

Supporting Information

Iron^{III}-Catalytic Asymmetric Inverse-Electron-Demand

Hetero-Diels–Alder Reaction of Dioxopyrrolidines with Simple Olefins

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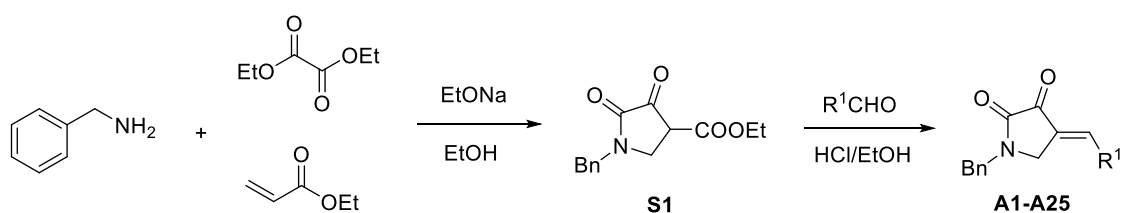
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1. General

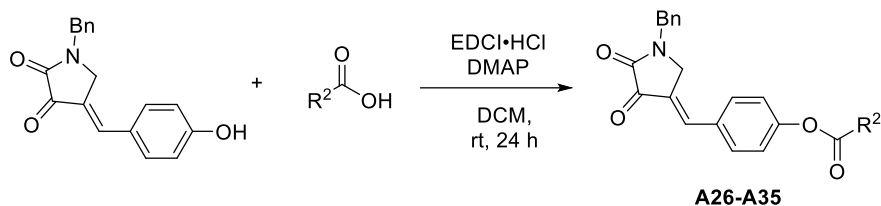
Optical rotations were reported as follows: $[\alpha]_D^{25} = (c: \text{g}/100 \text{ mL, in solvent})$. ^1H NMR spectra were recorded on commercial instruments (400 MHz or 600MHz). Chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration. $^{13}\text{C}\{^1\text{H}\}$ NMR data were collected on commercial instruments (101 MHz or 151 MHz) with complete proton decoupling. Chemical shifts were reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. $^{19}\text{F}\{^1\text{H}\}$ NMR spectra were collected on commercial instruments (376 MHz or 377 MHz) with complete proton decoupling. IR spectra were recorded on BRUKER TENSOR II IR spectrophotometer. Enantiomeric excesses (ee) were determined by Ultra Performance Convergence Chromatography (UPCC) on systems on Daicel chiralcel in the experimental procedures at 23 °C or Daicel Chiralcel IA, IB, IC, ID, IE at 23 °C with UV detector at 210 nm in comparison with the authentic racemates. HRMS was recorded on a commercial apparatus (FTMS+c ESI). UV-vis absorbance spectra were recorded on SHIMADZU UV-2600 UV-vis spectrophotometer in a 10.0 mm quartz cuvette. Reagents obtained from commercial sources were used without further purification. $\text{CH}_2\text{ClCHCl}_2$ was distilled over K_2CO_3 before use. Metal salts were purchased from Strem Chemicals, Inc. The N,N' -dioxides were prepared according to the previous reports.¹⁻³ Chromatography: Qingdao Haiyang silica gel, HG/T2354-92, H CP.

2: General procedure for the preparation of dioxopyrrolidines substrates



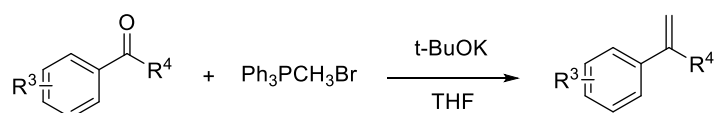
A mixture of benzylamine (7.26 g, 66.0 mmol), ethyl acrylate (7.2 mL, 66.0 mmol) in EtOH (15 mL) was stirred at room temperature for 16 h. Diethyl oxalate (9.0 mL, 66 mmol) and freshly-made sodium ethoxide solution in EtOH (generated from 2.0 g of sodium metal, 80.0 mmol, in 15 mL EtOH) was added. The mixture was heated at reflux in oil bath for 1 h and then solidified. The volatiles were removed in vacuo. The crude product was diluted with H_2O (80 mL) and adjusted the pH of the mixture to 1 by adding conc.HCl. The mixture was subjected to filtration to afford **S1** as a white solid (12.75 g, yield 75%).

A mixture of **S1** (2.6 g, 9.8 mmol, 1.0 equiv.), benzaldehyde or its derivatives (9.8 mmol, 1.0 equiv.) in EtOH (20 mL)/ 20 % aq. HCl (50 mL) was heated at reflux for 14 h in oil bath. After cooling down to ambient temperature, the aqueous layer was decanted. The obtained chunky solid was collected and further recrystallized from EtOAc to generate **A1-A25** as a bright yellow solid (yield: 25% to 70%).



A mixture of the carboxylic acid (4 mmol), phenol/phenol derivative (4 mmol), DMAP (0.4 mmol), and 1-ethyl-3-(3-(dimethylamino)propyl)carbodiimide hydrochloride (EDC·HCl, 6 mmol) in DCM (30 mL) was stirred overnight at rt. The resulting mixture was filtered, and the filtrate was evaporated in vacuo. The residue was purified by flash column chromatography (silica gel, ethyl acetate/petroleum ether = 1/2 to 1/1 as the eluent), affording the corresponding bright yellow solid.

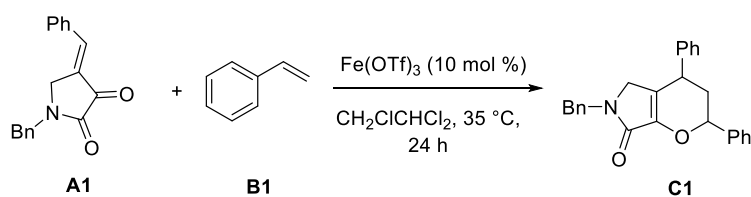
3: General procedure for the synthesis of alkenes according to the literature procedure.



In a dried flask, methyl triphenylphosphonium bromide (4.29 g, 12 mmol, 1.2 equiv.) was dissolved in THF (20 mL). Then t-BuOK (1.35 g, 12 mmol, 1.2 equiv.) was added and the resulting yellow suspension was stirred at room temperature for 30 min. Then aldehyde or ketone (10 mmol, 1.0 equiv.) was added and the resulting mixture was further stirred at room temperature overnight. Water was added to the reaction mixture and the aqueous phase was extracted with ethyl acetate. The combined organic phases were dried over Na₂SO₄ and concentrated in vacuo. The residue was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (19/1, v/v) to give corresponding alkenes.

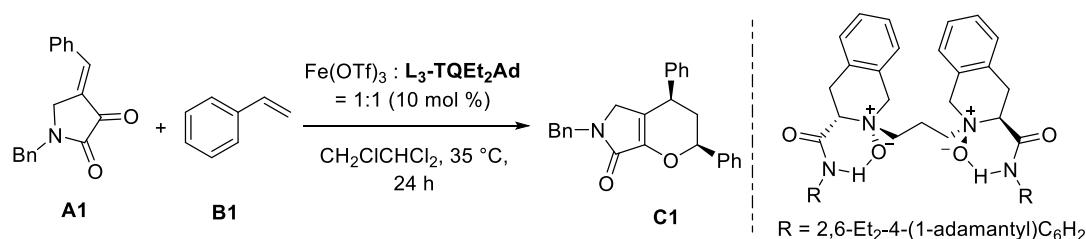
Note: All substituted olefins were synthesized by this method or obtained from commercial sources without further purification.

4: General procedure for the preparation of the racemic products (A1 as an example)



A mixture of (E)-1-benzyl-4-benzylidenepyrrolidine-2,3-dione **A1** (27.7 mg, 0.1 mmol), Fe(OTf)₃ (5.1 mg, 0.01 mmol, 10 mol %) was added to a test tube under an inert atmosphere. Anhydrous CH₂ClCHCl₂ (1.0 mL) was added, and the solution was stirred at 35 °C for 0.5 h. Subsequently, styrene **B1** (5 eq, 0.5 mmol) was added at 35 °C, and the reaction mixture was stirred for an additional 24 h. The product **C1** was purified by flash chromatography (PE/EtOAc = 2:1).

5: General experimental procedure for the catalytic asymmetric reaction (**A1** as an example)



A mixture of (E)-1-benzyl-4-benzylidenepyrrolidine-2,3-dione **A1** (27.7 mg, 0.1 mmol), Fe(OTf)₃ (5.1 mg, 0.01 mmol, 10 mol %), and *N,N'*-dioxide ligand **L3-TQEt₂Ad** (9.6 mg, 0.01 mmol, 10 mol %) was added to a test tube under an inert atmosphere. Anhydrous CH₂ClCHCl₂ (1.0 mL) was added, and the solution was stirred at 35 °C for 0.5 h. Subsequently, styrene **B1** (5 eq, 0.5 mmol) was added at 35 °C, and the reaction mixture was stirred for an additional 48 h. The product **C1** was purified by flash chromatography (PE/EtOAc = 2:1).

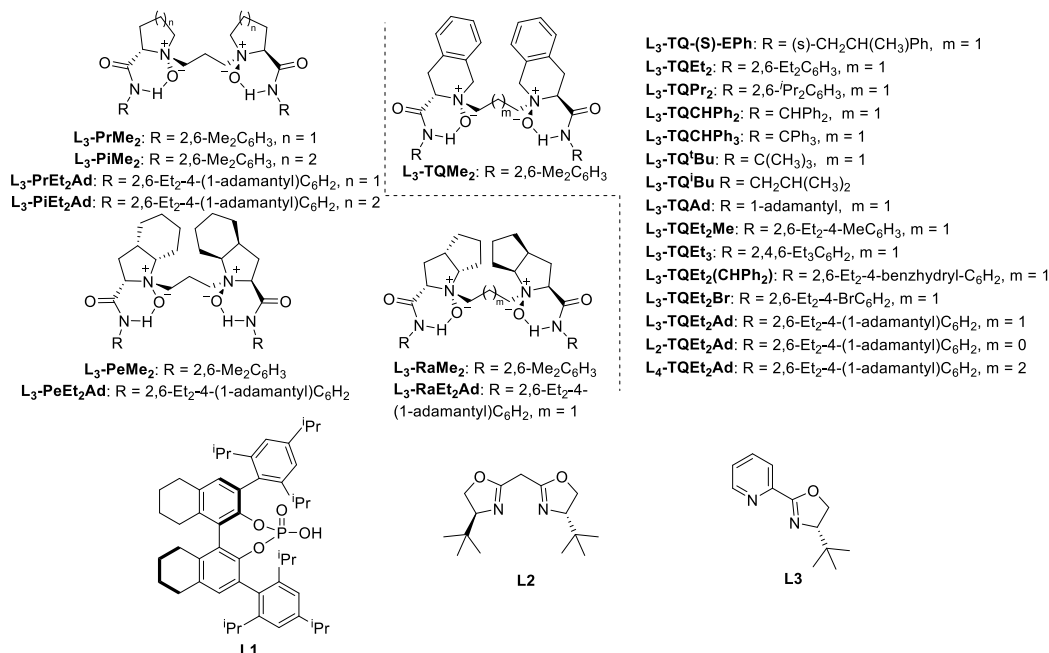


Figure S1 Chiral *N,N'*-dioxide used

6: Optimization of the reaction conditions.

Table S1. Ligand effect^a

<chem>O=C1C(=O)N(C1/C=C/c2ccccc2)Cc3ccccc3</chem> + <chem>C=Cc1ccccc1</chem> $\xrightarrow[\text{DCM, 35 } ^\circ\text{C}]{\text{In(OTf)}_3/\text{Ligand (1:1, 10 mol\%)}}$ <chem>O=C1C(=O)N(C1/C=C/c2ccccc2)C2C(=O)C(c3ccccc3)OC2Cc4ccccc4</chem> A1 (0.1 mmol) + B1 (1 mmol) → C1				
Entry	Ligand	Yield (%) ^b	Endo/exo ^c	Ee (%) ^c
1	L₃-RaMe₂	37	46/54	4/0
2	L₃-PrMe₂	20	52/48	28/22
3	L₃-PiMe₂	65	60/40	26/23
4	L₃-PeMe₂	48	48/52	9/0
5	L₃-TQMe₂	84	56/44	43/44
6	L₃-TQⁱBu	65	50/50	25/25
7	L₃-TQⁱBu	59	55/45	5/16
8	L₃-TQAd	48	53/47	13/0
9	L₃-TQCHPh₂	60	59/41	55/45
10	L₃-TQCPh₃	87	56/44	21/0
11	L₂-TQⁱBu	72	54/46	3/14
12	L₃-TQ-(S)-Eph	61	55/45	30/5
13	L₃-TQEt₂	99	68/32	59/40
14	L₃-TQPr₂	92	62/38	45/-5
15	L₃-TQE₂Me	98	73/27	75/53

^aThe reactions were carried out with **A1** (0.1 mmol), **B1** (10 eq, 1.0 mmol) and **Ligand**/In(OTf)₃ (1:1, 10 mol %) in CH₂Cl₂ (1.0 mL) at 35 °C for 24 h. ^bYield of isolated product. ^cDetermined by chiral SFC.

Table S2. Solvent effect^a

Entry	Solvent	Yield (%) ^b	Endo/exo ^c	Ee (%) ^c
1	THF	Trace	-	-
2	CHCl ₃	50	70/30	58/62
3	DCE	79	71/29	76/43
4	acetone	Trace	-	-
5	CH ₃ CN	NR	-	-
6	CH ₂ ClCHCl ₂	91	73/27	84/50
7	CHCl ₂ CHCl ₂	49	67/33	79/51

^aThe reactions were carried out with **A1** (0.1 mmol), **B1** (10 eq, 1.0 mmol) and **L₃-TQEt₂Me**/In(OTf)₃ (1:1, 10 mol %) in **solvent** (1.0 mL) at 35 °C for 24 h. ^bYield of isolated product. ^c Determined by chiral SFC.

Table S3. Temperature effect^a

Entry	T (°C)	Yield (%) ^b	Endo/exo ^c	Ee (%) ^c
1	0	26	78/22	88/53
2	20	73	76/24	81/45
3	35	90	73/27	84/50
4	50	99	66/34	72/39
5	-20	NR	-	-

^aThe reactions were carried out with **A1** (0.1 mmol), **B1** (10 eq, 1.0 mmol) and **L₃-TQEt₂Me**/In(OTf)₃ (1:1, 10 mol %) in CH₂ClCHCl₂ (1.0 mL) at T °C for 24 h. ^bYield of isolated product. ^c Determined by

chiral SFC.

Table S4. Additive effect^a

Entry	Additive	Yield (%) ^b	Endo/exo ^c	Ee (%) ^c
1	3Å MS (20 mg)	31	66/34	67/31
2	4Å MS (20 mg)	44	66/34	76/37
3	5Å MS (20 mg)	99	63/37	61/25
4	NaBAR ^F ₄ (10 %)	95	61/39	70/48
5	Na ₂ SO ₄ (20mg)	79	71/29	81/45
6	-	90	73/27	84/50

^aThe reactions were carried out with **A1** (0.1 mmol), **B1** (10 eq, 1.0 mmol) and **L₃-TQEt₂Me**/**In(OTf)₃** (1:1, 10 mol %) in CH₂ClCHCl₂ (1.0 mL) at 35 °C for 24 h. ^bYield of isolated product. ^c Determined by chiral SFC.

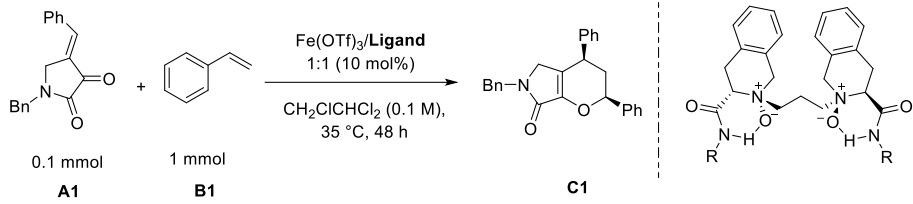
Table S5. Metal salts effect^a

Entry	Metal	Yield (%) ^b	Endo/exo ^c	Ee (%) ^c
1	Ni(OTf) ₂	NR	-	-
2	Zn(OTf) ₂	NR	-	-
3	Cu(OTf) ₂	NR	-	-
4	Fe(OTf) ₃	87	83/17	93/19
5	Sc(OTf) ₃	NR	-	-
6	Y(OTf) ₃	NR	-	-

7	La(OTf) ₃	NR	-	-
8	Al(OTf) ₃	58	67/33	68/-9
9	Bi(OTf) ₃	NR	-	-
10	Ga(OTf) ₃	NR	-	-
11	Fe(OTf) ₂	NR	-	-
12	Fe(ClO ₄) ₃ ·XH ₂ O	88	82/18	93/47
13	In(OTf) ₃	90	73/27	84/50

^aThe reactions were carried out with **A1** (0.1 mmol), **B1** (10 eq, 1.0 mmol) and **L₃-TQEt₂Me**/Metal (1:1, 10 mol %) in CH₂ClCHCl₂ (1.0 mL) at 35 °C for 24 h. ^bYield of isolated product. ^c Determined by chiral SFC.

Table S6. Ligand effect^a

				
Entry	Ligand	Yield (%) ^b	Endo/exo ^c	Ee (%) ^c
1	L₃-TQEt₂Ad	95	90/10	97/72
2	L₃-TQEt₂Br	29	78/22	65/0
3	L₄-TQEt₂Ad	Trace	-	-
4	L₂-TQEt₂Ad	35	78/22	19/22
5	L₃-TQEt₂CHPh₂	80	84/16	84/35
6	L₃-TQEt₂Me	87	83/17	93/19
7 ^d	L₃-TQEt₂Ad	45	89/11	96/68
8	L₃-PrEt₂Ad	44	77/23	39/31
9	L₃-PiEt₂Ad	36	87/13	92/69
10	L₃-RaEt₂Ad	40	92/18	37/37
11	L1	86	73/27	0/0

12	L2	trace	-	-
13	L3	trace	-	-

^aThe reactions were carried out with **A1** (0.1 mmol), **B1** (10 eq, 1.0 mmol) and **Ligand**/Fe(OTf)₃ (1:1, 10 mol %) in CH₂ClCHCl₂ (1.0 mL) at 35 °C for 24 h. ^bYield of isolated product. ^c Determined by chiral SFC. ^dwith 5 mol % Fe(OTf)₃/**L3-TQEt₂Ad** as the catalyst.

Table S7. Effect of the amount of B1

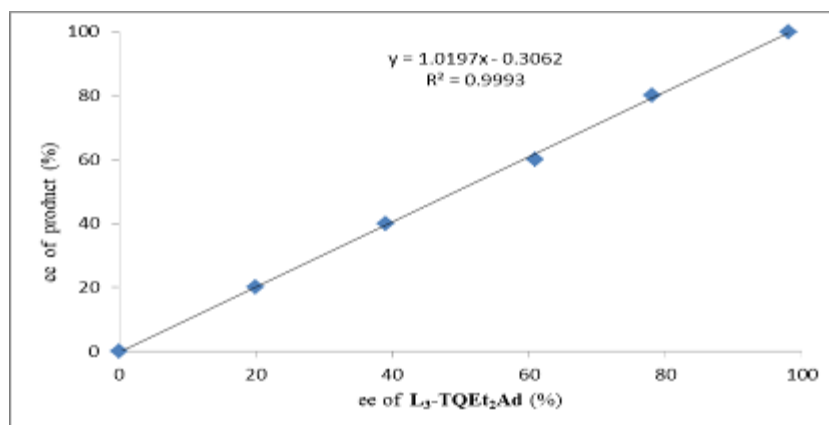
A1 (0.1 mmol) + **B1** (styrene) $\xrightarrow[\text{CH}_2\text{ClCHCl}_2 \text{ (0.1 M), } 35^\circ\text{C, 48 h}]{\text{Fe(OTf)}_3/\text{L}_3\text{-TQEt}_2\text{Ad (1:1, 10 mol\%)}}$ **C1**

R = 2,6-Et₂-4-(1-adamantyl)C₆H₂

Entry	B1 (X eq)	Yield (%) ^b	Endo/exo ^c	Ee (%) ^c
1	1	47	90/10	96/61
2	2	71	90/10	97/68
3	3	74	90/10	96/74
4	5	93	90/10	97/73
5	10	93	90/10	97/73
6 ^d	5	27	85/15	0/0
7 ^e	5	NR	-	-
8 ^f	5	trace	-	-
9 ^g	5	10	77/23	80/68

^aThe reactions were carried out with **A1** (0.1 mmol), **B1** (x eq) and **L3-TQEt₂Ad**/Fe(OTf)₃ (1:1, 10 mol %) in CH₂ClCHCl₂ (1.0 mL) at 35 °C for 48 h. ^bYield of isolated product. ^c Determined by chiral SFC. ^dNo ligand added and Sc(OTf)₃ instead of Fe(OTf)₃. ^e**L3-PiMe₂** instead of **L3-TQEt₂Ad**, Sc(OTf)₃ instead of Fe(OTf)₃. ^f**L3-PrMe₂** instead of **L3-TQEt₂Ad**. ^g**L3-PiMe₂** instead of **L3-TQEt₂Ad**.

7: The relationship of the ee value of product with the optical purity of the chiral ligand



entry	ee of Ligand (%)	ee of product (%)
1	0	0
2	20	20
3	40	39
4	60	61
5	80	78
6	100	98

UV-Vis absorption spectra

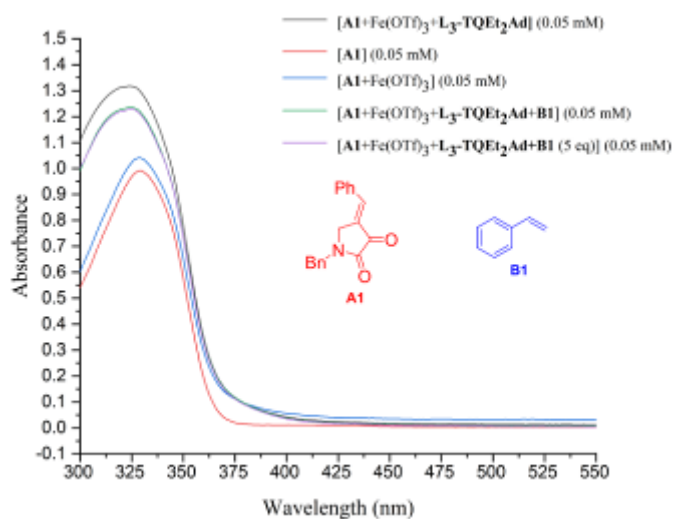


Figure S2. Lewis acid effects on UV-Vis absorption of (E)-1-benzyl-4-benzylidenepyrrolidine-2,3-dione **A1**. All measurements were carried out at ambient temperature at a concentration of 0.05 mM (E)-1-benzyl-4-benzylidenepyrrolidine-2,3-dione **A1** in $\text{CH}_2\text{ClCHCl}_2$. (E)-1-benzyl-4-benzylidenepyrrolidine-2,3-dione **A1** (red), (E)-1-benzyl-4-benzylidenepyrrolidine-2,3-dione **A1** + $\text{Fe}(\text{OTf})_3$ (1:1; blue), (E)-1-benzyl-4-benzylidenepyrrolidine-2,3-dione **A1** + $\text{Fe}(\text{OTf})_3$ + $\text{L}_3\text{-TQEt}_2\text{Ad}$ (1:1:1; black), (E)-1-benzyl-4-benzylidenepyrrolidine-2,3-dione **A1** + $\text{Fe}(\text{OTf})_3$ + $\text{L}_3\text{-TQEt}_2\text{Ad}$ + **B1** (1:1:1:1; green), (E)-1-benzyl-4-benzylidenepyrrolidine-2,3-dione **A1** + $\text{Fe}(\text{OTf})_3$ + $\text{L}_3\text{-TQEt}_2\text{Ad}$ + **B1** (1:1:1:5; pink).

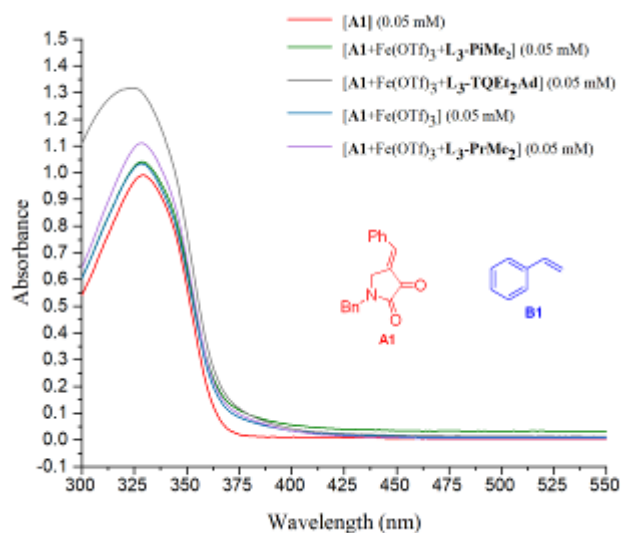


Figure S3. Lewis acid effects on UV-Vis absorption of (E)-1-benzyl-4-benzylidenepyrrolidine-2,3-dione **A1**. All measurements were carried out at ambient temperature at a concentration of 0.05 mM (E)-1-benzyl-4-benzylidenepyrrolidine-2,3-dione **A1** in $\text{CH}_2\text{ClCHCl}_2$. (E)-1-benzyl-4-benzylidenepyrrolidine-2,3-dione **A1** (red), (E)-1-benzyl-4-benzylidenepyrrolidine-2,3-dione **A1** + $\text{Fe}(\text{OTf})_3$ (1:1; blue), (E)-1-benzyl-4-benzylidenepyrrolidine-2,3-dione **A1** + $\text{Fe}(\text{OTf})_3$ + $\text{L}_3\text{-TQEt}_2\text{Ad}$ (1:1:1; black), (E)-1-benzyl-4-benzylidenepyrrolidine-2,3-dione **A1** + $\text{Fe}(\text{OTf})_3$ + $\text{L}_3\text{-PrMe}_2$ (1:1:1:1; pink), (E)-1-benzyl-4-benzylidenepyrrolidine-2,3-dione **A1** + $\text{Fe}(\text{OTf})_3$ + $\text{L}_3\text{-PiMe}_2$ (1:1:1:5; green).

8. Determination of the Absolute Configuration of the products C1, D13 and E1 via the X-ray crystal analysis

The absolute configuration of the optically active product **C1** was Determined to be (2*S*,4*R*) by X-ray crystal analysis.

The single crystal of **C1** was obtained from mixed solvents of CH₂Cl₂ and Hexane CCDC 2282511 contains the supplementary crystallographic data which can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

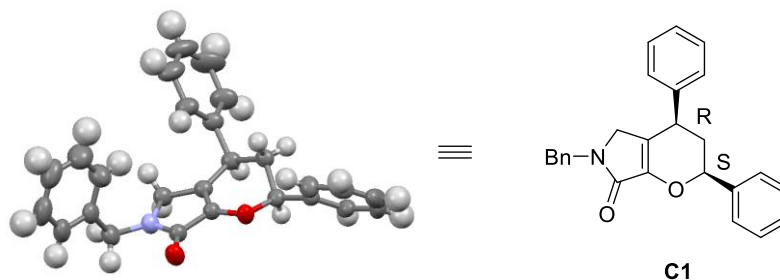


Figure S4. Crystal structure for **C1**

Crystallographic Data for C₂₆H₂₃NO₂.

Formula	C ₂₆ H ₂₃ NO ₂
Formula mass (amu)	381.45
Space group	P 21 21 21
<i>a</i> (Å)	6.0177(1)
<i>b</i> (Å)	14.5243(3)
<i>c</i> (Å)	23.7109(5)
<i>α</i> (deg)	90
<i>β</i> (deg)	90
<i>γ</i> (deg)	90
<i>V</i> (Å ³)	2072.40(7)
<i>Z</i>	4
<i>λ</i> (Å)	1.54178
<i>T</i> (K)	298 K
<i>ρ</i> _{calcd} (g cm ⁻³)	1.223
<i>μ</i> (mm ⁻¹)	0.605
Transmission factors	0.839,0.993
<i>θ</i> _{max} (deg)	68.216
No. of unique data, including <i>F</i> _o ² < 0	3779
No. of unique data, with <i>F</i> _o ² > 2σ(<i>F</i> _o ²)	3550
No. of variables	262

$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ ^a	0.0350
$R_w(F_o^2)$ ^b	0.0824
Goodness of fit	1.044

^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 $p = [\max(F_o^2, 0) + 2F_c^2] / 3$.

The colourless crystal in block-shape, with approximate dimensions of $0.148 \times 0.223 \times 0.249$ mm³, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 298(2)K equipped with micro-focus Cu radiation source ($K_\alpha = 1.54178\text{\AA}$). 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^{a, b, c}.^d The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested^e.

References:

^a Sheldrick, G. M. *Acta Cryst.* **2008**, A64, 112–122.

^b Sheldrick, G. M. *Acta Cryst.* **2015**, A71, 3–8.

^c Sheldrick, G. M. *Acta Cryst.* **2015**, C71, 3–8.

^d Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J. A. K., Puschmann, H. *J. Appl. Cryst.* **2009**, 42, 339–341.

^e Spek, A. L. *J. Appl. Cryst.* **2003**, 36, 7–13.

The absolute configuration of the optically active product **D13** was Determined to be (**2S,4R**) by X-ray crystal analysis.

The single crystal of **D13** was obtained from mixed solvents of CH₂Cl₂ and Hexane CCDC 2282510 contains the supplementary crystallographic data which can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

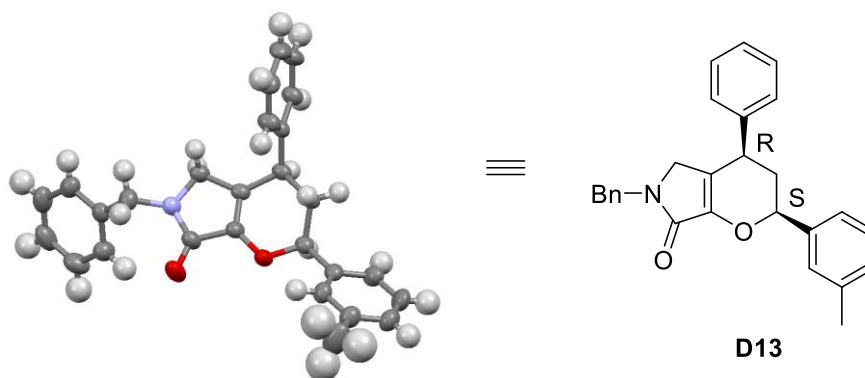


Figure S5. Crystal structure for **D13**

Crystallographic Data for C₂₇H₂₅NO₂.

Formula	C ₂₇ H ₂₅ NO ₂
Formula mass (amu)	395.48
Space group	P 21
<i>a</i> (Å)	10.8789(2)
<i>b</i> (Å)	8.8689(1)
<i>c</i> (Å)	11.6944(2)
<i>α</i> (deg)	90
<i>β</i> (deg)	110.898(1)
<i>γ</i> (deg)	90
<i>V</i> (Å ³)	1054.10(3)
<i>Z</i>	2
<i>λ</i> (Å)	1.54178
<i>T</i> (K)	298 K
ρ_{calcd} (g cm ⁻³)	1.246
μ (mm ⁻¹)	0.612
Transmission factors	0.729,1.000
θ_{max} (deg)	68.323
No. of unique data, including $F_o^2 < 0$	3810
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	3743
No. of variables	273
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ ^a	0.0317
$R_w(F_o^2)$ ^b	0.0842
Goodness of fit	1.039

^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 $p = [\max(F_o^2, 0) + 2F_c^2] / 3$.

The colourless crystal in flake-shape, with approximate dimensions of 0.058 × 0.335 × 0.600 mm³, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 298(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^{a, b, c}. ^d. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested^e.

References:

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

The absolute configuration of the optically active product **E1** was Determined to be (**7R,9S**) by X-ray crystal analysis.

The single crystal of **E1** was obtained from mixed solvents of CH₂Cl₂ and Hexane CCDC 2321465 contains the supplementary crystallographic data which can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

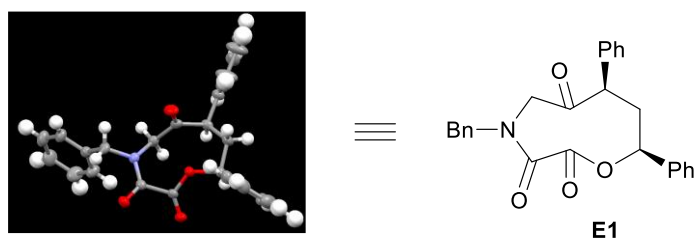


Figure S6. Crystal structure for **E1**

Crystallographic Data for C₂₆H₂₃NO₄.

Formula	C ₂₆ H ₂₃ NO ₄
Formula mass (amu)	413.45
Space group	P 21 21 21
<i>a</i> (Å)	8.7506(2)
<i>b</i> (Å)	9.9990(2)
<i>c</i> (Å)	25.0270(6)
α (deg)	90
β (deg)	90
γ (deg)	90
<i>V</i> (Å ³)	2189.79(8)
<i>Z</i>	4
λ (Å)	1.54178
<i>T</i> (K)	173 K
ρ_{calcd} (g cm ⁻³)	1.254
μ (mm ⁻¹)	0.683
Transmission factors	0.612,0.936

$\theta_{\max}$ (deg)	79.473
No. of unique data, including $F_o^2 < 0$	4660
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	4580
No. of variables	280
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ ^a	0.0364
$R_w(F_o^2)$ ^b	0.0958
Goodness of fit	1.054

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

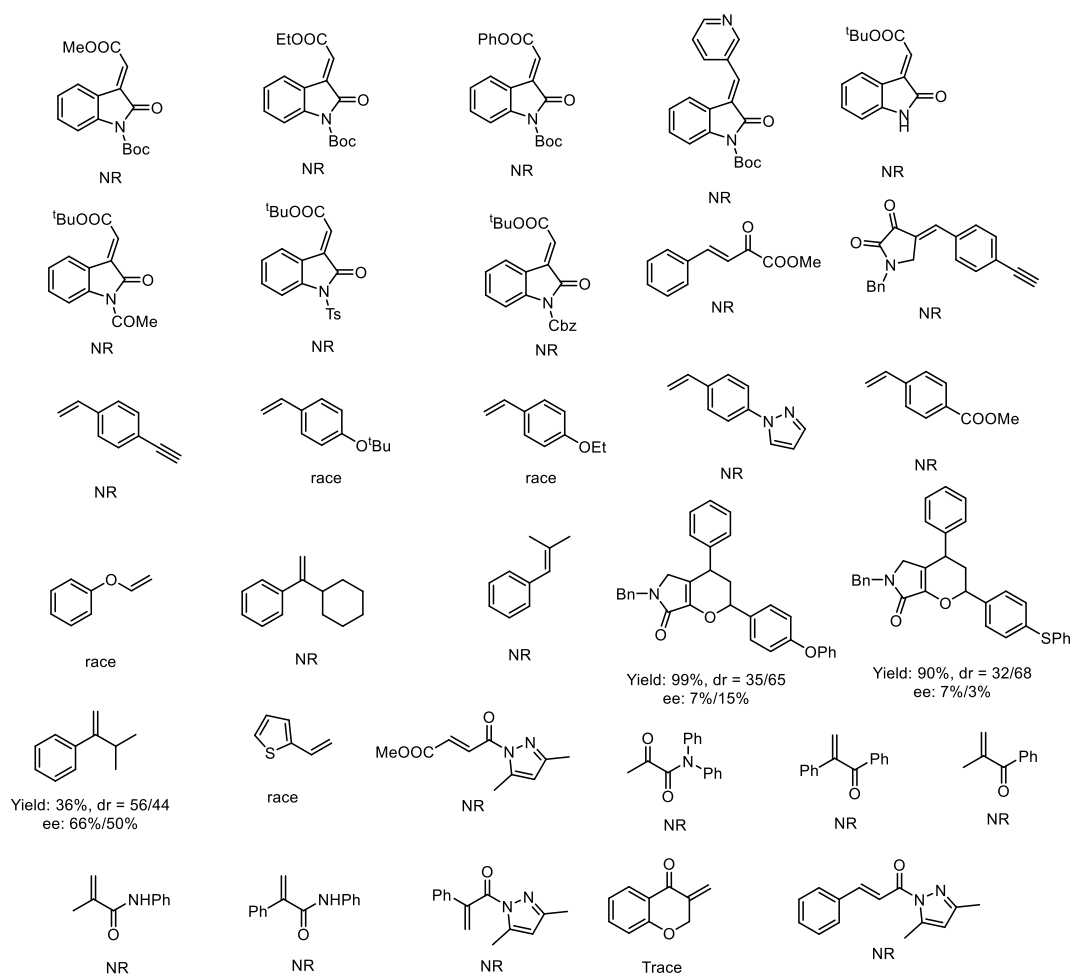
^b $R_w(F_o^2) = [\sum [w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2, 0) + 2F_c^2] / 3$.

The colourless crystal in rod-shape, with approximate dimensions of $0.167 \times 0.185 \times 0.866$ mm³, 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 ($K_\alpha = 1.54178\text{\AA}$). 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^{a, b, c}. ^d The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested^e.

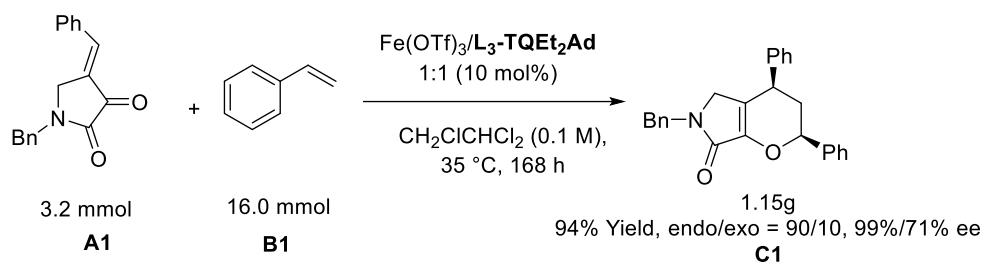
References:

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

9. Substrates Scope Limitation

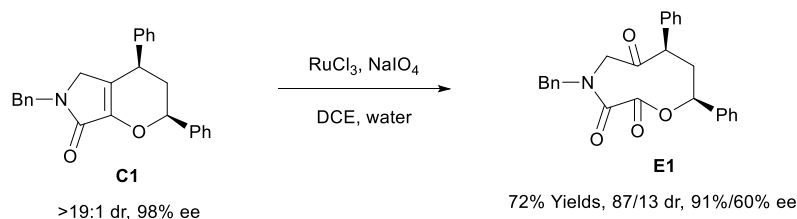


10. Gram-Scale Synthesis and Further Transformation of C1

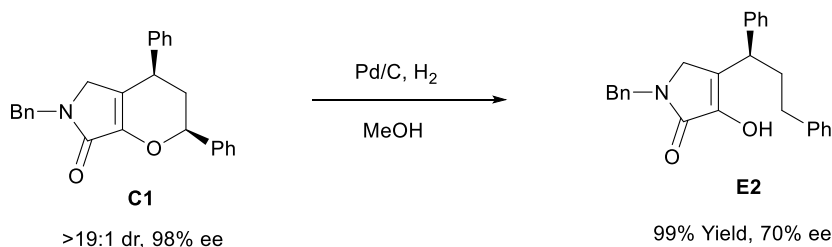


A mixture of (E)-1-benzyl-4-benzylidenepyrrolidine-2,3-dione **A1** (871 mg, 3.2 mmol), $\text{Fe}(\text{OTf})_3$ (160.1 mg, 0.32 mmol, 10 mol %), and *N,N*-dioxide ligand **L3-TQEt₂Ad** (307.2 mg, 0.32 mmol, 10 mol %) was added to a test tube under an inert atmosphere. Anhydrous $\text{CH}_2\text{ClCHCl}_2$ (32.0 mL) was added, and the solution was stirred at 35 °C for 12 h. Subsequently, styrene **B1** (1.84 mL, 16.0 mmol) was added at 35 °C, and the reaction mixture was stirred for an additional 168 h. The product **C1** was purified by flash chromatography (PE/EtOAc = 2:1).

further transformations.



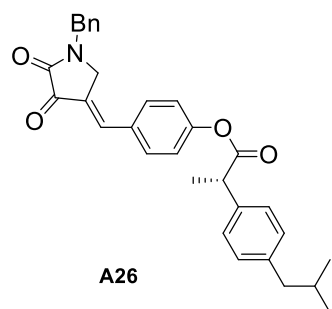
C1 was dissolved in 1,2-dichloroethane (5.50 ml per mmol substrate). Water (4.50 ml per mmol substrate) was added, followed by a solution of RuCl_3 (0.035 M in water, 3.5 mol%). Neat NaIO_4 (2.00 equiv.) was added in one portion, and the resulting biphasic mixture was stirred until the reaction was judged complete by TLC analysis of a reaction aliquot (quenched with satd aq $\text{Na}_2\text{S}_2\text{O}_3$, extracted with EtOAc). Satd aqueous $\text{Na}_2\text{S}_2\text{O}_3$ was added, and the resulting mixture was stirred for 10 min and then extracted with CH_2Cl_2 . The combined organic extracts were washed with water and then brine, and then they were dried (MgSO_4) and the solvents were removed by rotary evaporation. Purification by silica flash chromatography (PE:EA = 3:1).



C1 (38.1 mg, 0.10 mmol) and Pd/C (100 g%, 34.9 mg) were added into a dry reaction tube, and then methanol (2.0 mL) was added; the mixture was stirred under H_2 at 0 °C for 24 h, which could be monitored by TLC. Upon completion of the reaction, Pd/C was removed by suction filtration, and the solvent was evaporated off under reduced pressure; the crude material was purified by silica gel chromatography to give the compound **E2** (99% yield, 70% ee) as a colorless oil.

11. Characterization of the substrates

A26: (E)-4-((1-benzyl-4,5-dioxopyrrolidin-3-ylidene)methyl) phenyl (S)-2-(4-isobutylphenyl) propanoate



Yellow solid, m.p. 120–122 °C.

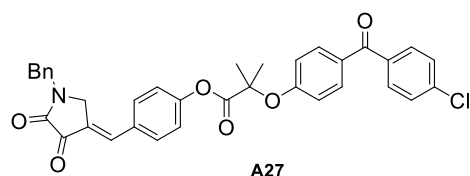
¹H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 2.0 Hz, 1H), 7.42 – 7.31 (m, 7H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 4.79 (s, 2H), 4.36 (d, *J* = 1.8 Hz, 2H), 3.94 (q, *J* = 7.2 Hz, 1H), 2.47 (d, *J* = 7.2 Hz, 2H), 1.90 – 1.82 (m, 1H), 1.60 (d, *J* = 7.2 Hz, 3H), 0.91 (d, *J* = 6.6 Hz, 6H) ppm.

¹³C NMR (101 MHz, CDCl₃) δ 186.4, 172.8, 160.5, 153.2, 141.1, 137.1, 136.8, 134.6, 132.5, 130.9, 129.6, 129.4, 129.2, 128.6, 128.5, 127.2, 124.6, 122.6, 48.1, 46.3, 45.3, 45.0, 30.2, 22.4, 18.4 ppm.

ESI-HRMS calcd for [C₃₁H₃₁NO₄+Na⁺] = 504.2145, found 504.2137.

IR $\tilde{\nu}$ (cm⁻¹) 2954, 2360, 1755, 1709, 1630, 1596, 1506, 1454, 1419, 1281, 1210, 1155, 1067, 894, 738, 529.

A27: (E)-4-((1-benzyl-4,5-dioxopyrrolidin-3-ylidene)methyl) phenyl 2-(4-(4-chlorobenzoyl) phenoxy)-2-methylpropanoate



Yellow solid, m.p. 160–163 °C.

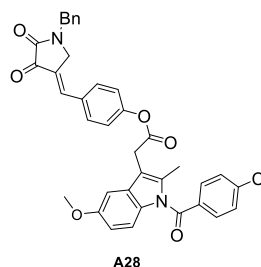
¹H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.8 Hz, 2H), 7.71 (d, *J* = 8.8 Hz, 2H), 7.64 (m, 1H), 7.50 – 7.40 (m, 4H), 7.39 – 7.31 (m, 5H), 7.09 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 4.80 (s, 2H), 4.46 – 4.20 (m, 2H), 1.83 (s, 6H) ppm.

¹³C NMR (101 MHz, CDCl₃) δ 194.2, 186.4, 172.1, 160.4, 159.4, 152.5, 138.6, 136.7, 136.2, 134.5, 132.6, 132.2, 131.5, 131.2, 130.8, 129.2, 128.8, 128.7, 128.6, 128.5, 127.9, 124.9, 122.4, 117.2, 79.4, 48.1, 46.3, 25.4 ppm.

ESI-HRMS calcd for [C₃₅H₂₈ClNO₆+Na⁺] = 616.1497, found 616.1493.

IR $\tilde{\nu}$ (cm⁻¹) 2360, 1757, 1712, 1632, 1596, 1504, 1275, 1250, 1157, 1110, 927, 852, 762, 701, 531.

A28: (E)-4-((1-benzyl-4,5-dioxopyrrolidin-3-ylidene)methyl)phenyl 2-(1-(4-chlorobenzoyl)-2-methyl-1H-indol-3-yl)acetate



Yellow solid, m.p. 125–128 °C.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.62 (s, 1H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.41 – 7.39 (m, 2H), 7.38 – 7.35 (m, 2H), 7.34 – 7.32 (m, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 2.8 Hz, 1H), 6.88 (s, 1H), 6.69 (dd, *J* = 9.0, 2.8 Hz, 1H), 4.78 (s, 2H), 4.35 (d, *J* = 1.8 Hz, 2H), 3.92 (s, 2H), 3.82 (s, 3H), 2.45 (s, 3H) ppm.

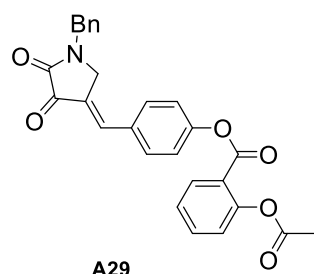
¹³C NMR (151 MHz, CDCl₃) δ 186.4, 168.8, 168.3, 160.5, 156.1, 152.9, 139.5, 136.9, 136.4, 134.5, 133.7, 132.5, 131.2, 131.1, 130.8, 130.4, 129.2, 129.1, 128.5, 128.4, 124.7,

122.6, 115.1, 111.7, 111.5, 101.2, 60.4, 55.8, 48.1, 46.3, 30.6, 14.2, 13.5 ppm.

ESI-HRMS calcd for $[C_{37}H_{29}ClN_2O_6+Na^+]$ = 655.1606, found 655.1609.

IR $\tilde{\nu}$ (cm^{-1}) 2360, 1756, 1711, 1629, 1596, 1504, 1476, 1357, 1320, 1213, 1155, 926, 834, 754, 701.

A29: (E)-4-((1-benzyl-4,5-dioxopyrrolidin-3-ylidene)methyl)phenyl 2-acetoxybenzoate



A29

Yellow solid, m.p. 130–133 °C.

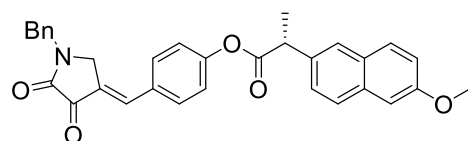
1H NMR (400 MHz, Chloroform-*d*) δ 8.19 (d, J = 7.6 Hz, 1H), 7.66 (d, J = 12.0 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 14.0 Hz, 6H), 7.27 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.4 Hz, 1H), 4.79 (s, 2H), 4.41 (s, 2H), 2.29 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 186.5, 169.7, 162.4, 160.5, 152.8, 151.3, 136.9, 135.1, 134.6, 132.7, 132.2, 131.3, 129.2, 128.6, 128.4, 126.4, 124.9, 124.2, 122.9, 121.9, 48.0, 46.3, 21.0 ppm.

ESI-HRMS calcd for $[C_{27}H_{21}NO_6+Na^+]$ = 478.1261, found 478.1255.

IR $\tilde{\nu}$ (cm^{-1}) 2360, 1756, 1710, 1711, 1629, 1597, 1506, 1452, 1368, 1284, 1207, 1156, 916, 750, 700, 529.

A30: (E)-4-((1-benzyl-4,5-dioxopyrrolidin-3-ylidene)methyl)phenyl (R)-2-(6-methoxynaphthalen-2-yl)propanoate



A30

Yellow solid, m.p. 149–152 °C.

1H NMR (400 MHz, Chloroform-*d*) δ 7.73 (t, J = 9.8 Hz, 3H), 7.61 (m, 1H), 7.46 (dd, J = 8.6, 1.6 Hz, 1H), 7.39 – 7.29 (m, 7H), 7.18 – 7.12 (m, 2H), 7.10 – 7.03 (m, 2H), 4.77 (s, 2H), 4.32 (d, J = 1.8 Hz, 2H), 4.09 (q, J = 7.2 Hz,

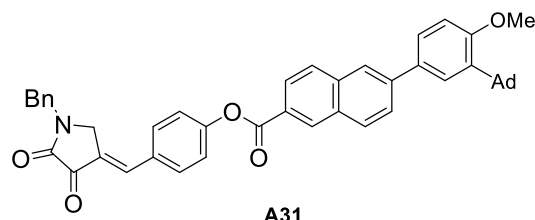
1H), 3.92 (s, 3H), 1.68 (d, J = 7.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 186.4, 172.7, 160.5, 157.9, 153.2, 137.1, 134.6, 134.6, 133.9, 132.5, 130.9, 129.3, 129.2, 128.9, 128.5, 128.4, 127.5, 126.2, 125.9, 124.6, 122.6, 119.3, 105.6, 55.4, 48.1, 46.3, 45.6, 18.4 ppm.

ESI-HRMS calcd for $[C_{32}H_{27}NO_5+Na^+]$ = 528.1781, found 528.1776.

IR $\tilde{\nu}$ (cm^{-1}) 2936, 2360, 1754, 1711, 1630, 1599, 1505, 1454, 1213, 1156, 1069, 892, 747, 701, 529.

A31: 4-((E)-((1-benzyl-4,5-dioxopyrrolidin-3-ylidene)methyl)phenyl 6-(3-((3s)-adamantan-1-yl)-4-methoxyphenyl)-2-naphthoate



A31

Yellow solid, m.p. 270–273 °C.

1H NMR (400 MHz, Chloroform-*d*) δ 8.77 (s, 1H), 8.21 – 8.13 (m, 1H), 8.07 – 7.98 (m, 3H), 7.87 – 7.83 (m, 1H), 7.73 (s, 1H), 7.62 (d, J = 2.0 Hz, 1H), 7.57 (dd, J = 8.4, 2.0 Hz, 1H), 7.53 (d, J = 8.4 Hz, 2H), 7.41 – 7.39 (m, 2H), 7.37 (d, J = 6.8 Hz, 3H),

7.31 (dd, J = 13.0, 7.8 Hz, 2H), 7.02 (d, J = 8.4 Hz, 1H), 4.83 (s, 2H), 4.44 (s, 2H), 3.92 (s, 3H), 2.19 (m, 5H), 2.11 (m, 3H), 1.81 (m, 5H), 1.59 (m, 2H) ppm.

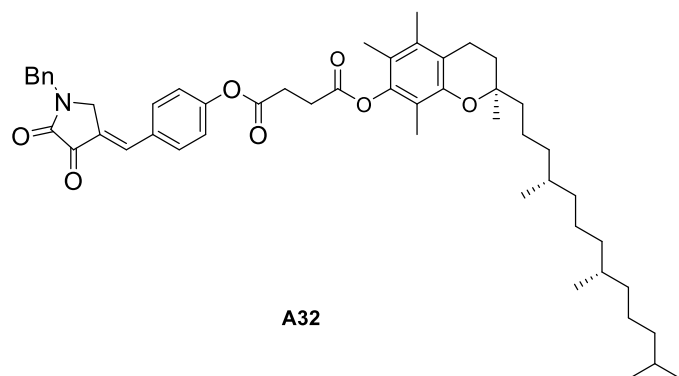
^{13}C NMR (101 MHz, $CDCl_3$) δ 186.0, 164.9, 159.1, 139.1, 137.2, 134.6, 132.7, 132.3, 132.0, 131.2,

129.9, 129.2, 128.9, 128.7, 128.6, 127.9, 126.9, 126.0, 125.8, 125.7, 124.8, 124.6, 123.0, 112.1, 55.2, 48.2, 46.4, 40.6, 37.2, 37.1, 29.7, 29.1 ppm.

ESI-HRMS calcd for $[C_{46}H_{41}NO_5+Na^+]$ = 710.2877, found 710.2879.

IR $\tilde{\nu}$ (cm⁻¹) 2902, 2361, 1726, 1708, 1627, 1596, 1505, 1472, 1277, 1205, 1156, 1058, 883, 810, 741, 700, 529.

A32: 4-((E)-(1-benzyl-4,5-dioxopyrrolidin-3-ylidene)methyl)phenyl ((R)-2,5,6,8-tetramethyl-2-((4S,8S)-4,8,12-trimethyltridecyl)chroman-7-yl) succinate



yellow liquid.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.65 (s, 1H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.40 – 7.36 (m, 2H), 7.34 (d, *J* = 7.2 Hz, 3H), 7.19 (d, *J* = 8.4 Hz, 2H), 4.80 (s, 2H), 4.38 (s, 2H), 3.11 – 2.98 (m, 4H), 2.58 (t, *J* = 5.4 Hz, 2H), 2.08 (d, *J* = 3.6 Hz, 3H), 2.00 (s, 3H), 1.96 (s, 3H), 1.83 – 1.79 (m, 1H), 1.77 – 1.72 (m, 1H), 1.53 (dq, *J* =

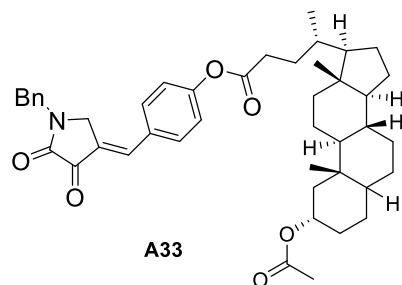
13.2, 6.8 Hz, 4H), 1.46 – 1.42 (m, 1H), 1.40 – 1.36 (m, 3H), 1.30 – 1.23 (m, 10H), 1.15 – 1.11 (m, 3H), 1.09 – 1.05 (m, 3H), 0.86 (dd, *J* = 11.8, 6.6 Hz, 12H) ppm.

¹³C NMR (151 MHz, CDCl₃) δ 186.4, 170.9, 170.5, 160.6, 152.9, 149.6, 140.4, 137.1, 134.6, 132.6, 131.1, 129.2, 128.6, 128.5, 126.6, 124.9, 124.8, 124.7, 123.2, 123.1, 122.7, 117.5, 75.1, 48.1, 46.3, 39.4, 37.5, 37.5, 37.3, 32.8, 32.7, 29.3, 28.7, 28.0, 24.8, 24.5, 22.8, 22.7, 21.1, 20.6, 19.8, 19.7, 13.0, 12.2, 11.9 ppm.

ESI-HRMS calcd for $[C_{51}H_{67}NO_7+Na^+]$ = 828.4810, found 828.4800.

IR $\tilde{\nu}$ (cm⁻¹) 2925, 2360, 1752, 1712, 1630, 1596, 1506, 1456, 1361, 1205, 1155, 1126, 927, 736, 701, 528.

A33: 4-((E)-(1-benzyl-4,5-dioxopyrrolidin-3-ylidene)methyl)phenyl (4S)-4-((2S,8R,9S,10S,13R,14S,17R)-2-acetoxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate



yellow liquid.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.67 (s, 1H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.39 – 7.33 (m, 4H), 7.30 – 7.26 (m, 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 4.81 (s, 2H), 4.72 (dt, *J* = 10.8, 6.4 Hz, 1H), 4.39 (s, 2H), 2.62 (ddd, *J* = 14.0, 9.2, 4.0 Hz, 1H), 2.49 (dt, *J* = 15.6, 7.8 Hz, 1H), 2.28 (m, 1H), 2.03 (s, 5H), 1.85 (m, 5H), 1.69 (d, *J* = 9.4 Hz, 2H), 1.61 – 1.51 (m, 3H), 1.47 – 1.37 (m,

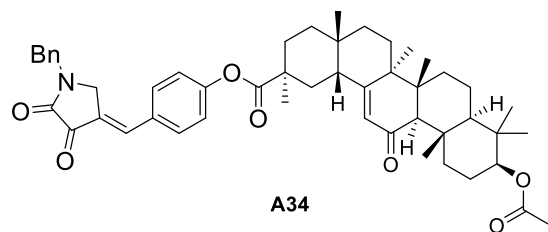
8H), 1.33 – 1.22 (m, 5H), 1.10 (m, 6H), 0.98 (d, *J* = 5.8 Hz, 3H), 0.93 (s, 3H), 0.86 (d, *J* = 7.0 Hz, 1H), 0.67 (m, 4H) ppm.

¹³C NMR (101 MHz, CDCl₃) δ 186.4, 172.2, 170.6, 160.5, 153.1, 137.1, 134.6, 132.5, 130.9, 129.2, 128.8, 128.5, 128.4, 127.9, 124.6, 122.7, 74.4, 56.5, 56.0, 48.1, 46.3, 42.8, 41.9, 40.4, 40.2, 35.8, 35.4, 35.1, 34.6, 32.3, 31.4, 30.9, 28.3, 27.0, 26.7, 26.3, 24.2, 23.3, 21.5, 20.9, 18.3, 12.1 ppm.

ESI-HRMS calcd for $[C_{44}H_{55}NO_6+Na^+]$ = 716.3922, found 716.3925.

IR $\tilde{\nu}$ (cm⁻¹) 2931, 2360, 1758, 1714, 1630, 1597, 1506, 1453, 1361, 1241, 1155, 1116, 829, 733, 700, 528.

A34: 4-((E)-(1-benzyl-4,5-dioxopyrrolidin-3-ylidene)methyl)phenyl (2S,4aS,6aS,6bR,8aR,10S,12aS,12bR,14bR)-10-acetoxy-2,4a,6a,6b,9,9,12a-heptamethyl-13-oxo-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-icosahydricene-2-carboxylate



Yellow solid, m.p. 253–256 °C.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.69 (s, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.37 (q, *J* = 7.2, 6.4 Hz, 5H), 7.15 (d, *J* = 8.4 Hz, 2H), 5.65 (s, 1H), 4.82 (s, 2H), 4.54 – 4.49 (m, 1H), 4.40 (s, 2H), 2.78 (d, *J* = 13.6 Hz, 1H), 2.37 (s, 1H), 2.23 –

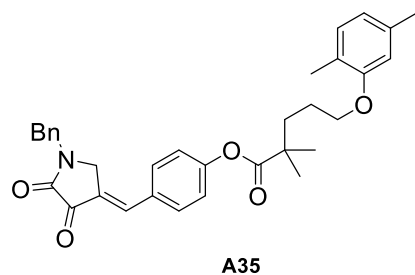
2.16 (m, 1H), 2.06 (s, 6H), 1.86 (dt, *J* = 14.8, 7.4 Hz, 1H), 1.79 (d, *J* = 13.6 Hz, 1H), 1.73 – 1.57 (m, 6H), 1.52 – 1.43 (m, 4H), 1.40 (d, *J* = 7.4 Hz, 3H), 1.35 (s, 3H), 1.27 – 1.21 (m, 1H), 1.15 (d, *J* = 10.2 Hz, 6H), 1.07 (d, *J* = 13.6 Hz, 2H), 0.87 (m, 10H) ppm.

¹³C NMR (101 MHz, CDCl₃) δ 200.1, 186.4, 174.6, 171.1, 168.8, 160.5, 153.1, 137.1, 134.5, 132.6, 131.0, 129.2, 128.7, 128.6, 128.5, 124.7, 122.7, 80.6, 61.8, 55.0, 48.7, 48.1, 46.3, 45.5, 44.5, 43.2, 41.1, 38.77, 38.1, 37.7, 36.9, 32.7, 31.9, 31.1, 28.6, 28.1, 28.0, 26.5, 26.4, 23.6, 23.4, 21.4, 18.7, 17.4, 16.7, 16.4 ppm.

ESI-HRMS calcd for [C₅₀H₆₁NO₇+Na⁺] = 810.4340, found 810.4345.

IR $\tilde{\nu}$ (cm⁻¹) 2947, 2360, 1725, 1656, 1631, 1597, 1507, 1455, 1247, 1205, 1156, 1120, 1069, 985, 750, 700, 531.

A35: (E)-4-((1-benzyl-4,5-dioxopyrrolidin-3-ylidene)methyl)phenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate



yellow liquid.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.65 (s, 1H), 7.50 – 7.27 (m, 7H), 7.11 (d, *J* = 8.4 Hz, 2H), 7.00 (m, 1H), 6.64 (d, *J* = 18.6 Hz, 2H), 4.80 (s, 2H), 4.37 (s, 2H), 3.98 (d, *J* = 5.2 Hz, 2H), 2.29 (s, 3H), 2.15 (s, 3H), 1.87 (s, 4H), 1.37 (s, 6H) ppm.

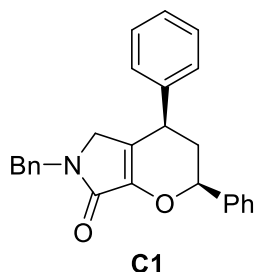
¹³C NMR (101 MHz, CDCl₃) δ 186.4, 175.9, 160.5, 156.8, 153.4, 137.1, 136.6, 134.6, 132.5, 130.9, 130.4, 129.2, 128.6, 128.5, 124.6, 123.6, 122.8, 120.8, 111.9, 67.6, 48.1, 46.3, 42.6, 37.1, 25.3, 25.1, 21.5, 15.9 ppm.

ESI-HRMS calcd for [C₃₃H₃₅NO₅+Na⁺] = 548.2407, found 548.2400.

IR $\tilde{\nu}$ (cm⁻¹) 2923, 2360, 1749, 1709, 1630, 1596, 1507, 1417, 1264, 1210, 1155, 1103, 1046, 806, 701, 531.

12. Characterization of the products

C1: (2S,4R)-6-benzyl-2,4-diphenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



C1: 93% yield, endo/exo = 90/10, 97%/73% ee; Colorless liquid, $[\alpha]^{25}_D = -38.2$ ($c = 1.43$, in CH_2Cl_2).

SFC Chiralcel OD-3, $\text{CO}_2/\text{MeOH}=80/20$. 1.5mL/ min, $\lambda = 210$ nm, retention time: $t_1 = 6.06$ min, $t_2 = 6.47$ min, $t_3 = 7.96$ min, $t_4 = 8.36$ min.

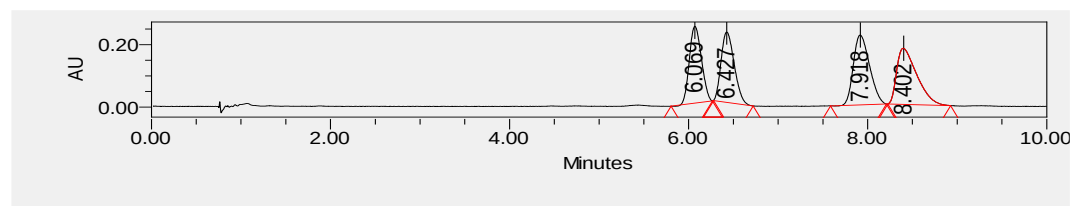
^1H NMR (400 MHz, CHCl_3) δ 7.43 (d, $J = 7.0$ Hz, 2H), 7.35 – 7.31 (m, 2H), 7.28 (ddd, $J = 7.0, 5.2, 1.4$ Hz, 4H), 7.25 – 7.17 (m, 5H), 7.13 (t, $J = 8.8$ Hz, 2H), 5.14 (d, $J = 10.4$ Hz, 1H), 4.81 (d, $J = 15.0$ Hz, 1H), 4.38 (d, $J = 15.0$ Hz, 1H), 3.89 (dd, $J = 10.4, 6.0$ Hz, 1H), 3.66 – 3.31 (m, 2H), 2.50 – 2.33 (m, 1H), 2.21 – 2.05 (m, 1H) ppm.

Endo C1: ^{13}C NMR (101 MHz, CDCl_3) δ 165.5, 146.8, 141.3, 139.7, 137.1, 129.0, 128.8, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.4, 123.6, 80.2, 47.4, 46.5, 40.8, 39.9 ppm.

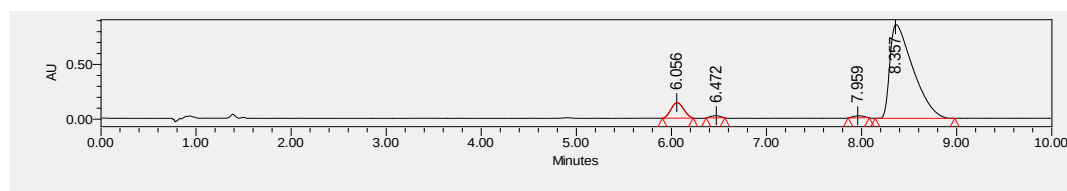
Exo C1: ^{13}C NMR (101 MHz, CDCl_3) δ 165.5, 146.7, 143.0, 139.7, 137.1, 129.0, 128.8, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.6, 127.4, 121.1, 75.6, 48.1, 46.6, 38.5, 36.9 ppm.

ESI-HRMS calcd for $[\text{C}_{26}\text{H}_{23}\text{NO}_2 + \text{Na}^+] = 404.1621$, found 404.1615.

IR $\tilde{\nu}$ (cm^{-1}) 3029, 2360, 1692, 1493, 1452, 1392, 1240, 1110, 1046, 819, 750, 698.

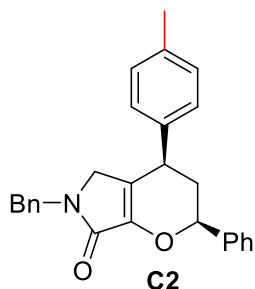


	Retention Time	Area	% Area	Height
1	6.069	2322936	22.67	245945
2	6.427	2298450	22.43	225047
3	7.918	2824562	27.57	224047
4	8.402	2799670	27.33	179727



	Retention Time	Area	% Area	Height
1	6.056	1313189	8.18	142147
2	6.472	142823	0.89	20187
3	7.959	152804	0.95	19302
4	8.357	14449795	89.98	856322

C2: (2S,4R)-6-benzyl-2-phenyl-4-(p-tolyl)-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



C2: 98% yield, endo/exo = 91/9, 98%/75% ee; Colorless liquid, $[\alpha]_D^{24} = -39.0$ ($c = 0.70$, in CH_2Cl_2).

HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, $\lambda = 210$ nm), $t_1 = 11.04$ min, $t_2 = 12.53$ min, $t_3 = 13.39$ min, $t_4 = 27.79$ min.

^1H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.25 (m, 8H), 7.24 – 7.17 (m, 2H), 7.10 (d, $J = 7.7$ Hz, 2H), 7.02 (d, $J = 7.8$ Hz, 2H), 5.21 – 5.06 (m, 1H), 4.83 (d, $J = 15.0$ Hz, 1H), 4.53 – 4.35 (d, $J = 15.0$ Hz, 1H), 3.87 (dd, $J = 11.0$, 6.0 Hz, 1H), 3.63 – 3.33 (m, 2H), 2.41 (m, 1H), 2.32 (s, 3H), 2.14 (m, 1H)

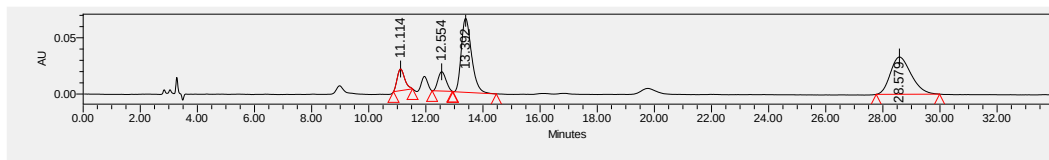
ppm.

Endo C2: ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.4, 146.7, 139.7, 138.2, 137.2, 137.0, 129.6, 128.7, 128.4, 128.2, 128.1, 127.7, 127.6, 127.4, 126.4, 123.7, 80.3, 47.3, 46.5, 40.8, 39.6, 21.6 ppm.

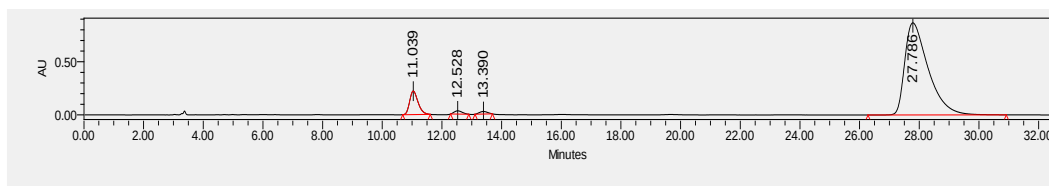
Exo C2: ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.4, 146.6, 139.8, 138.2, 137.1, 136.9, 129.6, 128.7, 128.4, 128.2, 128.0, 127.6, 127.5, 127.4, 126.2, 122.4, 75.6, 48.0, 46.6, 38.6, 36.5, 22.7 ppm.

ESI-HRMS calcd for $[\text{C}_{27}\text{H}_{25}\text{NO}_2 + \text{Na}^+] = 418.1778$, found 418.1780.

IR $\tilde{\nu}$ (cm^{-1}) 3029, 2360, 1692, 1512, 1453, 1240, 1107, 1047, 819, 735, 699.

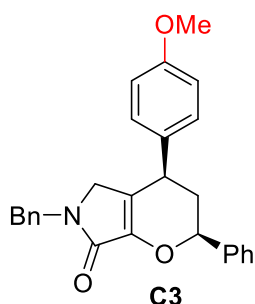


	Retention Time	Area	% Area	Height
1	11.114	348931	8.75	19230
2	12.554	335564	8.41	17197
3	13.392	1637633	41.06	65774
4	28.579	1666476	41.78	33121



	Retention Time	Area	% Area	Height
1	11.039	4334738	8.25	221336
2	12.528	573525	1.09	30511
3	13.390	459405	0.87	23937
4	27.786	47177138	89.78	866100

C3: (2S,4R)-6-benzyl-4-(4-methoxyphenyl)-2-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



C3: 96% yield, endo/exo = 95/5, 99%/83% ee; Colorless liquid, $[\alpha]_D^{24} = -44.9$ ($c = 0.76$, in CH_2Cl_2).

SFC Chiralcel OD-3, $\text{CO}_2/\text{MeOH}=80/20$. 1.5mL/ min, $\lambda = 210$ nm, retention time: $t_1 = 7.29$ min, $t_2 = 9.93$ min, $t_3 = 10.43$ min, $t_4 = 14.38$ min.

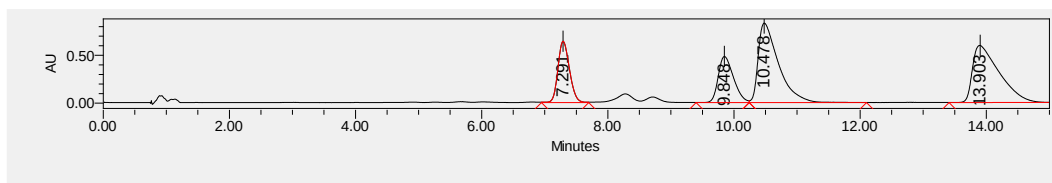
^1H NMR (400 MHz, Chloroform- d) δ 7.53 – 7.25 (m, 8H), 7.24 – 7.16 (m, 2H), 7.05 (d, $J = 8.6$ Hz, 2H), 6.82 (d, $J = 8.6$ Hz, 2H), 5.15 (d, $J = 10.4$ Hz, 1H), 4.83 (d, $J = 15.0$ Hz, 1H), 4.39 (d, $J = 15.0$ Hz, 1H), 3.86 (dd, $J = 10.8$, 6.0 Hz, 1H), 3.77 (s, 3H), 3.62 – 3.34 (m, 2H), 2.40 (ddd, $J = 14.0$, 6.0, 1.6

Hz, 1H), 2.12 (dt, $J = 14.0$, 11.2 Hz, 1H) ppm.

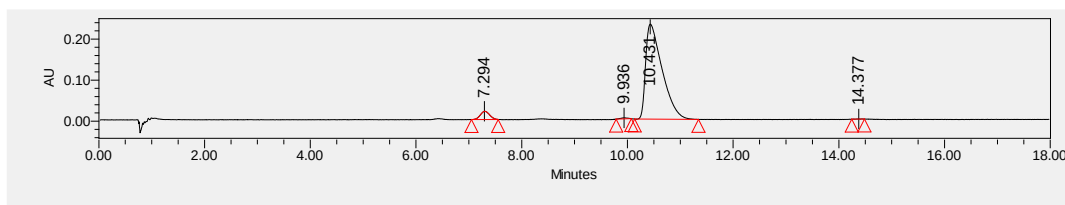
^{13}C NMR (101 MHz, Chloroform- d) δ 158.8, 146.6, 139.7, 137.2, 133.1, 128.7, 128.5, 128.4, 128.2, 128.1, 127.6, 126.4, 123.9, 114.3, 80.3, 55.3, 47.3, 46.5, 40.9, 39.2 ppm.

ESI-HRMS calcd for $[\text{C}_{27}\text{H}_{25}\text{NO}_3 + \text{Na}^+] = 434.1727$, found 434.1731.

IR $\tilde{\nu}$ (cm^{-1}) 3029, 2360, 1695, 1487, 1453, 1241, 1107, 1047, 841, 732, 697.

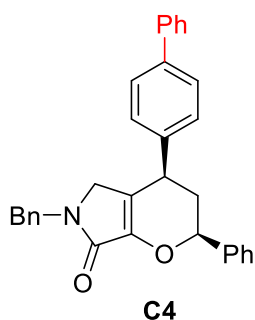


	Retention Time	Area	% Area	Height
1	7.291	8161881	15.58	640184
2	9.848	8118697	15.50	482410
3	10.478	18559778	35.44	830957
4	13.903	17532734	33.48	596689



	Retention Time	Area	% Area	Height
1	7.294	242434	4.60	20021
2	9.936	22646	0.43	2526
3	10.431	5000435	94.93	231332
4	14.377	2058	0.04	512

C4: (2S,4R)-4-([1,1'-biphenyl]-4-yl)-6-benzyl-2-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



C4: 95% yield, endo/exo = 94/6, 99%/84% ee; Colorless liquid, $[\alpha]_D^{24} = -34.1$ ($c = 0.73$, in CH_2Cl_2).

HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/ min, $\lambda = 210$ nm), $t_1 = 46.60$ min, $t_2 = 51.85$ min, $t_3 = 65.73$ min, $t_4 = 70.14$ min.

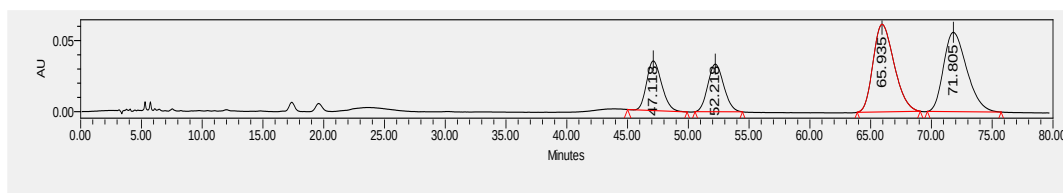
^1H NMR (400 MHz, Chloroform-*d*) δ 7.69 – 7.48 (m, 4H), 7.48 – 7.37 (m, 4H), 7.31 (ddd, $J = 21.0, 10.8, 4.6$ Hz, 6H), 7.25 – 7.17 (m, 5H), 5.17 (d, $J = 10.6$ Hz, 1H), 4.84 (d, $J = 15.0$ Hz, 1H), 4.41 (d, $J = 15.0$ Hz, 1H), 3.95 (dd, $J = 10.8, 6.0$ Hz, 1H), 3.53 (q, $J = 18.2$ Hz, 2H), 2.46 (ddd, $J = 14.0, 6.0, 1.6$ Hz, 1H), 2.19 (dt, $J = 14.0, 11.2$ Hz, 1H) ppm.

Endo C4: ^{13}C NMR (101 MHz, CDCl_3) δ 165.4, 146.9, 140.1, 140.3, 140.3, 139.6, 137.2, 128.9, 128.8, 128.8, 128.5, 128.3, 128.1, 128.0, 127.8, 127.7, 127.6, 127.5, 127.0, 126.4, 123.3, 80.2, 47.4, 46.5, 40.8, 39.7 ppm.

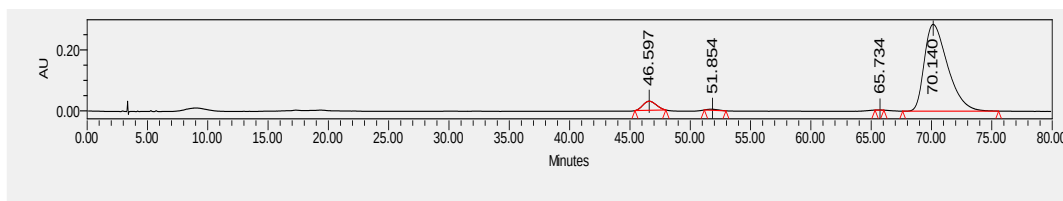
Exo C4: ^{13}C NMR (101 MHz, CDCl_3) δ 165.4, 146.9, 140.1, 140.3, 140.3, 139.7, 137.1, 128.9, 128.8, 128.8, 128.5, 128.3, 128.1, 128.0, 127.8, 127.7, 127.6, 127.5, 127.0, 126.2, 120.8, 75.6, 48.0, 46.6, 38.5, 36.6 ppm.

ESI-HRMS calcd for $[\text{C}_{32}\text{H}_{27}\text{NO}_2 + \text{Na}^+] = 480.1934$, found 480.1944.

IR $\tilde{\nu}$ (cm^{-1}) 3029, 2360, 1694, 1487, 1453, 1240, 1107, 1047, 855, 732, 697.

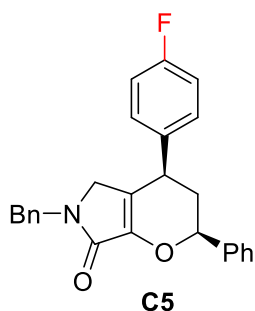


	Retention Time	Area	% Area	Height
1	47.118	3003749	14.38	34900
2	52.218	3053605	14.62	33476
3	65.935	7422314	35.54	61586
4	71.805	7402002	35.45	55756



	Retention Time	Area	% Area	Height
1	46.597	2289433	5.61	29835
2	51.854	207866	0.51	3443
3	65.734	12448	0.03	438
4	70.140	38291778	93.85	284705

C5: (2S,4R)-6-benzyl-4-(4-fluorophenyl)-2-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



C5: 98% yield, endo/exo = 92/8, 96%/69% ee; Colorless liquid, $[\alpha]_D^{24} = -38.9$ ($c = 0.66$, in CH_2Cl_2).

SFC Chiralcel OD-3, $\text{CO}_2/\text{MeOH}=80/20$. 1.5mL/ min, $\lambda = 210$ nm, retention time: $t_1 = 5.06$ min, $t_2 = 5.68$ min, $t_3 = 6.26$ min, $t_4 = 8.02$ min.

^1H NMR (400 MHz, Chloroform- d) δ 7.53 – 7.26 (m, 8H), 7.25 – 7.18 (m, 2H), 7.17 – 7.07 (m, 2H), 7.06 – 6.93 (m, 2H), 5.23 – 5.04 (d, $J = 12.0$ Hz, 1H), 4.83 (d, $J = 15.0$ Hz, 1H), 4.52 – 4.36 (d, $J = 15.0$ Hz, 1H), 3.91 (dd, $J = 10.8, 6.0$ Hz, 1H), 3.66 – 3.35 (m, 2H), 2.42 (ddd, $J = 14.0, 6.1, 1.8$ Hz, 1H), 2.11 (dt, $J = 14.0, 11.2$ Hz, 1H) ppm.

Endo C5: ^{13}C NMR (101 MHz, Chloroform- d) δ 165.3, 160.7(d, $J_{\text{C-F}} = 246.0$), 146.9, 139.5, 137.1, 136.9, 129.3(d, $J_{\text{C-F}} = 8.0$), 129.1, 129.0, 128.8, 128.5, 128.2, 128.1, 127.9, 127.6, 126.3, 123.0, 116.0, 115.8(d, $J_{\text{C-F}} = 21.0$), 80.2, 47.2, 46.5, 40.9, 39.3 ppm.

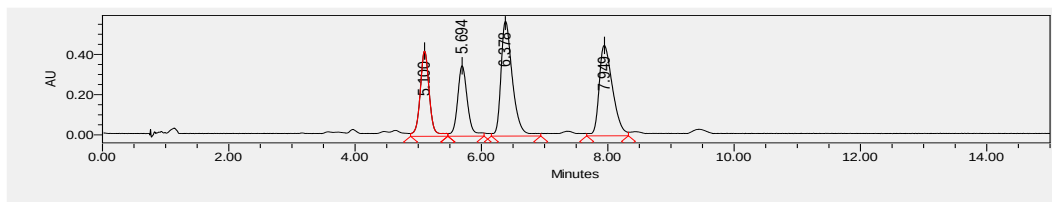
Exo C5: ^{13}C NMR (101 MHz, Chloroform- d) δ 163.2, 159.3(d, $J_{\text{C-F}} = 246.0$), 146.9, 139.5, 137.0, 136.9, 129.3(d, $J_{\text{C-F}} = 8.0$), 129.1, 129.0, 128.8, 128.5, 128.2, 128.1, 127.9, 127.6, 126.2, 120.6, 115.9, 115.7(d, $J_{\text{C-F}} = 21.0$), 75.5, 47.9, 46.6, 38.6, 36.2 ppm.

Endo C5: ^{19}F NMR (377 MHz, CDCl_3) δ -114.96 ppm.

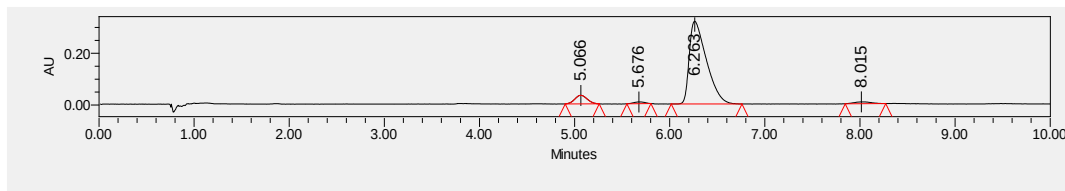
Exo C5: ^{19}F NMR (377 MHz, CDCl_3) δ -115.35 ppm.

ESI-HRMS calcd for $[\text{C}_{26}\text{H}_{22}\text{FNO}_2 + \text{Na}^+] = 422.1527$, found 422.1528.

IR $\tilde{\nu}$ (cm^{-1}) 3032, 2360, 1692, 1506, 1454, 1240, 1157, 1111, 838, 736, 699.

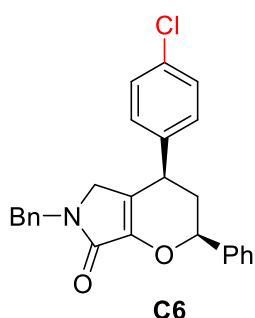


	Retention Time	Area	% Area	Height
1	5.100	4301485	19.58	423349
2	5.694	3798440	17.29	350072
3	6.378	7234863	32.92	570114
4	7.949	6639022	30.21	449186



	Retention Time	Area	% Area	Height
1	5.066	302908	6.81	33240
2	5.676	53702	1.21	6679
3	6.263	4007002	90.08	320047
4	8.015	84822	1.91	6980

C6: (2S,4R)-6-benzyl-4-(4-chlorophenyl)-2-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



C6: 98% yield, endo/exo = 92/8, 99%/89% ee; Colorless liquid, $[\alpha]_D^{25} = -43.5$ ($c = 0.69$, in CH_2Cl_2).

SFC Chiralcel OD-3, $\text{CO}_2/\text{MeOH}=90/10$. 1.5mL/ min, $\lambda = 210$ nm, retention time: $t_1 = 7.78$ min, $t_2 = 8.63$ min, $t_3 = 10.80$ min, $t_4 = 13.24$ min.

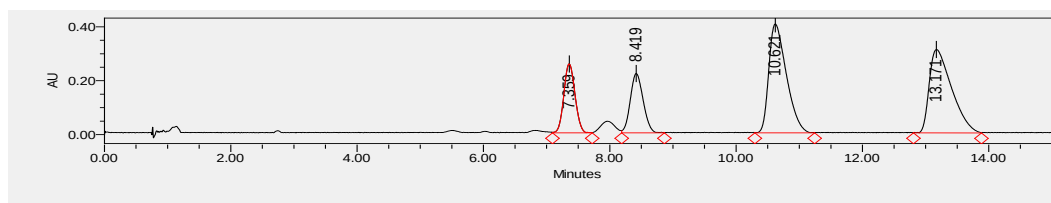
^1H NMR (400 MHz, Chloroform- d) δ 7.47 – 7.25 (m, 8H), 7.26 – 7.18 (m, 2H), 7.17 – 7.07 (m, 2H), 6.99 (q, $J = 9.7, 8.6$ Hz, 2H), 5.22 – 5.01 (m, 1H), 4.83 (d, $J = 15.0$ Hz, 1H), 4.54 – 4.33 (m, 1H), 3.91 (dd, $J = 10.8, 6.0$ Hz, 1H), 3.66 – 3.28 (m, 2H), 2.42 (ddd, $J = 14.2, 6.0, 1.8$ Hz, 1H), 2.18 – 2.03 (m, 1H) ppm.

Endo C6: ^{13}C NMR (101 MHz, Chloroform- d) δ 165.3, 146.9, 139.5, 137.1, 136.9, 129.1, 129.0, 128.8, 128.5, 128.3, 128.1, 127.6, 126.3, 123.0, 116.0, 115.8, 80.2, 47.2, 46.5, 40.9, 39.3 ppm.

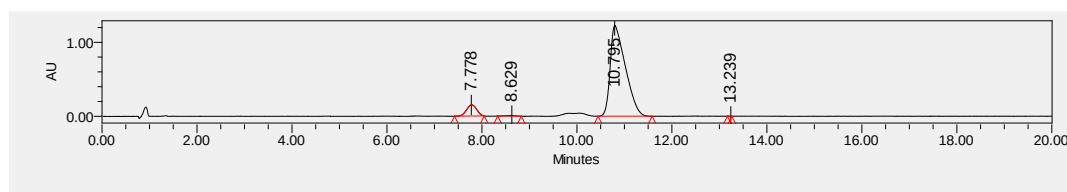
Exo C6: ^{13}C NMR (101 MHz, Chloroform- d) δ 165.2, 146.9, 139.5, 137.0, 136.9, 129.3, 129.2, 128.8k, 128.5, 128.3, 128.2, 127.7, 126.2, 120.6, 116.0, 115.7, 75.5, 47.9, 46.6, 38.6, 36.2 ppm.

ESI-HRMS calcd for $[\text{C}_{26}\text{H}_{22}\text{ClNO}_2 + \text{Na}^+] = 438.1231$, found 438.1245.

IR $\tilde{\nu}$ (cm^{-1}) 3032, 2360, 1694, 1507, 1454, 1240, 1157, 1110, 884, 733, 698.

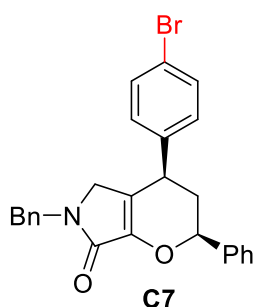


	Retention Time	Area	% Area	Height
1	7.359	3140208	14.50	255442
2	8.419	3108411	14.35	220542
3	10.621	7816213	36.08	404622
4	13.171	7597129	35.07	309448



	Retention Time	Area	% Area	Height
1	7.778	2249254	7.60	152128
2	8.629	127720	0.43	7881
3	10.795	27203979	91.96	1226535
4	13.239	1578	0.01	-940

C7: (2S,4R)-6-benzyl-4-(4-bromophenyl)-2-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



C7: 91% yield, endo/exo = 91/9, 94%/74% ee; Colorless liquid, $[\alpha]_D^{24} = -32.7$ ($c = 0.74$, in CH_2Cl_2).

SFC Chiralcel OD-3, $\text{CO}_2/\text{MeOH}=80/20$. 1.5mL/ min, $\lambda = 210$ nm, retention time: $t_1 = 9.05$ min, $t_2 = 10.23$ min, $t_3 = 13.72$ min, $t_4 = 17.31$ min.

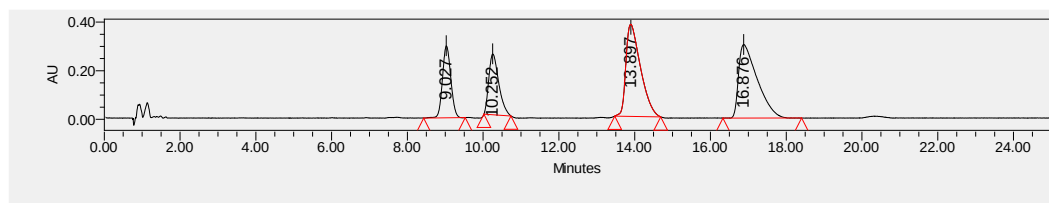
^1H NMR (400 MHz, $\text{Chloroform-}d$) δ 7.49 – 7.26 (m, 10H), 7.25 – 7.16 (m, 2H), 7.04 (dd, $J = 17.2, 8.4$ Hz, 2H), 5.15 (d, $J = 10.4$ Hz, 1H), 4.82 (d, $J = 15.0$ Hz, 1H), 4.53 – 4.37 (m, 1H), 3.88 (dd, $J = 10.8, 6.0$ Hz, 1H), 3.64 – 3.35 (m, 2H), 2.42 (ddd, $J = 14.0, 6.0, 1.6$ Hz, 1H), 2.10 (dt, $J = 14.0, 11.2$ Hz, 1H) ppm.

Endo C7: ^{13}C NMR (101 MHz, CDCl_3) δ 165.2, 147.0, 140.3, 139.4, 137.0, 132.1, 129.5, 129.3, 128.8, 128.5, 128.4, 128.2, 128.1, 127.7, 126.3, 126.2, 122.5, 121.1, 80.1, 75.5, 47.2, 46.5, 40.6, 39.5 ppm.

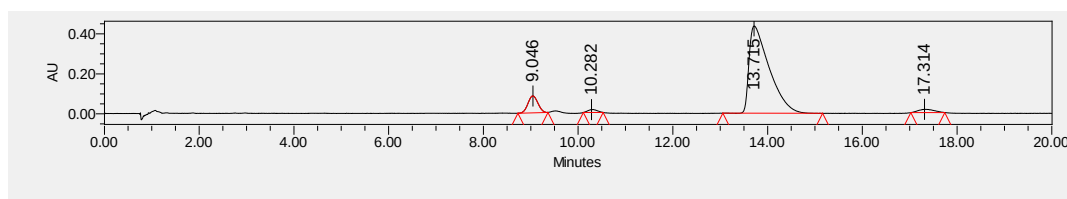
Exo C7: ^{13}C NMR (101 MHz, CDCl_3) δ 165.2, 147.1, 140.3, 139.3, 137.0, 132.1, 129.5, 129.2, 128.8, 128.6, 128.4, 128.2, 128.1, 127.7, 126.3, 126.2, 122.2, 121.1, 75.5, 75.5, 47.9, 46.6, 38.4, 36.4 ppm.

ESI-HRMS calcd for $[\text{C}_{26}\text{H}_{22}\text{BrNO}_2 + \text{Na}^+] = 482.0726$, found 482.0736.

IR $\tilde{\nu}$ (cm^{-1}) 3030, 2360, 1694, 1487, 1453, 1241, 1112, 1047, 884, 733, 698.

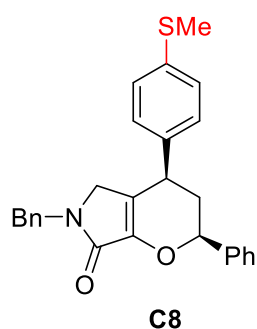


	Retention Time	Area	% Area	Height
1	9.027	4531073	15.31	296867
2	10.252	4583984	15.49	250303
3	13.897	10146572	34.28	379162
4	16.876	10339787	34.93	302587



	Retention Time	Area	% Area	Height
1	9.046	1233488	8.37	84746
2	10.282	200586	1.36	14766
3	13.715	12915100	87.61	436128
4	17.314	392855	2.66	16865

C8: (2S,4R)-6-benzyl-4-(4-(methylthio)phenyl)-2-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7 (2H)-one



C8: 90% yield, endo/exo = 95/5, 99%/67% ee; Colorless liquid, $[\alpha]_D^{24} = -35.9$ ($c = 0.78$, in CH_2Cl_2).

HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/ min, $\lambda = 210$ nm), $t_1 = 15.20$ min, $t_2 = 17.51$ min, $t_3 = 18.91$ min, $t_4 = 36.40$ min.

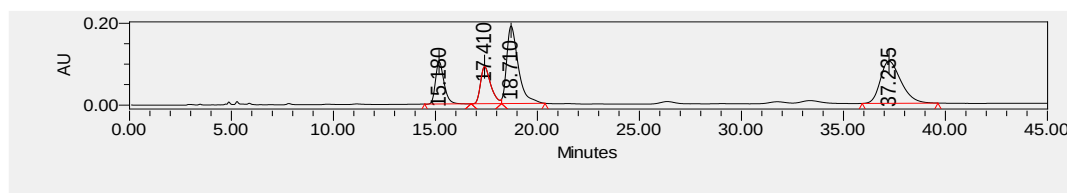
^1H NMR (400 MHz, Chloroform-*d*) δ 7.43 (d, $J = 7.0$ Hz, 2H), 7.36 (d, $J = 6.8$ Hz, 1H), 7.34 – 7.27 (m, 4H), 7.26 (s, 1H), 7.25 – 7.20 (m, 2H), 7.17 (d, $J = 8.4$ Hz, 2H), 7.06 (d, $J = 8.4$ Hz, 2H), 5.15 (d, $J = 10.6$ Hz, 1H), 4.82 (d, $J = 15.0$ Hz, 1H), 4.40 (d, $J = 15.0$ Hz, 1H), 3.87 (dd, $J = 10.8, 6.0$ Hz, 1H), 3.67 – 3.37 (m, 2H), 2.45 (s, 3H), 2.41 (ddd, $J = 14.0, 6.4, 1.8$ Hz, 1H), 2.12

(dt, $J = 14.0, 11.2$ Hz, 1H) ppm.

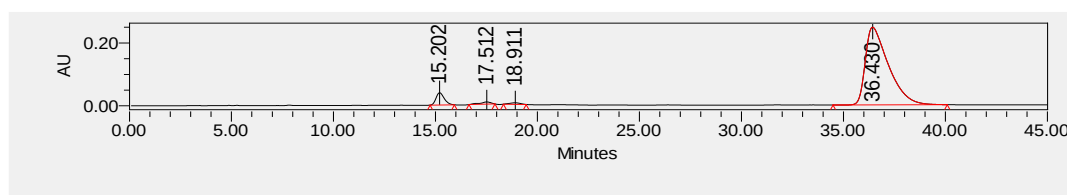
^{13}C NMR (101 MHz, CDCl_3) δ 165.3, 146.8, 139.6, 138.0, 137.5, 137.1, 128.7, 128.5, 128.4, 128.3, 128.1, 128.0, 127.6, 127.1, 126.4, 123.3, 80.2, 47.3, 46.5, 40.7, 39.5, 15.8 ppm.

ESI-HRMS calcd for $[\text{C}_{27}\text{H}_{25}\text{NO}_2\text{S} + \text{Na}^+] = 450.1498$, found 450.1504.

IR $\tilde{\nu}$ (cm^{-1}) 2918, 2360, 1692, 1492, 1453, 1240, 1088, 1046, 883, 731, 698.

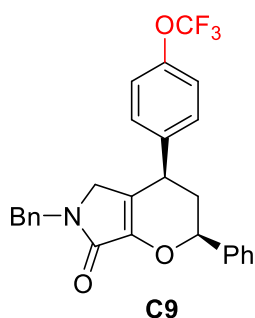


	Retention Time	Area	% Area	Height
1	15.180	3007420	14.43	103383
2	17.410	3157536	15.15	90680
3	18.710	7457423	35.78	189534
4	37.235	7221839	34.65	103054



	Retention Time	Area	% Area	Height
1	15.202	1090549	5.18	39146
2	17.512	268763	1.28	7062
3	18.911	177901	0.85	4859
4	36.430	19509628	92.70	247473

C9: (2S,4R)-6-benzyl-2-phenyl-4-(4-(trifluoromethoxy)phenyl)-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



C9: 96% yield, endo/exo = 95/5, 96%/55% ee; Colorless liquid, $[\alpha]^{25}_D = -32.2$ ($c = 0.83$, in CH_2Cl_2).

SFC Chiralcel IB-3, $\text{CO}_2/\text{MeOH}=90/10$. 1.5mL/ min, $\lambda = 210$ nm, retention time: $t_1 = 7.39$ min, $t_2 = 8.54$ min, $t_3 = 9.36$ min, $t_4 = 11.07$ min.

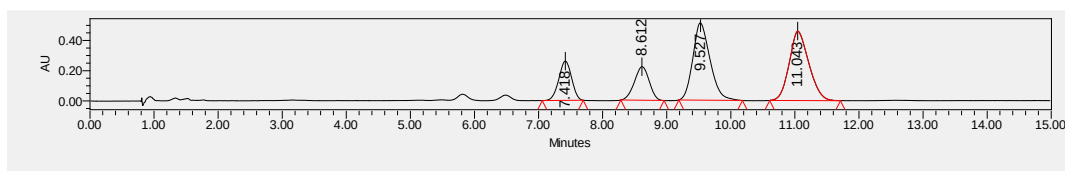
^1H NMR (400 MHz, $\text{Chloroform-}d$) δ 7.43 (d, $J = 7.0$ Hz, 2H), 7.38 – 7.31 (m, 4H), 7.29 (dd, $J = 6.8, 2.0$ Hz, 2H), 7.25 – 7.21 (m, 2H), 7.16 (t, $J = 6.4$ Hz, 4H), 5.16 (d, $J = 10.4$ Hz, 1H), 4.85 (dd, $J = 14.8, 4.8$ Hz, 1H), 4.52 – 4.36 (m, 1H), 3.94 (dd, $J = 10.4, 6.0$ Hz, 1H), 3.64 – 3.33 (m, 2H), 2.44 (ddd, $J = 14.0, 6.0, 1.6$ Hz, 1H), 2.11 (dt, $J = 14.0, 11.2$ Hz, 1H) ppm.

^{13}C NMR (101 MHz, CDCl_3) δ 165.2, 148.3, 147.1(d, $J_{\text{C-F}} = 14.0$), 140.0, 139.4, 137.1, 122.5, 121.5(d, $J_{\text{C-F}} = 255.0$), 80.1, 47.2, 46.5, 40.9, 39.4 ppm.

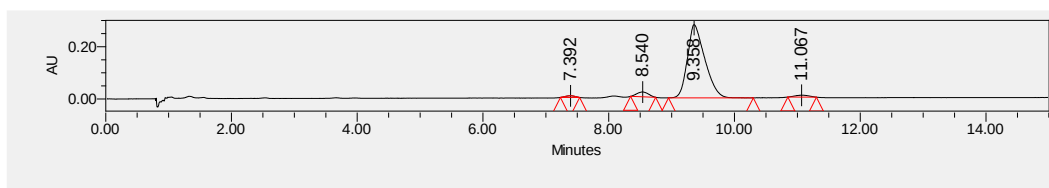
^{19}F NMR (377 MHz, CDCl_3) δ -57.89 ppm.

ESI-HRMS calcd for $[\text{C}_{27}\text{H}_{22}\text{F}_3\text{NO}_3 + \text{Na}^+] = 488.1444$, found 488.1455.

IR $\tilde{\nu}$ (cm^{-1}) 2919, 2360, 1694, 1505, 1454, 1253, 1110, 1048, 884, 735, 698.

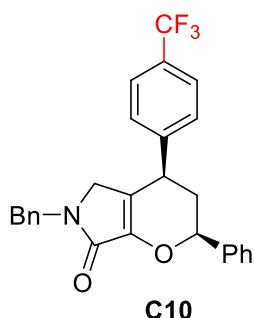


	Retention Time	Area	% Area	Height
1	7.418	3604693	13.68	259483
2	8.612	3556591	13.49	221850
3	9.527	9501339	36.05	510368
4	11.043	9695125	36.78	458555



	Retention Time	Area	% Area	Height
1	7.392	67313	1.17	6466
2	8.540	235083	4.08	18283
3	9.358	5354200	92.84	279937
4	11.067	110500	1.92	7351

C10: (2S,4R)-6-benzyl-2-phenyl-4-(4-(trifluoromethyl)phenyl)-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



C10: 86% yield, endo/exo = 91/9, 86%/68% ee; Colorless liquid, $[\alpha]_D^{25} = -27.3$ ($c = 0.79$, in CH_2Cl_2).

SFC Chiralcel OX-3, $\text{CO}_2/\text{MeOH}=80/20$. 1.5mL/ min, $\lambda = 210$ nm, retention time: $t_1 = 3.57$ min, $t_2 = 3.78$ min, $t_3 = 4.45$ min, $t_4 = 5.99$ min.

^1H NMR (400 MHz, CHCl_3) δ 7.71 – 7.54 (m, 2H), 7.45 – 7.37 (m, 2H), 7.38 – 7.30 (m, 5H), 7.29 (d, $J = 5.8$ Hz, 3H), 7.25 – 7.13 (m, 2H), 5.17 (d, $J = 10.6$ Hz, 1H), 4.84 (dd, $J = 14.9, 4.2$ Hz, 1H), 4.40 (d, $J = 15.0$ Hz, 1H), 4.00 (dd, $J = 10.6, 6.0$ Hz, 1H), 3.68 – 3.30 (m, 2H), 2.57 – 2.32 (m, 1H), 2.25 – 2.07 (m, 1H).

Endo C10: ^{13}C NMR (101 MHz, CDCl_3) δ 165.1, 147.3, 145.4, 139.3, 137.0, 136.0, 131.2, 129.9(d, $J_{\text{C-F}} = 33.2$), 129.6, 128.9, 128.5, 128.4, 128.1, 128.0, 127.7, 126.3, 126.2, 126.1(d, $J_{\text{C-F}} = 20.0$), 126.0, 125.9(d, $J_{\text{C-F}} = 4.0$), 125.9, 125.3, 122.0(d, $J_{\text{C-F}} = 287.0$), 80.0, 47.1, 46.5, 40.6, 39.8 ppm.

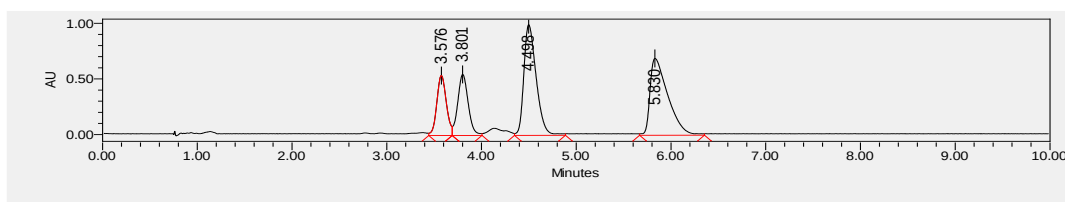
Exo C10: ^{13}C NMR (101 MHz, CDCl_3) δ 165.1, 147.3, 145.4, 139.3, 136.9, 136.0, 131.2, 129.9(d, $J_{\text{C-F}} = 33.2$), 129.6, 129.2, 128.6, 128.4, 128.2, 128.1, 127.8, 126.3, 126.2, 126.1(d, $J_{\text{C-F}} = 20.0$), 126.0, 125.9(d, $J_{\text{C-F}} = 4.0$), 125.9, 125.3, 122.0(d, $J_{\text{C-F}} = 287.0$), 75.5, 48.2, 47.9, 38.2, 36.8 ppm.

Endo C10: ^{19}F NMR (377 MHz, CDCl_3) δ -62.51 ppm.

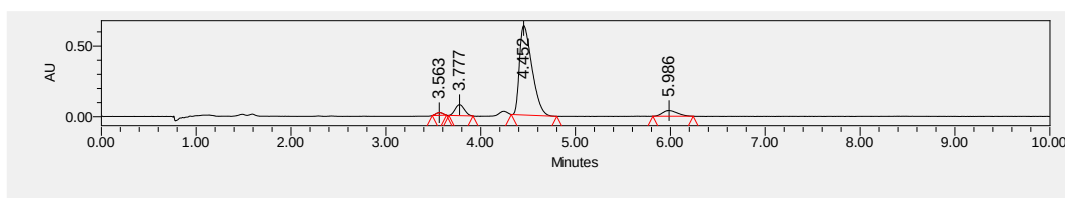
Exo C10: ^{19}F NMR (377 MHz, CDCl_3) δ -63.08 ppm.

ESI-HRMS calcd for $[\text{C}_{27}\text{H}_{22}\text{F}_3\text{NO}_2 + \text{Na}^+] = 472.1495$, found 472.1497.

IR $\tilde{\nu}$ (cm^{-1}) 3030, 2360, 1694, 1454, 1241, 1162, 1114, 885, 735, 698.

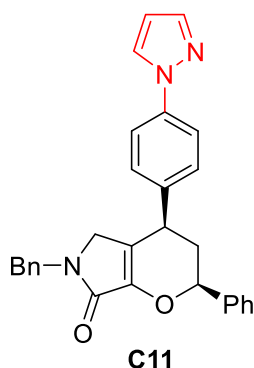


	Retention Time	Area	% Area	Height
1	3.576	3766084	14.46	539050
2	3.801	4217645	16.19	549436
3	4.498	9024479	34.65	994475
4	5.830	9037048	34.70	690039



	Retention Time	Area	% Area	Height
1	3.563	99503	1.46	19701
2	3.777	526610	7.72	77843
3	4.452	5761148	84.41	632680
4	5.986	437795	6.41	39787

C11: (2S,4R)-4-(4-(1H-pyrazol-1-yl)phenyl)-6-benzyl-2-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



C11: 93% yield, endo/exo = 95/5, 99%/78% ee; Colorless liquid, $[\alpha]_D^{25} = -37.8$ ($c = 0.74$, in CH_2Cl_2).

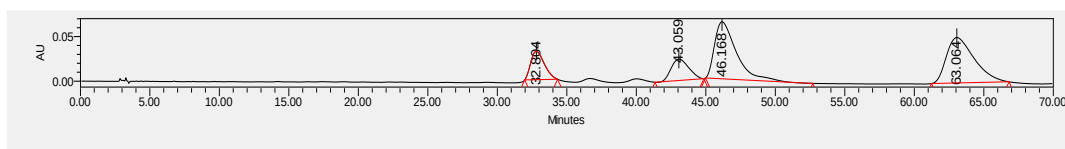
HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, $\lambda = 210$ nm), $t_1 = 34.00$ min, $t_2 = 44.50$ min, $t_3 = 48.54$ min, $t_4 = 63.94$ min.

^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, $J = 2.4$ Hz, 1H), 7.71 (d, $J = 1.4$ Hz, 1H), 7.62 (d, $J = 8.4$ Hz, 2H), 7.45 (d, $J = 7.0$ Hz, 2H), 7.39 – 7.28 (m, 5H), 7.27 (s, 1H), 7.23 (dt, $J = 6.4, 4.4$ Hz, 4H), 6.46 (q, $J = 3.2, 2.2$ Hz, 1H), 5.17 (d, $J = 10.8$ Hz, 1H), 4.81 (d, $J = 15.0$ Hz, 1H), 4.42 (d, $J = 15.0$ Hz, 1H), 3.96 (dd, $J = 10.6, 6.0$ Hz, 1H), 3.68 – 3.35 (m, 2H), 2.54 – 2.38 (m, 1H), 2.17 (dt, $J = 14.0, 11.2$ Hz, 1H) ppm.

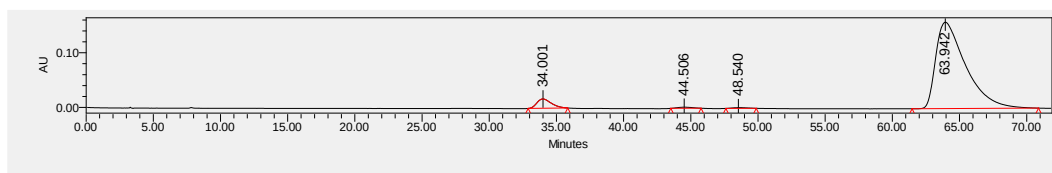
^{13}C NMR (101 MHz, CDCl_3) δ 165.2, 146.9, 141.2, 139.5, 139.4, 139.4, 137.1, 128.8, 128.7, 128.6, 128.5, 128.3, 128.1, 127.7, 126.7, 126.4, 122.9, 119.8, 107.8, 80.2, 47.2, 46.6, 40.6, 39.5 ppm.

ESI-HRMS calcd for $[\text{C}_{29}\text{H}_{25}\text{N}_3\text{O}_2 + \text{Na}^+] = 470.1839$, found 470.1848.

IR $\tilde{\nu}$ (cm^{-1}) 2918, 2360, 1692, 1523, 1454, 1241, 1107, 1047, 841, 753, 699.

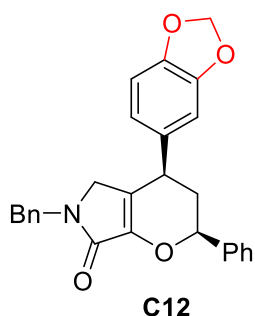


	Retention Time	Area	% Area	Height
1	32.804	2169117	11.80	31974
2	43.059	2111465	11.48	23955
3	46.168	7019135	38.18	63979
4	63.064	7086613	38.54	51033



	Retention Time	Area	% Area	Height
1	34.001	1270598	4.89	17109
2	44.506	151515	0.58	1985
3	48.540	101040	0.39	1306
4	63.942	24480136	94.14	158100

C12: (2S,4R)-4-(benzo[d][1,3]dioxol-5-yl)-6-benzyl-2-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



C12: 95% yield, endo/exo = 97/3, 99%/65% ee; Colorless liquid, $[\alpha]_D^{25} = -50.4$ ($c = 0.96$, in CH_2Cl_2).

SFC Chiralcel OD-3, $\text{CO}_2/\text{MeOH}=80/20$. 1.5mL/ min, $\lambda = 210$ nm, retention time: $t_1 = 7.91$ min, $t_2 = 8.94$ min, $t_3 = 10.20$ min, $t_4 = 11.43$ min.

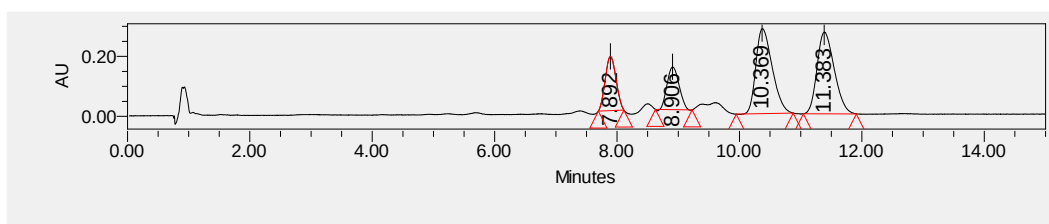
^1H NMR (400 MHz, Chloroform- d) δ 7.43 (d, $J = 7.2$ Hz, 2H), 7.36 (d, $J = 7.2$ Hz, 1H), 7.34 – 7.27 (m, 4H), 7.26 (s, 1H), 7.22 (d, $J = 7.0$ Hz, 2H), 6.71 (d, $J = 8.4$ Hz, 1H), 6.68 – 6.49 (m, 2H), 5.92 (d, $J = 2.4$ Hz, 2H), 5.13 (d, $J = 10.8$ Hz, 1H), 4.85 (d, $J = 15.0$ Hz, 1H), 4.39 (d, $J = 15.0$ Hz, 1H), 3.83 (dd, $J = 10.8, 6.0$ Hz, 1H), 3.49 (q, $J = 18.2$ Hz, 2H), 2.52 – 2.29 (m, 1H), 2.11

(dt, $J = 14.0, 11.2$ Hz, 1H) ppm.

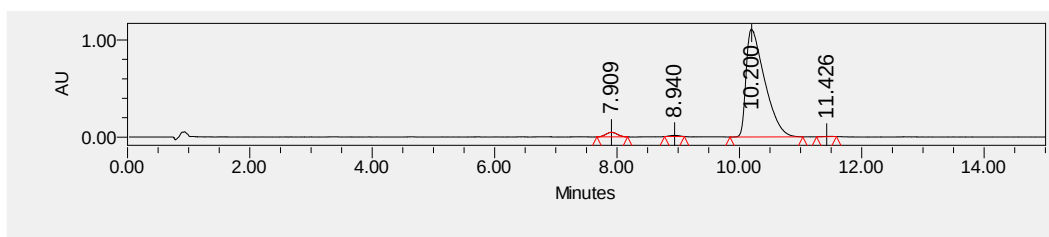
^{13}C NMR (101 MHz, CDCl_3) δ 165.3, 148.1, 146.8, 146.7, 139.6, 137.2, 134.9, 128.7, 128.5, 128.3, 128.1, 127.6, 126.4, 123.5, 120.8, 108.6, 107.6, 101.2, 80.2, 47.3, 46.5, 40.8, 39.7 ppm.

ESI-HRMS calcd for $[\text{C}_{27}\text{H}_{23}\text{NO}_4 + \text{Na}^+] = 448.1519$, found 448.1523.

IR $\tilde{\nu}$ (cm^{-1}) 2916, 2360, 1693, 1487, 1452, 1243, 1036, 914, 841, 754, 699.

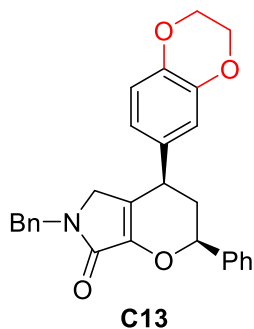


	Retention Time	Area	% Area	Height
1	7.892	2209527	14.96	180362
2	8.906	1953887	13.23	142404
3	10.369	5271838	35.70	283503
4	11.383	5330617	36.10	272565



	Retention Time	Area	% Area	Height
1	7.909	610015	2.53	47501
2	8.940	132373	0.55	12169
3	10.200	23293751	96.80	1110352
4	11.426	28307	0.12	2876

C13: (2S,4R)-6-benzyl-4-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-2-phenyl-3,4,5,6-tetrahydro-pyrano[2,3-c]pyrrol-7(2H)-one



C13: 95% yield, endo/exo = 96/4, 99%/62% ee; Colorless liquid, $[\alpha]^{25}_D = -44.0$ ($c = 0.70$, in CH_2Cl_2).

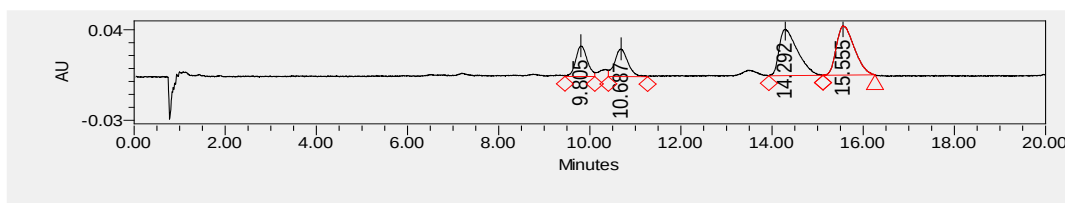
SFC Chiralcel OD-3, $\text{CO}_2/\text{MeOH}=80/20$. 1.5mL/ min, $\lambda = 210$ nm, retention time: $t_1 = 9.80$ min, $t_2 = 10.71$ min, $t_3 = 13.94$ min, $t_4 = 15.74$ min.

^1H NMR (400 MHz, $\text{Chloroform-}d$) δ 7.43 (d, $J = 7.0$ Hz, 2H), 7.35 (d, $J = 7.0$ Hz, 1H), 7.33 – 7.28 (m, 3H), 7.28 – 7.24 (m, 2H), 7.24 – 7.18 (m, 2H), 6.77 (d, $J = 8.2$ Hz, 1H), 6.71 – 6.45 (m, 2H), 5.12 (d, $J = 10.6$ Hz, 1H), 4.86 (d, $J = 15.0$ Hz, 1H), 4.37 (d, $J = 15.0$ Hz, 1H), 4.21 (s, 4H), 3.79 (dd, $J = 10.8, 6.0$ Hz, 1H), 3.50 (q, $J = 18.2$ Hz, 2H), 2.39 (ddd, $J = 14.0, 6.0, 1.6$ Hz, 1H), 2.12 (dt, $J = 14.0, 11.2$ Hz, 1H) ppm.

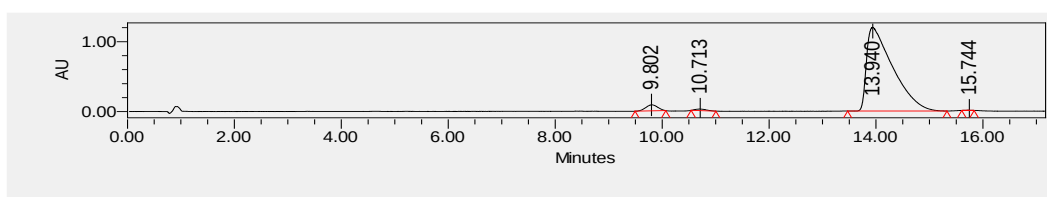
^{13}C NMR (101 MHz, CDCl_3) δ 165.4, 146.5, 143.7, 142.7, 139.7, 137.2, 134.4, 128.7, 128.4, 128.2, 128.1, 127.6, 126.4, 123.7, 120.4, 117.7, 116.3, 80.2, 64.4, 64.3, 47.3, 46.5, 40.7, 39.3 ppm.

ESI-HRMS calcd for $[\text{C}_{28}\text{H}_{25}\text{NO}_4 + \text{Na}^+] = 462.1676$, found 462.1678.

IR $\tilde{\nu}$ (cm^{-1}) 2874, 2360, 1692, 1588, 1454, 1240, 1106, 1066, 817, 733, 698.

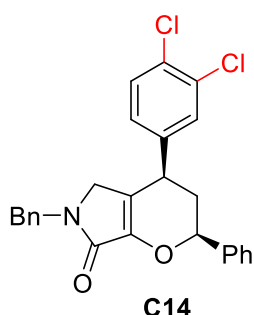


	Retention Time	Area	% Area	Height
1	9.805	413621	14.31	23819
2	10.687	431268	14.92	21470
3	14.292	1003200	34.71	35883
4	15.555	1042389	36.06	38236



	Retention Time	Area	% Area	Height
1	9.802	1347654	3.18	86844
2	10.713	315610	0.75	22690
3	13.940	40671016	96.02	1196691
4	15.744	21738	0.05	2845

C14: (2S,4R)-6-benzyl-4-(3,4-dichlorophenyl)-2-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7 (2H)-one



C14: 88% yield, endo/exo = 87/13, 89%/57% ee; Colorless liquid, $[\alpha]_D^{25} = -25.7$ ($c = 0.75$, in CH_2Cl_2).

SFC Chiralcel IB-3, $\text{CO}_2/\text{MeOH}=80/20$. 1.5mL/ min, $\lambda = 210$ nm, retention time: $t_1 = 7.28$ min, $t_2 = 7.76$ min, $t_3 = 9.31$ min, $t_4 = 10.03$ min.

^1H NMR (400 MHz, Chloroform- d) δ 7.58 – 7.27 (m, 10H), 7.25 – 7.16 (m, 3H), 6.98 (dd, $J = 8.4, 2.0$ Hz, 1H), 5.09 (d, $J = 8.0$ Hz, 1H), 4.87 – 4.80 (d, $J = 15.2$ Hz, 1H), 4.53 – 4.38 (d, $J = 15.2$ Hz, 1H), 3.88 (dd, $J = 10.8, 6.0$ Hz, 1H), 3.65 – 3.36 (m, 2H), 2.43 (ddd, $J = 14.0, 6.0, 1.6$ Hz, 1H), 2.09 (dt, $J = 14.2, 11.2$ Hz, 1H) ppm.

Endo C14: ^{13}C NMR (101 MHz, CDCl_3) δ 165.0, 147.3, 143.2, 141.5, 139.2, 136.9, 135.3, 133.1, 132.5, 131.4, 129.9, 129.6, 129.2, 128.8, 128.5, 128.1, 127.7, 126.9, 126.3, 121.8, 80.0, 47.0, 46.6, 40.4, 39.2 ppm.

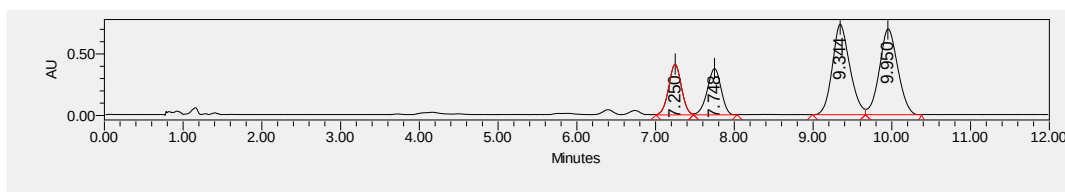
Exo C14: ^{13}C NMR (101 MHz, CDCl_3) δ 165.0, 147.4, 143.2, 141.5, 139.2, 136.9, 135.3, 133.1, 132.5, 131.4, 129.9, 129.6, 129.2, 128.8, 128.5, 128.1, 127.7, 126.9, 126.3, 119.3, 75.4, 48.2, 47.8, 38.2, 36.2 ppm.

HRMS (ESI) Calculated for $\text{C}_{26}\text{H}_{21}^{35}\text{Cl}^{35}\text{ClNO}_2$ ($[\text{M}]+\text{Na}^+$) = 472.0842, Found 472.0847.

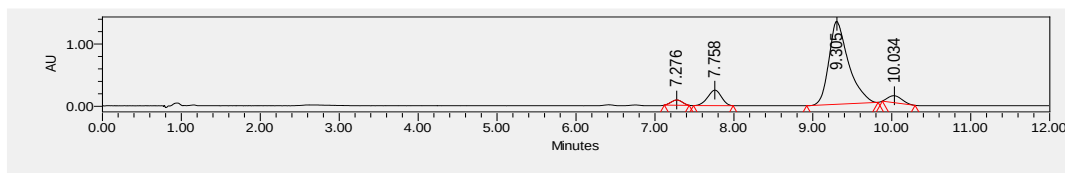
HRMS (ESI) Calculated for $\text{C}_{26}\text{H}_{21}^{35}\text{Cl}^{37}\text{ClNO}_2$ ($[\text{M}]+\text{Na}^+$) = 473.0875, Found 473.0876.

HRMS (ESI) Calculated for $\text{C}_{26}\text{H}_{21}^{37}\text{Cl}^{37}\text{ClNO}_2$ ($[\text{M}]+\text{Na}^+$) = 474.0812, Found 474.0816.

IR $\tilde{\nu}$ (cm^{-1}) 2916, 2360, 1693, 1487, 1452, 1243, 1036, 917, 814, 754, 699.

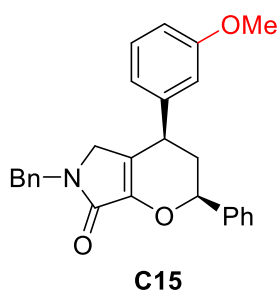


	Retention Time	Area	% Area	Height
1	7.250	4635374	14.57	412247
2	7.748	4580575	14.40	376010
3	9.344	11316164	35.58	735768
4	9.950	11276377	35.45	697365



	Retention Time	Area	% Area	Height
1	7.276	814119	2.90	83835
2	7.758	3008017	10.70	249496
3	9.305	22929501	81.58	1333364
4	10.034	1356106	4.82	112135

C15: (2S,4R)-6-benzyl-4-(3-methoxyphenyl)-2-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



C15: 34% yield, endo/exo = 89/11, 91%/75% ee; Colorless liquid, $[\alpha]_D^{25} = -33.2$ ($c = 0.34$, in CH_2Cl_2).

SFC Chiralcel OJ-3, $\text{CO}_2/\text{MeOH}=80/20$. 1.5mL/ min, $\lambda = 210$ nm, retention time: $t_1 = 3.13$ min, $t_2 = 3.47$ min, $t_3 = 3.83$ min, $t_4 = 4.89$ min.

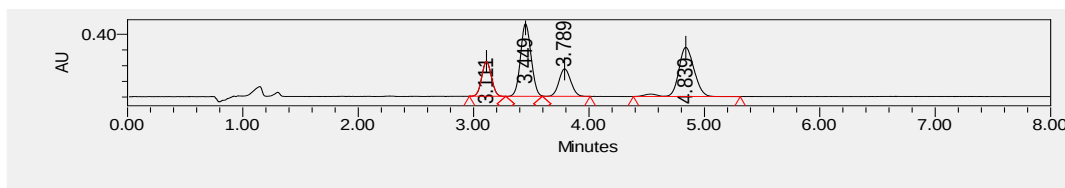
^1H NMR (400 MHz, CHCl_3) δ 7.44 (d, $J = 7.0$ Hz, 2H), 7.36 (m, 1H), 7.31 (dd, $J = 13.8, 6.4$ Hz, 4H), 7.26 (t, $J = 3.2$ Hz, 1H), 7.22 (q, $J = 7.8, 7.2$ Hz, 3H), 6.89 – 6.71 (m, 2H), 6.68 (d, $J = 19.2$ Hz, 1H), 5.21 – 5.07 (d, $J = 15.0$ Hz, 1H), 4.82 (d, $J = 15.0$ Hz, 1H), 4.47 (d, $J = 15.0$ Hz, 1H), 3.88 (dd, $J = 10.8, 6.0$ Hz, 1H), 3.75 (s, 3H), 3.51 (q, $J = 18.2$ Hz, 2H), 2.50 – 2.35 (m, 1H), 2.16 (dt, $J = 14.2, 11.2$ Hz, 1H) ppm.

Endo C15: ^{13}C NMR (101 MHz, CDCl_3) δ 165.4, 160.0, 146.8, 142.9, 139.6, 137.2, 130.0, 128.8, 128.2, 128.0, 126.2, 123.3, 119.9, 113.2, 112.6, 80.2, 55.2, 47.3, 46.5, 40.6, 40.0 ppm.

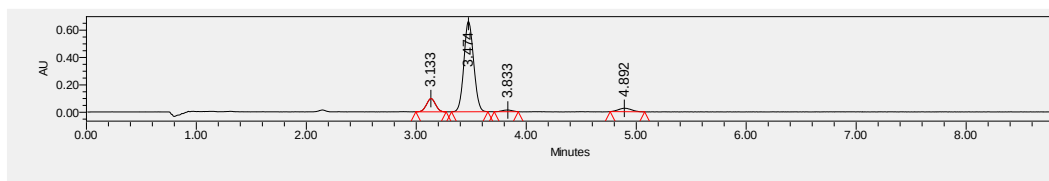
Exo C15: ^{13}C NMR (101 MHz, CDCl_3) δ 165.4, 160.0, 146.8, 142.9, 139.6, 137.2, 130.0, 128.8, 128.2, 128.0, 126.2, 123.3, 120.2, 113.8, 112.2, 75.7, 55.2, 48.1, 46.6, 38.4, 36.9 ppm.

ESI-HRMS calcd for $[\text{C}_{27}\text{H}_{25}\text{NO}_3 + \text{Na}^+] = 434.1727$, found 434.1729.

IR $\tilde{\nu}$ (cm^{-1}) 2920, 2360, 1696, 1557, 1540, 1454, 1242, 1154, 1046, 756, 700.

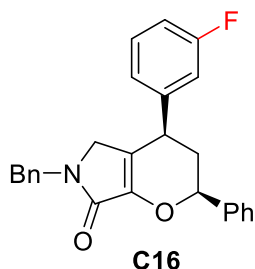


	Retention Time	Area	% Area	Height
1	3.111	1289760	15.27	220316
2	3.449	2941101	34.83	461815
3	3.789	1241726	14.70	175035
4	4.839	2972634	35.20	313337



	Retention Time	Area	% Area
1	3.133	551157	11.22
2	3.474	4073374	82.93
3	3.833	79105	1.61
4	4.892	208127	4.24

C16: (2S,4R)-6-benzyl-4-(3-fluorophenyl)-2-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7 (2H)-one



C16: 97% yield, endo/exo = 93/7, 96%/71% ee; Colorless liquid, $[\alpha]^{25}_D = -45.5$ ($c = 0.71$, in CH_2Cl_2).

SFC Chiralcel OJ-3, $\text{CO}_2/\text{MeOH}=90/10$. 1.5mL/ min, $\lambda = 210$ nm, retention time: $t_1 = 6.02$ min, $t_2 = 7.16$ min, $t_3 = 8.59$ min, $t_4 = 9.41$ min.

^1H NMR (400 MHz, Chloroform- d) δ 7.49 – 7.24 (m, 9H), 7.24 – 7.19 (m, 2H), 7.06 – 6.80 (m, 3H), 5.23 – 5.03 (d, $J = 10.4$ Hz, 1H), 4.85 (d, $J = 15.0$ Hz, 1H), 4.52 – 4.35 (d, $J = 15.0$ Hz, 1H), 3.92 (dd, $J = 10.7, 6.0$ Hz, 1H), 3.67 – 3.38 (m, 2H), 2.44 (ddd, $J = 14.0, 6.0, 1.6$ Hz, 1H), 2.13 (dt, $J = 14.0, 11.2$ Hz, 1H) ppm.

Endo C16: ^{13}C NMR (101 MHz, Chloroform- d) δ 165.2, 163.1(d, $J_{\text{C-F}} = 264.0$), 147.0, 143.9, 143.8, 139.4, 137.1, 130.6, 130.5, 128.8, 128.5, 128.3, 128.1, 127.6, 126.4, 123.2, 123.1, 122.5, 114.6, 114.5(d, $J_{\text{C-F}} = 24.0$), 114.4(d, $J_{\text{C-F}} = 8.0$), 114.3, 80.1, 47.2, 46.5, 40.6, 39.7 ppm.

