Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Catalytic asymmetric [4 + 1] cycloaddition to synthesize chiral pyrazoline-spirooxindoles

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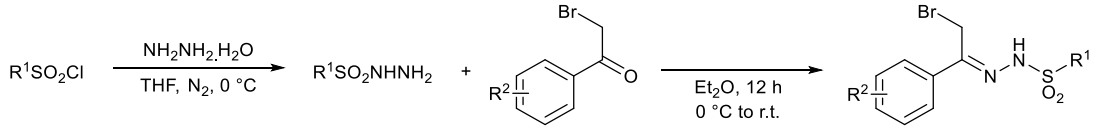
1. General remarks

^{1}H NMR spectra were recorded on Bruker ASCENDTM 400M (400 MHz) and ASCENDTM 600M (600 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26, acetone-d_6, δ = 2.05, DMSO-d_6, δ = 2.50). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets), coupling constants (Hz), integration and assignment. **^{13}C{^{1}H} NMR** spectra were collected on ASCENDTM 400M (101 MHz) and ASCENDTM 600M (153 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, δ = 77.0, acetone-d_6, δ = 29.8, 206.1, DMSO-d_6, δ = 39.5). **^{19}F{^{1}H} NMR** spectra were collected on ASCENDTM 400M (376 MHz) with complete proton decoupling. HRMS was recorded on a commercial apparatus (ESI Source). Enantiomeric excesses (ee) were determined by HPLC analysis using the corresponding commercial chiral column as stated in the experimental procedures at 23 °C. Optical rotations were measured on Rudolph Research Analytic Automatic Polarimeter and reported as follows: $[\alpha]_D^T$ (*c* g/100 mL, in solvent). Infrared spectra (IR) were recorded on Bruker Tensor II spectrometer with Plantium ATR accessory and the peaks were reported as absorption maxima (v, cm^{-1}). Circular dichroism spectra (CD) were recorded on Applied Photophysics Chirascan. X-ray crystallographic data were collected by a Bruker D8 Venture Photon II. Unless otherwise indicated, reagents obtained from commercial sources were used without further purification. Solvents were dried and distilled prior to use according to the standard methods. The size of typical stirring bar for the catalytic asymmetric reaction was 10 mm × 5 mm (Length × Diameter), for gram scale synthesis was 50 mm × 16 mm (Length × Diameter). The size of typical reaction tube was 130 mm × 17 mm (Length × Diameter). The 100 mL round-bottom flask for gram scale synthesis was purchased from Synthware Glass and the number was F309100. The chiral *N*,*N*′-dioxide ligands were synthesized by the same procedure in the literature.[1]

2. Synthesis of substrates and L_3-TQ-(*S*)-EPh

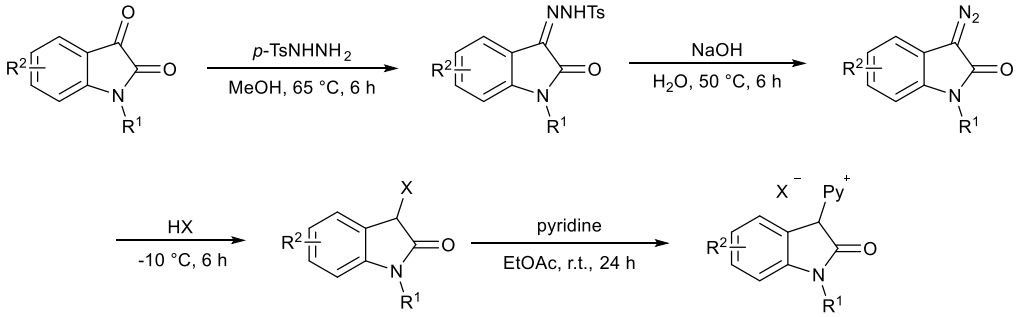
2.1 General procedure for the synthesis of *α*-bromo hydrazone derivatives



To a solution of sulfonyl chloride derivative (10.0 mmol, 1.0 equiv) at 0 °C in THF was slowly added hydrazine hydrate (12.0 mmol, 1.2 equiv) and stirred for 4 h. The mixture was filtered to provide hydrazine derivative.

To a solution of hydrazine derivative (10.0 mmol, 1.0 equiv) in cold (ice-water bath) Et_2O was added substituted *α*-bromo acetophenone (11.0 mmol, 1.1 equiv). The mixture was allowed to stir at room temperature for 12 h, filtered, rinsed with cold (ice-water bath) Et_2O (3 x 10 mL) to give the crude product. Then, it was recrystallized using CH_2Cl_2 as positive solvent while PE as negative one. After that it was filtered to give *α*-bromo hydrazone as white powder.

2.2 General procedure for the synthesis of oxindole 3-pyridinium salt[2]



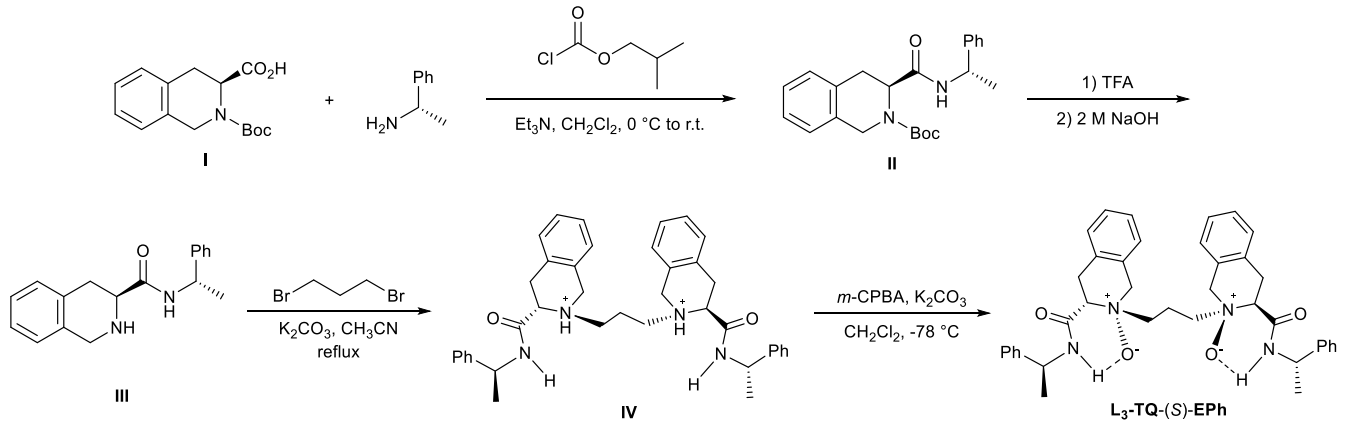
The corresponding isatin (20.0 mmol, 1.0 equiv) was suspended in CH_3OH (80 mL) at 65 °C. *p*-Toluenesulfonylhydrazine (22.0 mmol, 1.1 equiv) was added in one portion and the reaction mixture was refluxed until massive precipitates generated. The reaction mixture was concentrated to half of its volume and cooled to 0 – 5 °C. The precipitated mixture of (*Z*)/(*E*)-isomers of isatin *p*-tosylhydrazone was filtered off and washed with cold CH_3OH.

The corresponding isatin *p*-tosylhydrazone (17.2 mmol, 1.0 equiv) was suspended in water (10 mL per each 1 mmol of *p*-tosylhydrazone) and 10% aqueous NaOH (4.5 mmol per each 1 mmol of tosylhyrazone, 4.5 equiv) was added in one portion. The suspension was stirred at 50 °C until dissolution of all solid material accompanied by a change of the solution color to orange for approximately 12 hours (monitored by TLC; SiO_2 plates, PE/EtOAc = 2:1, v/v). Then, the reaction mixture was cooled and extracted with EtOAc (3 × 75 mL). The combined organic layers were washed with water (50 mL), dried with anhydrous Na_2SO_4 and evaporated.

The corresponding well-grinded diazooxindole (15.8 mmol, 1.0 equiv) was added in small portions to a stirred cold (-10 °C) aqueous HX (40.0 equiv) solution until the nitrogen emission ceased. Then, the reaction mixture was stirred for next 12 hours at room temperature to complete the reaction. The final suspension was filtered and washed with water until pH of the filtrate got neutral and the solid residue was dried to provide 3-halo-indolin-2-one.

A solution of 3-halo-indolin-2-one (10 mmol, 1.0 equiv) and pyridine (13 mmol, 1.3 equiv) in anhydrous EtOAc (20 mL) was stirred at room temperature for 24 h. The reaction mixture was directly filtered to collect the solid **B**. Then, it was recrystallized using MeOH as positive solvent while EtOAc as negative one. After that it was filtered to give oxindole 3-pyridinium salt **B**.

2.3 General procedure for the synthesis of L_3-TQ-(*S*)-EPh



To a solution of (*S*)-Boc-tetrahydroisoquinoline-3-carboxylic acid (2.77 g, 10.0 mmol) in DCM (20 mL) was added Et_3N (1.67 mL, 12.0 mmol), isobutyl carbonochloridate (1.52 mL, 12.0 mmol). It was allowed to stir at 0 °C for 25 minutes, and then (*S*)-1-phenylethan-1-amine (1.54 mL, 12.0 mmol) was added. The reaction was allowed to warm up to room temperature and monitored by TLC (R_f = 0.3, SiO_2 plates, PE/EtOAc = 1:1, v/v). After 48 h, the mixture was washed with 1 M $KHSO_4$ solution, saturated $NaHCO_3$ solution, brine, dried over anhydrous Na_2SO_4. After filtration, the mixture was concentrated, and the residue was used in the next step without other purification.

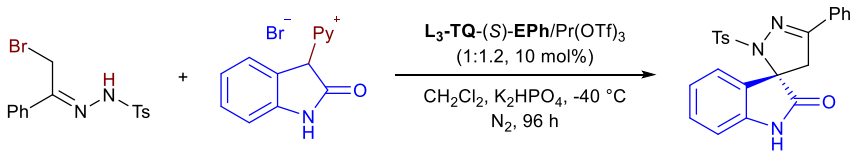
The residue in CH_2Cl_2 (20 mL) was added TFA (10 mL) at 0 °C. The reaction was allowed to warm up to room temperature and stirred for 1 h. The reaction was diluted with CH_2Cl_2 (20 mL). The pH value of the mixture was brought into the range of 10-12 by the addition of 2 M NaOH solution at 0 °C. The aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4 and evaporated in vacuo. The residue was subjected to flash column chromatography on silica gel and eluted with EtOAc to afford the product **III** (2.47 g, 8.82 mmol) as a white solid.

To a solution of compound **III** (2.47 g, 8.82 mmol) in CH_3CN (4 mL) was added K_2CO_3 (3.64 g, 26.4 mmol) and 1,3-dibromopropane (450 μL, 4.41 mmol). It was kept refluxing for 10 h. Then, K_2CO_3 was removed by filtration and washed by CH_2Cl_2. The filtrate was concentrated and was subjected to flash column chromatography on silica gel (Eluent: PE/EtOAc = 1:1 – 1:2, v/v) to give the product **IV** (1.72 g, 2.87 mmol) as a white solid.

To a solution of compound **IV** (0.60 g, 1.0 mmol) in CH_2Cl_2 (10 mL) was slowly added mixed solid of *m*-CPBA (0.345 g, 2.0 mmol) and K_2CO_3 (0.276 g, 2.0 mmol) at -78 °C. The reaction mixture was stirred at -78 °C for 0.5 h. Then the reaction was quenched with H_2O (20 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4 and evaporated in vacuo. The residue was subjected to flash column chromatography on silica gel (Eluent: EtOAc/MeOH = 10:1 – 8:1, v/v) to afford **L_3-TQ**-(*S*)-**EPh** (0.27 g, 0.43 mmol, 24% yield over four steps) as a white solid. (Note: The solvent was evaporated in vacuo at 20 °C and the **L_3-TQ**-(*S*)-**EPh** was stored at –20 °C.)

3. Typical procedure for the catalytic asymmetric reaction

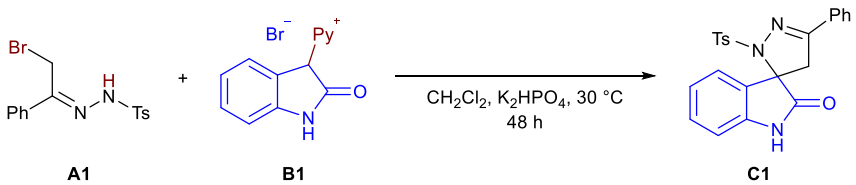
3.1 General procedure for the synthesis of chiral products



A dry reaction tube was charged with $Pr(OTf)_3$ (12 mol%, 7.1 mg), **L_3-TQ**-(*S*)-**EPh** (10 mol%, 6.3 mg), then, THF (1.0 mL) was added. The mixture was stirred at 30 °C for 2 h. The resulting mixture was concentrated under reduced pressure. Then to this very tube was added *α*-bromo hydrazone **A1** (0.10 mmol), oxindole 3-pyridinium salt **B1** (0.11 mmol) and K_2HPO_4 (0.45 mmol, 4.5 equiv) with CH_2Cl_2

(1 mL). It was allowed to stir at -40 °C for 96 h under nitrogen. The reaction process was monitored by TLC (R_f = 0.3, SiO_2 plates, PE/EtOAc = 3:2, v/v). The residue was purified by flash chromatography on silica gel (Eluent: PE/EtOAc = 2:1, v/v) to afford the chiral products **C1** as light yellow solid.

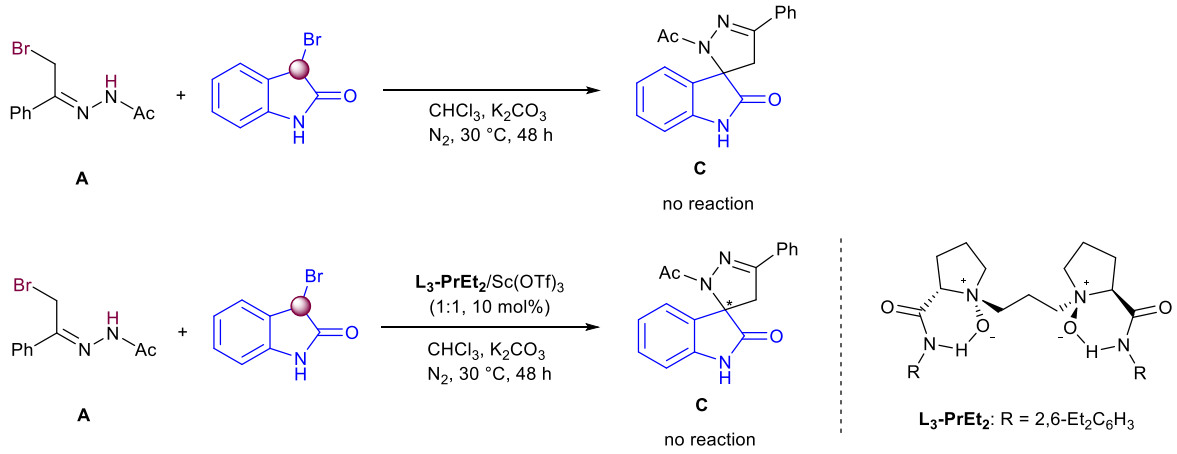
3.2 General procedure for the synthesis of racemic products



A1 **B1** **C1**

A dry reaction tube was charged with *α*-bromo hydrazone **A1** (0.10 mmol), oxindole 3-pyridinium salt **B1** (0.10 mmol) and K_2HPO_4 (0.30 mmol, 3.0 equiv). Then, CH_2Cl_2 (1.0 mL) was added and the mixture was allowed to stir at 30 °C for 48 h. The residue was purified by flash chromatography on silica gel (Eluent: PE/EtOAc = 2:1, v/v) to afford the racemic product **C1**.

4. Examination of C_1 synthons



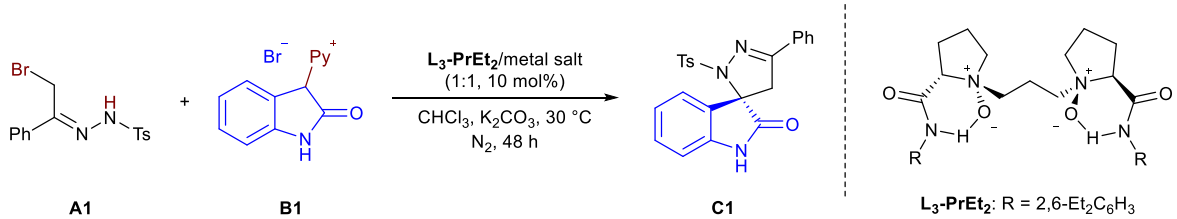
A **C** no reaction

A **C** no reaction

A dry reaction tube was charged with *α*-bromo hydrazone **A** (0.10 mmol), 3-bromooxindole (0.10 mmol) and K_2CO_3 (0.30 mmol, 3.0 equiv). Then, $CHCl_3$ (1.0 mL) was added and the mixture was allowed to stir under N_2 at 30 °C for 48 h. The reaction process was monitored by TLC (R_f = 0.3, SiO_2 plates, PE/EtOAc = 3:2, v/v).

5. Optimization of reaction conditions

5.1 Screening of the metal salt



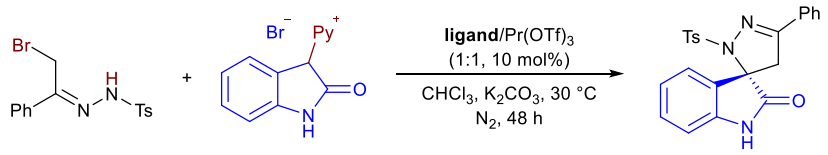
A1 **B1** **C1**

Entry[a]	Metal salt	Yield (%)[b]	ee (%)[c]
1	$Mg(OTf)_2$	84	0
2	$Sc(OTf)_3$	85	4
3	$Cu(OTf)_2$	87	1
4	$Y(OTf)_3$	83	8
5	$La(OTf)_3$	80	10
6	$Ce(OTf)_3$	84	13
7	$Pr(OTf)_3$	84	20
8	$Nd(OTf)_3$	87	10

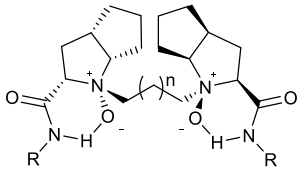
9	$Pm(OTf)_3$	99	13
10	$Eu(OTf)_3$	86	16
11	$Gd(OTf)_3$	83	4
12	$Tb(OTf)_3$	82	12
13	$Dy(OTf)_3$	74	20
14	$Ho(OTf)_3$	73	16
15	$Er(OTf)_3$	66	10
16	$Tm(OTf)_3$	87	10
17	$Yb(OTf)_3$	92	8
18	$Lu(OTf)_3$	80	6

[a] Unless otherwise noted, all reactions were carried out with **L_3-PrEt$_2$**/metal salt (1:1, 10 mol%), **A1** (0.10 mmol), **B1** (0.10 mmol) and K_2CO_3 (0.30 mmol, 3.0 equiv) in $CHCl_3$ (1.0 mL) at 30 °C under nitrogen for 48 h. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase.

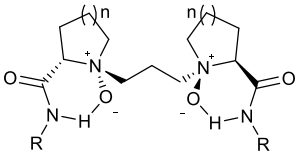
5.2 Screening of the *N*,*N*′-dioxide ligands



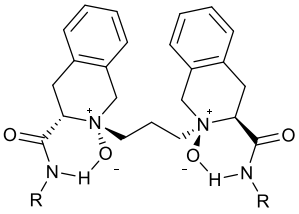
A1 **B1** **C1**



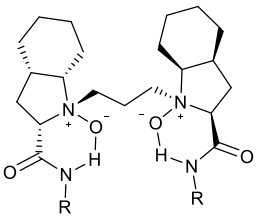
L_3-RaPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, n = 1
L_3-RaEt$_2$: R = 2,6-Et$_2$C$_6$H$_3$, n = 1



L_3-PrMe$_2$: R = 2,6-Me$_2$C$_6$H$_3$, n = 1
L_3-PiMe$_2$: R = 2,6-Me$_2$C$_6$H$_3$, n = 2
L_3-PrEt$_2$: R = 2,6-Et$_2$C$_6$H$_3$, n = 1
L_3-PiEt$_2$: R = 2,6-Et$_2$C$_6$H$_3$, n = 2
L_3-PrPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, n = 1
L_3-PiPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, n = 2



L_3-TQ-(*S*)-**EPh**: R = (*S*)-2-phenylethyl
L_3-TQ^{n}Pr: R = ^{n}Pr
L_3-TQ^{i}Pr: R = ^{i}Pr
L_3-TQ^{t}Bu: R = ^{t}Bu
L_3-TQ*c*P: R = cyclopropyl
L_3-TQ*c*H: R = cyclohexyl
L_3-TQAd: R = 1-adamantyl
L_3-TQCHPh$_2$: R = Ph$_2$CH
L_2-TQAd: R = 1-adamantyl
L_3-TQEt$_2$: R = 2,6-Et$_2$C$_6$H$_3$



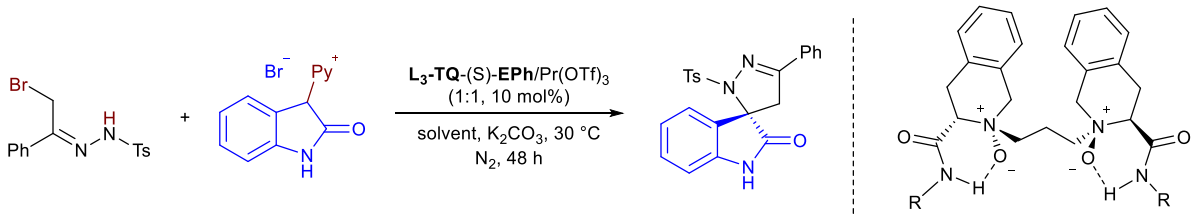
L_3-PePr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$

Entry[a]	Ligand	Yield (%)[b]	ee (%)[c]
1	**L_3-PrMe$_2$**	78	12
2	**L_3-PrEt$_2$**	83	20
3	**L_3-PrPr$_2$**	80	6
4	**L_3-PiMe$_2$**	75	10
5	**L_3-PiEt$_2$**	70	6
6	**L_3-PiPr$_2$**	68	6
7	**L_3-RaEt$_2$**	88	7
8	**L_3-RaPr$_2$**	89	4
9	**L_3-PePr$_2$**	62	4
10	**L_3-TQ-(*S*)-EPh**	83	44
11	**L_3-TQEt$_2$**	86	21
12	**L_3-TQ^{n}Pr**	84	20
13	**L_3-TQ^{i}Pr**	83	20
14	**L_3-TQ^{t}Bu**	92	22
15	**L_3-TQ*c*P**	77	22
16	**L_3-TQ*c*H**	72	28
17	**L_3-TQAd**	80	44

18	**L_3-TQCHPh$_2$**	87	5
19	**L_2-TQAd**	68	8

[a] Unless otherwise noted, all reactions were carried out with **ligand**/Pr(OTf)$_3$ (1:1, 10 mol%), **A1** (0.10 mmol), **B1** (0.10 mmol) and K_2CO_3 (0.30 mmol, 3.0 equiv) in $CHCl_3$ (1.0 mL) at 30 °C under nitrogen for 48 h. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase.

5.3 Screening of the solvent

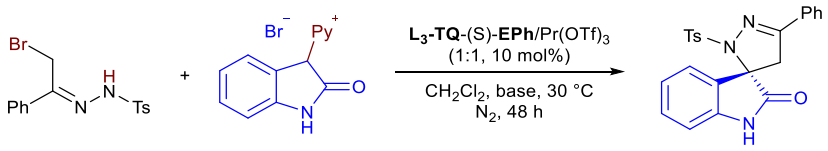


A1 **B1** **C1** **L_3-TQ**-(*S*)-**EPh**: R = (*S*)-2-phenylethyl

Entry[a]	Solvent	Yield (%)[b]	ee (%)[c]
1	CH_2Cl_2	90	54
2	THF	90	38
3	Et_2O	26	40
4	toluene	44	race
5	MeOH	87	race
6	HCO_2Et	91	6
7	1,2-DCE	88	52
8	1,1,2-TCE	90	50
9	1,1,2,2-TCE	85	52
10	chlorobenzene	80	40

[a] Unless otherwise noted, all reactions were carried out with **L_3-TQ**-(*S*)-**EPh**/Pr(OTf)$_3$ (1:1, 10 mol%), **A1** (0.10 mmol), **B1** (0.10 mmol) and K_2CO_3 (0.30 mmol, 3.0 equiv) in solvent (1.0 mL) at 30 °C under nitrogen for 48 h. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase.

5.4 Screening of the base



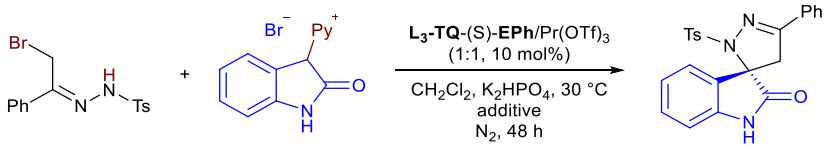
A1 **B1** **C1**

Entry[a]	Base	Yield (%)[b]	ee (%)[c]
1	Li_2CO_3	85	60
2	Na_2CO_3	91	46
3	Cs_2CO_3	79	48
4	$BaCO_3$	70	10
5	$NaHCO_3$	75	30
6	$KHCO_3$	73	4
7	K_2HPO_4	93	60
8	K_3PO_4	79	48
9	Na_3PO_4	83	10
10	Na_2HPO_4	89	48
11	NaOH	61	26
12	KOH	68	18
13	Et_3N	84	race
14	EtONa	51	race
15	HCOONa	48	race
16	DMAP	no reaction	-

17	$^{i}PrNH_2$	35	race
18	DABCO	30	race
19	KO^{t}Bu	no reaction	-
20	$NaNH_2$	85	race

[a] Unless otherwise noted, all reactions were carried out with **L$_3$-TQ**-(*S*)-**EPh**/Pr(OTf)$_3$ (1:1, 10 mol%), **A1** (0.10 mmol), **B1** (0.10 mmol) and base (0.30 mmol, 3.0 equiv) in CH_2Cl_2 (1.0 mL) at 30 °C under nitrogen for 48 h. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase.

5.5 Screening of the additive

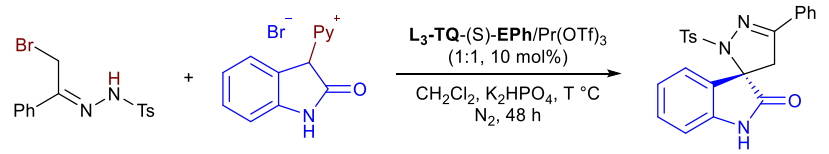


A1 **B1** **C1**

Entry[a]	Additive	Loading (mg)	Yield (%)[b]	ee (%)[c]
1	3Å MS	20	82	2
2	4Å MS	20	80	8
3	5Å MS	20	85	27
4	LiCl	4.2	82	5
5	$LiBF_4$	9.4	70	race
6	$LiNTf_2$	2.9	71	61
7	$NaBAr^{F}_4$	9	84	60

[a] Unless otherwise noted, all reactions were carried out with **L$_3$-TQ**-(*S*)-**EPh**/Pr(OTf)$_3$ (1:1, 10 mol%), **A1** (0.10 mmol), **B1** (0.10 mmol) and K_2HPO_4 (0.30 mmol, 3.0 equiv) with additive in CH_2Cl_2 (1.0 mL) at 30 °C under nitrogen for 48 h. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase.

5.6 Screening of the reaction temperature

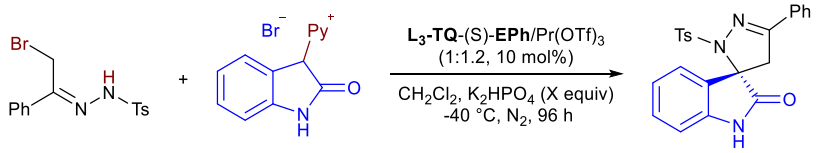


A1 **B1** **C1**

Entry[a]	T (°C)	Yield (%)[b]	ee (%)[c]
1	20	92	68
2	10	90	74
3	0	91	76
4	-10	95	76
5	-20	95	76
6	-30	74	82
7	-35	69	82
8	-40	52	88
9	-45	49	83
10	-50	49	80
11	-55	42	73
12[d]	-40	69	88
13[d,e]	-40	72	88
14[d,e,f]	-40	74	90

[a] Unless otherwise noted, all reactions were carried out with **L$_3$-TQ**-(*S*)-**EPh**/Pr(OTf)$_3$ (1:1, 10 mol%), **A1** (0.10 mmol), **B1** (0.10 mmol) and K_2HPO_4 (0.30 mmol, 3.0 equiv) in CH_2Cl_2 (1.0 mL) at T °C under nitrogen for 48 h. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase. [d] Reaction time was 96 h. [e] 0.11 mmol **B1** was used. [f] The ratio of **L$_3$-TQ**-(*S*)-**EPh**/Pr(OTf)$_3$ was 1:1.2 (10 mol%).

5.7 Screening of the base ratio

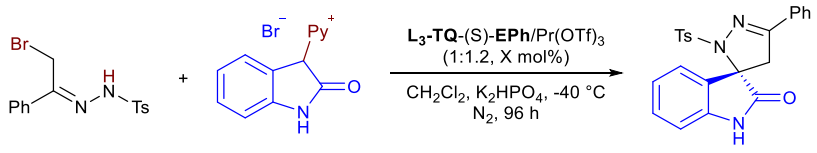


A1 B1 C1

Entry[a]	X (equiv)	Yield (%)[b]	ee (%)[c]
1	2.0	37	86
2	2.5	46	90
3	3.5	84	89
4	4.0	89	90
5	4.5	90	90
6	5.0	90	90

[a] Unless otherwise noted, all reactions were carried out with **L$_3$-TQ**-(*S*)-**EPh**/Pr(OTf)$_3$ (1:1.2, 10 mol%), **A1** (0.10 mmol), **B1** (0.11 mmol) and K_2HPO_4 (X equiv) in CH_2Cl_2 (1.0 mL) at -40 °C under nitrogen for 96 h. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase.

5.8 Screening of the catalyst loading

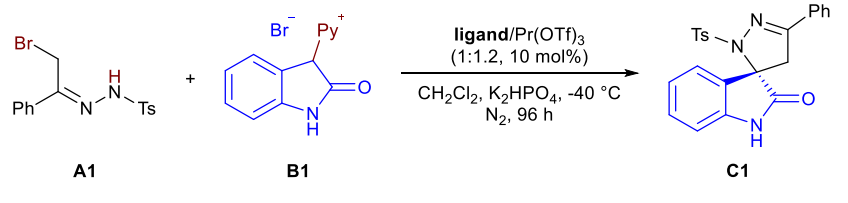


A1 B1 C1

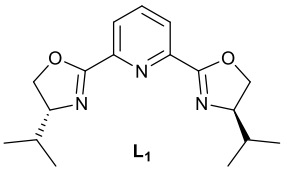
Entry[a]	X (mol%)	Yield (%)[b]	ee (%)[c]
1	1	59	71
2	2	73	78
3	5	92	87
4	10	90	90
5	20	93	90

[a] Unless otherwise noted, all reactions were carried out with **L$_3$-TQ**-(*S*)-**EPh**/Pr(OTf)$_3$ (1:1.2, X mol%), **A1** (0.10 mmol), **B1** (0.11 mmol) and K_2HPO_4 (0.45 mmol, 4.5 equiv) in CH_2Cl_2 (1.0 mL) at -40 °C under nitrogen for 96 h. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase.

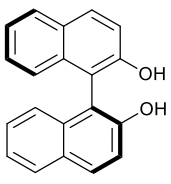
5.9 Screening of other ligands



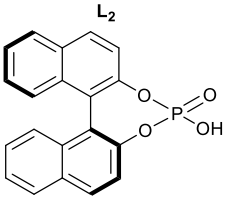
A1 B1 C1



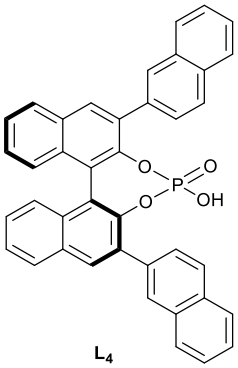
L$_1$



L$_2$



L$_3$

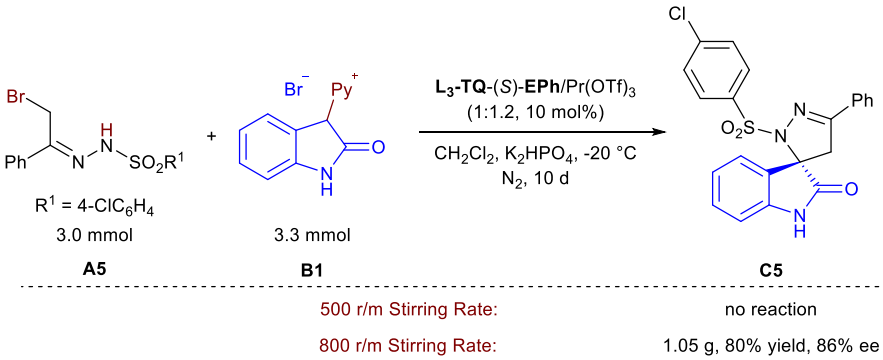


L$_4$

Entry[a]	Ligand	Yield (%)[b]	ee (%)[c]
1	L_1	31	-17
2	L_2	28	18
3	L_3	19	2
4	L_4	20	-35

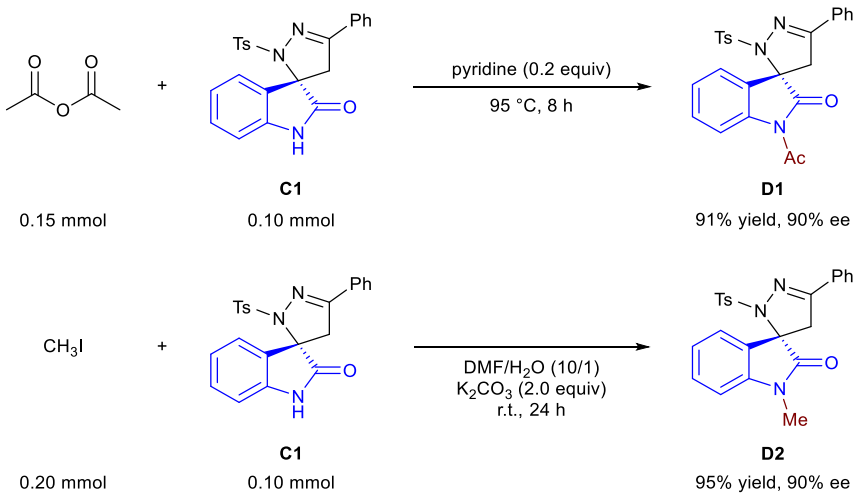
[a] Unless otherwise noted, all reactions were carried out with **ligand**/$Pr(OTf)_3$ (1:1.2, 10 mol%), **A1** (0.10 mmol), **B1** (0.11 mmol) and K_2HPO_4 (0.45 mmol, 4.5 equiv) in CH_2Cl_2 (1.0 mL) at -40 °C under nitrogen for 96 h. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase.

6. Typical procedure for the gram scale synthesis of product C5



A dry reaction 100 mL round-bottom flask was charged with $Pr(OTf)_3$ (12 mol%, 0.213 g), **L_3-TQ-(*S*)-EPh** (10 mol%, 0.189 g), THF (30 mL) and the mixture was stirred at 30 °C for 6 h. The resulting mixture was concentrated under reduced pressure. Substrate **A5** (3.0 mmol, 1.164 g), **B1** (3.3 mmol, 0.96 g) and K_2HPO_4 (13.5 mmol, 2.352 g) were added to the flask. The reaction mixture continued vigorously stirring (Note: 800 r/m, 500 r/m resulted in no reaction) at -20 °C for 240 h under nitrogen. The residue was purified by flash chromatography on silica gel (Eluent: PE/EtOAc = 2:1, v/v) to afford the product **C5** (80% yield, 86% ee).

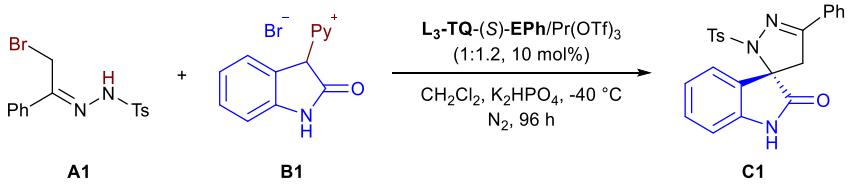
7. Transformation of C1



(a) A dry reaction tube was charged with **C1** (0.10 mmol), acetic anhydride (0.15 mmol), pyridine (0.2 equiv) without other solvent. The mixture was stirred at 95 °C for 8 h. It was washed with saturated $NaHCO_3$ solution, brine and was extracted with EtOAc (3 × 15 mL), and the organic phase was combined, dried over Na_2SO_4 and concentrated in vacuo. The residue was directly purified by flash chromatography on silica gel (Eluent: PE/EtOAc = 3:1, v/v) to afford the chiral product **D1** as light yellow oil.

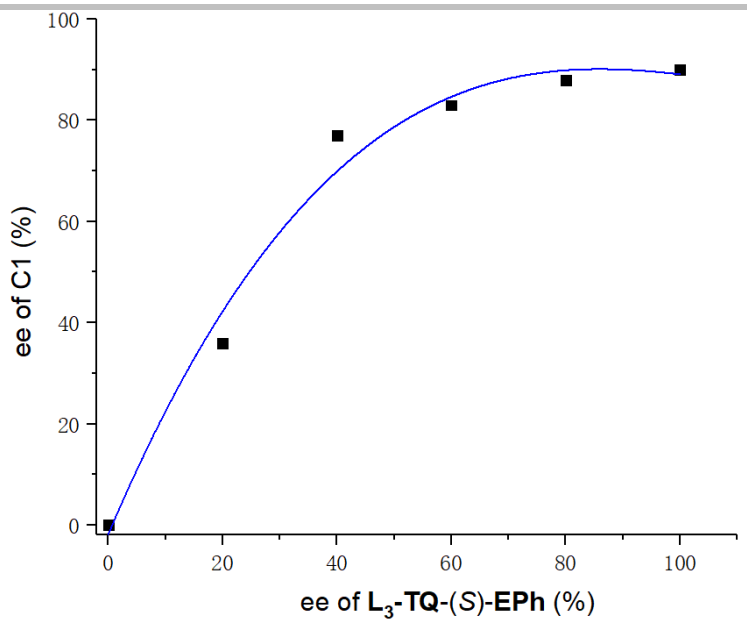
(b) A dry reaction tube was charged with **C1** (0.10 mmol), CH_3I (0.20 mmol), K_2CO_3 (2.0 equiv) in DMF/water (0.5 mL, v:v = 10:1) and it was stirred at room temperature for 24 h, then it was poured into icy water (20 mL), washed with brine and extracted with EtOAc (3 × 15 mL), and the organic phase was combined, dried over Na_2SO_4 and concentrated in vacuo. The residue was directly purified by flash chromatography on silica gel (Eluent: PE/EtOAc = 2:1, v/v) to afford the chiral product **D2** as yellow oil.

8. The nonlinear effect between the ee value of the ligand L_3-TQ-(*S*)-EPh and the product C1



Entry[a]	*ee* of L_3-TQ-(*S*)-EPh (%)	ee (%)[b]
1	0	0
2	20	36
3	40	77
4	60	83
5	80	88
6	100	90

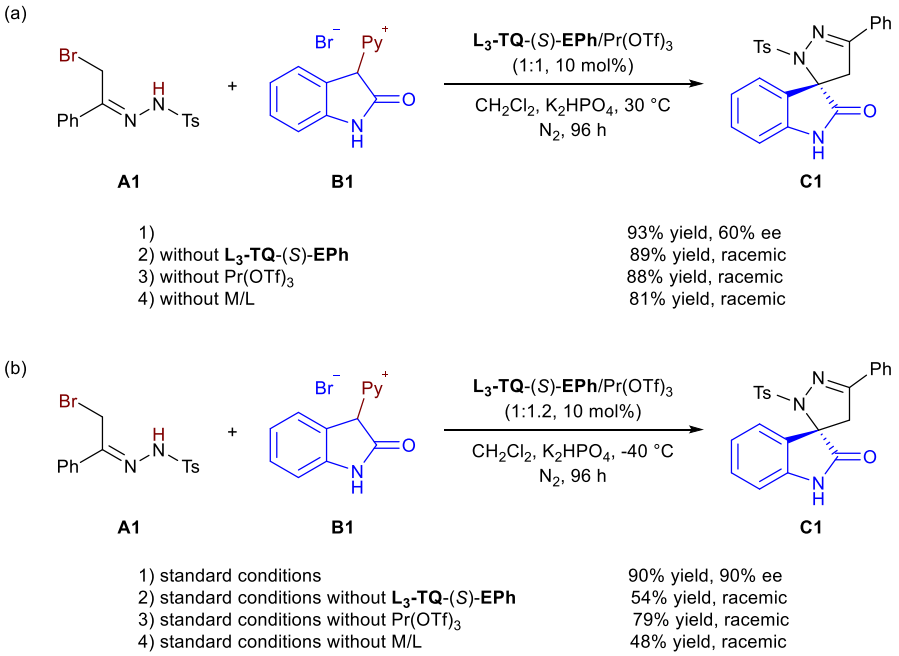
[a] Unless otherwise noted, all reactions were carried out with (*R*/*S*) **L_3-TQ**-(*S*)-**EPh**/Pr(OTf)$_3$ (1:1.2, 10 mol%), **A1** (0.10 mmol), **B1** (0.11 mmol) and K_2HPO_4 (0.45 mmol, 4.5 equiv) in CH_2Cl_2 (1.0 mL) at -40 °C under nitrogen for 96 h. [b] Determined by HPLC analysis on a chiral stationary phase.



A range of dry reaction tubes were charged with $Pr(OTf)_3$ (12 mol%, 7.1 mg), (*R*/*S*) **L_3-TQ**-*(S)*-**EPh** (10 mol%, 6.3 mg), then, THF (1.0 mL) was added. The mixtures were stirred at 30 °C for 2 h. The resulting mixtures were concentrated under reduced pressure. Then to these tubes were added *α*-bromo hydrazone **A1** (0.10 mmol), oxindole 3-pyridinium salt **B1** (0.11 mmol) and K_2HPO_4 (0.45 mmol, 4.5 equiv) with CH_2Cl_2 (1 mL). They were allowed to stir at -40 °C for 96 h under nitrogen. The reaction processes were monitored by TLC (R_f = 0.3, SiO_2 plates, PE/EtOAc = 3:2, v/v). The residues were purified by flash chromatography on silica gel (Eluent: PE/EtOAc = 2:1, v/v) to afford the products **C1** as light yellow solids.

9. Control experiments

9.1 Testing the background reaction

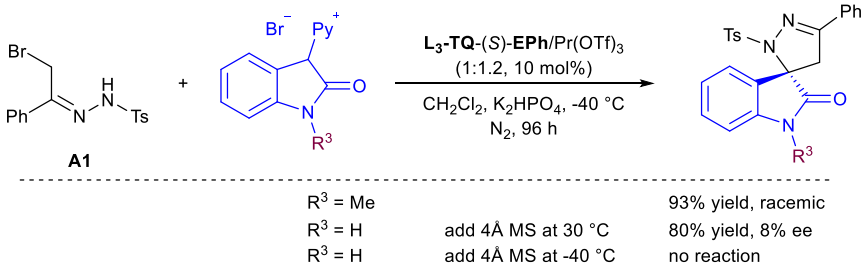


(a) Dry reaction tubes were charged with/without $Pr(OTf)_3$ (10 mol%, 5.9 mg), **L_3-TQ**-*(S)*-**EPh** (10 mol%, 6.3 mg), then, THF (1.0 mL) was added. The mixture was stirred at 30 °C under nitrogen for 2 h. The resulting mixture was concentrated under reduced pressure. Then to this very tube was added *α*-bromo hydrazone **A1** (0.10 mmol), oxindole 3-pyridinium salt **B1** (0.10 mmol) and K_2HPO_4 (0.30

mmol, 3.0 equiv). It was allowed to stir in CH_2Cl_2 (1 mL) at 30 °C for 48 h under nitrogen. The residue was purified by flash chromatography on silica gel (Eluent: PE/EtOAc = 2:1, v/v) to afford the product **C1** as light yellow solid.

(b) Dry reaction tubes were charged with/without $Pr(OTf)_3$ (12 mol%, 7.1 mg), **L_3-TQ**-*(S)*-**EPh** (10 mol%, 6.3 mg), then, THF (1.0 mL) was added. The mixture was stirred at 30 °C under nitrogen for 2 h. The resulting mixture was concentrated under reduced pressure. Then to this very tube was added *α*-bromo hydrazone **A1** (0.10 mmol), oxindole 3-pyridinium salt **B1** (0.11 mmol) and K_2HPO_4 (0.45 mmol, 4.5 equiv). It was allowed to stir in CH_2Cl_2 (1 mL) at -40 °C for 96 h under nitrogen. The residue was purified by flash chromatography on silica gel (Eluent: PE/EtOAc = 2:1, v/v) to afford the product **C1** as light yellow solid.

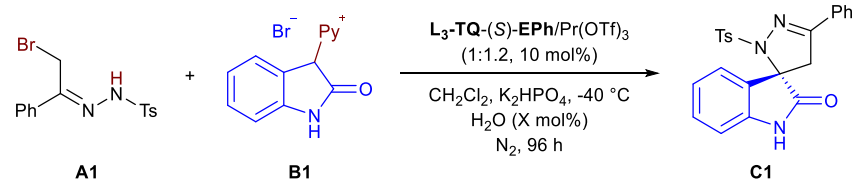
9.2 Proving the key role of water



(a) Dry reaction tube was charged with $Pr(OTf)_3$ (12 mol%, 7.1 mg), **L_3-TQ**-*(S)*-**EPh** (10 mol%, 6.3 mg), then, THF (1.0 mL) was added. The mixture was stirred at 30 °C for 2 h. The resulting mixture was concentrated under reduced pressure. Then to this very tube was added *α*-bromo hydrazone **A1** (0.10 mmol), oxindole 3-pyridinium salt **B2** (0.11 mmol) and K_2HPO_4 (0.45 mmol, 4.5 equiv). It was allowed to stir in CH_2Cl_2 (1 mL) at -40 °C under nitrogen for 96 h. The residue was purified by flash chromatography on silica gel (Eluent: PE/EtOAc = 3:1, v/v) to afford the racemic product **D2** as light yellow oil.

(b) Dry reaction tube was charged with $Pr(OTf)_3$ (12 mol%, 7.1 mg), **L_3-TQ**-*(S)*-**EPh** (10 mol%, 6.3 mg), then, THF (1.0 mL) was added. The mixture was stirred at 30 °C for 2 h. The resulting mixture was concentrated under reduced pressure. Then to this very tube was added *α*-bromo hydrazone **A1** (0.10 mmol), oxindole 3-pyridinium salt **B1** (0.11 mmol), K_2HPO_4 (0.45 mmol, 4.5 equiv) and 4Å MS (20 mg). It was allowed to stir in CH_2Cl_2 (1 mL) at -40 °C under nitrogen for 96 h. The residue was purified by flash chromatography on silica gel (Eluent: PE/EtOAc = 2:1, v/v) to afford the product **C1** as light yellow solid.

9.3 Evaluating the amount of water needed or tolerated

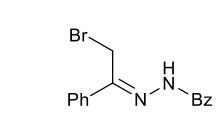


Entry[a]	X (mol%)	Yield (%)[b]	ee (%)[c]
1	5	91	90
2	10	90	90
3	50	89	87
4	100	85	85
5	150	85	84
6	200	88	84

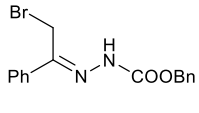
[a] Unless otherwise noted, all reactions were carried out with **L_3-TQ**-(*S*)-**EPh**/$Pr(OTf)_3$ (1:1.2, 10 mol%), **A1** (0.10 mmol), **B1** (0.11 mmol), K_2HPO_4 (0.45 mmol, 4.5 equiv) and H_2O (X mol%) in CH_2Cl_2 (1.0 mL) at -40 °C under nitrogen for 96 h. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase.

10. Unsuccessful substrates and screening attempt

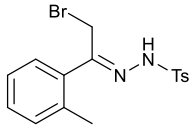
10.1 Poor results



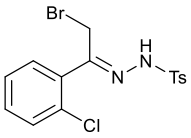
trace



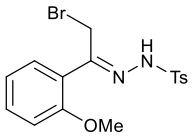
40% yield, racemic



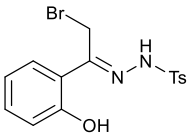
-20 °C : 19% yield, 73% ee
-40 °C : 4% yield, 78% ee



4% yield, 80% ee



6% yield, 90% ee



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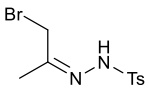

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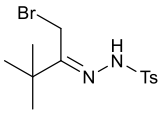
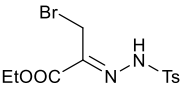
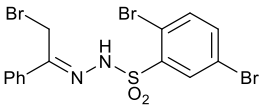


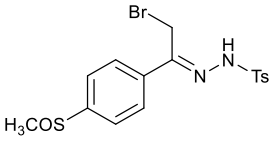
trace



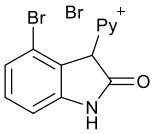
84% yield, 19% ee



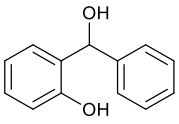
messy



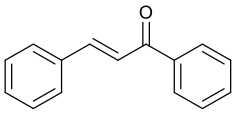
messy



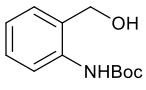
70% yield, 8% ee



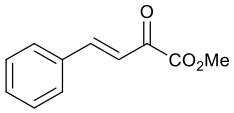
messy



messy

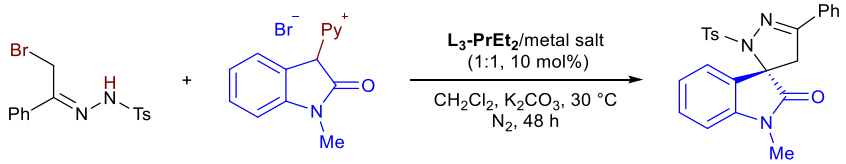


messy



messy

10.2 Screening of the metal salt

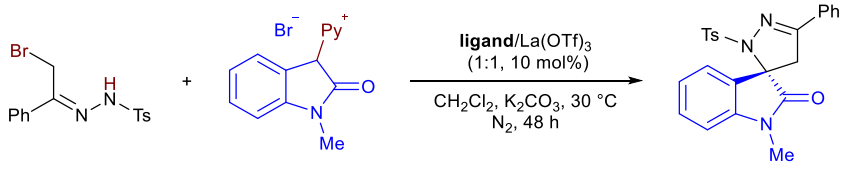


A1 **B2** **D2**

Entry[a]	Metal salt	Yield (%)[b]	ee (%)[c]
1	$Sc(OTf)_3$	97	0
2	$Mg(OTf)_2$	96	0
3	$Cu(OTf)_2$	65	0
4	$Ni(OTf)_2$	97	0
5	$Yb(OTf)_3$	90	0
6	$La(OTf)_3$	90	0
7	$Ga(OTf)_3$	92	0
8	$Lu(OTf)_3$	93	0
9	$Zn(OTf)_3$	60	0
10	$Fe(OTf)_2$	70	0
11	$Tb(OTf)_3$	89	0
12	$Dy(OTf)_3$	92	0
13	$Ho(OTf)_3$	93	0
14	$Er(OTf)_3$	90	0
15	$Tm(OTf)_3$	92	0
16	$Y(OTf)_3$	88	0

[a] Unless otherwise noted, all reactions were carried out with **L_3-PrEt$_2$**/metal salt (1:1, 10 mol%), **A1** (0.10 mmol), **B2** (0.10 mmol) and K_2CO_3 (0.30 mmol, 3.0 equiv) in CH_2Cl_2 (1.0 mL) at 30 °C under nitrogen for 48 h. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase.

10.3 Screening of the *N,N'*-dioxide ligands



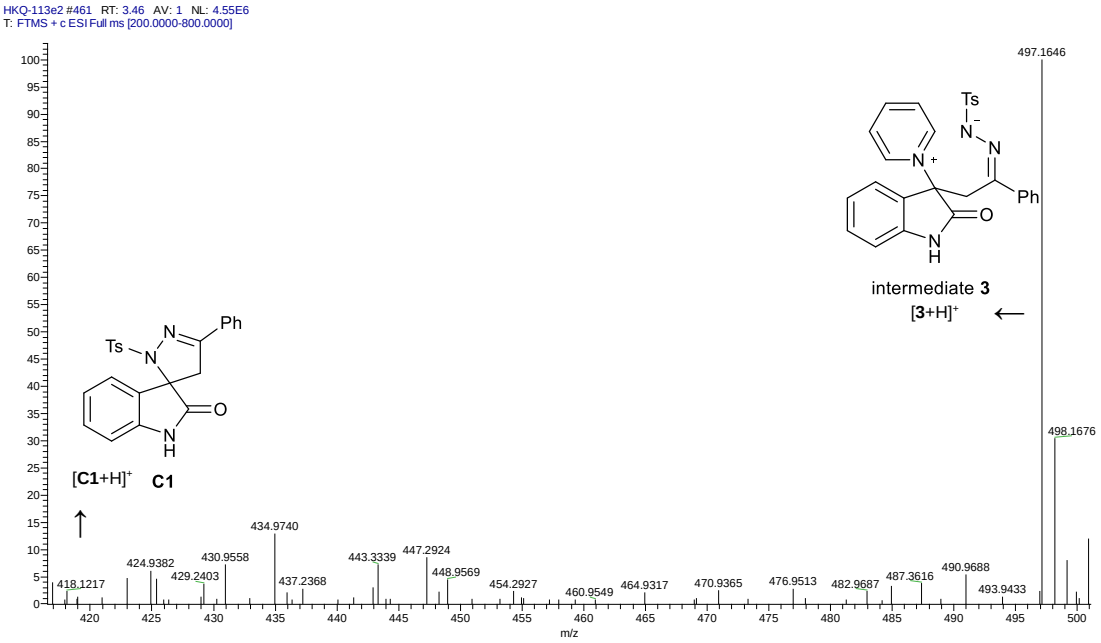
A1 **B2** **D2**

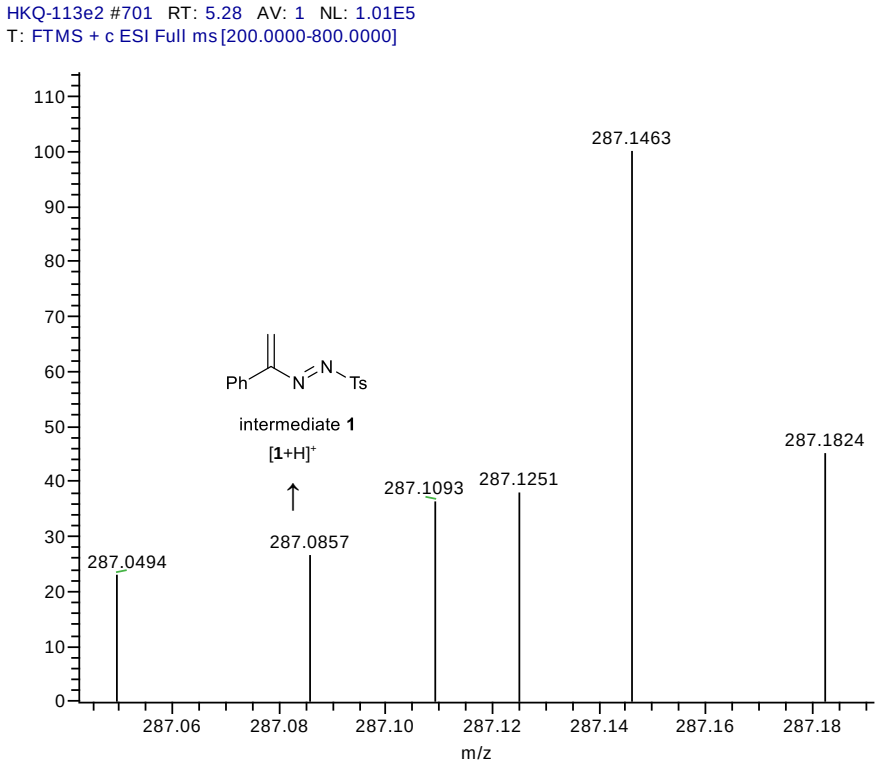
Entry[a]	Ligand	Yield (%)[b]	*ee* (%)[c]
1	**L_3-PiPr$_2$**	87	0
2	**L_3-PrPr$_2$**	66	0
3	**L_3-RaPr$_2$**	84	0
4	**L_3-TQPr$_2$**	87	0
5	**L_3-PePr$_2$**	79	0
6	**L_3-TQ**-(*S*)-**EPh**	82	0

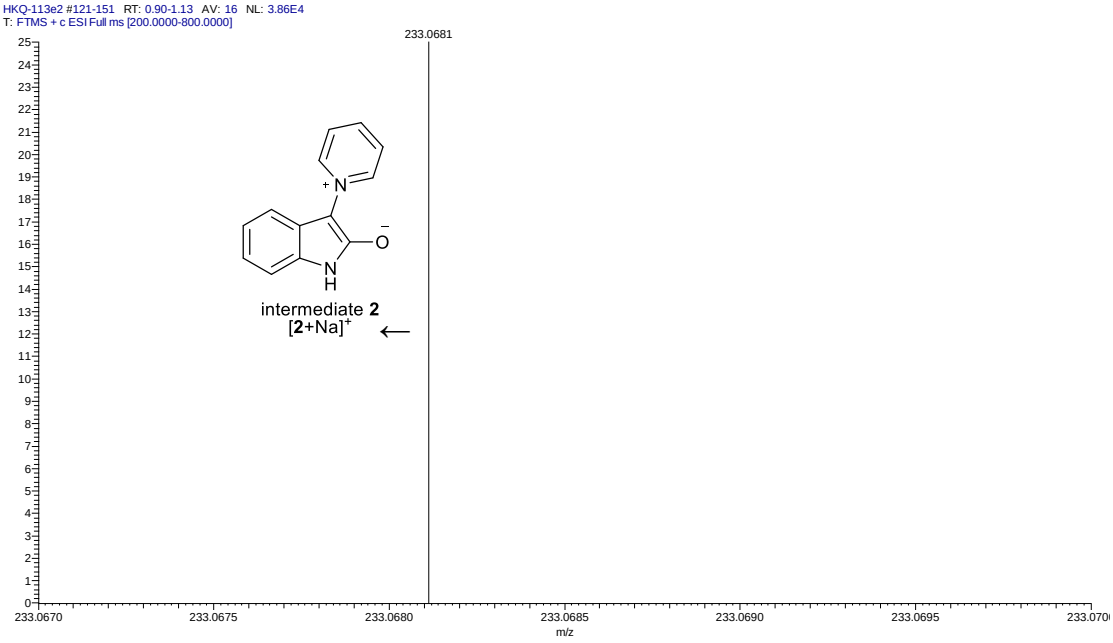
[a] Unless otherwise noted, all reactions were carried out with **ligand**/La(OTf)$_3$ (1:1, 10 mol%), **A1** (0.10 mmol), **B2** (0.10 mmol) and K_2CO_3 (0.30 mmol, 3.0 equiv) in CH_2Cl_2 (1.0 mL) at 30 °C under nitrogen for 48 h. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase.

11. Mass spectra of key intermediates 1, 2, 3 and product C1

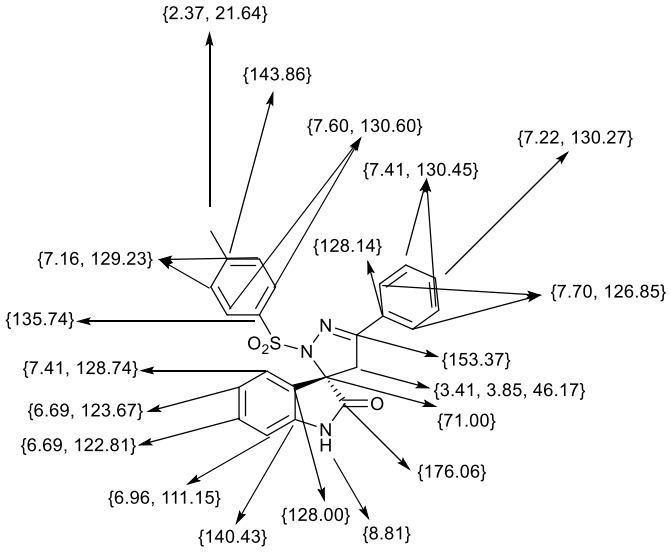
11.1 HRMS spectrum for the mixture of A1, B1 and K_2HPO_4



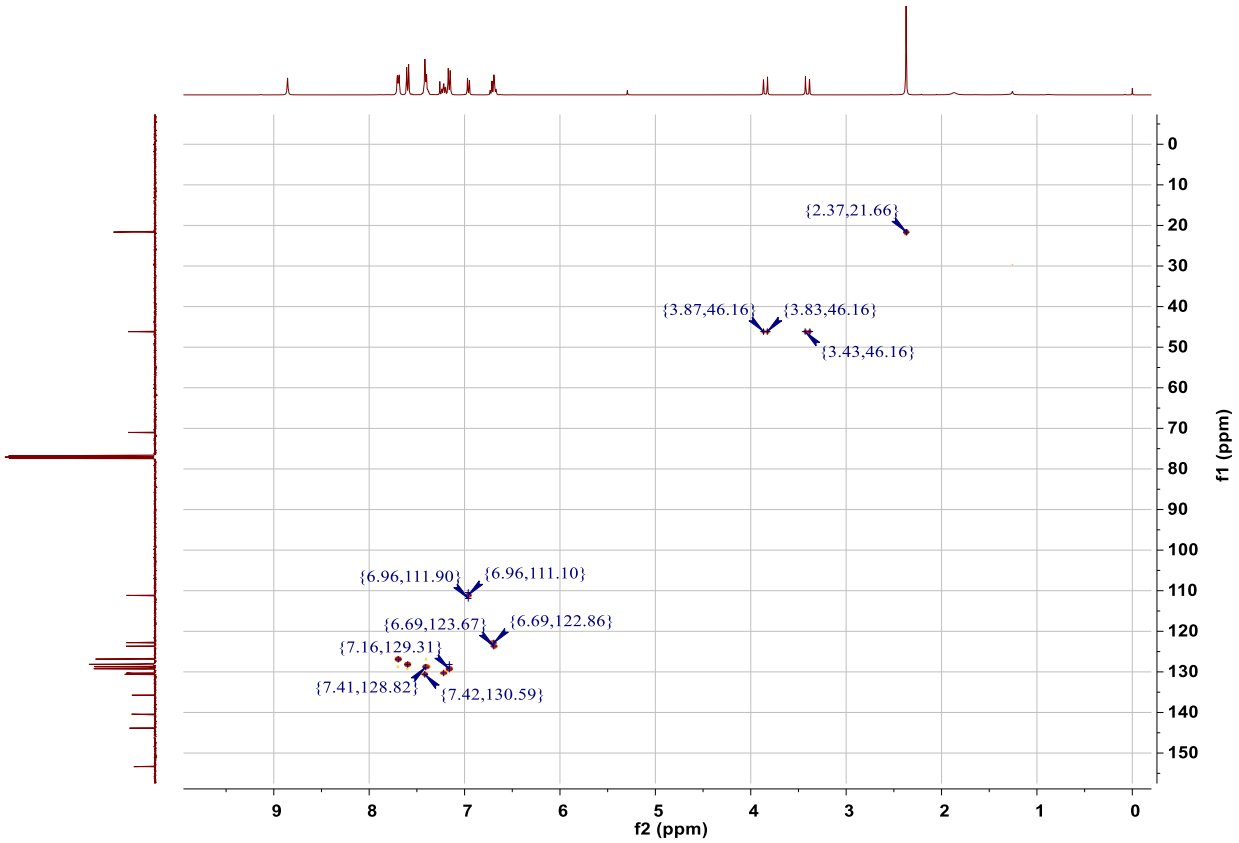




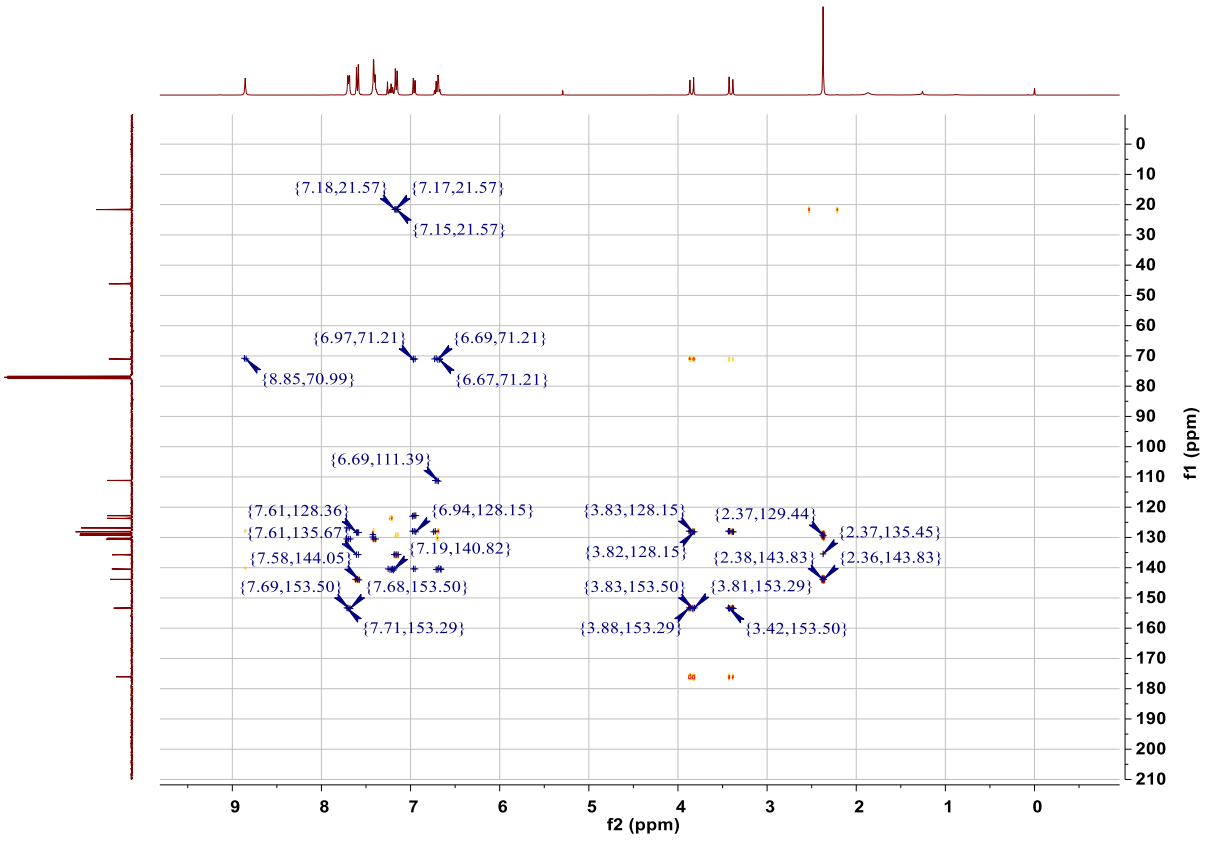
12. Copies of 2D NMR



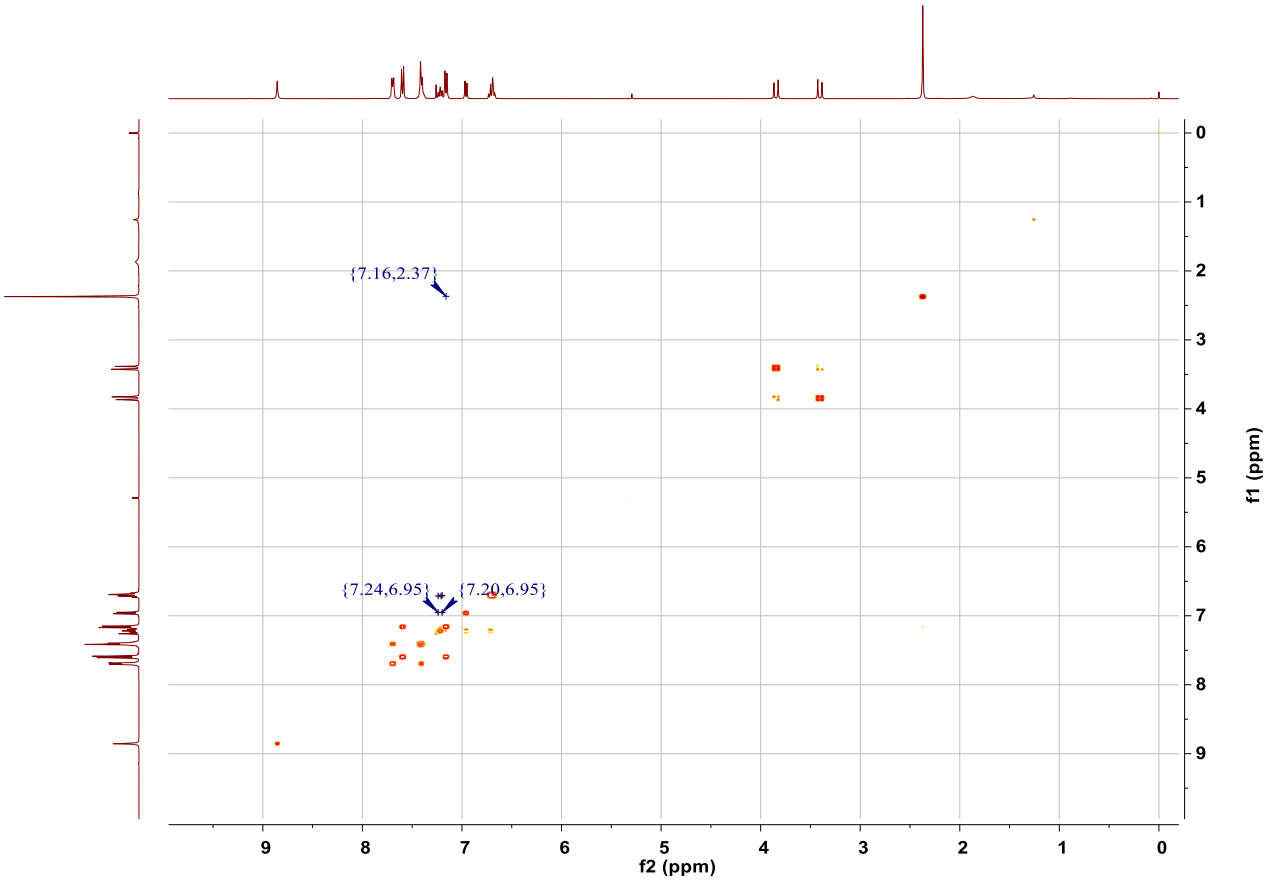
HSQC:


{2.37,21.66}
{3.87,46.16}
{3.83,46.16}
{3.43,46.16}
{6.96,111.90}
{6.96,111.10}
{6.69,123.67}
{6.69,122.86}
{7.16,129.31}
{7.41,128.82}
{7.42,130.59}
f2 (ppm)
f1 (ppm)

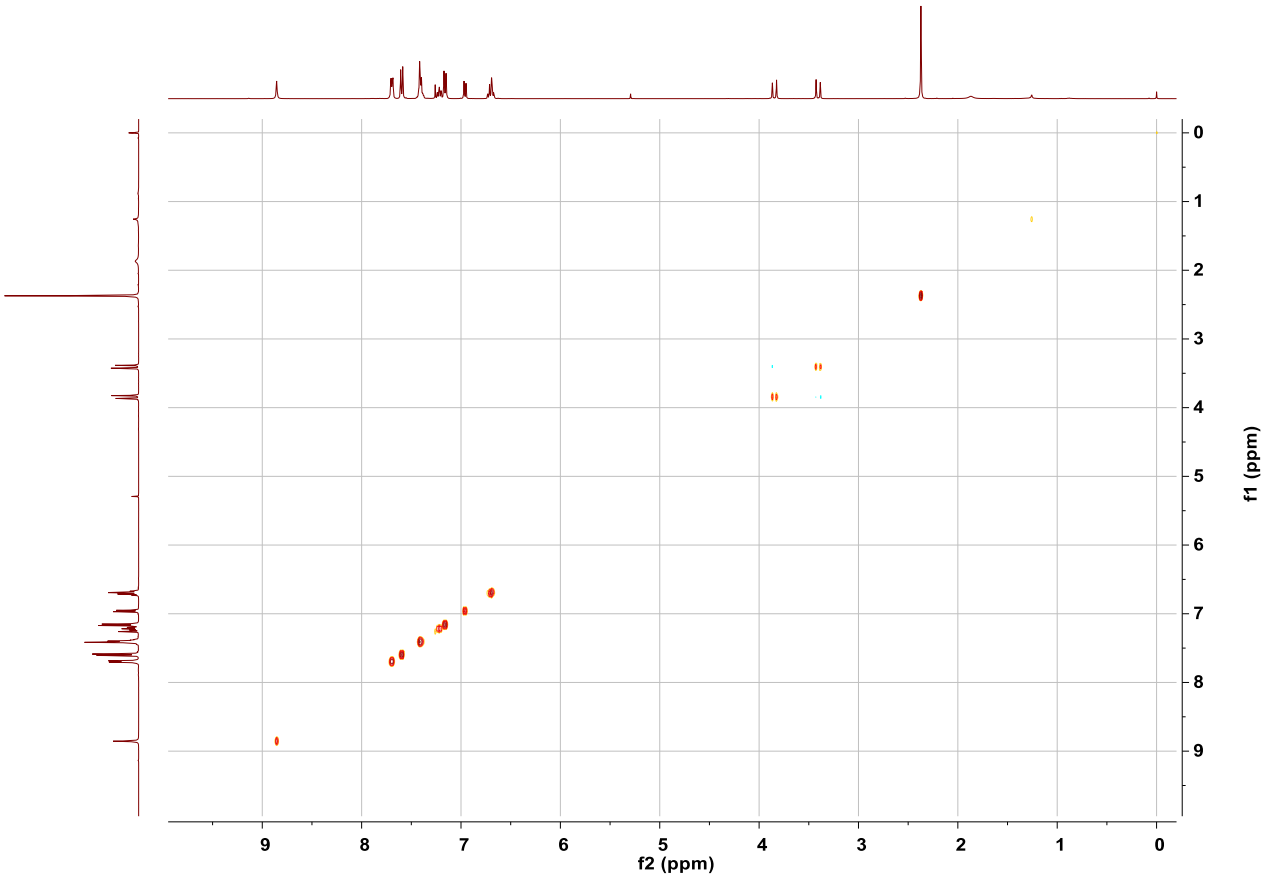
HMBC:


{7.18,21.57}
{7.17,21.57}
{7.15,21.57}
{6.97,71.21}
{6.69,71.21}
{8.85,70.99}
{6.67,71.21}
{6.69,111.39}
{7.61,128.36}
{6.94,128.15}
{7.61,135.67}
{7.58,144.05}
{7.19,140.82}
{7.69,153.50}
{7.68,153.50}
{7.71,153.29}
{3.83,128.15}
{2.37,129.44}
{2.37,135.45}
{3.82,128.15}
{2.38,143.83}
{2.36,143.83}
{3.83,153.50}
{3.81,153.29}
{3.88,153.29}
{3.42,153.50}
f2 (ppm)
f1 (ppm)

COSY:



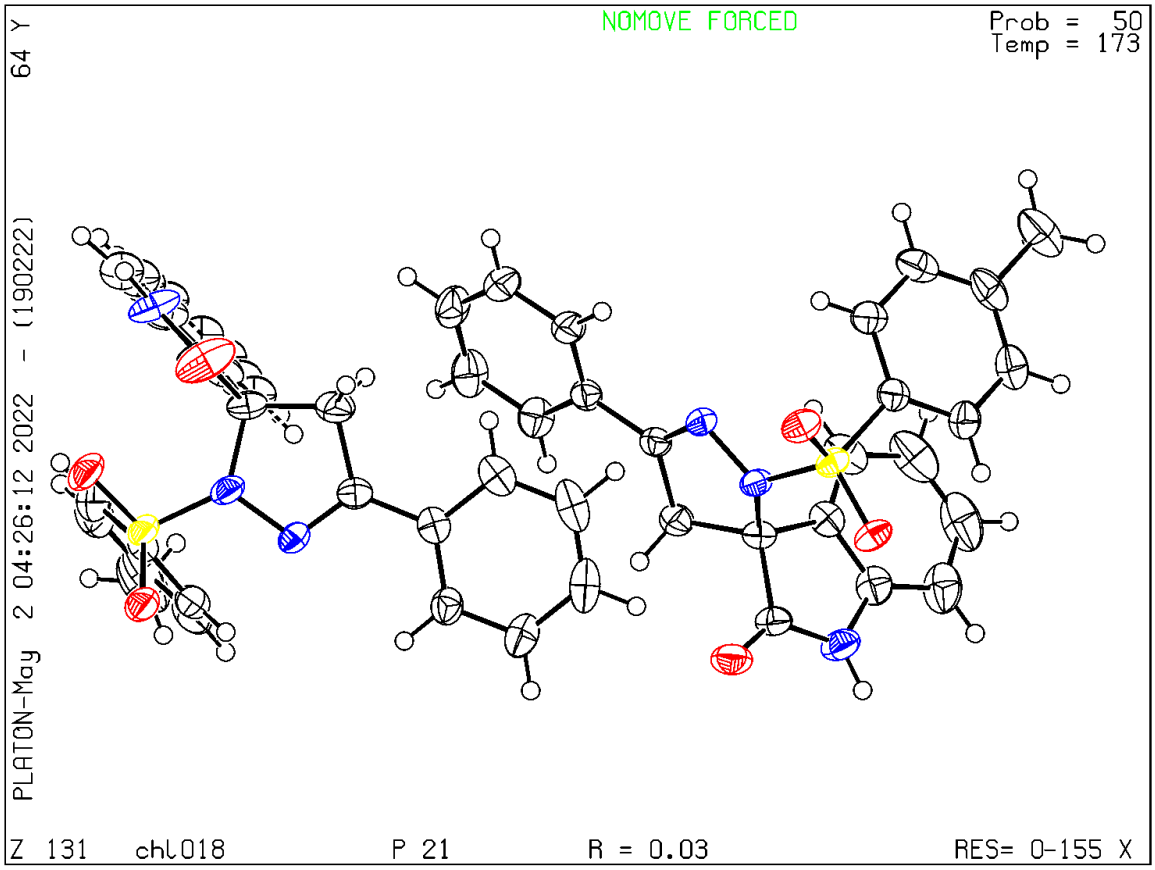
NOESY:



13. X-ray crystallography data

13.1 Determination of the absolute configuration of C1 by X-ray crystallography

The colourless crystal in block-shape, with approximate dimensions of 0.271 × 0.307 × 0.339 mm^3, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 173(2)K equipped with micro-focus Cu radiation source (K_α = 1.54178Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package.[3a-c] The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested.[3d]



The crystal of product **C1** was obtained in the solvents of dichloromethane and petroleum ether. CCDC: 2170044.
Crystallographic Data for C46 H38 N6 O6 S2

Formula	C46 H38 N6 O6 S2
Formula mass (amu)	834.94
Space group	P 21
a (Å)	8.3086 (3)
b (Å)	14.1838 (5)
c (Å)	17.5511 (6)
α (deg)	90
β (deg)	91.885 (1)
γ (deg)	90
V (Å^3)	2067.23 (13)
Z	2

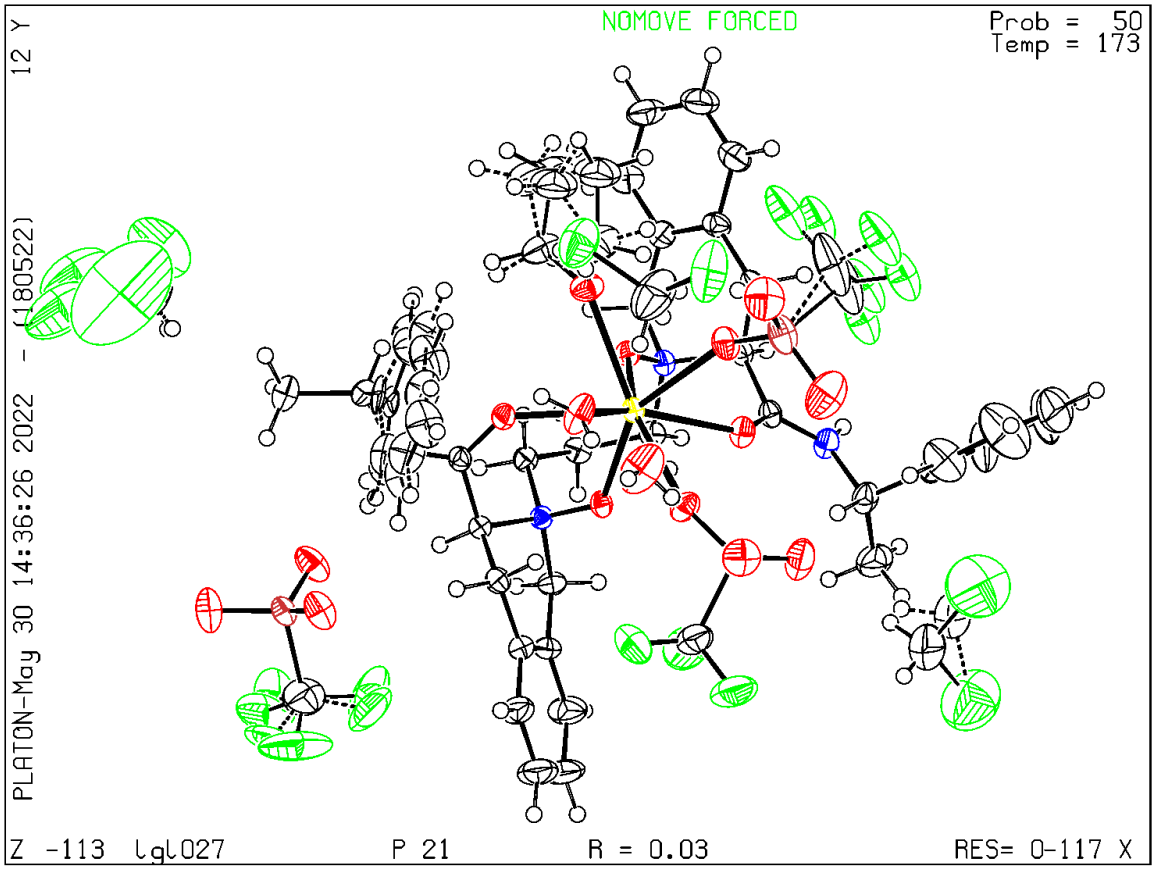
λ (Å)	1.54178
T (K)	173 K
ρ_{calcd} (g cm^{-3})	1.341
μ (mm^{-1})	1.641
Transmission factors	0.607, 0.743
θ_{max} (deg)	68.384
No. of unique data, including $F_o^2 < 0$	7503
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	7436
No. of variables	546
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.0265
$R_w(F_o^2)$ [b]	0.0692
Goodness of fit	1.051

[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$.

[b] $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2,0) + 2F_c^2] / 3$.

13.2 Determination of the absolute configuration of L$_3$-TQ-(*S*)-EPh/Pr(OTf)$_3$ by X-ray crystallography

The green crystal in block-shape, with approximate dimensions of 0.174 × 0.312 × 0.920 mm^3, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 173(2)K equipped with micro-focus Mo radiation source (K_α = 0.71073Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package.[3a-c] The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested.[3d]



The crystal of **L_3-TQ**-(*S*)-**EPh/**$Pr(OTf)_3$ was obtained in the solvents of tetrahydrofuran and petroleum ether. CCDC: 2181783.
Crystallographic Data for C49 H62 Cl6 F9 N4 O16 Pr S3

Formula	C49 H62 Cl6 F9 N4 O16 Pr S3
Formula mass (amu)	1583.81
Space group	P 21
a (Å)	12.3349 (9)
b (Å)	21.2246 (14)
c (Å)	12.9920 (8)
α (deg)	90
β (deg)	96.692 (2)
γ (deg)	90
V (Å^3)	3378.2 (4)
Z	2
λ (Å)	0.71073
T (K)	173 K
ρ_{calcd} (g cm^{-3})	1.557
μ (mm^{-1})	1.138
Transmission factors	0.708, 1.000
θ_{max} (deg)	27.519
No. of unique data, including $F_o^2 < 0$	15417
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	14334
No. of variables	933
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.0312
$R_w(F_o^2)$ [b]	0.0751
Goodness of fit	1.051

[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$.

[b] $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2,0) + 2F_c^2] / 3$.

14. References

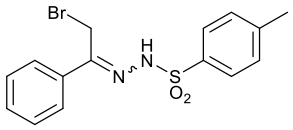
[1] (*a*) Y. H. Wen, X. Huang, J. L. Huang, Y. Xiong, B. Qin and X. M. Feng, Asymmetric Cyanosilylation of Aldehydes Catalyzed by Novel Organocatalysts, *Synlett.,* 2005, **16**, 2445–2448; (*b*) X. H. Liu, L. L. Lin and X. M. Feng, Chiral *N*,*N*'-Dioxides: New Ligands and Organocatalysts for Catalytic Asymmetric Reactions, *Acc. Chem. Res.*, 2011, **44**, 574–587; (*c*) X. H. Liu, L. L. Lin and X. M. Feng, Chiral *N*,*N*′-Dioxide Ligands: Synthesis, Coordination Chemistry and Asymmetric Catalysis, *Org. Chem. Front.,* 2014, **1**, 298–302; (*d*) Y. S. Chen, Y. Liu, Z. J. Li, S. X. Dong, X. H. Liu and X. M. Feng, Bimetallic Rhodium(II)/Indium(III) Relay Catalysis for Tandem Insertion/Asymmetric Claisen Rearrangement, *Angew. Chem. Int. Ed.,* 2018, **57**, 16554–16558.

[2] B. X. Quan, J. R. Zhuo, J. Q. Zhao, M. L. Zhang, M. Q. Zhou, X. M. Zhang and W. C. Yuan, [4 + 1] Annulation Reaction of Cyclic Pyridinium Ylides with *in situ* Generated Azoalkenes for the Construction of Spirocyclic Skeletons, *Org. Biomol. Chem.*, 2020, **18**, 1886–1891.

[3] (*a*) G. M. Sheldrick, Acta Cryst., 2008, **A64**, 112–122; (*b*) G. M. Sheldrick, Acta Cryst., 2015, **A71**, 3–8; (*c*) G. M. Sheldrick, Acta Cryst., 2015, **C71**, 3–8; (*d*) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, J. Appl. Cryst., 2009, **42**, 339–341; (*e*) A. L. Spek, J. Appl. Cryst., 2003, **36**, 7–13.

15. Characterization for the reaction substrates

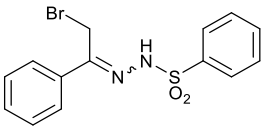
***N'*-(2-bromo-1-phenylethylidene)-4-methylbenzenesulfonohydrazide**



A1

Synthesized according to general method 2.1.
White solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.75 (m, 2H), 7.69 – 7.60 (m, 1H), 7.54 – 7.29 (m, 5H), 7.24 – 7.15 (m, 2H), 4.20 (s, 2H), 2.44 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.5, 135.1, 130.7, 130.3, 130.0, 129.8, 128.8, 128.1, 127.9, 127.5, 126.1, 34.1, 21.7, 19.1.
HRMS (ESI^{+}) m/z calcd for $C_{16}H_{18}KN_2O_3S^{+}$ ([M]-Br+OCH_3+K^{+}) = 357.0670, found 357.0668. (The bromo group would be replaced by -OMe in MeOH)
IR (neat, cm^{-1}) 3179, 1597, 1494, 1446, 1387, 1343, 1215, 1168, 1092, 1049, 908, 873, 816, 778, 740, 701, 668, 617, 579, 548, 525.
M. p. 143 – 144 °C

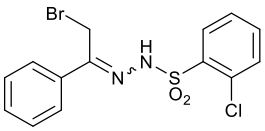
***N'*-(2-bromo-1-phenylethylidene)benzenesulfonohydrazide**



A2

Synthesized according to general method 2.1.
White solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 – 7.87 (m, 3H), 7.73 – 7.46 (m, 6H), 7.45 – 7.32 (m, 2H), 4.19 (s, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.8, 150.1, 138.1, 138.0, 134.4, 133.6, 133.5, 130.7, 130.4, 130.0, 129.8, 129.1, 128.8, 128.1, 127.9, 127.5, 126.2, 33.9, 19.1.
HRMS (ESI^{+}) m/z calcd for $C_{15}H_{16}KN_2O_3S^{+}$ ([M]-Br+OCH_3+K^{+}) = 343.0513, found 343.0515.
IR (neat, cm^{-1}) 3214, 1447, 1392, 1347, 1165, 1087, 1001, 873, 775, 752, 722, 687, 622, 577, 529.
M. p. 143 – 146 °C

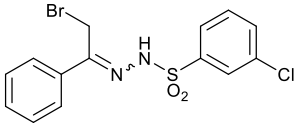
***N'*-(2-bromo-1-phenylethylidene)-2-chlorobenzenesulfonohydrazide**



A3

Synthesized according to general method 2.1.
White solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.72 – 7.99 (m, 2H), 7.78 – 7.31 (m, 8H), 4.25 (s, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.8, 151.8, 135.7, 135.6, 134.6, 134.1, 132.8, 132.7, 131.7, 131.6, 131.5, 131.2, 130.8, 130.5, 129.9, 129.7, 128.7, 127.6, 127.5, 127.3, 126.2, 33.8, 19.0.
HRMS (ESI^{+}) m/z calcd for $C_{15}H_{16}Cl^{34.9689}N_2O_3S^{+}$ ([M]-Br+OCH_3+H^{+}) = 339.0565, found 339.0567 and $C_{15}H_{16}Cl^{36.9659}N_2O_3S^{+}$ ([M]-Br+OCH_3+H^{+}) = 341.0535, found 341.0533.
IR (neat, cm^{-1}) 3235, 1575, 1452, 1391, 1351, 1320, 1165, 1131, 1108, 1042, 1001, 910, 877, 756, 702, 668, 622, 581.
M. p. 114 – 117 °C

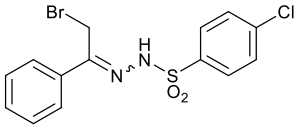
***N'*-(2-bromo-1-phenylethylidene)-3-chlorobenzenesulfonohydrazide**



A4

Synthesized according to general method 2.1.
White solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 – 7.99 (m, 1H), 7.94 – 7.86 (m, 1H), 7.85 – 7.55 (m, 3H), 7.54 – 7.36 (m, 4H), 7.25 – 7.18 (m, 1H), 4.21 (s, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.8, 139.7, 139.6, 135.3, 134.2, 133.7, 133.6, 130.8, 130.6, 130.4, 129.9, 128.8, 128.3, 127.9, 127.4, 126.2, 126.0, 33.7, 19.1.
HRMS (ESI^{+}) m/z calcd for $C_{15}H_{15}NaCl^{34.9689}N_2O_3S^{+}$ ([M]-Br+OCH_3+Na^{+}) = 361.0384, found 361.0386 and $C_{15}H_{15}NaCl^{36.9659}N_2O_3S^{+}$ ([M]-Br+OCH_3+Na^{+}) = 363.0355, found 363.0353.
IR (neat, cm^{-1}) 3218, 1464, 1409, 1351, 1319, 1165, 1076, 1000, 874, 775, 752, 674, 623, 579, 490.
M. p. 108 – 110 °C

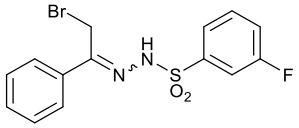
***N'*-(2-bromo-1-phenylethylidene)-4-chlorobenzenesulfonohydrazide**



A5

Synthesized according to general method 2.1.
White solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.82 (m, 2H), 7.70 – 7.60 (m, 1H), 7.57 – 7.35 (m, 5H), 7.25 – 7.18 (m, 2H), 4.21 (s, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.1, 136.5, 130.8, 129.9, 129.6, 129.5, 129.4, 128.8, 127.4, 126.1, 33.8.
HRMS (ESI^{+}) m/z calcd for $C_{15}H_{15}KCl^{34.9689}N_2O_3S^{+}$ ([M]-Br+OCH_3+K^{+}) = 377.0123, found 377.0126 and $C_{15}H_{15}KCl^{36.9659}N_2O_3S^{+}$ ([M]-Br+OCH_3+K^{+}) = 379.0094, found 379.0092.
IR (neat, cm^{-1}) 3216, 1583, 1475, 1397, 1349, 1165, 1089, 1014, 875, 828, 775, 757, 699, 634, 579, 528, 482.
M. p. 138 – 142 °C

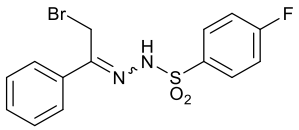
***N'*-(2-bromo-1-phenylethylidene)-4-fluorobenzenesulfonohydrazide**



A6

Synthesized according to general method 2.1.
White solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 – 7.78 (m, 1H), 7.77 – 7.60 (m, 3H), 7.60 – 7.46 (m, 2H), 7.46 – 7.28 (m, 3H), 7.25 – 7.17 (m, 1H), 4.21 (s, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.6, 161.1, 152.3, 150.7, 139.9, 134.2, 131.0, 130.9, 130.8, 130.6, 129.9, 128.8, 127.4, 126.2, 123.9, 123.8, 123.7, 121.0, 120.9, 120.8, 120.7, 115.7, 115.4, 115.2, 33.7, 19.1.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -109.5.
HRMS (ESI^{+}) m/z calcd for $C_{15}H_{15}FNaN_2O_3S^{+}$ ([M]-Br+OCH_3+Na^{+}) = 345.0680, found 345.0683.
IR (neat, cm^{-1}) 3216, 1593, 1476, 1435, 1391, 1350, 1272, 1226, 1165, 1084, 1068, 1002, 916, 870, 776, 753, 695, 677, 626, 579, 504.
M. p. 114 – 117 °C

***N'*-(2-bromo-1-phenylethylidene)-4-fluorobenzenesulfonohydrazide**

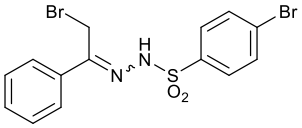


A7

Synthesized according to general method 2.1.
White solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 – 7.59 (m, 4H), 7.54 – 7.46 (m, 1H), 7.46 – 7.34 (m, 2H), 7.26 – 7.15 (m, 3H), 4.20 (s, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.0, 166.9, 164.4, 152.1, 150.4, 134.3, 134.0, 131.0, 130.9, 130.8, 130.7, 130.5, 129.9, 129.8, 128.8, 127.4, 126.1, 116.6, 116.3, 33.8, 19.1.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -103.6.

