.15 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.07 (d, *J* = 7.6 Hz, 1H, Ar-H), 6.95 (d, *J* = 11.6 Hz, 1H, =CH), 6.82 (dd, *J* = 8.6, 2.2 Hz, 1H, Ar-H), 6.74 (d, *J* = 8.0 Hz, 2H, Ar-H), 6.58 (d, *J* = 11.2 Hz, 1H, =CH), 3.87 (s, 3H, -OCH_3), 2.17 (s, 3H, -$SO_2PhC\underline{H}_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 158.4 (Ar-C), 144.2 (Ar-C), 142.4 (Ar-C), 141.7 (Ar-C), 139.0 (Ar-C), 138.0 (Ar-C), 136.0 (Ar-C), 133.6 (Ar-C), 133.4 (Ar-C), 132.7 (Ar-C), 131.4 (Ar-C), 130.5 (Ar-C), 129.1 (2C, Ar-C), 128.9 (Ar-C), 128.5 (Ar-C), 127.2 (Ar-C), 126.8 (Ar-C), 126.7 (2C, Ar-C), 126.3 (Ar-C), 124.4 (Ar-C), 124.0 (Ar-C), 123.7 (Ar-C), 119.9 (Ar-C), 113.1 (Ar-C), 100.5 (Ar-C), 100.0 (Ar-C), 55.9 (-OCH_3), 21.5 (-$SO_2Ph\underline{C}H_3$); HRMS (ESI) m/z calcd for $C_{30}H_{24}NO_3S$ [M+H]$^+$ 478.1477, found 478.1479.

*(Z)-12-Fluoro-15-tosyl-15H-dibenzo[5,6:7,8]cycloocta[1,2-b]indole (**7e**) :*

Pale yellow solid (27.4 mg, 95%), mp >250 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.06-8.02 (m, 1H, Ar-H), 7.54-7.38 (m, 4H, Ar-H), 7.35-7.28 (m, 2H, Ar-H), 7.24-7.22 (m, 1H, Ar-H), 7.13 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.07 (d, *J* = 7.6 Hz, 1H, Ar-H), 7.01-6.96 (m, 3H, Ar-H and =CH), 6.74 (d, *J* = 8.0 Hz, 2H, Ar-H), 6.54 (d, *J* = 11.2 Hz, 1H, =CH), 2.17 (s, 3H, -$SO_2PhC\underline{H}_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 161.1 (d, $J_{C\text{-}F}$ = 242.4 Hz, Ar-C), 144.5 (Ar-C), 142.1 (Ar-C), 141.9 (Ar-C), 139.7 (Ar-C), 137.6 (Ar-C), 136.6 (Ar-C), 133.5 (Ar-C), 132.8 (Ar-C), 132.6 (Ar-C), 131.5 (Ar-C), 130.7 (Ar-C), 129.1 (2C, Ar-C), 129.0 (Ar-C), 128.9 (Ar-C), 127.3 (Ar-C), 127.0 (Ar-C), 126.7 (2C, Ar-C), 126.4 (Ar-C), 123.9 (d, J_{C-F} = 4.0 Hz, Ar-C), 123.8 (d, J_{C-F} = 10.8 Hz, Ar-C), 123.1 (Ar-C), 117.2 (d, J_{C-F} = 9.2 Hz, Ar-C), 112.9 (d, J_{C-F} = 24.8 Hz, Ar-C), 105.2 (d, J_{C-F} = 24.1 Hz, Ar-C), 100.0 (Ar-C), 21.5 (-$SO_2Ph\underline{C}H_3$); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ = −118.2 (s, 1F); HRMS (ESI) m/z calcd for $C_{29}H_{20}FNaNO_2S$ $[M+Na]^+$ 488.1096, found 488.1097.

*(Z)-12-Chloro-15-tosyl-15H-dibenzo[5,6:7,8]cycloocta[1,2-b]indole (**7f**):*

White solid (25.3 mg, 85%), mp >250 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ_H 8.02 (d, J = 8.8 Hz, 1H, Ar-H), 7.54-7.38 (m, 4H, Ar-H), 7.35-7.26 (m, 3H, Ar-H), 7.24-7.21 (m, 2H, Ar-H), 7.13 (d, J = 8.4 Hz, 2H, Ar-H), 7.07 (d, J = 7.6 Hz, 1H, Ar-H), 6.98 (d, J = 11.6 Hz, 1H, =CH), 6.76 (d, J = 8.0 Hz, 2H, Ar-H), 6.55 (d, J = 11.6 Hz, 1H, =CH), 2.18 (s, 3H, -$SO_2PhC\underline{H_3}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 144.6 (Ar-C), 142.0 (Ar-C), 141.9 (Ar-C), 139.3 (Ar-C), 137.6 (Ar-C), 136.7 (Ar-C), 136.1 (Ar-C), 133.5 (Ar-C), 132.8 (Ar-C), 132.5 (Ar-C), 131.4 (Ar-C), 131.3 (Ar-C), 130.7 (Ar-C), 130.1 (Ar-C), 129.2 (2C, Ar-C), 129.1 (Ar-C), 128.9 (Ar-C), 127.3 (Ar-C), 127.0 (Ar-C), 126.7 (2C, Ar-C), 126.4 (Ar-C), 125.3 (Ar-C), 123.4 (Ar-C), 123.0 (Ar-C), 119.2 (Ar-C), 117.1 (Ar-C), 21.5 (-$SO_2Ph\underline{C}H_3$); HRMS (ESI) m/z calcd for $C_{29}H_{21}ClNO_2S$ $[M + H]^+$ 482.0982, found 482.0980.

*(Z)-12-Methoxy-15-tosyl-15H-dibenzo[5,6:7,8]cycloocta[1,2-b]indole (**7g**)* **:**

Pale yellow solid (24.5 mg, 83%), mp 224-226 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ_H 7.99 (d, J = 8.8 Hz, 1H, Ar-H), 7.55-7.53 (m, 1H, Ar-H), 7.49-7.39 (m, 3H, Ar-H), 7.34-7.29 (m, 2H, Ar-H), 7.24-7.21 (m, 1H, Ar-H), 7.14 (d, J = 8.4 Hz, 2H, Ar-H), 7.07 (d, J = 7.2 Hz, 1H, Ar-H), 6.97 (d, J = 11.6 Hz, 1H, =CH), 6.87 (dd, J = 9.0, 2.6 Hz, 1H, Ar-H), 6.77-6.72 (m, 3H, Ar-H), 6.57 (d, J = 11.6 Hz, 1H, =CH), 3.79 (s, 3H, -OCH_3), 2.16 (s, 3H, -$SO_2PhC\underline{H_3}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 157.1 (Ar-C), 144.1 (Ar-C), 142.3 (Ar-C), 141.8 (Ar-C), 137.8 (Ar-C), 136.2 (Ar-C), 133.6 (Ar-C), 133.0 (Ar-C), 132.8 (Ar-C), 132.2 (Ar-C), 131.5 (Ar-C), 131.1 (Ar-C), 130.6 (Ar-C), 129.0 (2C, Ar-C), 128.9 (Ar-C), 128.8 (Ar-C), 127.2 (Ar-C), 126.9 (Ar-C), 126.7 (2C, Ar-C), 126.3 (Ar-C), 124.3 (Ar-C), 123.7 (Ar-C), 117.0 (Ar-C), 113.8 (Ar-C), 101.9 (Ar-C), 100.0 (Ar-C), 55.6 (-OCH_3), 21.5 (-$SO_2Ph\underline{C}H_3$); HRMS (ESI) m/z calcd for $C_{30}H_{24}NO_3S$ $[M + H]^+$ 478.1477, found 478.1479.

*(Z)-3-Methoxy-15-tosyl-15H-dibenzo[5,6:7,8]cycloocta[1,2-b]indole (**7h**)***:**

Yellow solid (28.4 mg, 96%), mp 200-202 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ_H 8.10 (d, J = 8.0 Hz, 1H, Ar-H), 7.46 (d, J = 8.4 Hz, 1H, Ar-H), 7.40-7.36 (m, 1H, Ar-H), 7.33-7.24 (m, 4H, Ar-H), 7.21-7.14 (m, 3H, Ar-H), 7.07-7.05 (m, 1H, Ar-H), 7.00 (dd, J = 8.8, 2.8 Hz, 1H, Ar-H), 6.96 (d, J = 11.6 Hz, 1H, =CH), 6.75-6.73 (m, 3H, Ar-H), 6.61 (d, J = 11.6 Hz, 1H, =CH), 3.87 (s, 3H, -OCH_3), 2.15 (s, 3H, -$SO_2PhC\underline{H_3}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 159.8 (Ar-C), 144.2 (Ar-C), 143.3 (Ar-C), 142.1 (Ar-C), 137.9 (Ar-C), 137.8 (Ar-C), 137.7 (Ar-C), 135.9 (Ar-C), 134.2 (Ar-C), 133.8 (Ar-C), 131.2 (Ar-C), 130.2 (Ar-C), 129.0 (2C, Ar-C), 128.9 (Ar-C), 127.1 (Ar-C), 127.0 (Ar-C), 126.7 (2C, Ar-C), 125.1 (Ar-C), 125.0 (Ar-C), 124.1 (Ar-C), 123.9 (Ar-C), 123.6 (Ar-C), 119.2 (Ar-C), 116.1 (Ar-C), 115.4 (Ar-C), 112.7 (Ar-C), 55.4 (-OCH_3), 21.5 (-$SO_2Ph\underline{C}H_3$); HRMS (ESI) m/z calcd for $C_{30}H_{24}NO_3S$ $[M + H]^+$ 478.1477, found 478.1479.

*(Z)-Methyl 3-methoxy-15-tosyl-15H-dibenzo[5,6:7,8]cycloocta[1,2-b]indole-13-carboxylate (**7i**) :*

Yellow solid (24.5 mg, 74%), mp 238-240 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.79 (s, 1H, Ar-H), 7.91 (dd, *J* = 8.2, 1.4 Hz, 1H, Ar-H), 7.46 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.41-7.28 (m, 4H, Ar-H), 7.17 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.07 (d, *J* = 7.2 Hz, 1H, Ar-H), 7.03-6.96 (m, 2H, Ar-H), 6.77-6.75 (m, 3H, Ar-H), 6.60 (d, *J* = 11.6 Hz, 1H, =CH), 3.95 (s, 3H, $-CO_2CH_3$/$-OCH_3$), 3.87 (s, 3H, $-OCH_3$/$-CO_2CH_3$), 2.16 (s, 3H, $-SO_2PhC\underline{H_3}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 167.3 ($-\underline{C}O_2CH_3$), 160.2 (Ar-C), 144.5 (Ar-C), 143.4 (Ar-C), 141.8 (Ar-C), 141.0 (Ar-C), 137.5 (Ar-C), 137.2 (Ar-C), 136.5 (Ar-C), 134.3 (Ar-C), 133.7 (Ar-C), 133.6 (Ar-C), 131.3 (Ar-C), 129.2 (2C, Ar-C), 129.0 (Ar-C), 127.2 (Ar-C), 127.1 (Ar-C), 126.8 (Ar-C), 126.7 (2C, Ar-C), 125.5 (Ar-C), 124.5 (Ar-C), 123.4 (Ar-C), 123.2 (Ar-C), 118.9 (Ar-C), 117.7 (Ar-C), 115.6 (Ar-C), 112.7 (Ar-C), 55.4 ($-CO_2\underline{C}H_3$/$-OCH_3$), 52.3 ($-OCH_3$/$-CO_2\underline{C}H_3$), 21.5 ($-SO_2Ph\underline{C}H_3$); HRMS (ESI) m/z calcd for $C_{32}H_{26}NO_5S$ $[M + H]^+$ 536.1532, found 536.1535.

*(Z)-7-Methoxy-15-tosyl-15H-dibenzo[5,6:7,8]cycloocta[1,2-b]indole (**7j**)* **:**

Pale yellow solid (17.7 mg, 60%), mp 238-240 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 8.12 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.52 (d, *J* = 7.2 Hz, 1H, Ar-H), 7.47-7.44 (m, 1H, Ar-H), 7.42-7.40 (m, 1H, Ar-H), 7.35 (d, *J* = 7.2 Hz, 1H, Ar-H), 7.29 (t, *J* = 7.5 Hz, 1H, Ar-H), 7.22-7.19 (m, 5H, Ar-H), 6.96 (dd, *J* = 8.4, 2.4 Hz, 1H, Ar-H), 6.92 (d, *J* = 11.4 Hz, 1H, =CH), 6.78 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.62 (d, *J* = 11.4 Hz, 1H, =CH), 6.59-6.58 (m, 1H, Ar-H), 3.82 (s, 3H, $-OCH_3$), 2.17 (s, 3H, $-SO_2PhC\underline{H_3}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz) δ_C 158.4 (Ar-C), 144.1 (Ar-C), 141.5 (Ar-C), 138.9 (Ar-C), 137.8 (Ar-C), 137.7 (Ar-C), 135.9 (Ar-C), 134.6 (Ar-C), 133.7 (Ar-C), 133.0 (Ar-C), 132.7 (Ar-C), 132.4 (Ar-C), 130.6 (Ar-C), 130.0 (Ar-C), 129.0 (2C, Ar-C), 128.6 (Ar-C), 126.7 (2C, Ar-C), 125.9 (Ar-C), 125.1 (Ar-C), 124.1 (Ar-C), 124.0 (Ar-C), 123.6 (Ar-C), 119.2 (Ar-C), 115.9 (Ar-C), 113.7 (Ar-C), 113.0 (Ar-C) , 55.3 ($-OCH_3$), 21.4 ($-SO_2Ph\underline{C}H_3$); HRMS (ESI) m/z calcd for $C_{30}H_{24}NO_3S$ $[M + H]^+$ 478.1477, found 478.1468.

15. General procedure for the synthesis of products 8:

To a well stirred solution of $Pd(OAc)_2bpy$ (3.21 mg, 0.008 mmol, 6 mol %) in dry NMA (0.5 mL) was added D-CSA (65.3 mg, 0.28 mmol, 2 equiv) and the resulting mixture was heated at 100 °C under argon atmosphere. Next, amino-acetylene substrate **5** (0.14 mmol, 1 equiv) was added dropwise dissolving in NMA (1.0 mL) at the same temperature and the resulting mixture was allowed to stir for another 3.5-12 h. Upon completion of reaction (TLC), the mixture was diluted with water (15 mL) and extracted with ethyl acetate (3 x 15 mL). The combined organic extracts were then washed with brine (10 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Then the resulting residue was purified by silica gel (100-200 mesh) column chromatography eluting with 8-20% ethyl acetate-petroleum ether (v/v) to obtain the pure product **8** in 60-95% yield.

16. Spectral data of products 8a-8i :

*15-Tosyl-9H-dibenzo[5,6:7,8]cycloocta[1,2-b]indol-10(15H)-one (**8a**)* **:**

Yellow solid (59.6 mg, 92%), mp 220-222 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 8.33 (d, *J* = 7.2 Hz, 1H, Ar-H), 8.07 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.71 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.62 (t, *J* = 7.5 Hz, 1H, Ar-H), 7.52 (d, *J* = 7.6 Hz, 1H, Ar-H), 7.50 (t, *J* = 6.3 Hz, 2H, Ar-H), 7.37-7.26 (m, 5H, Ar-H), 7.06 (d, *J* = 7.8 Hz, 2H, Ar-H), 6.82 (d, *J* = 8.4 Hz, 2H, Ar-H), 3.71 (s, 2H, $-CH_2-$), 2.20 (s, 3H, $-SO_2PhC\underline{H_3}$); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz) δ_C 196.1 (C=O), 144.7 (Ar-C), 144.6 (Ar-C), 144.2 (Ar-C), 140.2 (Ar-C), 139.8 (Ar-C), 138.7 (Ar-C), 137.0 (Ar-C), 136.2 (Ar-C), 134.2 (Ar-C), 134.1 (Ar-C), 130.4 (Ar-C), 129.8 (Ar-C), 129.2 (Ar-C), 129.03 (Ar-C), 129.00 (Ar-C), 128.6 (Ar-C), 128.4 (Ar-C), 126.8 (Ar-C), 126.5 (2C, Ar-C)), 126.4 (Ar-C), 125.8 (Ar-C), 125.2 (Ar-C), 122.8 (Ar-C), 121.5 (Ar-C), 115.2 (Ar-C), 49.8 ($-CH_2-$), 21.4 ($-SO_2Ph\underline{C}H_3$); HRMS (ESI) m/z calcd for $C_{29}H_{22}NO_3S$ $[M + H]^+$ 464.1320, found 464.1318.

*12-Methoxy-15-tosyl-9H-dibenzo[5,6:7,8]cycloocta[1,2-b]indol-10(15H)-one (**8b**)* **:**

Pale yellow solid (65.6 mg, 95%), mp 206-208 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 7.96 (d, *J* = 9.0 Hz, 1H, Ar-H), 7.83 (s, 1H, Ar-H), 7.72 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.61 (t, *J* = 7.5 Hz, 1H, Ar-H), 7.54-7.48 (m, 3H, Ar-H), 7.38-7.32 (m, 3H, Ar-H), 7.04 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.90 (dd, *J* = 9.0, 2.4 Hz, 1H, Ar-H), 6.81 (d, *J* = 8.4 Hz, 2H, Ar-H), 3.83 (s, 3H, $-OCH_3$), 3.73 (d, *J* = 13.2 Hz, 1H, H_a of $-CH_2-$), 3.69 (d, *J* = 13.8 Hz, 1H, H_b of $-CH_2-$), 2.20 (s, 3H, $-SO_2PhC\underline{H_3}$); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz) δ_C 196.2 (C=O), 157.6 (Ar-C), 144.8 (Ar-C), 144.7 (Ar-C), 140.2 (Ar-C), 139.7 (Ar-C), 136.2 (Ar-C), 134.3 (Ar-C), 134.1 (Ar-C), 131.4 (Ar-C), 130.4 (Ar-C), 129.8 (Ar-C), 129.2 (3C, Ar-C), 129.1 (Ar-C), 129.0 (Ar-C), 128.5 (Ar-C), 128.4 (Ar-C), 126.8 (Ar-C), 126.5 (2C, Ar-C), 126.4 (Ar-C), 121.5 (Ar-C), 116.2 (Ar-C), 115.3 (Ar-C), 104.4 (Ar-C), 55.5 ($-OCH_3$), 49.7 ($-CH_2-$), 21.4 ($-SO_2Ph\underline{C}H_3$); HRMS (ESI) m/z calcd for $C_{30}H_{24}NO_4S$ $[M + H]^+$ 494.1426, found 494.1428.

*12-Methyl-15-tosyl-9H-dibenzo[5,6:7,8]cycloocta[1,2-b]indol-10(15H)-one (**8c**):*

White solid (58.1 mg, 87%), 220-222 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 8.14 (s, 1H, Ar-H), 7.94 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.72 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.61 (t, *J* = 7.5 Hz, 1H, Ar-H), 7.53-7.48 (m, 3H, Ar-H), 7.37-7.32 (m, 3H, Ar-H), 7.11 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.06 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.82 (d, *J* = 7.8 Hz, 2H, Ar-H), 3.71 (s, 2H, $-CH_2-$), 2.39 (s, 3H, $-CH_3$), 2.20 (s, 3H, $-SO_2PhC\underline{H_3}$); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz) δ_C 196.2 (C=O), 144.6 (Ar-C), 144.3 (Ar-C), 140.2 (Ar-C), 139.7 (Ar-C), 136.3 (Ar-C), 135.1 (Ar-C), 135.0 (Ar-C), 134.2 (Ar-C), 134.1 (Ar-C), 130.5 (Ar-C), 129.7 (Ar-C), 129.2 (2C, Ar-C), 129.0 (2C, Ar-C), 128.5 (Ar-C), 128.3 (Ar-C), 128.1 (Ar-C), 127.2 (Ar-C), 126.8 (Ar-C), 126.5 (2C, Ar-C), 126.4 (Ar-C), 122.6 (Ar-C), 121.4 (Ar-C), 114.9 (Ar-C), 49.8 ($-CH_2-$), 21.4 ($-CH_3/-SO_2Ph\underline{C}H_3$), 21.3 ($-SO_2Ph\underline{C}H_3$ $/-CH_3$); HRMS (ESI) m/z calcd for $C_{30}H_{24}NO_3S$ $[M + H]^+$ 478.1477, found 478.1481.

*Methyl 10-oxo-15-tosyl-10,15-dihydro-9H-dibenzo[5,6:7,8]cycloocta[1,2-b]indole-12-carboxylate (**8d**) :*

White solid (54.0 mg, 74%), mp 196-198 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.98 (s, 1H, Ar-H), 8.10 (d, *J* = 9.2 Hz, 1H, Ar-H), 7.98 (dd, *J* = 8.8, 2.0 Hz, 1H, Ar-H), 7.70 (dd, *J* = 7.8, 1.4 Hz, 1H, Ar-H), 7.63 (td, *J* = 7.5, 1.3 Hz, 1H, Ar-H), 7.55-7.46 (m, 3H, Ar-H), 7.38-7.32 (m, 3H, Ar-H), 7.05 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.83 (d, *J* = 8.4 Hz, 2H, Ar-H), 3.90 (s, 3H, $-CO_2CH_3$), 3.75-3.68 (m, 2H, $-CH_2-$), 2.21 (s, 3H, $-SO_2PhC\underline{H_3}$); $^{13}C\{^{1}H\}$ NMR

($CDCl_3$, 100 MHz) δ_C 195.7 (C=O), 167.1 (-$\underline{C}O_2CH_3$), 145.4 (Ar-C), 145.2 (Ar-C), 140.2 (Ar-C), 140.0 (Ar-C), 139.7 (Ar-C), 136.1 (Ar-C), 134.2 (Ar-C), 134.1 (Ar-C), 130.2 (Ar-C), 130.0 (Ar-C), 129.5 (2C, Ar-C), 129.2 (Ar-C), 129.1 (Ar-C), 128.8 (Ar-C), 128.6 (2C, Ar-C), 127.9 (Ar-C), 127.3 (Ar-C), 127.1 (Ar-C), 127.0 (Ar-C), 126.7 (Ar-C), 126.6 (Ar-C), 125.0 (Ar-C), 121.5 (Ar-C), 115.2 (Ar-C), 52.2 (-$CO_2\underline{C}H_3$), 49.9 (-CH_2-), 21.6 (-$SO_2Ph\underline{C}H_3$); HRMS (ESI) m/z calcd for $C_{31}H_{24}NO_5S$ $[M + H]^+$ 522.1375, found 522.1373.

*12-Chloro-15-tosyl-9H-dibenzo[5,6:7,8]cycloocta[1,2-b]indol-10(15H)-one (**8e**) :*

White solid (59.1 mg, 85%), mp 166-168 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.34-8.33 (m, 1H, Ar-H), 7.98 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.71-7.69 (m, 1H, Ar-H), 7.63 (td, *J* = 7.5, 1.3 Hz, 1H, Ar-H), 7.55-7.47 (m, 3H, Ar-H), 7.38-7.32 (m, 3H, Ar-H), 7.26-7.23 (m, 1H, Ar-H), 7.03 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.84 (d, *J* = 8.4 Hz, 2H, Ar-H), 3.69 (s, 2H, -CH_2-), 2.22 (s, 3H, -$SO_2PhC\underline{H_3}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 195.7 (C=O), 145.4 (Ar-C), 145.2 (Ar-C), 140.2 (Ar-C), 139.9 (Ar-C), 136.1 (Ar-C), 135.4 (Ar-C), 134.3 (Ar-C), 134.1 (Ar-C), 131.3 (Ar-C), 130.2 (Ar-C), 130.0 (Ar-C), 129.5 (2C, Ar-C), 129.3 (Ar-C), 129.2 (Ar-C), 129.1 (Ar-C), 128.7 (Ar-C), 128.6 (Ar-C), 127.0 (Ar-C), 126.7 (2C, Ar-C), 126.6 (Ar-C), 126.1 (Ar-C), 122.6 (Ar-C), 120.9 (Ar-C), 116.4 (Ar-C), 49.7 (-CH_2-), 21.6 (-$SO_2Ph\underline{C}H_3$); HRMS (ESI) m/z calcd for $C_{29}H_{21}ClNO_3S$ $[M + H]^+$ 498.0931, found 498.0906.

*13-Methoxy-15-tosyl-9H-dibenzo[5,6:7,8]cycloocta[1,2-b]indol-10(15H)-one (**8f**):*

Yellow solid (53.8 mg, 78%), mp 212-214 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.19 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.73-7.70 (m, 1H, Ar-H), 7.61-7.57 (m, 2H, Ar-H), 7.53-7.47 (m, 3H, Ar-H), 7.37-7.33 (m, 3H, Ar-H), 7.03 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.89 (dd, *J* = 8.8, 2.0 Hz, 1H, Ar-H), 6.81 (d, *J* = 8.0 Hz, 2H, Ar-H), 3.84 (s, 3H, -OCH_3), 3.69 (s, 2H, -CH_2-), 2.20 (s, 3H, -$SO_2PhC\underline{H_3}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 196.2 (C=O), 158.6 (Ar-C), 144.8 (Ar-C), 143.2 (Ar-C), 140.4 (Ar-C), 139.8 (Ar-C), 138.3 (Ar-C), 136.5 (Ar-C), 134.25 (Ar-C), 134.20 (Ar-C), 130.7 (Ar-C), 129.7 (Ar-C), 129.3 (2C, Ar-C), 129.1 (2C, Ar-C), 128.6 (Ar-C), 128.4 (Ar-C), 126.9 (Ar-C), 126.6 (Ar-C), 126.5 (2C, Ar-C), 123.6 (Ar-C), 121.8 (Ar-C), 121.7 (Ar-C), 114.2 (Ar-C), 99.7 (Ar-C), 55.8 (-OCH_3), 49.8 (-CH_2-), 21.5 (-$SO_2Ph\underline{C}H_3$); HRMS (ESI) m/z calcd for $C_{30}H_{24}NO_4S$ $[M + H]^+$ 494.1426, found 494.1427.

*Methyl 10-oxo-15-tosyl-10,15-dihydro-9H-dibenzo[5,6:7,8]cycloocta[1,2-b]indole-13-carboxylate (**8g**) :*
Yellow solid (45.2 mg, 62%), mp 212-214 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 8.77 (s, 1H, Ar-H), 8.37 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.96 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.70 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.64 (t, *J* = 7.5 Hz, 1H, Ar-H), 7.53 (t, *J* = 7.5 Hz, 1H, Ar-H), 7.50-7.49 (m, 2H, Ar-H), 7.38-7.34 (m, 3H, Ar-H), 7.09 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.84 (d, *J* = 7.8 Hz, 2H, Ar-H), 3.95 (s, 3H, -CO_2CH_3), 3.71 (s, 2H, -CH_2-), 2.21 (s, 3H, -$SO_2PhC\underline{H_3}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz) δ_C 195.7 (C=O), 166.9 (-$\underline{C}O_2CH_3$), 146.7 (Ar-C), 145.1 (Ar-C), 140.1 (Ar-C), 139.8 (Ar-C), 136.5 (Ar-C), 135.9 (Ar-C), 134.1 (Ar-C), 134.0 (Ar-C), 131.6 (Ar-C), 130.2 (Ar-C), 129.9 (Ar-C), 129.4 (2C, Ar-C), 129.2 (Ar-C), 129.0 (Ar-C), 128.7 (Ar-C), 128.5 (Ar-C), 127.4 (Ar-C), 127.0 (Ar-C), 126.6 (2C, Ar-C), 126.5 (Ar-C), 126.2 (Ar-C), 122.6 (Ar-C), 121.1 (Ar-C), 116.9 (Ar-C), 52.3 (-$CO_2\underline{C}H_3$), 49.7 (-CH_2-), 21.5 (-$SO_2Ph\underline{C}H_3$); HRMS (ESI) m/z calcd for $C_{31}H_{24}NO_5S$ $[M + H]^+$ 522.1375, found 522.1381.

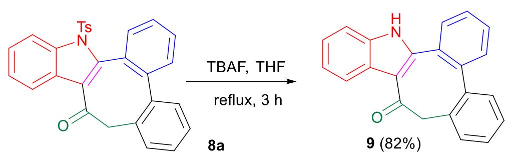
*3-Methoxy-15-tosyl-9H-dibenzo[5,6:7,8]cycloocta[1,2-b]indol-10(15H)-one (**8h**):*

Yellow solid (58.0 mg, 84%), mp 176-178 °C; ^{1}H NMR (CDCl$_3$, 400 MHz) δ_H 8.33-8.31 (m, 1H, Ar-H), 8.09-8.06 (m, 1H, Ar-H), 7.65 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.49-7.46 (m, 1H, Ar-H), 7.37-7.32 (m, 3H, Ar-H), 7.29-7.26 (m, 2H, Ar-H), 7.08-7.04 (m, 3H, Ar-H), 6.96 (d, *J* = 2.8 Hz, 1H, Ar-H), 6.81 (d, *J* = 8.0 Hz, 2H, Ar-H), 3.94 (s, 3H, -OCH$_3$), 3.75 (d, *J* = 13.6 Hz, 1H, H$_a$ of -CH$_2$-), 3.69 (d, *J* = 13.6 Hz, 1H, H$_b$ of -CH$_2$-), 2.19 (s, 3H, -SO$_2$PhC$\underline{H_3}$); ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz) δ_C 196.1 (C=O), 160.5 (Ar-C), 144.8 (2C, Ar-C), 141.4 (Ar-C), 140.3 (Ar-C), 137.0 (Ar-C), 136.2 (Ar-C), 136.0 (Ar-C), 134.4 (Ar-C), 129.3 (2C, Ar-C), 129.0 (Ar-C), 128.6 (Ar-C), 128.5 (Ar-C), 128.2 (Ar-C), 126.9 (Ar-C), 126.6 (2C, Ar-C), 125.7 (Ar-C), 125.3 (Ar-C), 122.9 (Ar-C), 122.8 (Ar-C), 121.4 (Ar-C), 115.5 (Ar-C), 114.1 (Ar-C), 112.6 (Ar-C), 55.5 (-OCH$_3$), 49.9 (-CH$_2$-), 21.5 (-SO$_2$Ph$\underline{C}$H$_3$); HRMS (ESI) m/z calcd for $C_{30}H_{24}NO_4S$ [M + H]$^+$ 494.1426, found 494.1423.

*15-Tosyl-9H-dibenzo[3',4':5',6']cycloocta[1',2':4,5]pyrrolo[2,3-b]pyridin-10(15H)-one (**8i**) :*

White solid (39.0 mg, 60%), mp 186-188 °C; ^{1}H NMR (CDCl$_3$, 600 MHz) δ_H 8.56 (d, *J* = 7.8 Hz, 1H, Ar-H), 8.42-8.41 (m, 1H, Ar-H), 7.65-7.57 (m, 5H, Ar-H), 7.53-7.51 (m, 2H, Ar-H), 7.41-7.37 (m, 1H, Ar-H), 7.34-7.33 (m, 2H, Ar-H), 7.23-7.20 (m, 1H, Ar-H), 7.00 (d, *J* = 7.8 Hz, 2H, Ar-H), 3.75-3.70 (m, 2H, -CH$_2$-), 2.27 (s, 3H, -SO$_2$PhC$\underline{H_3}$); ^{13}C{^{1}H} NMR (CDCl$_3$, 150 MHz) δ_C 195.8 (C=O), 149.1 (Ar-C), 145.8 (Ar-C), 145.1 (Ar-C), 144.0 (Ar-C), 140.3 (Ar-C), 139.9 (Ar-C), 135.9 (Ar-C), 135.1 (Ar-C), 132.8 (Ar-C), 131.4 (Ar-C), 130.4 (Ar-C), 130.0 (Ar-C), 129.1 (3C, Ar-C), 129.0 (Ar-C), 128.5 (Ar-C), 128.4 (Ar-C), 128.0 (2C, Ar-C), 127.2 (Ar-C), 126.7 (Ar-C), 120.6 (Ar-C), 120.4 (Ar-C), 118.4 (Ar-C), 49.7 (-CH$_2$-), 21.5 (-SO$_2$Ph$\underline{C}$H$_3$); HRMS (ESI) m/z calcd for $C_{28}H_{21}N_2O_3S$ [M + H]$^+$ 465.1273, found 465.1278.

17. Schematic representaion and general procedure of the synthesis of Product 9:



Scheme S3. *N*-Detosylation of product **8a.**

To a well stirred solution of **8a** (0.065 mmol, 1 equiv) in dry THF (2 mL), TBAF (93.64 µL, 0.324 mmol, 5 equiv) was added and the resulting mixture was refluxed under argon atmosphere. After 3 h, upon completion of reaction (TLC), the mixture was diluted with water (8 mL) and extracted with ethyl acetate (3 x 15 mL). The combined organic extracts were then washed with brine (10 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Then the resulting residue was purified by silica gel (100-200 mesh) column chromatography eluting with 15% ethyl acetate-petroleum ether (v/v) to obtain the pure product **9** in 82% yield.

18. Spectral data of product 9:

*9H-Dibenzo[5,6:7,8]cycloocta[1,2-b]indol-10(15H)-one (**9**)* :

White solid (16.5 mg, 82%), mp >250 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.52-8.48 (m, 1H, Ar-H), 8.40 (brs, 1H, -NH-), 7.69-7.67 (m, 1H, Ar-H), 7.62-7.53 (m, 3H, Ar-H), 7.43 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.34-7.30 (m, 3H, Ar-H), 7.29-7.22 (m, 3H, Ar-H), 3.88 (d, *J* = 12.4 Hz, 1H, H_a of -CH_2-), 3.67 (d, *J* = 12.4 Hz, 1H, H_b of -CH_2-); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 194.7 (C=O), 142.3 (Ar-C), 141.0 (Ar-C), 139.4 (Ar-C), 136.7 (Ar-C), 135.2 (Ar-C), 132.2 (Ar-C), 131.0 (Ar-C), 129.6 (Ar-C), 129.5 (Ar-C), 129.4 (Ar-C), 128.6 (Ar-C), 128.4 (Ar-C), 128.1 (Ar-C), 127.4 (Ar-C), 126.9 (Ar-C), 124.1 (Ar-C), 123.0 (Ar-C), 122.7 (Ar-C), 115.2 (Ar-C), 110.5 (Ar-C), 48.6 (-CH_2-); HRMS (ESI) m/z calcd for $C_{22}H_{16}NO$ $[M + H]^+$ 310.1232, found 310.1236.

19. References:

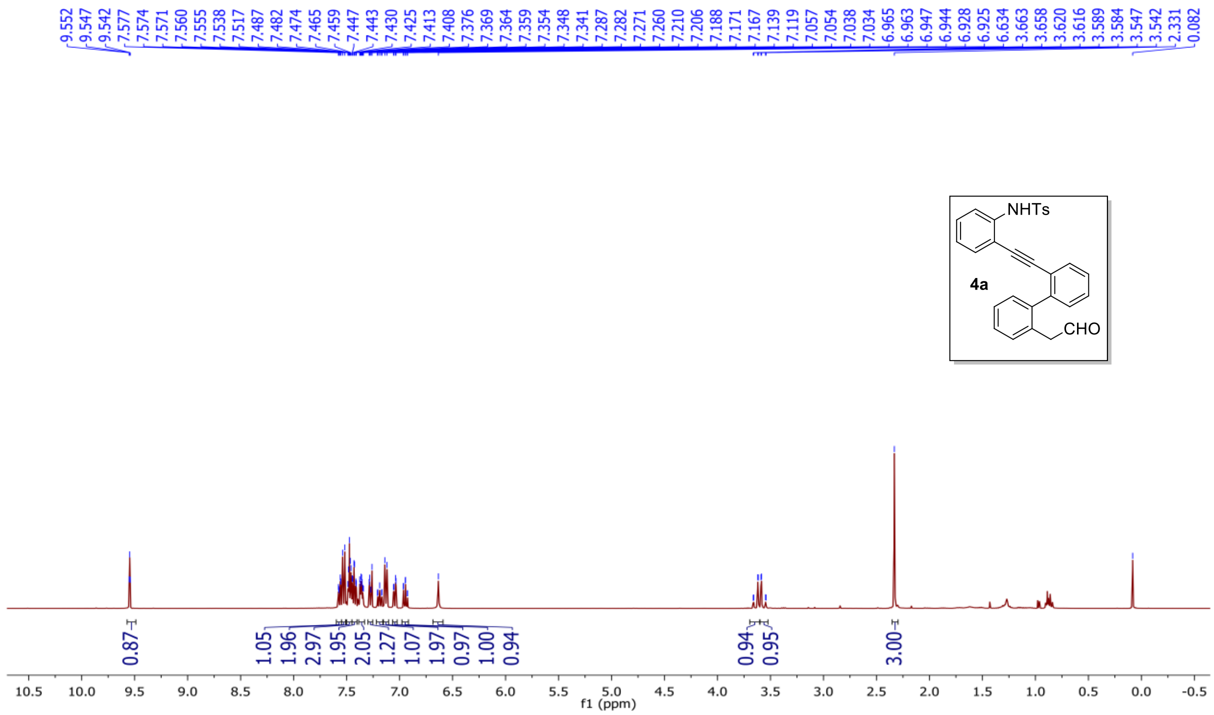
1. Sheldrick, G. M. *Acta Crystallogr., Sect. A,* Phase Annealing in *SHELX*-90: Direct Methods for Larger Structures. 1990, **46**, 467.

2. Sheldrick, G. M. SHELX - 97, Program for Crystallography Refinement, University of Gottingen: Gottingen, Germany, **1997**.

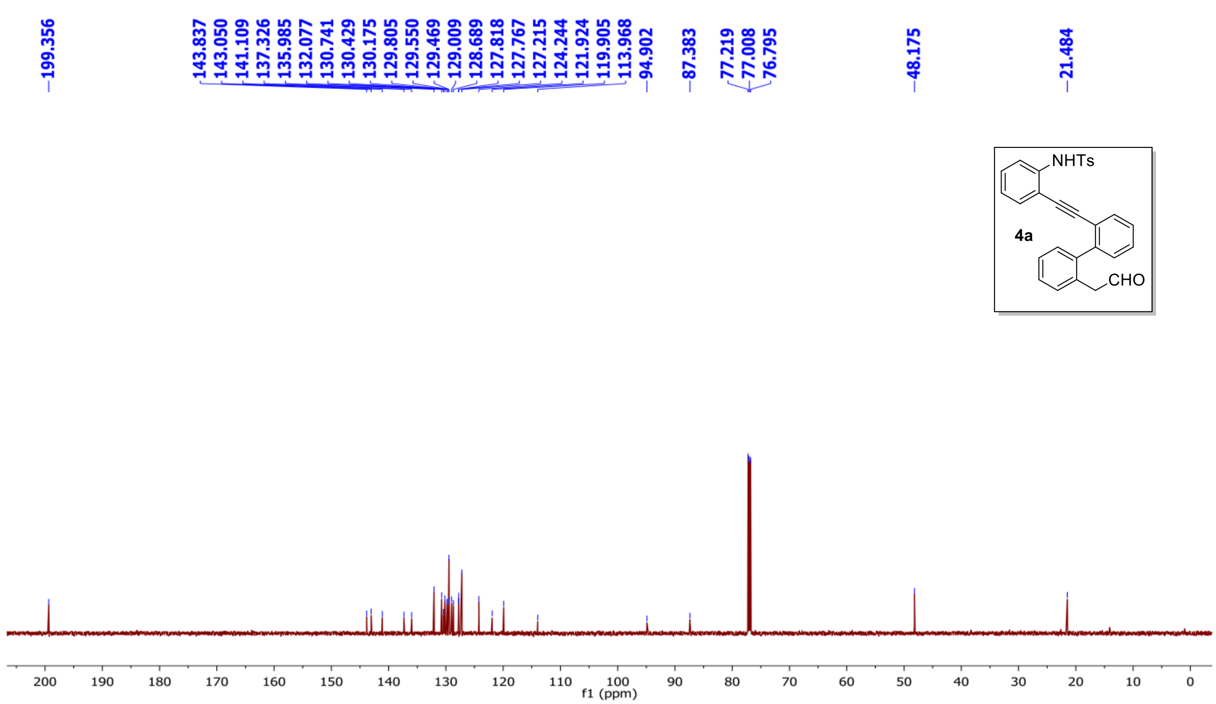
3. A. Kondoh, R. Ozawa, T. Aokib and M. Terada*, Org. Biomol. Chem.*, 2017, **15**, 7277.

20. NMR spectra of compounds 4a-4q :

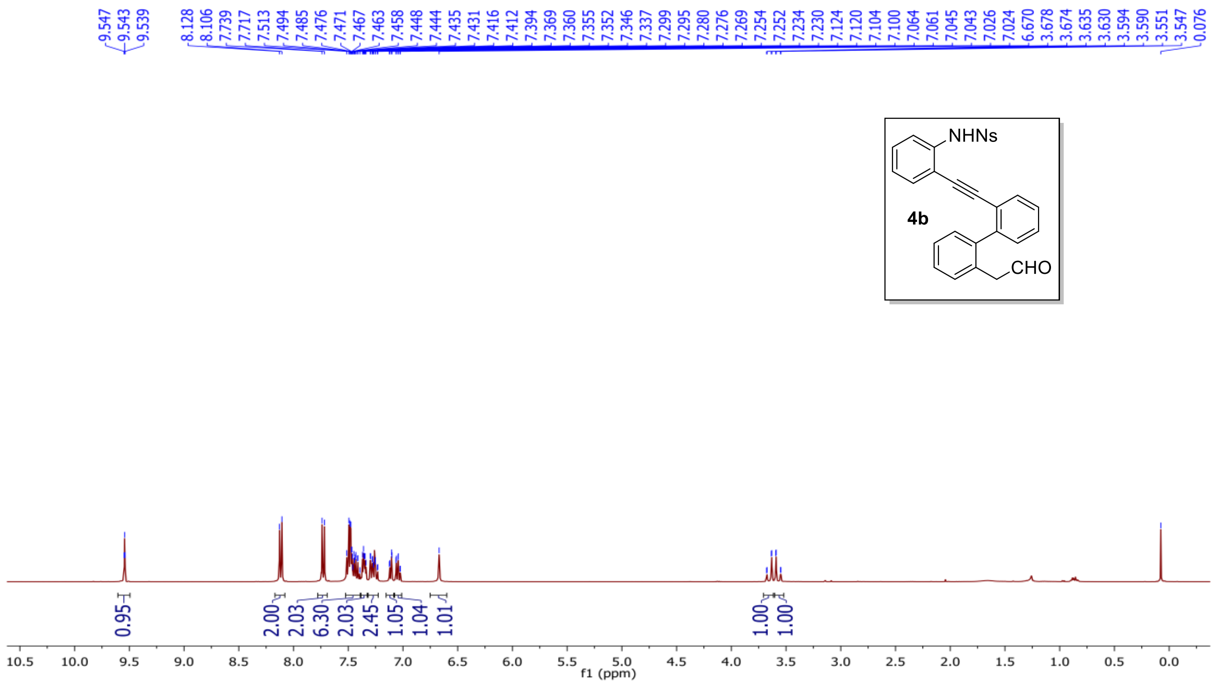
^{1}H NMR (400 MHz) of **4a :**



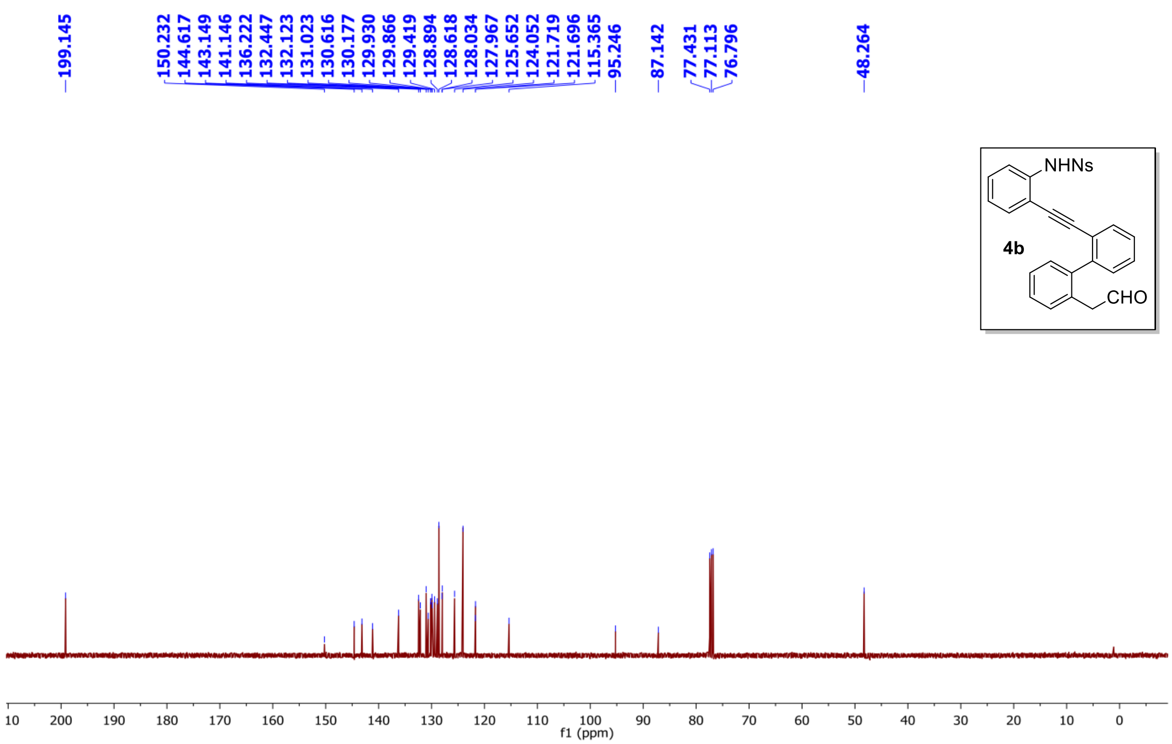
^{13}C{^{1}H} NMR (150 MHz) of **4a :**



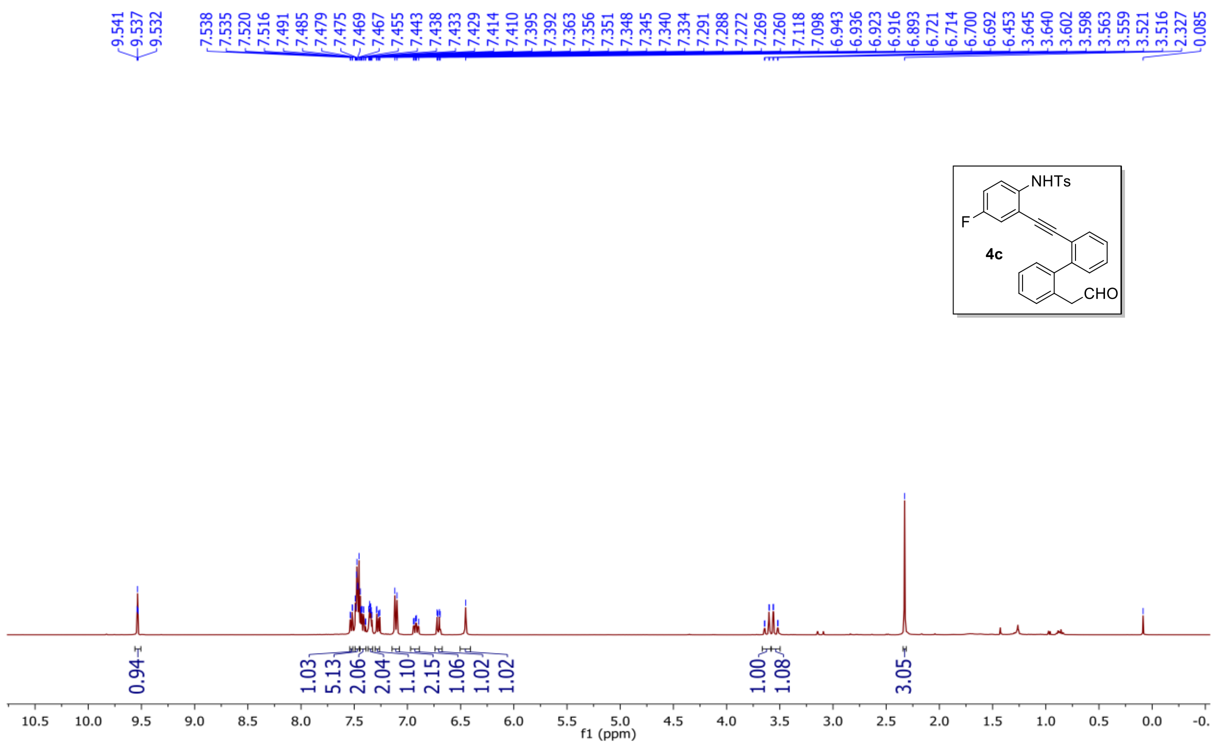
^{1}H NMR (400 MHz) of **4b :**



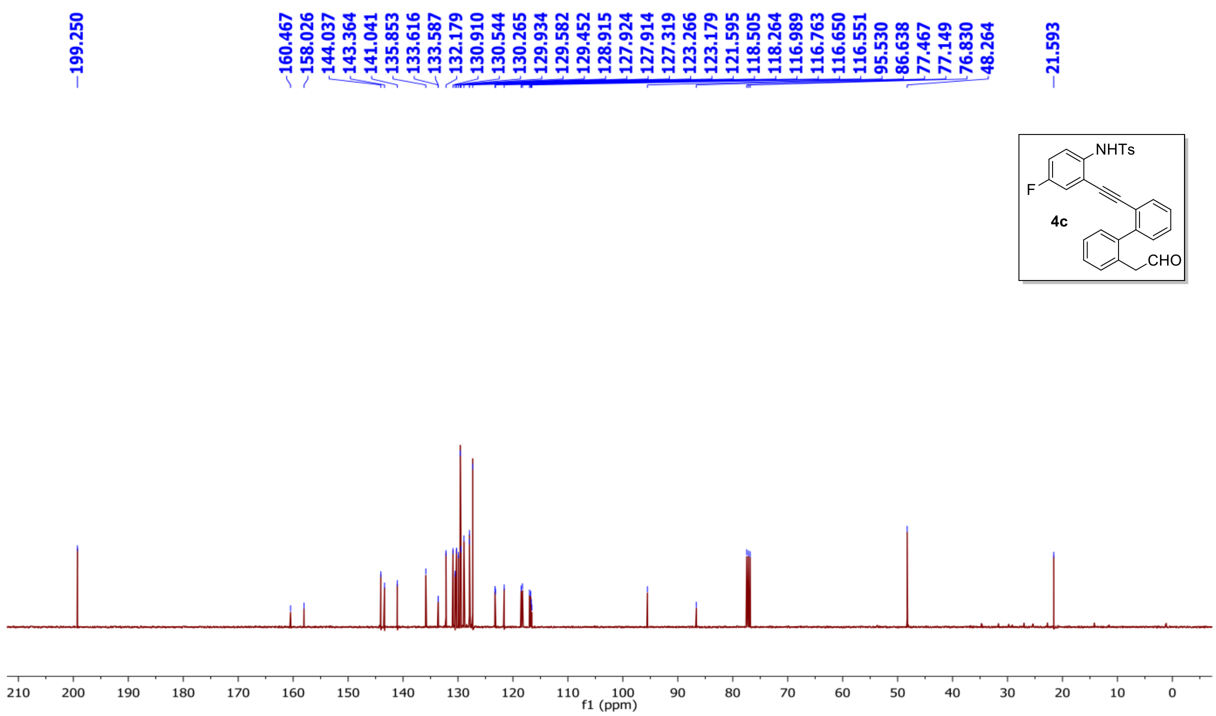
$^{13}C\{^{1}H\}$ NMR (100 MHz) of **4b :**



