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Electronic Supplementary information

Palladium(0)-catalysed regioselective cyclisations of 2-amino(tosyl) benzamides/sulphonamides: the stereoselective synthesis of 3-ylidene-[1,4]benzodiazepin-5-ones/benzo[*f*][1,2,5]thiadiazepine-1,1-dioxides

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Table of Contents : **Page No**

1**. General Information:**

All solvents were distilled prior to use. Petroleum ether refers to fraction boiling in the range 60−80 °C. DCE (Dichloroethane), CH_3CN (Acetonitrile) and BuCN (butyronitrile) was dried over phosphorous pentoxide, distilled, and stored over 3 Å molecular sieves in a sealed container. Commercial grade dry DMSO (Dimethylsulfonamide), Toluene were used as a solvent. THF (Tetrahydrofuran) were predried using KOH pellets and then dried by heating under reflux over sodium with benzophenone as indicator. 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 chromate gram was performed by UV absorbance. For purification, column chromatography was performed using 100−200 mesh silica gel. ^1H and ^{13}C NMR spectra were recorded on 300, 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 [$CDCl_3$: ^1H 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), p (pentet), m (multiplet), and brs (broad singlet). All ^{13}C NMR spectra were obtained with complete proton decoupling. Mass spectra were performed using ESI-TOF.

2.

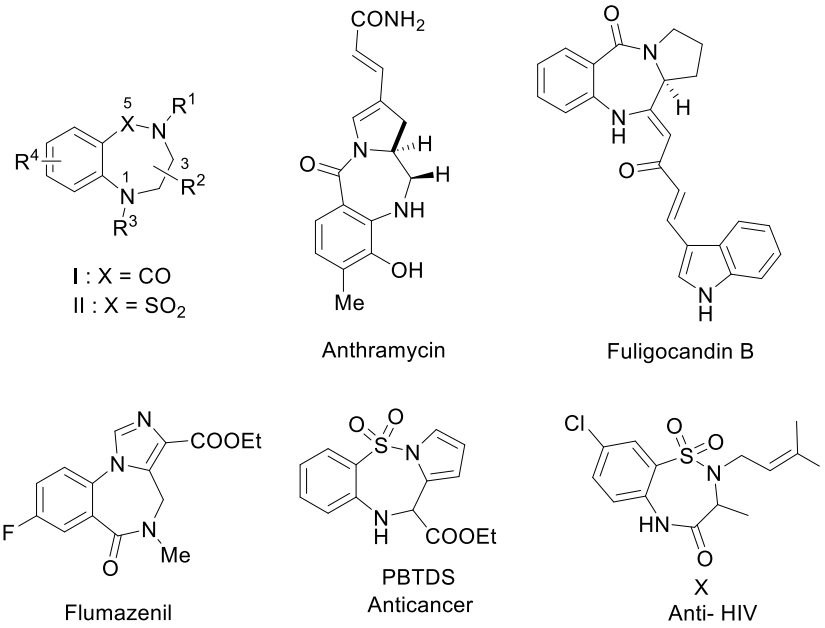
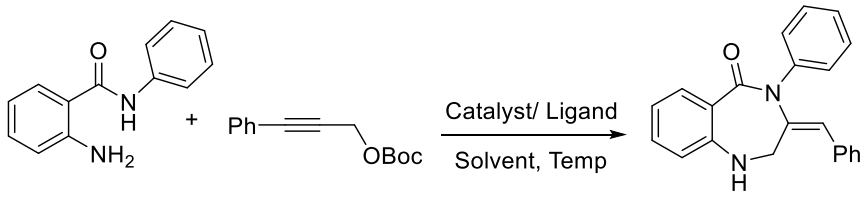


Fig. S1. Few biologically active 1,4-benzodiazepine-5-ones and their sulphur analogs

3. Optimisation of the reaction conditions for the synthesis of product 6a

Table S1. Optimisation of the reaction conditions for *(E)*-3-benzylidene-4-phenyl-3,4-dihydro-1*H*-benzo[*e*][1,4]diazepin-5(2*H)*-one **6a**[a]



C **2aa** **3b** **6a**

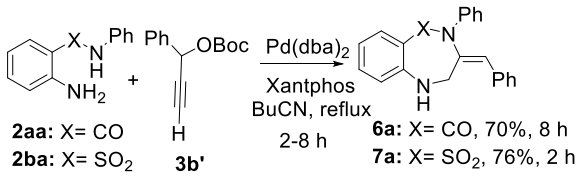
Entry	Catalyst	Ligand	Solvent	Temp(°C)	Time (h)	Yield(%)
1	$Pd(dba)_2$	Xantphos	CH_3CN	80	13	70
2	$Pd(PPh_3)_4$	Xantphos	CH_3CN	80	18	54
3	$Pd_2(dba)_3$	Xantphos	CH_3CN	80	18	51
4	$Pd_2(dba)_3.CHCl_3$	Xantphos	CH_3CN	80	18	45
5	$Pd(dba)_2$	DPEphos	CH_3CN	120	18	55
6	$Pd(dba)_2$	^{t}BuXantphos	CH_3CN	80	18	43
7	$Pd(dba)_2$	Xphos	CH_3CN	80	18	38
8	$Pd(dba)_2$	Xantphos	DCE	65	12	60
9	$Pd(dba)_2$	Xantphos	DMSO	120	18	24
10	$Pd(dba)_2$	Xantphos	THF	70	18	N.R.
11	$Pd(dba)_2$	Xantphos	BuCN	120	10	73
12[b]	**$Pd(dba)_2$**	**Xantphos**	**BuCN**	**120**	**10**	**72**
13[c]	$Pd(dba)_2$	Xantphos	BuCN	120	3	61
14[d]	$Pd(dba)_2$	Xantphos	BuCN	120	8	62
15[e]	$Pd(dba)_2$	Xantphos	BuCN	120	10	64

[a]Reaction conditions (Unless noted otherwise): A mixture of 1.0 equiv of **2aa** and 1.5 equiv of **3b** in 2.0 mL solvent in the presence of 10 mol% of the Pd(0) catalyst and 20 mol% ligand was refluxed under argon. [b]The reaction was performed with 7 mol% of $Pd(dba)_2$ along with 14 mol% Xantphos. [c]The reaction was performed with 2.0 equiv of t-butanol. [d]The reaction was performed with 5 mol% $Pd(dba)_2$ and 10 mol% Xantphos. [e]Using 2.0 equiv of **3b**.

To find the optimised reaction conditions, a model reaction was carried out between 2-amino-*N*-phenylbenzamide 2**aa** and *tert*-butyl propargyl carbonate **3b** with variation of the reaction parameters such as palladium catalyst, ligand, solvent, temperature etc. (Table S1). Initially, employment of $Pd(dba)_2$, Xantphos, and acetonitrile, respectively as catalyst, ligand, and solvent with **4a** (see, entry 14 of Table 1) required longer reaction time (13 h) to deliver **6a** with 70% yield (entry 1, Table S1). To reduce the reaction time, we replaced $Pd(dba)_2$ with other Pd(0) catalysts (viz., $Pd(PPh_3)_4$, $Pd_2(dba)_3$, $Pd_2(dba)_3.CHCl_3$). But to our disappointment, the product was isolated in lower yields (45-54%) even after 18 h of reaction time (entries 2-4, Table S1). We therefore decided to persist with $Pd(dba)_2$ and planned to vary the ligand. But use of DPEphos, ^{t}BuXantphos, or Xphos instead of Xantphos delivered **6a** in lower yields after 18 h (entries 5-7, Table S1).

Scrutiny of the solvent system revealed that the reaction provided **6a** with low yield in a polar solvent (i.e., DMSO) though DCE proved to be somewhat better (60% yield in 12 h, entries 8-9, Table S1). A medium polar solvent like THF failed to provide any product (entry 10, Table S1). To our pleasure, a remarkable improvement was noted when the reaction was carried out in refluxing BuCN which produced **6a** within 8 h and with 73% yield (entry 11 vs entry 1, Table S1). To decrease the reaction time, t-butanol was used as an additive to facilitate proton transfer (see, the reaction mechanism in the text as depicted under Scheme 2) as unprotected aniline is not acidic enough like tosylamide. Though this significantly enhanced the reaction rate resulting in the lowering of reaction time to 3h, the yield was only 61% (entry 13 vs entry 12, Table S1). Reduction of the catalyst loading from 10 mol% to 7 mol% slightly increased the reaction time and marginally decreased the yield of **6a** (entry 12, Table S1,). Further reduction of the either catalyst loading (to 5 mol%) or amount of the *tert*-butyl propargyl carbonate **3b** resulted in a substantial reduction of the yield (entries 14-15, Table S1). We therefore considered the reaction conditions used in entry 12 of Table S1 as the optimised one for further exploration of the scope this reaction.

4. Control experiments:



Scheme S1: Control experiment using propargyl carbonate 3b´

To support the mechanism as depicted in Scheme 2 in the main article, we carried out a control experiment (as shown under Scheme S1) in which propargyl carbonate 3b' (instead of 3b) was allowed to react separately with amines **2aa** and **2ba** under the optimised reaction conditions. These however delivered the products **6a** and **7a** which were previously Isolated from reactions of **3b** with **2aa** and **2ba**, respectively (see Table 3 in the main article). These observations indicate that the reaction might pass through an allenic-palladium intermediate IV (or V) as proposed in the mechanism under Scheme 2 in main article .

5. X-Ray crystallographic information of products 4n, 5a, 6k and 7a:

Single crystal of products **4n, 5a, 6k** and **7a** were obtained through slow evaporation (at room temperature) of a solution in dichloromethane-petroleum ether. A single crystal of **4n, 5a**, **6k** and **7a** 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 **4n, 5a, 6k, 7a** with MoKα radiation (λ = 0.71073 Å) at 293 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. Important crystal data of product **4n, 5a, 6k** and **7a** are given below.

Important crystal data of products 4n, 5a, 6k and 7a:

Table S2: Important crystal data of product **4n**

Empirical formula	$C_{24}H_{22}N_2O_3S$
Formula weight	418.49
Temperature	273 K
Wavelength	0.71073
Crystal system	'triclinic'
Space group	'P -1'
Unit cell dimensions	a = 8.130(3) Å α = 82.36(2)
	b = 10.804(6) Å β = 88.815(12)
	c = 12.330(5) Å γ = 80.34(2
Volume	1058.1(8) $Å^3$
Z	2
Density (calculated)	1.245 g/cm^3
Absorption coefficient (Mu)	0.181mm^{-1}
F(000)	440
Theta range for data collection	2.378^0 to 27.243^o
Index ranges	-10<=h<=10, -13<=k<=13, -15<=l<=15
Reflection collected	31258
Independent reflections	4724 [R(int) = 0.0518]
Completeness to theta	99.9 %
Absorption correction	multi-scan
Max. and min. transmission	0.7456 and 0.6875
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4724 /0/ 280
Goodness-of-fit on F^2	0.912
Final R indices [I>2sigma(I)]	R1 = 0.0476, wR2 = 0.1193
R indices (all data)	R1 = 0.0626, wR2 = 0.1318
Largest diff. peak and hole	0.268& -0.559e.A^{-3}

The single crystal of compound **4n** suitable for X-ray crystallographic determination was obtained by recrystallizing from a solution containing petroleum ether and dichloromethane at room temperature. The crystal data of product **4n** has already been deposited at Cambridge Crystallographic Data Centre. The CCDC reference number is **2062376.**

Table S3: Important crystal data of product **5a**

Empirical formula	C_{22} H_{20} N_2 O_4 S_2
Formula weight	440.52
Temperature	273 K
Wavelength	1.54184
Crystal system	'monoclinic'
Space group	'P 1 21/c 1'
Unit cell dimensions	a = 15.9293(11) Å α = 90 ^{0} b = 8.0486(5) Å β = 103.033(4) (12)^0 c = 16.3016(11) Å γ = 90 ^{0}
Volume	2036.2(2) Å^3
Z	8
Density (calculated)	1.437 g/cm^3
Absorption coefficient (Mu)	2.651 mm^{-1}
F(000)	920
Theta range for data collection	2.847 ^{o} to 69.883
Index ranges	-19<=h<=19, -9<=k<=9, -18<=l<=18
Reflection collected	58258
Independent reflections	3606 [R(int) = 0.0968]
Completeness to theta =	93.7 %
Absorption correction	multi-scan
Max. and min. transmission	0.7456 and 0.6875
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3606 / 0 / 278
Goodness-of-fit on F^2	1.274
Final R indices [I>2sigma(I)]	R1 = 0.0667, wR2 = 0.1408
R indices (all data)	R1 = 0.0670, wR2 = 0.1410
Largest diff. peak and hole	0.363 &- -0.367 e.A^{-3}

The single crystal of compound **5a** suitable for X-ray crystallographic determination was obtained by recrystallizing from a solution containing petroleum ether and dichloromethane at room temperature. The crystal data of product **5a** has already been deposited at Cambridge Crystallographic Data Centre. The CCDC reference number is **2062378.**

Table S4: Important crystal data of product **6k**

Empirical formula	'$C_{22}H_{17}ClN_2O$'
Formula weight	360.82
Temperature	273.15 K
Wavelength	1.54178
Crystal system	orthorhombic
Space group	'P 21 21 21'
Unit cell dimensions	a = 10.4364(17) Å α = 90.00°
	b = 12.3676(18) Å β = 90·00°(3)
	c = 14.215(2)Å γ = 90.00°
Volume	1834.8(5) $Å^3$
Z	4
Density (calculated)	1.306g/cm^3
Absorption coefficient (Mu)	1.936 mm^{-1}
F(000)	752.0
Theta range for data collection	4.739 to 66.876
Index ranges	-12<=h<=11, -14<=k<=14, -16<=l<=16
Reflection collected	20508
Independent reflections	3219 [R(int) = 0.0661]
Completeness to theta = 1.72/0.99	
Absorption correction	multi-scan
Max. and min. transmission	0.722 and 0.511
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3219 /0/236
Goodness-of-fit on F^2	1.034
Final R indices [I>2sigma(I)]	R1 = 0.0334, wR2 = 0.0823
R indices (all data)	R1 = 0.0351, wR2 = 0.0850
Largest diff. peak and hole	0.238 &--0.360 $e.A^{-3}$

Single crystal of compound **6k** suitable for X-ray crystallographic determination was obtained by recrystallizing from a solution containing petroleum ether and dichloromethane at room temperature. The crystal data of product **6k** has already been deposited at Cambridge Crystallographic Data Centre. The CCDC reference number is **2062375.**

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

Empirical formula	'C_{21} H_{18} N_2 O_2 S'
Formula weight	362.43
Temperature	100
Wavelength	1.54178
Crystal system	'monoclinic'
Space group	'P 1 21/n 1'
Unit cell dimensions	a = 9.4644(6) Å α = 90
	b = 18.1620(13) Å β = 113.232(2)
	c = 10.9259(7) Å γ = 90
Volume	1725.8(2) $Å^3$
Z	4
Density (calculated)	0.459 g/cm^3
Absorption coefficient (Mu)	1.813 mm^{-1}
F(000)	760
Theta range for data collection	5.033 to 58.925
Index ranges	-10<=h<=10, -20<=k<=20, -12<=l<=12
Reflection collected	19950
Independent reflections	2392 [R(int) = 0.0476]
Completeness to theta =	96.1 %
Absorption correction	multi-scan
Max.and min. transmission	0.713 and 0.496
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2392 /0/ 236
Goodness-of-fit on F^2	1.210
Final R indices [I>2sigma(I)]	R1 = 0.0486, wR2 = 0.1342
R indices (all data)	R1 = 0.0488, wR2 = 0.1344
Largest diff. peak and hole	0.428 &- -0.401e.A^{-3}

Single crystal of compound **7a** suitable for X-ray crystallographic determination was obtained by recrystallizing from a solution containing petroleum ether and dichloromethane at room temperature. The crystal data of product **7a** has already been deposited at Cambridge Crystallographic Data Centre. The CCDC reference number is **2062377**.

6. **ORTEP Diagrams of the products 4n, 5a, 6k and 7a:**

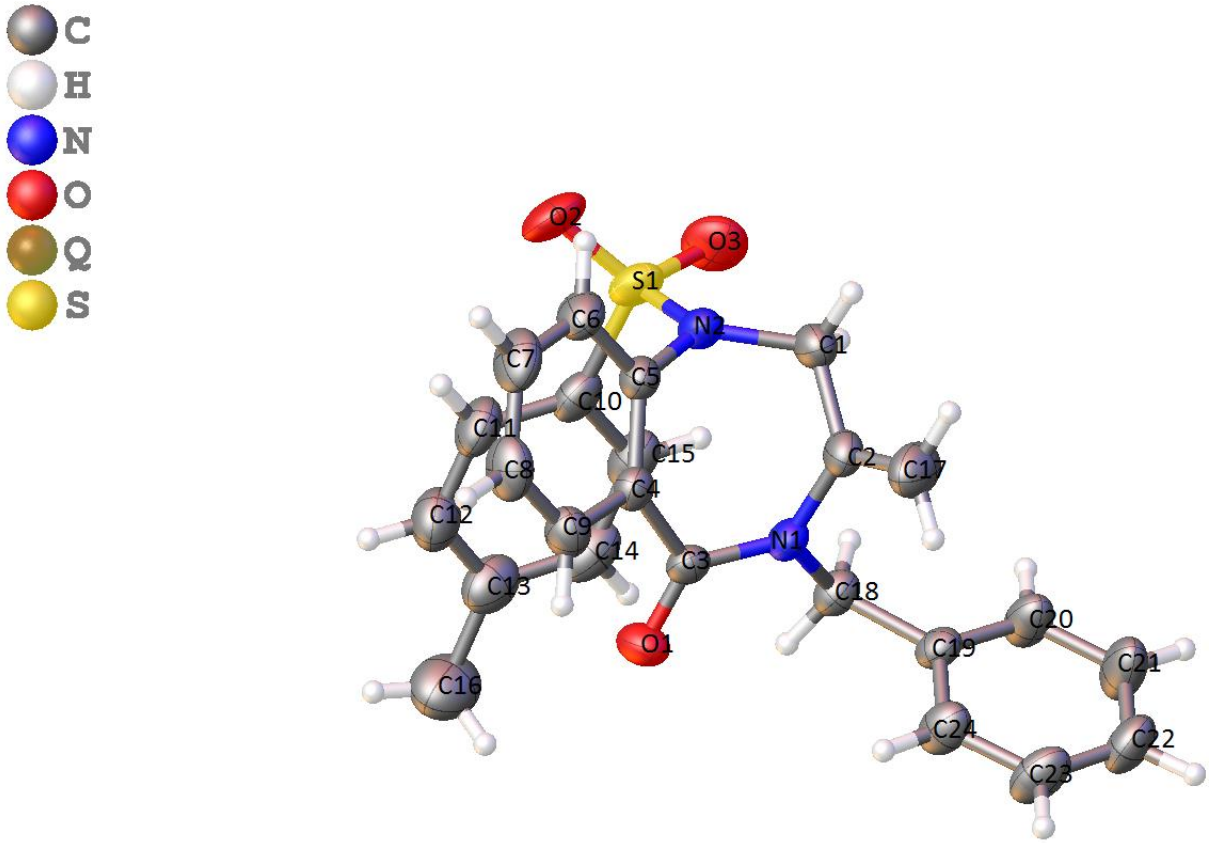


Figure S2. ORTEP Diagram (thermal ellipsoid plot) of Product **4n** (drawn at 50% probability level)

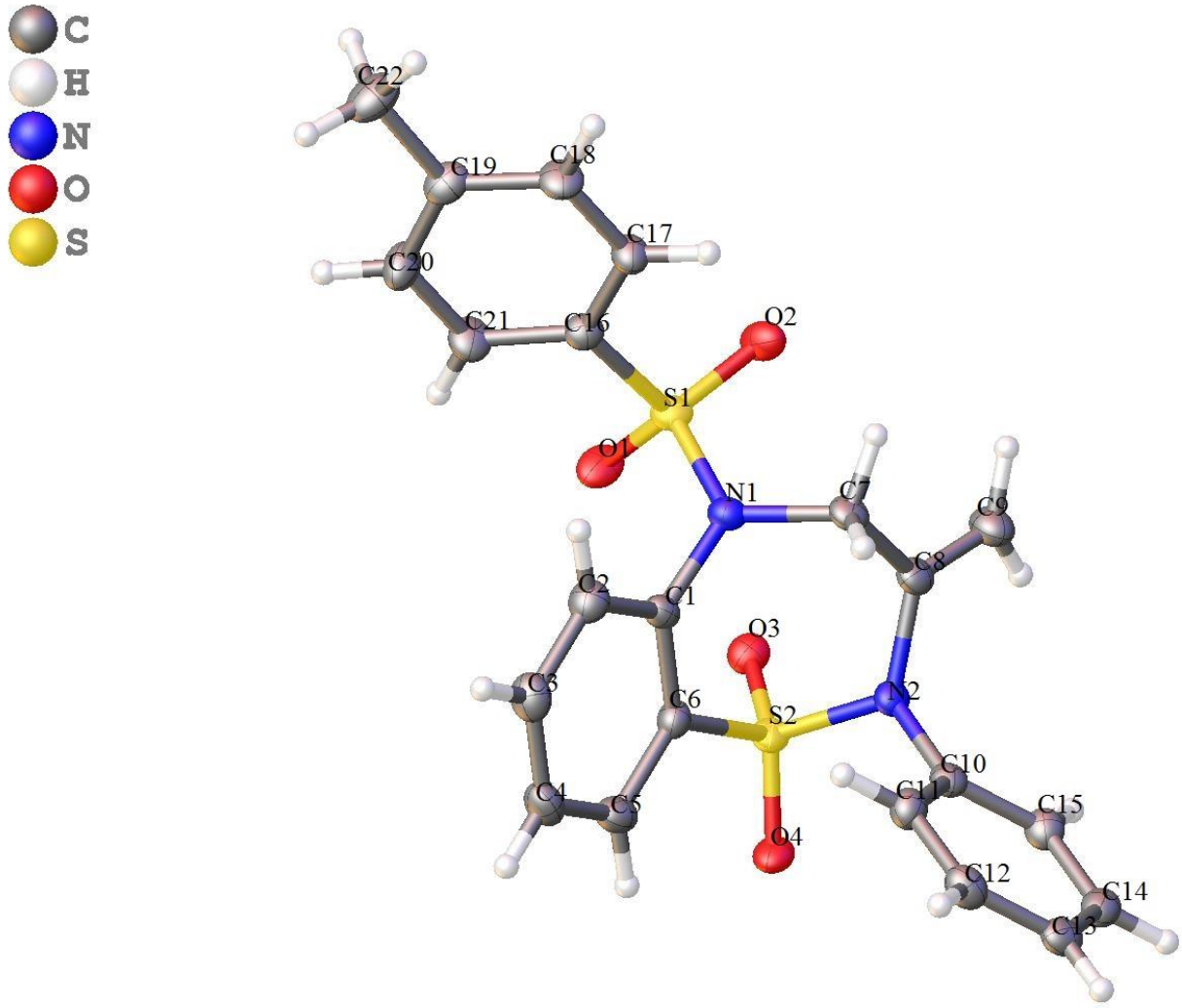


Figure S3. ORTEP Diagram (thermal ellipsoid plot) of Product **5a** (drawn at 50% probability level)

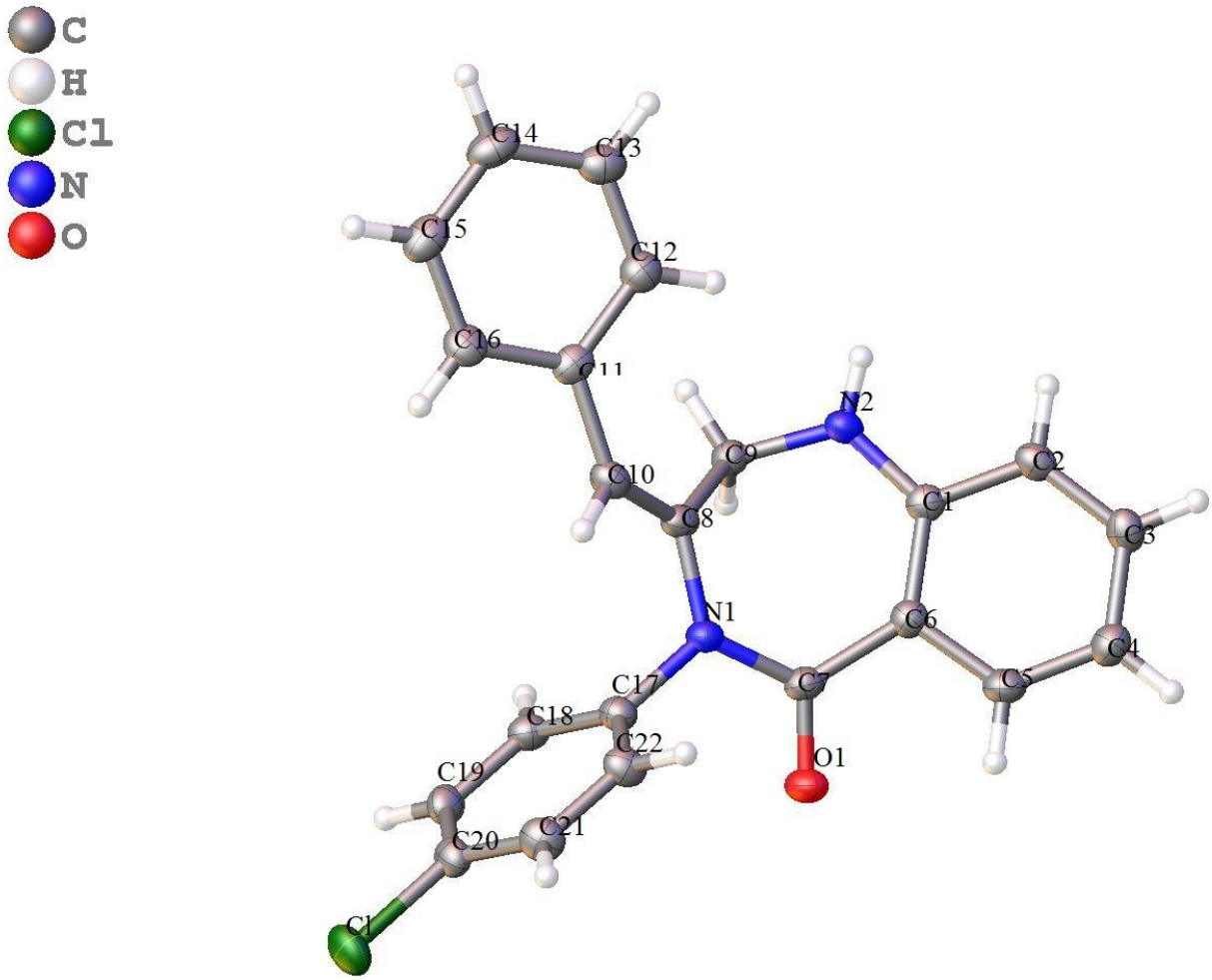


Figure S4. ORTEP Diagram (thermal ellipsoid plot) of Product **6k** (drawn at 50% probability level)

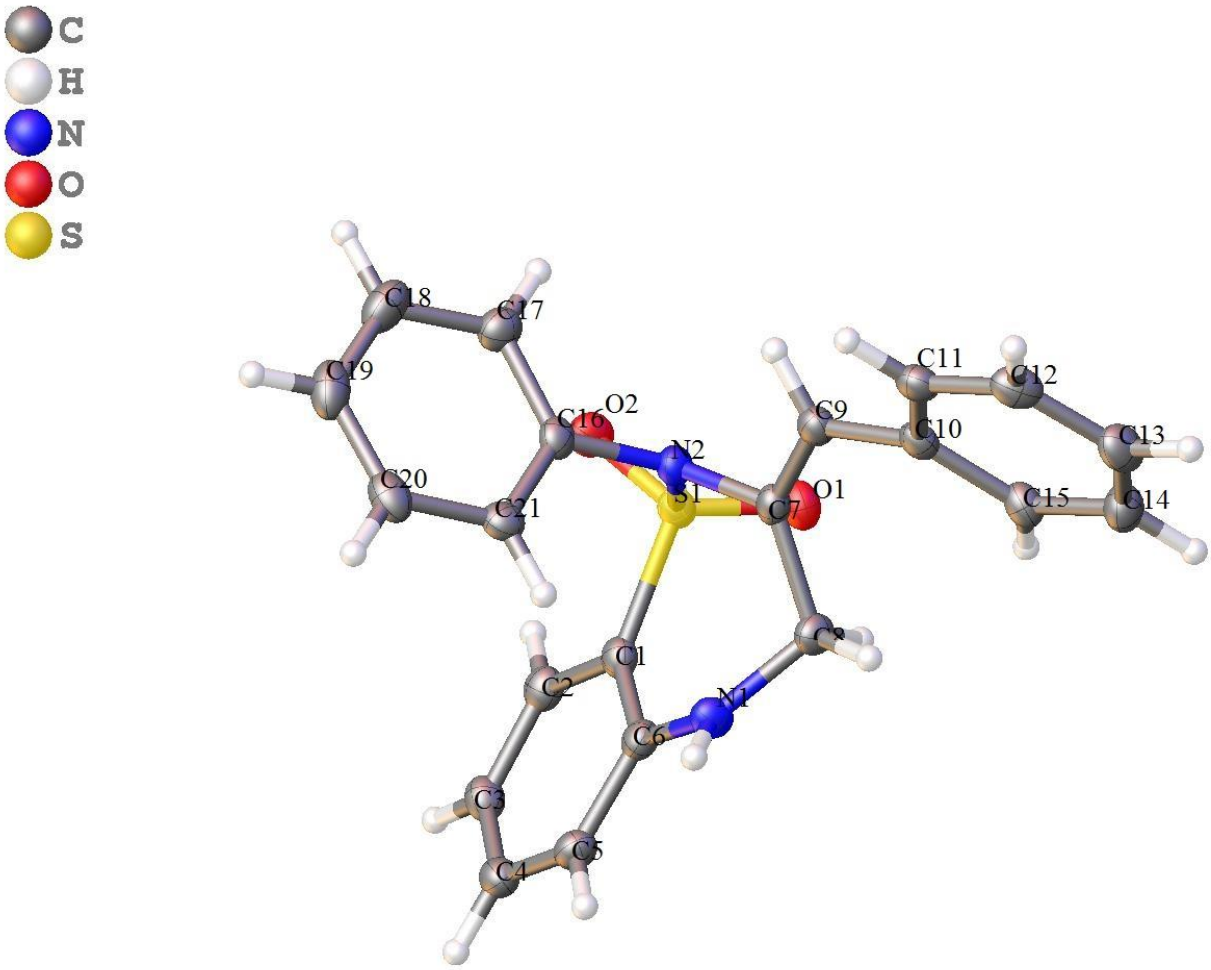
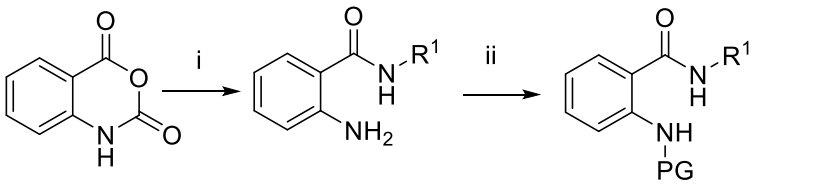


Figure S5. ORTEP Diagram (thermal ellipsoid plot) of Product **7a** (drawn at 50% probability level)

7. General procedure for the preparation of starting materials 1a and 2a[3]:

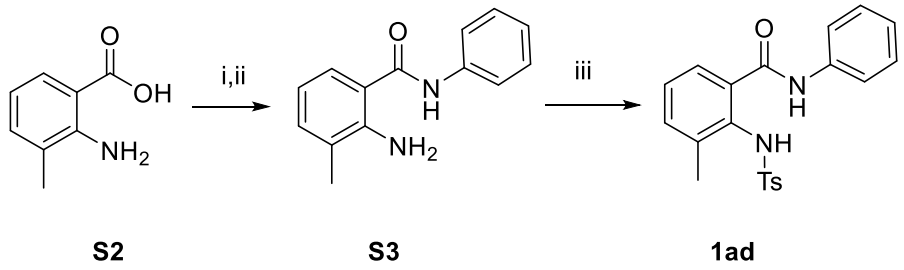


Scheme S2. Synthesis of substrate **1a**. Reagent and Conditions: (i) Aryl (or alkyl) amine (R^1NH_2), CH_3CN, reflux, 3-5 h, 70-91%; (ii) Arylsulphonyl chloride, Py, 0°C-rt, 2-3 h, 88-95%.

To a solution of isatoic anhydride **S1** (100 mg, 0.613 mmol, 1 equiv) in CH_3CN (5 mL), aryl (or alkyl) amine (62.6 mg, 0.674 mmol, 1.1 equiv) was added and the whole mixture was heated under reflux for 3-5 h. After completion of the reaction (TLC), the mixture was concentrated under reduced pressure, cooled and extracted with CH_2Cl_2 (3X10 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (100-200 mesh) using eluent 25-30% ethyl acetate-petroleum ether (v/v) to give the corresponding product **2a** in 70-91% yields.

Pyridine (38 µl, 0.47 mmol, 2 equiv) was added to a stirred solution of amino benzamide derivative **2a** (50 mg, 0.24 mmol, 1 equiv) in dry DCM (2 mL) at 0 ^oC under argon atmosphere. Next, arylsulphonyl chloride (59 mg, 0.31 mmol, 1.3 equiv) was added portion wise and the reaction was allowed to stir at room temperature for 2-3 h. After completion (TLC), the reaction mixture was diluted with DCM and washed with 1M HCl (3X10 mL,), satd. $NaHCO_3$ (3X10 mL), and brine (3X10 mL), respectively. The organic phase was dried over $MgSO_4$, concentrated, and purified by silica gel (100-200 mesh) column chromatography using 15-20% ethyl acetate-petroleum ether (v/v) as eluent to obtain 2-aminobenzenesulphonamide derivatives **1a** in 88-95% yield.

8. Typical procedure for preparation of starting material 1ad: [4]

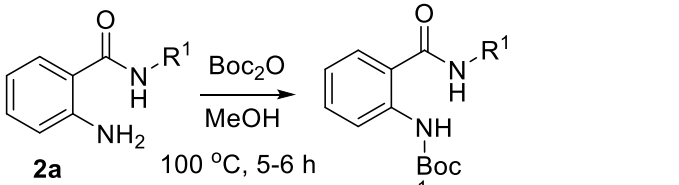


S2 **S3** **1ad**

Scheme S3. Synthesis of substrate **1ad**. Reagent and Conditions: (i) $SOCl_2$, toluene, reflux, 9 h; (ii) Aniline, Et_3N, DCM, 0°C-rt, 5 min; (iii) TsCl, 0°C-rt, 2 h, 92%

To a solution of 2-amino-3-methylbenzoic acid **S2** (148 mg, 0.98 mmol, 1 equiv) in toluene (5 mL) was added thionyl chloride (0.37 ml, 4.9 mmol, 5 equiv) at room temperature and the mixture was refluxed for 9 h under nitrogen atmosphere. After completion, the solvent was evaporated under reduced pressure to obtain the crude acid chloride as yellow oil, which was instantly used for the next reaction. In the next step to prepare the intermediate **S3**, Et_3N (0.16 ml, 1.2 mmol, 1.2 equiv) was added to a solution of aniline (0.1 ml, 1.2 mmol, 1.2 equiv) in dry DCM (5 mL) at 0 ^oC and stirred for 5 min. Then a solution of *p*-toluenesulphonyl chloride (185 mg, 0.98 mmol, 1 equiv) in dry DCM (2 mL) was added dropwise at 0 ^oC and stirring was continued for another 2 h. After completion (TLC), the solvent was removed under reduced pressure and the crude product was purified by silica gel (100-200 mesh) column chromatography using 20% ethyl acetate-petroleum ether (v/v) as eluent to obtain 3-methyl-2-((4-methylphenyl)sulfonamido)-*N*-phenylbenzamide (**1ad**) in 92% yield.

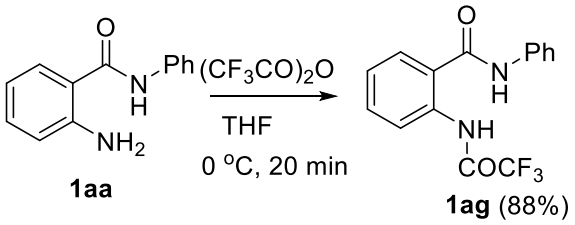
9. Typical procedure for the preparation of starting material 1ae, 1af:



Scheme S4. Preparation of the Boc-protected substrates **1ae** and **1af**

Di-*tert*-butyl dicarbonate (Boc_2O) (121 µl, 0.53 mmol, 2.2 equiv) was added to a solution of *N*-substituted-2-aminobenzamide (**2a**) (50 mg, 0.24 mmol, 1 equiv) in dry MeOH (2 mL) under argon atmosphere. Next, the mixture was allowed to stir at 100 °C for 5-6 h. After completion (TLC), the reaction mixture was poured into cold water (5 mL) and extracted with CH_2Cl_2 (3x 10 mL), dried over $MgSO_4$, and concentrated *in vacuo*. Then the residue was purified by silica gel (100-200 mesh) column chromatography eluting with 12% ethyl acetate-petroleum ether (v/v) to obtain pure *tert*-butyl(2-(arylcarbamoyl)phenyl)carbamate derivatives **1ae-1af** in 89% yield.

10. Typical procedure for the preparation of starting material 1ag:



1aa **1ag** (88%)

Scheme S5. Preparation of the $COCF_3$-protected substrate **1ag**

To a solution of 2-amino-N-phenylbenzamide **1aa** (100 mg, 0.47 mmol, 1 equiv) in dry THF (3 mL) was added Et_3N (0.10 ml, 0.71 mmol, 1.5 equiv) at room temperature and the mixture was cooled to 0 ^{0}C under nitrogen atmosphere. Trifluoroacetic andydride (0.13 ml, 0.94 mmol, 2 equiv) was added dropwise under ice cold conditions. After 20 min, the reaction mixture was poured into cold water (5 mL) and extracted with CH_2Cl_2 (3X 10 mL), dried over $MgSO_4$, and concentrated *in vacuo*. Then the residue was purified by silica gel (100-200 mesh) column chromatography eluting with 12% ethyl acetate-petroleum ether (v/v) to obtain pure *tert*-butyl(2-(arylcarbamoyl)phenyl)carbamate derivatives **1ag** in 88% yield.

11. Spectral Data of the substrates 1aa-1aq:

2-((4-Methylphenyl)sulfonamido)-*N*-phenylbenzamide (1aa)

White solid (78 mg, 90% yield); mp. 140-142 °C, R_f = 0.29 (15% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 10.13 (s, 1H), 7.66 (d, *J* = 9.2 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.50-7.46 (m, 3H), 7.42-7.34 (m, 3H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 7.2 Hz, 2H), 2.24 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 166.6, 143.8, 138.6, 137.1, 136.4, 132.9, 129.6, 127.3, 126.8, 125.3, 124.2, 123.2, 122.7, 120.7, 21.5; HRMS (ESI+) m/z calculated for $C_{20}H_{18}N_2NaO_3S$ $[M+Na]^+$ 389.0936, found 389.0937.

2-((4-Nitrophenyl)sulfonamido)-*N*-phenylbenzamide (1ab)

White solid (84 mg, 90% yield); mp. 166-168 °C, R_f = 0.40 (15% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 10.52 (s, 1H), 8.13-8.09 (m, 2H), 7.93-7.90 (m, 2H), 7.75 (dd, *J* = 8.6, 1.0 Hz, 1H), 7.55 (s, 1H), 7.52-7.48 (m, 2H), 7.42-7.35 (m, 4H), 7.23-7.18 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 166.4, 145.1, 137.9, 136.6, 133.3, 129.4, 128.7, 126.8, 125.8, 125.1, 124.2, 123.1, 120.6, 100.0; HRMS (ESI+) m/z calculated for $C_{19}H_{16}N_3O_5S$ $[M+H]^+$ 398.0811, found 398.0810.

2-((2-Bromophenyl)sulfonamido)-*N*-phenylbenzamide (1ac)

Yellow solid (93 mg, 92% yield); mp. 78-80 °C, R_f = 0.52 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 11.03 (s, 1H), 8.15 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.01 (s, 1H), 7.59-7.55 (m, 4H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.41-7.25 (m, 5H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 166.7, 138.6, 138.1, 137.2, 135.6, 134.1, 132.9, 132.0, 129.2, 127.6, 127.4, 125.4, 123.3, 121.4, 121.0, 120.5, 118.9; HRMS (ESI+) m/z calculated for $C_{19}H_{15}BrN_2NaO_3S$ $[M+Na]^+$ 452.9884, found 452.9867.

3-Methyl-2-((4-methylphenyl)sulfonamido)-*N*-phenylbenzamide (1ad)

White solid (77 mg, 92% yield); mp. >200 °C, R_f = 0.32 (15% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.57 (s, 1H), 7.44 (dd, *J* = 6.8, 2.0 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 4.4 Hz, 4H), 7.21 (d, *J* = 6.8 Hz, 2H), 7.16-7.13 (m, 1H), 6.94 (s, 1H), 6.86 (d, *J* = 8.4 Hz, 2H), 2.63 (s, 3H), 2.02 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 167.0, 143.6, 137.6, 135.01, 134.6, 133.9, 129.5, 129.0, 127.9, 127.0, 124.8 124.1, 119.3, 21.4, 19.7; HRMS (ESI+) m/z calculated for $C_{21}H_{21}N_2O_3S$ $[M+H]^+$ 381.1273, found 381.1276.

***Tert-butyl* (2-(phenylcarbamoyl)phenyl)carbamate (1ae)**

White solid (65 mg, 89% yield); mp. 148-150 °C, R_f = 0.25 (15% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 9.73 (s, 1H), 8.30 (d, *J* = 8.8 Hz, 1H), 8.04 (s, 1H), 7.59 (dd, *J* = 8.6, 1.0 Hz, 2H), 7.52 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.43-7.37 (m, 3H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.01 (t, *J* = 7.8 Hz, 1H), 1.50 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 167.4, 153.3, 140.1, 137.5, 132.7, 129.2, 126.8, 125.1, 121.8, 120.8, 120.5, 80.6, 28.4; HRMS (ESI+) m/z calculated for $C_{18}H_{20}N_2NaO_3$ $[M+Na]^+$ 335.1372, found 335.1367.

***Tert-butyl* (2-((3-nitrophenyl)carbamoyl)phenyl)carbamate (1af)**

Yellow solid (62 mg, 89% yield), mp. 170-172 °C, R_f = 0.33 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 9.52 (s, 1H), 8.75 (s 1H), 8.63 (t, *J* = 2.2 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 8.03-8.01 (m, 2H), 7.56 (t, *J* = 8.2 Hz, 1H), 7.48 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.33 (t, *J* = 8.0

Hz, 1H), 6.99 (t, *J* = 8.0 Hz, 1H), 1.55 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 167.4, 153.7, 148.8, 139.8, 139.2, 132.9, 130.0, 127.1, 125.9, 122.1, 120.9, 120.6, 119.3, 115.2, 100.0, 81.2, 28.5; HRMS (ESI+) m/z calculated for $C_{18}H_{19}N_3NaO_5$ $[M+Na]^+$ 380.1222, found 380.1221.

N-phenyl-2-(2,2,2-trifluoroacetamido)benzamide (1ag)

White solid (77 mg, 88% yield); mp. 145-147 °C, R_f = 0.32 (15% ethyl acetate-petroleum ether, v/v); ^1H NMR ($CDCl_3$, 400 MHz) δ_H 12.25 (brs, 1H), 8.60-8.53 (m, 1H), 8.07 (brs, 1H), 7.68-7.62 (m, 1H), 7.61 (d, *J* = 1.2 Hz, 2H), 7.57-7.52 (m, 1H), 7.43-7.39 (m, 2H), 7.28-7.20 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 166.7, 137.6, 136.8, 133.4, 139.4, 126.8, 125.7, 125.1, 122.1, 121.0, 100.0; HRMS (ESI+) m/z calculated $C_{15}H_{12}F_3N_2O_2$ $[M+H]^+$ 309.0851, found 309.0853.

***N*-(4-fluorophenyl)-2-((4-methylphenyl)sulfonamido)benzamide (1ah)**

White solid (77 mg, 92% yield); mp. 160-162 °C, R_f = 0.21 (15% ethyl acetate-petroleum ether, v/v); ^1H NMR ($CDCl_3$, 400 MHz) δ_H 10.25 (s, 1H), 7.70 (s, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 2H), 7.50-7.38 (m, 4H), 7.12-7.03 (m, 5H), 2.27 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 166.6, 160.0 (d, *J* = 244.0 Hz), 143.8, 138.7, 136.4, 133.1, 133.0, 129.7, 127.3, 126.8, 124.1, 122.7 (d, *J* = 5.0 Hz), 122.5 (d, *J* = 18.0 Hz), 115.9 (d, *J* = 22.0 Hz), 21.6; HRMS (ESI+) m/z calculated $C_{20}H_{18}FN_2O_3S$ $[M+H]^+$ 385.1022, found 385.1022.

***N*-(4-chlorophenyl)-2-((4-methylphenyl)sulfonamido)benzamide (1ai)**

White solid (74 mg, 91% yield); mp. 158-160 °C, R_f = 0.23 (15% ethyl acetate-petroleum ether, v/v); ^1H NMR ($CDCl_3$, 400 MHz) δ_H 10.13 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.58 (s, 1H), 7.47-7.41 (m, 4H), 7.35-7.32 (m, 2H), 7.14-7.08 (m, 3H), 2.27 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 166.5, 143.8, 138.7, 136.4, 135.7, 133.1, 130.4, 129.6, 129.3, 127.4, 126.7, 124.2, 122.8, 122.7, 121.8, 21.6; HRMS (ESI+) m/z calculated for $C_{20}H_{17}ClN_2NaO_3S$ $[M+Na]^+$ 423.0546, found 423.0549.

***N*-(4-bromophenyl)-2-((4-methylphenyl)sulfonamido)benzamide (1aj)**

White solid (69 mg, 90% yield); mp. 152-154 °C, R_f = 0.25 (15% ethyl acetate-petroleum ether, v/v); ^1H NMR ($CDCl_3$, 400 MHz) δ_H 10.11 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.56 (s, 1H), 7.50-7.38 (m, 6H), 7.13 (d, *J* = 7.2 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 2.27 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 166.5, 143.8, 138.7, 136.5, 136.2, 133.2, 132.2, 129.6, 127.4, 126.6, 124.2, 122.9, 122.7, 122.0, 118.1, 21.6; HRMS (ESI+) m/z calculated for $C_{20}H_{18}BrN_2O_3S$ $[M+H]^+$ 445.0222, found 445.0213.

***N*-(2,5-diethoxyphenyl)-2-((4-methylphenyl)sulfonamido)benzamide (1ak)**

White solid (71 mg, 94% yield); mp. 180-182 °C, R_f = 0.46 (20% ethyl acetate-petroleum ether, v/v); ^1H NMR ($CDCl_3$, 400 MHz) δ_H 10.50 (s, 1H), 8.31 (s, 1H), 8.08 (d, *J* = 3.2 Hz, 1H), 7.71 (dd, *J* =

8.6, 0.8 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.45-7.41 (m, 2H), 7.12 (td, *J* = 7.7, 0.8 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.80 (d, *J* = 9.2 Hz, 1H), 6.61 (dd, *J* = 8.8, 2.8 Hz, 1H), 4.09-4.03 (m, 4H), 2.22 (s, 3H), 1.15-1.39 (m, 6H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 166.0, 153.4, 143.7, 141.5, 139.0, 136.5, 132.8, 129.6,127.9, 127.4, 126.3, 124.01, 123.2, 122.4, 112.1, 110.2, 106.8, 100.0, 65.0, 64.3, 21.4, 15.1, 15.0; HRMS (ESI+) m/z calculated for $C_{24}H_{26}N_2NaO_5S$ $[M+Na]^+$ 477.1460, found 477.1460.

2-((4-Methylphenyl)sulfonamido)-*N*-(naphthalen-1-yl)benzamide (1al)

Brown solid (74 mg, 93% yield); mp. 194-196 °C, R_f = 0.45 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 10.43 (s, 1H), 8.00 (s, 1H), 7.92-7.89 (m, 1H), 7.79-7.76 (m, 3H), 7.70-7.67 (m, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.54-7.46 (m, 4H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 2.19 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 167.3, 143.7, 139.2, 136.6, 134.3, 133.2, 131.5, 129.6, 129.1, 127.5, 127.3, 127.0, 126.8, 126.4, 125.7, 124.1, 122.4, 122.3, 121.7, 120.6, 21.5; HRMS (ESI+) m/z calculated for $C_{24}H_{21}N_2O_3S$ $[M+H]^+$ 417.1273, found 417.1270.

2-((4-Methylphenyl)sulfonamido)-*N*-(pyridin-2-yl)benzamide (1am)

Yellow solid (76 mg, 88% yield); mp.116-118 °C, R_f = 0.33 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 10.12 (s, 1H), 8.53 (s, 1H), 8.25-8.19 (m, 2H), 7.81-7.77 (m, 1H), 7.72 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.55 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.49-7.44 (m, 1H), 7.15-7.09 (m, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 2.21 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 144.0, 139.0, 138.8, 136.2, 133.4, 129.6, 127.3, 127.0 124.4, 123.2, 122.9, 120.5, 100.0, 21.5; HRMS (ESI+) m/z calculated for $C_{19}H_{18}N_3O_3S$ $[M+H]^+$ 368.1069, found 368.1060.

***N*-benzyl-2-((4-methylphenyl)sulfonamido)benzamide (1an)**

Yellow solid (79 mg, 95% yield); mp. 138-140 °C, R_f = 0.50 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 10.82 (s, 1H), 7.70-7.68 (m, 3H), 7.40-7.33 (m, 5H), 7.30 (d, *J* = 7.2 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 2H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.33 (s, 1H), 4.52 (d, *J* = 5.4 Hz, 2H), 2.35 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz) δ_C 168.1, 143.5, 139.0, 137.3, 136.6, 132.7, 129.5, 128.9, 128.0, 127.9, 127.2, 126.6, 123.4, 121.3, 121.2, 44.1, 21.5; HRMS (ESI+) m/z calculated for $C_{21}H_{21}N_2O_3S$ $[M+H]^+$ 381.1273, found 381.1270.

***N*-(furan-2-ylmethyl)-2-((4-methylphenyl)sulfonamido)benzamide (1ao)**

White solid (81 mg, 95% yield); mp. 110-112 °C, R_f = 0.56 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 10.70 (s, 1H), 7.65-7.62 (m, 3H), 7.38-7.33 (m, 3H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.02-6.98 (m, 1H), 6.42 (s, 1H), 6.35-6.34 (m, 1H), 6.27-6.26 (m, 1H), 4.48 (d, *J* = 5.2 Hz, 2H), 2.31 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 168.1, 150.4, 143.7, 142.6, 139.0, 136.6, 132.8, 129.6, 127.3, 126.9, 123.6, 121.4, 121.3, 110.7, 108.2, 36.9, 21.6; HRMS (ESI+) m/z calculated for $C_{19}H_{18}N_2NaO_4S$ $[M+Na]^+$ 393.0885, found 393.0886.

***N*-ethyl-2-((4-methylphenyl)sulfonamido)benzamide (1ap)**

White solid (90 mg, 93% yield); mp. 126-128 °C, R_f = 0.50 (15% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 10.78 (s, 1H), 7.65-7.63 (m, 3H), 7.37-7.32 (m, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.03-6.99 (m, 1H), 6.09 (s, 1H), 3.37-3.30 (m, 2H), 2.33 (s, 3H), 1.15 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 168.3, 143.6, 138.8, 136.7, 132.5, 129.6, 127.3, 126.7, 123.6, 121.9, 121.5, 35.0, 21.6, 14.6; HRMS (ESI+) m/z calculated for $C_{16}H_{19}N_2O_3S$ $[M+H]^+$ 319.1116, found 319.1107.

***N*-butyl-2-((4-methylphenyl)sulfonamido)benzamide (1aq)**

White solid (85 mg, 94% yield); mp. 112-114 °C, R_f = 0.53 (15% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 10.93 (s, 1H), 7.61-7.58 (m, 3H), 7.37-7.29 (m, 2H), 7.13 (d, *J* = 6.8 Hz, 2H), 6.97 (t, *J* = 7.0 Hz, 1H), 6.41 (s, 1H), 3.26 (d, *J* = 5.2 Hz, 2H), 2.29 (s, 3H), 1.49-1.45 (m, 2H), 1.33-1.28 (m, 2H), 0.92-0.88 (m, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 168.4, 143.7, 138.8, 136.6, 136.5, 132.4, 129.6, 127.2, 127.0, 123.7, 121.8, 121.3, 39.8, 31.4, 21.6, 20.2, 13.8; HRMS (ESI+) m/z calculated for $C_{18}H_{23}N_2O_3S$ $[M+H]^+$ 347.1429, found 347.1428.

12. Spectral data of the substrates 2aa-2ae:

2-Amino-*N*-phenylbenzamide (2aa)[3]**:** White solid (118 mg, 91% yield), mp. 131-132 °C, R_f = 0.46 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.85 (brs, 1H), 7.57-7.55 (m, 2H), 7.48-7.45 (m, 1H), 7.38-7.33 (m, 2H), 7.27-7.22 (m, 1H), 7.17-7.12 (m, 1H), 6.72-6.67 (m, 2H), 5.12 (brs, 2H); HRMS (ESI+) m/z calculated for $C_{13}H_{13}N_2O$ $[M+H]^+$ 213.1028, found 213.1031.

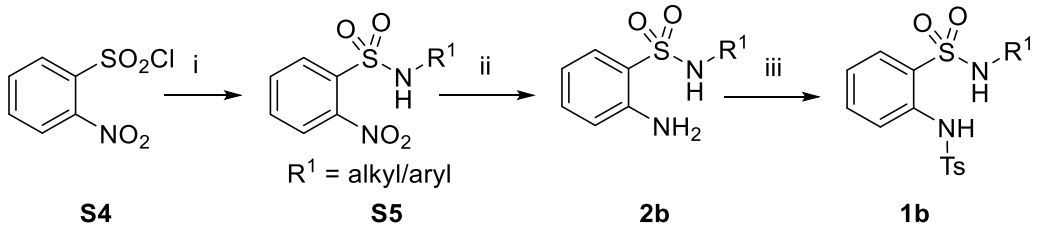
2-Amino-N-butylbenzamide (2ab): White solid (105 mg, 89% yield), mp. 127-129 °C, R_f = 0.63 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.27 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.19-7.15 (m, 2H), 6.66-6.60 (m, 2H), 6.10 (brs, 1H), 5.47 (brs, 2H), 3.39-3.37 (m, 2H), 1.57-1.54 (m, 2H), 1.41-1.36 (m, 2H), 0.95-0.91 (m, 3H); ^{13}C NMR ($CDCl_3$,100 MHz) δ_C 169.4, 148.7, 132.2, 127.2, 117.3, 116.7, 39.5, 31.8, 20.7, 13.9; HRMS (ESI+) m/z calculated for $C_{11}H_{17}N_2O$ $[M+H]^+$ 193.1341, found 193.1339.

2-Amino-*N*-(4-chlorophenyl)benzamide (2ac)[3]**:** White solid (130 mg, 85% yield), mp. 139-142°C , R_f = 0.46 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.82 (brs, 1H), 7.52-7.43 (m, 3H), 7.32-7.23 (m, 3H), 6.72-6.68 (m, 2H), 5.47 (brs, 2H); HRMS (ESI+) m/z calculated for $C_{13}H_{12}ClN_2O$ $[M+H]^+$ 247.0638, found 247.0639.

2-Amino-*N*-(2,5-diethoxyphenyl)benzamide (2ad):
White solid (129 mg, 70% yield); mp. 140-142 °C; R_f= 0.34 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.53 (s, 1H), 8.16 (d, *J* = 3.2 Hz, 1H), 7.45 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.26-7.22 (m, 1H), 6.80 (d, *J* = 8.8 Hz, 1H), 6.73-6.69 (m, 2H), 6.57 (dd, *J* = 9.0, 2.8 Hz, 1H), 4.09-4.01 (m, 4H), 1.44-1.37 (m, 6H); ^{13}C NMR ($CDCl_3$,100 MHz) δ_C 167.2, 153.3, 149.2, 141.8, 132.7, 128.9, 127.2, 117.7, 117.0, 116.7, 112.2, 109.4, 106.8, 65.0, 64.2, 15.1, 15.0; HRMS (ESI+) m/z calculated for $C_{17}H_{21}N_2O_3$ $[M+H]^+$ 301.1552, found 301.1551.

2-Amino-*N*-(4-(*tert*-butyl)phenyl)benzamide (2ae)[5]: White solid (145 mg, 88% yield, mp. 105-107°C, R_f = 0.60 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.85 (brs, 1H), 7.50-7.45 (m, 3H), 7.40-7.37 (m, 2H), 7.27-7.19 (m, 1H), 6.72-6.70 (m, 2H), 4.95 (brs, 2H), 1.33 (9H); HRMS (ESI+) m/z calculated for $C_{17}H_{21}N_2O$ $[M+H]^+$ 269.1654, found 269.1649.

13. Preparation of starting materials 1b and 2b:



Scheme S6. Synthesis of the sulphonamide substrates **1b**. Reagent and Conditions: (i) Amine (R^1NH_2), Et_3N, CH_2Cl_2, 0 °C to rt, 12 h, 80-90%; (ii) Zn, satd. NH_4Cl, MeOH, 0°C-rt, 2-3 h, 71-82%; (iii) TsCl, Py, 0°C-rt, 3-4 h, 84-87%.

To a solution of amine (R^1NH_2) (93 µl, 1.02 mmol, 1.5 equiv) and Et_3N (114 µl, 0.82 mmol, 1.2 equiv) in dry CH_2Cl_2 (3 mL) was added a solution of 2-nitrobenzenesulfonyl chloride **S4** (150 mg, 0.68 mmol, 1 equiv) in dry CH_2Cl_2 (1 mL) dropwise at 0 °C. Subsequently, the mixture was allowed to stir at room temperature for another 12 h. After completion (TLC) of the reaction, the reaction mixture was quenched with dilute hydrochloric acid (1N), washed with brine (3X10 mL), extracted with CH_2Cl_2 (3X10 mL), dried over $MgSO_4$, and concentrated in *vacuo*. Then the residue was purified by silica gel (100-200 mesh) column chromatography eluting with 15% ethyl acetate-petroleum ether (v/v) to obtain 2-nitro-*N*-arylbenzenesulfonamide derivatives **S5** in 80-90% yield.

To a well stirred solution of 2-nitro-*N*-arylbenzenesulfonamide **S5** (100 mg, 0.36 mmol, 1 equiv) in dry MeOH (2 mL) was added satd. NH_4Cl solution (125 mg, 2.34 mmol, 6.5 equiv) dropwise under argon

atmosphere. Thereafter, activated Zn (118 mg, 1.8 mmol, 5 equiv,) was added portion-wise maintaining the temperature of the reaction mixture at 0 °C. Then the whole reaction mixture was allowed to stir at rt for 2-3 h. Upon completion of the reaction (TLC), the reaction mixture was filtered through celite, neutralized with NaOH (2N). Then the mixture was washed with brine (3X10 mL), extracted with ethyl acetate (3X10 mL), and dried over anhydrous $MgSO_4$, and concentrated in *vaccuo*. Then the crude product was purified by silica gel (100-200 mesh) column chromatography eluting with 17% ethyl acetate-petroleum ether (v/v) to obtain the pure 2-amino-*N*-aryl/alkylbenzenesulfonamide **2b** in 71-82% yield.

Pyridine (32 µl, 0.40 mmol, 2 equiv) was added to a stirred solution of 2-amino-*N*-arylbenzenesulfonamide derivative **2b** (50 mg, 0.2 mmol, 1 equiv) in dry CH_2Cl_2 (2 mL) at 0 °C under argon atmosphere. After 2 minute, tosyl chloride (50 mg, 0.26 mmol, 1.3 equiv) was added portion wise and the reaction was allowed to stir at room temperature for 3-4 h. After completion (TLC) of the reaction, the mixture was diluted with CH_2Cl_2 (10 mL) and washed with 1M HCl (3X10 mL,), satd. $NaHCO_3$ (3X10 mL), and brine (3X10 mL). The organic phase was dried over anhydrous $MgSO_4$, concentrated, and purified by silica gel (100-200 mesh) column chromatography using 15-20% ethyl acetate-petroleum ether (v/v) as eluent to afford *N*-substituted-*N*'-protected-2-aminobenzamide **1b** in 84-87% yield.

14. Spectral data of substrates 1ba-1bc:

2-((4-Methylphenyl)sulfonamido)-*N*-phenylbenzenesulfonamide (1ba)

White solid (69 mg, 84% yield), mp. 194-196 °C, R_f = 0.25 (15% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.74 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.56-7.50 (m, 2H), 7.43-7.39 (m, 1H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.21-7.12 (m, 3H),7.03-6.99 (m, 1H), 6.93-6.91 (m, 2H), 6.87 (s, 1H), 2.36 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C, 144.9, 136.4, 135.3, 135.1, 134.5, 130.2, 130.1, 129.4, 127.7, 127.6, 126.6, 124.3, 123.6, 122.1, 21.7; HRMS (ESI+) m/z calculated for $C_{19}H_{19}N_2O_4S_2$ $[M+H]^+$ 403.0786, found 403.0786.

***N*-(4-chlorophenyl)-2-((4-methylphenyl)sulfonamido)benzenesulfonamide (1bb)**

Yellow gum (67 mg, 87% yield),R_f = 0.35 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.85 (d, *J* = 8.4 Hz, 2H), 7.57 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.52 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.42-7.38 (m, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.15-7.11 (m, 2H), 7.05-7.00 (m, 1H), 6.93-6.89 (m, 2H), 2.36 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C, 144.9, 136.2, 135.2, 134.7, 134.2, 131.9, 130.3, 130.1, 129.5, 127.6, 127.3, 124.3, 124.2, 121.6, 21.7; HRMS (ESI+) m/z calculated for $C_{19}H_{17}ClN_2NaO_4S_2$ $[M+Na]^+$ 459.0216, found 459.0213.

***N*-(2,5-diethoxyphenyl)-2-((4-methylphenyl)sulfonamido)benzenesulfonamide (1bc)**

Yellow solid (63 mg, 86% yield), mp. 124-126 ^{o}C, R_f = 0.32 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.97 (s, 1H), 7.76-7.73 (m, 2H), 7.58 (dd, *J* = 8.0,1.6 Hz, 1H), 7.54 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.36-7.32 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.09 (s, 1H), 6.98-6.93 (m, 2H), 6.64-6.58 (m, 2H), 3.94 (q, *J* = 6.9 Hz, 2H), 3.76 (q, *J* = 6.9 Hz, 2H), 2.34 (s, 3H), 1.36 (t, *J* = 7.0 Hz, 3H), 1.24 (t, *J* = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 153.1, 144.4, 143.8, 136.2, 136.1, 134.4, 129.9, 127.5, 125.9, 125.2, 123.0, 119.1, 112.5, 109.3, 64.7, 64.3, 21.6, 14.9, 14.7; HRMS (ESI+) m/z calculated for $C_{23}H_{27}N_2O_6S_2$ $[M+H]^+$ 491.1311, found 491.1314.

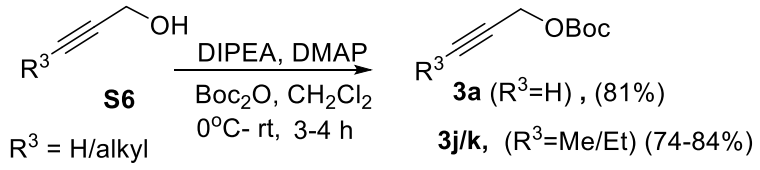
15. Spectral data of substrates 2ba-2bc:

2-Amino-*N*-phenylbenzenesulfonamide (2ba):[6] Brownish solid (68 mg, 76% yield), mp. 113-115 ^{o}C, R_f = 0.26 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.52 (dd, *J* = 10.8, 1.6 Hz, 1H), 7.28-7.16 (m, 4H), 7.10-7.04 (m, 2H), 6.73-6.62 (m, 2H), 4.68 (brs, 2H); HRMS (ESI+) m/z calculated for $C_{12}H_{13}N_2O_2S$ $[M+H]^+$ 249.0698, found 249.0700.

2-Amino-*N*-ethylbenzenesulfonamide (2bb): Brownish gum (72 mg, 82% yield), R_f = 0.17 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.64 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.28-7.24 (m, 1H), 6.75-6.71 (m, 2H), 5.08 (brs, 1H), 4.41 (brs, 2H), 2.87 (p, *J* = 7.2 Hz, 2H), 1.00 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 145.1, 134.2, 129.7, 121.5, 118.0, 117.8, 38.3, 14.9; HRMS (ESI+) m/z calculated for $C_8H_{13}N_2O_2S$ $[M+H]^+$ 201.0698, found 201.0696.

2-Amino-*N*-butylbenzenesulfonamide (2bc): Blackish liquid (81 mg, 71% yield), R_f = 0.28 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.69 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.33-7.29 (m, 1H), 6.82-6.76 (m, 2H), 4.80 (brs, 1H), 4.07 (brs, 2H), 2.85 (q, *J* = 6.4 Hz, 2H), 1.42-1.35 (m, 2H), 1.29-1.20 (m, 2H), 0.81 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 144.7, 134.1, 129.8, 122.7, 118.2, 118.0, 43.0, 31.5, 19.7, 13.6; HRMS (ESI+) m/z calculated for $C_{10}H_{17}N_2O_2S$ $[M+H]^+$ 343.1480, found 343.1481.

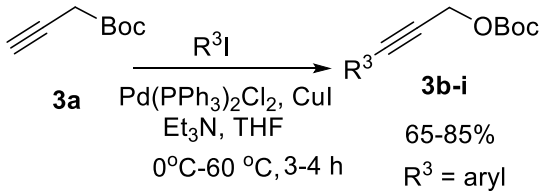
16. Procedure[2] for the preparation of starting material 3a, 3j-k:



Scheme S7. Synthesis of Boc-protected propargyl alcohols **3a**, **3j-k**

To a solution of propargyl alcohol or substituted propargyl alcohol **S6** (2.68 mmol, 1 equiv) in dry CH_2Cl_2 was added DIPEA (1.17 ml, 6.70 mmol, 2.5 equiv) and DMAP (33 mg, 0.27 mmol, 0.1 equiv) under argon. The reaction mixture was then cooled to 0 °C and di-*tert*-butyl dicarbonate (Boc_2O) (0.8 mL, 3.48 mmol, 1.3 equiv) was added portion wise over a period of two minutes. The reaction mixture was slowly warmed to ambient temperature over a period of 3-4 h. After completion (TLC) of the reaction, the reaction mixture was diluted with CH_2Cl_2 (10 mL) and washed with water (3X10 mL), 10% aq. HCl (3X10 mL), saturated aq. $NaHCO_3$ solution and brine (3X10 mL), respectively. The organic layer was then dried over anhydrous $MgSO_4$ and concentrated in *vacuo*. The residue was purified by flash column chromatography to give the desired product **3a** or **3j-k** in 74-84% yield.

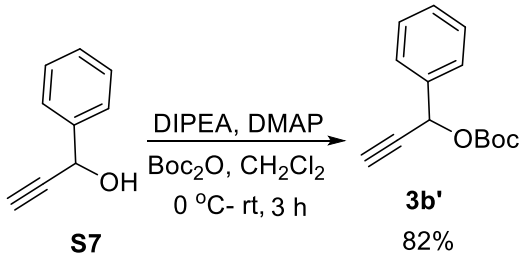
17. Schematic representation and procedure for preparation of starting material 3b-3i:



Scheme S8. Synthesis of substrates **3b-i** having substitution at acetylenic carbon

Substituted *tert*-butyl propargyl carbonate derivatives **3b-i** were prepared using "*Sonogashira reaction"* between aryl iodides (R^3I) and propargyl alcohol (**3a**) protected with Boc group (Scheme **S6**). Thus, to a solution of aryl iodide (86 µl, 0.77 mmol, 1.2 equiv) in dry THF (1 mL), $Pd(PPh_3)_2Cl_2$ (14 mg, 0.019 mmol, 3 mol %) was added at room temperature under argon. Next, dry Et_3N (0.9 mL, 6.4 mmol, 10 equiv) was added to the resulting mixture at 0 °C followed by the subsequent addition of a solution of **3a** (0.64 mmol, 1 equiv) in dry THF (2 mL) and copper(I) iodide (6.1 mg, 0.032 mmol, 5 mol %). The reaction mixture was heated at 60 °C for 3-4 h. Upon completion of the reaction (TLC), the reaction mixture was extracted with ethyl acetate (3X10 mL), and dried over anhydrous $MgSO_4$, and concentrated *in vaccuo*. Then the crude product was purified by silica gel (100-200 mesh) column chromatography eluting with 2-4% ethyl acetate-petroleum ether (v/v) to obtain the pure *tert*-butyl propargyl carbonates **3b-i** in 65-85% yield.

18. Schematic representation and procedure for preparation of starting material 3b':



Scheme S9. Synthesis of Boc-protected substrate **3b'**

To a solution of 1-phenylprop-2-yn-1-ol **S7** (0.76 mmol, 1 equiv), in dry CH_2Cl_2 (5mL) were added DIPEA (3.2 mL, 1.9 mmol, 2.5 equiv) and DMAP (0.93 mg, 0.076 mmol, 0.1 equiv). The reaction mixture was then cooled to 0 °C, and di-*tert*-butyl dicarbonate (Boc_2O) (2.2 g, 0.23ml, 0.99 mmol, 1.3 equiv) was added dropwise. The reaction mixture was slowly warmed to ambient temperature over a period of 3 h. After completion (TLC) of the reaction, the reaction mixture was diluted with CH_2Cl_2 and washed with water (3X10 mL), 10% aq. HCl (3X10 mL), sat. aq. $NaHCO_3$ (3X10 mL), and brine (3X10 mL), respectively. The crude residue was purified by silica gel (100-200 mesh) column chromatography to give the desired product **3b'** in 82% yield.

19. Spectral data of substrates 3a-3k

***Tert*-butyl (3-phenylprop-2-yn-1-yl) carbonate (3a)** [7]**:**
Colorless liquid (252 mg, 81% yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 4.64 (d, *J* = 2.4 Hz, 2H), 2.48 (t, *J* = 2.4 Hz, 1H), 1.47 (s, 9H).

***Tert*-butyl (3-phenylprop-2-yn-1-yl) carbonate (3b)** [7]**:**
Yellowish liquid (103 mg, 69% yield), R_f = 0.77 (2% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.46-7.43 (m, 2H), 7.33-7.30 (m, 3H), 4.90 (s, 2H), 1.51 (s, 9H).

***Tert*-butyl (3-(naphthalen-1-yl)prop-2-yn-1-yl) carbonate (3c):**
Brownish liquid (130 mg, 72% yield), R_f = 0.68 (2% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 8.35-8.33 (m, 1H), 7.85-7.83 (m, 2H), 7.71-7.69 (m, 1H), 7.60-7.49 (m, 2H), 7.44-7.39 (m, 1H), 5.07 (s, 2H), 1.55 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 153.1, 133.5, 133.2, 131.0, 129.4, 128.3, 127.0, 126.6, 126.2, 125.2, 119.9, 87.7, 85.1, 83.1, 55.6, 27.9; HRMS (ESI+) m/z calculated for $C_{18}H_{19}O_3$ $[M+H]^+$ 283.1334, found 283.1329.

***Tert*-butyl (3-(thiophen-2-yl)prop-2-yn-1-yl) carbonate (3d)[8]:**
Yellowish liquid (126 mg, 83% yield), R_f = 0.7 (2% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.26-7.22 (m, 2H), 6.96-6.94 (m, 1H), 4.89 (s, 2H), 1.49 (s, 9H).

***T*ert-butyl (3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl) carbonate (3e):**
Brownish liquid (146 mg, 76% yield), R_f = 0.47 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.56-7.50 (m, 4H), 4.88 (s, 2H), 1.49 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 152.9, 132.1, 125.34, 125.31, 125.27, 125.23, 85.4, 85.2, 83.2, 55.0, 27.7; HRMS (ESI+) m/z calculated for $C_{15}H_{16}F_3O_3$ $[M+H]^+$ 301.1052, found 301.1050.

***Tert*-butyl (3-(4-fluorophenyl)prop-2-yn-1-yl) carbonate (3f)[8]:**
Yellowish liquid (136 mg, 85% yield), R_f = 0.7 (2% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.43 (d, *J* = 8.8 Hz, 2H,), 7.28 (*J* = 8.4 Hz, 2H), 4.86 (s, 2H), 1.49 (s, 9H).

***Tert*-butyl (3-(4-nitrophenyl)prop-2-yn-1-yl) carbonate (3g)[8]:**
Yellowish solid (145 mg, 82% yield), mp. 70-71^{o}C, R_f = 0.56 (2% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 8.18-8.12 (m, 2H), 7.58-7.56 (m, 2H), 4.87 (s, 2H), 1.47 (s, 9H).

***Tert*-butyl (3-(*p*-tolyl)prop-2-yn-1-yl) carbonate (3h)[8]:**

Yellowish liquid (103 mg, 65% yield, R_f = 0.56 (1% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.35-7.32 (m, 2H), 7.13-7.10 (m, 2H), 4.89 (s, 2H), 2.34 (s, 3H), 1.51 (s, 9H).

***Tert*-butyl (3-(4-methoxyphenyl)prop-2-yn-1-yl) carbonate (3i)[8]:**
White solid; mp. 56-57 ^{o}C (110 mg, 65% yield), R_f = 0.48 (2% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.38-7.36 (m, 2H), 6.83-6.80 (m, 2H), 4.87 (s, 2H), 3.79 (s, 3H), 1.49 (s, 9H).

But-2-yn-1-yl *tert*-butyl carbonate (3j):
Yellowish liquid (138 mg, 84% yield), ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 4.59 (q, *J* = 2.4 Hz, 2H), 1.81 (t, *J* = 2.4 Hz, 3H), 1.45 (s, 9H);); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 153.0, 83.6, 82.7, 73.0, 56.7, 55.2, 27.8, 3.7; HRMS (ESI+) m/z calculated for $C_9H_{15}O_3$ $[M+H]^+$ 171.1021, found 171.1025.

***Tert*-butyl pent-2-yn-1-yl carbonate (3k):**
Colourless liquid (162 mg, 74% yield), ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 4.63 (t, *J* = 2.4 Hz, 2H), 2.23-2.19 (m, 2H), 1.47 (s, 9H), 1.18 (t, *J* = 10 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 153.0, 89.4, 82.7, 73.1, 55.3, 27.8, 13.6, 12.5; HRMS (ESI+) m/z calculated for $C_{10}H_{17}O_3$ $[M+H]^+$ 425.1284, found 425.1281.

20. Spectral data of substrate 3b'[7]

***Tert*-butyl (1-phenylprop-2-yn-1-yl) carbonate (3b'):**

Yellowish liquid (144 mg, 82% yield), R_f = 0.77 (2% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.55-7.53 (m, 2H), 7.39-7.36 (m, 3H), 6.23 (d, *J* = 2.0 Hz, 1H), 2.67 (d, *J* = 2.0 Hz, 2H), 1.48 (s, 9H).

21. General procedure for the Synthesis of Products 4a-q and 5a-c:

An oven dried two-neck round bottomed flask was charged with $Pd(dba)_2$ (1.6 mg, 0.003 mmol, 5 mol%) and Xantphos (3.1 mg, 0.005 mmol, 10 mol%) followed by the addition of dry CH_3CN (1 mL) *via* syringe. The reaction flask was then purged with argon. After 5 minutes of stirring at room temperature, *tert*-butyl propargyl carbonate **3a** (11 mg, 0.07 mmol, 1.3 equiv) dissolved in CH_3CN (0.5 mL) and 2-amino benzamide **1a** (0.05 mmol, 1 equiv) [or 2-amino benzsulphonamide **1b** (0.05 mmol, 1 equiv)] dissolved in CH_3CN (1 mL) were added subsequently. The reaction mixture was heated under reflux until the completion of the reaction (5 -12 h). The reaction mixture was cooled to room temperature and diluted with 5.0 mL of water. The water layer was extracted with (3x10 mL) of ethyl acetate and the combined ethyl acetate extracts were washed with brine (1x10 mL), dried over anhydrous sodium sulfate and concentrated under reduced pressure to obtained a crude product which was purified over silica gel (100-200 mesh) column chromatography using 10-15% ethyl acetate-petroleum ether (v/v) as eluent to afford the desired product **4** (or **5**) in 80-95% yield.

22. Spectral data of products 4a-q:

3-Methylene-4-phenyl-1-tosyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (4a)

Yellow solid (20 mg, 92% yield); mp. 148-150 ^oC; R_f = 0.31 (15% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.74-7.72 (m, 1H), 7.54-7.52 (m, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.45-7.41 (m, 1H), 7.27-7.24 (m, 2H), 7.21-7.17 (m, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.98-6.95 (m, 2H), 5.18 (s, 1H), 4.99 (s, 1H), 4.65 (s, 2H), 2.33 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 166.2, 144.0, 143.4, 140.7, 136.4, 135.2, 135.1, 132.1, 130.9, 130.8, 129.9, 128.9, 128.0, 127.5, 127.4, 126.5, 124.6, 118.8, 100.0, 58.0, 21.6; HRMS (ESI+) m/z calculated for $C_{23}H_{21}N_2O_3S$ $[M+H]^+$ 405.1273, found 405.1278.

3-Methylene-1-((4-nitrophenyl)sulfonyl)-4-phenyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (4b)

Yellow solid (20 mg, 91% yield); mp. 198-200 °C; R_f = 0.42 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.02 (d, *J* = 8.8 Hz, 2H), 7.70-7.65 (m, 3H), 7.60-7.47 (m, 4H), 7.26 (s, 1H), 7.17 (d, *J* = 8.8 Hz, 3H), 5.29 (s, 1H), 5.09 (s, 1H), 4.76 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 165.7, 144.3, 142.8, 140.7, 135.7, 133.7, 132.4, 131.1, 130.8, 129.8, 129.0, 128.7, 128.4, 126.3, 124.5, 124.2, 122.7, 120.8, 120.6, 100.0, 58.7; HRMS (ESI+) m/z calculated for $C_{22}H_{18}N_3O_5S$ $[M+H]^+$ 436.0967, found 436.0967.

1-((2-Bromophenyl)sulfonyl)-3-methylene-4-phenyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (4c)

White solid (19 mg, 90% yield); mp. 126-128 °C; R_f = 0.36 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.92 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.87 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.66 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.58 (td, *J* = 7.6, 1.6 Hz, 1H), 7.52-7.41 (m, 3H), 7.39 (d, *J* = 4.4 Hz, 4H), 7.29-7.26 (m, 1H), 7.76 (dd, *J* = 7.8, 1.0 Hz, 1H), 5.37 (s, 1H), 5.30 (s, 1H), 4.82 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 168.8, 144.2, 137.6, 136.6, 135.2, 134.9, 131.8, 130.4, 130.2, 130.0, 129.3, 129.0, 128.8, 128.0, 127.9, 57.6, 52.8, 21.6, 16.0; HRMS (ESI+) m/z calculated for $C_{22}H_{18}BrN_2O_3S$ $[M+H]^+$ 469.0222, found 469.0229.

9-Methyl-3-methylene-4-phenyl-1-tosyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (4d)

White solid (20 mg, 90% yield); mp. 176-178 °C; R_f = 0.35 (15% ethyl acetate-petroleum ether, v/v); ^{1}H NMR (DMSO-d_6, 400 MHz) δ_H 7.55 (d, *J* = 8.4 Hz, 2H), 7.48-7.47 (m, 1H), 7.46-7.36 (m, 2H), 7.24-7.13 (m, 5H), 6.98-6.96 (m, 2H), 5.24 (d, *J* = 1.2 Hz, 1H), 4.99 (d, *J* = 1.2 Hz, 1H), 4.89-4.85 (m, 1H), 4.35 (d, *J* = 15.2 Hz, 1H), 2.25 (s, 3H), 2.24 (s, 3H); ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz) δ_C 166.5, 144.2, 141.8, 139.9, 137.2, 137.0, 134.3, 134.2, 130.4, 129.5, 128.9, 127.8, 126.6, 125.5, 119.6, 57.4, 21.5, 18.8; HRMS (ESI+) m/z calculated for $C_{24}H_{23}N_2O_3S$ $[M+H]^+$ 419.1429, found 419.1423.

***Tert*-butyl 3-methylene-5-oxo-4-phenyl-2,3,4,5-tetrahydro-1*H*-benzo[*e*][1,4]diazepine-1-carboxylate (4e)**

White solid (19 mg, 87%yield); mp. 136-138 °C; R_f = 0.31 (15% ethyl acetate-petroleum ether, v/v); ^{1}H NMR (DMSO-d_6, 400 MHz) δ_H 7.63 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.56 (td, *J* = 7.6, 1.6 Hz, 1H), 7.48-7.39 (m, 3H), 7.31-7.25 (m, 4H), 5.21 (s, 1H), 5.04 (s, 1H), 4.14 (s, 2H), 1.29 (s, 9H); ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz) δ_C 167.5, 153.2, 143.5, 137.6, 133.5, 132.1, 129.8, 129.6, 129.5,

128.7, 127.3, 126.7, 105.6, 81.6, 55.3, 28.2; HRMS (ESI+) m/z calculated for $C_{21}H_{23}N_2O_3$ $[M+H]^+$ 351.1709, found 351.1707.

Tert-butyl 3-methylene--4-(3-nitrophenyl)-5-oxo-2,3,4,5-tetrahydro-1H- benzo[*e*][1,4] diazepine-1-carboxylate (4f)

Yellow solid (18 mg, 80% yield); mp. 98-100 °C; R_f = 0.35 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.31 (t, *J* = 2.2 Hz, 1H), 8.16-8.13 (m, 1H), 7.81-7.77 (m, 2H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.54 (td, *J* = 7.8, 1.9 Hz, 1H), 7.45 (td, *J* = 7.6, 1.2 Hz, 1H), 7.28 (dd, *J* = 7.8, 1.0 Hz, 1H), 5.44 (s, 1H), 5.01 (s, 1H), 4.19 (s, 2H), 1.36 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 168.0, 153.2, 148.7, 143.2, 142.6, 137.7, 132.5, 132.4, 132.0, 130.1, 129.7, 129.5, 128.4, 121.9, 121.5, 105.3, 82.4, 55.8, 28.1; HRMS (ESI+) m/z calculated for $C_{21}H_{22}N_3O_5$ $[M+H]^+$ 396.1559, found 396.1558.

4-(4-Fluorophenyl)-3-methylene-1-tosyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (4h)

White solid (21 mg, 94% yield); mp. 150-152 °C; R_f = 0.23 (15% ethyl acetate-petroleum ether, v/v); ^{1}H NMR (DMSO-d_6, 400 MHz) δ_H 7.59 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.57-7.53 (m, 3H), 7.46 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.24 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.15 (d, *J* = 6.8 Hz, 4H) 5.31 (s, 1H), 5.15 (s, 1H), 4.62 (s, 2H), 2.32 (s, 3H); ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz) δ_C 166.2, 160.7 (d, *J* = 242 Hz), 144.4, 143.6, 137.7 (d, *J* = 3.0 Hz), 137.1, 135.6 (d, *J* = 23.6 Hz), 132.6, 130.7, 130.6, 130.3, 129.5, 127.9 (d, *J* = 8.4 Hz), 127.5 , 120.1, 116.1 (d, *J* = 23.0 Hz), 57.8, 21.5; HRMS (ESI+) m/z calculated for $C_{23}H_{20}FN_2O_3S$ $[M+H]^+$ 423.1179, found 423.1178.

4-(4-Chlorophenyl)-3-methylene-1-tosyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (4i)

White solid (21 mg, 95% yield); mp. 144-146 °C; R_f = 0.25 (15% ethyl acetate-petroleum ether, v/v); ^{1}H NMR (DMSO-d_6, 400 MHz) δ_H 7.60-7.53 (m, 2H), 7.51-7.44 (m, 3H), 7.35 (d, *J* = 8.8 Hz, 2H), 7.27-7.23 (m, 3H), 7.18 (d, *J* = 8.8 Hz, 2H), 5.36 (s, 1H), 5.17 (s, 1H), 4.63 (s, 2H), 2.29 (s, 3H); ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz) δ_C 166.1, 144.3, 143.3, 140.1, 136.9, 135.7, 135.3, 132.7, 130.9, 130.7, 130.6, 130.5, 129.5, 129.1, 127.4, 126.9, 121.0, 57.7, 21.5; HRMS (ESI+) m/z calculated for $C_{23}H_{20}ClN_2O_3S$ $[M+H]^+$ 439.0883, found 439.0881.

4-(4-Bromophenyl)-3-methylene-1-tosyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (4j)

White solid (19 mg, 89% yield); mp. 146-148 °C; R_f = 0.27 (15% ethyl acetate-petroleum ether, v/v); ^{1}H NMR (DMSO-d_6, 400 MHz) δ_H 7.60-7.54 (m, 2H), 7.50-7.47 (m, 5H), 7.27-7.22 (m, 3H),

7.15-7.13 (m, 2H), 5.37 (s, 1H), 5.17 (s, 1H), 4.63 (s, 2H), 2.29 (s, 3H); $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 100 MHz) δ_C 166.1, 144.3, 143.2, 140.6, 136.9, 135.7, 135.3, 132.7, 132.1, 130.7, 130.5, 129.5, 127.4, 127.1, 121.1, 119.1, 57.7, 21.5; HRMS (ESI+) m/z calculated for $C_{23}H_{20}BrN_2O_3S$ $[M+H]^+$ 483.0378, found 483.0381.

4-(2,5-Diethoxyphenyl)-3-methylene-1-tosyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (4k)

White solid (20 mg, 91% yield); mp. 174-176 °C; R_f = 0.51 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR (DMSO-d_6, 400 MHz) δ_H 7.63 (d, *J* = 8.4 Hz, 2H), 7.55-7.50 (m, 2H), 7.44 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 9.2 Hz, 1H), 6.81 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.34 (d, *J* = 2.8 Hz, 1H), 5.07 (s, 1H), 4.92 (s, 1H), 4.69 (s, 2H), 3.97 (q, *J* = 7.2 Hz, 2H), 3.90 (q, *J* = 7.0 Hz, 2H), 2.32 (s, 3H), 1.29 (t, *J* = 6.8 Hz, 3H), 1.25 (t, *J* = 7.0 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 100 MHz) δ_C 166.3, 152.7, 148.4, 144.3, 144.0, 137.2, 135.7, 135.6, 132.3, 132.0, 130.5, 129.6, 129.3, 127.6, 115.9, 115.4, 114.7, 114.2, 64.7, 64.1, 58.2, 21.6, 15.3; HRMS (ESI+) m/z calculated for $C_{27}H_{29}N_2O_5S$ $[M+H]^+$ 493.1797, found 493.1793.

3-Methylene-4-(naphthalen-1-yl)-1-tosyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (4l)

Yellow solid (19 mg, 90% yield); mp. 148-150 °C; R_f = 0.47 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 7.94 (dd, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.88-7.86 (m, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.71-7.66 (m, 5H), 7.58 (td, *J* = 7.8, 1.4 Hz, 1H), 7.50-7.47 (m, 4H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 6.50 (d, *J* = 7.2 Hz, 1H), 4.86 (s, 1H), 4.69 (s, 1H), 2.40 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz) δ_C 166.3, 144.2, 143.0, 138.9, 136.5, 134.7, 133.7, 132.1, 131.5, 129.9, 129.8, 129.6, 128.6, 128.5, 127.7, 127.1, 126.3, 125.4, 124.6, 123.0, 112.2, 57.5, 21.6; HRMS (ESI+) m/z calculated for $C_{27}H_{23}N_2O_3S$ $[M+H]^+$ 455.1429, found 455.1432.

3-Methylene-4-(pyridin-2-yl)-1-tosyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (4m)

Yellow solid (20 mg, 89% yield); mp.116-118 °C; R_f = 0.35 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.29 (d, *J* = 4.8 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.60-7.54 (m, 3H), 7.46-7.42 (m, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.06-7.03 (m, 1H), 6.79 (d, *J* = 8.0 Hz, 2H), 5.27 (s, 1H), 5.02 (s, 1H), 4.83 (s, 2H), 2.17 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 166.4, 153.5, 147.6, 143.4, 137.2, 136.0, 135.7, 134.8, 132.4, 132.1, 130.4, 129.4, 129.1, 127.0, 120.3, 120.2, 117.1, 58.6, 21.5; HRMS (ESI+) m/z calculated for $C_{22}H_{20}N_3O_3S$ $[M+H]^+$ 406.1225, found 406.1226.