HRMS (ESI$^+$) m/z calcd for $C_{15}H_{15}FKN_2O_3S^+$ ([M]-Br+OCH_3+K^+) = 361.0419, found 361.0421.
IR (neat, cm^{-1}) 3217, 1592, 1494, 1407, 1352, 1320, 1295, 1239, 1174, 1155, 1086, 991, 874, 837, 775, 754, 691, 673, 615, 547.
M. p. 119 – 124 °C

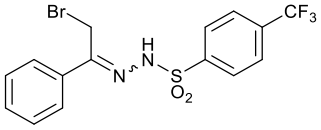
***N'*-4-bromo-(2-bromo-1-phenylethylidene)benzenesulfonohydrazide**



A8

Synthesized according to general method 2.1.
White solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (s, 1H), 7.91 – 7.75 (m, 2H), 7.73 – 7.61 (m, 3H), 7.55 – 7.46 (m, 2H), 7.46 – 7.35 (m, 1H), 7.25 – 7.19 (m, 1H), 4.20 (s, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.7, 132.5, 130.8, 130.6, 129.9, 129.6, 129.4, 128.8, 128.7, 127.4, 126.1, 33.8, 19.2.
HRMS (ESI$^+$) m/z calcd for $C_{15}H_{15}Br^{78.9183}NaN_2O_3S^+$ ([M]-Br+OCH_3+Na^+) = 404.9879, found 404.9877 and $C_{15}H_{15}Br^{80.9163}NaN_2O_3S^+$ ([M]-Br+OCH_3+Na^+) = 406.9859, found 406.9860.
IR (neat, cm^{-1}) 3217, 1574, 1470, 1392, 1350, 1319, 1165, 1085, 1069, 1008, 873, 822, 775, 740, 696, 627, 593, 531,419.
M. p. 157 – 158 °C

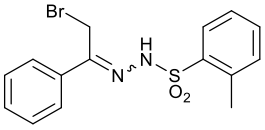
***N'*-(2-bromo-1-phenylethylidene)-4-(trifluoromethyl)benzenesulfonohydrazide**



A9

Synthesized according to general method 2.1.
White solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 (t, *J* = 8.4 Hz, 2H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.80 (m, 2H), 7.69 – 7.61 (m, 1H), 7.55 – 7.47 (m, 1H), 7.47 – 7.35 (m, 2H), 7.25 – 7.19 (m, 1H), 4.21 (s, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.5, 151.0, 141.6, 141.5, 135.3, 135.0, 134.2, 130.9, 130.6, 129.9, 129.8, 128.9, 128.7, 128.5, 127.4, 126.3, 126.2, 124.5, 121.8, 33.7, 19.1.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.1.
HRMS (ESI$^+$) m/z calcd for $C_{16}H_{15}F_3KN_2O_3S^+$ ([M]-Br+OCH_3+K^+) = 411.0387, found 411.0390.
IR (neat, cm^{-1}) 3220, 1406, 1353, 1322, 1171, 1132, 1109, 1089, 1062, 1018, 991, 876, 842, 775, 754, 713, 628, 599, 526, 428.
M. p. 108 – 111 °C

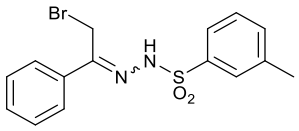
***N'*-(2-bromo-1-phenylethylidene)-2-methylbenzenesulfonohydrazide**



A10

Synthesized according to general method 2.1.
White solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 – 7.95 (m, 2H), 7.78 – 7.45 (m, 4H), 7.44 – 7.27 (m, 4H), 4.21 (s, 2H), 2.65 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.2, 149.2, 137.9, 137.7, 136.3, 134.4, 133.6, 132.6, 130.8, 130.7, 130.5, 130.3, 130.0, 129.9, 128.7, 127.5, 126.5, 126.4, 126.1, 34.0, 20.8, 20.6, 19.2.
HRMS (ESI$^+$) m/z calcd for $C_{16}H_{19}N_2O_3S^+$ ([M]-Br+OCH_3+H^+) = 319.1111, found 319.1116.
IR (neat, cm^{-1}) 3222, 1596, 1448, 1389, 1165, 1133, 1103, 1063, 1001, 944, 872, 807, 773, 752, 691, 620, 584, 541, 491.
M. p. 114 – 117 °C

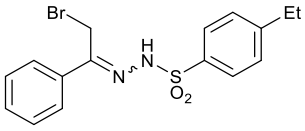
***N'*-(2-bromo-1-phenylethylidene)-3-methylbenzenesulfonohydrazide**



A11

Synthesized according to general method 2.1.
White solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (s, 1H), 7.90 – 7.77 (m, 2H), 7.74 – 7.61 (m, 2H), 7.53 – 7.33 (m, 5H), 4.19 (s, 2H), 2.42 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.9, 139.3, 137.8, 134.4, 130.3, 129.8, 129.0, 128.7, 128.4, 127.5, 126.2, 125.2, 21.3, 19.1.
HRMS (ESI$^+$) m/z calcd for $C_{16}H_{19}N_2O_3S^+$ ([M]-Br+OCH_3+H^+) = 319.1111, found 319.1115.
IR (neat, cm^{-1}) 3218, 1447, 1395, 1347, 1306, 1220, 1165, 1086, 1002, 877, 775, 753, 688, 624, 583, 487.
M. p. 113 – 115 °C

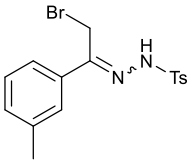
***N'*-(2-bromo-1-phenylethylidene)-4-ethylbenzenesulfonohydrazide**



A12

Synthesized according to general method 2.1.
White solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.69 – 7.58 (m, 1H), 7.53 – 7.45 (m, 1H), 7.44 – 7.31 (m, 4H), 7.24 – 7.15 (m, 1H), 4.20 (s, 2H), 2.73 (dq, *J* = 15.2, 7.6 Hz, 2H), 1.31 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.5, 150.6, 149.8, 135.3, 135.2, 134.4, 130.6, 130.3, 130.0, 129.8, 128.7, 128.6, 128.2, 128.0, 127.5, 126.2, 34.1, 28.9, 28.9, 19.1, 15.1, 15.0.
HRMS (ESI$^+$) m/z calcd for $C_{17}H_{20}NaN_2O_3S^+$ ([M]-Br+OCH_3+Na^+) = 355.1087, found 355.1089.
IR (neat, cm^{-1}) 3214, 2968, 1597, 1447, 1409, 1346, 1165, 1088, 1002, 873, 834, 775, 752, 693, 661, 616, 582, 559.
M. p. 108 – 110 °C

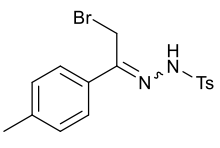
***N'*-(2-bromo-1-(*m*-tolyl)ethylidene)-4-methylbenzenesulfonohydrazide**



A15

Synthesized according to general method 2.1.
White solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 7.65 (m, 3H), 7.48 – 7.41 (m, 1H), 7.39 – 7.27 (m, 3H), 7.25 – 7.17 (m, 1H), 6.99 – 6.95 (m, 1H), 4.18 (s, 2H), 2.43 (s, 3H), 2.37 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.9, 150.0, 144.5, 144.4, 139.8, 138.5, 135.2, 135.1, 134.4, 131.4, 131.1, 129.9, 129.8, 129.7, 128.6, 128.1, 127.9, 127.8, 126.8, 124.4, 123.3, 53.5, 34.1, 21.7, 21.5, 19.3.
HRMS (ESI$^+$) m/z calcd for $C_{17}H_{21}N_2O_3S^+$ ([M]-Br+OCH_3+H^+) = 333.1267, found 333.1275.
IR (neat, cm^{-1}) 3215, 2362, 1598, 1401, 1345, 1165, 1086, 1023, 861, 814, 794, 667, 621, 584, 549.
M. p. 139 – 142 °C

***N'*-(2-bromo-1-(*p*-tolyl)ethylidene)-4-methylbenzenesulfonohydrazide**

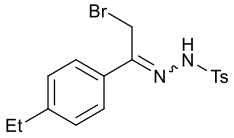


A16

Synthesized according to general method 2.1.
White solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 – 7.61 (m, 3H), 7.56 – 7.27 (m, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 4.26 – 4.11 (s, 2H), 2.43 (s, 3H), 2.38 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.1, 144.5, 140.7, 135.1, 130.4, 129.7, 129.5, 128.1, 127.9, 127.4, 126.1, 21.7, 21.4, 19.1.
HRMS (ESI$^+$) m/z calcd for $C_{17}H_{20}NaN_2O_3S^+$ ([M]-Br+OCH_3+Na^+) = 355.1087, found 355.1092.
IR (neat, cm^{-1}) 3208, 1596, 1470, 1407, 1342, 1319, 1305, 1165, 1082, 992, 869, 820, 731, 714, 689, 671, 584, 563.
M. p. 161 – 164 °C

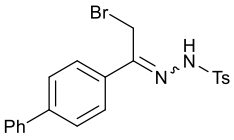
***N'*-(2-bromo-1-(4-ethylphenyl)ethylidene)-4-methylbenzenesulfonohydrazide**



A17

Synthesized according to general method 2.1.
White solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 – 7.65 (m, 3H), 7.62 – 7.28 (m, 4H), 7.24 – 7.06 (m, 2H), 4.18 (s, 2H), 2.68 (q, *J* = 7.6 Hz, 2H), 2.43 (s, 3H), 1.25 (t, *J* = 7.6 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.1, 147.0, 144.5, 135.1, 131.8, 129.7, 129.3, 128.3, 128.1, 127.9, 127.5, 126.2, 28.8, 28.7, 21.7, 19.2, 15.3, 15.2.
HRMS (ESI$^+$) m/z calcd for $C_{18}H_{23}NaN_2O_3S^+$ ([M]-Br+OCH_3+Na^+) = 347.1424, found 347.1428.
IR (neat, cm^{-1}) 3217, 2967, 1596, 1465, 1405, 1343, 1314, 1165, 1083, 994, 868, 840, 814, 707, 666, 586, 551.
M. p. 155 – 157 °C

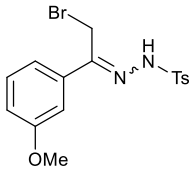
***N'*-(1-([1,1'-biphenyl]-4-yl)-2-bromoethylidene)-4-methylbenzenesulfonohydrazide**



A18

Synthesized according to general method 2.1.
Yellow solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (s, 1H), 7.94 – 7.79 (m, 2H), 7.78 – 7.54 (m, 6H), 7.50 – 7.27 (m, 5H), 4.23 (s, 2H), 2.43 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.3, 149.5, 144.6, 144.5, 143.6, 143.1, 140.0, 139.7, 135.1, 135.0, 133.2, 129.8, 129.0, 128.9, 128.6, 128.4, 128.2, 128.1, 128.0, 127.9, 127.4, 127.2, 127.1, 126.6, 34.1, 21.7, 21.7, 19.0.
HRMS (ESI$^+$) m/z calcd for $C_{22}H_{22}NaN_2O_3S^+$ ([M]-Br+OCH_3+Na^+) = 417.1243, found 417.1244.
IR (neat, cm^{-1}) 3216, 1599, 1487, 1402, 1348, 1319, 1165, 1084, 997, 871, 846, 813, 769, 734, 698, 666, 614, 551.
M. p. 138 – 140 °C

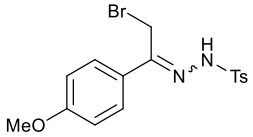
***N'*-(2-bromo-1-(3-methoxyphenyl)ethylidene)-4-methylbenzenesulfonohydrazide**



A19

Synthesized according to general method 2.1.
White solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 7.69 (m, 3H), 7.42 – 7.27 (m, 3H), 7.22 – 7.16 (m, 1H), 7.03 – 6.90 (m, 1H), 6.78 – 6.68 (m, 1H), 4.18 (s, 2H), 3.82 (s, 3H), 2.43 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.4, 159.8, 151.4, 149.6, 144.6, 144.4, 135.8, 135.2, 135.0, 131.2, 131.1, 129.8, 129.7, 128.1, 127.9, 119.3, 118.6, 116.1, 116.0, 113.1, 111.5, 55.4, 55.3, 33.9, 21.7, 21.7, 19.2.
HRMS (ESI$^+$) m/z calcd for $C_{17}H_{20}NaN_2O_4S^+$ ([M]-Br+OCH_3+Na^+) = 371.1036, found 371.1040.
IR (neat, cm^{-1}) 3214, 1598, 1575, 1464, 1429, 1400, 1310, 1237, 1165, 1084, 1042, 1009, 858, 814, 787, 731, 706, 666, 616, 548.
M. p. 136 – 139 °C

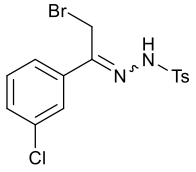
***N'*-(2-bromo-1-(4-methoxyphenyl)ethylidene)-4-methylbenzenesulfonohydrazide**



A20

Synthesized according to general method 2.1.
White solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.86 (m, 2H), 7.84 – 7.76 (m, 1H), 7.70 – 7.56 (m, 2H), 7.36 – 7.29 (m, 2H), 7.22 – 6.87 (m, 2H), 4.18 (s, 2H), 3.84 (s, 3H), 2.43 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.4, 150.2, 144.4, 135.1, 129.7, 129.1, 128.1, 127.9, 127.7, 126.8, 115.1, 114.1, 55.4, 21.7, 19.1.
HRMS (ESI$^+$) m/z calcd for $C_{17}H_{20}NaN_2O_4S^+$ ([M]-Br+OCH_3+Na^+) = 371.1036, found 371.1041.
IR (neat, cm^{-1}) 3207, 1602, 1513, 1462, 1403, 1317, 1255, 1165, 1083, 1030, 993, 872, 837, 813, 716, 665, 587, 548.
M. p. 137 – 140 °C

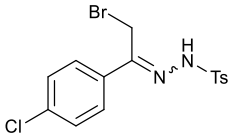
***N'*-(2-bromo-1-(3-chlorophenyl)ethylidene)-4-methylbenzenesulfonohydrazide**



A21

Synthesized according to general method 2.1.
White solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (s, 1H), 7.94 – 7.75 (m, 2H), 7.66 – 7.58 (m, 1H), 7.55 – 7.41 (m, 1H), 7.41 – 7.28 (m, 3H), 7.23 – 7.08 (m, 1H), 4.16 (s, 2H), 2.44 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.8, 148.1, 144.8, 144.6, 136.2, 135.9, 134.9, 131.7, 131.1, 130.9, 130.2, 130.0, 129.8, 128.1, 127.9, 127.6, 126.3, 125.8, 124.2, 33.7, 21.7, 18.7.
HRMS (ESI$^+$) m/z calcd for $C_{16}H_{17}Cl^{34.9689}NaN_2O_3S^+$ ([M]-Br+OCH_3+Na^+) = 375.0541, found 375.0545 and $C_{16}H_{17}Cl^{36.9659}NaN_2O_3S^+$ ([M]-Br+OCH_3+Na^+) = 377.0511, found 377.0511.
IR (neat, cm^{-1}) 3213, 1596, 1564, 1465, 1403, 1345, 1307, 1165, 1118, 1085, 1014, 872, 808, 665, 618, 583, 548.
M. p. 129 – 133 °C

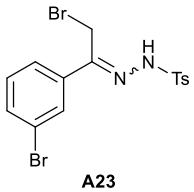
***N'*-(2-bromo-1-(4-chlorophenyl)ethylidene)-4-methylbenzenesulfonohydrazide**



A22

Synthesized according to general method 2.1.
White solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.62 – 7.54 (m, 2H), 7.50 – 7.29 (m, 4H), 4.17 (s, 2H), 2.44 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.6, 144.7, 136.5, 134.9, 132.8, 130.1, 129.8, 129.0, 128.1, 127.9, 127.4, 33.8, 21.7, 18.7.
HRMS (ESI$^+$) m/z calcd for $C_{16}H_{17}Cl^{34.9689}NaN_2O_3S^+$ ([M]-Br+OCH_3+Na^+) = 375.0541, found 375.0544 and $C_{16}H_{17}Cl^{36.9659}NaN_2O_3S^+$ ([M]-Br+OCH_3+Na^+) = 377.0511, found 377.0511.
IR (neat, cm^{-1}) 3202, 1596, 1493, 1474, 1399, 1341, 1313, 1165, 1083, 995, 943, 872, 834, 813, 771, 736, 701, 672, 551.
M. p. 149 – 152 °C

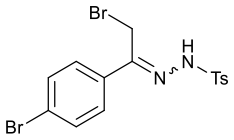
***N'*-(2-bromo-1-(3-bromophenyl)ethylidene)-4-methylbenzenesulfonohydrazide**



A23

Synthesized according to general method 2.1.
White solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (s, 1H), 7.93 – 7.78 (m, 2H), 7.76 (t, *J* = 2.0 Hz, 1H), 7.64 – 7.48 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.25 (t, *J* = 8.0 Hz, 1H), 4.13 (s, 2H), 2.43 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.1, 144.8, 136.4, 134.8, 133.2, 130.2, 129.8, 129.2, 128.1, 124.7, 123.0, 21.7, 18.7.
HRMS (ESI$^+$) m/z calcd for $C_{16}H_{17}Br^{78.9183}NaN_2O_3S^+$ ([M]-Br+OCH_3+Na^+) = 419.0035, found 419.0040 and $C_{16}H_{17}Br^{80.9163}NaN_2O_3S^+$ ([M]-Br+OCH_3+Na^+) = 421.0015, found 421.0018.
IR (neat, cm^{-1}) 3212, 1596, 1559, 1466, 1403, 1345, 1306, 1165, 1086, 1009, 871, 813, 786, 672, 617, 583, 548.
M. p. 130 – 133 °C

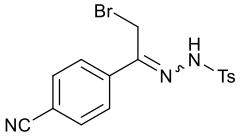
***N'*-(2-bromo-1-(4-bromophenyl)ethylidene)-4-methylbenzenesulfonohydrazide**



A24

Synthesized according to general method 2.1.
White solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (s, 1H), 7.93 – 7.73 (m, 2H), 7.67 – 7.58 (m, 1H), 7.51 (s, 3H), 7.40 – 7.29 (m, 2H), 4.16 (s, 2H), 2.44 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.6, 144.7, 134.9, 133.3, 133.1, 132.0, 129.8, 129.2, 128.1, 127.9, 127.6, 124.8, 33.8, 21.7, 18.6.
HRMS (ESI$^+$) m/z calcd for $C_{16}H_{17}Br^{78.9183}NaN_2O_3S^+$ ([M]-Br+OCH_3+Na^+) = 419.0035, Found 419.0042 and $C_{16}H_{17}Br^{80.9163}NaN_2O_3S^+$ ([M]-Br+OCH_3+Na^+) = 421.0015, found 421.0020.
IR (neat, cm^{-1}) 3214, 1594, 1469, 1396, 1345, 1313, 1165, 1084, 995, 871, 832, 814, 763, 688, 578, 549.
M. p. 160 – 162 °C

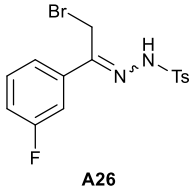
***N'*-(2-bromo-1-(4-cyanophenyl)ethylidene)-4-methylbenzenesulfonohydrazide**



A25

Synthesized according to general method 2.1.
White solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20 (s, 1H), 7.88 (m, 2H), 7.84 – 7.72 (m, 2H), 7.71 – 7.55 (m, 2H), 7.42 – 7.30 (m, 2H), 4.18 (s, 2H), 2.44 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.0, 144.9, 138.5, 134.8, 133.5, 132.5, 129.9, 128.1, 126.6, 118.2, 113.6, 21.7, 18.2.
HRMS (ESI$^+$) m/z calcd for $C_{17}H_{17}NaN_3O_3S^+$ ([M]-Br+OCH_3+Na^+) = 366.0883, found 366.0887.
IR (neat, cm^{-1}) 3207, 2231, 1595, 1405, 1350, 1318, 1165, 1086, 999, 869, 846, 814, 706, 663, 564.
M. p. 174 – 177 °C

***N'*-(2-bromo-1-(4-(trifluoromethoxy)phenyl)ethylidene)-4-methylbenzenesulfonohydrazide**



A26

Synthesized according to general method 2.1.

White solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.26 – 7.61 (m, 3H), 7.54 – 7.30 (m, 4H), 7.23 – 7.04 (m, 1H), 4.17 (s, 2H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.2, 161.9, 161.7, 148.3, 144.7, 144.6, 136.7, 134.9, 131.8, 131.7, 130.3, 129.8, 128.1, 127.9, 123.3, 121.8, 121.7, 118.0, 117.8, 117.4, 117.2, 115.0, 114.8, 113.3, 113.0, 33.7, 21.7, 18.8.

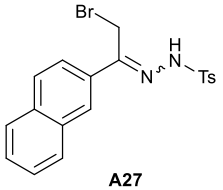
^{19}F NMR (376 MHz, Chloroform-*d*) δ -109.1, -111.9.

HRMS (ESI^{+}) m/z calcd for $C_{16}H_{17}NaFN_2O_3S^{+}$ ([M]-Br+OCH_3+Na^{+}) = 359.0836, found 359.0839.

IR (neat, cm^{-1}) 3214, 1597, 1438, 1401, 1346, 1313, 1165, 1086, 1019, 886, 814, 791, 727, 707, 666, 618, 548.

M. p. 112 – 116 °C

***N'*-(2-bromo-1-(naphthalen-2-yl)ethylidene)-4-methylbenzenesulfonohydrazide**



A27

Synthesized according to general method 2.1.

White solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (s, 1H), 7.99 (s, 1H), 7.96 – 7.91 (m, 2H), 7.91 – 7.79 (m, 4H), 7.57 – 7.46 (m, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 4.30 (s, 2H), 2.40 (s, 3H).

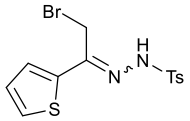
^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.7, 144.6, 135.0, 134.1, 132.8, 131.7, 129.8, 128.7, 128.1, 127.7, 127.4, 126.7, 126.1, 123.2, 21.7, 19.0.

HRMS (ESI^{+}) m/z calcd for $C_{20}H_{20}NaN_2O_3S^{+}$ ([M]-Br+OCH_3+Na^{+}) = 391.1087, found 391.1090.

IR (neat, cm^{-1}) 3217, 1597, 1401, 1344, 1311, 1165, 1081, 1007, 942, 862, 815, 753, 664, 579, 547, 476.

M. p. 153 – 156 °C

***N'*-(2-bromo-1-(thiophen-2-yl)ethylidene)-4-methylbenzenesulfonohydrazide**



A28

Synthesized according to general method 2.1.

Light yellow solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 – 7.76 (m, 3H), 7.45 – 7.29 (m, 3H), 7.25 – 7.16 (m, 1H), 7.05 – 6.98 (m, 1H), 4.21 (s, 2H), 2.43 (s, 3H).

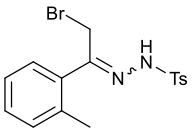
^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.5, 144.6, 139.3, 134.8, 129.7, 129.6, 129.5, 128.3, 128.1, 128.0, 127.4, 127.1, 21.7, 18.9.

HRMS (ESI^{+}) m/z calcd for $C_{14}H_{16}NaN_2O_3S_2^{+}$ ([M]-Br+OCH_3+Na^{+}) = 347.0495, found 347.0497.

IR (neat, cm^{-1}) 3211, 2361, 1597, 1400, 1341, 1309, 1165, 1088, 1050, 966, 870, 814, 709, 666, 548.

M. p. 155 – 157 °C

***N'*-(2-bromo-1-(*o*-tolyl)ethylidene)-4-methylbenzenesulfonohydrazide**



A30

Synthesized according to general method 2.1.

White solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.42 – 7.25 (m, 6H), 6.97 (d, *J* = 6.8 Hz, 1H), 4.26 (d, *J* = 10.4 Hz, 1H), 4.15 (d, *J* = 10.4 Hz, 1H), 2.46 (s, 3H), 2.07 (s, 3H).

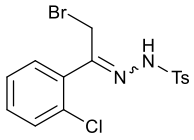
^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.0, 144.5, 135.8, 135.2, 131.3, 130.6, 129.8, 129.5, 127.8, 127.7, 126.9, 34.3, 21.7, 19.2.

HRMS (ESI^{+}) m/z calcd for $C_{17}H_{20}NaN_2O_3S^{+}$ ([M]-Br+OCH_3+Na^{+}) = 355.1087, found 355.1082.

IR (neat, cm^{-1}) 3199, 2964, 1598, 1491, 1384, 1345, 1300, 1261, 1165, 1090, 1042, 908, 878, 809, 772, 733, 709, 667, 593, 549, 463.

M. p. 162 – 163 °C

***N'*-(2-bromo-1-(2-chlorophenyl)ethylidene)-4-methylbenzenesulfonohydrazide**



A31

Synthesized according to general method 2.1.

White solid.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.52 – 7.37 (m, 4H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.22 – 7.14 (m, 1H), 4.29 (d, *J* = 10.4 Hz, 1H), 4.19 (d, *J* = 10.4 Hz, 1H), 2.45 (s, 3H).

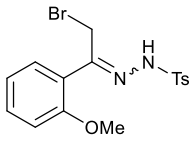
^{13}C NMR (101 MHz, Chloroform-d) δ 148.8, 144.5, 135.0, 132.0, 131.6, 130.6, 130.5, 129.7, 129.0, 127.9, 127.9, 33.4, 21.7.

HRMS (ESI$^+$) m/z calcd for $C_{16}H_{17}Cl^{34.9689}NaN_2O_3S^+$ ([M]-Br+OCH_3+Na^+) = 375.0541, found 375.0540 and $C_{16}H_{17}Cl^{36.9659}NaN_2O_3S^+$ ([M]-Br+OCH_3+Na^+) = 377.0511, found 377.0511.

IR (neat, cm^{-1}) 3196, 1597, 1432, 1391, 1347, 1303, 1261, 1168, 1069, 1037, 909, 879, 812, 763, 738, 703, 667, 589, 548, 461.

M. p. 162 – 164 °C

***N'*-(2-bromo-1-(2-methoxyphenyl)ethylidene)-4-methylbenzenesulfonohydrazide**



A32

Synthesized according to general method 2.1.

Light red solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.63 (s, 1H), 7.49 – 7.40 (m, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.10 – 7.01 (m, 2H), 6.97 (d, *J* = 8.4 Hz, 1H), 4.25 (s, 2H), 3.68 (s, 3H), 2.46 (s, 3H).

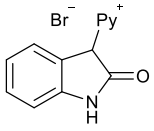
^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.8, 150.0, 144.2, 135.5, 132.2, 129.6, 129.5, 127.8, 121.5, 118.6, 111.9, 55.7, 34.4, 21.7.

HRMS (ESI$^+$) m/z calcd for $C_{17}H_{20}NaN_2O_4S^+$ ([M]-Br+OCH_3+Na^+) = 371.1036, found 371.1040.

IR (neat, cm^{-1}) 3210, 1598, 1491, 1460, 1435, 1385, 1344, 1304, 1246, 1165, 1092, 1047, 1021, 909, 879, 814, 757, 721, 668, 593, 549.

M. p. 134 – 136 °C

3-(pyridin-2-yl)indolin-2-one, bromide salt



B1

Synthesized according to general method 2.2.

Dark red solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.25 (s, 1H), 9.01 (d, *J* = 5.6 Hz, 2H), 8.75 (t, *J* = 8.0 Hz, 1H), 8.24 (t, *J* = 6.8 Hz, 2H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 6.79 (s, 1H).

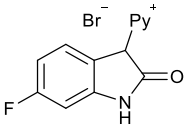
^{13}C NMR (101 MHz, DMSO-d_6) δ 171.2, 147.8, 145.0, 143.9, 132.1, 129.2, 126.8, 123.4, 122.2, 111.6, 69.9.

HRMS (ESI$^+$) m/z calcd for $C_{13}H_{10}NaN_2O^+$ ([M]-Br+Na^+) = 233.0685, found 233.0686.

IR (neat, cm^{-1}) 2361, 2340, 1720, 1620, 1471, 757, 702, 671, 584, 550, 498, 481, 451, 422.

M. p. 216 – 218 °C

6-fluoro-3-(pyridin-2-yl)indolin-2-one, bromide salt



B2

Synthesized according to general method 2.2.

Red solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 11.40 (s, 1H), 9.01 (d, *J* = 5.6 Hz, 2H), 8.75 (t, *J* = 7.8 Hz, 1H), 8.28 – 8.20 (m, 2H), 7.57 (dd, *J* = 8.0, 5.6 Hz, 1H), 7.04 – 6.95 (m, 1H), 6.93 (dd, *J* = 9.2, 2.4 Hz, 1H), 6.72 (s, 1H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 171.6, 163.3, 147.8, 146.0 (*J* = 12.6 Hz), 145.0, 129.2, 129.0 (*J* = 10.3 Hz), 126.9, 118.2 (*J* = 2.8 Hz), 109.8 (*J* = 22.8 Hz), 99.9 (*J* = 27.3 Hz), 69.4.

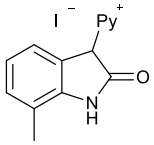
^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ -107.8.

HRMS (ESI$^+$) m/z calcd for $C_{13}H_9FNaN_2O^+$ ([M]-Br+Na$^+$) = 252.0669, found 252.0657.

IR (neat, cm^{-1}) 3028, 2361, 1742, 1625, 1499, 1462, 1330, 1290, 1240, 1198, 1142, 1094, 964, 846, 811, 772, 730, 678, 625, 598, 562, 514, 453.

M. p. ＞400 °C

7-methyl-3-(pyridin-2-yl)indolin-2-one, iodide salt



B3

Synthesized according to general method 2.2.

Dark brown solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 11.16 (s, 1H), 9.00 (d, *J* = 5.6 Hz, 2H), 8.75 (t, *J* = 8.0 Hz, 1H), 8.30 – 8.16 (m, 2H), 7.38 – 7.24 (m, 2H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.75 (s, 1H), 2.28 (s, 3H).

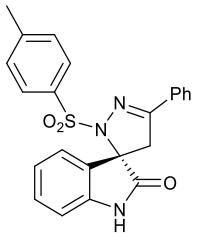
^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 171.1, 147.7, 145.0, 141.3, 132.6, 132.4, 129.3, 127.2, 122.3, 111.4, 70.0, 21.1.

HRMS (ESI$^+$) m/z calcd for $C_{14}H_{12}NaN_2O^+$ ([M]-I+Na$^+$) = 248.0920, found 248.0923.

IR (neat, cm^{-1}) 2360, 2339, 1711, 1626, 1484, 1207, 841, 752, 676, 584, 504.

M. p. ＞400 °C

16. Characterization and HPLC conditions for products



C1

(*S*)-5'-phenyl-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one

The crude material was directly purified by flash chromatography on silica gel (R_f = 0.3, PE/EtOAc = 3:2) to afford the light yellow solid (37.5 mg) in 90% yield with 90% ee. The ee was determined by HPLC analysis (Daicel chiralcel **IA**, 2-propanol/hexane = 30/70, flow rate = 1.0 mL/min, λ = 300 nm). $t_{R(major)}$ = 34.25 min, $t_{R(minor)}$ = 16.95 min; $[\alpha]_D^{17}$ = +44.6 (c = 0.24, in CH_2Cl_2).

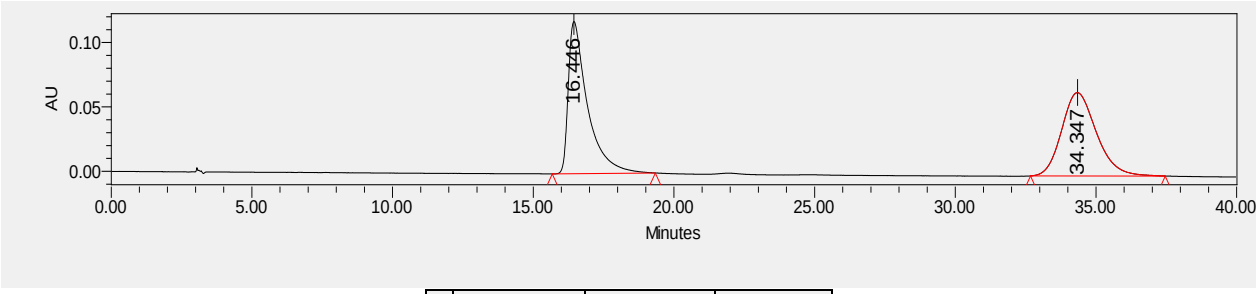
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.81 (s, 1H), 7.70 (d, *J* = 6.8 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.41 (s, 3H), 7.22 (td, *J* = 7.6, 2.0 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.78 – 6.65 (m, 2H), 3.85 (d, *J* = 16.8 Hz, 1H), 3.41 (d, *J* = 16.8 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.0, 153.3, 143.9, 140.4, 135.8, 130.6, 130.5, 130.3, 129.2, 128.7, 128.2, 128.0, 126.9, 123.7, 122.8, 111.2, 71.0, 46.2, 21.6.

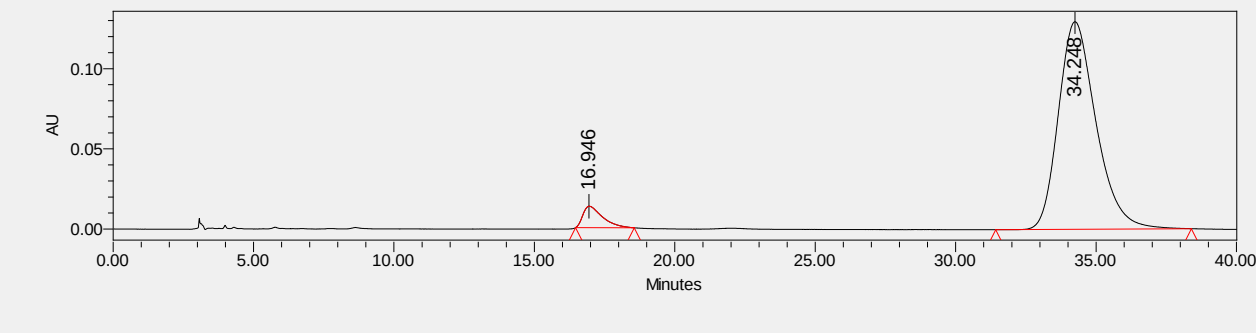
HRMS (ESI$^+$) m/z calcd for $C_{23}H_{20}N_3O_3S^+$ ([M]+H$^+$) = 418.1220, found 418.1218.

IR (neat, cm^{-1}) 3318, 1729, 1620, 1600, 1472, 1355, 1214, 1166, 1123, 1037, 1019, 758, 735, 705, 665, 592, 546.

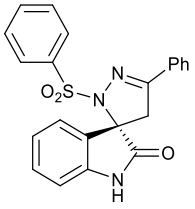
M. p. 236 – 240 °C



	Retention Time	Area	% Area
1	16.446	5595234	50.21
2	34.347	5548447	49.79



	Retention Time	Area	% Area
1	16.946	645680	5.08
2	34.248	12054166	94.92



C2

(*S*)-5'-phenyl-2'-(phenylsulfonyl)-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one

The crude material was directly purified by flash chromatography on silica gel (R_f = 0.3, PE/EtOAc = 3:2) to afford the light yellow solid (33.9 mg) in 84% yield with 90% ee. The ee was determined by HPLC analysis (Daicel chiralcel **IB$_{N-5}$**, 2-propanol/hexane = 30/70, flow rate = 1.0 mL/min, λ = 300 nm). $t_{R(major)}$ = 9.84 min, $t_{R(minor)}$ = 13.13 min; $[\alpha]_D^{20}$ = +30.6 (c = 1.39, in CH_2Cl_2).

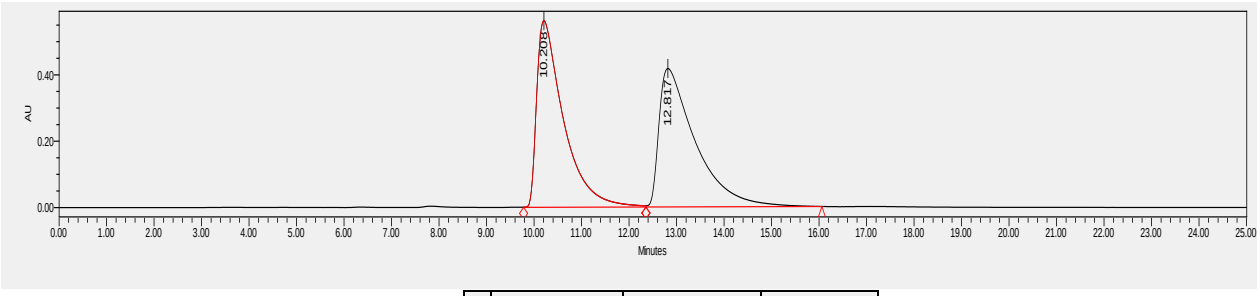
^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ 9.75 (s, 1H), 7.87 – 7.75 (m, 2H), 7.72 – 7.55 (m, 3H), 7.54 – 7.39 (m, 5H), 7.31 – 7.23 (m, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.77 – 6.54 (m, 2H), 3.81 (d, *J* = 17.2 Hz, 1H), 3.62 (d, *J* = 17.2 Hz, 1H).

^{13}C NMR (101 MHz, Acetone-*d*$_6$) δ 175.8, 154.4, 142.5, 140.2, 133.7, 131.5, 131.3, 130.8, 129.5, 129.4, 128.9, 128.6, 127.5, 124.6, 122.8, 111.0, 71.7, 46.7.

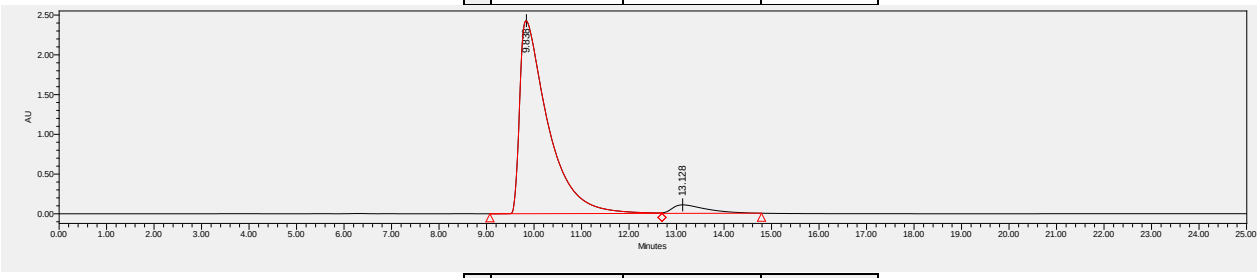
HRMS (ESI$^+$) m/z calcd for $C_{22}H_{17}N_3O_3NaS^+$ ([M]+Na$^+$) = 426.0883, found 426.0883.

IR (neat, cm^{-1}) 3259, 1729, 1620, 1473, 1447, 1355, 1262, 1215, 1168, 1125, 1036, 1019, 755, 724, 687, 631, 598, 568, 543, 486.

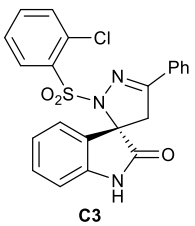
M. p. 223 – 226 °C



	Retention Time	Area	% Area
1	10.208	22018606	49.91
2	12.817	22095007	50.09



	Retention Time	Area	% Area
1	9.838	99926750	94.92
2	13.128	5344275	5.08



C3

(*S*)-2'-((2-chlorophenyl)sulfonyl)-5'-phenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one

The crude material was directly purified by flash chromatography on silica gel (R_f = 0.3, PE/EtOAc = 3:2) to afford the light yellow solid (36.4 mg) in 83% yield with 90% ee. The ee was determined by HPLC analysis (Daicel chiralcel **IB$_{N-5}$**, 2-propanol/hexane = 30/70, flow rate = 1.0 mL/min, λ = 300 nm). $t_{R(major)}$ = 11.94 min, $t_{R(minor)}$ = 18.32 min; $[\alpha]_D^{20}$ = +52.3 (c = 1.09, in CH_2Cl_2).

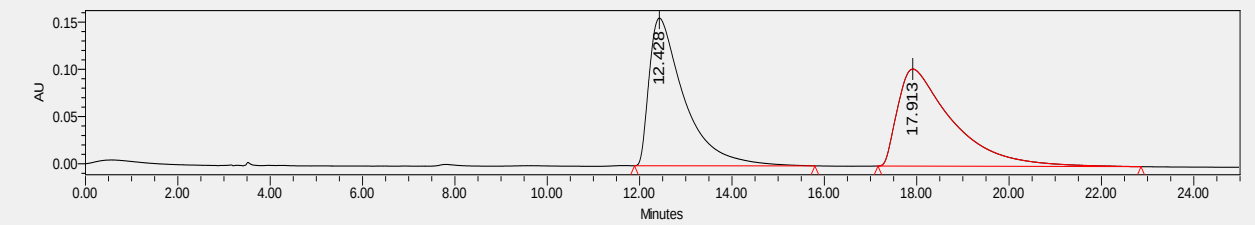
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.83 (s, 1H), 7.78 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.74 – 7.66 (m, 2H), 7.49 – 7.35 (m, 5H), 7.20 (t, *J* = 7.6 Hz, 2H), 6.94 (t, *J* = 7.6 Hz, 2H), 6.75 (t, *J* = 7.6 Hz, 1H), 3.91 (d, *J* = 16.8 Hz, 1H), 3.48 (d, *J* = 16.8 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.9, 153.2, 140.4, 136.8, 133.9, 133.2, 132.1, 132.1, 130.7, 130.5, 130.4, 128.8, 128.0, 127.0, 126.8, 123.7, 123.0, 111.2, 70.9, 46.4.

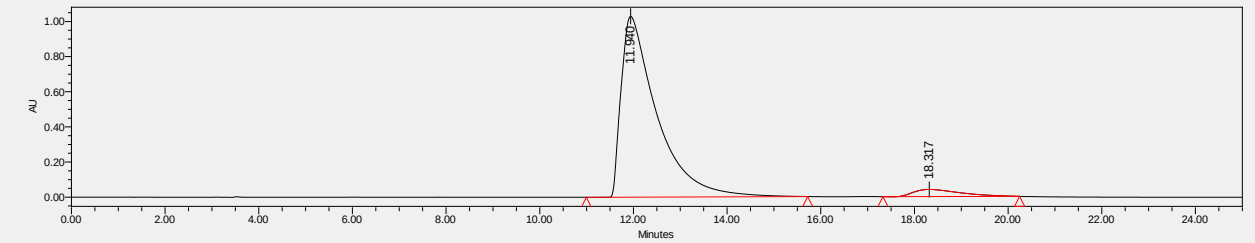
HRMS (ESI$^+$) m/z calcd for $C_{22}H_{16}Cl^{34.9689}N_3O_3NaS^+$ ([M]+Na$^+$) = 460.0493, found 460.0497 and $C_{22}H_{16}Cl^{36.9659}N_3O_3NaS^+$ ([M]+Na$^+$) = 462.0464, found 462.0465.

IR (neat, cm^{-1}) 3253, 1727, 1620, 1573, 1473, 1452, 1426, 1357, 1260, 1214, 1171, 1133, 1113, 1040, 755, 694, 665, 630, 600, 569, 541, 482.

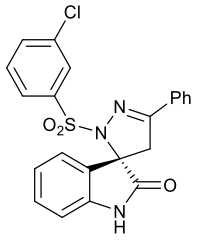
M. p. 207 – 210 °C



	Retention Time	Area	% Area
1	12.428	8254342	49.43
2	17.913	8446163	50.57



	Retention Time	Area	% Area
1	11.940	54377639	95.04
2	18.317	2835036	4.96



C4

(*S*)-2'-((3-chlorophenyl)sulfonyl)-5'-phenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one

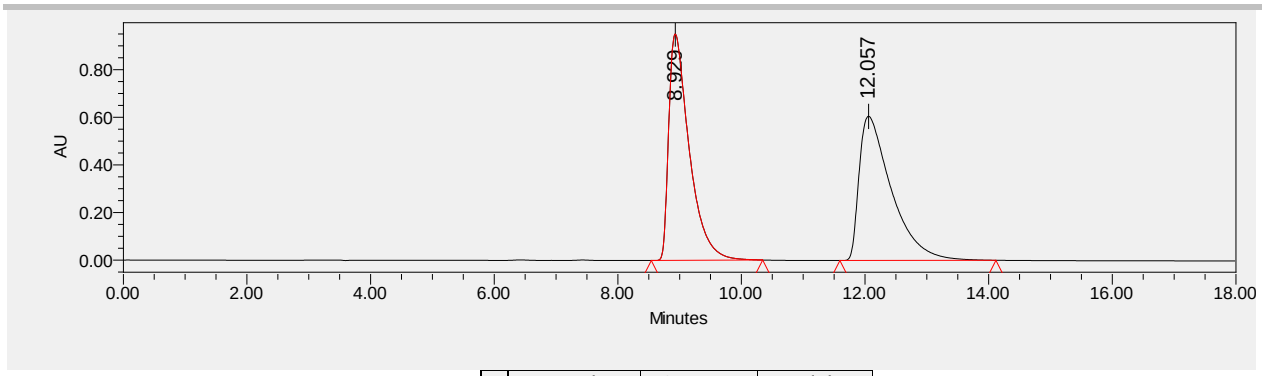
The crude material was directly purified by flash chromatography on silica gel (R_f = 0.3, PE/EtOAc = 3:2) to afford the light yellow oil (31.1 mg) in 71% yield with 95% ee. The ee was determined by HPLC analysis (Daicel chiralcel **IB$_{N-5}$**, 2-propanol/hexane = 30/70, flow rate = 1.0 mL/min, λ = 300 nm). $t_{R(major)}$ = 9.04 min, $t_{R(minor)}$ = 12.61 min; $[\alpha]_D^{20}$ = -7.2 (c = 0.42, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.66 (s, 1H), 7.78 – 7.69 (m, 2H), 7.68 – 7.62 (m, 1H), 7.52 – 7.38 (m, 5H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.29 – 7.23 (m, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.70 (td, *J* = 7.6, 0.8 Hz, 1H), 6.58 (d, *J* = 7.2 Hz, 1H), 3.88 (d, *J* = 16.8 Hz, 1H), 3.43 (d, *J* = 16.8 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.5, 155.3, 142.6, 141.6, 134.8, 133.8, 131.5, 131.4, 131.3, 131.1, 129.6, 128.4, 128.3, 127.7, 127.1, 124.8, 122.7, 111.1, 71.7, 46.6.

HRMS (ESI$^+$) m/z calcd for $C_{22}H_{16}Cl^{34.9689}N_3O_3NaS^+$ ([M]+Na$^+$) = 460.0493, found 460.0496 and $C_{22}H_{16}Cl^{36.9659}N_3O_3NaS^+$ ([M]+Na$^+$) = 462.0464, found 462.0465.

IR (neat, cm^{-1}) 3253, 1727, 1620, 1575, 1472, 1416, 1358, 1215, 1174, 1128, 1020, 792, 758, 705, 676, 632, 605, 572.



	Retention Time	% Area	Height
1	8.929	50.00	951176
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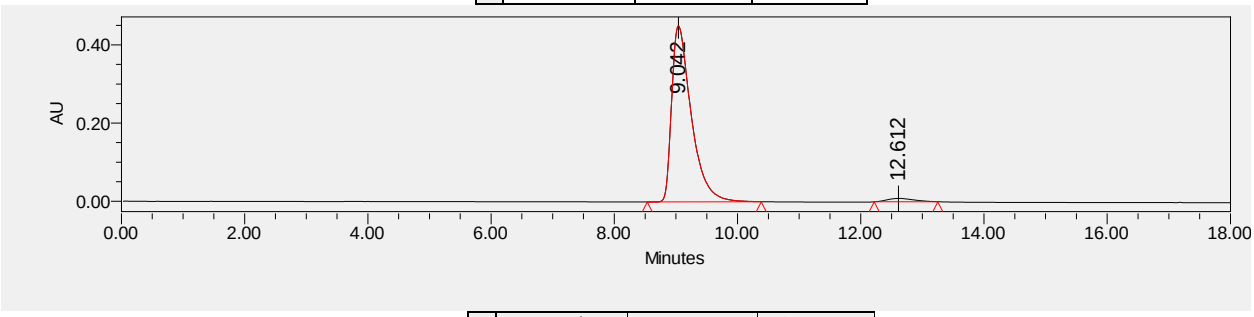
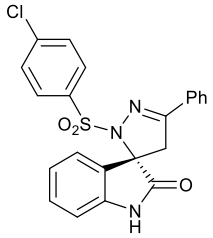


	Retention Time	Area	% Area
1	9.042	9926065	97.46
2	12.612	258237	2.54



C5

(*S*)-2'-((4-chlorophenyl)sulfonyl)-5'-phenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one

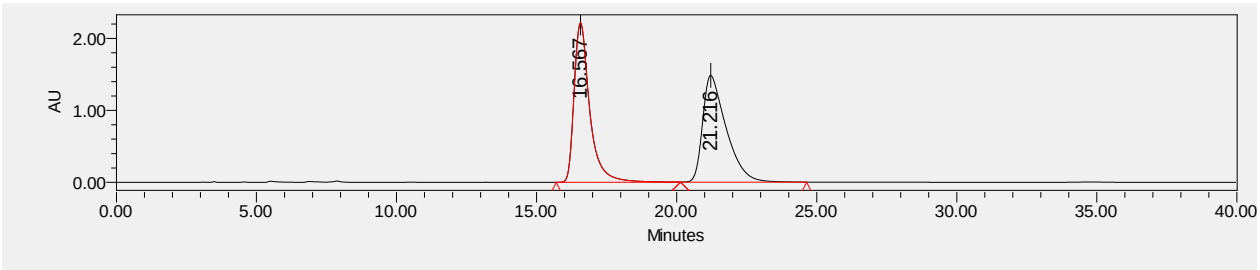
The crude material was directly purified by flash chromatography on silica gel (R_f = 0.3, PE/EtOAc = 3:2) to afford the white oil (39.9 mg) in 91% yield with 90% ee. The ee was determined by HPLC analysis (Daicel chiralcel **IA**, 2-propanol/hexane = 30/70, flow rate = 1.0 mL/min, λ = 300 nm). $t_{R(major)}$ = 21.59 min, $t_{R(minor)}$ = 17.01 min; $[\alpha]_D^{21}$ = +49.5 (c = 0.21, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.34 (s, 1H), 7.59 (d, *J* = 6.8 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.32 (s, 3H), 7.23 – 7.10 (m, 3H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.62 (t, *J* = 7.6 Hz, 1H), 6.53 (d, *J* = 7.6 Hz, 1H), 3.74 (d, *J* = 16.8 Hz, 1H), 3.29 (d, *J* = 16.8 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.2, 154.2, 140.7, 139.5, 137.1, 130.9, 130.6, 130.2, 129.5, 128.9, 128.9, 127.7, 127.0, 123.5, 122.9, 111.6, 71.1, 46.1.

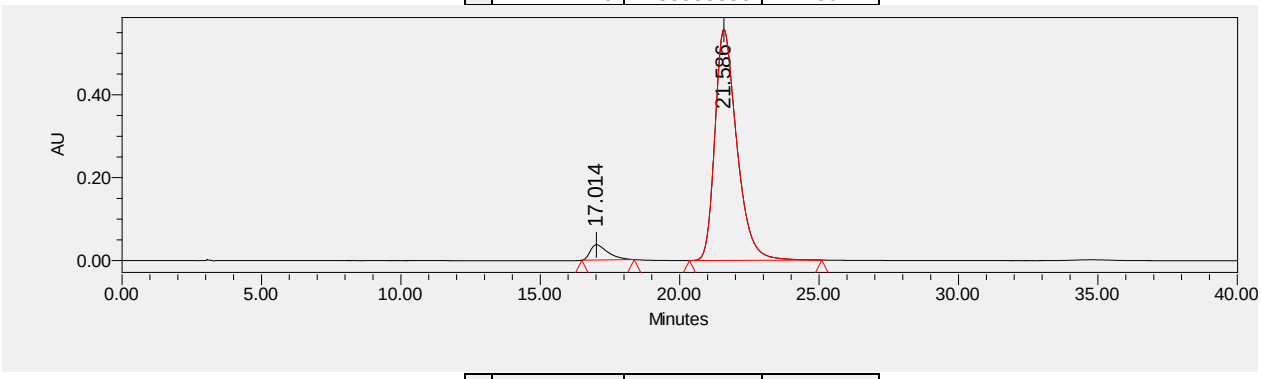
HRMS (ESI$^+$) m/z calcd for $C_{22}H_{16}Cl^{34.9689}N_3O_3NaS^+$ ([M]+Na$^+$) = 460.0493, found 460.0497 and $C_{22}H_{16}Cl^{36.9659}N_3O_3NaS^+$ ([M]+Na$^+$) = 462.0464, found 462.0460.

IR (neat, cm^{-1}) 3327, 1727, 1620, 1583, 1474, 1358, 1215, 1171, 1126, 1089, 1037, 1016, 827, 758, 705, 637, 615, 586, 532, 483.

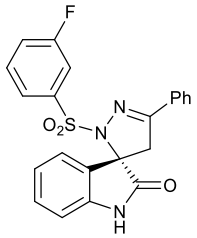


	Retention Time	Area	% Area

1	16.566	83183871	49.88
2	21.219	83593386	50.12



	Retention Time	Area	% Area
1	17.014	1633195	5.10
2	21.586	30413414	94.90



C6

(*S*)-2'-((3-fluorophenyl)sulfonyl)-5'-phenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one

The crude material was directly purified by flash chromatography on silica gel (R_f = 0.3, PE/EtOAc = 3:2) to afford the light yellow oil (24.4 mg) in 58% yield with 90% ee. The ee was determined by HPLC analysis (Daicel chiralcel **IA**, 2-propanol/hexane = 30/70, flow rate = 1.0 mL/min, λ = 300 nm). $t_{R(major)}$ = 18.37 min, $t_{R(minor)}$ = 13.76 min; $[\alpha]_D^{20}$ = +24.5 (c = 0.74, in CH_2Cl_2).

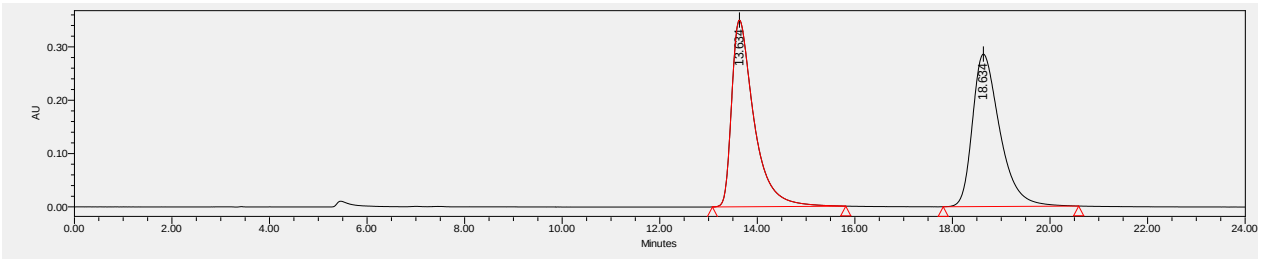
^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ 9.80 (s, 1H), 7.89 – 7.73 (m, 2H), 7.61 – 7.52 (m, 2H), 7.51 – 7.44 (m, 3H), 7.44 – 7.35 (m, 1H), 7.34 – 7.15 (m, 2H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.79 – 6.59 (m, 2H), 3.84 (d, *J* = 17.2 Hz, 1H), 3.66 (d, *J* = 17.2 Hz, 1H).

^{13}C NMR (101 MHz, Acetone-*d*$_6$) δ 175.5, 162.6 (*J* = 249.5 Hz), 155.1, 142.5, 141.8 (*J* = 7.1 Hz), 131.6 (*J* = 8.1 Hz), 131.4, 131.3, 130.9, 129.5, 128.6, 127.6, 124.6, 124.6, 122.7, 120.8 (*J* = 21.2 Hz), 115.4 (*J* = 25.3 Hz), 111.1, 71.6, 46.6.

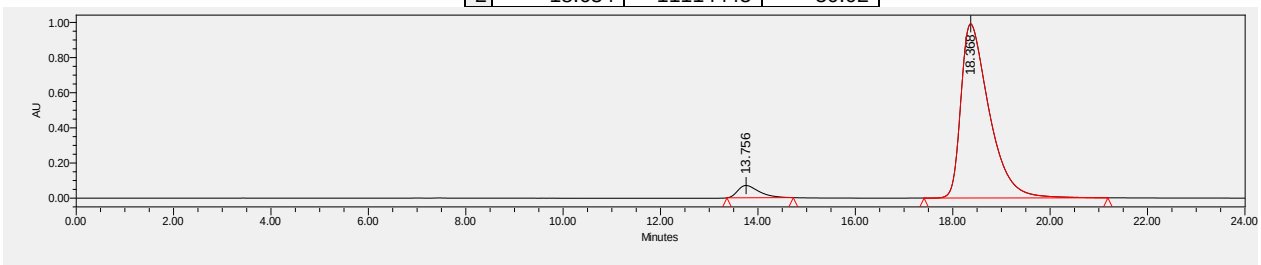
^{19}F NMR (376 MHz, Acetone-*d*$_6$) δ -112.2.

HRMS (ESI$^+$) m/z calcd for $C_{22}H_{16}FN_3O_3NaS^+$ ([M]+Na$^+$) = 444.0789, found 444.0791.

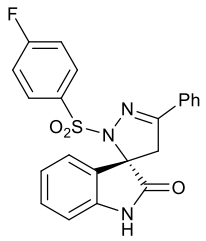
IR (neat, cm^{-1}) 3259, 1727, 1620, 1597, 1474, 1343, 1359, 1306, 1271, 1222, 1169, 1126, 1020, 873, 792, 759, 695, 677, 633, 611, 576, 544.



	Retention Time	Area	% Area
1	13.634	11106651	49.98
2	18.634	11114445	50.02



	Retention Time	Area	% Area
1	13.756	2123745	5.06
2	18.368	39860226	94.94



C7

(*S*)-2'-((4-fluorophenyl)sulfonyl)-5'-phenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one

The crude material was directly purified by flash chromatography on silica gel (R_f = 0.3, PE/EtOAc = 3:2) to afford the light yellow oil (40.4 mg) in 96% yield with 89% ee. The ee was determined by HPLC analysis (Daicel chiralcel **IB$_{N-5}$**, 2-propanol/hexane = 30/70, flow rate = 1.0 mL/min, λ = 300 nm). $t_{R(major)}$ = 9.85 min, $t_{R(minor)}$ = 13.75 min; $[\alpha]_D^{19}$ = +27.2 (c = 1.16, in CH_2Cl_2).

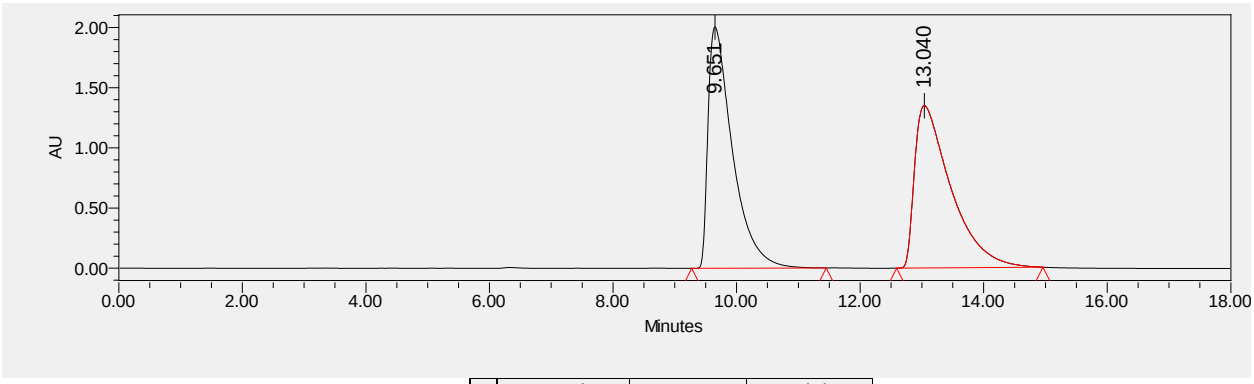
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.84 (s, 1H), 7.76 – 7.66 (m, 4H), 7.47 – 7.39 (m, 3H), 7.25 – 7.22 (m, 1H), 7.07 – 7.00 (m, 2H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.80 – 6.60 (m, 2H), 3.86 (d, *J* = 16.8 Hz, 1H), 3.44 (d, *J* = 16.8 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.9, 165.4 (*J* = 256.5 Hz), 153.9, 140.4, 134.7 (*J* = 3.0 Hz), 131.0, 130.8 (*J* = 3.0 Hz), 130.5, 130.2, 128.8, 127.8, 126.9, 123.6, 122.9, 115.9 (*J* = 22.2 Hz), 111.2, 71.0, 46.2.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -104.5.

HRMS (ESI$^+$) m/z calcd for $C_{22}H_{16}FN_3O_3NaS^+$ ([M]+Na$^+$) = 444.0789, found 444.0791.

IR (neat, cm^{-1}) 3265, 1729, 1620, 1591, 1492, 1473, 1358, 1236, 1215, 1173, 1156, 1125, 1037, 1019, 837, 759, 708, 693, 670, 628, 592, 545.



	Retention Time	% Area	Height
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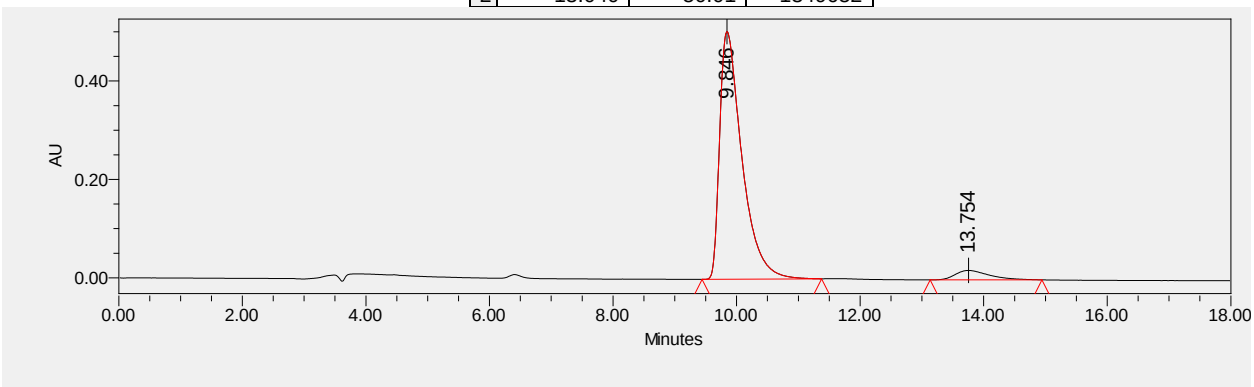
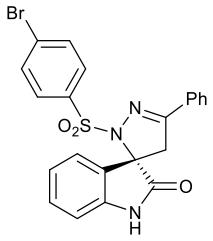
2	13.040	50.01	1349652



	Retention Time	Area	% Area
1	9.846	12588846	94.49
2	13.754	734567	5.51



C8

(*S*)-2'-((4-bromophenyl)sulfonyl)-5'-phenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one

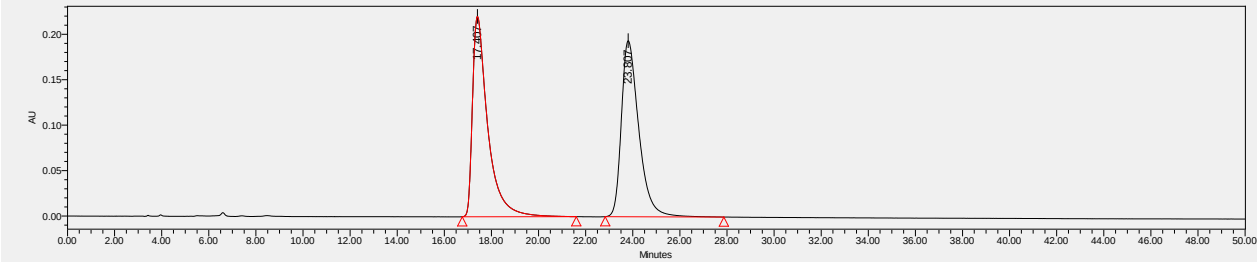
The crude material was directly purified by flash chromatography on silica gel (R_f = 0.3, PE/EtOAc = 3:2) to afford the light yellow oil (47.7 mg) in 91% yield with 86% ee. The ee was determined by HPLC analysis (Daicel chiralcel **IA**, 2-propanol/hexane = 30/70, flow rate = 1.0 mL/min, λ = 300 nm). $t_{R(major)}$ = 23.37 min, $t_{R(minor)}$ = 17.58 min; $[\alpha]_D^{20}$ = +47.7 (c = 0.39, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.58 (s, 1H), 7.75 – 7.67 (m, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.48 – 7.39 (m, 3H), 7.30 – 7.25 (m, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.83 – 6.64 (m, 2H), 3.86 (d, *J* = 16.8 Hz, 1H), 3.45 (d, *J* = 16.8 Hz, 1H).

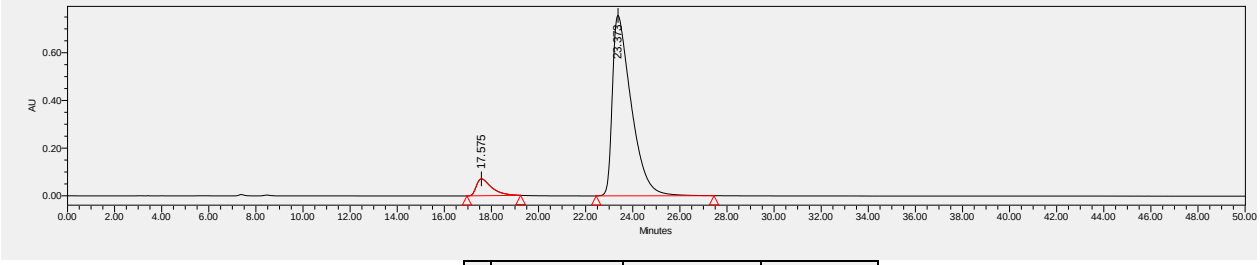
^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.7, 153.9, 140.3, 137.6, 131.9, 130.9, 130.5, 130.2, 129.6, 128.8, 128.2, 128.0, 126.9, 123.7, 123.0, 111.1, 70.9, 46.2.

HRMS (ESI$^+$) m/z calcd for $C_{22}H_{16}Br^{78.9183}N_3O_3NaS^+$ ([M]+Na$^+$) = 503.9988, found 503.9992 and $C_{22}H_{16}Br^{80.9163}N_3O_3NaS^+$ ([M]+Na$^+$) = 505.9967, found 505.9970.

IR (neat, cm^{-1}) 3216, 1727, 1620, 1573, 1472, 1390, 1358, 1215, 1171, 1126, 1068, 1037, 1012, 869, 823, 758, 741, 694, 633, 606, 583, 543.



	Retention Time	Area	% Area
1	17.407	9926447	50.00
2	23.807	9927769	50.00



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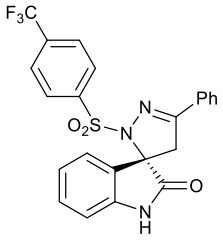
1	17.575	3199720	7.07
2	23.373	42080318	92.93

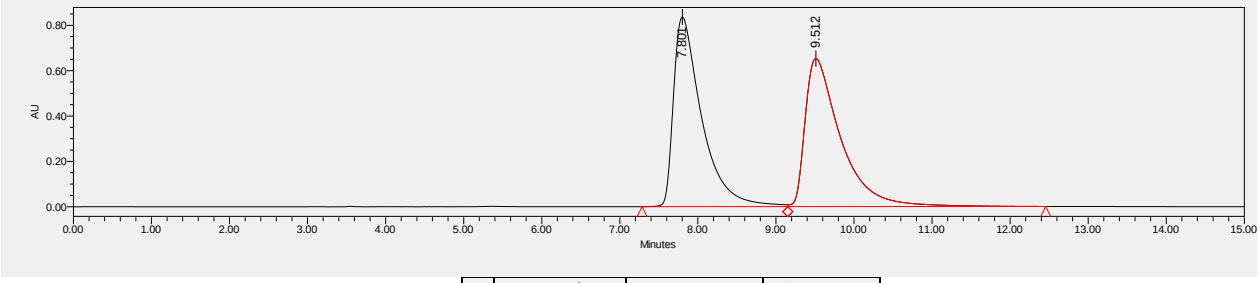


C9

(*S*)-5'-phenyl-2'-((4-(trifluoromethyl)phenyl)sulfonyl)-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one

The crude material was directly purified by flash chromatography on silica gel (R_f = 0.3, PE/EtOAc = 3:2) to afford the light yellow oil (37.2 mg) in 79% yield with 84% ee. The ee was determined by HPLC analysis (Daicel chiralcel **IB$_{N-5}$**, 2-propanol/hexane = 30/70, flow rate = 1.0 mL/min, λ = 300 nm). $t_{R(major)}$ = 7.70 min, $t_{R(minor)}$ = 9.66 min; $[\alpha]_D^{20}$ = +12.3 (c = 0.31, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.89 (s, 1H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.76 – 7.68 (m, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.51 – 7.38 (m, 3H), 7.31 – 7.20 (m, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.76 – 6.63 (m, 2H), 3.88 (d, *J* = 16.8 Hz, 1H), 3.46 (d, *J* = 16.8 Hz, 1H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.8, 154.3, 142.1, 140.4, 134.5 (*J* = 32.8 Hz), 131.0, 130.6, 130.1, 128.9, 128.5, 127.8, 126.9, 125.8 (*J* = 3.6 Hz), 124.6, 123.5, 123.0, 121.9, 111.2, 71.0, 46.1.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.1.
HRMS (ESI^{+}) m/z calcd for $C_{23}H_{16}F_3N_3O_3NaS^{+}$ ([M]+Na^{+}) = 494.0757, found 494.0760.
IR (neat, cm^{-1}) 3260, 1737, 1620,1474, 1405, 1359, 1323, 1215, 1173, 1132, 1109, 1062, 1037, 1017, 841, 759, 692, 635, 610, 429.



	Retention Time	Area	% Area
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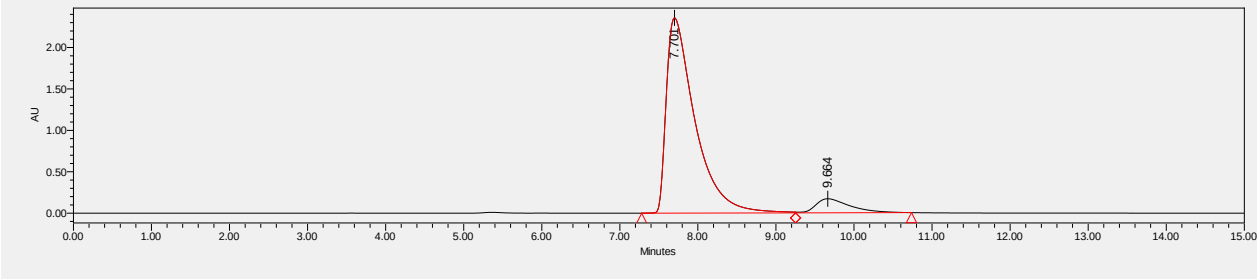
2	9.512	20601547	49.48



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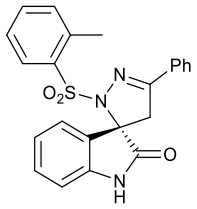
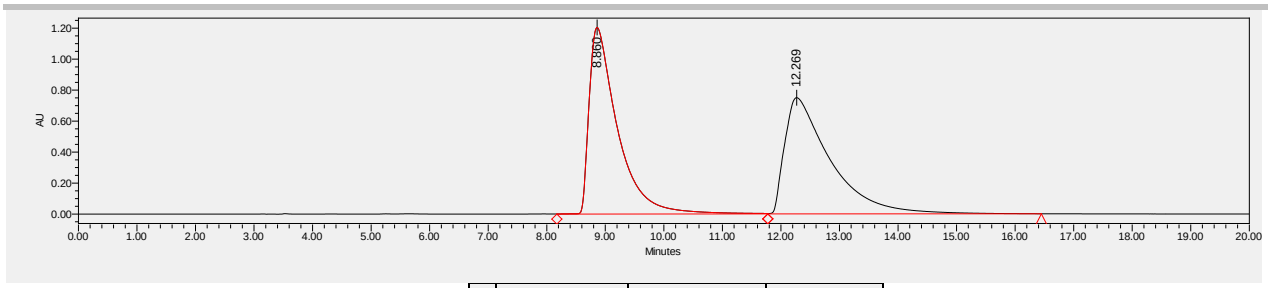
1	7.701	60011450	92.10
2	9.664	5148512	7.90



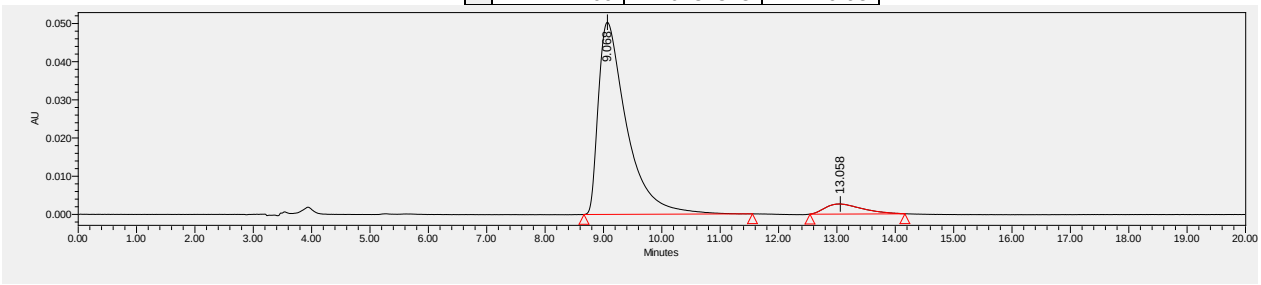
C10

(*S*)-5'-phenyl-2'-(*o*-tolylsulfonyl)-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one

The crude material was directly purified by flash chromatography on silica gel (R_f = 0.3, PE/EtOAc = 3:2) to afford the white oil (37.5 mg) in 96% yield with 87% ee. The ee was determined by HPLC analysis (Daicel chiralcel **IB$_{N-5}$**, 2-propanol/hexane = 30/70, flow rate = 1.0 mL/min, λ = 300 nm). $t_{R(major)}$ = 13.06 min, $t_{R(minor)}$ = 9.07 min; $[\alpha]_D^{21}$ = +16.1 (c = 0.74, in CH_2Cl_2).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.91 (s, 1H), 7.62 – 7.53 (m, 3H), 7.35 – 7.28 (m, 4H), 7.17 – 7.09 (m, 2H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 7.2 Hz, 1H), 6.69 (t, *J* = 7.6 Hz, 1H), 3.76 (d, *J* = 16.8 Hz, 1H), 3.34 (d, *J* = 16.8 Hz, 1H), 2.67 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.3, 152.0, 139.2, 138.1, 136.1, 132.1, 131.4, 129.5, 129.4, 129.3, 127.7, 127.1, 125.8, 125.0, 122.8, 121.9, 110.1, 70.1, 45.2, 20.1.
HRMS (ESI^{+}) m/z calcd for $C_{23}H_{19}N_3NaO_3S^{+}$ ([M]+Na^{+}) = 440.1039, found 440.1044.
IR (neat, cm^{-1}) 3259, 1734, 1620, 1474, 1404, 1359, 1323, 1215, 1172, 1131, 1062, 1037, 1017, 841, 758, 713, 635, 610, 577, 429.



	Retention Time	Area	% Area
1	8.860	40559899	50.05
2	12.269	40481878	49.95



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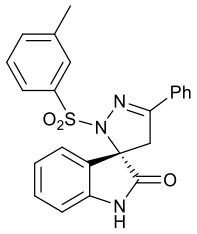


C11

(*S*)-5'-phenyl-2'-(*m*-tolylsulfonyl)-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one

The crude material was directly purified by flash chromatography on silica gel (R_f = 0.3, PE/EtOAc = 3:2) to afford the light yellow solid (37.5 mg) in 89% yield with 90% ee. The ee was determined by HPLC analysis (Daicel chiralcel **IA**, 2-propanol/hexane = 30/70, flow rate = 1.0 mL/min, λ = 300 nm). $t_{R(major)}$ = 21.01 min, $t_{R(minor)}$ = 12.81 min; $[\alpha]_D^{17}$ = +3.0 (c = 0.67, in $(CH_3)_2CO$).

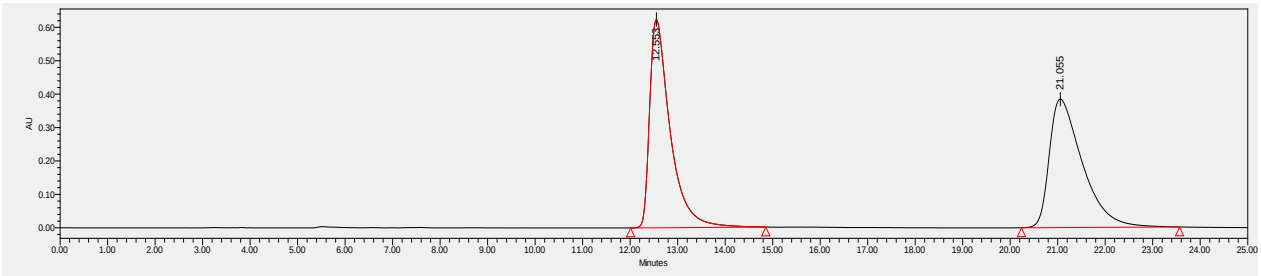
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.82 (s, 1H), 7.78 – 7.67 (m, 2H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.47 – 7.39 (m, 3H), 7.34 – 7.26 (m, 3H), 7.25 – 7.20 (m, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.64 (t, *J* = 7.6 Hz, 1H), 6.54 (d, *J* = 7.2 Hz, 1H), 3.88 (d, *J* = 16.8 Hz, 1H), 3.42 (d, *J* = 16.8 Hz, 1H), 2.28 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.1, 153.5, 140.5, 138.6, 138.4, 133.8, 130.7, 130.5, 130.3, 128.8, 128.5, 128.5, 127.4, 126.9, 125.3, 123.8, 122.5, 111.1, 71.0, 46.1, 21.3.

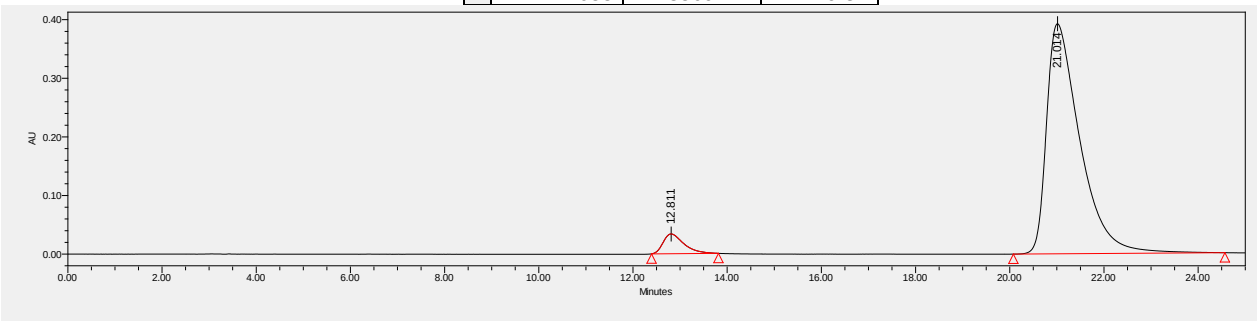
HRMS (ESI$^+$) m/z calcd for $C_{23}H_{20}N_3O_3S^+$ ([M]+H$^+$) = 418.1220, found 418.1218.

IR (neat, cm^{-1}) 3321, 1735, 1620, 1473, 1356, 1323, 1216, 1165, 1124, 1037, 865, 759, 689, 632, 605, 575, 478.

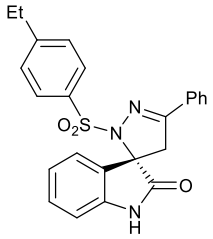
M. p. 242 – 245 °C



	Retention Time	Area	% Area
1	12.553	18666948	50.13
2	21.055	18569174	49.87



	Retention Time	Area	% Area
1	12.811	1028712	5.06
2	21.014	19294626	94.94



C12

(*S*)-2'-((4-ethylphenyl)sulfonyl)-5'-phenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one

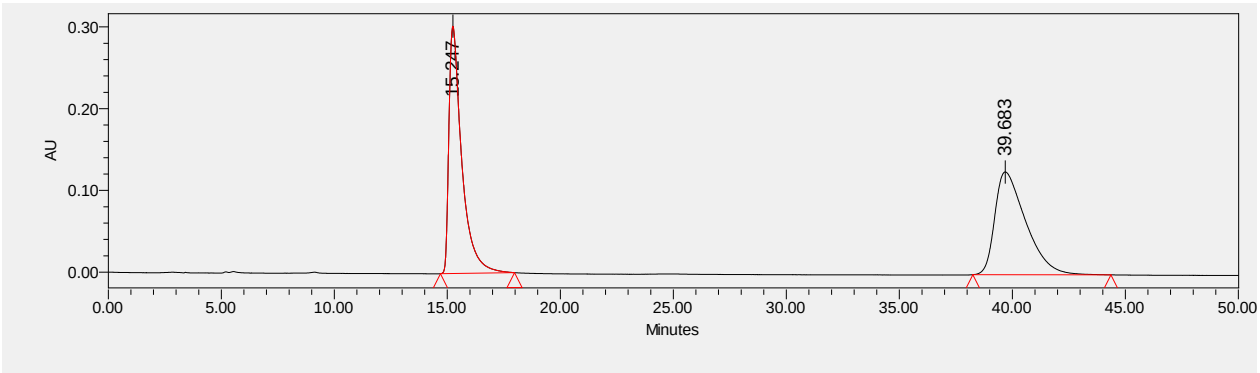
The crude material was directly purified by flash chromatography on silica gel (R_f = 0.3, PE/EtOAc = 3:2) to afford the light yellow oil (33.3 mg) in 77% yield with 90% ee. The ee was determined by HPLC analysis (Daicel chiralcel **IA**, 2-propanol/hexane = 30/70, flow rate = 1.0 mL/min, λ = 300 nm). $t_{R(major)}$ = 38.15 min, $t_{R(minor)}$ = 15.50 min; $[\alpha]_D^{21}$ = +54.2 (c = 1.08, in CH_2Cl_2).

^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ 9.76 (s, 1H), 7.84 – 7.74 (m, 2H), 7.60 – 7.53 (m, 2H), 7.51 – 7.40 (m, 3H), 7.32 – 7.20 (m, 3H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.73 – 6.65 (m, 1H), 6.65 – 6.59 (m, 1H), 3.79 (d, *J* = 17.2 Hz, 1H), 3.59 (d, *J* = 17.2 Hz, 1H), 2.69 (q, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H).

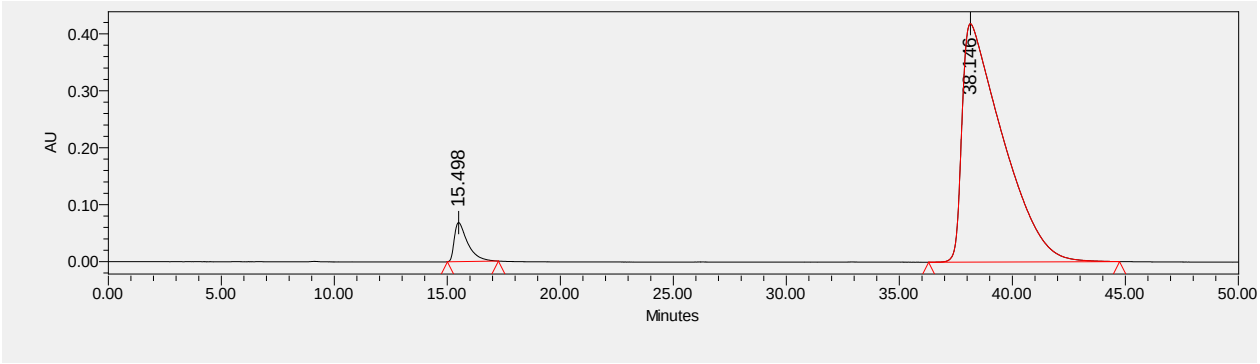
^{13}C NMR (101 MHz, Acetone-*d*$_6$) δ 175.8, 154.2, 150.7, 142.3, 137.4, 131.5, 131.1, 130.6, 129.5, 128.9, 128.7, 128.6, 127.4, 124.5, 122.7, 110.9, 71.6, 46.6, 15.5.

HRMS (ESI$^+$) m/z calcd for $C_{24}H_{21}N_3O_3NaS^+$ ([M+Na$^+$) = 454.1196, found 454.1196.

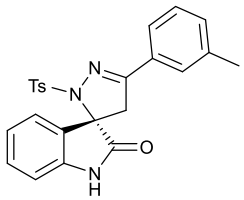
IR (neat, cm^{-1}) 3259, 1737, 1620, 1597, 1474, 1434, 1359, 1222, 1169, 1126, 1037, 873, 841, 759, 695, 677, 633, 611, 576, 544, 518, 482.



	Retention Time	Area	% Area
1	15.247	11966589	49.98
2	39.683	11974892	50.02



	Retention Time	Area	% Area
1	15.498	2808266	5.09
2	38.146	52318559	94.91



C15

(*S*)-5'-(*m*-tolyl)-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one

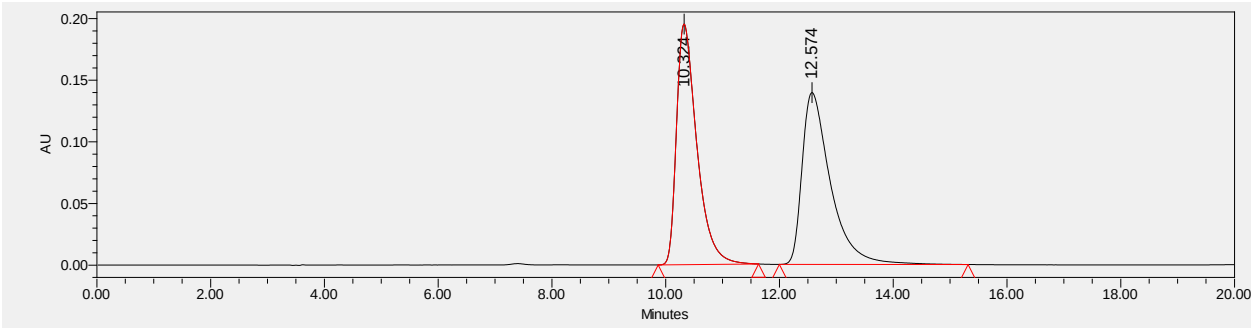
The crude material was directly purified by flash chromatography on silica gel (R_f = 0.3, PE/EtOAc = 3:2) to afford the white oil (37.9 mg) in 88% yield with 91% ee. The ee was determined by HPLC analysis (Daicel chiralcel **IB$_{N-5}$**, 2-propanol/hexane = 30/70, flow rate = 1.0 mL/min, λ = 300 nm). $t_{R(major)}$ = 10.21 min, $t_{R(minor)}$ = 12.73 min; $[\alpha]_D^{18}$ = +45.3 (c = 1.07, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.80 (s, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.55 (s, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.25 – 7.19 (m, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.74 – 6.62 (m, 2H), 3.83 (d, *J* = 16.8 Hz, 1H), 3.40 (d, *J* = 16.8 Hz, 1H), 2.37 (s, 6H).

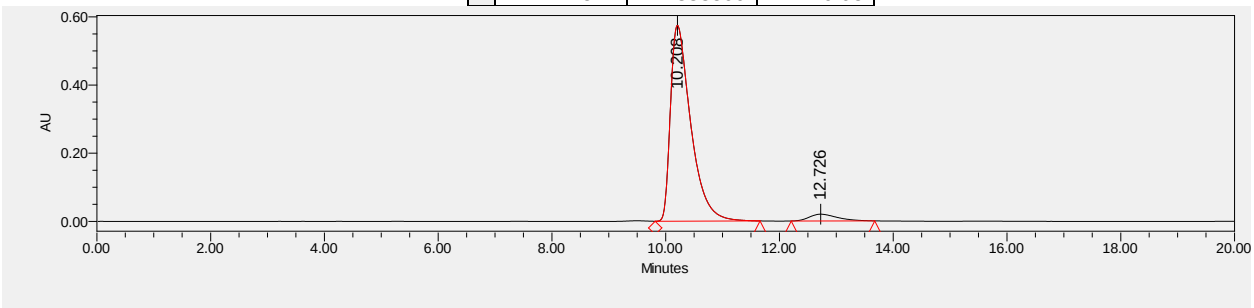
^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.1, 153.6, 143.8, 140.4, 138.5, 135.8, 131.4, 130.4, 130.2, 129.2, 128.6, 128.1, 128.0, 127.4, 124.1, 123.7, 122.8, 111.1, 70.9, 46.2, 21.6, 21.4.

HRMS (ESI$^+$) m/z calcd for $C_{24}H_{21}N_3O_3NaS^+$ ([M]+Na$^+$) = 454.1196, found 454.1198.

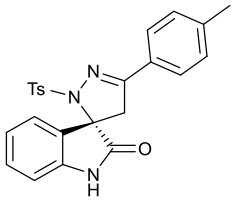
IR (neat, cm^{-1}) 3260, 1730, 1620, 1600, 1473, 1357, 1215, 1166, 1123, 1036, 788, 758, 735, 696, 665, 631, 594, 548.



	Retention Time	Area	% Area
1	10.324	4848121	50.05
2	12.574	4838599	49.95



	Retention Time	Area	% Area
1	10.208	14230316	95.47
2	12.726	675149	4.53



C16

(*S*)-5'-(*p*-tolyl)-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one

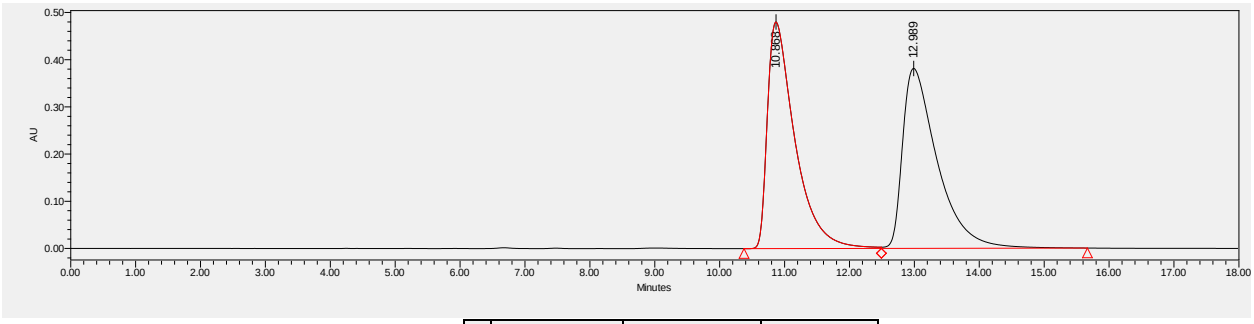
The crude material was directly purified by flash chromatography on silica gel (R_f = 0.3, PE/EtOAc = 3:2) to afford the white oil (37.9 mg) in 88% yield with 92% ee. The ee was determined by HPLC analysis (Daicel chiralcel **IB$_{N-5}$**, 2-propanol/hexane = 30/70, flow rate = 1.0 mL/min, λ = 300 nm). $t_{R(major)}$ = 10.75 min, $t_{R(minor)}$ = 13.31 min; $[\alpha]_D^{20}$ = +45.1 (c = 1.13, in CH_2Cl_2).

^{1}H NMR (400 MHz, Acetone-d_6) δ 9.74 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.32 – 7.20 (m, 5H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.75 – 6.68 (m, 1H), 6.63 (d, *J* = 6.8 Hz, 1H), 3.75 (d, *J* = 17.2 Hz, 1H), 3.54 (d, *J* = 17.2 Hz, 1H), 2.38 (s, 3H), 2.36 (s, 3H).

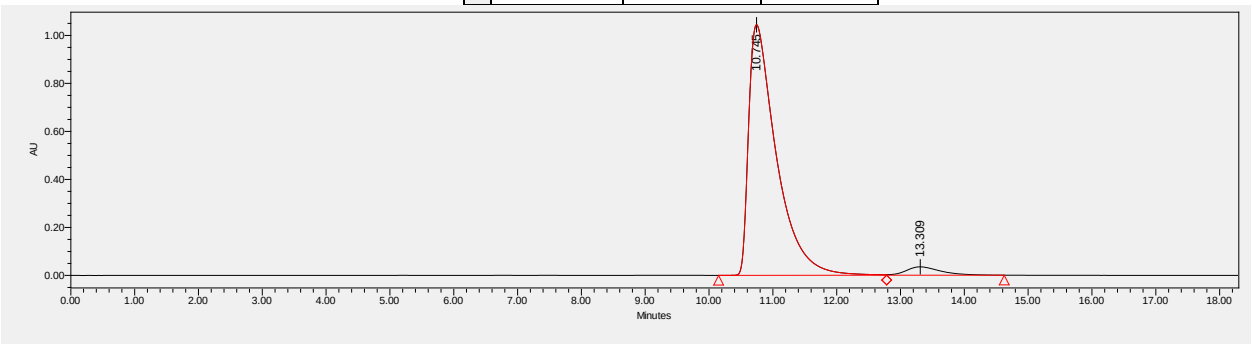
^{13}C NMR (101 MHz, Acetone-d_6) δ 175.8, 154.2, 144.5, 142.3, 141.4, 137.2, 130.6, 130.1, 129.8, 129.0, 128.7, 128.6, 127.4, 124.5, 122.7, 110.9, 71.5, 46.7, 21.3, 21.3.

HRMS (ESI$^+$) m/z calcd for $C_{24}H_{21}N_3O_3NaS^+$ ([M]+Na$^+$) = 454.1196, found 454.1200.

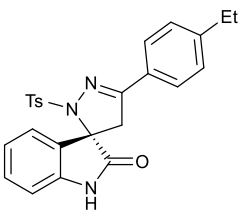
IR (neat, cm^{-1}) 3258, 1726, 1619, 1600, 1472, 1453, 1353, 1214, 1165, 1107, 1037, 814, 757, 735, 702, 665, 544, 522.