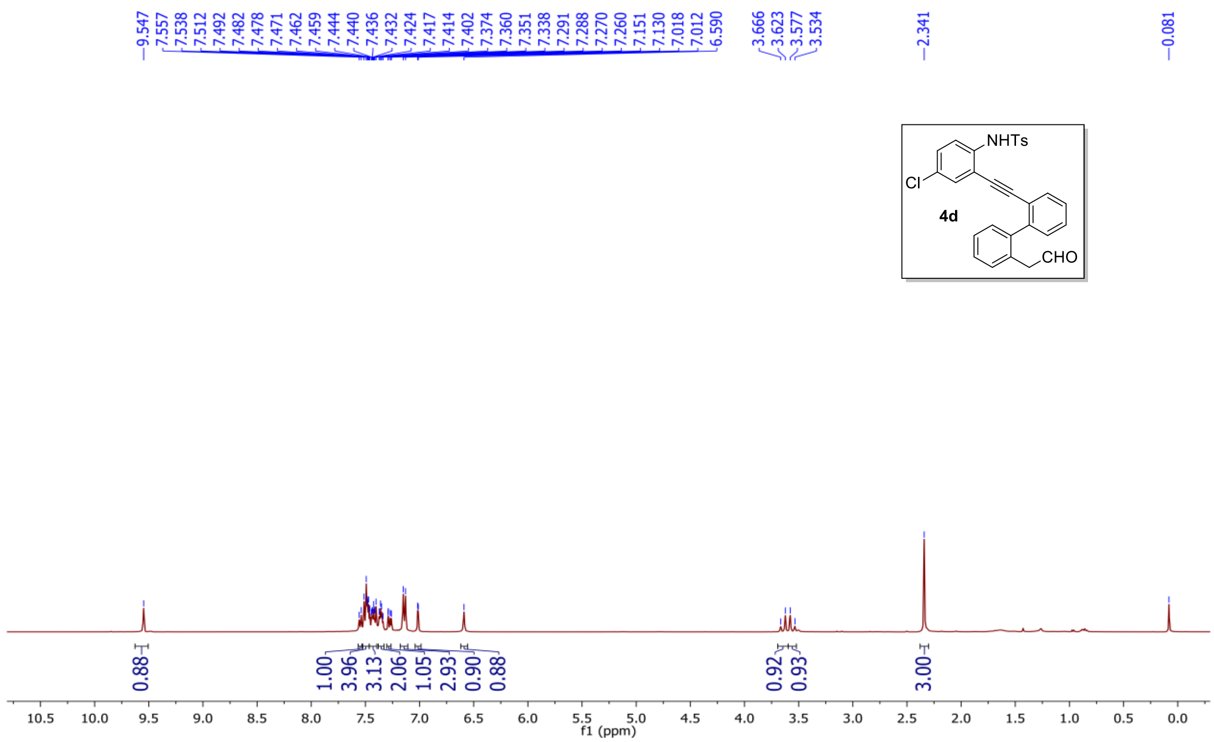
^{1}H NMR (400 MHz) of **4c :**



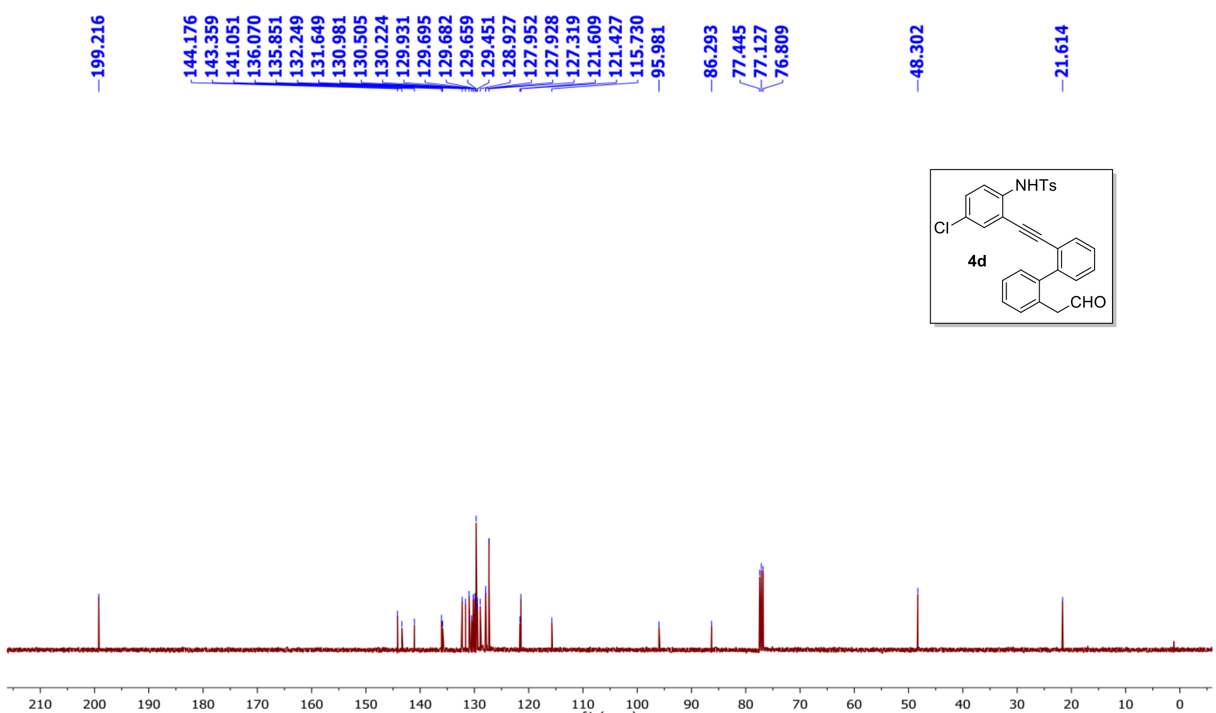
^{13}C{^{1}H} NMR (100 MHz) of **4c :**



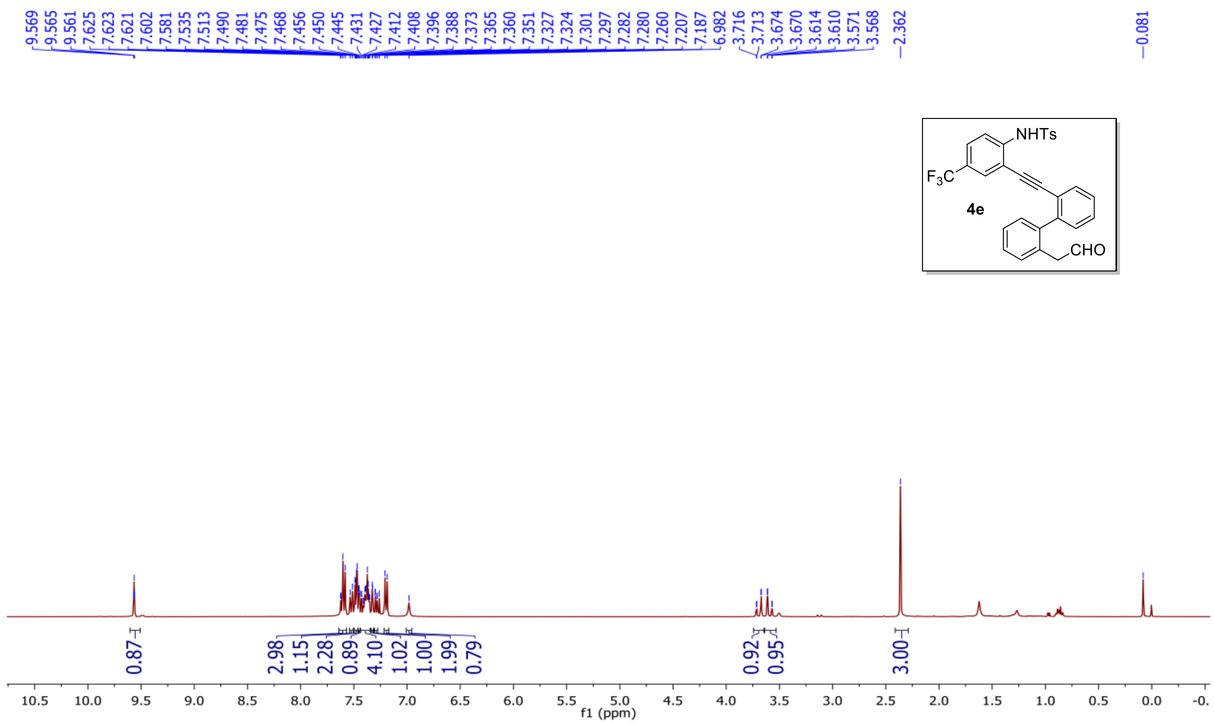
^{1}H NMR (400 MHz) of **4d :**



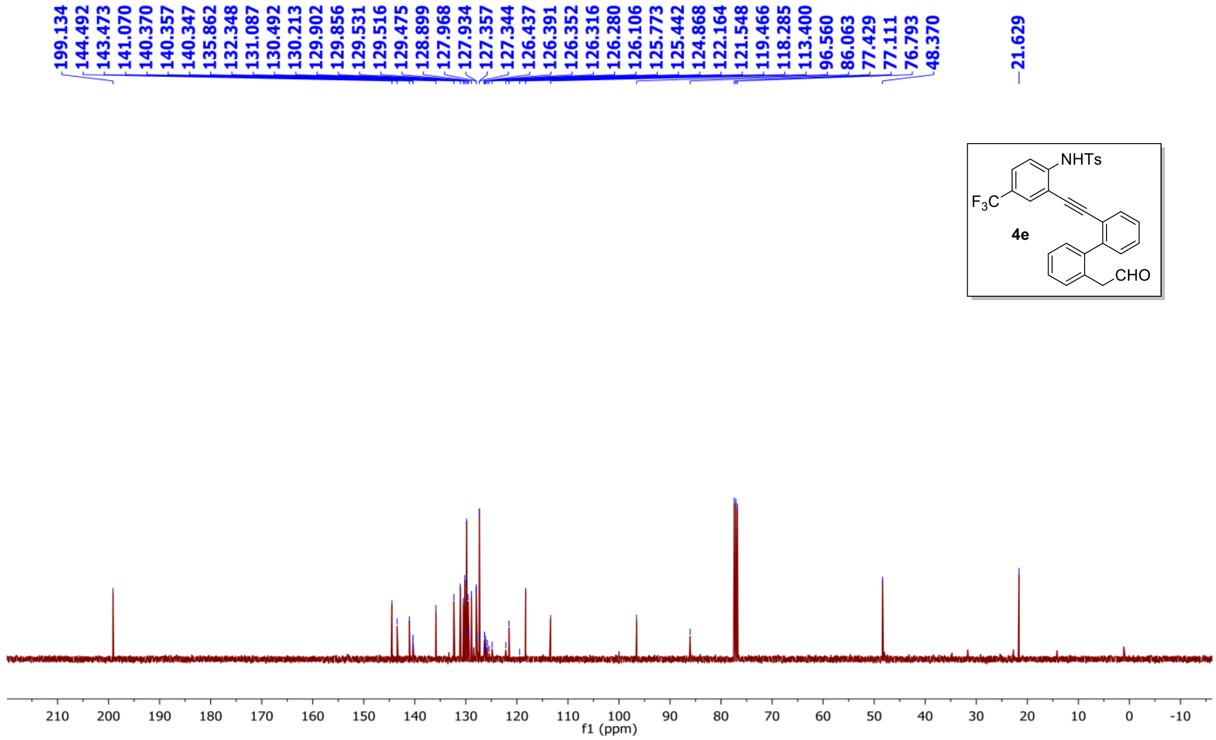
^{13}C{^{1}H} NMR (100 MHz) of **4d:**



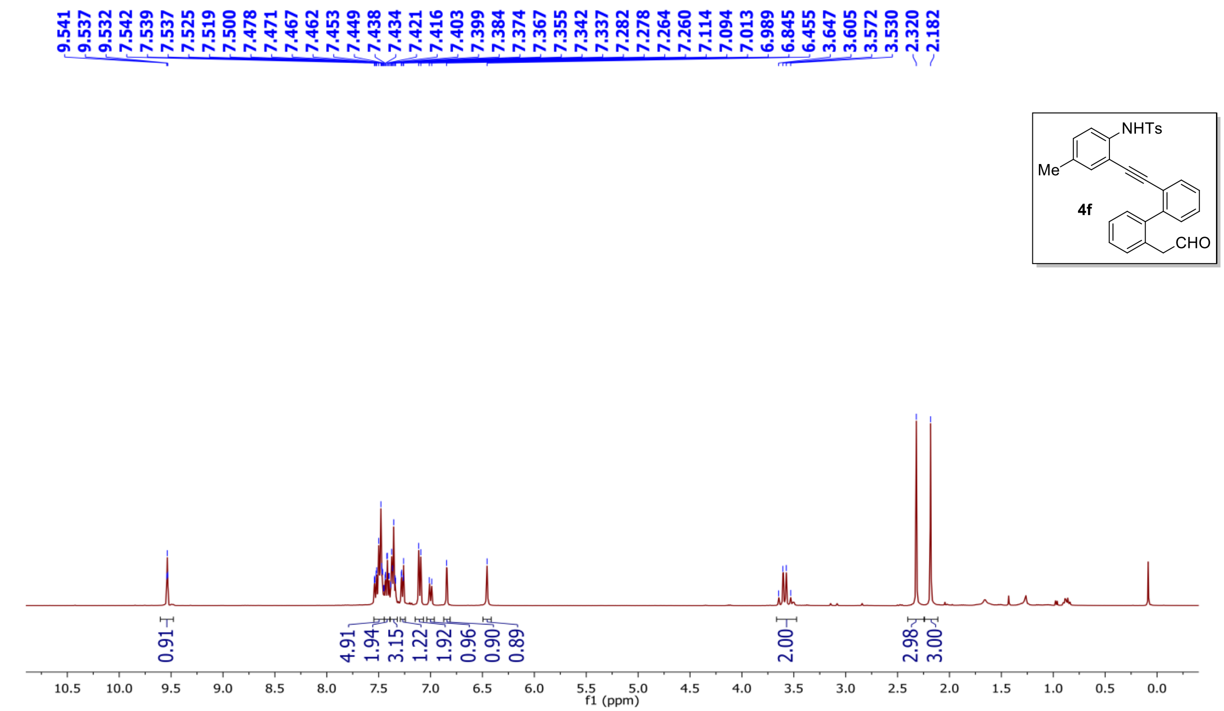
^{1}H NMR (400 MHz) of **4e :**



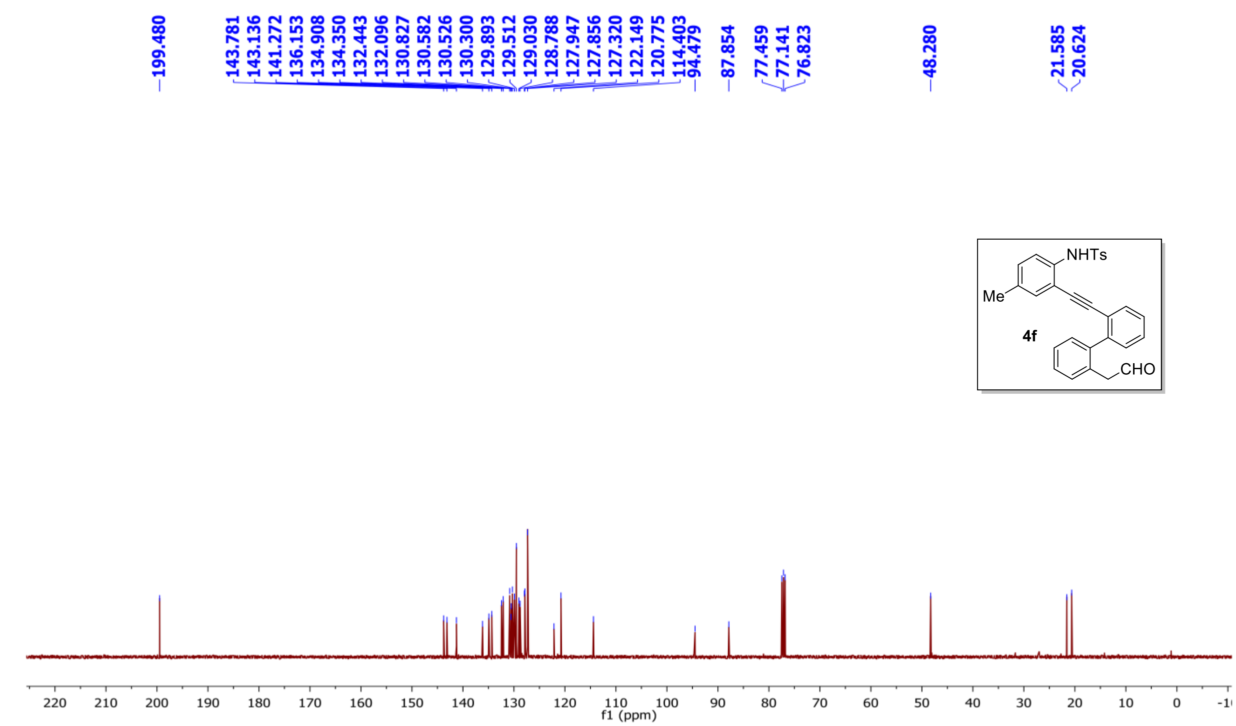
^{13}C{^{1}H} NMR (100 MHz) of **4e :**



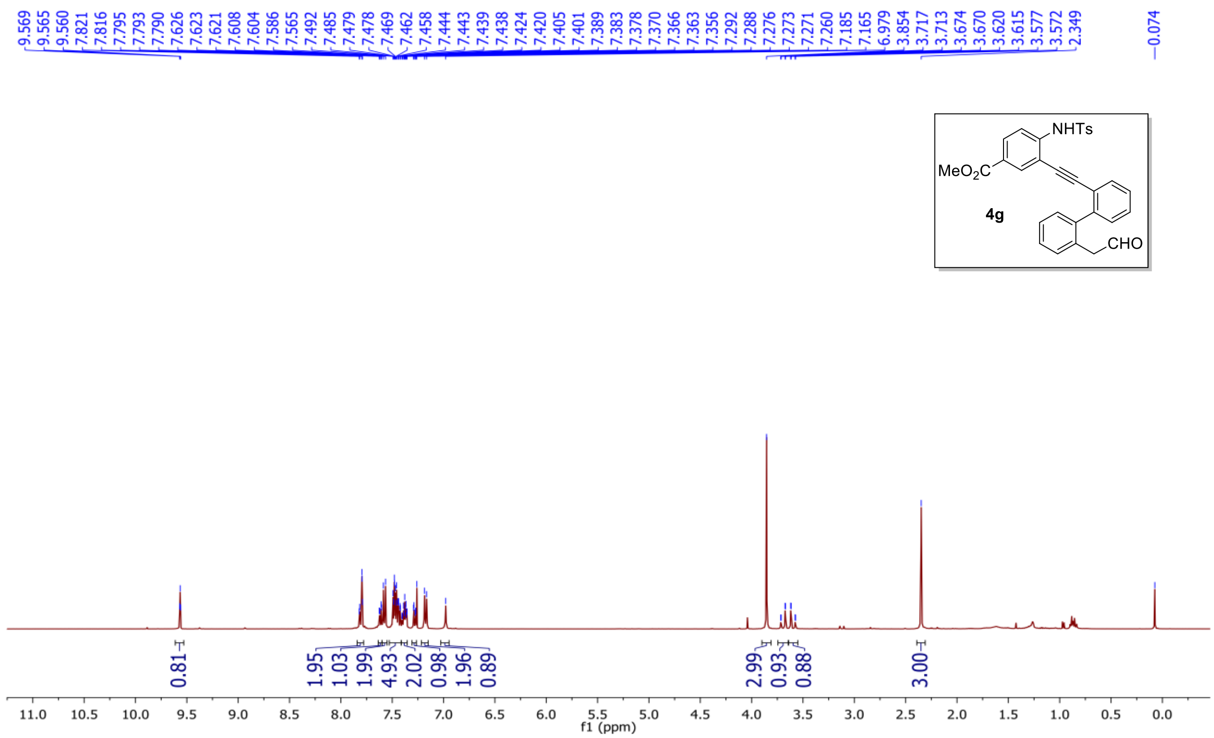
^{1}H NMR (400 MHz) of **4f :**



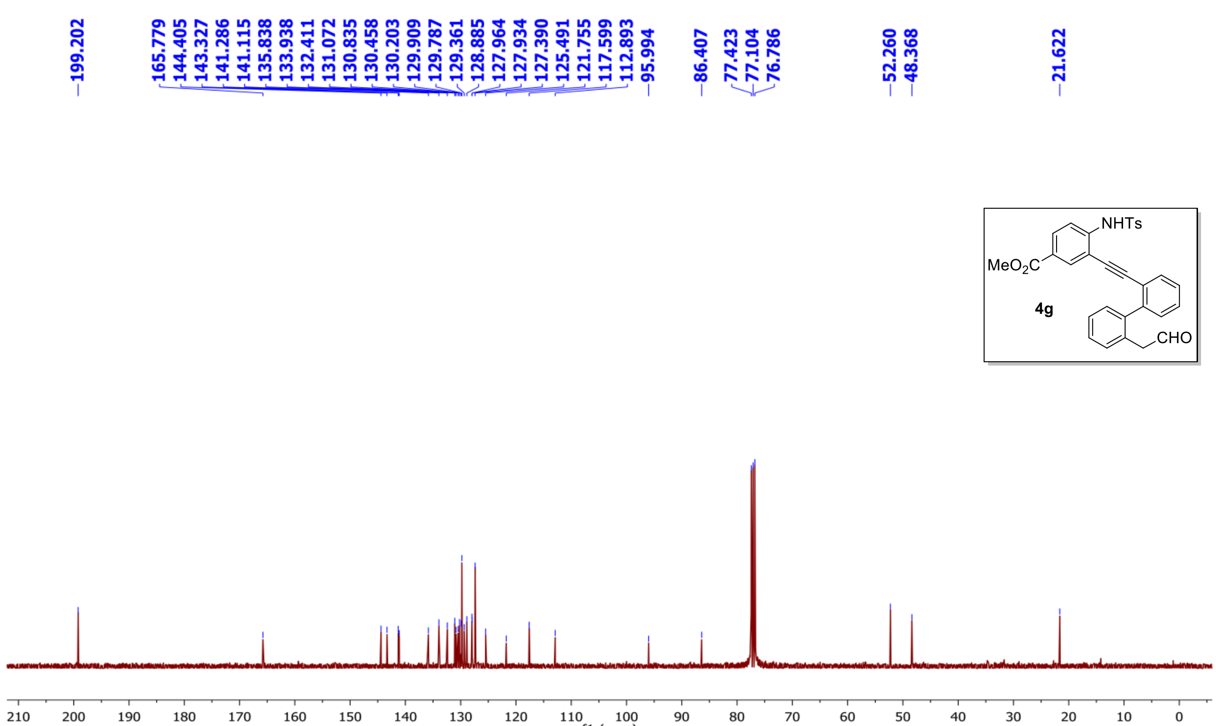
^{13}C{^{1}H} NMR (100 MHz) of **4f :**



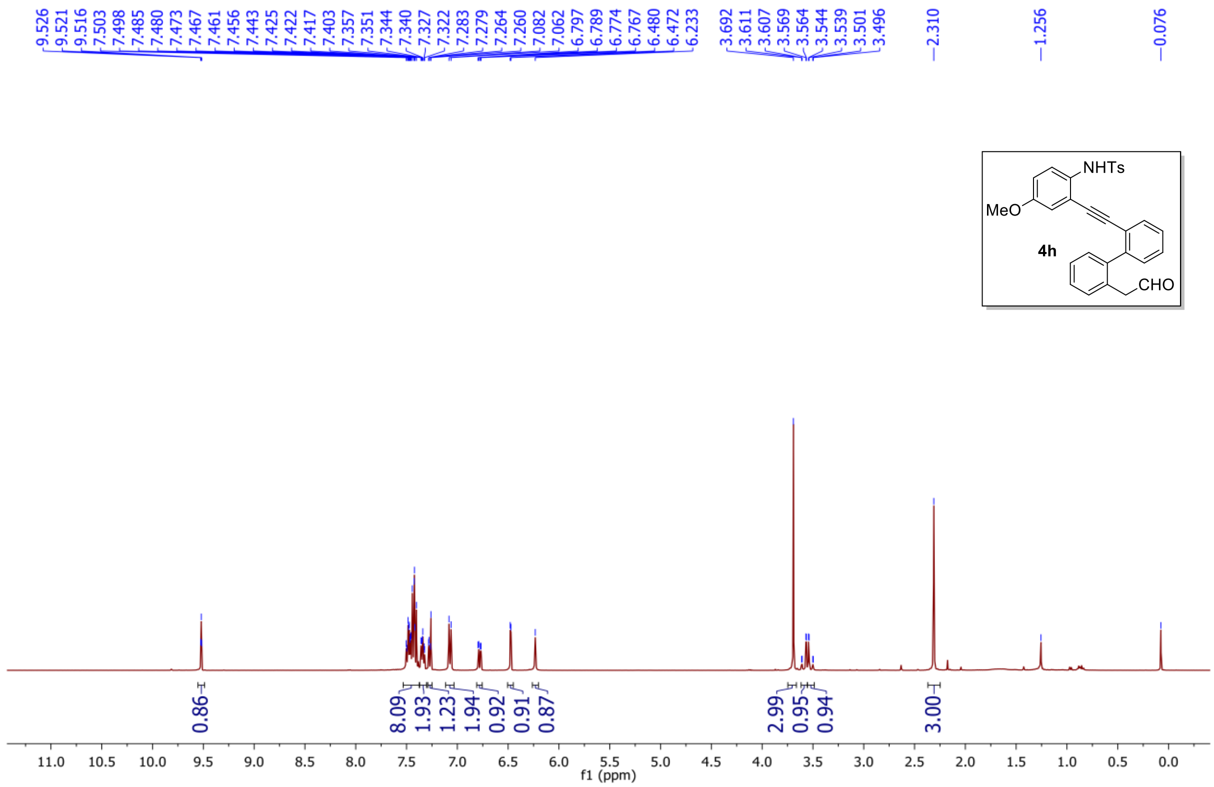
^{1}H NMR (400 MHz) of **4g :**



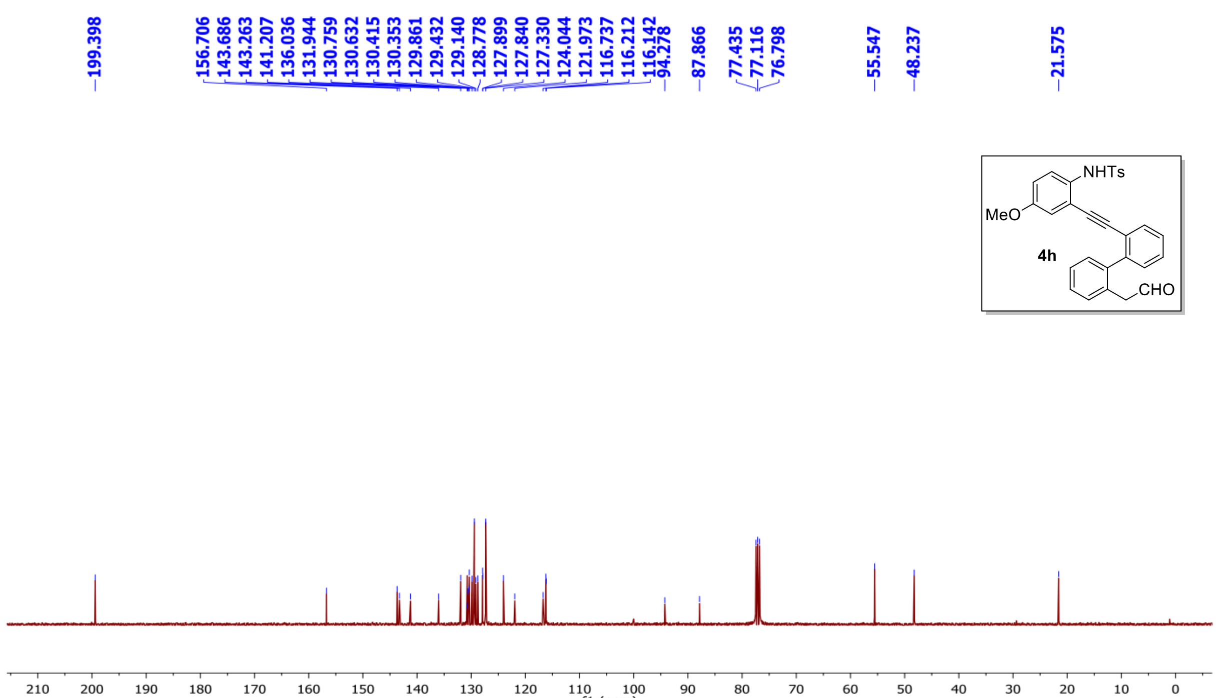
^{13}C{^{1}H} NMR (100 MHz) of **4g :**



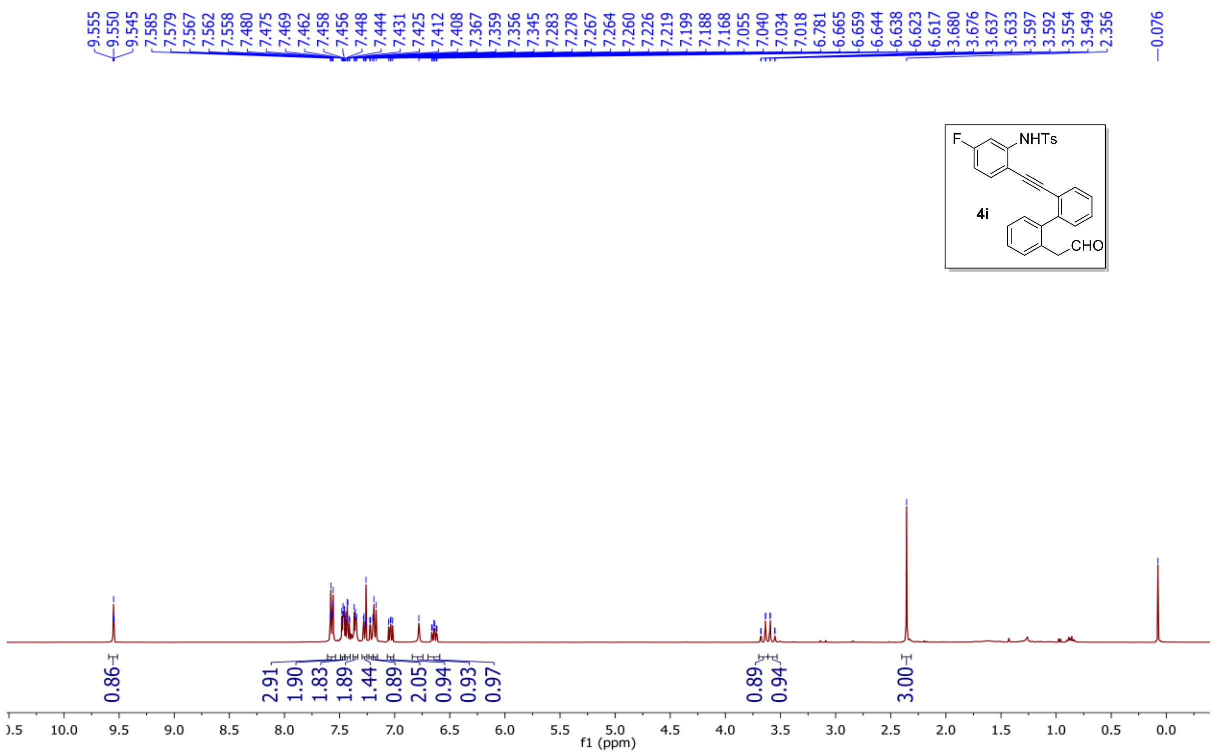
^{1}H NMR (400 MHz) of **4h :**



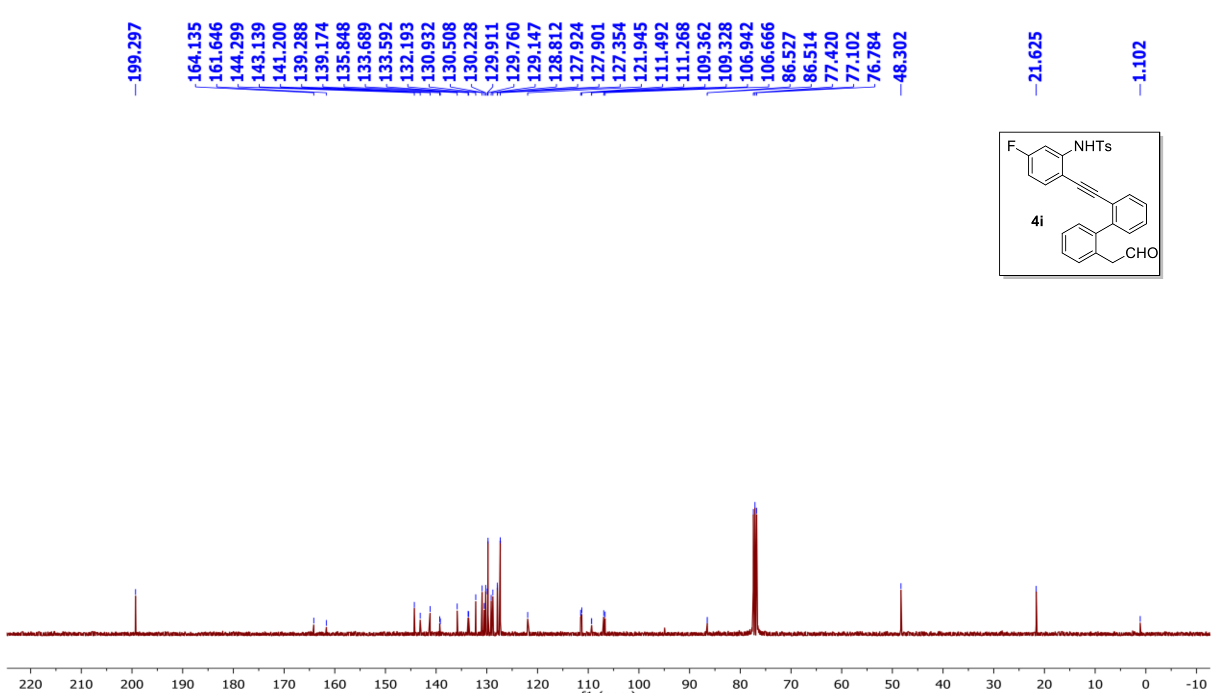
$^{13}C\{^{1}H\}$ NMR (100 MHz) of **4h :**



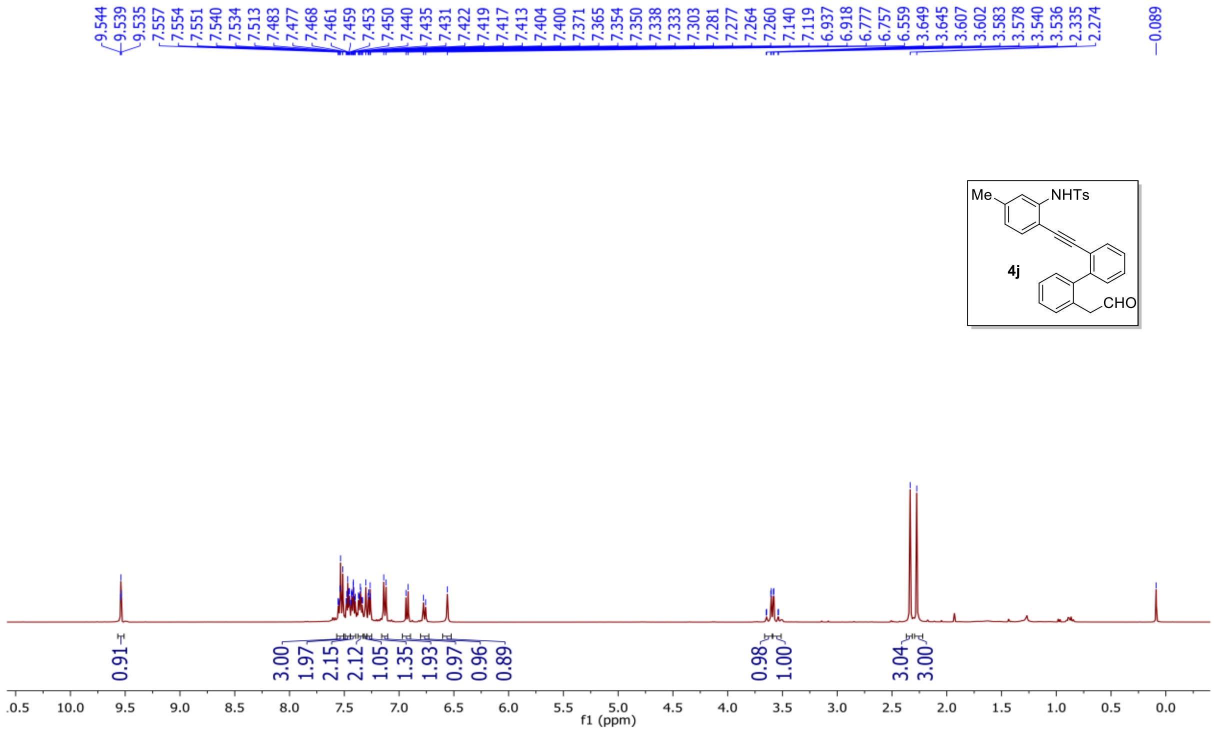
^{1}H NMR (400 MHz) of **4i :**



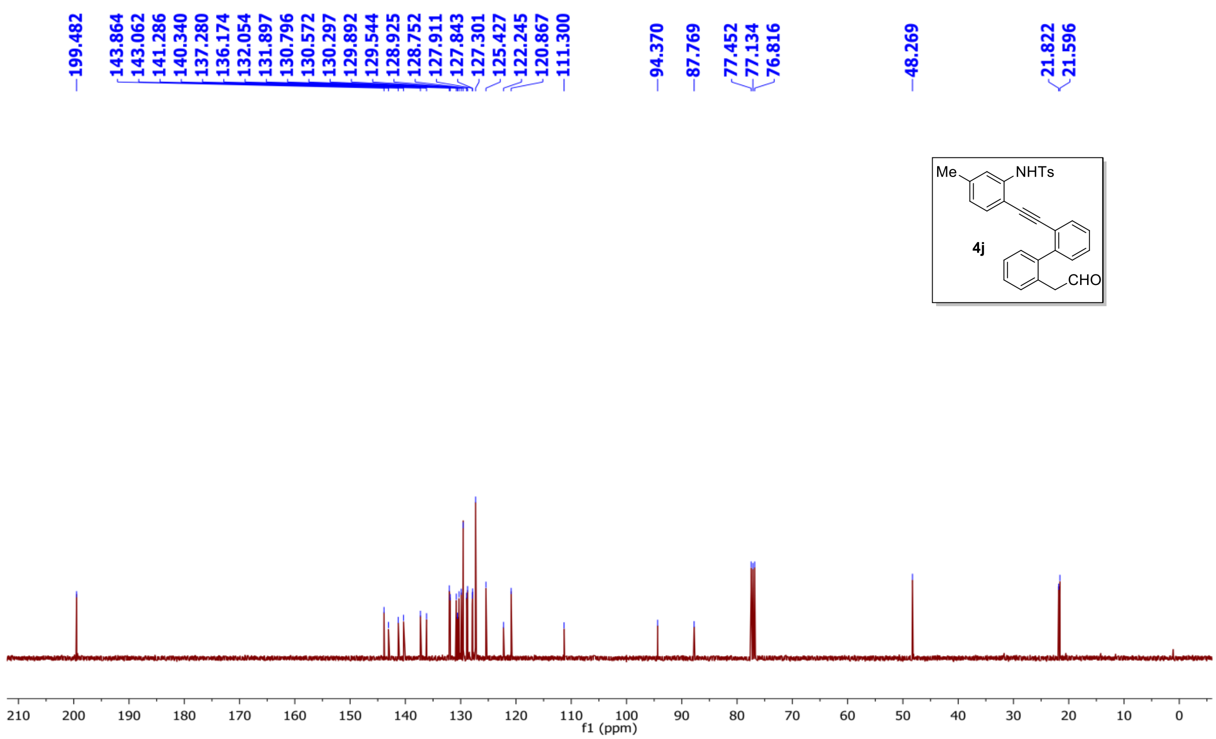
$^{13}C\{^{1}H\}$ NMR (100 MHz) of **4i :**



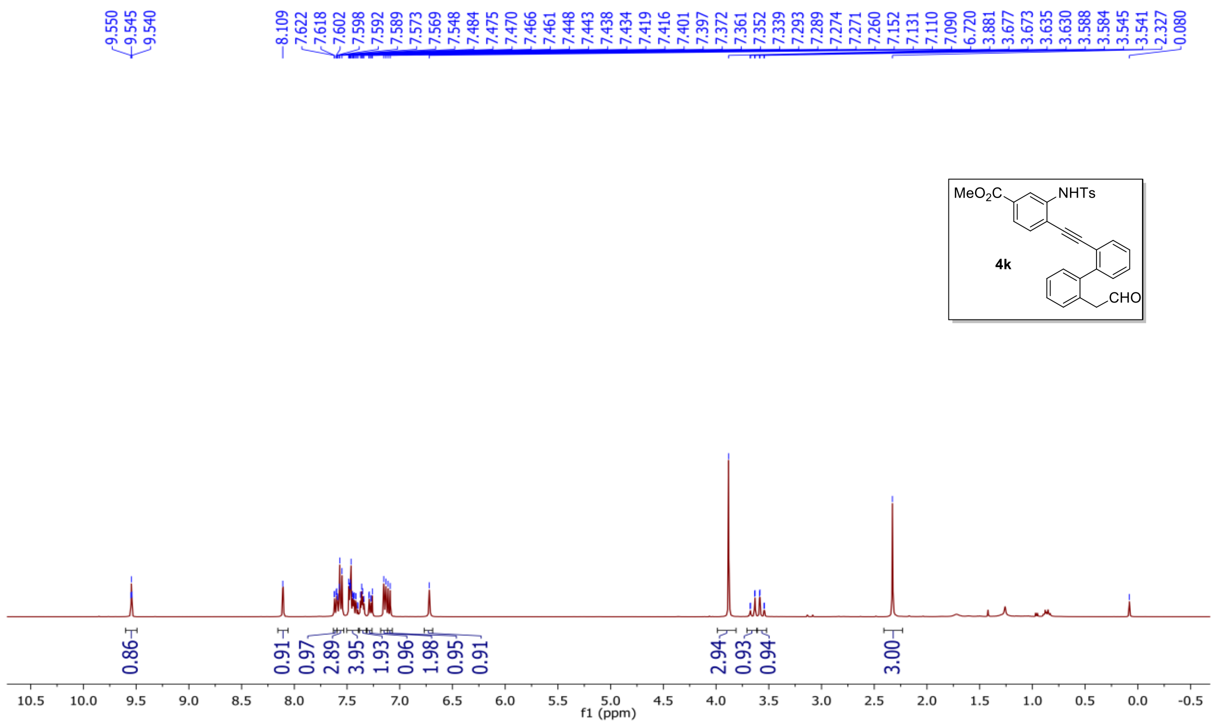
^{1}H NMR (400 MHz) of **4j :**



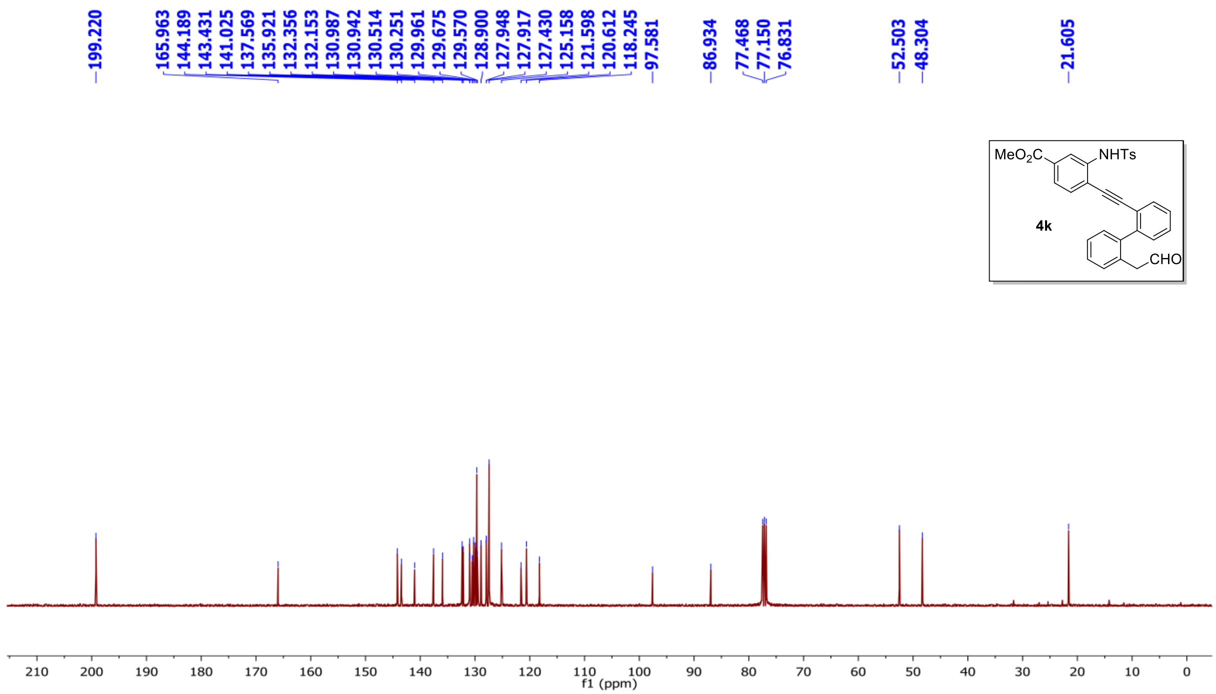
^{13}C{^{1}H} NMR (100 MHz) of **4j :**



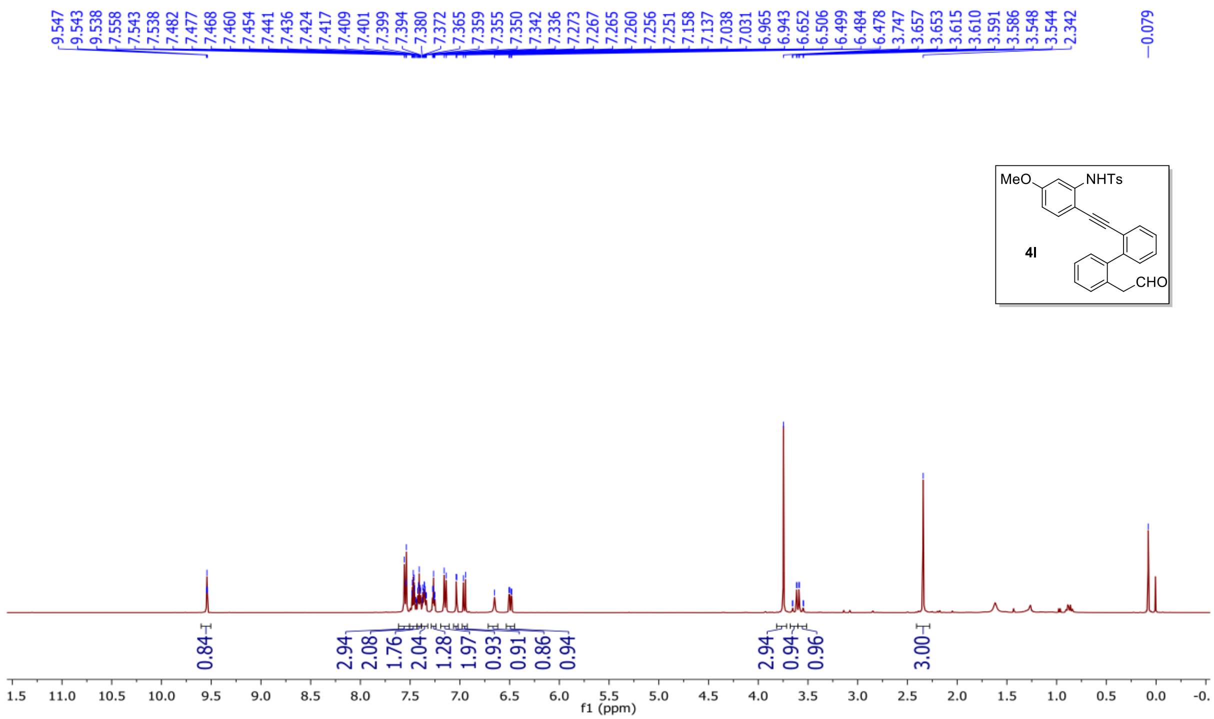
^{1}H NMR (400 MHz) of **4k :**



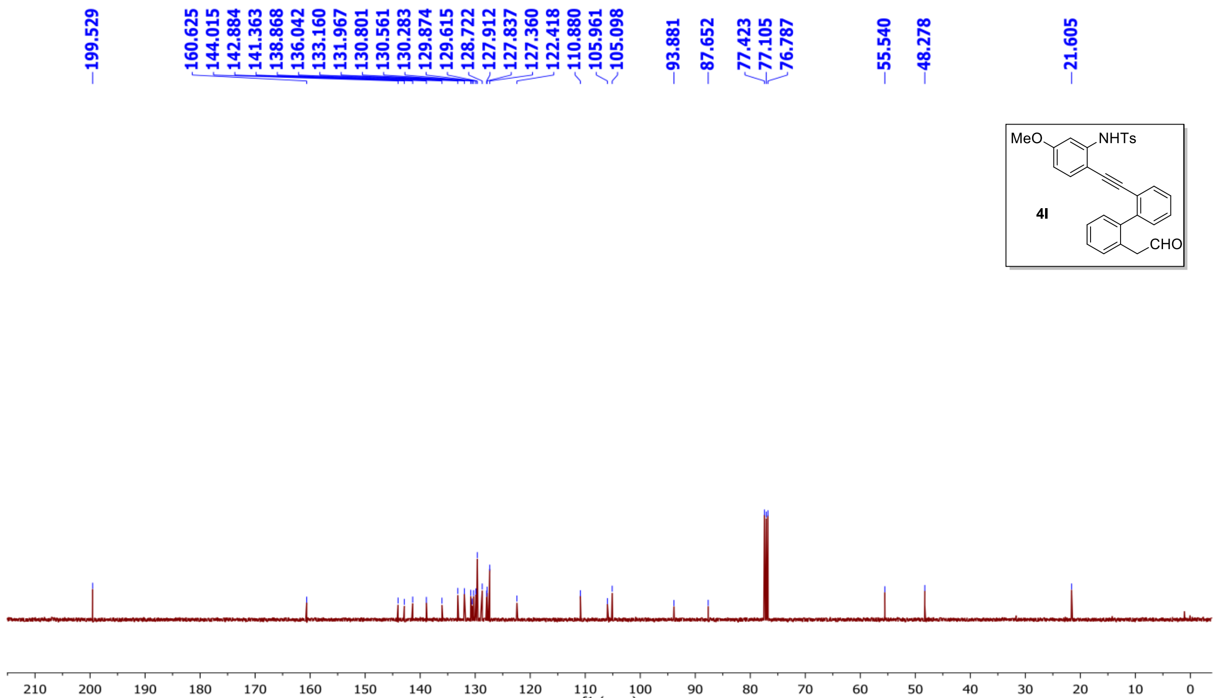
^{13}C{^{1}H} NMR (100 MHz) of **4k :**



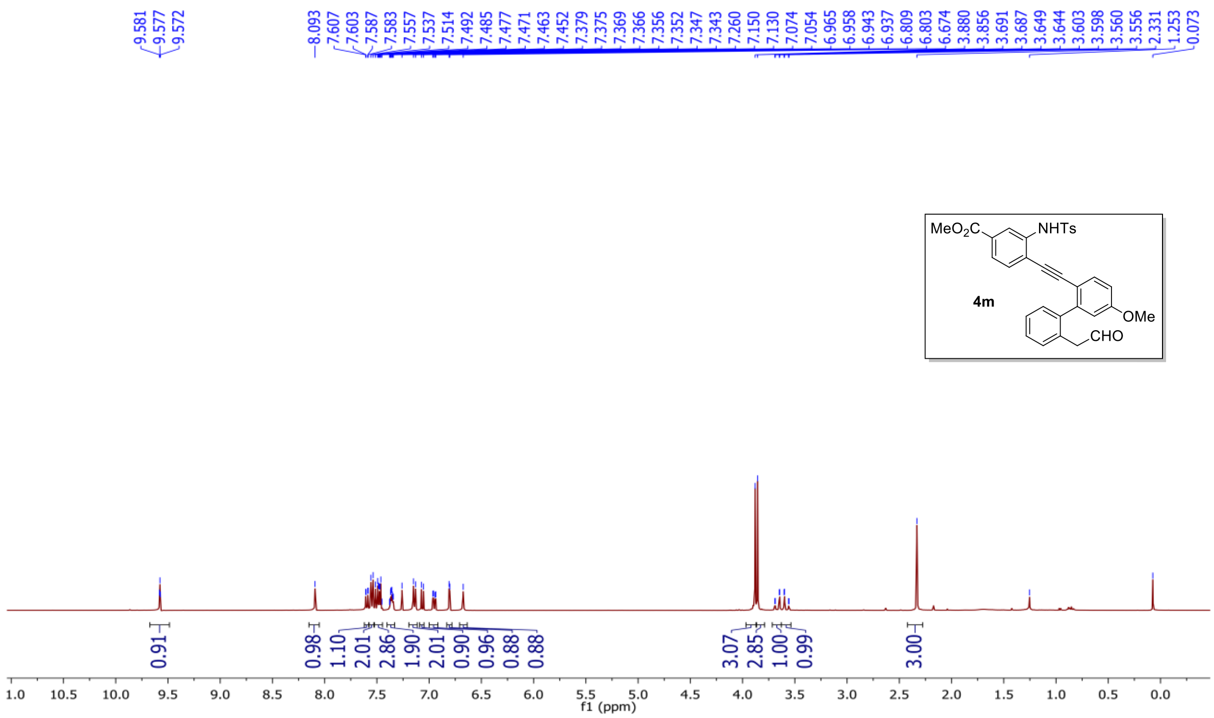
^{1}H NMR (400 MHz) of **4l :**



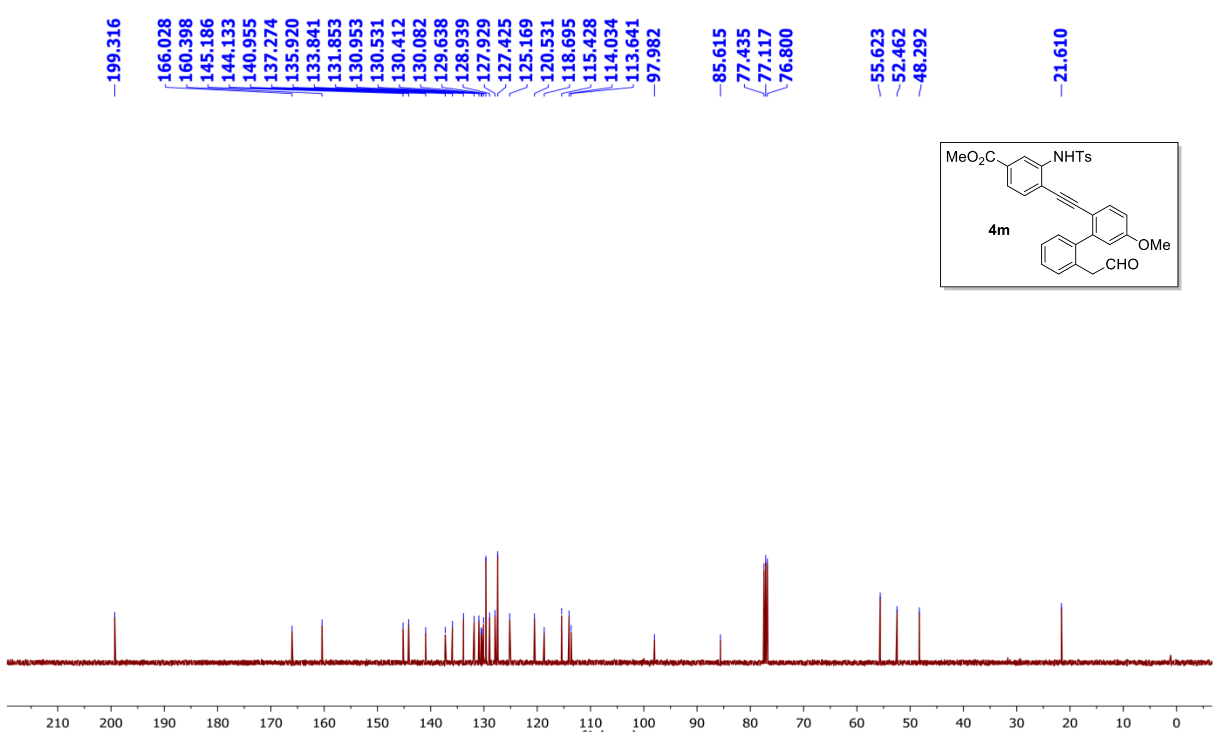
$^{13}C\{^{1}H\}$ NMR (100 MHz) of **4l :**



