Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Synthesis of Trifluoroethoxy/Aryloxy Cinnolines, Cinnolinones and Indazoles from *o*-Alkynylanilines via Metal-Free Diazotization Reagent

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1. General information:

All the reactions were carried out under an inert atmosphere using the schlenk technique unless stated. All solvents were dried and stored over molecular sieves under argon atmosphere. All chemicals and reagents were purchased from commercial suppliers and used without further purification. Thin-layer chromatography (TLC) was performed using pre-coated plates purchased from E. Merck (silica gel 60 PF254, 0.25 mm). Column chromatography was performed using E. Merck silica gel 60 (100–200 mesh). ^{1}H, $^{13}C\{^{1}H\}$ NMR spectra were recorded either in DMSO-d_6 or in $CDCl_3$, on JEOL JNM-ECS spectrometer at operating frequencies of 400 MHz (^{1}H) or 101 MHz ($^{13}C\{^{1}H\}$) as indicated in the individual spectrum. Chemical shifts (δ) are given in parts per million (ppm) relative to residual solvent (For ^{1}H: DMSO-d_6, δ= 2.50; $CDCl_3$, δ= 7.26; for $^{13}C\{^{1}H\}$: DMSO-d_6, δ= 39.52; $CDCl_3$, δ= 77.16) and coupling constants (*J*) in Hz. Multiplicity is tabulated as s for singlet, d for doublet, dd for doublet of doublet, t for triplet, q for quartet, and m for multiplet. High-resolution mass spectra (HRMS) were recorded using electron spray ionization (ESI) methods on waters mass spectrometer (XEVO G2-XS QTOF). Melting points were taken on the Staurt digital melting point apparatus and X-ray data were recorded on a Bruker D8 venture instrument.

2. Experimental procedures:

2.1. Synthesis of known alkynylanilines (1):

All the alkynylanilines **1a–1z,** and diynedianilines **1a'–1b'** were synthesized according to our previous reported work and reference cited theirin.[1]

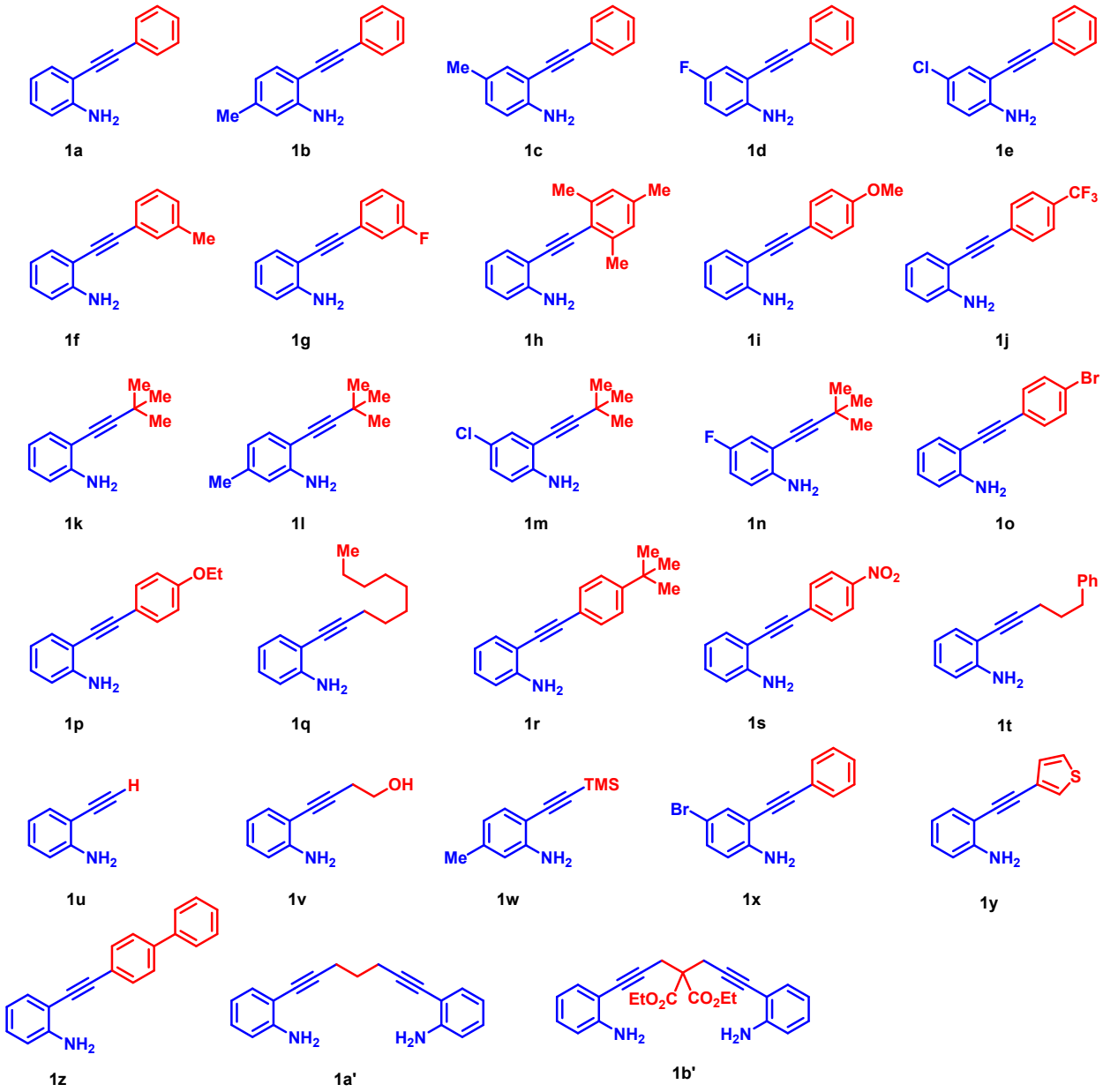


Figure 1. List of alkynylanilines derivatives **1**

2.2. General procedure for the synthesis of trifluoroethoxy cinnolines (3):

In a schlenk tube, *o*-alkynylaniline 1 (0.3 mmol, 1 equiv) was dissolved in 1.5 mL TFE under N_2 atmosphere. The reaction mixture was stirred and at first $BF_3{\cdot}OEt_2$ (2 equiv) was added followed by addition of TBN (2 equiv) in a dropwise manner at room temperature. After addition, reaction mixture was placed to pre-heated oil-bath of temperature at 70 °C. On completion of reaction as monitored by TLC, the crude mixture was cooled to room temperature, H_2O was added and extracted the organic layer thrice with EtOAc. The combined organic layer was once washed with brine, dried over anhydrous Na_2SO_4, filtered

and concentrated under reduced pressure. The collected crude product was purified through column chromatography over silica-gel (*n*-hexane:EtOAc = 10:1).

2.3. General procedure for the synthesis of aryloxy cinnolines (5):

In a schlenk tube, appropriate *o*-alkynylaniline 1 (0.3 mmol, 1 equiv) and aromatic alcohol 4 1.5 ml were dissolved in 0.5 mL DCE subsequently under N_2 atmosphere. The reaction mixture was stirred and $BF_3{\cdot}OEt_2$ (2 equiv) was added followed by TBN (2 equiv) in a dropwise manner at room temperature. After addition, reaction mixture was placed to pre-heated oil-bath of temperature at 70 °C. On completion of reaction as monitored by TLC, crude mixture was cooled to room temperature, added 30-40 ml saturated NaOH and extracted the organic layer thrice with DCM. The combined organic layer was once washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The collected crude product was purified through column chromatography over silica-gel (*n*-hexane:EtOAc = 10:1).

2.4. General procedure for the synthesis of cinnolin-4(1*H*)-one (6):

In a schlenk tube, suitable *o*-alkynylaniline 1 (0.3 mmol, 1 equiv) was dissolved in 1.0 mL AcOH under N_2 atmosphere. The reaction mixture was stirred and $BF_3{\cdot}OEt_2$ (2 equiv) was added followed by TBN (2 equiv) in a dropwise manner at room temperature. After addition, reaction mixture was placed to pre-heated oil-bath of temperature at 70 °C. On completion of reaction as monitored by TLC, the crude mixture was cooled to room temperature, quenched with saturated $NaHCO_3$ and extracted the organic layer thrice with EtOAc. The combined organic layer was once washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The collected crude product was purified through column chromatography over silica-gel (*n*-hexane:EtOAc = 10:1).

2.5. General procedure for the synthesis of (1*H*-indazol-3-yl)methanone (7):

In a schlenk tube, appropriate *o*-alkynylaniline 1 (0.3 mmol, 1 equiv) was dissolved in 1.0 mL DMF under N_2 atmosphere. The reaction mixture was stirred and $BF_3{\cdot}OEt_2$ (2 equiv) was added followed by TBN (2 equiv) in a dropwise manner at room temperature. After addition, reaction mixture was placed to pre-heated oil-bath of temperature at 70 °C. On completion of reaction as monitored by TLC, crude mixture was cooled to room temperature, added ice-cold water and extracted the organic layer thrice with EtOAc. The combined organic layer was again washed with ice-cold water and brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The collected crude product was purified through column chromatography over silica-gel (*n*-hexane:EtOAc = 100:5).

2.6. Gram scale synthesis of 6a:

In a schlenk RBF, alkynylaniline 1a (5 mmol, 1 equiv) was dissolved in 12 mL AcOH under N_2 atmosphere. The reaction mixture was stirred and added $BF_3{\cdot}OEt_2$ (2 equiv) followed by

TBN (2 equiv) in a dropwise manner at room temperature. After addition, reaction mixture was shifted to pre-heated oil-bath of temperature 70 °C. On completion of reaction as monitored by TLC, crude mixture was cooled to room temperature, quenched with saturated $NaHCO_3$ and extracted the organic layer thrice with EtOAc. The combined organic layer was once washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The collected crude was purified through column chromatography over silica-gel (*n*-hexane:EtOAc = 10:1).

2.7. General procedure for the synthesis of bis(cinnolin-4(1*H*)-one (8a & 8b):

In a schlenk tube, alkynylaniline 1a' or 1b' (0.3 mmol, 1 equiv), was dissolved in 1 mL AcOH under N_2 atmosphere. The reaction mixture was stirred and $BF_3{\cdot}OEt_2$ (5 equiv) was added followed by TBN (5 equiv) in a dropwise manner at room temperature. After addition, reaction mixture was placed to pre-heated oil-bath of temperature at 70 °C. On completion of reaction as monitored by TLC, the crude mixture was cooled to room temperature, quenched with saturated $NaHCO_3$ and extracted the organic layer thrice with EtOAc. The combined organic layer was once washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The collected crude product was purified through column chromatography over silica-gel (*n*-hexane:EtOAc = 10:8).

2.8. Synthesis of product 10:

At 0.1 mmol scale, iodo derivative of aryloxy cinnoline 5l (1 equiv), CuI (0.02 equiv), $PdCl_2(PPh_3)_2$ (0.01 equiv), and Et_3N (1 ml) were added subsequently under N_2 atm. in a schlenk tube. After stirring of reaction mixture at room temperature for 2 minutes, ethynyl trimethylsilane 9 (1.1 equiv) was added dropwise. The reaction was allowed to run for 8 h and after completion (monitored by TLC analysis) crude product was dissolved in EtOAc and filtered through small celite pad. The collected solution was concentrated under reduced pressure and performed column chromatography over silica gel (*n*-hexane:EtOAc = 10:1).

2.9. General procedure for the synthesis of *N*-propargylated cinnolinones 12a/12b:

In a 50 ml round-bottom flask, 6a/6l (0.2 mmol, 1 equiv) was dissolved in 15 ml ACN. After adding, propargyl bromide 11 (1.5 equiv) and K_2CO_3 (3 equiv) subsequently reaction was stirred on pre-heated oil bath of temperature 80 °C for 8 h. After completion of reaction, as monitored by TLC, reaction was allowed to come to room temperature, added H_2O and extracted the organic layer thrice with EtOAc. The combined organic layer was once washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The collected crude product was purified through column chromatography over silica-gel (*n*-hexane:EtOAc = 10:1).

2.10. Synthesis of *N*-boc protected indazole 14:

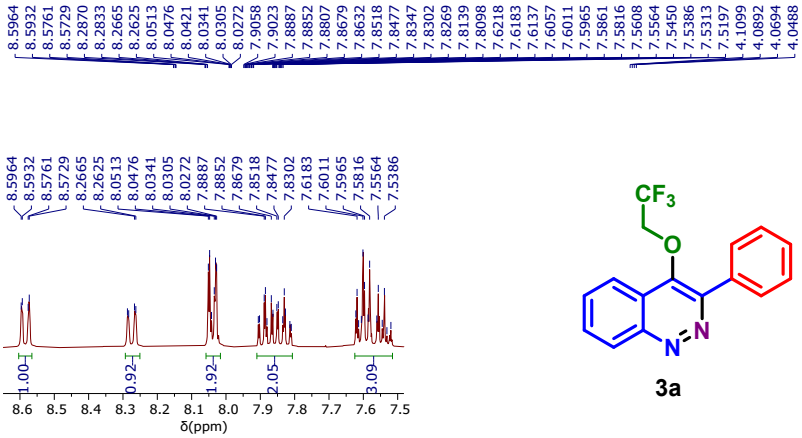
In a 10 ml round bottom flask, charged with 0.1 mmol, 1 equiv of **7g** was added THF (2 ml) at room temperature. Subsequently, $(Boc)_2O$ (1.2 equiv) and DMAP (5 mol%) was added under stirring condition at room temperature. After completion of reaction, as monitored by TLC analysis crude mixture was diluted with H_2O and extracted thrice with DCM. Then the combined organic layer was once washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The collected crude fraction was further purified through column chromatography over silica-gel (*n*-hexane:EtOAc = 100:1).

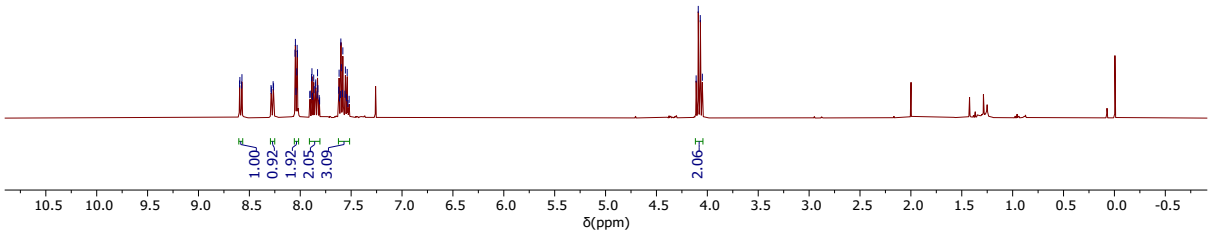
2.10. Synthesis of *N*-boc protected cinnolinones 15-17:

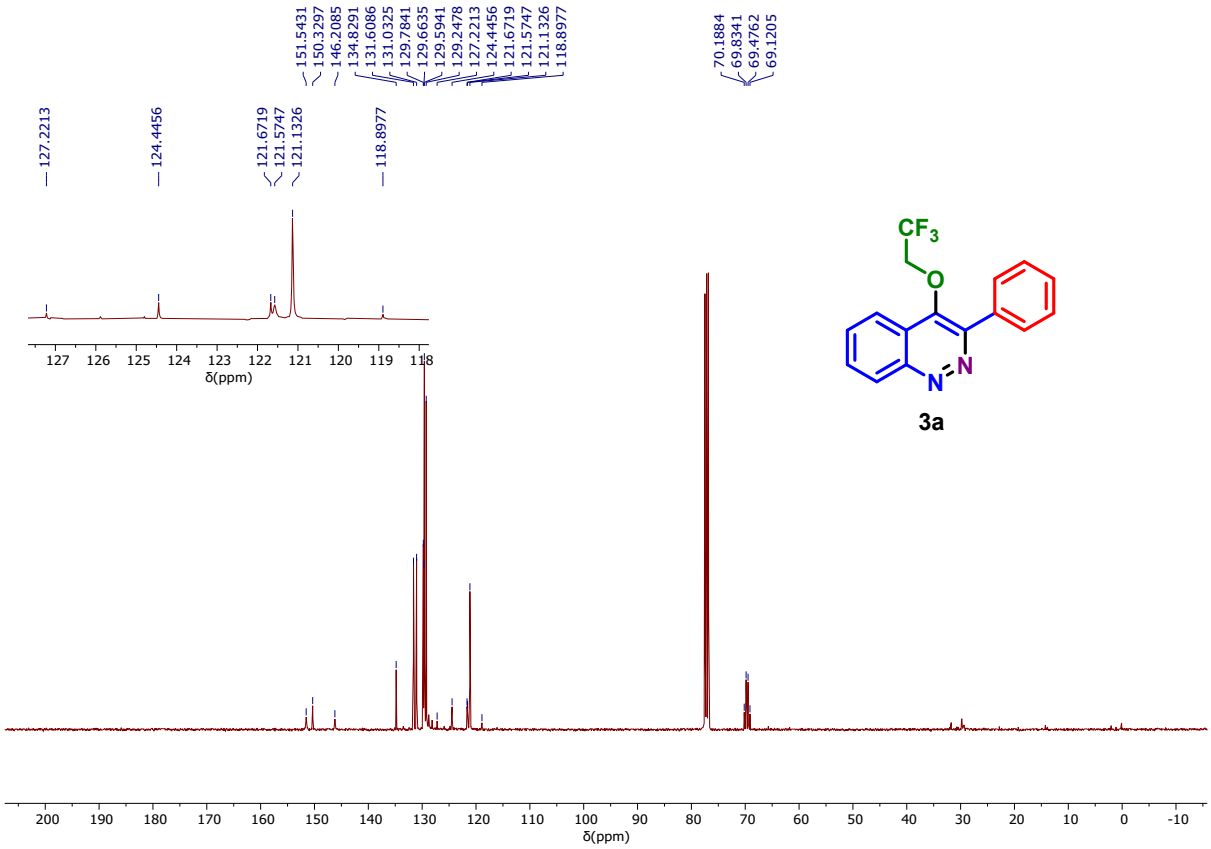
In a 10 ml round bottom flask, charged with 0.1 mmol, 1 equiv of **3j-3l**/**6m-6o** mixture was added THF (2 ml) at room temperature. Subsequently, $(Boc)_2O$ (1.2 equiv) and DMAP (5 mol%) was added under stirring condition at room temperature. After completion of reaction, as monitored by TLC analysis crude mixture was diluted with H_2O and extracted thrice with DCM. Then the combined organic layer was once washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The collected crude fraction was further purified through column chromatography over silica-gel (*n*-hexane:EtOAc = 100:1).

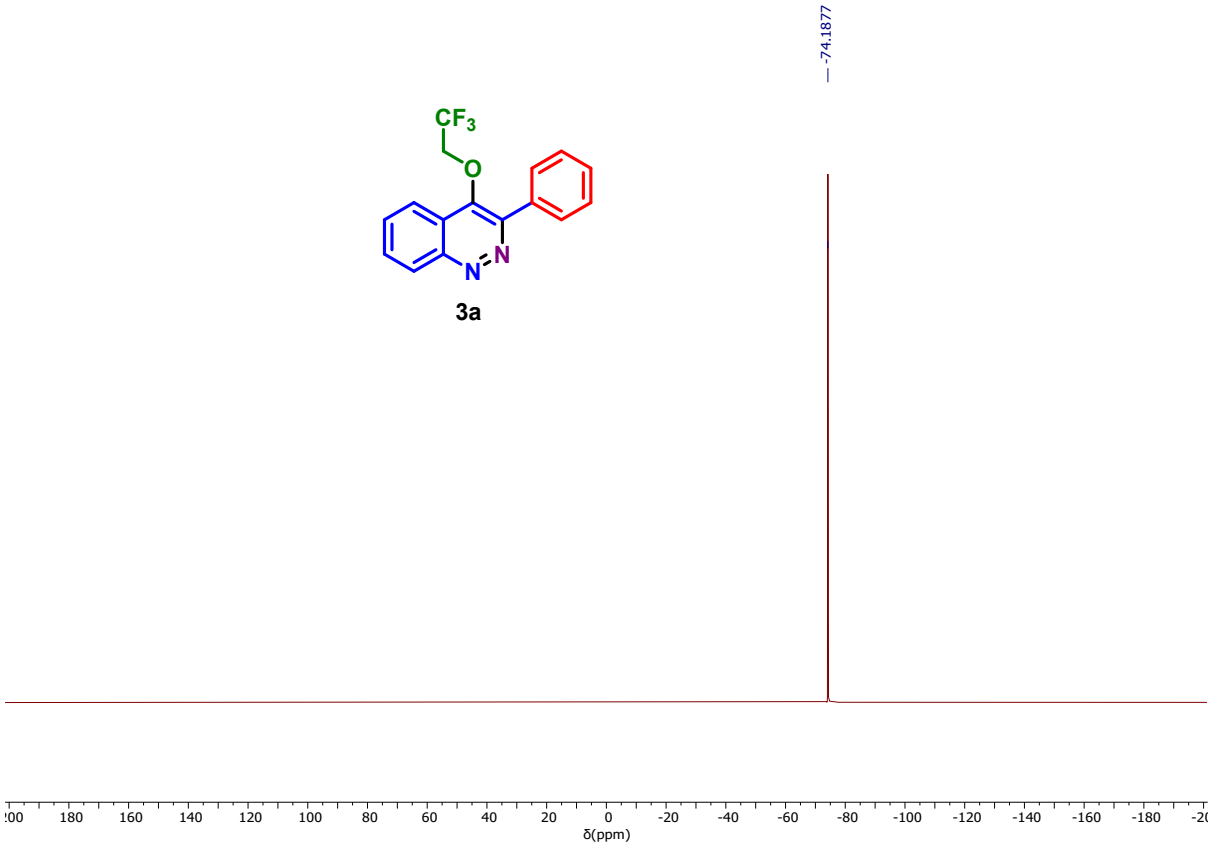
S4. Copies of ^{1}H, ^{13}C, & ^{19}F, NMR spectra

^{1}H, $^{13}C\{^{1}H\}$ and ^{19}F NMR ($CDCl_3$, 400, 101 and 376 MHz) of compound 3a:

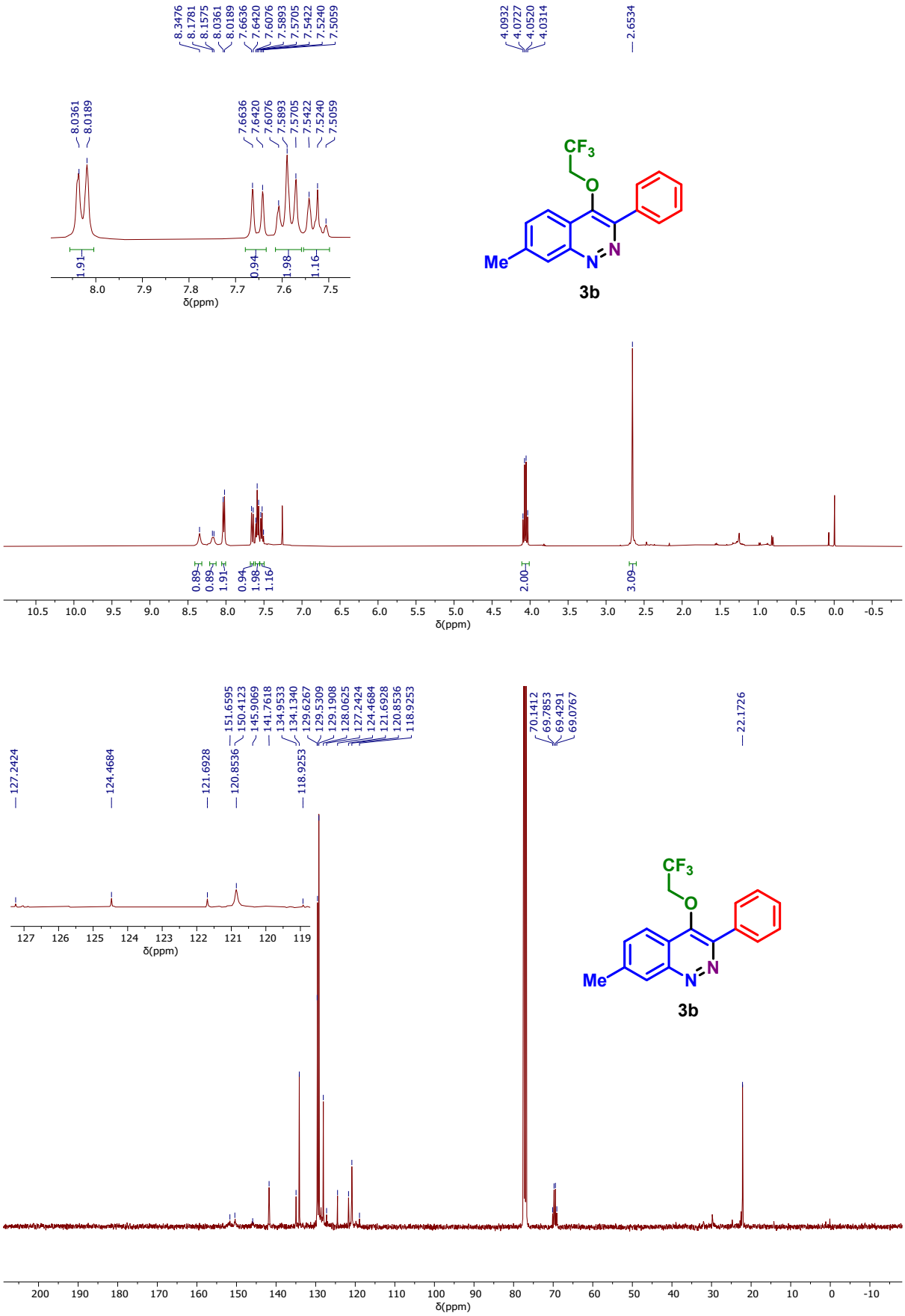


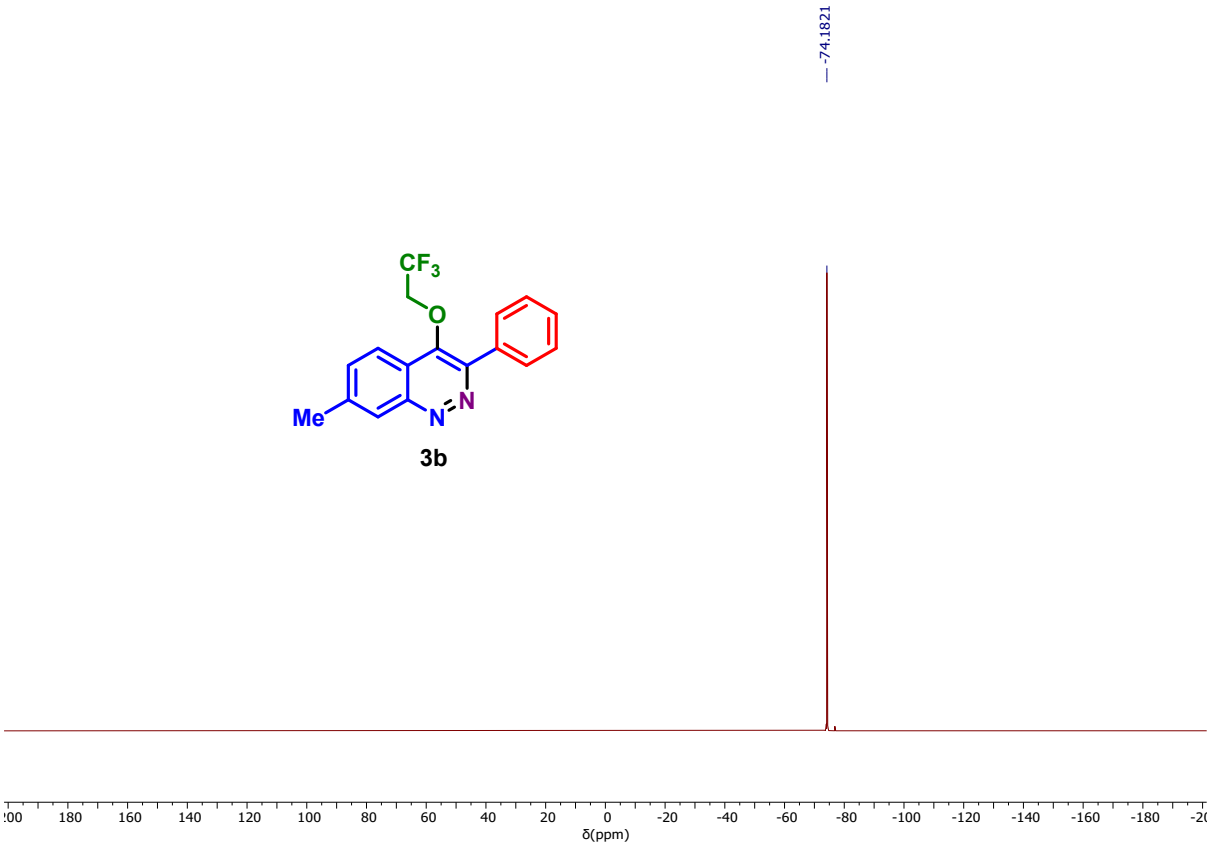




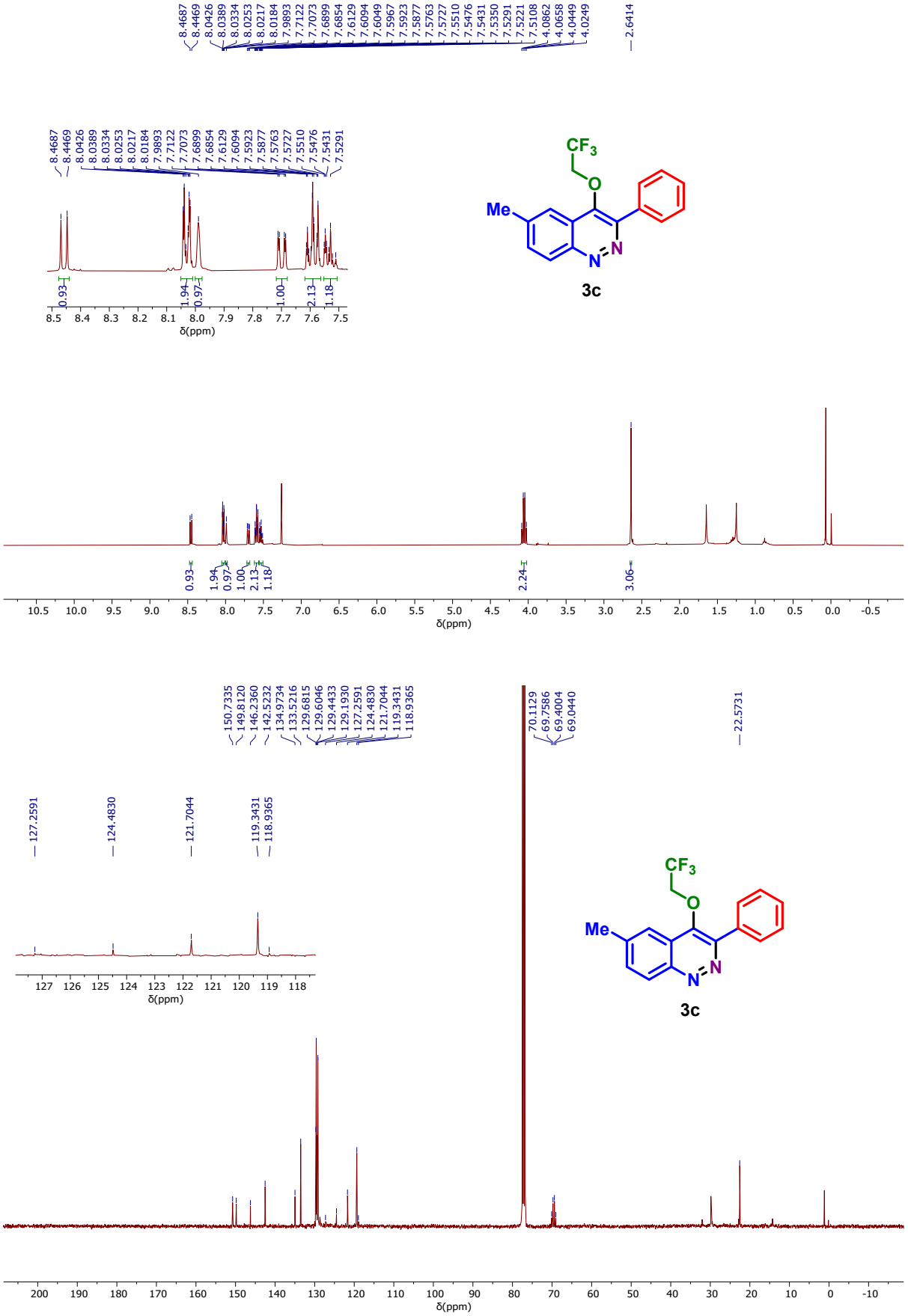

-74.1877
CF3
O
N
N
3a
δ(ppm)

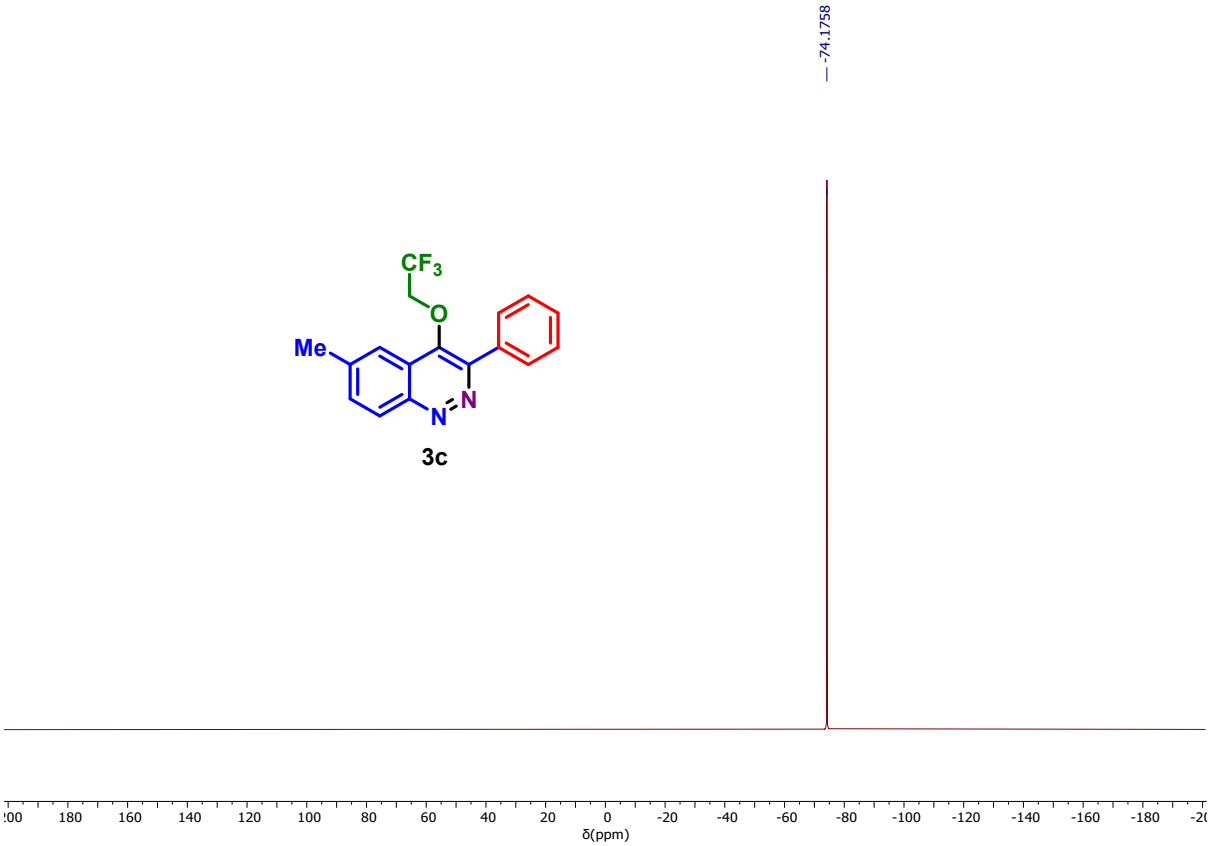
^{1}H, $^{13}C\{^{1}H\}$ and ^{19}F NMR ($CDCl_3$, 400, 101 and 376 MHz) of compound 3b:



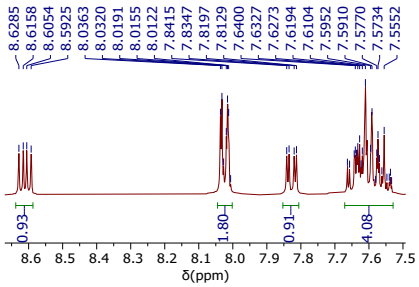

-74.1821
CF3
O
N
Me
N
3b
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
δ(ppm)

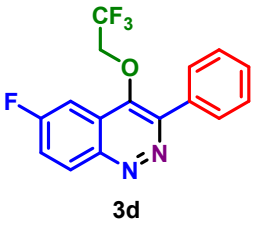
^{1}H, $^{13}C\{^{1}H\}$ and ^{19}F NMR ($CDCl_3$, 400, 101 and 376 MHz) of compound 3c:



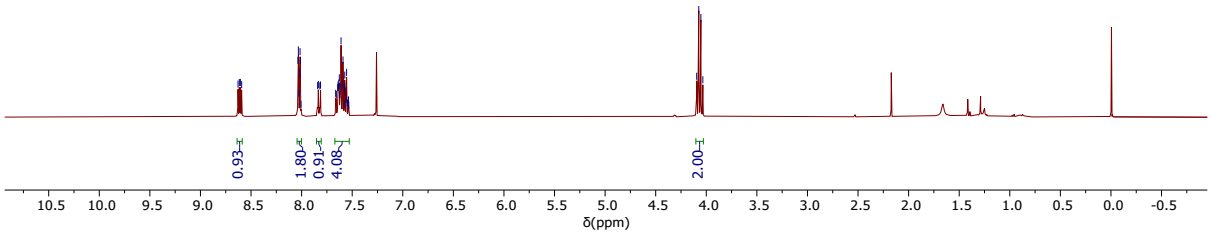

-74.1758
CF3
O
Me
N
N
3c
δ(ppm)

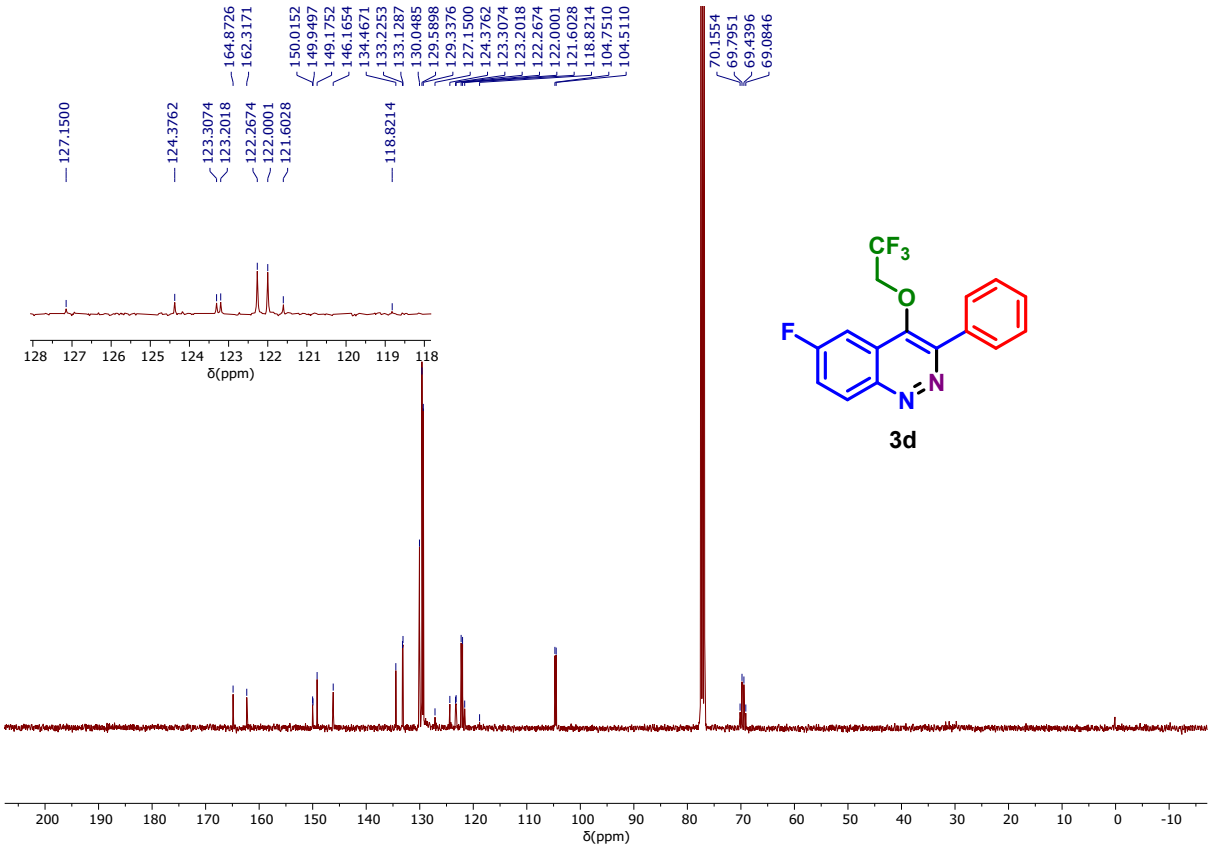
^{1}H, $^{13}C\{^{1}H\}$ and ^{19}F NMR ($CDCl_3$, 400, 101 and 376 MHz) of compound 3d:



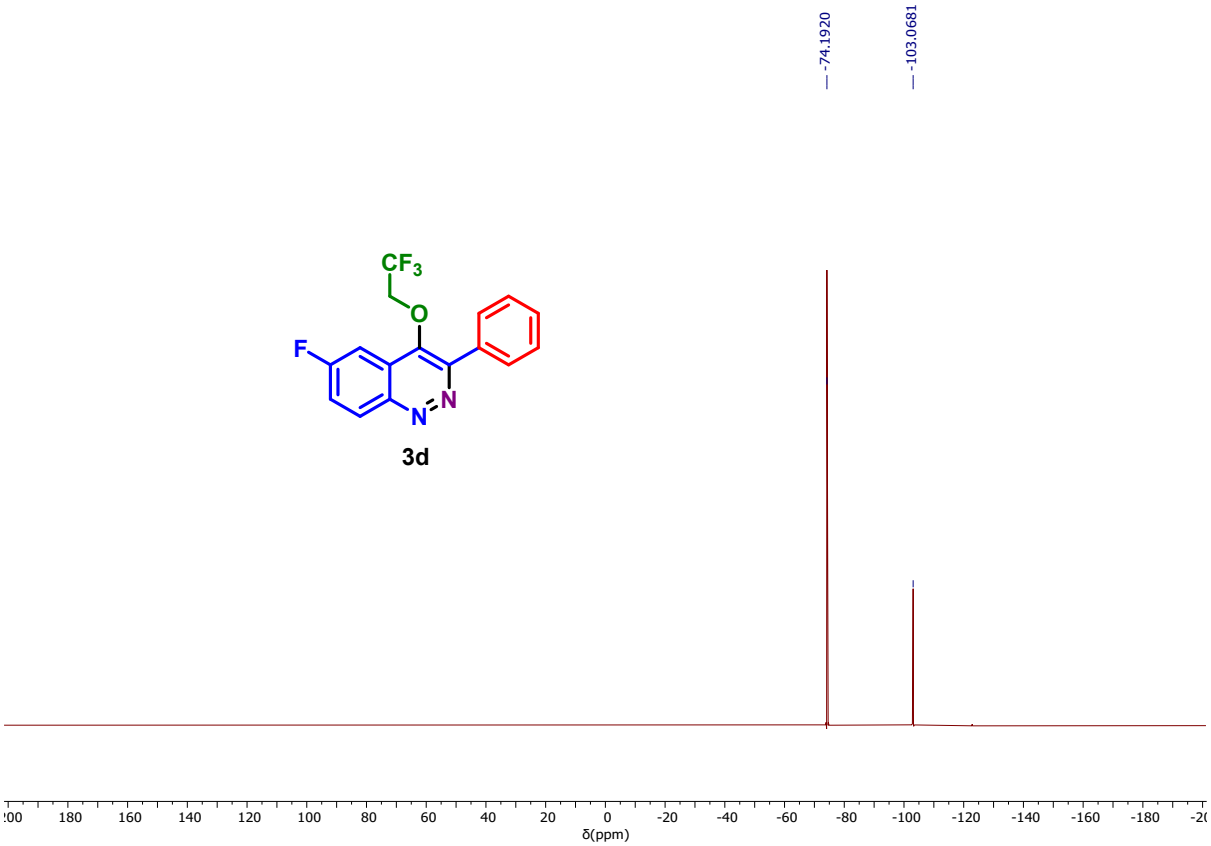


3d

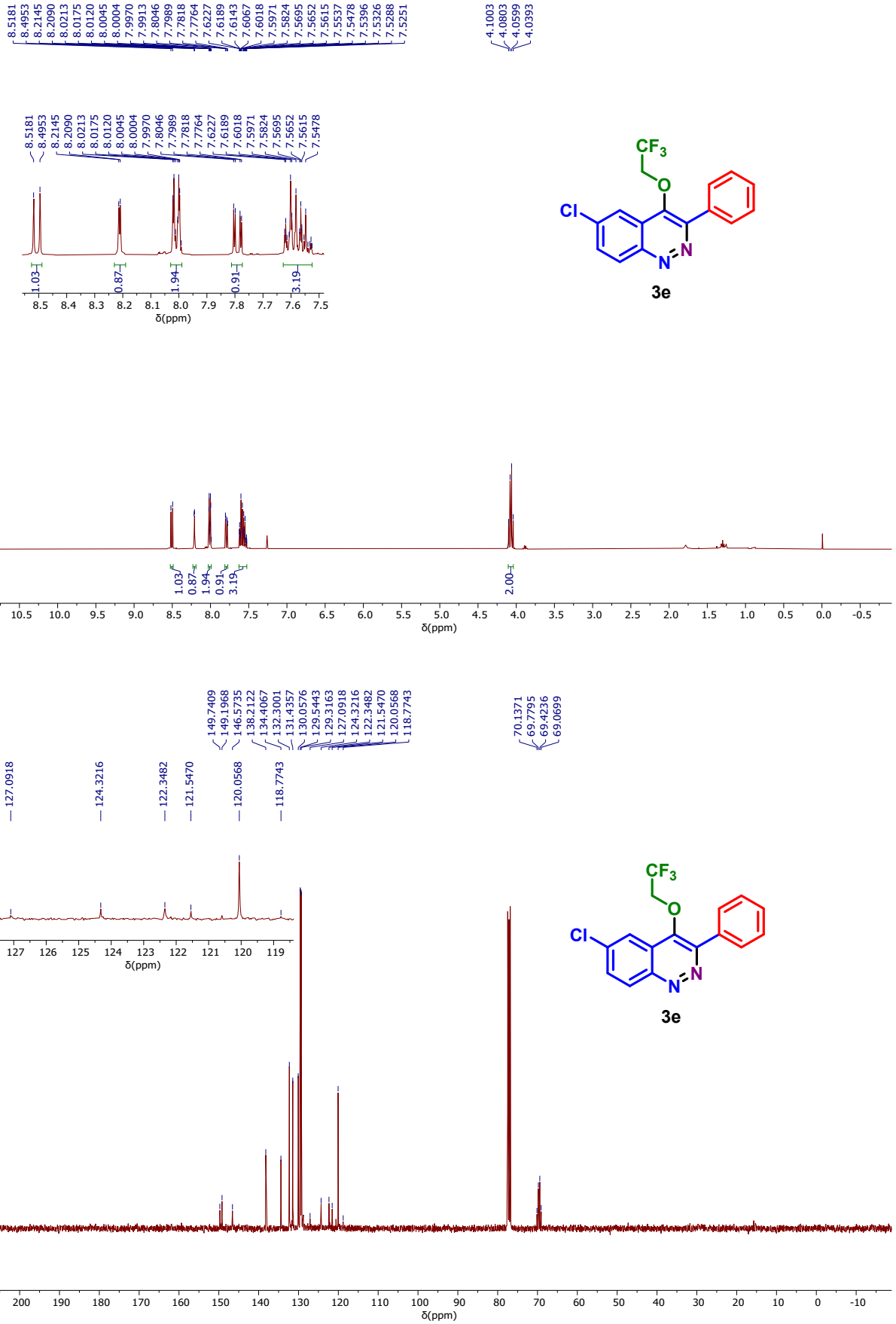


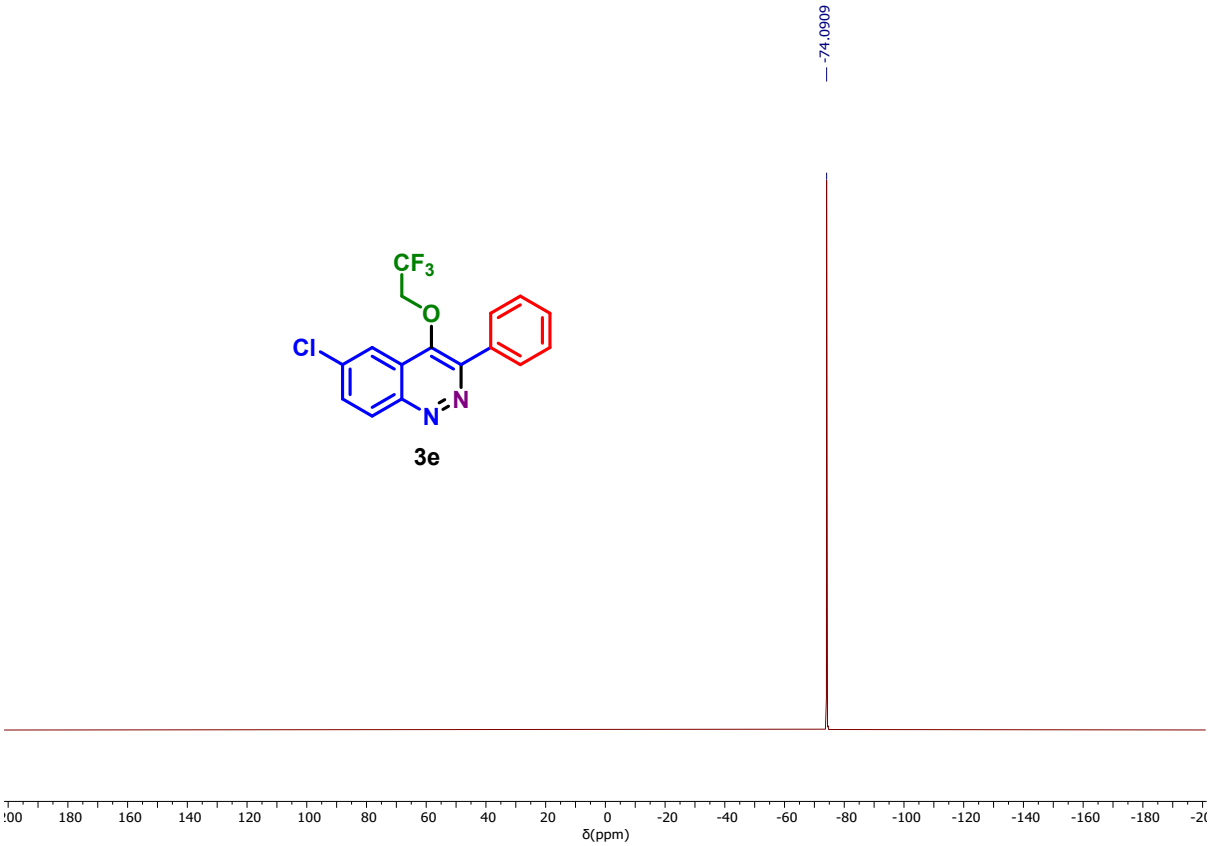


3d

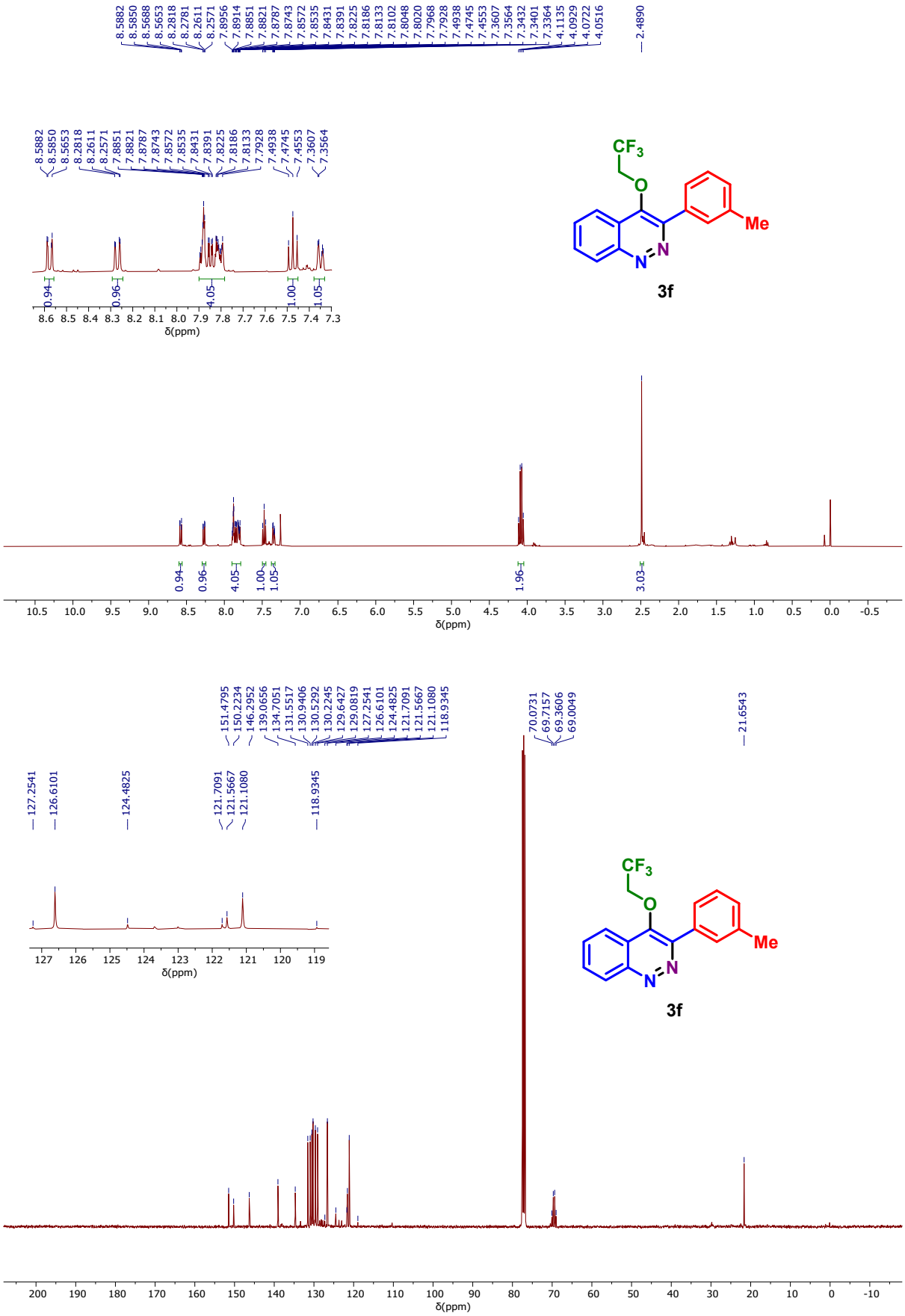

-74.1920
-103.0681
CF3
O
F
N
N
3d
δ(ppm)

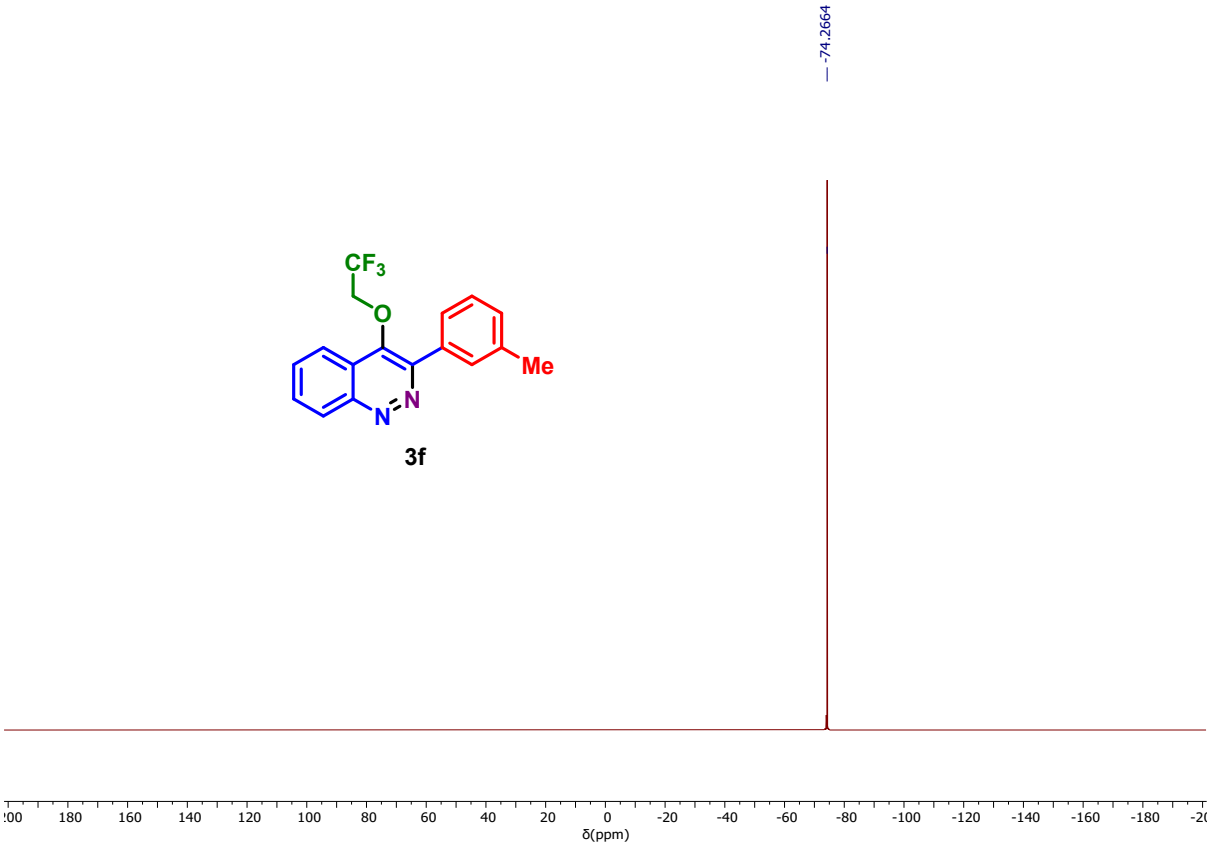
^{1}H, $^{13}C\{^{1}H\}$ and ^{19}F NMR ($CDCl_3$, 400, 101 and 376 MHz) of compound 3e:



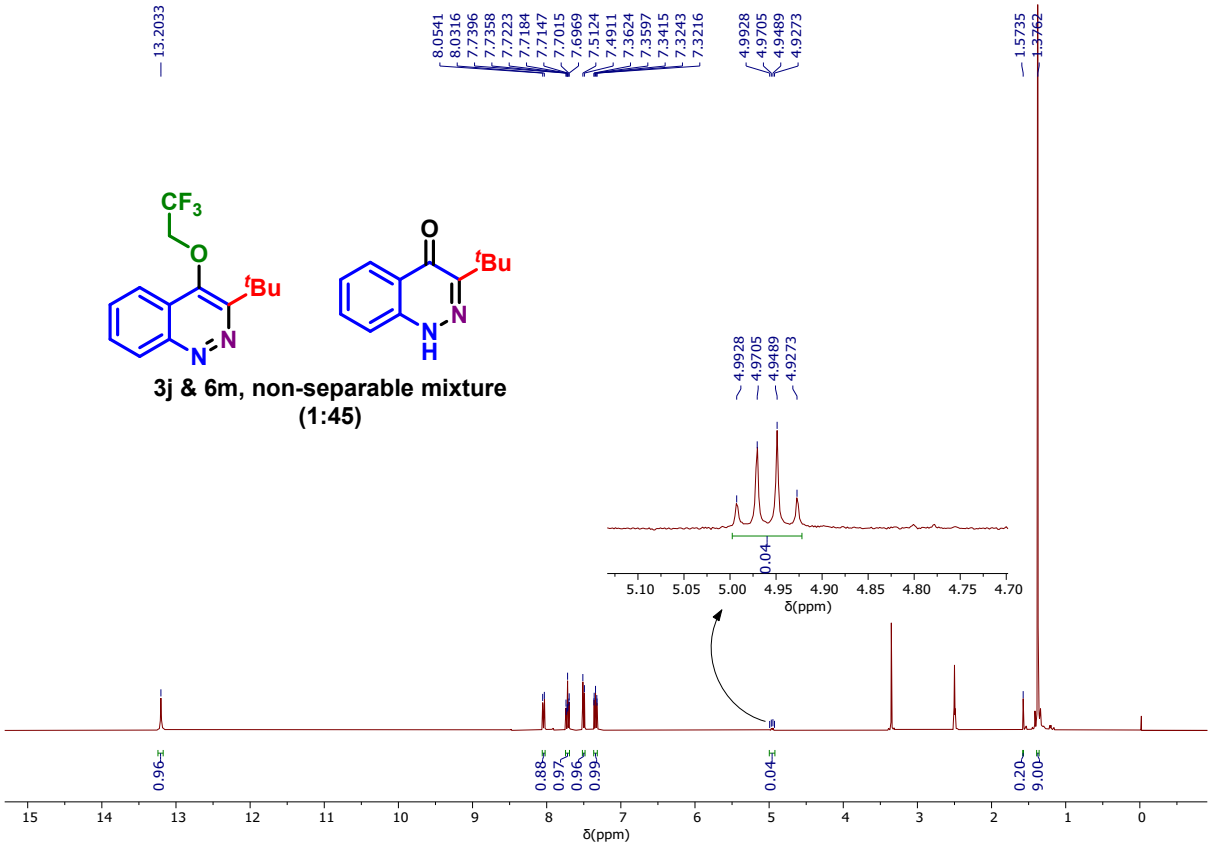

-74.0909
CF3
O
Cl
N
N
3e
δ(ppm)

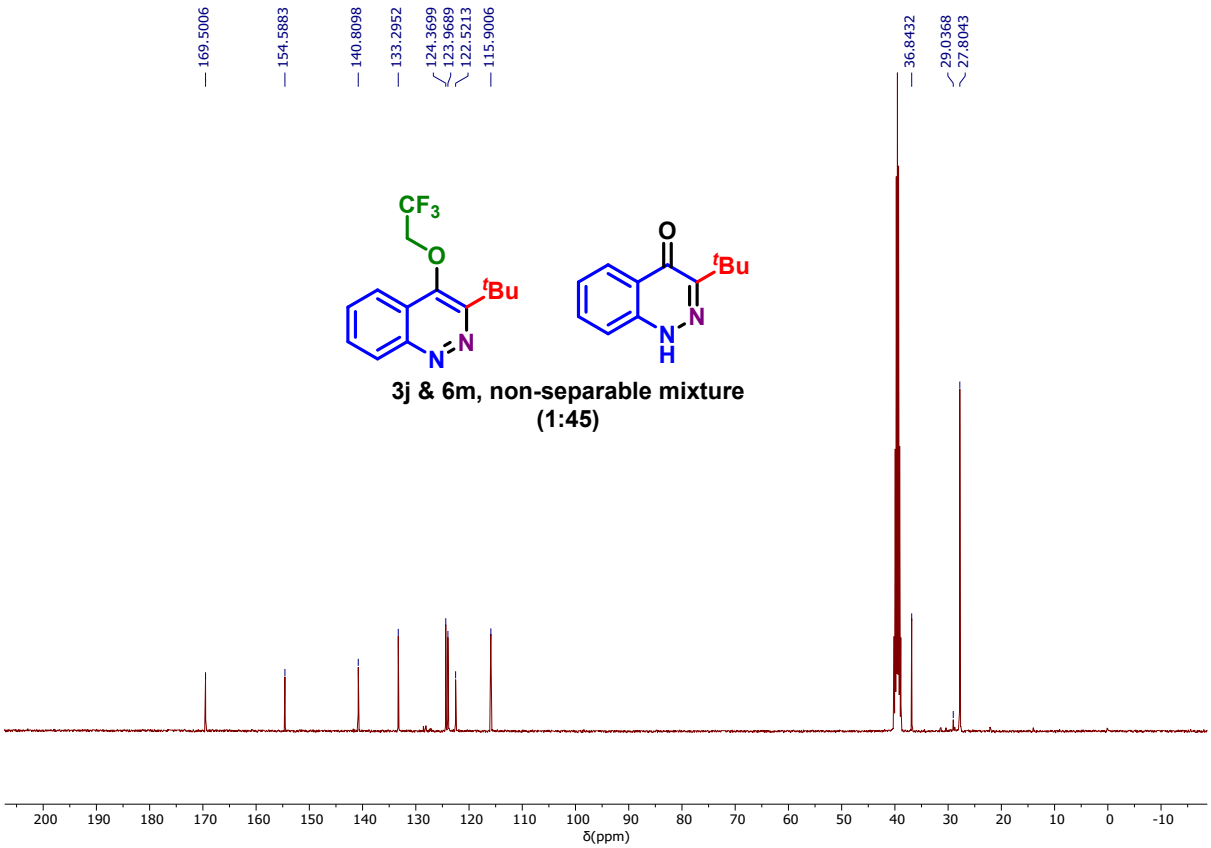
^{1}H, $^{13}C\{^{1}H\}$ and ^{19}F NMR ($CDCl_3$, 400, 101 and 376 MHz) of compound 3f:

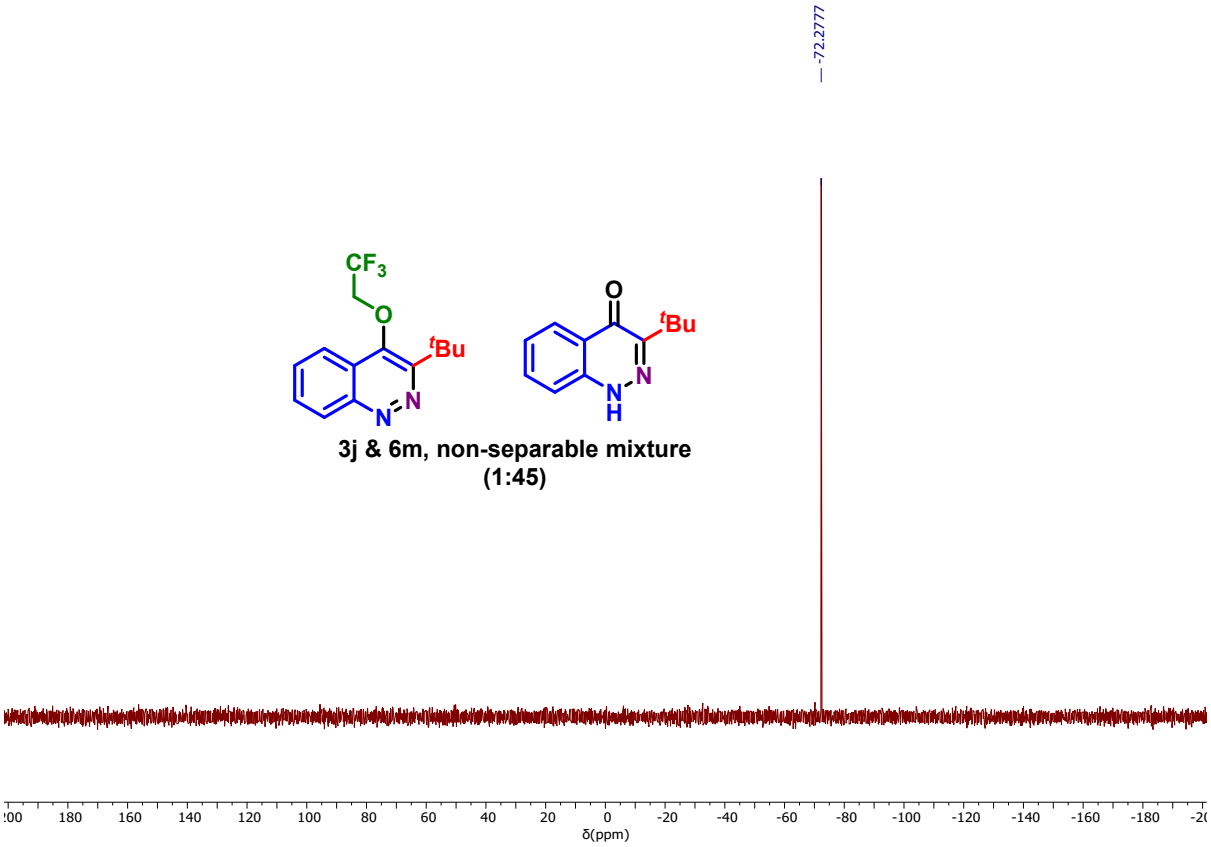



-74.2664
CF3
O
Me
N
N
3f
δ(ppm)

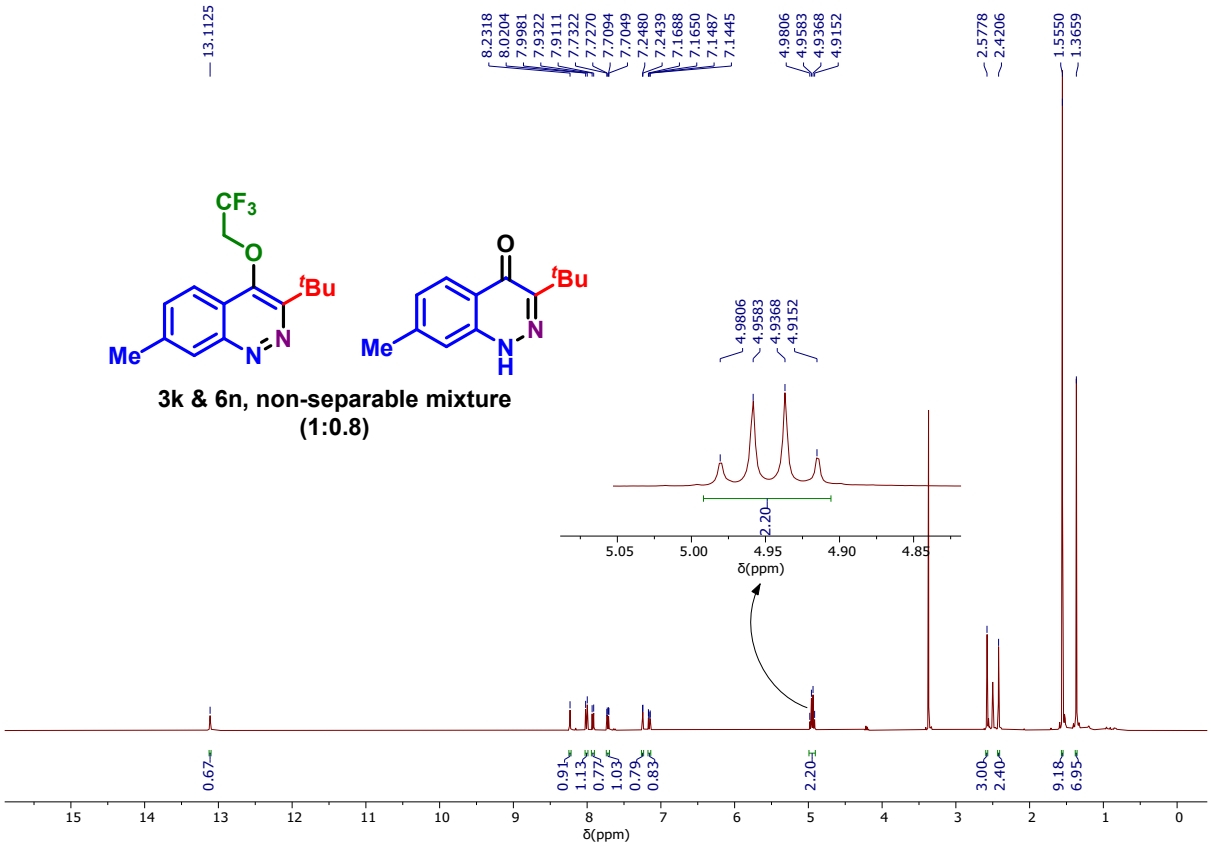
^{1}H, ^{13}C{^{1}H} and ^{19}F NMR (DMSO-d_6, 400, 101 and 376 MHz) of non-separable mixture 3j and 6m:

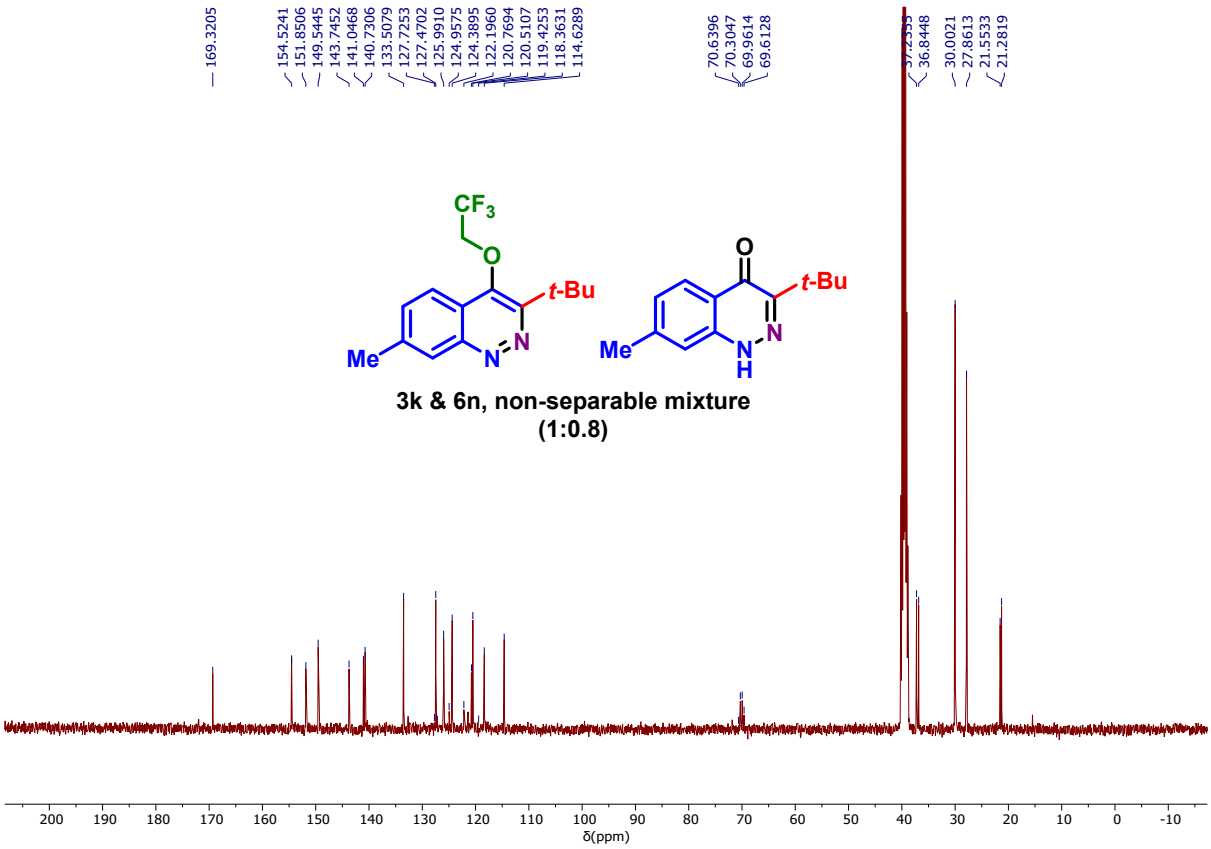


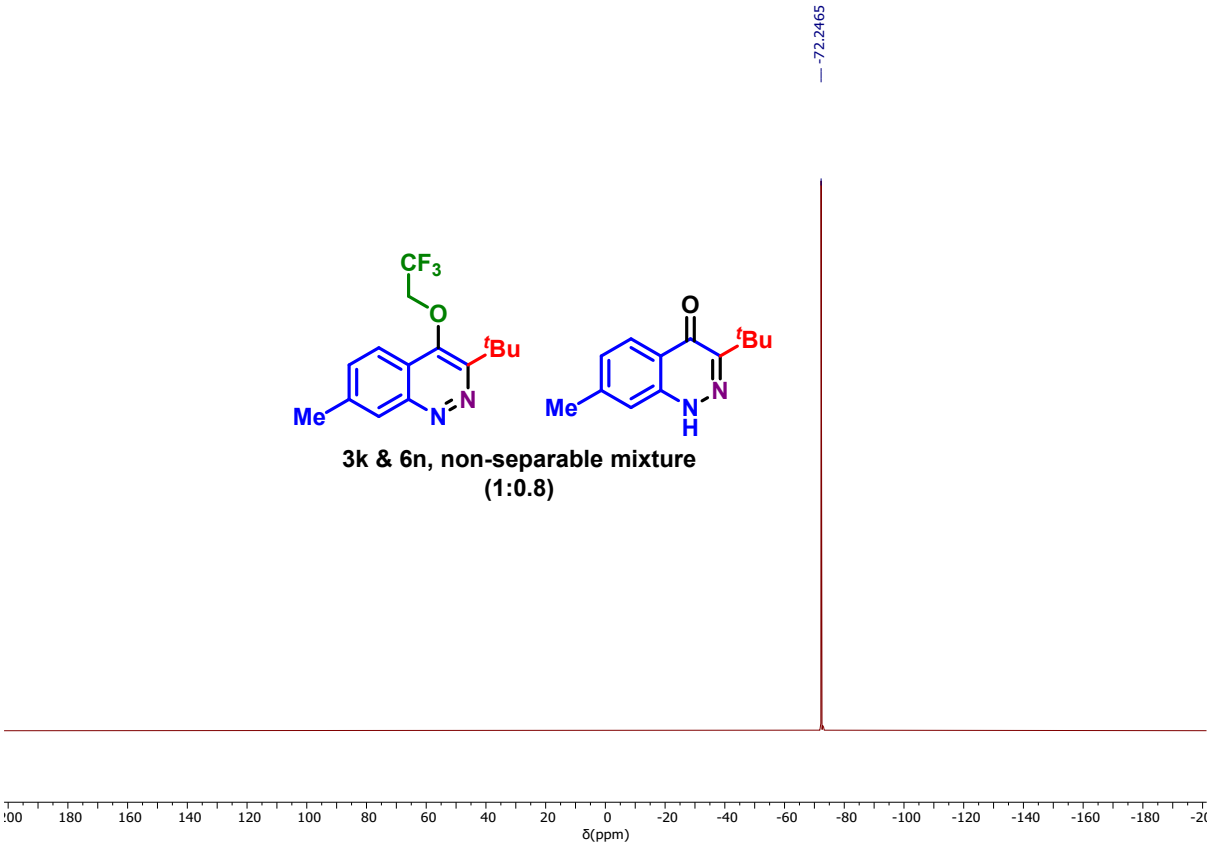



-72.2777
CF3
O
tBu
N
N
O
tBu
N
N
H
3j & 6m, non-separable mixture
(1:45)
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
δ(ppm)

^{1}H, ^{13}C{^{1}H} and ^{19}F NMR (DMSO-d_6, 400, 101 and 376 MHz) of non-separable mixture 3k and 6n:

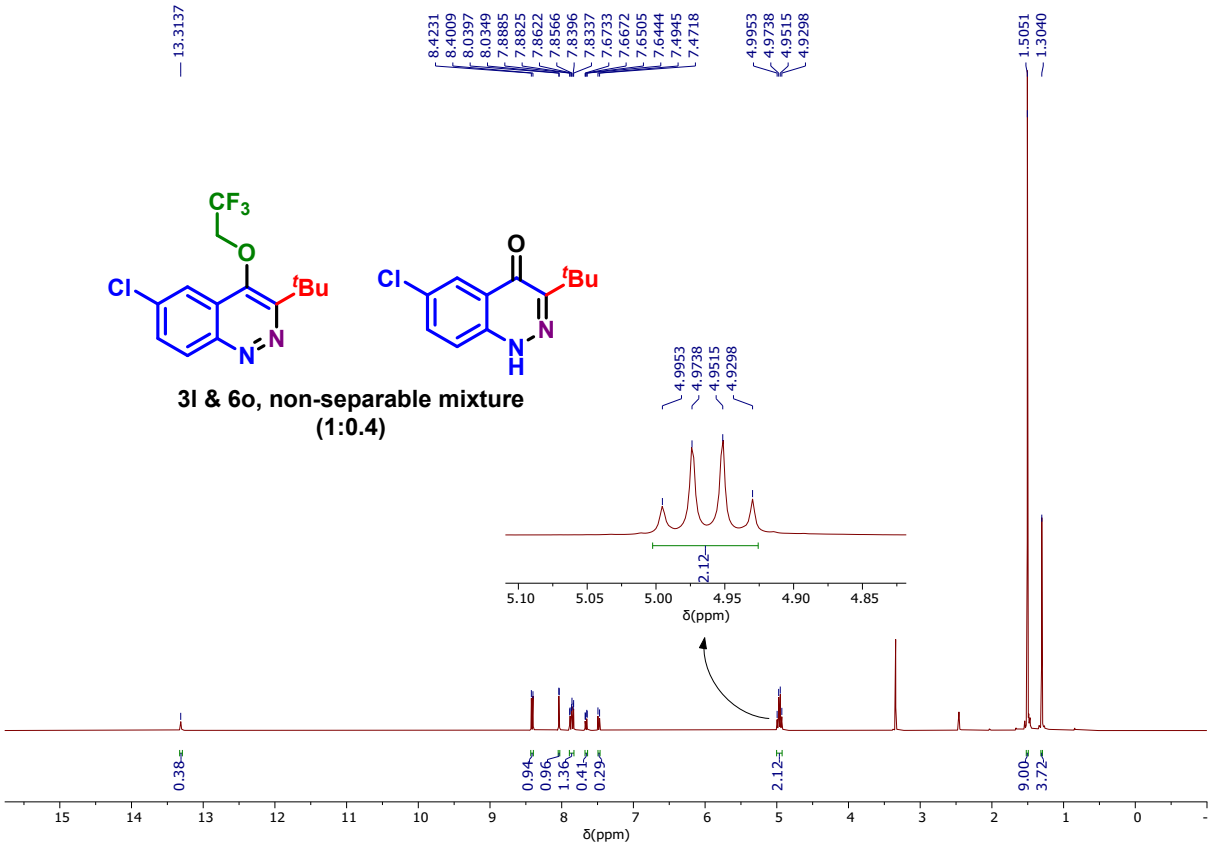


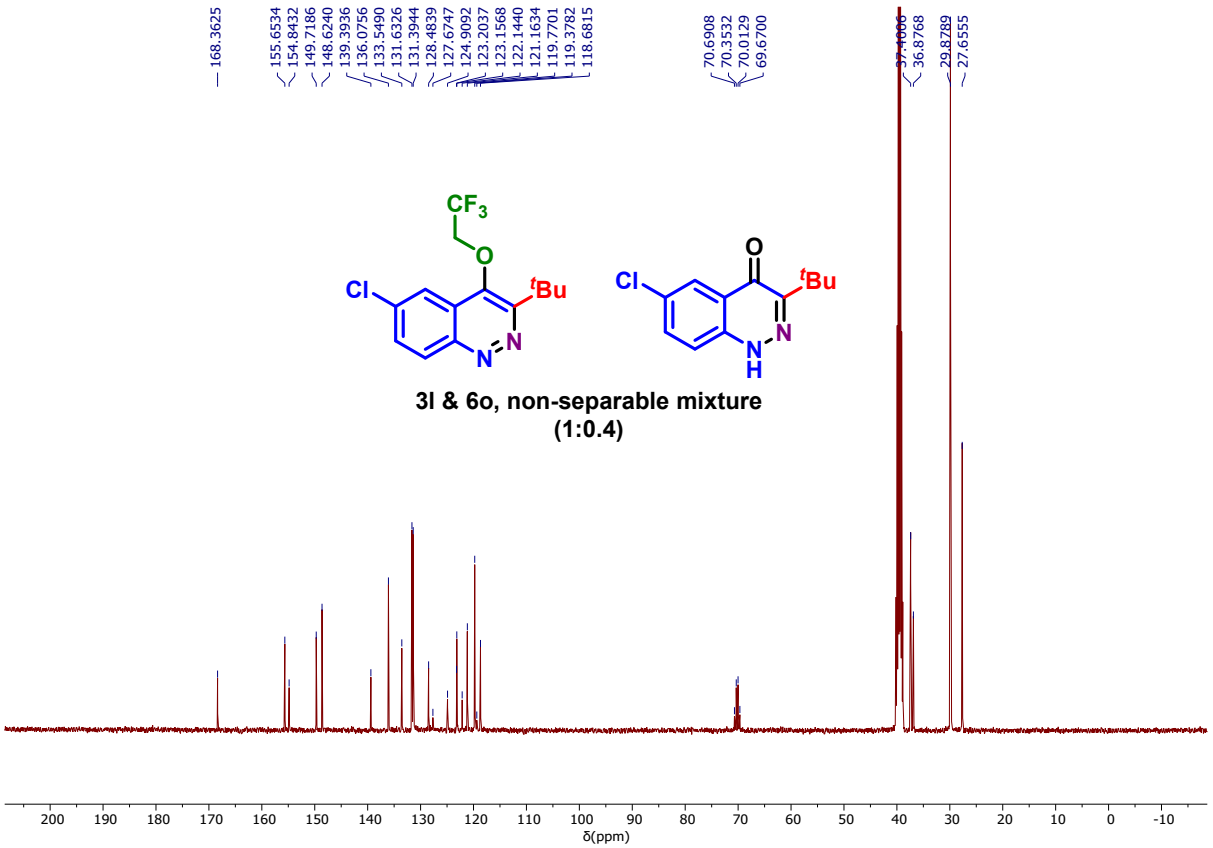


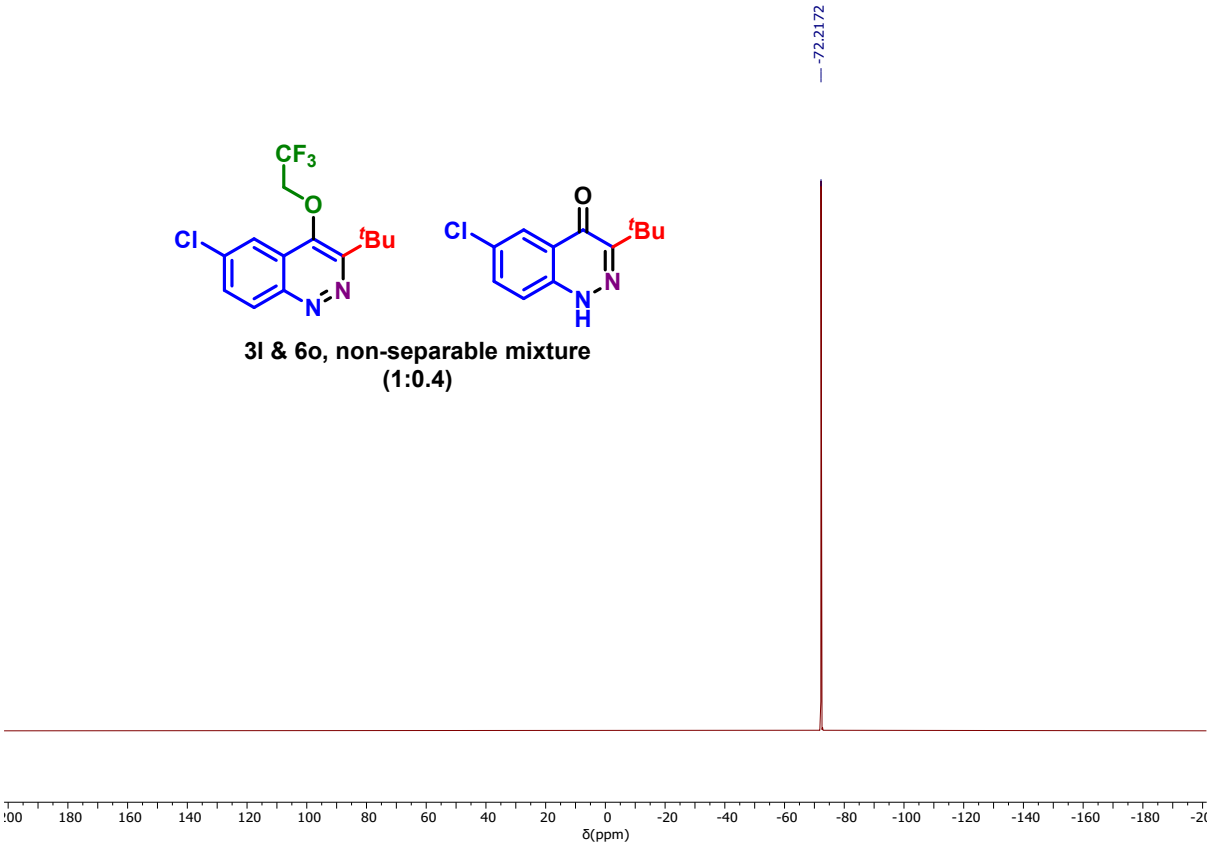


3k & 6n, non-separable mixture
(1:0.8)

^{1}H, ^{13}C{^{1}H} and ^{19}F NMR (DMSO-d_6, 400, 101 and 376 MHz) of non-separable mixture 3l and 6o:







3l & 6o, non-separable mixture
(1:0.4)

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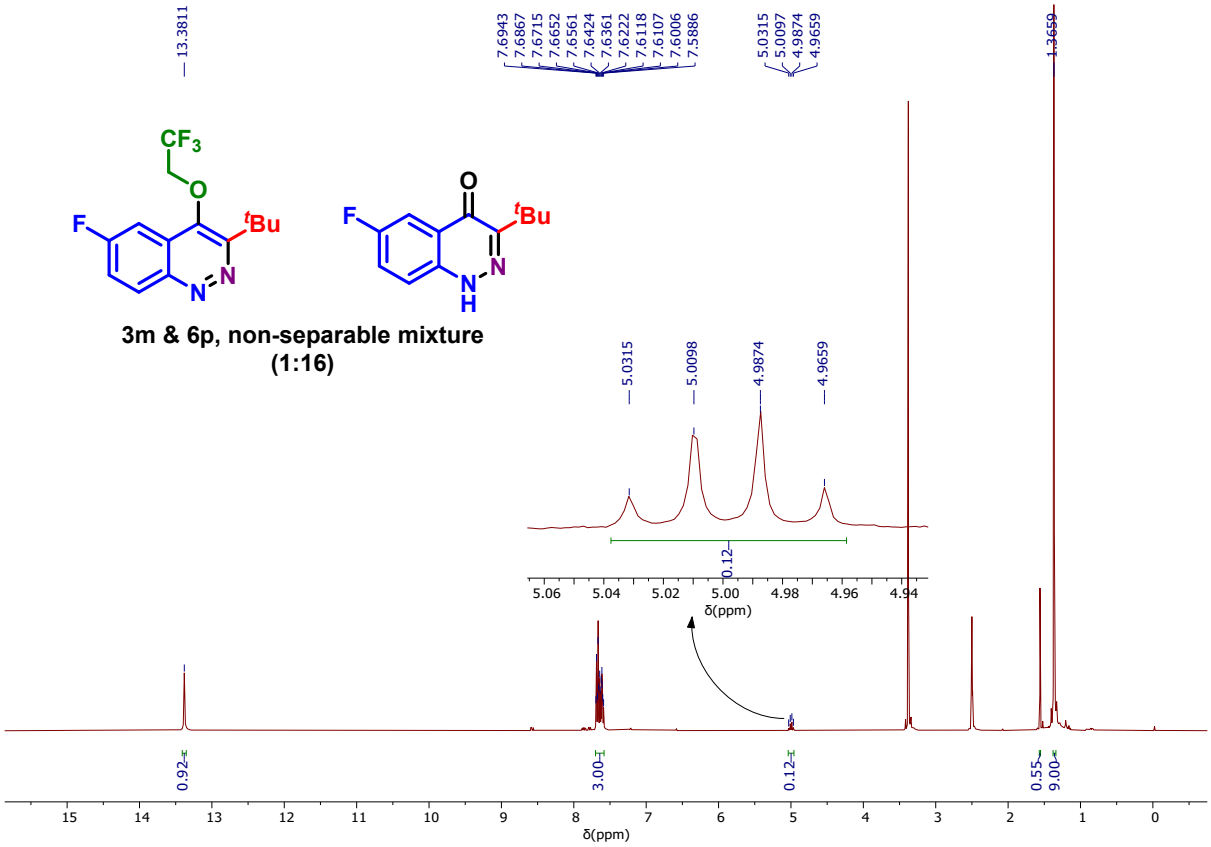

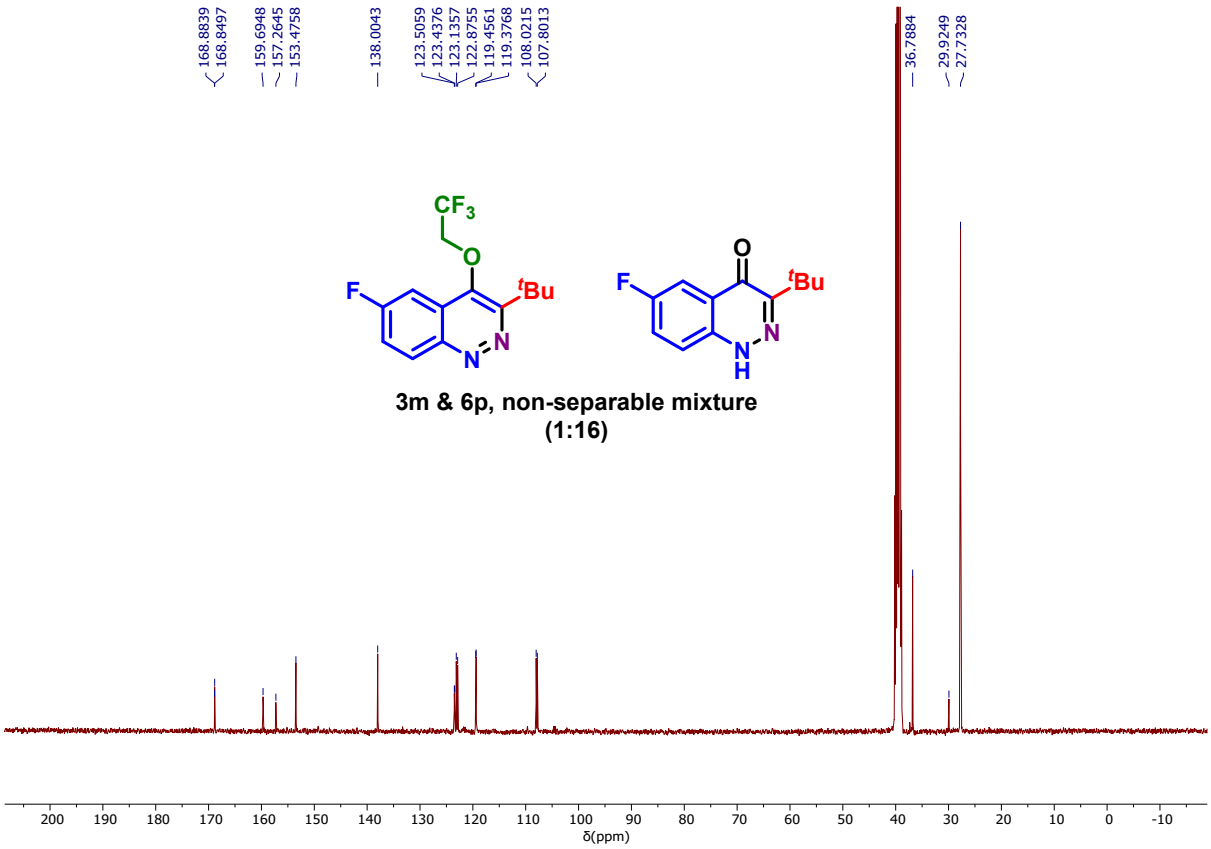

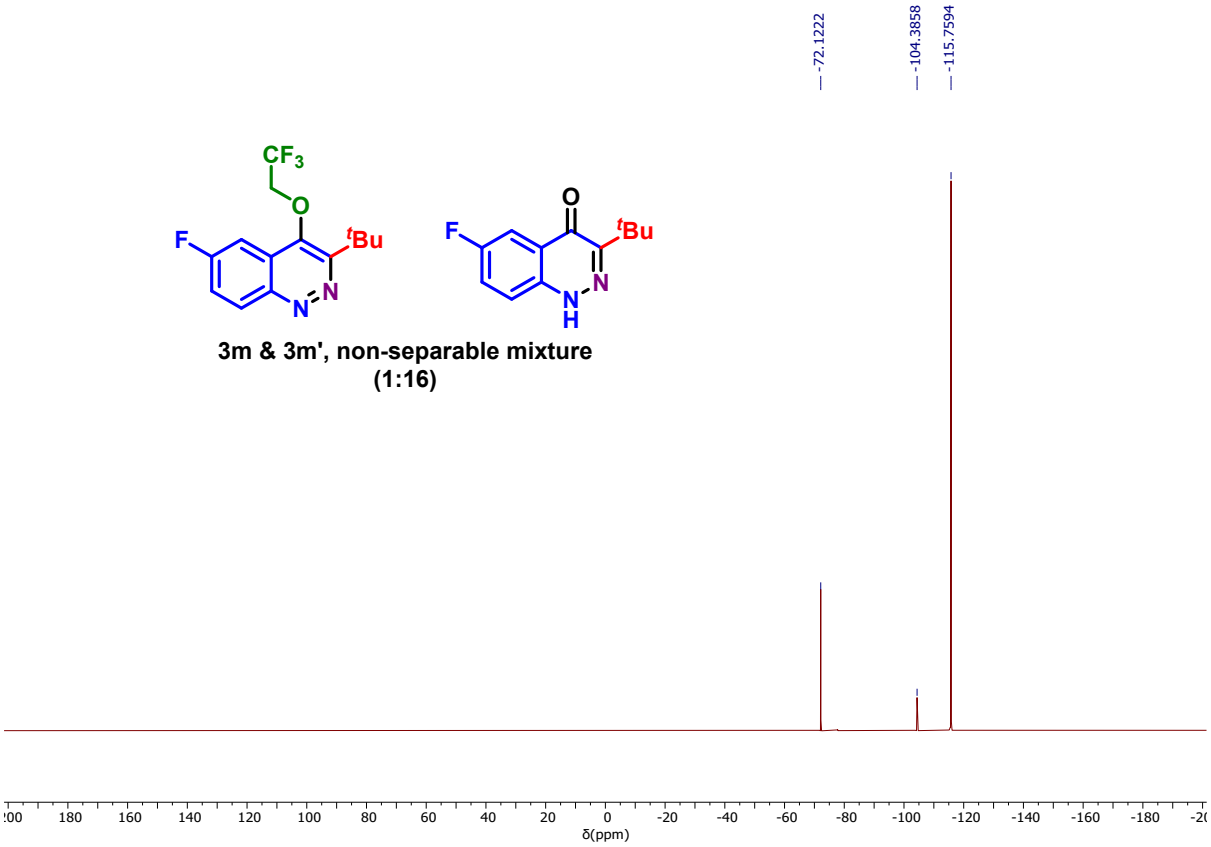

3m & 3m', non-separable mixture (1:16)

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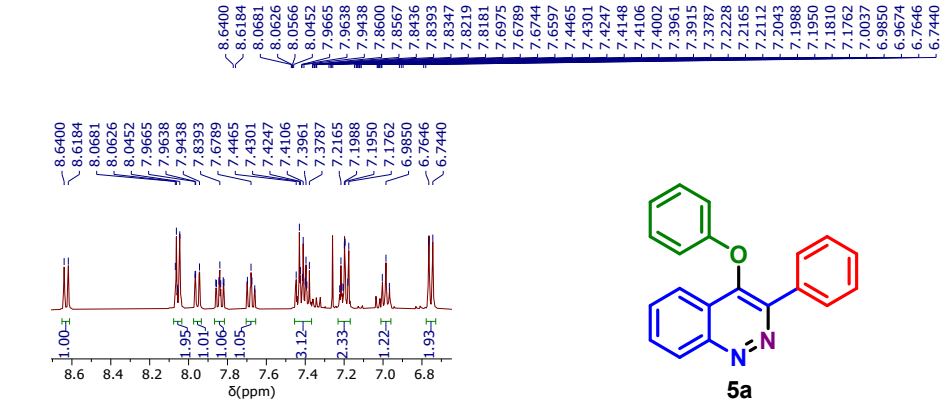
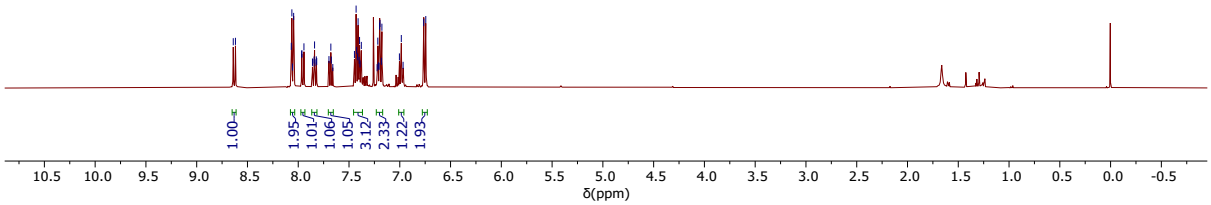
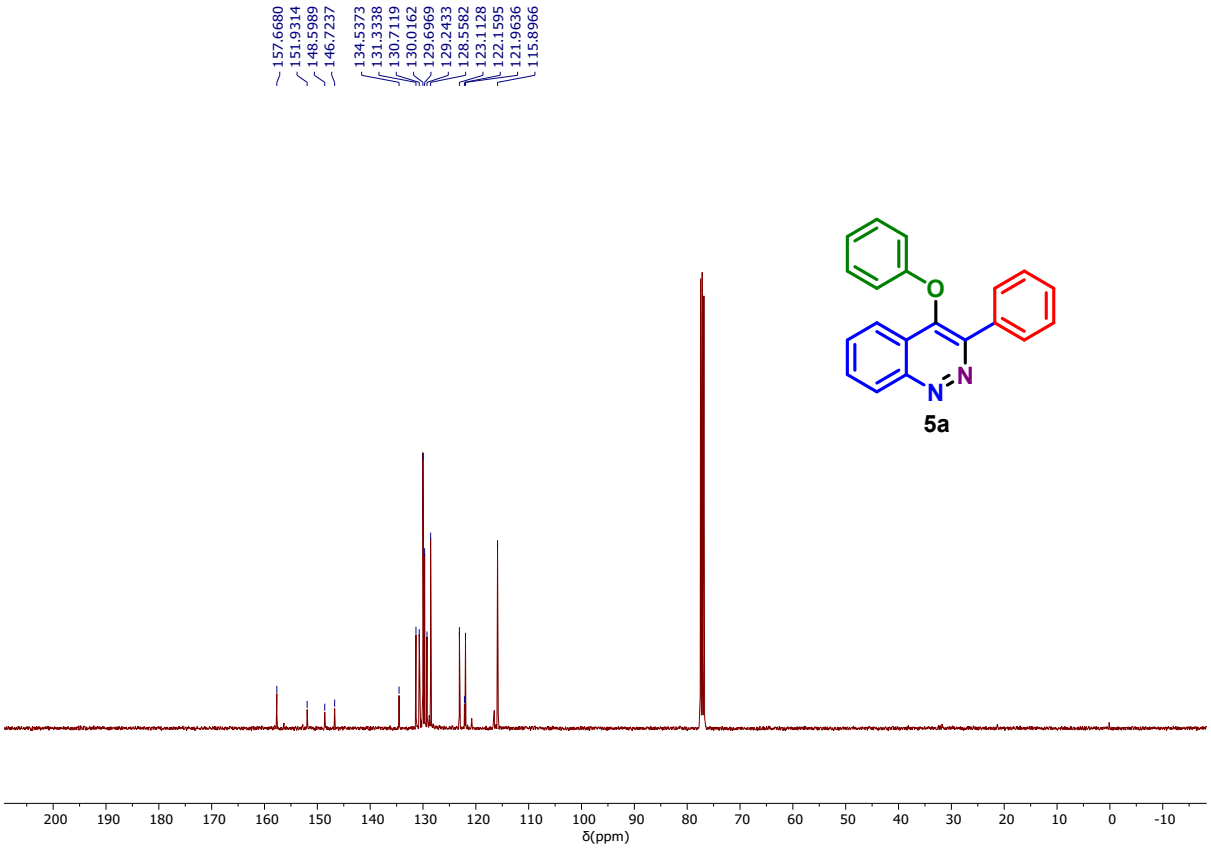
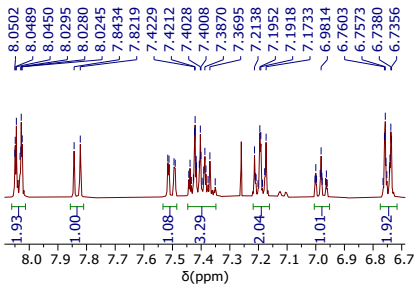
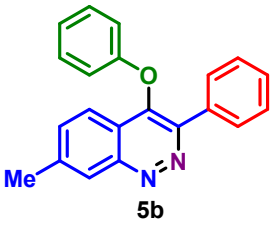


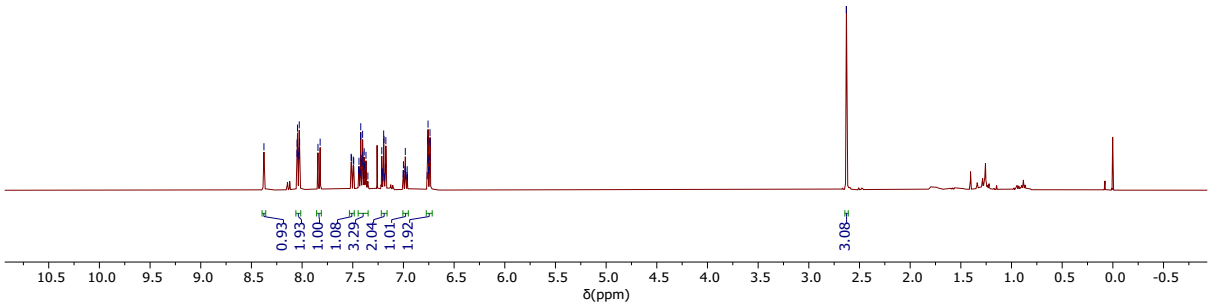


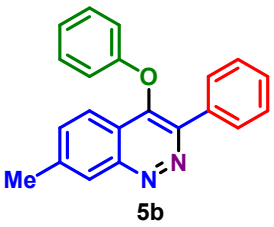


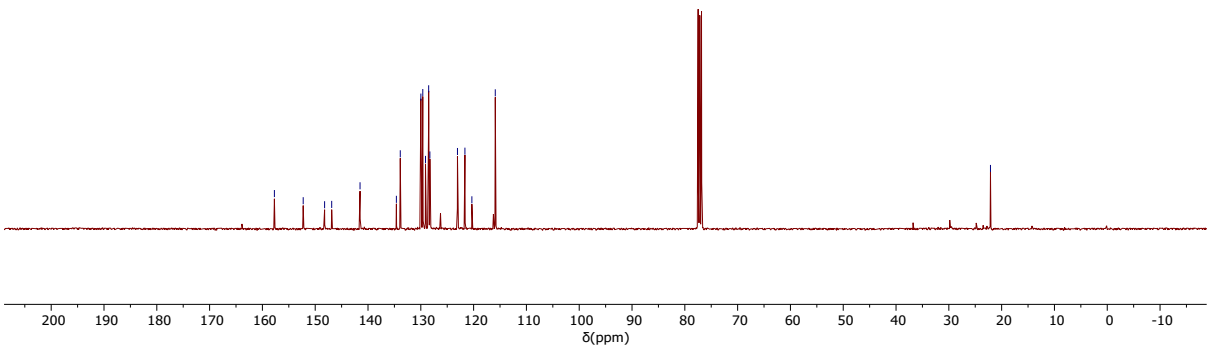
^{1}H and $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 400 and 101 MHz) of compound 5b:



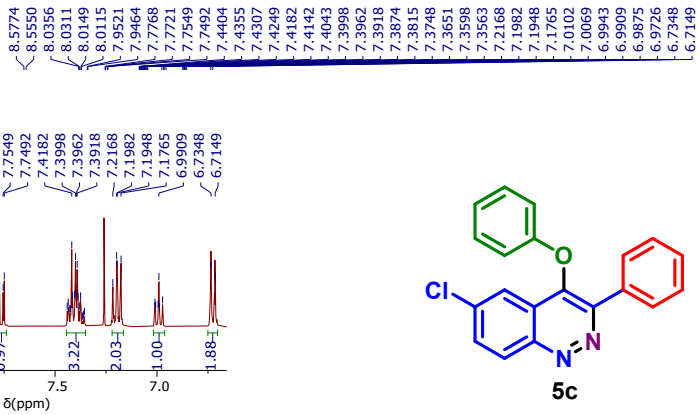


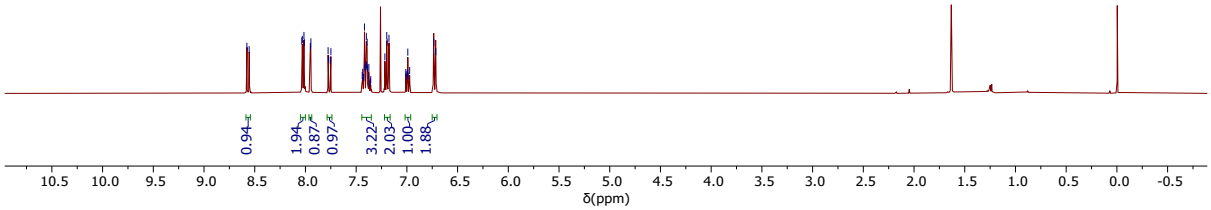


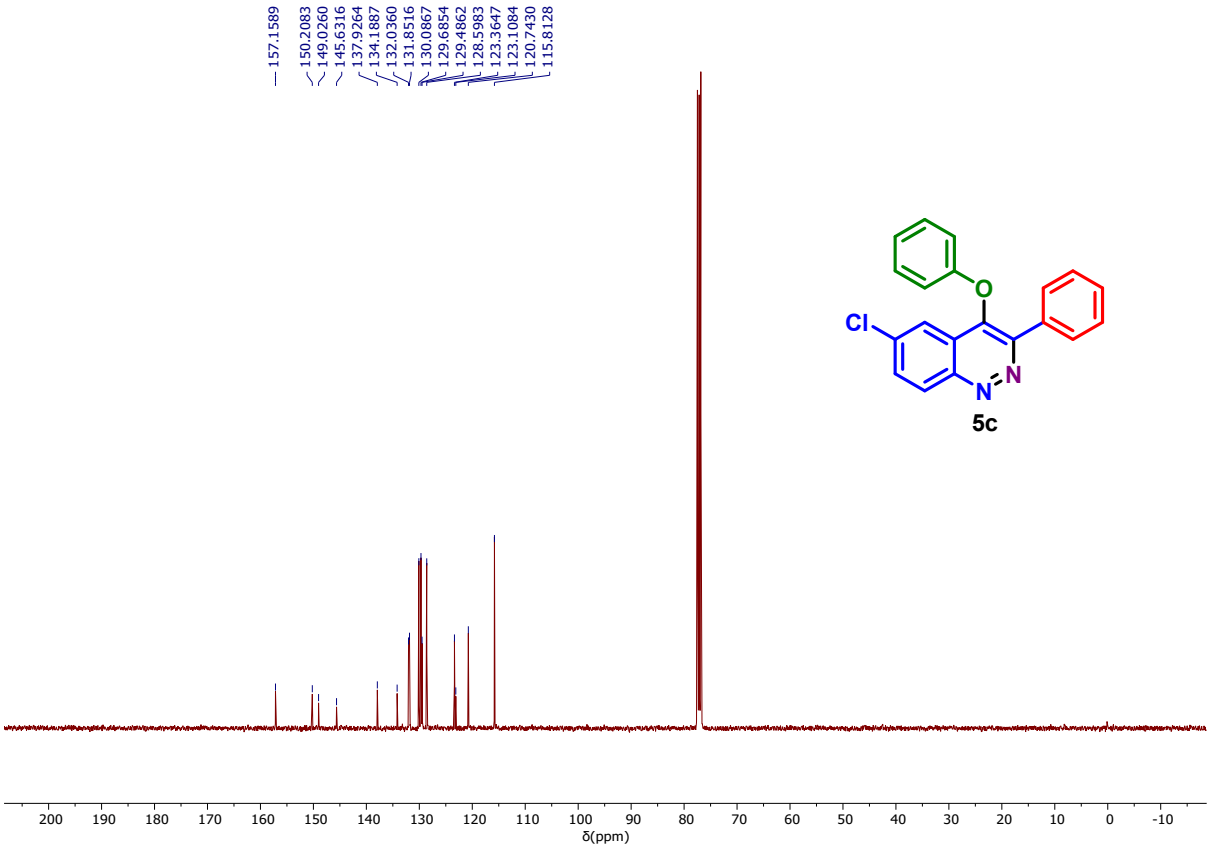




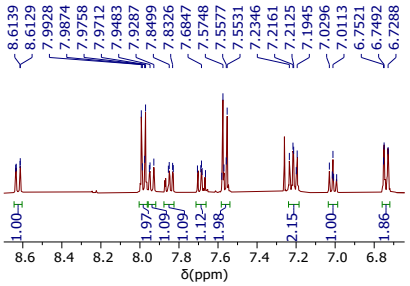
^{1}H and $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 400 and 101 MHz) of compound 5c:

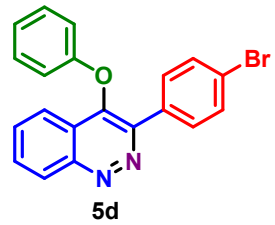


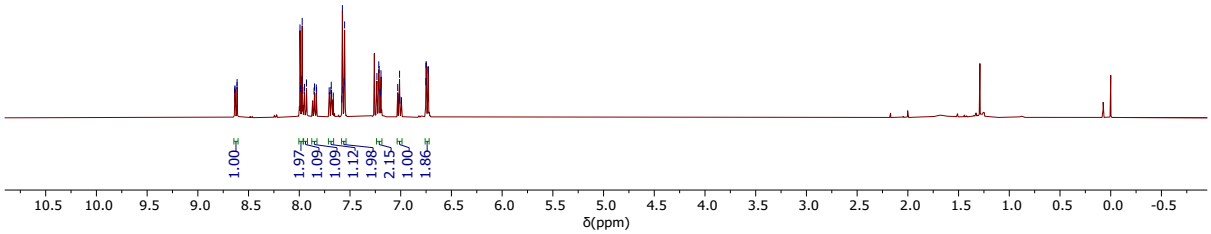


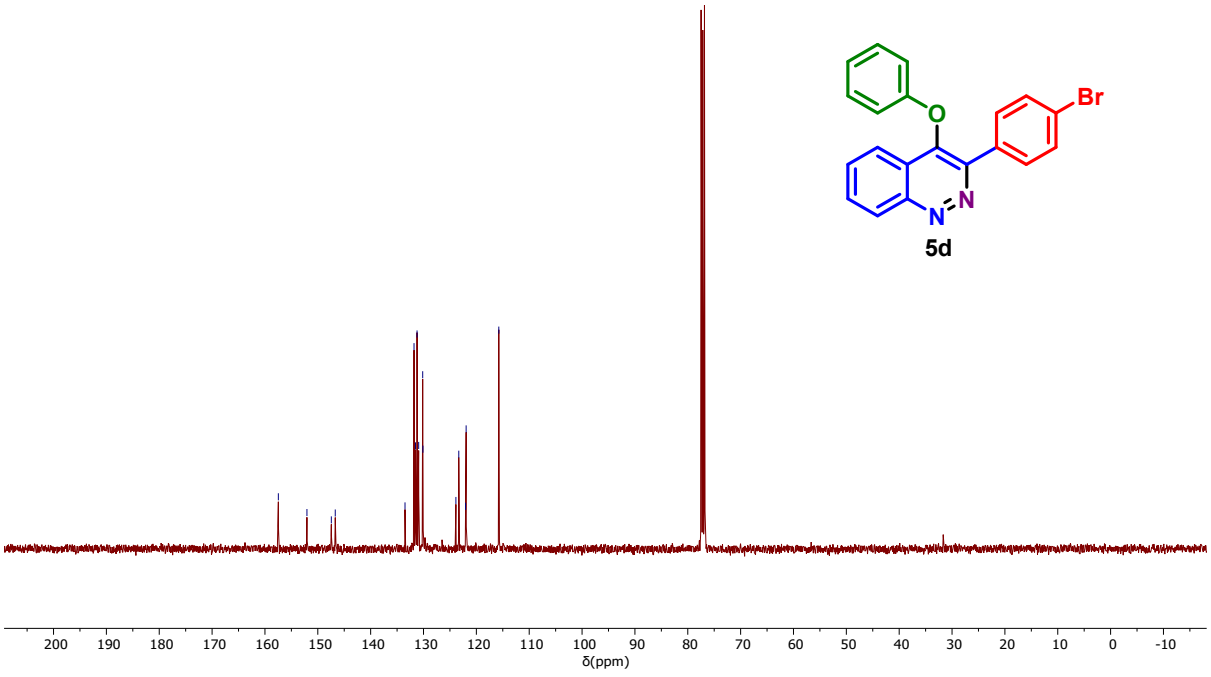


^{1}H and $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 400 and 101 MHz) of compound 5d:

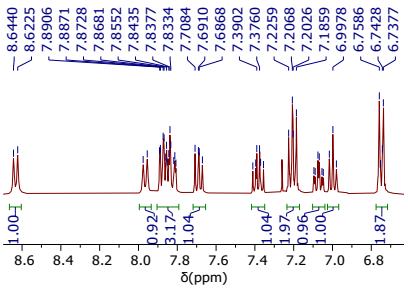


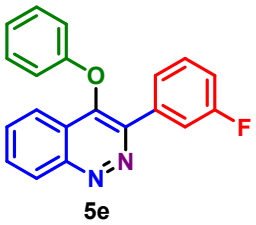


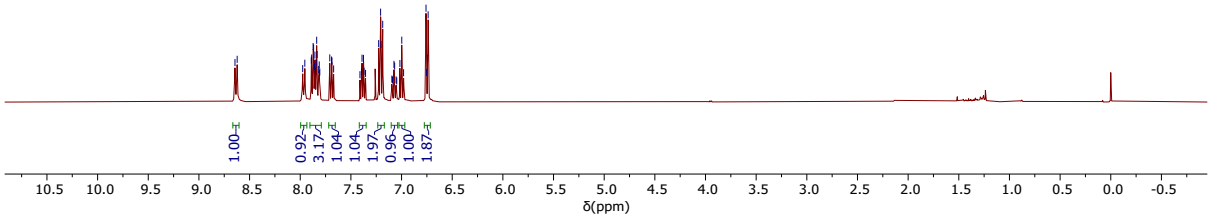


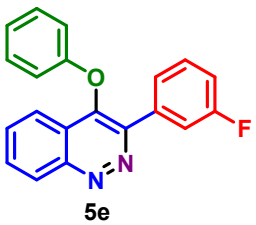


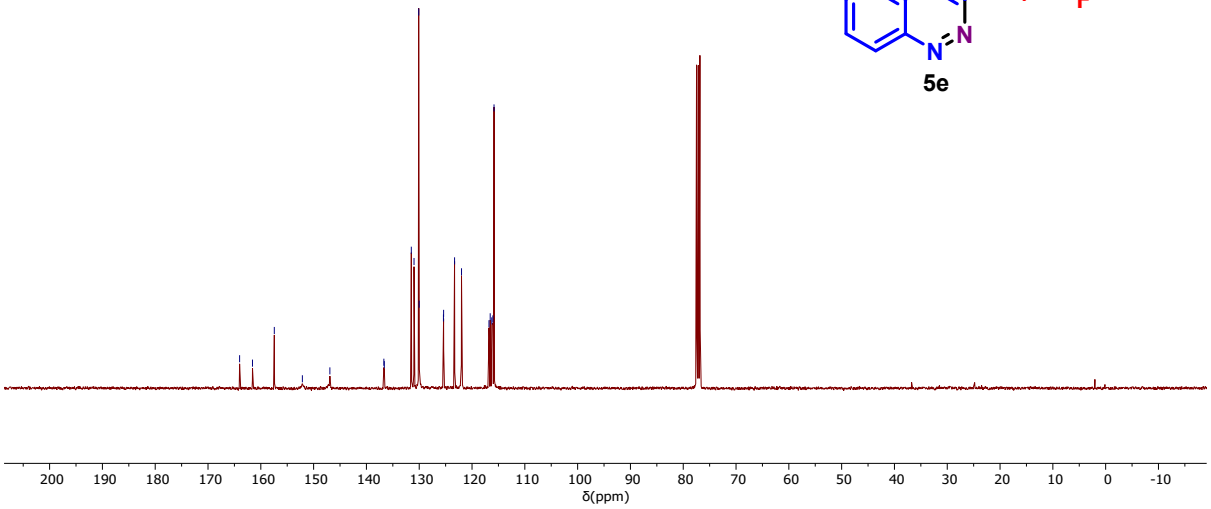
^{1}H, $^{13}C\{^{1}H\}$ and ^{19}F NMR ($CDCl_3$, 400, 101 and 376 MHz) of compound 5e:

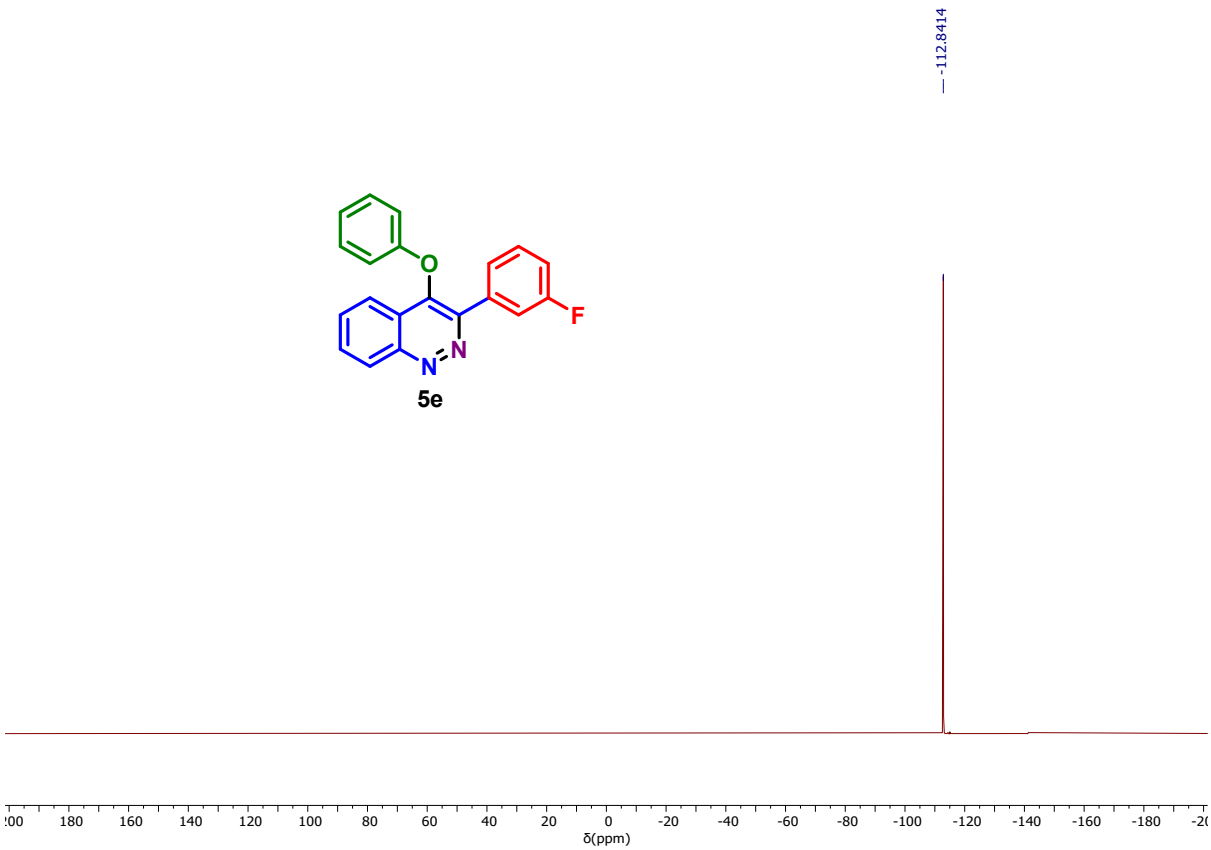




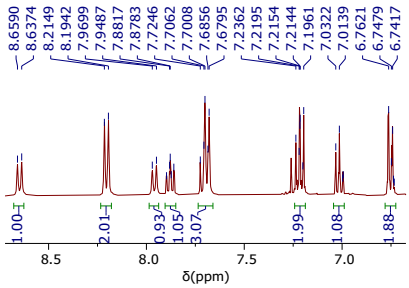


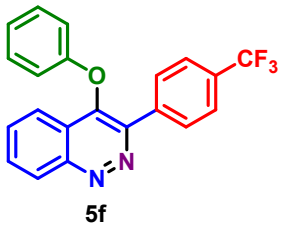


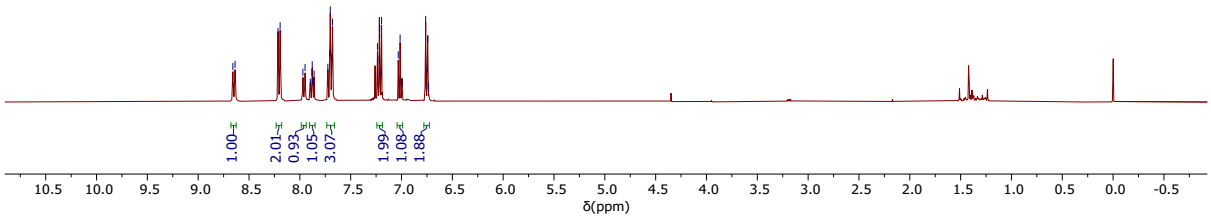


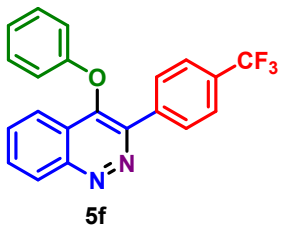

-112.8414
O
F
N
N
5e
δ(ppm)

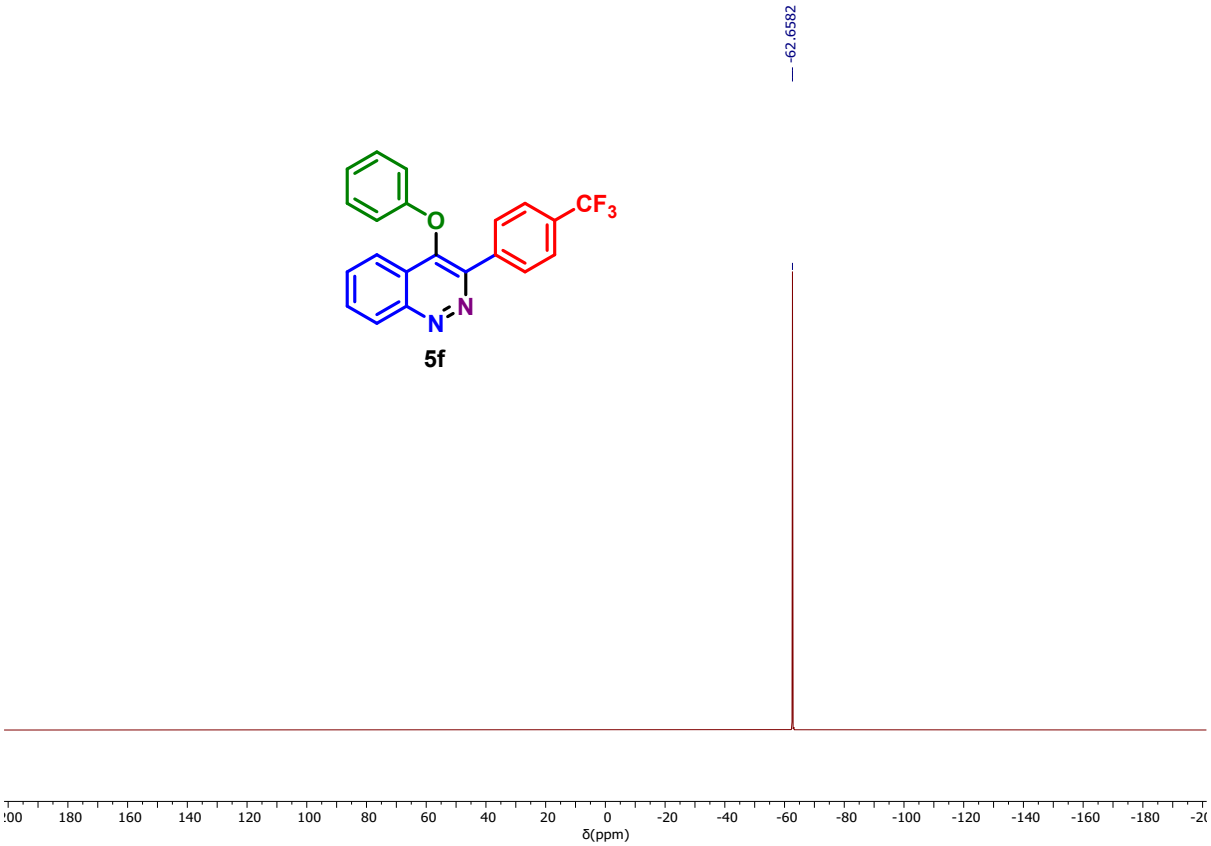
^{1}H, $^{13}C\{^{1}H\}$ and ^{19}F NMR ($CDCl_3$, 400, 101 and 376 MHz) of compound 5f:



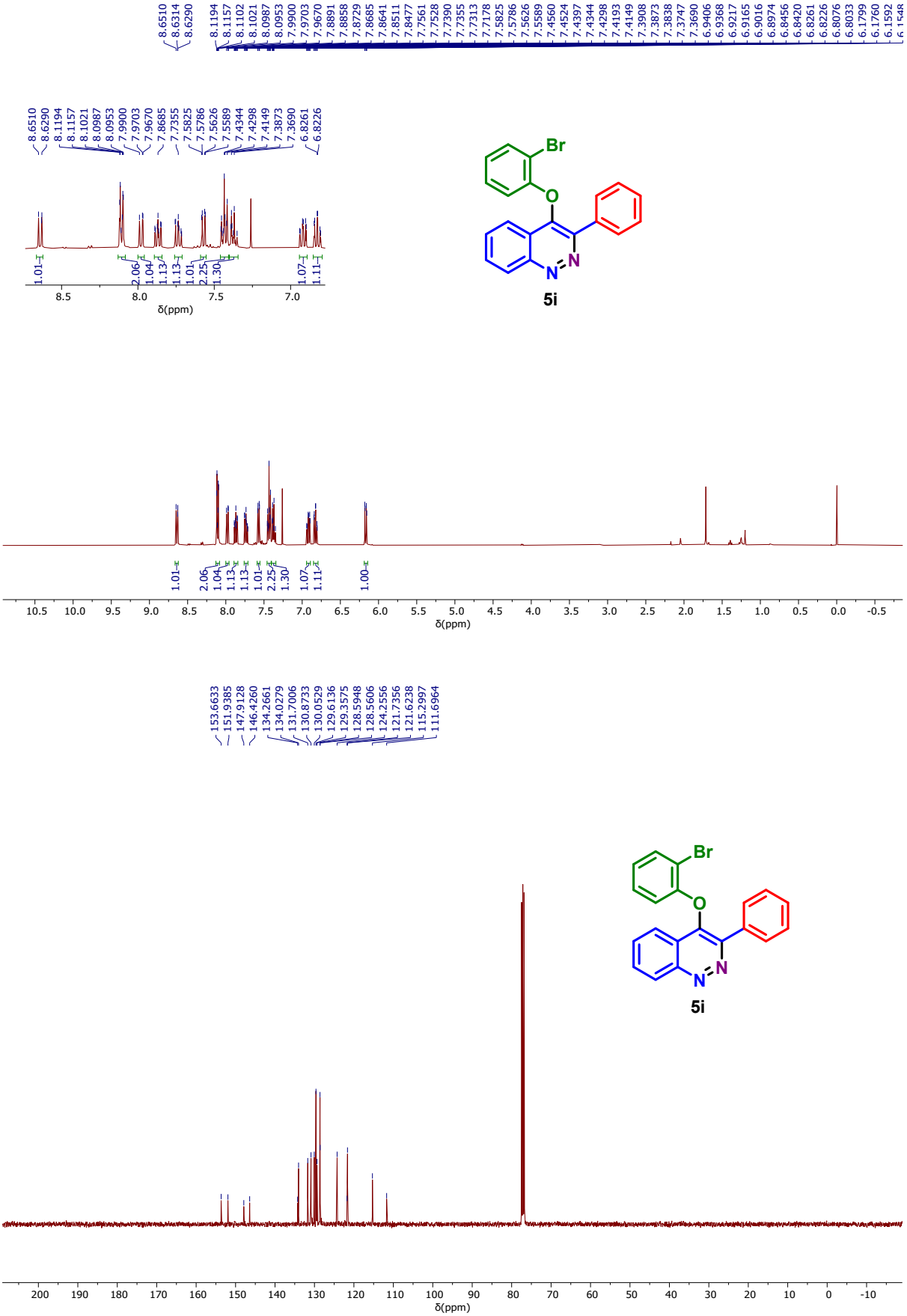




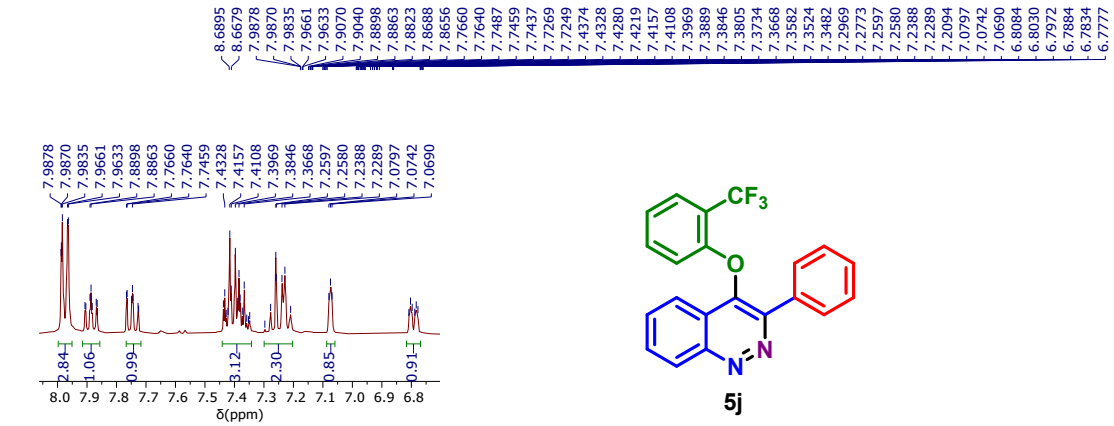



-62.6582
O
CF3
N
N
5f
δ(ppm)

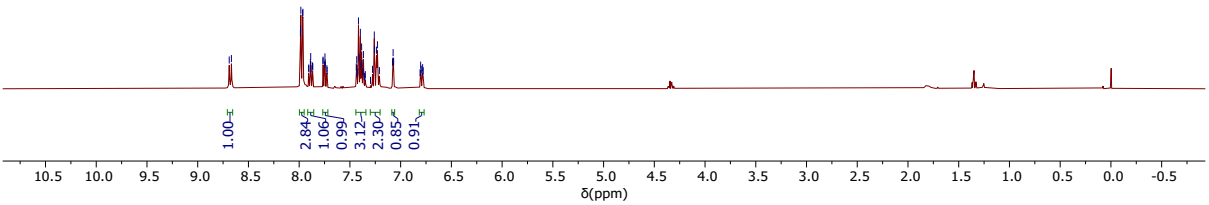
^{1}H and $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 400 and 101 MHz) of compound 5i:

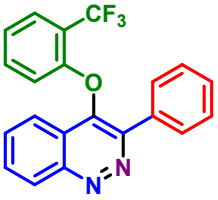


^{1}H, $^{13}C\{^{1}H\}$ and ^{19}F NMR ($CDCl_3$, 400, 101 and 376 MHz) of compound 5j:

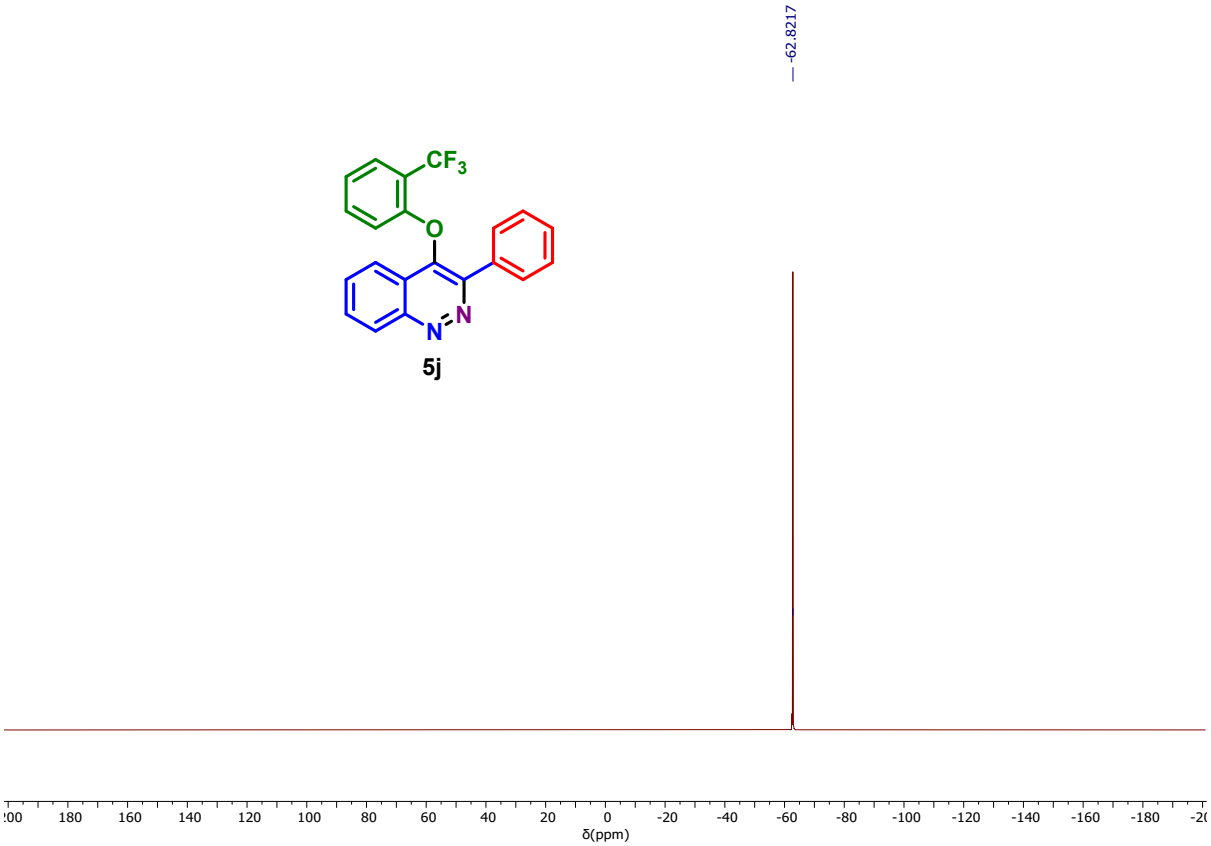


5j

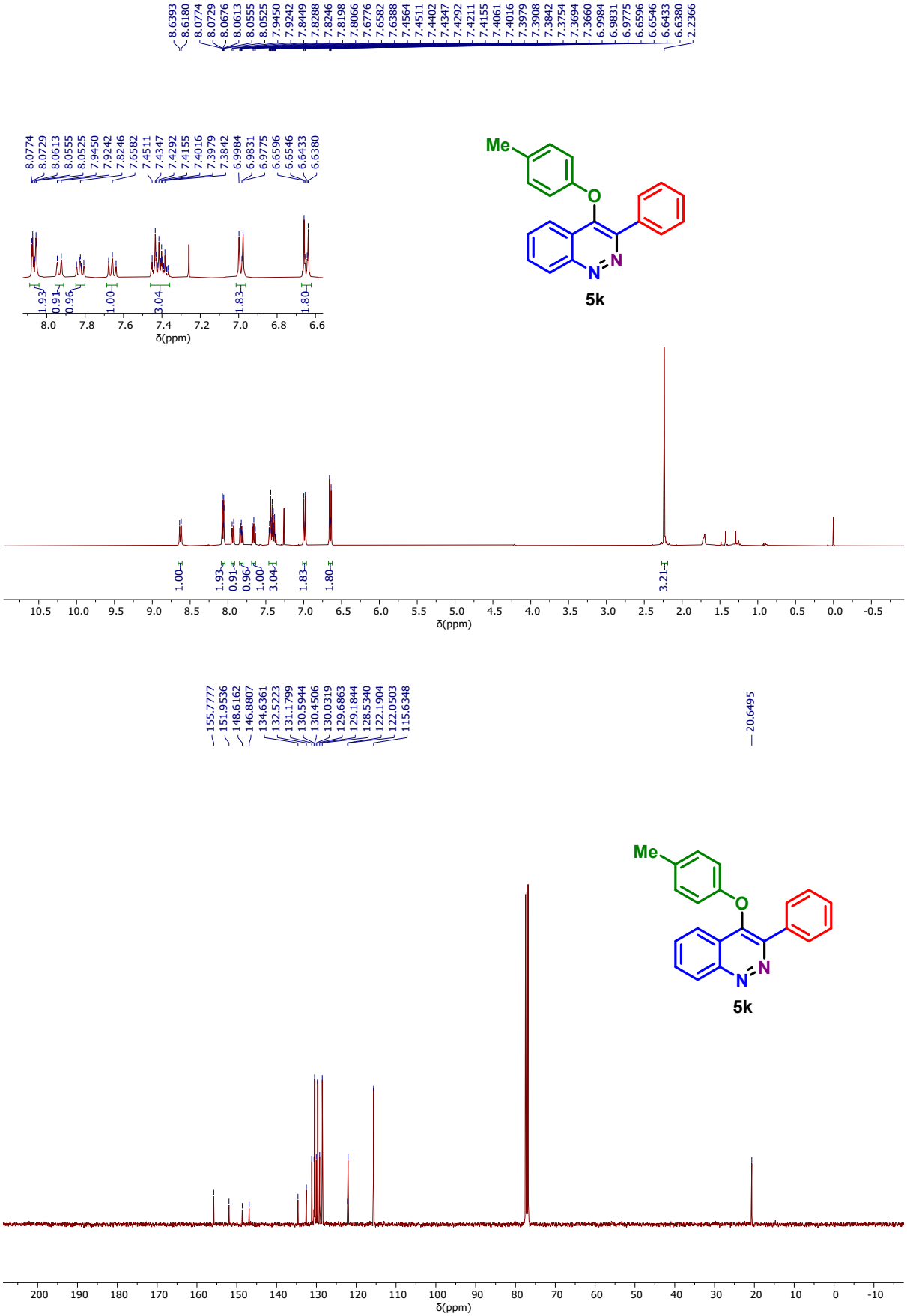




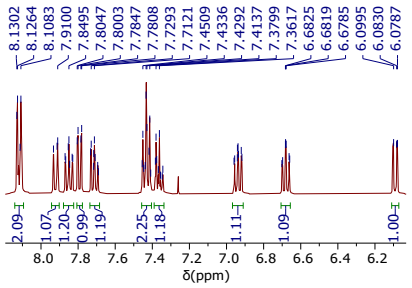
5j

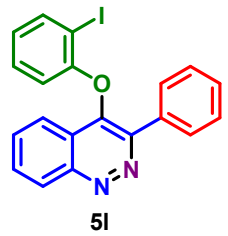

−62.8217
CF3
O
N
N
5j
δ(ppm)

^{1}H and $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 400 and 101 MHz) of compound 5k:

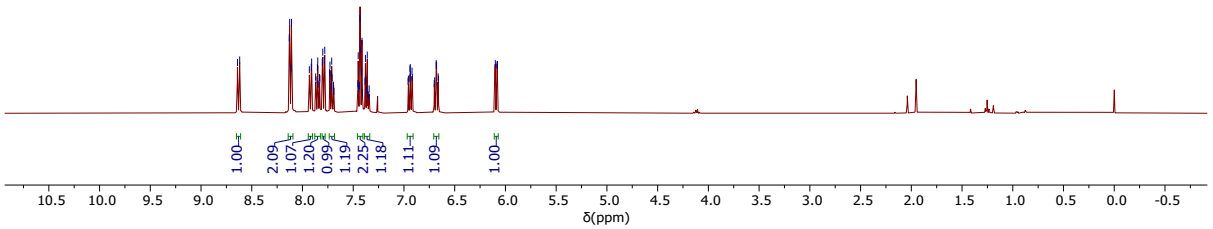


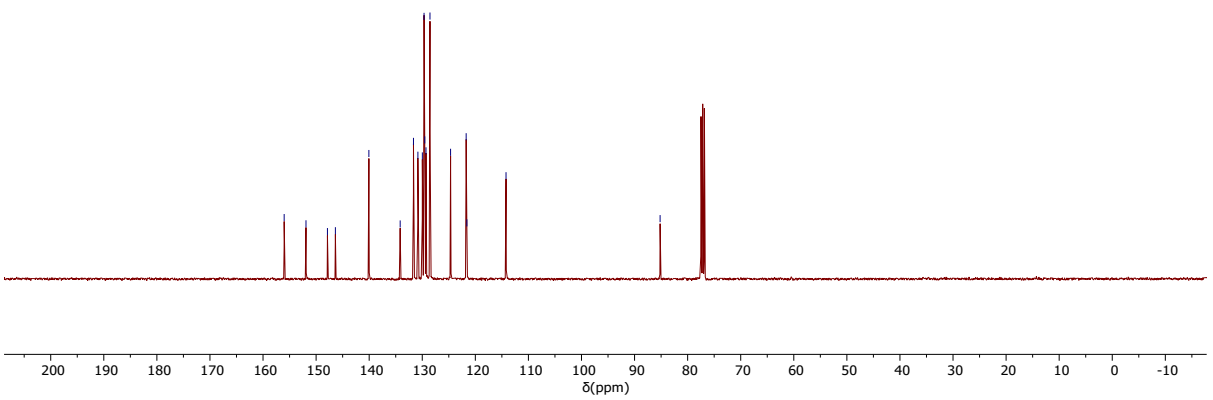
^{1}H and $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 400 and 101 MHz) of compound 5l:

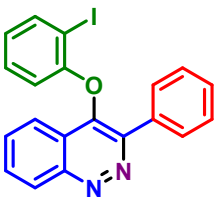




5l

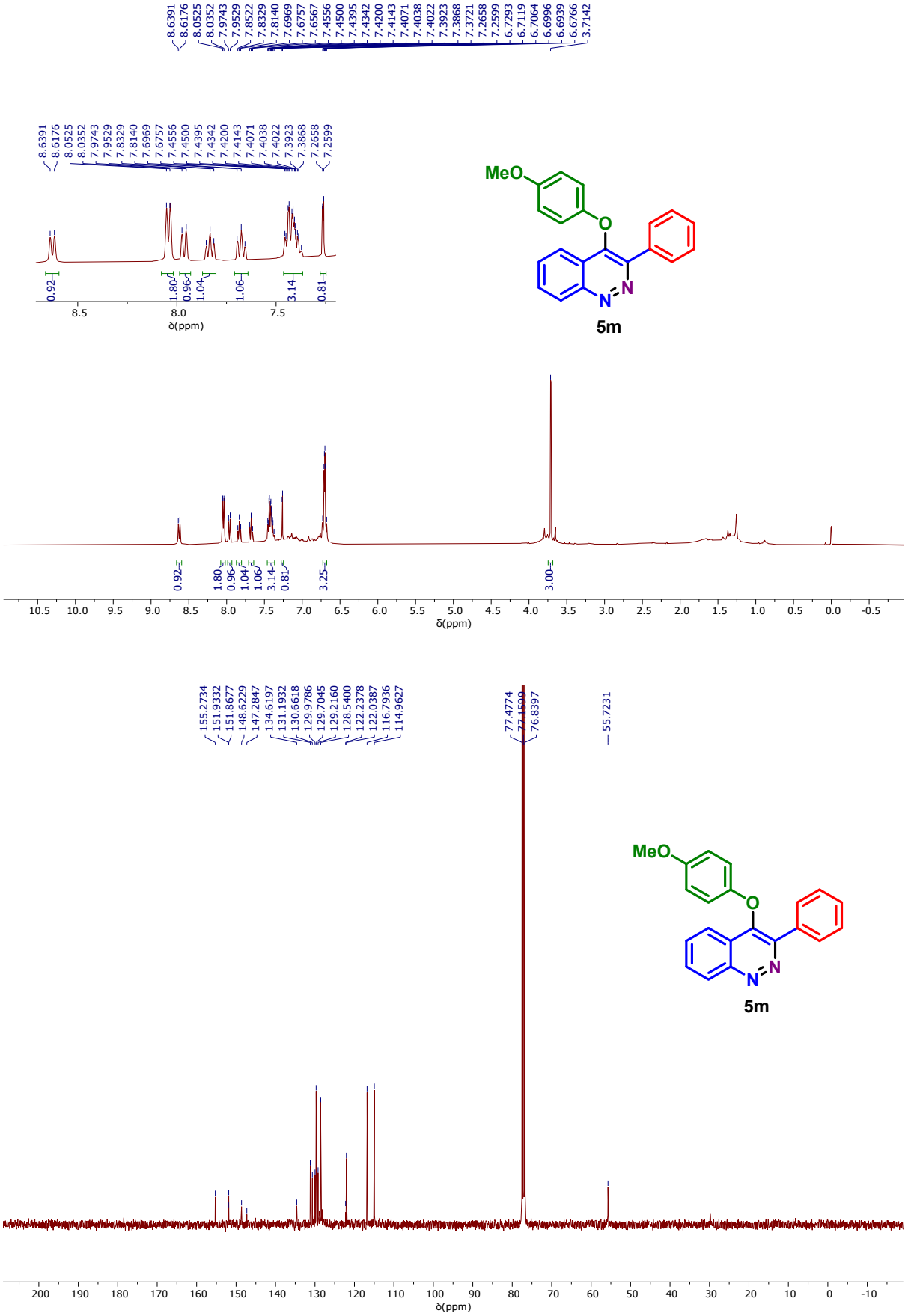




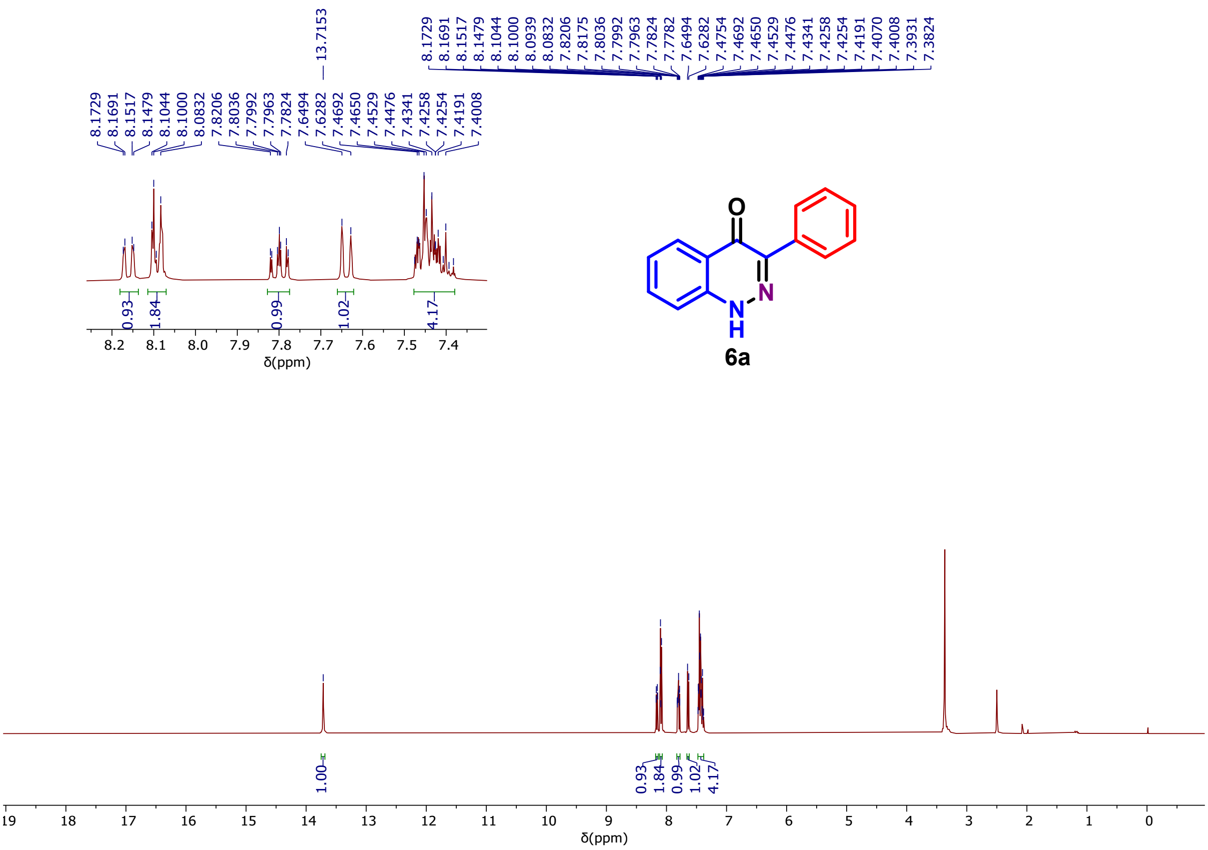


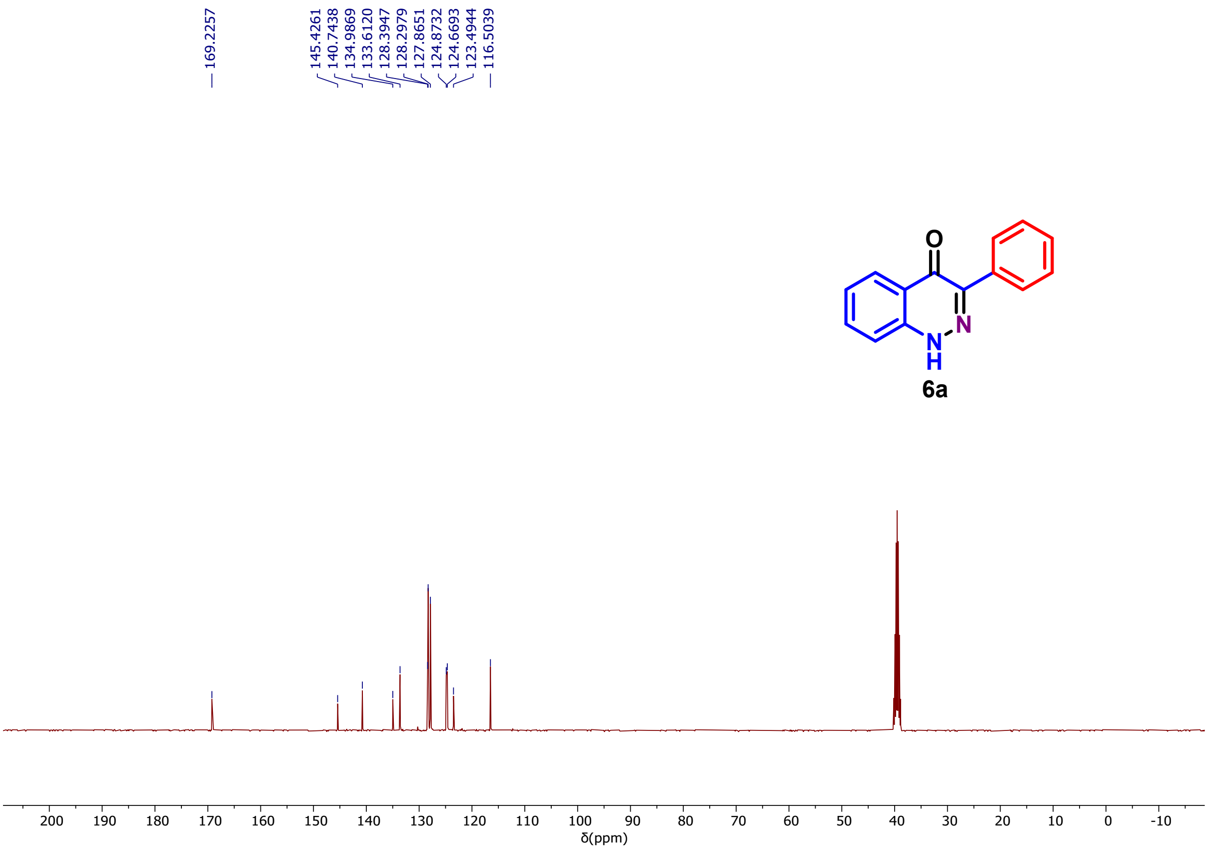
5l

^{1}H and $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 400 and 101 MHz) of compound 5m (<5% yield):

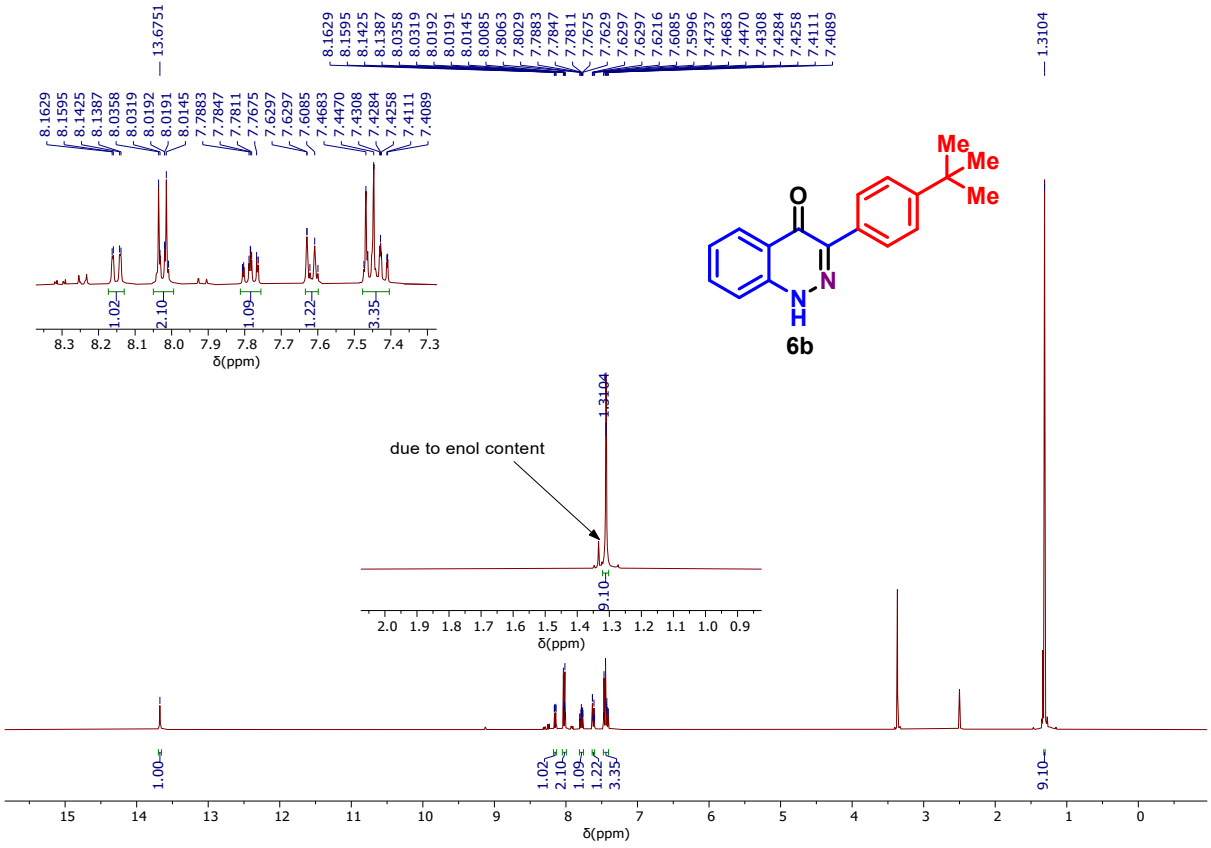


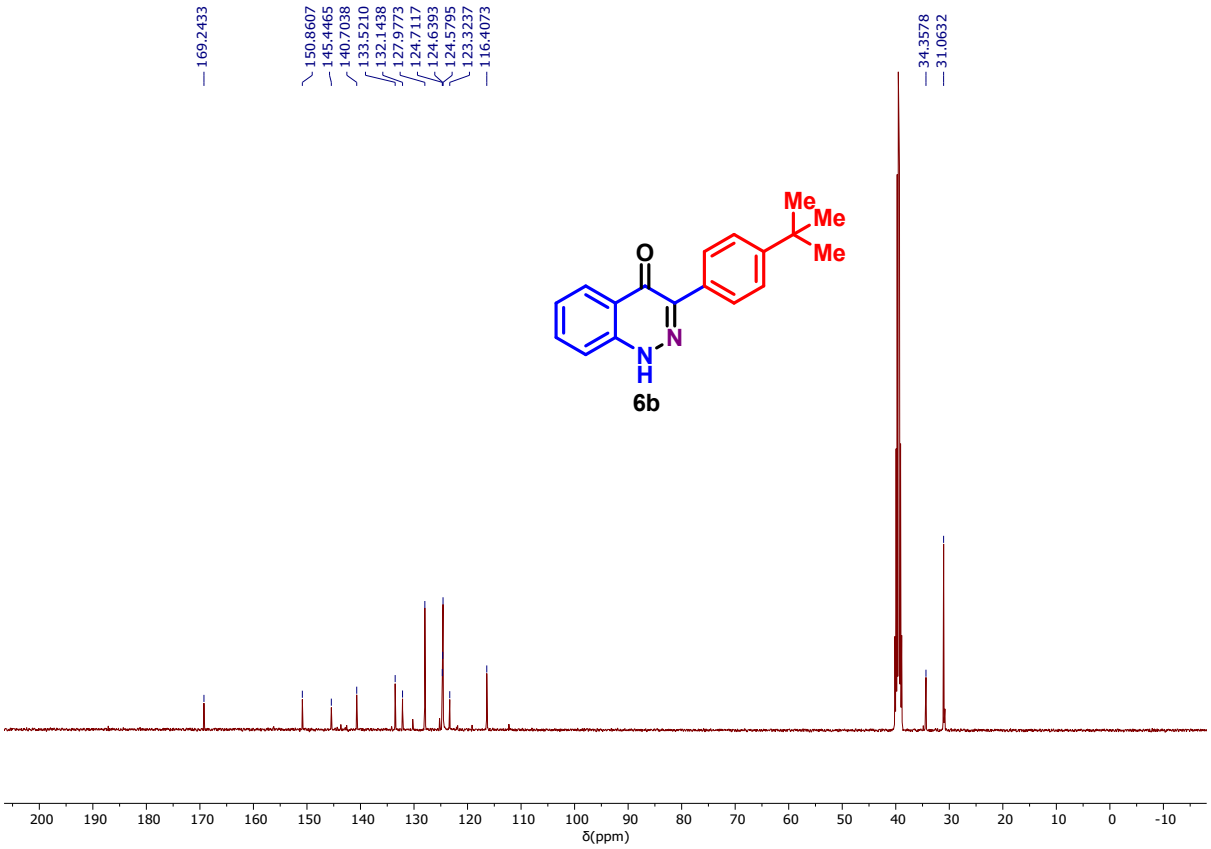
[1]H and [13]C{[1]H} NMR (DMSO-d_6, 400 and 101 MHz) of compound 6a:



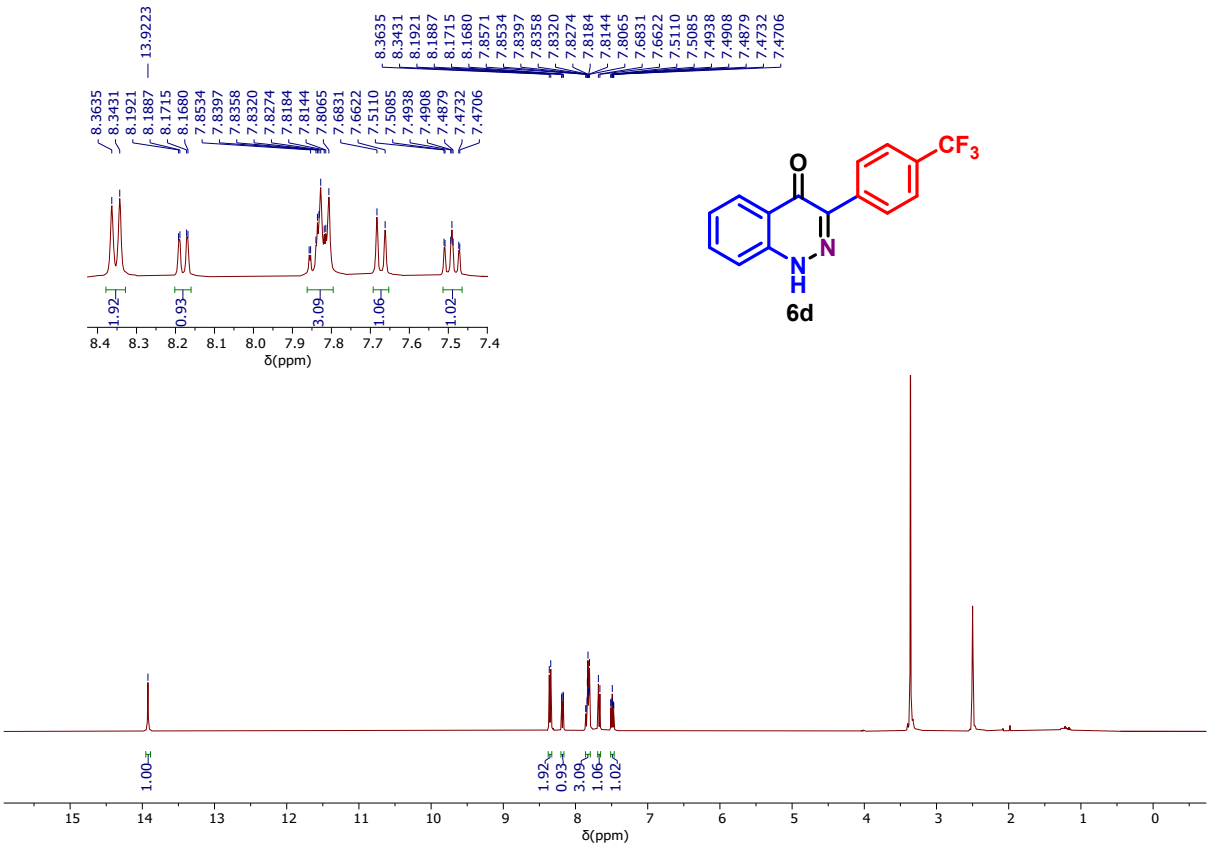


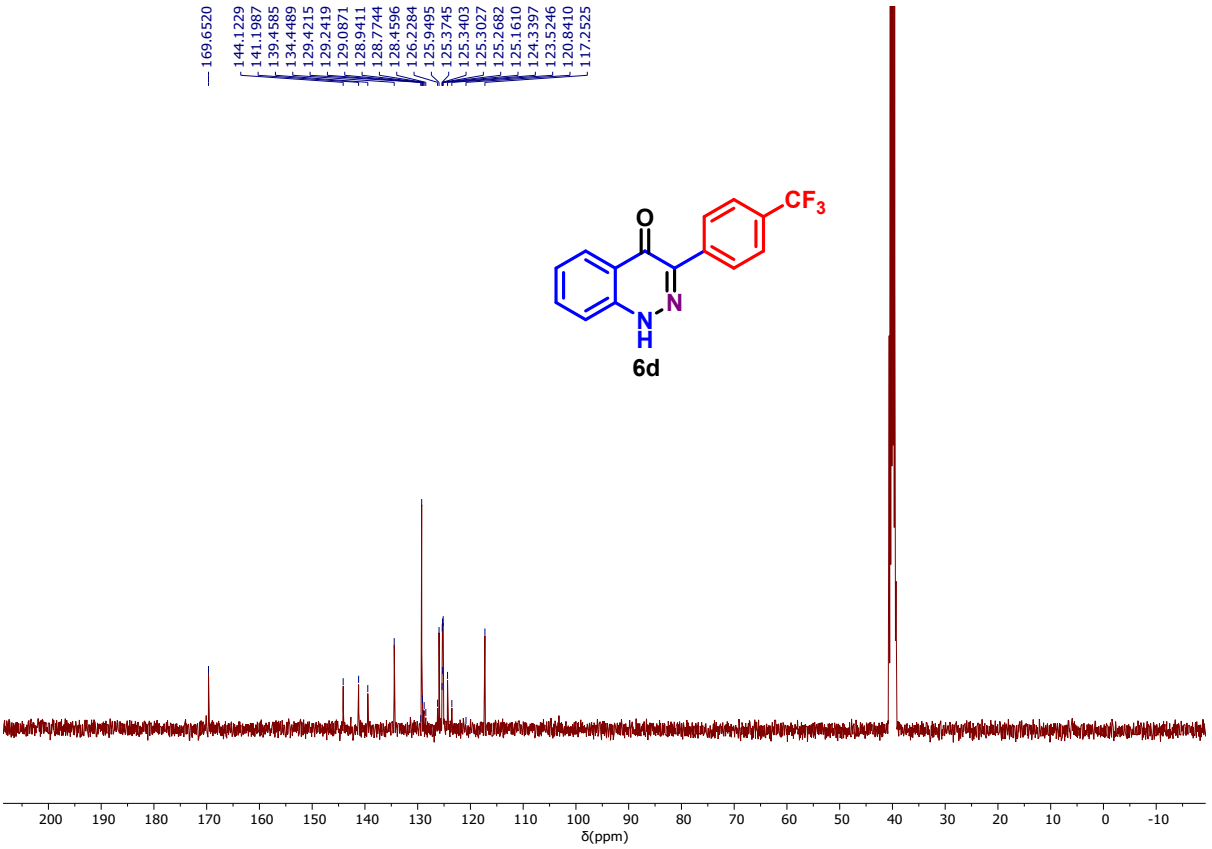
^{1}H and ^{13}C{^{1}H} NMR (DMSO-d_6, 400 and 101 MHz) of compound 6b:

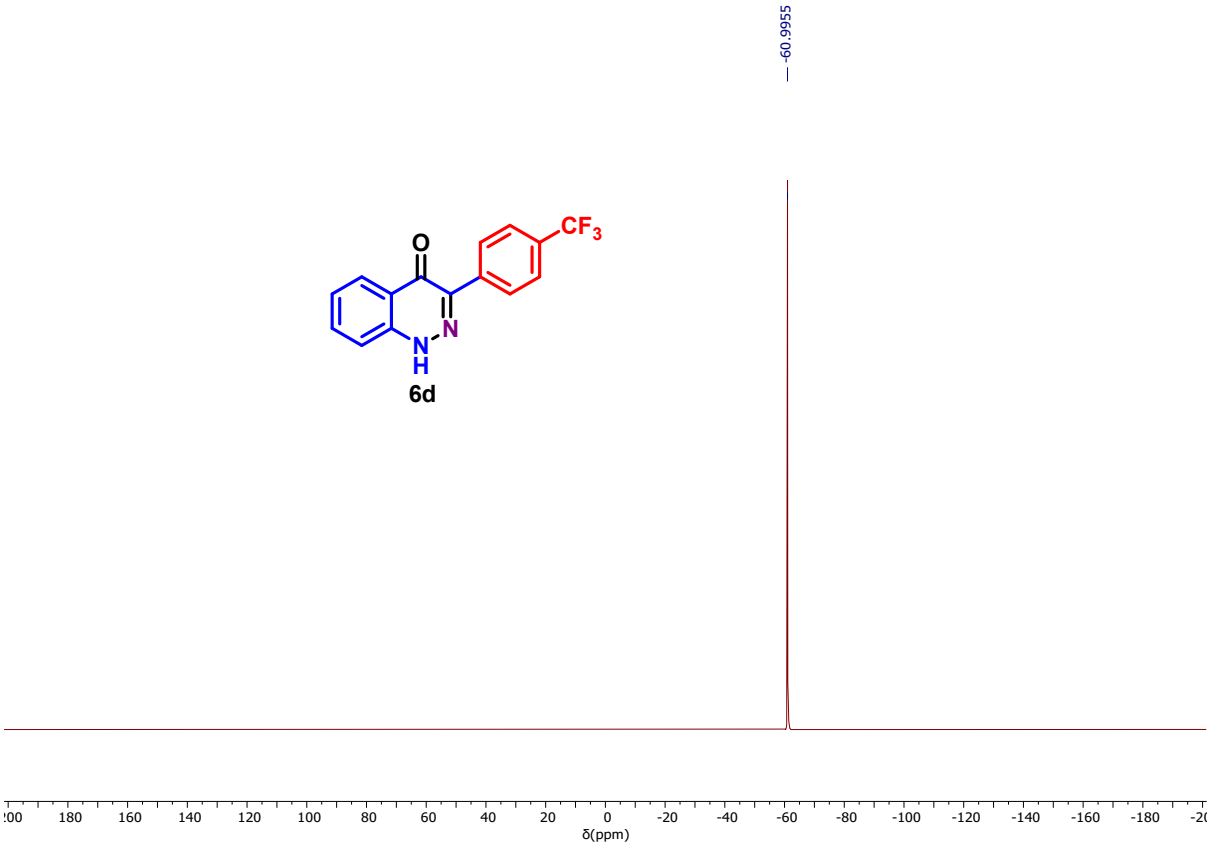




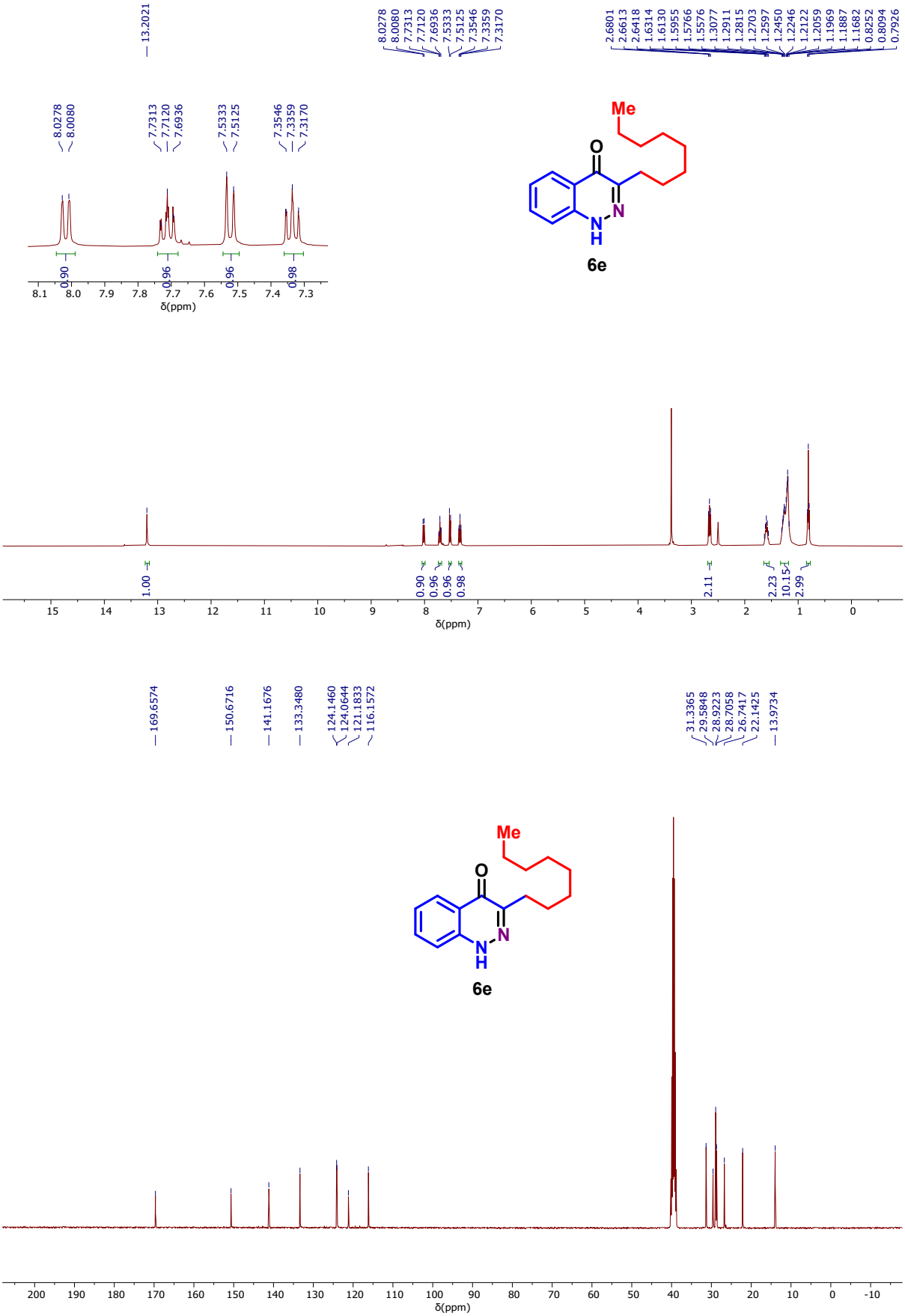
^{1}H, ^{13}C{^{1}H} and ^{19}F NMR (DMSO-d_6, 400, 101 and 376 MHz) of compound 6d:



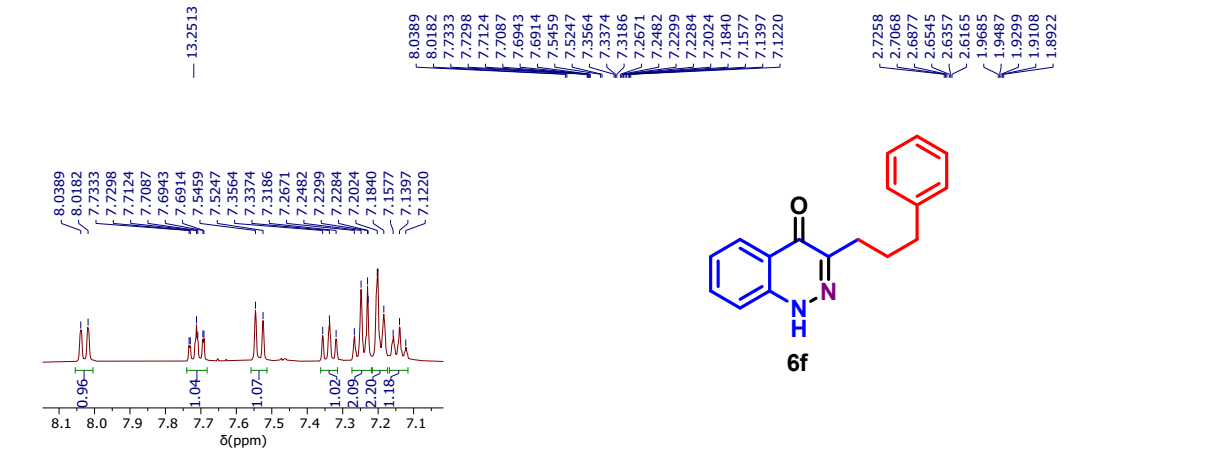


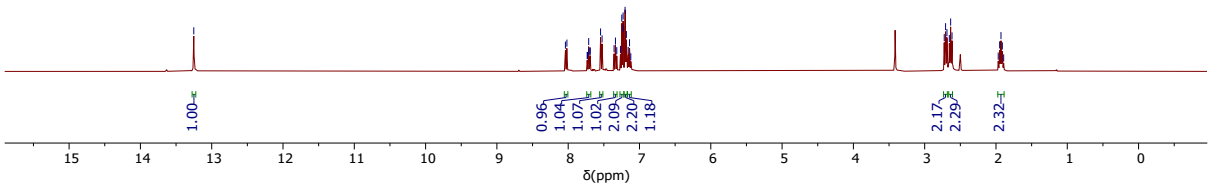

-60.9955
O
CF3
N
N
H
6d
δ(ppm)

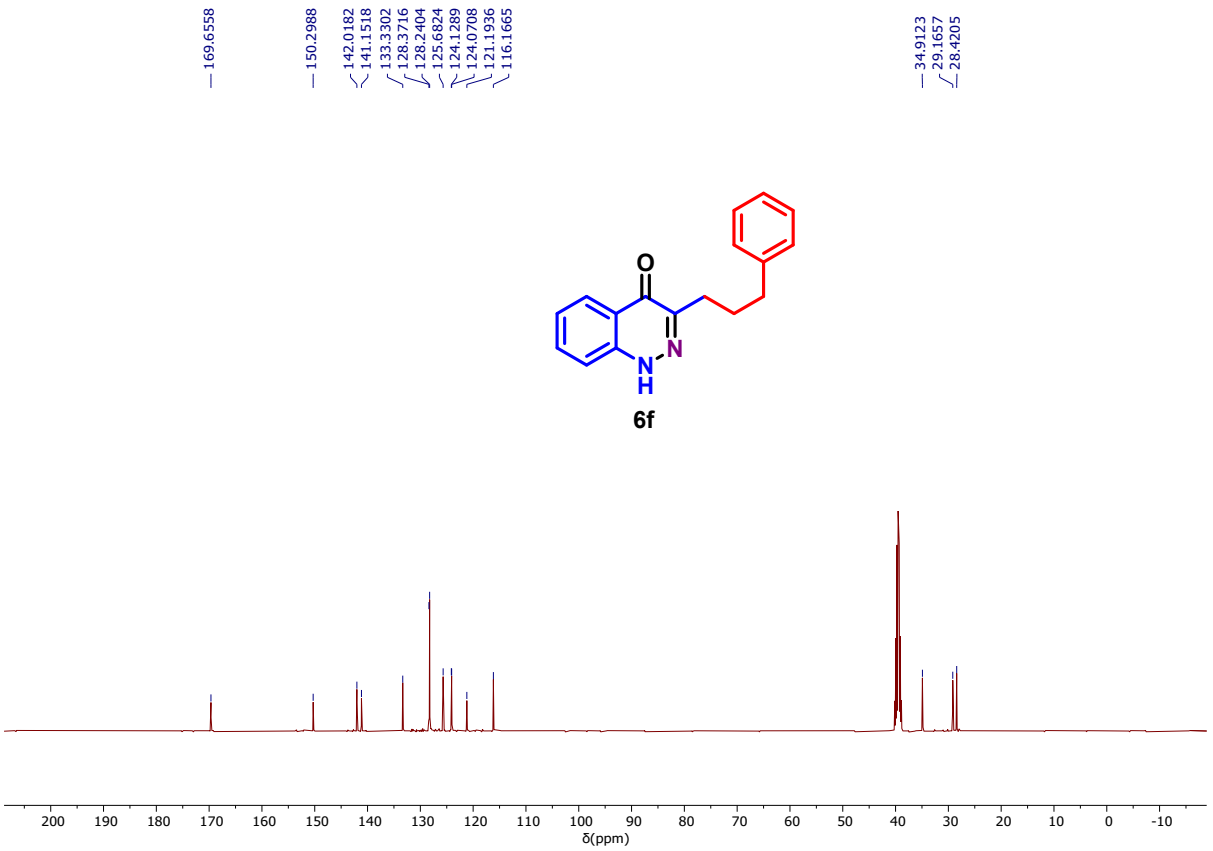
^{1}H and ^{13}C{^{1}H} NMR (DMSO-d_6, 400 and 101 MHz) of compound 6e:



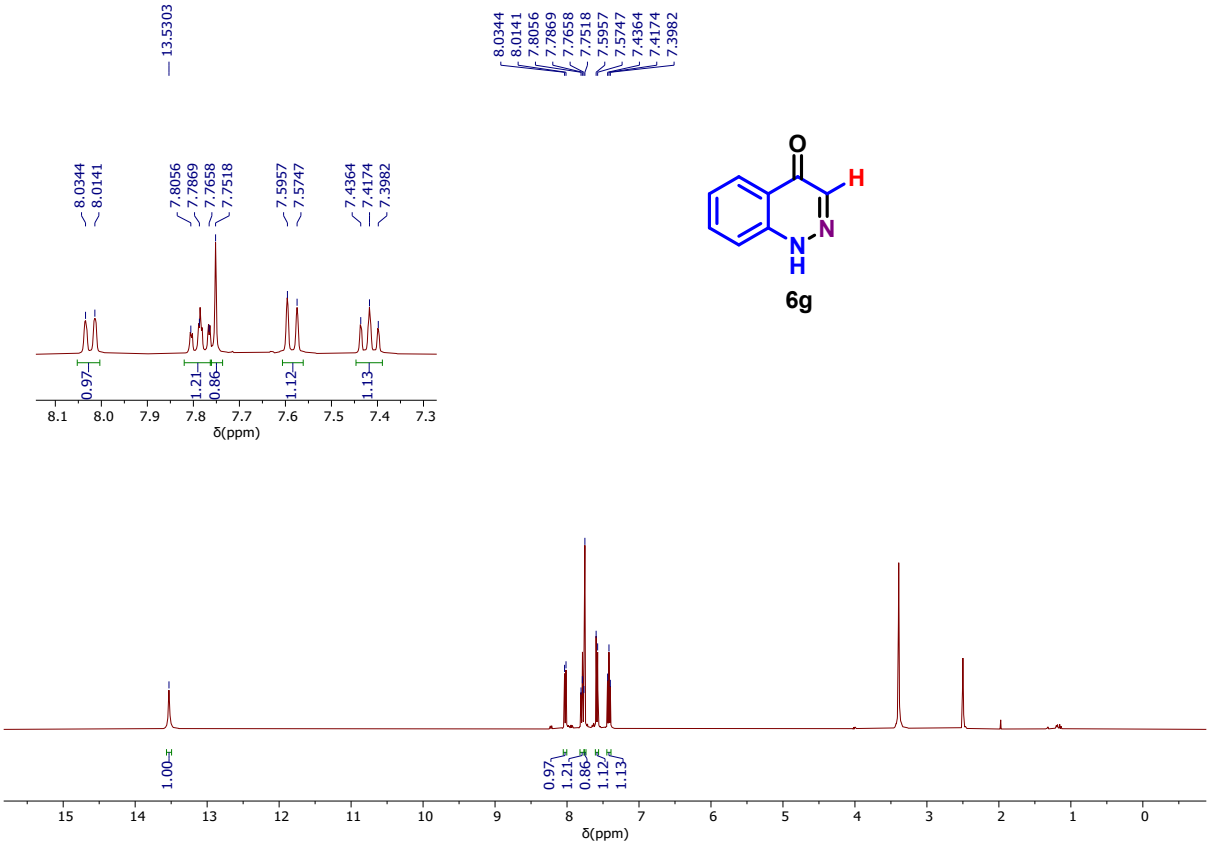
^{1}H and ^{13}C{^{1}H} NMR (DMSO-d_6, 400 and 101 MHz) of compound 6f:

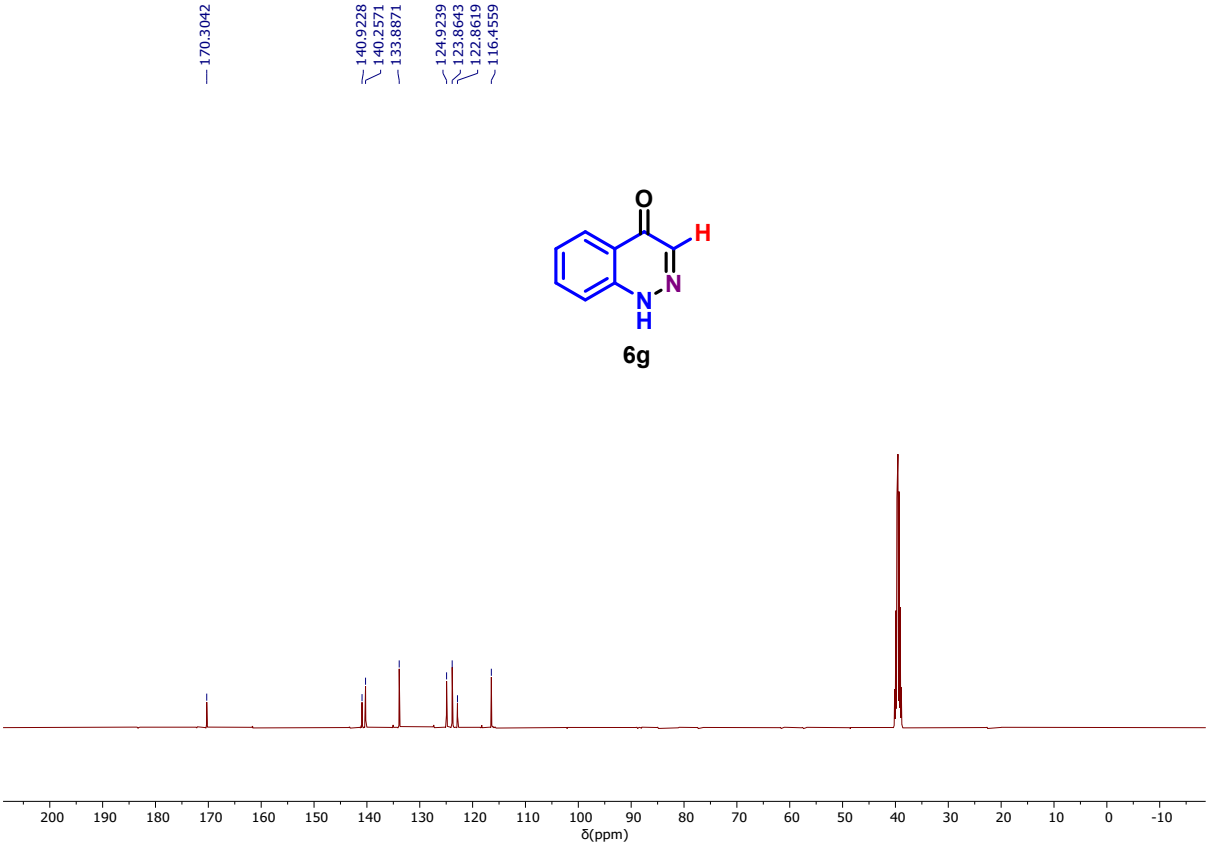




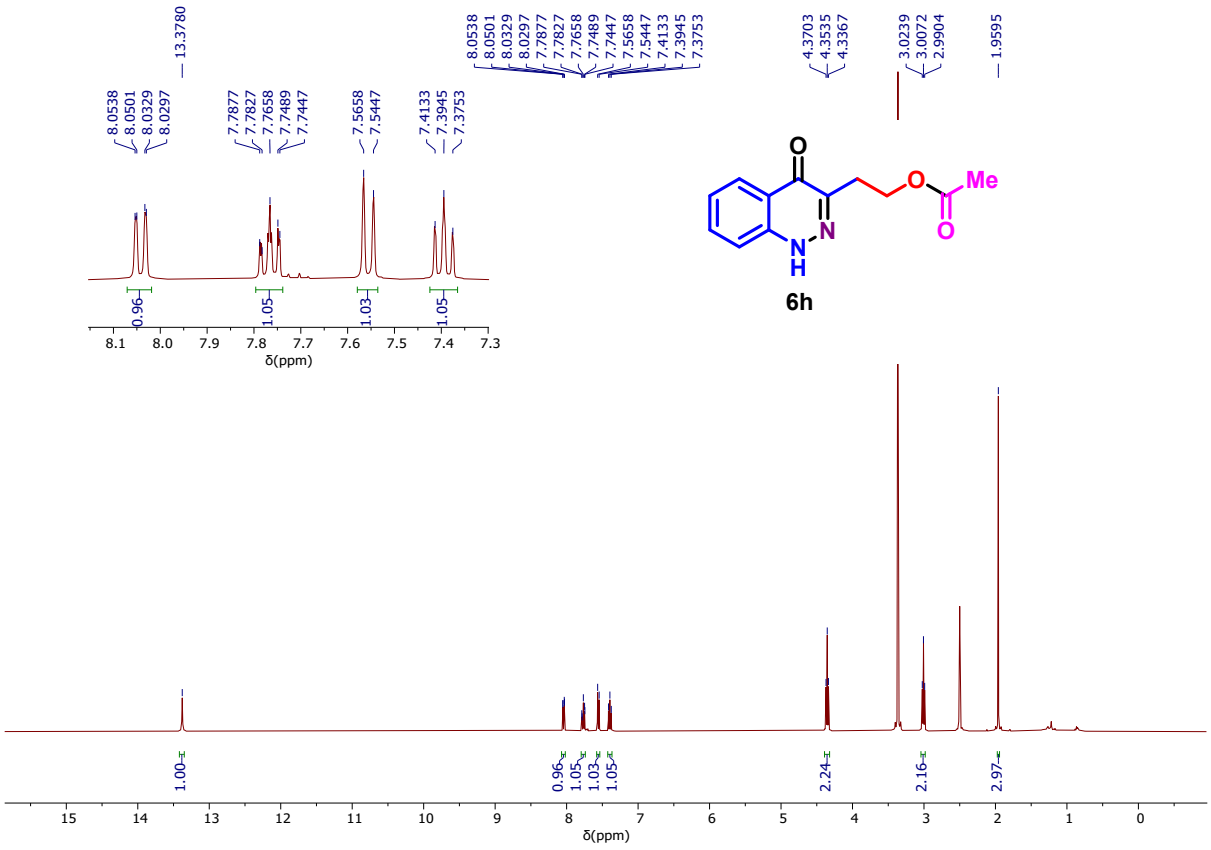


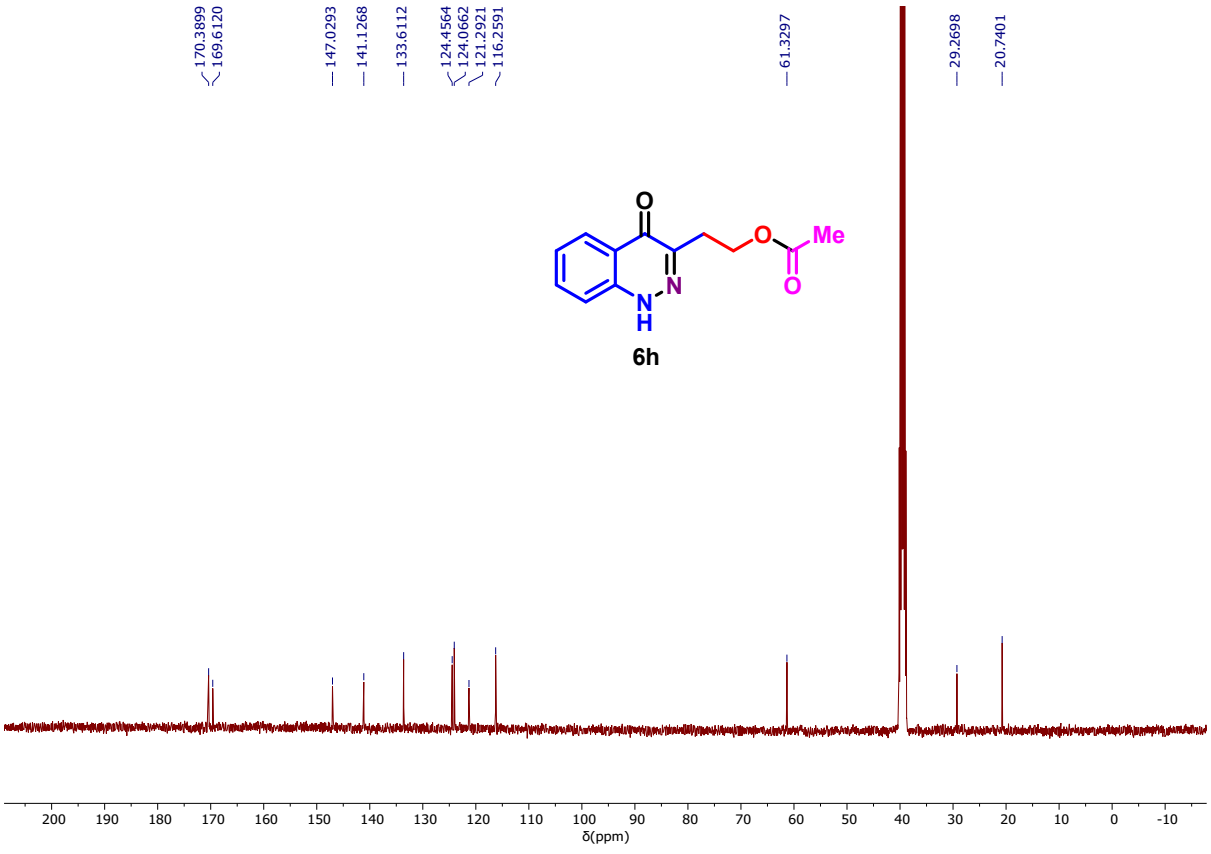
^{1}H and $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 400 and 101 MHz) of compound 6g:



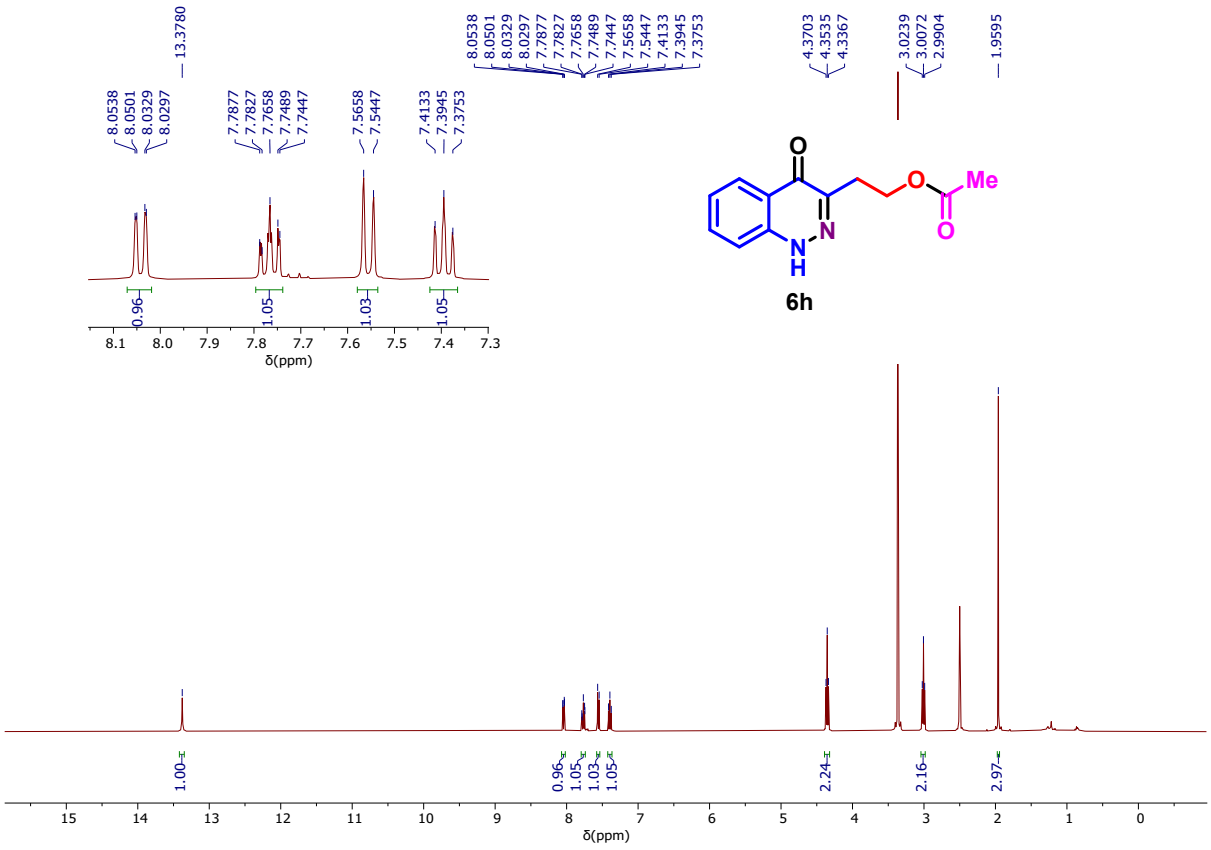


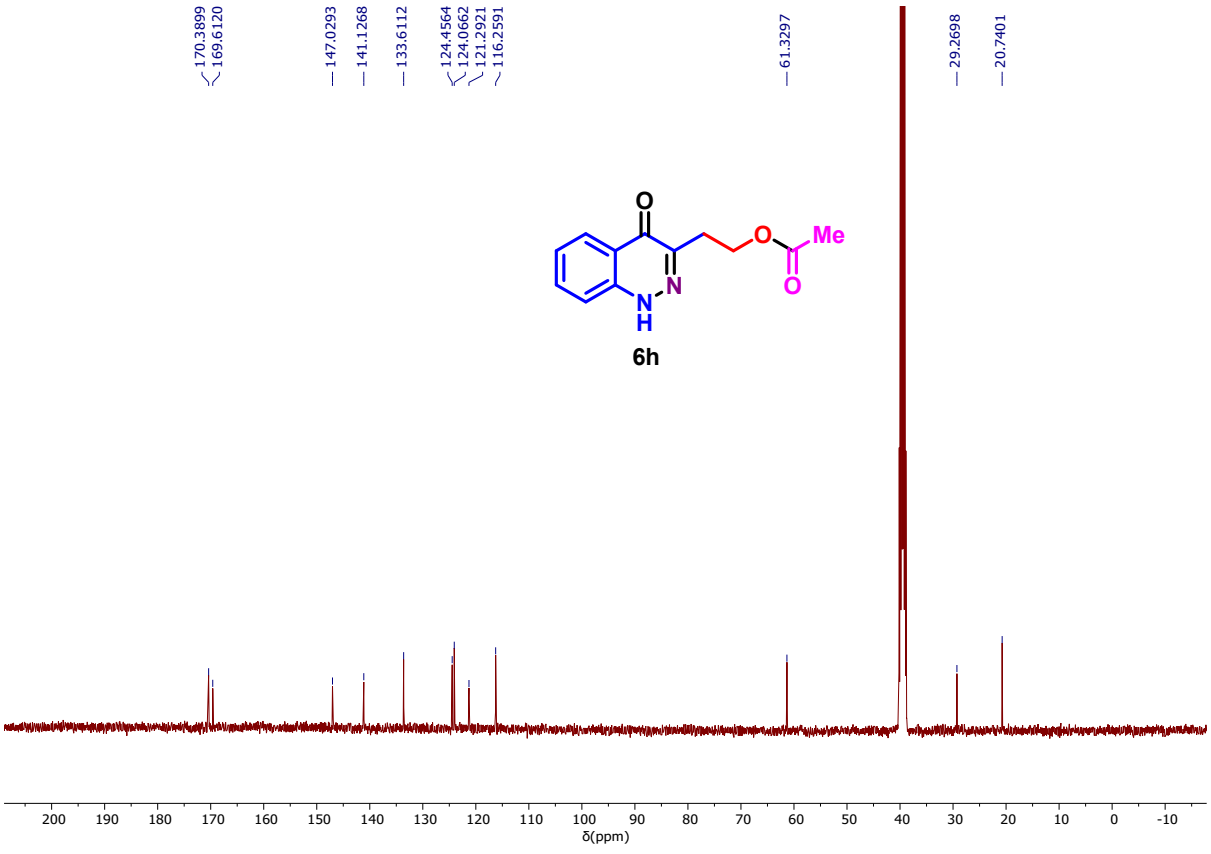
^{1}H and ^{13}C{^{1}H} NMR (DMSO-d_6, 400 and 101 MHz) of compound 6h:



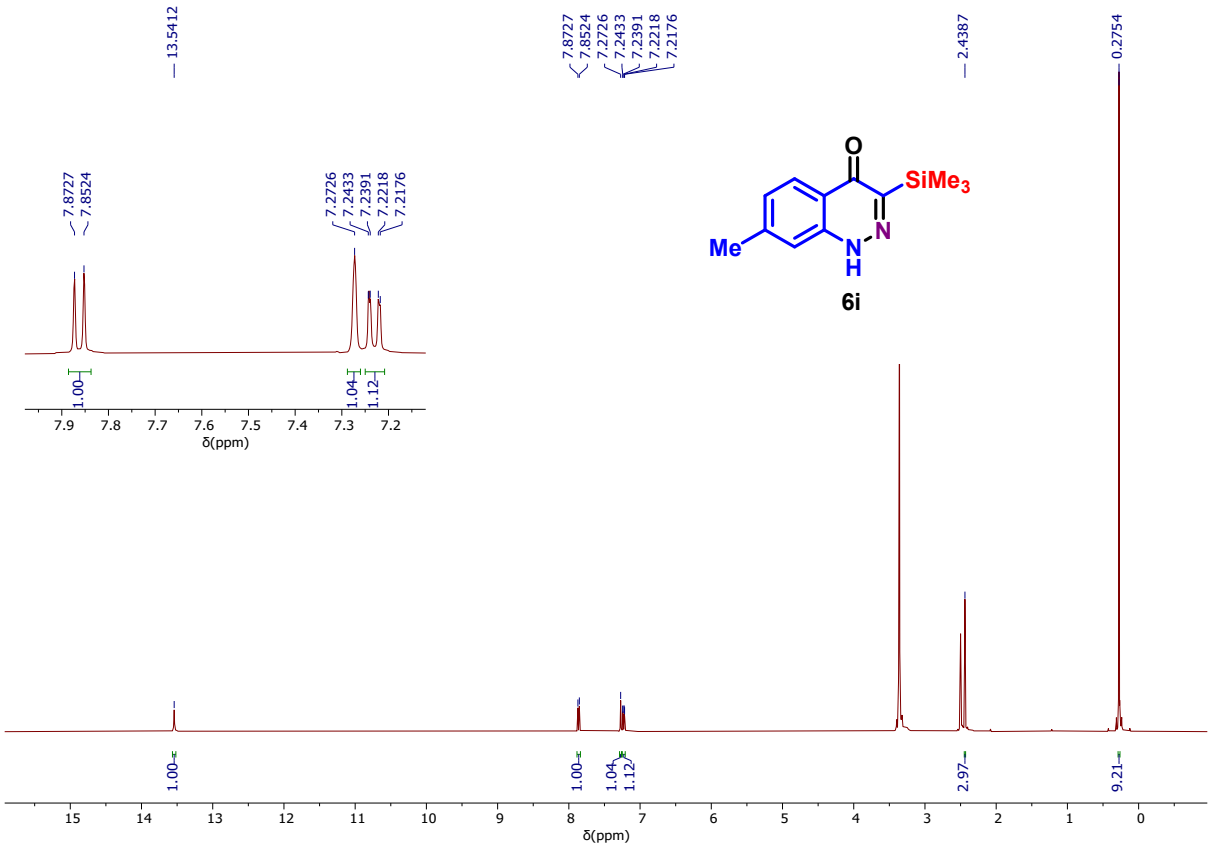


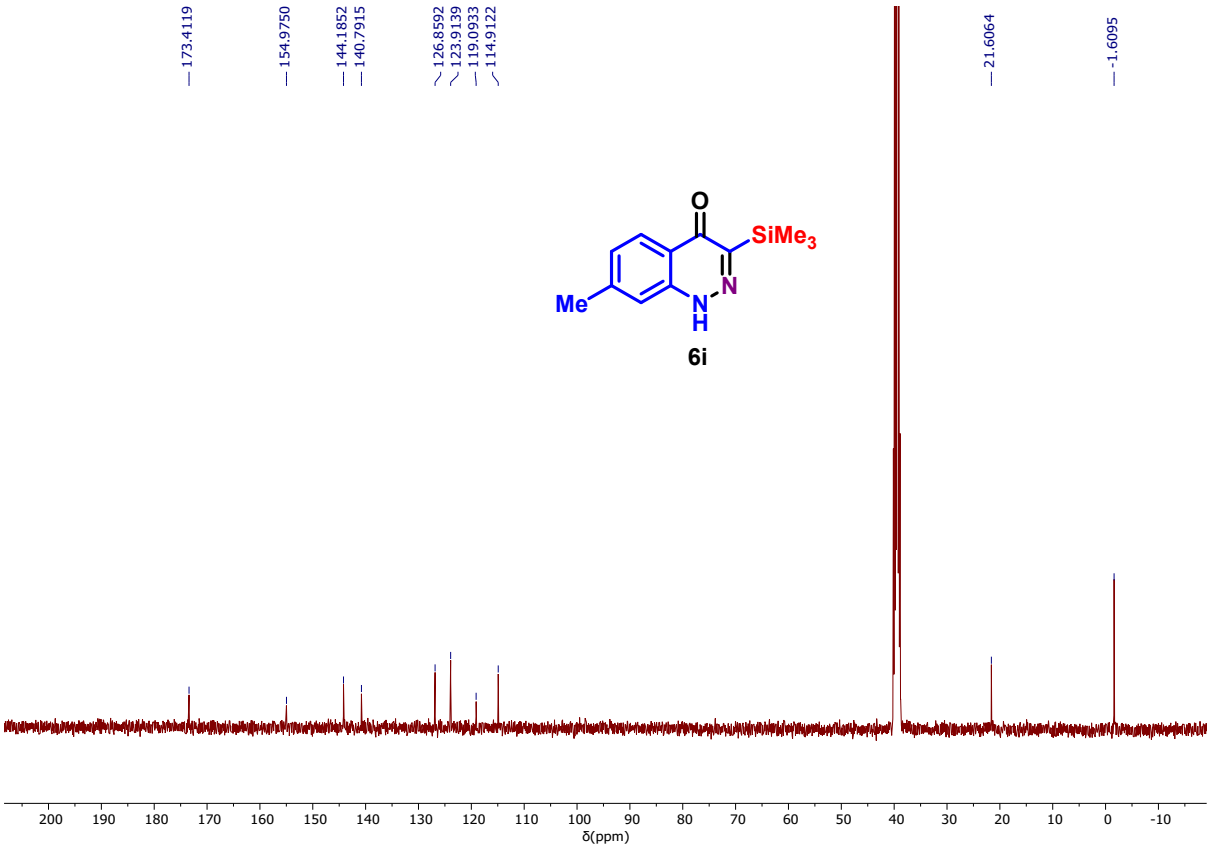
^{1}H and ^{13}C{^{1}H} NMR (DMSO-d_6, 400 and 101 MHz) of compound 6h:



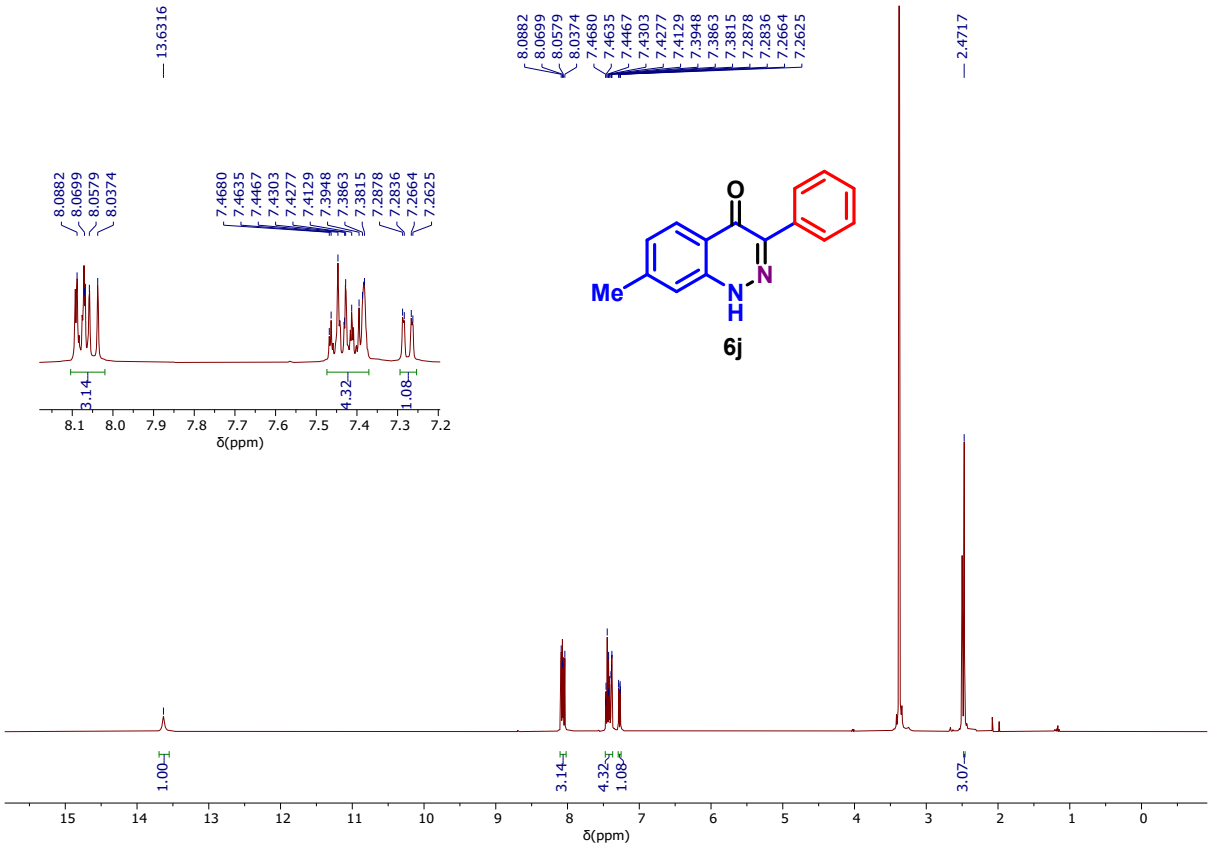


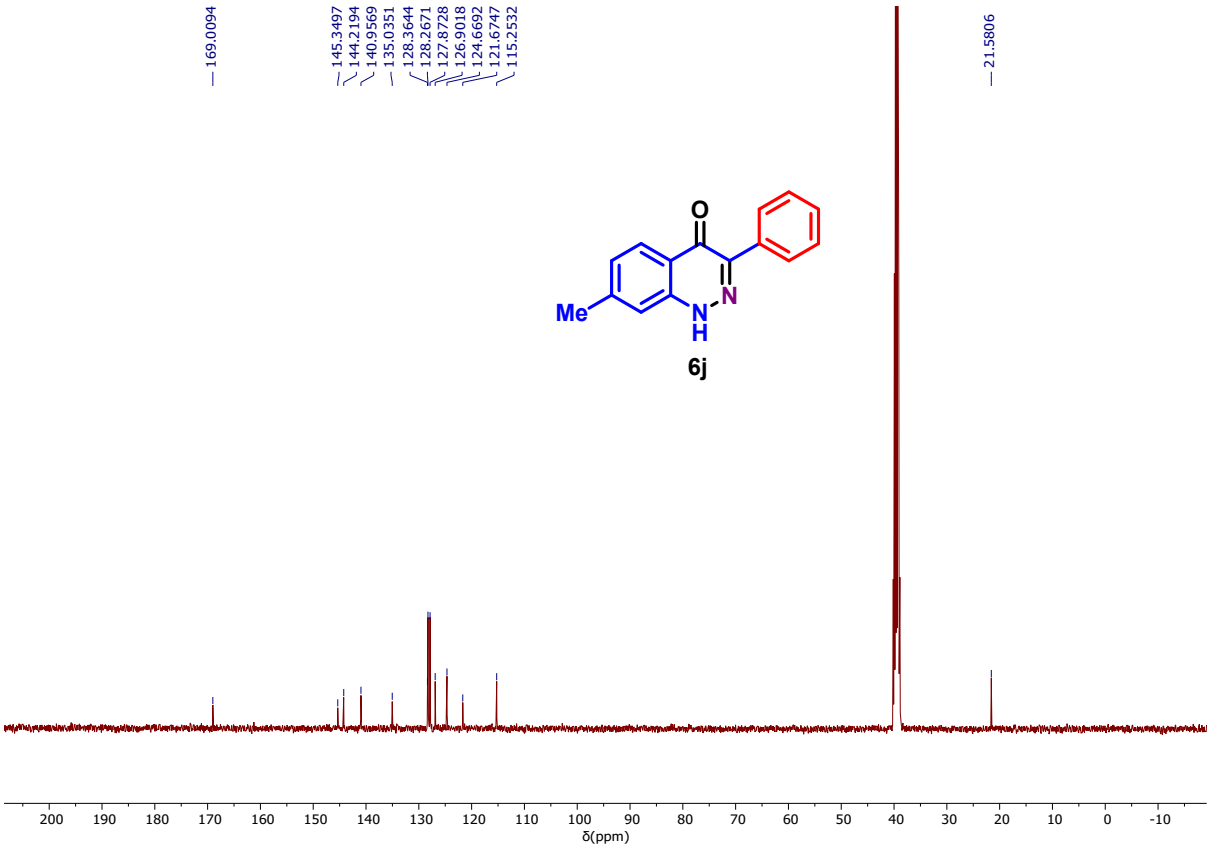
^{1}H and $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 400 and 101 MHz) of compound 6i:



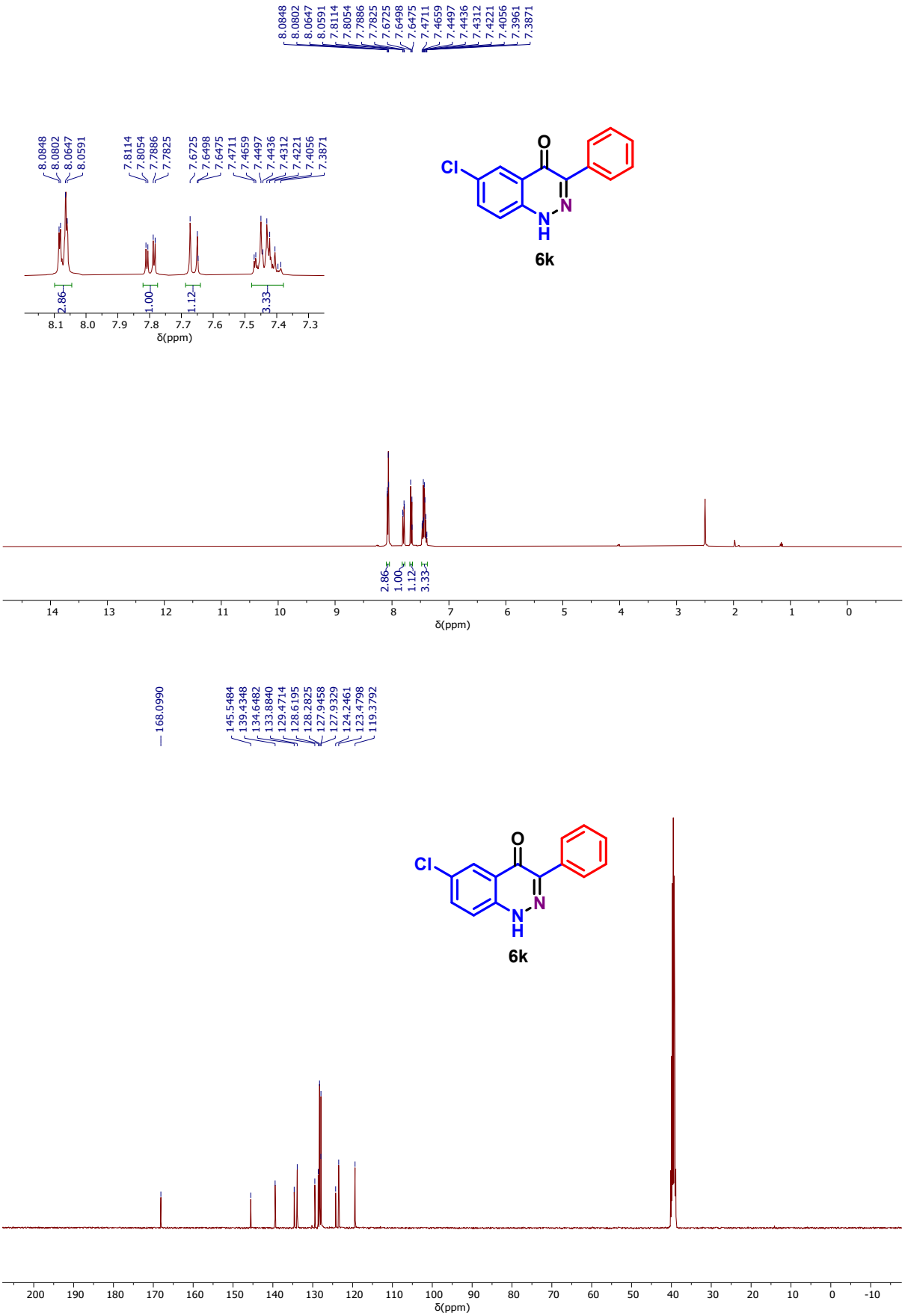


^{1}H and ^{13}C{^{1}H} NMR (DMSO-d_6, 400 and 101 MHz) of compound 6j:

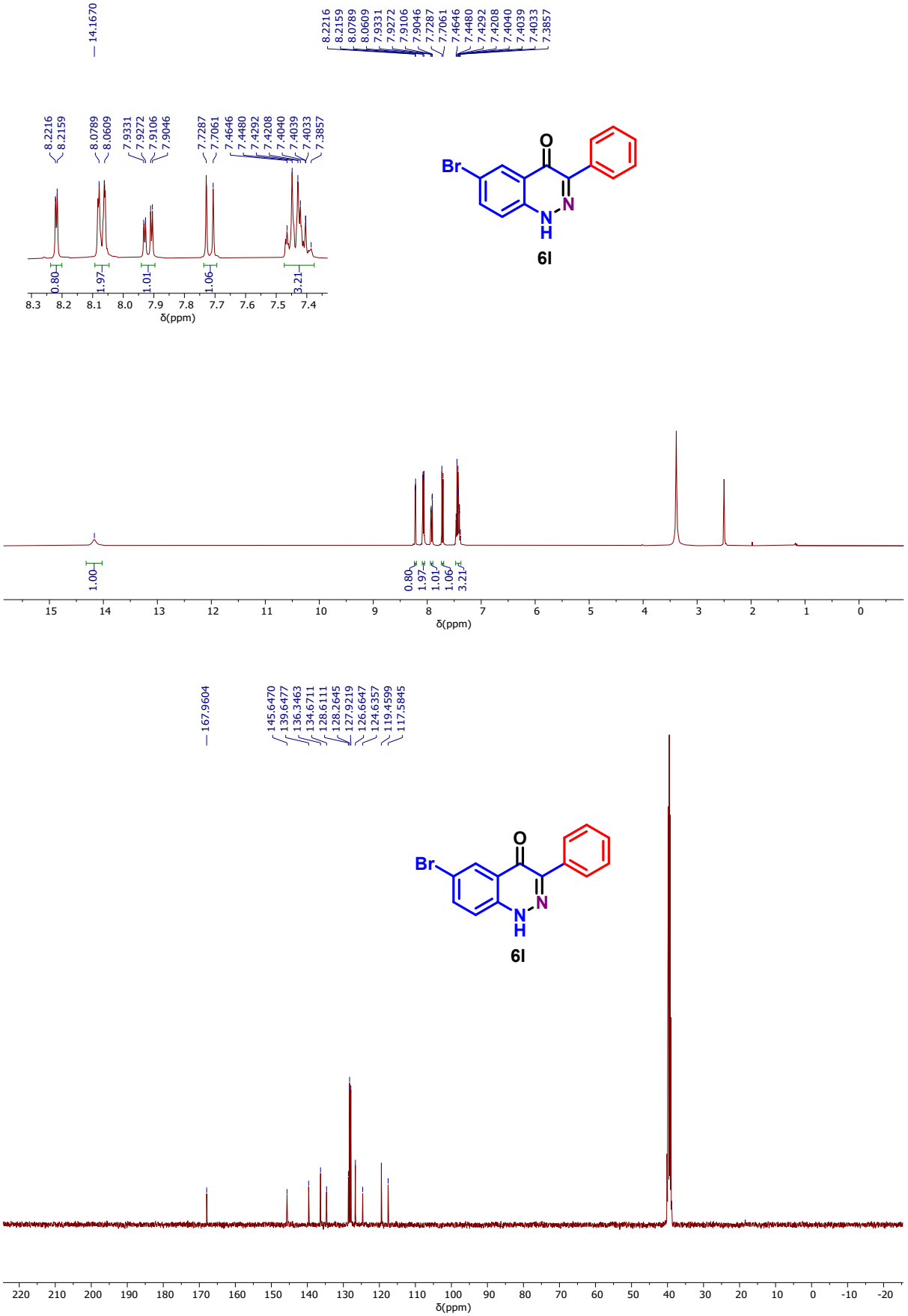




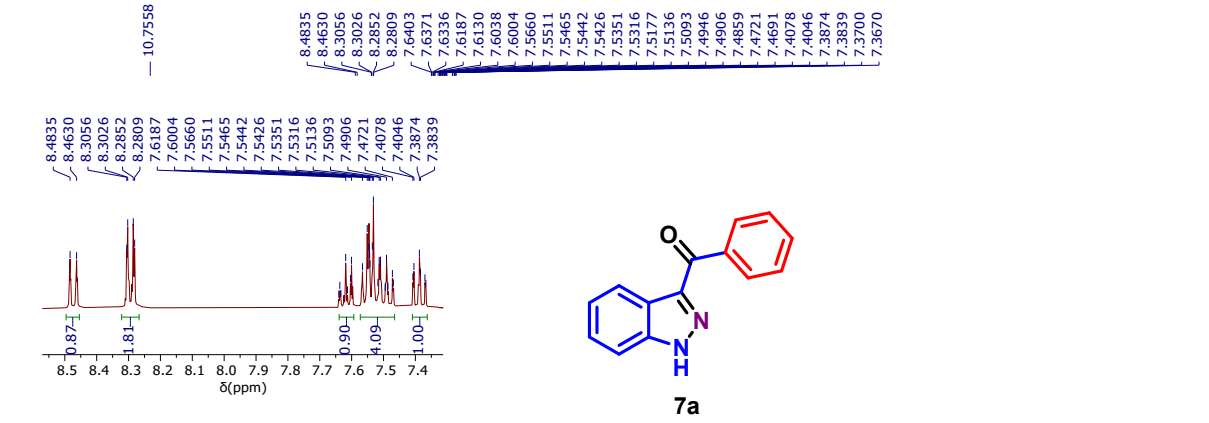
^{1}H and ^{13}C{^{1}H} NMR (DMSO-d_6, 400 and 101 MHz) of compound 6k:

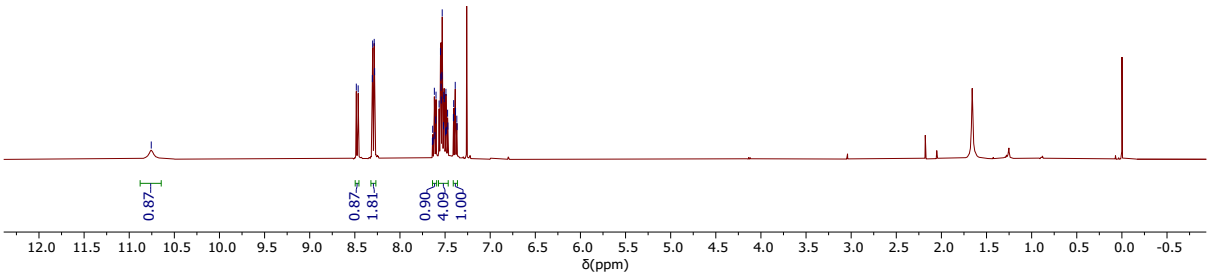


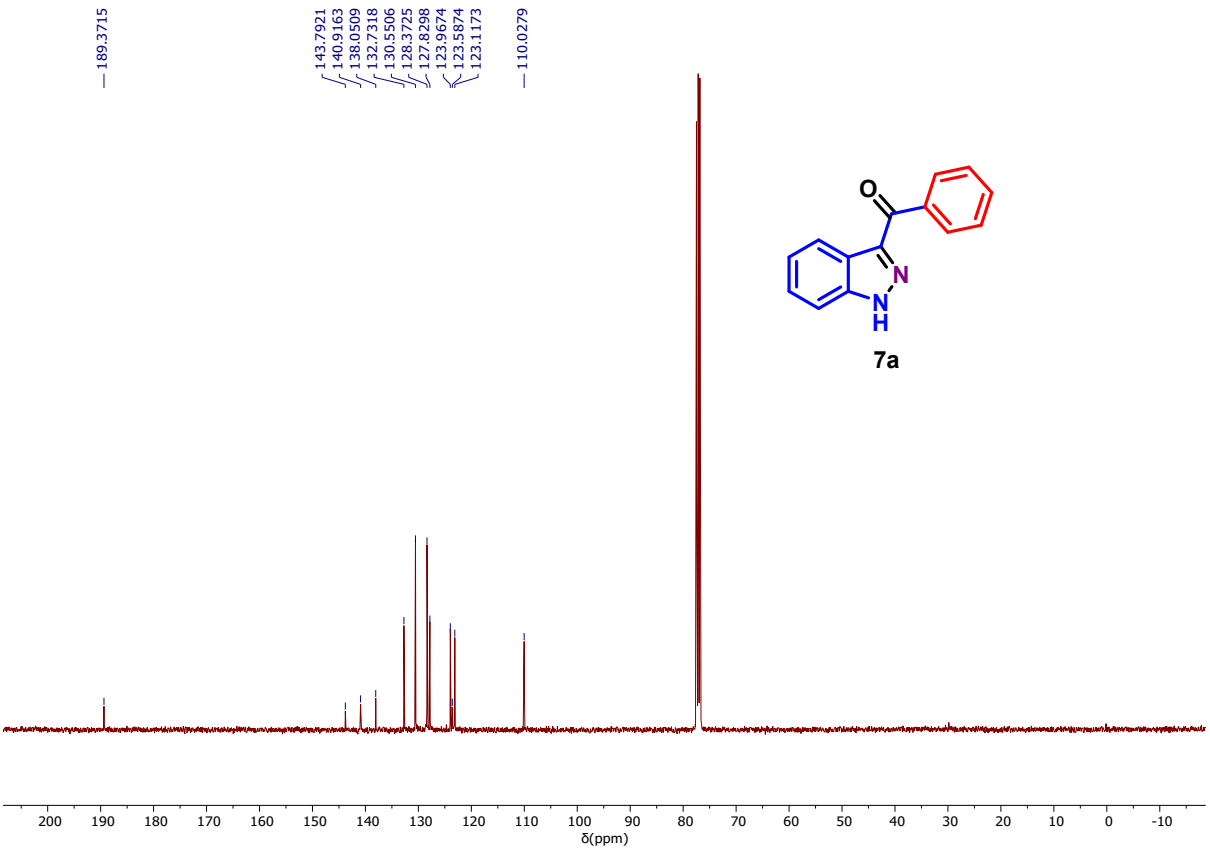
^{1}H and ^{13}C{^{1}H} NMR (DMSO-d_6, 400 and 101 MHz) of compound 6l:



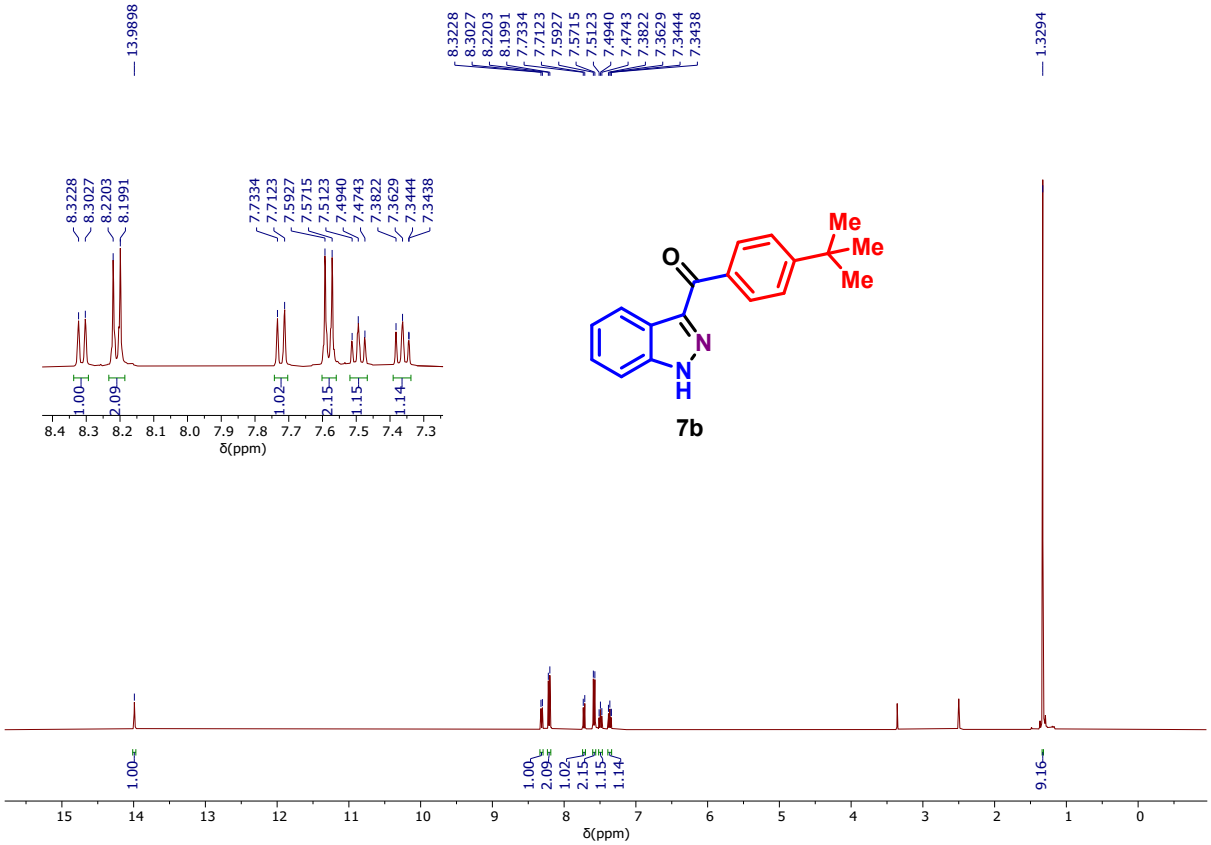
^{1}H and $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 400 and 101 MHz) of compound 7a:

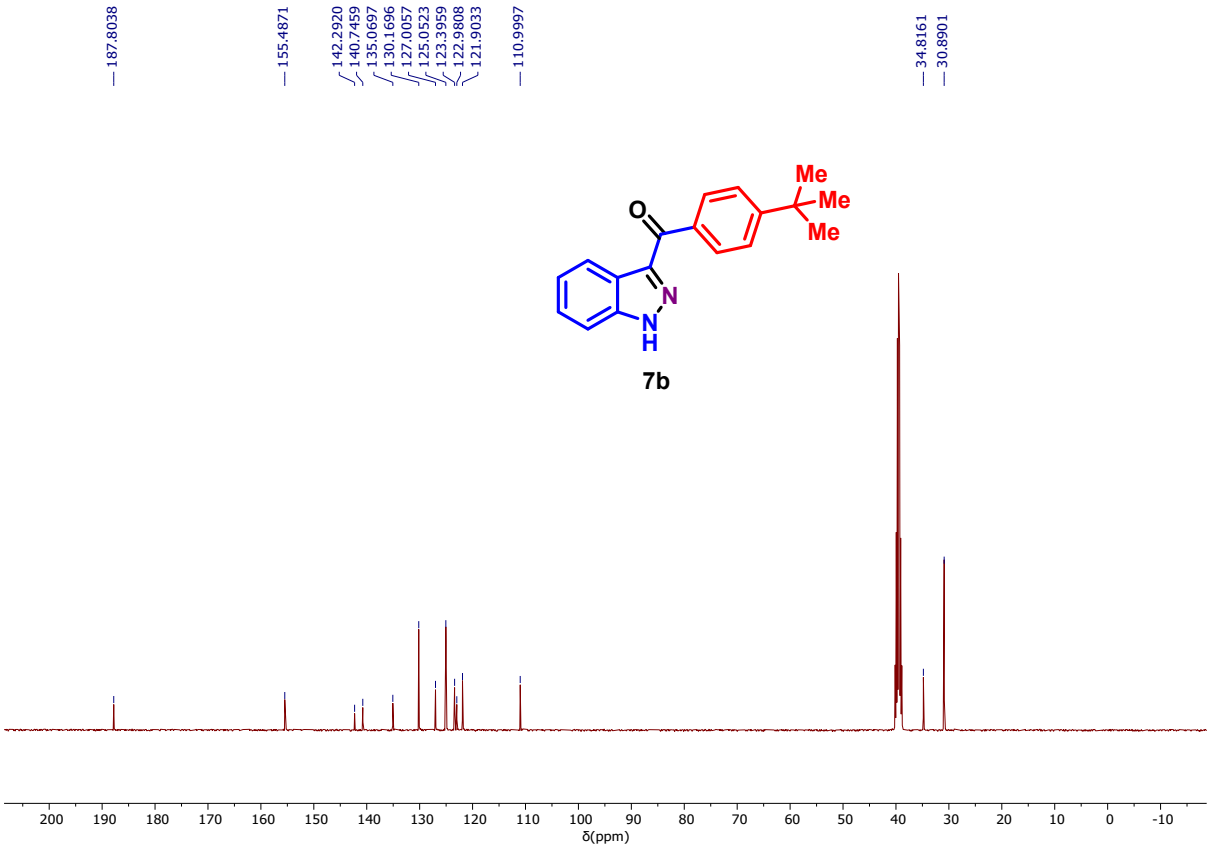




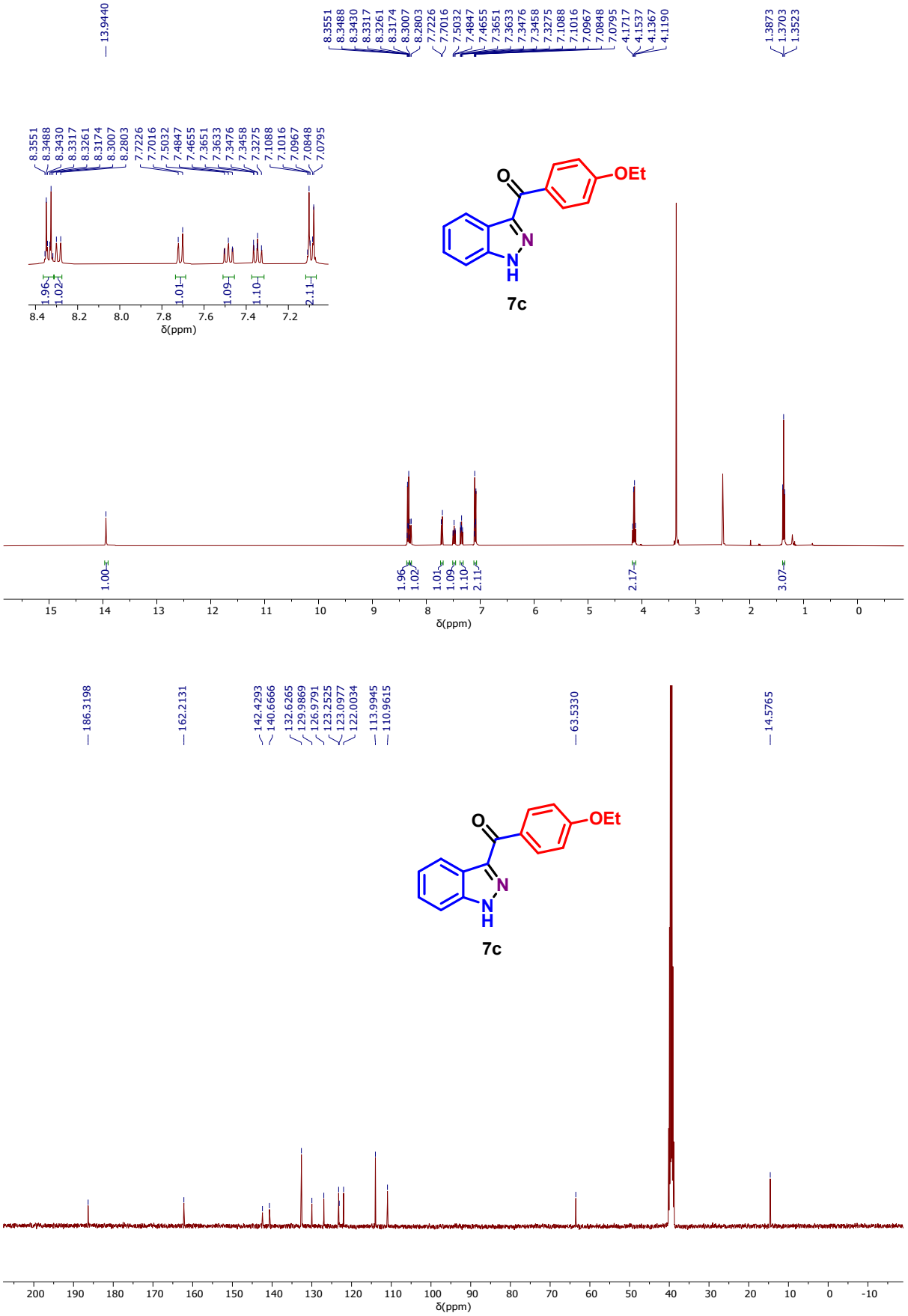


^{1}H and $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 400 and 101 MHz) of compound 7b:

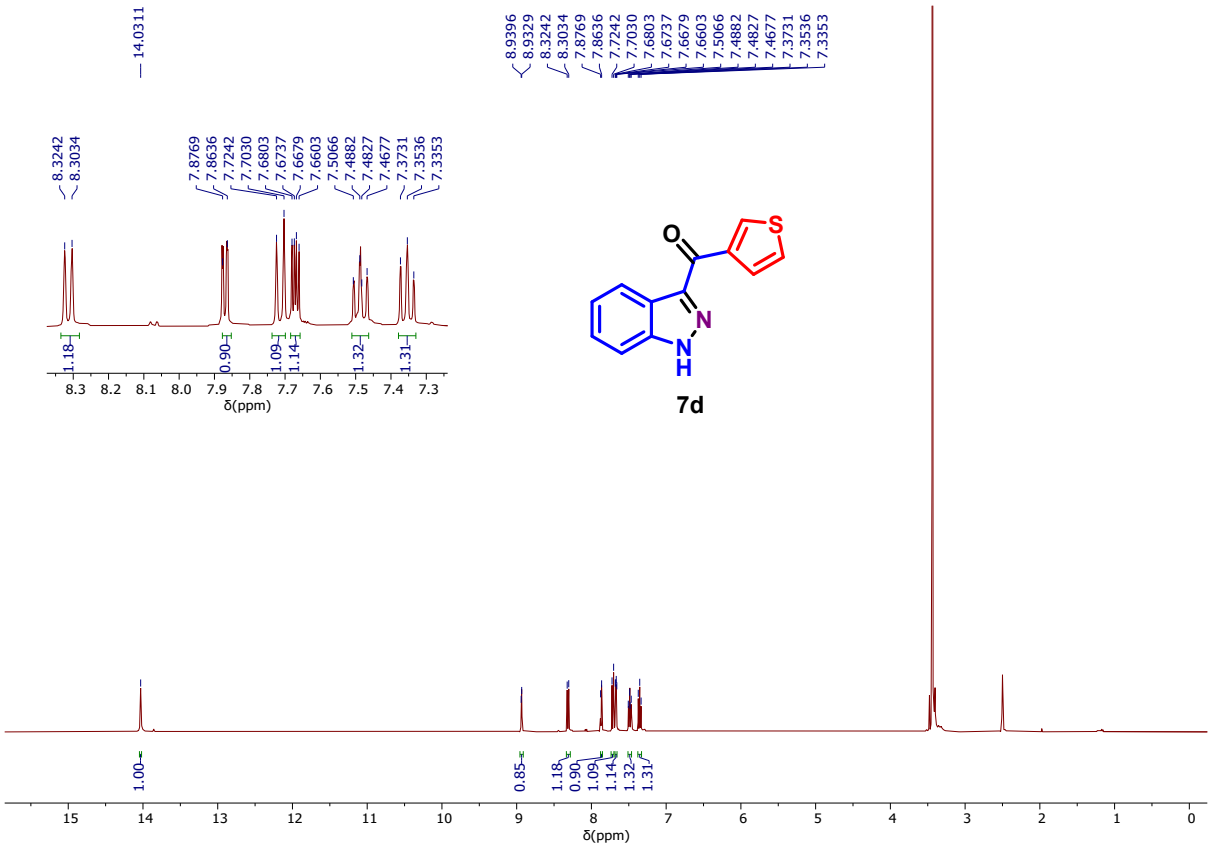


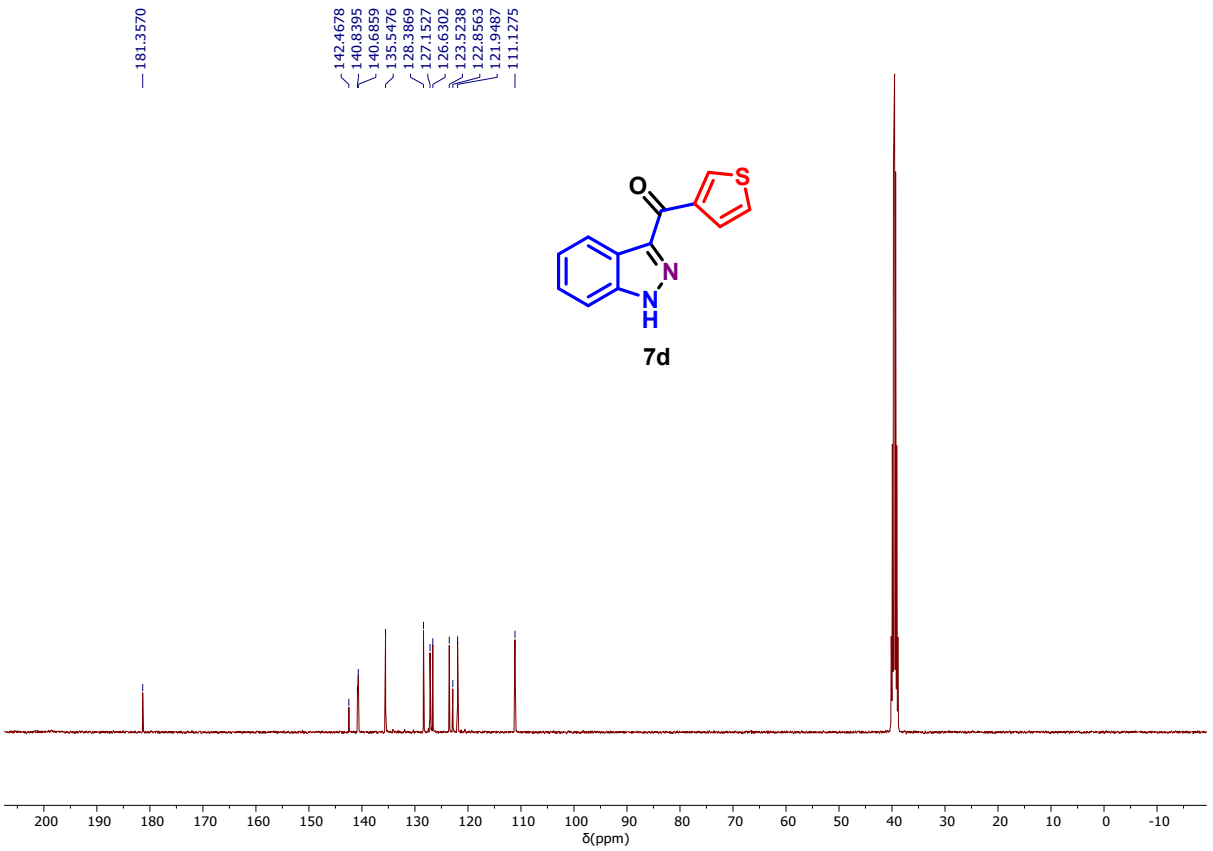


^{1}H and $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 400 and 101 MHz) of compound 7c:

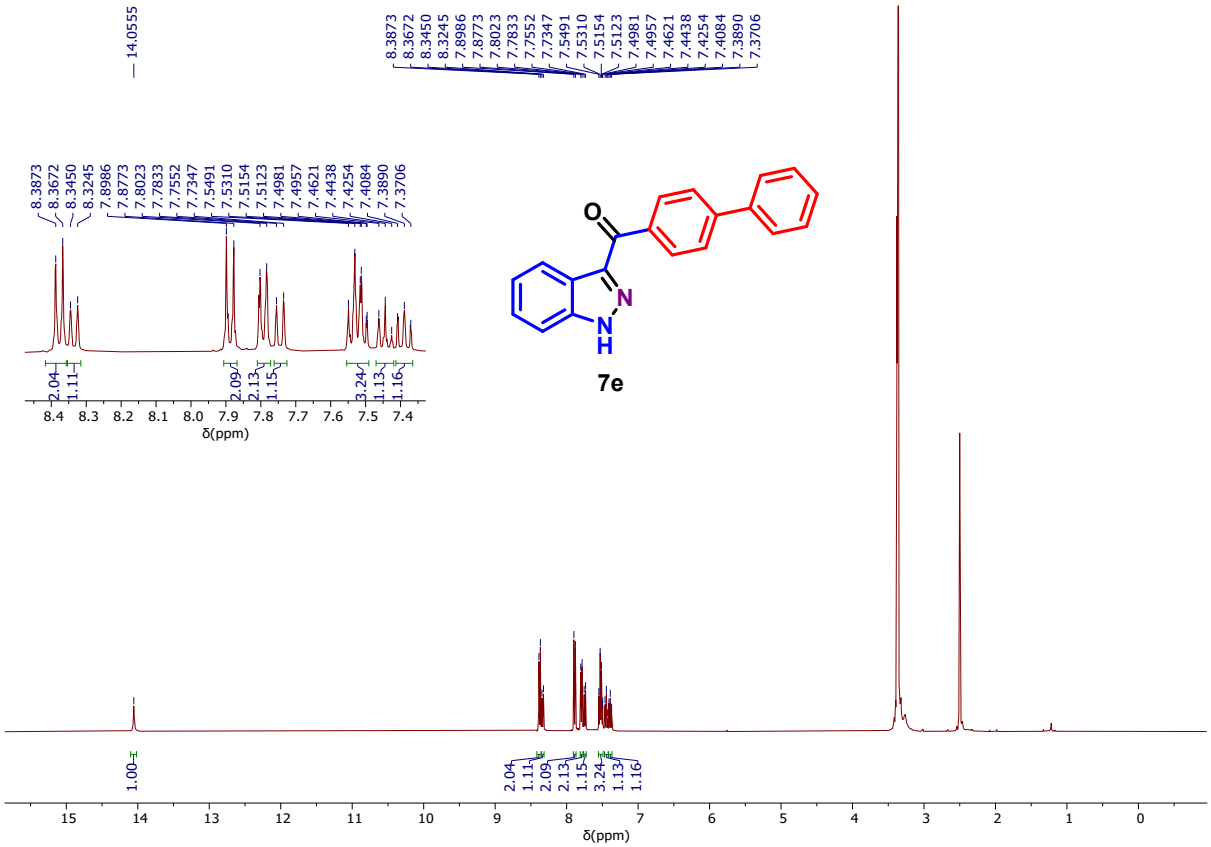


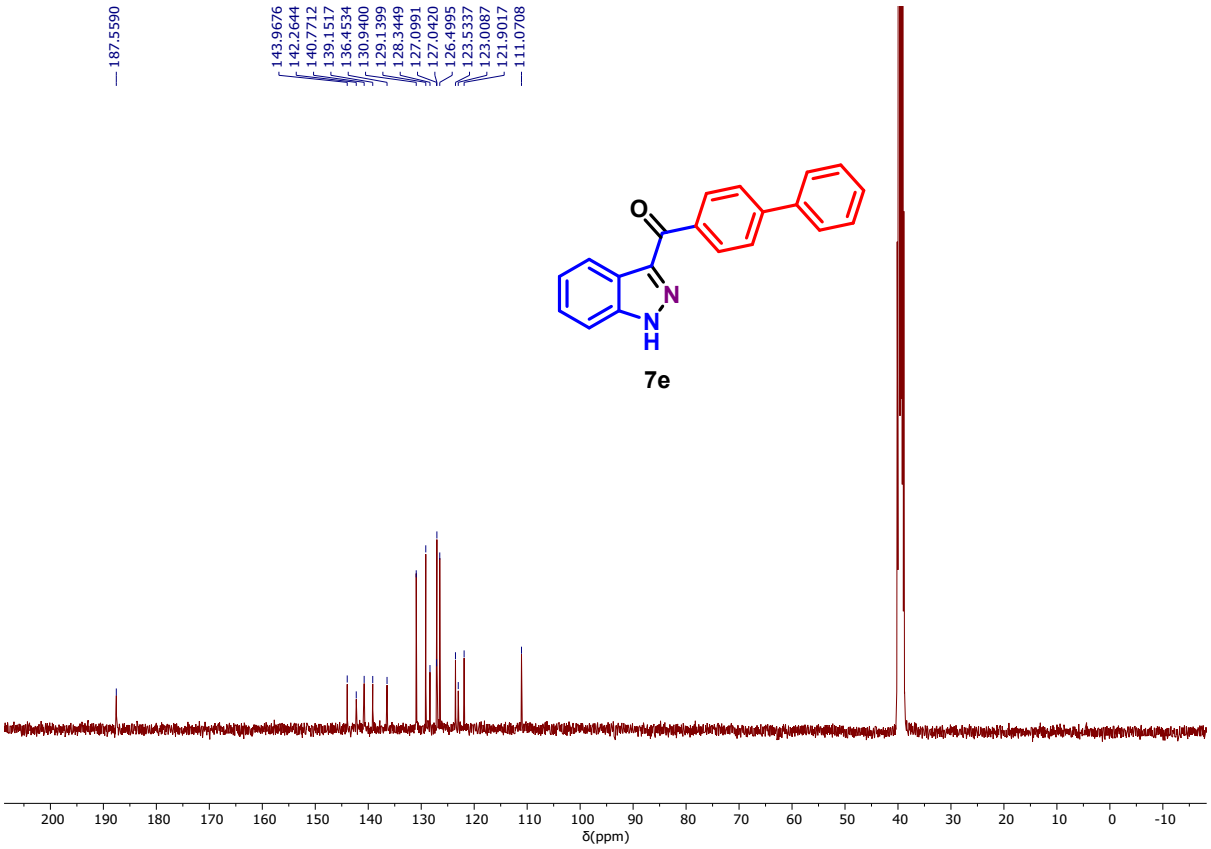
^{1}H and ^{13}C{^{1}H} NMR (DMSO-d_6, 400 and 101 MHz) of compound 7d:



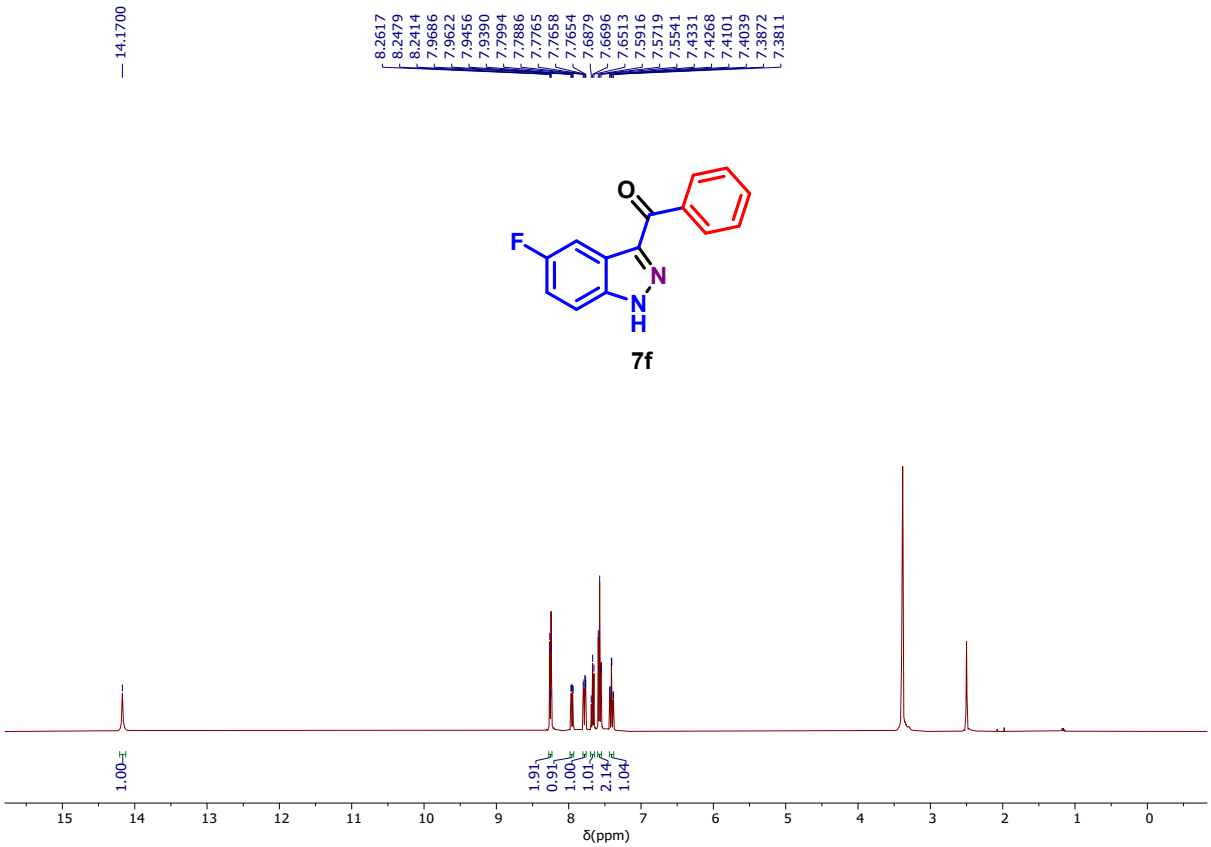


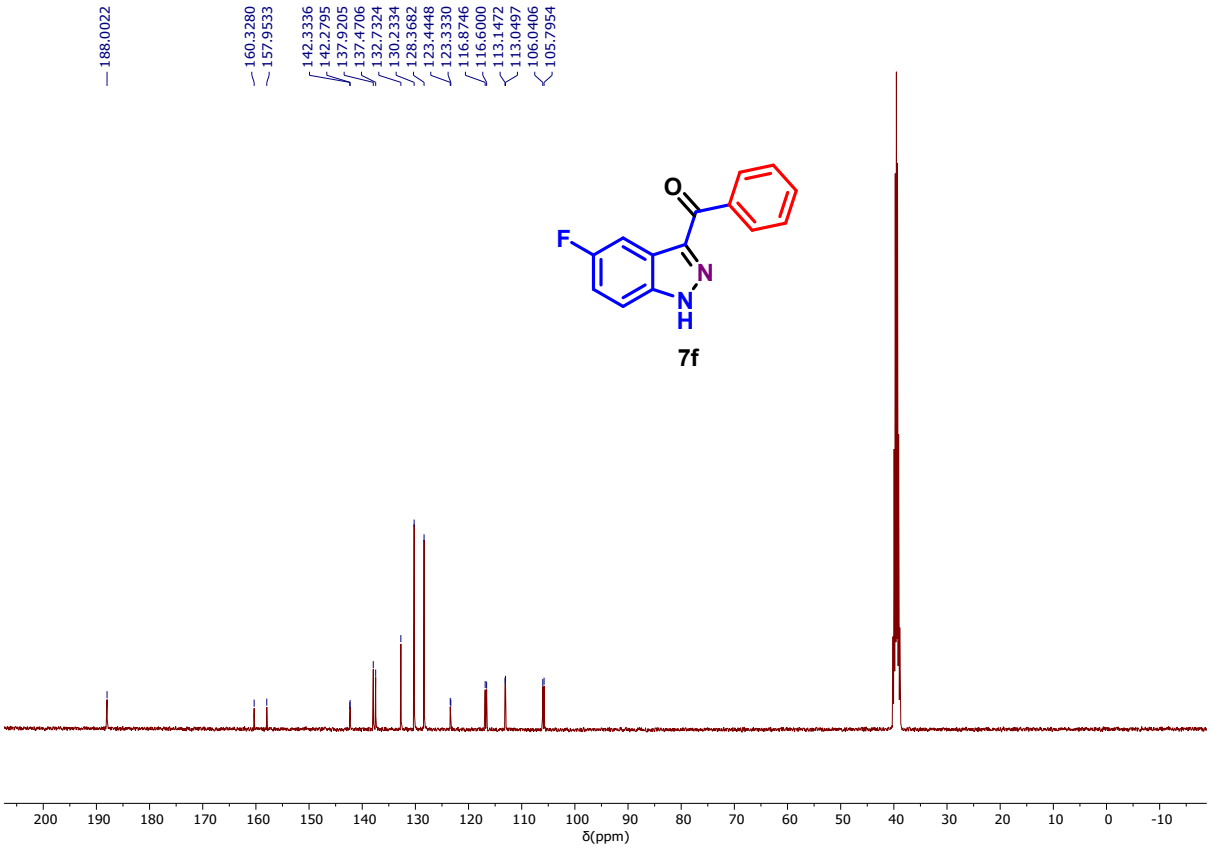
^{1}H and ^{13}C{^{1}H} NMR (DMSO-d_6, 400 and 101 MHz) of compound 7e:

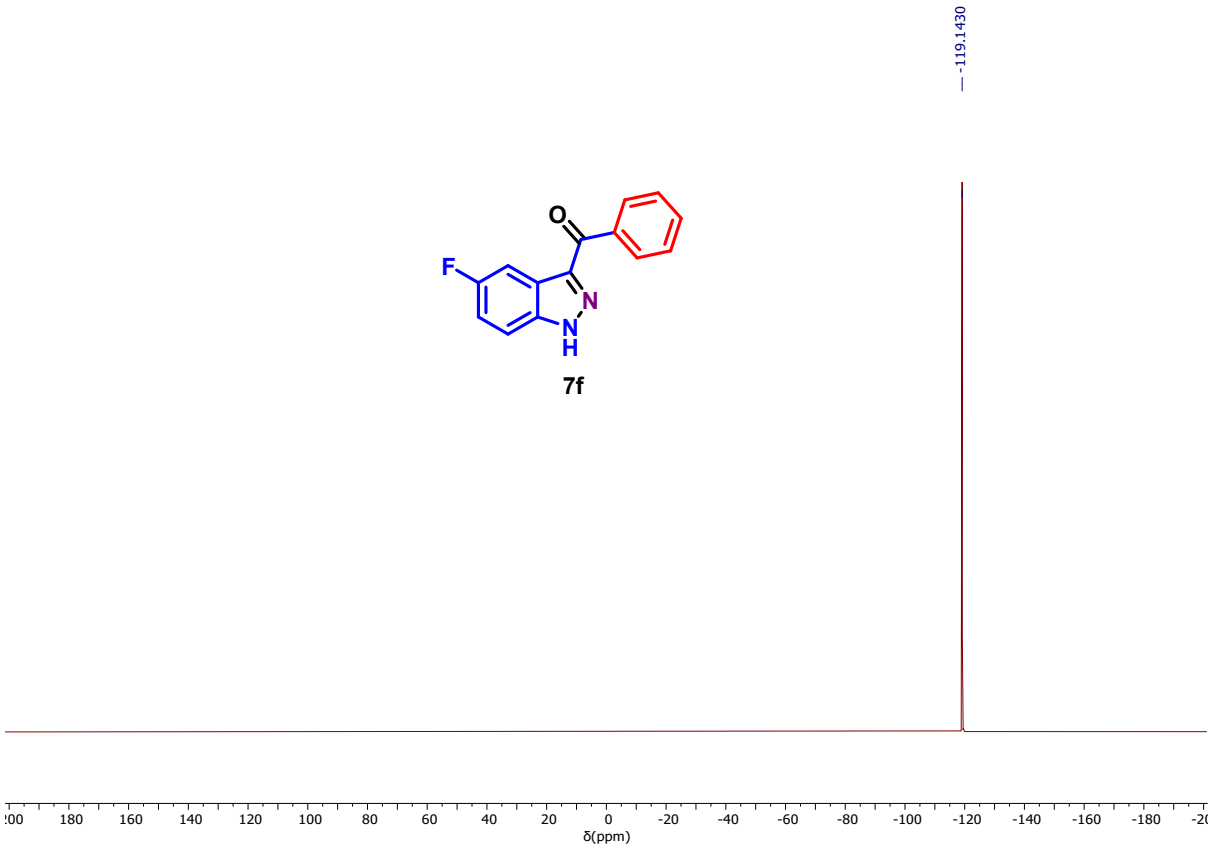




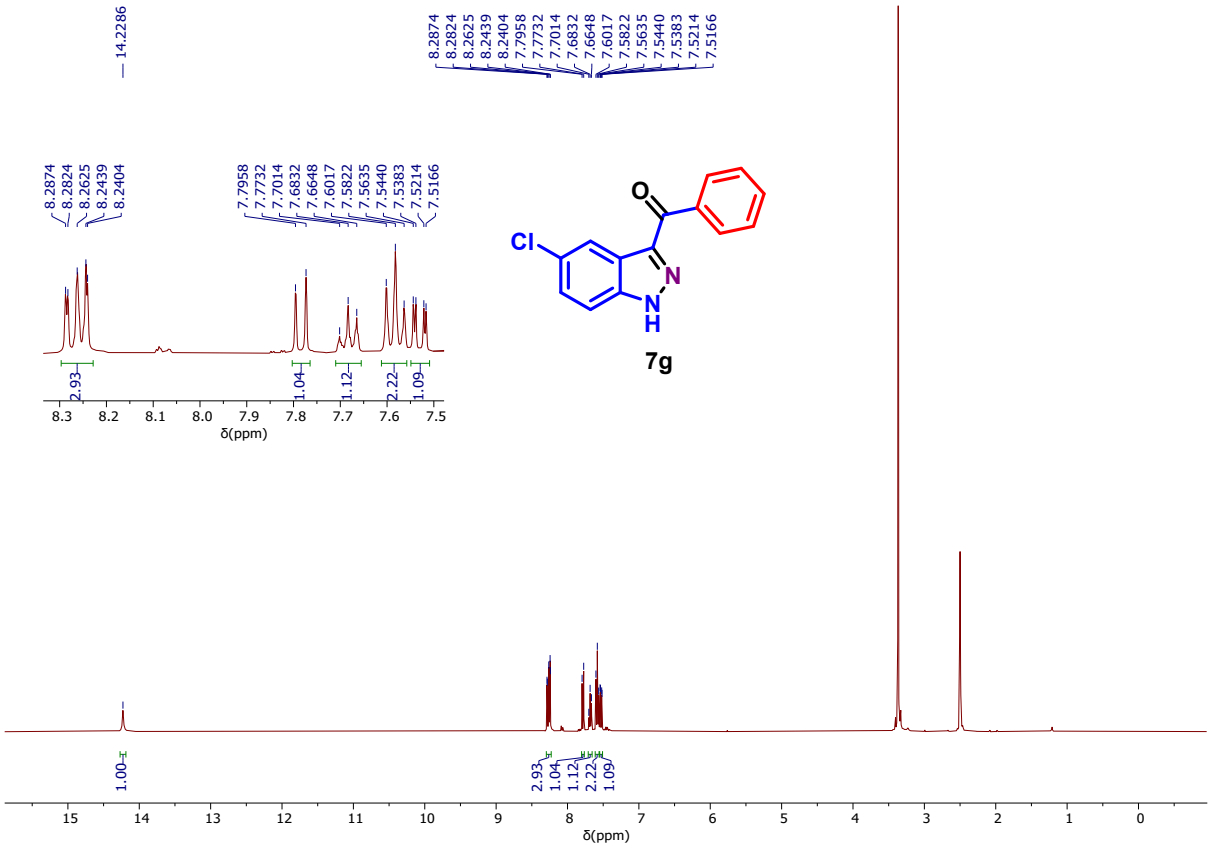
^{1}H, ^{13}C{^{1}H} and ^{19}F NMR (DMSO-d_6, 400, 101 and 376 MHz) of compound 7f:

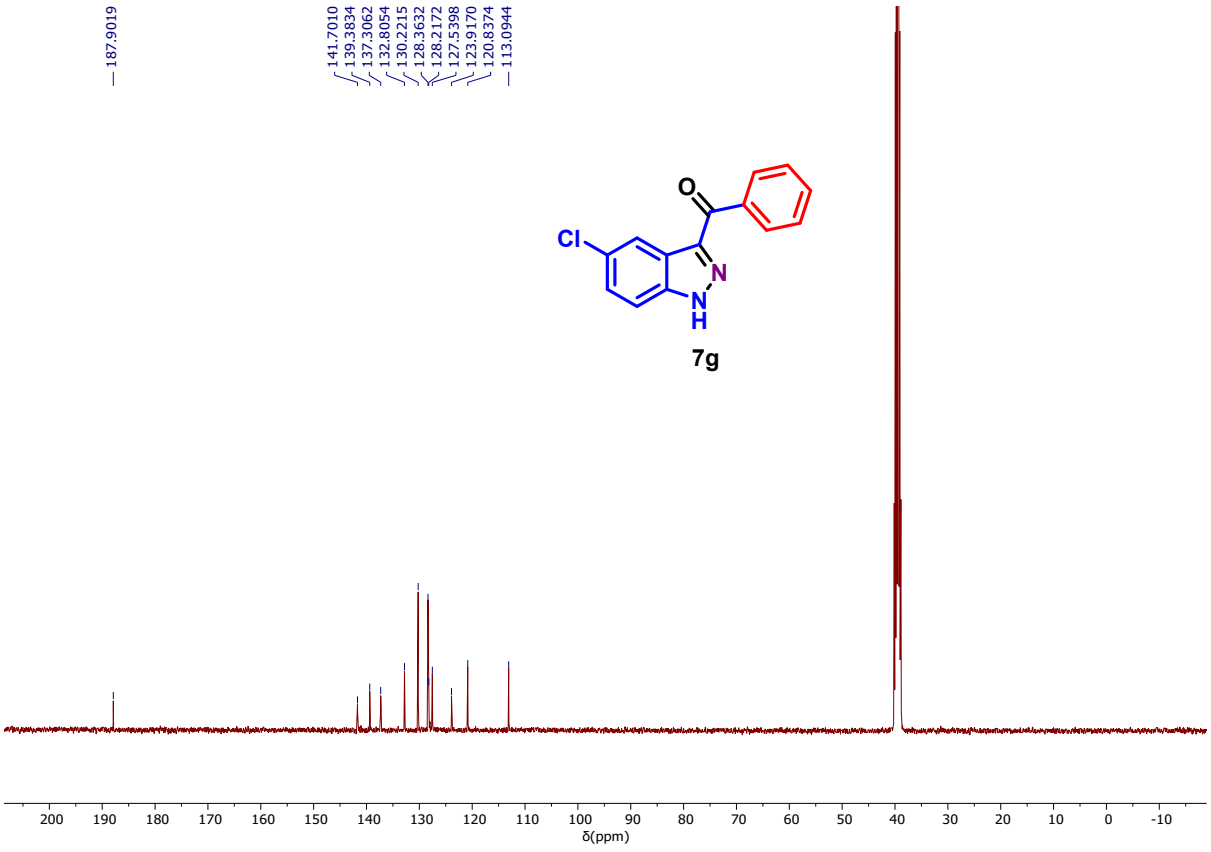




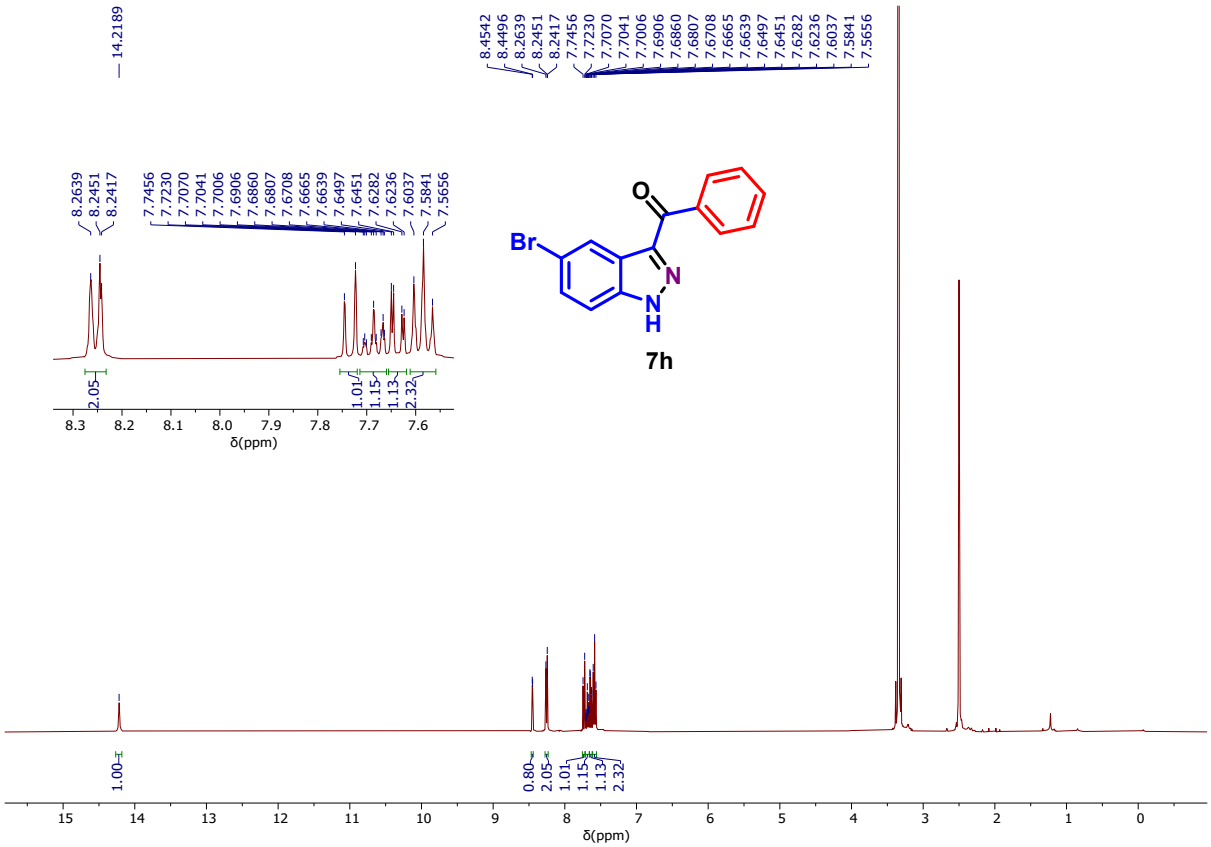

-119.1430
O
F
N
N
H
7f
δ(ppm)

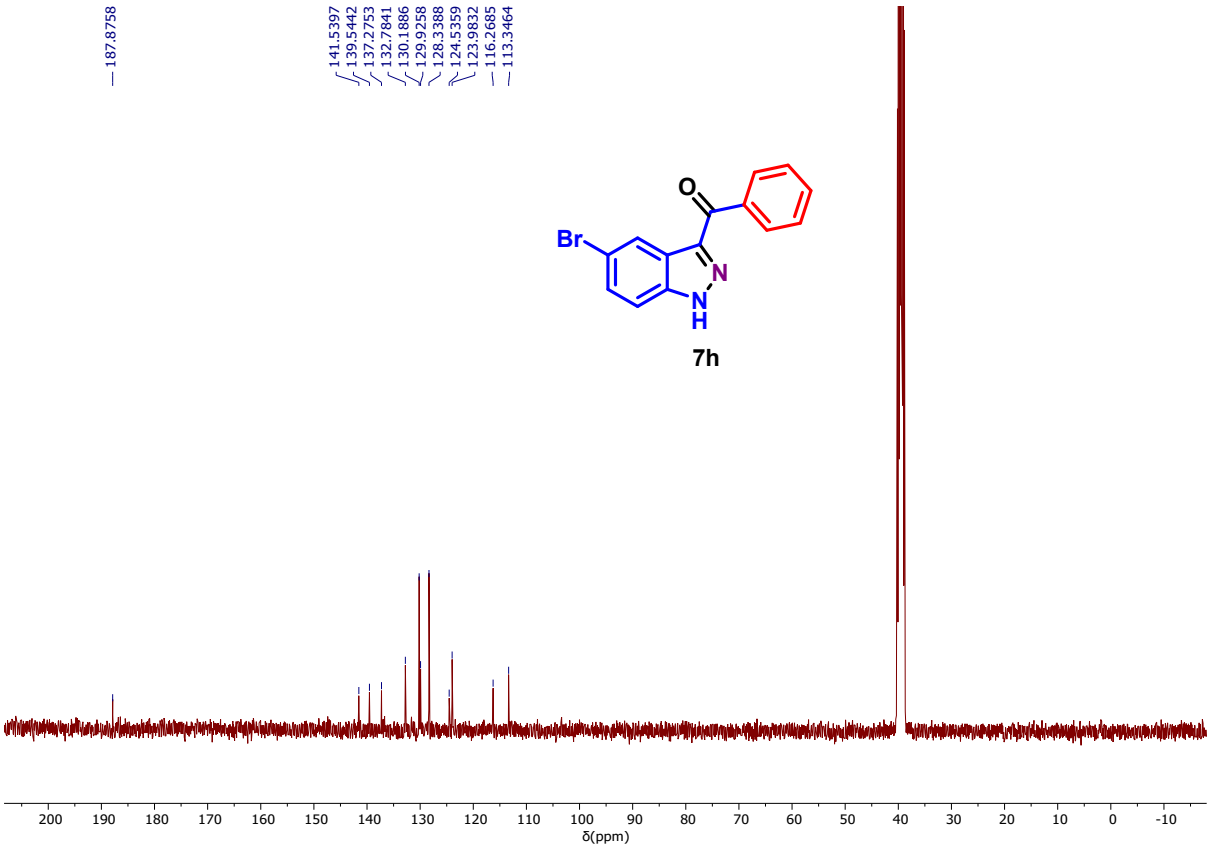
^{1}H and ^{13}C{^{1}H} NMR (DMSO-d_6, 400 and 101 MHz) of compound 7g:



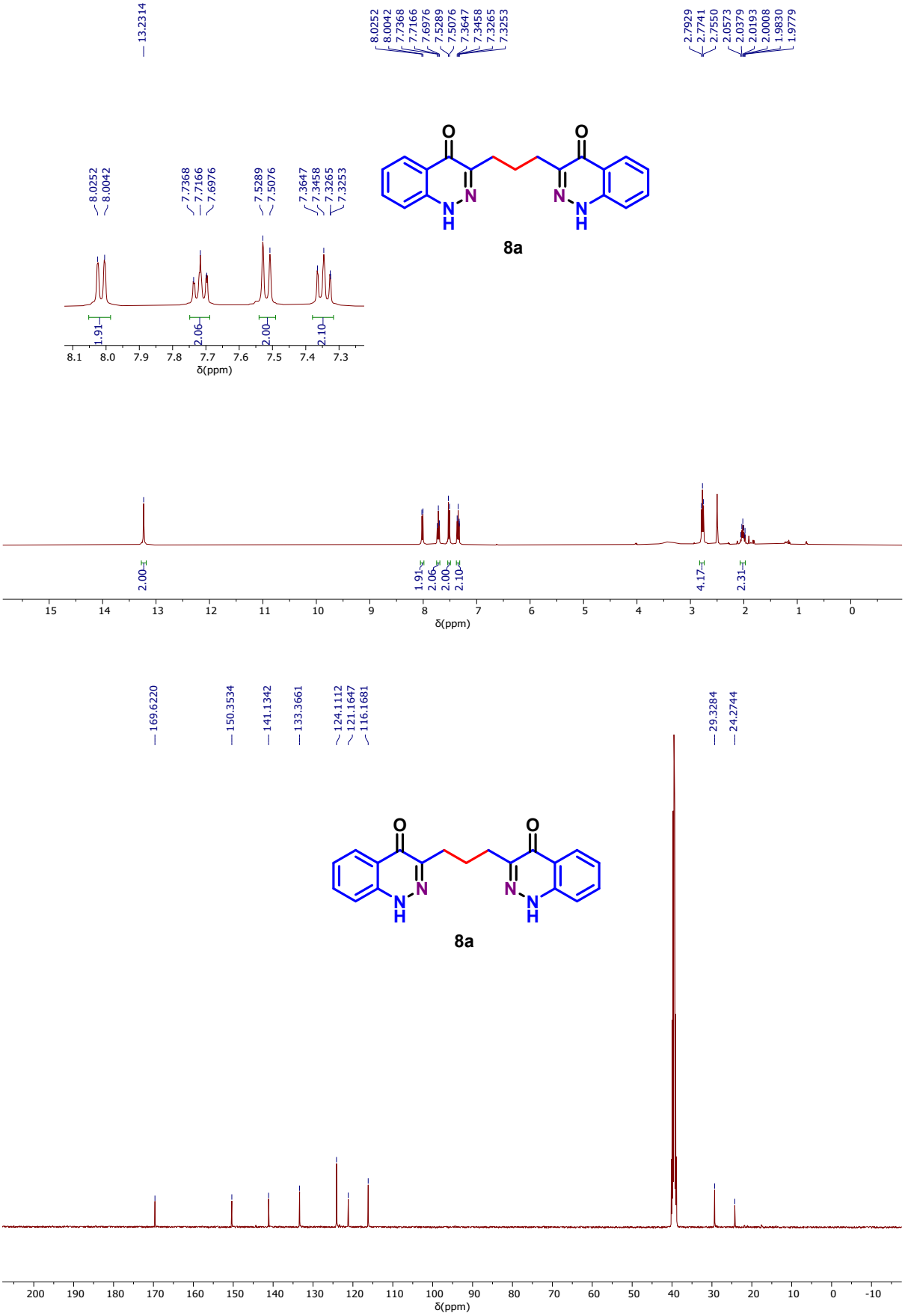


^{1}H and ^{13}C{^{1}H} NMR (DMSO-d_6, 400 and 101 MHz) of compound 7h:

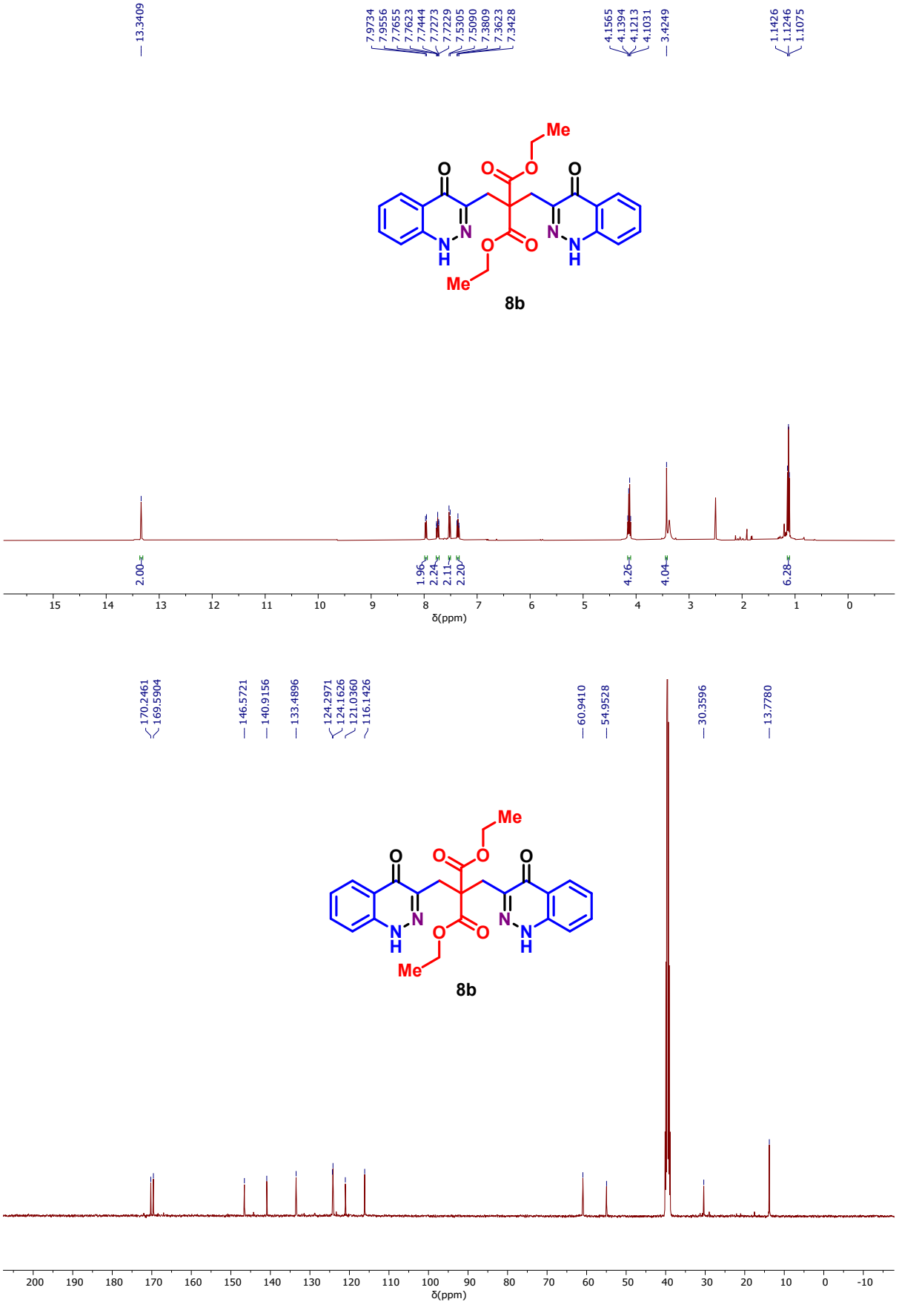




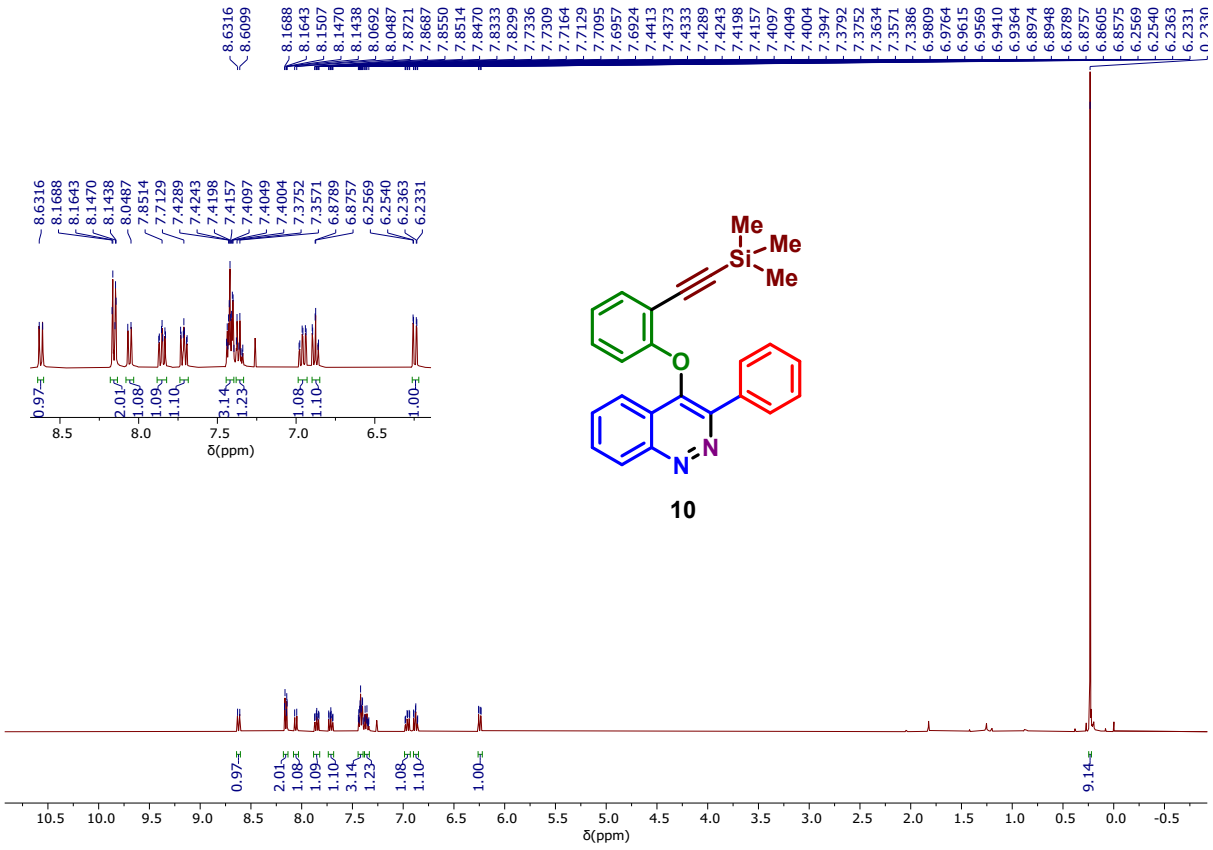
^{1}H and $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 400 and 101 MHz) of compound 8a:

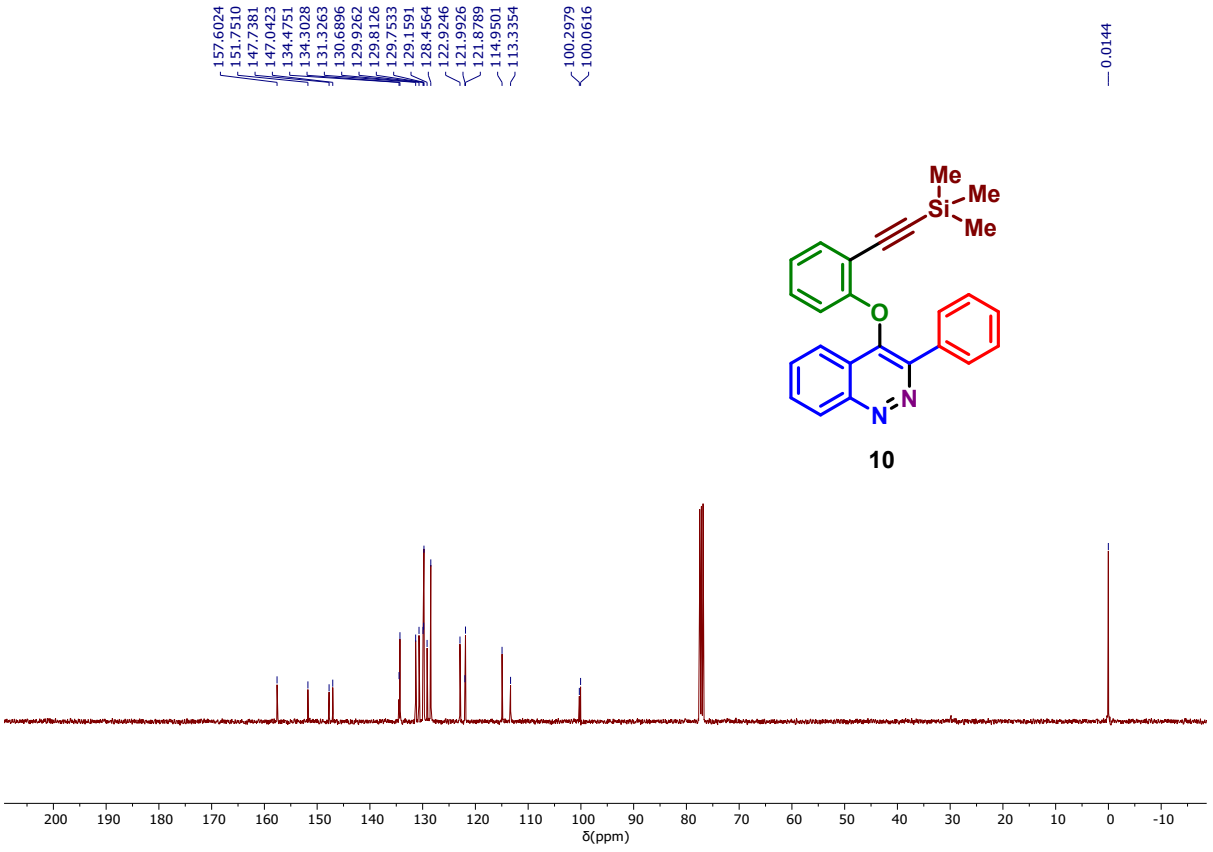


^{1}H and $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 400 and 101 MHz) of compound 8b:



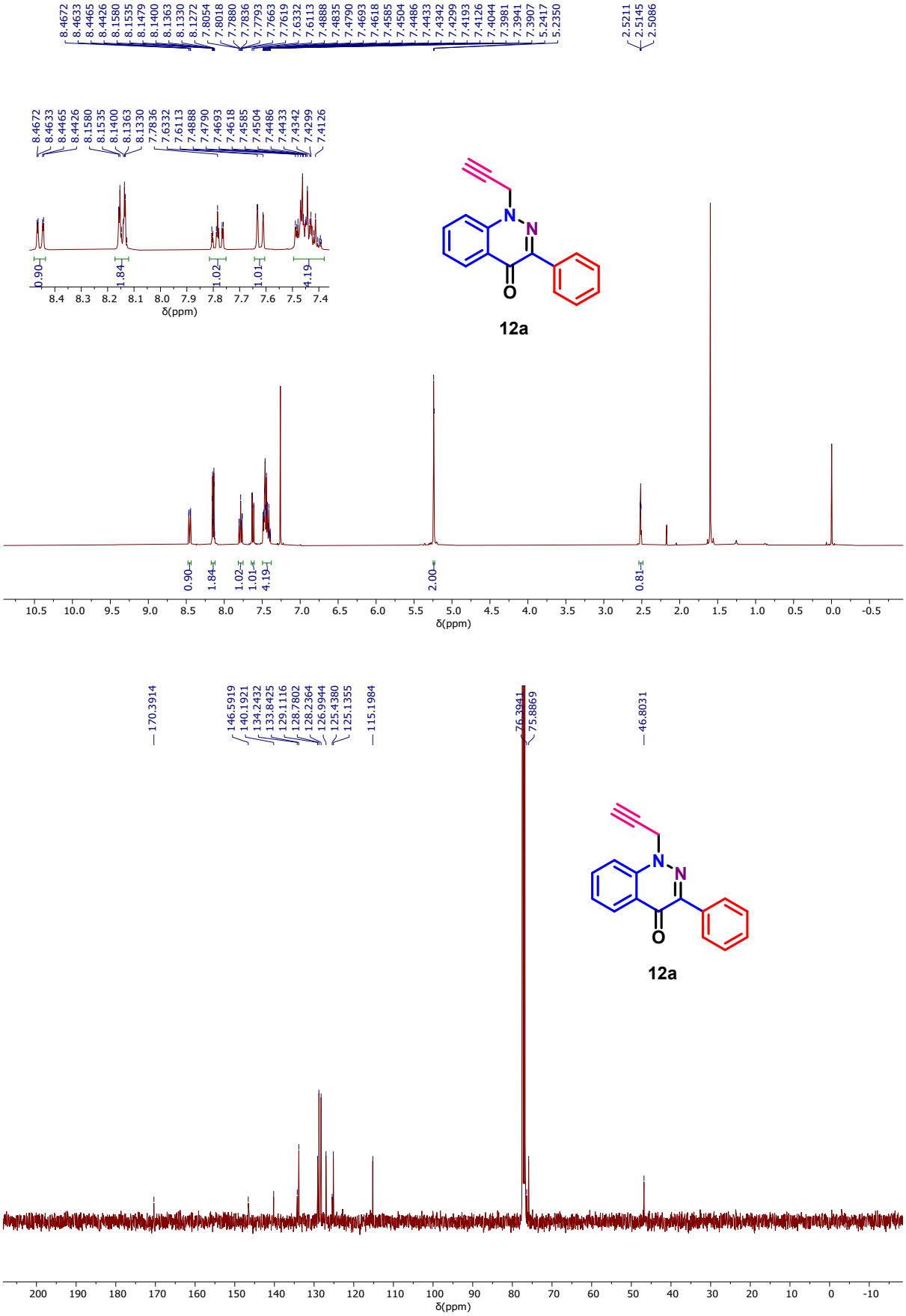
^{1}H and $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 400 and 101 MHz) of compound 10:



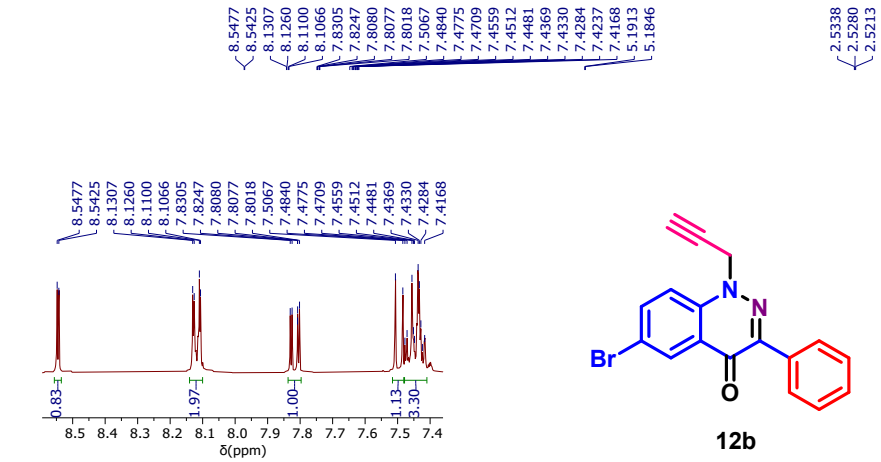


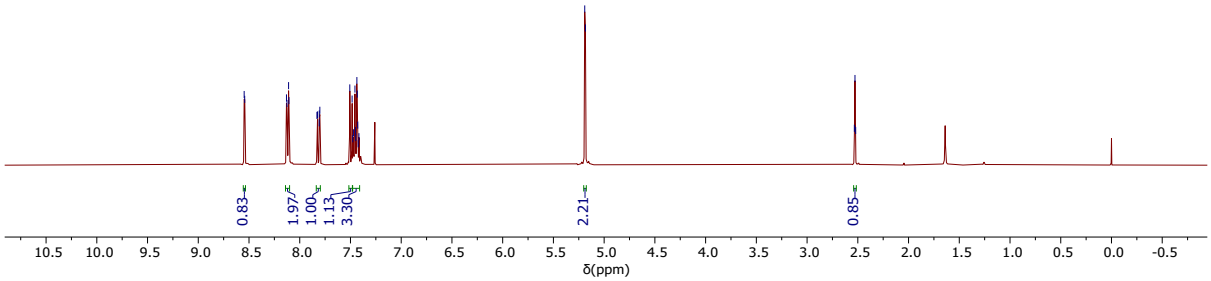
10

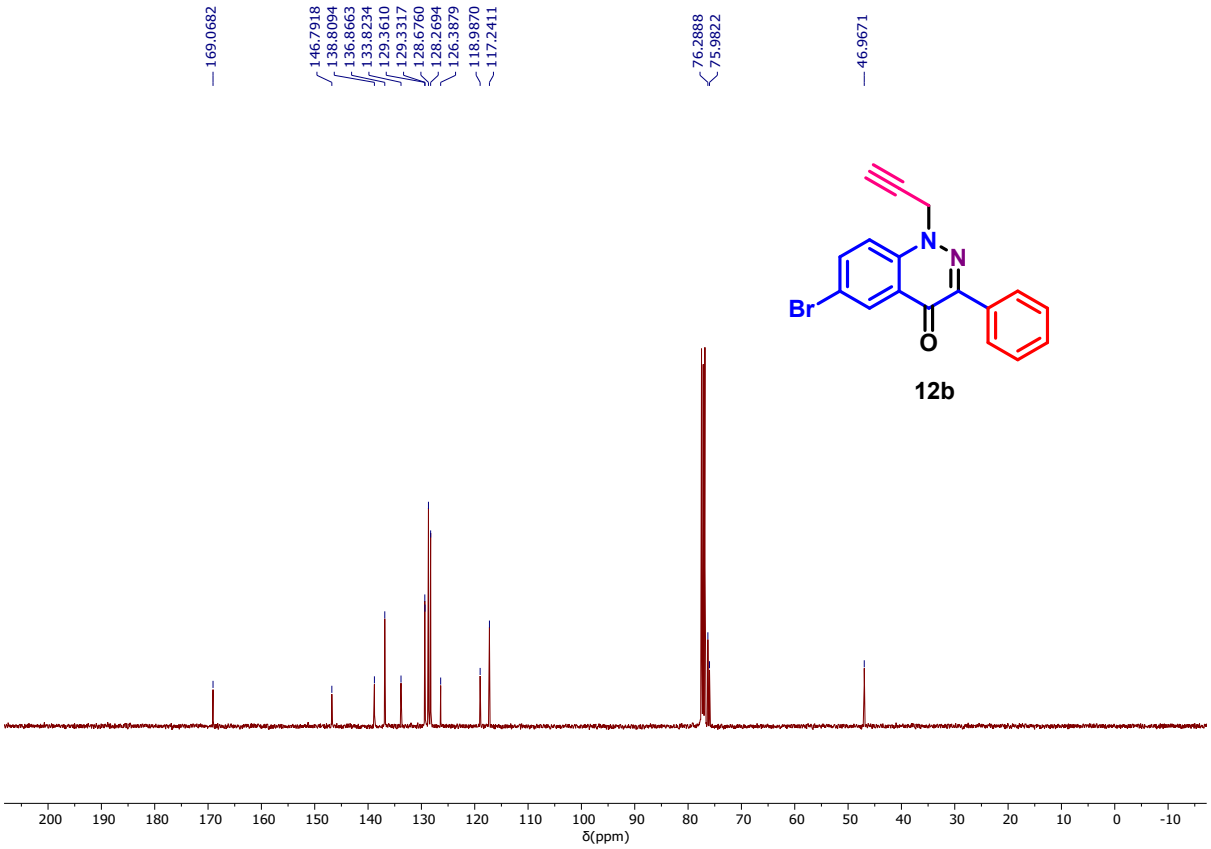
^{1}H and $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 400 and 101 MHz) of compound 12a:



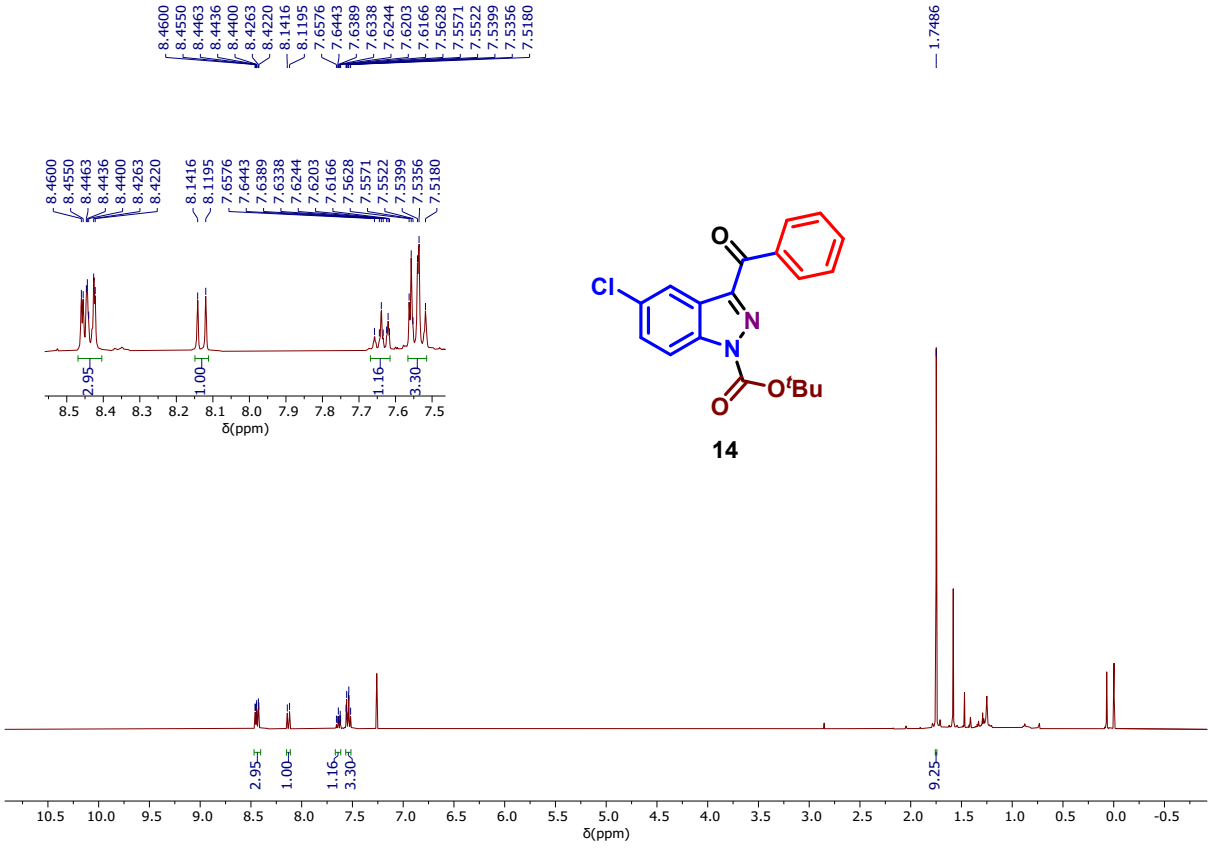
^{1}H and $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 400 and 101 MHz) of compound 12b:

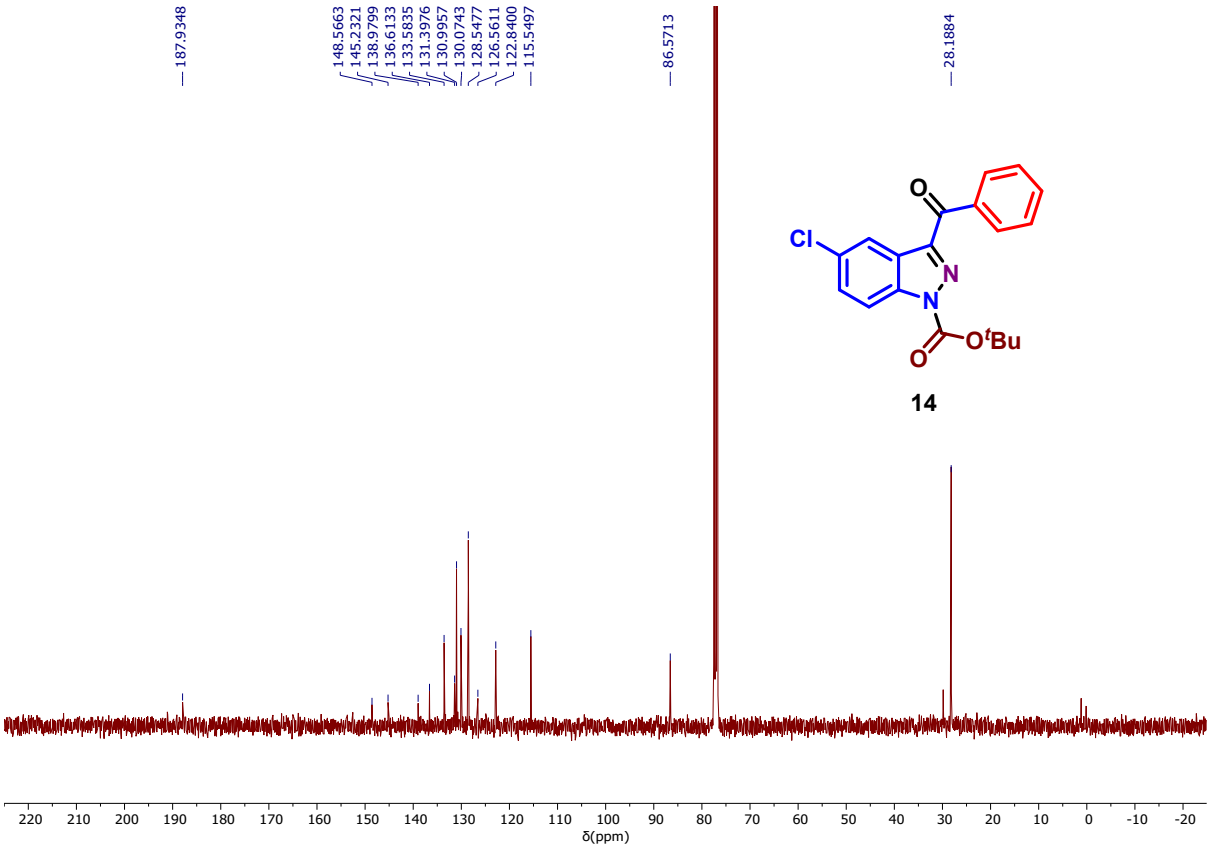




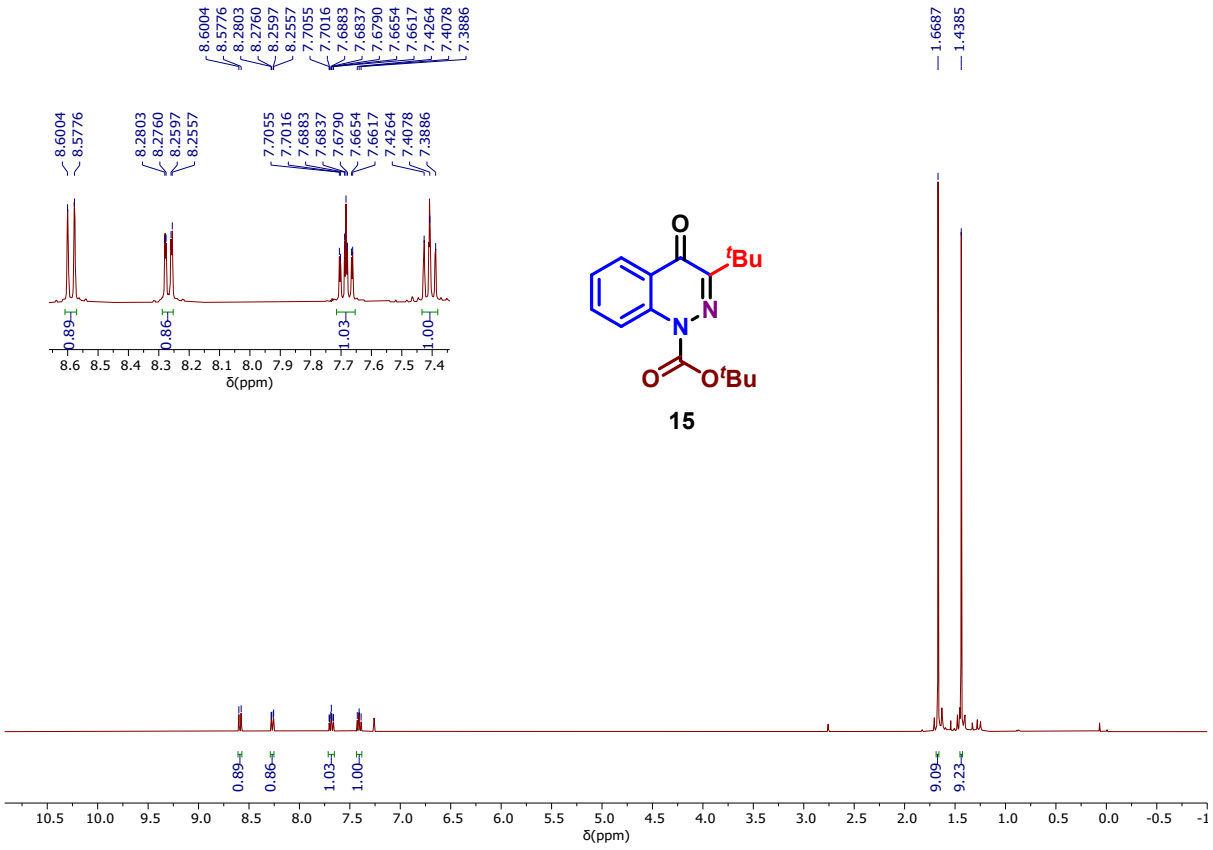


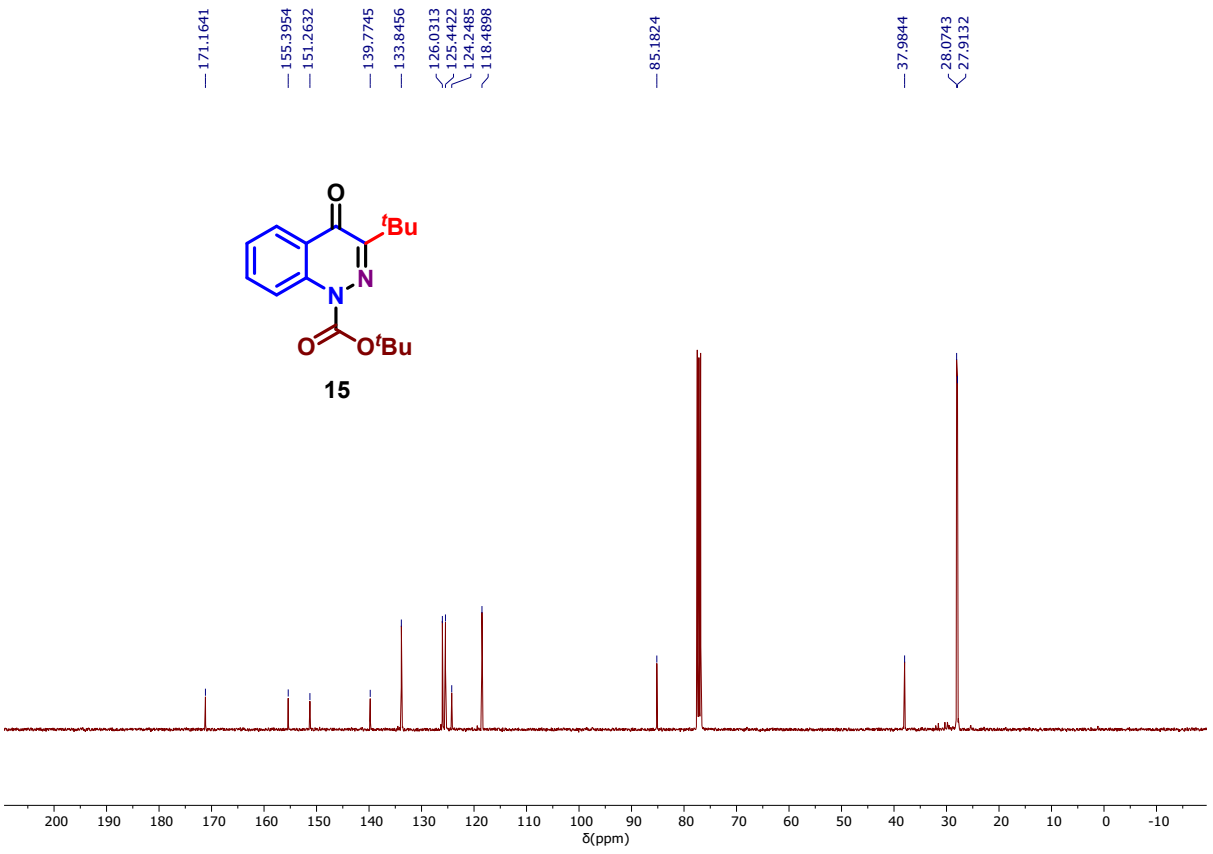
^{1}H and $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 400 and 101 MHz) of compound 14:



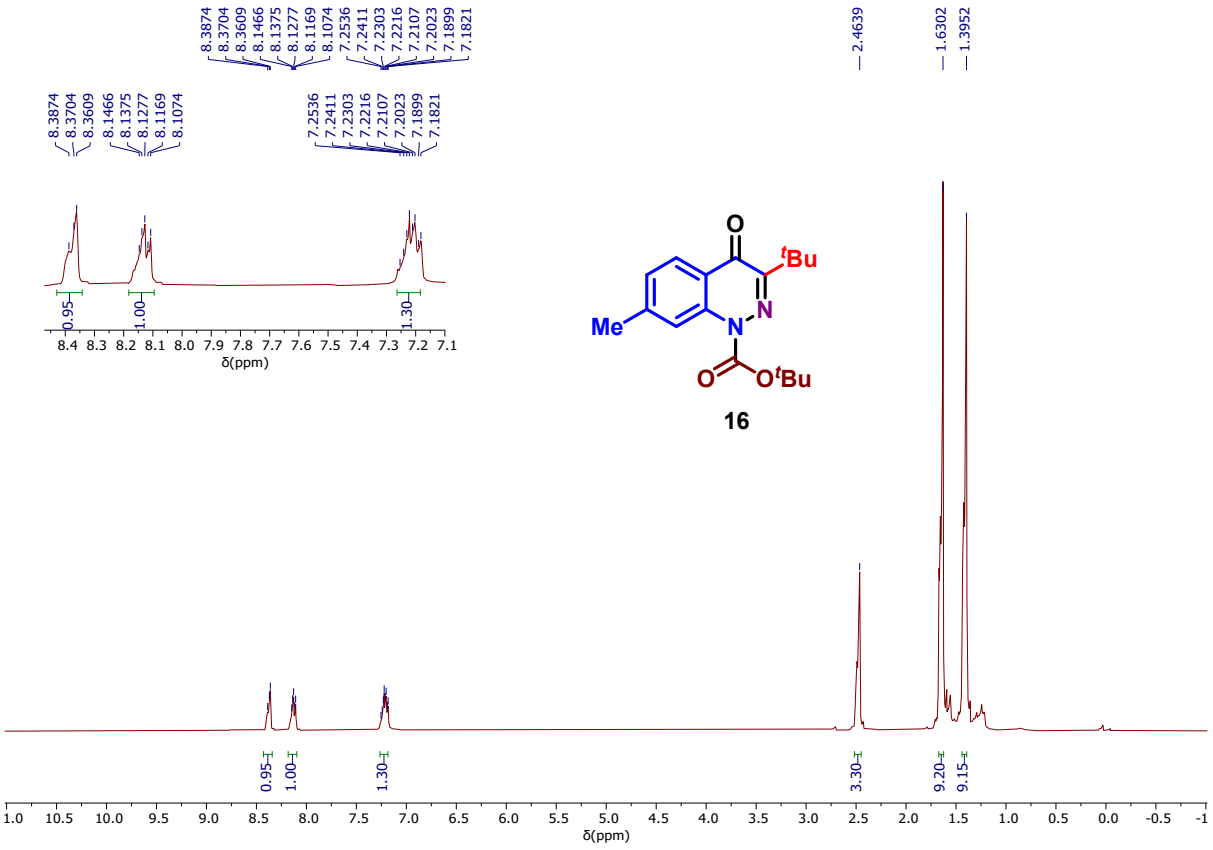


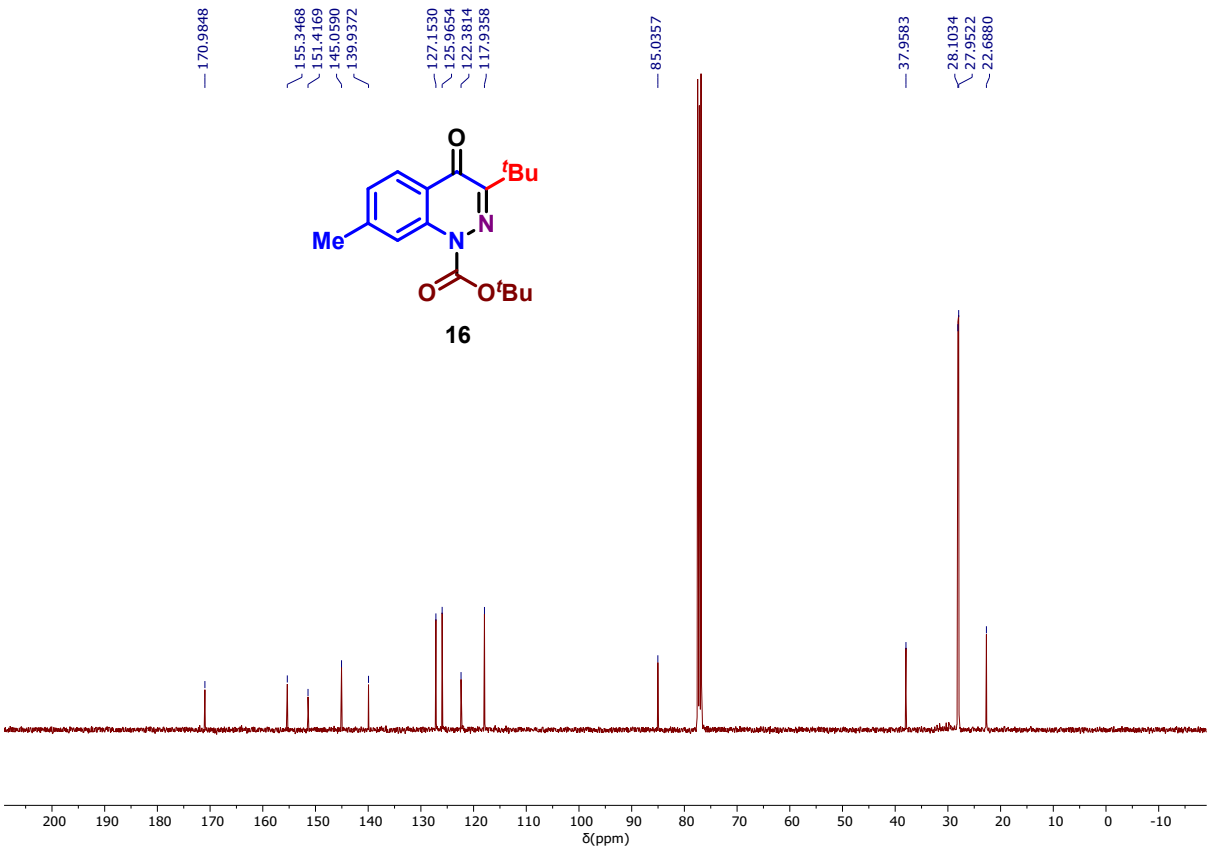
^{1}H and $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 400 and 101 MHz) of compound 15:



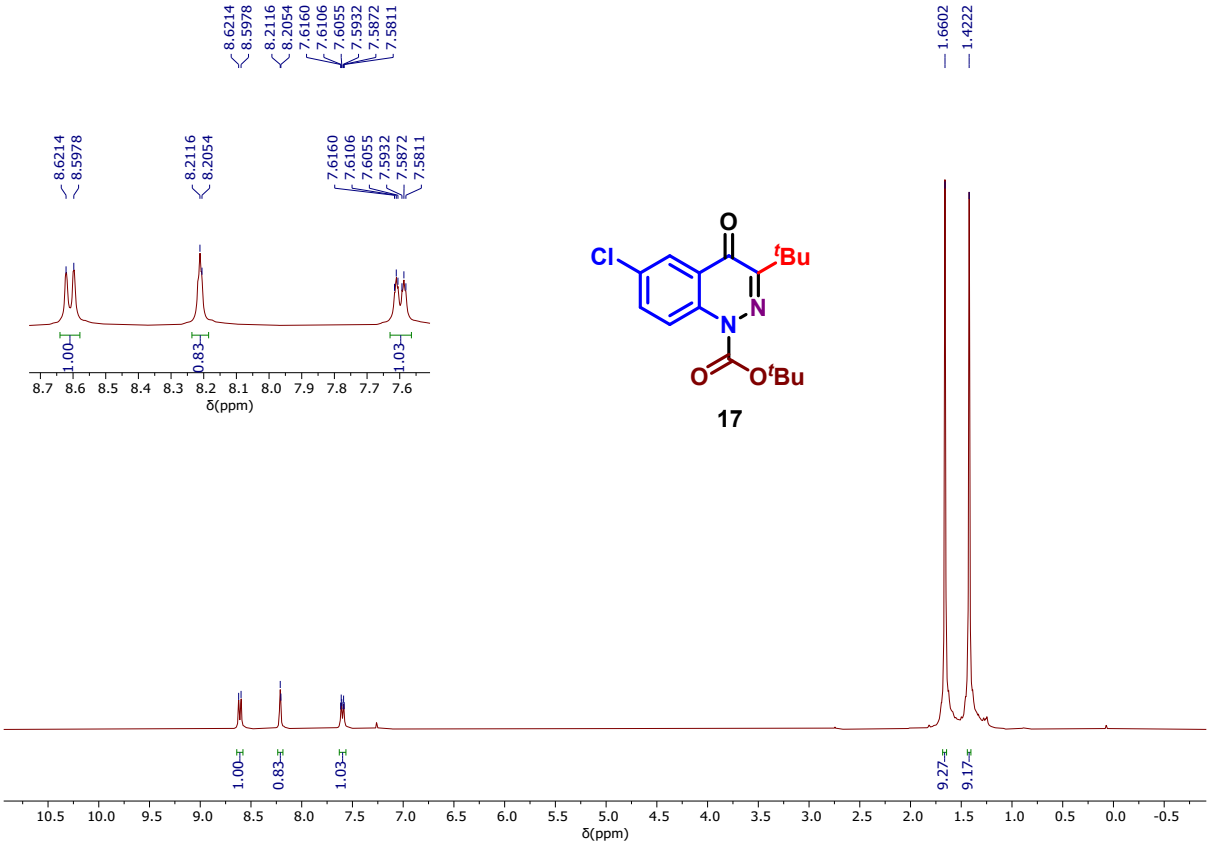


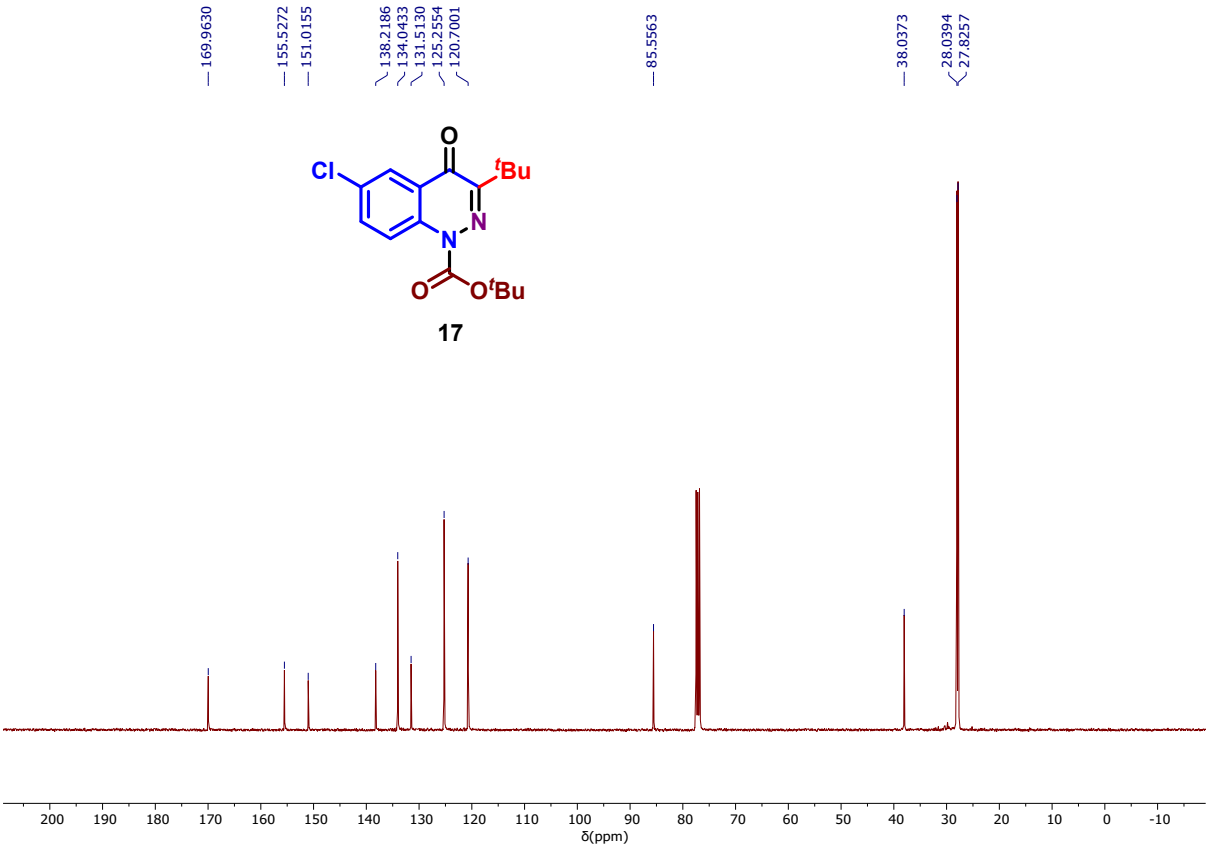
^{1}H and $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 400 and 101 MHz) of compound 16:





^{1}H and $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 400 and 101 MHz) of compound 17:





S5. X-ray crystallographic data

For the determination of X-ray crystal structures, single crystals were selected and mounted with paratone oil on a glass fiber using gum. The data were collected at 298 K on a CMOS based Bruker D8 Venture PHOTON 100 diffractometer equipped with a INCOATEC micro-focus source with graphite monochromatic Mo Kα radiation (λ = 0.71073 Å) operating at 50 kV and 30 mA. For the integration of diffraction profiles SAINT program[2] was used. Adsorption correction was done applying SADABS program.[3] The crystal structure was solved by SIR 92[4] and refined by full matrix least square method using SHELXL-97[5] WinGX system, Ver 1.70.01.[6] All the non-hydrogen atoms in the structure were located from the Fourier map and refined anisotropically. The hydrogen atoms were fixed by HFIX in their ideal positions and refined using riding model with isotropic thermal parameters.

1. **Crystal structure of 3e:**

The crystal structure of **3e** has been deposited to Cambridge Crystallographic Data Centre and allotted deposition number is 2282503. Suitable single–crystals X-ray analysis were grown up from slow evaporation in $CDCl_3$ at 25 ^oC.

Crystal structure of 3e (thermal ellipsoids with 50% probability level):

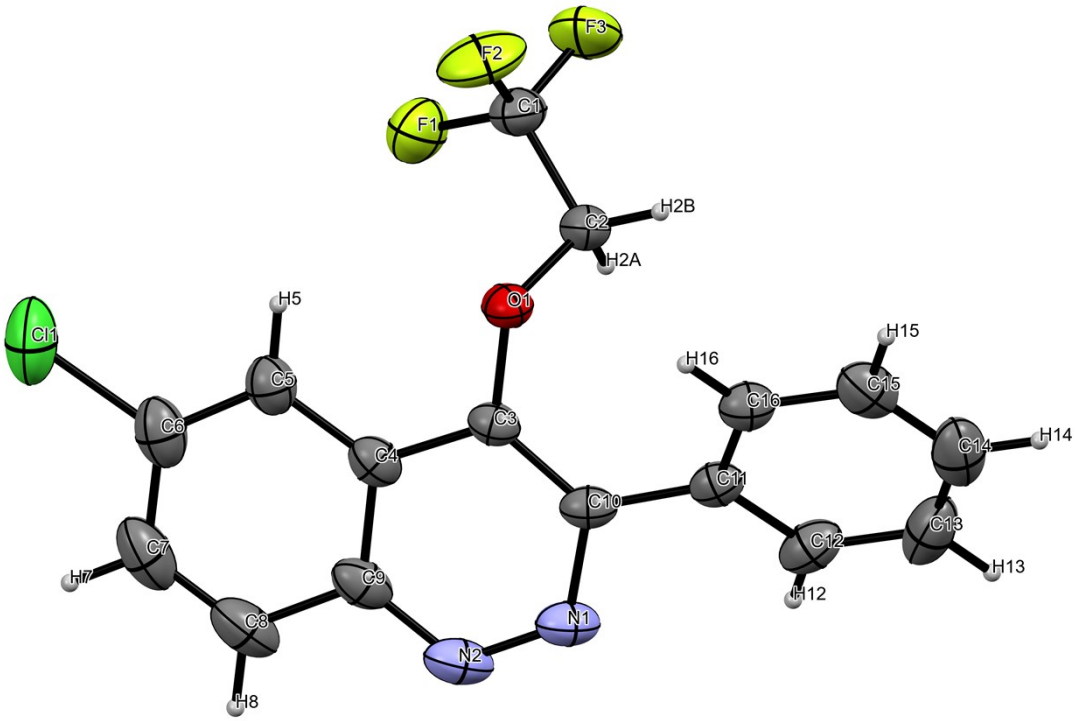


Table 2 Crystal data and structure refinement for 3e.	
CCDC no.	2282503
Empirical formula	$C_{16}H_{10}ClF_3N_2O$
Formula weight	338.71
Temperature/K	298
Crystal system	orthorhombic

Space group	Pbca
a/Å	13.347(2)
b/Å	7.581(2)
c/Å	29.868(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3022.0(10)
Z	8
ρ_{calc}g/cm^3	1.489
μ/mm^{-1}	0.290
F(000)	1376.0
Crystal size/mm^3	0.321 × 0.126 × 0.056
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.252 to 51.442
Index ranges	-16 ≤ h ≤ 16, -9 ≤ k ≤ 9, -36 ≤ l ≤ 36
Reflections collected	60482
Independent reflections	2863 [R_{int} = 0.0744, R_{sigma} = 0.0258]
Data/restraints/parameters	2863/0/208
Goodness-of-fit on F^2	1.063
Final R indexes [I>=2σ (I)]	R_1 = 0.0530, wR_2 = 0.1366
Final R indexes [all data]	R_1 = 0.0641, wR_2 = 0.1446
Largest diff. peak/hole / e Å^{-3}	0.23/-0.35

2. Crystal structure of 5i:

The crystal structure of **5i** has been deposited to Cambridge Crystallographic Data Centre and allotted deposition number is 2257365. Suitable single–crystals X-ray analysis were grown up from slow evaporation in ACN:Hexane, 3:1 (v/v) at 25 °C.

Crystal structure of 5i (thermal ellipsoids with 50% probability level):

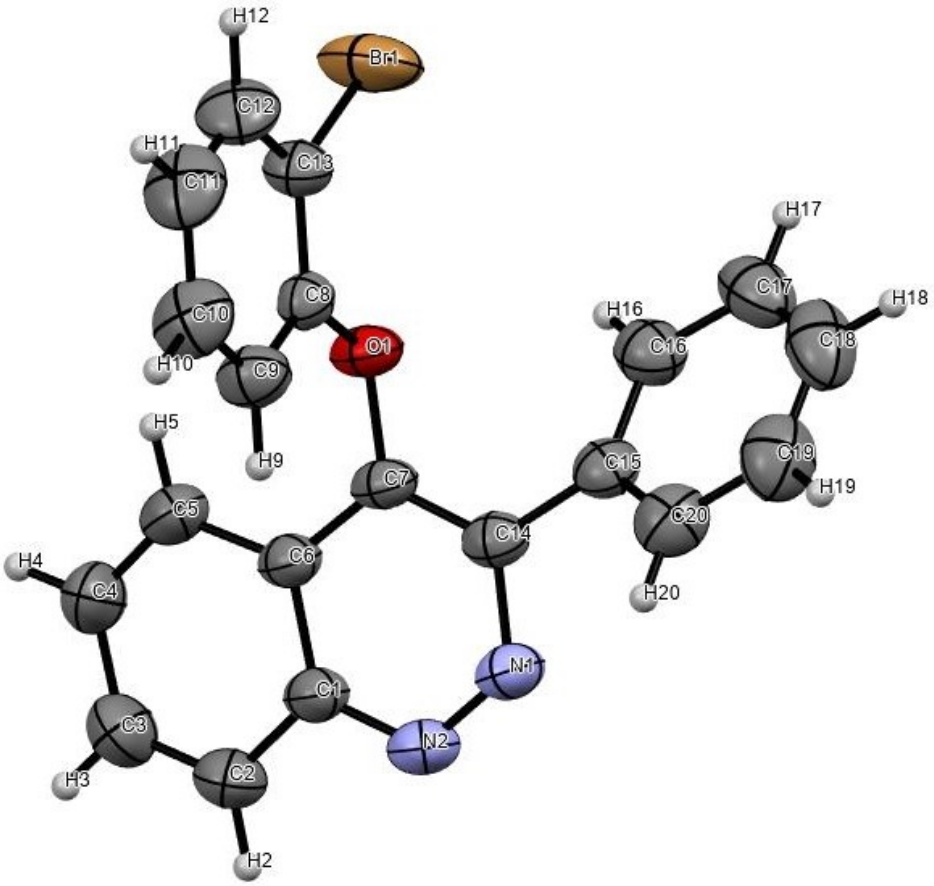


Table 3 Crystal data and structure refinement for 5i	
CCDC no.	2257365
Empirical formula	$C_{20}H_{13}BrN_2O$
Formula weight	377.23
Temperature/K	298
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.1714(6)
b/Å	10.7451(6)
c/Å	15.1448(10)
α/°	90
β/°	91.646(2)
γ/°	90

Volume/Å^3	1654.53(17)
Z	4
ρ_{calc}g/cm^3	1.514
μ/mm^{-1}	2.493
F(000)	760.0
Crystal size/mm^3	0.235 × 0.123 × 0.056
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.648 to 52.814
Index ranges	-12 ≤ h ≤ 11, -13 ≤ k ≤ 13, -18 ≤ l ≤ 15
Reflections collected	10102
Independent reflections	3388 [R_{int} = 0.0414, R_{sigma} = 0.0482]
Data/restraints/parameters	3388/0/217
Goodness-of-fit on F^2	1.015
Final R indexes [I>=2σ (I)]	R_1 = 0.0454, wR_2 = 0.0990
Final R indexes [all data]	R_1 = 0.0791, wR_2 = 0.1126
Largest diff. peak/hole / e Å^{-3}	0.48/-0.59

3. Crystal structure of 6f:

The crystal structure of **6f** has been deposited to Cambridge Crystallographic Data Centre and allotted deposition number is 2282504. Suitable single–crystals X-ray analysis were grown up from slow evaporation in MeOH:DCM, 3:1 (v/v) at 25 °C.

Crystal structure of 6f (thermal ellipsoids with 50% probability level):

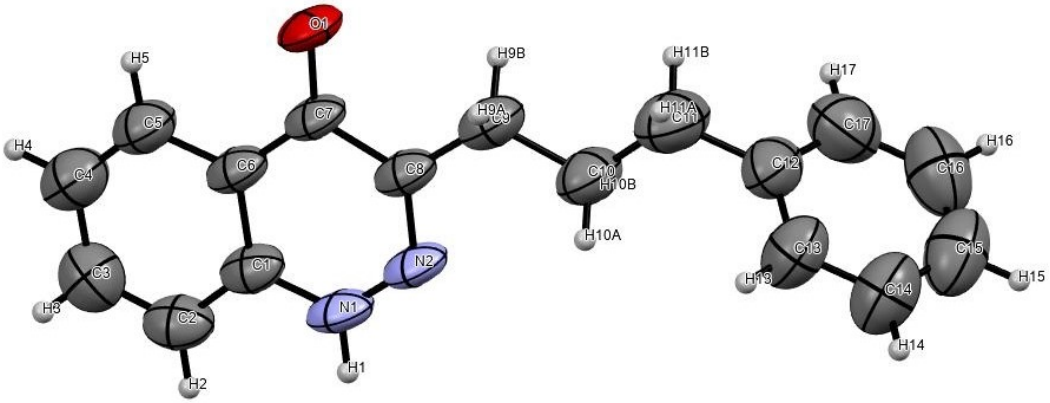


Table 4 Crystal data and structure refinement for 6f.	
CCDC no.	2282504
Empirical formula	$C_{17}H_{16}N_2O$
Formula weight	264.32
Temperature/K	298
Crystal system	Orthorhombic
Space group	Pbca
a/Å	12.7391(7)
b/Å	9.0644(5)
c/Å	24.8179(14)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2865.8(3)
Z	8
ρ_{calc}g/cm^3	1.225
μ/mm^{-1}	0.077
F(000)	1120.0
Crystal size/mm^3	0.231 × 0.156 × 0.023
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.582 to 51.42
Index ranges	$-15 \leq h \leq 14$, $-11 \leq k \leq 11$, $-30 \leq l \leq 30$
Reflections collected	27514
Independent reflections	2716 [R_{int} = 0.0979, R_{sigma} = 0.0473]
Data/restraints/parameters	2716/0/181

Goodness-of-fit on F^2	1.097
Final R indexes [I>=2σ (I)]	R_1 = 0.0924, wR_2 = 0.2234
Final R indexes [all data]	R_1 = 0.1315, wR_2 = 0.2452
Largest diff. peak/hole / e $Å^{-3}$	0.36/-0.20

4. Crystal structure of 7b:

The crystal structure of **7b** has been deposited to Cambridge Crystallographic Data Centre and allotted deposition number is 2270376. Suitable single–crystals X-ray analysis were grown up from slow evaporation in MeOH:DCM, 3:1 (v/v) at 25 °C.

Crystal structure of 7b (thermal ellipsoids with 50% probability level):

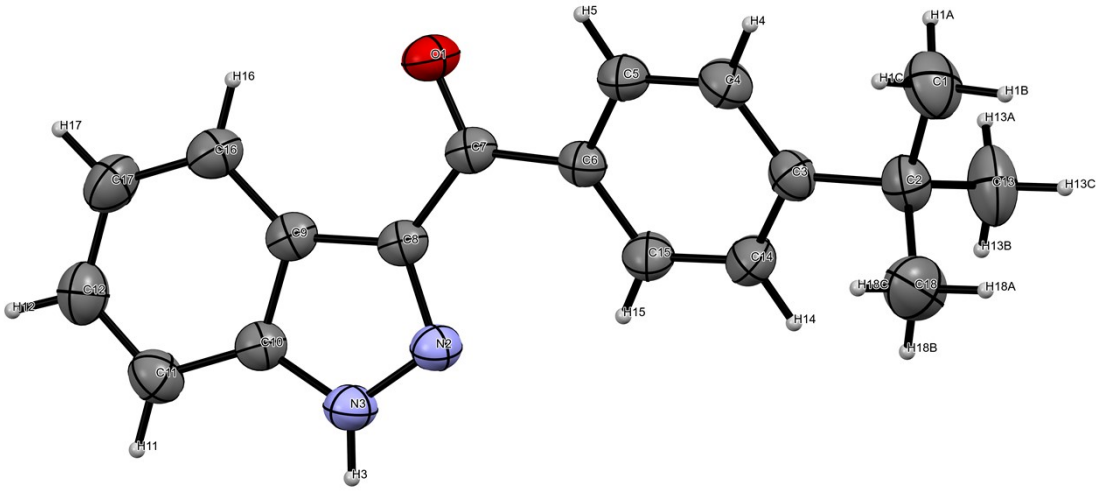


Table 5 Crystal data and structure refinement for 7b.	
CCDC no.	2270376
Empirical formula	$C_{18}H_{18}N_2O$
Formula weight	278.34
Temperature/K	298
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.7784(19)
b/Å	7.2071(9)
c/Å	13.3839(14)
α/°	90
β/°	97.417(3)
γ/°	90
Volume/Å^3	1509.2(3)
Z	4
ρ_{calc}g/cm^3	1.225
μ/mm^{-1}	0.077
F(000)	592.0
Crystal size/mm^3	0.356 × 0.125 × 0.056
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.208 to 52.752
Index ranges	-19 ≤ h ≤ 19, -9 ≤ k ≤ 9, -16 ≤ l ≤ 14
Reflections collected	15953
Independent reflections	3067 [R_{int} = 0.0438, R_{sigma} = 0.0333]

Data/restraints/parameters	3067/0/193
Goodness-of-fit on F^2	1.122
Final R indexes [I>=2σ (I)]	R_1 = 0.0611, wR_2 = 0.1422
Final R indexes [all data]	R_1 = 0.0789, wR_2 = 0.1519
Largest diff. peak/hole / e $Å^{-3}$	0.15/-0.13

5 Crystal structure of 12b:

The crystal structure of **12b** has been deposited to Cambridge Crystallographic Data Centre and allotted deposition number is 2282505. Suitable single–crystals X-ray analysis were grown up from slow evaporation in MeOH:DCM, 3:1 (v/v) at 25 °C.

Crystal structure of 12b (thermal ellipsoids with 50% probability level):

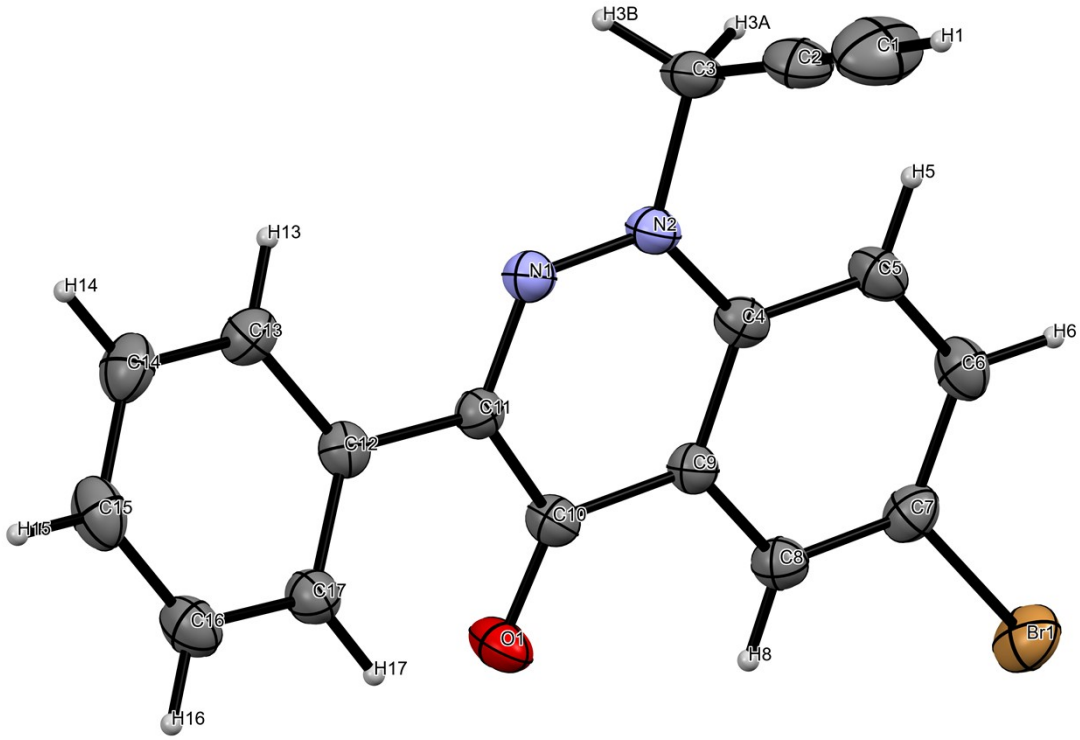


Table 6 Crystal data and structure refinement for 12b.	
CCDC no.	2282505
Empirical formula	$C_{17}H_{11}BrN_2O$
Formula weight	339.19
Temperature/K	298
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	5.1247(5)
b/Å	13.5141(15)
c/Å	20.781(2)
α/°	90
β/°	94.934(5)
γ/°	90
Volume/Å^3	1433.8(3)
Z	4
ρ_{calc}g/cm^3	1.571
μ/mm^{-1}	2.866

F(000)	680.0
Crystal size/mm^3	0.258 × 0.231 × 0.137
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.956 to 56.67
Index ranges	-6 ≤ h ≤ 6, -17 ≤ k ≤ 18, -27 ≤ l ≤ 22
Reflections collected	12448
Independent reflections	3463 [R_{int} = 0.0547, R_{sigma} = 0.0495]
Data/restraints/parameters	3463/0/190
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0440, wR_2 = 0.1072
Final R indexes [all data]	R_1 = 0.0626, wR_2 = 0.1172
Largest diff. peak/hole / e Å^{-3}	0.55/-0.85

6. References:

1 M. Kumar and A. Goswami, *Org. Lett.*, 2023, **25**, 3254–3259.
2 Bruker, SAINT V7.68A, Bruker AXS Inc., Madison (WI, USA), 2005.
3 G. M. Sheldrick, SADABS 2008/2, Göttingen, 2008.
4 A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Cryst*., 1993, **26**, 343–350.
5 G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Solution and Refinement; University of Göttingen, Göttingen, 43, Germany, 1997.
6 L. Farrugia, WinGX-A Windows Program for Crystal Structure Analysis, *J. Appl. Cryst.* 1999, **32**, 837–838.