	Retention Time	Area	% Area
1	10.868	14134163	50.00
2	12.989	14135019	50.00



	Retention Time	Area	% Area
1	10.745	31466928	96.01
2	13.309	1309156	3.99



C17

(*S*)-5'-(4-ethylphenyl)-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one

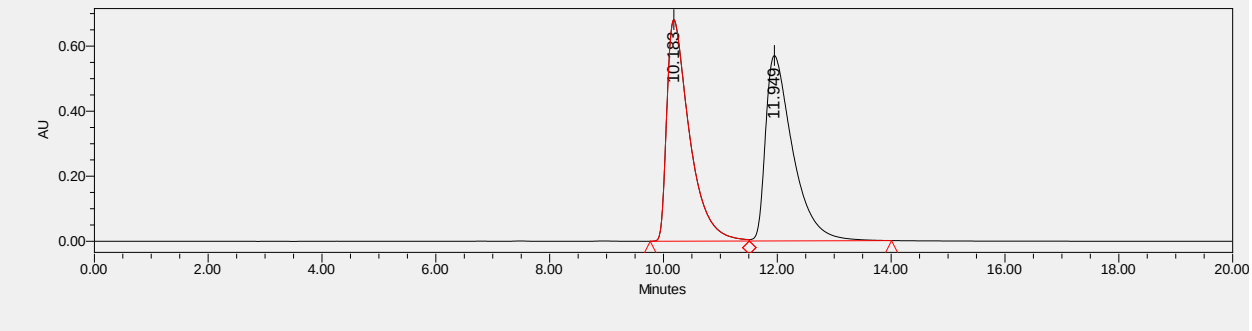
The crude material was directly purified by flash chromatography on silica gel (R_f = 0.3, PE/EtOAc = 3:2) to afford the light yellow oil (44.2 mg) in 99% yield with 86% ee. The ee was determined by HPLC analysis (Daicel chiralcel **IB$_{N-5}$**, 2-propanol/hexane = 30/70, flow rate = 1.0 mL/min, λ = 300 nm). $t_{R(major)}$ = 10.09 min, $t_{R(minor)}$ = 12.18 min; $[\alpha]_D^{19}$ = +29.6 (c = 1.38, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.04 (s, 1H), 7.60 (dd, *J* = 16.4, 8.4 Hz, 4H), 7.25 – 7.17 (m, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.65 (dt, *J* = 16.0, 7.2 Hz, 2H), 3.83 (d, *J* = 16.8 Hz, 1H), 3.38 (d, *J* = 16.8 Hz, 1H), 2.67 (q, *J* = 7.6 Hz, 2H), 2.36 (s, 3H), 1.23 (t, *J* = 7.6 Hz, 3H).

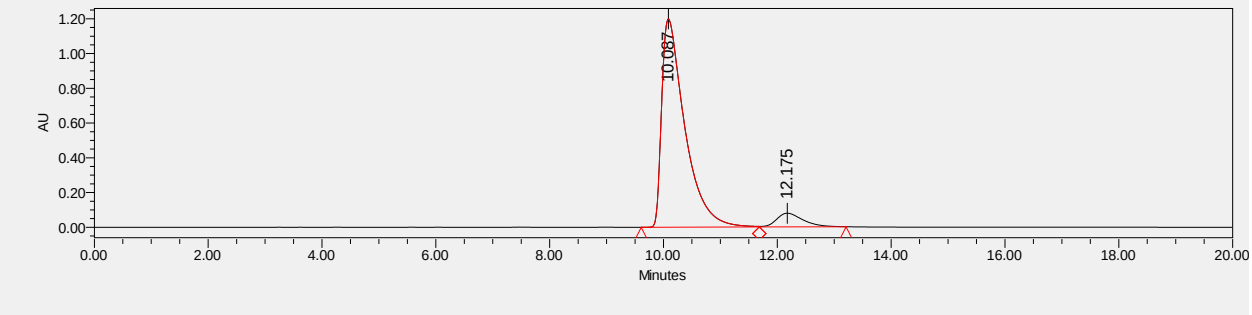
^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.2, 153.6, 147.3, 143.8, 140.5, 135.8, 130.2, 129.2, 128.3, 128.1, 128.0, 127.9, 127.0, 123.6, 122.7, 111.3, 77.4, 77.3, 77.1, 76.8, 71.0, 46.2, 28.9, 21.6, 15.4.

HRMS (ESI$^+$) m/z calcd for $C_{25}H_{23}N_3O_3NaS^+$ ([M]+Na$^+$) = 468.1352, found 468.1357.

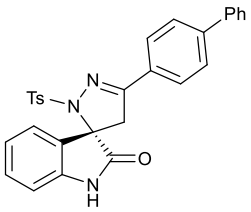
IR (neat, cm^{-1}) 3320, 1727, 1619, 1599, 1472, 1419, 1354, 1214, 1165, 1118, 1035, 843, 814, 756, 735, 703, 665, 590, 545, 491.



	Retention Time	Area	% Area
1	10.183	18808282	49.93
2	11.949	18863892	50.07



	Retention Time	Area	% Area
1	10.087	33726505	93.00
2	12.175	2539115	7.00



C18

(*S*)-5'-([1,1'-biphenyl]-4-yl)-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one

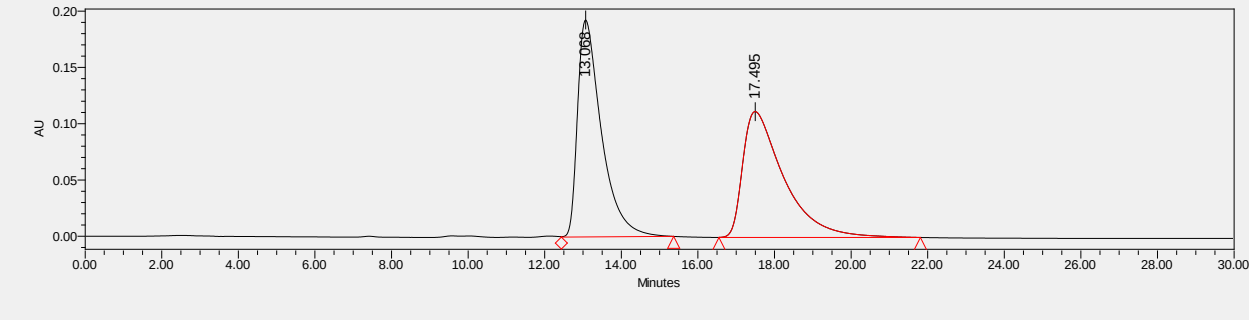
The crude material was directly purified by flash chromatography on silica gel (R_f = 0.3, PE/EtOAc = 3:2) to afford the yellow oil (43.5 mg) in 88% yield with 88% ee. The ee was determined by HPLC analysis (Daicel chiralcel **IB$_{N-5}$**, 2-propanol/hexane = 30/70, flow rate = 1.0 mL/min, λ = 300 nm). $t_{R(major)}$ = 12.69 min, $t_{R(minor)}$ = 17.80 min; $[\alpha]_D^{19}$ = -16.9 (c = 1.33, in CH_3CN).

^{1}H NMR (400 MHz, Acetone-d_6) δ 9.79 (s, 1H), 7.90 – 7.81 (m, 2H), 7.78 – 7.64 (m, 4H), 7.61 – 7.51 (m, 2H), 7.52 – 7.42 (m, 2H), 7.42 – 7.33 (m, 1H), 7.31 – 7.21 (m, 3H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.77 – 6.63 (m, 2H), 3.81 (d, *J* = 17.2 Hz, 1H), 3.59 (d, *J* = 17.2 Hz, 1H), 2.37 (s, 3H).

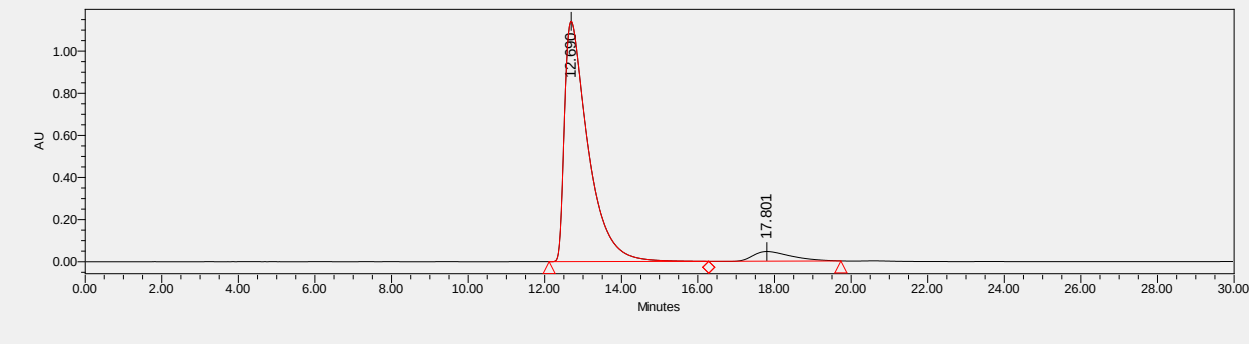
^{13}C NMR (101 MHz, Acetone-d_6) δ 175.2, 153.2, 143.9, 142.8, 141.7, 139.9, 136.5, 130.0, 129.7, 129.2, 129.0, 128.3, 128.0, 127.4, 127.2, 126.9, 123.9, 122.1, 110.3, 71.0, 45.9, 20.7.

HRMS (ESI$^+$) m/z calcd for $C_{29}H_{23}N_3O_3NaS^+$ ([M+Na$^+$]) = 516.1352, found 516.1359.

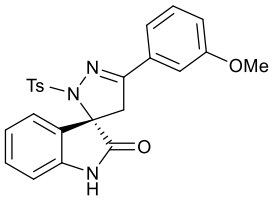
IR (neat, cm^{-1}) 3217, 1728, 1619, 1599, 1472, 1407, 1354, 1214, 1165, 1108, 1037, 848, 814, 754, 731, 697, 664, 624, 592, 548, 489.



	Retention Time	Area	% Area
1	13.068	8346291	50.07
2	17.495	8324462	49.93



	Retention Time	Area	% Area
1	12.690	48764205	93.94
2	17.801	3147165	6.06



C19

(*S*)-5'-(3-methoxyphenyl)-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one

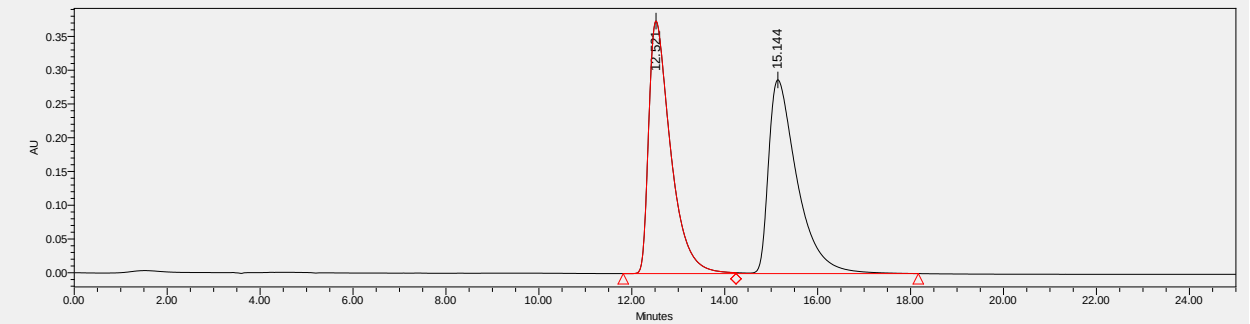
The crude material was directly purified by flash chromatography on silica gel (R_f = 0.3, PE/EtOAc = 3:2) to afford the light yellow oil (38.0 mg) in 85% yield with 91% ee. The ee was determined by HPLC analysis (Daicel chiralcel **IB$_{N-5}$**, 2-propanol/hexane = 30/70, flow rate = 1.0 mL/min, λ = 300 nm). $t_{R(major)}$ = 12.47 min, $t_{R(minor)}$ = 15.55 min; $[\alpha]_D^{18}$ = +32.7 (c = 1.47, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.80 (s, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.35 – 7.27 (m, 2H), 7.24 – 7.19 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.99 – 6.92 (m, 2H), 6.76 – 6.65 (m, 2H),3.84 (s, 3H), 3.83 (d, *J* = 16.8 Hz, 1H), 3.39 (d, *J* = 16.8 Hz, 1H), 2.37 (s, 3H).

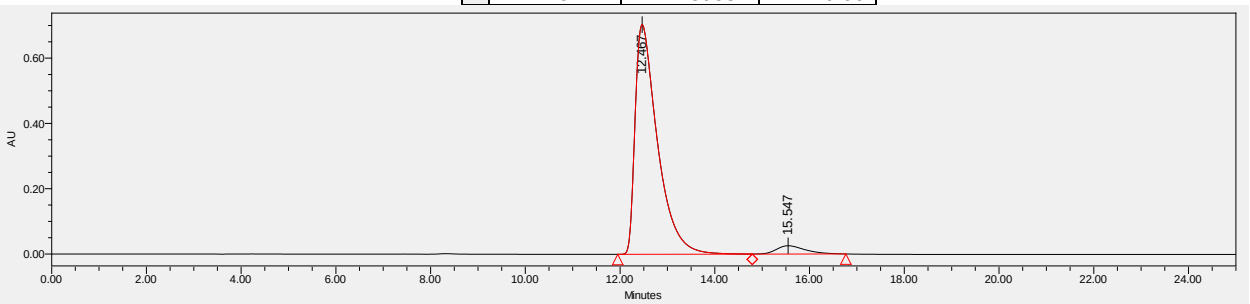
^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.0, 159.7, 153.3, 143.9, 140.4, 135.8, 131.8, 130.3, 129.8, 129.2, 128.1, 128.0, 123.7, 122.8, 119.5, 116.6, 111.7, 111.1, 71.0, 55.5, 46.3, 21.6.

HRMS (ESI$^+$) m/z calcd for $C_{24}H_{21}N_3O_4NaS^+$ ([M+Na$^+$]) = 470.1145, found 470.1149.

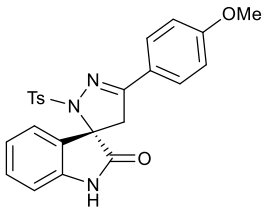
IR (neat, cm^{-1}) 3215, 1726, 1619, 1600, 1575, 1471, 1344, 1218, 1164, 1122, 1034, 813, 759, 665, 592, 547.



	Retention Time	Area	% Area
1	12.521	12262394	50.01
2	15.144	12259584	49.99



	Retention Time	Area	% Area
1	12.467	23069488	95.52
2	15.547	1082994	4.48



C20

(*S*)-5'-(4-methoxyphenyl)-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one

The crude material was directly purified by flash chromatography on silica gel (R_f = 0.3, PE/EtOAc = 3:2) to afford the yellow solid (42.5 mg) in 95% yield with 86% ee. The ee was determined by HPLC analysis (Daicel chiralcel **IB$_{N-5}$**, 2-propanol/hexane = 30/70, flow rate = 1.0 mL/min, λ = 300 nm). $t_{R(major)}$ = 16.00 min, $t_{R(minor)}$ = 21.58 min; $[\alpha]_D^{18}$ = +29.8 (c = 1.54, in CH_2Cl_2).

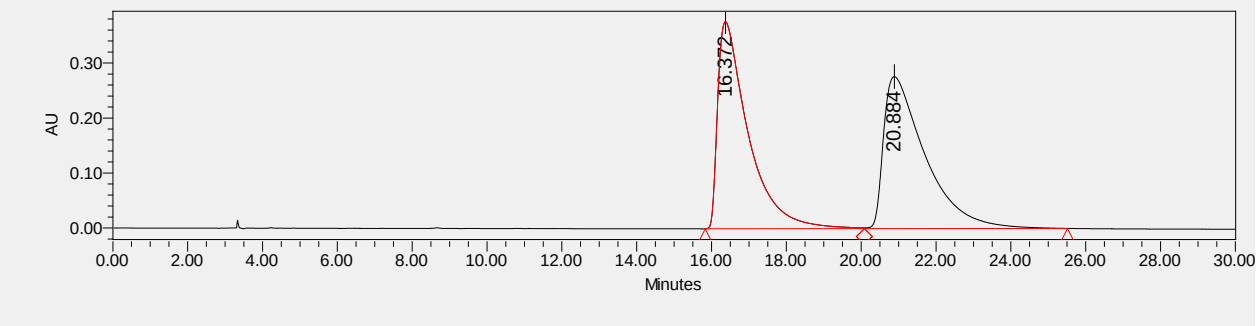
^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ 9.75 (s, 1H), 7.76 – 7.69 (m, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.30 – 7.21 (m, 3H), 7.04 – 6.94 (m, 3H), 6.74 – 6.66 (m, 1H), 6.61 (d, *J* = 7.6 Hz, 1H), 3.83 (s, 3H), 3.74 (d, *J* = 17.2 Hz, 1H), 3.52 (d, *J* = 17.2 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, Acetone-*d*$_6$) δ 175.8, 162.3, 153.9, 144.4, 142.2, 137.2, 130.5, 129.7, 129.0, 128.9, 128.5, 124.4, 123.9, 122.6, 114.8, 110.8, 71.4, 55.6, 46.7, 21.2.

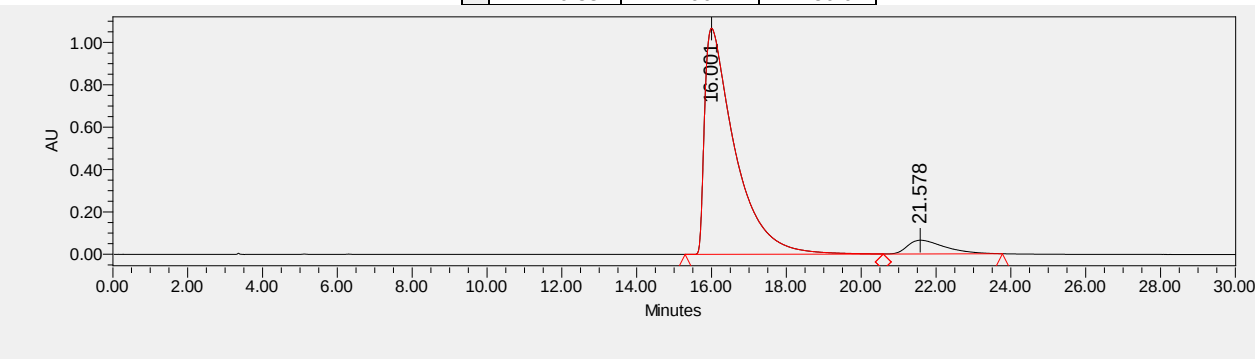
HRMS (ESI$^+$) m/z calcd for $C_{24}H_{21}N_3O_4NaS^+$ ([M+Na$^+$) = 470.1145, found 470.1148.

IR (neat, cm^{-1}) 3207, 1727, 1605, 1515, 1471, 1422, 1353, 1307, 1164, 1108, 1037, 1017, 840, 814, 757, 734, 701, 664, 590, 545.

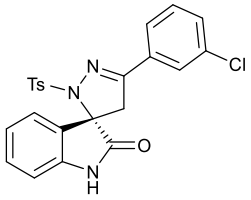
M. p. 217 – 220 °C



	Retention Time	Area	% Area
1	16.372	21282702	49.98
2	20.884	21296477	50.02



	Retention Time	Area	% Area
1	16.001	59809081	93.02
2	21.578	4488043	6.98



C21

(*S*)-5'-(3-chlorophenyl)-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one

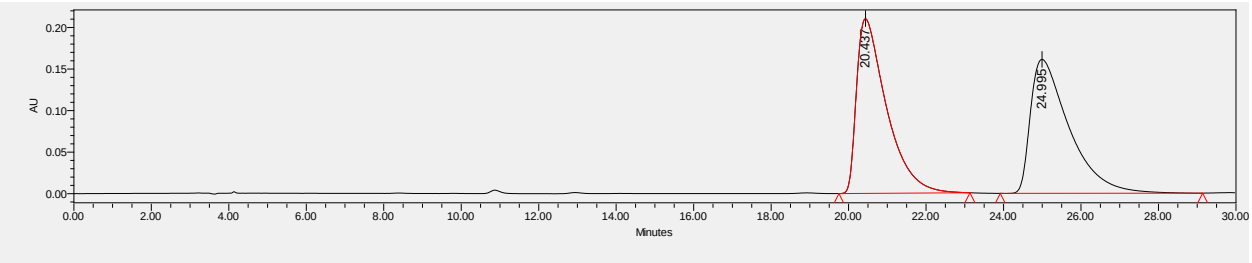
The crude material was directly purified by flash chromatography on silica gel (R_f = 0.3, PE/EtOAc = 3:2) to afford the light yellow oil (36.6 mg) in 81% yield with 91% ee. The ee was determined by HPLC analysis (Daicel chiralcel **IB$_{N\text{-}5}$**, 2-propanol/hexane = 30/70, flow rate = 1.0 mL/min, λ = 300 nm). $t_{R(major)}$ = 20.00 min, $t_{R(minor)}$ = 25.22 min; $[\alpha]_D^{19}$ = +24.8 (c = 1.34, in CH_3CN).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.72 (s, 1H), 7.70 (t, *J* = 2.0 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.53 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.39 (dt, *J* = 8.4, 1.6 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.80 – 6.68 (m, 2H), 3.82 (d, *J* = 16.8 Hz, 1H), 3.38 (d, *J* = 16.8 Hz, 1H), 2.38 (s, 3H).

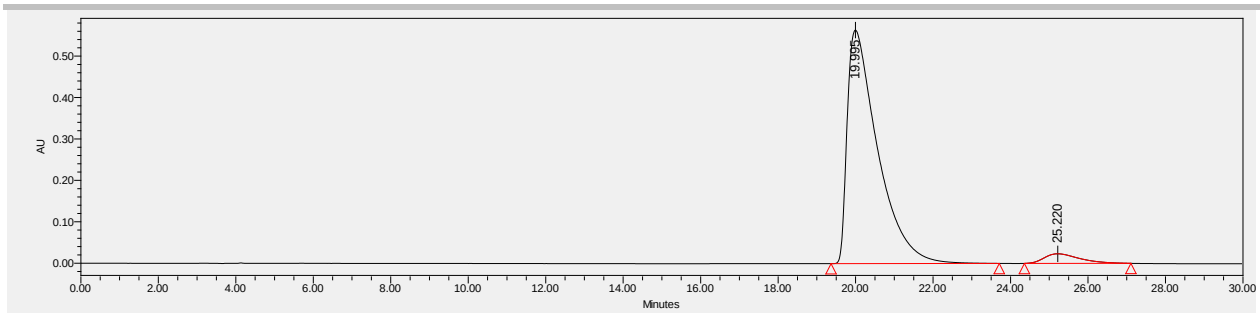
^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.8, 151.9, 144.1, 140.4, 135.6, 134.9, 132.2, 130.5, 130.4, 130.1, 129.3, 128.1, 128.0, 126.7, 124.9, 123.7, 123.0, 111.2, 71.1, 46.0, 21.7.

HRMS (ESI$^+$) m/z calcd for $C_{23}H_{18}Cl^{34.9689}N_3O_3NaS^+$ ([M]+Na$^+$) = 474.0650, found 474.0652 and $C_{23}H_{18}Cl^{36.9659}N_3O_3NaS^+$ ([M]+Na$^+$) = 476.0620, found 476.0620.

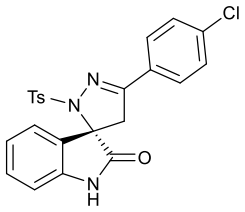
IR (neat, cm^{-1}) 3260, 1620, 1598, 1563, 1491, 1473, 1340, 1215, 1166, 1126, 1086, 1037, 736, 688, 665, 593, 547.



	Retention Time	Area	% Area
1	20.437	11270873	50.17
2	24.995	11194218	49.83



	Retention Time	Area	% Area
1	19.995	30689342	95.47
2	25.220	1457836	4.53



C22

(*S*)-5'-(4-chlorophenyl)-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one

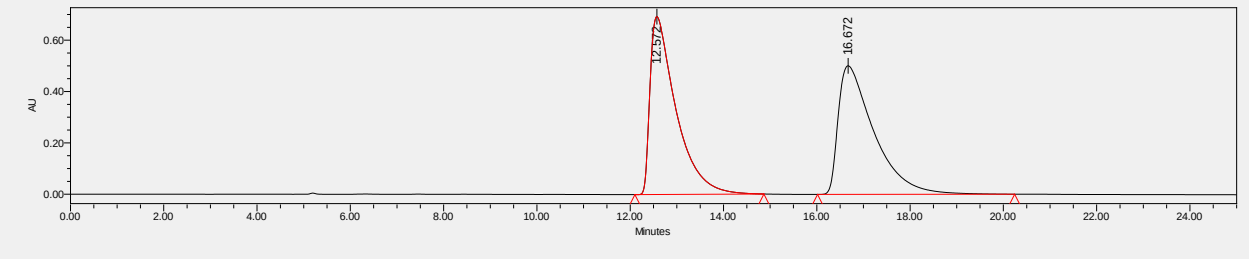
The crude material was directly purified by flash chromatography on silica gel (R_f = 0.3, PE/EtOAc = 3:2) to afford the white oil (38.9 mg) in 86% yield with 91% ee. The ee was determined by HPLC analysis (Daicel chiralcel **IB$_{N-5}$**, 2-propanol/hexane = 30/70, flow rate = 1.0 mL/min, λ = 300 nm). $t_{R(major)}$ = 12.16 min, $t_{R(minor)}$ = 17.11 min; $[\alpha]_D^{18}$ = +34.0 (c = 1.34, in CH_2Cl_2).

^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ 9.76 (s, 1H), 7.83 – 7.73 (m, 2H), 7.58 – 7.51 (m, 2H), 7.51 – 7.44 (m, 2H), 7.32 – 7.20 (m, 3H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.81 – 6.60 (m, 2H), 3.79 (d, *J* = 17.2 Hz, 1H), 3.60 (d, *J* = 17.2 Hz, 1H), 2.38 (s, 3H).

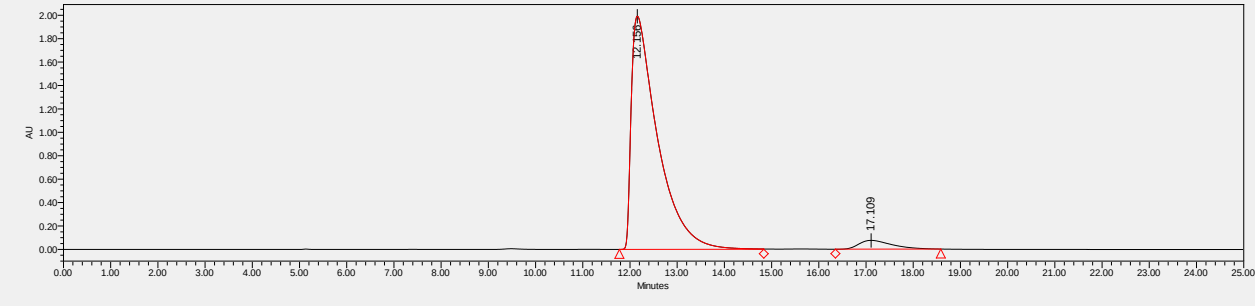
^{13}C NMR (101 MHz, Acetone-*d*$_6$) δ 175.7, 153.1, 144.6, 142.3, 137.1, 136.4, 130.7, 130.3, 129.8, 129.6, 129.0, 128.9, 128.6, 124.6, 122.8, 110.9, 71.8, 46.5, 21.3.

HRMS (ESI$^+$) m/z calcd for $C_{23}H_{18}Cl^{34.9689}N_3O_3NaS^+$ ([M]+Na$^+$) = 474.0650, found 474.0653 and $C_{23}H_{18}Cl^{36.9659}N_3O_3NaS^+$ ([M]+Na$^+$) = 476.0620, found 476.0622.

IR (neat, cm^{-1}) 3322, 1736, 1620, 1598, 1491, 1473, 1404, 1355, 1215, 1125, 1095, 1039, 1013, 815, 758, 705, 691, 666, 641, 594, 560, 540.

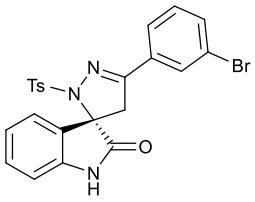


	Retention Time	Area	% Area
1	12.572	26742572	50.08
2	16.672	26660958	49.92



	Retention Time	Area	% Area
1	12.156	77013798	95.52

2	17.109	3615520	4.48



C23

(*S*)-5'-(3-bromophenyl)-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one

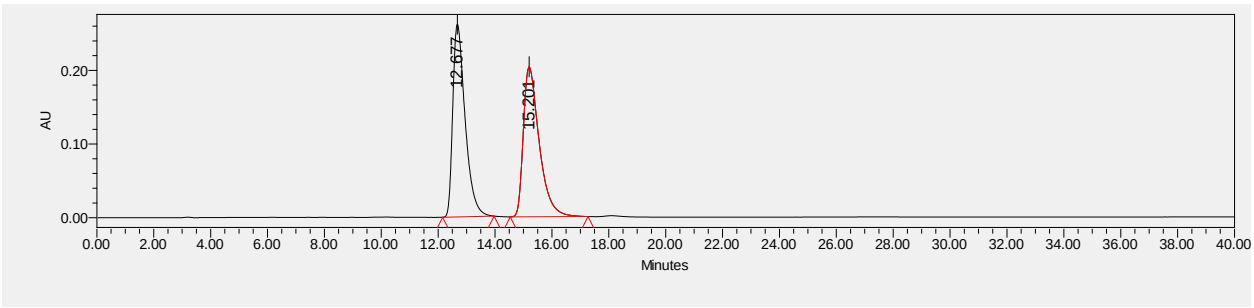
The crude material was directly purified by flash chromatography on silica gel (R_f = 0.3, PE/EtOAc = 3:2) to afford the yellow oil (45.1 mg) in 91% yield with 84% ee. The ee was determined by HPLC analysis (Daicel chiralcel **IB$_{N-5}$**, 2-propanol/hexane = 30/70, flow rate = 1.0 mL/min, λ = 300 nm). $t_{R(major)}$ = 12.57 min, $t_{R(minor)}$ = 15.38 min; $[\alpha]_D^{17}$ = +23.7 (c = 1.62, in $(CH_3)_2CO$).

^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ 9.77 (s, 1H), 7.93 (t, *J* = 1.6 Hz, 1H), 7.78 – 7.73 (m, 1H), 7.67 – 7.58 (m, 1H), 7.59 – 7.48 (m, 2H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.30 – 7.22 (m, 3H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.78 – 6.68 (m, 2H), 3.81 (d, *J* = 17.2 Hz, 1H), 3.62 (d, *J* = 17.2 Hz, 1H), 2.38 (s, 3H).

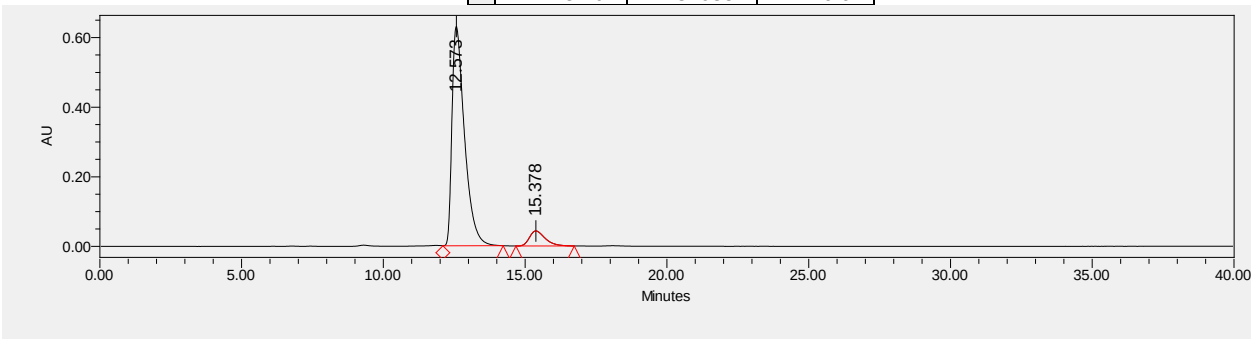
^{13}C NMR (101 MHz, Acetone-*d*$_6$) δ 175.6, 152.8, 144.7, 142.3, 137.0, 133.8, 133.7, 131.4, 130.7, 129.9, 129.9, 128.8, 128.6, 126.3, 124.6, 123.0, 122.8, 110.9, 71.8, 46.4, 21.3.

HRMS (ESI$^+$) m/z calcd for $C_{23}H_{18}Br^{78.9183}N_3O_3NaS^+$ ([M]+Na$^+$) = 518.0144, found 538.0148 and $C_{23}H_{18}Br^{80.9163}N_3O_3NaS^+$ ([M]+Na$^+$) = 520.0124, found 520.0129.

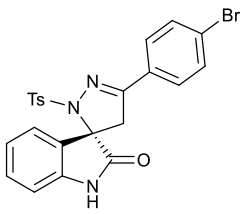
IR (neat, cm^{-1}) 3258, 1619, 1598, 1473,1358, 1337, 1215, 1166, 1126, 998, 759, 734, 703, 686, 665, 592, 547.



	Retention Time	Area	% Area
1	12.677	7889635	50.06
2	15.201	7870851	49.94



	Retention Time	Area	% Area
1	12.573	19345389	92.09
2	15.378	1661112	7.91



C24

(*S*)-5'-(4-bromophenyl)-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one

The crude material was directly purified by flash chromatography on silica gel (R_f = 0.3, PE/EtOAc = 3:2) to afford the yellow solid (47.1 mg) in 95% yield with 88% ee. The ee was determined by HPLC analysis (Daicel chiralcel **IB$_{N-5}$**, 2-propanol/hexane = 30/70, flow rate = 1.0 mL/min, λ = 300 nm). $t_{R(major)}$ = 13.31 min, $t_{R(minor)}$ = 19.63 min; $[\alpha]_D^{17}$ = +18.4 (c = 0.97, in $(CH_3)_2CO$).

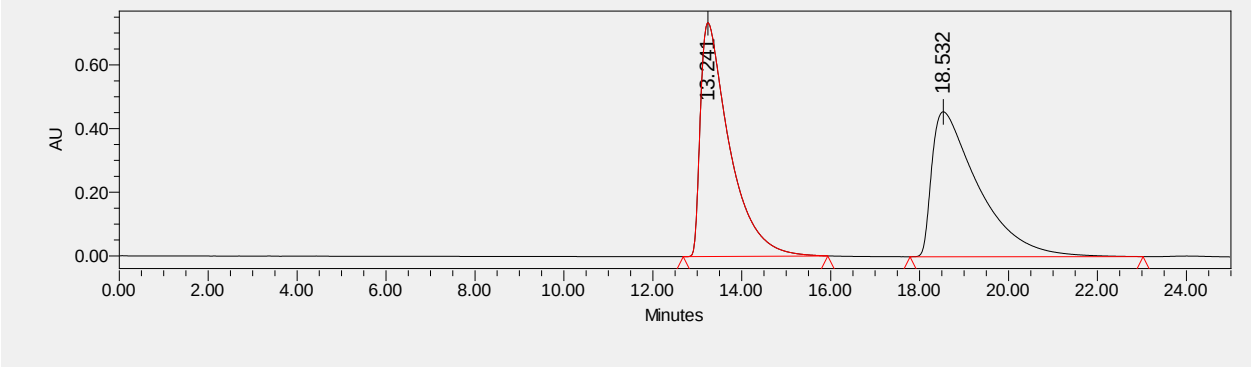
^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ 9.74 (s, 1H), 7.77 – 7.70 (m, 2H), 7.69 – 7.59 (m, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.31 – 7.22 (m, 3H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.78 – 6.64 (m, 2H), 3.80 (d, *J* = 17.2 Hz, 1H), 3.62 (d, *J* = 17.2 Hz, 1H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, Acetone-*d*$_6$) δ 175.7, 153.3, 144.7, 142.5, 137.2, 132.7, 130.8, 130.8, 129.9, 129.3, 129.0, 128.7, 124.9, 124.7, 122.8, 111.0, 71.9, 46.5, 21.4.

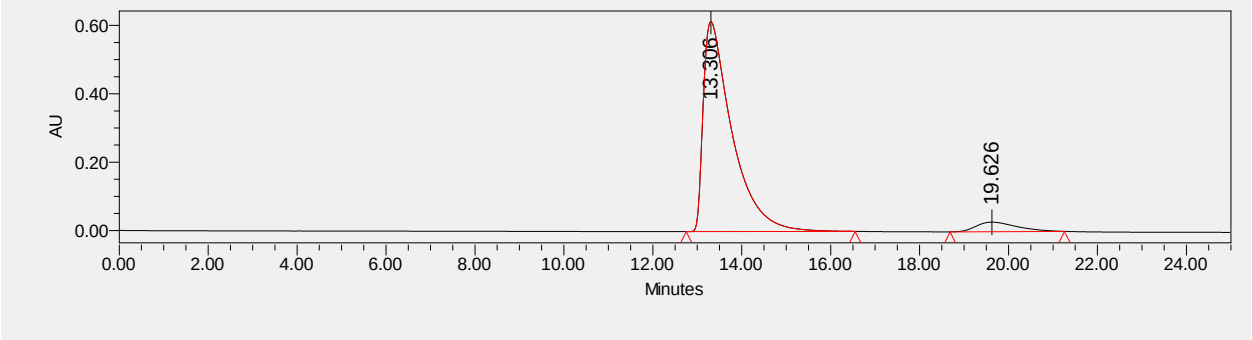
HRMS (ESI$^+$) m/z calcd for $C_{23}H_{18}Br^{78.9183}N_3O_3NaS^+$ ([M]+Na$^+$) = 518.0144, found 538.0148 and $C_{23}H_{18}Br^{80.9163}N_3O_3NaS^+$ ([M]+Na$^+$) = 520.0124, found 520.0124.

IR (neat, cm^{-1}) 3333, 1620, 1593, 1473, 1401, 1349, 1214, 1164, 1127, 1103, 1042, 1008, 845, 815, 754, 687, 664, 641, 596, 551, 538.

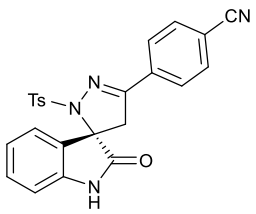
M. p. 265 – 267 °C



	Retention Time	Area	% Area
1	13.241	33296867	50.05
2	18.532	33233812	49.95



	Retention Time	Area	% Area
1	13.306	27580950	93.98
2	19.626	1767875	6.02



C25

(*S*)-4-(2-oxo-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-5'-yl)benzonitrile

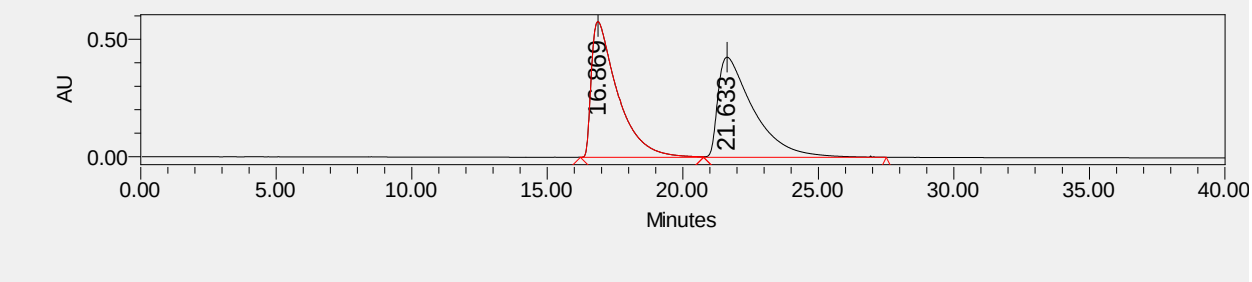
The crude material was directly purified by flash chromatography on silica gel (R_f = 0.4, PE/EtOAc = 3:2) to afford the light yellow oil (41.5 mg) in 94% yield with 74% ee. The ee was determined by HPLC analysis (Daicel chiralcel **IB$_{N-5}$**, 2-propanol/hexane = 30/70, flow rate = 1.0 mL/min, λ = 300 nm). $t_{R(major)}$ = 16.44 min, $t_{R(minor)}$ = 22.19 min; $[\alpha]_D^{19}$ = -10.0 (c = 1.48, in CH_3CN).

^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ 9.79 (s, 1H), 7.99 – 7.91 (m, 2H), 7.89 – 7.78 (m, 2H), 7.59 – 7.51 (m, 2H), 7.33 – 7.22 (m, 3H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.80 – 6.71 (m, 2H), 3.85 (d, *J* = 17.2 Hz, 1H), 3.67 (d, *J* = 17.2 Hz, 1H), 2.39 (s, 3H).

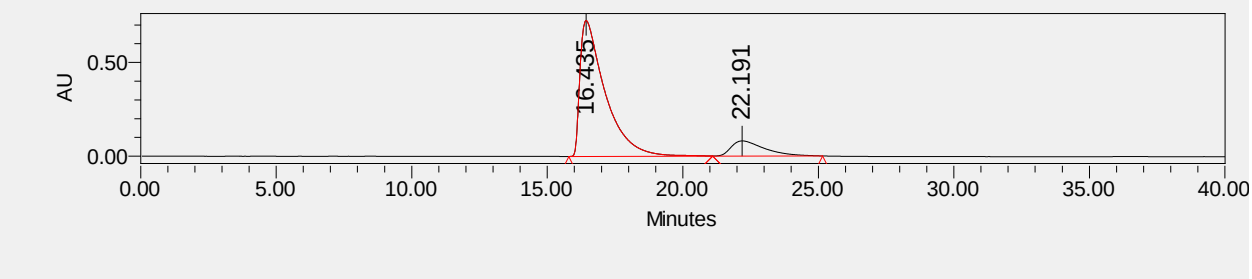
^{13}C NMR (101 MHz, Acetone-*d*$_6$) δ 175.6, 152.6, 144.8, 142.3, 136.9, 135.5, 133.1, 130.8, 129.9, 128.7, 128.5, 128.0, 124.7, 122.8, 118.8, 113.9, 110.9, 72.0, 46.2, 21.3.

HRMS (ESI$^+$) m/z calcd for $C_{24}H_{18}N_4O_3NaS^+$ ([M+Na$^+$) = 465.0992, found 465.0992.

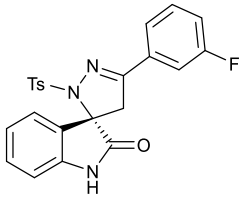
IR (neat, cm^{-1}) 3317, 2117, 1729, 1620, 1596, 1472, 1412, 1354, 1215, 1165, 1124, 1104, 1040, 1020, 848, 735, 702, 664, 594, 572, 543.



	Retention Time	Area	% Area
1	16.869	38980175	50.07
2	21.633	38865300	49.93



	Retention Time	Area	% Area
1	16.435	46811088	87.06
2	22.191	6959893	12.94



C26

***(S)*-5'-(3-fluorophenyl)-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one**

The crude material was directly purified by flash chromatography on silica gel (R_f = 0.3, PE/EtOAc = 3:2) to afford the light yellow solid (41.6 mg) in 83% yield with 78% ee. The ee was determined by HPLC analysis (Daicel chiralcel **IB$_{N-5}$**, 2-propanol/hexane = 30/70, flow rate = 1.0 mL/min, λ = 300 nm). $t_{R(major)}$ = 11.99 min, $t_{R(minor)}$ = 14.54 min; $[\alpha]_D^{19}$ = +37.8 (c = 1.46, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.67 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 9.6 Hz, 1H), 7.42 – 7.33 (m, 2H), 7.25 – 7.21 (m, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.12 (t, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.80 – 6.72 (m, 2H), 3.83 (d, *J* = 16.8 Hz, 1H), 3.39 (d, *J* = 16.8 Hz, 1H), 2.38 (s, 3H).

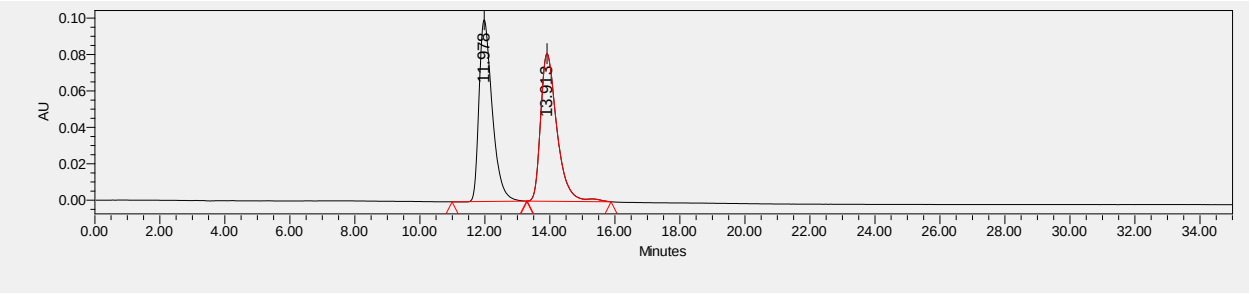
^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.8, 162.8 (*J* = 247.5 Hz), 152.1 (*J* = 3.0 Hz), 144.1, 140.4, 135.6, 132.6 (*J* = 8.1 Hz), 130.5, 130.4, 129.3, 128.2, 128.0, 123.7, 123.0, 122.6 (*J* = 3.0 Hz), 117.6 (*J* = 22.2 Hz), 113.5 (*J* = 22.2 Hz), 111.1, 71.1, 46.1, 21.7.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -112.0.

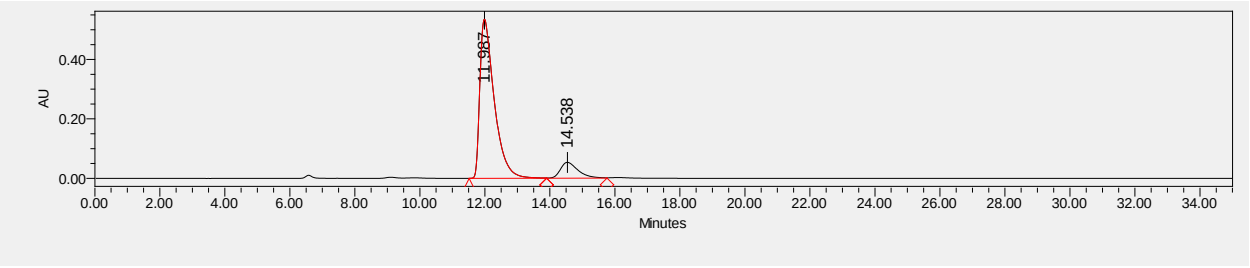
HRMS (ESI$^+$) m/z calcd for $C_{23}H_{18}FNaN_3O_3S^+$ ([M+Na$^+$) = 458.0945, found 458.0947.

IR (neat, cm^{-1}) 3259, 1729, 1619, 1577, 1473, 1452, 1345, 1272, 1215, 1198, 1165, 1122, 1001, 789, 758, 736,702, 666, 592, 548.

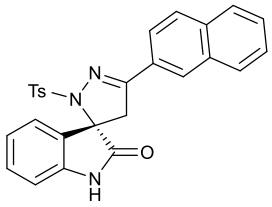
M. p. 213 – 215 °C



	Retention Time	Area	% Area
1	11.978	2823328	49.97
2	13.913	2827011	50.03



	Retention Time	Area	% Area
1	11.987	16397883	89.06
2	14.538	2014183	10.94



C27

(*S*)-5'-(naphthalen-2-yl)-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one

The crude material was directly purified by flash chromatography on silica gel (R_f = 0.3, PE/EtOAc = 3:2) to afford the yellow solid (43.9 mg) in 94% yield with 90% ee. The ee was determined by HPLC analysis (Daicel chiralcel **IB$_{N-5}$**, 2-propanol/hexane = 30/70, flow rate = 1.0 mL/min, λ = 300 nm). $t_{R(major)}$ = 13.75 min, $t_{R(minor)}$ = 17.51 min; $[\alpha]_D^{19}$ = +79.0 (c = 1.73, in CH_3CN).

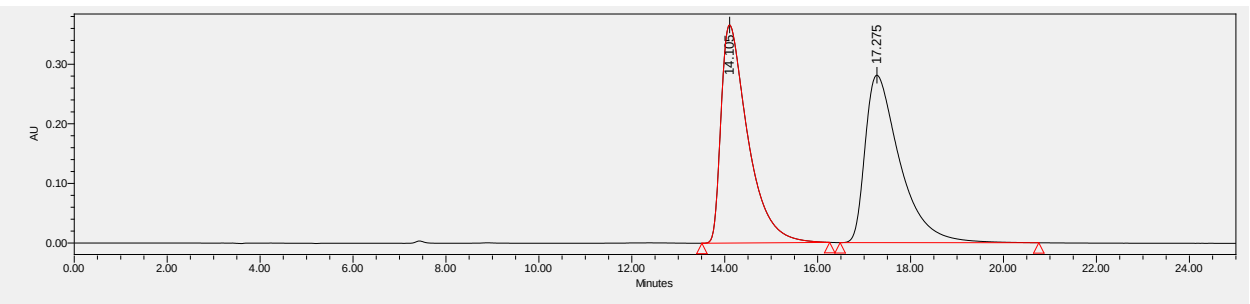
^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ 9.81 (s, 1H), 8.11 (s, 1H), 8.04 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.96 – 7.89 (m, 3H), 7.60 – 7.50 (m, 4H), 7.30 – 7.23 (m, 3H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.74 – 6.66 (m, 2H), 3.89 (d, *J* = 17.2 Hz, 1H), 3.69 (d, *J* = 17.2 Hz, 1H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, Acetone-*d*$_6$) δ 175.8, 154.2, 144.5, 142.3, 137.1, 134.8, 133.7, 130.6, 129.8, 129.2, 129.1, 128.9, 128.5, 128.4, 128.2, 128.0, 127.5, 124.5, 123.8, 122.7, 110.9, 71.7, 46.5, 21.3.

HRMS (ESI$^+$) m/z calcd for $C_{27}H_{21}N_3O_3NaS^+$ ([M]+Na$^+$) = 490.1196, found 490.1199.

IR (neat, cm^{-1}) 3260, 1727, 1620, 1600, 1472, 1419, 1355, 1214, 1165, 1120, 1103, 1037, 963, 893, 863, 815, 753, 702, 665, 625, 588, 544, 493.

M. p. 204 – 206 °C



	Retention Time	Area	% Area
1	14.105	14672610	50.17
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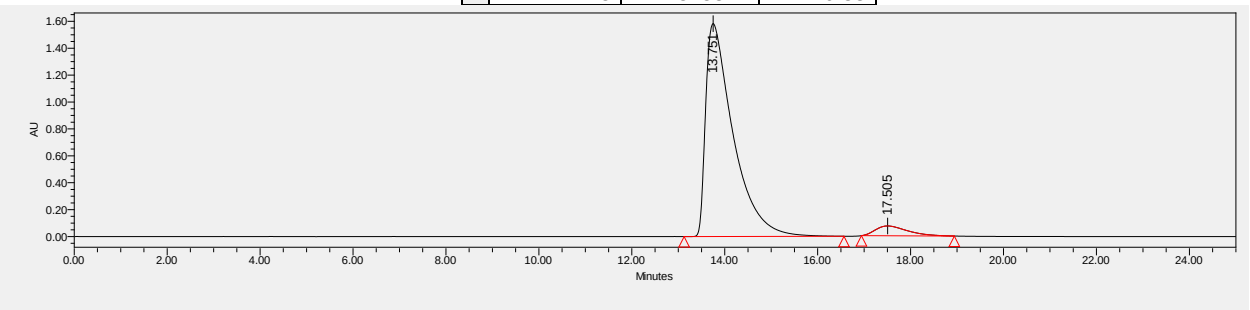

	Retention Time	Area	% Area
1	13.751	64686341	94.86
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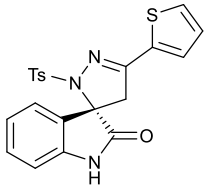


C28

(*S*)-5'-(thiophen-2-yl)-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one

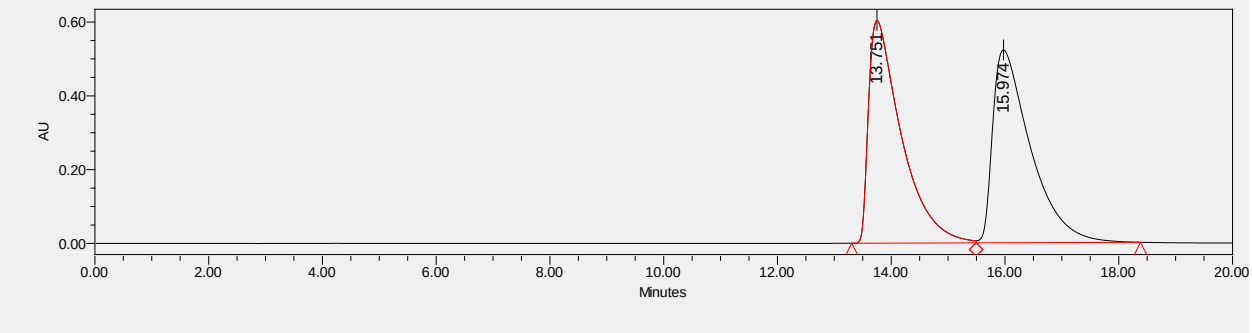
The crude material was directly purified by flash chromatography on silica gel (R_f = 0.3, PE/EtOAc = 3:2) to afford the light yellow oil (33.8 mg) in 80% yield with 80% ee. The ee was determined by HPLC analysis (Daicel chiralcel **IB$_{N-5}$**, 2-propanol/hexane = 30/70, flow rate = 1.0 mL/min, λ = 300 nm). $t_{R(major)}$ = 14.02 min, $t_{R(minor)}$ = 16.63 min; $[\alpha]_D^{19}$ = +16.2 (c = 1.02, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.84 (s, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.44 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.24 – 7.18 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.04 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.73 – 6.62 (m, 2H), 3.85 (d, *J* = 16.8 Hz, 1H), 3.38 (d, *J* = 16.8 Hz, 1H), 2.37 (s, 3H).

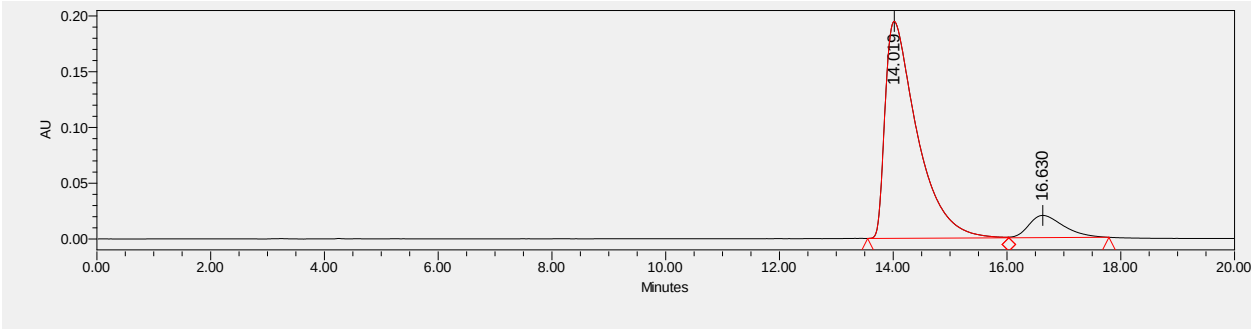
^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.7, 149.0, 143.9, 140.5, 135.6, 133.8, 130.3, 129.3, 129.2, 129.2, 129.0, 128.2, 127.7, 127.6, 123.7, 122.8, 111.2, 71.0, 46.8, 21.6.

HRMS (ESI$^+$) m/z calcd for $C_{21}H_{17}N_3NaO_3S_2^+$ ([M]+H$^+$) = 446.0604, found 446.0611.

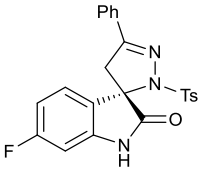
IR (neat, cm^{-1}) 3266, 1727, 1620, 1598, 1437, 1400, 1214, 1166, 1123, 1103, 1034, 842, 815, 759, 705, 665, 593, 547, 529.



	Retention Time	Area	% Area
1	13.751	24095886	50.00
2	15.974	24094142	50.00



	Retention Time	Area	% Area
1	14.019	7597868	89.98
2	16.630	846016	10.02



C31

(*S*)-6-fluoro-5'-phenyl-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one

The crude material was directly purified by flash chromatography on silica gel (R_f = 0.5, PE/EtOAc = 3:2) to afford the orange oil (27.8 mg) in 64% yield with 86% ee. The ee was determined by HPLC analysis (Daicel chiralcel **IB$_{N-5}$**, 2-propanol/hexane = 20/80, flow rate = 1.0 mL/min, λ = 300 nm). $t_{R(major)}$ = 21.19 min, $t_{R(minor)}$ = 17.88 min; $[\alpha]_{405}^{25}$ = -36.3 (c = 0.85, in CH_2Cl_2).

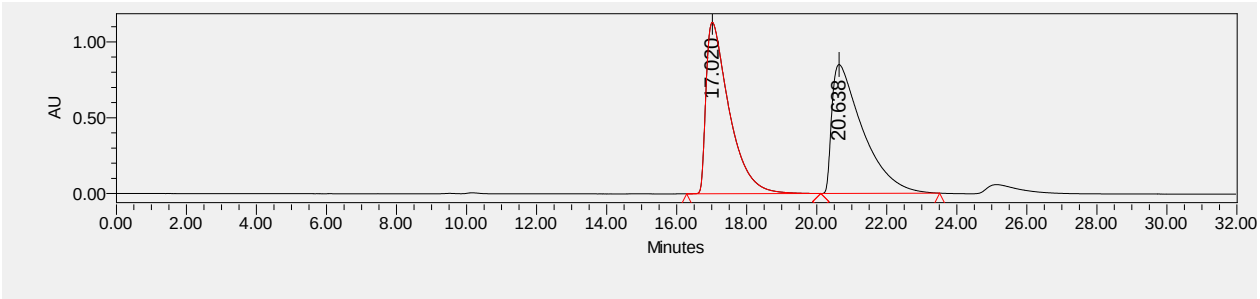
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.12 (s, 1H), 7.74 – 7.66 (m, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.47 – 7.36 (m, 3H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.71 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.65 (dd, *J* = 8.4, 5.2 Hz, 1H), 6.40 (td, *J* = 8.8, 2.4 Hz, 1H), 3.82 (d, *J* = 16.8 Hz, 1H), 3.37 (d, *J* = 16.8 Hz, 1H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.5, 163.9 (*J* = 248.8 Hz), 153.4, 144.2, 142.2 (*J* = 12.4 Hz), 135.6, 130.7, 130.3, 129.3, 129.3, 128.8, 128.1, 126.9, 125.0 (*J* = 10.1 Hz), 123.7 (*J* = 2.8 Hz), 109.2 (*J* = 22.8 Hz), 99.9 (*J* = 27.4 Hz), 70.6, 46.1, 21.6.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -108.4.

HRMS (ESI$^+$) m/z calcd for $C_{23}H_{18}FN_3NaO_3S^+$ ([M]+Na$^+$) = 458.0945, found 458.0941.

IR (neat, cm^{-1}) 3313, 1743, 1627, 1501, 1462, 1356, 1269, 1215, 1166, 1141, 1120, 1036, 968, 847, 811, 761, 734, 707, 690, 667, 600, 574, 544.



	Retention Time	Area	% Area
1	17.020	51824497	49.82
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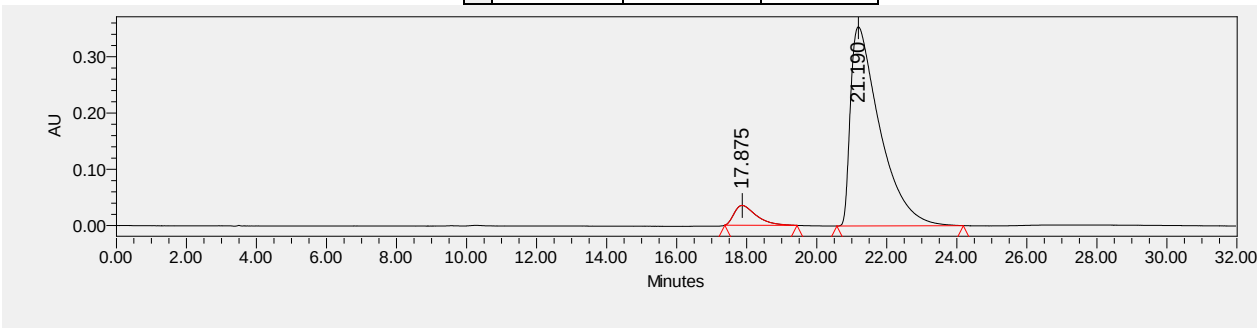
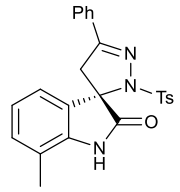


	Retention Time	Area	% Area
1	17.875	1557905	7.05
2	21.190	20550897	92.95



C32

(*S*)-7-methyl-5'-phenyl-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one

The crude material was directly purified by flash chromatography on silica gel (R_f = 0.4, PE/EtOAc = 3:2) to afford the light pink solid (39.1 mg) in 84% yield with 70% ee. The ee was determined by HPLC analysis (Daicel chiralcel **IB$_{N-5}$**, 2-propanol/hexane = 20/80, flow rate = 1.0 mL/min, λ = 300 nm). $t_{R(major)}$ = 18.00 min, $t_{R(minor)}$ = 21.57 min; $[\alpha]_{405}^{24}$ = +66.9 (c = 1.33, in CH_2Cl_2).

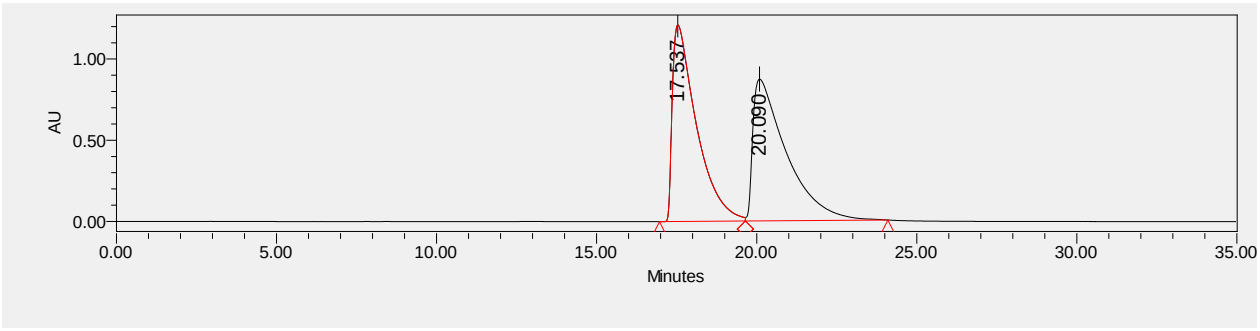
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.12 (s, 1H), 7.79 – 7.70 (m, 2H), 7.50 (dd, *J* = 8.4, 6.4 Hz, 2H), 7.46 – 7.39 (m, 3H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.95 – 6.87 (m, 1H), 6.19 (s, 1H), 3.85 (d, *J* = 16.8 Hz, 1H), 3.36 (d, *J* = 16.8 Hz, 1H), 2.37 (s, 3H), 1.93 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.2, 153.6, 143.6, 138.2, 135.8, 132.0, 130.7, 130.6, 130.5, 129.1, 129.1, 128.8, 128.1, 127.1, 126.9, 124.5, 111.1, 71.2, 46.1, 21.6, 20.6.

HRMS (ESI$^+$) m/z calcd for $C_{24}H_{21}N_3NaO_3S^+$ ([M]+Na$^+$) = 454.1196, found 454.1188.

IR (neat, cm^{-1}) 3326, 1730, 1626, 1598, 1494, 1448, 1356, 1263, 1217, 1167, 1114, 1036, 858, 815, 763, 734, 691, 664, 636, 599, 547, 488.

M. p. 246 – 249 °C



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1	17.537	63343733	49.96
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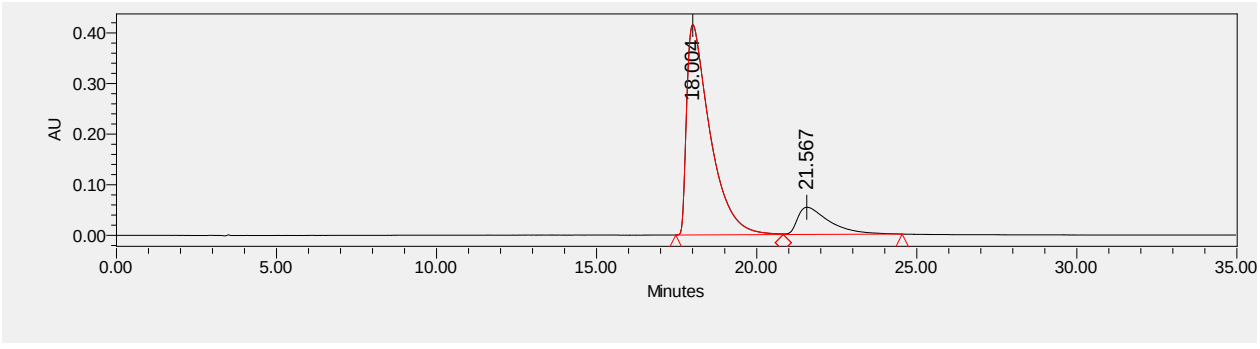
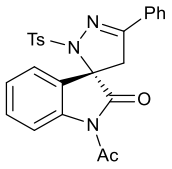


	Retention Time	Area	% Area
1	18.004	21065322	84.97
2	21.567	3726770	15.03



D1

(*S*)-1-acetyl-5'-phenyl-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one

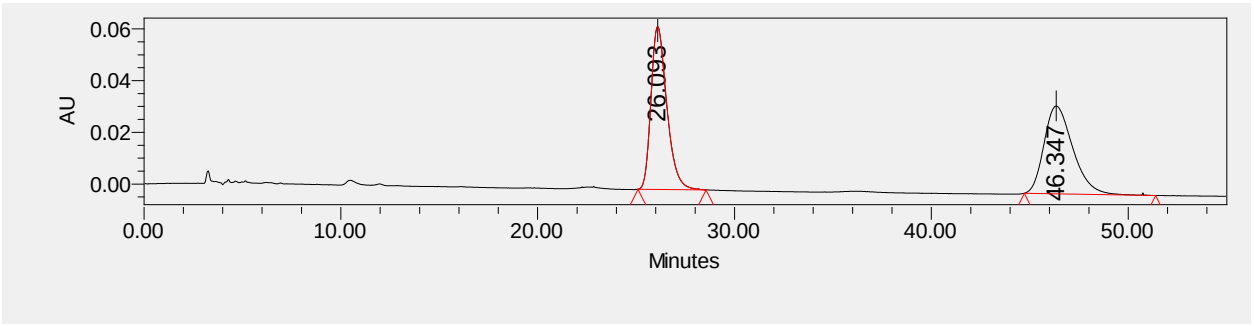
The crude material was directly purified by flash chromatography on silica gel (R_f = 0.4, PE/EtOAc = 3:2) to afford the light yellow oil (41.9 mg) in 91% yield with 90% ee. The ee was determined by HPLC analysis (Daicel chiralcel **ID** 2-propanol/hexane = 30/70, flow rate = 1.0 mL/min, λ = 300 nm). $t_{R(major)}$ = 25.53 min, $t_{R(minor)}$ = 46.25 min; $[\alpha]_D^{16}$ = +32.7 (c = 0.44, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 (d, *J* = 8.4 Hz, 1H), 7.75 – 7.67 (m, 2H), 7.47 – 7.31 (m, 6H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.81 (t, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 7.6 Hz, 1H), 3.89 (d, *J* = 16.8 Hz, 1H), 3.43 (d, *J* = 16.8 Hz, 1H), 2.76 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.0, 169.8, 151.8, 143.0, 138.5, 134.4, 129.8, 129.6, 129.1, 128.2, 127.8, 126.7, 125.8, 125.2, 124.3, 122.1, 116.0, 69.9, 46.0, 25.6, 20.6.

HRMS (ESI$^+$) m/z calcd for $C_{25}H_{21}N_3NaO_4S^+$ ([M]+Na$^+$) = 482.1145, found 482.1150.

IR (neat, cm^{-1}) 2924, 2854, 2360, 1770, 1714, 1600, 1466, 1418, 1357, 1337, 1310, 1274, 1101, 1055, 1016, 915, 863, 801, 760, 736, 693, 671, 602, 587, 546, 494.



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1	26.093	3518983	50.44
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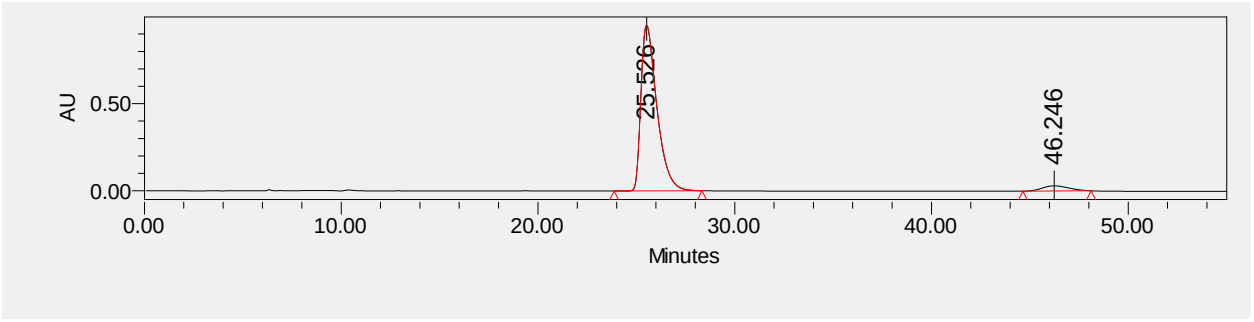

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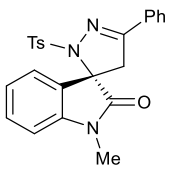


D2

(*S*)-1-methyl-5'-phenyl-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one

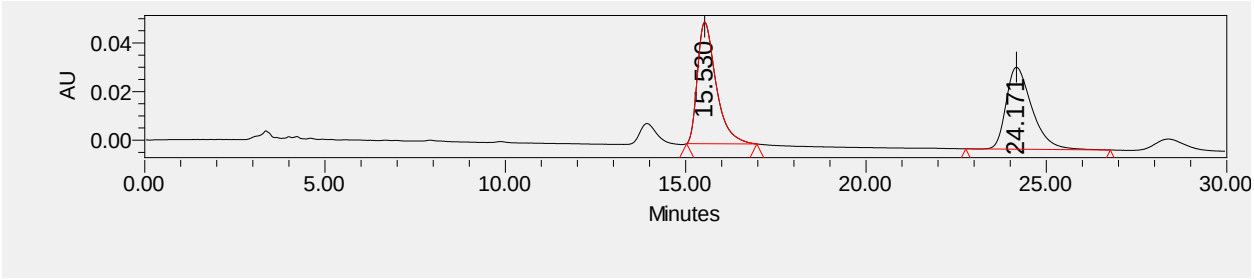
The crude material was directly purified by flash chromatography on silica gel (R_f = 0.5, PE/EtOAc = 2:1) to afford the yellow oil (41.0 mg) in 95% yield with 90% ee. The ee was determined by HPLC analysis (Daicel chiralcel **IA**, 2-propanol/hexane = 30/70, flow rate = 1.0 mL/min, λ = 300 nm). $t_{R(major)}$ = 15.12 min, $t_{R(minor)}$ = 24.05 min; $[\alpha]_D^{15}$ = +59.1 (c = 0.25, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.64 (m, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.43 – 7.35 (m, 3H), 7.35 – 7.29 (m, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.81 – 6.67 (m, 2H), 3.81 (d, *J* = 16.8 Hz, 1H), 3.38 (d, *J* = 16.8 Hz, 1H), 3.32 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.1, 153.2, 143.8, 143.2, 135.9, 130.6, 130.5, 130.3, 129.2, 128.7, 128.1, 127.7, 126.8, 123.5, 122.9, 108.8, 70.6, 45.9, 27.0, 21.6.

HRMS (ESI$^+$) m/z calcd for $C_{24}H_{21}N_3NaO_3S^+$ ([M]+Na$^+$) = 454.1196, found 454.1194.

IR (neat, cm^{-1}) 2927, 2360, 1727, 1672, 1612, 1493, 1471, 1449, 1421, 1351, 1306, 1260, 1160, 1117, 1090, 1058, 1011, 953, 867, 815, 755, 732, 697, 666, 546, 492.



	Retention Time	% Area	Height
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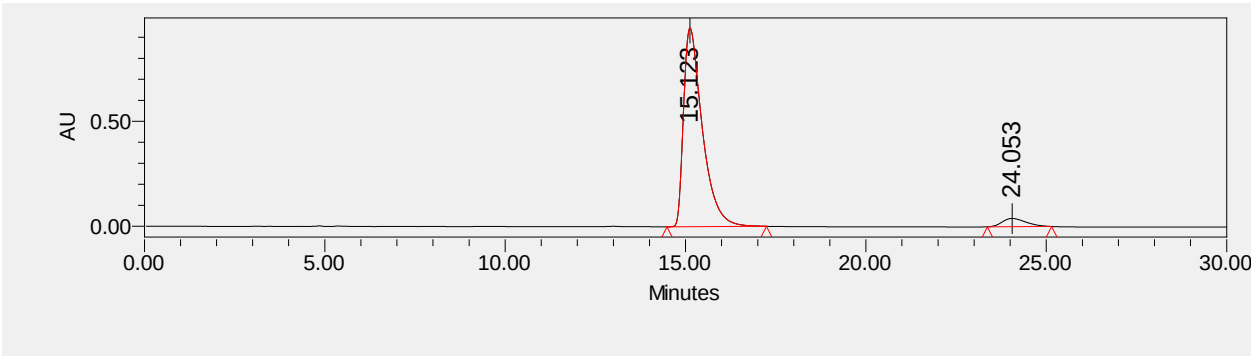

	Retention Time	% Area	Height
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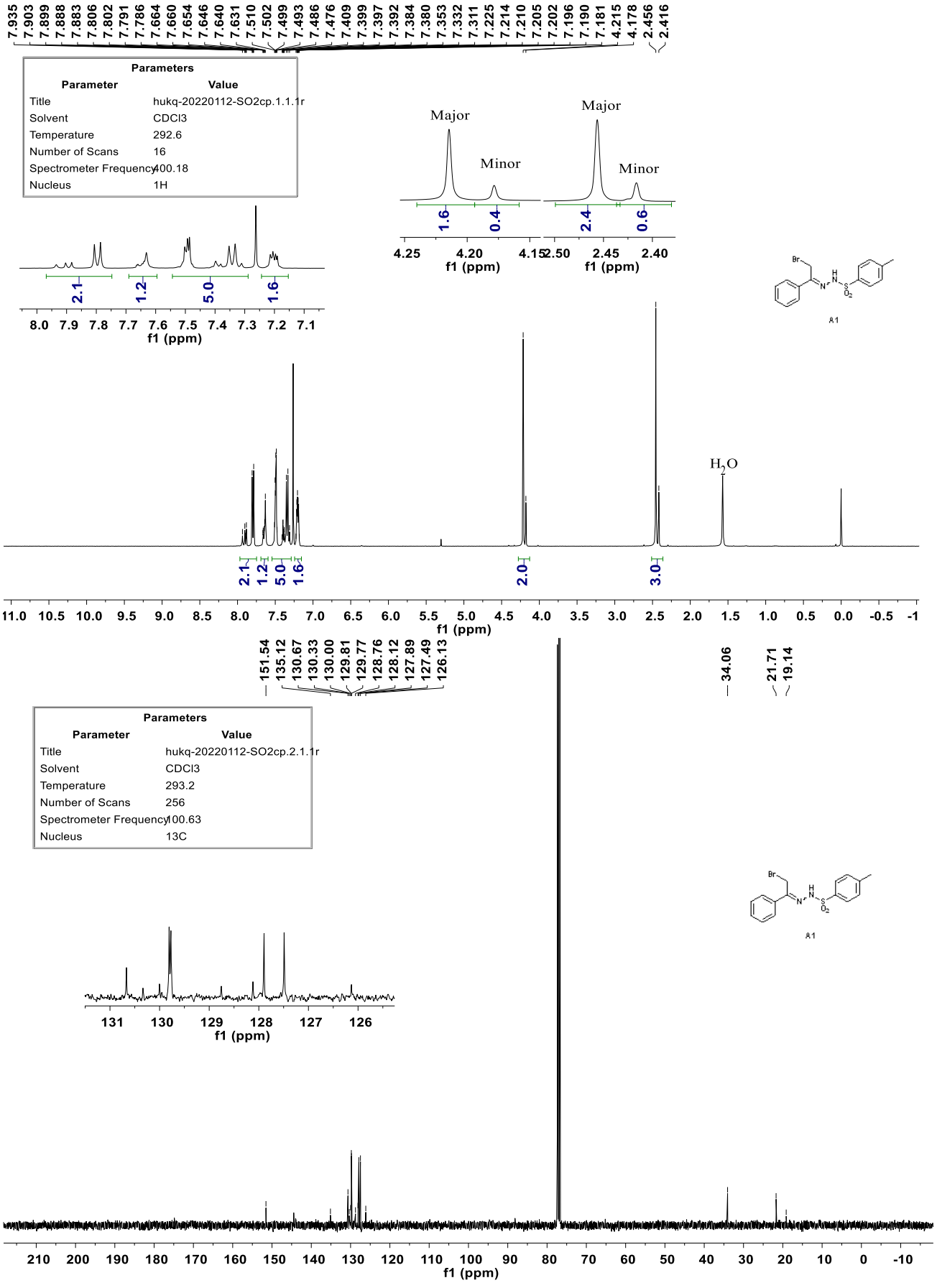
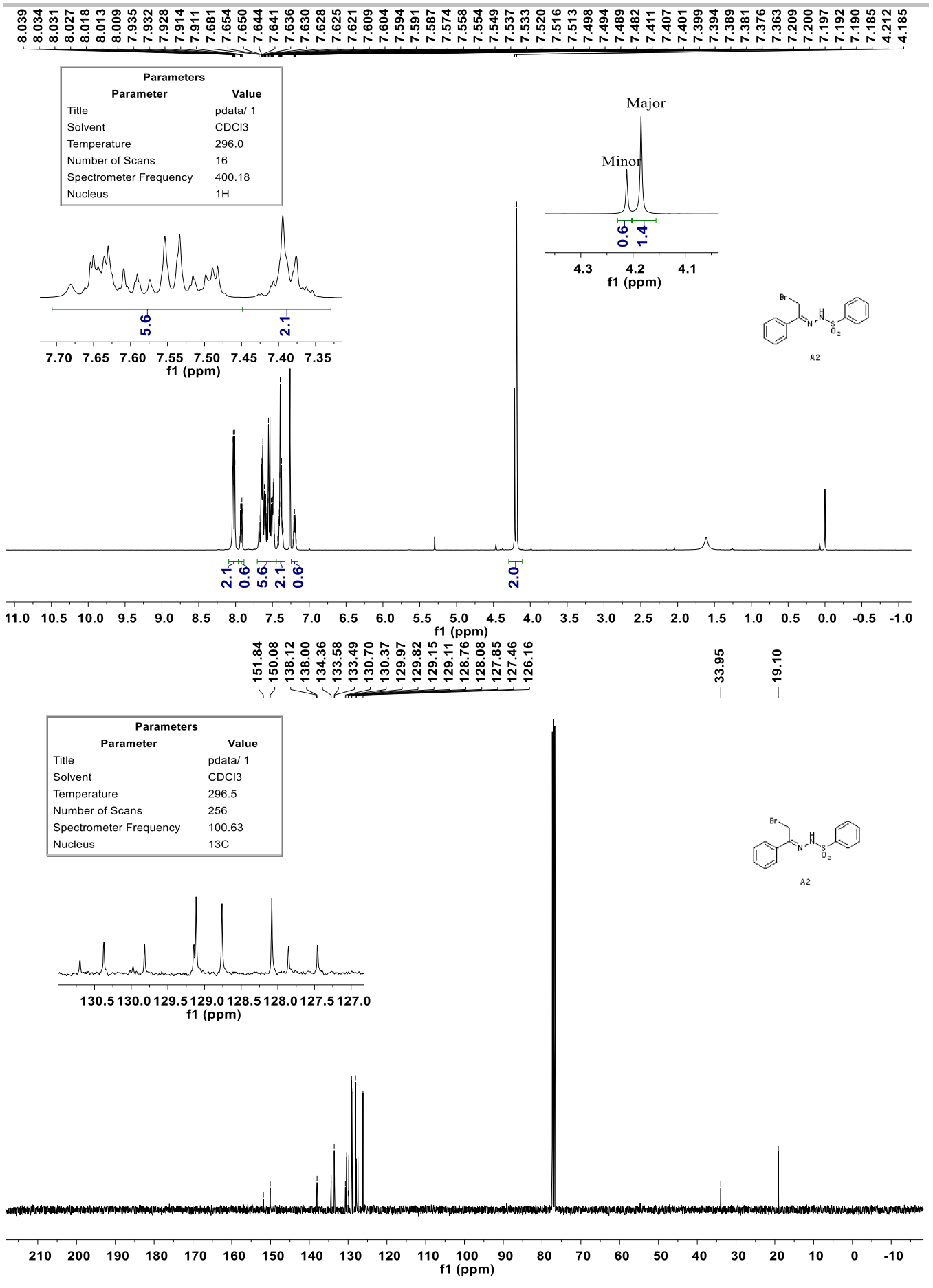
2	24.053	5.04	39265

17. Copies of NMR spectra for the reaction substrates and products

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Spectrometer Frequency 400.18
Nucleus 1H
Major
Minor
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4.3 4.2 4.1
f1 (ppm)
5.6
2.1
7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35
f1 (ppm)
A2
2.1 0.6 5.6 2.1 0.6
2.0
11.0 10.5 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 -0.5 -1.0
f1 (ppm)
151.84 150.08 138.12 138.00 134.36 133.58 133.49 130.70 130.37 129.97 129.82 129.15 129.11 128.76 128.08 127.85 127.46 126.16
33.95
19.10
Parameters
Parameter Value
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Solvent CDCl3
Temperature 296.5
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
A2
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f1 (ppm)
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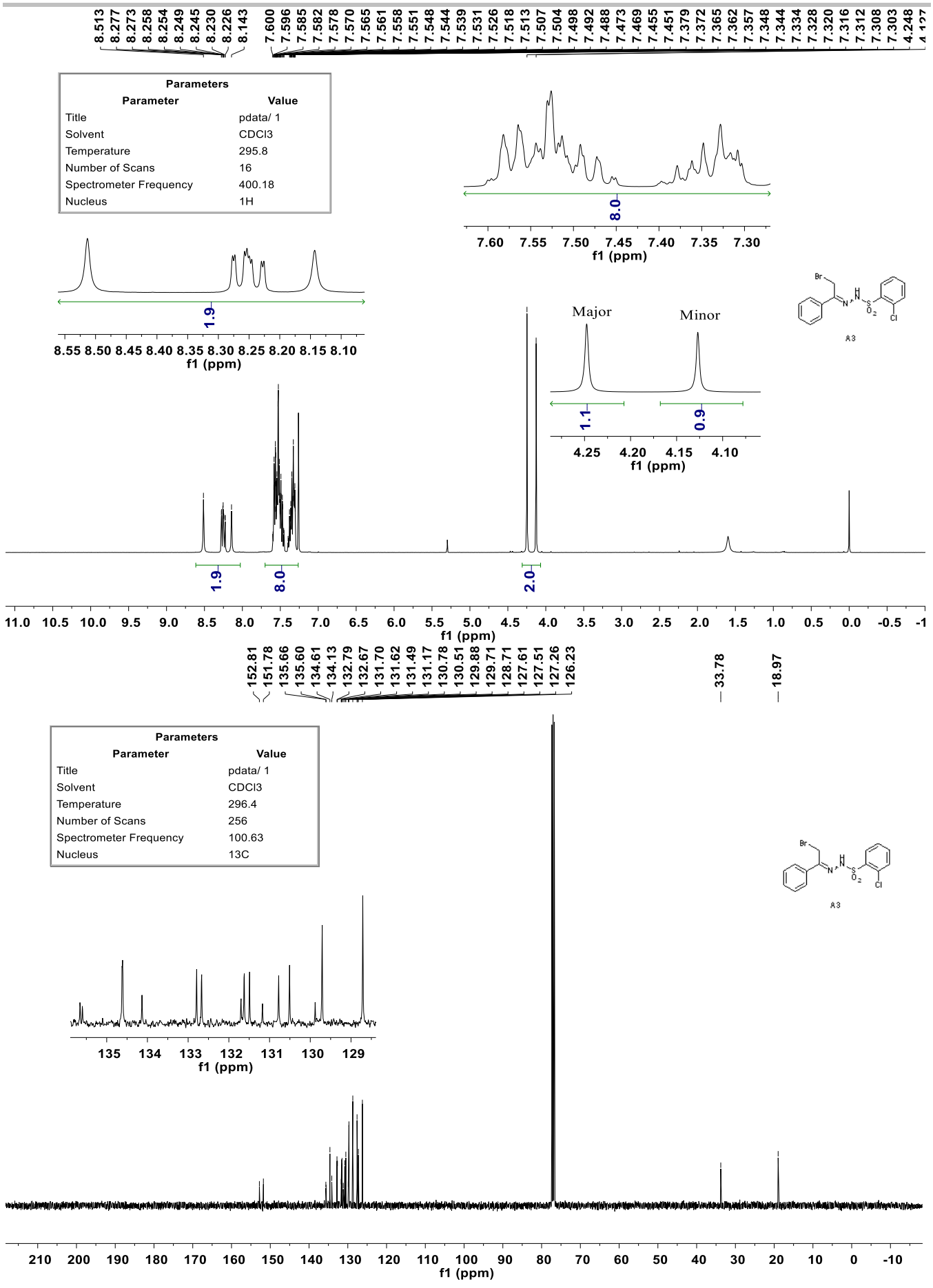
f1 (ppm)


8.513 8.277 8.273 8.258 8.254 8.249 8.245 8.230 8.226 8.143
7.600 7.596 7.585 7.582 7.578 7.570 7.565 7.561 7.558 7.551 7.548 7.544 7.539 7.531 7.526 7.518 7.513 7.507 7.504 7.498 7.492 7.488 7.473 7.469 7.455 7.451 7.379 7.372 7.365 7.362 7.357 7.348 7.344 7.334 7.328 7.320 7.316 7.312 7.308 7.303 4.248
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8.55 8.50 8.45 8.40 8.35 8.30 8.25 8.20 8.15 8.10
f1 (ppm)
Br
N
H
S
O2
Cl
A3
Major
Minor
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0.9
4.25 4.20 4.15 4.10
f1 (ppm)
1.9
8.0
2.0
11.0 10.5 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 -0.5 -1
f1 (ppm)
152.81 151.78 135.66 135.60 134.61 134.13 132.79 132.67 131.70 131.62 131.49 131.17 130.78 130.51 129.88 129.71 128.71 127.61 127.51 127.26 126.23
33.78
18.97
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H
S
O2
Cl
A3
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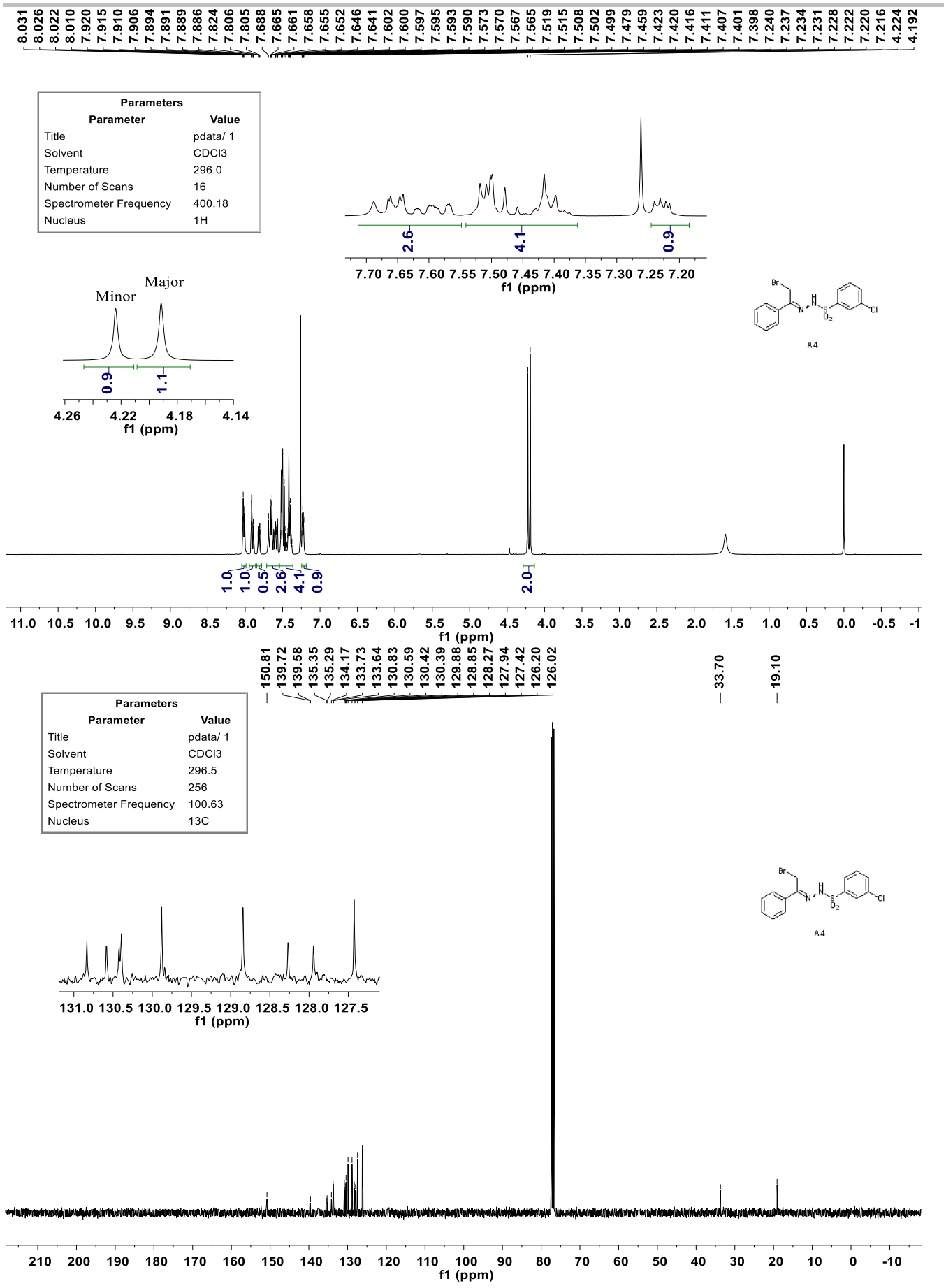
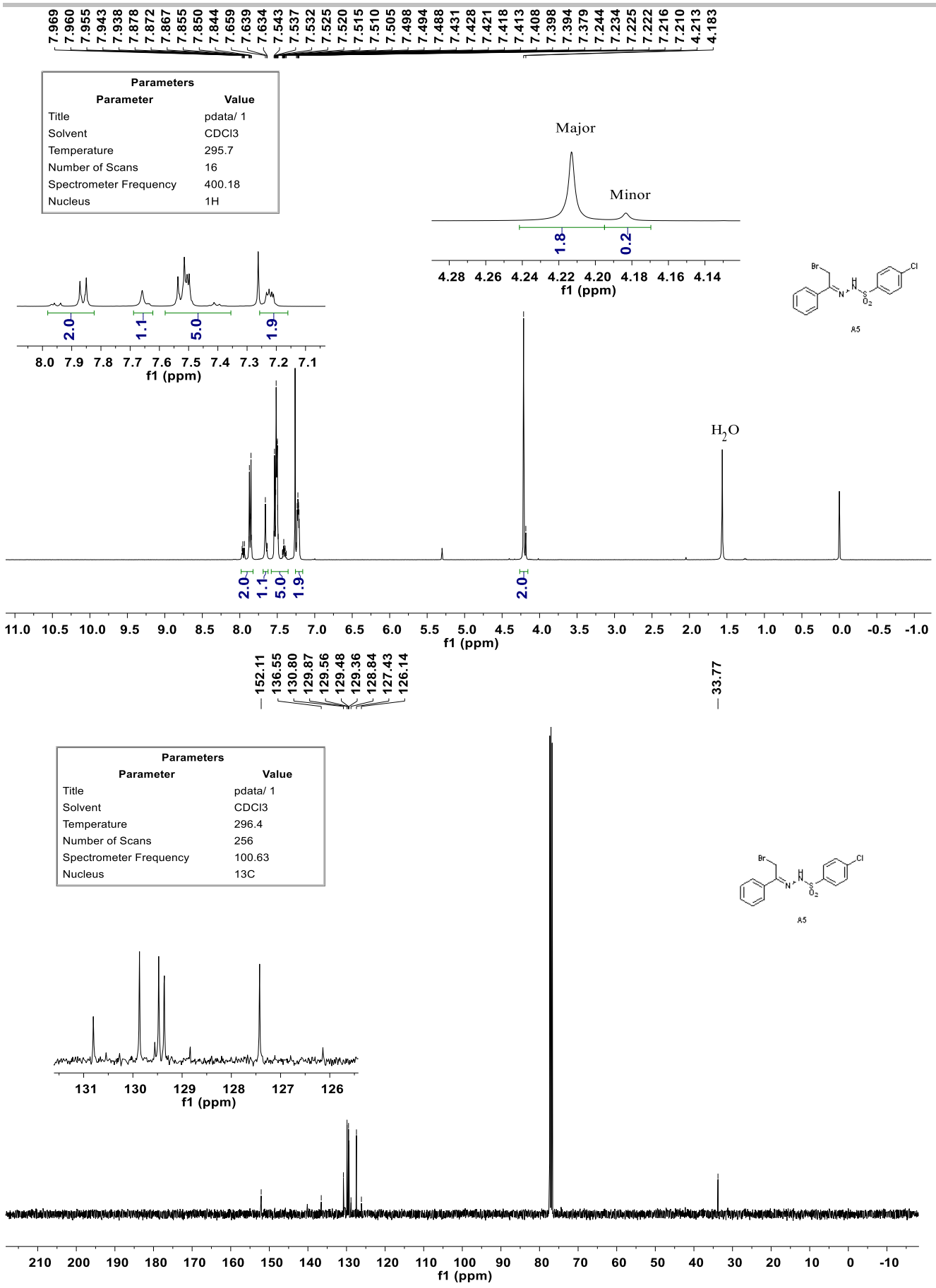
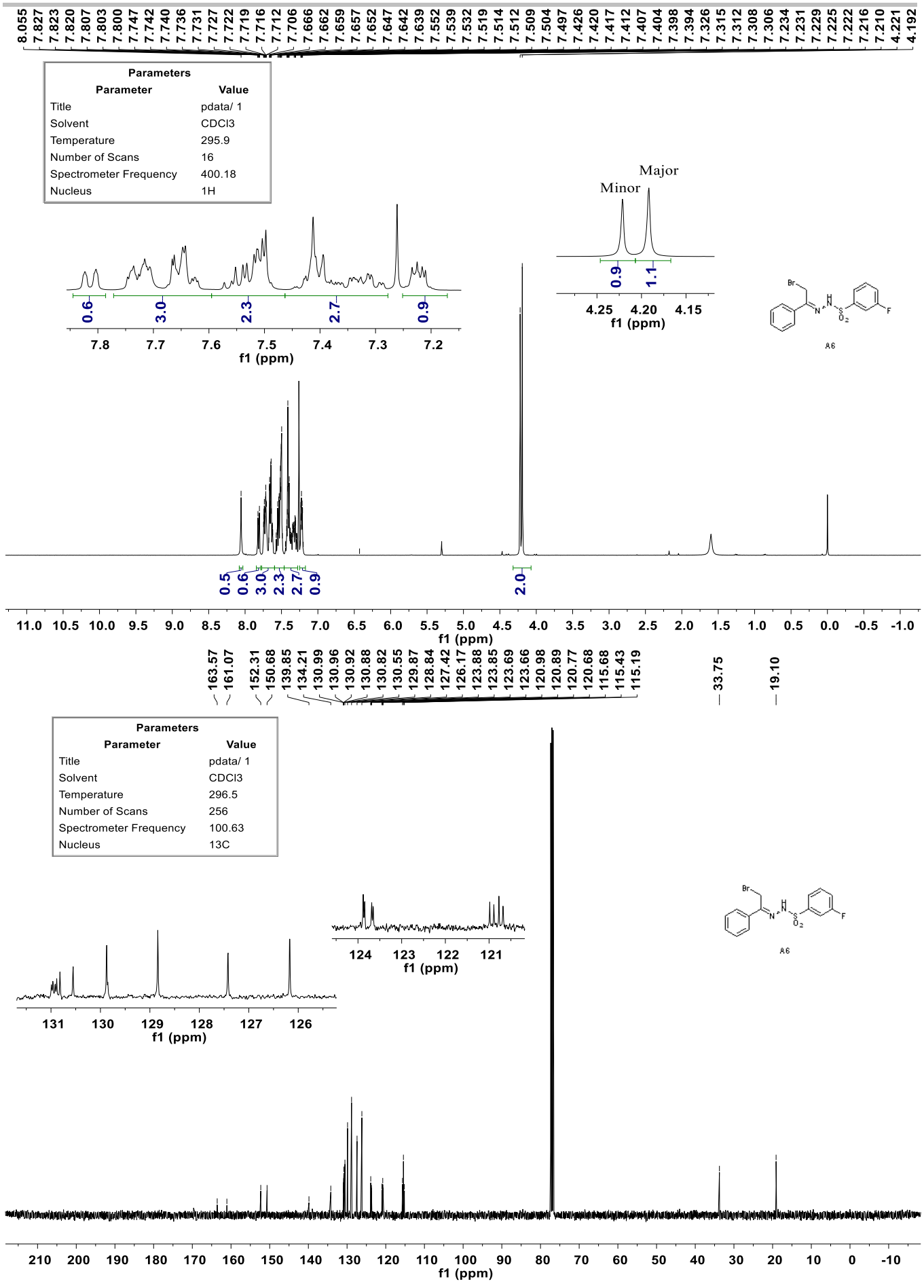
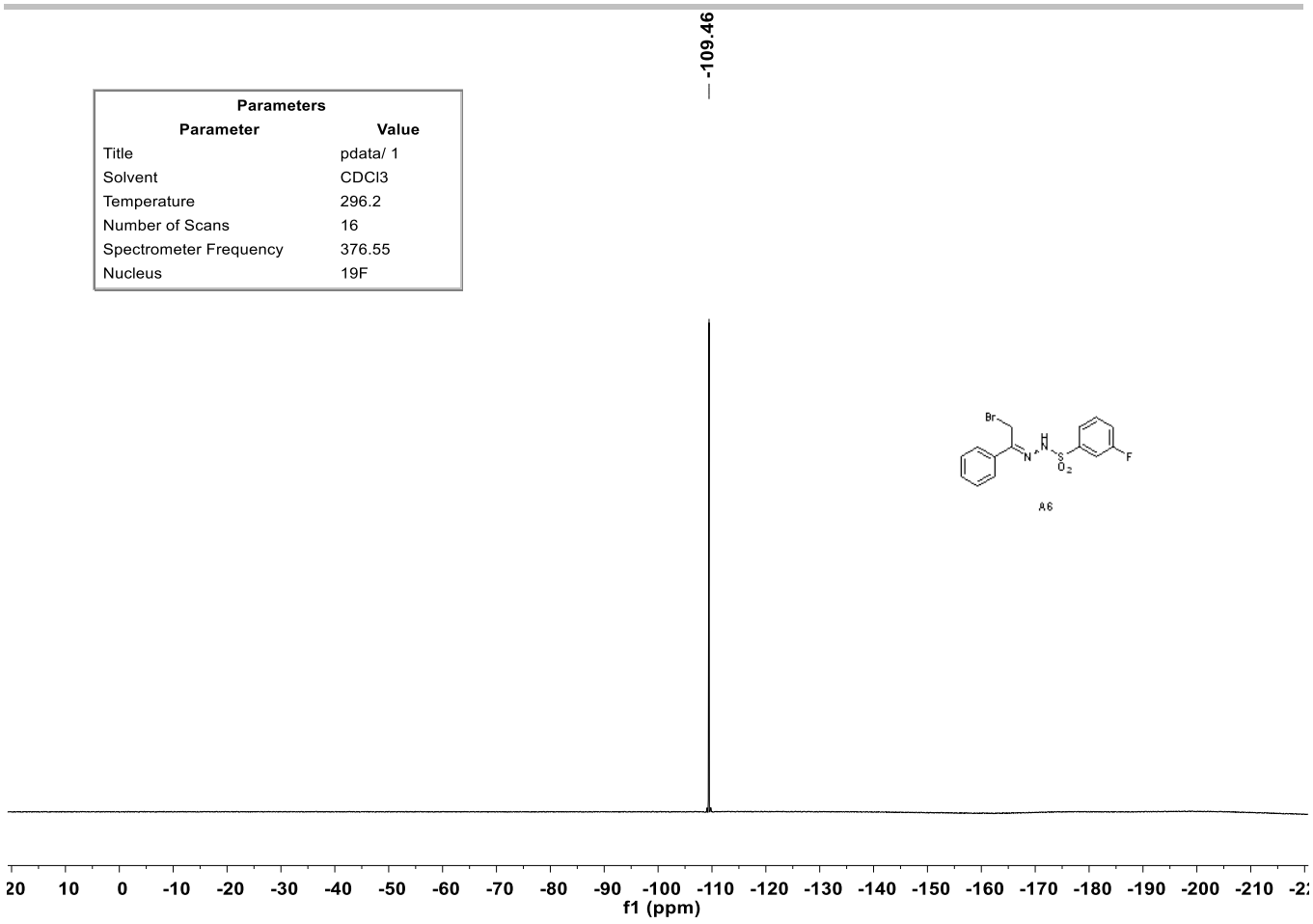
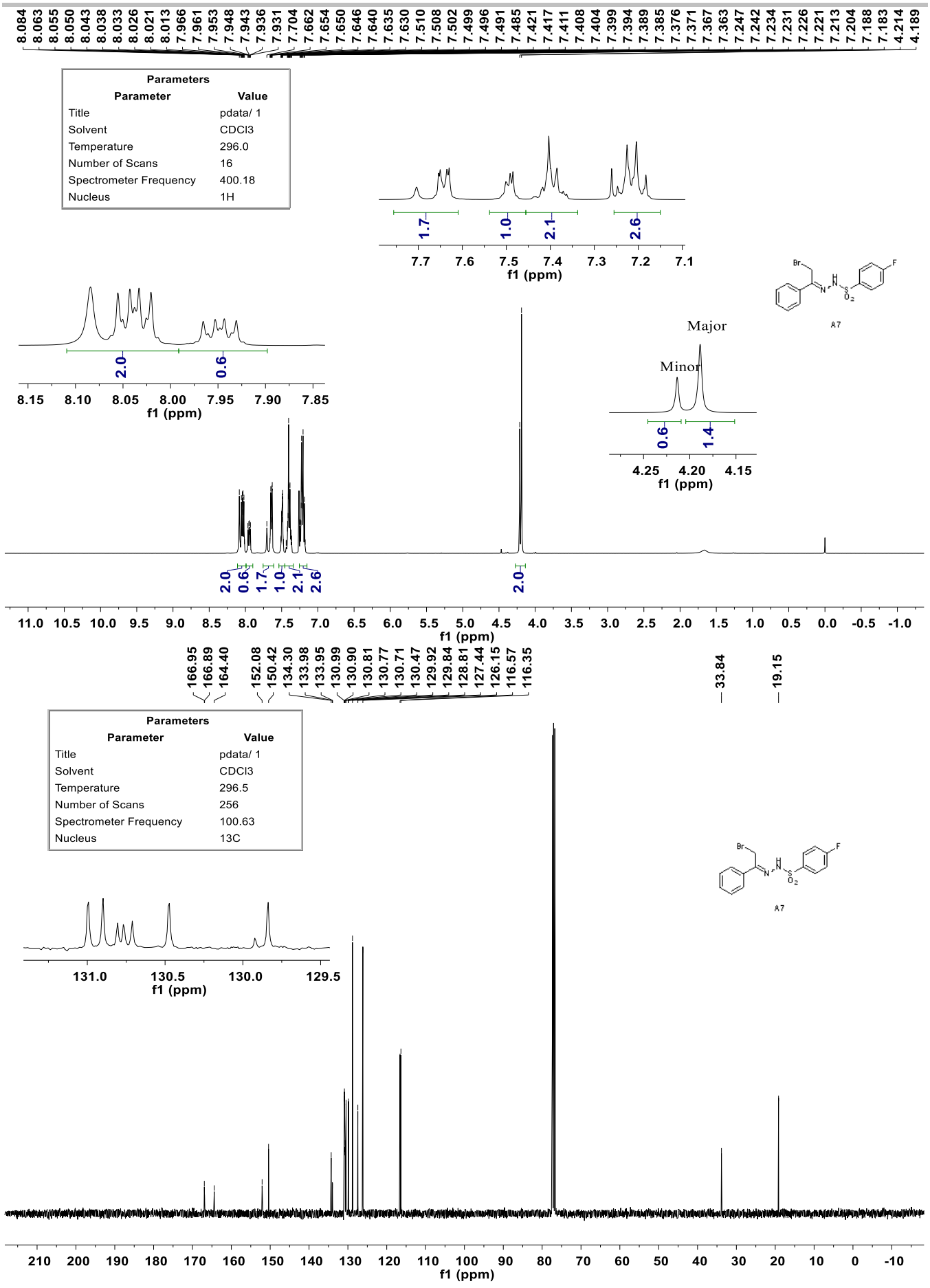
f1 (ppm)

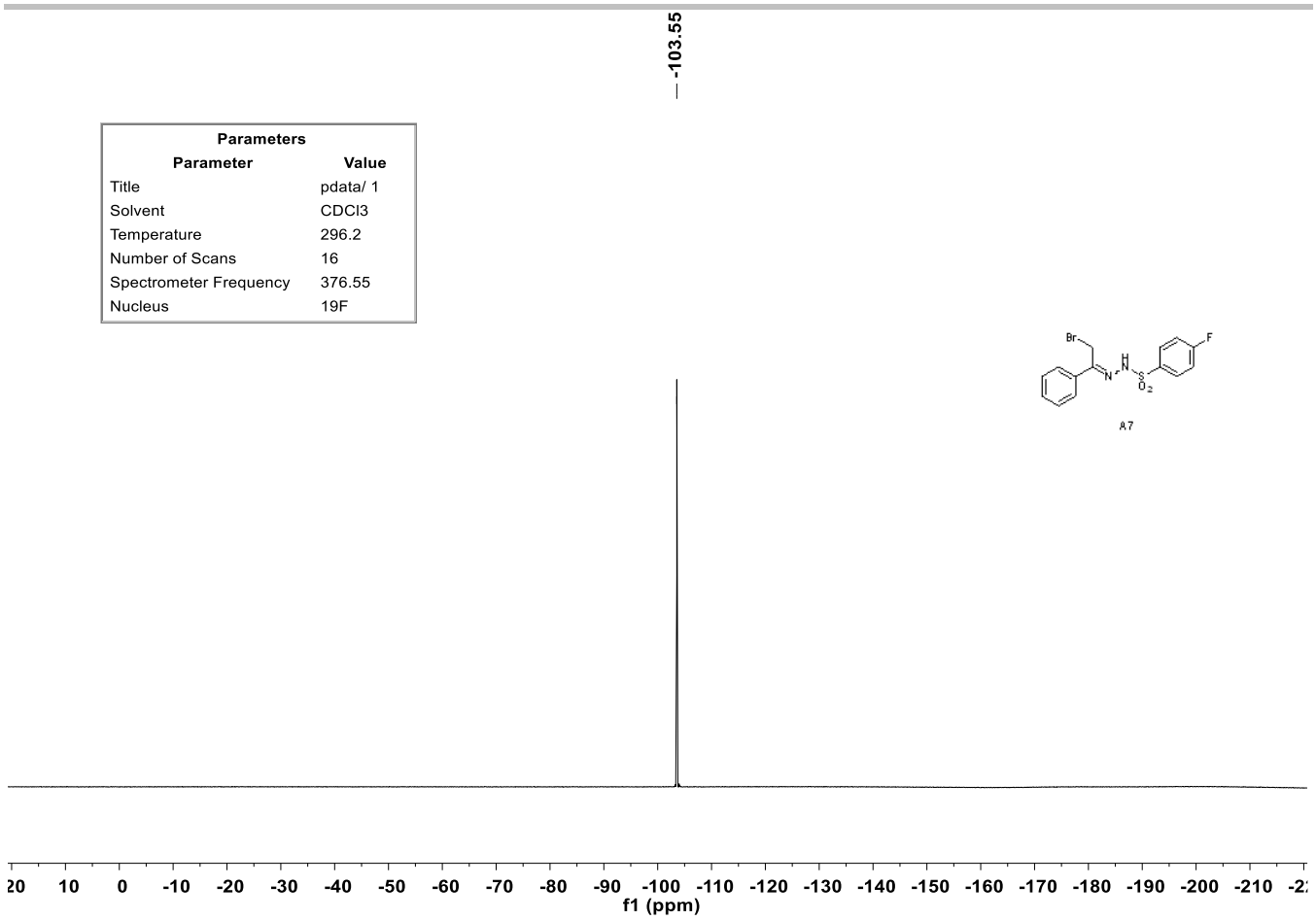

8.031 8.026 8.022 8.010 7.920 7.915 7.910 7.906 7.894 7.891 7.889 7.886 7.824 7.806 7.805 7.688 7.665 7.661 7.658 7.655 7.652 7.646 7.641 7.602 7.600 7.597 7.595 7.593 7.590 7.573 7.570 7.567 7.565 7.519 7.515 7.508 7.502 7.499 7.479 7.459 7.423 7.420 7.416 7.411 7.407 7.401 7.398 7.240 7.237 7.234 7.231 7.228 7.222 7.220 7.216 4.224 4.192
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.0
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
2.6 4.1 0.9
7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20
f1 (ppm)
Major
Minor
0.9 1.1
4.26 4.22 4.18 4.14
f1 (ppm)
A4
1.0 1.0 0.5 2.6 4.1 0.9 2.0
11.0 10.5 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 -0.5 -1
f1 (ppm)
150.81 139.72 139.58 135.35 135.29 134.17 133.73 133.64 130.83 130.59 130.42 130.39 129.88 128.85 128.27 127.94 127.42 126.20 126.02
33.70
19.10
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.5
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
131.0 130.5 130.0 129.5 129.0 128.5 128.0 127.5
f1 (ppm)
A4
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

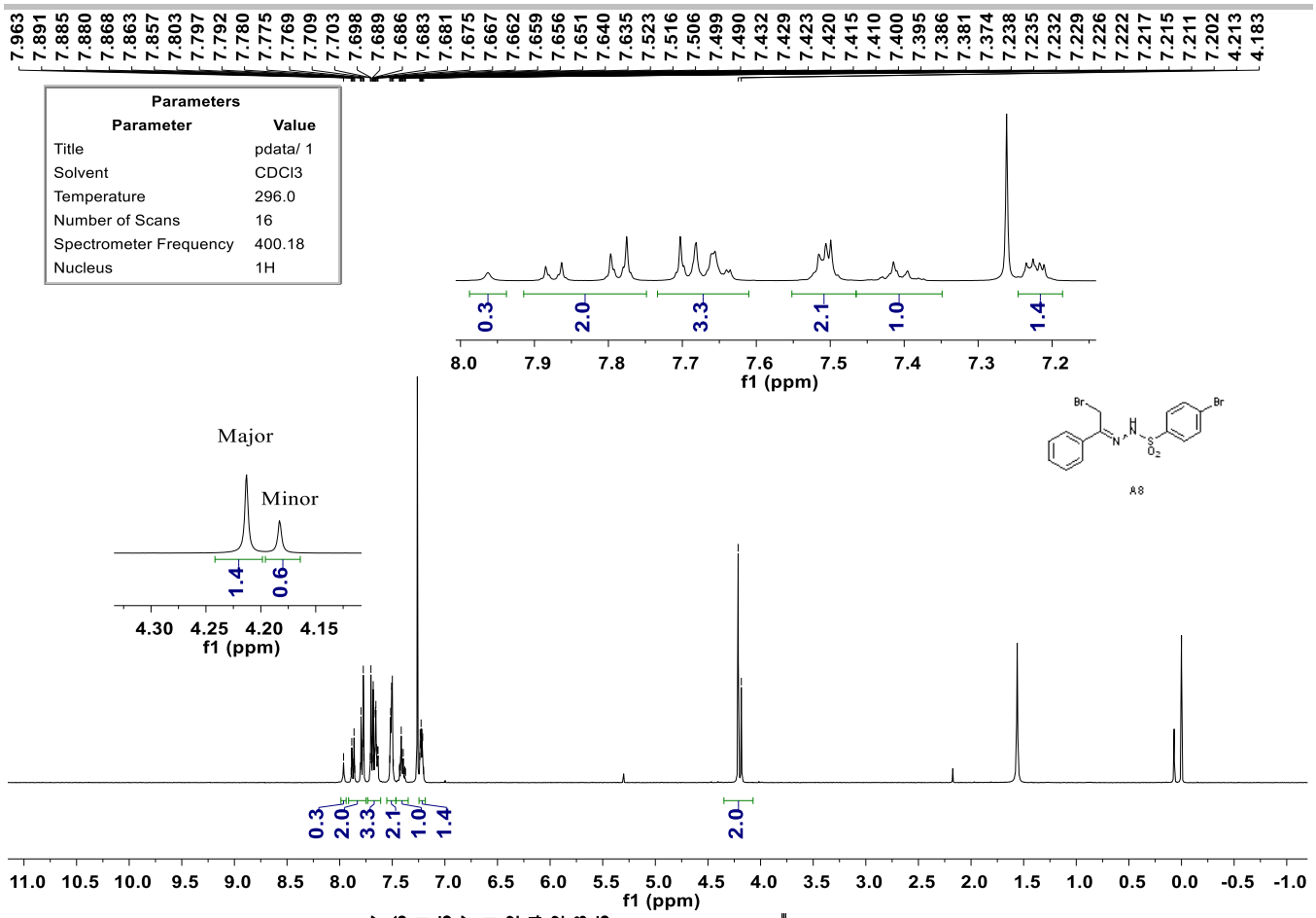

7.969 7.960 7.955 7.943 7.938 7.878 7.872 7.867 7.855 7.850 7.844 7.659 7.639 7.634 7.543 7.537 7.532 7.525 7.520 7.515 7.510 7.505 7.498 7.494 7.488 7.431 7.428 7.421 7.418 7.413 7.408 7.398 7.394 7.379 7.244 7.234 7.225 7.222 7.216 7.210 4.213 4.183
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 295.7
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
Major
Minor
1.8
0.2
4.28 4.26 4.24 4.22 4.20 4.18 4.16 4.14
f1 (ppm)
2.0
1.1
5.0
1.9
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)
Br
Cl
N
H
S
O2
A5
H2O
2.0
1.1
5.0
1.9
2.0
11.0 10.5 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 -0.5 -1.0
f1 (ppm)
152.11 136.55 130.80 129.87 129.56 129.48 129.36 128.84 127.43 126.14
33.77
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.4
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
Br
Cl
N
H
S
O2
A5
131 130 129 128 127 126
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

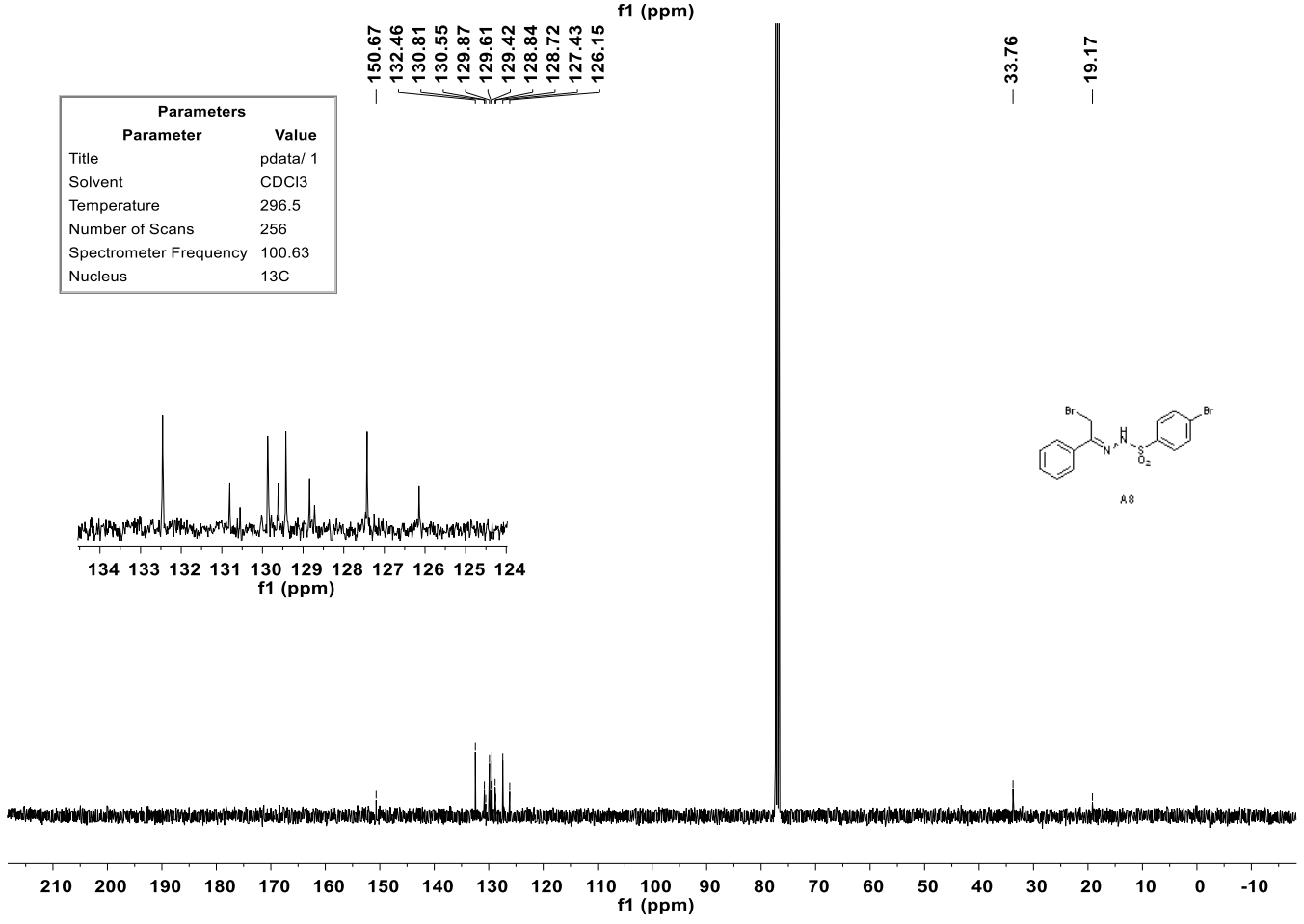

8.055 7.827 7.823 7.820 7.807 7.803 7.800 7.747 7.742 7.740 7.736 7.731 7.727 7.722 7.719 7.716 7.712 7.706 7.666 7.662 7.659 7.657 7.652 7.647 7.642 7.639 7.552 7.539 7.532 7.519 7.514 7.512 7.509 7.504 7.497 7.426 7.420 7.417 7.412 7.407 7.404 7.398 7.394 7.326 7.315 7.312 7.308 7.306 7.234 7.231 7.229 7.225 7.222 7.216 7.210 4.221 4.192
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 295.9
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
Major
Minor
0.6 3.0 2.3 2.7 0.9
0.9 1.1
f1 (ppm)
A6
0.5 0.6 3.0 2.3 2.7 0.9 2.0
f1 (ppm)
163.57 161.07 152.31 150.68 139.85 134.21 130.99 130.96 130.92 130.88 130.82 130.55 129.87 128.84 127.42 126.17 123.88 123.85 123.69 123.66 120.98 120.89 120.77 120.68 115.68 115.43 115.19 33.75 19.10
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.5
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
f1 (ppm)
f1 (ppm)
A6
f1 (ppm)

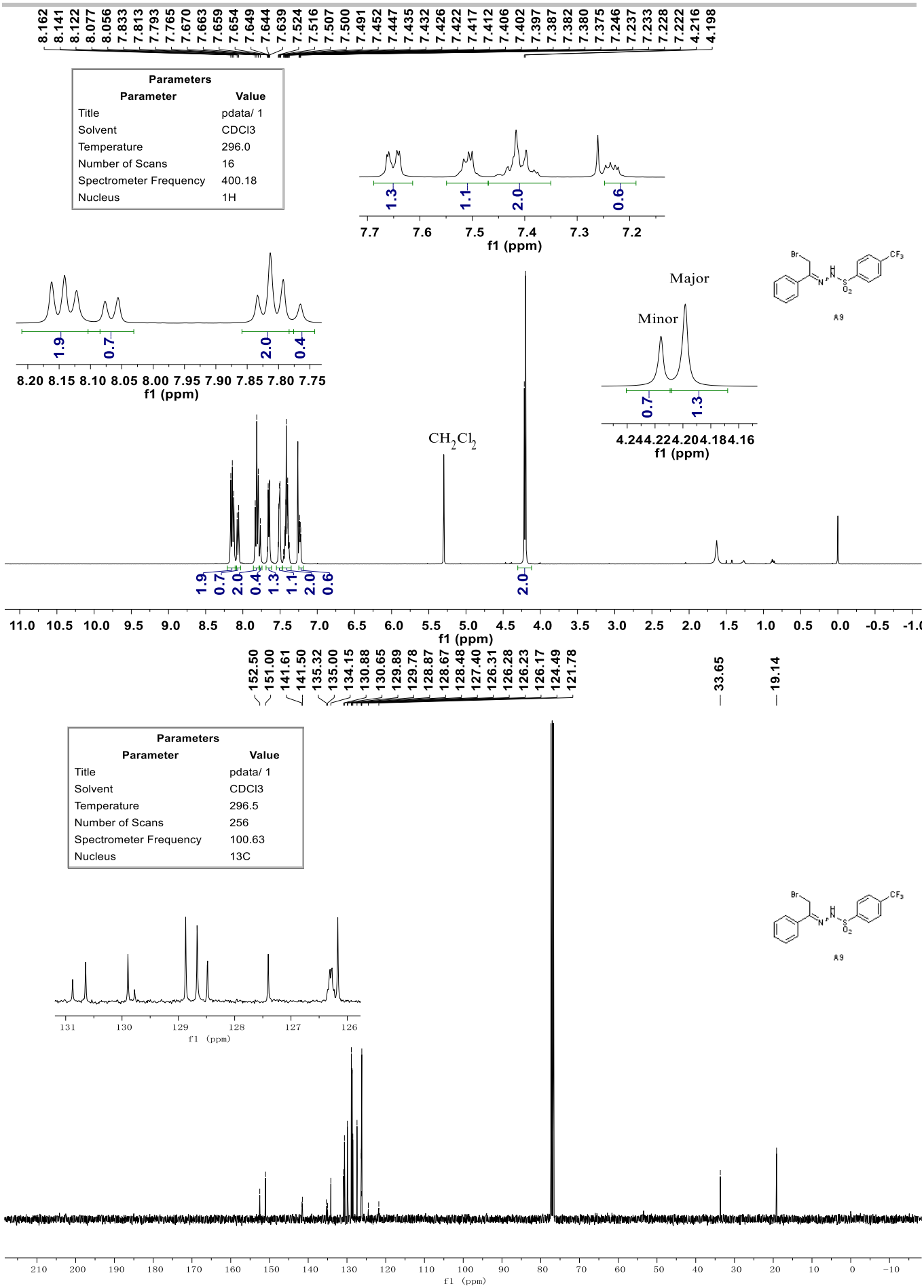

-109.46
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.2
Number of Scans 16
Spectrometer Frequency 376.55
Nucleus 19F
Br
N
H
N
S
O
O
F
A6
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

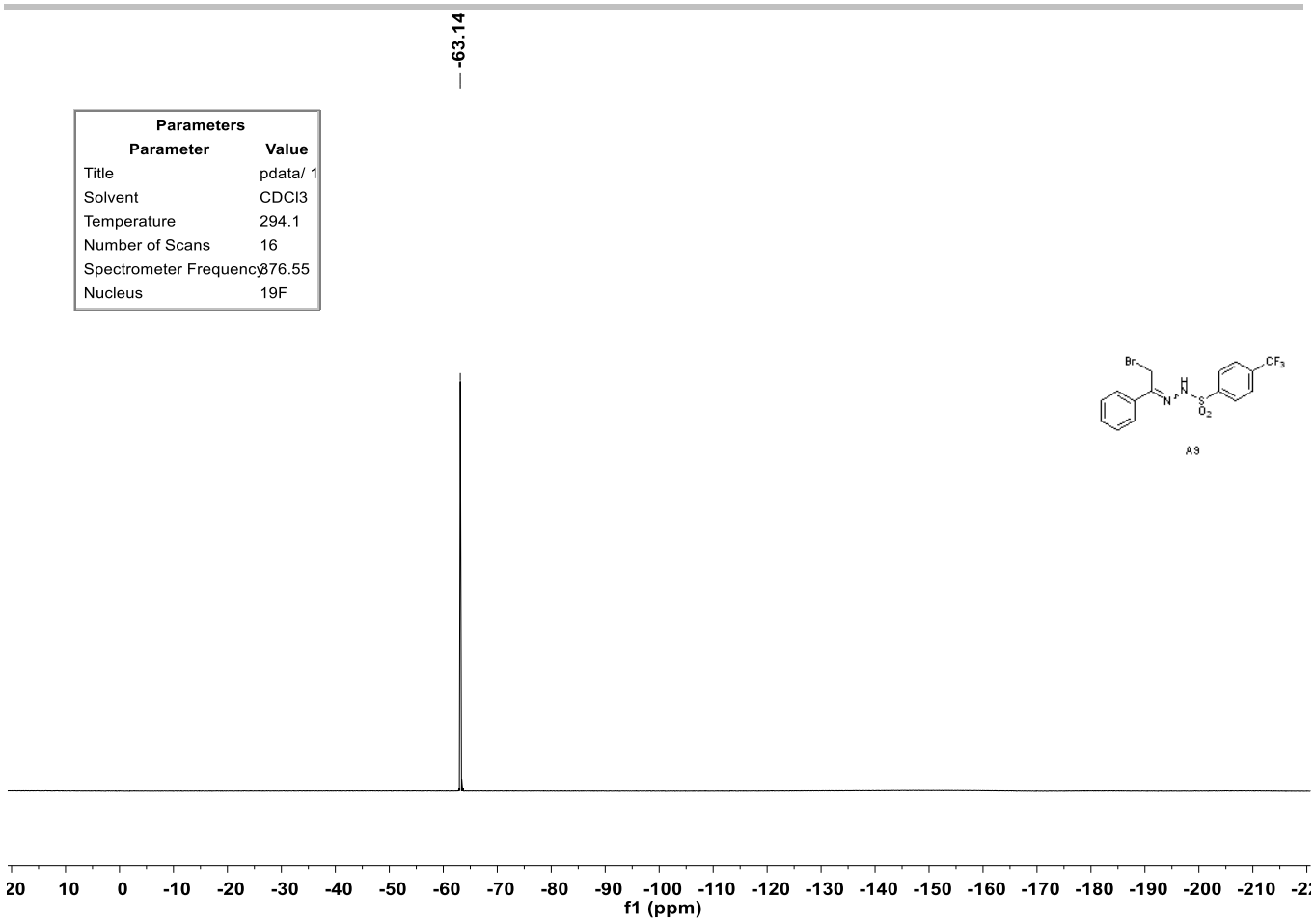

8.084 8.063 8.055 8.050 8.043 8.038 8.033 8.026 8.021 8.013 7.966 7.961 7.953 7.948 7.943 7.936 7.931 7.704 7.662 7.654 7.650 7.646 7.640 7.635 7.630 7.510 7.508 7.502 7.499 7.496 7.491 7.485 7.421 7.417 7.411 7.408 7.404 7.399 7.394 7.389 7.385 7.376 7.371 7.367 7.363 7.247 7.242 7.234 7.231 7.226 7.221 7.213 7.204 7.188 7.183 4.214 4.189
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.0
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
1.7 1.0 2.1 2.6
7.7 7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)
2.0 0.6
8.15 8.10 8.05 8.00 7.95 7.90 7.85
f1 (ppm)
Br F N H S O2
A7
Major
Minor
0.6 1.4
4.25 4.20 4.15
f1 (ppm)
2.0 0.6 1.7 1.0 2.1 2.6
2.0
11.0 10.5 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 -0.5 -1.0
f1 (ppm)
166.95 166.89 164.40 152.08 150.42 134.30 133.98 133.95 130.99 130.90 130.81 130.77 130.71 130.47 129.92 129.84 128.81 127.44 126.15 116.57 116.35
33.84 19.15
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.5
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
131.0 130.5 130.0 129.5
f1 (ppm)
Br F N H S O2
A7
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

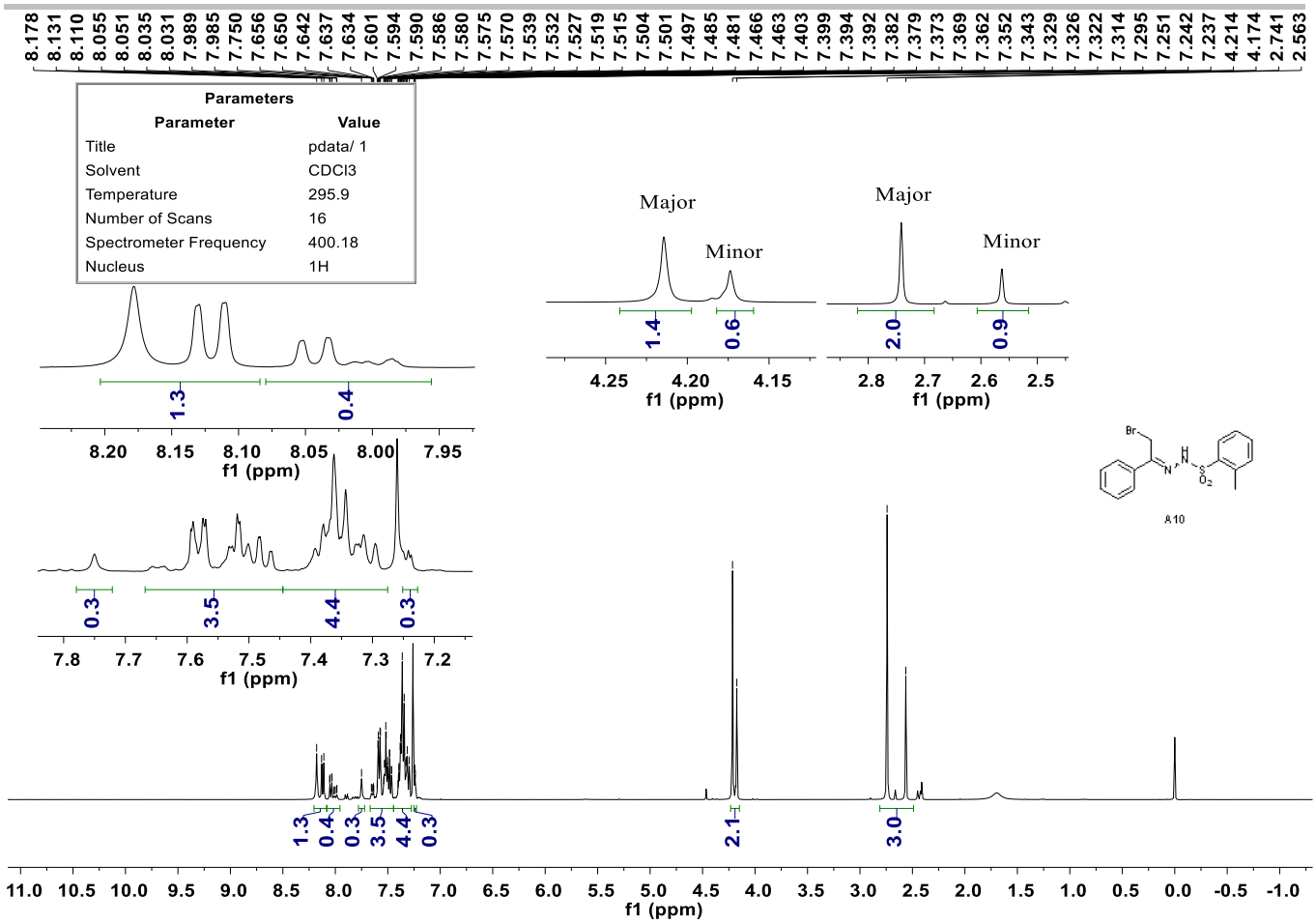

-103.55
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.2
Number of Scans 16
Spectrometer Frequency 376.55
Nucleus 19F
Br
F
A7
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

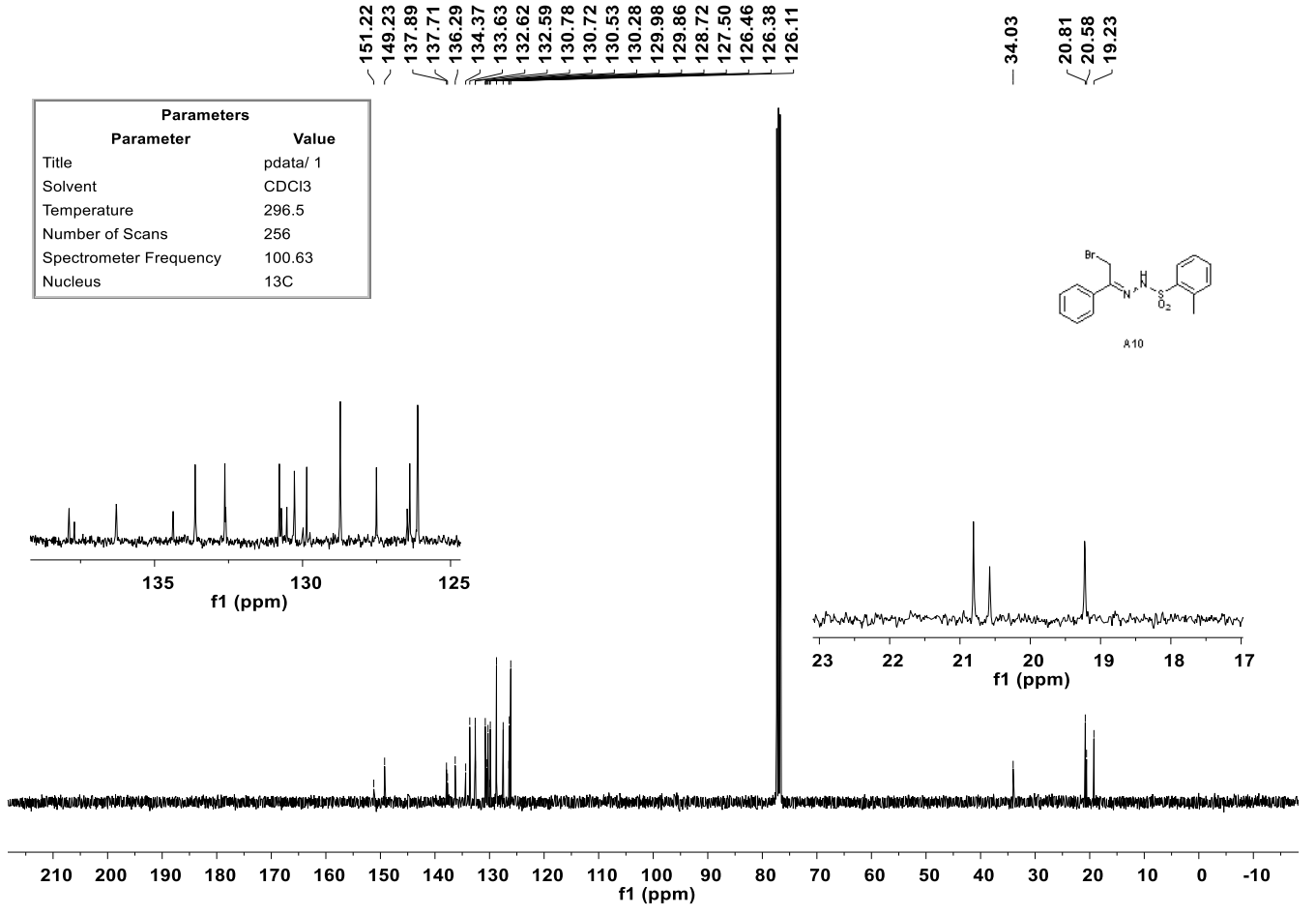

7.963 7.891 7.885 7.880 7.868 7.863 7.857 7.803 7.797 7.792 7.780 7.775 7.769 7.709 7.703 7.698 7.689 7.686 7.683 7.681 7.675 7.667 7.662 7.659 7.656 7.651 7.640 7.635 7.523 7.516 7.506 7.499 7.490 7.432 7.429 7.423 7.420 7.415 7.410 7.400 7.395 7.386 7.381 7.374 7.238 7.235 7.232 7.229 7.226 7.222 7.217 7.215 7.211 7.202 4.213 4.183
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.0
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
0.3 2.0 3.3 2.1 1.0 1.4
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
f1 (ppm)
Major
Minor
1.4 0.6
4.30 4.25 4.20 4.15
f1 (ppm)
Br
Br
N
H
S
O2
A8
0.3 2.0 3.3 2.1 1.0 1.4
2.0
11.0 10.5 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 -0.5 -1.0
f1 (ppm)

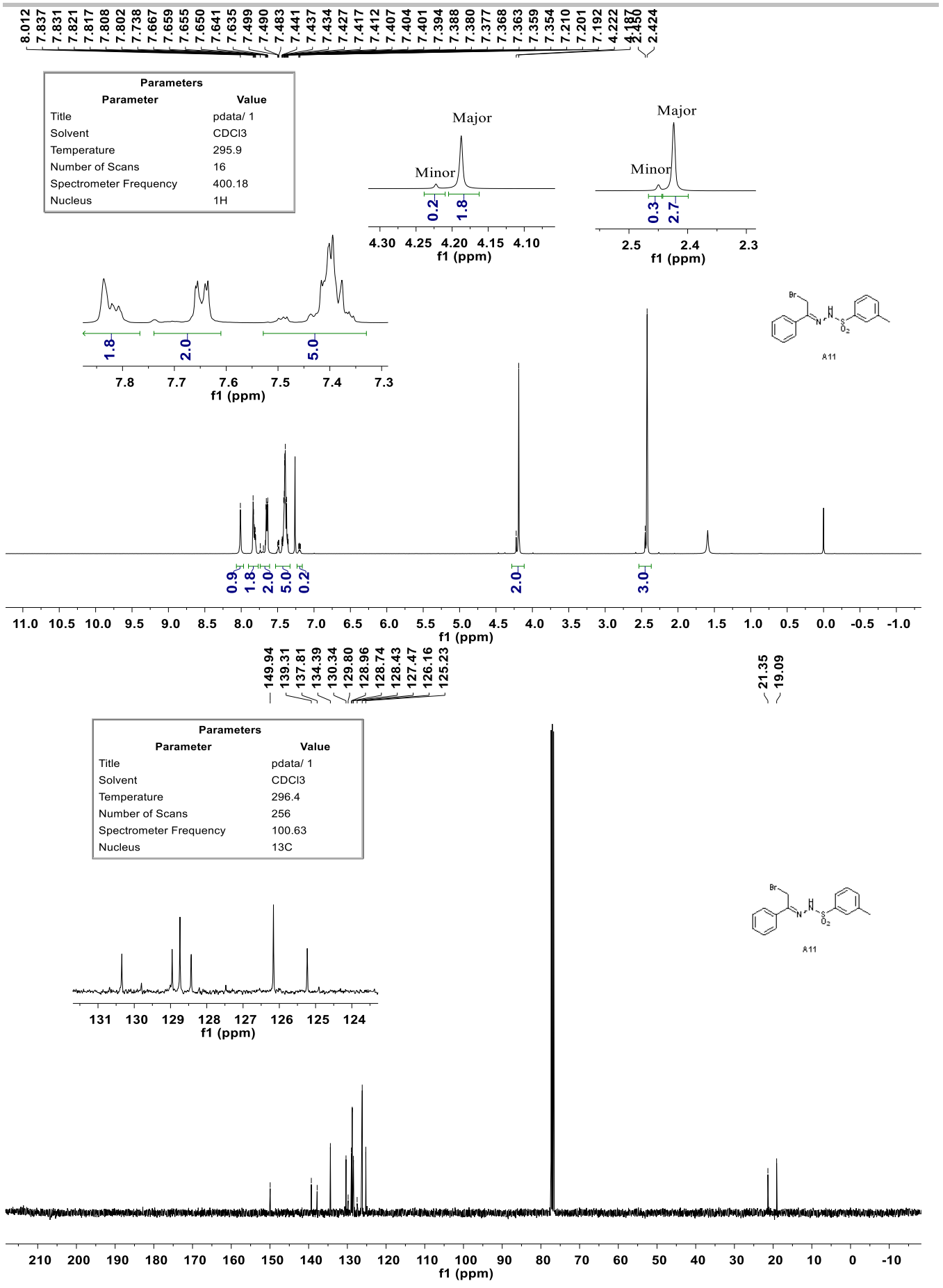

150.67 132.46 130.81 130.55 129.87 129.61 129.42 128.84 128.72 127.43 126.15
33.76
19.17
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.5
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
134 133 132 131 130 129 128 127 126 125 124
f1 (ppm)
Br
Br
N
H
S
O2
A8
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

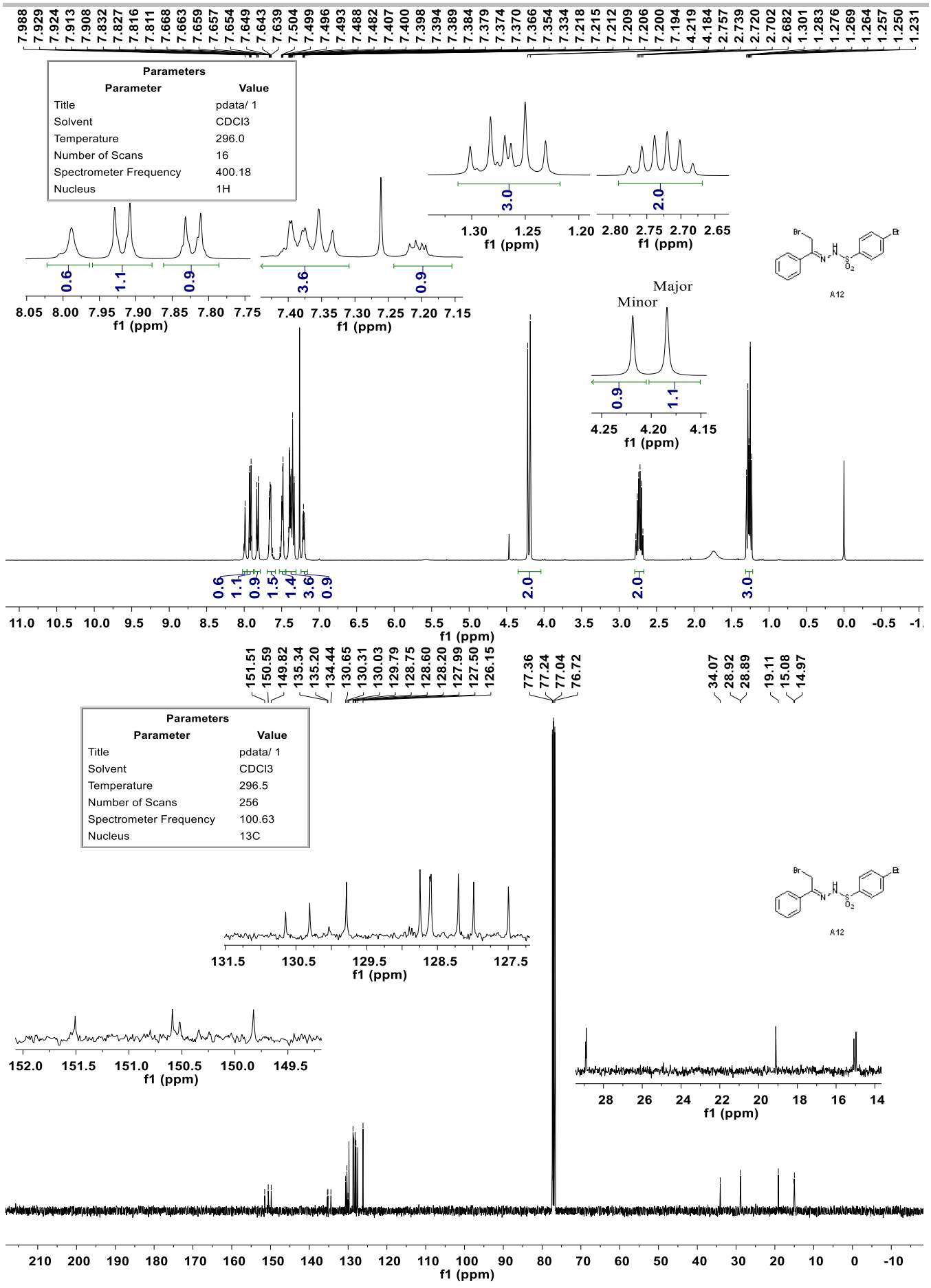

8.162 8.141 8.122 8.077 8.056 7.833 7.813 7.793 7.765 7.670 7.663 7.659 7.654 7.649 7.644 7.639 7.524 7.516 7.507 7.500 7.491 7.452 7.447 7.435 7.432 7.426 7.422 7.417 7.412 7.406 7.402 7.397 7.387 7.382 7.380 7.375 7.246 7.237 7.233 7.228 7.222 4.216 4.198
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.0
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
1.3 1.1 2.0 0.6
7.7 7.6 7.5 7.4 7.3 7.2
f1 (ppm)
1.9 0.7 2.0 0.4
8.20 8.15 8.10 8.05 8.00 7.95 7.90 7.85 7.80 7.75
f1 (ppm)
Major
Minor
0.7 1.3
4.244.224.204.184.16
f1 (ppm)
A9
CH2Cl2
1.9 0.7 2.0 0.4 1.3 1.1 2.0 0.6
2.0
11.0 10.5 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 -0.5
f1 (ppm)
152.50 151.00 141.61 141.50 135.32 135.00 134.15 130.88 130.65 129.89 129.78 128.87 128.67 128.48 127.40 126.31 126.28 126.23 126.17 124.49 121.78
33.65
19.14
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.5
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
A9
131 130 129 128 127 126
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

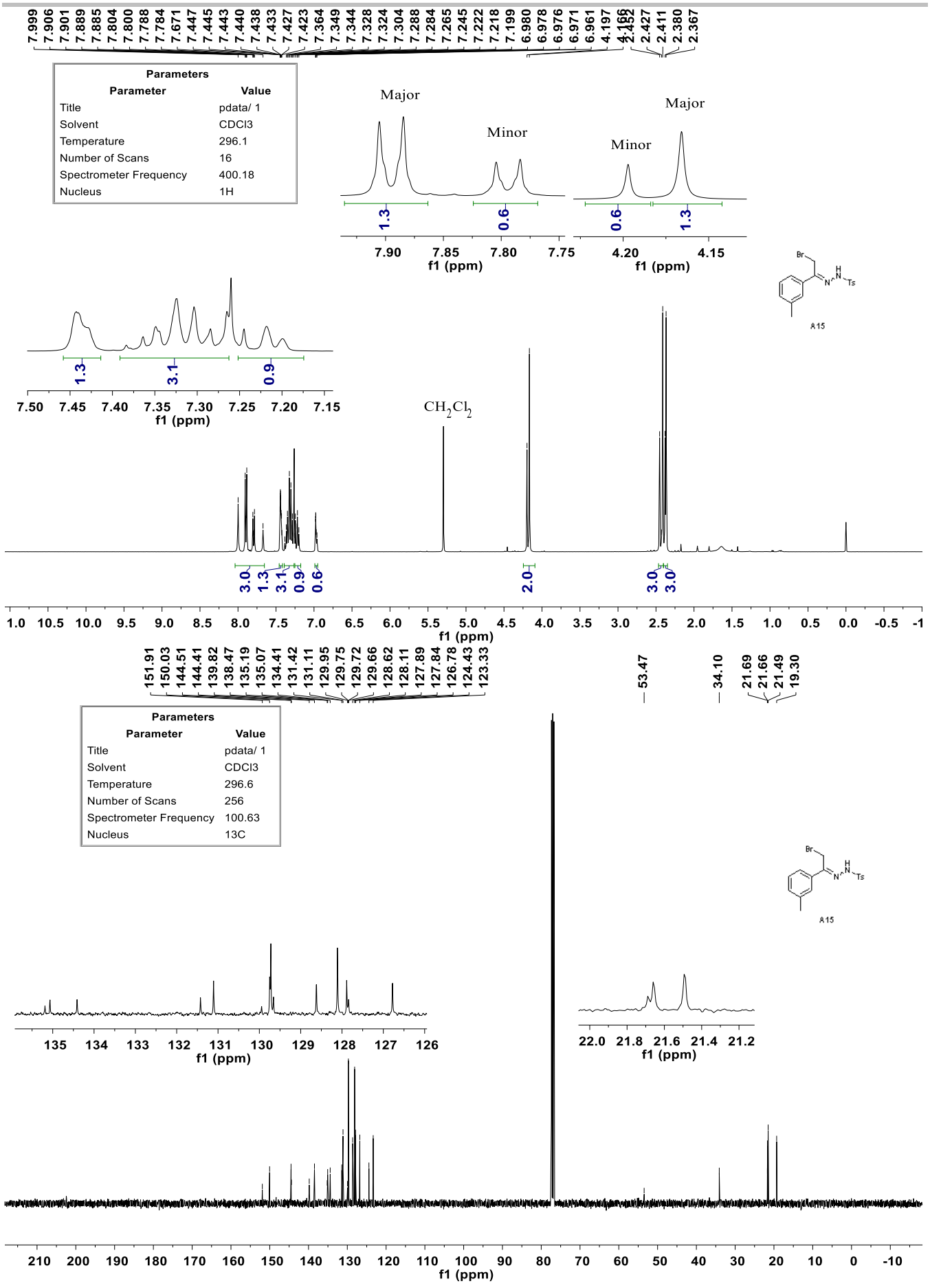

-63.14
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.1
Number of Scans 16
Spectrometer Frequency 376.55
Nucleus 19F
Br
CF3
A9
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

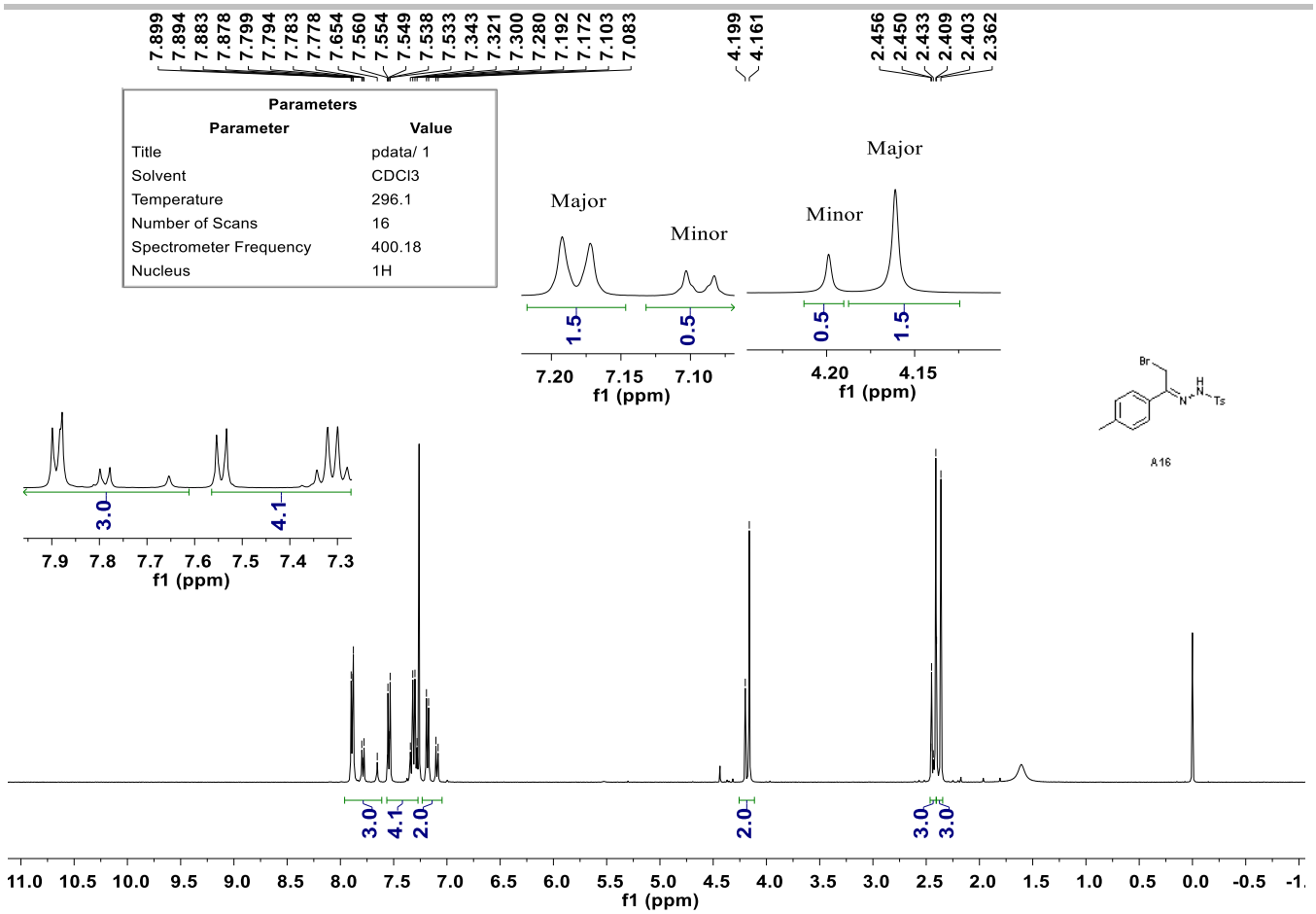

8.178 8.131 8.110 8.055 8.051 8.035 8.031 7.989 7.985 7.750 7.656 7.650 7.642 7.637 7.634 7.601 7.594 7.590 7.586 7.580 7.575 7.570 7.539 7.532 7.527 7.519 7.515 7.504 7.501 7.497 7.485 7.481 7.466 7.463 7.403 7.399 7.394 7.392 7.382 7.379 7.373 7.369 7.362 7.352 7.343 7.329 7.326 7.322 7.314 7.295 7.251 7.242 7.237 4.214 4.174 2.741 2.563
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 295.9
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
Major
Minor
Major
Minor
1.4
0.6
2.0
0.9
4.25 4.20 4.15
2.8 2.7 2.6 2.5
f1 (ppm)
1.3
0.4
8.20 8.15 8.10 8.05 8.00 7.95
f1 (ppm)
0.3
3.5
4.4
0.3
7.8 7.7 7.6 7.5 7.4 7.3 7.2
f1 (ppm)
Br
N
H
S
O2
A10
1.3 0.4 0.3 3.5 4.4 0.3
2.1
3.0
11.0 10.5 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 -0.5 -1.0
f1 (ppm)

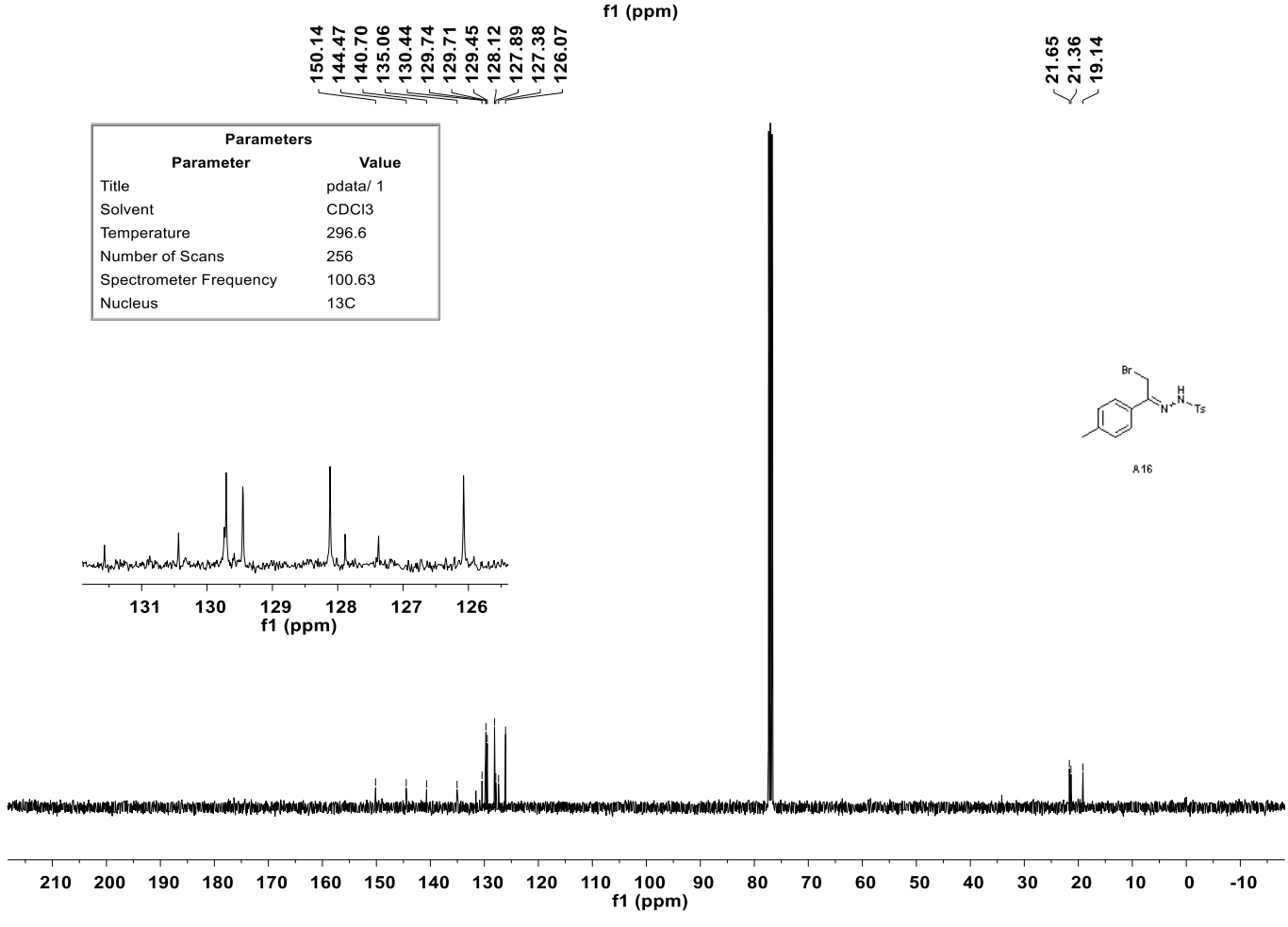

151.22 149.23 137.89 137.71 136.29 134.37 133.63 132.62 132.59 130.78 130.72 130.53 130.28 129.98 129.86 128.72 127.50 126.46 126.38 126.11
34.03
20.81 20.58 19.23
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.5
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
Br
N
H
S
O2
A10
135 130 125
f1 (ppm)
23 22 21 20 19 18 17
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

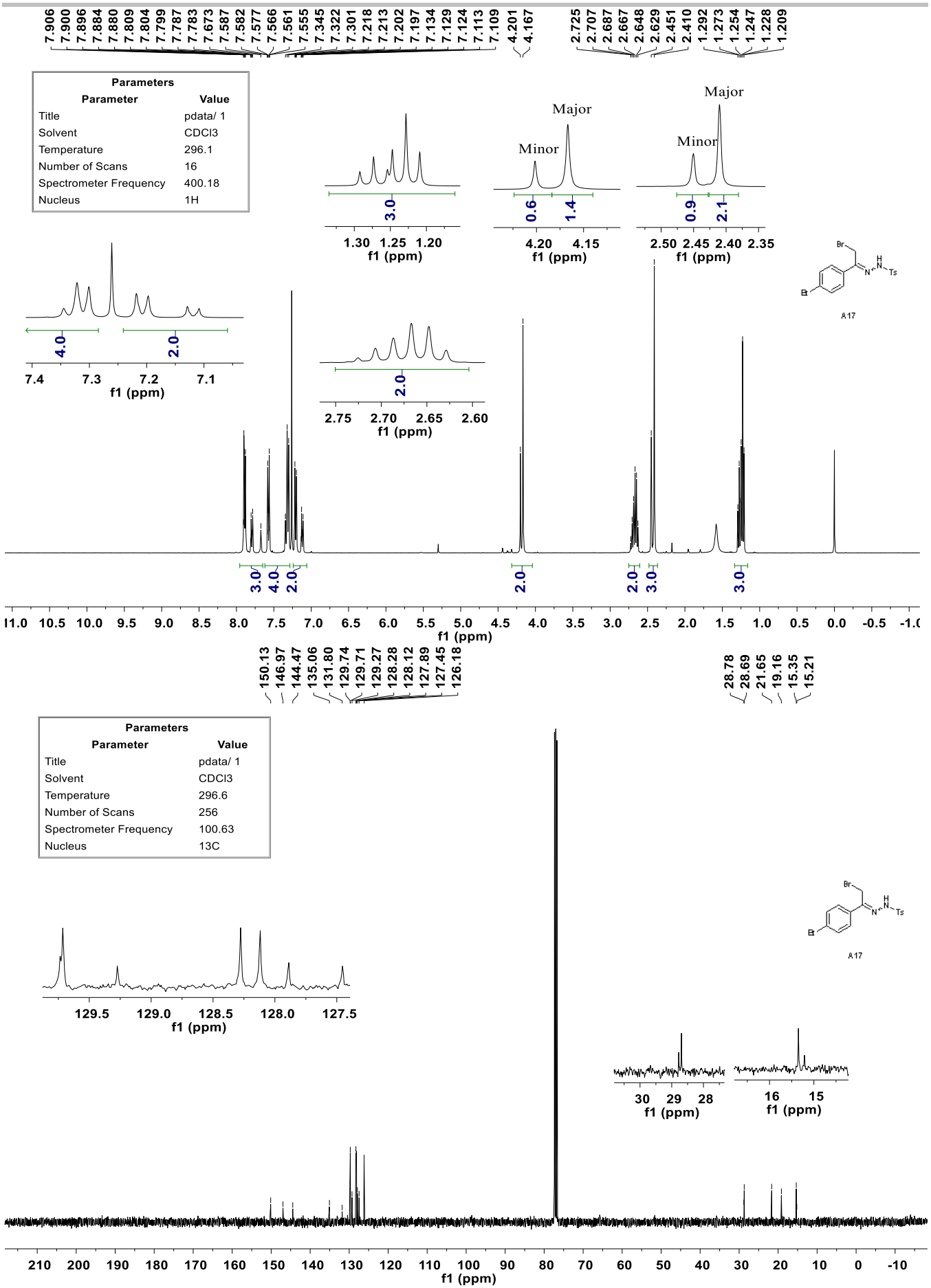

8.012 7.837 7.831 7.821 7.817 7.808 7.802 7.738 7.667 7.659 7.655 7.650 7.641 7.635 7.499 7.490 7.483 7.441 7.437 7.434 7.427 7.417 7.412 7.407 7.404 7.401 7.394 7.388 7.380 7.377 7.368 7.363 7.359 7.354 7.210 7.201 7.192 4.222 4.187 4.150 2.424
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 295.9
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
Major
Minor
0.2
1.8
4.30 4.25 4.20 4.15 4.10
f1 (ppm)
Major
Minor
0.3
2.7
2.5 2.4 2.3
f1 (ppm)
1.8
2.0
5.0
7.8 7.7 7.6 7.5 7.4 7.3
f1 (ppm)
A11
0.9 1.8 2.0 5.0 0.2 2.0 3.0
11.0 10.5 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 -0.5 -1.0
f1 (ppm)
149.94 139.31 137.81 134.39 130.34 129.80 128.96 128.74 128.43 127.47 126.16 125.23
21.35 19.09
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.4
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
131 130 129 128 127 126 125 124
f1 (ppm)
A11
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

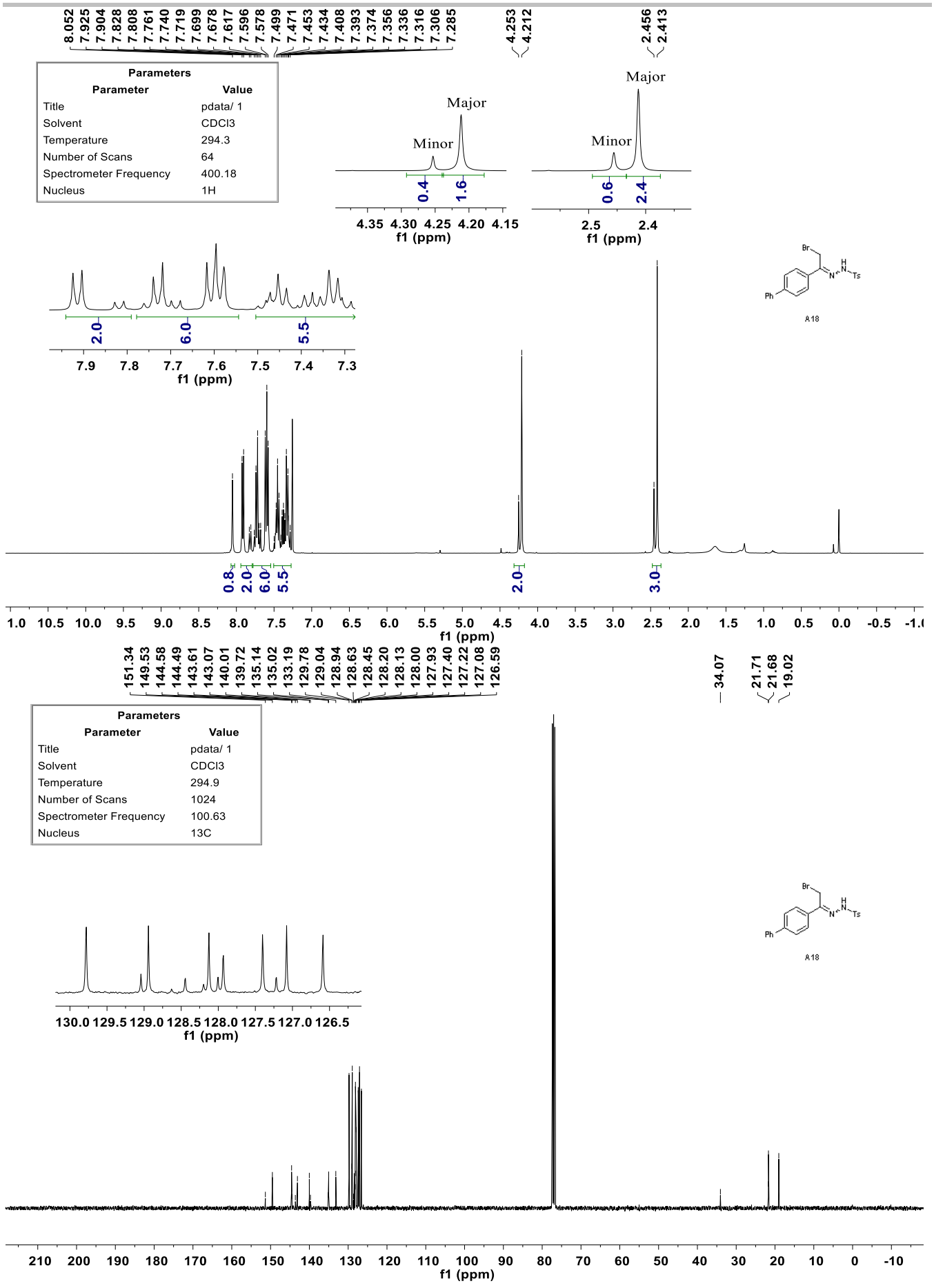

Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.0
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
Major
Minor
A12
f1 (ppm)
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.5
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
A12
f1 (ppm)

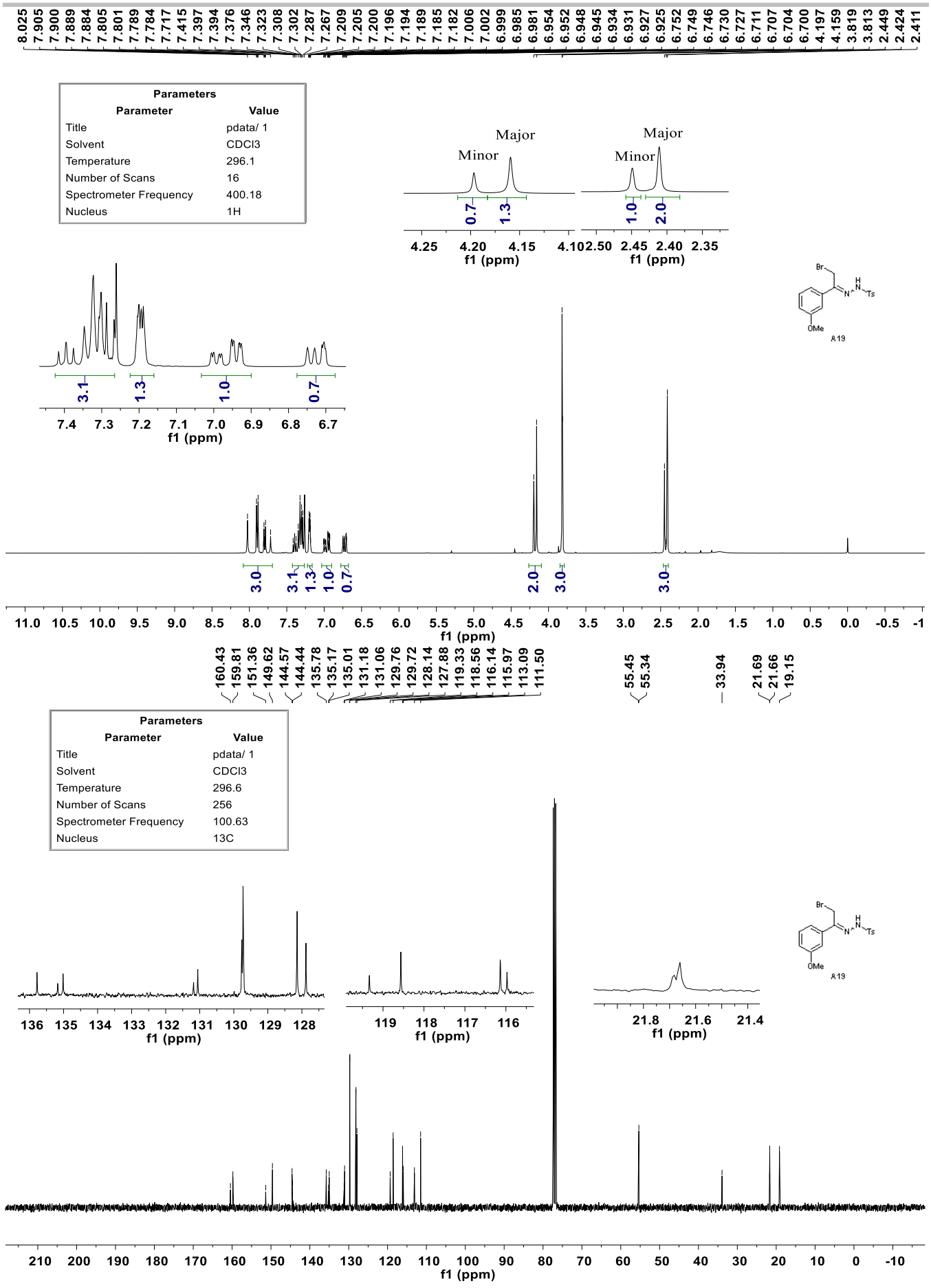

7.999 7.906 7.901 7.889 7.885 7.804 7.800 7.788 7.784 7.671 7.447 7.445 7.443 7.440 7.438 7.433 7.427 7.423 7.364 7.349 7.344 7.328 7.324 7.304 7.288 7.284 7.265 7.245 7.222 7.218 7.199 6.980 6.978 6.976 6.971 6.961 4.197 4.166 2.432 2.427 2.411 2.380 2.367
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.1
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
Major
Minor
Major
Minor
1.3
0.6
0.6
1.3
7.90 7.85 7.80 7.75
f1 (ppm)
4.20 4.15
f1 (ppm)
Br
N
H
N
Ts
A15
1.3
3.1
0.9
7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15
f1 (ppm)
CH2Cl2
3.0 1.3 3.1 0.9 0.6 2.0 3.0 3.0
1.0 10.5 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 -0.5 -1
f1 (ppm)
151.91 150.03 144.51 144.41 139.82 138.47 135.19 135.07 134.41 131.42 131.11 129.95 129.75 129.72 129.66 128.62 128.11 127.89 127.84 126.78 124.43 123.33
53.47
34.10
21.69 21.66 21.49 19.30
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.6
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
Br
N
H
N
Ts
A15
135 134 133 132 131 130 129 128 127 126
f1 (ppm)
22.0 21.8 21.6 21.4 21.2
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

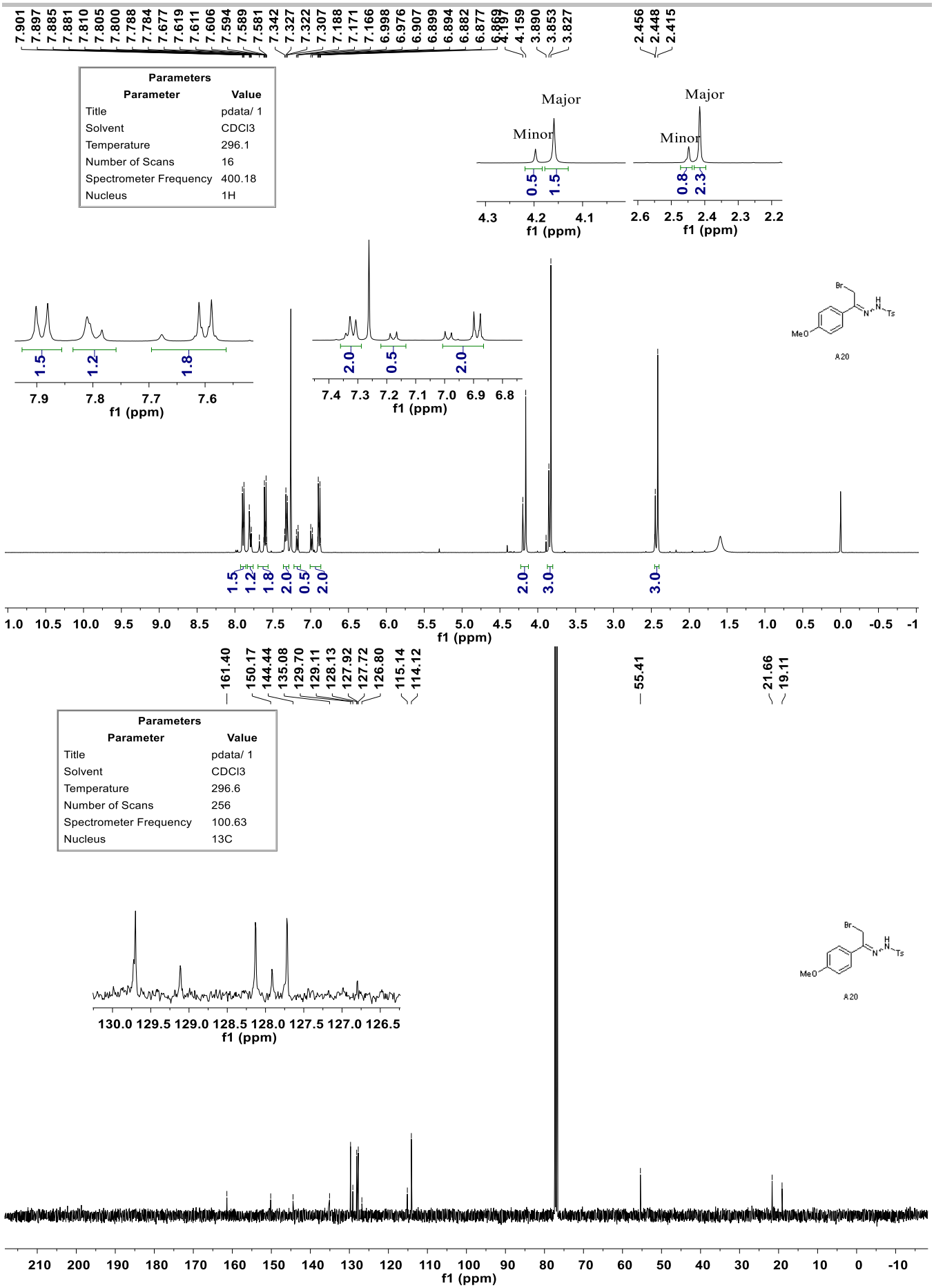

7.899 7.894 7.883 7.878 7.799 7.794 7.783 7.778 7.654 7.560 7.554 7.549 7.538 7.533 7.343 7.321 7.300 7.280 7.192 7.172 7.103 7.083
4.199 4.161
2.456 2.450 2.433 2.409 2.403 2.362
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.1
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
Major
Minor
Major
Minor
1.5 0.5
0.5 1.5
7.20 7.15 7.10
4.20 4.15
f1 (ppm)
A16
3.0 4.1
7.9 7.8 7.7 7.6 7.5 7.4 7.3
f1 (ppm)
3.0 4.1 2.0 2.0 3.0 3.0
11.0 10.5 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 -0.5
f1 (ppm)

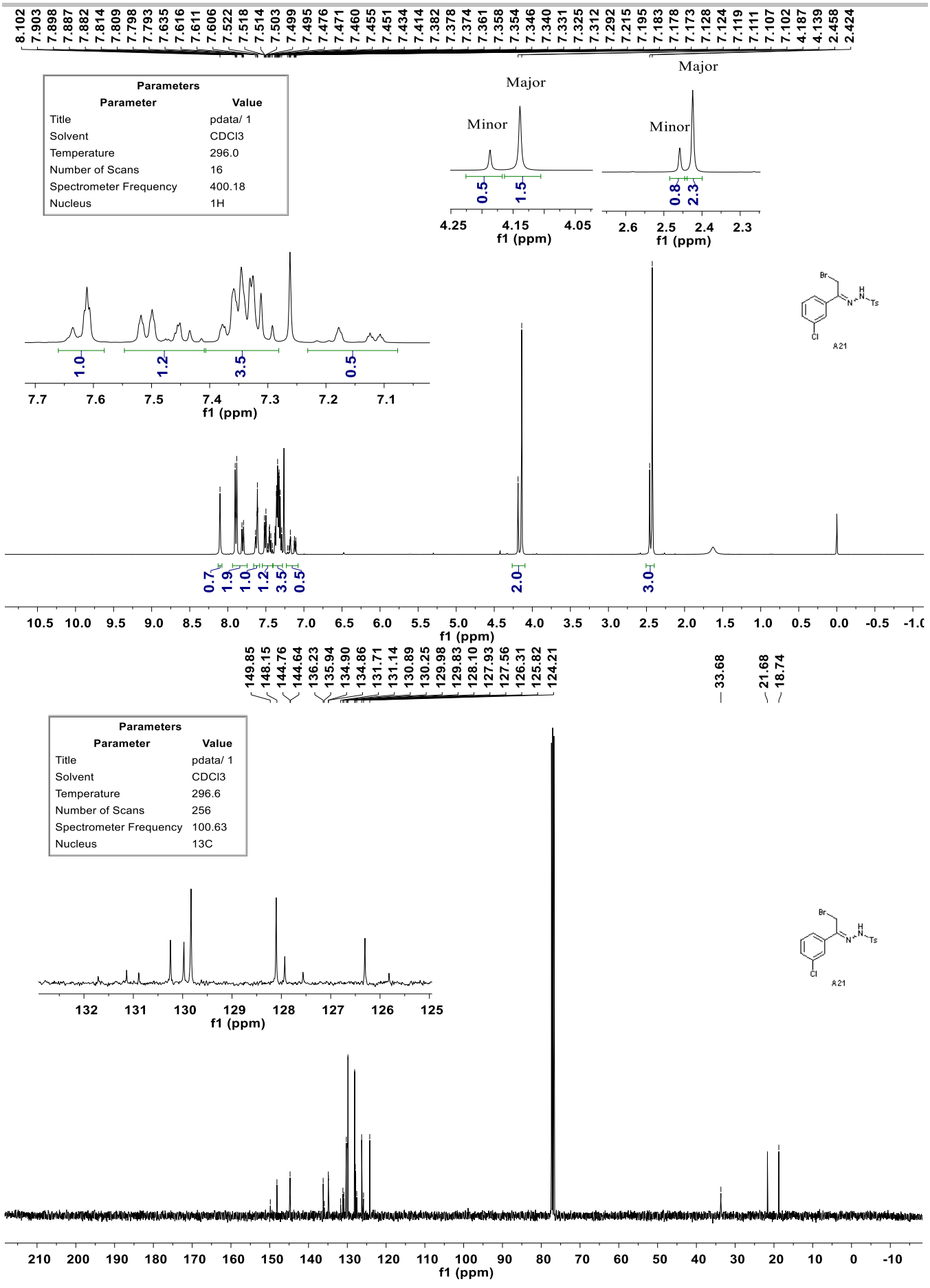

150.14 144.47 140.70 135.06 130.44 129.74 129.71 129.45 128.12 127.89 127.38 126.07
21.65 21.36 19.14
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.6
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
A16
131 130 129 128 127 126
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

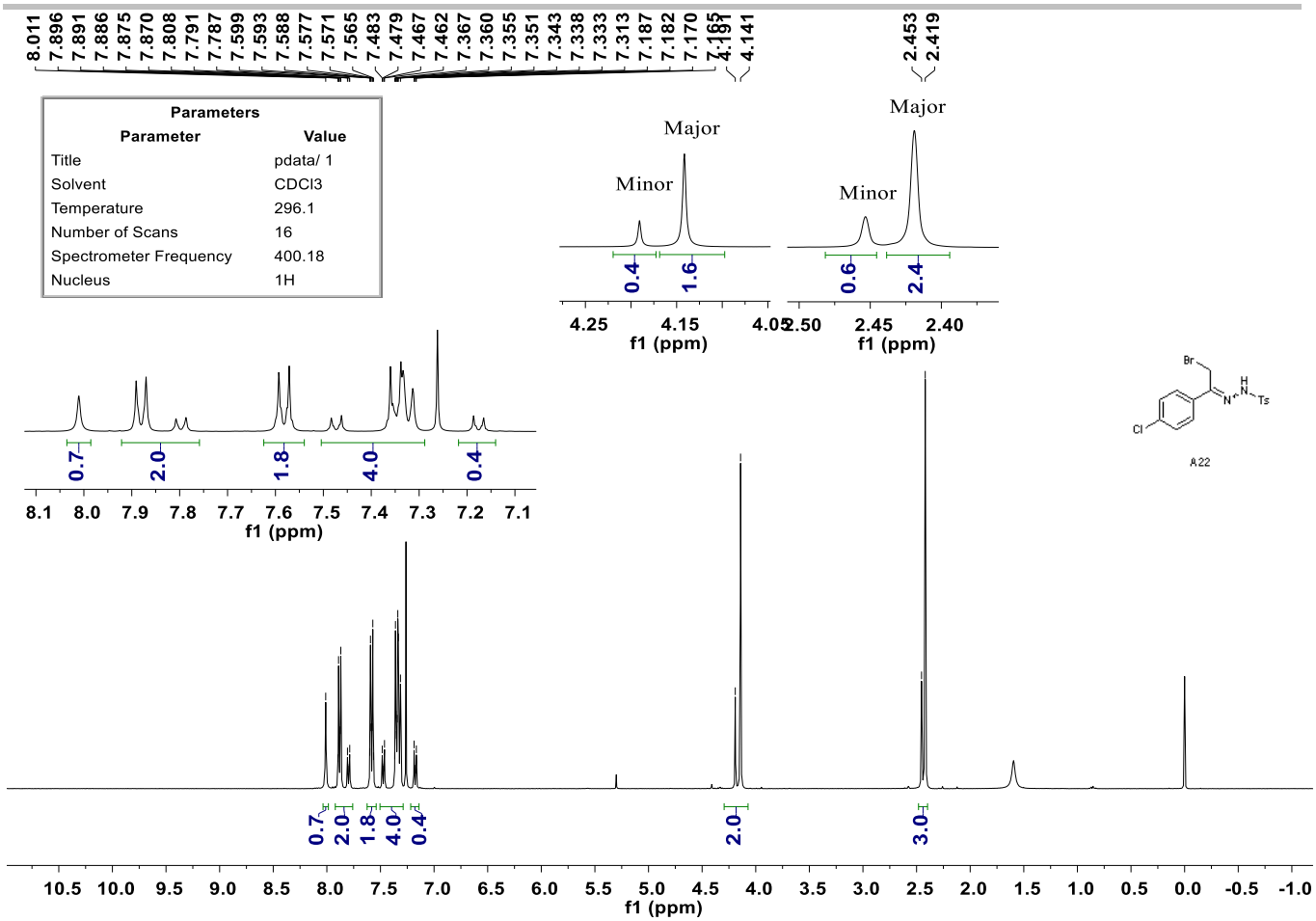

7.906 7.900 7.896 7.884 7.880 7.809 7.804 7.799 7.787 7.783 7.673 7.587 7.582 7.577 7.566 7.561 7.555 7.345 7.322 7.301 7.218 7.213 7.202 7.197 7.134 7.129 7.124 7.113 7.109 4.201 4.167 2.725 2.707 2.687 2.667 2.648 2.629 2.451 2.410 1.292 1.273 1.254 1.247 1.228 1.209
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.1
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
Major
Minor
Major
Minor
3.0
0.6
1.4
0.9
2.1
1.30 1.25 1.20
4.20 4.15
2.50 2.45 2.40 2.35
f1 (ppm)
A17
4.0
2.0
2.0
7.4 7.3 7.2 7.1
2.75 2.70 2.65 2.60
f1 (ppm)
3.0 4.0 2.0 2.0 2.0 3.0 3.0
f1 (ppm)
150.13 146.97 144.47 135.06 131.80 129.74 129.71 129.27 128.28 128.12 127.89 127.45 126.18
28.78 28.69 21.65 19.16 15.35 15.21
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.6
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
A17
129.5 129.0 128.5 128.0 127.5
30 29 28
16 15
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