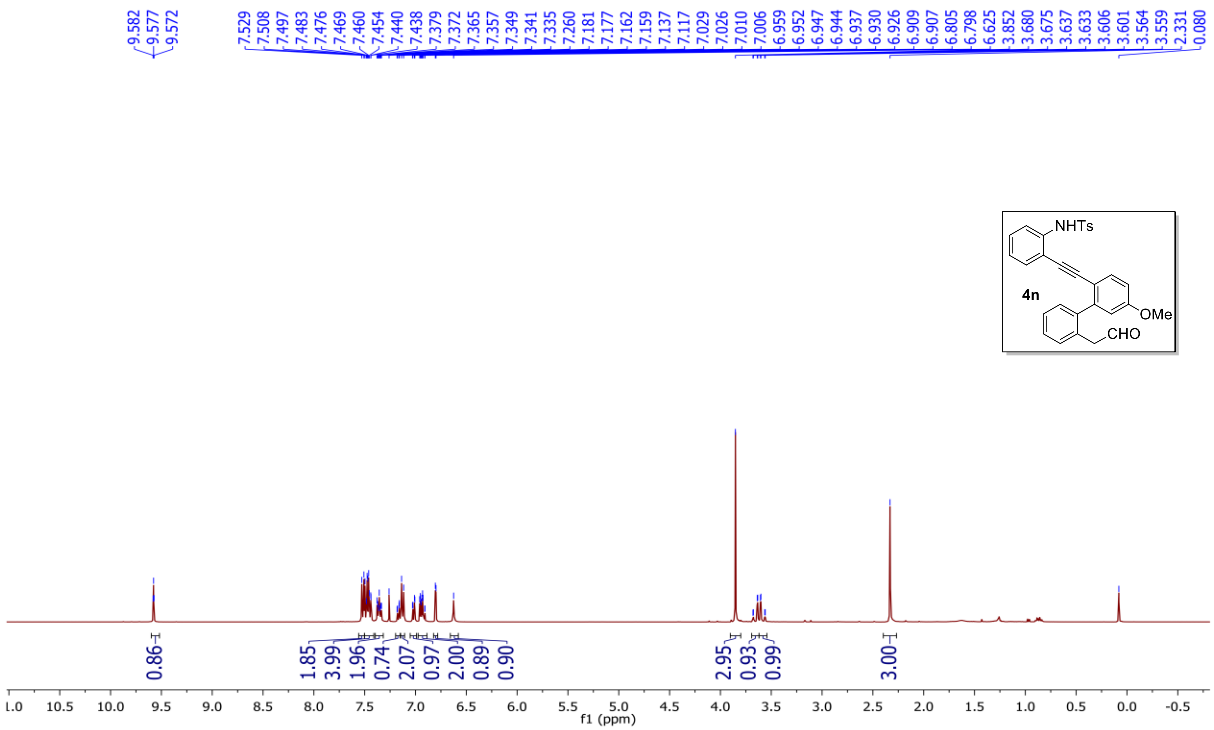
^{1}H NMR (400 MHz) of **4m :**



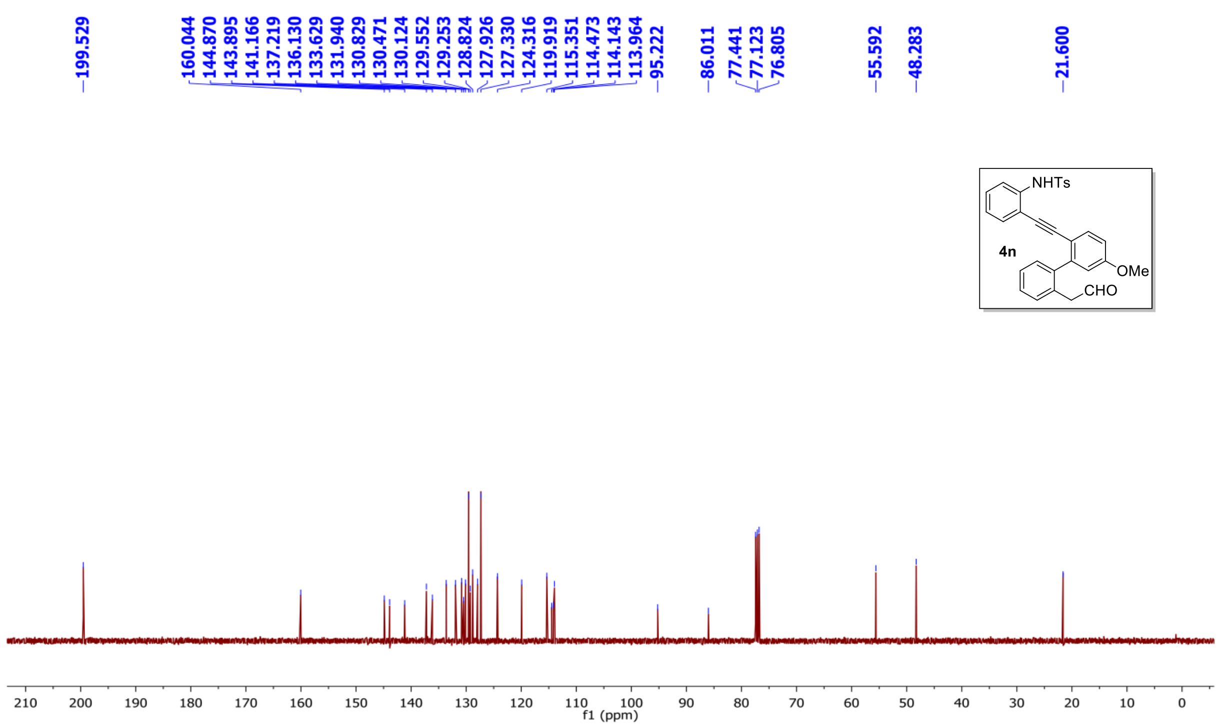
$^{13}C\{^{1}H\}$ NMR (100 MHz) of **4m :**



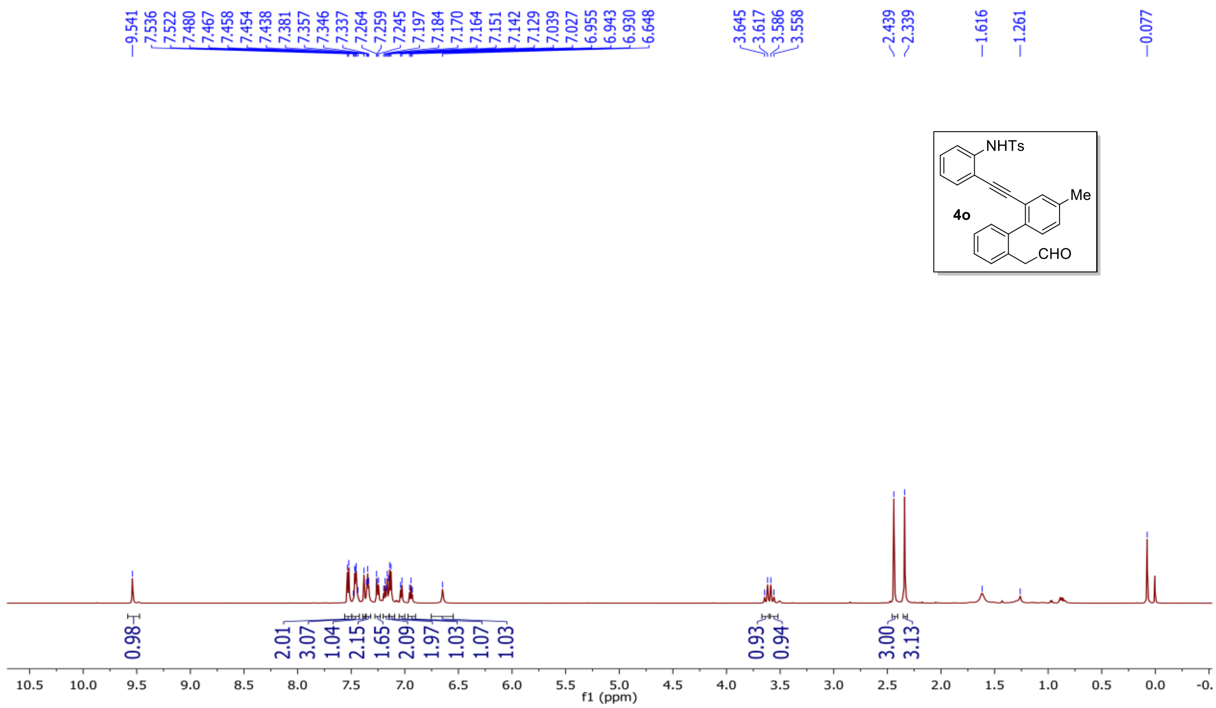
^{1}H NMR (400 MHz) of **4n :**



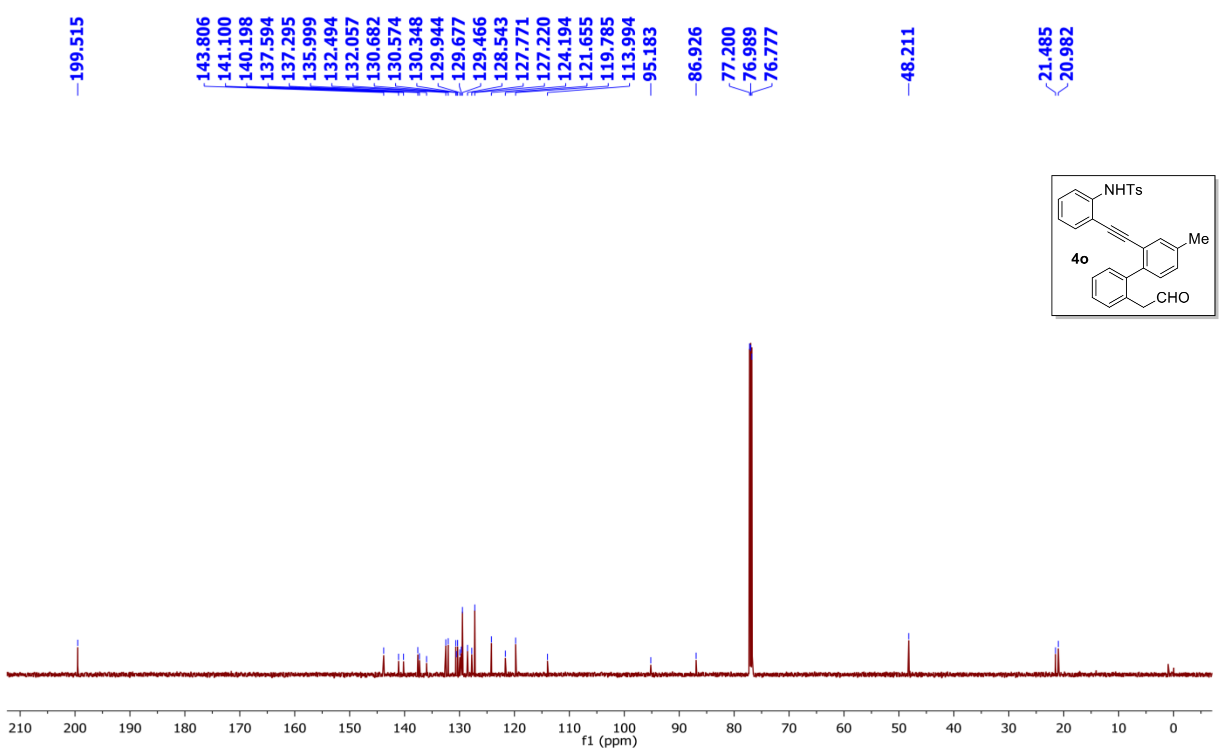
$^{13}C\{^{1}H\}$ NMR (100 MHz) of **4n :**



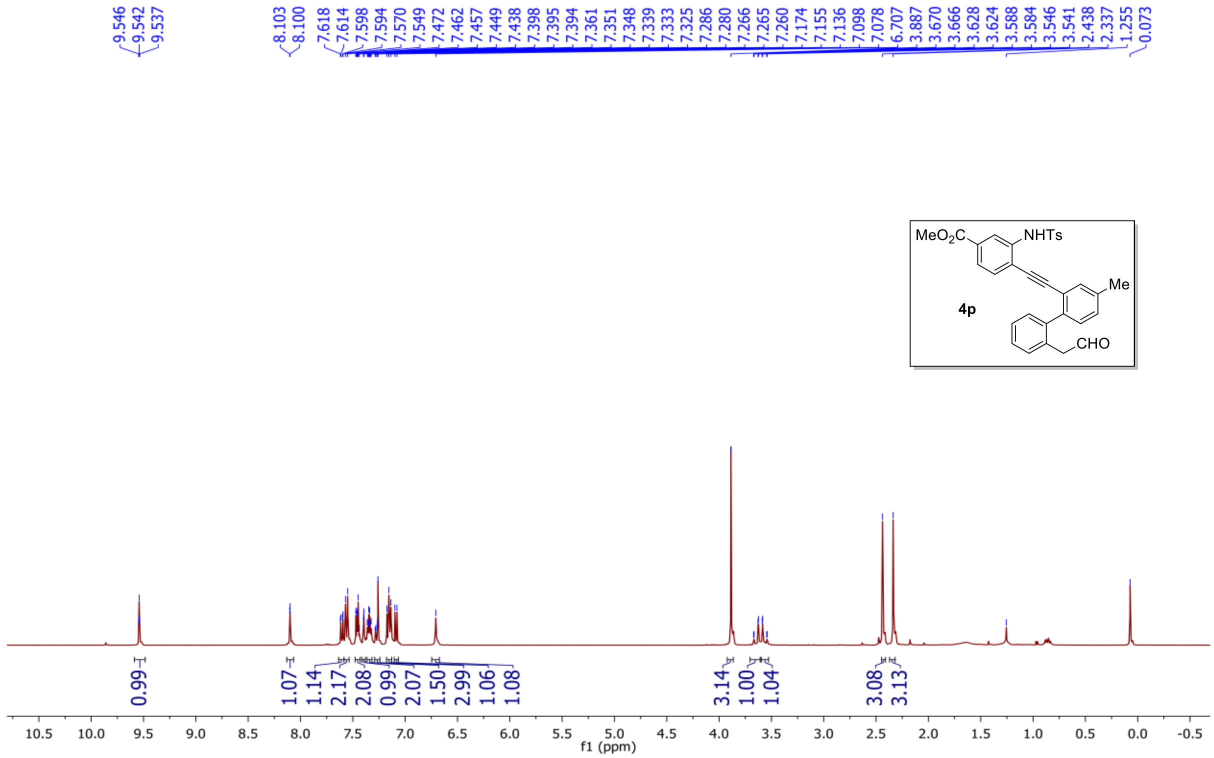
^{1}H NMR (600 MHz) of **4o :**



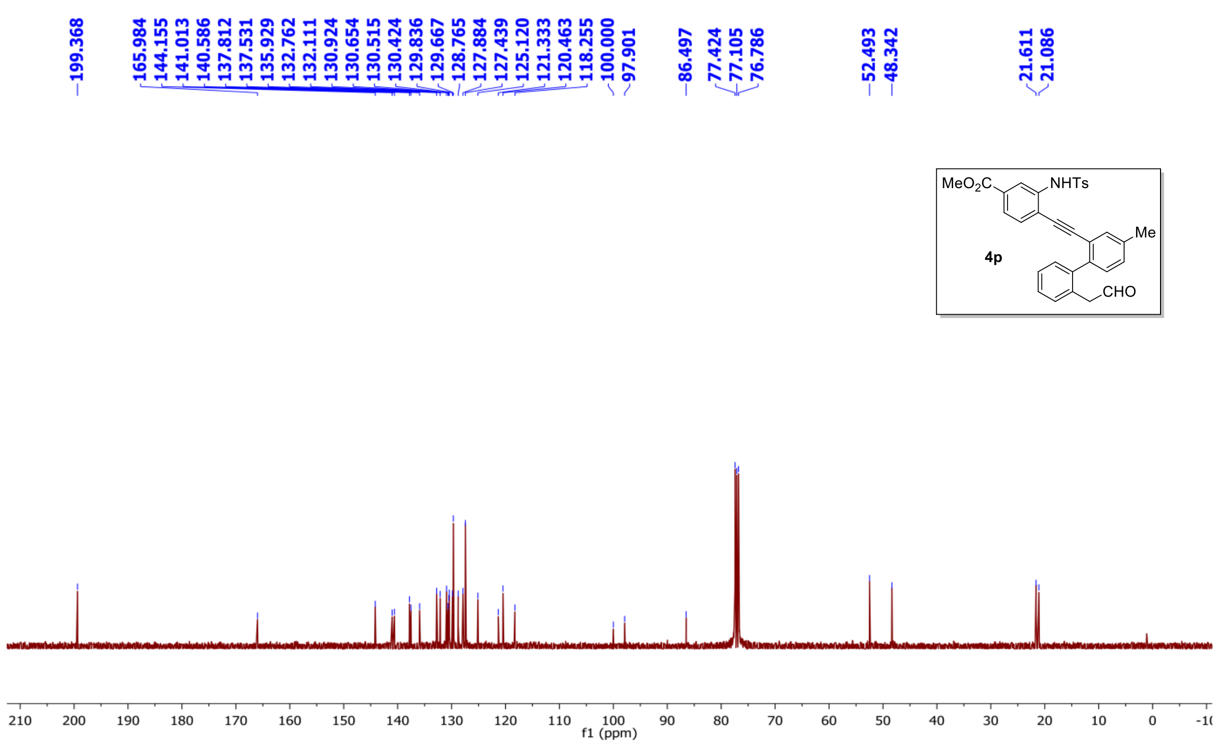
$^{13}C\{^{1}H\}$ NMR (150 MHz) of **4o :**



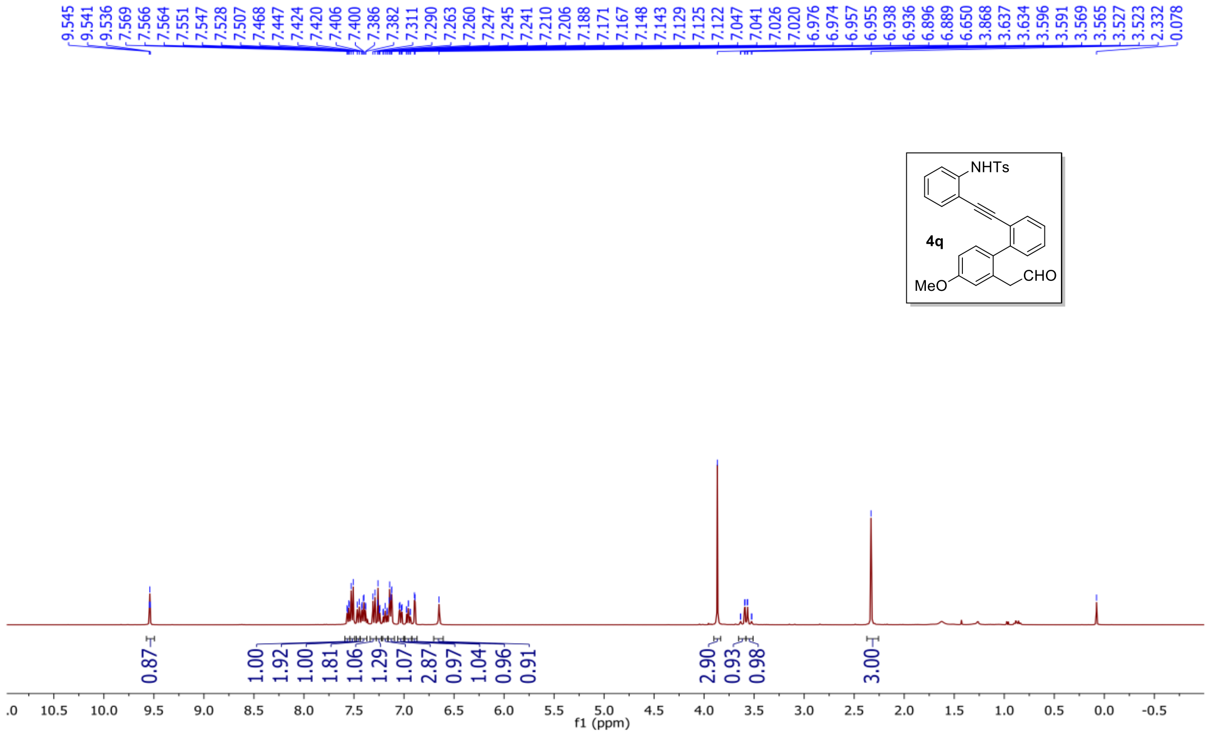
^{1}H NMR (400 MHz) of **4p :**



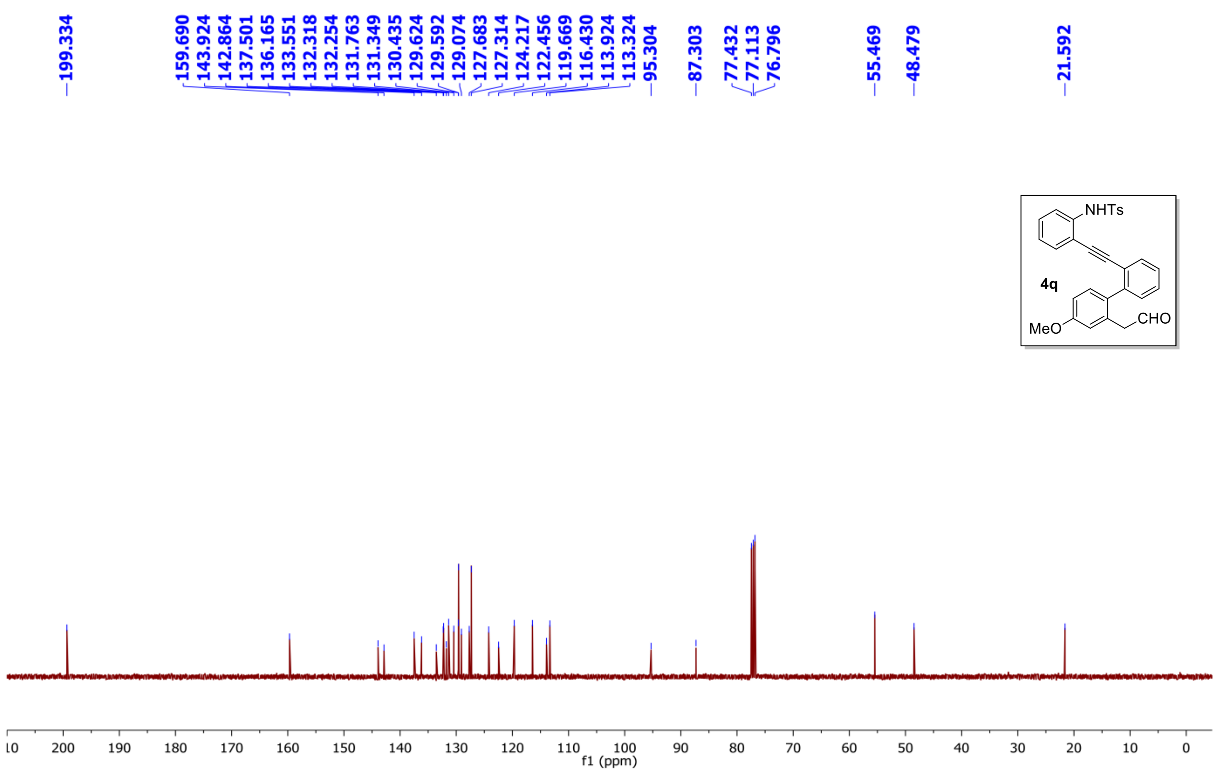
^{13}C{^{1}H} NMR (100 MHz) of **4p :**



^{1}H NMR (400 MHz) of **4q :**

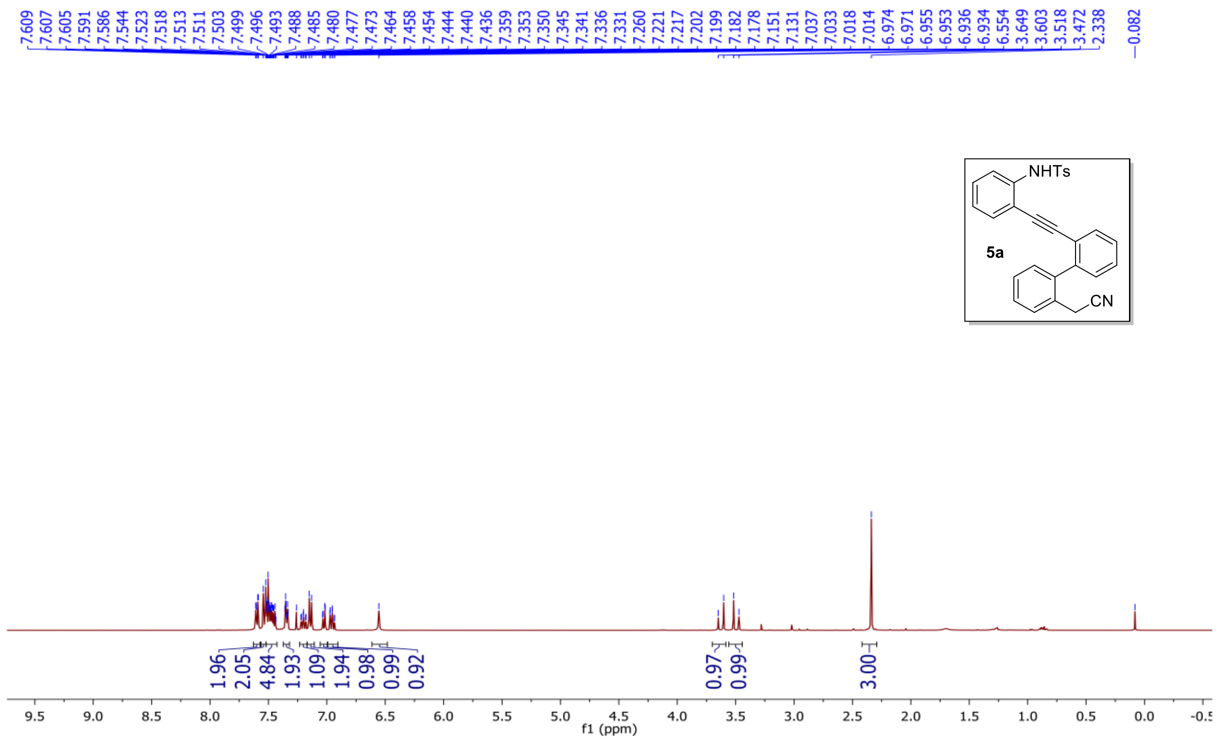


$^{13}C\{^{1}H\}$ NMR (100 MHz) of **4q :**

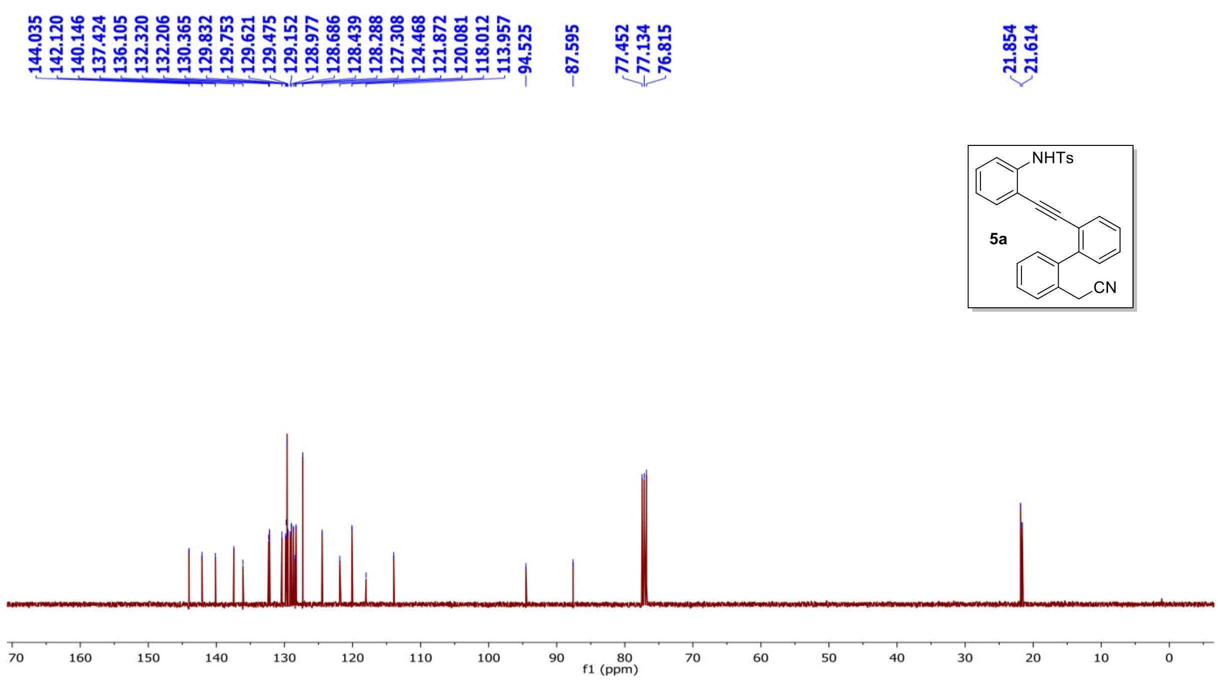


21. NMR Spectra of Compounds 5a-5i :

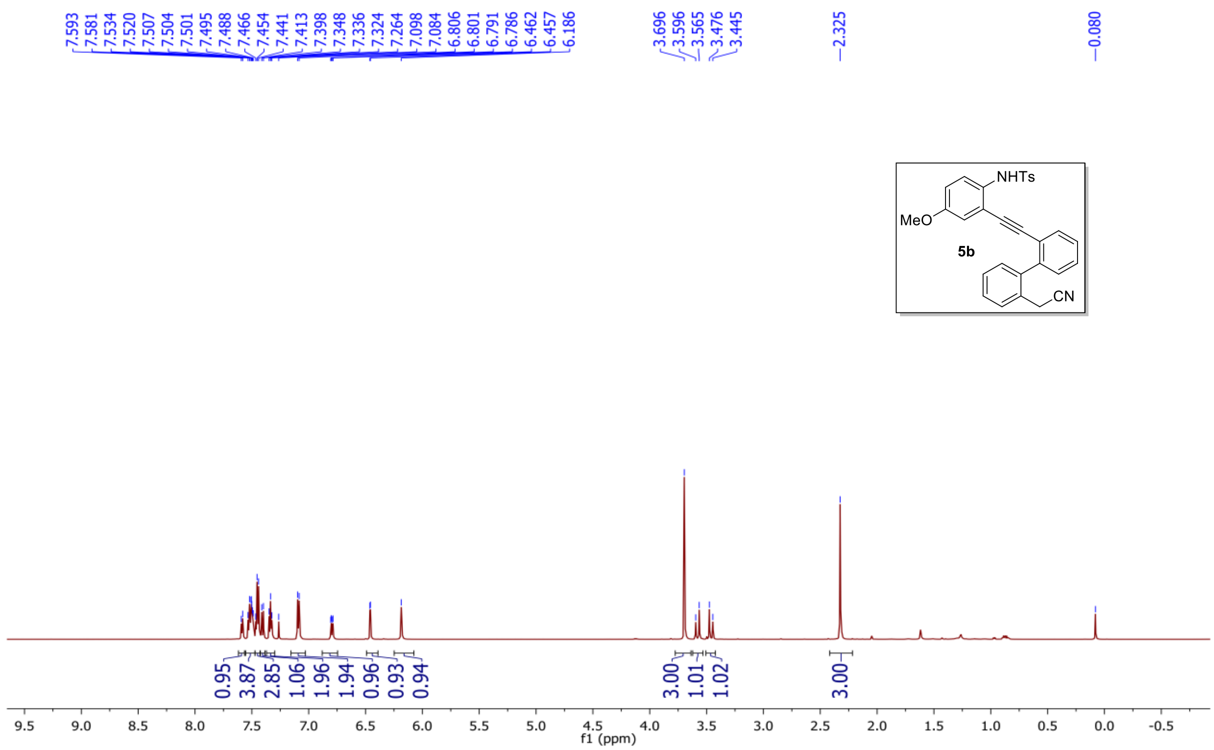
^{1}H NMR (400 MHz) of **5a :**



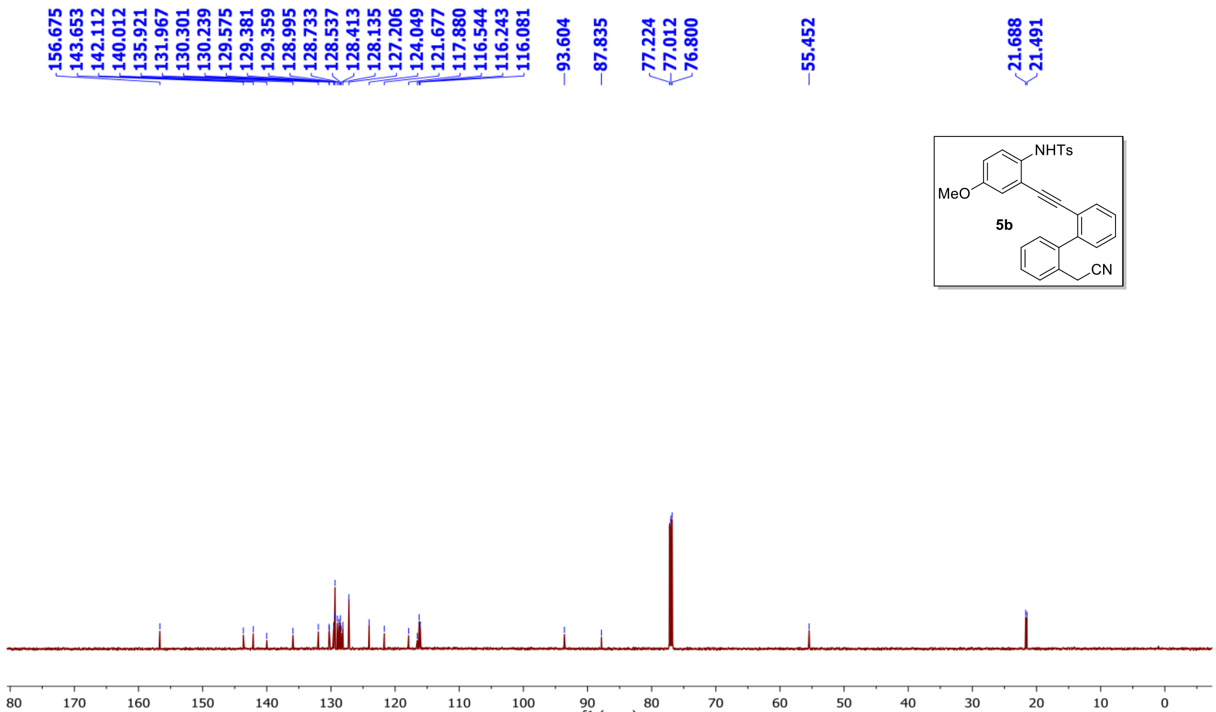
^{13}C{^{1}H} NMR (100 MHz) of **5a:**



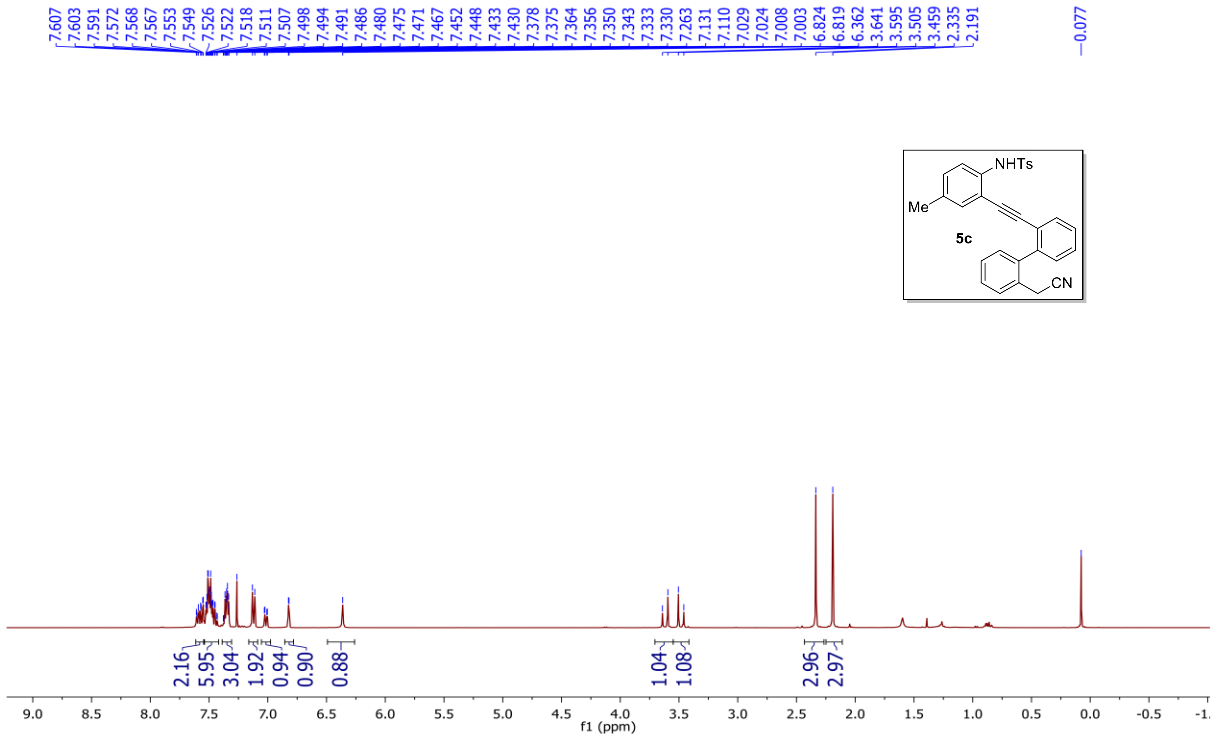
^{1}H NMR (600 MHz) of **5b :**



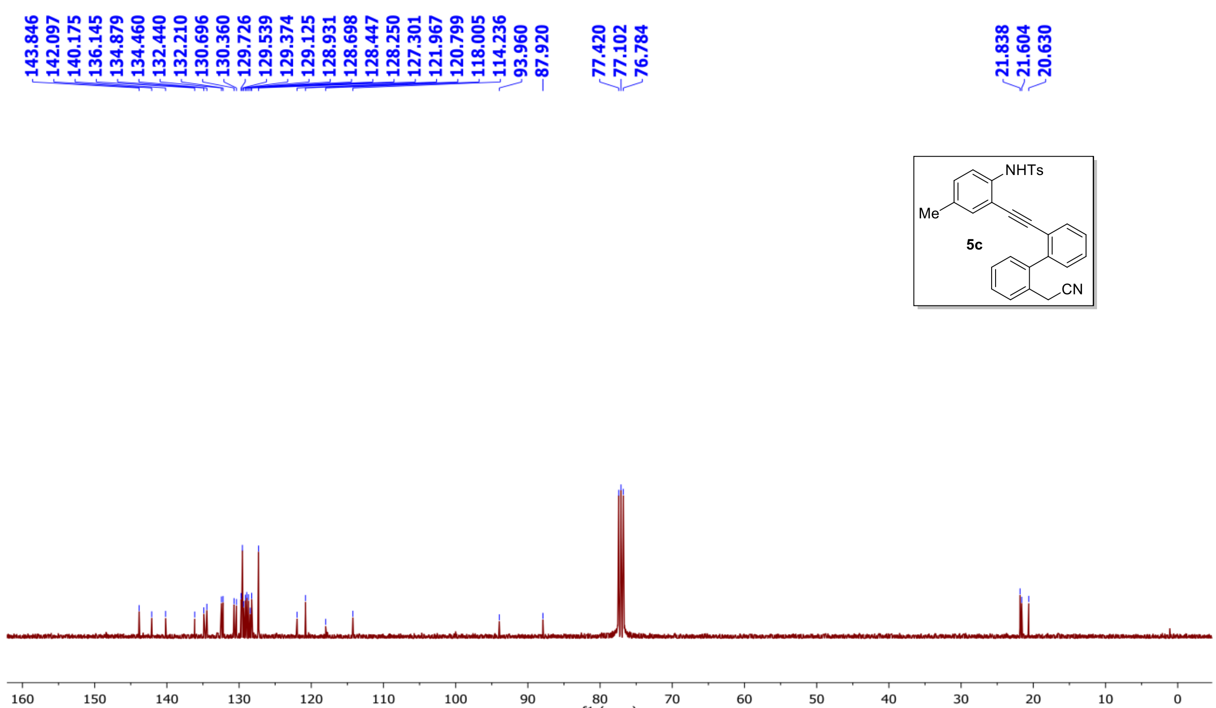
$^{13}C\{^{1}H\}$ NMR (150 MHz) of **5b :**