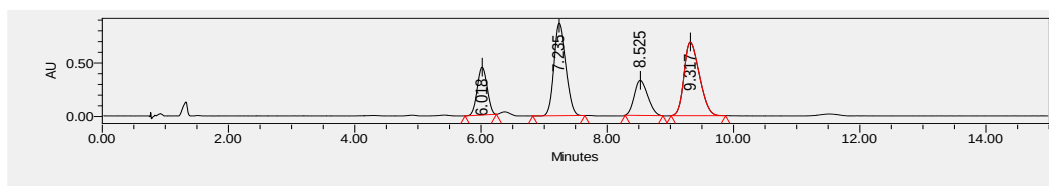
Exo C16: ^{13}C NMR (101 MHz, Chloroform- d) δ 165.2, 163.1(d, $J_{\text{C-F}} = 264.0$), 147.0, 143.9, 143.8, 139.4, 137.1, 130.6, 130.5, 128.8, 128.5, 128.3, 128.1, 127.6, 126.2, 123.2, 123.1, 122.5, 114.6, 114.5(d, $J_{\text{C-F}} = 24.0$), 114.4(d, $J_{\text{C-F}} = 8.0$), 114.3, 75.5, 47.9, 46.5, 38.3, 36.7 ppm.

Endo C16: ^{19}F NMR (377 MHz, CDCl_3) δ -112.01 ppm.

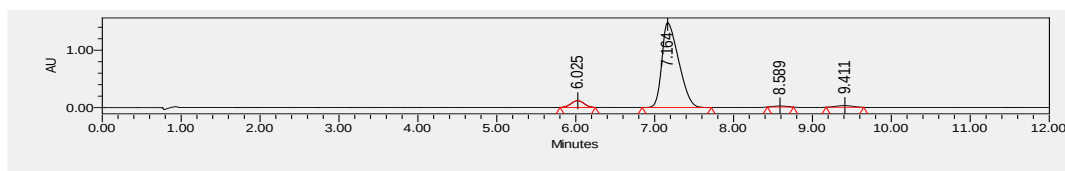
Exo C16: ^{19}F NMR (377 MHz, CDCl_3) δ -112.08 ppm.

ESI-HRMS calcd for $[\text{C}_{26}\text{H}_{22}\text{FNO}_2 + \text{Na}^+] = 422.1527$, found 422.1527.

IR $\tilde{\nu}$ (cm^{-1}) 2919, 2360, 1695, 1588, 1489, 1242, 1144, 1109, 877, 757, 699.

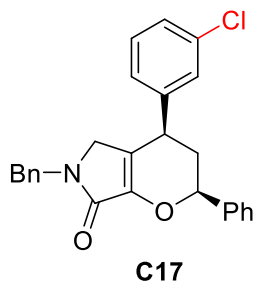


	Retention Time	Area	% Area	Height
1	6.018	4881712	14.88	447425
2	7.235	11492655	35.03	864061
3	8.525	4854179	14.80	328141
4	9.317	11579250	35.29	688290



	Retention Time	Area	% Area	Height
1	6.025	1345353	5.66	117468
2	7.164	21766825	91.54	1483329
3	8.589	219825	0.92	18941
4	9.411	445502	1.87	29844

C17: (2S,4R)-6-benzyl-4-(3-chlorophenyl)-2-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



C17: 84% yield, endo/exo = 89/11, 90%/61% ee; Colorless liquid, $[\alpha]_D^{25} = -30.9$ ($c = 0.66$, in CH_2Cl_2).

SFC Chiralcel IJ-3, $\text{CO}_2/\text{MeOH}=80/20$. 1.5mL/ min, $\lambda = 210$ nm, retention time: $t_1 = 3.30$ min, $t_2 = 3.83$ min, $t_3 = 4.67$ min, $t_4 = 5.65$ min.

^1H NMR (400 MHz, $\text{Chloroform-}d$) δ 7.45 – 7.35 (m, 3H), 7.34 – 7.28 (m, 4H), 7.27 (d, $J = 7.0$ Hz, 2H), 7.22 (dd, $J = 5.8, 2.8$ Hz, 3H), 7.15 (d, $J = 16.2$ Hz, 1H), 7.09 – 7.00 (m, 1H), 5.20 – 5.03 (d, $J = 11.2$ Hz, 1H), 4.86 (d, $J = 15.0$ Hz, 1H), 4.45 (d, $J = 15.0$ Hz, 1H), 3.89 (dd, $J = 10.8, 6.0$ Hz, 1H),

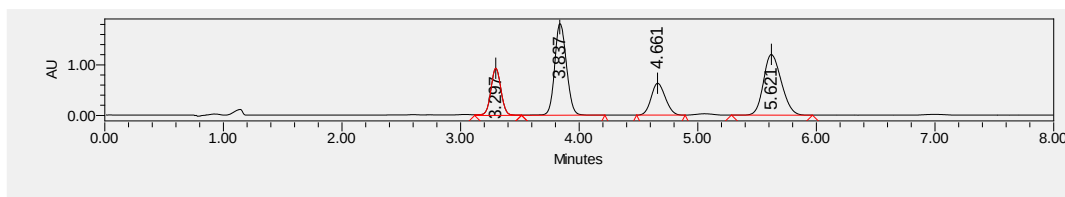
3.66 – 3.37 (m, 2H), 2.43 (ddd, $J = 14.0, 6.0, 1.8$ Hz, 1H), 2.13 (dt, $J = 14.0, 11.2$ Hz, 1H) ppm.

Endo C17: ^{13}C NMR (101 MHz, CDCl_3) δ 165.2, 163.5, 147.1, 143.3, 139.4, 137.0, 134.8, 130.3, 128.5, 128.4, 128.1, 128.0, 127.8, 127.7, 127.6, 126.3, 125.7, 122.4, 80.1, 47.1, 46.5, 40.6, 39.7 ppm.

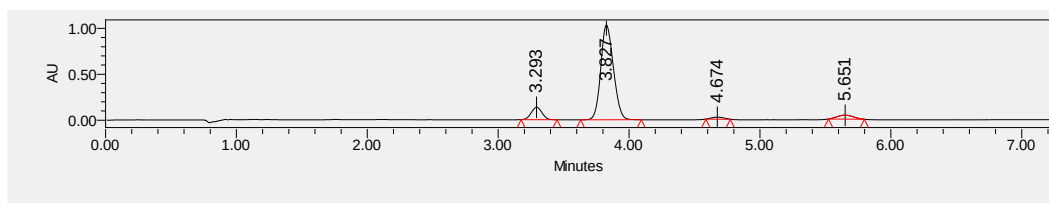
Exo C17: ^{13}C NMR (101 MHz, CDCl_3) δ 165.2, 163.5, 147.1, 143.3, 139.4, 137.0, 134.8, 130.3, 128.5, 128.4, 128.1, 128.0, 127.8, 127.7, 127.6, 126.2, 125.7, 119.9, 75.5, 47.9, 46.6, 38.3, 36.6 ppm.

ESI-HRMS calcd for $[\text{C}_{26}\text{H}_{22}\text{ClNO}_2 + \text{Na}^+] = 438.1231$, found 438.1236.

IR $\tilde{\nu}$ (cm^{-1}) 2919, 2360, 1694, 1595, 1453, 1241, 1112, 891, 733, 697.

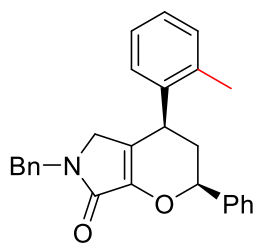


	Retention Time	Area	% Area	Height
1	3.297	5581267	15.54	933614
2	3.837	12556199	34.97	1810924
3	4.661	5220827	14.54	630733
4	5.621	12550379	34.95	1202098



	Retention Time	Area	% Area	Height
1	3.293	769869	9.38	135239
2	3.827	6925842	84.38	1033710
3	4.674	138831	1.69	21846
4	5.651	373510	4.55	43057

C18: (2S,4R)-6-benzyl-2-phenyl-4-(o-tolyl)-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



C18

C18: 25% yield, endo/exo = 91/9, 91%/73% ee; Colorless liquid, $[\alpha]^{25}_D = -16.4$ ($c = 0.22$, in CH_2Cl_2).

SFC Chiralcel OD-3, $\text{CO}_2/\text{MeOH}=80/20$. 1.5mL/ min, $\lambda = 210$ nm, retention time: $t_1 = 6.08$ min, $t_2 = 6.57$ min, $t_3 = 7.00$ min, $t_4 = 7.78$ min.

^1H NMR (400 MHz, CHCl_3) δ 7.44 (d, $J = 7.0$ Hz, 2H), 7.37 – 7.29 (m, 6H), 7.25 – 7.19 (m, 2H), 7.19 – 7.10 (m, 3H), 7.02 (d, $J = 6.4$ Hz, 1H), 5.16 (d, $J = 10.6$ Hz, 1H), 4.85 (d, $J = 6.2$ Hz, 1H), 4.50 (d, $J = 6.2$ Hz, 1H),

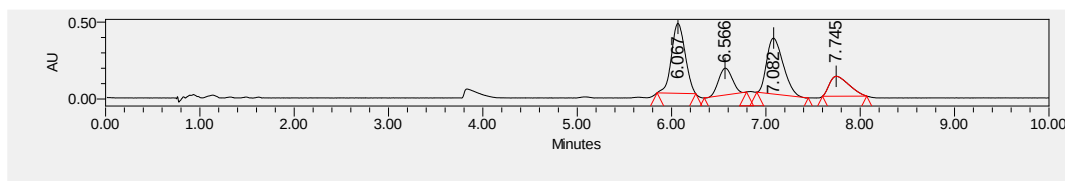
4.15 (dq, $J = 12.8, 7.1$ Hz, 1H), 3.51 (m, 2H), 2.41 (dd, $J = 14.0, 4.8$ Hz, 1H), 2.32 (s, 3H), 2.15 – 1.96 (m, 1H) ppm.

Endo C18: ^{13}C NMR (101 MHz, CDCl_3) δ 165.4, 139.6, 137.2, 135.7, 128.9, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.6, 127.0, 126.8, 126.5, 126.4, 123.7, 80.3, 47.3, 46.5, 43.8, 19.4 ppm.

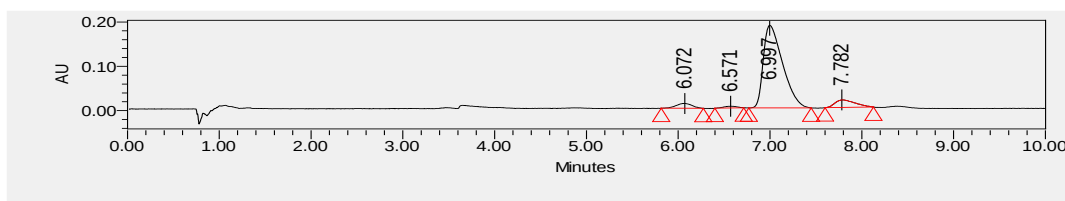
Exo C18: ^{13}C NMR (101 MHz, CDCl_3) δ 159.6, 139.4, 136.7, 135.1, 128.9, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.6, 127.0, 126.8, 126.5, 126.4, 120.5, 80.3, 47.3, 46.6, 43.7, 19.2 ppm.

ESI-HRMS calcd for $[\text{C}_{27}\text{H}_{25}\text{NO}_2 + \text{Na}^+] = 418.1778$, found 418.1777.

IR $\tilde{\nu}$ (cm^{-1}) 2922, 2360, 1693, 1492, 1454, 1241, 1120, 1045, 732, 699.

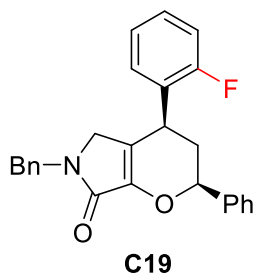


	Retention Time	Area	% Area	Height
1	6.067	4549583	36.20	454530
2	6.566	1756141	13.97	174585
3	7.082	4404268	35.04	363917
4	7.745	1858292	14.79	129960



	Retention Time	Area	% Area	Height
1	6.072	130601	4.15	10882
2	6.571	39626	1.26	4048
3	6.997	2719099	86.40	186300
4	7.782	257867	8.19	17041

C19: (2S,4S)-6-benzyl-4-(2-fluorophenyl)-2-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7 (2H)-one



C19: 86% yield, endo/exo = 86/14, 80%/77% ee; Colorless liquid, $[\alpha]_D^{25} = -23.3$ ($c = 0.57$, in CH_2Cl_2).

SFC Chiralcel OJ-3, $\text{CO}_2/\text{MeOH}=90/10$. 1.5mL/ min, $\lambda = 210$ nm, retention time: $t_1 = 4.92$ min, $t_2 = 5.22$ min, $t_3 = 5.95$ min, $t_4 = 7.30$ min.

^1H NMR (400 MHz, CHCl_3) δ 7.45 (d, $J = 7.2$ Hz, 2H), 7.37 – 7.28 (m, 5H), 7.28 – 7.20 (m, 4H), 7.17 – 7.07 (m, 2H), 7.06 – 6.98 (m, 1H), 5.29 – 4.99 (d, $J = 10.8$ Hz, 1H), 4.83 (dd, $J = 15.0, 4.6$ Hz, 1H), 4.48 (dd, $J = 15.0$ Hz, 4.6 Hz, 1H), 4.31 – 4.01 (m, 1H), 3.75 – 3.41 (m, 2H), 2.59 – 2.36 (m, 1H), 2.19 (dt, $J = 14.0, 11.2$ Hz, 1H) ppm.

Endo C19: ^{13}C NMR (101 MHz, CDCl_3) δ 165.3, 160.8(d, $J_{\text{C-F}} = 246.0$), 147.0, 139.5, 137.1, 129.0, 128.9, 128.8, 128.7, 128.5, 128.3, 128.2, 128.0, 126.4, 124.7(d, $J_{\text{C-F}} = 4.0$), 122.3, 119.5, 115.9, 115.7(d, $J_{\text{C-F}} = 22.0$), 80.2, 47.3, 46.5, 38.8, 32.7, ppm.

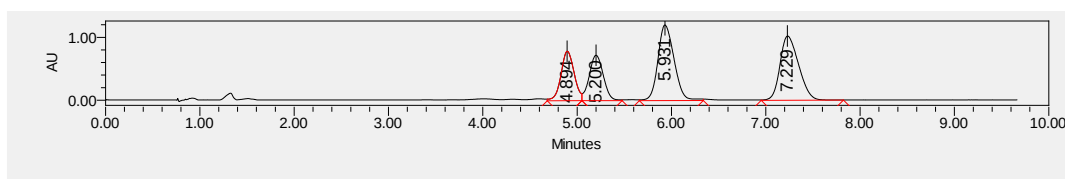
Exo C19: ^{13}C NMR (101 MHz, CDCl_3) δ 165.3, 160.8(d, $J_{\text{C-F}} = 246.0$), 147.0, 139.4, 137.0, 129.0, 128.9, 128.8, 128.7, 128.5, 128.3, 128.2, 128.0, 126.4, 124.7(d, $J_{\text{C-F}} = 4.0$), 122.3, 119.5, 115.9, 115.7(d, $J_{\text{C-F}} = 22.0$), 75.8, 48.0, 46.6, 36.8, 30.2 ppm.

Endo C19: ^{19}F NMR (377 MHz, CDCl_3) δ -118.71 ppm.

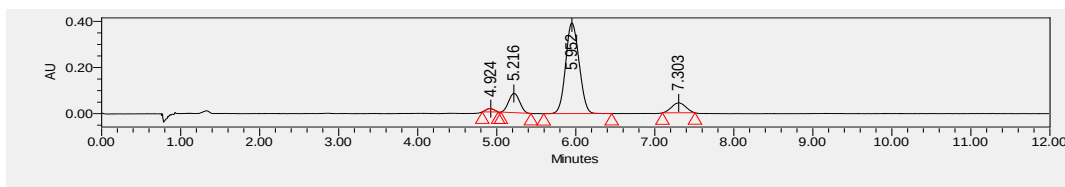
Exo C19: ^{19}F NMR (377 MHz, CDCl_3) δ -119.20 ppm.

ESI-HRMS calcd for $[\text{C}_{26}\text{H}_{22}\text{FNO}_2 + \text{Na}^+] = 422.1527$, found 422.1530.

IR $\tilde{\nu}$ (cm^{-1}) 2921, 2360, 1694, 1490, 1453, 1241, 1113, 1048, 887, 756, 699.

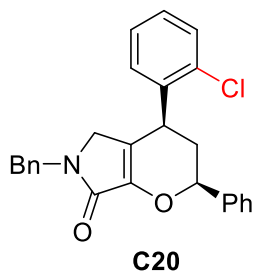


	Retention Time	Area	% Area	Height
1	4.894	7627918	17.53	786020
2	5.200	7512276	17.27	722225
3	5.931	14332319	32.95	1202506
4	7.229	14030450	32.25	1021481



	Retention Time	Area	% Area	Height
1	4.924	101562	1.67	14552
2	5.216	803306	13.19	83498
3	5.952	4652439	76.41	392871
4	7.303	531139	8.72	43049

C20: (2S,4S)-6-benzyl-4-(2-chlorophenyl)-2-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



C20: 62% yield, endo/exo = 76/24, 72%/90% ee; Colorless liquid, $[\alpha]^{22}_D = -8.4$ ($c = 0.06$, in CH_2Cl_2).

SFC Chiralcel OD-3, $\text{CO}_2/\text{MeOH}=80/20$. 1.5mL/ min, $\lambda = 210$ nm, retention time: $t_1 = 6.90$ min, $t_2 = 7.40$ min, $t_3 = 7.98$ min, $t_4 = 10.75$ min.

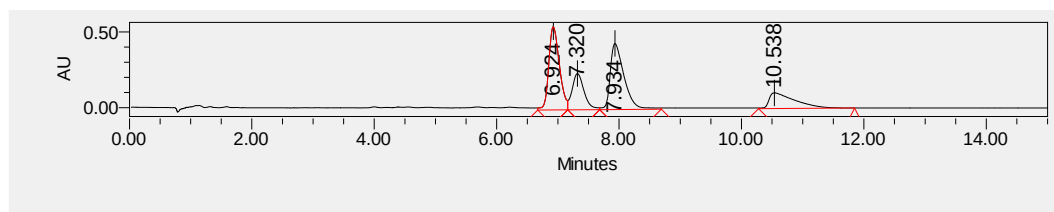
^1H NMR (400 MHz, CHCl_3 - d) δ 7.57 – 7.38 (m, 2H), 7.38 – 7.30 (m, 5H), 7.29 (d, $J = 8.0$ Hz, 2H), 7.26 (s, 1H), 7.24 – 7.23 (m, 1H), 7.22 – 7.20 (m, 1H), 7.19 – 7.15 (m, 1H), 7.15 – 7.02 (m, 1H), 5.22 – 4.93 (d, $J = 11.6$ Hz, 1H), 4.91 – 4.72 (d, $J = 14.4$ Hz, 1H), 4.48 (dd, $J = 19.0, 15.0$ Hz, 2H), 3.75 – 3.44 (m, 2H), 2.63 – 2.35 (m, 1H), 2.23 – 1.96 (m, 1H) ppm.

Endo C20: ^{13}C NMR (101 MHz, CDCl_3) δ 165.3, 148.0, 139.9, 139.5, 139.4, 137.1, 133.8, 130.2, 129.5, 128.8, 128.5, 128.3, 128.2, 128.1, 127.7, 127.6, 127.5, 127.1, 126.4, 122.4, 119.6, 80.2, 47.3, 46.5, 36.4, 34.2 ppm.

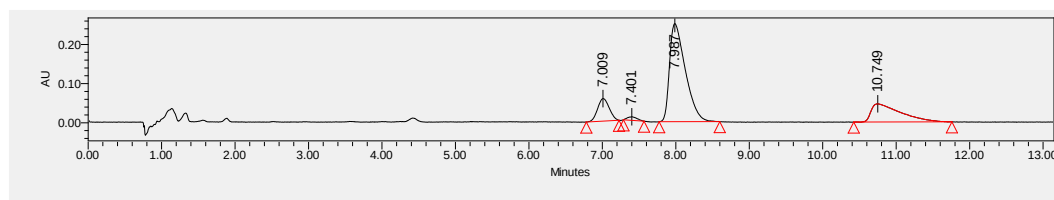
Exo C20: ^{13}C NMR (101 MHz, CDCl_3) δ 165.2, 148.0, 139.9, 139.5, 139.4, 137.0, 133.6, 130.2, 129.5, 128.8, 128.5, 128.3, 128.2, 128.1, 127.7, 127.6, 127.5, 127.1, 126.4, 122.4, 119.6, 75.6, 47.9, 46.7, 36.4, 34.2 ppm.

ESI-HRMS calcd for $[\text{C}_{26}\text{H}_{22}\text{NO}_2 + \text{Na}^+] = 438.1231$, found 438.1234.

IR $\tilde{\nu}$ (cm^{-1}) 2919, 2360, 1696, 1453, 1394, 1242, 1110, 1047, 754, 699.

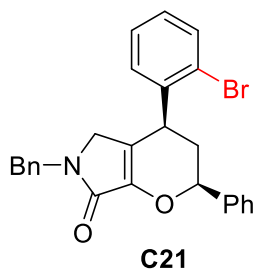


	Retention Time	Area	% Area	Height
1	6.924	6645098	33.43	549003
2	7.320	3263328	16.42	239609
3	7.934	6887492	34.65	436112
4	10.538	3079287	15.49	103700



	Retention Time	Area	% Area
1	7.009	631288	10.99
2	7.401	83561	1.45
3	7.987	3740464	65.11
4	10.749	1289129	22.44

C21: (2S,4S)-6-benzyl-4-(2-bromophenyl)-2-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7 (2H)-one



C21: 59% yield, endo/exo = 66/34, 57%/89% ee; Colorless liquid, $[\alpha]_D^{25} = -10.2$ ($c = 0.49$, in CH_2Cl_2).

SFC Chiralcel OJ-3, $\text{CO}_2/\text{MeOH}=90/10$. 1.5mL/ min, $\lambda = 210$ nm, retention time: $t_1 = 8.21$ min, $t_2 = 9.20$ min, $t_3 = 9.66$ min, $t_4 = 12.23$ min.

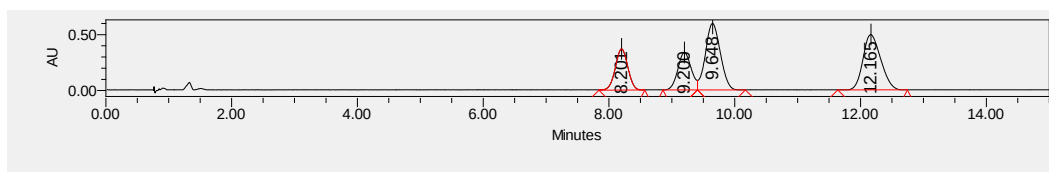
^1H NMR (400 MHz, $\text{Chloroform-}d$) δ 7.62 – 7.50 (m, 1H), 7.47 – 7.29 (m, 7H), 7.28 – 7.21 (m, 4H), 7.08 (t, $J = 6.9$ Hz, 2H), 5.24 – 4.93 (d, $J = 12.0$ Hz, 1H), 4.91 – 4.77 (d, $J = 12.0$ Hz, 1H), 4.48 (d, $J = 12.0$ Hz, 2H), 3.75 – 3.45 (m, 2H), 2.53 (d, $J = 8.4$ Hz, 1H), 2.17 (d, $J = 2.0$ Hz, 1H) ppm.

Endo C21: ^{13}C NMR (101 MHz, CDCl_3) δ 165.3, 147.9, 141.5, 139.4, 137.1, 137.0, 133.6, 133.2, 129.6, 128.8, 128.5, 128.3, 128.2, 128.1, 127.7, 126.4, 124.2, 122.5, 119.7, 80.2, 47.2, 46.6, 36.7, 36.6 ppm.

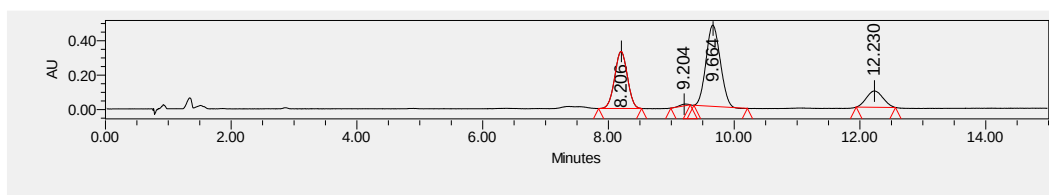
Exo C21: ^{13}C NMR (101 MHz, CDCl_3) δ 165.1, 147.9, 141.5, 139.4, 137.1, 137.0, 133.6, 133.2, 129.6, 128.8, 128.5, 128.3, 128.2, 128.1, 127.6, 126.4, 124.2, 122.5, 119.7, 75.5, 47.9, 46.7, 36.7, 36.6 ppm.

ESI-HRMS calcd for $[\text{C}_{26}\text{H}_{22}\text{BrNO}_2 + \text{Na}^+] = 482.0726$, found 482.0738.

IR $\tilde{\nu}$ (cm^{-1}) 2919, 2360, 1695, 1494, 1468, 1242, 1131, 1110, 894, 733, 699.

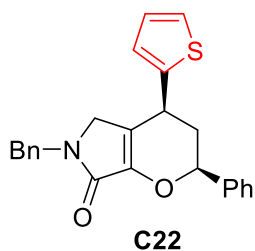


	Retention Time	Area	% Area	Height
1	8.201	5088542	17.20	368122
2	9.200	4962470	16.78	334000
3	9.648	9812654	33.17	594750
4	12.165	9715013	32.84	495615



	Retention Time	Area	% Area	Height
1	8.206	4658345	33.47	331038
2	9.204	89074	0.64	9886
3	9.664	7453019	53.54	472449
4	12.230	1718975	12.35	94517

C22: (2S,4S)-6-benzyl-2-phenyl-4-(thiophen-2-yl)-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



C22: 29% yield, endo/exo = 97/3, 99%/0% ee; Colorless liquid, $[\alpha]^{25}_D = -49.5$ ($c = 0.41$, in CH_2Cl_2).

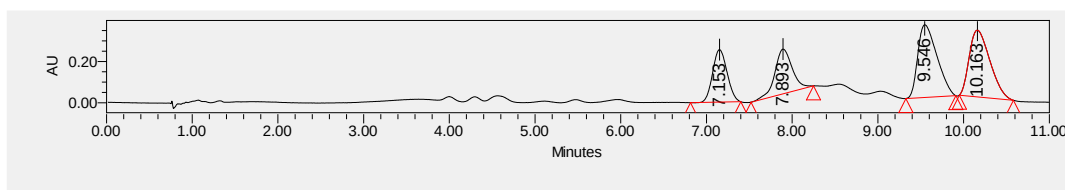
SFC Chiralcel OD-3, $\text{CO}_2/\text{MeOH}=80/20$. 1.5mL/ min, $\lambda = 210$ nm, retention time: $t_1 = 7.14$ min, $t_2 = 7.92$ min, $t_3 = 9.55$ min, $t_4 = 10.30$ min.

^1H NMR (400 MHz, $\text{Chloroform-}d$) δ 7.45 (d, $J = 7.2$ Hz, 2H), 7.37 (t, $J = 7.2$ Hz, 2H), 7.35 – 7.29 (m, 3H), 7.28 (m, 1H), 7.22 (d, $J = 6.8$ Hz, 2H), 7.17 (d, $J = 4.8$ Hz, 1H), 6.99 – 6.79 (m, 2H), 5.16 (d, $J = 10.4$ Hz, 1H), 4.83 (d, $J = 15.0$ Hz, 1H), 4.51 (d, $J = 15.0$ Hz, 0H), 4.42 (d, $J = 15.0$ Hz, 1H), 4.29 (dd, $J = 10.4, 6.0$ Hz, 1H), 3.69 – 3.48 (m, 2H), 2.54 (ddd, $J = 14.0, 6.0, 1.6$ Hz, 1H), 2.27 (dt, $J = 14.0, 11.2$ Hz, 1H) ppm.

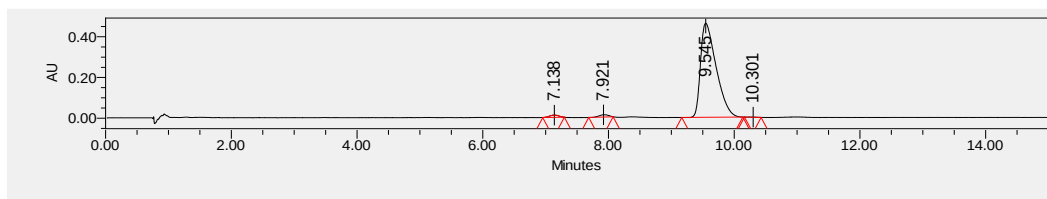
^{13}C NMR (101 MHz, CDCl_3) δ 165.2, 145.9, 143.9, 139.3, 137.1, 128.7, 128.5, 128.4, 128.0, 127.6, 126.9, 126.4, 124.9, 124.3, 122.7, 80.3, 47.3, 46.5, 40.8, 35.1 ppm.

ESI-HRMS calcd for $[\text{C}_{24}\text{H}_{21}\text{NO}_2\text{S}+\text{Na}^+] = 410.1185$, found 410.1188.

IR $\tilde{\nu}$ (cm^{-1}) 2917, 2360, 1690, 1494, 1453, 1240, 1102, 1047, 850, 734, 697.

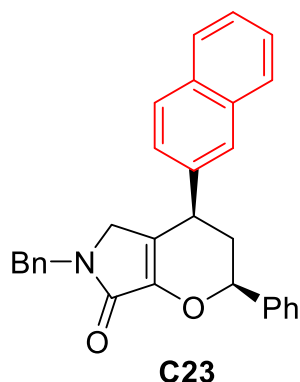


	Retention Time	Area	% Area	Height
1	7.153	2984668	17.66	254189
2	7.893	3031083	17.93	216450
3	9.546	5463652	32.33	352217
4	10.163	5422287	32.08	323135



	Retention Time	Area	% Area	Height
1	7.138	114864	1.40	11181
2	7.921	116923	1.42	11196
3	9.545	7981838	97.12	462523
4	10.301	4666	0.06	794

C23: (2S,4R)-6-benzyl-4-(naphthalen-2-yl)-2-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



C23: 69% yield, endo/exo = 86/14, 92%/68% ee; Colorless liquid, $[\alpha]^{25}_D = -24.0$ ($c = 0.52$, in CH_2Cl_2).

HPLC (Daicel chiralcel ID, n -hexane/ i -PrOH 70/30, 1.0 mL/min, $\lambda = 210$ nm), $t_1 = 32.66$ min, $t_2 = 34.91$ min, $t_3 = 38.97$ min, $t_4 = 59.80$ min.

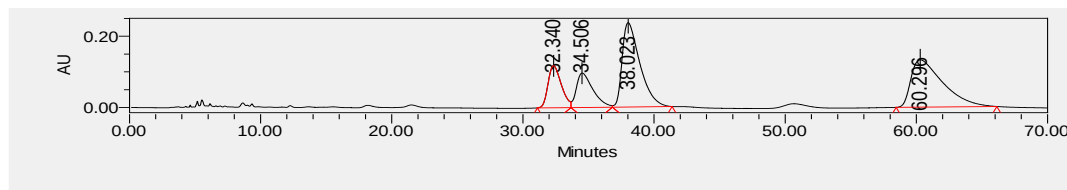
^1H NMR (400 MHz, Chloroform- d) δ 7.78 (ddt, $J = 13.2, 9.0, 5.0$ Hz, 3H), 7.59 (d, $J = 15.0$ Hz, 1H), 7.47 (dq, $J = 11.2, 5.2$ Hz, 4H), 7.39 – 7.29 (m, 4H), 7.29 – 7.26 (m, 2H), 7.25 – 7.13 (m, 4H), 5.18 (d, $J = 9.2$ Hz, 1H), 4.89 – 4.80 (d, $J = 15.0$ Hz, 1H), 4.37 (d, $J = 15.0$ Hz, 1H), 4.09 (td, $J = 11.0, 6.8$ Hz, 1H), 3.76 – 3.36 (m, 2H), 2.49 (ddd, $J = 14.2, 6.0, 1.6$ Hz, 1H), 2.34 – 2.19 (m, 1H) ppm.

Endo C23: ^{13}C NMR (101 MHz, CDCl_3) δ 165.4, 146.9, 140.4, 139.6, 138.6, 137.1, 133.5, 132.7, 132.5, 128.9, 128.8, 128.5, 128.4, 128.3, 128.2, 128.1, 127.8, 127.7, 127.6, 126.6, 126.5, 126.4, 126.2, 126.0, 125.2, 123.4, 80.2, 47.4, 46.5, 40.5, 40.2, ppm.

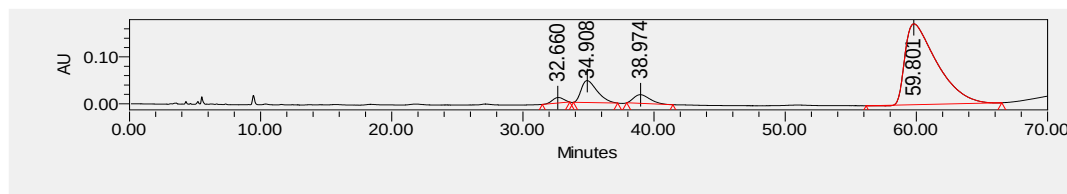
Exo C23: ^{13}C NMR (101 MHz, CDCl_3) δ 165.4, 146.9, 140.4, 139.6, 138.6, 137.1, 133.4, 132.7, 132.5, 128.9, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 127.8, 127.7, 127.5, 126.6, 126.5, 126.4, 126.2, 126.0, 125.2, 123.4, 75.6, 48.1, 46.7, 38.3, 37.1 ppm.

ESI-HRMS calcd for $[\text{C}_{30}\text{H}_{25}\text{NO}_2 + \text{Na}^+] = 454.1778$, found 454.1783.

IR $\tilde{\nu}$ (cm^{-1}) 3054, 2360, 1693, 1494, 1453, 1240, 1106, 1047, 821, 732, 698.

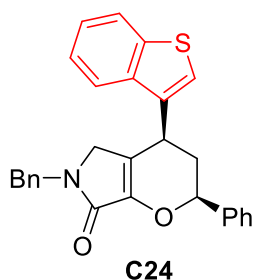


	Retention Time	Area	% Area	Height
1	32.340	8308514	13.54	117874
2	34.506	8430368	13.74	96469
3	38.023	22219063	36.20	236507
4	60.296	22413087	36.52	132686



	Retention Time	Area	% Area	Height
1	32.660	703477	1.99	11834
2	34.908	3963171	11.19	47014
3	38.974	1571625	4.44	18425
4	59.801	29164097	82.38	172723

C24: (2S,4S)-4-(benzo[b]thiophen-3-yl)-6-benzyl-2-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



C24: 95% yield, endo/exo = 99/1, 99%/20% ee; Colorless liquid, $[\alpha]_D^{25} = -59.9$ ($c = 0.86$, in CH_2Cl_2).

HPLC (Daicel chiralcel IB(N5), *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, $\lambda = 210$ nm), $t_1 = 22.65$ min, $t_2 = 31.09$ min, $t_3 = 33.41$ min, $t_4 = 38.82$ min.

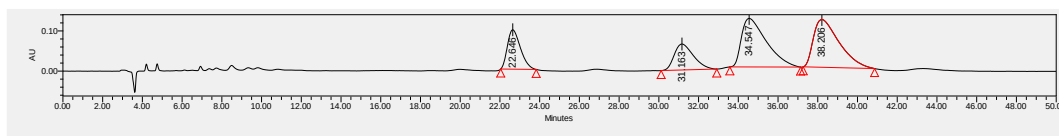
^1H NMR (400 MHz, Chloroform- d) δ 7.84 (dd, $J = 6.0, 2.8$ Hz, 1H), 7.70 (dq, $J = 7.0, 3.6$ Hz, 1H), 7.46 (d, $J = 7.0$ Hz, 2H), 7.33 (dtd, $J = 13.6, 7.0, 6.6, 2.0$ Hz, 5H), 7.27 (dd, $J = 8.4, 1.8$ Hz, 2H), 7.24 – 7.21 (m, 1H), 7.17 (d, $J = 8.4$ Hz, 3H), 5.27 – 5.20 (m, 1H), 4.77 (d, $J = 15.0$ Hz, 1H), 4.40 (dd, $J =$

16.0, 8.4 Hz, 2H), 3.66 – 3.58 (m, 1H), 3.40 (d, $J = 18.2$ Hz, 1H), 2.50 – 2.42 (m, 2H) ppm.

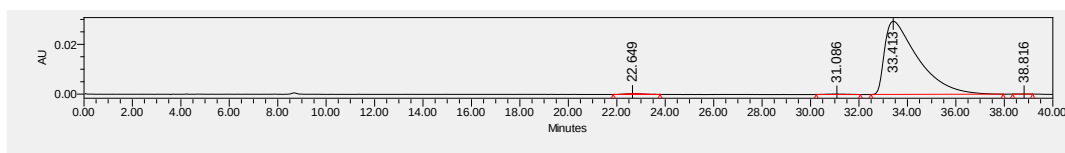
^{13}C NMR (101 MHz, CDCl_3) δ 165.3, 146.6, 141.0, 139.4, 137.3, 137.1, 135.0, 128.7, 128.5, 128.3, 127.9, 127.6, 126.4, 124.6, 124.4, 123.5, 123.3, 122.6, 121.5, 80.3, 47.6, 46.4, 38.0, 34.4, 25.4 ppm.

ESI-HRMS calcd for $[\text{C}_{28}\text{H}_{23}\text{NO}_2\text{S} + \text{Na}^+] = 460.1342$, found 460.1346.

IR $\tilde{\nu}$ (cm^{-1}) 3061, 2360, 1692, 1494, 1454, 1241, 1119, 1045, 931, 734, 698.

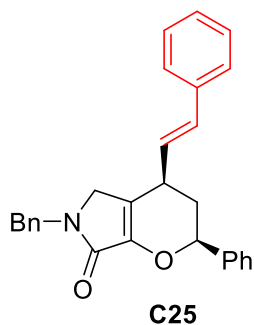


	Retention Time	Area	% Area	Height
1	22.646	4465135	14.84	98022
2	31.163	4351132	14.46	64668
3	34.547	10521388	34.97	120724
4	38.206	10749983	35.73	118913



	Retention Time	Area	% Area	Height
1	22.649	16445	0.58	347
2	31.086	11301	0.40	196
3	33.413	2807565	98.98	29356
4	38.816	1095	0.04	48

C25: (2S,4R)-6-benzyl-2-phenyl-4-((E)-styryl)-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



C25: 30% yield, endo/exo = 85/15, 97%/83% ee; Colorless liquid, $[\alpha]_D^{25} = -15.0$ ($c = 0.20$, in CH_2Cl_2).

SFC Chiralcel OJ-3, $\text{CO}_2/\text{MeOH}=80/20$. 1.5mL/ min, $\lambda = 210$ nm, retention time: $t_1 = 10.90$ min, $t_2 = 14.28$ min, $t_3 = 15.20$ min, $t_4 = 17.69$ min.

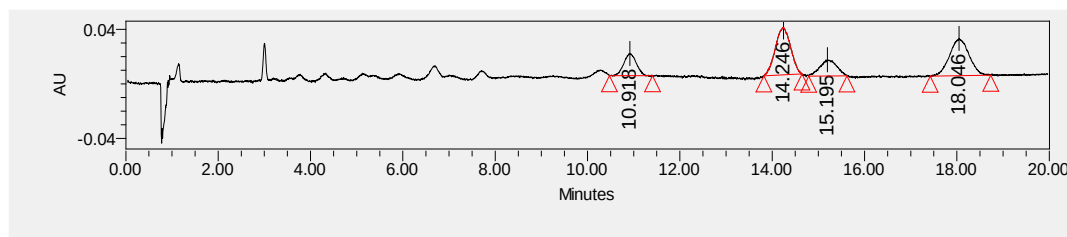
^1H NMR (400 MHz, $\text{CHloroform-}d$) δ 7.44 (d, $J = 7.0$ Hz, 2H), 7.38 (d, $J = 7.0$ Hz, 2H), 7.35 (d, $J = 3.4$ Hz, 2H), 7.34 – 7.31 (m, 4H), 7.30 (d, $J = 4.4$ Hz, 5H), 7.27 (m, 1H), 6.51 (d, $J = 15.0$ Hz, 1H), 5.94 (dd, $J = 15.0, 8.8$ Hz, 1H), 5.09 (d, $J = 10.6$ Hz, 1H), 4.74 (d, $J = 15.0$ Hz, 1H), 4.57 – 4.49 (m, 2H), 3.68 (s, 2H), 2.37 – 2.25 (m, 1H), 2.06 – 1.99 (m, 1H) ppm.

Endo C25: ^{13}C NMR (101 MHz, CDCl_3) δ 165.3, 145.8, 139.7, 137.2, 136.4, 132.5, 129.2, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.2, 127.9, 127.9, 127.8, 127.6, 126.4, 126.3, 126.2, 122.6, 79.7, 47.6, 46.6, 43.8, 37.9, 37.5 ppm.

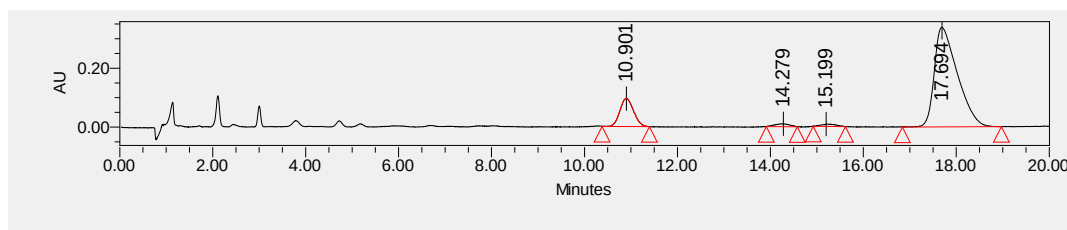
Exo C25: ^{13}C NMR (101 MHz, CDCl_3) δ 159.6, 145.8, 139.7, 137.2, 136.4, 132.5, 129.2, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.2, 127.9, 127.9, 127.8, 127.6, 126.4, 126.3, 126.2, 122.6, 70.5, 47.6, 46.6, 43.8, 37.9, 37.5 ppm.

ESI-HRMS calcd for $[\text{C}_{28}\text{H}_{25}\text{NO}_2 + \text{Na}^+] = 430.1778$, found 430.1784.

IR $\tilde{\nu}$ (cm^{-1}) 2918, 2360, 1698, 1521, 1454, 1243, 751, 698.

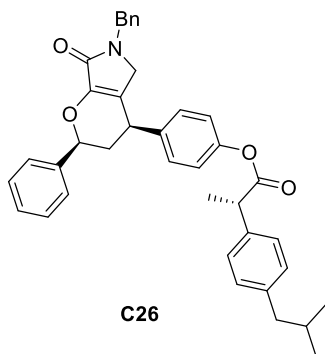


	Retention Time	Area	% Area	Height
1	10.918	306278	13.94	16246
2	14.246	795094	36.19	35035
3	15.195	300587	13.68	11839
4	18.046	795254	36.19	27285



	Retention Time	Area	% Area	Height
1	10.901	1938658	13.86	95149
2	14.279	223234	1.60	10349
3	15.199	179979	1.29	8237
4	17.694	11643277	83.25	337598

C26: 4-((2S,4R)-6-benzyl-7-oxo-2-phenyl-2,3,4,5,6,7-hexahydropyrano[2,3-c]pyrrol-4-yl)phenyl (S)-2-(4-isobutylphenyl)propanoate



C26: 97% yield, endo/exo = 92.3/7.7, dr (endo) = 90.8:1.5, dr (exo) = 6.8:0.9; Colorless liquid, $[\alpha]_D^{26} = 27.0$ ($c = 1.09$, in CH_2Cl_2).

HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/ min, $\lambda = 210$ nm), retention time: $t_1 = 14.67$ min, $t_2 = 23.51$ min, $t_3 = 25.66$ min, $t_4 = 46.26$ min.

^1H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.36 (m, 2H), 7.35 (d, $J = 6.8$ Hz, 1H), 7.32 (dd, $J = 4.0, 2.0$ Hz, 2H), 7.30 – 7.24 (m, 5H), 7.23 – 7.18 (m, 2H), 7.12 (dt, $J = 13.8, 6.0$ Hz, 4H), 6.99 – 6.86 (m, 2H), 5.13 (d, $J = 10.6$ Hz, 1H), 4.84 (d, $J = 14.8$ Hz, 1H), 4.35 (d, $J =$

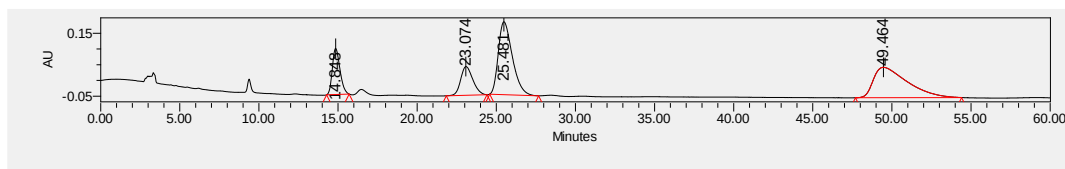
14.8 Hz, 1H), 3.90 (dq, $J = 12.8, 6.4, 6.0$ Hz, 2H), 3.59 – 3.33 (m, 2H), 2.46 (d, $J = 7.2$ Hz, 2H), 2.40 (ddd, $J = 14.0, 6.0, 1.6$ Hz, 1H), 2.10 (dt, $J = 14.0, 11.2$ Hz, 1H), 1.86 (dt, $J = 13.6, 6.8$ Hz, 1H), 1.58 (d, $J = 7.2$ Hz, 3H), 0.90 (d, $J = 6.6$ Hz, 6H) ppm.

Endo C26: ^{13}C NMR (101 MHz, CDCl_3) δ 173.3, 165.2, 149.9, 146.8, 140.9, 139.5, 138.6, 137.1, 137.0, 129.6, 128.8, 128.7, 128.5, 128.4, 128.3, 128.2, 127.6, 127.2, 126.4, 123.1, 121.9, 80.2, 47.3, 46.5, 45.2, 45.1, 40.7, 39.4, 30.2, 22.4, 18.2 ppm.

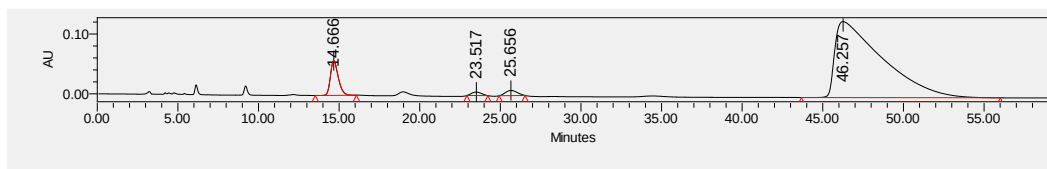
Exo C26: ^{13}C NMR (101 MHz, CDCl_3) δ 173.3, 165.2, 149.8, 146.9, 141.2, 139.7, 138.7, 137.2, 137.0, 129.6, 128.8, 128.7, 128.5, 128.4, 128.3, 128.2, 127.7, 127.3, 126.2, 123.1, 120.5, 75.5, 48.0, 46.6, 45.2, 45.1, 38.5, 36.4, 30.2, 22.4, 18.5 ppm.

ESI-HRMS calcd for $[\text{C}_{39}\text{H}_{39}\text{NO}_4 + \text{Na}^+] = 608.2771$, found 608.2778.

IR $\tilde{\nu}$ (cm^{-1}) 2954, 2360, 1752, 1697, 1540, 1454, 1241, 1139, 1071, 869, 848, 752, 699.

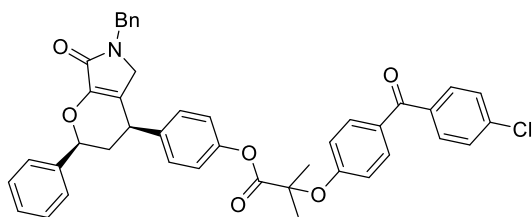


	Retention Time	Area	% Area	Height
1	14.848	4921416	12.82	146608
2	23.074	4861410	12.67	91292
3	25.481	14250248	37.13	231630
4	49.464	14342419	37.37	96553



	Retention Time	Area	% Area	Height
1	14.666	1961781	6.83	58116
2	23.517	251123	0.87	5883
3	25.656	442558	1.54	8698
4	46.257	26057609	90.75	126990

C27: 4-((2S,4R)-6-benzyl-7-oxo-2-phenyl-2,3,4,5,6,7-hexahydropyrano[2,3-c]pyrrol-4-yl)phenyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate



C27

C27: 86% yield, endo/exo = 90.5/9.5, ee: 98%/93%; Colorless liquid, $[\alpha]_D^{26} = -16.1$ ($c = 0.99$, in CH_2Cl_2).

HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, $\lambda = 210$ nm), retention time: $t_1 = 32.33$ min, $t_2 = 40.16$ min, $t_3 = 45.46$ min, $t_4 = 79.81$ min.

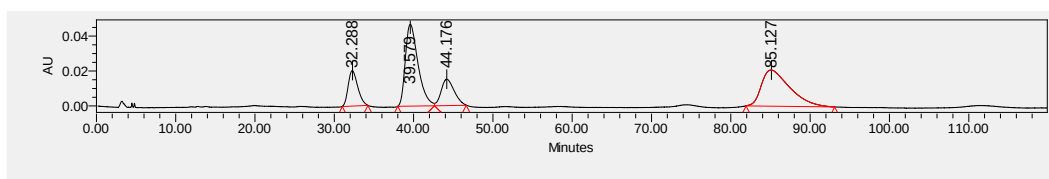
^1H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.68 (m, 4H), 7.54 – 7.37 (m, 4H), 7.37 – 7.26 (m, 6H), 7.24 – 7.18 (m, 2H), 7.18 – 7.11 (m, 2H), 7.02 – 6.87 (m, 4H), 5.14 (d, $J = 10.4$ Hz, 1H), 4.83 (dd, $J = 15.0, 11.2$ Hz, 1H), 4.36 (d, $J = 15.0$ Hz, 1H), 3.92 (dd, $J = 10.8, 6.0$ Hz, 1H), 3.61 – 3.34 (m, 2H), 2.50 – 2.34 (m, 1H), 2.11 (dt, $J = 14.0, 11.2$ Hz, 1H), 1.81 (s, 6H) ppm.

Endo C27: ^{13}C NMR (101 MHz, CDCl_3) δ 194.2, 172.5, 165.2, 159.5, 149.5, 146.9, 139.4, 139.3, 138.6, 137.0, 136.2, 132.6, 131.5, 130.2, 128.8, 128.7, 128.6, 128.5, 128.3, 128.1, 127.6, 126.3, 122.8, 121.7, 117.3, 80.1, 79.4, 47.2, 46.5, 40.8, 39.4, 25.5, 25.4 ppm.

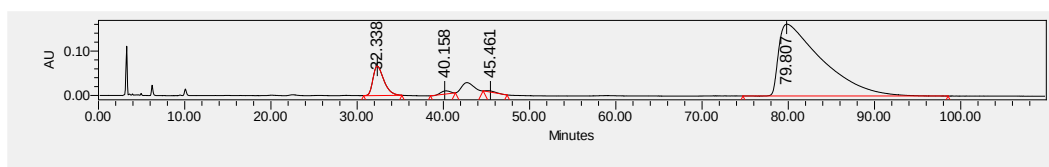
Exo C27: ^{13}C NMR (101 MHz, CDCl_3) δ 194.2, 172.5, 164.7, 159.4, 149.4, 146.8, 139.4, 139.3, 138.6, 137.0, 136.2, 132.2, 131.2, 130.7, 128.8, 128.7, 128.6, 128.5, 128.3, 128.1, 127.7, 126.2, 122.4, 120.8, 117.3, 76.0, 75.5, 47.9, 46.6, 38.3, 36.4, 25.5, 25.4 ppm.

ESI-HRMS calcd for $[\text{C}_{43}\text{H}_{36}\text{ClNO}_6 + \text{Na}^+] = 720.2123$, found 720.2129.

IR $\tilde{\nu}$ (cm^{-1}) 2922, 2360, 1752, 1697, 1651, 1596, 1504, 1243, 1166, 1113, 927, 852, 699.

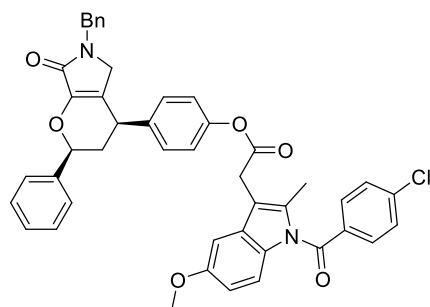


	Retention Time	Area	% Area	Height
1	32.288	1695673	12.32	20361
2	39.579	5199088	37.79	46938
3	44.176	1720197	12.50	15163
4	85.127	5143992	37.39	20743



	Retention Time	Area	% Area	Height
1	32.338	5806013	9.21	66239
2	40.158	528425	0.84	7097
3	45.461	197839	0.31	2766
4	79.807	56476754	89.63	161743

C28: 4-((2S,4R)-6-benzyl-7-oxo-2-phenyl-2,3,4,5,6,7-hexahydropyrano[2,3-c]pyrrol-4-yl)phenyl 2-(1-(4-chlorobenzoyl)-2-methyl-1H-indol-3-yl)acetate



C28

C28: 86% yield, endo/exo = 91.6/8.4, ee: 99%/80%; Colorless liquid, $[\alpha]_D^{26} = -18.6$ ($c = 1.16$, in CH_2Cl_2).

HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, $\lambda = 210$ nm), retention time: $t_1 = 54.56$ min, $t_2 = 70.49$ min, $t_3 = 80.90$ min, $t_4 = 89.36$ min.

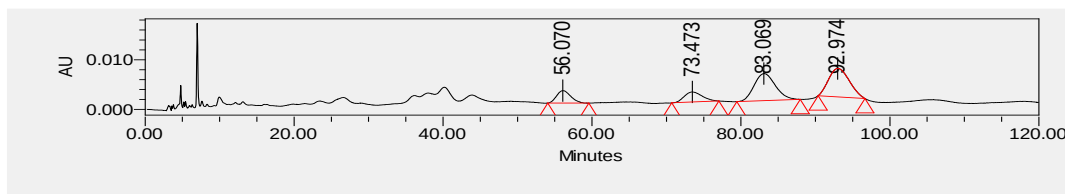
^1H NMR (400 MHz, Chloroform- d) δ 7.66 (dd, $J = 8.8, 2.0$ Hz, 2H), 7.51 – 7.44 (m, 2H), 7.42 (d, $J = 7.0$ Hz, 2H), 7.34 (m, 1H), 7.33 – 7.26 (m, 4H), 7.26 (m, 1H), 7.24 – 7.18 (m, 2H), 7.12 (d, $J = 8.8$ Hz, 2H), 7.09 – 6.93 (m, 3H), 6.88 (d, $J = 9.0$ Hz, 1H), 6.69 (dd, $J = 9.0, 2.4$ Hz, 1H), 5.13 (d, $J = 10.8$ Hz, 1H), 4.83 (d, $J = 15.0$ Hz, 1H), 4.36 (d, $J = 15.0$ Hz, 1H), 3.91 (d, $J = 7.6$ Hz, 3H), 3.82 (s, 3H), 3.65 – 3.38 (m, 2H), 2.45 (d, $J = 5.2$ Hz, 4H), 2.10 (dt, $J = 14.0, 11.2$ Hz, 1H) ppm.

Endo C28: ^{13}C NMR (101 MHz, CDCl_3) δ 169.3, 168.3, 165.2, 156.1, 149.8, 146.9, 139.5, 139.4, 138.9, 137.1, 136.3, 133.8, 131.2, 130.9, 130.5, 129.2, 128.8, 128.6, 128.5, 128.3, 128.2, 128.1, 127.6, 126.4, 122.9, 121.9, 115.1, 111.9, 111.7, 101.3, 80.2, 47.3, 46.5, 40.8, 39.4, 30.6, 13.5 ppm.

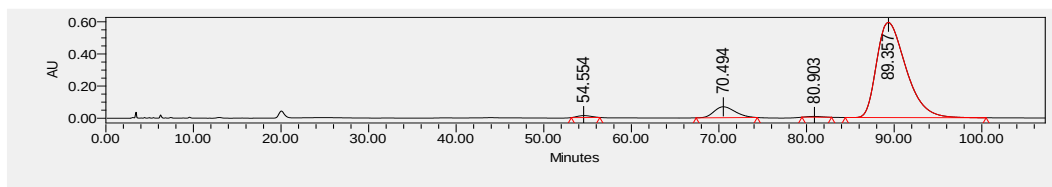
Exo C28: ^{13}C NMR (101 MHz, CDCl_3) δ 169.4, 168.3, 165.2, 156.1, 149.7, 147.0, 140.6, 139.5, 138.5, 137.0, 136.3, 133.8, 131.2, 130.9, 130.5, 129.2, 128.8, 128.5, 128.4, 128.3, 128.2, 128.1, 127.7, 126.2, 122.9, 120.4, 116.0, 111.9, 111.7, 101.3, 75.5, 47.9, 46.6, 40.8, 36.6, 30.6, 14.2 ppm.

ESI-HRMS calcd for $[\text{C}_{44}\text{H}_{35}\text{ClN}_2\text{O}_5 + \text{Na}^+] = 759.2232$, found 729.2239.

IR $\tilde{\nu}$ (cm^{-1}) 2924, 2360, 1947, 1699, 1650, 1557, 1540, 1521, 1747, 1318, 1260, 1128, 699.

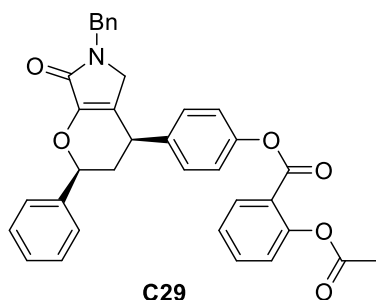


	Retention Time	Area	% Area	Height
1	56.070	330500	11.54	2510
2	73.473	337888	11.79	2033
3	83.069	1082810	37.80	5467
4	92.974	1113739	38.87	5738



	Retention Time	Area	% Area	Height
1	54.554	1292177	0.86	12053
2	70.494	11386510	7.55	67907
3	80.903	573030	0.38	4808
4	89.357	137655870	91.22	592959

C29: 4-((2S,4R)-6-benzyl-7-oxo-2-phenyl-2,3,4,5,6,7-hexahydropyrano[2,3-c]pyrrol-4-yl)phenyl 2-acetoxybenzoate



C29: 91% yield, endo/exo = 94.0/6.0, ee: 97%/85%; Colorless liquid, $[\alpha]_D^{26} = -25.5$ ($c = 0.80$, in CH_2Cl_2).

HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, $\lambda = 210$ nm), retention time: $t_1 = 12.72$ min, $t_2 = 14.54$ min, $t_3 = 16.69$ min, $t_4 = 25.10$ min.

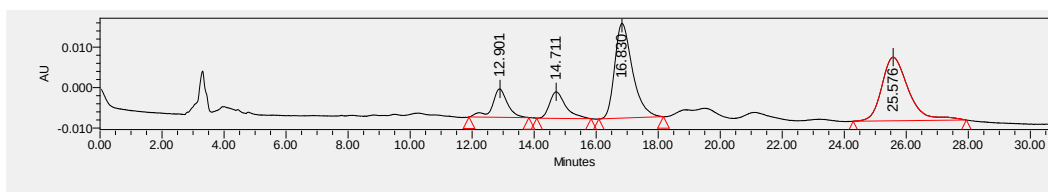
^1H NMR (400 MHz, Chloroform-*d*) δ 8.42 – 8.04 (m, 1H), 7.89 – 7.51 (m, 1H), 7.43 (t, $J = 9.6$ Hz, 2H), 7.37 (d, $J = 8.4$ Hz, 2H), 7.34 – 7.27 (m, 4H), 7.23 (dd, $J = 13.6, 6.4$ Hz, 4H), 7.20 – 7.15

(m, 2H), 7.11 (d, $J = 8.4$ Hz, 2H), 5.16 (d, $J = 11.2$ Hz, 1H), 4.86 (d, $J = 14.8$ Hz, 1H), 4.55 – 4.34 (m, 1H), 3.95 (dd, $J = 10.8, 6.0$ Hz, 1H), 3.70 – 3.42 (m, 2H), 2.44 (dd, $J = 13.2, 5.6$ Hz, 1H), 2.30 (s, 3H), 2.15 (q, $J = 11.4$ Hz, 1H) ppm.

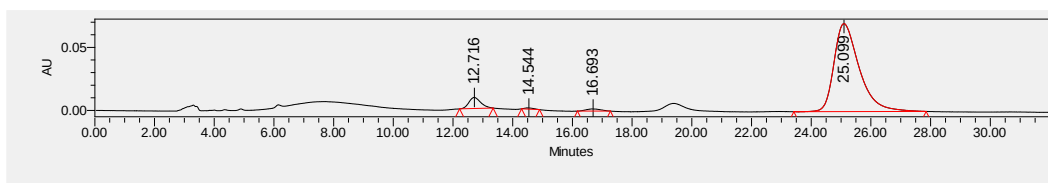
^{13}C NMR (101 MHz, CDCl_3) δ 169.7, 165.2, 162.9, 151.2, 149.6, 146.9, 139.5, 139.1, 137.1, 134.8, 132.2, 128.8, 128.7, 128.5, 128.3, 128.2, 127.7, 126.4, 126.3, 126.2, 124.1, 122.9, 122.4, 122.3, 80.2, 47.3, 46.5, 40.9, 39.5, 21.1 ppm.

ESI-HRMS calcd for $[\text{C}_{35}\text{H}_{29}\text{NO}_6 + \text{Na}^+]$ = 582.1887, found 582.1889.

IR $\tilde{\nu}$ (cm^{-1}) 2925, 2360, 1739, 1693, 1605, 1504, 1453, 1287, 1242, 1190, 1164, 1050, 751, 700.

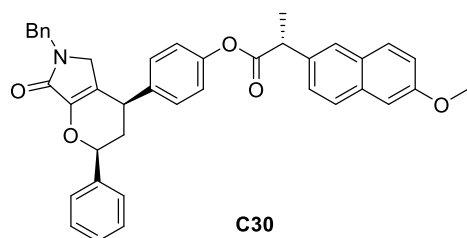


	Retention Time	Area	% Area	Height
1	12.901	240202	10.24	7043
2	14.711	236696	10.09	6581
3	16.830	931134	39.71	23413
4	25.576	936732	39.95	15711



	Retention Time	Area	% Area	Height
1	12.716	242901	5.49	8824
2	14.544	19590	0.44	948
3	16.693	59629	1.35	1718
4	25.099	4098870	92.71	69813

C30: 4-((2S,4R)-6-benzyl-7-oxo-2-phenyl-2,3,4,5,6,7-hexahydropyrano[2,3-c]pyrrol-4-yl)phenyl (R)-2-(6-methoxynaphthalen-2-yl)propanoate



C30: 95% yield, endo/exo = 87.7/12.3, dr (endo) = 83.6:4.1, dr (exo) = 9.9:2.4; Colorless liquid, $[\alpha]^{26}_D = 36.4$ ($c = 0.98$, in CH_2Cl_2).

SFC Chiralcel OD-3, $\text{CO}_2/i\text{-PrOH} = 70/30$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 22.67$ min, $t_2 = 24.67$ min, $t_3 = 26.55$ min, $t_4 = 31.38$ min.

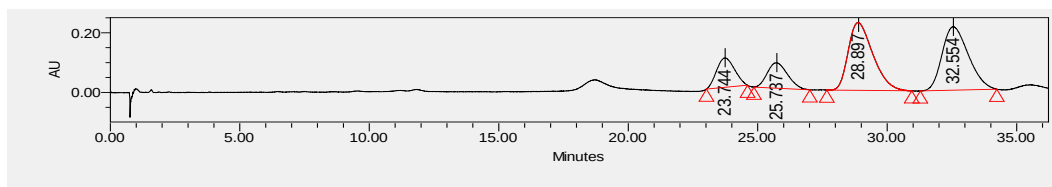
^1H NMR (400 MHz, Chloroform- d) δ 7.72 (t, $J = 7.0$ Hz, 3H), 7.52 – 7.44 (m, 1H), 7.44 – 7.35 (m, 2H), 7.31 (dd, $J = 12.8, 7.0$ Hz, 4H), 7.26 (d, $J = 8.2$ Hz, 2H), 7.19 (d, $J = 7.0$ Hz, 2H), 7.17 – 7.12 (m, 2H), 7.07 (d, $J = 8.2$ Hz, 2H), 6.93 (dd, $J = 16.8, 8.2$ Hz, 2H), 5.11 (d, $J = 10.8$ Hz, 1H), 4.82 (d, $J = 14.8$ Hz, 1H), 4.34 (d, $J = 14.8$ Hz, 1H), 4.06 (q, $J = 7.2$ Hz, 1H), 3.91 (s, 3H), 3.87 (dd, $J = 10.8, 6.2$ Hz, 1H), 3.62 – 3.26 (m, 2H), 2.48 – 2.31 (m, 1H), 2.08 (dd, $J = 11.2, 2.4$ Hz, 1H), 1.67 (d, $J = 7.0$ Hz, 3H) ppm.

Endo C30: ^{13}C NMR (101 MHz, CDCl_3) δ 173.2, 165.2, 157.8, 149.9, 146.8, 139.6, 138.4, 137.0, 134.7, 133.8, 129.3, 129.0, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.6, 127.4, 126.3, 126.2, 126.1, 123.0, 121.9, 121.9, 119.2, 105.7, 80.1, 55.4, 47.3, 46.5, 45.6, 40.7, 39.4, 18.5 ppm.

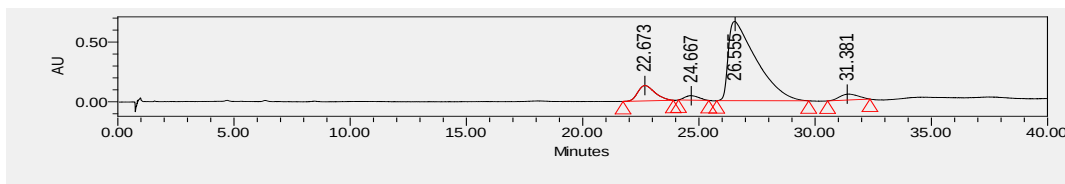
Exo C30: ^{13}C NMR (101 MHz, CDCl_3) δ 173.3, 165.2, 157.8, 149.9, 146.9, 139.5, 138.7, 137.1, 135.0, 133.9, 129.3, 129.0, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.6, 127.4, 126.3, 126.2, 126.1, 123.0, 121.9, 121.9, 119.2, 105.7, 75.5, 60.4, 47.9, 46.5, 45.6, 38.5, 36.4, 20.6 ppm.

ESI-HRMS calcd for $[\text{C}_{40}\text{H}_{35}\text{NO}_5 + \text{Na}^+] = 632.2407$, found 632.2415.

IR $\tilde{\nu}$ (cm^{-1}) 2934, 2360, 1750, 1696, 1604, 1504, 1454, 1240, 1198, 1165, 1029, 852, 733, 698.

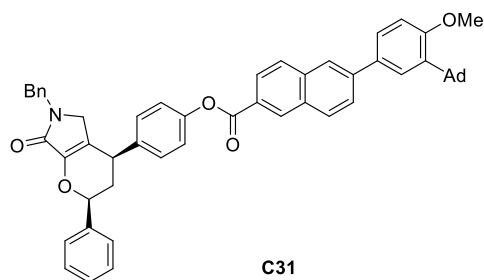


	Retention Time	Area	% Area	Height
1	23.744	4749125	12.04	99042
2	25.737	4647809	11.78	85828
3	28.897	15040896	38.12	227468
4	32.554	15022967	38.07	213430



	Retention Time	Area	% Area	Height
1	22.673	6582080	9.92	129613
2	24.667	1564949	2.36	37652
3	26.555	55452828	83.59	663066
4	31.381	2739471	4.13	49501

C31: 4-((2S,4R)-6-benzyl-7-oxo-2-phenyl-2,3,4,5,6,7-hexahydropyrano[2,3-c]pyrrol-4-yl)phenyl 6-(3-((3S)-adamantan-1-yl)-4-methoxyphenyl)-2-naphthoate



C31

C31: 62% yield, endo/exo = 95.3/4.7, ee: 98%/73%;

Colorless liquid, $[\alpha]_D^{26} = -12.6$ ($c = 0.53$, in CH_2Cl_2).

HPLC (Daicel chiralcel IB-N5, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, $\lambda = 210$ nm), retention time: $t_1 = 203.20$ min, $t_2 = 227.70$ min, $t_3 = 244.04$ min, $t_4 = 268.95$ min.

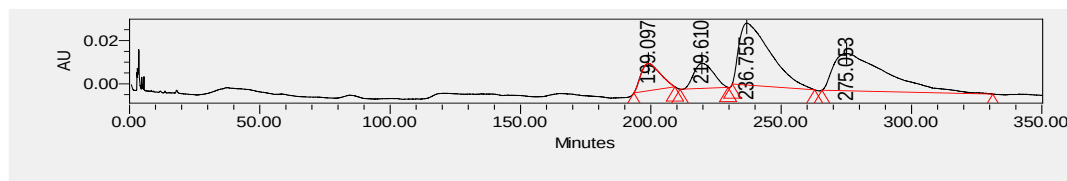
^1H NMR (400 MHz, CHCl_3 - d) δ 8.76 (d, $J = 5.8$ Hz, 1H), 8.19 – 8.14 (m, 1H), 8.06 – 8.01 (m, 2H), 7.97 (d, $J = 8.8$ Hz, 1H), 7.85 – 7.81 (m, 1H), 7.63 – 7.61 (m,

1H), 7.58 – 7.55 (m, 1H), 7.46 (d, $J = 7.0$ Hz, 2H), 7.38 (d, $J = 7.0$ Hz, 2H), 7.32 (dd, $J = 10.8, 6.4$ Hz, 4H), 7.27 – 7.22 (m, 6H), 7.01 (d, $J = 8.8$ Hz, 1H), 5.18 (d, $J = 11.2$ Hz, 1H), 4.87 (d, $J = 15.0$ Hz, 1H), 4.40 (d, $J = 15.0$ Hz, 1H), 3.97 (dd, $J = 10.8, 6.4$ Hz, 1H), 3.91 (s, 3H), 3.71 – 3.44 (m, 2H), 2.47 (dd, $J = 12.8, 6.0$ Hz, 1H), 2.19 (m, 6H), 2.11 (m, 3H), 1.81 (m, 7H) ppm.

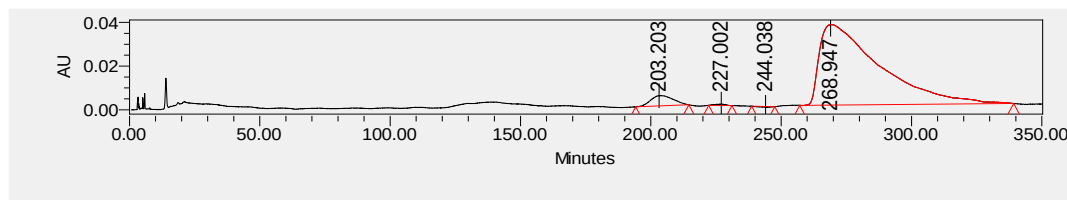
^{13}C NMR (101 MHz, CDCl_3) δ 165.4, 165.3, 159.1, 150.2, 146.9, 141.9, 139.1, 139.0, 138.8, 137.1, 136.3, 132.4, 131.8, 131.2, 129.9, 128.9, 128.8, 128.6, 128.5, 128.4, 128.3, 128.2, 127.9, 127.7, 126.7, 126.4, 126.0, 125.9, 125.8, 125.8, 124.78, 123.1, 122.4, 112.2, 80.2, 55.2, 47.4, 46.6, 40.9, 40.6, 39.5, 37.2, 37.1, 29.1 ppm.

ESI-HRMS calcd for $[\text{C}_{54}\text{H}_{49}\text{NO}_5 + \text{Na}^+] = 814.3503$, found 814.3514.

IR $\tilde{\nu}$ (cm^{-1}) 2903, 2360, 1734, 1684, 1557, 1507, 1472, 1276, 1175, 699, 420.

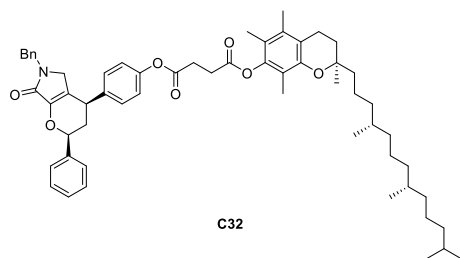


	Retention Time	Area	% Area	Height
1	199.097	6441818	10.48	12668
2	219.610	6102853	9.93	11651
3	236.755	24252912	39.45	28619
4	275.053	24681666	40.15	17222



	Retention Time	Area	% Area	Height
1	203.203	2774993	4.49	4687
2	227.002	172413	0.28	653
3	244.038	113402	0.18	-406
4	268.947	58777612	95.05	36953

C32: 4-((2S,4R)-6-benzyl-7-oxo-2-phenyl-2,3,4,5,6,7-hexahydropyrano[2,3-c]pyrrol-4-yl)phenyl ((R)-2,5,6,8-tetramethyl-2-((4S,8S)-4,8,12-trimethyltridecyl)chroman-7-yl) succinate



C32: 70% yield, endo/exo = 94.3/5.7, dr (endo) = 93.8:0.5, dr (exo) = 5.2:0.5; Colorless liquid, $[\alpha]^{26}_D = -12.9$ ($c = 0.90$, in CH_2Cl_2).

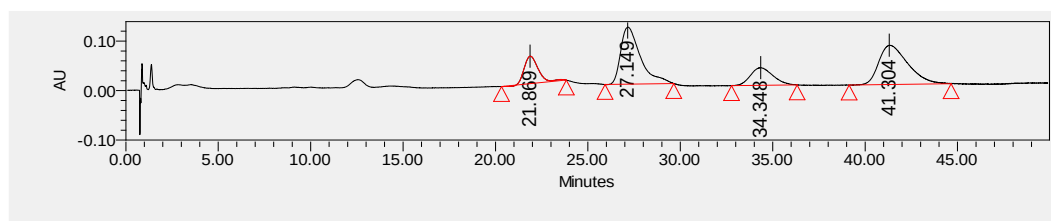
SFC Chiralcel OD-3, $\text{CO}_2/\text{i-PrOH} = 70/30$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 22.43$ min, $t_2 = 27.08$ min, $t_3 = 35.92$ min, $t_4 = 43.53$ min.

^1H NMR (400 MHz, $\text{Chloroform-}d$) δ 7.48 – 7.37 (m, 2H), 7.35 (m, 1H), 7.34 – 7.28 (m, 4H), 7.28 – 7.25 (m, 1H), 7.25 – 7.20 (m, 2H), 7.14 (d, $J = 8.4$ Hz, 2H), 7.02 (d, $J = 8.4$ Hz, 2H), 5.15 (d, $J = 10.8$ Hz, 1H), 4.85 (d, $J = 14.8$ Hz, 1H), 4.38 (d, $J = 15.0$ Hz, 1H), 3.91 (dd, $J = 10.8, 6.0$ Hz, 1H), 3.49 (q, $J = 18.4$ Hz, 2H), 3.13 – 2.92 (m, 4H), 2.58 (t, $J = 6.4$ Hz, 2H), 2.47 – 2.38 (m, 1H), 2.18 – 2.10 (m, 1H), 2.08 (s, 3H), 2.01 (s, 3H), 1.96 (s, 3H), 1.77 (dt, $J = 13.2, 6.8$ Hz, 2H), 1.57 – 1.49 (m, 3H), 1.48 – 1.31 (m, 6H), 1.29 – 1.20 (m, 10H), 1.17 – 1.11 (m, 3H), 1.11 – 1.00 (m, 4H), 0.86 (d, $J = 6.8$ Hz, 10H) ppm.

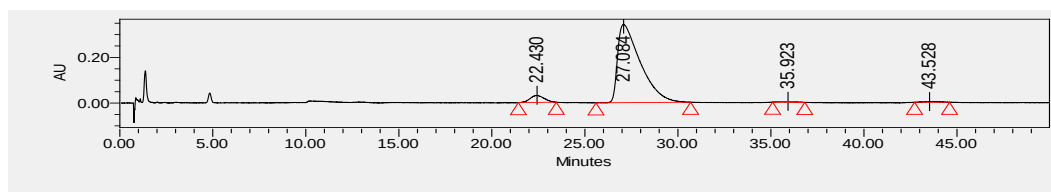
^{13}C NMR (101 MHz, CDCl_3) δ 170.9, 170.8, 165.3, 149.7, 149.5, 146.9, 140.4, 139.5, 138.8, 137.1, 128.8, 128.6, 128.5, 128.3, 128.2, 127.6, 126.7, 126.4, 124.9, 123.1, 123.0, 122.1, 117.5, 80.2, 75.1, 47.3, 46.6, 40.8, 39.5, 39.4, 37.5, 37.5, 37.3, 32.8, 32.7, 29.3, 28.8, 28.0, 24.8, 24.5, 22.8, 22.7, 21.1, 20.6, 19.8, 19.7, 13.0, 12.2, 11.9 ppm.

ESI-HRMS calcd for $[\text{C}_{59}\text{H}_{75}\text{NO}_7 + \text{Na}^+] = 932.5436$, found 932.5450.

IR $\tilde{\nu}$ (cm^{-1}) 2924, 2360, 1750, 1698, 1673, 1540, 1456, 1360, 1241, 1199, 1131, 888, 751, 699.



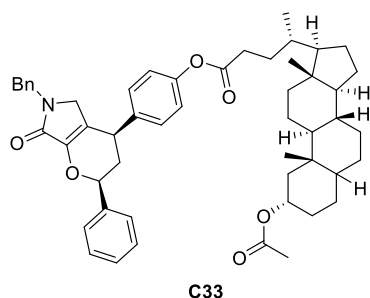
	Retention Time	Area	% Area	Height
1	21.869	2952997	12.73	55702
2	27.149	8593097	37.03	115412
3	34.348	3006625	12.96	35746
4	41.304	8650463	37.28	79353



	Retention Time	Area	% Area	Height
1	22.430	1615169	5.21	31601
2	27.084	29054850	93.81	343713
3	35.923	152038	0.49	4340

4	43.528	150868	0.49	3245
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C33: 4-((2S,4R)-6-benzyl-7-oxo-2-phenyl-2,3,4,5,6,7-hexahydropyrano[2,3-c]pyrrol-4-yl)Phenyl(4S)-4-((2S,8R,9S,10S,13R,14S,17R)-2-acetoxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate



C33: 75% yield, endo/exo = 91.5/8.5, dr (endo) = 90.3:1.2, dr (exo) = 7.4:1.1; Colorless liquid, $[\alpha]^{26}_D = 8.7$ ($c = 0.78$, in CH_2Cl_2).

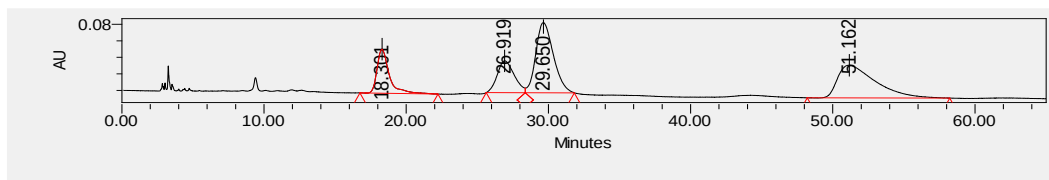
HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, $\lambda = 210$ nm), retention time: $t_1 = 18.42$ min, $t_2 = 27.45$ min, $t_3 = 30.00$ min, $t_4 = 47.57$ min.

^1H NMR (400 MHz, CHCl_3) δ 7.43 (d, $J = 7.2$ Hz, 2H), 7.33 (dt, $J = 17.4, 7.2$ Hz, 5H), 7.26 (m, 1H), 7.22 (d, $J = 7.0$ Hz, 2H), 7.15 (d, $J = 8.4$ Hz, 2H), 7.01 (d, $J = 8.4$ Hz, 2H), 5.15 (d, $J = 11.2$ Hz, 1H), 4.86 (d, $J = 14.8$ Hz, 1H), 4.72 (dt, $J = 11.2, 6.4$ Hz, 1H), 4.37 (d, $J = 14.8$ Hz, 1H), 3.92 (dd, $J = 10.6, 6.0$ Hz, 1H), 3.49 (q, $J = 18.4$ Hz, 2H), 2.63 – 2.54 (m, 1H), 2.45 (dq, $J = 12.8, 6.8, 5.0$ Hz, 2H), 2.18 – 2.08 (m, 1H), 2.03 (s, 3H), 1.98 (d, $J = 11.2$ Hz, 1H), 1.90 – 1.78 (m, 5H), 1.69 (d, $J = 10.4$ Hz, 1H), 1.54 (d, $J = 13.0$ Hz, 2H), 1.47 – 1.37 (m, 7H), 1.24 (q, $J = 13.6$ Hz, 4H), 1.17 – 1.02 (m, 6H), 0.97 (d, $J = 6.0$ Hz, 3H), 0.93 (s, 3H), 0.65 (d, $J = 6.0$ Hz, 3H) ppm.

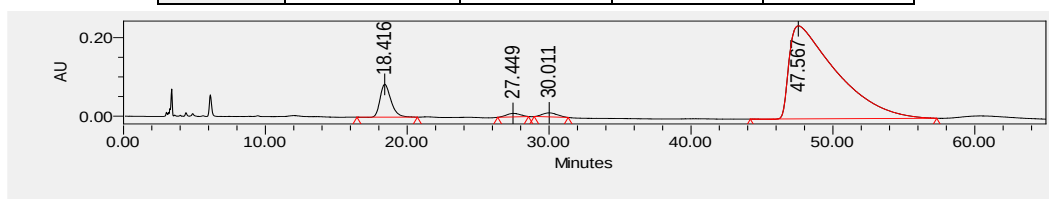
^{13}C NMR (101 MHz, CDCl_3) δ 172.8, 170.7, 165.3, 149.9, 146.9, 139.5, 138.6, 137.1, 128.8, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 127.6, 126.4, 123.0, 122.1, 80.2, 74.4, 56.5, 56.0, 47.3, 46.5, 42.8, 41.9, 40.8, 40.4, 40.2, 39.5, 35.8, 35.4, 35.1, 34.6, 32.3, 31.4, 30.9, 28.3, 27.0, 26.6, 26.3, 24.2, 23.4, 21.5, 20.9, 18.3, 12.1 ppm.

ESI-HRMS calcd for $[\text{C}_{52}\text{H}_{63}\text{NO}_6 + \text{Na}^+] = 820.4548$, found 820.4557.

IR $\tilde{\nu}$ (cm^{-1}) 2930, 2360, 1732, 1698, 1673, 1540, 1453, 1241, 1200, 1136, 1023, 885, 734, 699.



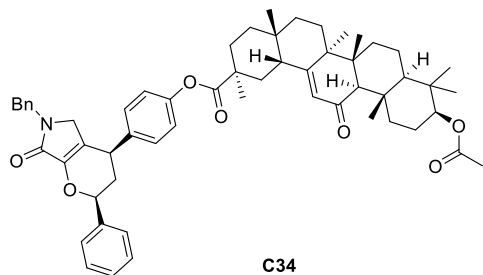
	Retention Time	Area	% Area	Height
1	18.301	3165031	15.09	53315
2	26.919	3199420	15.26	38747
3	29.650	7312099	34.87	85025
4	51.162	7292171	34.78	39600



	Retention Time	Area	% Area	Height
1	18.416	4480002	7.41	83646
2	27.449	605163	1.00	9005
3	30.011	752849	1.25	10312

4	47.567	54615740	90.34	236937
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C34: 4-((2S,4R)-6-benzyl-7-oxo-2-phenyl-2,3,4,5,6,7-hexahydropyrano[2,3-c]pyrrol-4-yl)phenyl (2S,4aS,6aS,6bR,8aR,10S,12aS,12bR,14bR)-10-acetoxy-2,4a,6a,6b,9,9,12a-heptamethyl-13-oxo-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-icosahydronicene-2-carboxylate



C34: 82% yield, endo/exo = 93.0/7.0, dr (endo) = 92.1:0.9, dr (exo) = 6.6:0.4; Colorless liquid, $[\alpha]_D^{26} = 114.4$ ($c = 1.06$, in CH_2Cl_2).

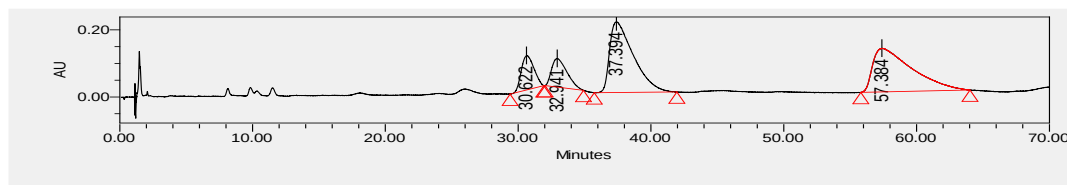
SFC Chiralcel OD-3, $\text{CO}_2/i\text{-PrOH} = 70/30$. 1.0 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 30.53$ min, $t_2 = 33.23$ min, $t_3 = 35.86$ min, $t_4 = 60.89$ min.

^1H NMR (400 MHz, $\text{Chloroform-}d$) δ 7.44 (d, $J = 7.2$ Hz, 2H), 7.38 – 7.28 (m, 5H), 7.26 (d, $J = 4.6$ Hz, 1H), 7.23 (d, $J = 7.2$ Hz, 2H), 7.17 (q, $J = 7.2$, 6.8 Hz, 2H), 7.05 – 6.94 (m, 2H), 5.65 (s, 1H), 5.15 (d, $J = 10.8$ Hz, 1H), 4.88 (d, $J = 15.0$ Hz, 1H), 4.52 (dd, $J = 11.6$, 4.8 Hz, 1H), 4.35 (d, $J = 15.0$ Hz, 1H), 3.93 (dd, $J = 10.8$, 6.0 Hz, 1H), 3.50 (q, $J = 18.4$ Hz, 2H), 2.78 (d, $J = 13.6$ Hz, 1H), 2.48 – 2.39 (m, 1H), 2.37 (s, 1H), 2.25 – 2.18 (m, 1H), 2.17 – 2.08 (m, 2H), 2.05 (m, 5H), 1.92 – 1.76 (m, 2H), 1.78 – 1.54 (m, 5H), 1.45 (d, $J = 7.6$ Hz, 5H), 1.39 (s, 3H), 1.33 (s, 3H), 1.21 (d, $J = 13.2$ Hz, 2H), 1.15 (d, $J = 10.2$ Hz, 5H), 1.10 – 0.99 (m, 2H), 0.87 (d, $J = 13.6$ Hz, 9H) ppm.

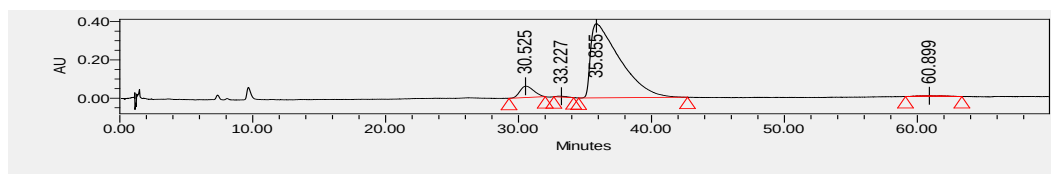
^{13}C NMR (101 MHz, CDCl_3) δ 200.1, 175.1, 171.1, 168.9, 165.2, 149.9, 146.9, 139.5, 138.7, 137.1, 128.9, 128.8, 128.6, 128.5, 128.3, 128.2, 128.1, 127.6, 126.4, 123.0, 121.9, 80.6, 80.2, 61.8, 55.0, 48.6, 47.3, 46.5, 45.4, 44.3, 43.2, 41.1, 40.7, 39.5, 38.8, 38.1, 37.7, 36.9, 32.7, 31.9, 31.2, 28.6, 28.1, 28.0, 26.5, 26.4, 23.6, 23.4, 21.4, 18.7, 17.4, 16.7, 16.4 ppm.

ESI-HRMS calcd for $[\text{C}_{58}\text{H}_{69}\text{NO}_7 + \text{Na}^+] = 914.4966$, found 914.4980.

IR $\tilde{\nu}$ (cm^{-1}) 2947, 2360, 1729, 1698, 1670, 1655, 1504, 1455, 1364, 1242, 1198, 1124, 1073, 1027, 883, 733, 699.



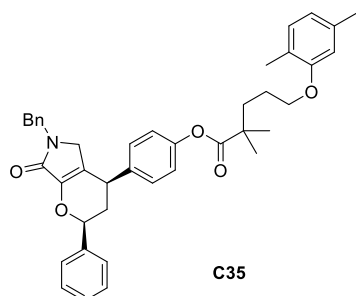
	Retention Time	Area	% Area	Height
1	30.622	6792765	10.22	102868
2	32.941	6885518	10.36	85341
3	37.394	26194821	39.40	210464
4	57.384	26618050	40.03	130480



	Retention Time	Area	% Area	Height
1	30.525	4283094	6.63	59399
2	33.227	248234	0.38	4841

3	35.855	59455006	92.08	387414
4	60.899	580792	0.90	4296

C35: 4-((2S,4R)-6-benzyl-7-oxo-2-phenyl-2,3,4,5,6,7-hexahydropyrano[2,3-c]pyrrol-4-yl)phenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate



C35: 76% yield, endo/exo = 87.7/12.3, ee; 90%/65%; Colorless liquid, $[\alpha]_D^{26} = -16.3$ ($c = 0.83$, in CH_2Cl_2).

SFC Chiralcel IA-3, $\text{CO}_2/i\text{-PrOH} = 70/30$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 9.13$ min, $t_2 = 13.88$ min, $t_3 = 14.53$ min, $t_4 = 23.27$ min.

^1H NMR (400 MHz, CHCl_3) δ 7.43 (d, $J = 7.2$ Hz, 2H), 7.36 – 7.28 (m, 5H), 7.26 – 7.19 (m, 3H), 7.13 (d, $J = 8.4$ Hz, 2H), 7.02 – 6.91 (m, 3H), 6.69 – 6.58 (m, 2H), 5.15 (d, $J = 11.0$ Hz, 1H),

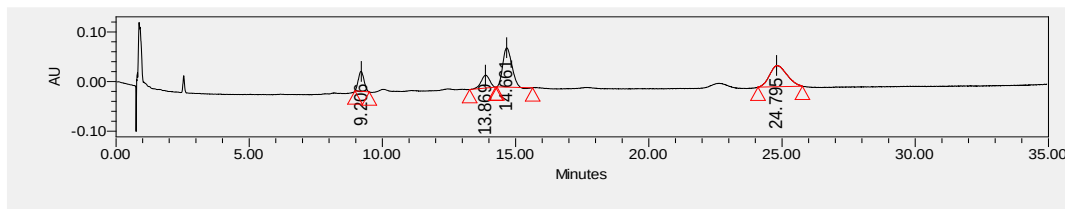
4.84 (d, $J = 14.8$ Hz, 1H), 4.37 (d, $J = 14.8$ Hz, 1H), 3.97 (d, $J = 3.8$ Hz, 2H), 3.91 (dd, $J = 10.8, 6.0$ Hz, 1H), 3.66 – 3.33 (m, 2H), 2.47 – 2.38 (m, 1H), 2.29 (s, 3H), 2.16 (m, 4H), 1.86 (m, 4H), 1.36 (d, $J = 6.0$ Hz, 6H) ppm.

Endo C35: ^{13}C NMR (101 MHz, CDCl_3) δ 176.4, 165.2, 156.9, 150.1, 146.9, 139.5, 138.6, 137.1, 136.5, 130.4, 128.9, 128.8, 128.5, 128.3, 128.2, 128.1, 127.6, 126.4, 126.2, 123.6, 123.0, 122.1, 122.0, 120.8, 111.9, 80.2, 67.8, 47.3, 46.6, 42.5, 40.8, 39.5, 37.1, 25.3, 25.1, 21.4, 15.8 ppm.

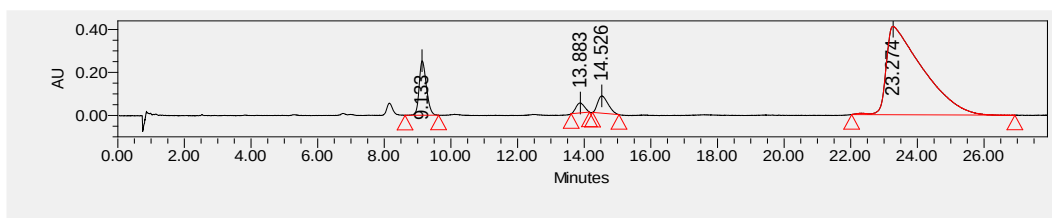
Exo C35: ^{13}C NMR (101 MHz, CDCl_3) δ 176.4, 166.0, 157.4, 150.1, 146.9, 139.6, 138.6, 137.0, 136.5, 130.4, 128.9, 128.8, 128.5, 128.3, 128.2, 128.1, 127.6, 126.4, 126.2, 123.6, 123.0, 122.1, 122.0, 120.6, 108.6, 75.5, 67.8, 50.4, 46.7, 42.5, 40.8, 38.5, 36.4, 25.3, 25.1, 22.7, 14.2 ppm.

ESI-HRMS calcd for $[\text{C}_{41}\text{H}_{43}\text{NO}_5 + \text{Na}^+] = 652.3033$, found 652.3041.

IR $\tilde{\nu}$ (cm^{-1}) 2921, 2360, 1746, 1697, 1506, 1242, 1200, 1162, 1111, 890, 805, 752, 699.



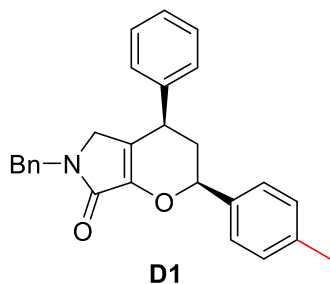
	Retention Time	Area	% Area	Height
1	9.206	597531	11.96	40379
2	13.869	579108	11.59	26053
3	14.661	1906634	38.16	79408
4	24.795	1913551	38.30	42810



	Retention Time	Area	% Area	Height
1	9.133	3802507	10.12	252879

2	13.883	822592	2.19	47173
3	14.526	1641426	4.37	78484
4	23.274	31301892	83.32	411786

D1: (2S,4R)-6-benzyl-4-phenyl-2-(p-tolyl)-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



D1: 67% yield, endo/exo = 80/20, 90%/35% ee; Colorless liquid, $[\alpha]_D^{25} = -22.1$ ($c = 0.52$, in CH_2Cl_2).

SFC Chiralcel OD-3, $\text{CO}_2/\text{MeOH} = 80/20$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 6.23$ min, $t_2 = 6.85$ min, $t_3 = 8.50$ min, $t_4 = 8.93$ min.

^1H NMR (400 MHz, CHCl_3 - d) δ 7.33 (d, $J = 8.0$ Hz, 3H), 7.30 – 7.27 (m, 3H), 7.26 (d, $J = 3.6$ Hz, 1H), 7.23 – 7.18 (m, 3H), 7.14 (t, $J = 7.4$ Hz, 4H), 5.12 (d, $J = 10.9$ Hz, 1H), 4.83 (d, $J = 15.0$ Hz, 1H),

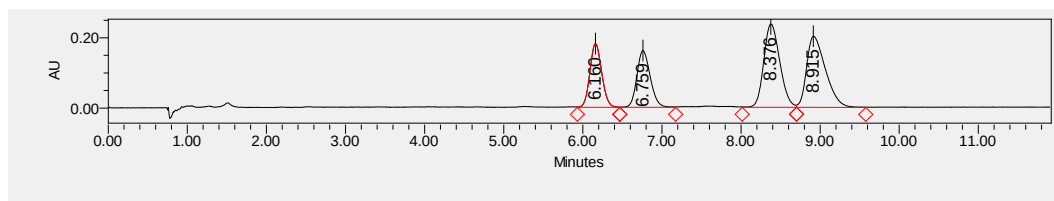
4.38 (d, $J = 15.0$ Hz, 1H), 3.89 (dd, $J = 10.8, 6.0$ Hz, 1H), 3.65 – 3.35 (m, 2H), 2.44 – 2.38 (m, 1H), 2.33 (s, 3H), 2.15 (dt, $J = 14.0, 11.2$ Hz, 1H) ppm.

Endo D1: ^{13}C NMR (101 MHz, CDCl_3) δ 165.5, 146.8, 141.3, 137.9, 137.2, 136.7, 129.1, 128.9, 128.8, 128.1, 127.8, 127.6, 127.3, 127.1, 126.4, 123.4, 80.1, 47.3, 46.5, 40.7, 40.1, 21.2 ppm.

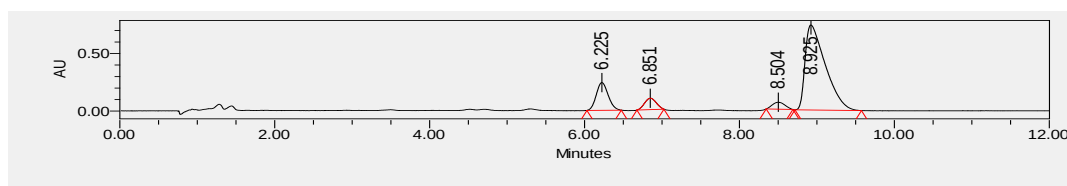
Exo D1: ^{13}C NMR (101 MHz, CDCl_3) δ 165.5, 146.8, 143.1, 137.7, 137.1, 136.7, 130.2, 128.9, 128.7, 128.2, 127.8, 127.7, 127.3, 127.1, 126.1, 120.1, 75.5, 48.0, 46.6, 38.4, 40.5, 21.2 ppm.

ESI-HRMS calcd for $[\text{C}_{27}\text{H}_{25}\text{NO}_2 + \text{Na}^+] = 418.1778$, found 418.1779.

IR $\tilde{\nu}$ (cm^{-1}) 2919, 2360, 1693, 1493, 1452, 1241, 1110, 1048, 815, 735, 700.

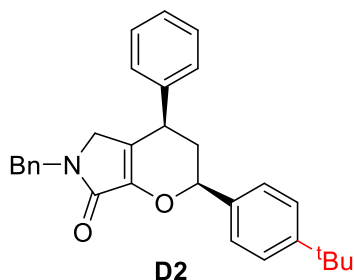


	Retention Time	Area	% Area	Height
1	6.160	1886121	18.00	181259
2	6.759	1897329	18.11	161463
3	8.376	3342353	31.90	237245
4	8.915	3350479	31.98	202215



	Retention Time	Area	% Area	Height
1	6.225	2561398	14.48	241178
2	6.851	1039832	5.88	99628
3	8.504	681403	3.85	61344
4	8.925	13403587	75.79	739829

D2: (2S,4R)-6-benzyl-2-(4-(tert-butyl)phenyl)-4-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7 (2H)-one



D2: 49% yield, endo/exo = 74/26, 73%/0% ee; Colorless liquid, $[\alpha]_D^{26} = -9.0$ ($c = 0.41$, in CH_2Cl_2).

SFC Chiralcel OD-3, $\text{CO}_2/\text{MeOH} = 80/20$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 2.26$ min, $t_2 = 2.68$ min, $t_3 = 3.67$ min, $t_4 = 3.99$ min.

^1H NMR (400 MHz, Chloroform- d) δ 7.37 (m, 3H), 7.35 – 7.31 (m, 2H), 7.31 – 7.27 (m, 3H), 7.23 (dd, $J = 14.4, 4.0$ Hz, 4H), 7.18 – 7.09 (m, 2H), 5.21 – 5.04 (d, $J = 11.2$, 1H), 4.83 (d, $J = 15.0$, Hz,

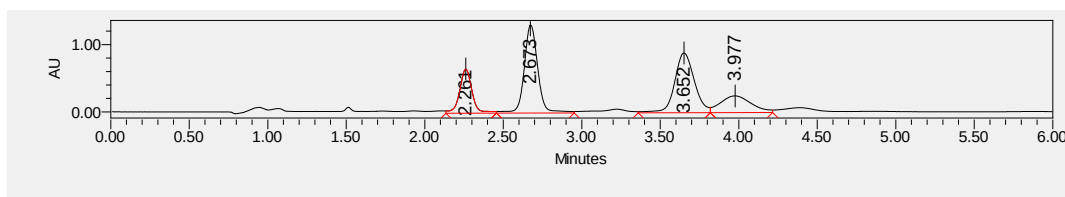
1H), 4.44 (d, $J = 15.0$ Hz, 1H), 3.90 (dd, $J = 10.4, 6.0$ Hz, 1H), 3.65 – 3.33 (m, 2H), 2.53 – 2.36 (m, 1H), 2.17 (m, 1H), 1.30 (s, 9H) ppm.

Endo D2: ^{13}C NMR (101 MHz, CDCl_3) δ 165.4, 151.3, 146.8, 143.1, 141.4, 137.2, 136.6, 128.9, 128.8, 128.1, 127.9, 127.6, 127.3, 127.1, 126.2, 126.0, 125.3, 123.3, 80.0, 47.3, 46.5, 40.5, 40.0, 34.6, 31.3 ppm.

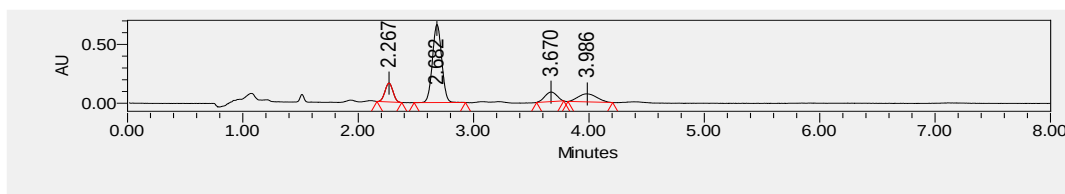
Exo D2: ^{13}C NMR (101 MHz, CDCl_3) δ 165.4, 151.1, 146.9, 143.1, 141.0, 137.1, 136.6, 129.0, 128.9, 128.2, 127.9, 127.6, 127.3, 127.1, 126.2, 126.0, 125.3, 120.7, 75.5, 48.0, 46.6, 38.1, 36.9, 34.6, 31.1 ppm.

ESI-HRMS calcd for $[\text{C}_{30}\text{H}_{31}\text{NO}_2 + \text{Na}^+] = 460.2247$, found 460.2248.

IR $\tilde{\nu}$ (cm^{-1}) 2961, 2360, 1694, 1493, 1454, 1242, 1113, 833, 763, 701, 581.

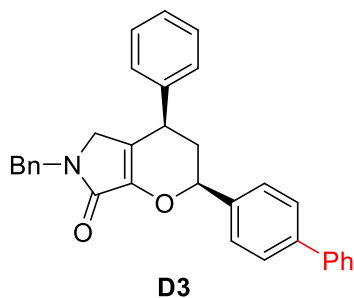


	Retention Time	Area	% Area	Height
1	2.261	3614515	15.97	655024
2	2.673	7882323	34.83	1308206
3	3.652	7733663	34.17	886306
4	3.977	3402240	15.03	248690



	Retention Time	Area	% Area	Height
1	2.267	772702	13.23	160705
2	2.682	3706346	63.45	662602
3	3.670	585995	10.03	81694
4	3.986	776303	13.29	68491

D3: (2S,4R)-2-([1,1'-biphenyl]-4-yl)-6-benzyl-4-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7 (2H)-one



D3: 94% yield, endo/exo = 80/20, 86%/30% ee; Colorless liquid, $[\alpha]_D^{25} = -17.7$ ($c = 0.81$, in CH_2Cl_2).

SFC Chiralcel ID-3, $\text{CO}_2/\text{MeOH} = 80/20$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 25.00$ min, $t_2 = 28.47$ min, $t_3 = 32.57$ min, $t_4 = 36.00$ min.

^1H NMR (400 MHz, CHCl_3) δ 7.64 – 7.55 (m, 4H), 7.52 (t, $J = 7.0$ Hz, 2H), 7.40 (dt, $J = 16.4, 7.2$ Hz, 3H), 7.36 – 7.31 (m, 2H), 7.31 – 7.25 (m, 4H), 7.24 – 7.20 (m, 2H), 7.20 – 7.05 (m, 2H), 5.20

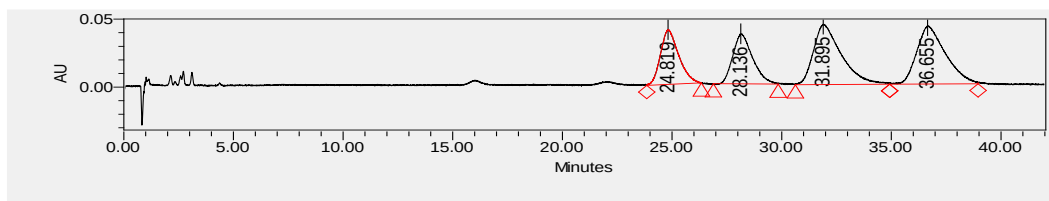
(d, $J = 10.6$ Hz, 1H), 4.84 (d, $J = 15.0$ Hz, 1H), 4.39 (d, $J = 15.0$ Hz, 1H), 3.92 (dd, $J = 10.6, 6.0$ Hz, 1H), 3.68 – 3.39 (m, 2H), 2.58 – 2.37 (m, 1H), 2.25 – 2.11 (m, 1H) ppm.

Endo D3: ^{13}C NMR (101 MHz, CDCl_3) δ 165.4, 146.8, 146.8, 142.9, 141.3, 141.1, 140.8, 140.7, 138.7, 137.1, 129.0, 128.9, 128.8, 128.7, 128.2, 128.1, 127.9, 127.7, 127.6, 127.5, 127.4, 127.4, 127.2, 127.1, 126.9, 126.7, 123.5, 79.9, 47.3, 46.5, 40.7, 40.0 ppm.

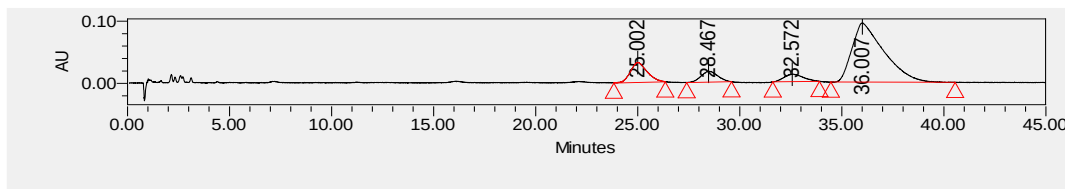
Exo D3: ^{13}C NMR (101 MHz, CDCl_3) δ 165.4, 146.8, 146.8, 143.0, 141.3, 141.1, 140.9, 140.8, 138.7, 137.2, 129.0, 128.9, 128.8, 128.7, 128.2, 128.1, 127.9, 127.7, 127.6, 127.5, 127.4, 127.4, 127.2, 127.1, 126.9, 126.7, 120.9, 75.4, 48.0, 46.6, 38.5, 36.9 ppm.

ESI-HRMS calcd for $[\text{C}_{32}\text{H}_{27}\text{NO}_2 + \text{Na}^+] = 480.1934$, found 480.1938.

IR $\tilde{\nu}$ (cm^{-1}) 3028, 2360, 1694, 1489, 1452, 1240, 1110, 1048, 1005, 732, 698.

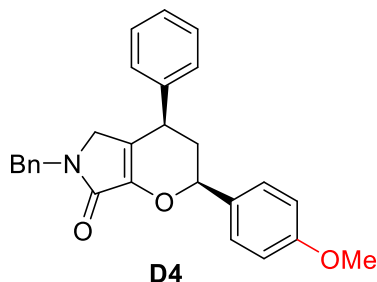


	Retention Time	Area	% Area	Height
1	24.819	2316000	18.61	40309
2	28.136	2309805	18.56	36876
3	31.895	3916160	31.46	44513
4	36.655	3904146	31.37	42960



	Retention Time	Area	% Area	Height
1	25.002	1816902	13.01	32166
2	28.467	988454	7.08	17684
3	32.572	792368	5.67	12238
4	36.007	10372067	74.25	95262

D4: (2S,4R)-6-benzyl-2-(4-methoxyphenyl)-4-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7 (2H)-one



D4: 86% yield, endo/exo = 65/35, 31%/27% ee; Colorless liquid, $[\alpha]_D^{25} = -2.9$ ($c = 0.82$, in CH_2Cl_2).

SFC Chiralcel OD-3, $\text{CO}_2/\text{MeOH} = 80/20$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 8.17$ min, $t_2 = 8.68$ min, $t_3 = 10.87$ min, $t_4 = 19.28$ min.

^1H NMR (400 MHz, Chloroform- d) δ 7.40 – 7.33 (m, 2H), 7.30 (d, $J = 7.6$ Hz, 2H), 7.29 – 7.22 (m, 5H), 7.22 – 7.16 (m, 2H), 7.14 (d, $J = 7.0$ Hz, 1H), 6.86 (dd, $J = 12.4, 8.8$ Hz, 2H), 5.18 –

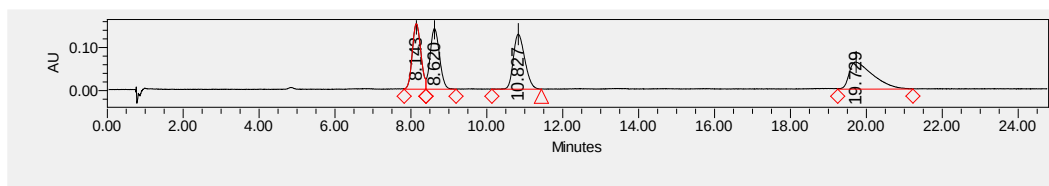
4.98 (d, $J = 10.8$ Hz, 1H), 4.83 (d, $J = 4.2$ Hz, 1H), 4.44 (d, $J = 4.2$ Hz, 1H), 3.93 – 3.77 (m, 4H), 3.67 – 3.38 (m, 2H), 2.48 – 2.35 (m, 1H), 2.21 – 2.06 (m, 1H) ppm.

Endo D4: ^{13}C NMR (101 MHz, CDCl_3) δ 165.4, 159.6, 146.9, 143.1, 141.4, 137.2, 131.8, 129.0, 128.9, 128.8, 128.7, 128.2, 128.1, 127.8, 127.6, 127.5, 127.3, 127.1, 123.3, 113.8, 113.7, 79.9, 55.3, 47.3, 46.5, 40.6, 40.1 ppm.

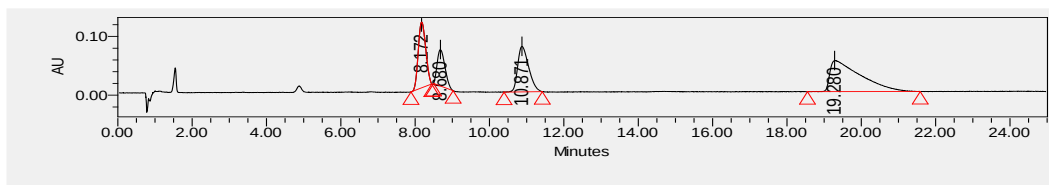
Exo D4: ^{13}C NMR (101 MHz, CDCl_3) δ 165.4, 159.4, 146.8, 143.1, 141.4, 137.1, 131.8, 129.0, 128.9, 128.8, 128.7, 128.2, 128.1, 127.8, 127.6, 127.5, 127.3, 127.1, 120.7, 113.8, 113.7, 75.3, 55.3, 48.0, 46.6, 38.4, 37.0 ppm.

ESI-HRMS calcd for $[\text{C}_{27}\text{H}_{25}\text{NO}_3 + \text{Na}^+] = 434.1727$, found 434.1728.

IR $\tilde{\nu}$ (cm^{-1}) 2920, 2361, 1696, 1512, 1455, 1177, 1111, 1032, 831, 761, 702.

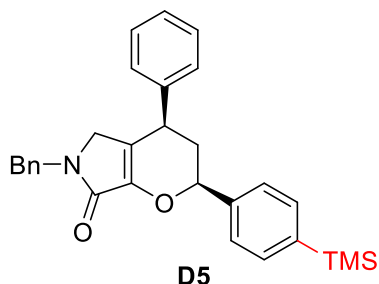


	Retention Time	Area	% Area	Height
1	8.143	2388349	23.37	152244
2	8.620	2411637	23.60	141182
3	10.827	2677550	26.21	127616
4	19.729	2740110	26.82	62857



	Retention Time	Area	% Area	Height
1	8.172	1574838	22.17	112216
2	8.680	900591	12.68	61874
3	10.871	1592920	22.42	77595
4	19.280	3036331	42.74	52855

D5: (2S,4R)-6-benzyl-4-phenyl-2-(4-(trimethylsilyl)phenyl)-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



D5: 22% yield, endo/exo = 86/14, 87%/19% ee; Colorless liquid, $[\alpha]_D^{26} = -19.1$ ($c = 0.22$, in CH_2Cl_2).

SFC Chiralcel OD-3, $\text{CO}_2/\text{MeOH} = 80/20$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 4.68$ min, $t_2 = 4.97$ min, $t_3 = 5.89$ min, $t_4 = 10.31$ min.

^1H NMR (400 MHz, CHCl_3) δ 7.51 (d, $J = 8.0$ Hz, 2H), 7.47 – 7.41 (m, 2H), 7.35 – 7.28 (m, 4H), 7.27 (d, $J = 1.8$ Hz, 1H), 7.25 – 7.19 (m, 3H), 7.18 – 7.10 (m, 2H), 5.16 (d, $J = 10.4$

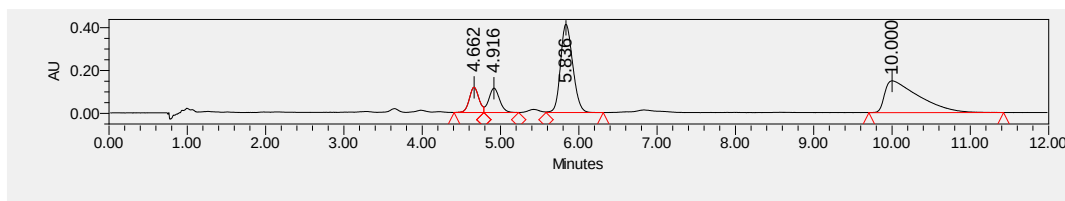
Hz, 1H), 4.84 (d, $J = 15.0$ Hz, 1H), 4.39 (d, $J = 15.0$ Hz, 1H), 3.90 (dd, $J = 10.8, 6.0$ Hz, 1H), 3.65 – 3.38 (m, 2H), 2.44 (ddd, $J = 14.0, 6.0, 1.6$ Hz, 1H), 2.21 – 2.09 (m, 1H), 0.25 (s, 9H) ppm.

Endo D5: **^{13}C NMR** (101 MHz, CDCl_3) δ 166.5, 147.9, 142.4, 141.7, 141.2, 138.3, 134.6, 130.1, 130.1, 129.9, 129.8, 129.3, 129.2, 128.9, 128.7, 128.6, 128.5, 126.8, 126.6, 124.5, 81.2, 48.4, 47.6, 41.8, 41.1, -0.00 ppm.

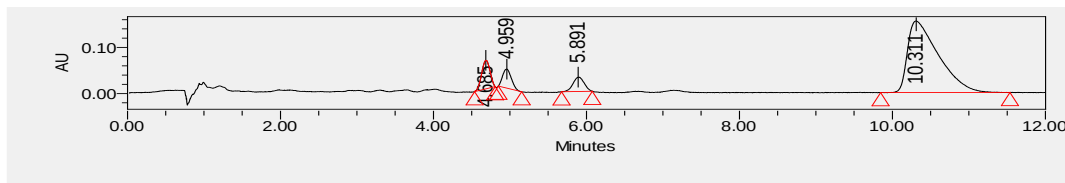
Exo D5: **^{13}C NMR** (101 MHz, CDCl_3) δ 166.5, 147.9, 142.4, 141.7, 141.2, 138.3, 134.6, 130.1, 130.1, 129.9, 129.8, 129.3, 129.2, 128.9, 128.7, 128.6, 128.5, 126.8, 126.6, 124.5, 76.7, 49.1, 47.7, 39.4, 38.0, -0.00 ppm.

ESI-HRMS calcd for $[\text{C}_{29}\text{H}_{31}\text{NO}_2\text{Si} + \text{Na}^+] = 476.2106$, found 476.2020.

IR $\tilde{\nu}$ (cm^{-1}) 2953, 2360, 1693, 1494, 1453, 1244, 1104, 1048, 754, 700.

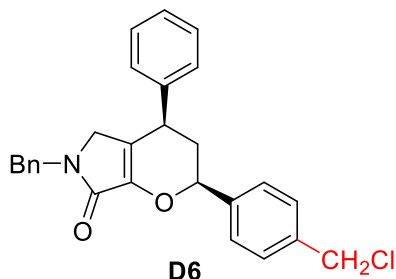


	Retention Time	Area	% Area	Height
1	4.662	1006512	9.11	117572
2	4.916	1089567	9.86	113680
3	5.836	4477118	40.50	411790
4	10.000	4480344	40.53	148065



	Retention Time	Area	% Area	Height
1	4.685	466958	8.57	61892
2	4.959	323584	5.94	41193
3	5.891	315436	5.79	31336
4	10.311	4342824	79.70	155044

D6: (2S,4R)-6-benzyl-2-(4-(chloromethyl)phenyl)-4-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



D6: 61% yield, endo/exo = 89/11, 97%/33% ee; Colorless liquid, $[\alpha]_D^{25} = -34.2$ ($c = 0.53$, in CH_2Cl_2).

SFC Chiralcel OD-3, $\text{CO}_2/\text{MeOH} = 80/20$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 10.00$ min, $t_2 = 11.75$ min, $t_3 = 15.14$ min, $t_4 = 16.31$ min.

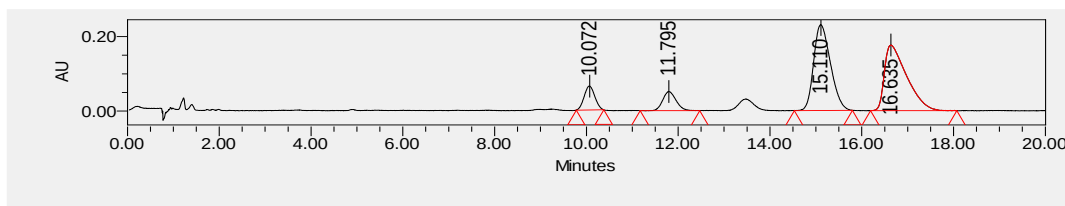
^1H NMR (400 MHz, $\text{Chloroform-}d$) δ 7.43 (m, 2H), 7.37 (d, $J = 8.2$ Hz, 2H), 7.35 – 7.31 (m, 1H), 7.31 – 7.27 (m, 3H), 7.26 (t, $J = 3.6$ Hz, 2H), 7.23 – 7.18 (m, 2H), 7.18 – 7.08 (m, 2H), 5.17 (d, $J = 10.4$ Hz, 1H), 4.84 (d, $J = 15.0$ Hz, 1H), 4.58 (s, 2H), 4.39 (d, $J = 15.0$ Hz, 1H), 3.91 (dd, $J = 10.8, 6.0$ Hz, 1H), 3.67 – 3.39 (m, 2H), 2.43 (ddd, $J = 14.0, 6.0, 1.6$ Hz, 1H), 2.13 (dt, $J = 14.0, 11.2$ Hz, 1H) ppm.

Endo D6: ^{13}C NMR (101 MHz, CDCl_3) δ 165.3, 146.7, 141.1, 139.9, 137.5, 137.1, 129.0, 128.7, 128.2, 128.1, 127.8, 127.6, 127.5, 127.4, 126.7, 126.6, 123.5, 79.7, 47.3, 46.5, 45.9, 40.7, 39.9 ppm.

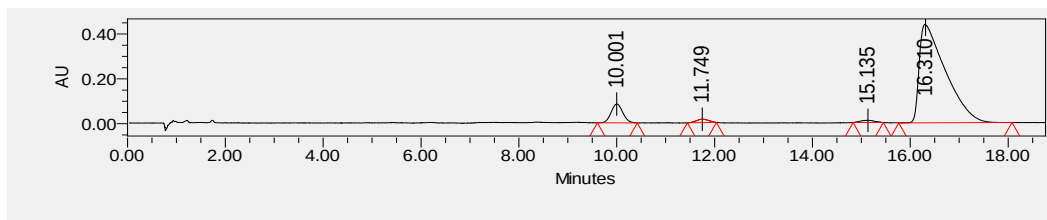
Exo D6: ^{13}C NMR (101 MHz, CDCl_3) δ 165.3, 146.7, 141.1, 140.0, 137.5, 137.1, 129.0, 128.8, 128.2, 128.1, 127.8, 127.6, 127.5, 127.4, 126.7, 126.6, 123.5, 75.2, 48.0, 46.6, 45.9, 38.5, 36.9 ppm.

ESI-HRMS calcd for $[\text{C}_{27}\text{H}_{24}\text{ClNO}_2 + \text{Na}^+] = 452.1388$, found 452.1395.

IR $\tilde{\nu}$ (cm^{-1}) 3029, 2360, 1694, 1493, 1453, 1242, 1110, 1048, 828, 746, 701.

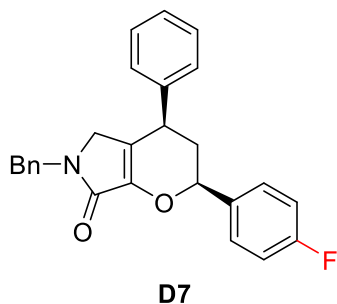


	Retention Time	Area	% Area	Height
1	10.072	1034776	7.50	64198
2	11.795	1031362	7.47	51337
3	15.110	5854753	42.42	230075
4	16.635	5882202	42.62	175754



	Retention Time	Area	% Area	Height
1	10.001	1384618	7.61	84330
2	11.749	267054	1.47	15589
3	15.135	197365	1.08	10140
4	16.310	16353127	89.84	439054

D7: (2S,4R)-6-benzyl-2-(4-fluorophenyl)-4-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7 (2H)-one



D7: 89% yield, endo/exo = 91/9, 96%/63% ee; Colorless liquid, $[\alpha]_D^{25} = -35.9$ ($c = 0.69$, in CH_2Cl_2).

SFC Chiralcel OD-3, $\text{CO}_2/\text{MeOH} = 80/20$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 4.63$ min, $t_2 = 5.63$ min, $t_3 = 6.55$ min, $t_4 = 9.13$ min.

^1H NMR (400 MHz, $\text{Chloroform-}d$) δ 7.42 (dd, $J = 8.6, 5.4$ Hz, 2H), 7.30 (t, $J = 7.0$ Hz, 4H), 7.25 (q, $J = 5.8, 4.8$ Hz, 2H), 7.21 (d, $J = 7.6$ Hz, 2H), 7.18 – 7.08 (m, 2H), 7.04 (t, $J = 8.8$ Hz, 2H), 5.14 (d, $J =$

11.2 Hz, 1H), 4.84 (d, $J = 15.0$ Hz, 1H), 4.39 (d, $J = 15.0$ Hz, 1H), 3.90 (dd, $J = 10.8, 6.0$ Hz, 1H), 3.66 – 3.26 (m, 2H), 2.41 (ddd, $J = 14.0, 6.0, 1.6$ Hz, 1H), 2.13 (dt, $J = 14.0, 11.2$ Hz, 1H) ppm.

Endo D7: **^{13}C NMR** (101 MHz, CDCl_3) δ 165.3, 162.6(d, $J_{\text{C-F}} = 244.0$), 146.7, 141.1, 137.1, 135.5, 135.5, 129.0, 128.9, 128.8, 128.7, 128.3, 128.2, 128.1, 127.8, 127.6, 127.5, 127.4, 123.5, 115.5(d, $J_{\text{C-F}} = 4.0$), 115.4(d, $J_{\text{C-F}} = 17.0$), 115.3, 79.5, 47.3, 46.5, 40.8, 39.9 ppm.

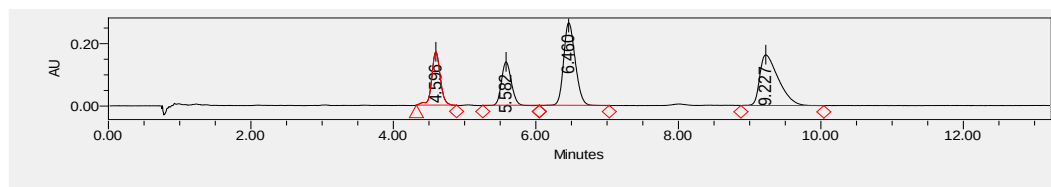
Exo D7: **^{13}C NMR** (101 MHz, CDCl_3) δ 165.3, 162.6(d, $J_{\text{C-F}} = 244.0$), 146.7, 141.1, 137.1, 135.5, 135.5, 129.0, 128.9, 128.8, 128.7, 128.3, 128.2, 128.1, 127.8, 127.6, 127.5, 127.4, 123.5, 115.5(d, $J_{\text{C-F}} = 4.0$), 115.4(d, $J_{\text{C-F}} = 17.0$), 115.3, 74.9, 48.0, 46.6, 38.6, 37.0 ppm.

Endo D7: **^{19}F NMR** (377 MHz, CDCl_3) δ -113.85 ppm.

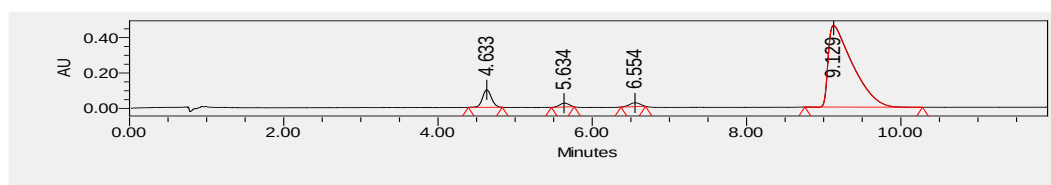
Exo D7: **^{19}F NMR** (377 MHz, CDCl_3) δ -114.16 ppm.

ESI-HRMS calcd for $[\text{C}_{26}\text{H}_{22}\text{FNO}_2 + \text{Na}^+] = 422.1527$, found 422.1529.

IR $\tilde{\nu}$ (cm^{-1}) 3029, 2360, 1693, 1510, 1453, 1390, 1224, 1109, 1048, 733, 699.

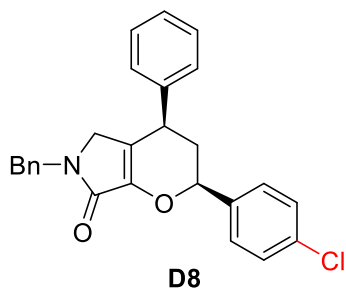


	Retention Time	Area	% Area	Height
1	4.596	1423705	16.38	170741
2	5.582	1338526	15.40	138818
3	6.460	2979805	34.29	264586
4	9.227	2947447	33.92	162615



	Retention Time	Area	% Area	Height
1	4.633	793730	7.01	98939
2	5.634	184728	1.63	21959
3	6.554	209726	1.85	21737
4	9.129	10142138	89.51	462333

D8: (2S,4R)-6-benzyl-2-(4-chlorophenyl)-4-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



D8: 81% yield, endo/exo = 91/9, 92%/40% ee; Colorless liquid, $[\alpha]_D^{25} = -37.1$ ($c = 1.02$, in CH_2Cl_2).

SFC Chiralcel OD-3, $\text{CO}_2/\text{MeOH} = 80/20$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 6.42$ min, $t_2 = 7.99$ min, $t_3 = 10.56$ min, $t_4 = 15.26$ min.

^1H NMR (400 MHz, Chloroform- d) δ 7.38 (d, $J = 8.4$ Hz, 2H), 7.34 – 7.29 (m, 4H), 7.29 – 7.23 (m, 4H), 7.20 (dd, $J = 9.4, 2.8$ Hz, 2H), 7.17 – 7.02 (m, 2H), 5.14 (d, $J = 10.4$ Hz, 1H), 4.83 (d, $J = 15.0$ Hz,

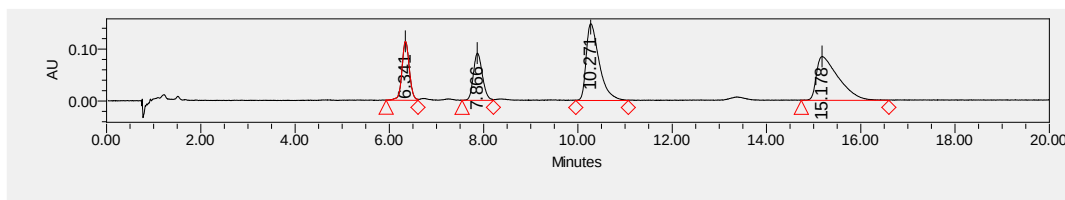
1H), 4.39 (d, $J = 15.0$ Hz, 1H), 3.90 (dd, $J = 10.8, 6.0$ Hz, 1H), 3.66 – 3.34 (m, 2H), 2.41 (ddd, $J = 14.0, 6.0, 1.6$ Hz, 1H), 2.15 – 2.00 (m, 1H) ppm.

Endo D8: ^{13}C NMR (101 MHz, CDCl_3) δ 165.2, 146.6, 141.0, 138.2, 137.1, 133.9, 129.0, 128.8, 128.7, 128.6, 128.5, 128.2, 128.1, 127.9, 127.8, 127.6, 127.5, 127.4, 123.6, 79.4, 47.3, 46.5, 40.8, 39.9 ppm.

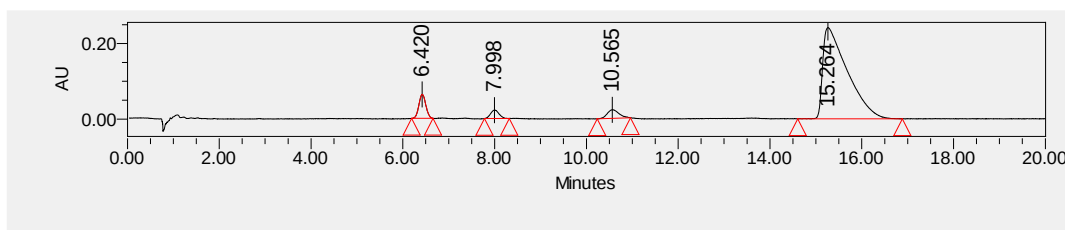
Exo D8: ^{13}C NMR (101 MHz, CDCl_3) δ 165.2, 146.6, 142.8, 138.3, 137.0, 133.8, 129.0, 128.8, 128.7, 128.6, 128.5, 128.2, 128.1, 127.9, 127.8, 127.6, 127.5, 127.3, 121.1, 75.8, 48.0, 46.6, 38.6, 36.9 ppm.

ESI-HRMS calcd for $[\text{C}_{26}\text{H}_{22}\text{ClNO}_2 + \text{Na}^+] = 438.1231$, found 438.1238.

IR $\tilde{\nu}$ (cm^{-1}) 3029, 2360, 1693, 1492, 1453, 1241, 1108, 1048, 1014, 762, 700.

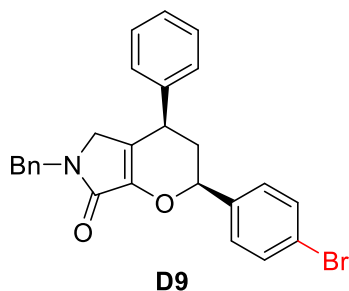


	Retention Time	Area	% Area	Height
1	6.341	1236382	15.43	113308
2	7.866	1208242	15.07	90840
3	10.271	2839785	35.43	147833
4	15.178	2730678	34.07	84204



	Retention Time	Area	% Area	Height
1	6.420	662525	6.42	63473
2	7.998	285200	2.76	22434
3	10.565	404367	3.92	22936
4	15.264	8965247	86.89	241212

D9: (2S,4R)-6-benzyl-2-(4-bromophenyl)-4-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



D9: 66% yield, endo/exo = 91/9, 97%/57% ee; Colorless liquid, $[\alpha]_D^{25} = -33.4$ ($c = 0.90$, in CH_2Cl_2).

SFC Chiralcel OD-3, $\text{CO}_2/\text{MeOH} = 80/20$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 7.76$ min, $t_2 = 9.69$ min, $t_3 = 13.77$ min, $t_4 = 19.61$ min.

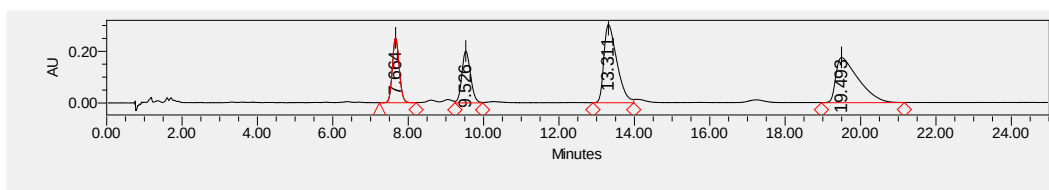
^1H NMR (400 MHz, Chloroform- d) δ 7.47 (d, $J = 8.4$ Hz, 2H), 7.30 (dd, $J = 13.6, 7.6$ Hz, 6H), 7.25 (d, $J = 8.8$ Hz, 2H), 7.20 (d, $J = 7.2$ Hz, 2H), 7.12 (d, $J = 7.2$ Hz, 2H), 5.12 (d, $J = 11.2$ Hz, 1H), 4.83 (d, $J = 15.0$ Hz, 1H), 4.39 (d, $J = 15.0$ Hz, 1H), 3.90 (dd, $J = 10.6, 6.0$ Hz, 1H), 3.68 – 3.32 (m, 2H), 2.52 – 2.28 (m, 1H), 2.21 – 2.02 (m, 1H) ppm.

Endo D9: ^{13}C NMR (101 MHz, CDCl_3) δ 165.2, 146.6, 140.9, 138.7, 137.1, 131.6, 129.0, 128.7, 128.1, 127.9, 127.6, 127.5, 127.4, 123.6, 122.1, 79.4, 47.3, 46.5, 40.7, 39.9 ppm.

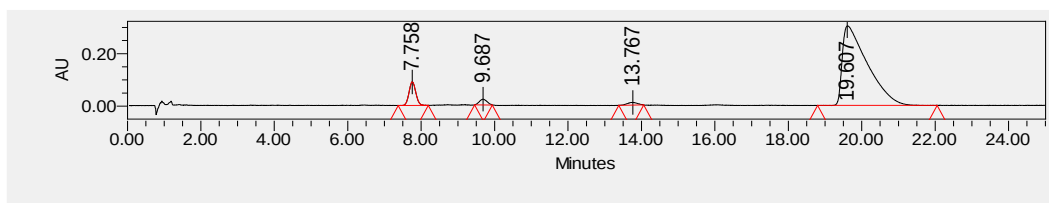
Exo D9: ^{13}C NMR (101 MHz, CDCl_3) δ 165.2, 146.6, 140.9, 138.8, 137.0, 131.6, 129.0, 128.8, 128.2, 127.9, 127.6, 127.5, 127.4, 123.6, 121.9, 74.9, 48.0, 46.6, 38.6, 36.9 ppm.

ESI-HRMS calcd for $[\text{C}_{26}\text{H}_{22}\text{BrNO}_2 + \text{Na}^+] = 482.0726$, found 482.0733.

IR $\tilde{\nu}$ (cm^{-1}) 3028, 2360, 1696, 1490, 1454, 1241, 1109, 1072, 1048, 762, 700.

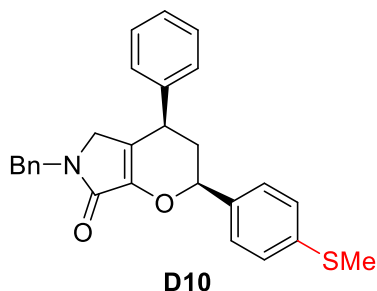


	Retention Time	Area	% Area	Height
1	7.664	3191173	15.28	250907
2	9.526	3198159	15.31	200075
3	13.311	7253345	34.73	301804
4	19.493	7243421	34.68	174393



	Retention Time	Area	% Area	Height
1	7.758	1150820	7.18	89837
2	9.687	320048	2.00	22156
3	13.767	194112	1.21	10290
4	19.607	14370554	89.62	303325

D10: (2S,4R)-6-benzyl-2-(4-(methylthio)phenyl)-4-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



D10: 60% yield, endo/exo = 76/24, 92%/36% ee; Colorless liquid, $[\alpha]_D^{26} = -14.2$ ($c = 0.45$, in CH_2Cl_2).

SFC Chiralcel OJ-3, $\text{CO}_2/\text{MeOH} = 80/20$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 5.98$ min, $t_2 = 8.72$ min, $t_3 = 10.40$ min, $t_4 = 13.33$ min.

^1H NMR (400 MHz, Chloroform- d) δ 7.39 – 7.33 (m, 2H), 7.32 (d, $J = 2.0$ Hz, 1H), 7.31 – 7.29 (m, 2H), 7.29 – 7.27 (m, 2H), 7.25 – 7.23 (m, 2H), 7.22 (dd, $J = 2.8, 1.6$ Hz, 2H), 7.20 – 7.18

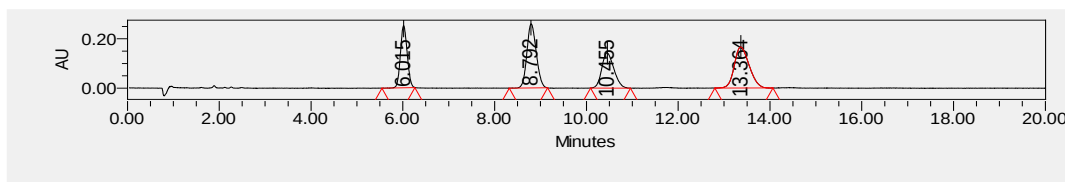
(m, 1H), 7.17 – 7.10 (m, 2H), 5.17 – 5.03 (d, $J = 10.4$ Hz, 1H), 4.83 (dt, $J = 8.8, 4.4$ Hz, 1H), 4.38 (d, $J = 15.0$ Hz, 1H), 3.89 (dd, $J = 10.8, 6.0$ Hz, 1H), 3.61 – 3.39 (m, 2H), 2.47 (s, 3H), 2.41 (ddd, $J = 14.0, 6.0, 1.8$ Hz, 1H), 2.18 – 2.08 (m, 1H) ppm.

Endo D10: ^{13}C NMR (101 MHz, CDCl_3) δ 165.3, 146.7, 141.2, 138.5, 137.1, 136.5, 129.0, 128.8, 128.7, 128.2, 128.1, 127.8, 127.7, 127.6, 127.5, 127.4, 127.2, 126.9, 126.7, 126.5, 125.1, 123.4, 79.8, 47.3, 46.5, 40.7, 39.9, 15.7 ppm.

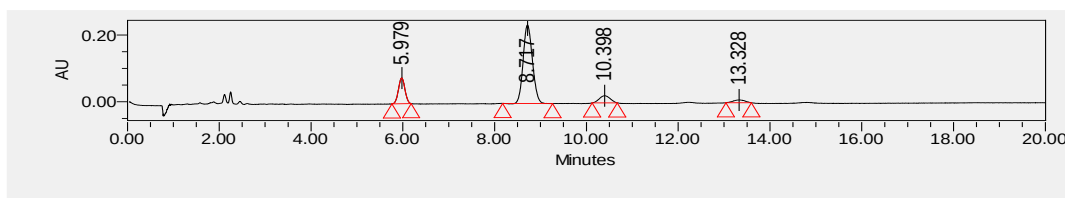
Exo D10: ^{13}C NMR (101 MHz, CDCl_3) δ 163.3, 146.8, 142.9, 138.3, 137.1, 136.5, 129.0, 128.8, 128.7, 128.2, 128.0, 127.8, 127.7, 127.6, 127.5, 127.4, 127.2, 126.9, 126.7, 126.5, 121.0, 120.1, 75.2, 48.0, 46.5, 38.4, 36.9, 14.7 ppm.

ESI-HRMS calcd for $[\text{C}_{27}\text{H}_{25}\text{NO}_2\text{S} + \text{Na}^+] = 450.1498$, found 450.1505.

IR $\tilde{\nu}$ (cm^{-1}) 2919, 2360, 1694, 1493, 1453, 1242, 1091, 1048, 968, 763, 702.

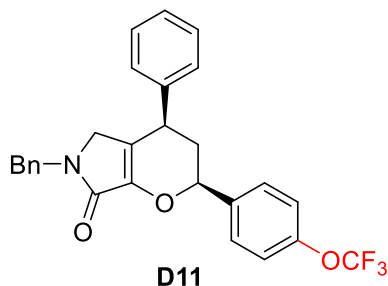


	Retention Time	Area	% Area	Height
1	6.015	2566310	20.37	251290
2	8.792	3680706	29.21	259533
3	10.455	2612233	20.73	143074
4	13.364	3739751	29.68	166529



	Retention Time	Area	% Area	Height
1	5.979	757407	16.53	77316
2	8.717	3321150	72.46	235383
3	10.398	356204	7.77	21869
4	13.328	148602	3.24	8494

D11: (2S,4R)-6-benzyl-4-phenyl-2-(4-(trifluoromethoxy)phenyl)-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



D11: 46% yield, endo/exo = 92/8, 96%/53% ee; Colorless liquid, $[\alpha]_D^{26} = -18.2$ ($c = 0.22$, in CH_2Cl_2).

SFC Chiralcel OD-3, $\text{CO}_2/\text{MeOH} = 80/20$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 3.23$ min, $t_2 = 3.71$ min, $t_3 = 4.48$ min, $t_4 = 5.94$ min.

^1H NMR (400 MHz, Chloroform- d) δ 7.99 (d, $J = 8.8$ Hz, 1H), 7.48 (d, $J = 8.8$ Hz, 2H), 7.36 – 7.28 (m, 5H), 7.21 (dd, $J = 7.4$, 2.8 Hz, 4H), 7.17 – 7.09 (m, 2H), 5.18 (d, $J = 10.8$ Hz, 1H), 4.84

(d, $J = 15.0$ Hz, 1H), 4.40 (d, $J = 15.0$ Hz, 1H), 3.91 (dd, $J = 10.8$, 6.0 Hz, 1H), 3.68 – 3.37 (m, 2H), 2.44 (ddd, $J = 14.0$, 6.0, 1.6 Hz, 1H), 2.13 (dt, $J = 14.0$, 11.2 Hz, 1H) ppm.

Endo D11: **^{13}C NMR** (101 MHz, CDCl_3) δ 165.3, 149.0, 146.6, 140.9, 138.3, 137.0, 129.8, 129.0, 128.8, 128.1, 127.8, 127.6, 127.5, 127.4, 122.2(d, $J_{\text{C-F}} = 290.0$), 121.0, 79.3, 47.3, 46.5, 40.8, 39.9 ppm.

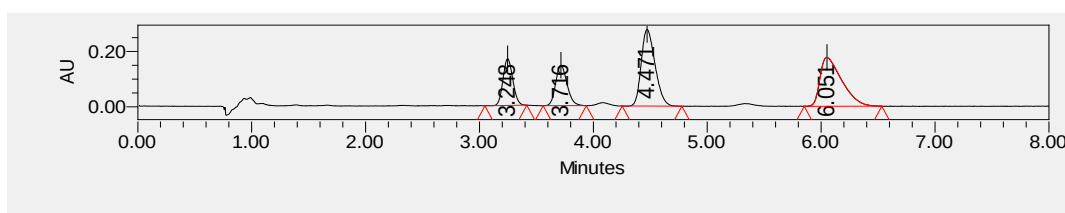
Exo D11: **^{13}C NMR** (101 MHz, CDCl_3) δ 165.3, 149.0, 146.6, 140.9, 138.3, 137.0, 129.8, 129.0, 128.8, 128.1, 127.8, 127.6, 127.5, 127.4, 122.2(d, $J_{\text{C-F}} = 290.0$), 121.0, 65.5, 45.3, 44.5, 40.8, 39.9 ppm.

Endo D11: **^{19}F NMR** (377 MHz, CDCl_3) δ -57.59 ppm.

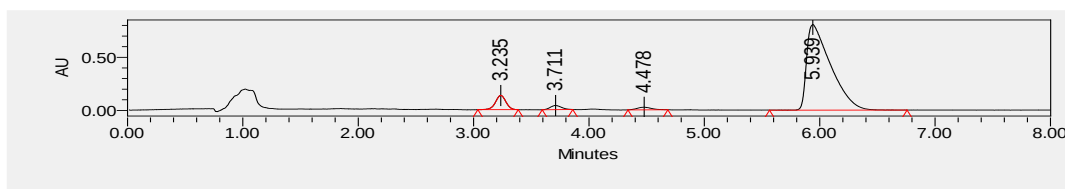
Exo D11: **^{19}F NMR** (377 MHz, CDCl_3) δ -57.88 ppm.

ESI-HRMS calcd for $[\text{C}_{27}\text{H}_{22}\text{F}_3\text{NO}_2 + \text{Na}^+] = 488.1444$, found 488.1451.

IR $\tilde{\nu}$ (cm^{-1}) 2923, 2360, 1673, 1509, 1454, 1255, 1218, 1163, 852, 763, 701.

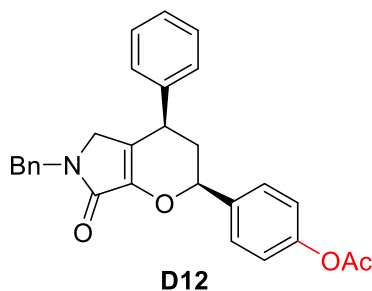


	Retention Time	Area	% Area	Height
1	3.248	1007686	15.11	168221
2	3.716	1011927	15.17	145795
3	4.471	2324298	34.85	275994
4	6.051	2325221	34.87	176326



	Retention Time	Area	% Area	Height
1	3.235	849610	6.55	134426
2	3.711	265195	2.04	39756
3	4.478	211999	1.63	24568
4	5.939	11647553	89.77	806874

D12: 4-((2S,4R)-6-benzyl-7-oxo-4-phenyl-2,3,4,5,6,7-hexahydropyrano[2,3-c]pyrrol-2-yl)phenyl acetate



D12: 99% yield, endo/exo = 87/13, 95%/43% ee; Colorless liquid, $[\alpha]_D^{26} = -30.6$ ($c = 0.77$, in CH_2Cl_2).

SFC Chiralcel OJ-3, $\text{CO}_2/\text{MeOH} = 80/20$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 3.41$ min, $t_2 = 4.33$ min, $t_3 = 5.39$ min, $t_4 = 7.56$ min.

^1H NMR (400 MHz, Chloroform- d) δ 7.46 (d, $J = 8.4$ Hz, 2H), 7.35 – 7.31 (m, 1H), 7.29 (d, $J = 6.0$ Hz, 3H), 7.25 (d, $J = 4.8$ Hz, 2H), 7.21 (t, $J = 6.8$ Hz, 2H), 7.13 (d, $J = 7.0$ Hz, 2H), 7.08 (d, $J =$

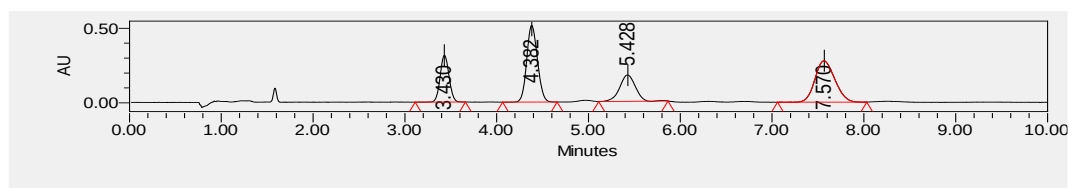
8.6 Hz, 2H), 5.16 (d, $J = 10.8$ Hz, 1H), 4.83 (d, $J = 15.0$ Hz, 1H), 4.39 (d, $J = 15.0$ Hz, 1H), 3.90 (dd, $J = 10.8, 6.1$ Hz, 1H), 3.67 – 3.25 (m, 2H), 2.43 (ddd, $J = 14.0, 6.0, 1.6$ Hz, 1H), 2.28 (s, 3H), 2.13 (dt, $J = 14.0, 11.2$ Hz, 1H) ppm.

Endo D12: ^{13}C NMR (101 MHz, CDCl_3) δ 169.4, 165.3, 150.5, 146.7, 141.1, 137.2, 137.1, 129.0, 128.9, 128.8, 128.7, 128.2, 128.1, 127.8, 127.6, 127.5, 127.4, 127.3, 123.5, 121.6, 121.5, 79.6, 47.3, 46.5, 40.7, 39.9, 21.2 ppm.

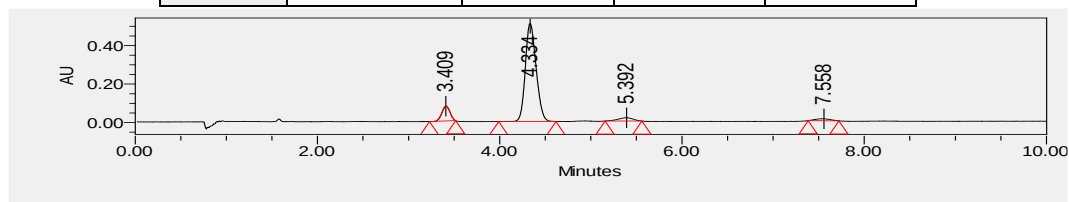
Exo D12: ^{13}C NMR (101 MHz, CDCl_3) δ 169.4, 165.3, 150.3, 146.6, 142.9, 137.3, 137.1, 129.0, 128.9, 128.8, 128.7, 128.2, 128.1, 127.8, 127.6, 127.5, 127.4, 127.3, 123.5, 121.6, 121.5, 75.0, 48.0, 46.6, 38.5, 36.9, 18.2 ppm.

ESI-HRMS calcd for $[\text{C}_{28}\text{H}_{25}\text{NO}_4 + \text{Na}^+] = 462.1676$, found 462.1678.

IR $\tilde{\nu}$ (cm^{-1}) 2919, 2360, 1759, 1693, 1453, 1194, 1109, 1016, 911, 762, 702.

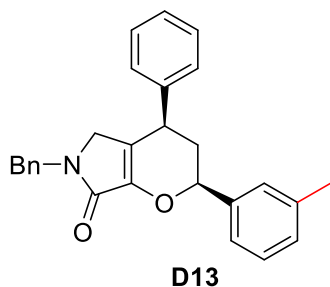


	Retention Time	Area	% Area	Height
1	3.430	2110469	16.80	313565
2	4.382	4180579	33.28	514691
3	5.428	2111714	16.81	176966
4	7.570	4160180	33.11	277255



	Retention Time	Area	% Area	Height
1	3.409	479171	9.64	77325
2	4.334	4187205	84.23	509862
3	5.392	189289	3.81	17053
4	7.558	115783	2.33	10097

D13: (2S,4R)-6-benzyl-4-phenyl-2-(m-tolyl)-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



D13: 85% yield, endo/exo = 92/8, 98%/93% ee; Colorless liquid, $[\alpha]_D^{25} = -38.2$ ($c = 0.56$, in CH_2Cl_2).

SFC Chiralcel ID-3, $\text{CO}_2/\text{MeOH} = 80/20$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 7.77$ min, $t_2 = 8.51$ min, $t_3 = 9.26$ min, $t_4 = 10.74$ min.

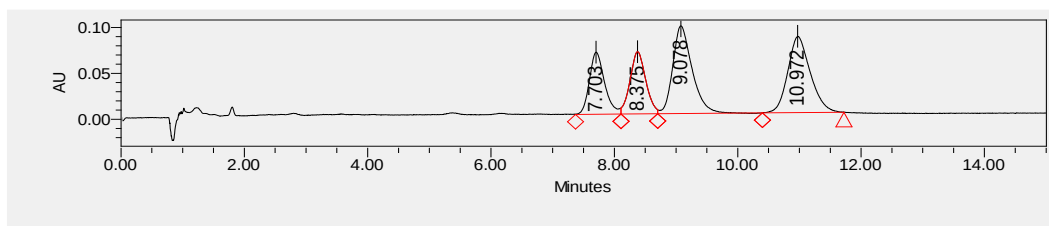
^1H NMR (400 MHz, CHCl_3) δ 7.30 (ddt, $J = 9.6, 5.4, 2.8$ Hz, 5H), 7.27 – 7.24 (m, 2H), 7.22 (t, $J = 6.4$ Hz, 4H), 7.17 – 7.05 (m, 3H), 5.22 – 5.03 (m, 1H), 4.83 (d, $J = 15.0$ Hz, 1H), 4.40 (d, $J = 15.0$ Hz, 1H), 3.90 (dd, $J = 10.8, 6.0$ Hz, 1H), 3.67 – 3.28 (m, 2H), 2.43 (ddd, $J = 14.0, 6.0, 1.6$ Hz, 1H), 2.35 (s, 3H), 2.15 (dt, $J = 14.0, 11.2$ Hz, 1H) ppm.

Endo D13: ^{13}C NMR (101 MHz, CDCl_3) δ 165.4, 146.8, 141.3, 139.5, 138.1, 137.2, 128.9, 128.7, 128.7, 128.3, 128.1, 127.6, 127.5, 127.3, 127.0, 123.5, 123.4, 80.2, 47.3, 46.5, 40.8, 40.0, 21.5 ppm.

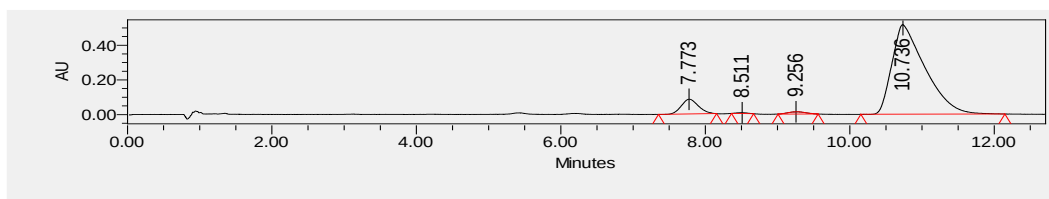
Exo D13: ^{13}C NMR (101 MHz, CDCl_3) δ 165.4, 146.8, 141.3, 139.5, 138.1, 137.2, 128.9, 128.7, 128.7, 128.3, 128.1, 127.6, 127.5, 127.3, 127.0, 123.5, 123.4, 75.6, 48.0, 46.6, 38.6, 37.0, 14.2 ppm.

ESI-HRMS calcd for $[\text{C}_{27}\text{H}_{25}\text{NO}_2 + \text{Na}^+] = 418.1778$, found 418.1777.

IR $\tilde{\nu}$ (cm^{-1}) 2918, 2360, 1694, 1492, 1453, 1240, 1110, 1048, 935, 733, 699.

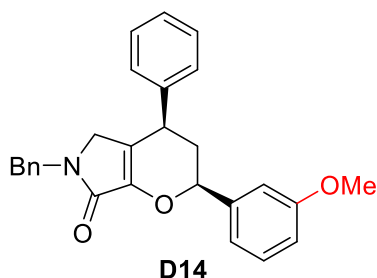


	Retention Time	Area	% Area	Height
1	7.703	1158434	17.71	67641
2	8.375	1194119	18.26	67786
3	9.078	2088660	31.93	95611
4	10.972	2099326	32.10	83078



	Retention Time	Area	% Area	Height
1	7.773	1390418	7.68	85234
2	8.511	52605	0.29	5213
3	9.256	212166	1.17	12967
4	10.736	16443440	90.85	516554

D14: (2S,4R)-6-benzyl-2-(3-methoxyphenyl)-4-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7 (2H)-one



D14: 50% yield, endo/exo = 90/10, 96%/85% ee; Colorless liquid, $[\alpha]_D^{26} = -33.9$ ($c = 0.43$, in CH_2Cl_2).

SFC Chiralcel AD-3, $\text{CO}_2/\text{MeOH} = 80/20$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 9.73$ min, $t_2 = 10.08$ min, $t_3 = 14.46$ min, $t_4 = 18.69$ min.

^1H NMR (400 MHz, Chloroform- d) δ 7.36 – 7.27 (m, 4H), 7.26 (t, $J = 3.6$ Hz, 2H), 7.21 (qd, $J = 6.0, 2.4$ Hz, 3H), 7.19 – 7.09 (m, 2H), 7.01 (d, $J = 7.2$ Hz, 2H), 6.89 – 6.82 (m, 1H), 5.13 (d, $J =$

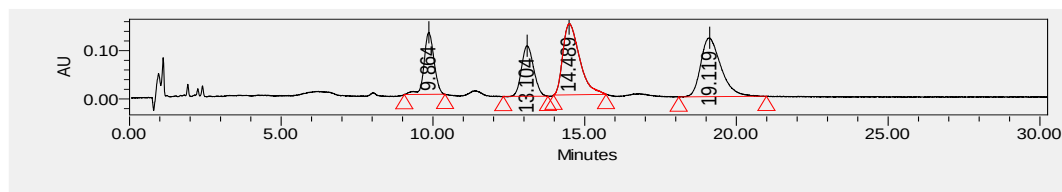
10.4 Hz, 1H), 4.84 (d, $J = 15.0$ Hz, 1H), 4.39 (d, $J = 15.0$ Hz, 1H), 3.90 (dd, $J = 10.8, 6.0$ Hz, 1H), 3.81 (s, 3H), 3.67 – 3.36 (m, 2H), 2.43 (ddd, $J = 14.0, 6.0, 1.6$ Hz, 1H), 2.21 – 2.09 (m, 1H) ppm.

Endo D14: ^{13}C NMR (101 MHz, CDCl_3) δ 165.3, 159.7, 146.7, 141.2, 141.1, 137.2, 129.5, 129.0, 128.9, 128.8, 128.7, 128.1, 127.7, 127.6, 127.4, 123.5, 118.7, 113.9, 111.8, 80.1, 55.4, 47.3, 46.5, 40.9, 40.0 ppm.

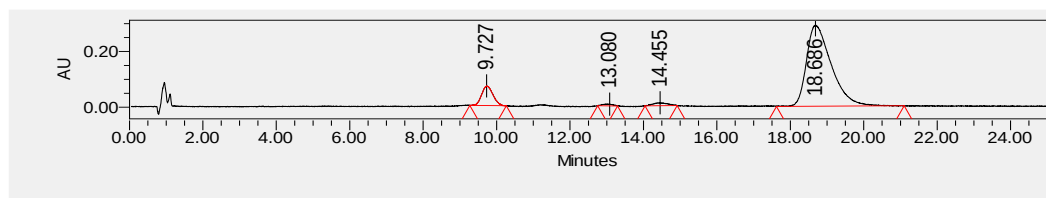
Exo D14: ^{13}C NMR (101 MHz, CDCl_3) δ 165.3, 159.7, 146.7, 141.2, 141.1, 137.2, 129.5, 129.0, 128.9, 128.8, 128.7, 128.1, 127.7, 127.6, 127.4, 123.5, 118.5, 113.6, 111.7, 75.5, 54.3, 48.0, 46.6, 38.5, 36.9 ppm.

ESI-HRMS calcd for $[\text{C}_{27}\text{H}_{25}\text{NO}_3 + \text{Na}^+] = 434.1727$, found 434.1735.

IR $\tilde{\nu}$ (cm^{-1}) 2918, 2360, 1695, 1540, 1454, 1241, 1110, 1044, 936, 751, 699.

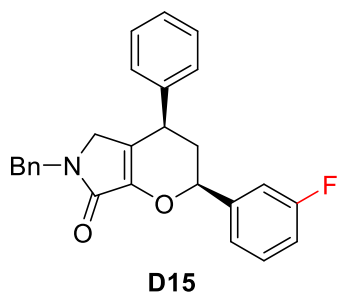


	Retention Time	Area	% Area	Height
1	9.864	2926824	17.15	128364
2	13.104	2905088	17.02	104529
3	14.489	5633326	33.01	147379
4	19.119	5599129	32.81	121708



	Retention Time	Area	% Area	Height
1	9.727	1484181	9.55	70408
2	13.080	120426	0.77	6881
3	14.455	290015	1.87	10568
4	18.686	13652110	87.81	292746

D15: (2S,4R)-6-benzyl-2-(3-fluorophenyl)-4-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7 (2H)-one



D15: 51% yield, endo/exo = 91/9, 98%/86% ee; Colorless liquid, $[\alpha]_D^{25} = -35.8$ ($c = 0.40$, in CH_2Cl_2).

SFC Chiralcel OD-3, $\text{CO}_2/\text{MeOH} = 80/20$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 4.56$ min, $t_2 = 5.09$ min, $t_3 = 5.68$ min, $t_4 = 6.84$ min.

^1H NMR (400 MHz, Chloroform- d) δ 7.38 – 7.27 (m, 5H), 7.27 – 7.24 (m, 2H), 7.21 (q, $J = 10.0, 8.4$ Hz, 4H), 7.16 – 7.05 (m, 2H), 6.98 (qd, $J = 8.8, 2.0$ Hz, 1H), 5.16 (d, $J = 10.6$ Hz, 1H), 4.84 (d, $J = 15.0$ Hz, 1H), 4.40 (d, $J = 15.0$ Hz, 1H), 3.91 (dd, $J = 10.8, 6.0$ Hz, 1H), 3.67 – 3.26 (m, 2H), 2.44 (ddd, $J = 14.0, 6.0, 1.8$ Hz, 1H), 2.16 – 2.00 (m, 1H) ppm.

Endo D15: ^{13}C NMR (101 MHz, CDCl_3) δ 165.2, 162.9(d, $J_{\text{C-F}} = 245.0$), 146.6, 142.2, 142.1(d, $J_{\text{C-F}} = 7.0$), 140.9, 137.1, 130.1, 129.9, 129.0(d, $J_{\text{C-F}} = 3.0$), 128.8, 128.7, 128.2, 128.1, 127.8, 127.6, 127.5, 127.4, 123.6, 121.9, 115.2, 115.0, 113.5, 113.3(d, $J_{\text{C-F}} = 22.0$), 79.4, 47.3, 46.5, 40.8, 39.9 ppm.

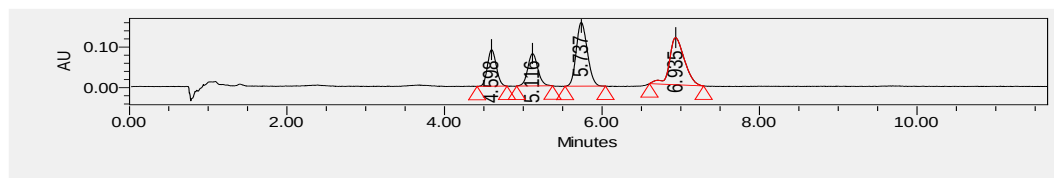
Exo D15: ^{13}C NMR (101 MHz, CDCl_3) δ 165.2, 162.9(d, $J_{\text{C-F}} = 245.0$), 146.6, 142.2, 142.1(d, $J_{\text{C-F}} = 7.0$), 140.9, 137.1, 130.1, 129.9, 129.0(d, $J_{\text{C-F}} = 3.0$), 128.8, 128.7, 128.2, 128.1, 127.8, 127.6, 127.5, 127.4, 123.6, 121.8, 115.2, 114.8, 113.5, 113.3(d, $J_{\text{C-F}} = 22.0$), 74.8, 48.0, 46.5, 36.9, 34.1 ppm.

Endo D15: ^{19}F NMR (377 MHz, CDCl_3) δ -112.80 ppm.

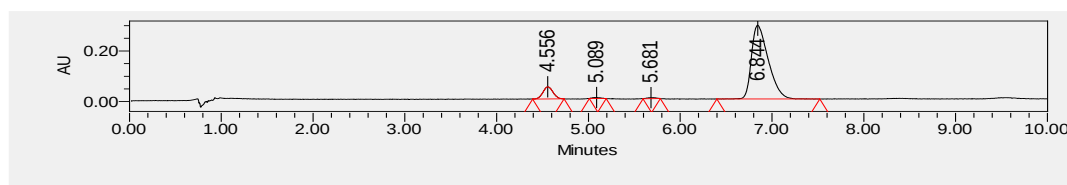
Exo D15: ^{19}F NMR (377 MHz, CDCl_3) δ -112.80 ppm.

ESI-HRMS calcd for $[\text{C}_{26}\text{H}_{22}\text{FNO}_2 + \text{Na}^+] = 422.1527$, found 422.1531.

IR $\tilde{\nu}$ (cm^{-1}) 2919, 2360, 1694, 1493, 1454, 1240, 1111, 1048, 787, 762, 698.

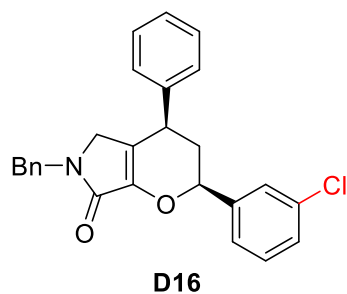


	Retention Time	Area	% Area	Height
1	4.598	699348	15.64	89915
2	5.116	707763	15.83	79781
3	5.737	1531327	34.25	156731
4	6.935	1533107	34.29	115851



	Retention Time	Area	% Area	Height
1	4.556	363601	8.82	47917
2	5.089	27366	0.66	4573
3	5.681	30848	0.75	4694
4	6.844	3702648	89.77	291386

D16: (2S,4R)-6-benzyl-2-(3-chlorophenyl)-4-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



D16: 50% yield, endo/exo = 93/7, 98%/87% ee; Colorless liquid, $[\alpha]_D^{25} = -41.8$ ($c = 0.61$, in CH_2Cl_2).

SFC Chiralcel OD-3, $\text{CO}_2/\text{MeOH} = 80/20$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 6.10$ min, $t_2 = 7.22$ min, $t_3 = 8.71$ min, $t_4 = 9.34$ min.

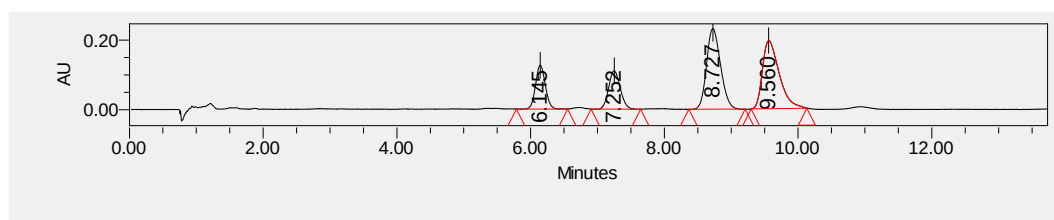
^1H NMR (400 MHz, CHCl_3) δ 7.47 (m, 1H), 7.34 – 7.31 (m, 1H), 7.31 – 7.29 (m, 2H), 7.28 (dd, $J = 4.0, 1.6$ Hz, 4H), 7.26 – 7.23 (m, 2H), 7.23 – 7.18 (m, 2H), 7.18 – 7.08 (m, 2H), 5.21 – 5.01 (m, 1H), 4.83 (d, $J = 15.0$ Hz, 1H), 4.40 (d, $J = 15.0$ Hz, 1H), 3.90 (dd, $J = 10.8, 6.0$ Hz, 1H), 3.68 – 3.36 (m, 2H), 2.43 (ddd, $J = 14.0, 6.0, 1.8$ Hz, 1H), 2.11 (dt, $J = 14.0, 11.2$ Hz, 1H) ppm.

Endo D16: ^{13}C NMR (101 MHz, CDCl_3) δ 165.2, 146.6, 141.6, 140.9, 137.1, 134.4, 129.8, 129.0, 128.7, 128.4, 128.1, 127.6, 127.5, 127.4, 126.5, 124.5, 123.6, 79.4, 47.3, 46.5, 40.8, 39.9 ppm.

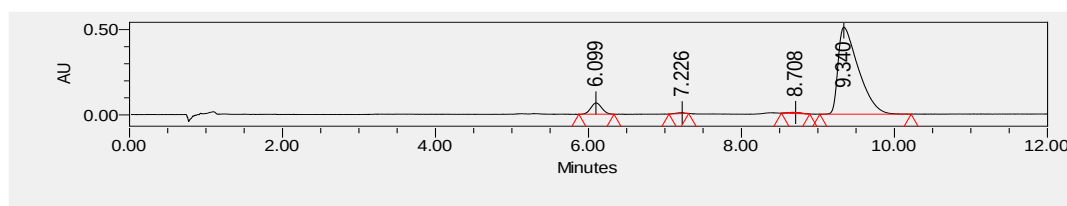
Exo D16: ^{13}C NMR (101 MHz, CDCl_3) δ 165.2, 146.6, 141.7, 140.9, 137.1, 134.4, 129.8, 129.0, 128.8, 128.4, 128.2, 127.6, 127.5, 127.4, 126.4, 124.5, 123.6, 74.8, 48.0, 46.5, 38.6, 36.9 ppm.

ESI-HRMS calcd for $[\text{C}_{26}\text{H}_{22}\text{ClNO}_2 + \text{Na}^+] = 438.1231$, found 438.1238.

IR $\tilde{\nu}$ (cm^{-1}) 2919, 2360, 1694, 1493, 1454, 1240, 1111, 1048, 787, 762, 698.

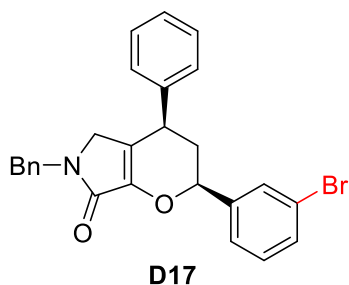


	Retention Time	Area	% Area	Height
1	6.145	1279391	13.67	125654
2	7.252	1324434	14.15	110053
3	8.727	3361908	35.91	231070
4	9.560	3396620	36.28	195332



	Retention Time	Area	% Area	Height
1	6.099	654094	6.43	66299
2	7.226	43381	0.43	5332
3	8.708	75066	0.74	6806
4	9.340	9407193	92.41	510324

D17: (2S,4R)-6-benzyl-2-(3-bromophenyl)-4-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



D17: 53% yield, endo/exo = 93/7, 98%/87% ee; Colorless liquid, $[\alpha]_D^{25} = -36.4$ ($c = 0.42$, in CH_2Cl_2).

SFC Chiralcel OJ-3, $\text{CO}_2/\text{MeOH} = 80/20$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 3.79$ min, $t_2 = 4.10$ min, $t_3 = 4.94$ min, $t_4 = 6.76$ min.

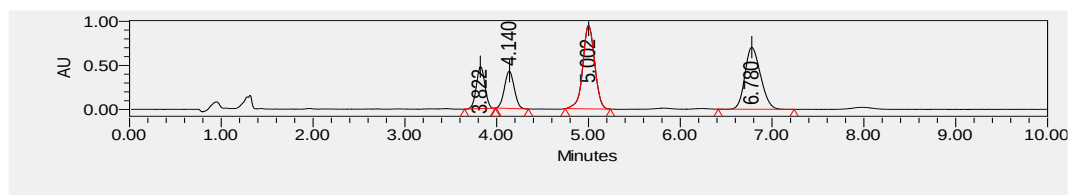
^1H NMR (400 MHz, Chloroform- d) δ 7.62 (m, 1H), 7.49 – 7.41 (m, 1H), 7.37 (d, $J = 7.8$ Hz, 1H), 7.30 (ddd, $J = 10.0, 6.0, 2.4$ Hz, 4H), 7.25 (dd, $J = 7.2, 2.4$ Hz, 2H), 7.21 (d, $J = 8.0$ Hz, 3H), 7.17 – 7.07 (m, 2H), 5.13 (d, $J = 10.6$ Hz, 1H), 4.83 (d, $J = 15.0$ Hz, 1H), 4.40 (d, $J = 15.0$ Hz, 1H), 3.90 (dd, $J = 10.8, 6.0$ Hz, 1H), 3.68 – 3.34 (m, 2H), 2.43 (ddd, $J = 14.2, 6.0, 1.6$ Hz, 1H), 2.11 (dt, $J = 14.2, 11.2$ Hz, 1H).

Endo D17: ^{13}C NMR (101 MHz, Chloroform- d) δ 165.2, 146.6, 137.1, 131.3, 130.1, 129.4, 129.0, 128.7, 128.1, 127.6, 127.5, 127.4, 124.9, 123.6, 122.6, 79.3, 47.3, 46.5, 40.8, 39.9 ppm.

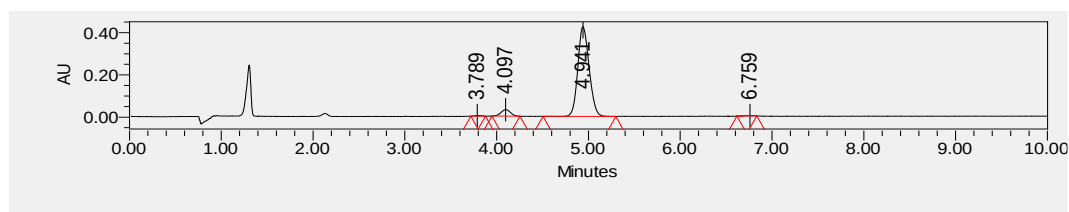
Exo D17: ^{13}C NMR (101 MHz, Chloroform- d) δ 165.2, 146.6, 137.1, 130.7, 130.1, 129.4, 129.0, 128.7, 128.1, 127.6, 127.5, 127.4, 124.9, 123.6, 122.6, 74.7, 47.3, 46.5, 42.2, 36.9 ppm.

ESI-HRMS calcd for $[\text{C}_{26}\text{H}_{22}\text{BrNO}_2 + \text{Na}^+] = 482.0726$, found 482.0738.

IR $\tilde{\nu}$ (cm^{-1}) 2919, 2360, 1693, 1493, 1454, 1241, 1110, 1074, 762, 700.

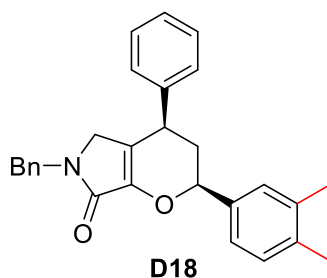


	Retention Time	Area	% Area	Height
1	3.822	3085173	13.44	475836
2	4.140	3110620	13.55	422280
3	5.002	8470788	36.90	949700
4	6.780	8291412	36.12	703912



	Retention Time	Area	% Area	Height
1	3.789	13653	0.35	2951
2	4.097	220122	5.69	30559
3	4.941	3621215	93.65	424371
4	6.759	11756	0.30	2074

D18: (2S,4R)-6-benzyl-2-(3,4-dimethylphenyl)-4-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7 (2H)-one



D18: 84% yield, endo/exo = 85/15, 93%/80% ee; Colorless liquid, $[\alpha]_D^{26} = -26.9$ ($c = 0.62$, in CH_2Cl_2).

SFC Chiralcel OJ-3, $\text{CO}_2/\text{MeOH} = 90/10$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 6.83$ min, $t_2 = 7.51$ min, $t_3 = 8.14$ min, $t_4 = 11.25$ min.

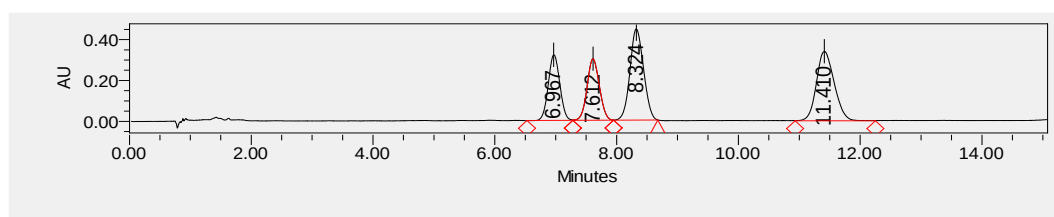
^1H NMR (400 MHz, CHCl_3) δ 7.35 – 7.27 (m, 4H), 7.22 (dq, $J = 10.4, 5.8, 3.6$ Hz, 4H), 7.13 (dq, $J = 14.4, 7.4$ Hz, 4H), 7.04 (dd, $J = 12.0, 6.4$ Hz, 1H), 5.10 (d, $J = 10.6$ Hz, 1H), 4.83 (d, $J = 15.0$ Hz, 1H), 4.39 (d, $J = 15.0$ Hz, 1H), 3.89 (dd, $J = 10.8, 6.0$ Hz, 1H), 3.61 – 3.32 (m, 2H), 2.41 (ddd, $J = 14.0, 6.0, 1.6$ Hz, 1H), 2.26 – 2.22 (m, 6H), 2.18 – 2.11 (m, 1H).

Endo D18: ^{13}C NMR (101 MHz, CDCl_3) δ 165.5, 146.9, 141.4, 137.2, 137.1, 136.7, 136.6, 129.6, 129.0, 128.9, 128.8, 128.7, 128.2, 128.1, 127.9, 127.7, 127.6, 127.3, 123.8, 123.3, 80.1, 47.3, 46.5, 40.7, 40.1, 19.8, 19.6 ppm.

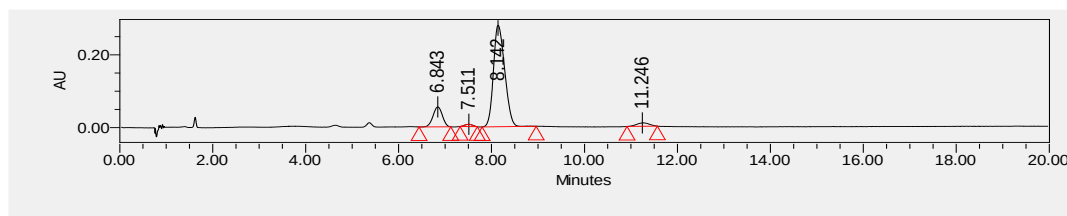
Exo D18: ^{13}C NMR (101 MHz, CDCl_3) δ 165.5, 146.9, 141.1, 137.2, 137.1, 136.7, 136.4, 129.6, 129.0, 128.9, 128.8, 128.7, 128.2, 128.1, 127.9, 127.6, 127.5, 127.1, 123.6, 120.8, 75.5, 48.0, 46.6, 38.5, 37.0, 19.8, 19.6 ppm.

ESI-HRMS calcd for $[\text{C}_{28}\text{H}_{27}\text{NO}_2 + \text{Na}^+] = 432.1934$, found 432.1938.

IR $\tilde{\nu}$ (cm^{-1}) 3027, 2360, 1695, 1494, 1453, 1241, 1109, 1050, 821, 762, 701.

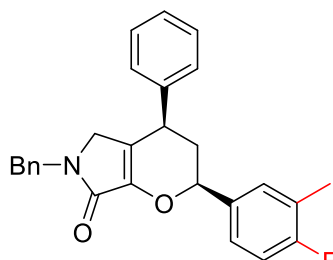


	Retention Time	Area	% Area	Height
1	6.967	4205956	18.95	320596
2	7.612	4206042	18.95	300372
3	8.324	6914772	31.16	445904
4	11.410	6866408	30.94	339460



	Retention Time	Area	% Area	Height
1	6.843	761709	13.36	54858
2	7.511	77514	1.36	6422
3	8.142	4680823	82.12	278954
4	11.246	179886	3.16	9464

D19: (2S,4R)-6-benzyl-2-(4-fluoro-3-methylphenyl)-4-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



D19

D19: 99% yield, endo/exo = 89/11, 96%/70% ee; Colorless liquid, $[\alpha]_D^{25} = -31.8$ ($c = 0.76$, in CH_2Cl_2).

SFC Chiralcel OD-3, $\text{CO}_2/\text{MeOH} = 80/20$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 4.37$ min, $t_2 = 5.40$ min, $t_3 = 5.83$ min, $t_4 = 7.83$ min.

^1H NMR (400 MHz, $\text{Chloroform-}d$) δ 7.33 (d, $J = 12.0$ Hz, 1H), 7.31 – 7.27 (m, 4H), 7.27 – 7.23 (m, 2H), 7.23 – 7.16 (m, 3H), 7.16 – 7.05 (m, 2H), 7.00 – 6.90 (m, 1H), 5.10 (d, $J = 10.4$ Hz, 1H), 4.84 (dd, $J = 14.8, 3.6$ Hz, 1H), 4.39 (d, $J = 15.0$ Hz, 1H), 3.89 (dd, $J = 10.8, 6.0$ Hz, 1H), 3.69 – 3.15 (m, 2H), 2.40 (ddd, $J = 14.0, 6.0, 1.8$ Hz, 1H), 2.25 (dd, $J = 10.4, 1.6$ Hz, 3H), 2.12 (dt, $J = 14.0, 11.2$ Hz, 1H).

Endo D19: **^{13}C NMR** (101 MHz, CDCl_3) δ 165.3, 161.1(d, $J_{\text{C-F}} = 244.0$), 146.7, 143.0, 141.2, 137.1, 137.1, 135.1, 135.0, 129.6(d, $J_{\text{C-F}} = 6.0$), 129.0, 128.9, 128.8, 128.7, 128.6, 128.2, 128.1, 127.8, 127.7, 127.6, 127.5, 127.4, 127.2, 125.4, 125.4, 125.0(d, $J_{\text{C-F}} = 17.0$), 124.8, 123.4, 114.9(d, $J_{\text{C-F}} = 23.0$), 79.6, 47.3, 46.5, 40.9, 39.9, 14.6 ppm.

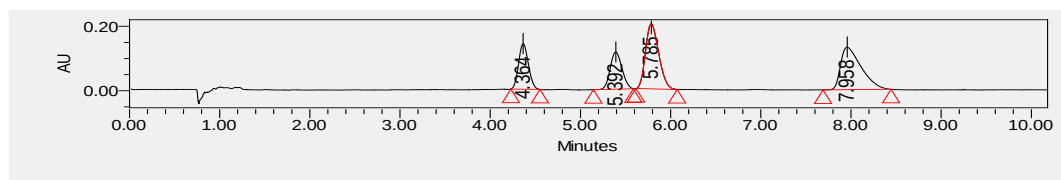
Exo D19: **^{13}C NMR** (101 MHz, CDCl_3) δ 165.3, 161.1(d, $J_{\text{C-F}} = 244.0$), 146.9, 143.0, 141.2, 137.1, 137.1, 135.1, 135.0, 129.5(d, $J_{\text{C-F}} = 6.0$), 129.0, 128.9, 128.8, 128.7, 128.6, 128.2, 128.1, 127.8, 127.7, 127.6, 127.5, 127.4, 127.2, 125.4, 125.4, 125.0(d, $J_{\text{C-F}} = 17.0$), 124.8, 120.8, 114.9(d, $J_{\text{C-F}} = 23.0$), 75.0, 48.0, 46.6, 38.7, 37.0, 14.2 ppm.

Endo D19: **^{19}F NMR** (377 MHz, CDCl_3) δ -118.27 ppm.

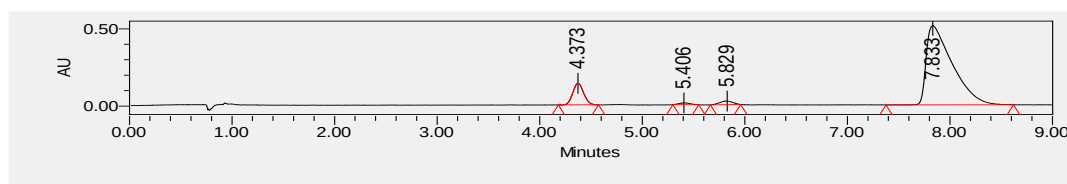
Exo D19: **^{19}F NMR** (377 MHz, CDCl_3) δ -118.56 ppm.

ESI-HRMS calcd for $[\text{C}_{27}\text{H}_{24}\text{FNO}_2 + \text{Na}^+] = 436.1683$, found 436.1689.

IR $\tilde{\nu}$ (cm^{-1}) 2918, 2360, 1697, 1503, 1454, 1243, 1118, 1049, 822, 750, 701.



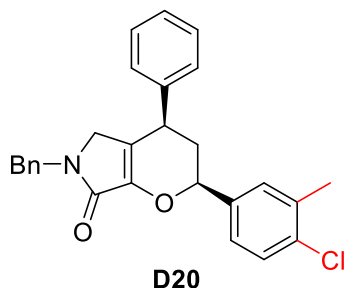
	Retention Time	Area	% Area	Height
1	4.364	1067797	17.07	141370
2	5.392	1048777	16.77	115171
3	5.785	2056931	32.88	202028
4	7.958	2081884	33.28	132322



	Retention Time	Area	% Area	Height
1	4.373	1031770	9.95	140050
2	5.406	93329	0.90	11966
3	5.829	204833	1.98	23503

4	7.833	9035783	87.17	513951
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D20: (2S,4R)-6-benzyl-2-(4-chloro-3-methylphenyl)-4-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



D20: 70% yield, endo/exo = 92/8, 98%/77% ee; Colorless liquid, $[\alpha]^{25}_D = -34.7$ ($c = 0.58$, in CH_2Cl_2).

SFC Chiralcel OD-3, $\text{CO}_2/\text{MeOH} = 80/20$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 6.06$ min, $t_2 = 7.77$ min, $t_3 = 9.17$ min, $t_4 = 13.02$ min.

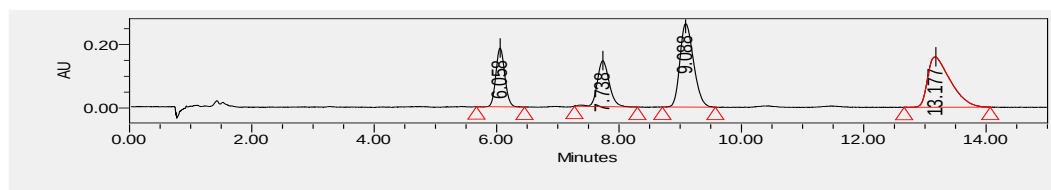
^1H NMR (400 MHz, Chloroform- d) δ 7.37 – 7.33 (m, 1H), 7.32 (d, $J = 2.8$ Hz, 1H), 7.30 (d, $J = 2.0$ Hz, 2H), 7.27 (dd, $J = 4.4$, 2.0 Hz, 2H), 7.26 – 7.23 (m, 2H), 7.22 (d, $J = 1.4$ Hz, 1H), 7.21 – 7.16 (m, 2H), 7.16 – 7.04 (m, 2H), 5.11 (d, $J = 10.4$ Hz, 1H), 4.83 (d, $J = 15.0$ Hz, 1H), 4.39 (d, $J = 15.0$ Hz, 1H), 3.89 (dd, $J = 10.8$, 6.0 Hz, 1H), 3.68 – 3.34 (m, 2H), 2.49 – 2.30 (m, 4H), 2.10 (dt, $J = 14.0$, 11.2 Hz, 1H) ppm.

Endo D20: ^{13}C NMR (101 MHz, CDCl_3) δ 165.3, 146.7, 141.1, 138.2, 137.1, 136.2, 134.2, 129.0, 128.9, 128.8, 128.7, 128.1, 127.6, 127.5, 127.4, 125.1, 123.5, 79.5, 47.3, 46.5, 40.8, 39.9, 20.1 ppm.

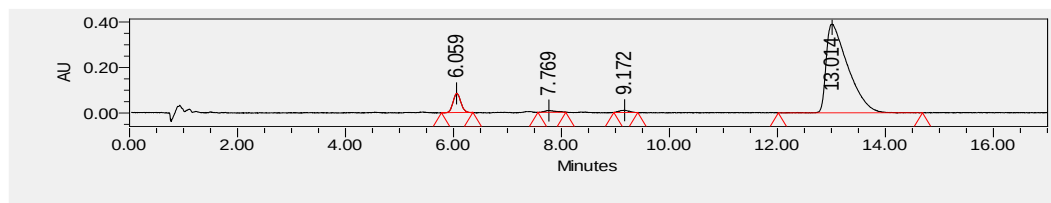
Exo D20: ^{13}C NMR (101 MHz, CDCl_3) δ 165.3, 146.7, 141.6, 138.2, 137.0, 136.2, 134.2, 129.0, 128.9, 128.8, 128.7, 128.1, 127.6, 127.5, 127.4, 124.9, 123.1, 74.9, 48.0, 46.5, 38.7, 36.9, 14.2 ppm.

ESI-HRMS calcd for $[\text{C}_{27}\text{H}_{24}\text{ClNO}_2 + \text{Na}^+] = 452.1388$, found 452.1394.

IR $\tilde{\nu}$ (cm^{-1}) 2918, 2360, 1696, 1454, 1242, 1110, 1047, 821, 751, 701.

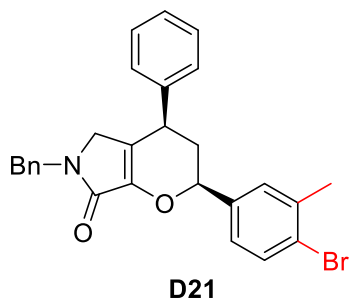


	Retention Time	Area	% Area	Height
1	6.058	1885146	15.74	185248
2	7.738	1951744	16.29	144885
3	9.088	4066369	33.95	263121
4	13.177	4075741	34.02	158486



	Retention Time	Area	% Area	Height
1	6.059	835562	6.98	84567
2	7.769	111859	0.93	8146
3	9.172	123372	1.03	10336
4	13.014	10897669	91.05	390475

D21: (2S,4R)-6-benzyl-2-(4-bromo-3-methylphenyl)-4-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



D21: 80% yield, endo/exo = 92/8, 98%/82% ee; Colorless liquid, $[\alpha]_D^{25} = -29.6$ ($c = 0.72$, in CH_2Cl_2).

SFC Chiralcel OD-3, $\text{CO}_2/\text{MeOH} = 80/20$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 7.27$ min, $t_2 = 9.37$ min, $t_3 = 11.57$ min, $t_4 = 16.66$ min.

^1H NMR (400 MHz, Chloroform- d) δ 7.49 (d, $J = 8.2$ Hz, 1H), 7.34 (m, 1H), 7.32 – 7.29 (m, 2H), 7.29 – 7.25 (m, 3H), 7.25 – 7.17 (m, 3H), 7.17 – 6.95 (m, 3H), 5.09 (d, $J = 11.2$ Hz, 1H), 4.83 (d, $J =$

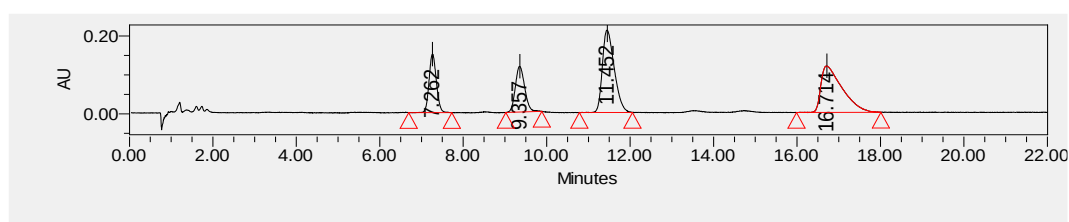
15.0 Hz, 1H), 4.39 (d, $J = 15.0$ Hz, 1H), 3.89 (dd, $J = 10.8, 6.0$ Hz, 1H), 3.68 – 3.38 (m, 2H), 2.46 – 2.33 (m, 4H), 2.10 (dt, $J = 14.0, 11.2$ Hz, 1H) ppm.

Endo D21: ^{13}C NMR (101 MHz, CDCl_3) δ 165.3, 146.6, 141.1, 138.9, 138.1, 137.1, 132.3, 129.0, 128.7, 128.1, 127.6, 127.5, 127.4, 125.3, 124.5, 123.5, 79.5, 47.3, 46.5, 40.8, 39.9, 22.9 ppm.

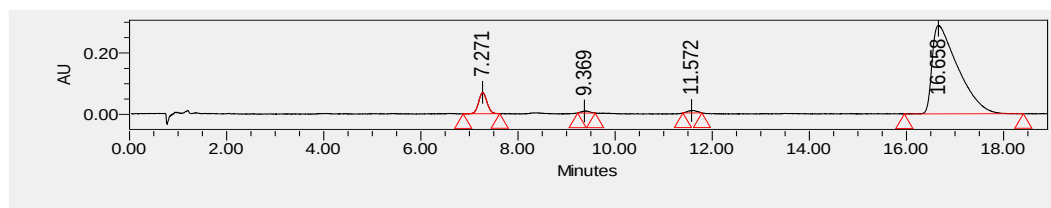
Exo D21: ^{13}C NMR (101 MHz, CDCl_3) δ 165.3, 146.6, 141.1, 138.8, 138.0, 137.0, 132.3, 129.0, 128.6, 128.2, 127.6, 127.5, 127.2, 125.1, 124.5, 123.5, 74.8, 48.0, 46.6, 38.7, 36.9, 23.7 ppm.

ESI-HRMS calcd for $[\text{C}_{27}\text{H}_{24}\text{BrNO}_2 + \text{Na}^+] = 496.0883$, found 496.0893.

IR $\tilde{\nu}$ (cm^{-1}) 2918, 2360, 1694, 1453, 1240, 1198, 1026, 819, 734, 700.

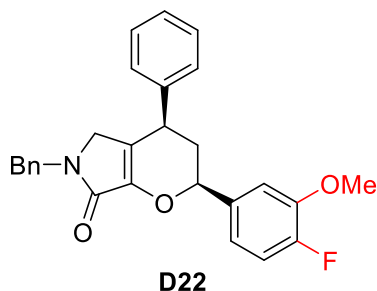


	Retention Time	Area	% Area	Height
1	7.262	1816327	15.12	150143
2	9.357	1820785	15.16	117320
3	11.452	4179691	34.80	211833
4	16.714	4193139	34.91	119543



	Retention Time	Area	% Area	Height
1	7.271	838176	7.19	70124
2	9.369	79844	0.68	7032
3	11.572	106403	0.91	8241
4	16.658	10634465	91.21	288675

D22: (2S,4R)-6-benzyl-2-(4-fluoro-3-methoxyphenyl)-4-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



D22: 92% yield, endo/exo = 90/10, 99%/93% ee; Colorless liquid, $[\alpha]_D^{26} = -25.5$ ($c = 0.74$, in CH_2Cl_2).

SFC Chiralcel OJ-3, $\text{CO}_2/\text{MeOH} = 80/20$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 3.27$ min, $t_2 = 3.80$ min, $t_3 = 4.05$ min, $t_4 = 5.94$ min.

^1H NMR (400 MHz, CHCl_3) δ 7.43 (tt, $J = 11.6, 5.4$ Hz, 1H), 7.38 – 7.33 (m, 1H), 7.33 – 7.27 (m, 4H), 7.24 – 7.19 (m, 2H), 7.14 (d, $J = 7.0$ Hz, 2H), 7.11 – 7.05 (m, 1H), 7.05 – 6.96 (m, 1H), 6.92 (ddd, $J = 8.2, 4.0, 1.6$ Hz, 1H), 5.12 (d, $J = 11.0$ Hz, 1H), 4.83 (d, $J = 15.2$ Hz, 1H), 4.40 (d, $J = 15.2$ Hz, 1H), 3.88 (d, $J = 15.2$ Hz, 4H), 3.71 – 3.35 (m, 2H), 2.65 – 2.32 (m, 1H), 2.12 (dt, $J = 14.0, 11.2$ Hz, 1H) ppm.

Endo D22: ^{13}C NMR (101 MHz, CDCl_3) δ 165.3, 152.2(d, $J_{\text{C-F}} = 244.0$), 151.0, 147.7, 147.6(d, $J_{\text{C-F}} = 11.0$), 146.7, 141.1, 138.3, 137.1, 136.1, 131.3, 129.4, 129.2, 129.0, 128.8, 128.5, 128.4, 128.0, 127.7, 127.6, 127.5, 123.6, 118.8, 115.9, 115.7(d, $J_{\text{C-F}} = 18.0$), 111.6(d, $J_{\text{C-F}} = 2.0$), 79.8, 56.3, 47.3, 46.5, 40.9, 39.9 ppm.

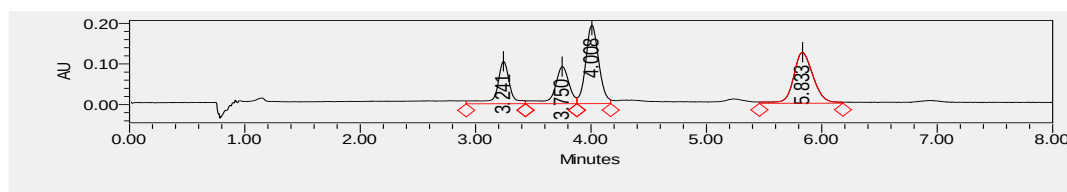
Exo D22: ^{13}C NMR (101 MHz, CDCl_3) δ 160.6, 152.2(d, $J_{\text{C-F}} = 244.0$), 150.8, 147.7, 147.6(d, $J_{\text{C-F}} = 11.0$), 146.8, 142.9, 138.3, 137.1, 136.1, 131.6, 129.4, 129.2, 129.0, 128.7, 128.5, 128.4, 128.1, 127.8, 127.6, 127.4, 123.6, 118.8, 115.9, 115.7(d, $J_{\text{C-F}} = 18.0$), 111.6(d, $J_{\text{C-F}} = 2.0$), 75.1, 54.8, 48.1, 46.4, 38.7, 37.0 ppm.

Endo D22: ^{19}F NMR (377 MHz, CDCl_3) δ -135.82 ppm.

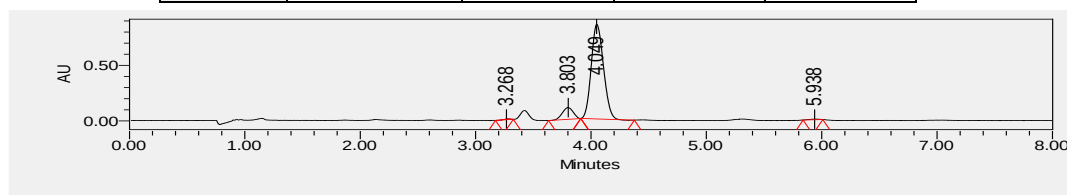
Exo D22: ^{19}F NMR (377 MHz, CDCl_3) δ -136.08 ppm.

ESI-HRMS calcd for $[\text{C}_{27}\text{H}_{24}\text{FNO}_3 + \text{Na}^+]$ = 452.1632, found 452.1636.

IR $\tilde{\nu}$ (cm^{-1}) 2920, 2360, 1698, 1540, 1455, 1276, 1155, 1117, 1029, 750, 701.



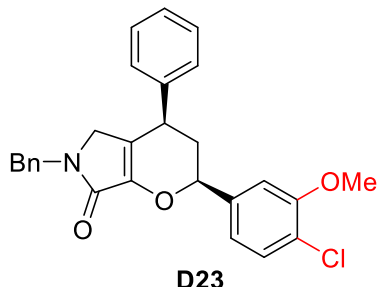
	Retention Time	Area	% Area	Height
1	3.241	792721	17.26	104581
2	3.750	794501	17.29	91339
3	4.008	1514602	32.97	193049
4	5.833	1492048	32.48	125654



	Retention Time	Area	% Area	Height
1	3.268	25444	0.36	7085
2	3.803	690165	9.79	105527

3	4.049	6296922	89.32	851689
4	5.938	37346	0.53	6247

D23: (2S,4R)-6-benzyl-2-(4-chloro-3-methoxyphenyl)-4-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



D23: 72% yield, endo/exo = 91/9, 97%/88% ee; Colorless liquid, $[\alpha]_D^{26} = -26.4$ ($c = 0.67$, in CH_2Cl_2).

SFC Chiralcel OD-3, $\text{CO}_2/\text{MeOH} = 80/20$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 6.73$ min, $t_2 = 8.93$ min, $t_3 = 10.47$ min, $t_4 = 16.54$ min.

^1H NMR (400 MHz, Chloroform- d) δ 7.46 – 7.36 (m, 1H), 7.33 – 7.28 (m, 4H), 7.27 (d, $J = 3.6$ Hz, 2H), 7.23 – 7.19 (m, 2H), 7.19 – 7.11 (m, 2H), 7.05 (d, $J = 1.6$ Hz, 1H), 6.93 (dd, $J = 8.0$,

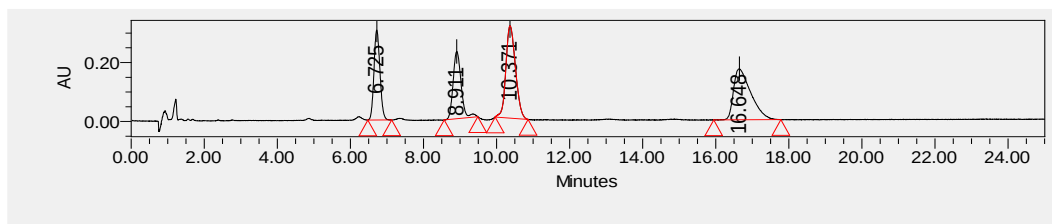
1.6 Hz, 1H), 5.13 (d, $J = 10.4$ Hz, 1H), 4.83 (d, $J = 15.0$ Hz, 1H), 4.40 (d, $J = 15.0$ Hz, 1H), 3.90 (d, $J = 16.0$ Hz, 4H), 3.69 – 3.40 (m, 2H), 2.43 (ddd, $J = 14.0$, 6.0, 1.6 Hz, 1H), 2.11 (dt, $J = 14.0$, 11.2 Hz, 1H) ppm.

Endo D23: ^{13}C NMR (101 MHz, CDCl_3) δ 165.2, 155.1, 146.6, 140.9, 139.8, 137.1, 130.1, 129.2, 128.8, 128.0, 127.6, 127.5, 123.7, 122.1, 119.1, 110.0, 79.6, 56.3, 47.3, 46.5, 40.9, 39.9 ppm.

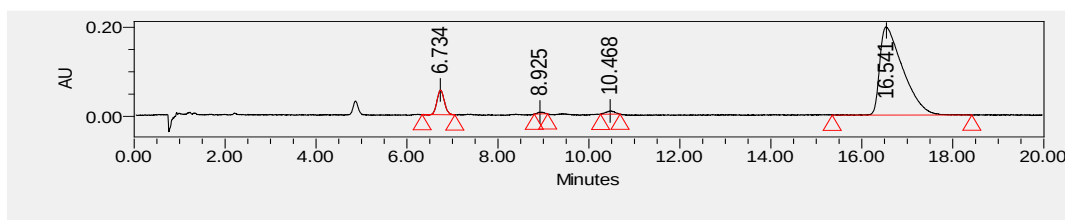
Exo D23: ^{13}C NMR (101 MHz, CDCl_3) δ 165.2, 155.1, 146.6, 140.9, 139.8, 138.3, 129.4, 129.0, 128.8, 128.1, 127.8, 127.5, 124.7, 121.1, 118.9, 110.0, 75.3, 56.3, 48.1, 46.5, 38.7, 36.9 ppm.

ESI-HRMS calcd for $[\text{C}_{27}\text{H}_{24}\text{ClNO}_3 + \text{Na}^+] = 468.1337$, found 468.1345.

IR $\tilde{\nu}$ (cm^{-1}) 2920, 2360, 1695, 1540, 1454, 1240, 1200, 1060, 1028, 846, 749, 699.

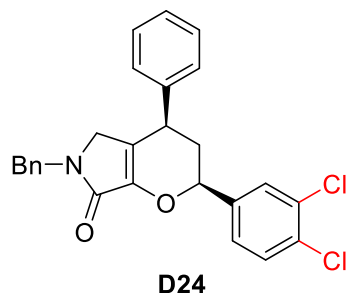


	Retention Time	Area	% Area	Height
1	6.725	3466084	18.92	305550
2	8.911	3479249	19.00	228238
3	10.371	5711842	31.19	313435
4	16.648	5658738	30.90	173443



	Retention Time	Area	% Area	Height
1	6.734	629938	8.14	55628
2	8.925	38701	0.50	4424
3	10.468	95491	1.23	7405
4	16.541	6978931	90.13	197796

D24: (2S,4R)-6-benzyl-2-(3,4-dichlorophenyl)-4-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7 (2H)-one



D24: 22% yield, endo/exo = 97/3, 97%/94% ee; Colorless liquid, $[\alpha]_D^{25} = -31.9$ ($c = 0.46$, in CH_2Cl_2).

SFC Chiralcel OD-3, $\text{CO}_2/\text{MeOH} = 80/20$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 7.83$ min, $t_2 = 10.37$ min, $t_3 = 12.40$ min, $t_4 = 16.50$ min.

^1H NMR (400 MHz, Chloroform- d) δ 7.57 (d, $J = 2.0$ Hz, 1H), 7.43 (d, $J = 8.4$ Hz, 1H), 7.31 (dd, $J = 10.4$, 3.6 Hz, 4H), 7.28 – 7.23 (m, 3H), 7.23 – 7.18 (m, 2H), 7.17 – 7.07 (m, 2H), 5.12 (d, $J = 10.4$ Hz,

1H), 4.84 (d, $J = 15.0$ Hz, 1H), 4.40 (d, $J = 15.0$ Hz, 1H), 3.90 (dd, $J = 10.8$, 6.0 Hz, 1H), 3.65 – 3.32 (m, 2H), 2.42 (ddd, $J = 14.0$, 6.0, 1.8 Hz, 1H), 2.11 – 2.03 (m, 1H) ppm.

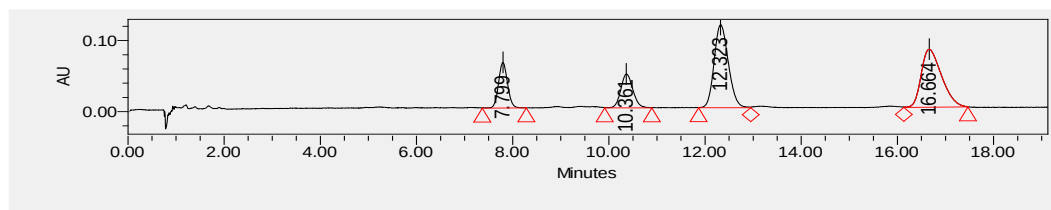
^{13}C NMR (101 MHz, CDCl_3) δ 165.1, 146.4, 140.7, 139.8, 137.0, 132.7, 132.2, 130.5, 129.1, 128.8, 128.4, 128.1, 127.7, 127.5, 127.5, 125.6, 123.7, 78.7, 47.3, 46.5, 40.7, 39.8 ppm.

HRMS (ESI) Calculated for $\text{C}_{26}\text{H}_{21}^{35}\text{Cl}^{35}\text{ClNO}_2$ ($[\text{M}] + \text{Na}^+$) = 472.0842, Found 472.0847.

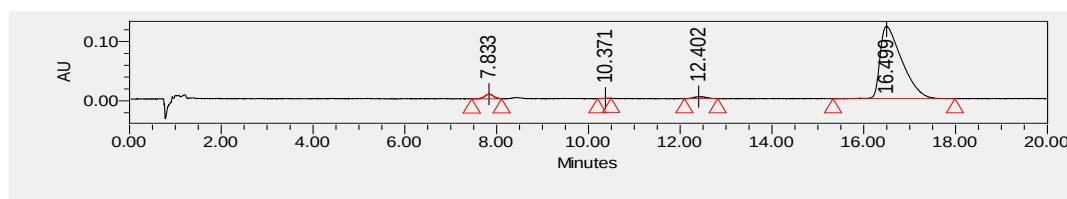
HRMS (ESI) Calculated for $\text{C}_{26}\text{H}_{21}^{35}\text{Cl}^{37}\text{ClNO}_2$ ($[\text{M}] + \text{Na}^+$) = 473.0875, Found 473.0878.

HRMS (ESI) Calculated for $\text{C}_{26}\text{H}_{21}^{37}\text{Cl}^{37}\text{ClNO}_2$ ($[\text{M}] + \text{Na}^+$) = 474.0812, Found 474.0818.

IR $\tilde{\nu}$ (cm^{-1}) 2920, 2360, 1692, 1493, 1454, 1241, 1110, 1049, 1029, 762, 701.

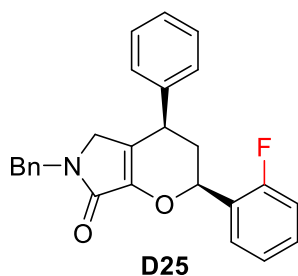


	Retention Time	Area	% Area	Height
1	7.799	832805	12.91	64179
2	10.361	829439	12.86	47602
3	12.323	2397748	37.17	116811
4	16.664	2390416	37.06	81624



	Retention Time	Area	% Area	Height
1	7.833	106543	2.54	8083
2	10.371	3448	0.08	695
3	12.402	61238	1.46	3518
4	16.499	4019321	95.91	122286

D25: C(2S,4R)-6-benzyl-2-(2-fluorophenyl)-4-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7 (2H)-one



D25: 20% yield, endo/exo = 89/11, 94%/71% ee; Colorless liquid, $[\alpha]^{22}_D = -66.3$ ($c = 0.08$, in CH_2Cl_2).

SFC Chiralcel OJ-3, $\text{CO}_2/\text{MeOH} = 90/10$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 4.59$ min, $t_2 = 5.08$ min, $t_3 = 5.61$ min, $t_4 = 6.33$ min.

^1H NMR (600 MHz, $\text{Chloroform-}d$) δ 7.71 – 7.49 (m, 1H), 7.35 – 7.31 (m, 1H), 7.31 – 7.27 (m, 4H), 7.27 – 7.24 (m, 2H), 7.22 (t, $J = 7.2$ Hz, 2H), 7.18 (d, $J = 7.7$ Hz, 1H), 7.15 (t, $J = 7.4$ Hz, 2H), 7.06 – 6.94 (m, 1H), 5.49 (d, $J = 11.0$ Hz, 1H), 4.84 (dd, $J = 15.0, 5.5$ Hz, 1H), 4.41 (d, $J = 15.0$ Hz, 1H), 3.93 (dd, $J = 10.8, 6.1$ Hz, 1H), 3.69 – 3.29 (m, 2H), 2.62 – 2.40 (m, 1H), 2.10 (dt, $J = 14.0, 11.3$ Hz, 1H) ppm.

Endo D25: ^{13}C NMR (151 MHz, CDCl_3) δ 165.3, 160.2, 158.9(d, $J_{\text{C-F}} = 244.0$), 146.6, 141.1(d, $J_{\text{C-F}} = 11.0$), 137.1, 129.6, 128.9, 128.8, 128.2, 128.1, 127.9, 127.7, 127.6, 127.4, 127.1, 126.9, 124.4, 123.6, 115.2(d, $J_{\text{C-F}} = 18.0$), 115.1(d, $J_{\text{C-F}} = 2.0$), 74.1, 47.3, 46.5, 39.9. 39.7 ppm.

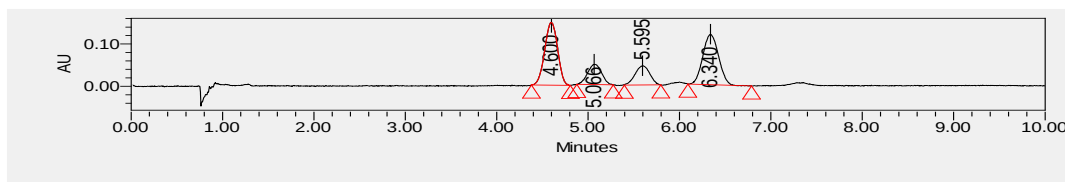
Exo D25: ^{13}C NMR (151 MHz, CDCl_3) δ 165.3, 160.2, 158.9(d, $J_{\text{C-F}} = 244.0$), 146.6, 141.1, 137.1, 129.6, 128.9, 128.8, 128.2, 128.1, 127.9, 127.7, 127.6, 127.4, 127.1, 126.9, 124.4, 123.6, 115.2(d, $J_{\text{C-F}} = 18.0$), 115.1(d, $J_{\text{C-F}} = 2.0$), 70.2, 48.1, 46.6, 37.2. 36.9 ppm.

Endo D25: ^{19}F NMR (565 MHz, CDCl_3) δ -119.80 ppm.

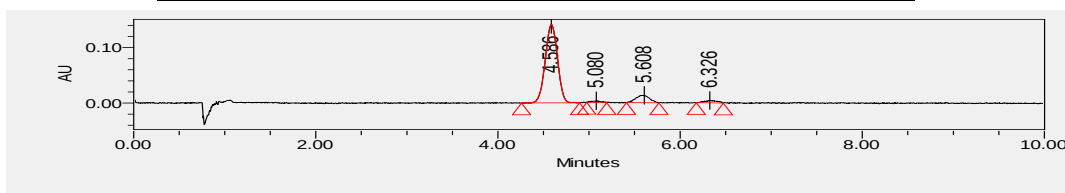
Exo D25: ^{19}F NMR (565 MHz, CDCl_3) δ -118.96 ppm.

ESI-HRMS calcd for $[\text{C}_{26}\text{H}_{22}\text{FNO}_2 + \text{Na}^+] = 422.1527$, found 422.1532.

IR $\tilde{\nu}$ (cm^{-1}) 3031, 2360, 1695, 1490, 1453, 1242, 1113, 1049, 756, 699

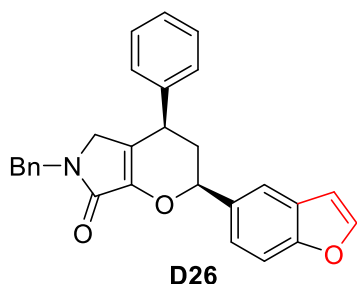


	Retention Time	Area	% Area	Height
1	4.600	1456441	37.35	147932
2	5.066	510518	13.09	48208
3	5.595	507019	13.00	45681
4	6.340	1425398	36.55	119091



	Retention Time	Area	% Area	Height
1	4.586	1318320	86.49	141183
2	5.080	23688	1.55	3455
3	5.608	140619	9.23	13545
4	6.326	41658	2.73	4367

D26: (2S,4R)-2-(benzofuran-5-yl)-6-benzyl-4-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7 (2H)-one



D26: 30% yield, endo/exo = 92/8, 98%/80% ee; Colorless liquid, $[\alpha]_D^{26} = -18.4$ ($c = 0.49$, in CH_2Cl_2).

SFC Chiralcel OD-3, $\text{CO}_2/\text{MeOH} = 80/20$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 8.40$ min, $t_2 = 9.78$ min, $t_3 = 12.29$ min, $t_4 = 20.42$ min.

^1H NMR (400 MHz, Chloroform- d) δ 7.81 – 7.65 (m, 1H), 7.62 (dd, $J = 4.6, 2.2$ Hz, 1H), 7.48 (d, $J = 8.4$ Hz, 1H), 7.37 – 7.34 (m, 1H), 7.34 – 7.26 (m, 5H), 7.25 – 7.20 (m, 3H), 7.20 – 7.10 (m, 2H),

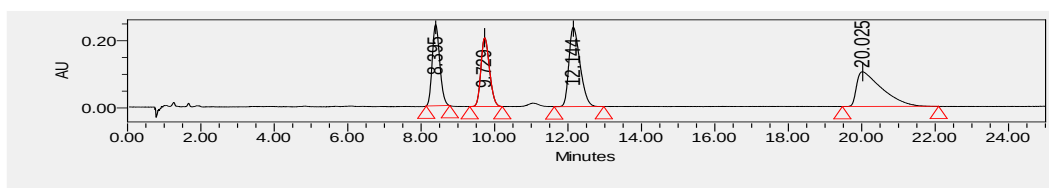
6.75 (d, $J = 1.6$ Hz, 1H), 5.26 (d, $J = 10.4$ Hz, 1H), 4.85 (d, $J = 15.0$ Hz, 1H), 4.40 (d, $J = 15.0$ Hz, 1H), 3.93 (dd, $J = 10.8, 6.0$ Hz, 1H), 3.70 – 3.35 (m, 2H), 2.47 (ddd, $J = 14.0, 6.0, 1.6$ Hz, 1H), 2.22 (dt, $J = 14.0, 11.2$ Hz, 1H) ppm.

Endo D26: ^{13}C NMR (101 MHz, CDCl_3) δ 165.4, 154.8, 146.9, 145.6, 141.3, 137.2, 134.4, 129.0, 128.9, 128.8, 128.7, 128.2, 128.1, 127.7, 127.6, 127.5, 127.3, 123.4, 122.9, 119.3, 111.3, 106.7, 80.4, 47.3, 46.5, 41.2, 40.1 ppm.

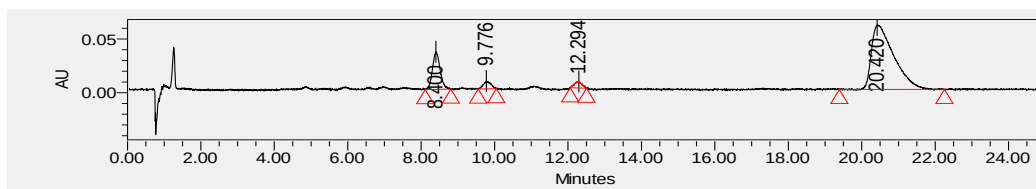
Exo D26: ^{13}C NMR (101 MHz, CDCl_3) δ 165.4, 154.8, 147.0, 145.6, 141.3, 137.1, 134.7, 129.0, 128.9, 128.8, 128.7, 128.2, 128.1, 127.7, 127.6, 127.5, 127.3, 123.1, 122.6, 119.2, 111.3, 106.7, 75.3, 48.1, 46.6, 39.1, 37.1 ppm.

ESI-HRMS calcd for $[\text{C}_{28}\text{H}_{23}\text{NO}_3 + \text{Na}^+] = 444.1570$, found 444.1575.

IR $\tilde{\nu}$ (cm^{-1}) 2920, 2360, 1693, 1493, 1453, 1242, 1110, 1049, 816, 760, 701.

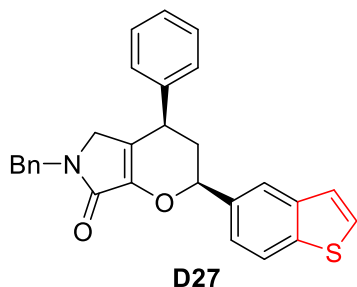


	Retention Time	Area	% Area	Height
1	8.395	3453721	20.73	241956
2	9.729	3334574	20.02	204625
3	12.144	4959053	29.77	236477
4	20.025	4909671	29.48	103396



	Retention Time	Area	% Area	Height
1	8.400	501409	15.48	35012
2	9.776	101754	3.14	7571
3	12.294	84837	2.62	6180
4	20.420	2551639	78.76	59971

D27: (2S,4R)-2-(benzo[b]thiophen-5-yl)-6-benzyl-4-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



D27: 25% yield, endo/exo = 92/8, 98%/80% ee; Colorless liquid, $[\alpha]_D^{25} = -32.7$ ($c = 0.22$, in CH_2Cl_2).

SFC Chiralcel OD-3, $\text{CO}_2/\text{MeOH} = 80/20$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 14.05$ min, $t_2 = 16.15$ min, $t_3 = 26.56$ min, $t_4 = 37.09$ min.

^1H NMR (400 MHz, Chloroform- d) δ 7.95 (m, 1H), 7.84 (dd, $J = 11.2, 7.2$ Hz, 1H), 7.45 (d, $J = 5.4$ Hz, 1H), 7.43 – 7.38 (m, 1H), 7.36 – 7.26 (m, 6H), 7.22 (d, $J = 8.0$ Hz, 3H), 7.19 – 7.07 (m, 2H),

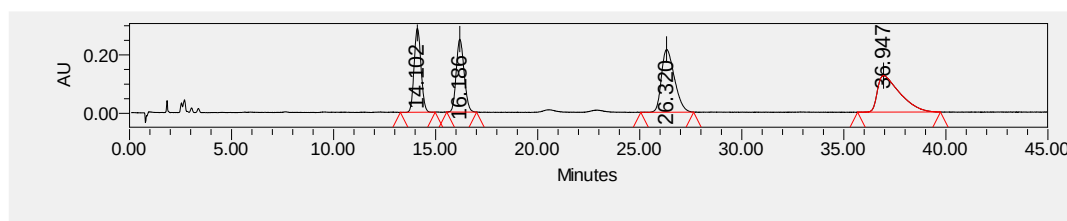
5.30 (d, $J = 10.8$ Hz, 1H), 4.85 (d, $J = 15.0$ Hz, 1H), 4.41 (d, $J = 15.0$ Hz, 1H), 3.94 (dd, $J = 10.8, 6.0$ Hz, 1H), 3.69 – 3.36 (m, 2H), 2.62 – 2.42 (m, 1H), 2.22 (dt, $J = 14.0, 11.2$ Hz, 1H) ppm.

Endo D27: **^{13}C NMR** (101 MHz, CDCl_3) δ 165.4, 146.8, 141.2, 139.7, 139.5, 137.2, 135.9, 129.0, 128.7, 128.1, 127.6, 127.5, 127.4, 127.0, 123.9, 123.5, 122.7, 122.5, 121.5, 80.3, 47.3, 46.5, 41.1, 40.1 ppm.

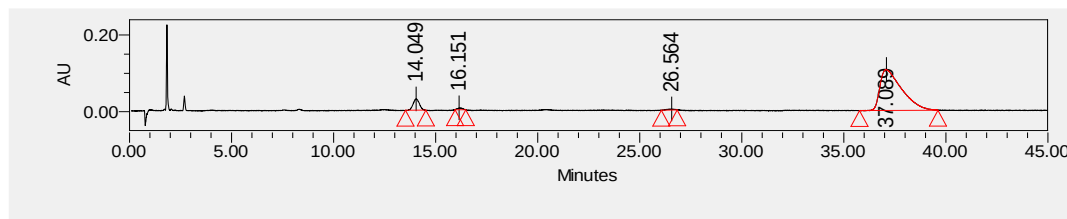
Exo D27: **^{13}C NMR** (101 MHz, CDCl_3) δ 165.4, 146.8, 141.2, 139.7, 139.5, 137.2, 135.9, 129.0, 128.7, 128.1, 127.6, 127.5, 127.4, 127.0, 123.9, 123.5, 122.7, 122.5, 121.5, 75.6, 48.0, 46.7, 39.2, 39.0 ppm.

ESI-HRMS calcd for $[\text{C}_{28}\text{H}_{23}\text{NO}_2\text{S} + \text{Na}^+] = 460.1342$, found 460.1351.

IR $\tilde{\nu}$ (cm^{-1}) 2920, 2360, 1694, 1540, 1454, 1241, 1108, 1046, 815, 754, 700.

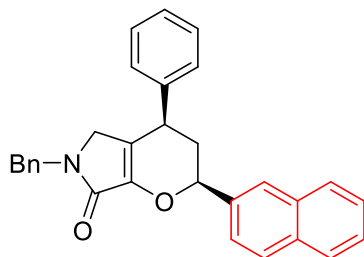


	Retention Time	Area	% Area	Height
1	14.102	6728668	20.73	287318
2	16.186	6688798	20.60	249505
3	26.320	9539178	29.38	214899
4	36.947	9507670	29.29	125363



	Retention Time	Area	% Area	Height
1	14.049	628455	7.26	29576
2	16.151	85996	0.99	5337
3	26.564	63498	0.73	3094
4	37.089	7878462	91.01	106722

D28: (2S,4R)-6-benzyl-2-(naphthalen-2-yl)-4-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



D28

D28: 75% yield, endo/exo = 90/10, 91%/51% ee; Colorless liquid, $[\alpha]_D^{26} = -36.7$ ($c = 0.63$, in CH_2Cl_2).

SFC Chiralcel IB-3, $\text{CO}_2/\text{MeOH} = 80/20$, 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 9.69$ min, $t_2 = 10.23$ min, $t_3 = 15.83$ min, $t_4 = 18.56$ min.

^1H NMR (400 MHz, $\text{Chloroform-}d$) δ 7.95 (s, 1H), 7.82 (dq, $J = 10.4$, 5.8, 5.0 Hz, 3H), 7.58 – 7.49 (m, 1H), 7.49 – 7.43 (m, 2H), 7.42 – 7.32 (m, 1H), 7.32 – 7.19 (m, 8H), 7.16 (t, $J = 10.4$ Hz, 2H),

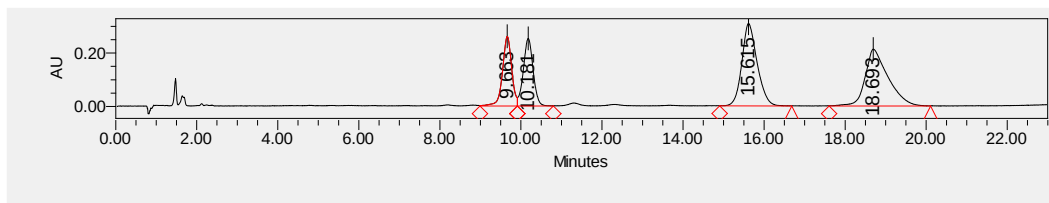
5.32 (d, $J = 11.0$ Hz, 1H), 4.85 (d, $J = 15.0$ Hz, 1H), 4.41 (d, $J = 15.0$ Hz, 1H), 3.94 (dd, $J = 10.8$, 6.0 Hz, 1H), 3.69 – 3.40 (m, 2H), 2.60 – 2.42 (m, 1H), 2.22 (dt, $J = 14.0$, 11.2 Hz, 1H) ppm.

Endo D28: **^{13}C NMR** (101 MHz, CDCl_3) δ 165.4, 146.8, 141.2, 137.2, 137.1, 133.2, 129.0, 128.9, 128.8, 128.3, 128.2, 128.1, 128.1, 127.8, 127.7, 127.6, 127.5, 127.4, 126.2, 126.1, 125.4, 124.2, 123.6, 80.2, 47.3, 46.5, 40.9, 40.1 ppm.

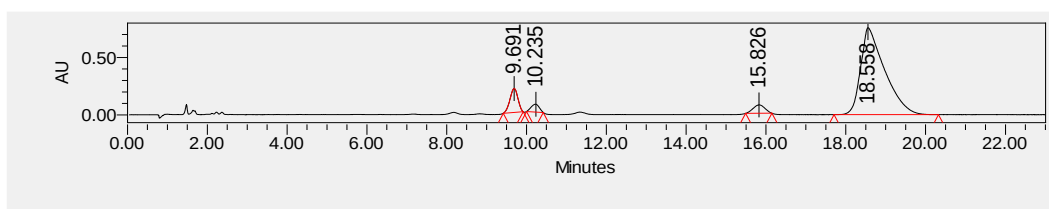
Exo D28: **^{13}C NMR** (101 MHz, CDCl_3) δ 164.3, 146.9, 141.2, 137.2, 137.1, 133.0, 129.0, 128.8, 128.7, 128.3, 128.2, 128.1, 128.1, 127.8, 127.7, 127.6, 127.5, 127.2, 126.2, 126.1, 125.1, 124.2, 121.0, 75.6, 48.0, 46.6, 38.7, 37.0 ppm.

ESI-HRMS calcd for $[\text{C}_{30}\text{H}_{25}\text{NO}_2 + \text{Na}^+] = 454.1778$, found 454.1781.

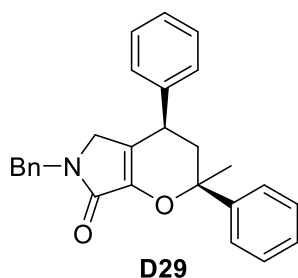
IR $\tilde{\nu}$ (cm^{-1}) 3057, 2360, 1694, 1493, 1453, 1240, 1197, 1107, 1048, 749, 700.



	Retention Time	Area	% Area	Height
1	9.663	4096298	16.58	260641
2	10.181	4212315	17.05	252547
3	15.615	8072123	32.68	308931
4	18.693	8322132	33.69	212732



	Retention Time	Area	% Area	Height
1	9.691	2897537	7.83	209131
2	10.235	966076	2.61	68962
3	15.826	1494854	4.04	73673
4	18.558	31656307	85.52	757114

D29: (2S,4R)-6-benzyl-2-methyl-2,4-diphenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one

D29: 56% yield, endo/exo = 52/48, 40%/74% ee; Colorless liquid, $[\alpha]^{22}_D = -0.71$ ($c = 0.42$, in CH_2Cl_2).

SFC Chiralcel OD-3, $\text{CO}_2/\text{MeOH} = 90/10$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 7.79$ min, $t_2 = 10.38$ min, $t_3 = 12.47$ min, $t_4 = 13.34$ min.

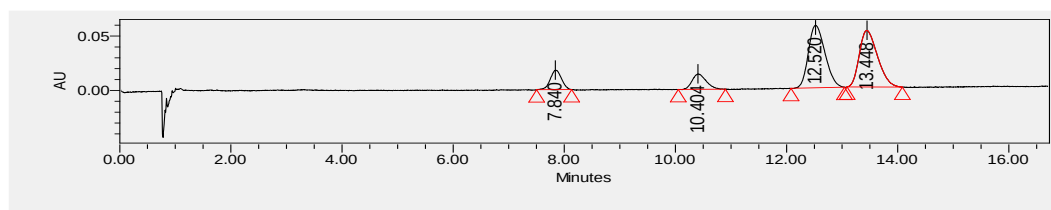
^1H NMR (400 MHz, $\text{Chloroform-}d$) δ 7.50 (d, $J = 7.5$ Hz, 1H), 7.45 – 7.37 (m, 2H), 7.37 – 7.31 (m, 2H), 7.30 (m, 3H), 7.21 (m, 4H), 7.17 – 7.13 (m, 1H), 7.06 (q, $J = 6.6, 5.6$ Hz, 2H), 4.75 (m, 1H), 4.54 – 4.43 (m, 1H), 3.61 – 3.44 (m, 1H), 3.37 – 3.21 (m, 1H), 2.93 – 2.66 (m, 1H), 2.36 (dd, $J = 14.0, 6.0$ Hz, 1H), 2.18 – 2.04 (m, 1H), 1.69 (s, 3H) ppm.

Endo D29: ^{13}C NMR (101 MHz, CDCl_3) δ 165.8, 145.0, 144.0, 141.1, 137.2, 128.9, 128.8, 128.7, 128.5, 128.2, 128.1, 127.9, 127.8, 127.7, 127.5, 127.2, 127.1, 127.0, 126.2, 124.7, 123.6, 82.2, 47.5, 46.6, 44.4, 37.3, 31.5 ppm.

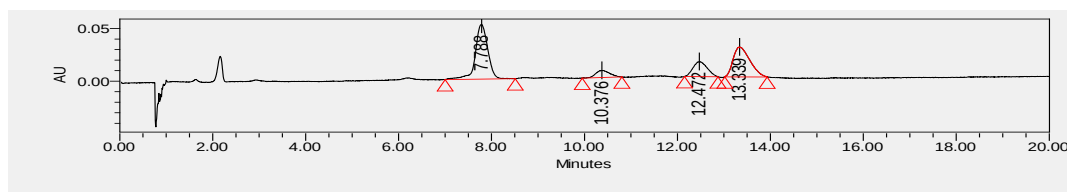
Exo D29: ^{13}C NMR (101 MHz, CDCl_3) δ 165.7, 145.0, 144.0, 141.0, 137.1, 128.9, 128.8, 128.7, 128.5, 128.2, 128.1, 127.9, 127.8, 127.6, 127.5, 127.2, 127.1, 127.0, 126.2, 124.5, 121.1, 81.11, 47.3, 46.5, 42.6, 37.3, 24.6 ppm.

HRMS (ESI) Calculated for $\text{C}_{27}\text{H}_{25}\text{NO}_2$ ($[\text{M}] + \text{Na}^+$) = 418.1778, Found 418.1776.

IR $\tilde{\nu}$ (cm^{-1}) 2929, 2360, 1693, 1494, 1448, 1383, 1244, 1116, 1029, 737, 700.



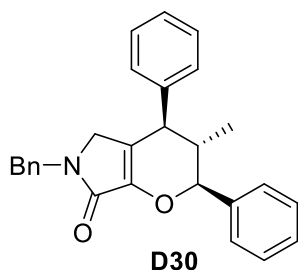
	Retention Time	Area	% Area	Height
1	7.840	249833	8.68	17856
2	10.404	248776	8.64	14209
3	12.520	1197545	41.60	57640
4	13.448	1182839	41.09	52190



	Retention Time	Area	% Area	Height
1	7.788	961160	45.62	52072
2	10.376	137361	6.52	6682
3	12.472	302607	14.36	14344
4	13.339	705631	33.49	28403

D30: (2S,3S,4R)-6-benzyl-3-methyl-2,4-diphenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)

-one



D30: 76% yield, endo/exo = 91/9, 99%/96% ee; Colorless liquid, $[\alpha]^{20}_D$ = -40.0 (c = 0.48, in CH_2Cl_2).

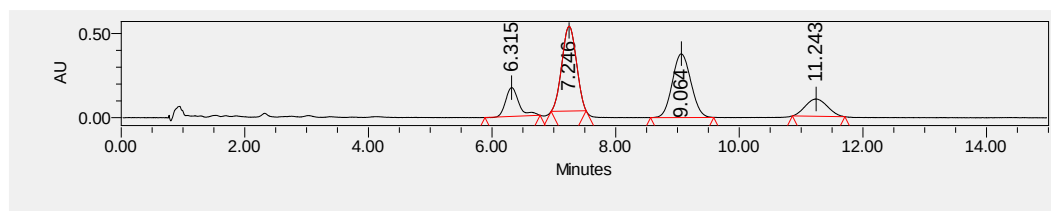
SFC Chiralcel AS-3, CO_2/MeOH = 80/20. 1.5 mL/min, λ = 210 nm, retention time: t_1 = 6.14 min, t_2 = 7.12 min, t_3 = 8.81 min, t_4 = 11.11 min.

^1H NMR (600 MHz, $\text{Chloroform-}d$) δ 7.39 (d, J = 7.2 Hz, 2H), 7.35 (t, J = 7.2 Hz, 2H), 7.31 (dt, J = 16.6, 7.2 Hz, 5H), 7.26 – 7.23 (m, 2H), 7.19 (d, J = 7.4 Hz, 2H), 7.14 (d, J = 7.4 Hz, 2H), 4.83 (d, J = 15.0 Hz, 1H), 4.73 (d, J = 10.2 Hz, 1H), 4.36 (d, J = 15.2 Hz, 1H), 3.49 (d, J = 18.4 Hz, 1H), 3.44 – 3.24 (m, 2H), 2.19 (ddt, J = 13.2, 10.0, 6.6 Hz, 1H), 0.62 (d, J = 6.6 Hz, 3H) ppm.

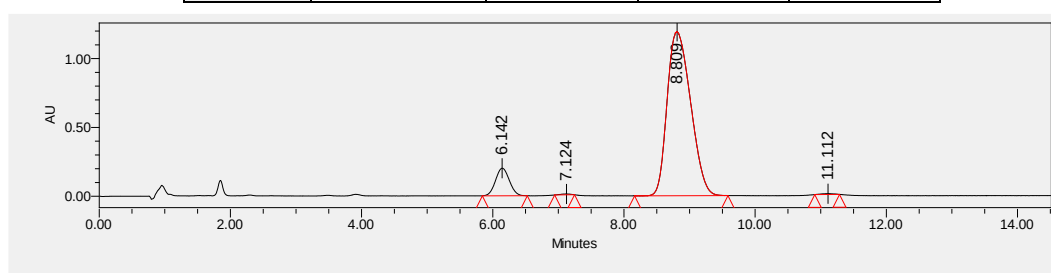
^{13}C NMR (151 MHz, CDCl_3) δ 165.4, 146.5, 140.6, 138.4, 137.2, 128.9, 128.7, 128.6, 128.4, 128.4, 128.0, 127.9, 127.6, 127.4, 123.7, 86.2, 47.4, 47.3, 46.5, 41.8, 15.2 ppm.

ESI-HRMS calcd for $[\text{C}_{27}\text{H}_{25}\text{NO}_2 + \text{Na}^+]$ = 418.1778, found 418.1782.

IR $\tilde{\nu}$ (cm^{-1}) 3029, 2360, 1694, 1494, 1454, 1241, 1116, 1078, 917, 751, 700, 522.



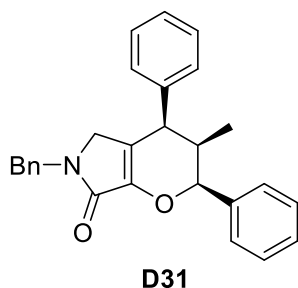
	Retention Time	Area	% Area	Height
1	6.315	2544087	12.04	171579
2	7.246	8156175	38.60	502532
3	9.064	7892301	37.35	378943
4	11.243	2536379	12.00	102942



	Retention Time	Area	% Area	Height
1	6.142	2925514	8.97	200662
2	7.124	69462	0.21	6486
3	8.809	29519511	90.55	1192838
4	11.112	84749	0.26	6206

D31: (2S,3R,4R)-6-benzyl-3-methyl-2,4-diphenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)

-one



D31: 68% yield, endo/exo = 70/30, 99%/87% ee; Colorless liquid, $[\alpha]^{20}_D$ = -16.5 (c = 0.17, in CH_2Cl_2).

SFC Chiralcel AS-3, CO_2/MeOH = 80/20. 1.5 mL/min, λ = 210 nm, retention time: t_1 = 6.11 min, t_2 = 6.88 min, t_3 = 8.82 min, t_4 = 10.91 min.

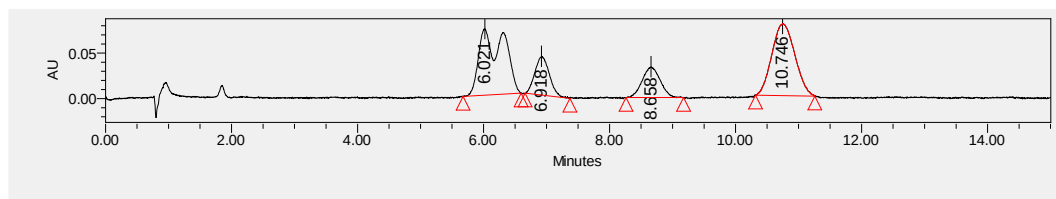
^1H NMR (600 MHz, Chloroform- d) δ 7.47 (d, J = 7.6 Hz, 2H), 7.36 (t, J = 7.6 Hz, 2H), 7.34 – 7.27 (m, 6H), 7.27 (m, 1H), 7.25 (d, J = 2.4 Hz, 2H), 7.10 (d, J = 7.6 Hz, 2H), 5.37 (s, 1H), 4.89 (d, J = 15.0 Hz, 1H), 4.45 (d, J = 15.0 Hz, 1H), 4.30 (d, J = 5.8 Hz, 1H), 3.78 (d, J = 18.0 Hz, 1H), 3.60 – 3.52 (m, 1H), 2.46 – 2.29 (m, 1H), 0.53 (d, J = 7.6 Hz, 3H) ppm.

Endo D31: ^{13}C NMR (151 MHz, CDCl_3) δ 165.2, 146.8, 139.0, 138.8, 137.2, 129.1, 128.5, 128.3, 128.2, 128.1, 127.6, 127.4, 127.2, 125.8, 122.4, 83.4, 47.5, 46.6, 45.3, 39.3, 7.4 ppm.

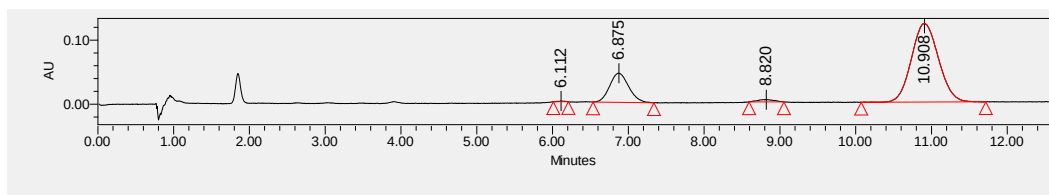
Exo D31: ^{13}C NMR (151 MHz, CDCl_3) δ 163.3, 147.2, 139.0, 138.8, 137.2, 128.8, 128.5, 128.3, 128.2, 128.1, 127.7, 127.4, 127.1, 126.0, 122.4, 81.2, 57.5, 46.6, 45.3, 39.0, 7.4 ppm.

ESI-HRMS calcd for $[\text{C}_{27}\text{H}_{25}\text{NO}_2 + \text{Na}^+]$ = 418.1778, found 418.1783.

IR $\tilde{\nu}$ (cm^{-1}) 2924, 2360, 1698, 1540, 1455, 1257, 749, 700.

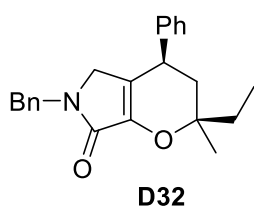


	Retention Time	Area	% Area	Height
1	6.021	1980635	37.28	73217
2	6.918	675118	12.71	42471
3	8.658	660860	12.44	33816
4	10.746	1995865	37.57	79136



	Retention Time	Area	% Area	Height
1	6.112	6403	0.16	1216
2	6.875	794310	20.35	45560
3	8.820	56698	1.45	3687
4	10.908	3045771	78.03	122851

D32: (4R)-6-benzyl-2-ethyl-2-methyl-4-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



D32: 34% yield, endo/exo = 70/30, 91%/6% ee; Colorless liquid, $[\alpha]_D^{26} = 42.9$ ($c = 0.21$, in CH_2Cl_2).

SFC Chiralcel AS-3, $\text{CO}_2/\text{MeOH} = 90/10$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 5.52$ min, $t_2 = 6.25$ min, $t_3 = 7.72$ min, $t_4 = 8.89$ min.

^1H NMR (400 MHz, Chloroform- d) δ 7.47 – 7.34 (m, 1H), 7.29 (ddd, $J = 8.8$, 5.2, 1.6 Hz, 3H), 7.26 – 7.23 (m, 2H), 7.21 (dd, $J = 10.0$, 1.6 Hz, 2H), 7.18 –

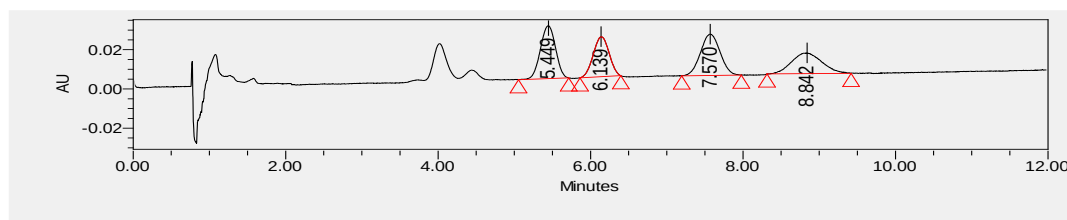
7.03 (m, 2H), 4.87 – 4.69 (m, 1H), 4.50 – 4.37 (m, 1H), 3.71 – 3.48 (m, 1H), 3.45 – 3.41 (m, 1H), 2.05 (m, 1H), 1.88 – 1.74 (m, 2H), 1.62 (m, 2H), 1.34 – 1.22 (m, 3H), 0.98 (td, $J = 7.6$, 3.6 Hz, 3H) ppm.

Endo D32: ^{13}C NMR (101 MHz, CDCl_3) δ 166.1, 144.9, 141.6, 137.2, 131.3, 129.4, 129.2, 128.9, 128.7, 128.5, 128.1, 127.8, 127.5, 127.2, 120.9, 80.9, 46.5, 41.5, 36.7, 28.5, 25.3, 21.8, 8.1, ppm.

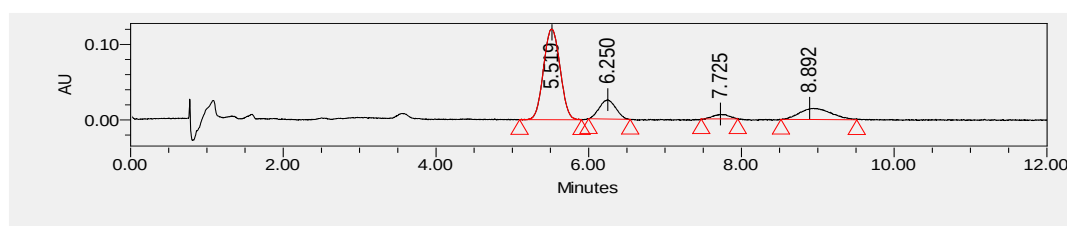
Exo D32: ^{13}C NMR (101 MHz, CDCl_3) δ 166.0, 145.1, 141.7, 137.3, 131.3, 129.4, 129.2, 128.9, 128.7, 128.6, 128.1, 127.8, 127.5, 127.2, 120.7, 80.7, 47.4, 40.9, 34.6, 30.2, 25.3, 21.8, 8.0 ppm.

ESI-HRMS calcd for $[\text{C}_{23}\text{H}_{25}\text{NO}_2 + \text{Na}^+] = 370.1778$, found 370.1778.

IR $\tilde{\nu}$ (cm^{-1}) 2925, 2360, 1695, 1540, 1454, 1249, 1164, 1106, 750, 700.

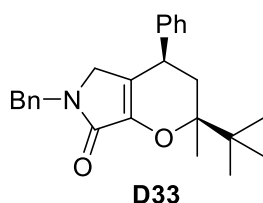


	Retention Time	Area	% Area	Height
1	5.449	370384	27.81	26945
2	6.139	293532	22.04	20372
3	7.570	375517	28.20	21014
4	8.842	292347	21.95	10558



	Retention Time	Area	% Area	Height
1	5.519	1808478	66.75	120007
2	6.250	381656	14.09	25863
3	7.725	89071	3.29	6549
4	8.892	430306	15.88	14962

D33: (2S,4R)-6-benzyl-2-(tert-butyl)-2-methyl-4-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7 (2H)-one



D33: 60% yield, endo/exo = 88/12, 96%/39% ee; Colorless liquid, $[\alpha]_D^{26} = -46.8$ ($c = 0.37$, in CH_2Cl_2).

SFC Chiralcel IE-3, $\text{CO}_2/\text{MeOH} = 80/20$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 3.78$ min, $t_2 = 4.10$ min, $t_3 = 4.68$ min, $t_4 = 5.97$ min.

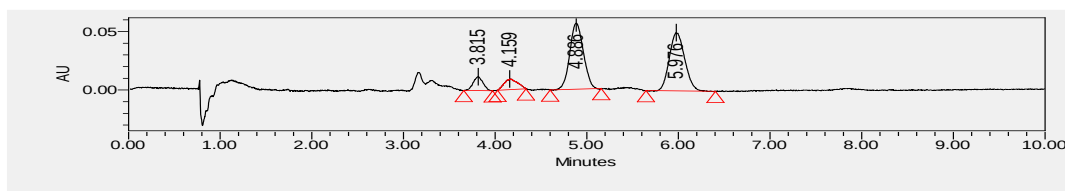
^1H NMR (400 MHz, $\text{Chloroform-}d$) δ 7.32 (m, 3H), 7.27 (q, $J = 3.6$ Hz, 4H), 7.19 (m, 3H), 4.80 (m, 1H), 4.51 (d, $J = 14.9$ Hz, 1H), 3.85 (d, $J = 17.8$ Hz, 1H), 3.74 (dd, $J = 7.2, 3.6$ Hz, 1H), 3.53 (d, $J = 17.8$ Hz, 1H), 2.45 (dd, $J = 14.4, 7.4$ Hz, 1H), 1.95 (dd, $J = 14.4, 3.6$ Hz, 1H), 1.05 (s, 3H), 1.02 (s, 9H) ppm.

Endo D33: ^{13}C NMR (101 MHz, CDCl_3) δ 166.0, 146.4, 143.3, 137.3, 128.9, 128.7, 128.6, 128.2, 128.1, 127.8, 127.6, 126.5, 117.7, 84.0, 48.4, 46.6, 38.4, 36.3, 36.2, 25.6, 20.7 ppm.

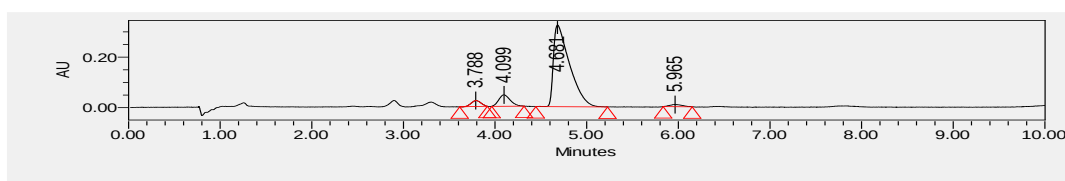
Exo D33: ^{13}C NMR (101 MHz, CDCl_3) δ 166.0, 146.4, 143.1, 137.3, 128.9, 128.7, 128.6, 128.2, 128.1, 127.8, 127.6, 126.5, 117.4, 79.6, 49.0, 47.2, 40.0, 36.3, 36.2, 25.3, 17.6 ppm.

ESI-HRMS calcd for $[\text{C}_{25}\text{H}_{29}\text{NO}_2 + \text{Na}^+] = 398.2091$, found 398.2095.

IR $\tilde{\nu}$ (cm^{-1}) 2965, 2360, 1696, 1540, 1453, 1229, 1130, 1077, 1028, 734, 701.

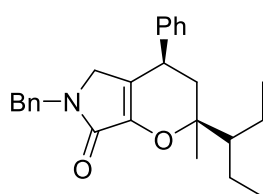


	Retention Time	Area	% Area	Height
1	3.815	88425	6.55	11975
2	4.159	92327	6.84	9172
3	4.886	586846	43.47	56673
4	5.976	582381	43.14	49787



	Retention Time	Area	% Area	Height
1	3.788	170122	3.69	23484
2	4.099	391156	8.49	45047
3	4.681	3964851	86.01	323020
4	5.965	83682	1.82	8514

D34: (R)-6-benzyl-2,2-diethyl-4-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



D34

D34: 46% yield, endo/exo = 75/25, 83%/5% ee; Colorless liquid, $[\alpha]_D^{26} = 15.4$ ($c = 0.28$, in CH_2Cl_2).

SFC Chiralcel IH-3, $\text{CO}_2/\text{MeOH} = 90/10$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 4.99$ min, $t_2 = 7.74$ min, $t_3 = 9.18$ min, $t_4 = 11.76$ min.

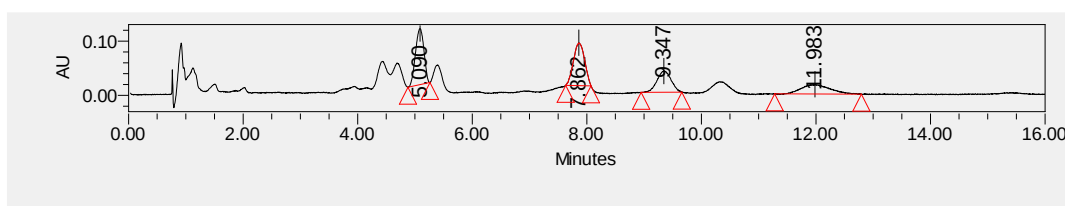
^1H NMR (400 MHz, CHCl_3) δ 7.29 (m, 5H), 7.23 – 7.16 (m, 3H), 7.12 (d, $J = 7.2$ Hz, 2H), 4.78 (d, $J = 15.0$ Hz, 1H), 4.42 (d, $J = 15.0$ Hz, 1H), 3.54 (dd, $J = 12.6, 6.8$ Hz, 1H), 3.52 – 3.21 (m, 2H), 2.34 (dd, $J = 14.2, 5.7$ Hz, 1H), 2.01 – 1.67 (m, 4H), 1.62 – 1.54 (m, 1H), 1.35 – 1.19 (m, 5H), 1.06 – 0.78 (m, 6H).ppm.

Endo D34: **^{13}C NMR** (101 MHz, CDCl_3) δ 165.9, 144.9, 141.7, 137.3, 128.9, 128.8, 128.7, 128.6, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.2, 121.3, 83.8, 47.3, 46.5, 44.1, 41.4, 36.8, 23.6, 22.3, 21.8, 14.5, 13.7 ppm.

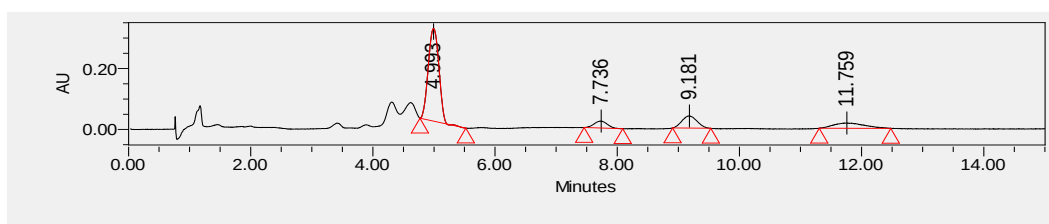
Exo D34: **^{13}C NMR** (101 MHz, CDCl_3) δ 166.1, 145.0, 141.9, 136.7, 128.9, 128.8, 128.7, 128.6, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.2, 121.3, 83.8, 47.8, 46.7, 44.1, 40.6, 38.8, 25.9, 22.8, 22.6, 14.5, 13.8 ppm.

ESI-HRMS calcd for $[\text{C}_{24}\text{H}_{27}\text{NO}_2 + \text{Na}^+] = 412.2247$, found 412.2251.

IR $\tilde{\nu}$ (cm^{-1}) 2962, 2360, 1698, 1540, 1454, 1254, 750, 701.

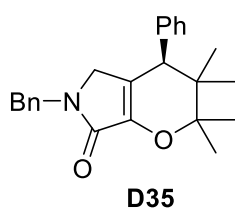


	Retention Time	Area	% Area	Height
1	5.090	1061914	31.12	103365
2	7.862	1066809	31.26	78921
3	9.347	666956	19.55	39000
4	11.983	616692	18.07	18054



	Retention Time	Area	% Area	Height
1	4.993	3694284	69.23	304595
2	7.736	345325	6.47	23132
3	9.181	678988	12.72	39836
4	11.759	617798	11.58	17764

(S)-6-benzyl-2,2,3,3-tetramethyl-4-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



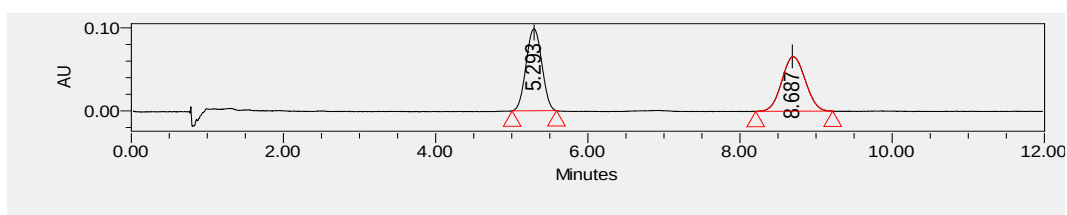
D35: 60% yield, 77% ee; Colorless liquid, $[\alpha]^{22}_D = -29.2$ ($c = 0.13$, in CH_2Cl_2). SFC Chiralcel AS-3, $\text{CO}_2/\text{MeOH} = 90/10$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 5.22$ min, $t_2 = 8.63$ min.

^1H NMR (400 MHz, CHCl_3) δ 7.32 – 7.28 (m, 2H), 7.28 – 7.27 (m, 2H), 7.25 (d, $J = 10.4$ Hz, 2H), 7.22 – 7.18 (m, 2H), 7.08 (s, 2H), 4.80 (d, $J = 15.0$ Hz, 1H), 4.43 (d, $J = 15.0$ Hz, 1H), 3.63 (d, $J = 18.2$ Hz, 1H), 3.53 (s, 1H), 3.38 (dd, $J = 18.2, 1.6$ Hz, 1H), 1.48 (s, 3H), 1.34 (s, 3H), 0.85 (s, 3H), 0.78 (s, 3H) ppm.

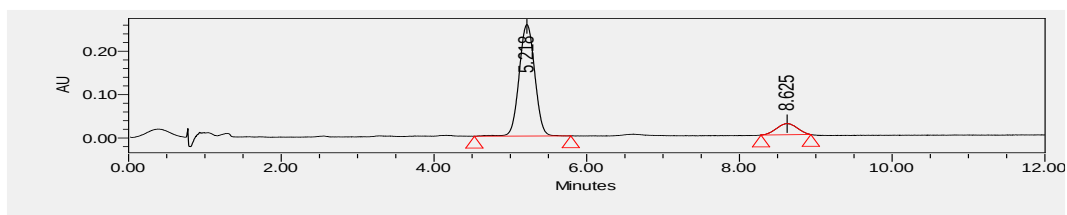
^{13}C NMR (101 MHz, CDCl_3) δ 166.0, 144.7, 137.7, 137.2, 128.7, 128.1, 127.8, 127.5, 127.2, 121.6, 84.7, 48.1, 47.7, 46.6, 38.4, 23.8, 22.9, 21.5, 17.8 ppm.

ESI-HRMS calcd for $[\text{C}_{24}\text{H}_{27}\text{NO}_2 + \text{Na}^+] = 384.1934$, found 384.1941.

IR $\tilde{\nu}$ (cm^{-1}) 2981, 2360, 1695, 1493, 1452, 1443, 1380, 1246, 1152, 1084, 754.



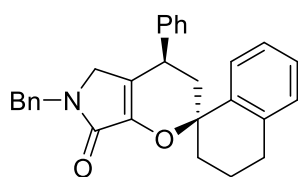
	Retention Time	Area	% Area	Height
1	5.293	456646	50.28	31752
2	8.687	451550	49.72	21383



	Retention Time	Area	% Area	Height
1	5.218	3657404	88.33	256907
2	8.625	483400	11.67	25639

D36:

(1S,4'R)-6'-benzyl-4'-phenyl-3,3',4,4',5',6'-hexahydro-2H,7'H-spiro[naphthalene-1,2'-pyrano[2,3-c]pyrrol]-7'-one

**D36**

D36: 52% yield, endo/exo > 19:1, 67% ee; Colorless liquid, $[\alpha]^{25}_D = 18.6$ ($c = 0.35$, in CH_2Cl_2).

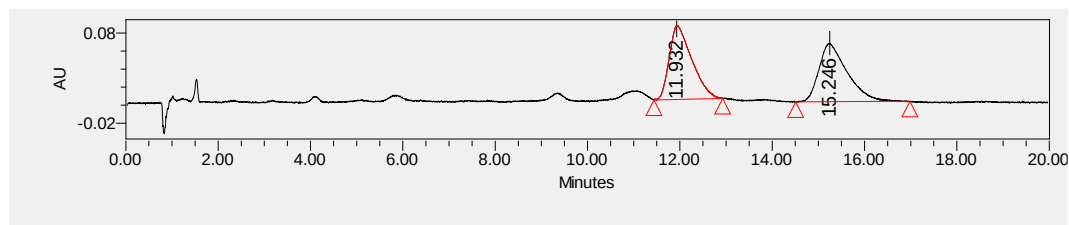
SFC Chiralcel ID-3, $\text{CO}_2/\text{MeOH} = 80/20$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 11.58$ min, $t_2 = 15.11$ min.

^1H NMR (600 MHz, $\text{Chloroform-}d$) δ 7.58 – 7.52 (m, 1H), 7.30 (q, $J = 7.1$ Hz, 4H), 7.27 – 7.23 (m, 2H), 7.22 (d, $J = 7.8$ Hz, 2H), 7.19 – 7.14 (m, 4H), 7.07 (d, $J = 6.2$ Hz, 1H), 4.75 (d, $J = 15.0$ Hz, 1H), 4.49 (d, $J = 15.0$ Hz, 1H), 3.72 (t, $J = 8.4$ Hz, 1H), 3.55 – 3.44 (m, 2H), 2.91 – 2.85 (m, 1H), 2.77 (dt, $J = 16.1, 5.6$ Hz, 1H), 2.25 (q, $J = 8.6$ Hz, 2H), 2.20 (t, $J = 10.5$ Hz, 1H), 2.03 (d, $J = 10.1$ Hz, 2H), 1.85 – 1.78 (m, 1H) ppm.

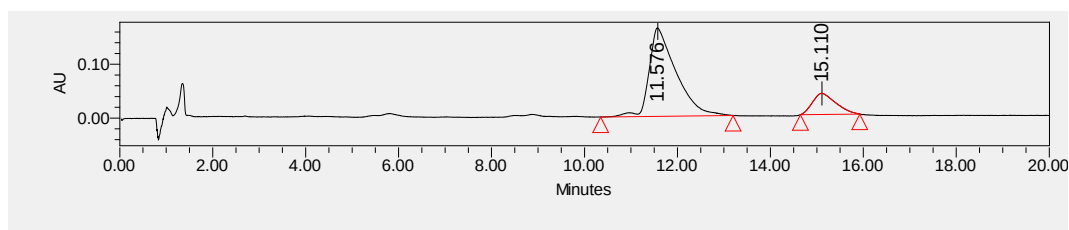
^{13}C NMR (101 MHz, CDCl_3) δ 165.9, 145.6, 141.2, 138.4, 137.2, 137.1, 128.9, 128.7, 128.6, 128.1, 127.8, 127.6, 127.4, 127.3, 126.2, 120.9, 79.9, 47.4, 46.6, 43.5, 37.3, 31.4, 29.7, 19.5 ppm.

ESI-HRMS calcd for $[\text{C}_{29}\text{H}_{27}\text{NO}_2 + \text{Na}^+] = 444.1934$, found 444.1927.

IR $\tilde{\nu}$ (cm^{-1}) 2934, 2360, 1697, 1540, 1492, 1246, 753, 701.



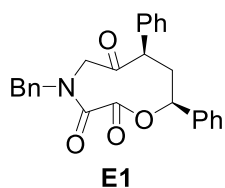
	Retention Time	Area	% Area	Height
1	11.932	2790557	50.42	82625
2	15.246	2743925	49.58	65098



	Retention Time	Area	% Area	Height
1	11.576	6591269	82.81	164277
2	15.110	1368081	17.19	39436

E1: (7R,9S)-4-benzyl-7,9-diphenyl-1,4-oxazonane-2,3,6-trione

E1: 72% yield, dr = 87/13, 91%/60% ee; Colorless liquid, $[\alpha]_D^{23} = -12.6$ ($c = 1.60$, in CH_2Cl_2)



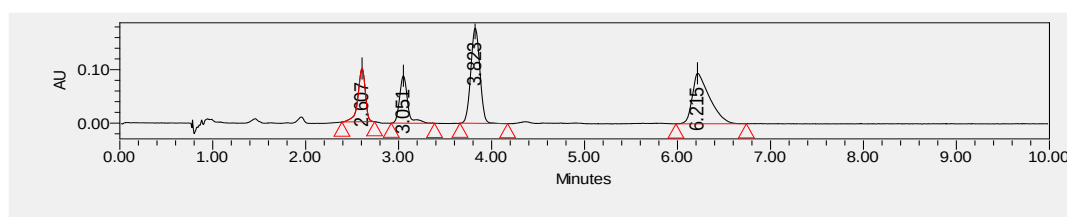
SFC Chiralcel IB-3, $\text{CO}_2/\text{MeOH} = 80/20$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 2.60$ min, $t_2 = 3.05$ min, $t_3 = 3.82$ min, $t_4 = 5.93$ min.

^1H NMR (400 MHz, CHCl_3) δ 7.43 (m, 1H), 7.40-7.35 (m, 4H), 7.32-7.27 (m, 6H), 7.24-7.20 (m, 3H), 7.13 (m, 1H), 6.10 (dd, $J = 12.0, 2.4$ Hz, 1H), 5.52 (d, $J = 14.8$ Hz, 1H), 4.18 (m, 2H), 4.00 (dd, $J = 12.0, 2.4$ Hz, 1H), 3.65 (d, $J = 16.0$ Hz, 1H), 3.14 – 3.04 (m, 1H), 2.30-2.25 (m, 1H) ppm.

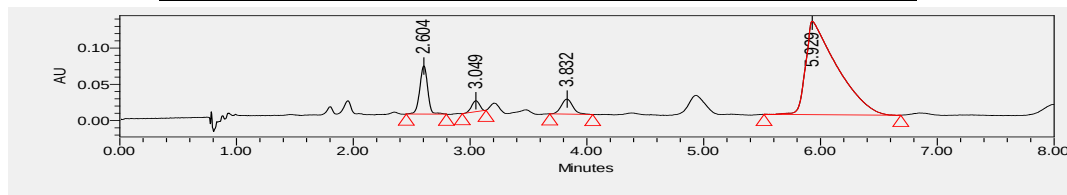
^{13}C NMR (101 MHz, CDCl_3) δ 207.4, 161.6, 161.5, 136.9, 136.8, 135.2, 129.4, 129.2, 129.0, 128.9, 128.7, 128.6, 128.4, 128.2, 127.9, 127.8, 127.5, 126.5, 126.3, 125.9, 79.4, 56.0, 55.4, 50.7, 46.1 ppm.

ESI-HRMS calcd for $[\text{C}_{26}\text{H}_{23}\text{NO}_4 + \text{Na}^+] = 436.1519$, found 436.1523.

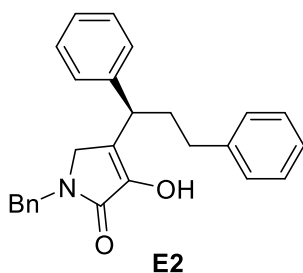
IR $\tilde{\nu}$ (cm^{-1}) 3031, 2929, 1759, 1727, 1674, 1496, 1454, 1424, 1359, 1256, 1153, 1084, 1067, 1029, 998, 757, 698.



	Retention Time	Area	% Area	Height
1	2.607	544458	15.52	99385
2	3.051	532990	15.19	88557
3	3.823	1212077	34.55	177996
4	6.215	1219083	34.75	94273



	Retention Time	Area	% Area	Height
1	2.604	312997	10.69	66453
2	3.049	71224	2.43	15145
3	3.832	142486	4.87	20748
4	5.929	2400349	82.01	128934

E2: (R)-1-benzyl-4-(1,3-diphenylpropyl)-3-hydroxy-1,5-dihydro-2H-pyrrol-2-one

E2: 99% yield, 70% ee ; Colorless liquid, $[\alpha]_D^{22} = -57.6$ ($c = 0.70$, in CH_2Cl_2)

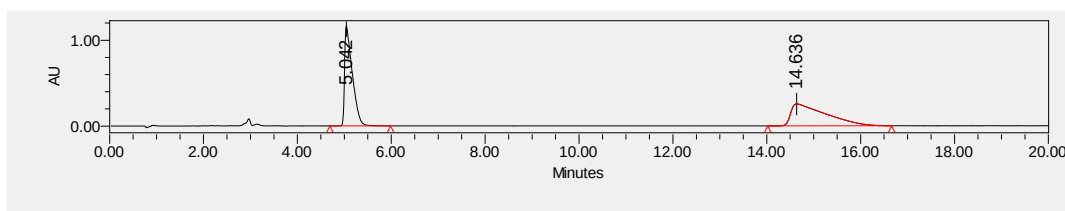
SFC Chiralcel OJ-3, $\text{CO}_2/\text{MeOH} = 80/20$. 1.5 mL/min, $\lambda = 210$ nm, retention time: $t_1 = 5.28$ min, $t_2 = 15.06$ min.

^1H NMR (400 MHz, CDCl_3) δ 8.09 (s, 1H), 7.35 – 7.27 (m, 4H), 7.27 – 7.21 (m, 5H), 7.21 – 7.14 (m, 4H), 7.13 – 7.09 (m, 2H), 4.66 – 4.51 (m, 2H), 3.79 (t, $J = 7.8$ Hz, 1H), 3.60 – 3.34 (m, 2H), 2.58 (t, $J = 7.8$ Hz, 2H), 2.40 – 2.28 (m, 1H), 2.20 (dq, $J = 13.4, 7.8$ Hz, 1H).

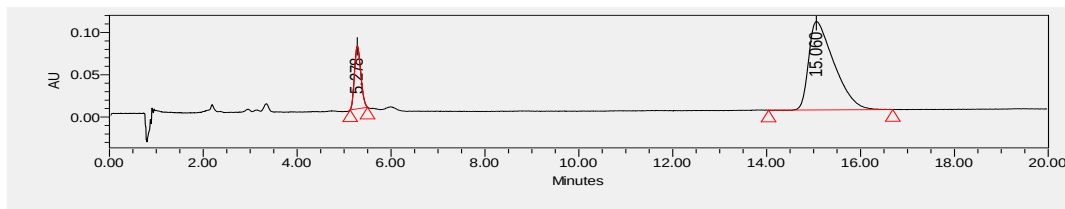
^{13}C NMR (101 MHz, CDCl_3) δ 168.22, 142.89, 141.92, 141.55, 136.68, 128.84, 128.73, 128.51, 128.37, 128.00, 127.95, 127.71, 126.93, 126.70, 125.87, 123.66, 47.99, 46.83, 42.69, 35.33, 34.19.

ESI-HRMS calcd for $[\text{C}_{26}\text{H}_{25}\text{NO}_2 + \text{Na}^+] = 406.1778$, found 406.1781.

IR $\tilde{\nu}$ (cm^{-1}) 3028, 2923, 2854, 1663, 1602, 1494, 1452, 1378, 1265, 1200, 1079, 1029, 911, 726, 698, 620, 492.



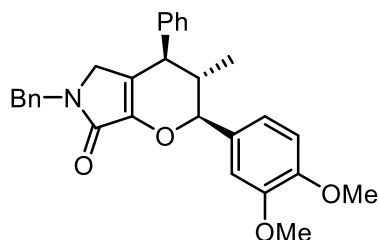
	Retention Time	Area	% Area	Height
1	5.042	13231624	50.00	1164938
2	14.636	13230629	50.00	254971



	Retention Time	Area	% Area	Height
1	5.278	692314	14.97	73821
2	15.060	3930907	85.03	104647

D37:

(2S,3S,4R)-6-benzyl-2-(3,4-dimethoxyphenyl)-3-methyl-4-phenyl-3,4,5,6-tetrahydropyrano[2,3-c]pyrrol-7(2H)-one



98% yield, endo/exo = 78/22, 45%/40% ee; Colorless liquid, $[\alpha]_D^{24} = 17.2$ ($c = 0.84$, in CH_2Cl_2).

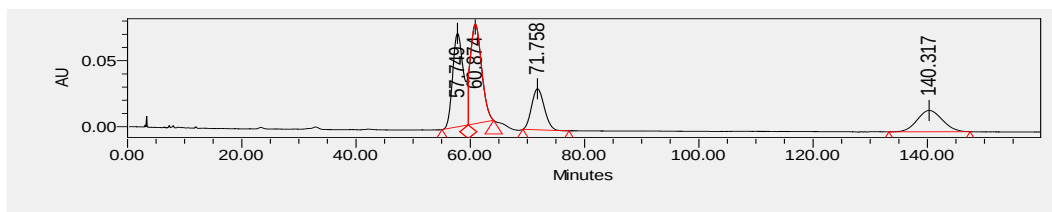
HPLC (Daicel chiralcel IK, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, $\lambda = 210$ nm), $t_1 = 58.41$ min, $t_2 = 61.27$ min, $t_3 = 72.28$ min, $t_4 = 140.38$ min.

^1H NMR (400 MHz, Chloroform-*d*) δ 7.32 (dq, $J = 12.2, 5.6, 4.8$ Hz, 5H), 7.26 – 7.23 (m, 2H), 7.21 – 7.07 (m, 3H), 6.93 – 6.78 (m, 3H), 4.85 (d, $J = 14.8$ Hz, 1H), 4.73 (d, $J = 10.2$ Hz, 1H), 4.43 (d, $J = 14.8$ Hz, 1H), 3.86 (d, $J = 2.8$ Hz, 6H), 3.62 – 3.57 (m, 2H), 3.35 (d, $J = 14.4$ Hz, 1H), 2.51 – 2.13 (m, 1H), 0.43 (d, $J = 7.2$ Hz, 3H) ppm.

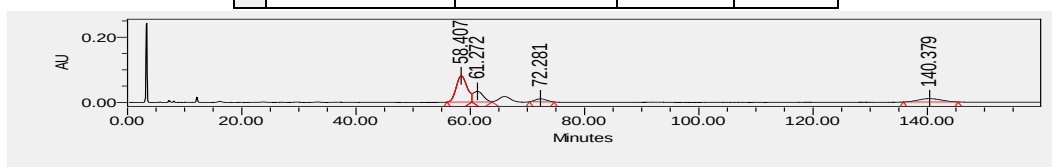
^{13}C NMR (101 MHz, CDCl_3) δ 165.4, 149.0, 148.9, 146.2, 139.3, 137.1, 131.1, 129.6, 128.8, 128.7, 128.6, 128.5, 128.2, 128.0, 127.6, 127.3, 121.5, 120.4, 110.6, 110.2, 81.0, 55.9, 55.9, 47.8, 46.6, 43.1, 37.6, 15.0 ppm.

ESI-HRMS calcd for $[\text{C}_{29}\text{H}_{29}\text{NO}_4 + \text{Na}^+] = 478.1989$, found 478.1994.

IR $\tilde{\nu}$ (cm^{-1}) 2932, 1690, 1598, 1515, 1455, 1419, 1261, 1237, 1141, 1080, 1026, 854, 760, 703.



	Retention Time	Area	% Area	Height
1	57.749	9575052	32.35	70776
2	60.874	10258963	34.66	75284
3	71.758	4804656	16.23	31089
4	140.317	4959502	16.76	16187

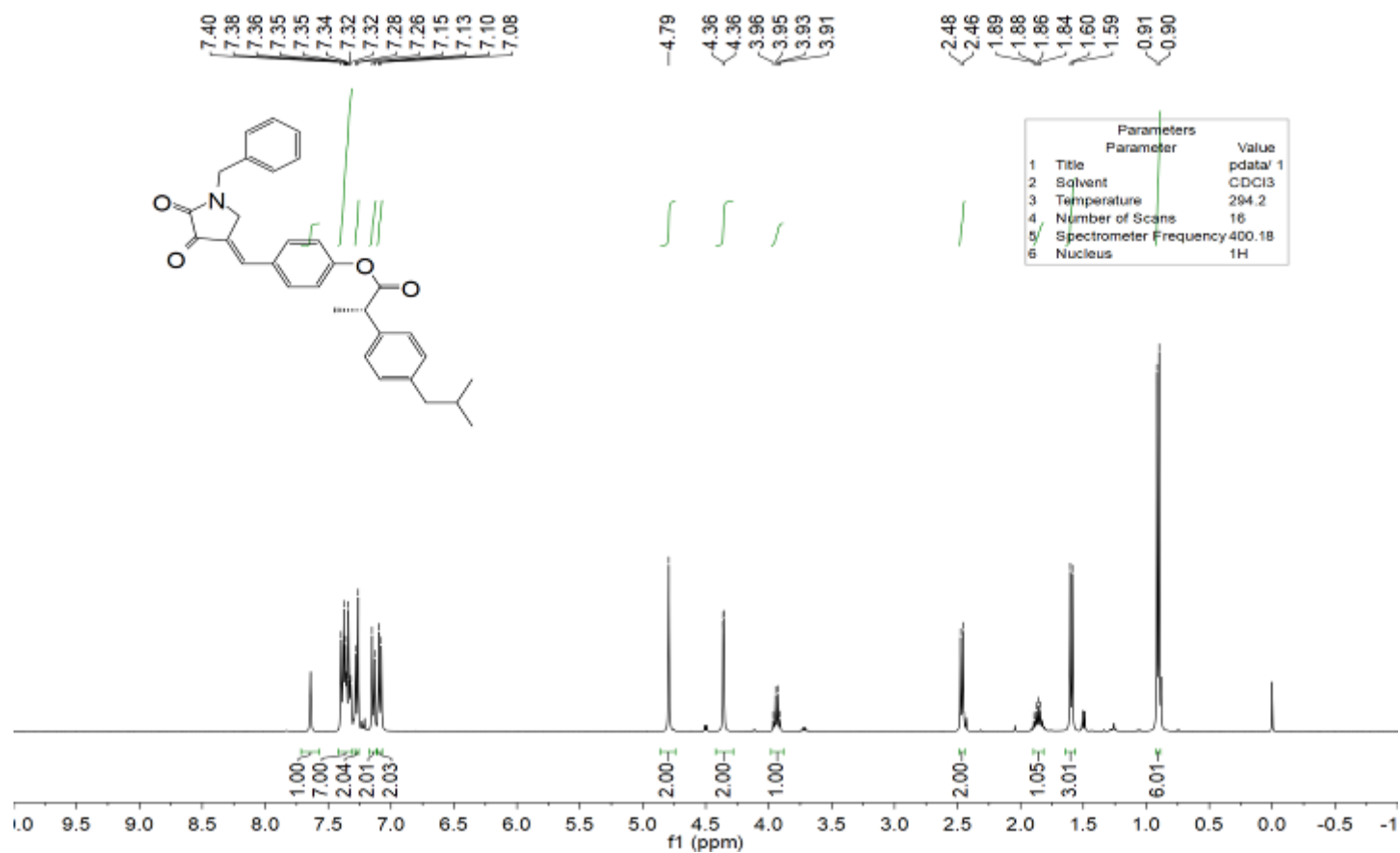


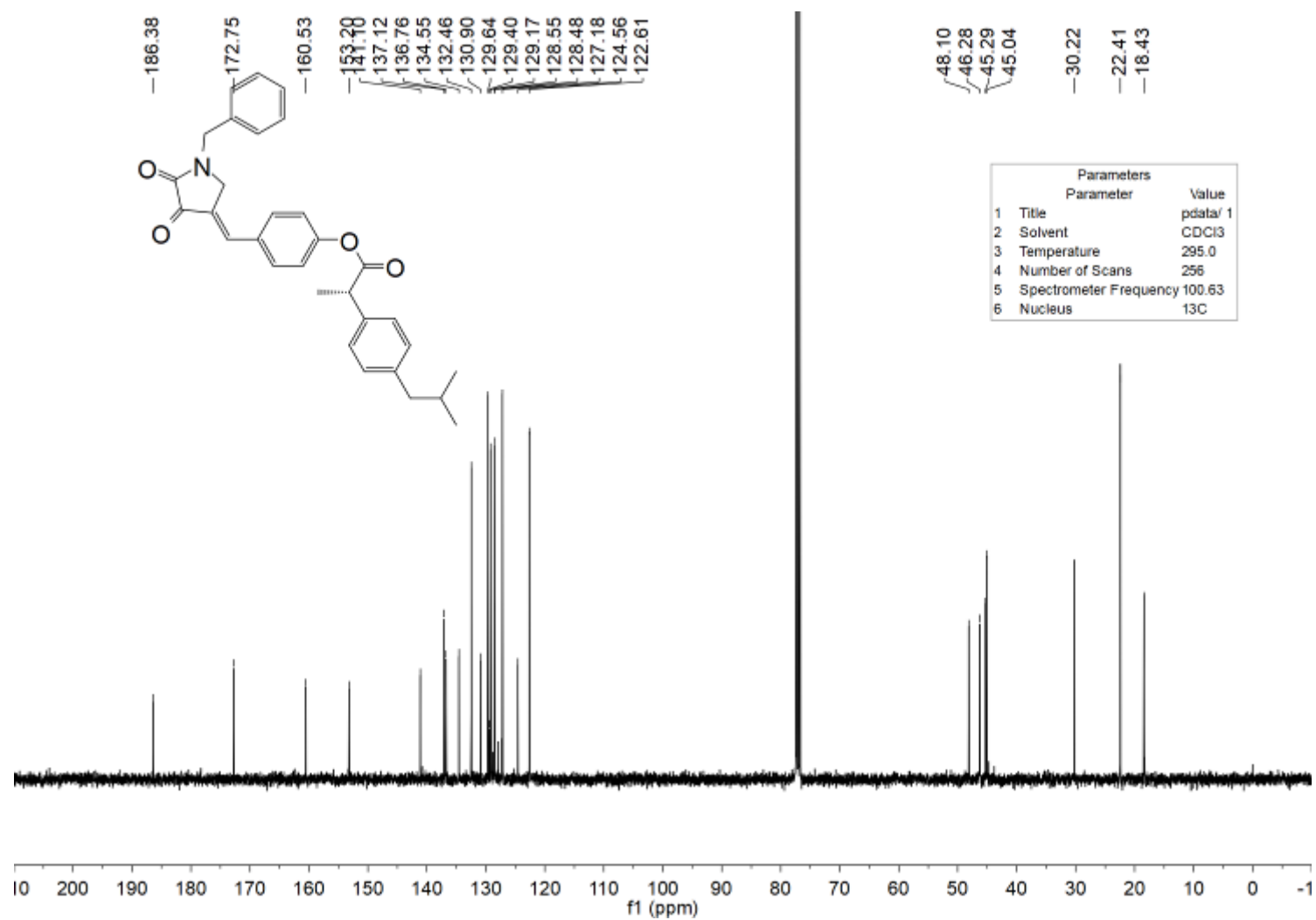
	Retention Time	Area	% Area	Height
1	58.407	10649243	56.50	80565
2	61.272	4054239	21.51	32750
3	72.281	1262372	6.70	9286
4	140.379	2881437	15.29	10236

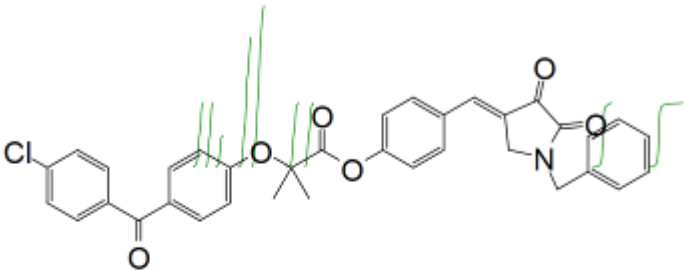
13. References.

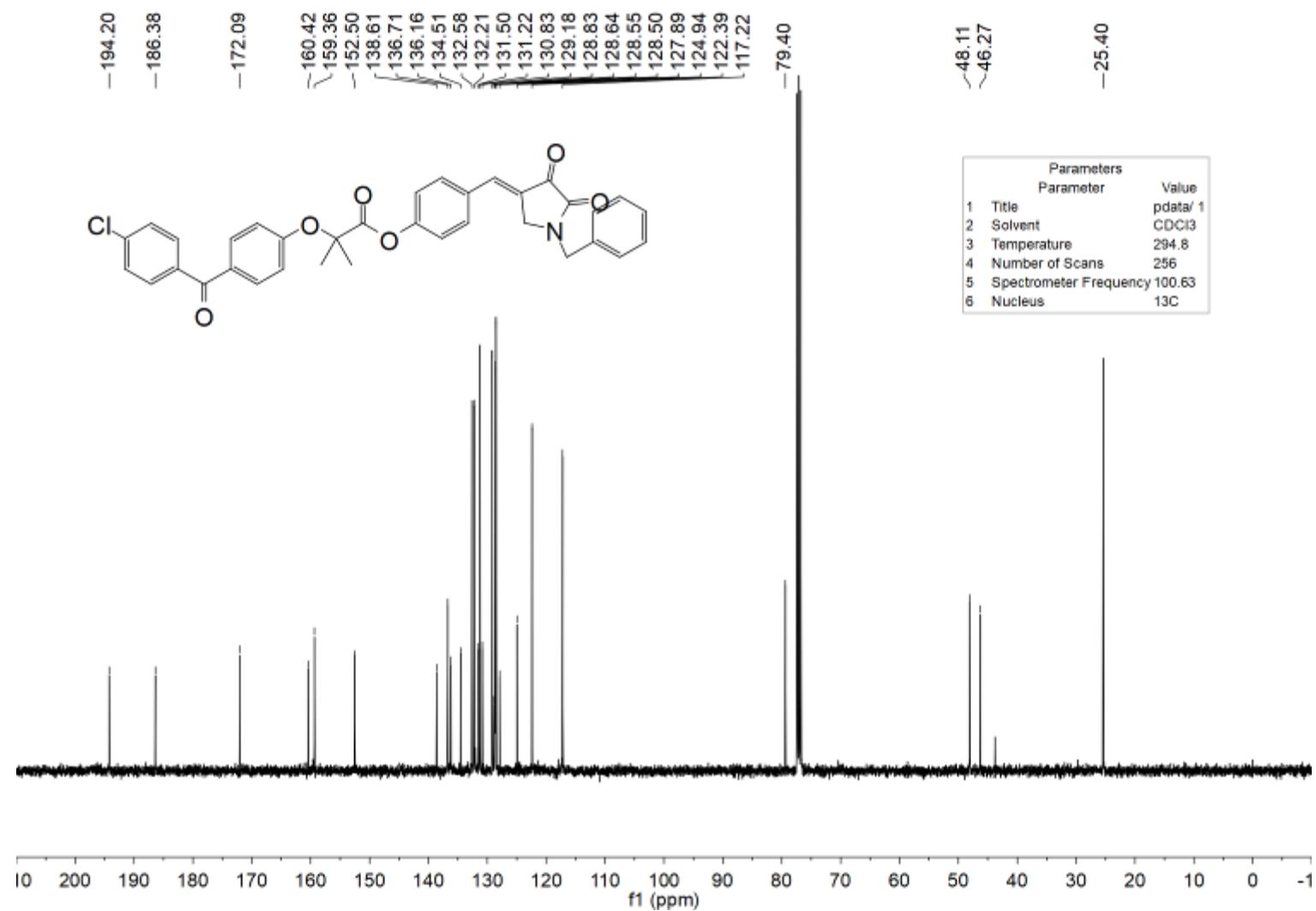
- 1: Wen, Y. H.; Huang, X.; Huang, J. L.; Xiong, Y.; Qin, B.; Feng, X. M. *Synlett*. **2005**, *16*, 2445–2448.
- 2: Liu, X. H.; Lin, L. L.; Feng, X. M. *Acc. Chem. Res.* **2011**, *44*, 574–587.
- 3: Liu, X. H.; Lin, L. L.; Feng, X. M. *Org. Chem. Front.* **2014**, *1*, 298–302.

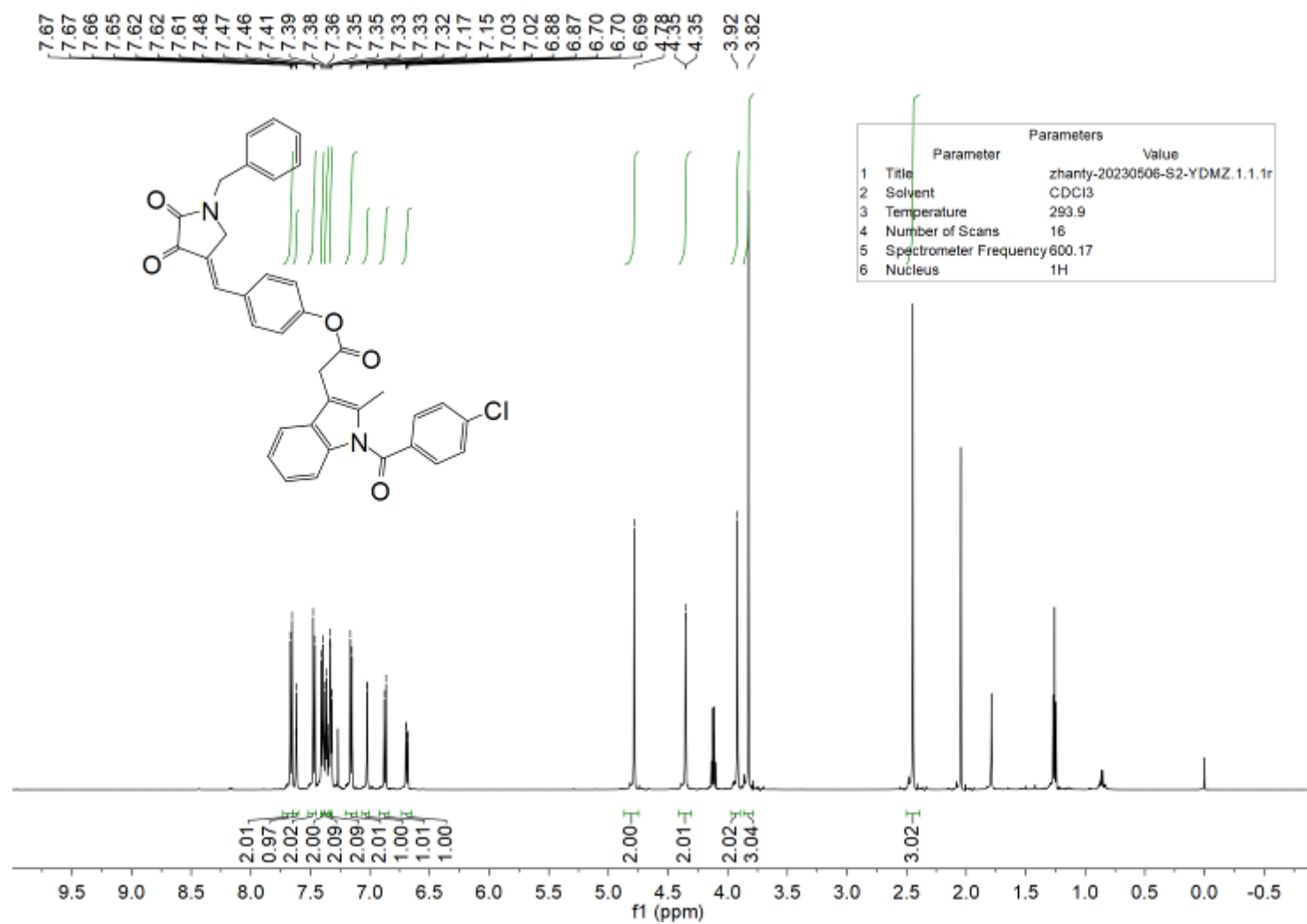
14. Copies of NMR spectra for the reaction products.

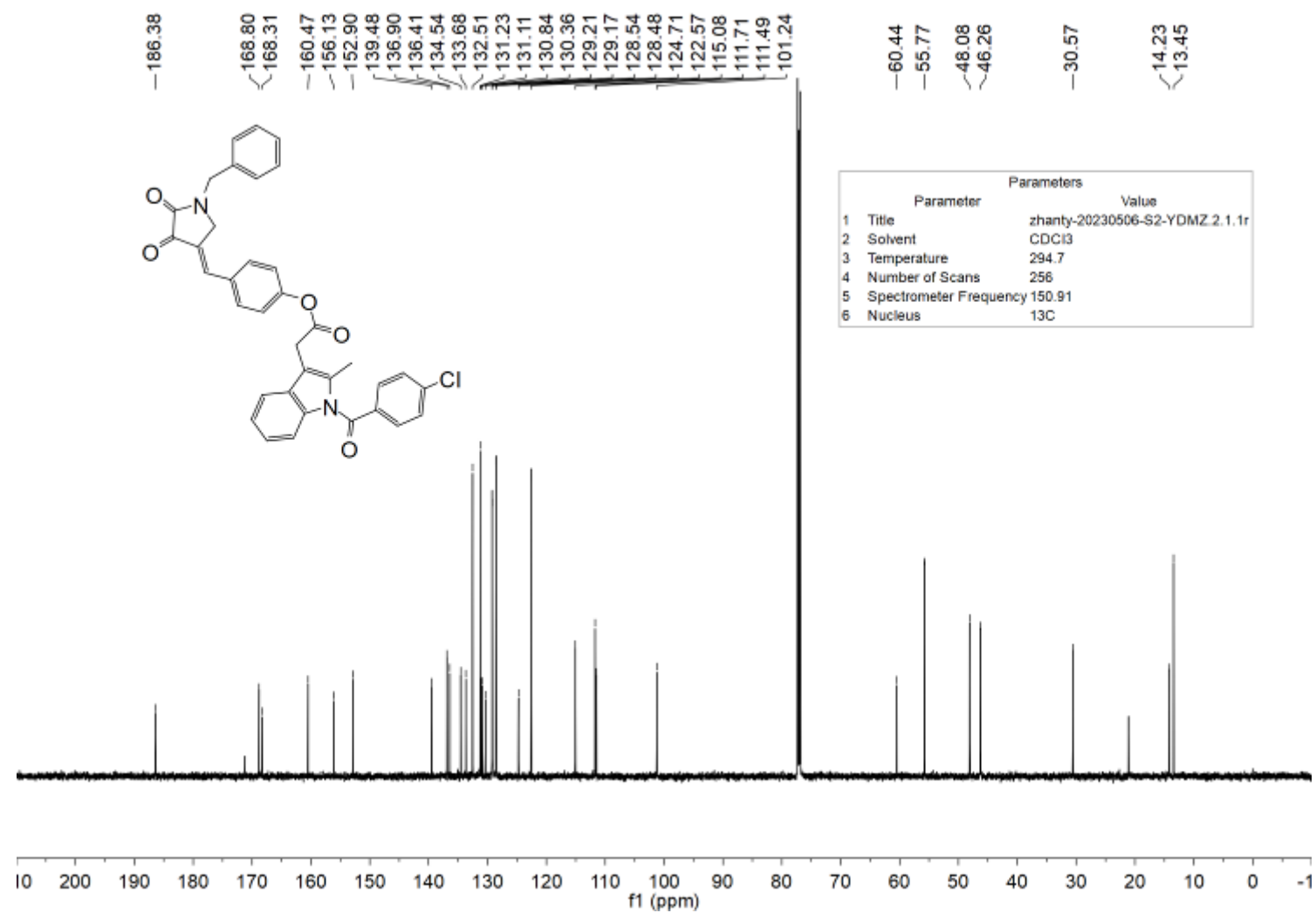


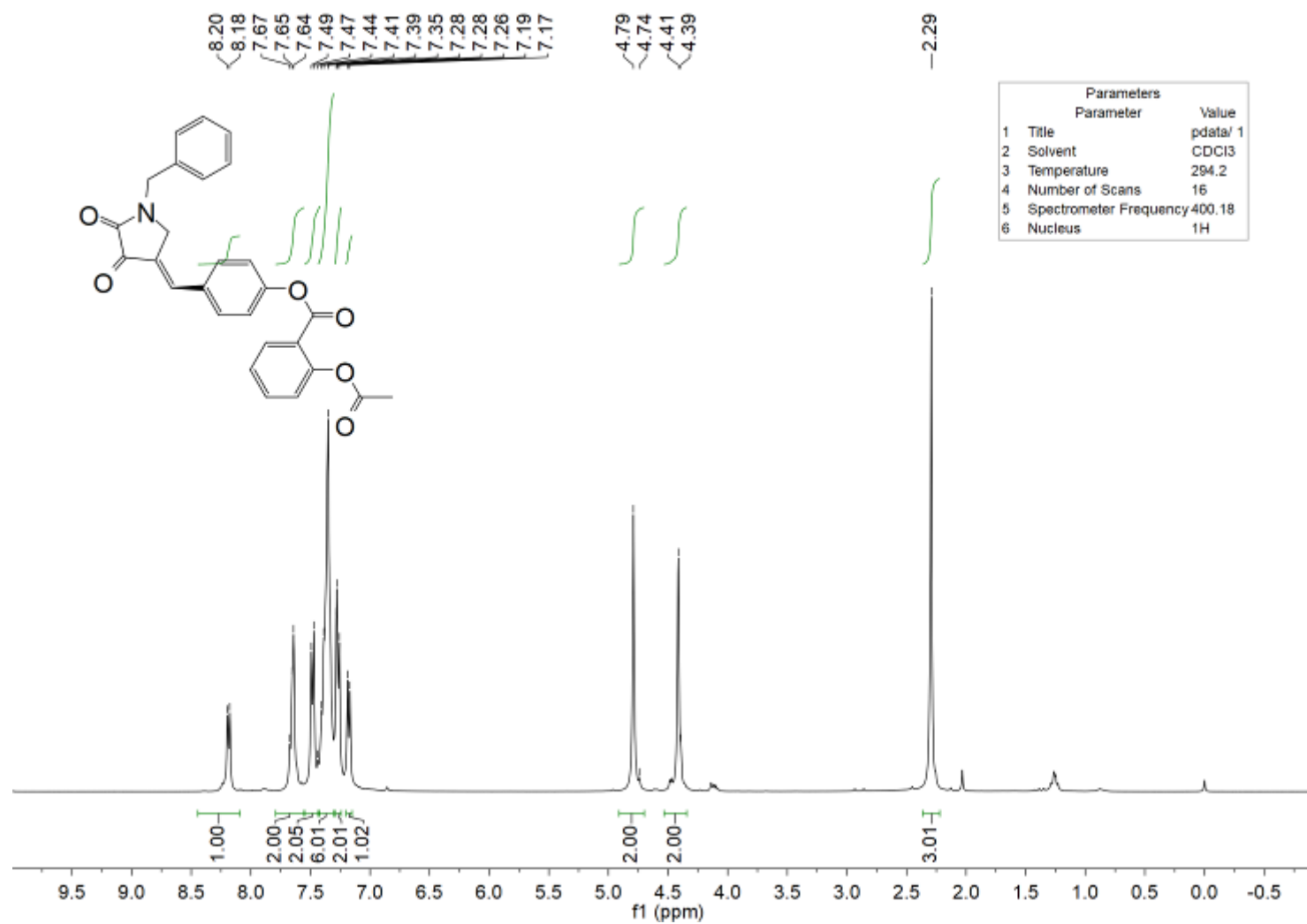


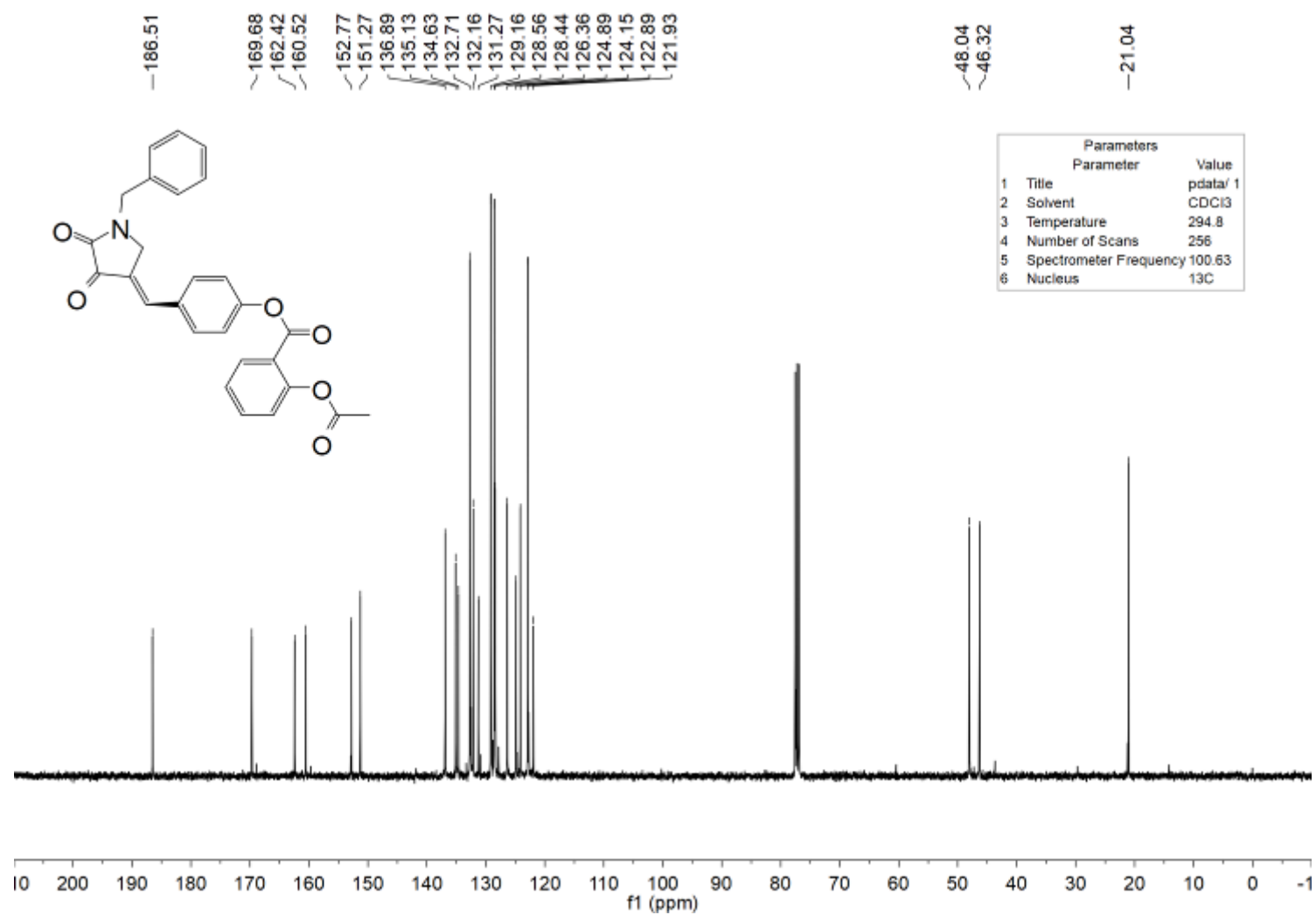


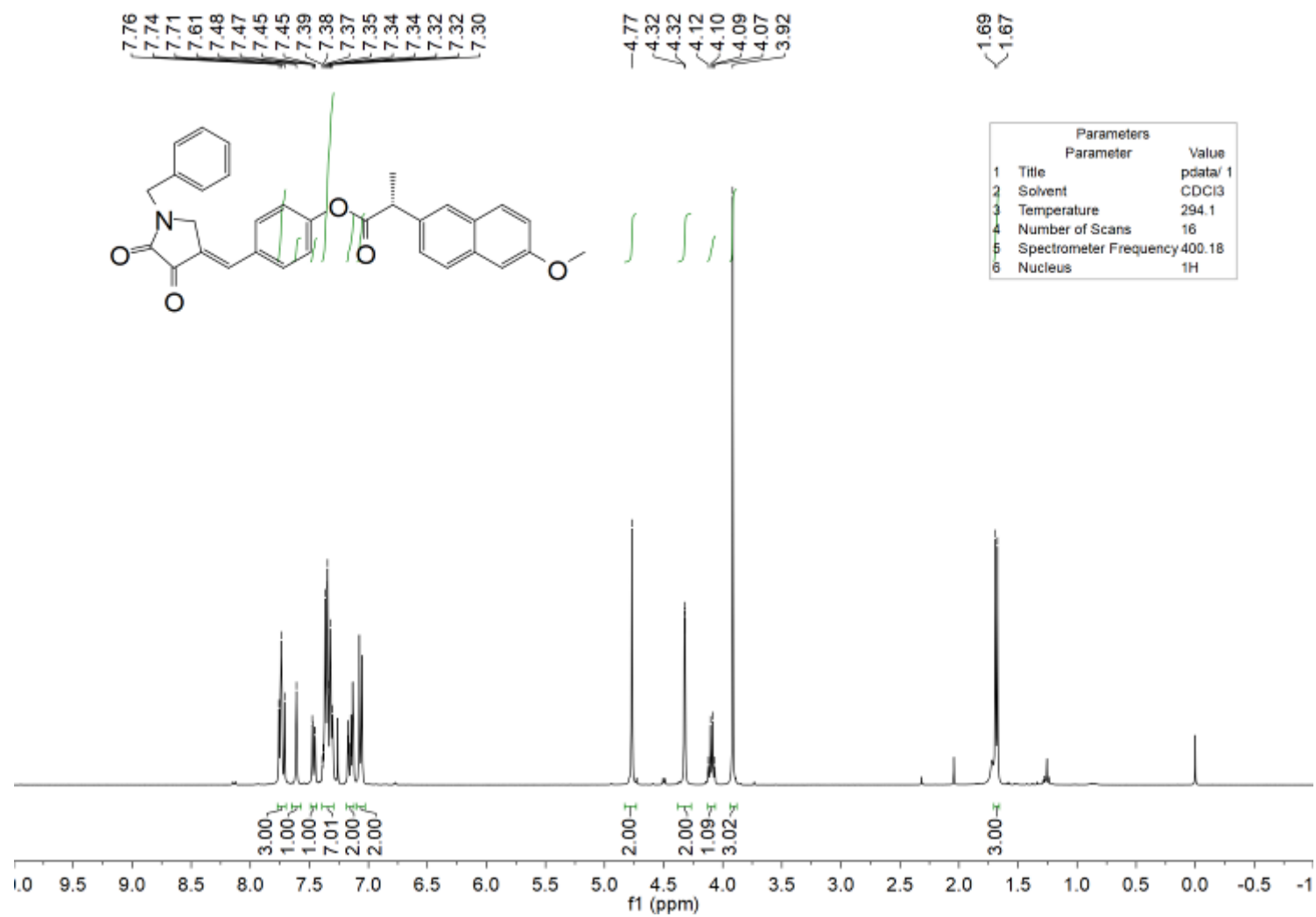


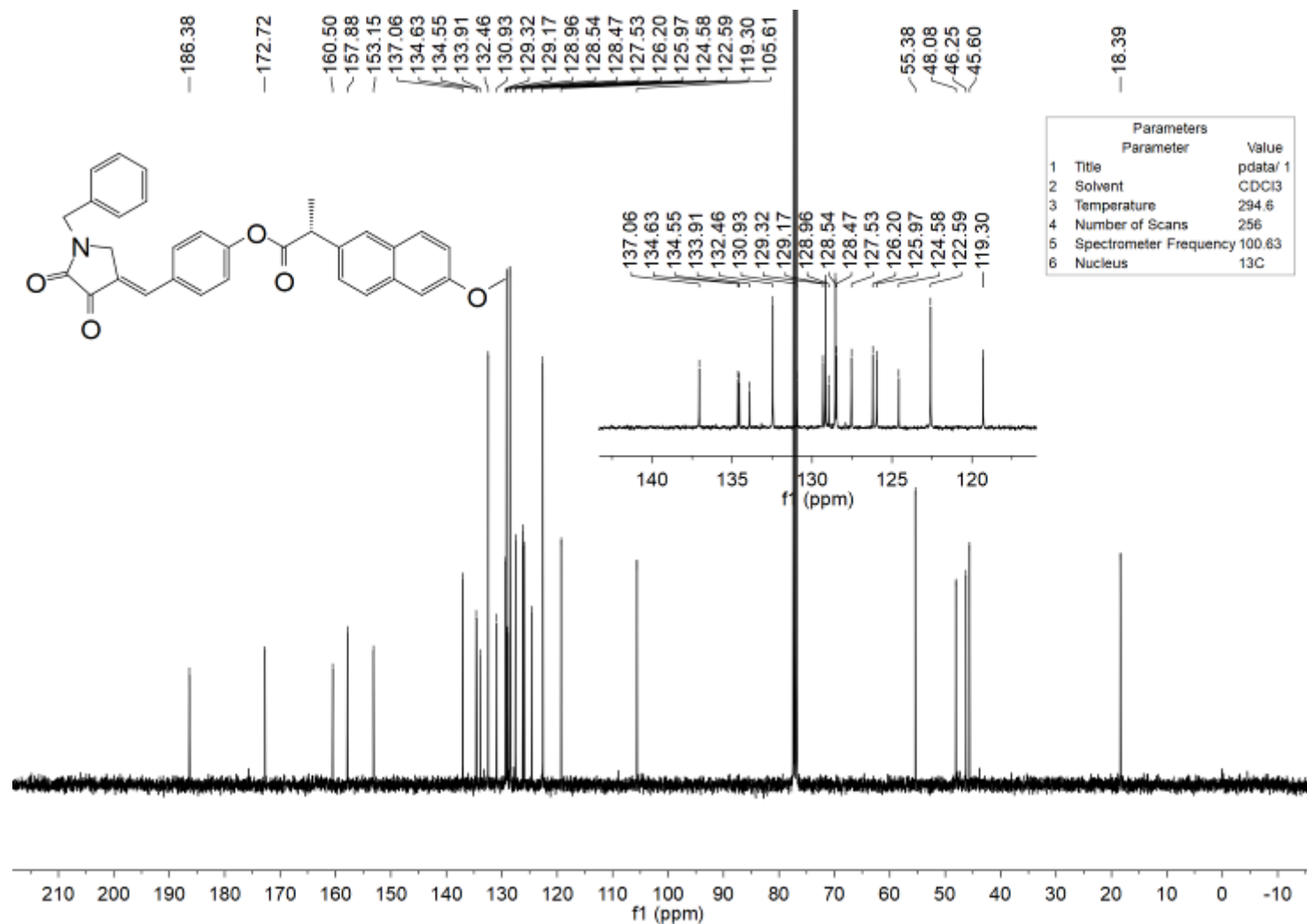


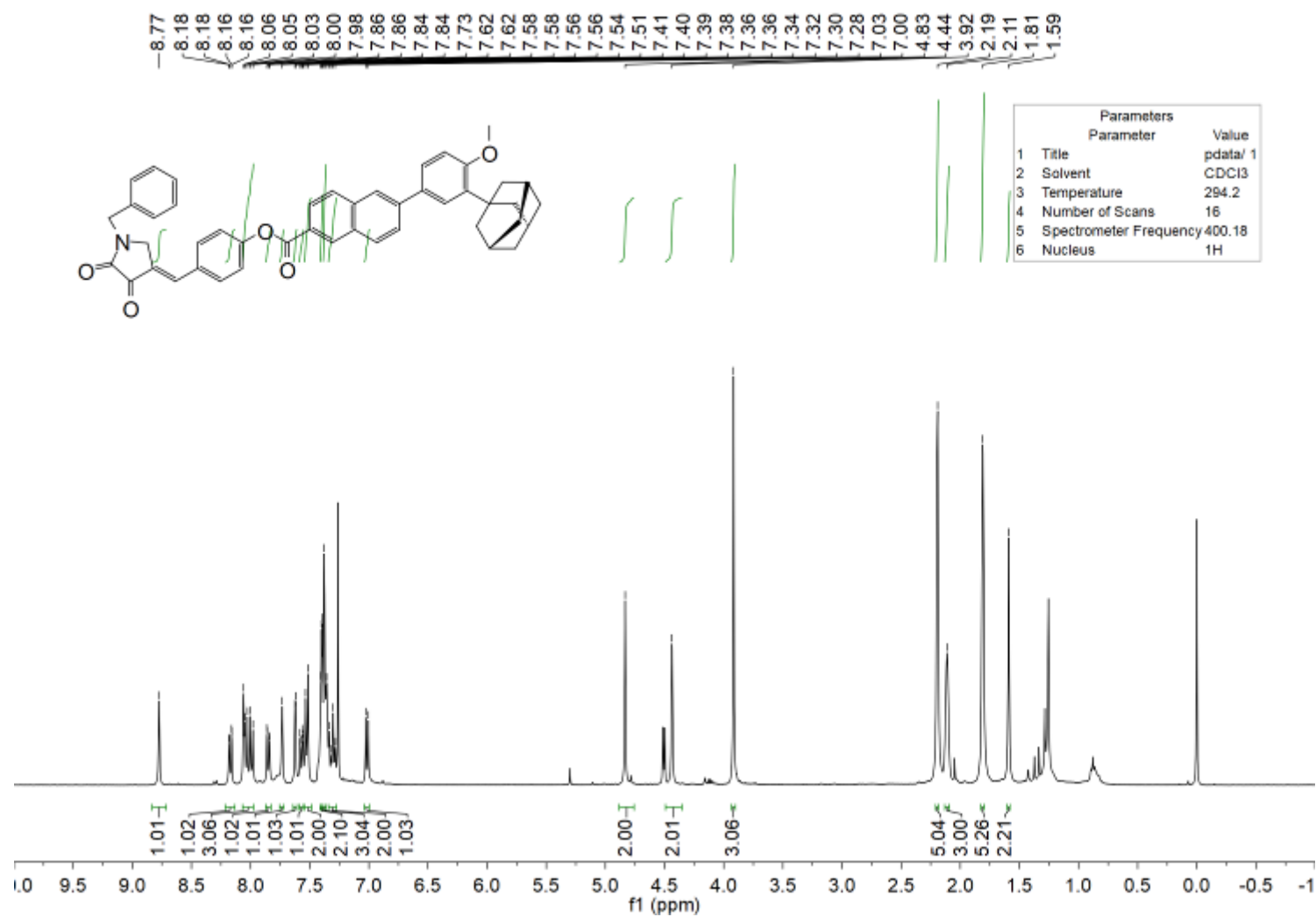


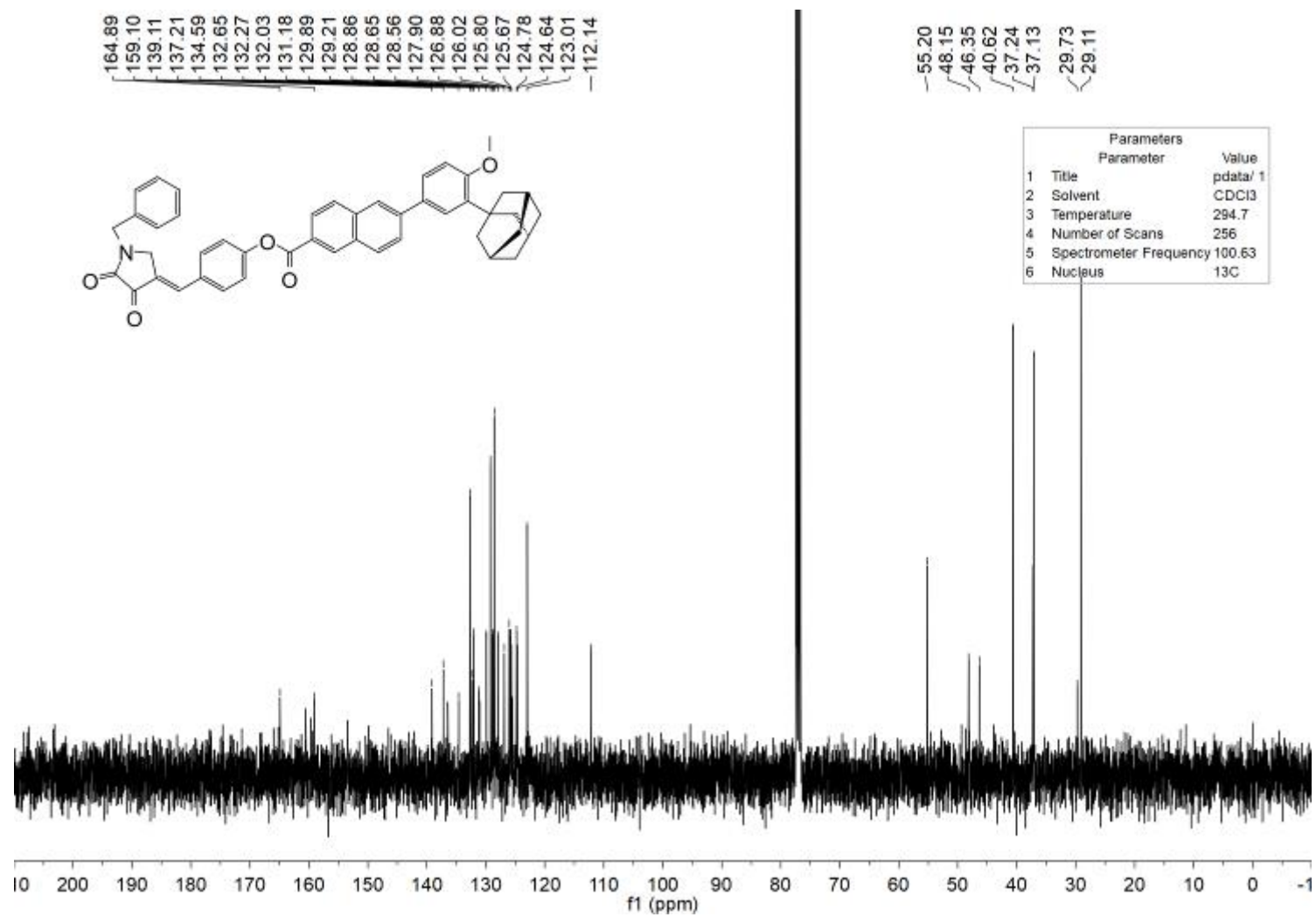


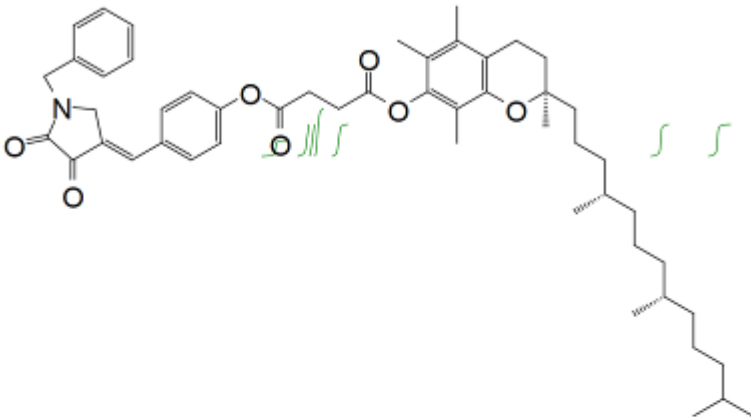


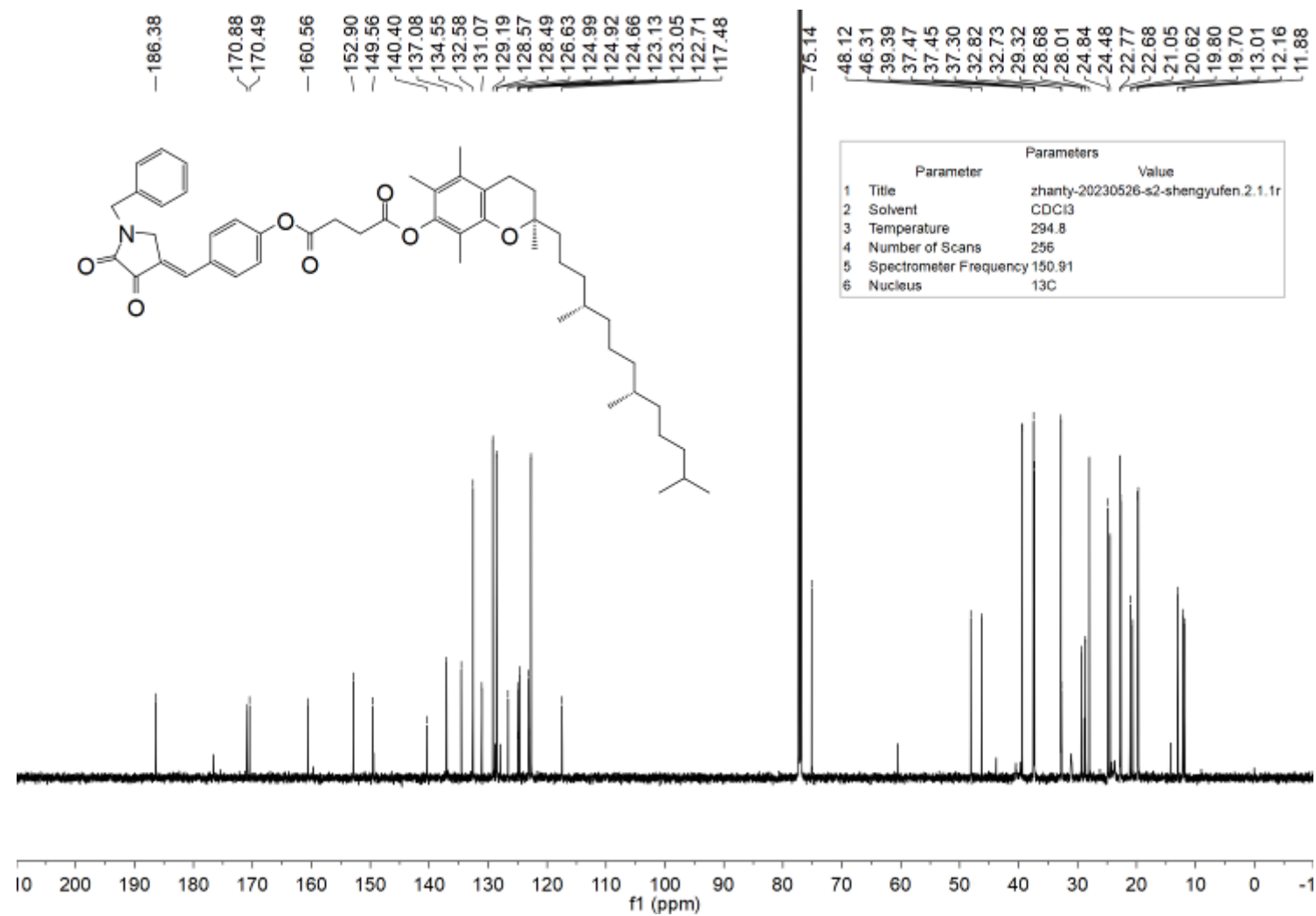


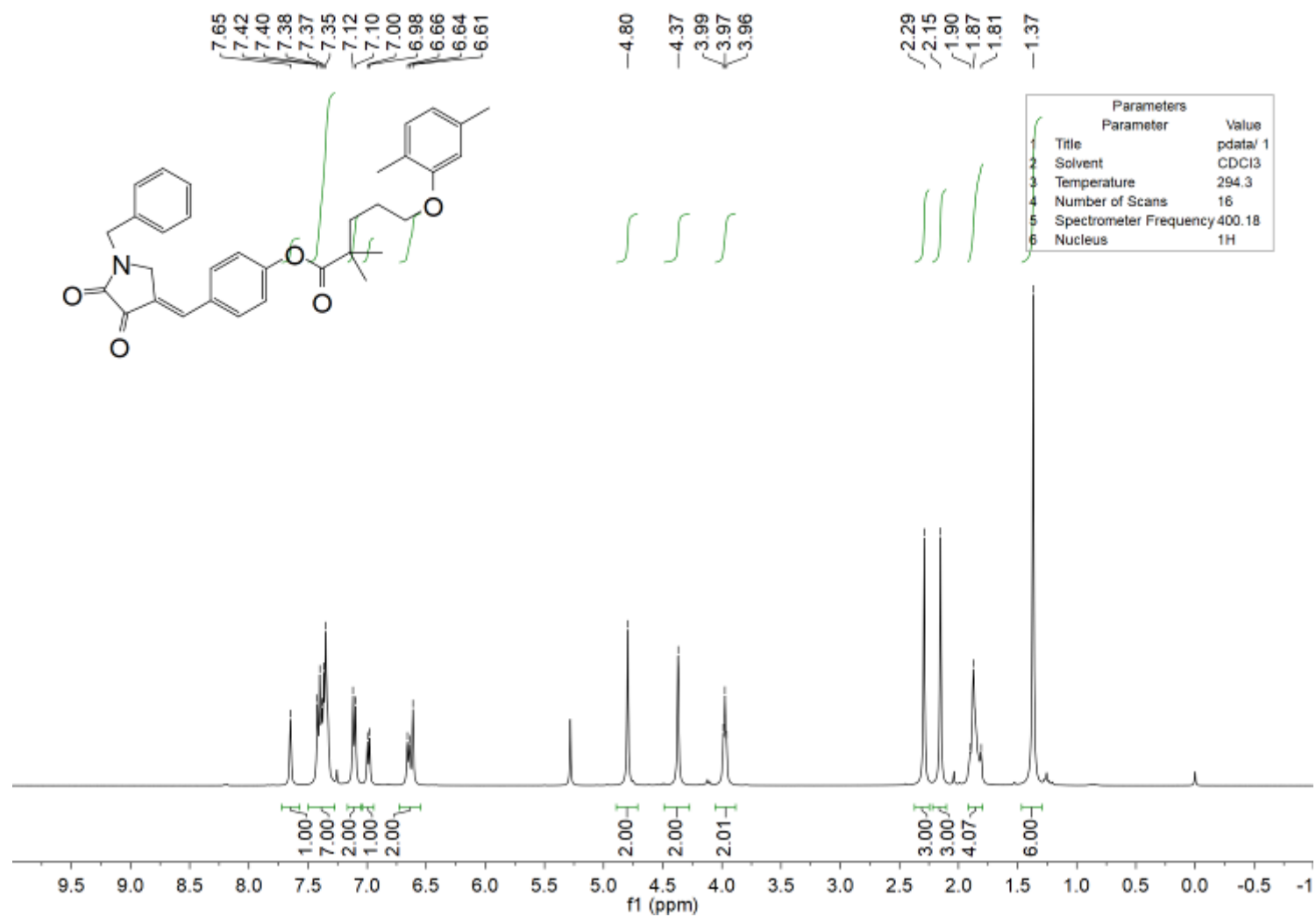


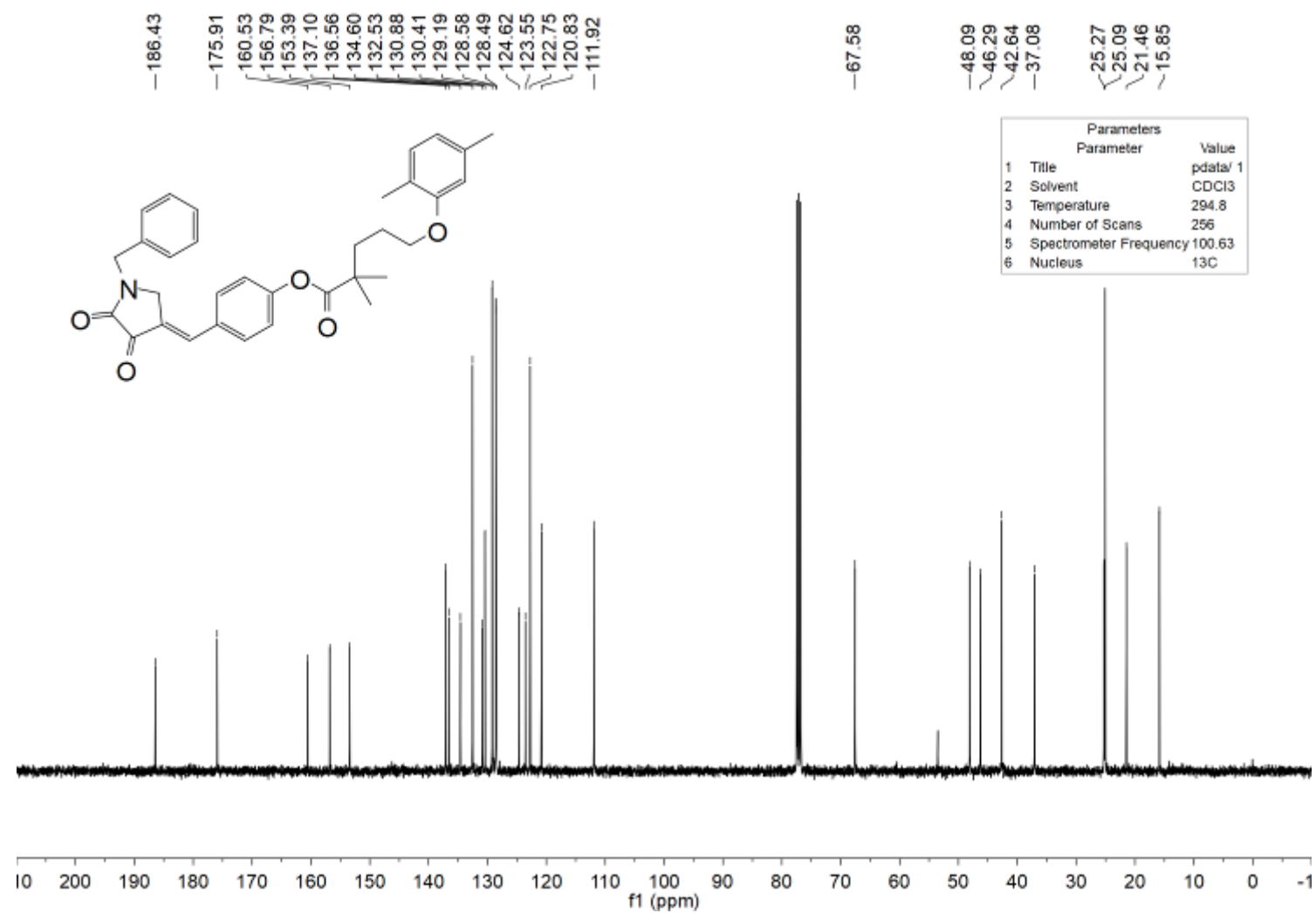


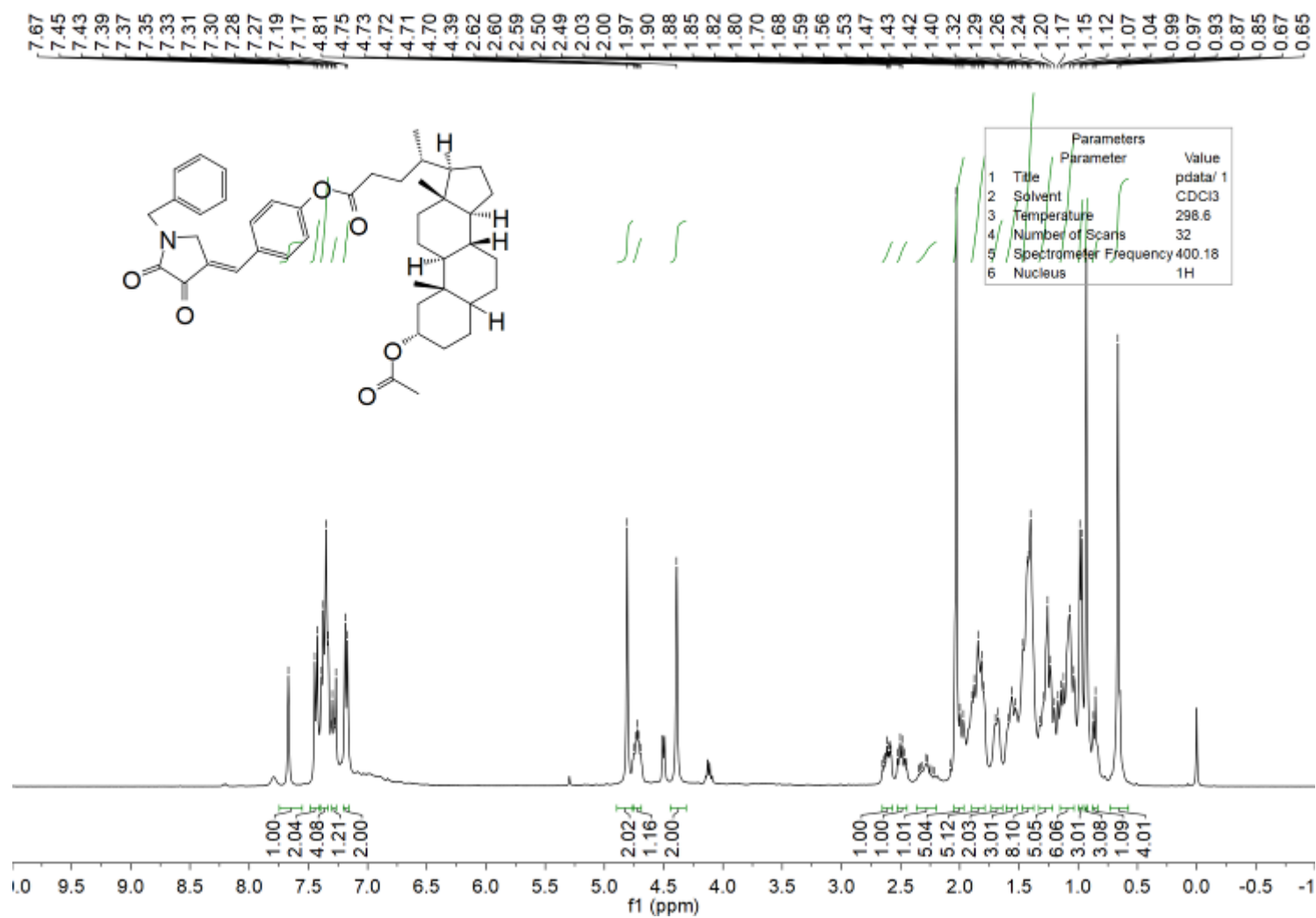


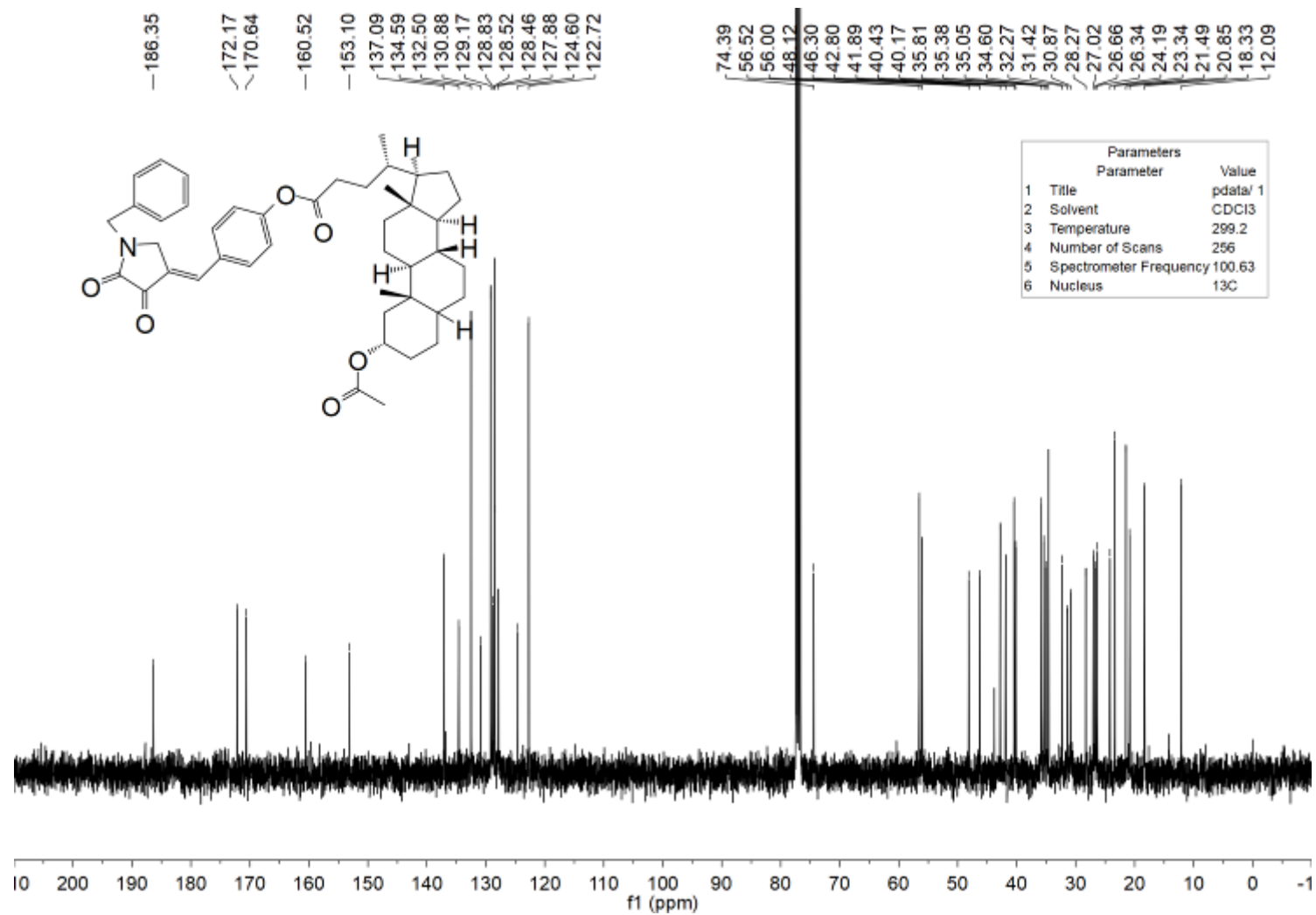


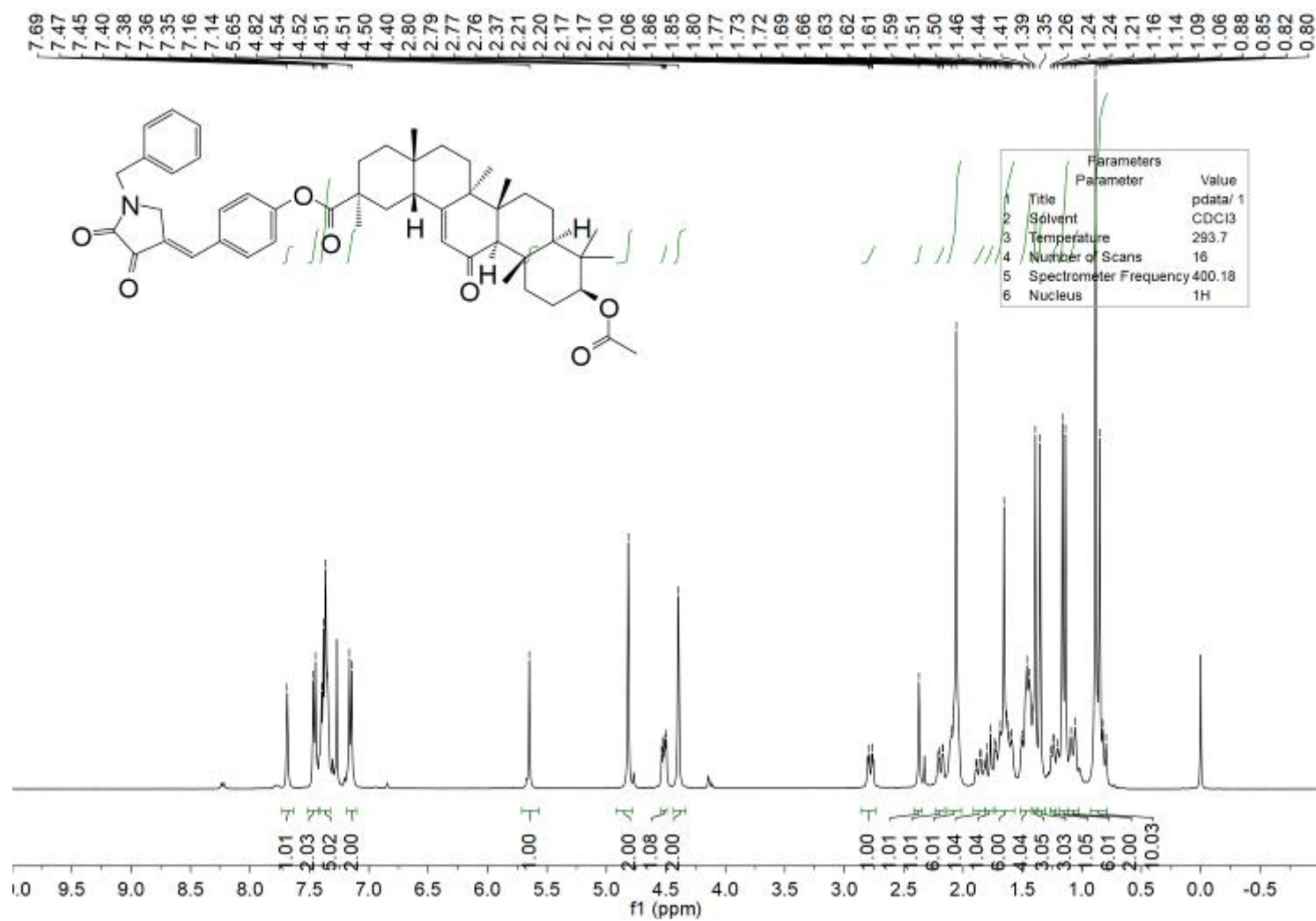


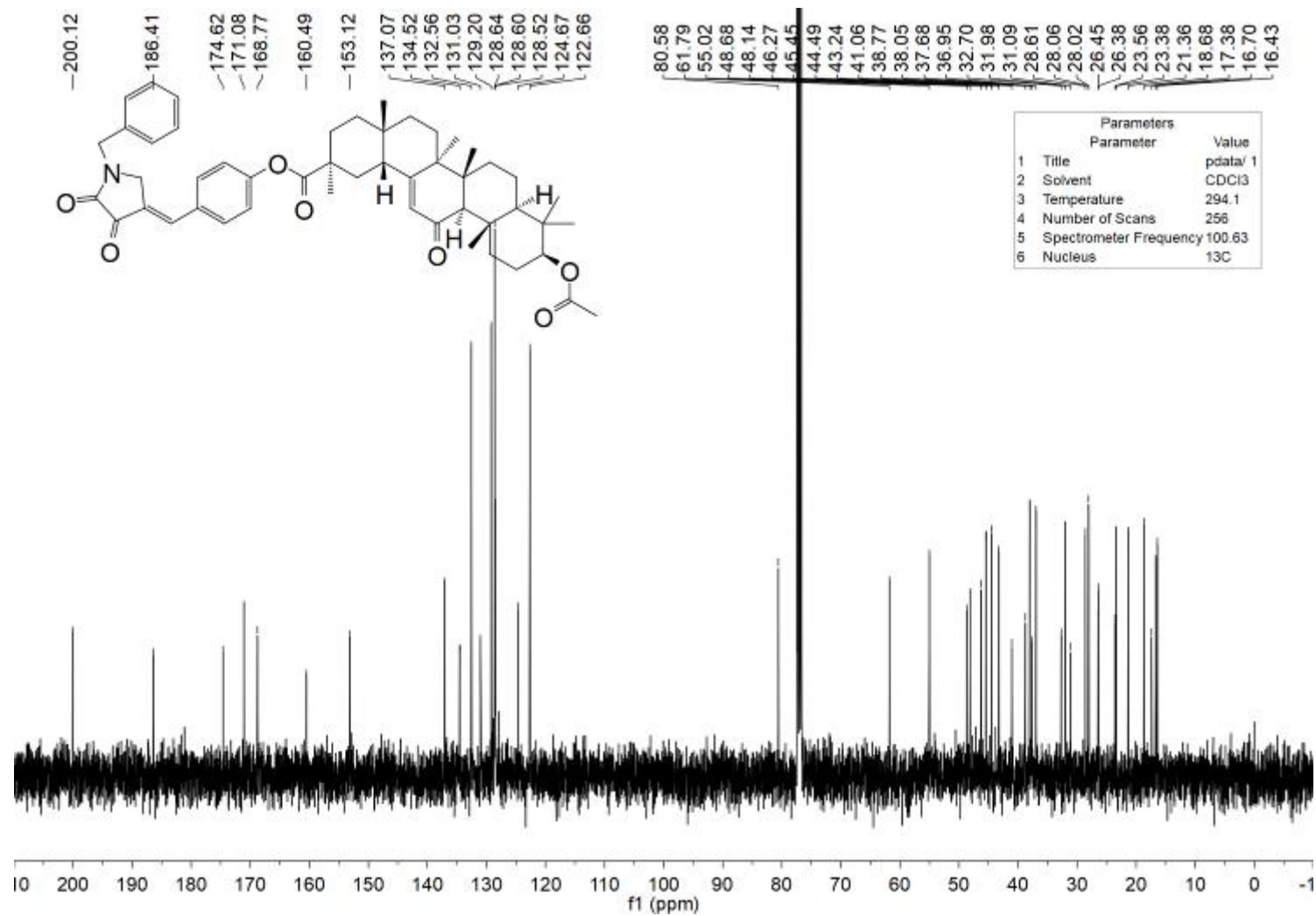


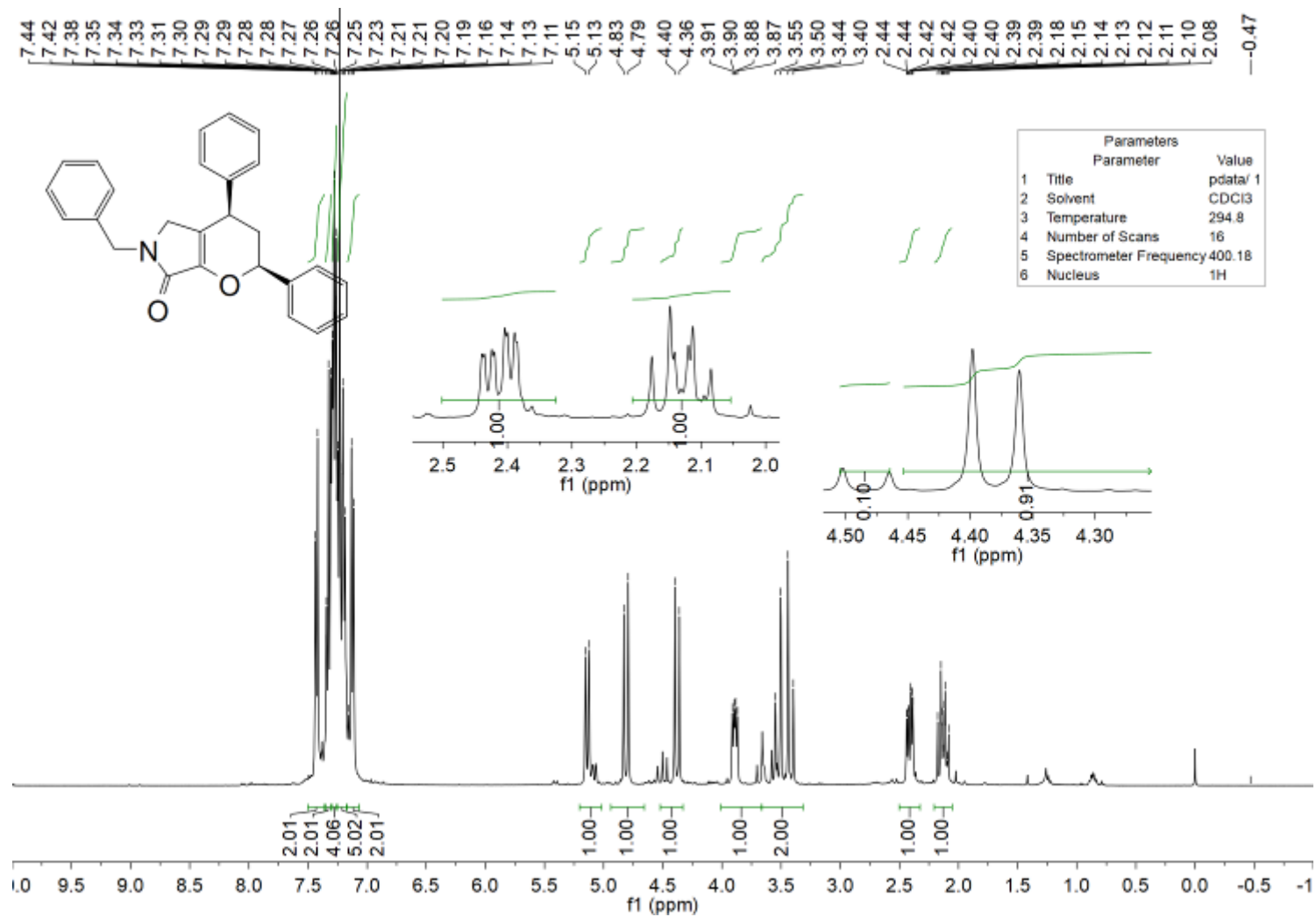


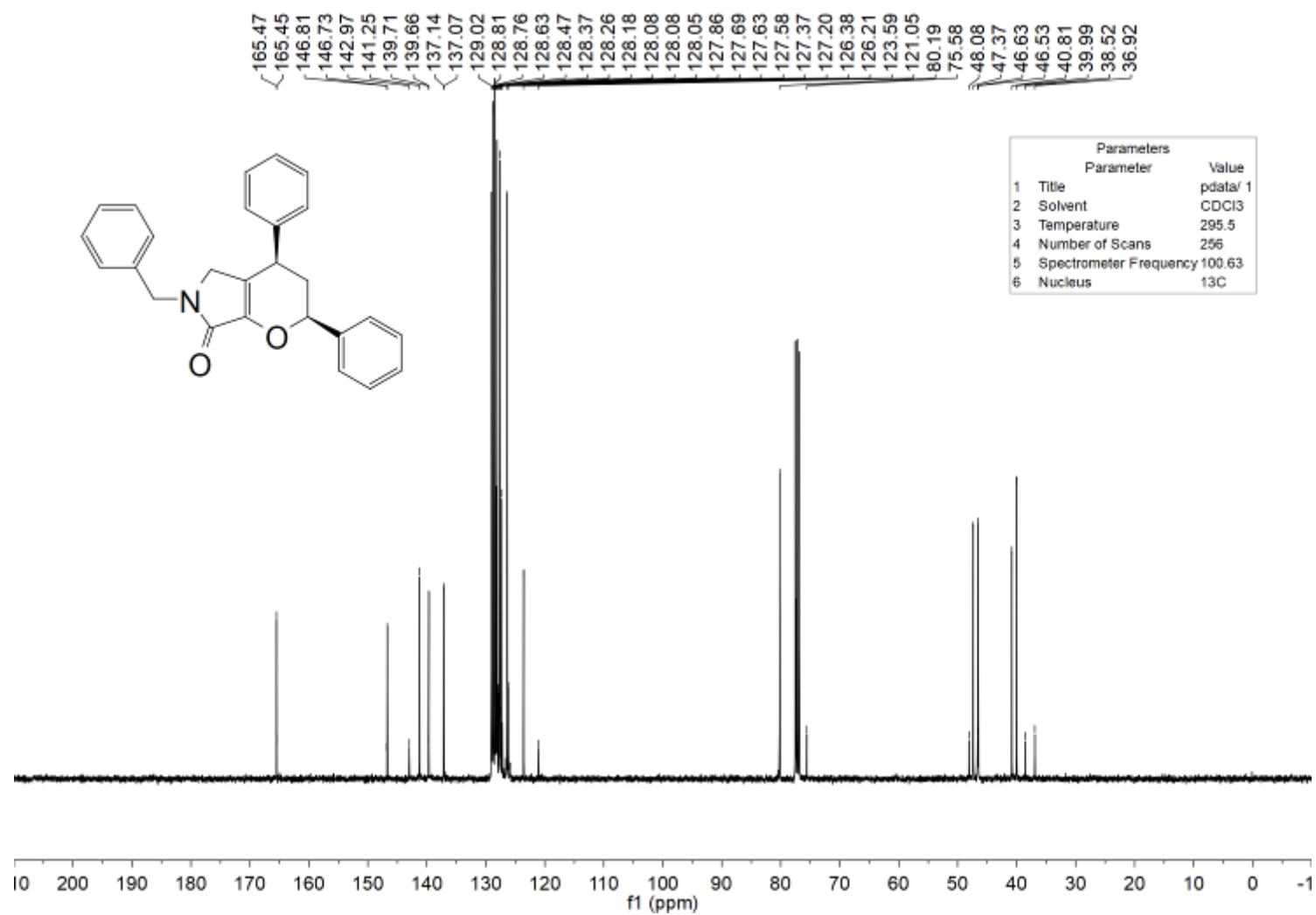


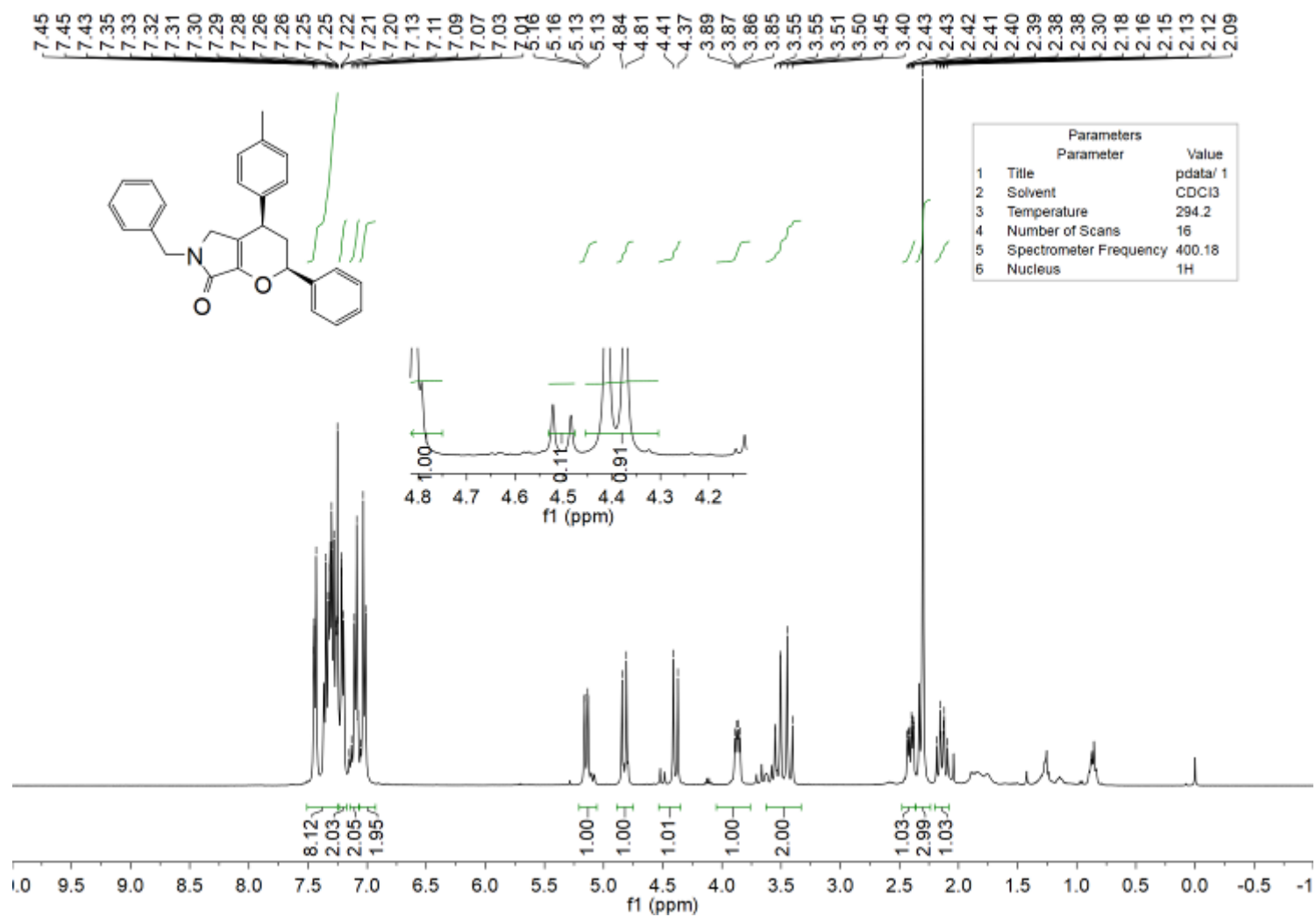


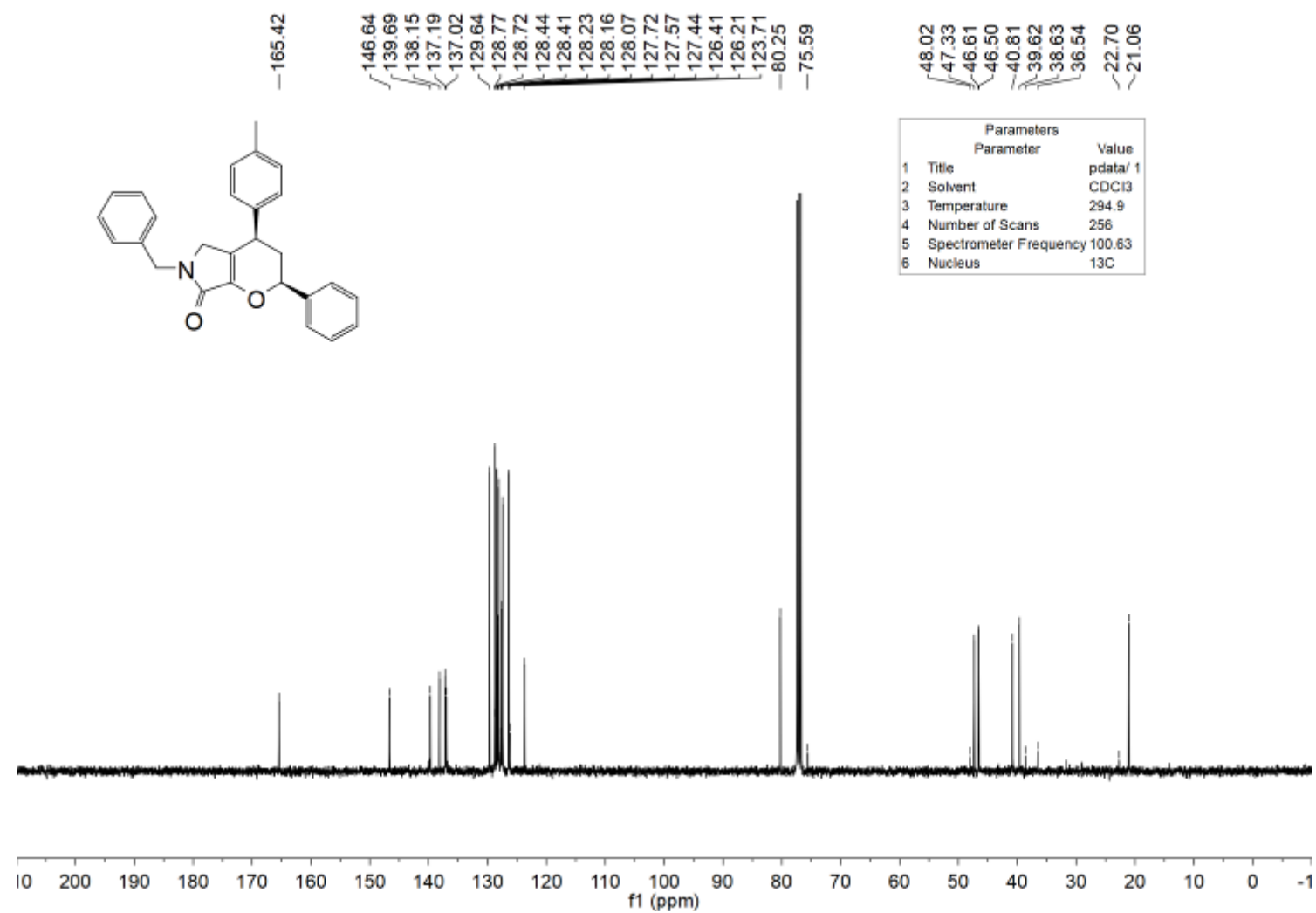


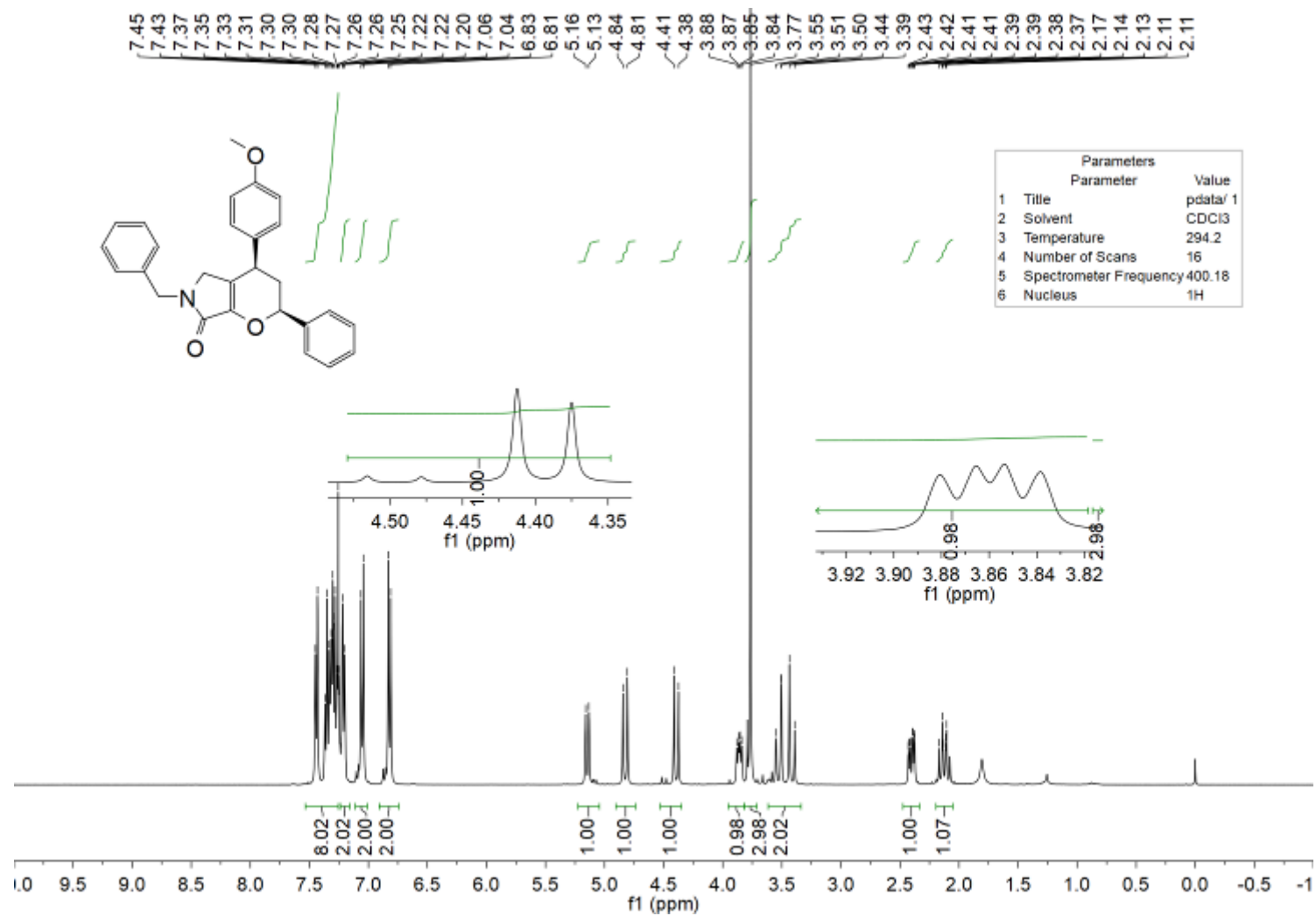


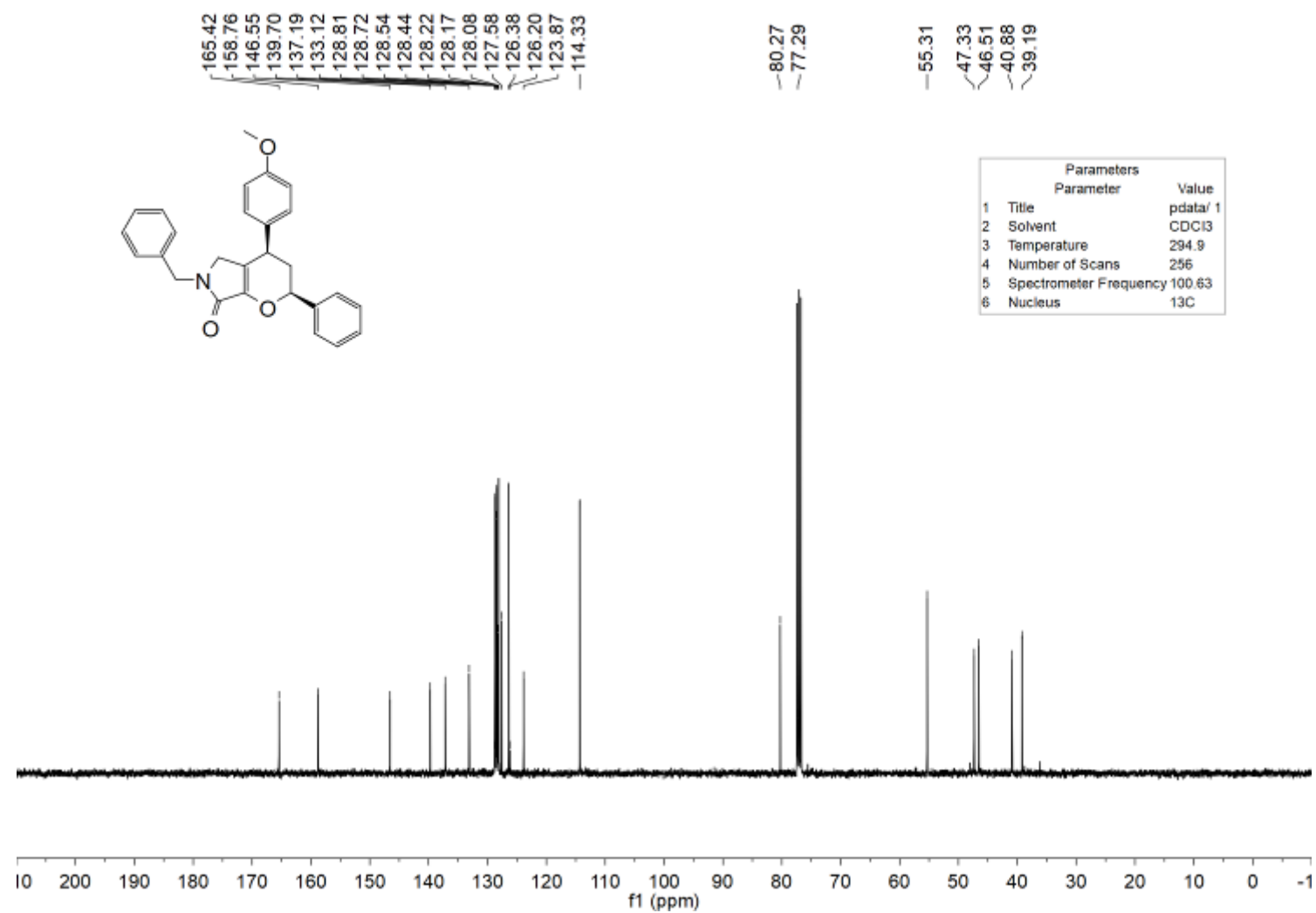


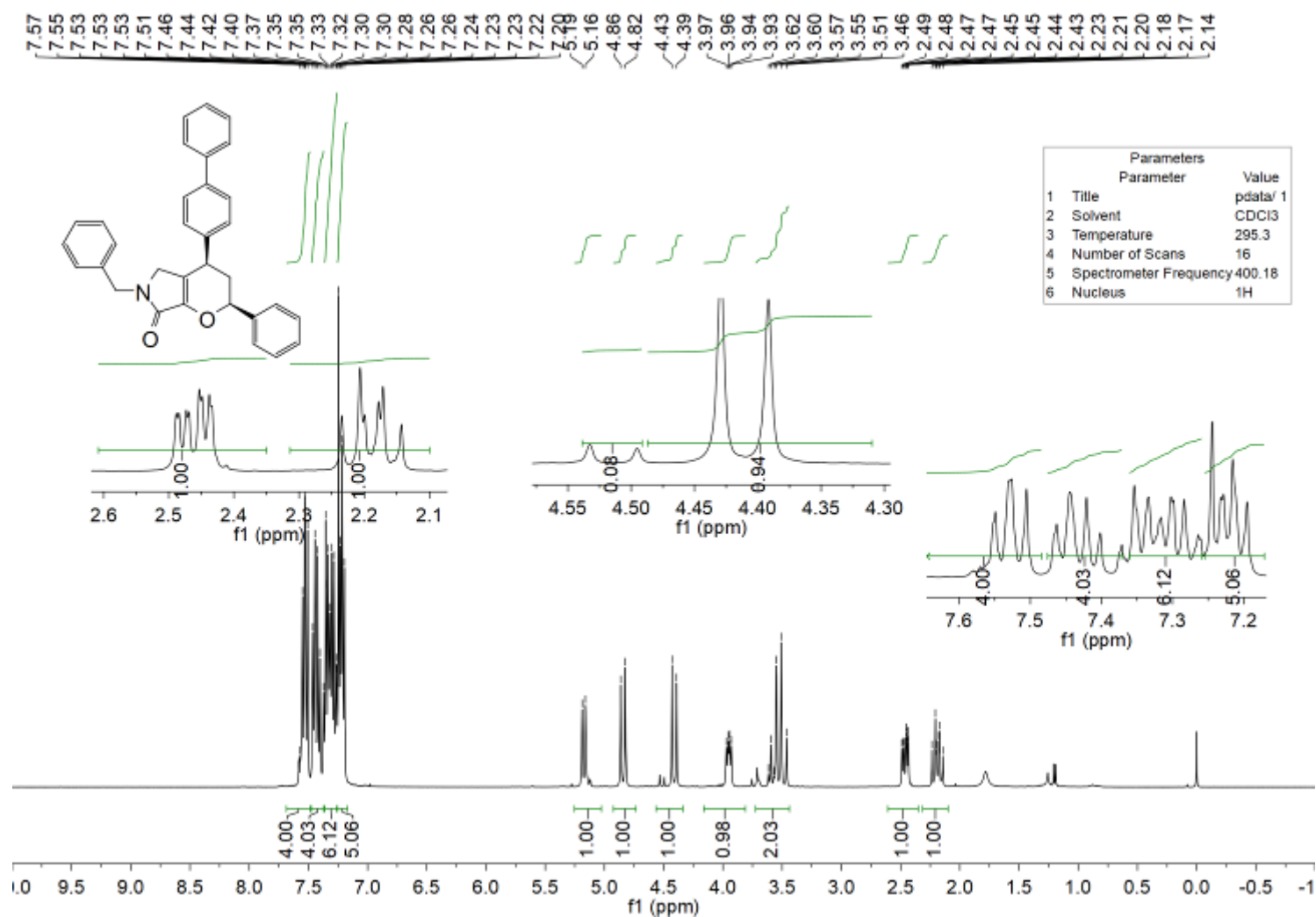


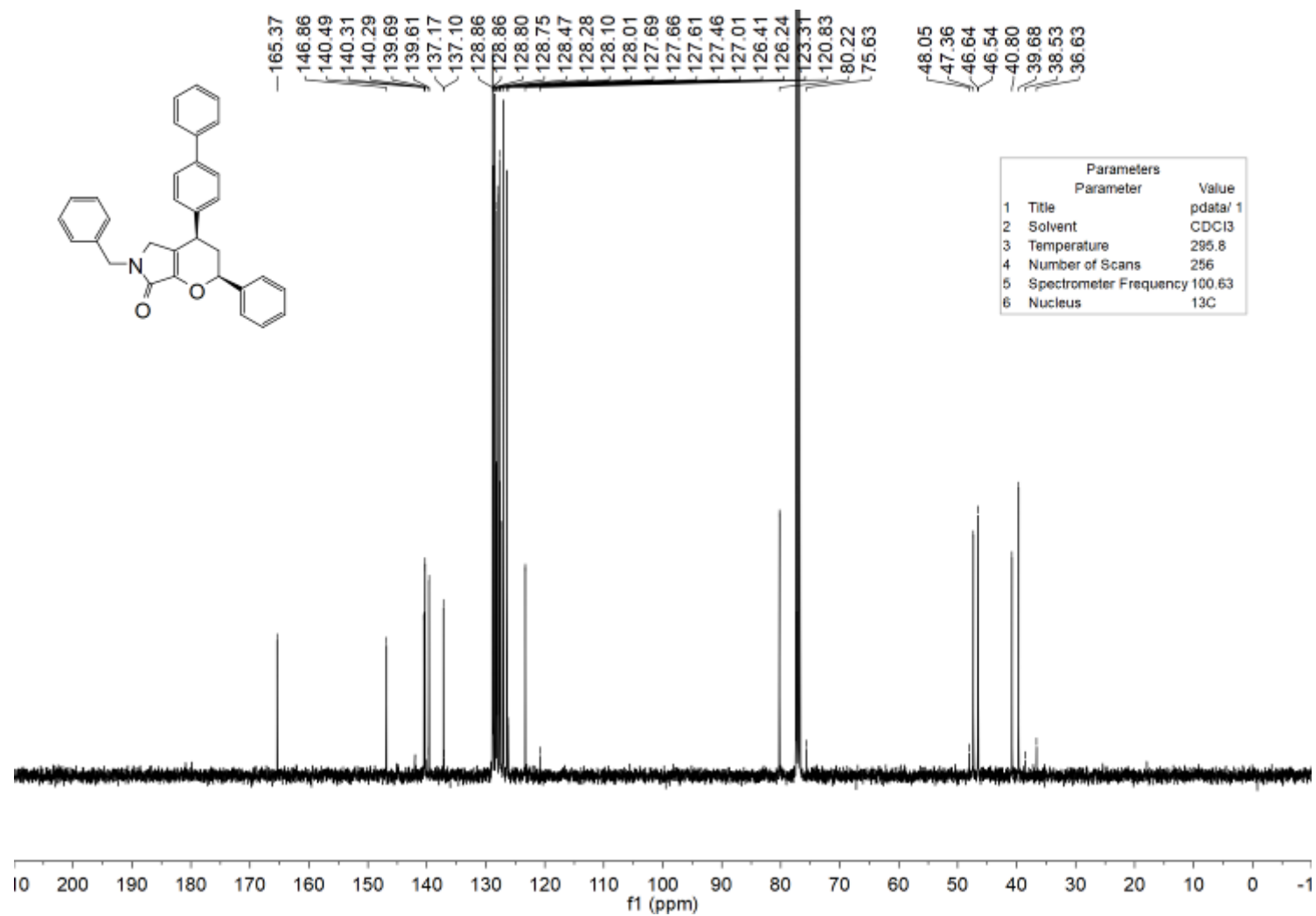


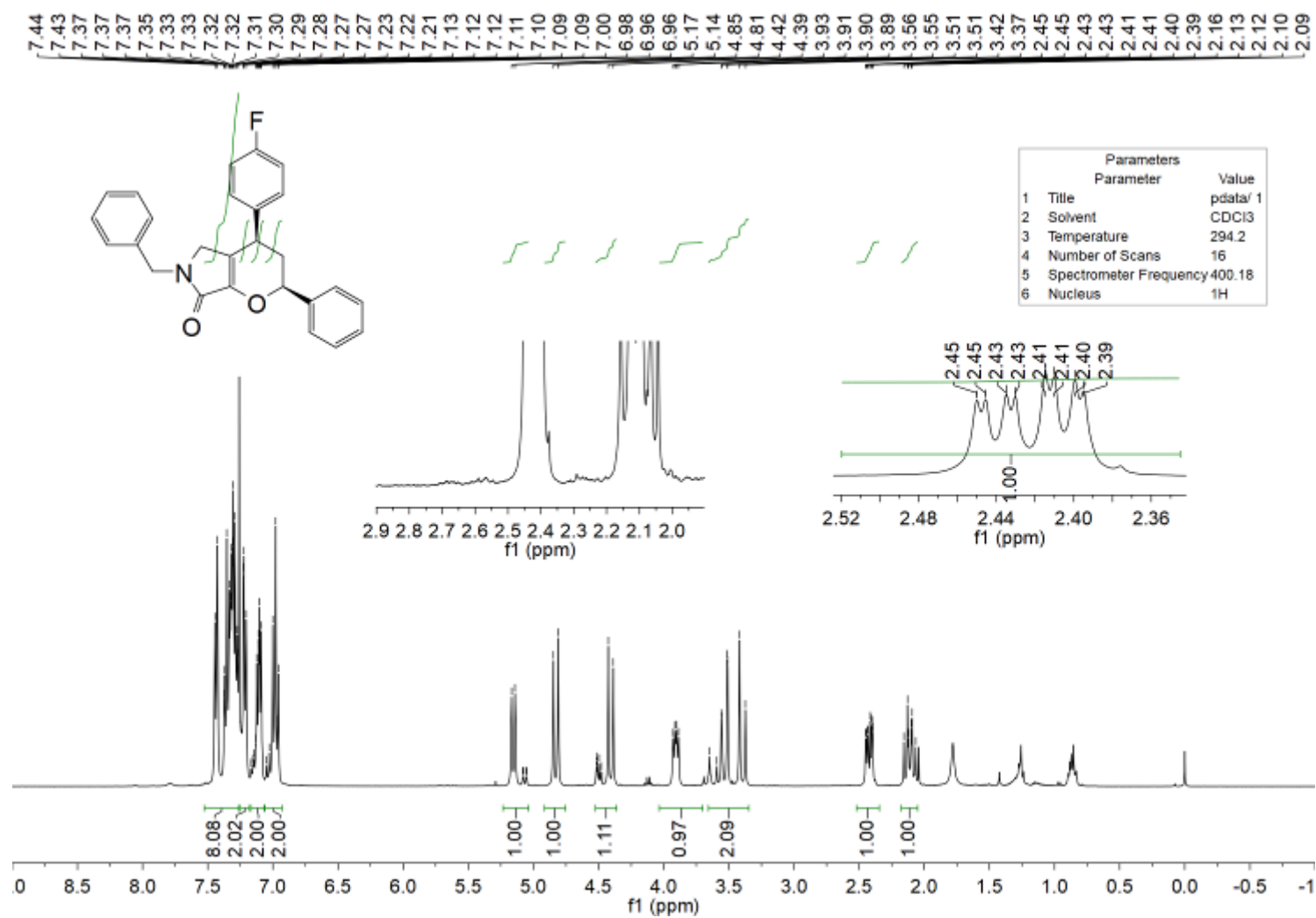


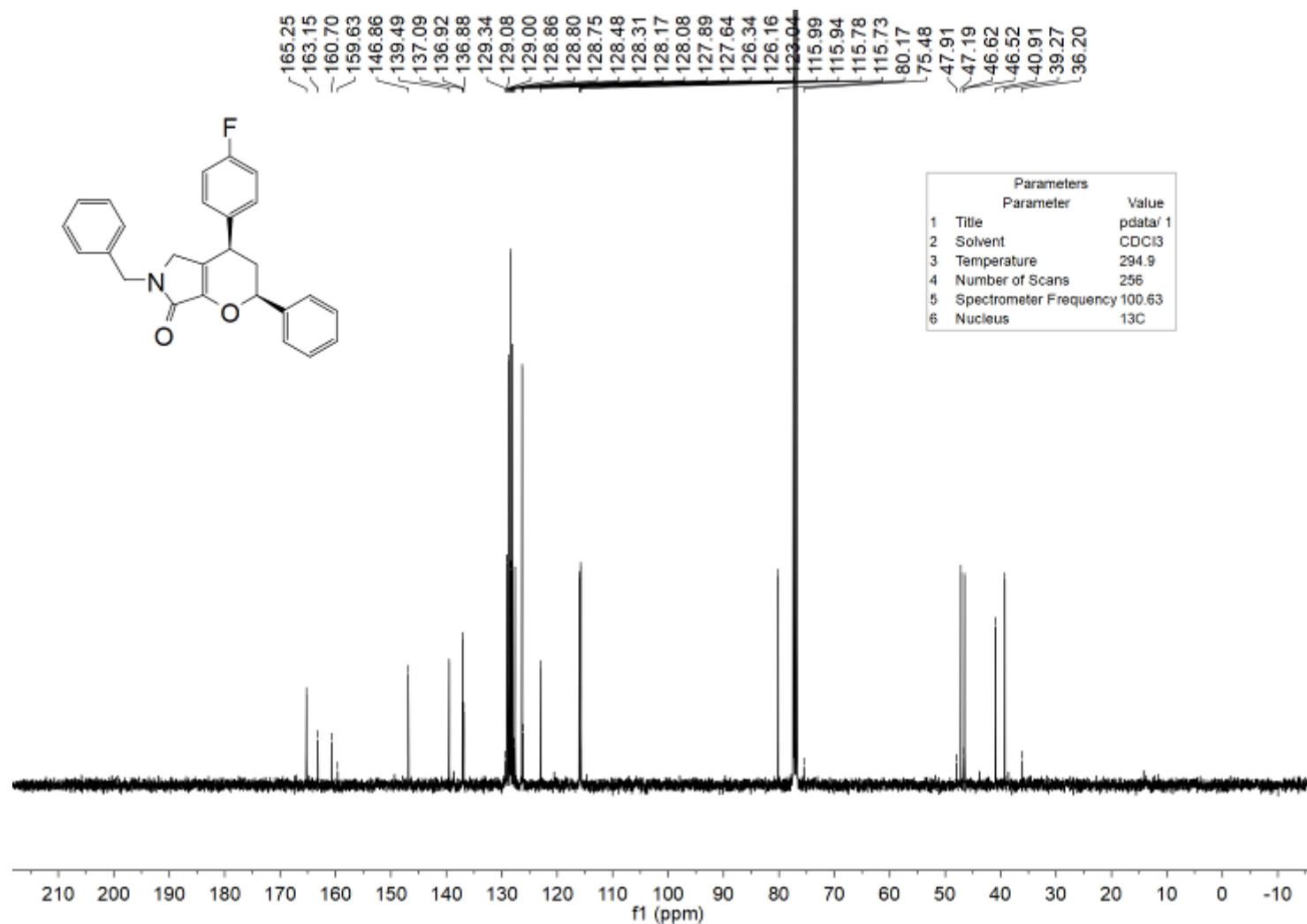


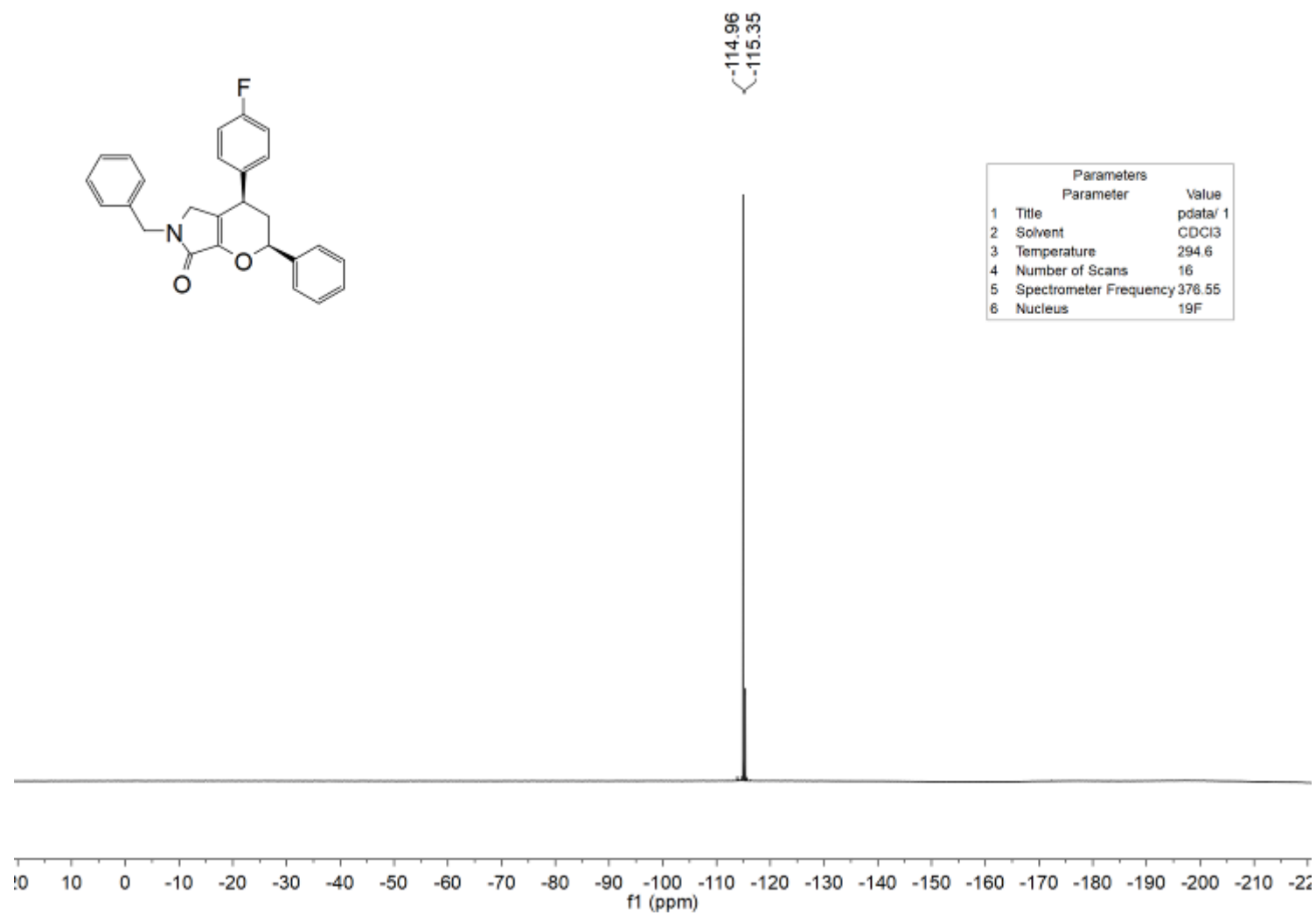


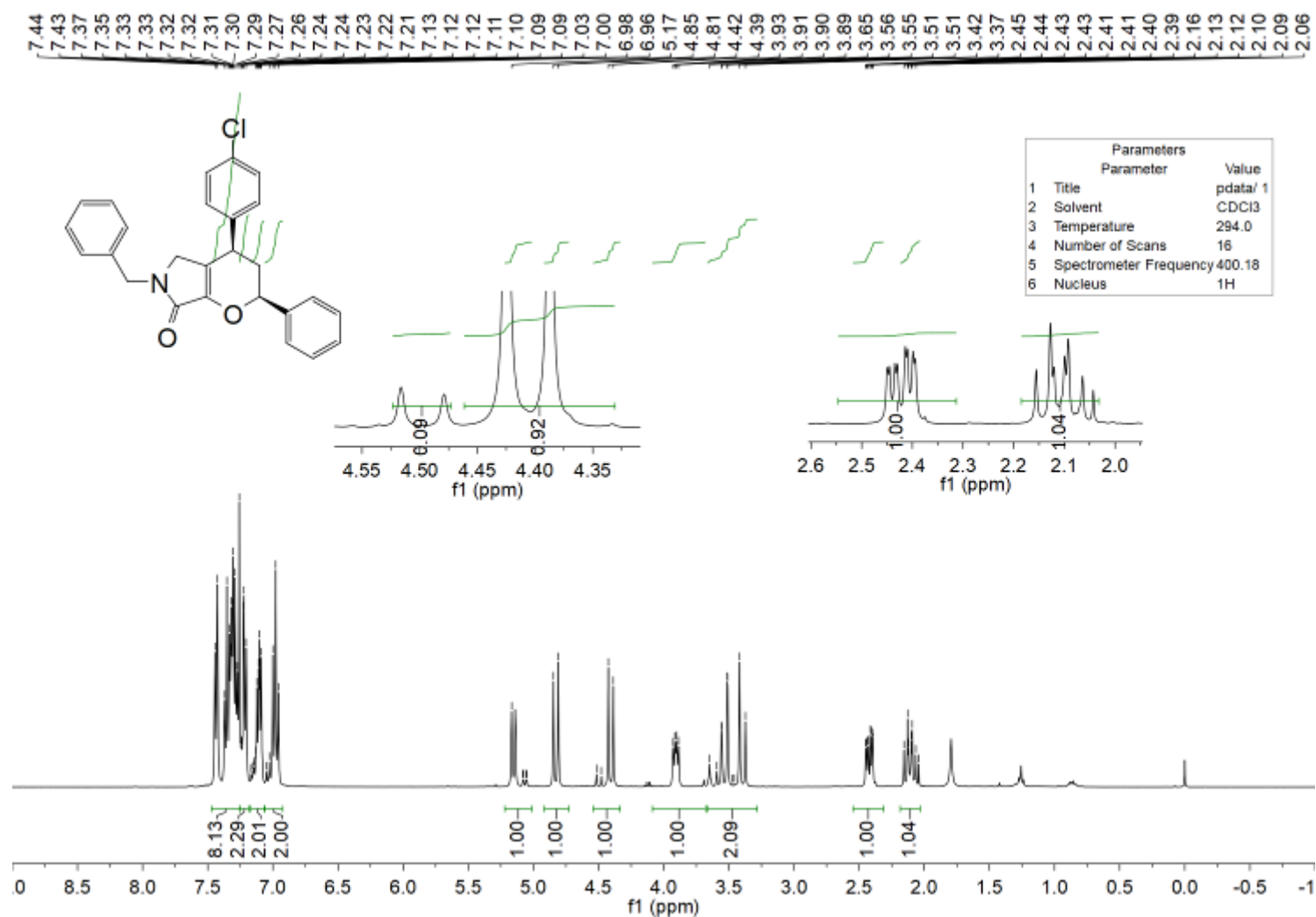


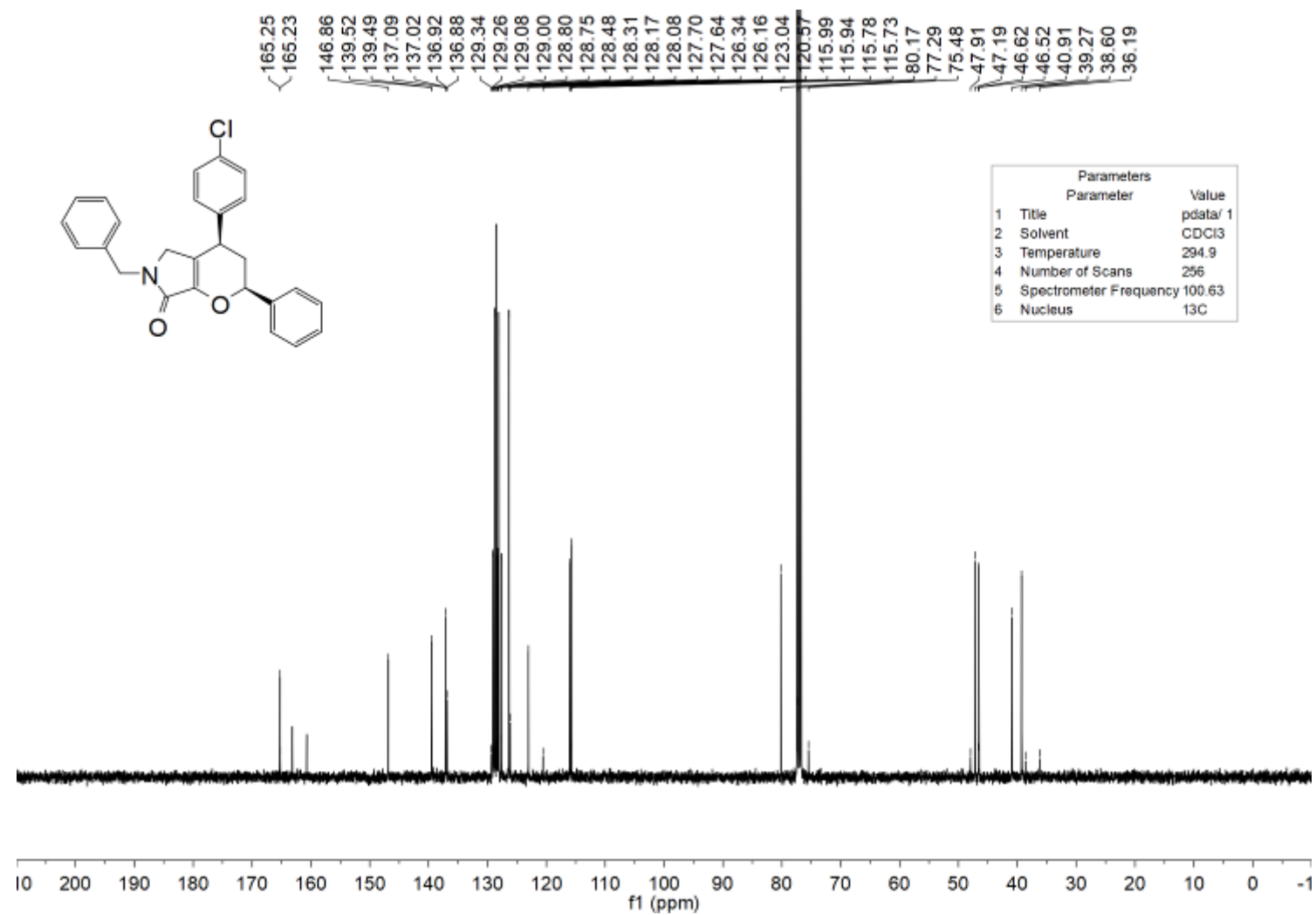


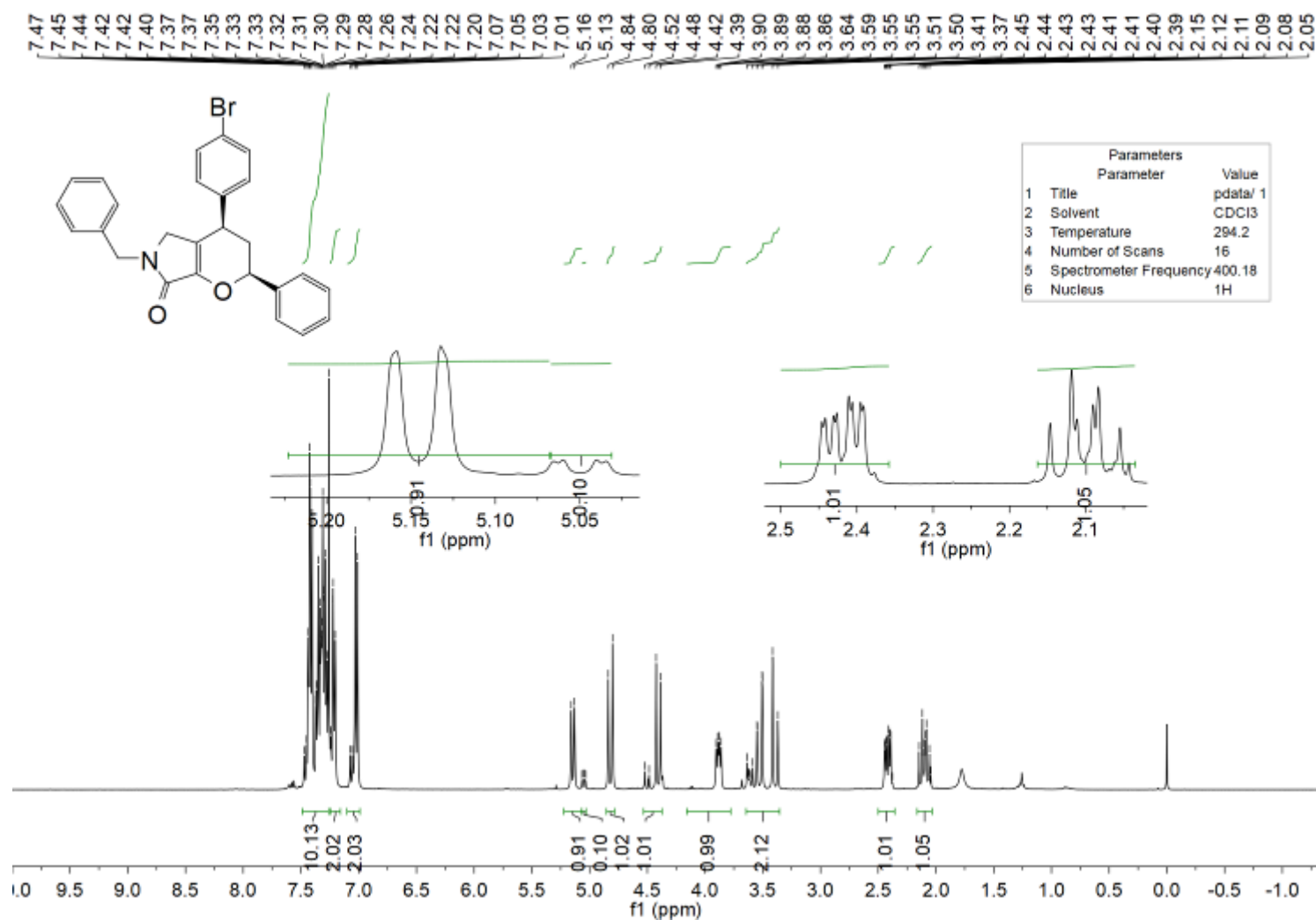


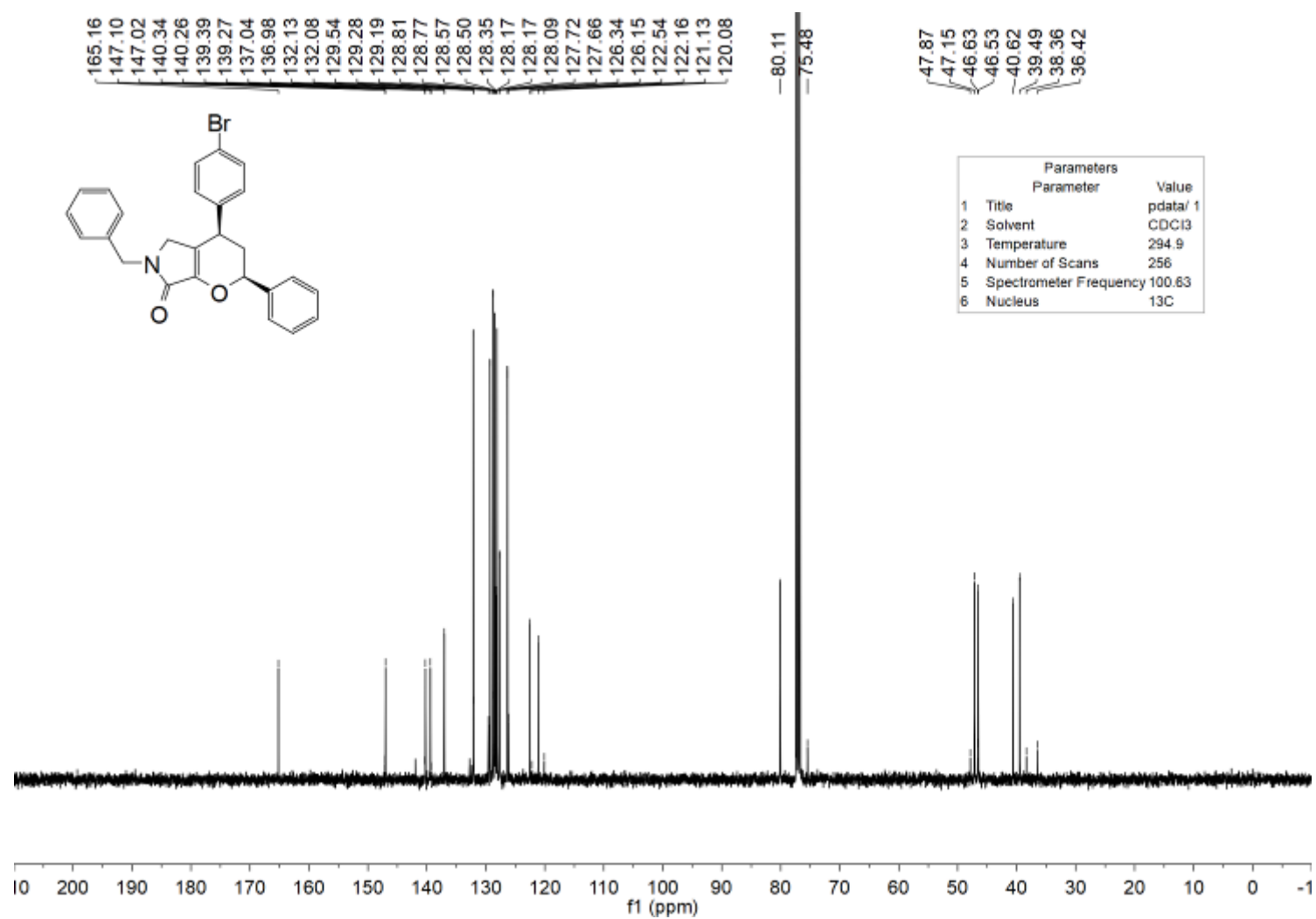


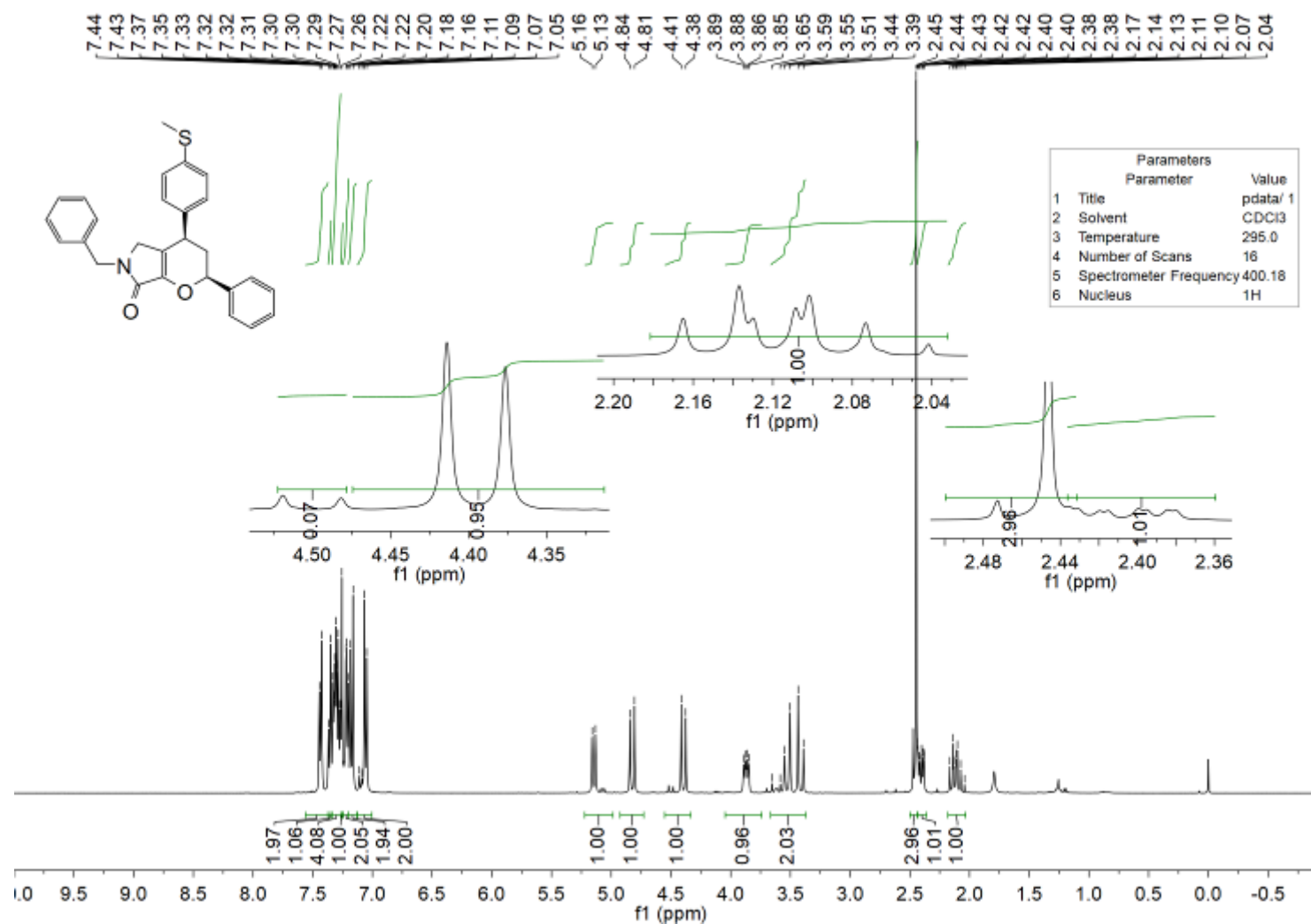


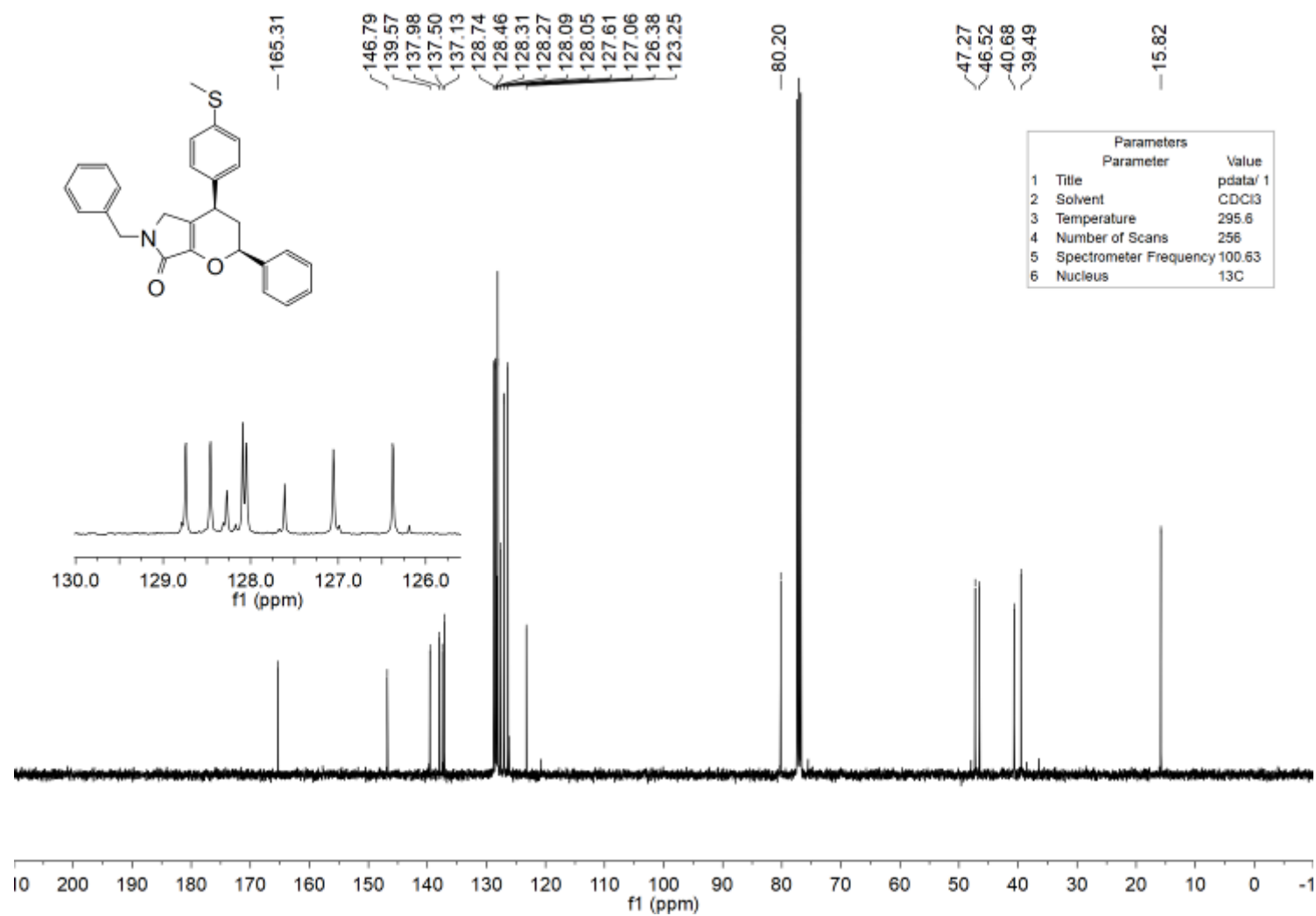


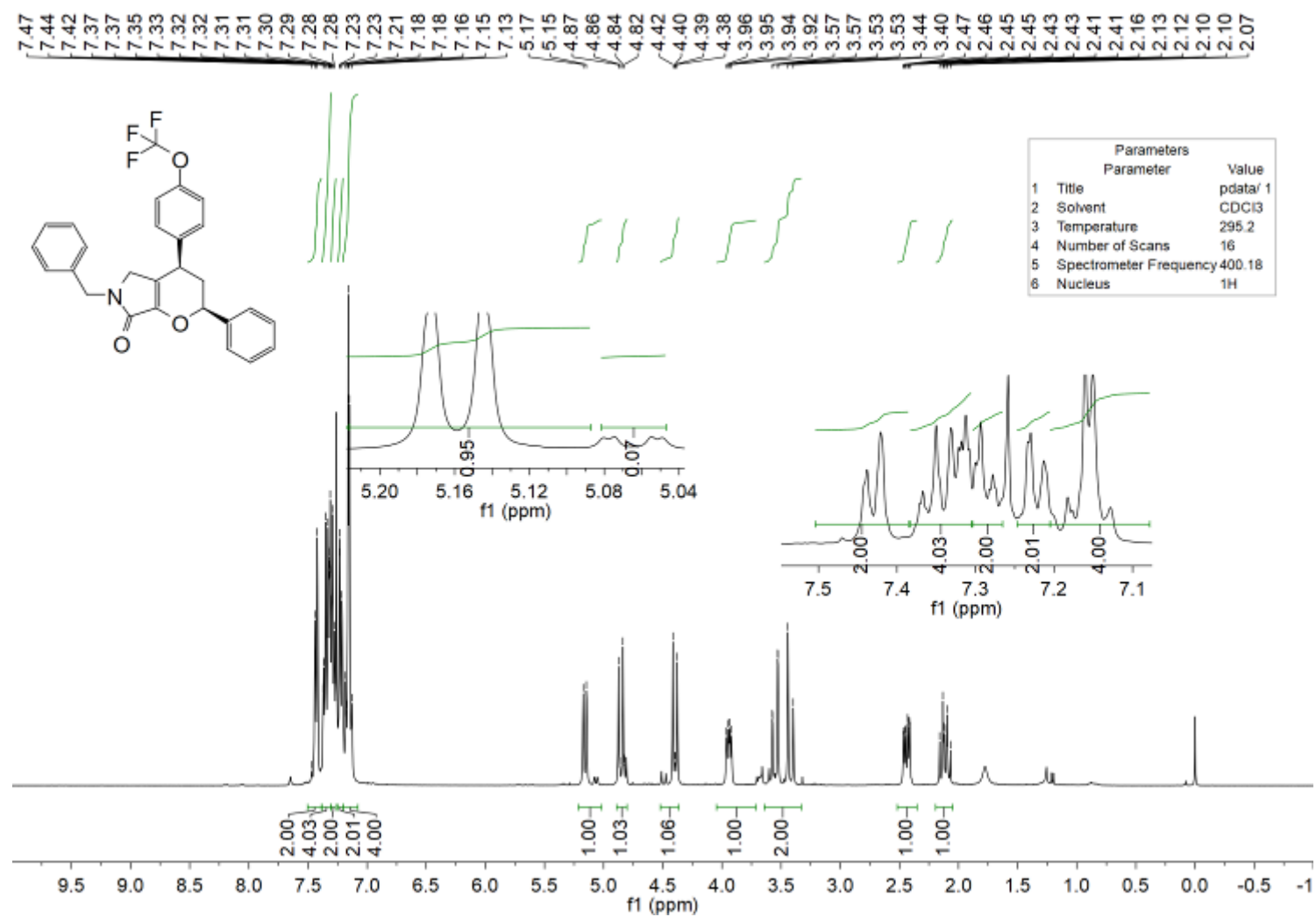


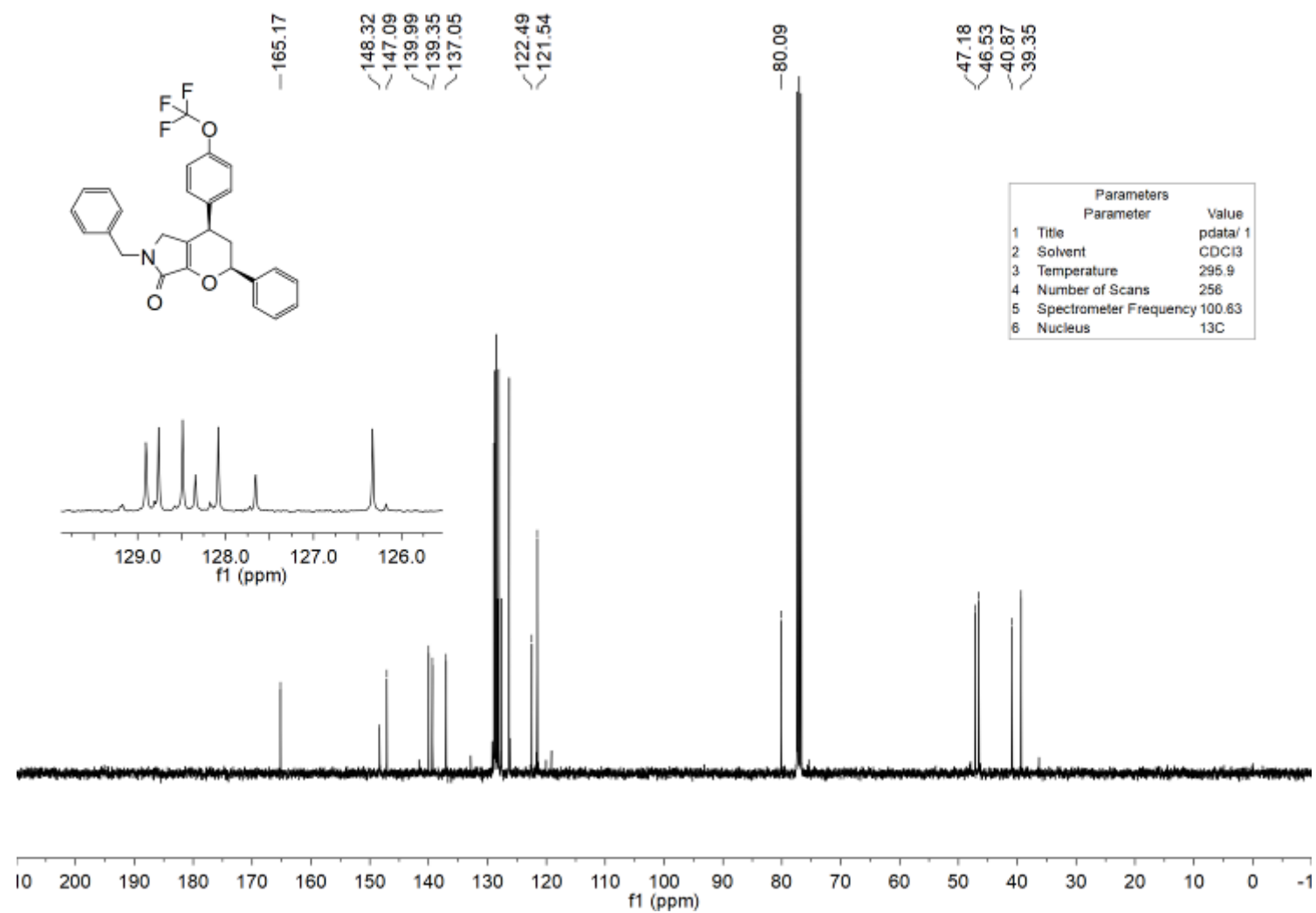


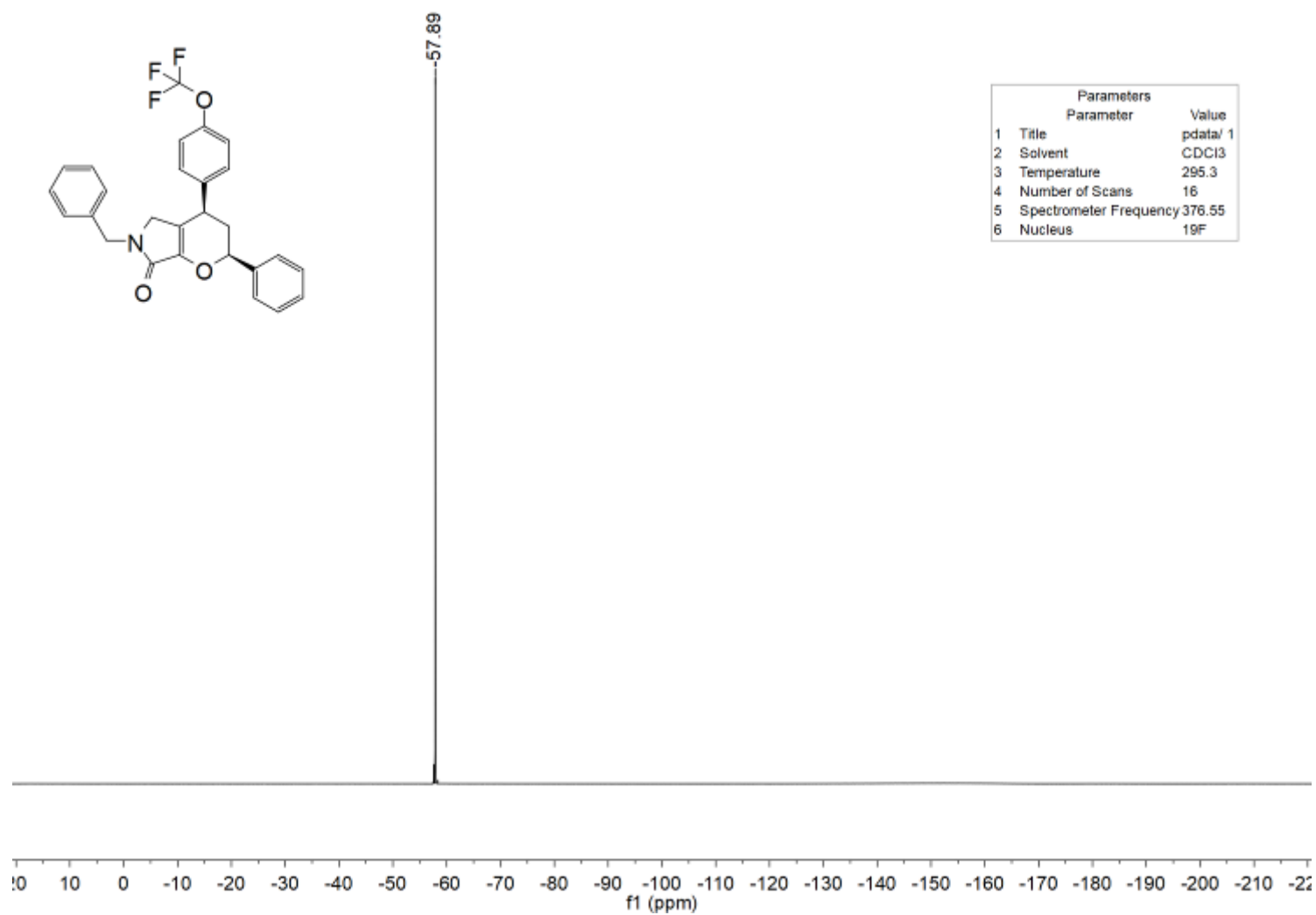


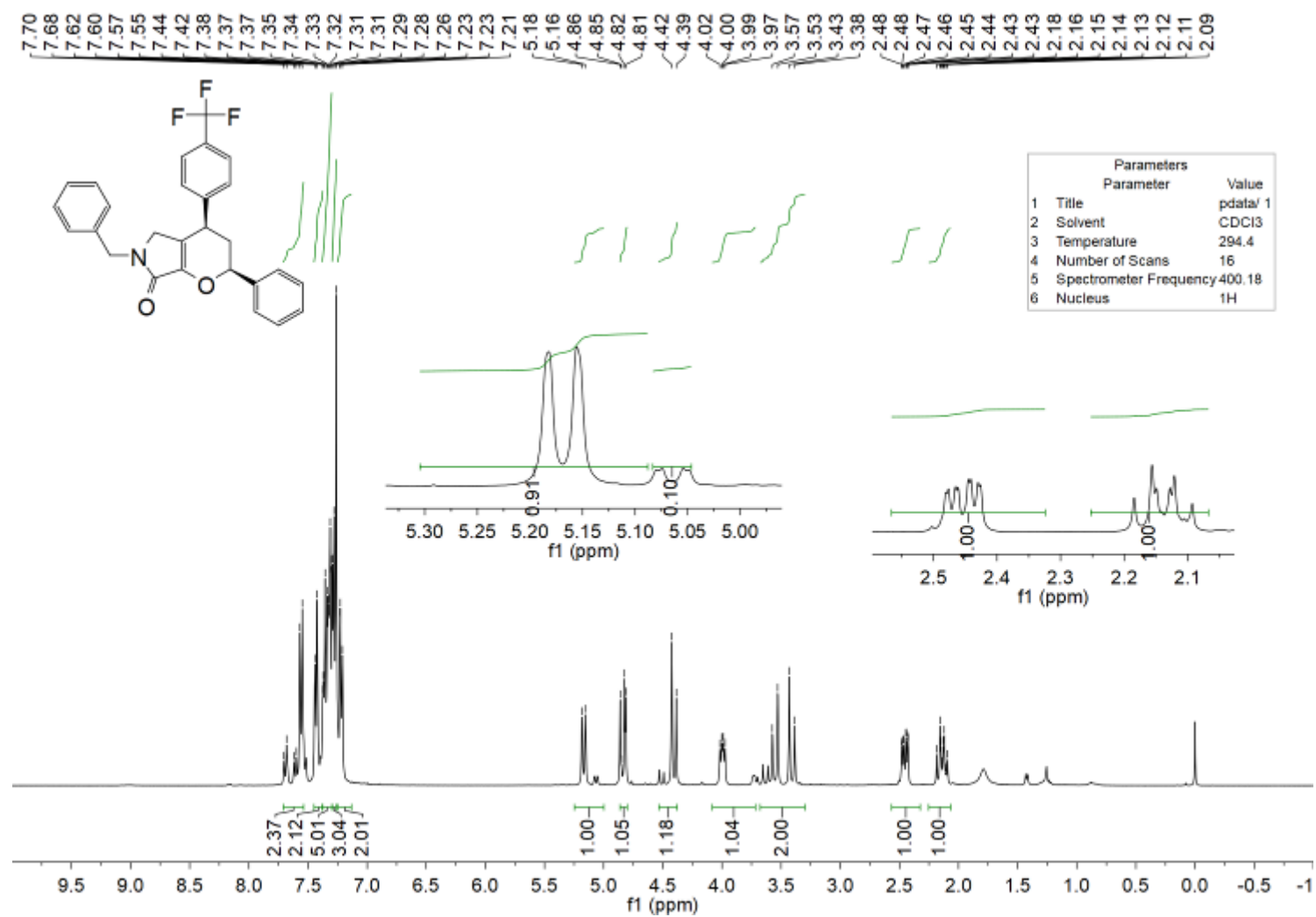


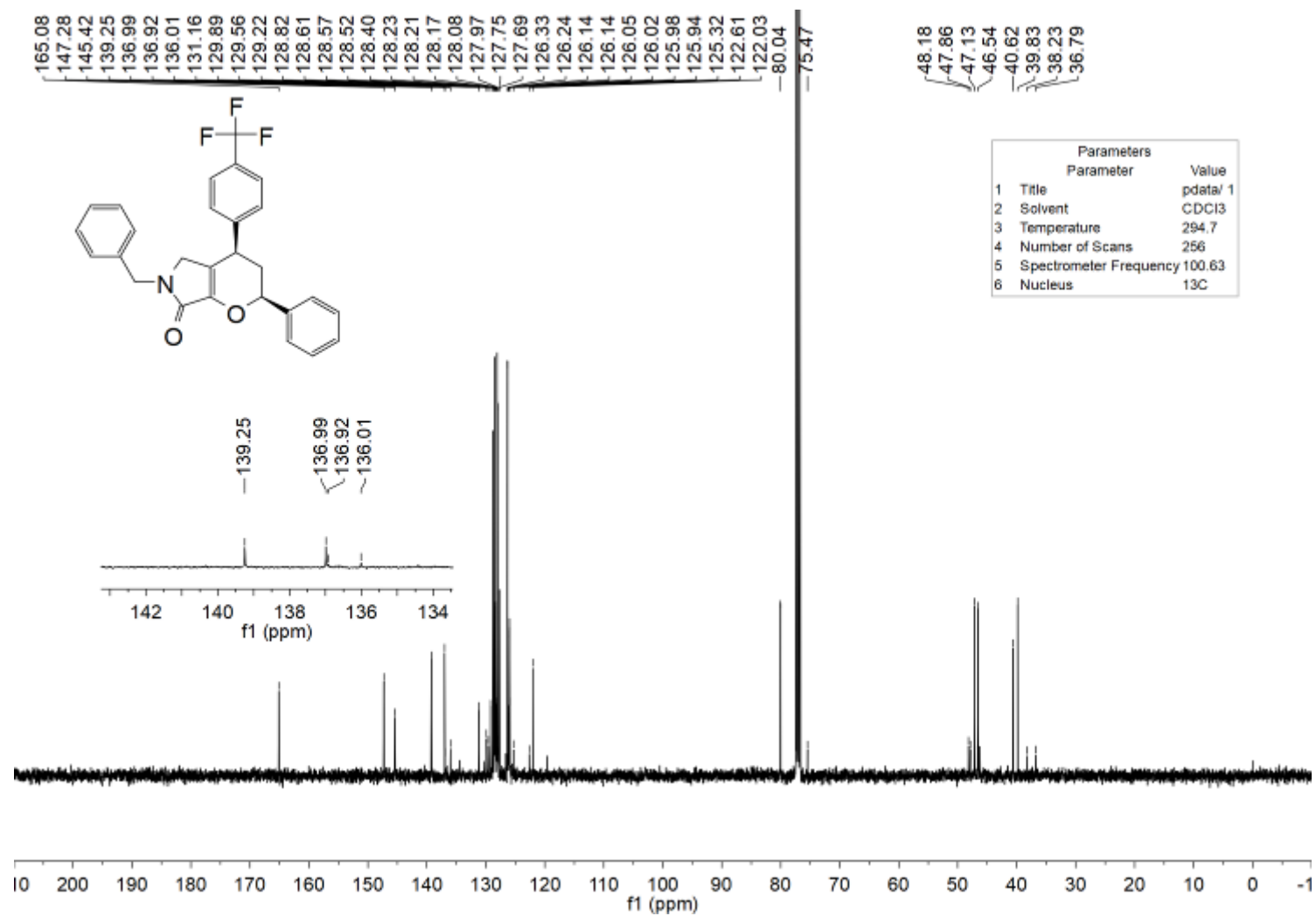


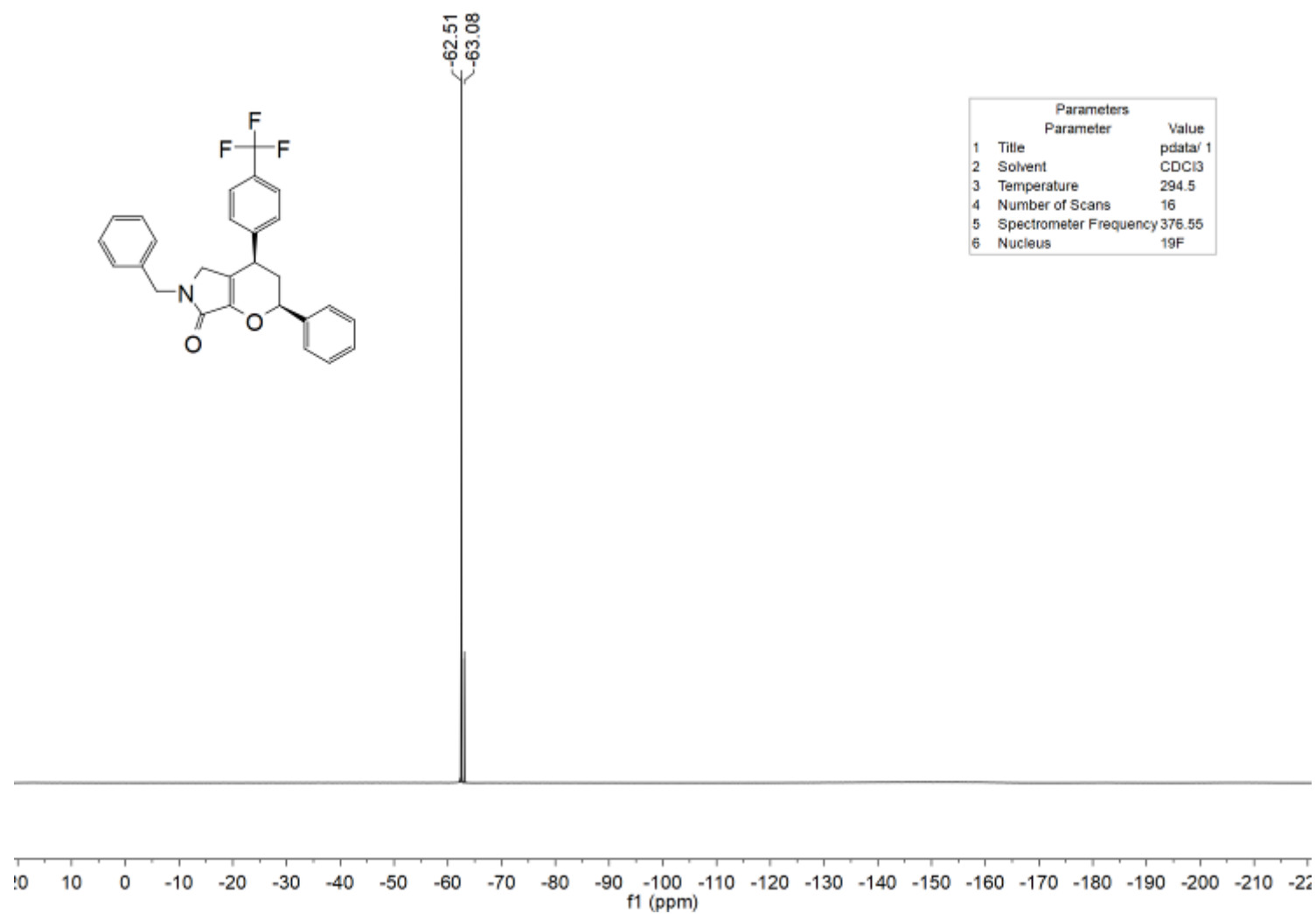


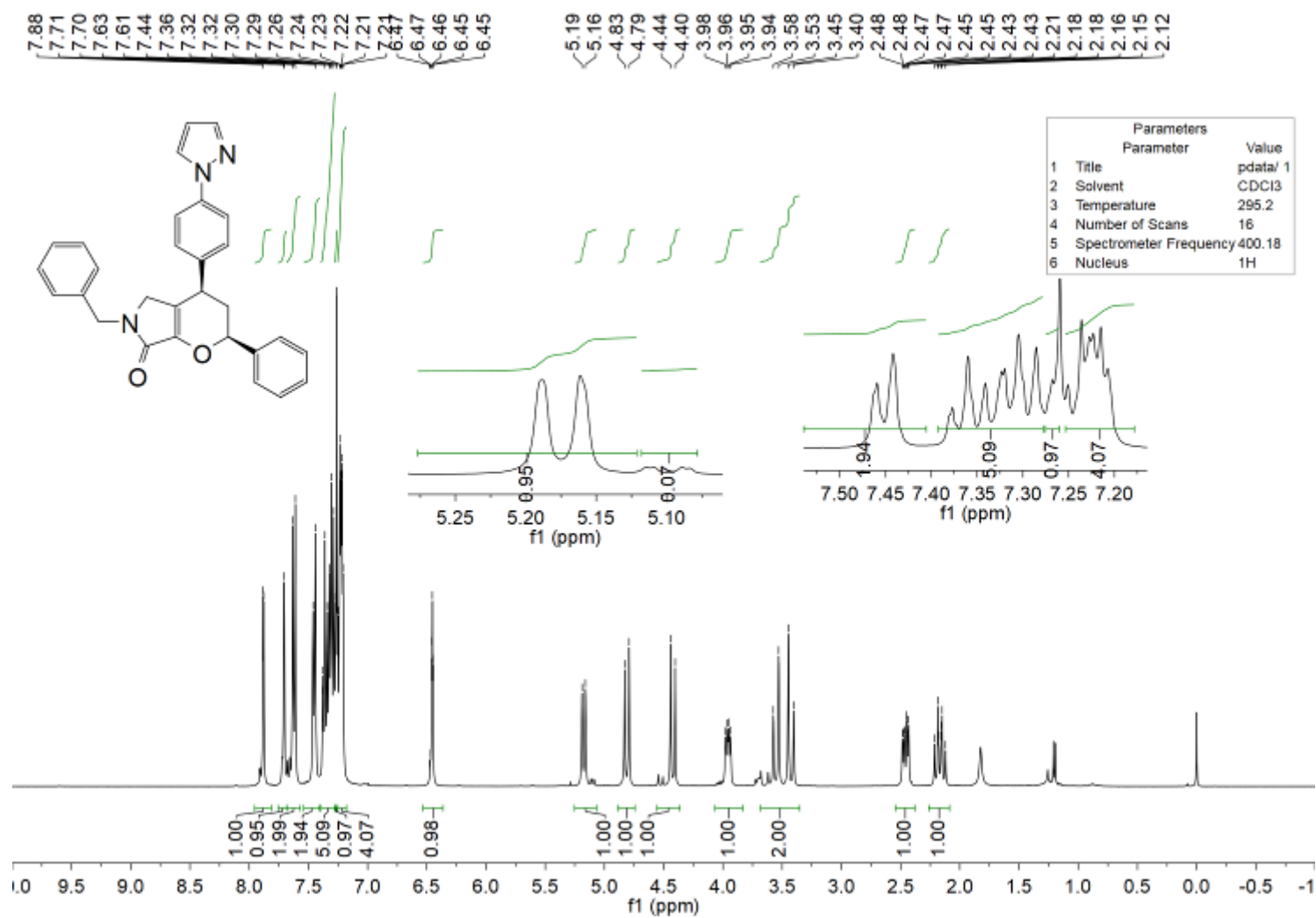


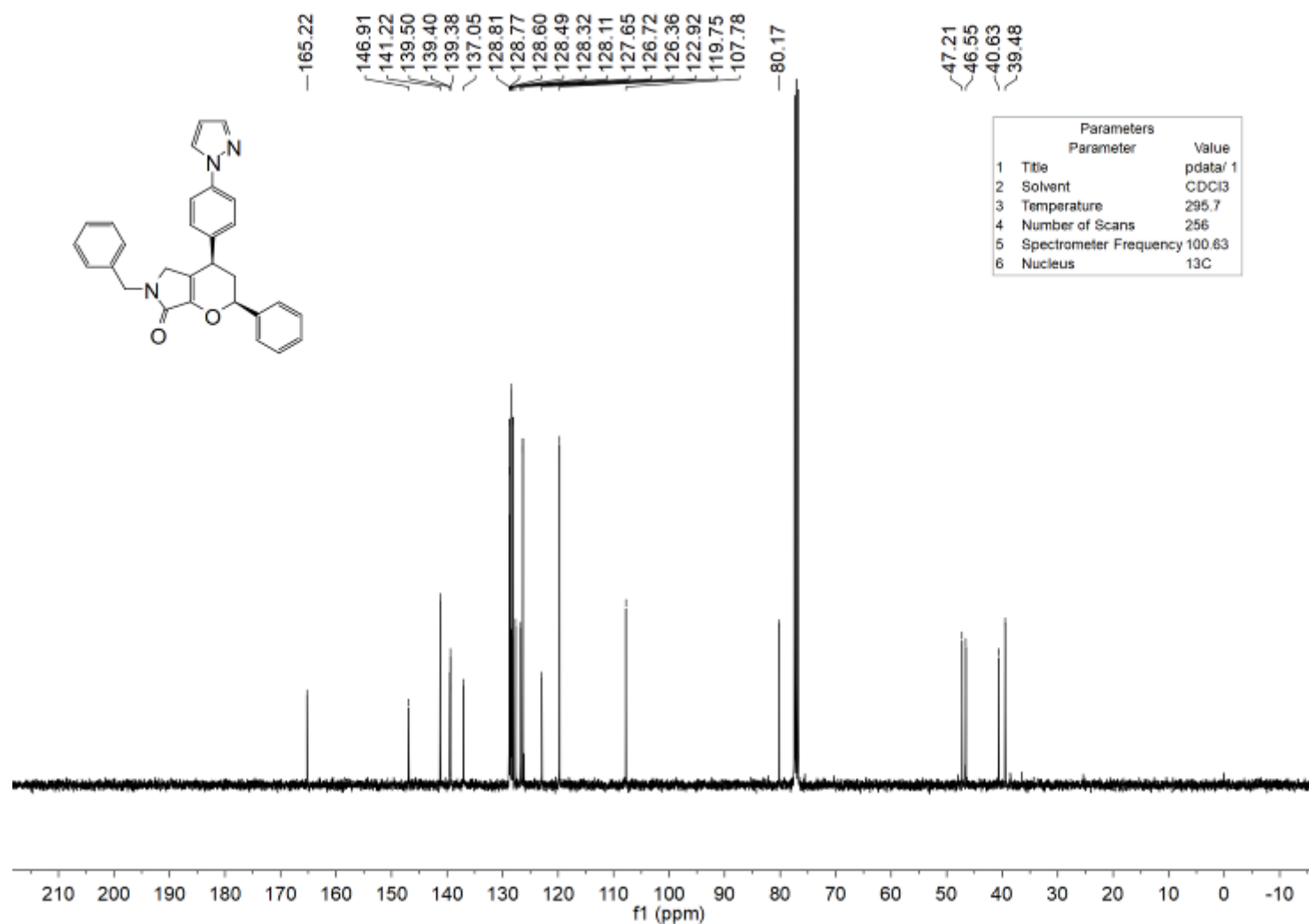


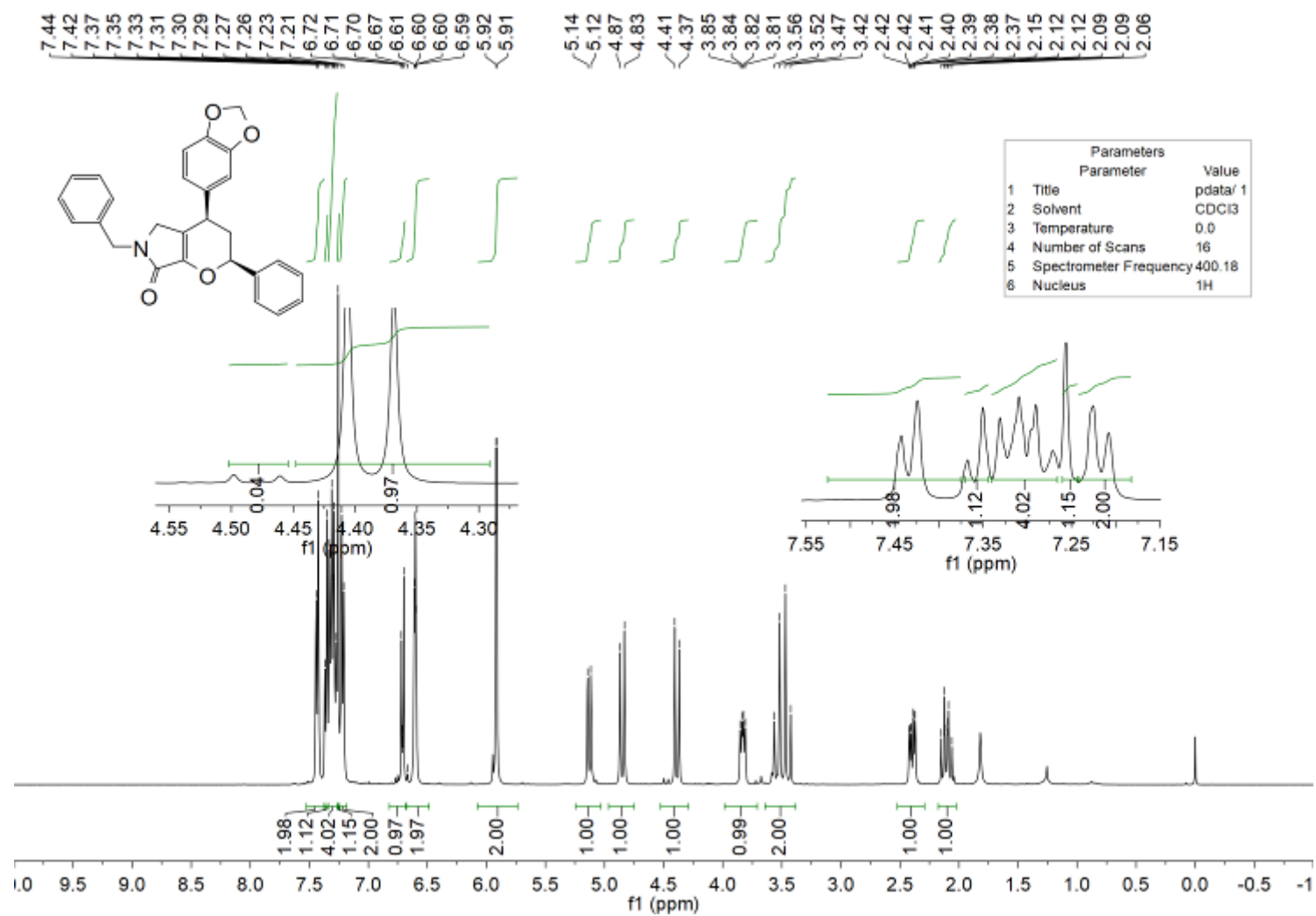


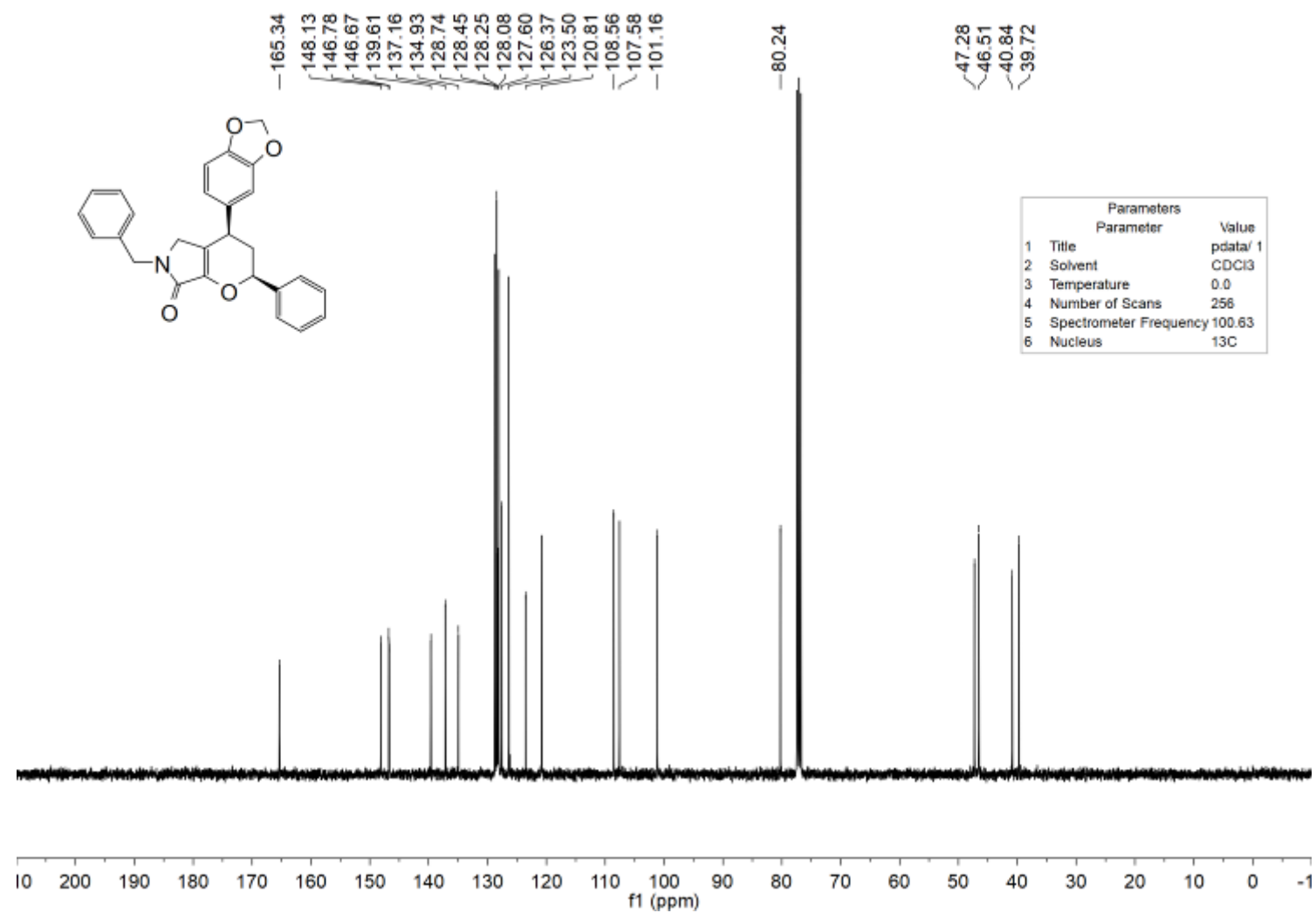


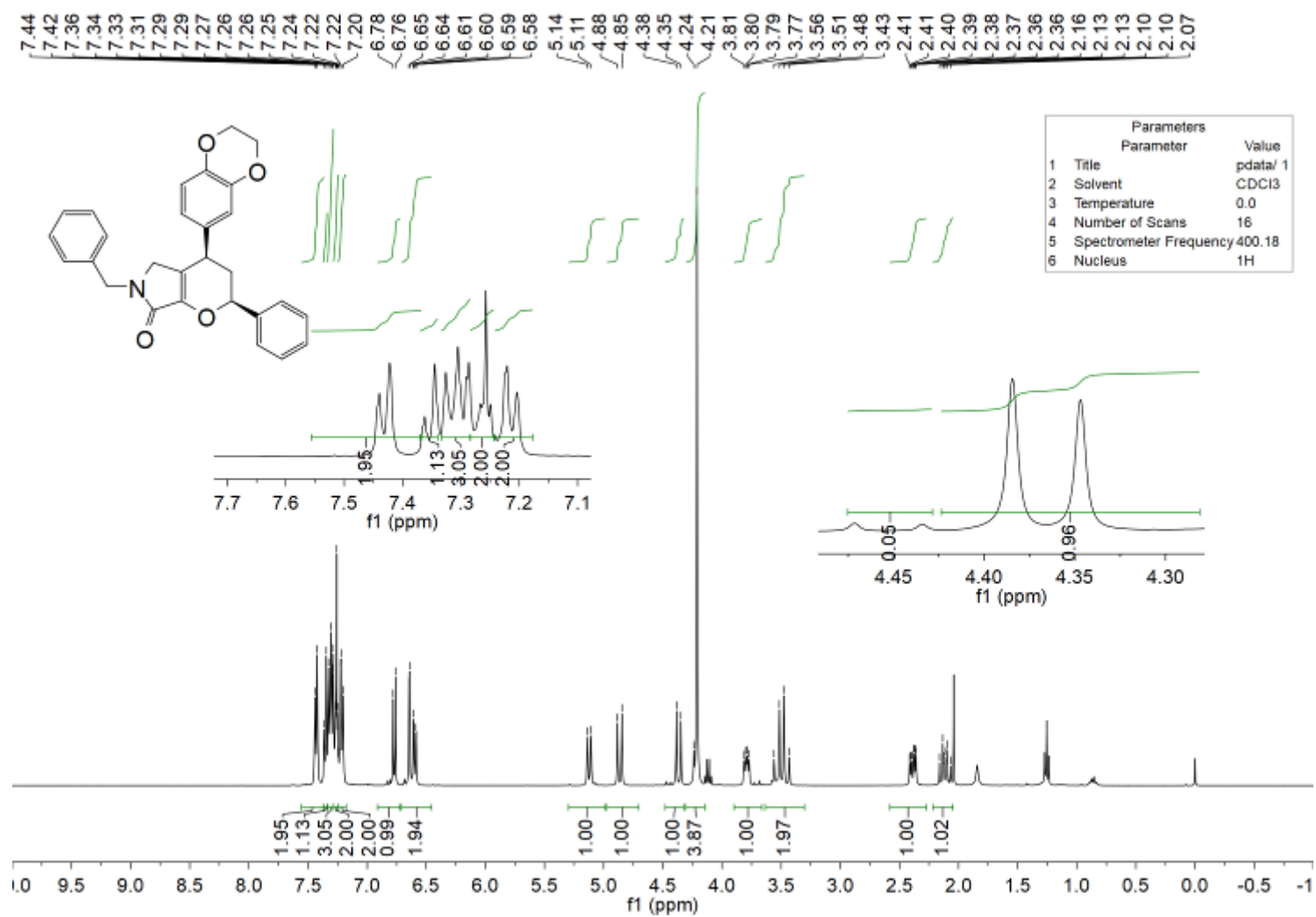


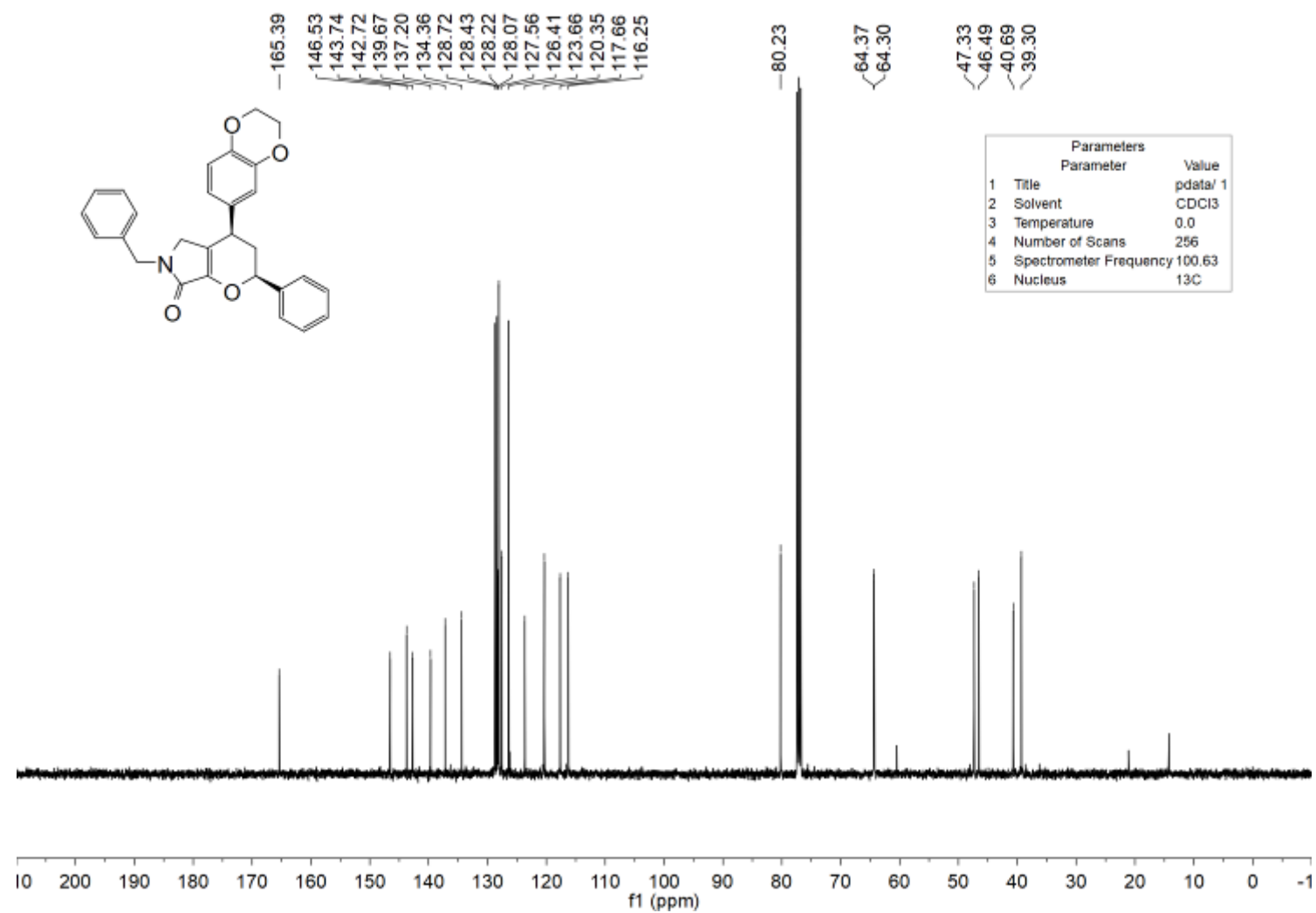


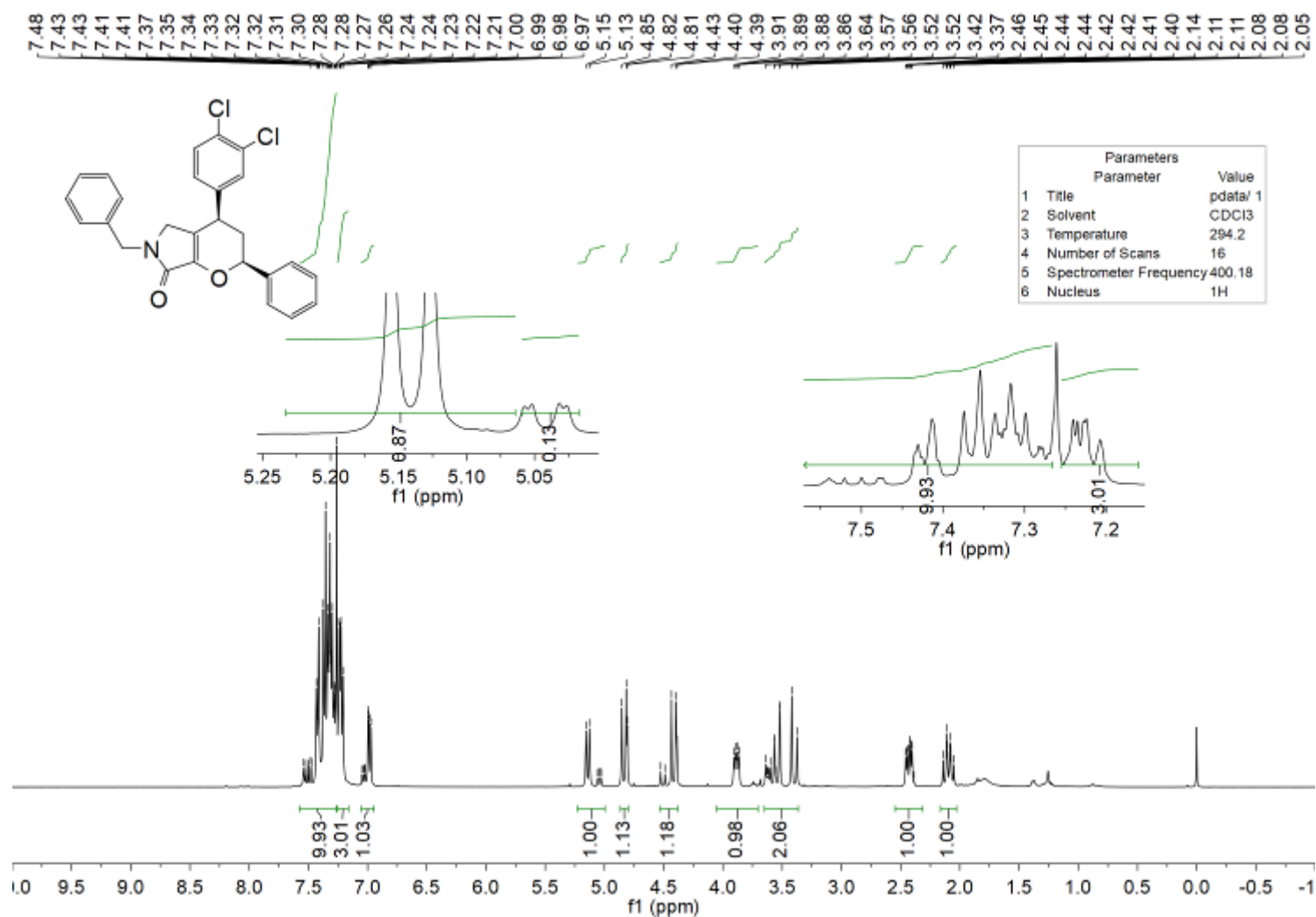


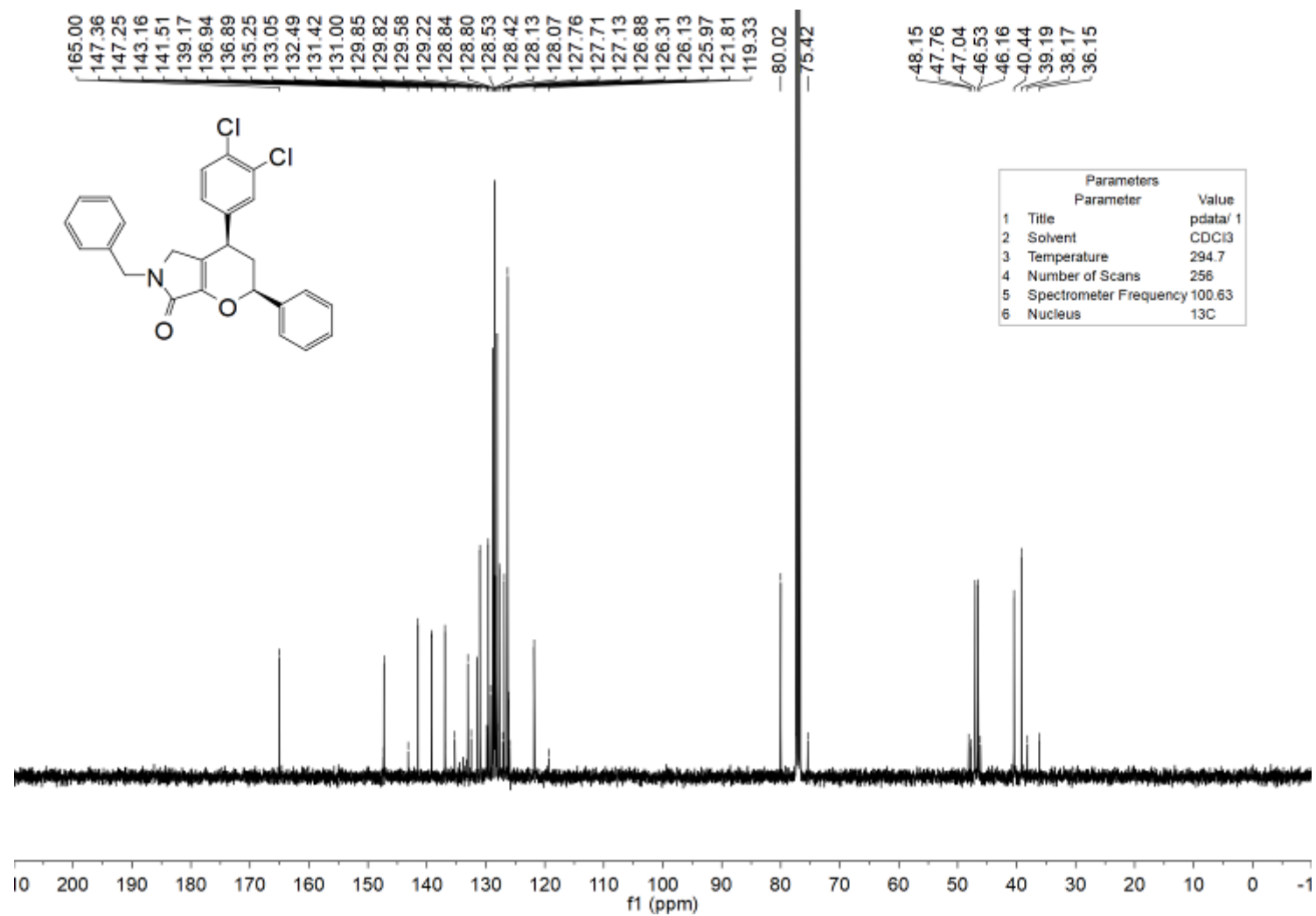


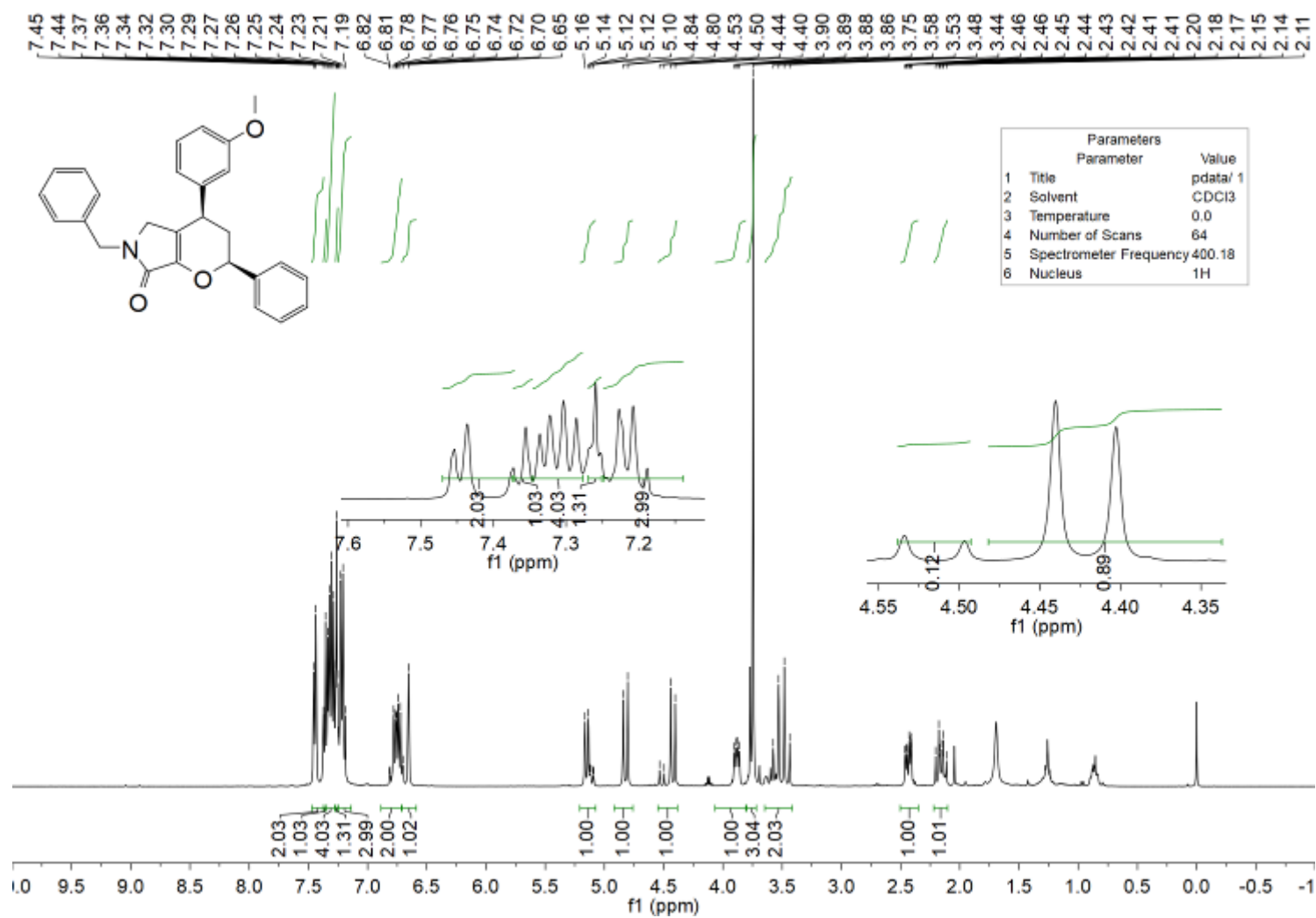


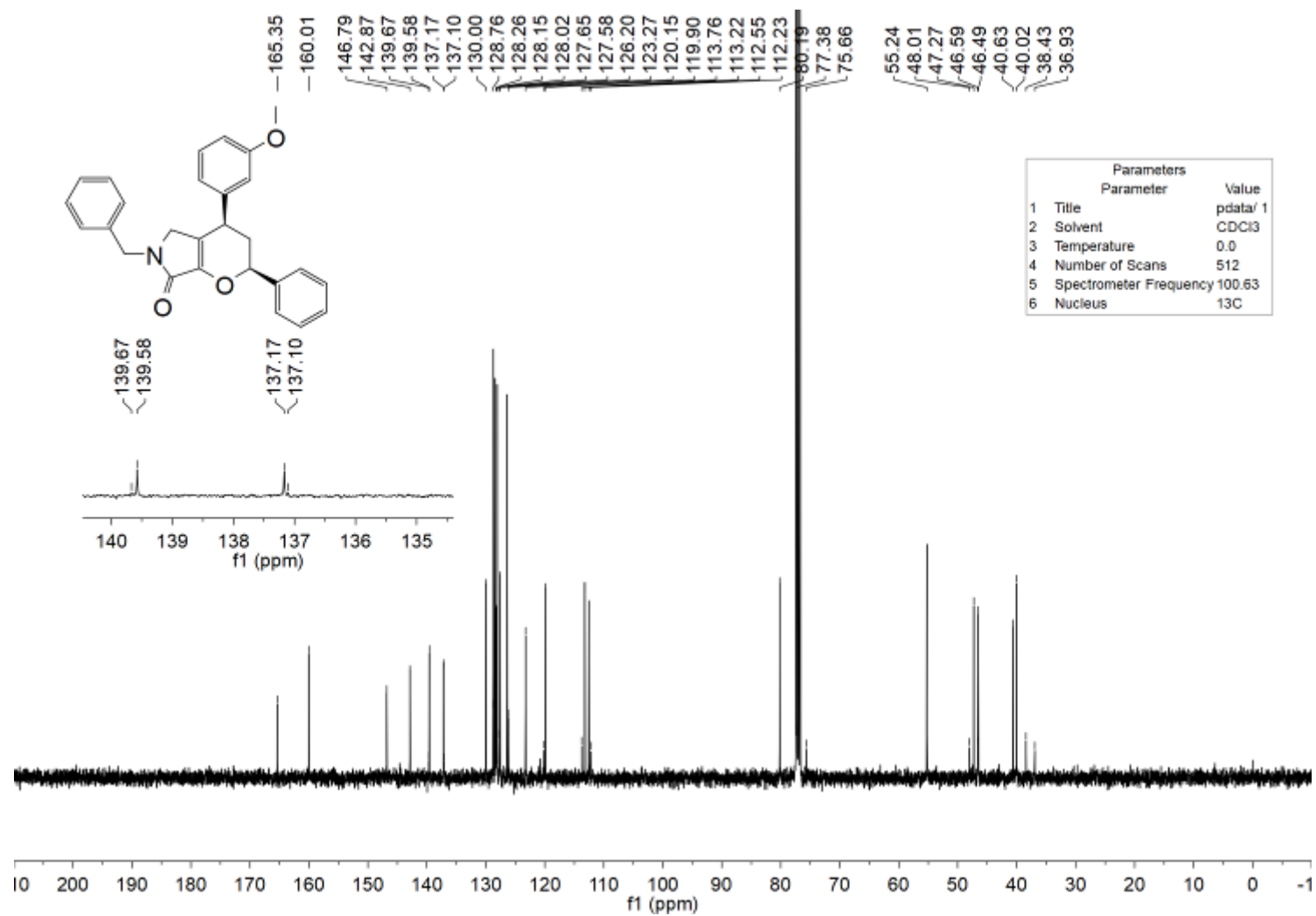


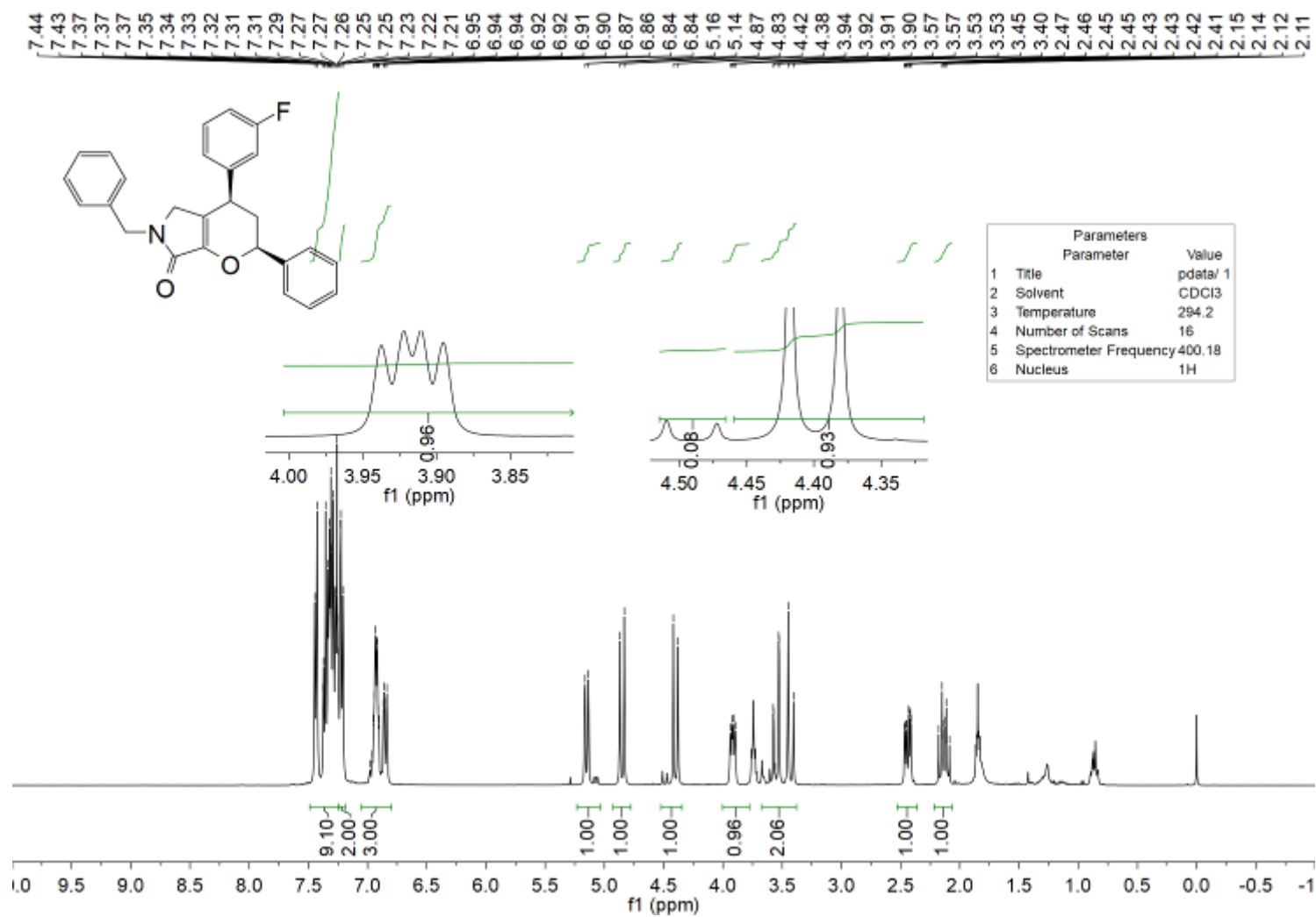


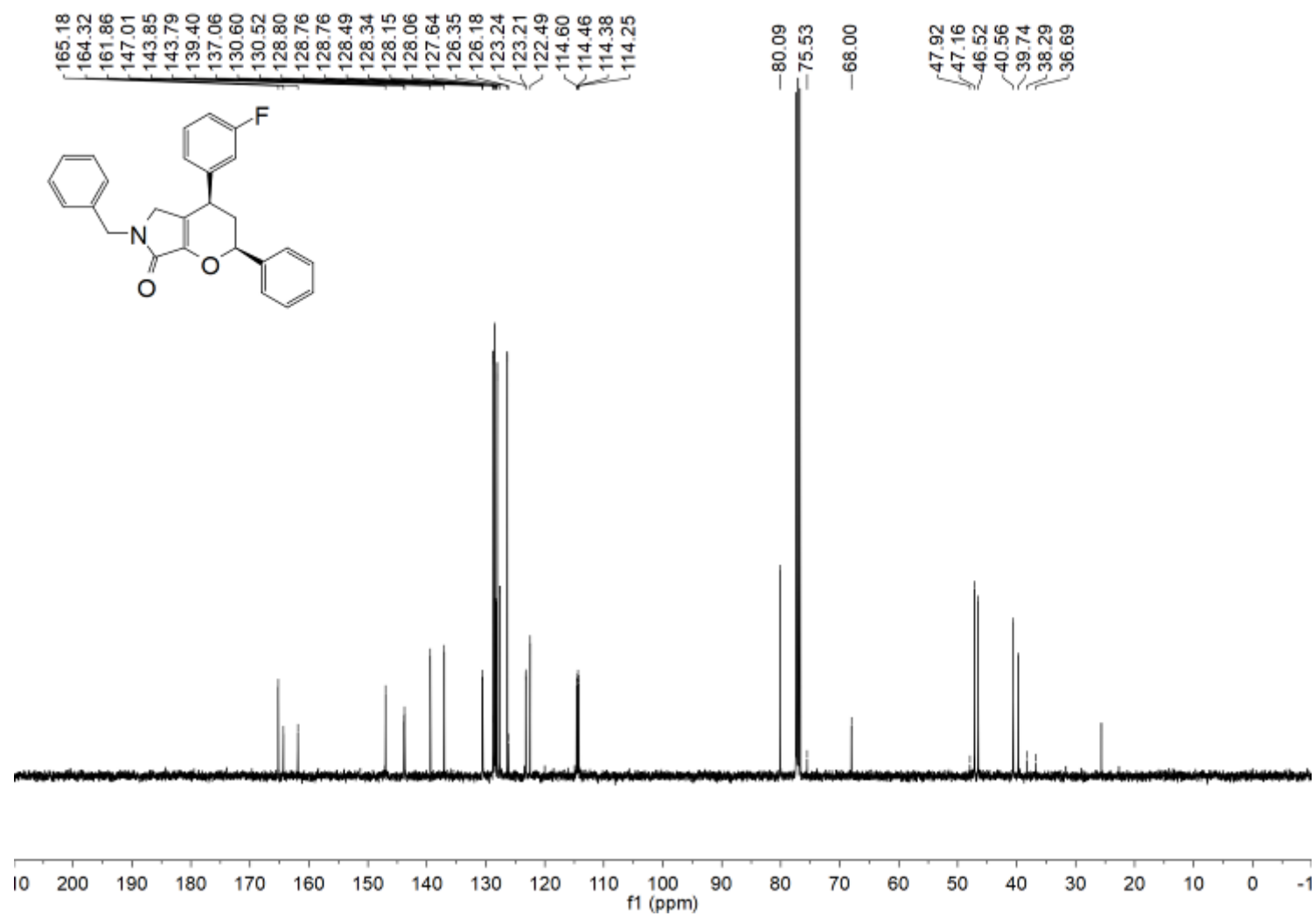




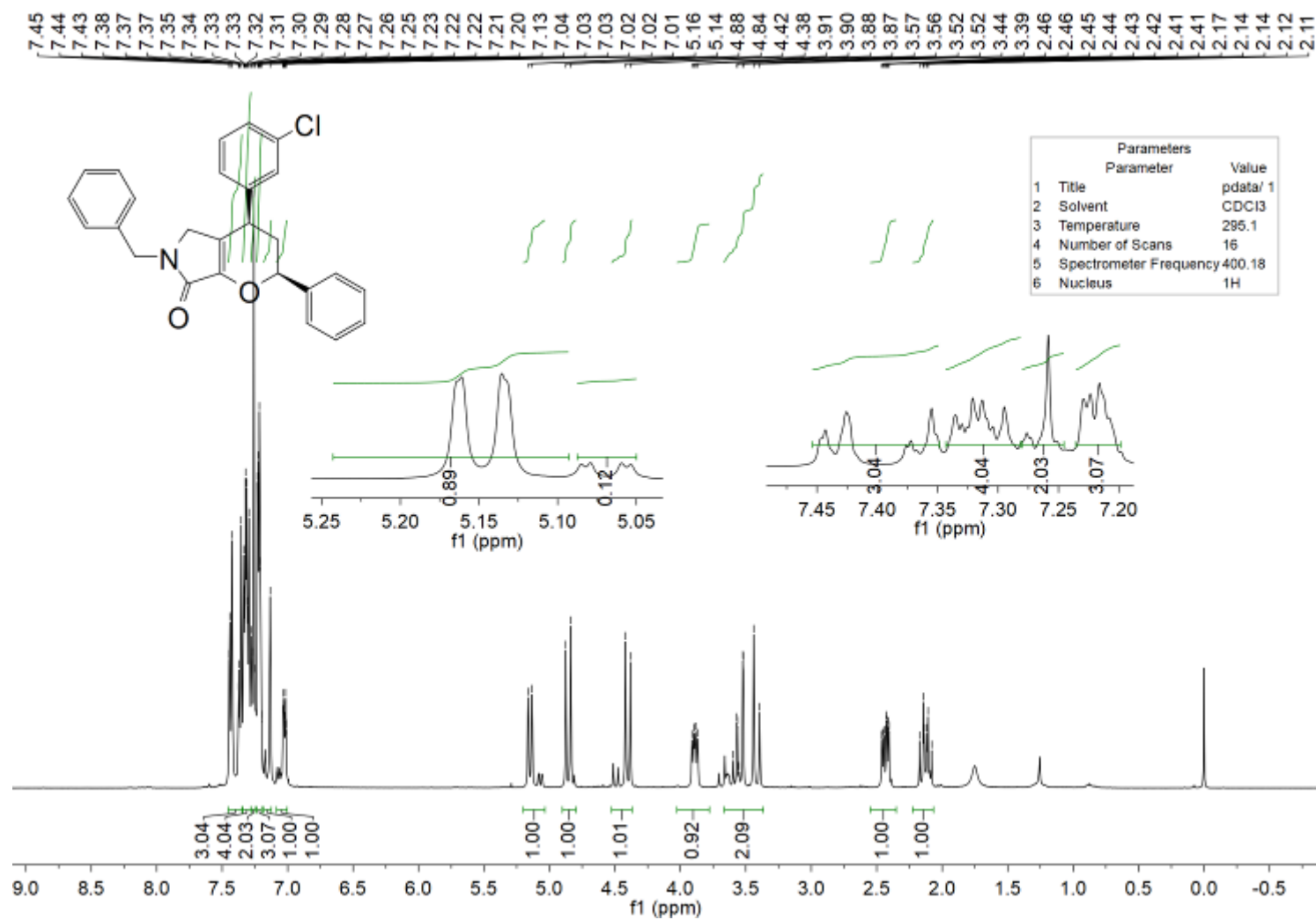


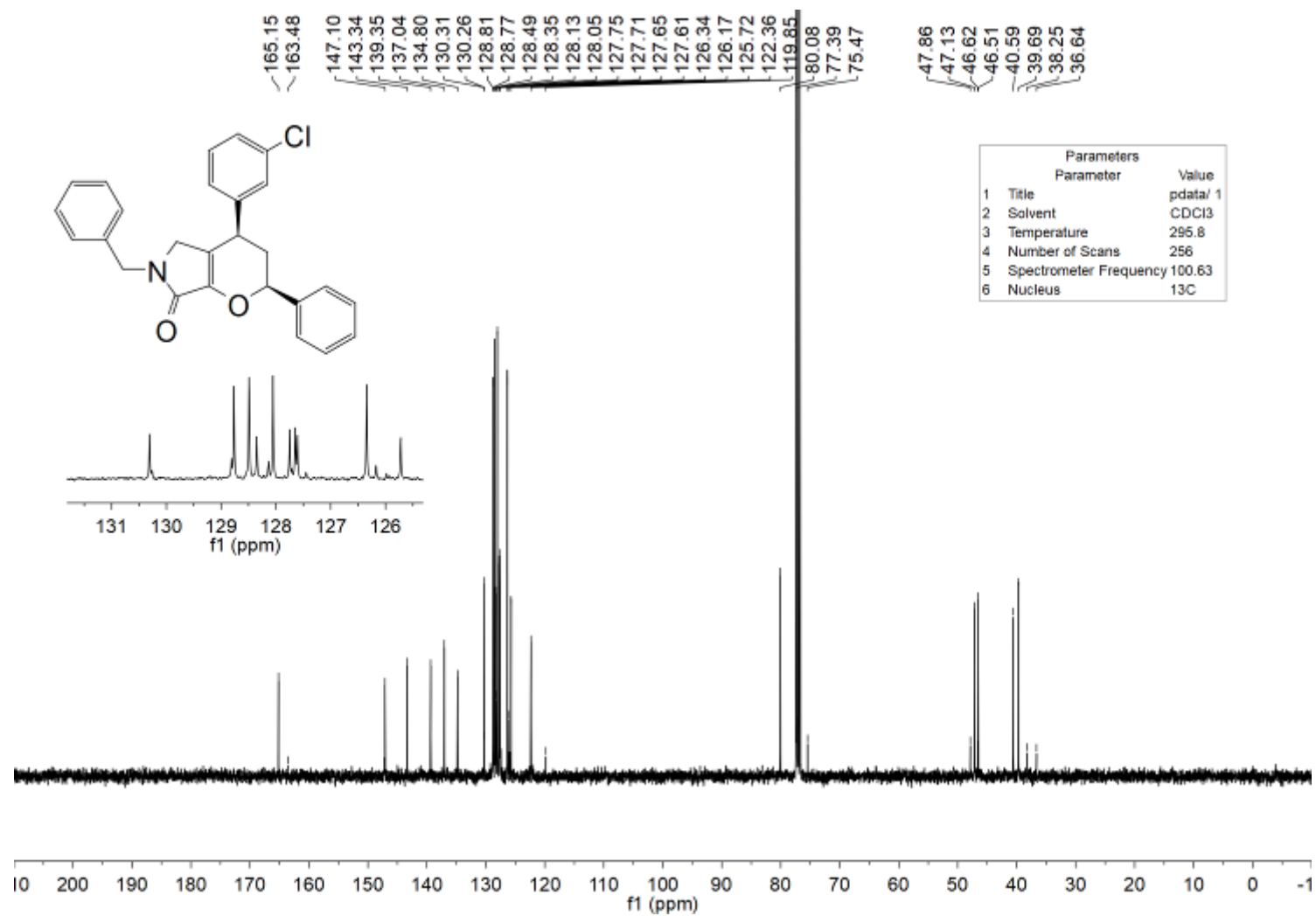


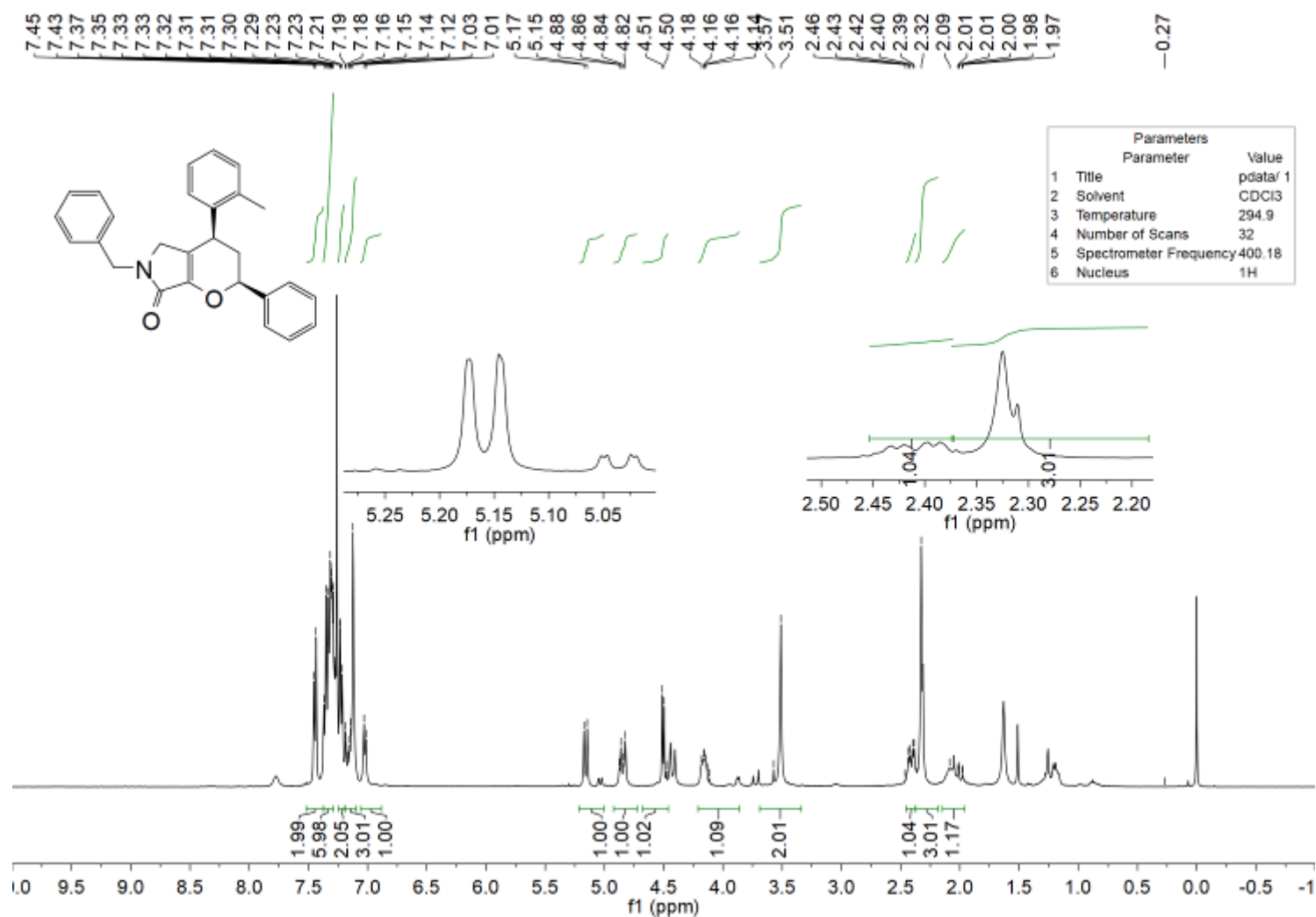


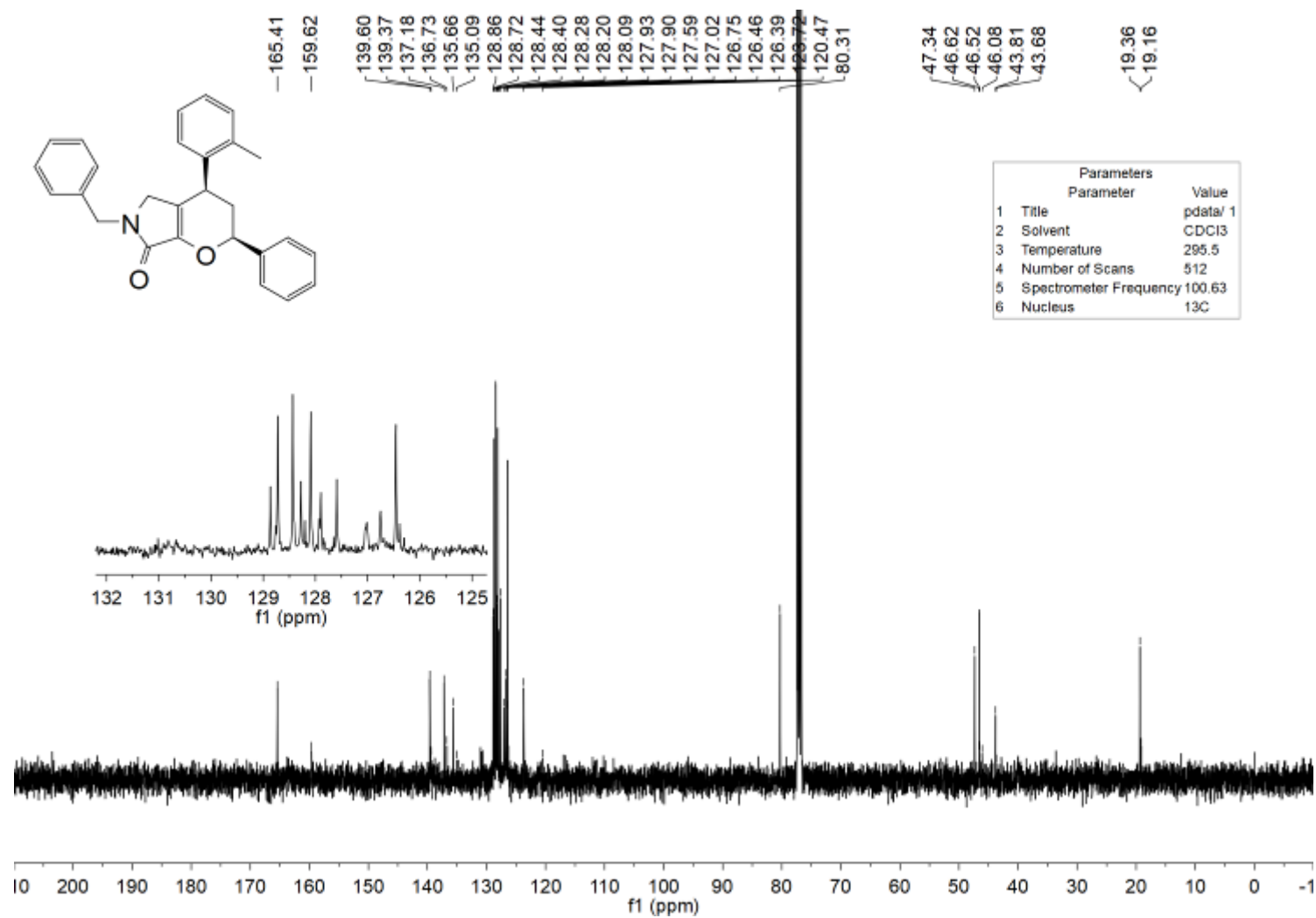


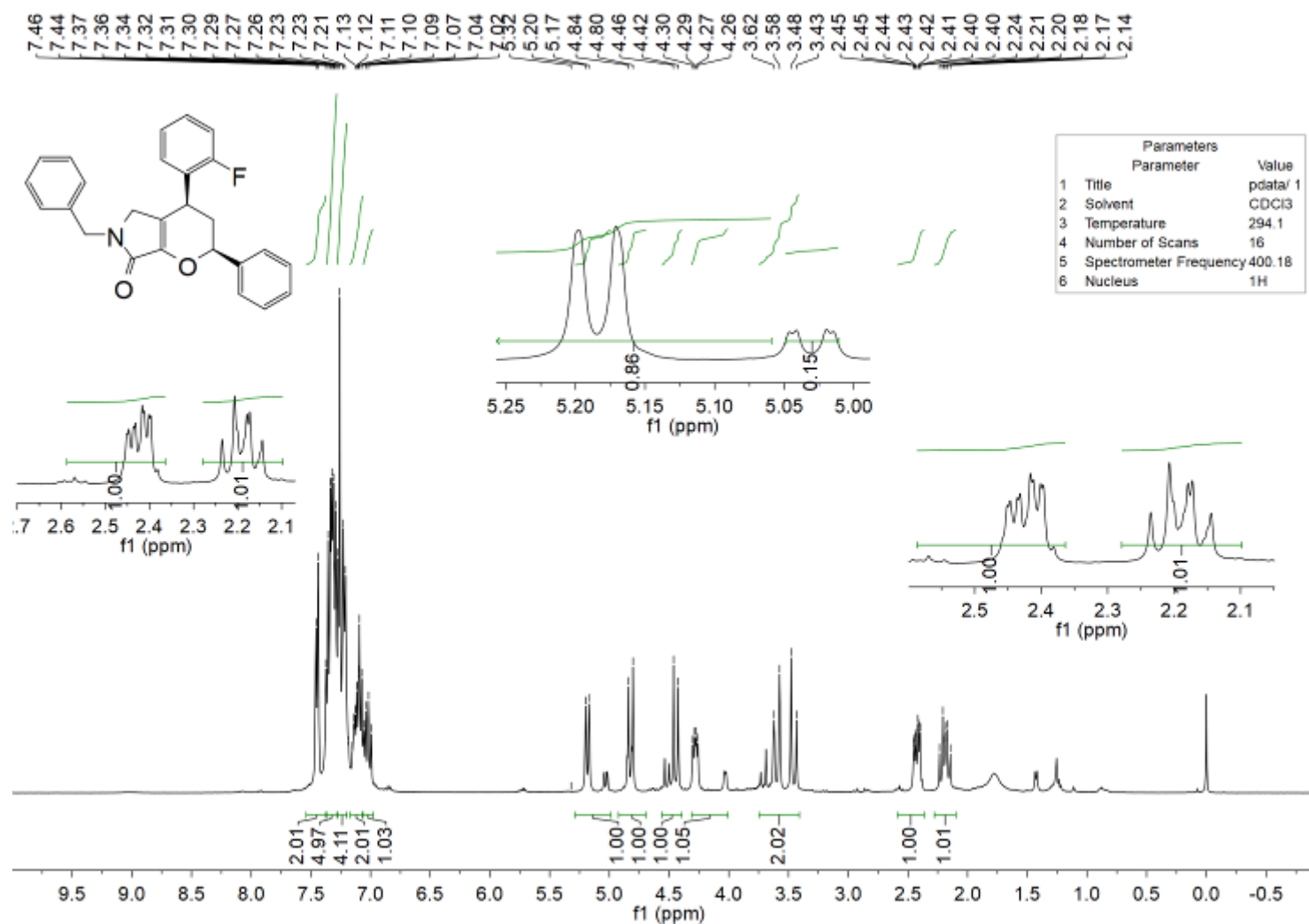


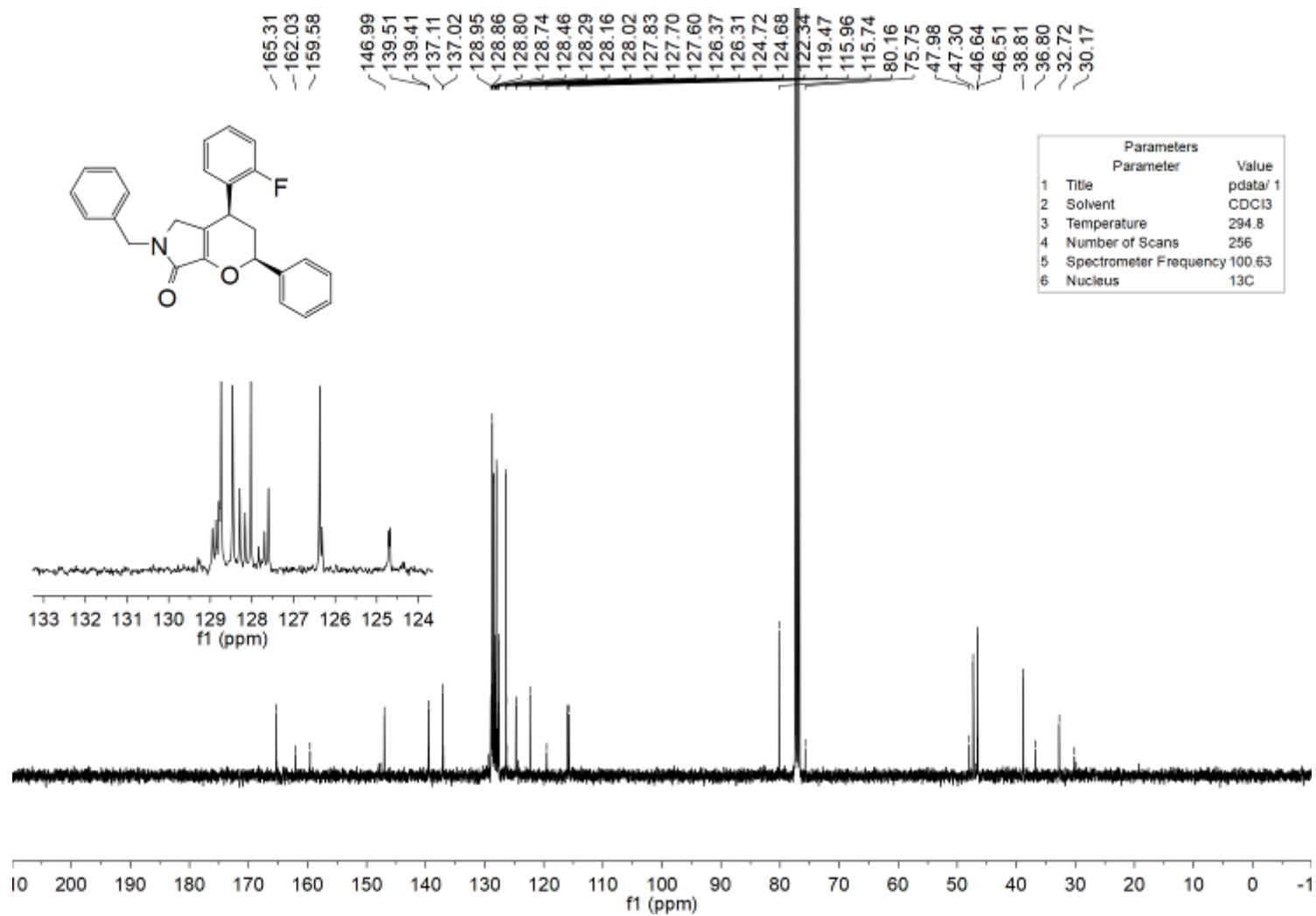


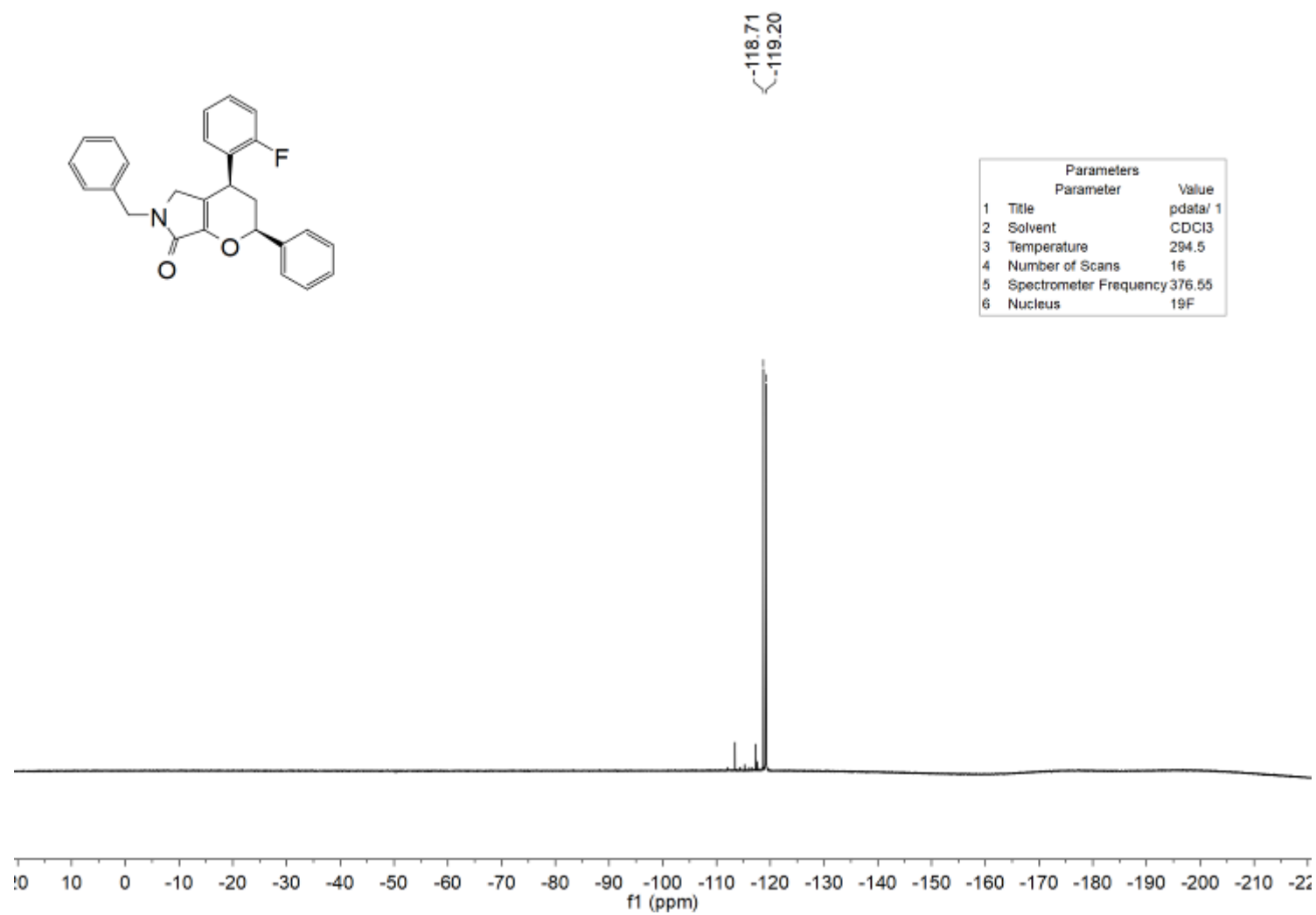


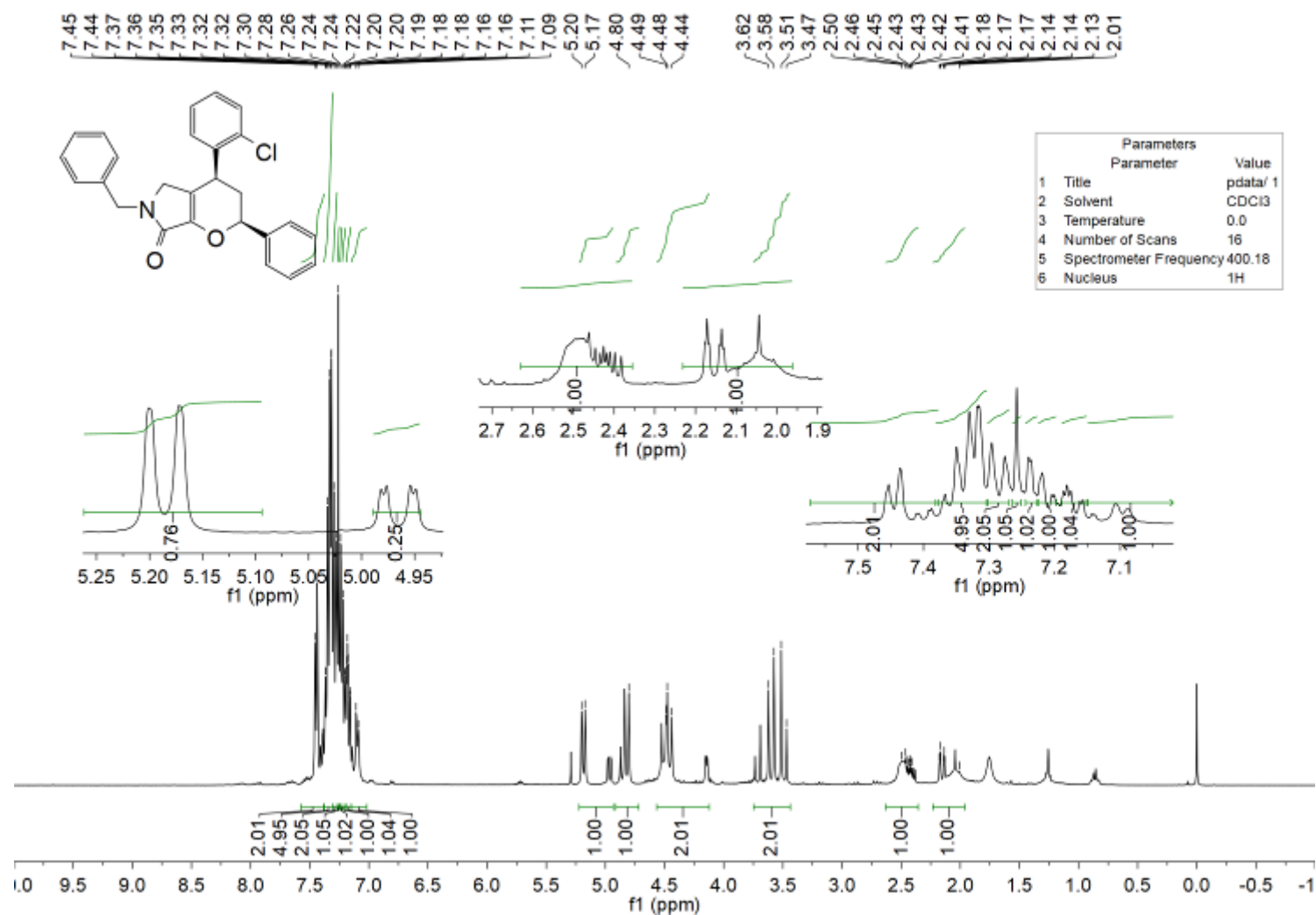


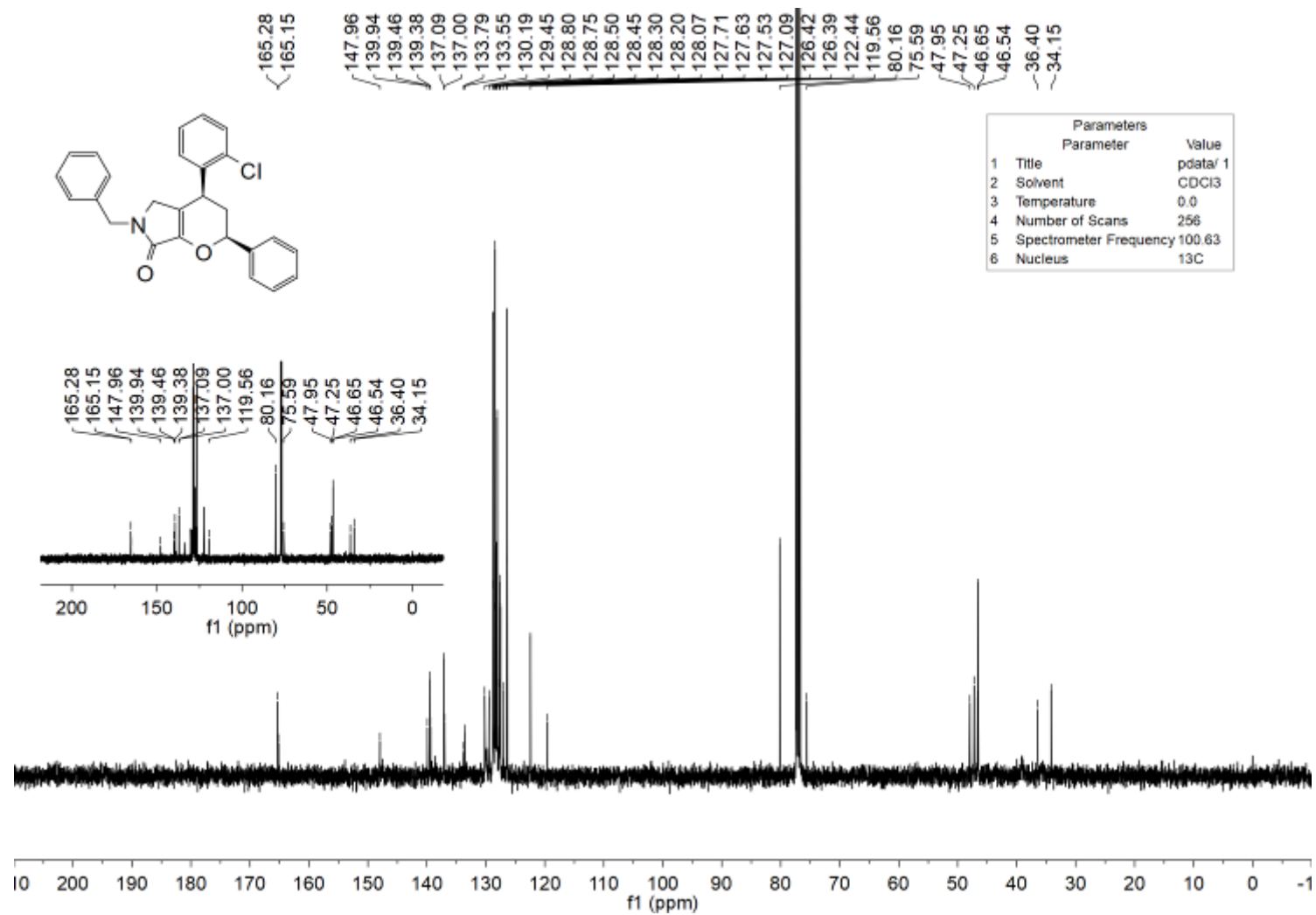


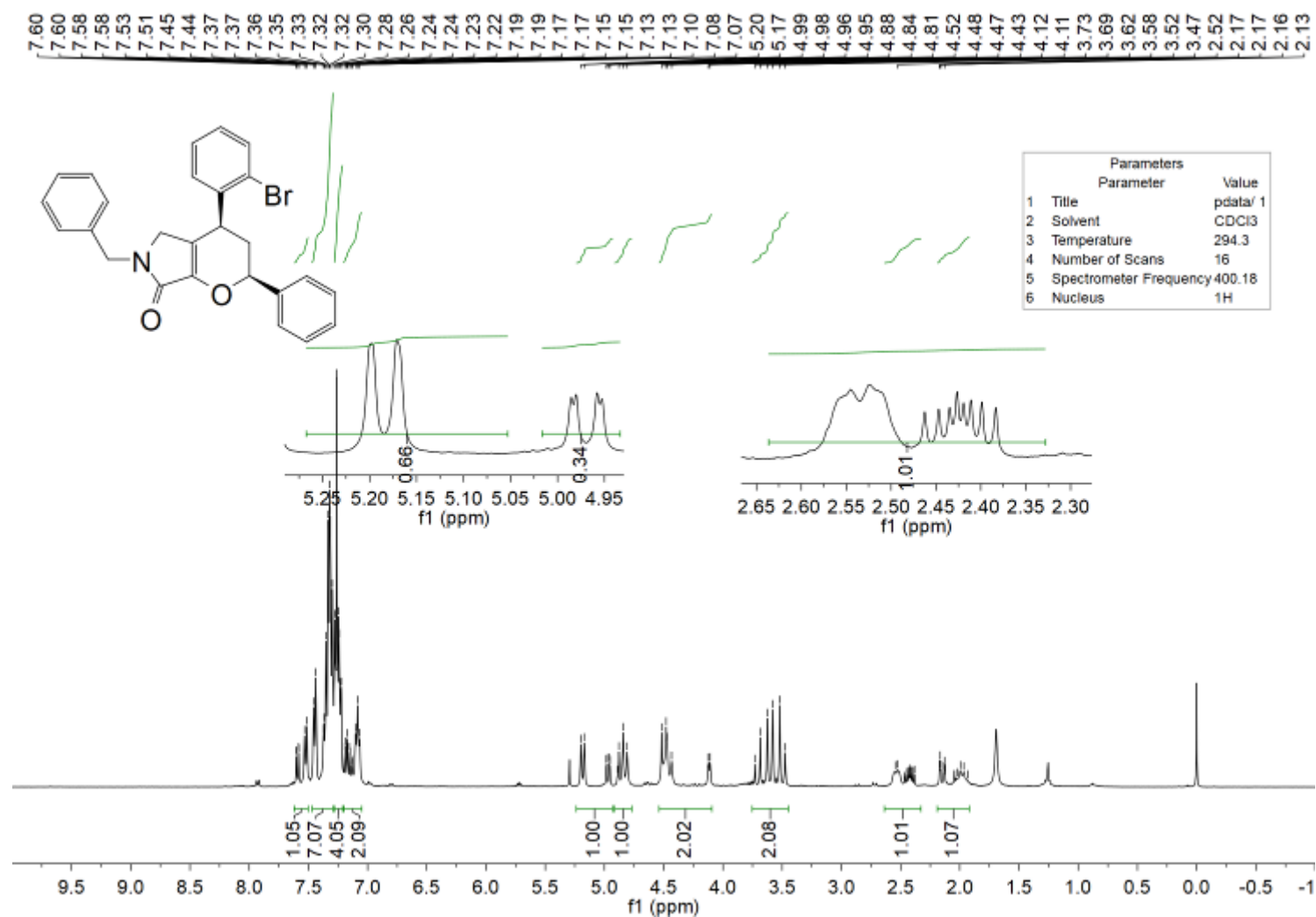


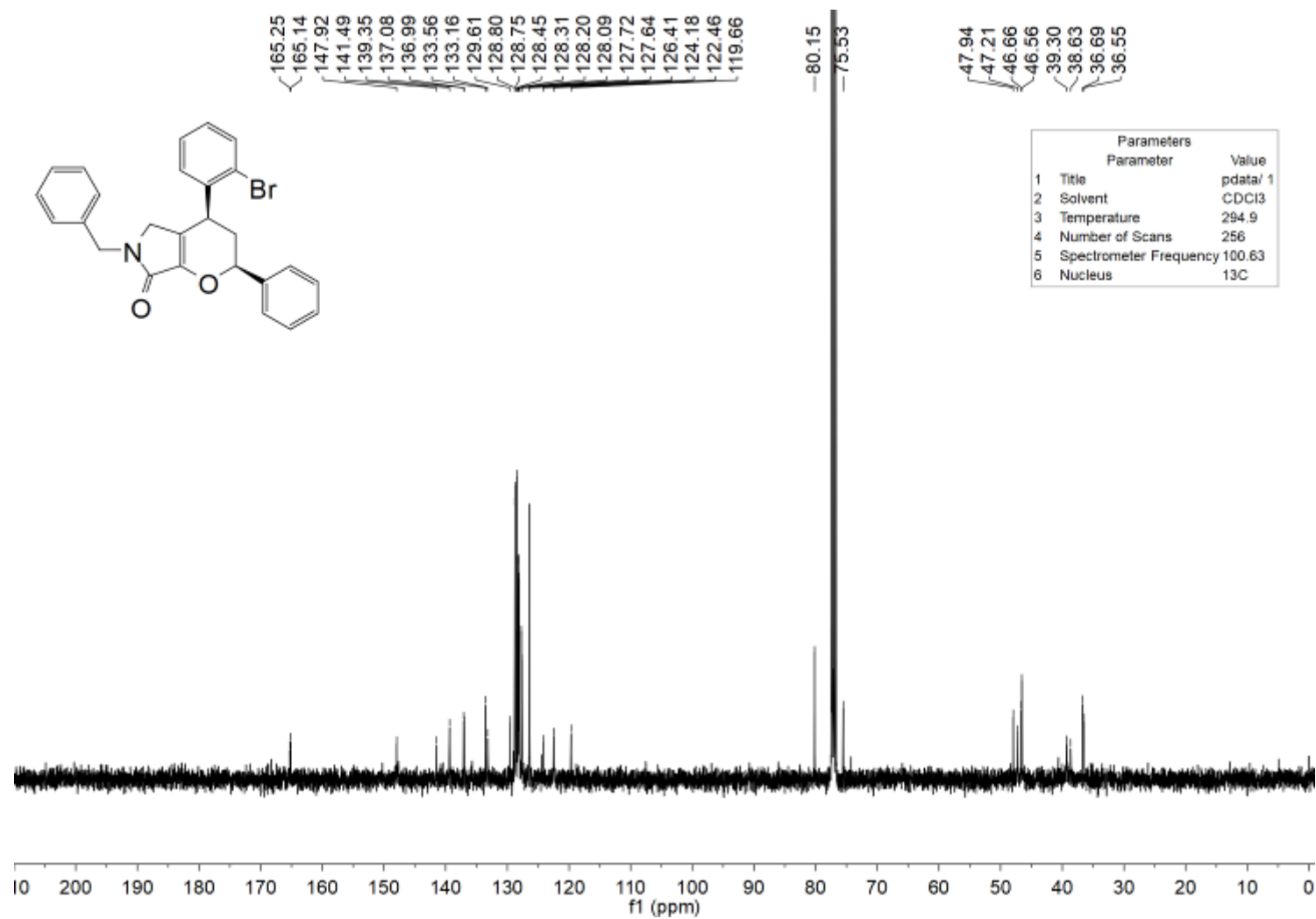


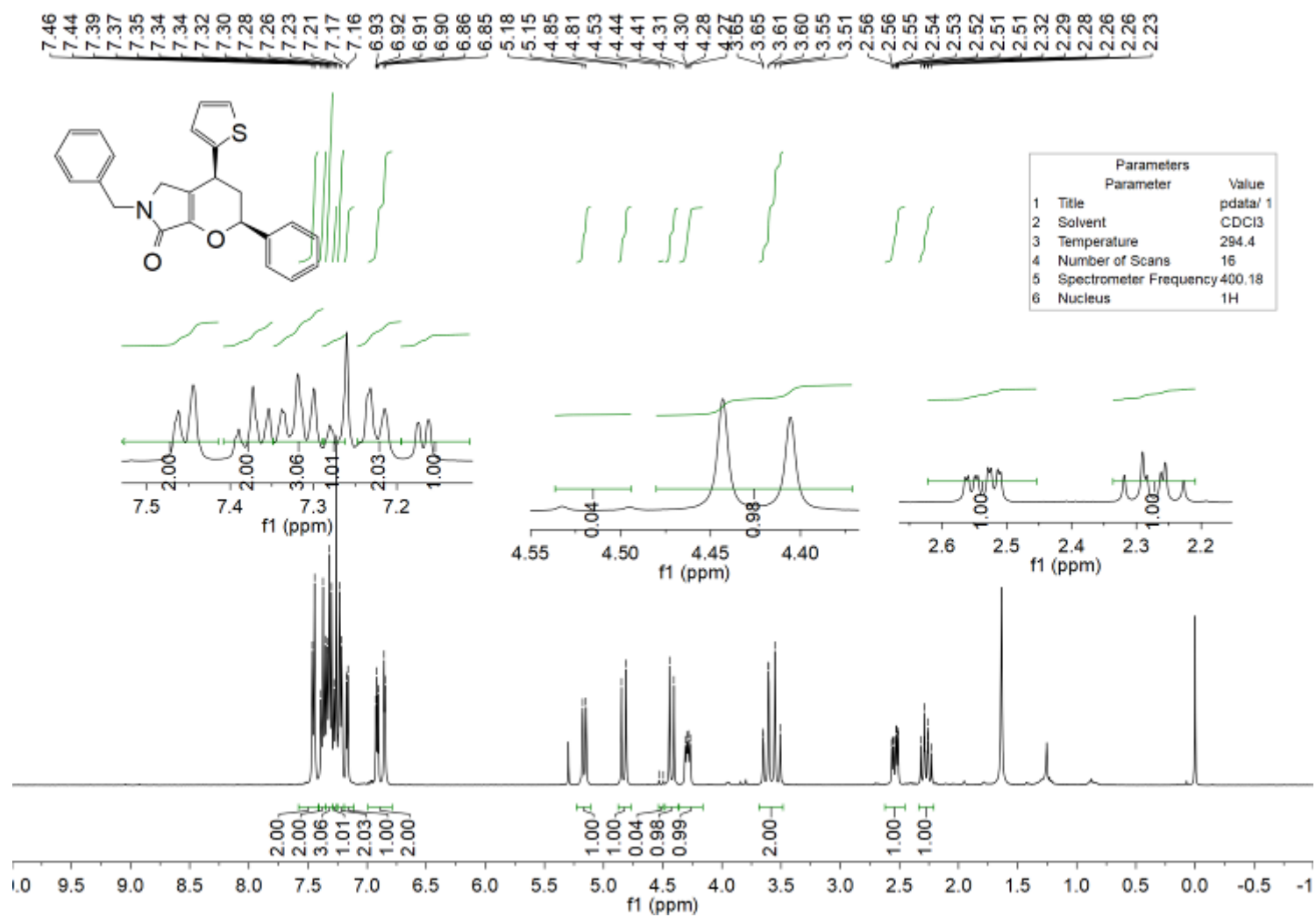


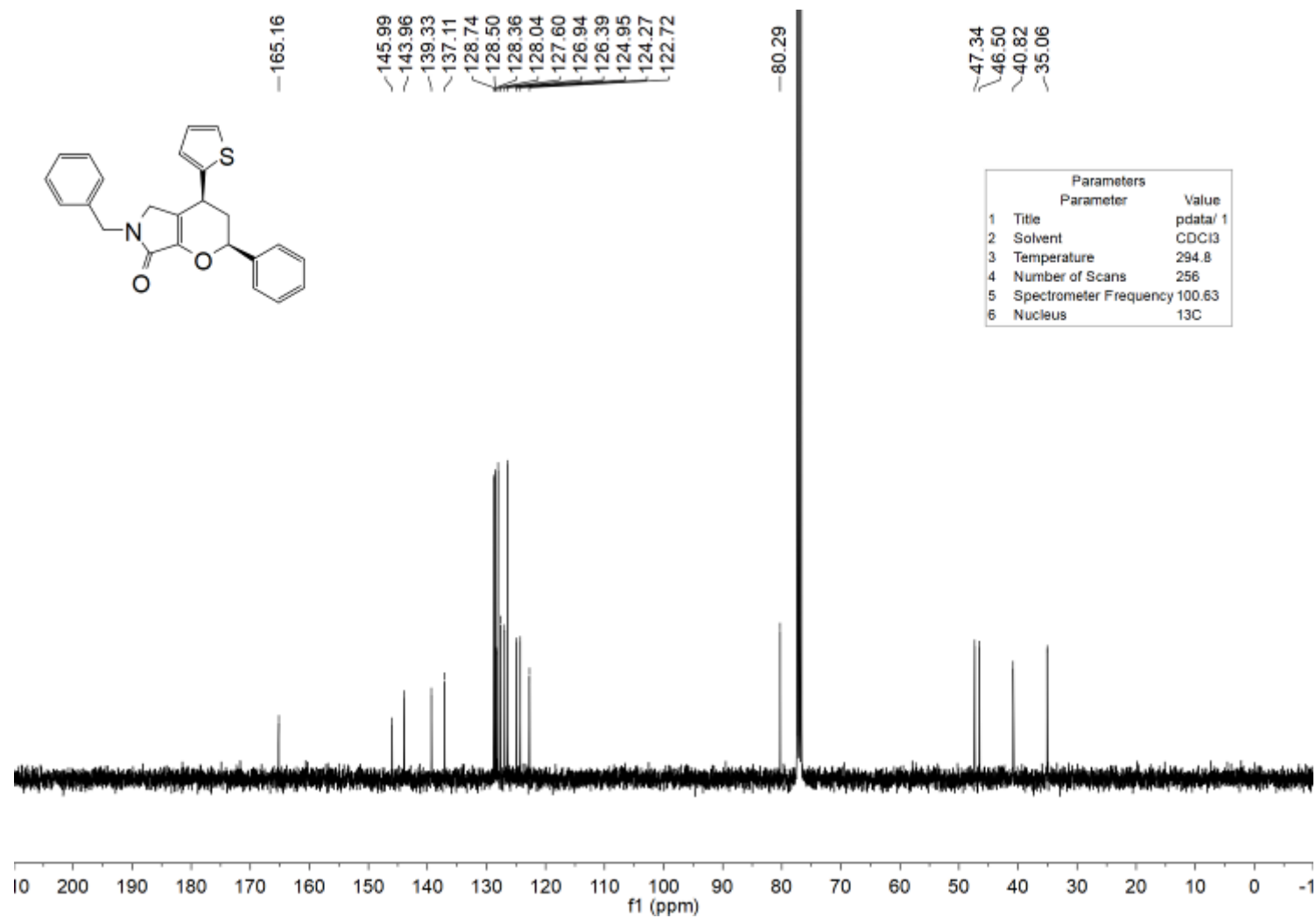


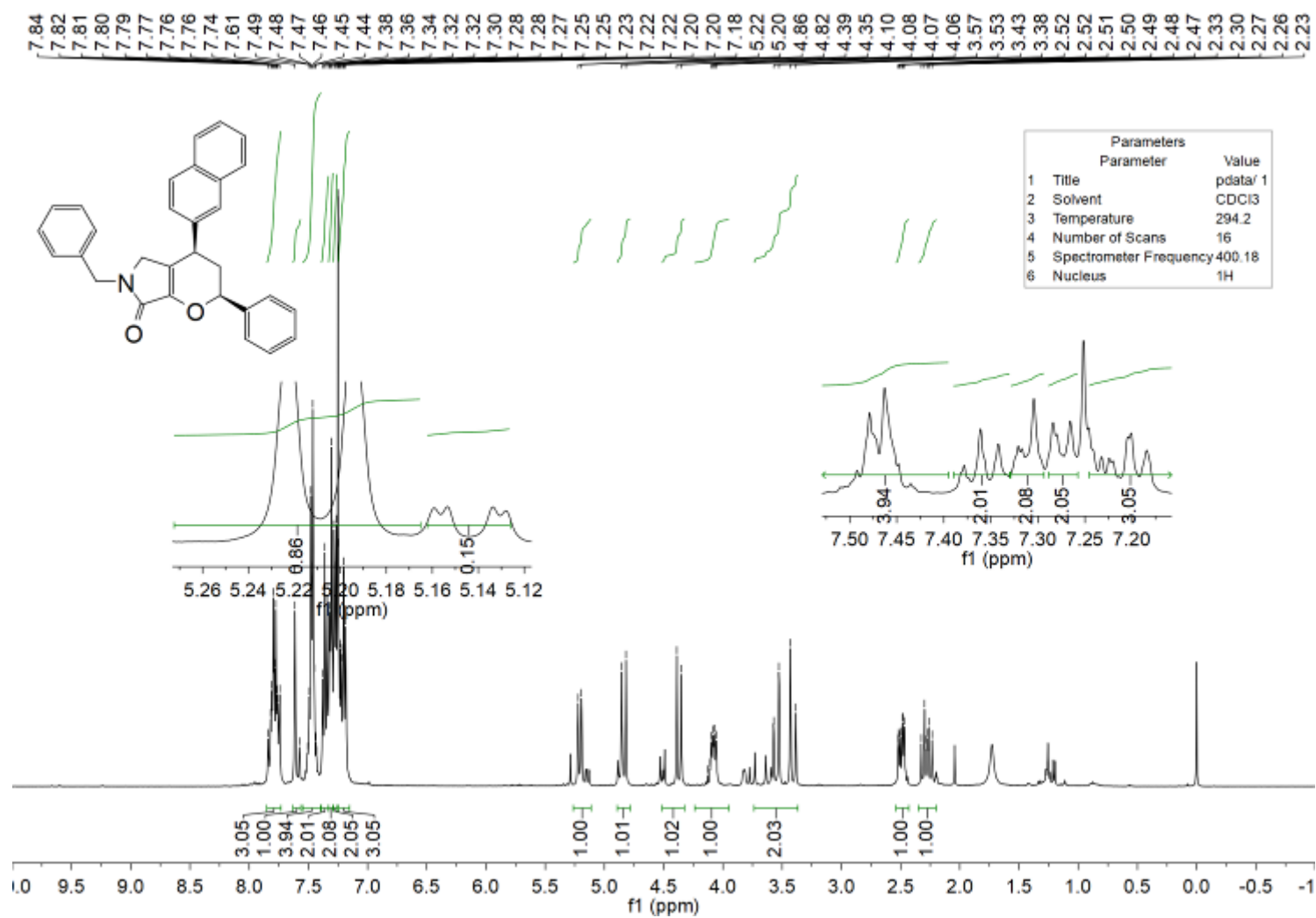


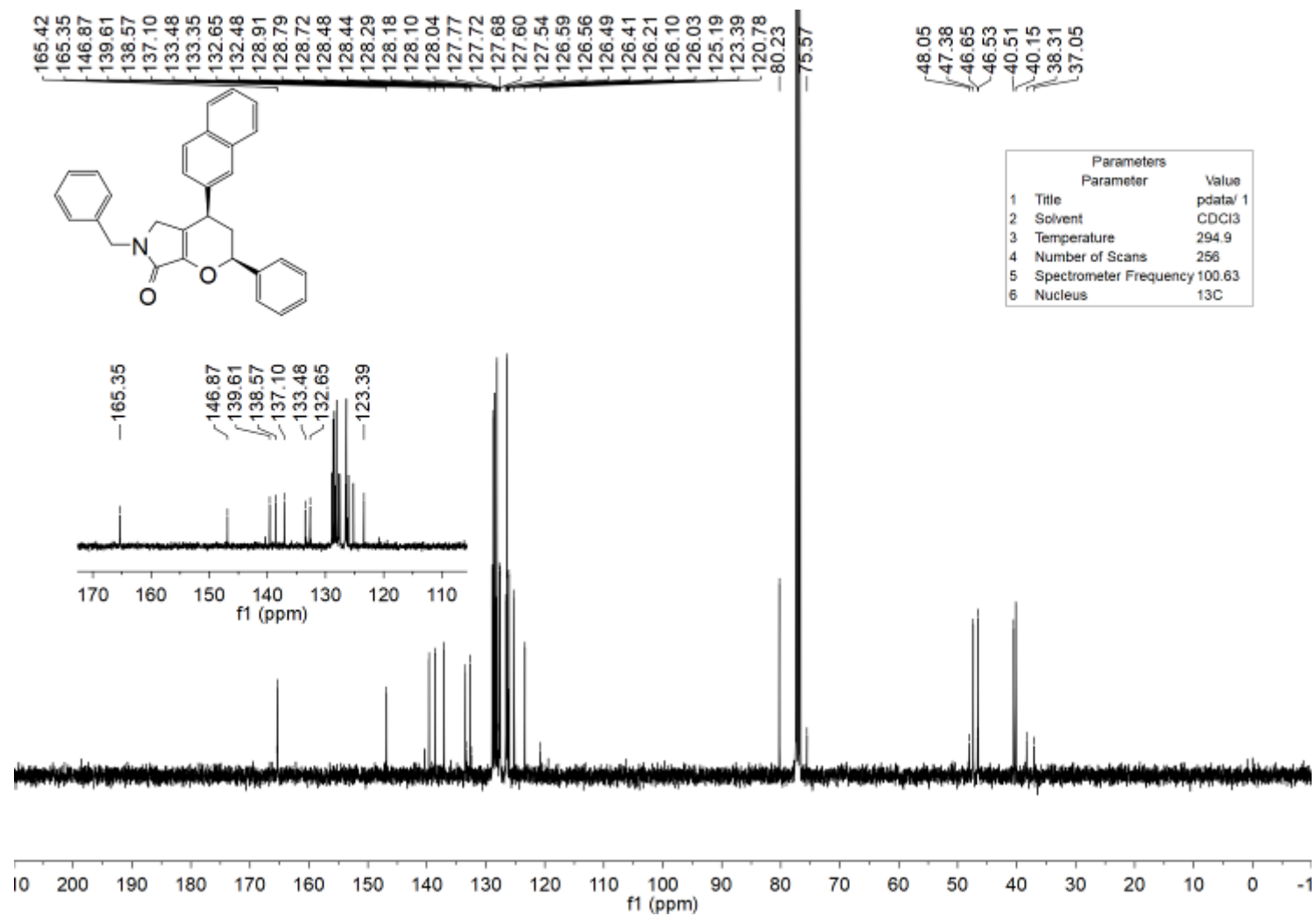


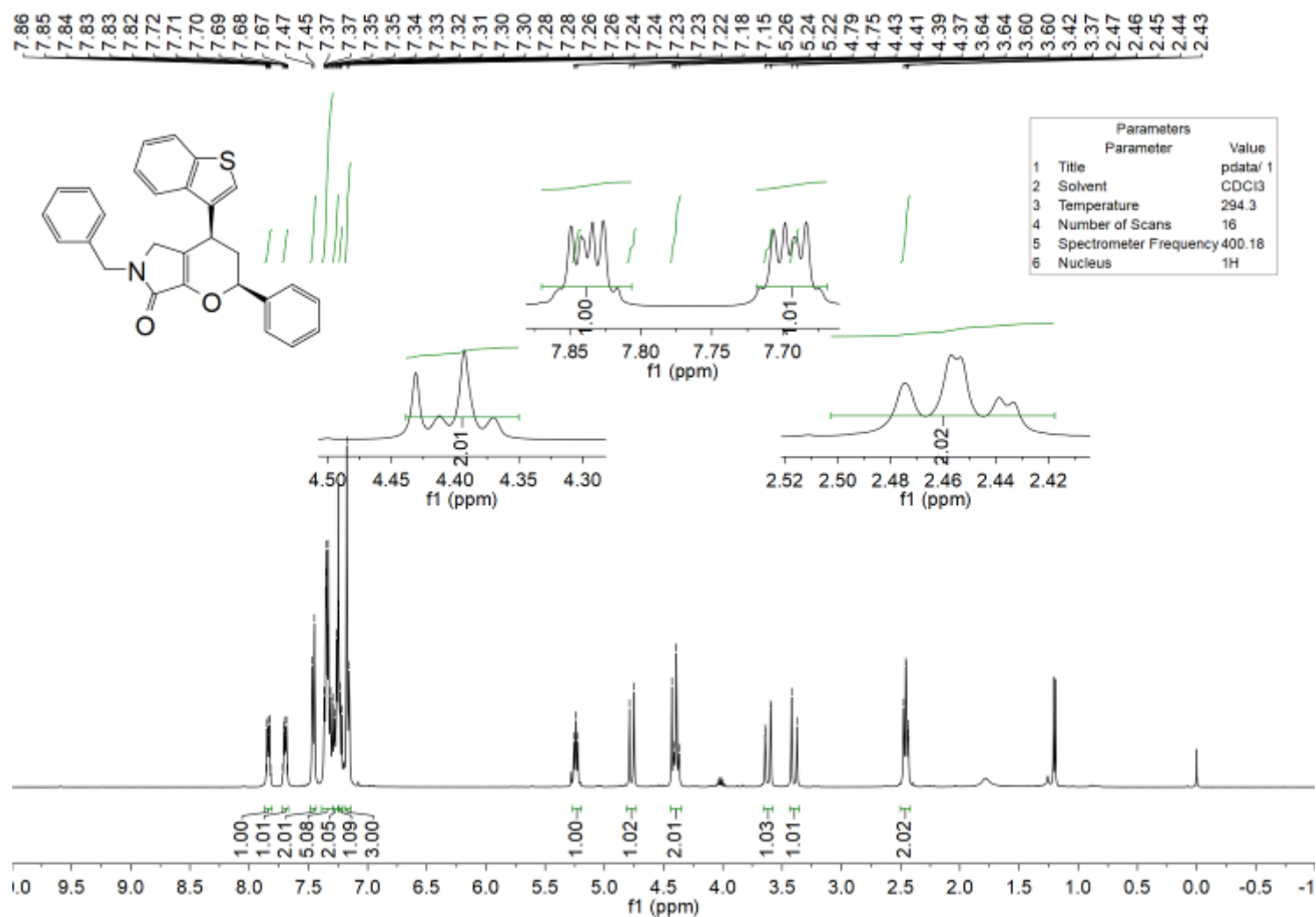


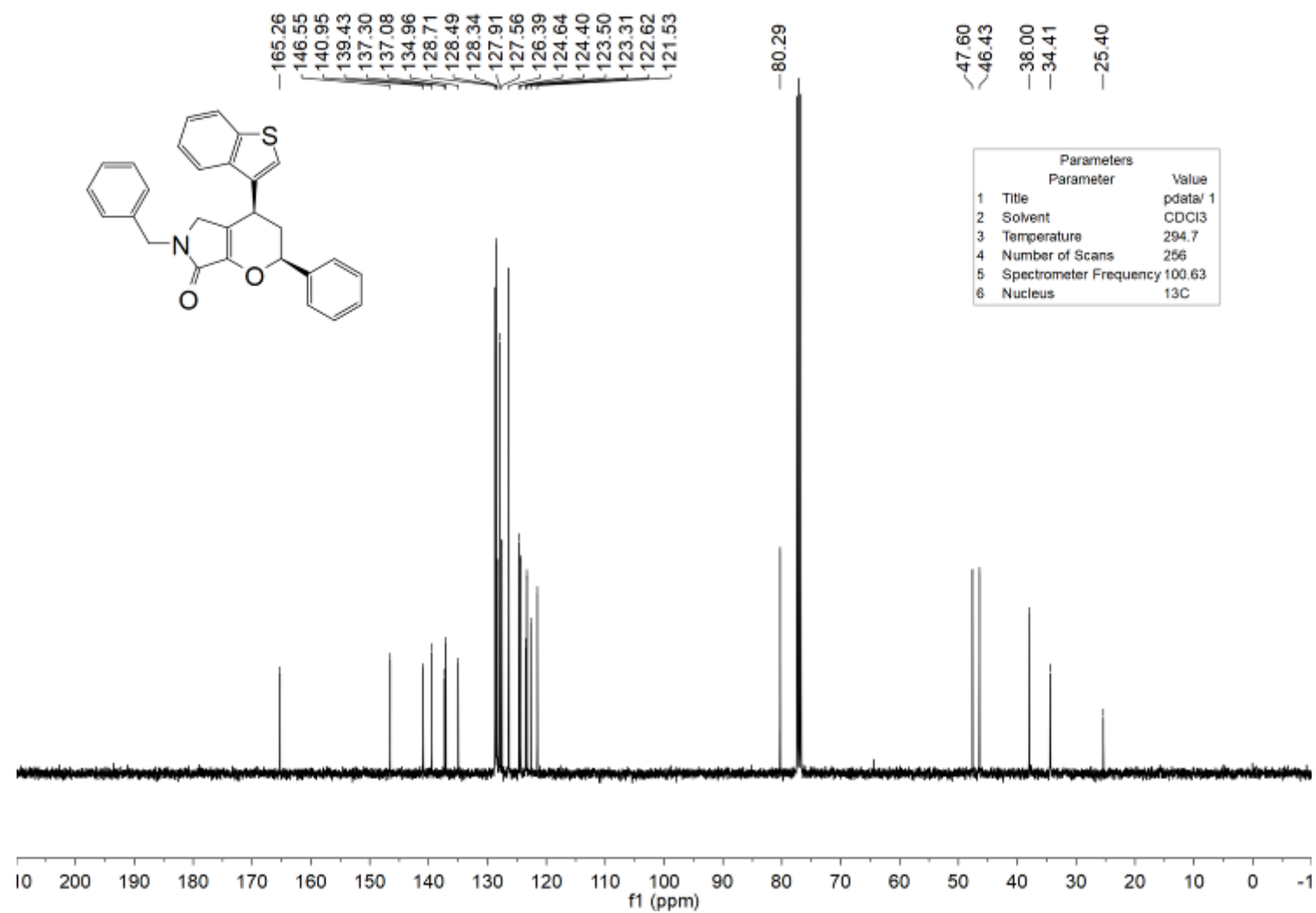


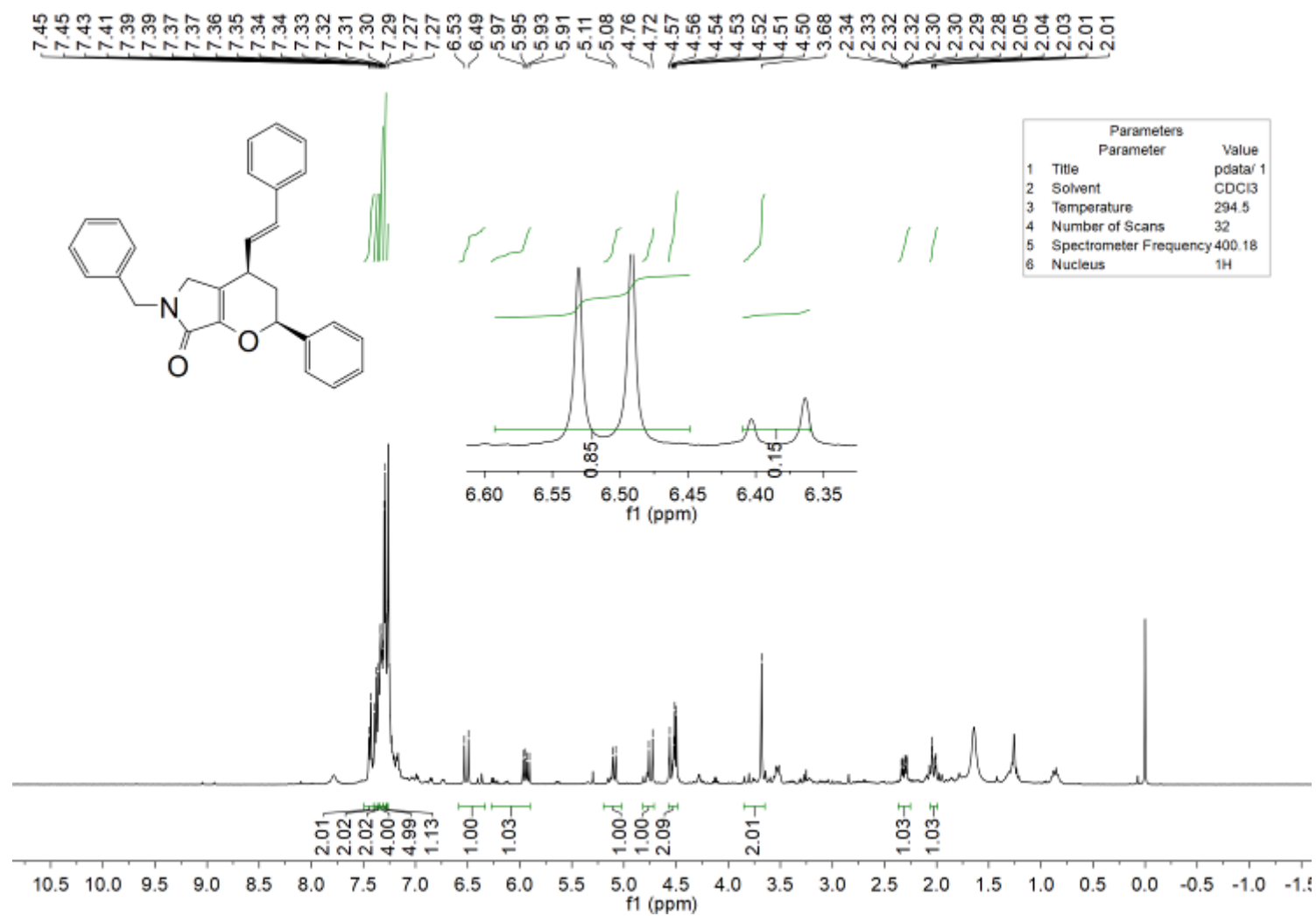


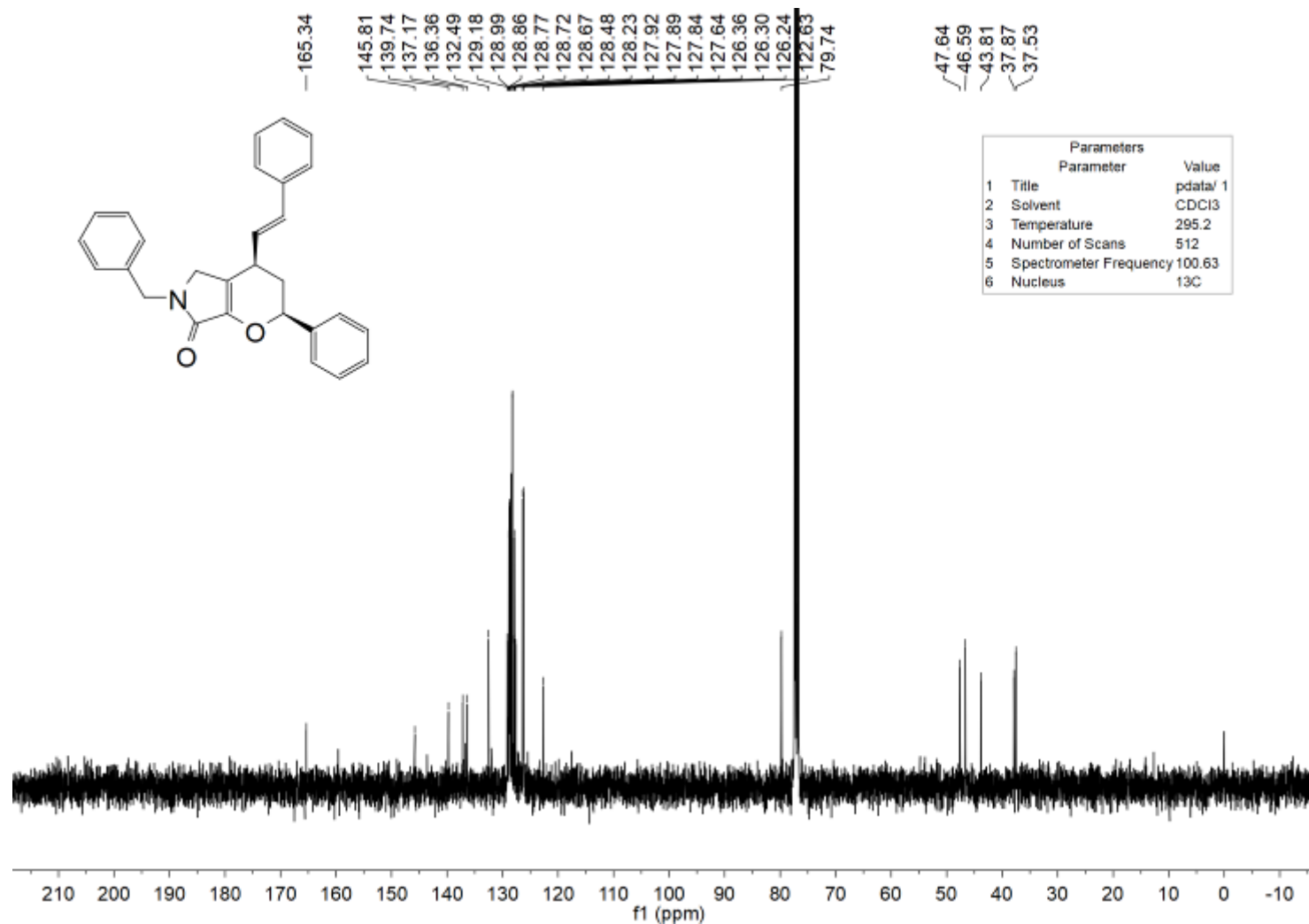


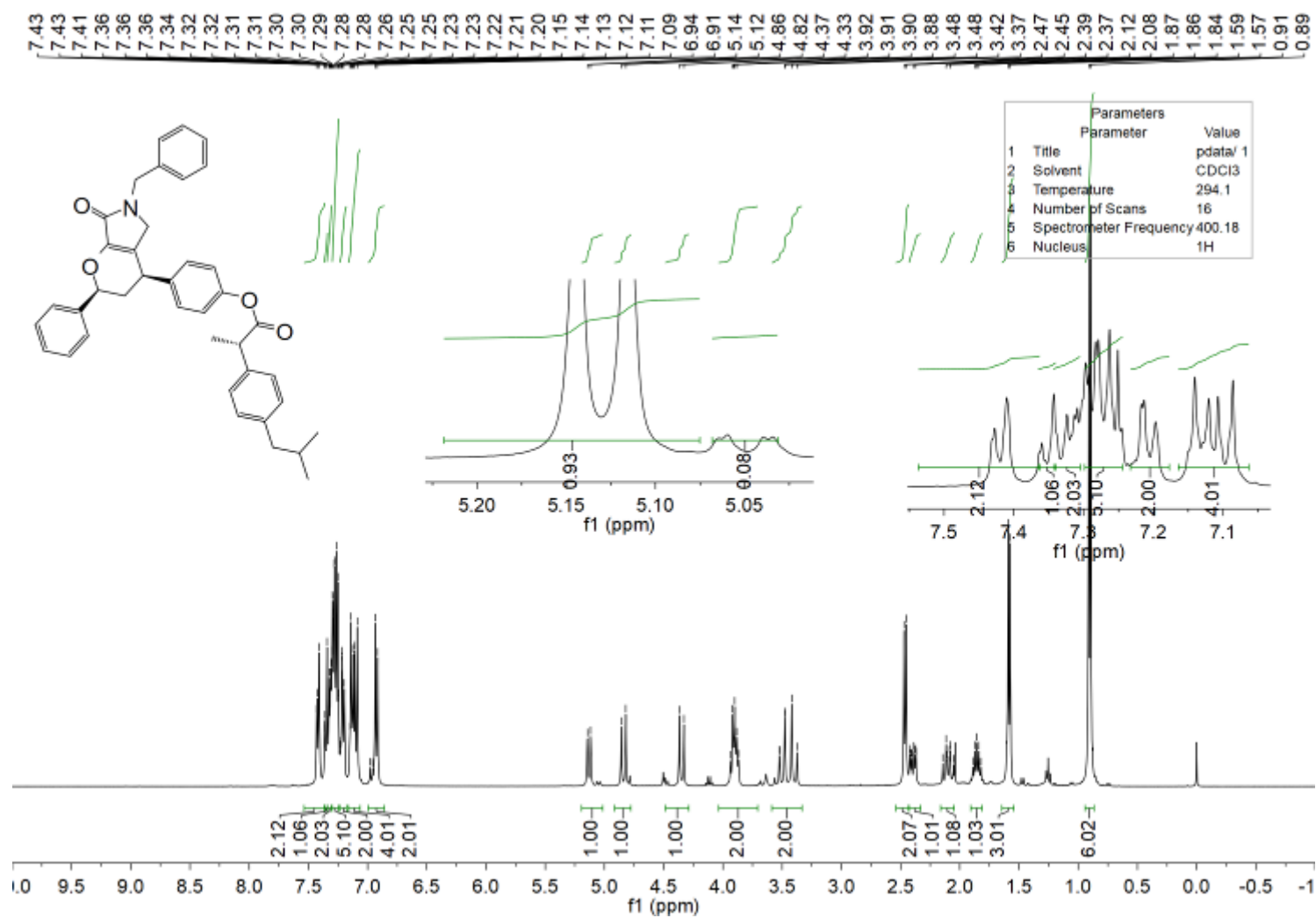


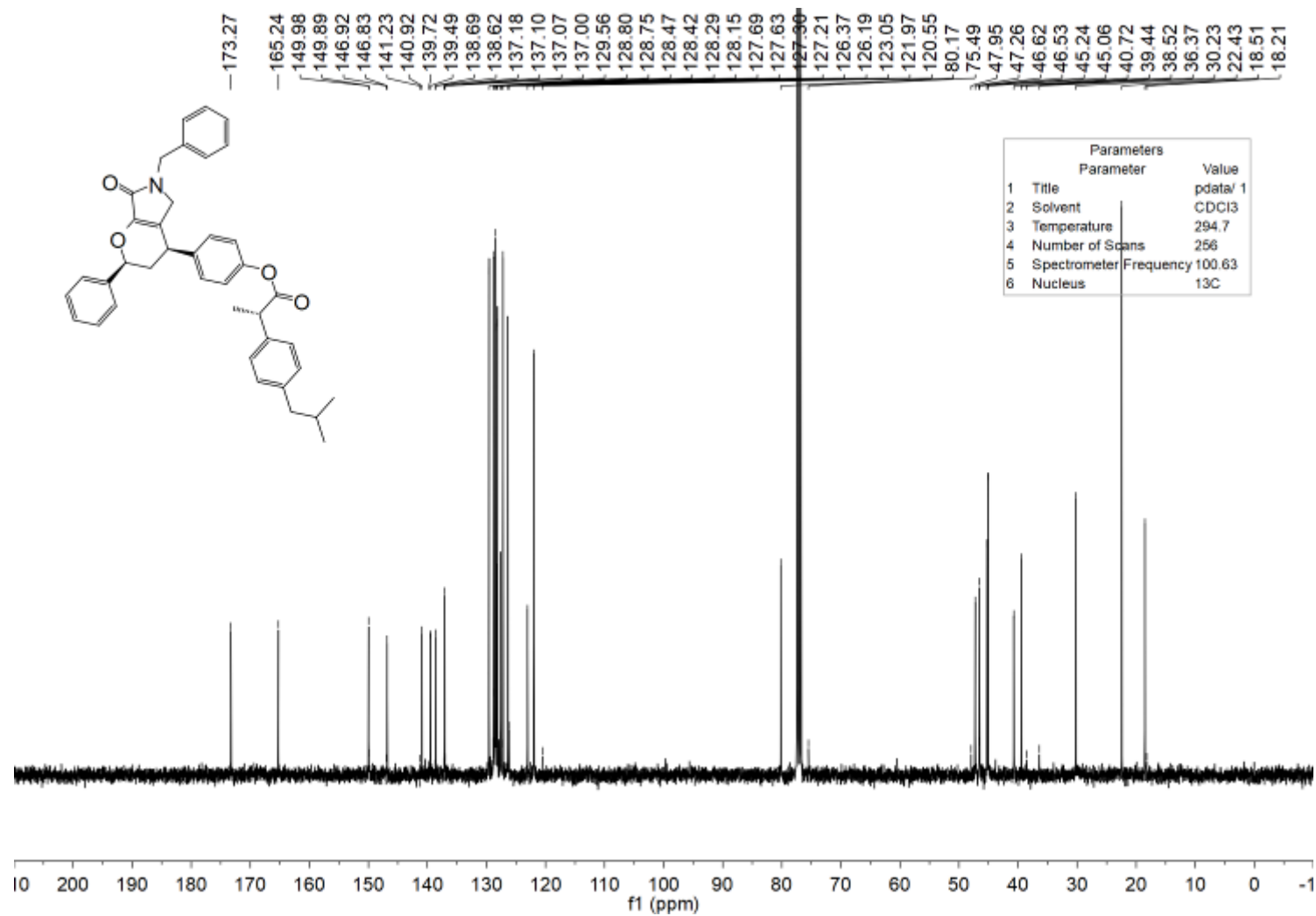


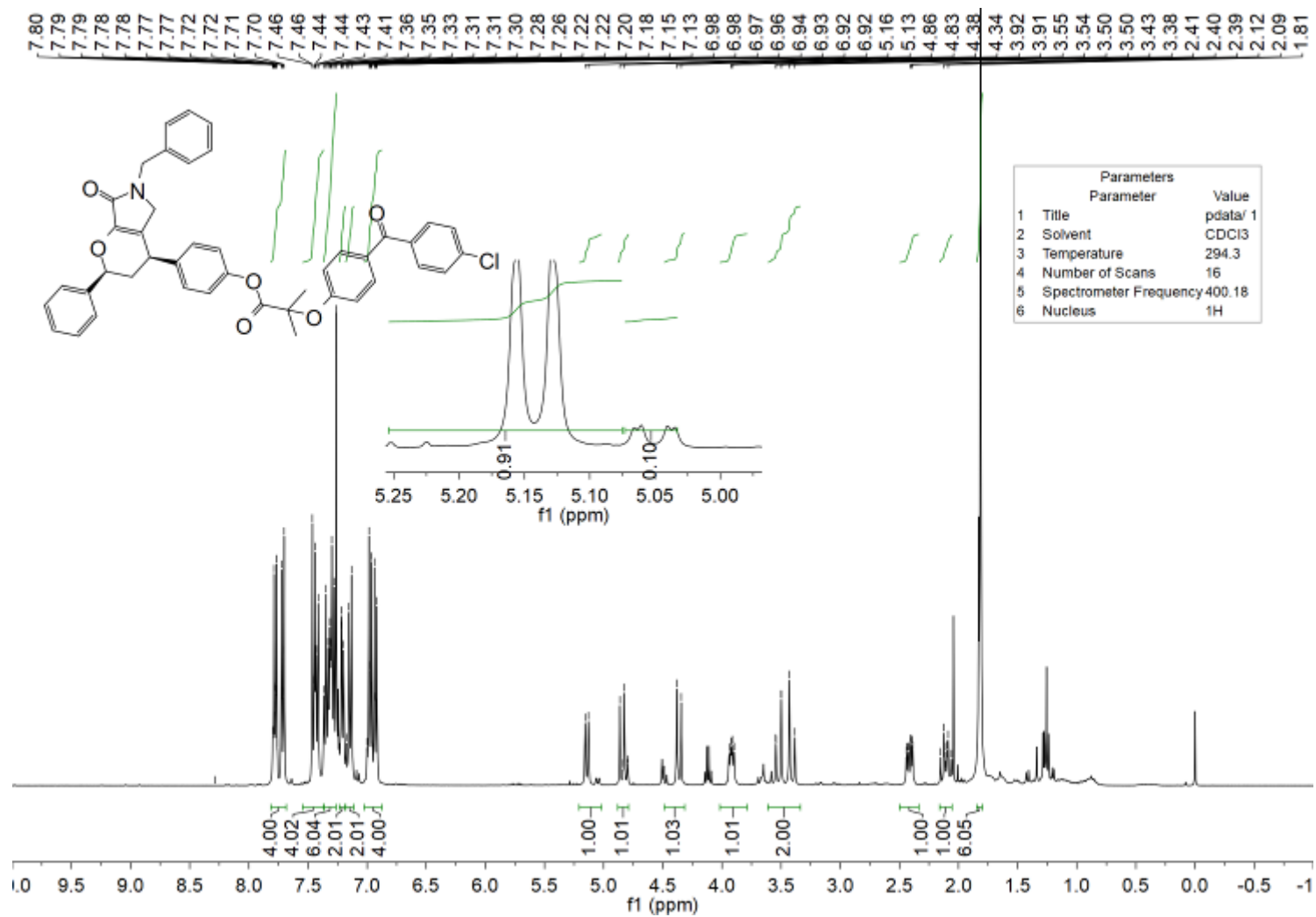


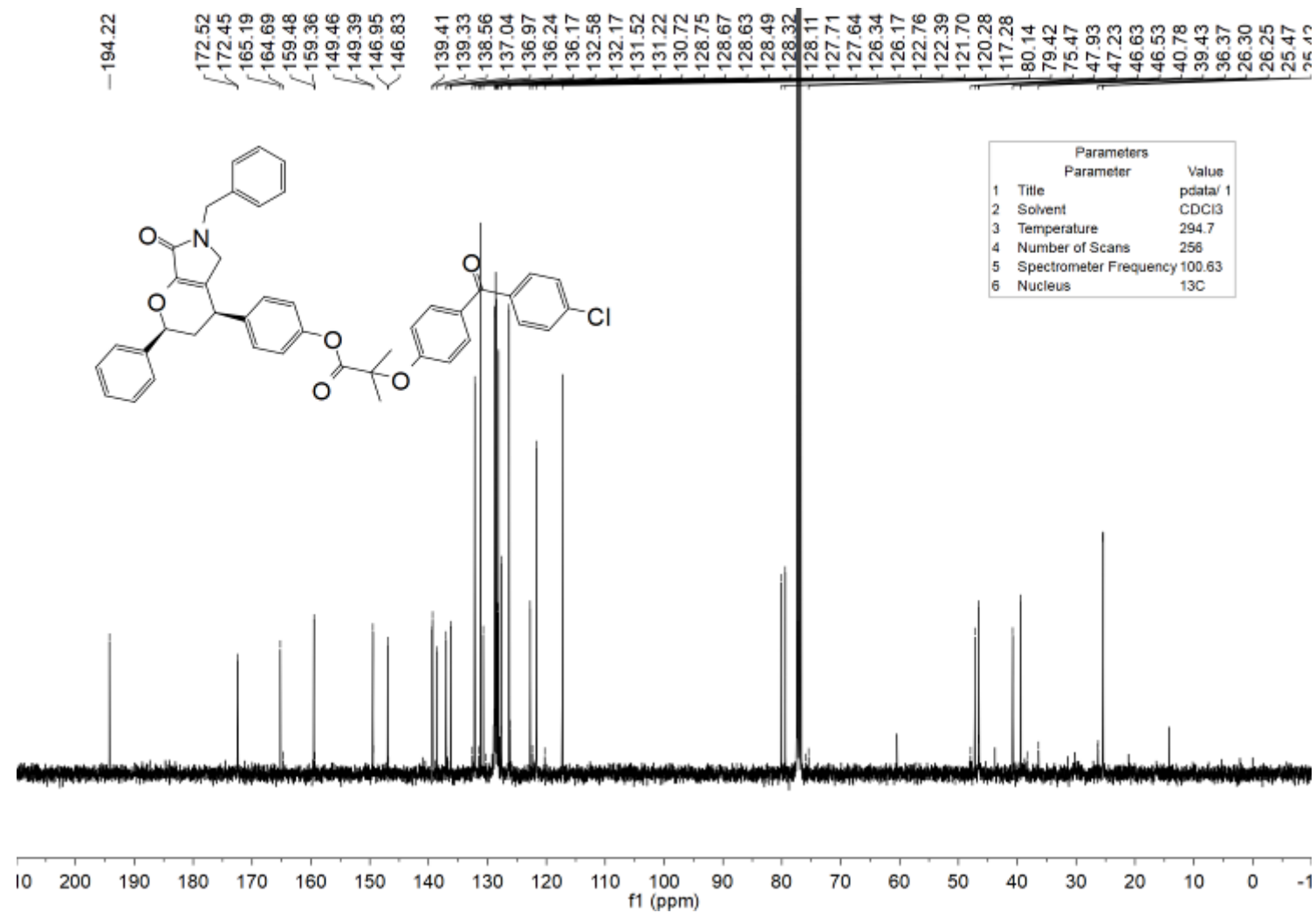


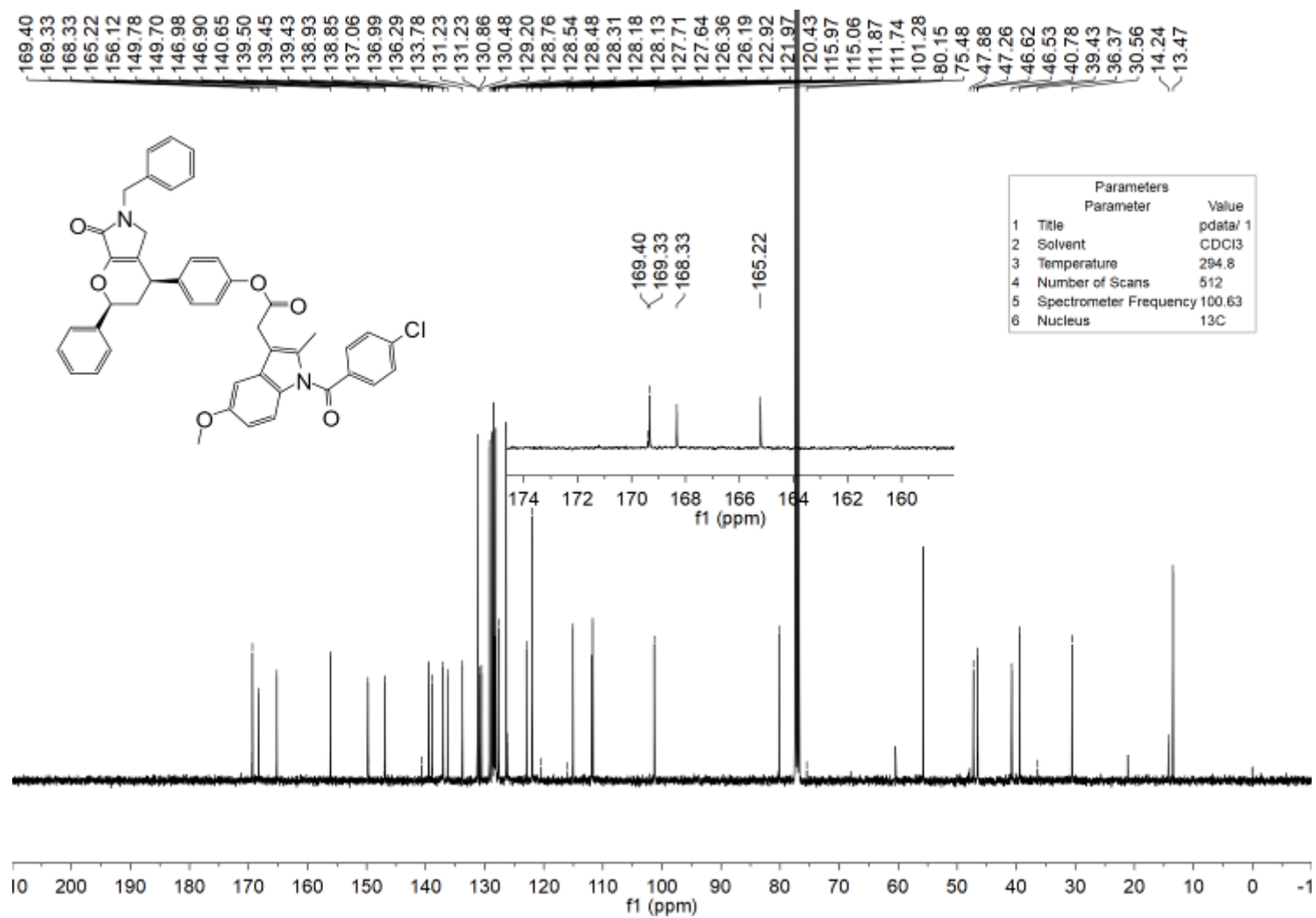


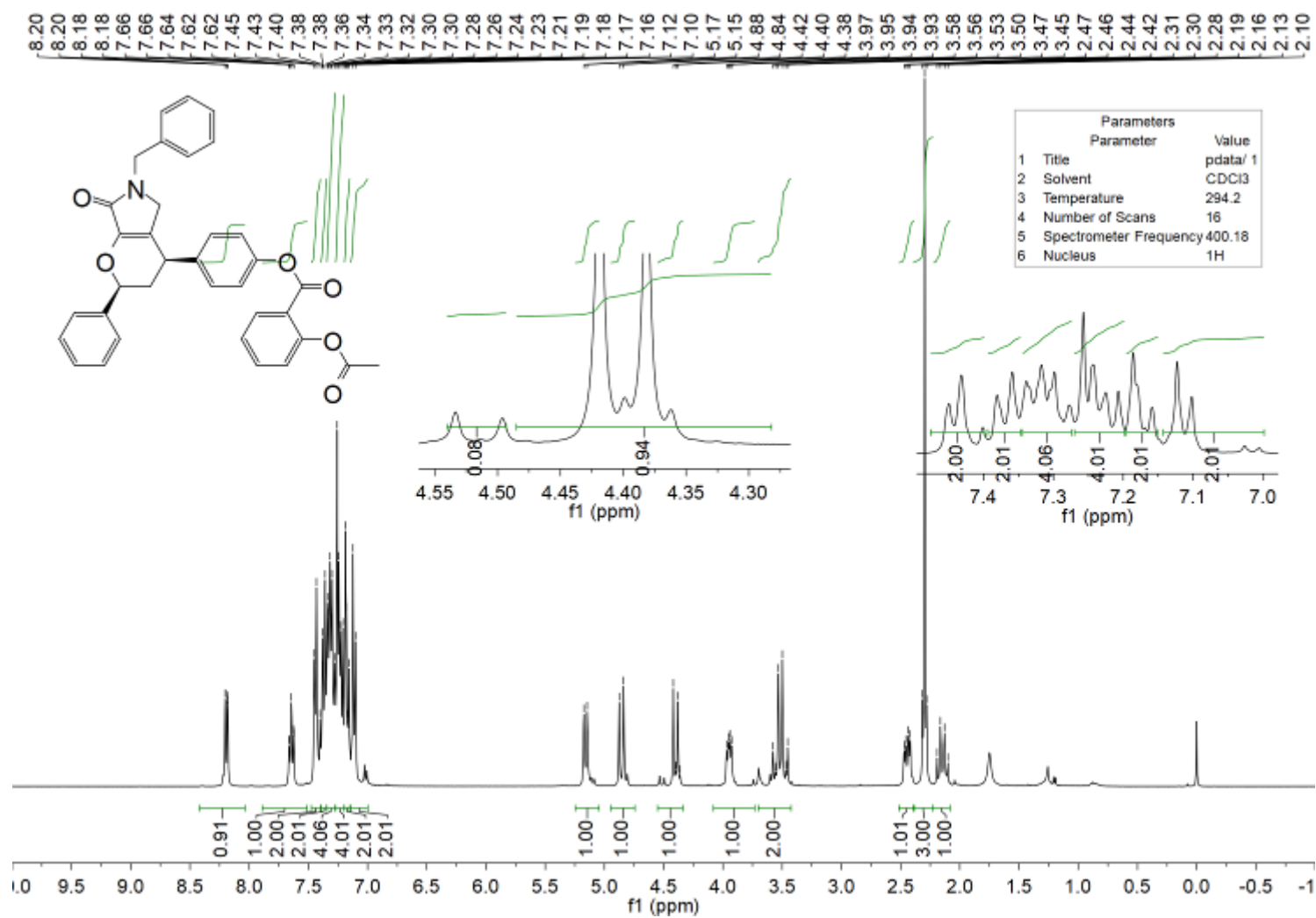


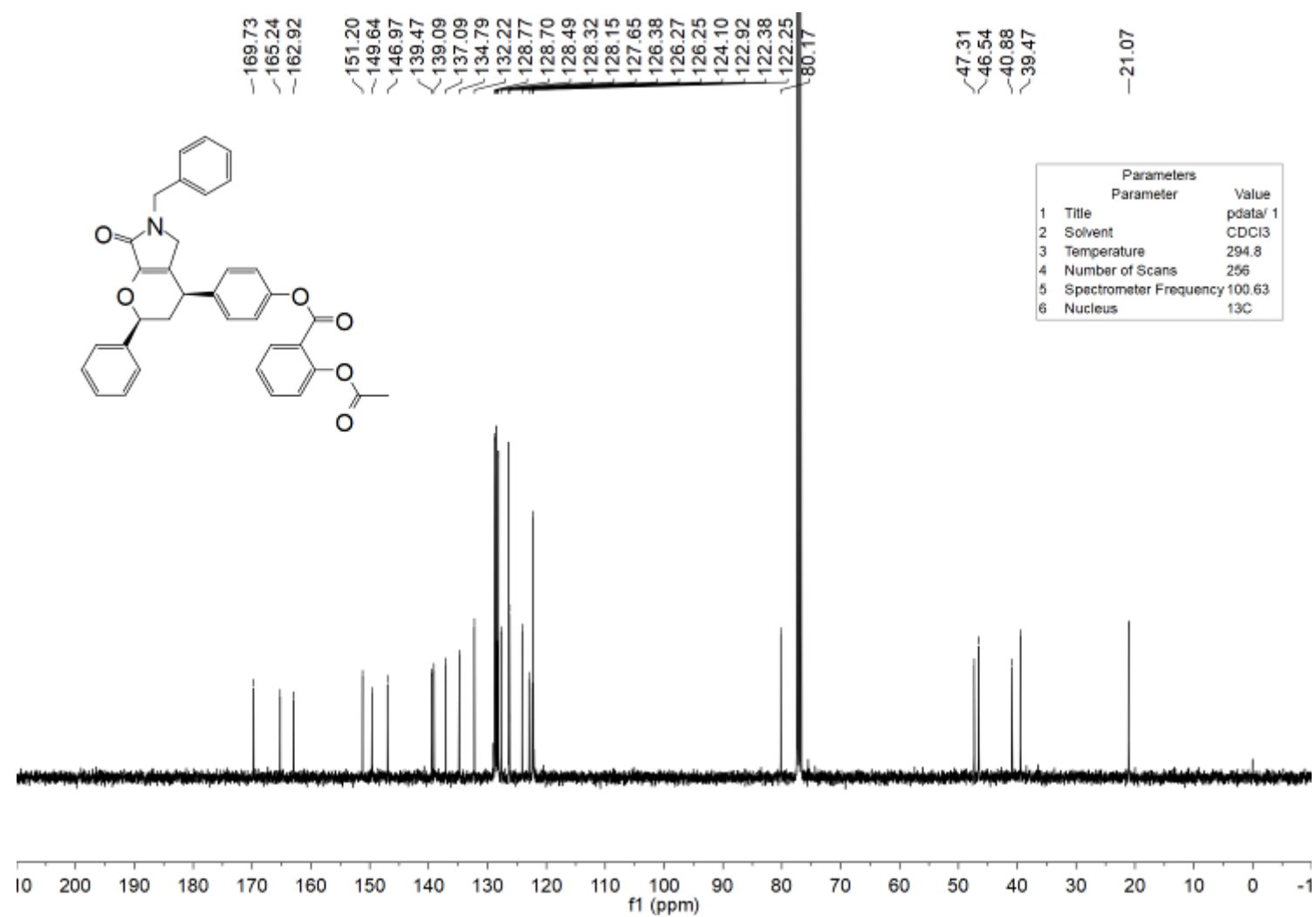


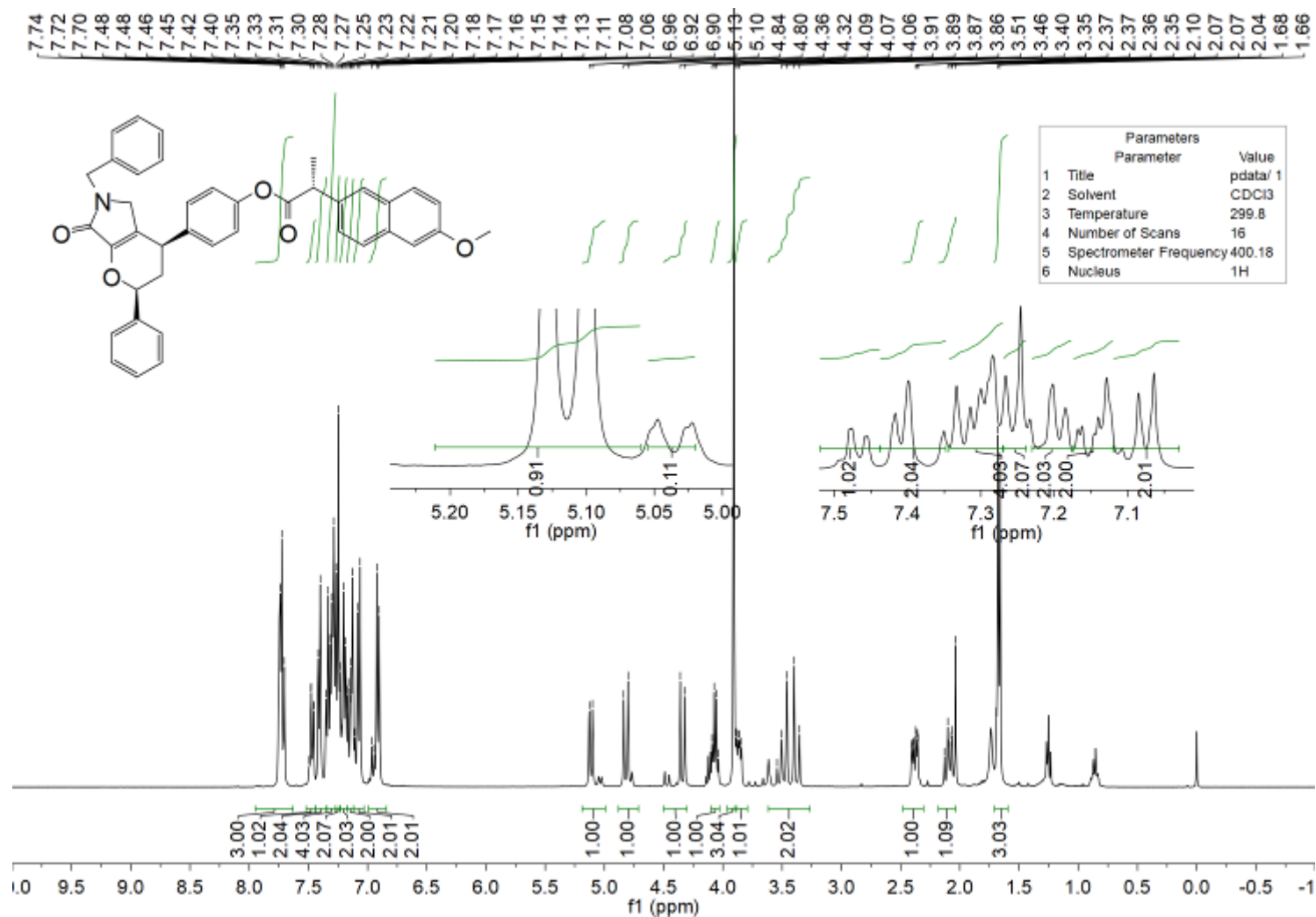


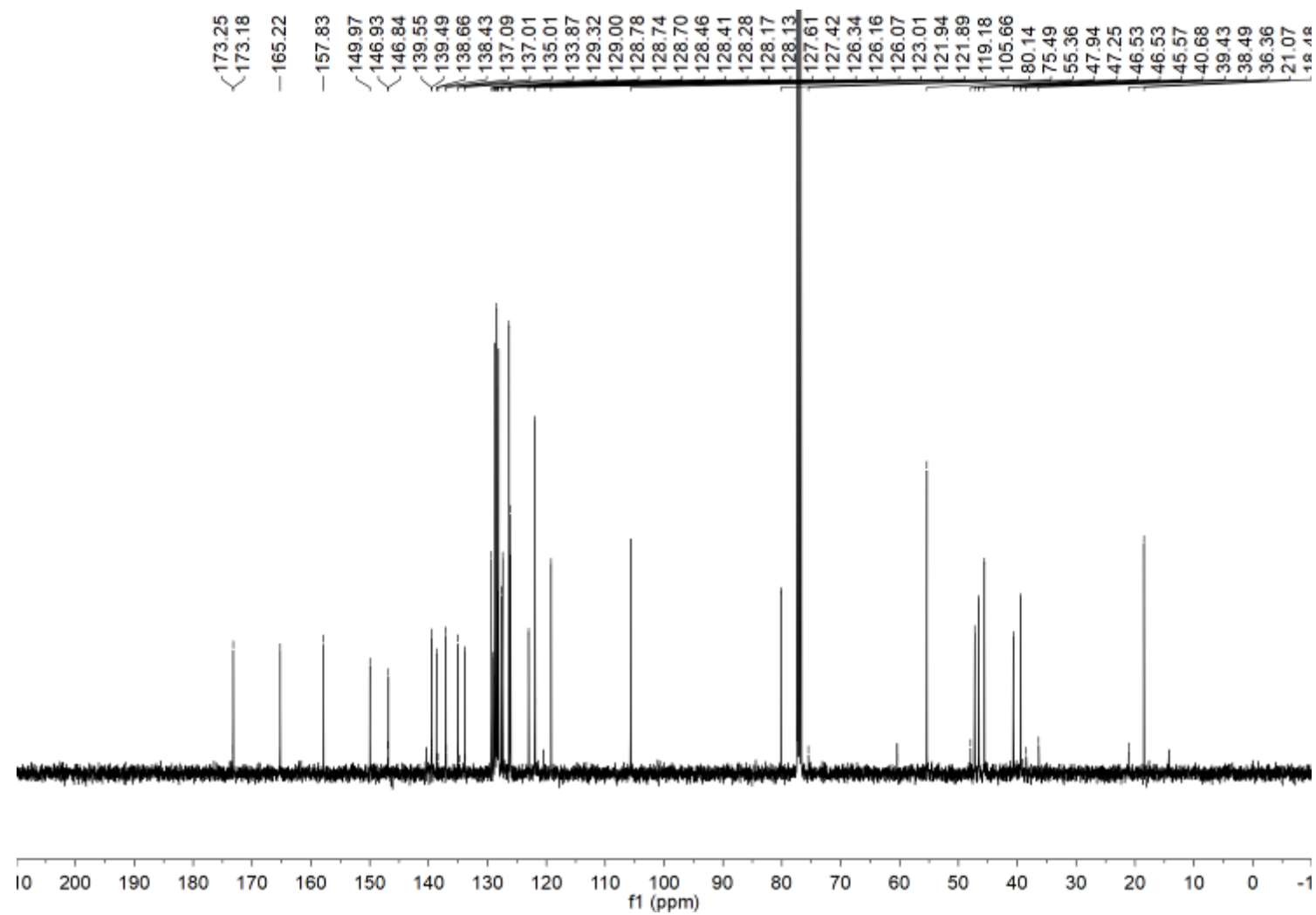


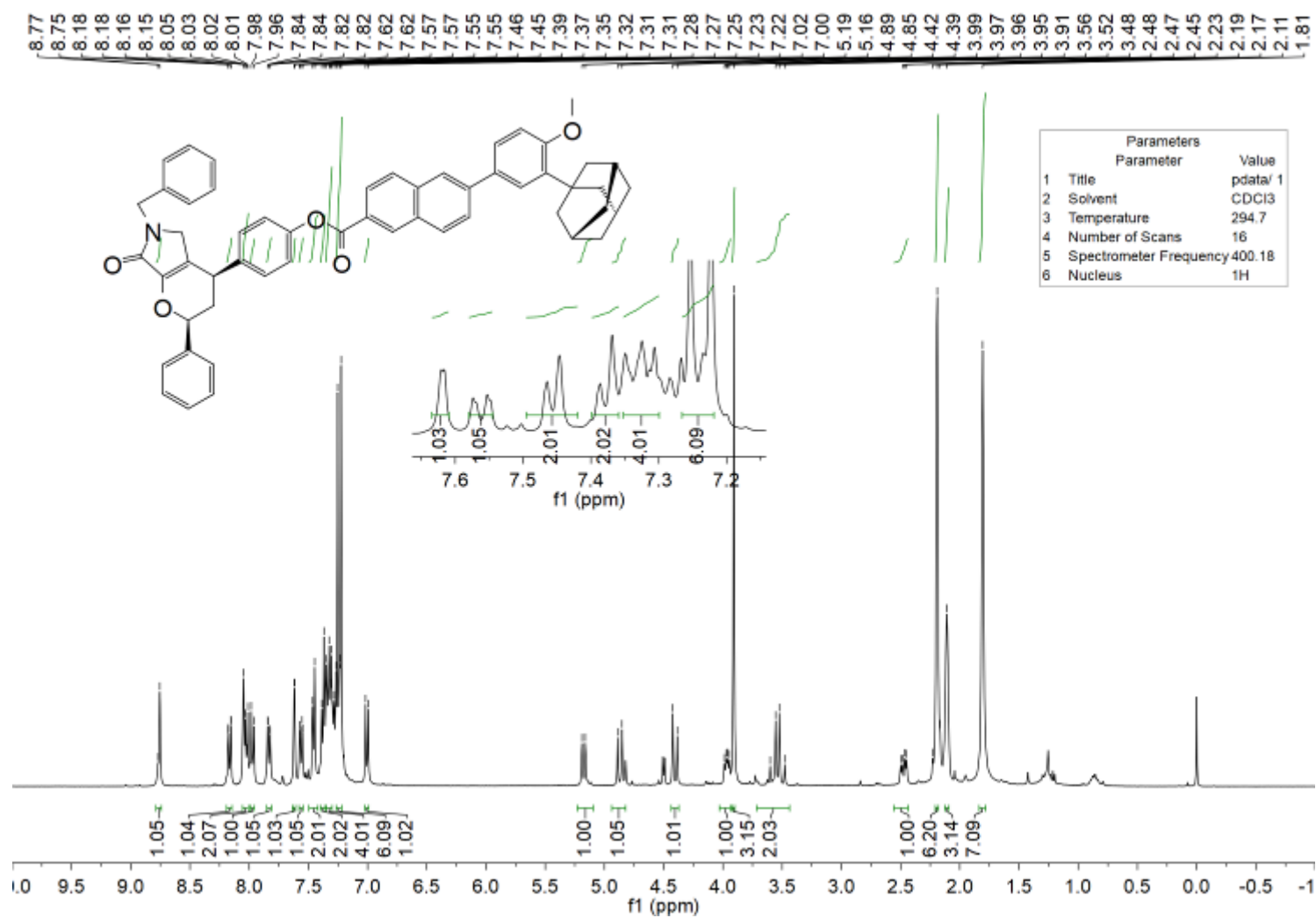


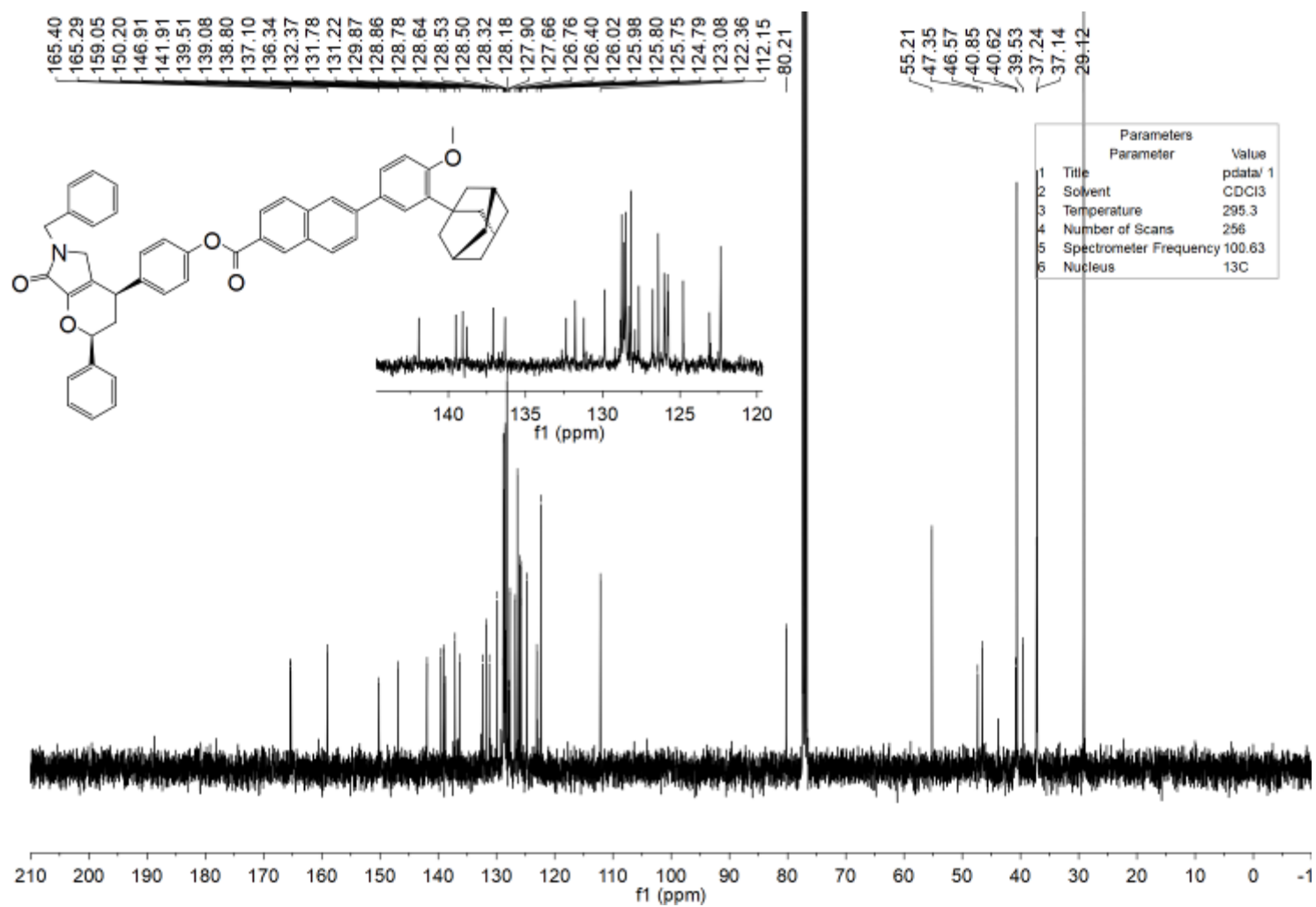


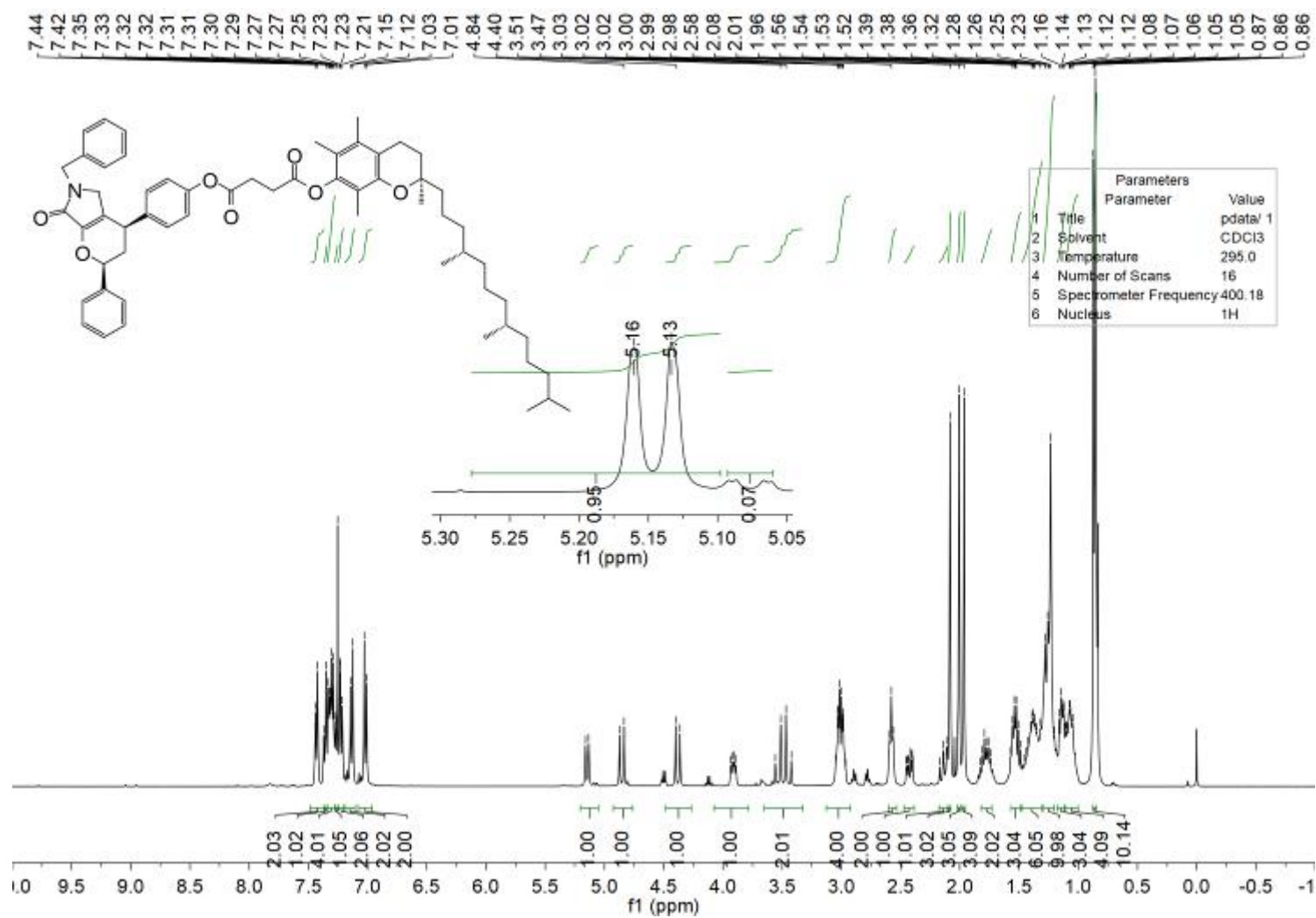


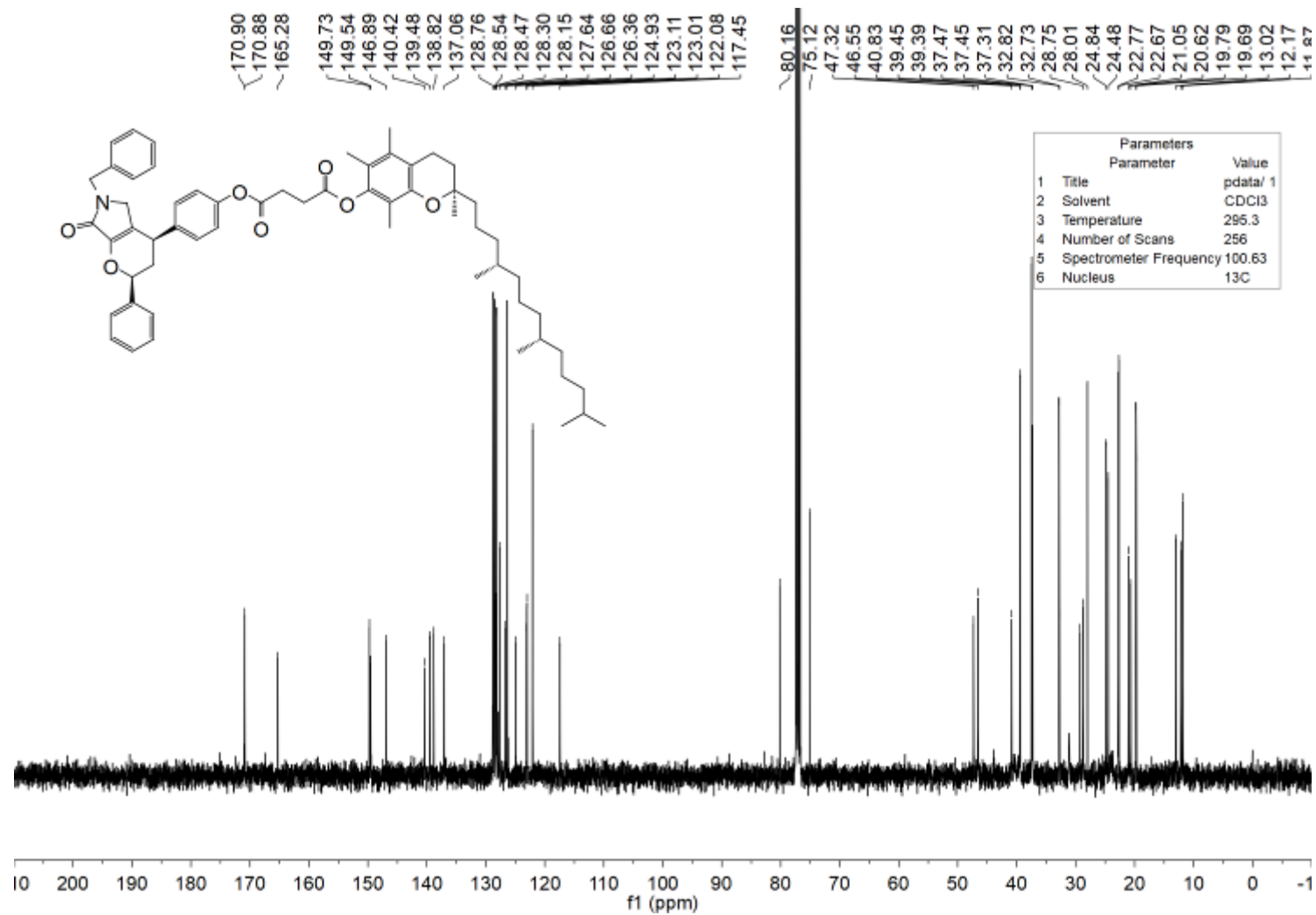


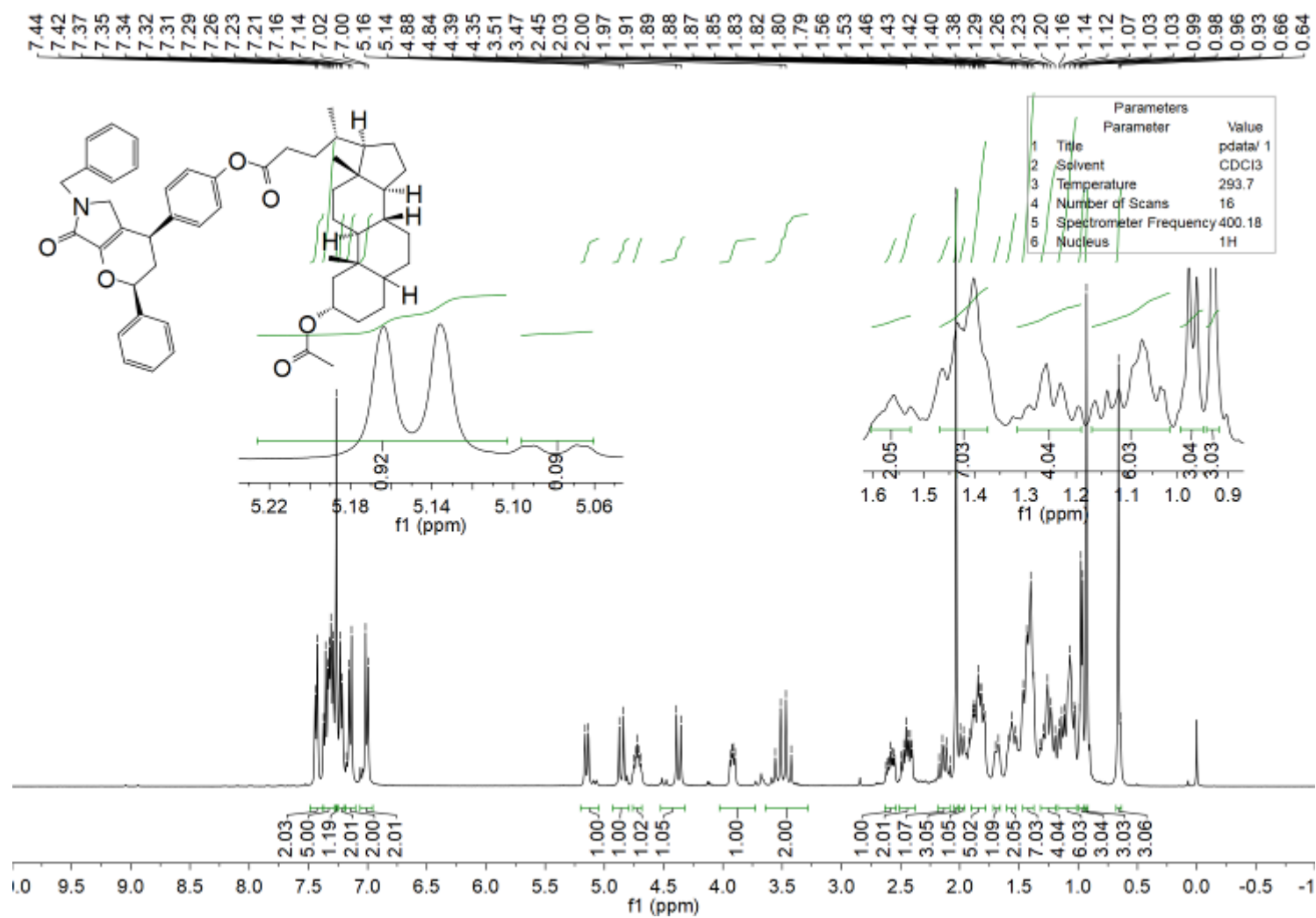


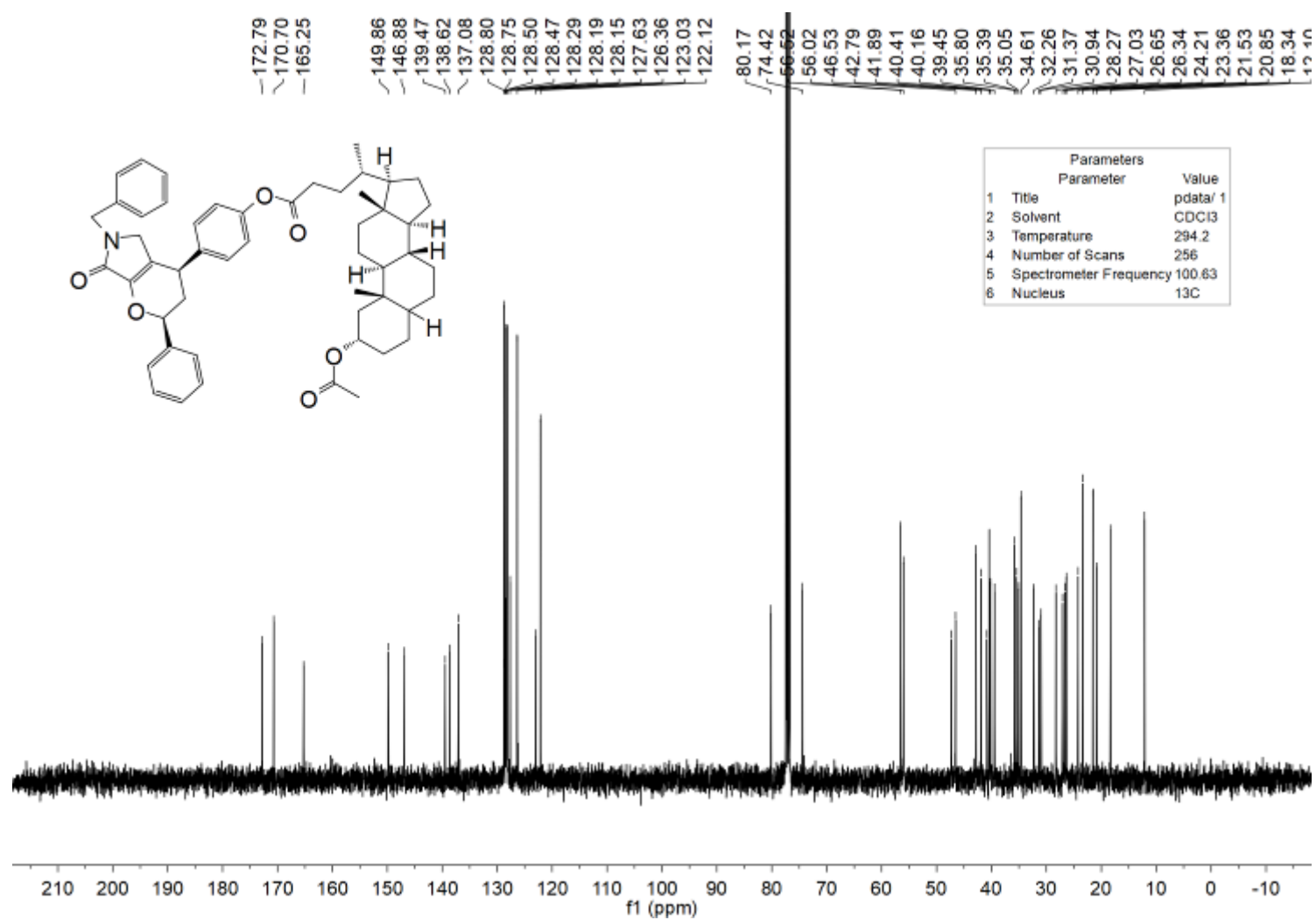


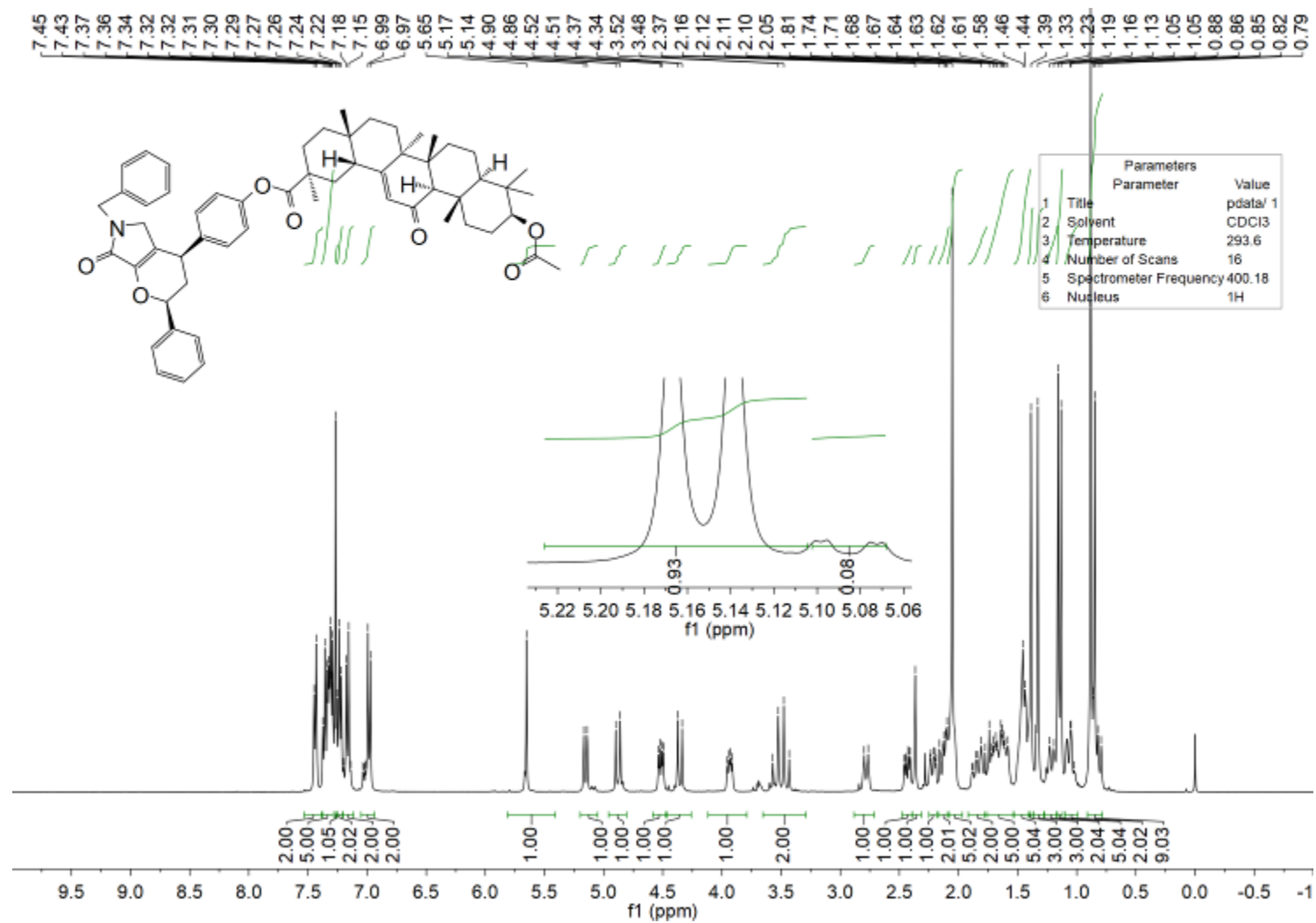


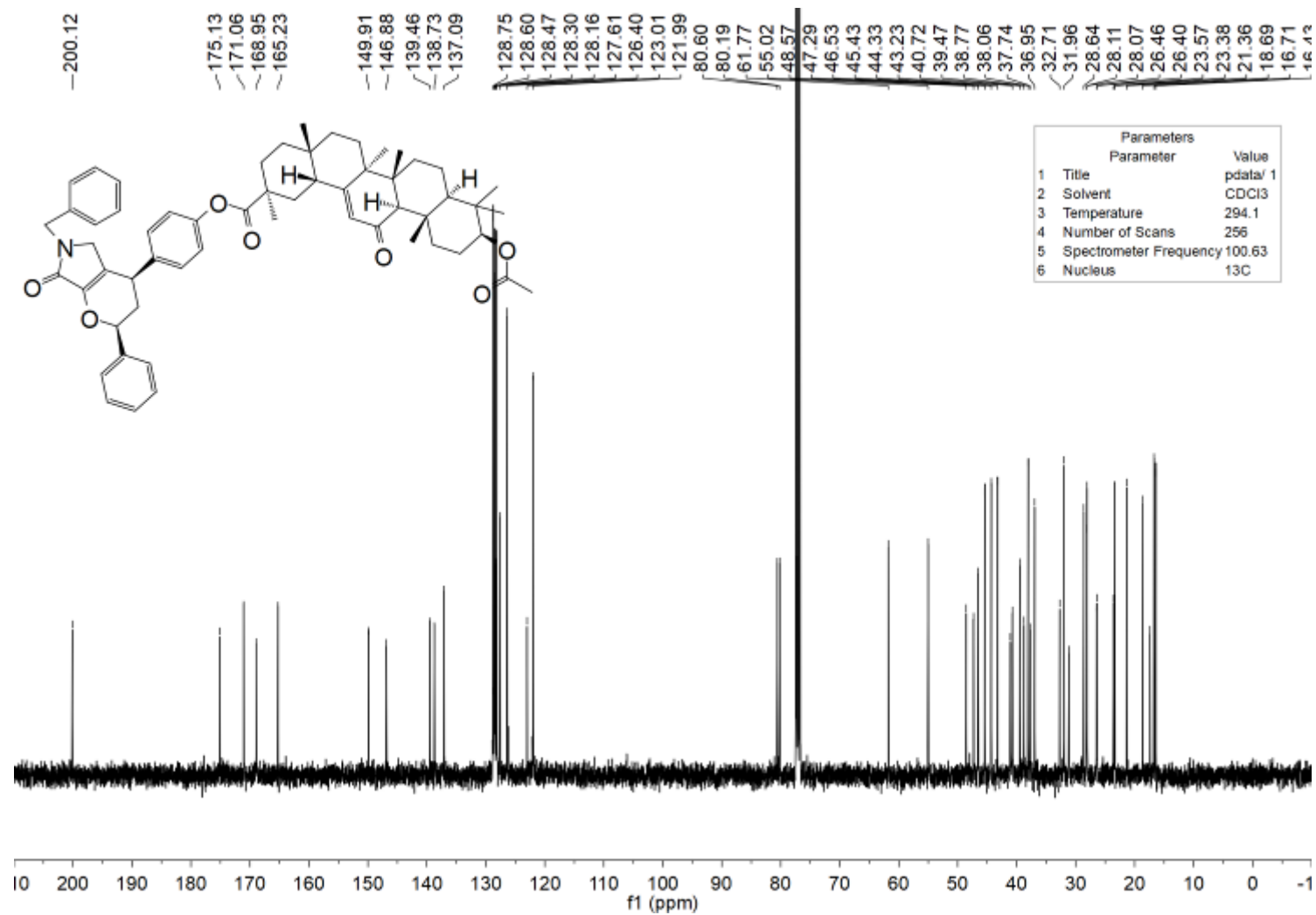


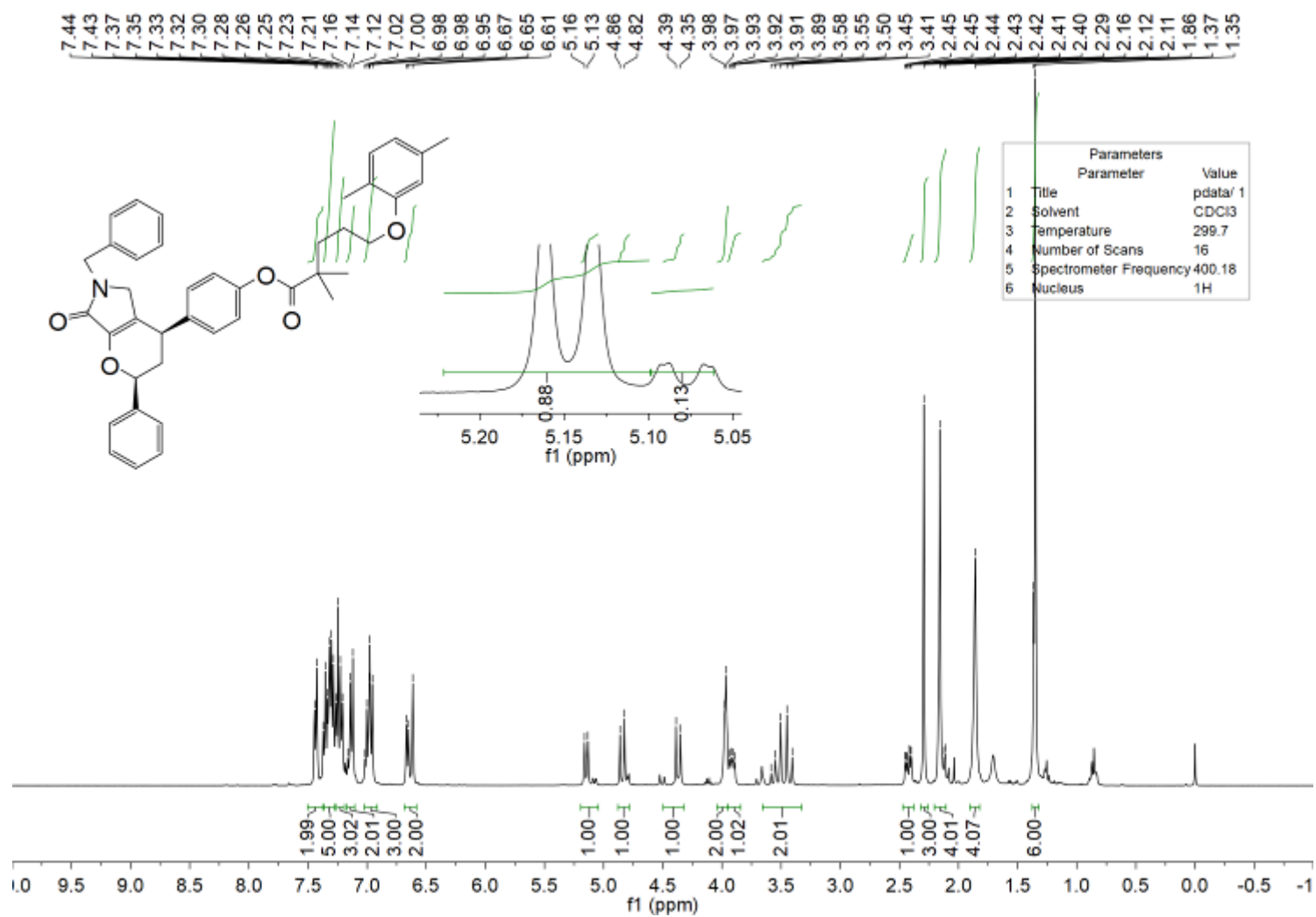


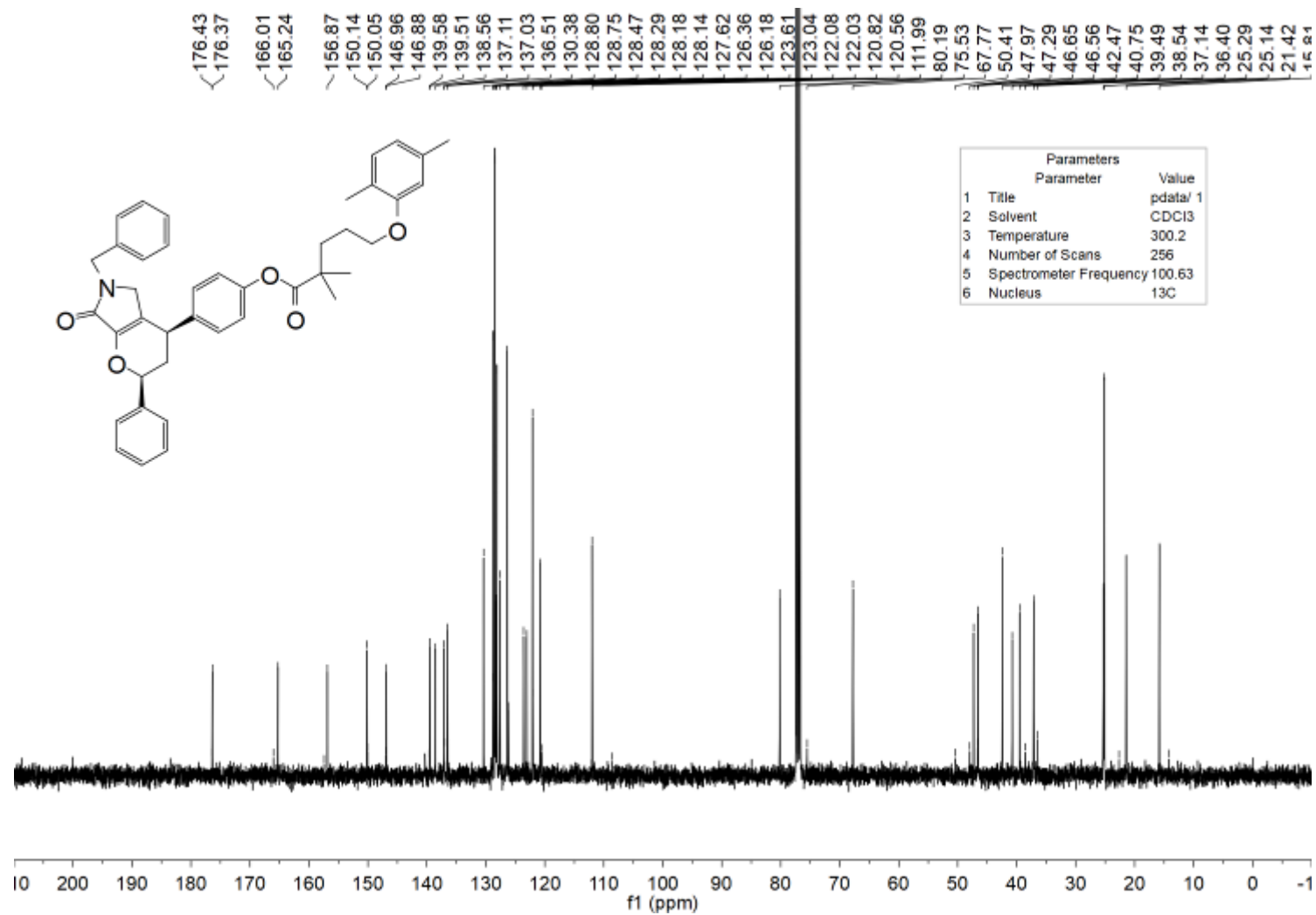


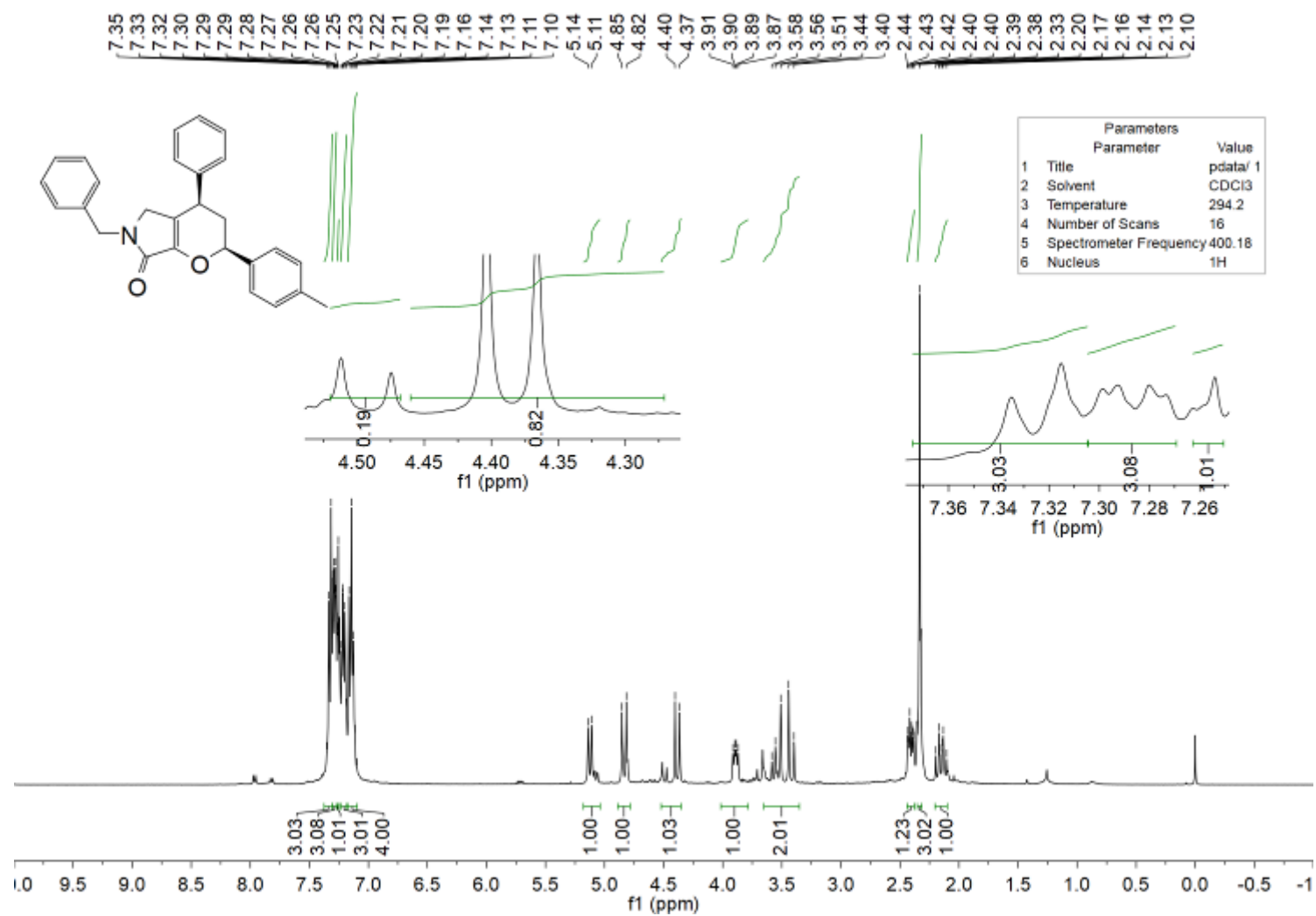


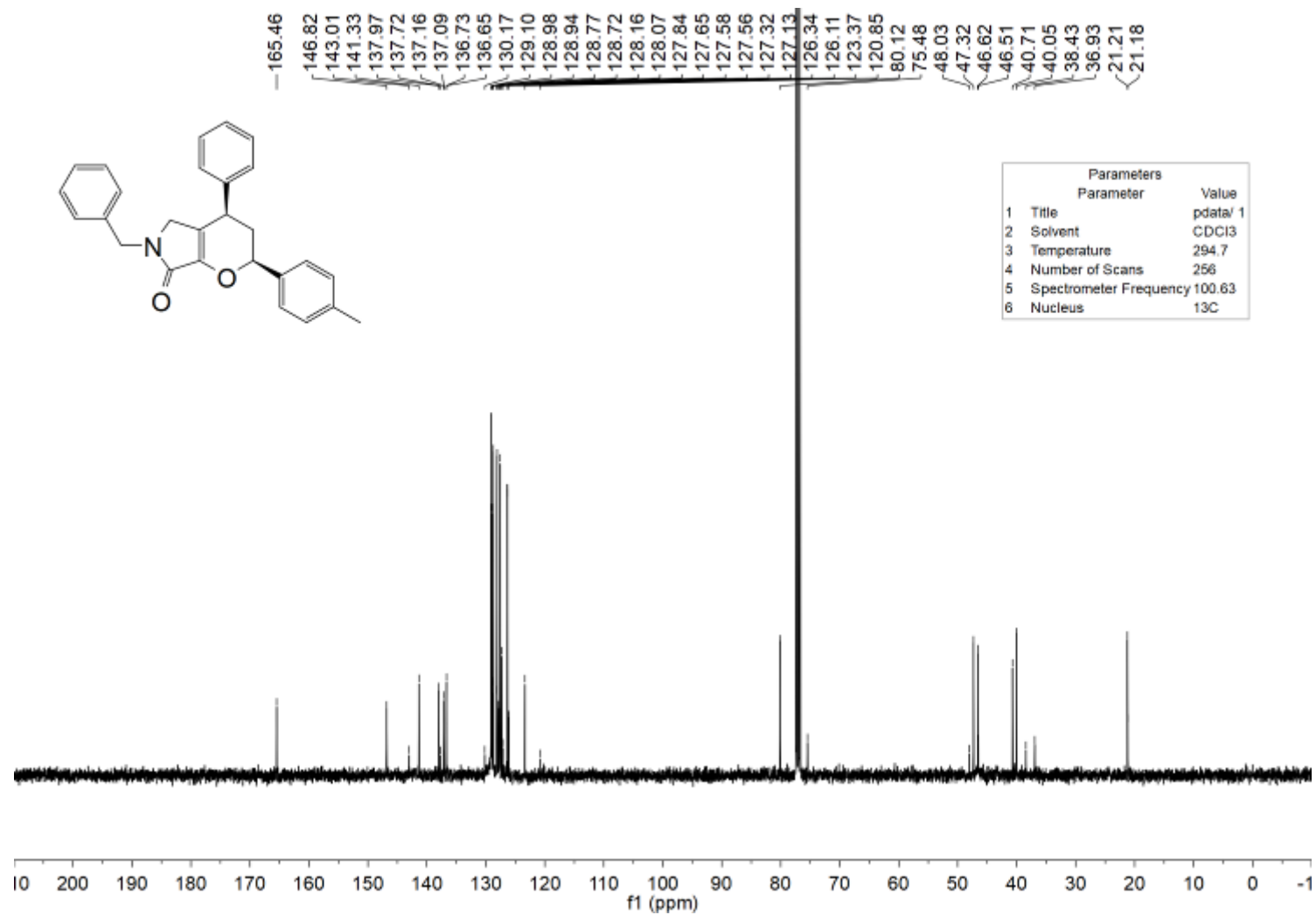


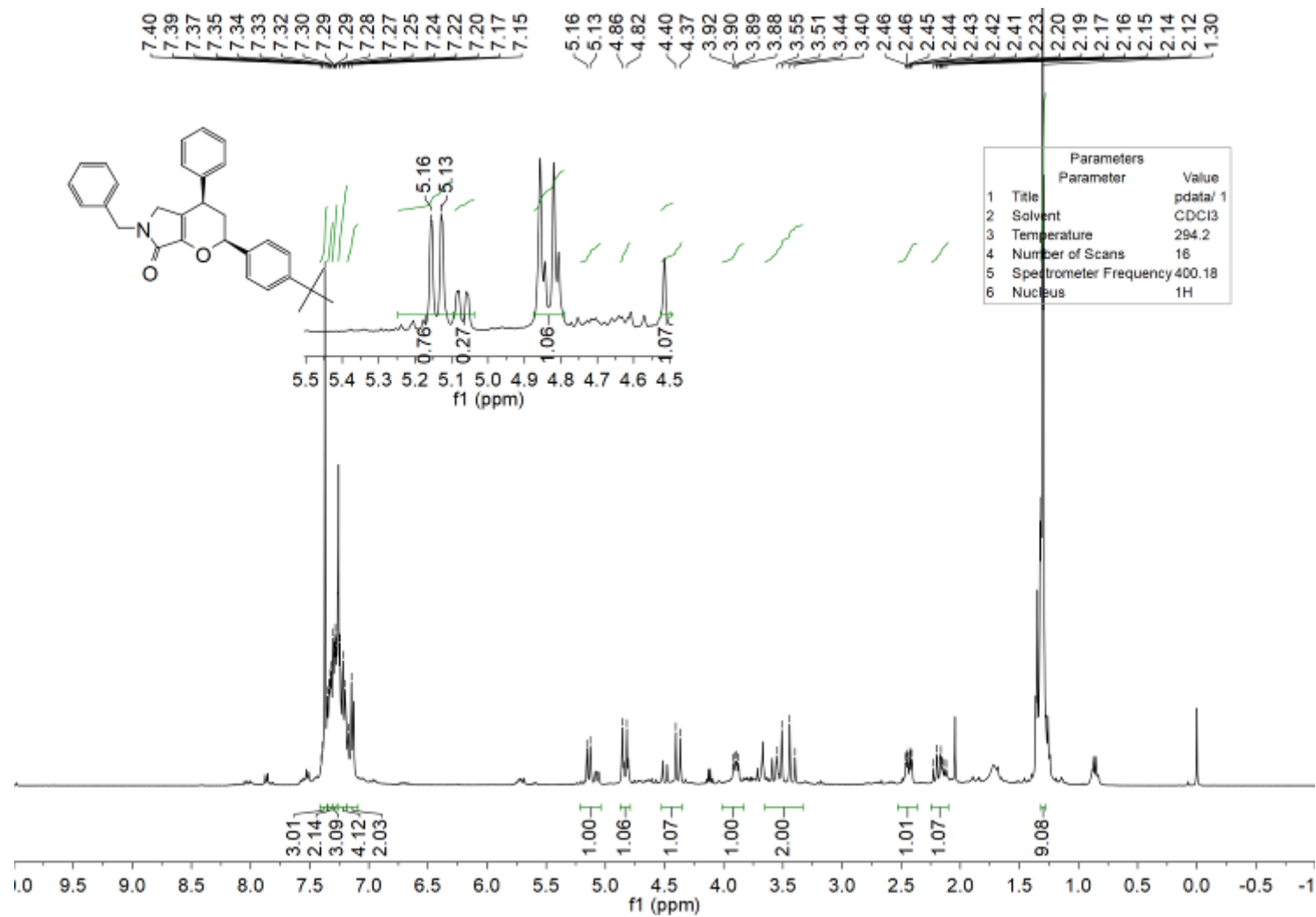


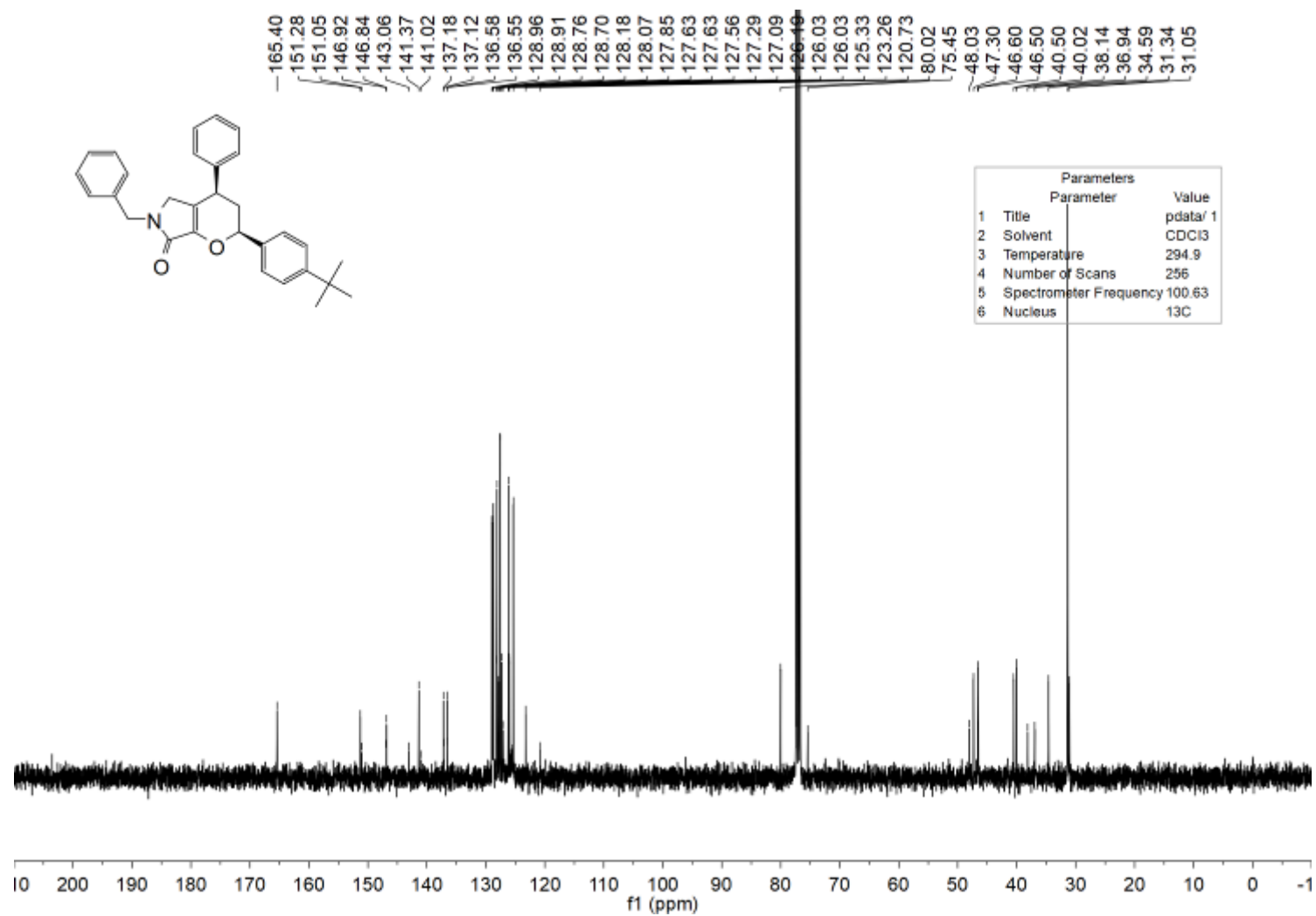


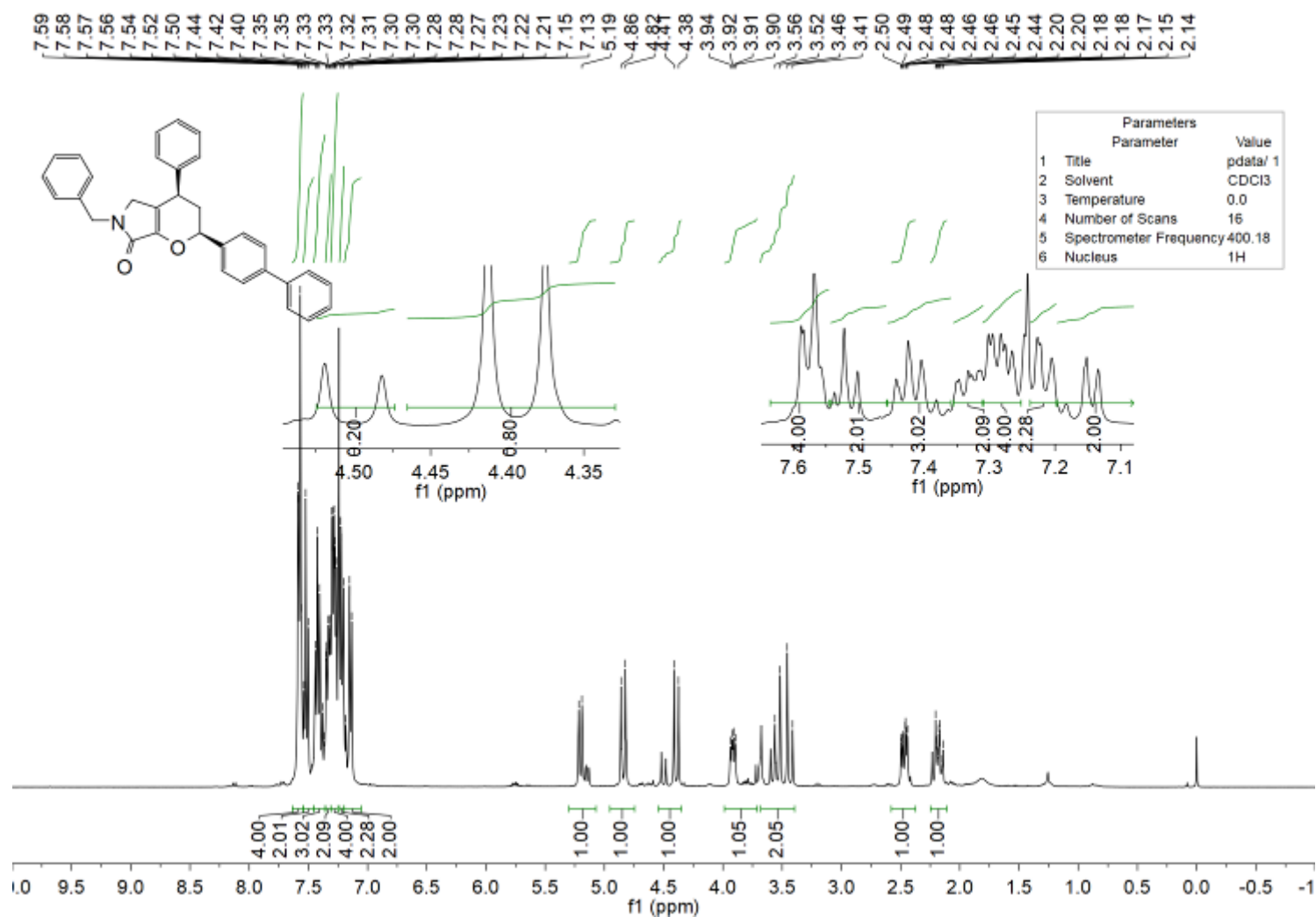


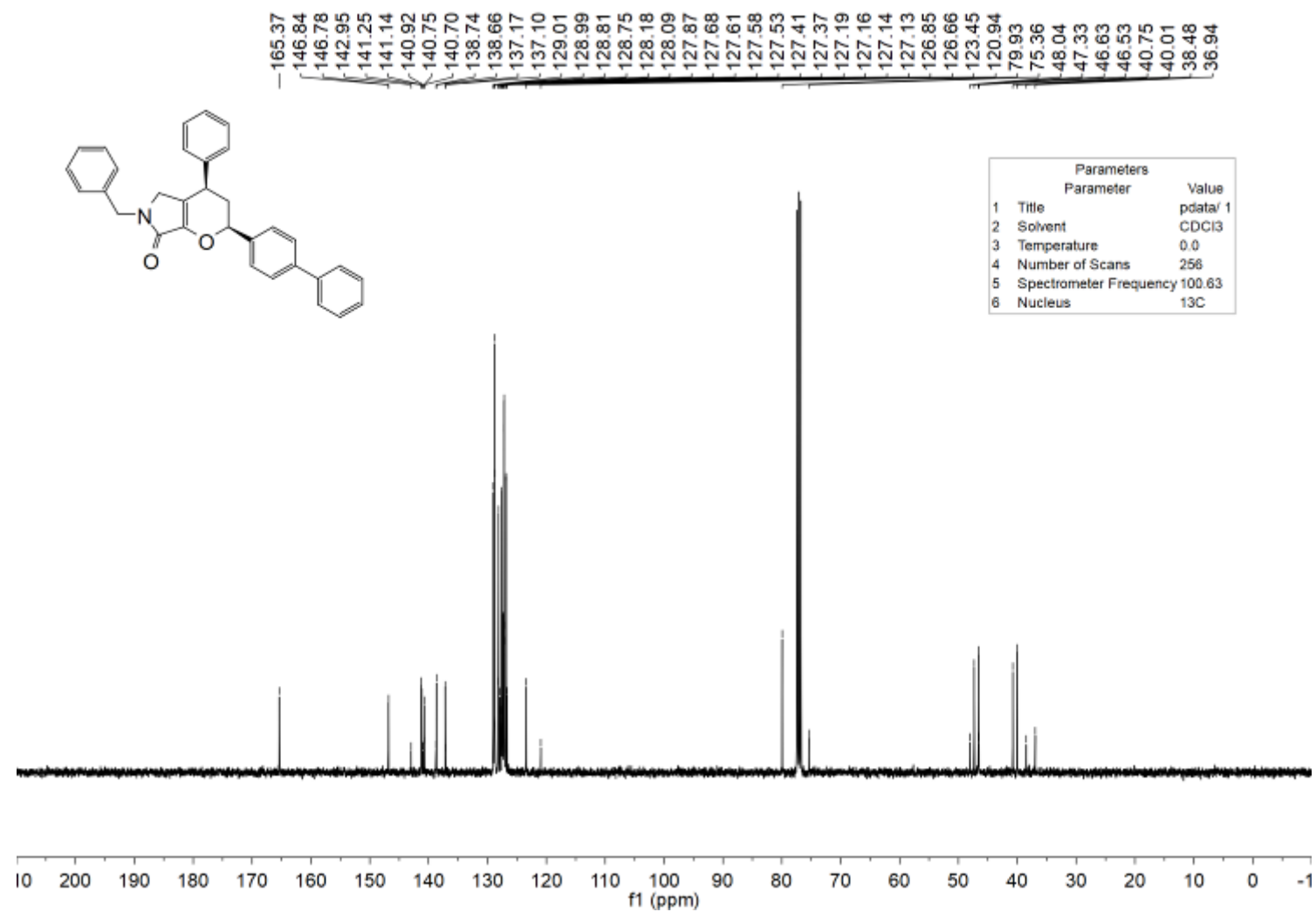


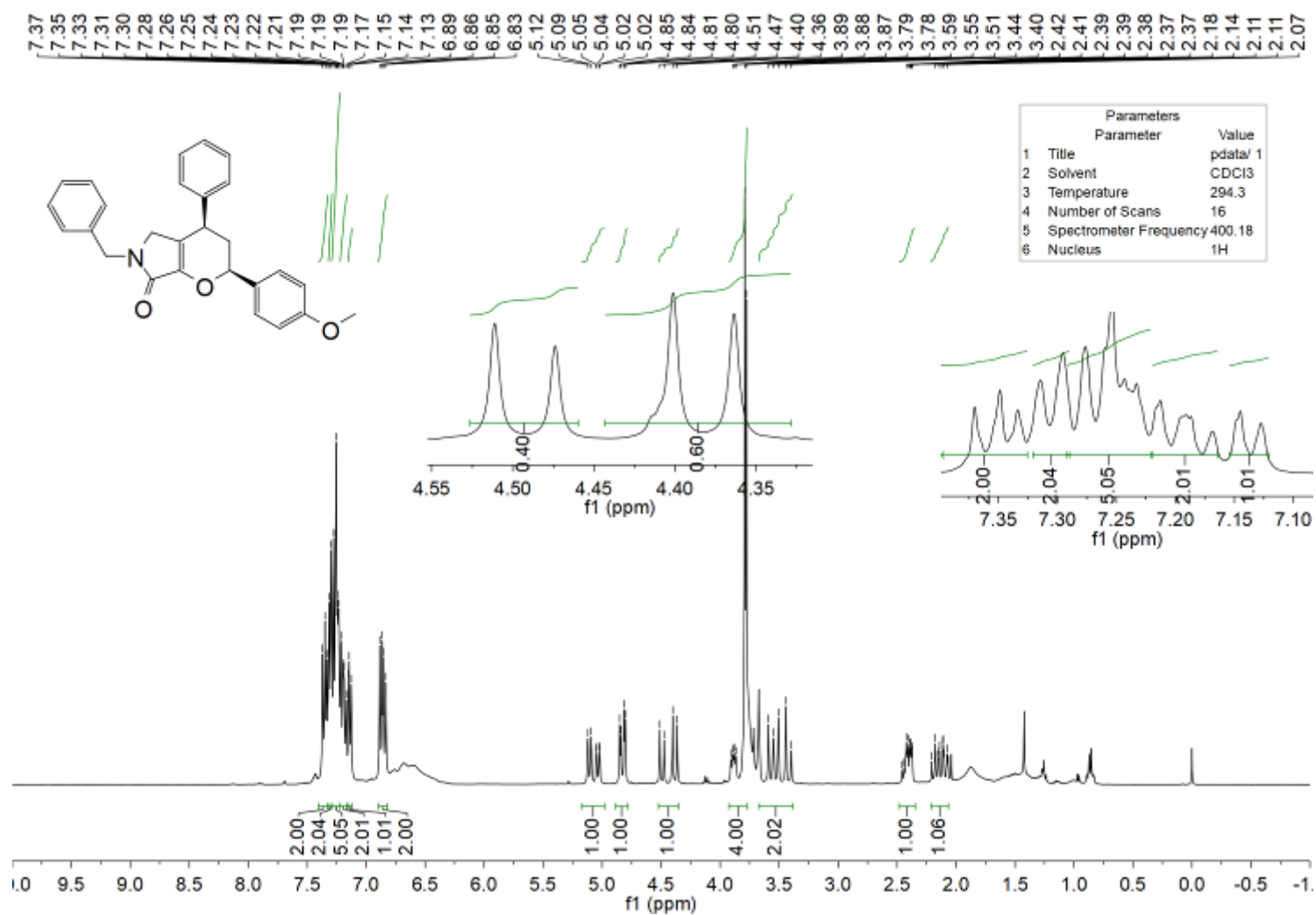


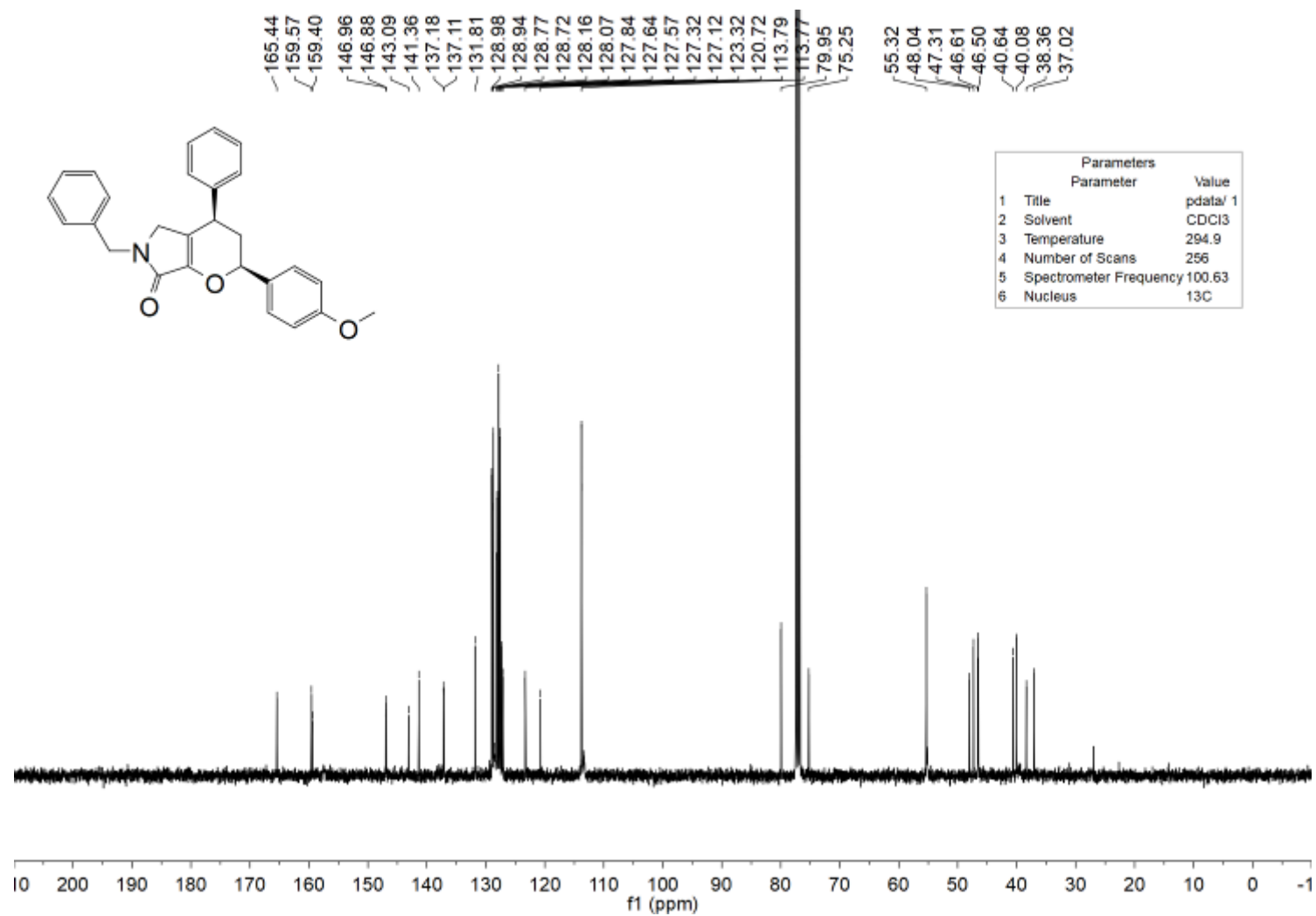


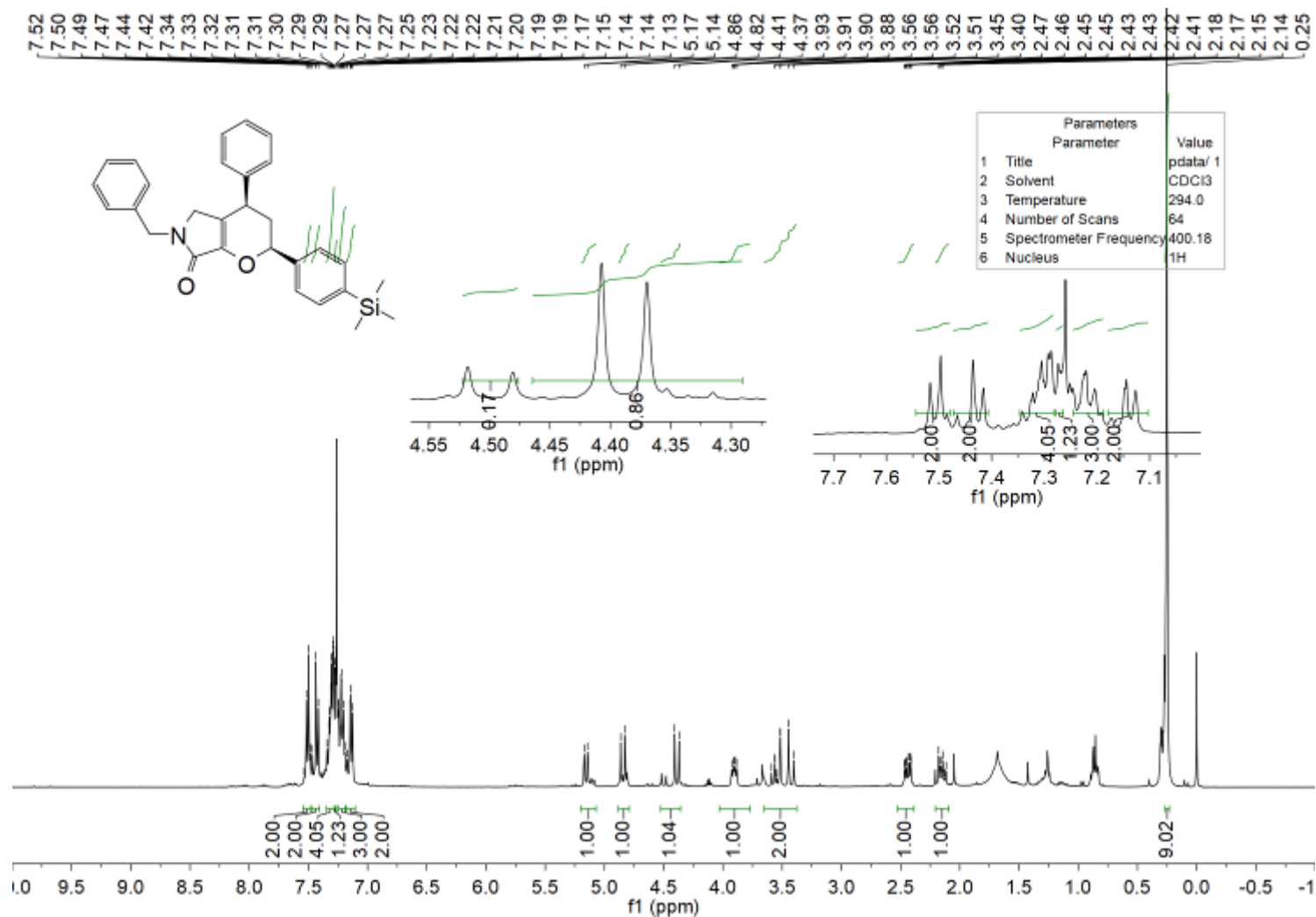


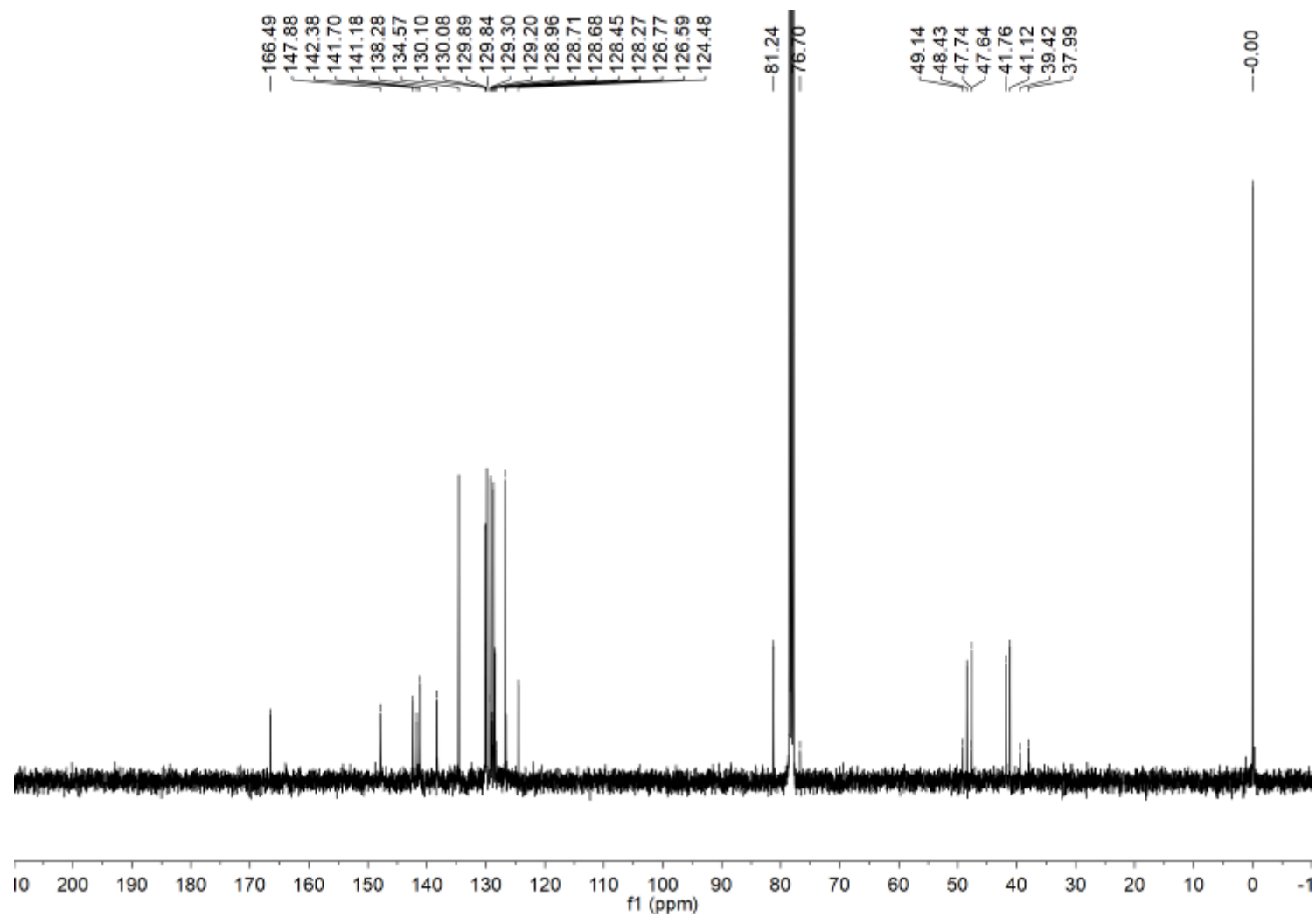


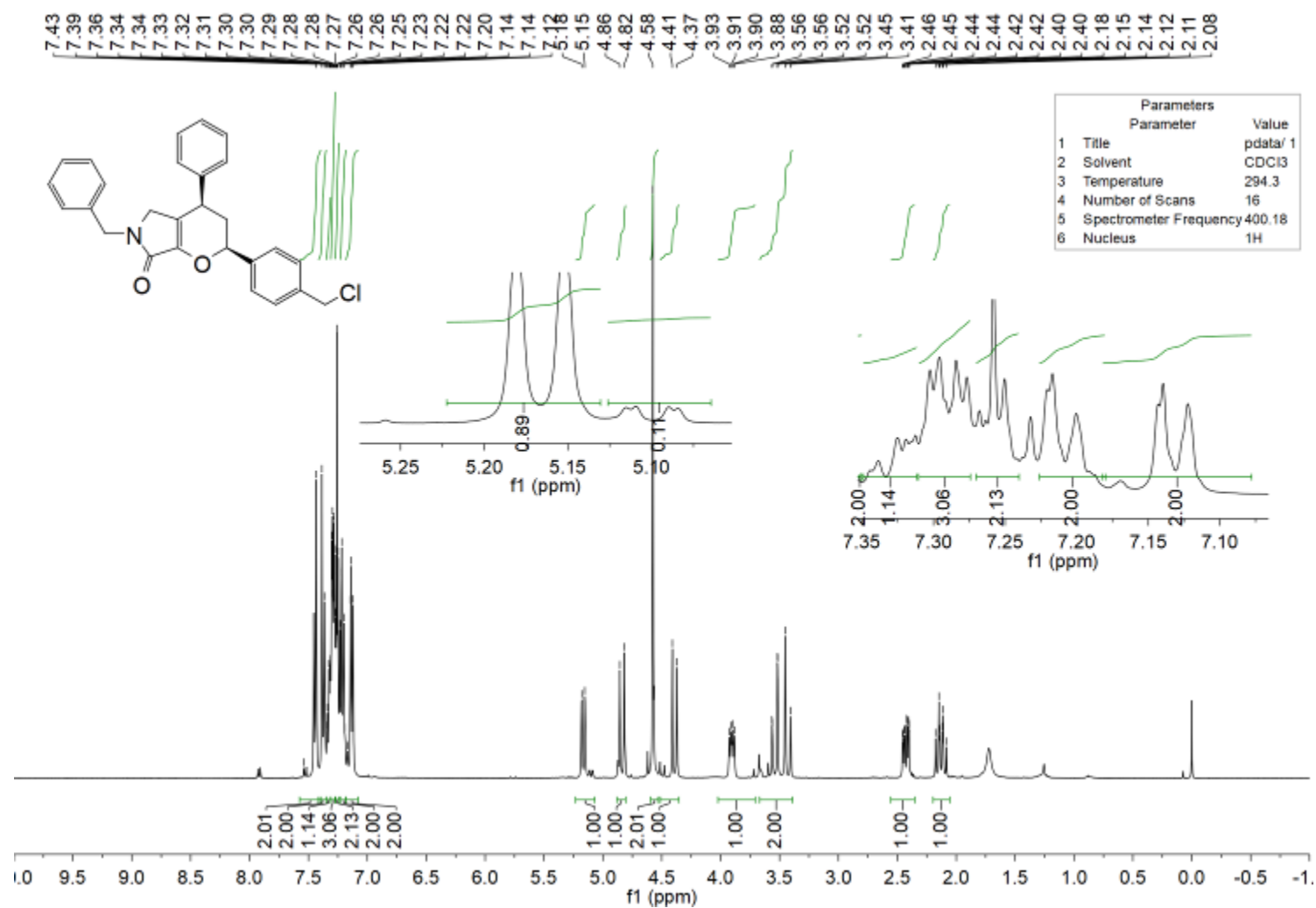


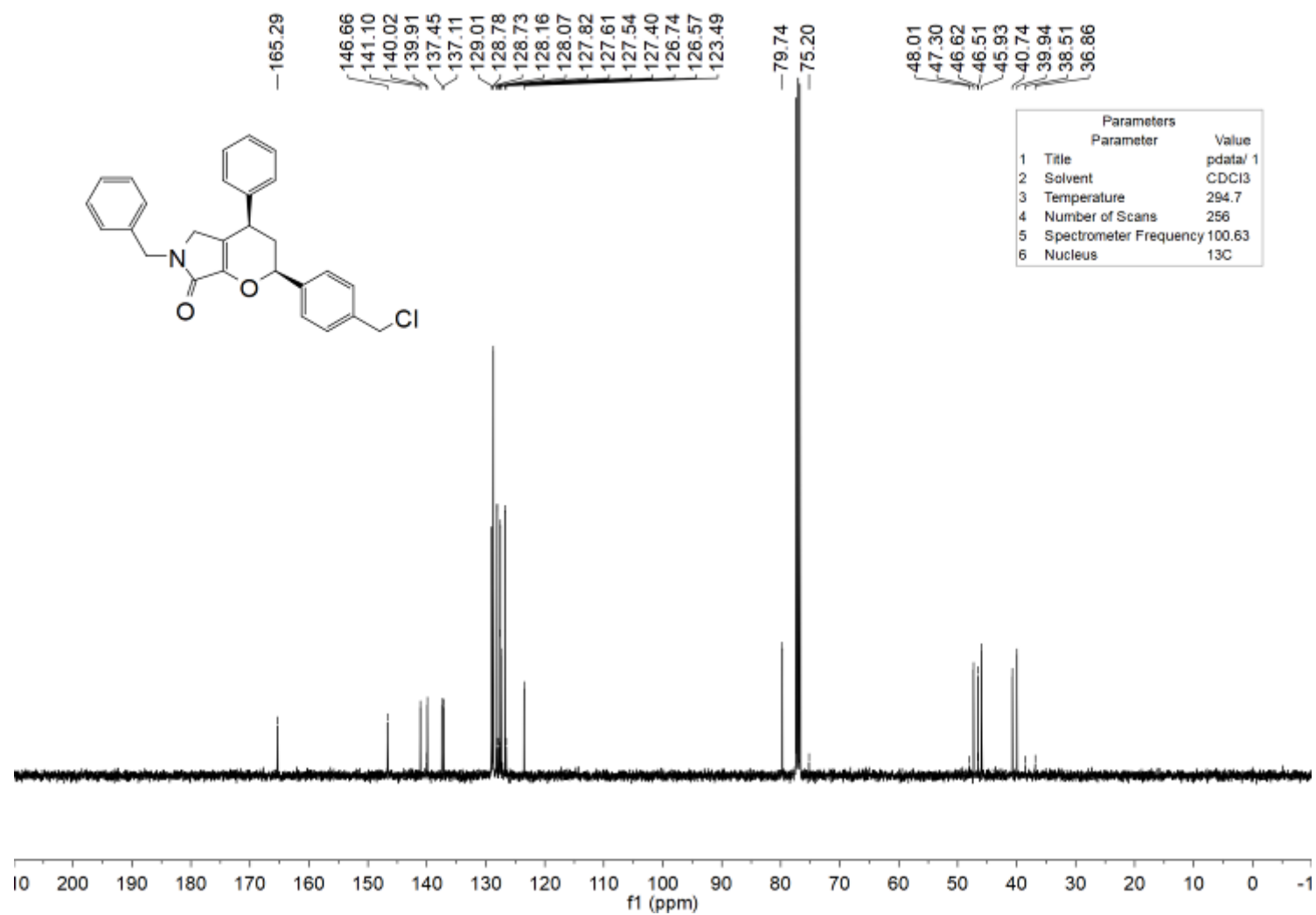


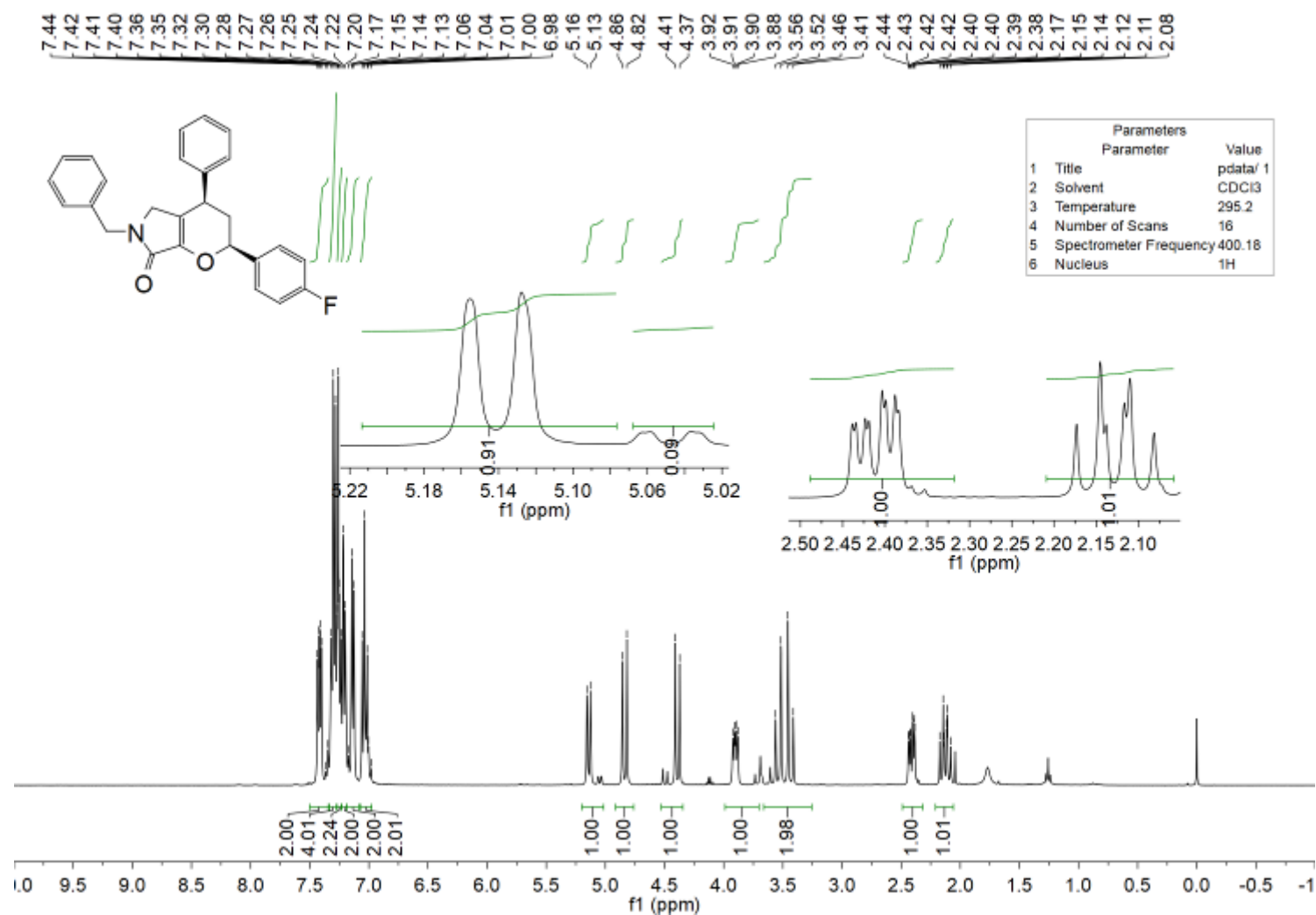


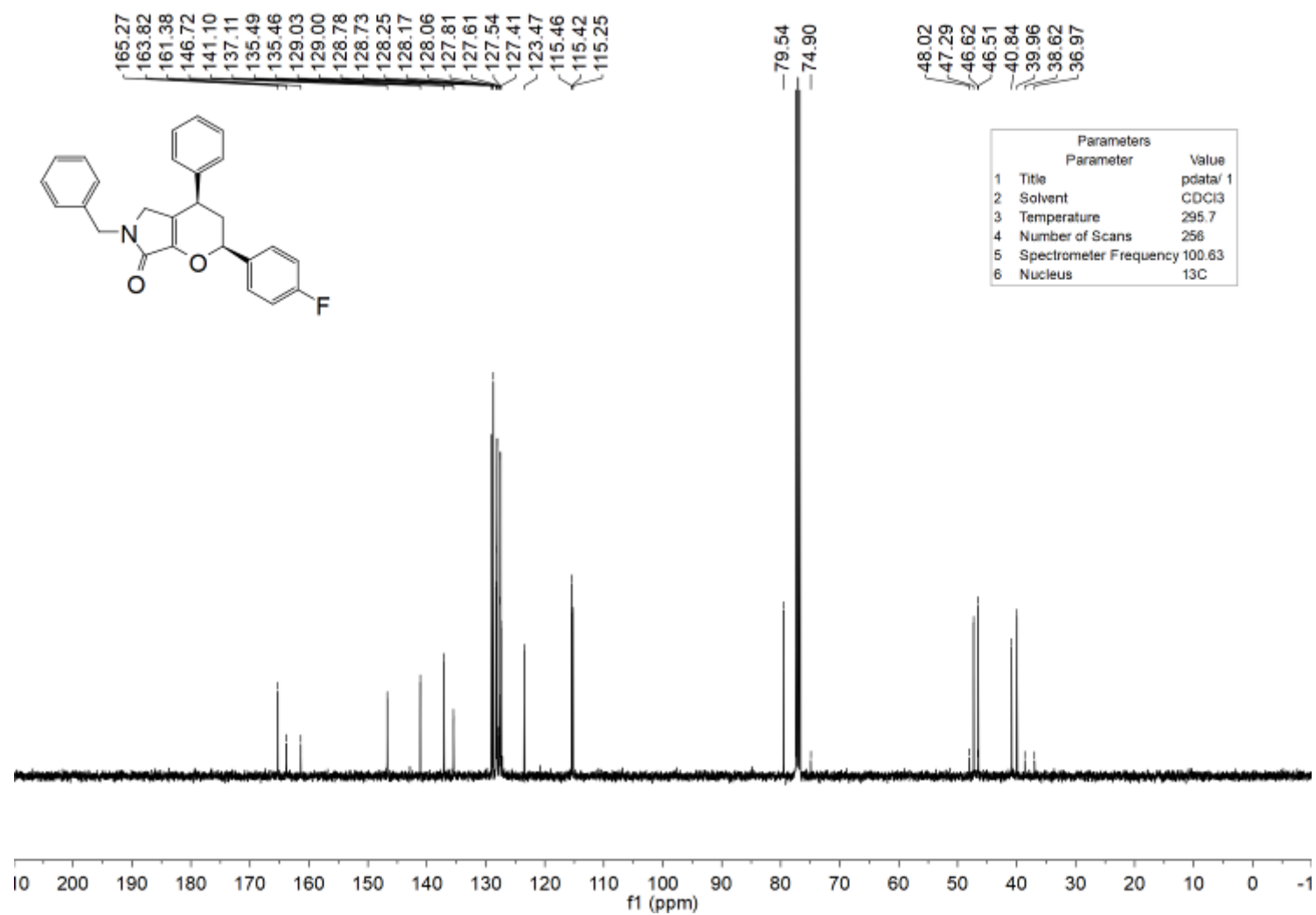


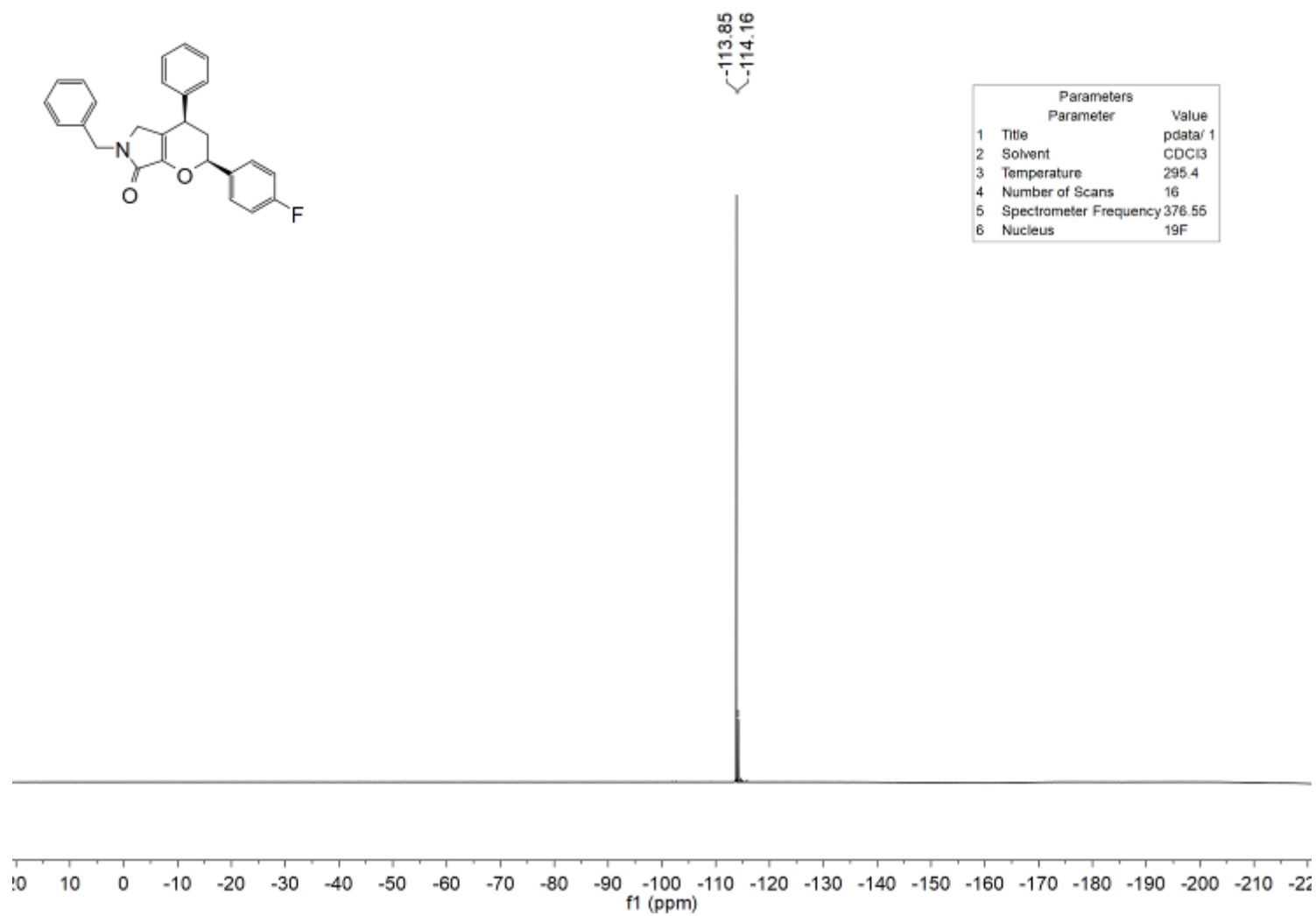


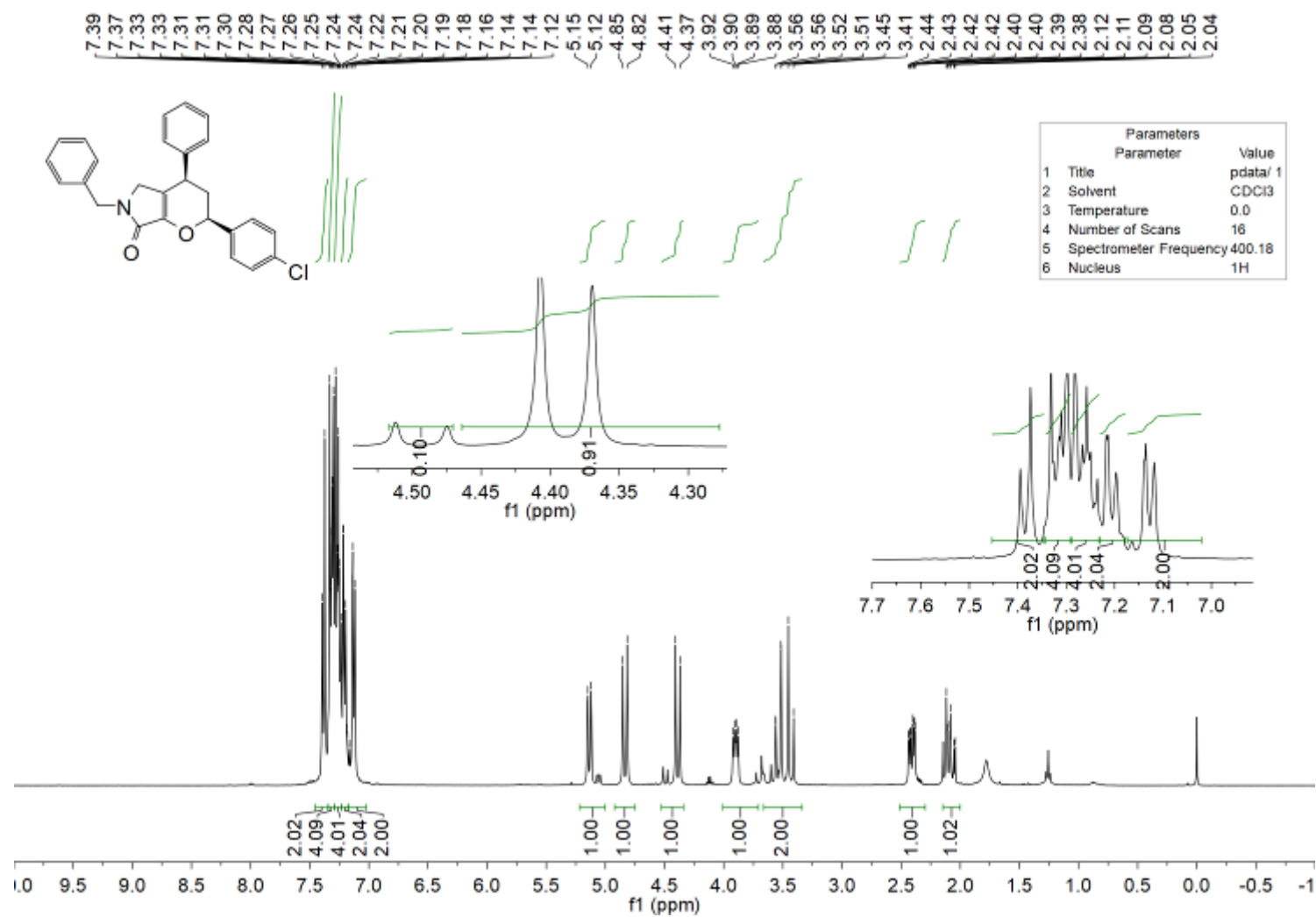


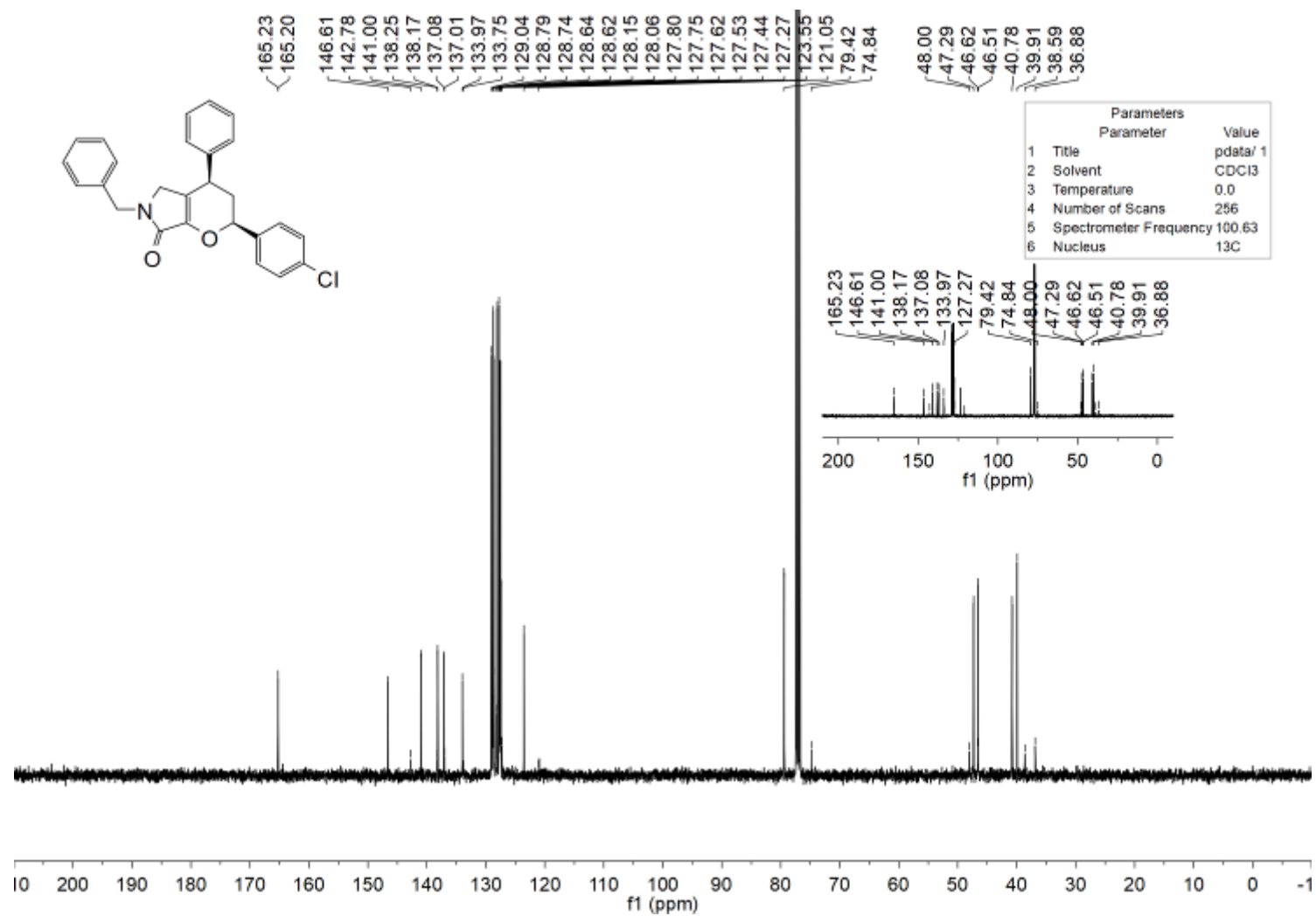


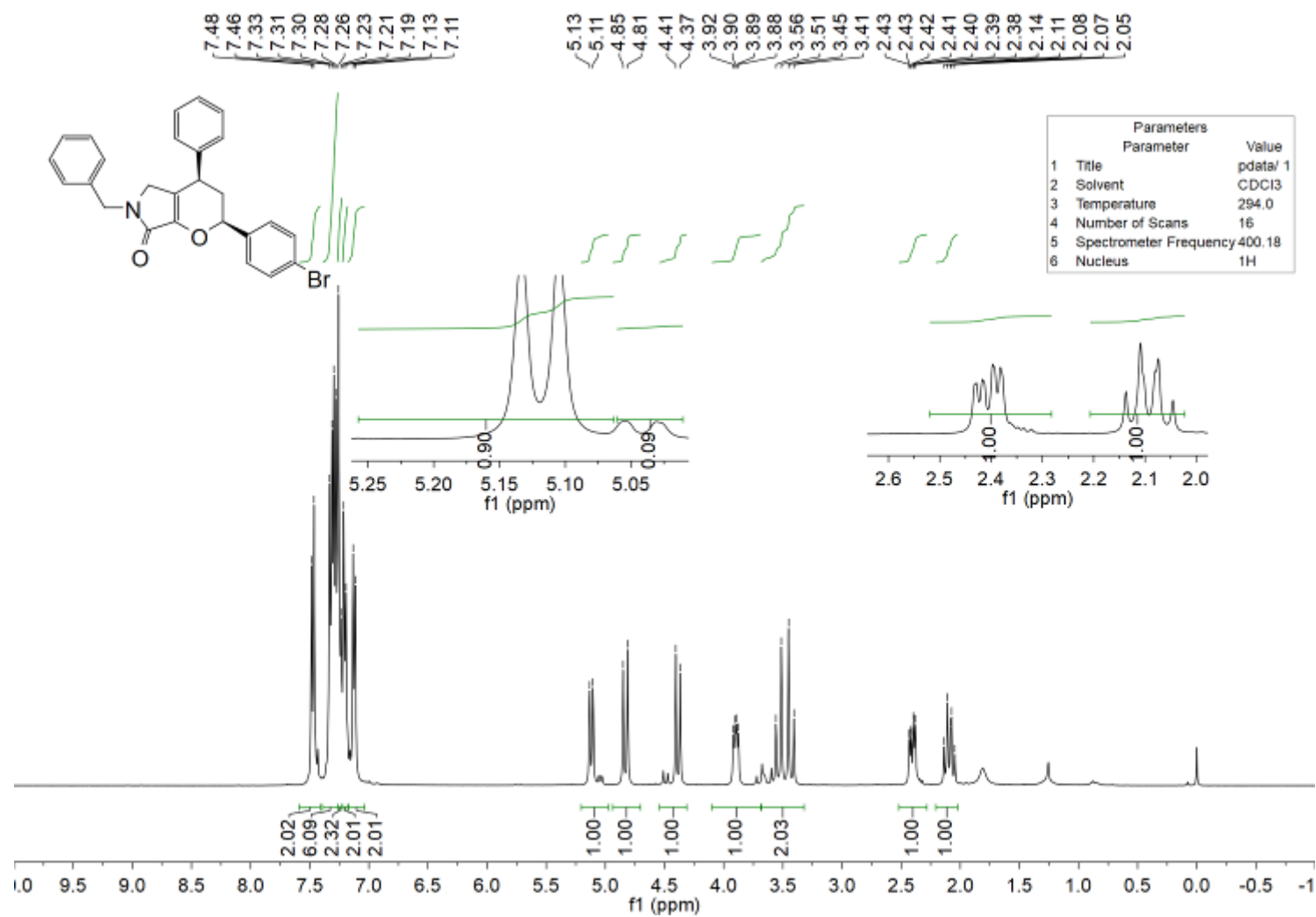


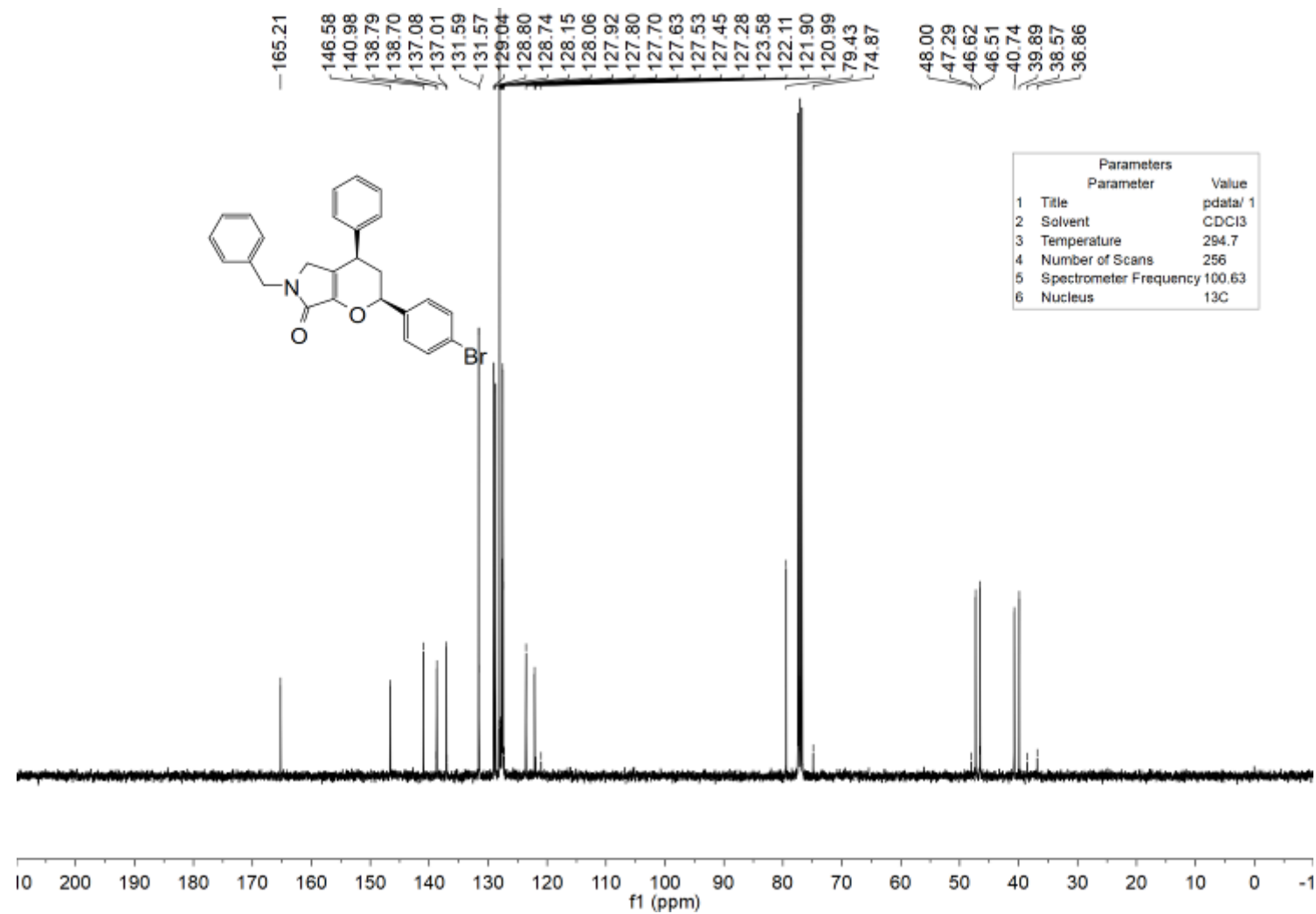


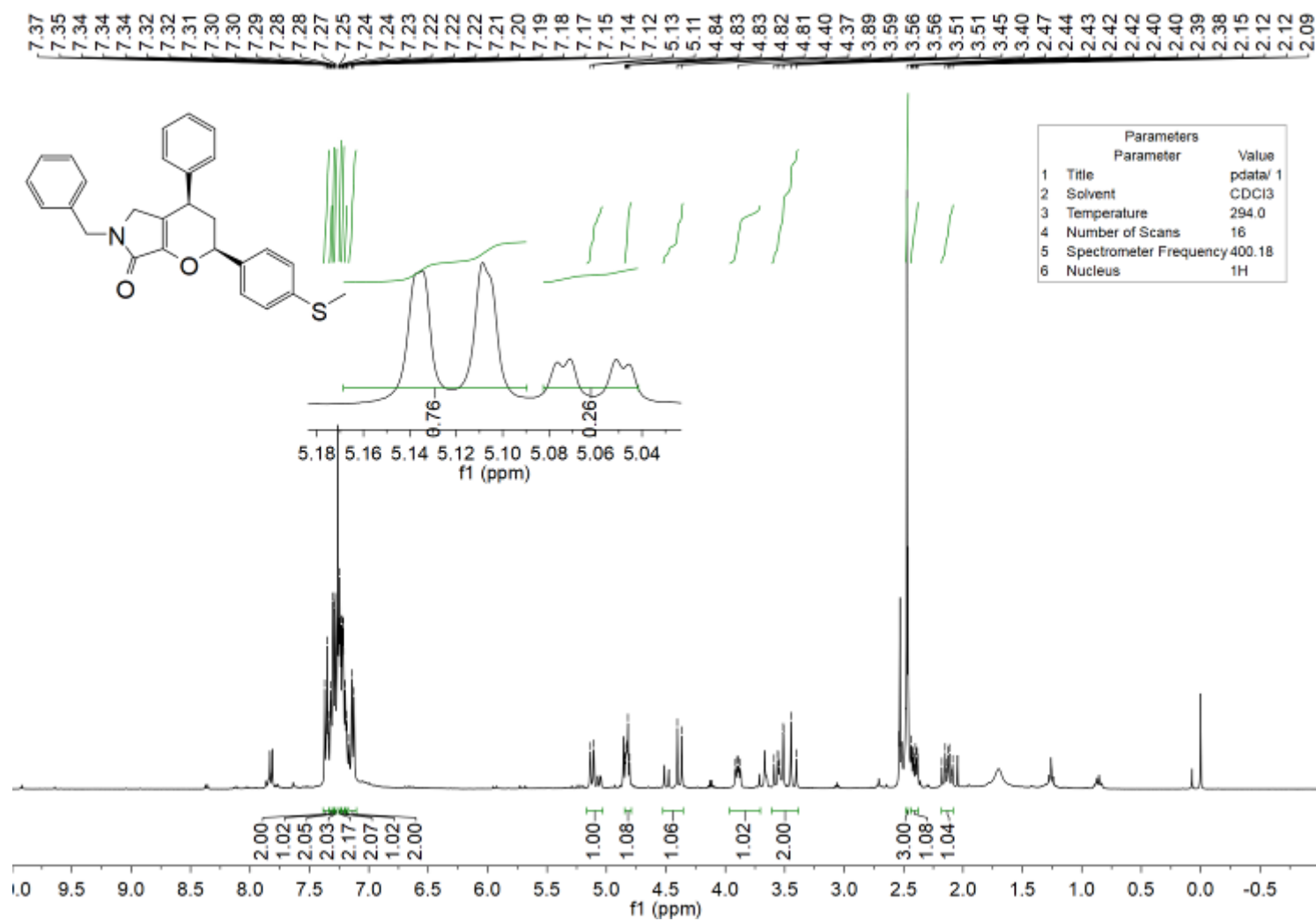


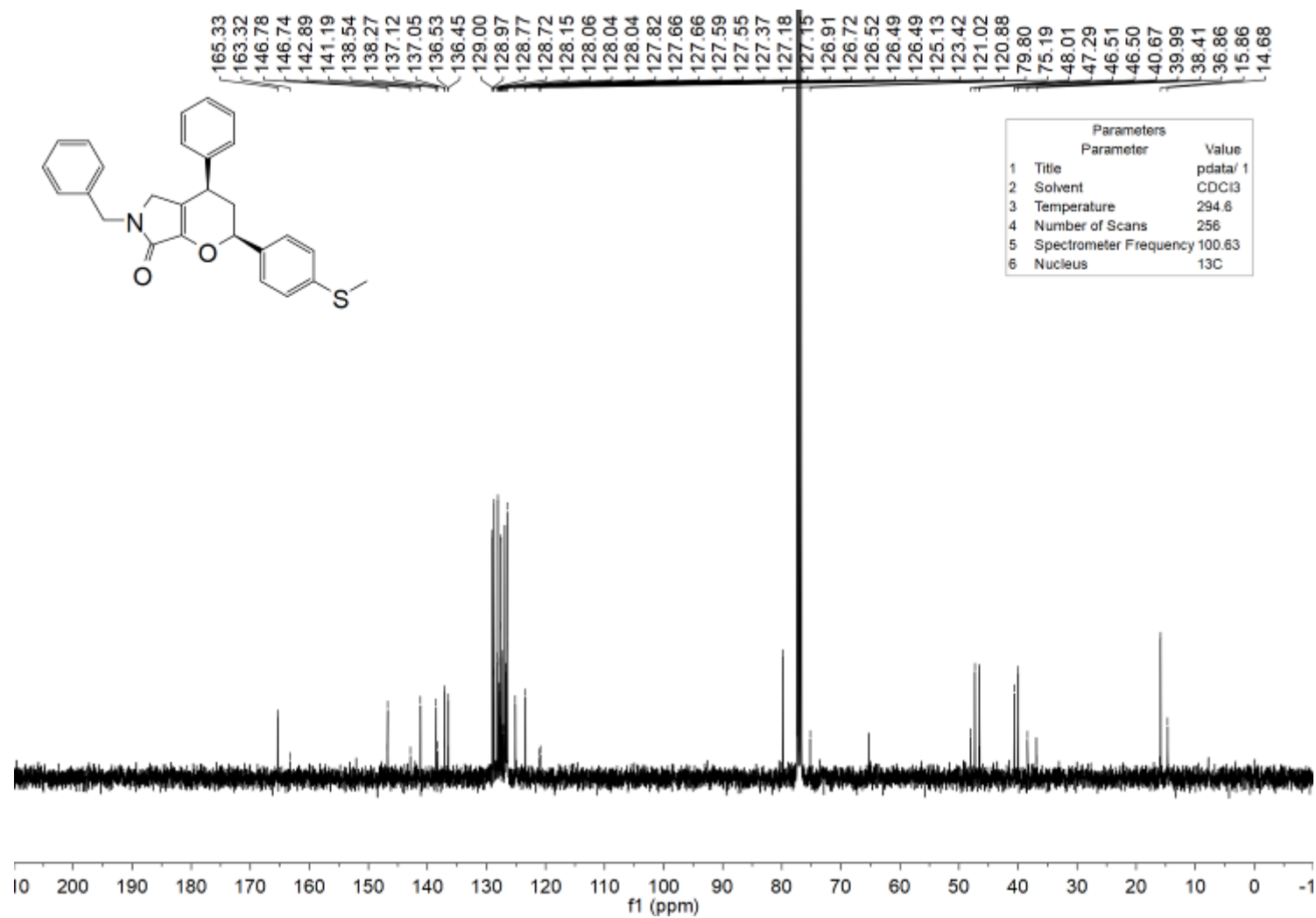


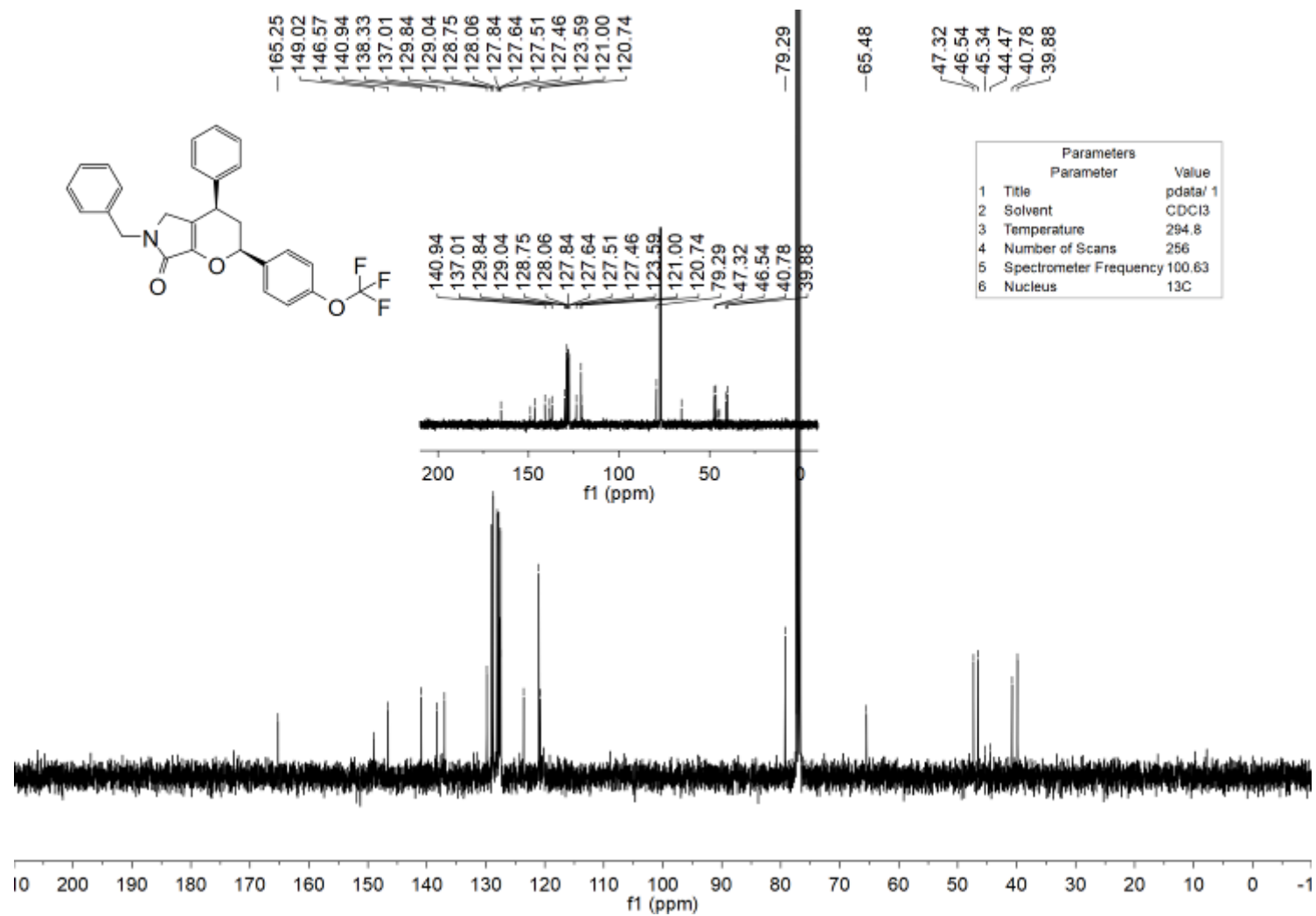


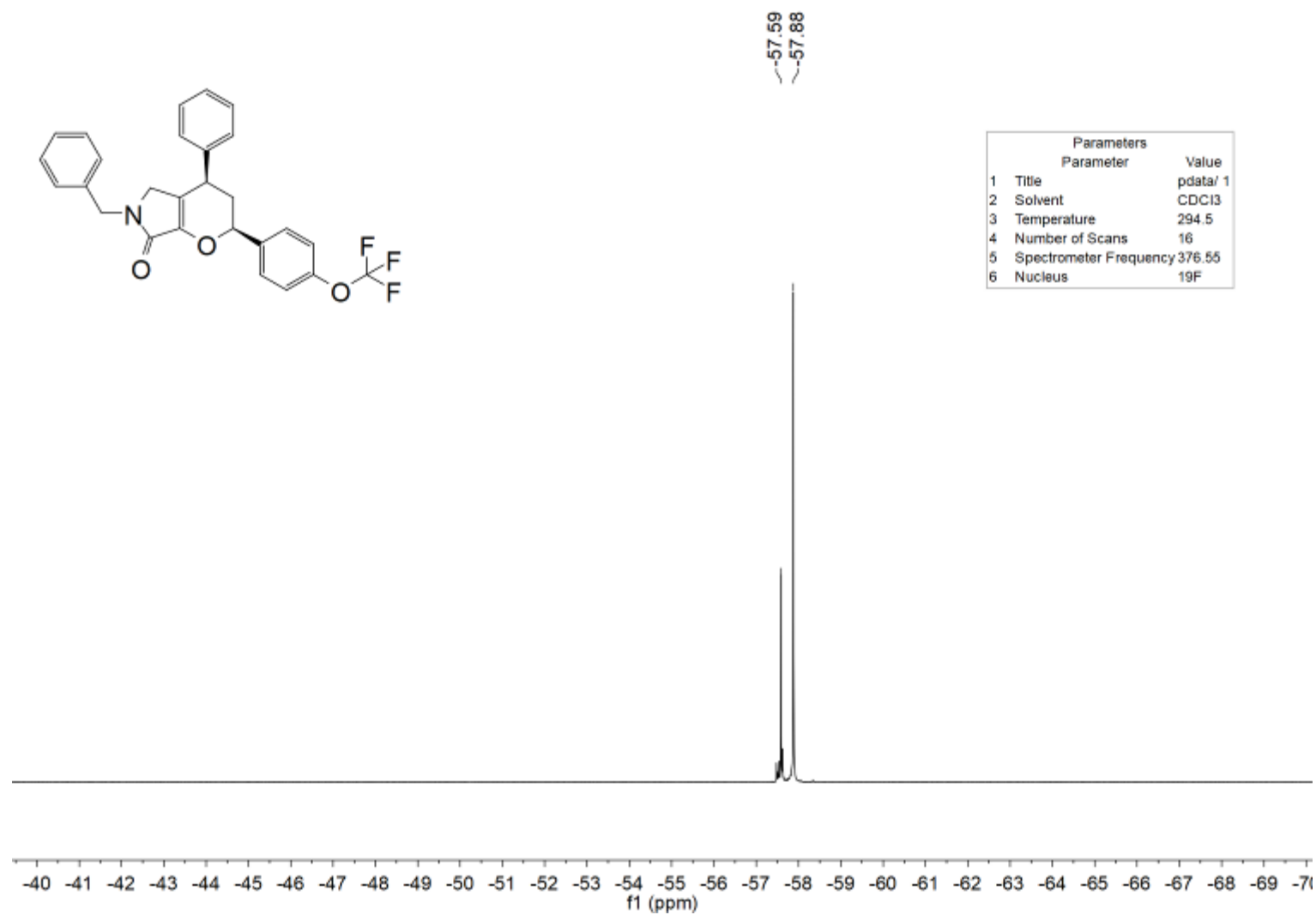


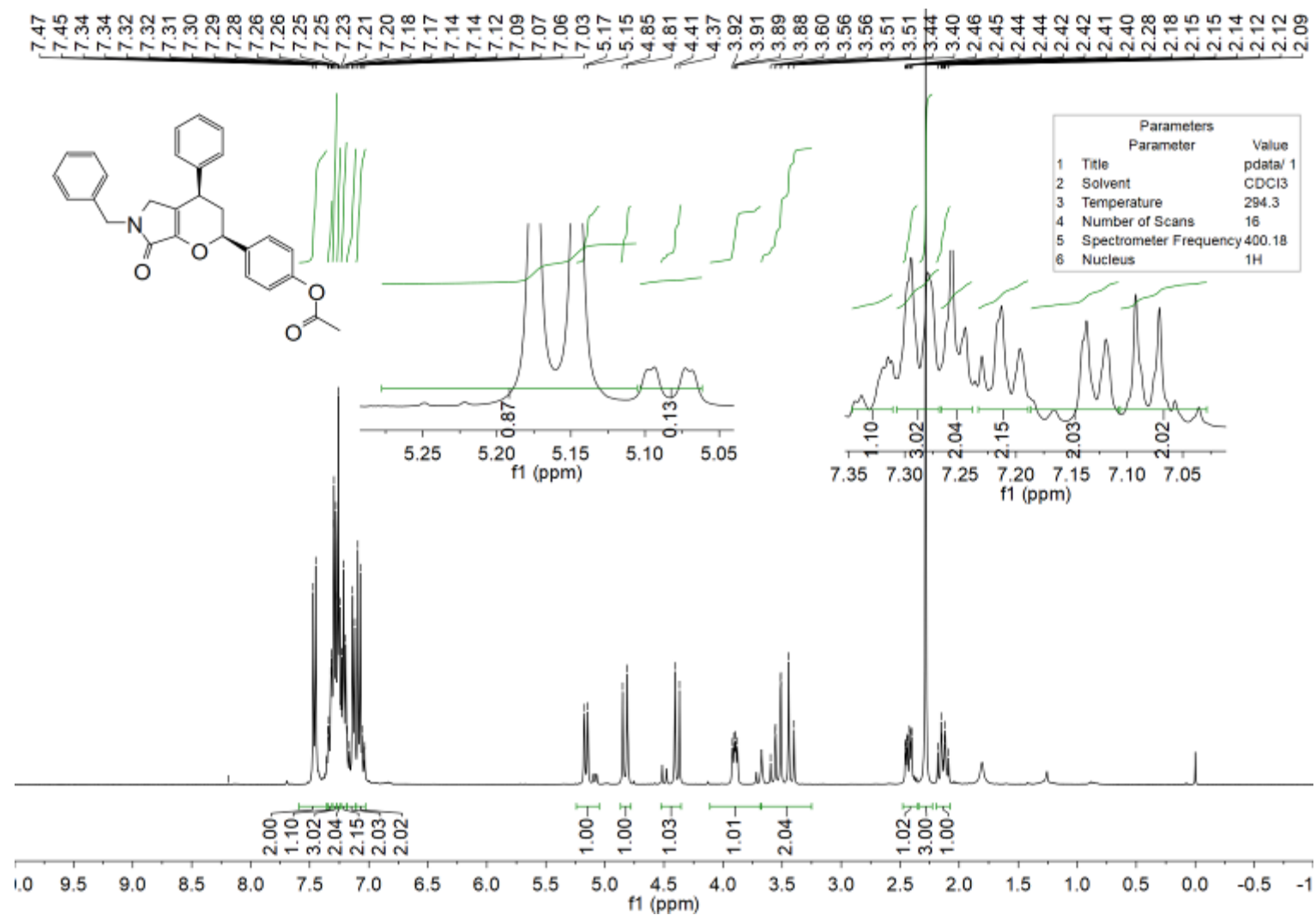


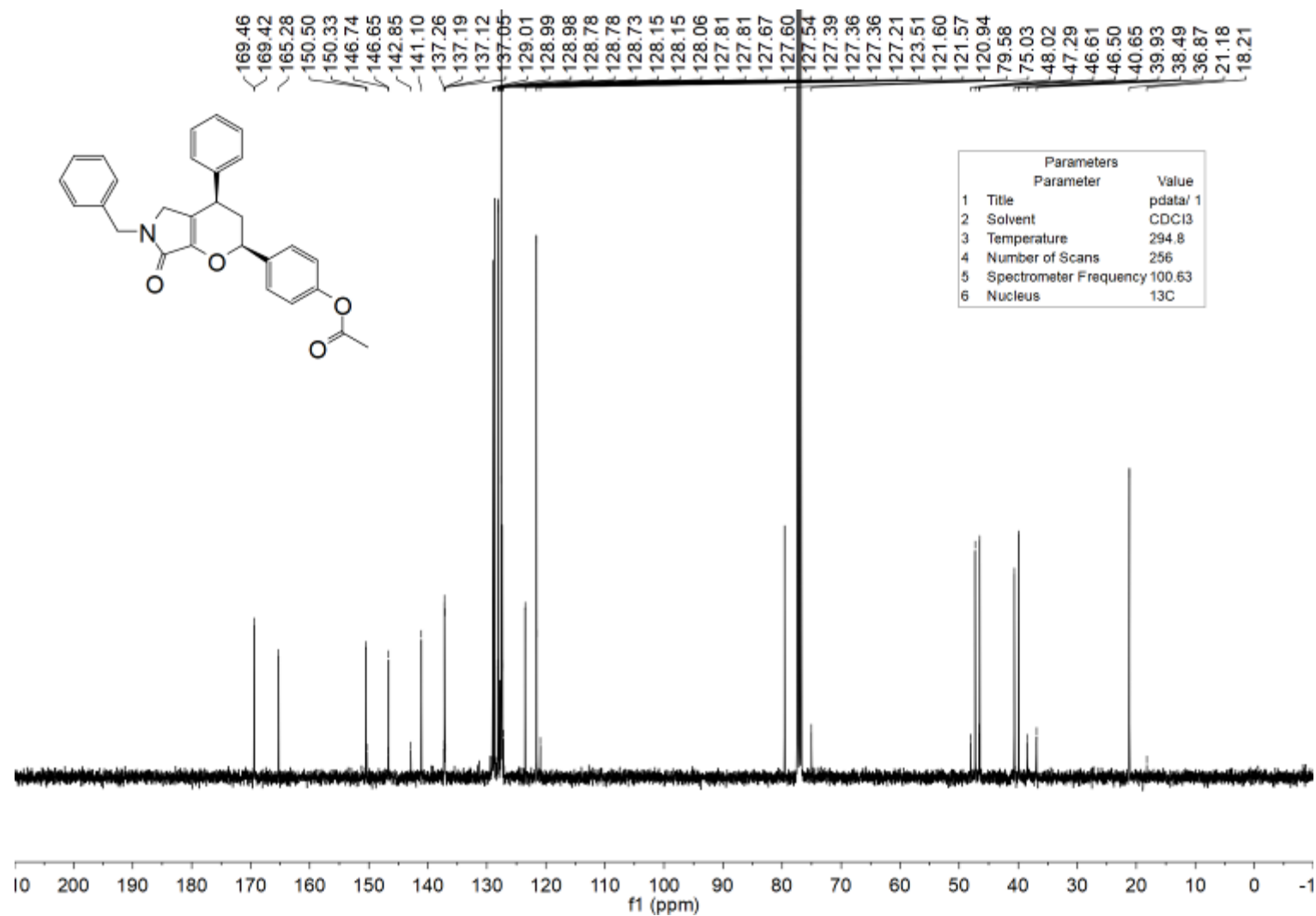


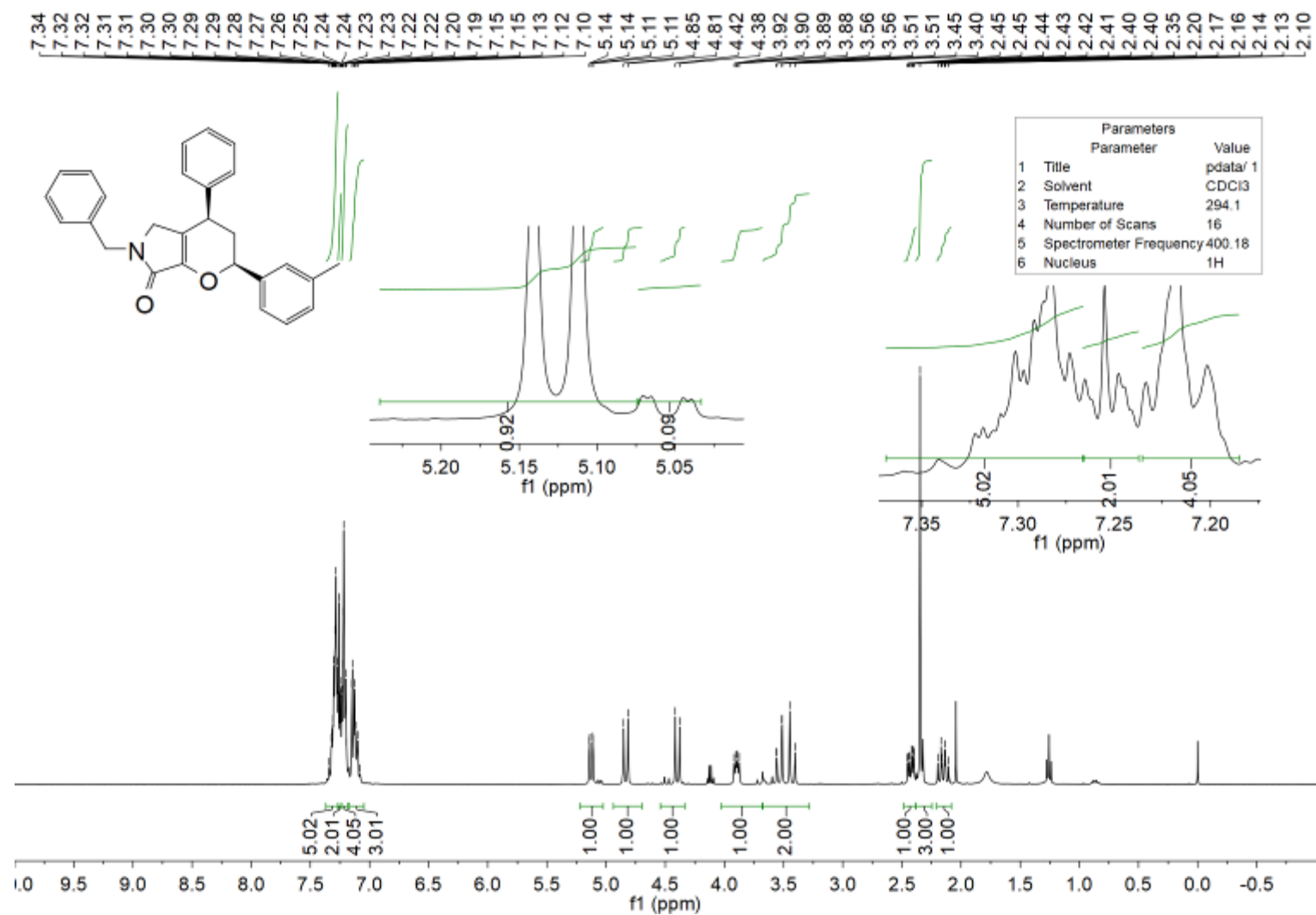


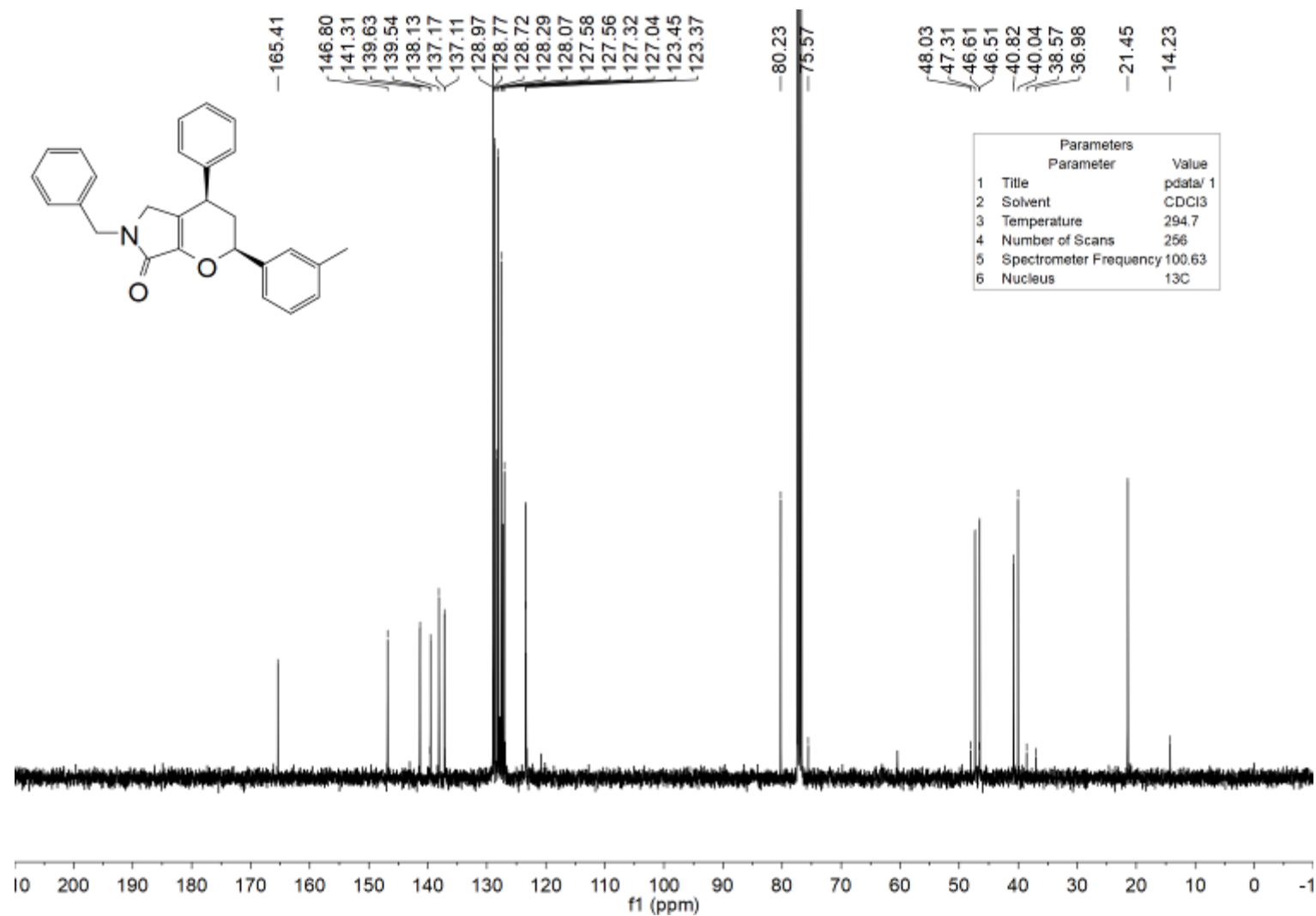


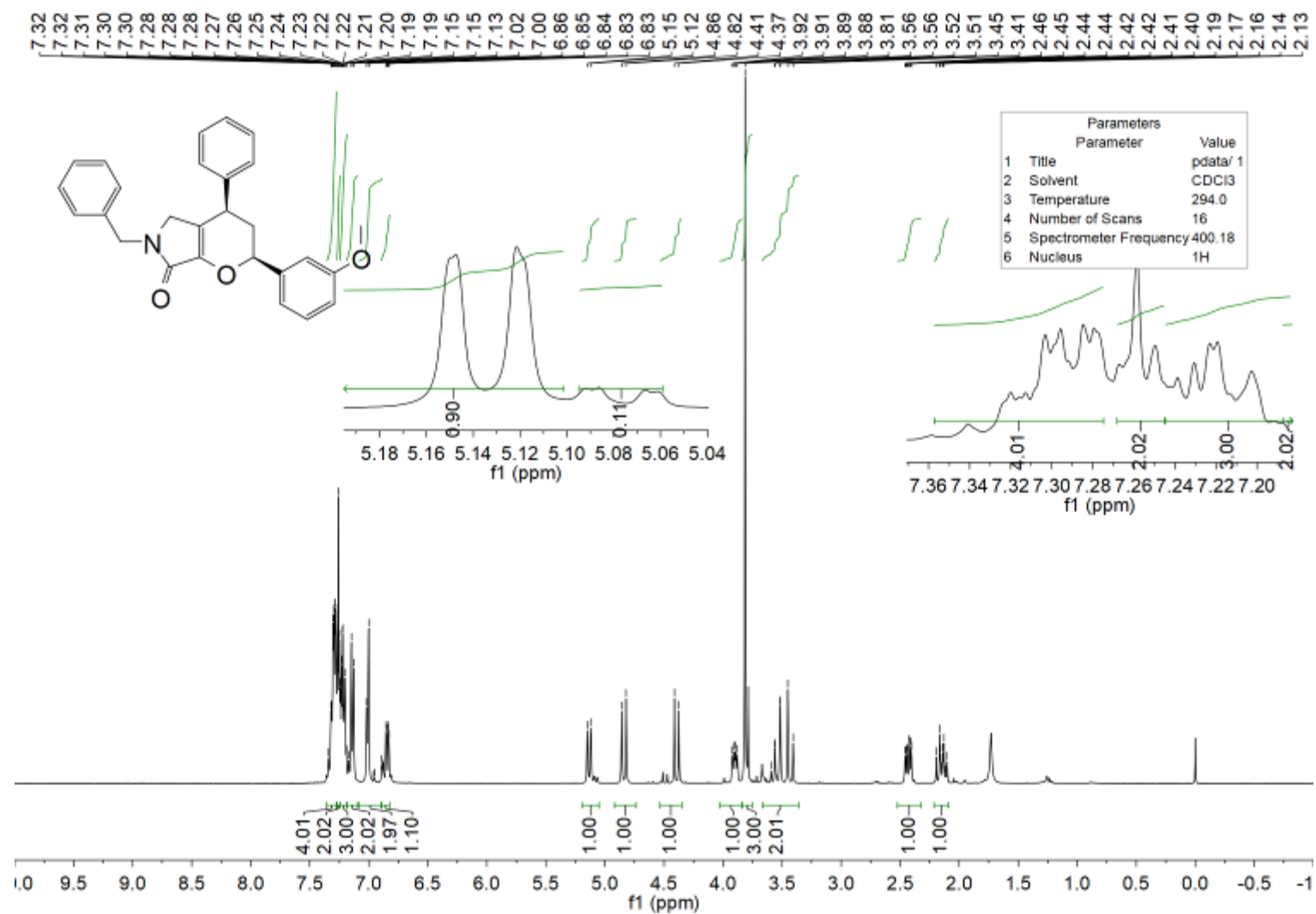


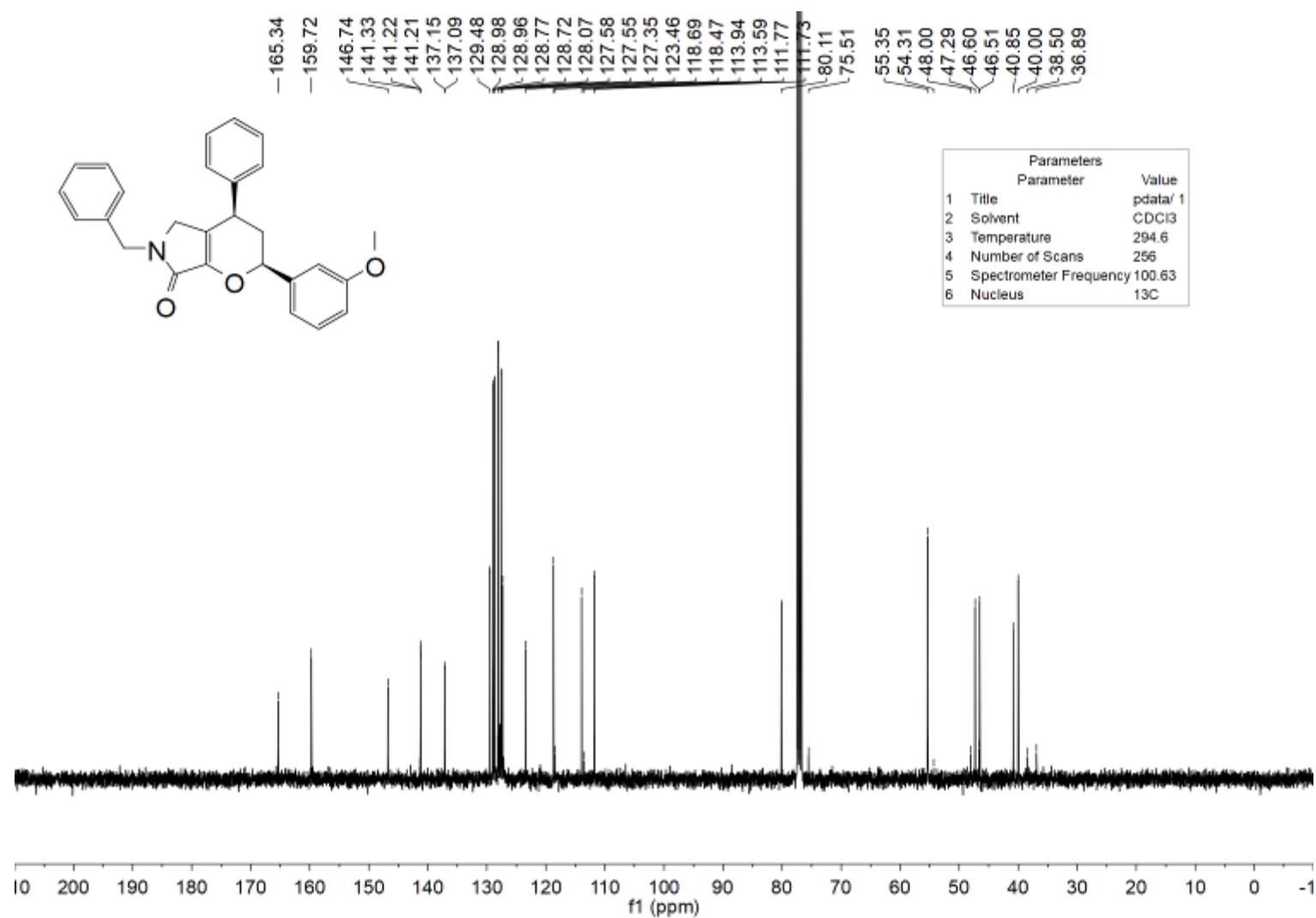


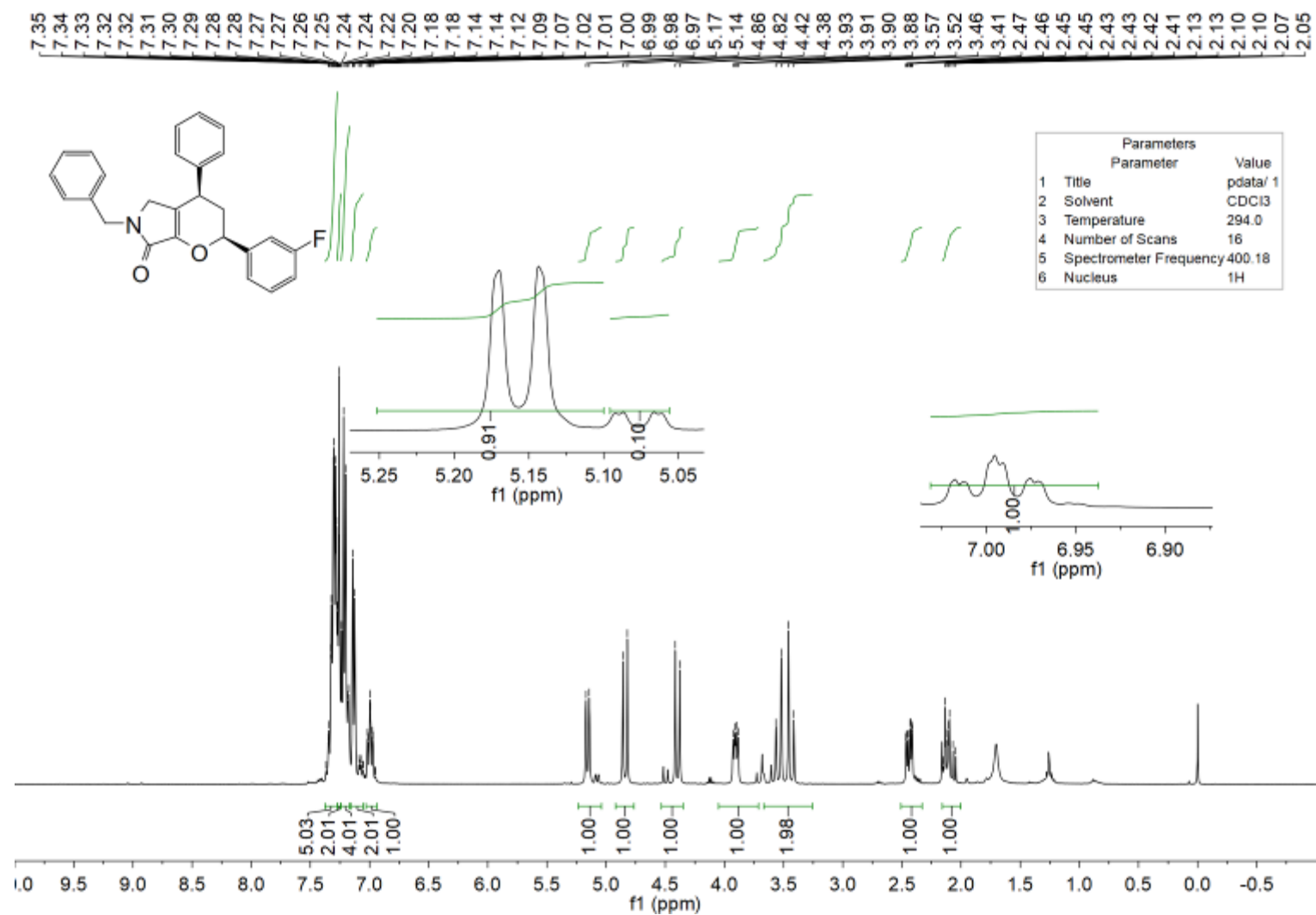


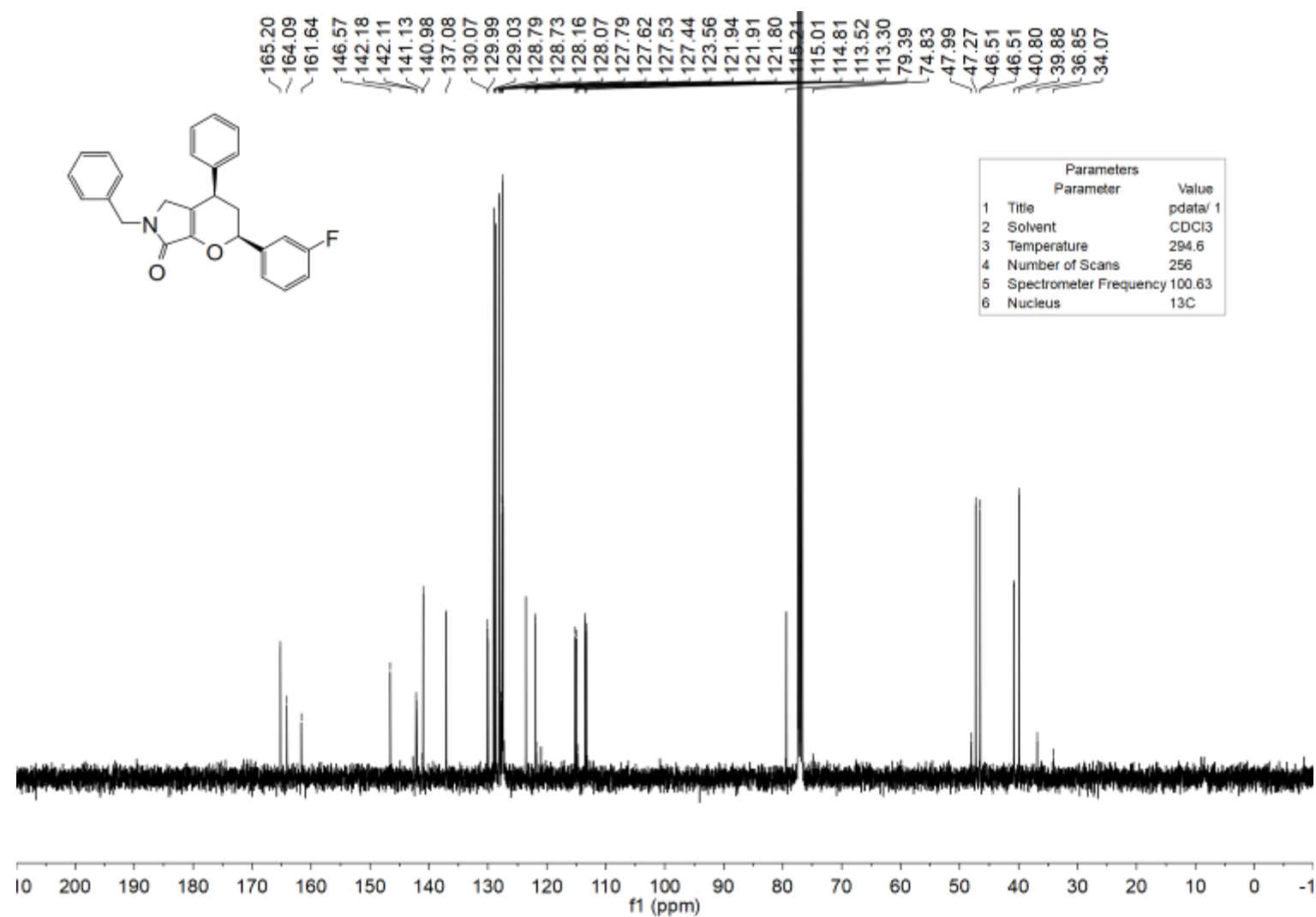


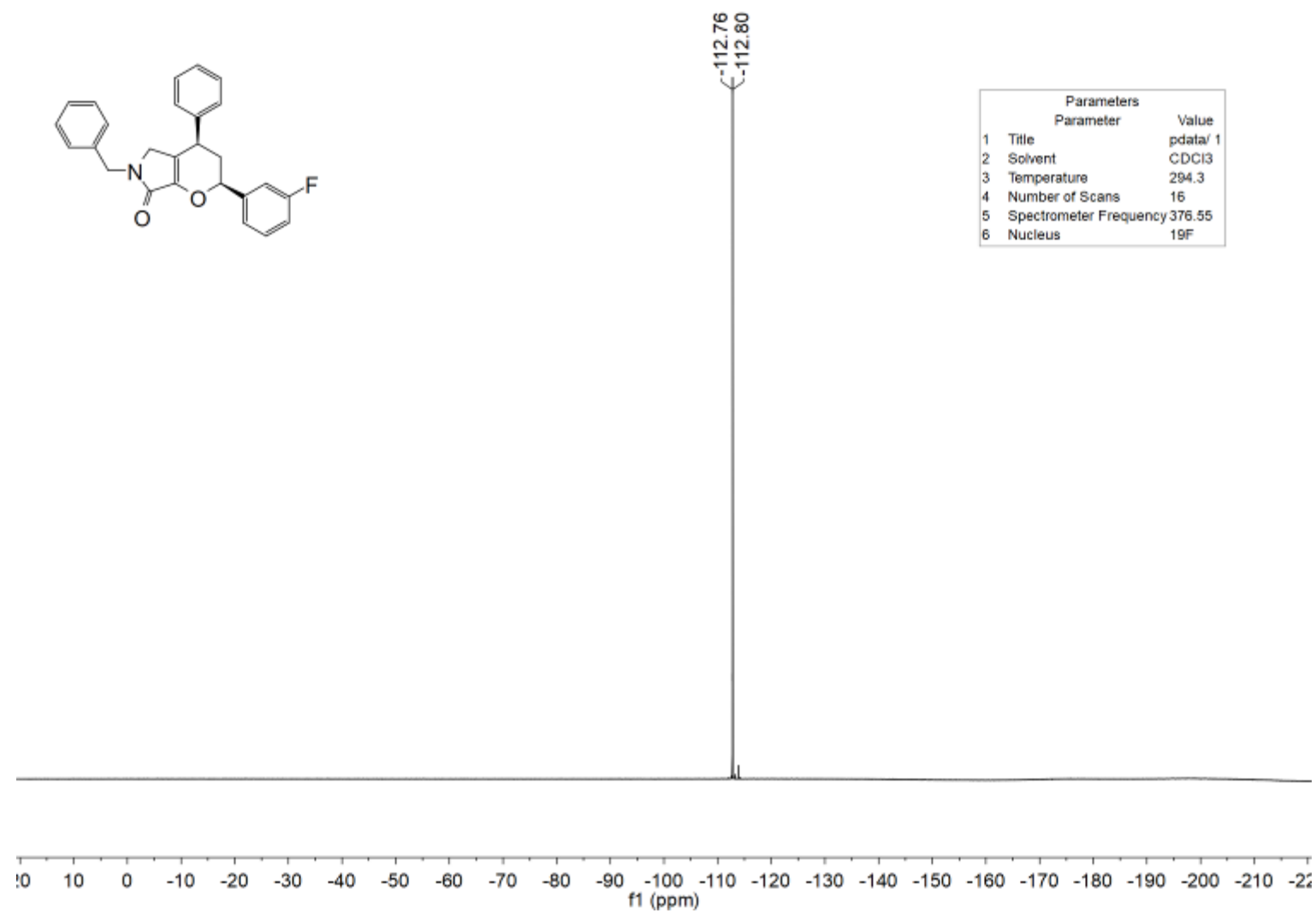


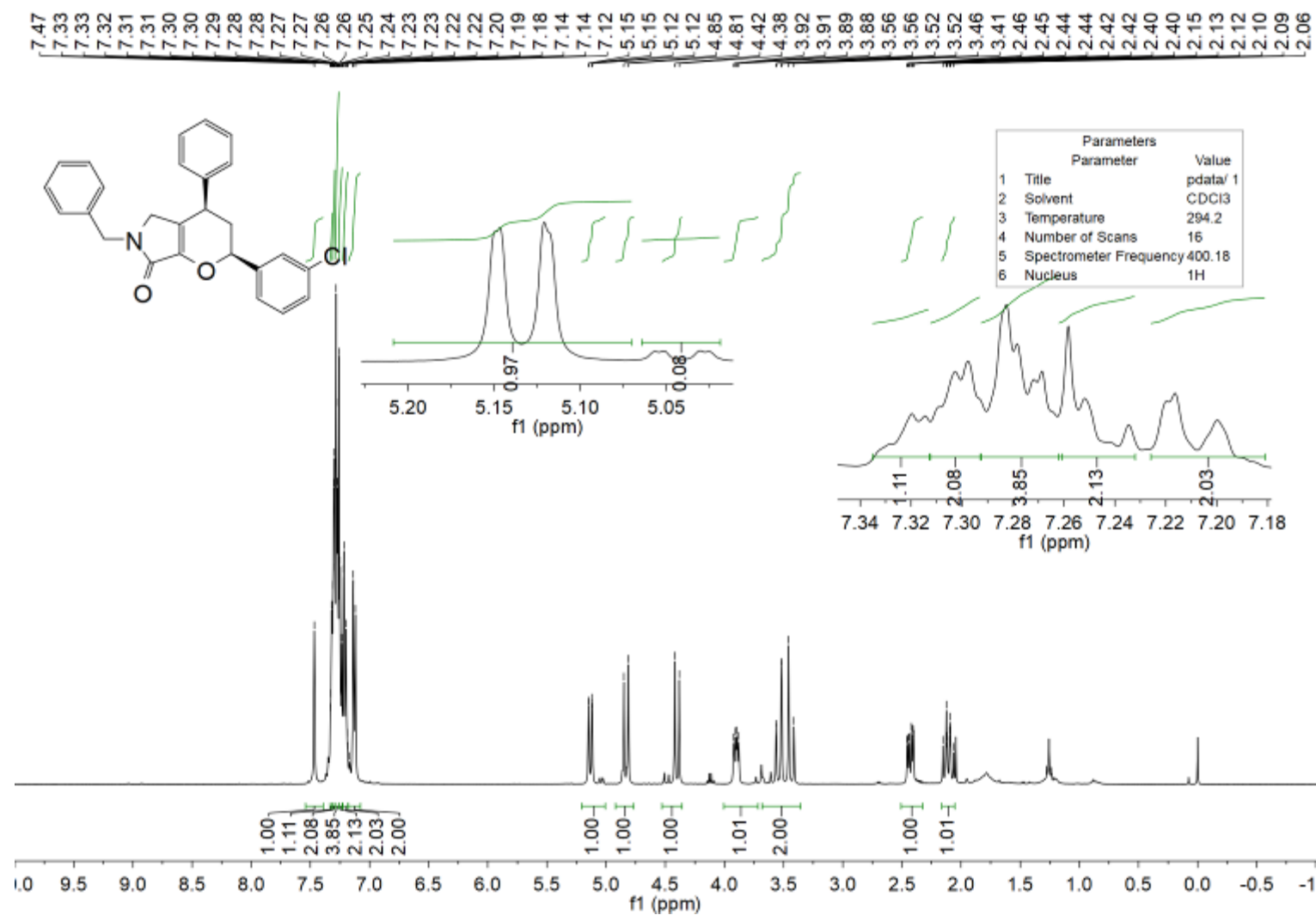


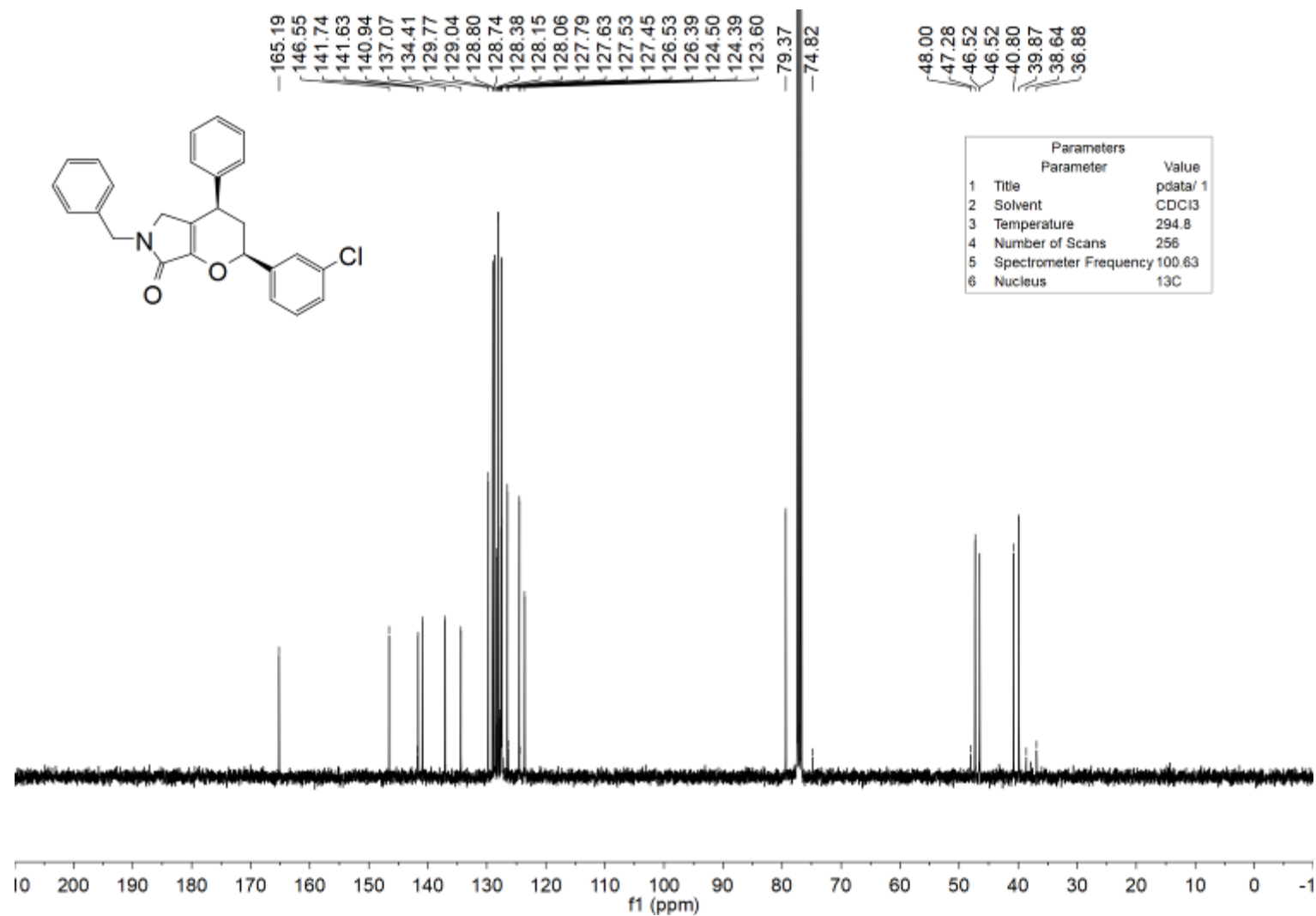


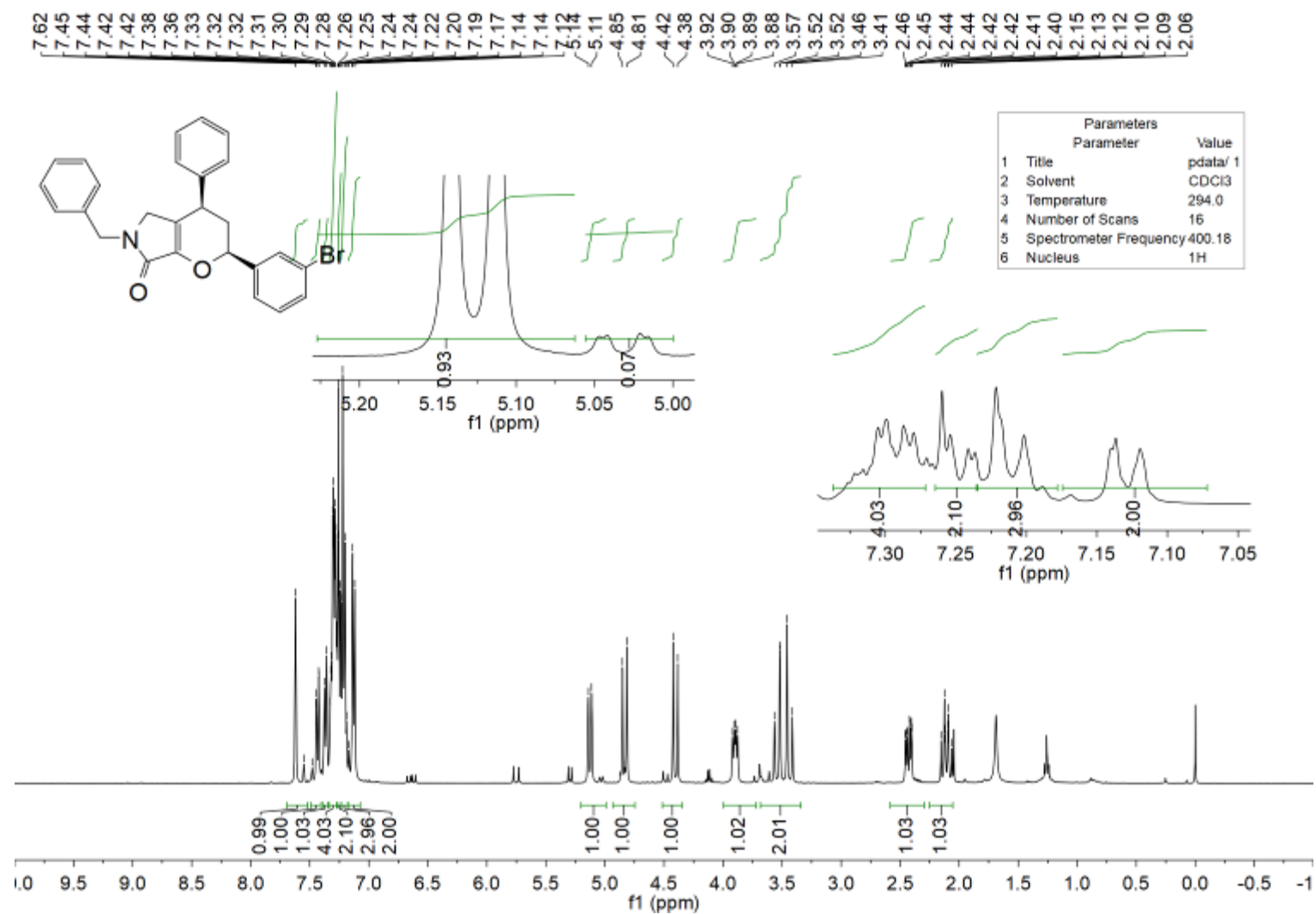


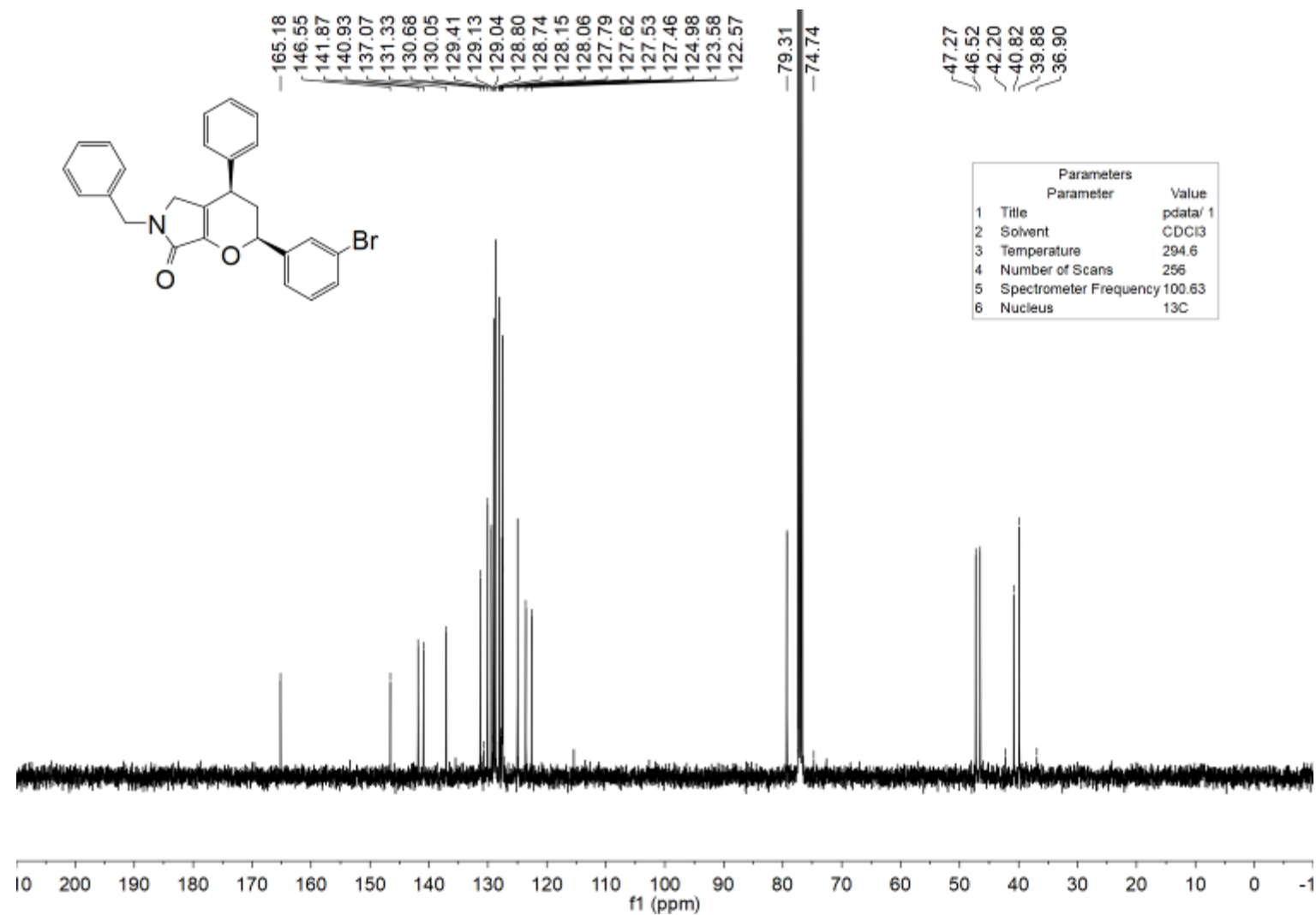


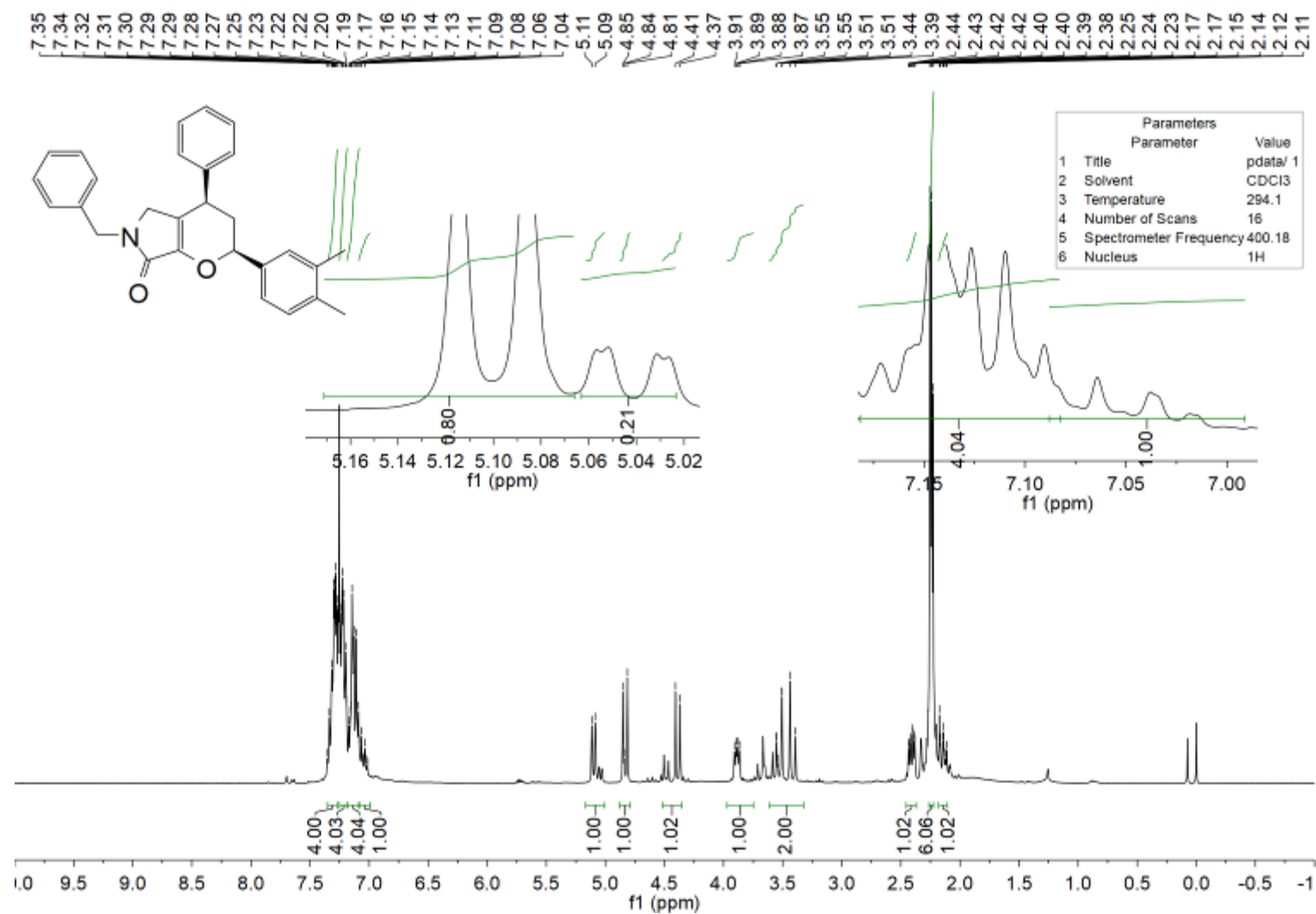


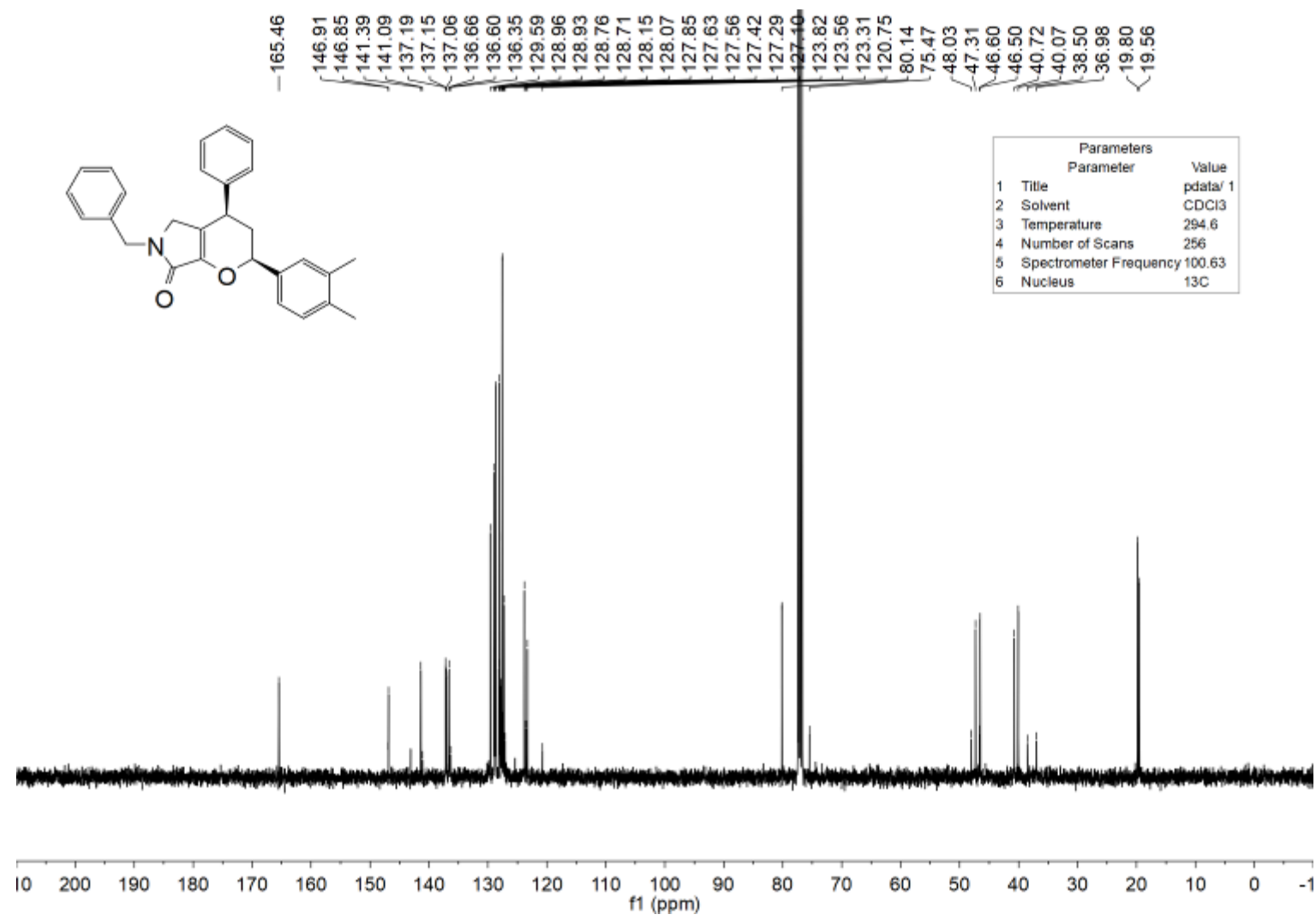


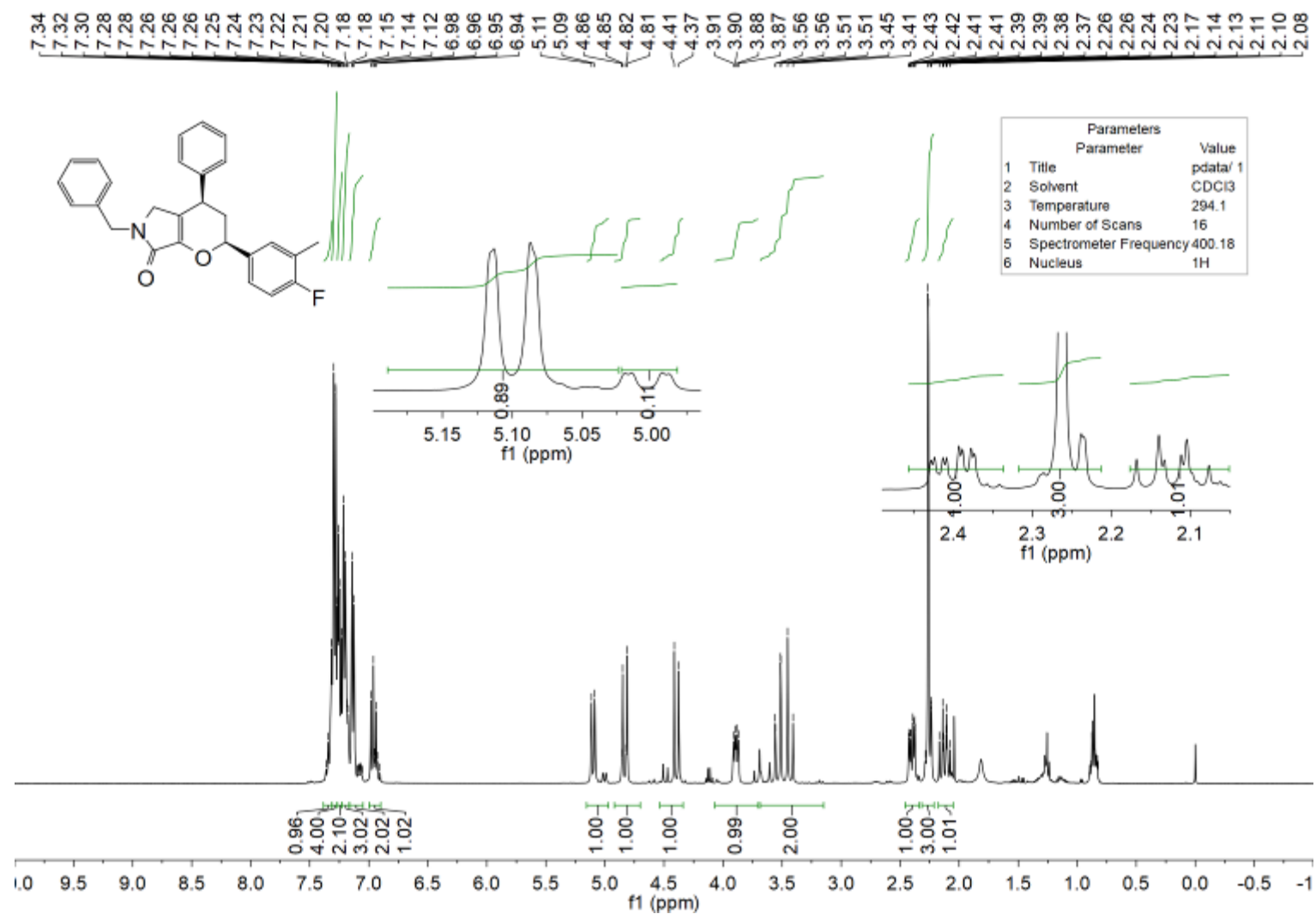


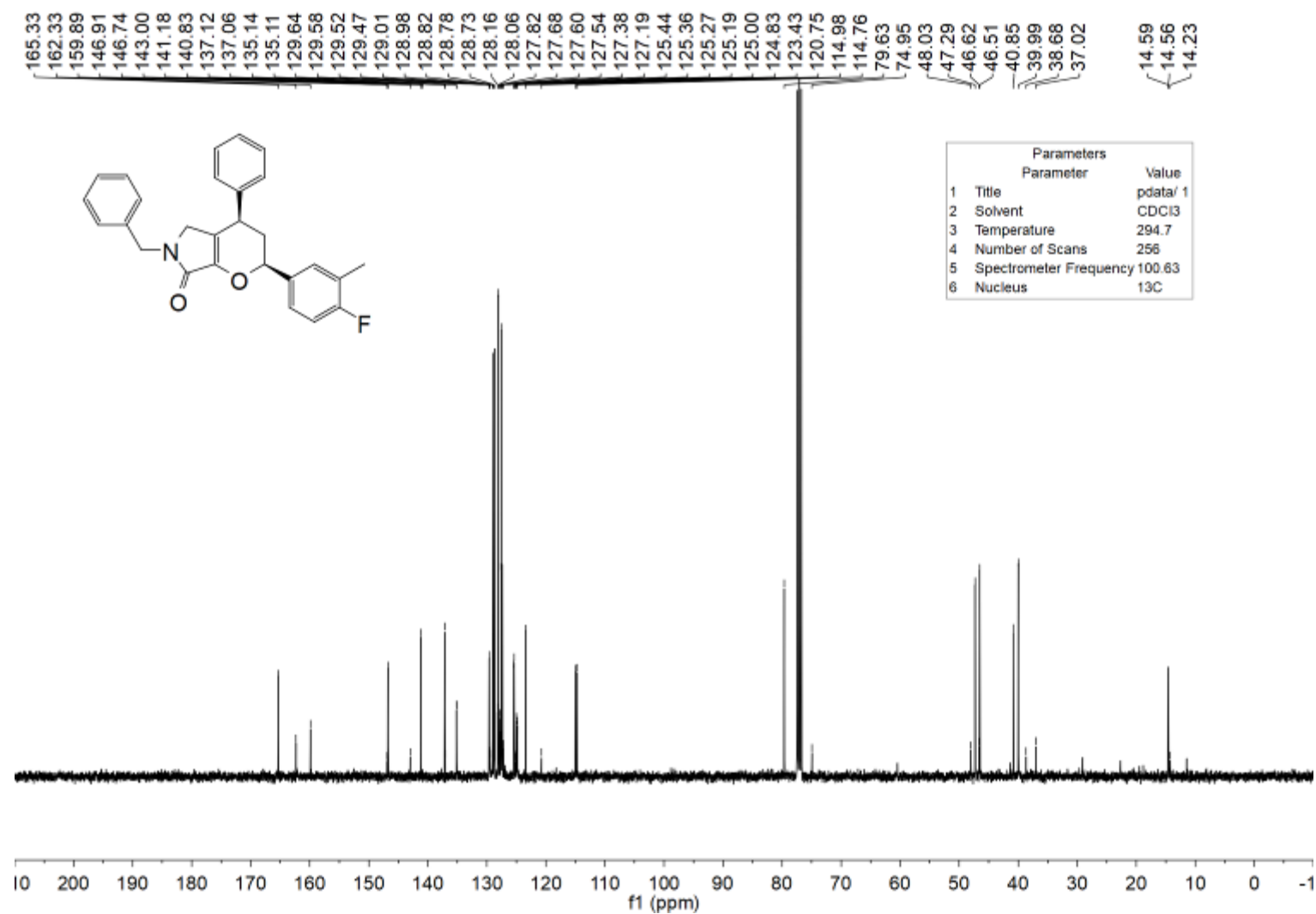


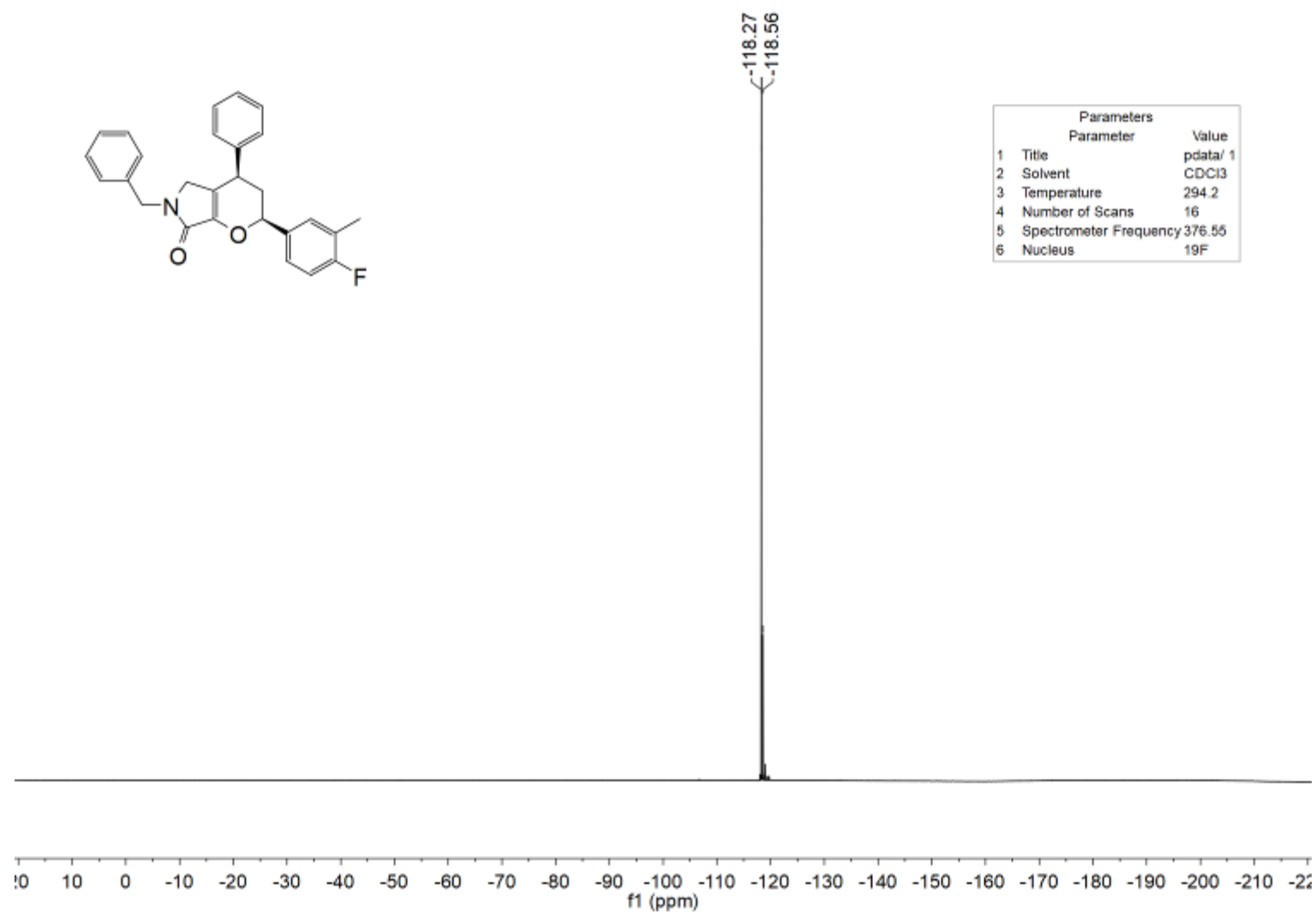


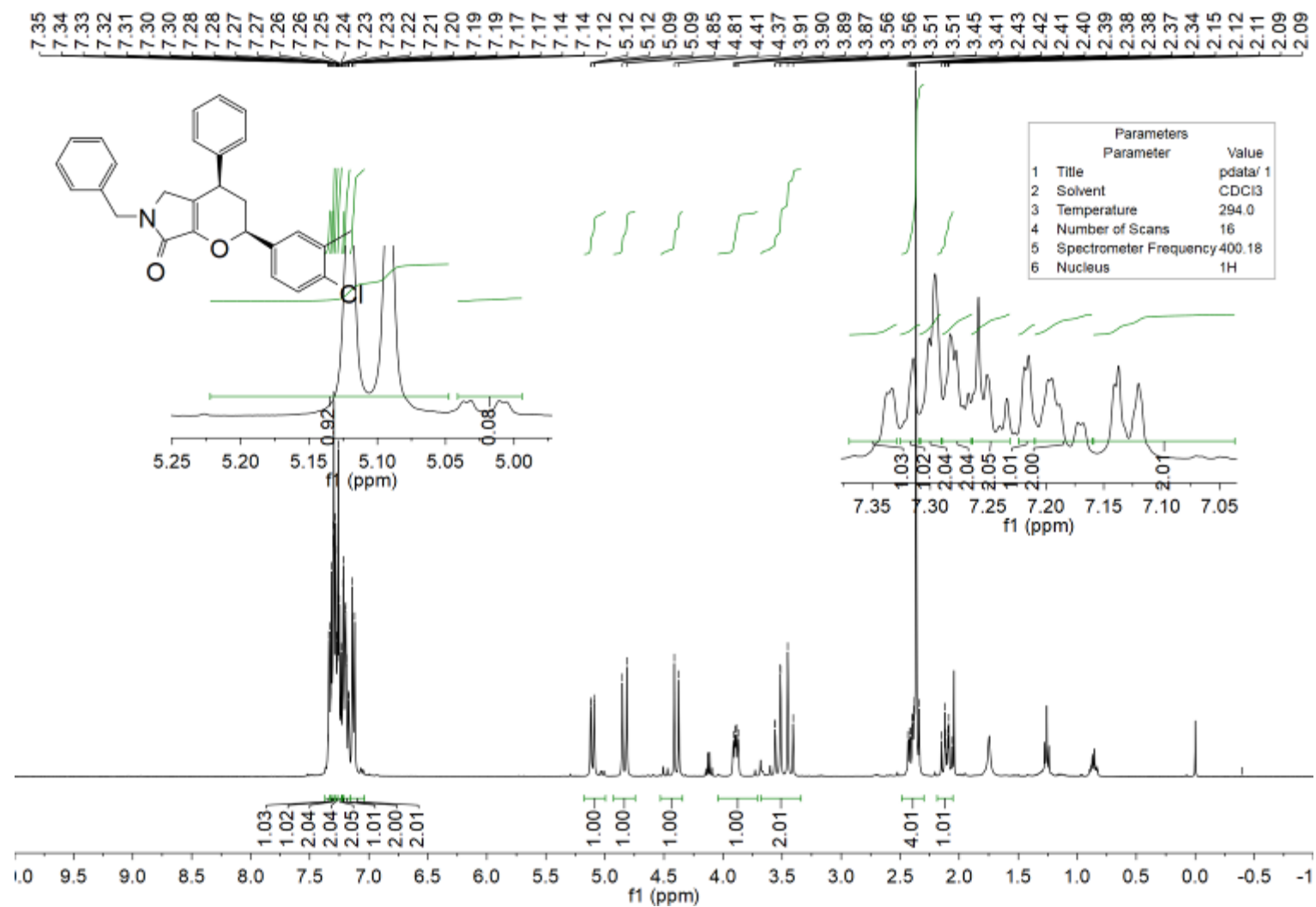


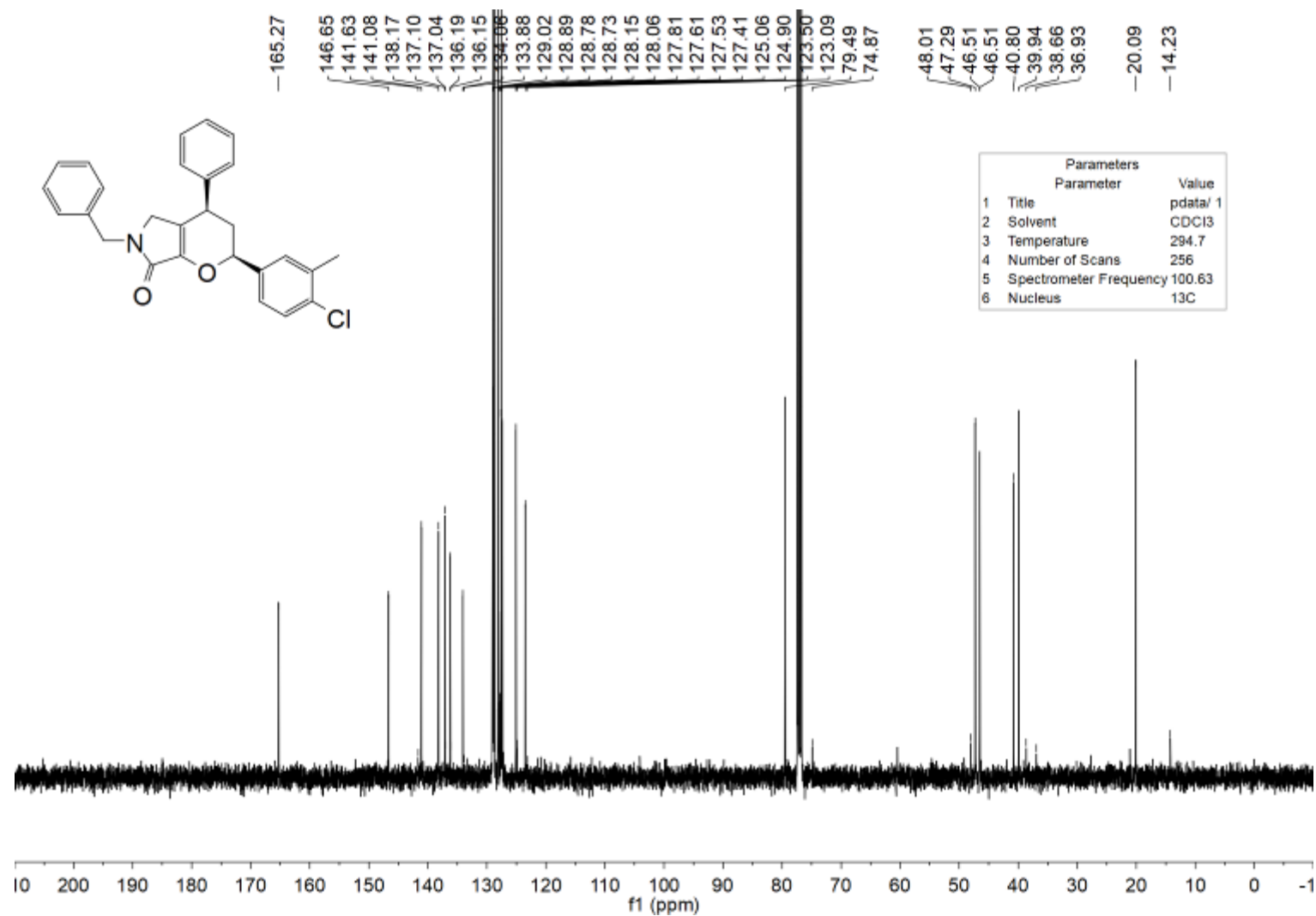


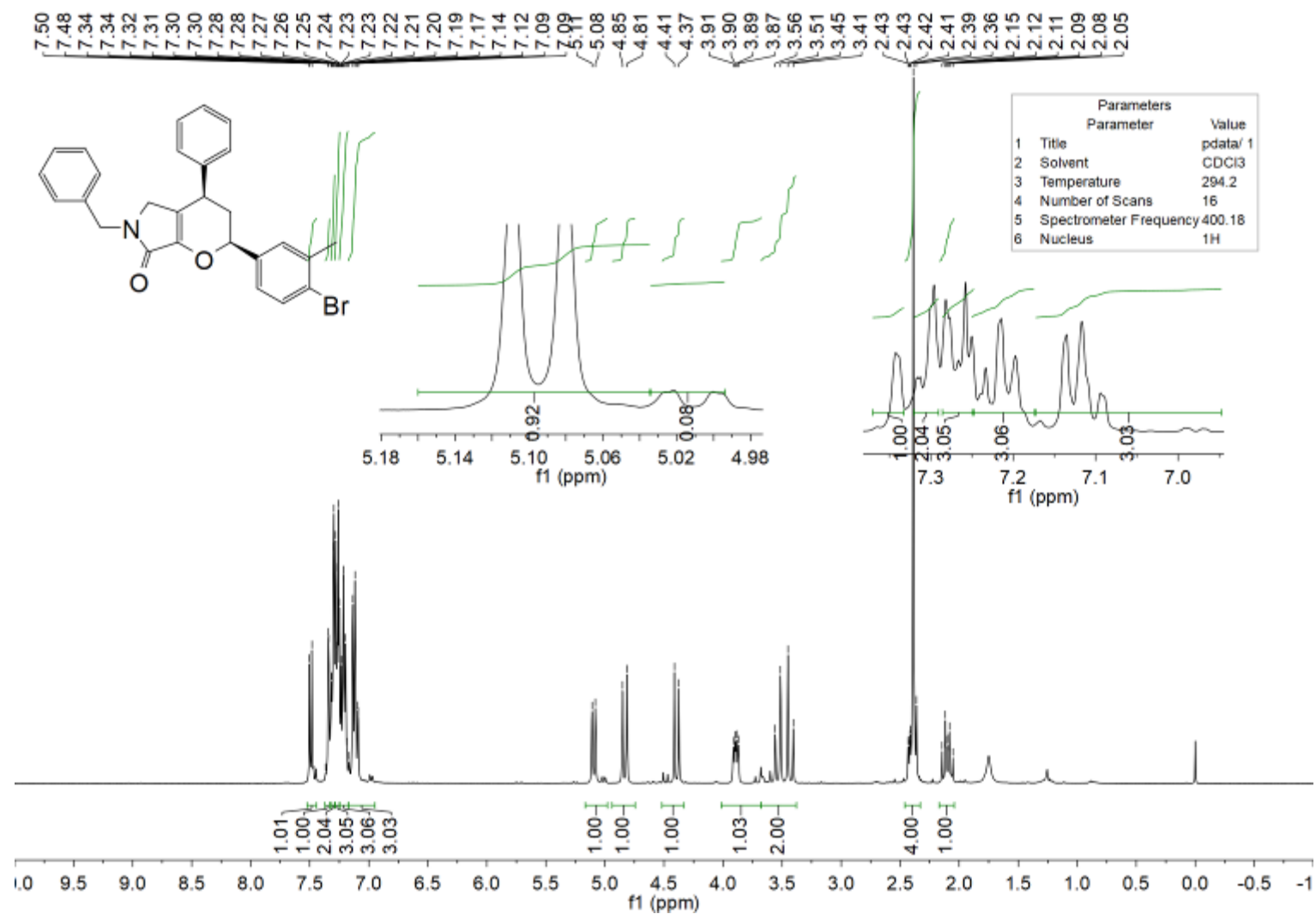


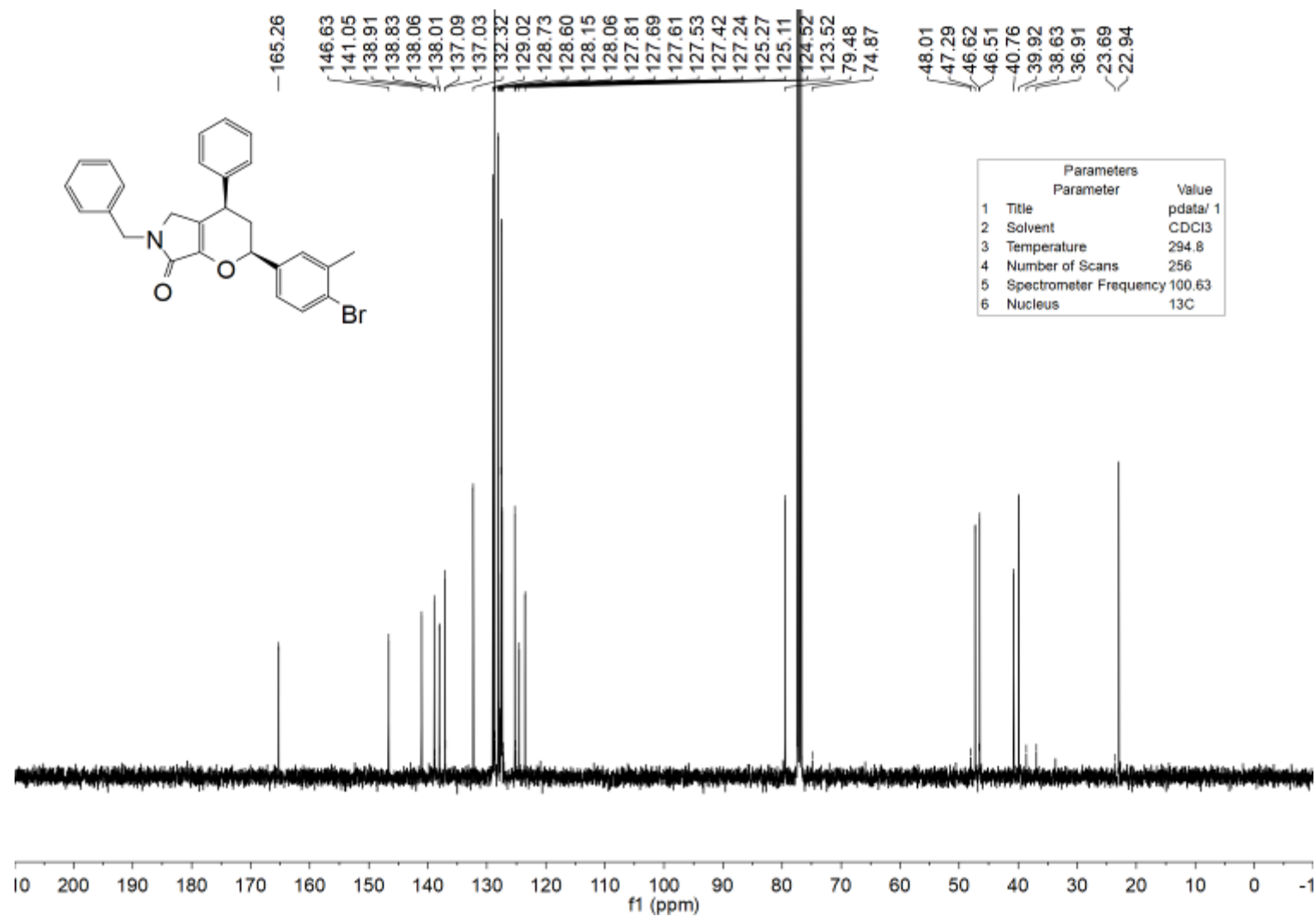


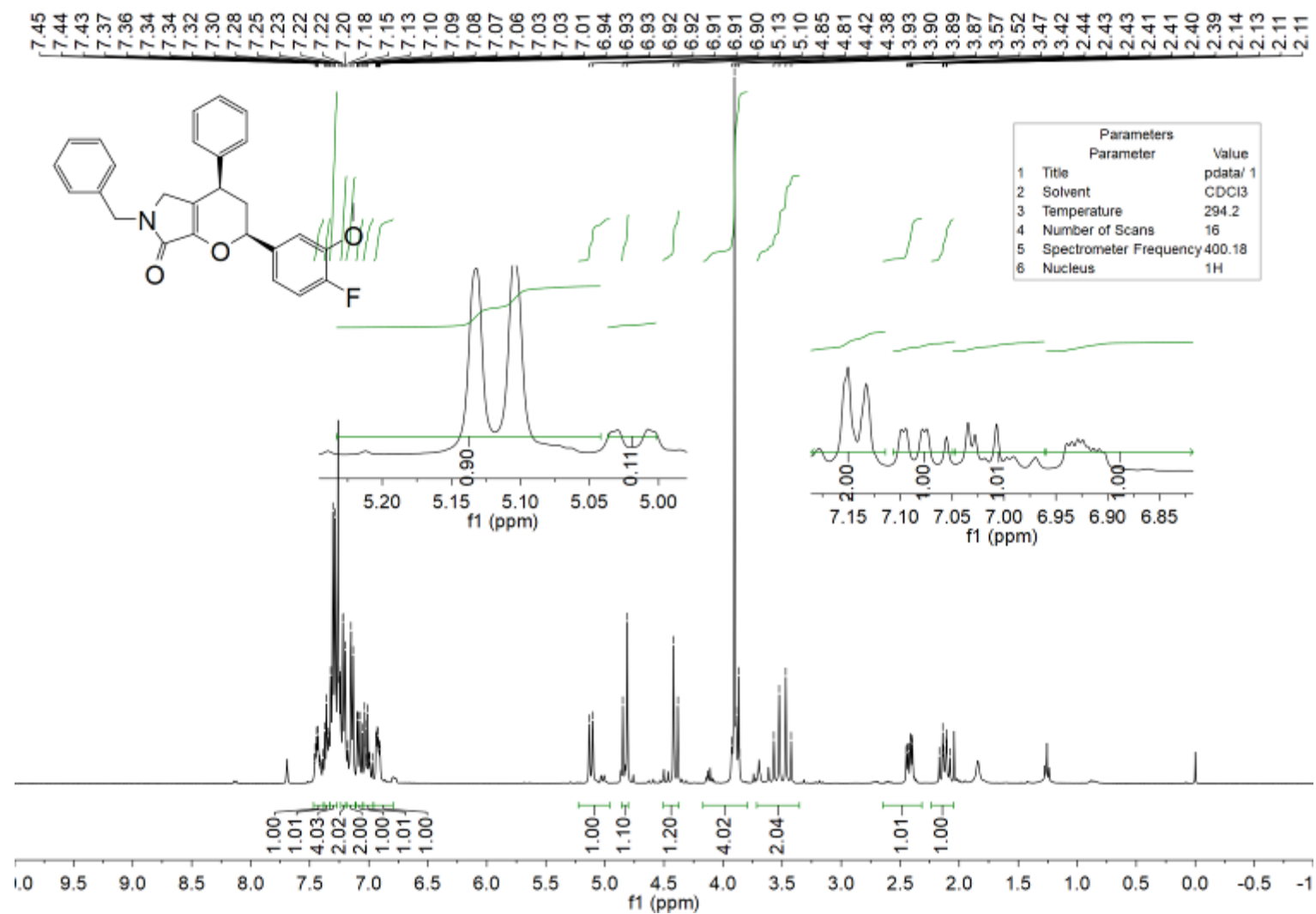


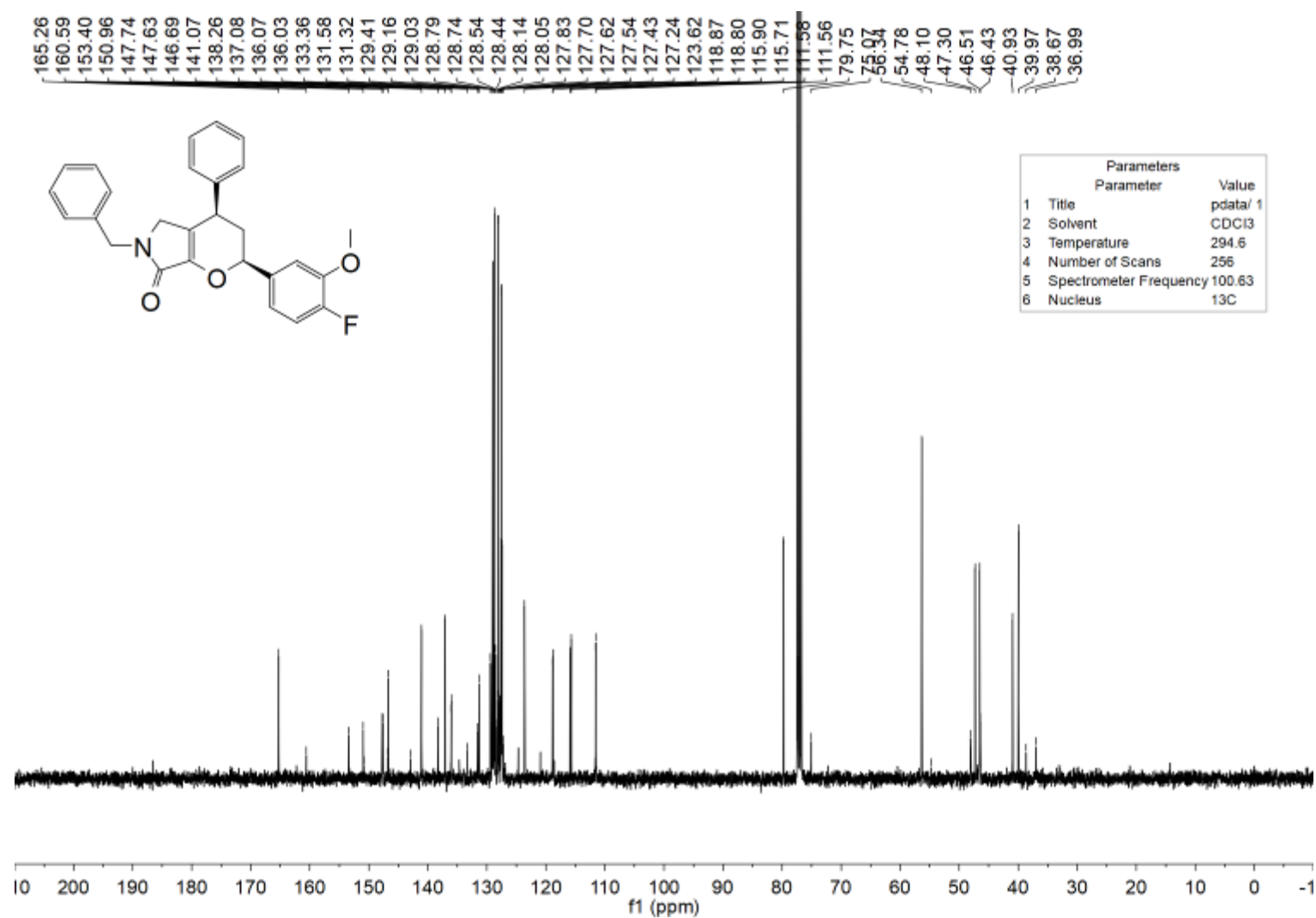


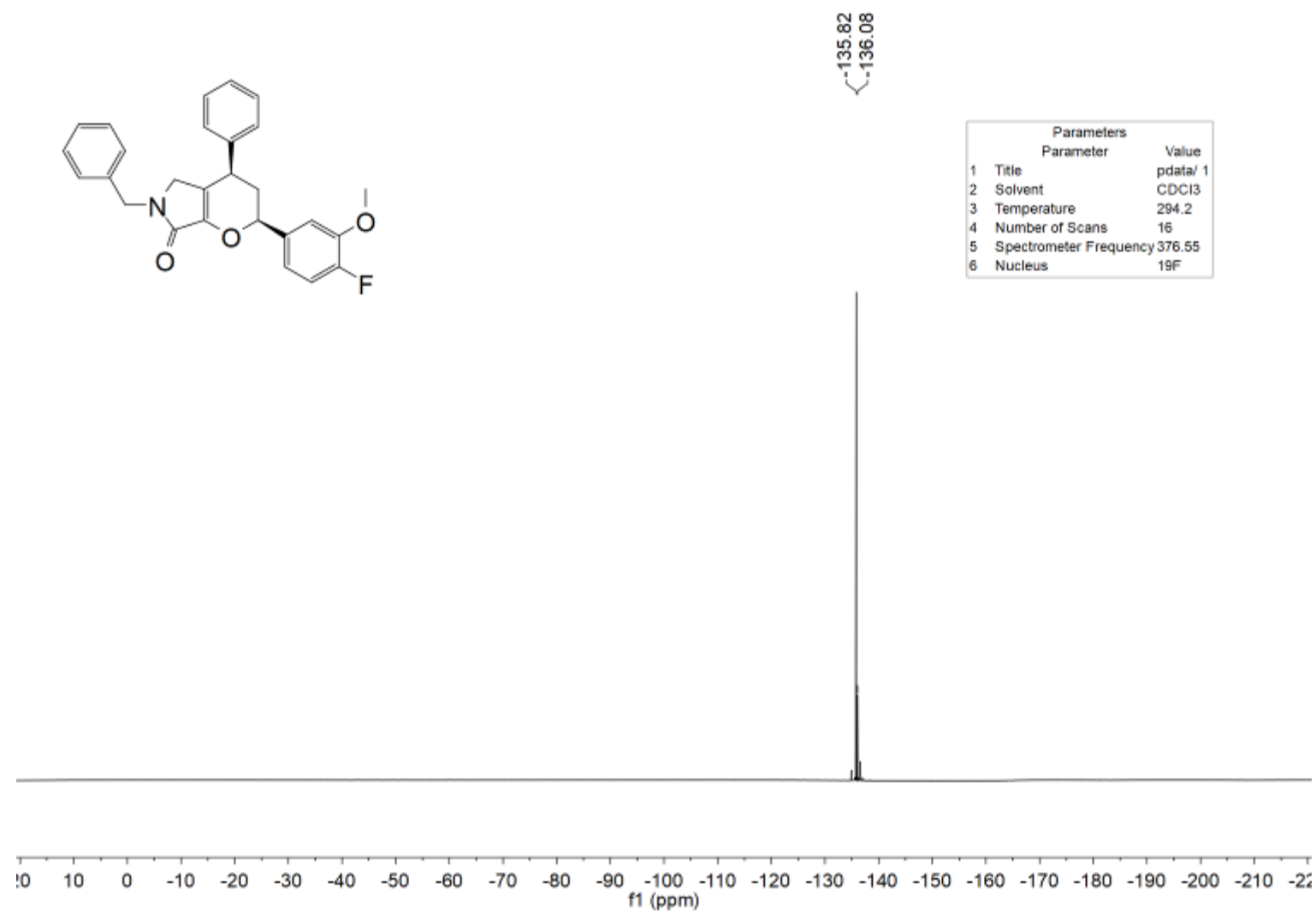


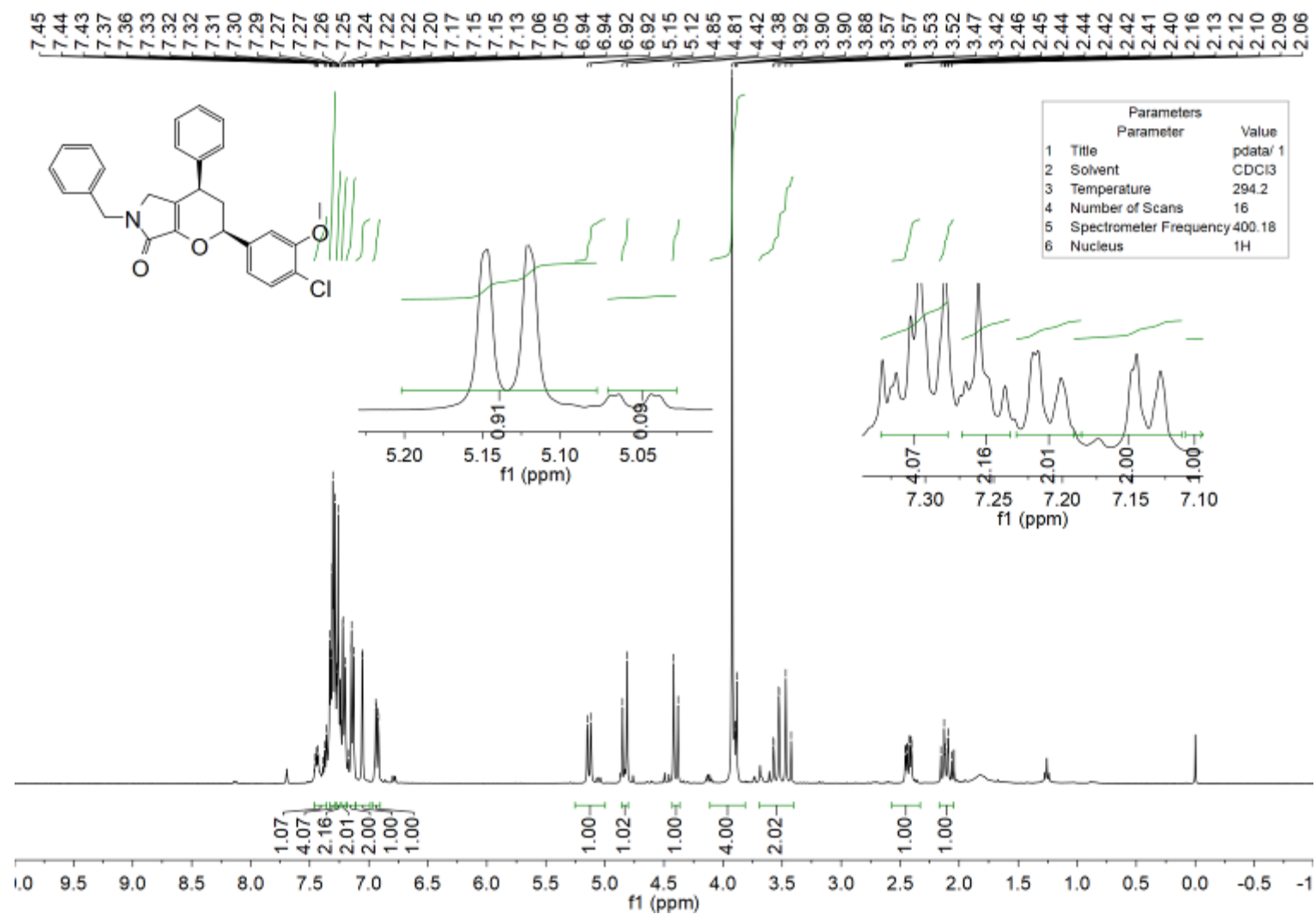


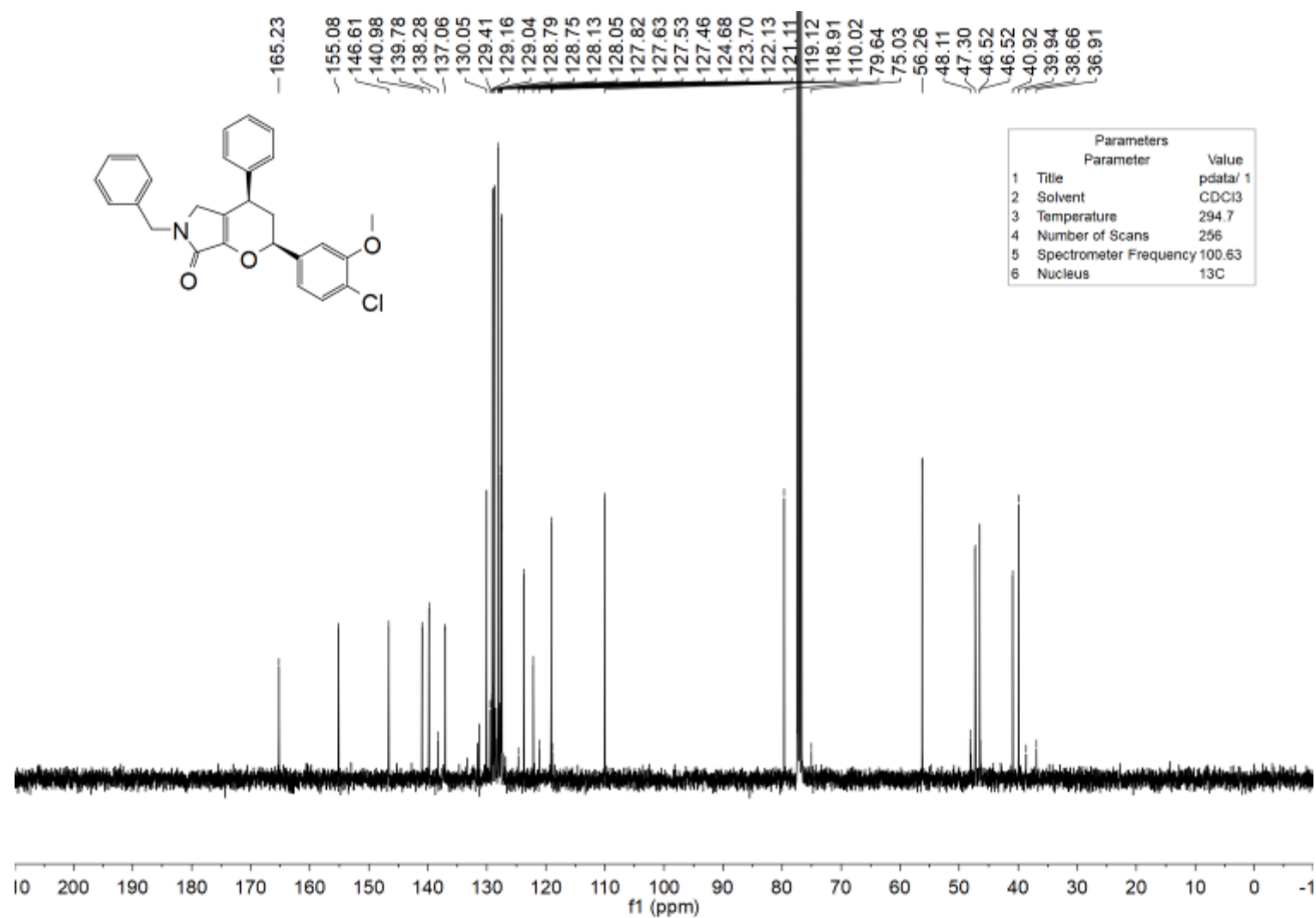


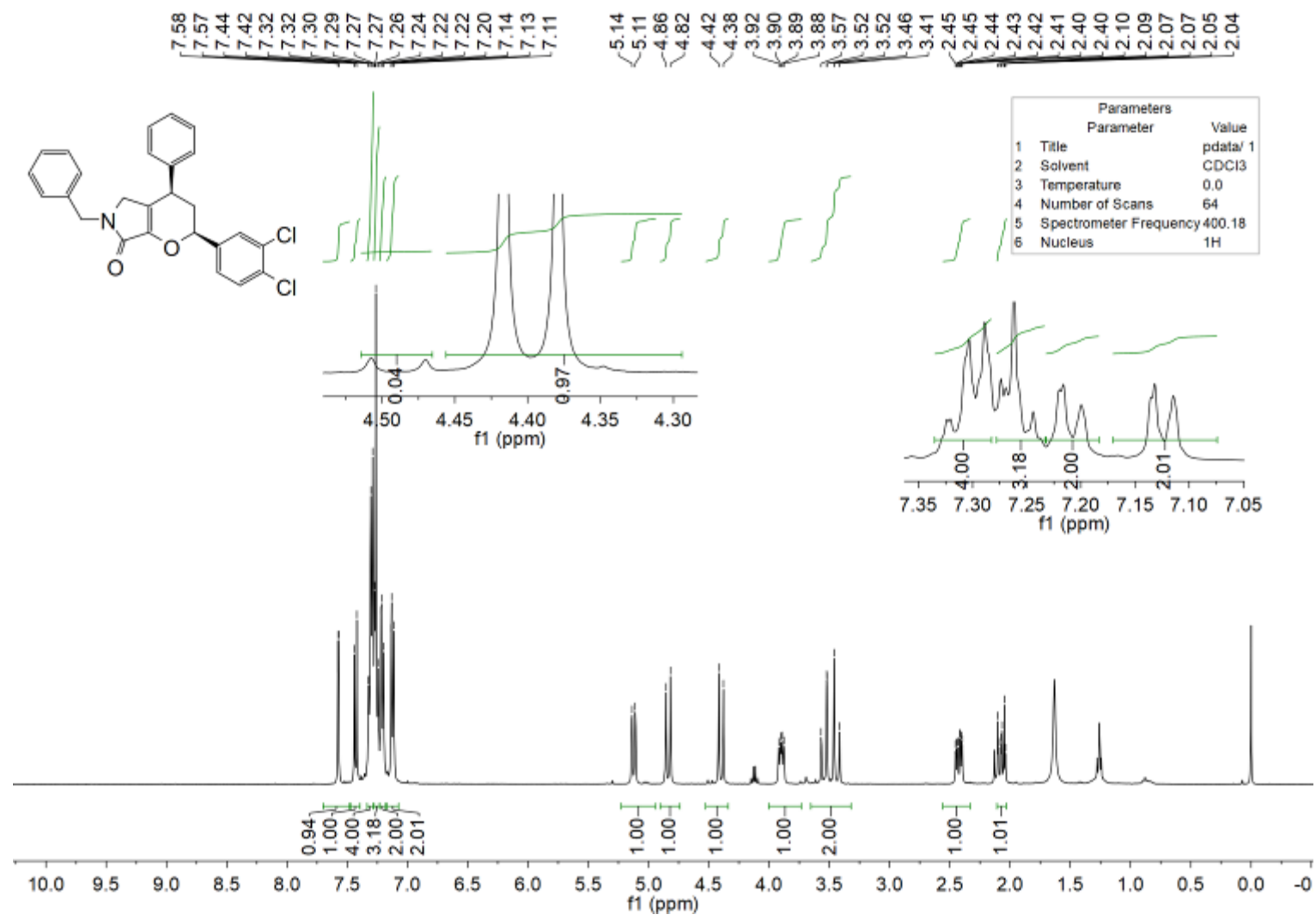


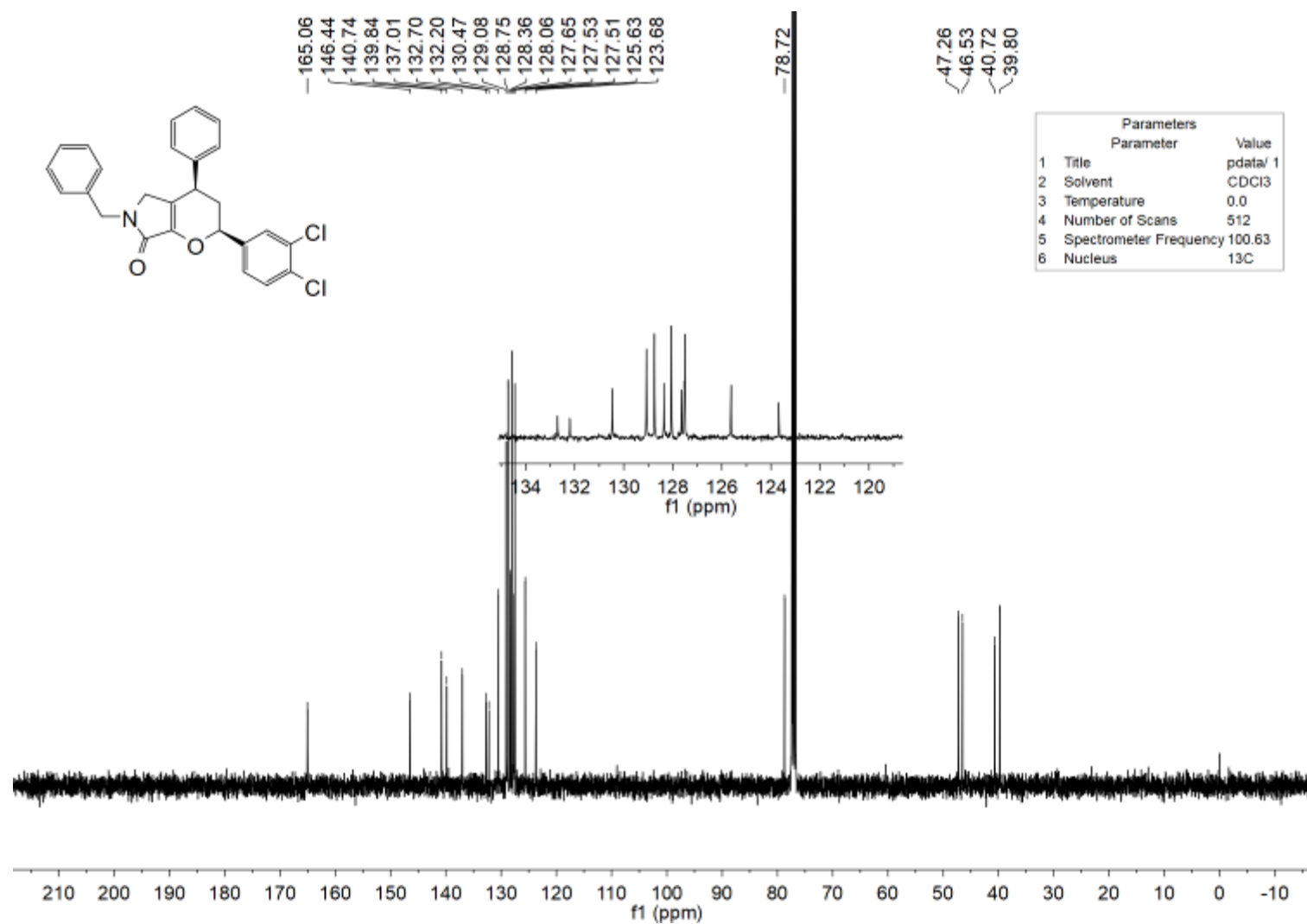


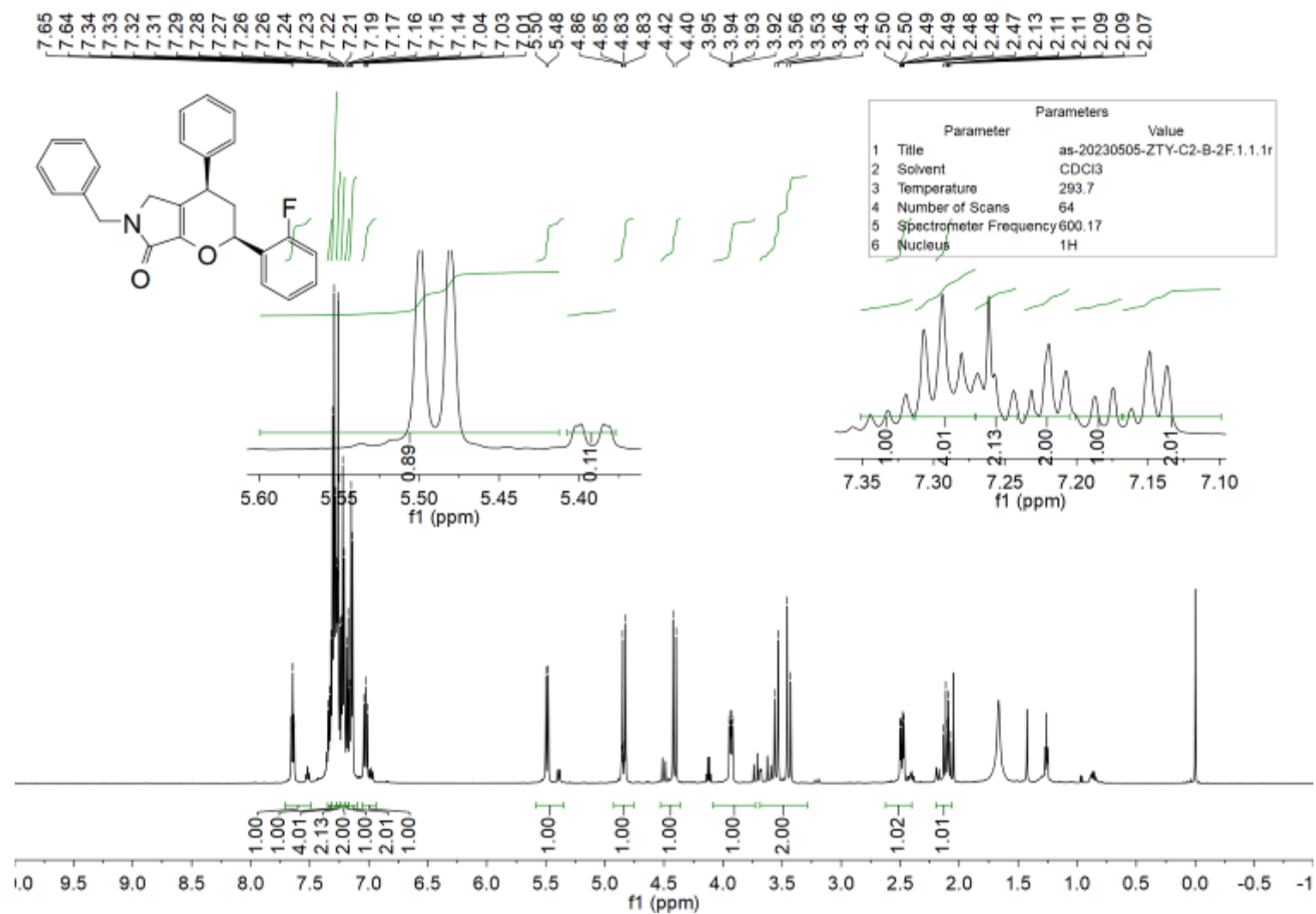


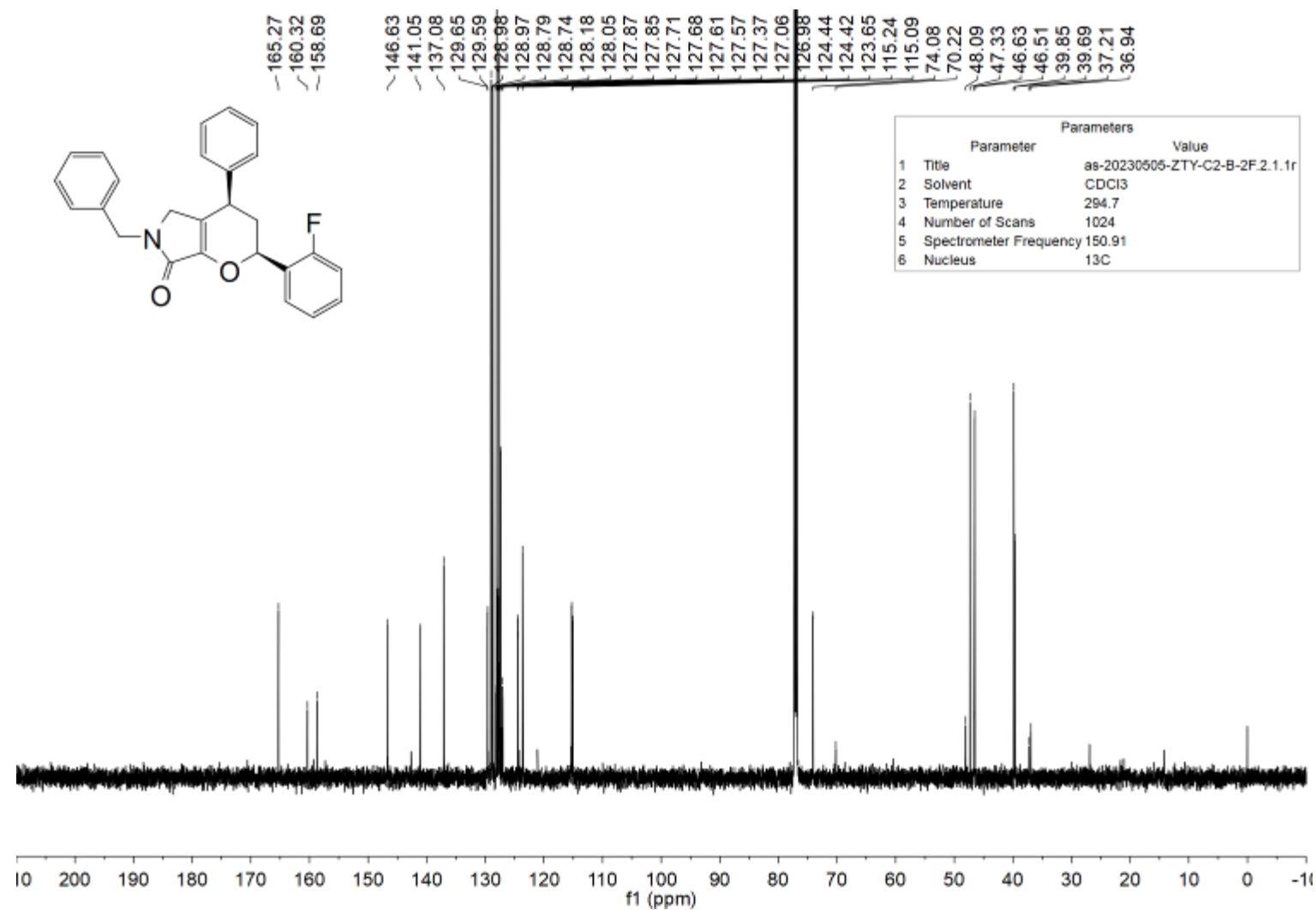


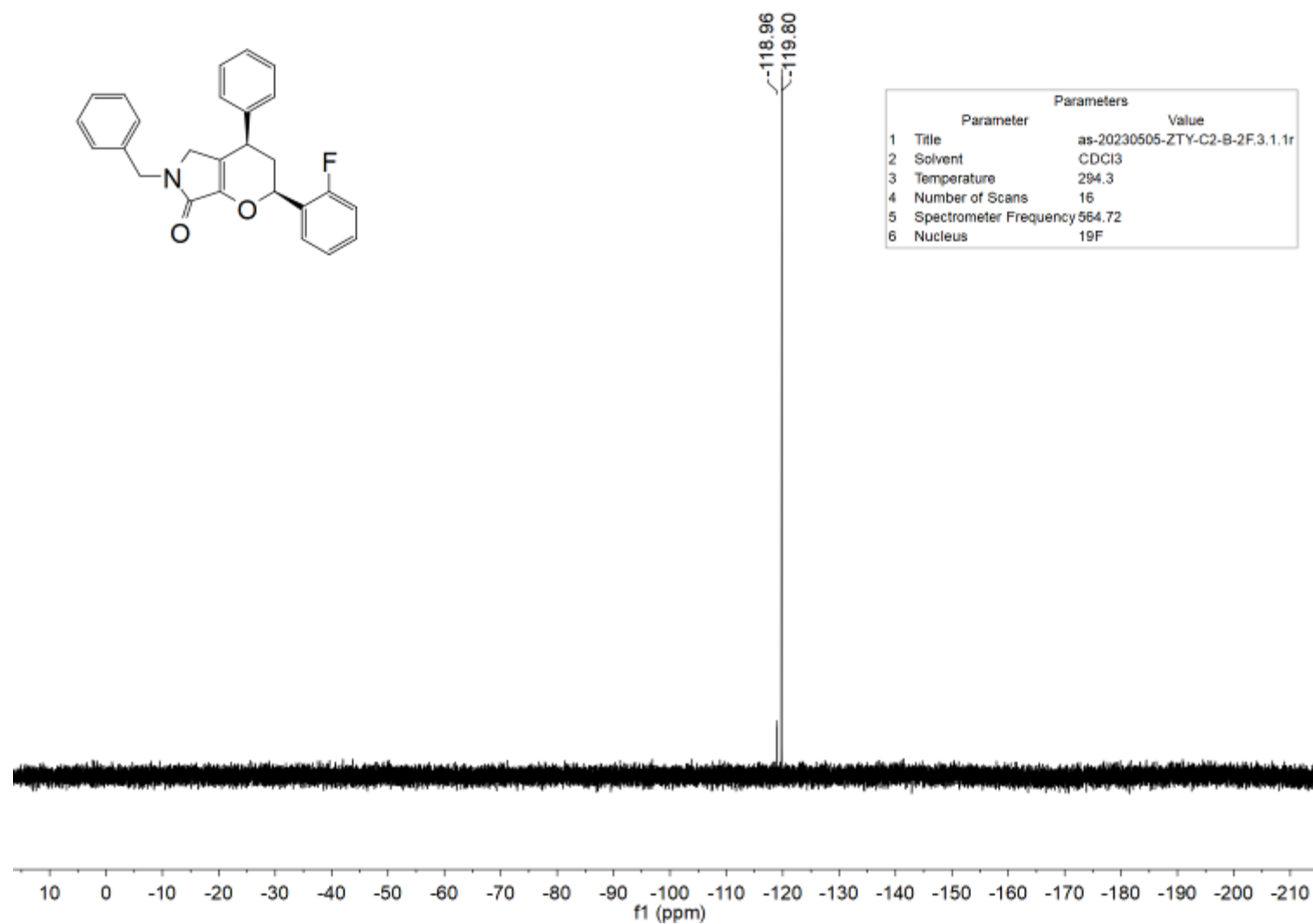


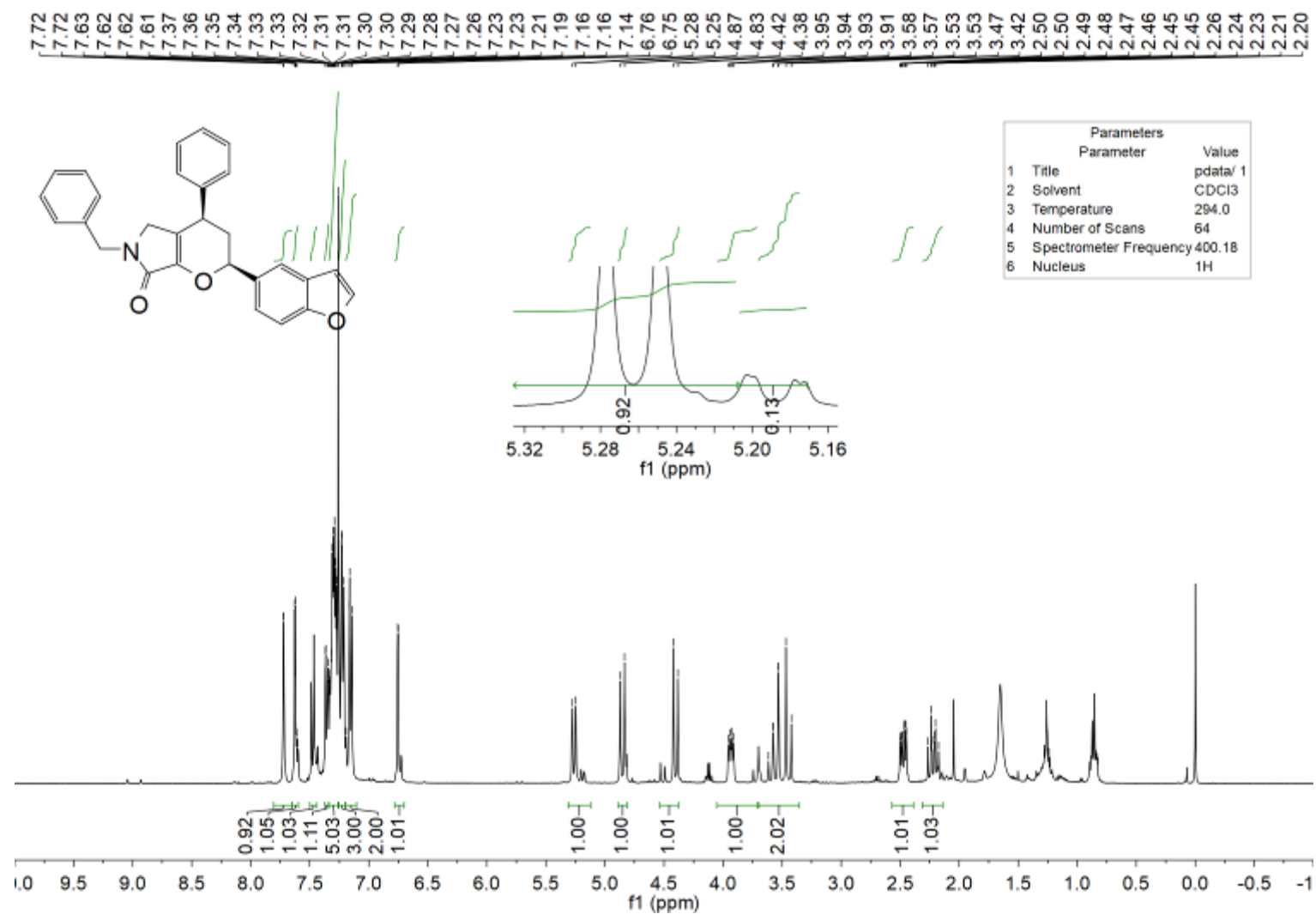


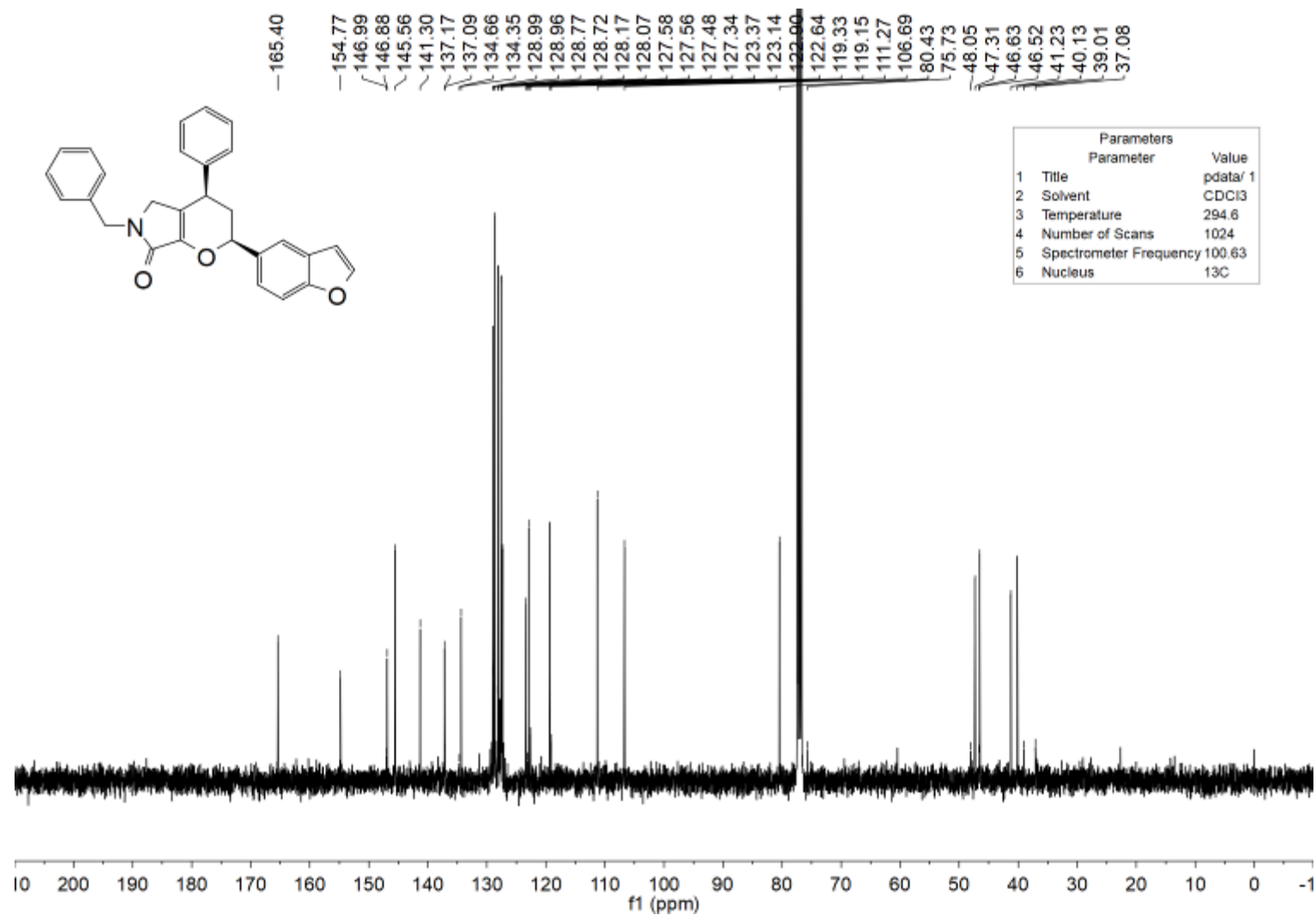


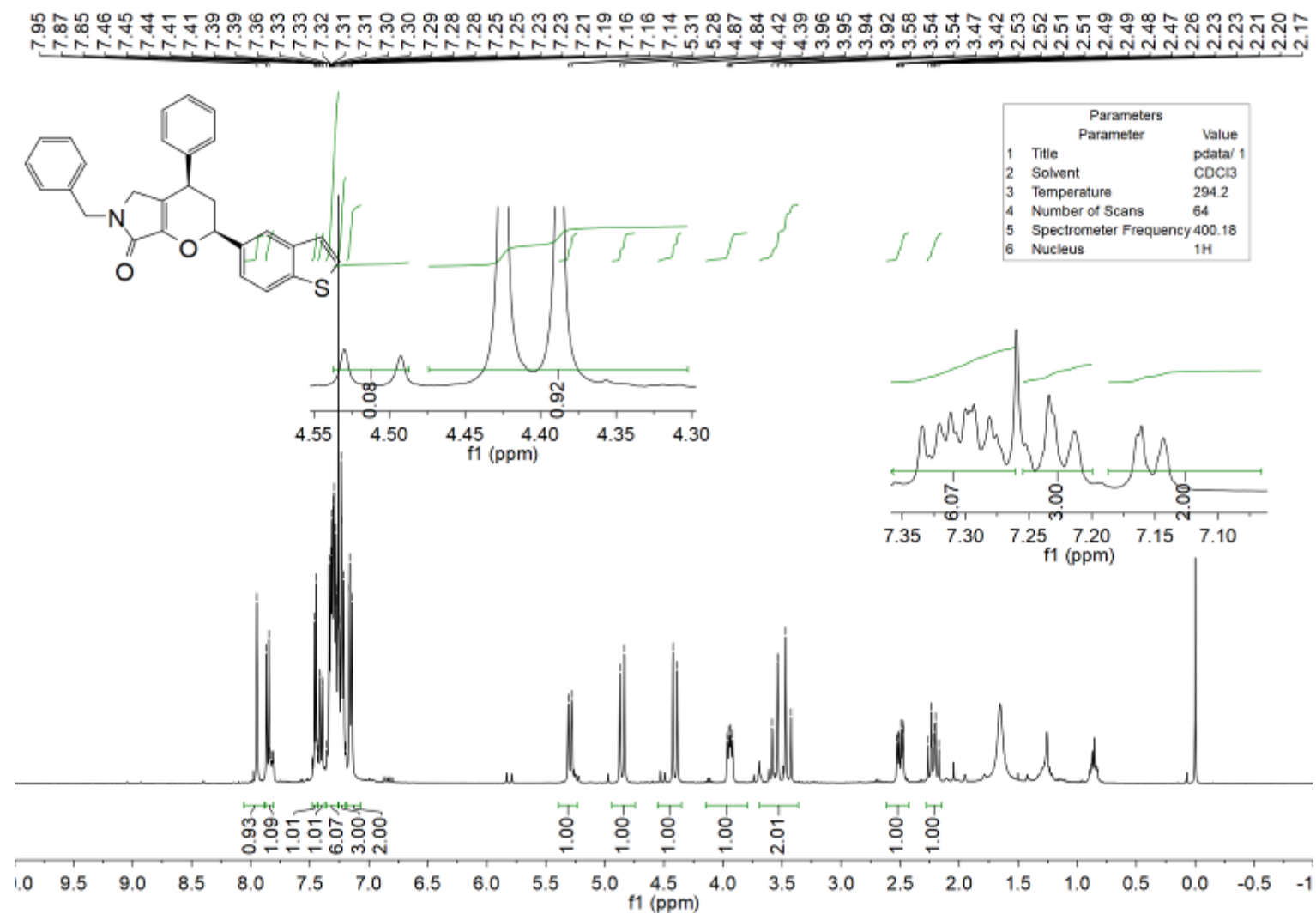


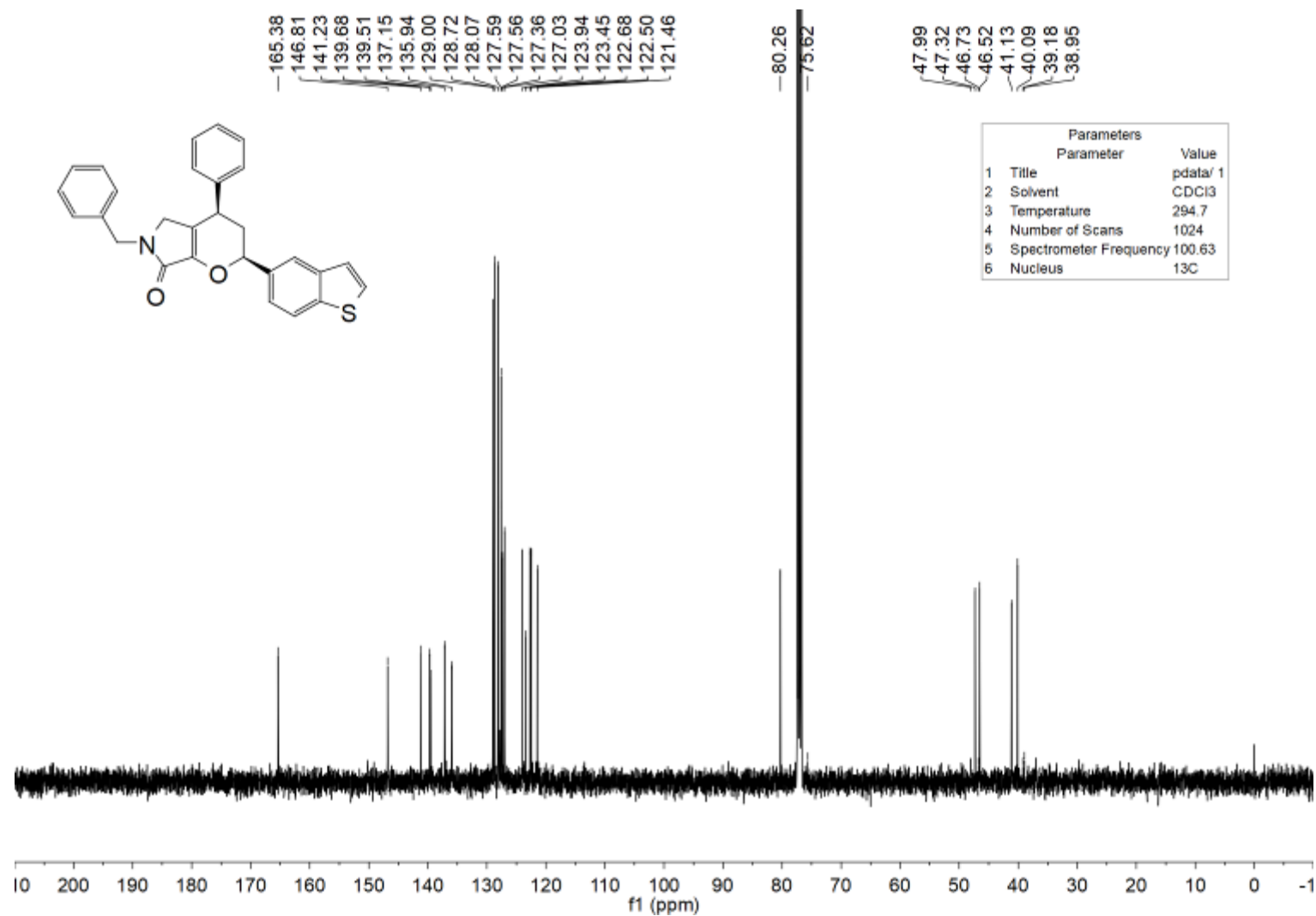


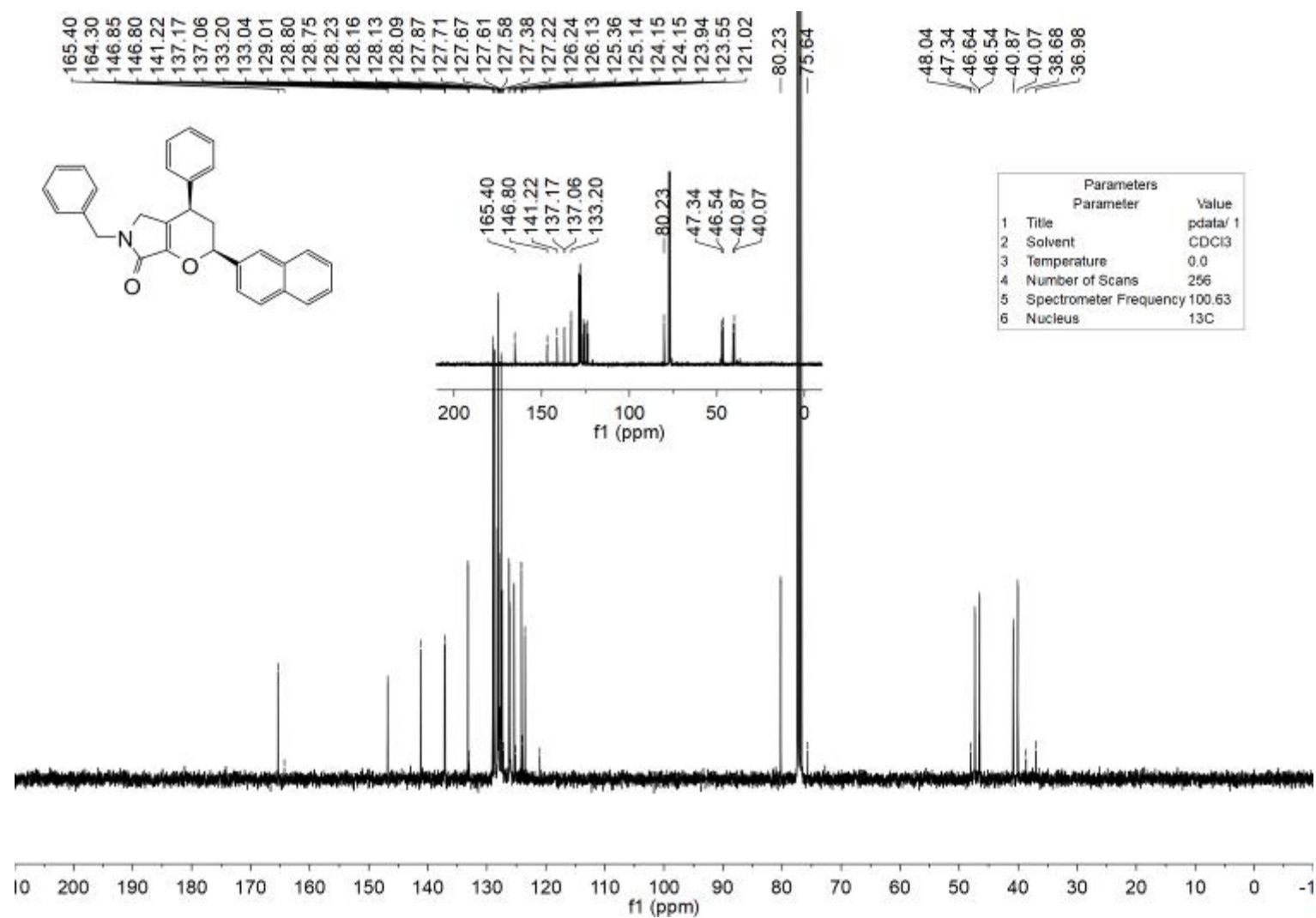


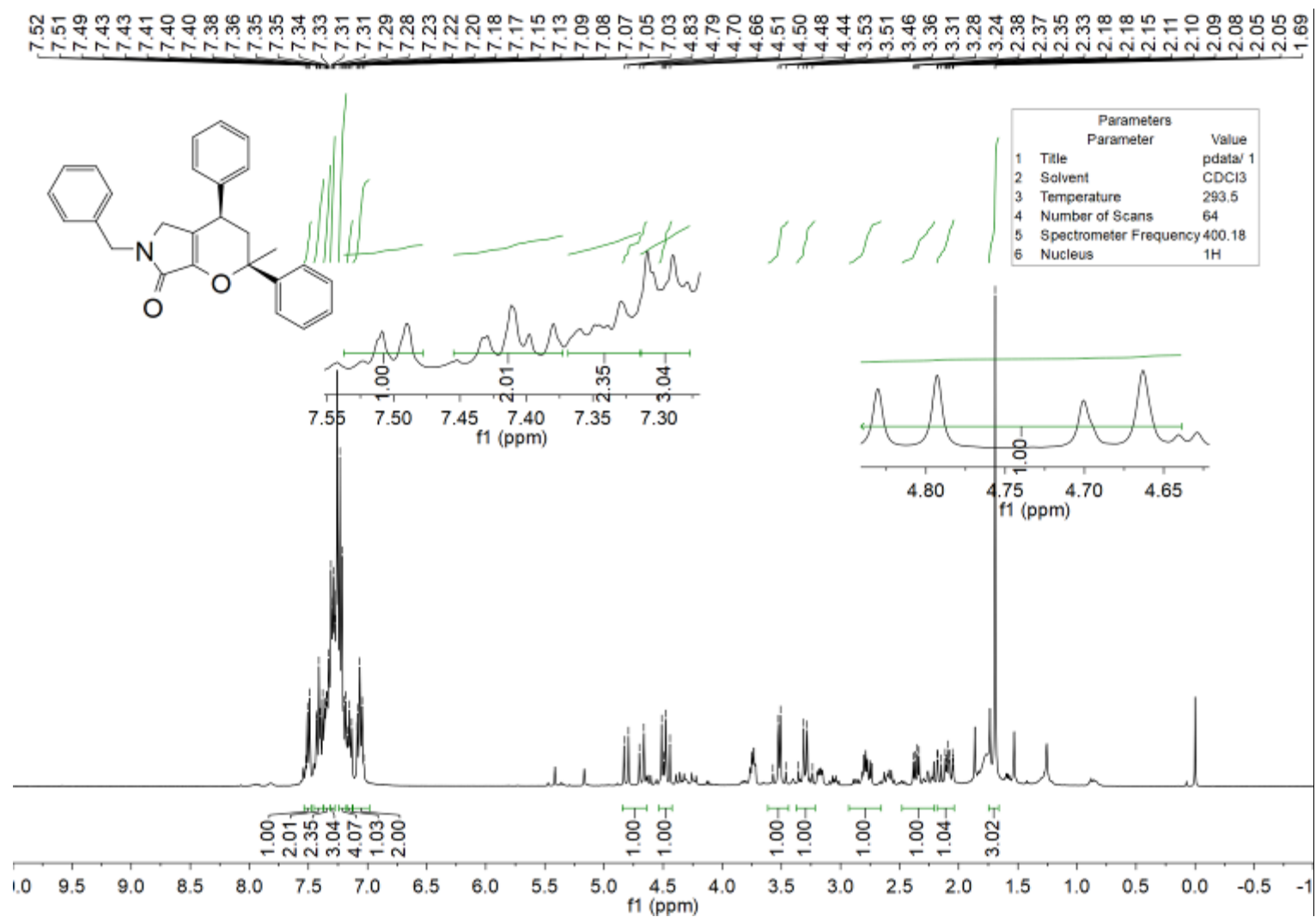


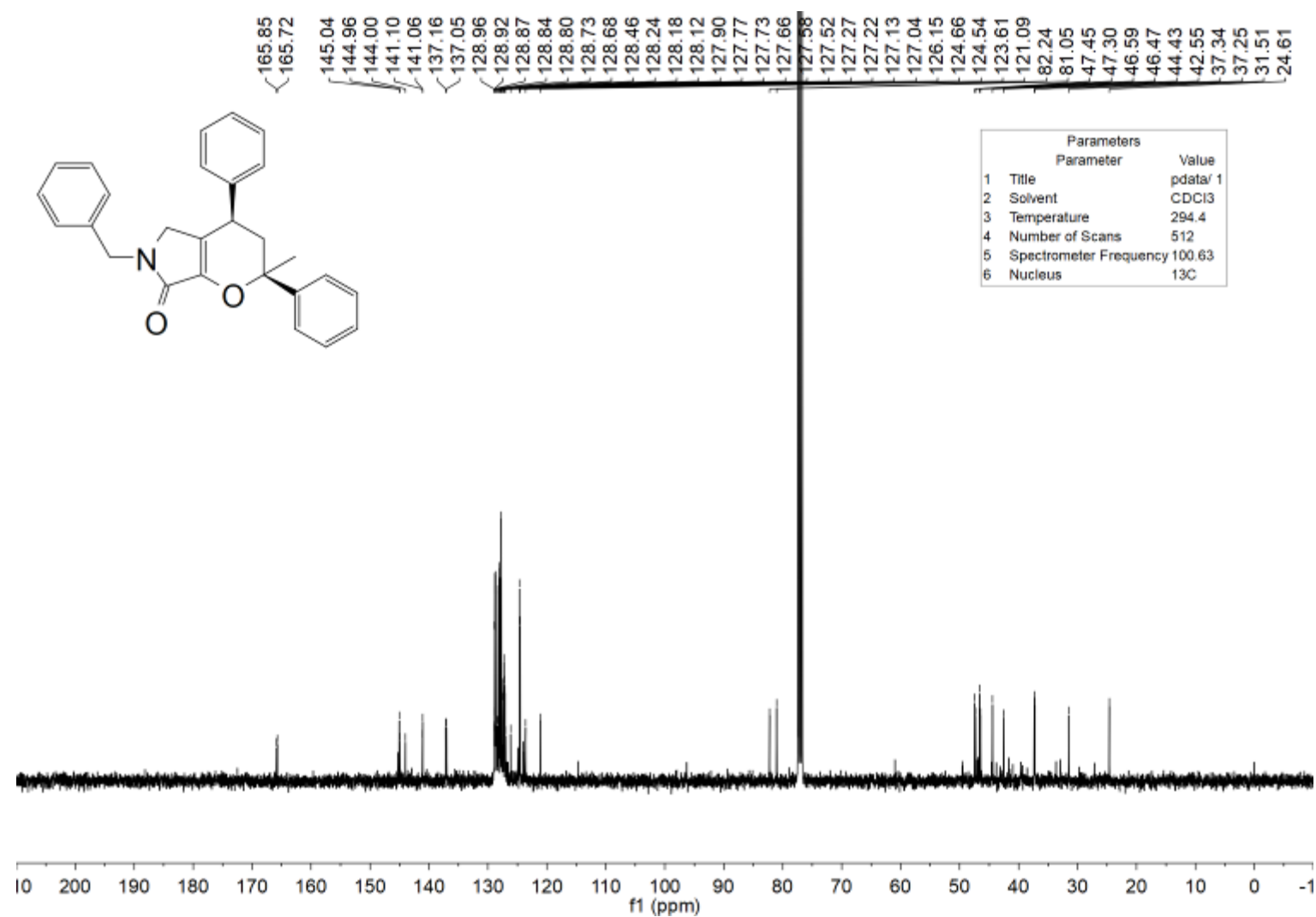


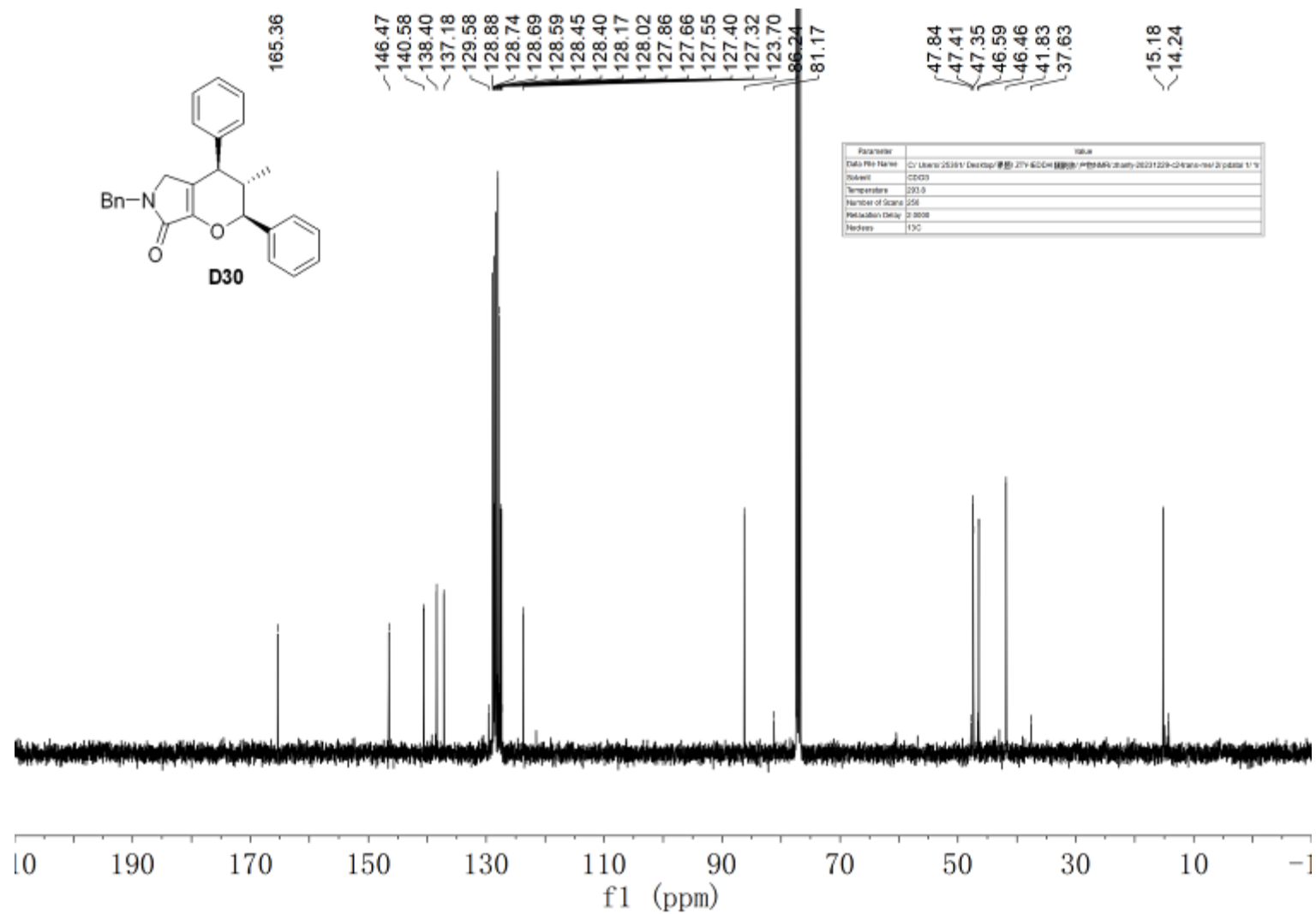


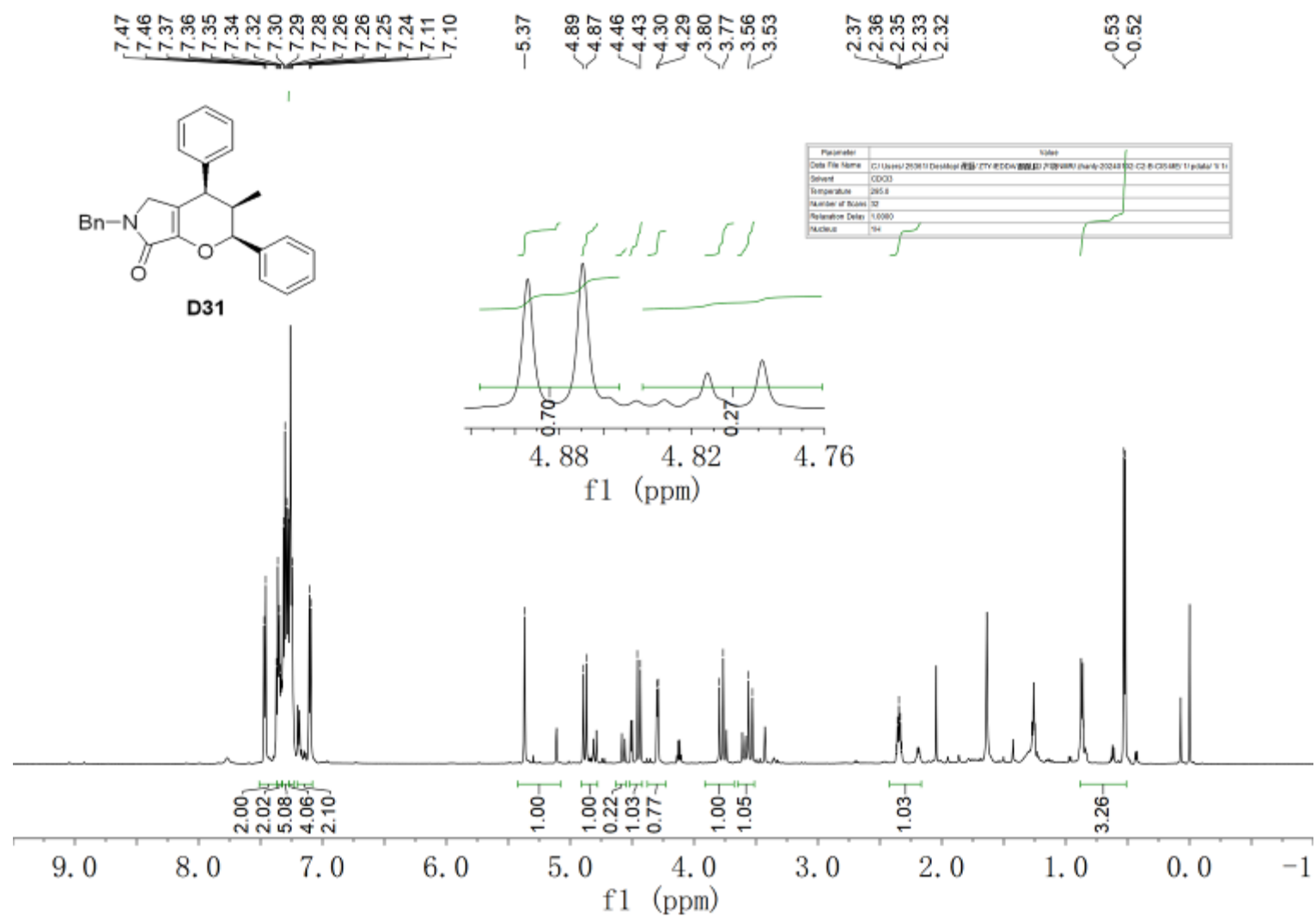


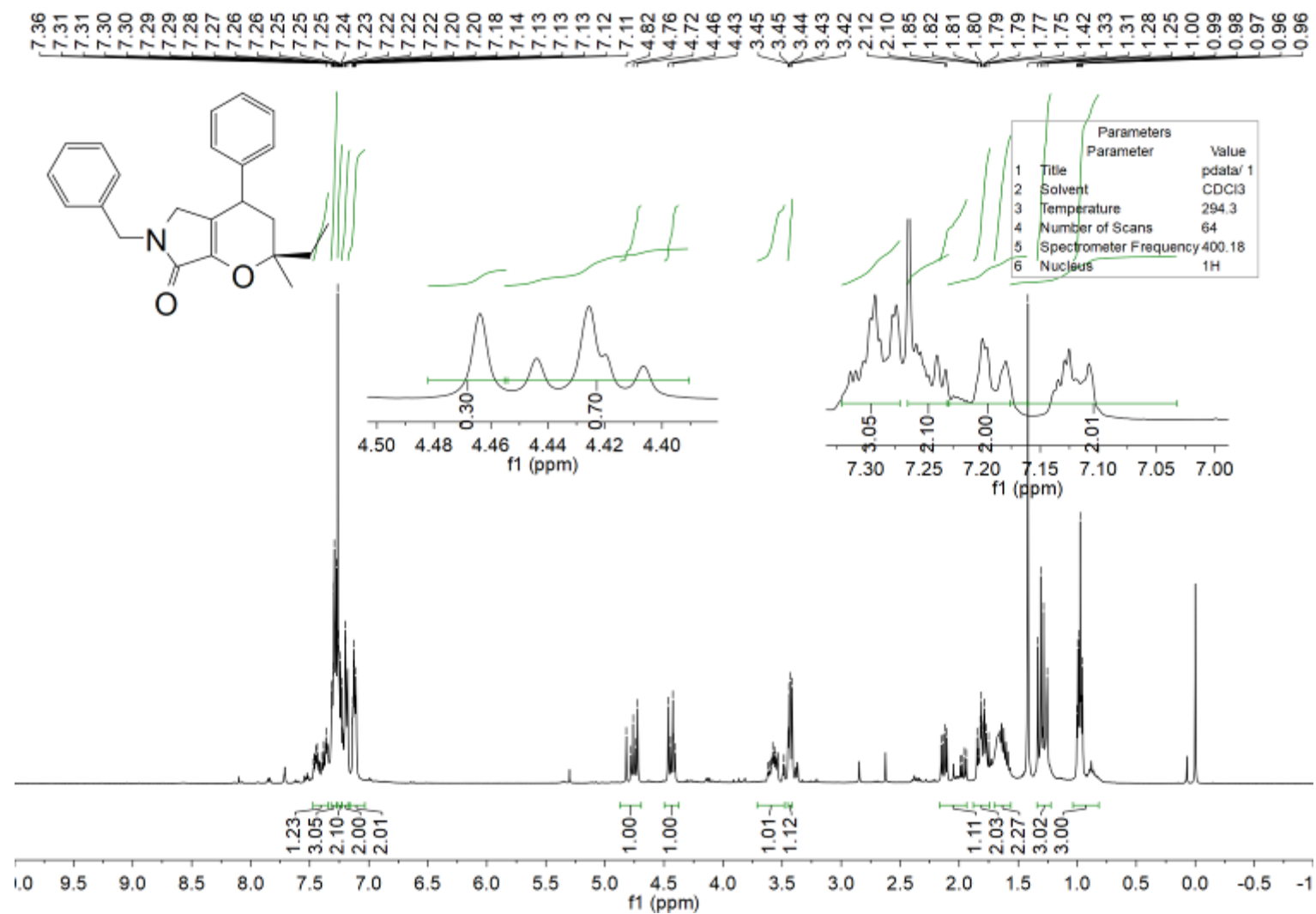


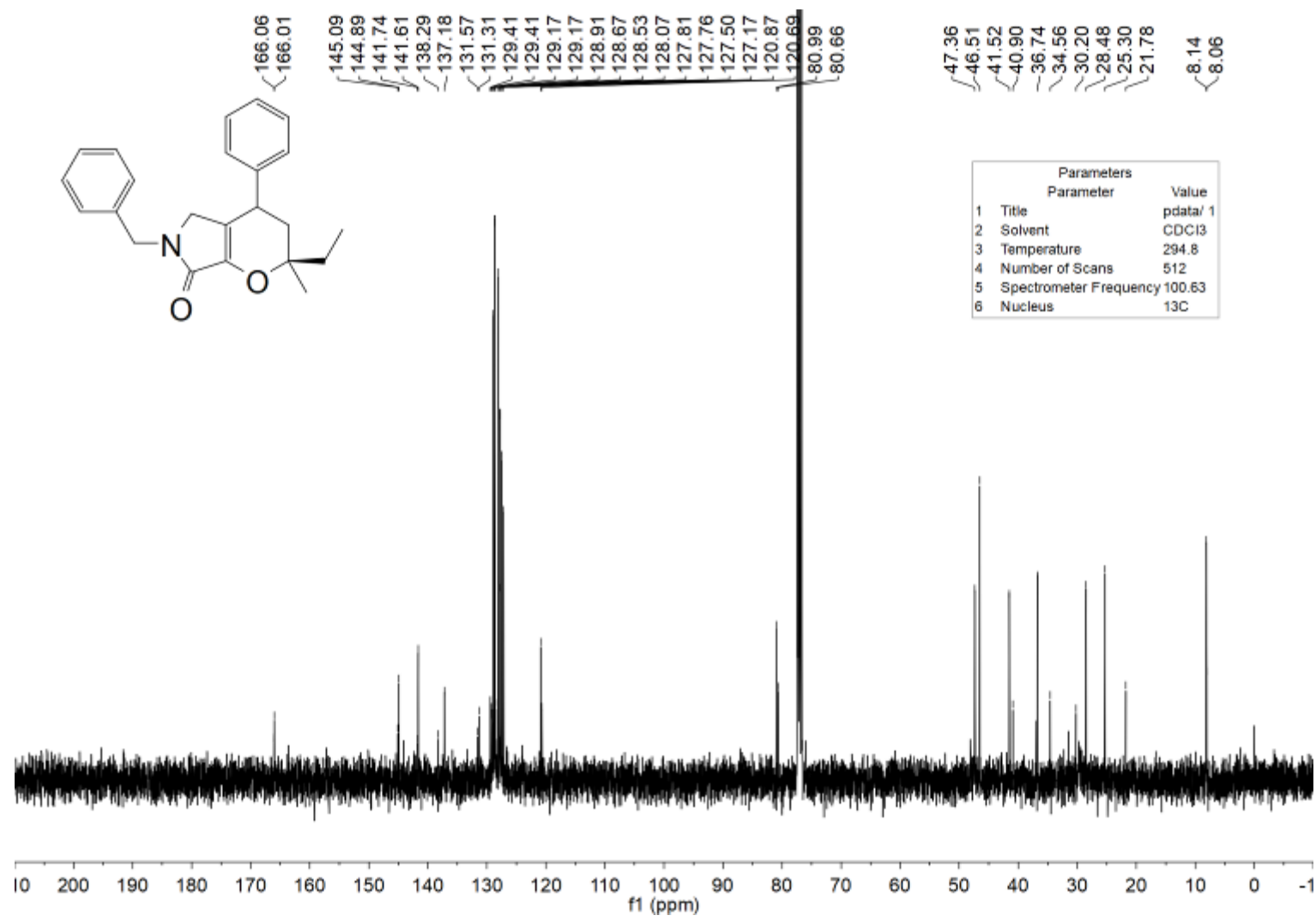


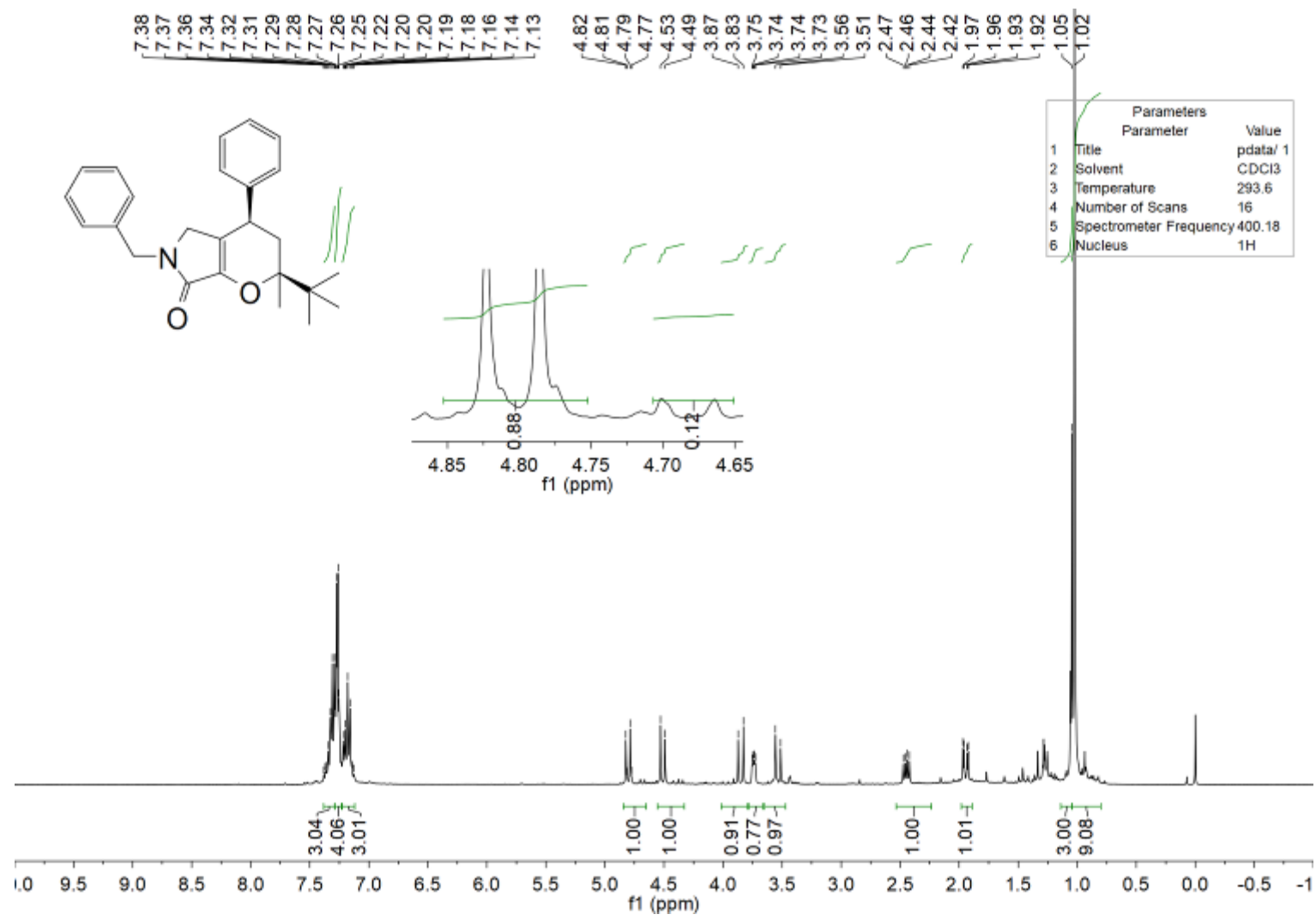


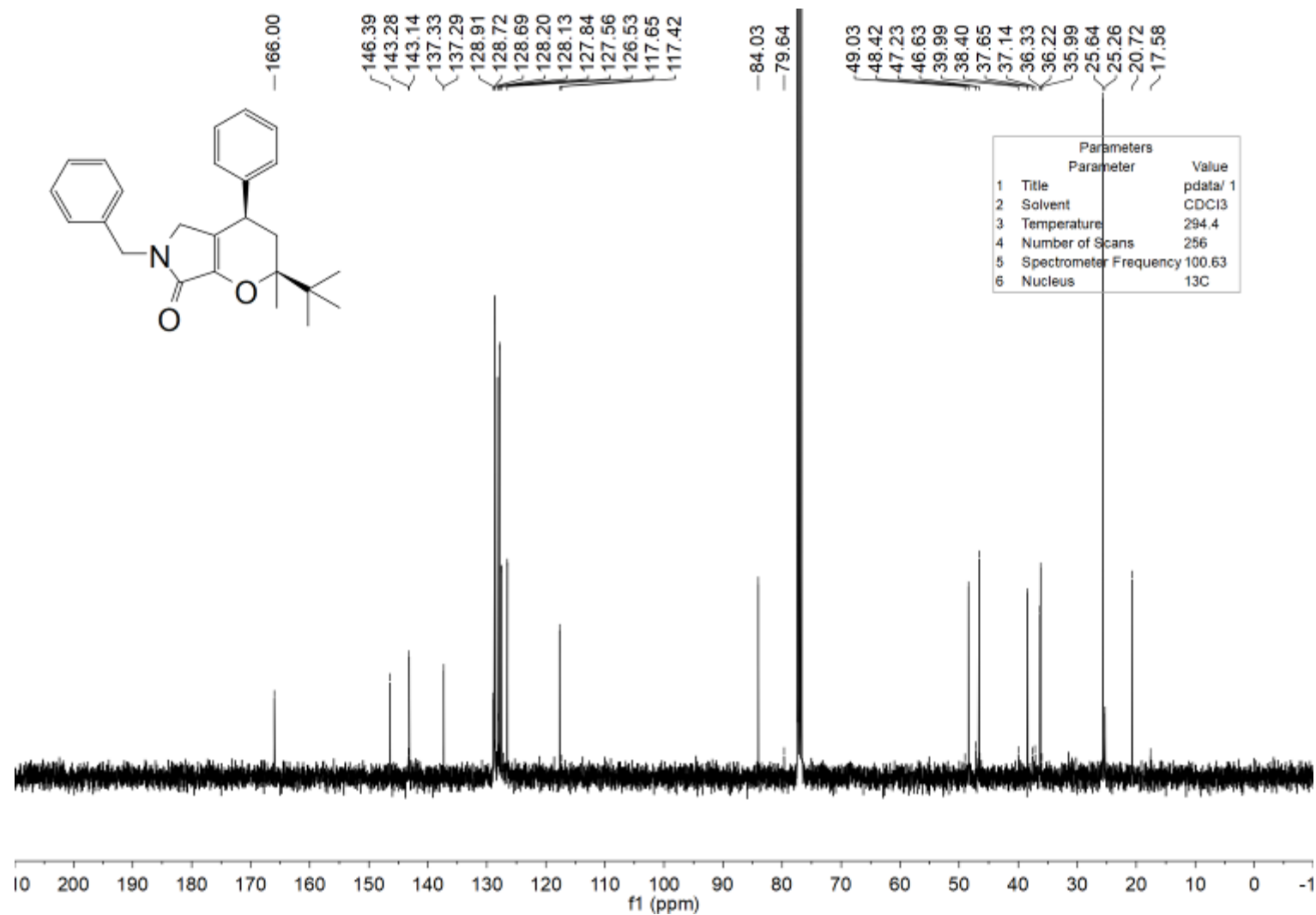


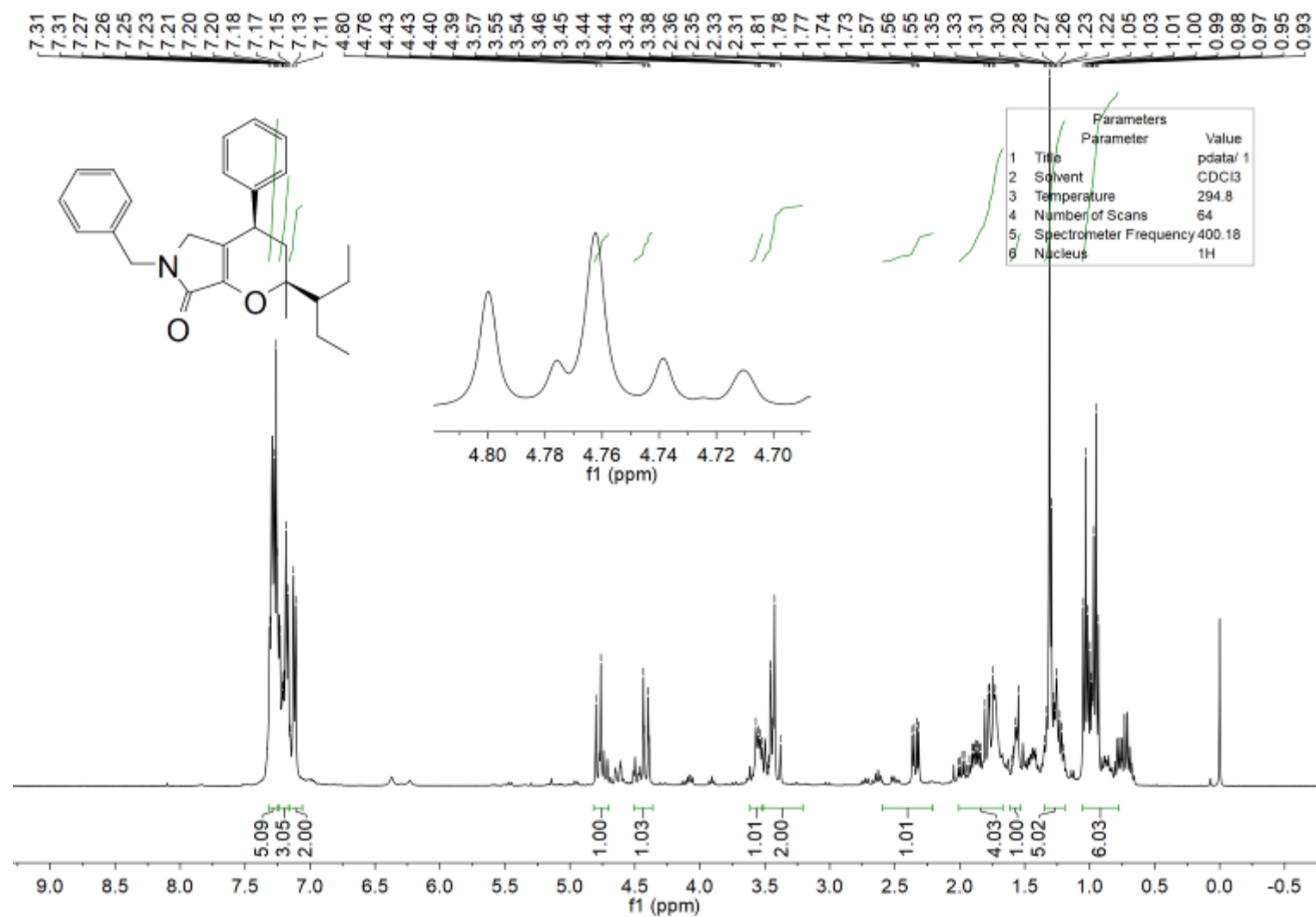


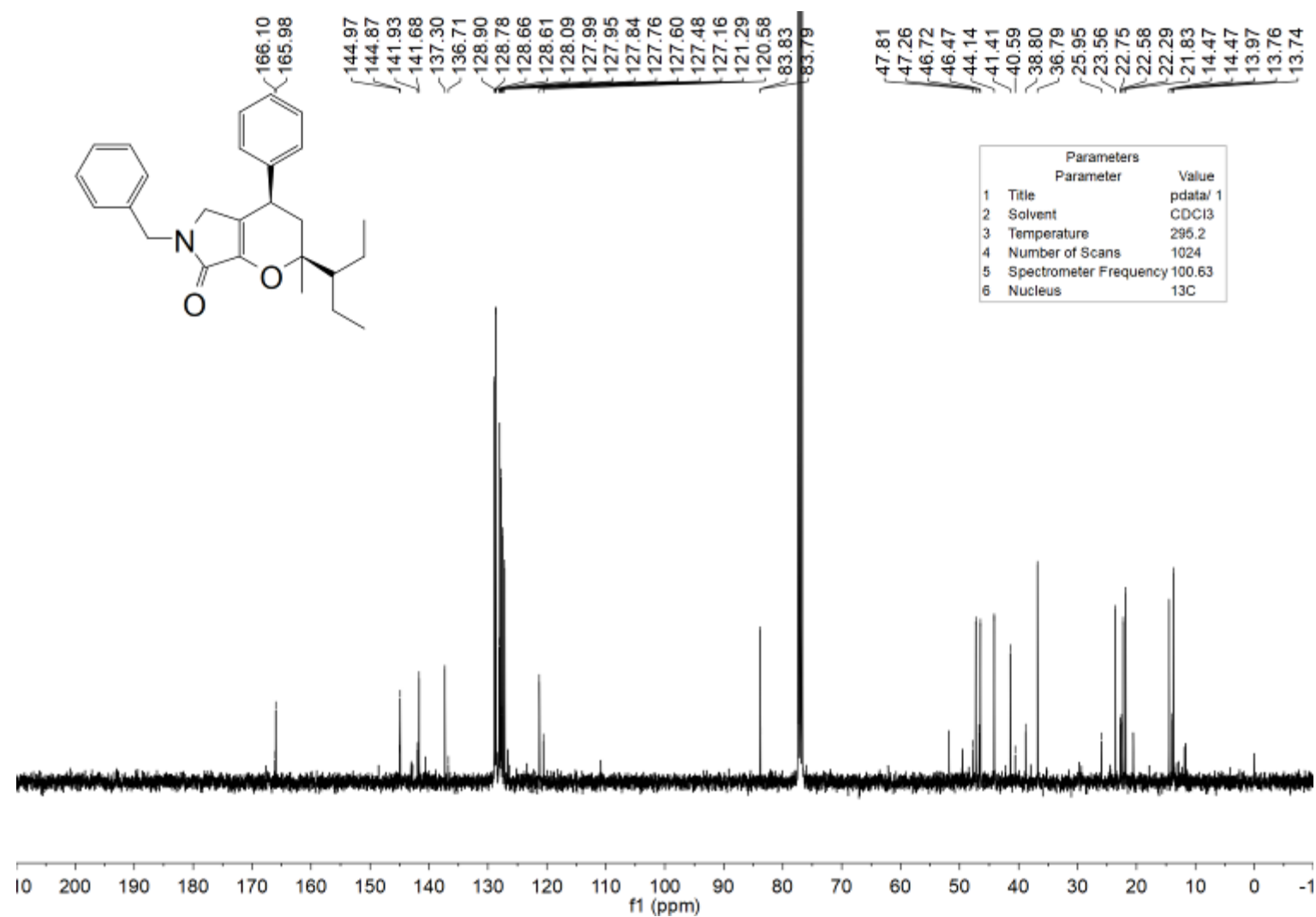


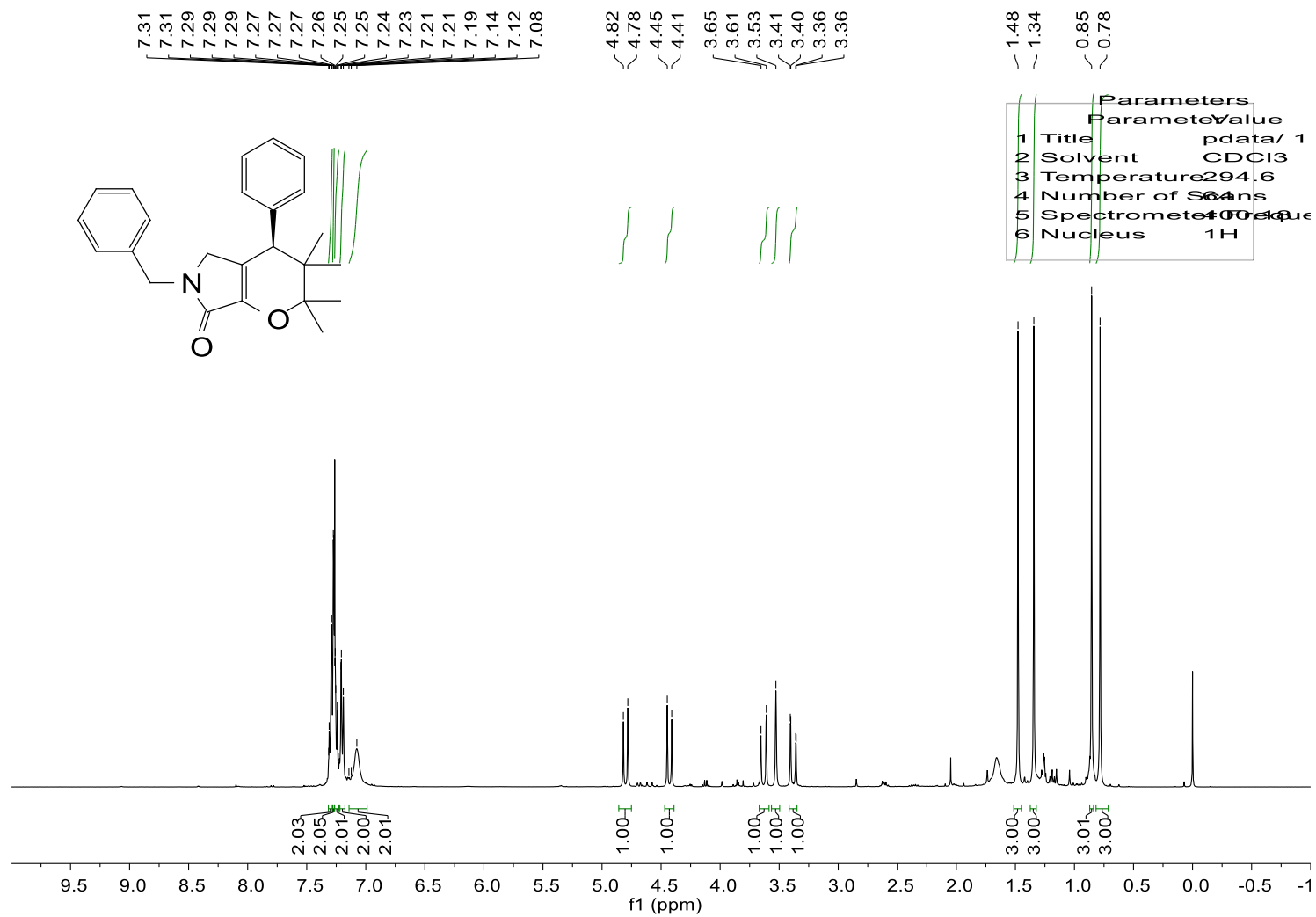


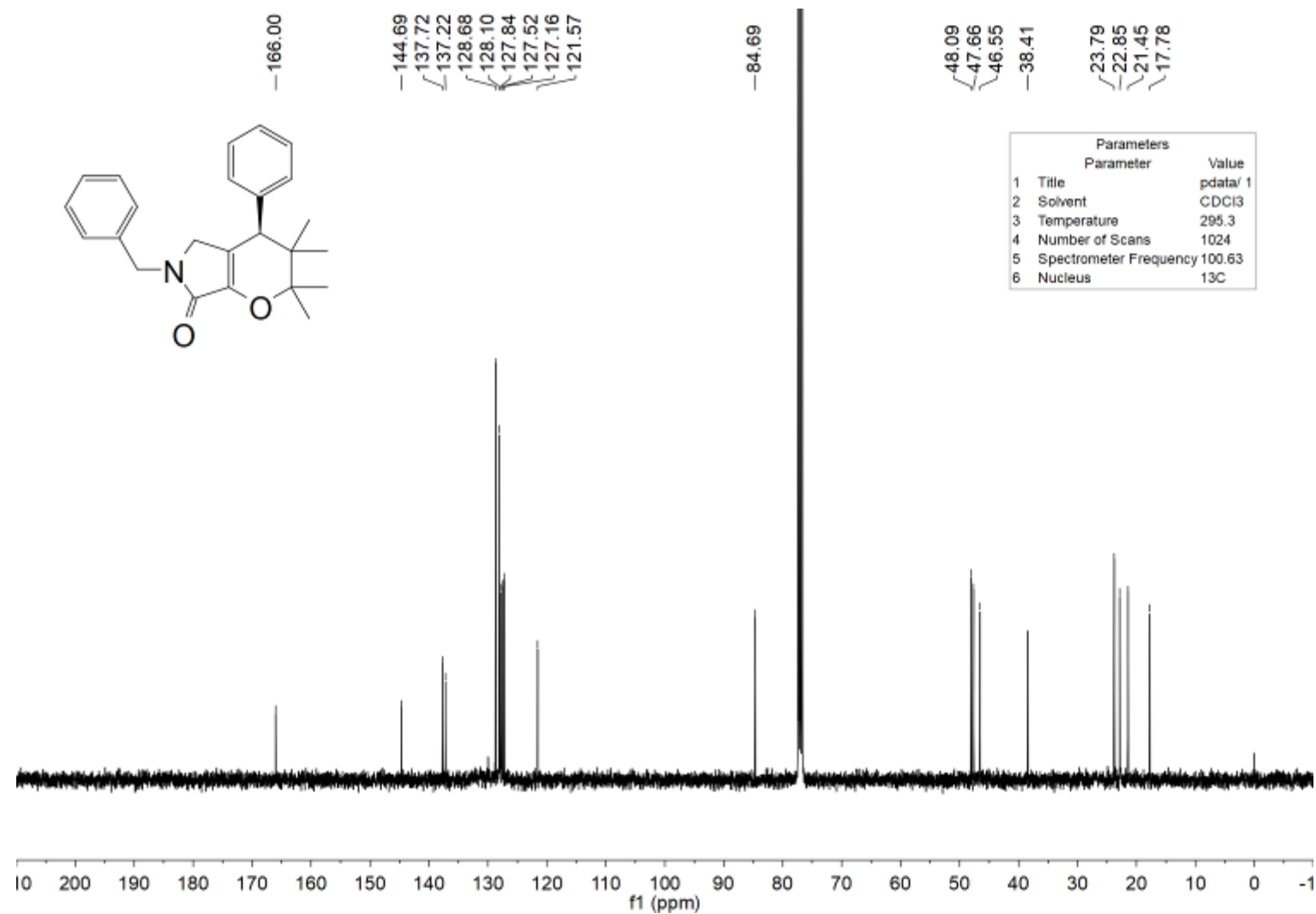


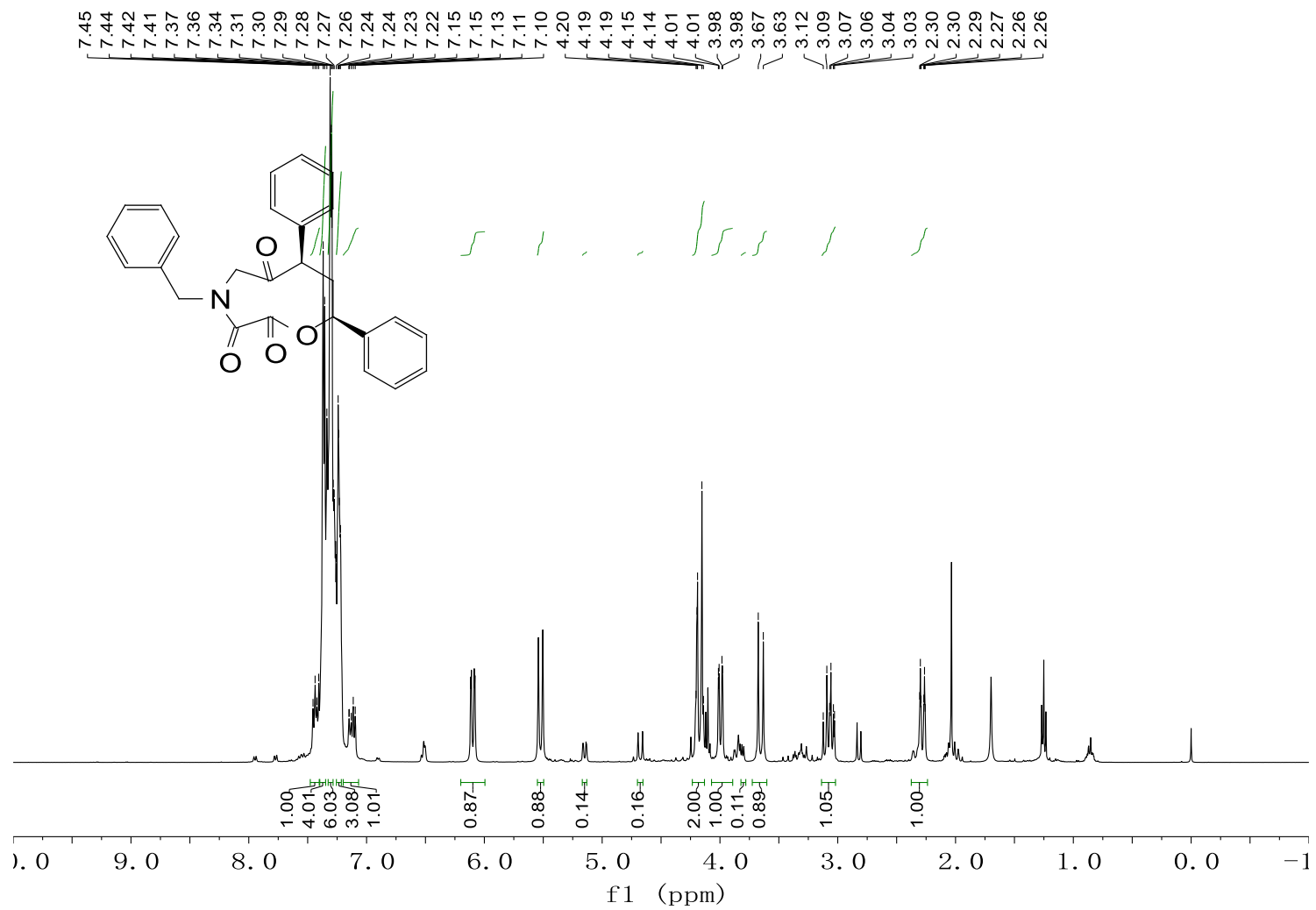


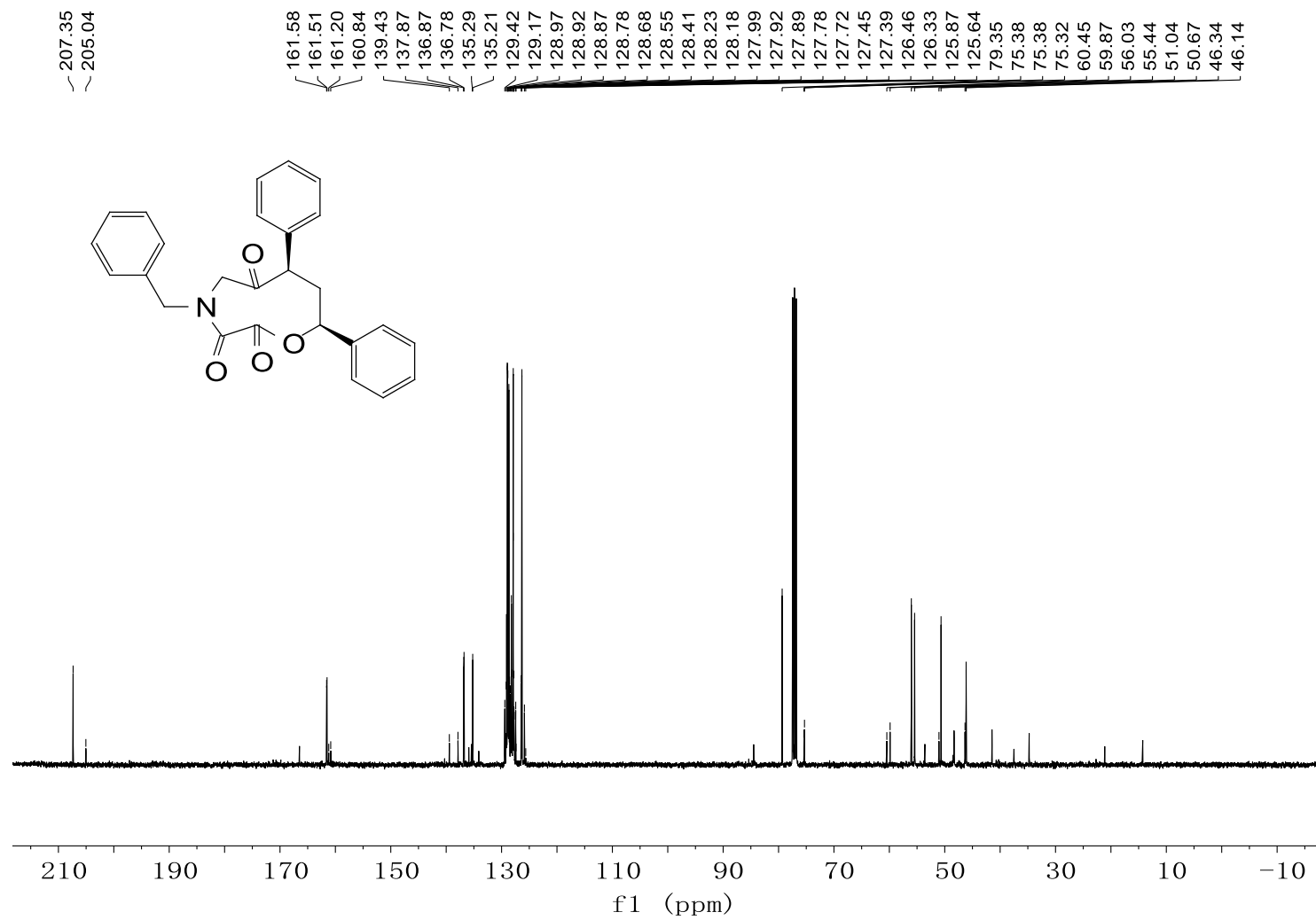


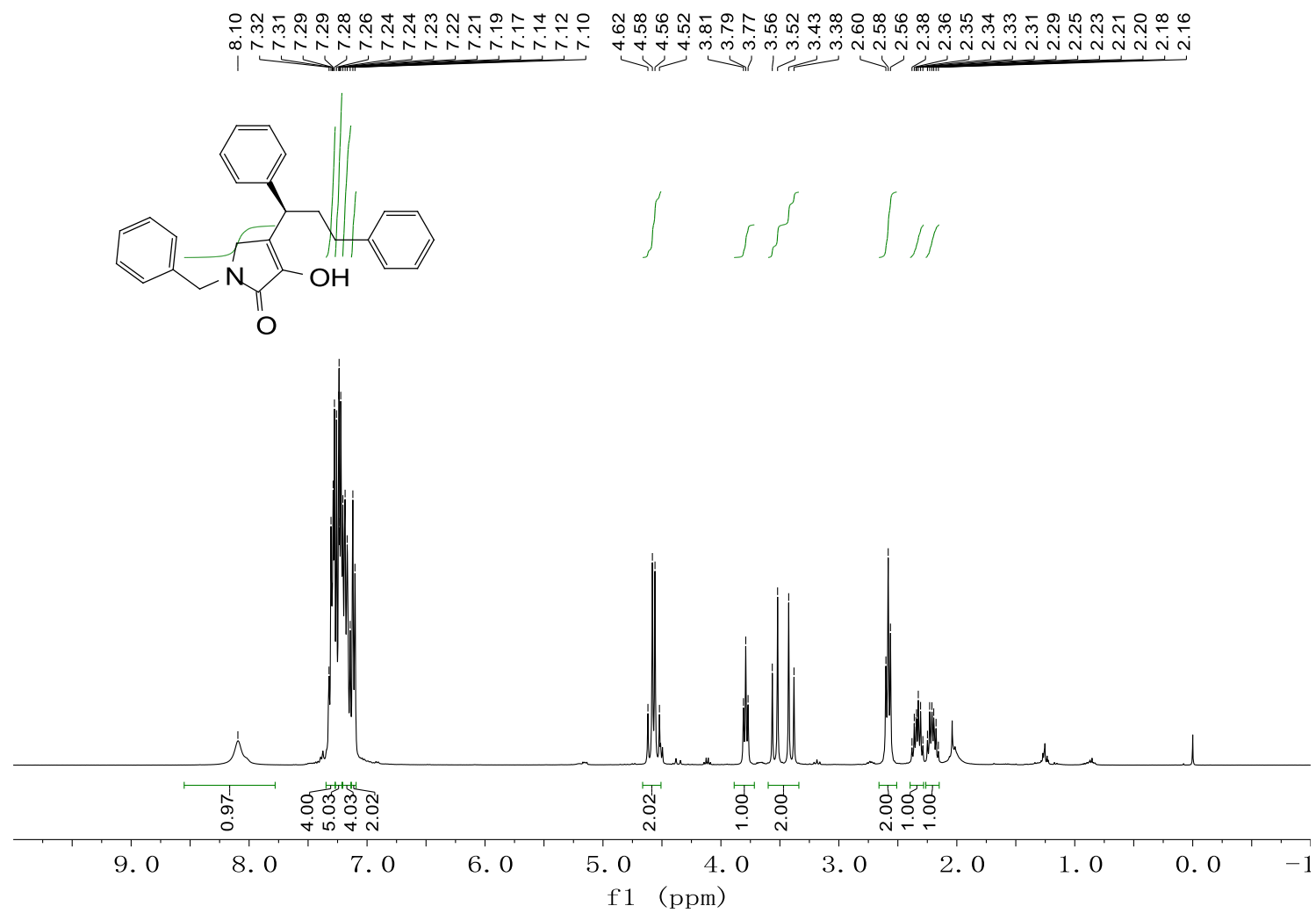


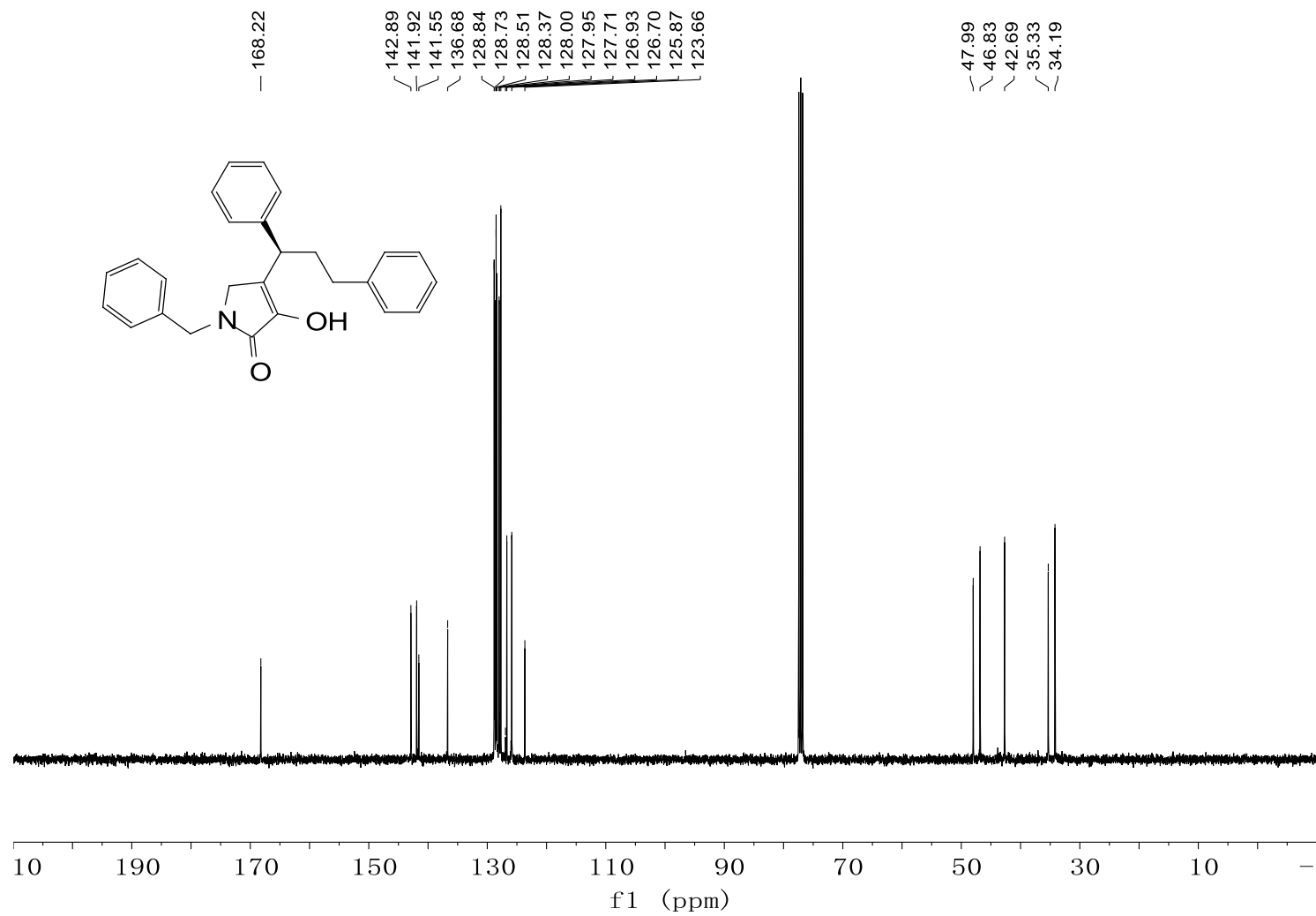


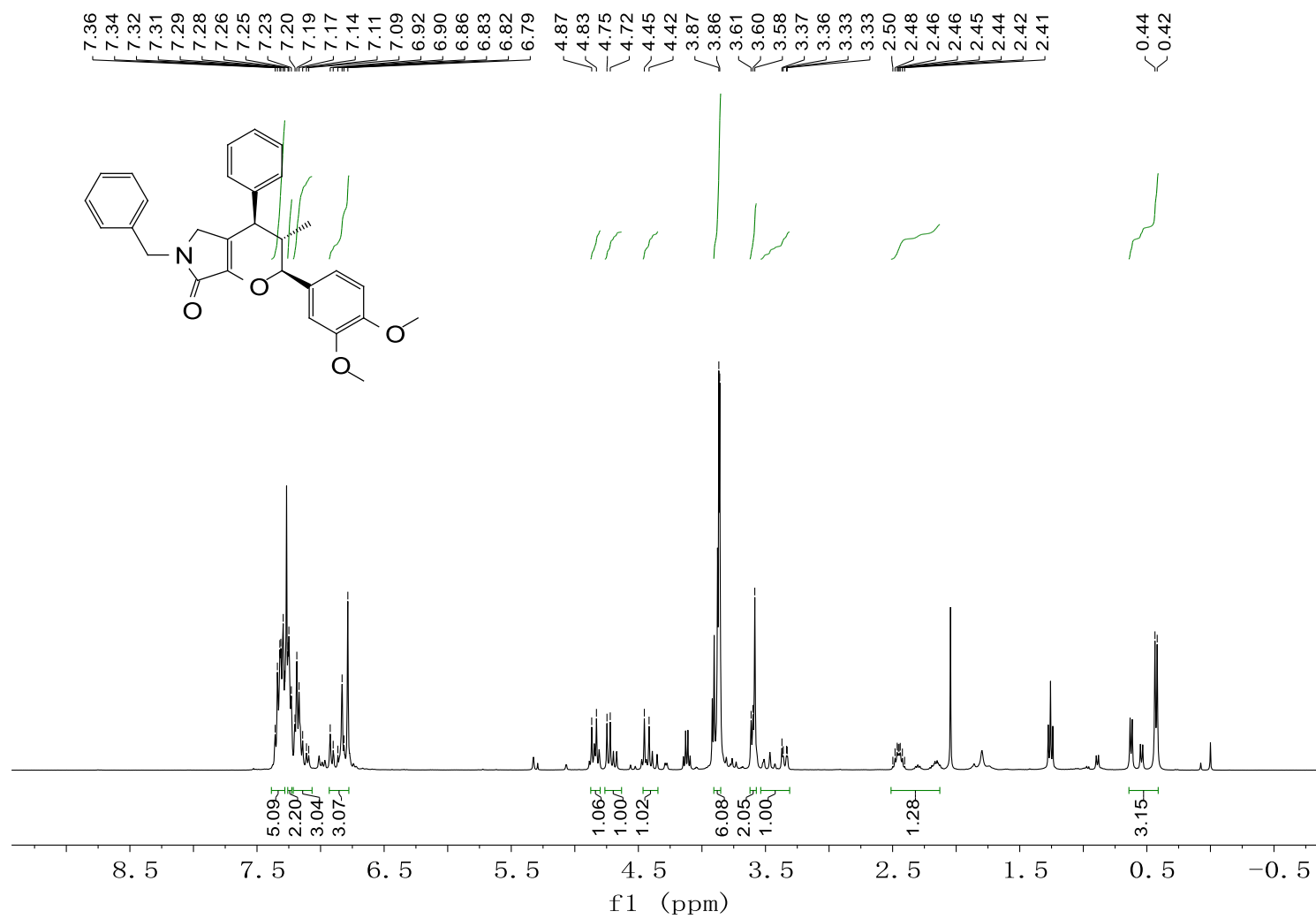


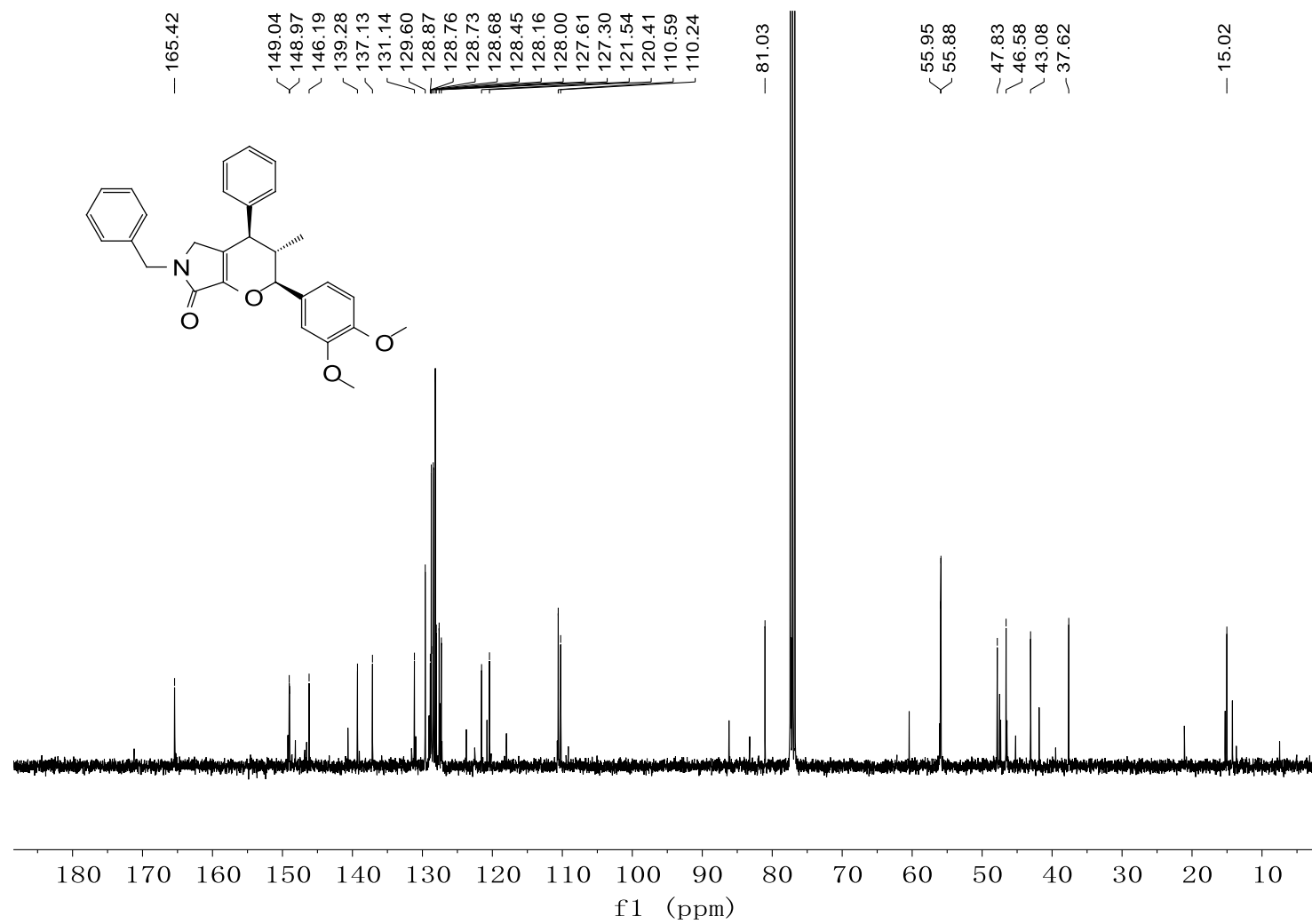


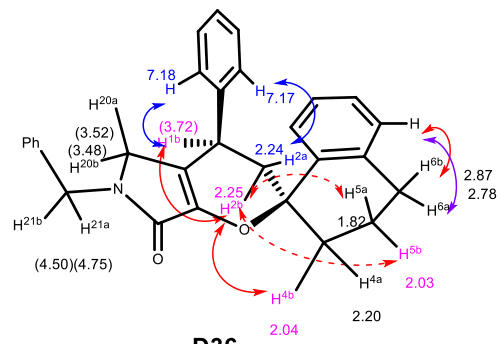
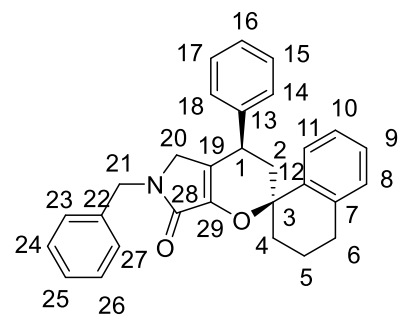












D36

Entry	H (ppm)	C (ppm)	entry	H (ppm)	C (ppm)
1	3.70	37.27	15	7.30	128.82
2	2.24, 2.25	43.36	16	7.18	126.36
3		79.94	17	7.30	128.81
4	2.20, 2.04	31.4, 31.4	18	7.17	127.66
5	2.03, 1.82	19.46, 19.44	19		121.03
6	2.87, 2.78	29.66, 29.58	20	3.52, 3.48	47.44, 47.41
7		137.41	21	4.75, 4.50	46.55, 46.58
8	7.07	128.77	22		137.01
9	7.17	127.87	23	7.22	128.01
10	7.29	128.84	24	7.21	127.13
11	7.54	127.38	25	7.22	128.47
12		136.86	26	7.22	127.13
13		141.32	27	7.22	128.01
14	7.17	127.66	28		165.93
			29		145.38