4-Benzyl-3-methylene-1-tosyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (4n)

Yellow solid (20 mg, 91% yield); Mp. 192-198 ^{o}C; R_f = 0.60 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.51 (d, *J* = 7.6 Hz, 2H), 7.48-7.39 (m, 4H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.27-7.23 (m, 3H), 7.15-7.13 (m, 2H), 5.06 (s, 1H), 4.65 (s, 1H), 4.44 (s, 2H), 4.42 (s, 2H), 2.35 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 166.3, 144.2, 142.4, 137.9, 136.8, 135.5, 135.3, 132.2, 130.5, 130.4, 129.3, 128.9, 128.8, 127.9, 127.5, 117.3, 58.4, 50.5, 21.6; HRMS (ESI+) m/z calculated for $C_{24}H_{23}N_2O_3S$ $[M+H]^+$ 419.1429, found 419.1430.

4-(Furan-2-ylmethyl)-3-methylene-1-tosyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (4o)

Yellow solid (20 mg, 90% yield); mp. 50-52 ^{o}C; R_f = 0.58 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.58 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.50-7.45 (m, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.37-7.34 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.30-6.29 (m, 1H), 6.19 (d, *J* = 3.2 Hz, 1H) 5.03 (s, 1H), 4.76 (s, 1H), 4.51 (s, 2H), 4.35 (s, 2H), 2.37 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 166.4, 150.0, 143.9, 142.6, 142.0, 136.2, 135.1, 134.9, 131.9, 131.2, 130.4, 129.8, 128.9, 127.4, 127.2, 116.8, 110.6, 109.8, 58.3, 43.6, 21.7; HRMS (ESI+) m/z calculated for $C_{22}H_{21}N_2O_4S$ $[M+H]^+$ 409.1222, found 409.1224.

4-Ethyl-3-methylene-1-tosyl-1,2,3,4-tetrahydro-*5H*-benzo[*e*][1,4]diazepin-5-one (4p)

White solid (20 mg, 91% yield); mp. 116-118 ^{o}C; R_f = 0.56 (15% ethyl acetate-petroleum ether, v/v); ^{1}H NMR (DMSO-d_6, 600 MHz) δ_H 7.54-7.46 (m, 4H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* =7.8 Hz, 1H), 5.23 (s, 1H), 5.09 (s, 1H), 4.55 (s, 2H), 3.28 (q, *J* =.7.2 Hz, 2H), 2.38 (s, 3H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz) δ_C 165.6, 144.0, 142.6, 136.8, 135.8, 135.2, 131.9, 130.7, 130.3, 130.2, 129.2, 127.4, 117.0, 58.7, 42.2, 21.5, 13.4 ;HRMS (ESI+) m/z calculated for $C_{19}H_{21}N_2O_3S$ $[M+H]^+$ 357.1273, found 357.1273.

4-Butyl-3-methylene-1-tosyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (4q)

White solid (20 mg, 90%yield); mp. 110-112 ^{o}C; R_f = 0.55 (15% ethyl acetate-petroleum ether, v/v); ^{1}H NMR (DMSO-d_6, 600 MHz) δ_H 7.52-7.50 (m, 3H), 7.47 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.26 (d, *J* = 7.8 Hz, 1H), 5.24 (s, 1H), 5.08 (s, 1H), 4.52 (s, , 2H), 3.23 (t, *J* = 7.8 Hz, 2H), 2.38 (s, 3H), 1.23-1.16 (m, 4H), 0.84 (t, *J* = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz) δ_C 165.9, 144.0, 142.8, 136.9, 135.8, 135.2, 131.9, 130.4, 130.1, 129.1, 127.4, 117.1, 58.5, 47.4, 29.9, 21.5, 20.1, 14.1; HRMS (ESI+) m/z calculated for $C_{21}H_{25}N_2O_3S$ $[M+H]^+$ 385.1586, found 385.1587.

23. Spectral data of products 5a-c:

3-Methylene-2-phenyl-5-tosyl-2,3,4,5-tetrahydrobenzo[*f*][1,2,5]thiadiazepine-1,1-dioxide (5a)
White solid (19 mg, 86% yield), mp. 154-156 °C R_f = 0.29 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR (DMSO-d^6, 400 MHz) δ_H 7.81 (d, *J* = 8.8 Hz, 2H), 7.75 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.68 (td, *J* = 7.8, 1.7 Hz 1H), 7.52-7.45 (m, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.29-7.27 (m, 3H), 7.05-7.03 (m, 2H), 5.29 (s, 1H), 5.08 (s, 1H), 4.55 (s, 2H), 2.39 (s, 3H); ^{13}C{^{1}H} NMR (DMSO-d^6, 100 MHz) δ_C 144.6, 142.8, 140.5, 138.2, 137.9, 137.5, 134.4, 130.5, 130.0, 129.2, 128.69, 128.50, 128.37, 128.01, 127.95, 117.2, 52.3, 21.6; HRMS (ESI+) m/z calculated for $C_{22}H_{21}N_2O_4S_2$ $[M+H]^+$ 441.0943, found 441.0945.

2-(4-Chlorophenyl)-3-methylene-5-tosyl-2,3,4,5-tetrahydrobenzo[*f*][1,2,5]thiadiazepine-1,1-dioxide (5b)

Yellow solid (19 mg, 88% yield), mp. 68-70 °C R_f = 0.39 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.87 (t, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.60-7.56 (m, 1H), 7.39 (t, *J* = 7.0 Hz, 1H), 7.26-7.22 (m, 4H), 6.89 (d, *J* = 8.8 Hz, 2H), 5.04 (s, 1H), 4.72 (s, 1H), 4.70 (s, 2H), 2.41 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C, 144.5, 141.7, 137.6, 136.9, 136.5, 136.3, 134.4, 133.5, 129.8, 129.7, 129.5, 129.4, 128.1, 128.0, 127.4, 112.3, 52.9, 21.7; HRMS (ESI+) m/z calculated for $C_{22}H_{20}ClN_2O_4S_2$ $[M+H]^+$ 475.0553, found 475.0557.

2-(2,5-Diethoxyphenyl)-3-methylene-5-tosyl-2,3,4,5-tetrahydrobenzo[*f*][1,2,5]thiadiazepine-1,1-dioxide (5c)

White solid (18 mg, 85% yield), mp. 125-127 °C R_f = 0.35 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR (DMSO-d_6, 400 MHz) δ_H 7.81 (d, *J* = 8.4 Hz, 2H), 7.70 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.64 (td, *J* = 7.8, 1.7 Hz, 1H), 7.49-7.43 (m, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 6.86-6.80 (m, 2H), 6.70 (d, *J* = 2.8 Hz, 1H), 5.14(s, 1H), 5.00 (s, 1H), 4.53 (s, 2H), 3.87 (q, *J* = 7.1 Hz, 2H), 3.64 (q, *J* = 7.1 Hz, 2H), 2.38 (s, 3H), 1.21 (t, *J* = 7.0 Hz, 3H), 0.71 (t, *J* = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz) δ_C 152.5, 149.7, 144.5, 142.5, 139.7, 137.8, 137.6, 133.9, 130.4, 129.8, 128.7, 128.1, 127.6, 118.5, 116.0, 115.1, 114.3, 64.3, 64.1, 52.6, 21.6, 15.1, 14.4; HRMS (ESI+) m/z calculated for $C_{26}H_{29}N_2O_6S_2$ $[M+H]^+$ 529.1467, found 529.1466.

24. Procedure for the synthesis of products 6a-m and 7a-k:

An oven dried two-neck round bottomed flask was charged with $Pd(dba)_2$ (3.8 mg, 0.006 mmol, 7 mol%) and Xantphos (7.6 mg, 0.013 mmol, 14 mol%) followed by addition of dry BuCN (1 mL) *via* syringe. The reaction flask was then purged with argon. After 5 minutes of stirring at room temperature, *tert*-butyl propargyl carbonate **3** (0.14 mmol, 1.5 equiv) having substitution at acetylenic carbon was added dropwise followed by the addition of 2-aminobenzamide derivative **2a** (0.094 mmol,1 equiv) dissolved in BuCN (1 mL). Next, the reaction mixture was heated under reflux until the completion of reaction (1.3 -24 h). The reaction mixture was cooled to room temperature and diluted with water (4.0 mL). The water layer was extracted with ethyl acetate (3x10 mL). The combined ethyl acetate extracts were washed with brine (1x10 mL), dried over anhydrous sodium sulfate and concentrated under reduced pressure to obtain the crude residue which was purified over silica gel (100-200 mesh) column chromatography using 10-15% ethyl acetate-petroleum ether (v/v) as eluent to afford desired product **6** in 42-76% yield. The same reaction procedure was adopted for the synthesis of **7** where 2-amino-N-aryl/alkylbenzenesulphonaamide **2b** was used instead of **2a**.

25. Spectral data of products 6a-m:

(*E*)-3-benzylidene-4-phenyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (6a):
Brownish solid (22.7 mg, 72% yield), mp. 148-150 °C, R_f = 0.32 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 8.17 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.47-7.45 (m, 2H), 7.36-7.31 (m, 5H), 7.30-7.26 (m, 2H), 7.16 (d, *J* = 4.8 Hz, 2H), 6.89-6.86 (m, 1H), 6.73 (d, *J* = 5.6 Hz, 1H), 6.20 (s, 1H), 4.64 (brs, 1H), 4.28 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz) δ_C 168.0, 143.6, 139.9, 135.5, 134.1, 132.4, 129.4, 128.7, 128.4, 127.4, 127.1, 126.9, 125.0, 118.9, 117.9, 99.9, 48.1; HRMS (ESI+) m/z calculated for $C_{22}H_{19}N_2O$ $[M+H]^+$ 327.1497, found 327.1491.

(*E*)-3-(naphthalen-1-ylmethylene)-4-phenyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (6b):
Brown solid (24.8 mg, 70% yield), mp. 152-153 °C, R_f = 0.44 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.22 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.83-7.76 (m, 3H), 7.54-7.50 (m, 2H), 7.47-7.43 (m, 3H), 7.40-7.36 (m, 3H), 7.33-7.28 (m, 2H), 6.91-6.87 (m, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.50 (s, 1H), 4.12 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 168.0, 144.0, 141.6, 134.4, 133.6, 132.9, 132.6, 132.2, 129.7, 129.1, 128.5, 128.2, 128.0,127.4, 127.2, 126.38, 126.35, 126.2, 125.9, 125.3, 124.8, 117.9, 100.0, 48.0; HRMS (ESI+) m/z calculated for $C_{26}H_{21}N_2O$ $[M+H]^+$ 377.1654, found 377.1651.

(*E*)-4-phenyl-3-(thiophen-2-ylmethylene)-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (6c):

Yellowish solid (22.2 mg, 71% yield), mp. 143-145 ^{o}C, R_f = 0.30, (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.14 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.45-7.41 (m, 2H), 7.31-7.29 (m, 5H), 7.00-6.97 (m, 1H), 6.87-6.83 (m, 2H), 6.73 (dd, *J* = 8.2, 1.0 Hz, 1H), 6.27 (s, 1H), 4.44 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)δ_C 168.3, 146.5, 143.5, 138.6, 137.4, 134.4, 132.5, 129.5, 128.4, 127.5, 127.2, 127.0, 126.4, 119.9, 118.9, 118.2, 117.9, 48.5; HRMS (ESI+) m/z calculated for $C_{20}H_{17}N_2OS$ $[M+H]^+$ 333.1062, found 333.1061.

(*E*)-4-phenyl-3-(4-(trifluoromethyl)benzylidene)-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (6d):

White solid (18 mg, 48% yield), mp. 166-167 ^{o}C, R_f = 0.47 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.19 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.48-7.44 (m, 3H), 7.36-7.34 (m, 1H), 7.32-7.29 (m, 3H), 7.27-7.26 (m, 1H), 6.89-6.85 (m, 1H), 6.73 (dd, *J* = 8.0, 0.4 Hz, 1H), 6.05 (s, 1H), 4.22 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 167.9, 147.2, 143.6, 142.0, 139.6, 134.6, 132.8, 129.7, 129.1, 127.7, 127.4, 125.41, 125.37, 121.1, 119.3, 119.0, 117.7, 100.0, 47.6; HRMS (ESI+) m/z calculated for $C_{23}H_{18}F_3N_2O$ $[M+H]^+$ 395.1371, found 395.1375.

(*E*)-3-(4-fluorobenzylidene)-4-phenyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (6e):

Yellowish solid (14.7 mg, 46% yield), mp. 134-136 ^{o}C, R_f = 0.34 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.13 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.35-7.26 (m, 6H), 7.14-7.12 (m, 4H), 6.90-6.86 (m, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 6.16 (s, 1H), 4.27 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 168.1, 146.9, 140.0, 139.6, 135.4, 134.3, 132.6, 129.0, 128.95, 128.70, 128.4, 127.5, 124.3, 119.5, 118.9, 117.7, 116.4, 116.3, 47.9; HRMS (ESI+) m/z calculated for $C_{22}H_{18}FN_2O$ $[M+H]^+$ 345.1403, found 345.1403.

(E)-3-(4-nitrobenzylidene)-4-phenyl-1,2,3,4-tetrahydro-5H-benzo[e][1,4]diazepin-5-one (6f):

Brownish solid (12.8 mg, 42% yield), mp. 156-158 ^{o}C, R_f = 0.45, (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.94 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.57 (d, *J* = 6.0 Hz, 2H), 7.37-7.27 (m, 6H), 7.16 (d, *J* = 6.8 Hz, 2H), 6.95-6.91 (m, 1H), 6.73 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.61 (s, 1H), 4.33 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 160.8, 152.7, 150.3, 146.0, 136.7, 134.3, 133.2, 133.0, 128.7, 128.5, 120.4, 119.2, 100.0, 49.5; HRMS (ESI+) m/z calculated for $C_{22}H_{18}N_3O_3$ $[M+H]^+$ 372.1348, found 372.1346.

(*E*)-3-(4-methylbenzylidene)-4-phenyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (6g):

Brownish solid (21.4 mg, 67% yield), mp. 142-143°C, R_f = 0.46 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.11 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.44-7.40 (m, 2H), 7.36-7.34 (m, 2H), 7.31-7.26 (m, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.87 (t, *J* = 7.2 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 6.21 (s, 1H), 4.29 (s, 2H), 2.32 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 168.1, 143.7, 137.6, 134.1, 132.5, 129.5, 129.2, 128.7, 127.1, 126.9, 118.1, 48.6, 21.3; HRMS (ESI+) m/z calculated for $C_{23}H_{21}N_2O$ $[M+H]^+$ 341.1654, found 341.1656.

(*E*)-3-(4-methoxybenzylidene)-4-phenyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (6h):

Brownish solid (23 mg, 69% yield), mp. 136-138 °C, R_f = 0.20 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.11 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.45-7.41 (m, 3H), 7.36-7.31 (m, 3H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.85-6.83 (m, 3H), 6.71 (dd, *J* = 7.8, 0.6 Hz, 1H), 6.20 (s, 1H), 4.27 (s, 2H), 3.78 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 159.1, 138.5, 134.1, 132.4, 130.7, 130.1, 129.4, 128.8, 128.0, 127.0, 126.8, 125.9, 122.7, 119.0, 118.0, 113.9, 100.0, 55.4, 48.6; HRMS (ESI+) m/z calculated for $C_{23}H_{21}N_2O_2$ $[M+H]^+$ 357.1603, found 357.1609.

(*E*)-3-ethylidene-4-phenyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (6i):

Brownish solid (16.5 mg, 67% yield), mp. 105-106 °C , R_f = 0.28 (15% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.81 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.55-7.53 (m, 2H), 7.37-7.33 (m, 3H), 7.18-7.13 (m, 1H), 6.93-6.89 (m, 1H), 6.72-6.65 (m, 1H), 5.63 (q, *J* = 6.9 Hz, 1H), 4.15 (s, 2H), 1.47 (d, *J* = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 168.7, 145.3, 141.0, 136.9, 132.1, 131.9, 129.1, 128.9, 125.3, 124.6, 123.3, 120.6, 120.4, 119.5, 100.0, 55.9, 13.0; HRMS (ESI+) m/z calculated for $C_{17}H_{17}N_2O$ $[M+H]^+$ 265.1341, found 265.1346.

(*E*)-3-benzylidene-4-(4-chlorophenyl)-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (6k):

Brownish solid (15.8 mg, 54% yield), mp. 120-122 °C, R_f = 0.80 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.18 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.416-7.410 (m, 1H), 7.40-7.39 (m, 1H), 7.32-7.27 (m, 5H), 7.14 (d, *J* = 7.6 Hz, 3H), 6.88-6.84 (m, 1H), 6.72 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.18 (s, 1H), 4.25 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 168.1, 146.8, 142.2, 139.8, 135.4, 134.2, 132.7, 132.5, 129.7, 128.8, 128.53, 128.52, 127.7, 125.4, 119.9, 119.1, 118.0, 100.0, 48.2; HRMS (ESI+) m/z calculated for $C_{22}H_{18}ClN_2O$ $[M+H]^+$ 361.1108, found 361.1111.

(*E*)-3-benzylidene-4-(2,5-diethoxyphenyl)-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (6l):

Brownish solid (16.6 mg, 60% yield), mp. 128-130 ^{o}C, R_f = 0.37 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.18 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.32-7.27 (m, 3H), 7.24-7.20 (m, 2H), 7.15 (d, *J* = 7.6 Hz, 2H), 6.92-6.90 (m, 1H), 6.85-6.84 (m, 1H), 6.83-6.81 (m, 1H), 6.70 (d, *J* = 8.4 Hz, 1H), 6.18 (s, 1H), 4.25 (s, 2H), 4.01-3.95 (m, 4H), 1.38 (t, 7.2 Hz, 3H), 1.27-1.24 (m, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 168.0, 153.2, 148.2, 146.9, 140.6, 136.2, 134.8, 133.7, 132.3, 128.8, 128.4, 127.2, 121.4, 118.6, 118.1, 117.5, 116.4, 114.6, 114.3, 100.0, 64.8, 64.1, 46.9, 15.0; HRMS (ESI+) m/z calculated for $C_{26}H_{27}N_2O_3$ $[M+H]^+$ 415.2022, found 415.2021.

(*E*)-3-benzylidene-4-(4-(tert-butyl)phenyl)-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (6m):

Yellowish solid (19 mg, 67% yield), mp. 194-196 ^{o}C, R_f = 0.42 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR (DMSO-d_6, 400 MHz) δ_H 7.79 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.43-7.41 (m, 2H), 7.33-7.30 (m, 3H), 7.22-7.21 (m, 1H), 7.201-7.196 (m, 2H), 7.18-7.17 (m, 2H), 6.79 (dd, *J* = 8.2, 1.0 Hz, 1H), 6.66-6.61 (m, 1H), 6.09 (s, 1H), 4.15 (d, *J* = 4.4 Hz, 2H), 1.28 (s, 9H); ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz) δ_C 168.0, 149.4, 148.2, 142.0, 141.0, 135.6, 133.9, 132.6, 129.2, 129.0, 127.9, 127.3, 126.4, 118.3, 116.9, 100.0, 34.8, 31.7; HRMS (ESI+) m/z calculated for $C_{26}H_{27}N_2O$ $[M+H]^+$ 383.2123, found 383.2139.

26. Spectral data of products 7a-k:

(*E*)-3-benzylidene-2-phenyl-2,3,4,5-tetrahydrobenzo[*f*][1,2,5]thiadiazepine-1,1-dioxide (7a):
Brownish solid (22 mg, 76% yield), mp. 185-187 ^{o}*C,* R_f = 0.32 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.65 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.47-7.45 (m, 2H), 7.35-7.28 (m, 6H), 7.25-7.20 (m, 1H), 7.06 (d, *J* = 7.2 Hz, 2H), 6.78-6.74 (m, 1H), 6.68 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.04 (s, 1H), 4.75 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 145.4, 143.3, 140.8, 135.5, 133.2, 129.5, 129.4, 129.1, 128.6, 128.5, 128.2, 127.3, 124.8, 121.3, 118.7, 118.1, 45.3; HRMS (ESI+) m/z calculated for $C_{21}H_{19}N_2O_2S$ $[M+H]^+$ 363.1167, found 363.1173.

(*E*)-3-(naphthalen-1-ylmethylene)-2-phenyl-2,3,4,5-tetrahydrobenzo[*f*][1,2,5]thiadiazepine-1,1-dioxide (7b):

Brownish solid (23.6 mg, 70% yield), mp. 183-185 ^{o}C, R_f = 0.48 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.82 (d, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.67 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.58-7.56 (m, 2H), 7.53-7.51 (m, 1H), 7.48-7.32 (m, 6H), 7.24-7.16 (m, 2H), 6.78-6.74 (m, 1H), 6.62 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.34 (s, 1H), 4.62 (d, *J* = 4.8 Hz, 2H); ^{13}C{^{1}H}

NMR ($CDCl_3$, 100 MHz) δ_C 145.4, 144.5, 141.0, 133.6, 133.2, 132.6, 132.2, 129.7, 129.6, 129.1, 128.6, 128.5, 128.4, 128.1, 127.2, 126.4, 126.2, 125.3, 124.9, 124.7, 118.6, 118.5, 118.0, 100.0, 45.3; HRMS (ESI+) m/z calculated for $C_{25}H_{21}N_2O_2S$ $[M+H]^+$ 413.1324, found 413.1324.

(*E*)-2-phenyl-3-(thiophen-2-ylmethylene)-2,3,4,5-tetrahydrobenzo[*f*][1,2,5]thiadiazepine-1,1-dioxide (7c):

Brownish solid (22.5 mg, 76% yield), mp. 109-111 °C, R_f = 0.27 (20% ethyl acetate-petroleum ether, v/v); ^1H NMR ($CDCl_3$, 400 MHz) δ_H 7.65 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.46-7.43 (m, 2H), 7.35-7.26 (m, 5H), 6.98-6.96 (m, 1H), 6.80-6.75 (m, 2H), 6.72 (dd, *J* = 8.0, 0.8 Hz, 1H), 6.07 (s, 1H), 4.91 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 145.2, 142.4, 140.4, 137.5, 133.3, 129.5, 129.3, 128.6, 128.2, 128.1, 127.4, 125.9, 124.8, 118.9, 118.3, 114.6, 100.0, 45.8; HRMS (ESI+) m/z calculated for $C_{19}H_{17}N_2O_2S_2$ $[M+H]^+$ 369.0731, found 369.0732.

(E)-2-phenyl-3-(4-(trifluoromethyl)benzylidene)-2,3,4,5 tetrahydrobenzo[f][1,2,5]thiadi-azepine-1,1-dioxide (7d):

Brownish solid (18 mg, 53% yield), mp. 163-165 °C, R_f = 0.45 (20% ethyl acetate-petroleum ether, v/v); ^1H NMR ($CDCl_3$, 400 MHz) δ_H 7.65 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.45-7.43 (m, 2H), 7.37-7.29 (m, 4H), 7.17 (d, *J* = 8.4 Hz, 2H), 6.80-6.76 (m, 1H), 6.70 (dd, *J* = 8.4, 0.8 Hz, 1H), 5.98 (s, 1H), 4.75 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 145.2, 140.4, 133.4, 129.9, 129.62, 129.59, 129.4, 129.2, 128.54, 128.50, 125.43, 125.39, 124.6, 122.6, 119.1, 118.8, 118.1, 112.6, 100.0, 45.1; HRMS (ESI+) m/z calculated for $C_{22}H_{18}F_3N_2O_2S$ $[M+H]^+$ 431.1041, found 431.1036.

(*E*)-3-(4-fluorobenzylidene)-2-phenyl-2,3,4,5-tetrahydrobenzo[*f*][1,2,5]thiadiazepine-1,1-dioxide (7e):

Brownish solid (20.9 mg, 68% yield), mp. 167-169 °C, R_f = 0.48 (20% ethyl acetate-petroleum ether, v/v); ^1H NMR ($CDCl_3$, 400 MHz) δ_H 7.66 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.47-7.45 (m, 2H), 7.34-7.32 (m, 2H), 7.31-7.30 (m, 1H), 7.29-7.28 (m, 1H), 7.23-7.21 (m, 2H), 7.06 (d, *J* = 6.8 Hz, 2H), 6.79-6.75 (m, 1H), 6.68 (dd, *J* = 8.6, 0.6 Hz, 1H), 6.04 (s, 1H), 4.77 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 136.5, 134.7, 131.1, 131.0, 130.7, 129.14, 129.08, 127.41, 127.39, 125.7, 122.7, 116.1, 115.9, 100.0, 46.5; HRMS (ESI+) m/z calculated for $C_{21}H_{18}FN_2O_2S$ $[M+H]^+$ 381.1073 found 381.1075.

(*E*)-3-(4-nitrobenzylidene)-2-phenyl-2,3,4,5-tetrahydrobenzo[*f*][1,2,5]thiadiazepine-1,1-dioxide (7f):

Yellow solid (25 mg, 76 % yield), mp. 208-210°C, R_f = 0.24 (20% ethyl acetate-petroleum ether, v/v); ^1H NMR (DMSO-d_6, 400 MHz) δ_H 8.14 (d, *J* = 8.8 Hz, 2H), 7.41-7.37 (m, 5H), 7.33-7.29 (m,

4H), 6.85 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.69-6.65 (m, 1H), 5.94 (s, 1H), 4.63 (d, *J* = 5.2 Hz, 2H); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 100 MHz) δ_C 147.2, 146.8, 146.5, 142.7, 140.9, 134.0, 130.5, 130.2, 129.7, 128.9, 127.9, 124.1, 122.8, 118.8, 118.3, 117.6, 100.0, 43.9; HRMS (ESI+) m/z calculated for $C_{21}H_{17}N_3NaO_4S$ $[M+Na]^+$ 429.0885, found 429.0887.

(*E*)-3-(4-methylbenzylidene)-2-phenyl-2,3,4,5-tetrahydrobenzo[*f*][1,2,5]thiadiazepine-1,1-dioxide (7g):

White solid (21.5 mg, 71% yield), mp. 184-186 °C, R_f = 0.40, (15% ethyl acetate-petroleum ether, v/v); ^1H NMR ($CDCl_3$, 600 MHz) δ_H 7.40-7.37 (m, 4H), 7.31-7.24 (m, 2H), 7.16 (d, *J* = 7.8 Hz, 2H), 7.13 (s, 1H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.68 (t, *J* = 7.2 Hz, 1H), 5.94 (s, 1H), 4.61 (d, *J* = 4.2 Hz, 2H), 3.33 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz) δ_C 146.9, 143.8, 141.4, 137.1, 133.6, 132.3, 129.8, 129.5, 129.3, 129.1, 128.3, 128.0, 123.1, 121.3, 118.7, 117.5, 44.4, 21.1; HRMS (ESI+) m/z calculated for $C_{22}H_{21}N_2O_2S$ $[M+H]^+$ 377.1324, found 377.1327.

(*E*)-3-ethylidene-2-phenyl-2,3,4,5-tetrahydrobenzo[*f*][1,2,5]thiadiazepine-1,1-dioxide (7h):

Reddish gum (17 mg, 72 % yield), R_f = 0.34 (20% ethyl acetate-petroleum ether, v/v); ^1H NMR ($CDCl_3$, 400 MHz) δ_H 7.63 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.60-7.57 (m, 1H), 7.27-7.26 (m, 1H), 7.24-7.12 (m, 4H), 6.76-6.72 (m, 1H), 6.68 (dd, *J* = 8.4, 0.8 Hz, 1H), 5.24 (q, *J* = 6.9 Hz, 2H), 4.64 (s, 2H), 1.37 (d, *J* = 6.8 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 145.7, 141.0, 140.8, 133.1, 129.4, 129.2, 129.0, 128.9, 127.9, 126.9, 125.1, 119.1, 118.48, 118.46, 50.8, 12.6; HRMS (ESI+) m/z calculated for $C_{16}H_{17}N_2O_2S$ $[M+H]^+$ 301.1011, found 301.1008.

(*E*)-2-phenyl-3-propylidene-2,3,4,5-tetrahydrobenzo[*f*][1,2,5]thiadiazepine-1,1-dioxide (7i):

Brownish gum (17.5 mg, 69% yield), R_f = 0.64 (20% ethyl acetate-petroleum ether, v/v); ^1H NMR ($CDCl_3$, 400 MHz) δ_H 7.63-7.58 (m, 3H), 7.21-7.14 (m, 4H), 6.75-6.66 (m, 2H), 5.09 (t, *J* = 7.2 Hz, 1H), 4.46 (s, 2H), 1.82 (p, *J* = 7.6 Hz, 2H), 0.66 (t, *J* = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 145.7, 141.4, 139.4, 133.1, 129.4, 129.2, 129.0, 128.9, 128.1, 127.0, 125.3, 125.0, 119.1, 118.4, 50.8, 20.4, 12.6; HRMS (ESI+) m/z calculated for $C_{17}H_{19}N_2O_2S$ $[M+H]^+$ 315.1167, found 315.1166.

(*E*)-3-benzylidene-2-ethyl-2,3,4,5-tetrahydrobenzo[*f*][1,2,5]thiadiazepine-1,1-dioxide (7j):

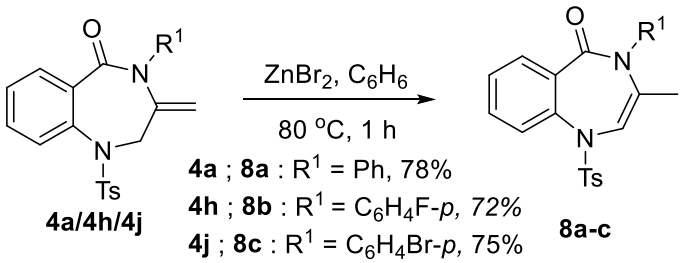
Yellowish solid (22 mg, 71% yield), mp. 127-129 °C, R_f = 0.45 (20% ethyl acetate-petroleum ether, v/v); ^1H NMR ($CDCl_3$, 400 MHz) δ_H 7.80 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.265-7.263 (m, 1H), 7.25-7.23 (m, 1H), 6.90-6.85 (m, 1H), 6.69 (d, *J* = 8.4 Hz, 1H), 6.17 (s, 1H), 4.36 (s, 2H), 3.37 (q, *J* = 7.2 Hz, 2H), 0.87 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 145.9, 138.3, 134.6, 133.0, 129.1, 129.0, 128.6, 128.0, 127.5, 121.2, 119.5,

118.8, 51.6, 45.8, 12.8; HRMS (ESI+) m/z calculated for $C_{17}H_{19}N_2O_2S$ $[M+H]^+$ 315.1167, found 361.1161.

(*E*)-3-benzylidene-2-butyl-2,3,4,5-tetrahydrobenzo[*f*][1,2,5]thiadiazepine-1,1-dioxide (7k):

Brownish gum (21 mg, 70% yield), R_f = 0.59 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.52 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.39-7.35 (m, 2H), 7.29-7.21 (m, 3H), 6.84-6.82 (m, 1H), 6.75-6.70 (m, 2H), 6.44 (s, 1H), 4.33 (d, *J* = 4.4 Hz, 2H), 3.54-3.50 (m, 2H), 1.60-1.53 (m, 2H), 1.23-1.17 (m, 2H), 0.77 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 147.2, 141.7, 135.9, 133.4, 129.6, 129.0, 128.0, 127.7, 124.6, 120.0, 118.8, 117.6, 50.8, 44.7, 31.2, 19.7, 14.0; HRMS (ESI+) m/z calculated for $C_{19}H_{23}N_2O_2S$ $[M+H]^+$ 343.1480, found 343.1481

27. Isomerisations of the exocyclic double bond of 4a/4h/4j into 1,4-dihydro-5*H*-benzo[*e*][1,4]diazepin-5-one derivatives 8a/8b/8c



Scheme S10. Isomerisations of the compound **4a/4h/4j** into **8a/8b/8c**

To a well stirred solution of the 1,4-benzodiazepinone **4a** (0.05 mmol, 1 equiv) in dry benzene (1 mL) was added anhydrous $ZnBr_2$ (23 mg, 0.1 mmol, 2 equiv) under argon atmosphere. The reaction mixture was then heated at 80 °C for 1 h until completion of the reaction (TLC). Upon completion of the reaction, the mixture was cooled to room temperature and quenched with water (2 mL). It was then extracted with ethyl acetate (3 x 15 mL) and the combined organic extracts were washed with brine (10 mL), dried over anhydrous sodium sulphate and concentrated under reduced pressure. The crude residue was purified over silica gel (100-200 mesh) column chromatography using 10% ethyl acetate–petroleum ether (v/v) as eluent to afford pure products **8a** in 72% yield.

The same reaction procedure was adopted in the isomerisations of **4h** and **4j** into **8b**(72%) and **8c**(75%), respectively.

28. Spectral data of products 8a–8c:

3-Methyl-4-phenyl-1-tosyl-1,4-dihydro-5*H*-benzo[*e*][1,4]diazepin-5-one (8a)

White solid (15.6 mg, 78% yield), mp. 152-154 ^{o}C, R_f = 0.58 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.85-7.83 (m, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.55-7.54 (m, 2H), 7.42-7.38 (m, 1H), 7.27 (s, 2H), 7.24-7.23 (m, 3H),, 6.46 (d, *J* = 7.2 Hz, 2H), 6.19 (d, *J* = 1.2 Hz, 1H), 2.38 (s, 3H), 1.45 (d, *J* = 0.8 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 167.1, 144.3, 143.6, 138.9, 137.8, 137.5, 132.5, 132.1, 131.7, 129.9, 128.8, 128.1, 128.0, 127.9, 127.5, 118.5, 21.6, 18.7; HRMS (ESI+) m/z calculated for $C_{23}H_{21}N_2O_3S$ $[M+H]^+$ 405.1273, found 405.1275.

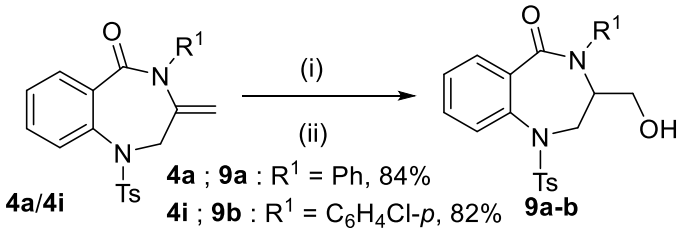
4-(4-Fluorophenyl)-3-methyl-1-tosyl-1,4-dihydro-5*H*-benzo[*e*][1,4]diazepin-5-one (8b)

White solid (14.5 mg, 72% yield), mp 165-167 ^{o}C, R_f = 0.55 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 7.85 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.59-7.55 (m, 2H), 7.44-7.42 (m, 1H), 7.28 (d, *J* = 7.8 Hz, 2H), 6.94 (t, *J* = 8.7 Hz, 2H), 6.44 (brs, 2H), 6.21 (s, 1H), 2.41 (s, 3H), 1.48 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz) δ_C 167.0, 161.7 (d, *J* = 247.5 Hz), 144.2, 143.5, 137.5 (d, *J* = 25.5 Hz), 134.6 (d, *J* = 3.0 Hz). 132.6, 132.0, 131.3, 129.8, 129.6 (d, *J* = 7.5 Hz), 128.0, 127.9, 127.4, 118.7, 115.7 (d, *J* = 22.4 Hz), 21.6, 18.6; HRMS (ESI+) m/z calculated for $C_{23}H_{20}FN_2O_3S$ $[M+H]^+$ 445.0998, found 445.0994.

4-(4-Bromophenyl)-3-methyl-1-tosyl-1,4-dihydro-5*H*-benzo[*e*][1,4]diazepin-5-one (8c):

White solid (15 mg, 75% yield), mp. 164-166 ^{0}C, R_f = 0.54 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.83-7.81 (m, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.58-7.53 (m, 2H), 7.43-7.39 (m, 1H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.26-7.24 (m, 2H), 6.36 (d, *J* = 8.4 Hz, 2H), 6.21 (d, *J* = 1.2 Hz, 1H), 2.39 (s, 3H), 1.46 (d, *J* = 1.2 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 166.9, 144.4, 143.5, 137.9, 137.5, 137.4, 132.7, 132.1, 132.0, 131.3, 129.9, 129.7, 128.1, 128.0, 127.5, 121.8, 119.2, 21.6, 18.6; HRMS (ESI+) m/z calculated for $C_{23}H_{20}BrN_2O_3S$ $[M+H]^+$ 483.0378, found 483.0380.

29. Transformations of 4a/4i into 3-(hydroxymethyl)-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-ones 9a/9b:



Scheme S11. Transformations of **4a/4i** into **9a/9b**. Reagent and Conditions: (i) $BH_3.SMe_2$,THF, 0 °C to rt, 3 h, (ii) H_2O_2, NaOH, 0 °C to rt, 1 h, 82-84%

To a well-stirred and cooled (0 °C) solution of **4** (0.05 mmol, 1 equiv) in dry THF (2 mL), borane dimethyl sulphide complex (2 M in THF) (0.12 mL, 0.25 mmol) and butylated hydroxytoluene (BHT) (1 mg) was added slowly under argon. The whole mixture was allowed to attain to rt and stirred at rt for another 3 h. Thereafter the reaction mixture was cooled to 0 °C and H_2O_2 (100 vol., 0.1 mL) was added followed by the addition of aqueous NaOH (4 M, 0.1mL).

After the completion of reaction (1 h), the reaction mixture was quenched with water (3 mL). It was then extracted with ethyl acetate (3x15 mL). The combined organic extracts were washed with brine (5 mL) and dried over anhydrous sodium sulphate. The ethyl acetate layer was then evaporated under reduced pressure to obtain a crude residue which was purified by silica gel (100-200 mesh) column chromatography using 50% ethyl acetate–petroleum ether (v/v) as the eluent to afford a pure product **9a/9b** in 82-84% yield.

30. Spectral Data of Compounds 9a and 9b:

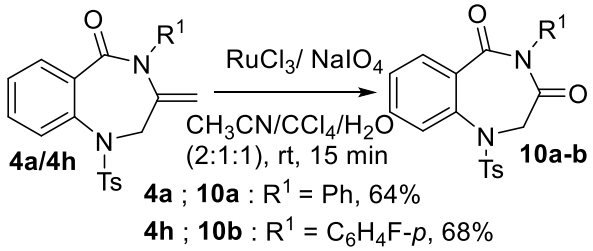
3-(Hydroxymethyl)-4-phenyl-1-tosyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (9a)

Brown solid (17.5 mg, 84% yield), mp. 169-171 °C, R_f = 0.40 (50% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.70 (d, *J* = 7.6 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.53-7.41 (m, 3H), 7.29-7.23 (m, 5H), 6.73 (d, *J* = 5.6 Hz, 2H), 4.10-4.05 (m, 1H), 3.97-3.91 (m, 1H), 3.77 (dd, *J* = 12.0, 3.8 Hz, 1H), 3.34 (s, 2H), 2.37 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 168.9, 144.2, 138.1, 136.7, 135.0, 132.0, 130.3, 130.2, 130.0, 129.3, 129.0, 128.9, 128.3, 127.9, 100.0, 60.7, 59.8, 53.6, 21.6; HRMS (ESI+) m/z calculated for $C_{23}H_{23}N_2O_4S$ $[M+H]^+$ 423.1379, found 423.1376.

4-(4-Chlorophenyl)-3-(hydroxymethyl)-1-tosyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (9b)

White solid (17 mg, 82% yield), mp. 150-152 °C, R_f = 0.39 (50% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.71 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.54-7.50 (m, 1H), 7.47-7.43 (m, 2H), 7.26-7.23 (m, 4H), 6.71 (d, *J* = 8.4 Hz, 2H), 4.07-4.02 (m, 1H), 3.98-3.91 (m, 1H), 3.78 (dd, *J* = 12.0, 4.0 Hz, 1H), 3.37 (d, *J* = 6.0 Hz, 2H), 2.39 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 168.9, 144.3, 136.7, 135.0, 134.9, 134.1, 132.2, 130.4, 130.3, 130.1, 129.4, 129.1, 127.9, 100.0, 60.6, 59.9, 53.4, 21.6; HRMS (ESI+) m/z calculated for $C_{23}H_{22}ClN_2O_4S$ $[M+H]^+$ 457.0989, found 457.0991.

31. Synthetic transformations of 4a/4h into 1,2-dihydro-3*H*-benzo[*e*][1,4]diazepine-3,5(4*H*)-diones 10a/10b



Scheme S12. Transformations of compounds **4a/4h** into products **10a**/**10b**

To a stirred solution of the substrate **4a** or **4h** (0.05 mmol, 1 equiv) in a mixture of $CH_3CN/CCl_4/H_2O$ (1 mL, 2:1:1) was added $RuCl_3$ (0.52 mg, 0.0025 mmol, 0.05 equiv) and $NaIO_4$ (64 mg, 0.3 mmol, 6 equiv) at 0 °C under an argon atmosphere. Stirring was continued at 0 °C for 15 min. The reaction mixture was then diluted with ethyl acetate (8 mL) and quenched with aqueous sodium thiosulfate. The ethyl acetate layer was then filtered through a plug of celite. The filtrate was washed with brine and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the crude product was purified by silica gel (100-200 mesh) column chromatography using 20% ethyl acetate–petroleum ether (v/v) as eluent to afford the pure product **10a** or **10b** in 64% or 68% yield.

32. **Spectral data of products 10a and 10b:**

4-Phenyl-1-tosyl-1,2-dihydro-3*H*-benzo*[e]*[1,4]diazepine-3,5*(4H)*-dione (10a) :

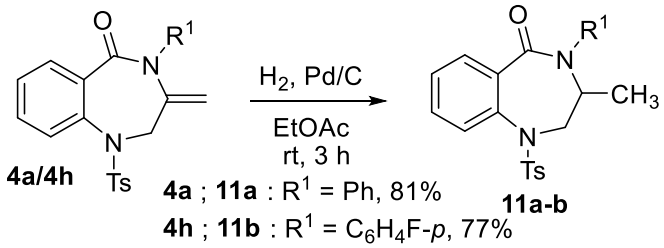
White Solid (12.8 mg, 64% yield), mp. 187-189 °C, R_f = 0.32 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.03-8.00 (m, 1H), 7.65-7.62 (m, 4H), 7.51-7.47 (m, 1H), 7.36-7.31 (m, 5H), 6.60-6.57 (m, 2H), 4.78 (s, 2H), 2.46 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C

202.5, 171.2, 165.9, 144.9, 136.6, 134.1, 131.2, 130.4, 129.1, 129.0, 128.9, 128.5, 128.1, 127.5, 100.0, 55.9, 21.7; HRMS (ESI+) m/z calculated for $C_{22}H_{18}N_2NaO_4S$ $[M+Na]^+$ 429.0885, found 429.0888.

4-(4-Fluorophenyl)-1-tosyl-1,2-dihydro-3*H*-benzo[*e*][1,4]diazepine-3,5(4*H*)-dione (10b):

White solid (13.6 mg, 68% yield), mp. 182-184 °C; R_f = 0.34 (20% ethyl acetate-petroleum ether, v/v), ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.02 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.64-7.62 (m, 3H), 7.58 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.52-7.47 (m, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.06-7.01 (m, 2H), 6.62-6.58 (m, 2H), 4.75 (s, 2H), 2.46 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 171.4, 165.8, 162.3 (d, *J* = 246.0 Hz), 145.0, 138.2, 136.6, 134.2 (d, *J* = 7.9 Hz) 133.6 (d, *J* = 3.5 Hz), 131.0, 130.4 129.9 (d, *J* = 8.3 Hz), 129.0 (d, *J* = 9.4 Hz), 127.6, 116.1 (d, *J* = 23.0 Hz), 55.9, 21.7; HRMS (ESI+) m/z calculated for $C_{22}H_{18}FN_2O_4S$ $[M+H]^+$ 425.0971, found 425.0970.

33. Procedure for the hydrogenation of 4a/4h into 3-methyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-ones 11a/ 11b:



Scheme S13. Hydrogenations of compounds **4a/4h**

To a well stirred solution of Compound **4a** (0.05 mmol, 1 equiv) in dry ethyl acetate (1 mL), 5 mg of 10% Pd/C catalyst was added and the whole reaction mixture was allowed to stir at rt under the balloon pressure of H_2. After 3 h, the catalyst was removed by filtration and washd with ethyl acetate (5 mL). The combined filtrate was evaporated to dryness to give a gummy material which was purified by silica gel column chromatography using 20% ethyl acetate–petroleum ether (v/v) as the eluent to afford pure products **11a** in 81% yield.

The same procedure was adopted for the hydrogenation of **4h** to obtain the product **11b** in 77% yield.

34. Spectral data of products 11a and 11b:

3-Methyl-4-phenyl-1-tosyl-1,2,3,4-tetrahydro-5*H*-benzo[*e*][1,4]diazepin-5-one (11a):

White solid (16.2 mg, 81% yield), mp. 152-154 °C; R_f = 0.36 (20% ethyl acetate-petroleum ether, v/v), mp 158-160 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.74-7.13 (m, 1H), 7.67 (d, *J* = 8.0 Hz, 2H),

7.55-7.49 (m, 2H), 7.46-7.42 (m, 1H), 7.26 (s, 3H), 7.25 (s, 3H), 6.57 (d, *J* = 5.2 Hz, 2H), 4.01-3.91 (m, 2H), 3.61 (dd, *J* = 12.0, 2.4 Hz, 1H), 2.37 (s, 3H), 0.83 (d, *J* = 6.8 Hz, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 168.8, 144.2, 137.6, 136.6, 135.2, 134.9, 131.8, 130.4, 130.2, 130.0, 129.3, 129.0, 128.8, 128.0, 127.9, 57.6, 52.8, 21.6, 16.0;HRMS (ESI+) m/z calculated for $C_{23}H_{23}N_2O_3S$ $[M+Na]^+$ 429.1249, found 429.1253.

4-(4-Fluorophenyl)-3-methyl-1-tosyl-1,2,3,4-tetrahydro-5H-benzo[e][1,4]diazepin-5-one (11b):

White Solid (15.4 mg, 77% yield), m.p. 156-157ºC , R_f = 0.40 (20% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.73-7.71 (m, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.54-7.49 (m, 2H), 7.47-7.43 (m, 1H), 7.27-7.25 (m, 2H), 6.96-6.92 (m, 2H), 6.56 (s, 2H), 4.00-3.90 (m, 2H), 3.61-3.57 (m, 1H), 2.38 (s, 3H), 0.83 (d, *J* = 6.4 Hz, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 169.0, 162.5 (d, *J* = 246.6 Hz) 144.2, 136.7, 135.0 (d, *J* = 9.1 Hz), 133.5, 132.0, 130.2 (d, *J* = 12.3 Hz), 130.0, 128.9, 127.9, 115.9 (d, *J* = 22.4 Hz), 57.5, 52.8, 21.6, 16.0; HRMS (ESI+) m/z calculated for $C_{23}H_{22}FN_2O_3S$ $[M+H]^+$ 425.1335, found 425.1338.

35. References:

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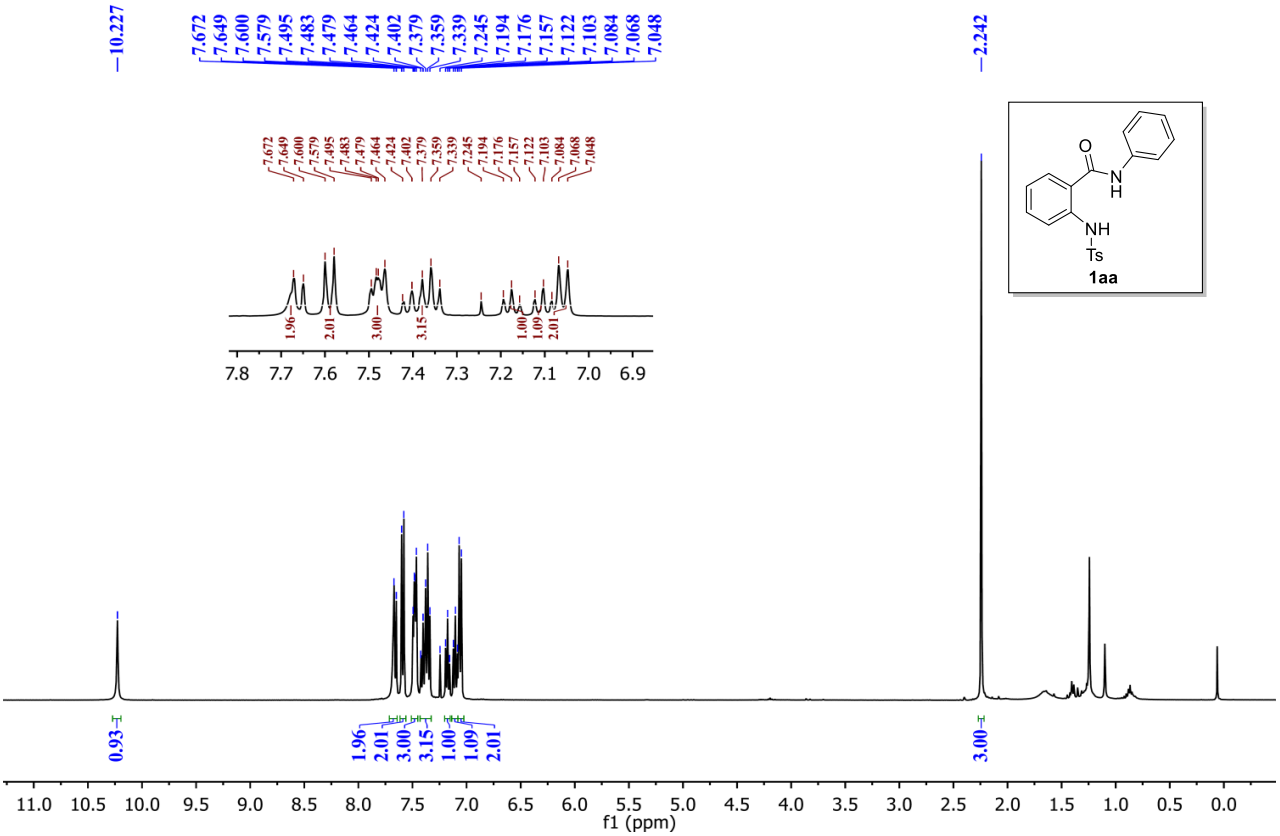
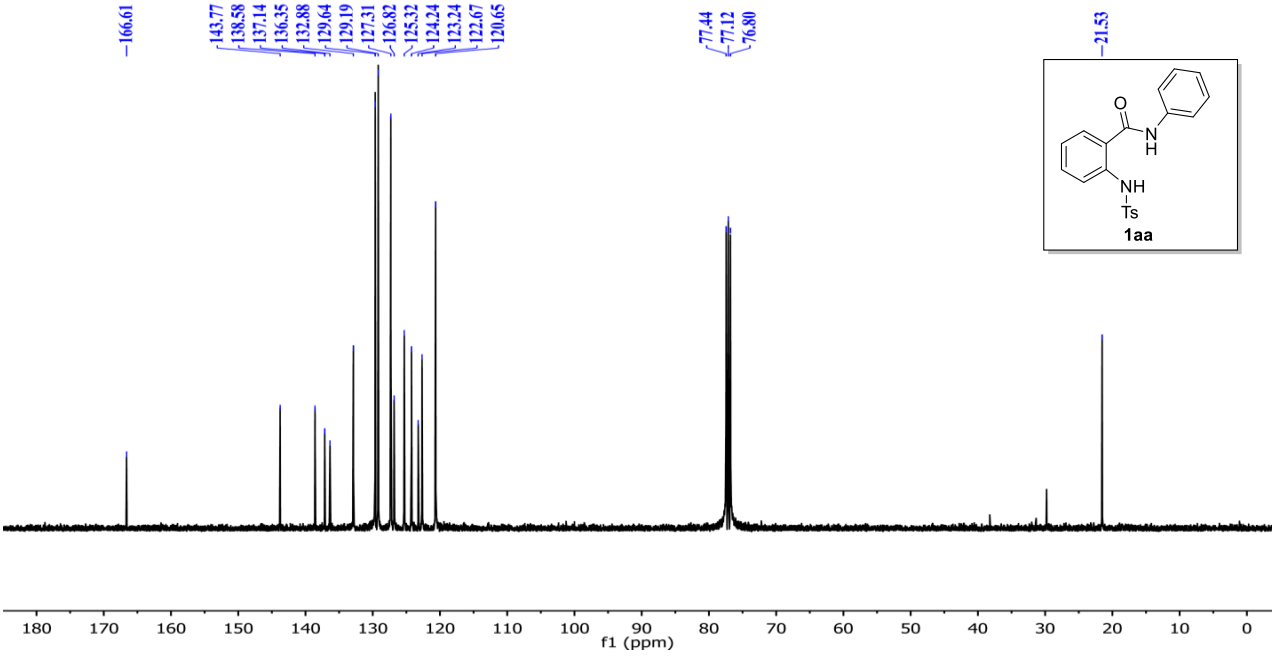
36. NMR Spectra of substrates 1aa-1aq:

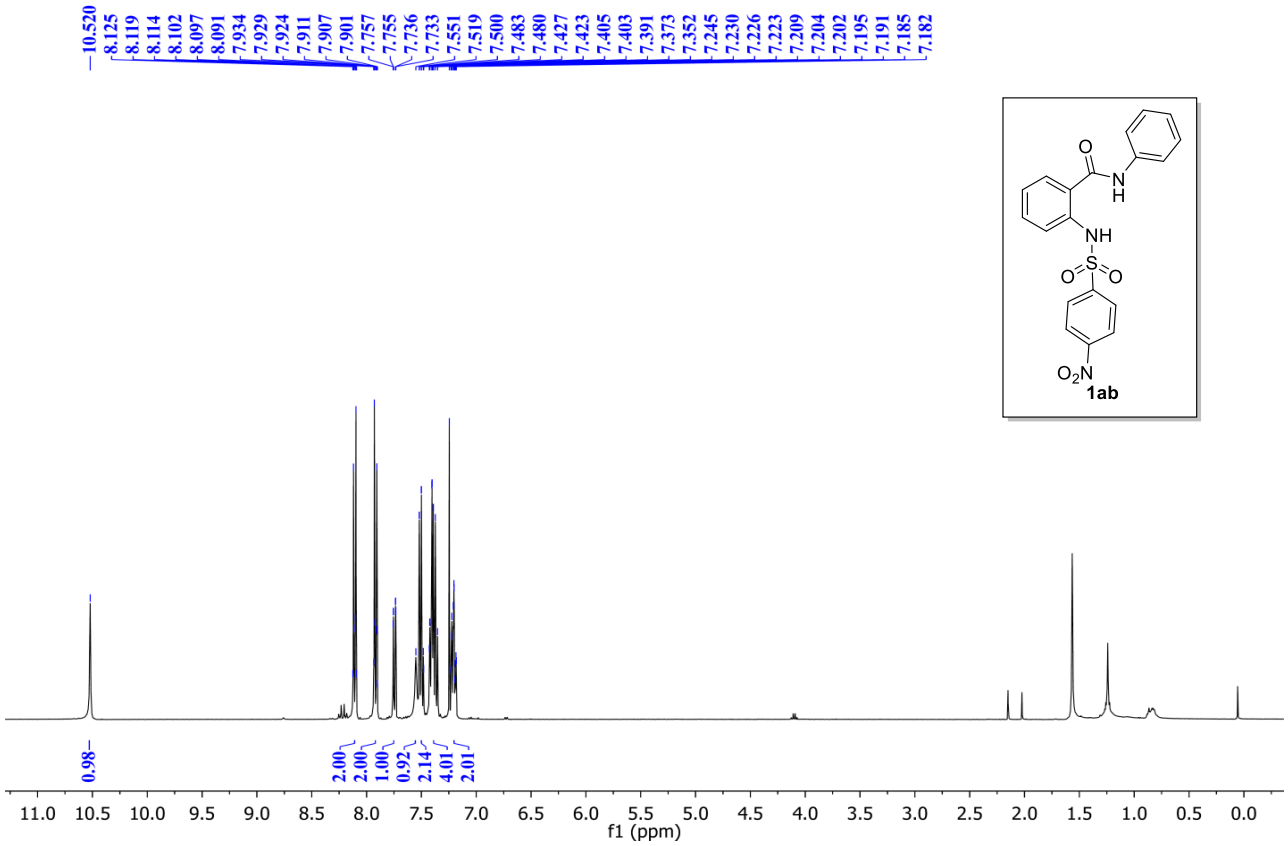
^{1}H NMR (400 MHz) of **1aa**:



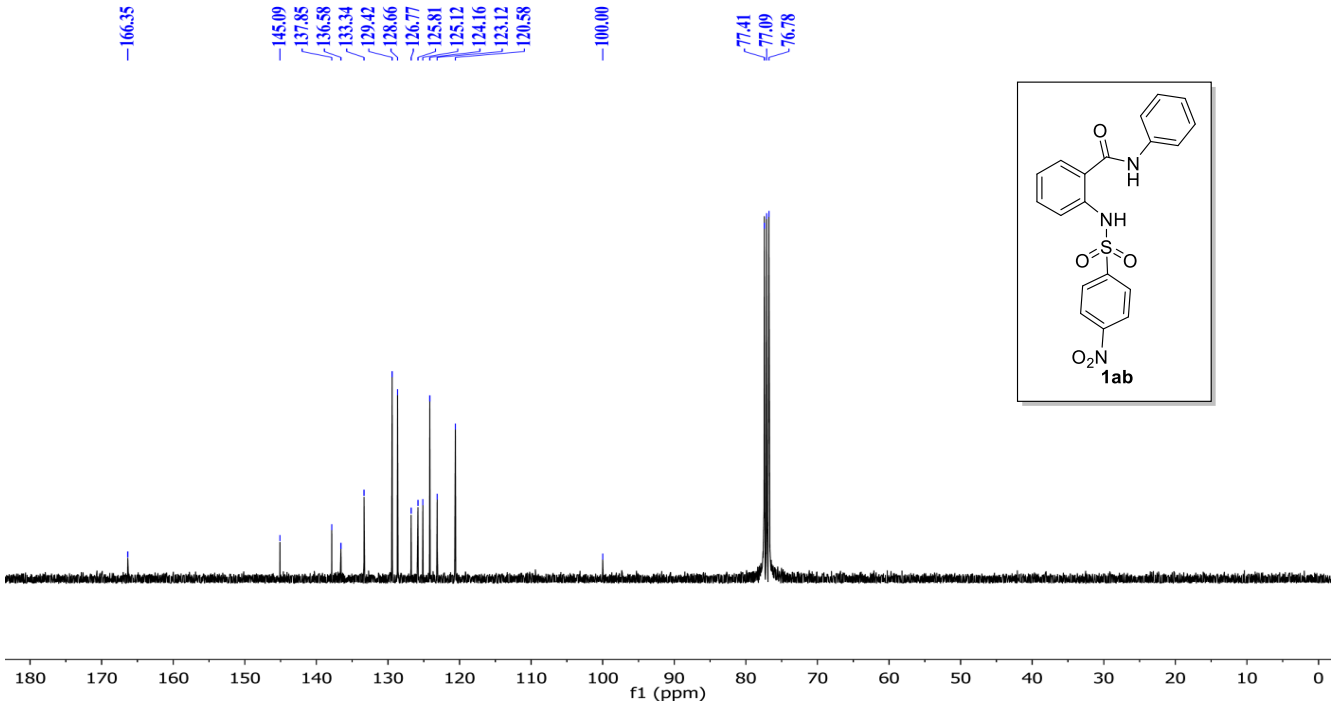
^{13}C{^{1}H} NMR (100 MHz) of **1aa**:



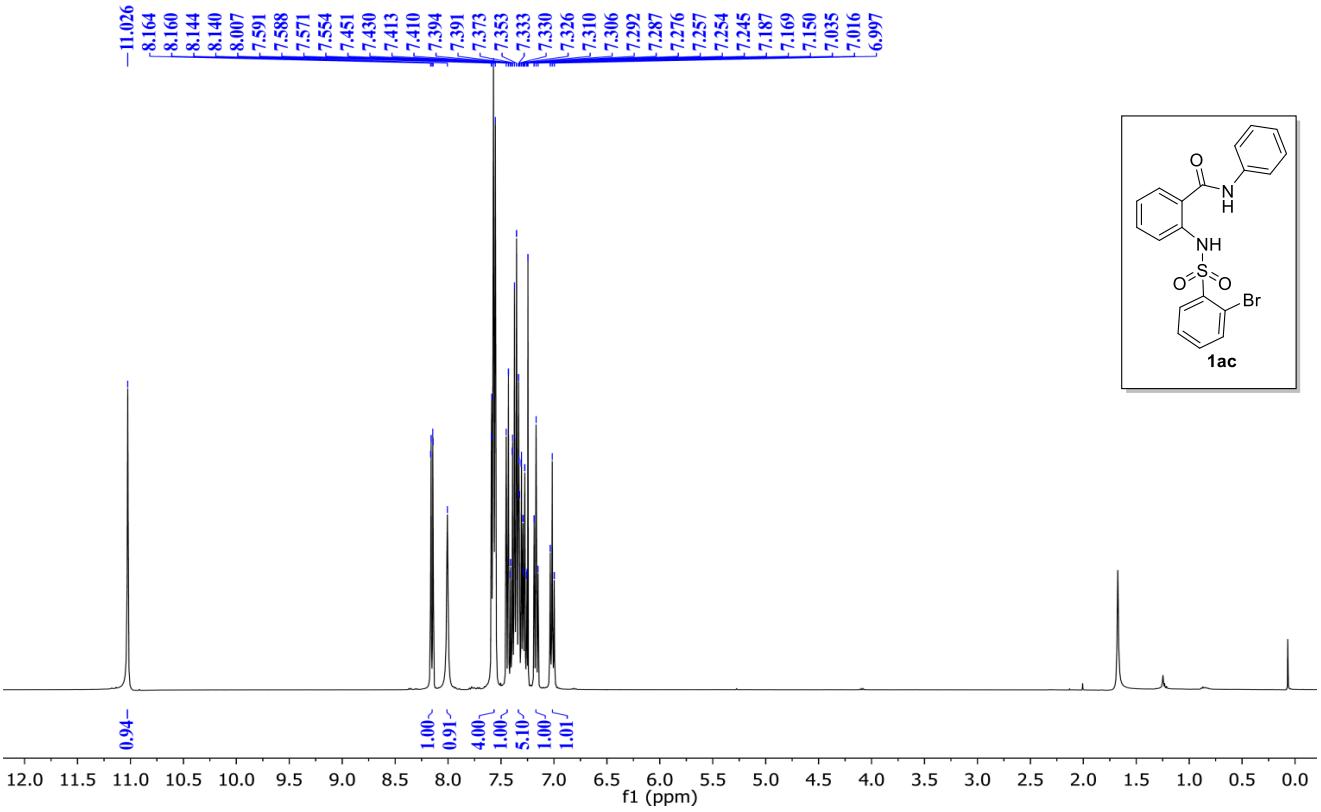
^{1}H NMR (400 MHz) of **1ab**:



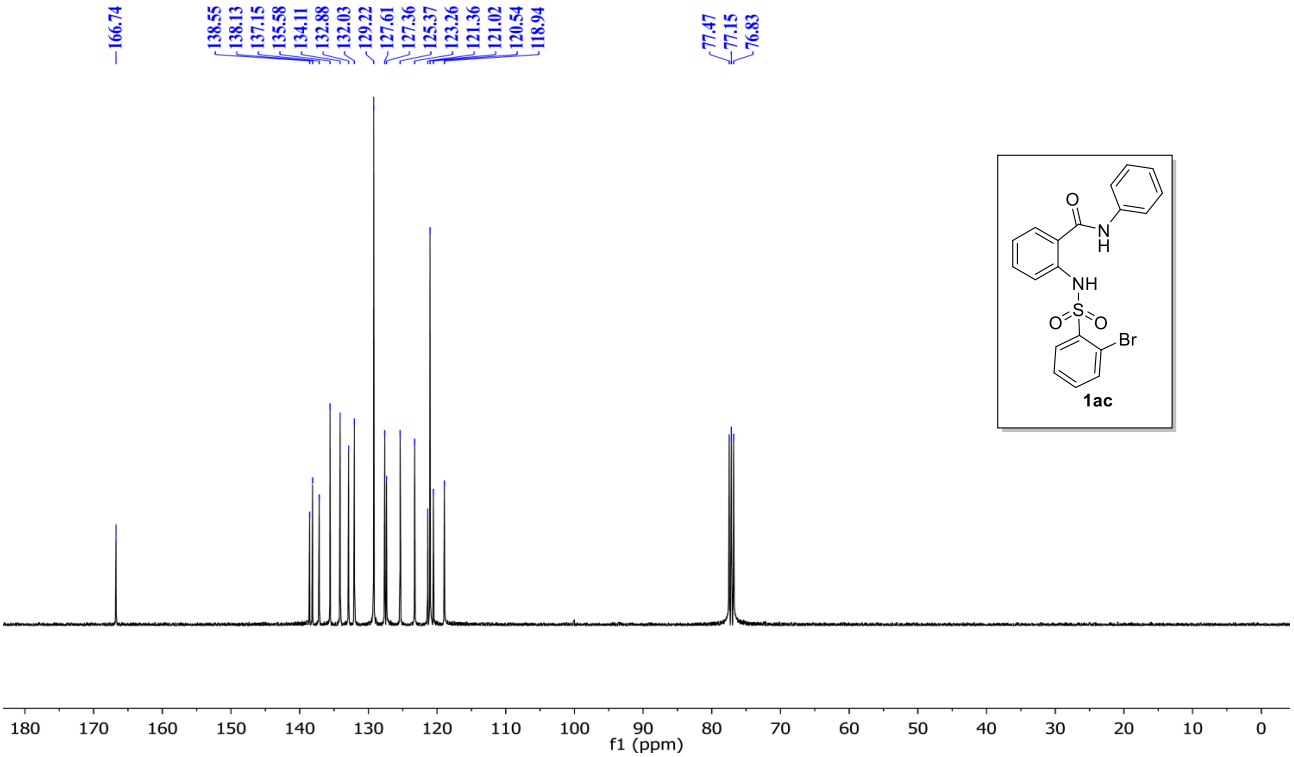
^{13}C{^{1}H} NMR (100 MHz) of **1ab**:



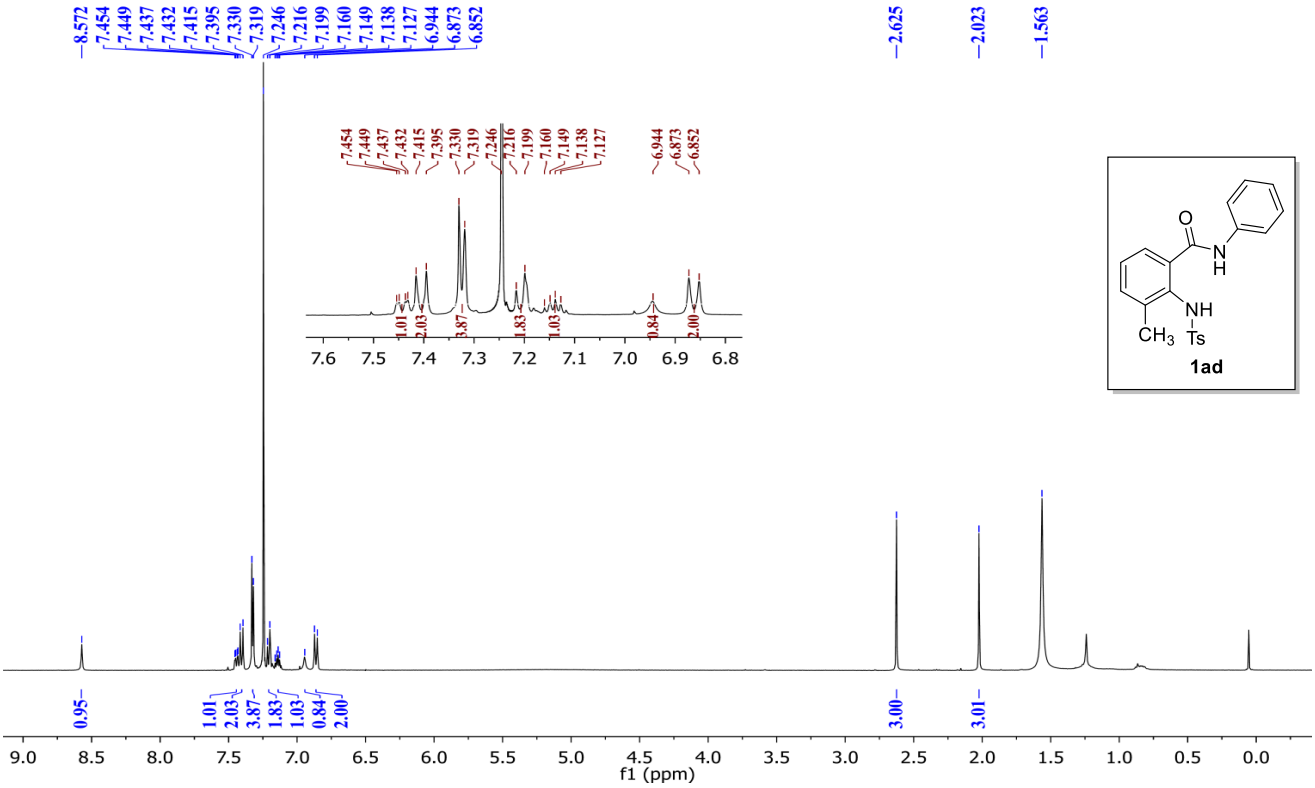
^{1}H NMR (400 MHz) of **1ac:**



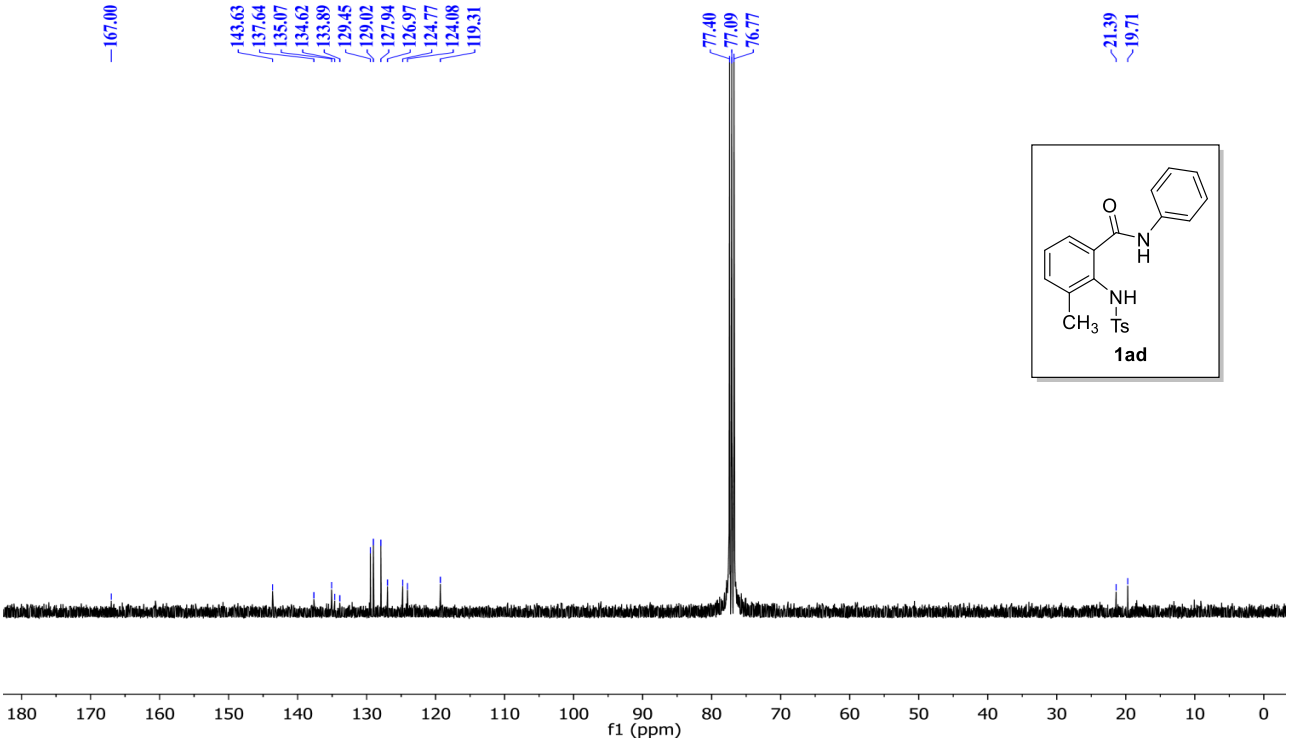
^{13}C{^{1}H} NMR (100 MHz) of **1ac**:



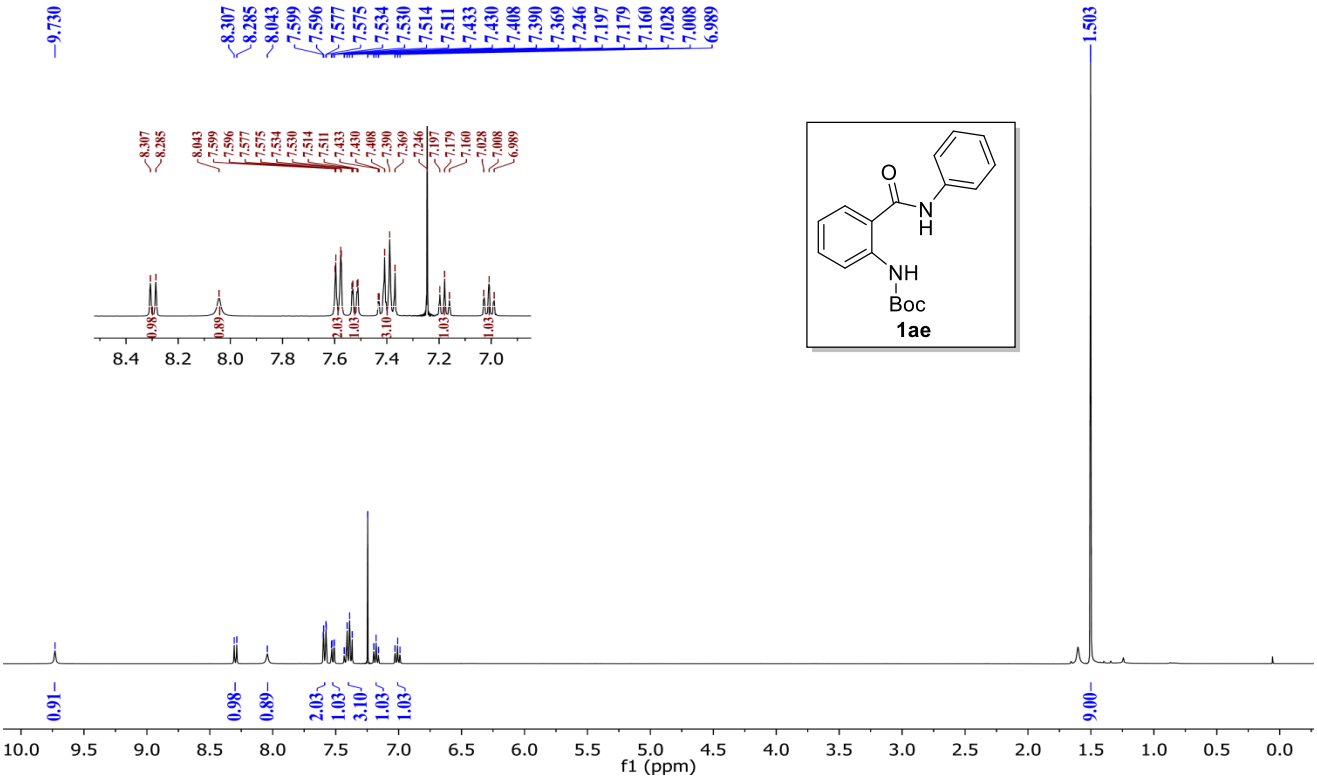
^{1}H NMR (400 MHz) of **1ad:**



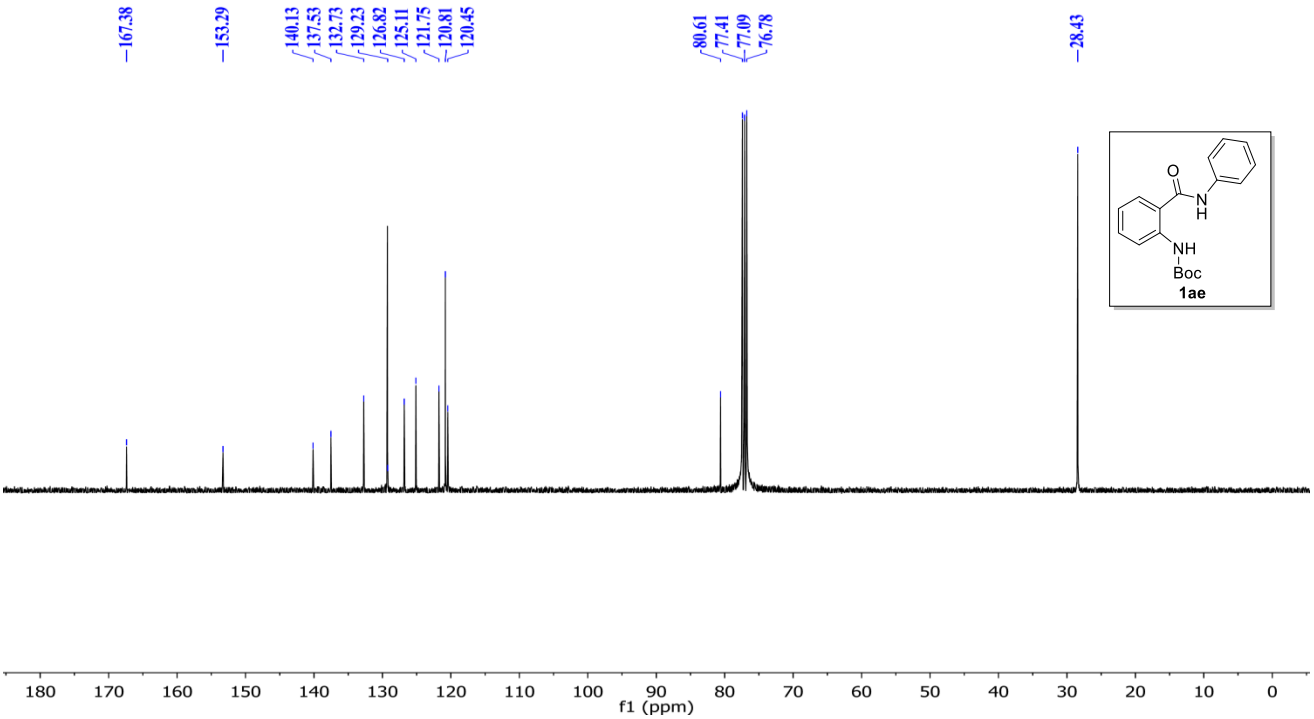
^{13}C{^{1}H} NMR (100 MHz) of **1ad**:



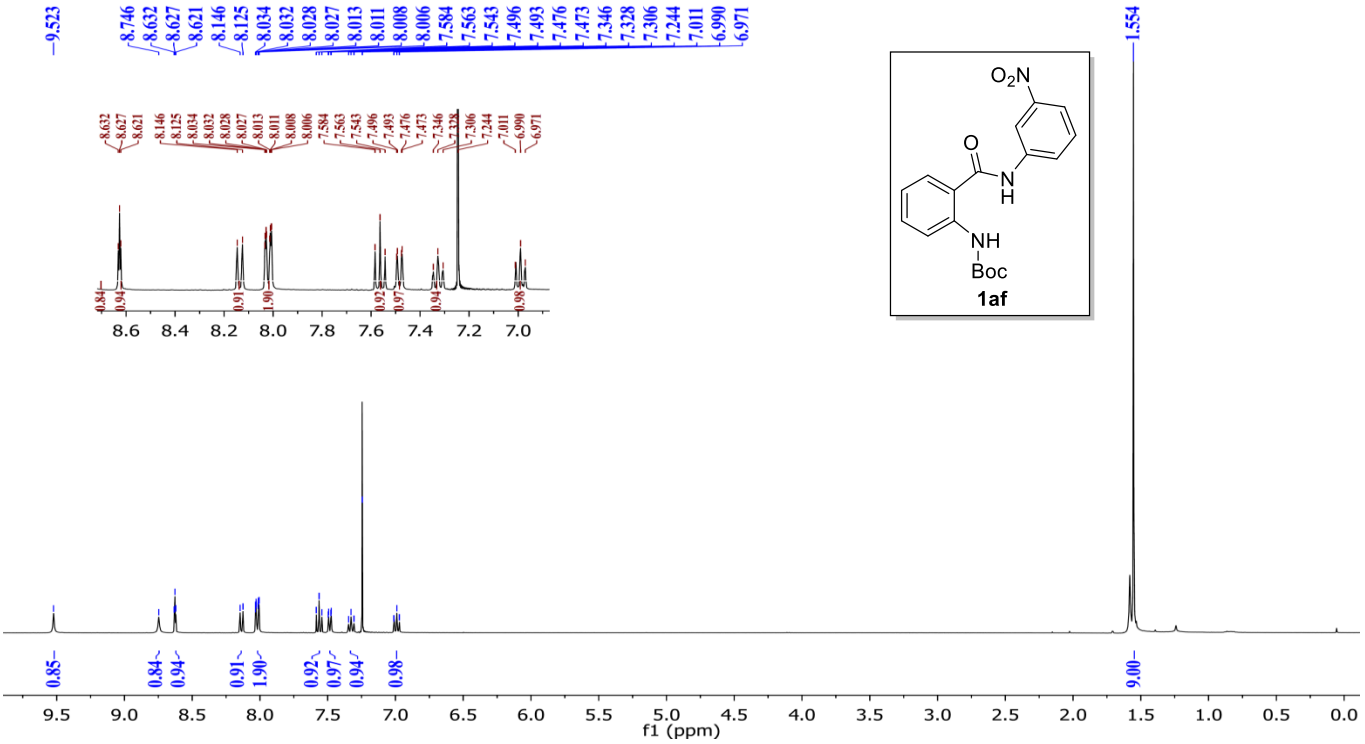
^{1}H NMR (600 MHz) of **1ae:**



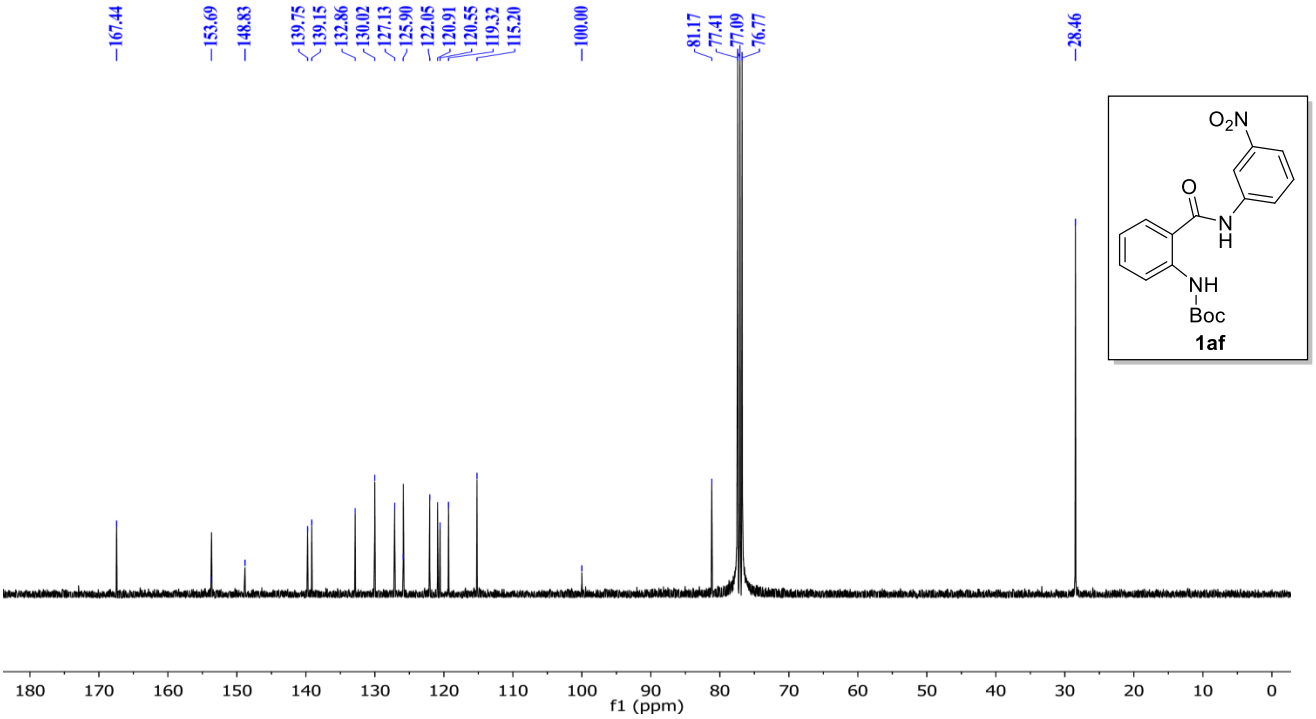
^{13}C{^{1}H} NMR (100 MHz) of **1ae**:



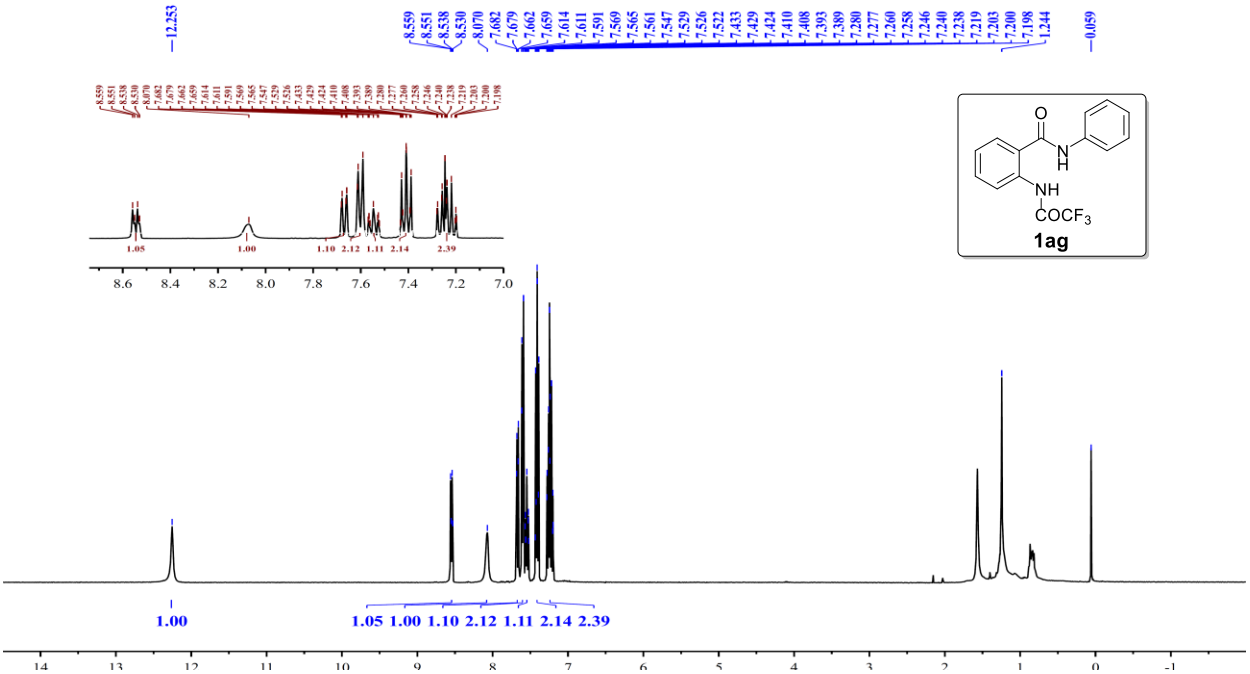
^{1}H NMR (400 MHz) of **1af**:



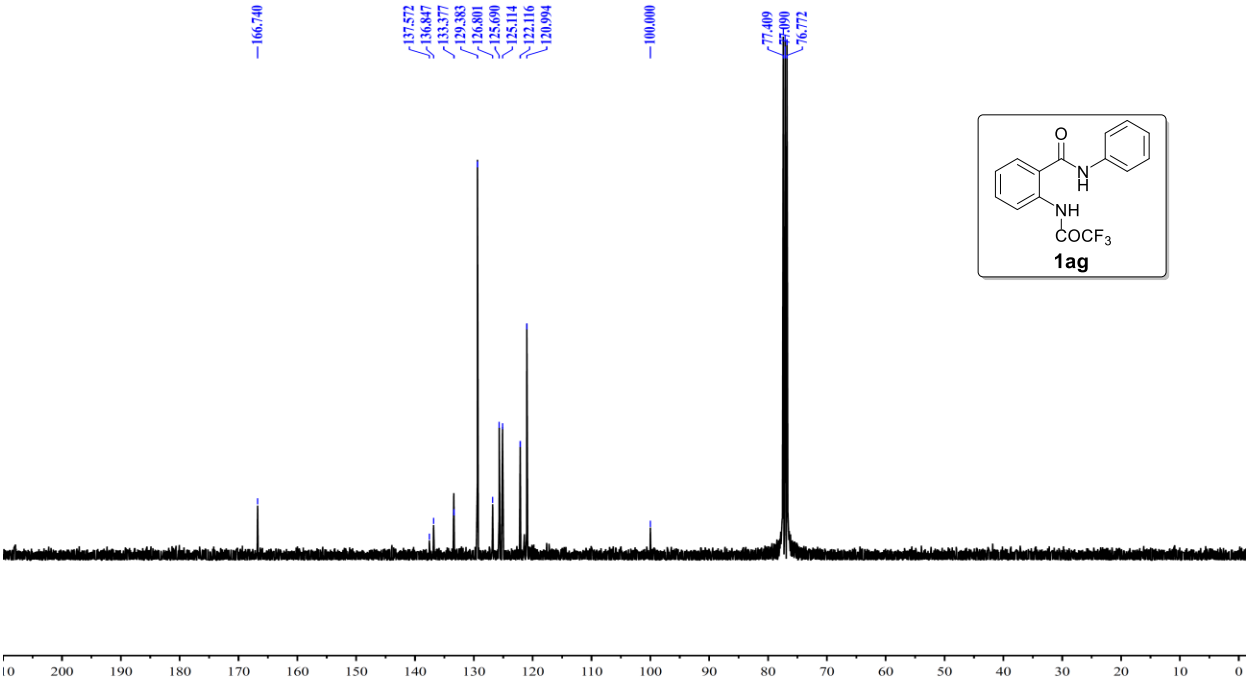
^{13}C{^{1}H} NMR (100 MHz) of **1af**:



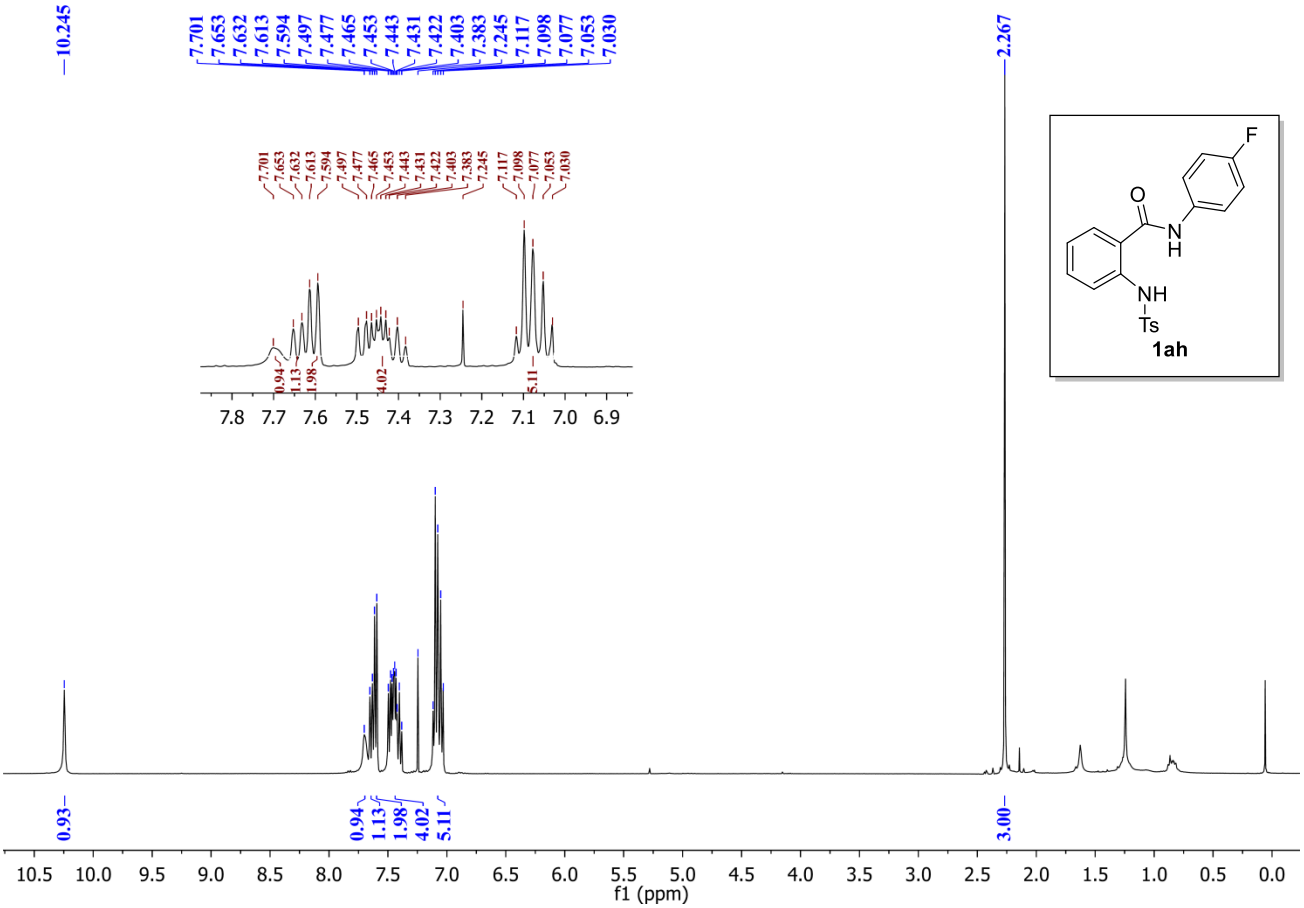
^{1}H NMR (400 MHz) of **1ag**:



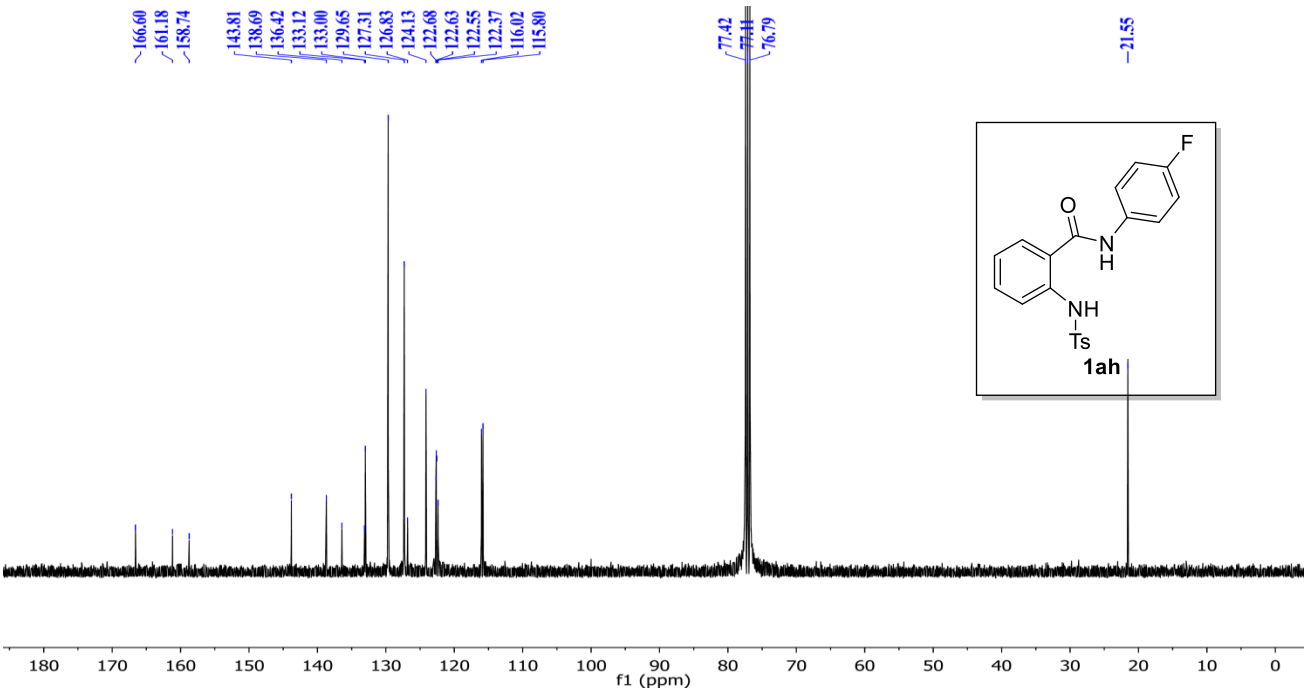
^{13}C{^{1}H} NMR (100 MHz) of 1**ag**:



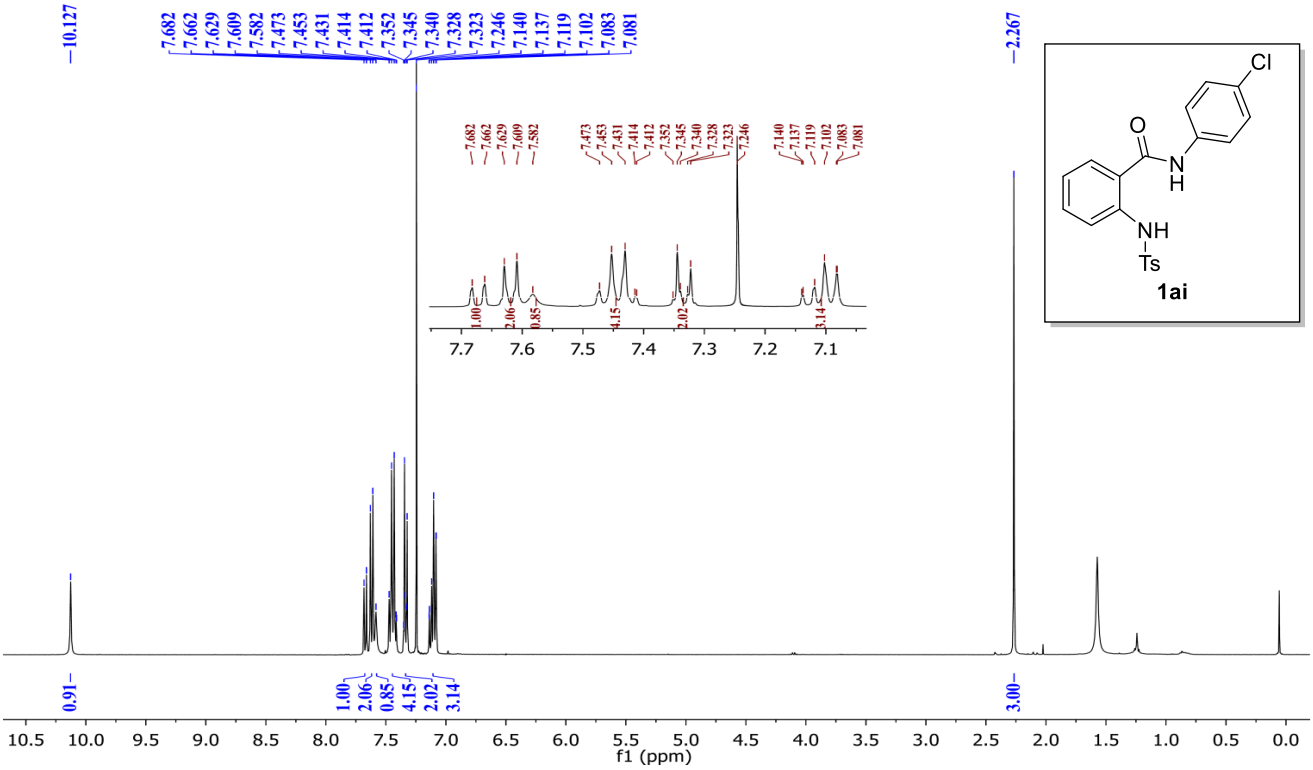
^{1}H NMR (400 MHz) of **1ah**:



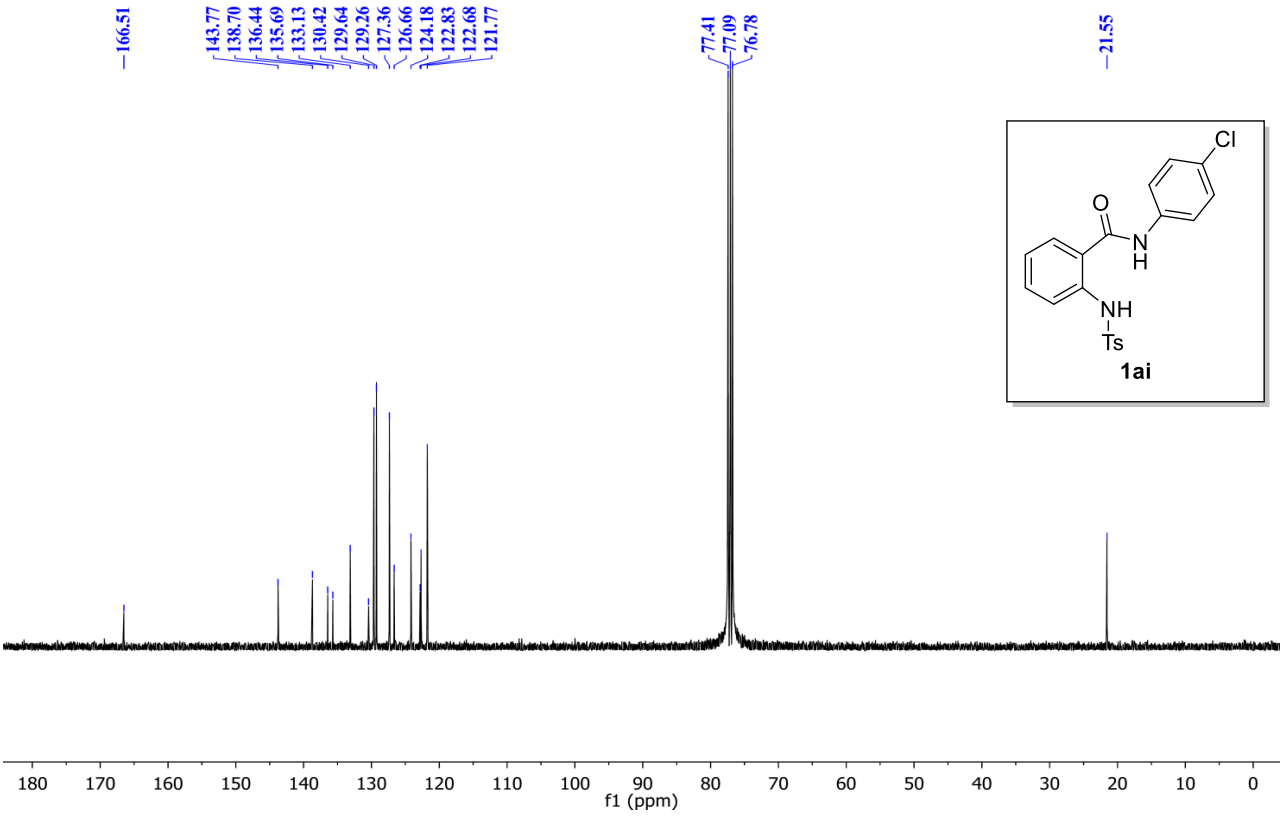
^{13}C{^{1}H} NMR (100 MHz) of 1**ah**:



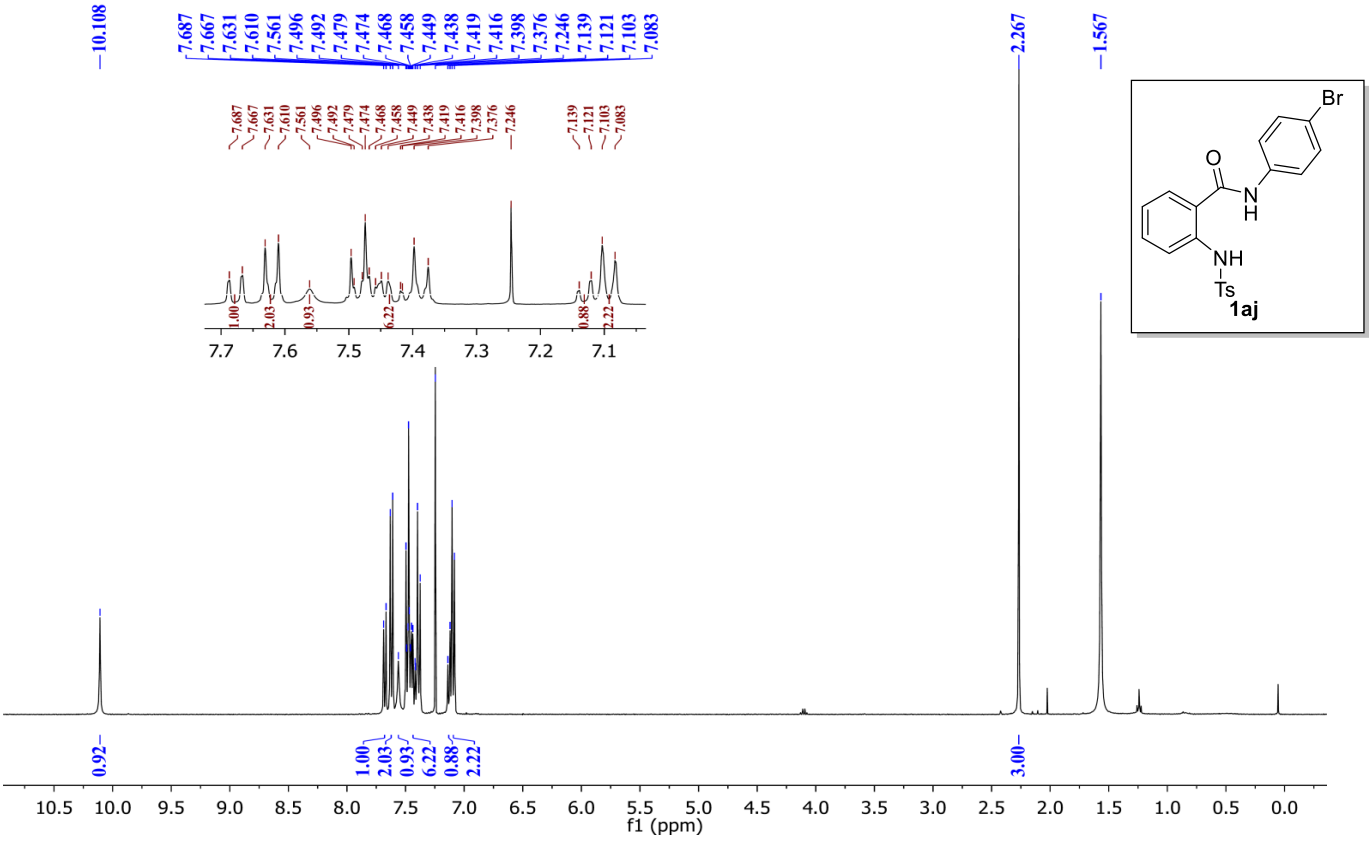
^{1}H NMR (400 MHz) of **1ai**:



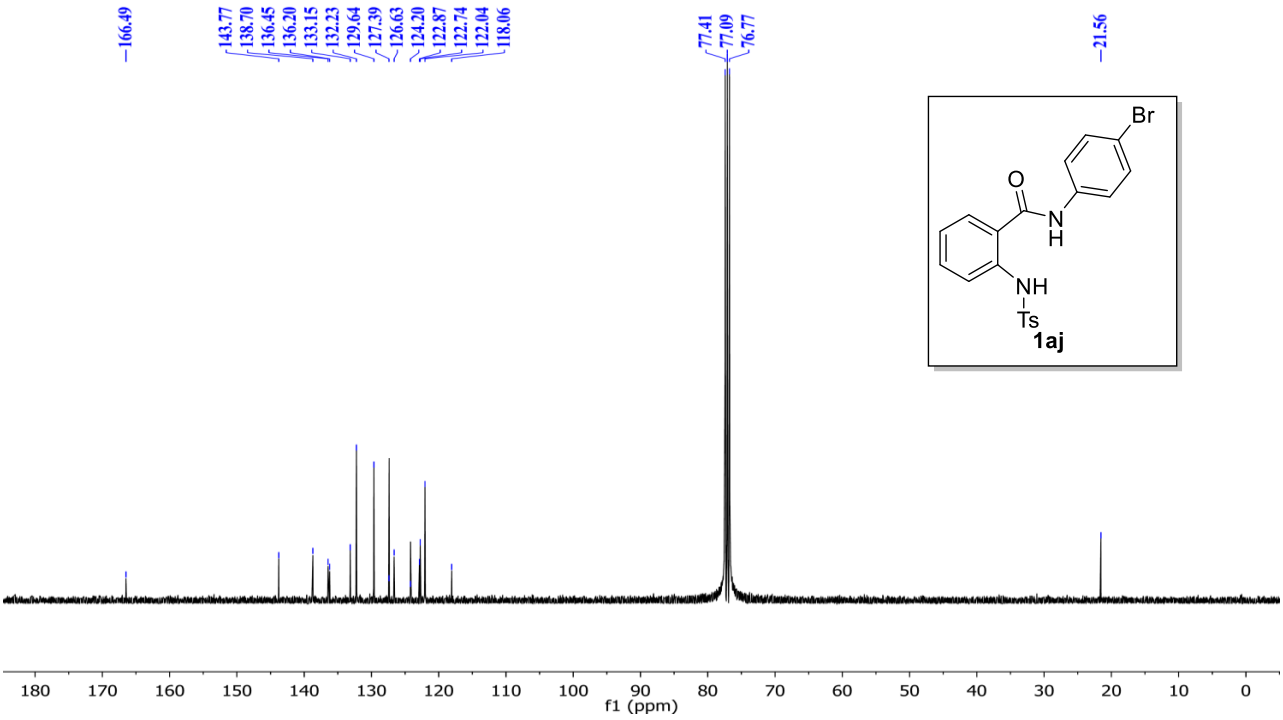
^{13}C{^{1}H} NMR (100 MHz) of **1ai**:



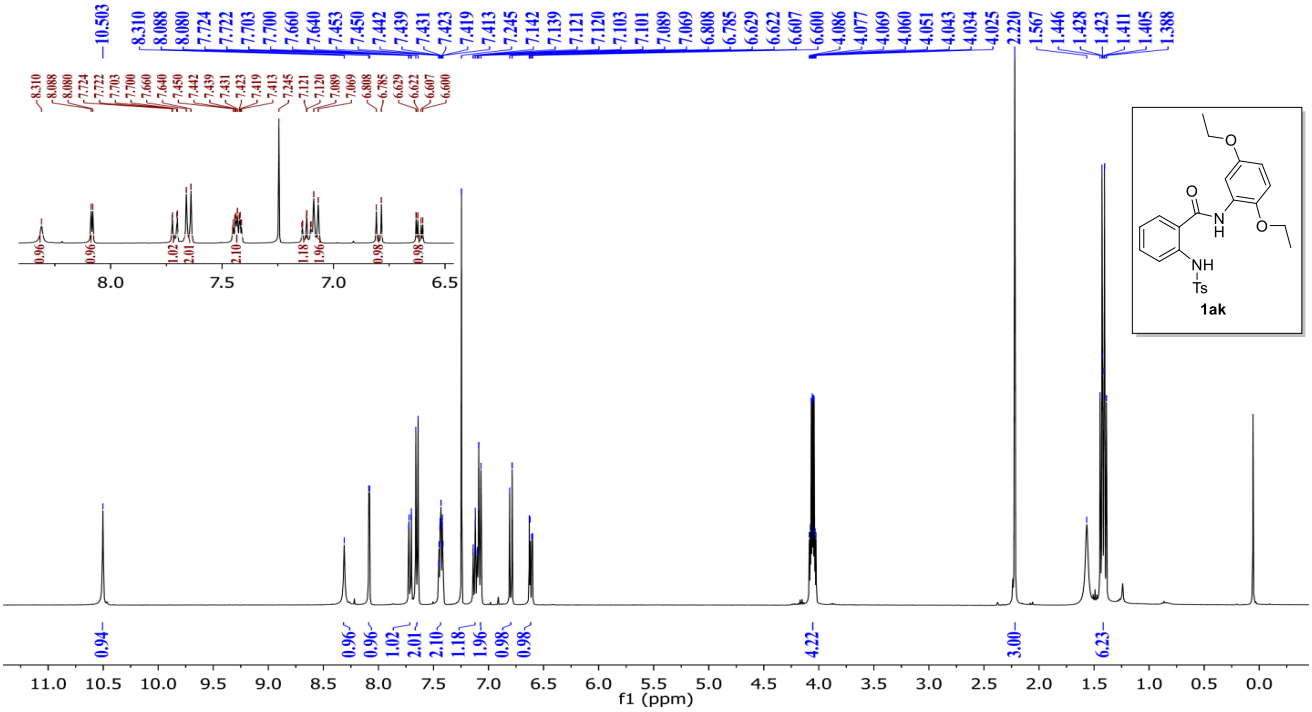
^{1}H NMR (400 MHz) of **1aj**:



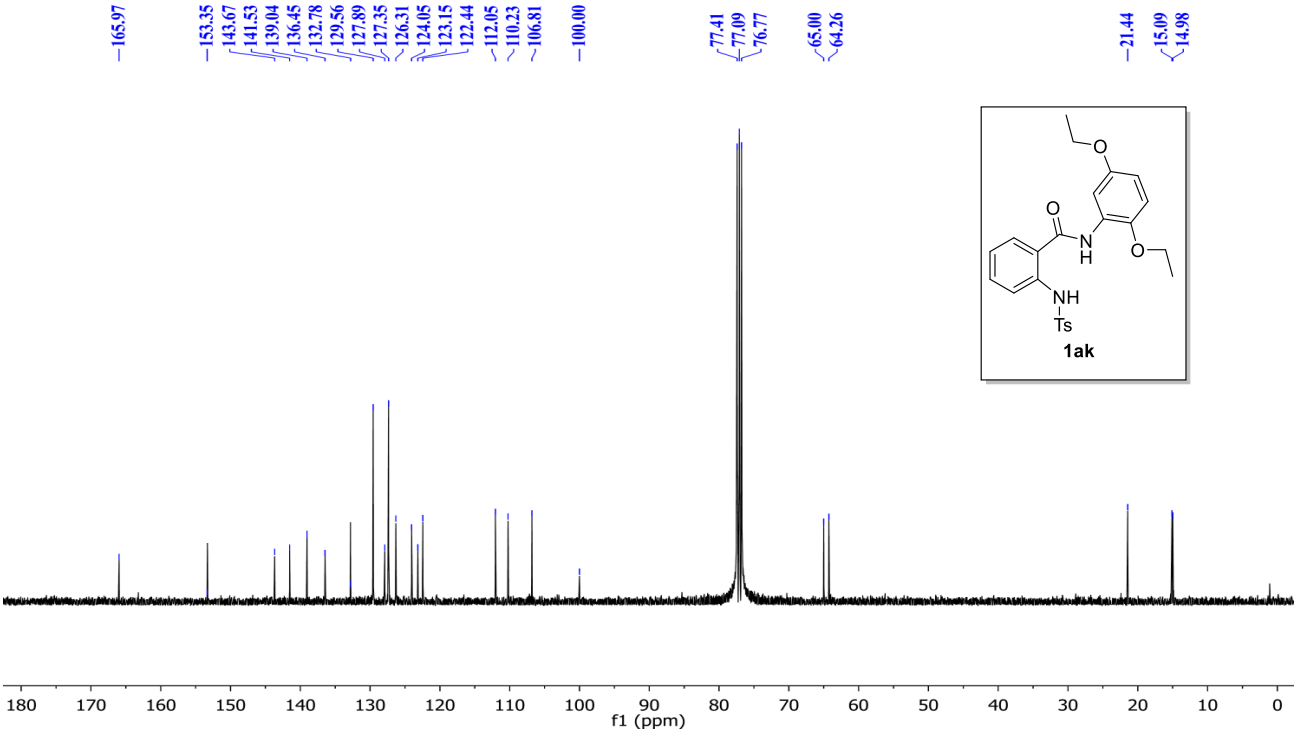
^{13}C{^{1}H} NMR (100 MHz) of **1aj**:



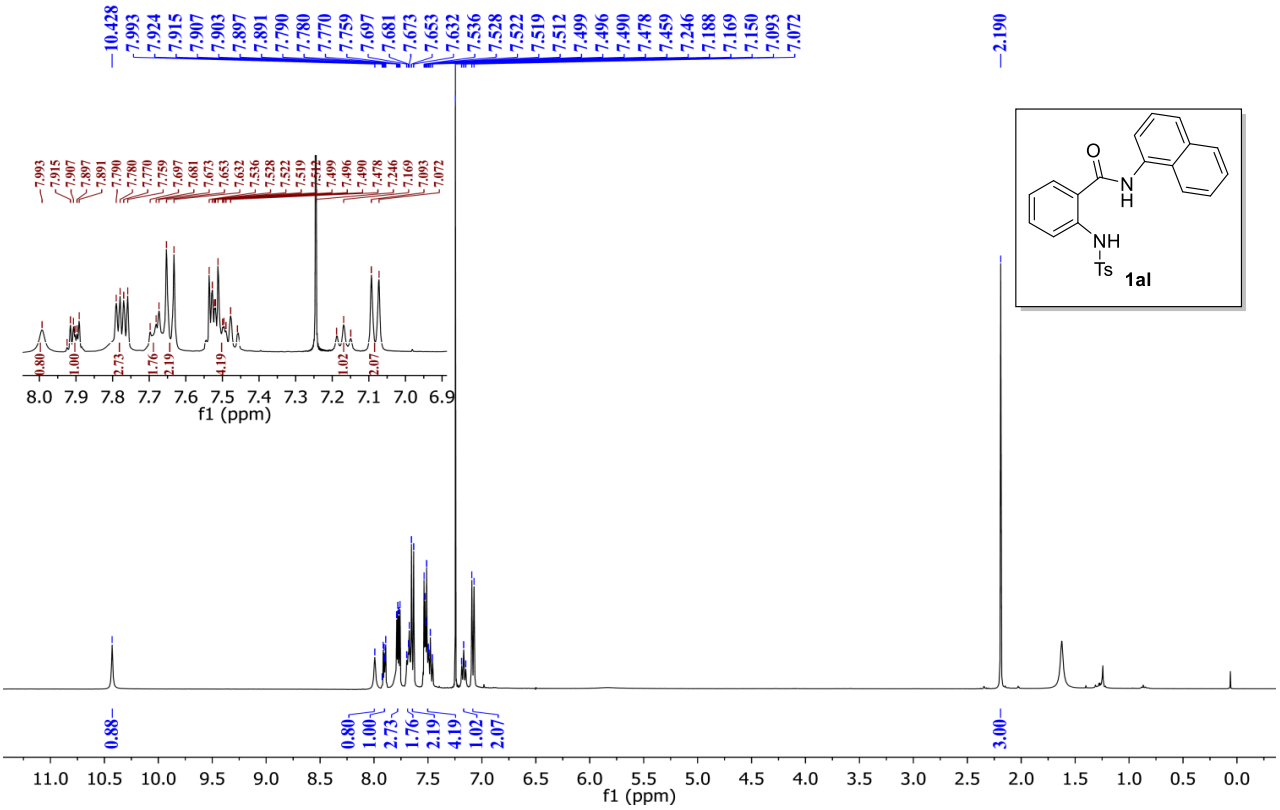
^{1}H NMR (400 MHz) of **1ak**:



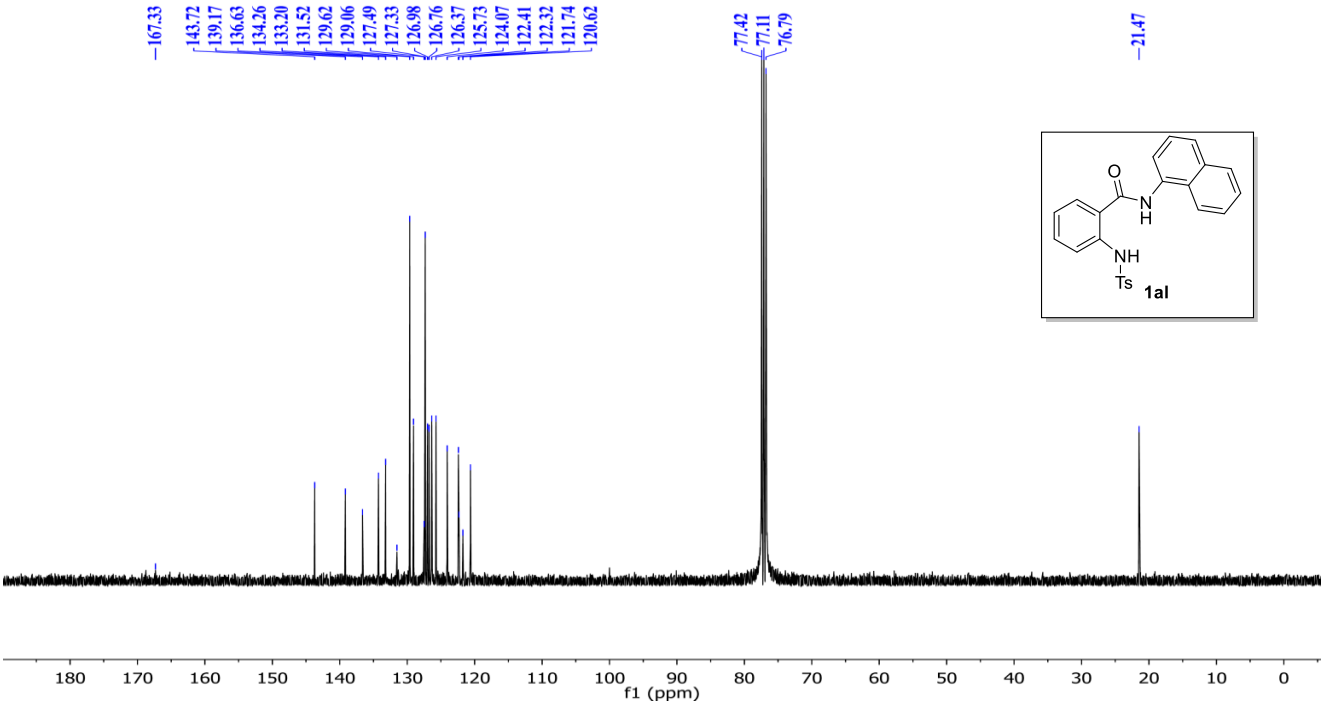
^{13}C{^{1}H} NMR (100 MHz) of **1ak**:



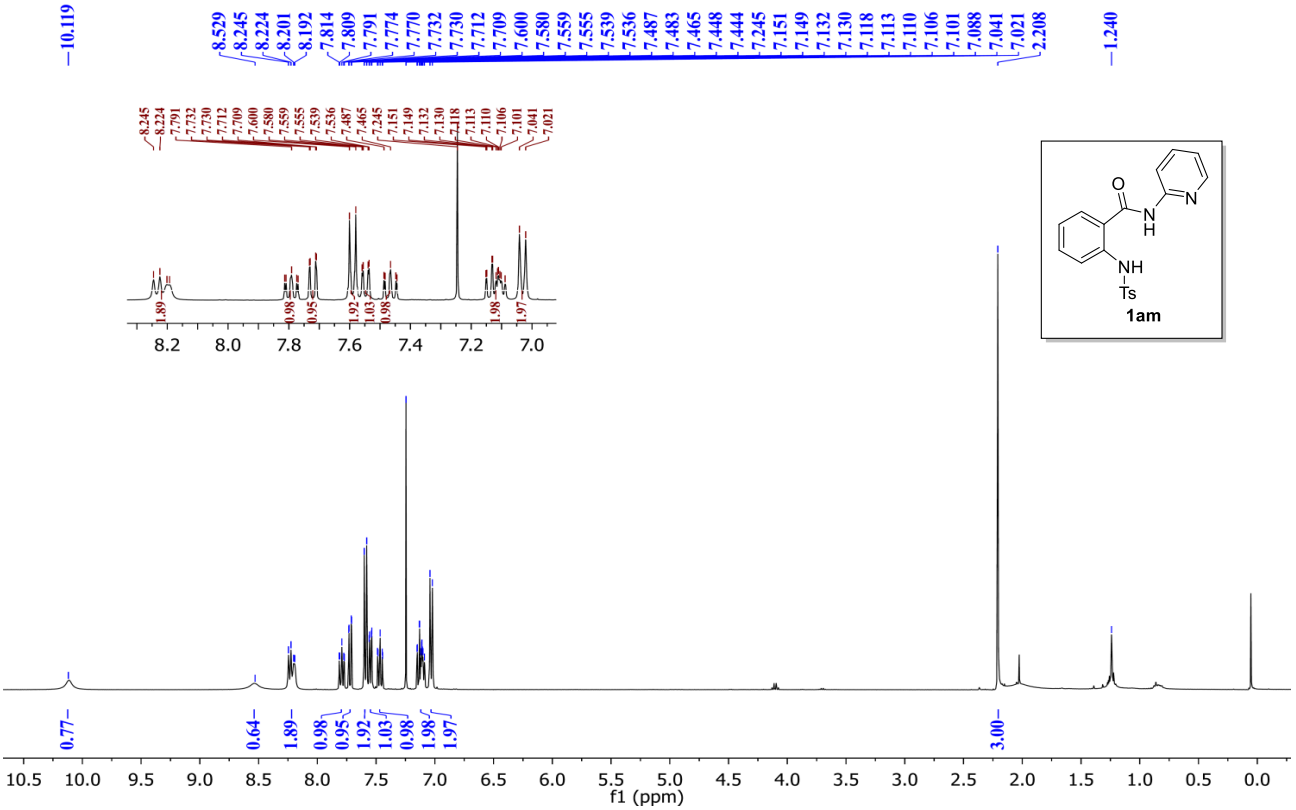
^{1}H NMR (600 MHz) of **1al:**



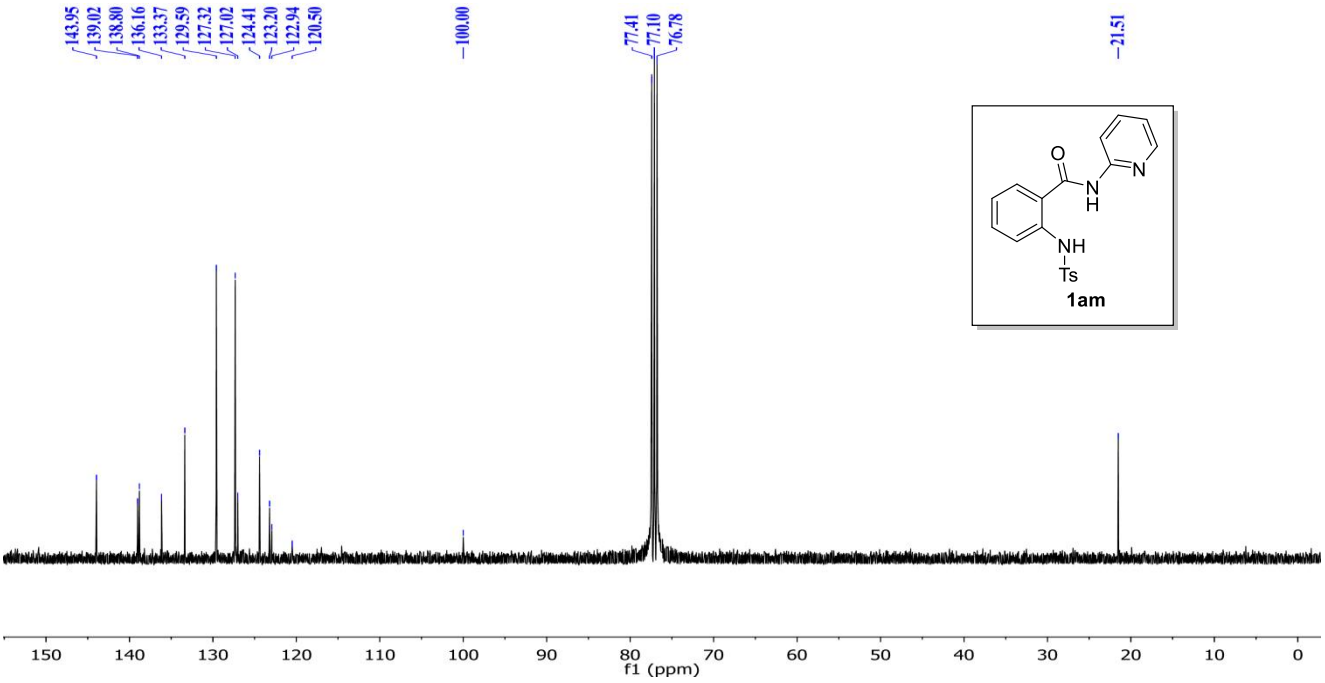
^{13}C{^{1}H} NMR (150 MHz) of **1al**:



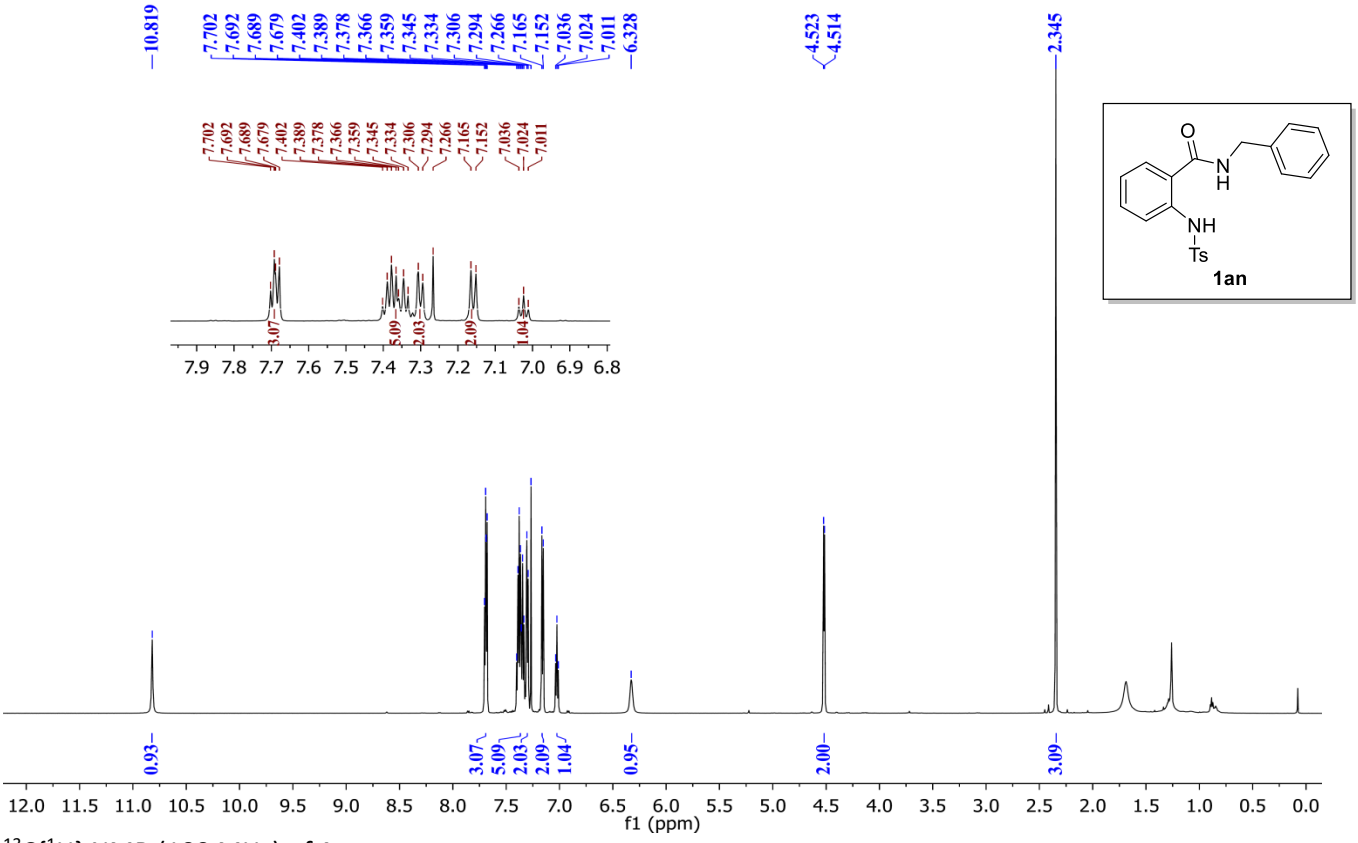
^{1}H NMR (400 MHz) of **1am**:



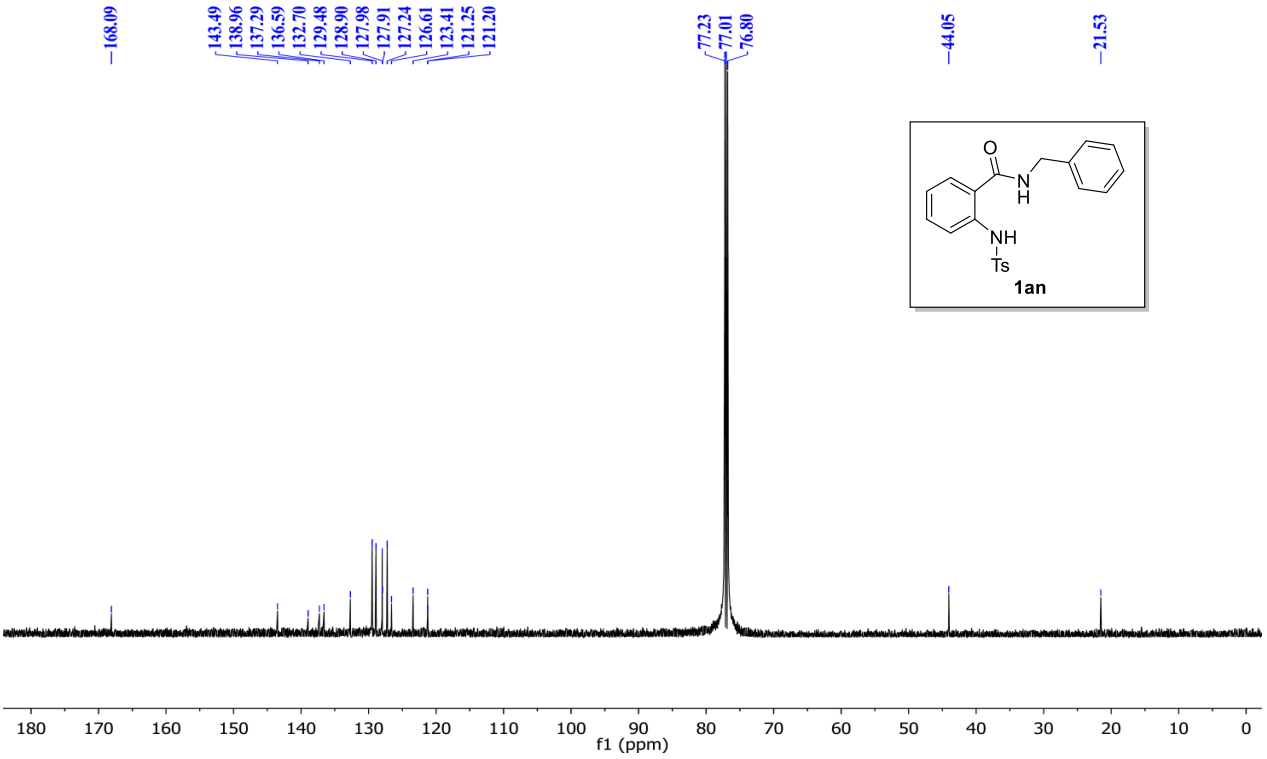
^{13}C{^{1}H} NMR (100 MHz) of **1am**:



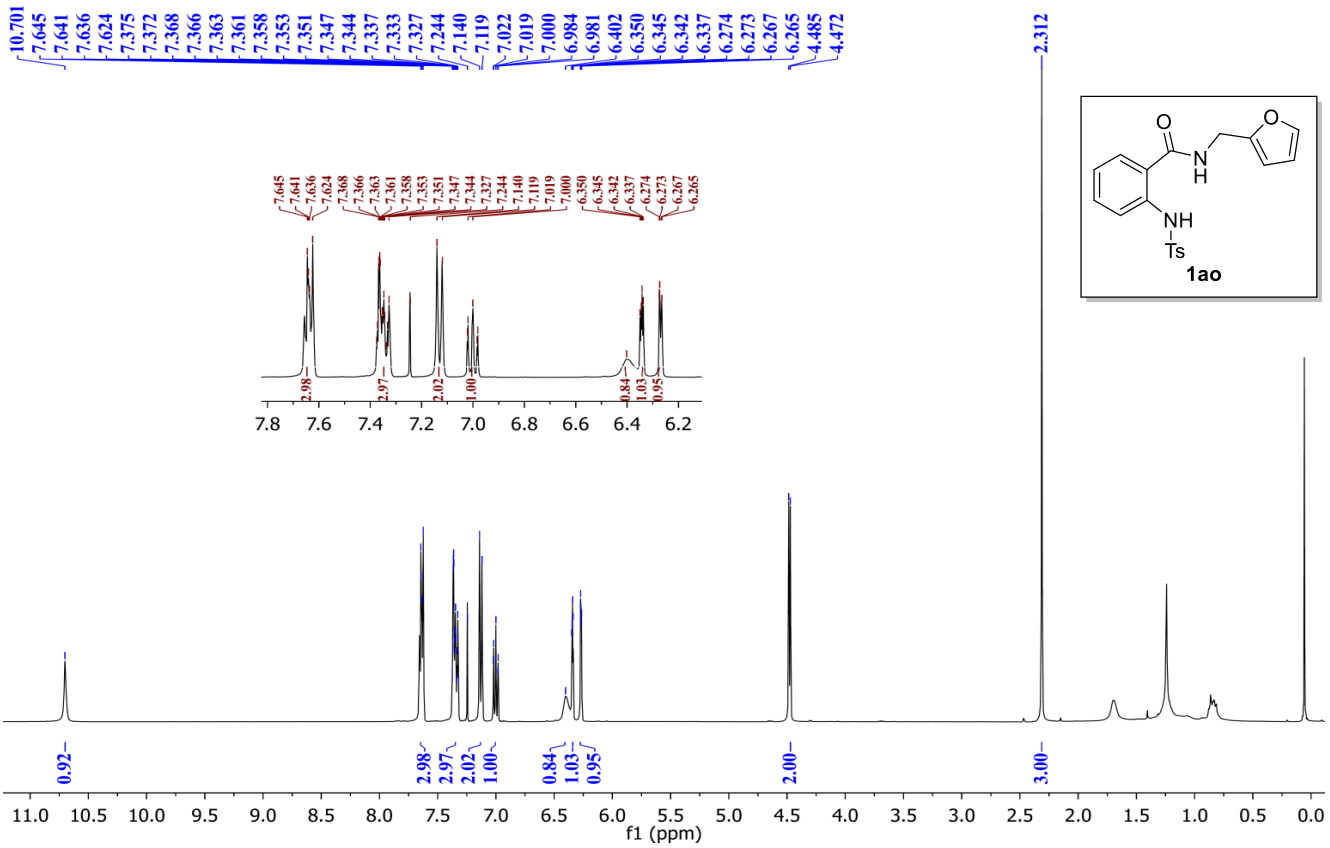
^{1}H NMR (400 MHz) of **1an**:



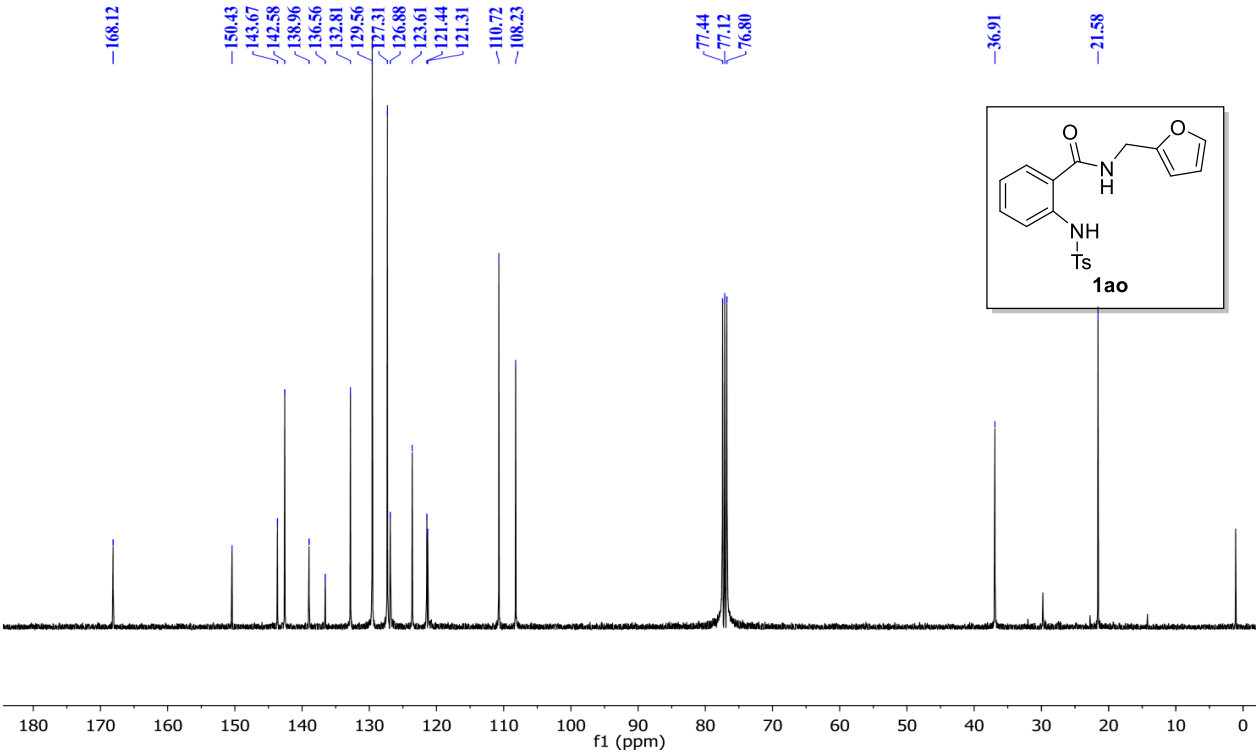
^{13}C{^{1}H} NMR (100 MHz) of **1an**:



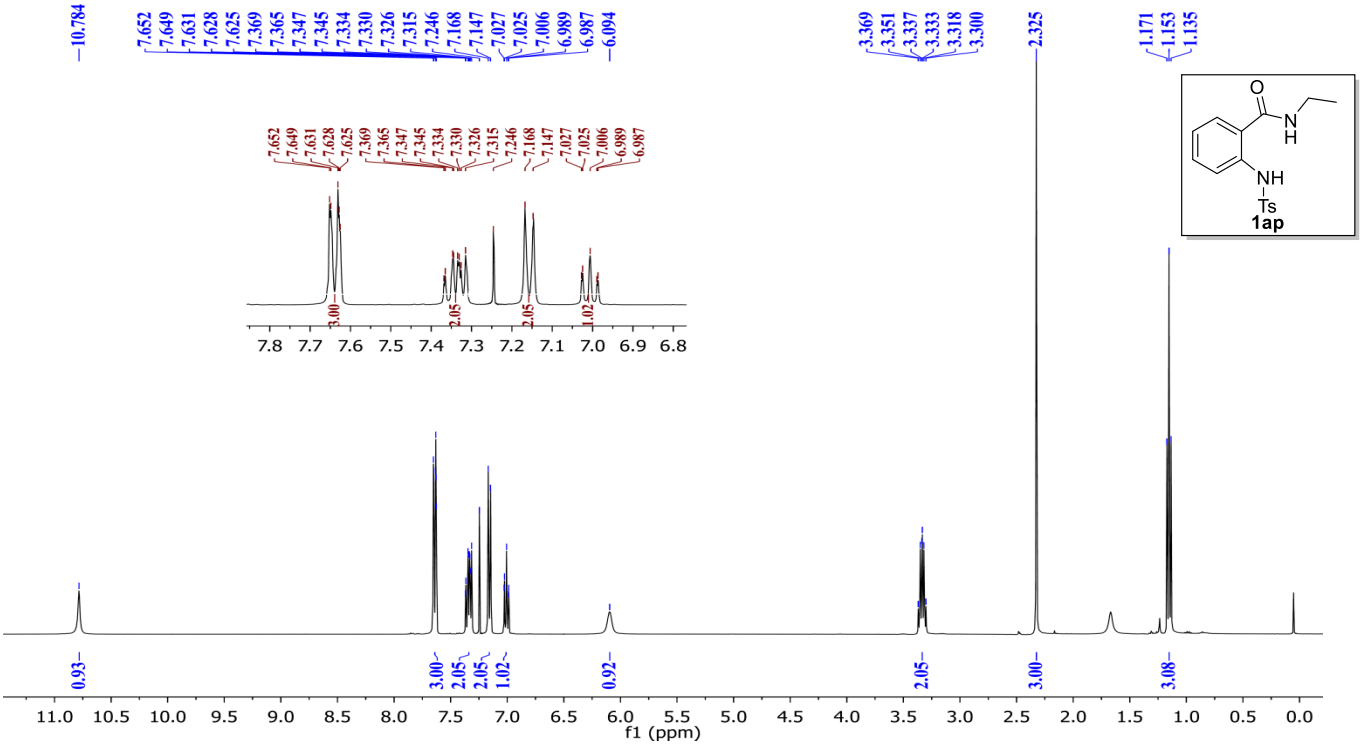
^{1}H NMR (400 MHz) of **1ao**:



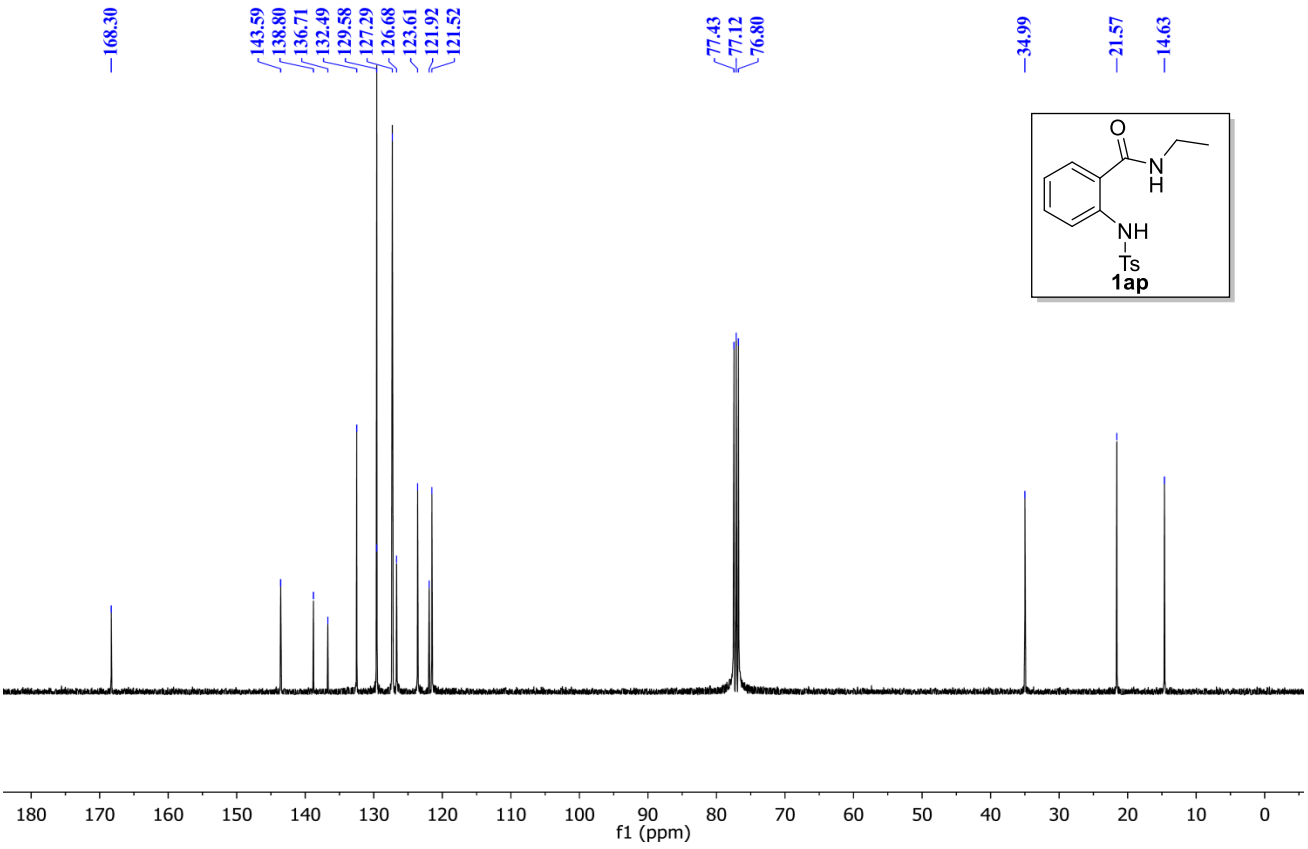
^{13}C{^{1}H} NMR (100 MHz) of **1ao**:



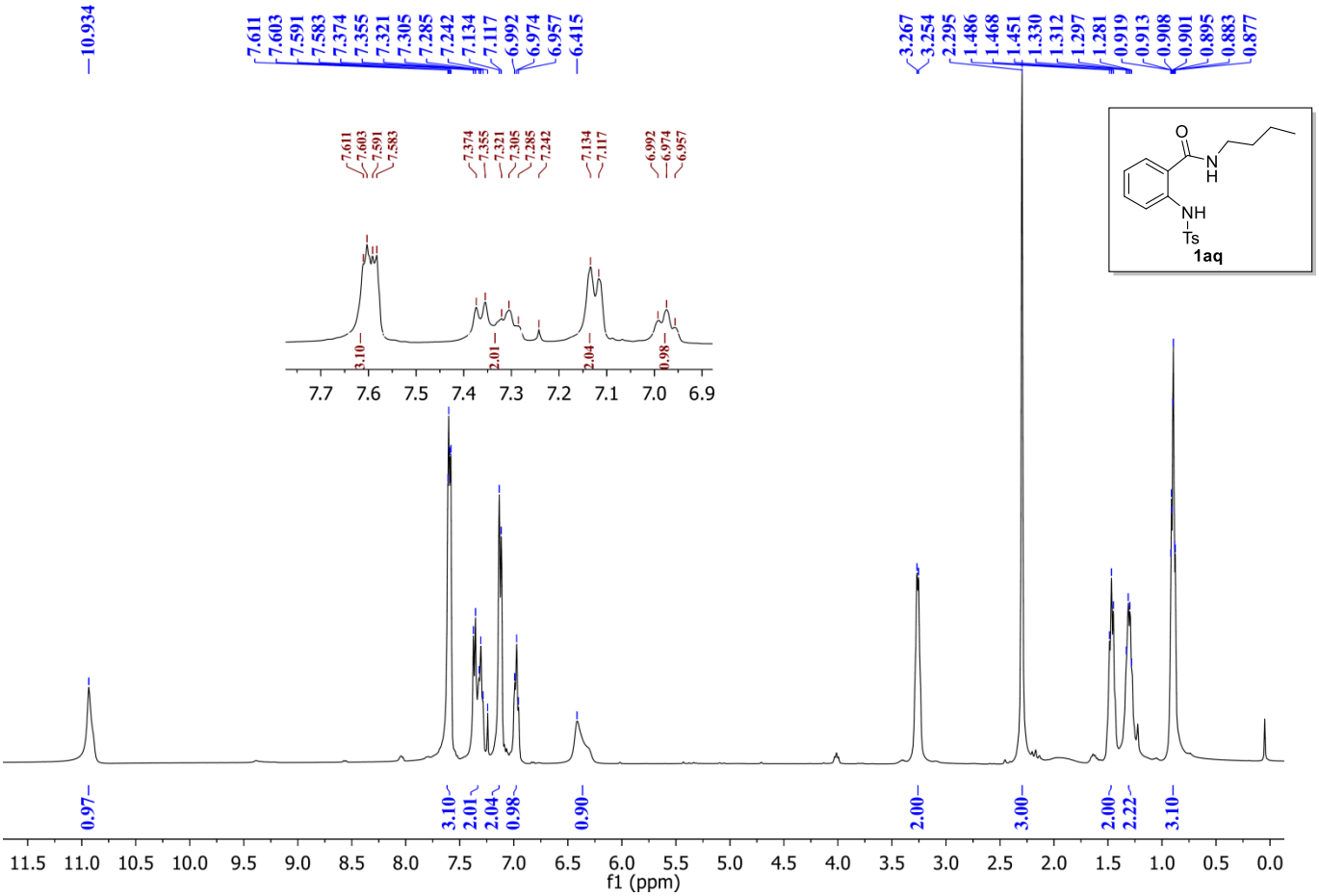
^{1}H NMR (600 MHz) of **1ap**:



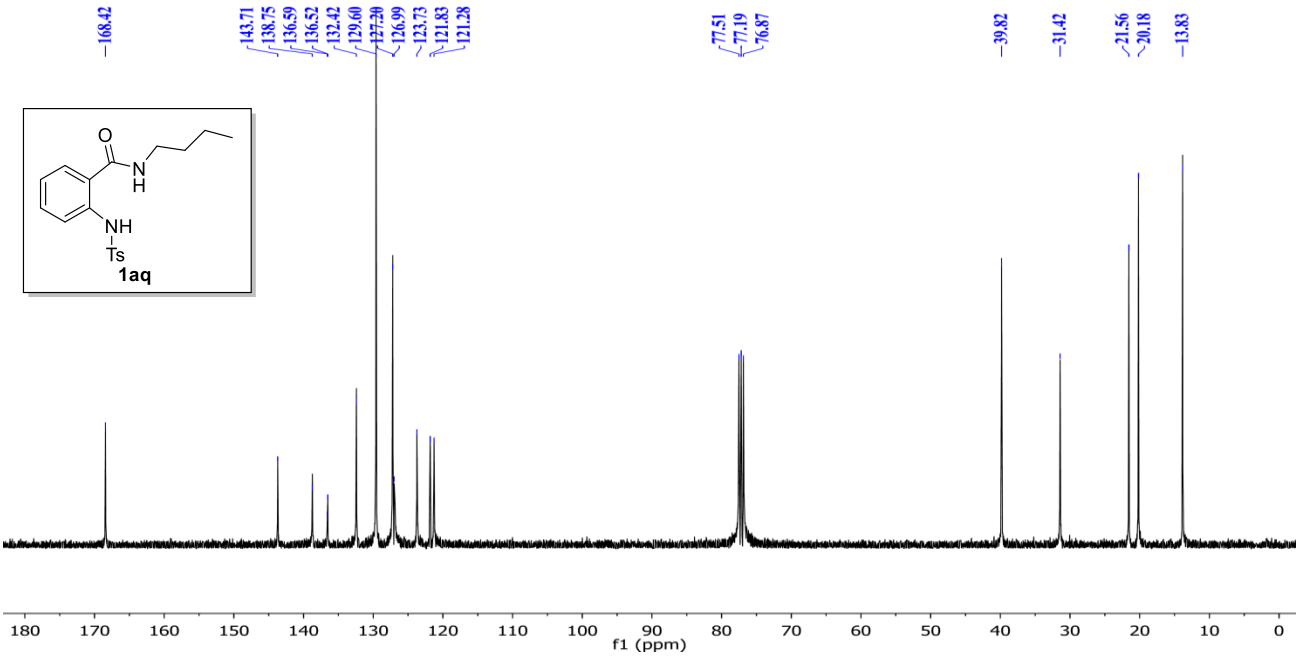
^{13}C{^{1}H} NMR (150 MHz) of **1ap**:



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

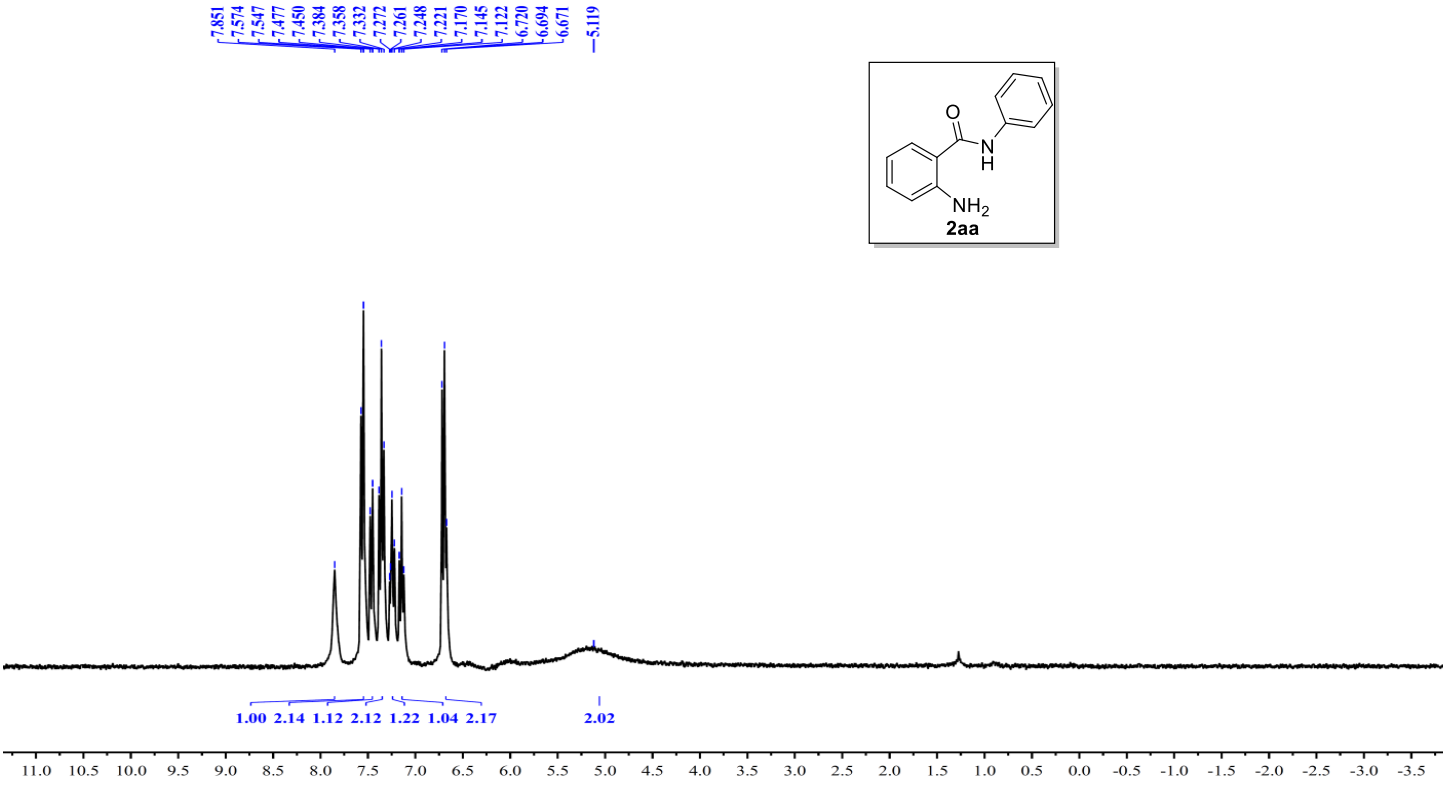


^{13}C{^{1}H} NMR (150 MHz) of **1aq**:

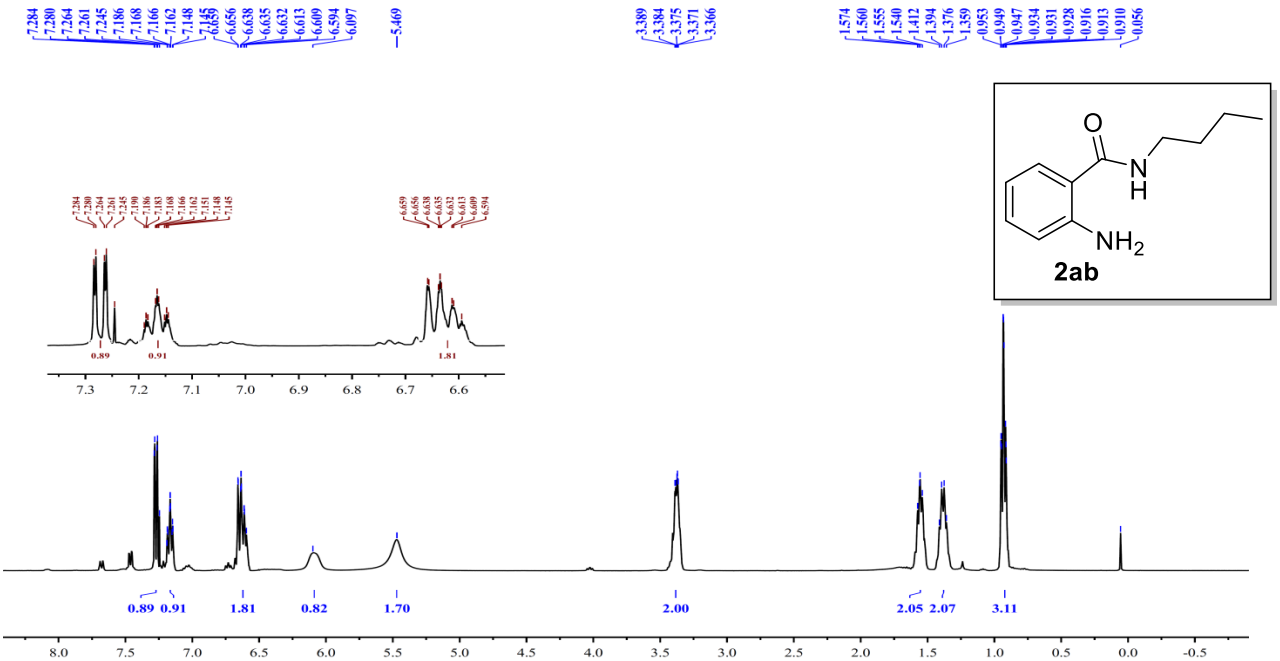


37. NMR Spectra of substrates 2aa-2ae

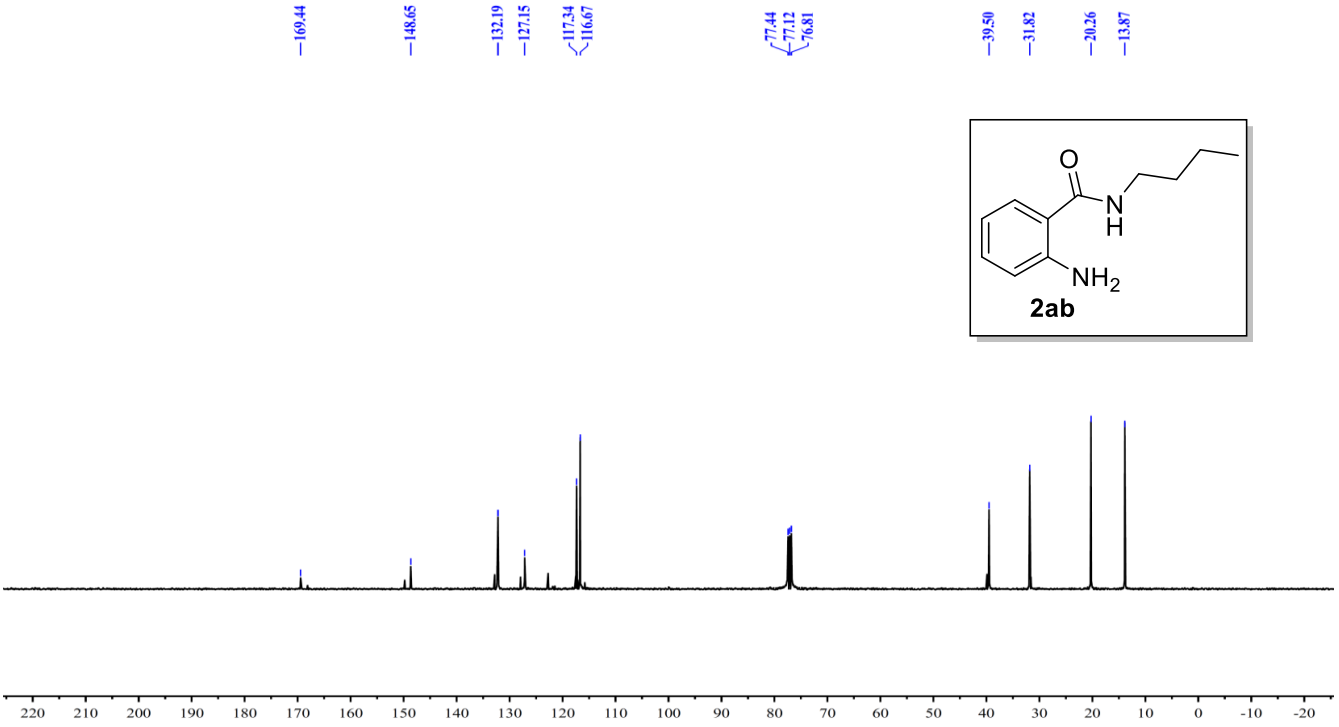
^{1}H NMR (300 MHz) of **2aa**:



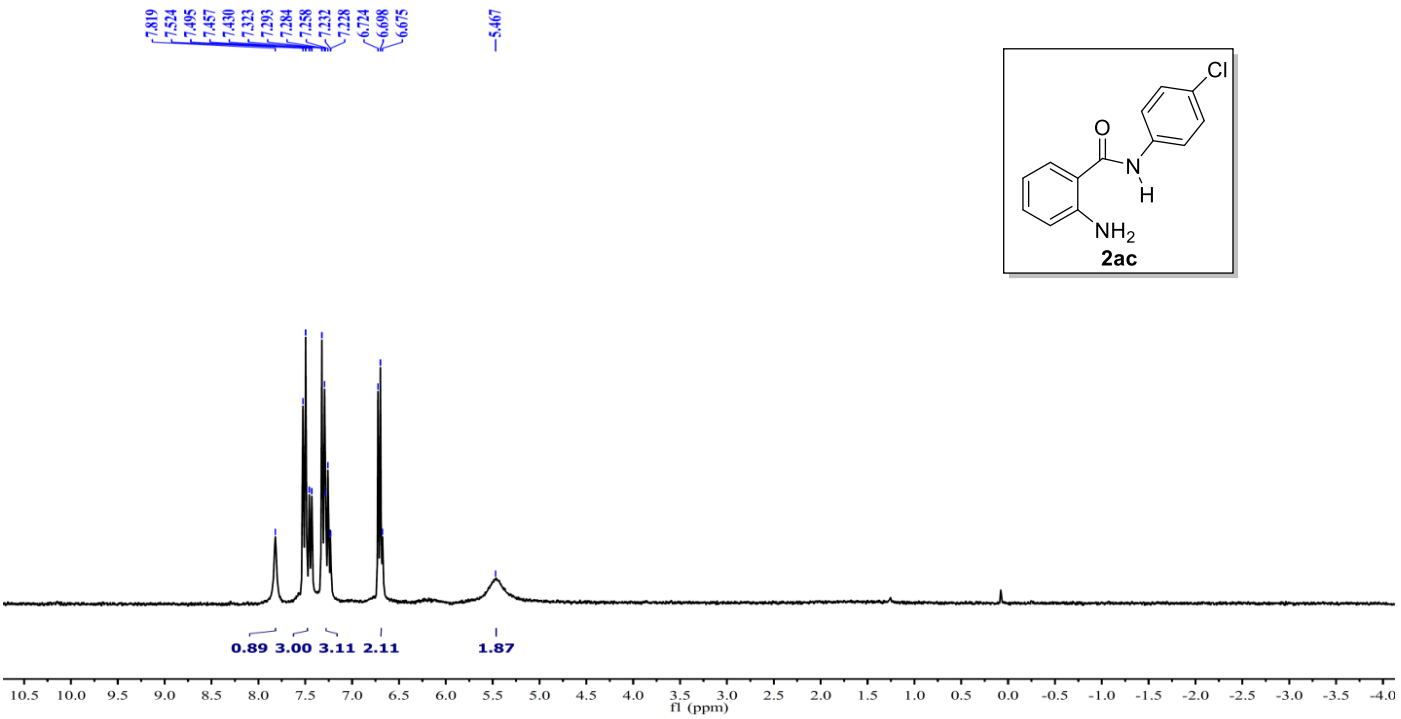
^{1}H NMR (400 MHz) of **2ab**:



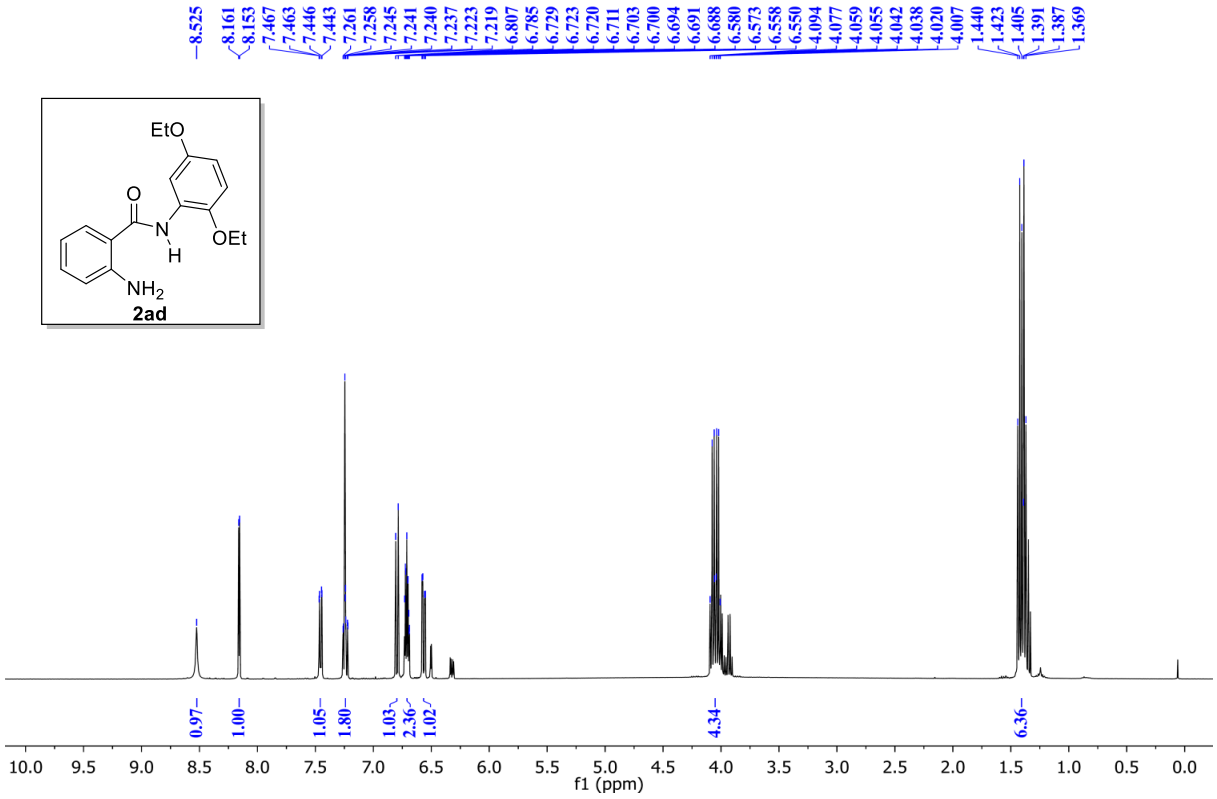
$^{13}C\{^{1}H\}$ NMR (100 MHz) of **2ab**:



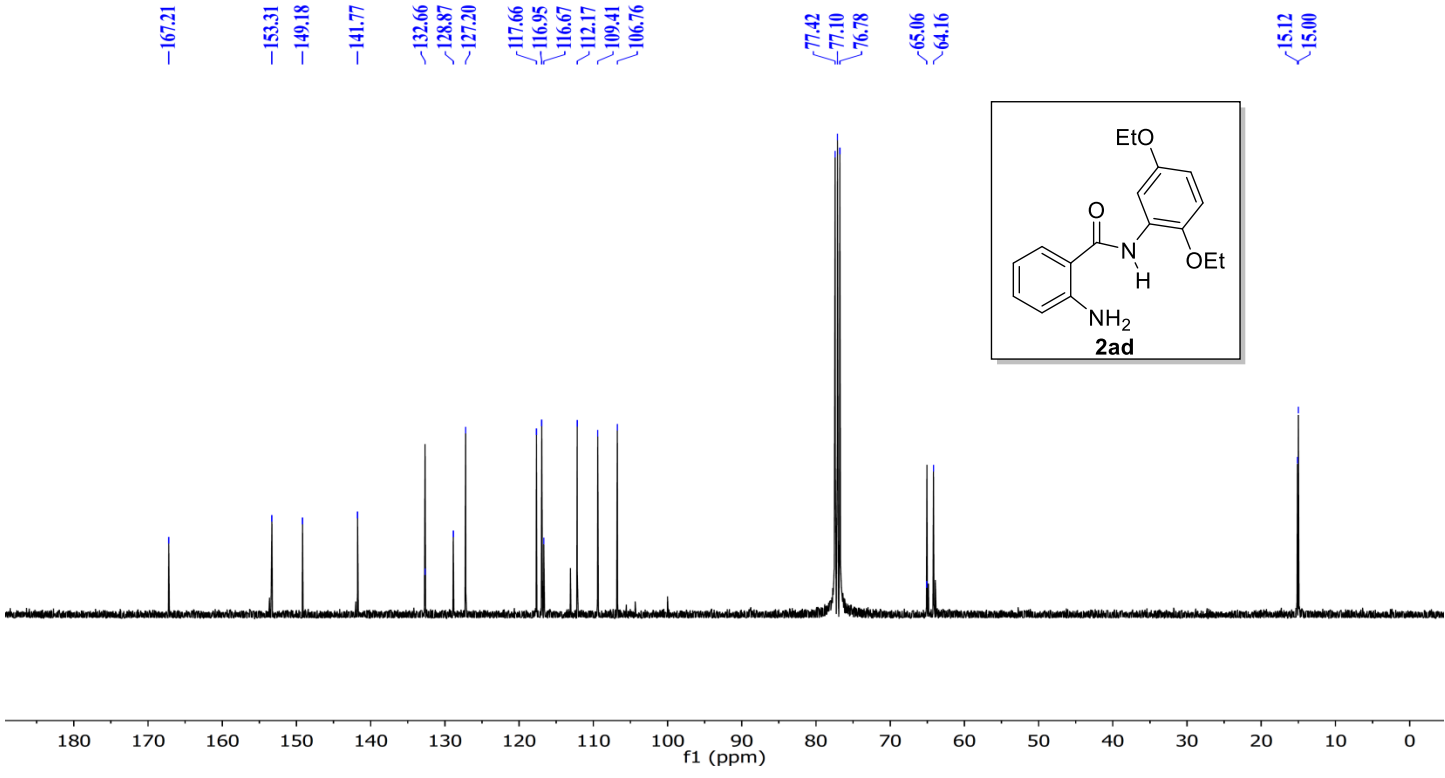
^{1}H NMR (300 MHz) of **2ac**:



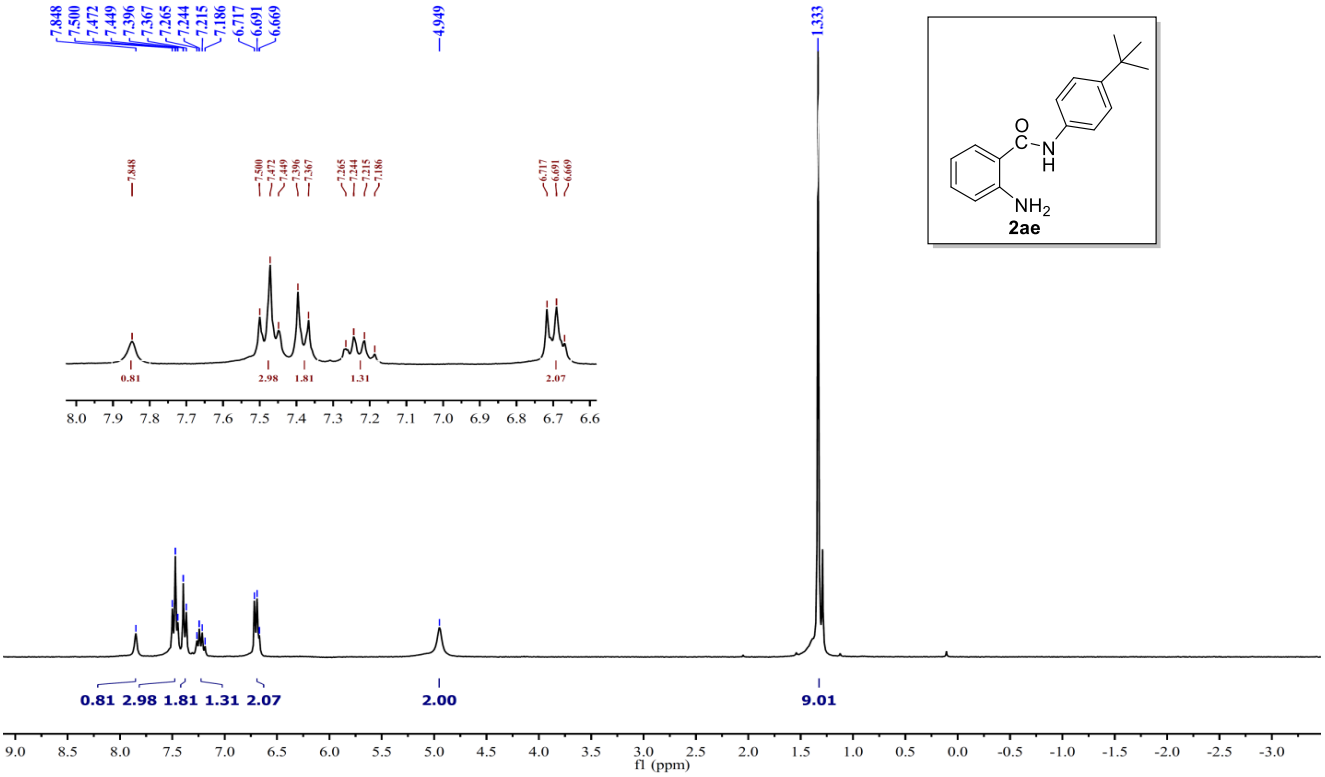
^{1}H NMR (300 MHz) of **2ad:**



^{13}C{^{1}H} NMR (100 MHz) of **2ad**:

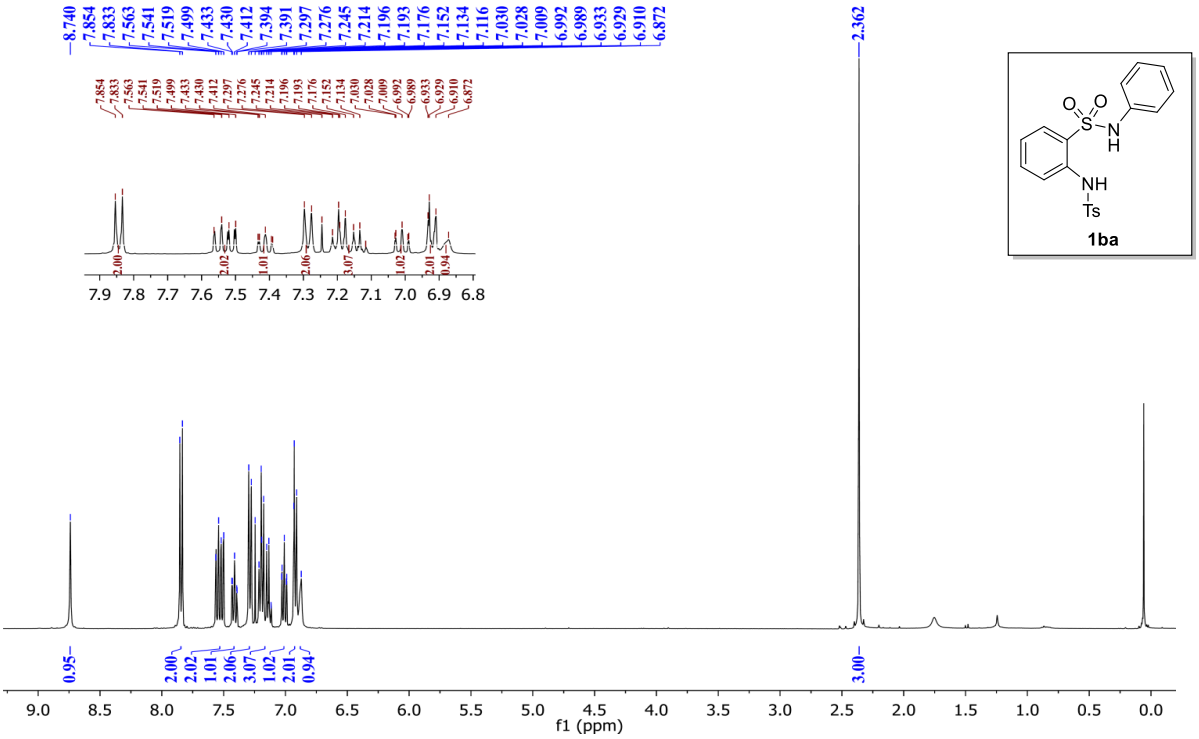


^{1}H NMR (300 MHz) of **2ae:**

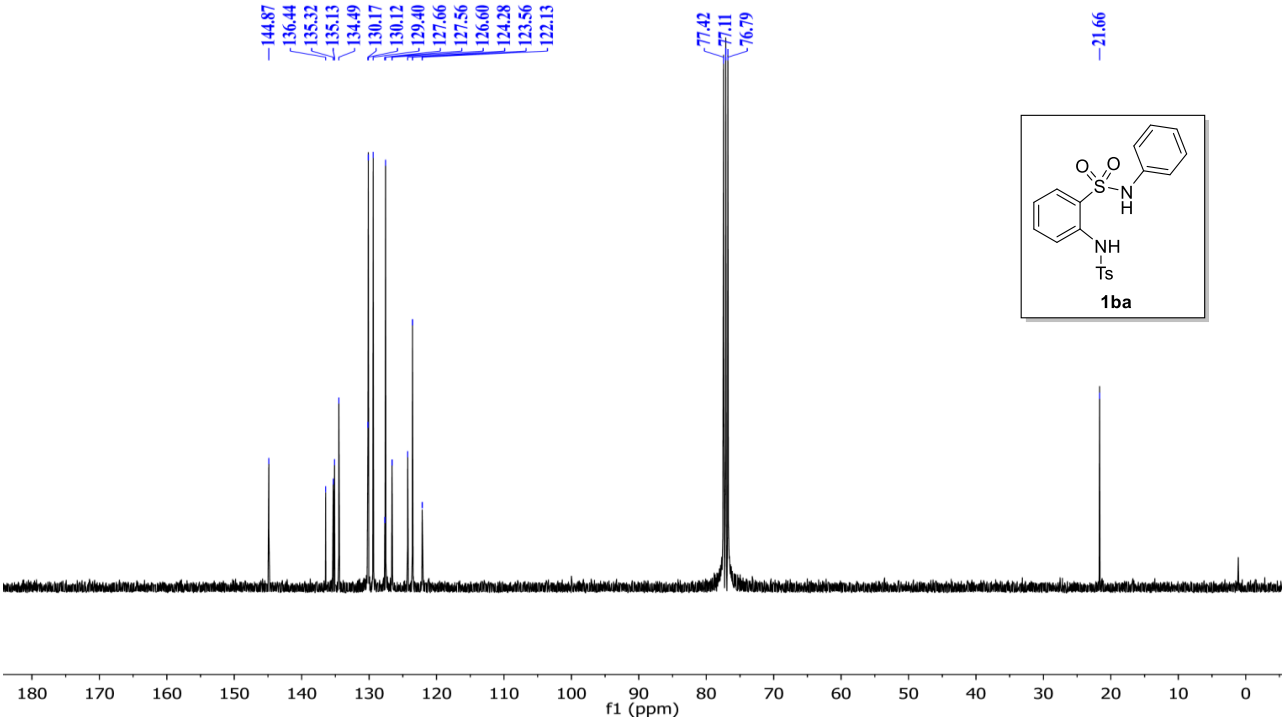


38. NMR spectra of substrates 1ba-1bc

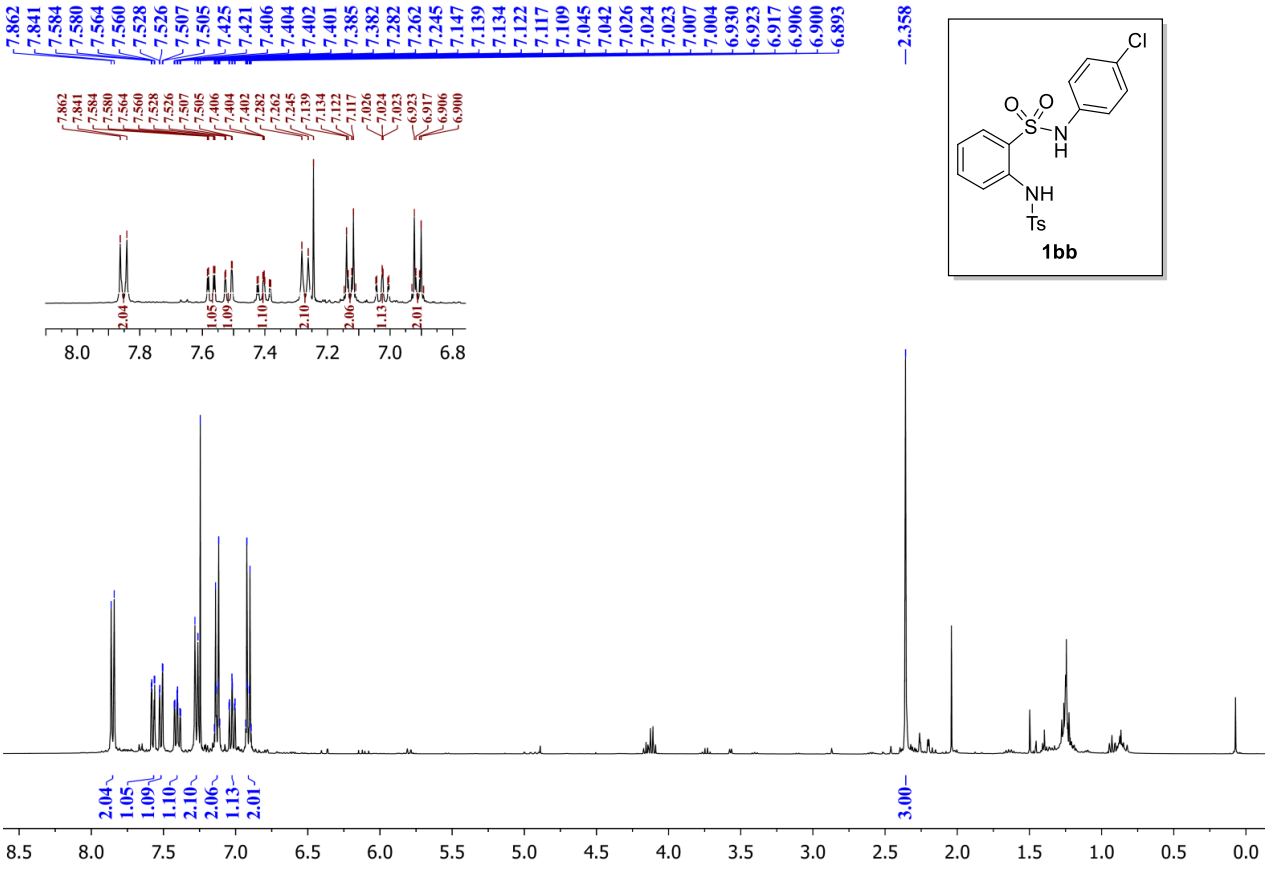
^{1}H NMR (400 MHz) of **1ba**:



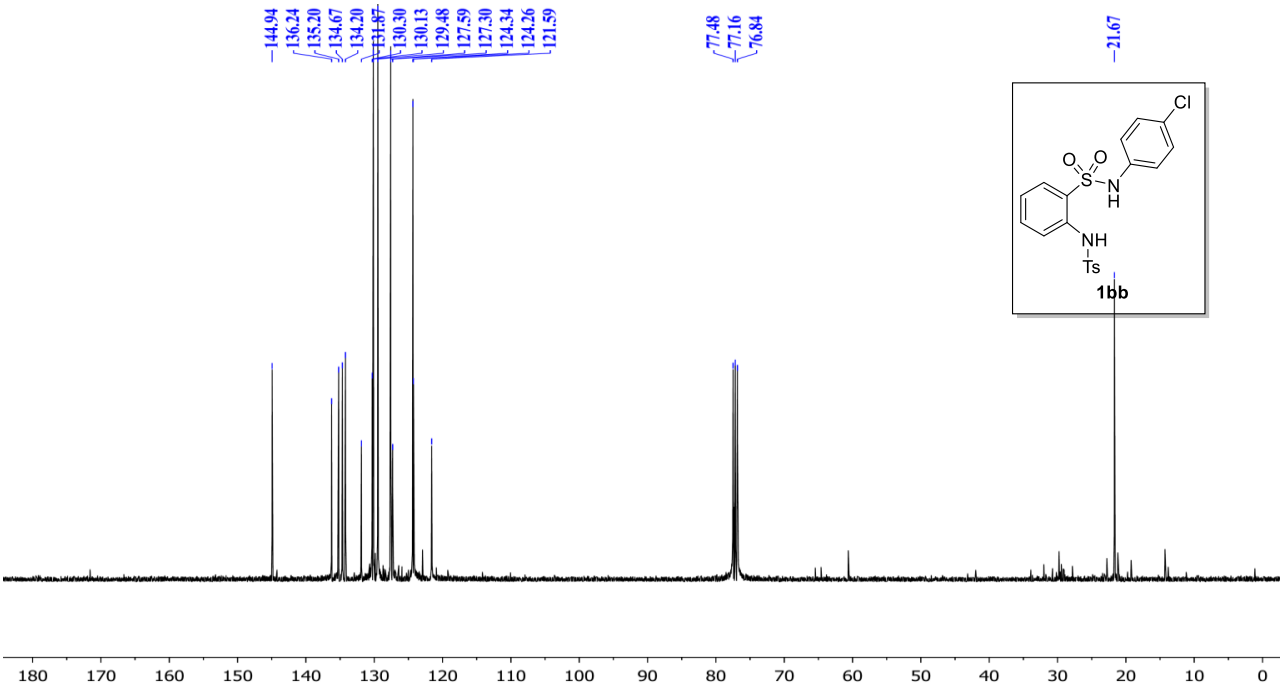
^{13}C{^{1}H} NMR (100 MHz) of **1ba**:



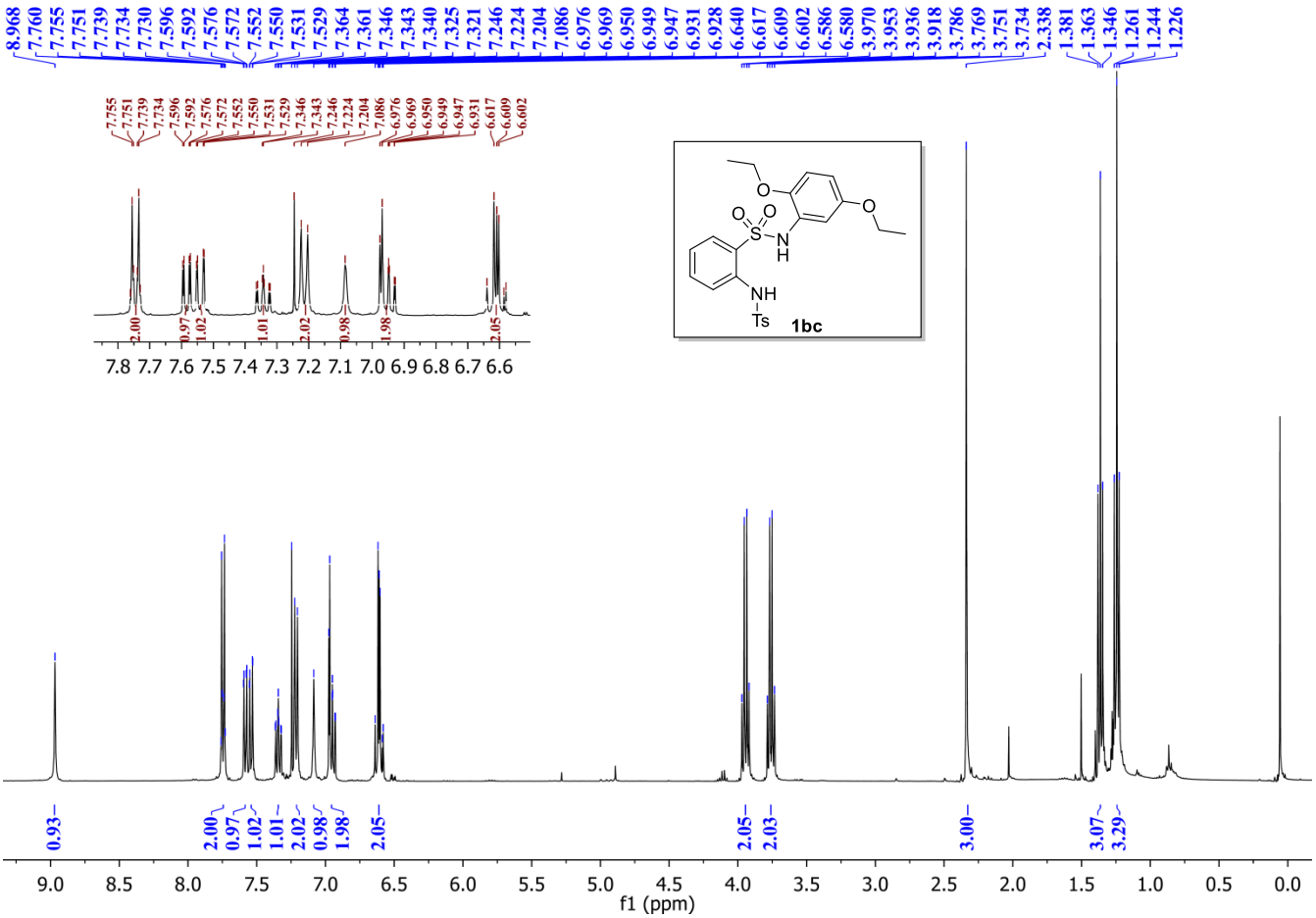
^{1}H NMR (400 MHz) of **1bb**:



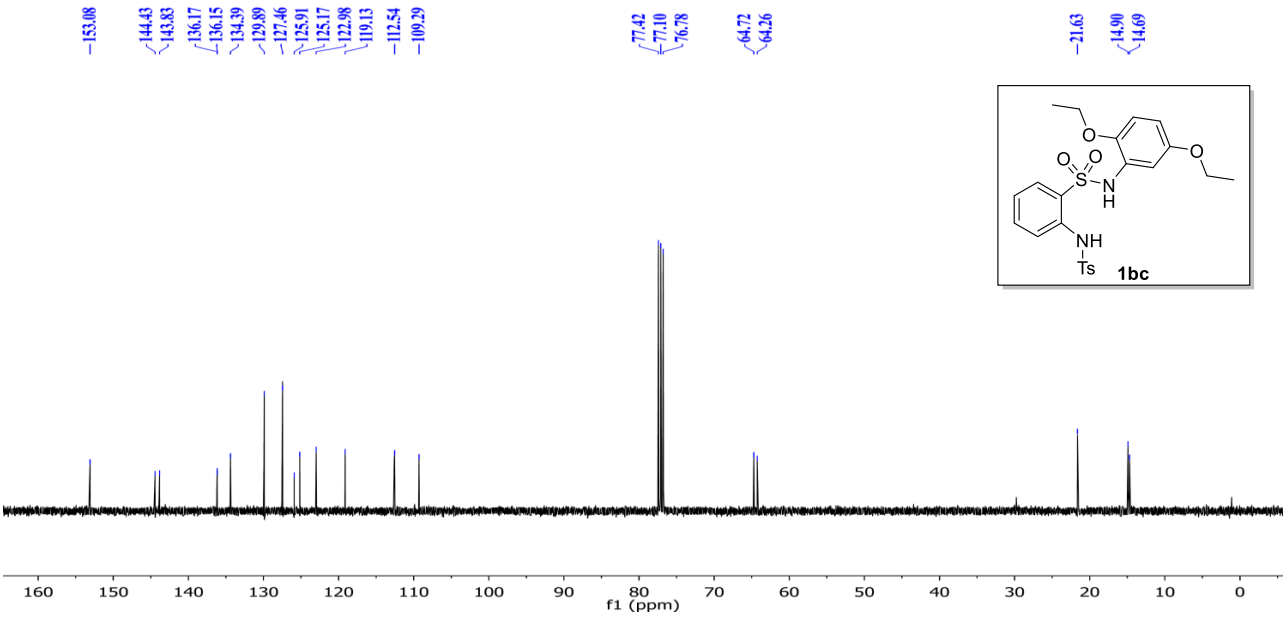
^{13}C{^{1}H} NMR (100 MHz) of **1bb**:



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

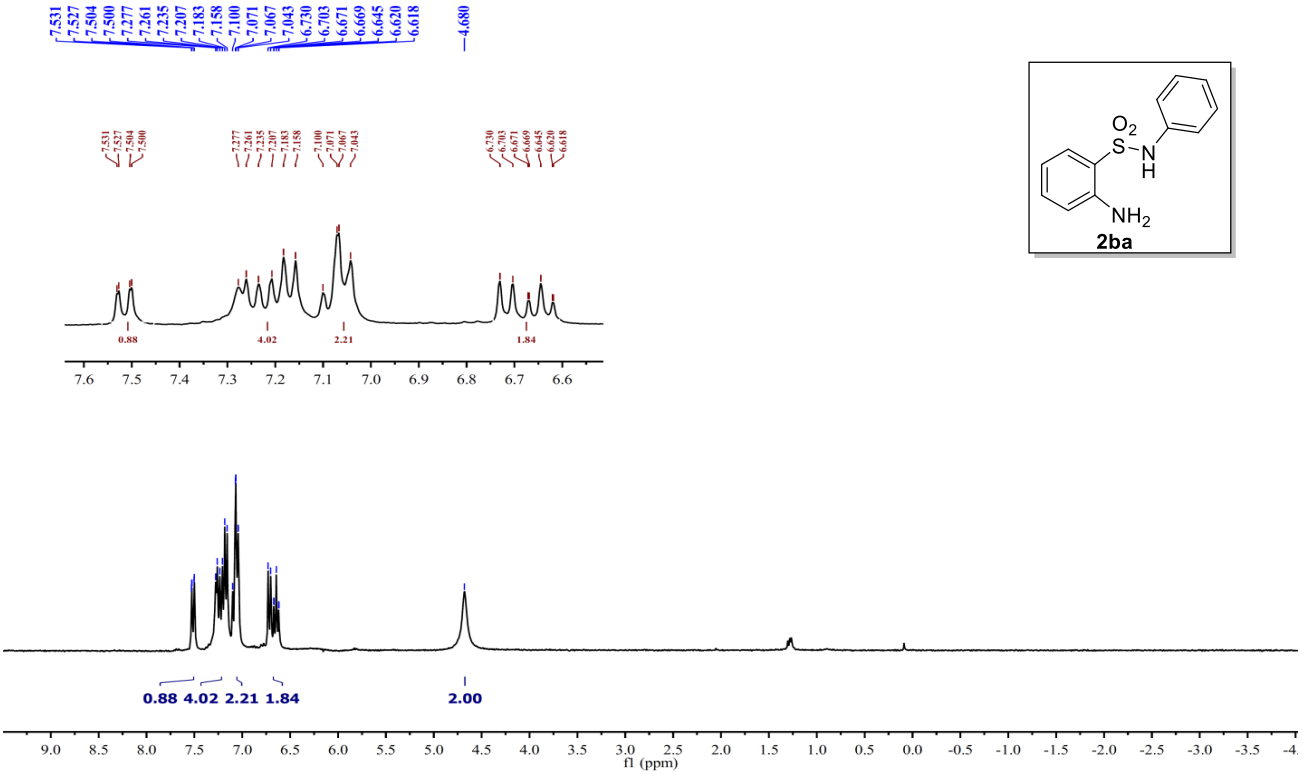


^{13}C{^{1}H} NMR (100 MHz) of **1bc**:



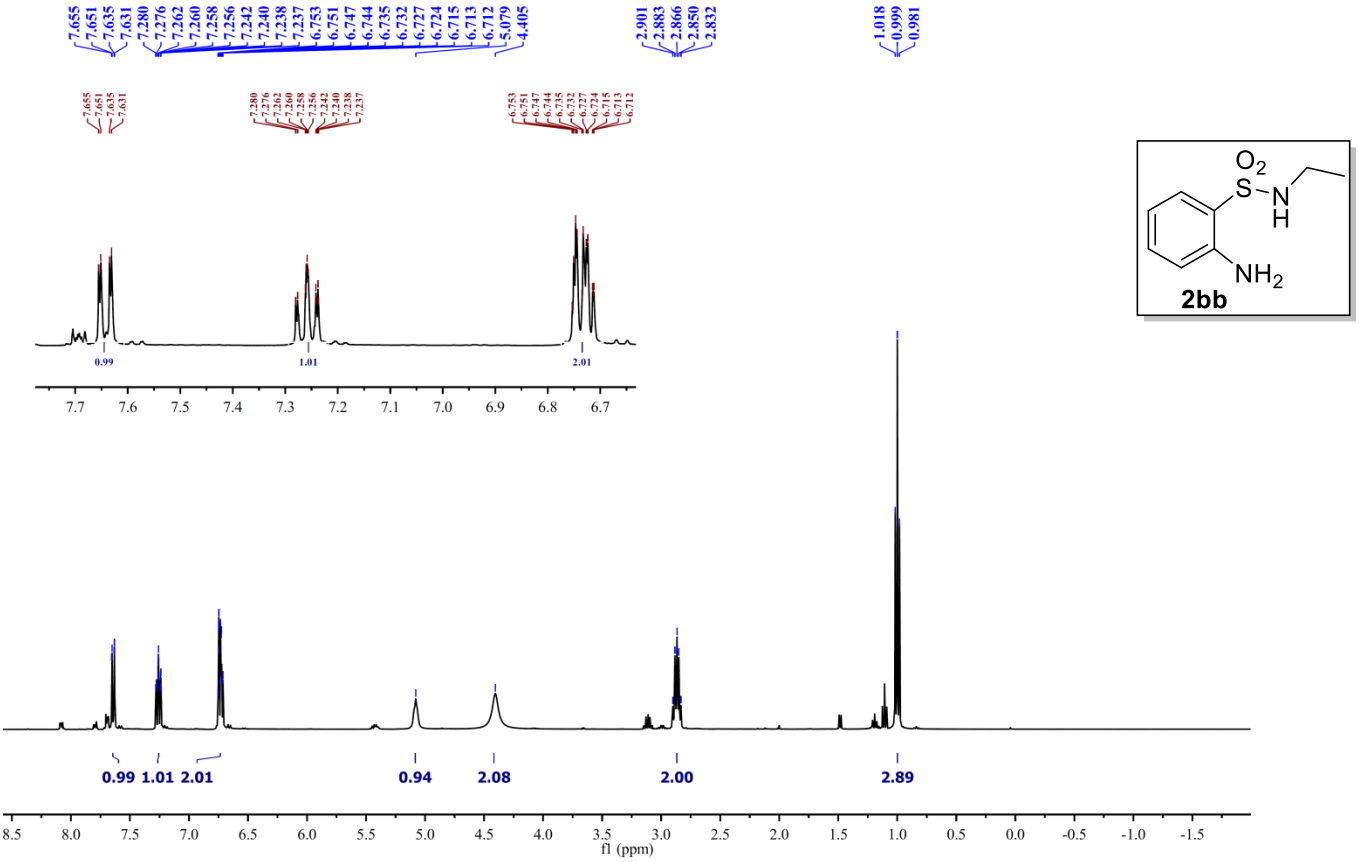
39. NMR spectra of substrates 2ba-2bc:

^{1}H NMR (300 MHz) of **2ba**:

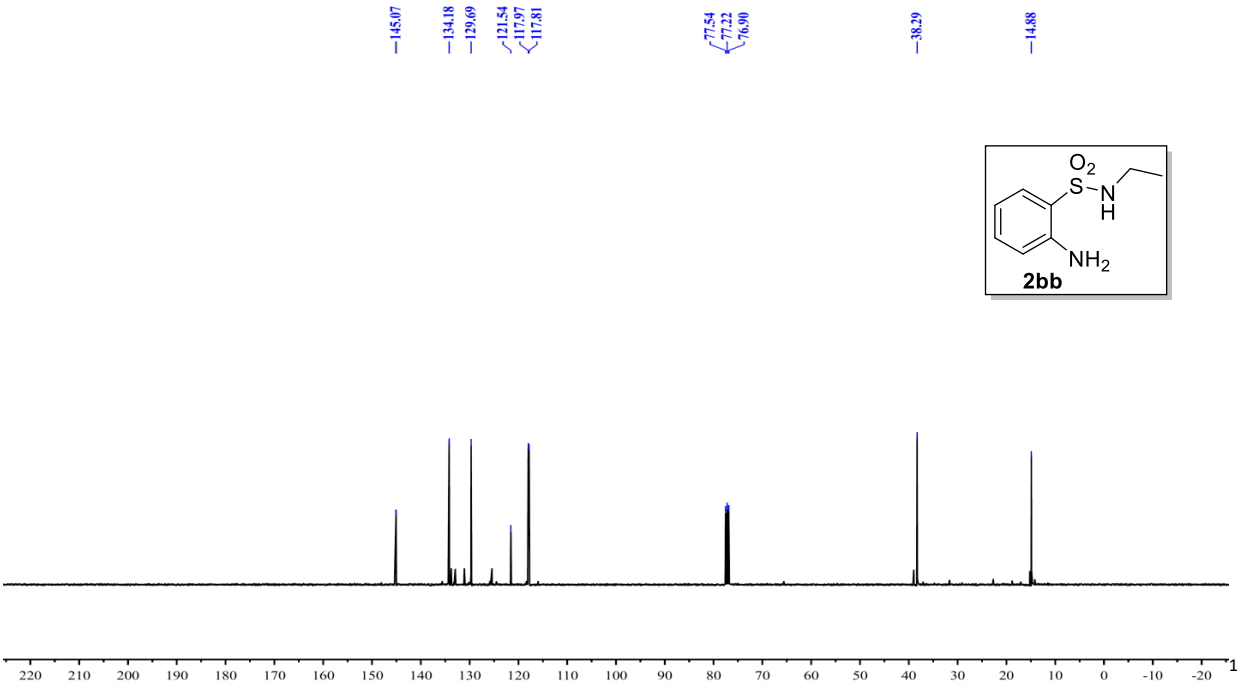


2ba

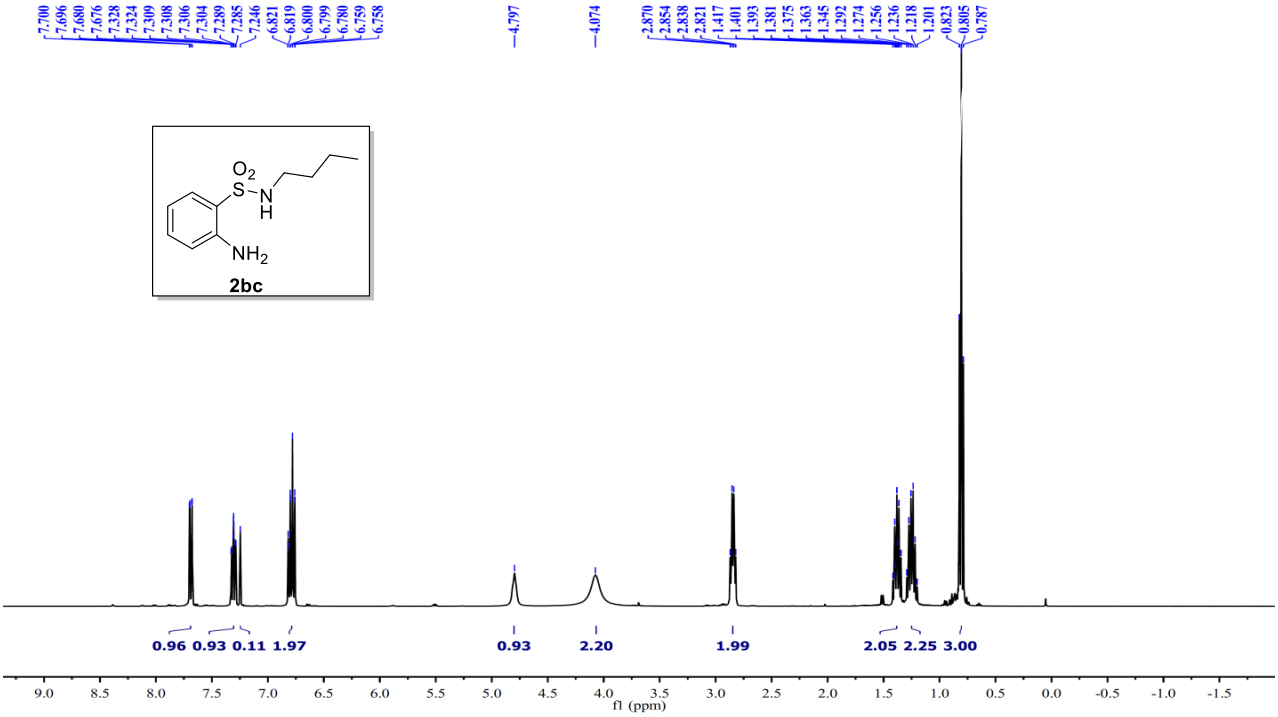
^{1}H NMR (400 MHz) of **2bb**:



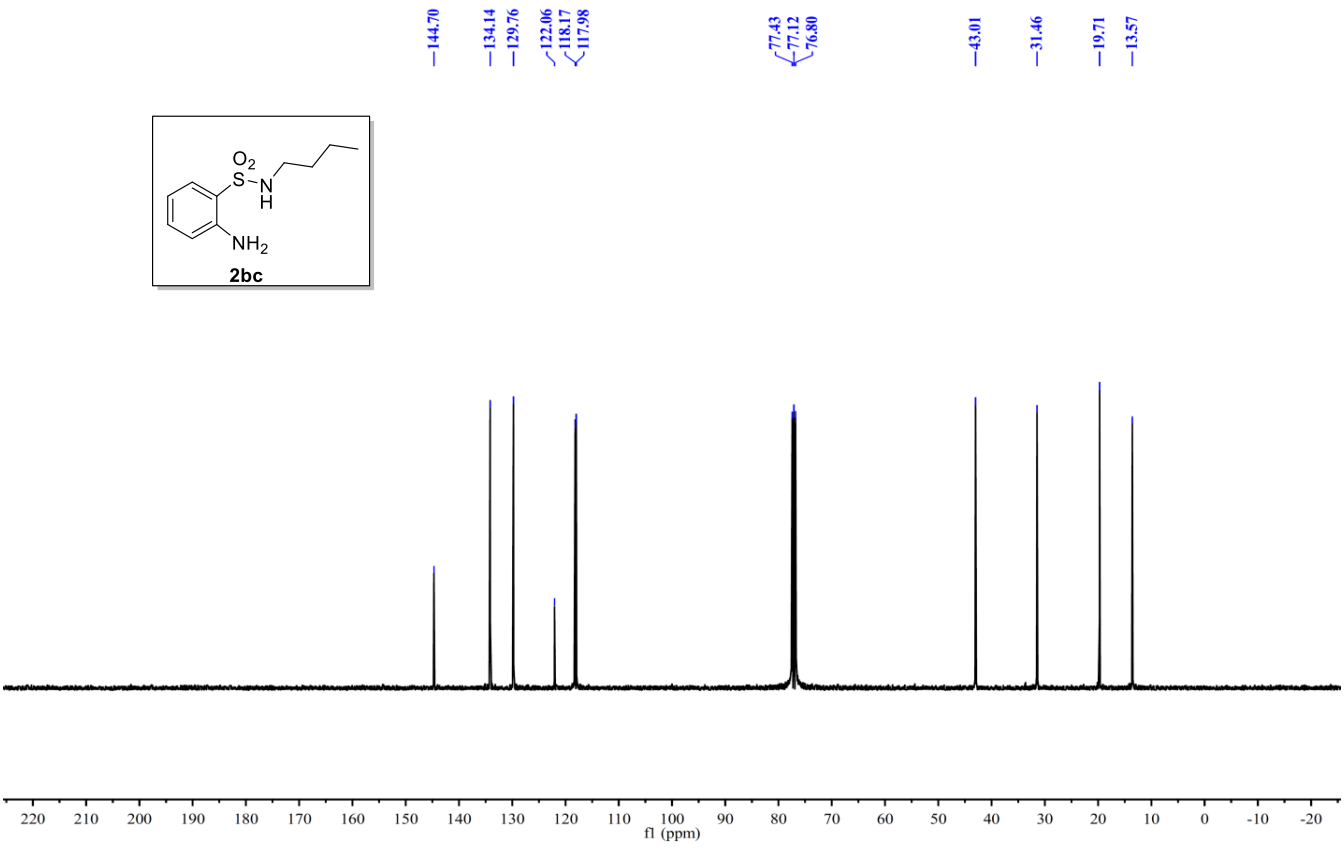
^{13}C{^{1}H} NMR (100 MHz) of **2bb**:



H NMR (400 MHz) of **2bc**:

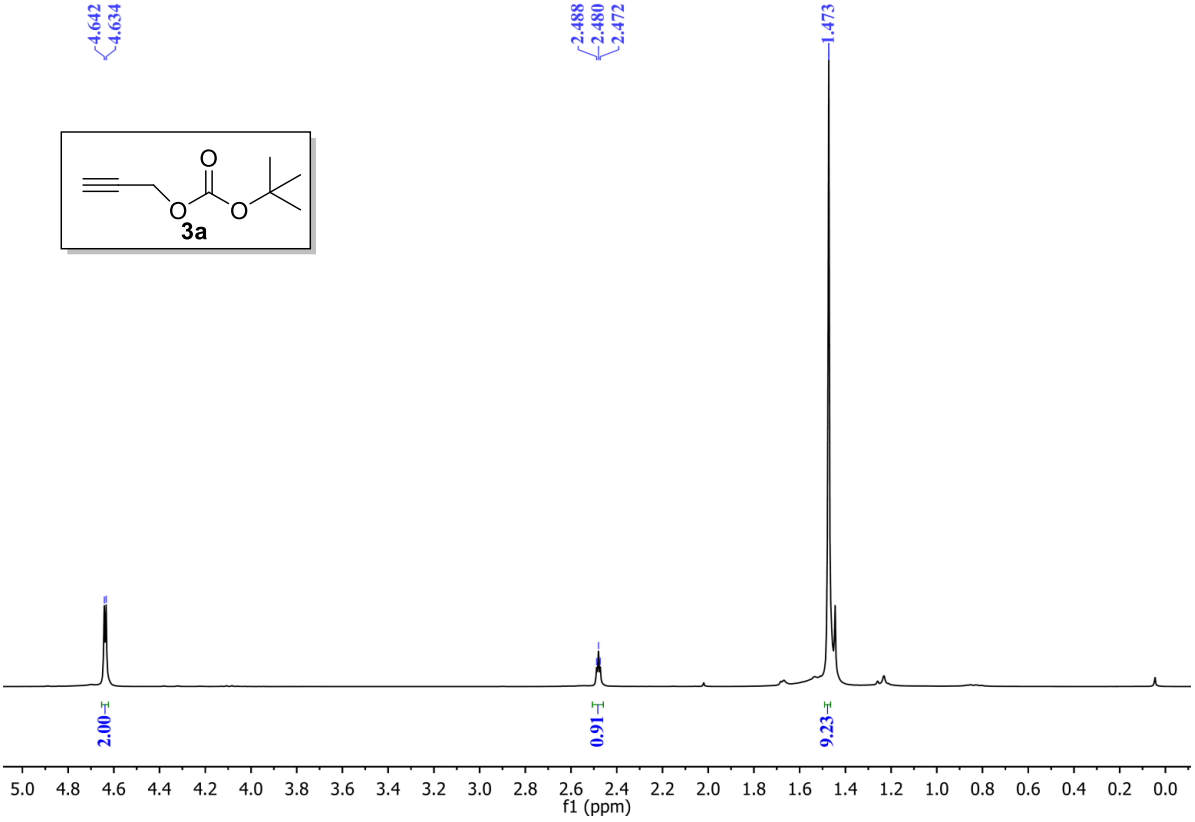


$^{13}C\{^{1}H\}$ NMR (100 MHz) of **2bc**:

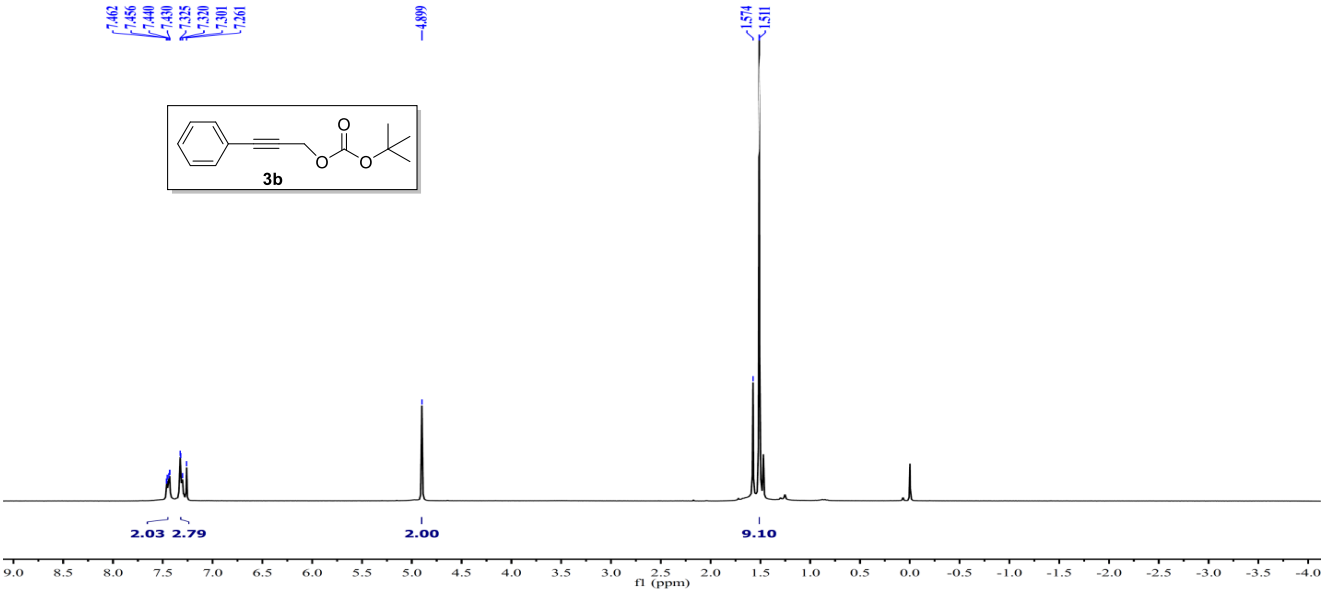


40. NMR spectra of substrates 3a-3k:

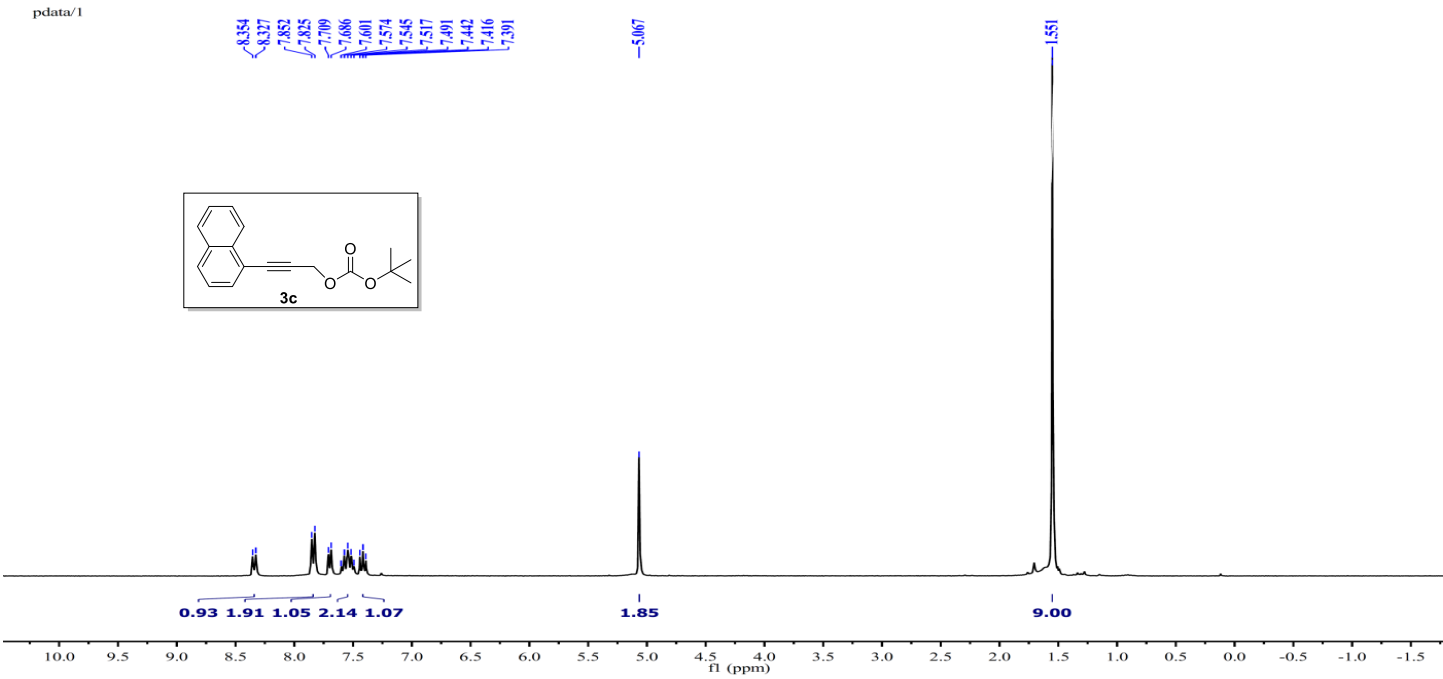
^{1}H NMR (300 MHz) of **3a** :



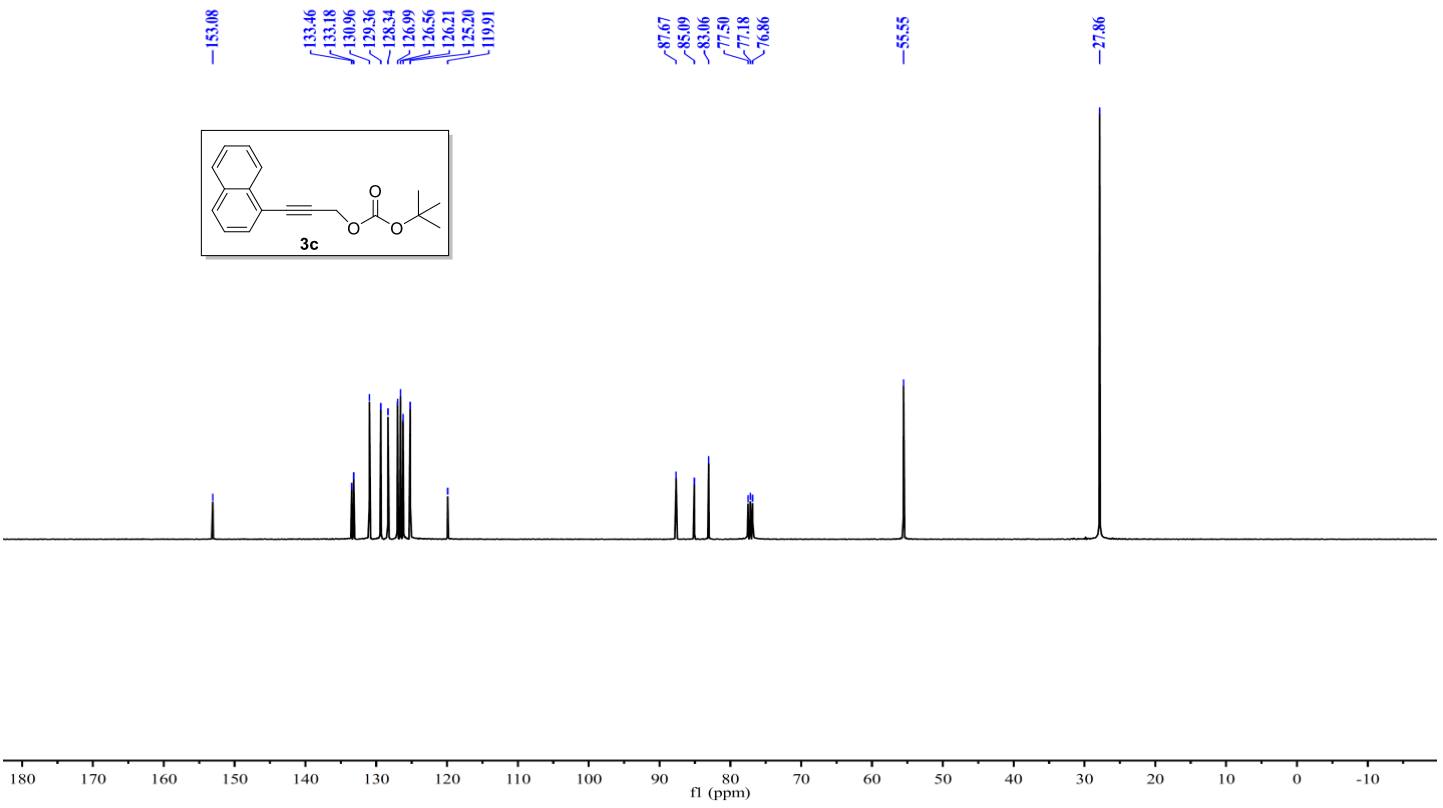
^{1}H NMR (300 MHz) of **3b** :



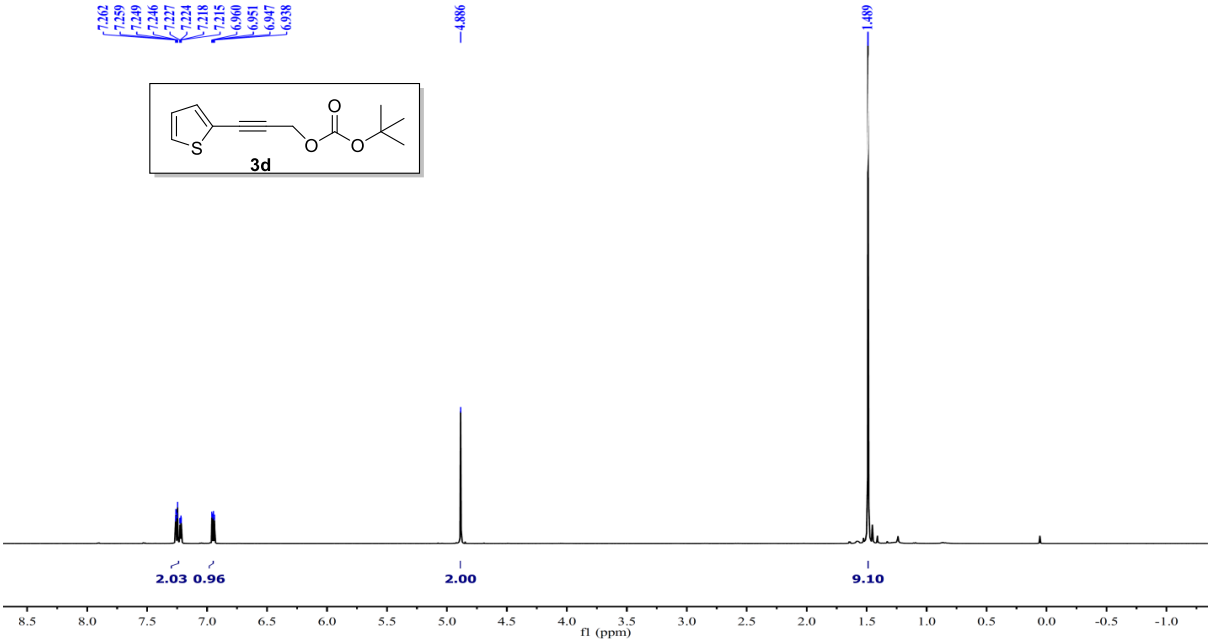
^{1}H NMR (400 MHz) of **3c :**



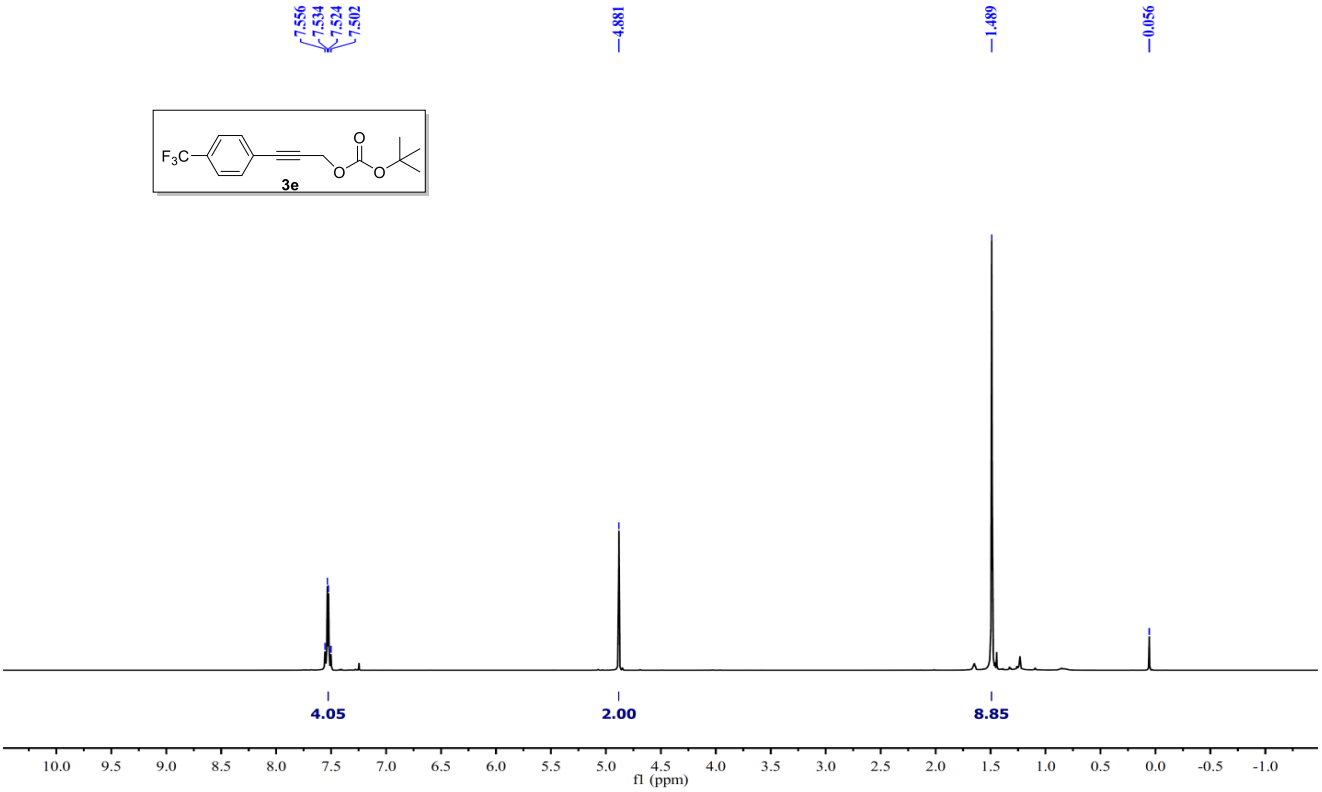
^{13}C{^{1}H} NMR (100 MHz) of **3c** :



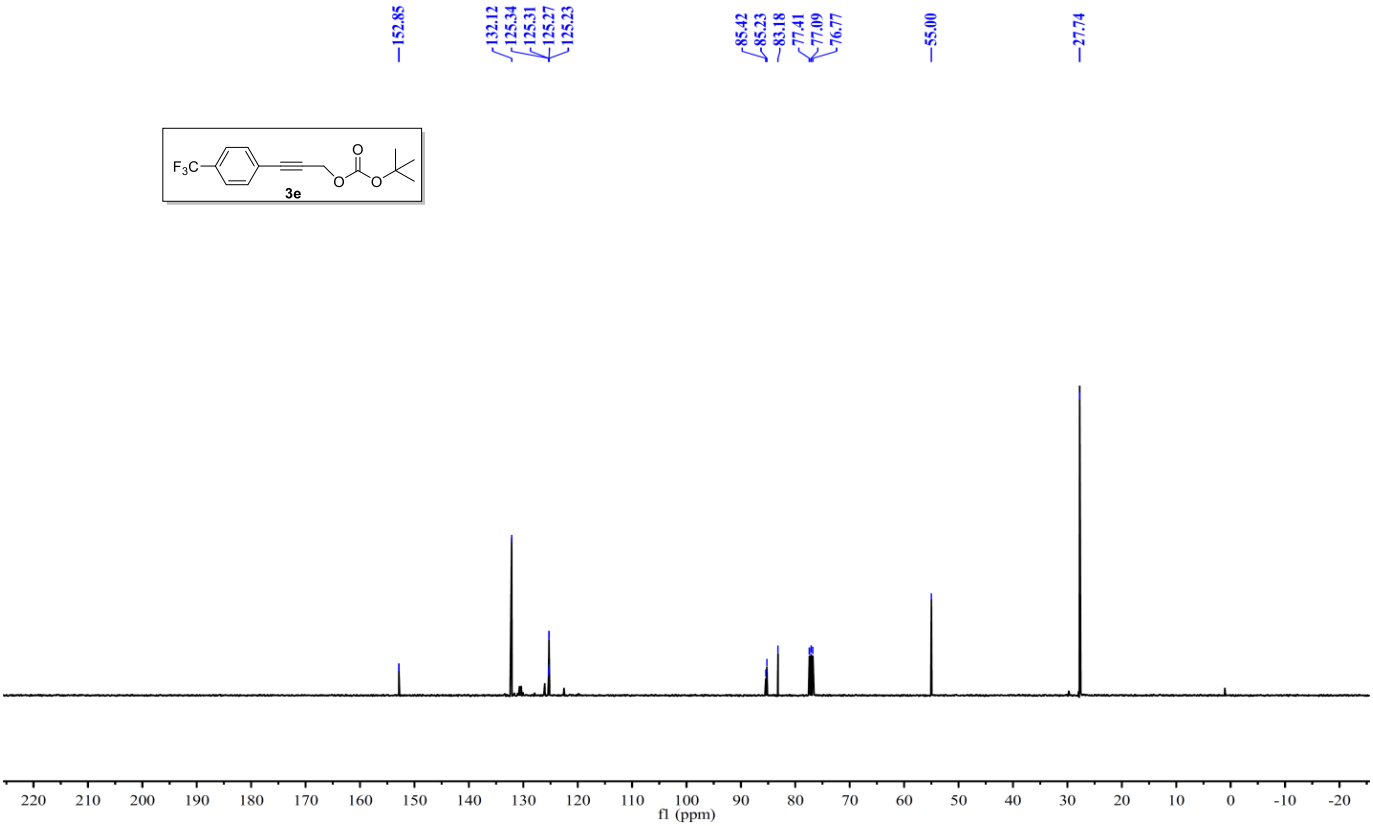
^{1}H NMR (400 MHz) of **3d :**



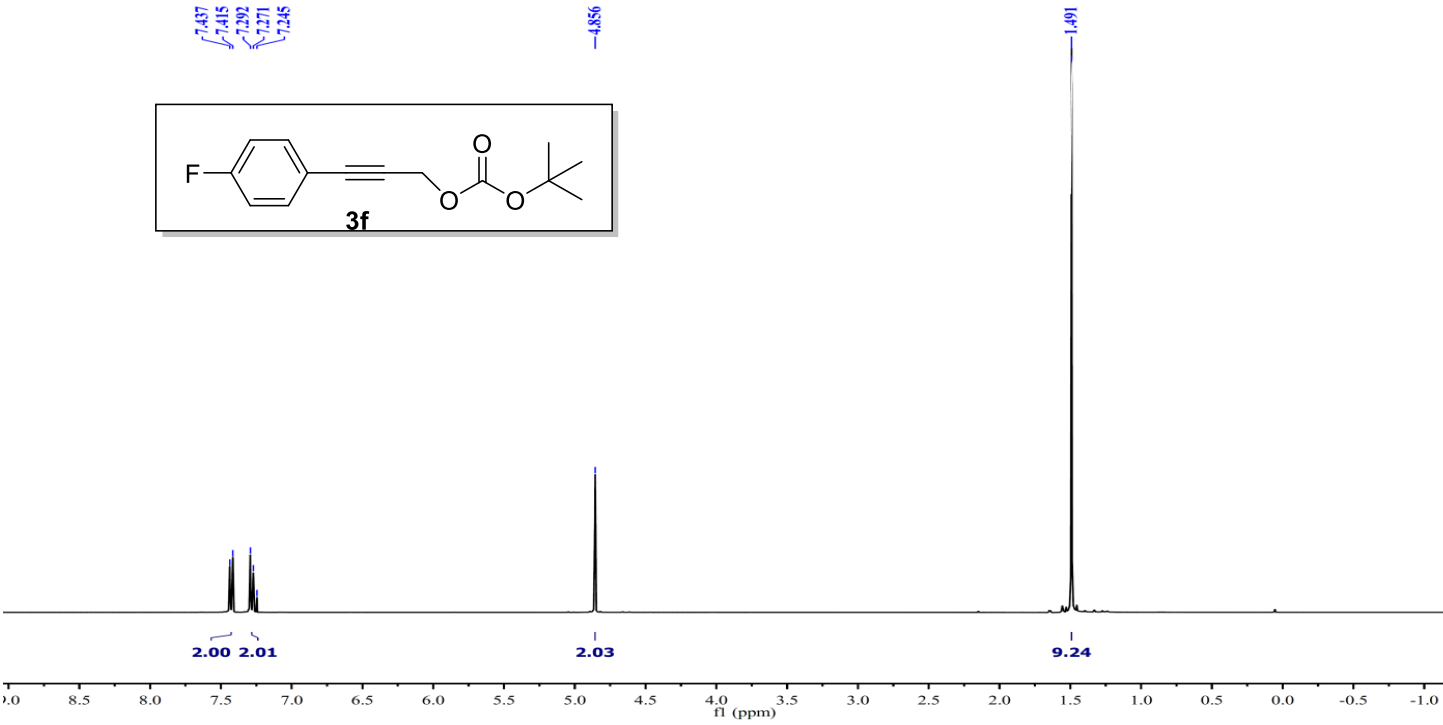
^{1}H NMR (400 MHz) of **3e:**



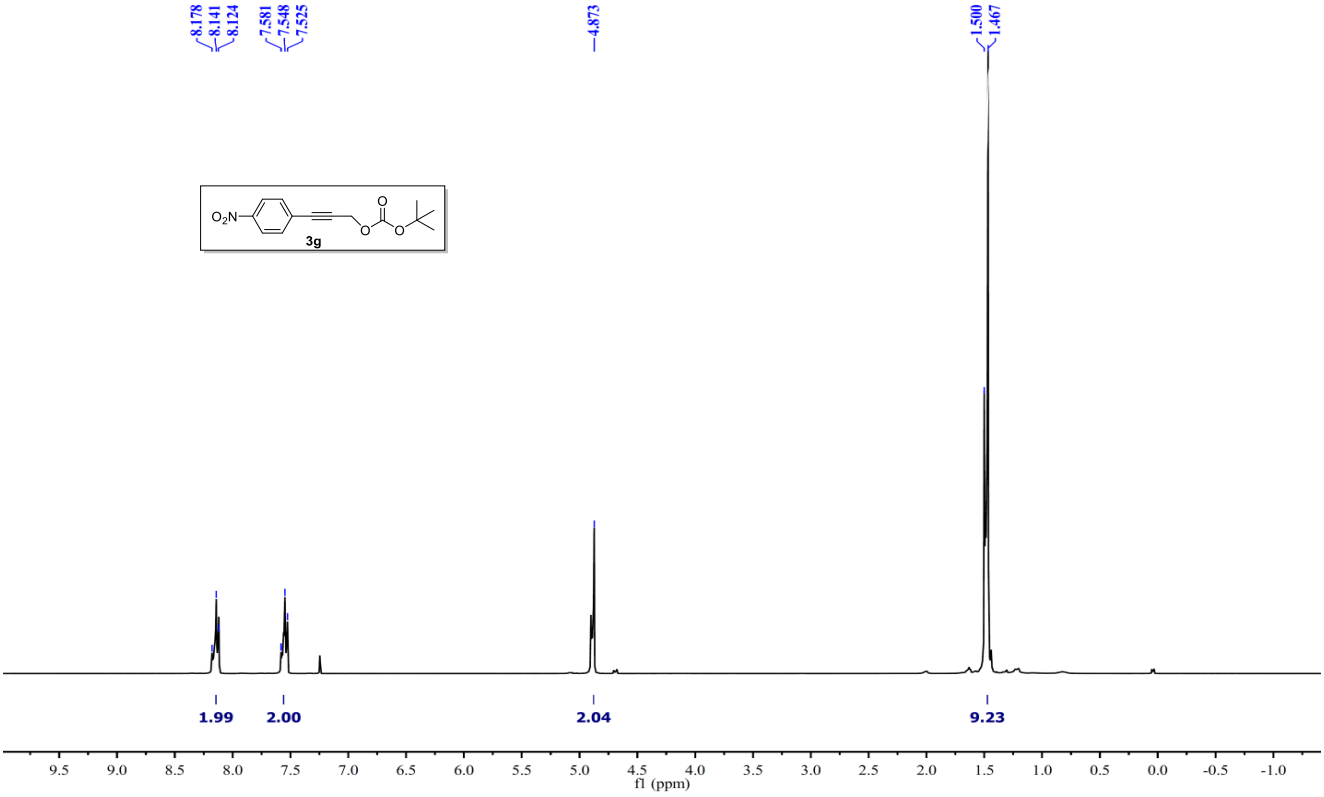
$^{13}C\{^{1}H\}$ NMR (100 MHz) of **3e** :



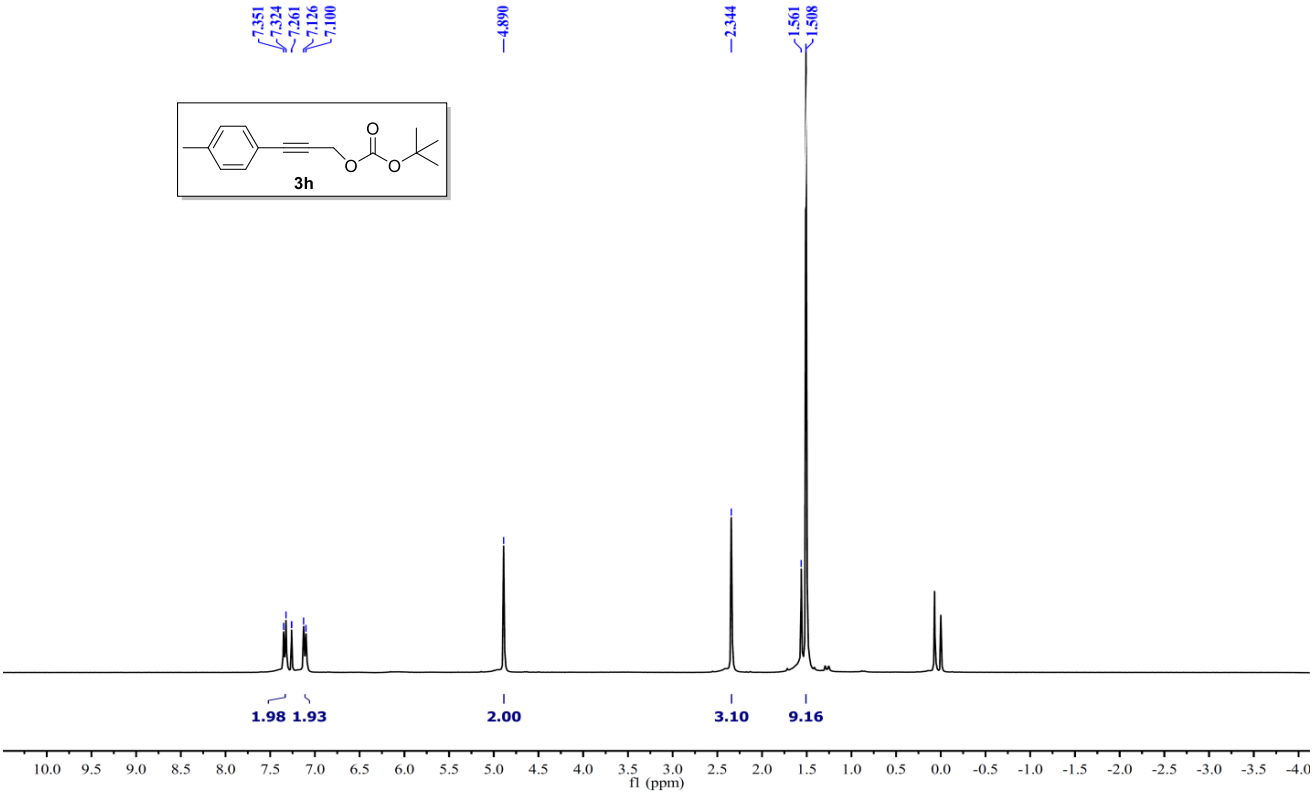
^{1}H NMR (400 MHz) of **3f :**



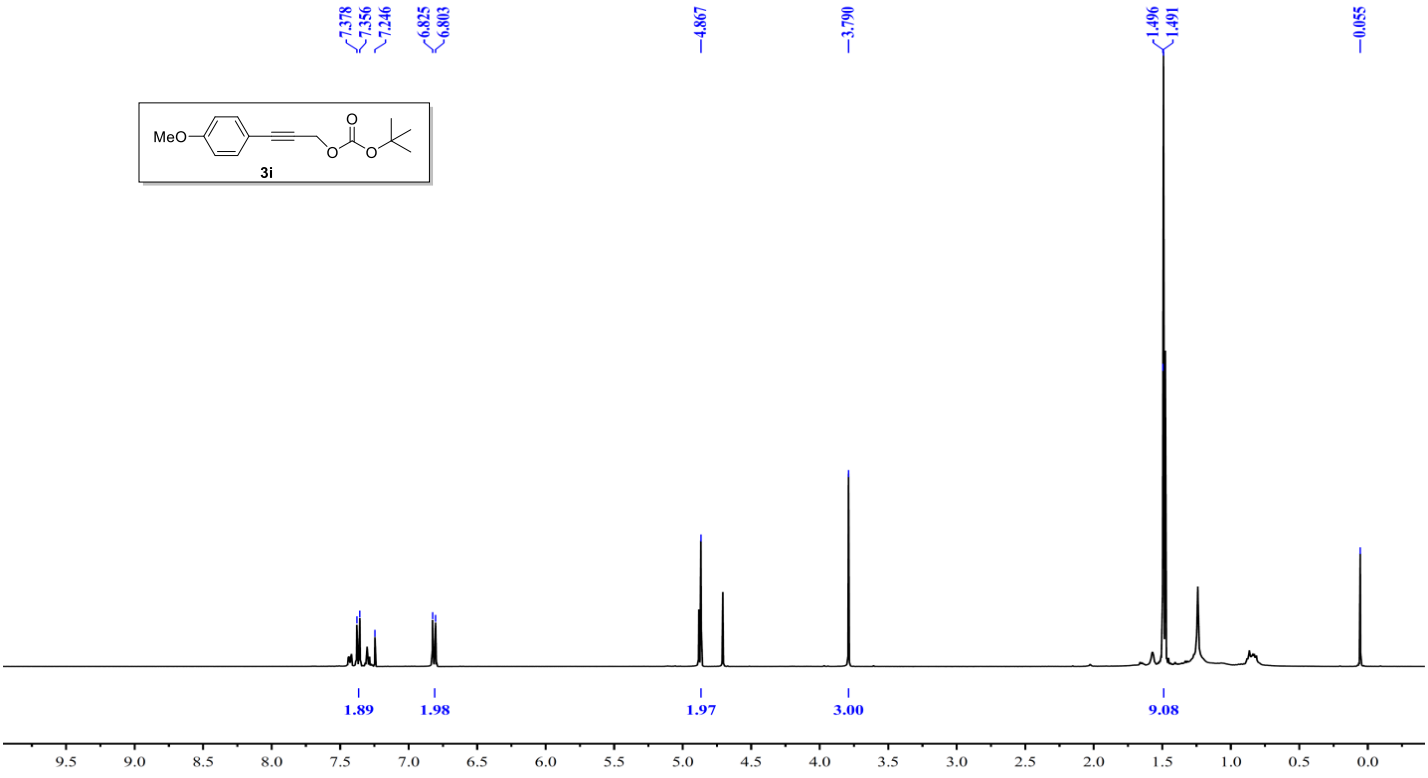
^{1}H NMR (400 MHz) of **3g :**



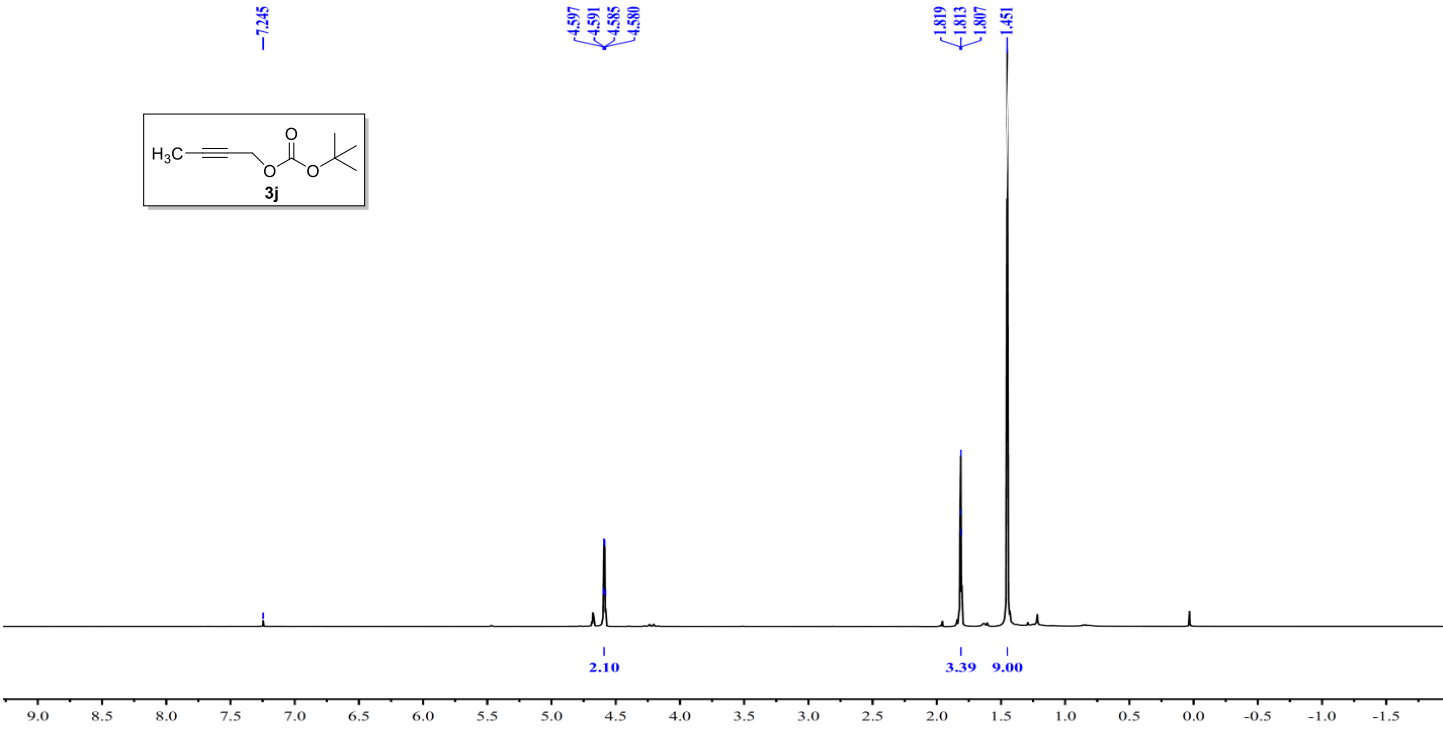
^{1}H NMR (400 MHz) of **3h :**



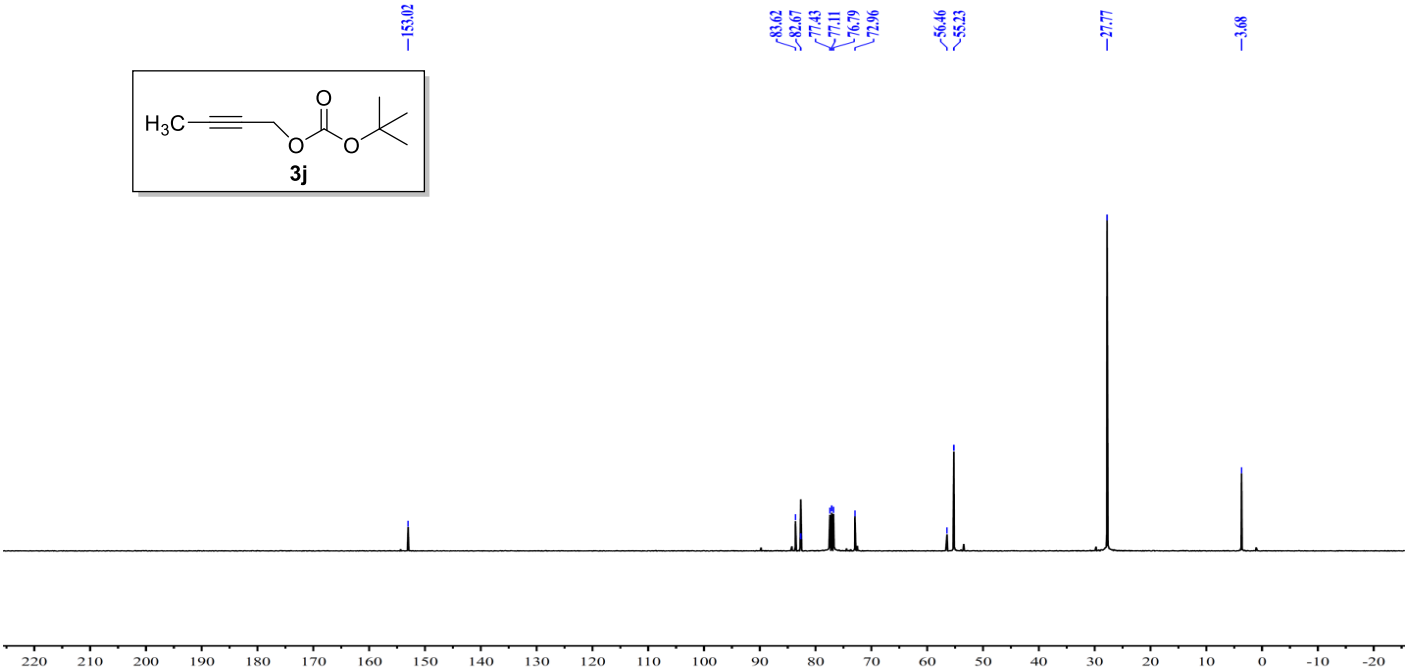
^{1}H NMR (400 MHz) of **3i :**



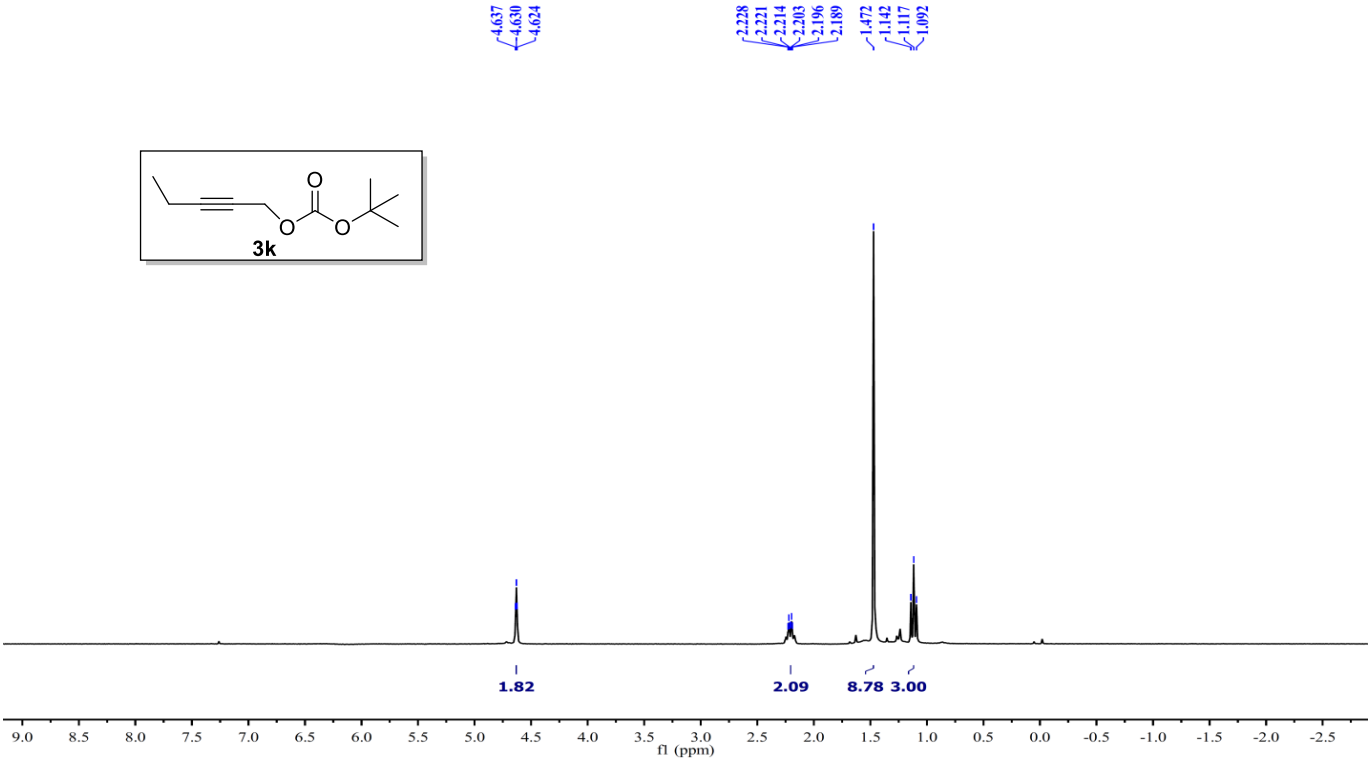
^{1}H NMR (400 MHz) of **3j :**



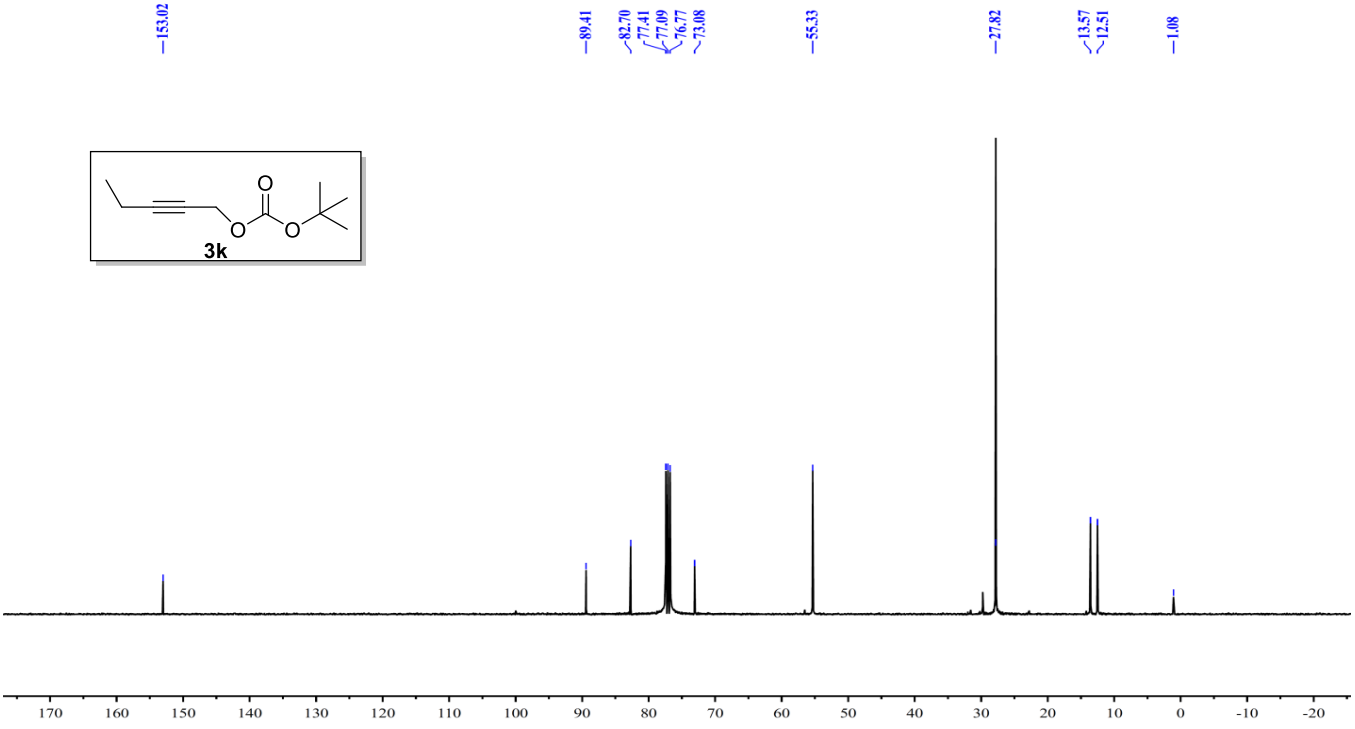
^{13}C{^{1}H} NMR (100 MHz) of **3j** :