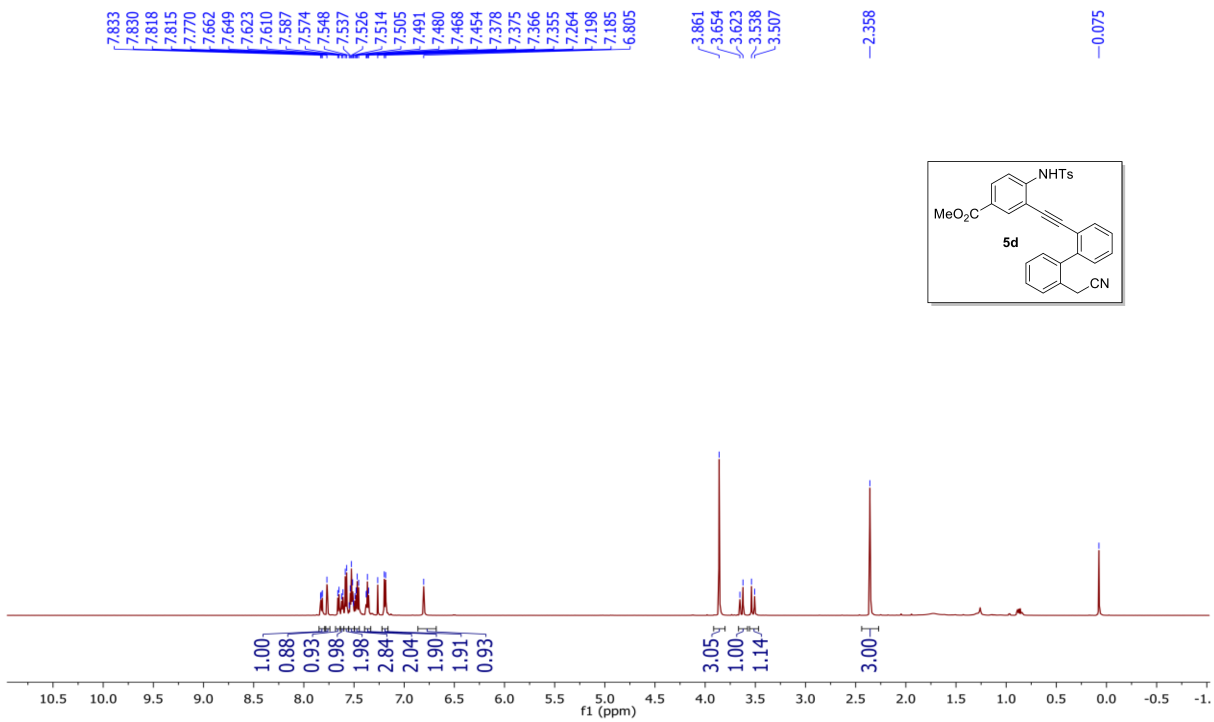
^{1}H NMR (400 MHz) of **5c :**



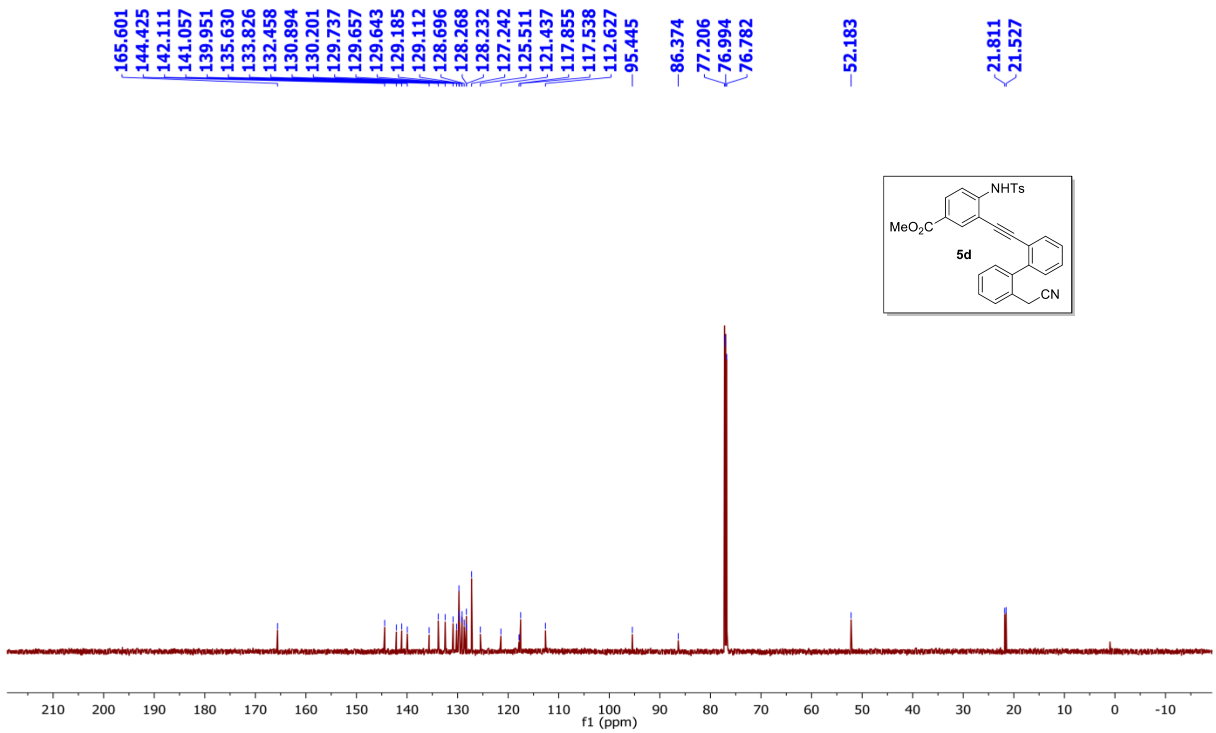
^{13}C{^{1}H} NMR (100 MHz) of **5c :**



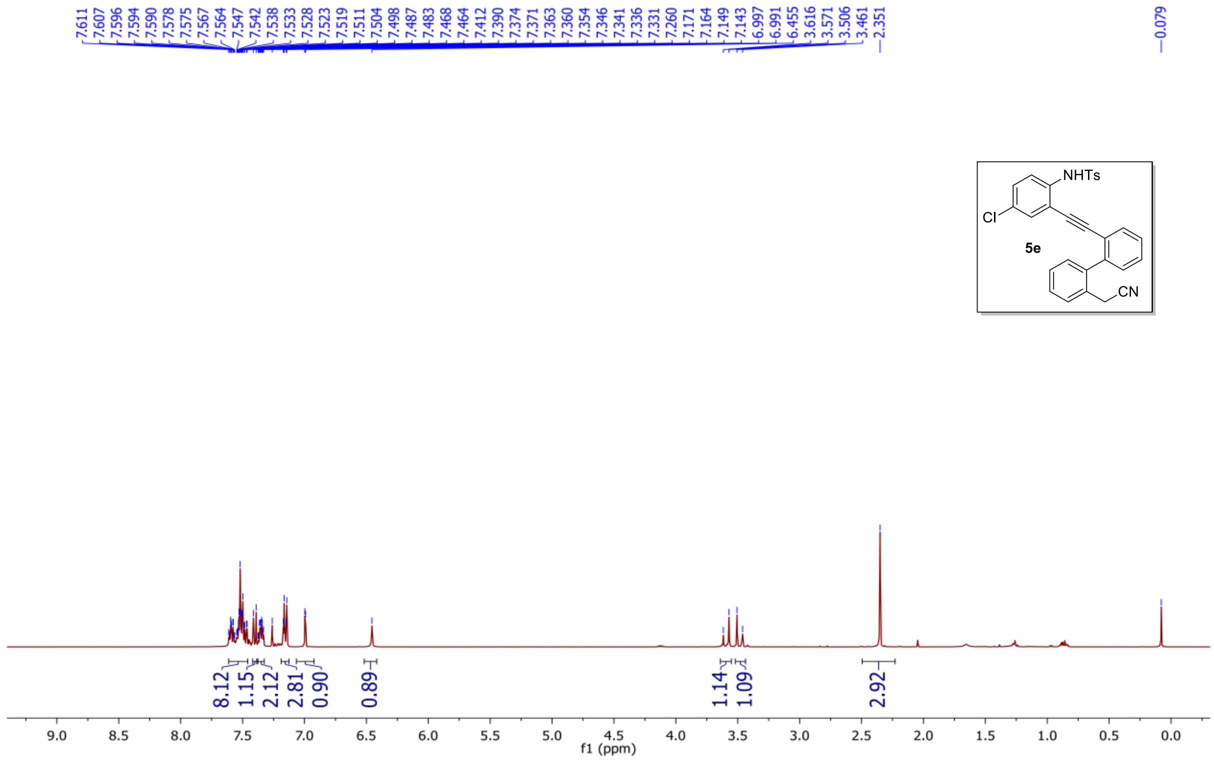
^{1}H NMR (600 MHz) of **5d :**



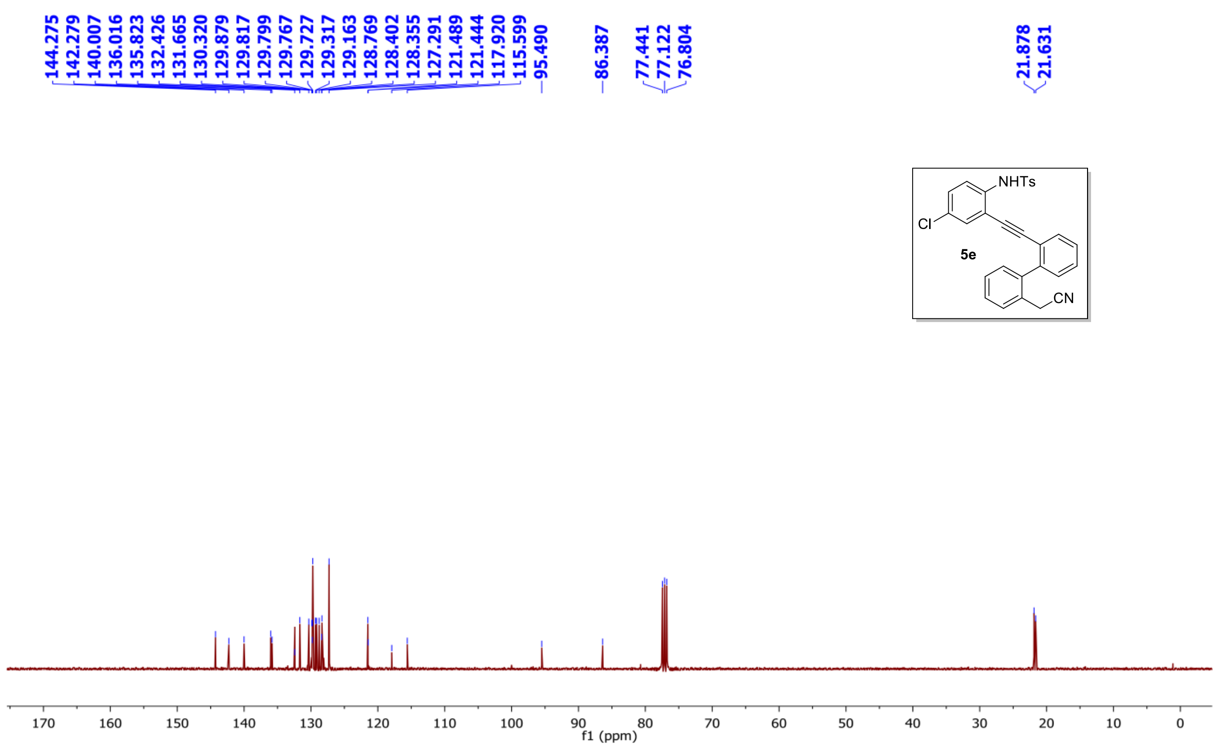
$^{13}C\{^{1}H\}$ NMR (150 MHz) of **5d :**



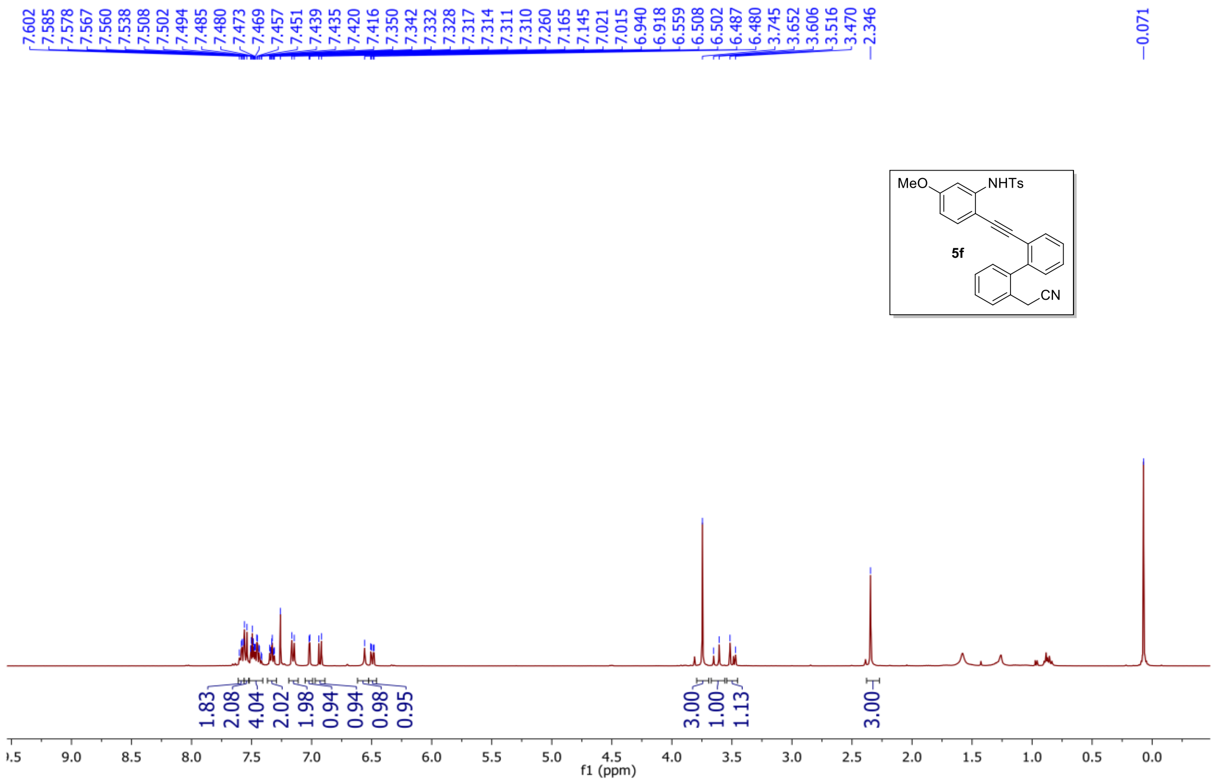
[1]H NMR (400 MHz) of **5e :**



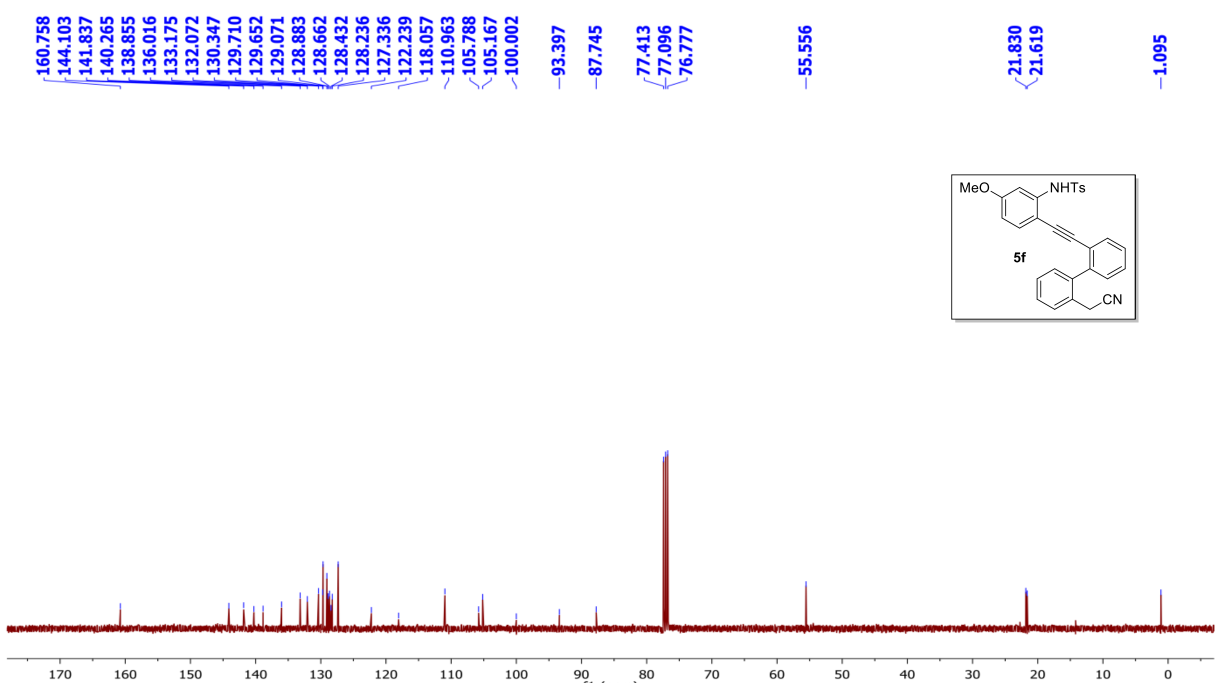
[13]C{[1]H} NMR (100 MHz) of **5e :**



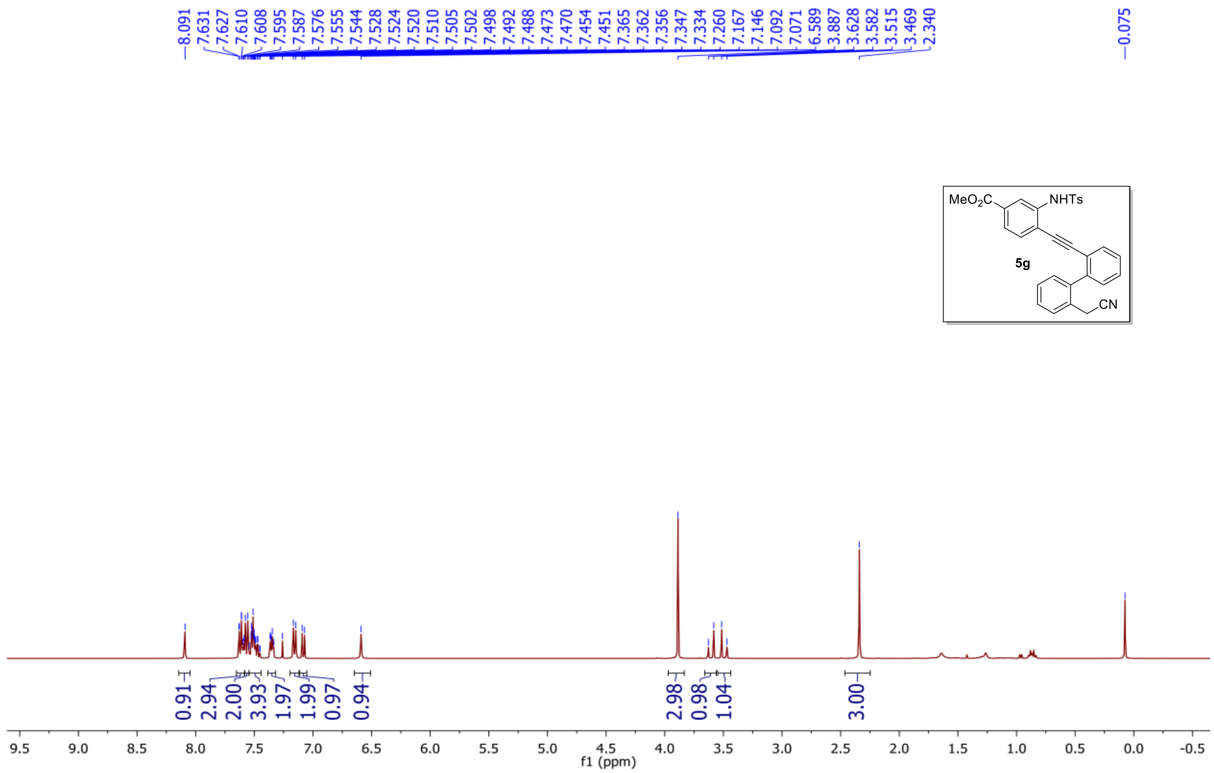
^{1}H NMR (400 MHz) of **5f :**



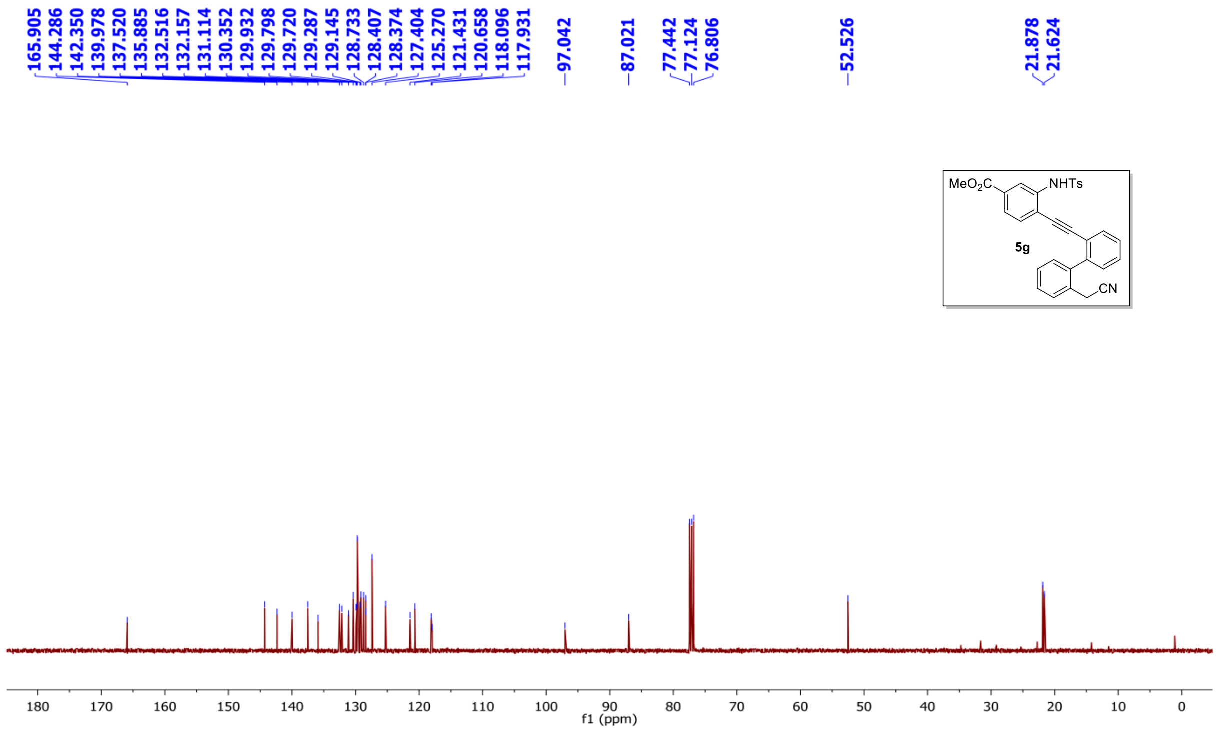
^{13}C{^{1}H} NMR (100 MHz) of **5f :**



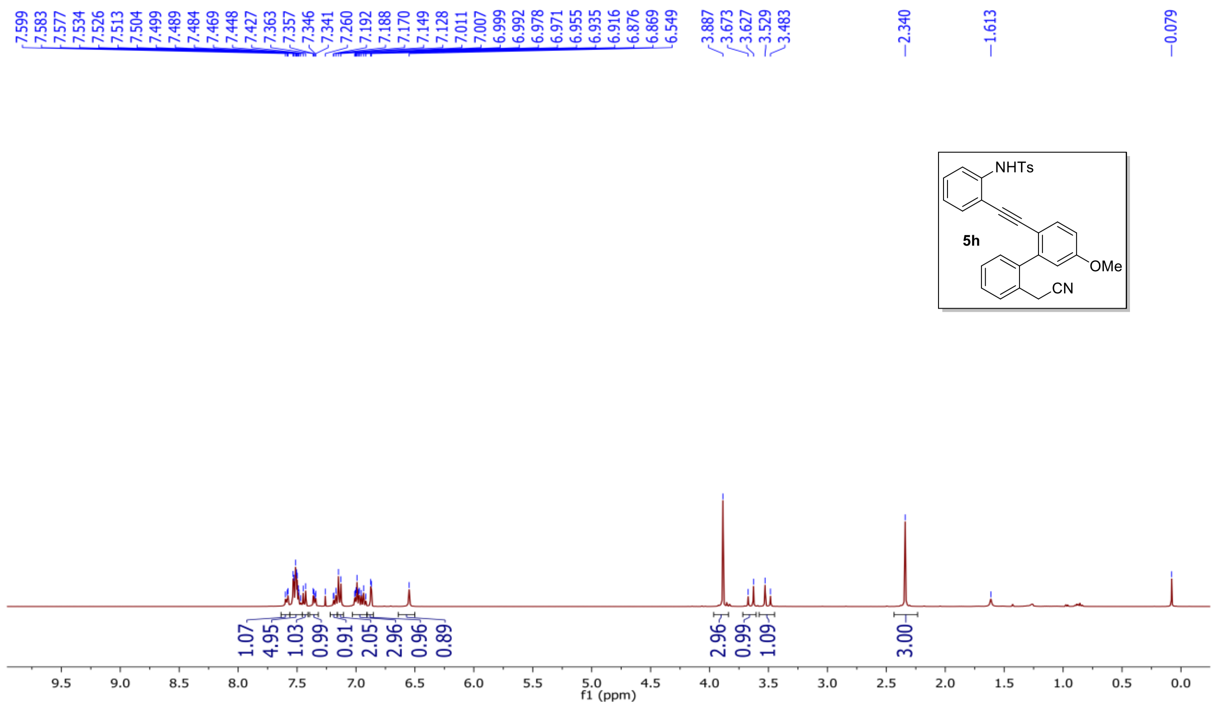
^{1}H NMR (400 MHz) of **5g :**



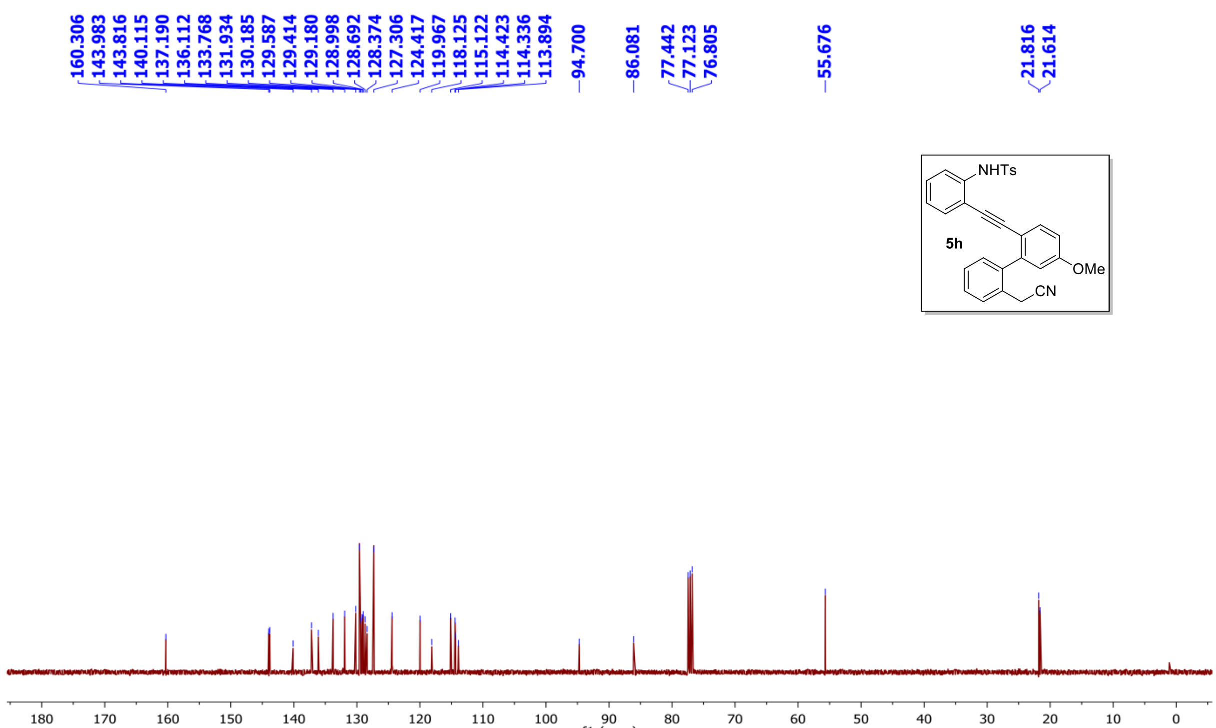
^{13}C{^{1}H} NMR (100 MHz) of **5g :**



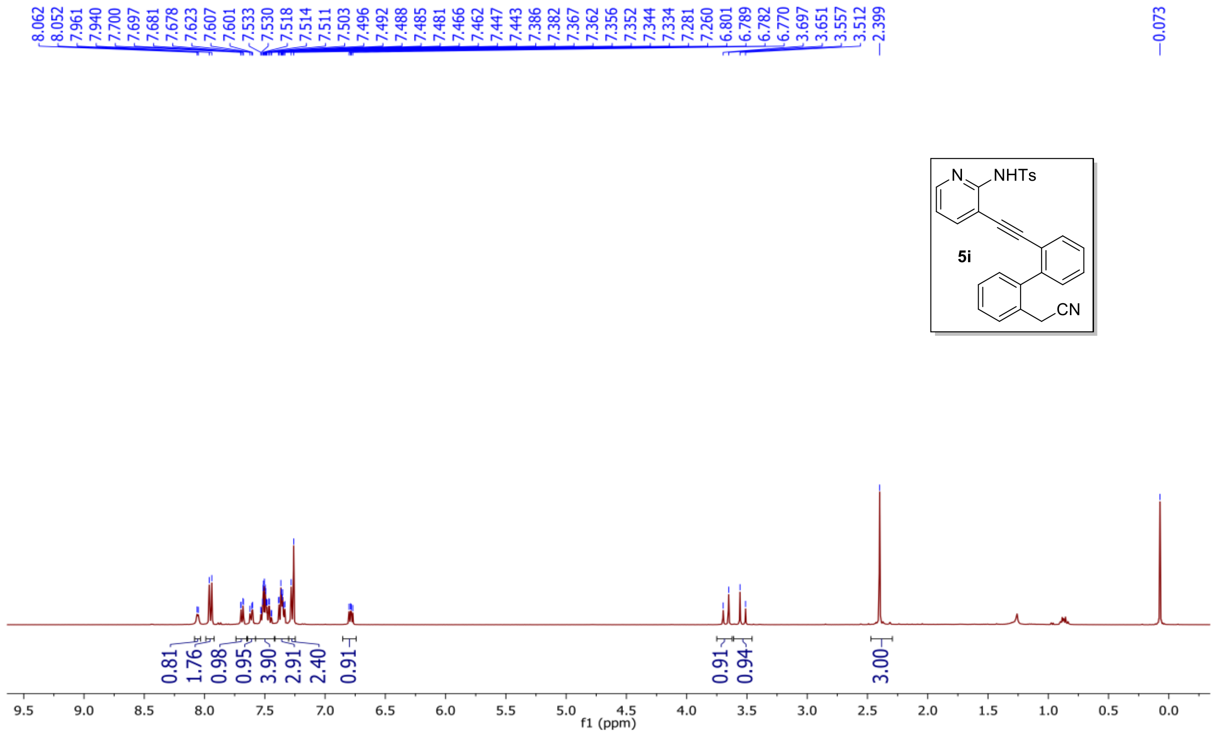
^{1}H NMR (400 MHz) of **5h :**



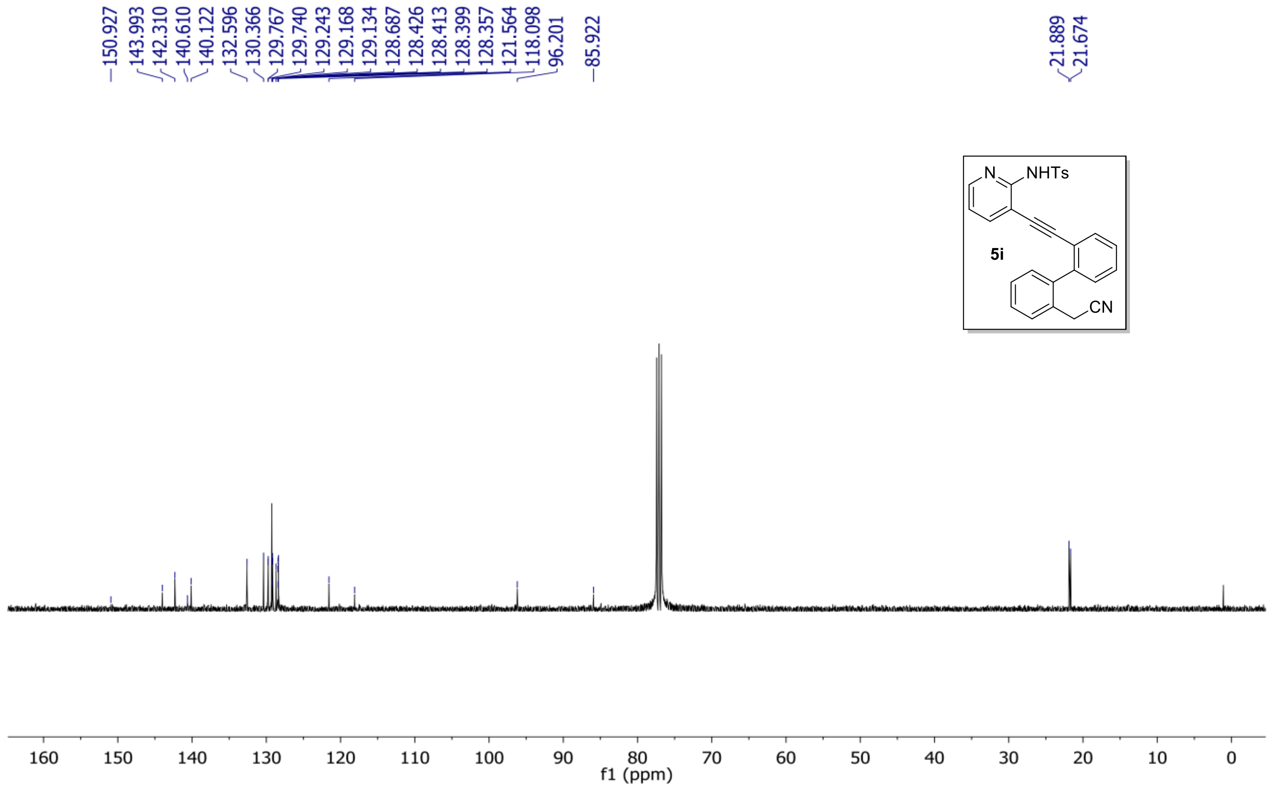
^{13}C{^{1}H} NMR (100 MHz) of **5h :**



^{1}H NMR (400 MHz) of **5i :**

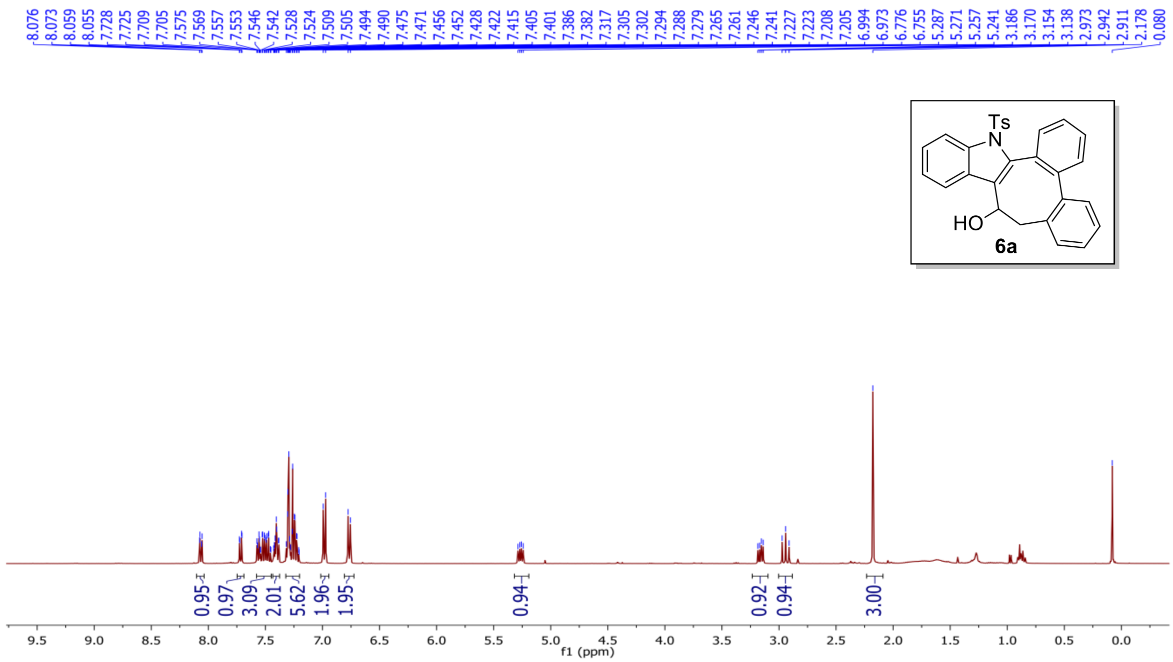


^{13}C{^{1}H} NMR (100 MHz) of **5i :**

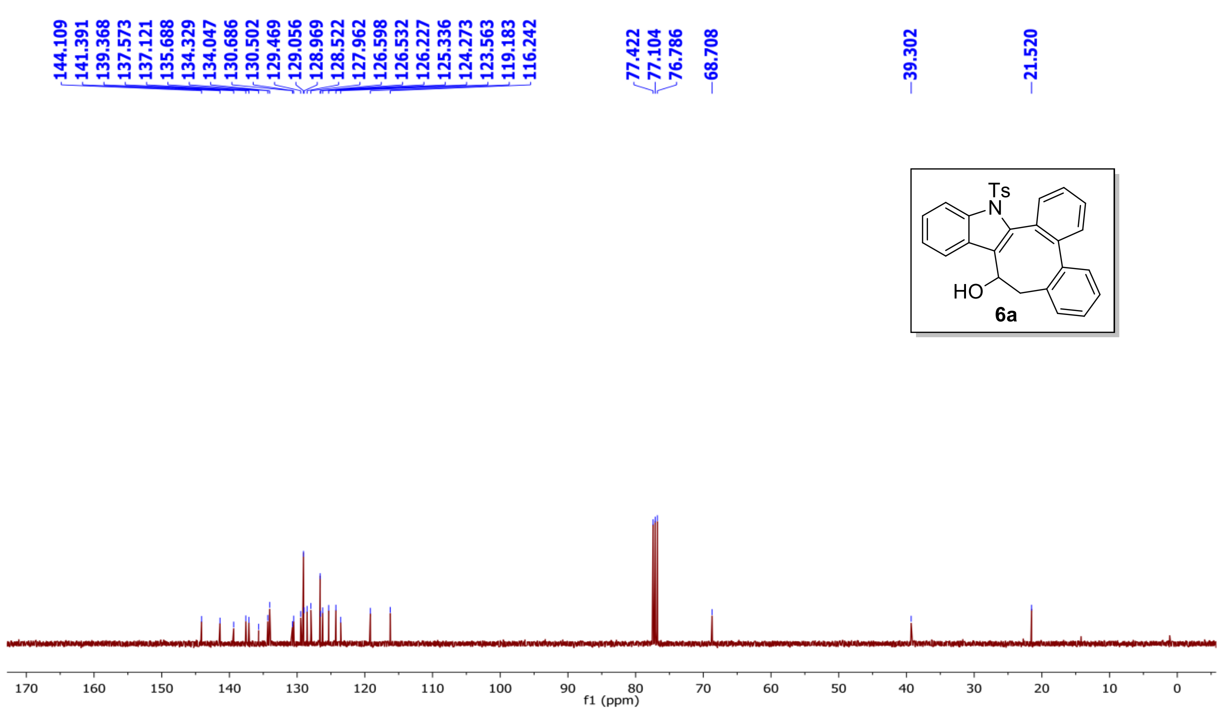


22. NMR Spectra of Compounds 6a-6q :

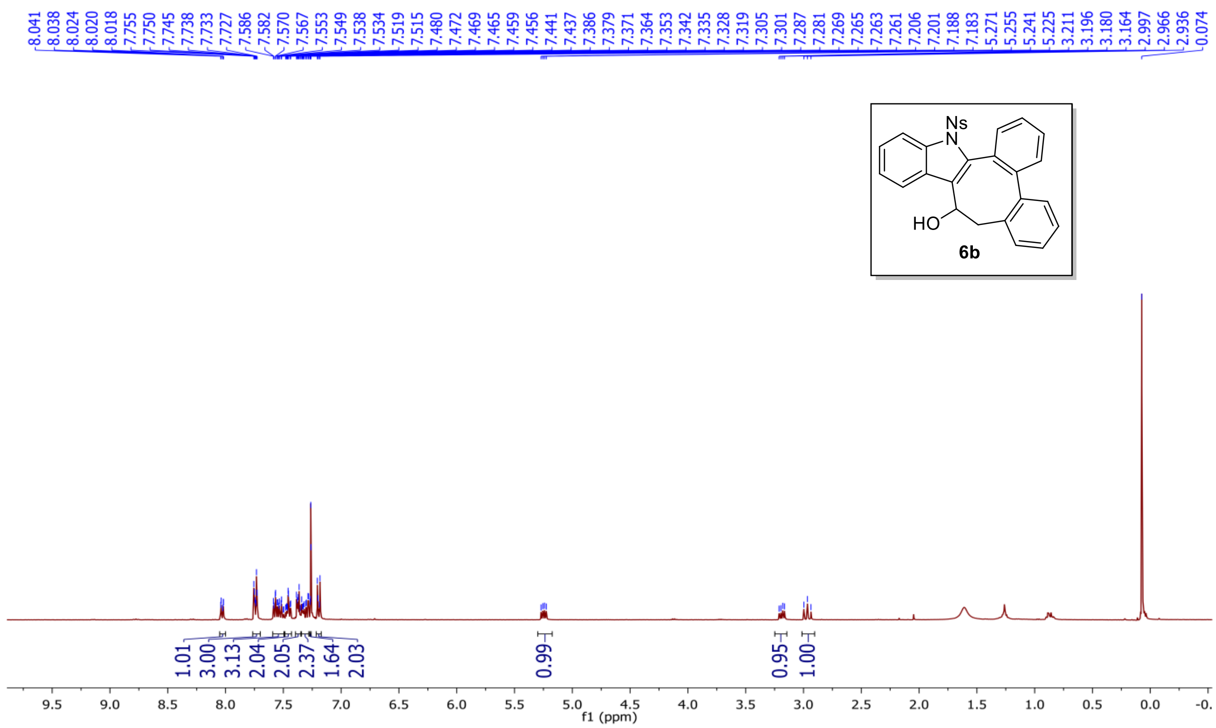
^{1}H NMR (400 MHz) of **6a :**



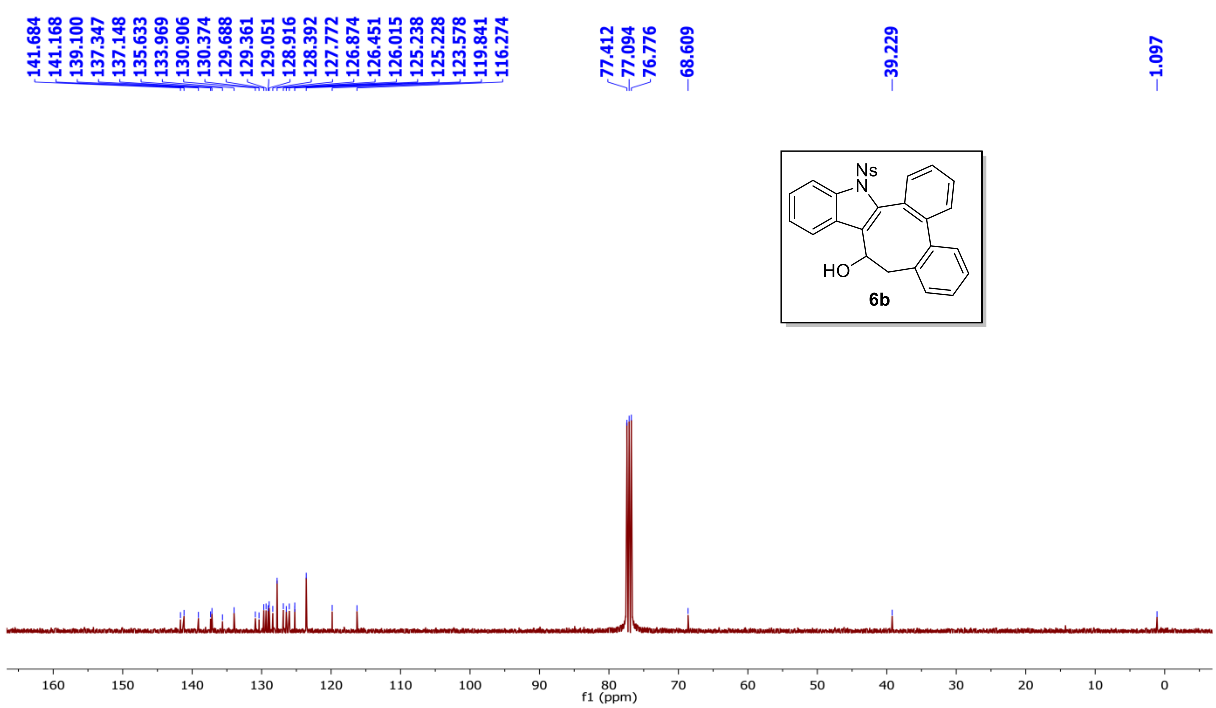
^{13}C{^{1}H} NMR (100 MHz) of **6a :**



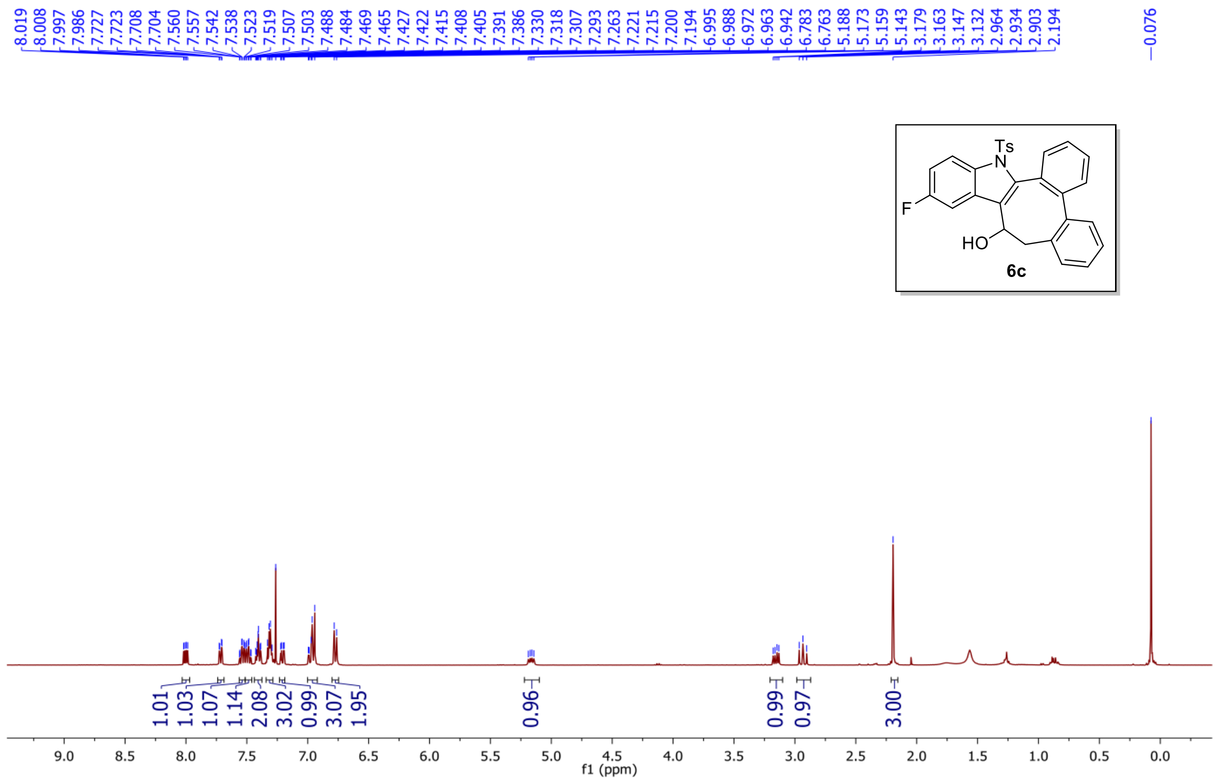
^{1}H NMR (400 MHz) of **6b :**



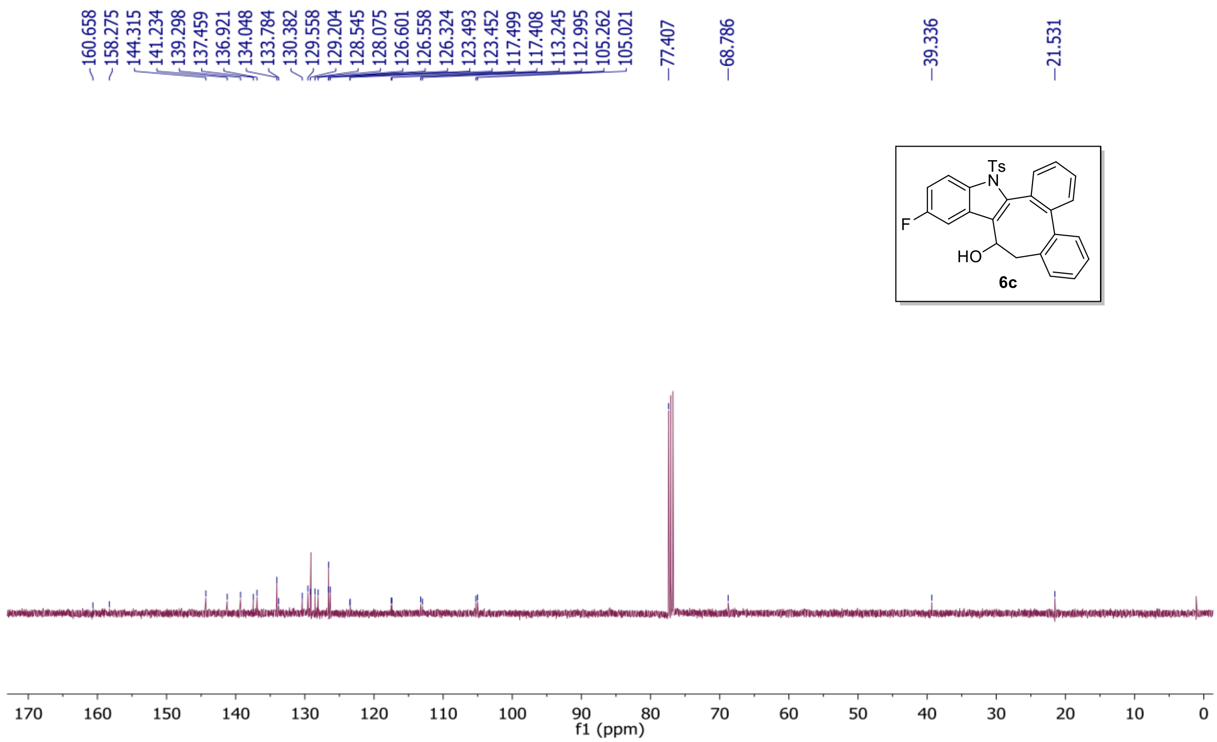
$^{13}C\{^{1}H\}$ NMR (100 MHz) of **6b :**



