Supporting Information

Copper-Catalyzed *N*-Arylation of Isatins Employing Aryl(TMP)-Iodonium Salts

Ankita Rakshit,[a] Raktim Abha Saikia,[b] Snata Deka[a] and Ashim Jyoti Thakur*[a]

[a]*Department of Chemical Sciences, Tezpur University, Napaam-784028, India*

[b]*National Institute for Research and Development of Isotopic and Molecular Technologies (INCDTIM), 67-103 Donat Street, 400293 Cluj-Napoca, Romania*

*E-mail: ashim@tezu.ernet.in

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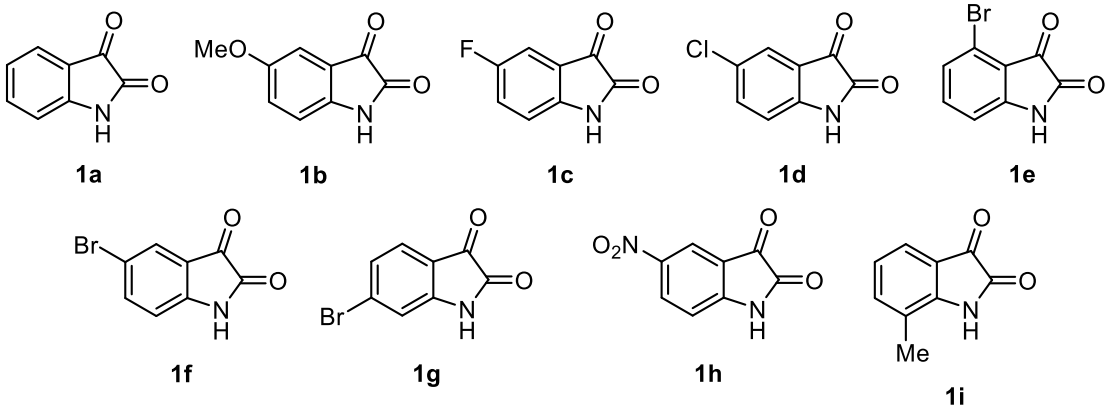
1. GENERAL EXPERIMENTAL INFORMATION

All reactions were performed in oven-dried Schlenk tubes or round-bottom flasks under ambient conditions, unless otherwise stated. Dichloromethane (DCM), 1,2-dichloroethane (DCE), and acetonitrile (ACN) were dried by refluxing over CaH_2 under nitrogen conditions and stored over 4Å molecular sieves. Toluene and 1,4-dioxane were dried utilising conventional drying procedures using sodium/benzophenone as an indicator and stored over 4Å molecular sieves. All chemicals were purchased from commercial suppliers and used as received unless otherwise stated. NaOH, Cs_2CO_3, K_3PO_4, and ^{t}BuOK were stored in a desiccator. The diaryliodonium salts were synthesized according to procedures described below. *m*-CPBA (Aldrich, >70% active oxidant) was dried at room temperature under high vacuum for 1 hour and titrated by iodometric titration[1] before use in the synthesis of diaryliodonium salts. Thin Layer Chromatography (TLC) analyses were performed on pre-coated Merck silica gel $60F_{254}$ plates using UV (254 nm) light and/or with $KMnO_4$-stain. Column chromatography was performed on 100-200 mesh silica gel using the gradient system, a freshly distilled ethyl acetate-hexane mixture. All NMR data were recorded in a 400 MHz instrument at 298 K using $CDCl_3$ and DMSO-d_6 as solvents. Chemical shifts are given in ppm relative to the residual solvent peak (^{1}H NMR: $CDCl_3$ δ 7.26 and sometimes δ 1.56 ($CDCl_3$-water) and in DMSO-d_6 δ 2.50 and δ 3.3 (DMSO-water); ^{13}C NMR: $CDCl_3$ δ 77.16, DMSO-d_6 δ 39.52) with multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sex = sextet, sep = septet, m = multiplet, app = apparent) coupling constants (in Hz) and integration. Chemical shifts for ^{19}F-NMR are given in ppm relative to mono-fluorobenzene (δ = -113.15 ppm) used as internal standard. The raw NMR data were processed by MestReNova software.

2. SELECTED STRUCTURES OF INDOLINE-2,3-DIONES

The following isatins (**1a-i**) were chosen for the synthesis of the desired *N*-arylated products. Isatin derivatives were purchased commercially and were used without any further purification.



3. SYNTHESIS OF DIARYLIODONIUM SALTS

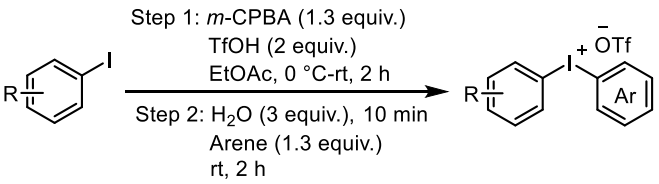
3.1 Diaryliodonium salts synthesized in this work

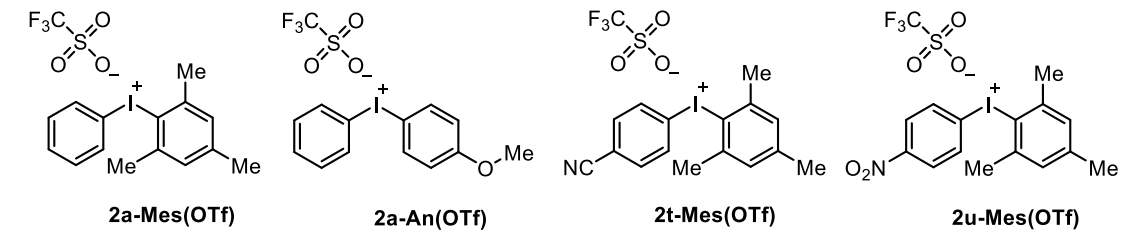
Most of the diaryliodonium salts used in our work were synthesized following reported methods. One-pot synthesis of aryl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate salts were accomplished according to the reported procedure as mentioned in Stuart's work (Method II). It is to be noted that these reactions were run without precautions to avoid air or moisture.

Olofsson's work:

Table S1. Synthesis of various diaryliodonium salts according to above mentioned procedures:

Method I[1]

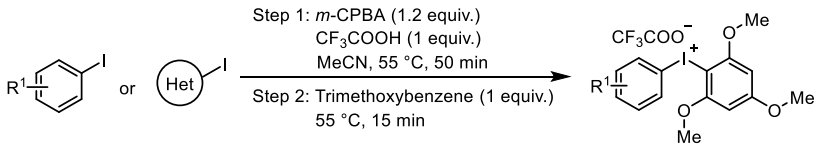


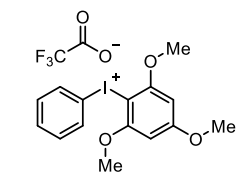


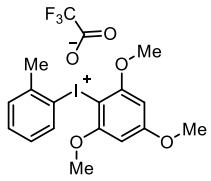
Stuart's work:

Table S2. Synthesis of various diaryliodonium salts according to above mentioned procedures:

Method II[2]




2a-TMP(TFA)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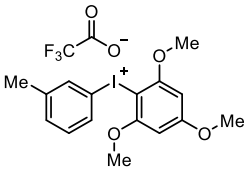
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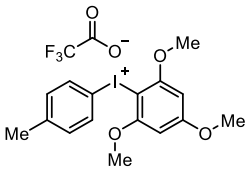
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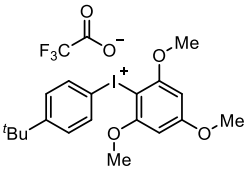
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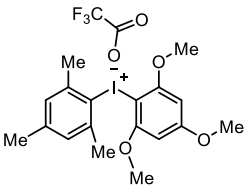
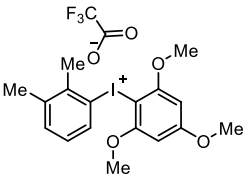

2f-TMP(TFA)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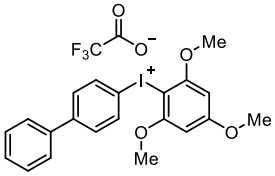
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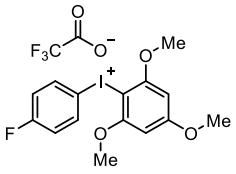
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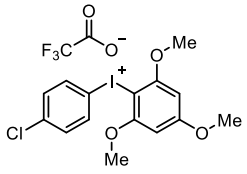
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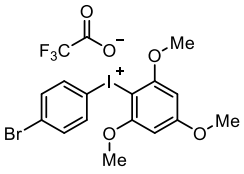
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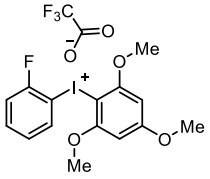
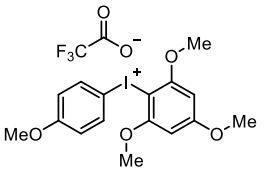
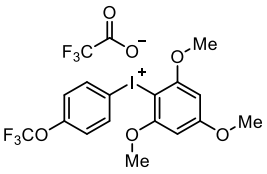

2l-TMP(TFA)


2m-TMP(TFA)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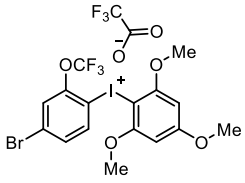
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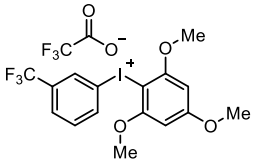
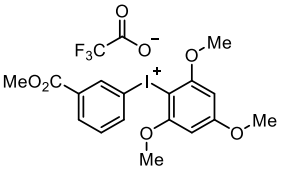
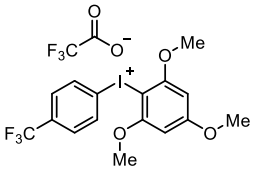
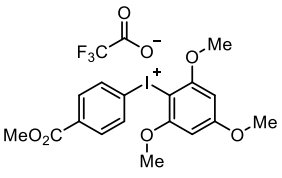
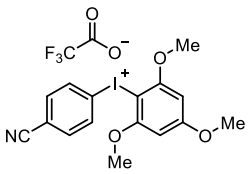
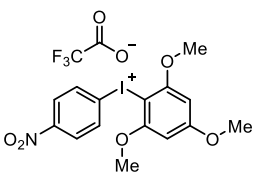

2p-TMP(TFA)

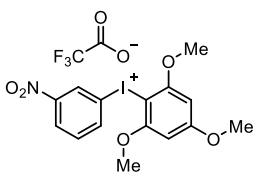

2q-TMP(TFA)

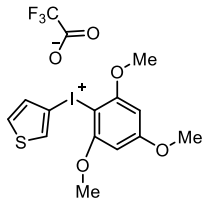

2r-TMP(TFA)

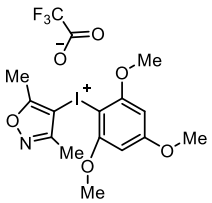

2s-TMP(TFA)


2t-TMP(TFA)

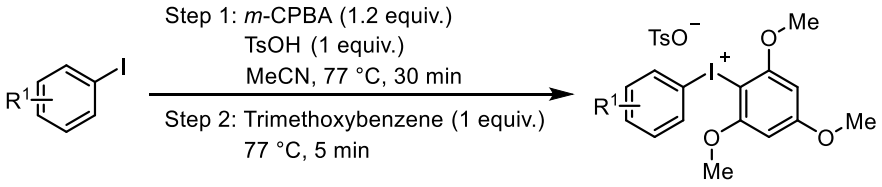

2u-TMP(TFA)

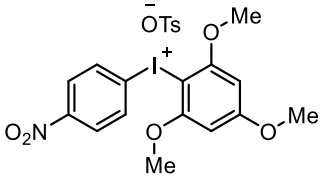

2v-TMP(TFA)


2w-TMP(TFA)


2z-TMP(TFA)

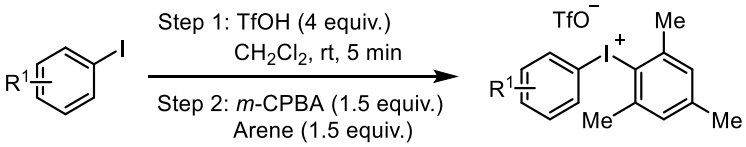
Method III[3]

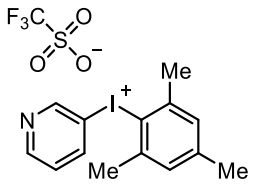




2u-TMP(OTs)

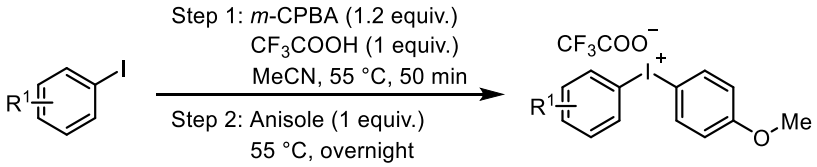
Method IV[4]

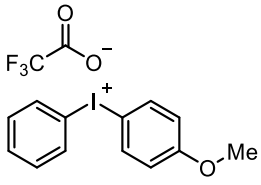




2x-Mes(OTf)

Method V





2a-An(TFA)

All diaryliodonium salts were prepared according to above mentioned procedures. The synthesis of iodonium salt, Ph-I-An(TFA) could not be achieved using reported procedure (method II). However, with slight moderation in the Stuart's method, it was be easily achieved

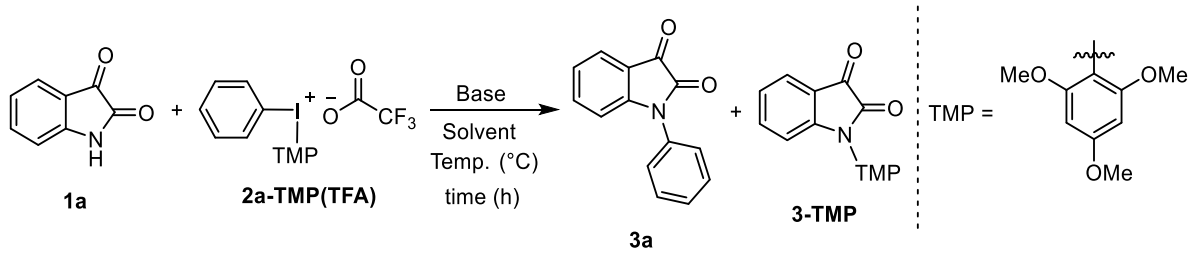
with 45% yield. Characterization data of these compounds were matched with those previously reported in the literature.

4. OPTIMIZATION OF REACTION CONDITIONS

4.1. Investigation for metal-free reaction conditions

The arylation was tried with indoline-2,3-dione **1a** (0.2 mmol) and phenyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate salt **2a-TMP(TFA)** (0.22 mmol) in 1,2-dicholoroethane at room temperature, delivering no significant yield of *N*-arylated product **3a** (Table S2). In order to maintain the metal-free prospect, various organic and inorganic bases with varying time and temperature were optimized (Entries 1-18, Table S3).

Table S3. Optimization under metal-free conditions[a]



Entry	Base (equiv.)	Solvent	Temp. (°C)	Time (h)	Yield[b] (%)
1[c,d]	NaH (1.5)	DMF	RT	12	trace
2[c,d]	NaH (1.5)	DMA	RT	12	trace
3[c,d]	NaH (1.5)	THF	RT	12	trace
4	Cs_2CO_3 (1.2)	DMF	RT	10	trace
5	Cs_2CO_3 (1.2)	DMF	70	12	trace
6	Cs_2CO_3 (2)	CH_3CN	75	12	NR
7	Cs_2CO_3 (2)	Toluene	100	12	NR
8	Cs_2CO_3 (1.5)	DMF	RT	12	trace
9	Cs_2CO_3 (1.5)	DMF	70	12	trace
10	Cs_2CO_3 (1.2)	DMSO	RT	12	NR
11	Cs_2CO_3 (1.5)	Toluene	100	12	NR
12	Na_2CO_3 (1.5)	Toluene	100	12	NR
13	*t*-BuOK (1.1)	DCE	0-RT	12	NR
14	*t*-BuOK (1.5)	Toluene	100	12	trace

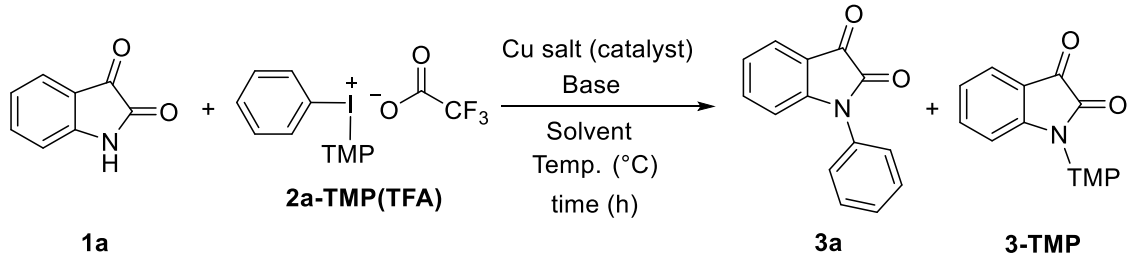
15	DBU (1.2)	CH_3CN	80	12	NR
16	K_3PO_4 (1.5)	Toluene	100	12	18
17	K_3PO_4 (1.5)	DMF	100	12	trace
18	K_3PO_4 (1.5)	1,4-Dioxane	100	12	NR

[a]Reaction conditions: **1a** (0.2 mmol), **2a-TMP(TFA)** (1.1 equiv.), and solvent (2 ml) were used. [b]Isolated yield. [c]The reaction was performed under a nitrogen atmosphere, [d]dry solvent was used, RT, i.e., room temperature, and NR, i.e., no reaction.

4.2. Investigation for Cu-catalyzed route

From Table S3, it was evident that metal-free conditions didn't show satisfactory results; therefore, it was further carried out under metal-catalyzed conditions, *namely*, using a copper catalyst. The *N*-arylation reaction proceeded with moderate to good yields (Table S4, entries 1-29). Variation of reaction parameters gave our optimized product (Table S4, entry 18).

Table S4. Optimization under copper-catalyzed condition[a]



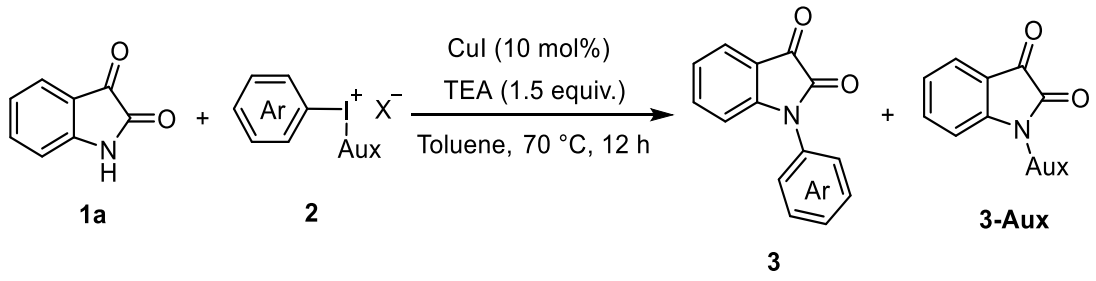
Entry	Catalyst	Base (equiv.)	Solvent	Temp (°C)	Time (h)	Yield[b] (%)
1	CuI	TEA (1.2)	DCE	0-RT	12	85
2	CuI	TEA (1.2)	DCE	60	12	76
3	CuI	TEA (1.2)	DCE	100	12	75
4	CuI	TEA (1.5)	DCE	0-RT	24	82
5	$Cu(OTf)_2$	TEA (1.2)	DCE	RT	24	44
6	$Cu(OTf)_2$	TEA (1.5)	DCE	RT	12	45
7	$Cu(OAc)_2$	TEA (1.2)	DCE	RT	12	trace
8	CuBr	TEA (1.2)	DCE	RT	12	83
9	$Cu(NO_3)_2{\cdot}3H_2O$	TEA (1.5)	DCE	RT	12	trace
10	CuI	TMEDA (1.2)	DCE	70	12	NR
11	CuI	DBU (1.2)	DCE	70	12	72
12	CuI	Na_2CO_3 (1.2)	DCE	70	12	72

13	CuI	K_3PO_4 (1.5)	DCE	RT	12	66
14	CuI	K_3PO_4 (1.5)	DCE	70	12	70
15	CuI	K_3PO_4 (1.5)	Toluene	70	12	72
16	CuI	TEA (1.5)	Toluene	RT	12	60
17	CuI	TEA (1.5)	Toluene	45	12	74
18	CuI	TEA (1.5)	Toluene	60	24	81
19	CuI	DIPEA (1.5)	Toluene	60	24	80
20	**CuI**	**TEA (1.5)**	**Toluene**	**70**	**12**	**88**
21	CuI	TEA (1.5)	Toluene	120	12	82
23	CuI	TEA (1.5)	CH_3CN	80	12	66
24	CuI	TEA (1.5)	1,4-Dioxane	70	12	trace
25	CuI	Cs_2CO_3 (1.5)	DMF	120	24	trace
26	CuI	Cs_2CO_3 (1.5)	DMSO	120	24	trace
27	CuCl	TEA (1.5)	Toluene	70	12	76
28	CuBr	TEA (1.5)	Toluene	70	12	81
29	$Cu(OTf)_2$	TEA (1.5)	Toluene	70	12	62

[a]Reaction conditions: **1a** (0.5 mmol), **2a-TMP(TFA)** (1.1 equiv.), Cu salt (10 mol%), base (1.5 equiv.), and solvent (3 ml) were used. [b]Isolated yield.

4.3. Effect of the nature of auxiliary group and counter-anions

Table S5. Variation of auxiliary group and counter-anions[a]



1a 2 3 3-Aux

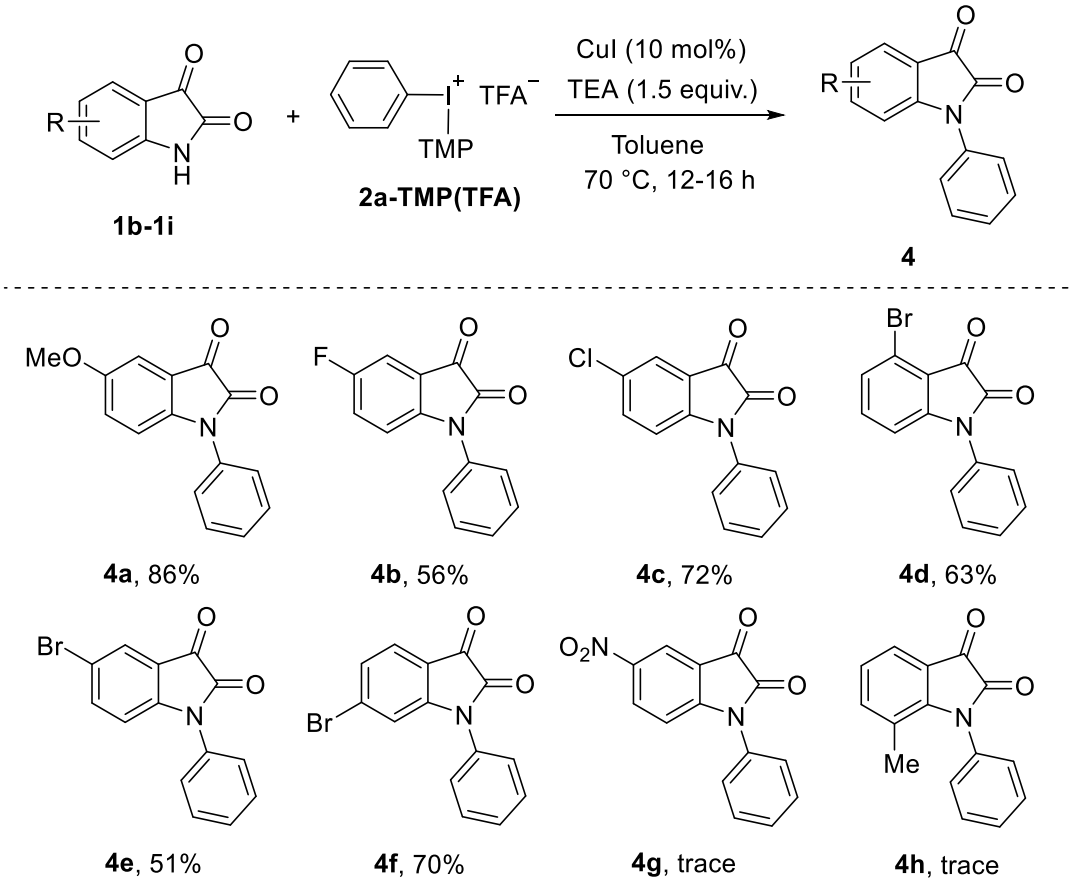
Entry	Ar	Aux	Counter anion (X)	Yield[b] (%)
1	Ph	TMP	TFA	88
2	Ph	TMP	OTs	74
3	Ph	TMP	OTf	76
4	Ph	Mes	OTf	78

5	Ph	Mes	OTs	72
6	Ph	An	OTf	**3a**: 66 and **3m**: 24
7	Ph	An	TFA	**3a**: 45 and **3m**: 42
8	TMP	DMIX	TFA	**3v**: 45

[a]Reaction conditions: **1a** (0.2 mmol), **2** (1.1 equiv.), CuI (10 mol%), TEA (1.5 equiv.), and solvent (3 ml) were used. [b]Isolated yield. Ph, i.e., Phenyl. TMP, i.e., 2,4,6-trimethoxyphenyl. Mes i.e, Mesityl. An, i.e, Anisyl. OTs, i.e, Tosylate. OTf, i.e., Triflate. TFA, i.e., trifluoroacetate anion.

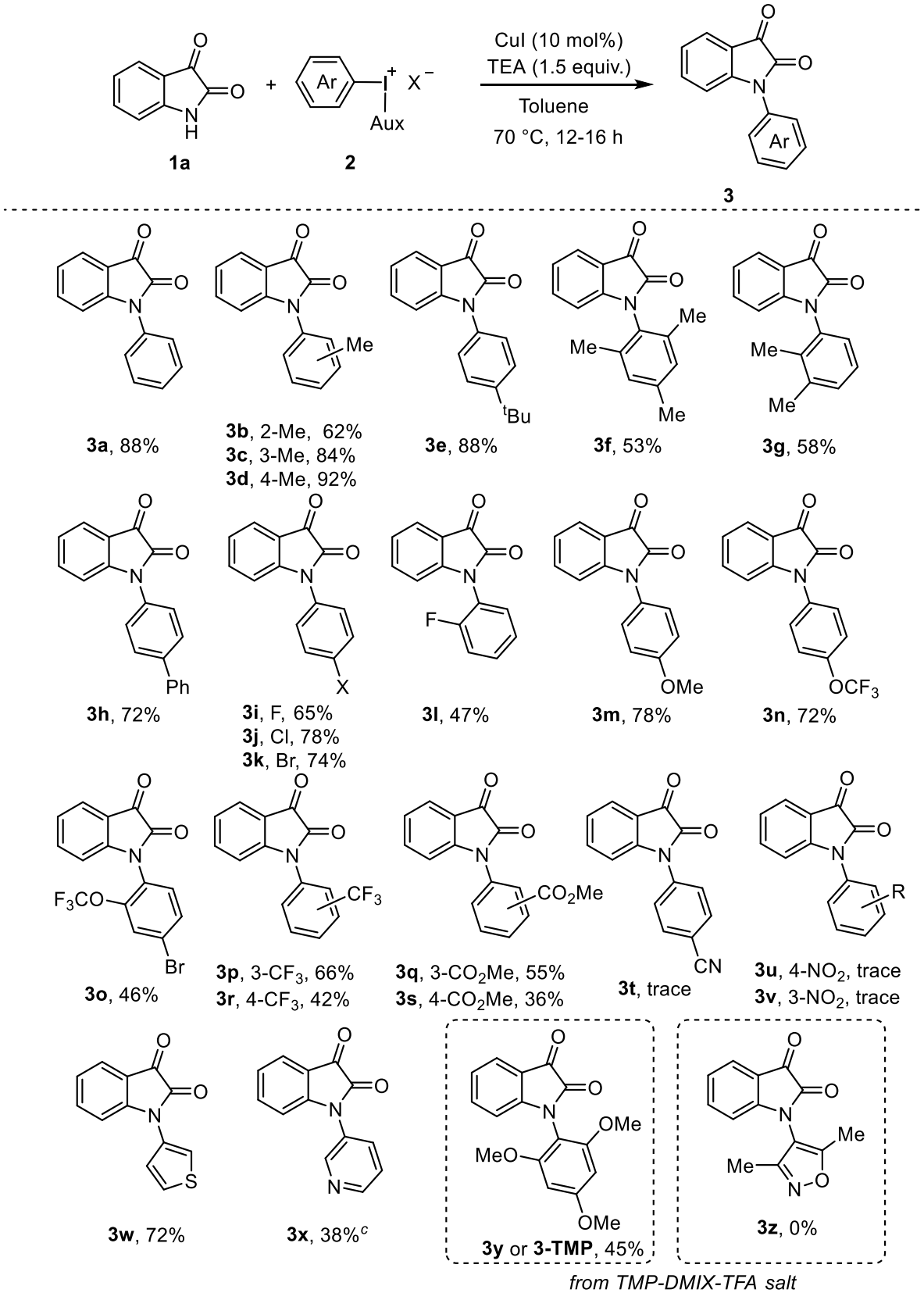
5. OVERALL ATTEMPTED SUBSTRATES

Scheme S6. Substrate scope of isatin derivatives[a]



[a]Reaction conditions: **1b-i** (0.2 mmol), **2a-TMP(TFA)** (1.1 equiv.), and solvent (3 ml) were used. [b]Isolated yield. TMP, i.e., 2,4,6-trimethoxyphenyl.

Scheme S7. Scope of the iodonium salts[a]



[a]Reaction conditions: **1a** (0.2 mmol), **2** (1.1 equiv.), and solvent (3 ml) were used. [b]Isolated yield. [c]Using Mes/OTf salt. TMP, i.e., 2,4,6-trimethoxyphenyl. Mes, i.e., Mesityl.

6. CRYSTALLOGRAPHIC DATA

6.1. Crystal structure of 3j (1-(4-chlorophenyl)indoline-2,3-dione):

Good quality crystals were obtained by slow evaporation of solvent from a solution of the compound **3j** in chloroform.

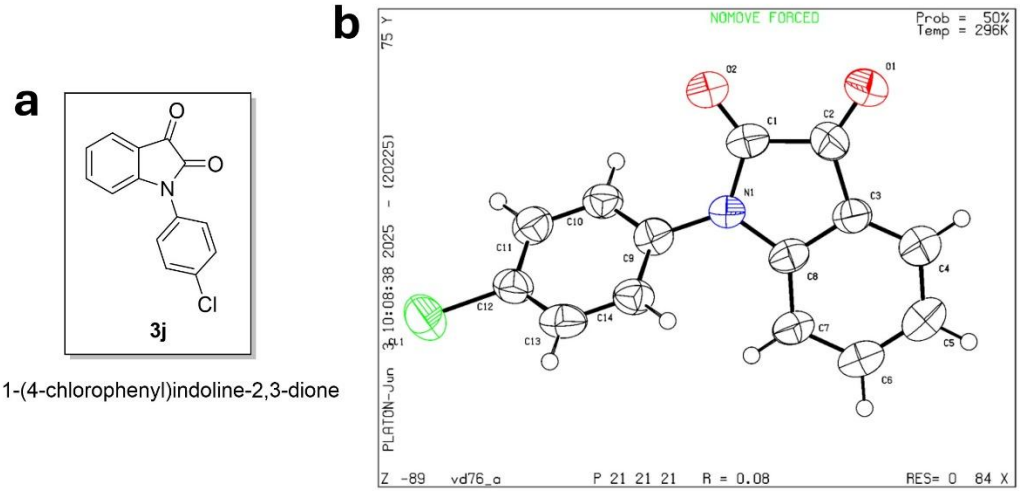


Figure 1. a) Chemical structure of **3j** and b) ORTEP diagram of the compound **3j** with 50% probability ellipsoid.

Obtained data for 3j:

Empirical formula	$C_{14}H_8ClNO_2$
CCDC No.	2456163
Formula weight	257.66
Temperature/K	100
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	3.9146(19)
b/Å	13.289(7)
c/Å	21.939(11)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1141.3(10)
Z	4

ρ_{calc}/cm^3	1.500
μ/mm^{-1}	0.325
F(000)	528.0
Reflections (R) collected	2903
Unique observed	1092
R1	0.0816
wR^2	0.2374

6.2. Crystal structure of 4b [5-fluoro-1-phenylindoline-2,3-dione]:

Good quality crystals were obtained by slow evaporation of solvent from a solution of the compound **4b** in chloroform.

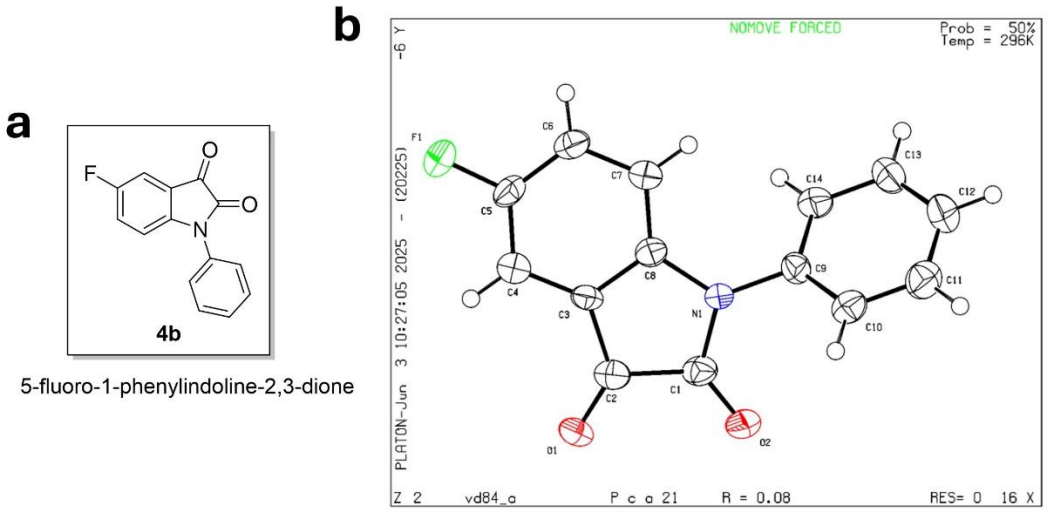


Figure 1. a) Chemical structure of **4b** and b) ORTEP diagram of the compound **4b** with 50% probability ellipsoid.

Obtained data for 4b:

Empirical formula	$C_{14}H_8FNO_2$
CCDC No.	2456164
Formula weight	241.21
Temperature/K	100
Crystal system	orthorhombic
Space group	$Pca2_1$

a/Å	21.146(14)
b/Å	6.933(5)
c/Å	7.634(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1119.1(13)
Z	4
ρ_{calc}/cm^3	1.432
μ/mm^{-1}	0.108
F(000)	496.0
Reflections (R) collected	2865
Unique observed	1380
R1	0.0837
wR^2	0.2420

6.1. Crystal structure of 4d (4-bromo-1-phenylindoline-2,3-dione):

Good quality crystals were obtained by slow evaporation of solvent from a solution of the compound **4d** in chloroform.

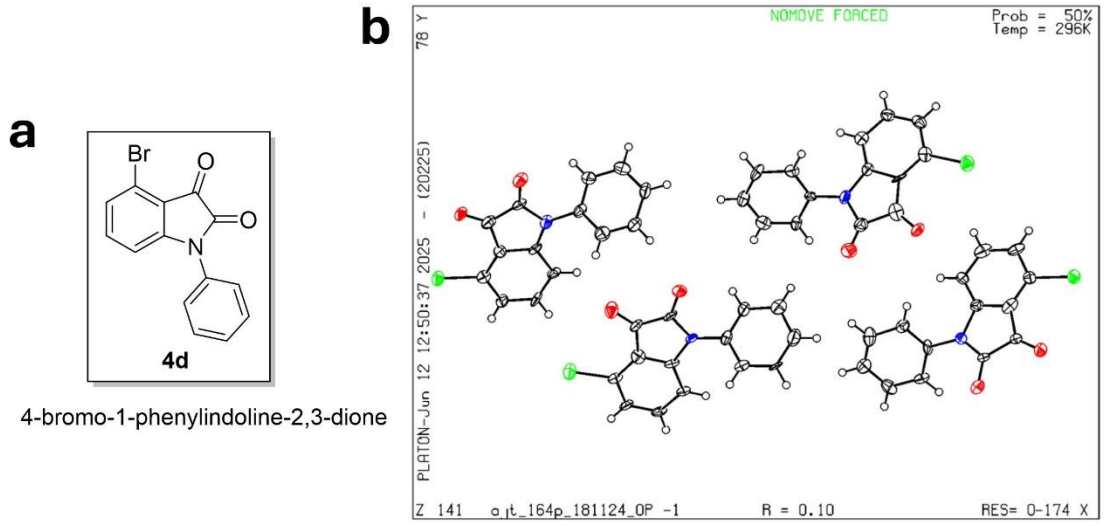


Figure 1. a) Chemical structure of **4d**. b) ORTEP diagram of the compound **4d** with 50% probability ellipsoid.

Obtained data for 4d:

Empirical formula	$C_{14}H_8BrNO_2$
CCDC No.	2463849
Formula weight	302.12
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	3.938(6)
b/Å	13.90(2)
c/Å	43.76(6)
α/°	98.65(5)
β/°	88.67(5)
γ/°	89.92(5)
Volume/Å^3	2367(6)
Z	8
ρ_{calc}/cm^3	1.696
μ/mm^{-1}	3.465
F(000)	1200.0
Reflections (R) collected	12756
Unique observed	4339
R1	0.0983
wR^2	0.3318

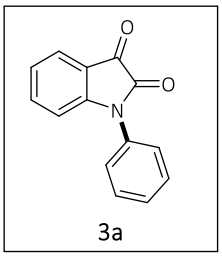
7. GENERAL PROCEDURE FOR *N*-ARYLATION OF INDOLINE-2,3-DIONES

General procedure (GP). To an oven-dried Schlenk tube, indoline-2,3-diones 1 (0.5 mmol), aryl(TMP)iodonium salt (0.55 mmol, 1.1 equiv.), CuI (0.025 mmol, 0.1 equiv.), and Et_3N (TEA, 0.75 mmol, 1.5 equiv.) were added. After adding dry toluene (3 mL, 0.1 M), the tube was sealed and stirred at room temperature to 70 °C. The reaction mixture was stirred for 10-12 h at 70 °C. The reaction mixture was then passed through Celite and washed with minimal EtOAc (15-20 mL). The organic mixture was then mixed with water, followed by a brine wash. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure.

Then, the crude product was purified using flash column chromatography (using 60-120 mesh silica with an eluent of 10:90 EtOAc/hexane) to obtain the desired product.

8. SYNTHESIS AND CHARACTERIZATION OF *N*-ARYL PRODUCTS

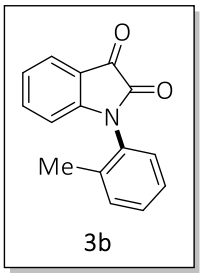
1-phenylindoline-2,3-dione (3a)[5]



Following **GP**, starting from isatin **1a** (74 mg, 0.5 mmol) and **2a-TMP(TFA)** (267 mg, 0.55 mmol). The reaction mixture was stirred for 12 h and purified by column chromatography (AcOEt/Hexane: 5/95→10/90) to afford **3a** (98 mg, 0.43 mmol, 88%) as an orange solid. R_f 0.2 (AcOEt /Hexane: 20/80).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8 Hz, 1H), 7.50-7.55 (m, 3H), 7.39-7.46 (m, 3H), 7.16 (t, *J* = 8 Hz, 1H), 6.88 (d, *J* = 8 Hz, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 183.0, 157.4, 151.7, 138.5, 132.9, 130.0, 128.9, 126.1, 125.7, 124.4, 117.5, 111.4. HRMS (ESI) *m/z*: $[M+Na]^+$ calculated for $C_{14}H_9NO_2Na$ 246.0525; found 246.0520.

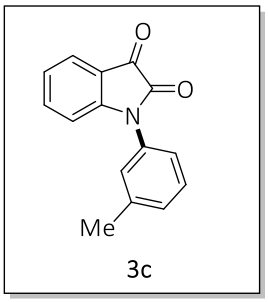
1-(*o*-tolyl)indoline-2,3-dione (3b)



Following **GP**, starting from isatin **1a** (74 mg, 0.5 mmol) and **2b-TMP(TFA)** (275 mg, 0.55 mmol). The reaction mixture was stirred for 12 h and purified by column chromatography (AcOEt/Hexane: 5/95→10/90) to afford **3b** (74 mg, 0.31 mmol, 62%) as an orange solid. R_f 0.6 (AcOEt /Hexane: 20/80).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8 Hz, 1H), 7.50 (t, *J* = 8 Hz, 1H), 7.31-7.41 (m, 3H), 7.22-7.25 (m, 1H), 7.14 (t, *J* = 8 Hz, 1H), 6.53 (d, *J* = 8 Hz, 1H), 2.21 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 182.3, 156.3, 152.6, 138.9, 136.2, 131.8, 131.5, 129.7, 127.5, 127.4, 125.4, 124.0, 117.4, 111.2, 17.1. HRMS (ESI) *m/z*: $[M+Na]^+$ calculated for $C_{15}H_{11}NO_2Na$ is 260.0682; found 260.0686.

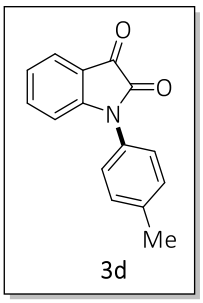
1-(*m*-tolyl)indoline-2,3-dione (3c)[6]



Following **GP**, starting from isatin **1a** (74 mg, 0.5 mmol) and **2c-TMP(TFA)** (275 mg, 0.55 mmol). The reaction mixture was stirred for 12 h and purified by column chromatography (AcOEt/Hexane: 5/95→10/90) to afford **3c** (100 mg, 0.42 mmol, 84%) as an orange solid. R_f 0.6 (AcOEt /Hexane: 20/80).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8 Hz, 1H), 7.54 (t, *J* = 8 Hz, 1H), 7.44 (t, *J* = 8 Hz, 1H), 7.26-7.28 (m, 1H), 7.19-7.22 (m, 2H), 7.15-7.18 (m, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 2.43 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 182.9, 157.2, 152.2, 140.1, 138.2, 133.4, 129.6, 129.6, 126.5, 125.4, 124.1, 122.9, 117.3, 111.2, 21.3. HRMS (ESI) *m/z*: $[M+Na]^+$ calculated for $C_{15}H_{11}NO_2Na$ is 260.0682; found 260.0682.

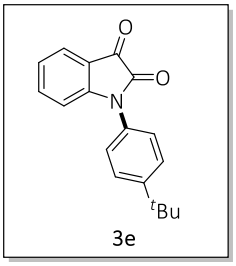
1-(*p*-tolyl)indoline-2,3-dione (3d)[7]



Following **GP**, starting from isatin **1a** (74 mg, 0.5 mmol) and **2d-TMP(TFA)** (275 mg, 0.55 mmol). The reaction mixture was stirred for 12 h and purified by column chromatography (AcOEt/Hexane: 5/95→10/90) to afford **3d** (109 mg, 0.45 mmol, 92%) as an orange solid. R_f 0.4 (AcOEt /Hexane: 20/80).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8 Hz, 1H), 7.53 (t, *J* = 8 Hz, 1H), 7.34-7.37 (m, 2H), 7.26-7.30 (m, 2H), 7.16 (t, *J* = 8 Hz, 1H), 6.87 (d, *J* = 8 Hz, 1H), 2.43 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 182.6, 157.7, 152.1, 139.2, 136.9, 130.8, 129.9, 126.1, 125.7, 124.4, 116.7, 111.5, 21.5. HRMS (ESI) *m/z*: $[M+Na]^+$ calculated for $C_{15}H_{11}NO_2Na$ is 260.0682; found 260.0684.

1-(4-(*tert*-butyl)phenyl)indoline-2,3-dione (3e)

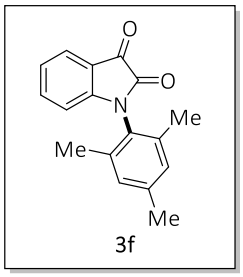


Following **GP**, starting from isatin **1a** (74 mg, 0.5 mmol) and **2e-TMP(TFA)** (298 mg, 0.55 mmol). The reaction mixture was stirred for 12 h and purified by column chromatography (AcOEt/Hexane: 5/95→10/90) to afford **3e** (123 mg, 0.44 mmol, 88%) as an orange solid. R_f 0.6 (AcOEt /Hexane: 20/80).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8 Hz, 1H), 7.51-7.55 (m, 3H) 7.32 (d, *J* = 8 Hz, 2H), 7.14 (t, *J* = 8 Hz, 1H), 6.90 (d, *J* = 8 Hz, 1H), 1.35 (s, 9H). **^{13}C{^{1}H} NMR** (100 MHz,

$CDCl_3$) δ 182.6, 156.4, 152.2, 152.1, 137.6, 130.3, 127.2, 125.7, 124.4, 116.4, 109.6, 34.3, 31.4. HRMS (ESI) *m/z*: $[M+Na]^+$ calculated for $C_{18}H_{17}NO_2Na$ is 302.1151; found 302.1150.

1-mesitylindoline-2,3-dione (3f)[8]

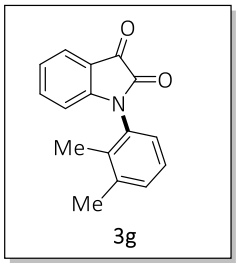


3f

Following **GP**, starting from isatin **1a** (74 mg, 0.5 mmol) and **2f-TMP(TFA)** (290 mg, 0.55 mmol). The reaction mixture was stirred for 12 h and purified by column chromatography (AcOEt/Hexane: 5/95→ 10/90) to afford **3f** (70 mg, 0.26 mmol, 53 %) as an orange solid. R_f 0.7 (AcOEt /Hexane: 20/80).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8 Hz, 1H), 7.50 (t, *J* = 8 Hz, 1H), 7.12-7.18 (m, 1H), 7.03 (s, 2H), 6.43 (d, *J* = 8 Hz, 1H), 2.35 (s, 3H), 2.13 (s, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 182.4, 156.4, 151.2, 139.9, 138.9, 137.6, 130.0, 127.5, 125.9, 123.8, 117.8, 110.2, 22.2, 19.3. HRMS (ESI) *m/z*: $[M+Na]^+$ calculated for $C_{17}H_{15}NO_2Na$ is 288.0995; found 288.0994.

1-(2,3-dimethylphenyl)indoline-2,3-dione (3g)

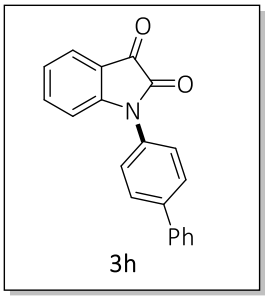


3g

Following **GP**, starting from isatin **1a** (74 mg, 0.5 mmol) and **2g-TMP(TFA)** (282 mg, 0.55 mmol). The reaction mixture was stirred for 12 h and purified by column chromatography (AcOEt/Hexane: 5/95→10/90) to afford **3g** (73 mg, 0.29 mmol, 58 %) as a red solid. R_f 0.7 (AcOEt /Hexane: 20/80).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8 Hz, 1H), 7.51 (t, *J* = 8 Hz, 1H), 7.23-7.32 (m, 2H), 7.15 (t, *J* = 8 Hz, 1H), 7.11 (d, *J* = 8 Hz, 1H), 6.55 (d, *J* = 8.0 Hz, 1H), 2.37 (s, 3H), 2.11 (s, 3H). **^{13}C NMR{^{1}H}** (100 MHz, $CDCl_3$) δ 182.7, 158.1, 152.9, 139.5, 138.7, 135.0, 131.8, 131.4, 127.2, 125.7, 125.2, 124.3, 117.6, 112.1, 20.6, 14.7. HRMS (ESI) *m/z*: $[M+Na]^+$ calculated for $C_{16}H_{13}NO_2Na$ is 274.0838; found 274.0837.

1-(1,1'-biphenyl]-4-yl)indoline-2,3-dione (3h)[6]

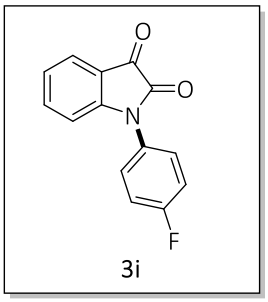


3h

Following **GP**, starting from isatin **1a** (74 mg, 0.5 mmol) and **2h-TMP(TFA)** (309 mg, 0.55 mmol). The reaction mixture was stirred for 12 h and purified by column chromatography (AcOEt/Hexane: 5/95→10/90) to afford **3h** (108 mg, 0.36 mmol, 72 %) as an orange solid. R_f 0.3 (AcOEt /Hexane: 20/80).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 80 Hz, 2H), 7.63 (d, *J* = 8 Hz, 1H), 7.54 (d, *J* = 8 Hz, 2H), 7.42-7.56 (m, 1H), 7.41 (t, *J* = 8 Hz, 4H), 7.30-7.36 (m, 1H), 7.08-7.14 (m, 1H), 6.90 (d, *J* = 8.0 Hz, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 181.8, 157.6, 151.8, 142.0, 140.1, 138.6, 132.1, 129.2, 128.8, 128.1, 127.4, 126.4, 125.9, 124.6, 117.7, 111.6. HRMS (ESI) *m/z*: $[M+Na]^+$ calculated for $C_{20}H_{13}NO_2Na$ is 276.0631; found 276.0633.

1-(4-fluorophenyl)indoline-2,3-dione (3i)[8]

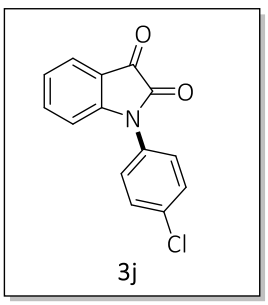


3i

Following **GP**, starting from isatin **1a** (74 mg, 0.5 mmol) and **2i-TMP(TFA)** (277 mg, 0.55 mmol). The reaction mixture was stirred for 12 h and purified by column chromatography (AcOEt/Hexane: 5/95→10/90) to afford **3i** (78 mg, 0.32 mmol, 65 %) as an orange solid. R_f 0.5 (AcOEt /Hexane: 20/80).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8 Hz, 1H), 7.56 (t, *J* = 8 Hz, 1H), 7.39-7.43 (m, 2H), 7.23-7.28 (m, 2H), 7.19 (t, *J* = 8 Hz, 1H), 6.85 (d, *J*= 8 Hz, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 182.8, 162.5 (d, $^1J_{C\text{-}F}$ = 248 Hz), 157.6, 138.6, 128.9 (d, $^4J_{C\text{-}F}$ = 4 Hz), 128.3 (d, $^3J_{C\text{-}F}$ = 8 Hz), 126.0, 124.7, 117.7, 117.2 (d, $^2J_{C\text{-}F}$ = 23 Hz), 111.3. **^{19}F NMR** (375 MHz, $CDCl_3$) δ -111.30. HRMS (ESI) *m/z*: $[M+Na]^+$ calculated for $C_{14}H_8FNO_2Na$ is 264.0431; found 264.0431.

1-(4-chlorophenyl)indoline-2,3-dione (3j)[8]

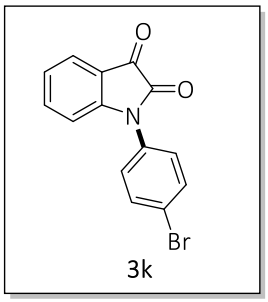


3j

Following **GP**, starting from isatin **1a** (74 mg, 0.5 mmol) and **2j-TMP(TFA)** (286 mg, 0.55 mmol). The reaction mixture was stirred for 12 h and purified by column chromatography (AcOEt/Hexane: 5/95→10/90) to afford **3j** (101 mg, 0.39 mmol, 78 %) as an orange solid. R_f 0.5 (AcOEt /Hexane: 20/80).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8 Hz, 1H), 7.53-7.59 (m Hz, 3H), 7.38 (d, *J* = 8 Hz, 2H), 7.20 (t, *J* = 8 Hz, 1H), 6.89 (d, *J* = 8 Hz, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 190.1, 165.4, 151.3, 137.9, 134.4, 129.8, 127.5, 126.5, 124.8, 117.0, 113.6, 111.8. HRMS (ESI) *m/z*: $[M+Na]^+$ calculated for $C_{18}H_{17}ClNO_2Na$ is 280.0136; found 280.0134.

1-(4-bromophenyl)indoline-2,3-dione (3k)[8]

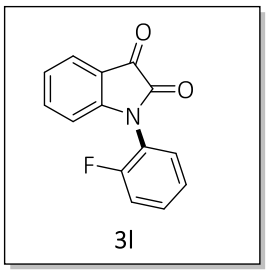


3k

Following **GP**, starting from isatin **1a** (74 mg, 0.5 mmol) and **2k-TMP(TFA)** (310 mg, 0.55 mmol). The reaction mixture was stirred for 12 h and purified by column chromatography (AcOEt/Hexane: 5/95→10/90) to afford **3k** (112 mg, 0.37 mmol, 74 %) as an orange solid. R_f 0.5 (AcOEt /Hexane: 20/80).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.72 (m, 3H), 7.55-7.59 (m, 1H), 7.32 (d, *J* = 8 Hz, 2H), 7.18-7.20 (m, 1H), 6.90 (d, *J* = 8.0 Hz, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 180.3, 158.4, 151.6, 140.4, 135.5, 131.9, 127.1, 126.3, 125.2, 123.0, 117.5, 111.7. HRMS (ESI) *m/z*: $[M+Na]^+$ calculated for $C_{14}H_8BrNO_2Na$ is 323.9631; found 323.9638.

1-(2-fluorophenyl)indoline-2,3-dione (3l)

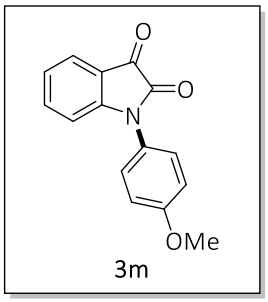


3l

Following **GP**, starting from isatin **1a** (74 mg, 0.5 mmol) and **2l-TMP(TFA)** (277 mg, 0.55 mmol). The reaction mixture was stirred for 12 h and purified by column chromatography (AcOEt/Hexane: 5/95→10/90) to afford **3l** (57 mg, 0.23 mmol, 47 %) as an orange solid. R_f 0.3 (AcOEt /Hexane: 20/80).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8 Hz, 1H), 7.56 (t, *J* = 8 Hz, 1H), 7.41-7.53 (m, 2H), 7.29-7.37 (m, 2H), 7.19 (t, *J* = 8 Hz, 1H), 6.72 (d, *J* = 8 Hz, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 182.4, 157.8 (d, $^{1}J_{C\text{-}F}$ = 252 Hz), 157.4, 151.2, 138.7, 131.3 (d, $^{3}J_{C\text{-}F}$ = 8 Hz), 129.2, 125.8, 125.5 (d, $^{3}J_{C\text{-}F}$ = 4 Hz), 124.6, 120.6 (d, $^{2}J_{C\text{-}F}$ = 13 Hz), 117.8, 117.6 (d, $^{2}J_{C\text{-}F}$ = 19 Hz), 111.5. **^{19}F NMR** (375 MHz, $CDCl_3$) δ -117.34. HRMS (ESI) *m/z*: $[M+Na]^+$ calculated for $C_{14}H_8FNO_2Na$ is 264.0431; found 264.0434.

1-(4-methoxyphenyl)indoline-2,3-dione (3m)[9]

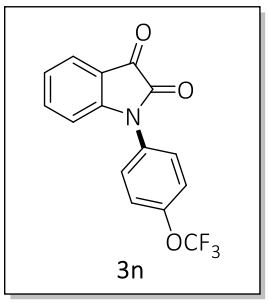


3m

Following **GP**, starting from isatin **1a** (74 mg, 0.5 mmol) and **2m-TMP(TFA)** (283 mg, 0.55 mmol). The reaction mixture was stirred for 12 h and purified by column chromatography (AcOEt/Hexane: 5/95→10/90) to afford **3m** (99 mg, 0.39 mmol, 78 %) as a red solid. R_f 0.3 (AcOEt /Hexane: 20/80).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8 Hz, 1H), 7.46 (t, *J* = 8 Hz, 1H), 7.25 (d, *J* = 8 Hz, 2H), 7.08 (t, *J* = 8 Hz, 1H), 6.99 (d, *J* = 8 Hz, 2H), 6.76 (d, *J* = 8 Hz, 1H), 3.80 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 183.3, 159.5, 157.8, 152.8, 138.5, 127.6, 125.6, 125.5, 124.3, 117.6, 115.4, 111.4, 55.8. HRMS (ESI) *m/z*: $[M+Na]^+$ calculated for $C_{15}H_{11}NO_3Na$ is 276.0631; found 276.0633.

1-(4-(trifluoromethoxy)phenyl)indoline-2,3-dione (3n)

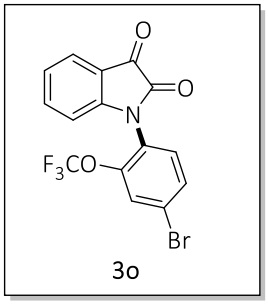


3n

Following **GP**, starting from isatin **1a** (74 mg, 0.5 mmol) and **2n-TMP(TFA)** (313 mg, 0.55 mmol). The reaction mixture was stirred for 12 h and purified by column chromatography (AcOEt/Hexane: 5/95→10/90) to afford **3n** (111 mg, 0.36 mmol, 72 %) as a yellow solid. R_f 0.3 (AcOEt /Hexane: 20/80).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8 Hz, 1H), 7.58 (t, *J* = 8 Hz, 1H), 7.49 (d, *J* = 8 Hz, 2H), 7.41 (d, *J* = 8 Hz, 2H), 7.21 (t, *J* = 8 Hz, 1H), 6.91 (d, *J* = 8 Hz, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 182.5, 158.3, 151.7 (q, *J* = 2 Hz), 149.1, 127.7, 126.1, 124.8, 122.7, 121.9 (q, $^1J_{C\text{-}F}$ = 257 Hz), 117.8, 111.3. **^{19}F NMR** (375 MHz, $CDCl_3$) δ -57.74. HRMS (ESI) *m/z*: $[M+Na]^+$ calculated for $C_{15}H_8F_3NO_2Na$ is 330.0348; found 330.0349.

1-(4-bromo-2-(trifluoromethoxy)phenyl)indoline-2,3-dione (3o)



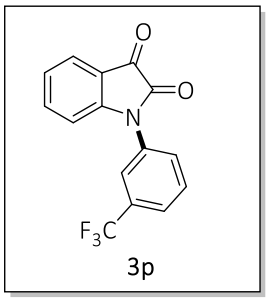
3o

Following **GP**, starting from isatin **1a** (74 mg, 0.5 mmol) and **2o-TMP(TFA)** (356 mg, 0.55 mmol). The reaction mixture was stirred for 12 h and purified by column chromatography (AcOEt/Hexane: 5/95→10/90) to afford **3o** (89 mg, 0.23 mmol, 46 %) as an orange solid. R_f 0.4 (AcOEt /Hexane: 20/80).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8 Hz, 1H), 7.68-7.62 (m, 2H), 7.60-7.55 (m, 1H), 7.36 (d, *J* = 8 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 6.64 (d, *J* = 8.0 Hz,

1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 181.8, 157.1, 145.7, 138.8, 130.9, 126.0, 125.6 (d, *J* = 2 Hz), 124.9, 124.6, 124.1, 120.2 (q, $^{1}J_{C\text{-}F}$ = 260 Hz), 117.7, 111.3. **^{19}F NMR** (375 MHz, $CDCl_3$) δ -57.46. HRMS (ESI) *m/z*: $[M+Na]^+$ calculated for $C_{15}H_7O_3NF_3BrNa$ 407.9454; found 407.9454.

1-(3-(trifluoromethyl)phenyl)indoline-2,3-dione (3p)[8]

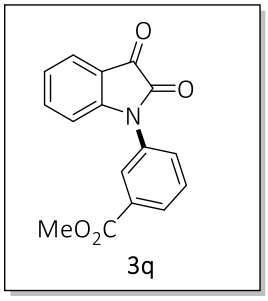


3p

Following **GP**, starting from isatin **1a** (74 mg, 0.5 mmol) and **2p-TMP(TFA)** (304 mg, 0.55 mmol). The reaction mixture was stirred for 12 h and purified by column chromatography (AcOEt/Hexane: 5/95→10/90) to afford **3p** (96 mg, 0.33 mmol, 66 %) as an orange solid. R_f 0.3 (AcOEt /Hexane: 20/80).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.61 (m, 4H), 7.59 (d, *J* = 6.5 Hz, 1H), 7.55-7.49 (m, 1H), 7.16 (t, *J* = 7.1 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 182.3, 151.0, 133.7, 132.9, 132.7 (q, $^{2}J_{C\text{-}F}$ = 33 Hz), 130.9, 129.7, 126.2, 125.8 (q, $^{3}J_{C\text{-}F}$ = 4 Hz), 125.0, 123.5 (q, $^{1}J_{C\text{-}F}$ = 271 Hz), 123.04 (q, $^{3}J_{C\text{-}F}$ = 4 Hz), 111.2. **^{19}F NMR** (375 MHz, $CDCl_3$) δ -62.60. HRMS (ESI) *m/z*: $[M+Na]^+$ calculated for $C_{15}H_8F_3NO_2Na$ 314.0399; found 314.0398.

methyl 3-(2,3-dioxoindolin-1-yl)benzoate (3q)[9]

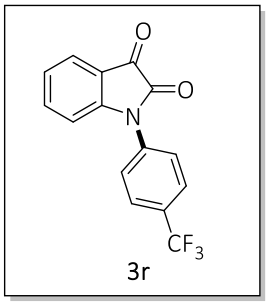


3q

Following **GP**, starting from isatin **1a** (74 mg, 0.5 mmol) and **2q-TMP(TFA)** (120 mg, 0.55 mmol). The reaction mixture was stirred for 12 h and purified by column chromatography (AcOEt/Hexane: 5/95→10/90) to afford **3q** (77 mg, 0.28 mmol, 55 %) as an orange solid. R_f 0.4 (AcOEt /Hexane: 20/80).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10-8.17 (m, 2H), 7.72 (d, *J* = 8 Hz, 1H), 7.65-7.67 (m, 2H), 7.57 (t, *J* = 8 Hz, 1H), 7.21 (t, *J* = 8 Hz, 1H), 6.91 (d, *J* = 8 Hz, 1H), 3.95 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 183.5, 166.0, 156.3, 151.4, 138.2, 133.4, 132.3, 130.8, 130.4, 130.0, 127.1, 126.0, 124.8, 117.7, 109.8, 52.2. HRMS (ESI) *m/z*: $[M+Na]^+$ calculated for $C_{16}H_{11}NO_4Na$ is 304.0580; found 304.0581.

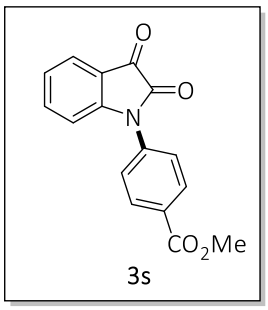
1-(4-(trifluoromethyl)phenyl)indoline-2,3-dione (3r)[9]



Following **GP**, starting from isatin **1a** (74 mg, 0.5 mmol) and **2r-TMP(TFA)** (304 mg, 0.55 mmol). The reaction mixture was stirred for 12 h and purified by column chromatography (AcOEt/Hexane: 5/95→10/90) to afford **3r** (61 mg, 0.21 mmol, 42 %) as an orange solid. R_f 0.4 (AcOEt /Hexane: 20/80).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8 Hz, 2H), 7.75 (d, *J* = 8 Hz, 1H), 7.56-7.62 (m, 3H), 7.24 (t, *J* = 8 Hz, 1H), 6.97 (d, *J* = 8 Hz, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 181.6, 156.7, 150.4, 140.1, 136.2, 130.9 (q, $^2J_{C\text{-}F}$ = 33 Hz), 127.3 (d, $^3J_{C\text{-}F}$ = 4 Hz), 126.3, 126.2, 125.1, 123.7 (q, $^1J_{C\text{-}F}$ = 270 Hz), 117.8, 113.4. **^{19}F NMR** (375 MHz, $CDCl_3$) δ -62.55. HRMS (ESI) *m/z*: $[M+Na]^+$ calculated for $C_{15}H_8F_3NO_2Na$ is 314.0399; found 314.0399.

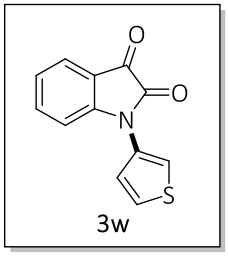
methyl-4-(2,3-dioxoindolin-1-yl)benzoate (3s)



Following **GP**, starting from isatin **1a** (74 mg, 0.5 mmol) and **2s-TMP(TFA)** (298 mg, 0.55 mmol). The reaction mixture was stirred for 12 h and purified by column chromatography (AcOEt/Hexane: 5/95→10/90) to afford **3s** (51 mg, 0.18 mmol, 36 %) as an orange solid. R_f 0.4 (AcOEt /Hexane: 20/80).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8 Hz, 2H), 7.72-7.75 (m, 1H), 7.58-7.61 (m, 1H), 7.55 (d, *J* = 8 Hz, 2H), 7.22 (t, *J* = 8 Hz, 1H), 6.98 (d, *J* = 8 Hz, 1H), 3.97 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.4, 166.2, 157.2, 151.5, 138.2, 137.1, 131.4, 130.4, 126.9, 125.7, 124.2, 117.9, 111.5, 52.7. HRMS (ESI) *m/z*: $[M+Na]^+$ calculated for $C_{16}H_{11}NO_4Na$ is 304.0580; found 304.0586.

1-(thiophen-3-yl)indoline-2,3-dione (3w)[9]

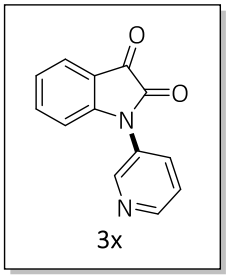


Following **GP**, starting from isatin **1a** (74 mg, 0.5 mmol) and **2w-TMP(TFA)** (270 mg, 0.55 mmol). The reaction mixture was stirred for 12 h and purified by column chromatography (AcOEt/Hexane: 5/95→10/90) to afford **3w** (83 mg, 0.36 mmol, 72 %) as a red solid. R_f 0.2 (AcOEt /Hexane: 20/80).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8 Hz, 1H), 7.59 (t, *J* = 8 Hz, 1H), 7.48-7.51 (m, 2H), 7.21-7.24 (m, 1H), 7.18 (t, *J* = 8 Hz, 1H), 7.04 (d, *J* = 8 Hz, 1H). **^{13}C{^{1}H} NMR** (100

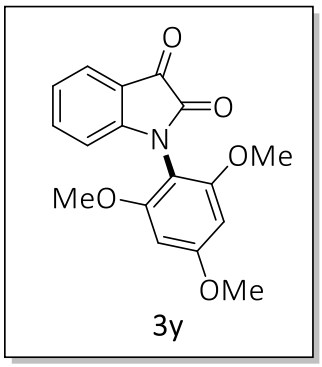
MHz, $CDCl_3$) δ 182.6, 157.4, 152.3, 139.5, 132.5, 127.6, 125.8, 124.6, 123.9, 120.8, 118.8, 111.6. HRMS (ESI) *m/z*: $[M+Na]^+$ calculated for $C_{12}H_7NO_2SNa$ is 252.0090; found 252.0089.

1-(pyridin-3-yl)indoline-2,3-dione (3x)



Following **GP**, starting from isatin **1a** (89 mg, 0.6 mmol) and **2x-Mes(OTf)** (312 mg, 0.66 mmol). The reaction mixture was stirred for 12 h and purified by column chromatography (AcOEt/Hexane: 20/80→30/70) to afford **3x** (51 mg, 0.23 mmol, 38 %) as a red solid. R_f 0.4 (AcOEt /Hexane: 30/70). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.72 (d, *J* = 8 Hz, 1H), 7.82 (dq, *J* = 8 and 1.6 Hz, 1H), 7.74-7.76 (m, 1H), 7.60 (dt, *J* = 8 and 1.2 Hz, 1H), 7.53-7.56 (m, 1H), 7.24 (t, *J* = 8 Hz, 1H), 6.93 (d, *J* = 8 Hz, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 182.2, 156.9, 150.9, 150.0, 146.7, 138.3, 133.5, 130.3, 126.3, 125.1, 123.7, 117.8, 111.6. HRMS (ESI) *m/z*: $[M+Na]^+$ calculated for $C_{13}H_8N_2O_2Na$ is 247.0478; found 247.0488.

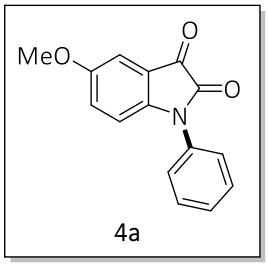
1-(2,4,6-trimethoxyphenyl)indoline-2,3-dione (3y)



Following **GP**, starting from isatin **1a** (74 mg, 0.5 mmol) and **2y-TMP(TFA)** (268 mg, 0.55 mmol). The reaction mixture was stirred for 12 h and purified by column chromatography (AcOEt/Hexane: 5/95→10/90) to afford **3y** (71 mg, 0.22 mmol, 45 %) as an orange solid. R_f 0.3 (AcOEt /Hexane: 20/80).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8 Hz, 1H), 7.47 (t, *J* = 8 Hz, 1H), 7.09 (t, *J* = 8 Hz, 1H), 6.50 (d, *J* = 8 Hz, 1H), 6.22 (s, 2H), 3.86 (s, 3H), 3.76 (s, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 182.6, 163.8, 158.3, 157.6, 153.8, 139.4, 138.4, 126.6, 125.2, 123.9, 123.6, 118.1, 113.8, 111.6, 105.0, 93.1, 57.5, 55.8. HRMS (ESI) *m/z*: $[M+Na]^+$ calculated for $C_{17}H_{15}NO_5Na$ is 336.0842; found 336.0845.

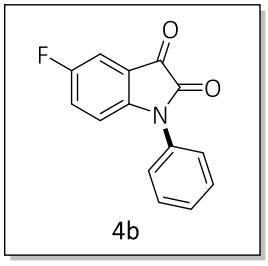
5-methoxy-1-phenylindoline-2,3-dione (4a)[9]



Following **GP**, starting from isatin **1b** (89 mg, 0.5 mmol) and **2a-TMP(TFA)** (266.3 mg, 0.55 mmol). The reaction mixture was stirred for 12 h and purified by column chromatography (AcOEt/Hexane: 5/95→10/90) to afford **4a** (109 mg, 0.43 mmol, 86 %) as a brown solid. R_f 0.3 (AcOEt /Hexane: 20/80).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.57 (m, 2H), 7.41-7.43 (m, 3H), 7.21 (d, J = 2 Hz, 1H), 7.08-7.11 (m, 1H), 6.85 (d, J = 8 Hz, 1H), 3.83 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 180.8, 157.6, 154.9, 145.8, 132.8, 129.4, 128.3, 125.9, 125.2, 118.1, 112.6, 108.1, 56.2. HRMS (ESI) *m/z*: $[M+Na]^+$ calculated for $C_{15}H_{11}NO_3Na$ is 276.0631; found 276.0639.

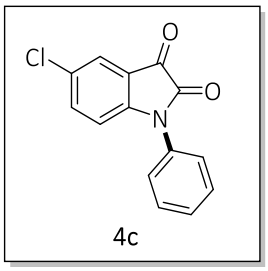
5-fluoro-1-phenylindoline-2,3-dione (4b)[9]



Following **GP**, starting from isatin **1c** (83 mg, mmol) and **2a-TMP(TFA)** (267 mg, 0.55 mmol). The reaction mixture was stirred for 12 h and purified by column chromatography (AcOEt/Hexane: 5/95→10/90) to afford **4b** (68 mg, 0.28 mmol, 56 %) as a deep red solid. R_f 0.4 (AcOEt /Hexane: 20/80).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.59 (m, 2H), 7.43-7.49 (m, 1H), 7.38-7.42 (m, 3H), 7.24-7.28 (m, 1H), 6.86-6.89 (m, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 181.9, 159.7 (d, $^1J_{C\text{-}F}$ = 245 Hz), 157.2, 148.0, 132.9, 130.3, 129.2, 126.1, 124.9 (d, $^2J_{C\text{-}F}$ = 24 Hz), 118.3 (d, $^3J_{C\text{-}F}$ = 7 Hz), 112.7 (d, $^3J_{C\text{-}F}$ = 1 Hz), 112.6 (d, $^2J_{C\text{-}F}$ = 33 Hz). **^{19}F NMR** (375 MHz, $CDCl_3$) δ -117.35. HRMS (ESI) *m/z*: $[M+Na]^+$ calculated for $C_{14}H_8FNO_2Na$ is 264.0431; found 264.0435.

5-chloro-1-phenylindoline-2,3-dione (4c)

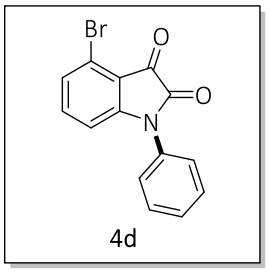


Following **GP**, starting from isatin **1d** (91 mg, 0.5 mmol) and **2a-TMP(TFA)** (267 mg, 0.55 mmol). The reaction mixture was stirred for 12 h and purified by column chromatography (AcOEt/Hexane: 5/95→10/90) to afford **4c** (93 mg, 0.36 mmol, 72 %) as an orange solid. R_f 0.5 (AcOEt /Hexane: 20/80).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 1.6 Hz, 1H), 7.66, 7.55-7.58 (m, 2H), 7.45-7.51 (m, 2H), 7.38-7.40 (m, 2H), 6.86 (d, J = 8 Hz, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ

192.7, 178.4, 156.3, 149.2, 137.3, 132.9, 130.6, 129.6, 126.4, 125.9, 118.4, 113.7. HRMS (ESI) *m/z*: $[M+Na]^+$ calculated for $C_{14}H_8ClNO_2Na$ is 280.0136; found 280.0147.

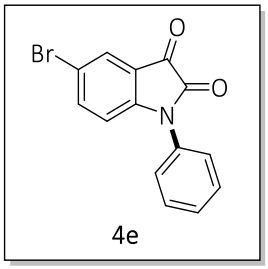
4-bromo-1-phenylindoline-2,3-dione (4d)



Following **GP**, starting from isatin **1e** (113 mg, 0.5 mmol) and **2a-TMP(TFA)** (267 mg, 0.55 mmol). The reaction mixture was stirred for 12 h and purified by column chromatography (AcOEt/Hexane: 5/95→10/90) to afford **4d** (95 mg, 0.31 mmol, 63 %) as an orange solid. R_f 0.4 (AcOEt /Hexane: 20/80).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (t, *J* = 8 Hz, 2H), 7.38-7.43 (m, 1H), 7.29-7.34 (m, 2H), 7.27 (d, *J* = 8 Hz, 1H), 7.21-7.24 (m, 1H), 6.75 (d, *J* = 8 Hz, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 179.9, 156.6, 153.4, 138.5, 132.1, 130.3, 129.4, 129.1, 126.4, 122.5, 116.9, 111.1. HRMS (ESI) *m/z*: $[M+Na]^+$ calculated for $C_{14}H_8BrNO_2Na$ 323.9631; found 325.9630.

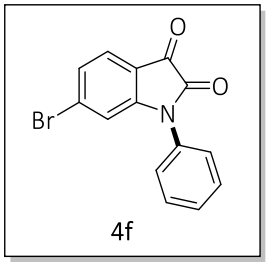
5-bromo-1-phenylindoline-2,3-dione (4e)



Following **GP**, starting from isatin **1f** (113 mg, 0.5 mmol) and **2a-TMP(TFA)** (267 mg, 0.55 mmol). The reaction mixture was stirred for 12 h and purified by column chromatography (AcOEt/Hexane: 5/95→10/90) to afford **4e** (77 mg, 0.25 mmol, 51 %) as a brown solid. R_f 0.4 (AcOEt /Hexane: 20/80).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 2 Hz, 1H), 7.63-7.65 (m, 1H), 7.54-7.60 (m, 2H), 7.45-7.50 (m, 1H), 7.37-7.40 (m, 2H), 6.81 (d, *J* = 8 Hz, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 182.0, 156.8, 151.2, 141.6, 132.7, 130.3, 129.4, 128.5, 126.1, 119.5, 117.3, 113.2. HRMS (ESI) *m/z*: $[M+Na]^+$ calculated for $C_{14}H_8BrNO_2Na$ is 323.9631; found 323.9631.

6-bromo-1-phenylindoline-2,3-dione (4f)



Following **GP**, starting from isatin **1g** (113 mg, 0.5 mmol) and **2a-TMP(TFA)** (267 mg, 0.55 mmol). The reaction mixture was stirred for 12 h and purified by column chromatography (AcOEt/Hexane: 5/95→10/90) to afford **4f** (106 mg, 0.35 mmol, 70 %) as an orange solid. R_f 0.4 (AcOEt /Hexane: 20/80).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.61 (m, 3H), 7.47-7.52 (m, 1H), 7.38-7.41 (m, 2H), 7.32-7.35 (m, 1H), 7.06 (s, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 181.0, 156.3, 151.9,

133.9, 132.6, 130.4, 129.5, 127.8, 126.8, 126.2, 116.3, 115.0. HRMS (ESI) *m/z*: $[M+Na]^+$ calculated for $C_{14}H_8BrNO_2Na$ is 323.9631; found 323.9637.

9. GRAM-SCALE SYNTHESIS

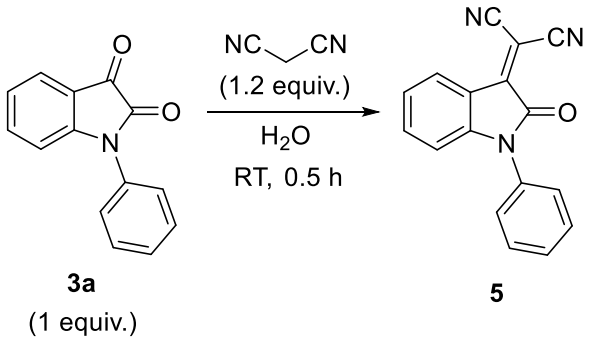
1-phenylindoline-2,3-dione (3a)

To an oven-dried 100 ml round-bottom flask, indoline-2,3-diones **1a** (5 mmol), **2a-TMP(TFA)** phenyl(TMP)iodonium salt (5.5 mmol, 1.1 equiv.), CuI (10 mol%, 0.5 mmol, equiv.), and Et_3N (TEA, 7.5 mmol, 1.5 equiv.) were added. After adding dry toluene (15 mL, 0.1 M), it was sealed with a rubber septum and stirred at 70 °C. The reaction mixture was stirred for 15 h. The reaction mixture was then passed through Celite and washed with minimal EtOAc (15−20 mL). The organic mixture was then mixed with water, followed by a brine wash. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Then, the crude product was purified using flash column chromatography (using 60-120 mesh silica with an eluent of 10:90 EtOAc/hexane) to obtain the desired product. The yield of the phenylated product was 76%.

10. METHODS FOR POST-MODIFICATIONS

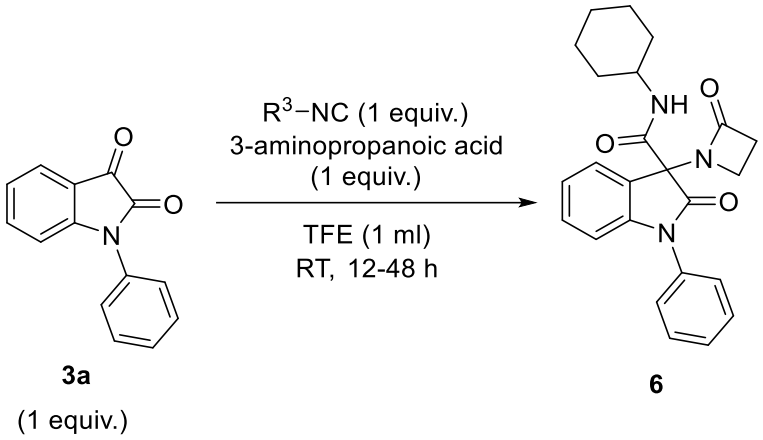
To illustrate the synthetic applicability of our method, an attempt was made to derivatize compound **3a** under different conditions (Scheme S8).

Mohsenzadeh and co-workers provided a general method for the preparation of isatylidene malononitriles from isatins (1 equiv.) and malononitrile (1.2 equiv.) in water (5 ml). The reaction was stirred at room temperature for 0.5 h (Scheme S8). The precipitated solid was filtered, washed with water, and dried to afford the corresponding products.[10]



Scheme S8. General procedure for the preparation of substituted isatylidene malononitriles

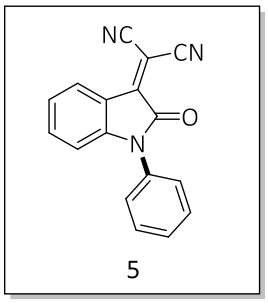
Pineiro and co-workers designed a three-component Ugi reaction employing substituted isatins (1 equiv.), 2-aminopropanoic acid (1 equiv.), and isocyanides (1 equiv.) as model substrates. They carried out the following reaction in the presence of 2,2,2-trifluoroethanol (1 ml) to synthesize β-lactam-oxindole hybrids under catalyst-free conditions (Scheme S9).[11]



Scheme S9. General procedure for the three-component Ugi reaction

11. CHARACTERIZATION DATA OF PRODUCTS OBTAINED FROM SYNTHETIC MODIFICATIONS

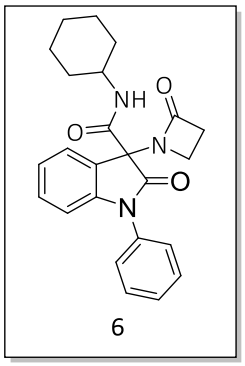
2-(2-oxo-1-phenylindolin-3-ylidene)malononitrile (5)[9]



Following the general method for preparation of **5,** starting from *N*-phenyl isatin **3a** (25 mg, 0.11 mmol) and malononitrile (8 mg, 0.11 mmol) in water (5 ml). The reaction was stirred at room temperature for 0.5 h. The heterogeneous mixture was filtered, washed with water, and dried to afford **5** (23 mg, 0.08 mmol, 77 %) as a deep red solid.

^{1}H NMR (400 MHz, DMSO-D_6) δ 8.01 (d, J = 8 Hz, 1H), 7.54-7.60 (m, 3H), 7.42-7.51 (m, 3H), 7.24 (t, J = 8 Hz, 1H), 6.78 (d, J = 8 Hz, 1H). **^{13}C NMR** (100 MHz, DMSO-D_6) δ 162.6, 151.2, 147.1, 137.8, 133.6, 129.8, 129.0, 127.2, 125.8, 124.0, 119.7, 114.4, 112.0, 110.8, 82.1. HRMS (ESI) *m/z*: $[M+Na]^+$ calculated for $C_{17}H_9N_3ONa$ is 294.0638; found 294.0636.

***N*-cyclohexyl-2-oxo-3-(2-oxoazetidin-1-yl)-1-phenylindoline-3-carboxamide (6)**[10]



Following the general method for preparation of **6** starting from *N*-phenyl isatin **3a** (40 mg, 0.18 mmol), 2-aminopropanoic acid (90 mg, 0.18 mmol), and cyclohexyl isocyanide (22 µl, 0.18 mmol). The reaction was stirred for 96 h at room temperature. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 20/80→30/70) to afford **6** (62 mg, 0.15 mmol, 85%) as an off-white solid. R_f 0.3 (AcOEt/Hexane: 30/70).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8 Hz, 1H), 7.53-7.57 (m, 2H), 7.45-7.48 (m, 3H), 7.29 (t, *J* = 8 Hz, 1H), 7.17 (t, *J* = 8 Hz, 1H), 6.80 (d, *J* = 8 Hz, 1H), 3.80-3.84 (m, 1NH), 3.60-3.64 (m, 1H), 3.40-3.43 (m, 1H), 2.94-2.97 (m, 1H), 1.97-2.00 (m, 1H), 1.83-1.87 (m, 1H), 1.57-1.76 (m, 4H), 1.21-1.39 (m, 6H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 171.0, 167.3, 162.4, 143.7, 133.7, 130.3, 130.0, 128.9, 127.1, 126.9, 125.4, 124.2, 110.2, 67.7, 49.3, 40.6, 36.3, 32.8, 32.6, 26.0, 24.7. HRMS (ESI) *m/z*: $[M+Na]^+$ calculated for $C_{24}H_{25}N_3O_3Na$ is 426.1788; found 426.1788.

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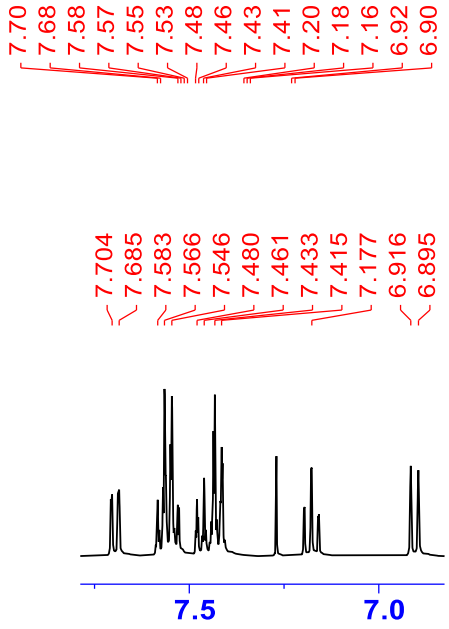
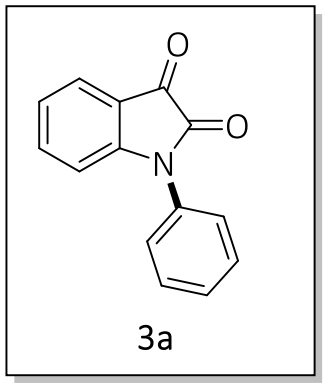
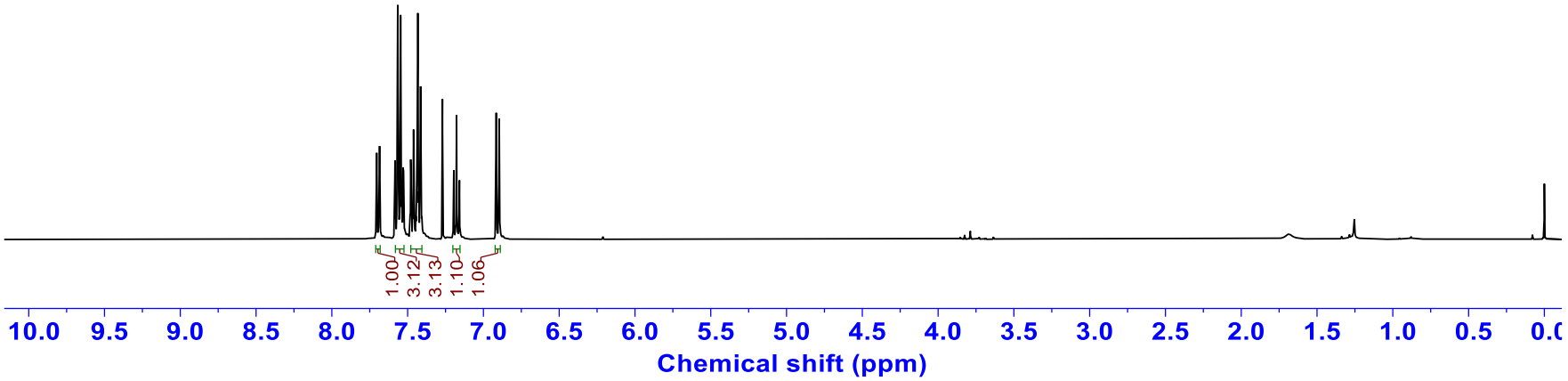
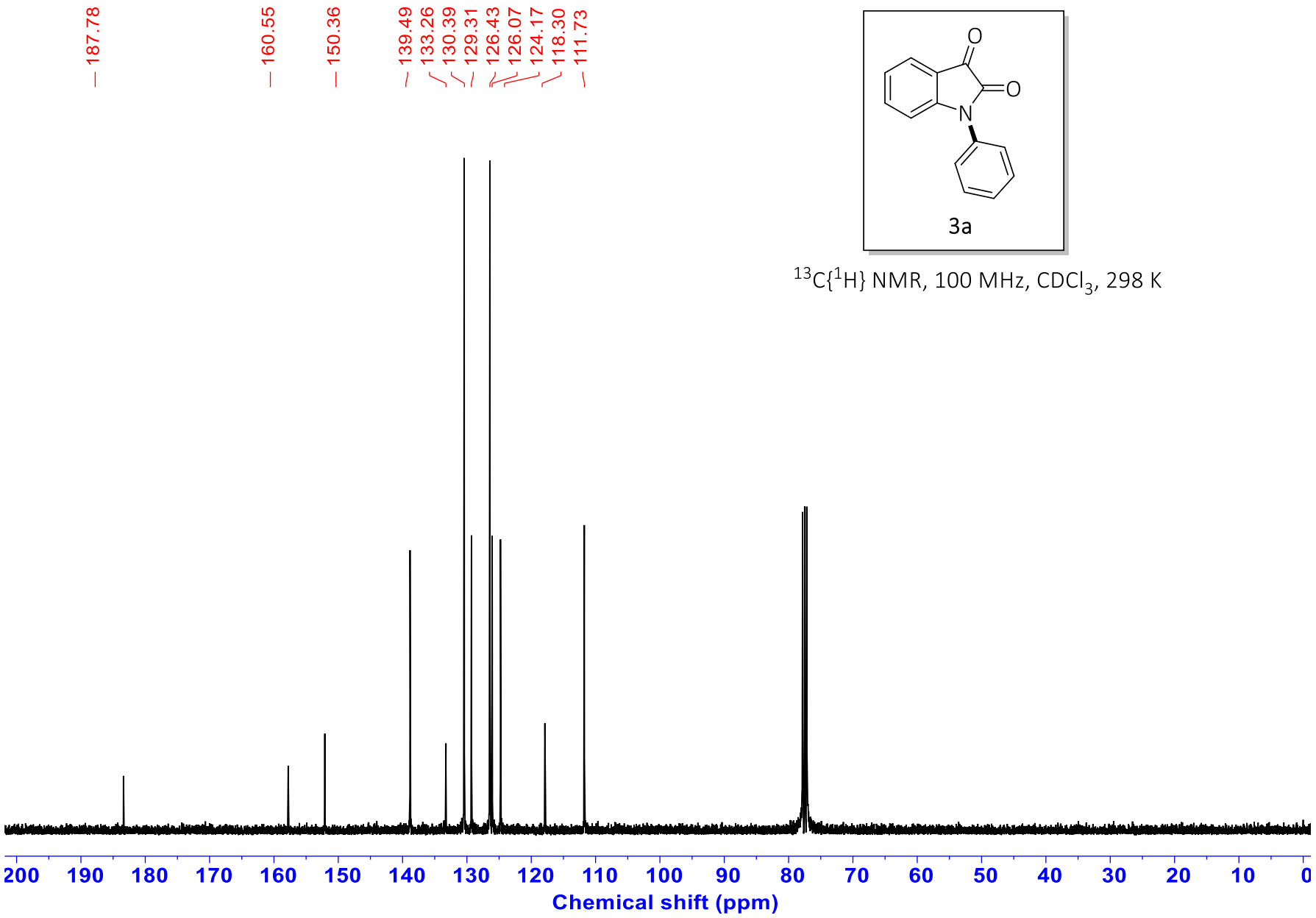
13. COPIES OF ^{1}H, ^{13}C and ^{19}F NMR SPECTRA



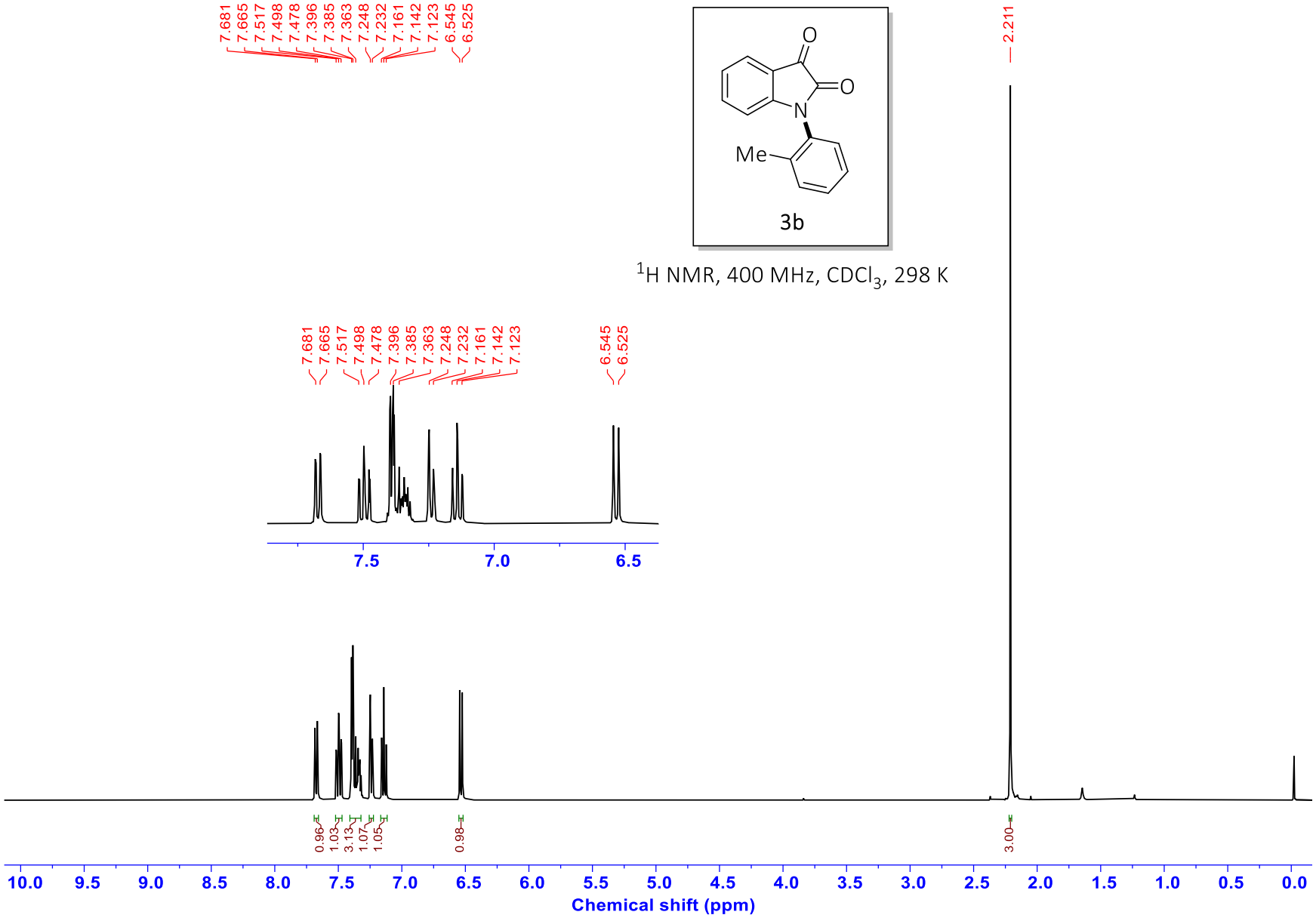


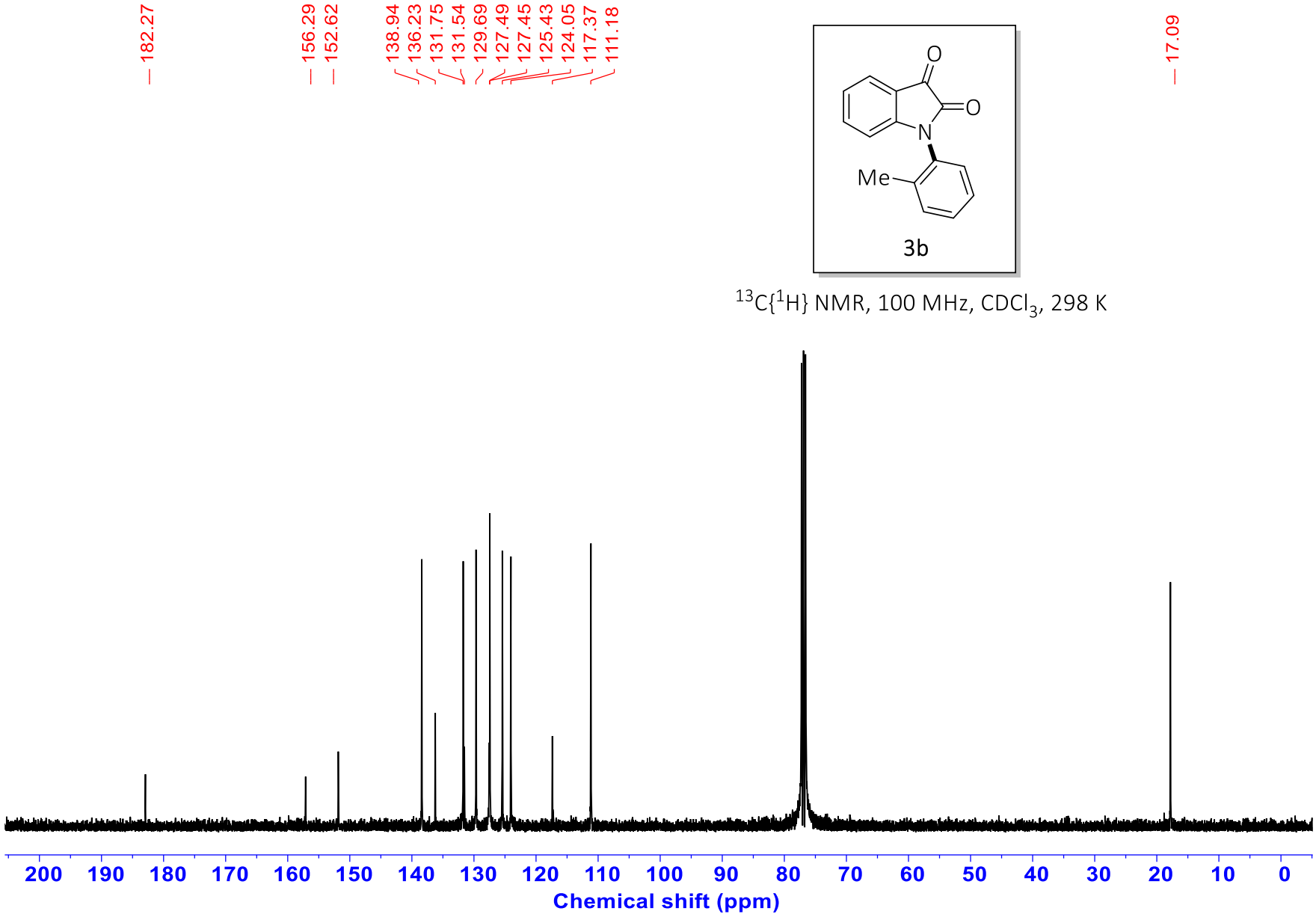
^{1}H NMR, 400 MHz, $CDCl_3$, 298 K



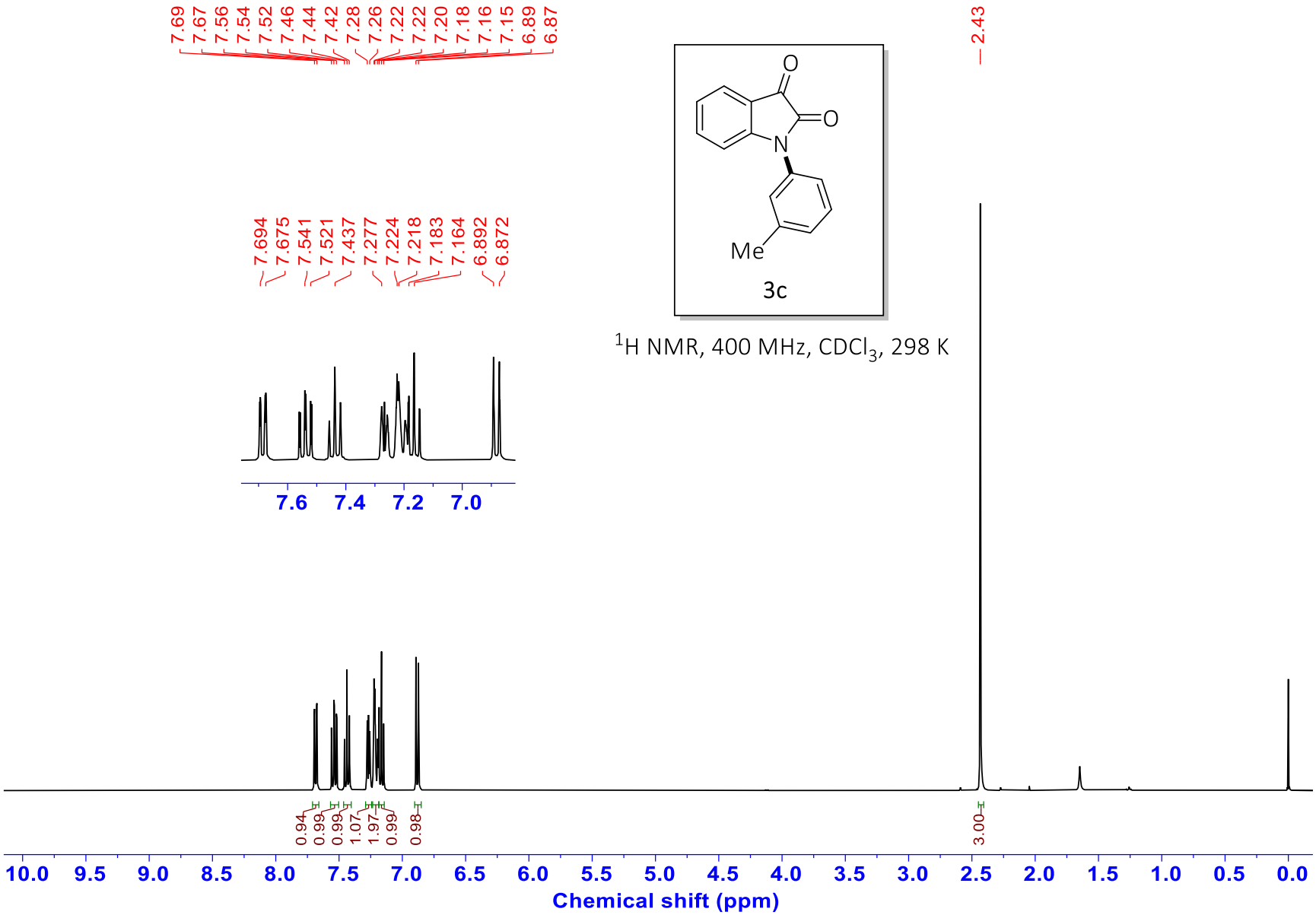


$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$, 298 K

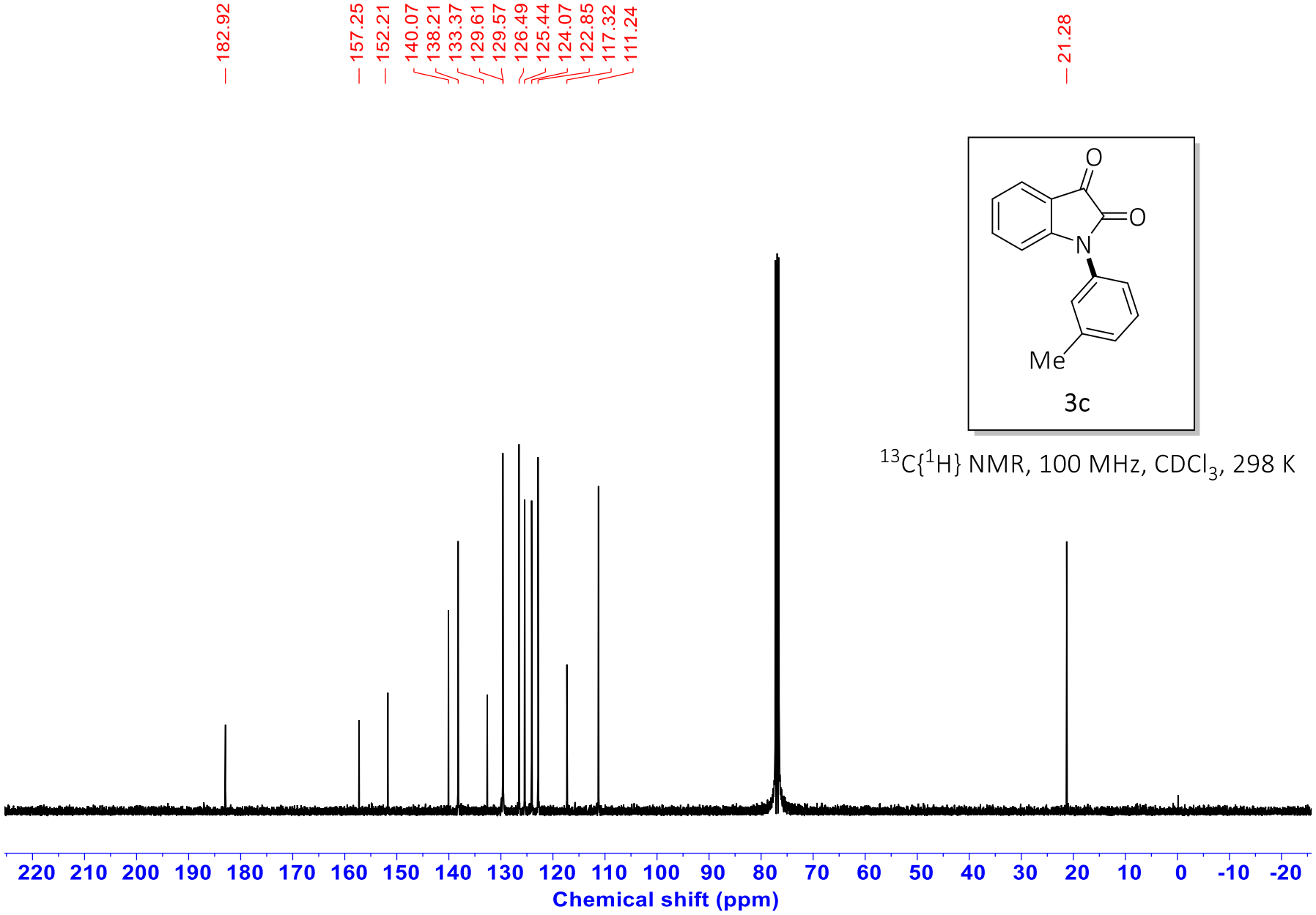

7.681
7.665
7.517
7.498
7.478
7.396
7.385
7.363
7.248
7.232
7.161
7.142
7.123
6.545
6.525
2.211
O
O
N
Me
3b
1H NMR, 400 MHz, CDCl3, 298 K
0.96
1.03
3.13
1.07
1.05
0.98
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical shift (ppm)



$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$, 298 K



^{1}H NMR, 400 MHz, $CDCl_3$, 298 K



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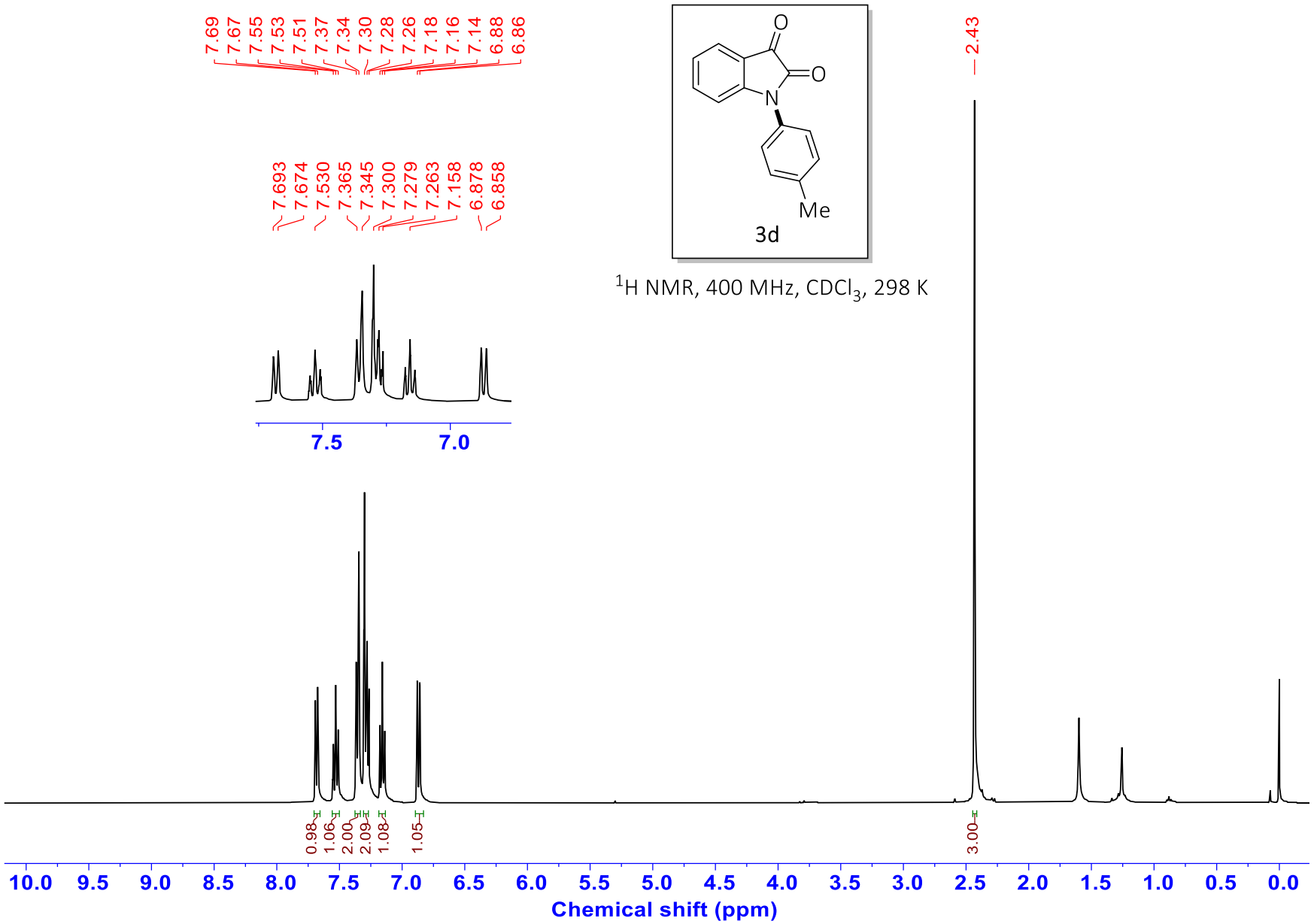

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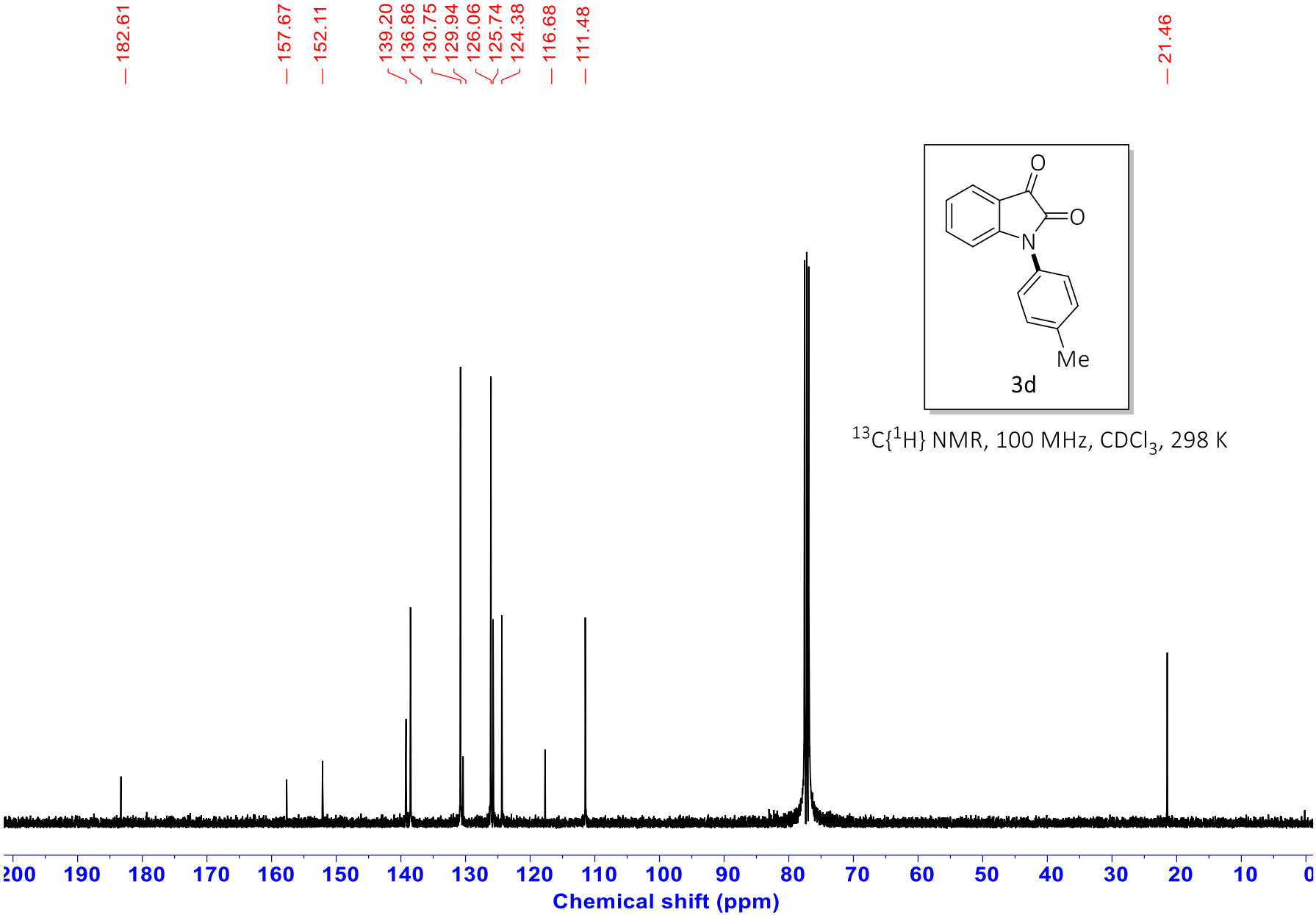
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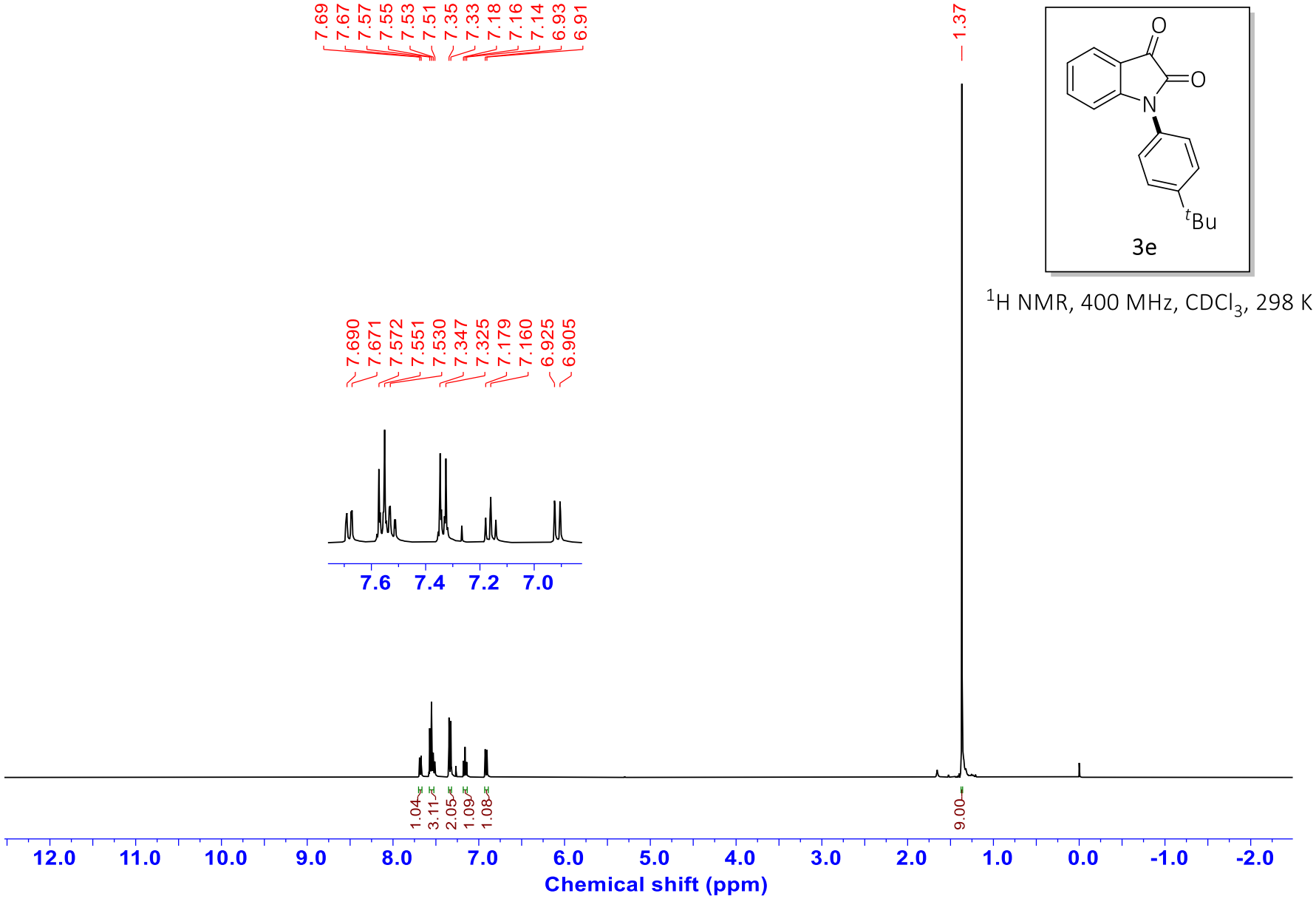
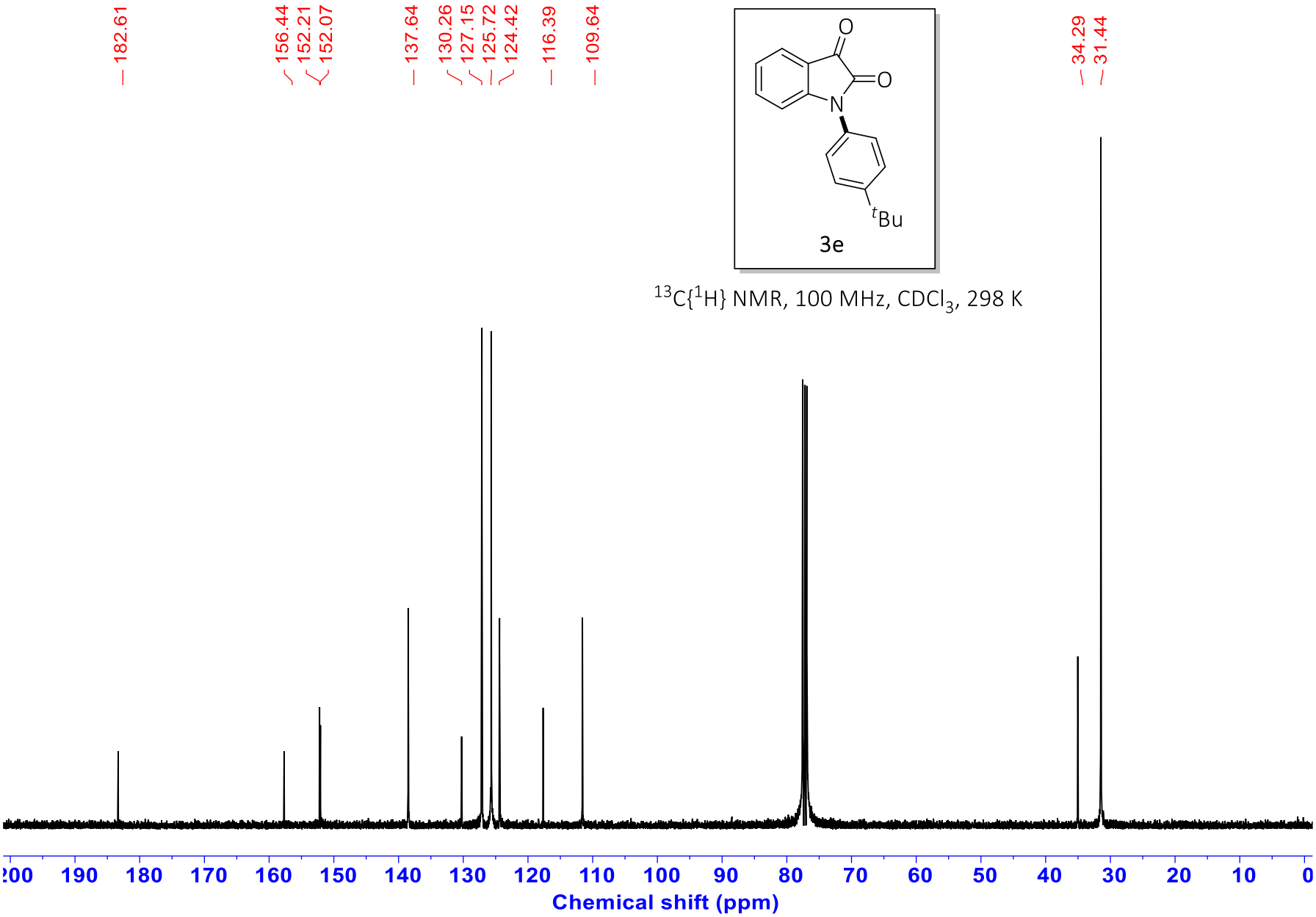
157.67
152.11
139.20
136.86
130.75
129.94
126.06
125.74
124.38
116.68
111.48
21.46
O
O
N
Me
3d
$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$, 298 K
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical shift (ppm)


7.69
7.67
7.57
7.55
7.53
7.51
7.35
7.33
7.18
7.16
7.14
6.93
6.91
1.37
O
O
N
tBu
3e
1H NMR, 400 MHz, CDCl3, 298 K
7.690
7.671
7.572
7.551
7.530
7.347
7.325
7.179
7.160
6.925
6.905
7.6
7.4
7.2
7.0
1.04
3.11
2.05
1.09
1.08
9.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
Chemical shift (ppm)


182.61
156.44
152.21
152.07
137.64
130.26
127.15
125.72
124.42
116.39
109.64
34.29
31.44
O
O
N
tBu
3e
13C{1H} NMR, 100 MHz, CDCl3, 298 K
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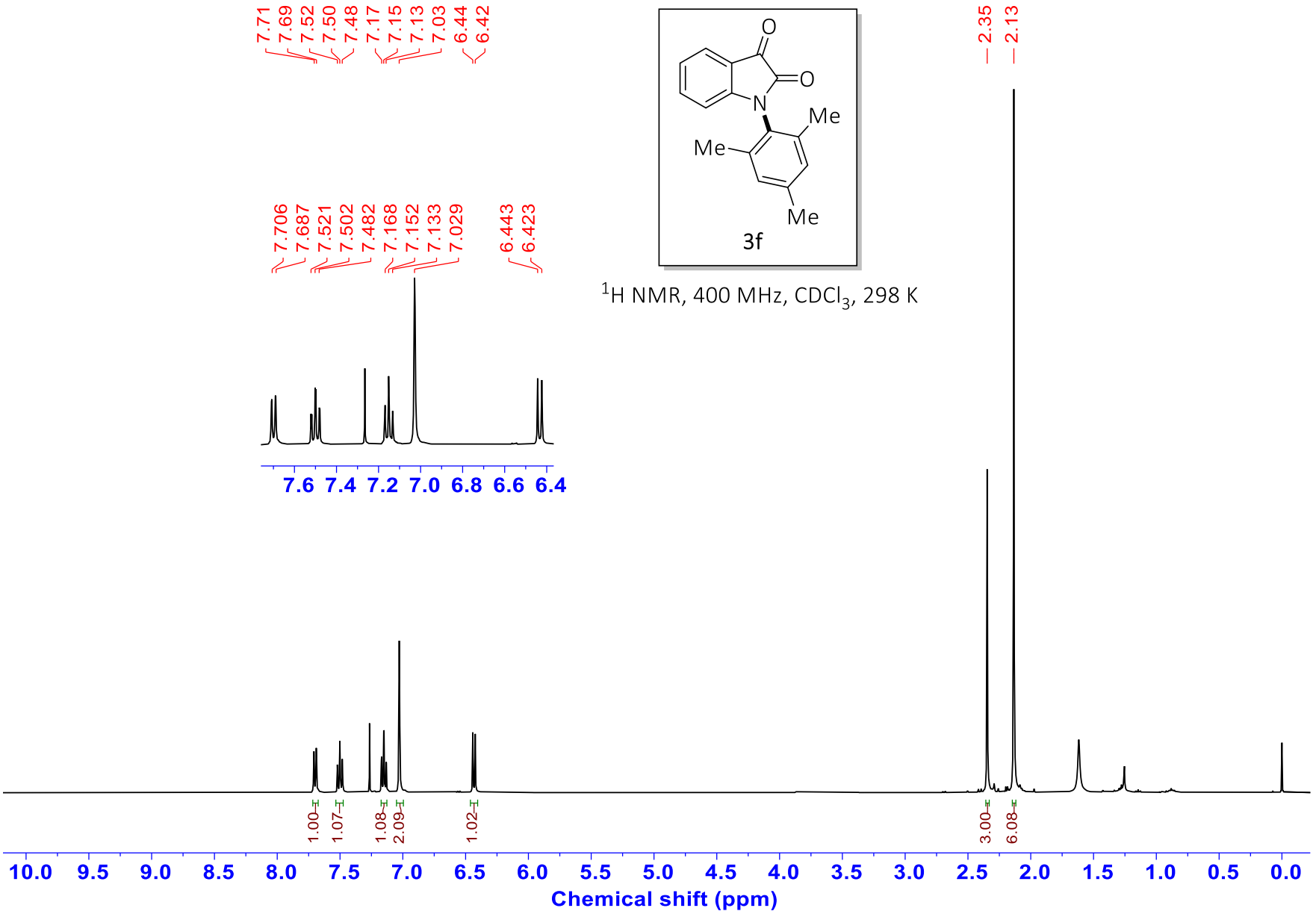
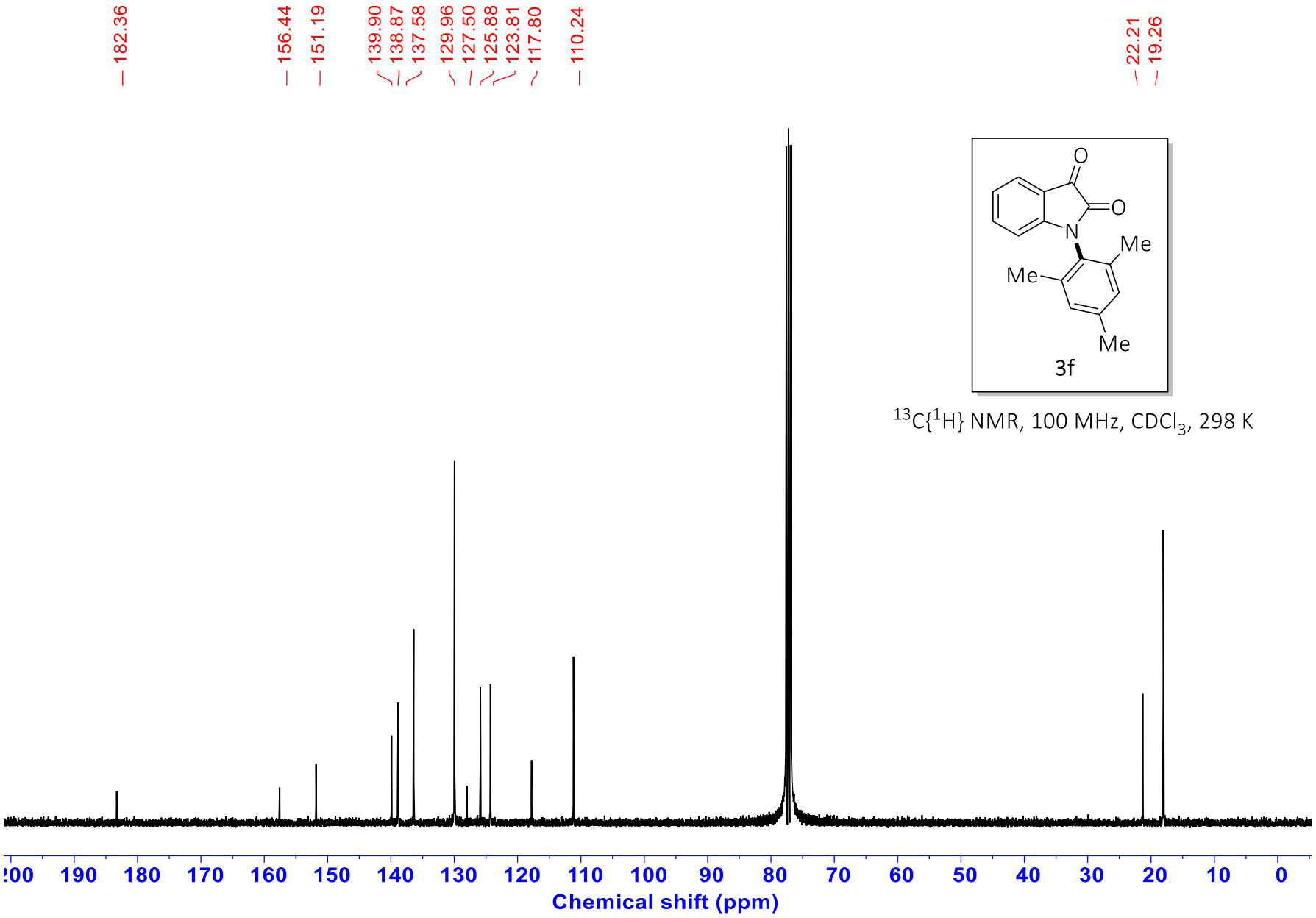
Chemical shift (ppm)



^{1}H NMR, 400 MHz, $CDCl_3$, 298 K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151.19
139.90
138.87
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129.96
127.50
125.88
123.81
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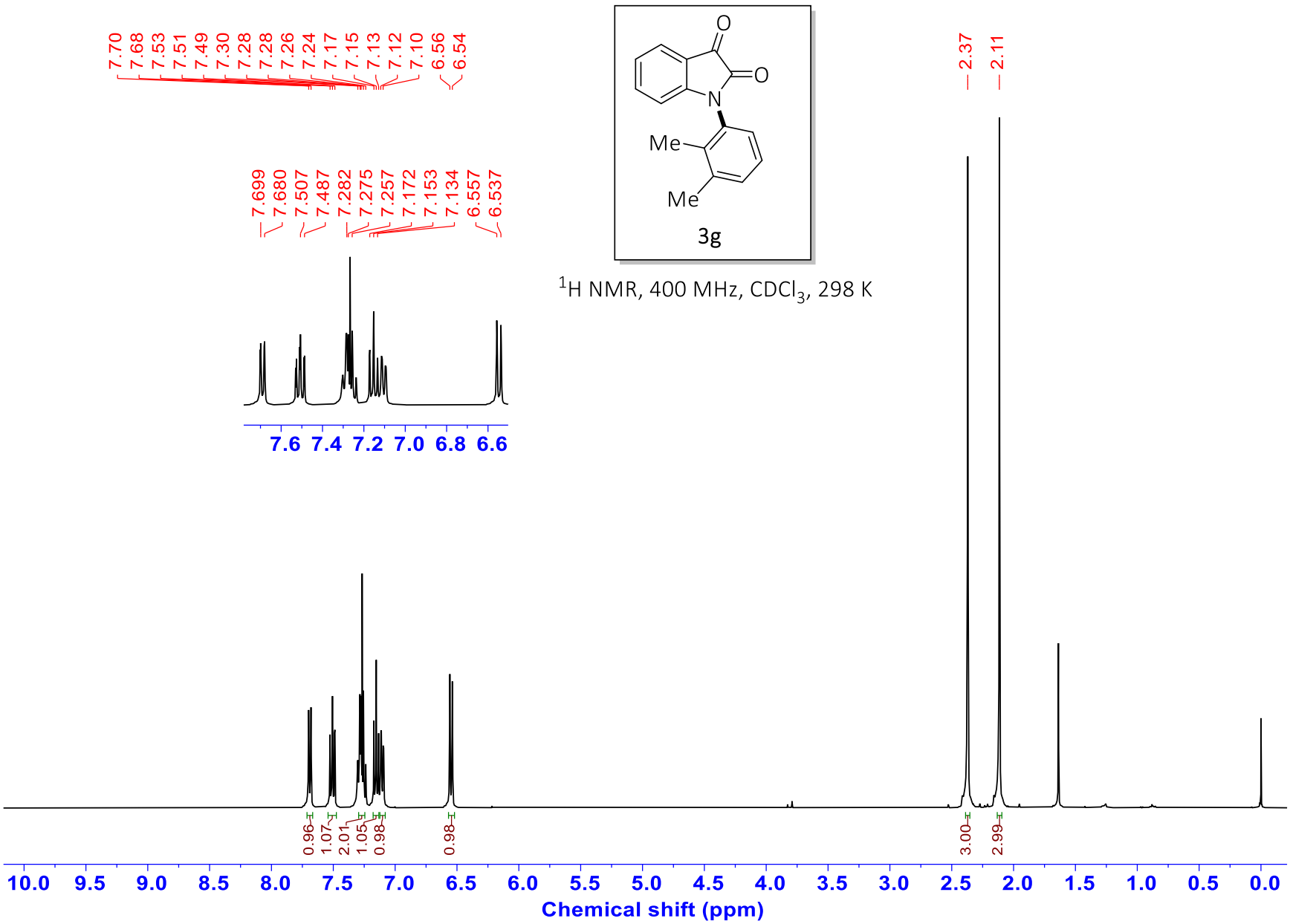
110.24
22.21
19.26
O
O
N
Me
Me
Me
3f
$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$, 298 K
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical shift (ppm)



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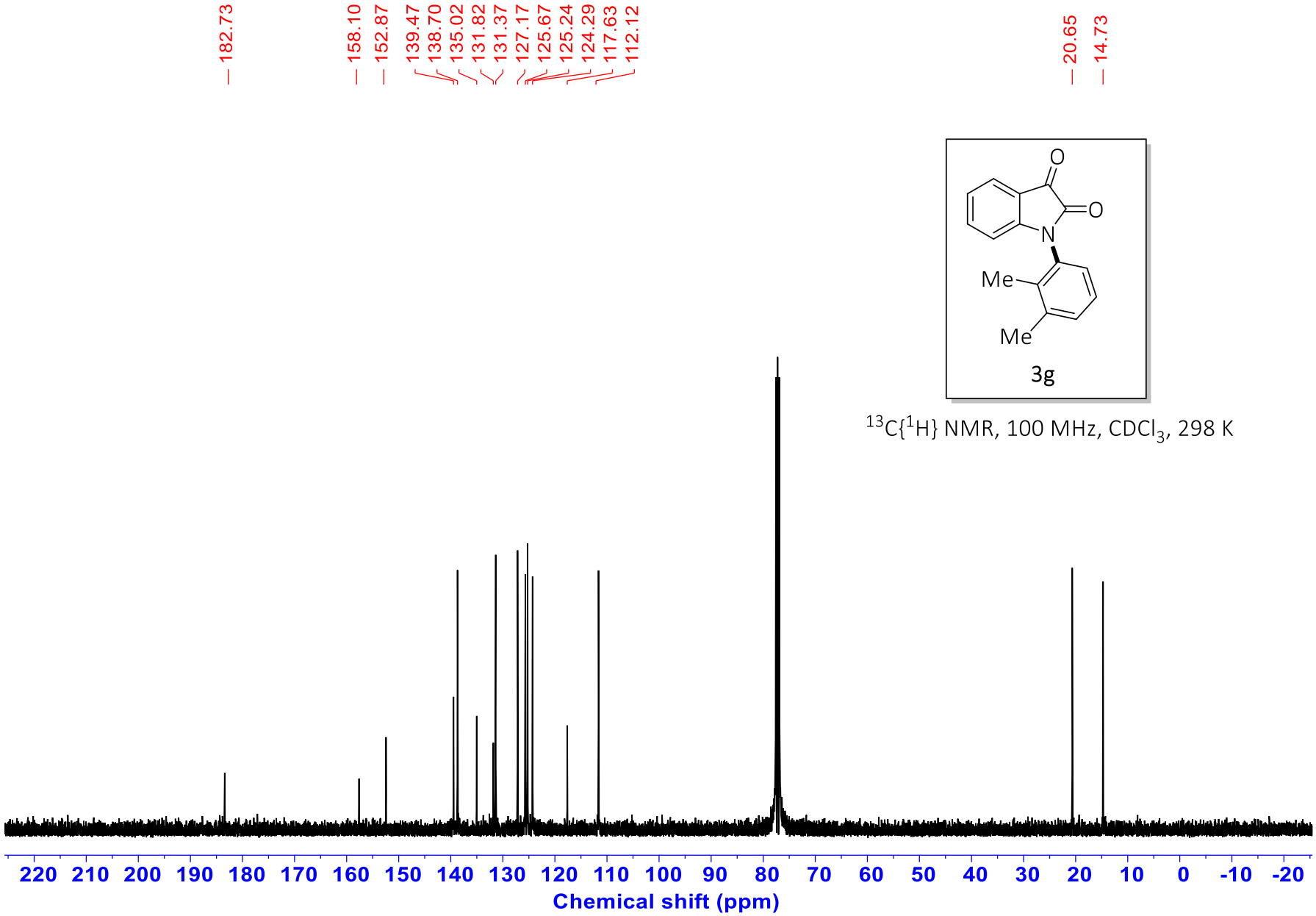
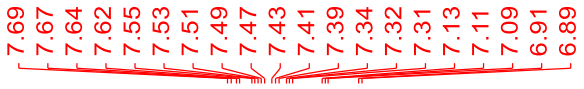
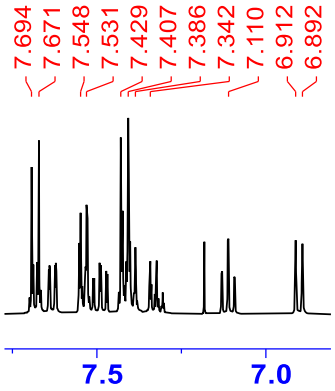
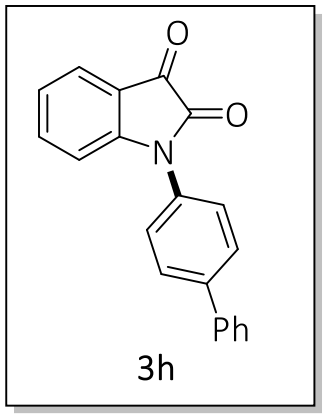


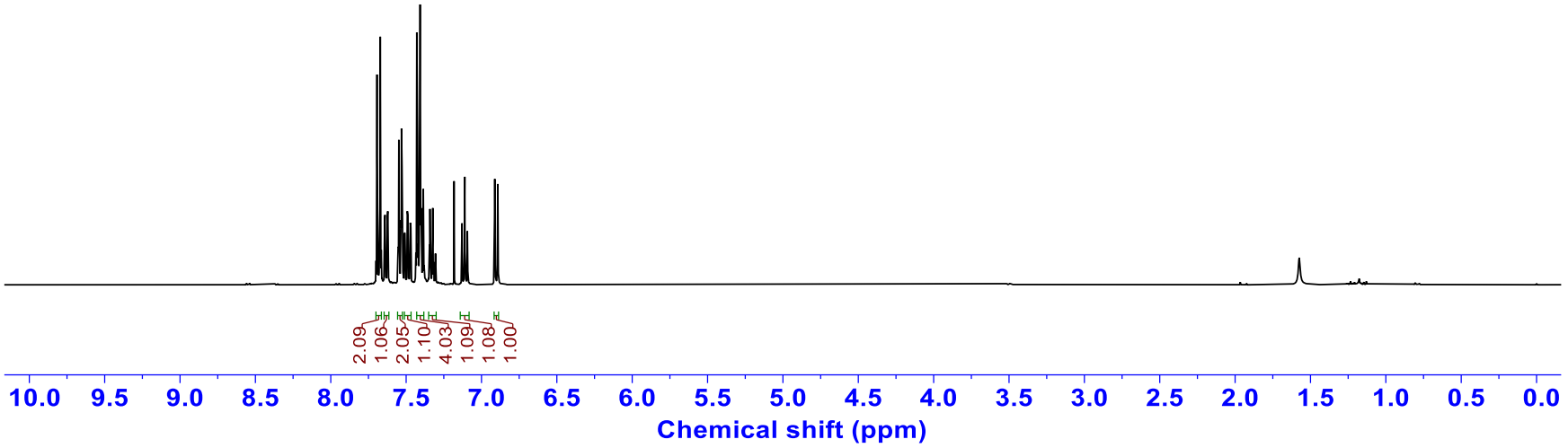
$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$, 298 K

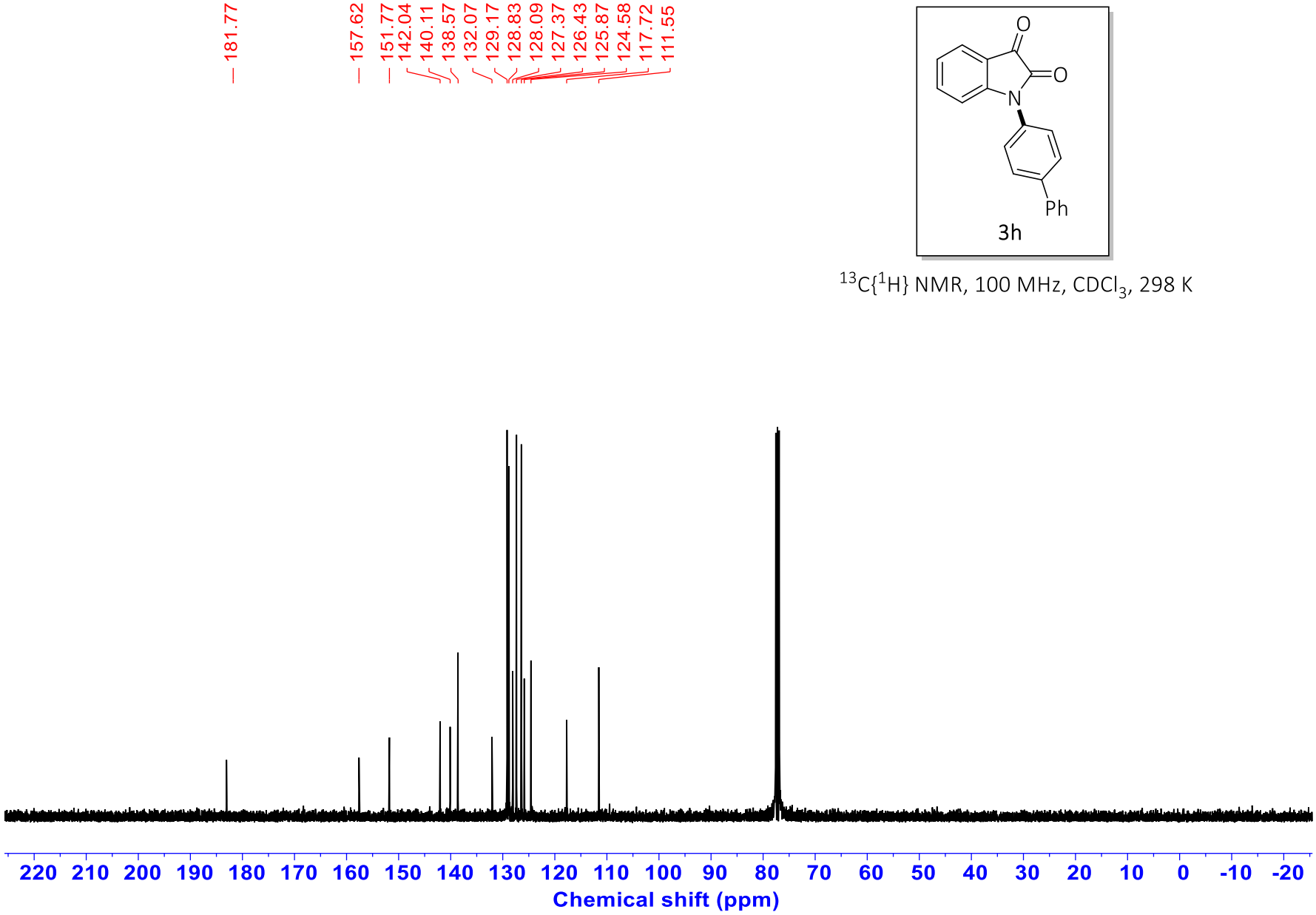




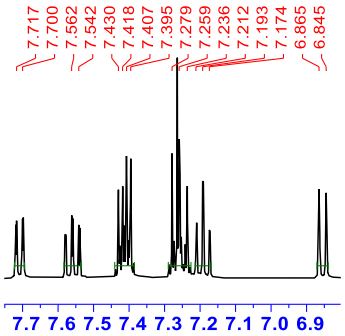


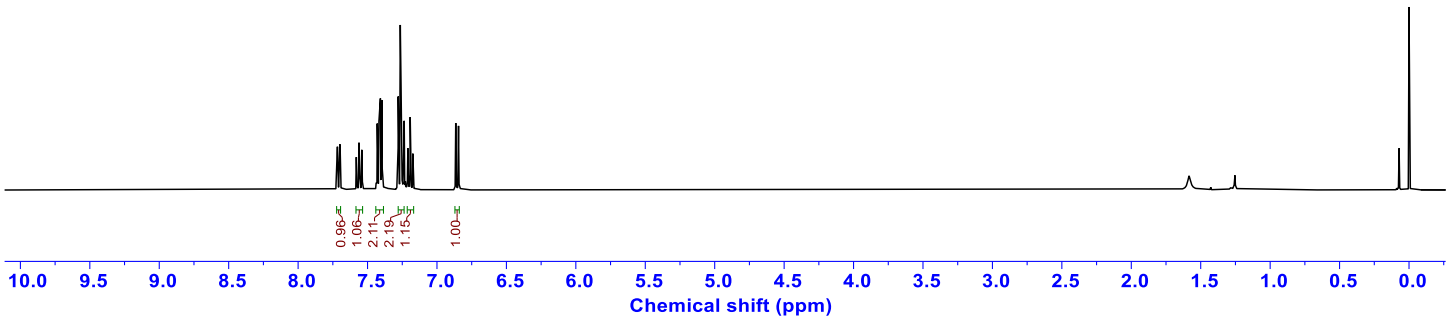
^{1}H NMR, 400 MHz, $CDCl_3$, 298 K

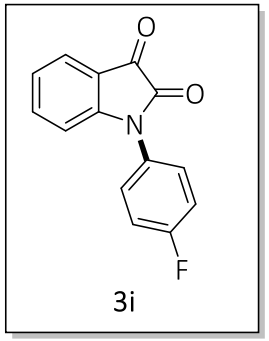




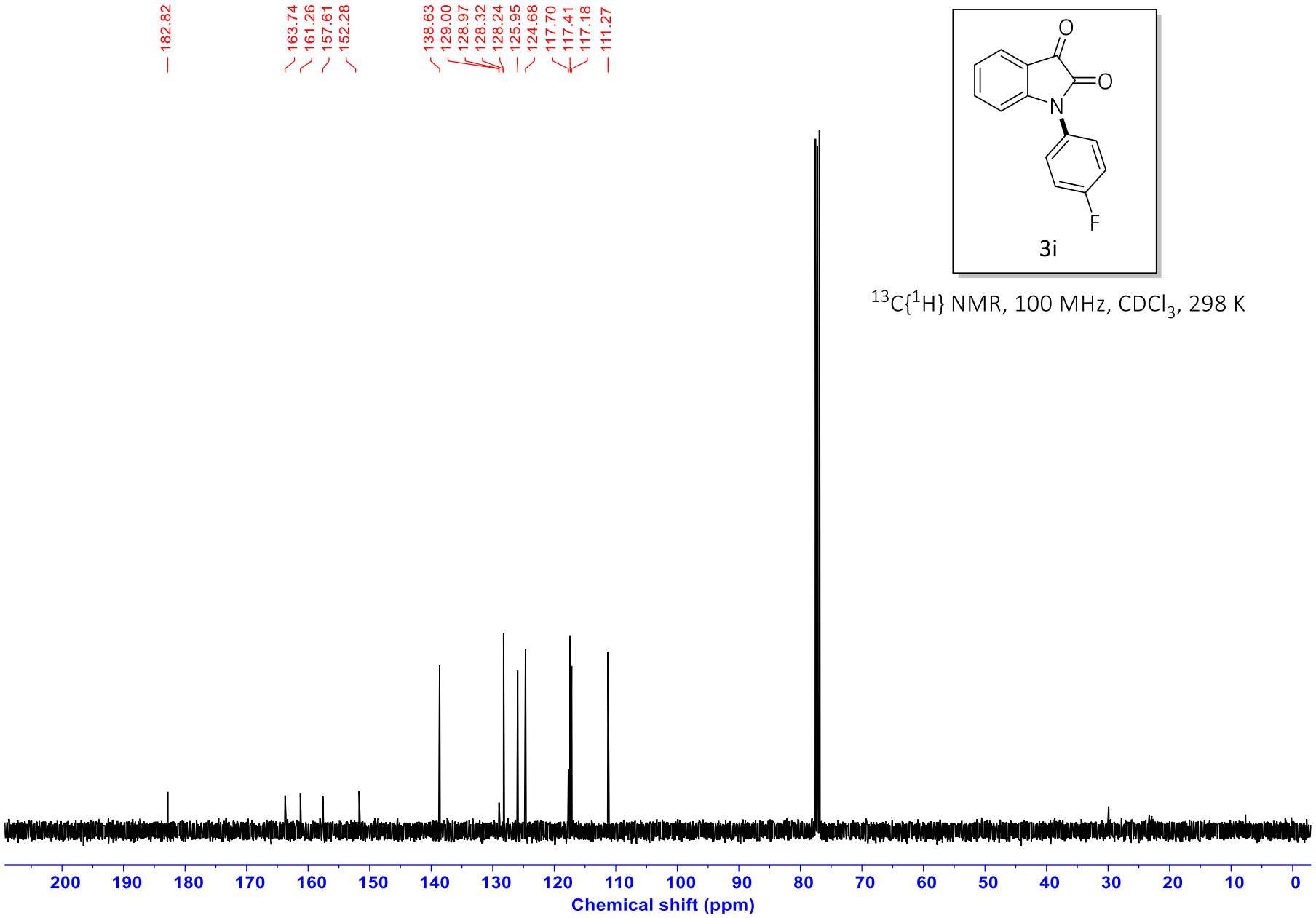
$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$, 298 K



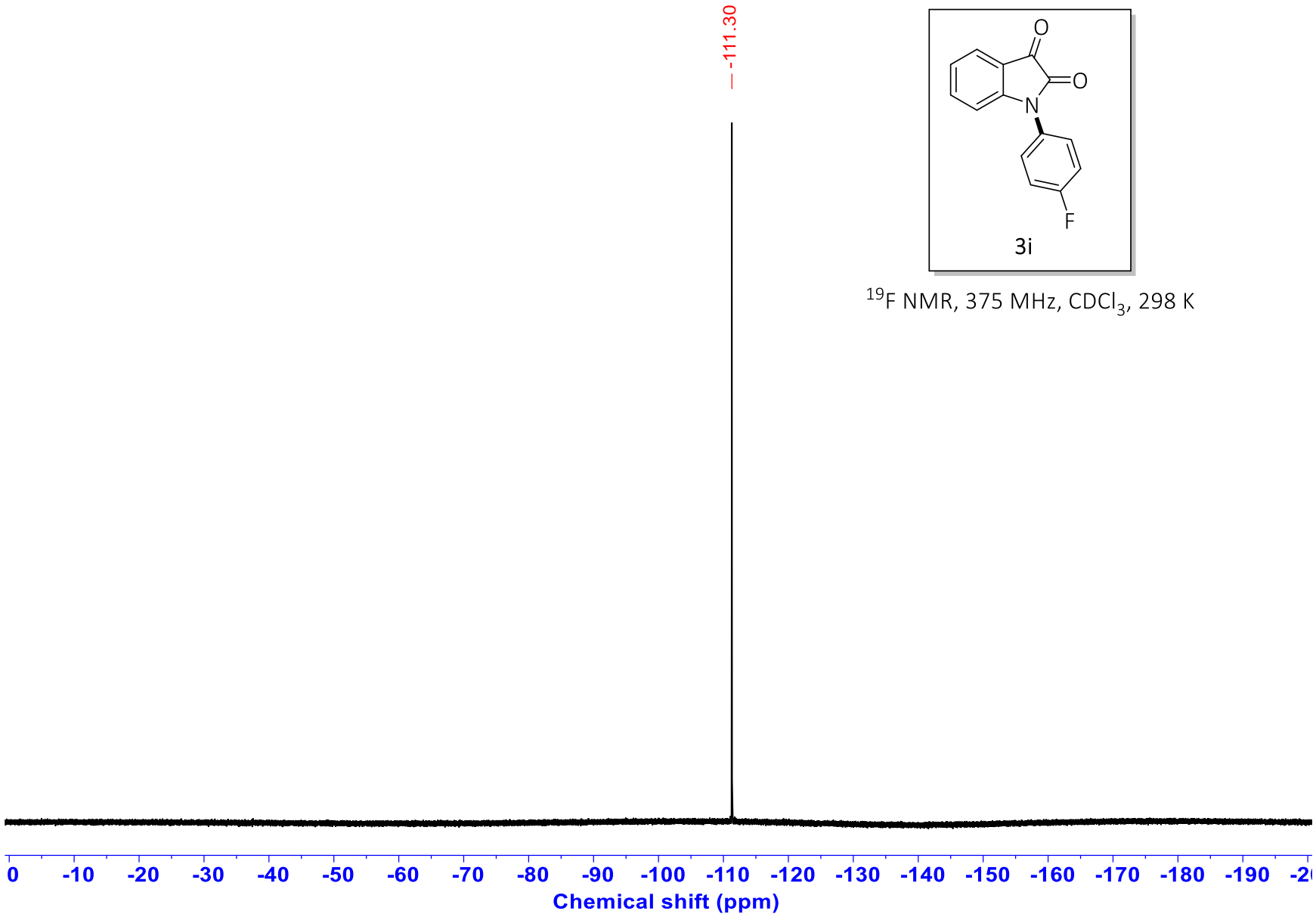




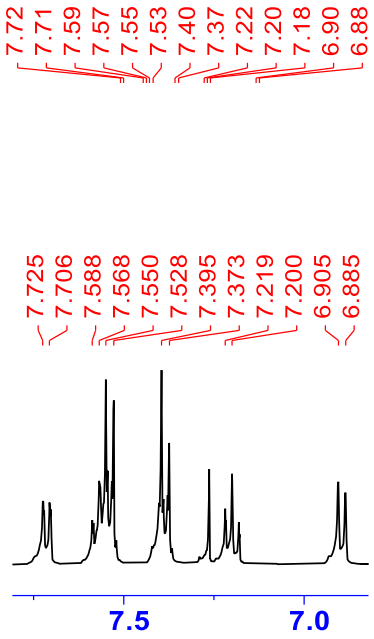
^{1}H NMR, 400 MHz, $CDCl_3$, 298 K

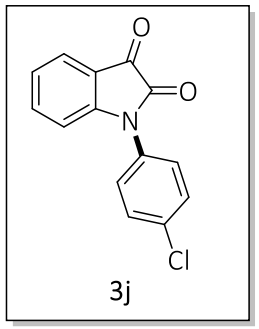


$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$, 298 K

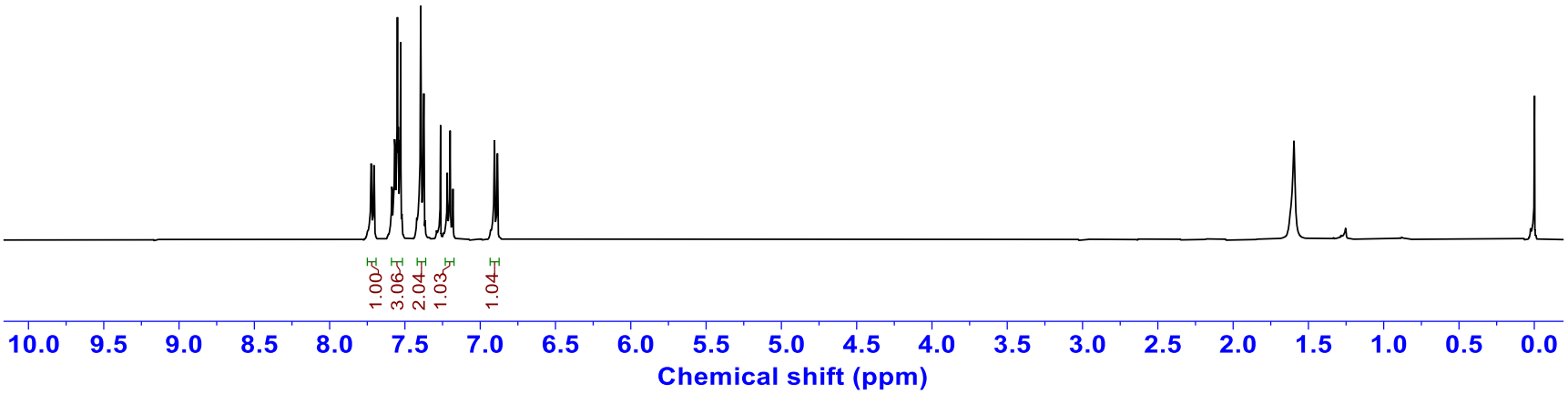


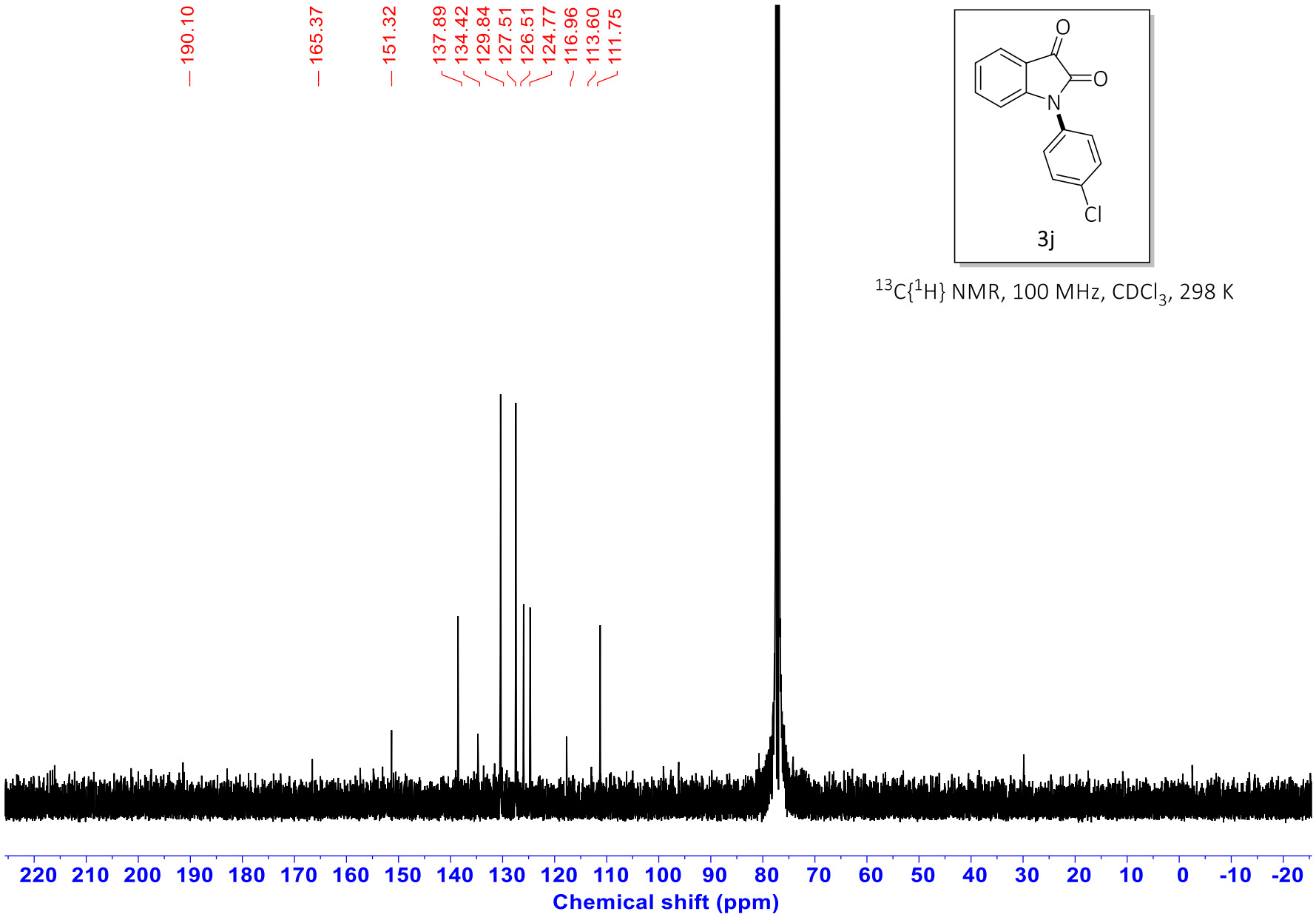
^{19}F NMR, 375 MHz, $CDCl_3$, 298 K



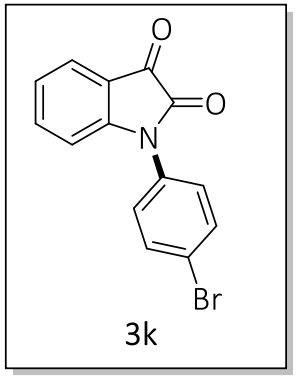


^{1}H NMR, 400 MHz, $CDCl_3$, 298 K

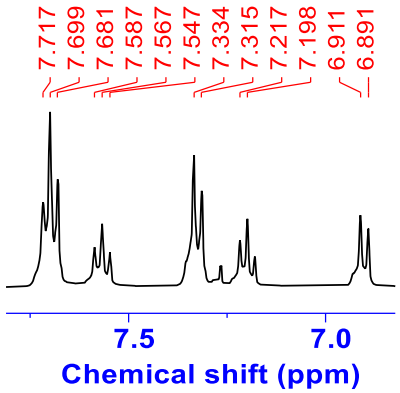


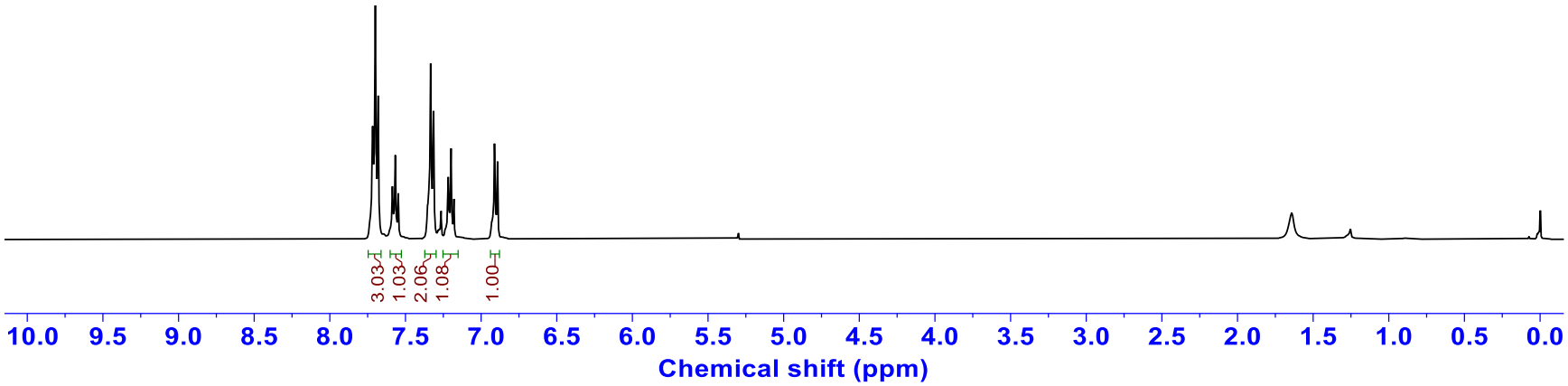


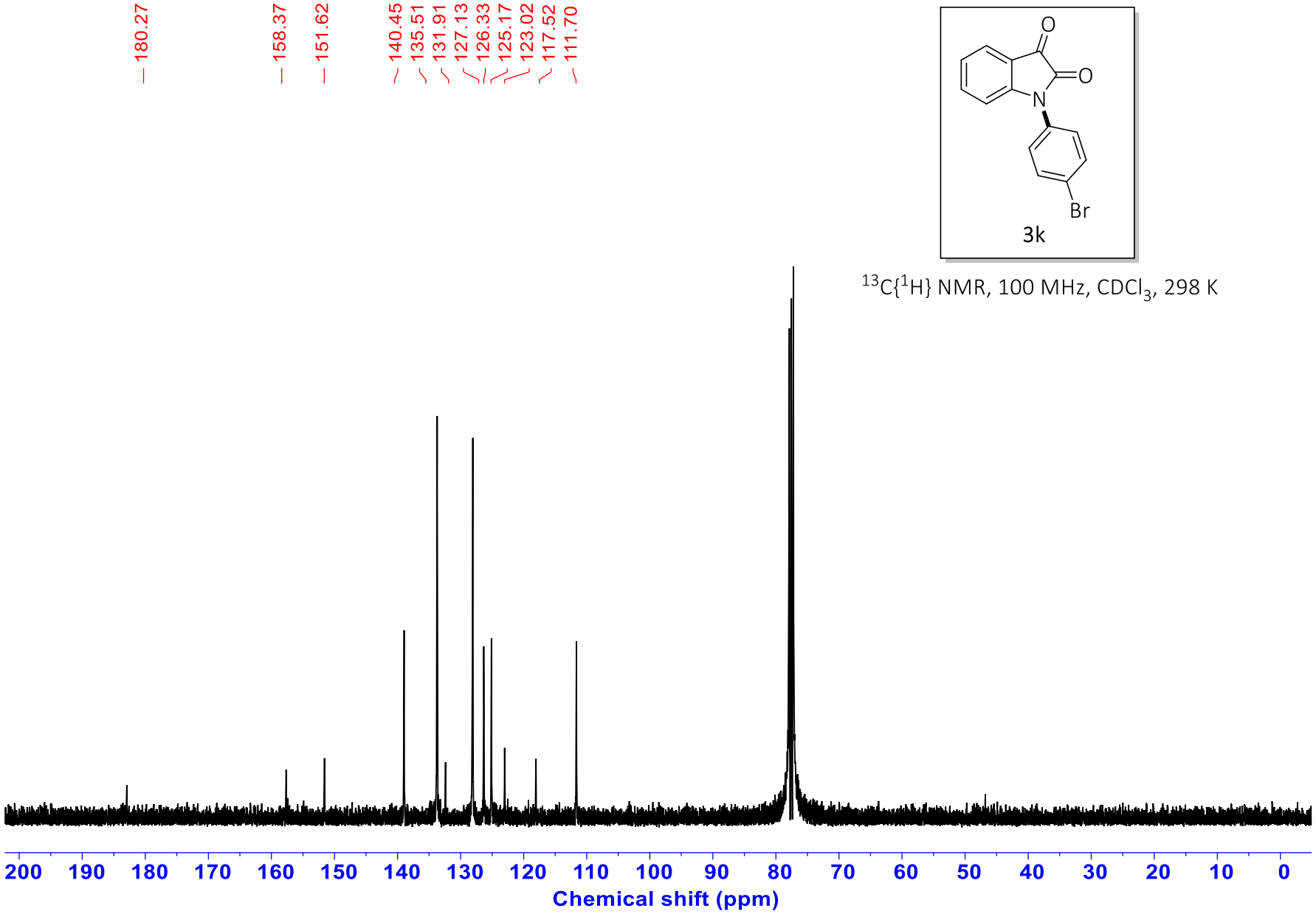
$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$, 298 K



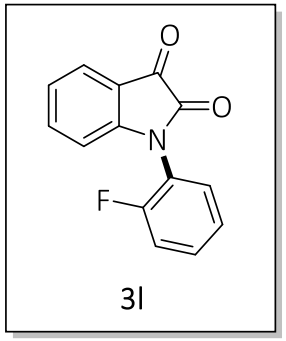
^{1}H NMR, 400 MHz, $CDCl_3$, 298 K





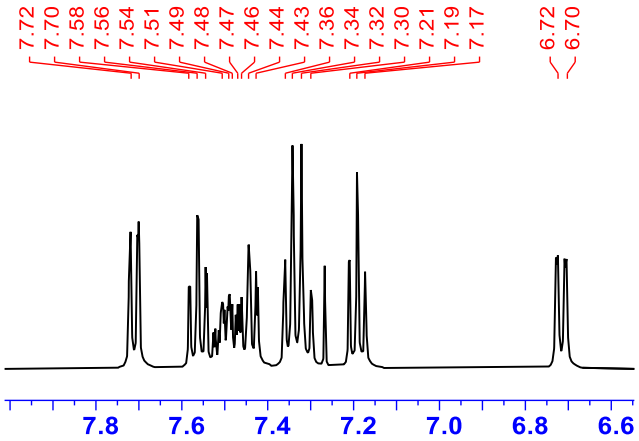


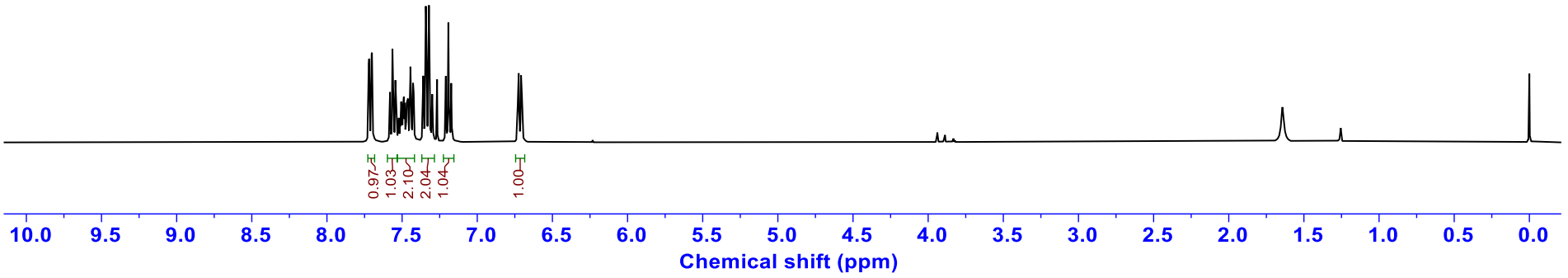
$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$, 298 K

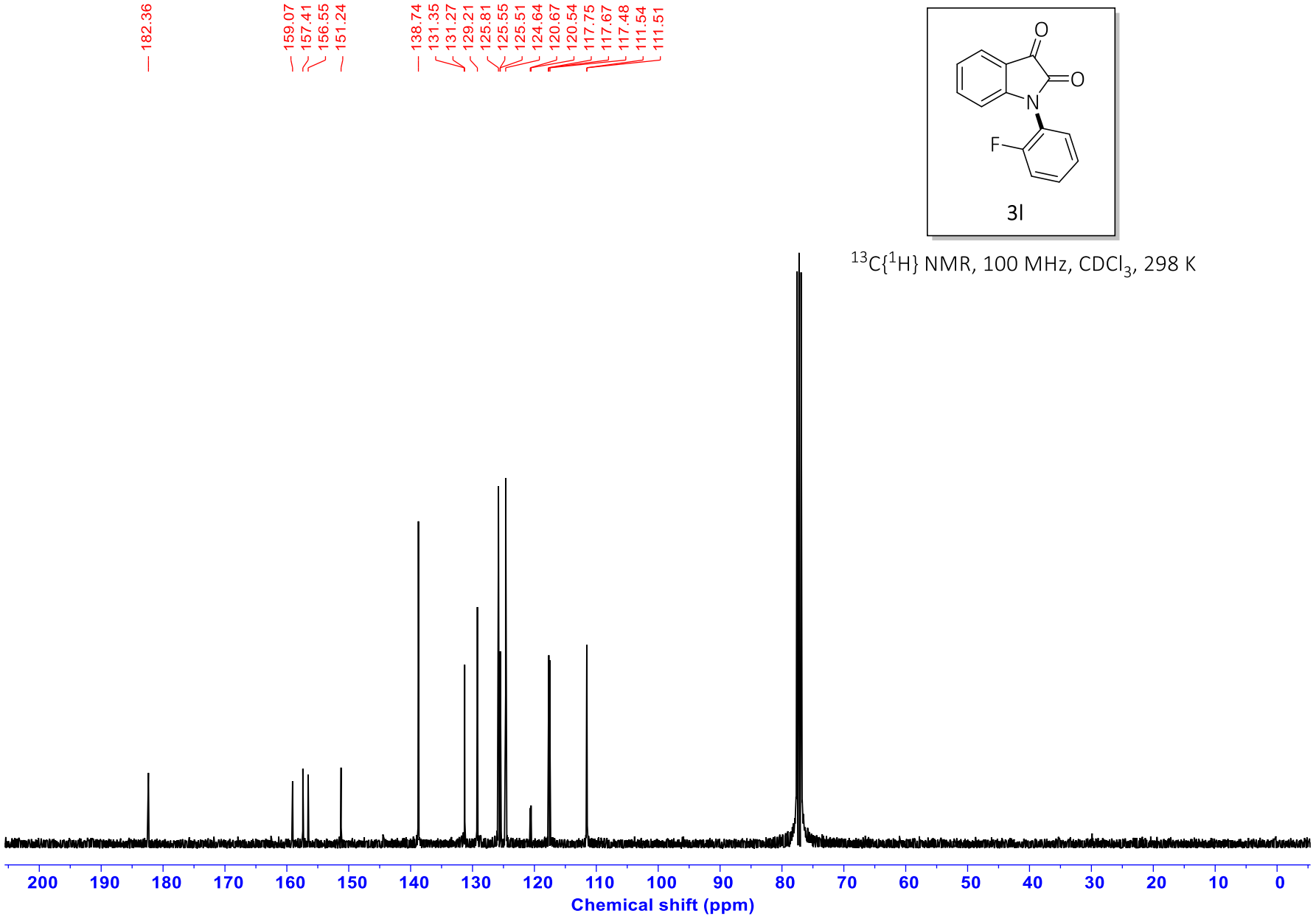


3l

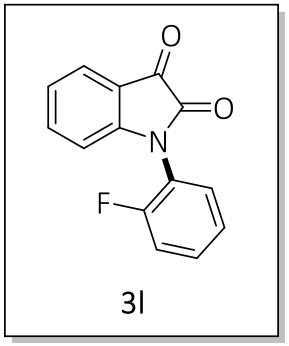
^{1}H NMR, 400 MHz, $CDCl_3$, 298 K





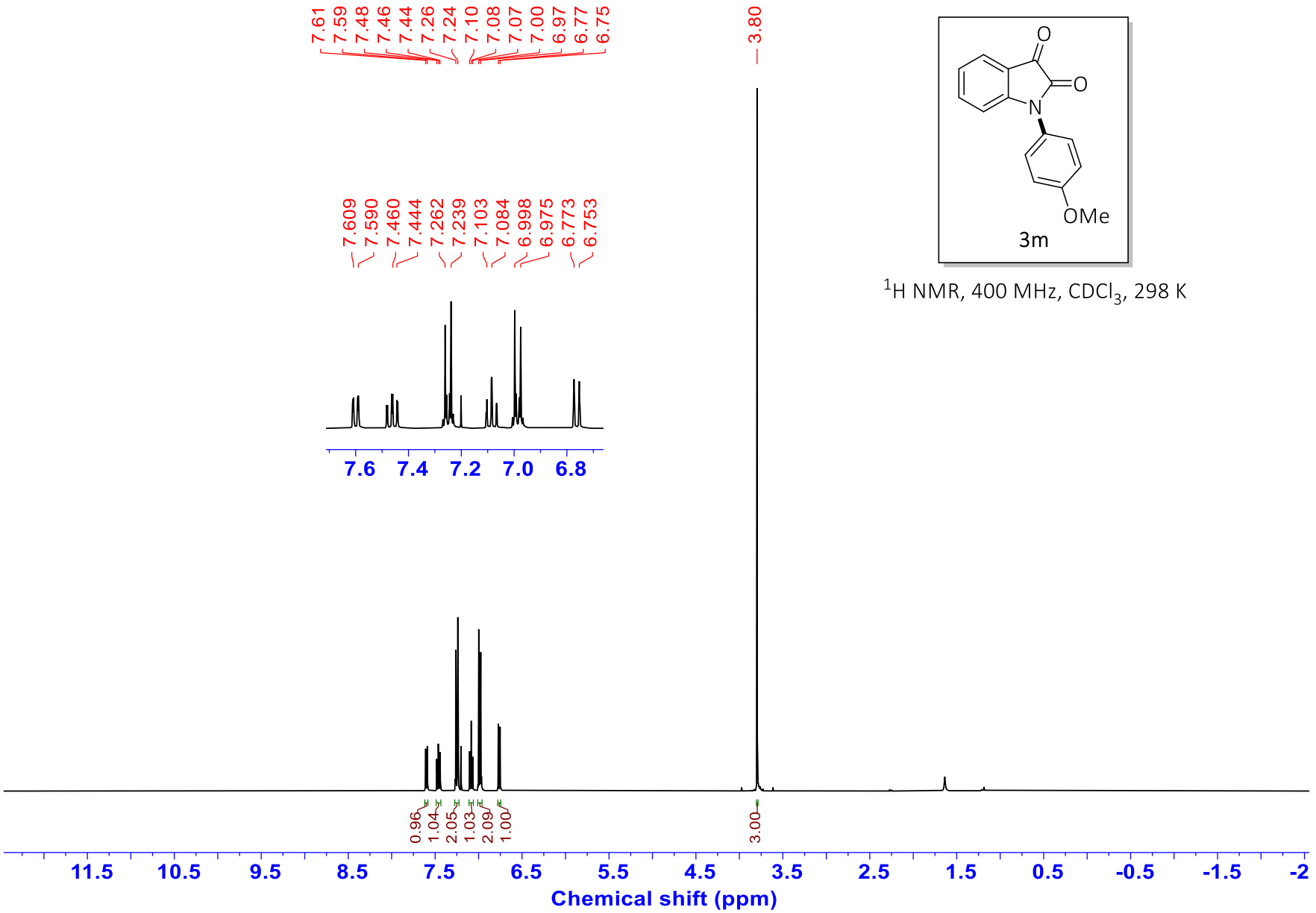


$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$, 298 K

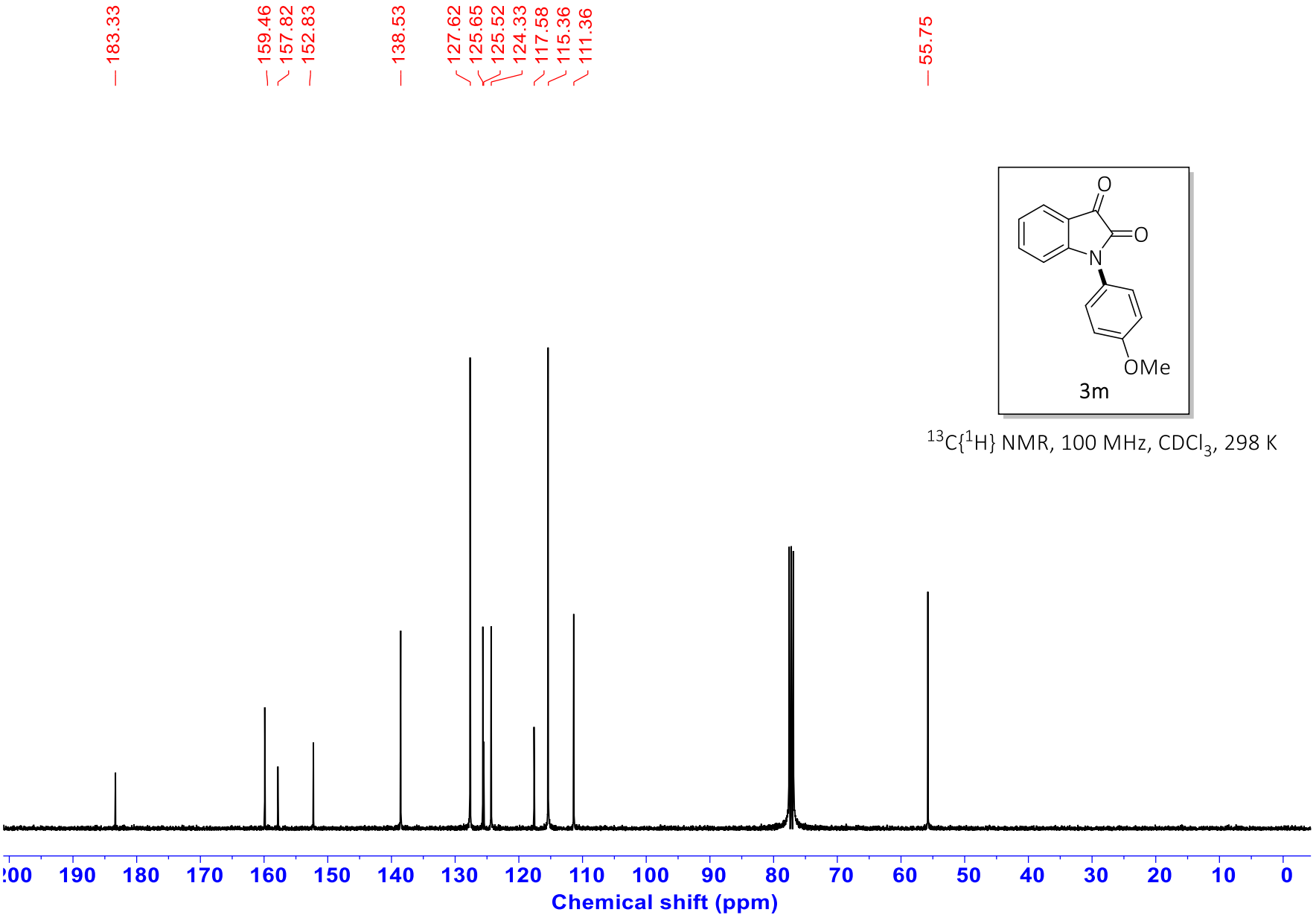


3l

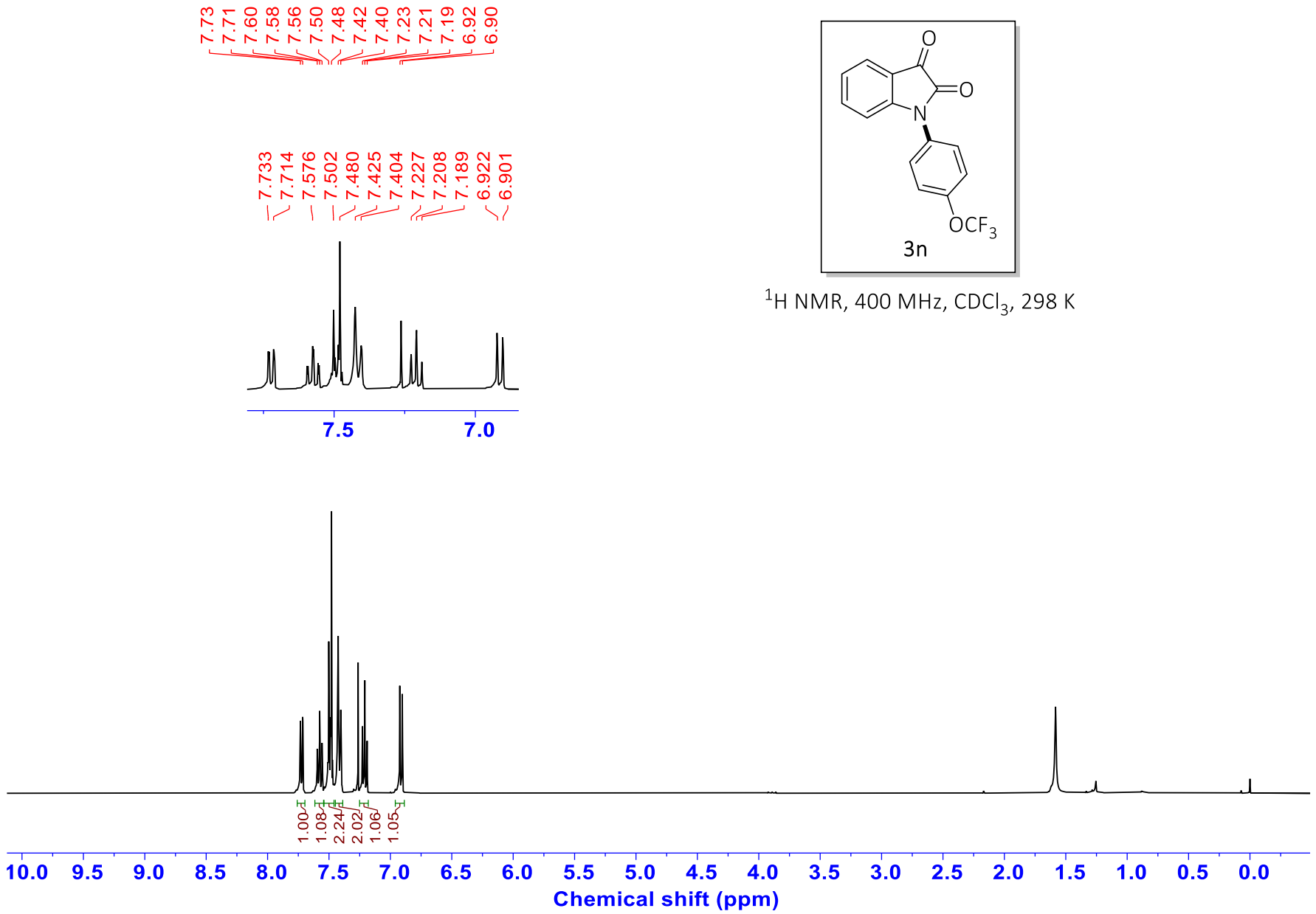
^{19}F NMR, 375 MHz, $CDCl_3$, 298 K



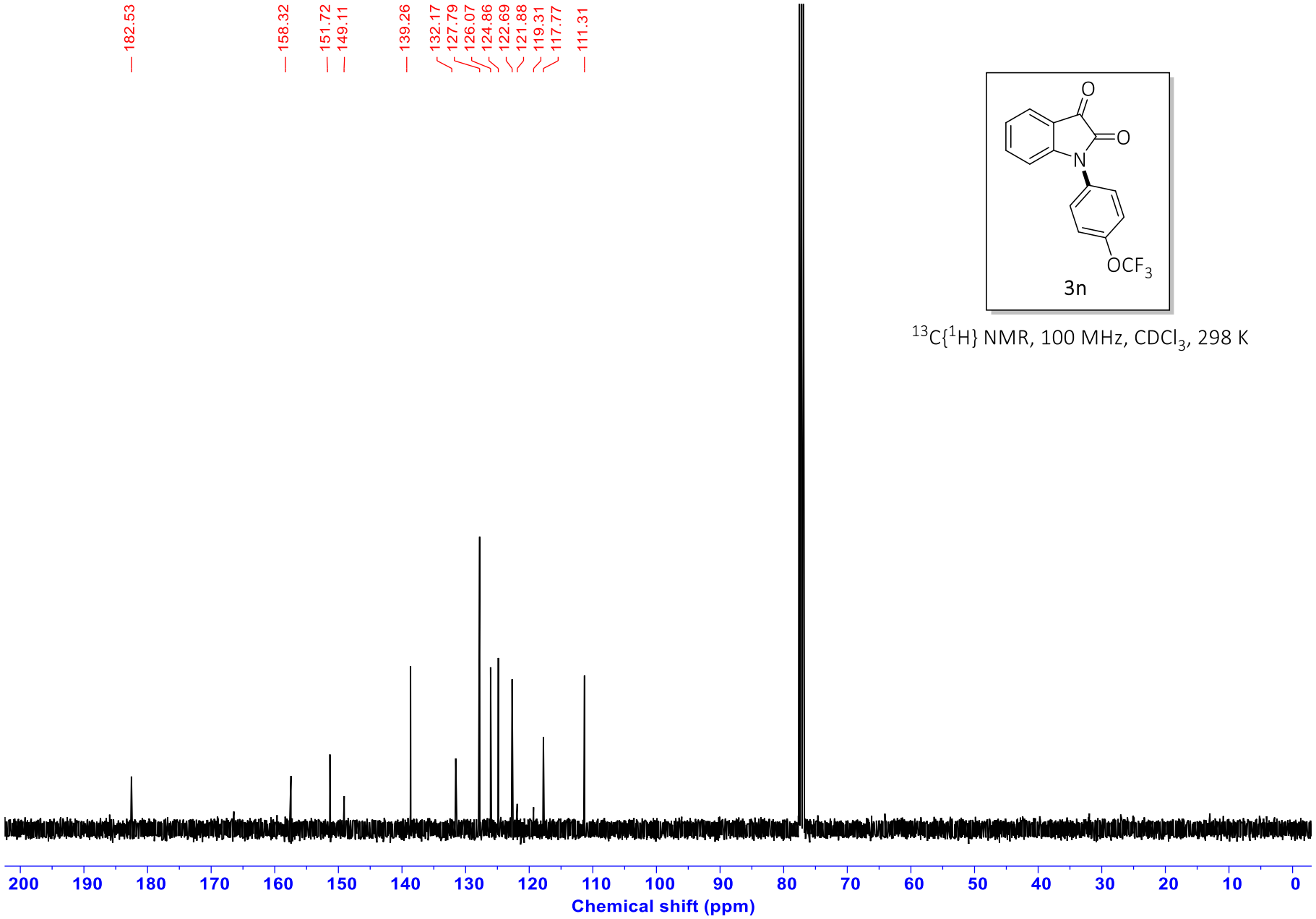
^{1}H NMR, 400 MHz, $CDCl_3$, 298 K



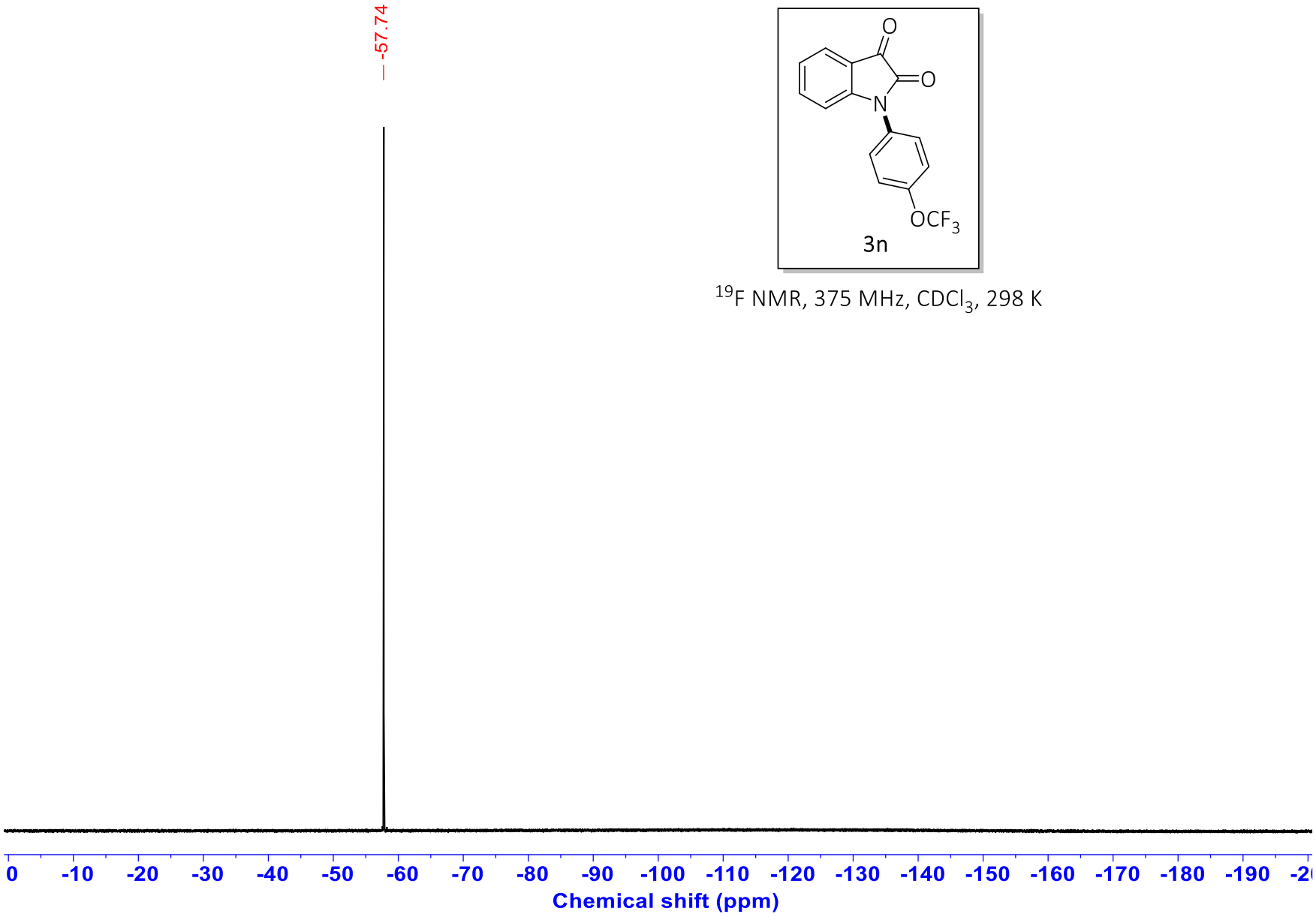
$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$, 298 K



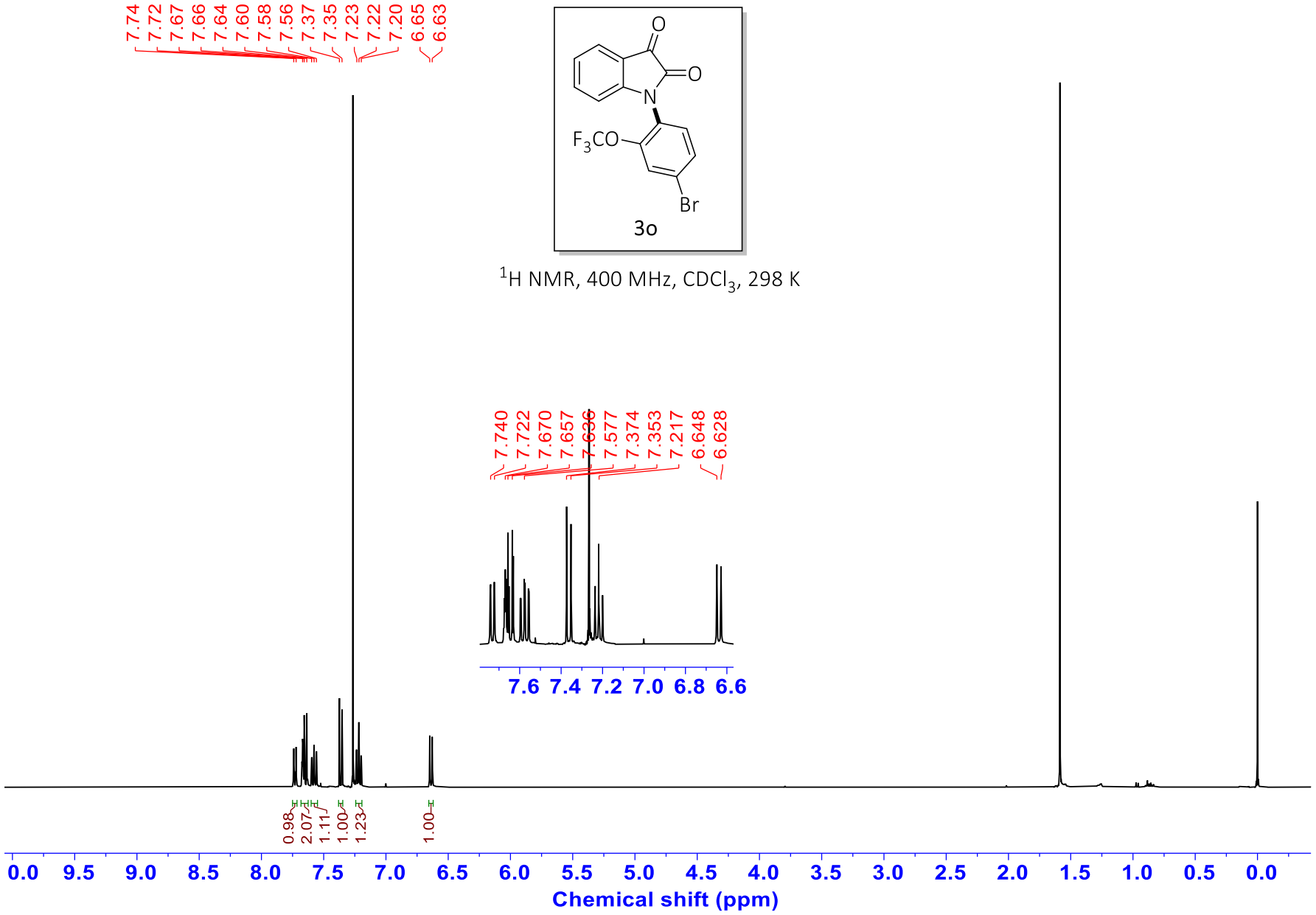
^{1}H NMR, 400 MHz, $CDCl_3$, 298 K

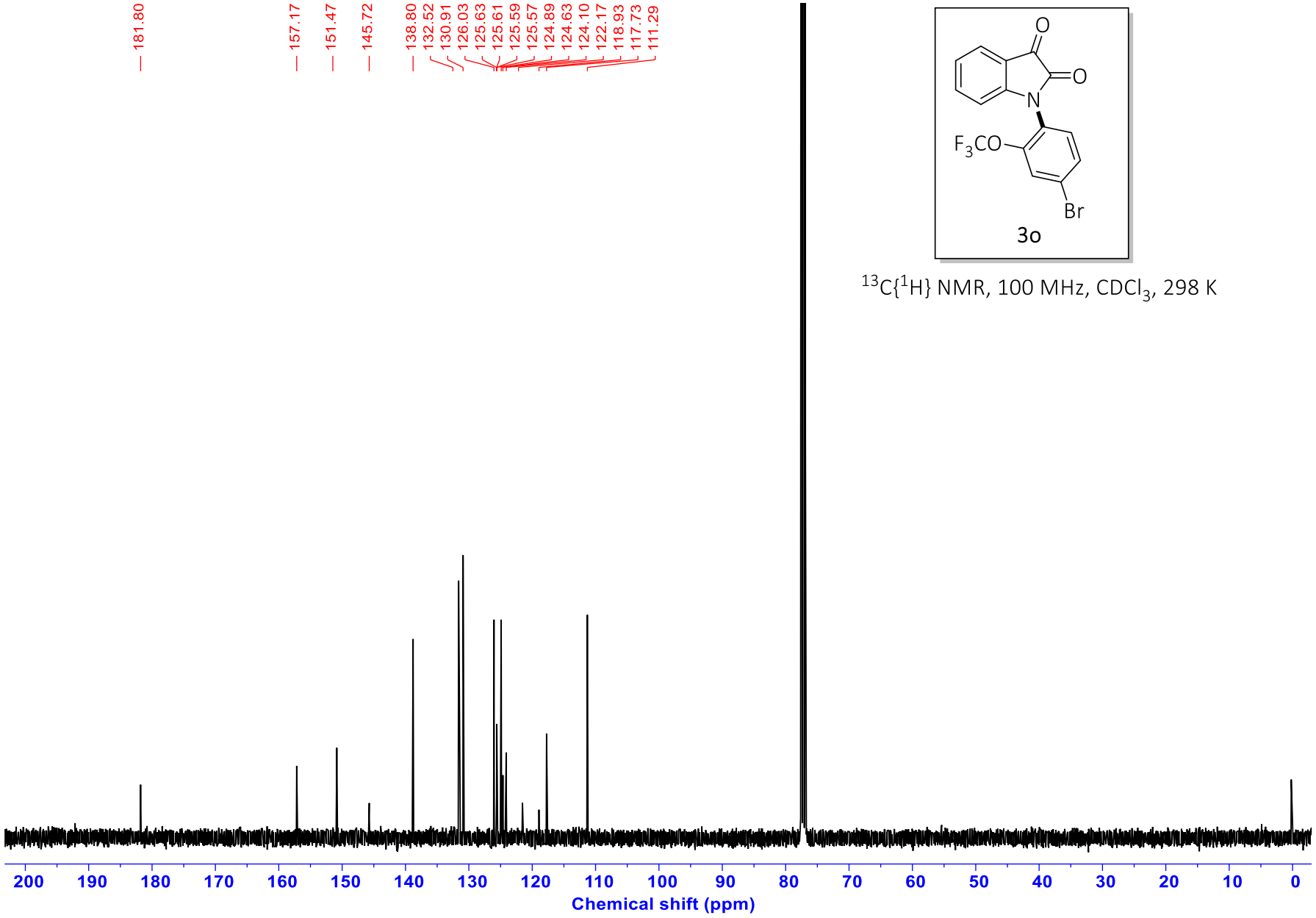


$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$, 298 K

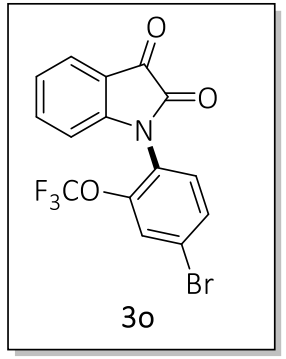


^{19}F NMR, 375 MHz, $CDCl_3$, 298 K

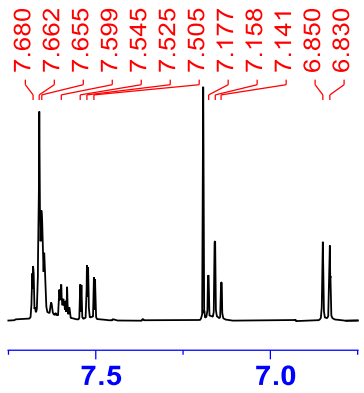

7.74
7.72
7.67
7.66
7.64
7.60
7.58
7.56
7.37
7.35
7.23
7.22
7.20
6.65
6.63
O
O
N
F3CO
Br
3o
1H NMR, 400 MHz, CDCl3, 298 K
7.740
7.722
7.670
7.657
7.636
7.577
7.374
7.353
7.217
6.648
6.628
7.6 7.4 7.2 7.0 6.8 6.6
0.98
2.07
1.11
1.00
1.23
1.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical shift (ppm)

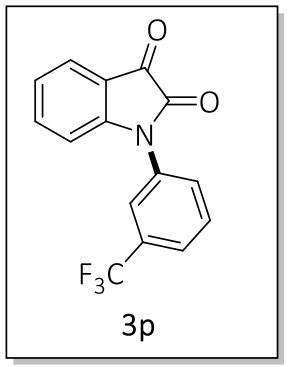


$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$, 298 K

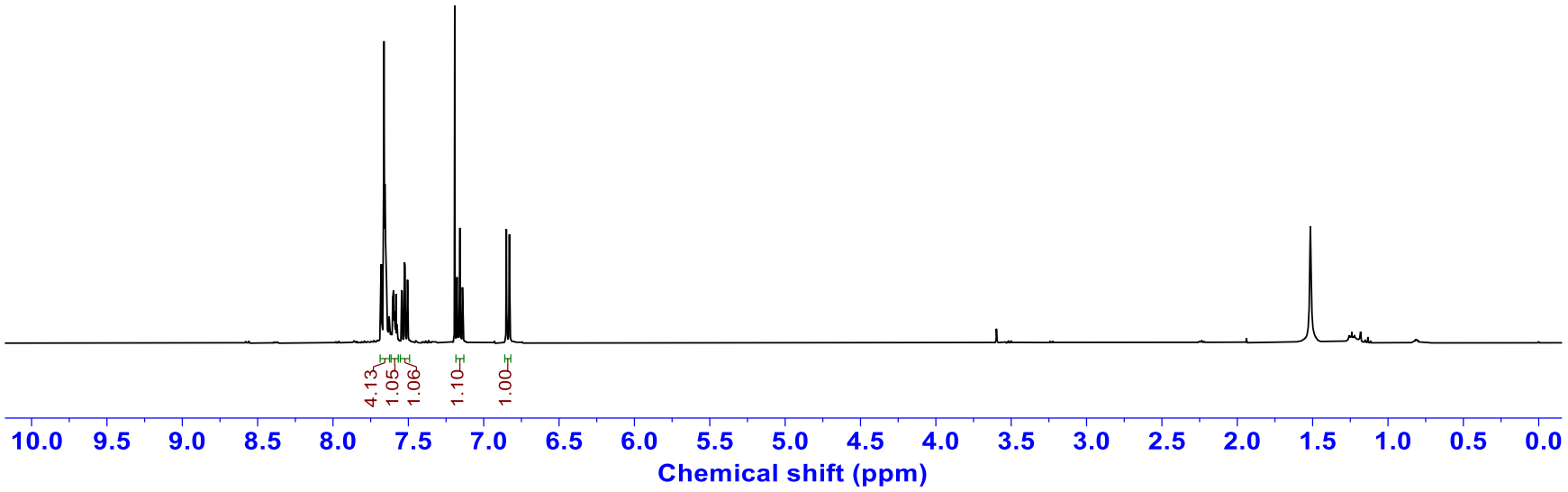


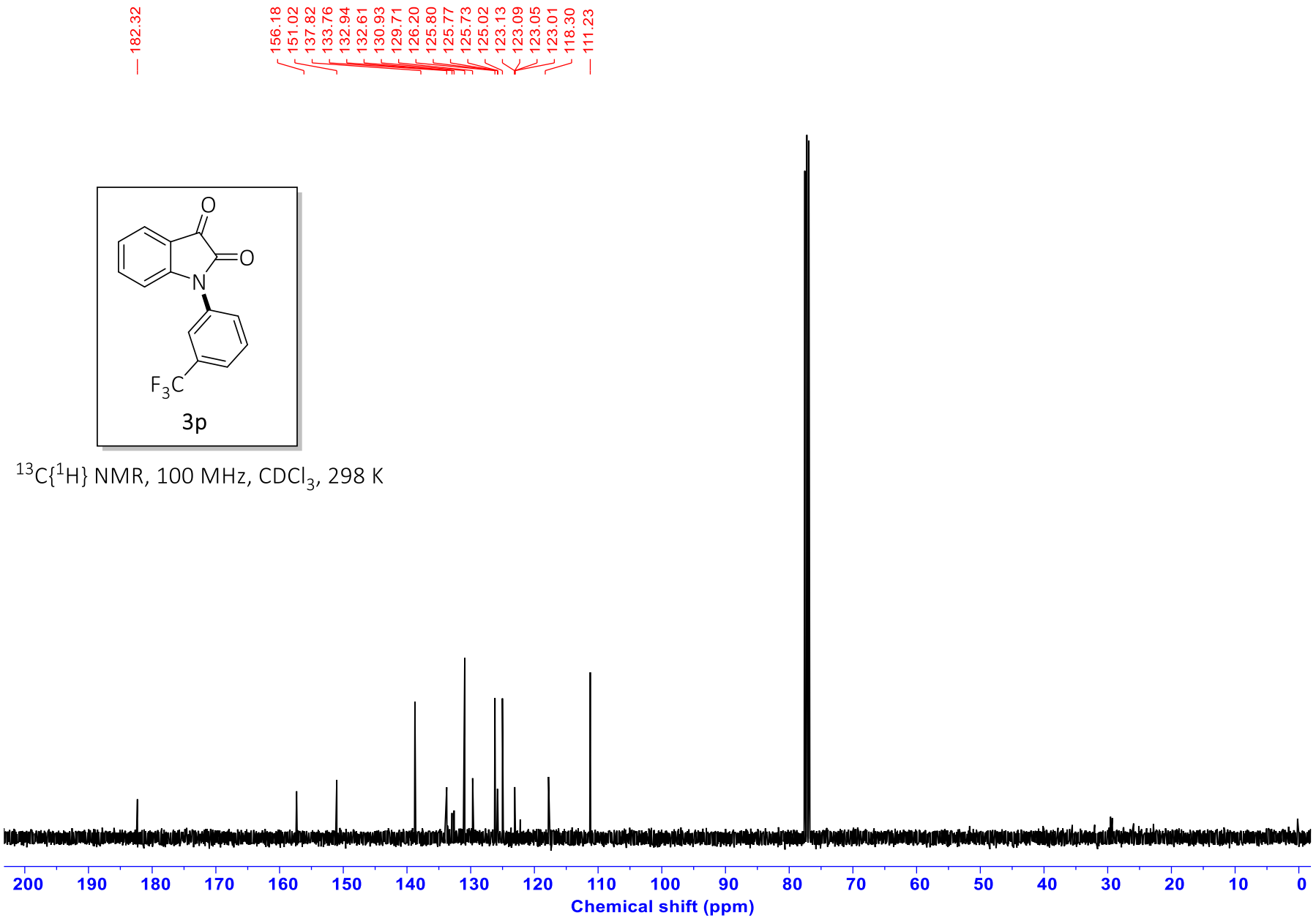
^{19}F NMR, 375 MHz, $CDCl_3$, 298 K



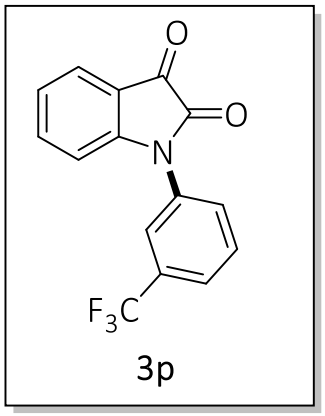


^{1}H NMR, 400 MHz, $CDCl_3$, 298 K



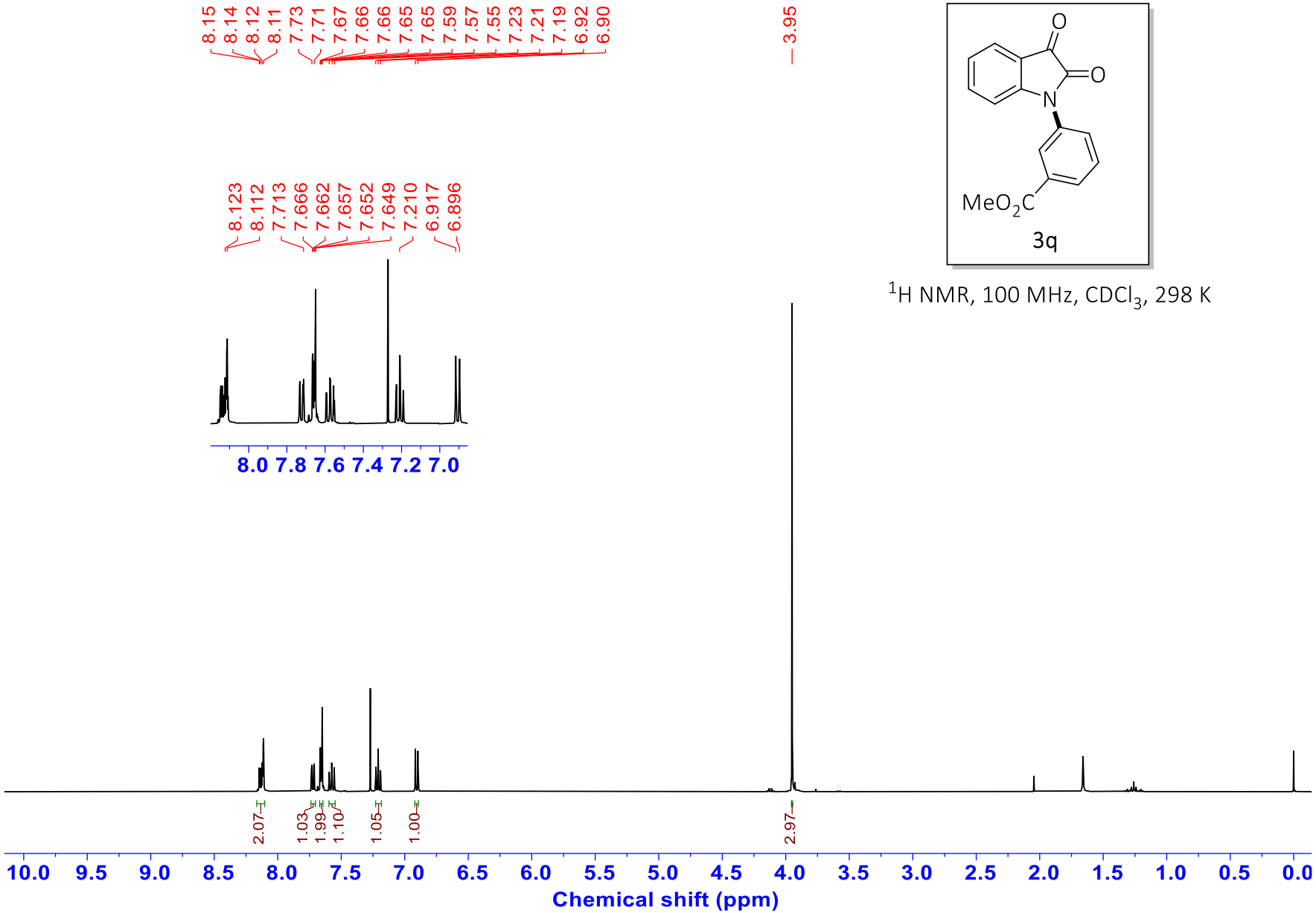


$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$, 298 K

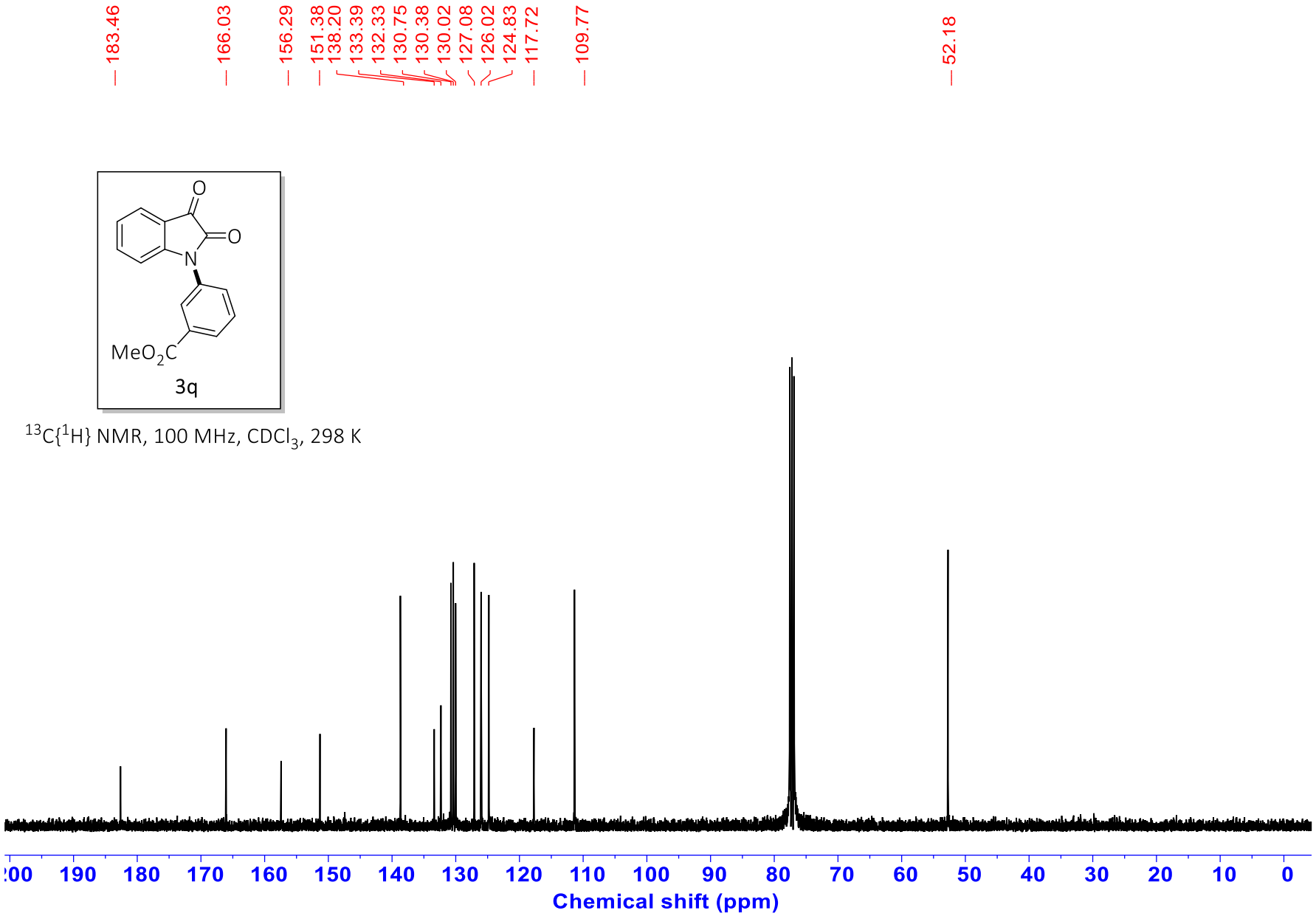


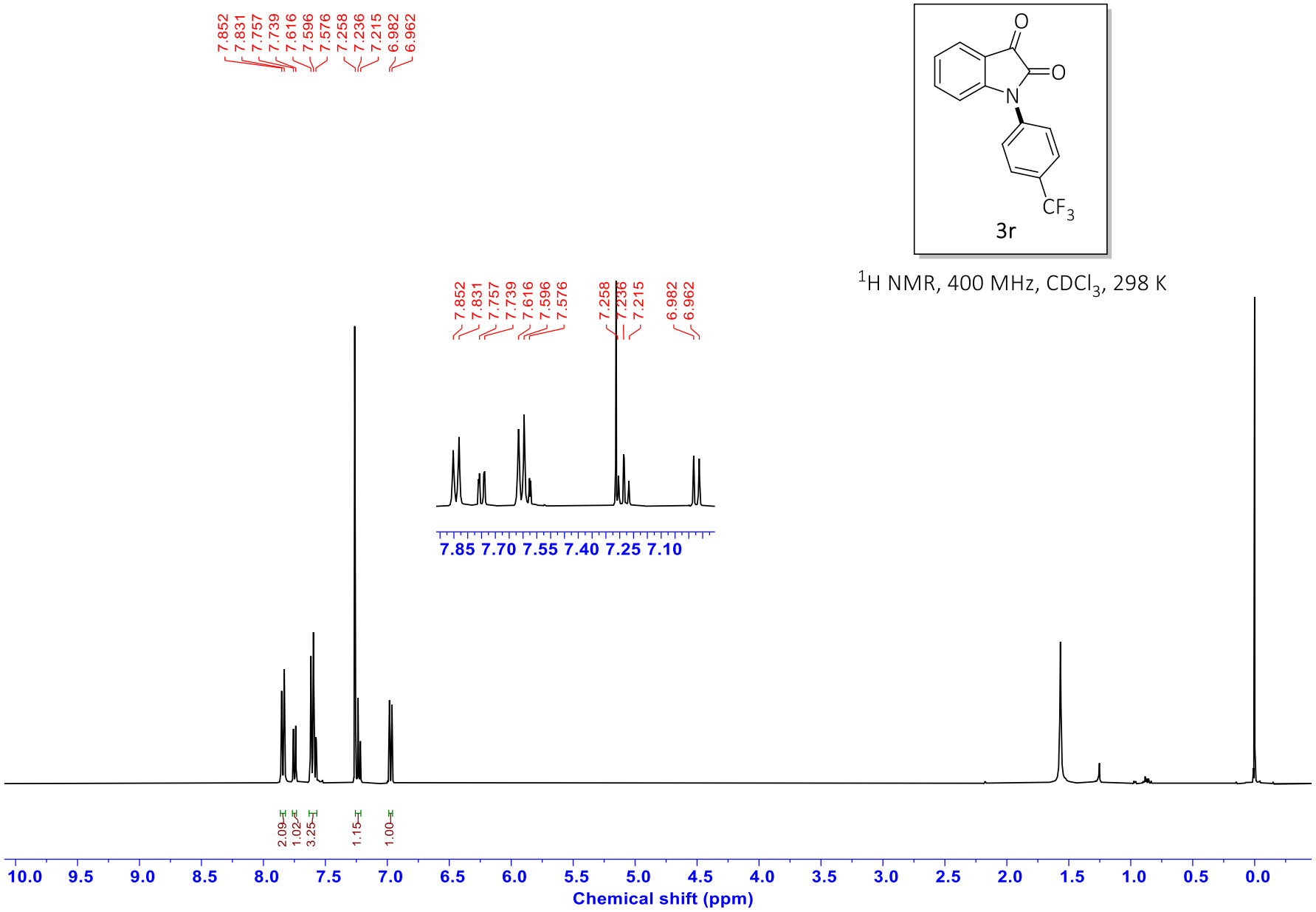
3p

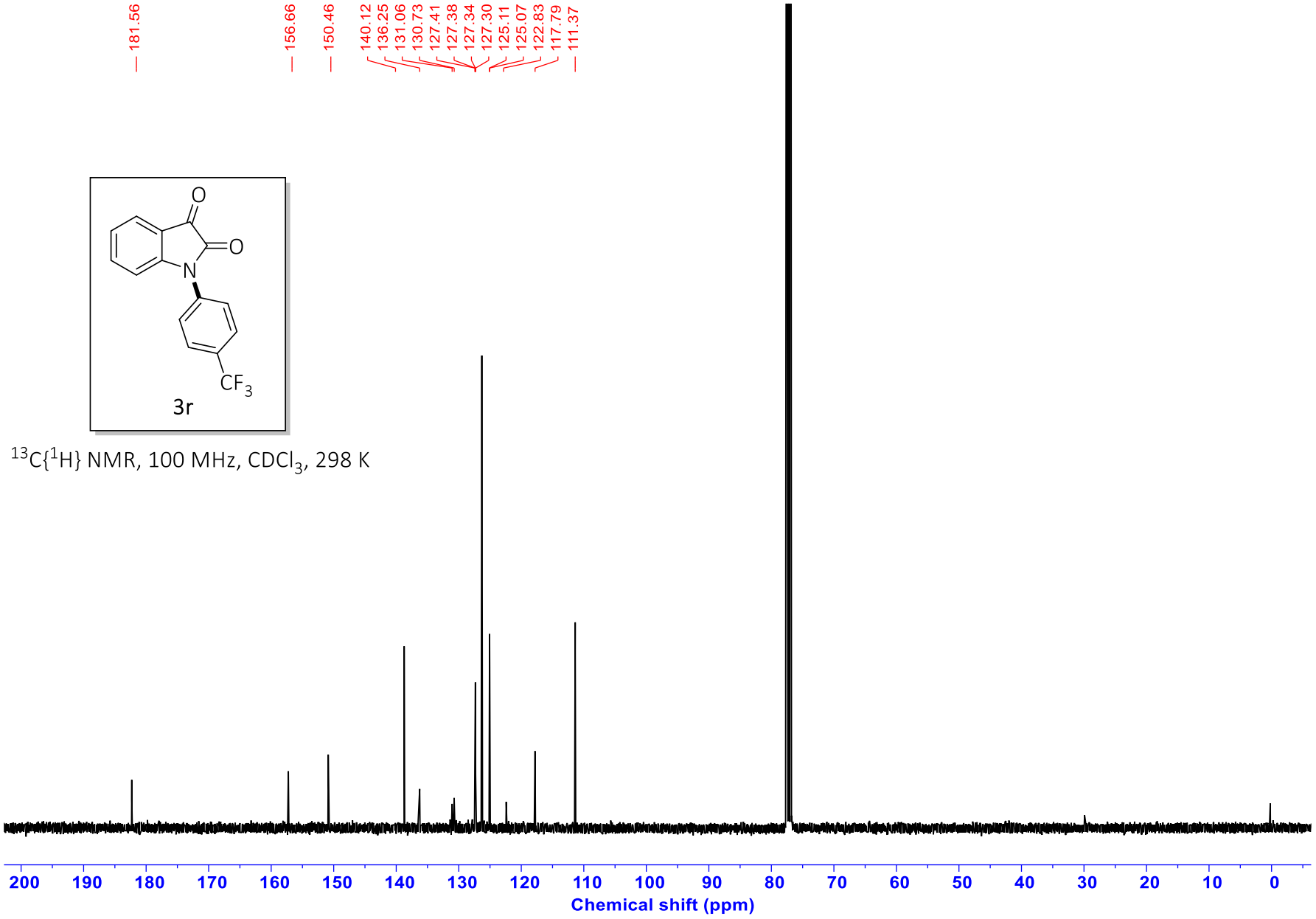
^{19}F NMR, 375 MHz, $CDCl_3$, 298 K



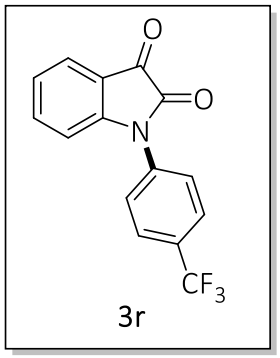
^{1}H NMR, 100 MHz, $CDCl_3$, 298 K


183.46
166.03
156.29
151.38
138.20
133.39
132.33
130.75
130.38
130.02
127.08
126.02
124.83
117.72
109.77
52.18
O
O
N
MeO2C
3q
13C{1H} NMR, 100 MHz, CDCl3, 298 K
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical shift (ppm)

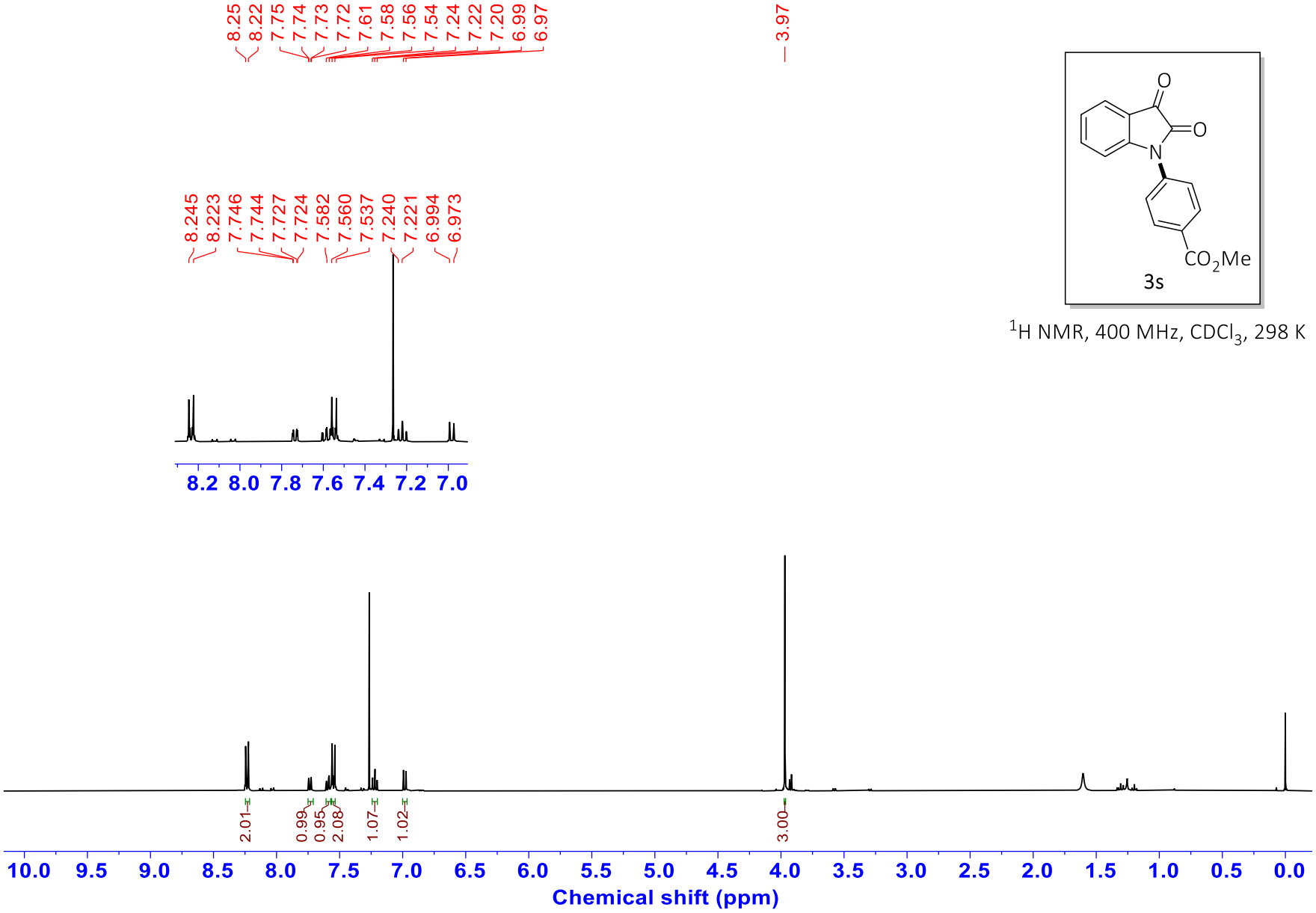

7.852
7.831
7.757
7.739
7.616
7.596
7.576
7.258
7.236
7.215
6.982
6.962
O
O
N
CF3
3r
1H NMR, 400 MHz, CDCl3, 298 K
7.85 7.70 7.55 7.40 7.25 7.10
2.09
1.02
3.25
1.15
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical shift (ppm)



$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$, 298 K

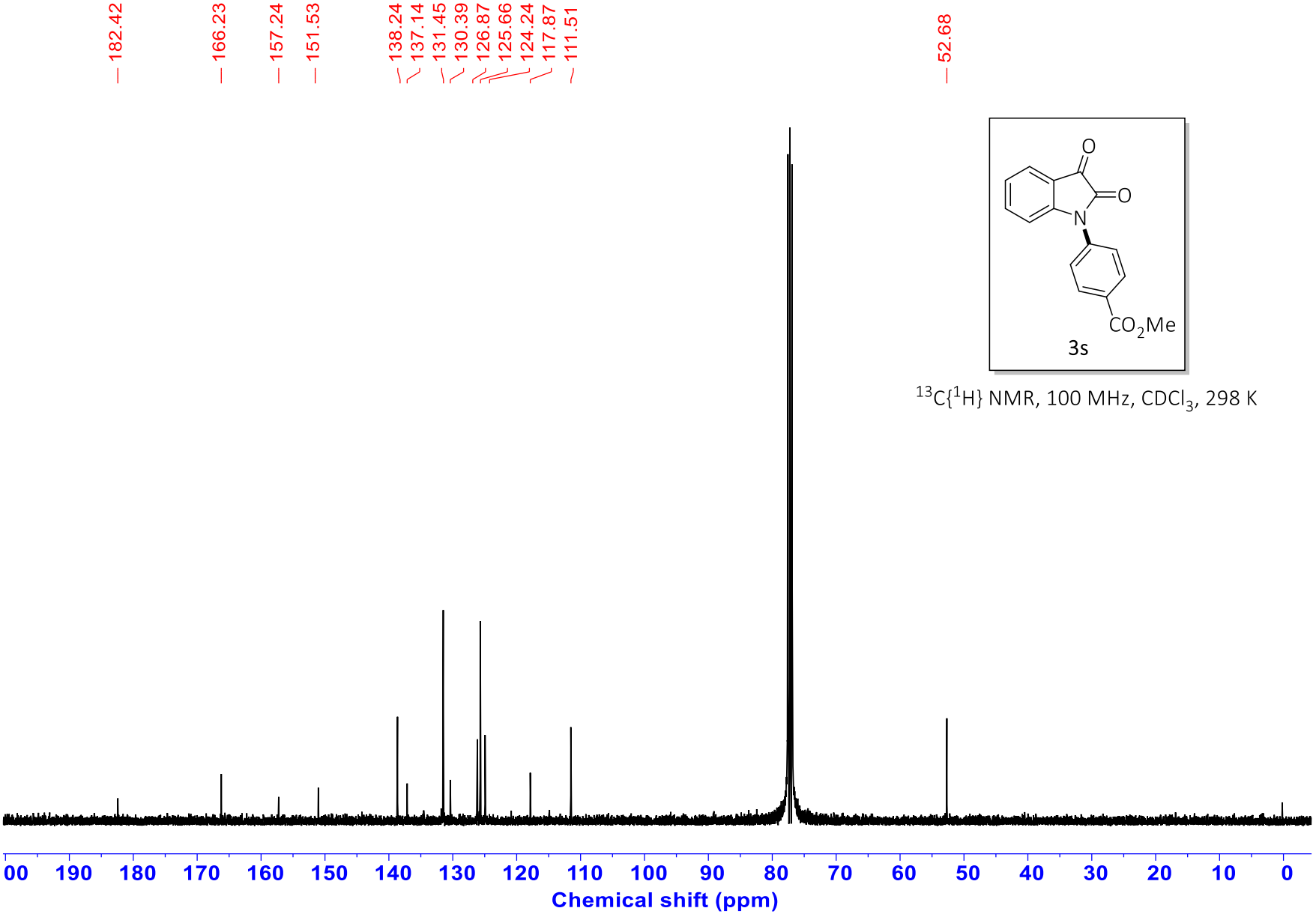


^{19}F NMR, 375 MHz, $CDCl_3$, 298 K

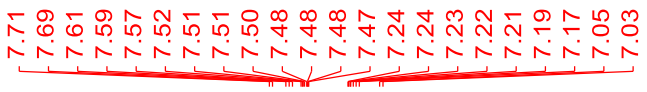


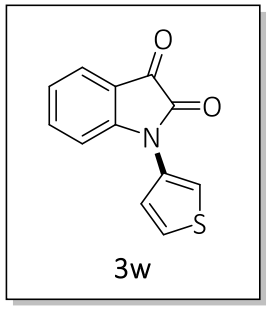
3s

^{1}H NMR, 400 MHz, $CDCl_3$, 298 K

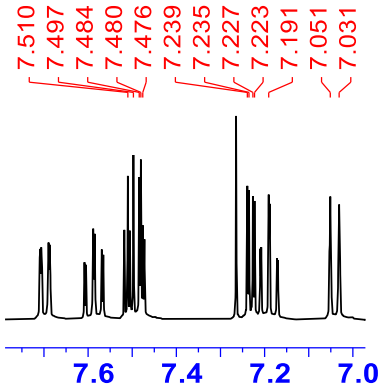


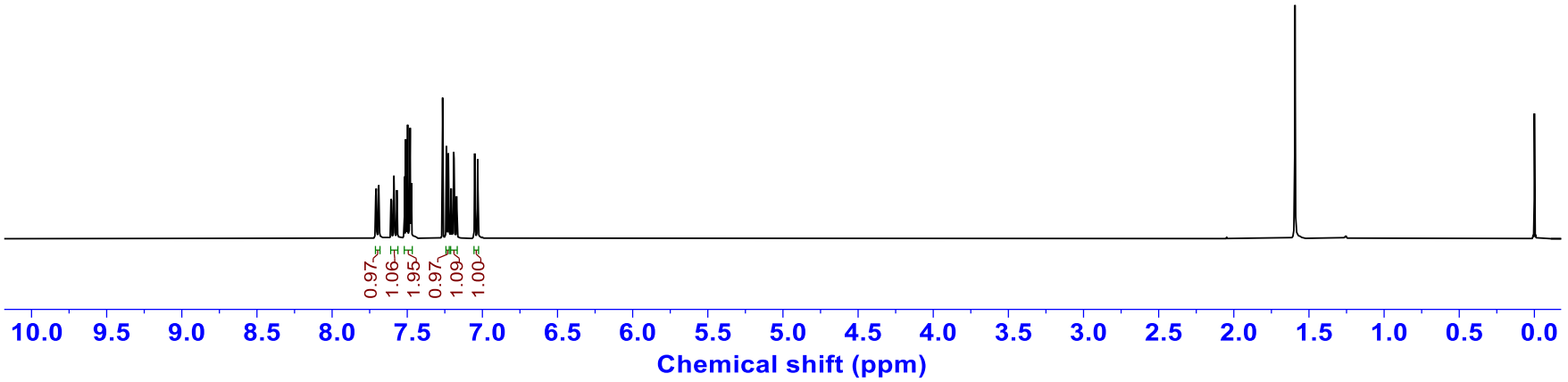
$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$, 298 K

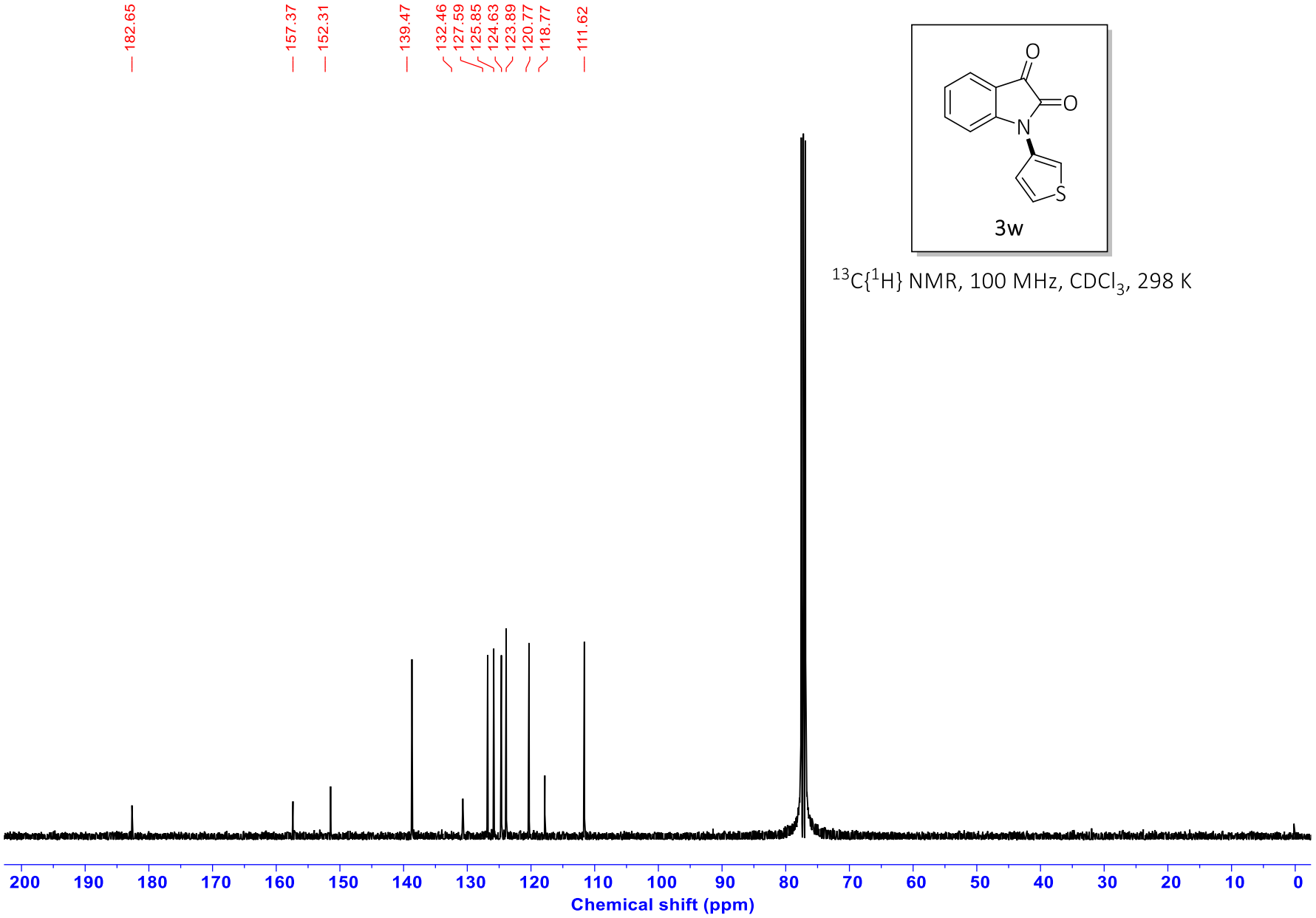




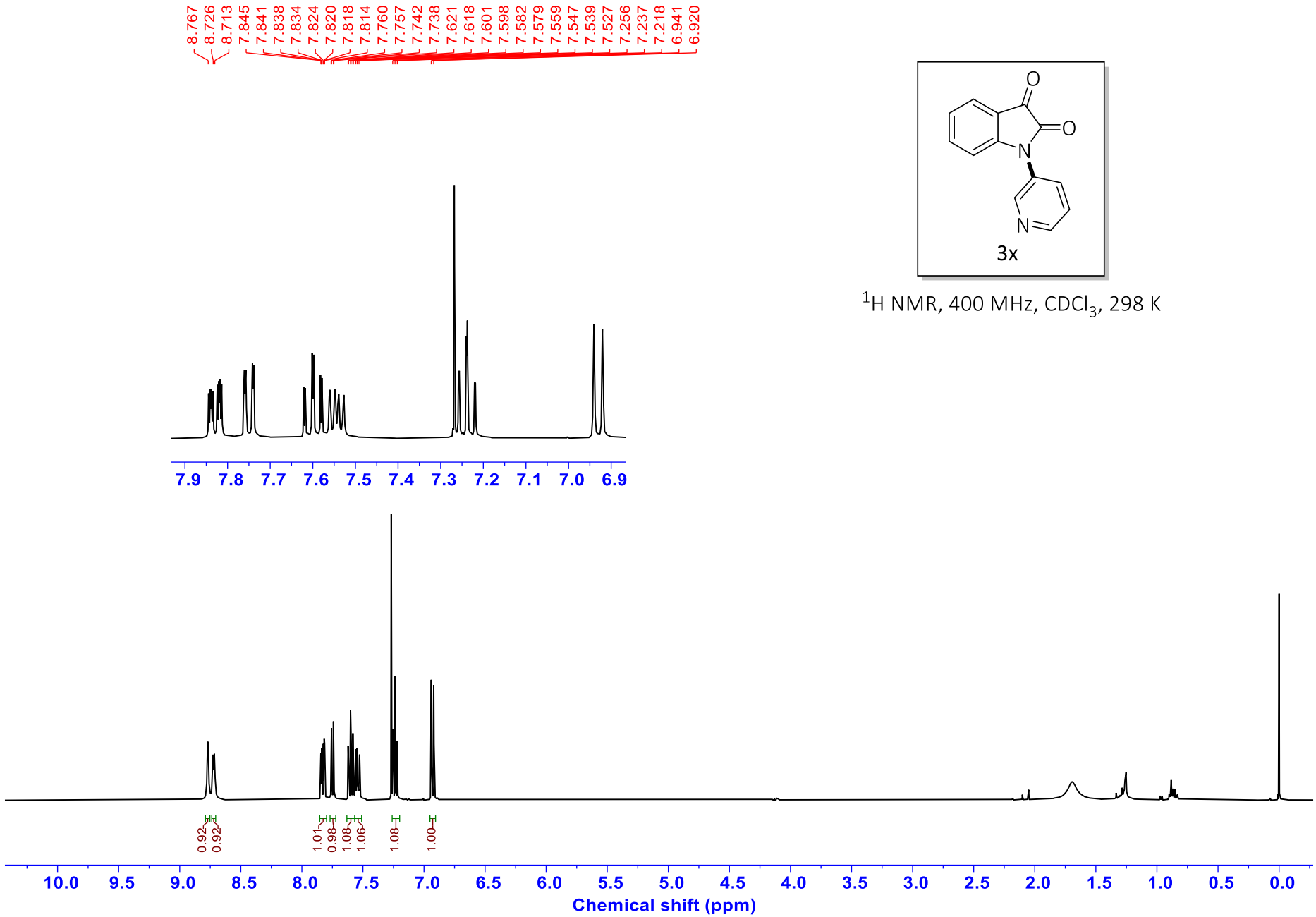
^{1}H NMR, 400 MHz, $CDCl_3$, 298 K



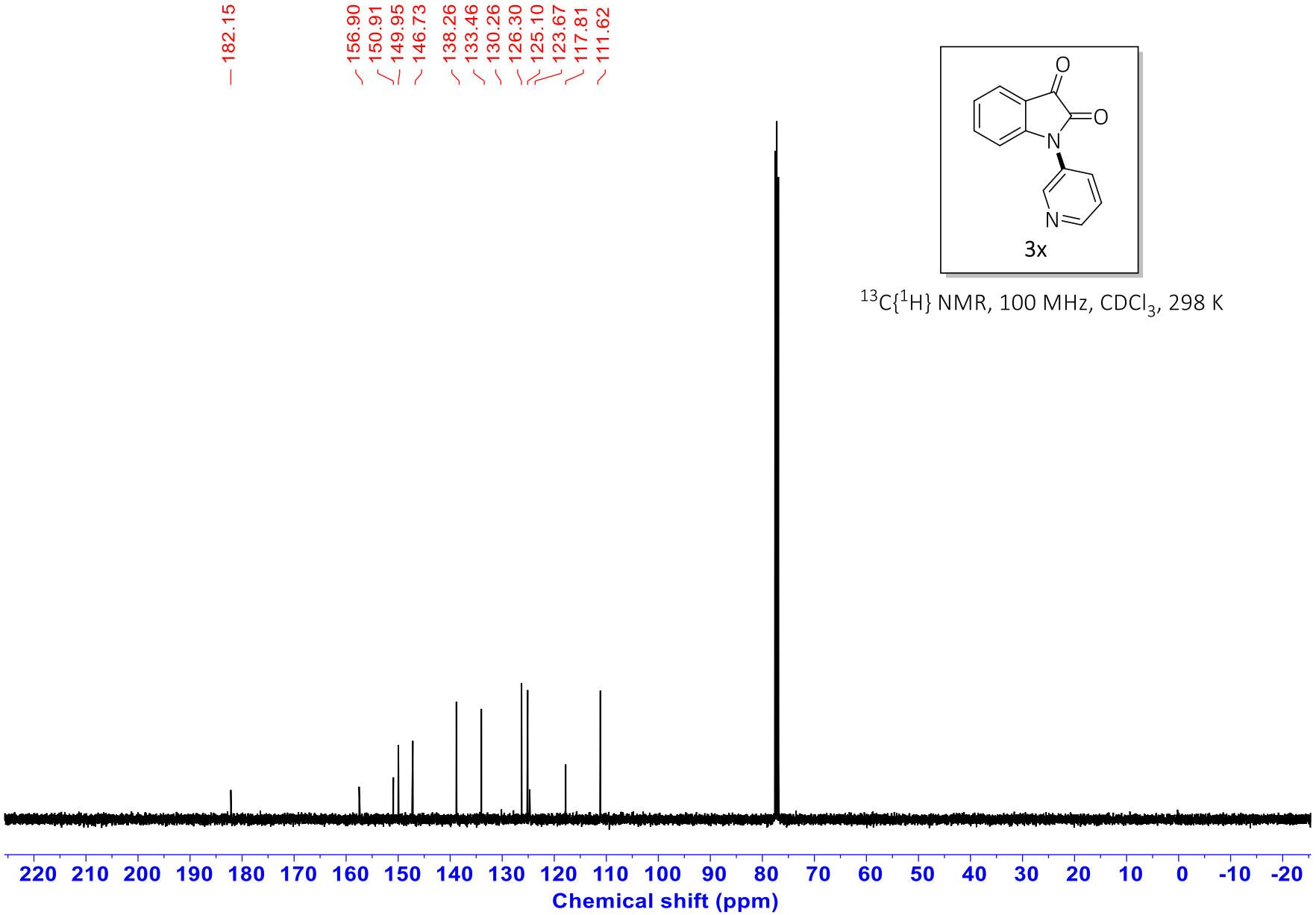




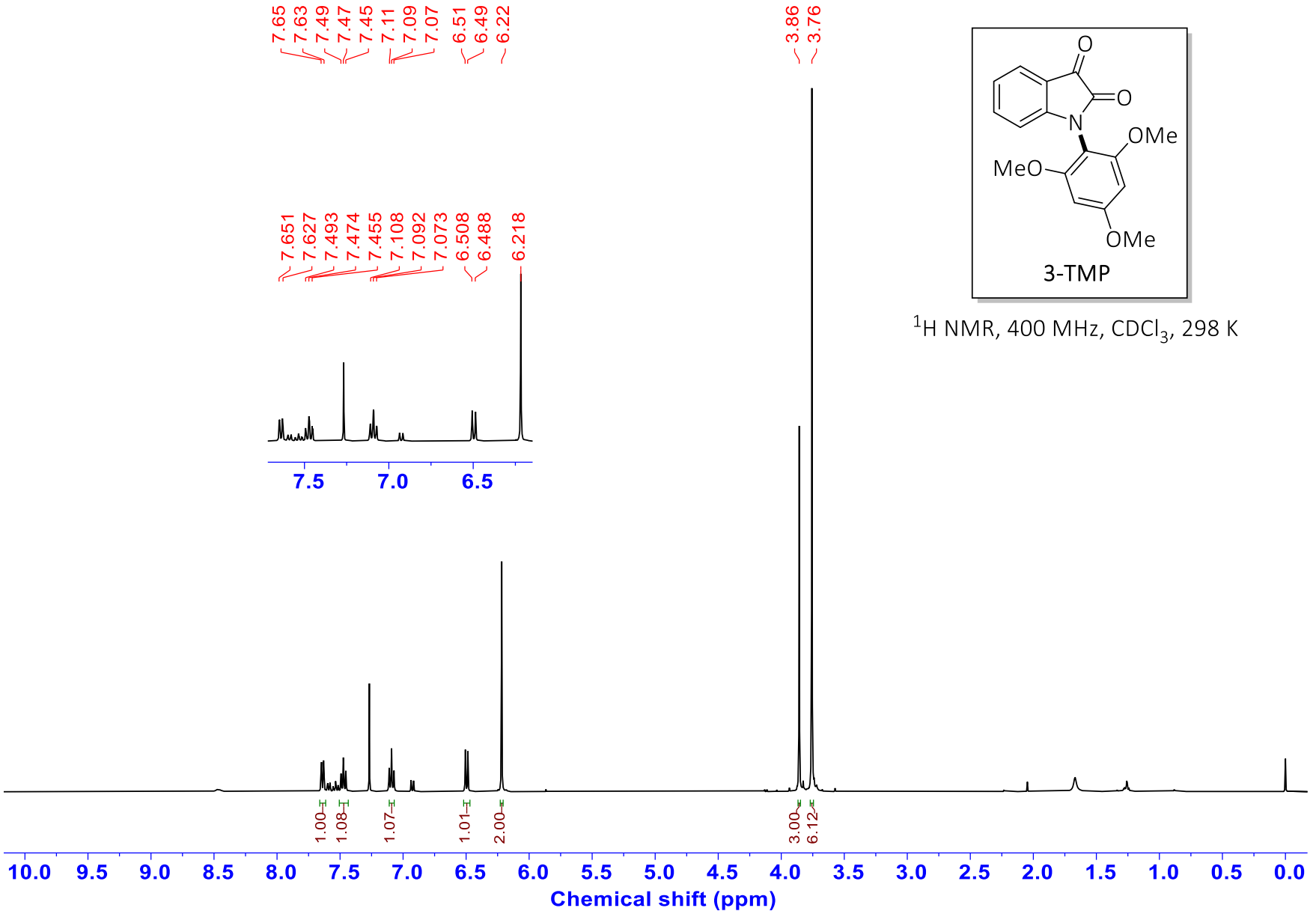
$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$, 298 K



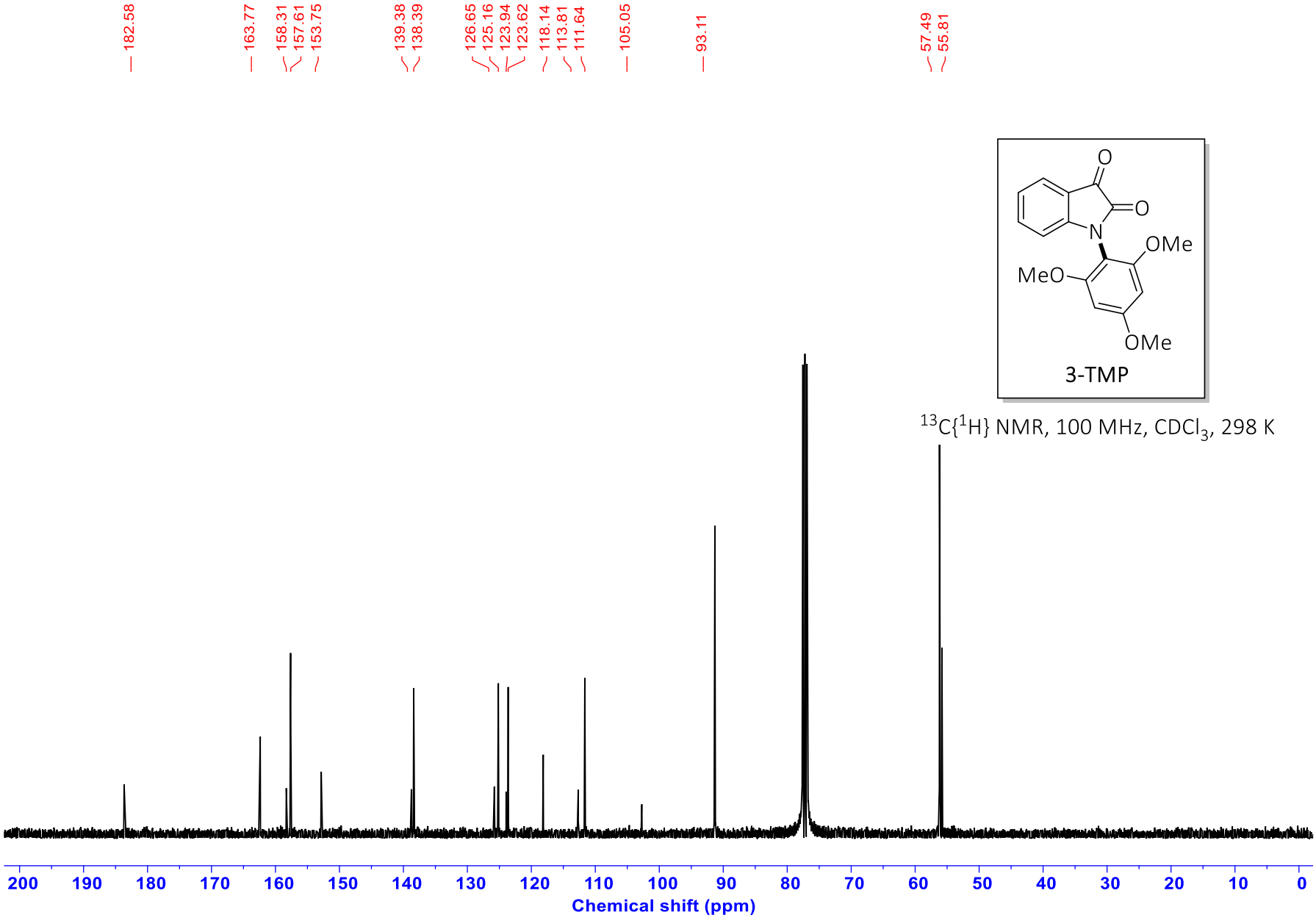
^{1}H NMR, 400 MHz, $CDCl_3$, 298 K

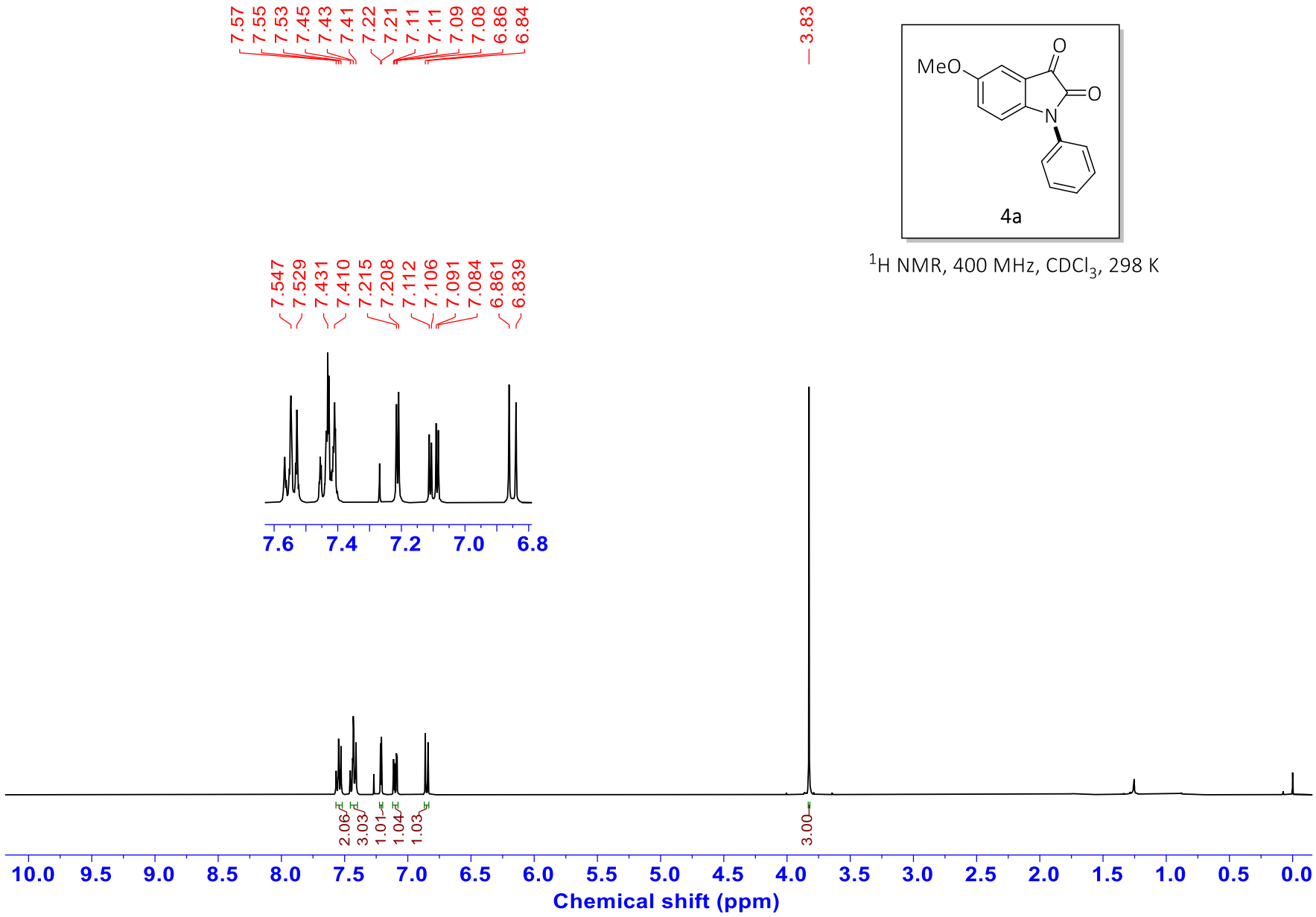


$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$, 298 K

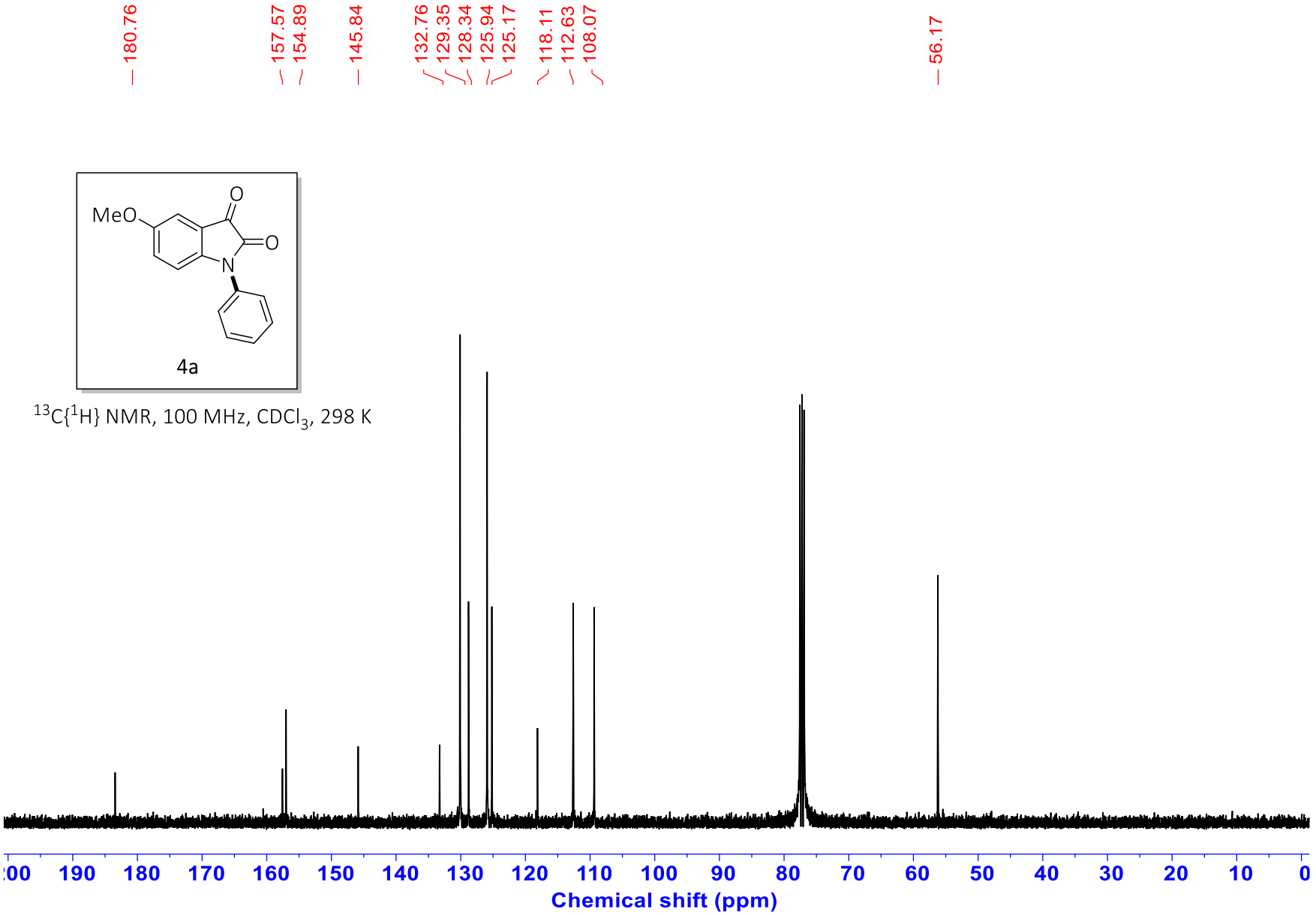


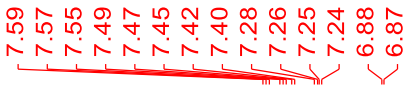
^{1}H NMR, 400 MHz, $CDCl_3$, 298 K

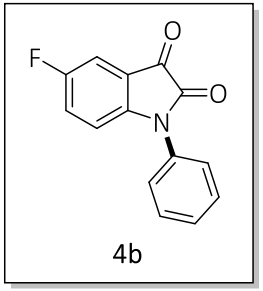

182.58
163.77
158.31
157.61
153.75
139.38
138.39
126.65
125.16
123.94
123.62
118.14
113.81
111.64
105.05
93.11
57.49
55.81
O
O
N
OMe
MeO
OMe
3-TMP
$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$, 298 K
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical shift (ppm)



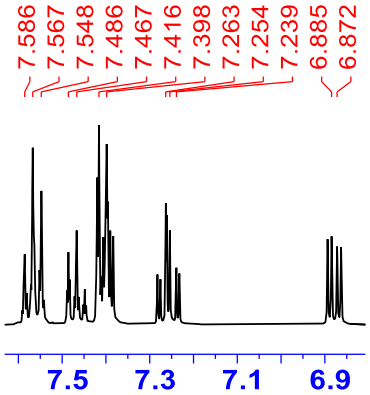
^{1}H NMR, 400 MHz, $CDCl_3$, 298 K

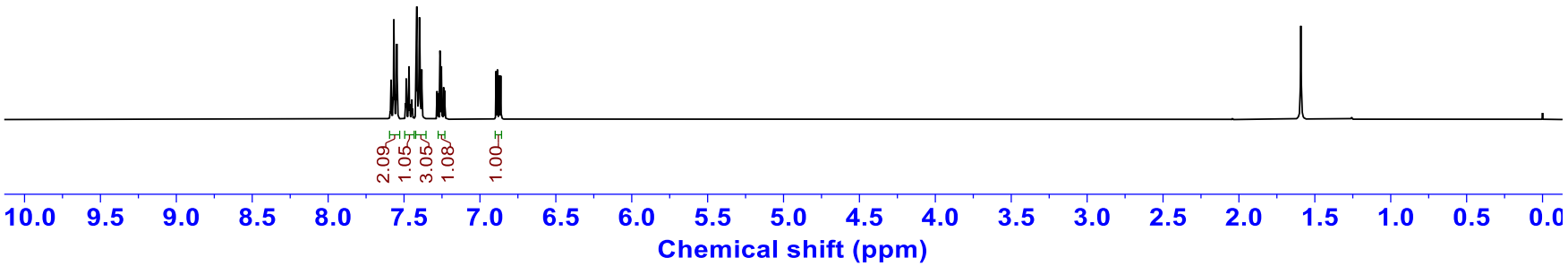

180.76
157.57
154.89
145.84
132.76
129.35
128.34
125.94
125.17
118.11
112.63
108.07
56.17
MeO
O
O
N
4a
$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$, 298 K
Chemical shift (ppm)

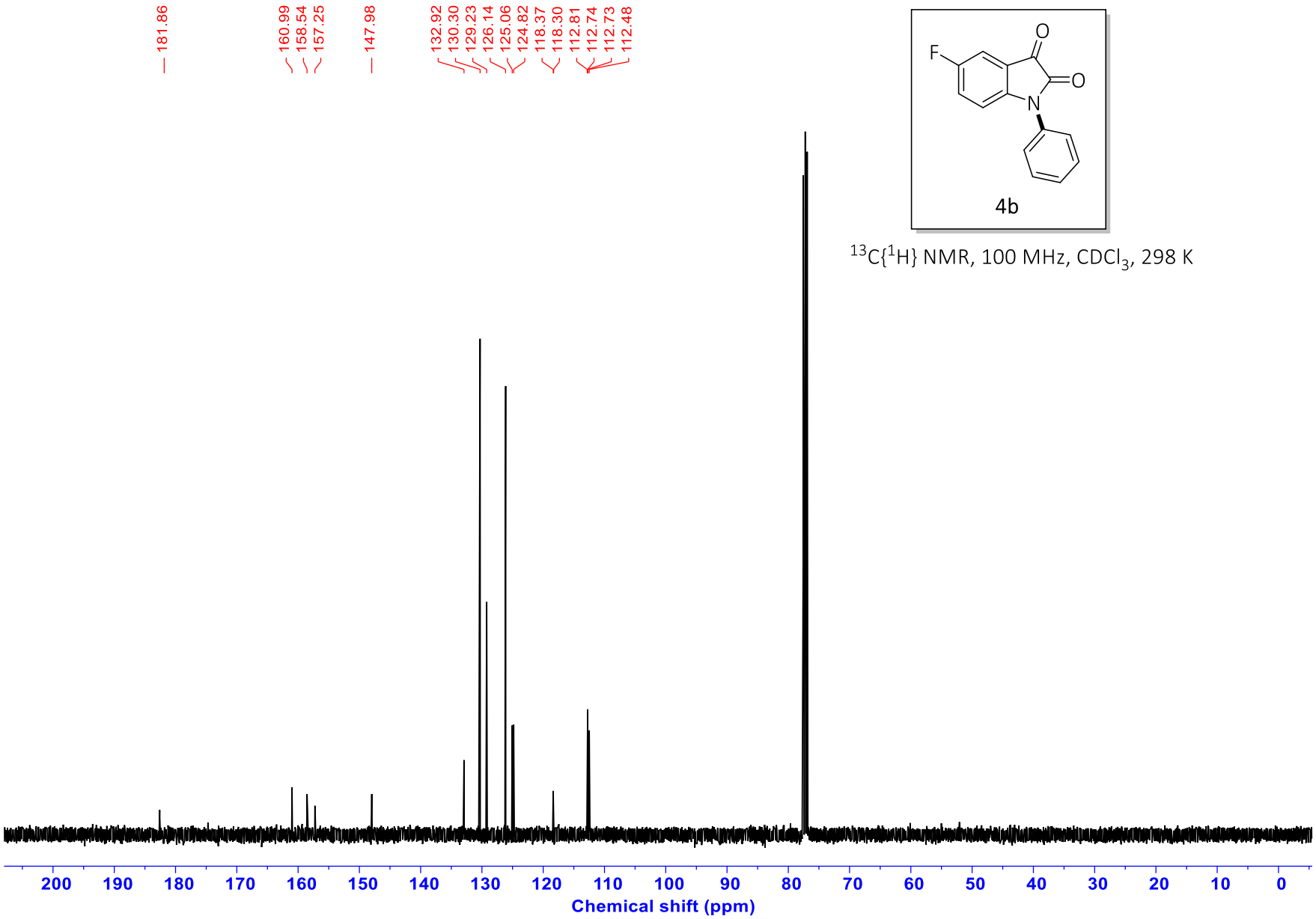




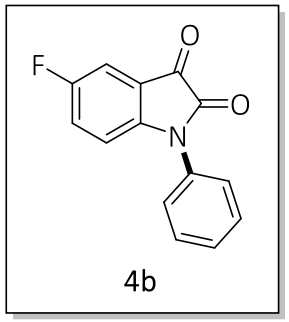
^{1}H NMR, 400 MHz, $CDCl_3$, 298 K





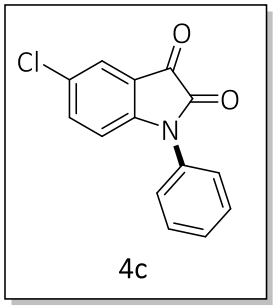


$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$, 298 K

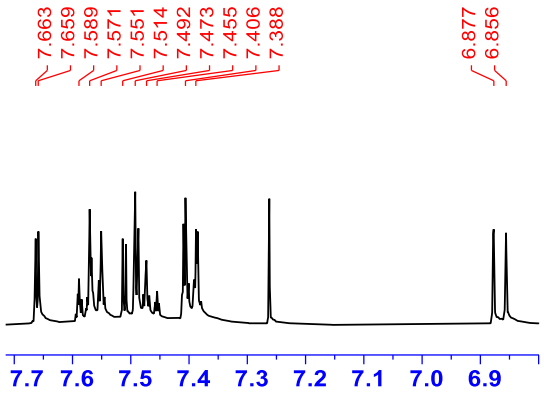


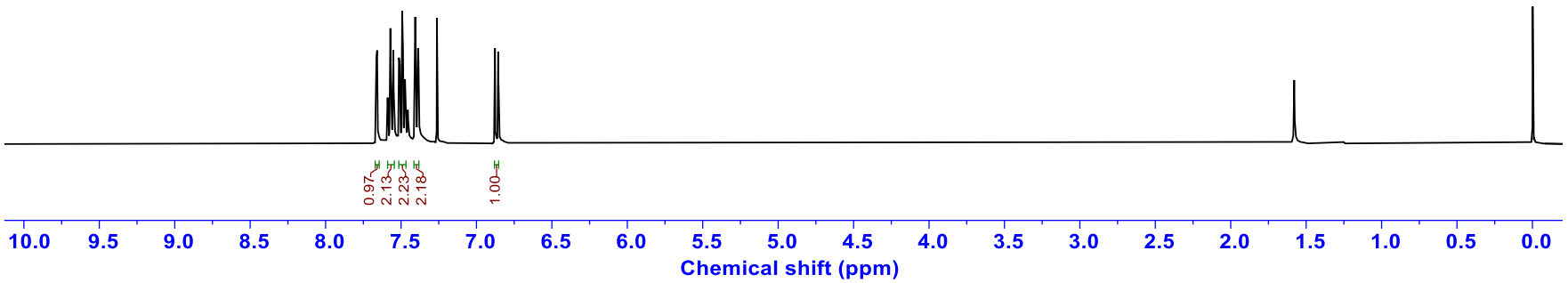
4b

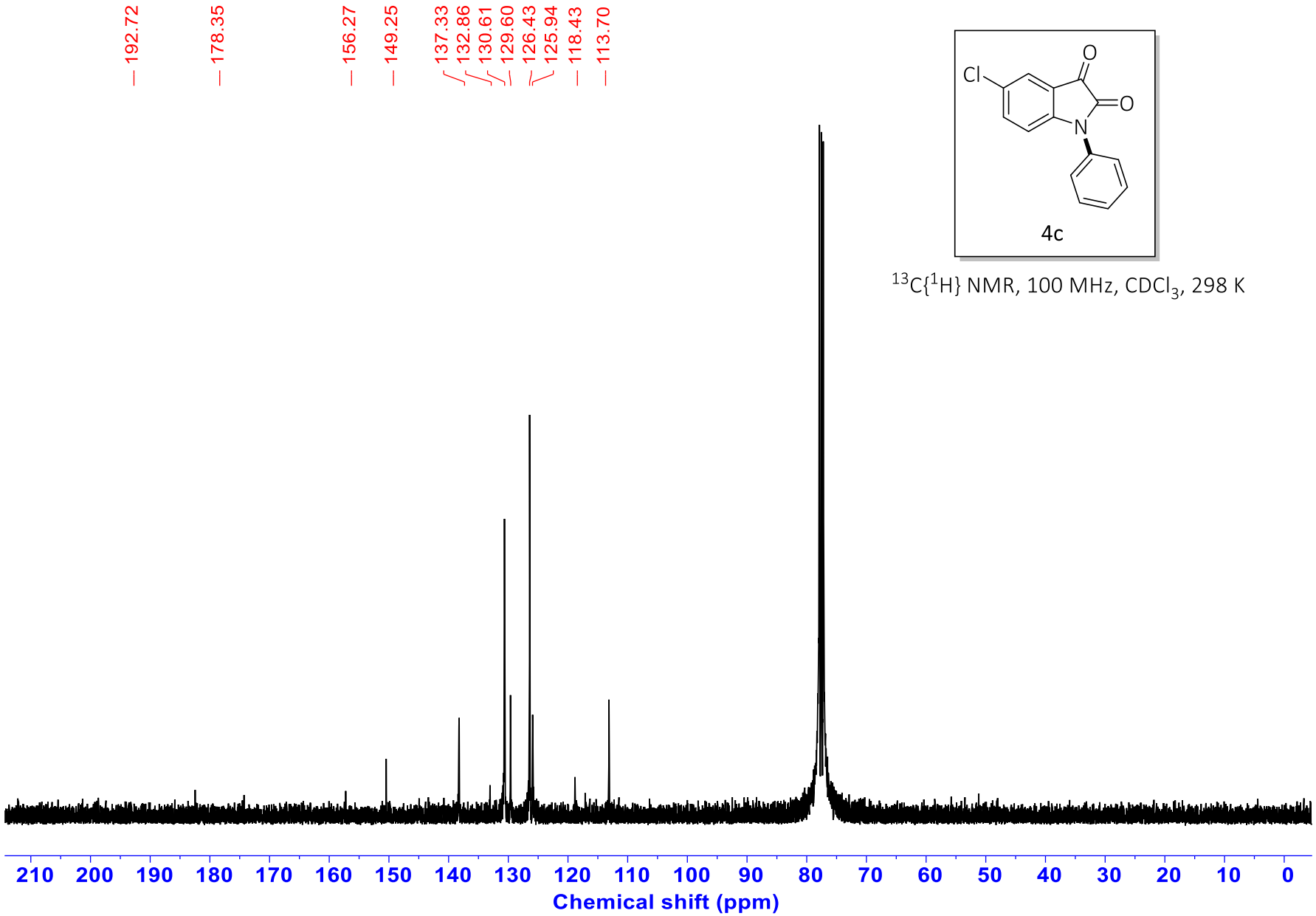
^{19}F NMR, 375 MHz, $CDCl_3$, 298 K

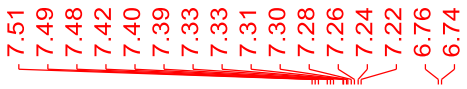


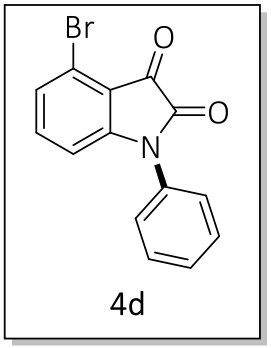
^{1}H NMR, 400 MHz, $CDCl_3$, 298 K

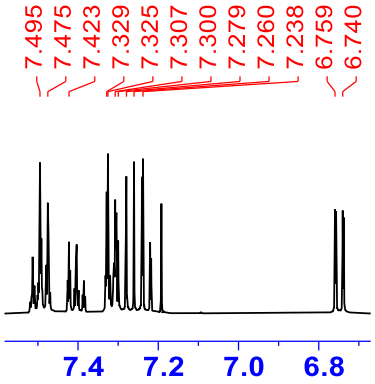




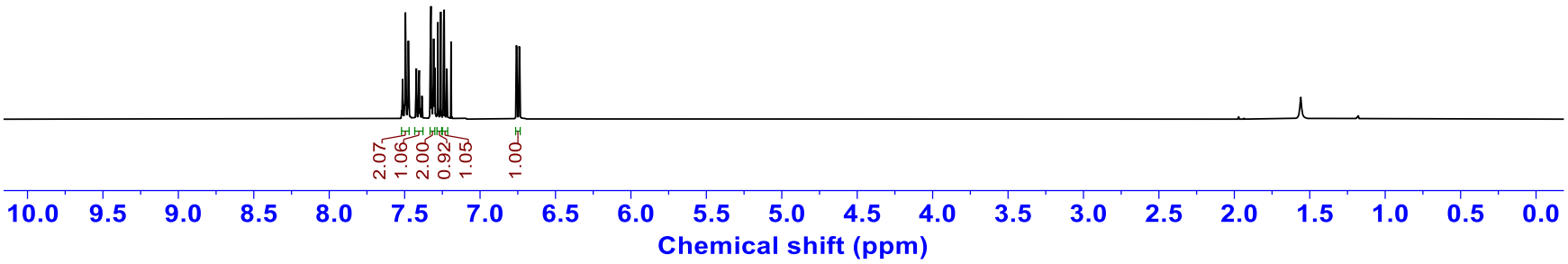

192.72
178.35
156.27
149.25
137.33
132.86
130.61
129.60
126.43
125.94
118.43
113.70
Cl
O
O
N
4c
$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$, 298 K
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical shift (ppm)

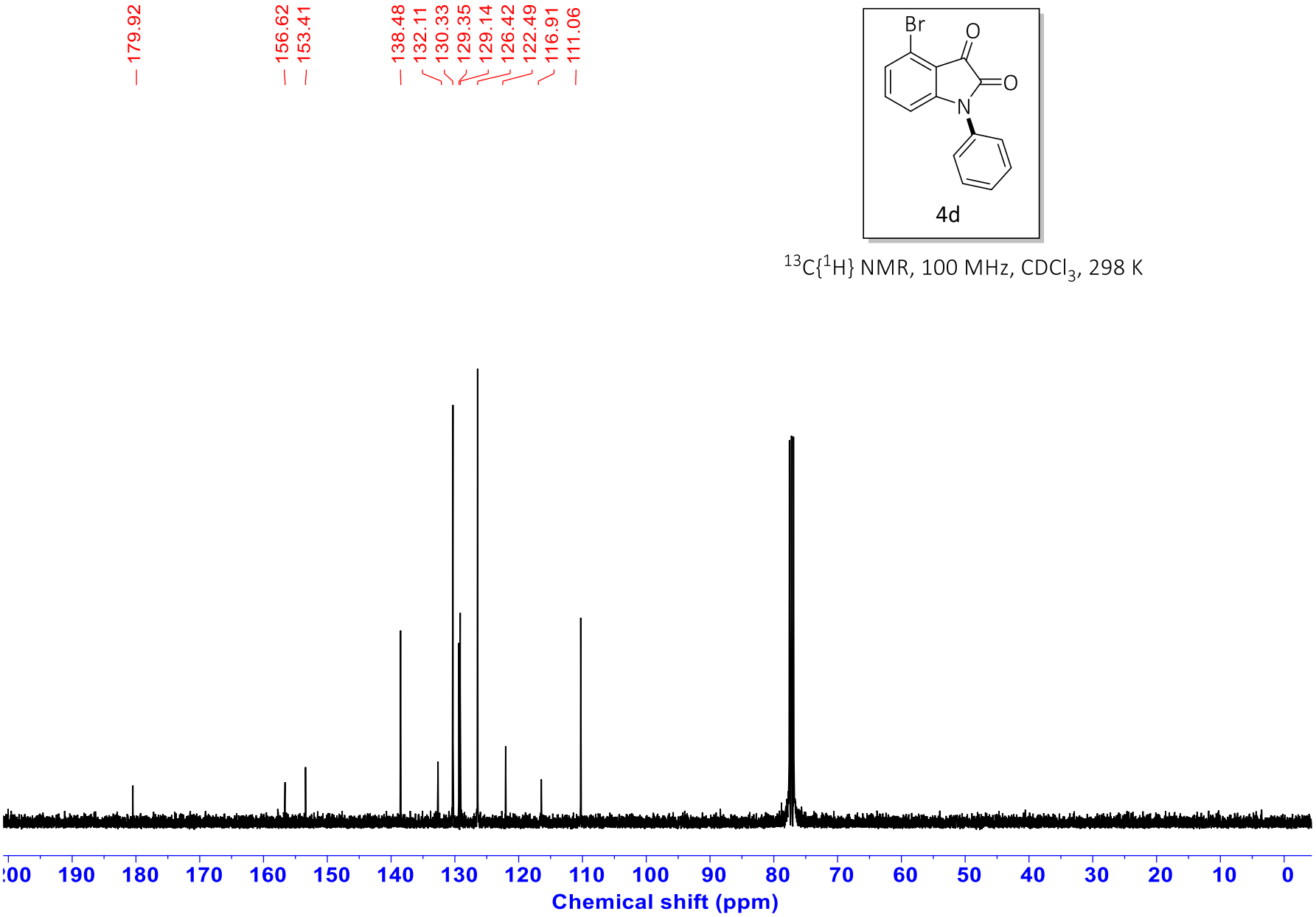




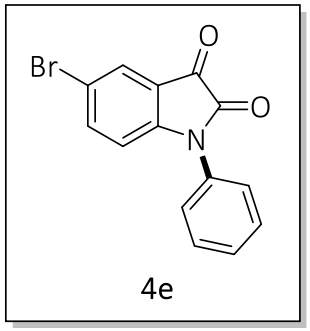


^{1}H NMR, 400 MHz, $CDCl_3$, 298 K

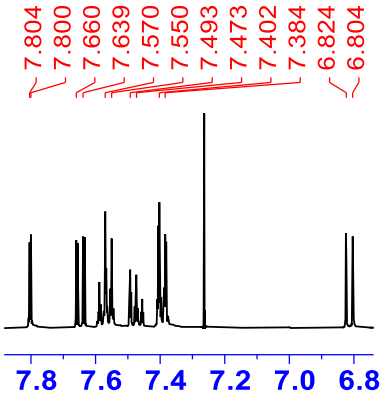


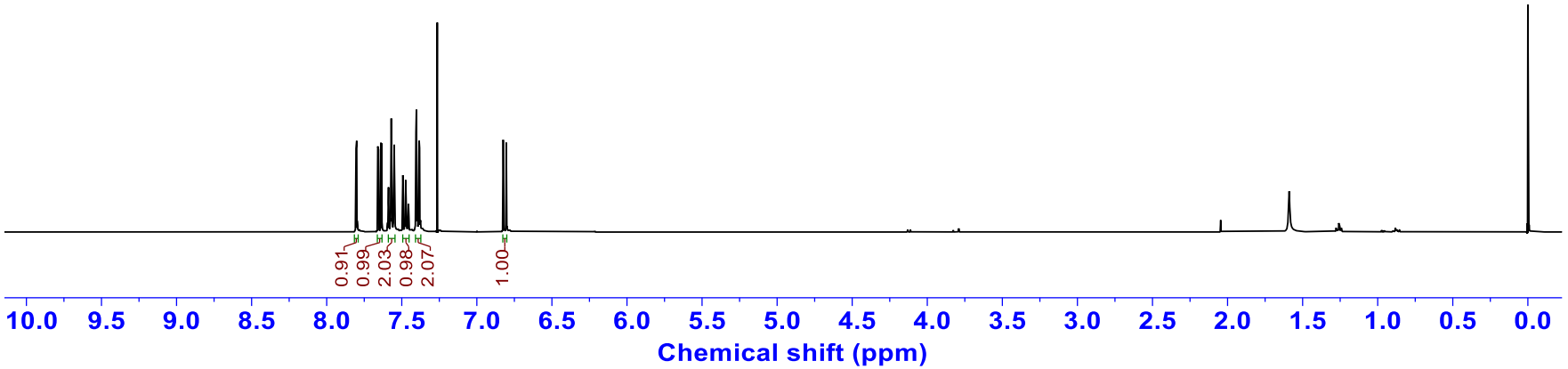


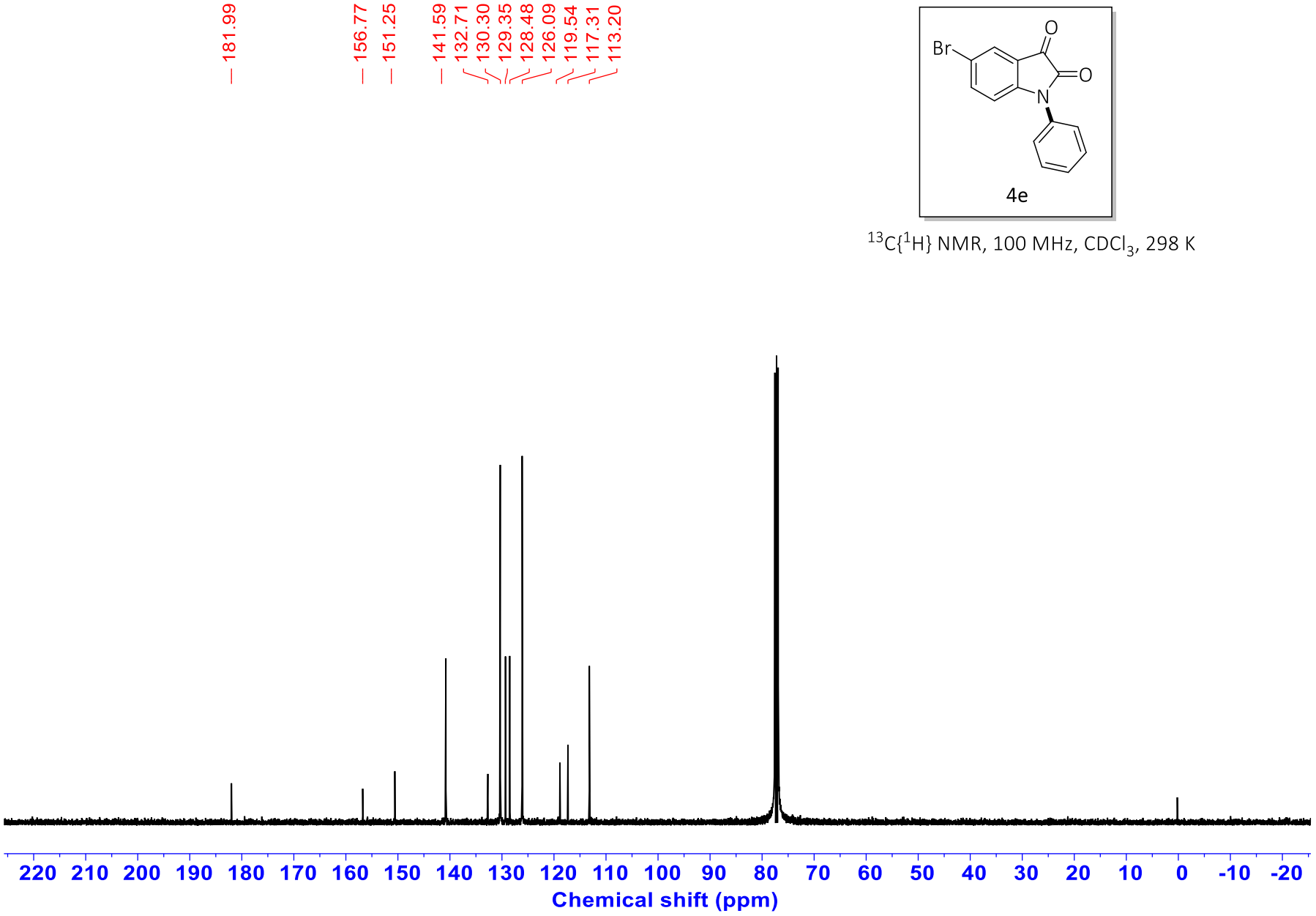
$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$, 298 K



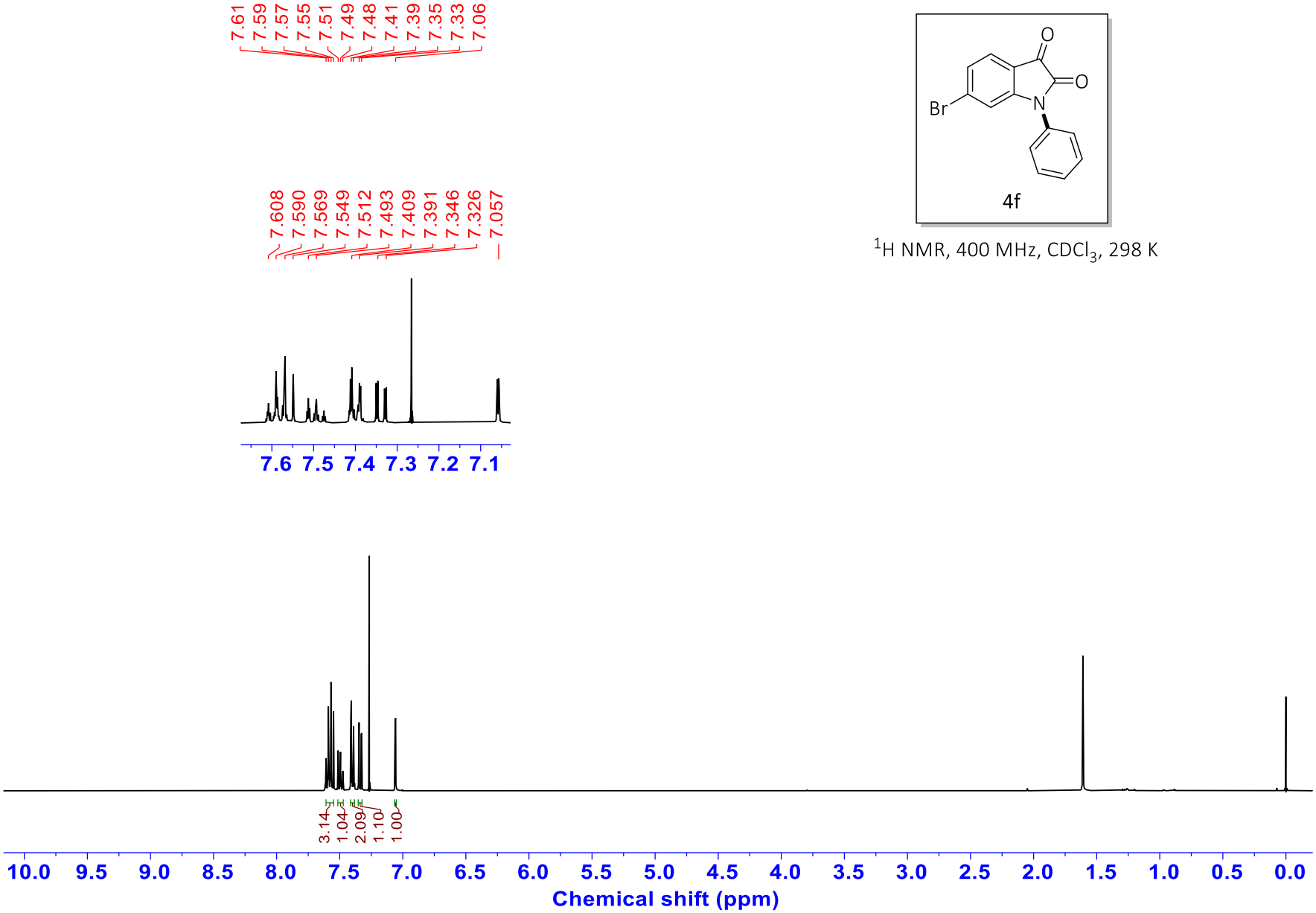
^{1}H NMR, 400 MHz, $CDCl_3$, 298 K



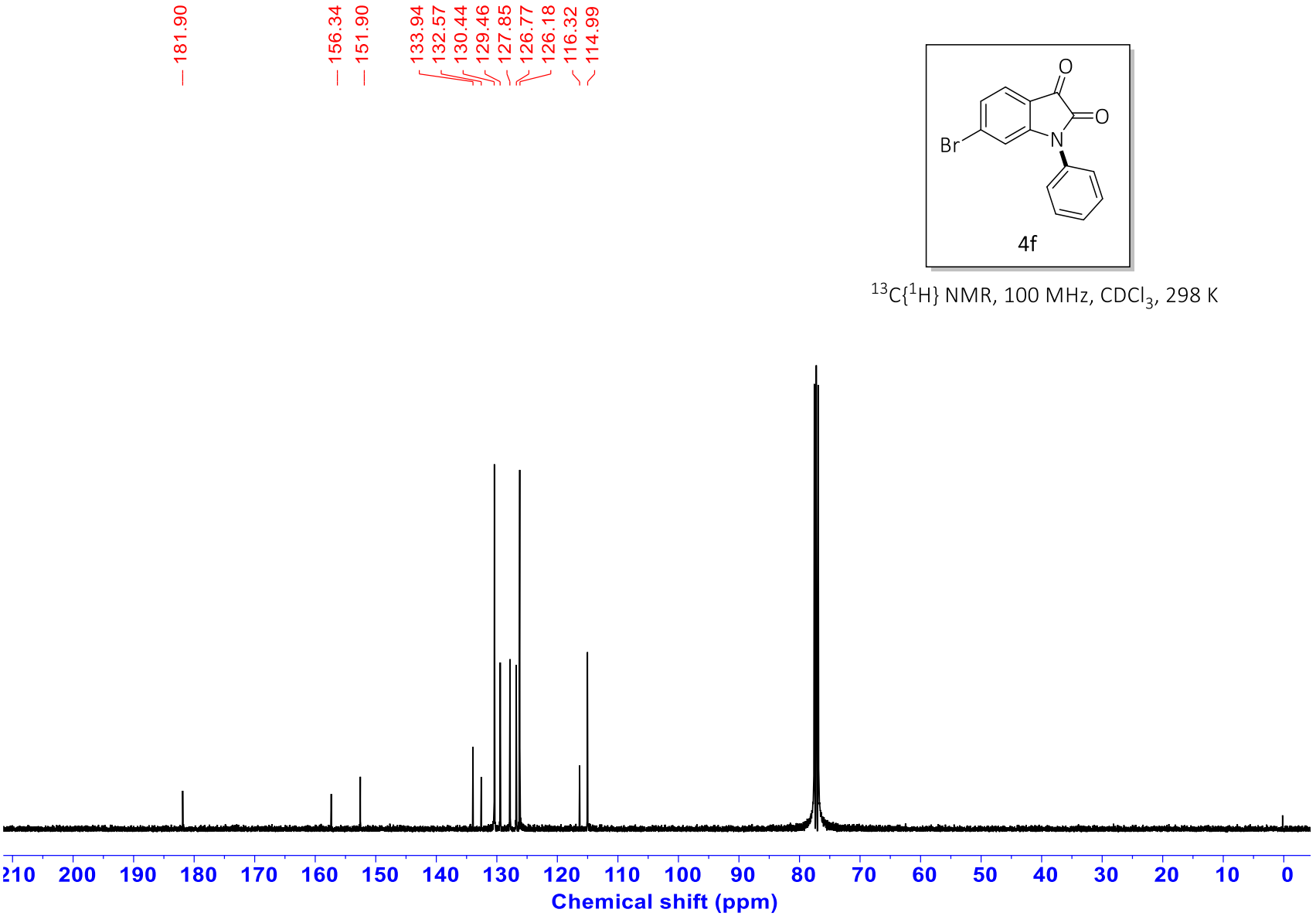




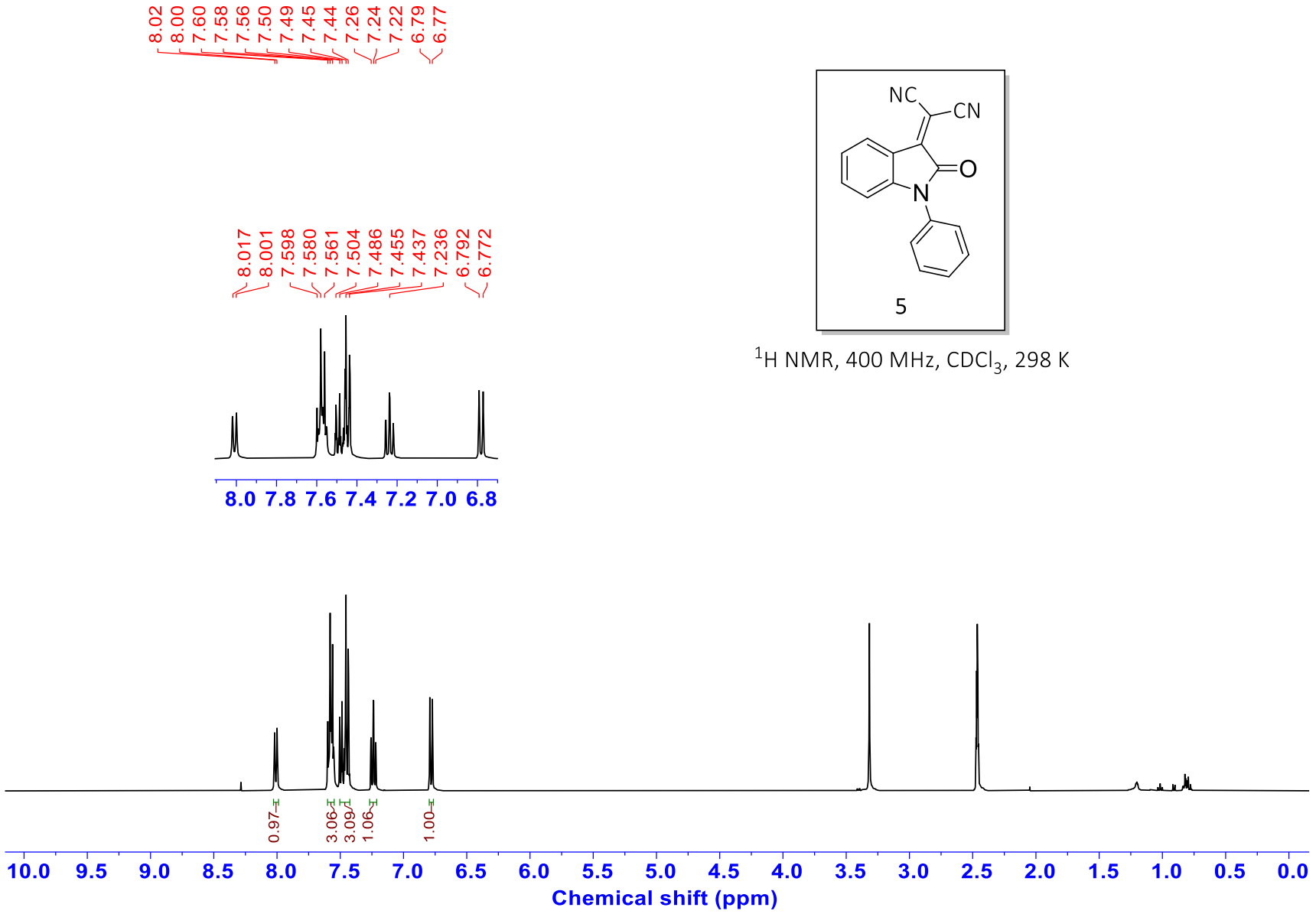
$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$, 298 K



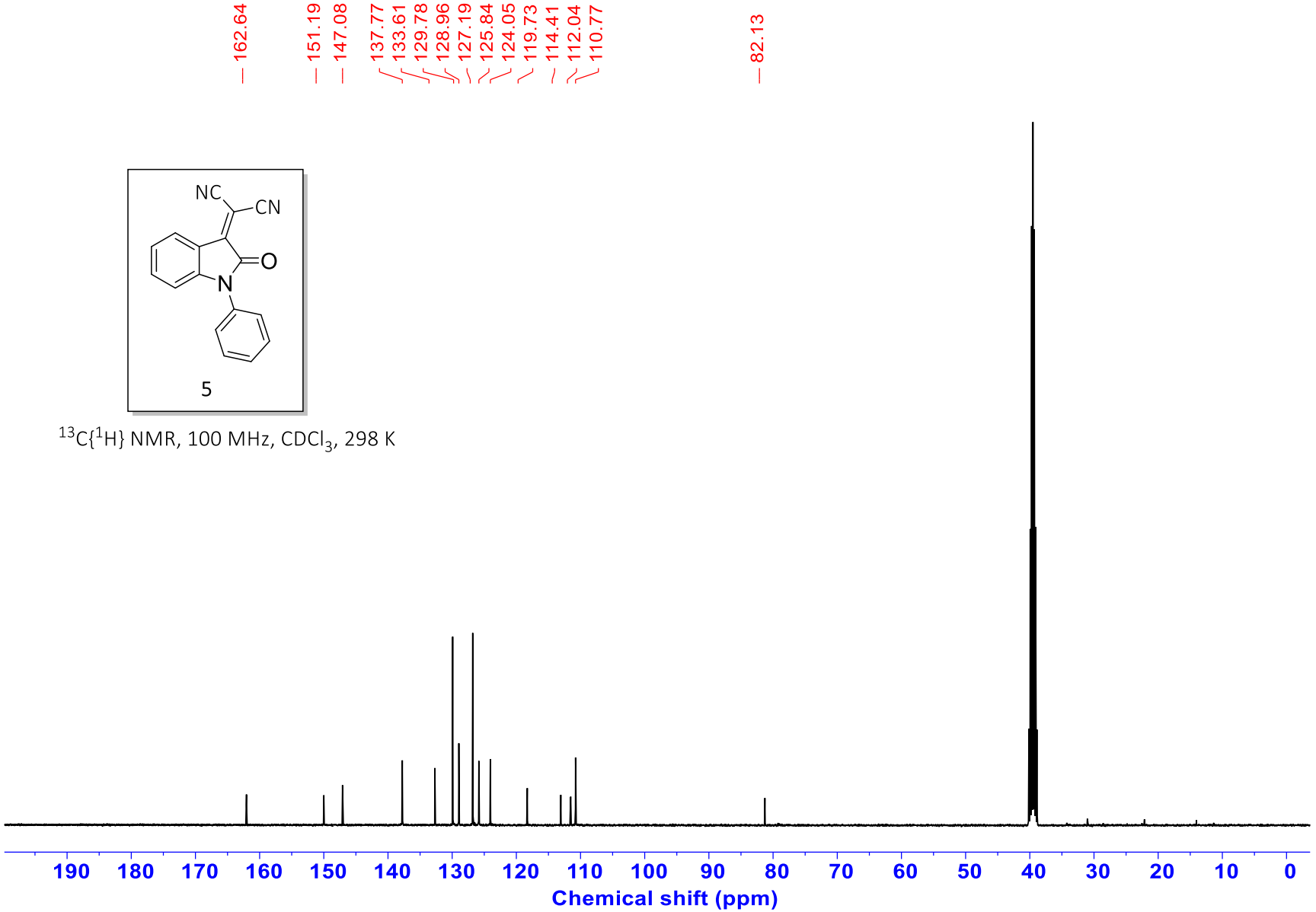
^{1}H NMR, 400 MHz, $CDCl_3$, 298 K



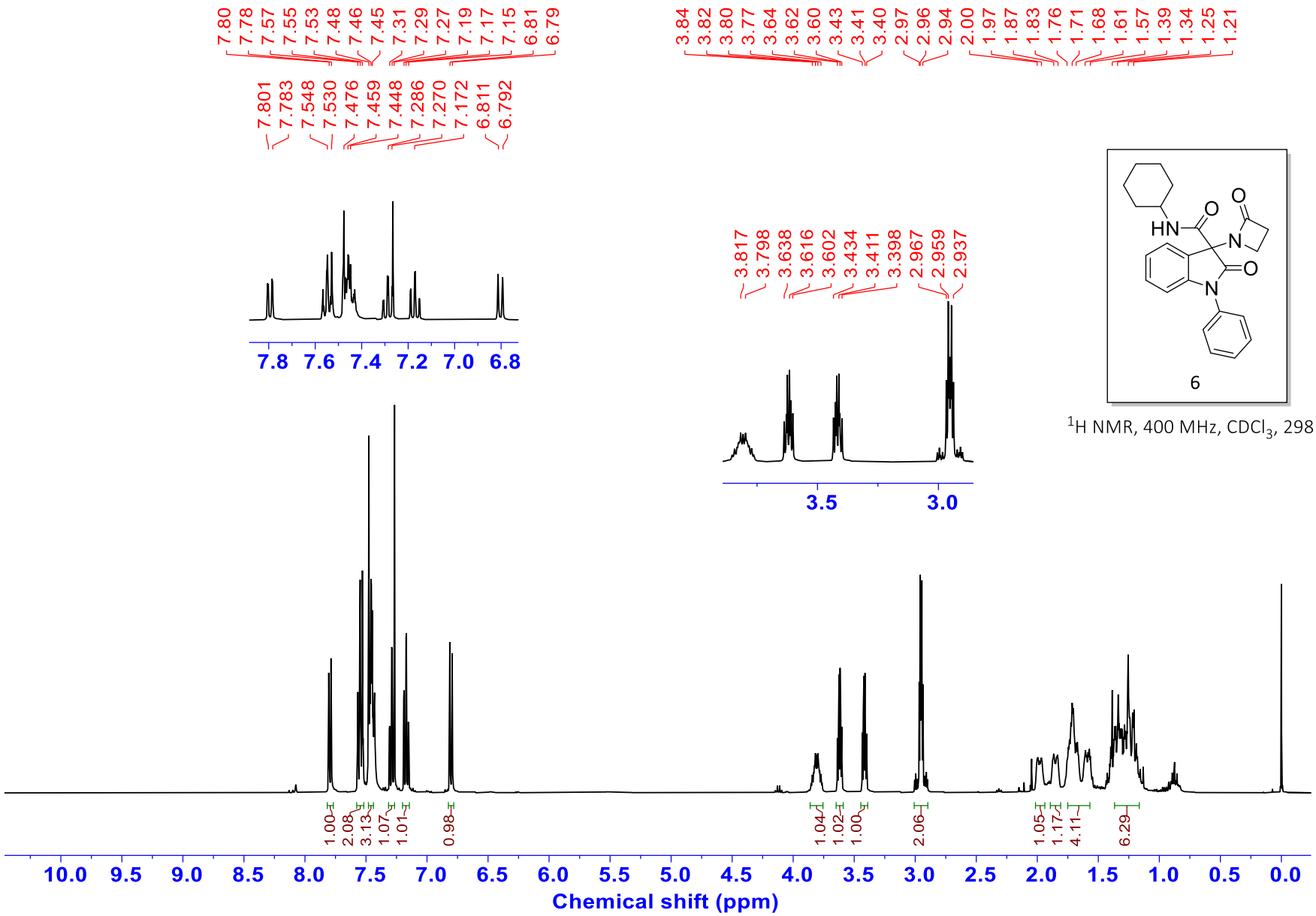
$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$, 298 K



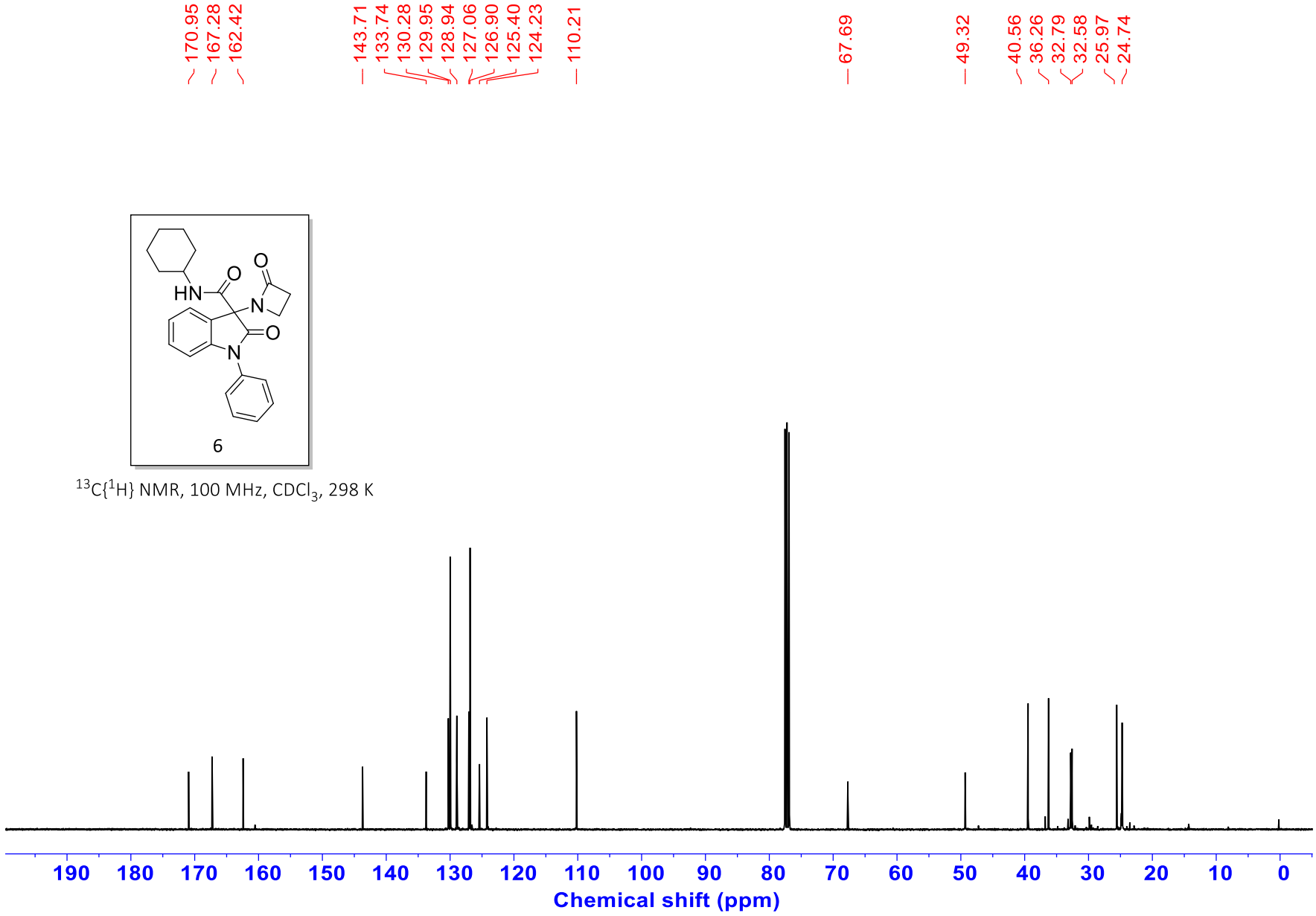
^{1}H NMR, 400 MHz, $CDCl_3$, 298 K



$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$, 298 K



^{1}H NMR, 400 MHz, $CDCl_3$, 298 K



$^{13}C\{^{1}H\}$ NMR, 100 MHz, $CDCl_3$, 298 K