^{1}H NMR (400 MHz) of **3k :**

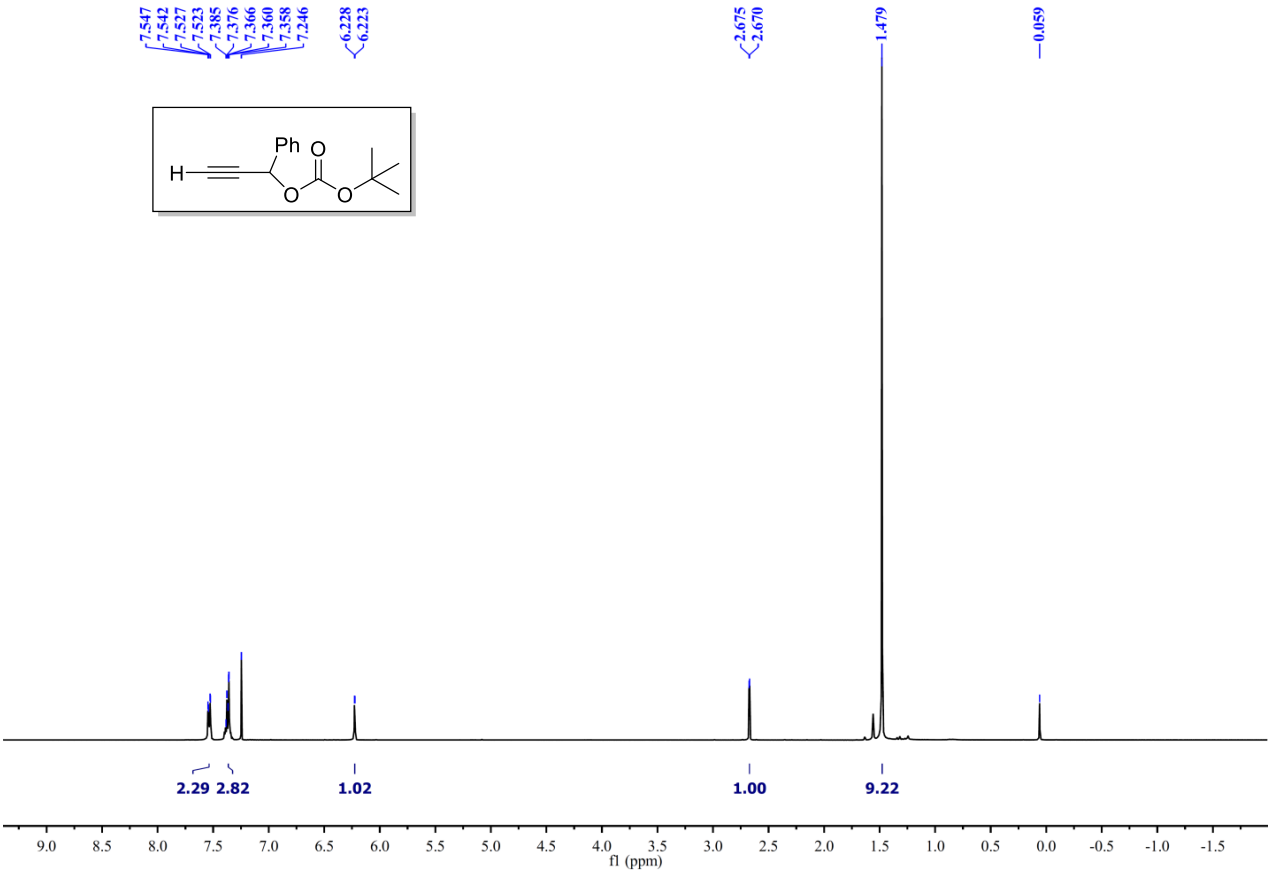


^{13}C{^{1}H} NMR (100 MHz) of **3k** :



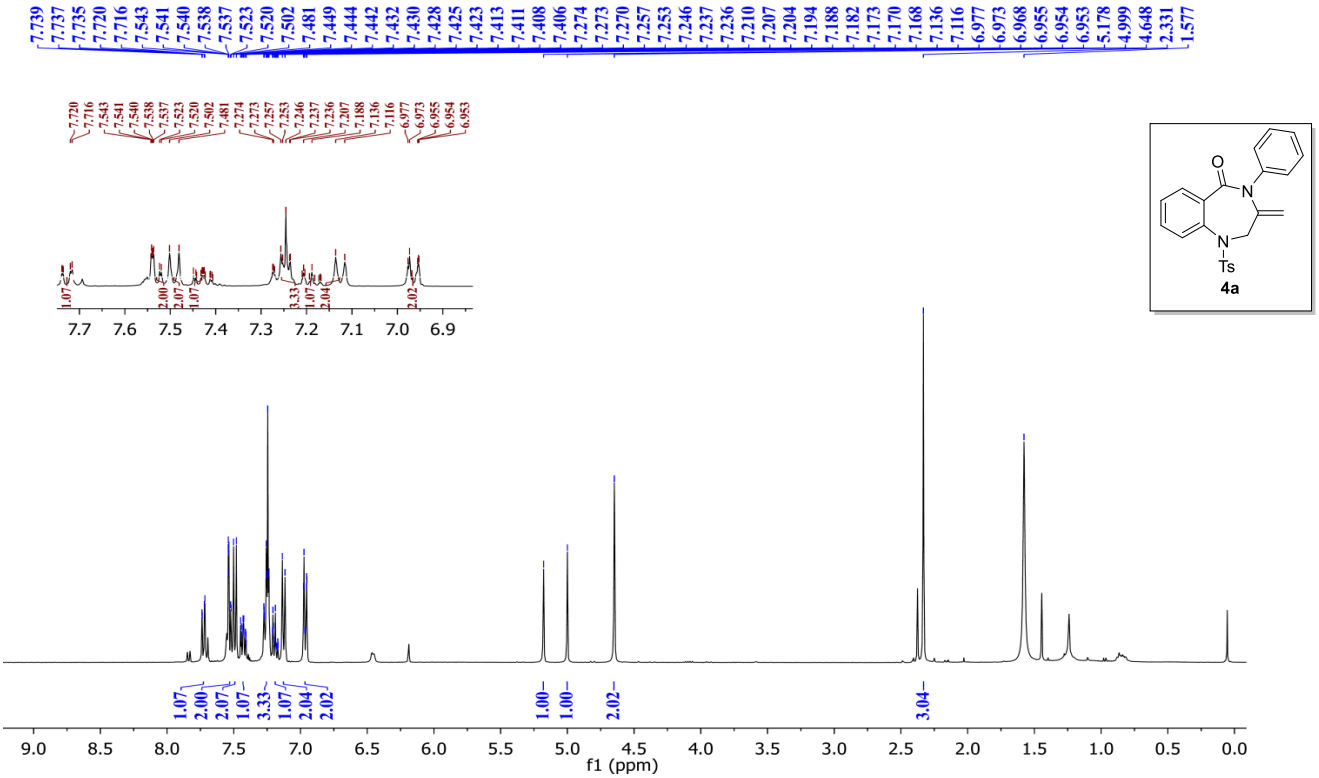
41. NMR spectra of substrates 3b':

^{1}H NMR (400 MHz) of **3b'** :

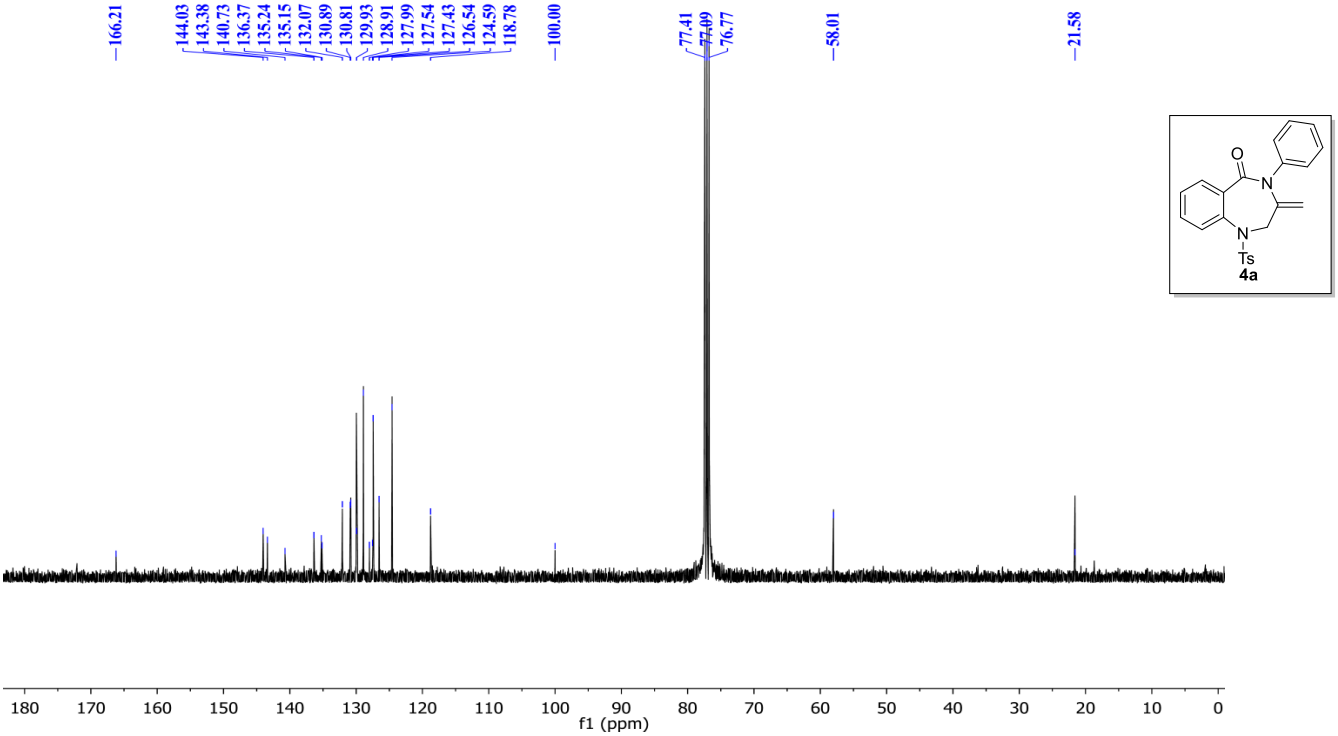


42. NMR spectra of products 4a-4q:

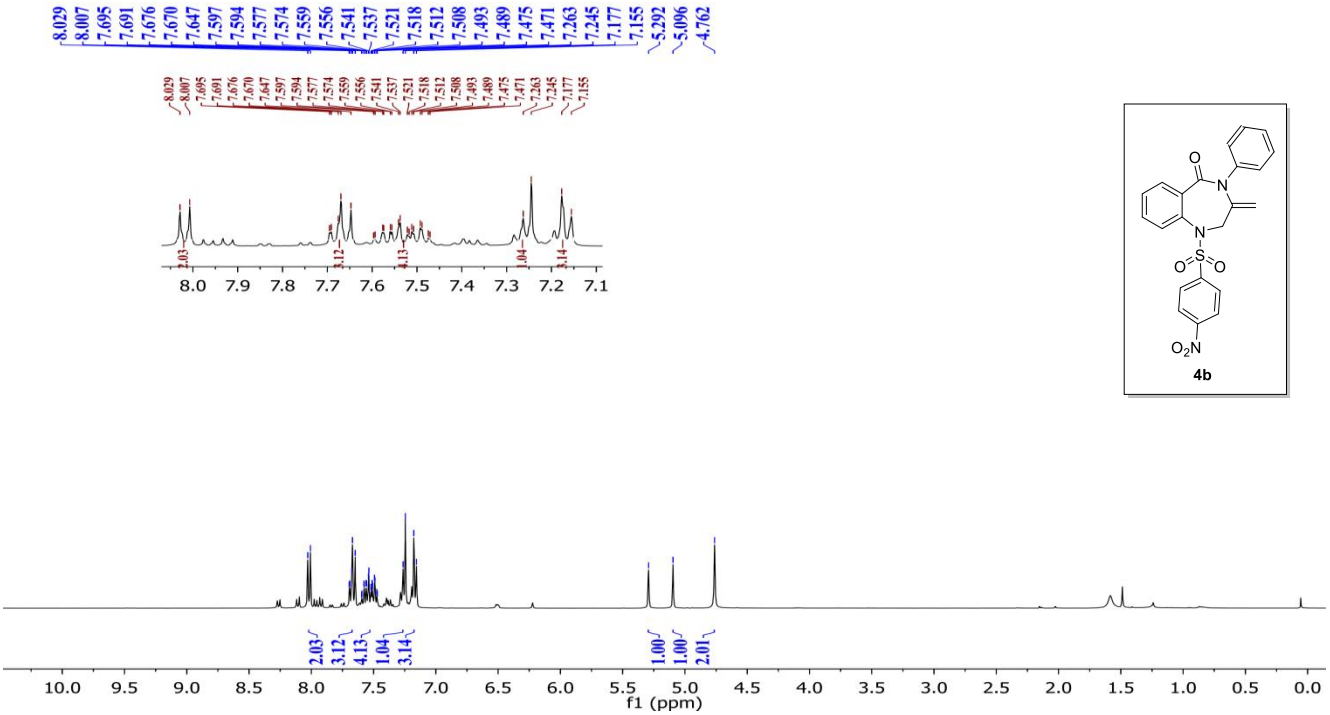
^{1}H NMR (400 MHz) of **4a**:



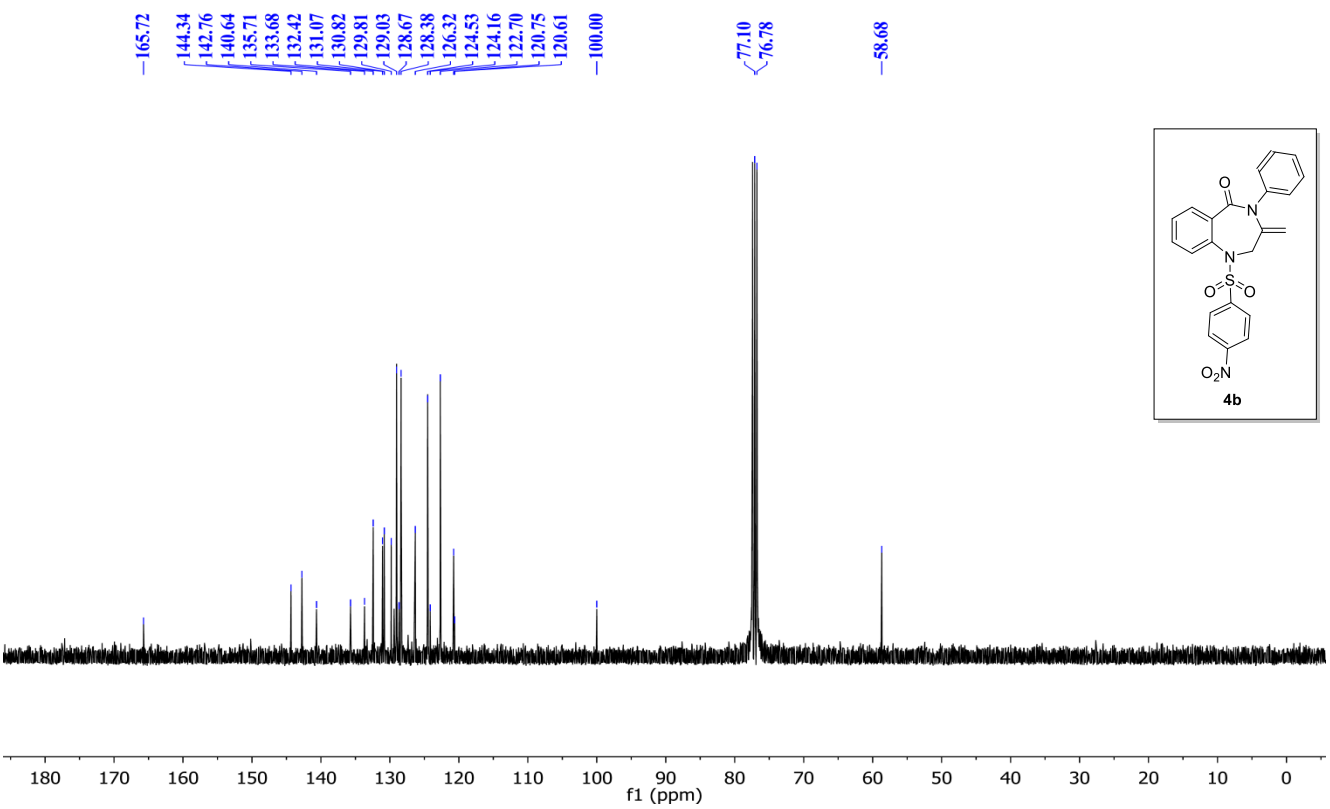
^{13}C{^{1}H} NMR (100 MHz) of **4a**:



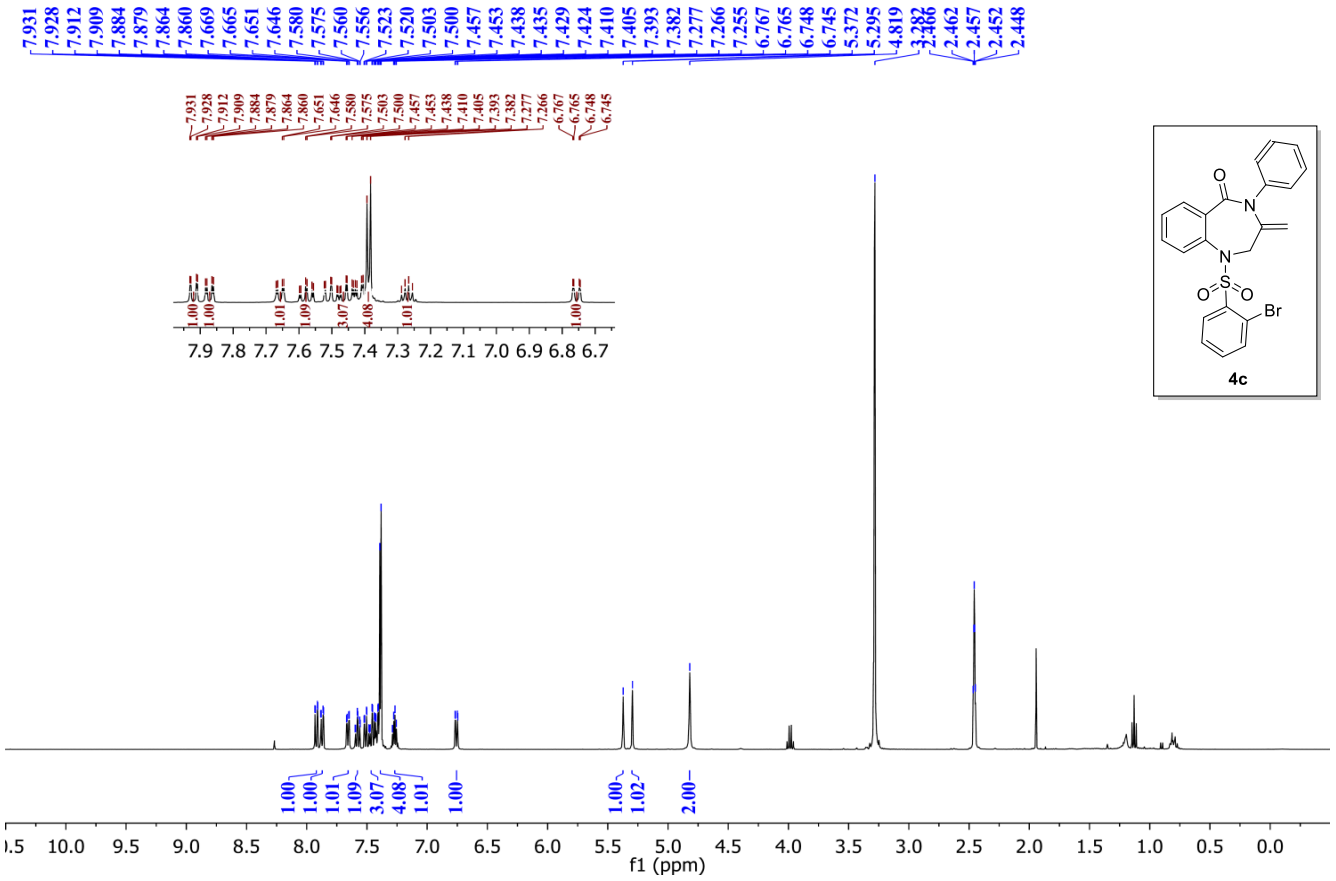
^{1}H NMR (400 MHz) of **4b**:



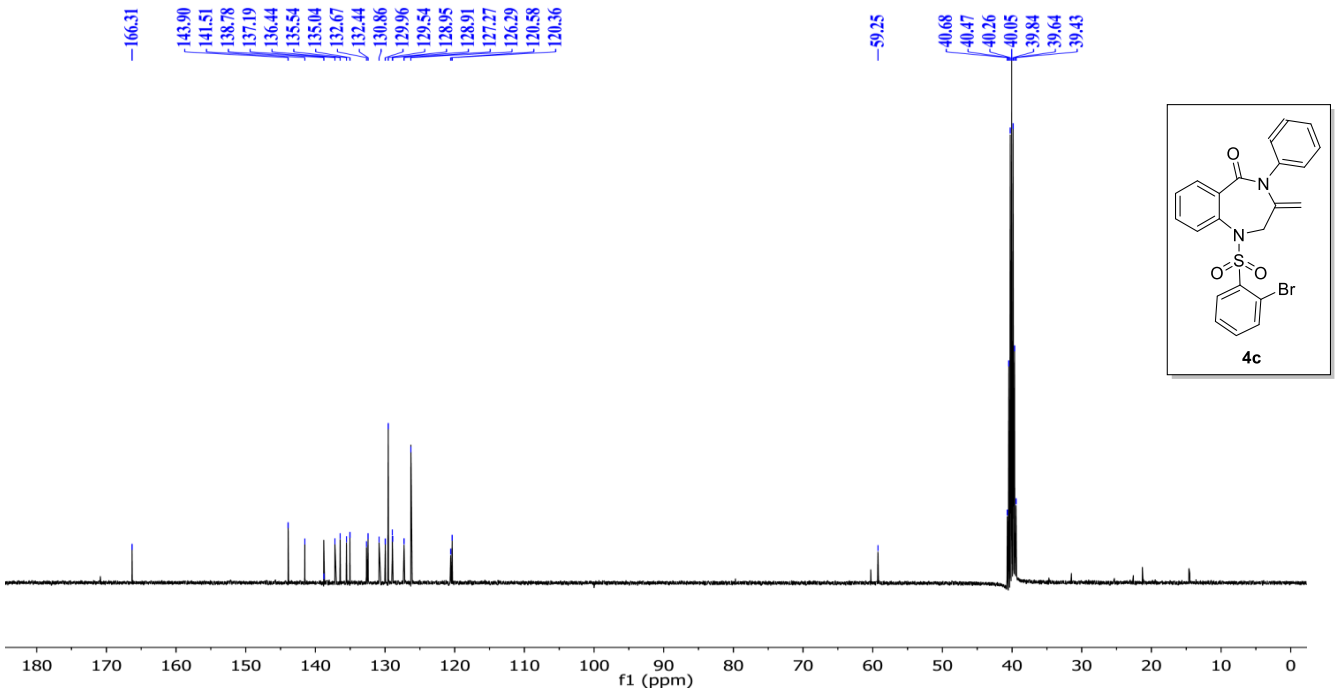
^{13}C{^{1}H} NMR (100 MHz) of **4b**:



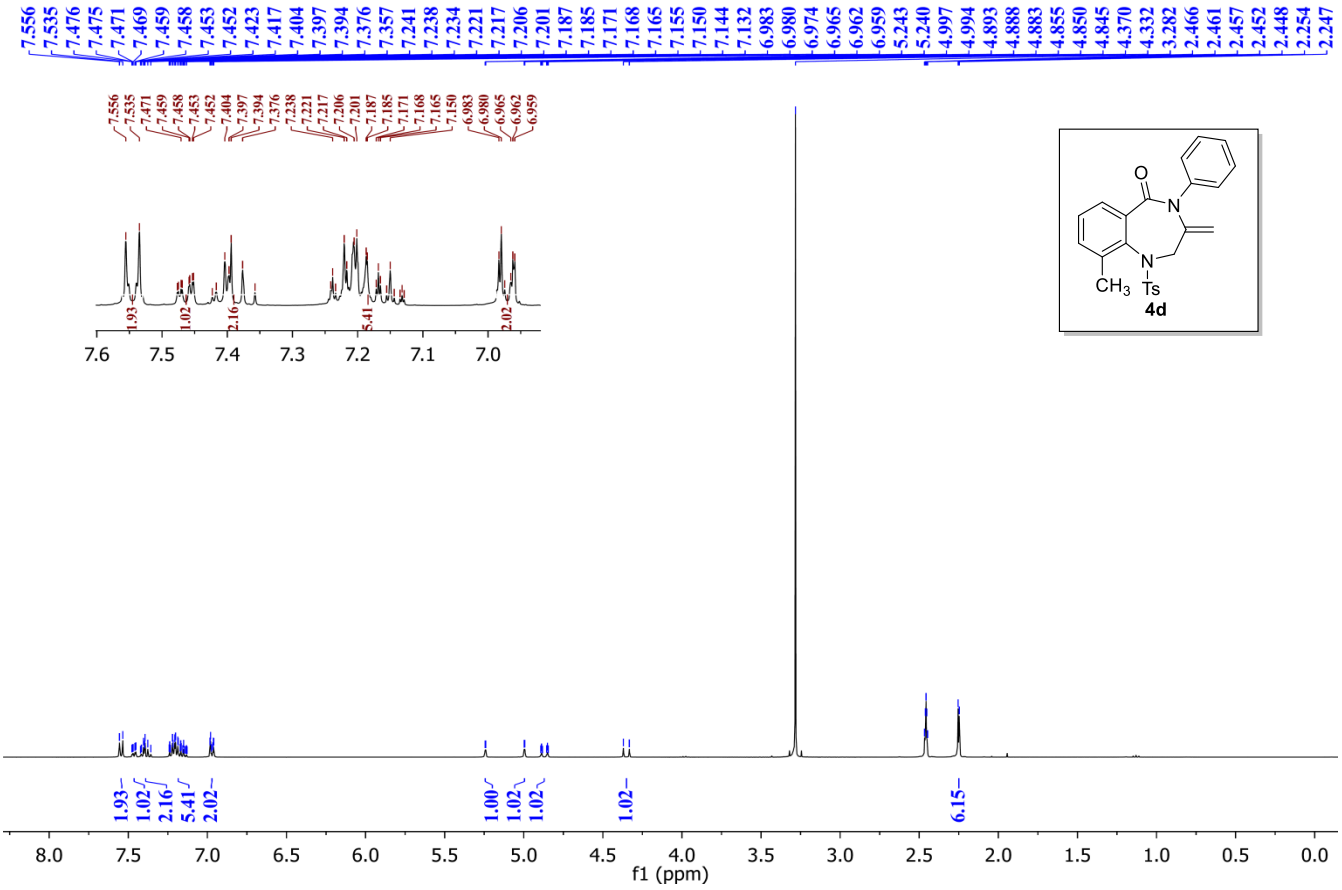
^{1}H NMR (400 MHz) of **4c:**



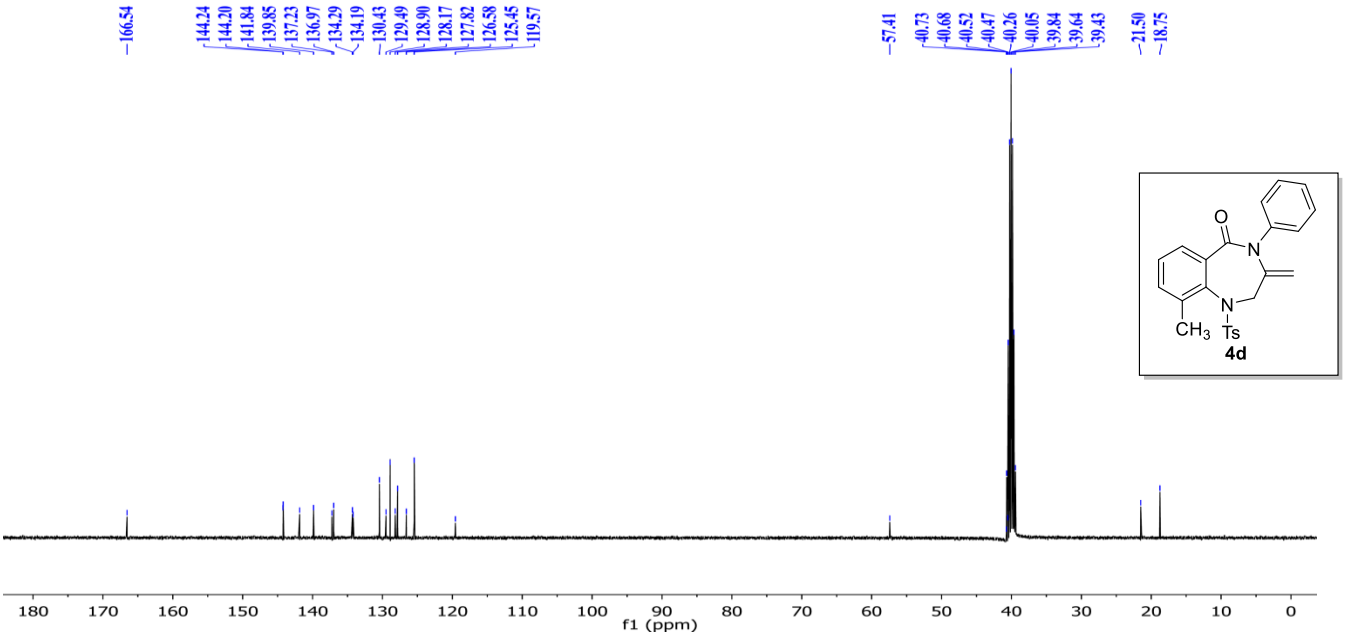
^{13}C{^{1}H} NMR (100 MHz) of **4c**:



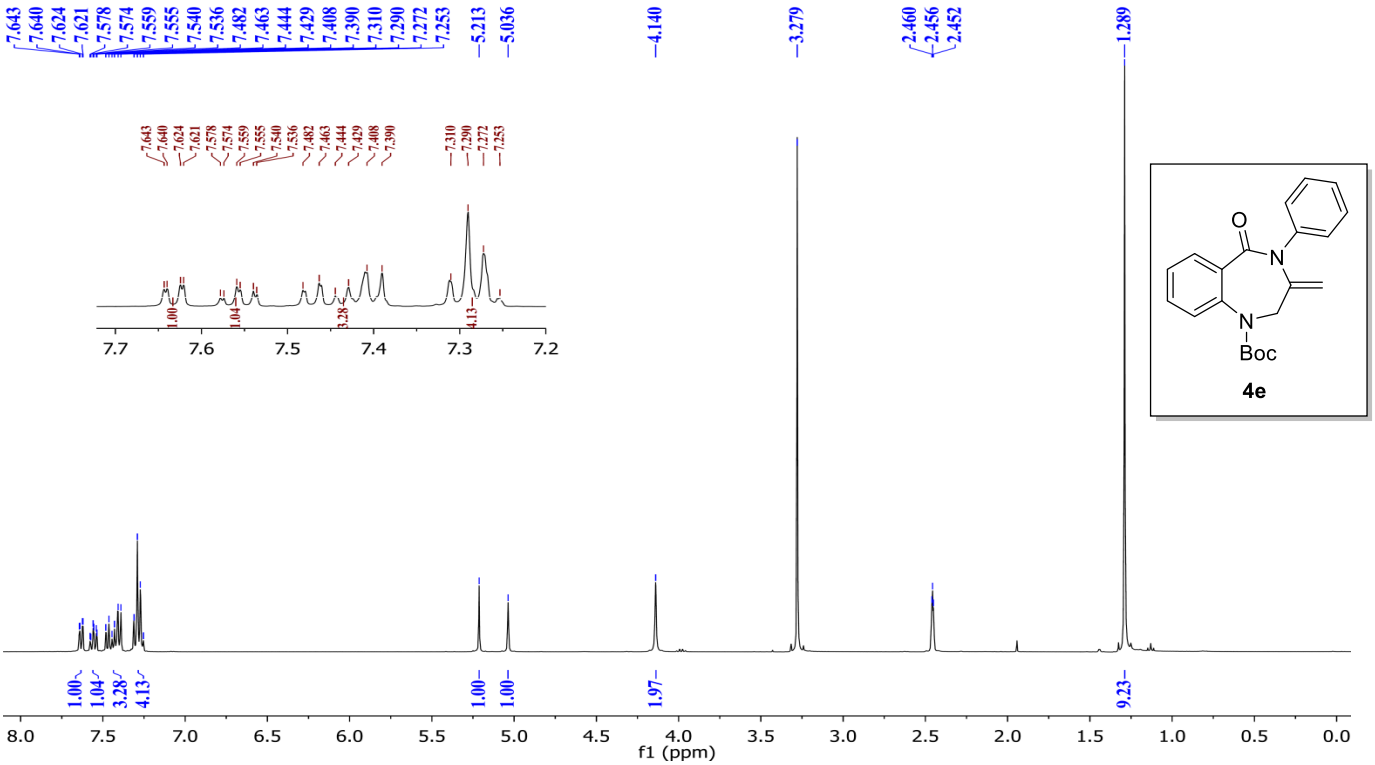
^{1}H NMR (400 MHz) of **4d:**



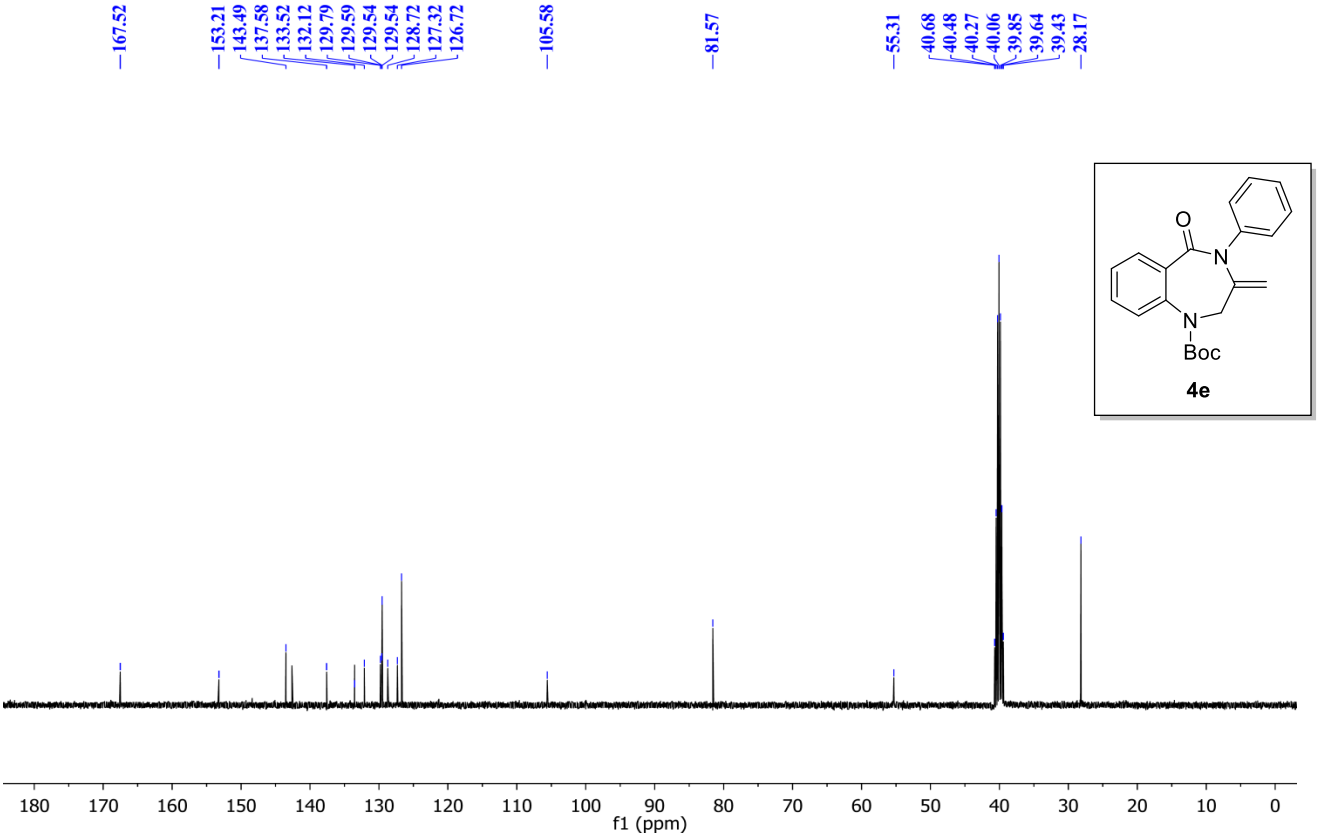
^{13}C{^{1}H} NMR (100 MHz) of **4d**:



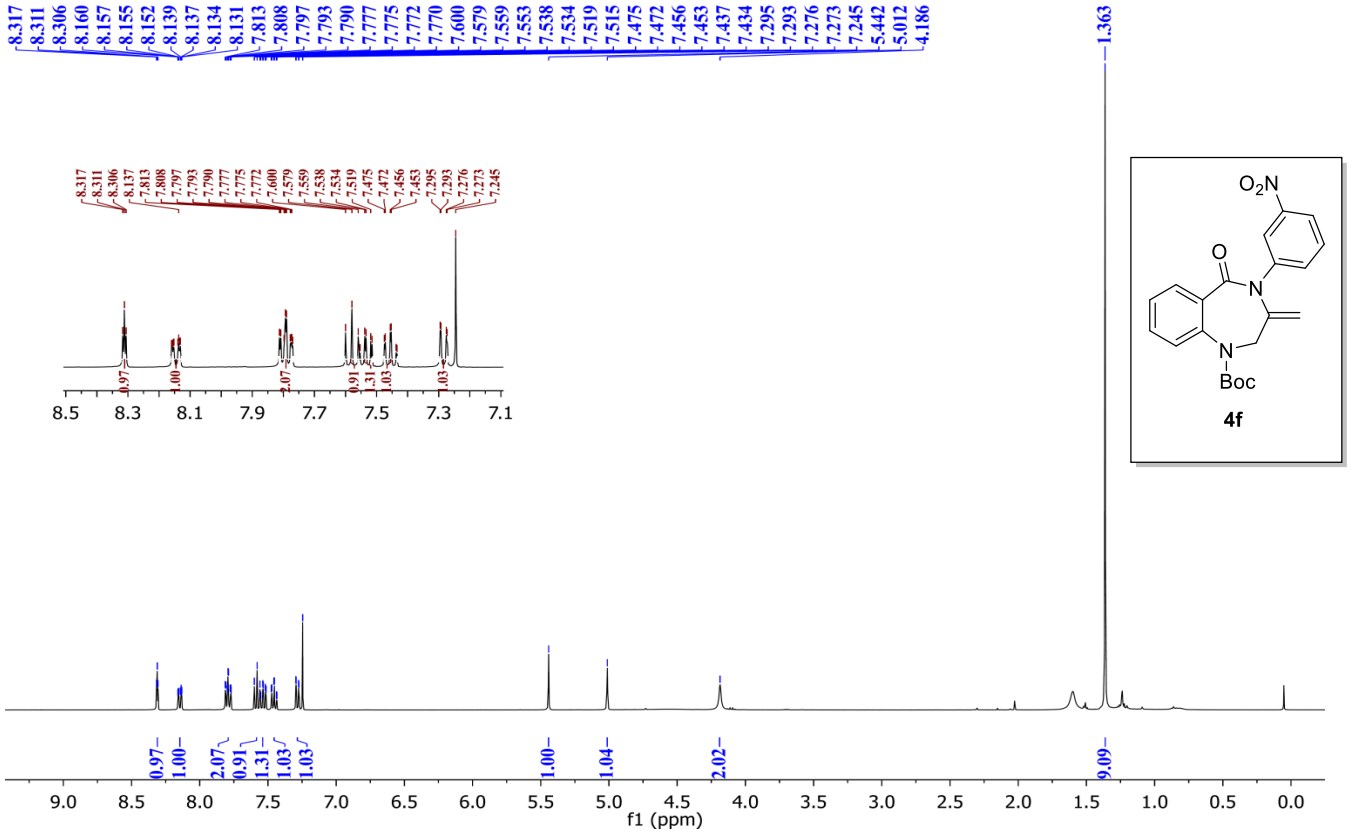
^{1}H NMR (400 MHz) of **4e**:



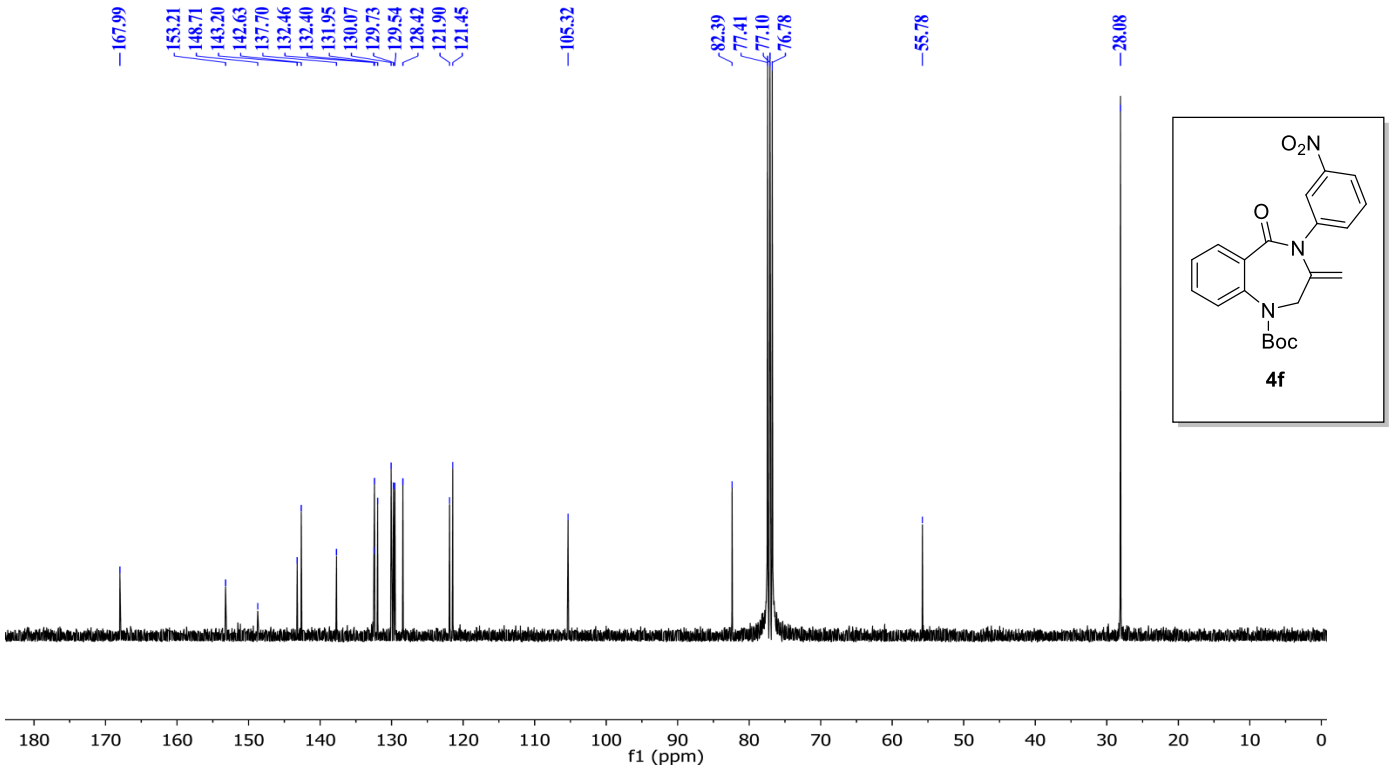
^{13}C{^{1}H} NMR (100 MHz) of **4e**:



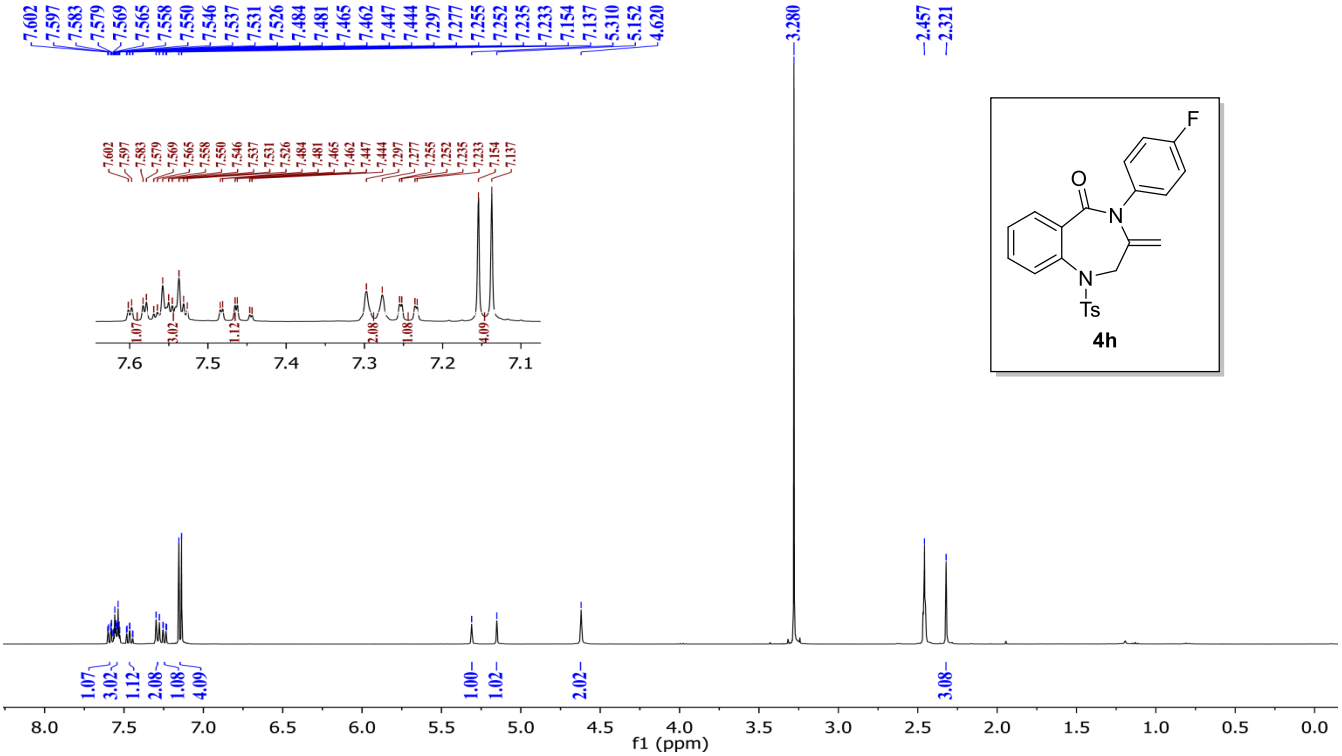
^{1}H NMR (400 MHz) of **4f**:



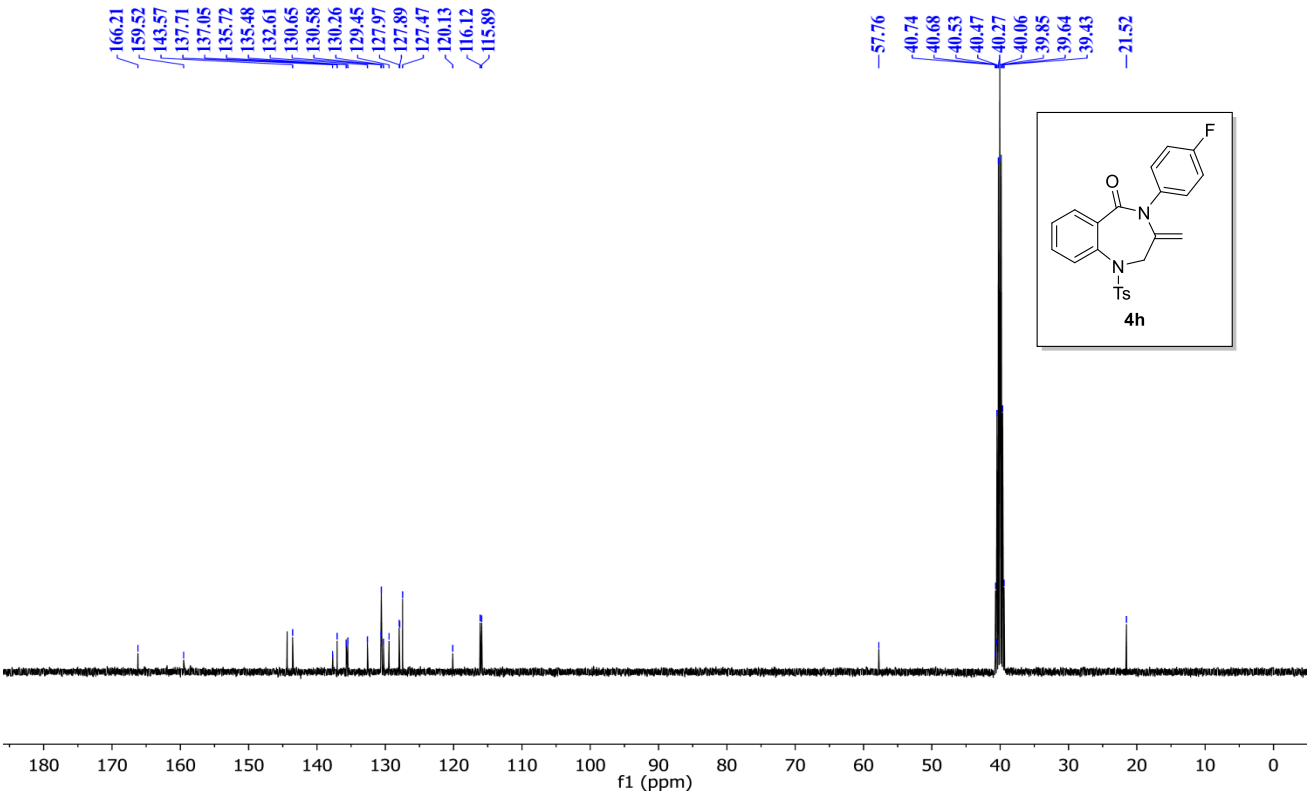
^{13}C{^{1}H} NMR (100 MHz) of **4f**:



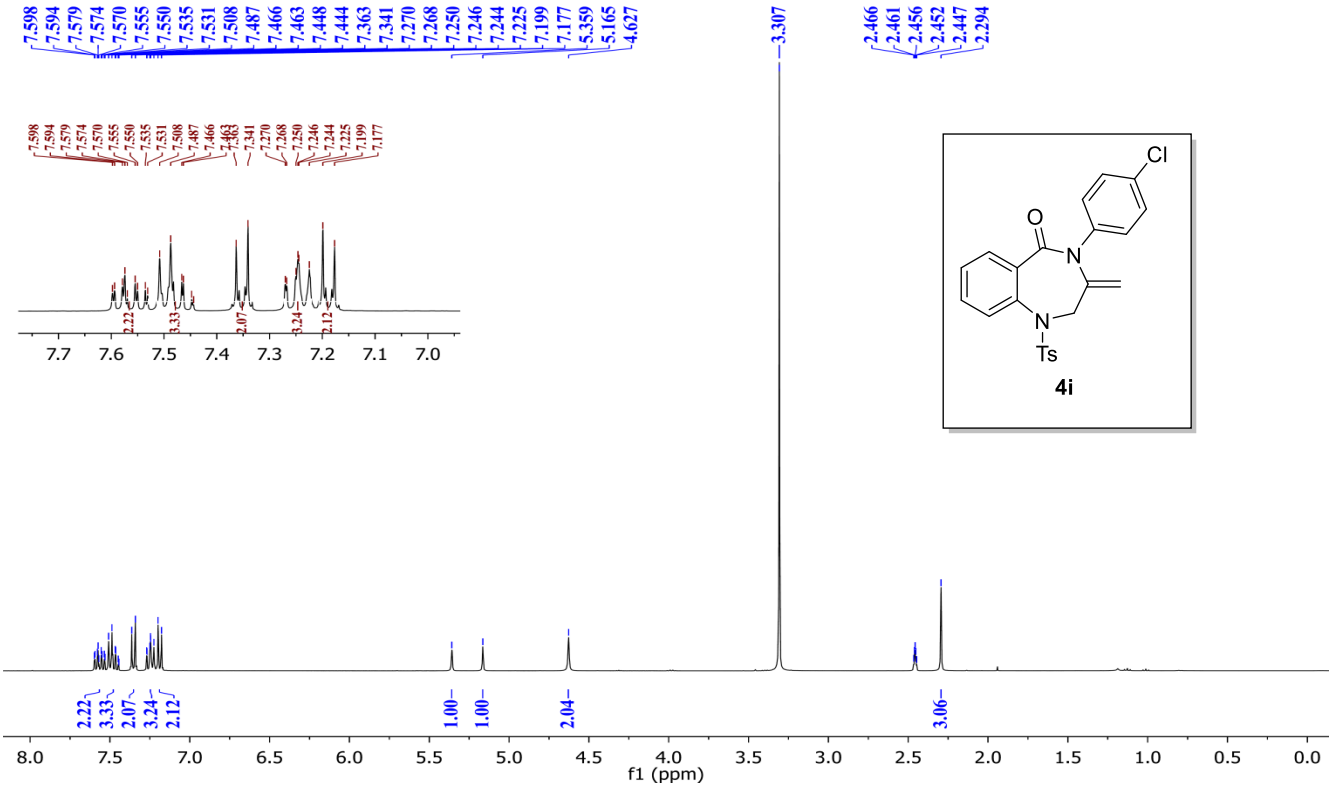
^{1}H NMR (400 MHz) of **4h**:



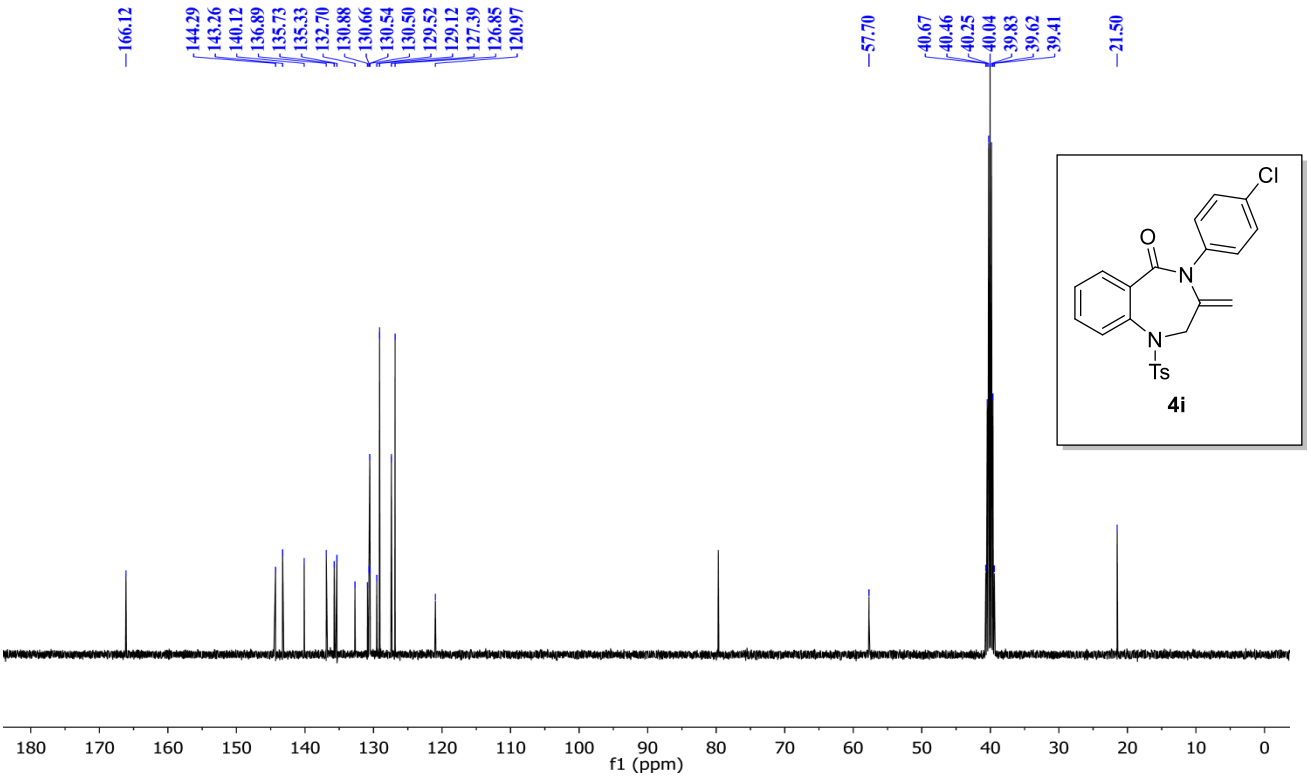
^{13}C{^{1}H} NMR (100 MHz) of **4h**:



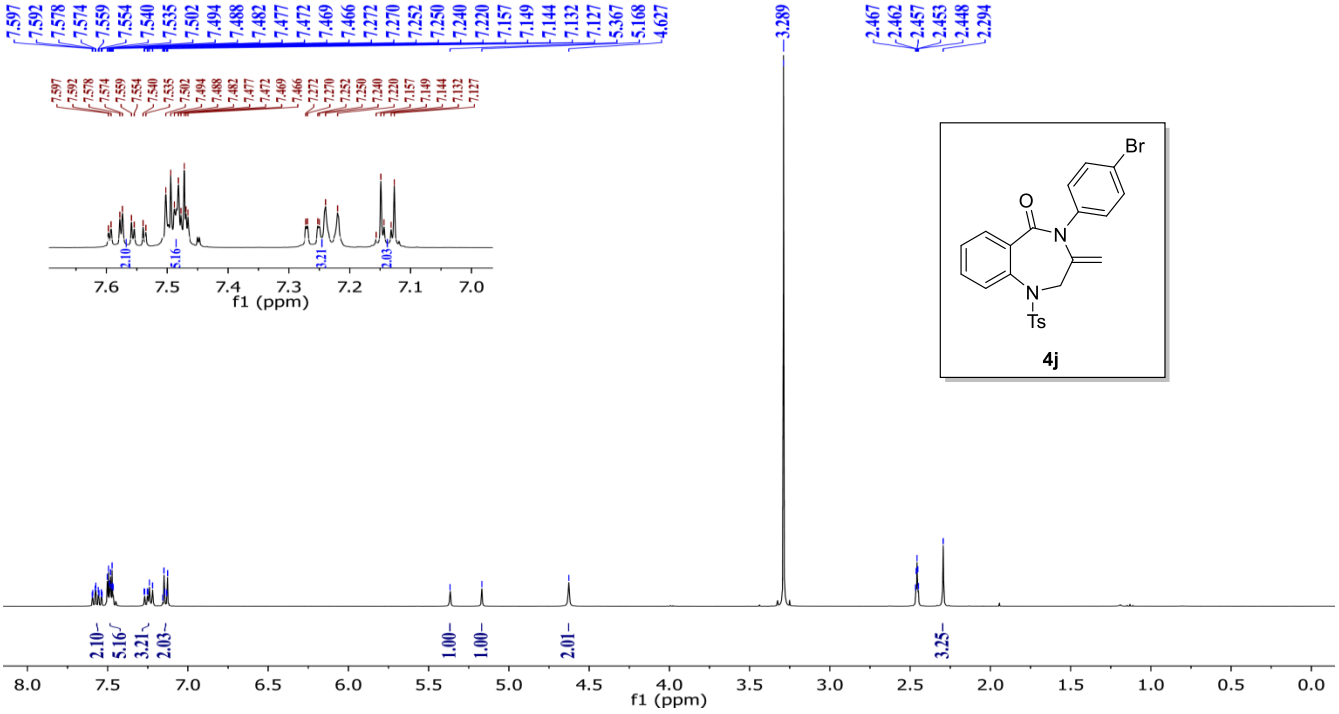
^{1}H NMR (400 MHz) of **4i**:



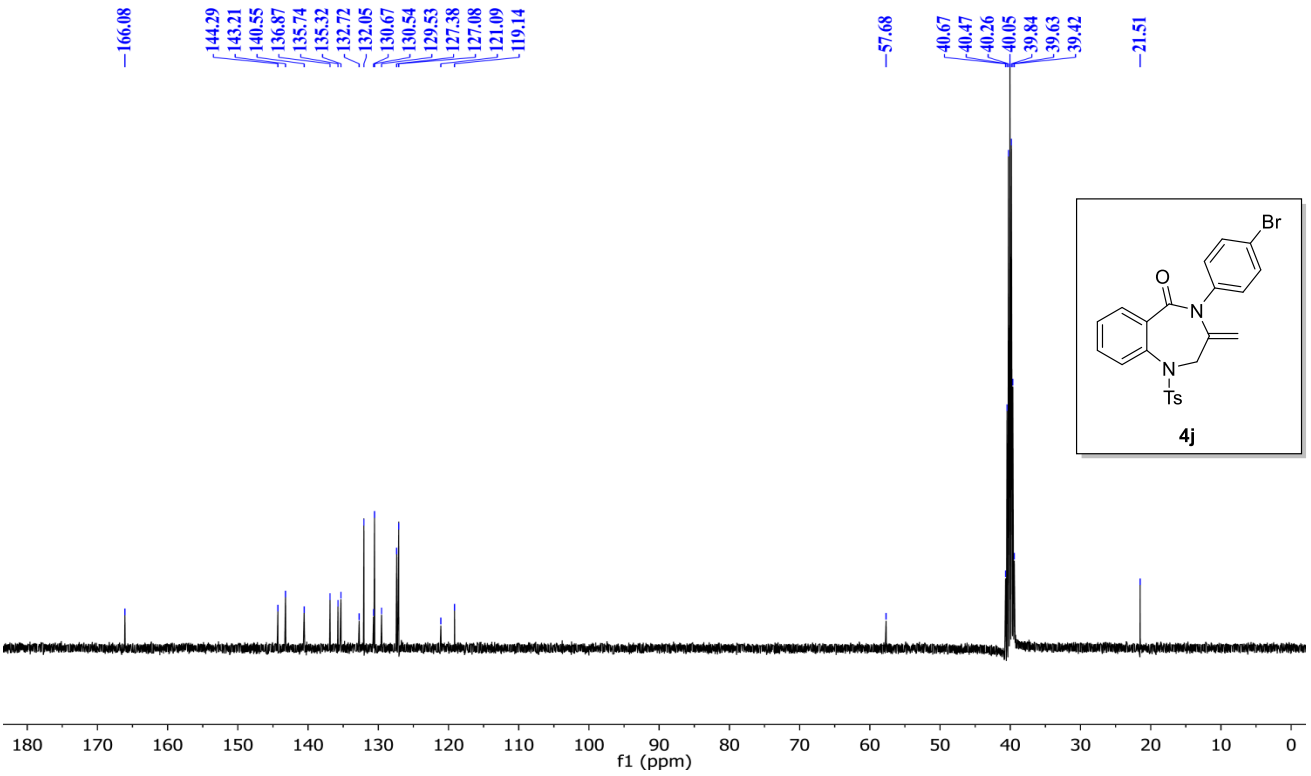
^{13}C{^{1}H} NMR (100 MHz) of **4i**:



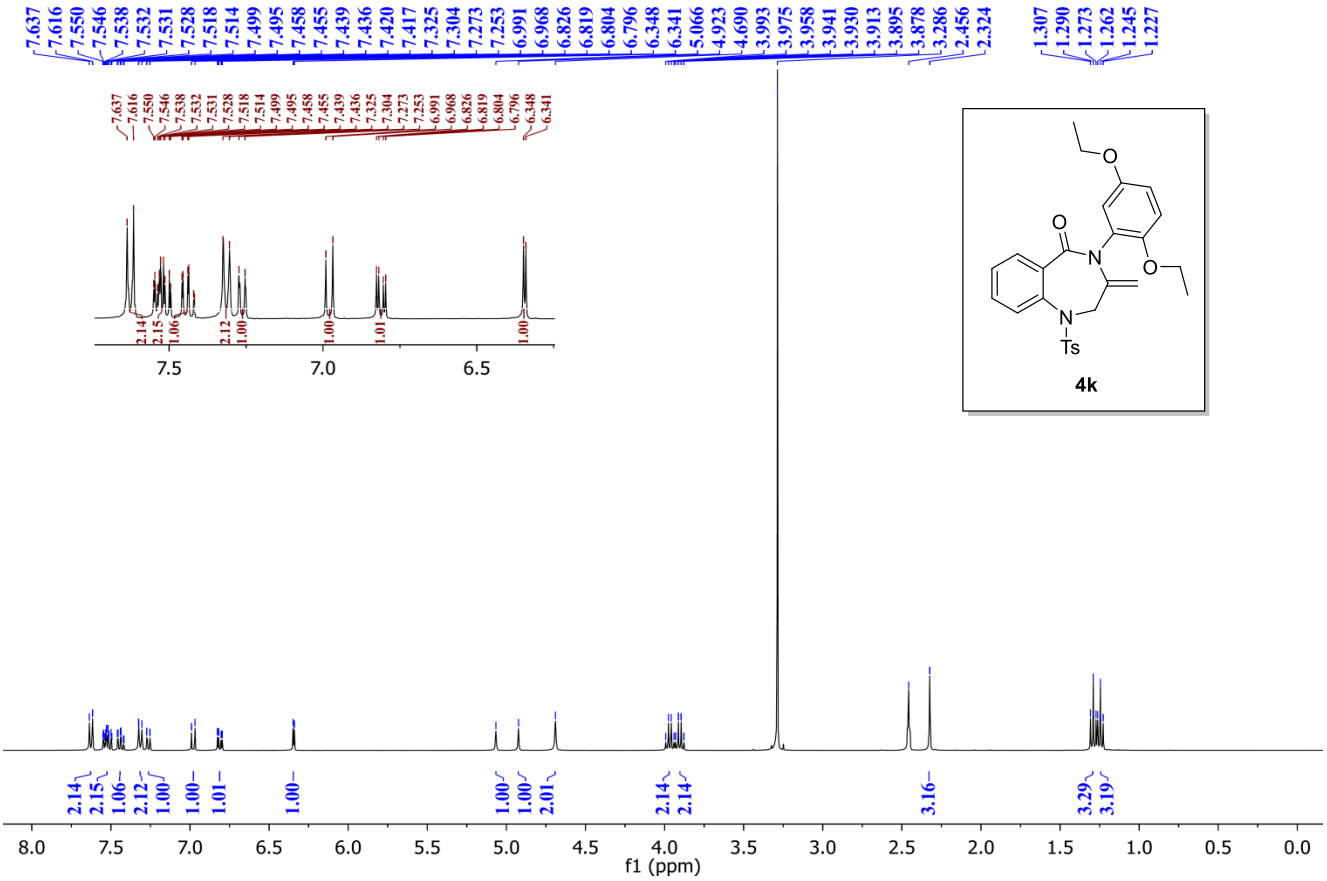
^{1}H NMR (400 MHz) of **4j**:



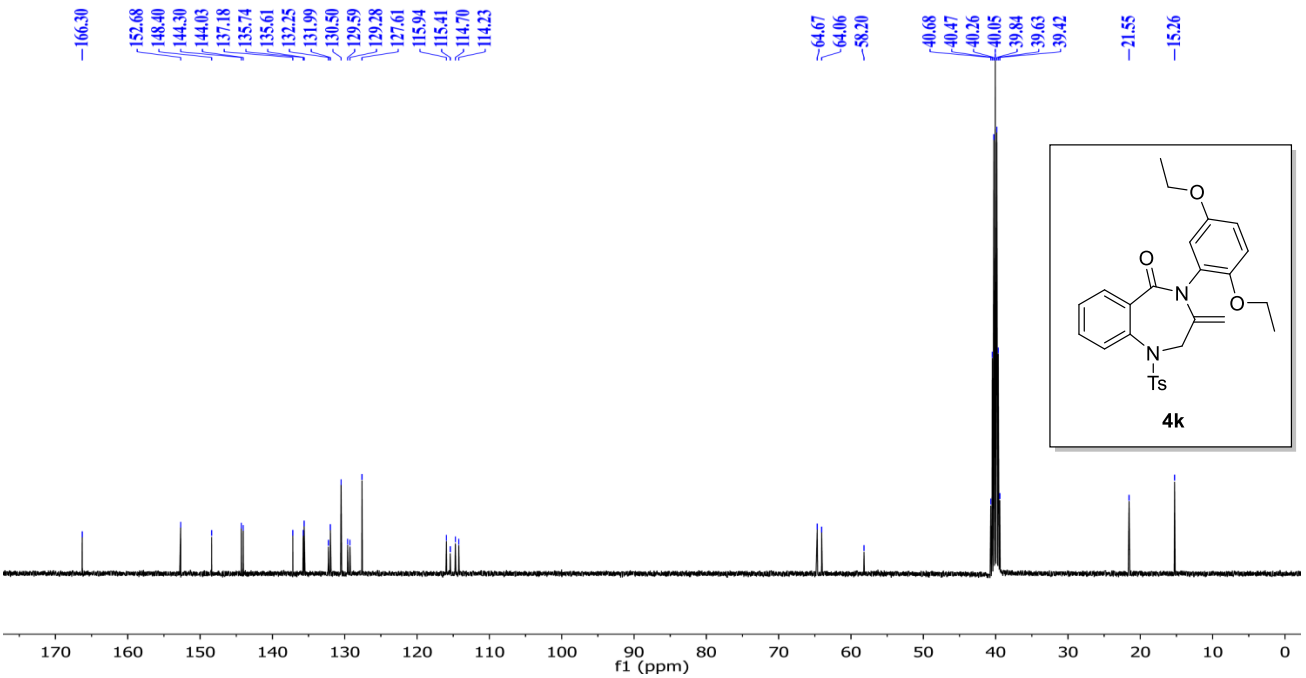
^{13}C{^{1}H} NMR (100 MHz) of **4j**:



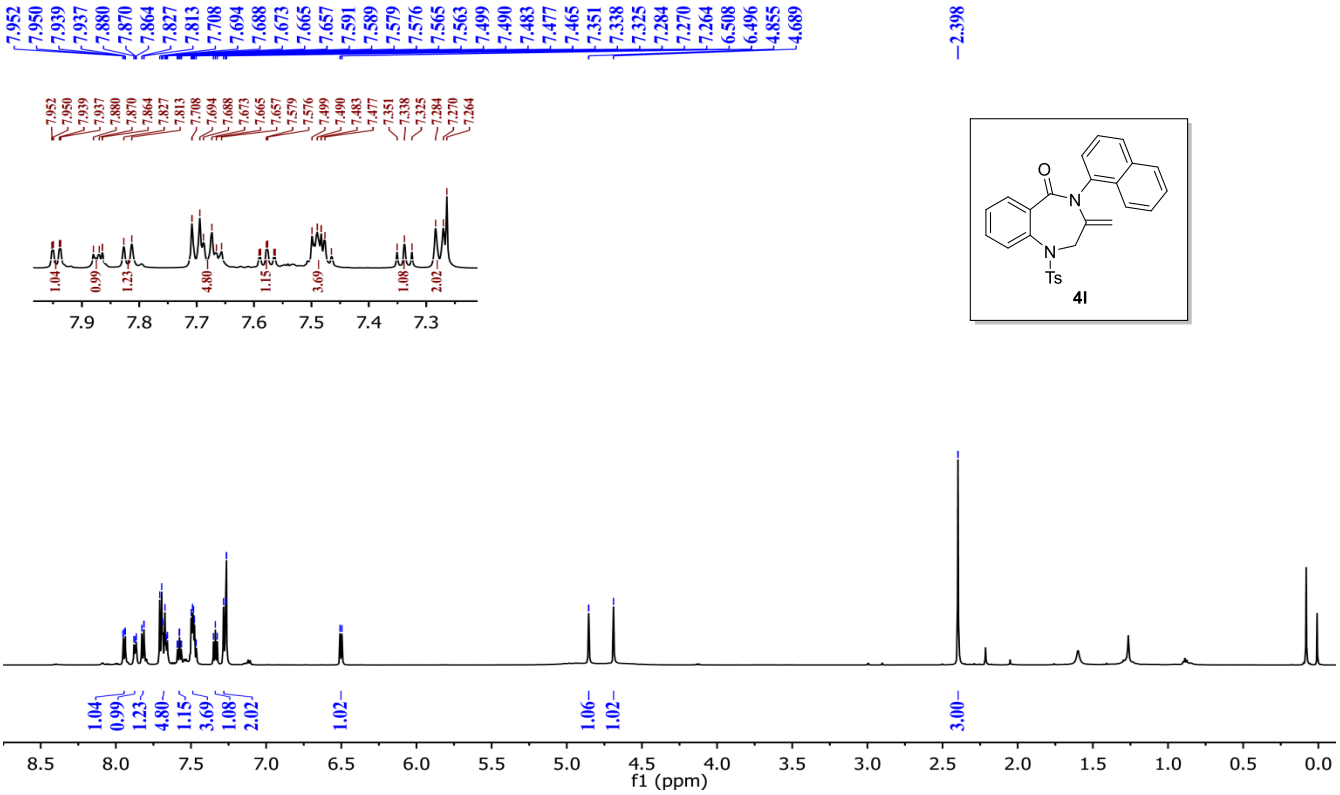
^{1}H NMR (400 MHz) of **4k**:



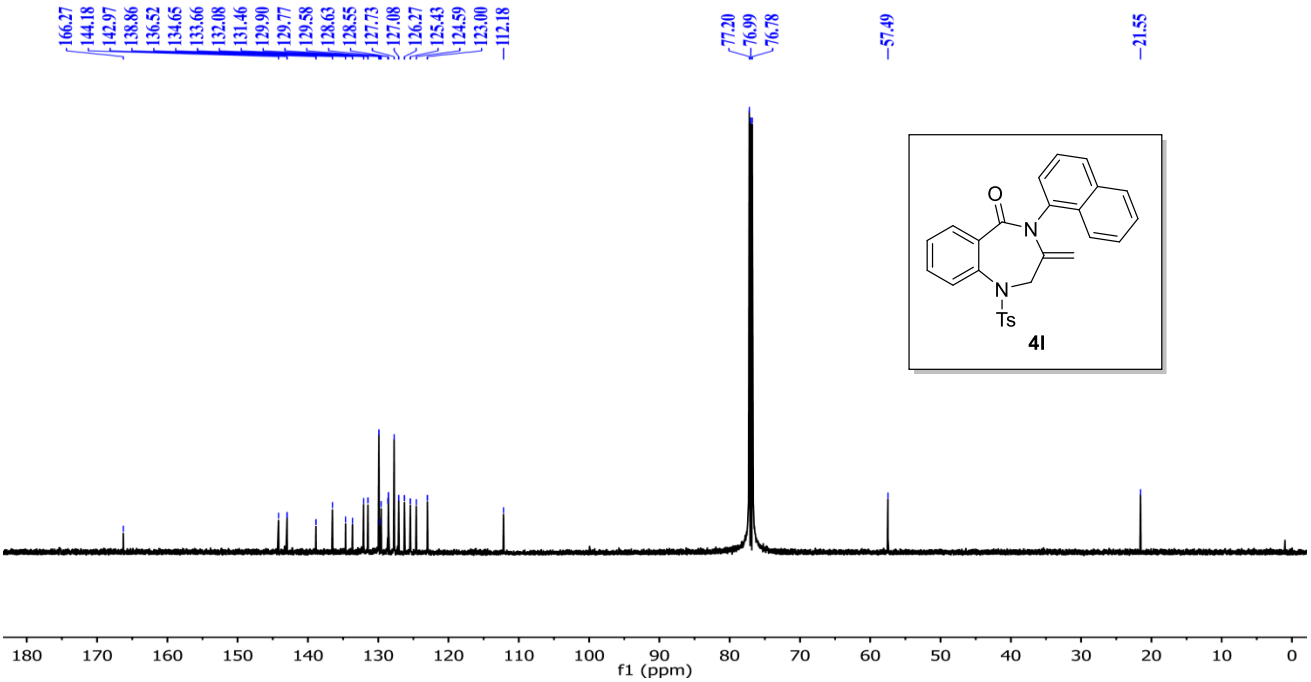
^{13}C{^{1}H} NMR (100 MHz) of **4k**:



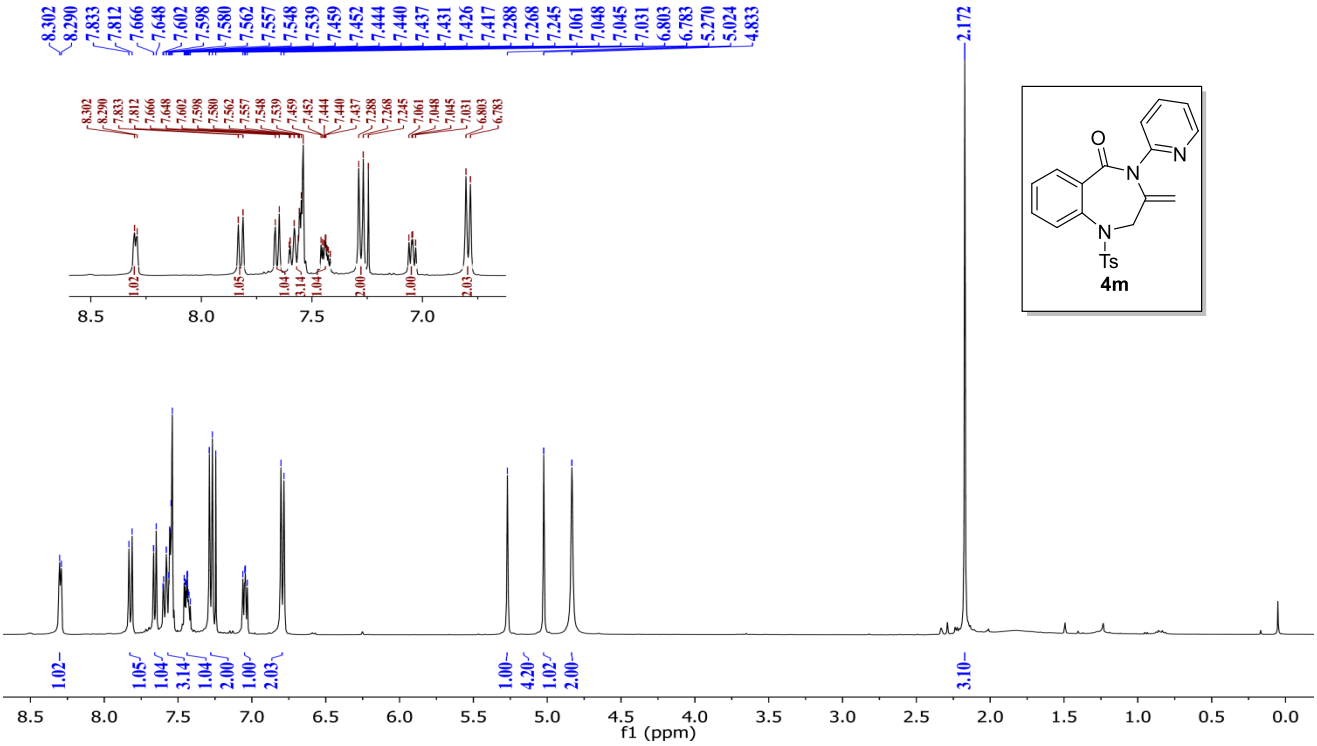
^{1}H NMR (600 MHz) of **4l:**



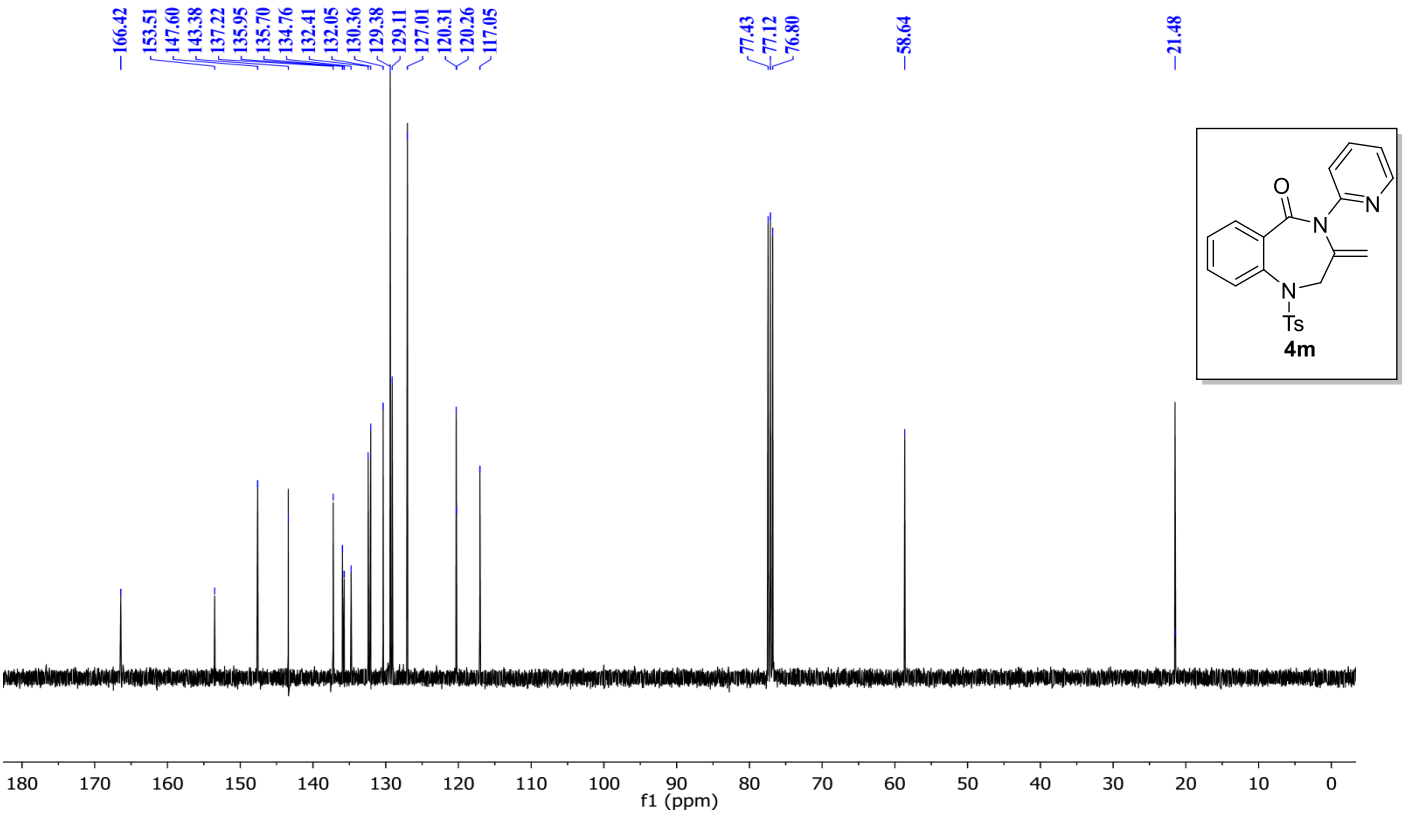
^{13}C{^{1}H} NMR (150 MHz) of **4l**:



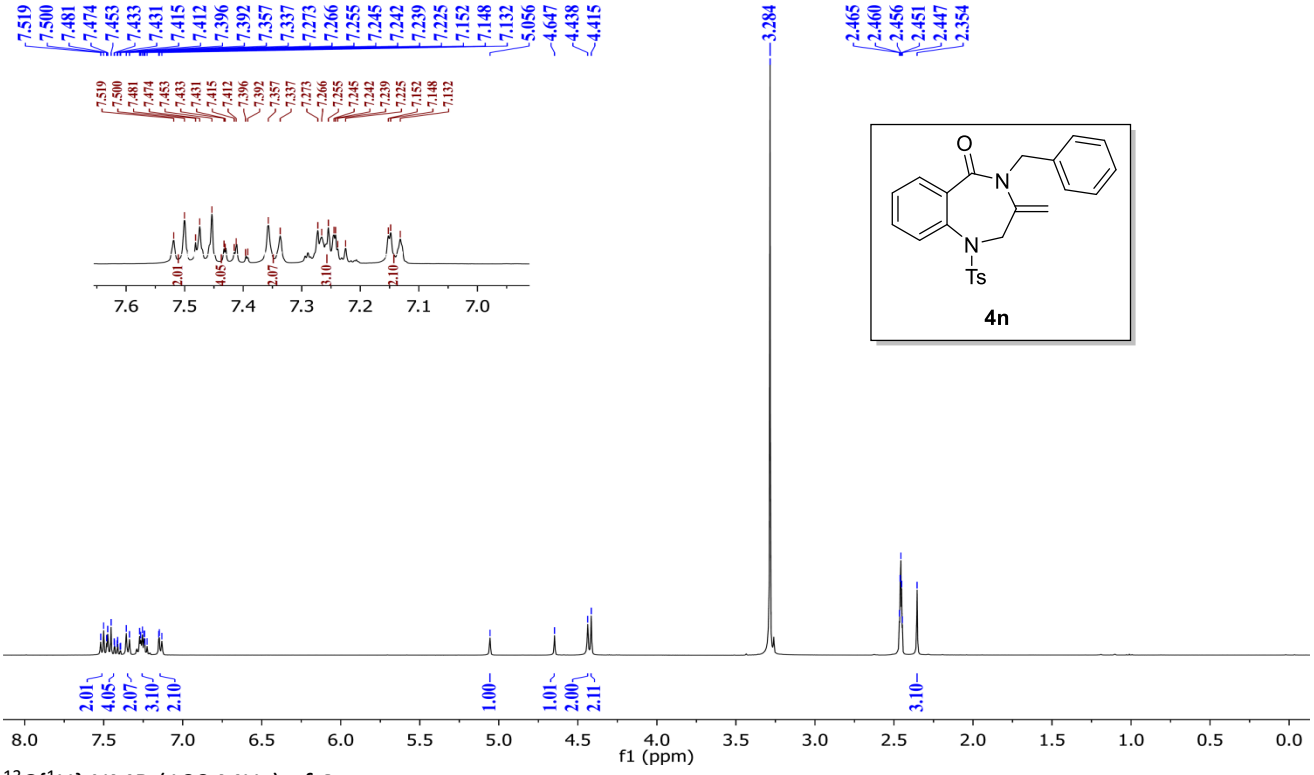
^{1}H NMR (400 MHz) of **4m**:



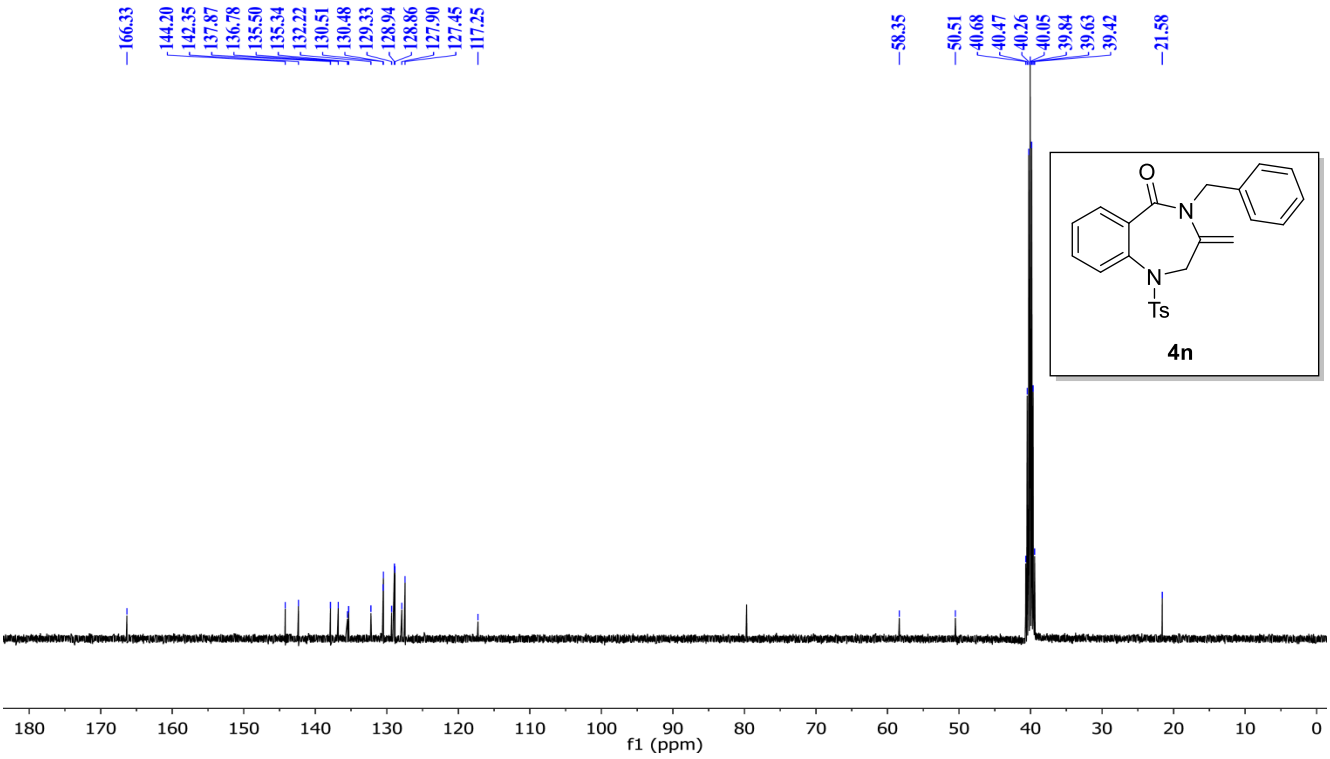
^{13}C{^{1}H} NMR (100 MHz) of **4m**:



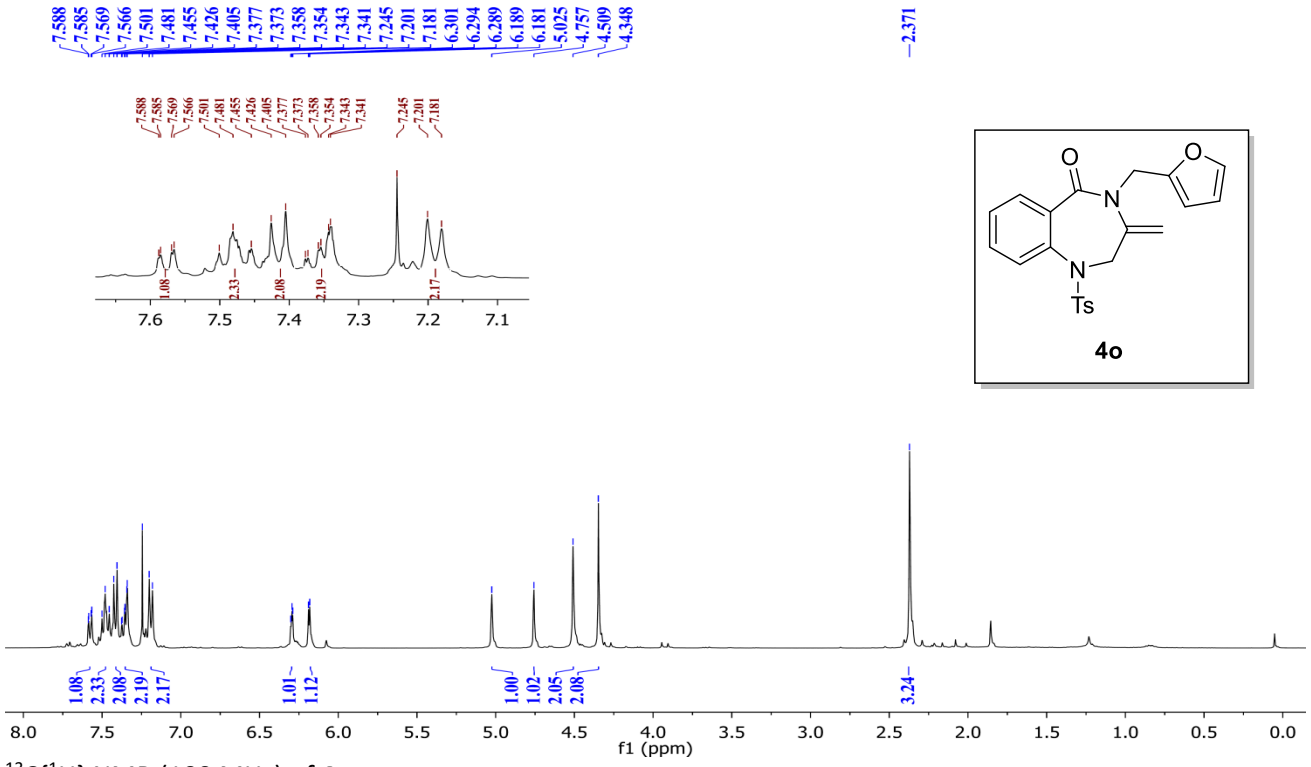
^{1}H NMR (400 MHz) of **4n**:



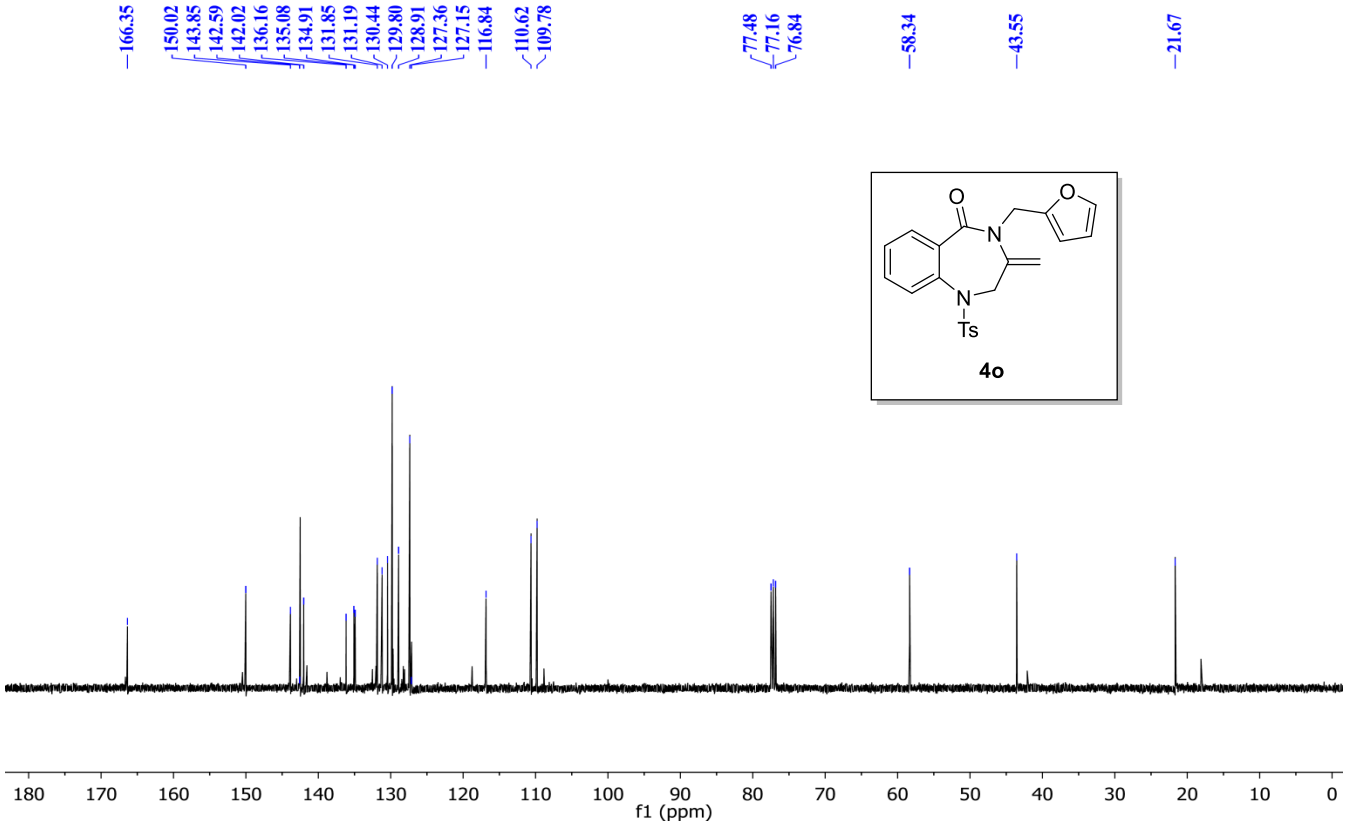
^{13}C{^{1}H} NMR (100 MHz) of **4n**:



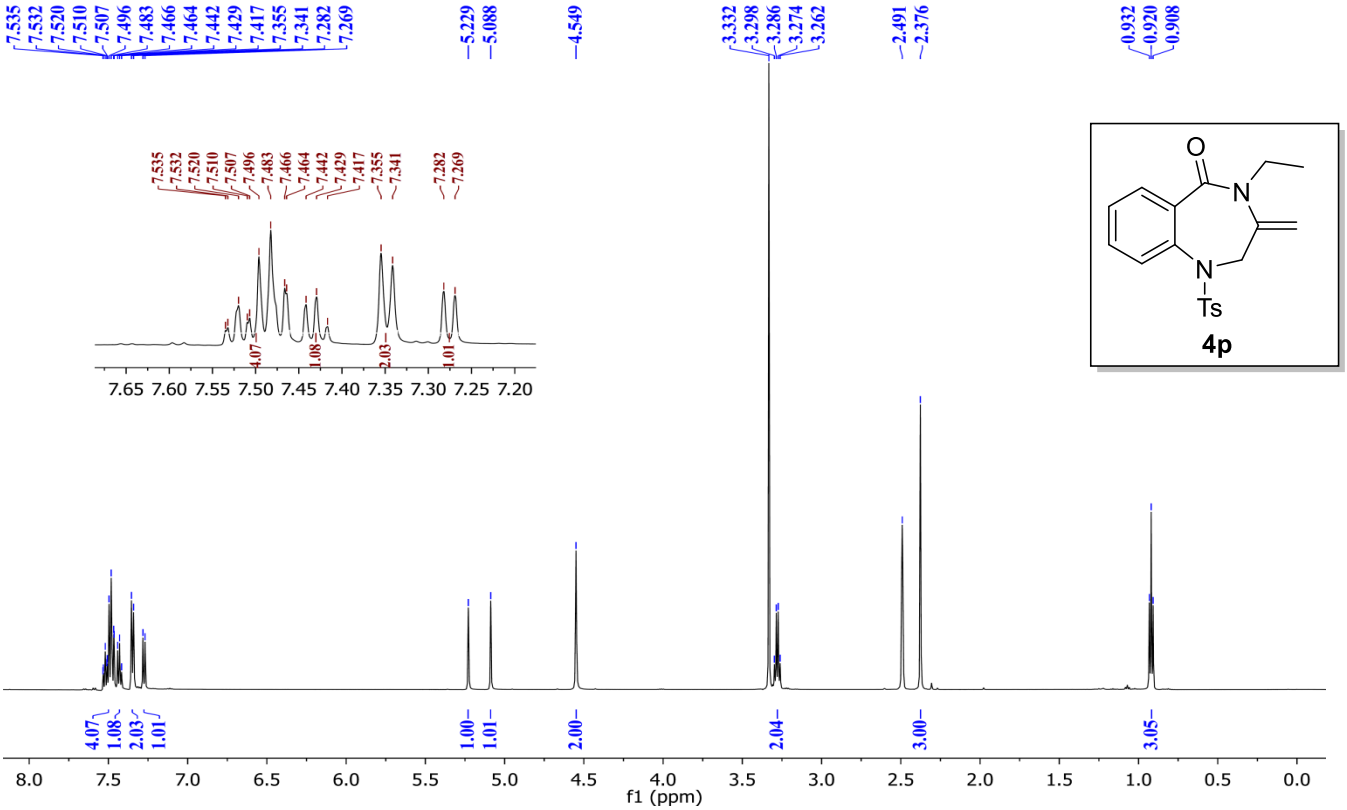
^{1}H NMR (400 MHz) of **4o**:



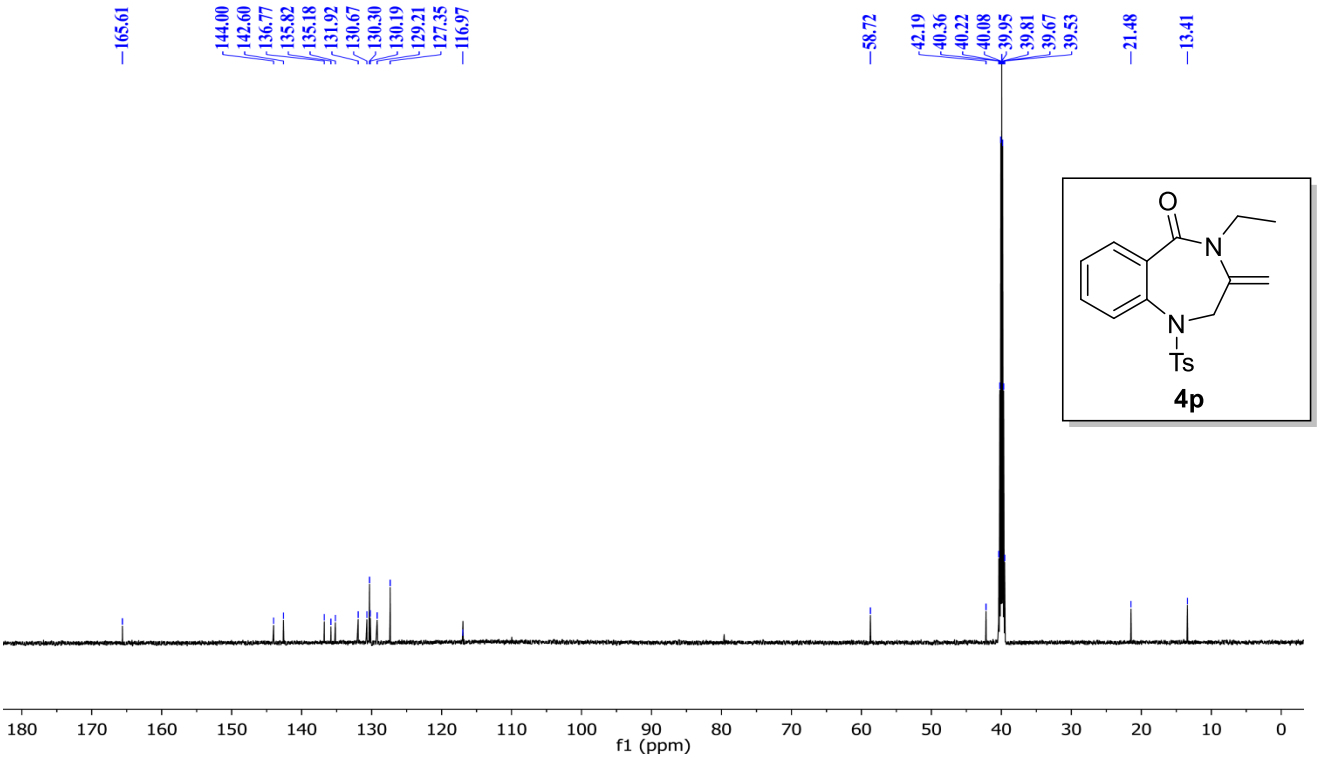
^{13}C{^{1}H} NMR (100 MHz) of **4o**:



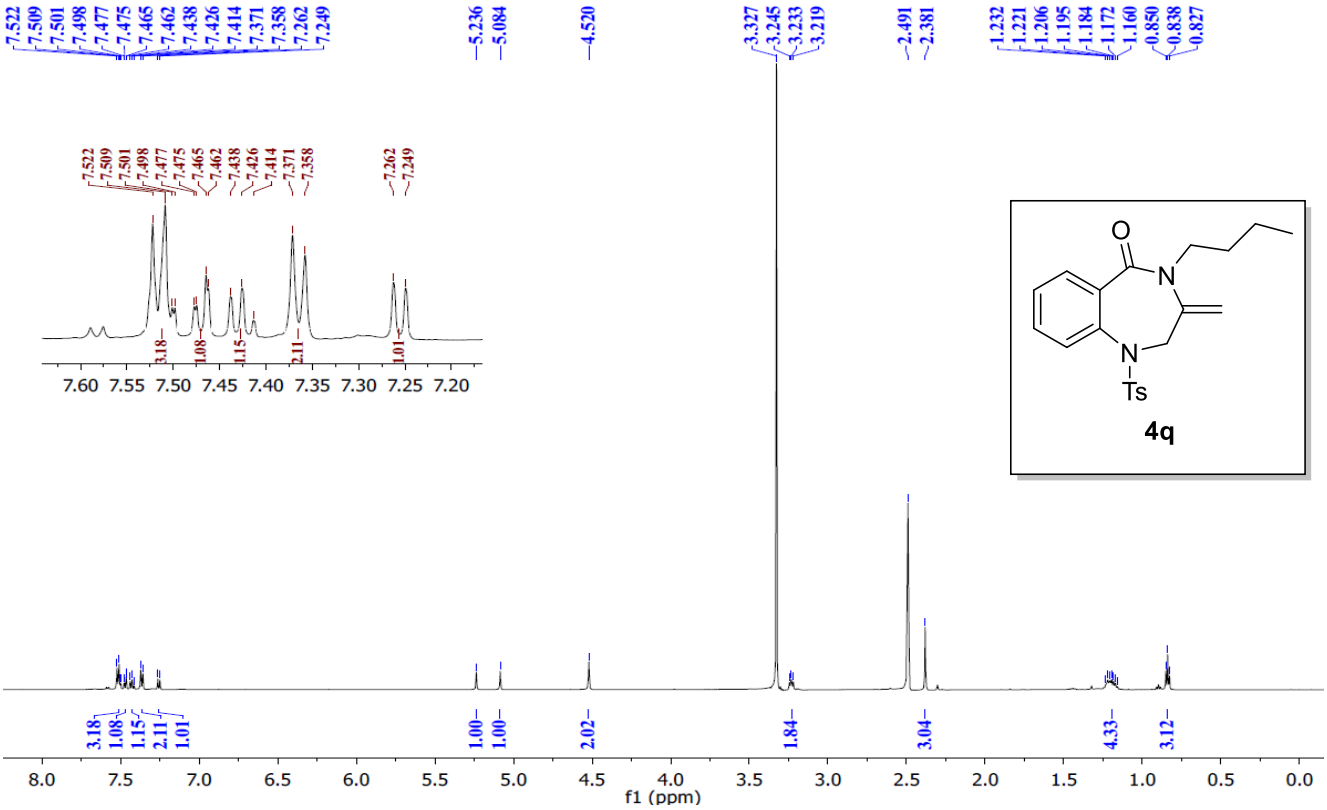
^{1}H NMR (600 MHz) of **4p**:



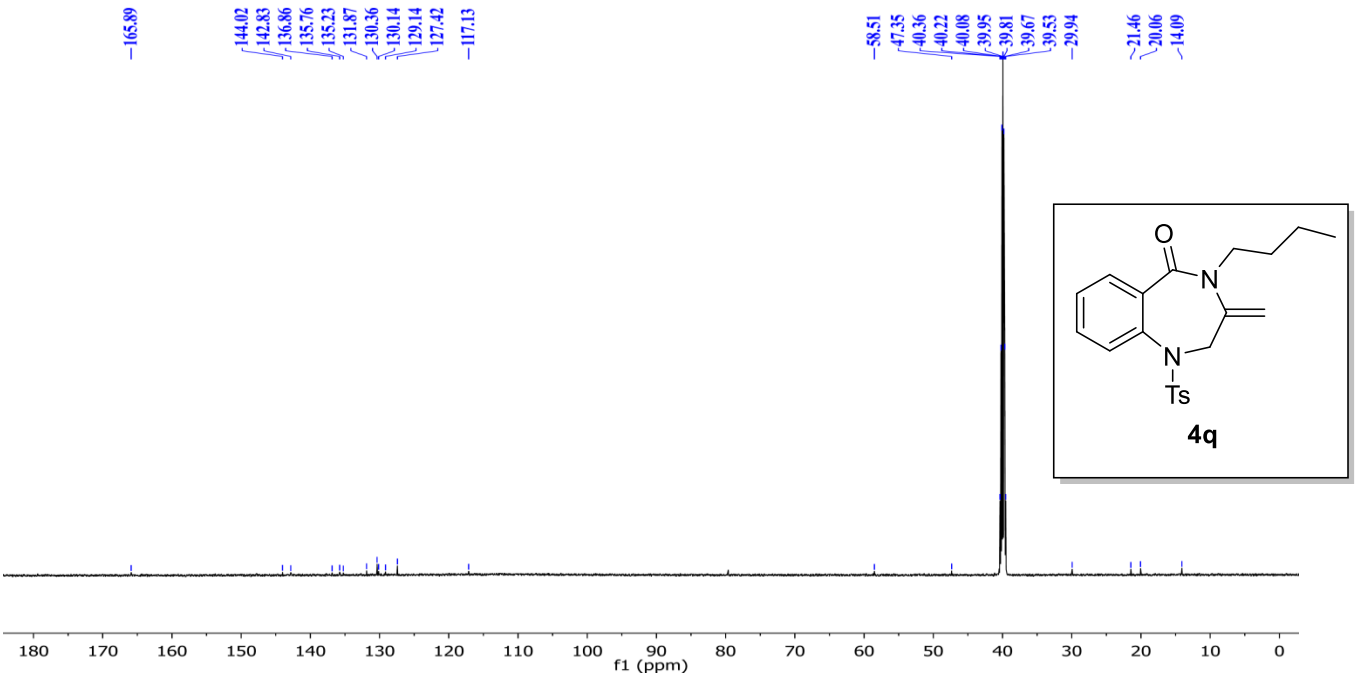
^{13}C{^{1}H} NMR (150 MHz) of **4p**:



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

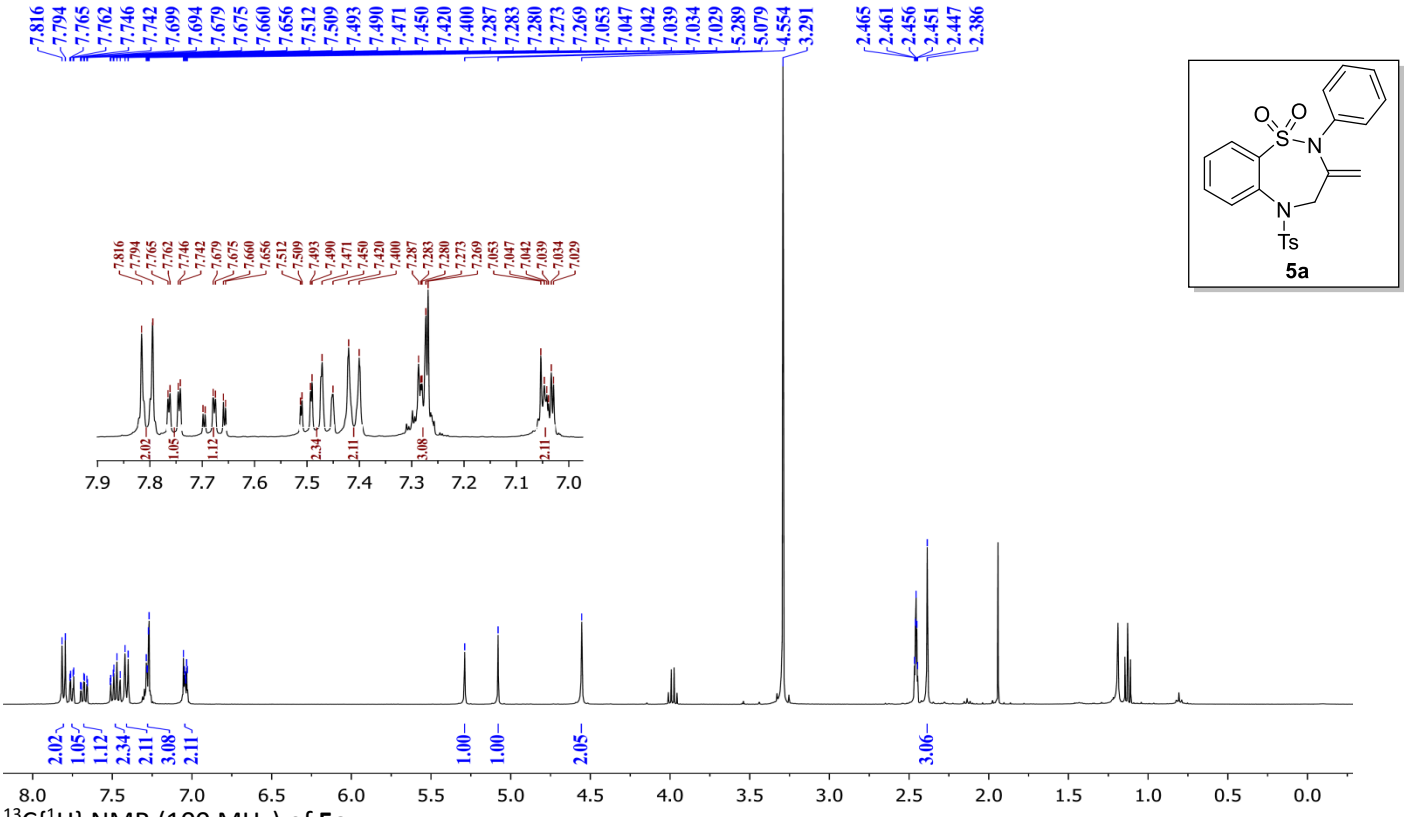


^{13}C{^{1}H} NMR (150 MHz) of **4q**:

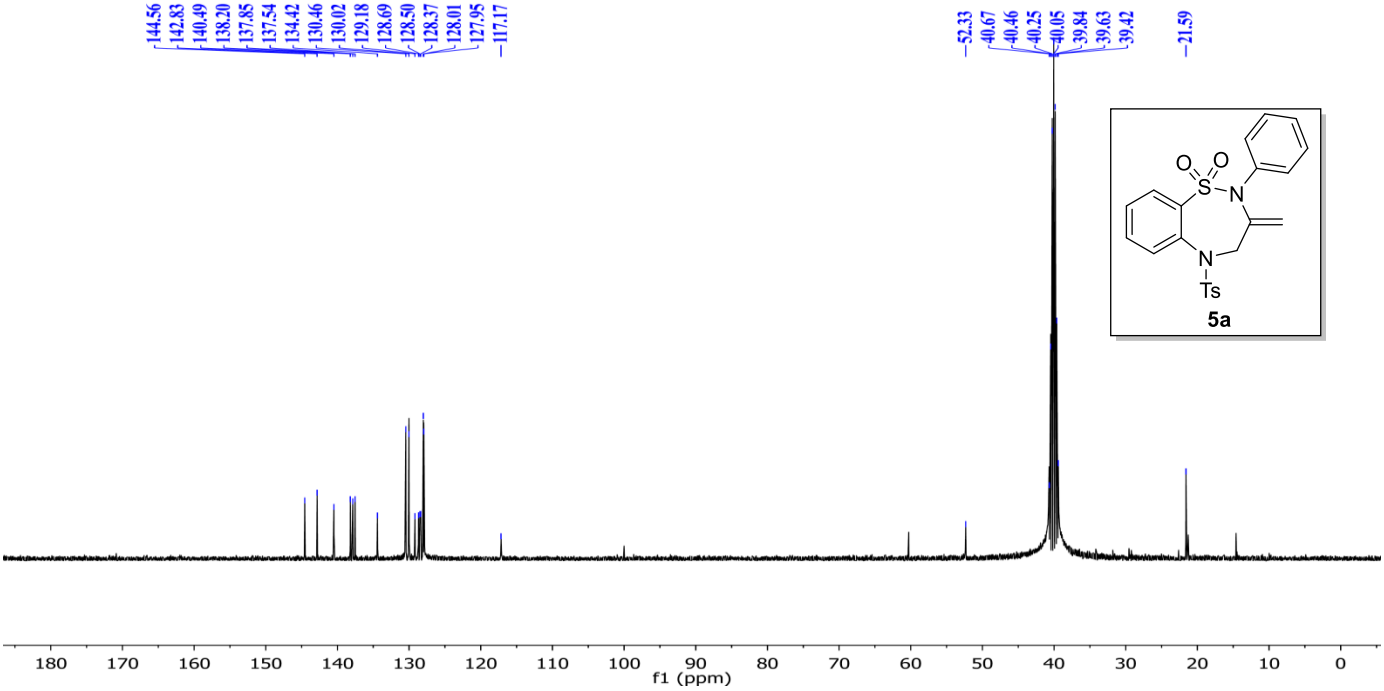


43. NMR spectra of products 5a-5c:

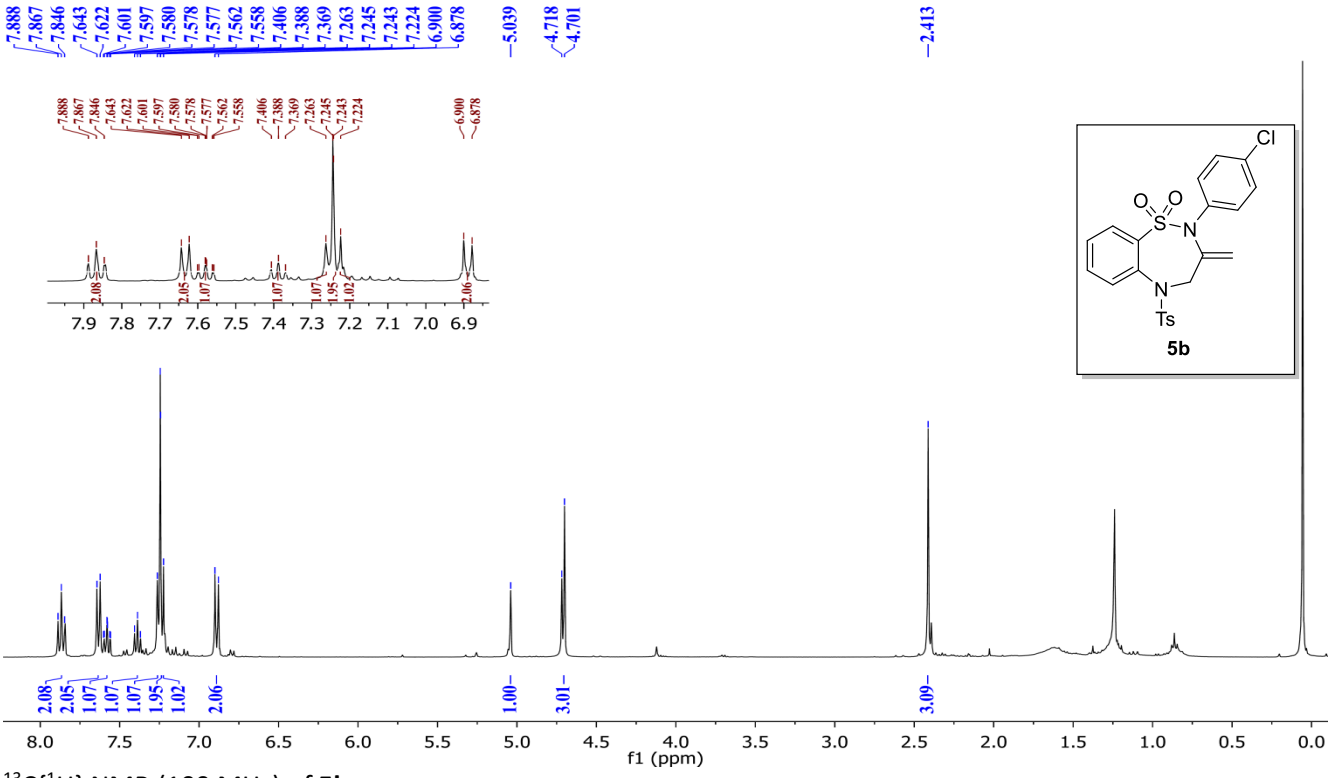
^{1}H NMR (400 MHz) of **5a**:



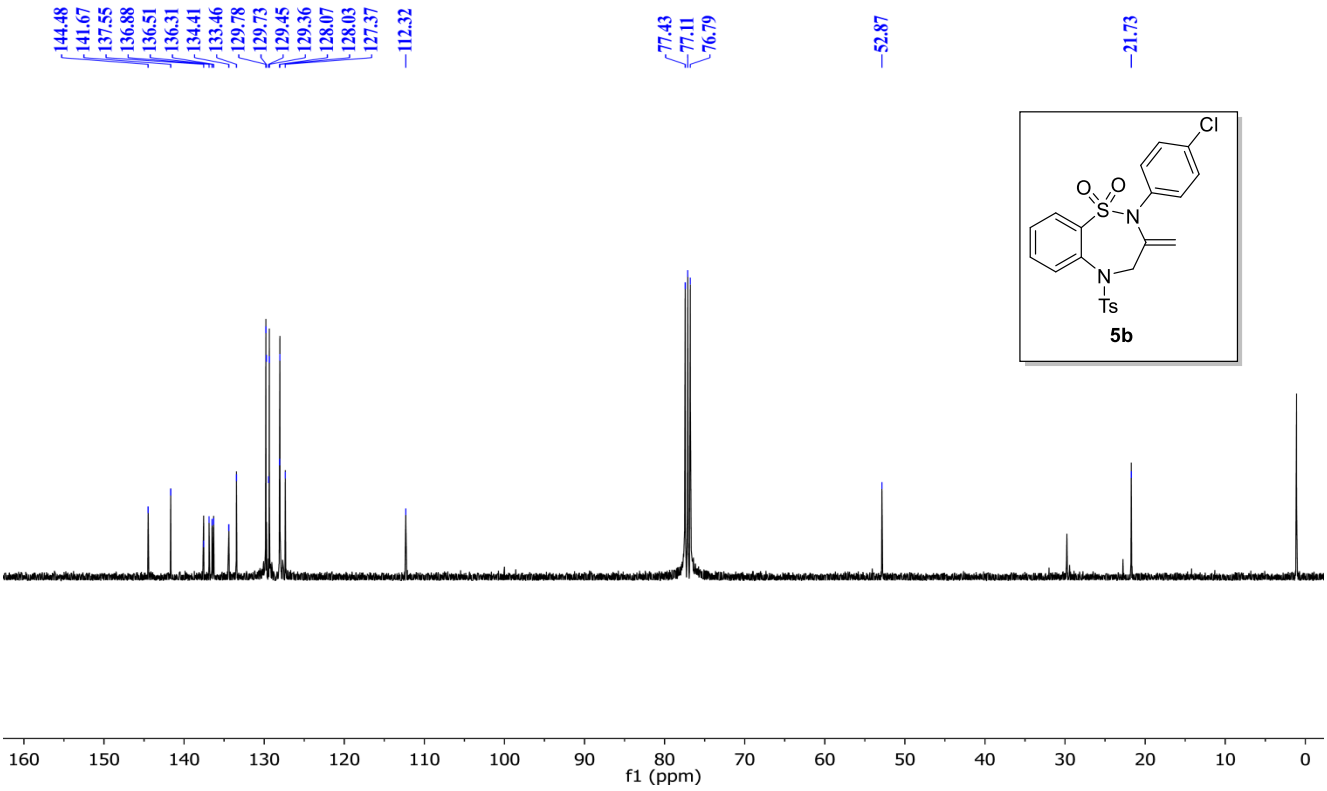
^{13}C{^{1}H} NMR (100 MHz) of **5a**:



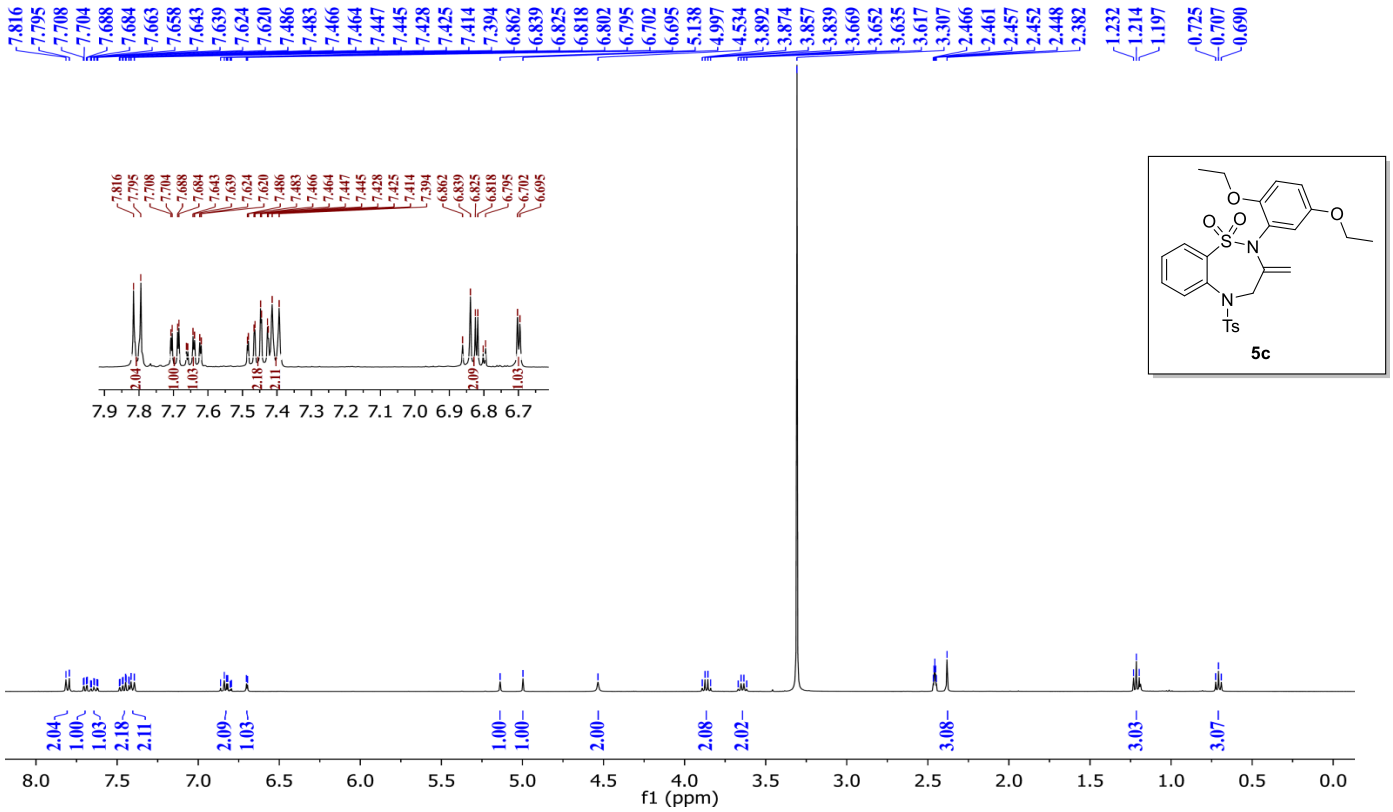
^{1}H NMR (400 MHz) of **5b**:



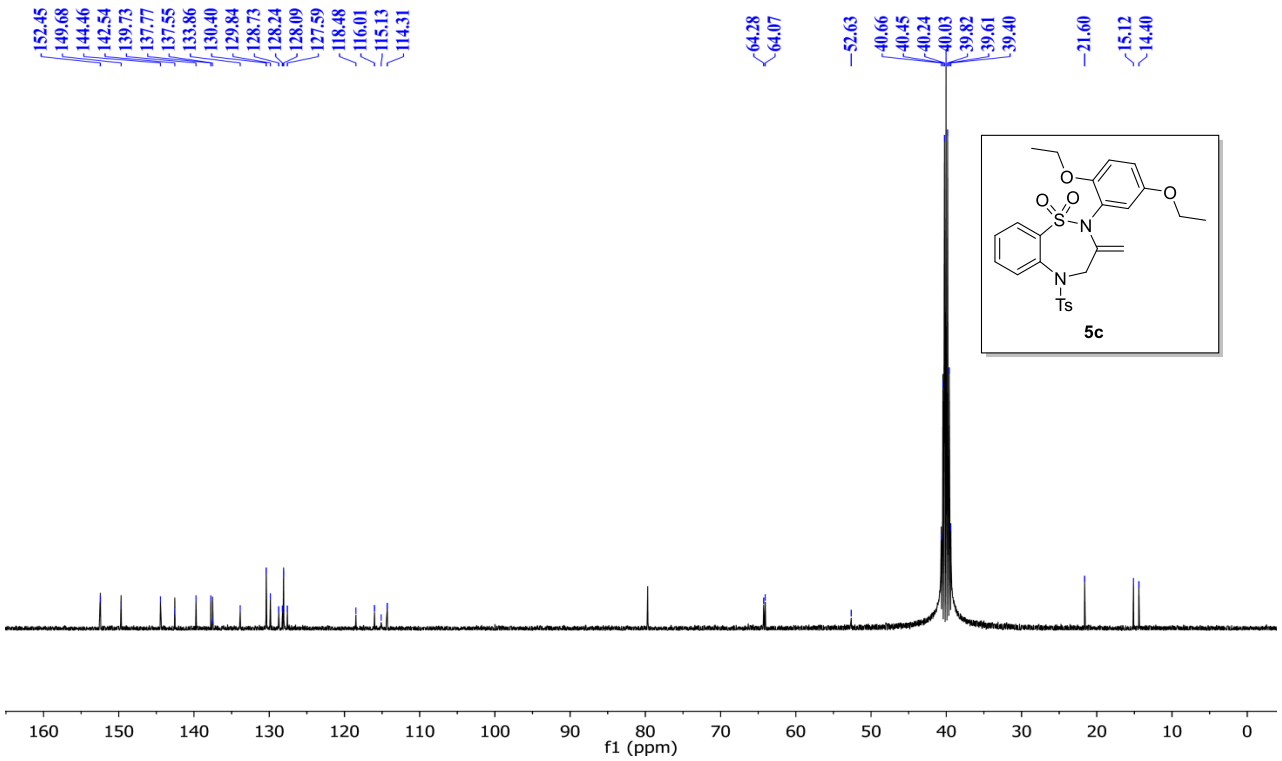
^{13}C{^{1}H} NMR (100 MHz) of **5b**:



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

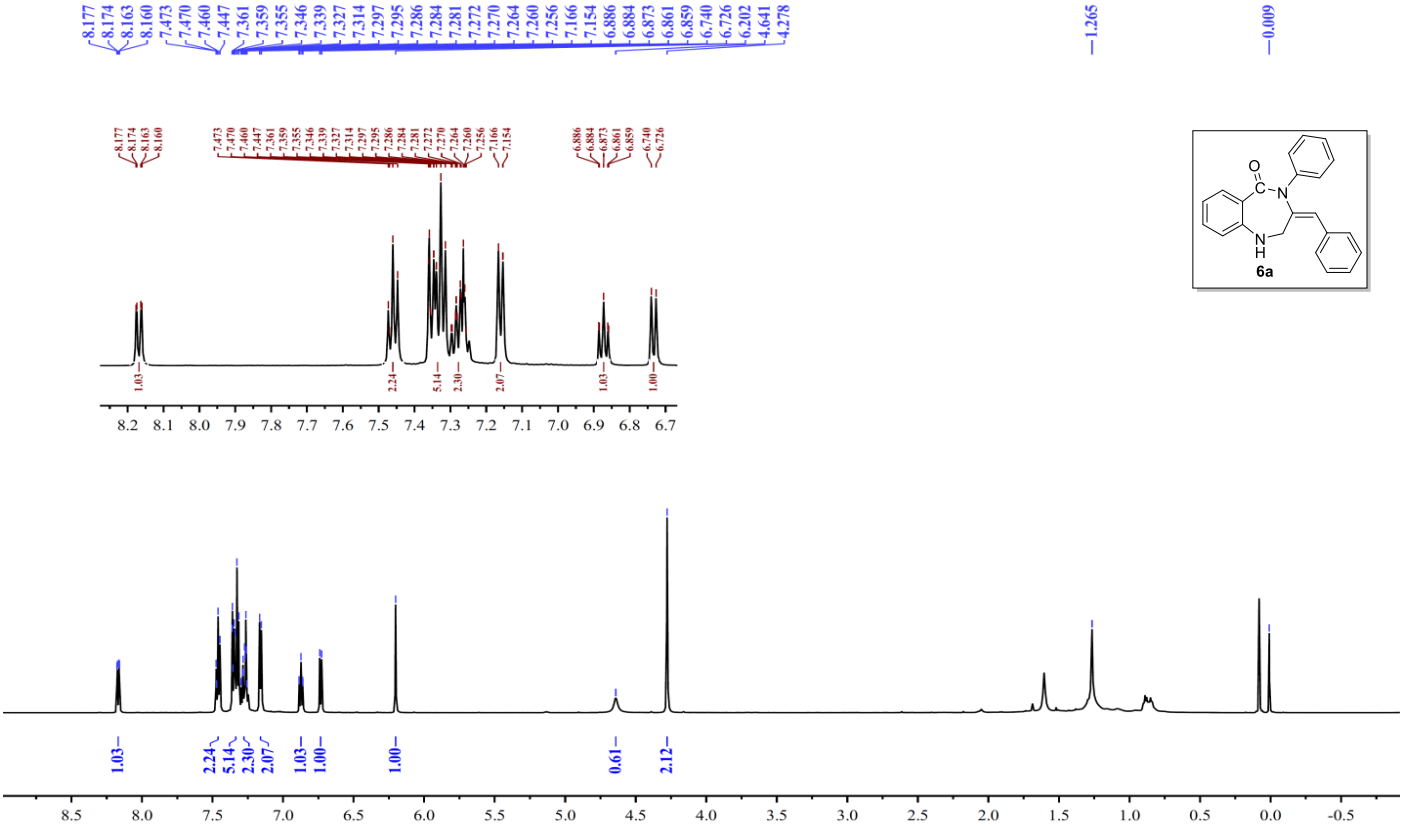


^{13}C{^{1}H} NMR (100 MHz) of **5c**:

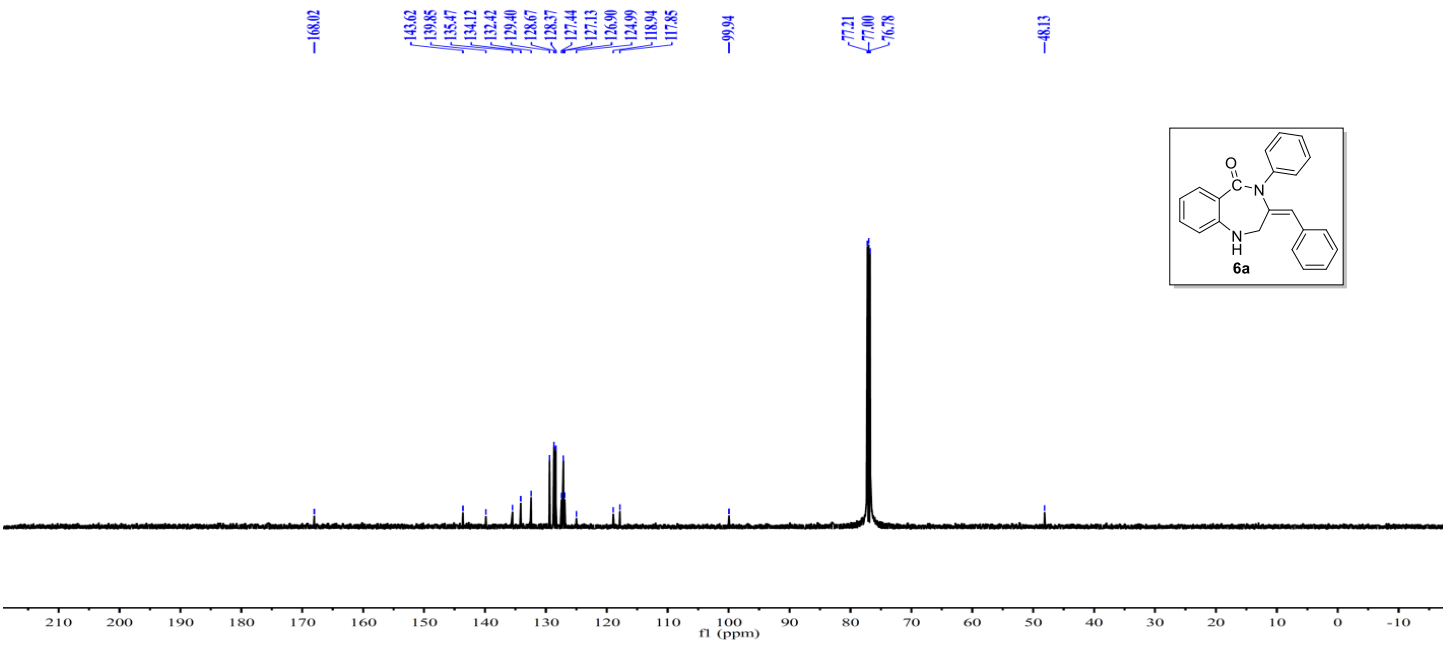


44. NMR spectra of products 6a-6m:

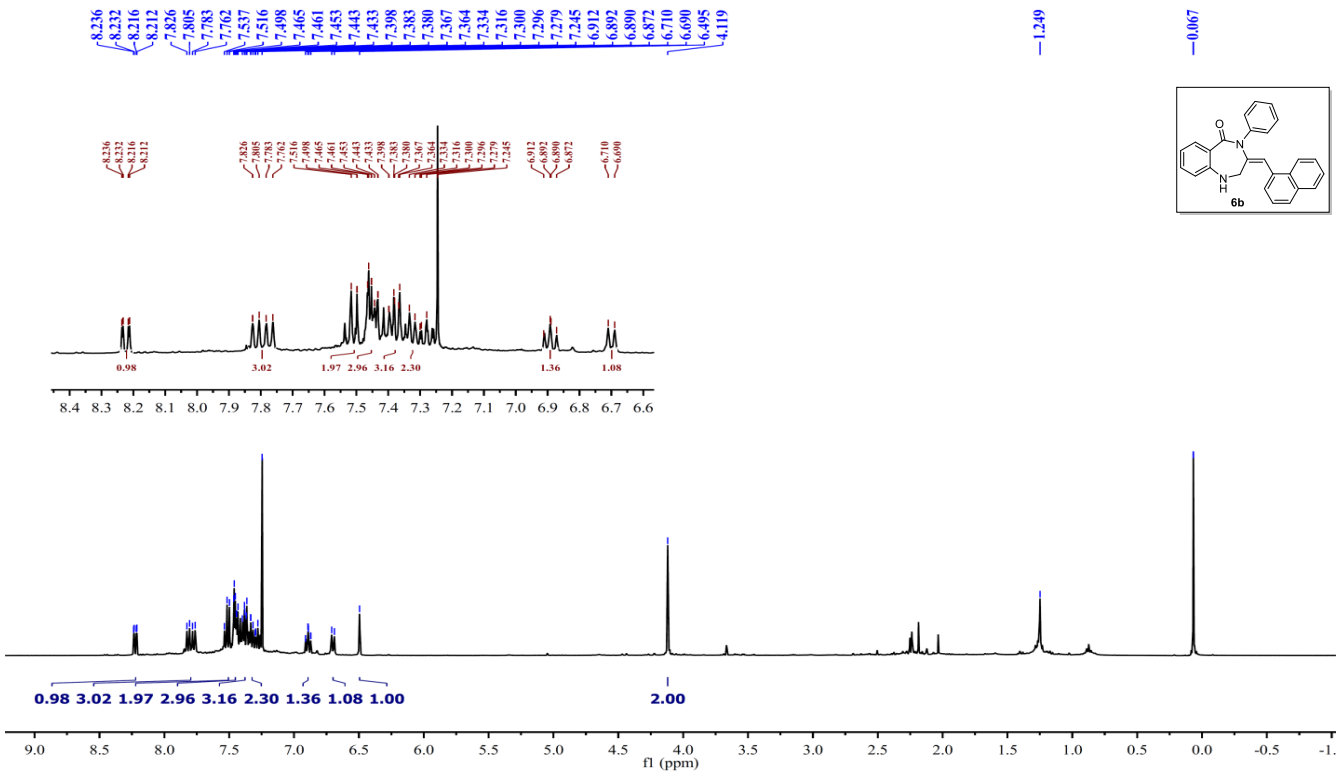
^{1}H NMR (600 MHz) of **6a** :



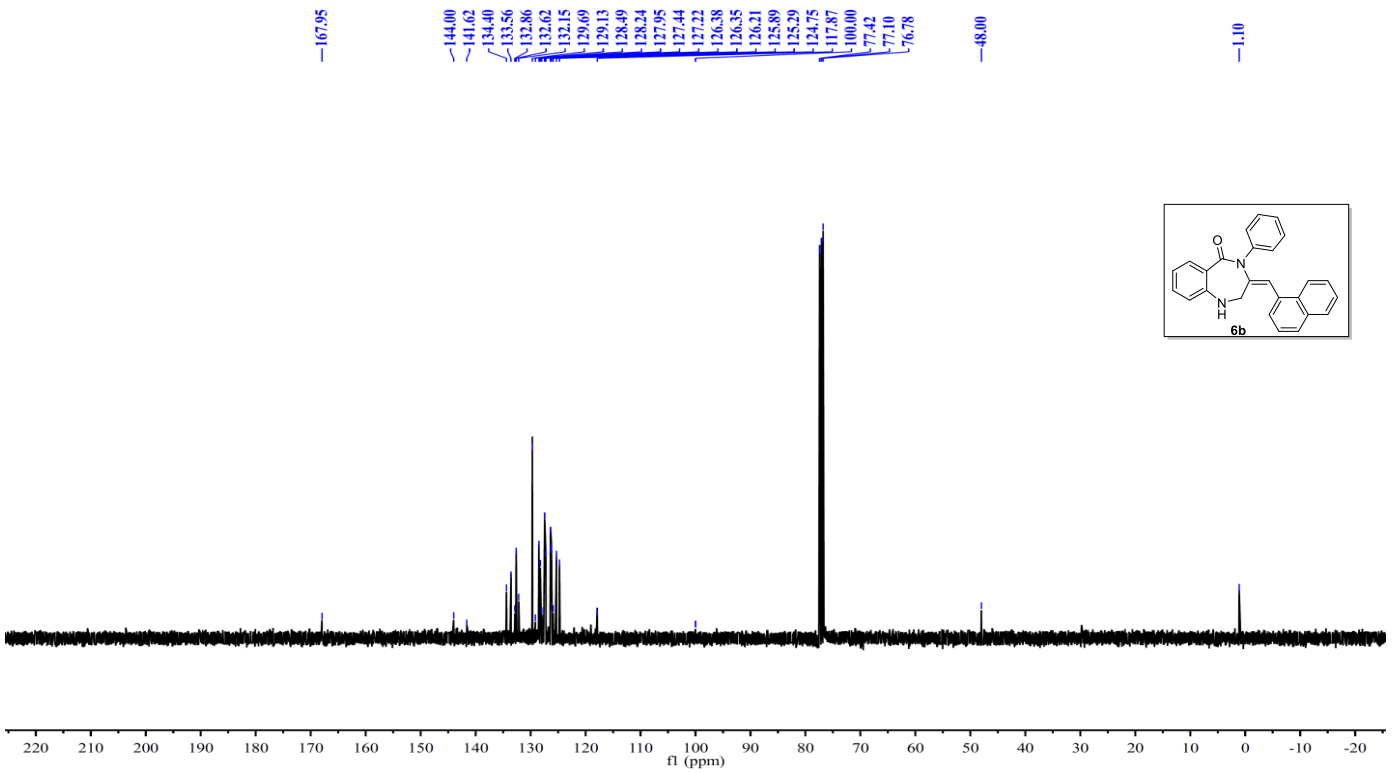
^{13}C{^{1}H} NMR (150 MHz) of **6a** :



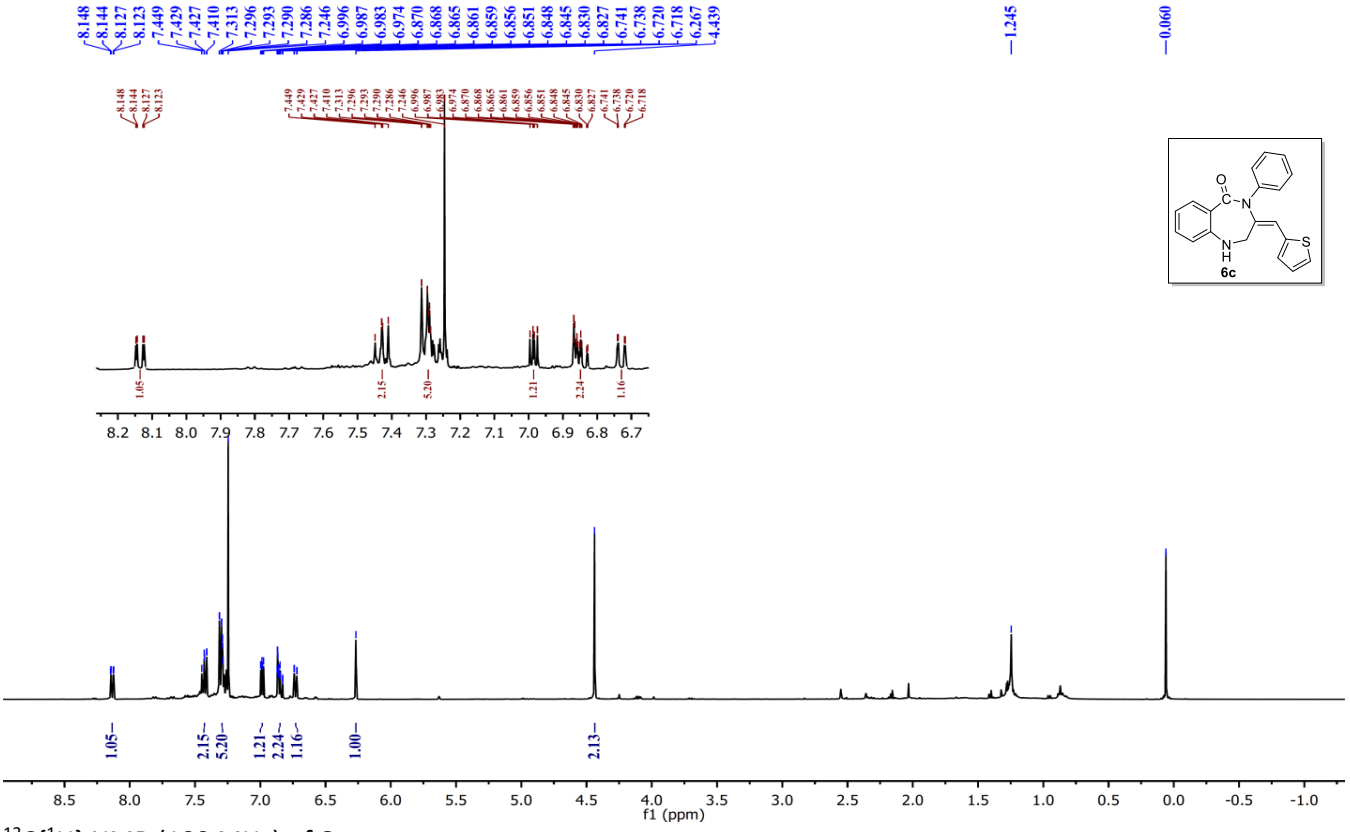
^{1}H NMR (400 MHz) of **6b** :



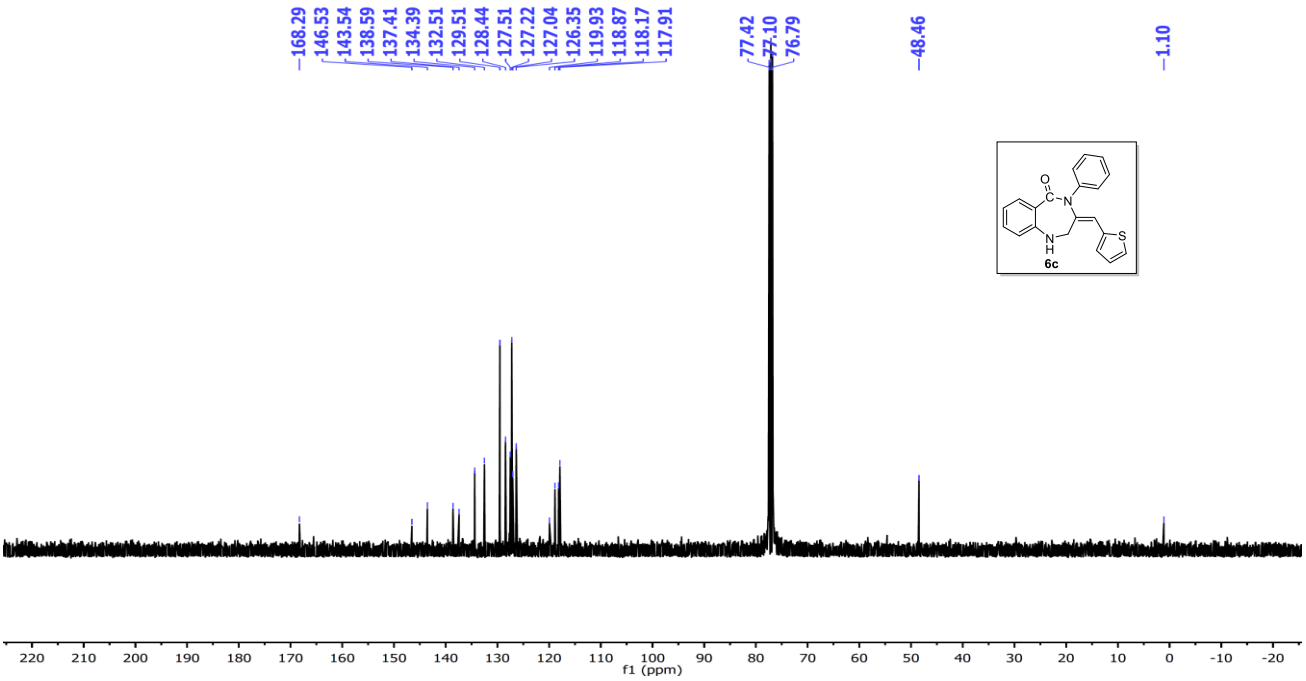
^{13}C{^{1}H} NMR (100 MHz) of **6b** :



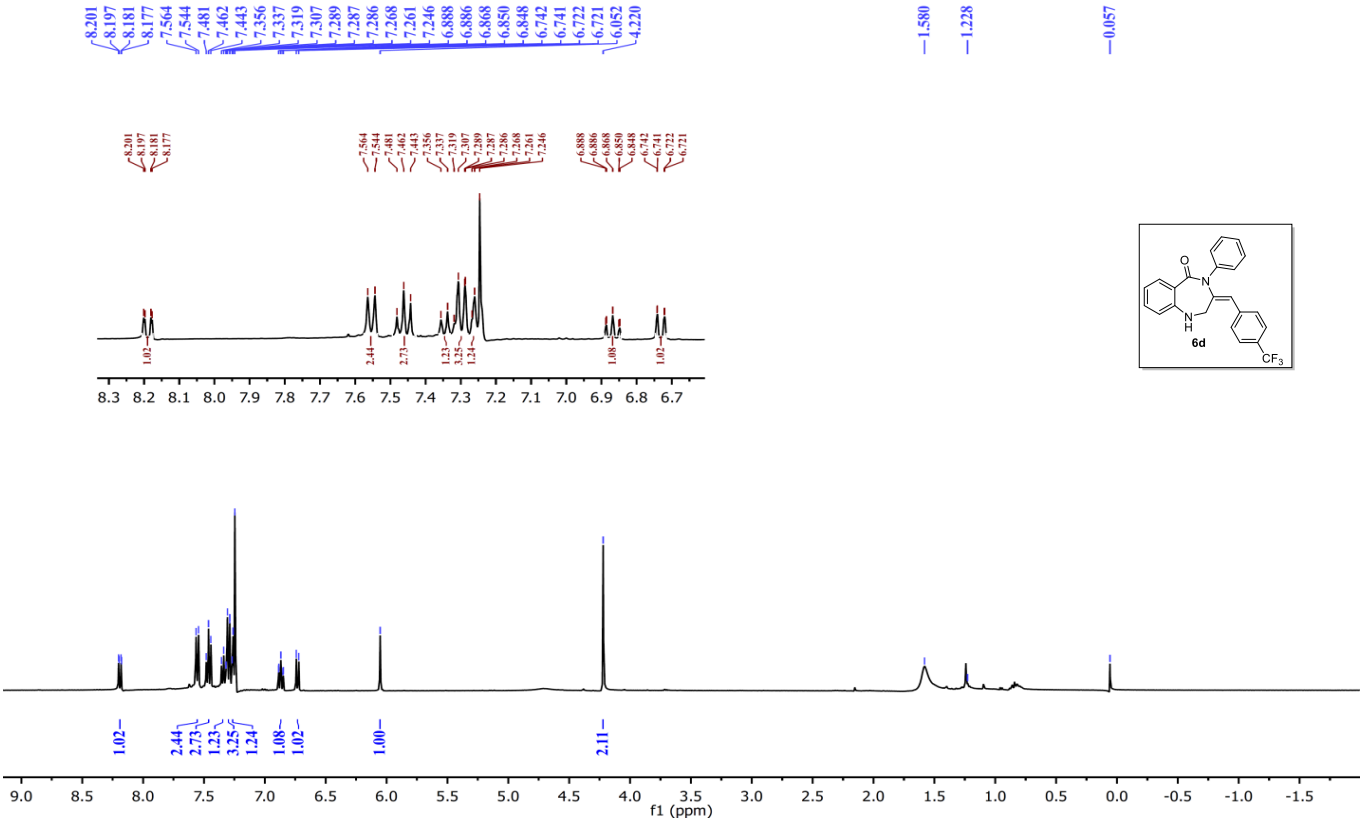
^{1}H NMR (400 MHz) of **6c** :



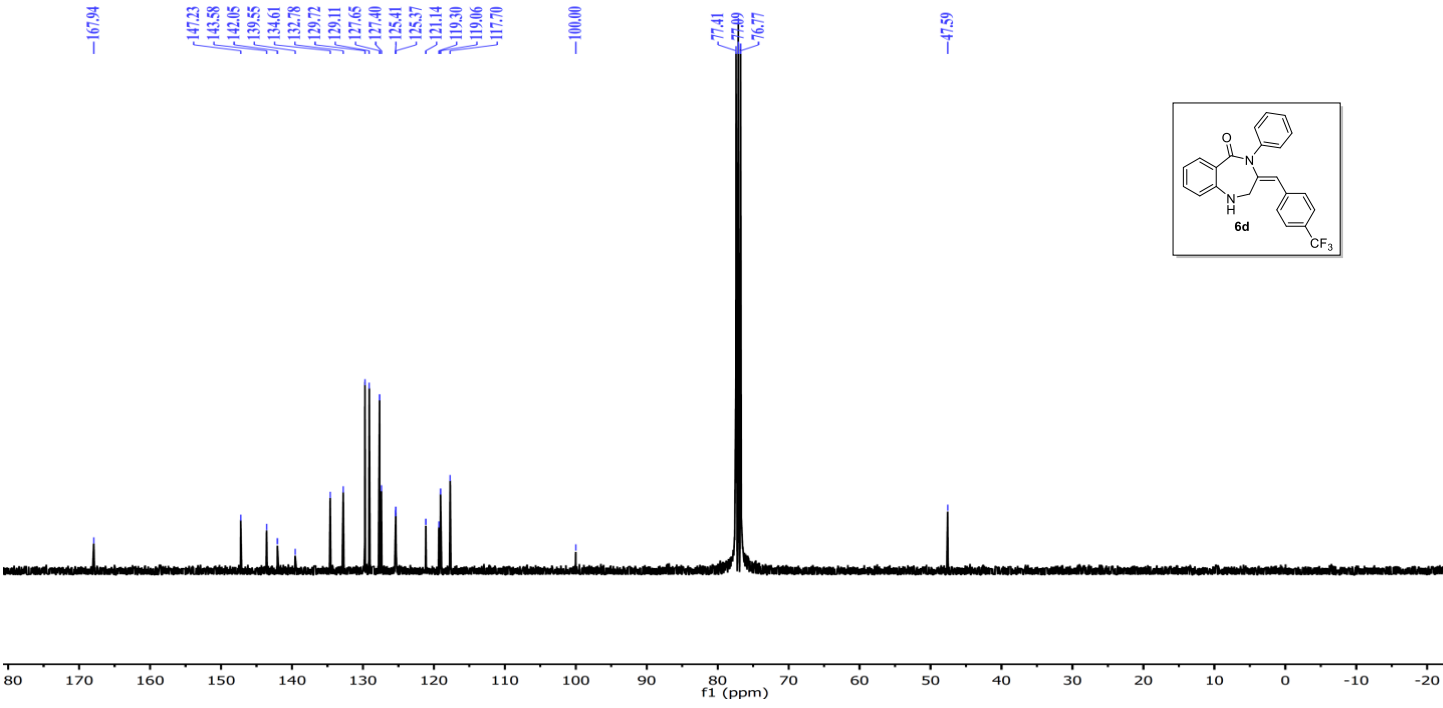
^{13}C{^{1}H} NMR (100 MHz) of **6c** :



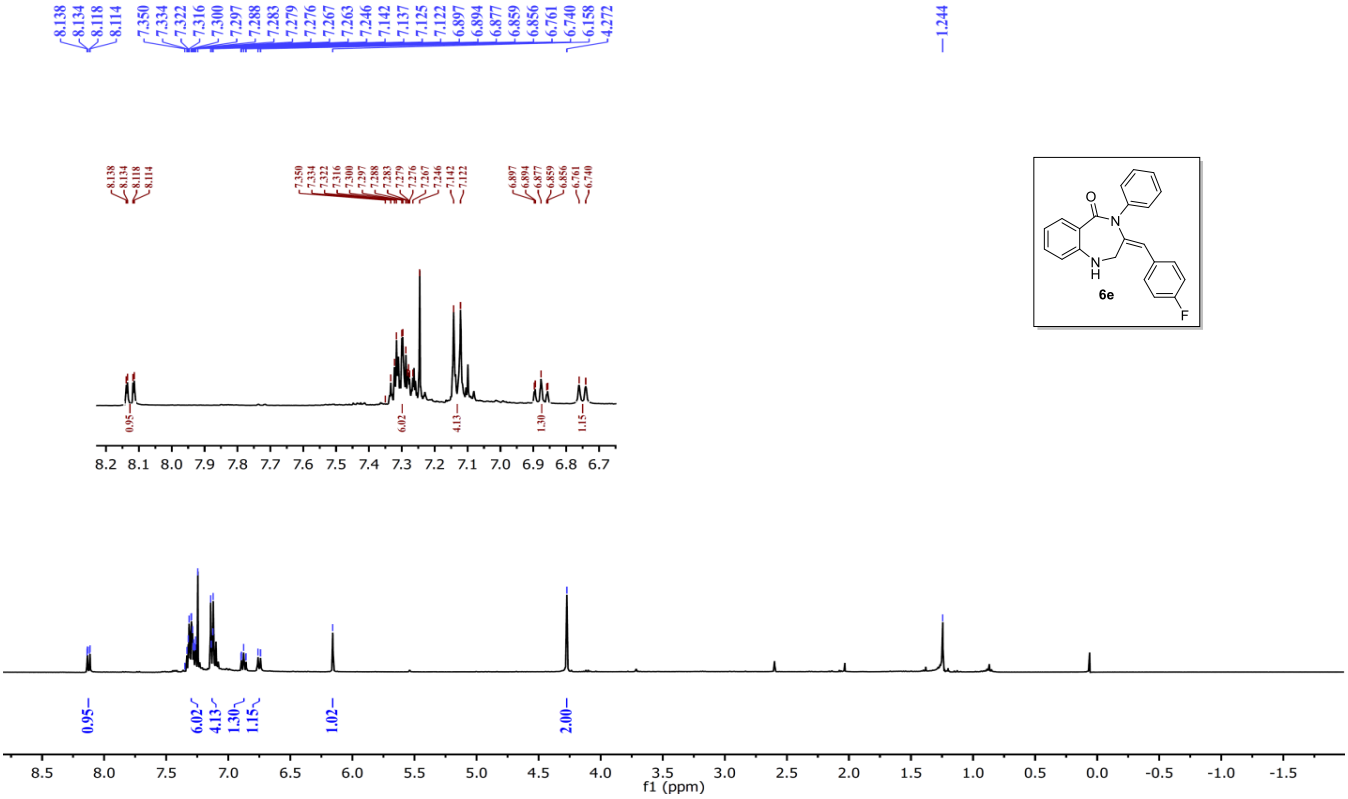
^{1}H NMR (400 MHz) of **6d** :



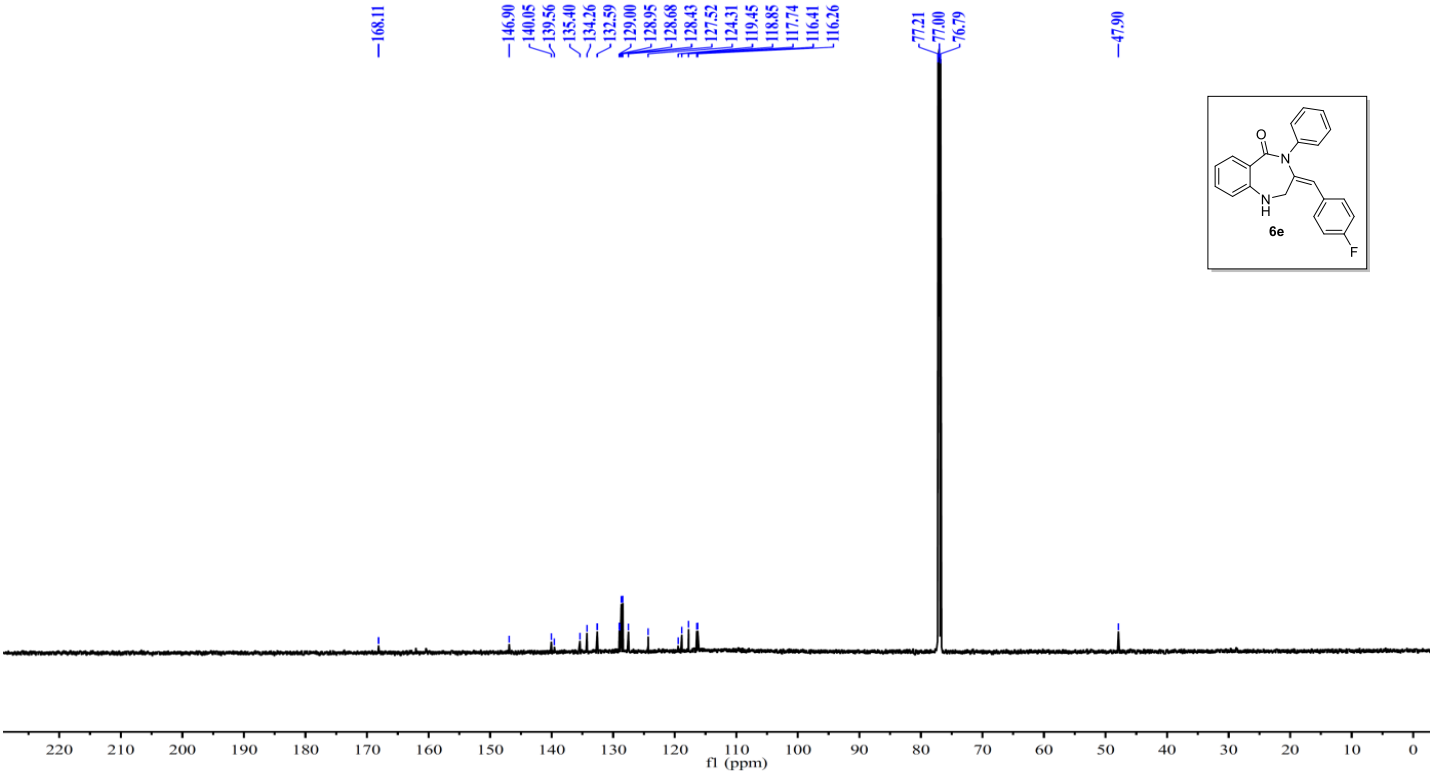
^{13}C{^{1}H} NMR (100 MHz) of **6d** :



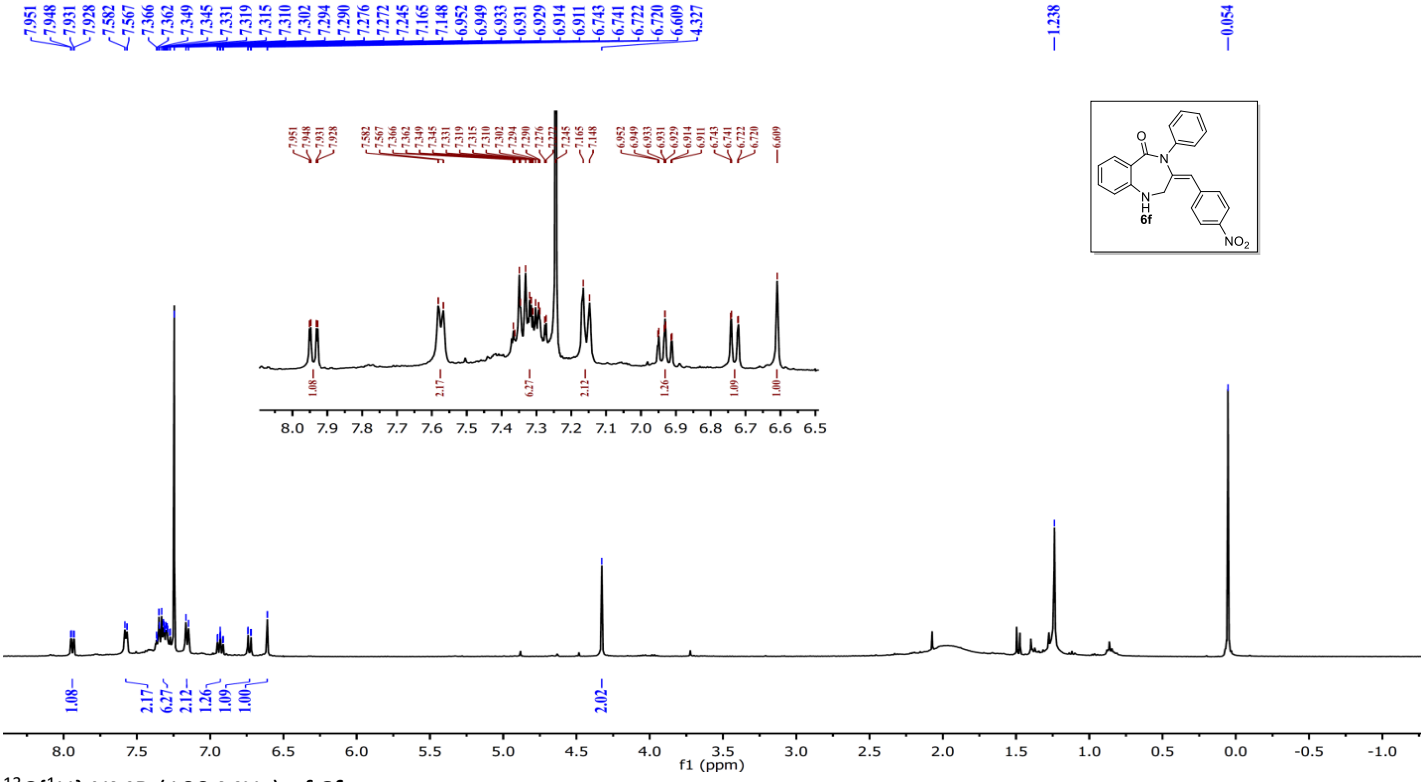
^{1}H NMR (400 MHz) of **6e** :



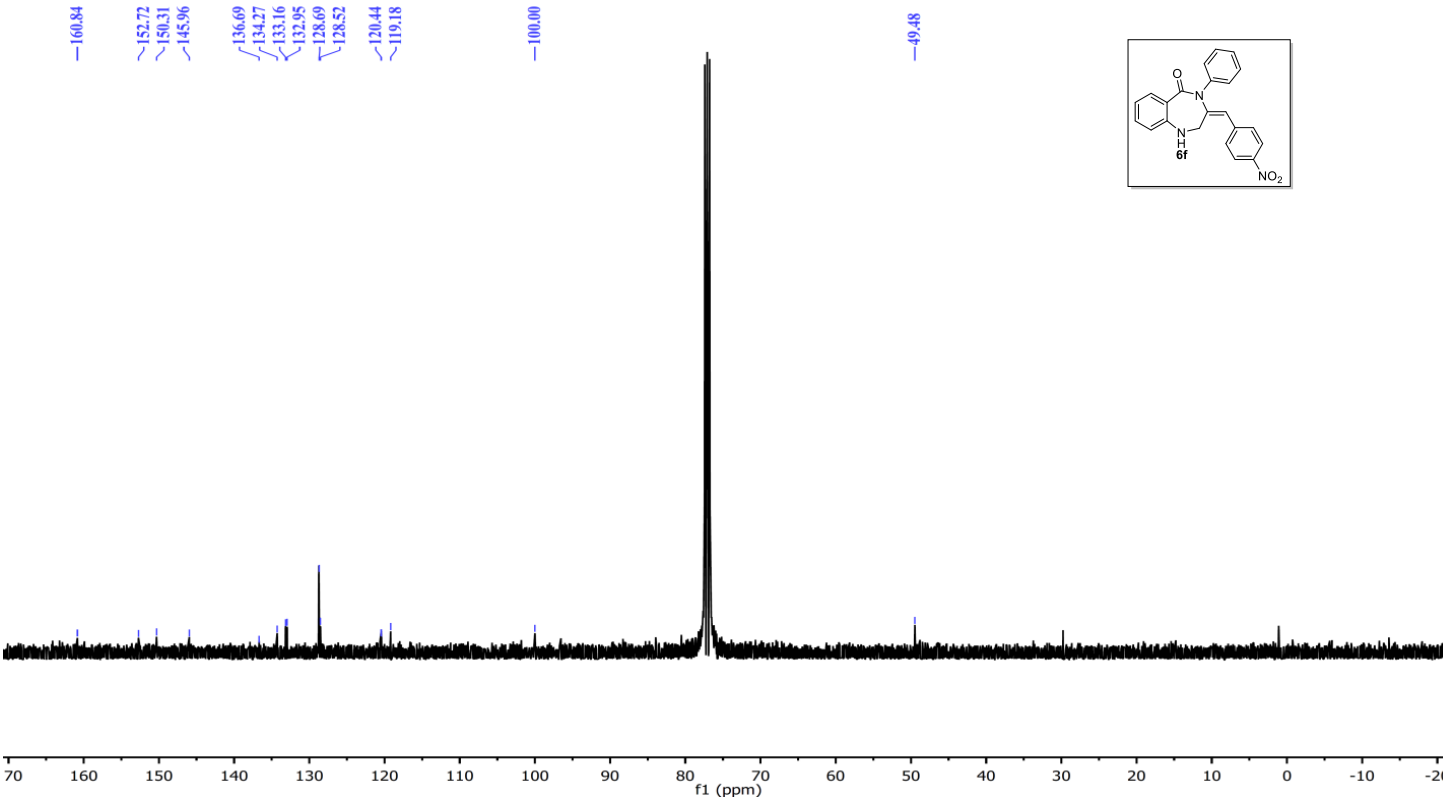
^{13}C{^{1}H} NMR (100 MHz) of **6e** :



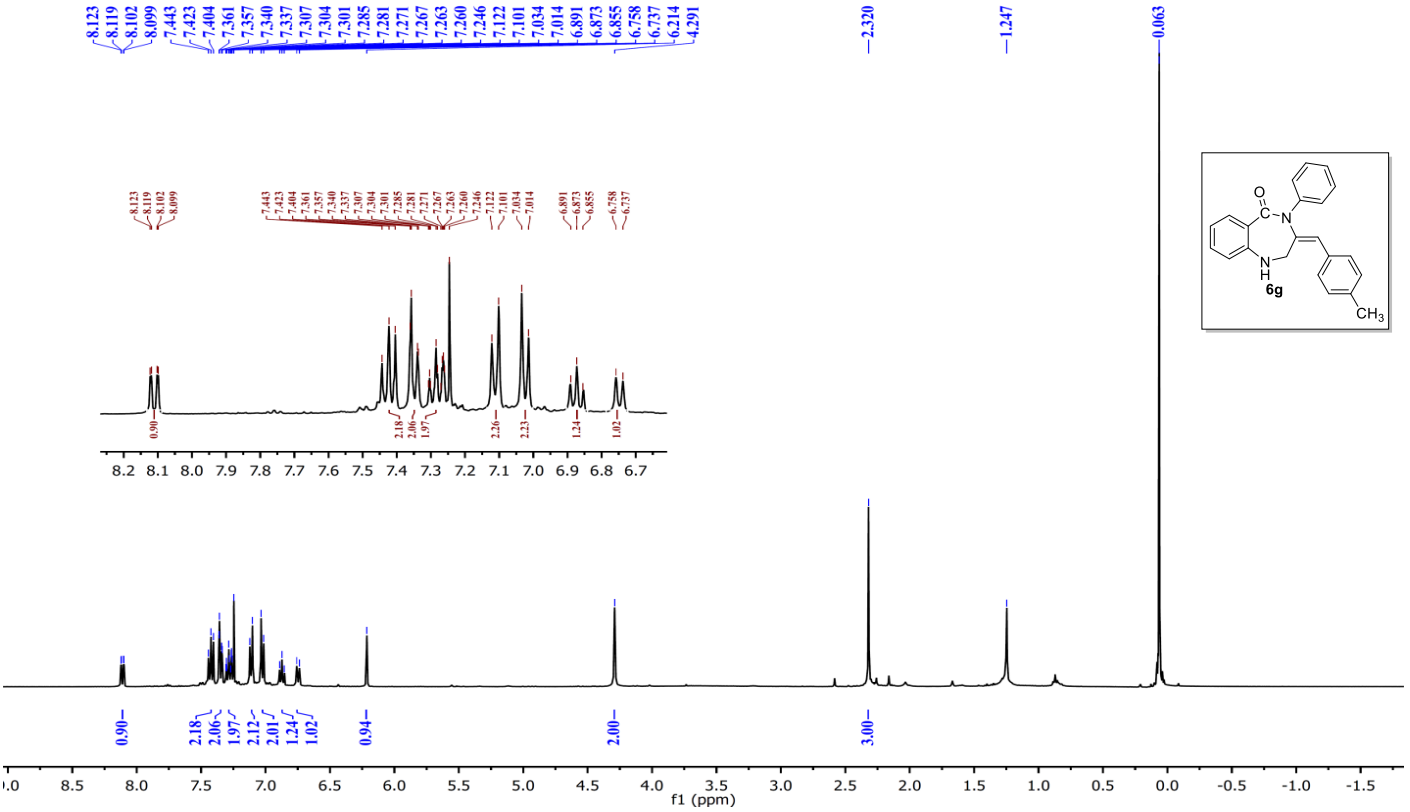
^{1}H NMR (400 MHz) of **6f** :



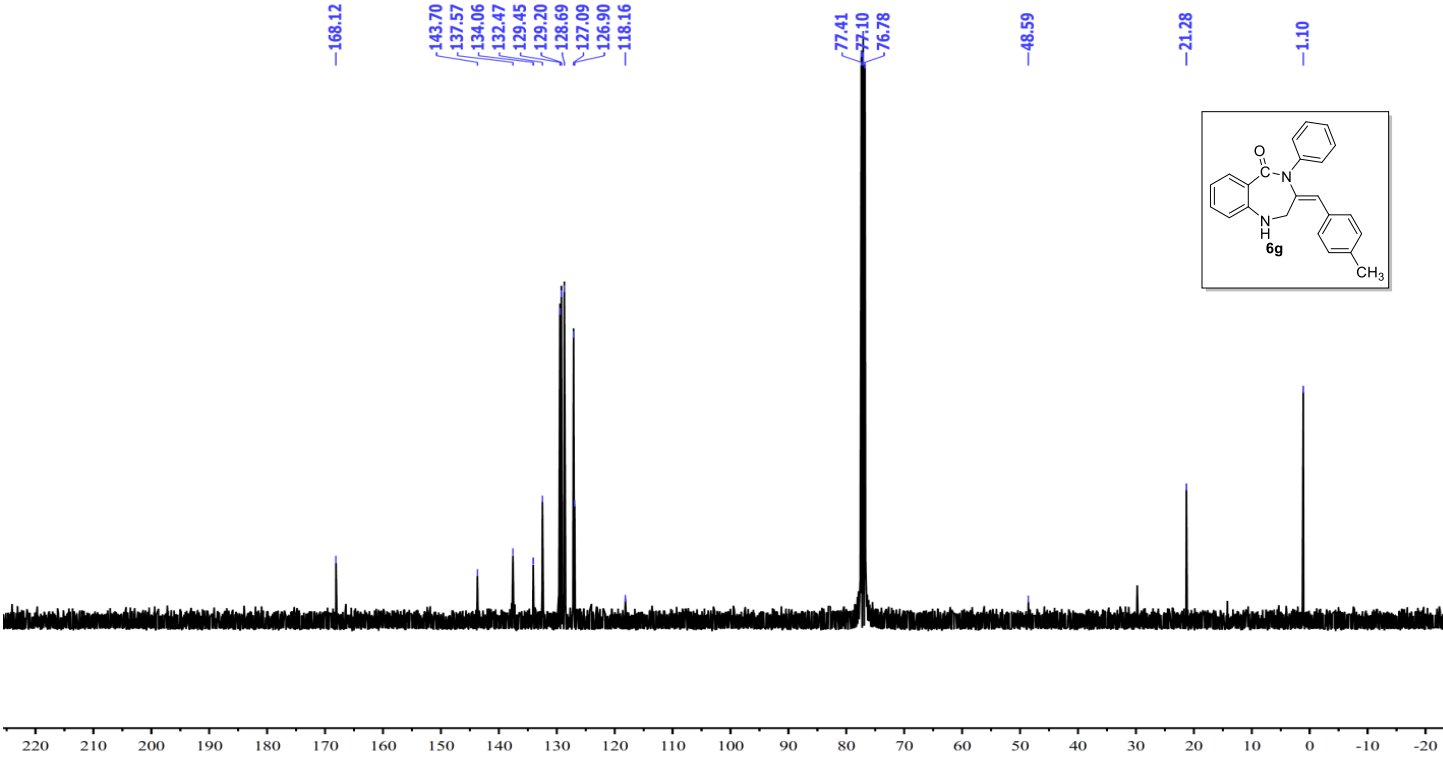
^{13}C{^{1}H} NMR (100 MHz) of **6f** :