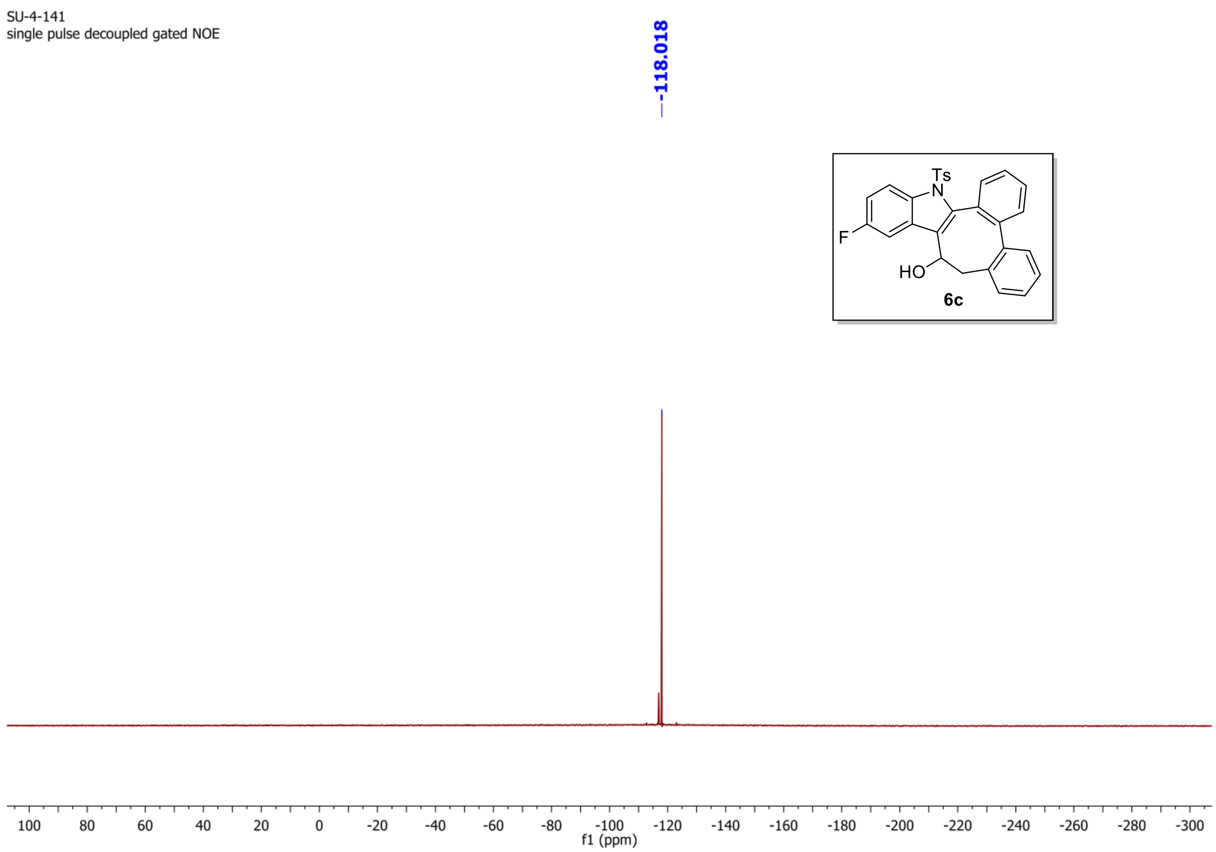
^{1}H NMR (400 MHz) of **6c :**



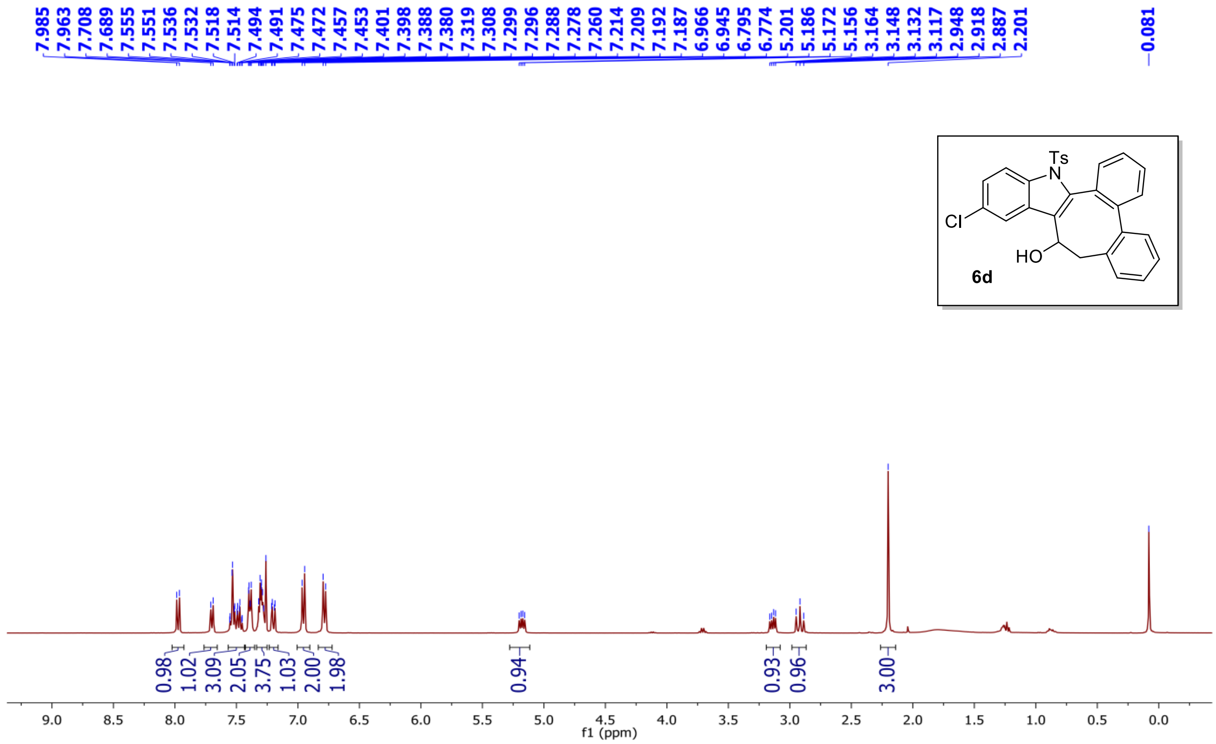
$^{13}C\{^{1}H\}$ NMR (100 MHz) of **6c :**



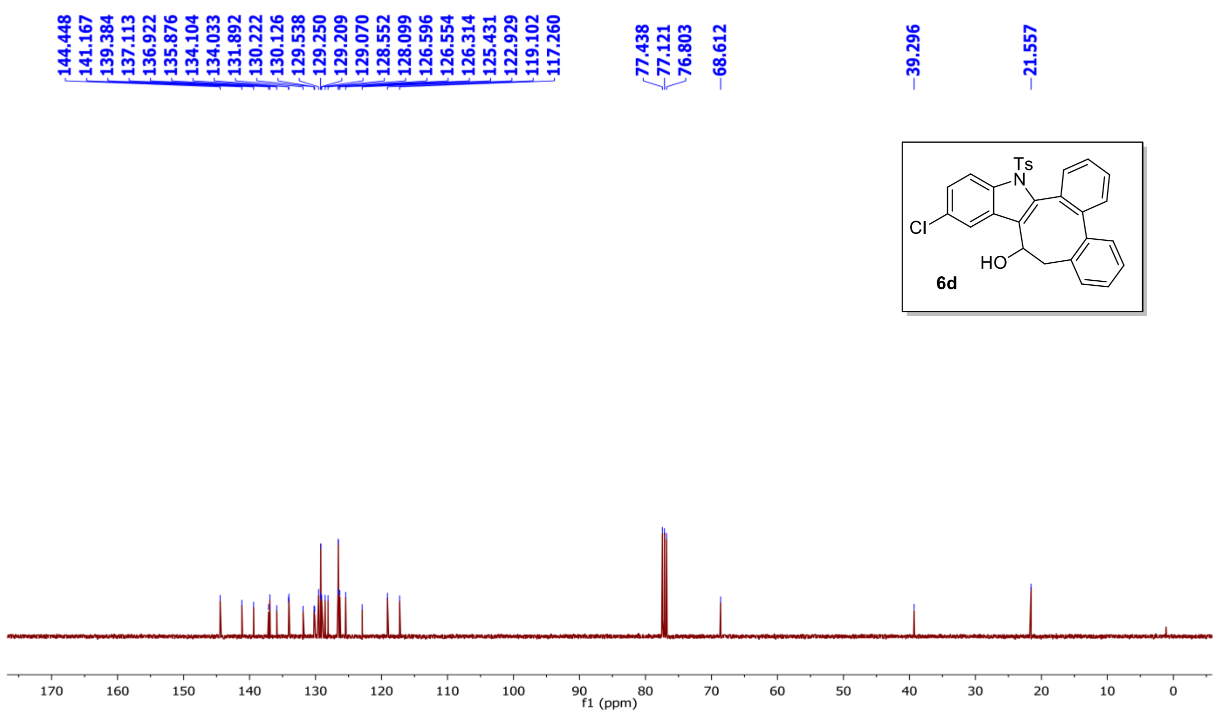
$^{19}F\{^1H\}$ NMR (376 MHz) of **6c**:



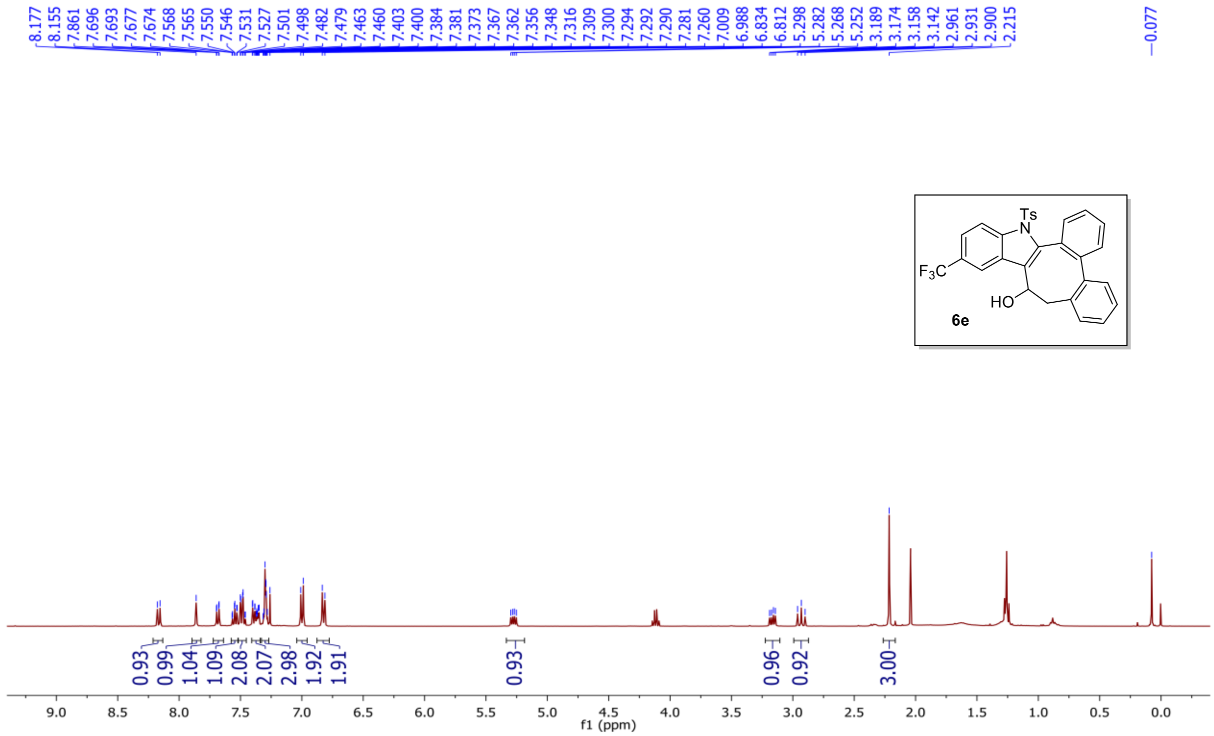
^{1}H NMR (400 MHz) of **6d :**



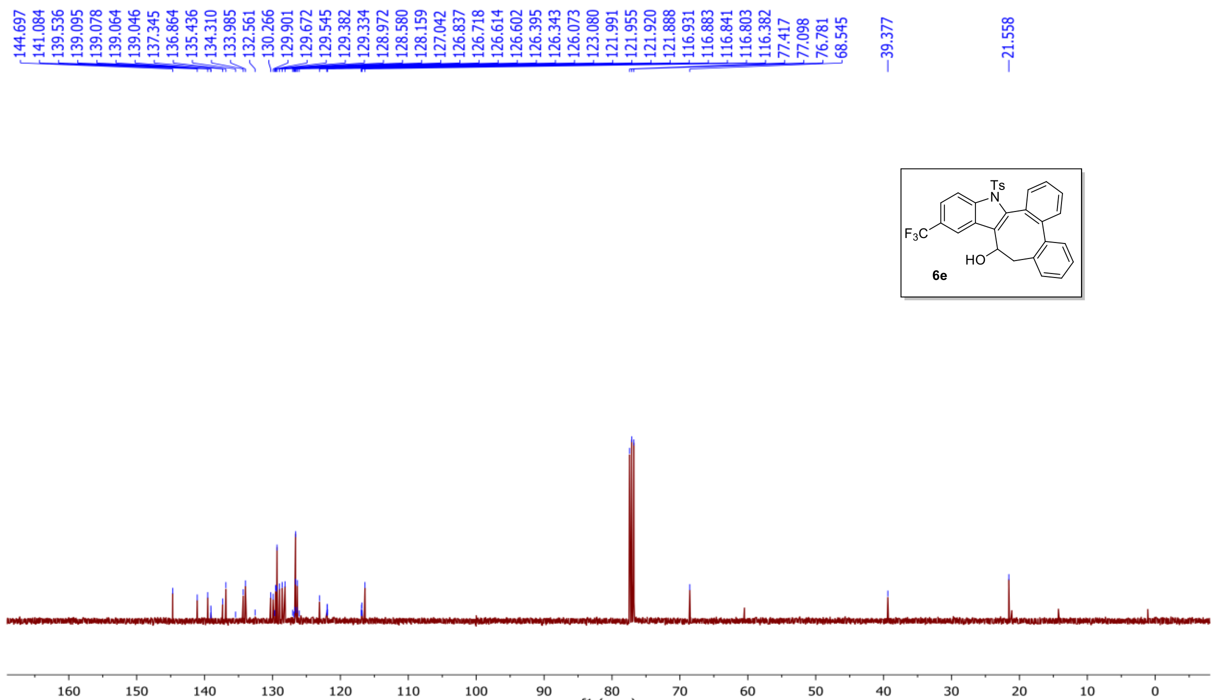
^{13}C{^{1}H} NMR (100 MHz) of **6d :**



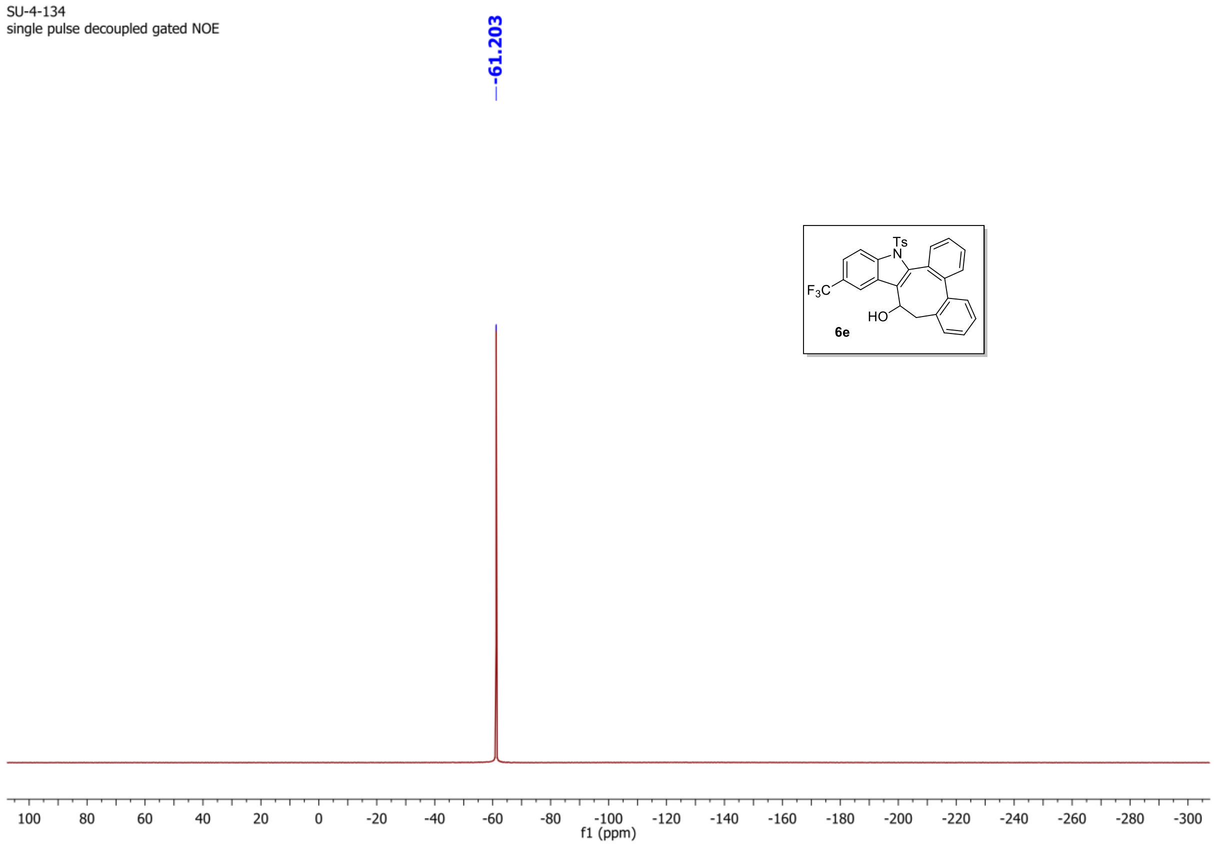
[1]H NMR (400 MHz) of **6e :**



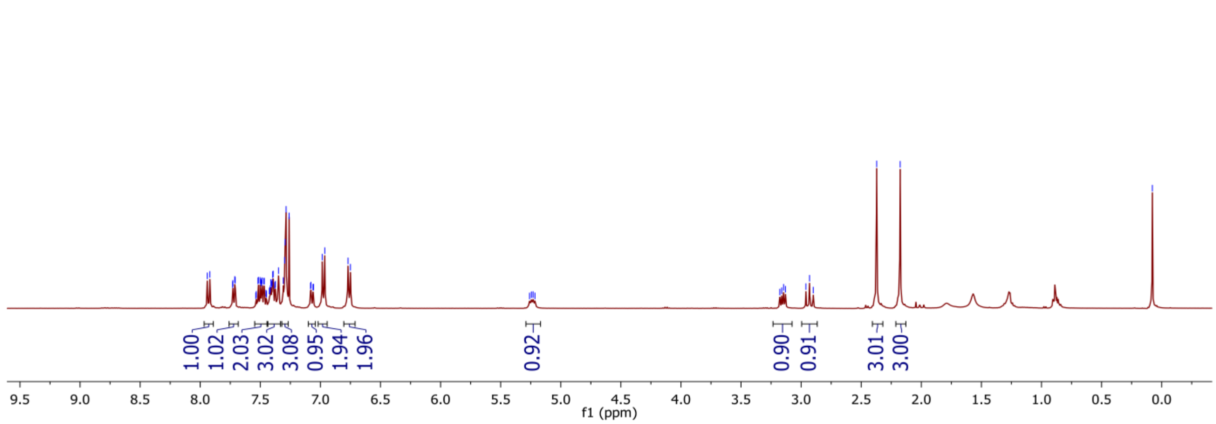
[13]C{[1]H} NMR (100 MHz) of **6e :**

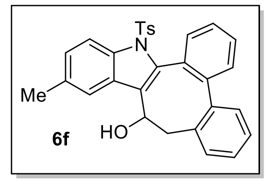


$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) **6e :**

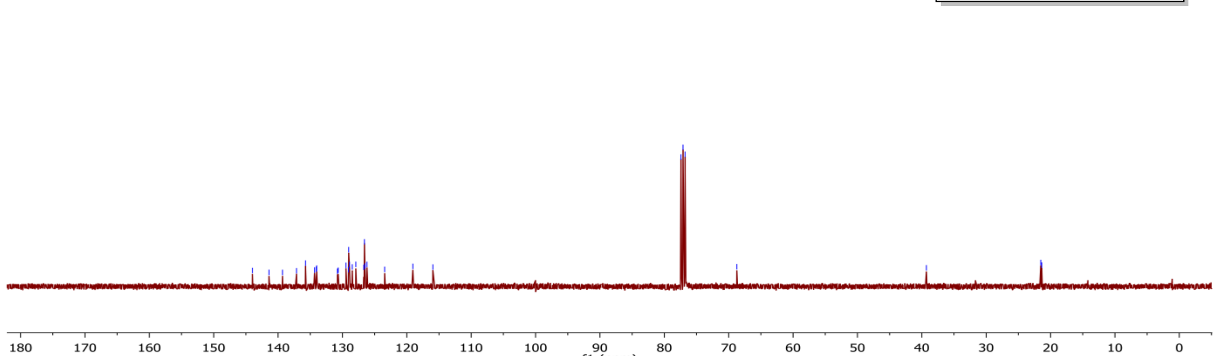


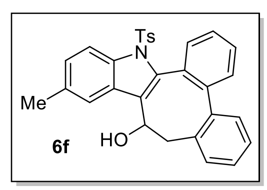
[1]H NMR (400 MHz) of **6f :**



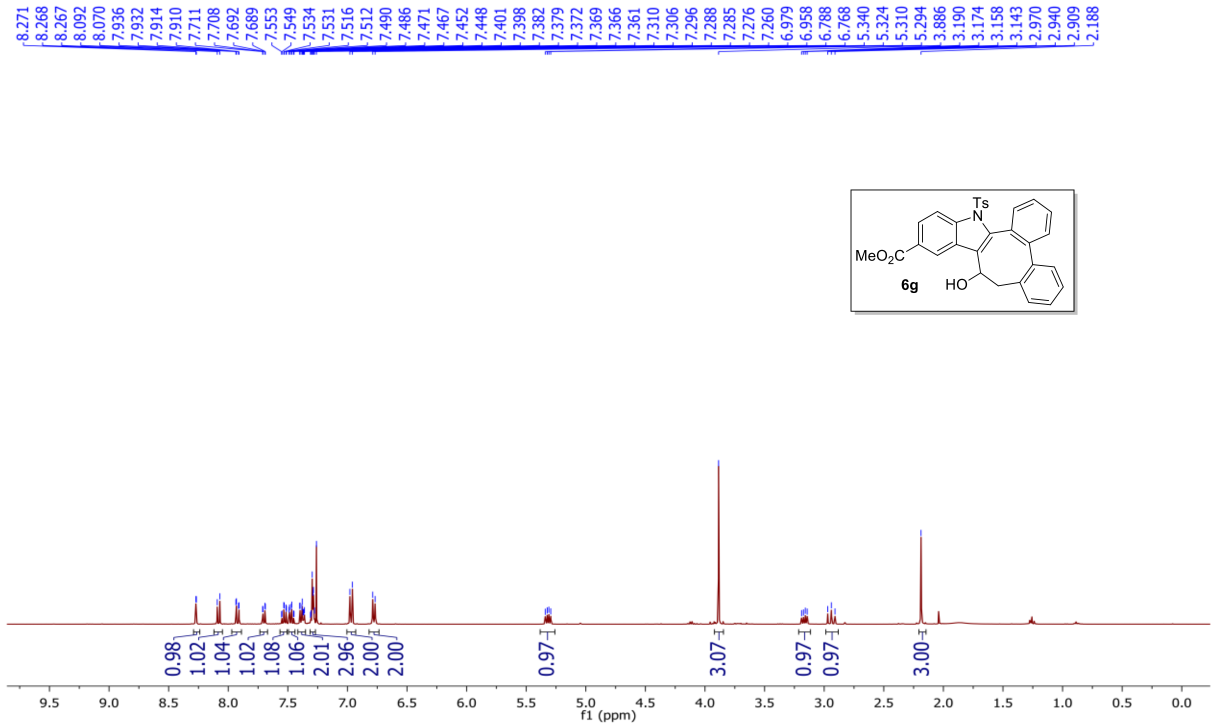


$^{13}C\{^1H\}$ NMR (100 MHz) of **6f :**

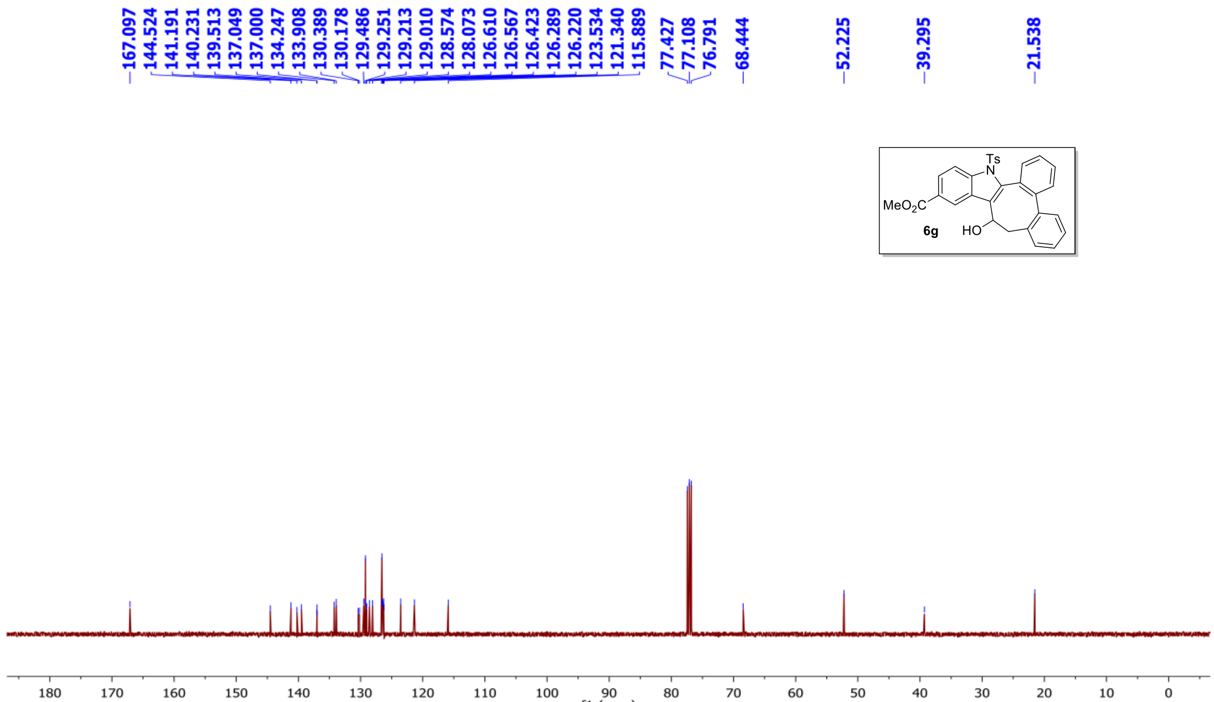




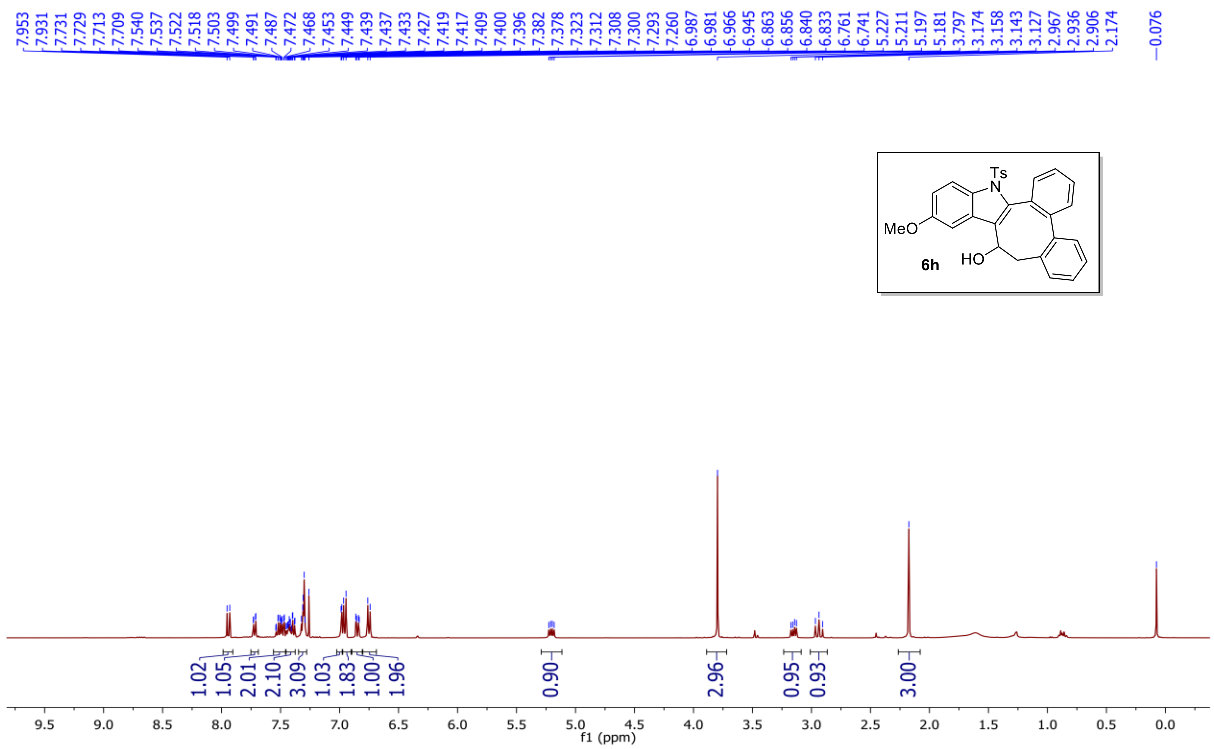
^{1}H NMR (400 MHz) of **6g :**



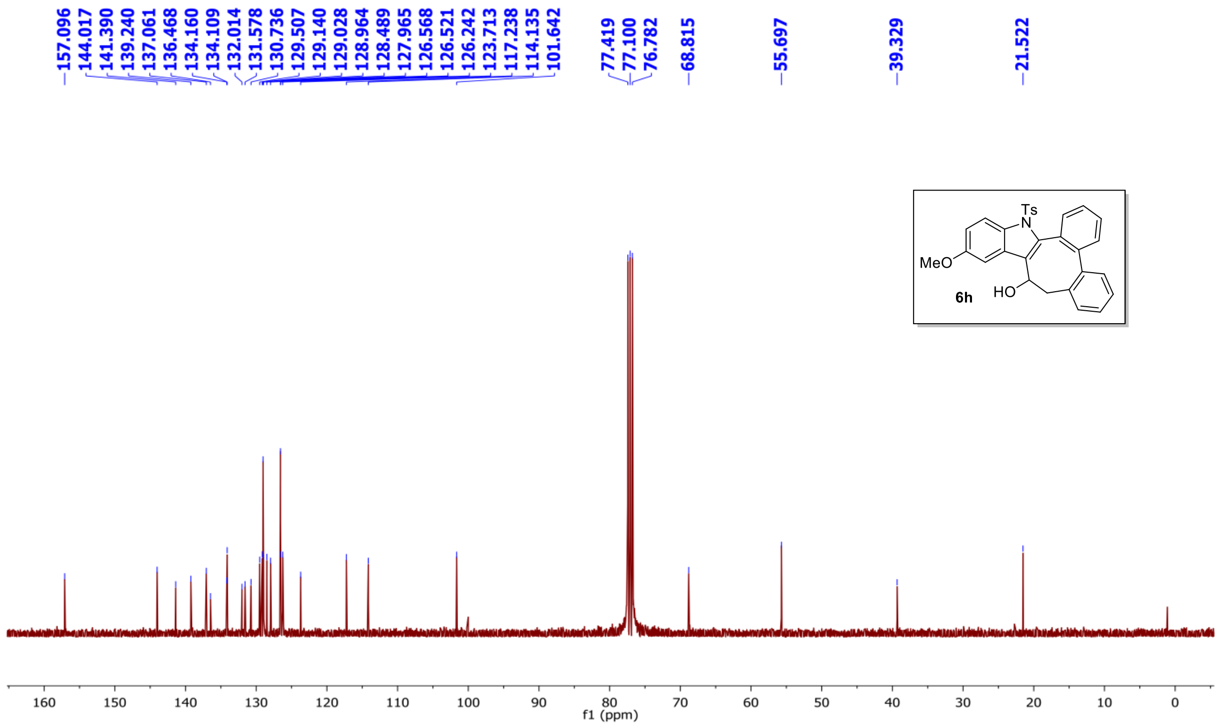
^{13}C{^{1}H} NMR (100 MHz) of **6g :**



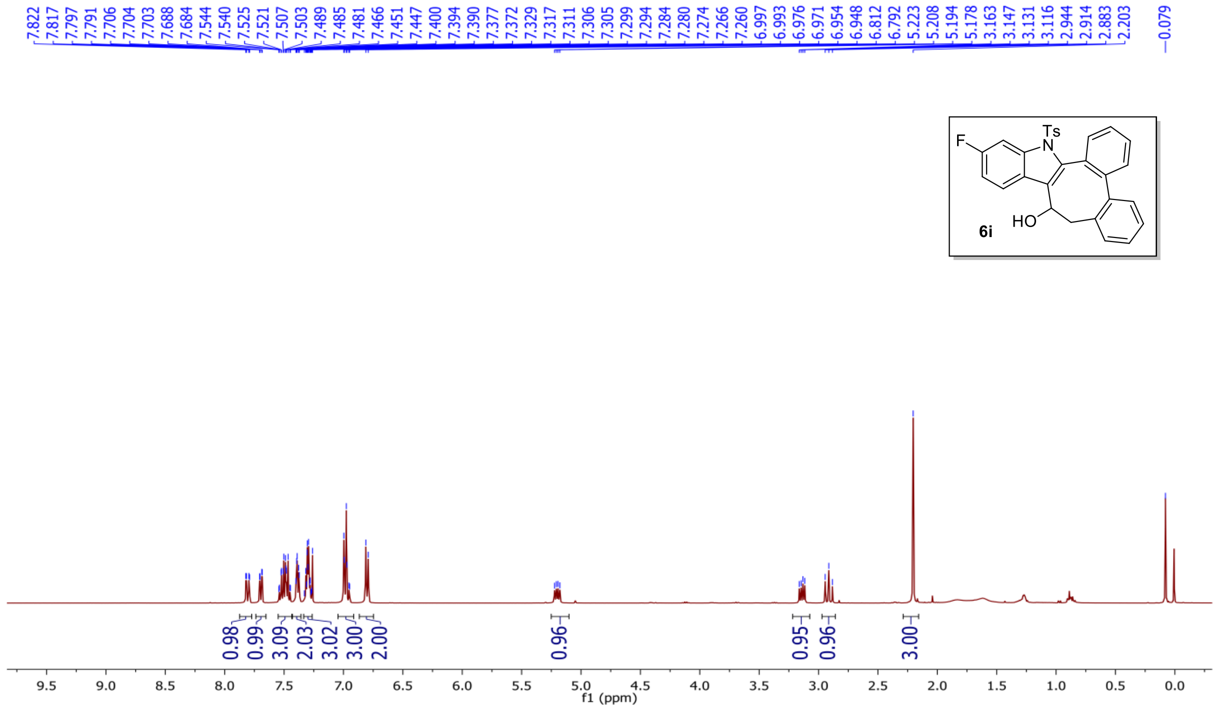
^{1}H NMR (400 MHz) of **6h :**



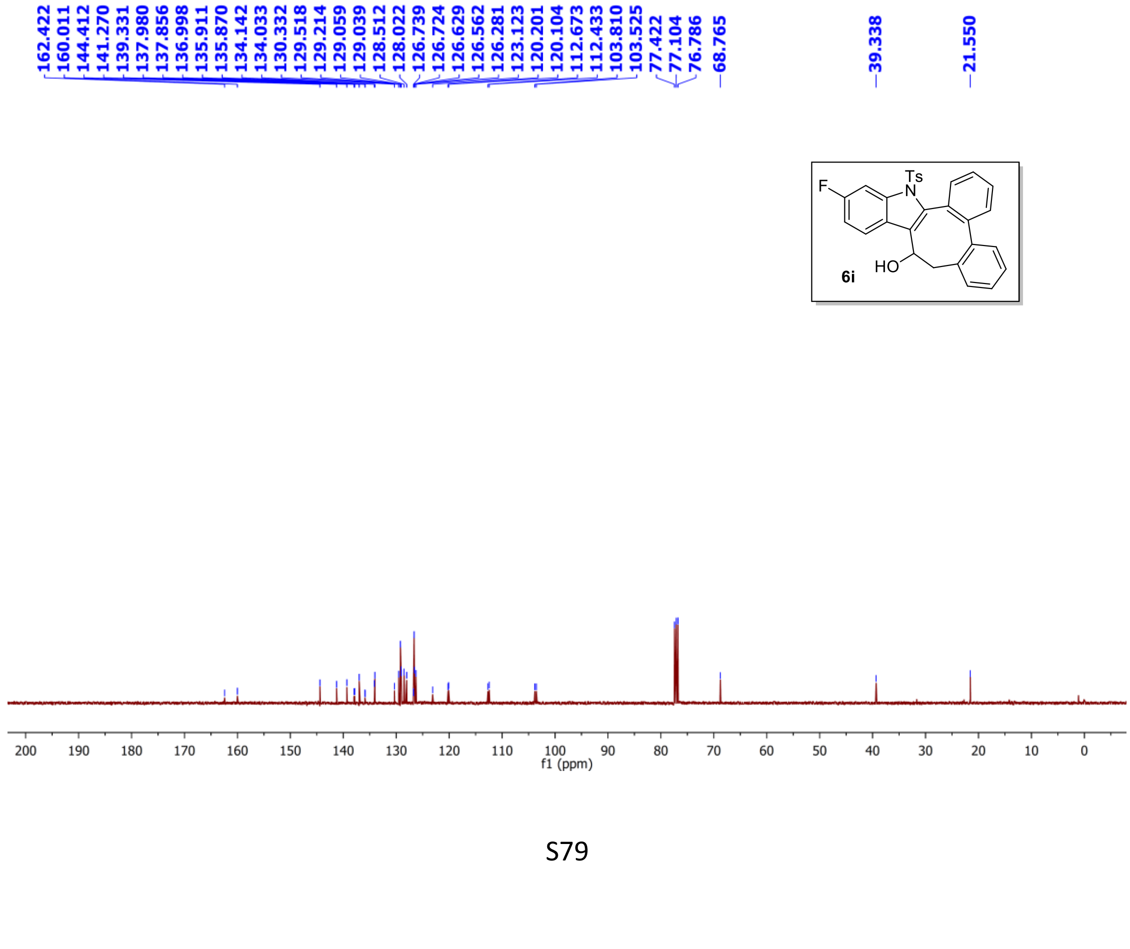
$^{13}C\{^{1}H\}$ NMR (100 MHz) of **6h :**



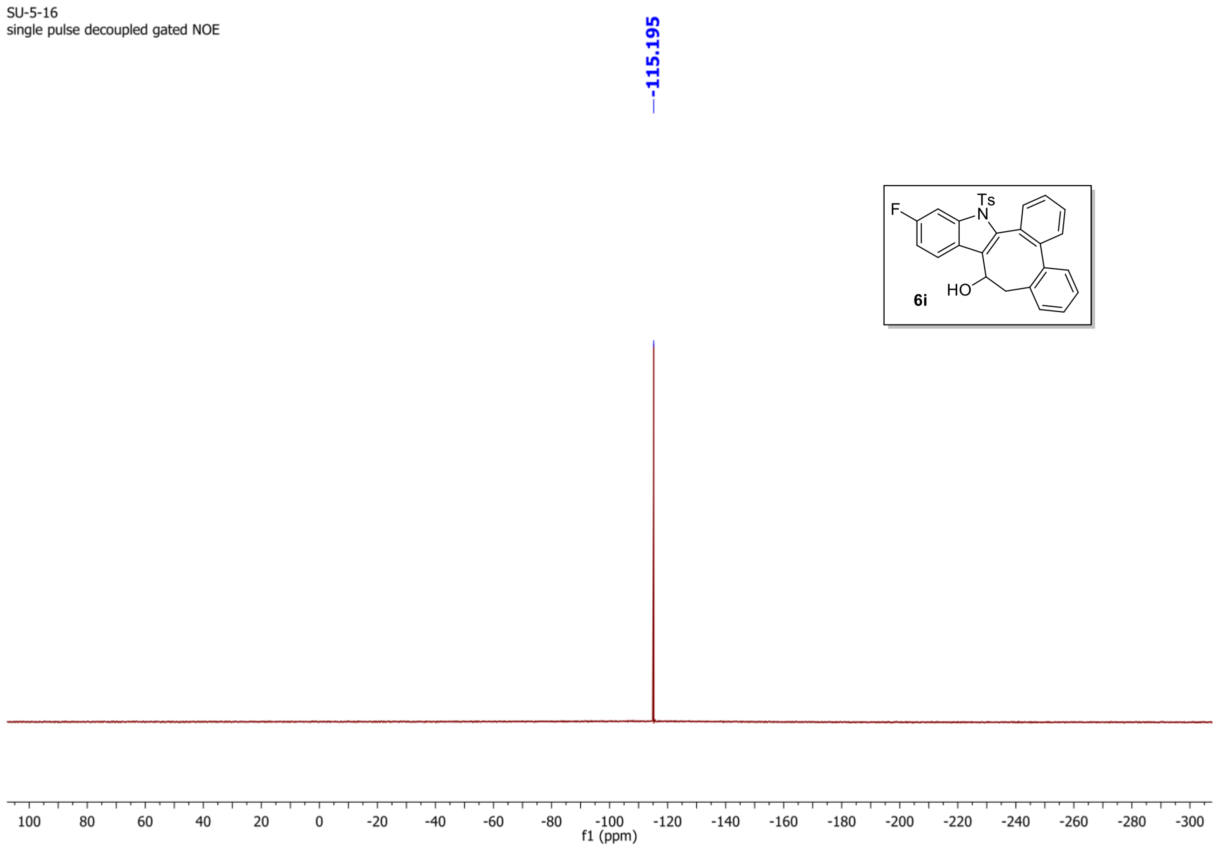
^{1}H NMR (400 MHz) of **6i :**



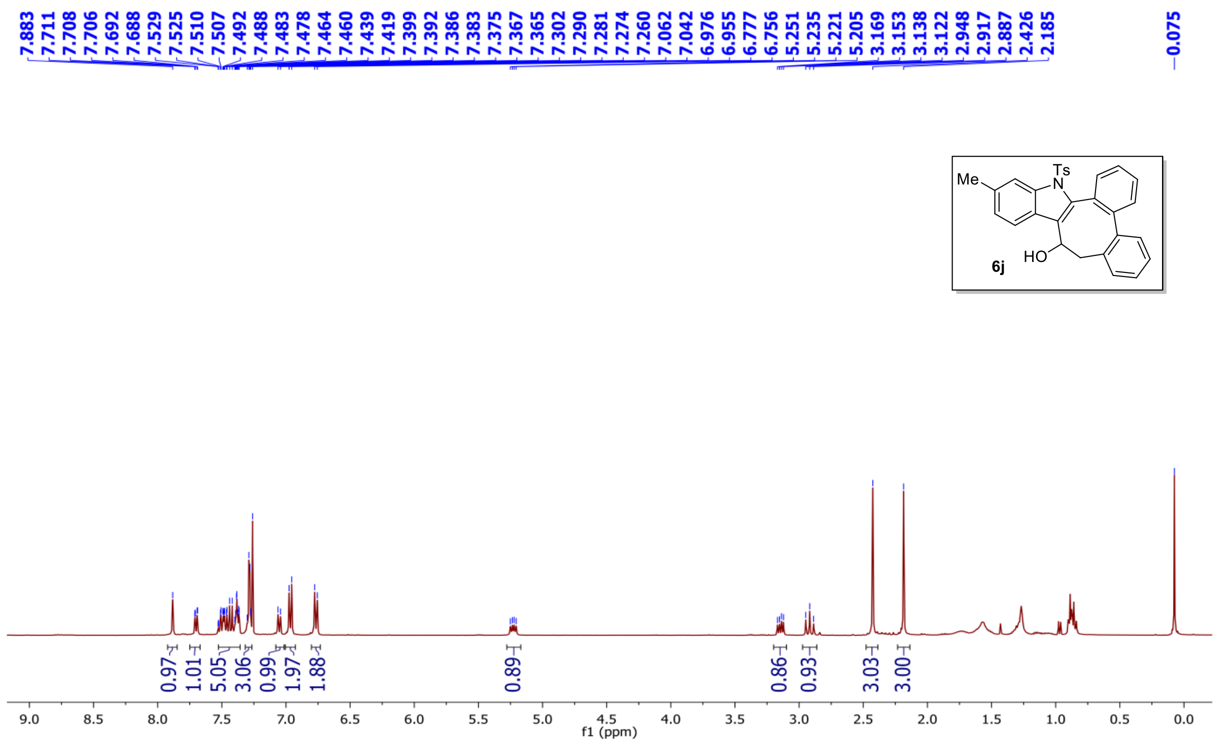
^{13}C{^{1}H} NMR (100 MHz) of **6i :**



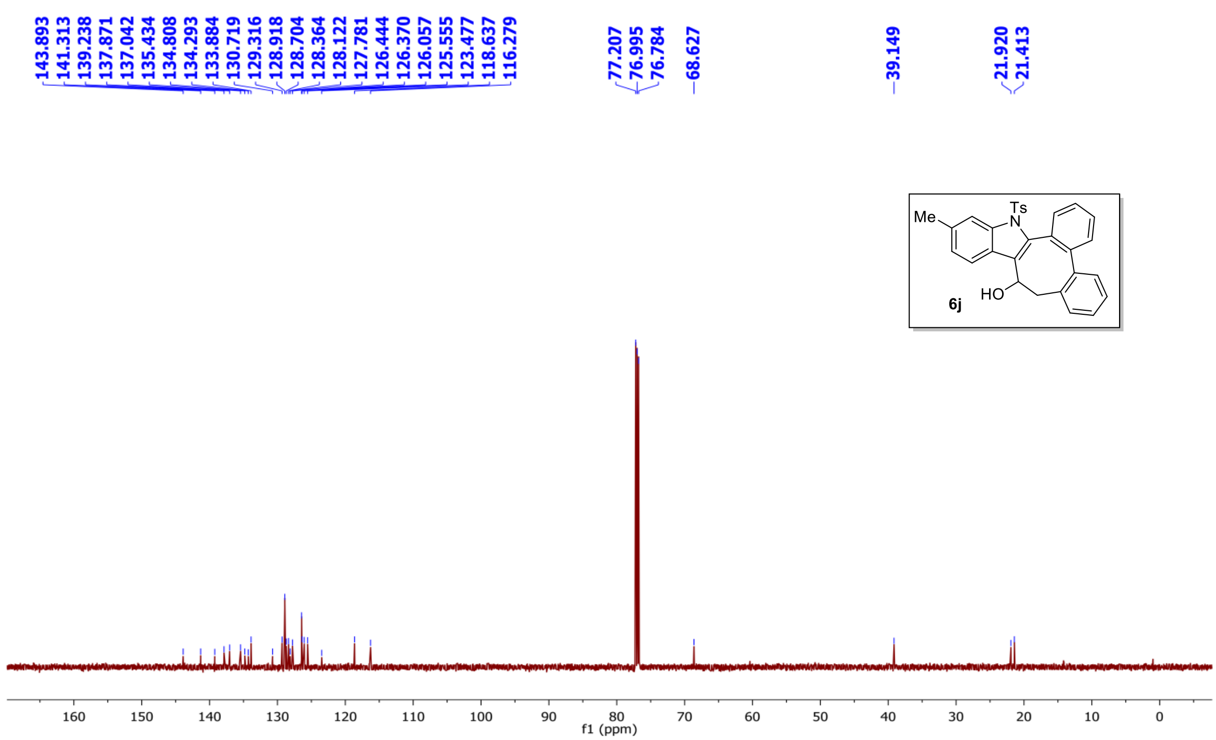
$^{19}F\{^1H\}$ NMR (376 MHz) of **6i** :