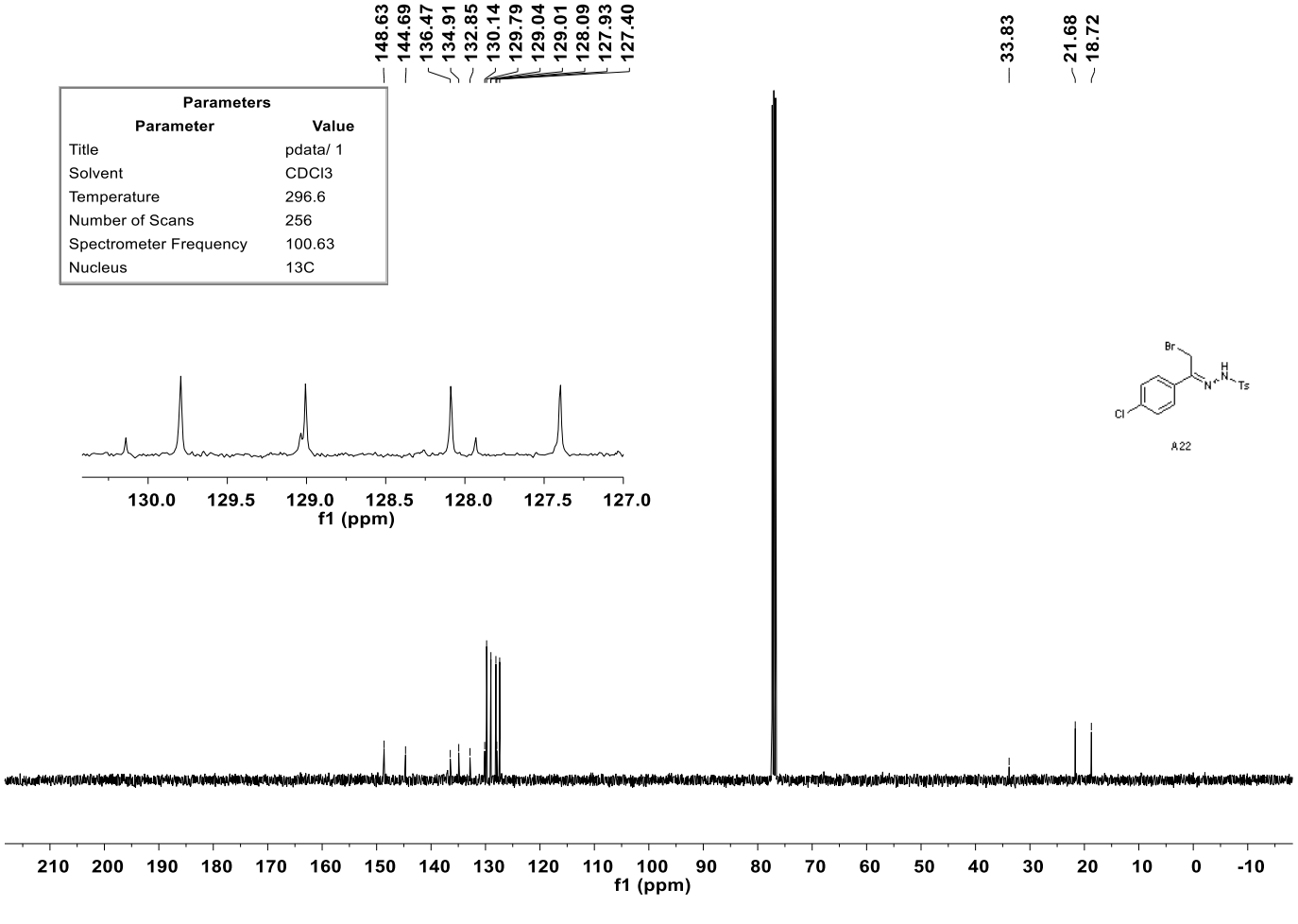

8.052 7.925 7.904 7.828 7.808 7.761 7.740 7.719 7.699 7.678 7.617 7.596 7.578 7.499 7.471 7.453 7.434 7.408 7.393 7.374 7.356 7.336 7.316 7.306 7.285
4.253 4.212
2.456 2.413
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.3
Number of Scans 64
Spectrometer Frequency 400.18
Nucleus 1H
Major
Minor
0.4 1.6
4.35 4.30 4.25 4.20 4.15
f1 (ppm)
Major
Minor
0.6 2.4
2.5 2.4
f1 (ppm)
2.0 6.0 5.5
7.9 7.8 7.7 7.6 7.5 7.4 7.3
f1 (ppm)
Br
Ph
Ts
A18
0.8 2.0 6.0 5.5 2.0 3.0
1.0 10.5 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 -0.5
f1 (ppm)
151.34 149.53 144.58 144.49 143.61 143.07 140.01 139.72 135.14 135.02 133.19 129.78 129.04 128.94 128.63 128.45 128.20 128.13 128.00 127.93 127.40 127.22 127.08 126.59
34.07
21.71 21.68 19.02
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.9
Number of Scans 1024
Spectrometer Frequency 100.63
Nucleus 13C
130.0 129.5 129.0 128.5 128.0 127.5 127.0 126.5
f1 (ppm)
Br
Ph
Ts
A18
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

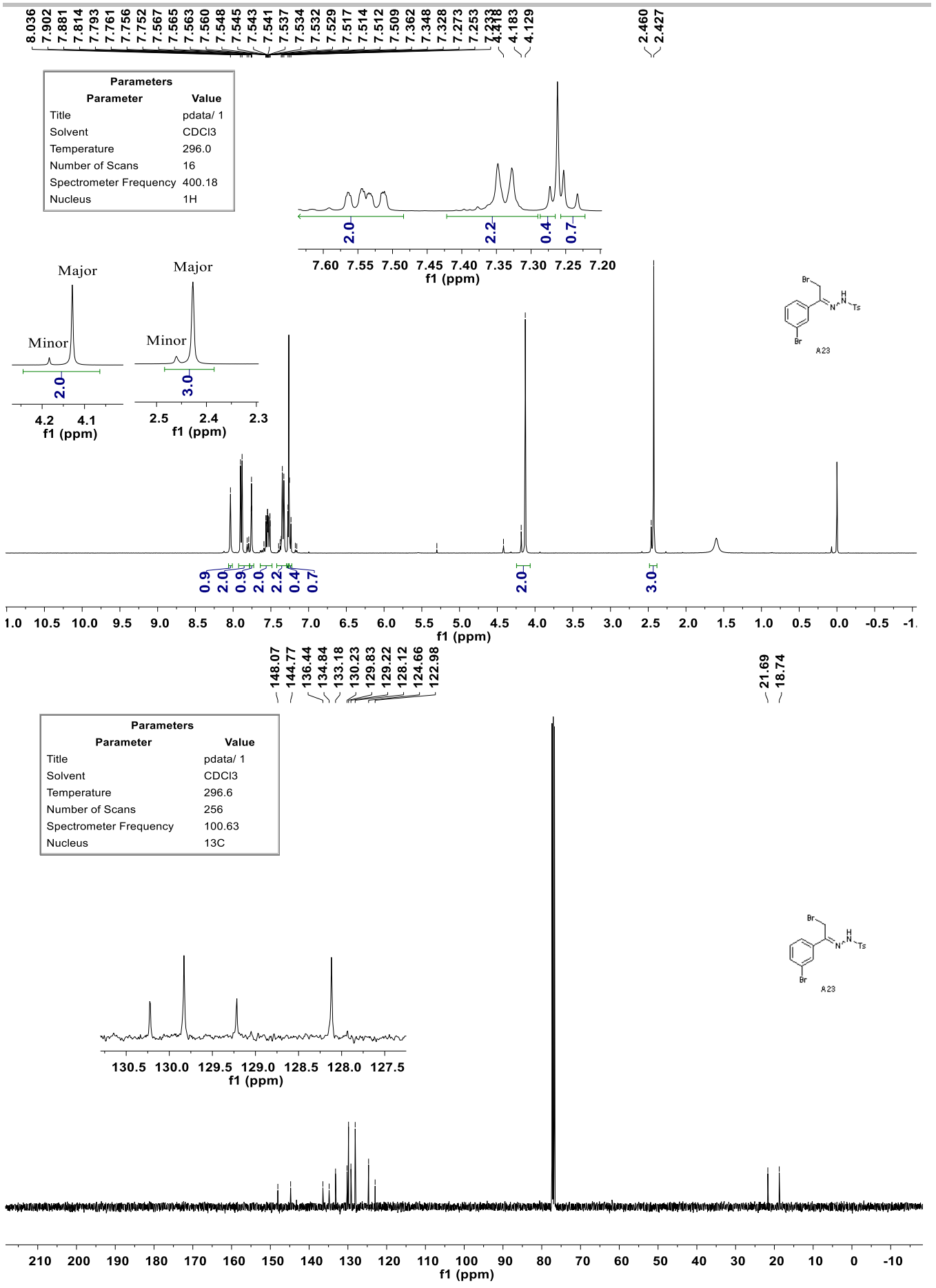

8.025 7.905 7.900 7.889 7.884 7.805 7.801 7.789 7.784 7.717 7.415 7.397 7.394 7.376 7.346 7.323 7.308 7.302 7.287 7.267 7.209 7.205 7.200 7.196 7.194 7.189 7.185 7.182 7.006 7.002 6.999 6.985 6.981 6.954 6.952 6.948 6.945 6.934 6.931 6.927 6.925 6.752 6.749 6.746 6.730 6.727 6.711 6.707 6.704 6.700 4.197 4.159 3.819 3.813 2.449 2.424 2.411
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.1
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
Major
Minor
0.7
1.3
4.25 4.20 4.15 4.10
f1 (ppm)
Major
Minor
1.0
2.0
2.50 2.45 2.40 2.35
f1 (ppm)
3.1
1.3
1.0
0.7
7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7
f1 (ppm)
Br
N
H
N
Ts
OMe
A19
3.0
3.1
1.3
1.0
0.7
2.0
3.0
3.0
11.0 10.5 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 -0.5 -1
f1 (ppm)
160.43 159.81 151.36 149.62 144.57 144.44 135.78 135.17 135.01 131.18 131.06 129.76 129.72 128.14 127.88 119.33 118.56 116.14 115.97 113.09 111.50
55.45 55.34
33.94
21.69 21.66 19.15
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.6
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
136 135 134 133 132 131 130 129 128
f1 (ppm)
119 118 117 116
f1 (ppm)
21.8 21.6 21.4
f1 (ppm)
Br
N
H
N
Ts
OMe
A19
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

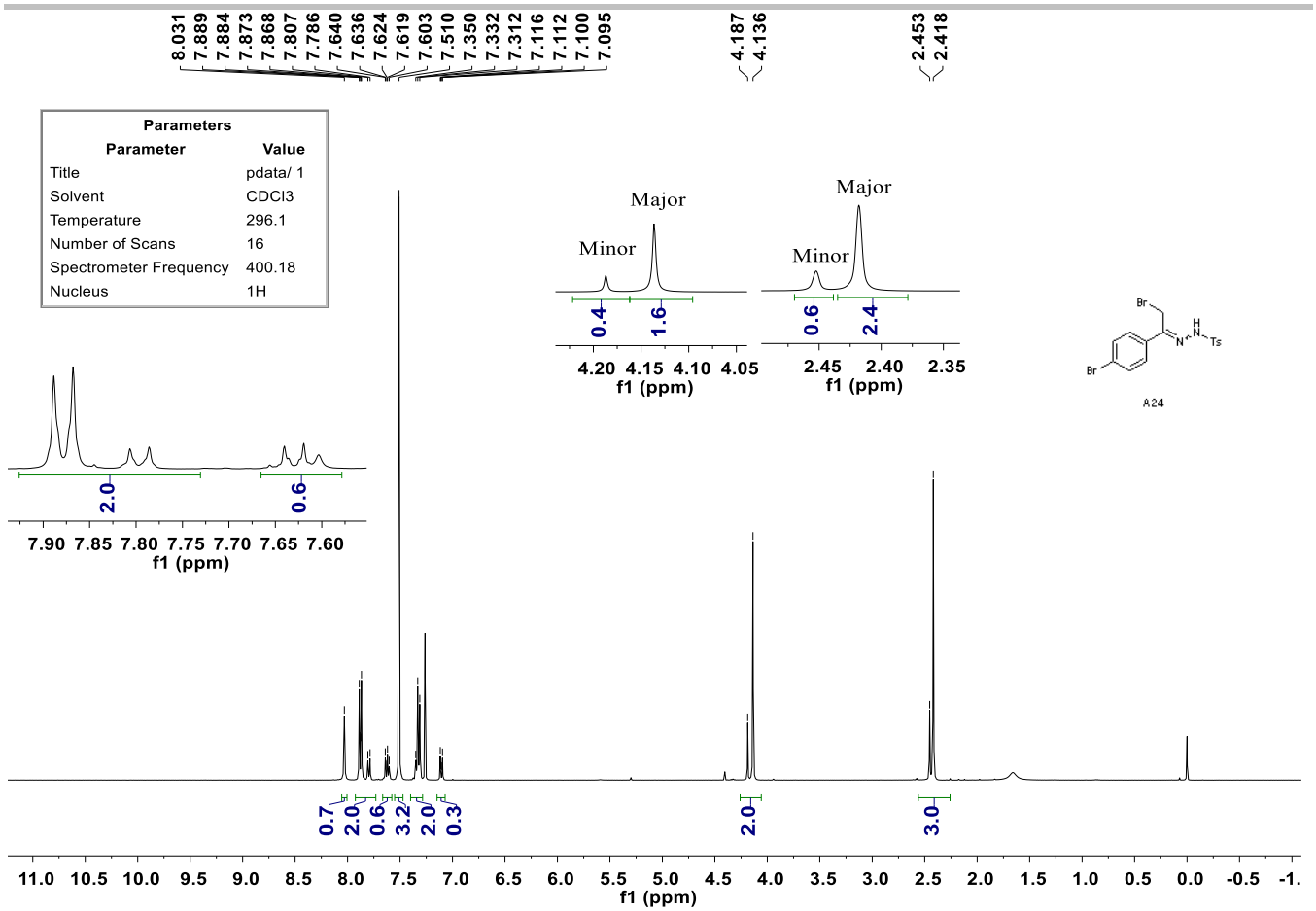

7.901 7.897 7.885 7.881 7.810 7.805 7.800 7.788 7.784 7.677 7.619 7.611 7.606 7.594 7.589 7.581 7.342 7.327 7.322 7.307 7.188 7.171 7.166 6.998 6.976 6.907 6.899 6.894 6.882 6.877 6.869 4.159 3.890 3.853 3.827
2.456 2.448 2.415
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.1
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
Major
Minor
0.5 1.5
4.3 4.2 4.1
f1 (ppm)
Major
Minor
0.8 2.3
2.6 2.5 2.4 2.3 2.2
f1 (ppm)
1.5 1.2 1.8
7.9 7.8 7.7 7.6
f1 (ppm)
2.0 0.5 2.0
7.4 7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)
Br
N
H
N
Ts
MeO
A20
1.5 1.2 1.8 2.0 0.5 2.0 2.0 3.0 3.0
1.0 10.5 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 -0.5 -1
f1 (ppm)
161.40 150.17 144.44 135.08 129.70 129.11 128.13 127.92 127.72 126.80 115.14 114.12
55.41
21.66 19.11
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.6
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
130.0 129.5 129.0 128.5 128.0 127.5 127.0 126.5
f1 (ppm)
Br
N
H
N
Ts
MeO
A20
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

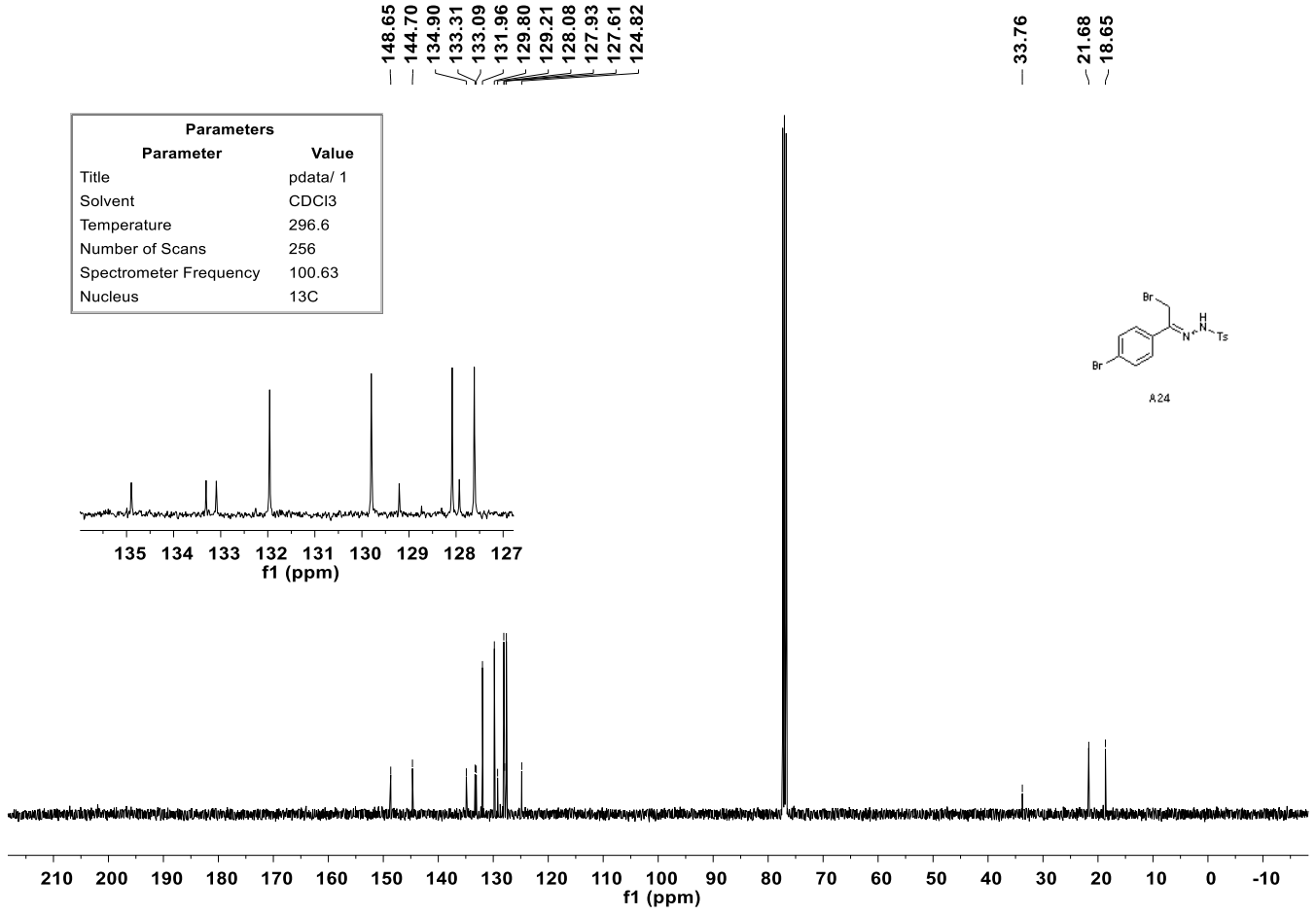

8.102 7.903 7.898 7.887 7.882 7.814 7.809 7.798 7.793 7.635 7.616 7.611 7.606 7.522 7.518 7.514 7.503 7.499 7.495 7.476 7.471 7.460 7.455 7.451 7.434 7.414 7.382 7.378 7.374 7.361 7.358 7.354 7.346 7.340 7.331 7.325 7.312 7.292 7.215 7.195 7.183 7.178 7.173 7.128 7.124 7.119 7.111 7.107 7.102 4.187 4.139 2.458 2.424
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.0
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
Major
Minor
0.5 1.5
4.25 4.15 4.05
f1 (ppm)
Major
Minor
0.8 2.3
2.6 2.5 2.4 2.3
f1 (ppm)
1.0 1.2 3.5 0.5
7.7 7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)
Br
N
H
N
Ts
Cl
A21
0.7 1.9 1.0 1.2 3.5 0.5
2.0
3.0
10.5 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 -0.5 -1.0
f1 (ppm)
149.85 148.15 144.76 144.64 136.23 135.94 134.90 134.86 131.71 131.14 130.89 130.25 129.98 129.83 128.10 127.93 127.56 126.31 125.82 124.21
33.68
21.68
18.74
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.6
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
132 131 130 129 128 127 126 125
f1 (ppm)
Br
N
H
N
Ts
Cl
A21
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

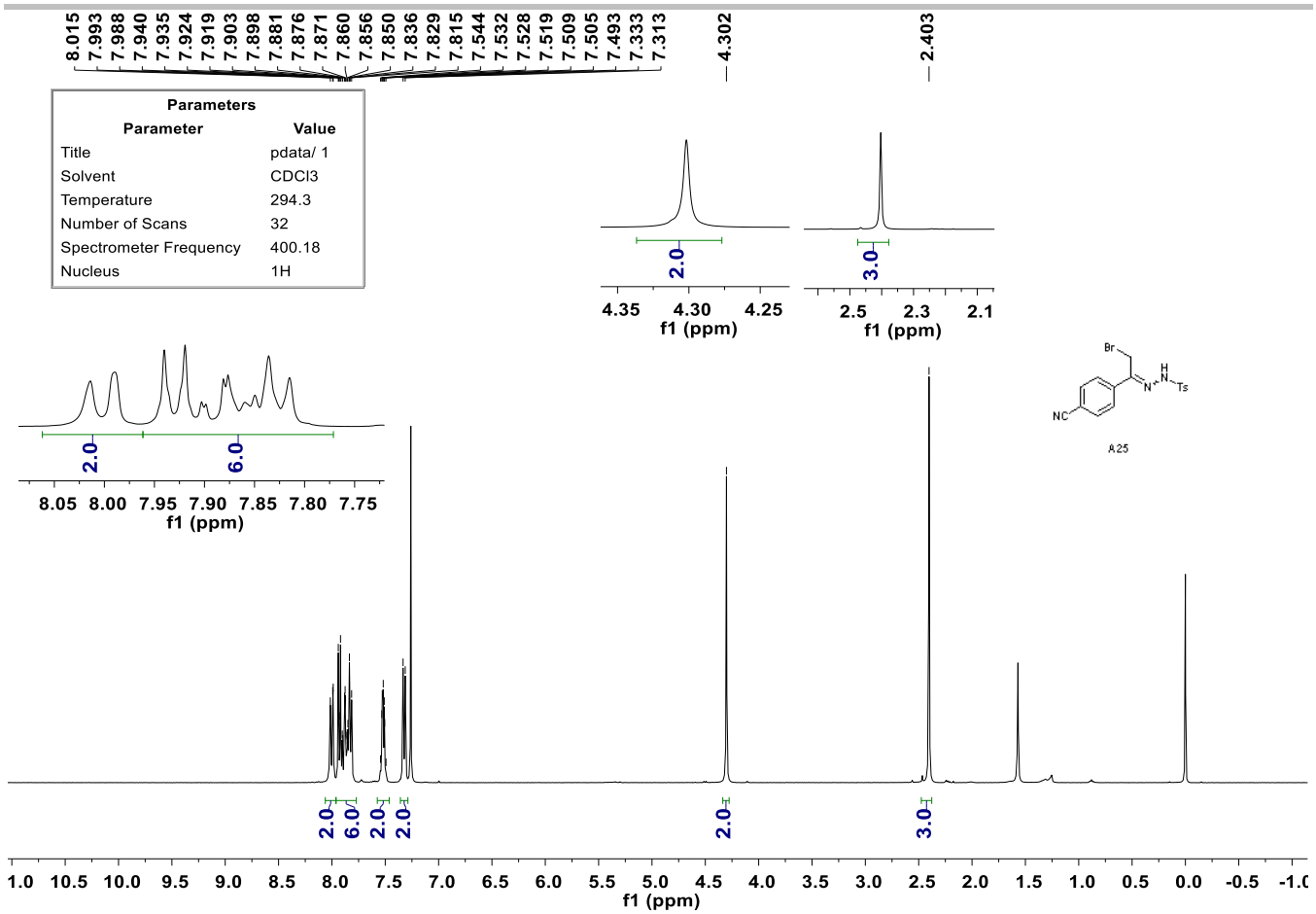

8.011
7.896
7.891
7.886
7.875
7.870
7.808
7.791
7.787
7.599
7.593
7.588
7.577
7.571
7.565
7.483
7.479
7.467
7.462
7.367
7.360
7.355
7.351
7.343
7.338
7.333
7.313
7.187
7.182
7.170
4.191
4.141
2.453
2.419
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.1
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
Major
Minor
0.4
1.6
0.6
2.4
f1 (ppm)
0.7
2.0
1.8
4.0
0.4
2.0
3.0
A22

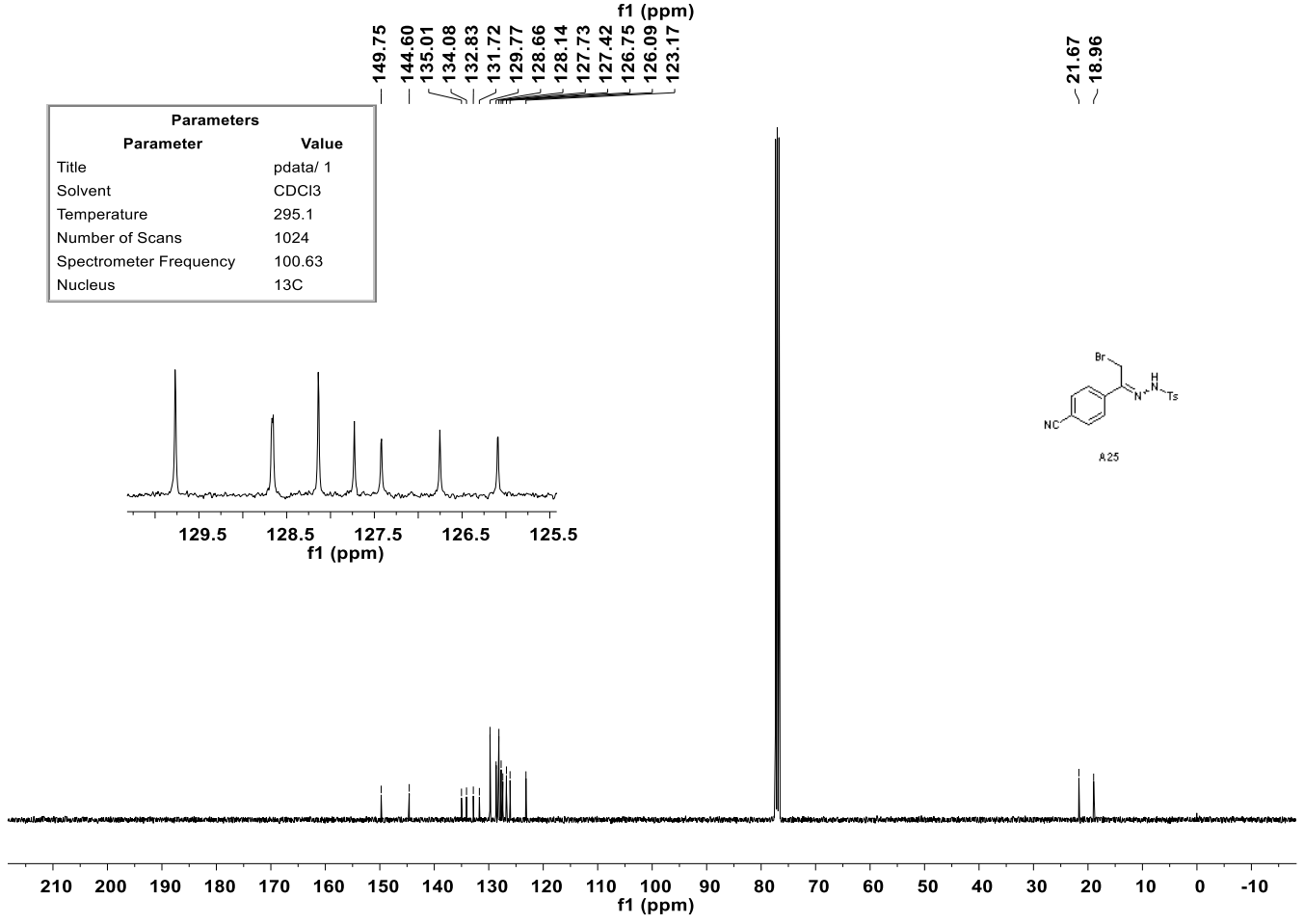

148.63
144.69
136.47
134.91
132.85
130.14
129.79
129.04
129.01
128.09
127.93
127.40
33.83
21.68
18.72
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.6
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
f1 (ppm)
A22

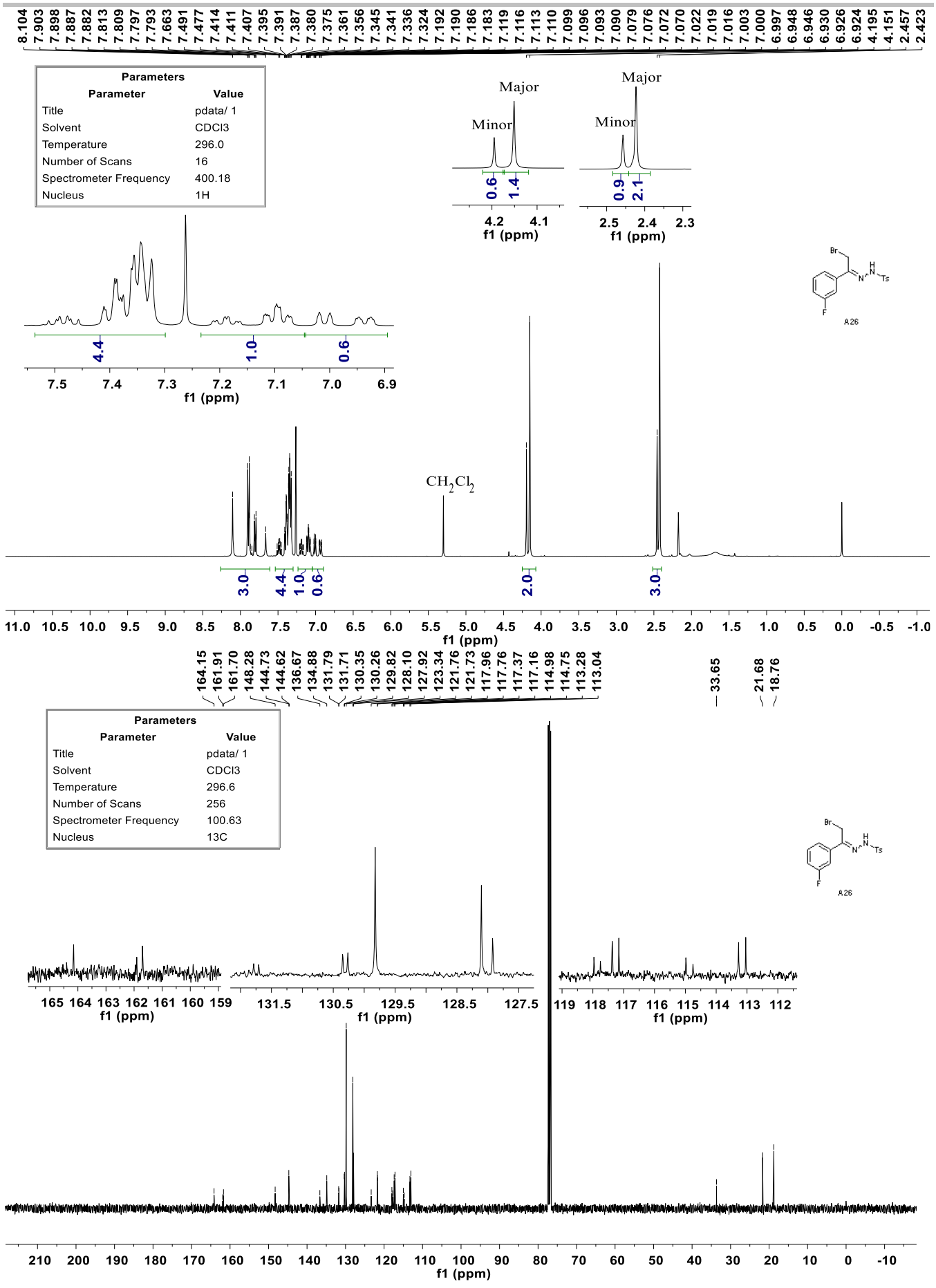

8.036 7.902 7.881 7.814 7.793 7.761 7.756 7.752 7.567 7.565 7.563 7.560 7.548 7.545 7.543 7.541 7.537 7.534 7.532 7.529 7.517 7.514 7.512 7.509 7.362 7.348 7.328 7.273 7.253 7.233 4.418 4.183 4.129 2.460 2.427
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.0
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
Major
Minor
Major
Minor
f1 (ppm)
f1 (ppm)
f1 (ppm)
A23
148.07 144.77 136.44 134.84 133.18 130.23 129.83 129.22 128.12 124.66 122.98 21.69 18.74
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.6
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
f1 (ppm)
f1 (ppm)
A23
f1 (ppm)

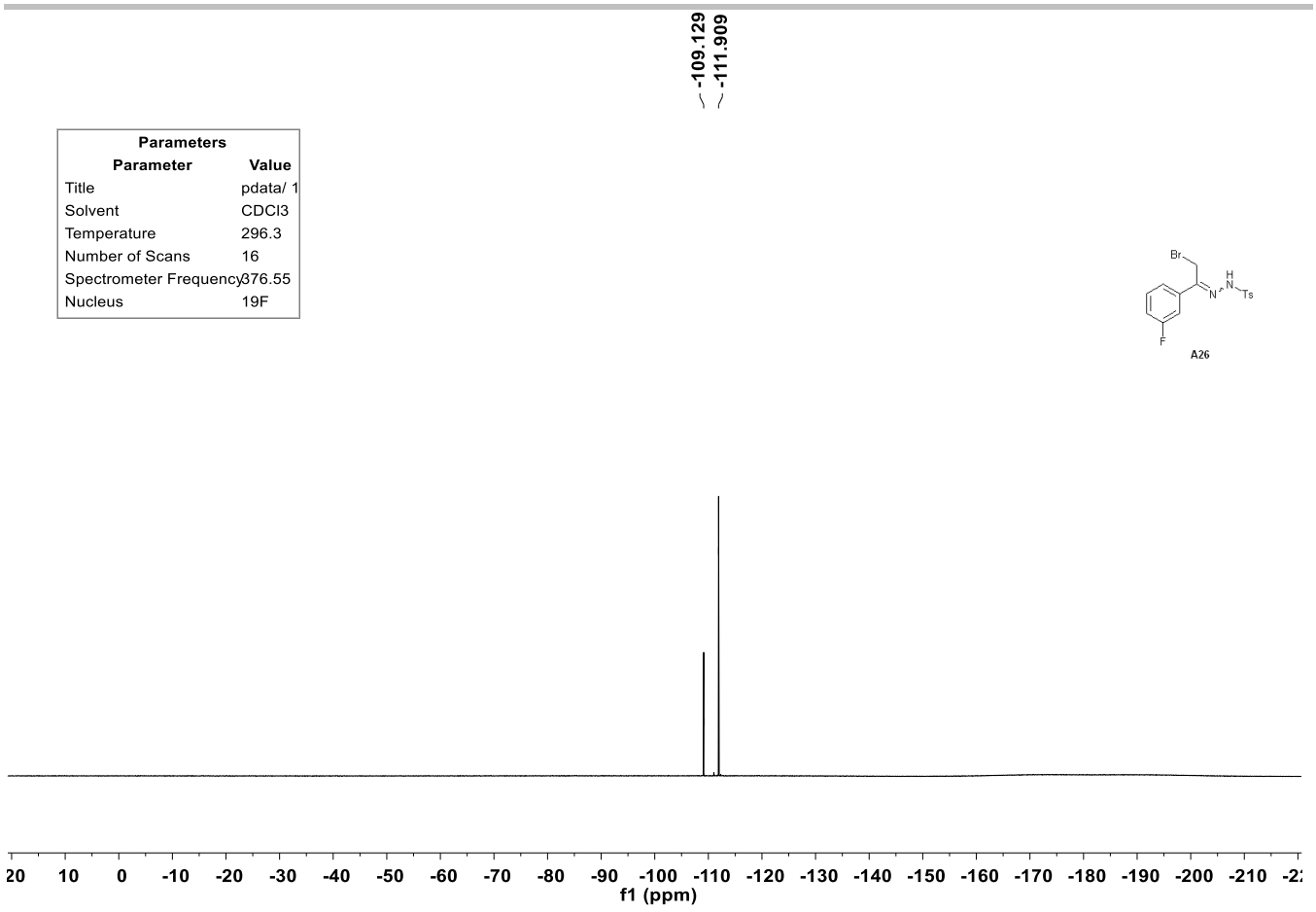

8.031
7.889
7.884
7.873
7.868
7.807
7.786
7.640
7.636
7.624
7.619
7.603
7.510
7.350
7.332
7.312
7.116
7.112
7.100
7.095
4.187
4.136
2.453
2.418
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.1
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
Major
Minor
0.4
1.6
4.20 4.15 4.10 4.05
f1 (ppm)
Major
Minor
0.6
2.4
2.45 2.40 2.35
f1 (ppm)
2.0
0.6
7.90 7.85 7.80 7.75 7.70 7.65 7.60
f1 (ppm)
A24
0.7
2.0
0.6
3.2
2.0
0.3
2.0
3.0
11.0 10.5 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 -0.5 -1.
f1 (ppm)

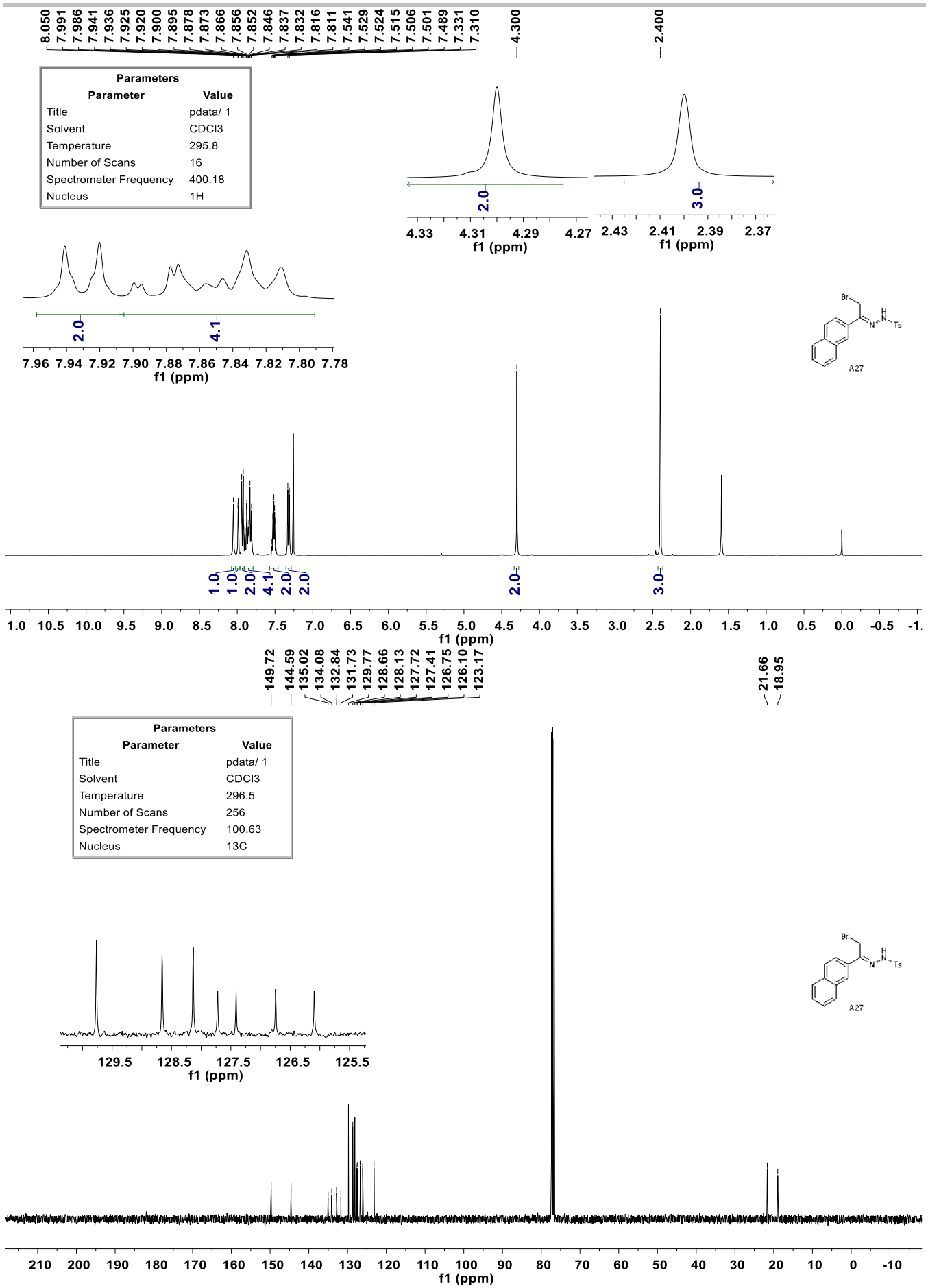

148.65
144.70
134.90
133.31
133.09
131.96
129.80
129.21
128.08
127.93
127.61
124.82
33.76
21.68
18.65
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.6
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
135 134 133 132 131 130 129 128 127
f1 (ppm)
A24
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

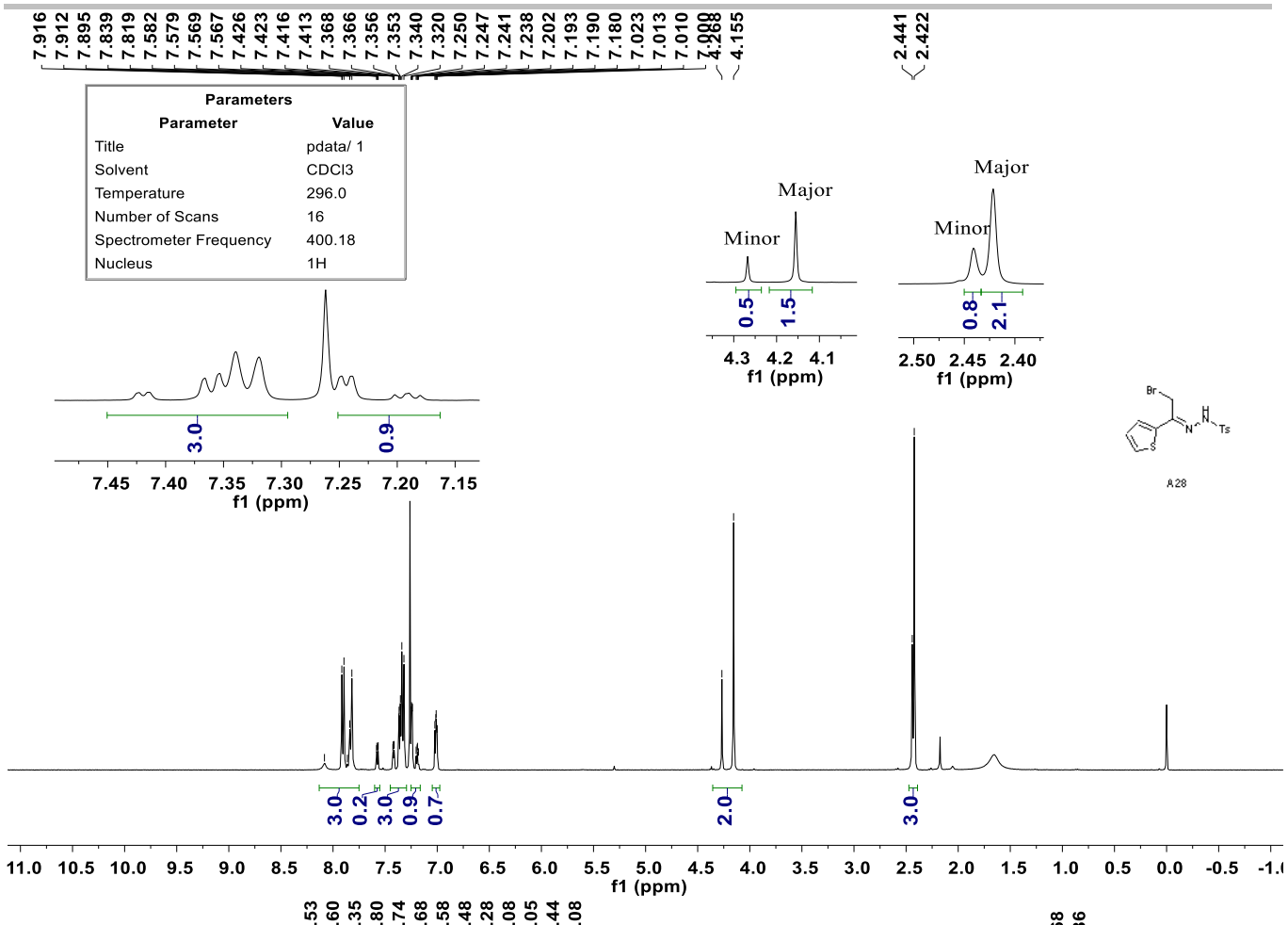

8.015
7.993
7.988
7.940
7.935
7.924
7.919
7.903
7.898
7.881
7.876
7.871
7.860
7.856
7.850
7.836
7.829
7.815
7.544
7.532
7.528
7.519
7.509
7.505
7.493
7.333
7.313
4.302
2.403
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.3
Number of Scans 32
Spectrometer Frequency 400.18
Nucleus 1H
2.0
3.0
4.35 4.30 4.25
2.5 2.3 2.1
f1 (ppm)
2.0
6.0
8.05 8.00 7.95 7.90 7.85 7.80 7.75
f1 (ppm)
Br
NC
Ts
A25
2.0
6.0
2.0
2.0
2.0
3.0
1.0 10.5 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 -0.5 -1.0
f1 (ppm)

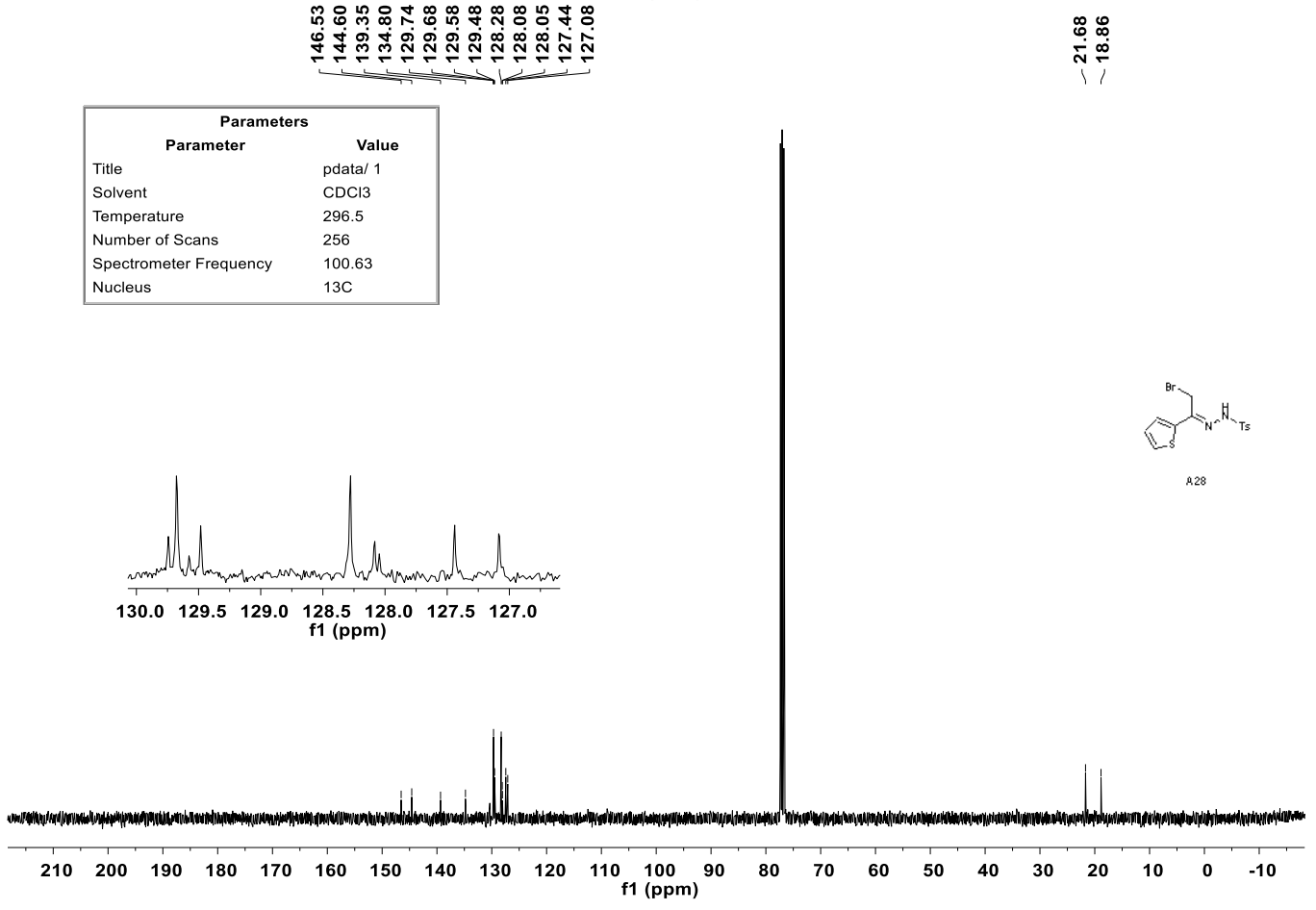

149.75
144.60
135.01
134.08
132.83
131.72
129.77
128.66
128.14
127.73
127.42
126.75
126.09
123.17
21.67
18.96
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 295.1
Number of Scans 1024
Spectrometer Frequency 100.63
Nucleus 13C
129.5 128.5 127.5 126.5 125.5
f1 (ppm)
Br
NC
Ts
A25
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

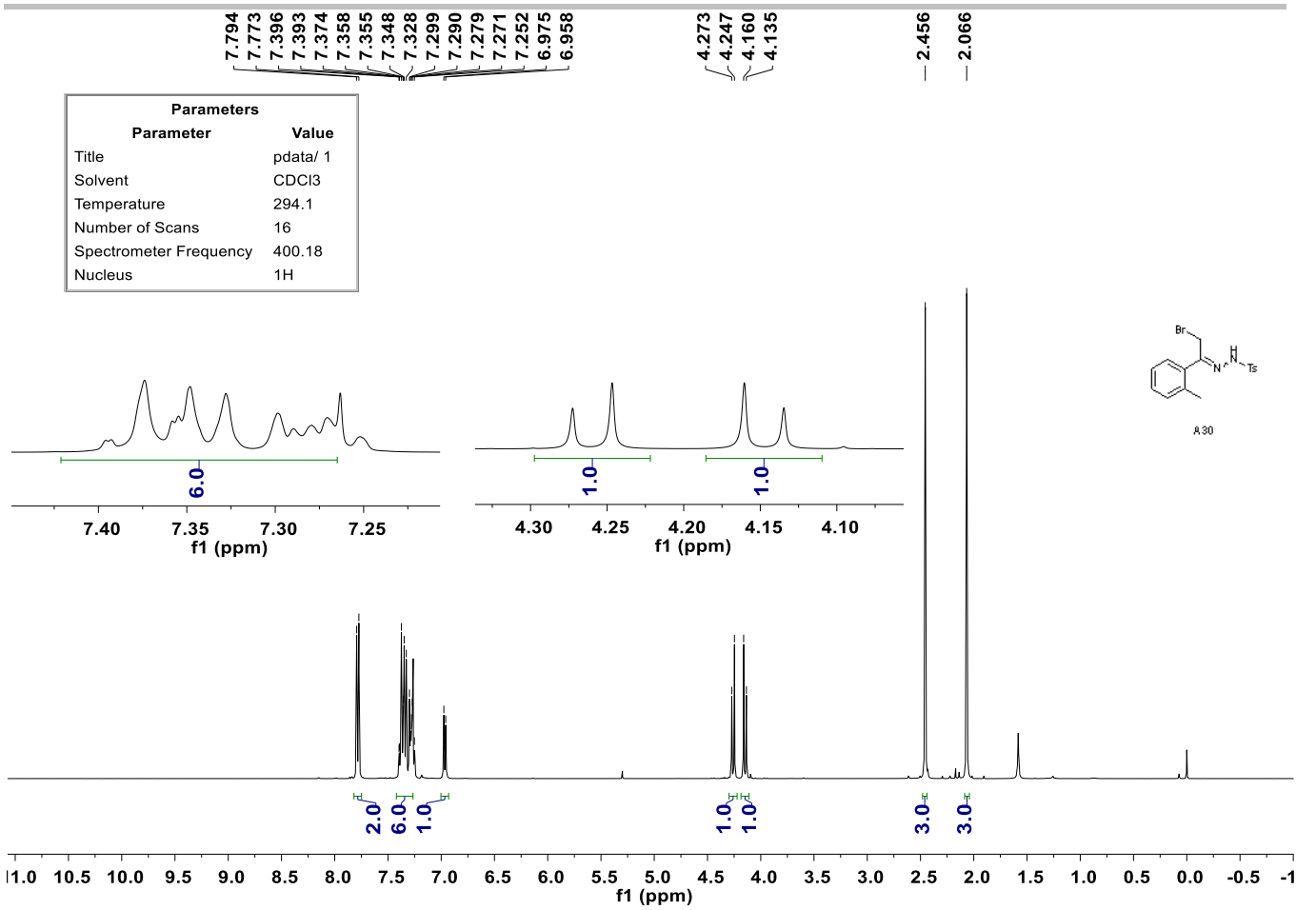

Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.0
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
Major
Minor
Major
Minor
0.6
1.4
0.9
2.1
4.2 4.1
2.5 2.4 2.3
f1 (ppm)
4.4
1.0
0.6
7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
A26
CH2Cl2
3.0
4.4
1.0
0.6
2.0
3.0
11.0 10.5 10.0 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 -0.5 -1.0
f1 (ppm)
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.6
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
A26
165 164 163 162 161 160 159
f1 (ppm)
131.5 130.5 129.5 128.5 127.5
f1 (ppm)
119 118 117 116 115 114 113 112
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

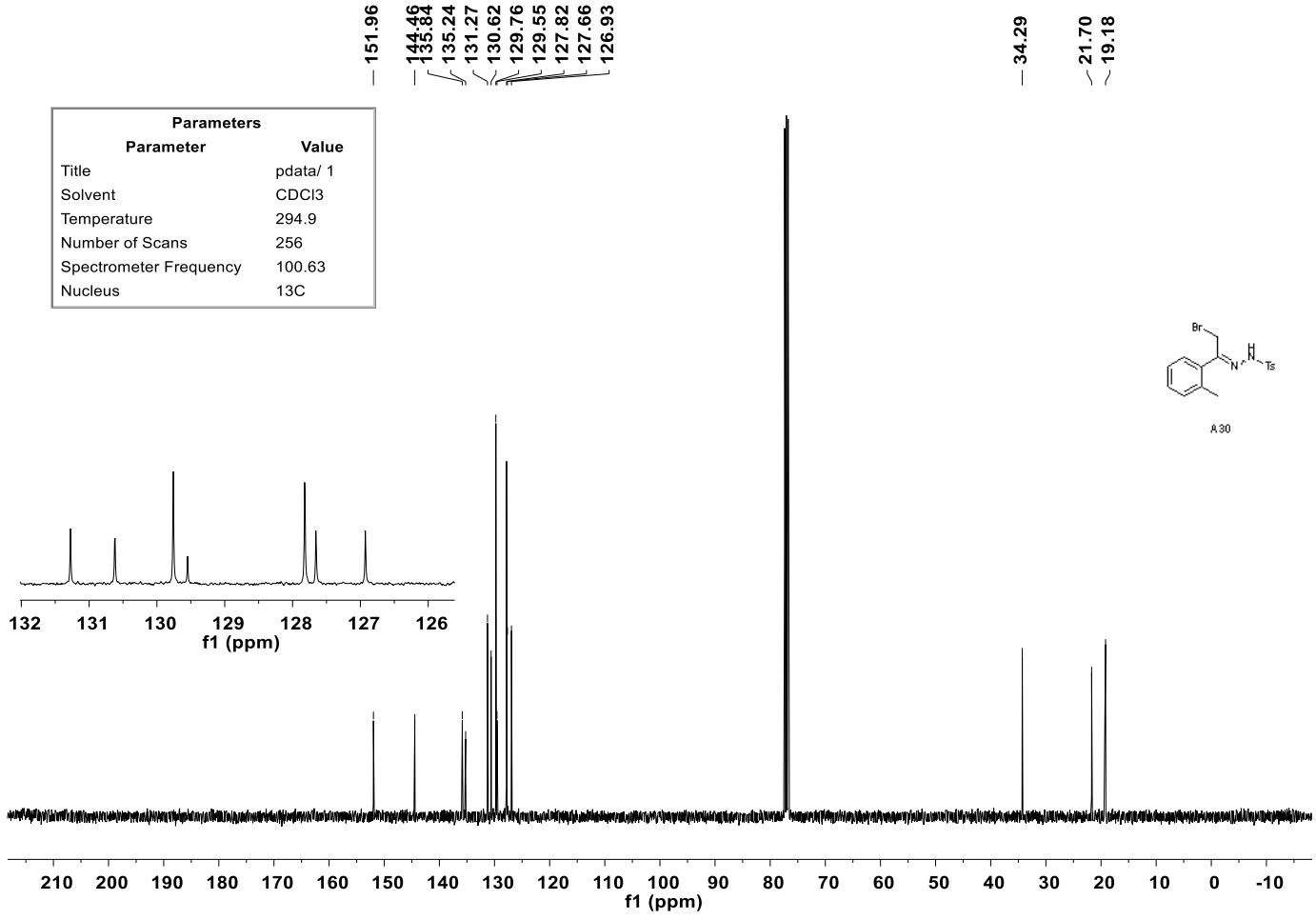

-109.129
-111.909
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.3
Number of Scans 16
Spectrometer Frequency 376.55
Nucleus 19F
Br
H
N
N
Ts
F
A26
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

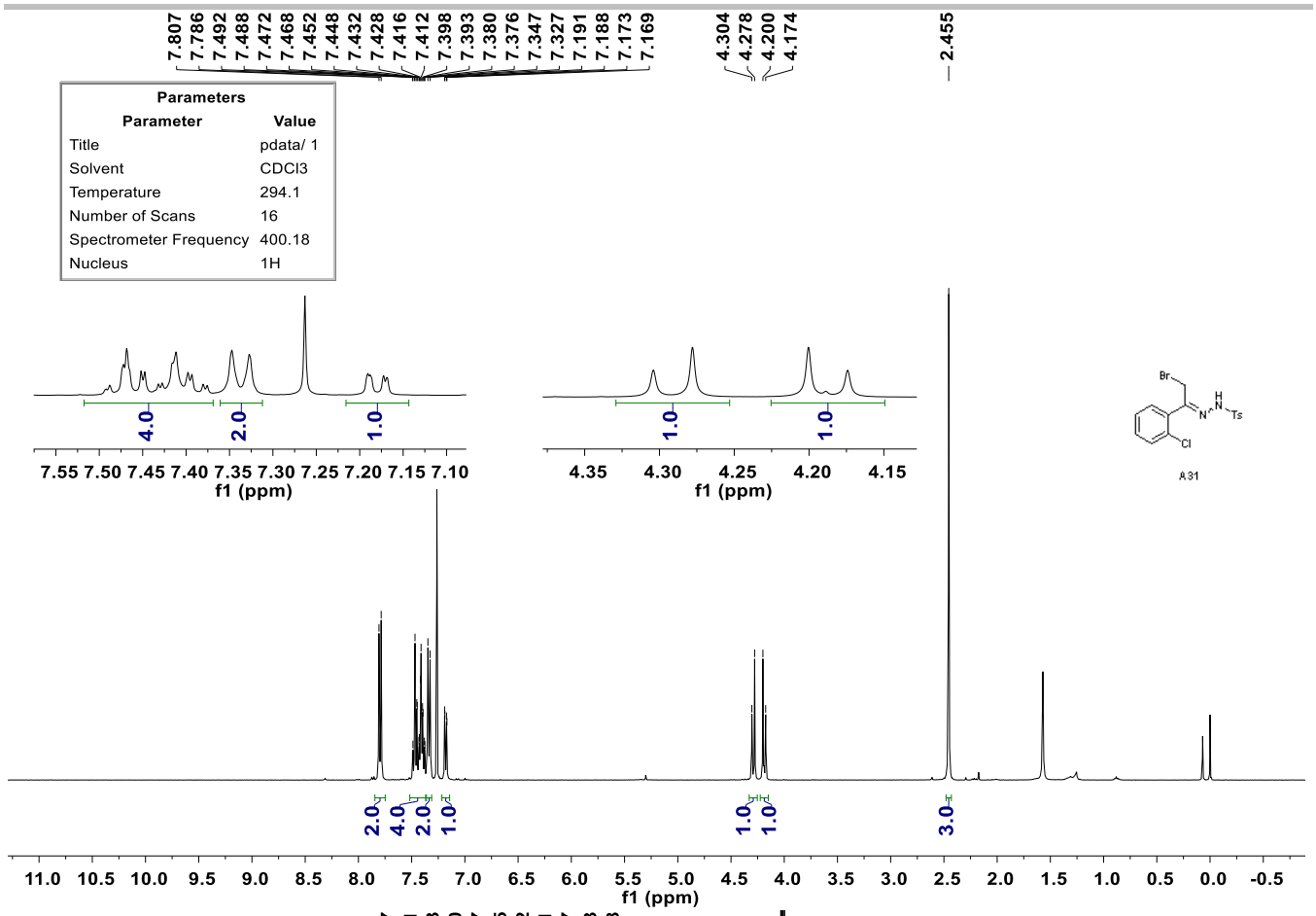

8.050 7.991 7.986 7.941 7.936 7.925 7.920 7.900 7.895 7.878 7.873 7.866 7.856 7.852 7.846 7.837 7.832 7.816 7.811 7.541 7.529 7.524 7.515 7.506 7.501 7.489 7.331 7.310
4.300
2.400
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 295.8
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
2.0
3.0
4.33 4.31 4.29 4.27
2.43 2.41 2.39 2.37
f1 (ppm)
2.0
4.1
7.96 7.94 7.92 7.90 7.88 7.86 7.84 7.82 7.80 7.78
f1 (ppm)
Br
N
H
N
Ts
A27
1.0 1.0 2.0 4.1 2.0 2.0
2.0
3.0
1.0 10.5 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 -0.5
f1 (ppm)
149.72 144.59 135.02 134.08 132.84 131.73 129.77 128.66 128.13 127.72 127.41 126.75 126.10 123.17
21.66 18.95
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.5
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
129.5 128.5 127.5 126.5 125.5
f1 (ppm)
Br
N
H
N
Ts
A27
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

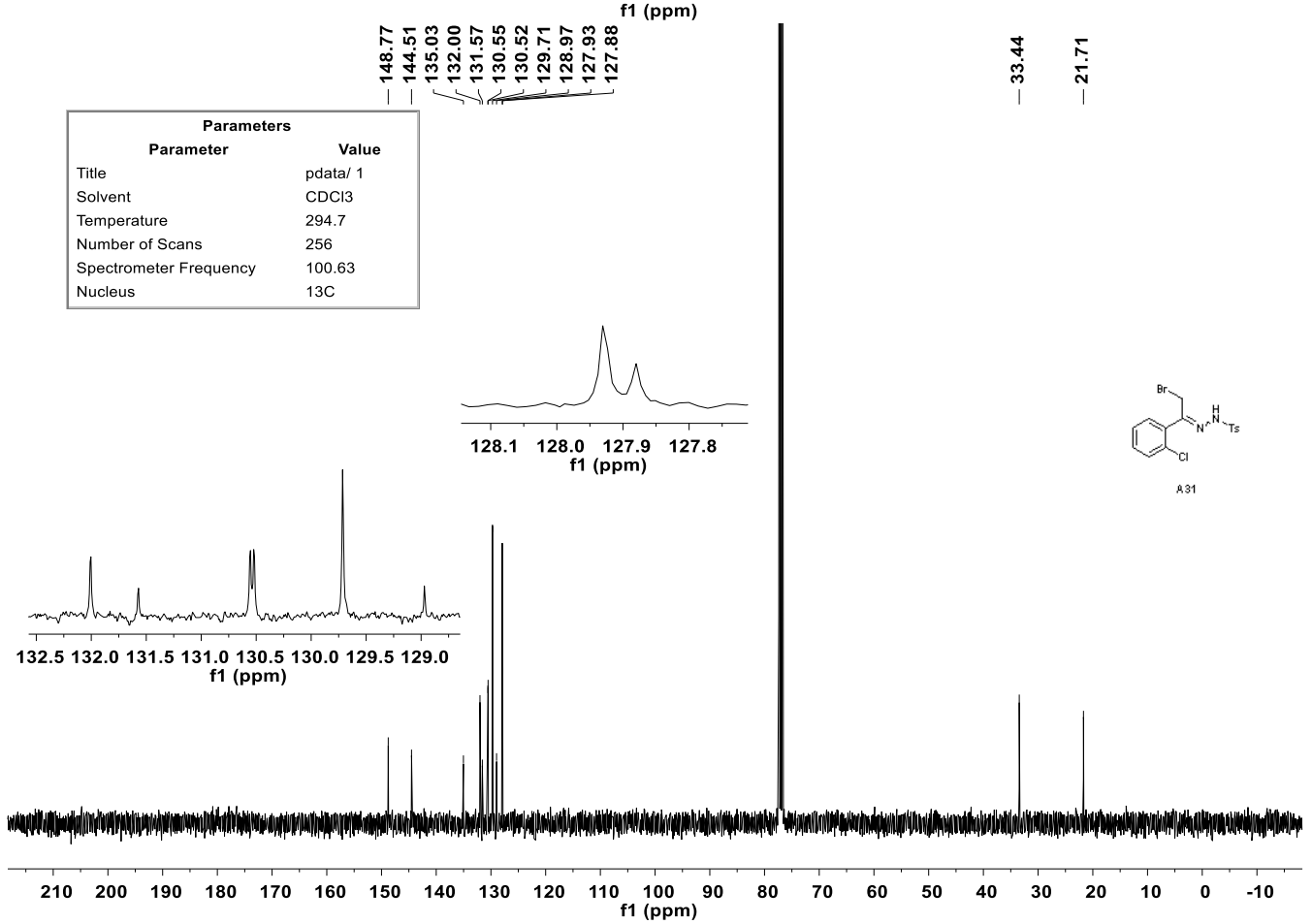

7.916 7.912 7.895 7.839 7.819 7.582 7.579 7.569 7.567 7.426 7.423 7.416 7.413 7.368 7.366 7.356 7.353 7.340 7.320 7.250 7.247 7.241 7.238 7.202 7.193 7.190 7.180 7.023 7.013 7.010 7.000 4.168 4.155
2.441 2.422
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.0
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
Major
Minor
0.5 1.5
4.3 4.2 4.1
f1 (ppm)
Major
Minor
0.8 2.1
2.50 2.45 2.40
f1 (ppm)
3.0 0.9
7.45 7.40 7.35 7.30 7.25 7.20 7.15
f1 (ppm)
A28
3.0 0.2 3.0 0.9 0.7 2.0 3.0
11.0 10.5 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 -0.5
f1 (ppm)

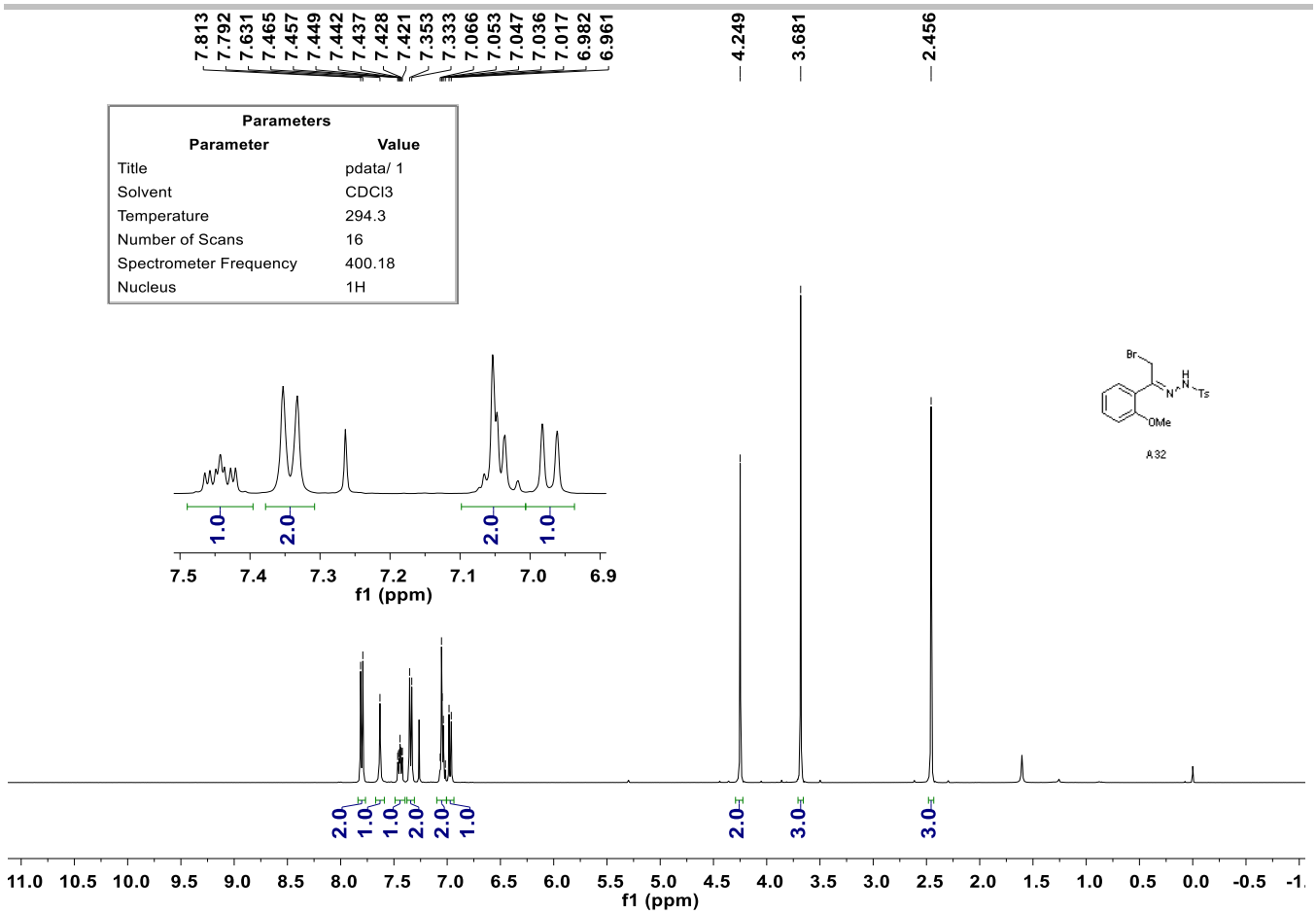

146.53 144.60 139.35 134.80 129.74 129.68 129.58 129.48 128.28 128.08 128.05 127.44 127.08
21.68 18.86
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 296.5
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
A28
130.0 129.5 129.0 128.5 128.0 127.5 127.0
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

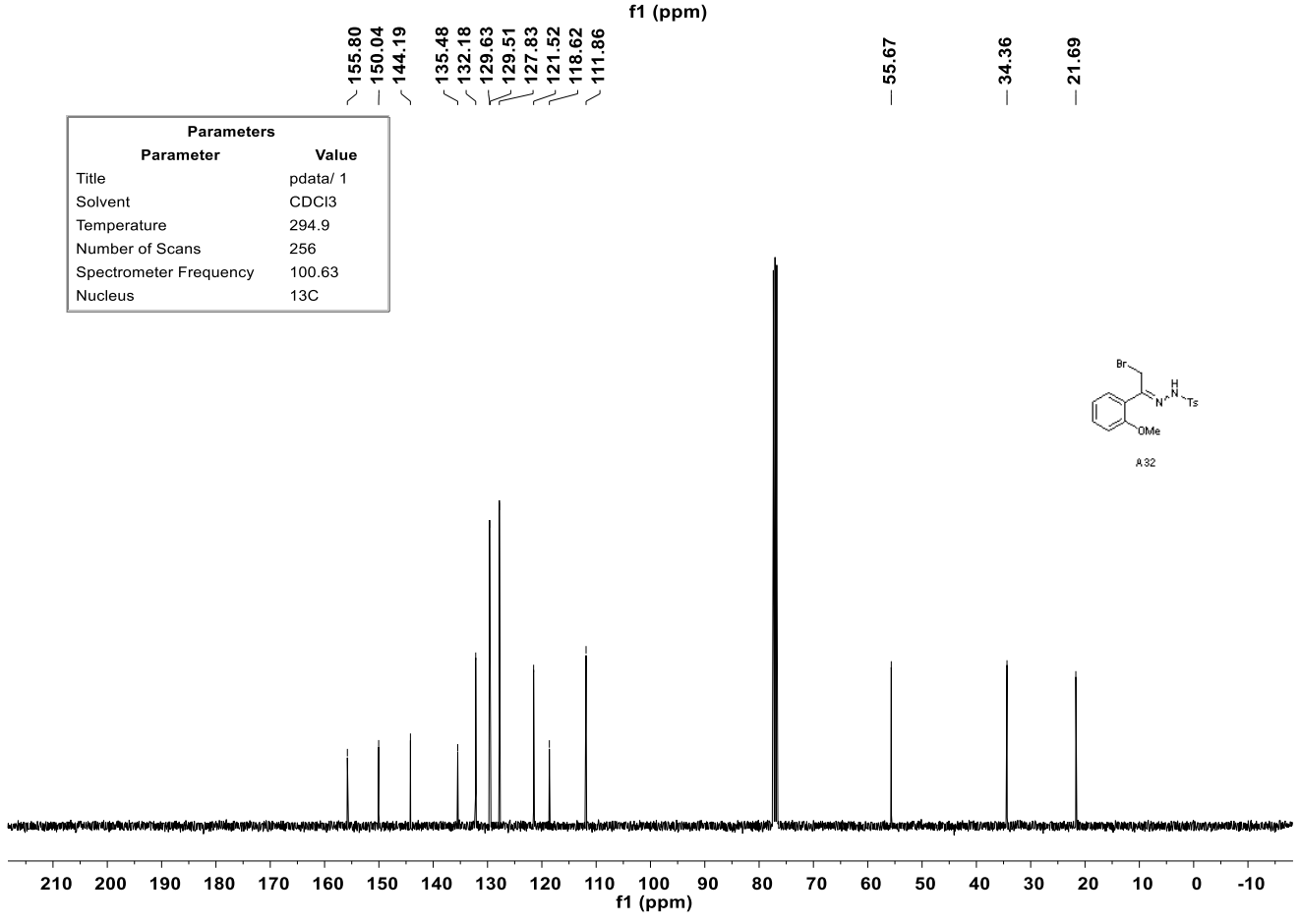

7.794
7.773
7.396
7.393
7.374
7.358
7.355
7.348
7.328
7.299
7.290
7.279
7.271
7.252
6.975
6.958
4.273
4.247
4.160
4.135
2.456
2.066
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.1
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
6.0
1.0
1.0
f1 (ppm)
A30
2.0
6.0
1.0
1.0
1.0
3.0
3.0
f1 (ppm)

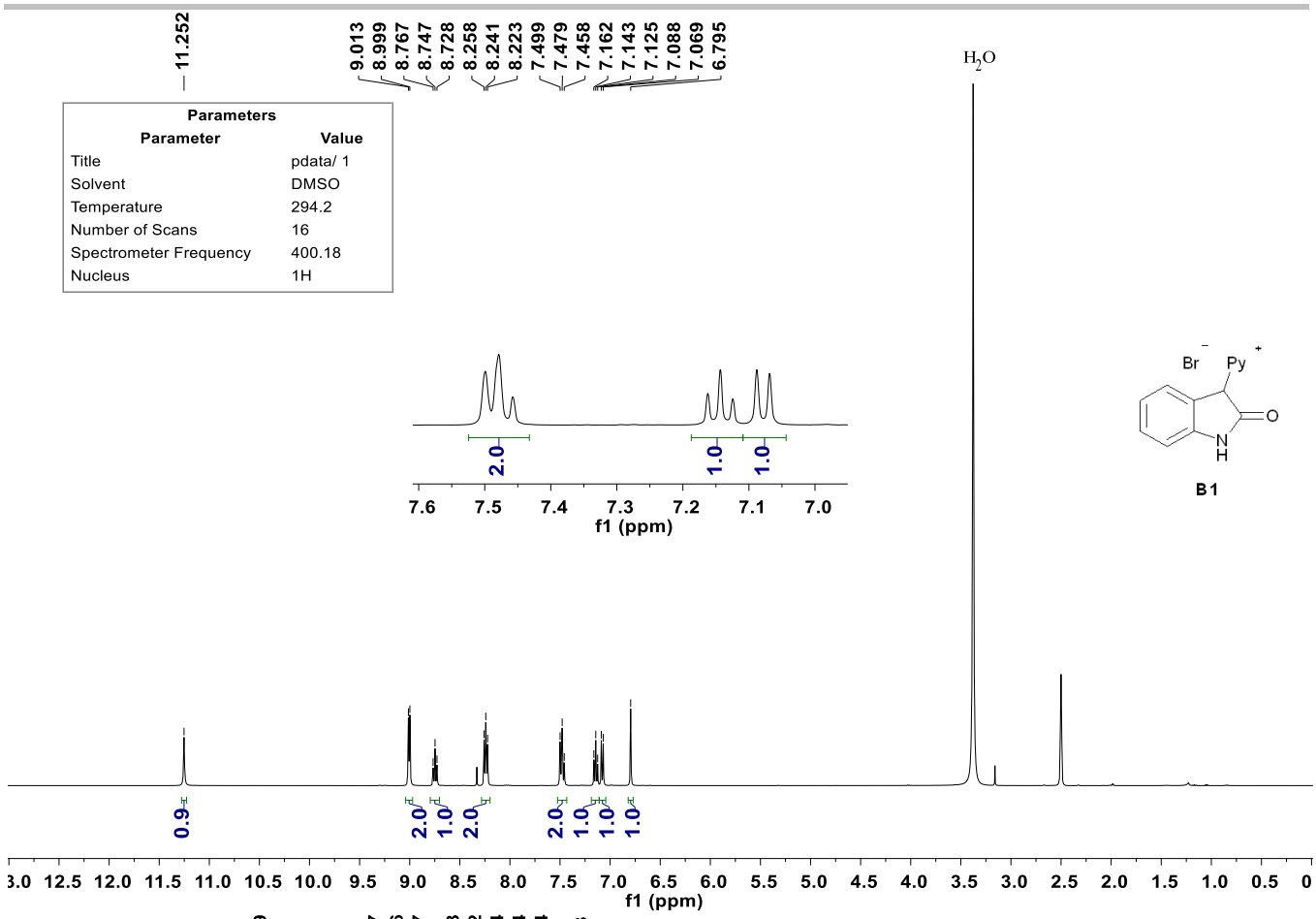

151.96
144.46
135.84
135.24
131.27
130.62
129.76
129.55
127.82
127.66
126.93
34.29
21.70
19.18
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.9
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
A30
f1 (ppm)
f1 (ppm)

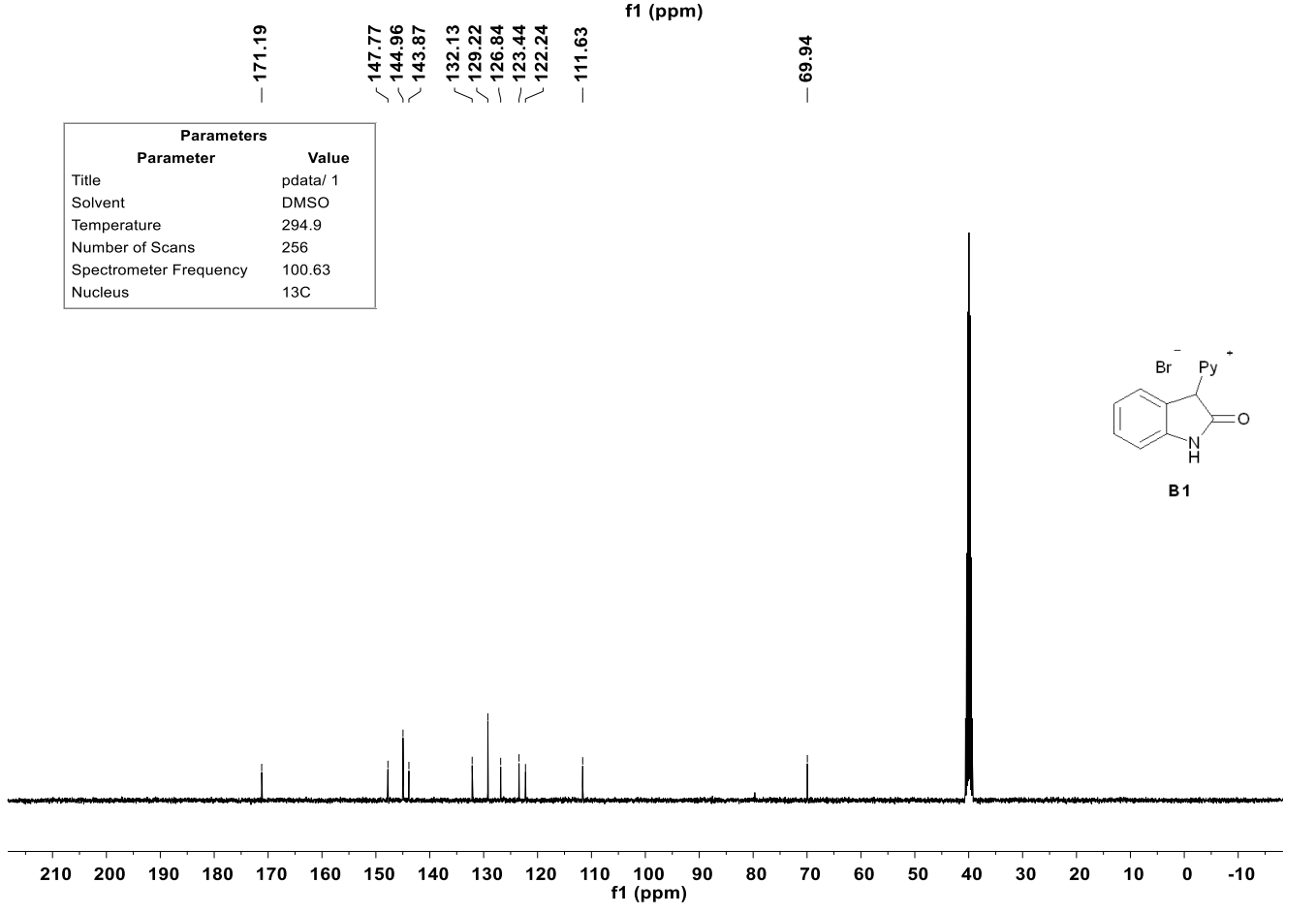

7.807
7.786
7.492
7.488
7.472
7.468
7.452
7.448
7.432
7.428
7.416
7.412
7.398
7.393
7.380
7.376
7.347
7.327
7.191
7.188
7.173
7.169
4.304
4.278
4.200
4.174
2.455
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.1
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
4.0
2.0
1.0
7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10
f1 (ppm)
1.0
1.0
4.35 4.30 4.25 4.20 4.15
f1 (ppm)
A31
2.0
4.0
2.0
1.0
1.0
1.0
3.0
11.0 10.5 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 -0.5
f1 (ppm)

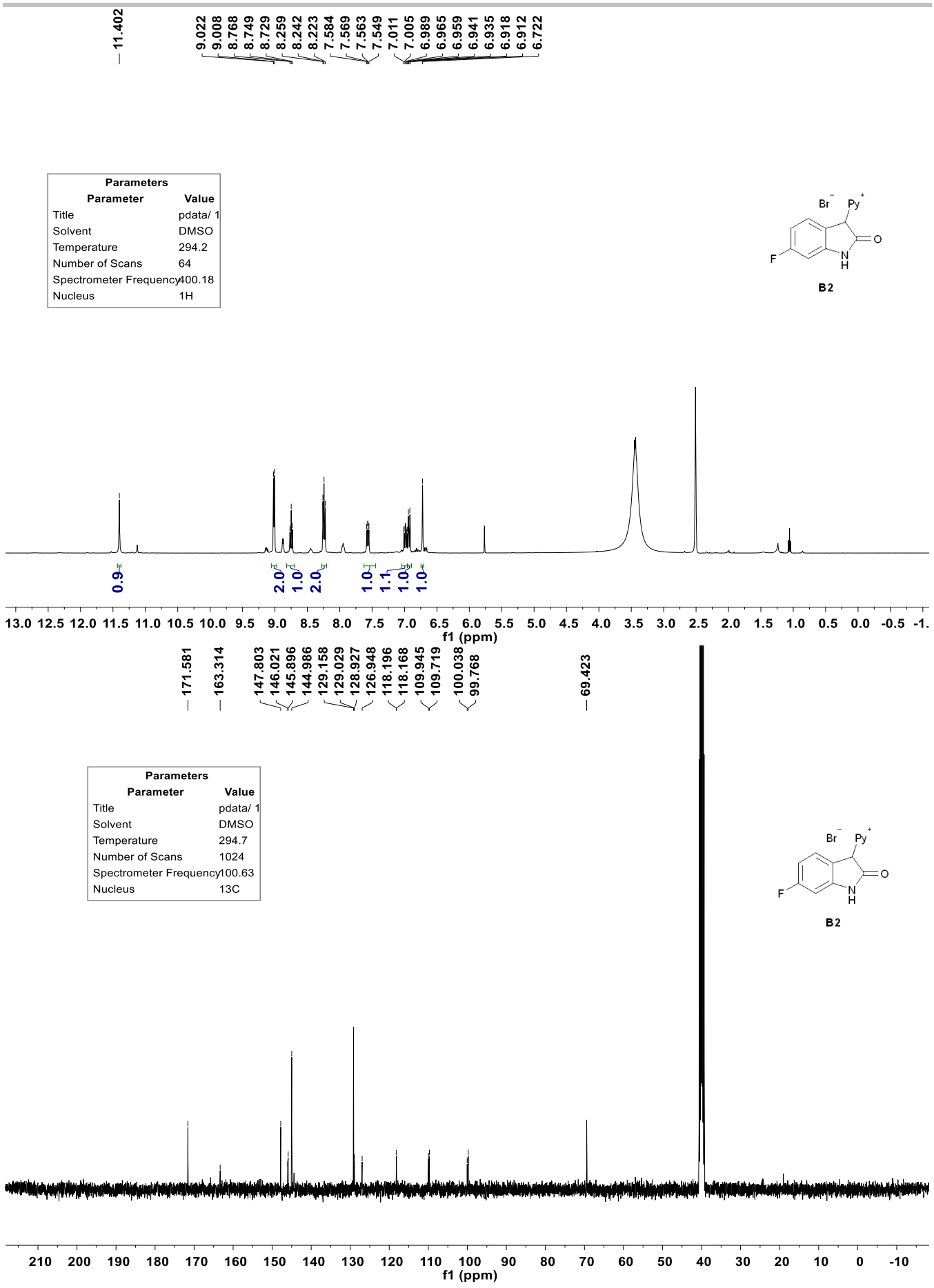

148.77
144.51
135.03
132.00
131.57
130.55
130.52
129.71
128.97
127.93
127.88
33.44
21.71
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.7
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
128.1 128.0 127.9 127.8
f1 (ppm)
A31
132.5 132.0 131.5 131.0 130.5 130.0 129.5 129.0
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

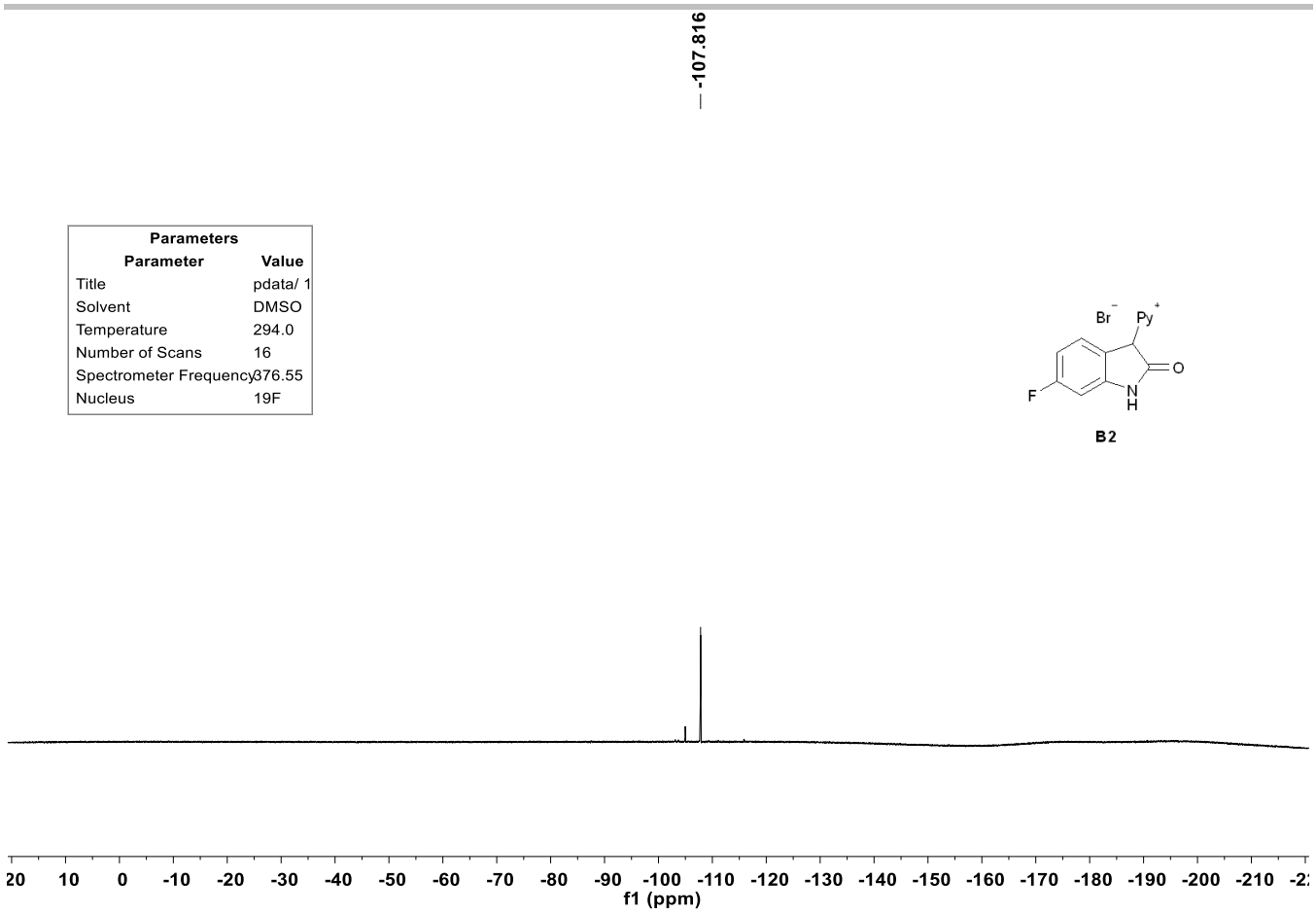

7.813
7.792
7.631
7.465
7.457
7.449
7.442
7.437
7.428
7.421
7.353
7.333
7.066
7.053
7.047
7.036
7.017
6.982
6.961
4.249
3.681
2.456
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.3
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
Br
N
H
N
Ts
OMe
A32
1.0
2.0
2.0
1.0
7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
2.0 1.0 1.0 2.0 2.0 1.0
2.0
3.0
3.0
11.0 10.5 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 -0.5
f1 (ppm)

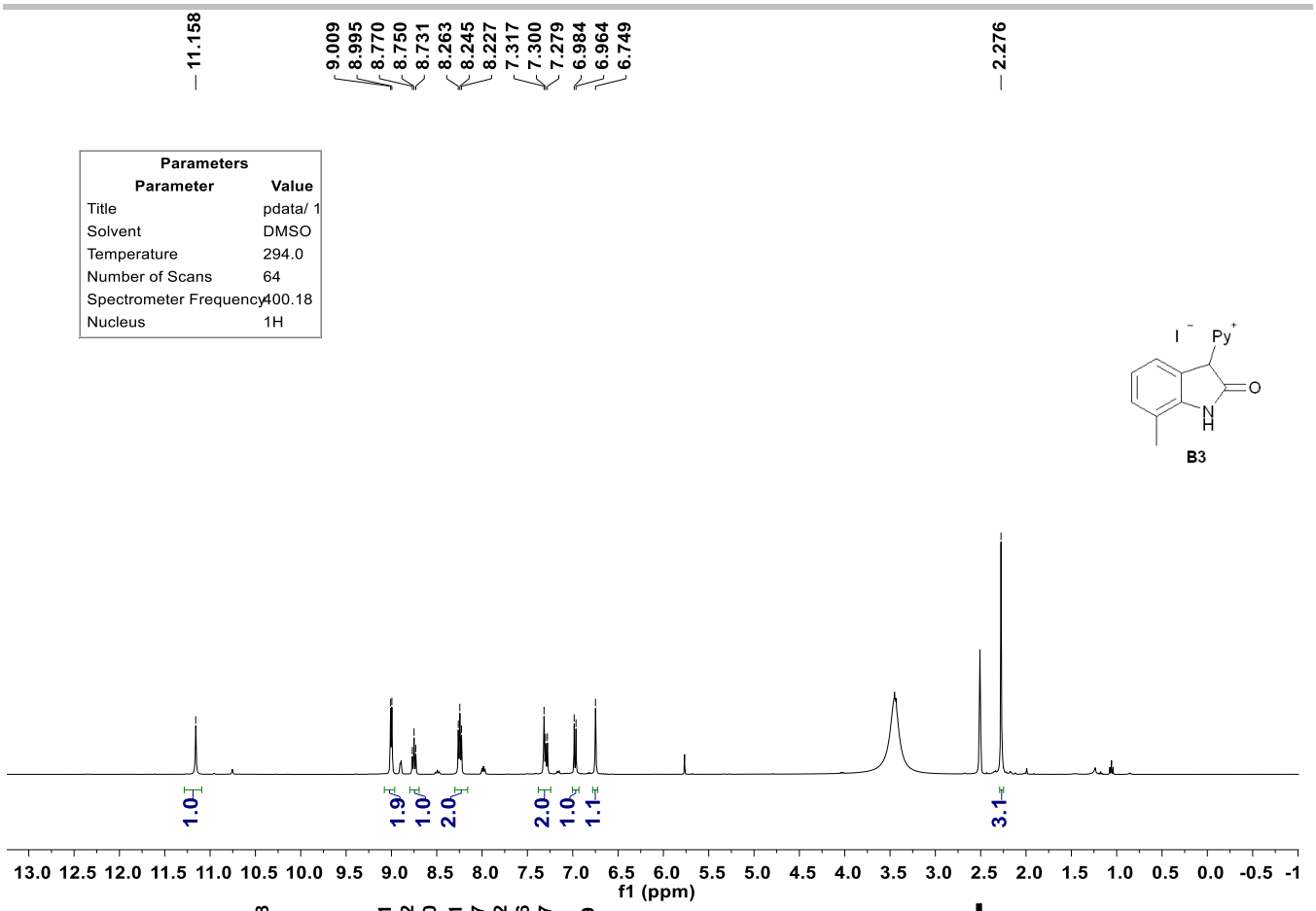

155.80
150.04
144.19
135.48
132.18
129.63
129.51
127.83
121.52
118.62
111.86
55.67
34.36
21.69
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.9
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
Br
N
H
N
Ts
OMe
A32
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

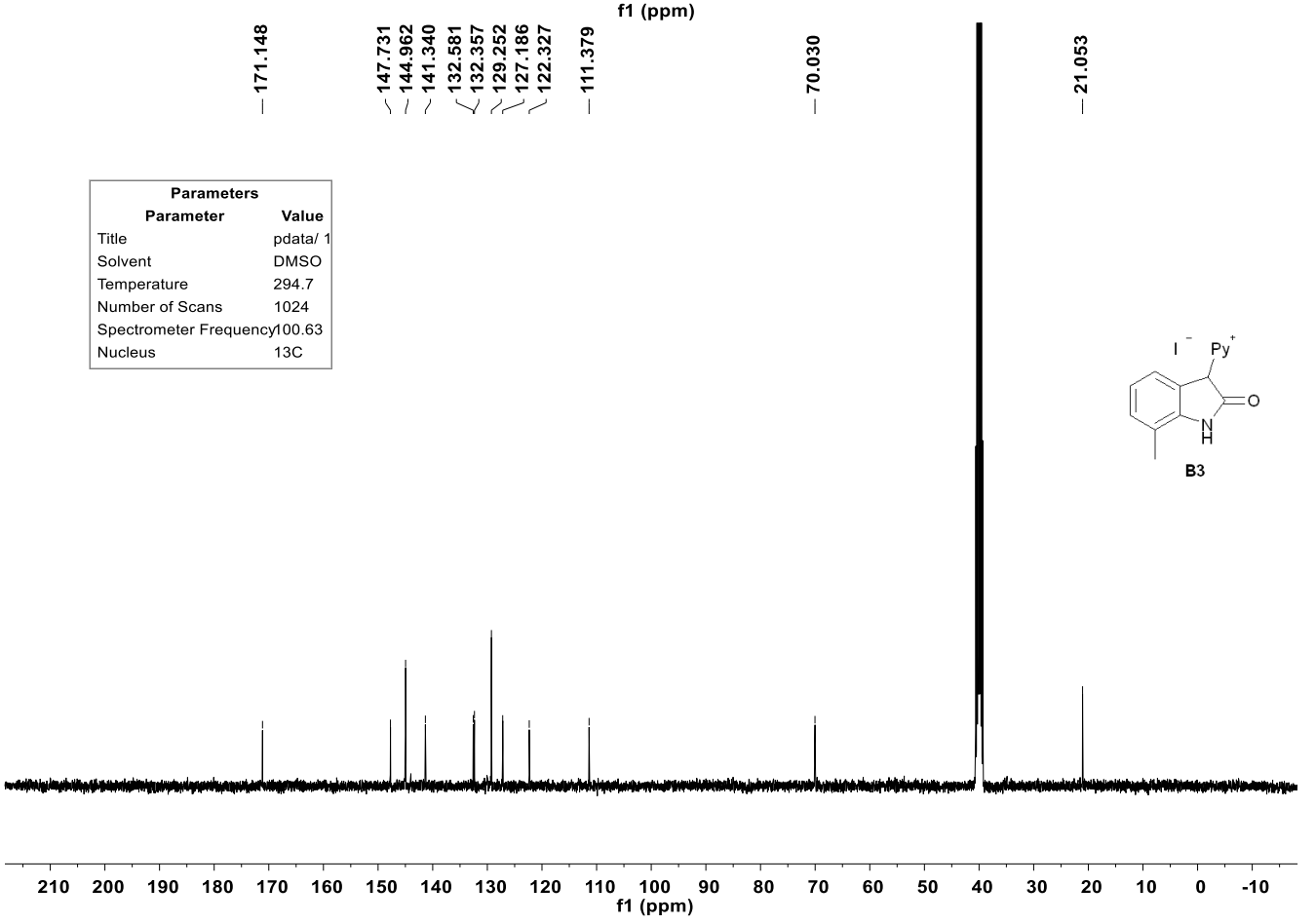

11.252
9.013
8.999
8.767
8.747
8.728
8.258
8.241
8.223
7.499
7.479
7.458
7.162
7.143
7.125
7.088
7.069
6.795
H2O
Parameters
Parameter Value
Title pdata/ 1
Solvent DMSO
Temperature 294.2
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
2.0
1.0
1.0
7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
Br
Py
O
N
H
B1
0.9
2.0
1.0
2.0
2.0
1.0
1.0
1.0
f1 (ppm)

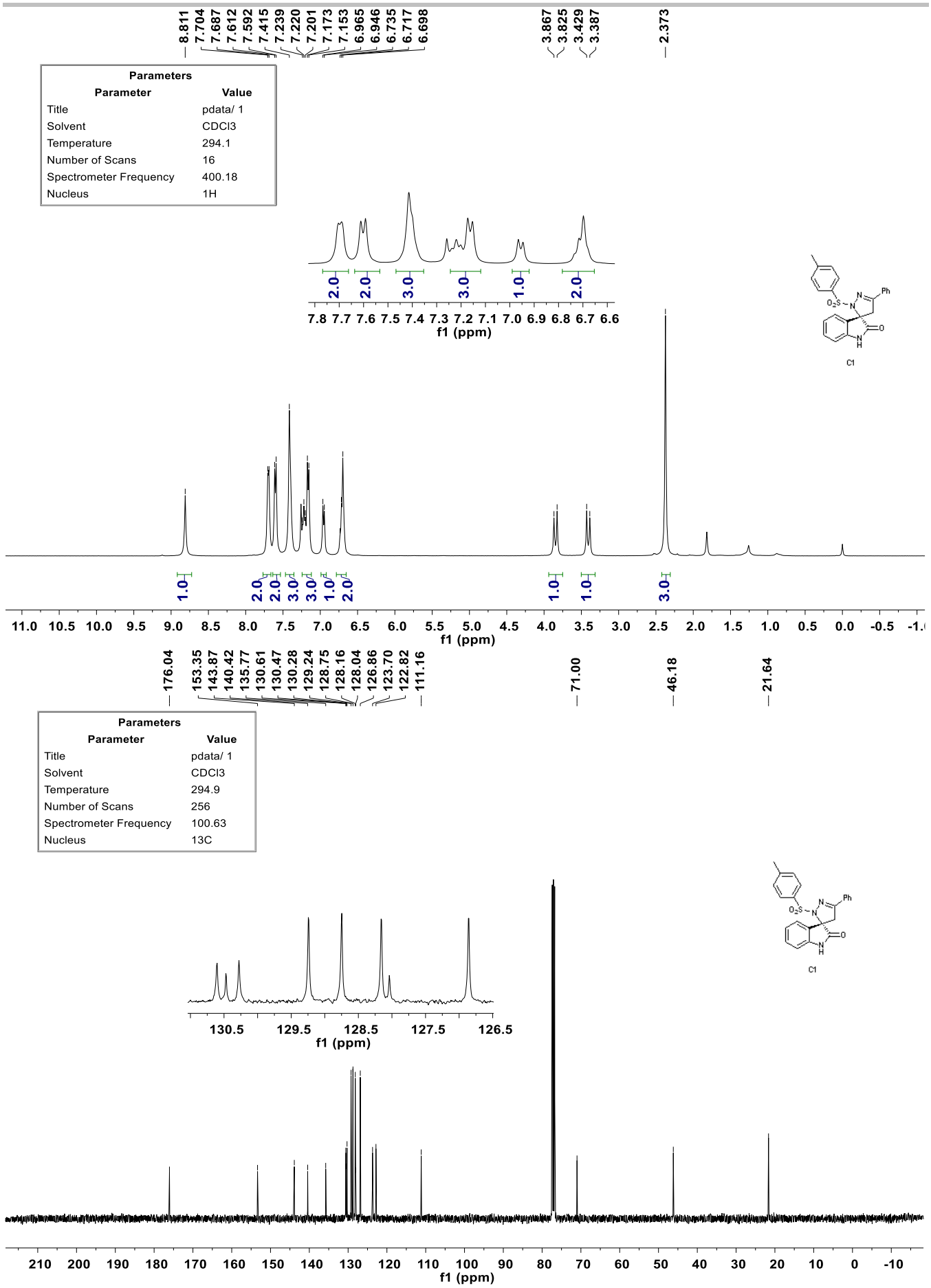

171.19
147.77
144.96
143.87
132.13
129.22
126.84
123.44
122.24
111.63
69.94
Parameters
Parameter Value
Title pdata/ 1
Solvent DMSO
Temperature 294.9
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
Br
Py
O
N
H
B1
f1 (ppm)

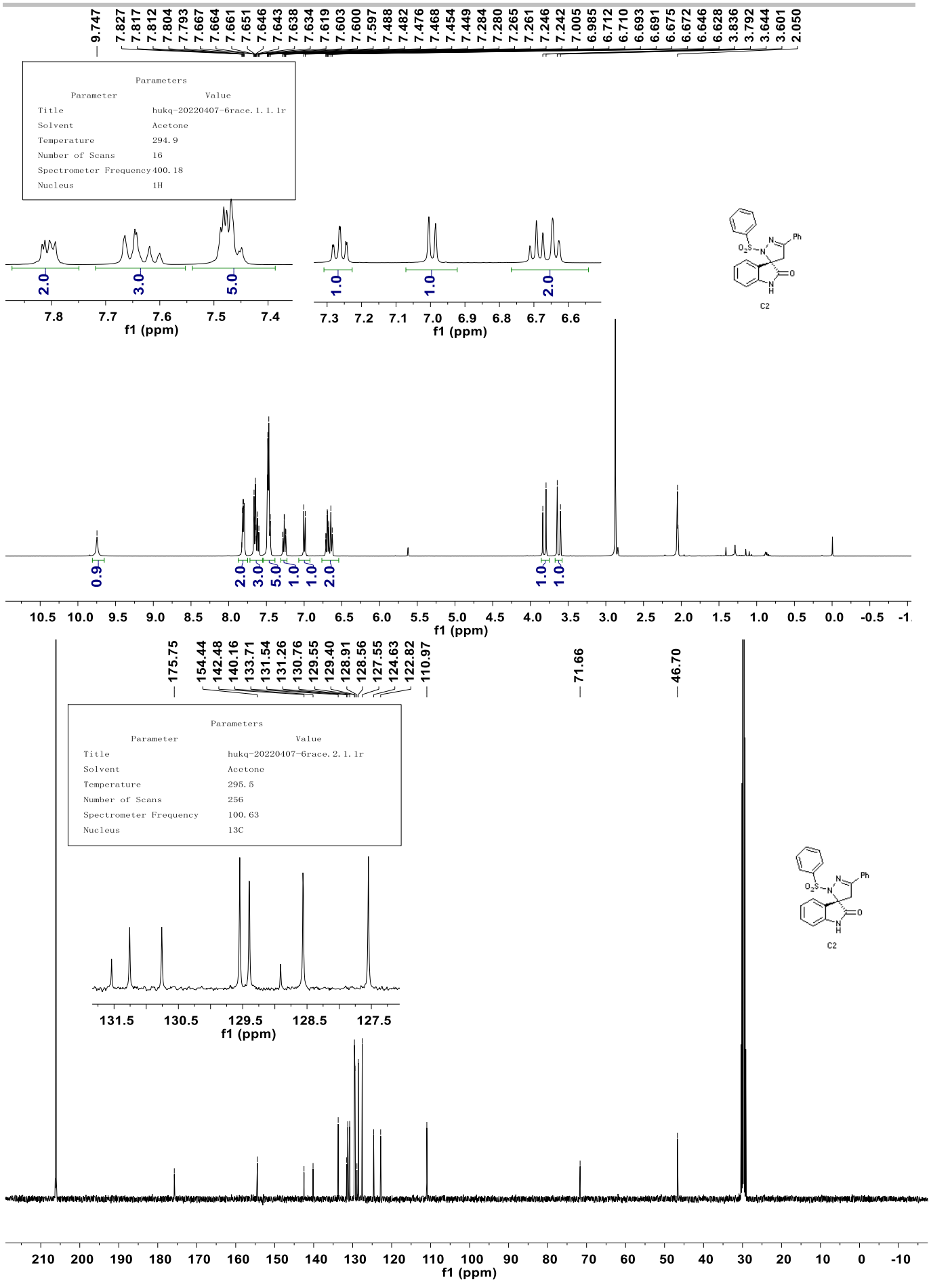

11.402
9.022
9.008
8.768
8.749
8.729
8.259
8.242
8.223
7.584
7.569
7.563
7.549
7.011
7.005
6.989
6.965
6.959
6.941
6.935
6.918
6.912
6.722
Parameters
Parameter Value
Title pdata/ 1
Solvent DMSO
Temperature 294.2
Number of Scans 64
Spectrometer Frequency 400.18
Nucleus 1H
Br
Py
F
O
N
H
B2
0.9
2.0
1.0
2.0
1.0
1.1
1.0
1.0
13.0 12.5 12.0 11.5 11.0 10.5 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 -0.5 -1.
f1 (ppm)
171.581
163.314
147.803
146.021
145.896
144.986
129.158
129.029
128.927
126.948
118.196
118.168
109.945
109.719
100.038
99.768
69.423
Parameters
Parameter Value
Title pdata/ 1
Solvent DMSO
Temperature 294.7
Number of Scans 1024
Spectrometer Frequency 100.63
Nucleus 13C
Br
Py
F
O
N
H
B2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

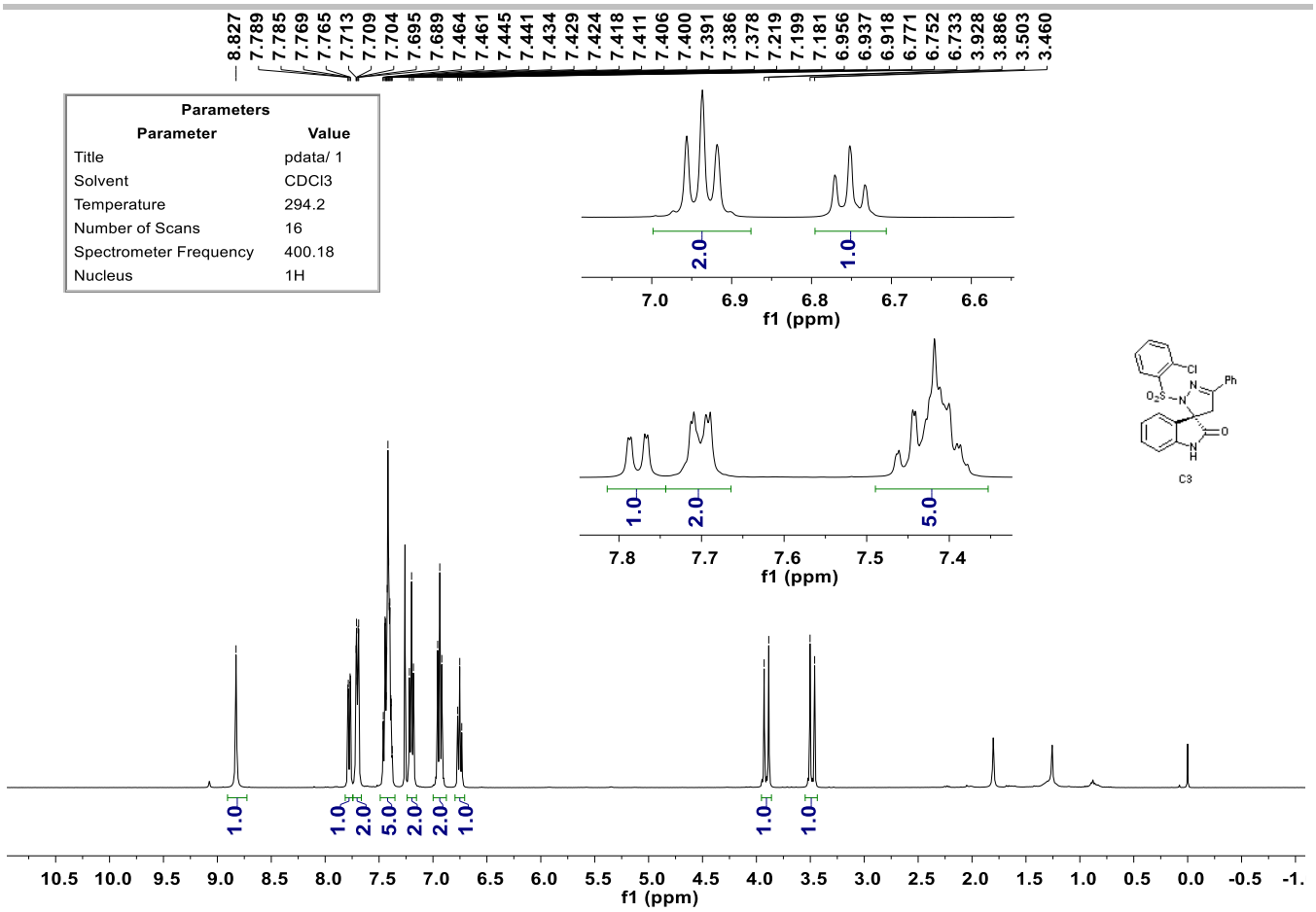

-107.816
Parameters
Parameter Value
Title pdata/ 1
Solvent DMSO
Temperature 294.0
Number of Scans 16
Spectrometer Frequency 376.55
Nucleus 19F
Br
Py
O
F
N
H
B2
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

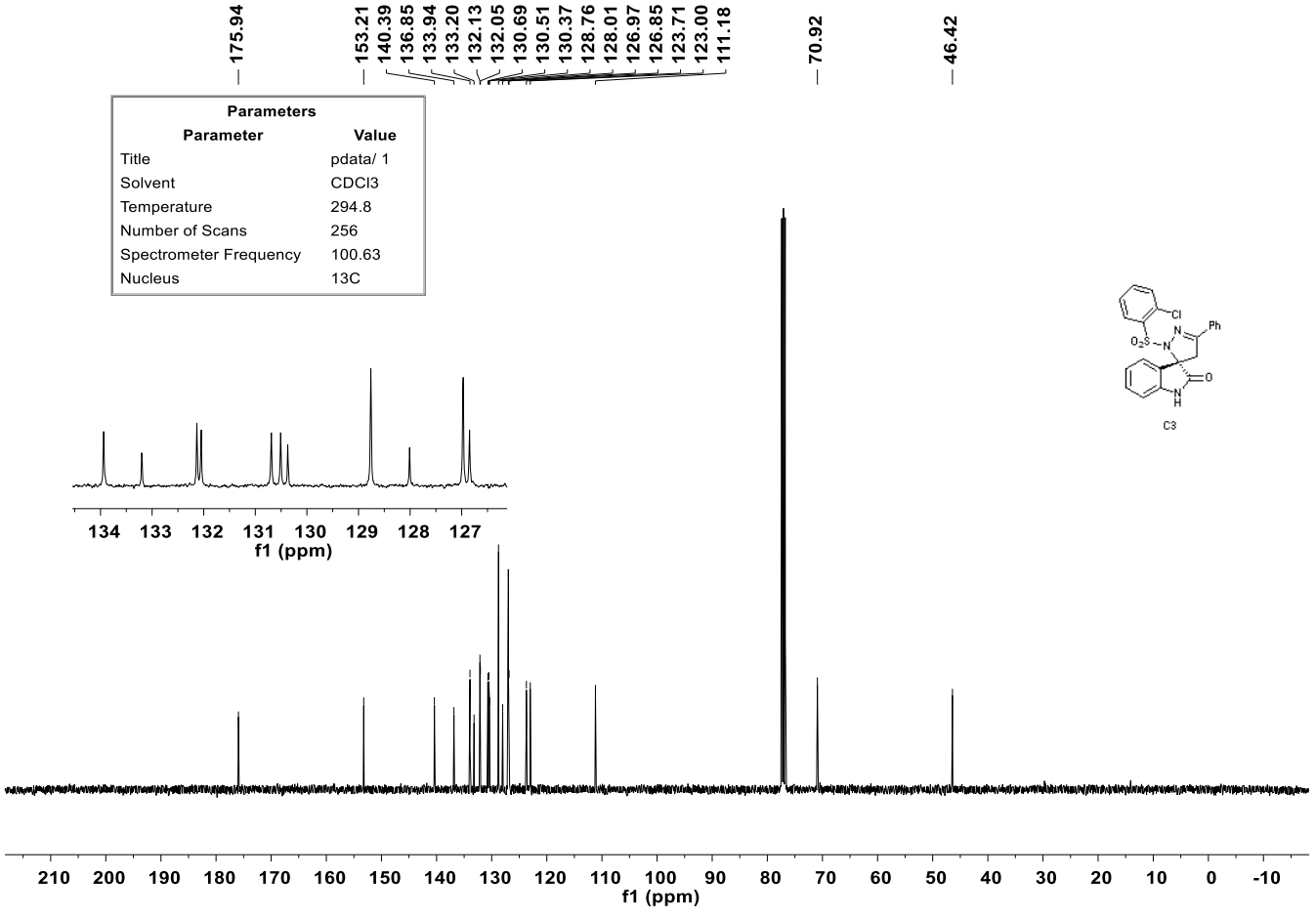

11.158
9.009
8.995
8.770
8.750
8.731
8.263
8.245
8.227
7.317
7.300
7.279
6.984
6.964
6.749
2.276
Parameters
Parameter Value
Title pdata/ 1
Solvent DMSO
Temperature 294.0
Number of Scans 64
Spectrometer Frequency 400.18
Nucleus 1H
I⁻ Py⁺
O
N
H
B3
1.0
1.9
1.0
2.0
2.0
1.0
1.1
3.1
13.0 12.5 12.0 11.5 11.0 10.5 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 -0.5 -1
f1 (ppm)

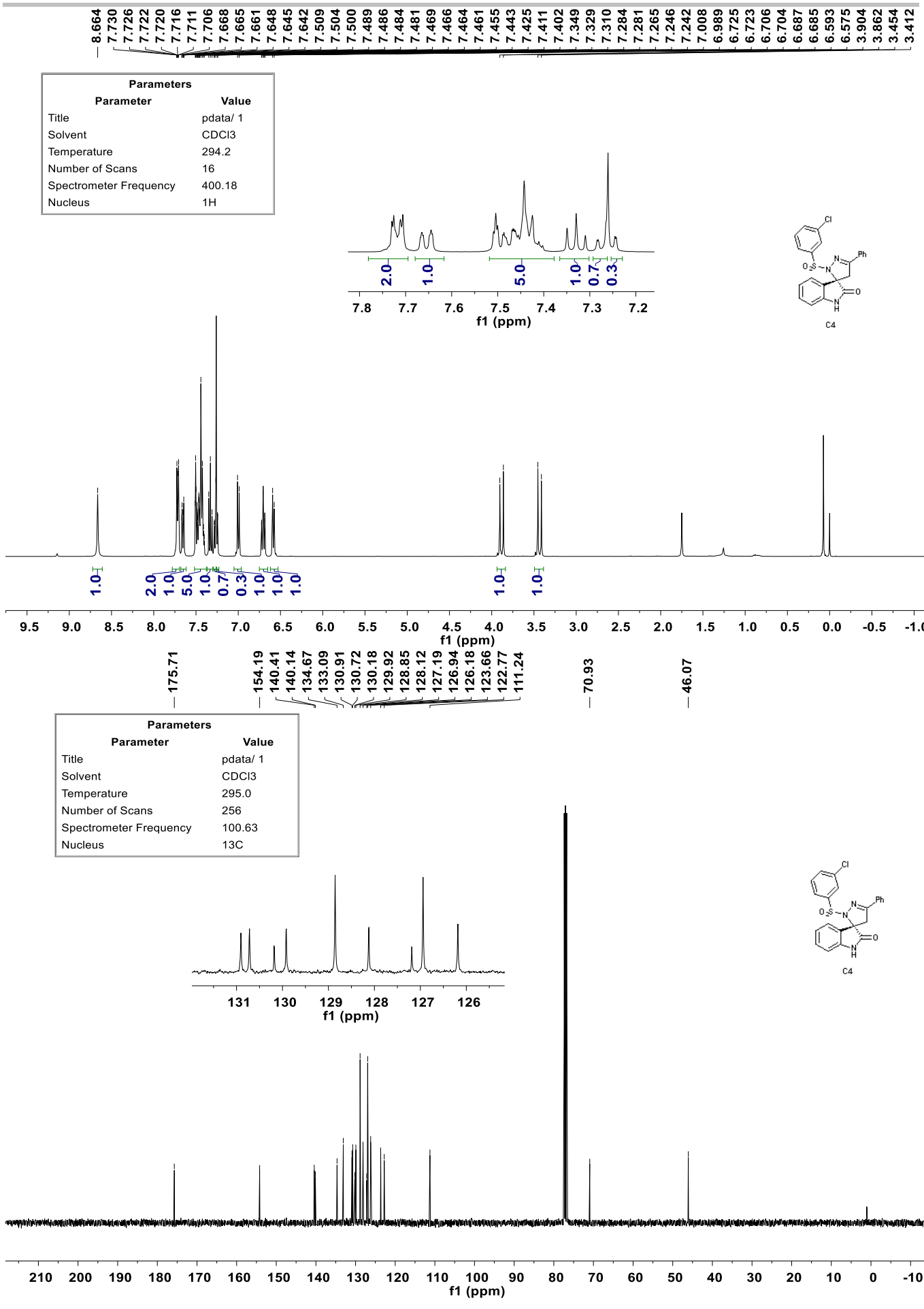

171.148
147.731
144.962
141.340
132.581
132.357
129.252
127.186
122.327
111.379
70.030
21.053
Parameters
Parameter Value
Title pdata/ 1
Solvent DMSO
Temperature 294.7
Number of Scans 1024
Spectrometer Frequency 100.63
Nucleus 13C
I⁻ Py⁺
O
N
H
B3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

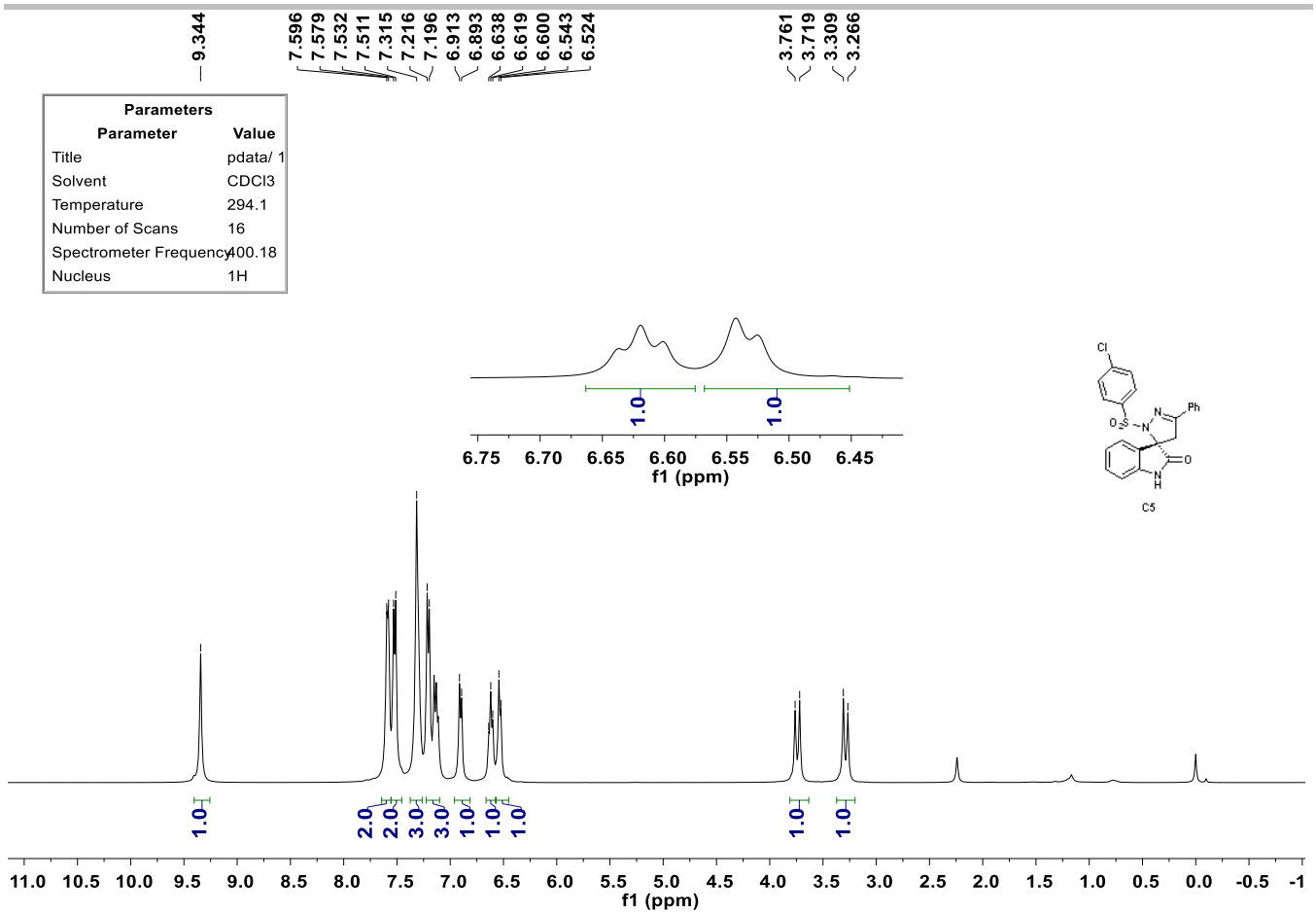

8.811
7.704
7.687
7.612
7.592
7.415
7.239
7.220
7.201
7.173
7.153
6.965
6.946
6.735
6.717
6.698
3.867
3.825
3.429
3.387
2.373
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.1
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
2.0
2.0
3.0
3.0
1.0
2.0
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6
f1 (ppm)
Ph
O
N
H
C1
1.0
2.0
2.0
3.0
3.0
1.0
2.0
1.0
1.0
3.0
11.0 10.5 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 -0.5
f1 (ppm)
176.04
153.35
143.87
140.42
135.77
130.61
130.47
130.28
129.24
128.75
128.16
128.04
126.86
123.70
122.82
111.16
71.00
46.18
21.64
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.9
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
130.5 129.5 128.5 127.5 126.5
f1 (ppm)
Ph
O
N
H
C1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

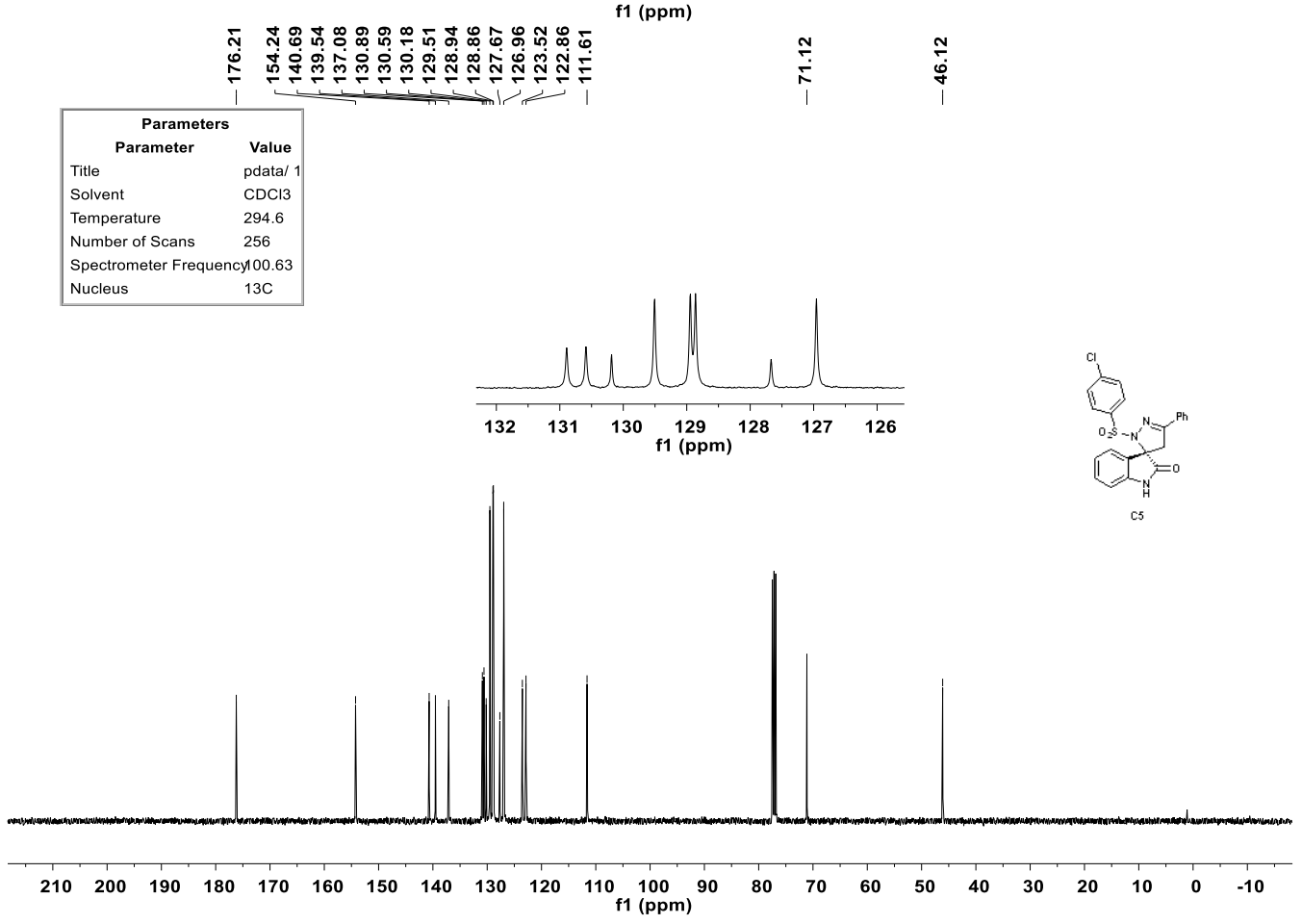

9.747
7.827
7.817
7.812
7.804
7.793
7.667
7.664
7.661
7.651
7.646
7.643
7.638
7.634
7.619
7.603
7.600
7.597
7.488
7.482
7.476
7.468
7.454
7.449
7.284
7.280
7.265
7.261
7.246
7.242
7.005
6.985
6.712
6.710
6.693
6.691
6.675
6.672
6.646
6.628
3.836
3.792
3.644
3.601
2.050
Parameters
Parameter Value
Title hukq-20220407-6race.1.1.1r
Solvent Acetone
Temperature 294.9
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
2.0
3.0
5.0
1.0
1.0
2.0
f1 (ppm)
Ph
C2
0.9
2.0
3.0
5.0
1.0
1.0
2.0
1.0
1.0
f1 (ppm)
175.75
154.44
142.48
140.16
133.71
131.54
131.26
130.76
129.55
129.40
128.91
128.56
127.55
124.63
122.82
110.97
71.66
46.70
Parameters
Parameter Value
Title hukq-20220407-6race.2.1.1r
Solvent Acetone
Temperature 295.5
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
f1 (ppm)
Ph
C2
f1 (ppm)

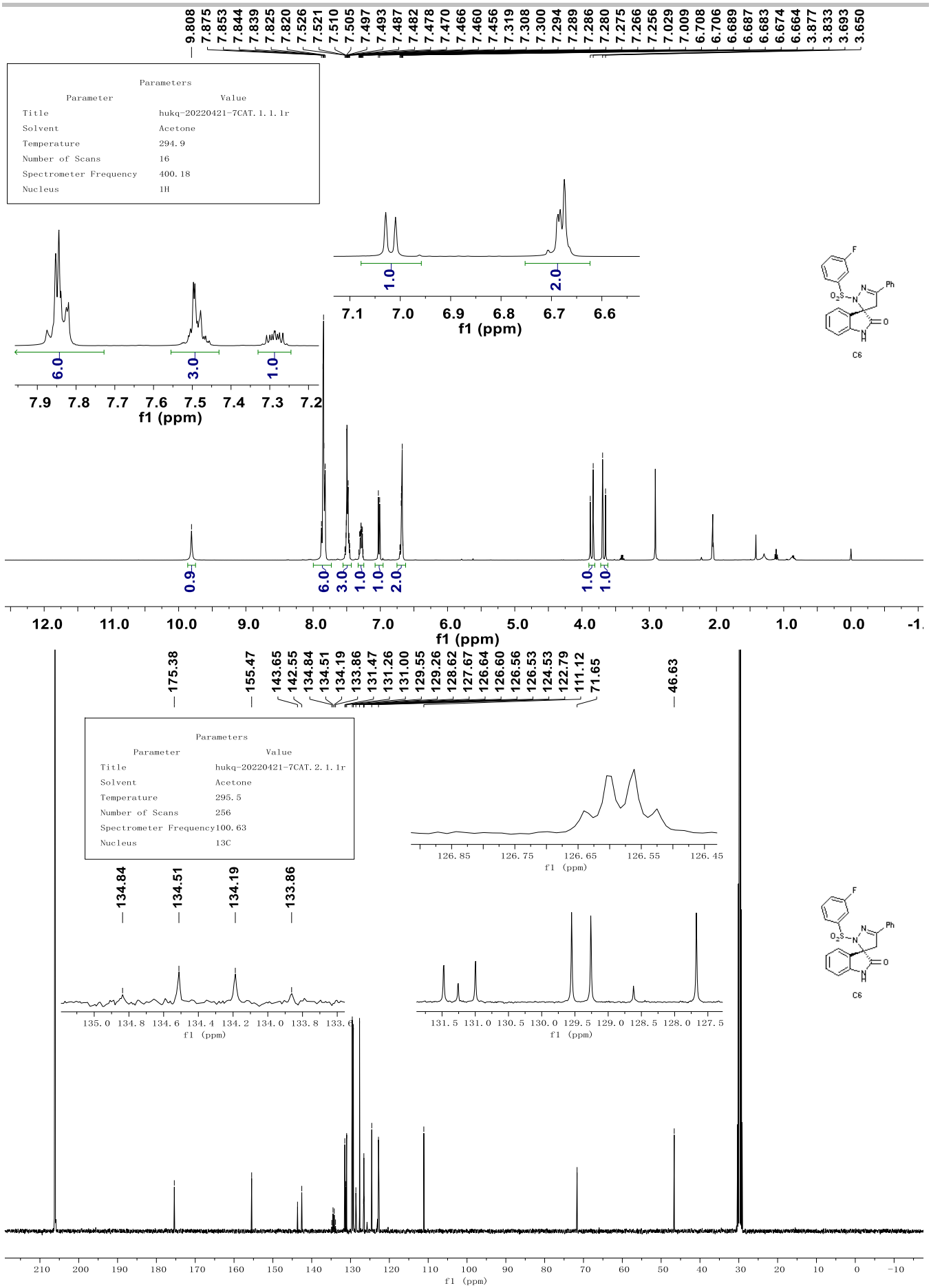

8.827
7.789
7.785
7.769
7.765
7.713
7.709
7.704
7.695
7.689
7.464
7.461
7.445
7.441
7.434
7.429
7.424
7.418
7.411
7.406
7.400
7.391
7.386
7.378
7.219
7.199
7.181
6.956
6.937
6.918
6.771
6.752
6.733
3.928
3.886
3.503
3.460
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.2
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
2.0
1.0
7.0 6.9 6.8 6.7 6.6
f1 (ppm)
1.0
2.0
5.0
7.8 7.7 7.6 7.5 7.4
f1 (ppm)
C3
1.0 1.0 2.0 5.0 2.0 2.0 1.0 1.0 1.0
10.5 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 -0.5 -1.
f1 (ppm)

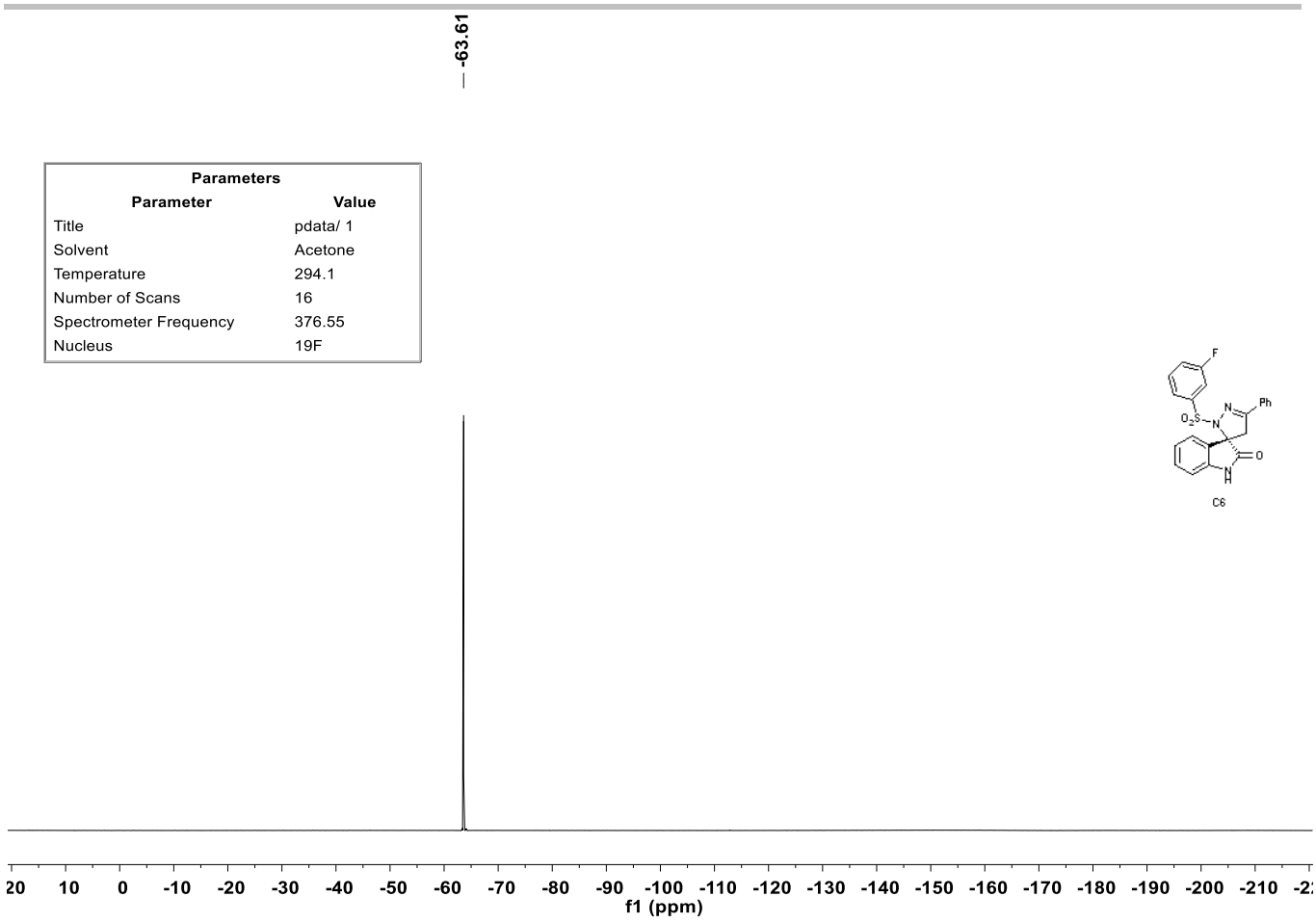

175.94
153.21
140.39
136.85
133.94
133.20
132.13
132.05
130.69
130.51
130.37
128.76
128.01
126.97
126.85
123.71
123.00
111.18
70.92
46.42
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.8
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
134 133 132 131 130 129 128 127
f1 (ppm)
C3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

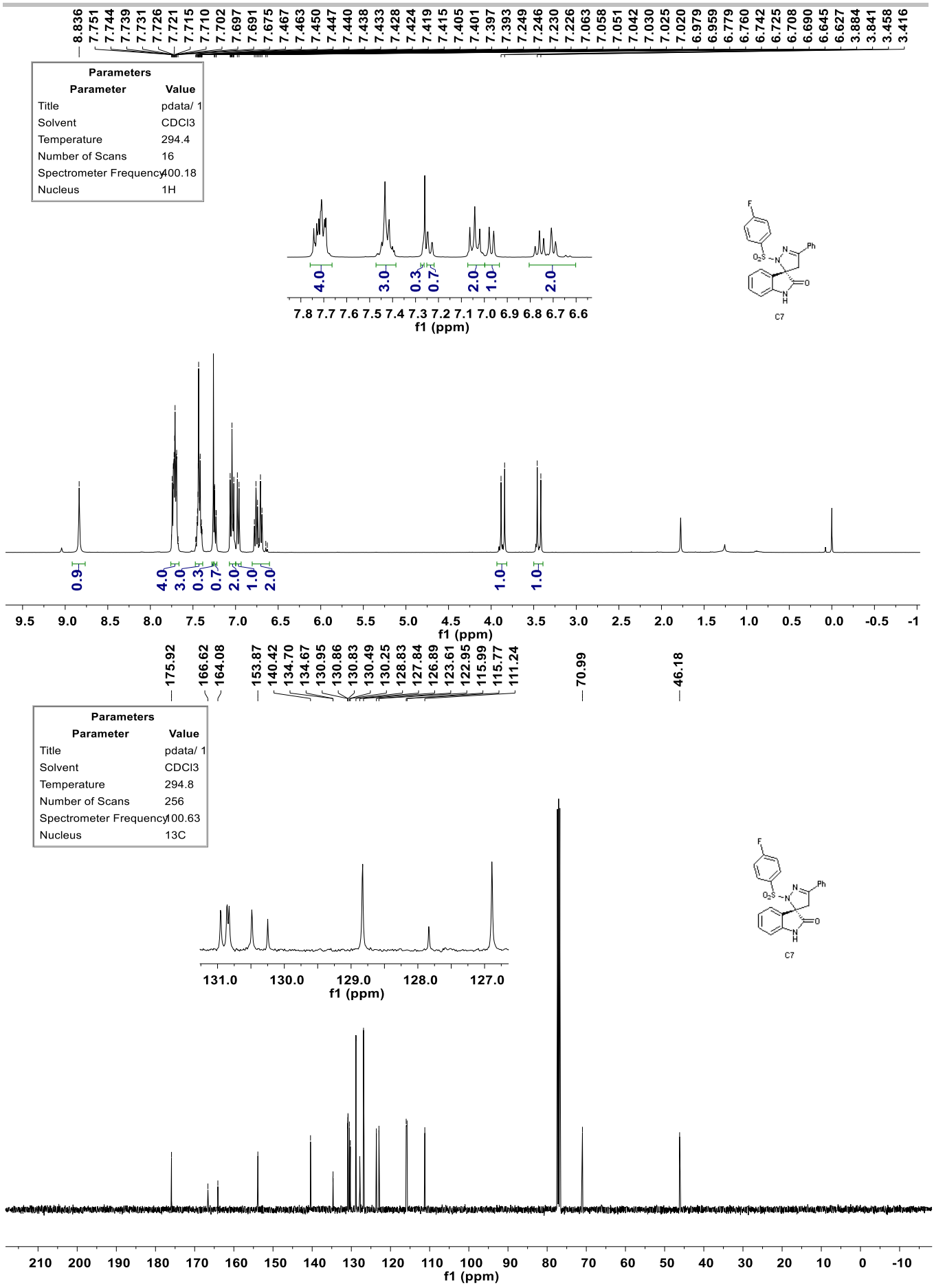

8.664 7.730 7.726 7.722 7.720 7.716 7.711 7.706 7.668 7.665 7.661 7.648 7.645 7.642 7.509 7.504 7.500 7.489 7.486 7.484 7.481 7.469 7.466 7.464 7.461 7.455 7.443 7.425 7.411 7.402 7.349 7.329 7.310 7.284 7.281 7.265 7.246 7.242 7.008 6.989 6.725 6.723 6.706 6.704 6.687 6.685 6.593 6.575 3.904 3.862 3.454 3.412
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.2
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
2.0 1.0 5.0 1.0 0.7 0.3
7.8 7.7 7.6 7.5 7.4 7.3 7.2
f1 (ppm)
Cl
Ph
O
N
S
O
N
H
O
C4
1.0 2.0 1.0 5.0 1.0 0.7 0.3 1.0 1.0 1.0 1.0 1.0
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 -0.5
f1 (ppm)
175.71 154.19 140.41 140.14 134.67 133.09 130.91 130.72 130.18 129.92 128.85 128.12 127.19 126.94 126.18 123.66 122.77 111.24 70.93 46.07
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 295.0
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
131 130 129 128 127 126
f1 (ppm)
Cl
Ph
O
N
S
O
N
H
O
C4
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


9.344
7.596
7.579
7.532
7.511
7.315
7.216
7.196
6.913
6.893
6.638
6.619
6.600
6.543
6.524
3.761
3.719
3.309
3.266
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.1
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
1.0
1.0
6.75 6.70 6.65 6.60 6.55 6.50 6.45
f1 (ppm)
Cl
Ph
O
N
H
C5
1.0 2.0 2.0 3.0 3.0 1.0 1.0 1.0 1.0 1.0
11.0 10.5 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 -0.5 -1
f1 (ppm)

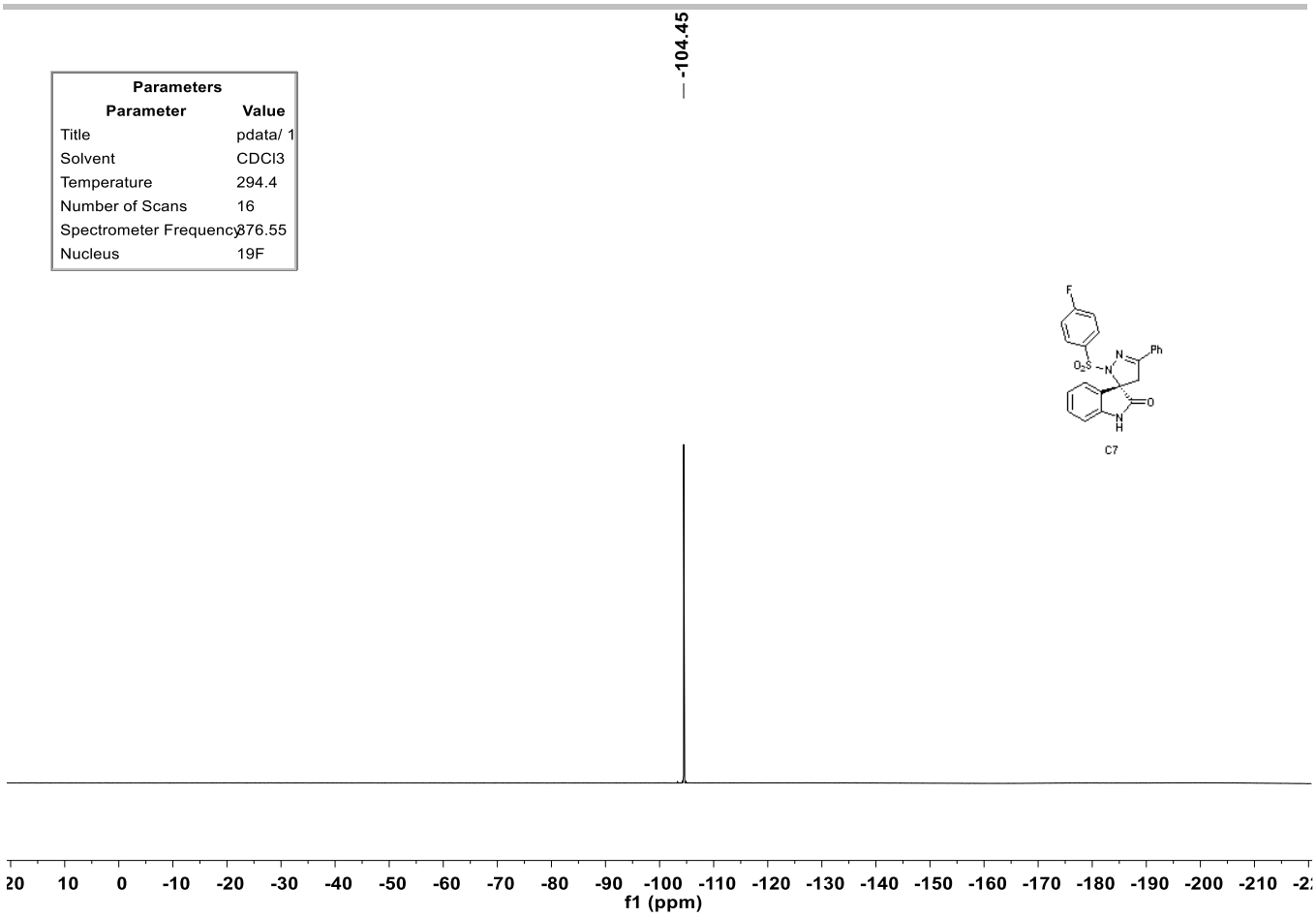

176.21
154.24
140.69
139.54
137.08
130.89
130.59
130.18
129.51
128.94
128.86
127.67
126.96
123.52
122.86
111.61
71.12
46.12
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.6
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
132 131 130 129 128 127 126
f1 (ppm)
Cl
Ph
O
N
H
C5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

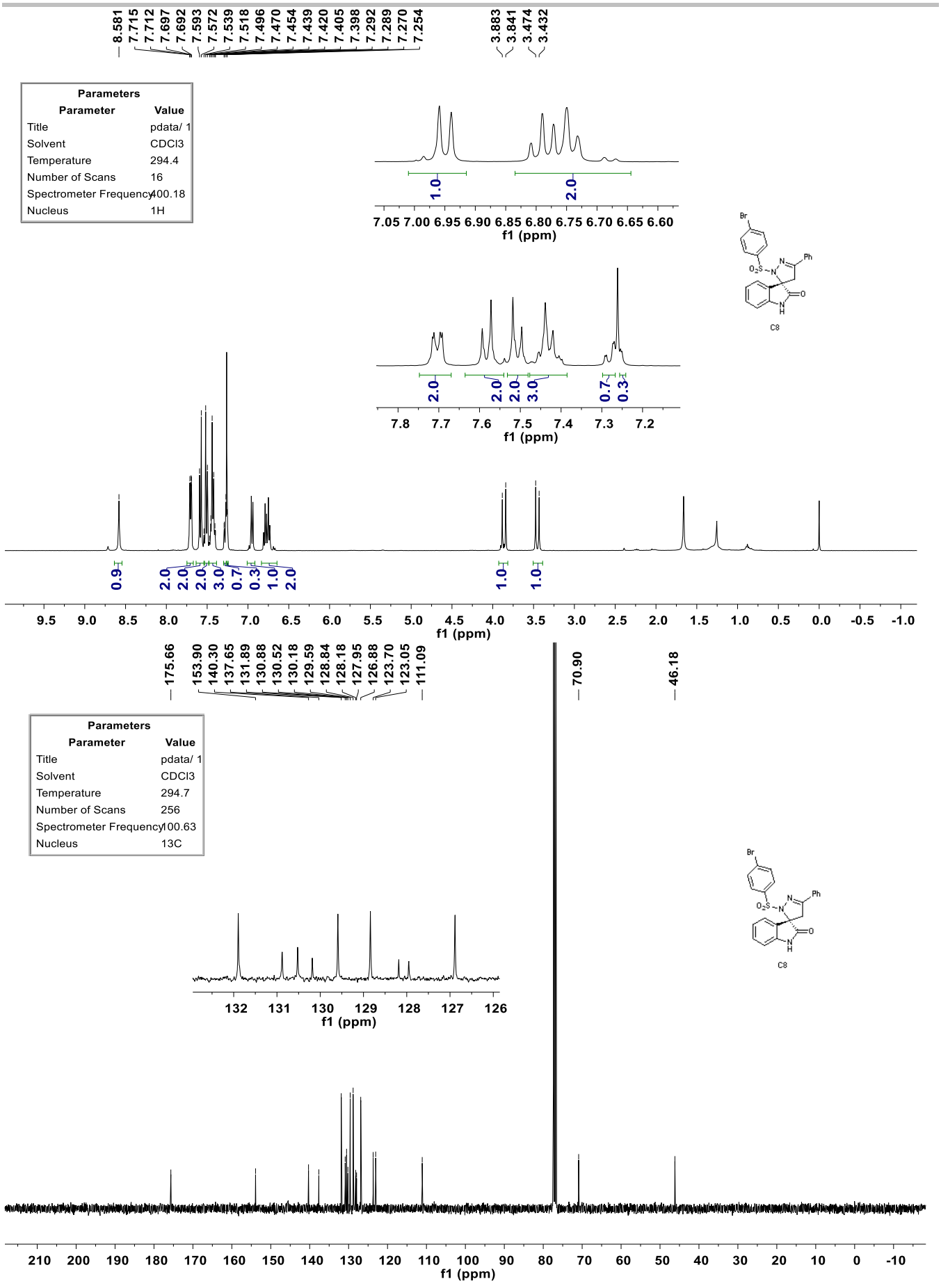

9.808
7.875
7.853
7.844
7.839
7.825
7.820
7.526
7.521
7.510
7.505
7.497
7.493
7.487
7.482
7.478
7.470
7.466
7.460
7.456
7.319
7.308
7.300
7.294
7.289
7.286
7.280
7.275
7.266
7.256
7.029
7.009
6.708
6.706
6.689
6.687
6.683
6.674
6.664
3.877
3.833
3.693
3.650
Parameters
Parameter Value
Title hukq-20220421-7CAT.1.1.1r
Solvent Acetone
Temperature 294.9
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
f1 (ppm)
C6
Parameters
Parameter Value
Title hukq-20220421-7CAT.2.1.1r
Solvent Acetone
Temperature 295.5
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
175.38
155.47
143.65
142.55
134.84
134.51
134.19
133.86
131.47
131.26
131.00
129.55
129.26
128.62
127.67
126.64
126.60
126.56
126.53
124.53
122.79
111.12
71.65
46.63
f1 (ppm)
C6

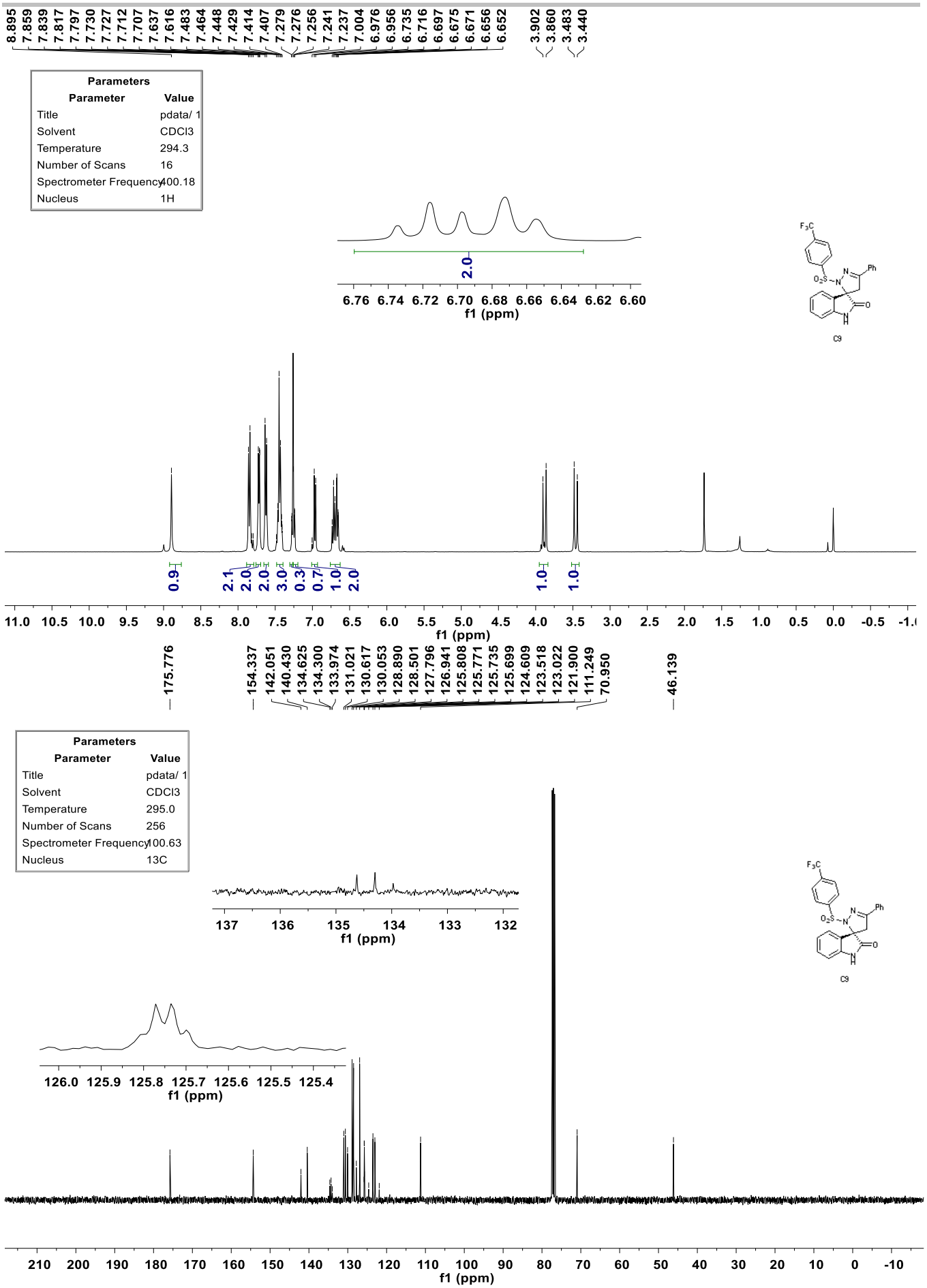

-63.61
Parameters
Parameter Value
Title pdata/ 1
Solvent Acetone
Temperature 294.1
Number of Scans 16
Spectrometer Frequency 376.55
Nucleus 19F
F
Ph
O
C6
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


8.836 7.751 7.744 7.739 7.731 7.726 7.721 7.715 7.710 7.702 7.697 7.691 7.675 7.467 7.463 7.450 7.447 7.440 7.438 7.433 7.428 7.424 7.419 7.415 7.405 7.401 7.397 7.393 7.249 7.246 7.230 7.226 7.063 7.058 7.051 7.042 7.030 7.025 7.020 6.979 6.959 6.779 6.760 6.742 6.725 6.708 6.690 6.645 6.627 3.884 3.841 3.458 3.416
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.4
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
4.0 3.0 0.3 0.7 2.0 1.0 2.0
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6
f1 (ppm)
F
Ph
O2S
N
O
H
C7
0.9 4.0 3.0 0.3 0.7 2.0 1.0 2.0 1.0 1.0
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 -0.5 -1
f1 (ppm)
175.92 166.62 164.08 153.87 140.42 134.70 134.67 130.95 130.86 130.83 130.49 130.25 128.83 127.84 126.89 123.61 122.95 115.99 115.77 111.24 70.99 46.18
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.8
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
131.0 130.0 129.0 128.0 127.0
f1 (ppm)
F
Ph
O2S
N
O
H
C7
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

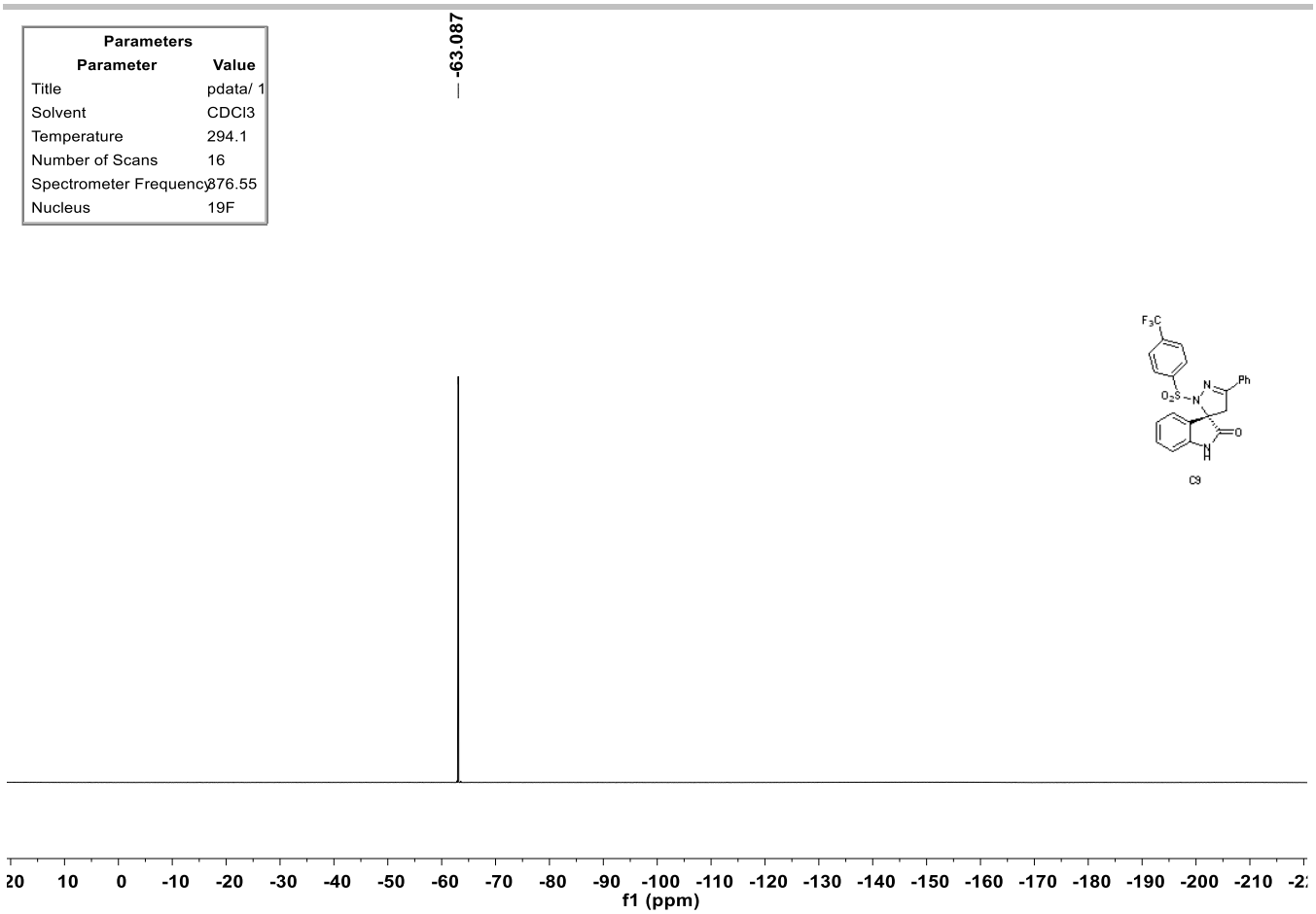
Parameters	
Parameter	**Value**
Title	pdata/ 1
Solvent	CDCl3
Temperature	294.4
Number of Scans	16
Spectrometer Frequency	376.55
Nucleus	19F

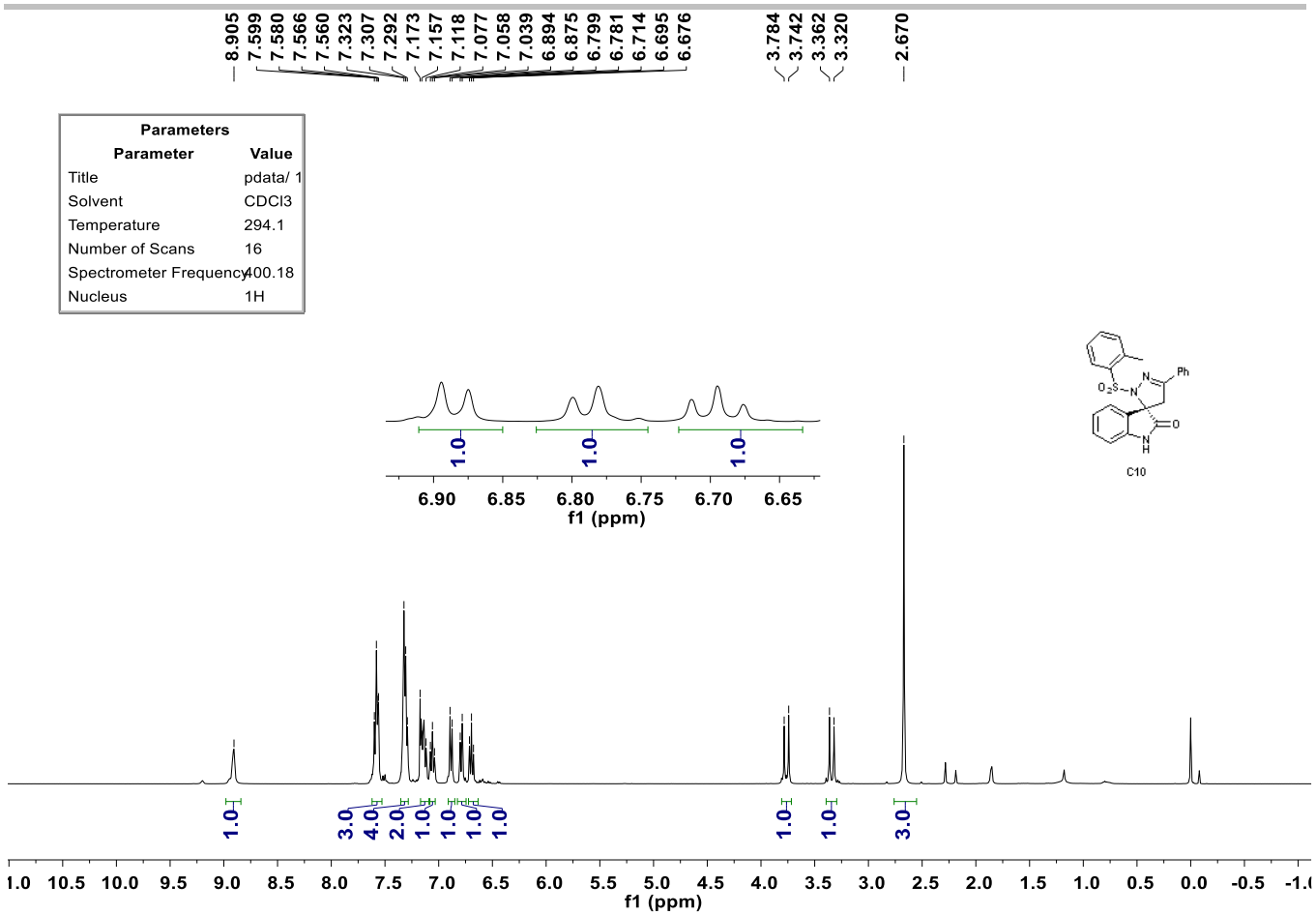


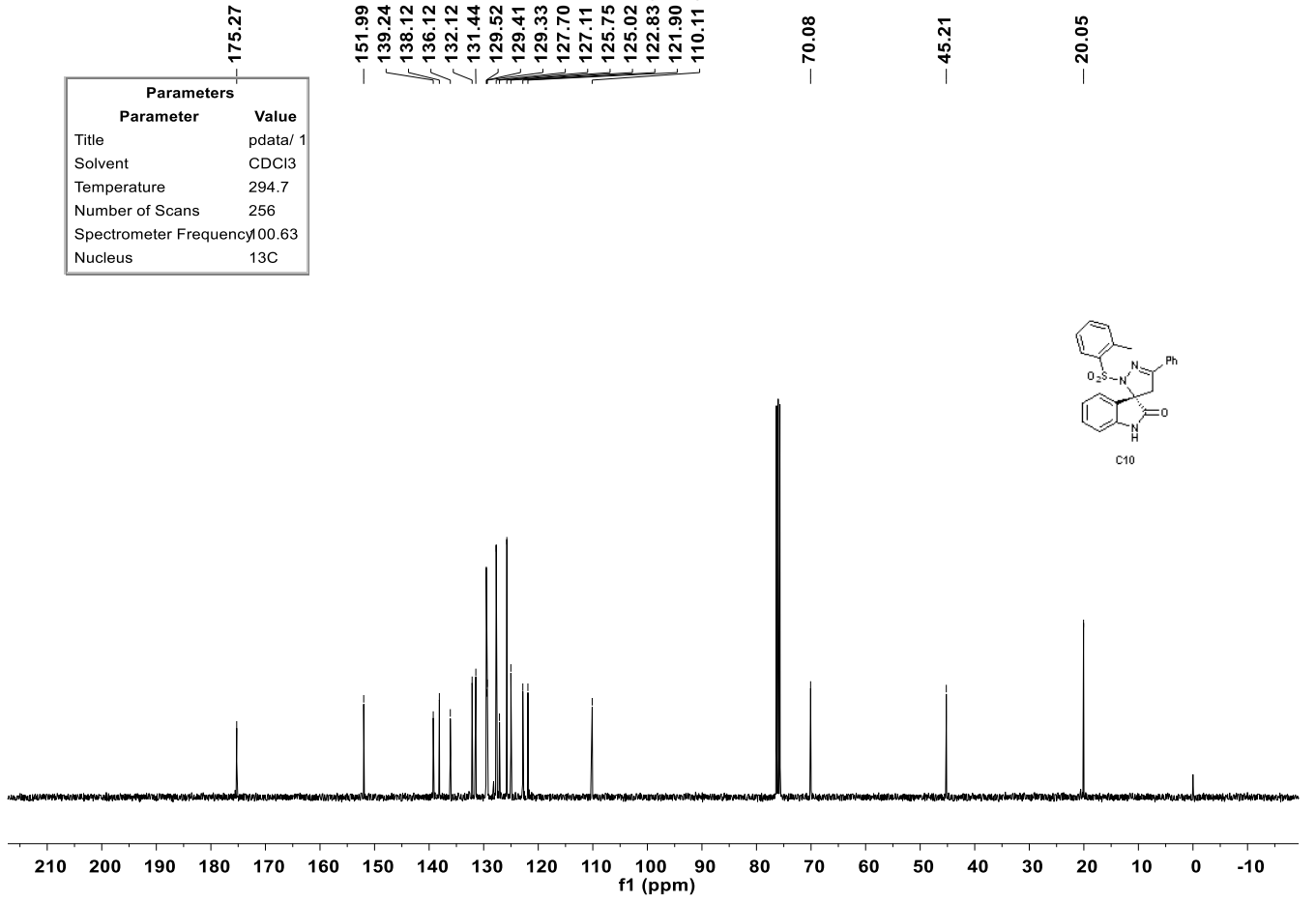

8.581
7.715
7.712
7.697
7.692
7.593
7.572
7.539
7.518
7.496
7.470
7.454
7.439
7.420
7.405
7.398
7.292
7.289
7.270
7.254
3.883
3.841
3.474
3.432
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.4
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
1.0
2.0
7.05 7.00 6.95 6.90 6.85 6.80 6.75 6.70 6.65 6.60
f1 (ppm)
Br
Ph
C8
2.0
2.0
2.0
3.0
0.7
0.3
7.8 7.7 7.6 7.5 7.4 7.3 7.2
f1 (ppm)
0.9
2.0
2.0
2.0
3.0
0.7
0.3
1.0
2.0
1.0
1.0
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 -0.5 -1.0
f1 (ppm)
175.66
153.90
140.30
137.65
131.89
130.88
130.52
130.18
129.59
128.84
128.18
127.95
126.88
123.70
123.05
111.09
70.90
46.18
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.7
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
Br
Ph
C8
132 131 130 129 128 127 126
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

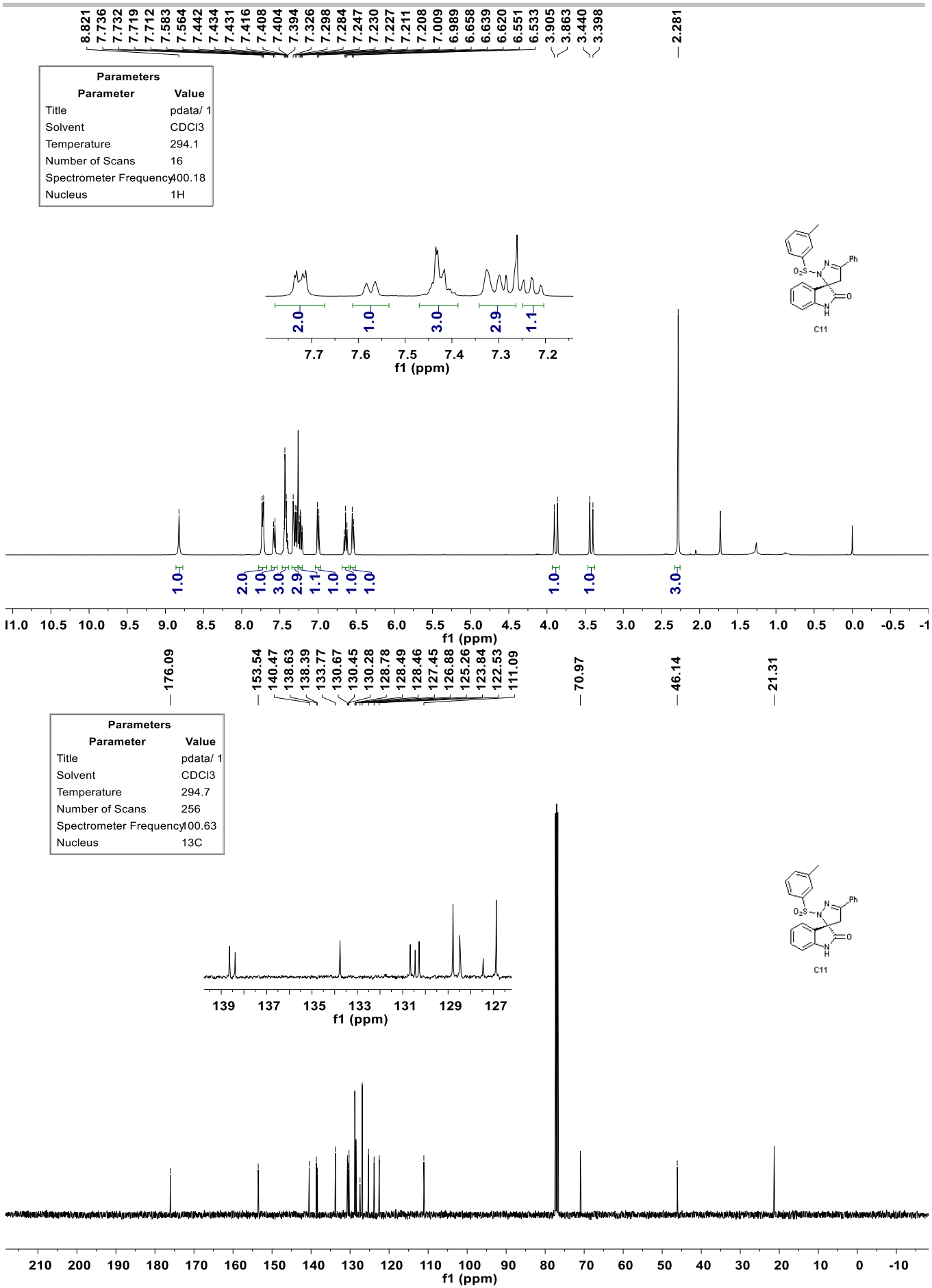

8.895 7.859 7.839 7.817 7.797 7.730 7.727 7.712 7.707 7.637 7.616 7.483 7.464 7.448 7.429 7.414 7.407 7.279 7.276 7.256 7.241 7.237 7.004 6.976 6.956 6.735 6.716 6.697 6.675 6.671 6.656 6.652
3.902 3.860 3.483 3.440
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.3
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
2.0
6.76 6.74 6.72 6.70 6.68 6.66 6.64 6.62 6.60
f1 (ppm)
F3C
Ph
N
O2S
O
H
C9
0.9 2.1 2.0 2.0 3.0 0.3 0.7 1.0 2.0 1.0 1.0
11.0 10.5 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 -0.5
f1 (ppm)
175.776
154.337 142.051 140.430 134.625 134.300 133.974 131.021 130.617 130.053 128.890 128.501 127.796 126.941 125.808 125.771 125.735 125.699 124.609 123.518 123.022 121.900 111.249 70.950
46.139
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 295.0
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
137 136 135 134 133 132
f1 (ppm)
126.0 125.9 125.8 125.7 125.6 125.5 125.4
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

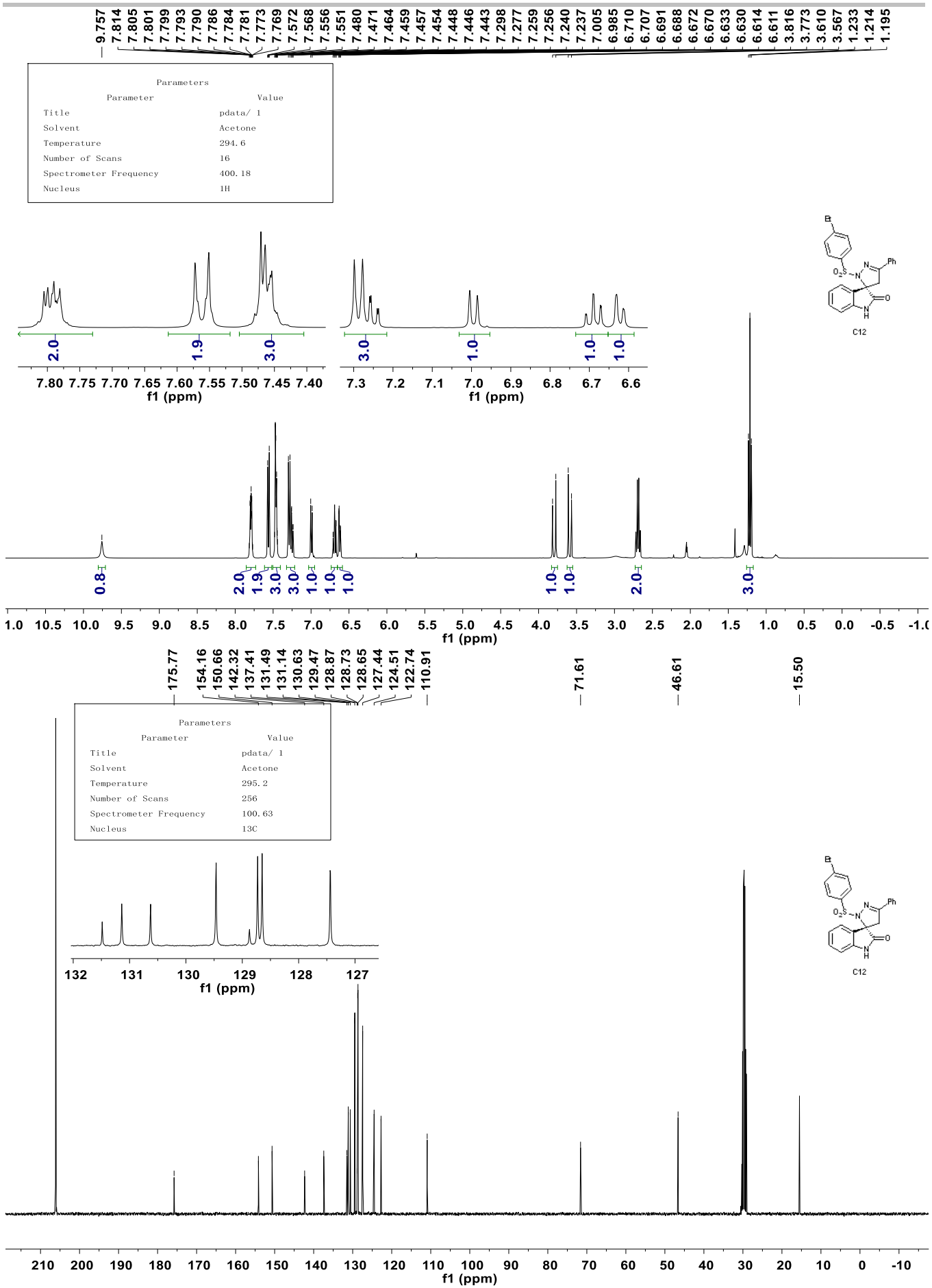
Parameters	
Parameter	**Value**
Title	pdata/ 1
Solvent	CDCl3
Temperature	294.1
Number of Scans	16
Spectrometer Frequency	376.55
Nucleus	19F

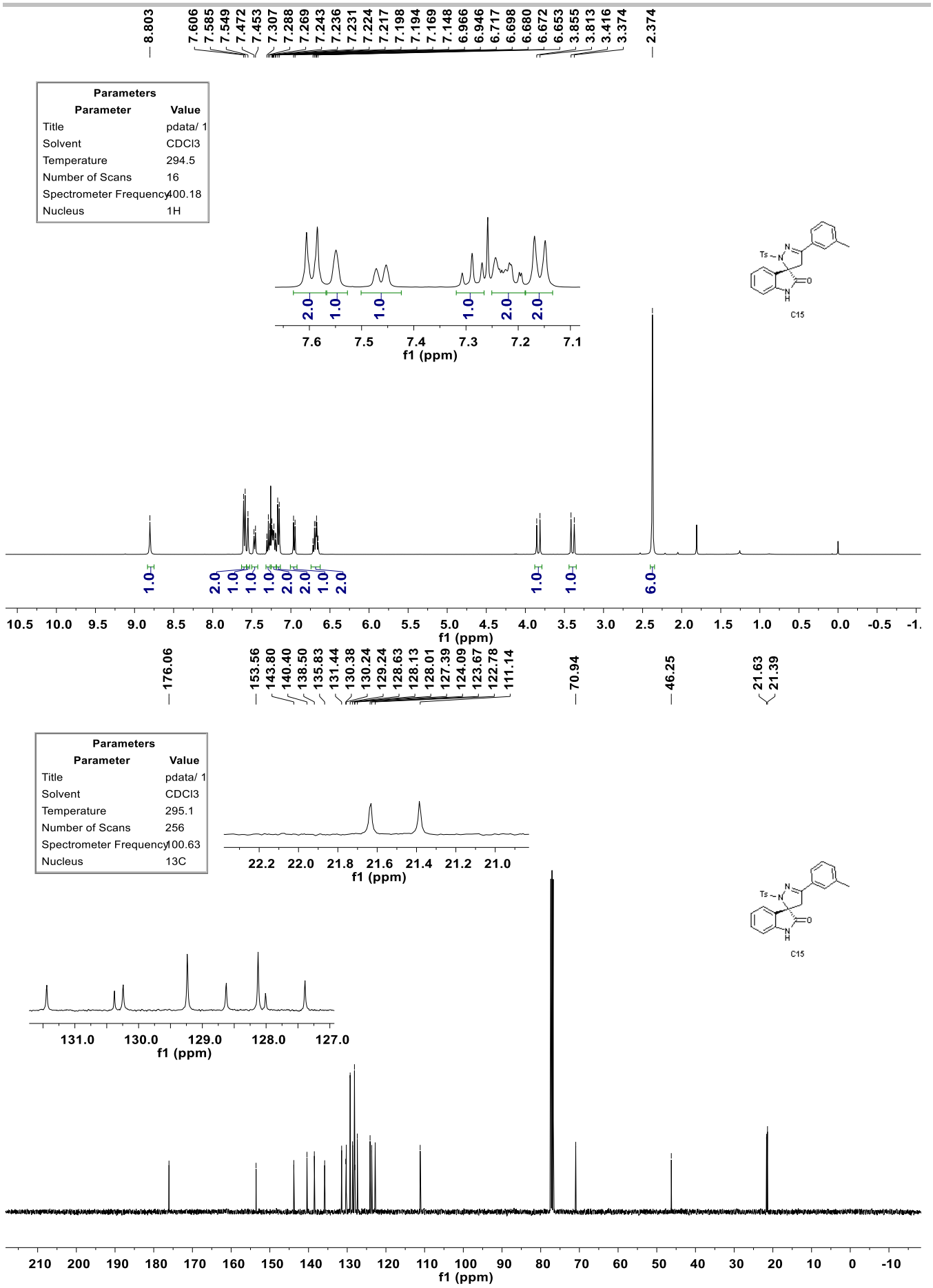


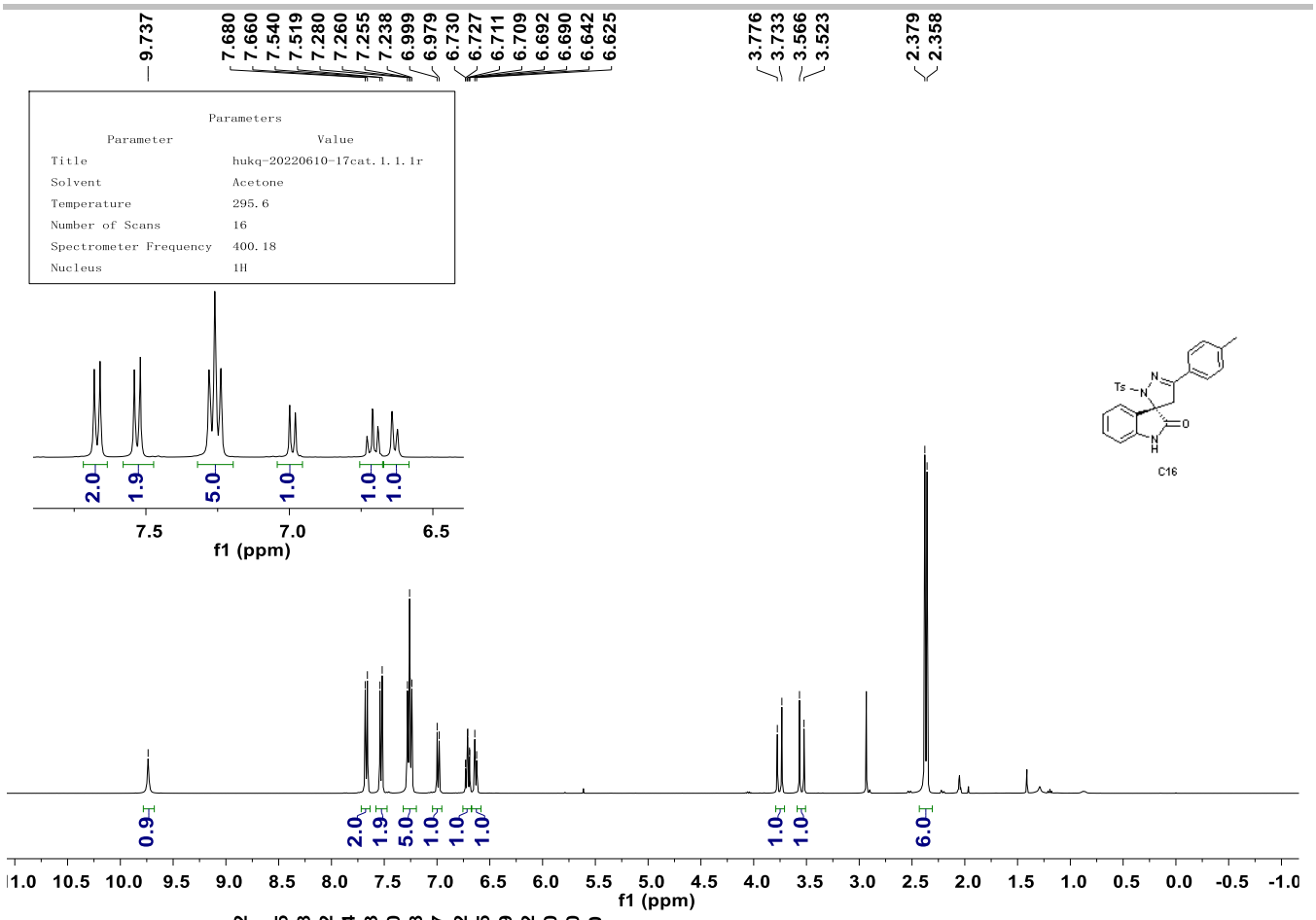

8.905
7.599
7.580
7.566
7.560
7.323
7.307
7.292
7.173
7.157
7.118
7.077
7.058
7.039
6.894
6.875
6.799
6.781
6.714
6.695
6.676
3.784
3.742
3.362
3.320
2.670
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.1
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
1.0
1.0
1.0
6.90
6.85
6.80
6.75
6.70
6.65
f1 (ppm)
Ph
O
N
H
C10
1.0
3.0
4.0
2.0
1.0
1.0
1.0
1.0
1.0
1.0
3.0
f1 (ppm)

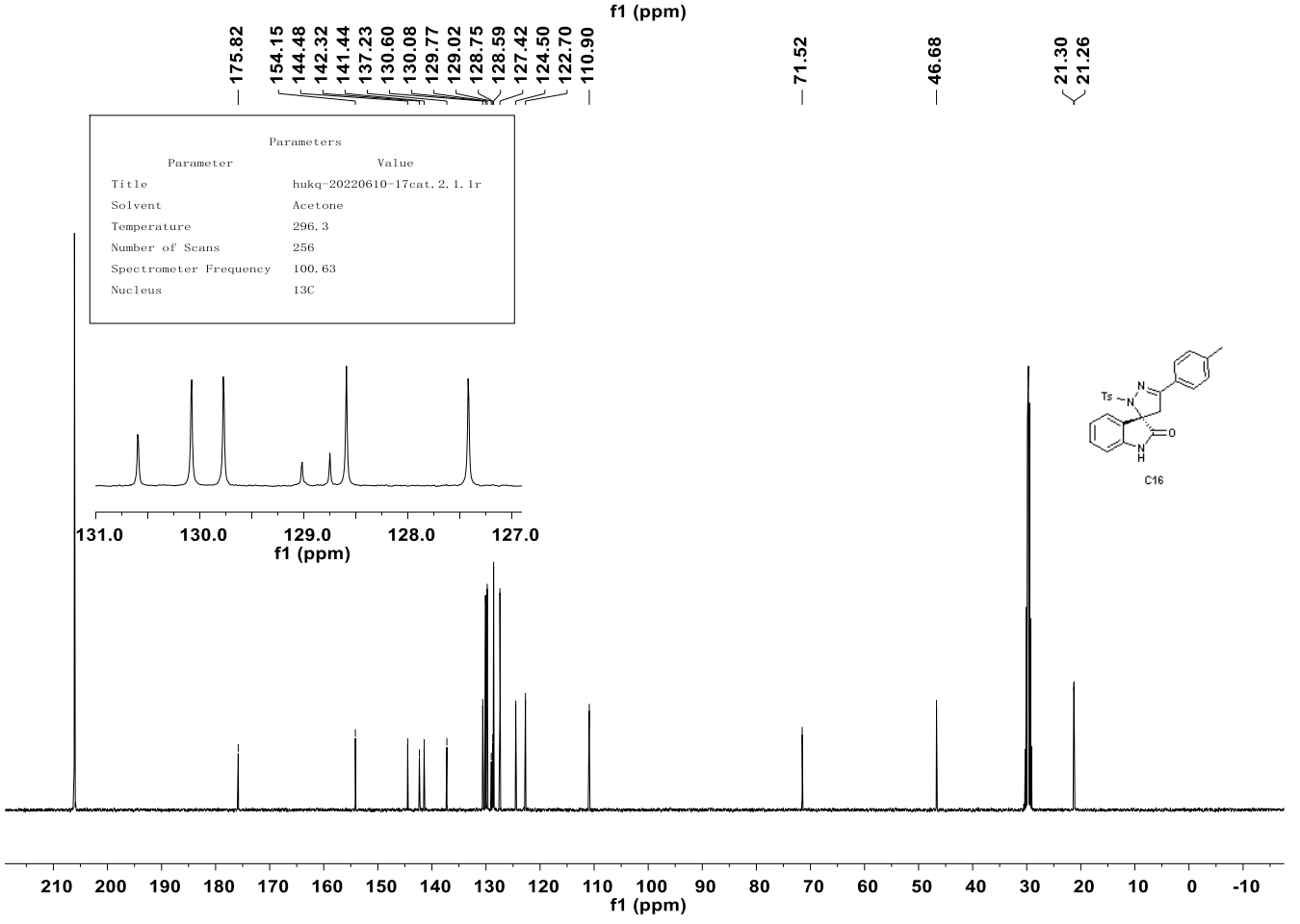

175.27
151.99
139.24
138.12
136.12
132.12
131.44
129.52
129.41
129.33
127.70
127.11
125.75
125.02
122.83
121.90
110.11
70.08
45.21
20.05
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.7
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
Ph
O
N
H
C10
f1 (ppm)