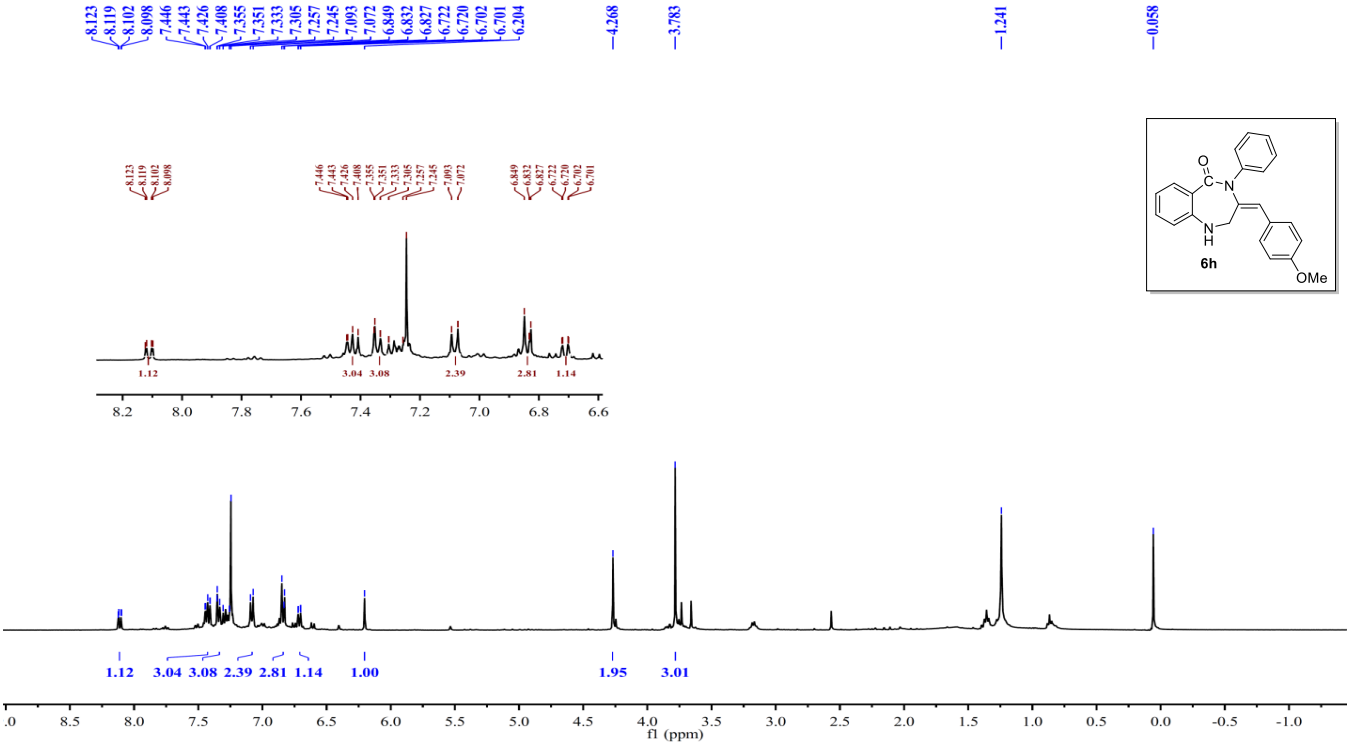
^{1}H NMR (400 MHz) of **6g**:



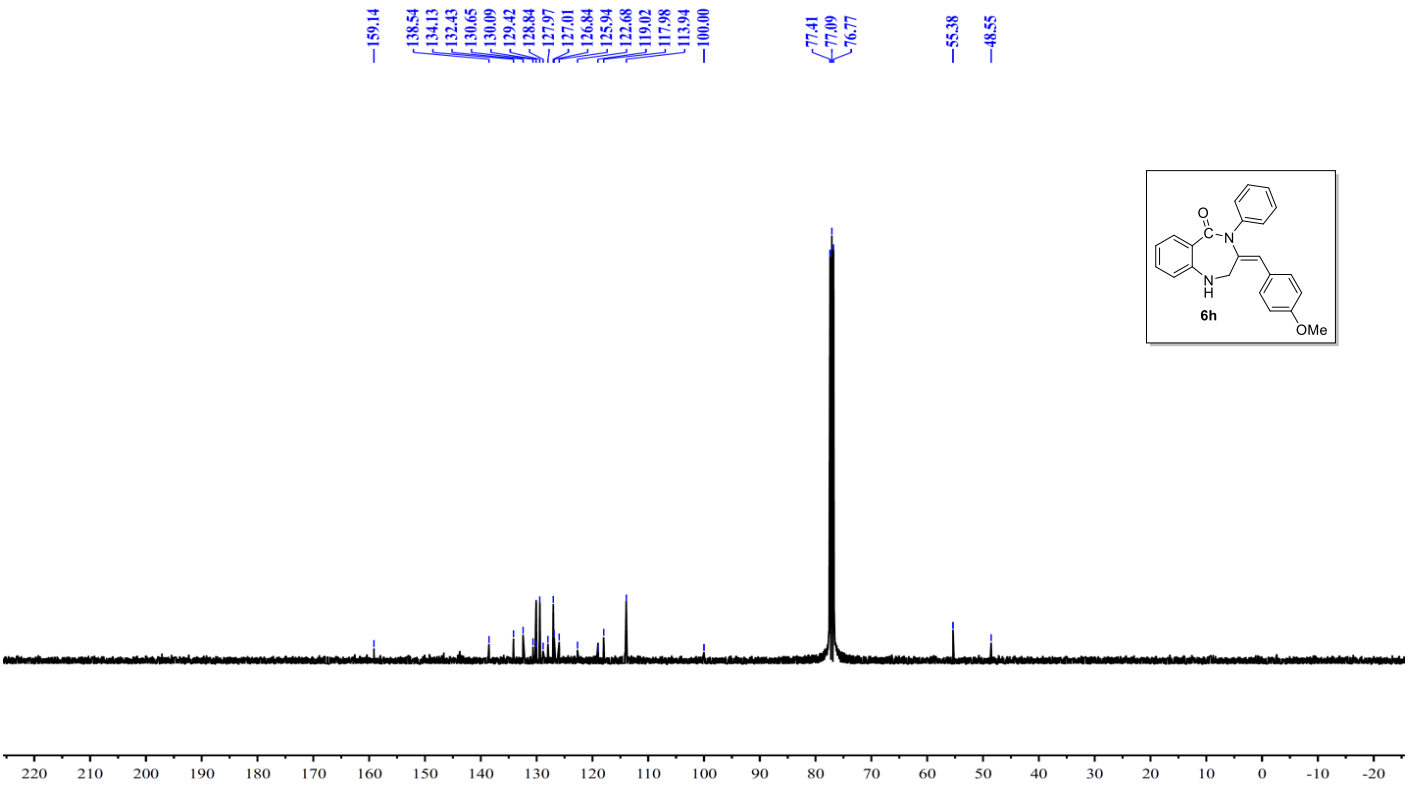
^{13}C{^{1}H} NMR (100 MHz) of **6g**:



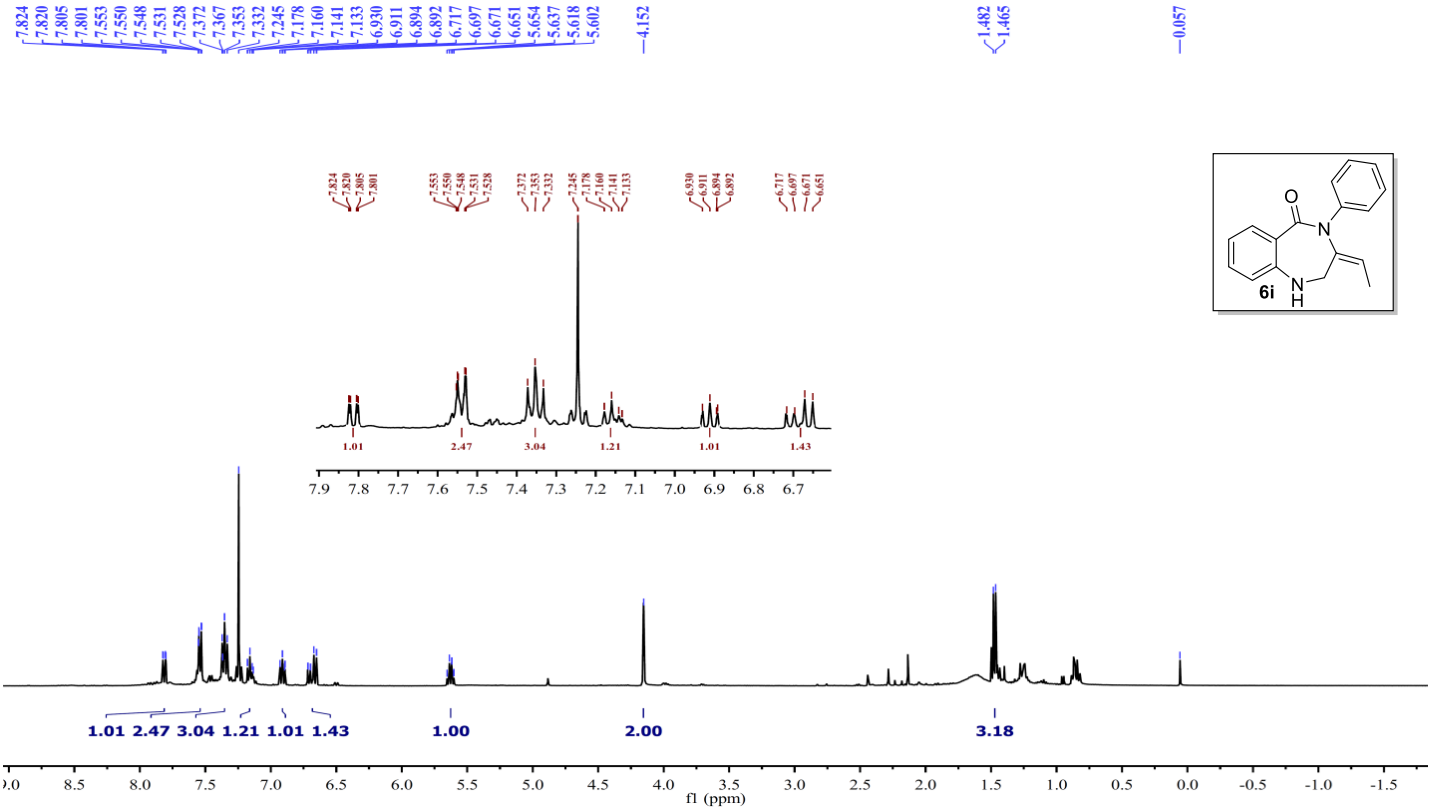
^{1}H NMR (400 MHz) of **6h** :



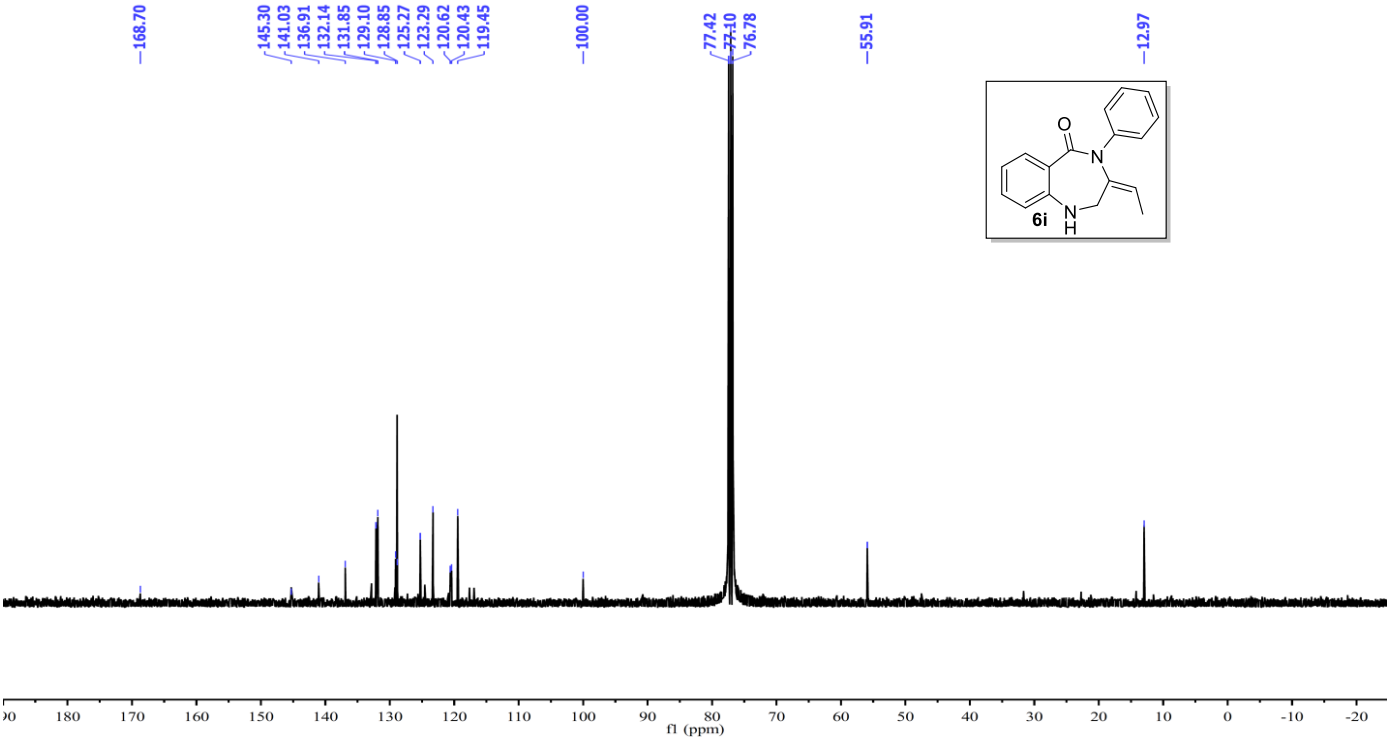
^{13}C{^{1}H} NMR (100 MHz) of **6h**:



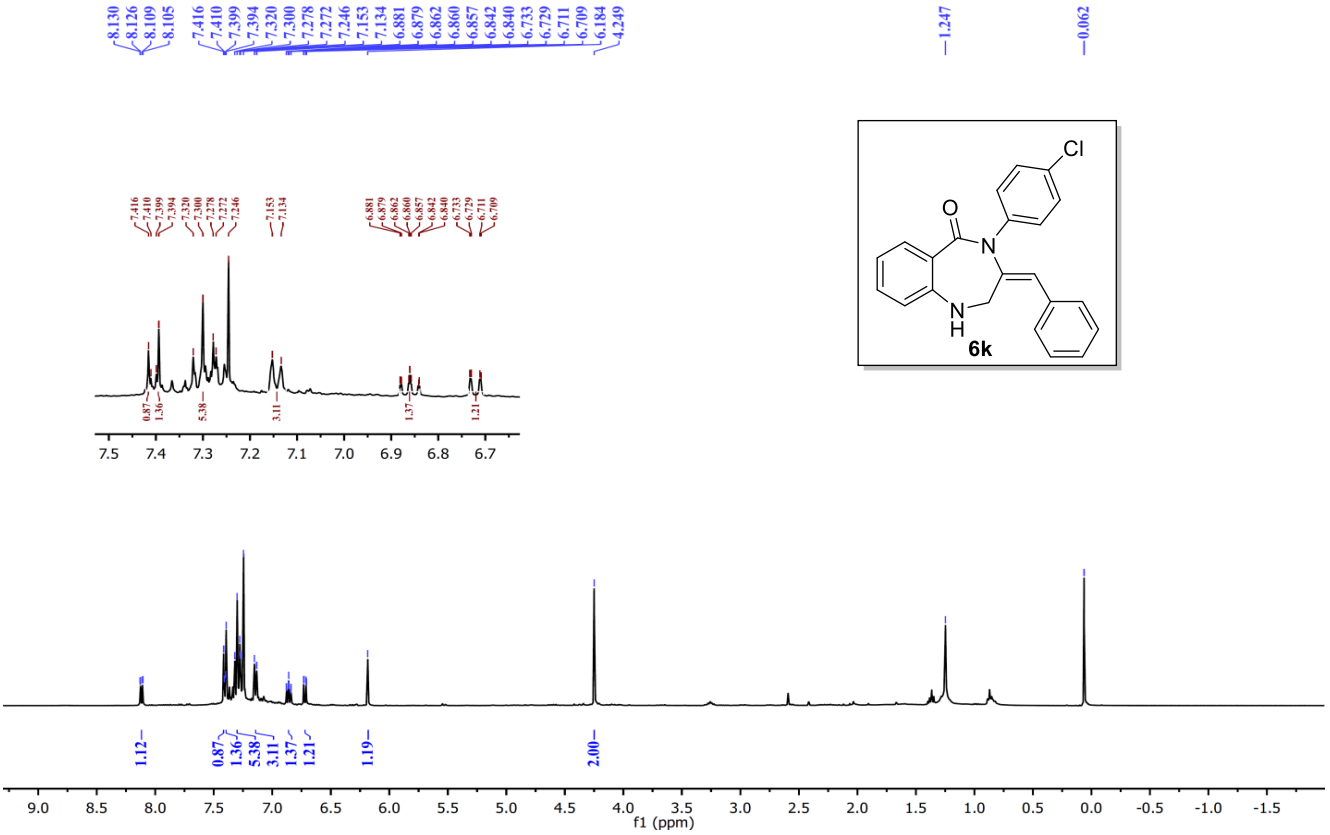
1H NMR (400 MHz) of **6i** :



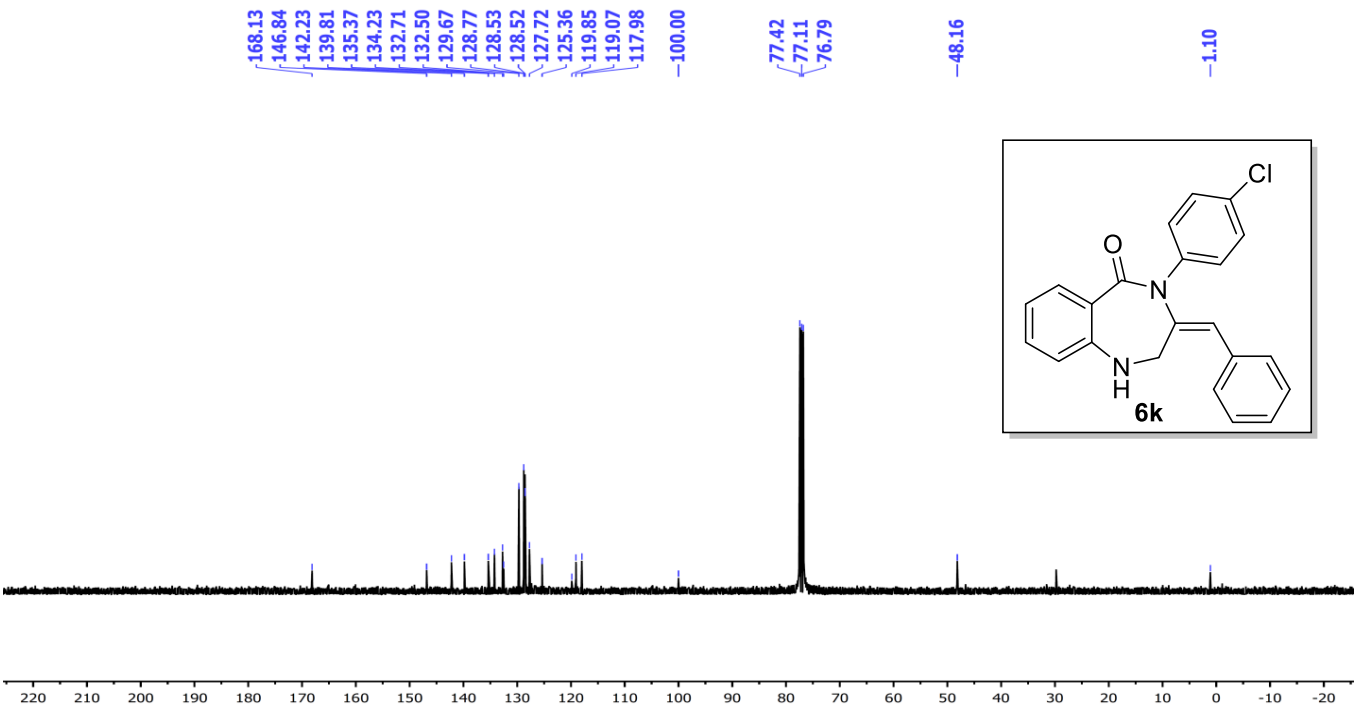
$^{13}C\{^{1}H\}$ NMR (100 MHz) of **6i :**



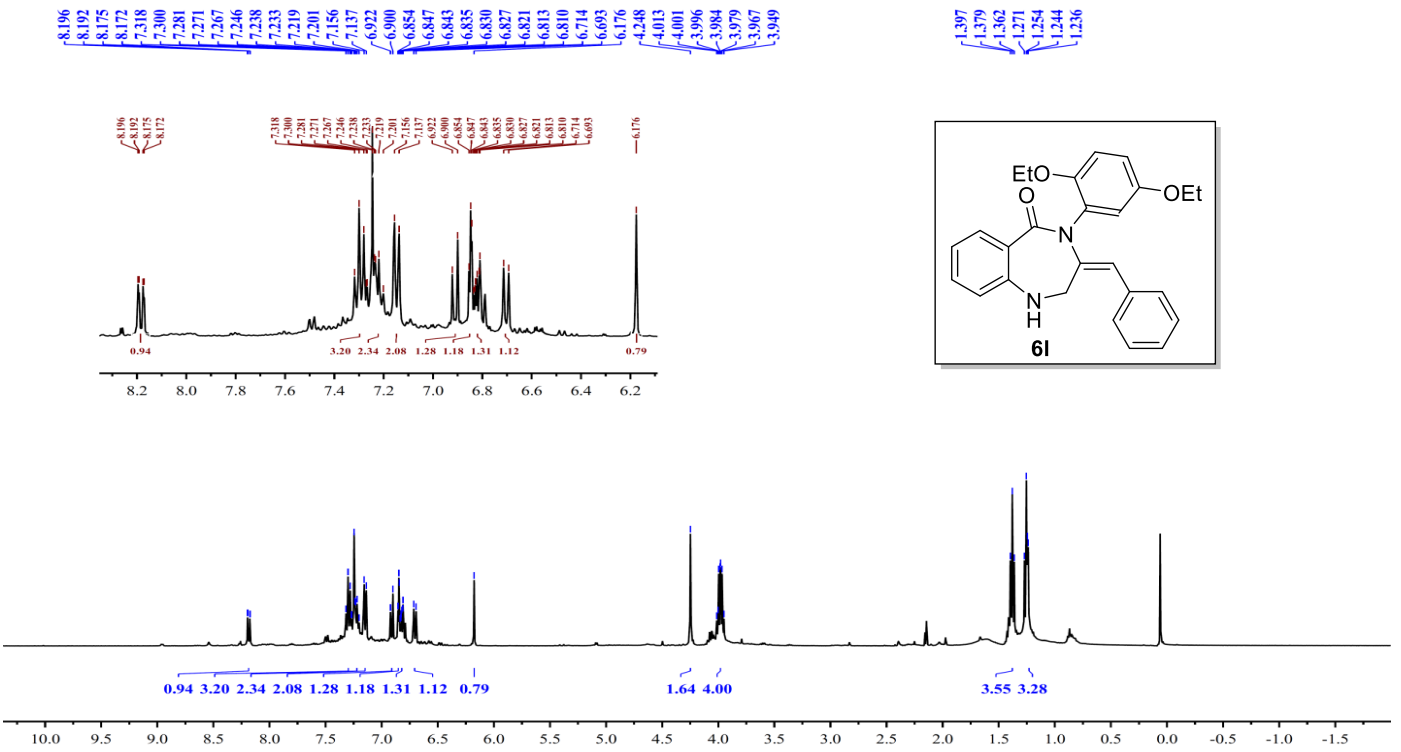
^{1}H NMR (400 MHz) of **6k**:



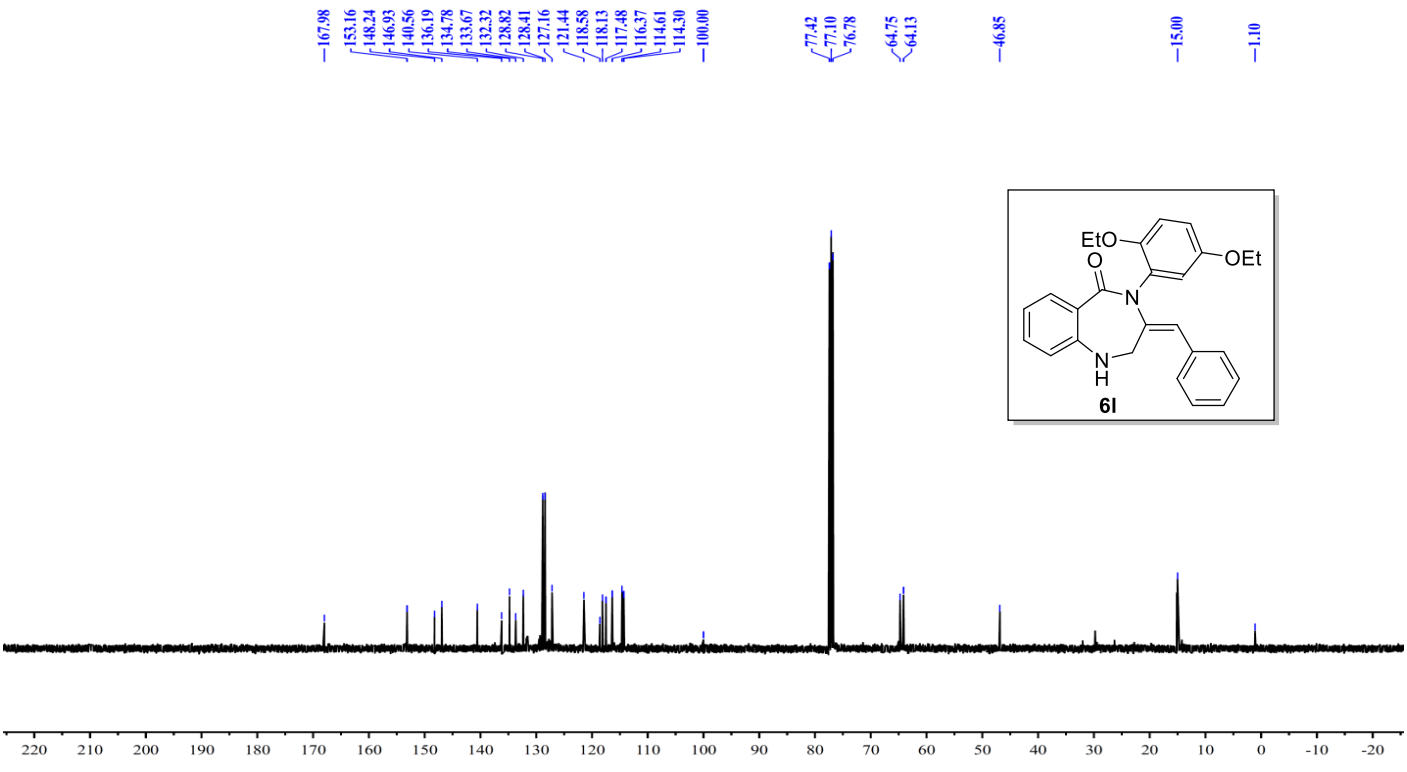
^{13}C{^{1}H} NMR (100 MHz) of **6k :**



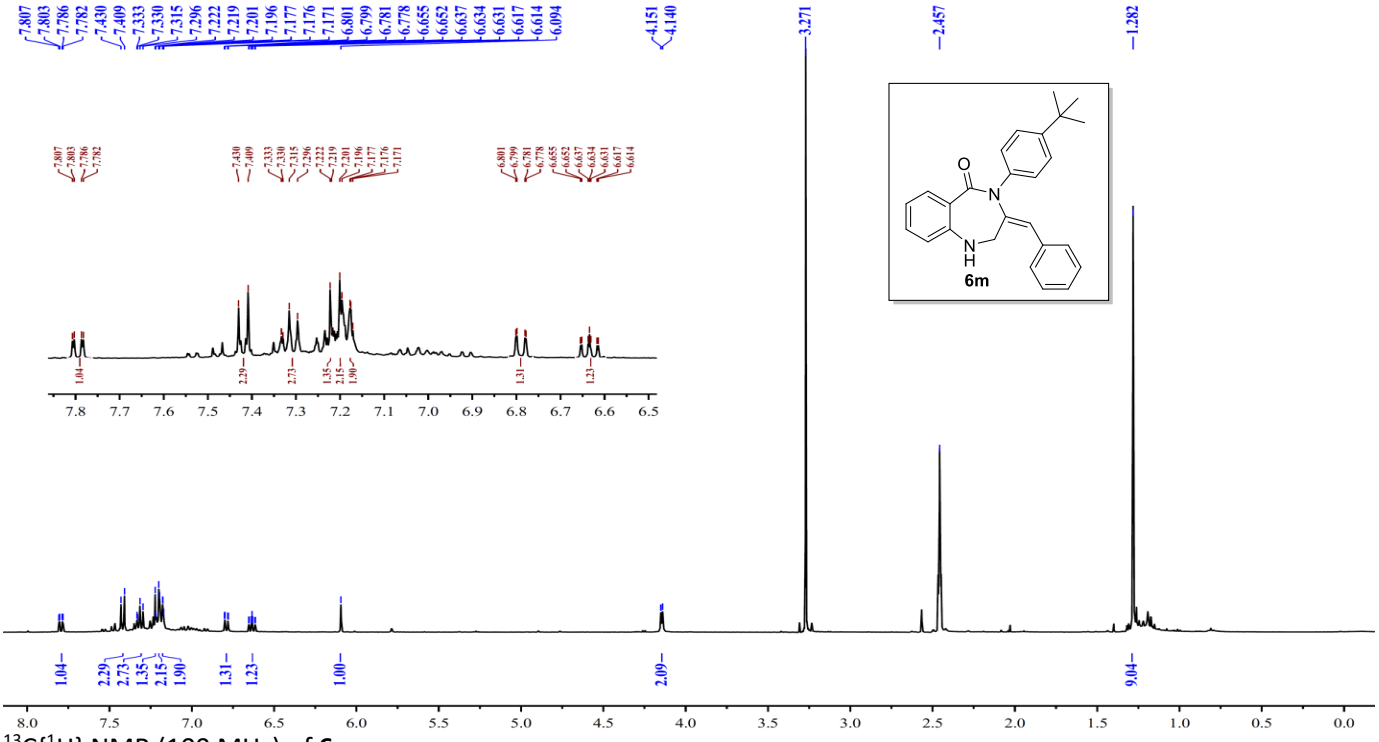
^{1}H NMR (400 MHz) of **6l** :



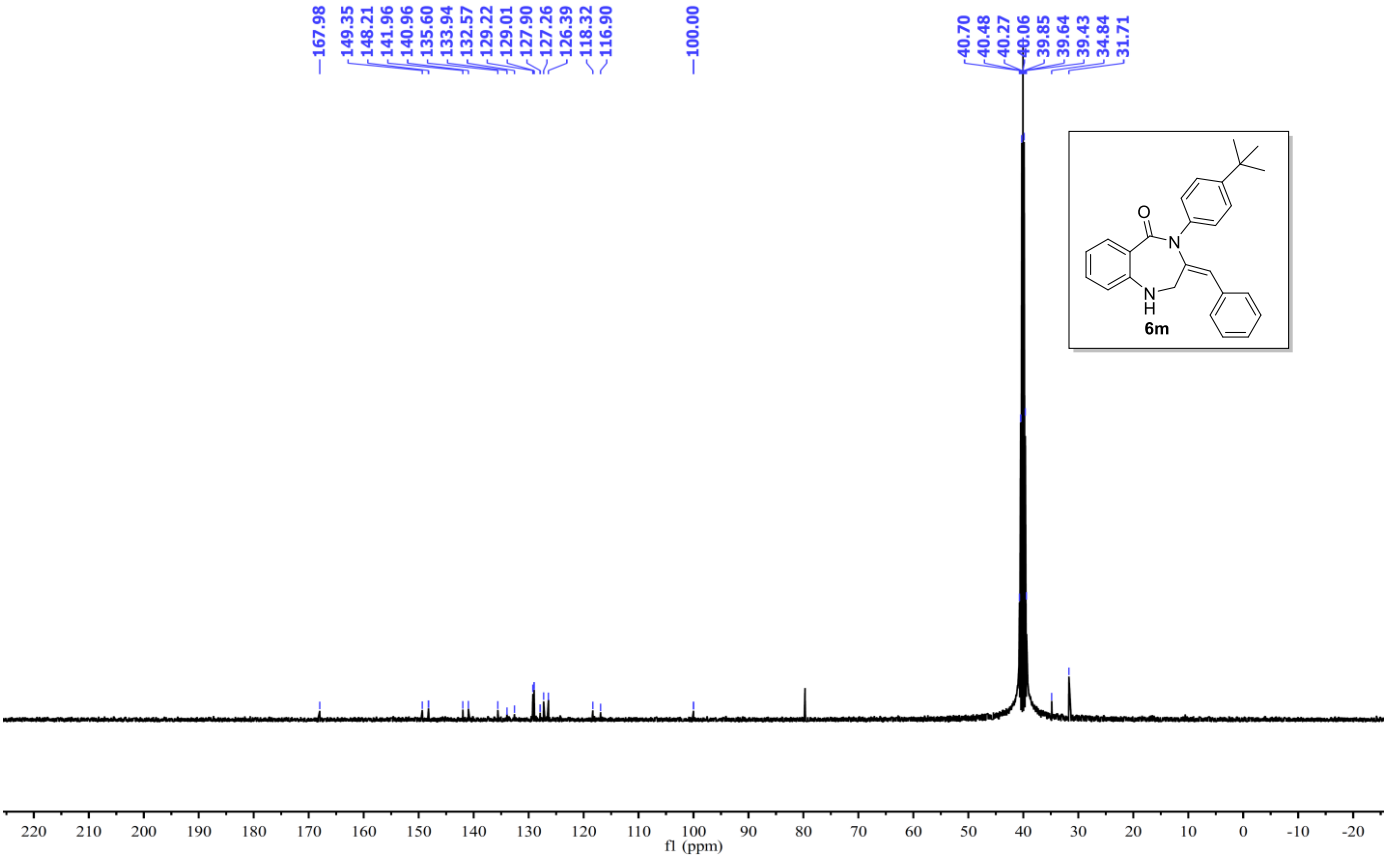
^{13}C{^{1}H} NMR (100 MHz) of **6l** :



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

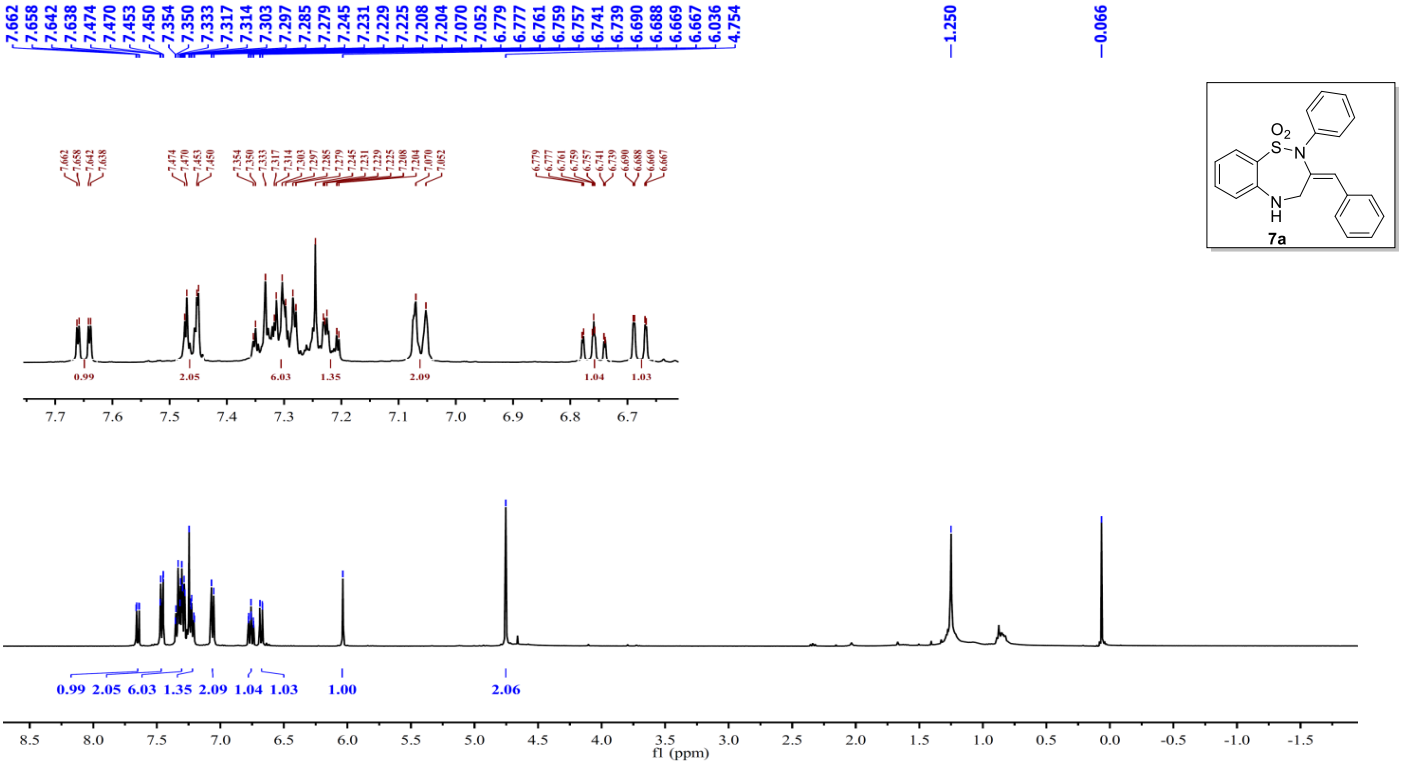


^{13}C{^{1}H} NMR (100 MHz) of **6m** :

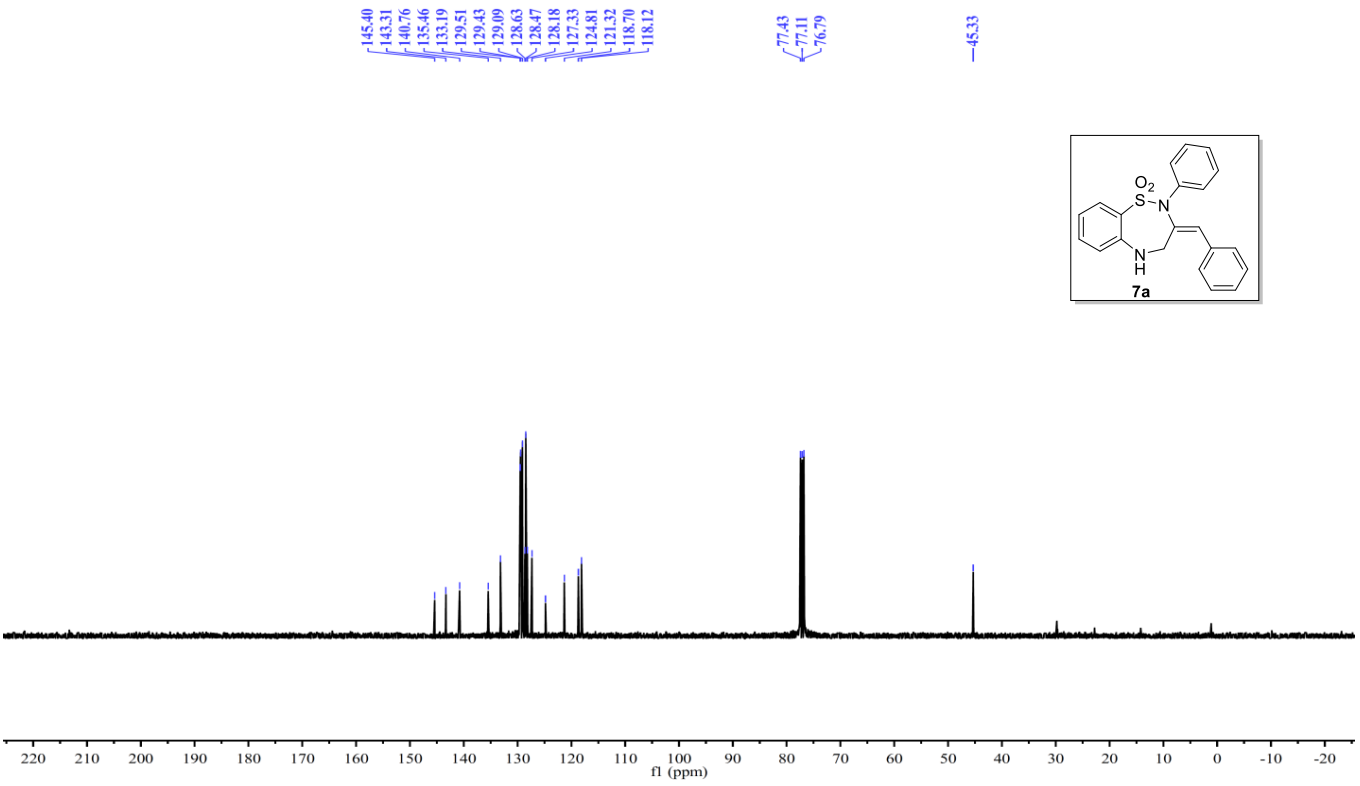


45. NMR spectra of products 7a-7k:

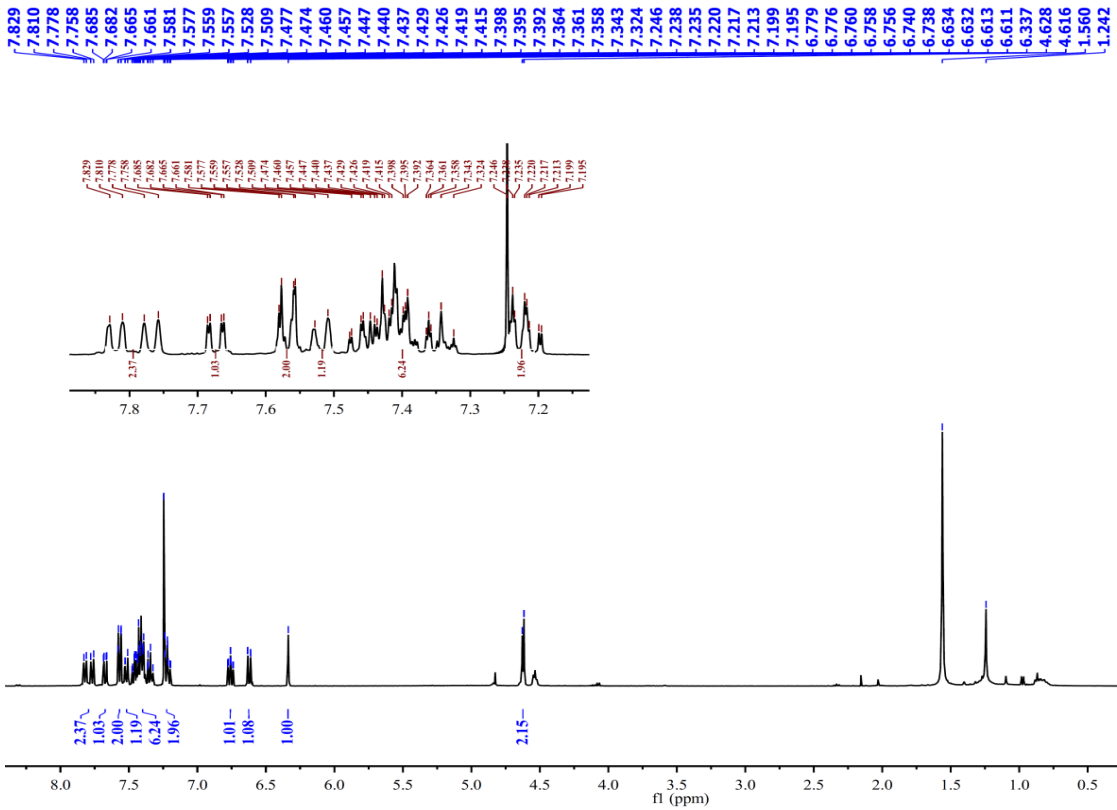
^{1}H NMR (400 MHz) of **7a**:

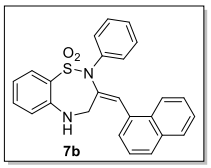


^{13}C{^{1}H} NMR (100 MHz) of **7a**:

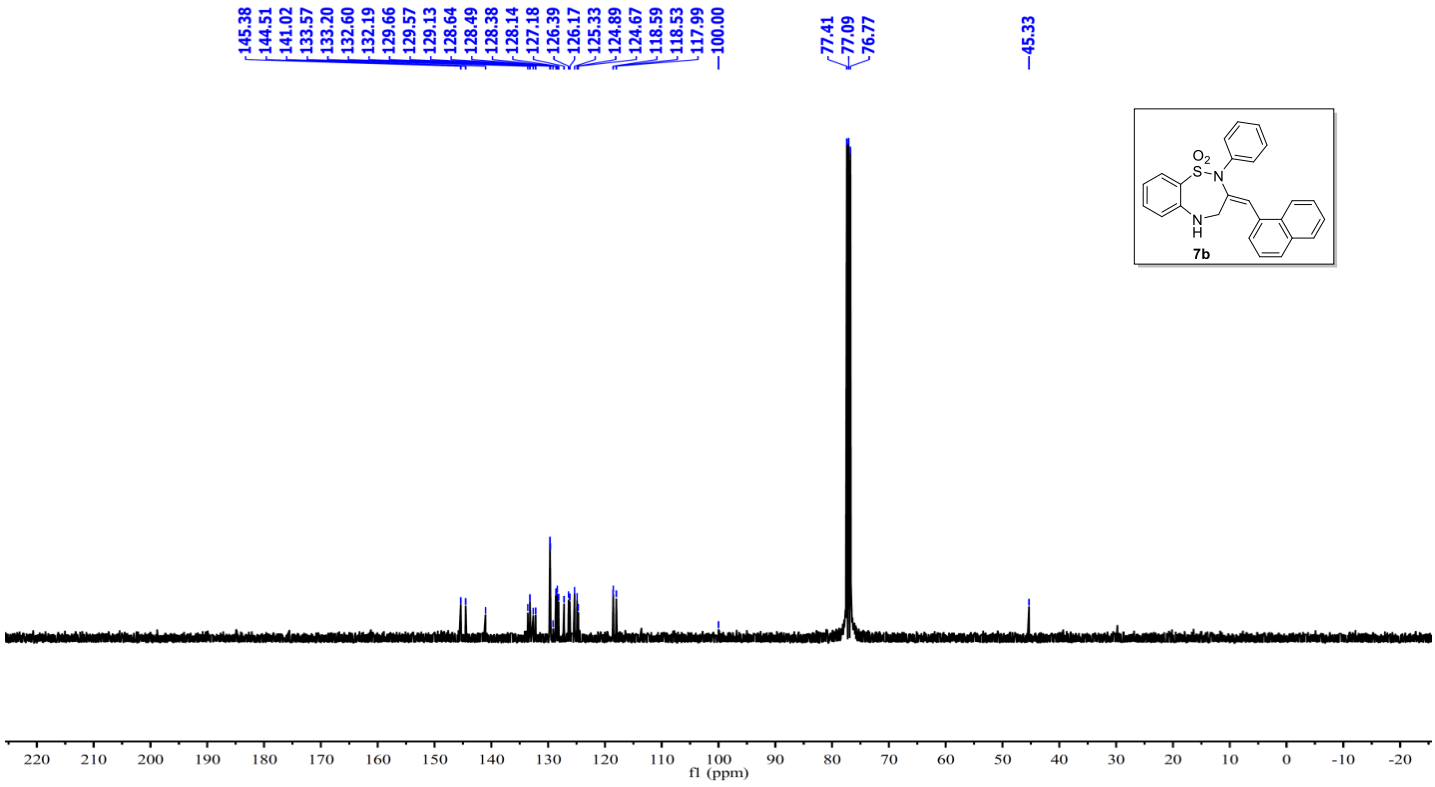


^{1}H NMR (400 MHz) of **7b**:

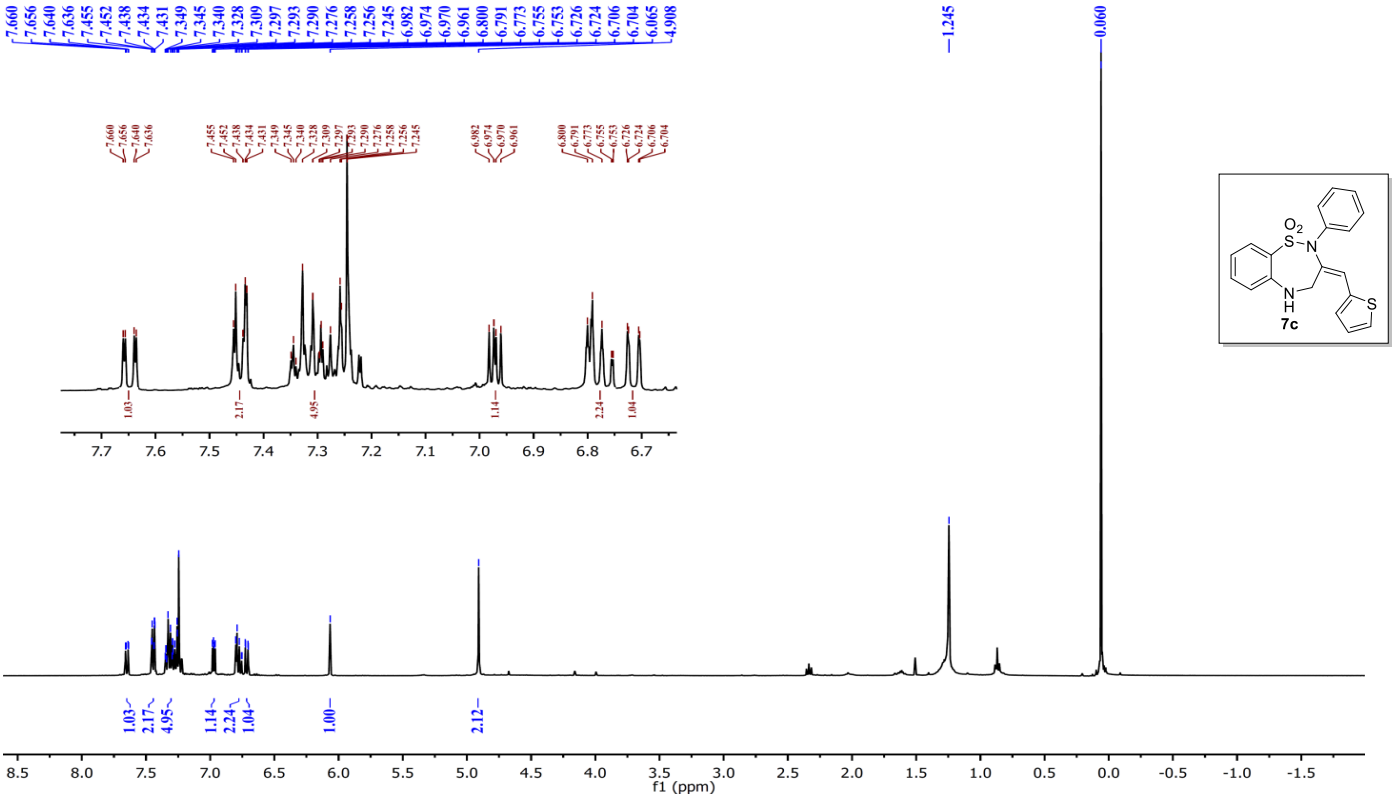




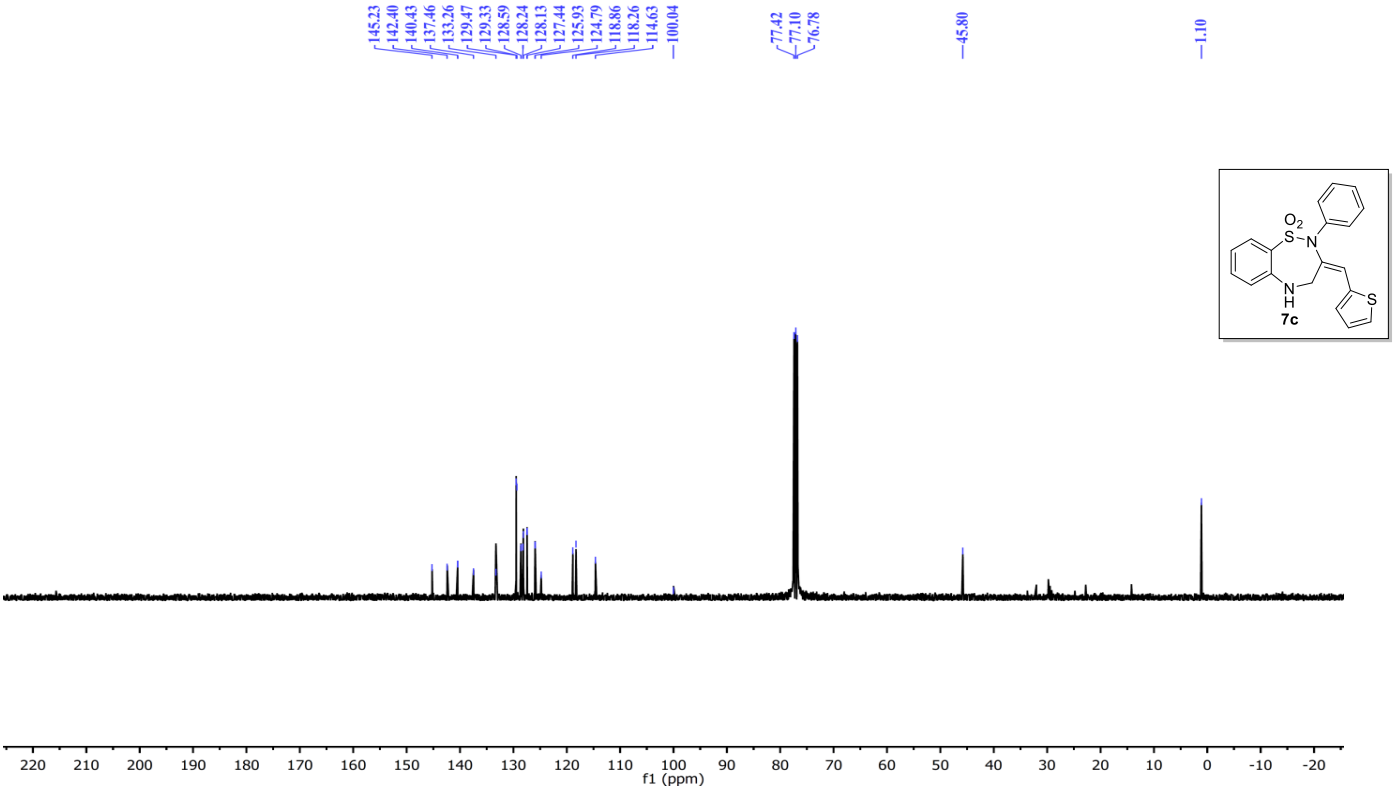
^{13}C{^{1}H} NMR (100 MHz) of **7b**:



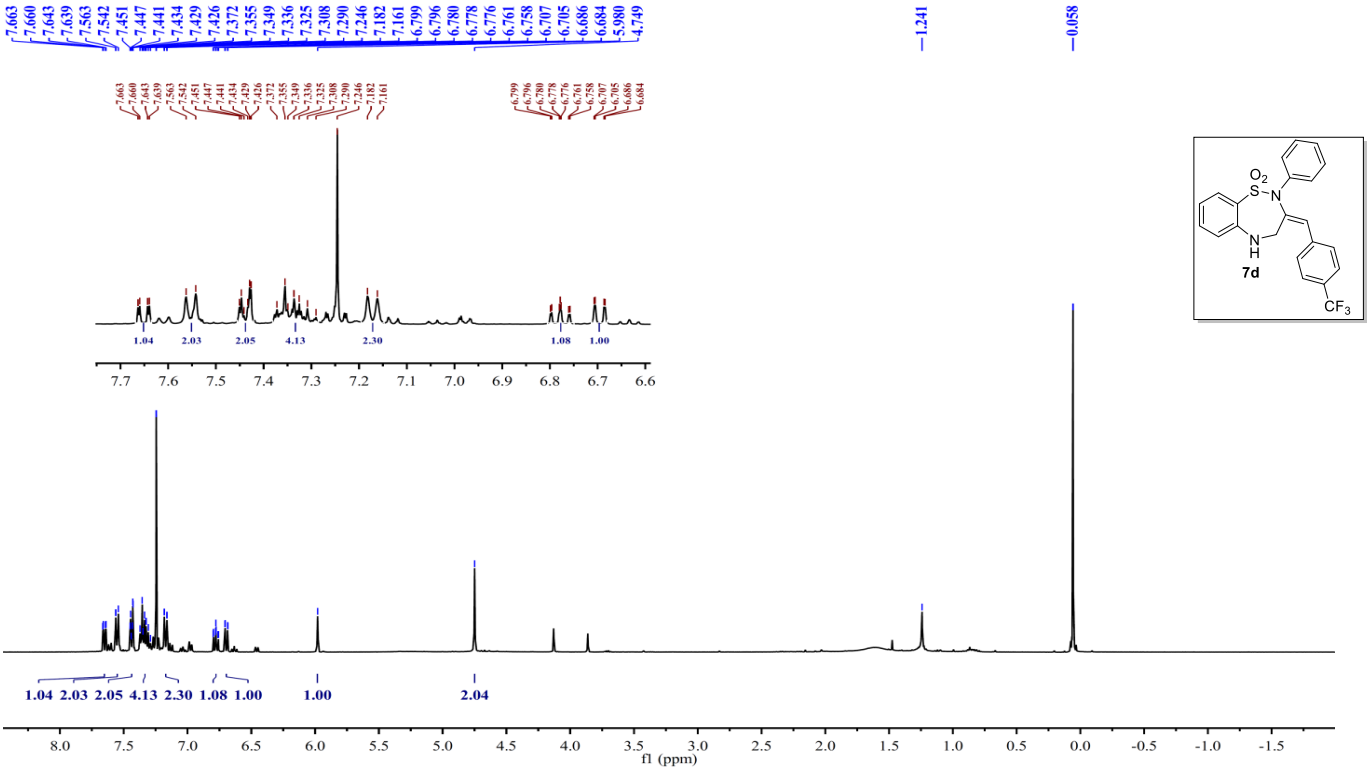
^{1}H NMR (400 MHz) of **7c**:



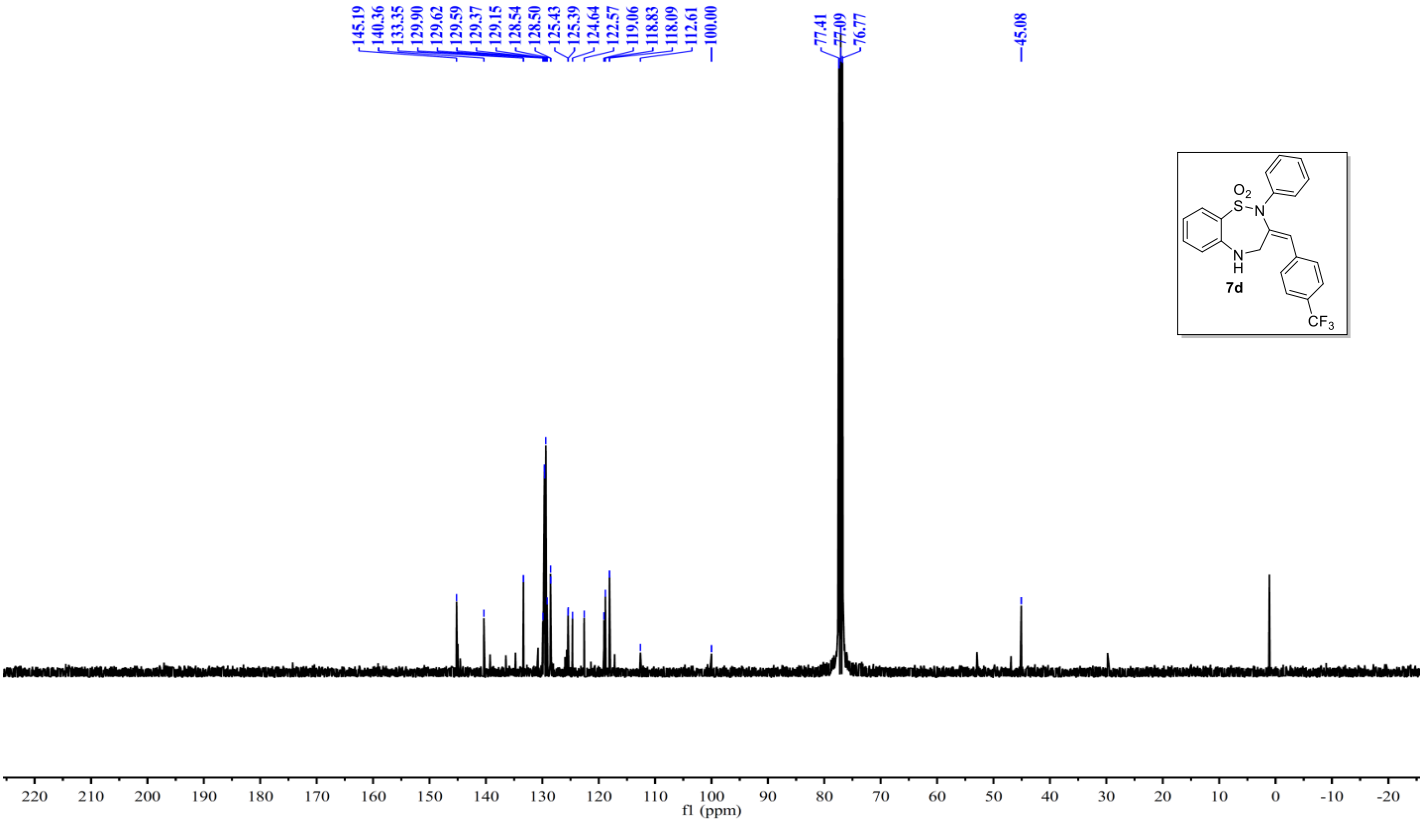
^{13}C{^{1}H} NMR (100 MHz) of **7c**:



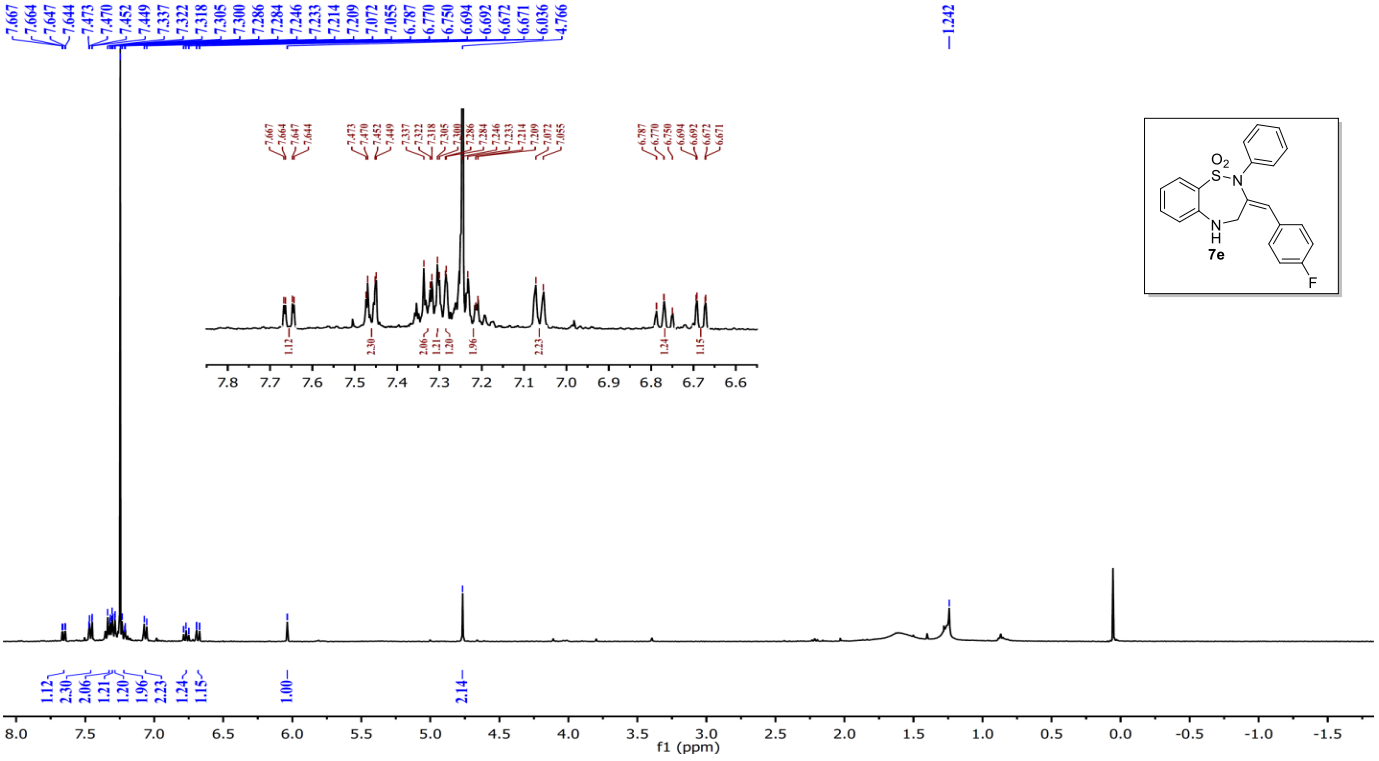
^{1}H NMR (400 MHz) of **7d**:



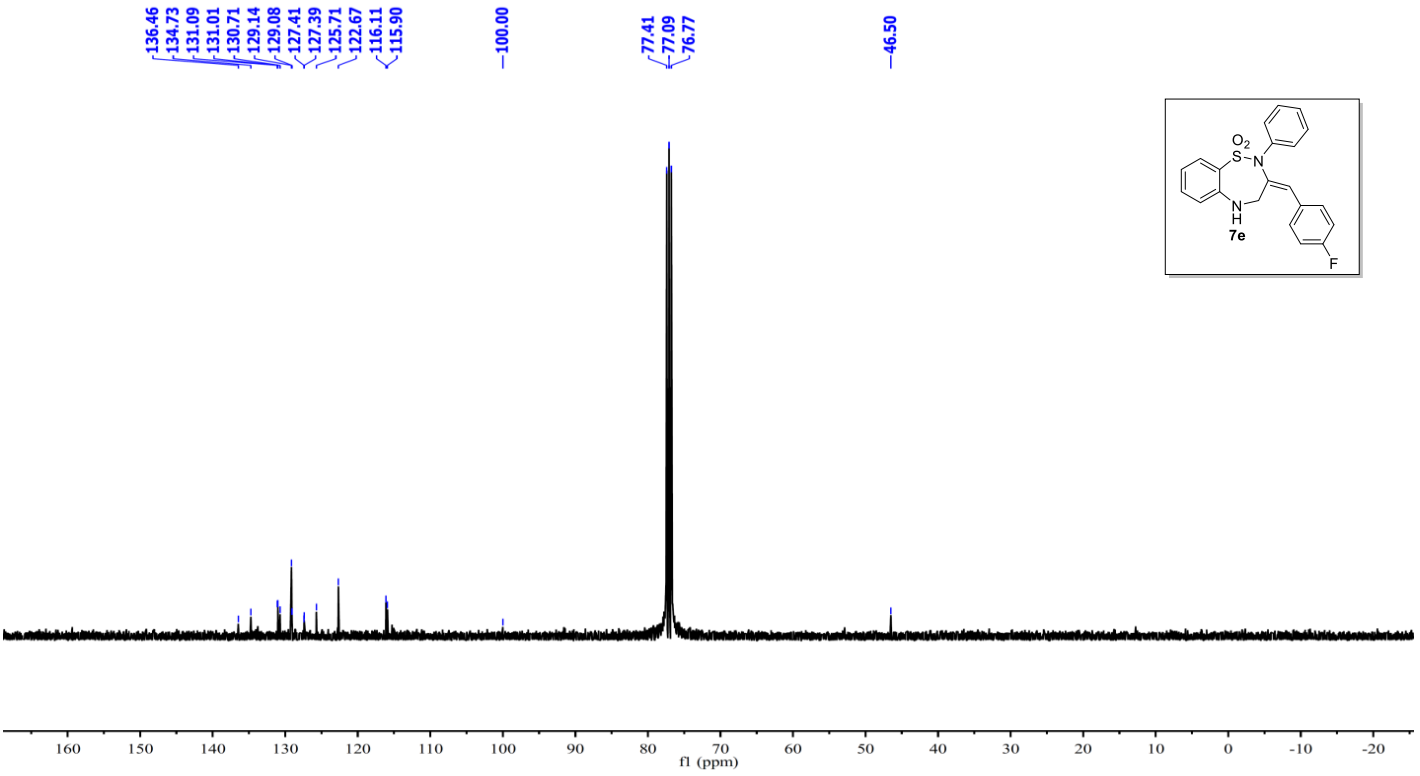
^{13}C{^{1}H} NMR (100 MHz) of **7d**:



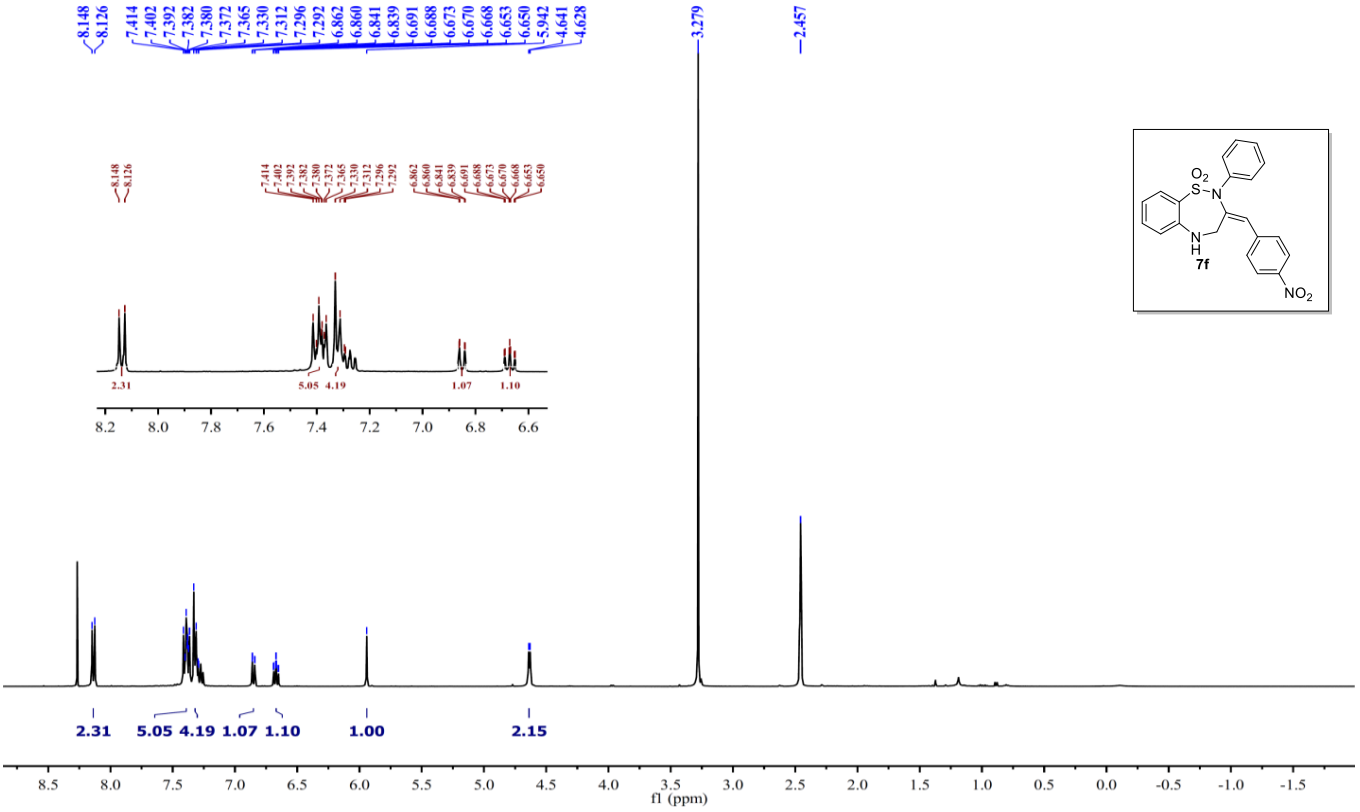
^{1}H NMR (400 MHz) of **7e**:



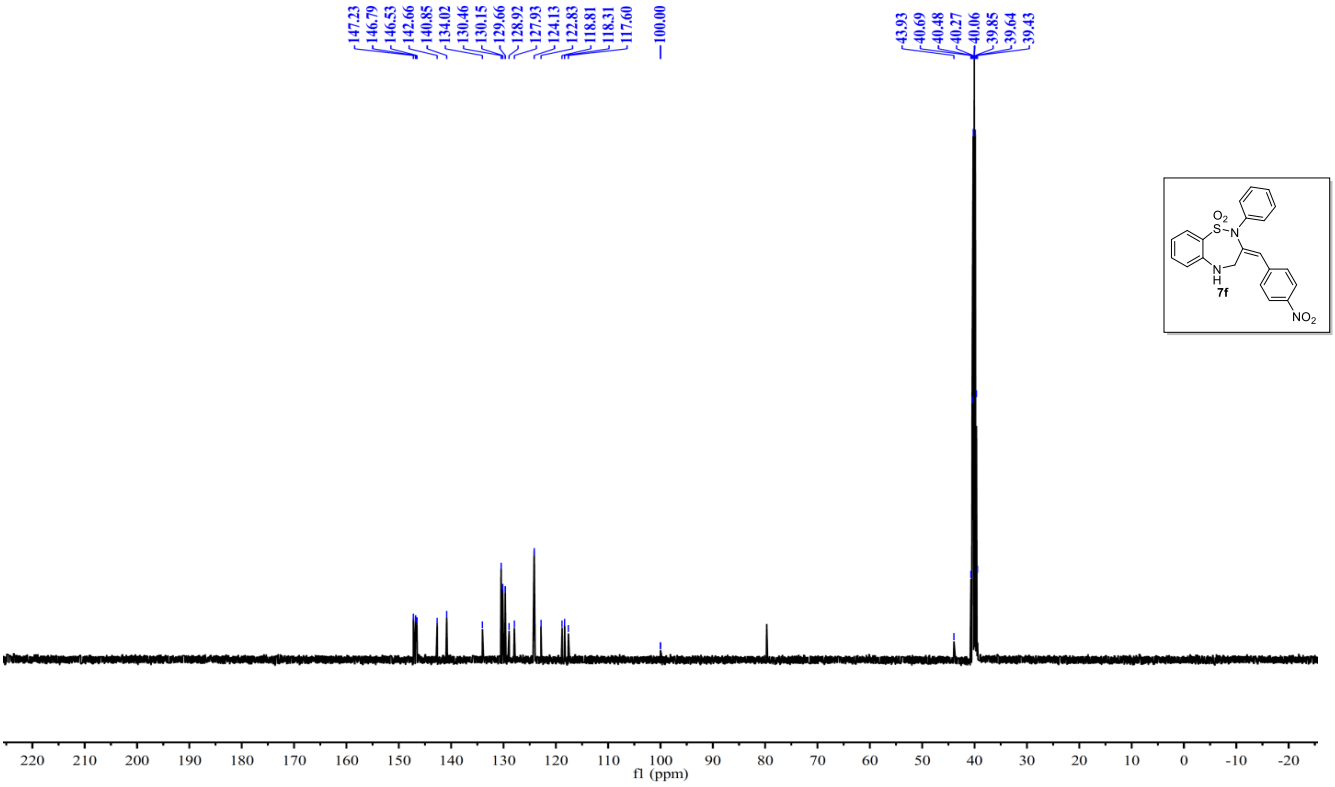
^{13}C{^{1}H} NMR (100 MHz) of **7e**:



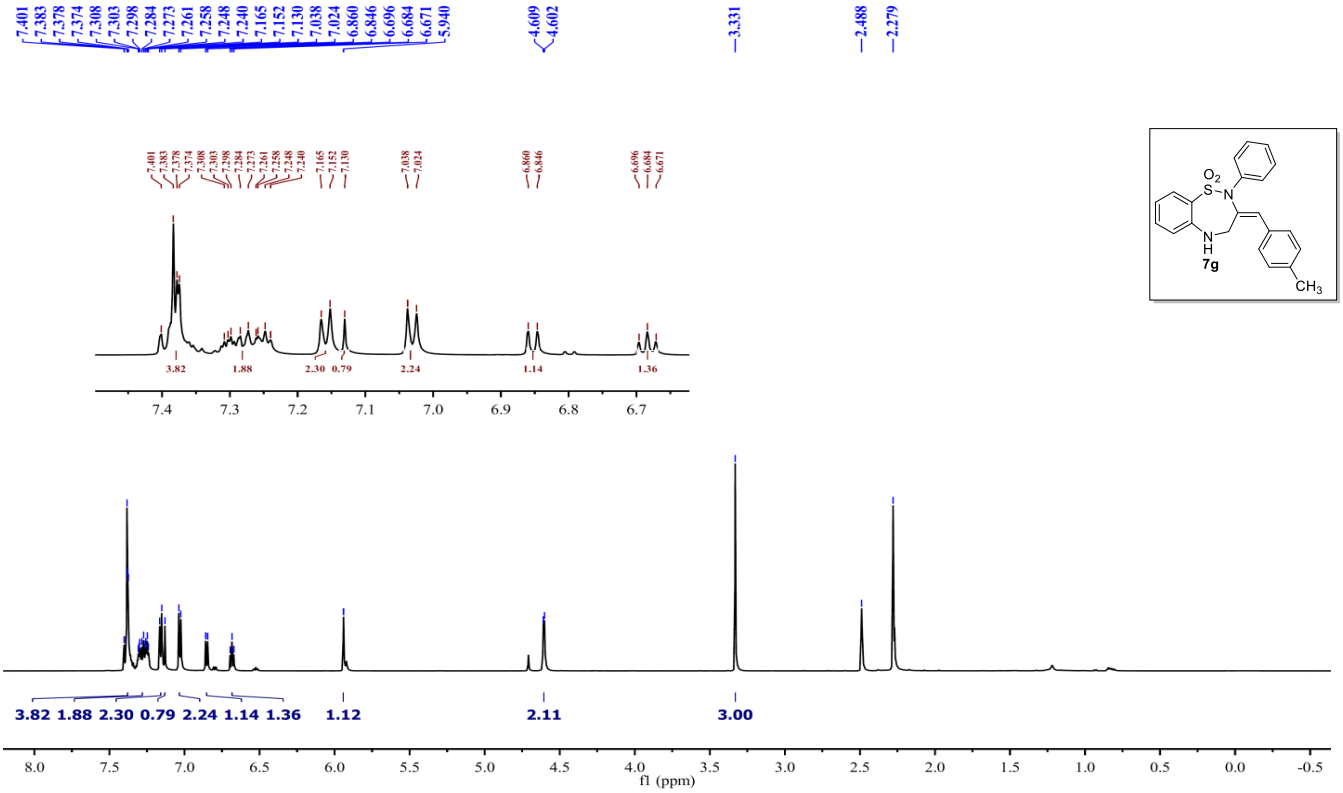
^{1}H NMR (400 MHz) of **7f** :



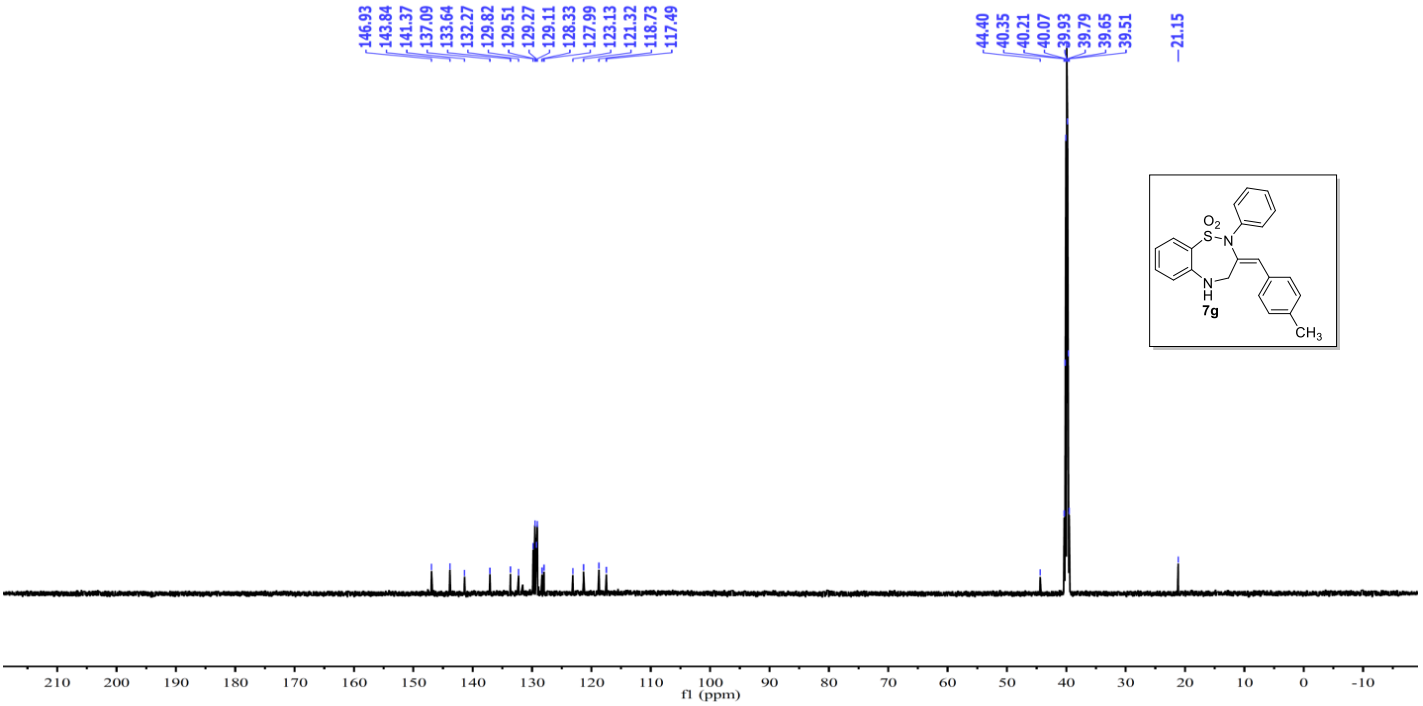
^{13}C{^{1}H} NMR (100 MHz) of **7f**:



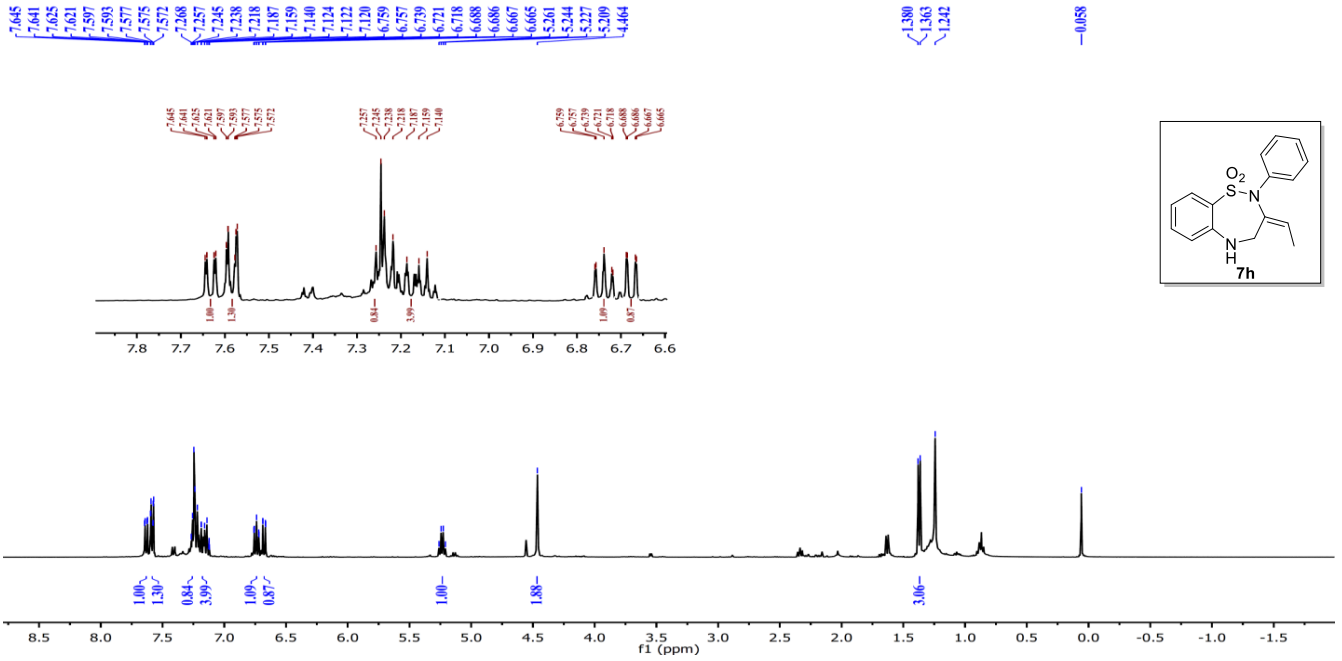
^{1}H NMR (600 MHz) of **7g** :