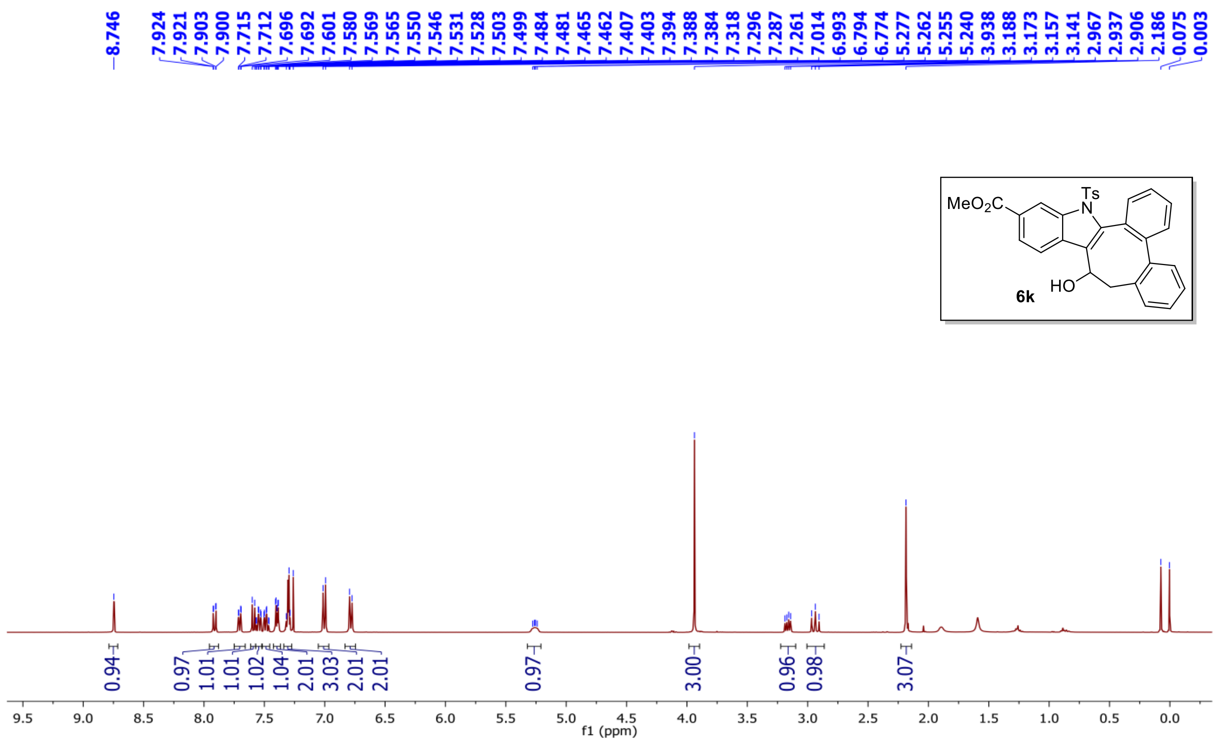
^{1}H NMR (400 MHz) of **6j :**



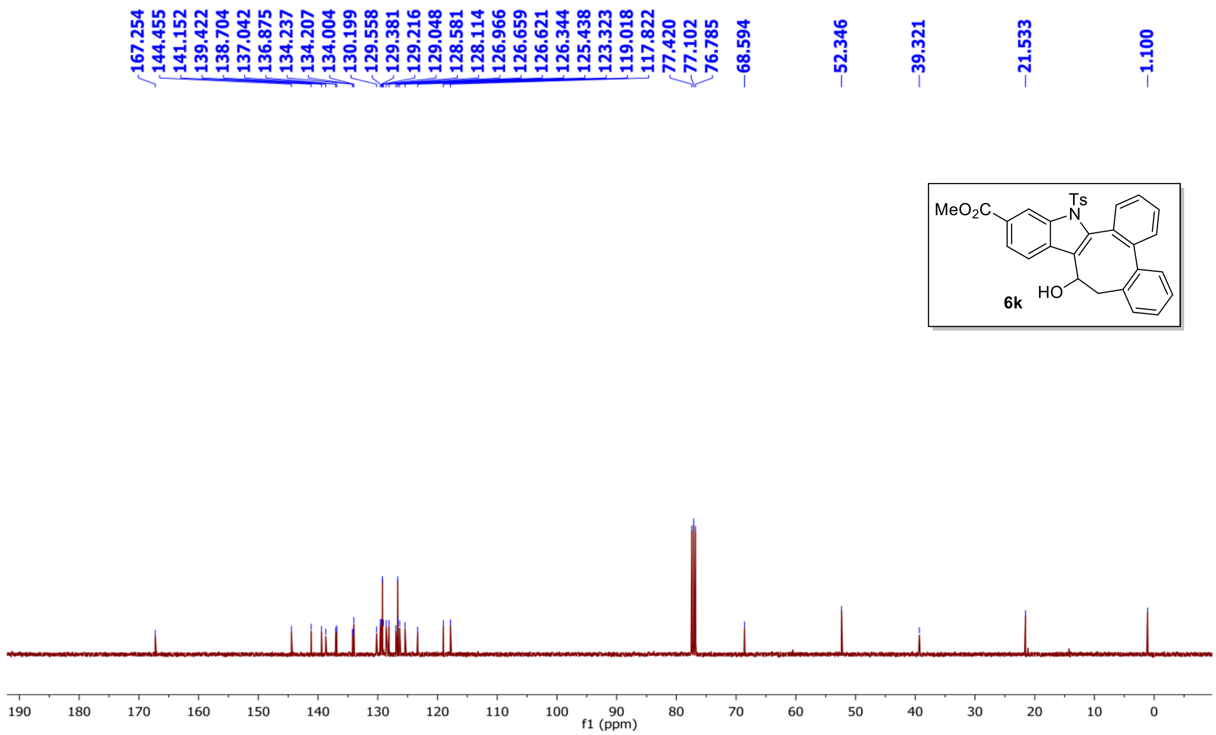
^{13}C{^{1}H} NMR (150 MHz) of **6j :**



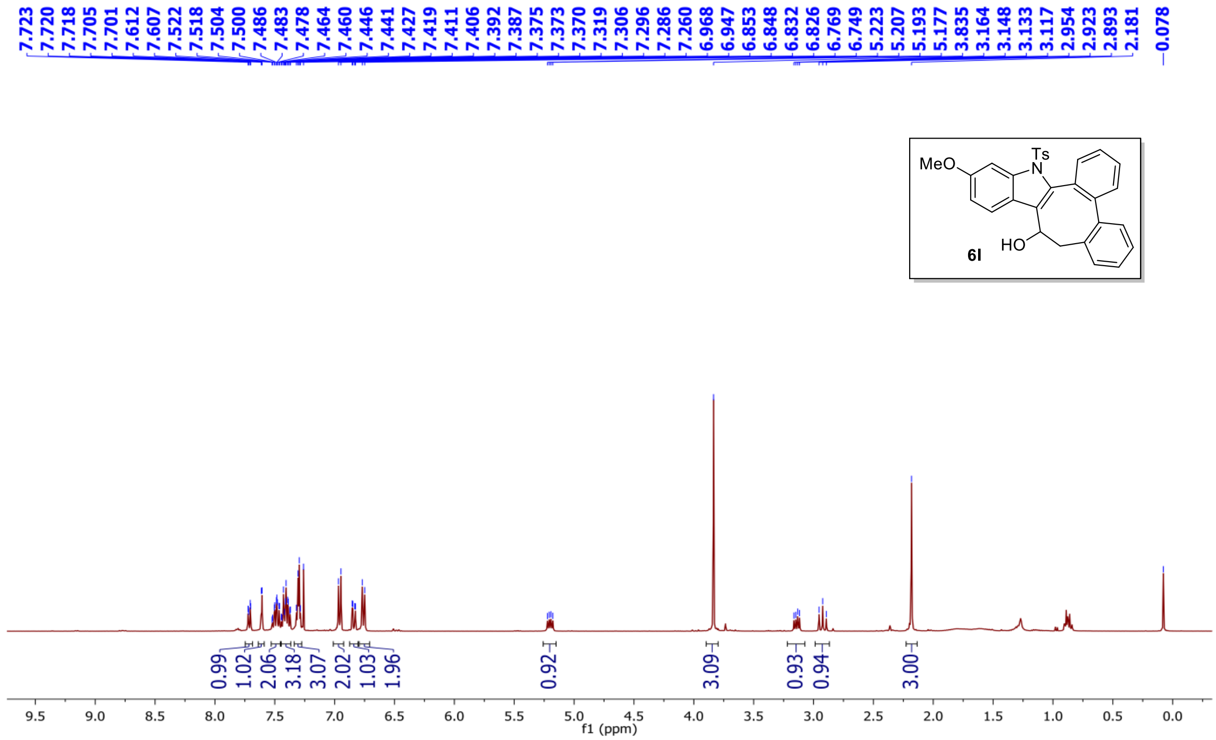
^{1}H NMR (400 MHz) of **6k :**



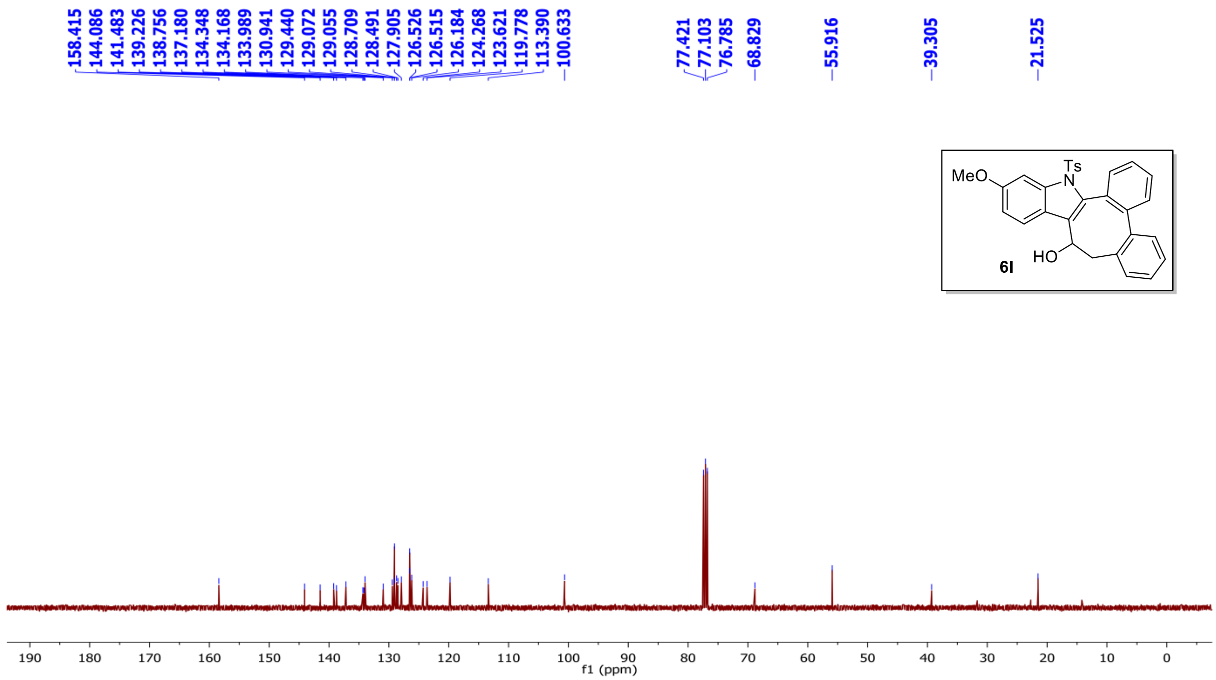
$^{13}C\{^{1}H\}$ NMR (100 MHz) of **6k :**



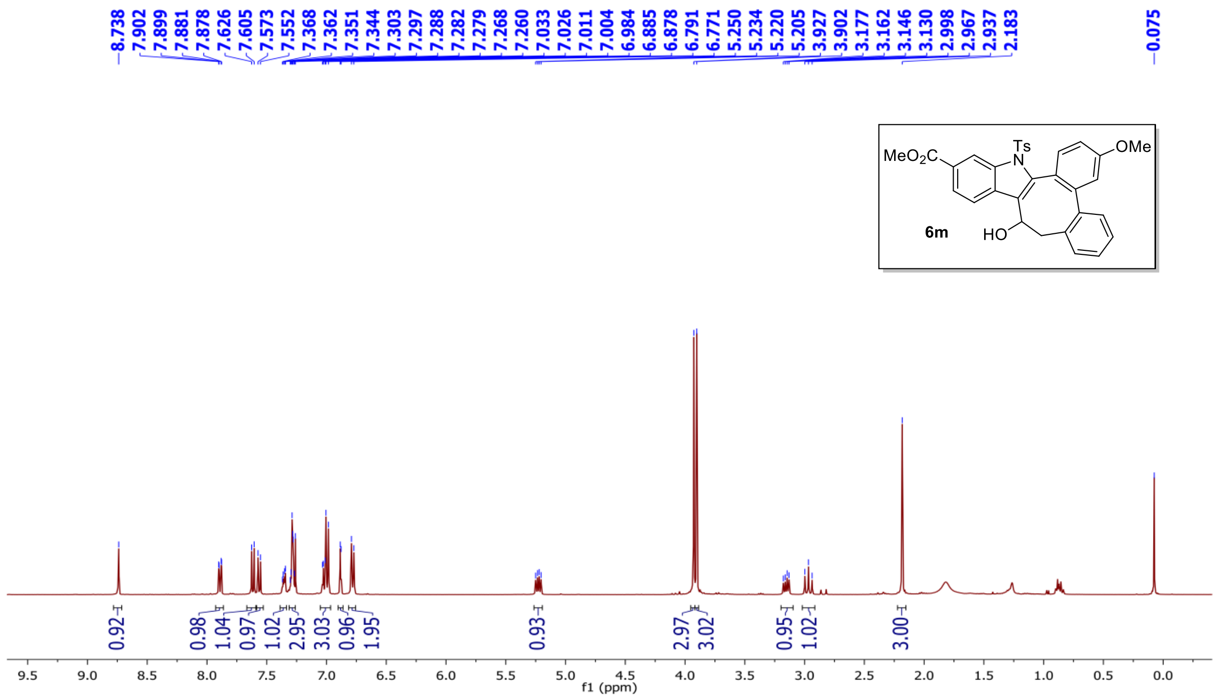
[1]H NMR (400 MHz) of **6l :**



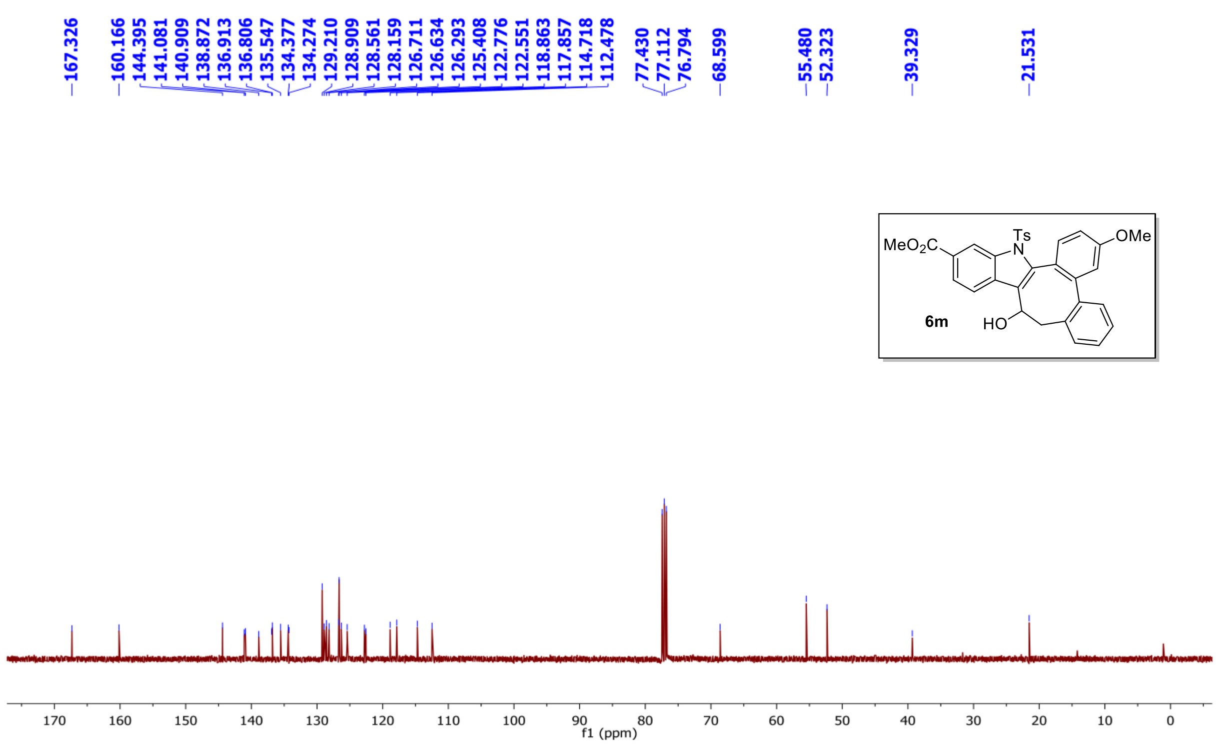
[13]C{[1]H} NMR (100 MHz) of **6l :**



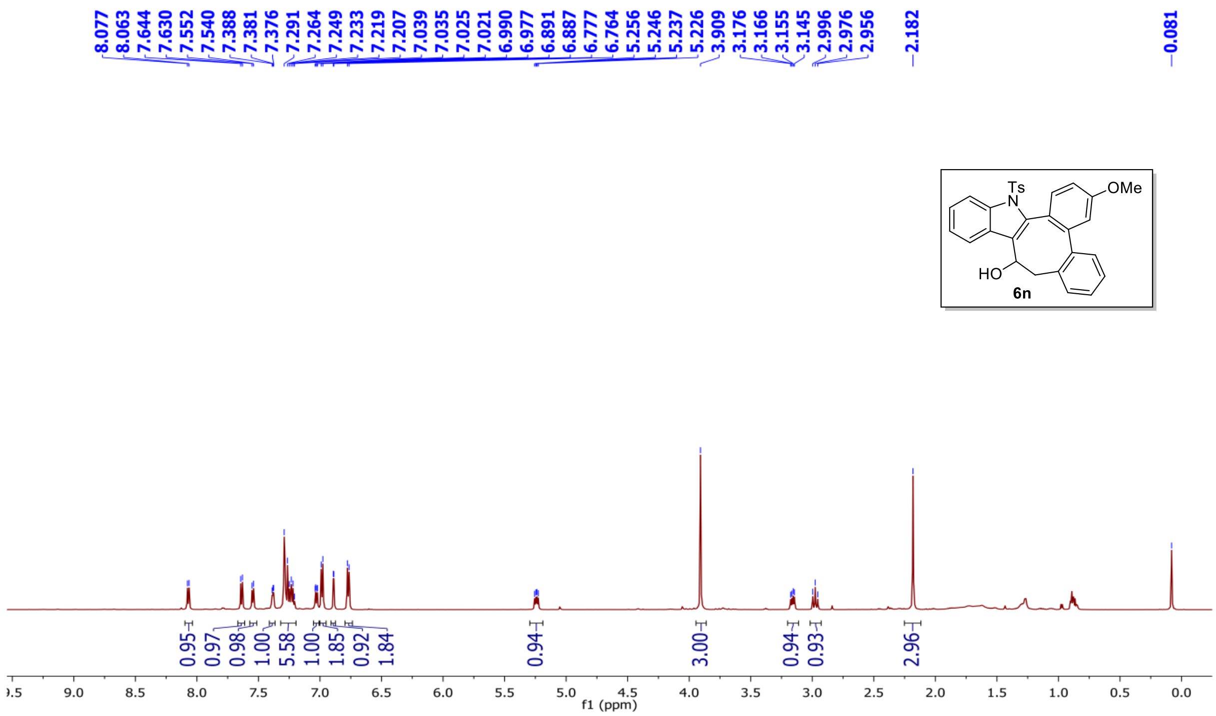
[1]H NMR (400 MHz) of **6m :**



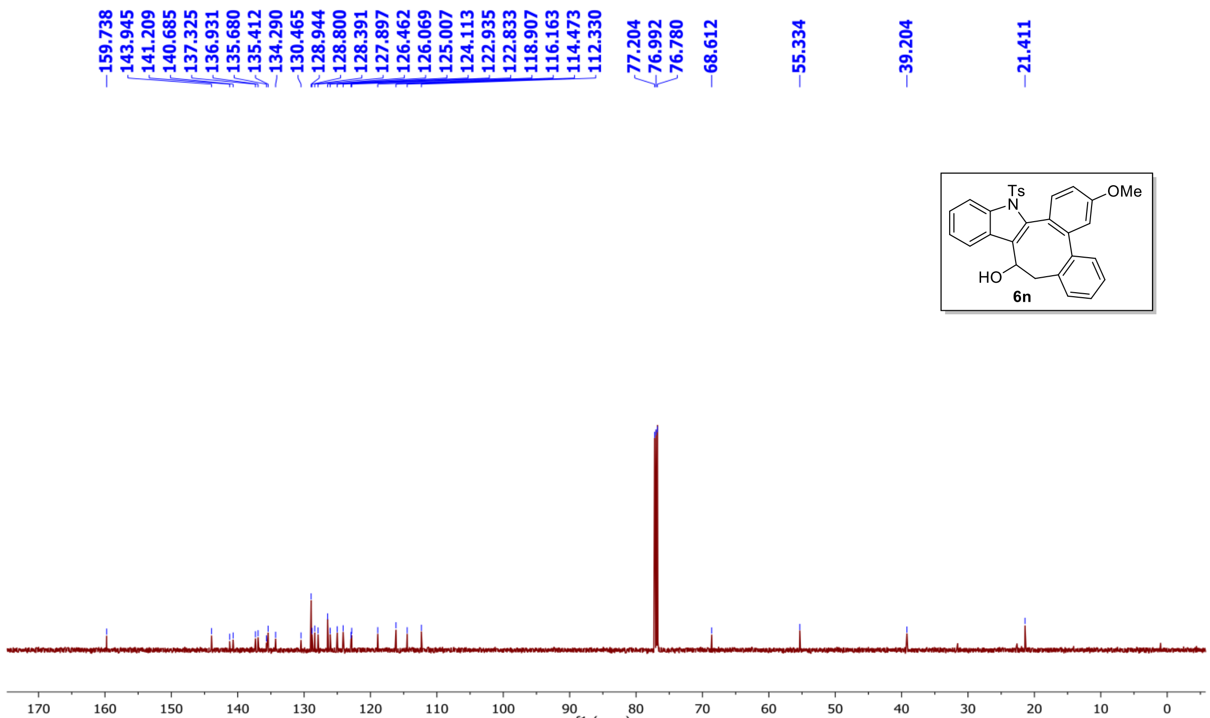
[13]C{[1]H} NMR (100 MHz) of **6m :**



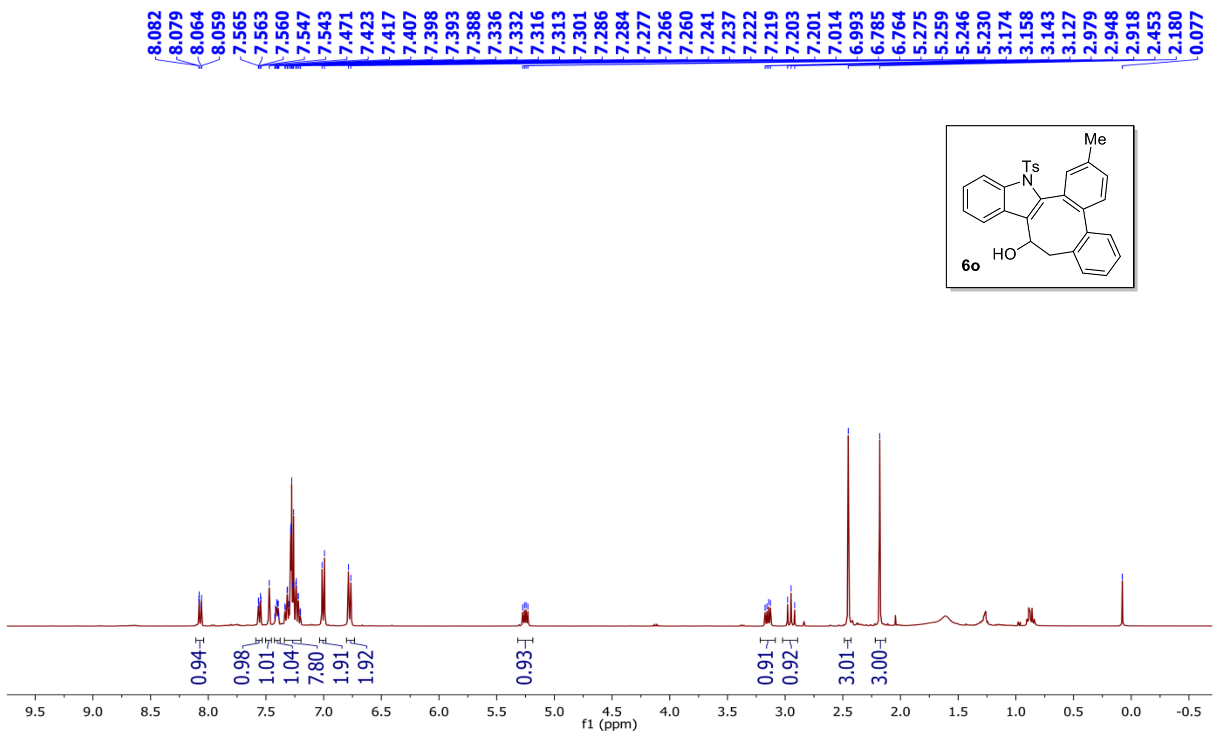
^{1}H NMR (600 MHz) of **6n :**



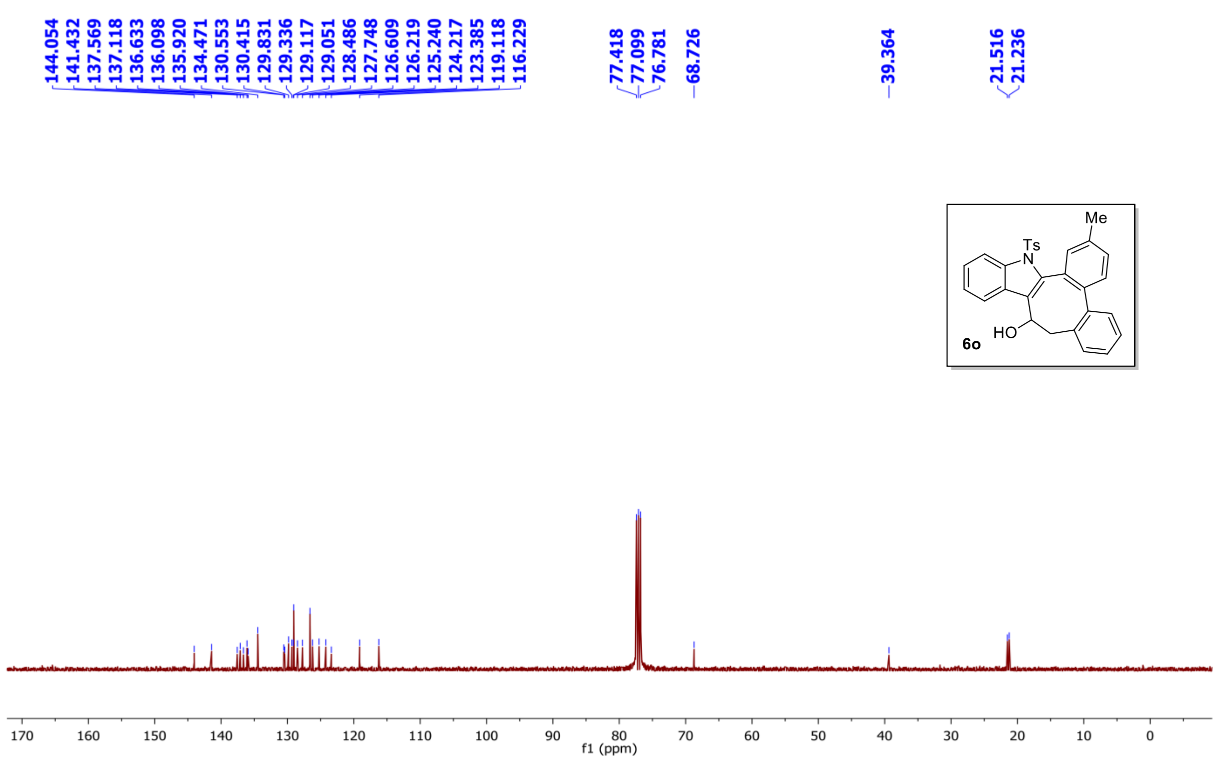
^{13}C{^{1}H} NMR (150 MHz) of **6n :**



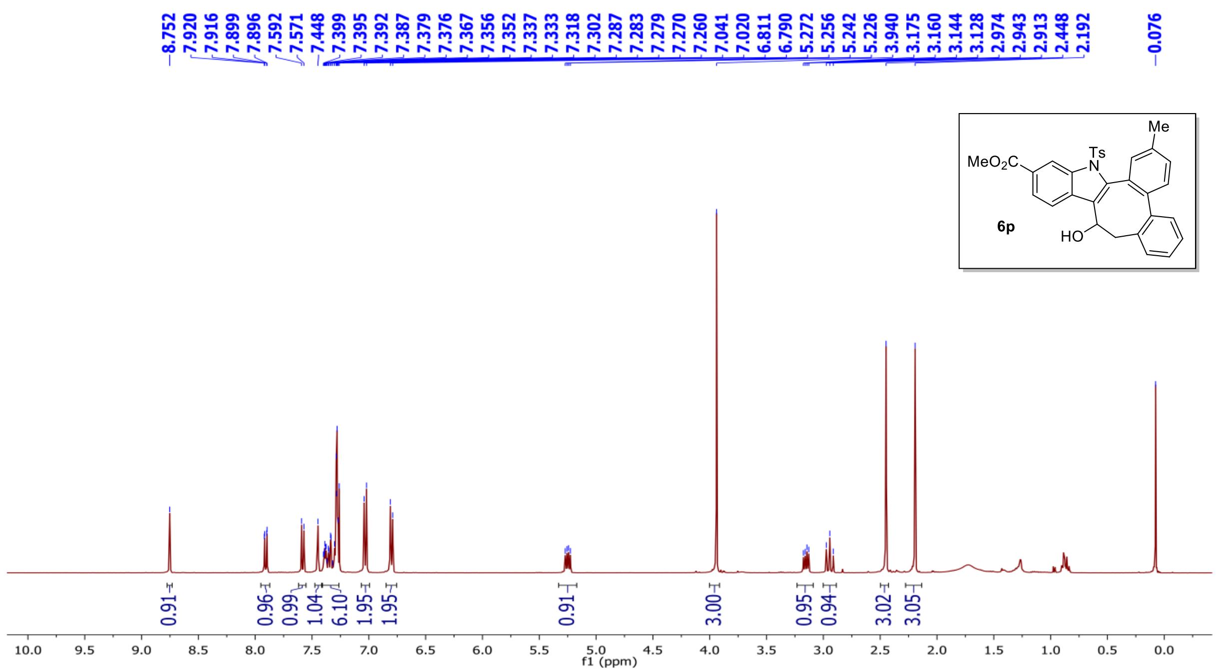
[1]H NMR (400 MHz) of **6o :**



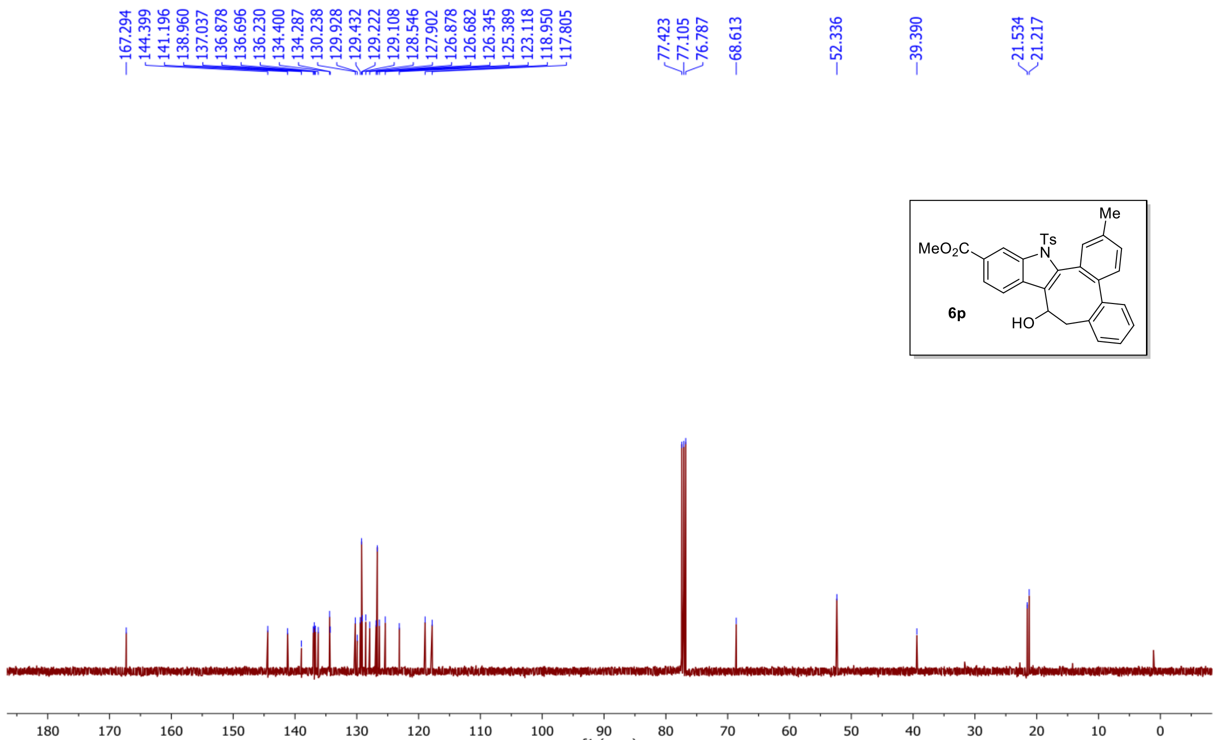
[13]C{[1]H} NMR (100 MHz) of **6o :**



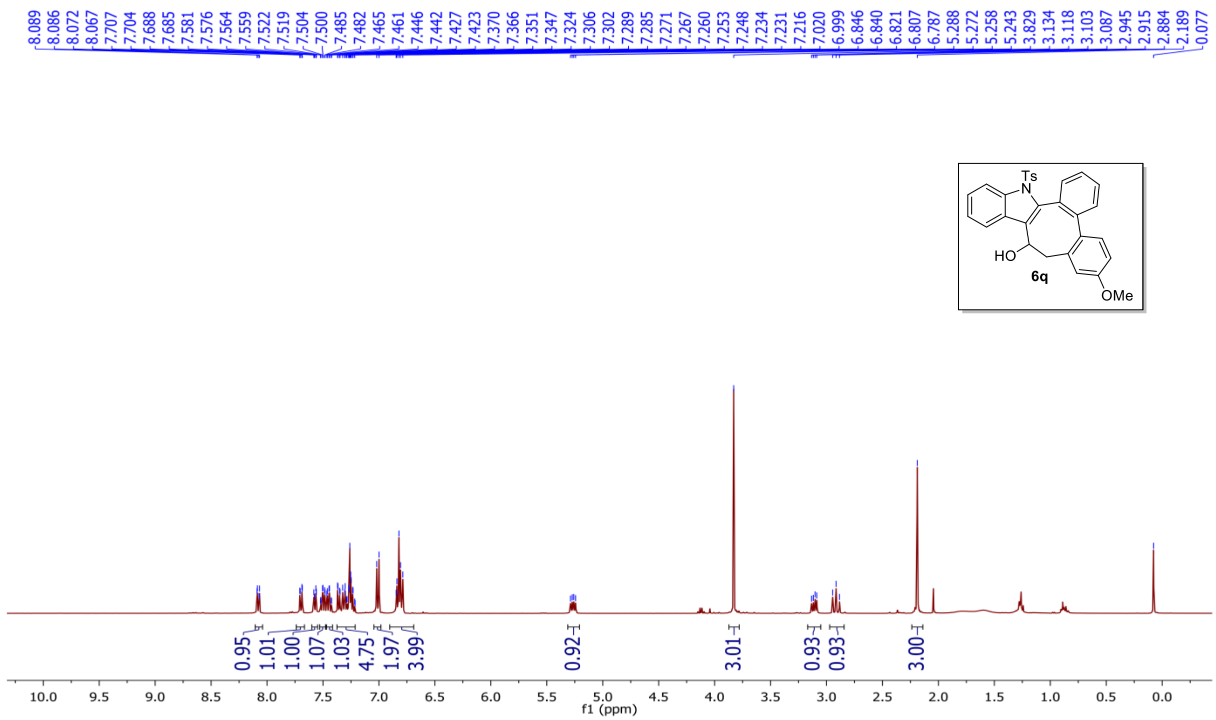
^{1}H NMR (400 MHz) of **6p :**



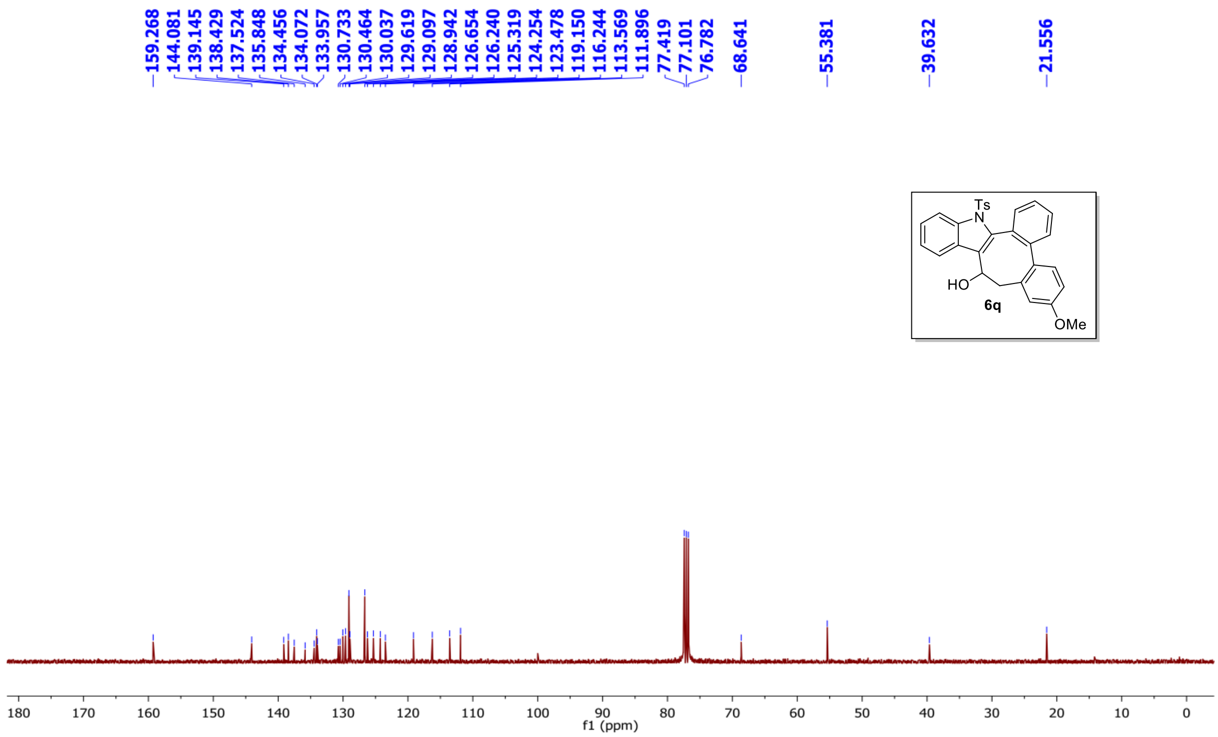
$^{13}C\{^{1}H\}$ NMR (100 MHz) of **6p :**



^{1}H NMR (400 MHz) of **6q :**

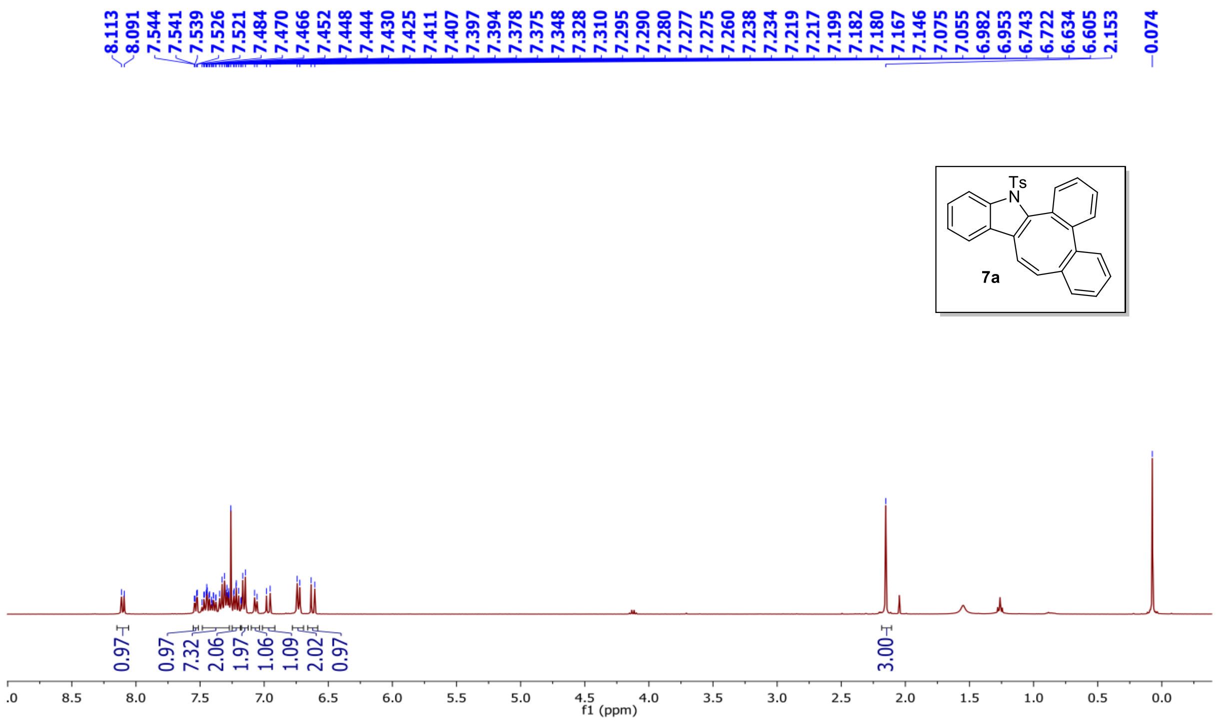


^{13}C{^{1}H} NMR (100 MHz) of **6q :**

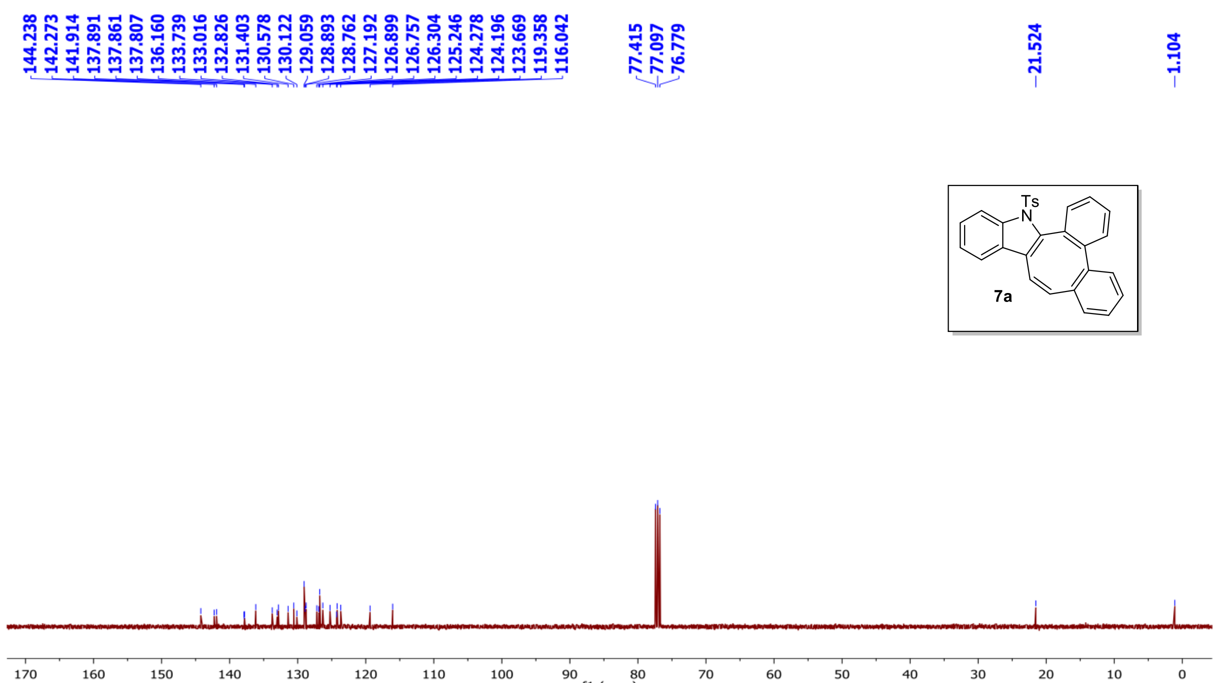


23. NMR Spectra of Compounds 7a-7j :

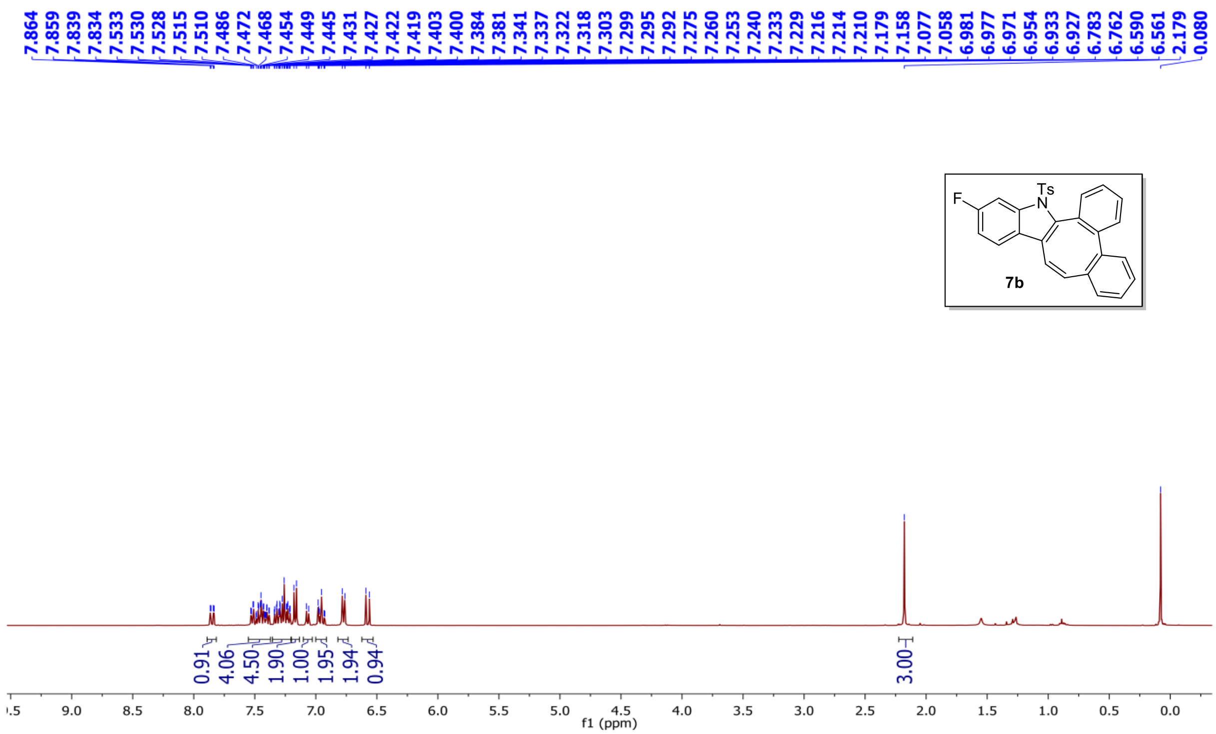
^{1}H NMR (400 MHz) of **7a :**



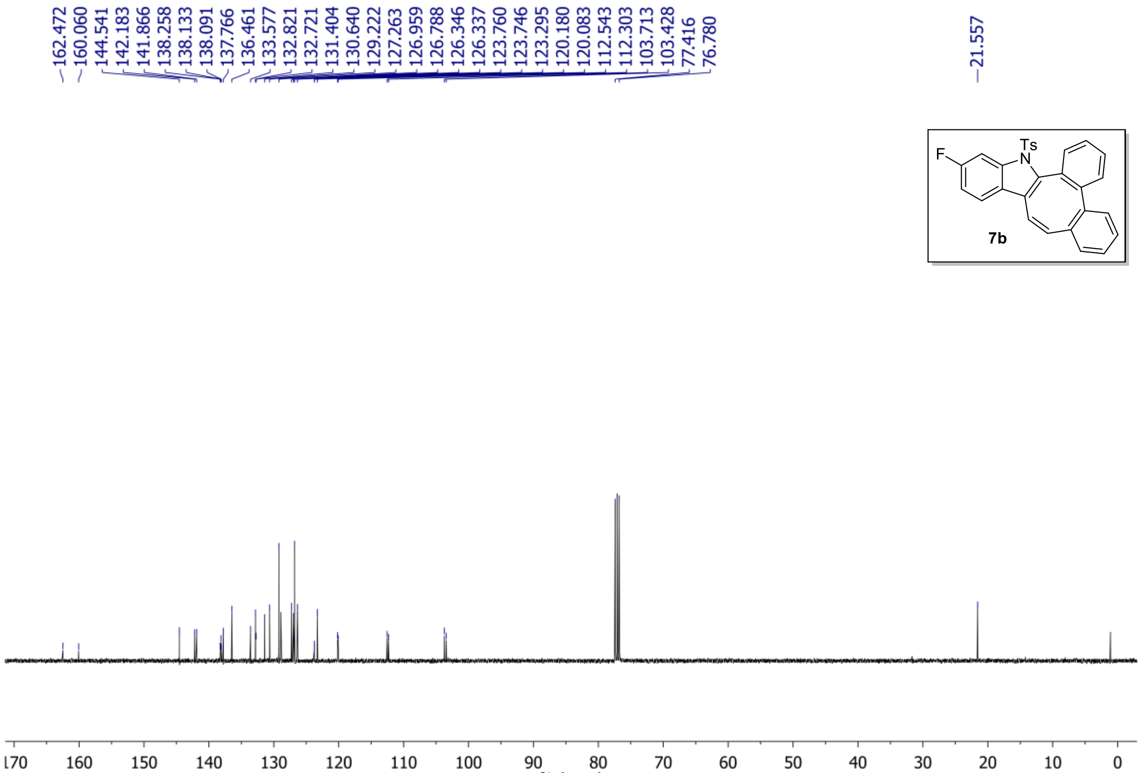
^{13}C{^{1}H} NMR (100 MHz) of **7a :**



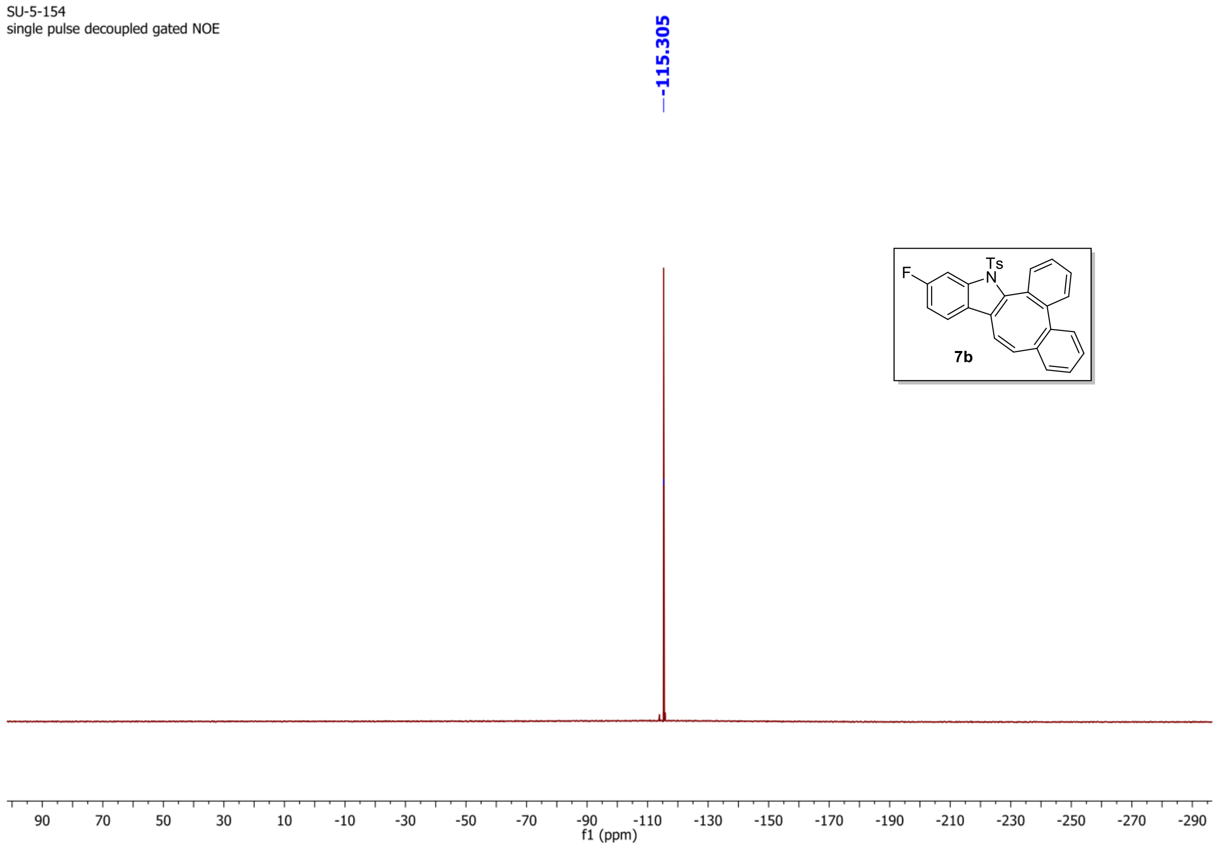
[1]H NMR (400 MHz) of **7b :**



[13]C{[1]H} NMR (100 MHz) of **7b :**

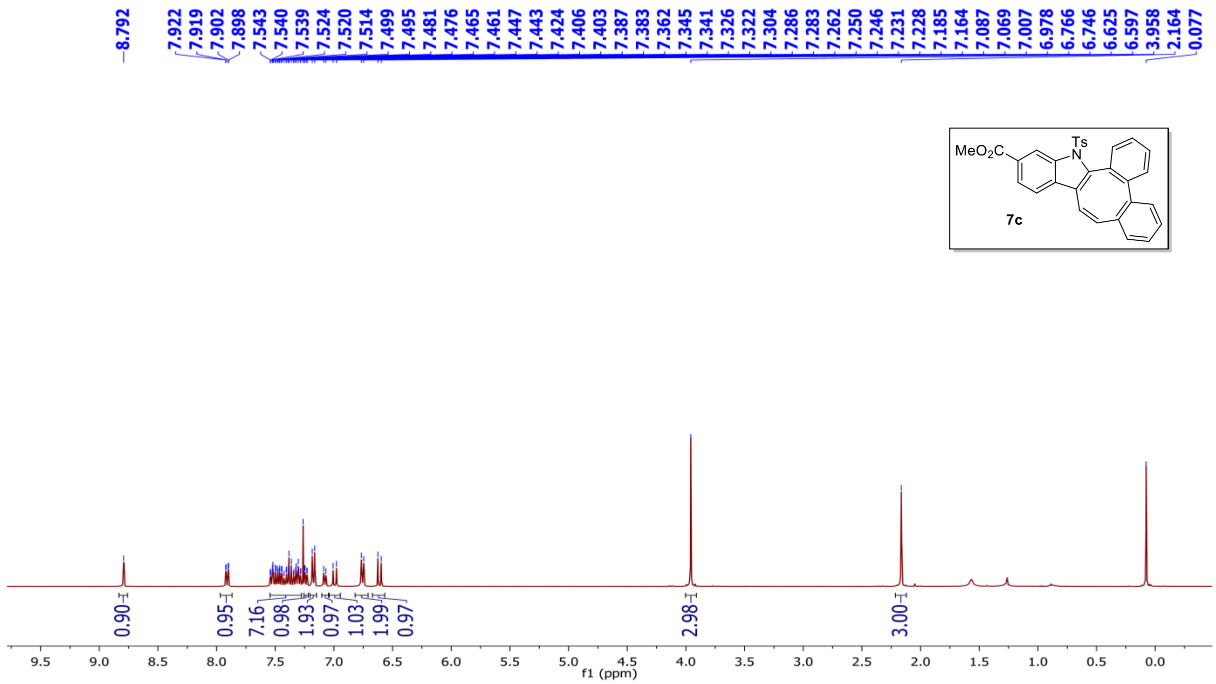


$^{19}F\{^{1}H\}$ NMR (376 MHz) of **7b :**

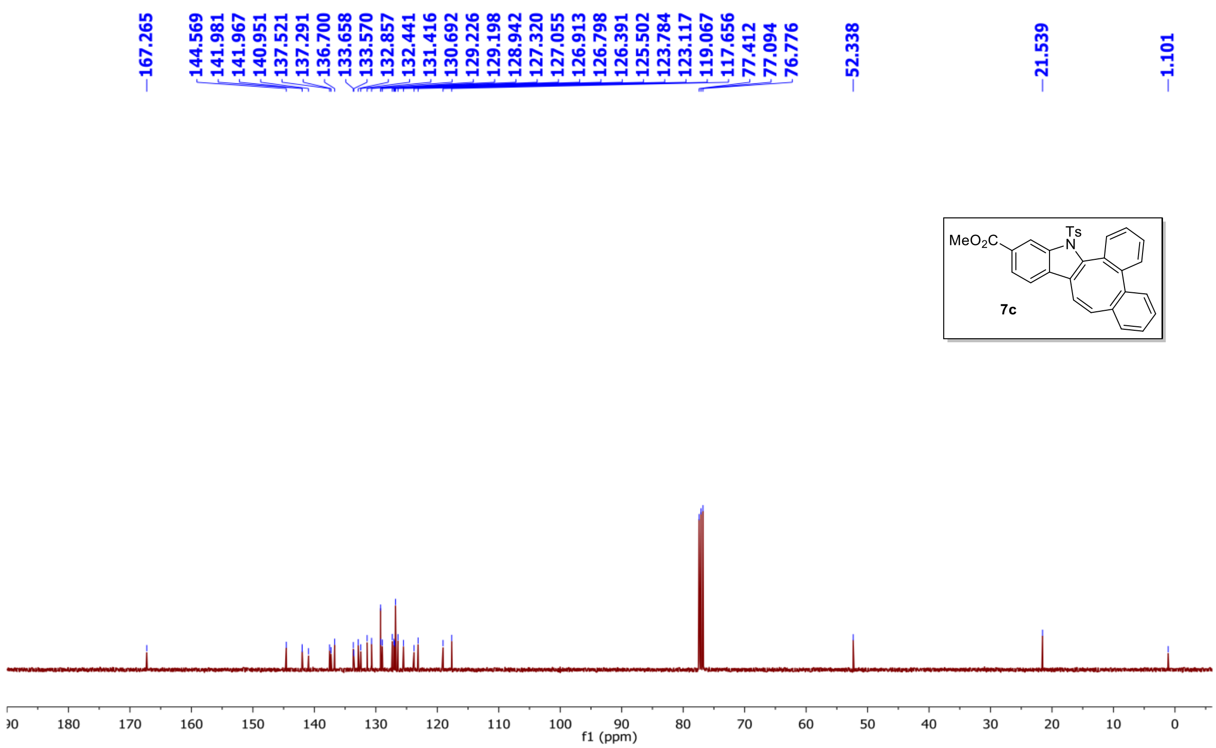


7b

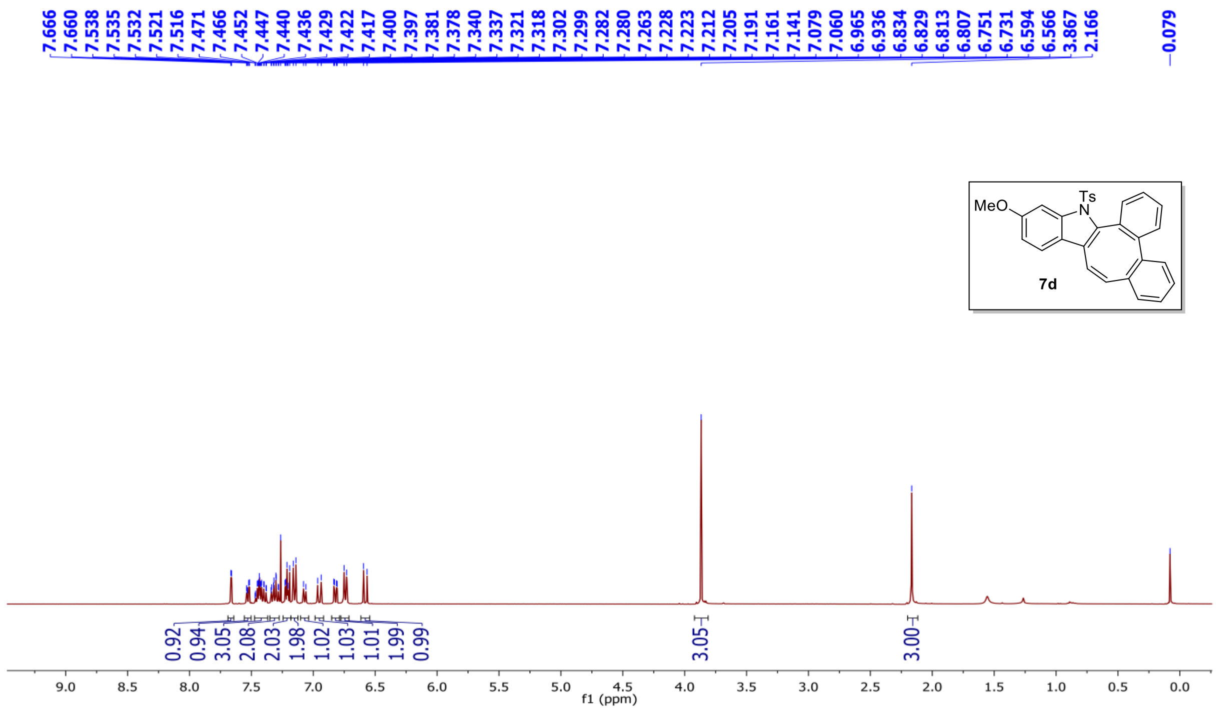
^{1}H NMR (400 MHz) of **7c :**



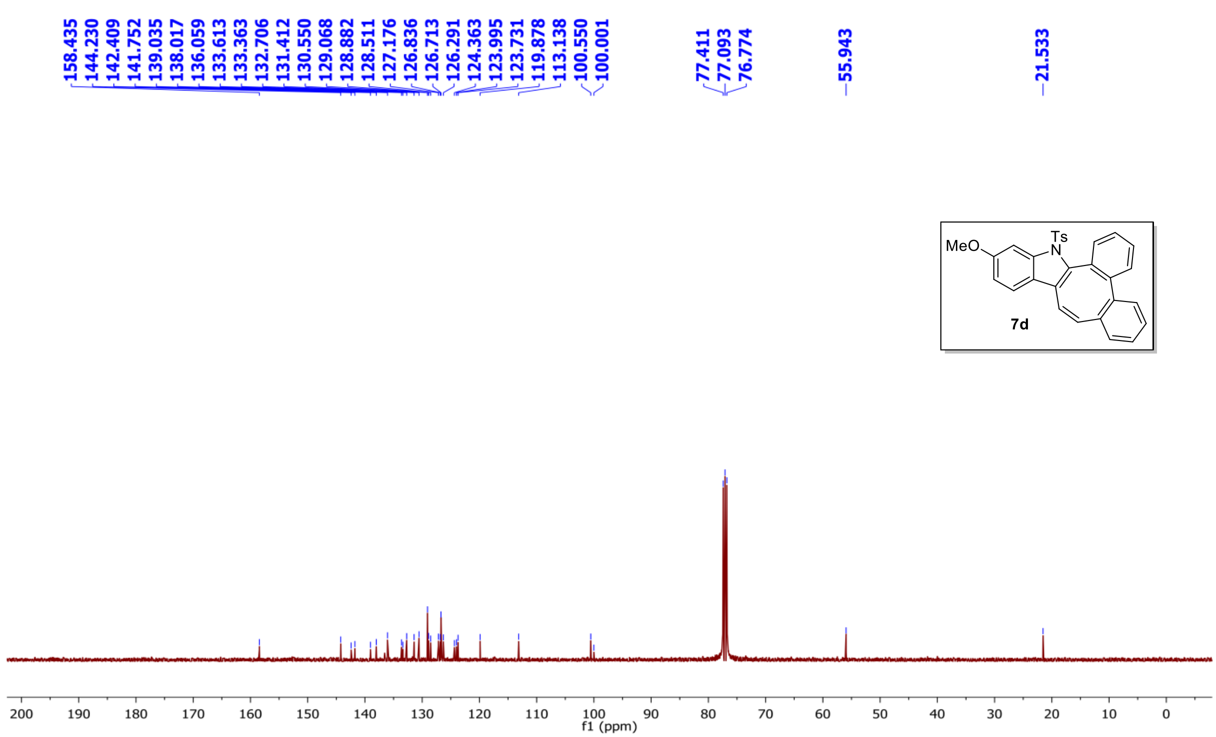
^{13}C{^{1}H} NMR (100 MHz) of **7c :**



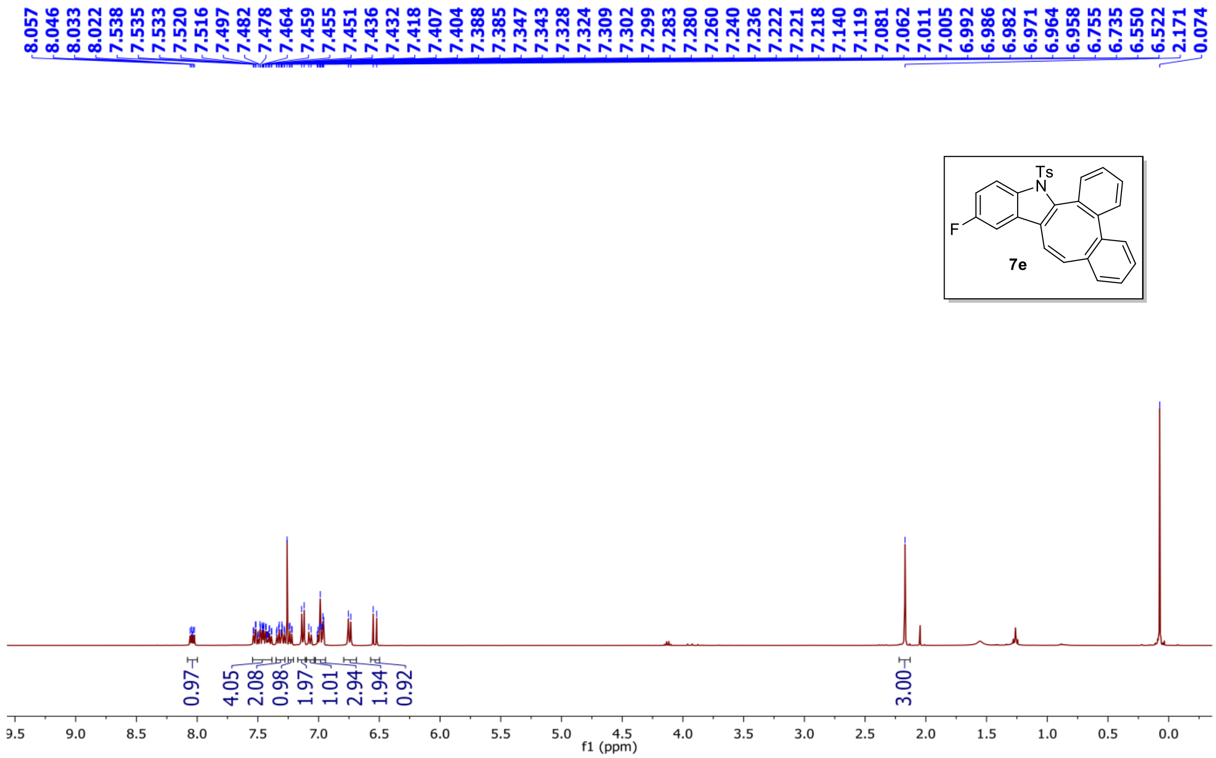
[1]H NMR (400 MHz) of **7d :**



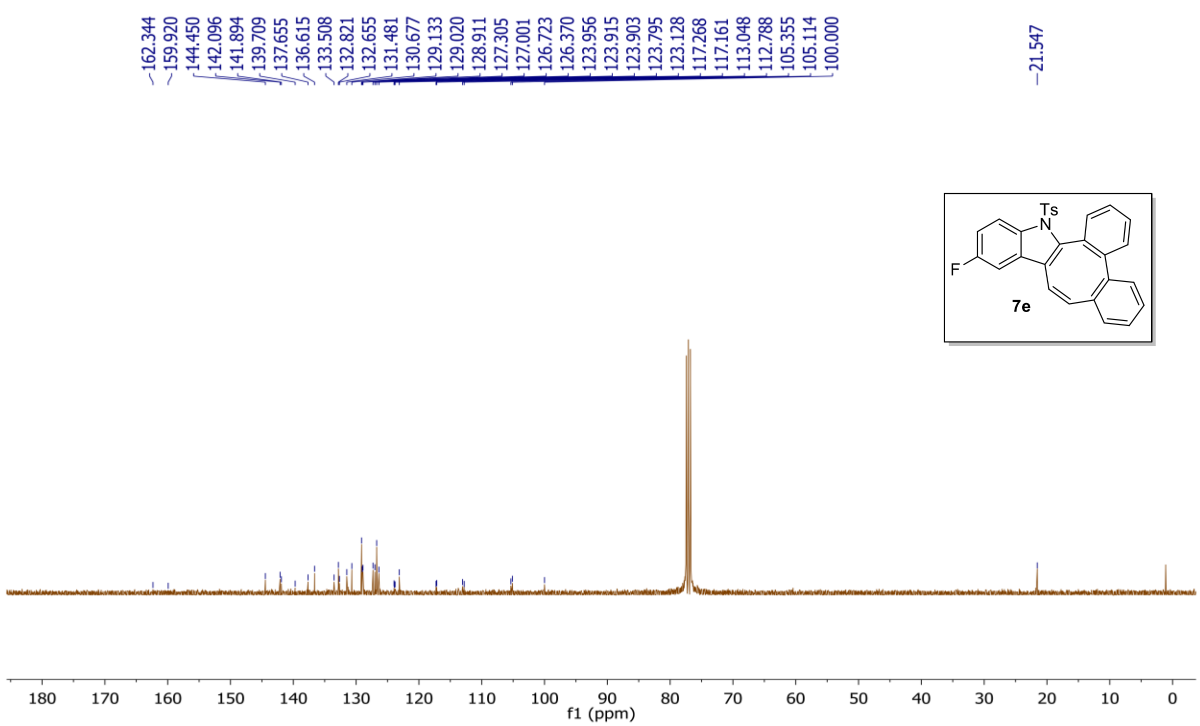
$^{13}C\{^1H\}$ NMR (100 MHz) of **7d :**



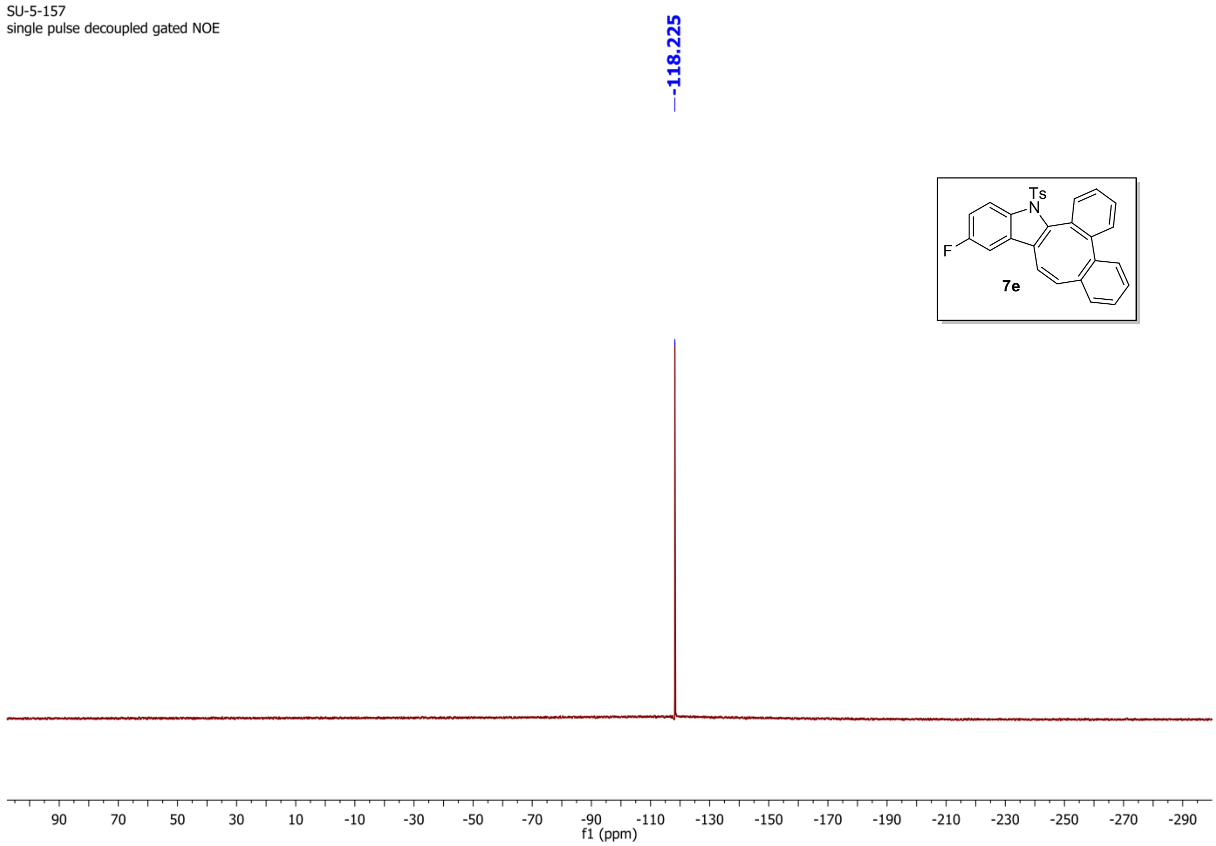
^{1}H NMR (400 MHz) of **7e :**



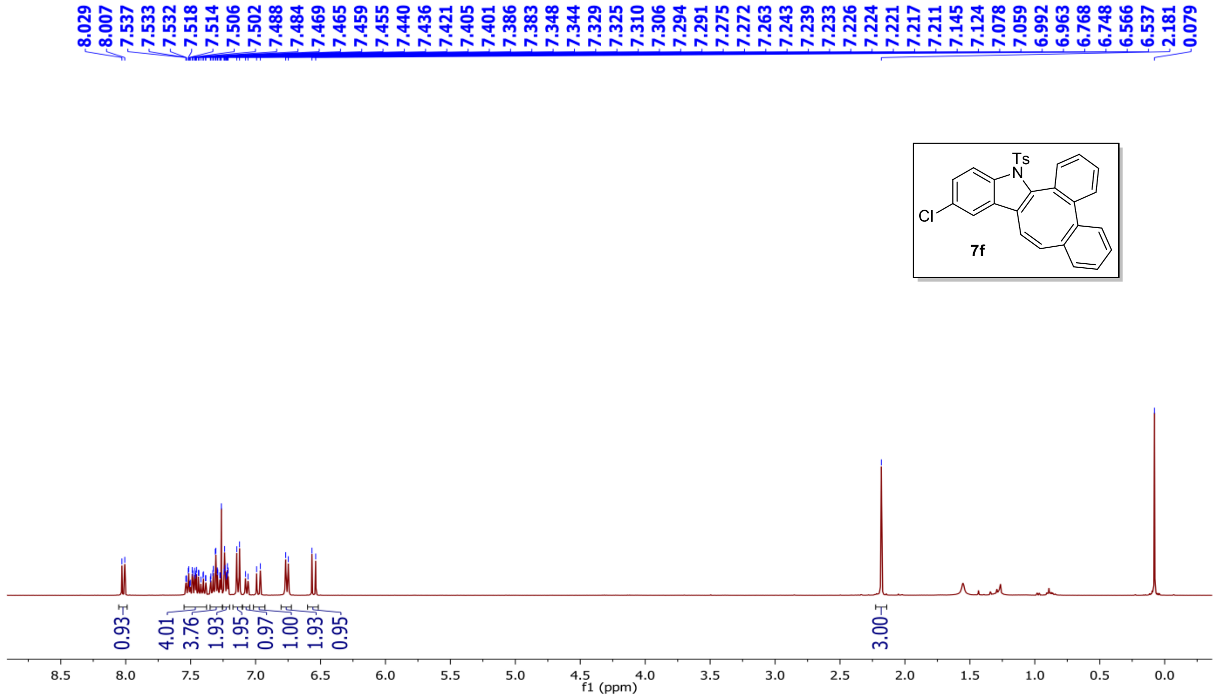
$^{13}C\{^{1}H\}$ NMR (100 MHz) of **7e :**



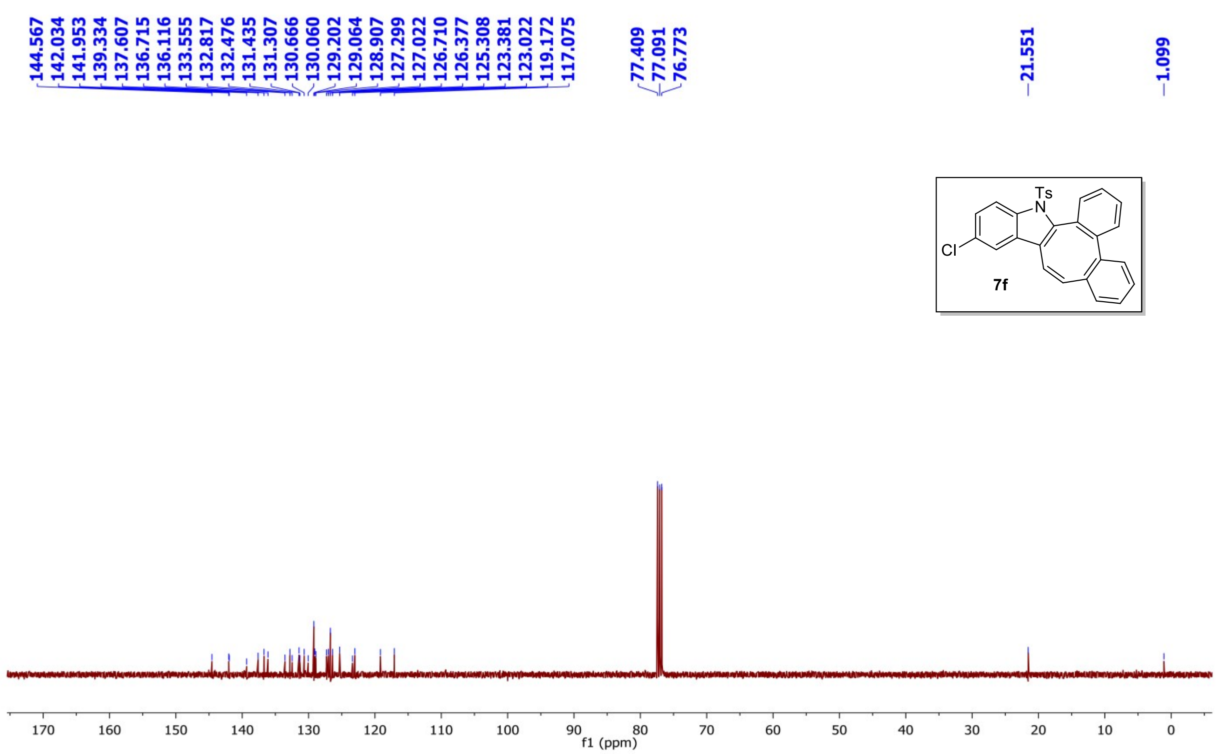
$^{19}F\{^1H\}$ NMR (376 MHz) of **7e :**



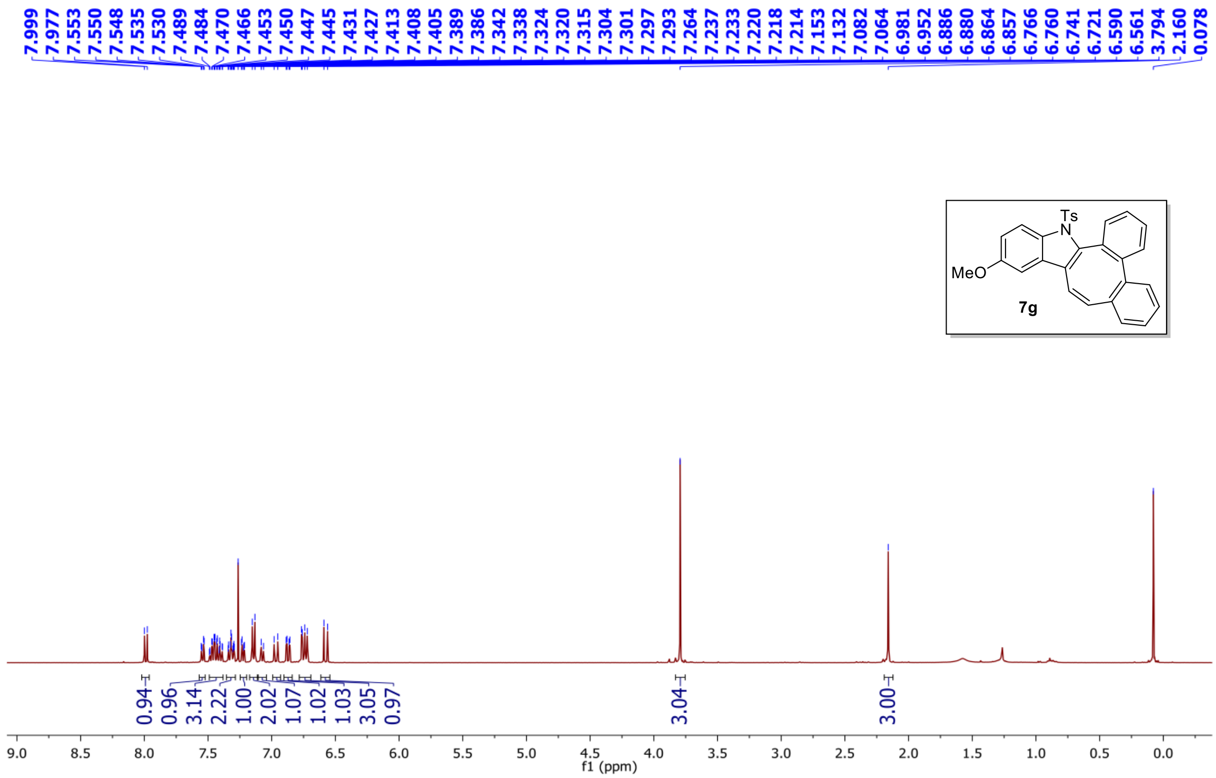
^{1}H NMR (400 MHz) of **7f :**



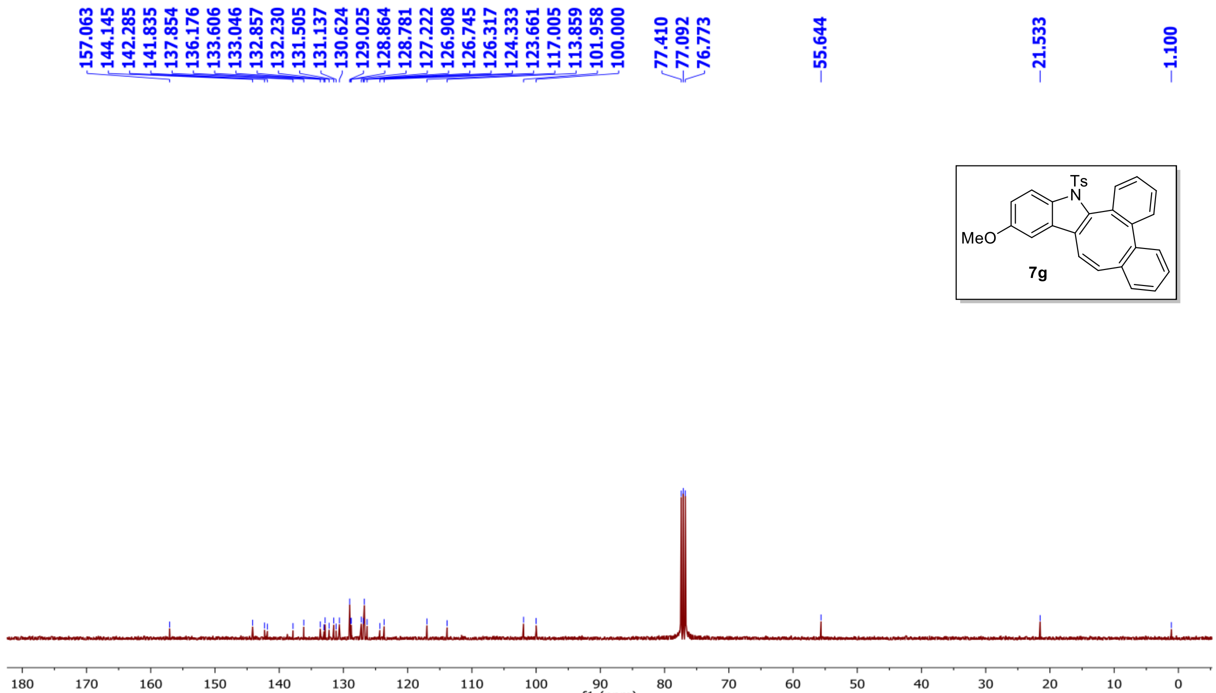
$^{13}C\{^{1}H\}$ NMR (100 MHz) of **7f :**



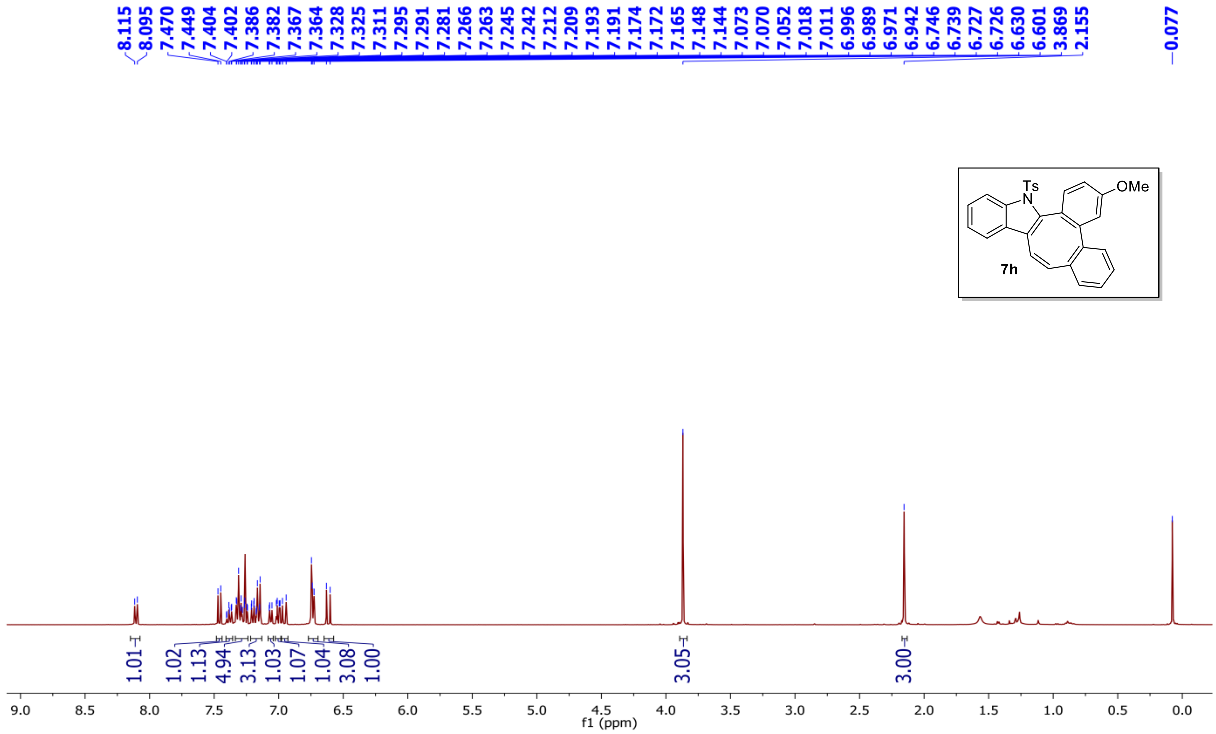
^{1}H NMR (400 MHz) of **7g :**



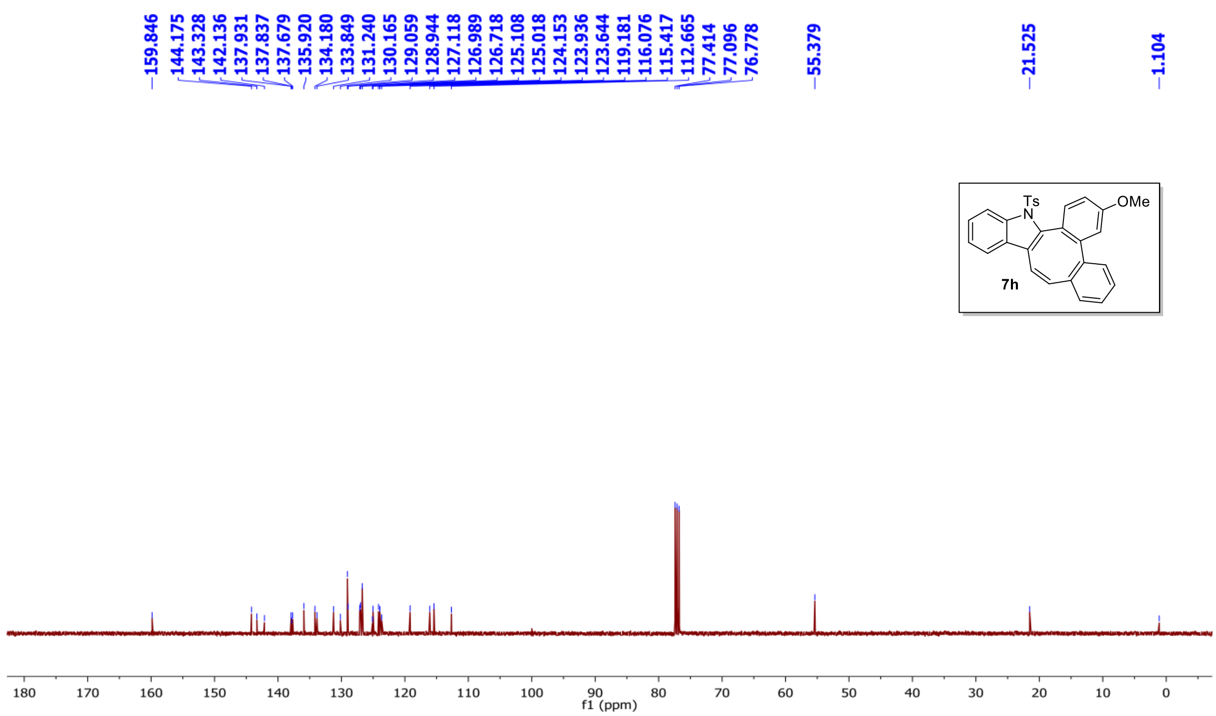
$^{13}C\{^{1}H\}$ NMR (100 MHz) of **7g :**



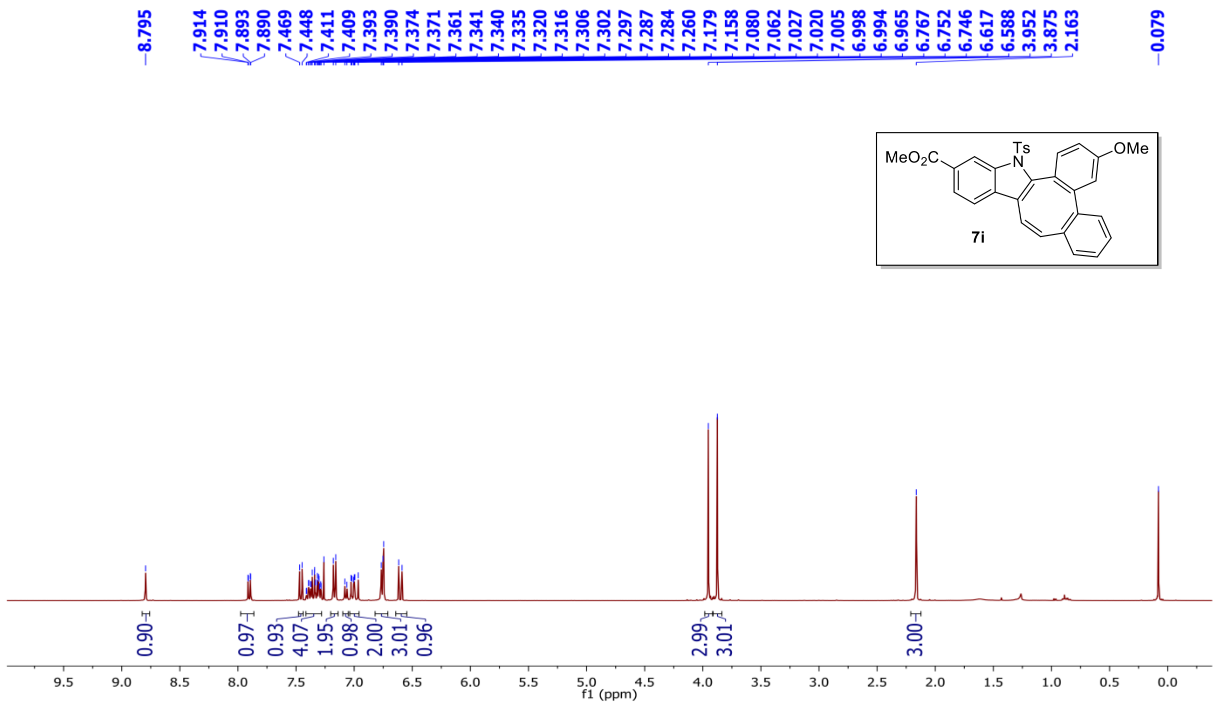
^{1}H NMR (400 MHz) of **7h :**



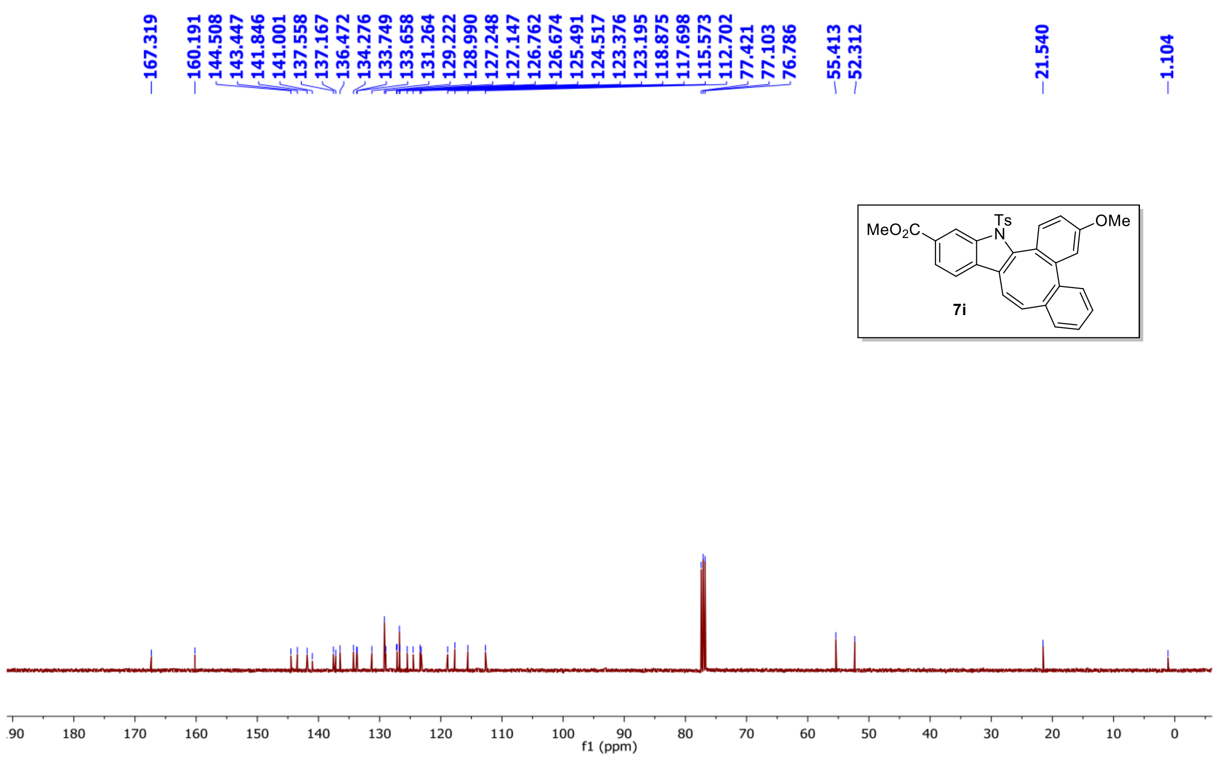
^{13}C{^{1}H} NMR (100 MHz) of **7h :**



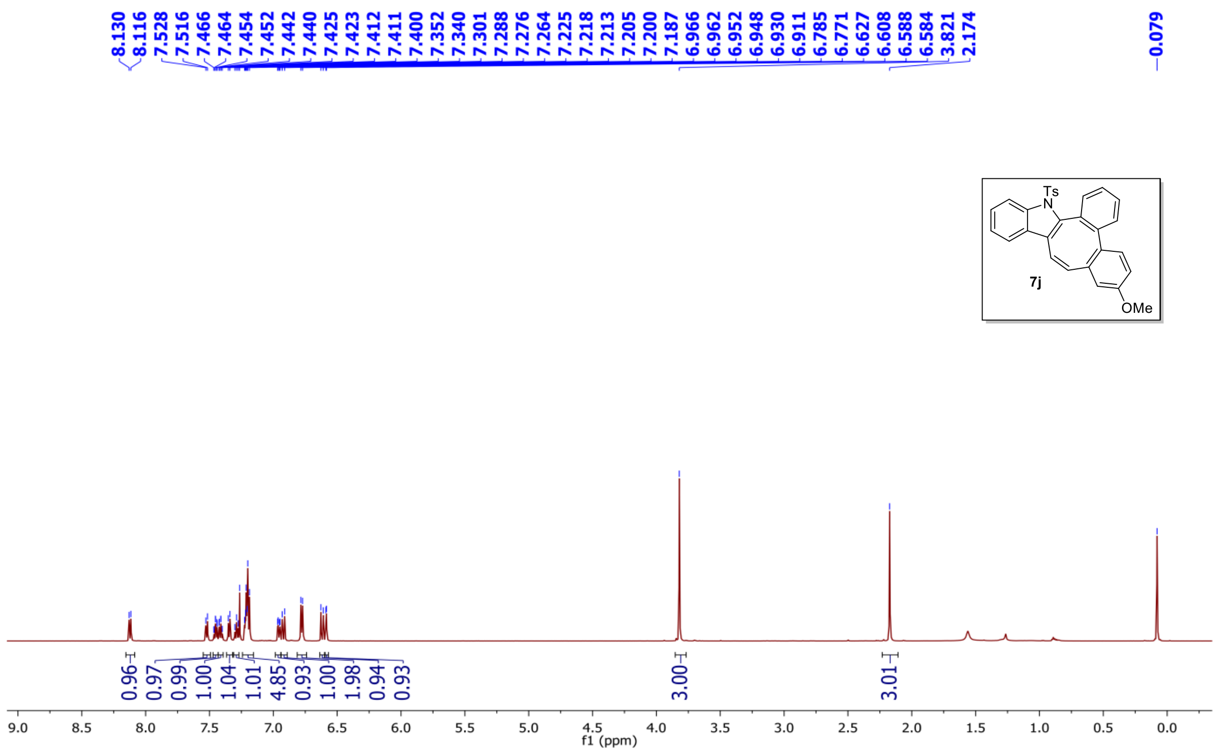
^{1}H NMR (400 MHz) of **7i :**



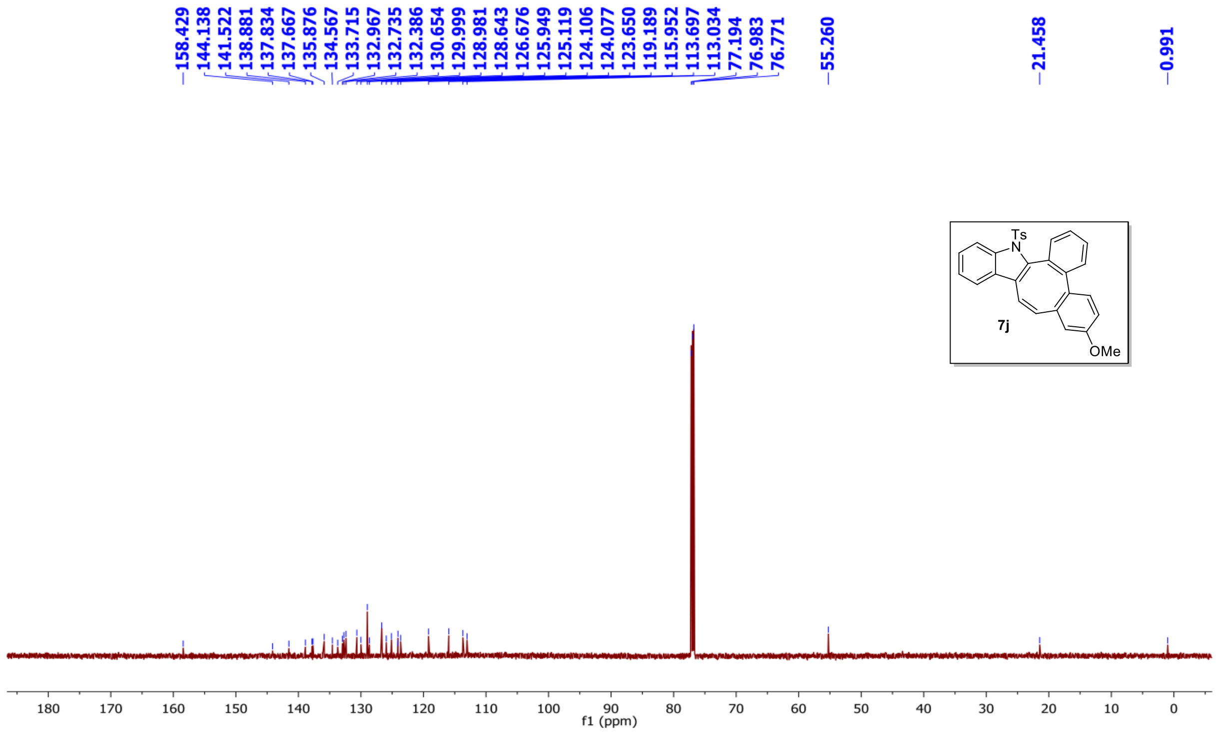
^{13}C{^{1}H} NMR (100 MHz) of **7i :**



^1H NMR (600 MHz) of **7j :**

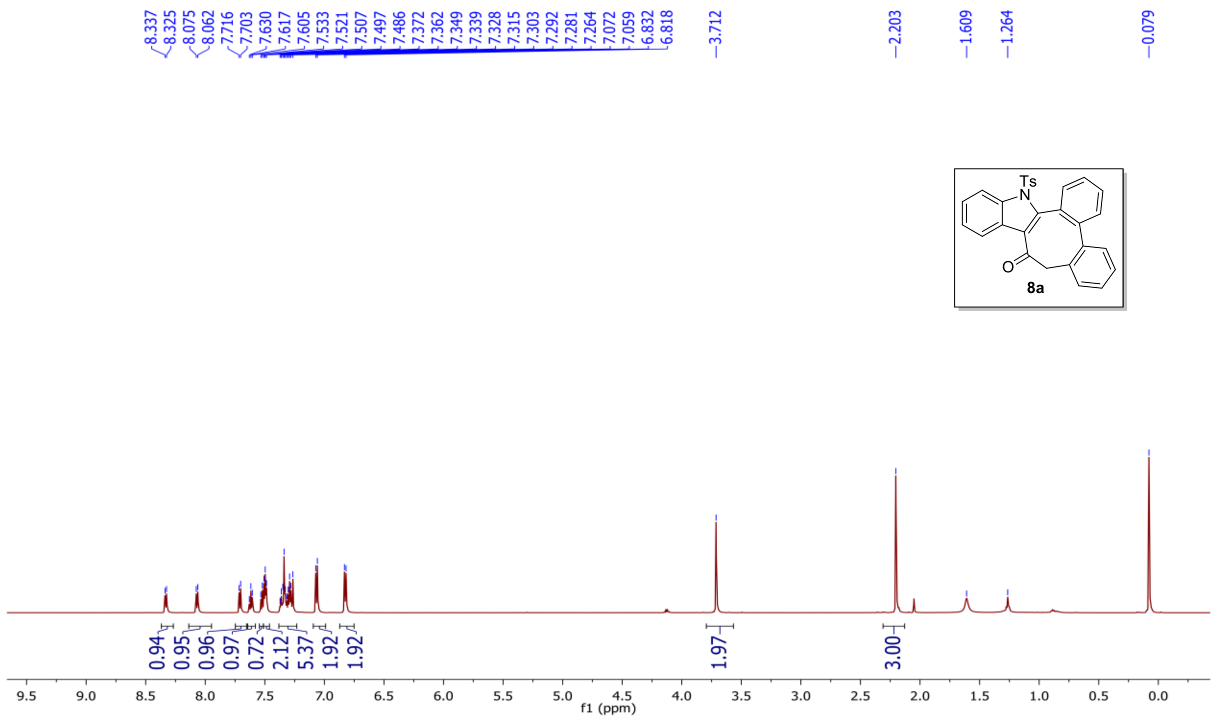


$^{13}C\{^1H\}$ NMR (150 MHz) of **7j :**

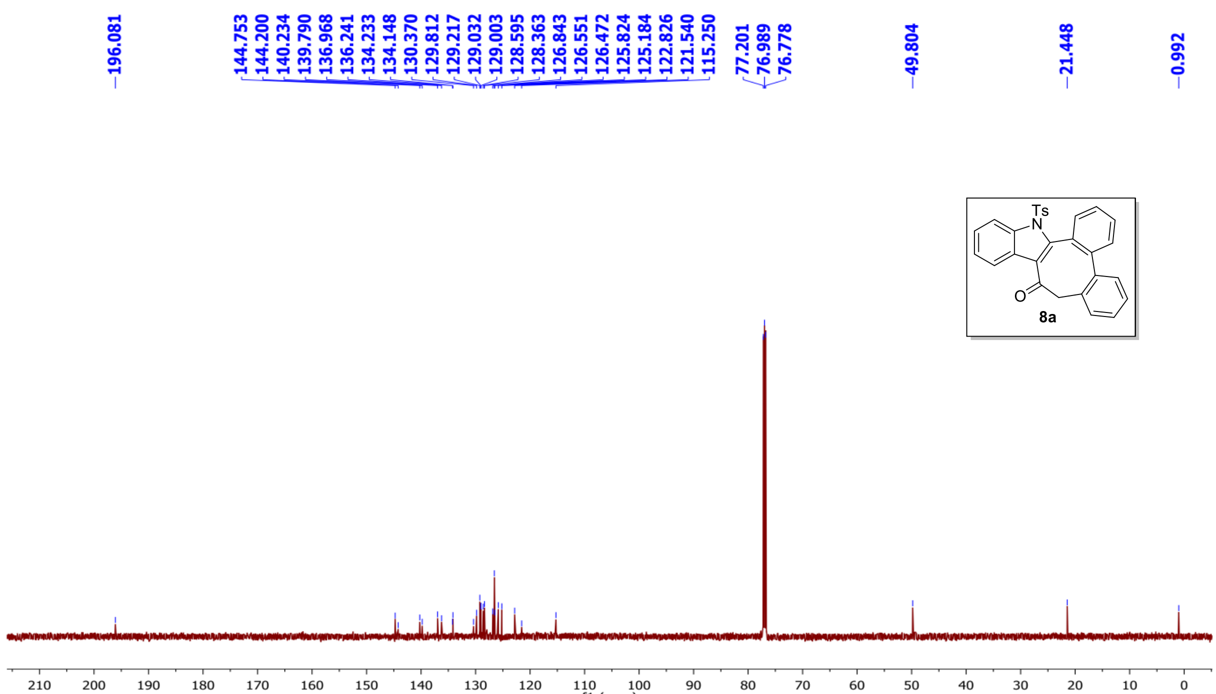


24. NMR Spectra of Compounds 8a-8i :

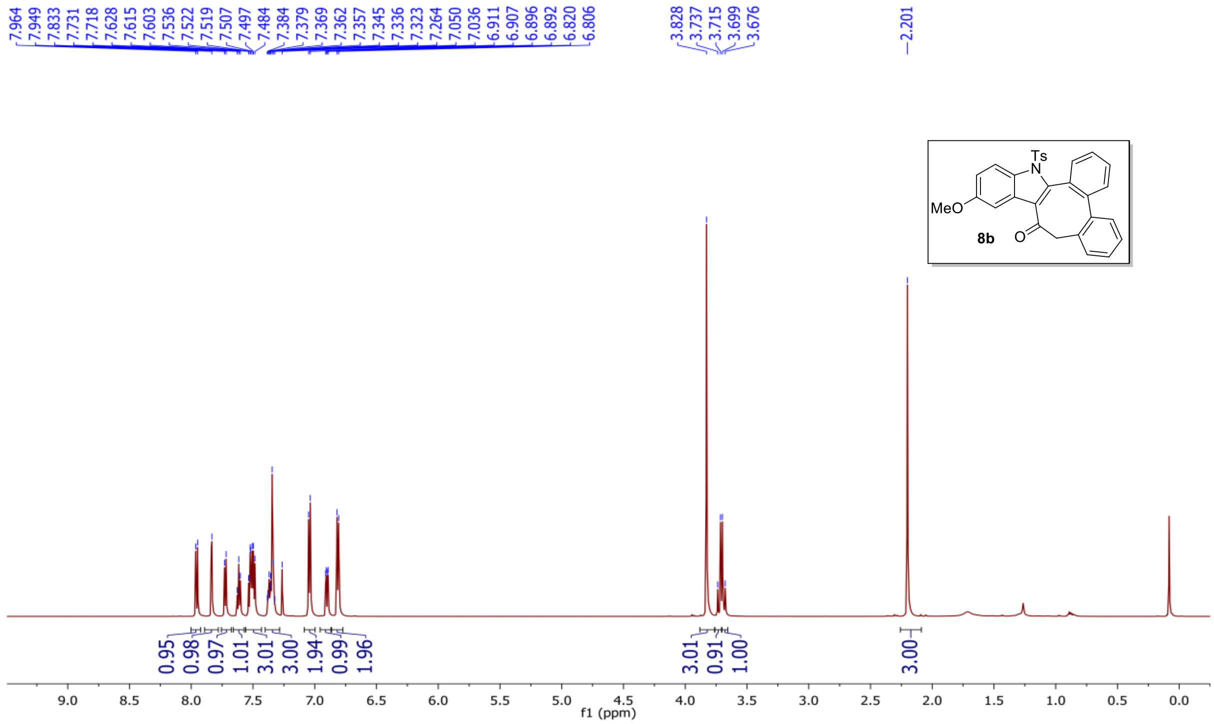
^{1}H NMR (600 MHz) of **8a :**



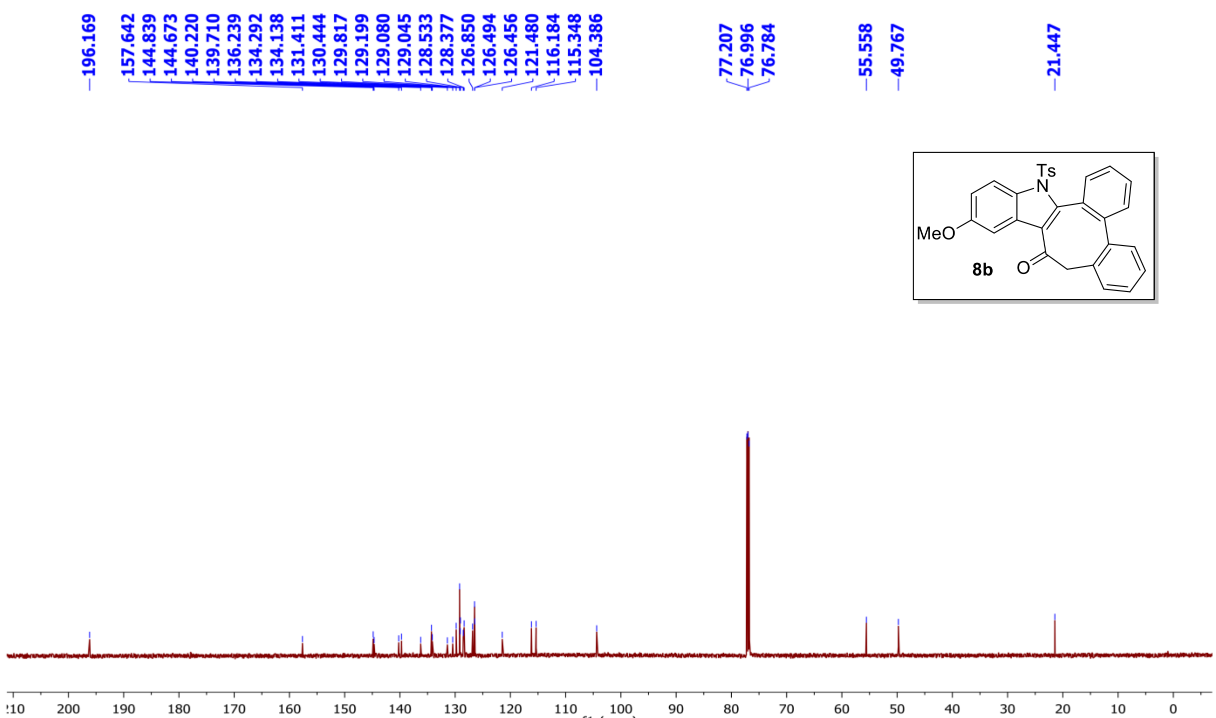
$^{13}C\{^{1}H\}$ NMR (150 MHz) of **8a :**



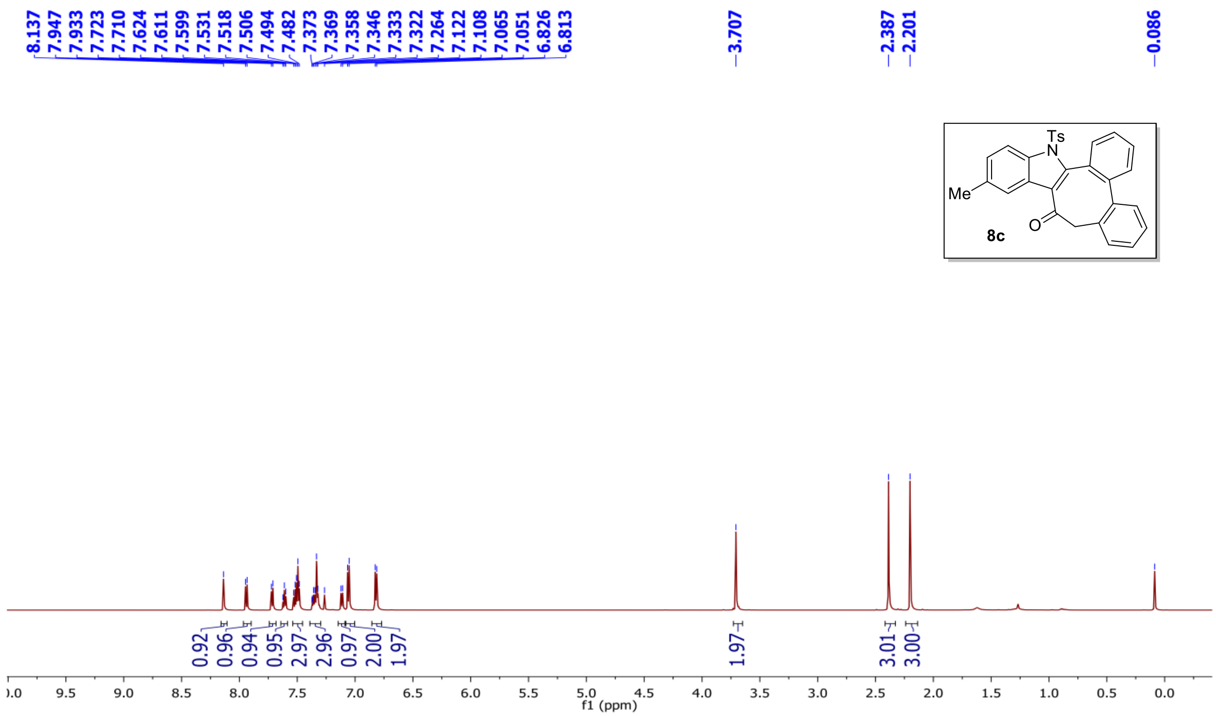
^{1}H NMR (600 MHz) of **8b :**



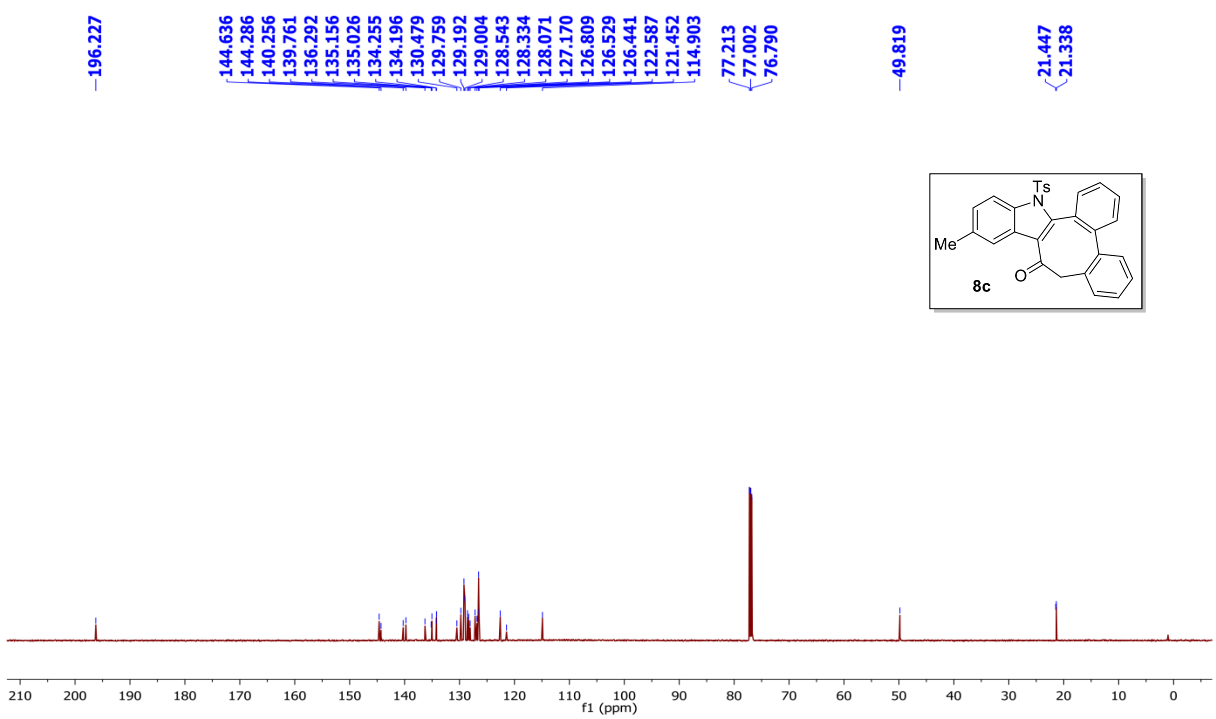
$^{13}C\{^{1}H\}$ NMR (150 MHz) of **8b :**



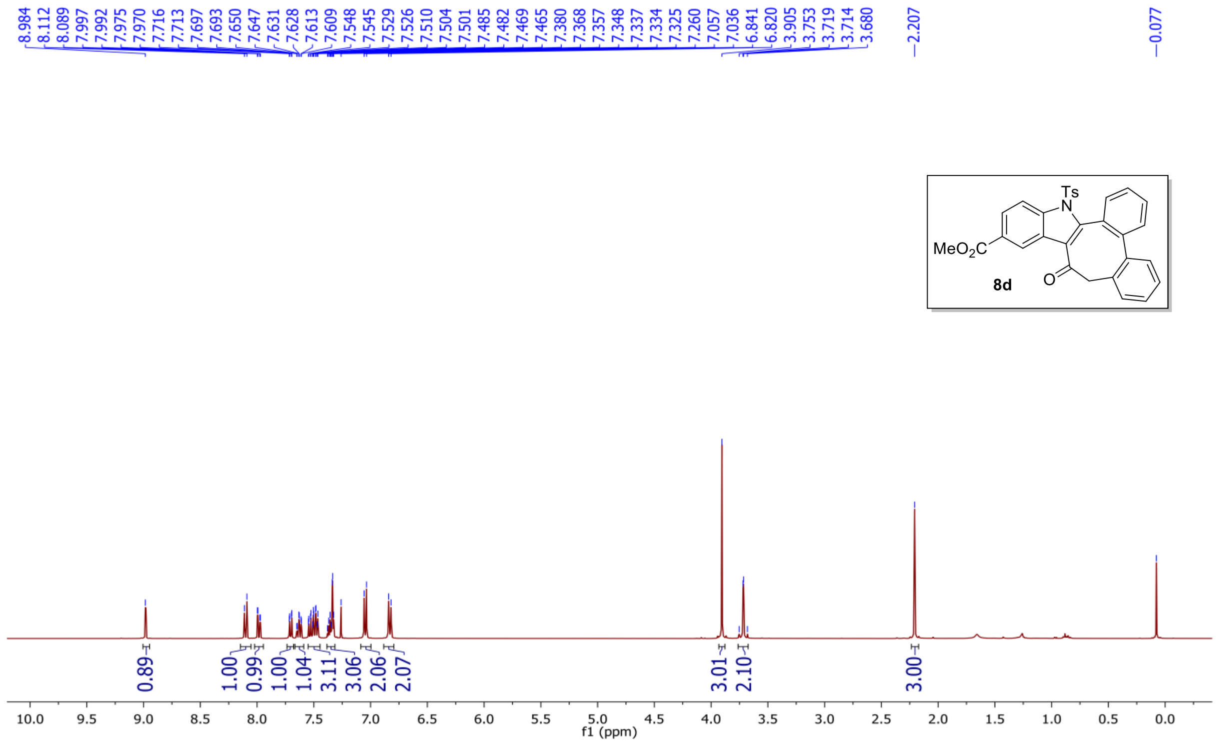
^{1}H NMR (600 MHz) of **8c :**



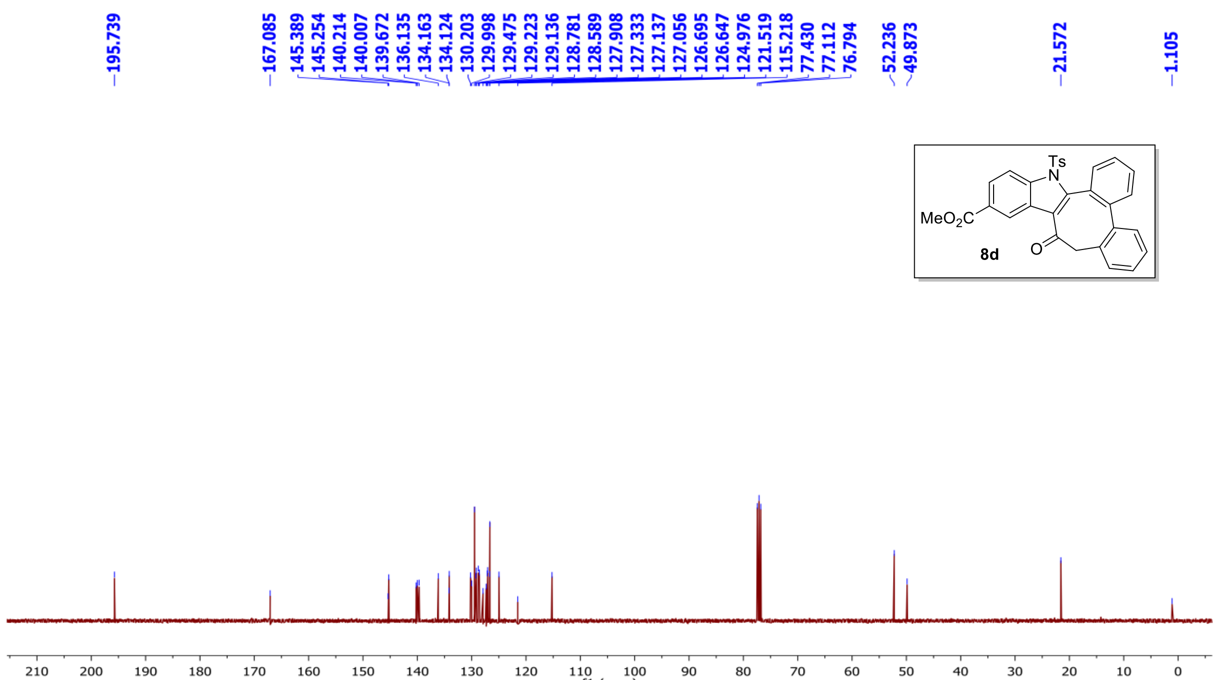
^{13}C{^{1}H} NMR (150 MHz) of **8c :**



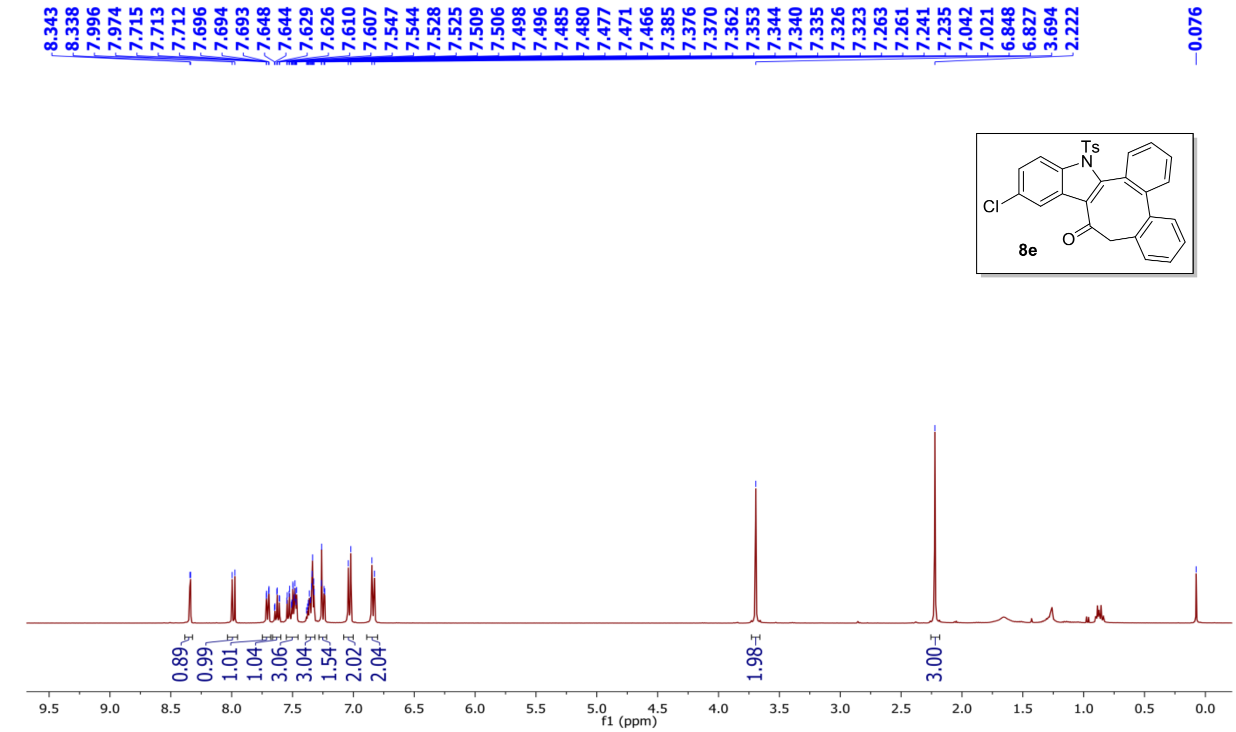
^{1}H NMR (400 MHz) of **8d :**



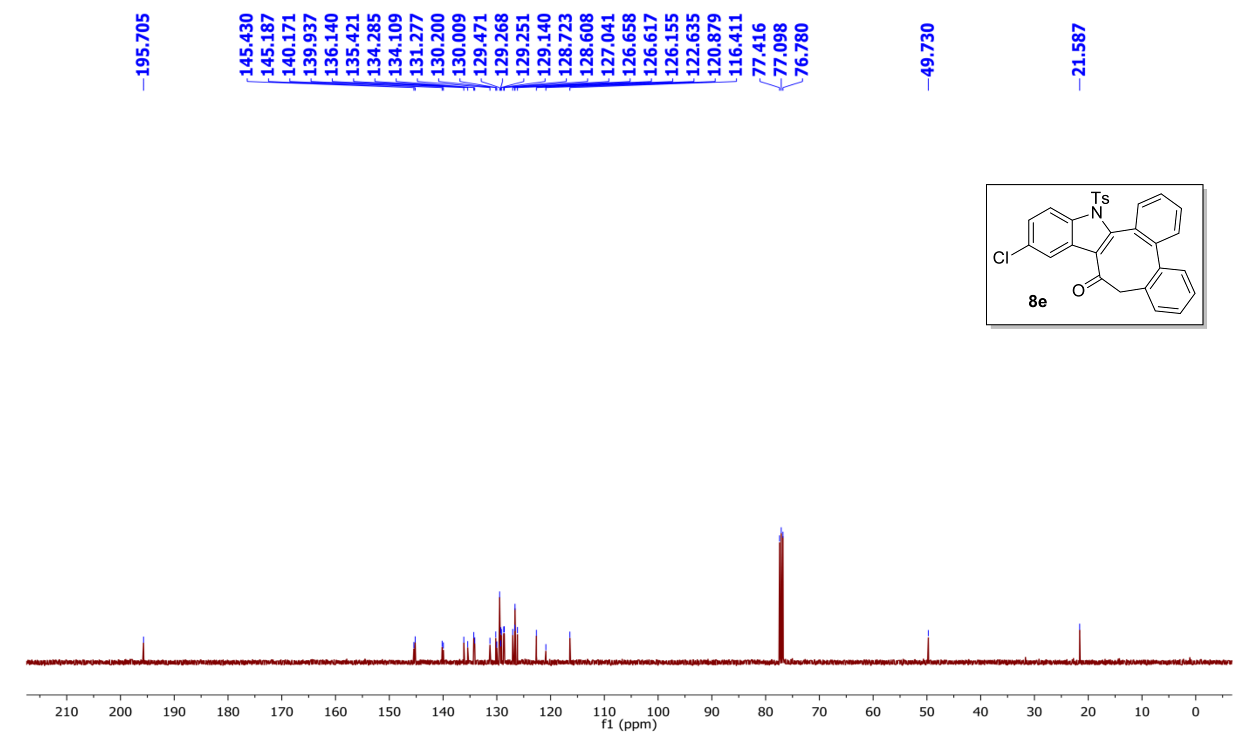
$^{13}C\{^{1}H\}$ NMR (100 MHz) of **8d :**



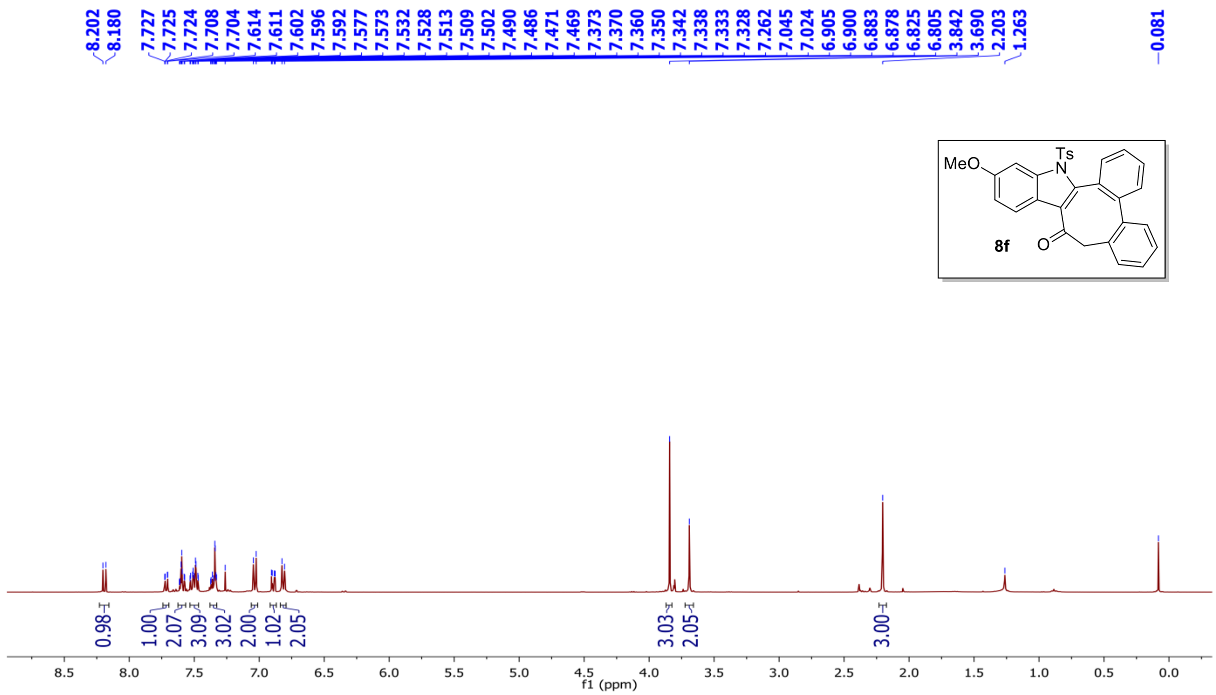
^{1}H NMR (400 MHz) of **8e :**



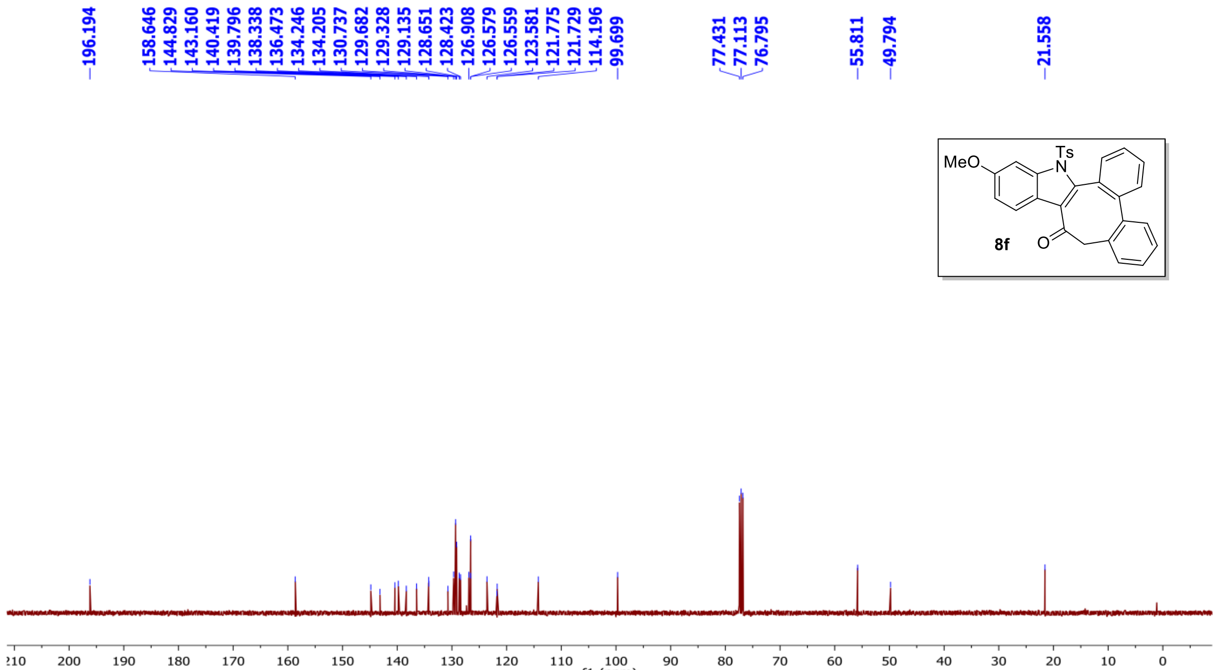
$^{13}C\{^{1}H\}$ NMR (100 MHz) of **8e :**



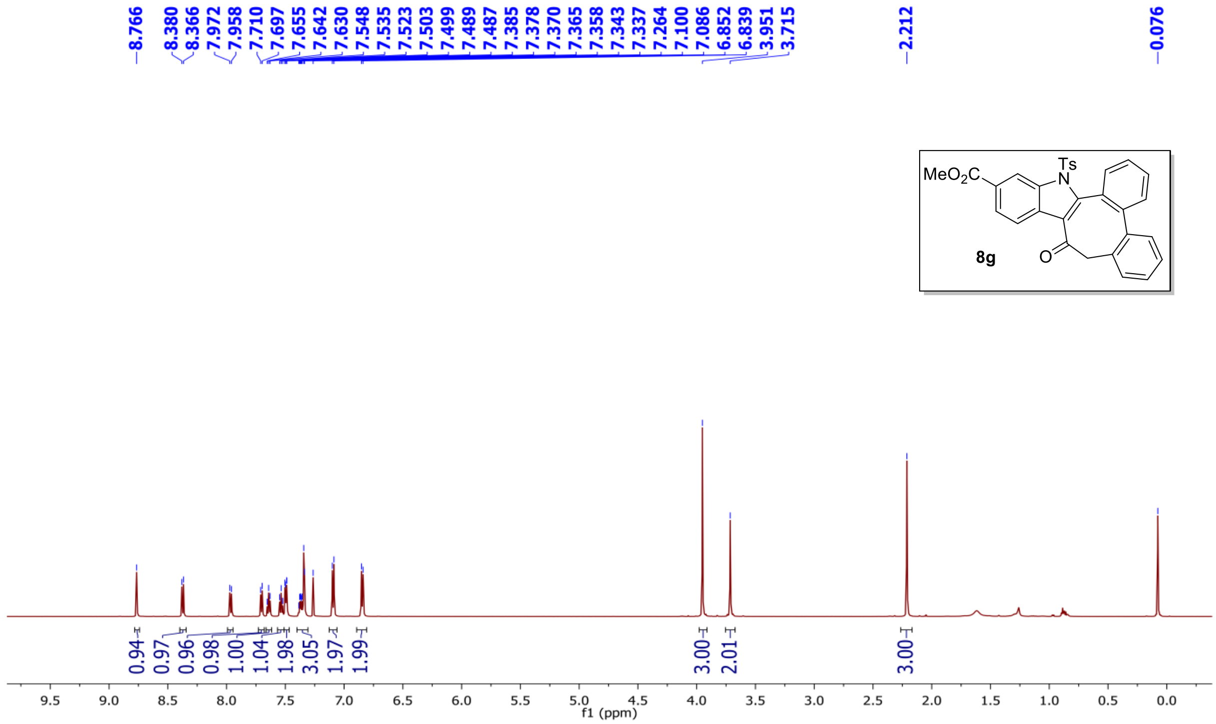
^{1}H NMR (400 MHz) of **8f :**



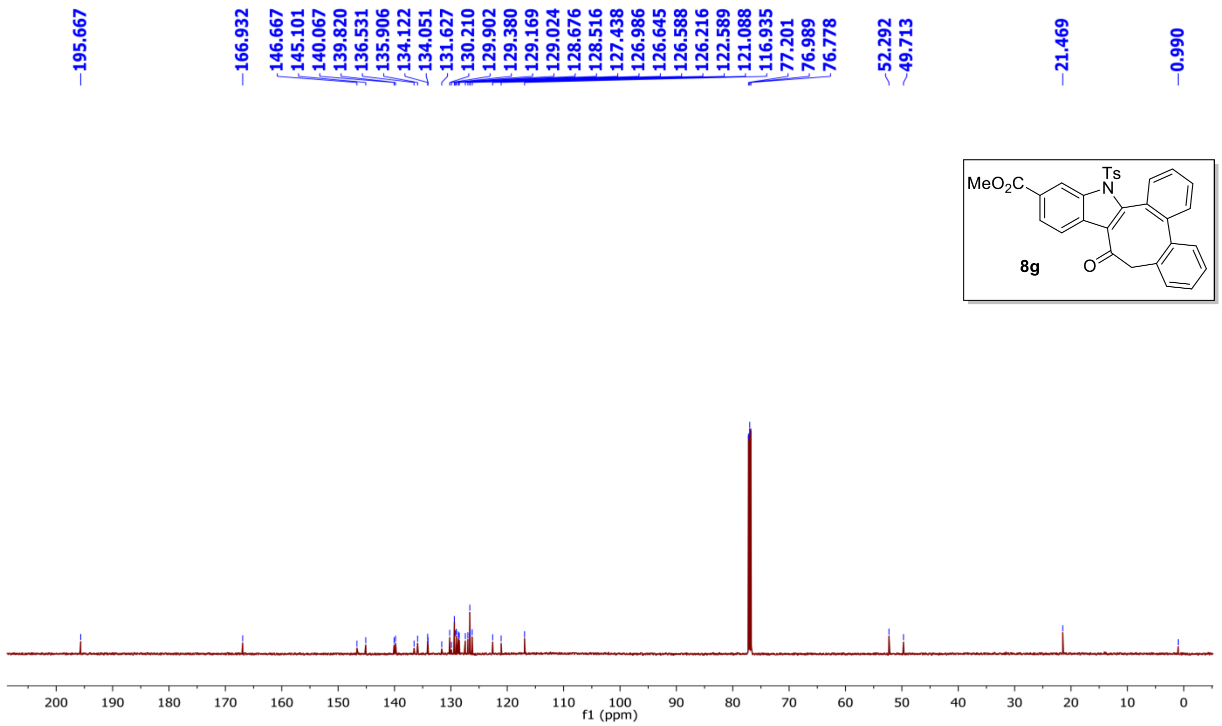
$^{13}C\{^{1}H\}$ NMR (100 MHz) of **8f :**



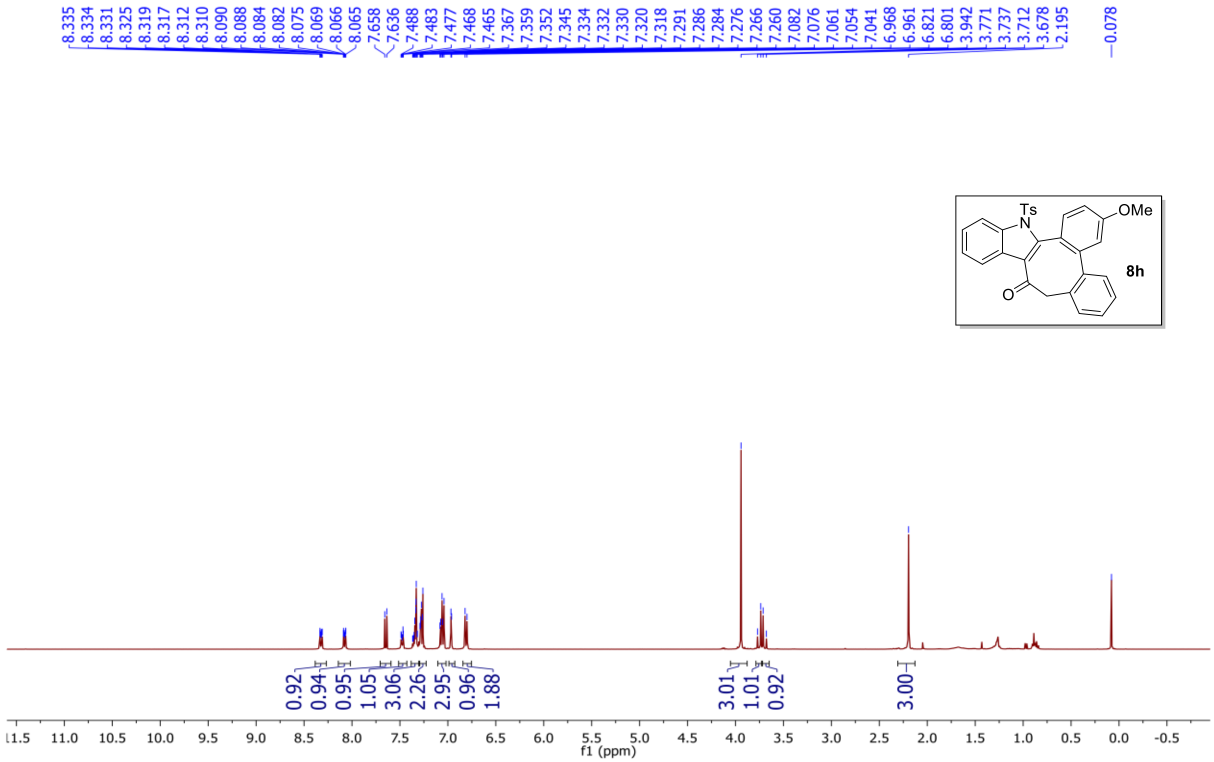
^{1}H NMR (600 MHz) of **8g :**



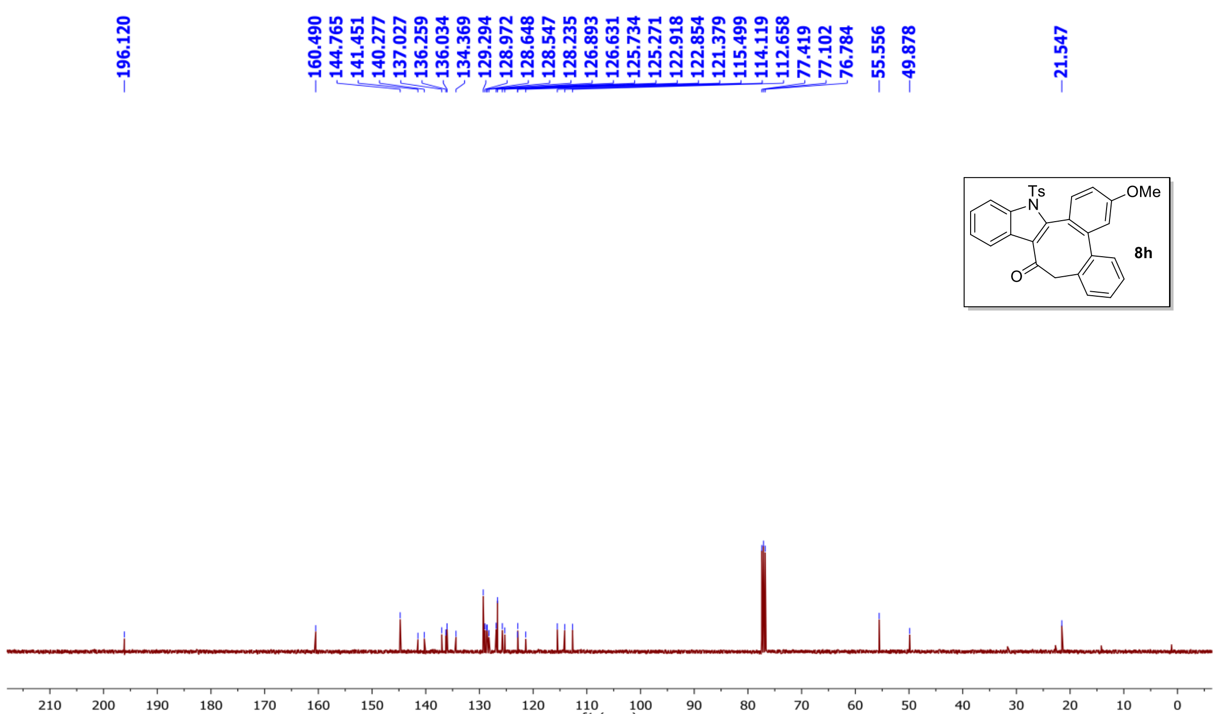
$^{13}C\{^{1}H\}$ NMR (150 MHz) of **8g :**



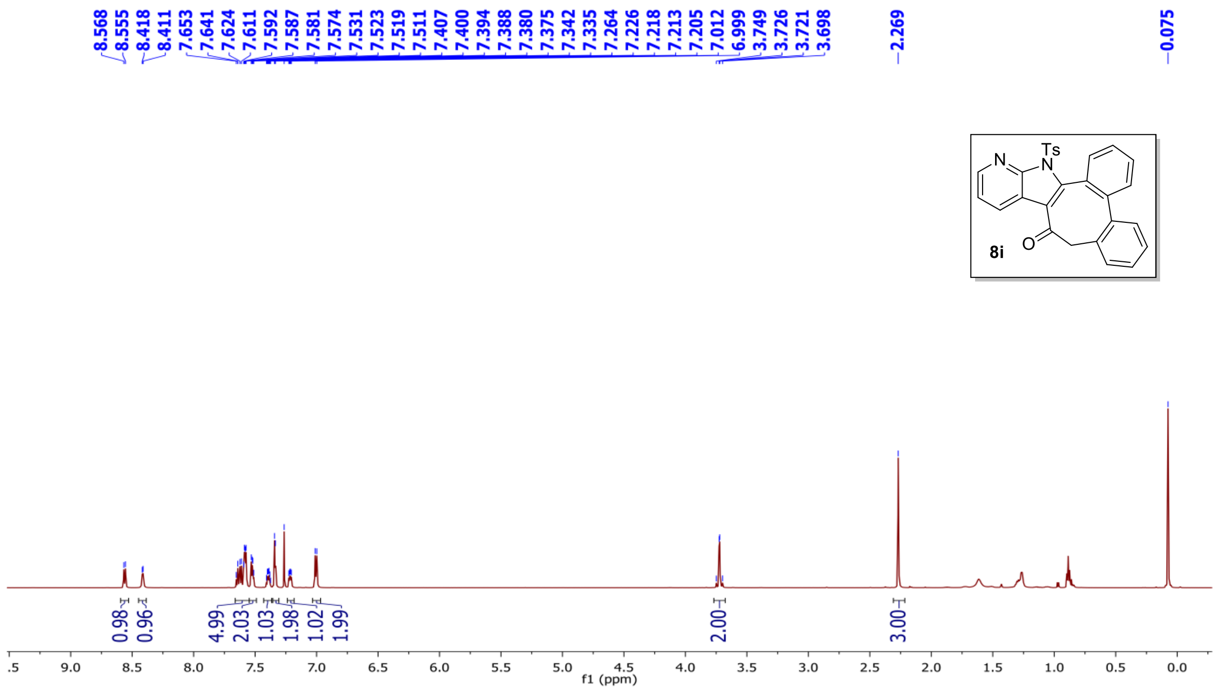
[1]H NMR (400 MHz) of **8h :**



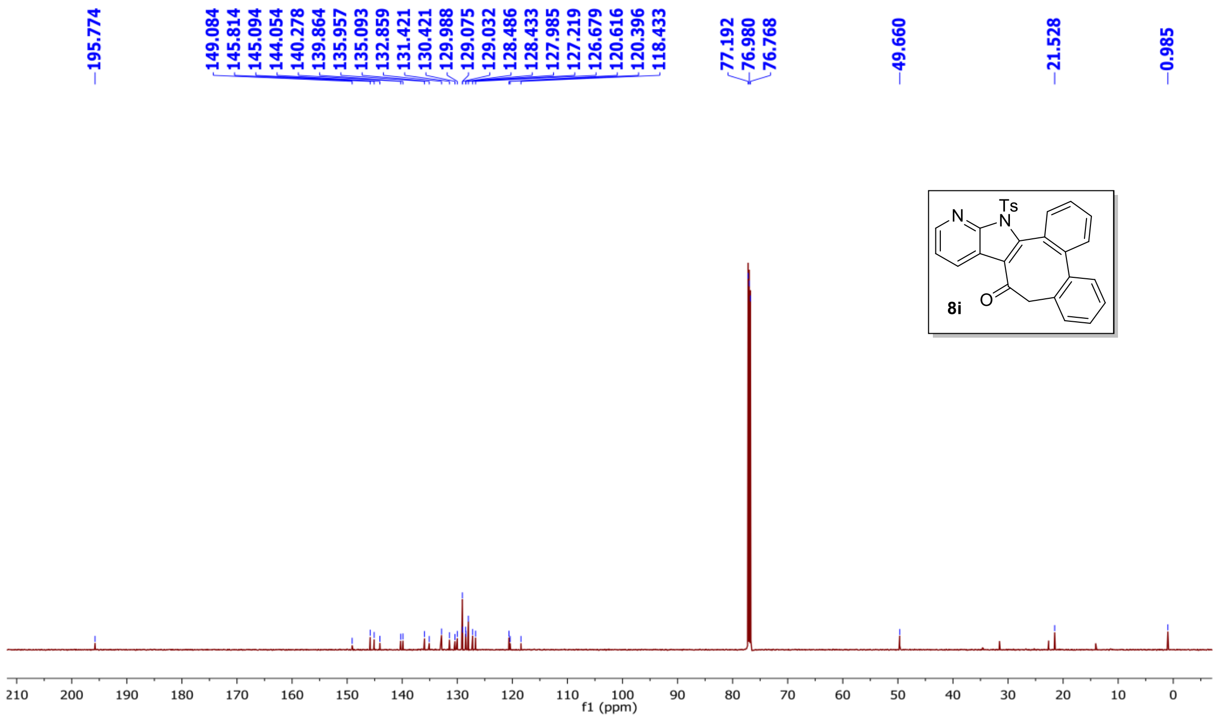
[13]C{[1]H} NMR (100 MHz) of **8h :**



^{1}H NMR (600 MHz) of **8i :**

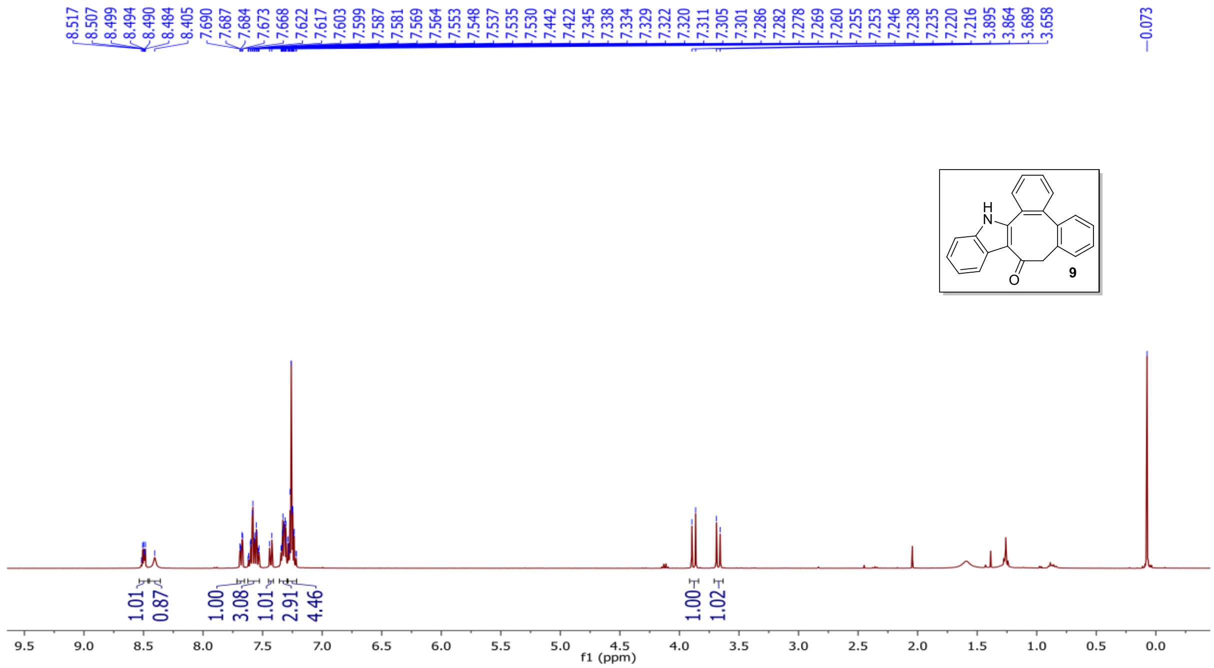


^{13}C{^{1}H} NMR (150 MHz) of **8i :**



25. NMR Spectra of Compound 9 :

^{1}H NMR (400 MHz) of **9 :**



^{13}C{^{1}H} NMR (100 MHz) of **9 :**