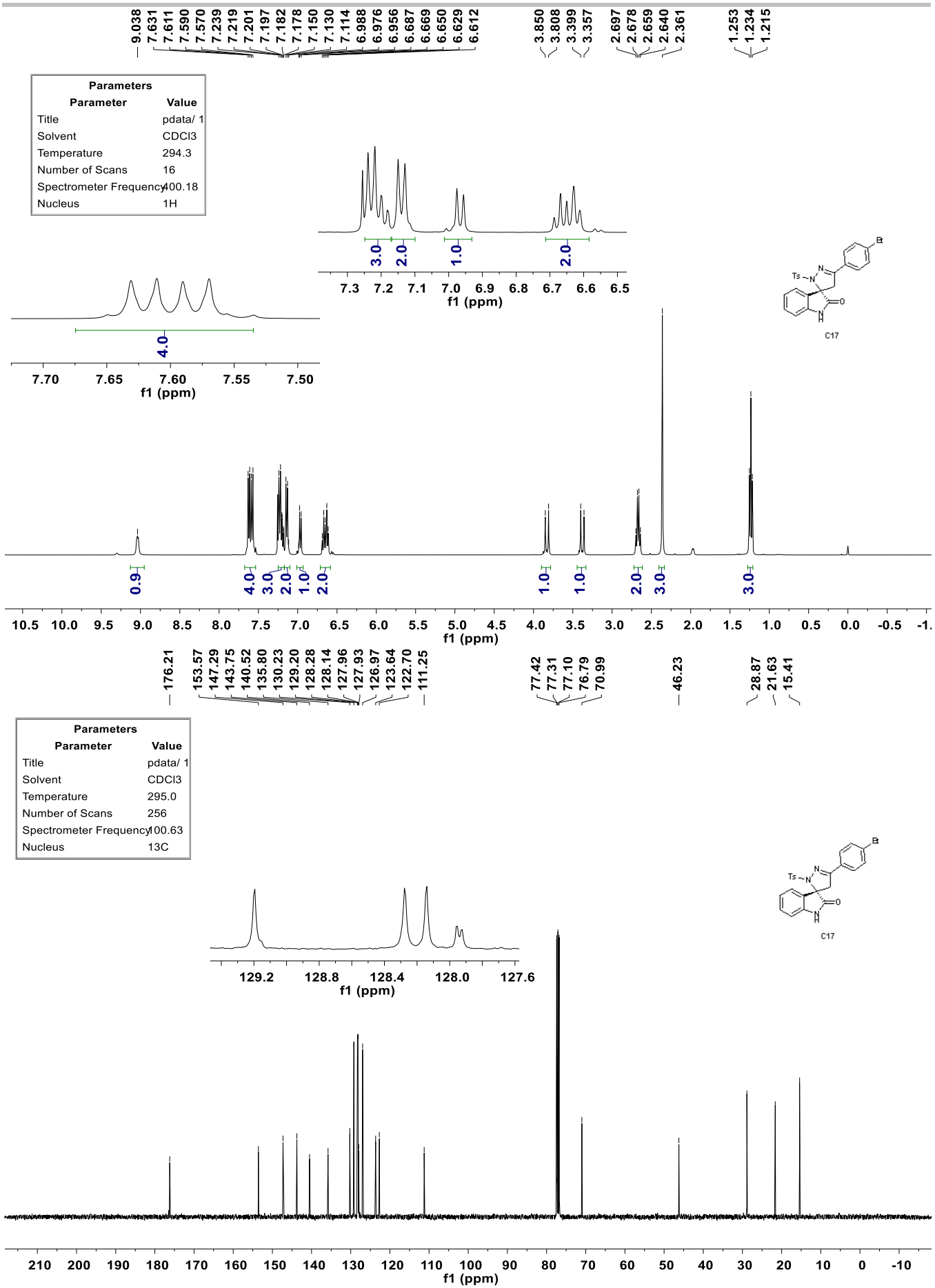

8.821 7.736 7.732 7.719 7.712 7.583 7.564 7.442 7.434 7.431 7.416 7.408 7.404 7.394 7.326 7.298 7.284 7.247 7.230 7.227 7.211 7.208 7.009 6.989 6.658 6.639 6.620 6.551 6.533 3.905 3.863 3.440 3.398 2.281
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.1
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
2.0 1.0 3.0 2.9 1.1
7.7 7.6 7.5 7.4 7.3 7.2
f1 (ppm)
C11
1.0 2.0 1.0 3.0 2.9 1.1 1.0 1.0 1.0 1.0 3.0
f1 (ppm)
176.09 153.54 140.47 138.63 138.39 133.77 130.67 130.45 130.28 128.78 128.49 128.46 127.45 126.88 125.26 123.84 122.53 111.09 70.97 46.14 21.31
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.7
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
139 137 135 133 131 129 127
f1 (ppm)
C11
f1 (ppm)

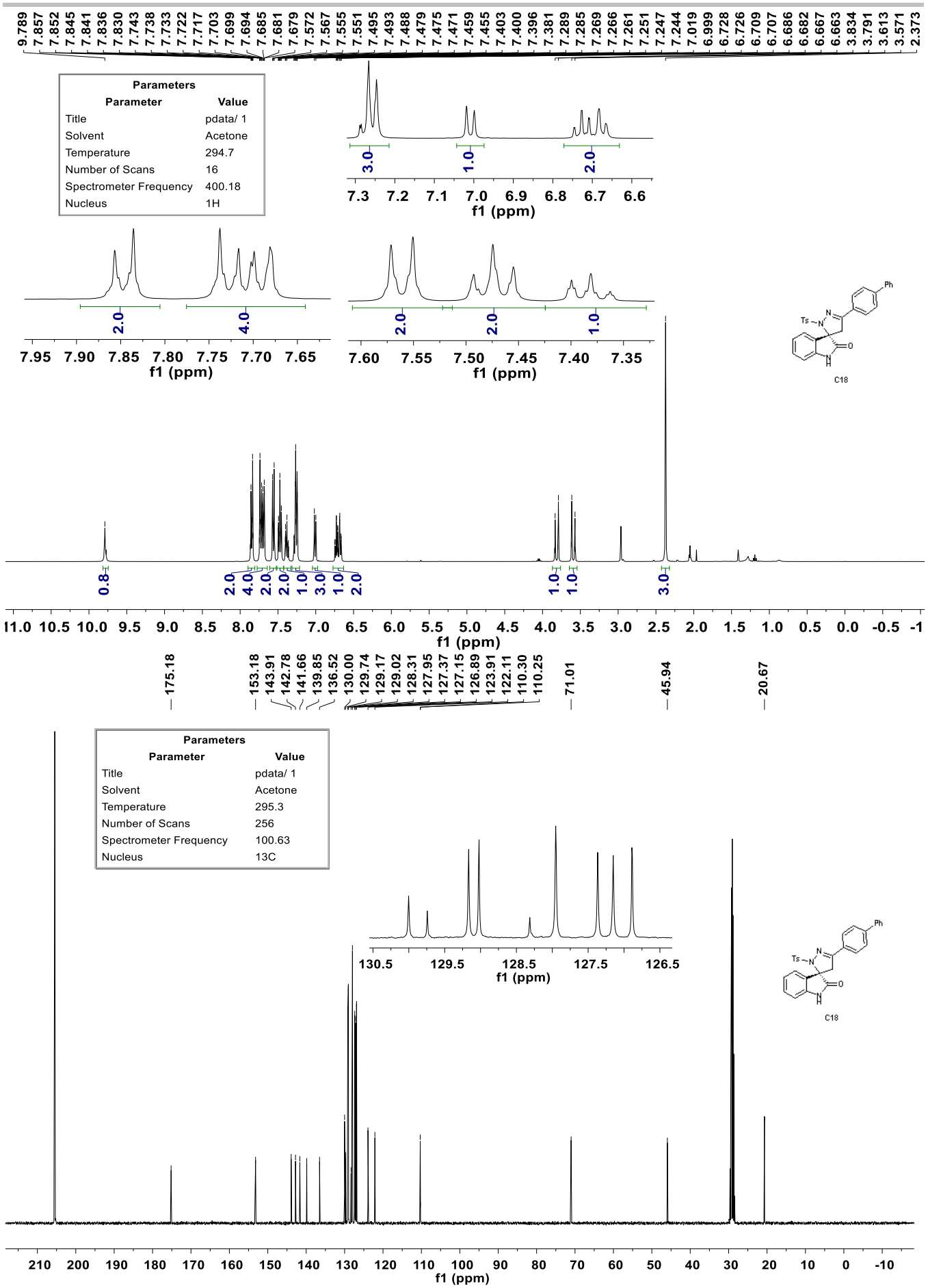

9.757 7.814 7.805 7.801 7.799 7.793 7.790 7.786 7.784 7.781 7.773 7.769 7.572 7.568 7.556 7.551 7.480 7.471 7.464 7.459 7.457 7.454 7.448 7.446 7.443 7.298 7.277 7.259 7.256 7.240 7.237 7.005 6.985 6.710 6.707 6.691 6.688 6.672 6.670 6.633 6.630 6.614 6.611 3.816 3.773 3.610 3.567 1.233 1.214 1.195
Parameters
Parameter Value
Title pdata/ 1
Solvent Acetone
Temperature 294.6
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
2.0 1.9 3.0
3.0 1.0 1.0 1.0
f1 (ppm)
C12
0.8 2.0 1.9 3.0 3.0 1.0 1.0 1.0 1.0 1.0 2.0 3.0
f1 (ppm)
175.77 154.16 150.66 142.32 137.41 131.49 131.14 130.63 129.47 128.87 128.73 128.65 127.44 124.51 122.74 110.91 71.61 46.61 15.50
Parameters
Parameter Value
Title pdata/ 1
Solvent Acetone
Temperature 295.2
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
f1 (ppm)
C12
f1 (ppm)

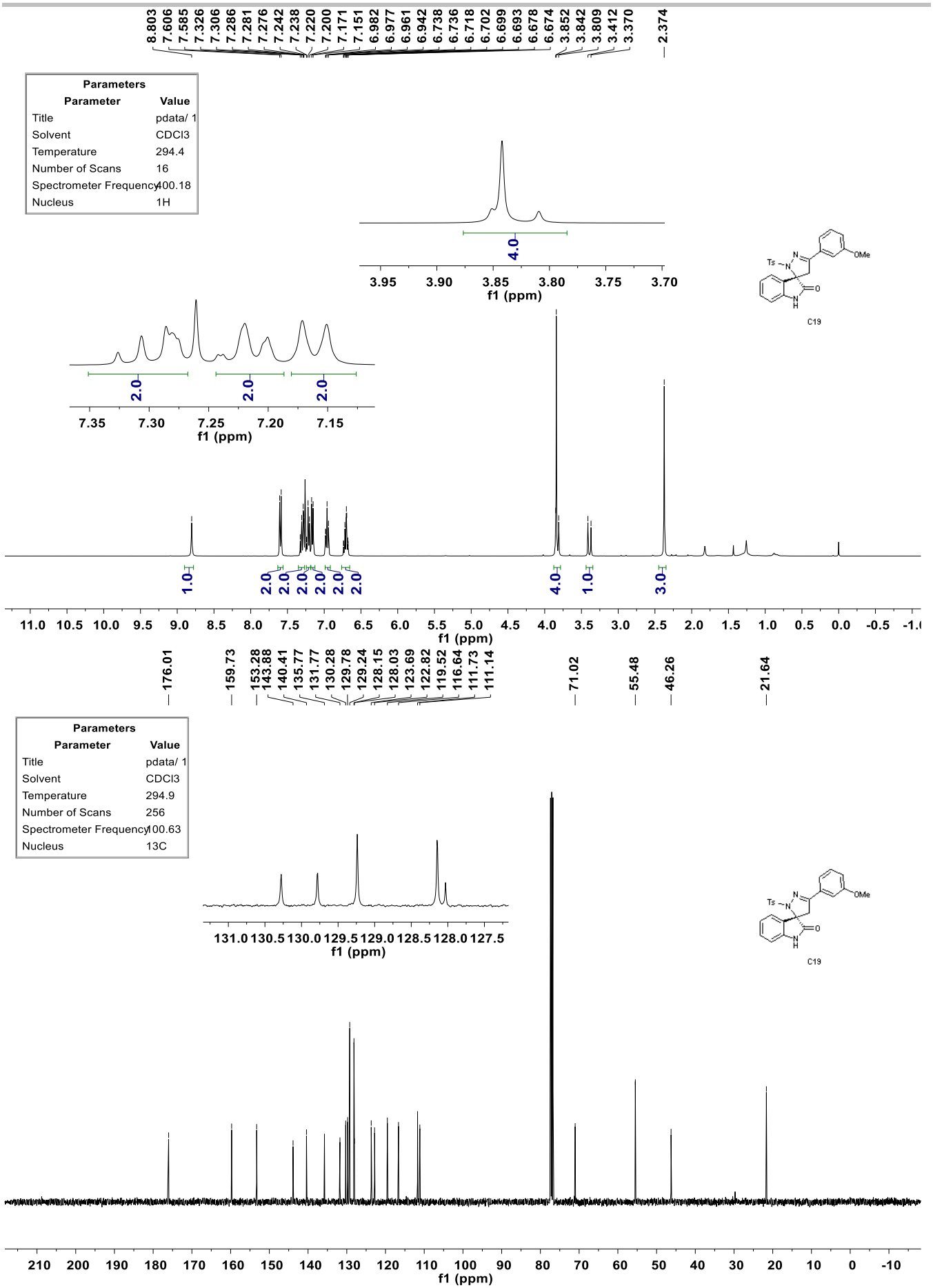

8.803
7.606
7.585
7.549
7.472
7.453
7.307
7.288
7.269
7.243
7.236
7.231
7.224
7.217
7.198
7.194
7.169
7.148
6.966
6.946
6.717
6.698
6.680
6.672
6.653
3.855
3.813
3.416
3.374
2.374
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.5
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
f1 (ppm)
C15
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 295.1
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
176.06
153.56
143.80
140.40
138.50
135.83
131.44
130.38
130.24
129.24
128.63
128.13
128.01
127.39
124.09
123.67
122.78
111.14
70.94
46.25
21.63
21.39

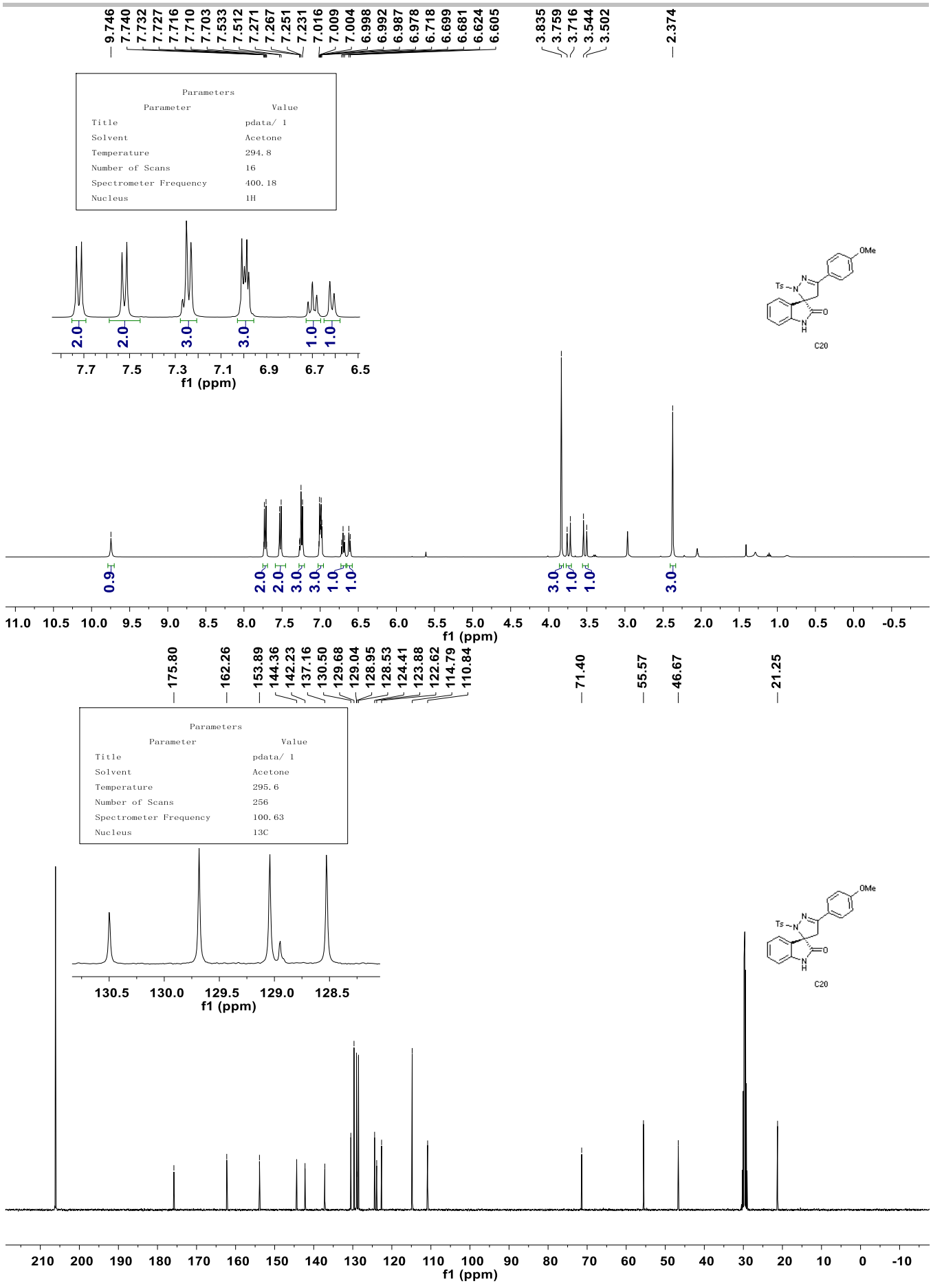

9.737
7.680
7.660
7.540
7.519
7.280
7.260
7.255
7.238
6.999
6.979
6.730
6.727
6.711
6.709
6.692
6.690
6.642
6.625
3.776
3.733
3.566
3.523
2.379
2.358
Parameters
Parameter Value
Title hukq-20220610-17cat.1.1.1r
Solvent Acetone
Temperature 295.6
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
2.0
1.9
5.0
1.0
1.0
1.0
7.5
7.0
6.5
f1 (ppm)
Ts
N
O
H
C16
0.9
2.0
1.9
5.0
1.0
1.0
1.0
1.0
1.0
6.0
f1 (ppm)

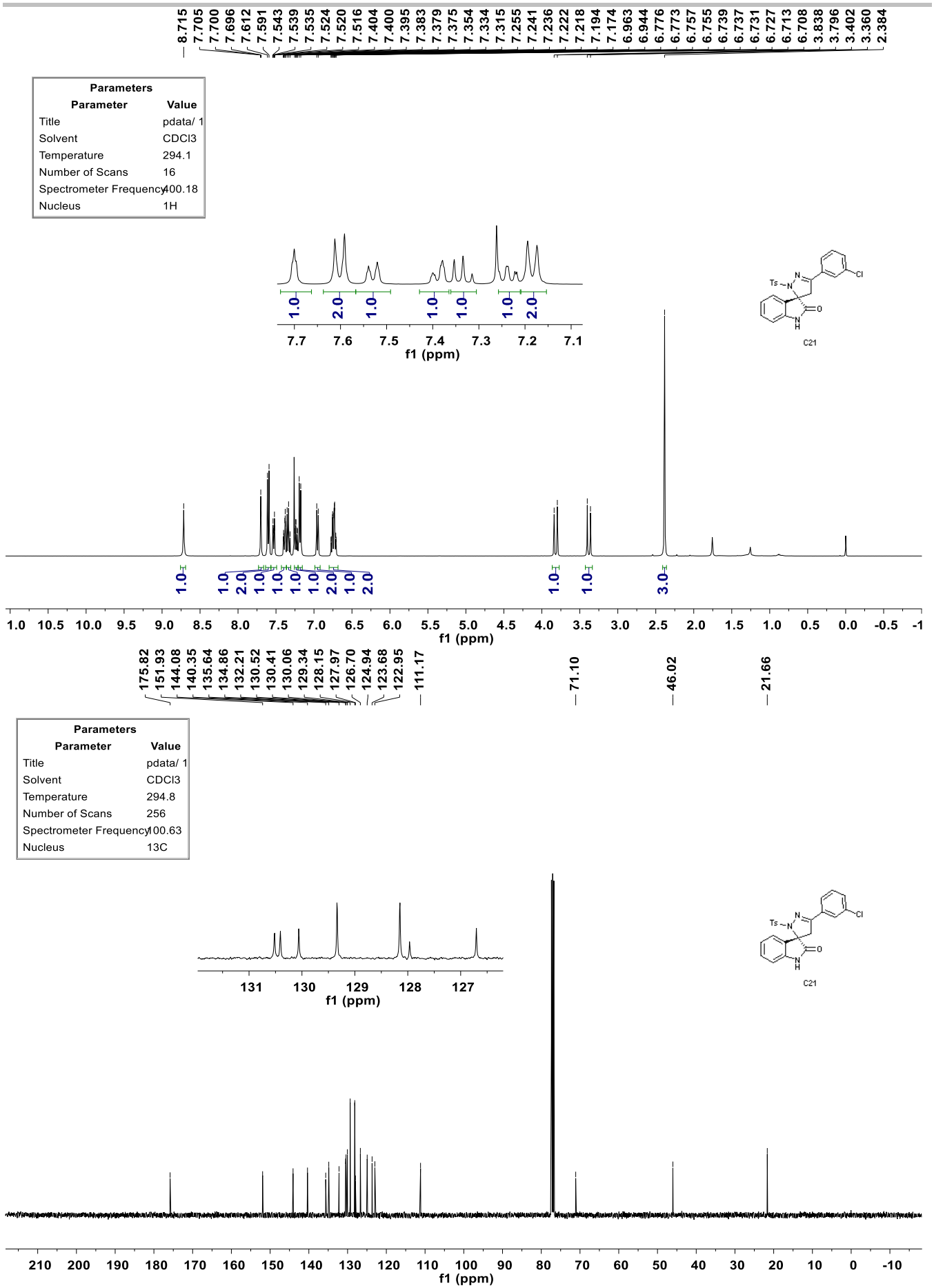

175.82
154.15
144.48
142.32
141.44
137.23
130.60
130.08
129.77
129.02
128.75
128.59
127.42
124.50
122.70
110.90
71.52
46.68
21.30
21.26
Parameters
Parameter Value
Title hukq-20220610-17cat.2.1.1r
Solvent Acetone
Temperature 296.3
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
131.0
130.0
129.0
128.0
127.0
f1 (ppm)
Ts
N
O
H
C16
f1 (ppm)

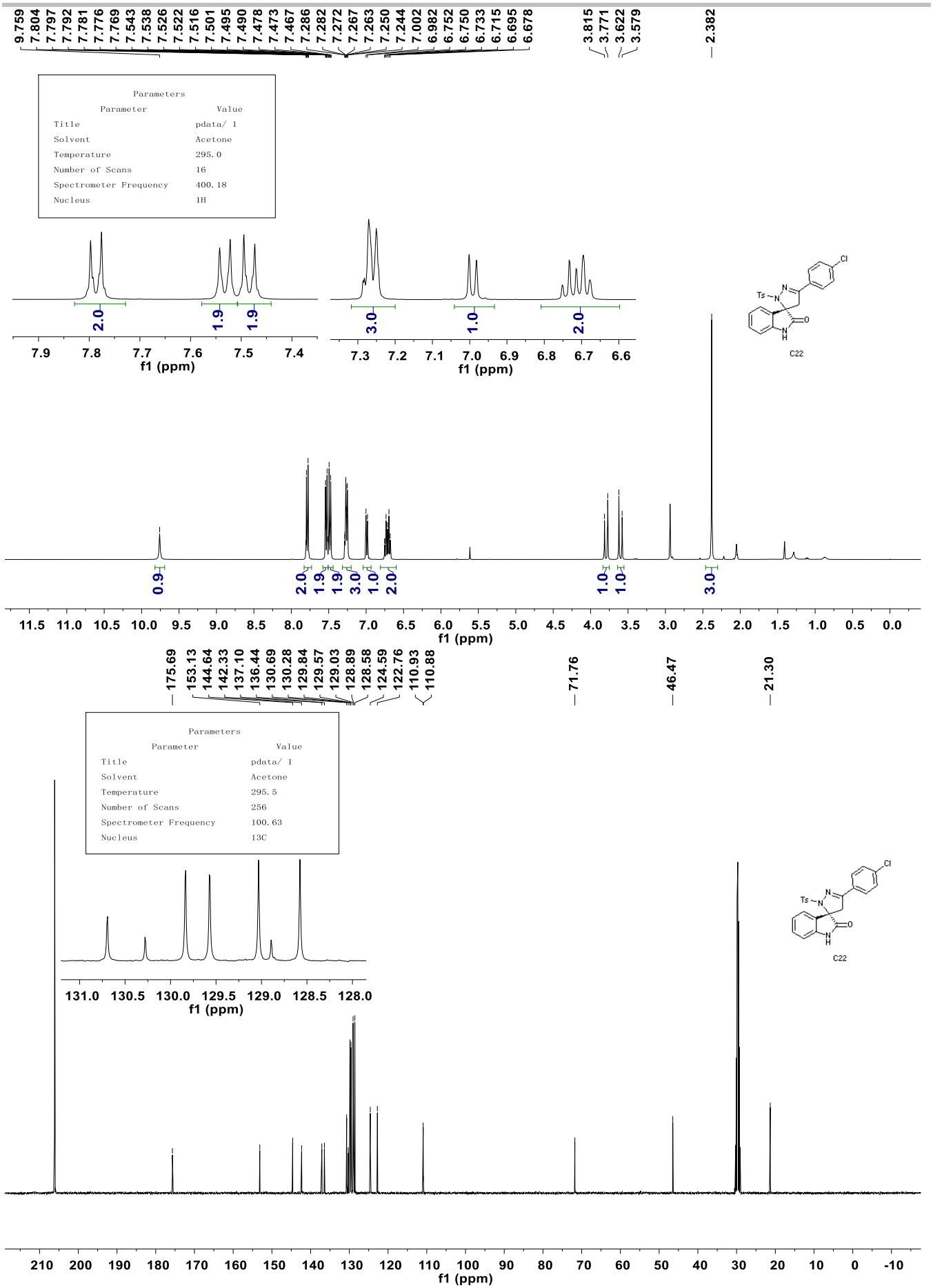

9.038
7.631
7.611
7.590
7.570
7.239
7.219
7.201
7.197
7.182
7.178
7.150
7.130
7.114
6.988
6.976
6.956
6.687
6.669
6.650
6.629
6.612
3.850
3.808
3.399
3.357
2.697
2.678
2.659
2.640
2.361
1.253
1.234
1.215
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.3
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
3.0
2.0
1.0
2.0
7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5
f1 (ppm)
4.0
7.70 7.65 7.60 7.55 7.50
f1 (ppm)
Ts
N
O
H
Br
C17
0.9
4.0
3.0
2.0
1.0
2.0
1.0
1.0
2.0
3.0
3.0
10.5 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 -0.5 -1.
f1 (ppm)
176.21
153.57
147.29
143.75
140.52
135.80
130.23
129.20
128.28
128.14
127.96
127.93
126.97
123.64
122.70
111.25
77.42
77.31
77.10
76.79
70.99
46.23
28.87
21.63
15.41
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 295.0
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
129.2 128.8 128.4 128.0 127.6
f1 (ppm)
Ts
N
O
H
Br
C17
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

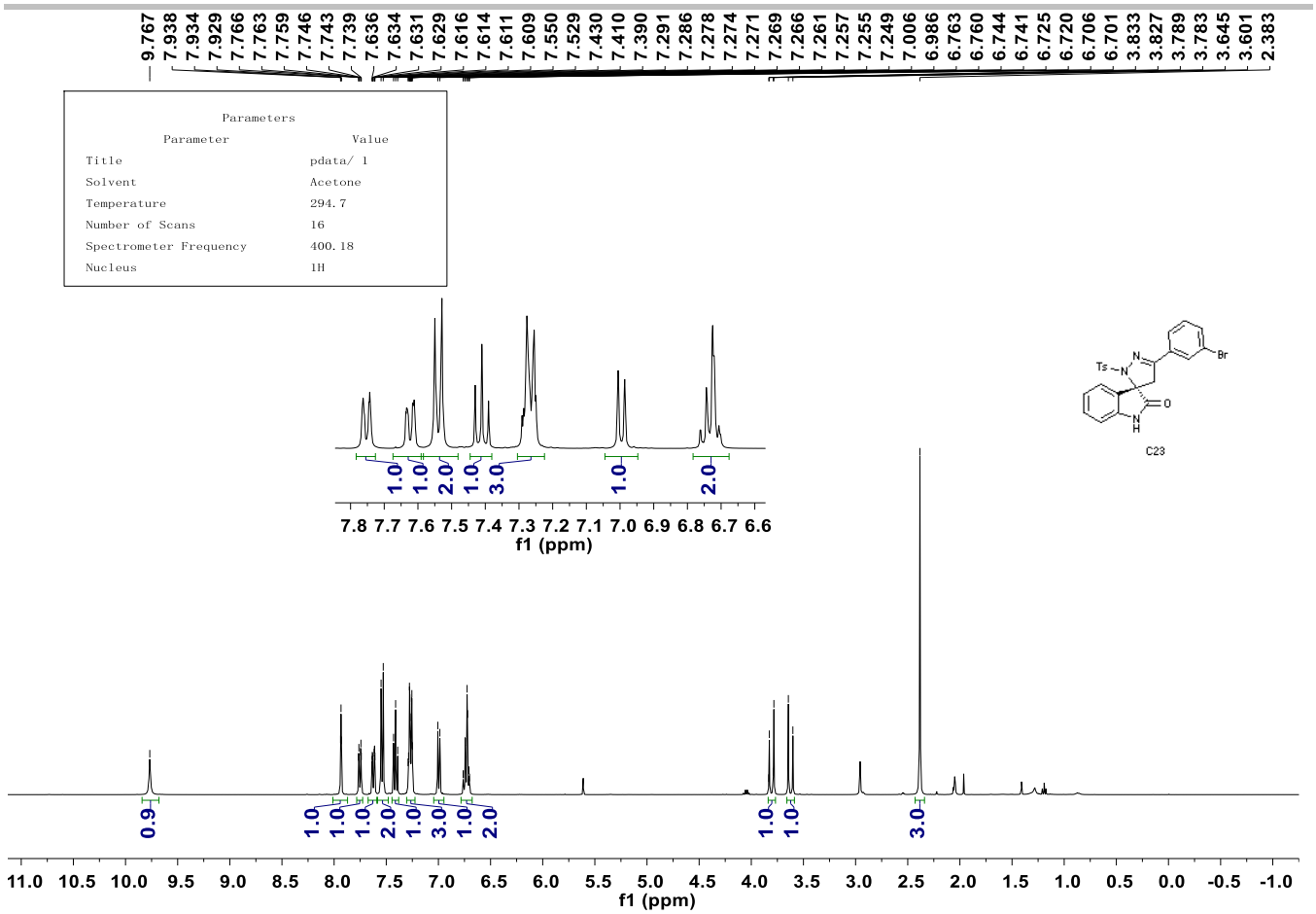

9.789 7.857 7.852 7.845 7.841 7.836 7.830 7.743 7.738 7.733 7.722 7.717 7.703 7.699 7.694 7.685 7.681 7.679 7.572 7.567 7.555 7.551 7.495 7.493 7.488 7.479 7.475 7.471 7.459 7.455 7.403 7.400 7.396 7.381 7.289 7.285 7.269 7.266 7.261 7.251 7.247 7.244 7.019 6.999 6.728 6.726 6.709 6.707 6.686 6.682 6.667 6.663 3.834 3.791 3.613 3.571 2.373
Parameters
Parameter Value
Title pdata/ 1
Solvent Acetone
Temperature 294.7
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
f1 (ppm)
Ph
Ts
N
O
H
C18
f1 (ppm)
175.18 153.18 143.91 142.78 141.66 139.85 136.52 130.00 129.74 129.17 129.02 128.31 127.95 127.37 127.15 126.89 123.91 122.11 110.30 110.25 71.01 45.94 20.67
Parameters
Parameter Value
Title pdata/ 1
Solvent Acetone
Temperature 295.3
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
f1 (ppm)
Ph
Ts
N
O
H
C18
f1 (ppm)

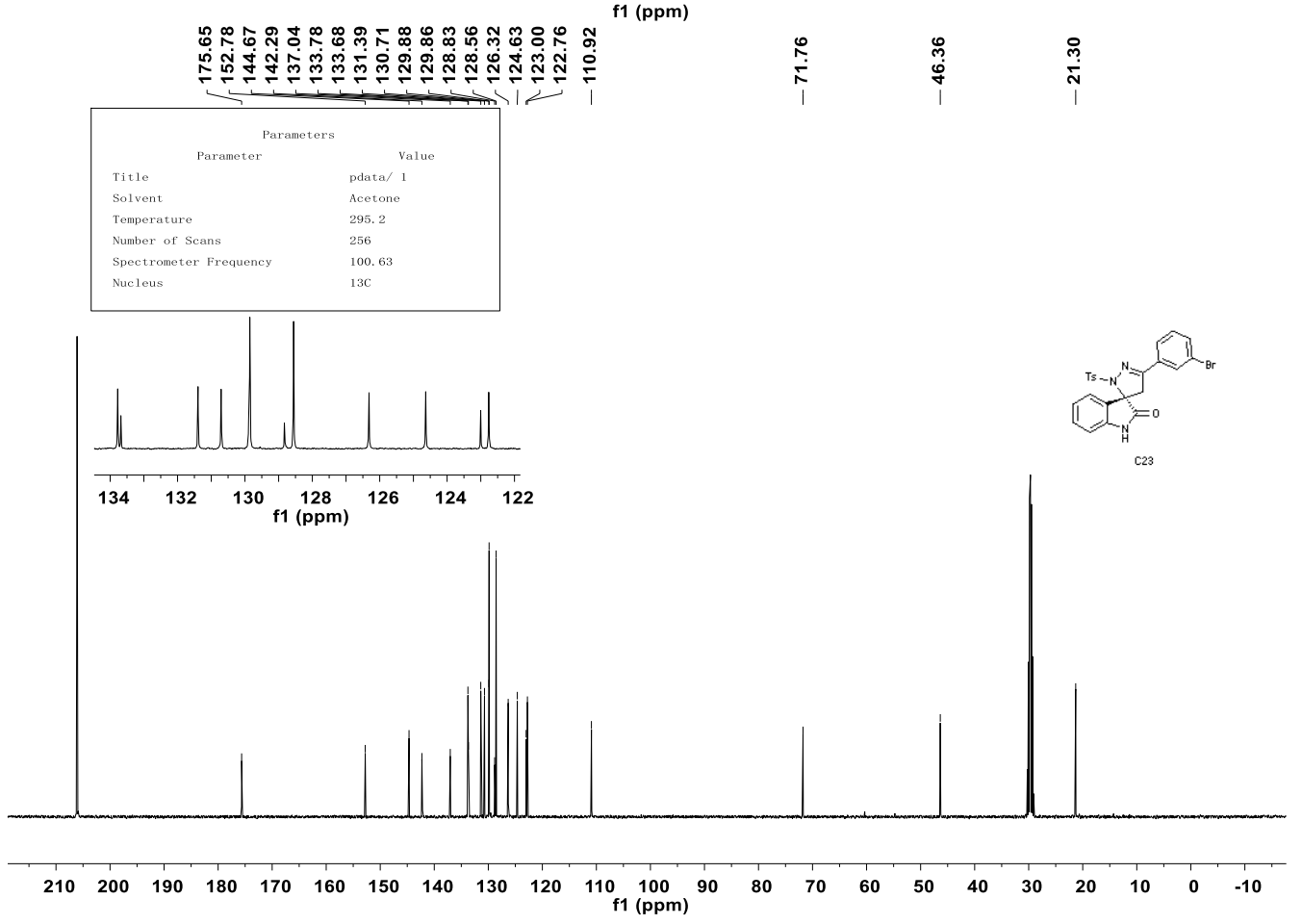

8.803 7.606 7.585 7.326 7.306 7.286 7.281 7.276 7.242 7.238 7.220 7.200 7.171 7.151 6.982 6.977 6.961 6.942 6.738 6.736 6.718 6.702 6.699 6.693 6.678 6.674 3.852 3.842 3.809 3.412 3.370 2.374
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.4
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
4.0
3.95 3.90 3.85 3.80 3.75 3.70
f1 (ppm)
2.0 2.0 2.0
7.35 7.30 7.25 7.20 7.15
f1 (ppm)
Ts
OMe
O
N
H
C19
1.0 2.0 2.0 2.0 2.0 2.0 2.0 4.0 1.0 3.0
11.0 10.5 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 -0.5
f1 (ppm)
176.01 159.73 153.28 143.88 140.41 135.77 131.77 130.28 129.78 129.24 128.15 128.03 123.69 122.82 119.52 116.64 111.73 111.14 71.02 55.48 46.26 21.64
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.9
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
131.0 130.5 130.0 129.5 129.0 128.5 128.0 127.5
f1 (ppm)
Ts
OMe
O
N
H
C19
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

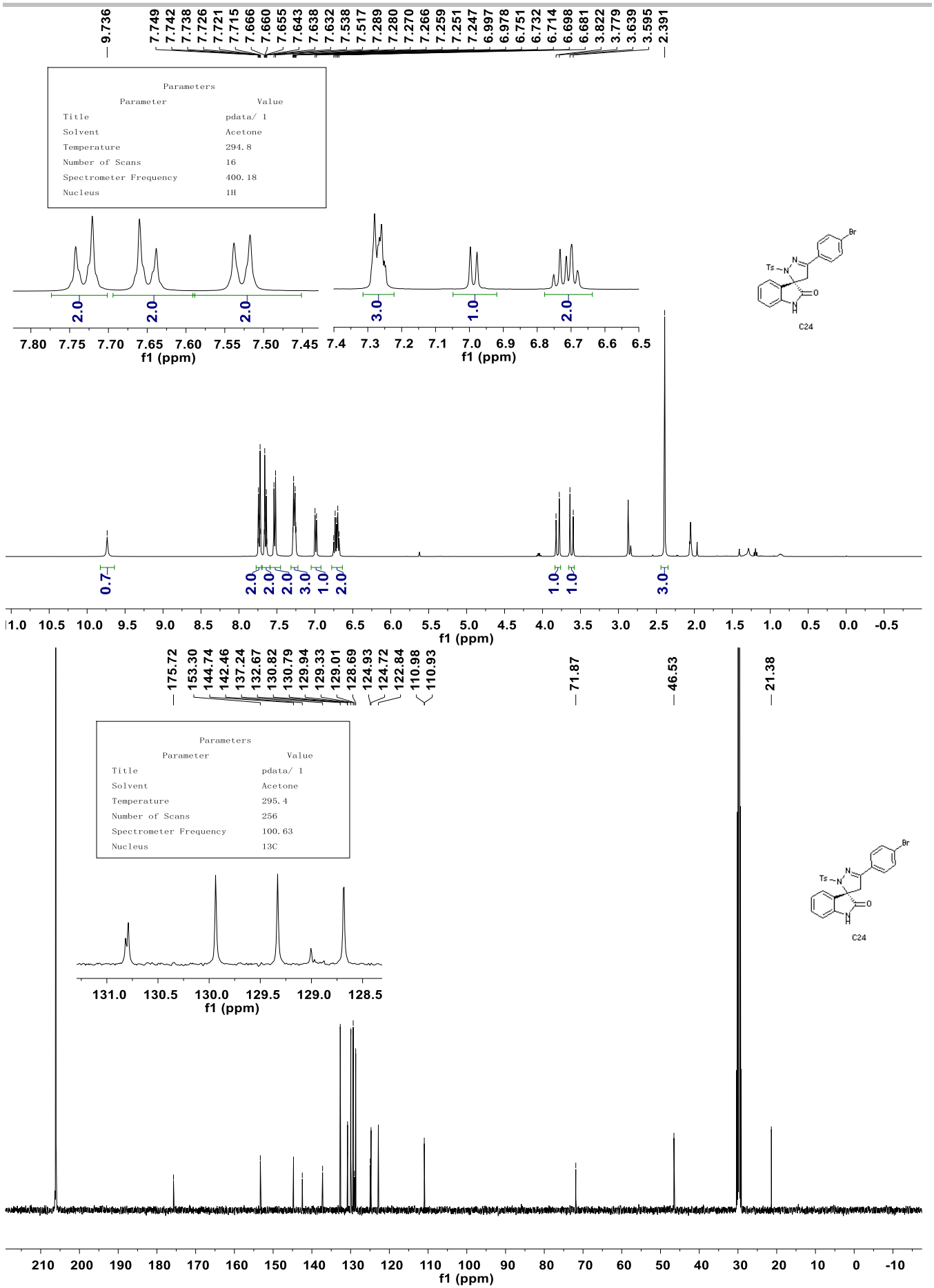

9.746
7.740
7.732
7.727
7.716
7.710
7.703
7.533
7.512
7.271
7.267
7.251
7.231
7.016
7.009
7.004
6.998
6.992
6.987
6.978
6.718
6.699
6.681
6.624
6.605
3.835
3.759
3.716
3.544
3.502
2.374
Parameters
Parameter Value
Title pdata/ 1
Solvent Acetone
Temperature 294.8
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
2.0
2.0
3.0
3.0
1.0
1.0
7.7 7.5 7.3 7.1 6.9 6.7 6.5
f1 (ppm)
OMe
Ts
N
O
H
C20
0.9
2.0
2.0
3.0
3.0
1.0
1.0
3.0
1.0
1.0
3.0
11.0 10.5 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 -0.5
f1 (ppm)
175.80
162.26
153.89
144.36
142.23
137.16
130.50
129.68
129.04
128.95
128.53
124.41
123.88
122.62
114.79
110.84
71.40
55.57
46.67
21.25
Parameters
Parameter Value
Title pdata/ 1
Solvent Acetone
Temperature 295.6
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
130.5 130.0 129.5 129.0 128.5
f1 (ppm)
OMe
Ts
N
O
H
C20
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

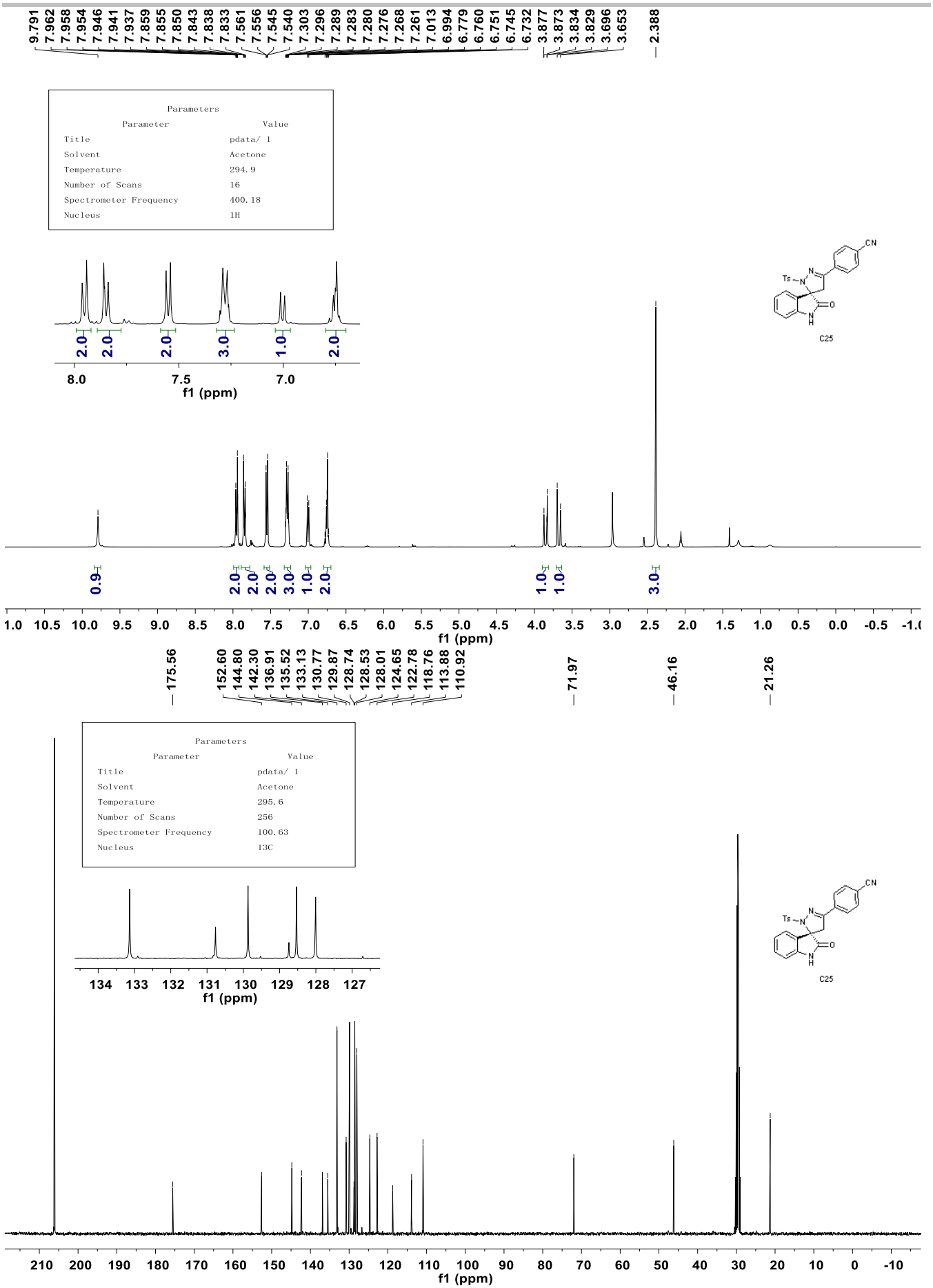

8.715 7.705 7.700 7.696 7.612 7.591 7.543 7.539 7.535 7.524 7.520 7.516 7.404 7.400 7.395 7.383 7.379 7.375 7.354 7.334 7.315 7.255 7.241 7.236 7.222 7.218 7.194 7.174 6.963 6.944 6.776 6.773 6.757 6.755 6.739 6.737 6.731 6.727 6.713 6.708 3.838 3.796 3.402 3.360 2.384
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.1
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
1.0 2.0 1.0 1.0 1.0 1.0 2.0
7.7 7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)
Ts N Cl O H
C21
1.0 1.0 2.0 1.0 1.0 1.0 2.0 1.0 2.0 1.0 1.0 3.0
1.0 10.5 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 -0.5 -1
f1 (ppm)
175.82 151.93 144.08 140.35 135.64 134.86 132.21 130.52 130.41 130.06 129.34 128.15 127.97 126.70 124.94 123.68 122.95 111.17 71.10 46.02 21.66
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.8
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
131 130 129 128 127
f1 (ppm)
Ts N Cl O H
C21
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

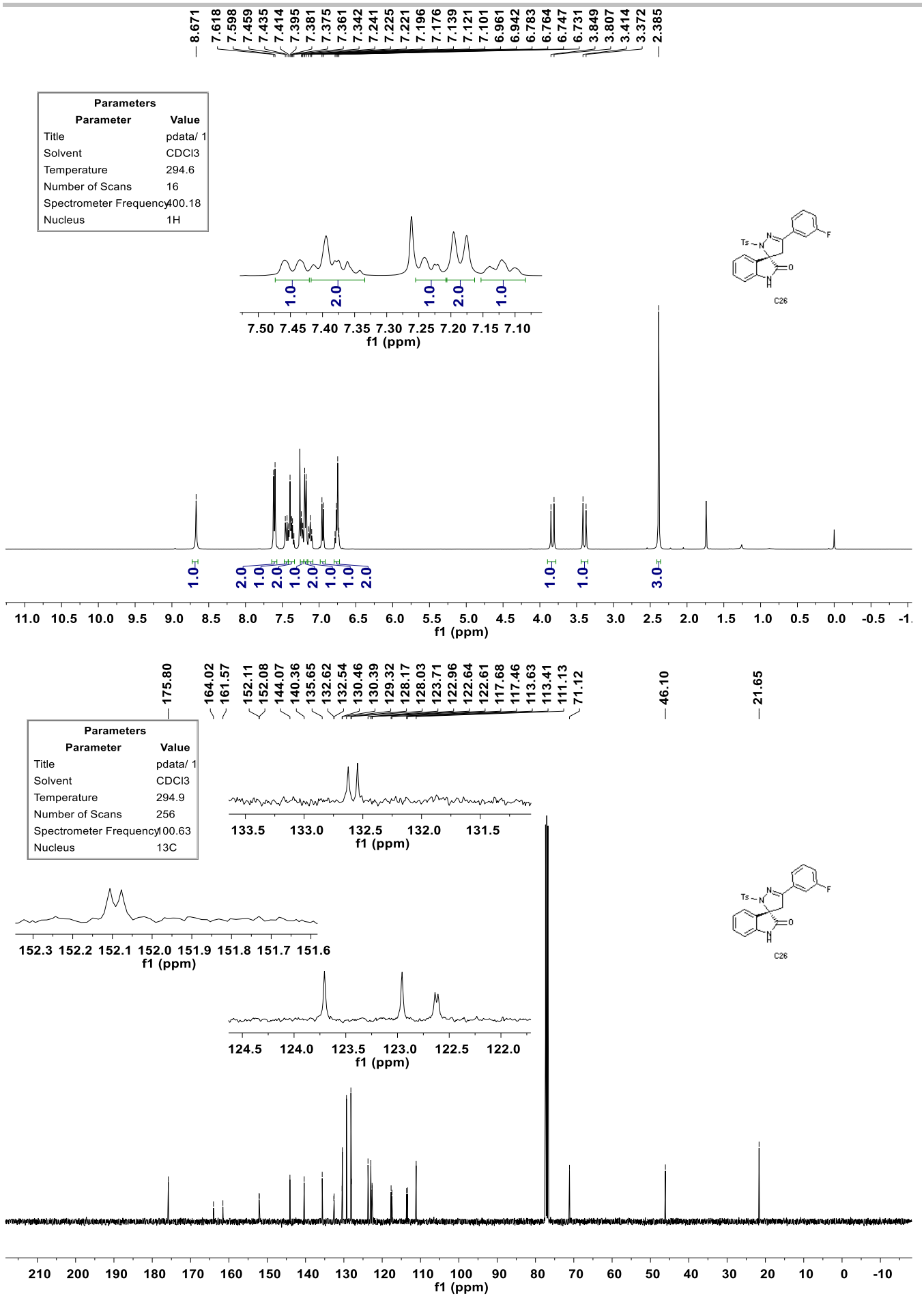

9.759 7.804 7.797 7.792 7.781 7.776 7.769 7.543 7.538 7.526 7.522 7.516 7.501 7.495 7.490 7.478 7.473 7.467 7.286 7.282 7.272 7.267 7.263 7.250 7.244 7.002 6.982 6.752 6.750 6.733 6.715 6.695 6.678
3.815 3.771 3.622 3.579
2.382
Parameters
Parameter Value
Title pdata/ 1
Solvent Acetone
Temperature 295.0
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
2.0 1.9 1.9
3.0 1.0 2.0
f1 (ppm)
Cl
Ts
N
O
H
C22
0.9 2.0 1.9 1.9 3.0 1.0 2.0 1.0 1.0 3.0
f1 (ppm)
175.69 153.13 144.64 142.33 137.10 136.44 130.69 130.28 129.84 129.57 129.03 128.89 128.58 124.59 122.76 110.93 110.88
71.76
46.47
21.30
Parameters
Parameter Value
Title pdata/ 1
Solvent Acetone
Temperature 295.5
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
f1 (ppm)
Cl
Ts
N
O
H
C22
f1 (ppm)

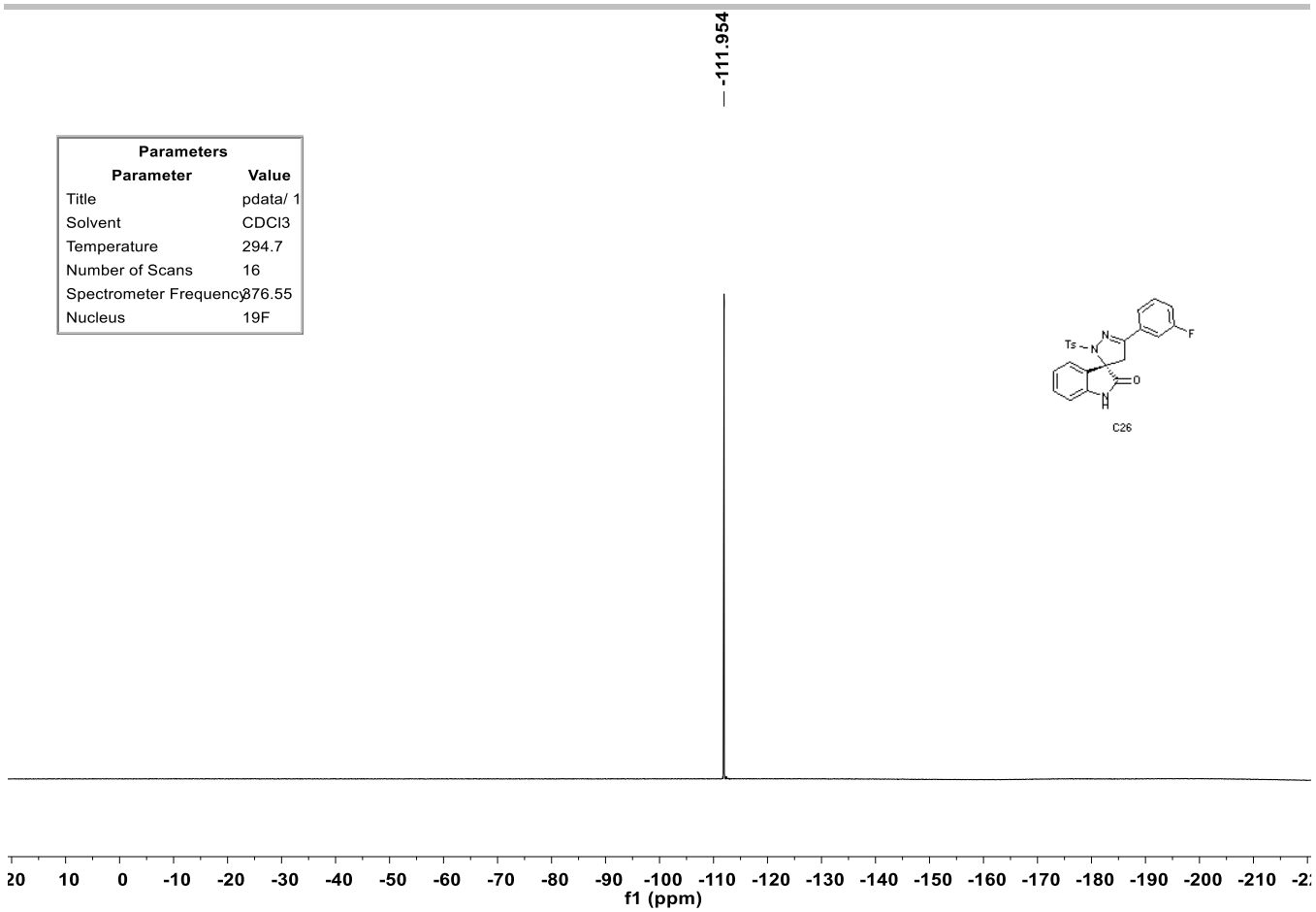

9.767 7.938 7.934 7.929 7.766 7.763 7.759 7.746 7.743 7.739 7.636 7.634 7.631 7.629 7.616 7.614 7.611 7.609 7.550 7.529 7.430 7.410 7.390 7.291 7.286 7.278 7.274 7.271 7.269 7.266 7.261 7.257 7.255 7.249 7.006 6.986 6.763 6.760 6.744 6.741 6.725 6.720 6.706 6.701 3.833 3.827 3.789 3.783 3.645 3.601 2.383
Parameters
Parameter Value
Title pdata/ 1
Solvent Acetone
Temperature 294.7
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
1.0 1.0 2.0 1.0 3.0 1.0 2.0
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6
f1 (ppm)
Ts
Br
O
N
H
C23
0.9 1.0 1.0 1.0 2.0 1.0 3.0 1.0 2.0 1.0 1.0 3.0
11.0 10.5 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 -0.5 -1.0
f1 (ppm)

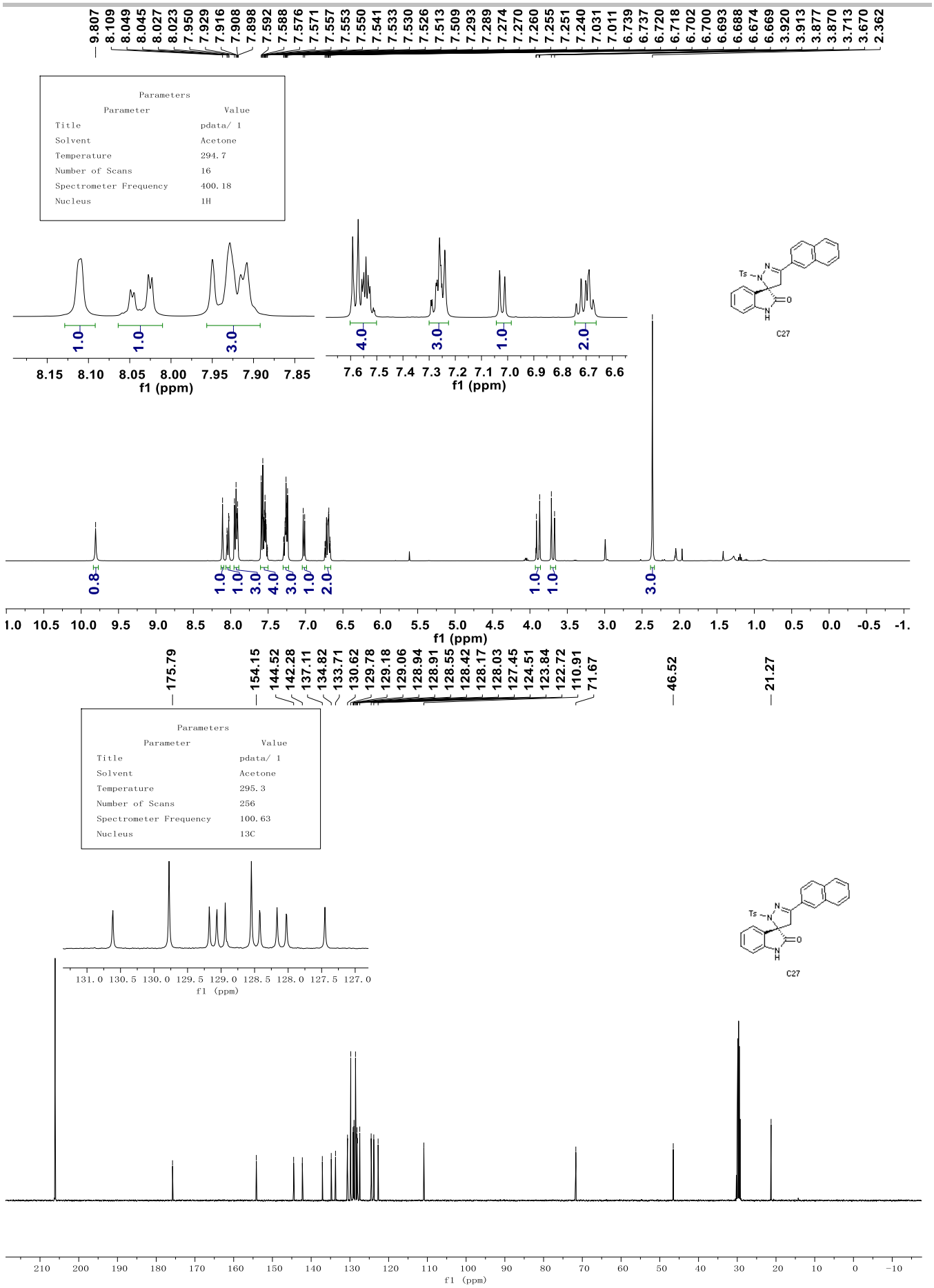

175.65 152.78 144.67 142.29 137.04 133.78 133.68 131.39 130.71 129.88 129.86 128.83 128.56 126.32 124.63 123.00 122.76 110.92 71.76 46.36 21.30
Parameters
Parameter Value
Title pdata/ 1
Solvent Acetone
Temperature 295.2
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
134 132 130 128 126 124 122
f1 (ppm)
Ts
Br
O
N
H
C23
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

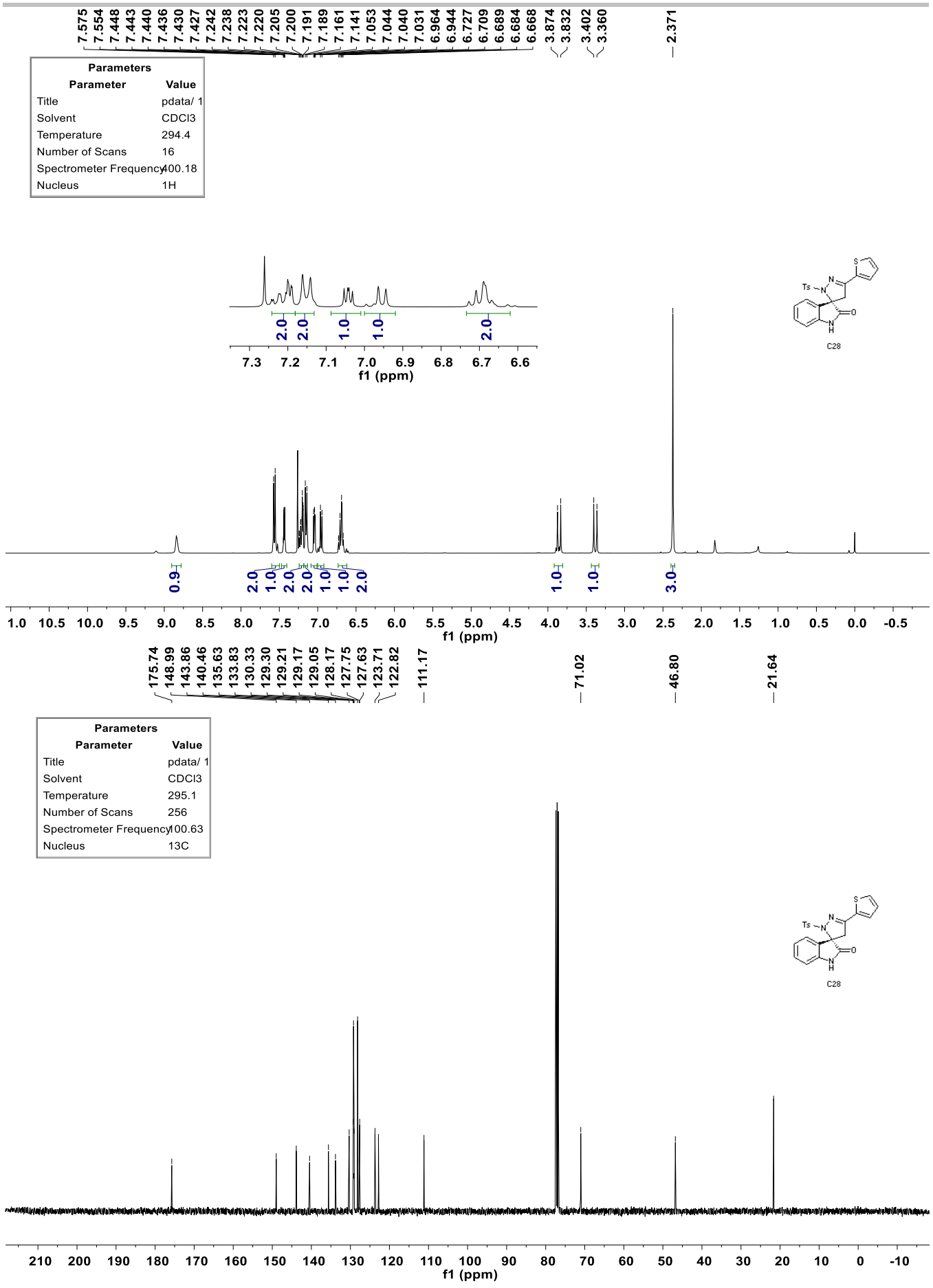

9.736
7.749
7.742
7.738
7.726
7.721
7.715
7.666
7.660
7.655
7.643
7.638
7.632
7.538
7.517
7.289
7.280
7.270
7.266
7.259
7.251
7.247
6.997
6.978
6.751
6.732
6.714
6.698
6.681
3.822
3.779
3.639
3.595
2.391
Parameters
Parameter Value
Title pdata/ 1
Solvent Acetone
Temperature 294.8
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
2.0
2.0
2.0
3.0
1.0
2.0
f1 (ppm)
Br
Ts
N
O
H
C24
0.7
2.0
2.0
2.0
3.0
1.0
2.0
1.0
1.0
3.0
f1 (ppm)
175.72
153.30
144.74
142.46
137.24
132.67
130.82
130.79
129.94
129.33
129.01
128.69
124.93
124.72
122.84
110.98
110.93
71.87
46.53
21.38
Parameters
Parameter Value
Title pdata/ 1
Solvent Acetone
Temperature 295.4
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
f1 (ppm)
Br
Ts
N
O
H
C24
f1 (ppm)

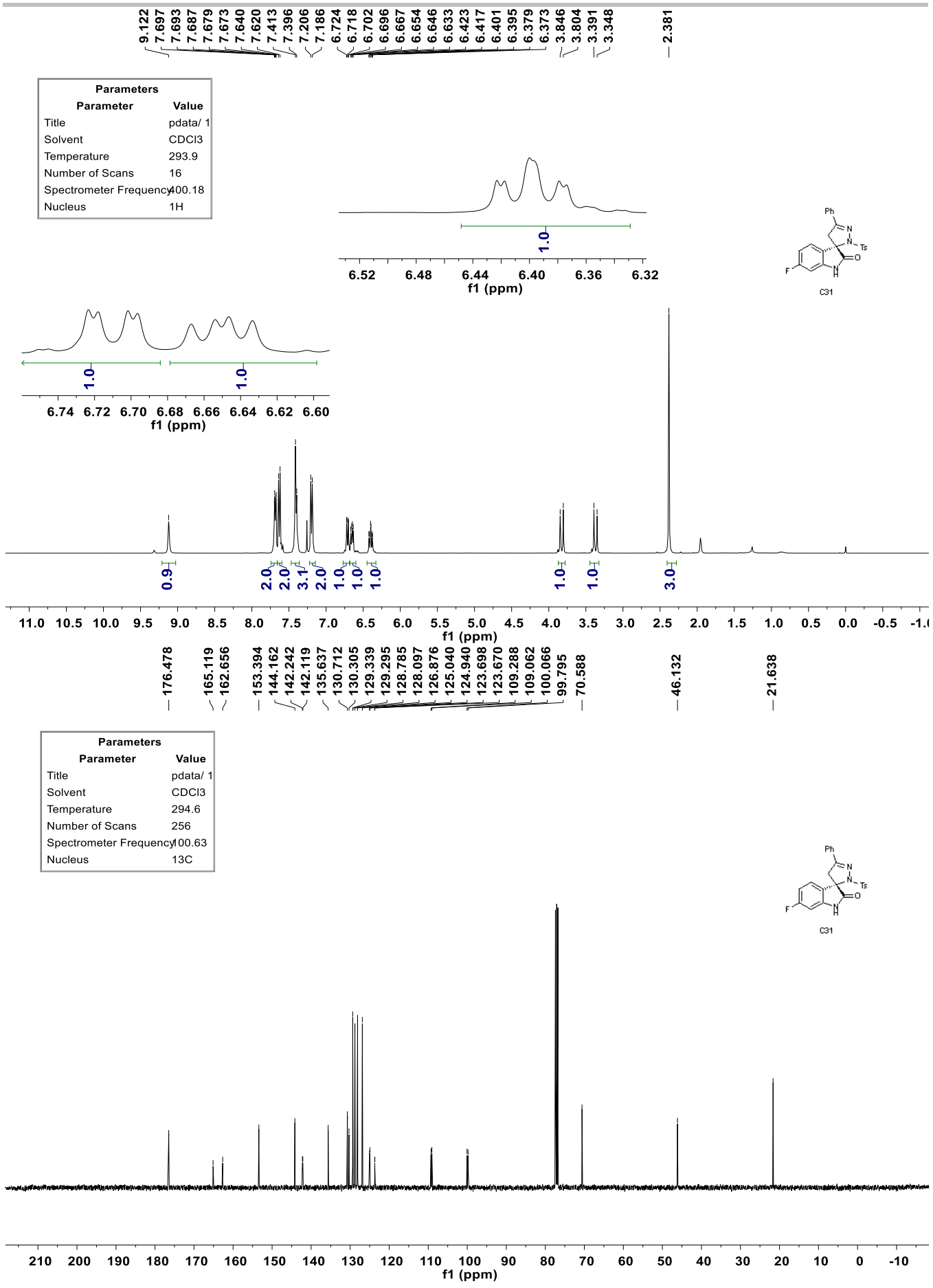

9.791 7.962 7.958 7.954 7.946 7.941 7.937 7.859 7.855 7.850 7.843 7.838 7.833 7.561 7.556 7.545 7.540 7.303 7.296 7.289 7.283 7.280 7.276 7.268 7.261 7.013 6.994 6.779 6.760 6.751 6.745 6.732 3.877 3.873 3.834 3.829 3.696 3.653 2.388
Parameters
Parameter Value
Title pdata/ 1
Solvent Acetone
Temperature 294.9
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
2.0 2.0 2.0 3.0 1.0 2.0
8.0 7.5 7.0
f1 (ppm)
CN
Ts
N
O
H
C25
0.9 2.0 2.0 2.0 3.0 1.0 2.0 1.0 1.0 3.0
1.0 10.5 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 -0.5
f1 (ppm)
175.56 152.60 144.80 142.30 136.91 135.52 133.13 130.77 129.87 128.74 128.53 128.01 124.65 122.78 118.76 113.88 110.92 71.97 46.16 21.26
Parameters
Parameter Value
Title pdata/ 1
Solvent Acetone
Temperature 295.6
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
134 133 132 131 130 129 128 127
f1 (ppm)
CN
Ts
N
O
H
C25
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

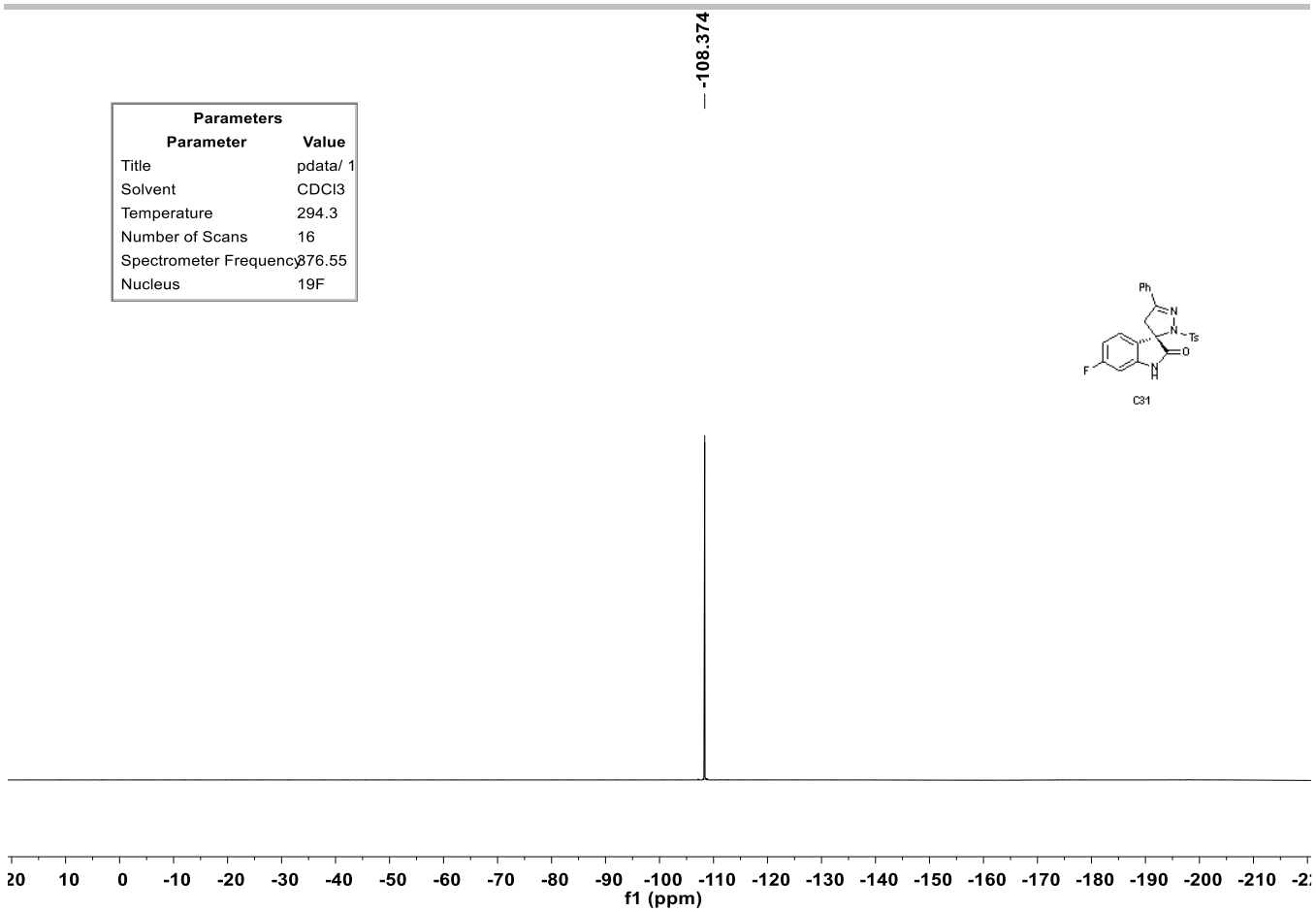

8.671
7.618
7.598
7.459
7.435
7.414
7.395
7.381
7.375
7.361
7.342
7.241
7.225
7.221
7.196
7.176
7.139
7.121
7.101
6.961
6.942
6.783
6.764
6.747
6.731
3.849
3.807
3.414
3.372
2.385
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.6
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
1.0
2.0
1.0
2.0
1.0
7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10
f1 (ppm)
Ts
N
F
O
H
C26
1.0
2.0
1.0
2.0
1.0
2.0
1.0
1.0
2.0
1.0
1.0
3.0
11.0 10.5 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 -0.5
f1 (ppm)
175.80
164.02
161.57
152.11
152.08
144.07
140.36
135.65
132.62
132.54
130.46
130.39
129.32
128.17
128.03
123.71
122.96
122.64
122.61
117.68
117.46
113.63
113.41
111.13
71.12
46.10
21.65
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.9
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
133.5 133.0 132.5 132.0 131.5
f1 (ppm)
152.3 152.2 152.1 152.0 151.9 151.8 151.7 151.6
f1 (ppm)
124.5 124.0 123.5 123.0 122.5 122.0
f1 (ppm)
Ts
N
F
O
H
C26
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-111.954
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.7
Number of Scans 16
Spectrometer Frequency 376.55
Nucleus 19F
Ts
N
F
O
H
C26
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

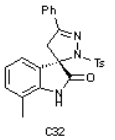

9.807 8.109 8.049 8.045 8.027 8.023 7.950 7.929 7.916 7.908 7.898 7.592 7.588 7.576 7.571 7.557 7.553 7.550 7.541 7.533 7.530 7.526 7.513 7.509 7.293 7.289 7.274 7.270 7.260 7.255 7.251 7.240 7.031 7.011 6.739 6.737 6.720 6.718 6.702 6.700 6.693 6.688 6.674 6.669 3.920 3.913 3.877 3.870 3.713 3.670 2.362
Parameters
Parameter Value
Title pdata/ 1
Solvent Acetone
Temperature 294.7
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
1.0 1.0 3.0
8.15 8.10 8.05 8.00 7.95 7.90 7.85
f1 (ppm)
4.0 3.0 1.0 2.0
7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6
f1 (ppm)
Ts
N
O
N
H
C27
0.8 1.0 1.0 3.0 4.0 3.0 1.0 2.0 1.0 1.0 3.0
f1 (ppm)
175.79 154.15 144.52 142.28 137.11 134.82 133.71 130.62 129.78 129.18 129.06 128.94 128.91 128.55 128.42 128.17 128.03 127.45 124.51 123.84 122.72 110.91 71.67 46.52 21.27
Parameters
Parameter Value
Title pdata/ 1
Solvent Acetone
Temperature 295.3
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
131.0 130.5 130.0 129.5 129.0 128.5 128.0 127.5 127.0
f1 (ppm)
Ts
N
O
N
H
C27
f1 (ppm)

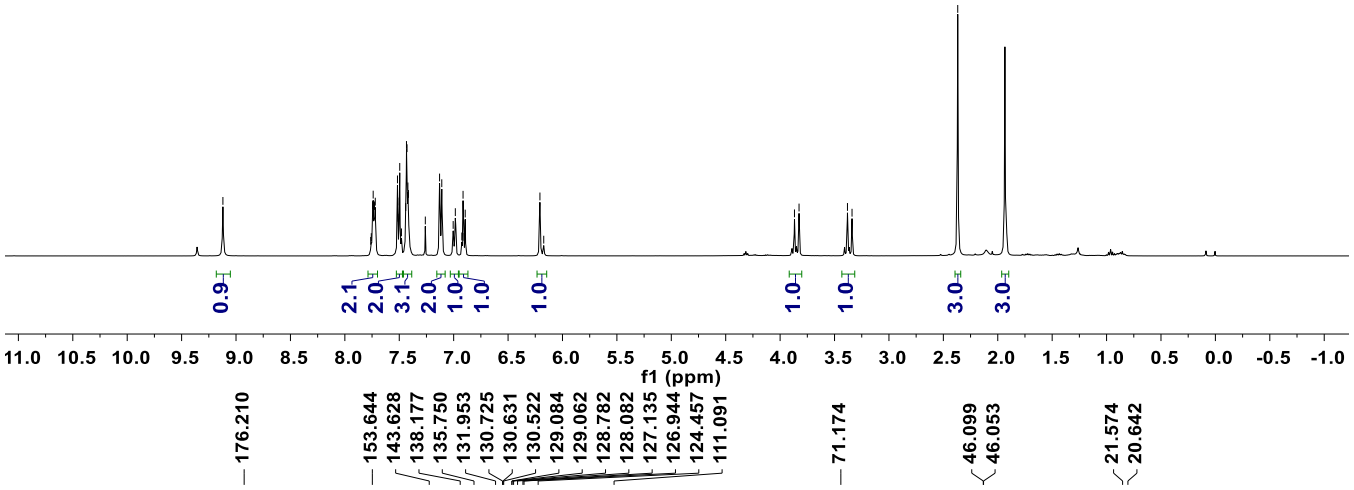

7.575 7.554 7.448 7.443 7.440 7.436 7.430 7.427 7.242 7.238 7.223 7.220 7.205 7.200 7.191 7.189 7.161 7.141 7.053 7.044 7.040 7.031 6.964 6.944 6.727 6.709 6.689 6.684 6.668 3.874 3.832 3.402 3.360 2.371
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.4
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
2.0 2.0 1.0 1.0 2.0
7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6
f1 (ppm)
Ts
S
N
O
H
C28
0.9 2.0 1.0 2.0 2.0 1.0 1.0 2.0 1.0 1.0 3.0
1.0 10.5 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 -0.5
f1 (ppm)
175.74 148.99 143.86 140.46 135.63 133.83 130.33 129.30 129.21 129.17 129.05 128.17 127.75 127.63 123.71 122.82 111.17 71.02 46.80 21.64
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 295.1
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
Ts
S
N
O
H
C28
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


9.122
7.697
7.693
7.687
7.679
7.673
7.640
7.620
7.413
7.396
7.206
7.186
6.724
6.718
6.702
6.696
6.667
6.654
6.646
6.633
6.423
6.417
6.401
6.395
6.379
6.373
3.846
3.804
3.391
3.348
2.381
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 293.9
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
1.0
6.52 6.48 6.44 6.40 6.36 6.32
f1 (ppm)
Ph
N
N
Ts
O
F
H
C31
1.0
1.0
6.74 6.72 6.70 6.68 6.66 6.64 6.62 6.60
f1 (ppm)
0.9
2.0
2.0
3.1
2.0
1.0
1.0
1.0
1.0
1.0
3.0
11.0 10.5 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 -0.5
f1 (ppm)
176.478
165.119
162.656
153.394
144.162
142.242
142.119
135.637
130.712
130.305
129.339
129.295
128.785
128.097
126.876
125.040
124.940
123.698
123.670
109.288
109.062
100.066
99.795
70.588
46.132
21.638
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.6
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
Ph
N
N
Ts
O
F
H
C31
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

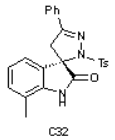

-108.374
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.3
Number of Scans 16
Spectrometer Frequency 376.55
Nucleus 19F
Ph
N
N
Ts
O
F
H
C31
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

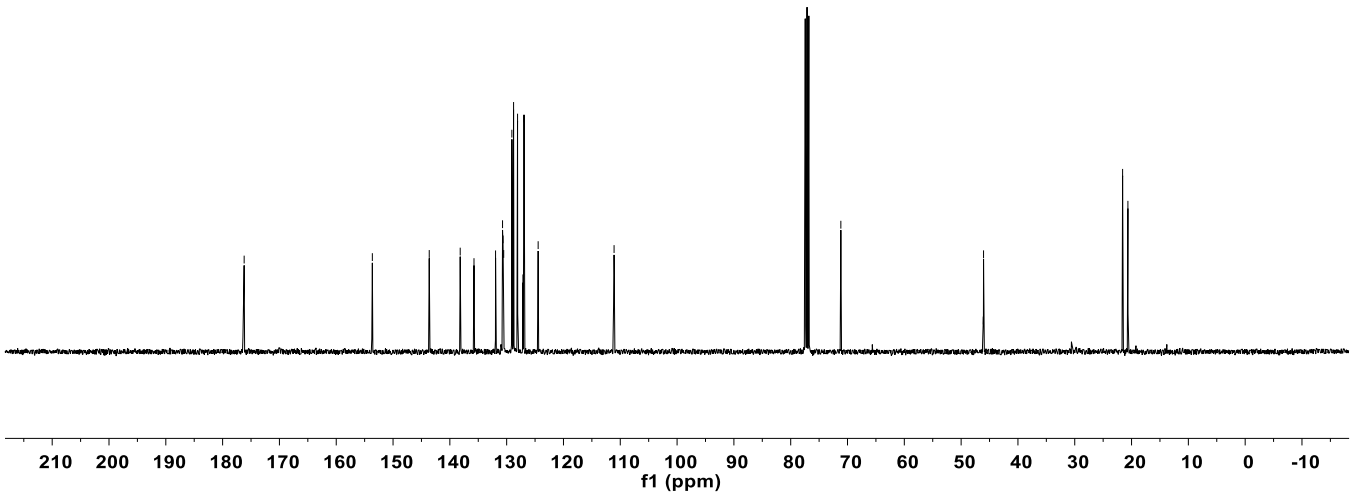
Parameters	
Parameter	**Value**
Title	pdata/ 1
Solvent	CDCl3
Temperature	294.1
Number of Scans	16
Spectrometer Frequency	400.18
Nucleus	1H



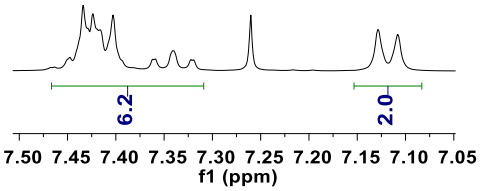


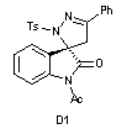
Parameters	
Parameter	**Value**
Title	pdata/ 1
Solvent	CDCl3
Temperature	294.5
Number of Scans	256
Spectrometer Frequency	100.63
Nucleus	13C

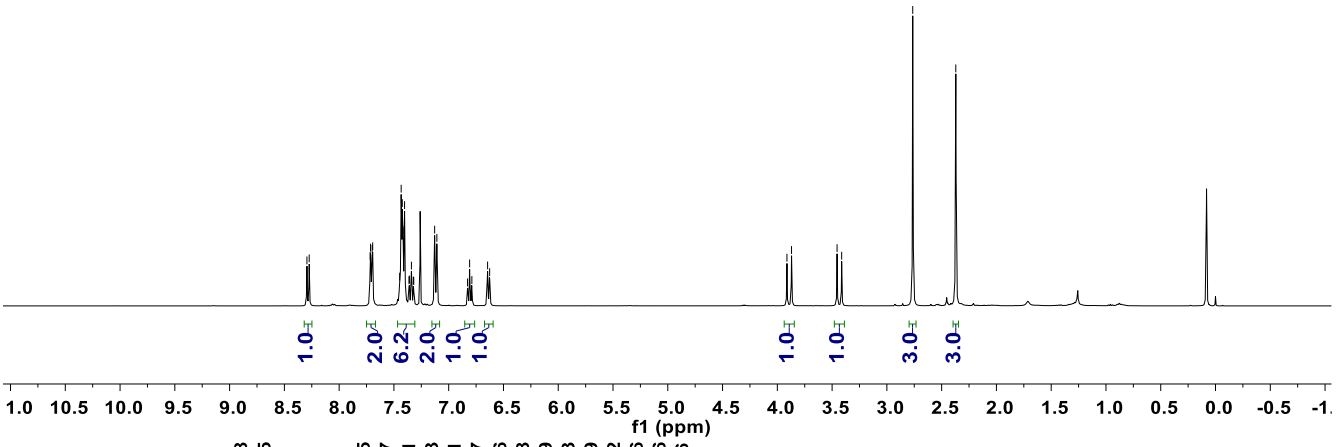


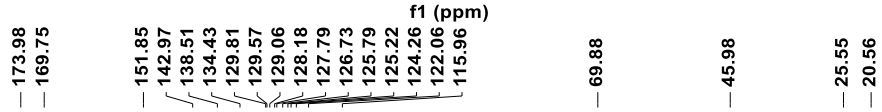


Parameters	
Parameter	**Value**
Title	pdata/ 1
Solvent	CDCl3
Temperature	294.3
Number of Scans	16
Spectrometer Frequency	400.18
Nucleus	1H

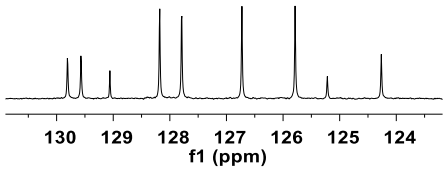


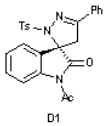


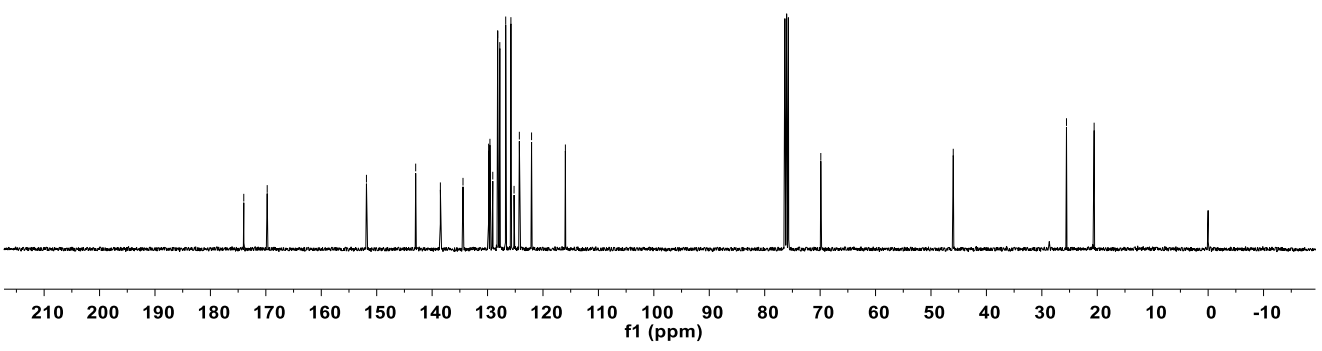


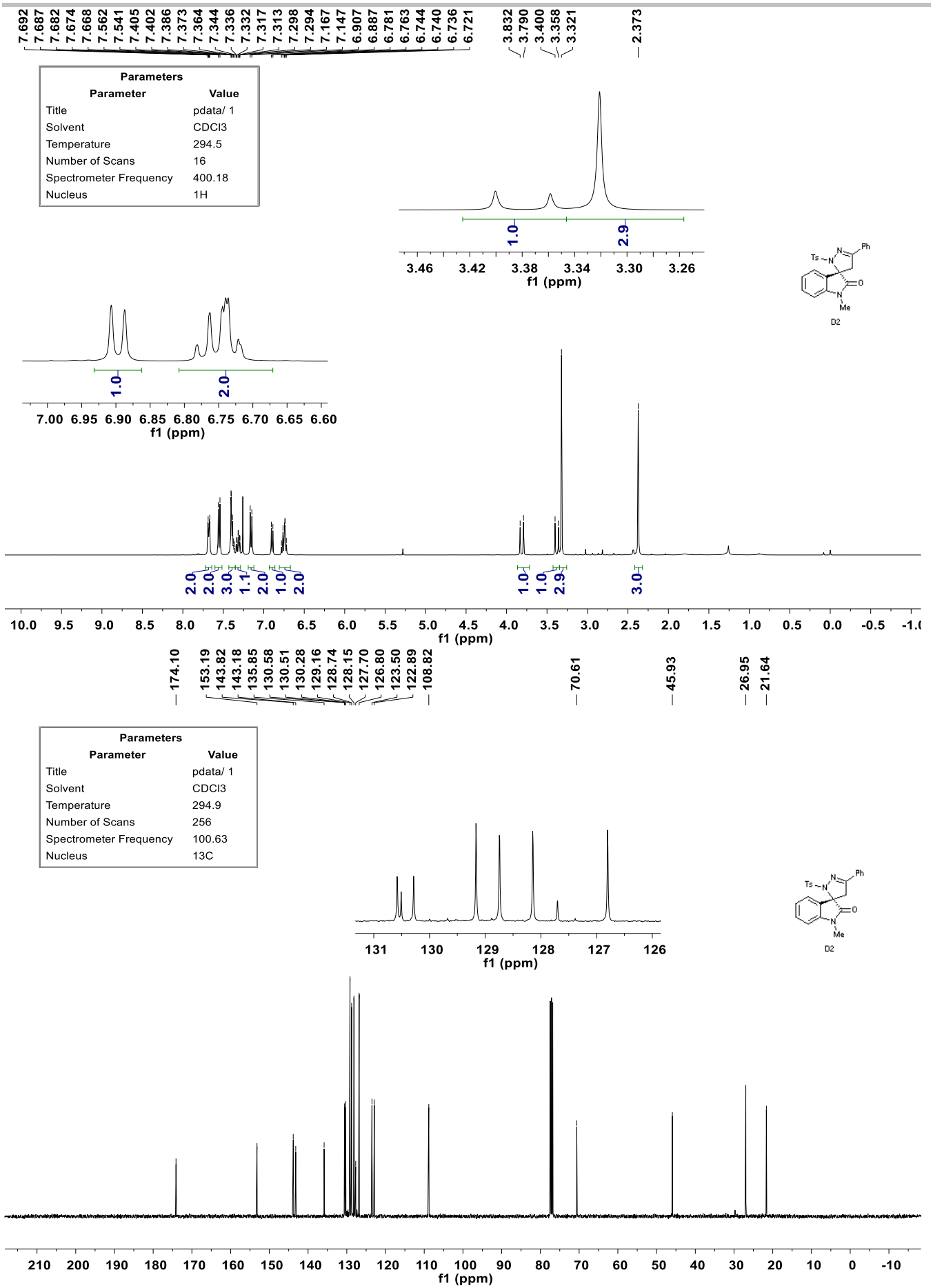


Parameters	
Parameter	**Value**
Title	pdata/ 1
Solvent	CDCl3
Temperature	295.0
Number of Scans	256
Spectrometer Frequency	100.63
Nucleus	13C

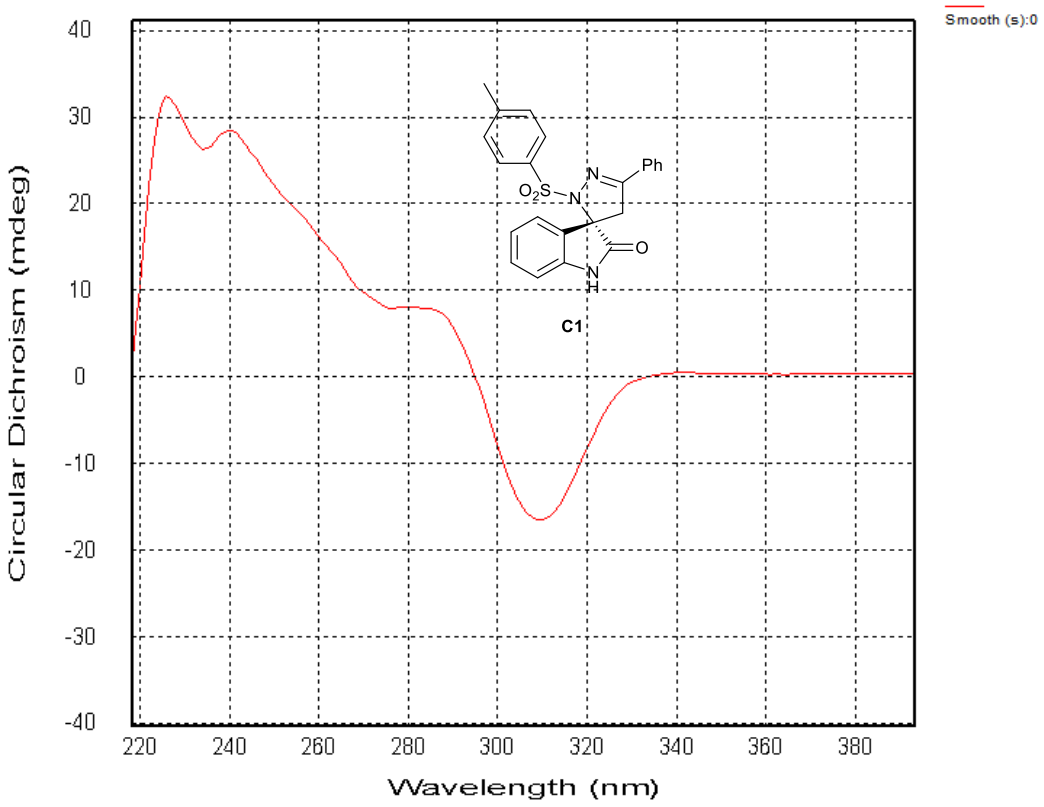


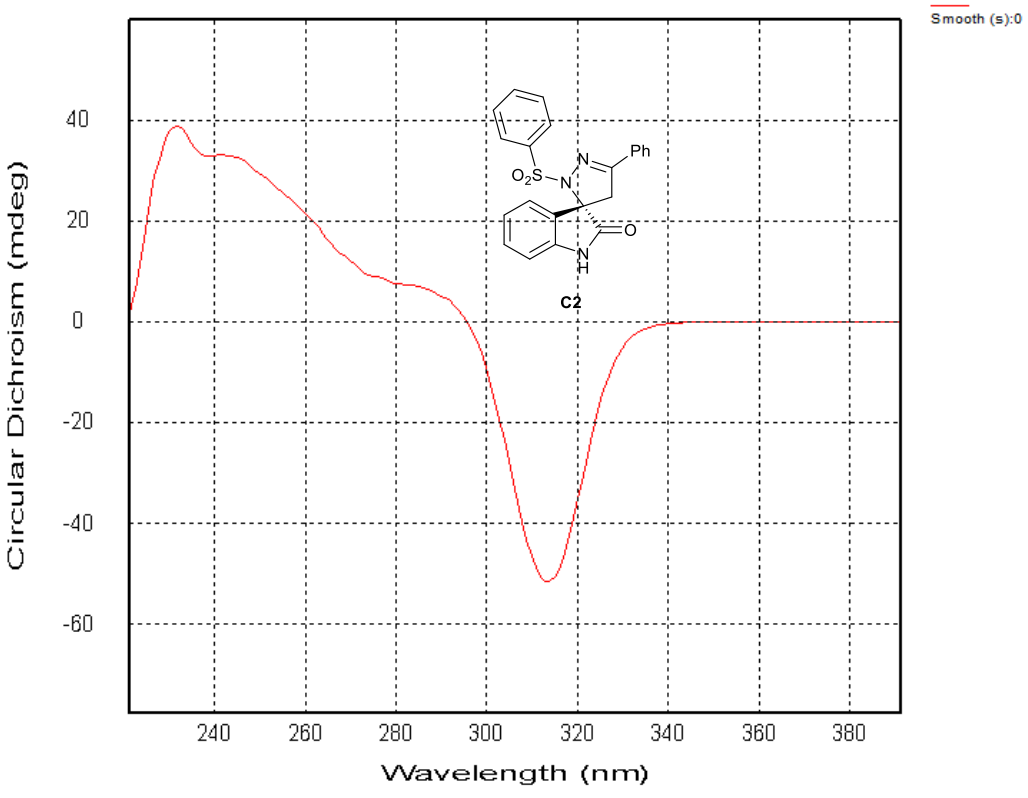


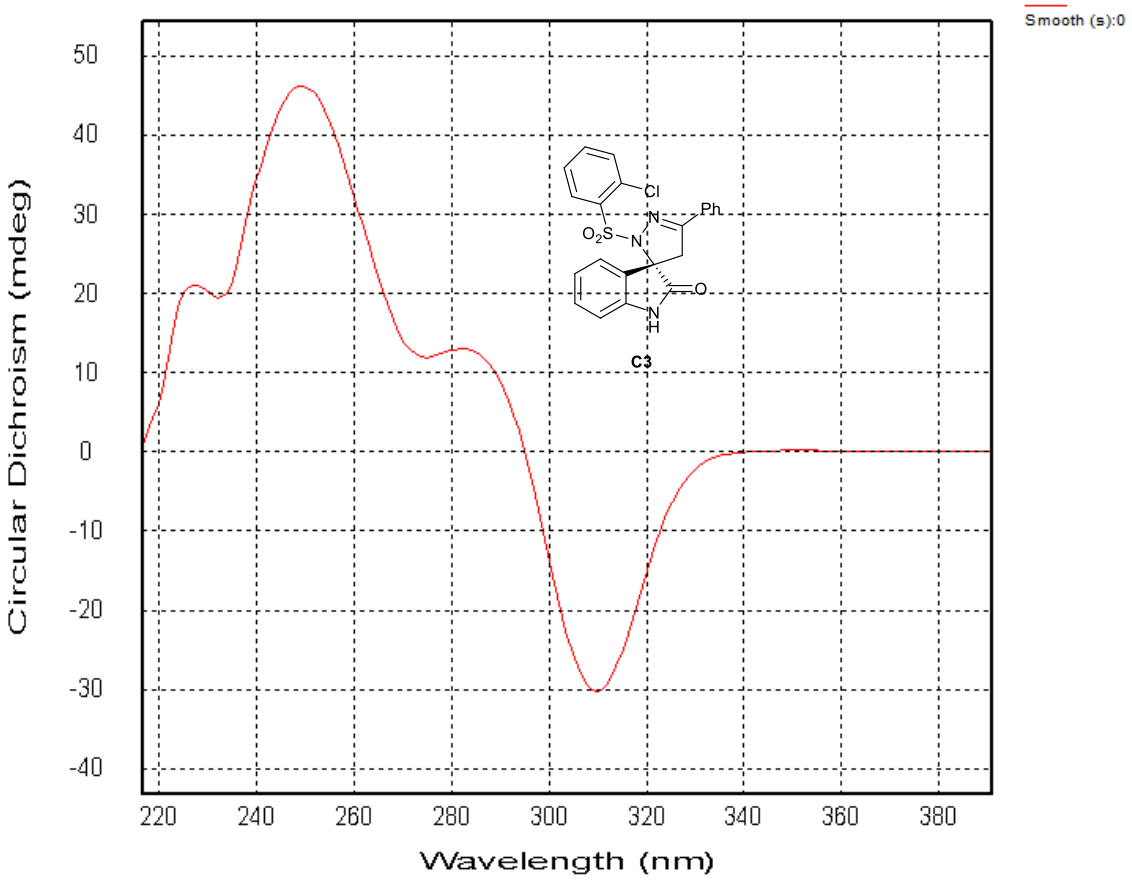


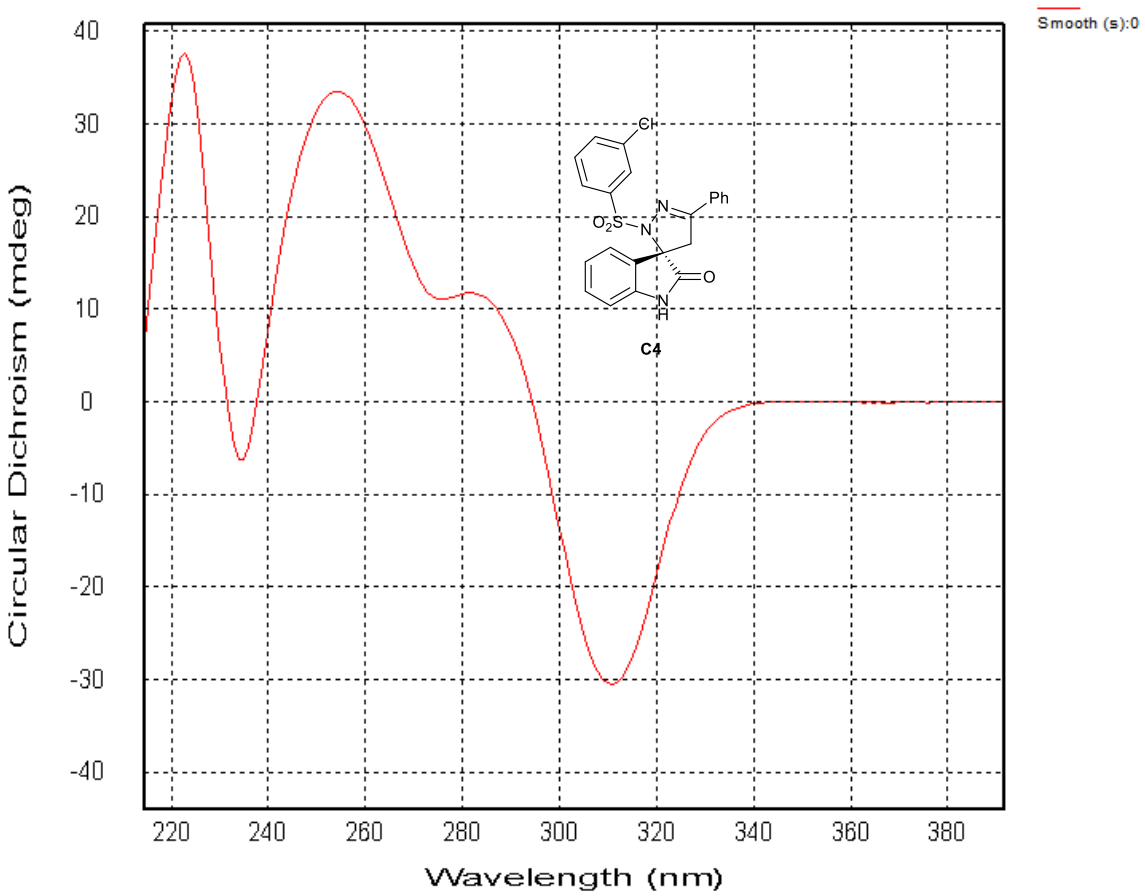

7.692 7.687 7.682 7.674 7.668 7.562 7.541 7.405 7.402 7.386 7.373 7.364 7.344 7.336 7.332 7.317 7.313 7.298 7.294 7.167 7.147 6.907 6.887 6.781 6.763 6.744 6.740 6.736 6.721
3.832 3.790 3.400 3.358 3.321
2.373
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.5
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
1.0 2.9
3.46 3.42 3.38 3.34 3.30 3.26
f1 (ppm)
Ts Ph N O Me
D2
1.0 2.0
7.00 6.95 6.90 6.85 6.80 6.75 6.70 6.65 6.60
f1 (ppm)
2.0 2.0 3.0 1.1 2.0 1.0 2.0 1.0 1.0 2.9 3.0
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 -0.5
f1 (ppm)
174.10 153.19 143.82 143.18 135.85 130.58 130.51 130.28 129.16 128.74 128.15 127.70 126.80 123.50 122.89 108.82
70.61 45.93 26.95 21.64
Parameters
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.9
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
131 130 129 128 127 126
f1 (ppm)
Ts Ph N O Me
D2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

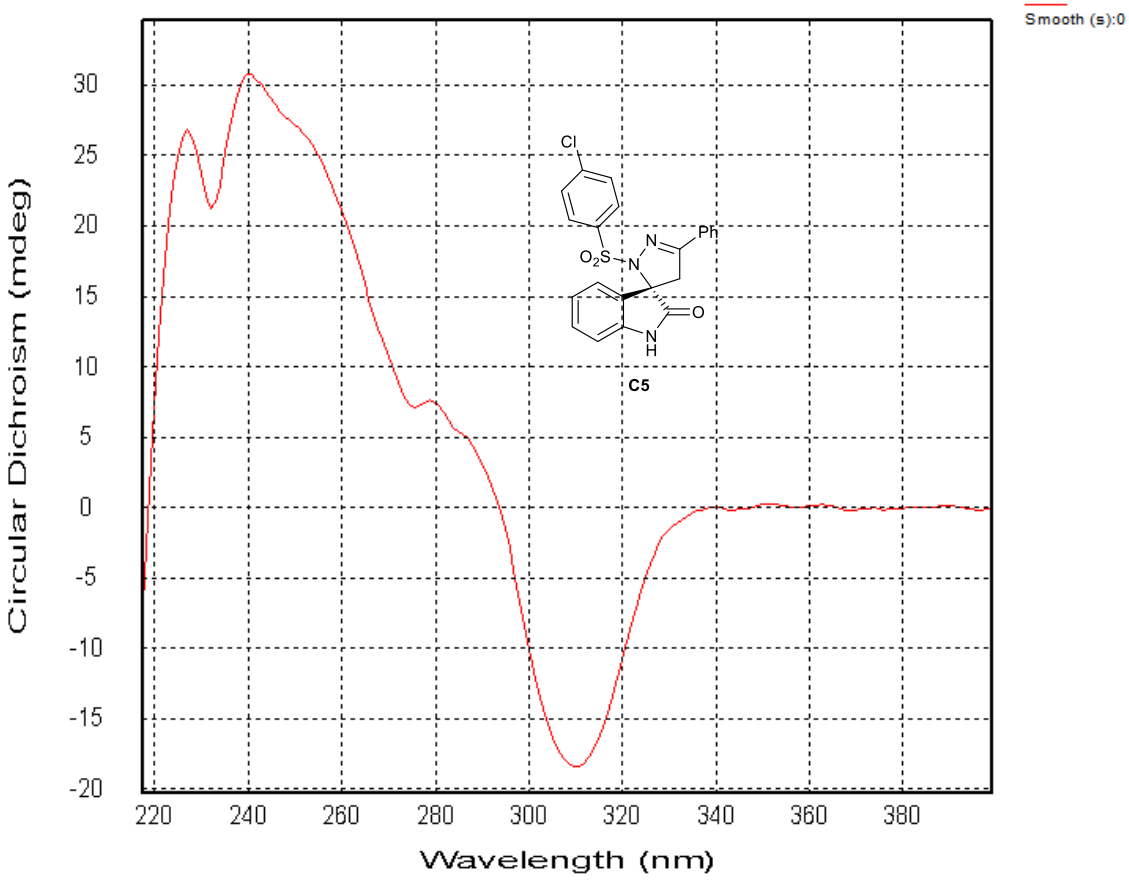
18. Copies of CD spectra in CH_3OH






Smooth (s):0
Circular Dichroism (mdeg)
50
40
30
20
10
0
-10
-20
-30
-40
220
240
260
280
300
320
340
360
380
Wavelength (nm)
Cl
Ph
O_2S
N
N
O
N
H
C3


Smooth (s):0
Circular Dichroism (mdeg)
40
30
20
10
0
-10
-20
-30
-40
220
240
260
280
300
320
340
360
380
Wavelength (nm)
Cl
Ph
N
O2S
N
O
N
H
C4


Smooth (s):0
Circular Dichroism (mdeg)
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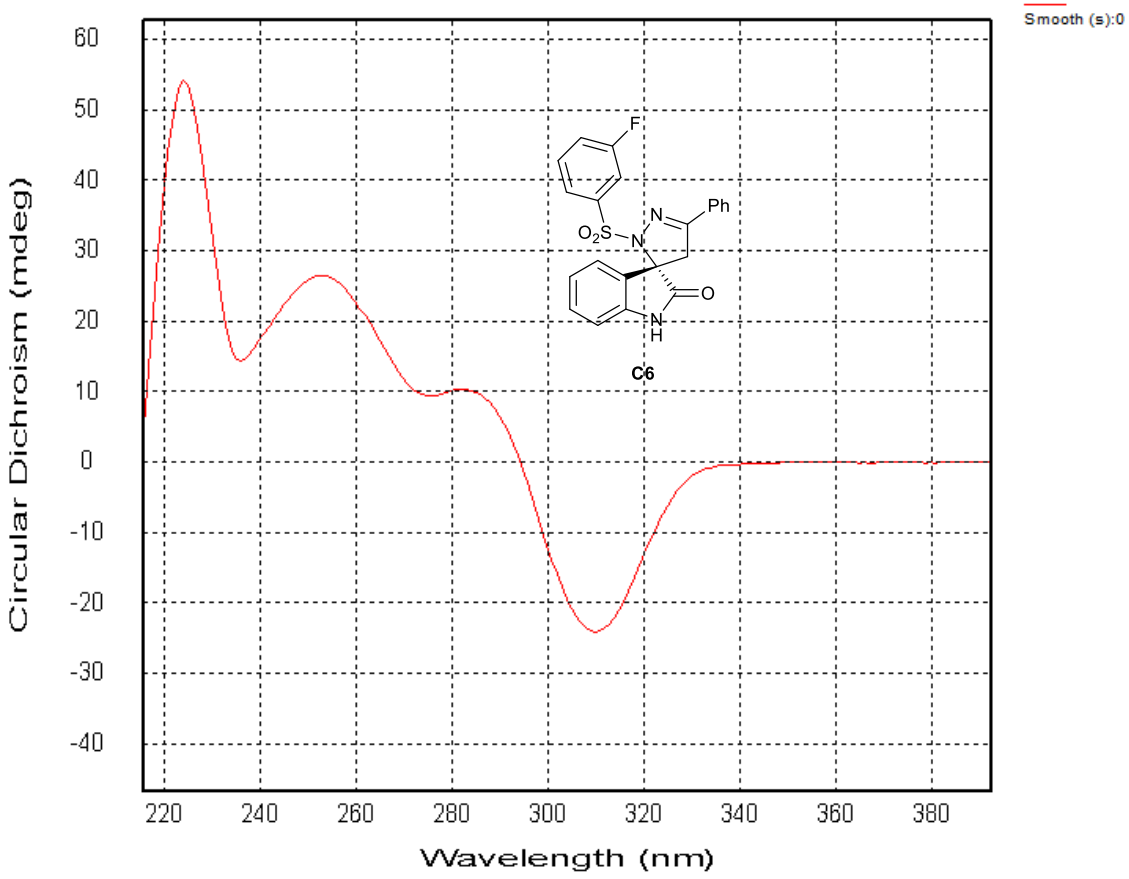
25
20
15
10
5
0
-5
-10
-15
-20
220
240
260
280
300
320
340
360
380
Wavelength (nm)
Cl
Ph
N
O_2S
N
O
N
H
C5


Smooth (s):0
Circular Dichroism (mdeg)
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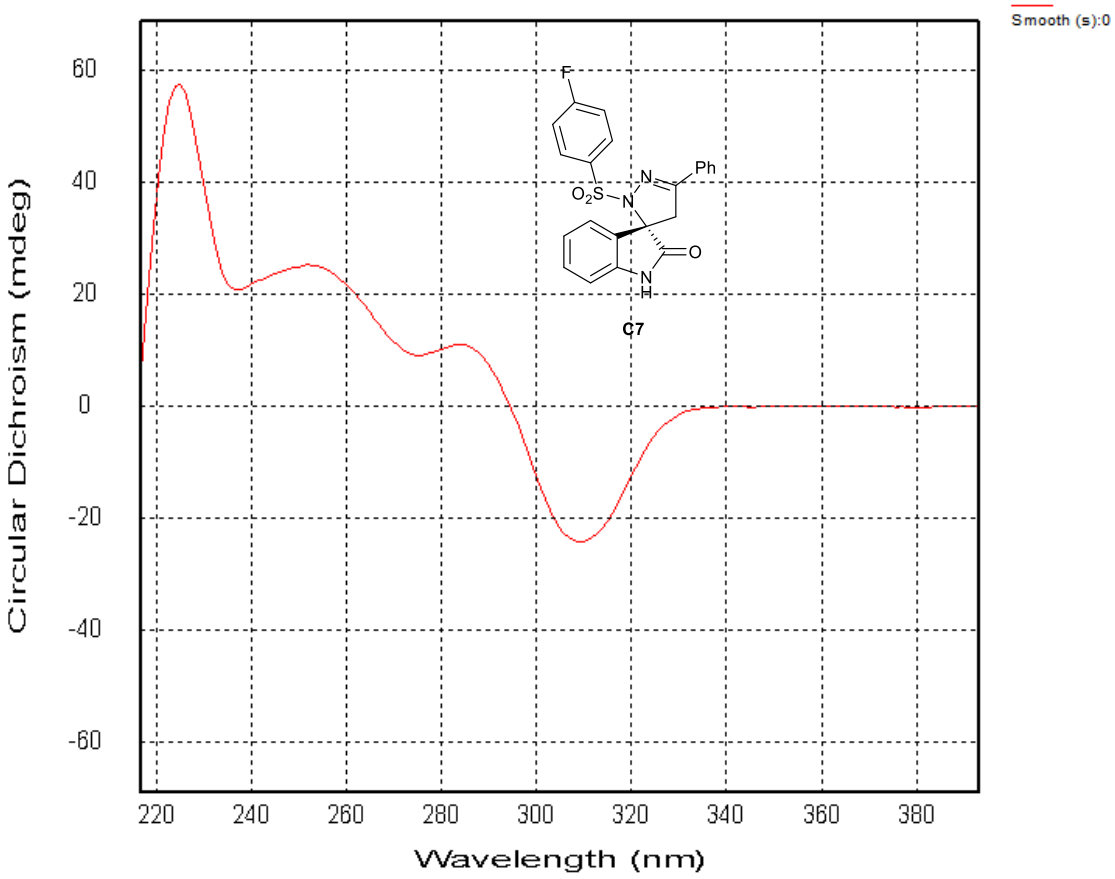
50
40
30
20
10
0
-10
-20
-30
-40
220
240
260
280
300
320
340
360
380
Wavelength (nm)
F
Ph
N
O_2S
N
O
N
H
C6


Smooth (s):0
Circular Dichroism (mdeg)
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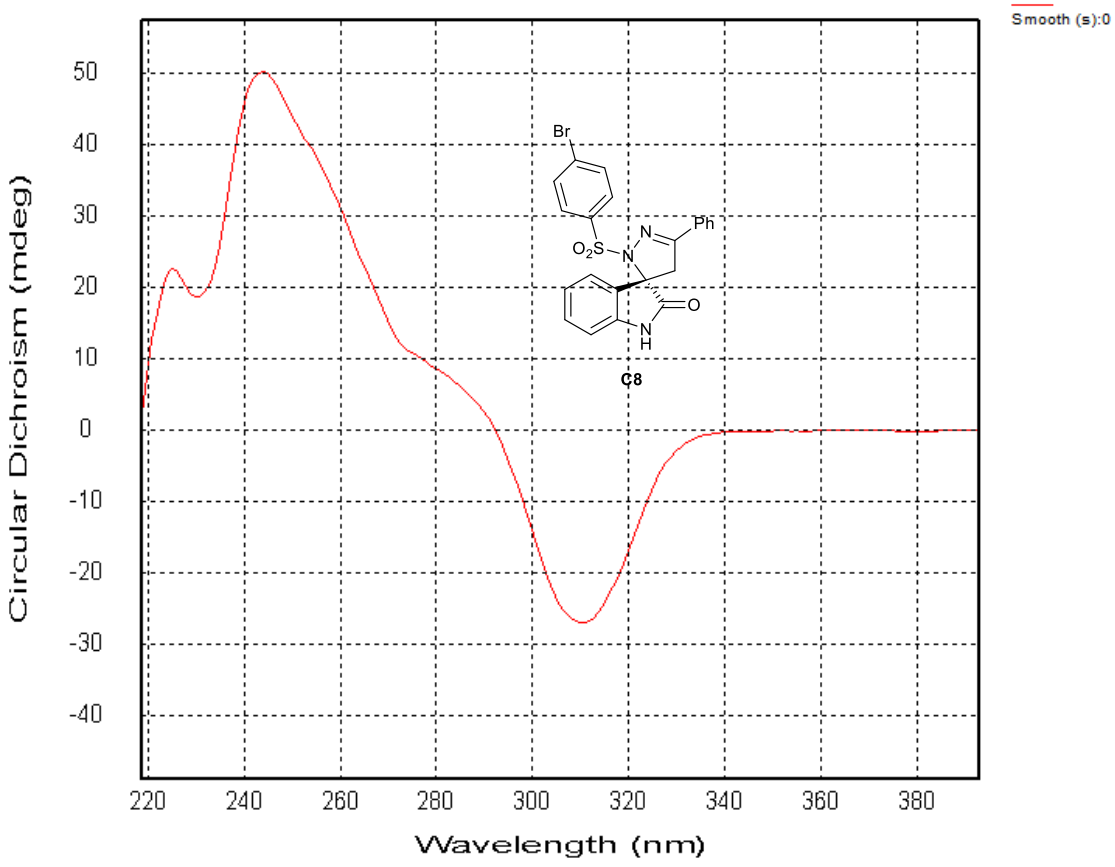
40
20
0
-20
-40
-60
220
240
260
280
300
320
340
360
380
Wavelength (nm)
F
Ph
N
O2S
N
O
N
H
C7


Smooth (s):0
Circular Dichroism (mdeg)
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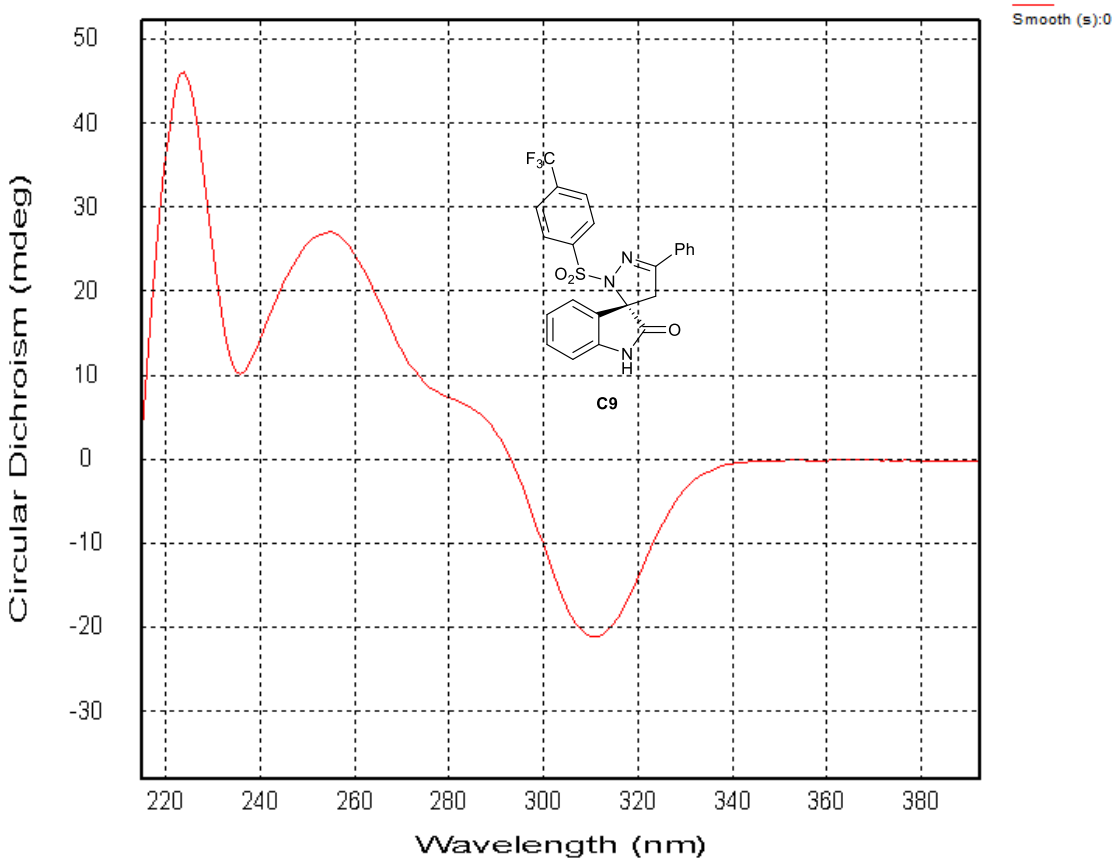
40
30
20
10
0
-10
-20
-30
-40
220
240
260
280
300
320
340
360
380
Wavelength (nm)
Br
Ph
N
O2S
N
O
N
H
C8


Smooth (s):0
Circular Dichroism (mdeg)
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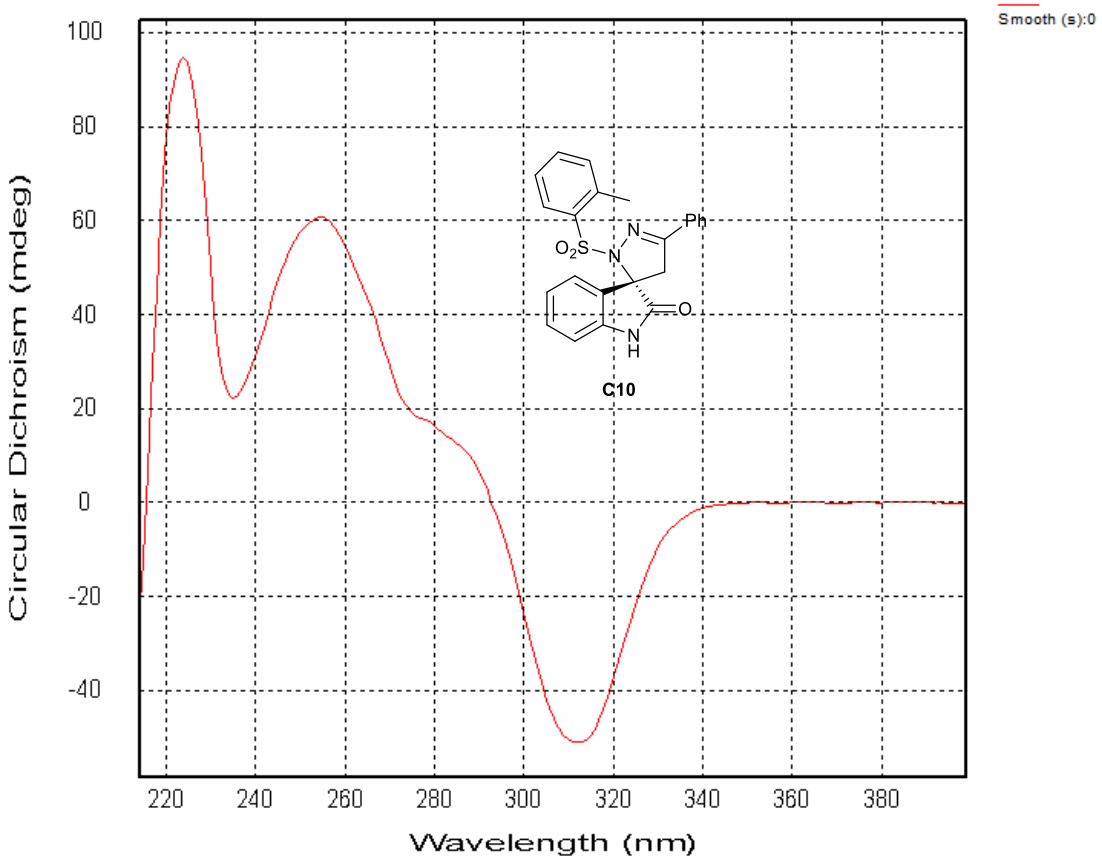
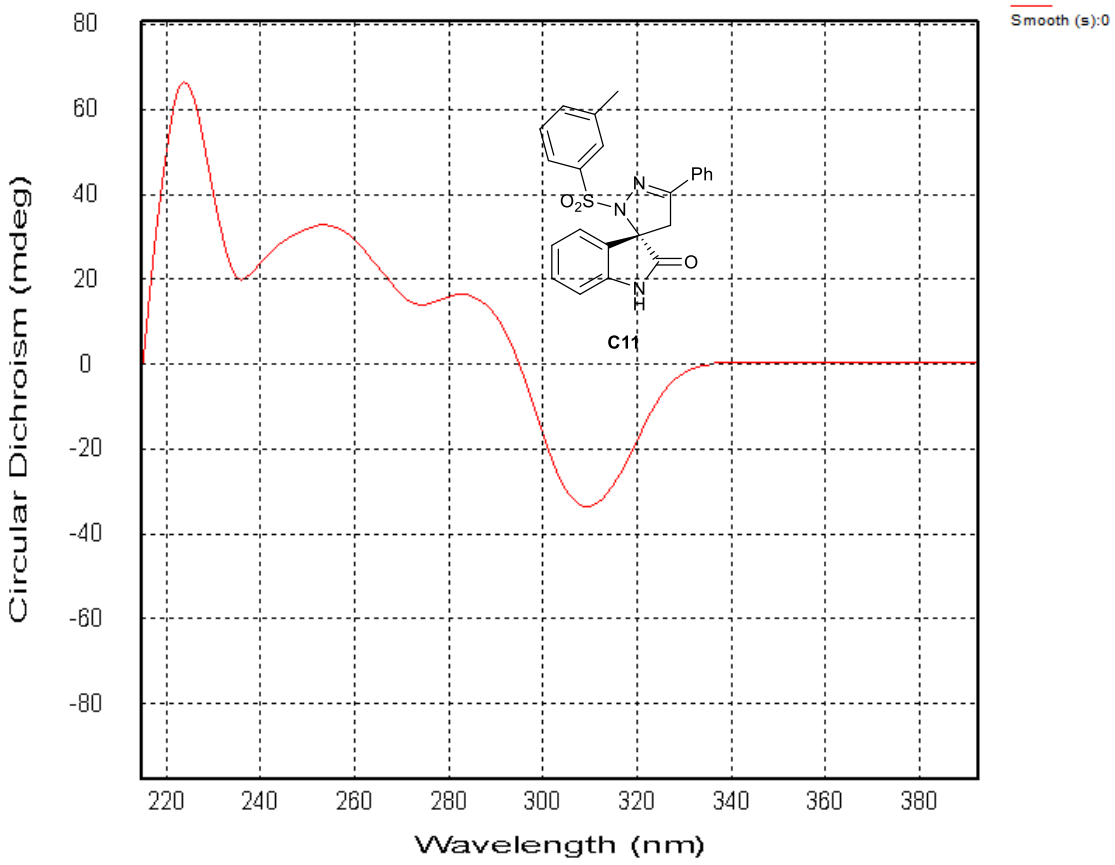
40
30
20
10
0
-10
-20
-30
220
240
260
280
300
320
340
360
380
Wavelength (nm)
F3C
O2S
N
Ph
O
H
C9


Smooth (s):0
Circular Dichroism (mdeg)
100
80
60
40
20
0
-20
-40
220
240
260
280
300
320
340
360
380
Wavelength (nm)
O2S
N
Ph
O
H
C10


Smooth (s):0
Circular Dichroism (mdeg)
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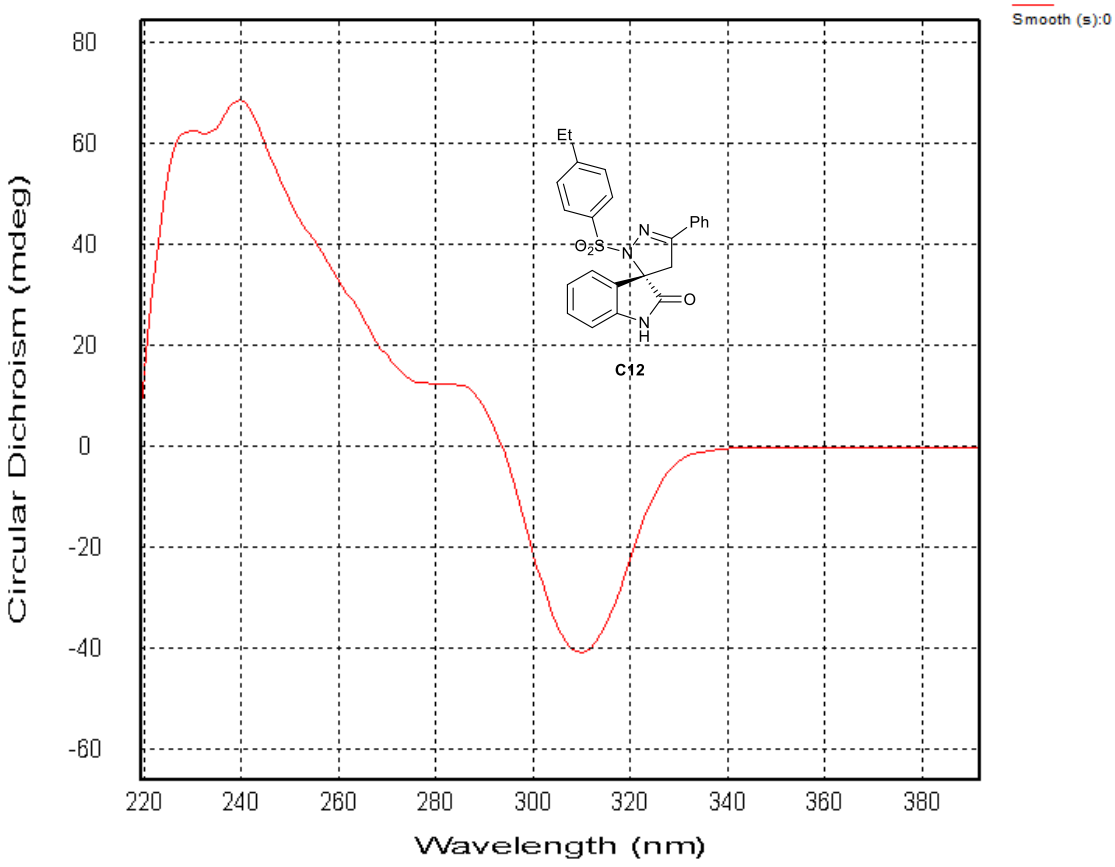
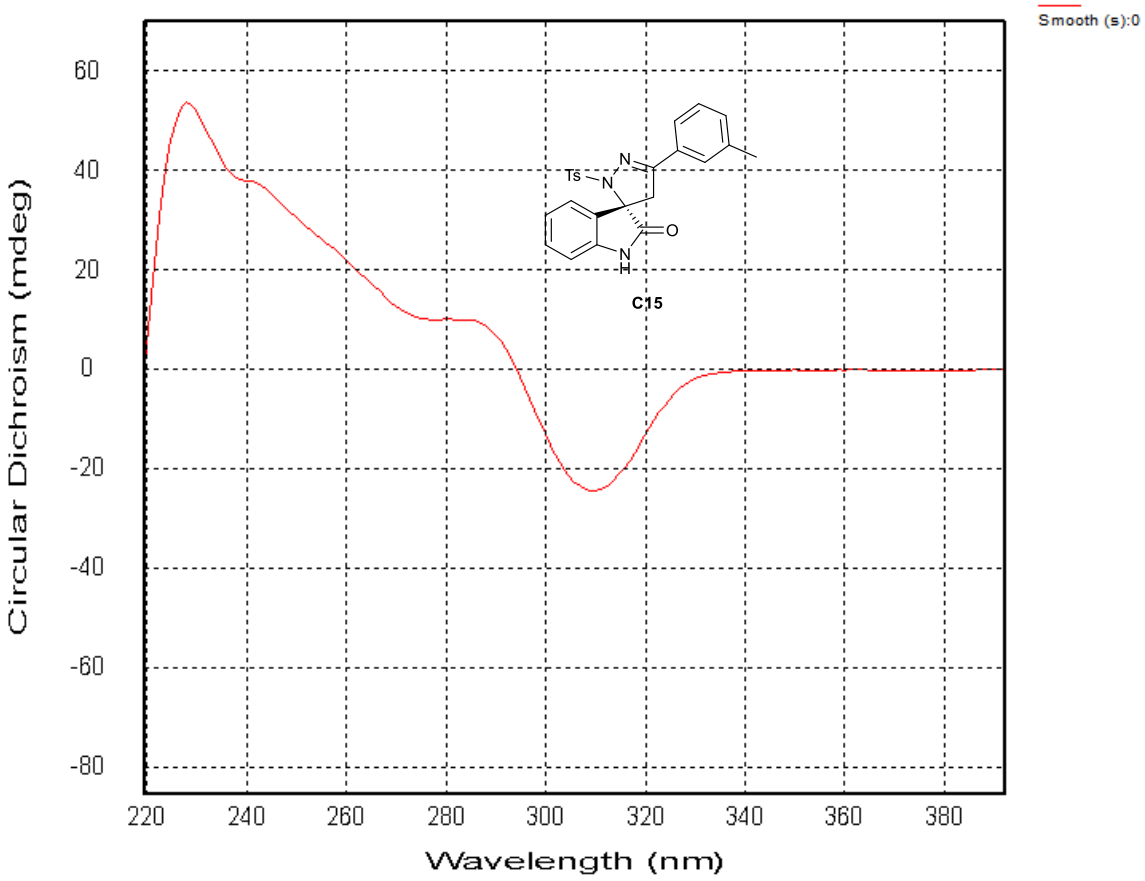
60
40
20
0
-20
-40
-60
-80
220
240
260
280
300
320
340
360
380
Wavelength (nm)
Ph
N
N
O2S
O
N
H
C11


Smooth (s):0
Circular Dichroism (mdeg)
80
60
40
20
0
-20
-40
-60
220
240
260
280
300
320
340
360
380
Wavelength (nm)
Et
Ph
N
N
O2S
O
N
H
C12


Smooth (s):0
Circular Dichroism (mdeg)
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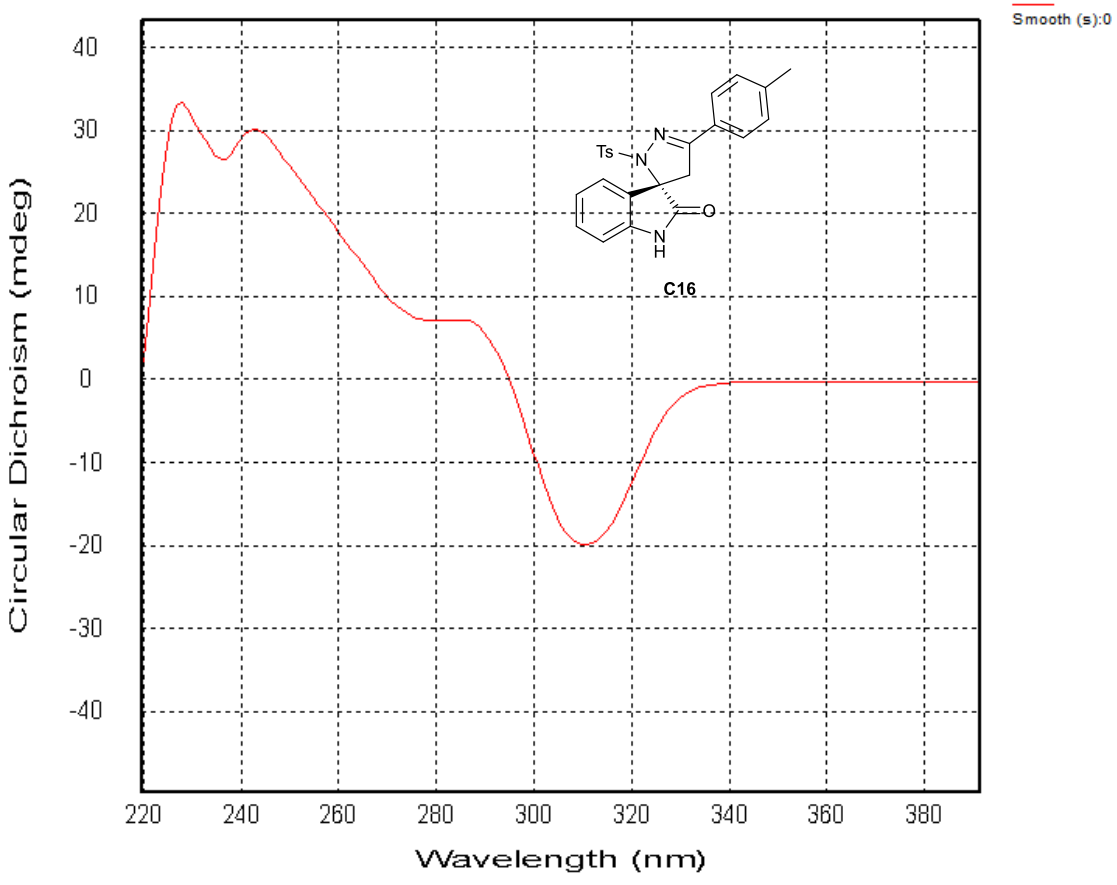
40
20
0
-20
-40
-60
-80
220
240
260
280
300
320
340
360
380
Wavelength (nm)
Ts
N
N
O
N
H
C15


Smooth (s):0
Circular Dichroism (mdeg)
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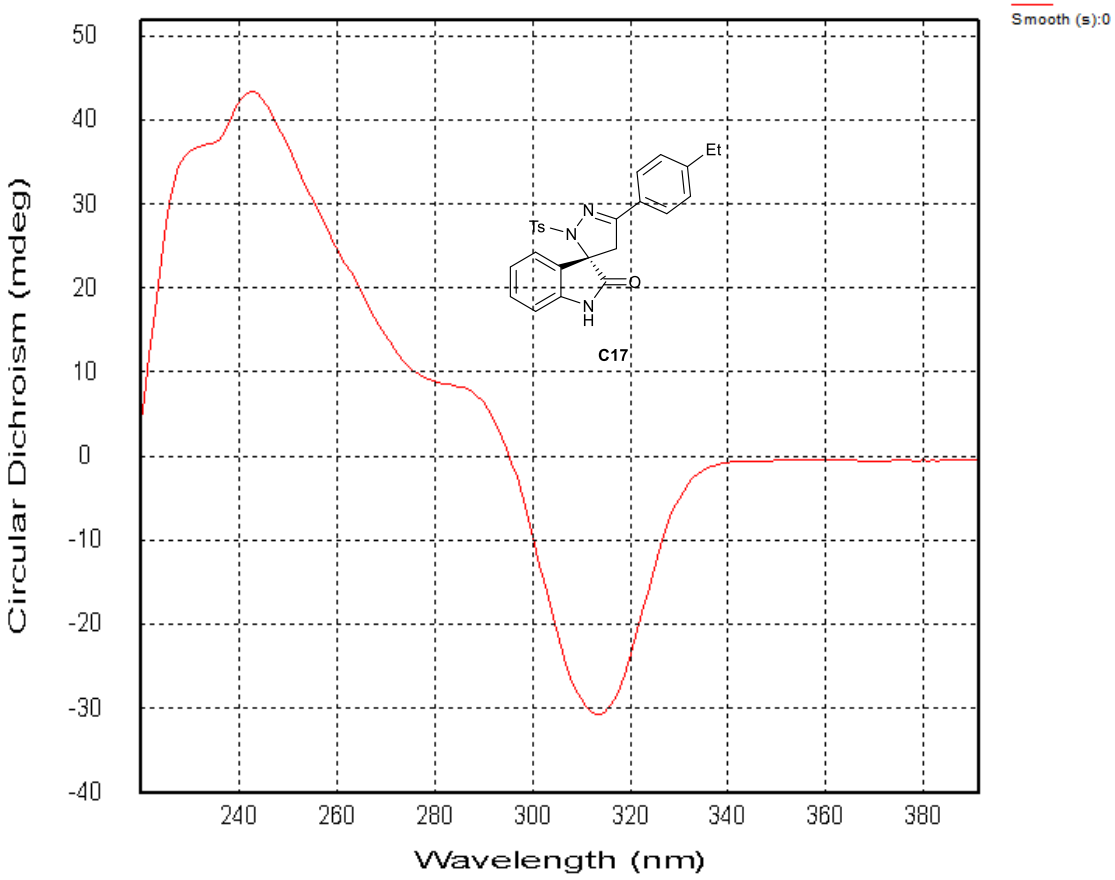
30
20
10
0
-10
-20
-30
-40
220
240
260
280
300
320
340
360
380
Wavelength (nm)
Ts
N
N
O
N
H
C16


Smooth (s):0
Circular Dichroism (mdeg)
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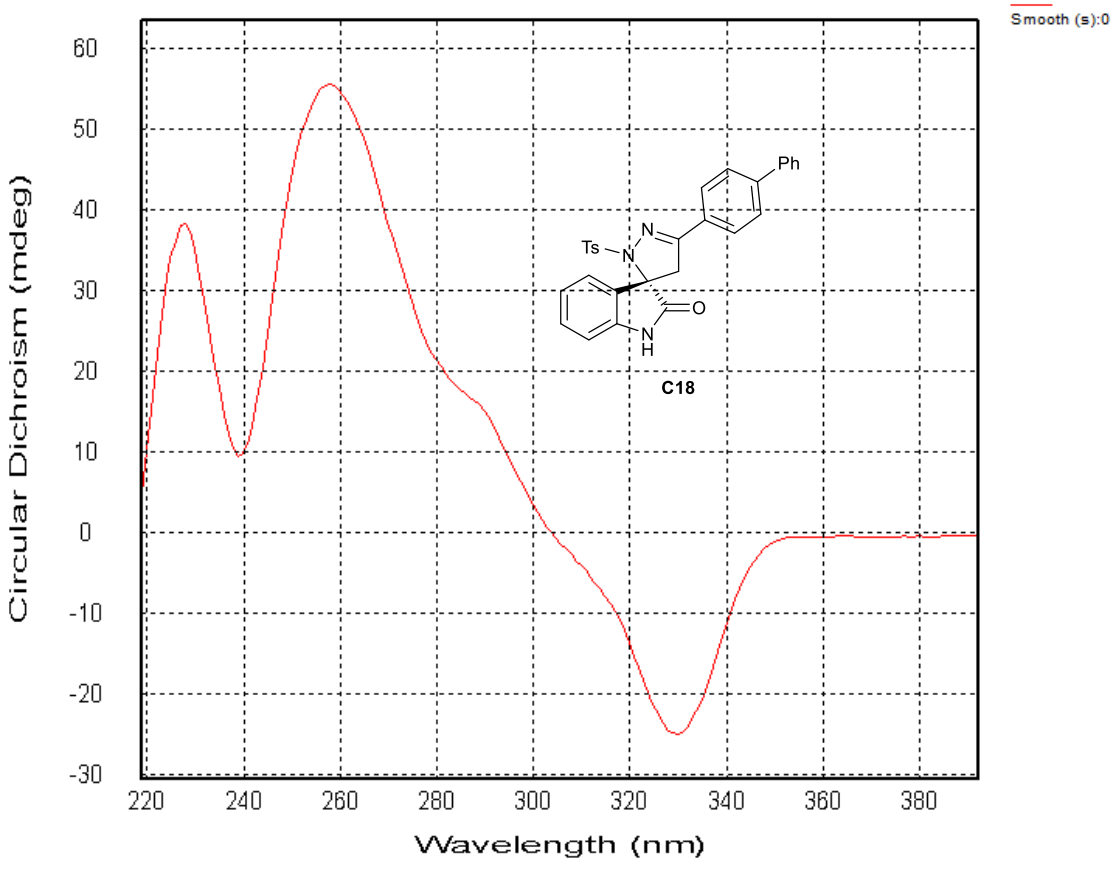
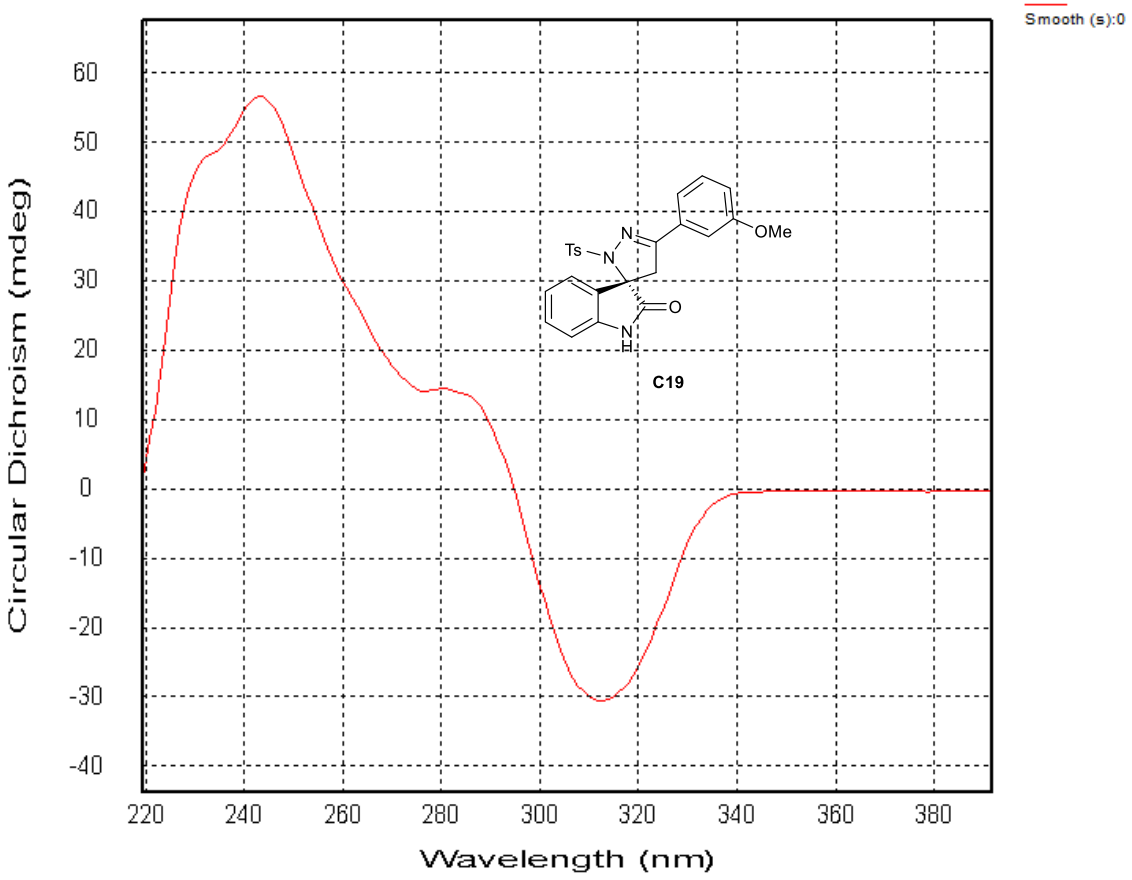
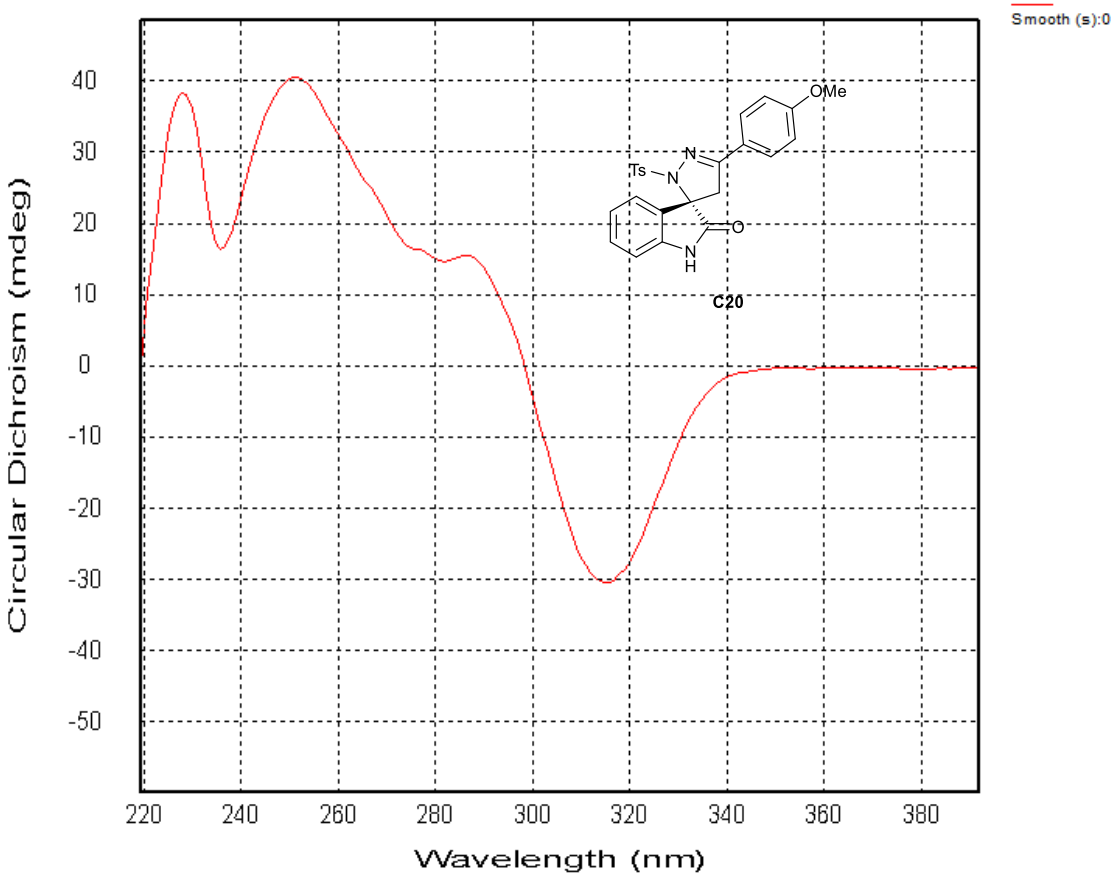
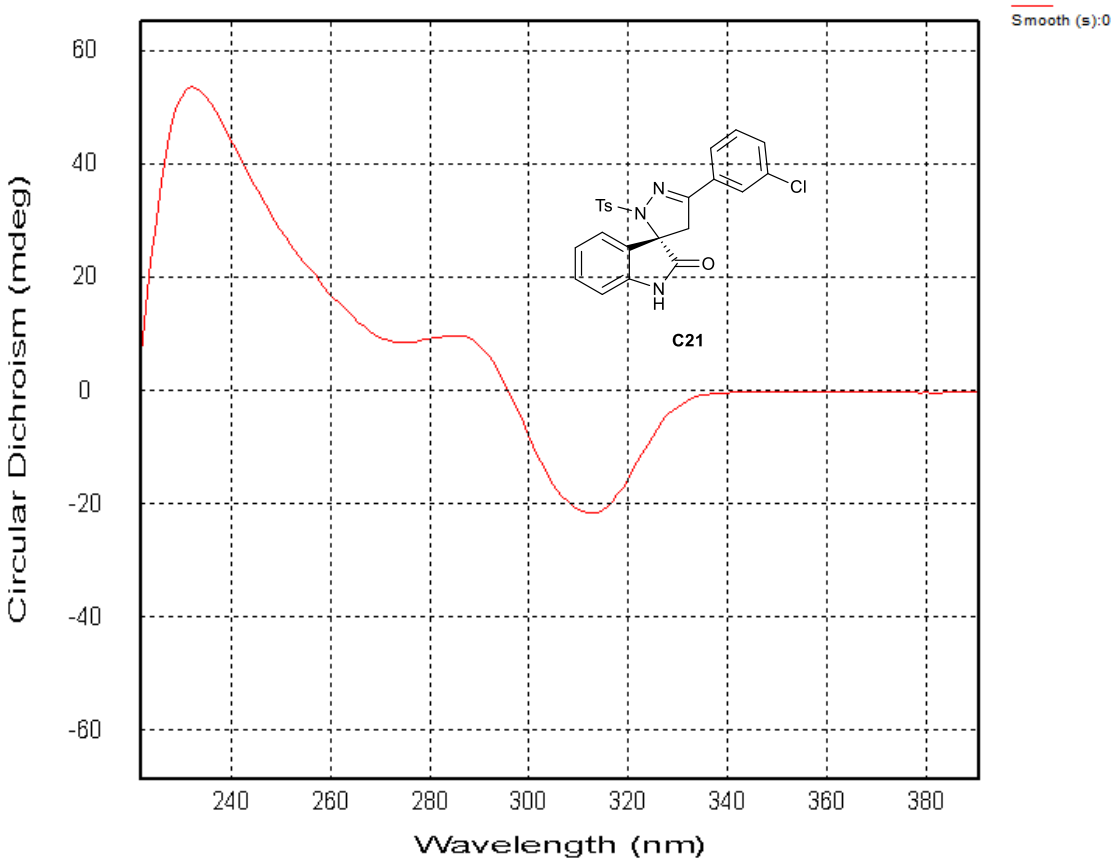
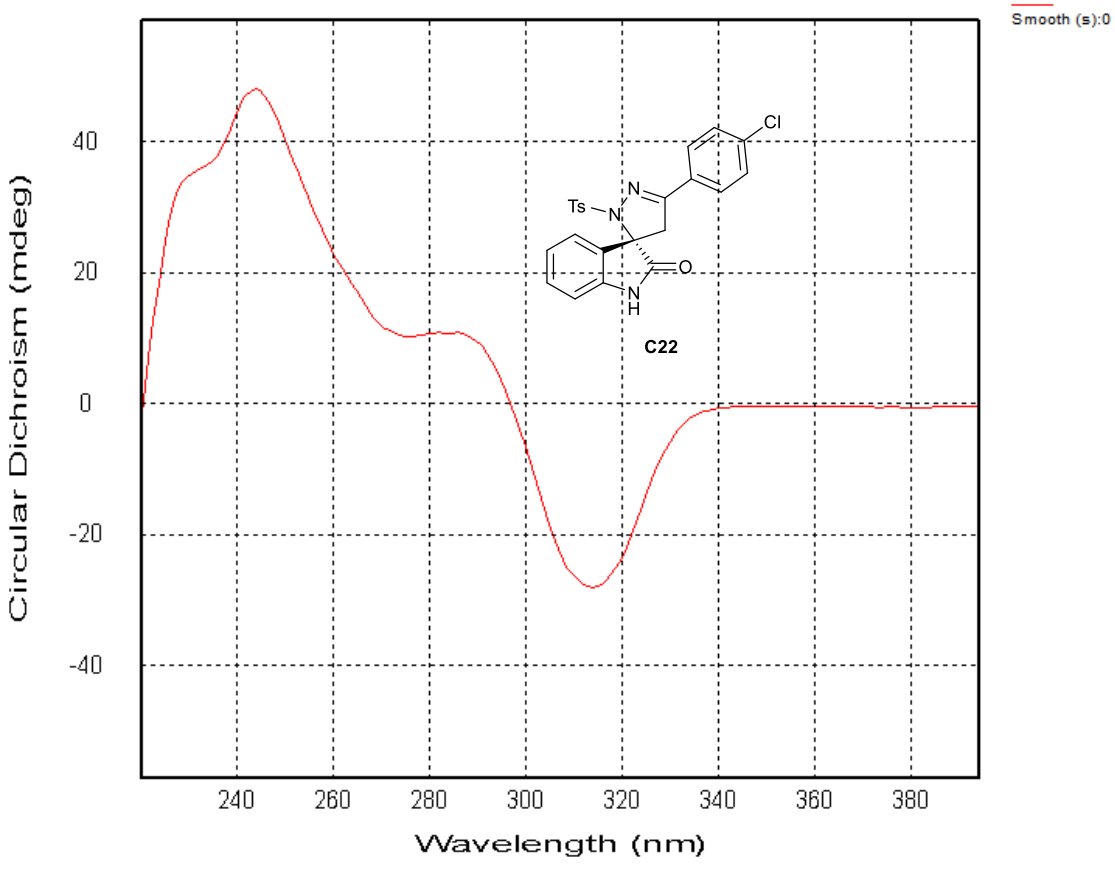
40
30
20
10
0
-10
-20
-30
-40
240
260
280
300
320
340
360
380
Wavelength (nm)
Et
Ts
N
N
O
N
H
C17


Smooth (s):0
Circular Dichroism (mdeg)
60
50
40
30
20
10
0
-10
-20
-30
220
240
260
280
300
320
340
360
380
Wavelength (nm)
Ph
Ts
N
N
O
N
H
C18

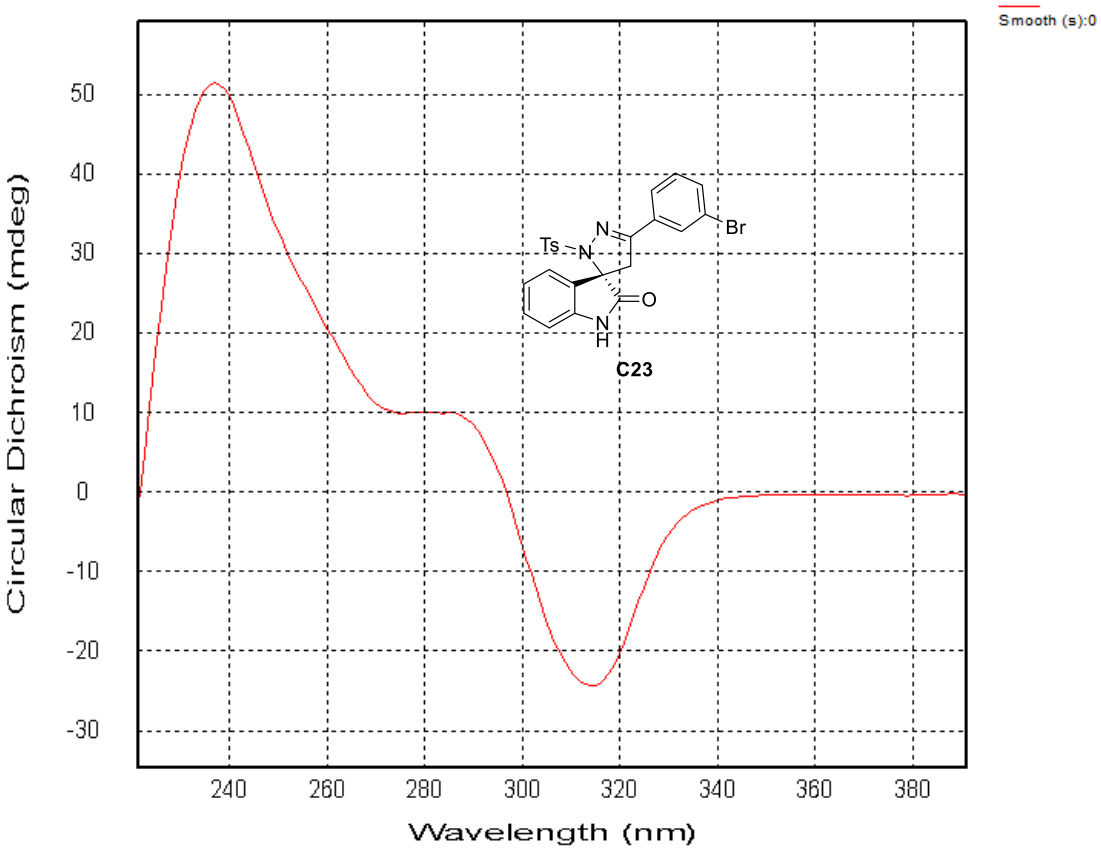

Smooth (s):0
Circular Dichroism (mdeg)
60
50
40
30
20
10
0
-10
-20
-30
-40
220
240
260
280
300
320
340
360
380
Wavelength (nm)
Ts
N
N
OMe
O
N
H
C19

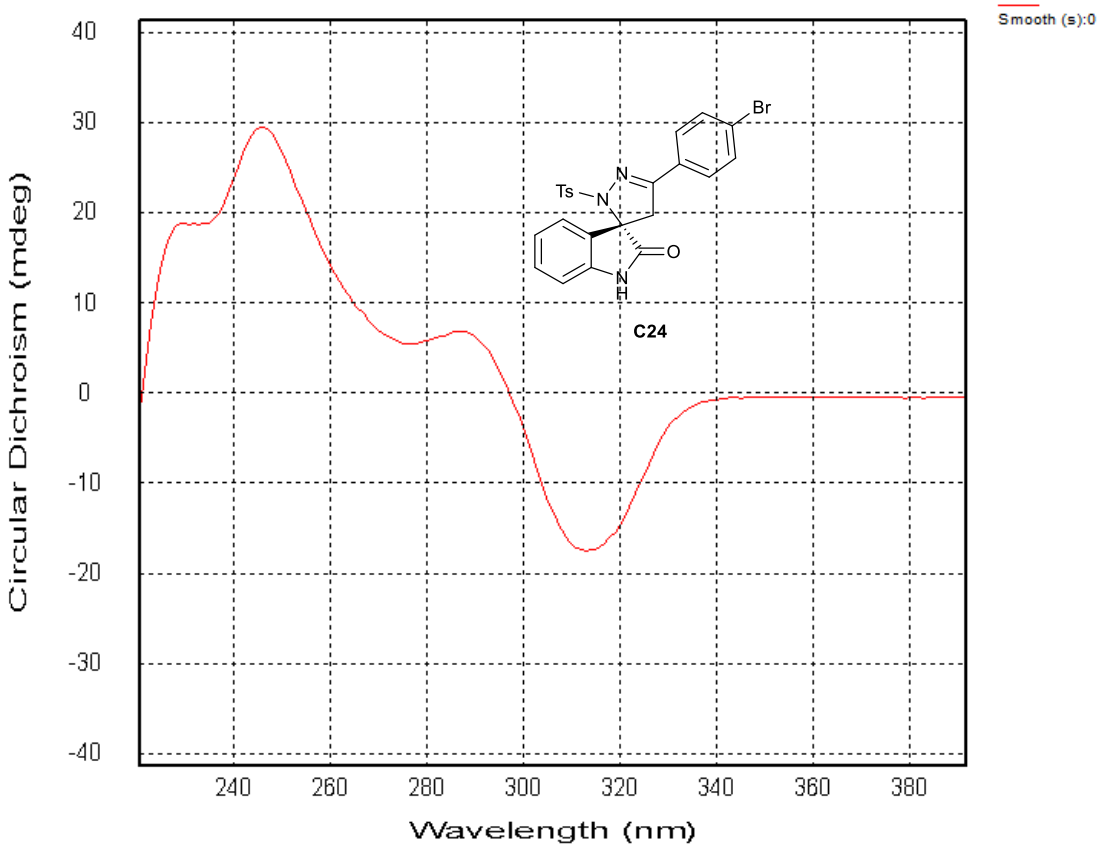

Smooth (s):0
Circular Dichroism (mdeg)
40
30
20
10
0
-10
-20
-30
-40
-50
220
240
260
280
300
320
340
360
380
Wavelength (nm)
OMe
Ts
N
N
O
N
H
C20

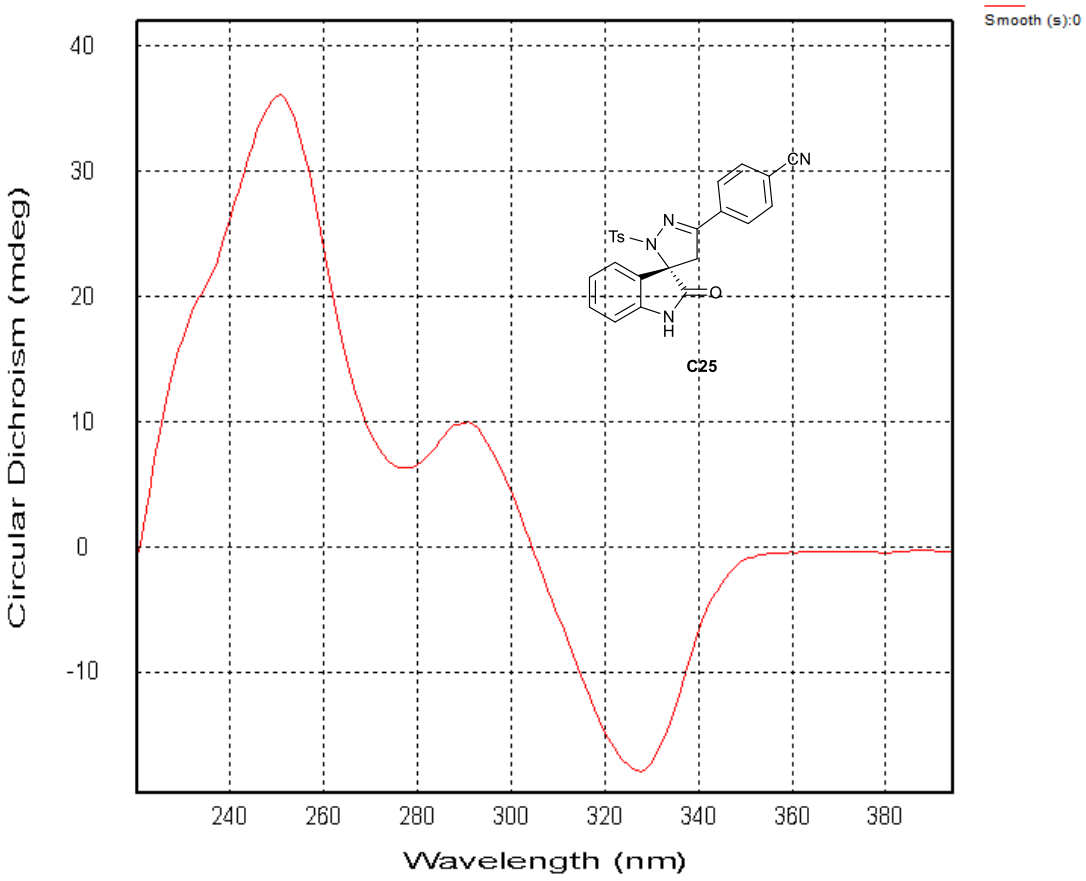

Smooth (s):0
Circular Dichroism (mdeg)
60
40
20
0
-20
-40
-60
240
260
280
300
320
340
360
380
Wavelength (nm)
Ts
N
N
Cl
O
N
H
C21

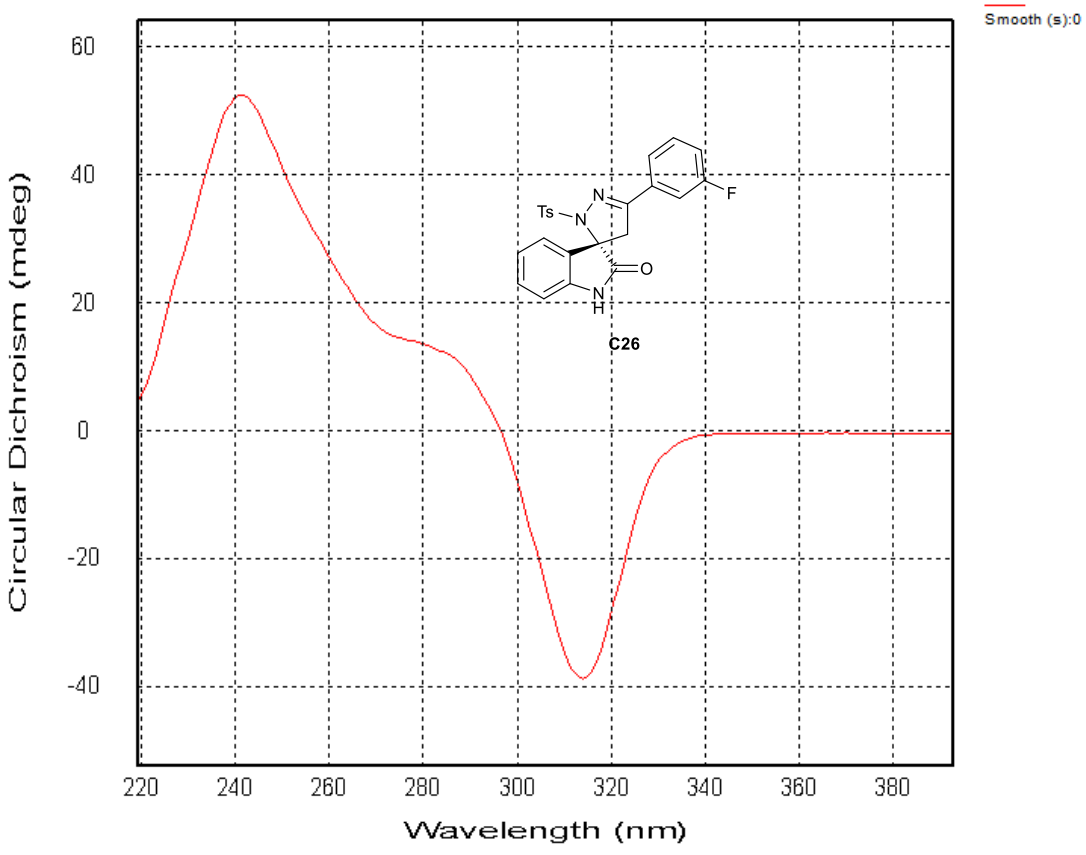

Smooth (s):0
Circular Dichroism (mdeg)
40
20
0
-20
-40
240
260
280
300
320
340
360
380
Wavelength (nm)
Ts
N
N
Cl
O
N
H
C22

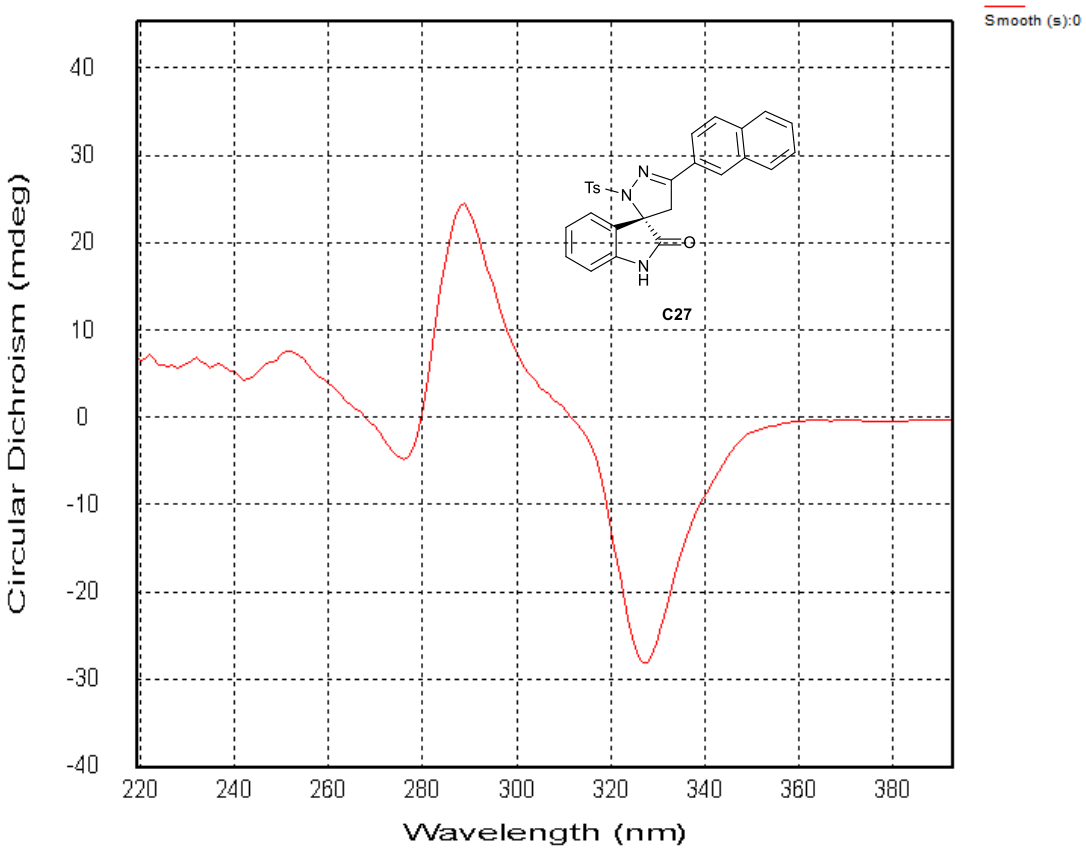
z

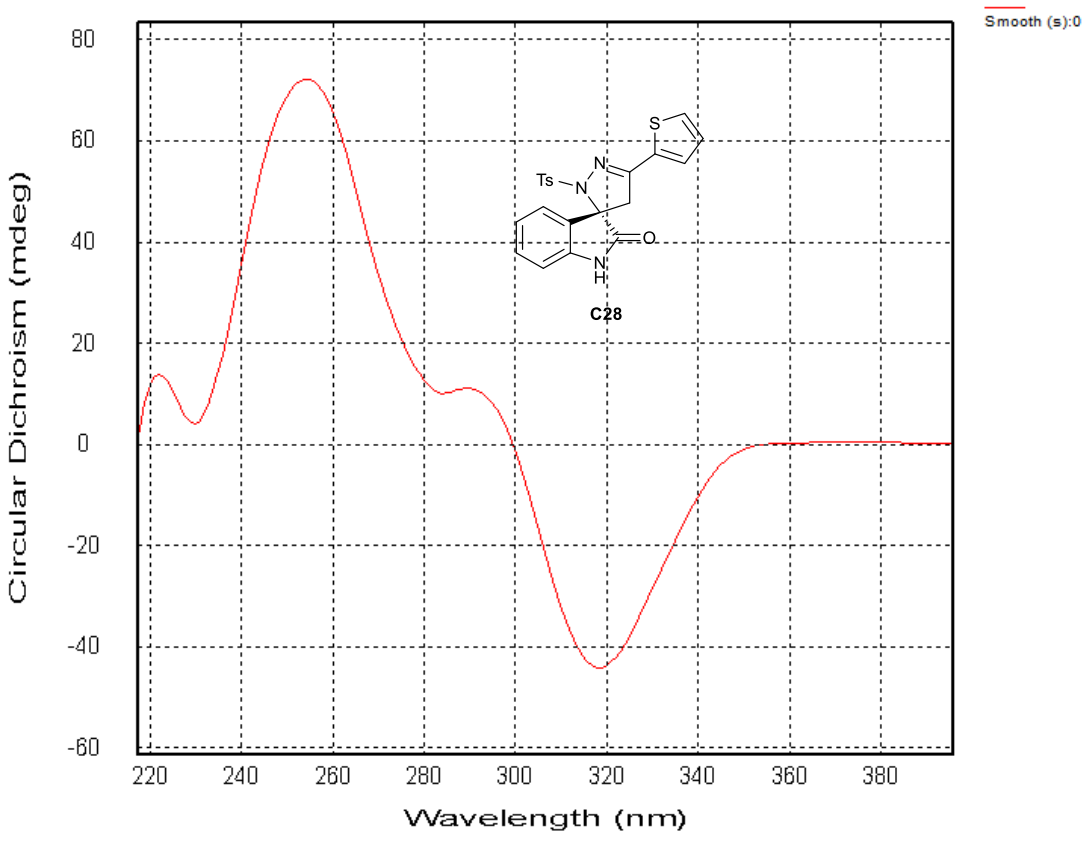

Smooth (s):0
Circular Dichroism (mdeg)
50
40
30
20
10
0
-10
-20
-30
240
260
280
300
320
340
360
380
Wavelength (nm)
Ts
N
N
Br
O
N
H
C23

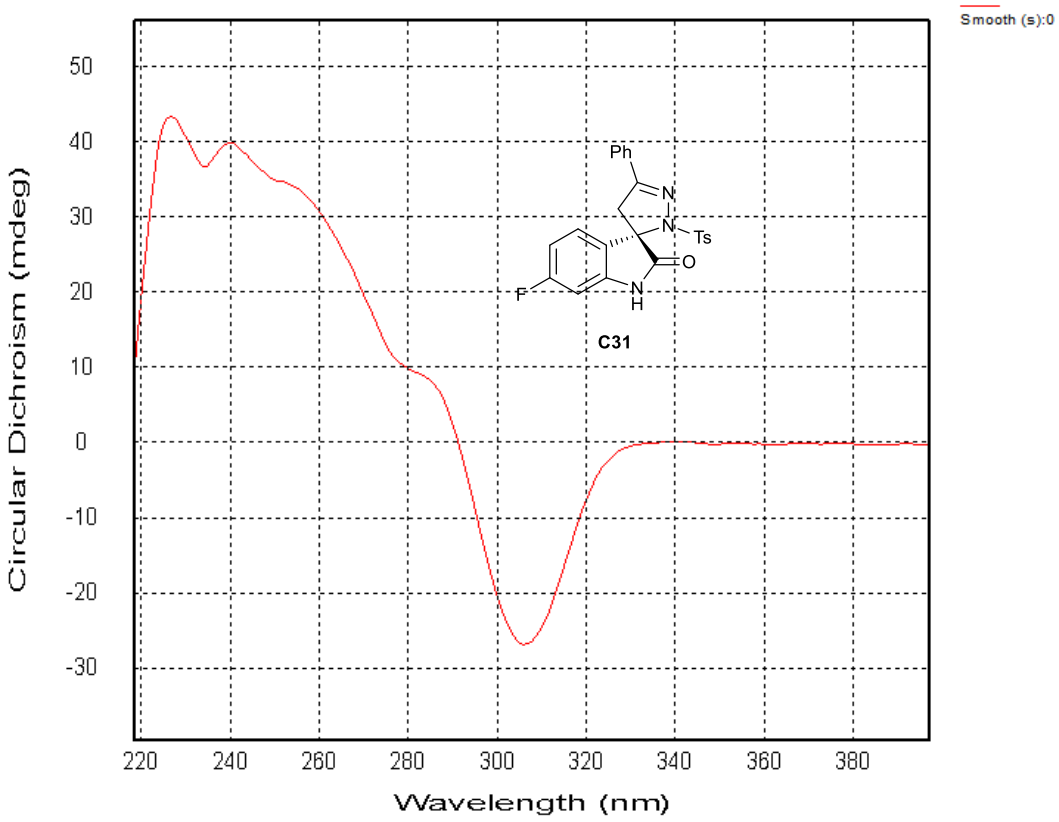

Smooth (s):0
Circular Dichroism (mdeg)
40
30
20
10
0
-10
-20
-30
-40
240
260
280
300
320
340
360
380
Wavelength (nm)
Ts
N
N
Br
O
N
H
C24

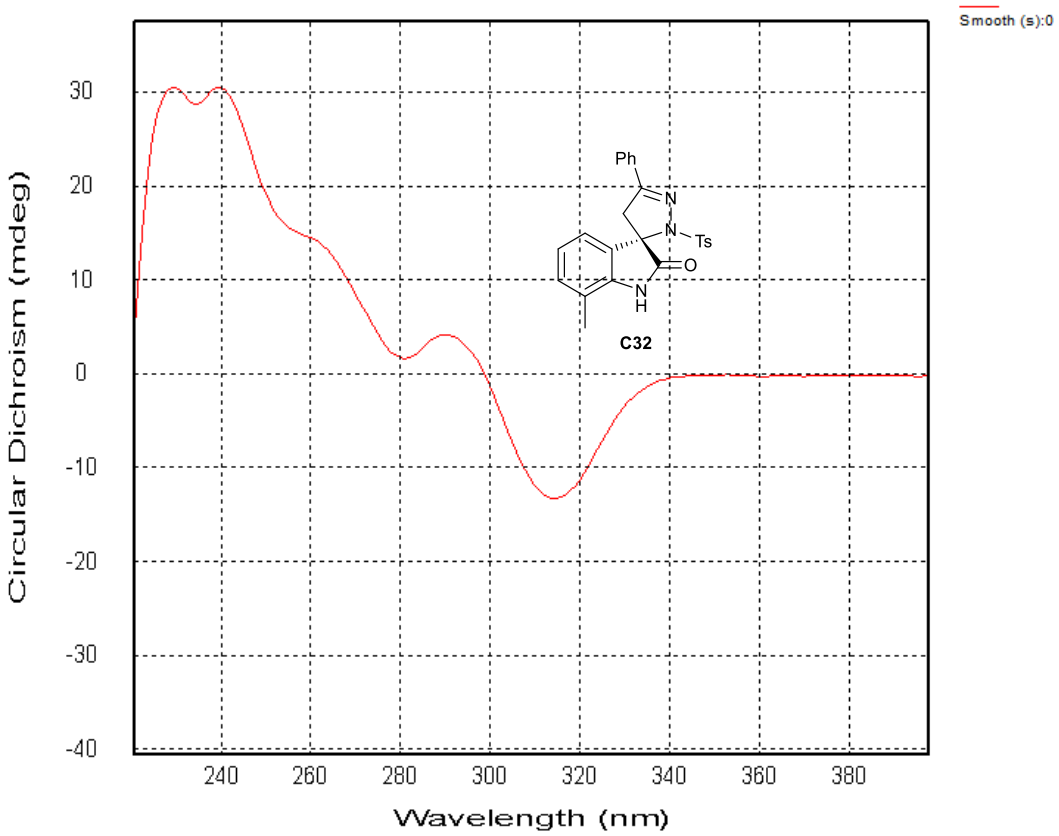

Smooth (s):0
Circular Dichroism (mdeg)
40
30
20
10
0
-10
240
260
280
300
320
340
360
380
Wavelength (nm)
CN
Ts
N
N
O
N
H
C25

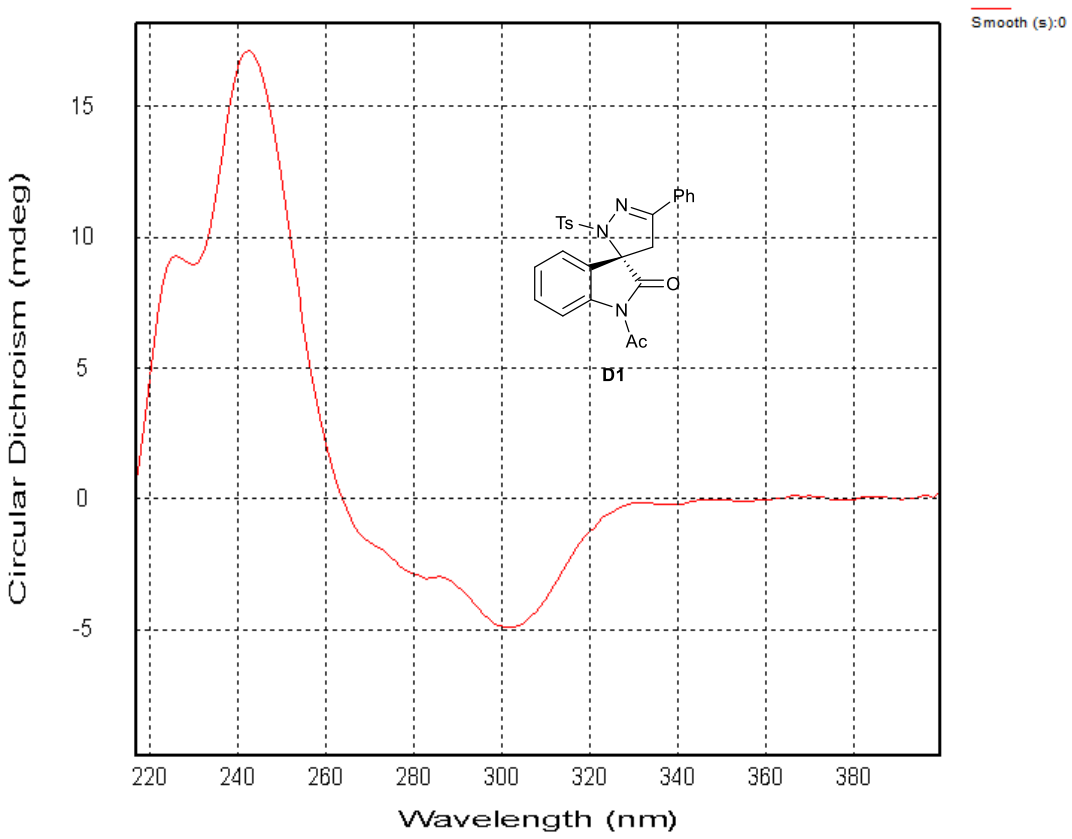

Smooth (s):0
Circular Dichroism (mdeg)
60
40
20
0
-20
-40
220
240
260
280
300
320
340
360
380
Wavelength (nm)
F
Ts
N
N
O
N
H
C26

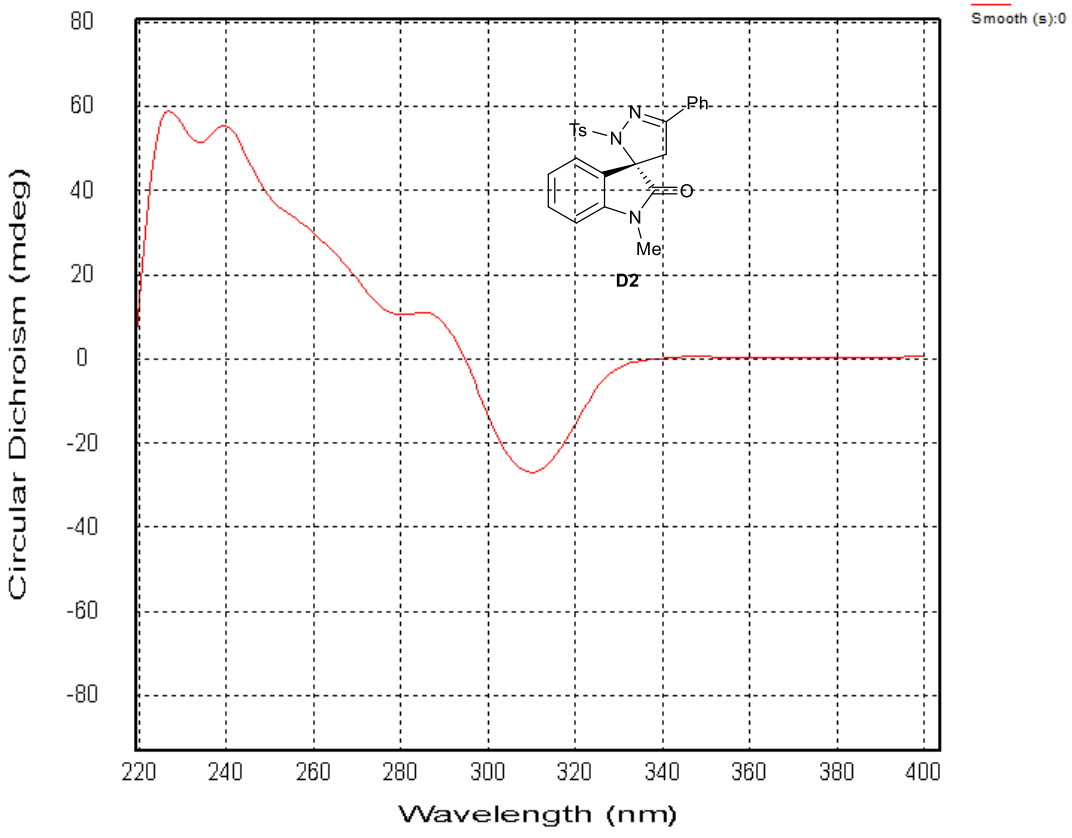

Smooth (s):0
Circular Dichroism (mdeg)
40
30
20
10
0
-10
-20
-30
-40
220
240
260
280
300
320
340
360
380
Wavelength (nm)
Ts
N
N
O
N
H
C27


Smooth (s):0
Circular Dichroism (mdeg)
80
60
40
20
0
-20
-40
-60
220
240
260
280
300
320
340
360
380
Wavelength (nm)
S
Ts
N
N
O
N
H
C28


Smooth (s):0
Circular Dichroism (mdeg)
50
40
30
20
10
0
-10
-20
-30
220
240
260
280
300
320
340
360
380
Wavelength (nm)
Ph
N
N
Ts
O
F
N
H
C31


Smooth (s):0
Circular Dichroism (mdeg)
30
20
10
0
-10
-20
-30
-40
240
260
280
300
320
340
360
380
Wavelength (nm)
Ph
N
N
Ts
O
N
H
C32


Smooth (s):0
Circular Dichroism (mdeg)
15
10
5
0
-5
220
240
260
280
300
320
340
360
380
Wavelength (nm)
Ts
N
N
Ph
O
N
Ac
D1


Smooth (s):0
Circular Dichroism (mdeg)
80
60
40
20
0
-20
-40
-60
-80
220
240
260
280
300
320
340
360
380
400
Wavelength (nm)
Ts
N
N
Ph
O
N
Me
D2