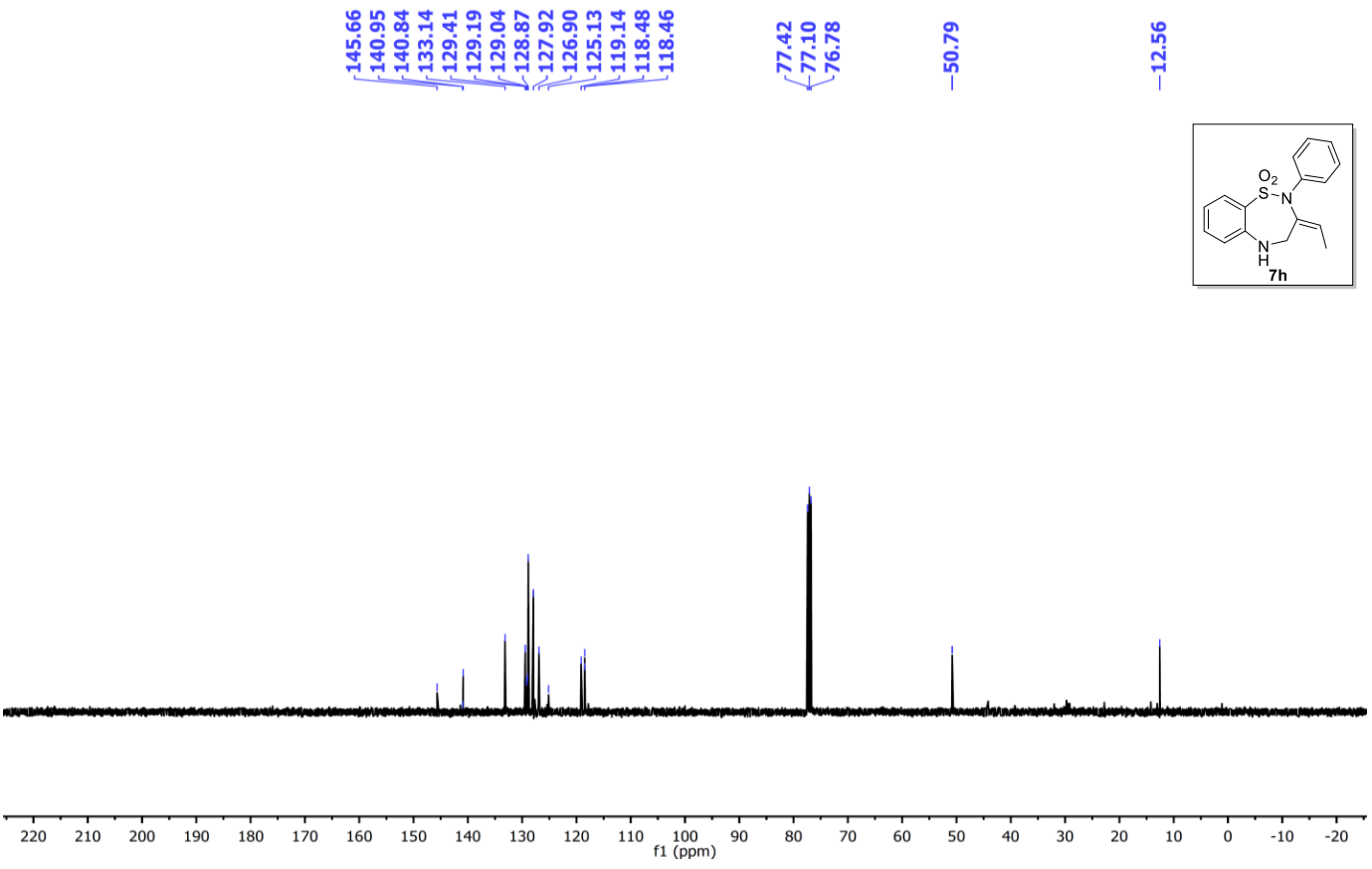
^{13}C{^{1}H} NMR (150 MHz) of **7g**:



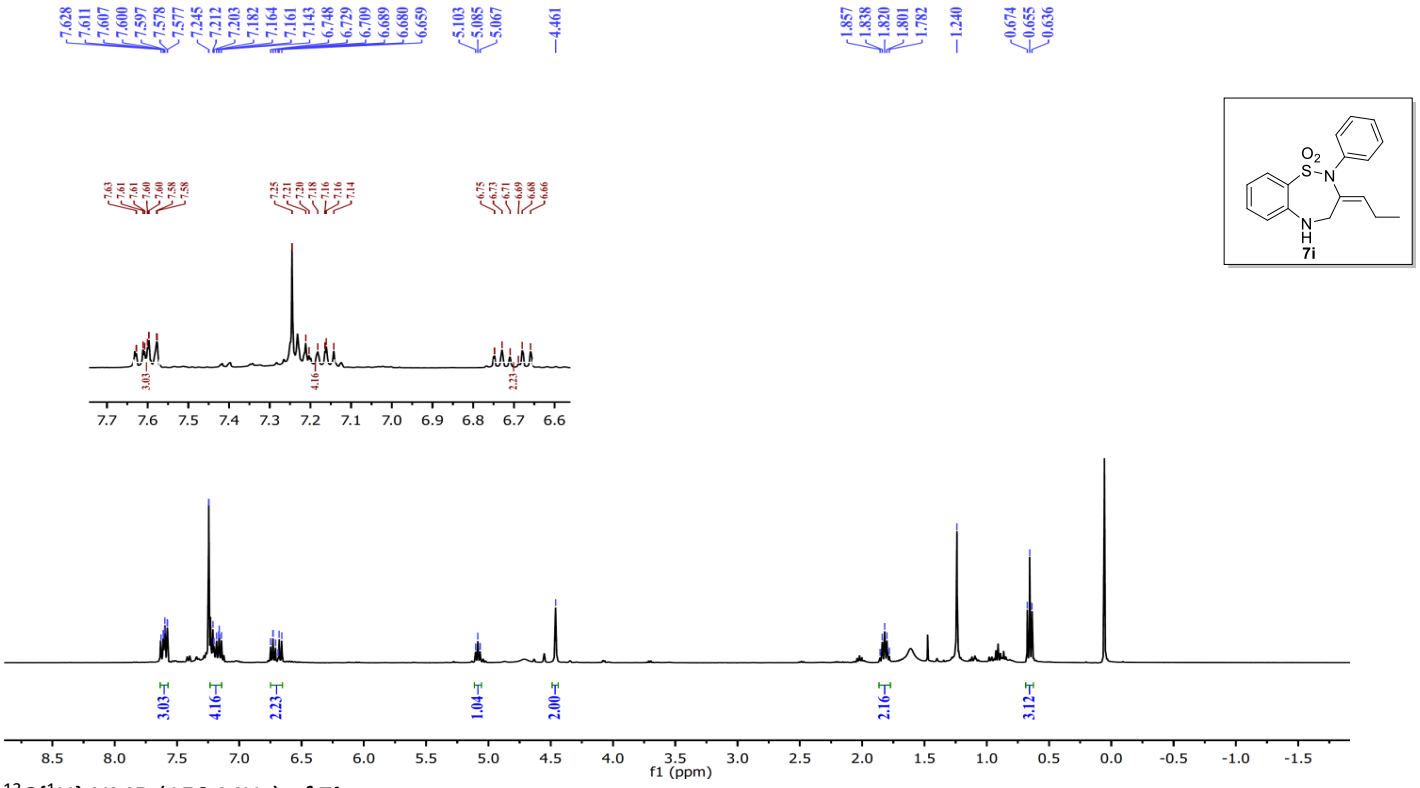
^{1}H NMR (400 MHz) of **7h** :



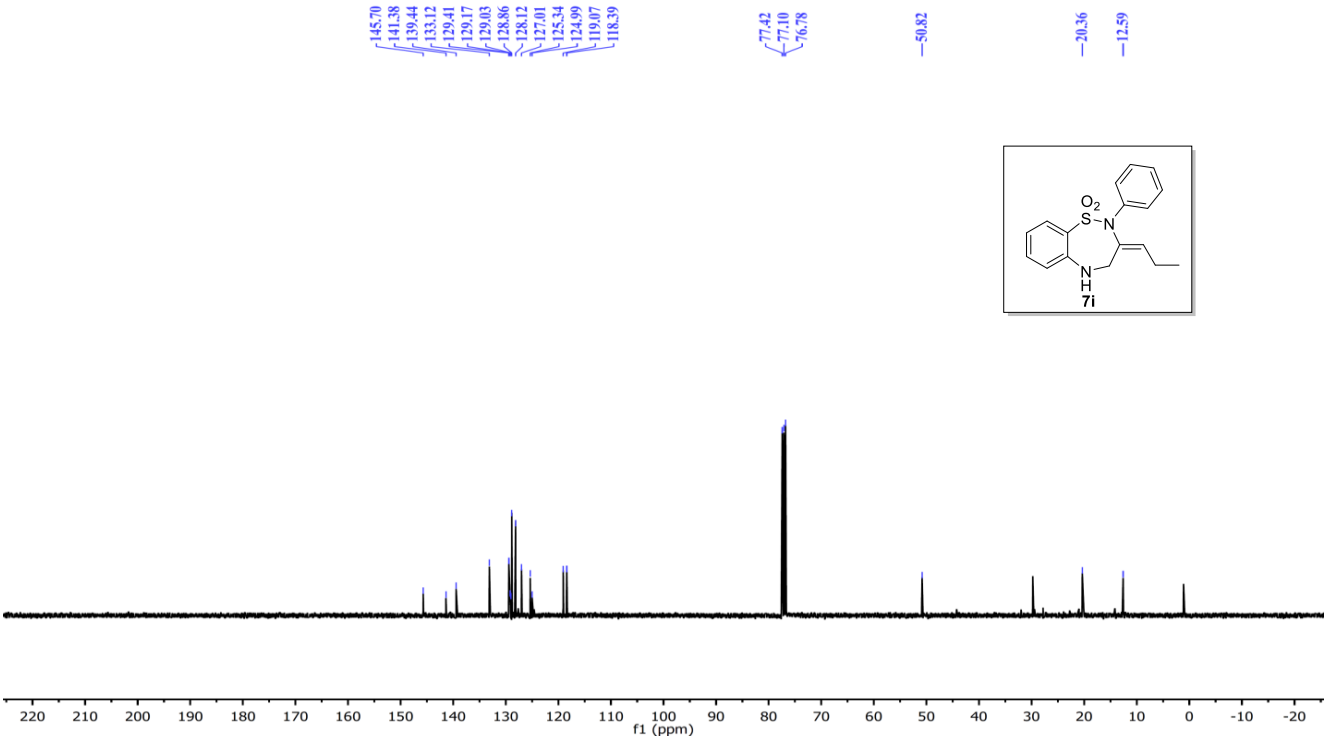
^{13}C{^{1}H} NMR (150 MHz) of **7h** :



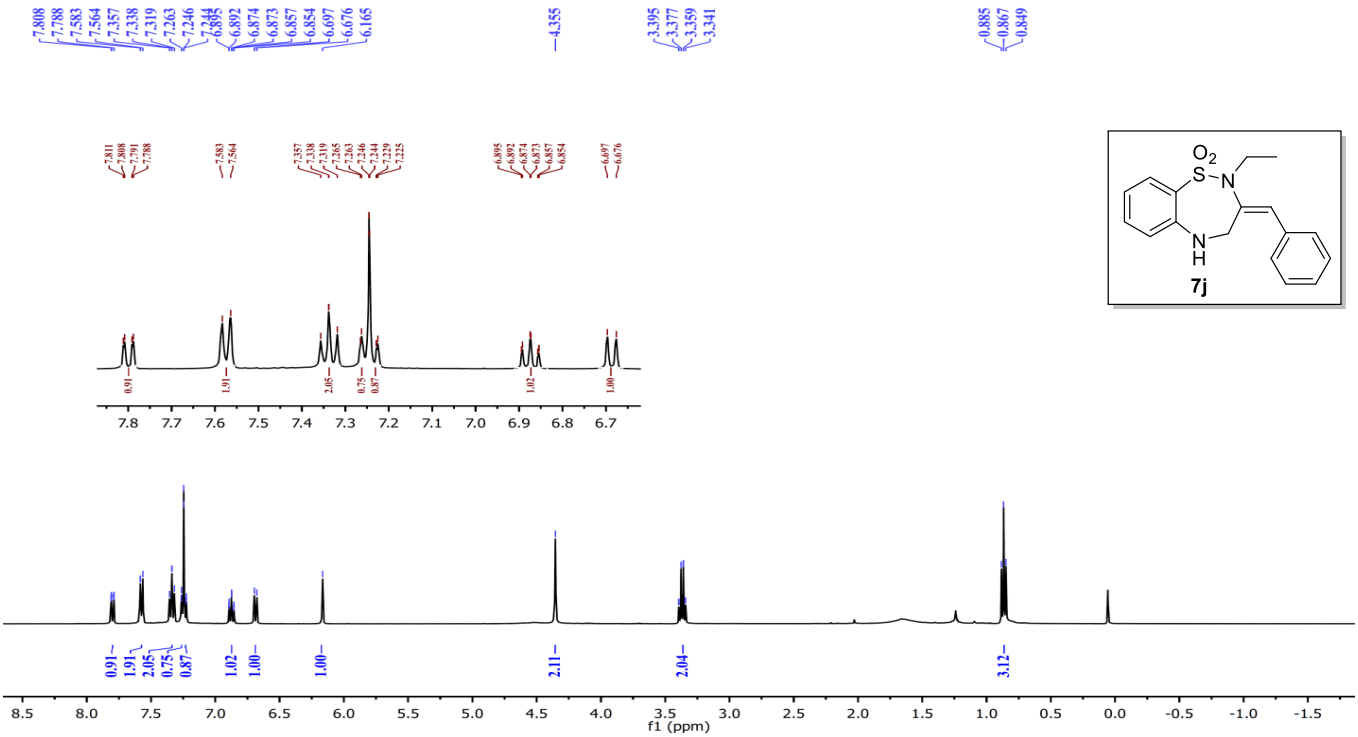
^{1}H NMR (400 MHz) of **7i** :



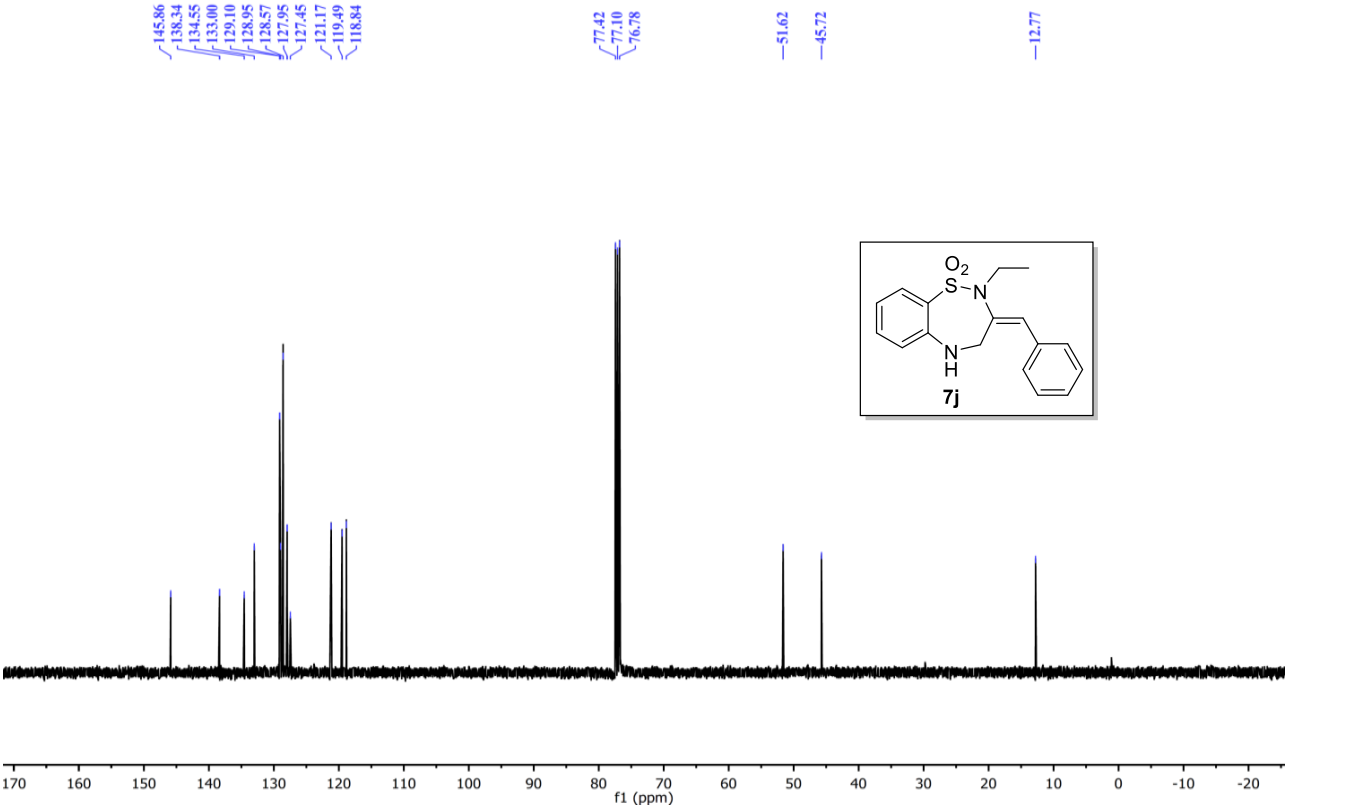
^{13}C{^{1}H} NMR (150 MHz) of **7i** :



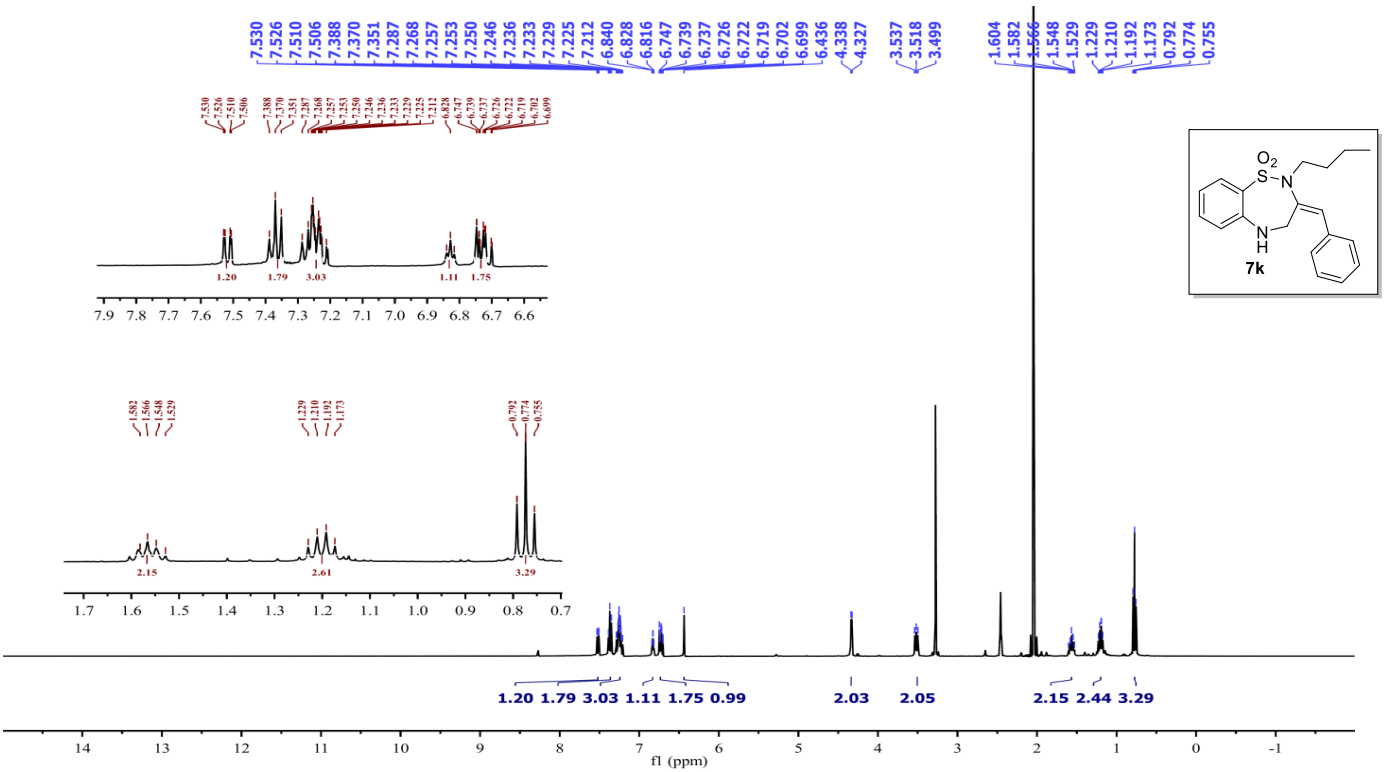
^{1}H NMR (400 MHz) of **7j** :



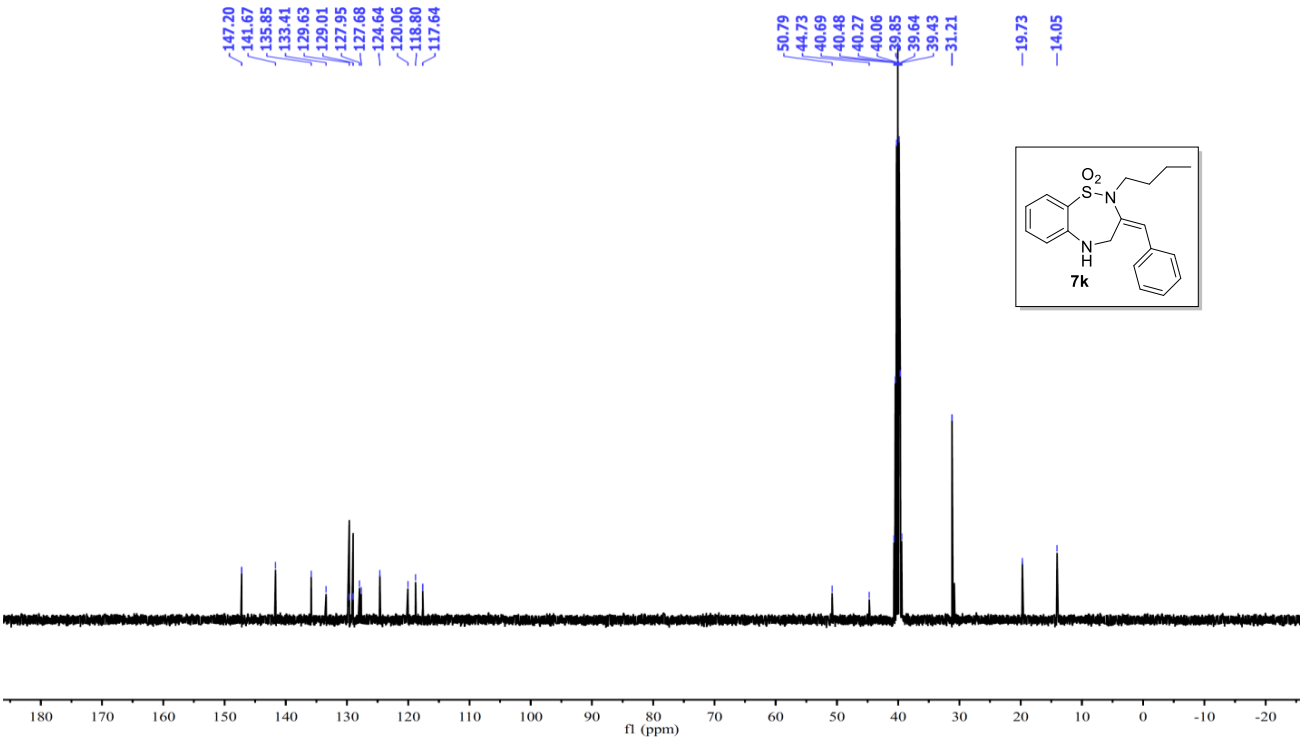
^{13}C{^{1}H} NMR (100 MHz) of **7j** :



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

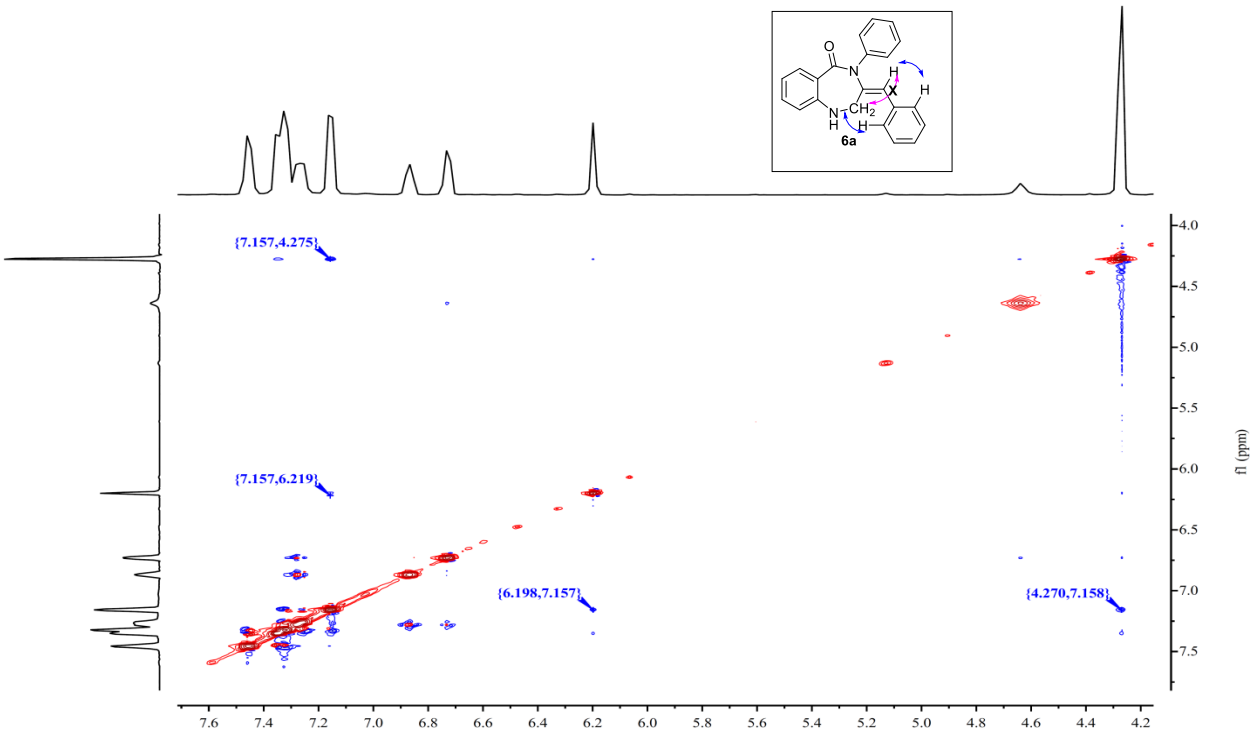


^{13}C{^{1}H} NMR (100 MHz) of **7k** :

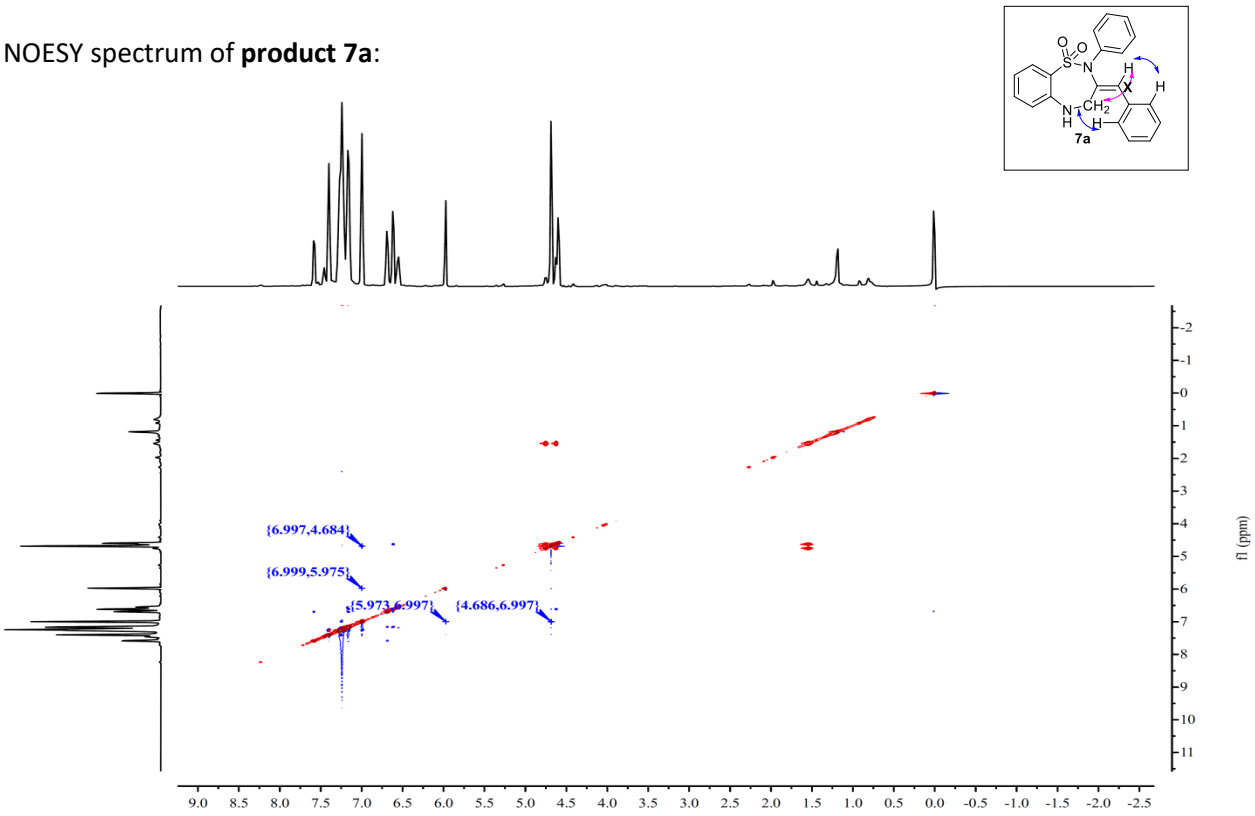


46. NOESY spectrum of products 6a, 7a, 7g:

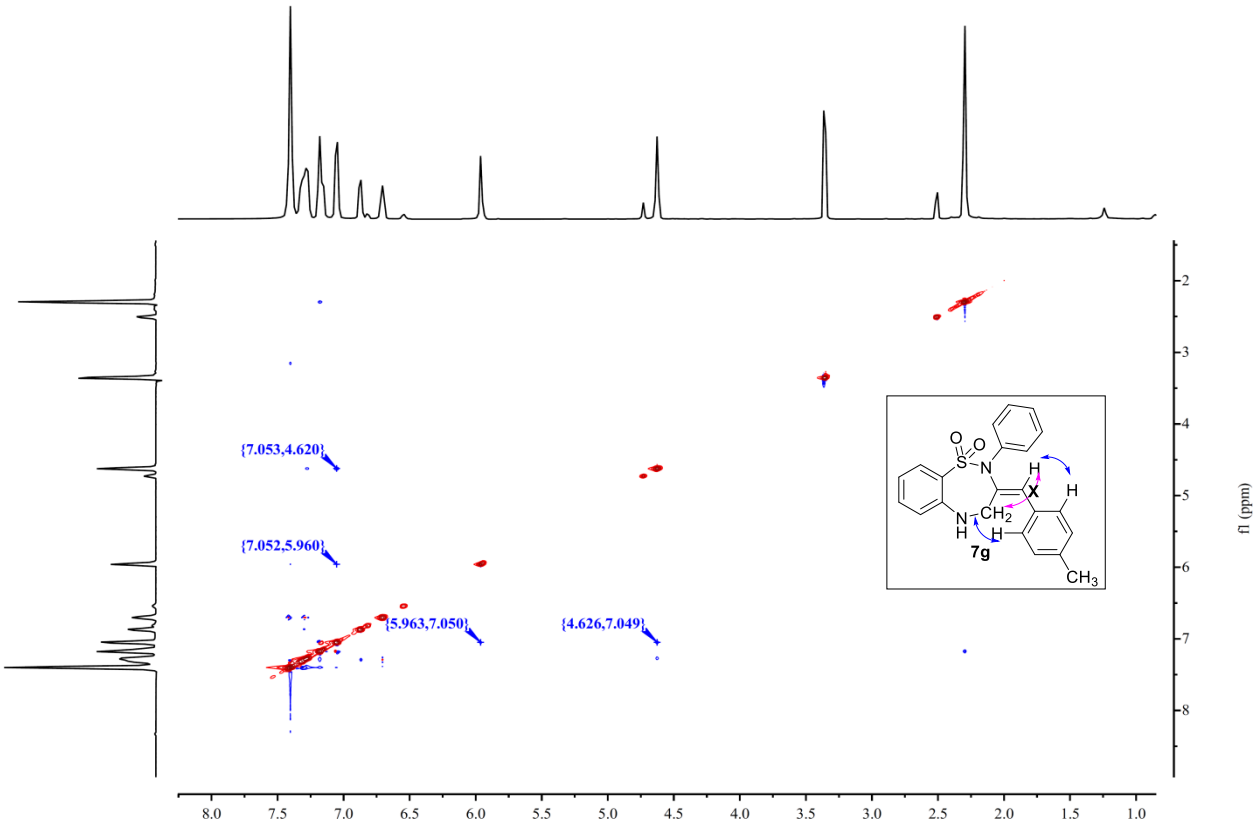
NOESY spectrum of **product 6a**:



NOESY spectrum of **product 7a**:

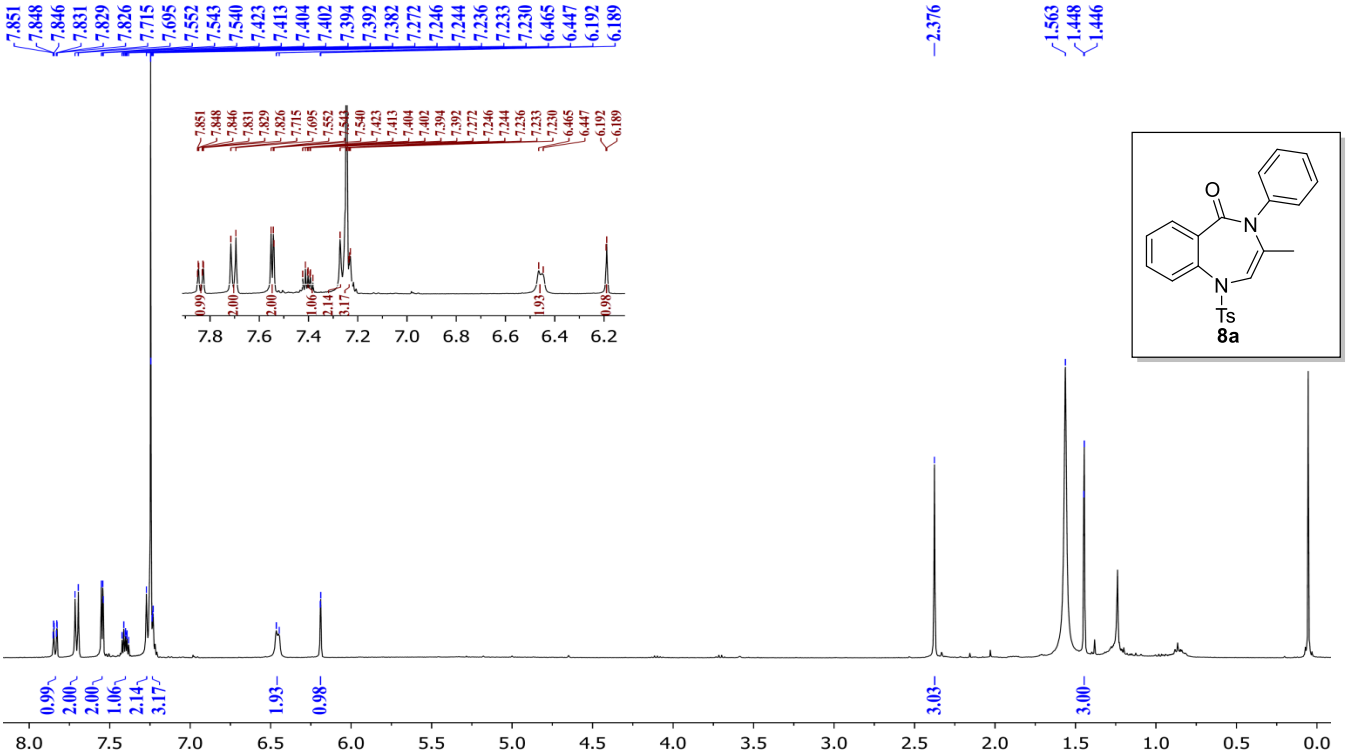


NOESY spectrum of **product 7g**:

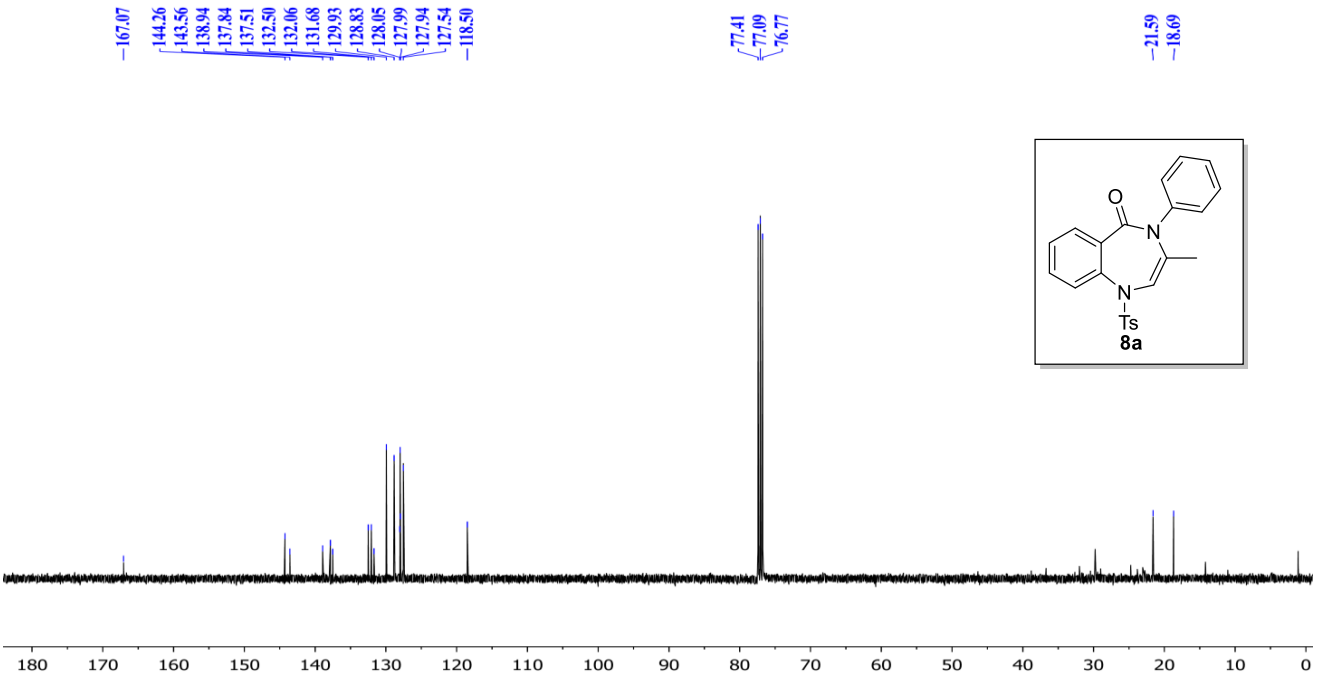


47. NMR spectra of products 8a–8c:

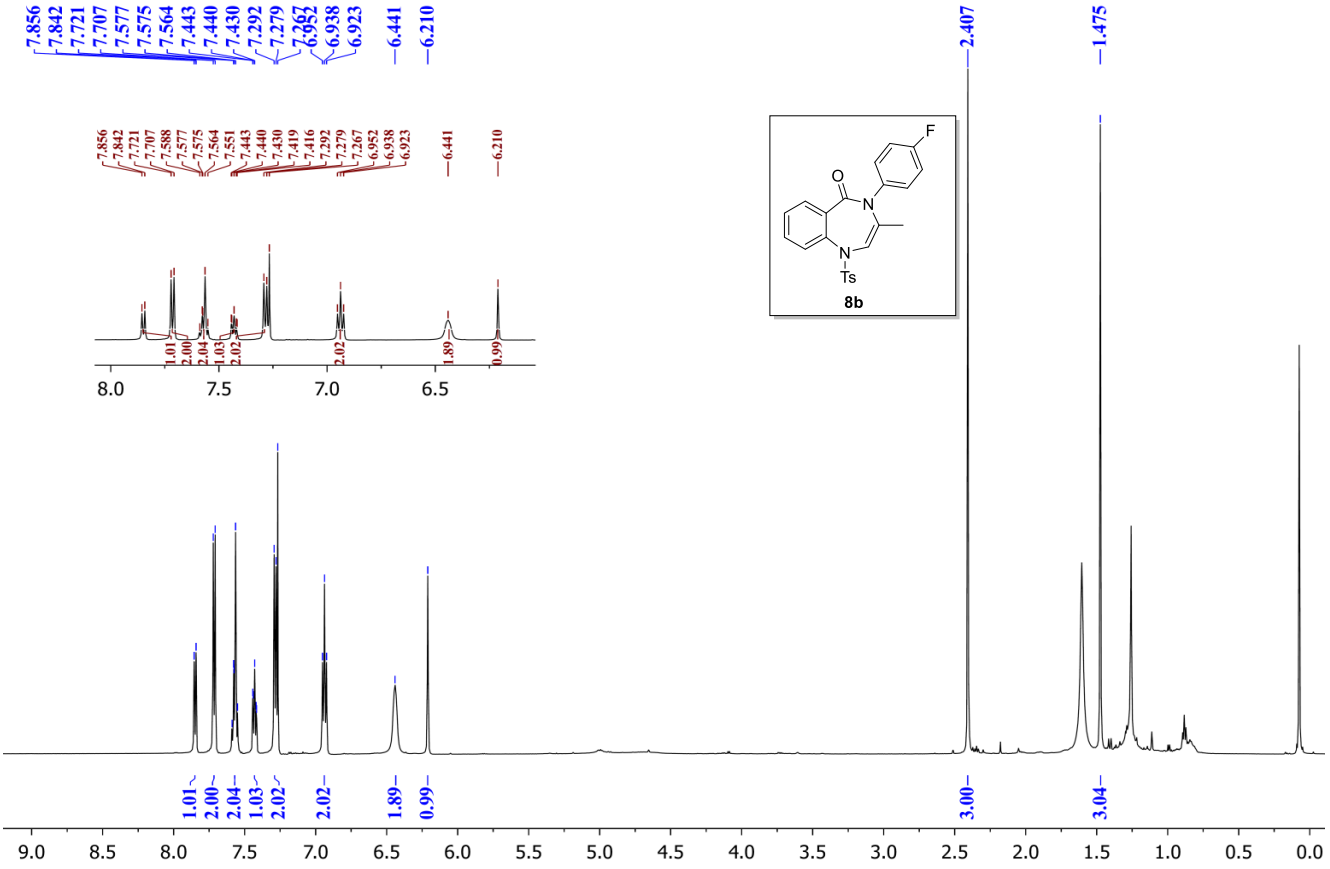
^{1}H NMR (400 MHz) of **8a**:



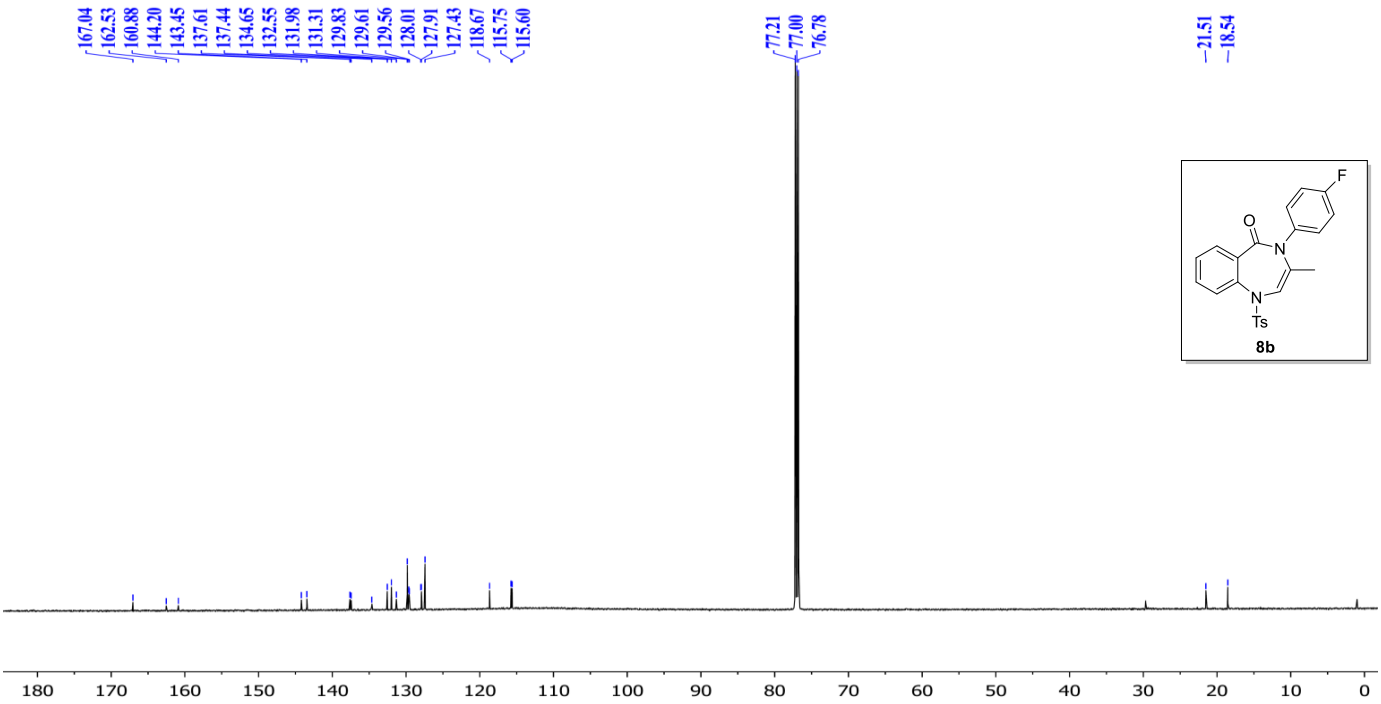
^{13}C{^{1}H} NMR (100 MHz) of **8a**:



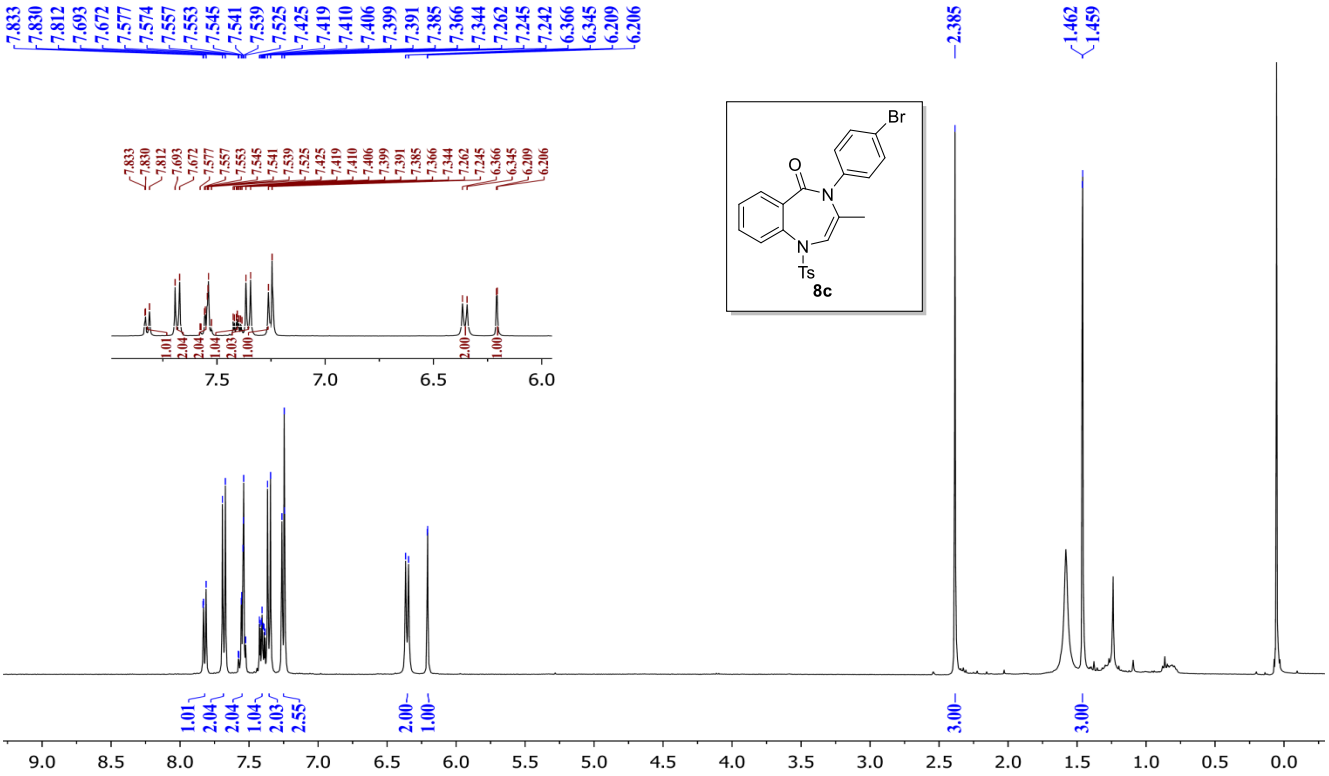
^{1}H NMR (600 MHz) of **8b:**



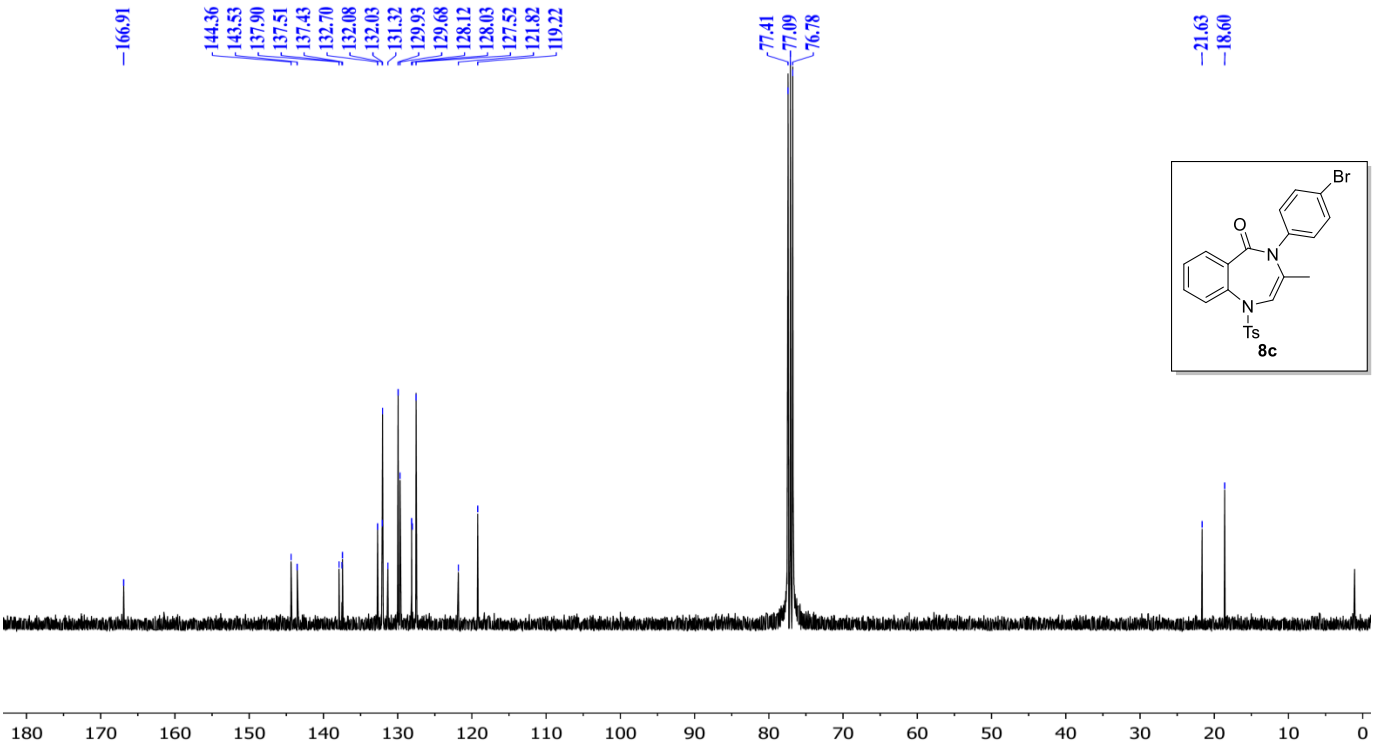
^{13}C{^{1}H} NMR (150 MHz) of **8b**:



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

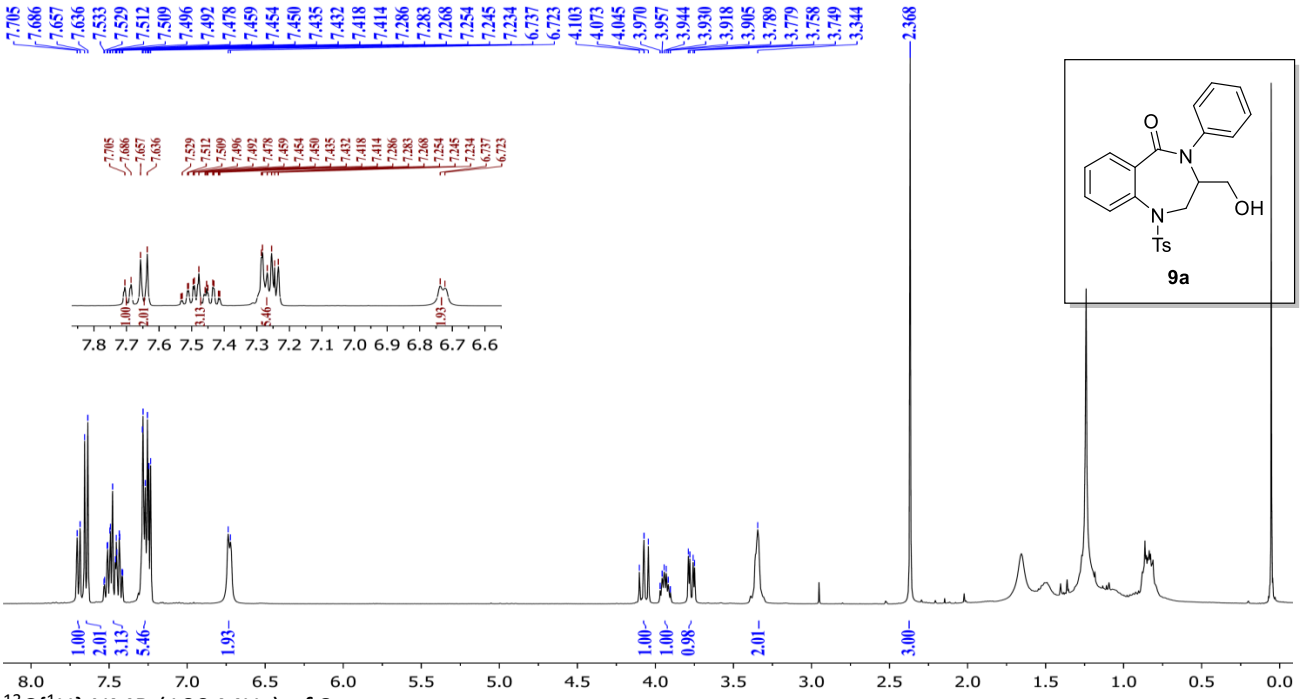


^{13}C{^{1}H} NMR (100 MHz) of **8c**:

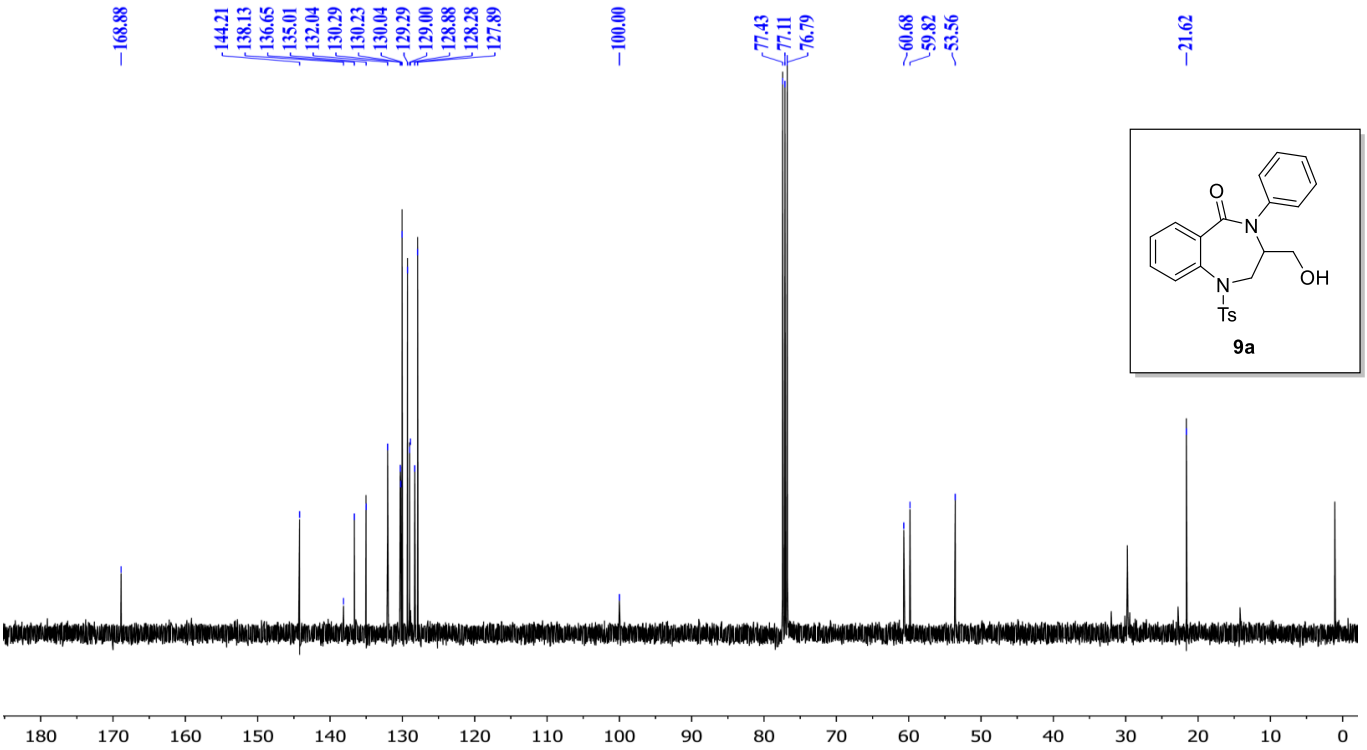


48. NMR spectra of products 9a and 9b:

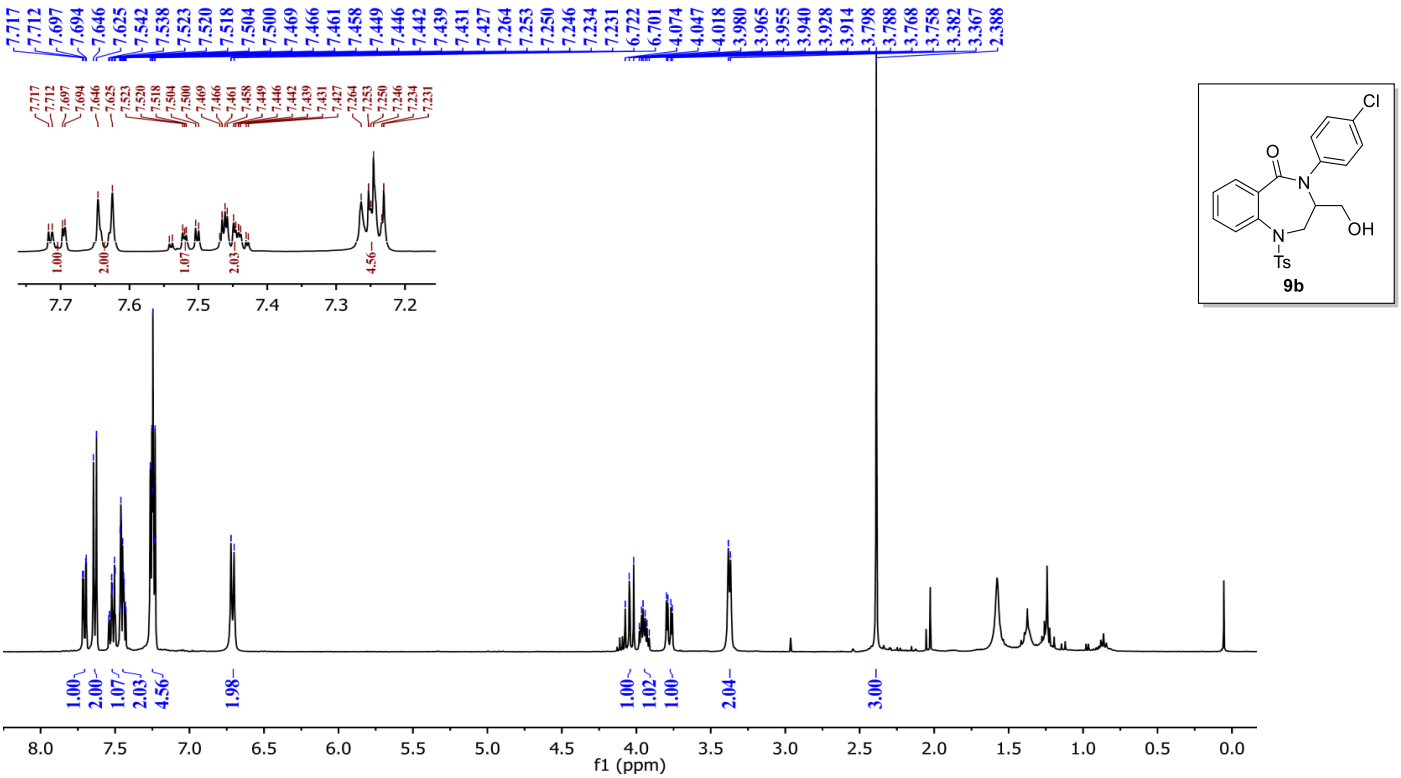
^{1}H NMR (400 MHz) of **9a**:



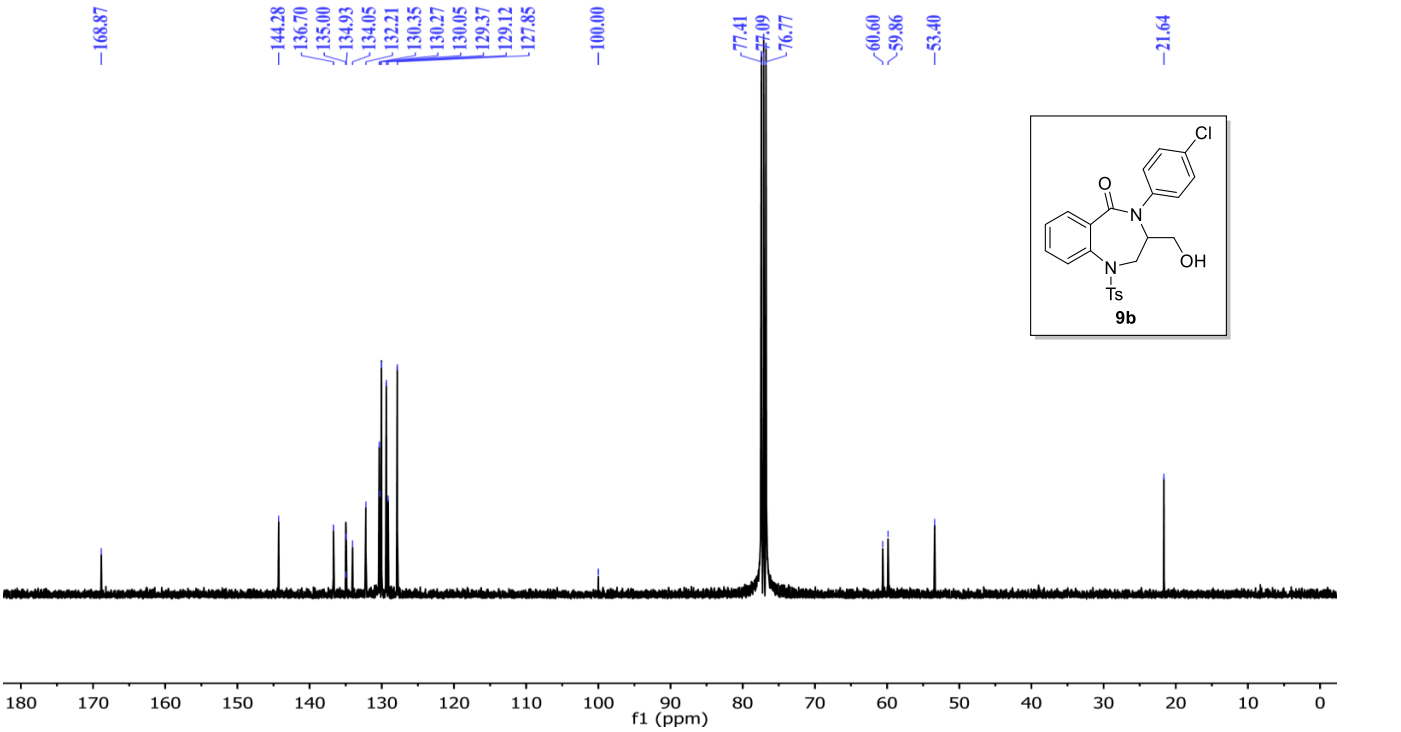
^{13}C{^{1}H} NMR (100 MHz) of **9a**:



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

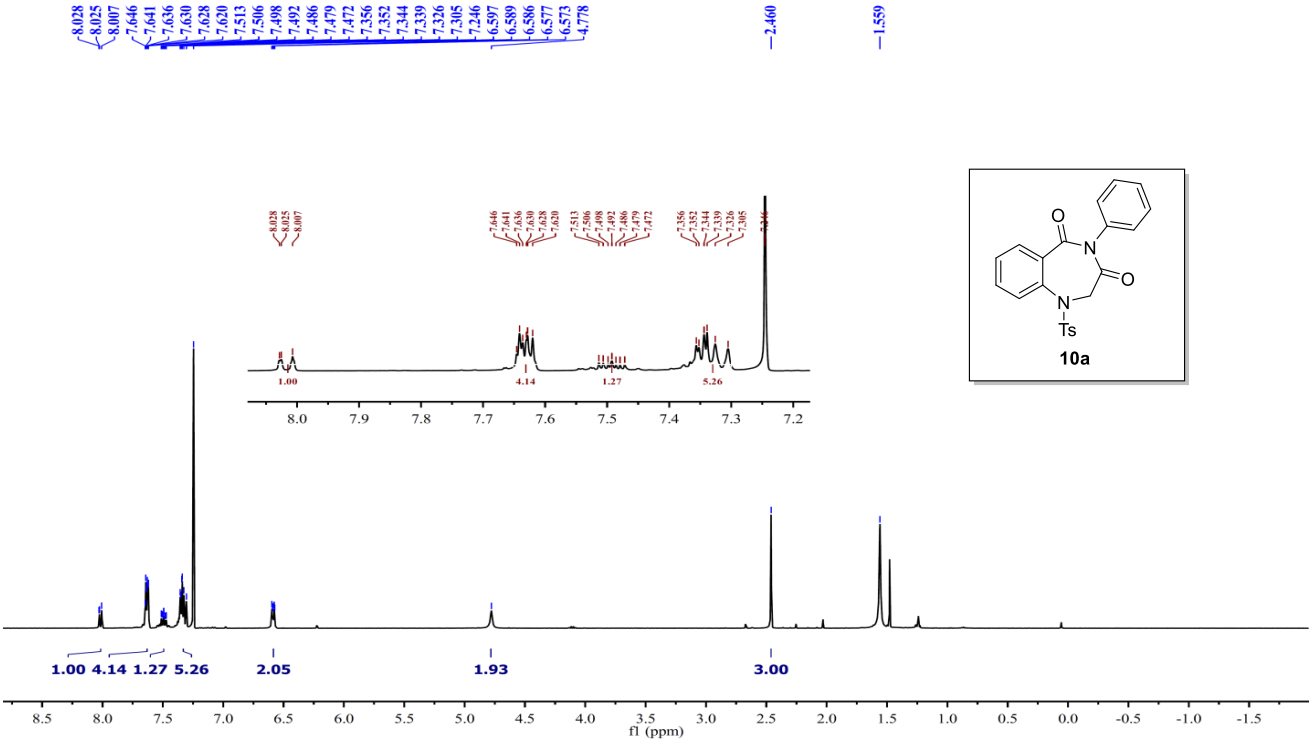


^{13}C{^{1}H} NMR (100 MHz) of **9b**:

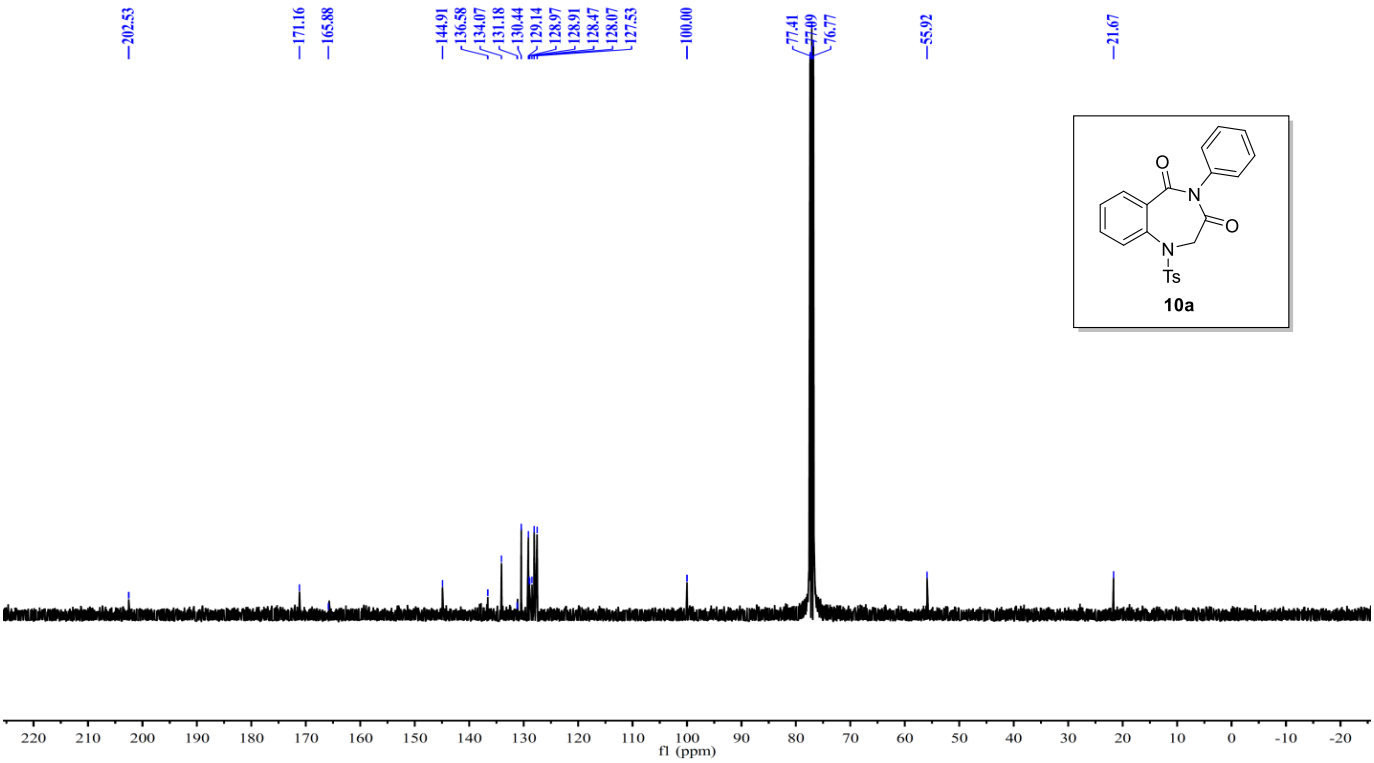


49. NMR spectra of products 10a and 10b:

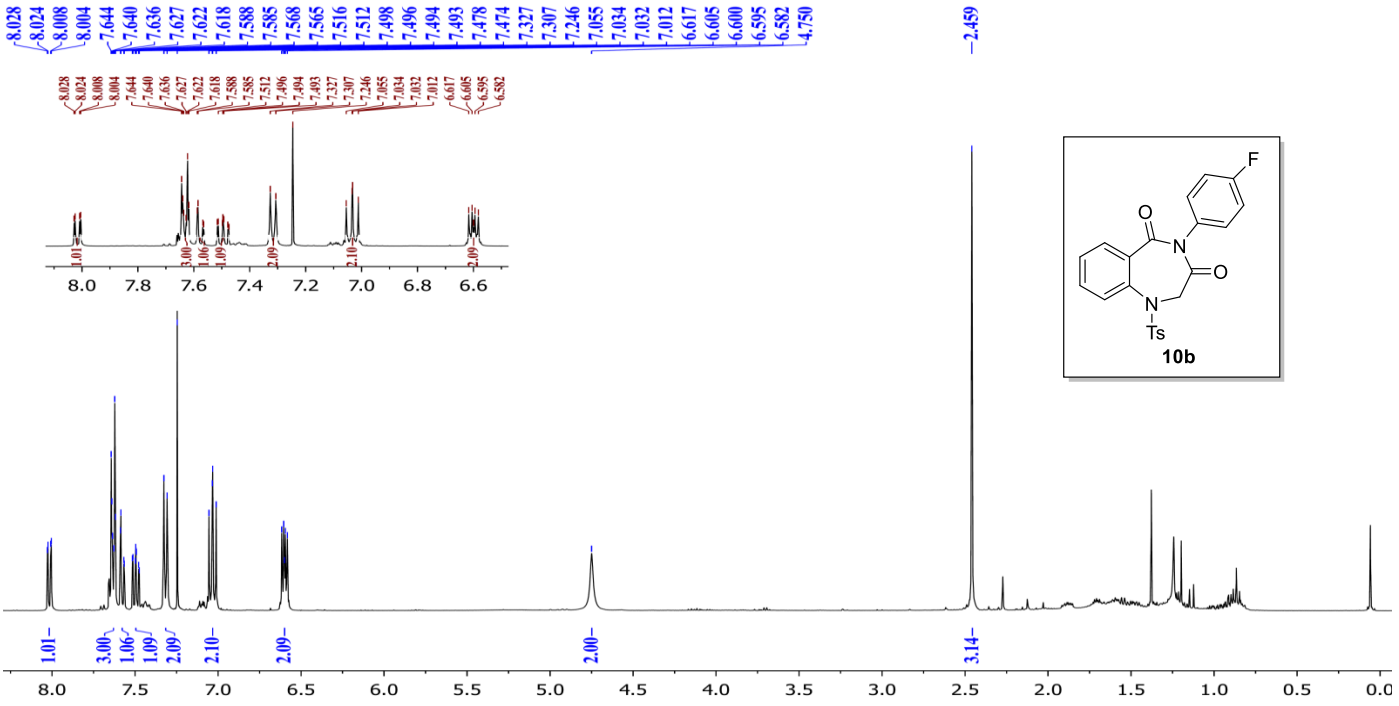
^{1}H NMR (400 MHz) of**10a**:



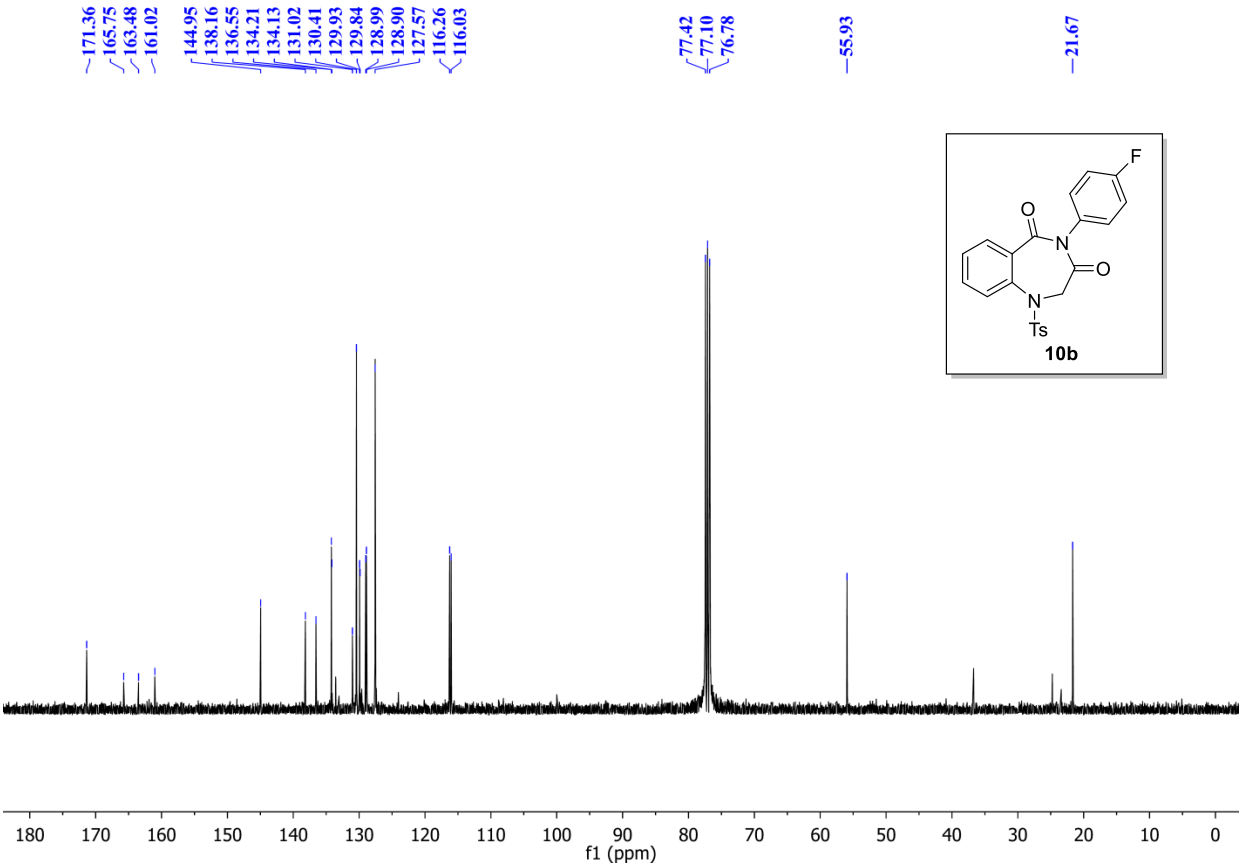
^{13}C{^{1}H} NMR (100 MHz) of **10a**:



^{1}H NMR (400 MHz) of**10b**:

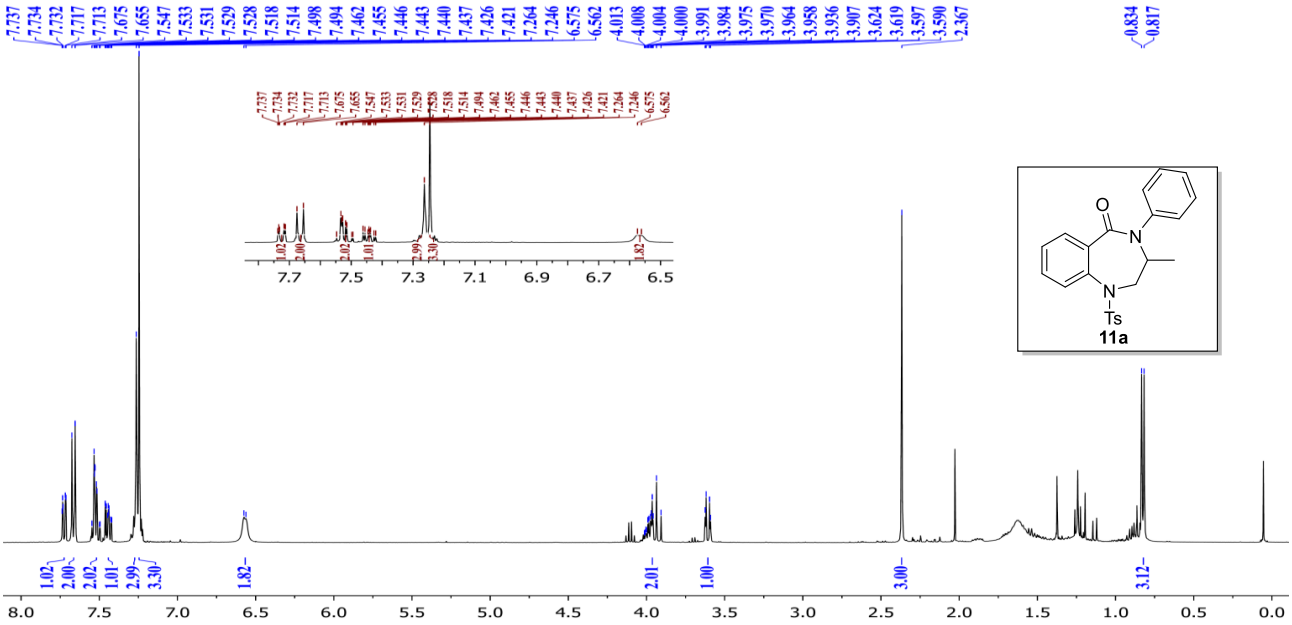


^{13}C{^{1}H} NMR (100 MHz) of **10b**:

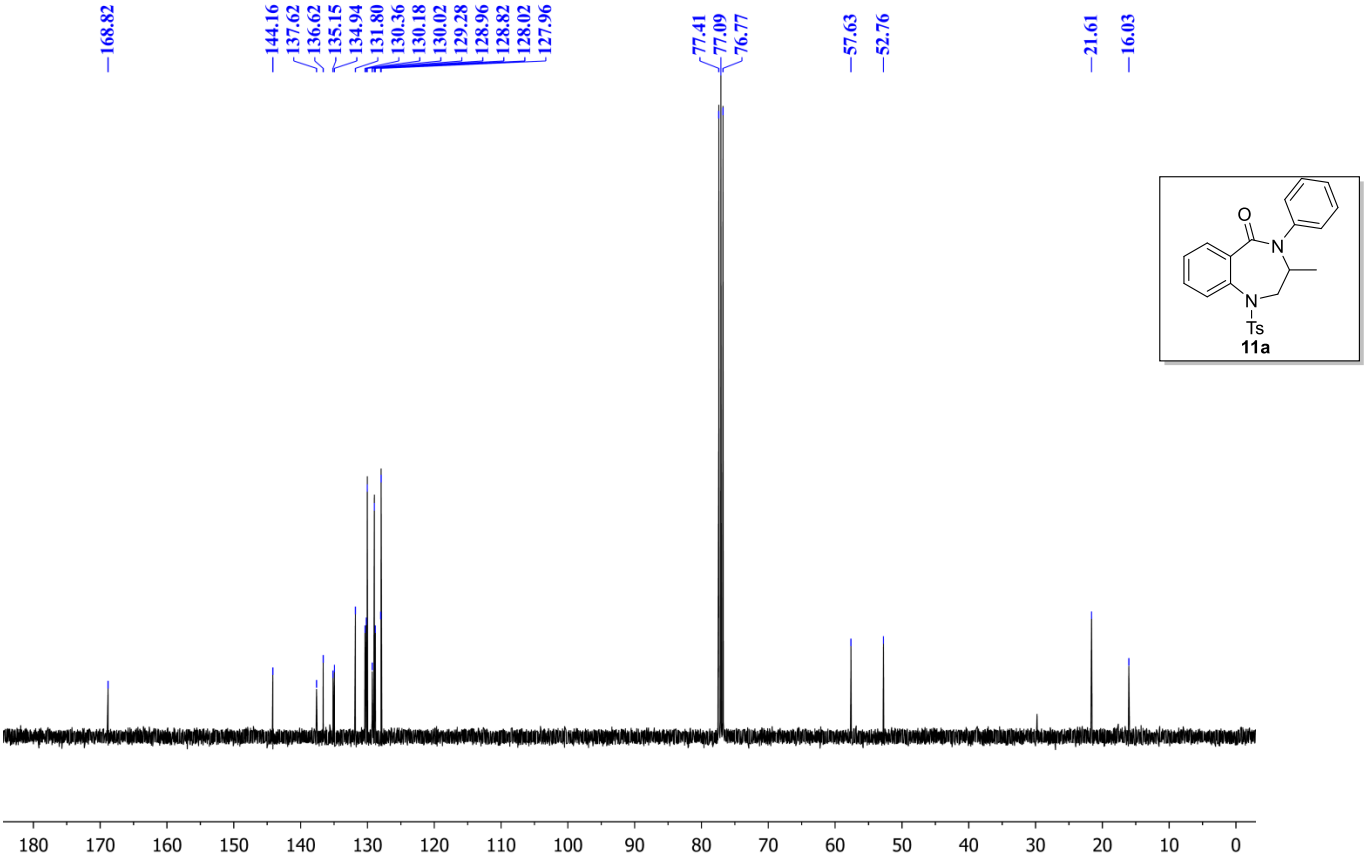


50. NMR spectra of products 11a and 11b:

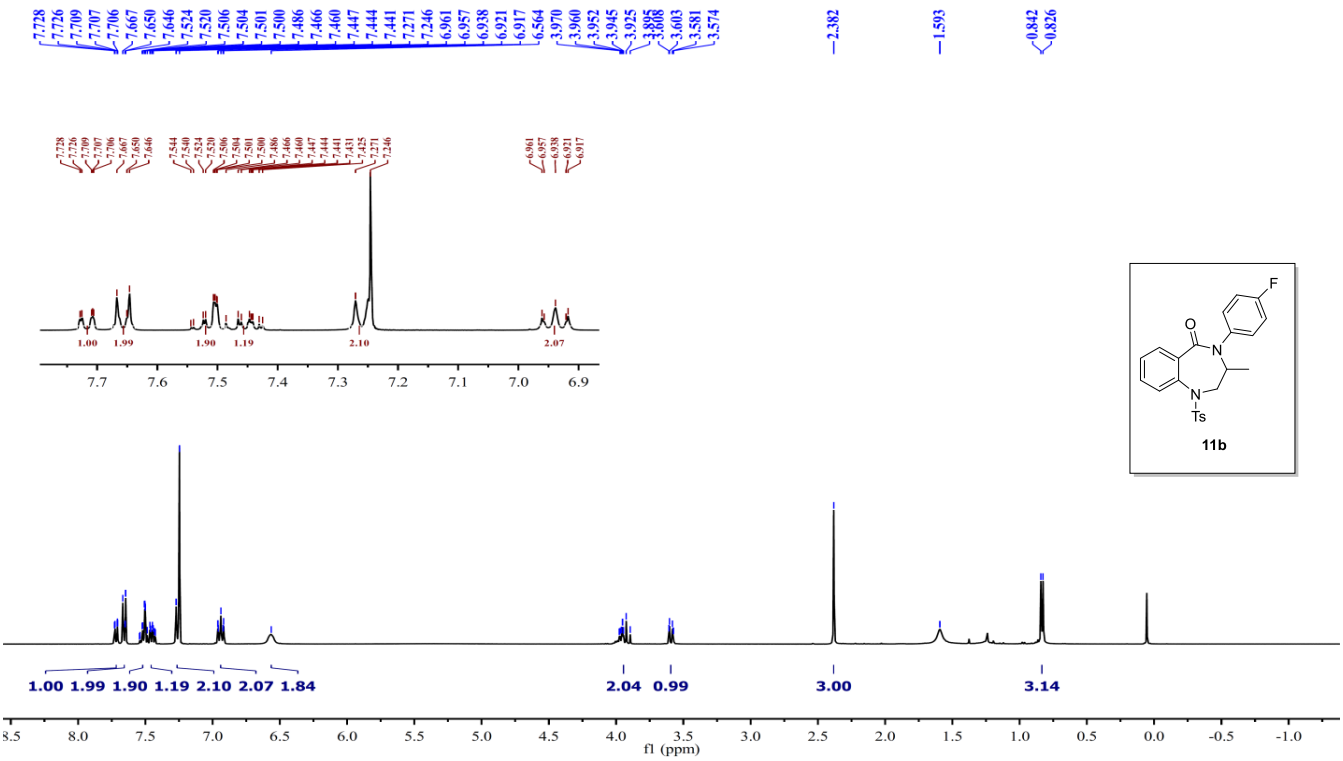
^{1}H NMR (400 MHz) of **11a**:



^{13}C{^{1}H} NMR (100 MHz) of **11a**:



^{1}H NMR (400 MHz) of **11b**:



^{13}C{^{1}H} NMR (100 MHz) of **11b**: