Water enables the tunable electrochemical synthesis of heterocyclic 3a- and 5a-bromoindolines

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Supporting Information

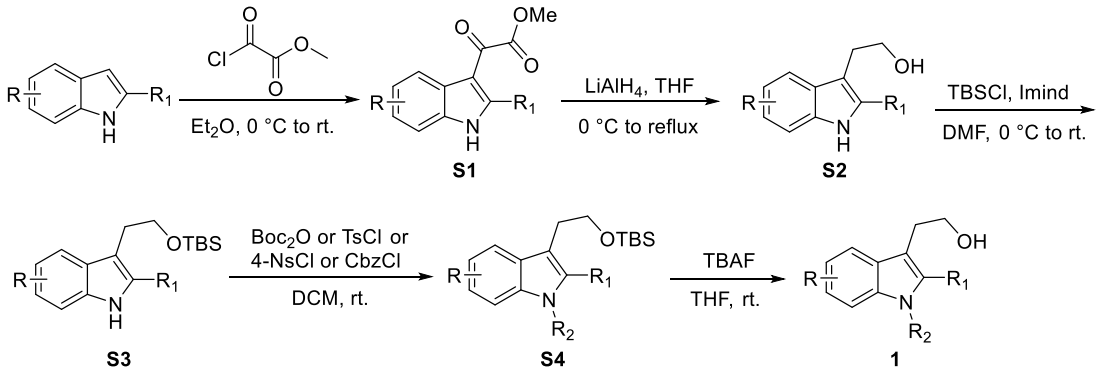
Content

1. General information

Unless stated, otherwise all reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. All the reactions that need to be heated, the oil bath is used as a heating source. All solvents and reagents were obtained from commercial sources and were purified according to standard procedures before use. Column chromatography was performed on silica gel (Qingdao, 300 - 400 mesh) using the indicated eluents. NMR spectra were recorded on an Agilent Mercury 600 MHz spectrometer (^{1}H: 600 MHz and ^{13}C: 150 MHz) in chloroform-*d*. ^{1}H and ^{13}C NMR spectra were internally referenced to the proton (^{1}H) of the internal TMS signal at 0.00 ppm or the solvent residue of DMSO at 2.54 ppm and the residual carbon nuclei (^{13}C) of the solvent at 77.0 or 39.5 ppm, respectively. Data for ^{1}H NMR were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, coupling constant(s) in Hz, integration). High resolution mass spectra were obtained using Bruker ESI-QTOF mass spectrometry.

2. Preparations of tryptophol and tryptamine substrates

2.1 Preparations of tryptophol substrates



Substrates **1a-1d**, **1f-1o** are known compounds, the general procedure for synthesis of these substrates are described as below according to previous literatures.[1-3, 7]

General procedures: To a solution of indole (10.0 mmol) in dry Et_2O (50 mL) at 0 ℃ was added dropwise methyl oxalyl chloride (2.7 mL, 30.0 mmol). The ice bath was removed and the resultant yellow slurry was stirred at room temperature for 6 h. The crude reaction mixture was filtered with celite and washed with cold Et_2O. The solid **S1** was used directly for the next step without further purification. A solution of **S1** in THF (20 mL) was added dropwise to a suspension of $LiAlH_4$ (1.52 g, 40 mmol) in THF (40 mL) at 0 ℃. The solution was stirred at 80 ℃ for 2 h and quenched carefully by H_2O (1.5 mL), 10% aqueous NaOH (3.0 mL), H_2O (4.5 mL) at 0 ℃. The solution was then filtered and washed with EtOAc. The combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure to give the crude product. The crude product was purified by silica gel column chromatography (EtOAc/hexane = 1:3) to afford the tryptophol **S2.**

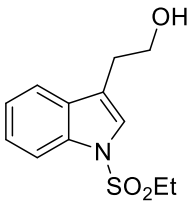
TBSCl (1.66 g, 11 mmol) was added to a solution of **S2** (10.0 mmol) and imidazole (1.36 g, 20.0 mmol) in DMF (50 mL) at 0 ℃. The ice bath was then removed and the reaction mixture was stirred at room temperature for 3 h. The mixture was quenched with water and extracted with EtOAc (3×30 mL), then the combined organic layers were washed with water, brine, dried over Na_2SO_4, filtered

and concentrated under reduced pressure. The residue was used directly for the next step without further purification.

To a solution of **S3** in THF (50 mL) was added NaH (400 mg, 10.0 mmol) at 0 ℃. After stirring at 0 ℃ for 15 min and then at room temperature for 1 h, the reaction mixture was cooled to 0 ℃, treated with Boc_2O or TsCl or CbzCl or 4-NsCl (11.0 mmol), and then allowed to stir at room temperature for 6-12 h. After the reaction was complete (monitored by TLC), aqueous saturated $NaHCO_3$ (30 mL) was added slowly. The organic layer was separated and the aqueous layer was extracted with EtOAc (3×30 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product **S4** was further treated with tetrabutylammonium fluoride (15 mmol), after 24 h, the mixture was worked up and purified by silica gel column chromatography (EtOAc/hexane = 1/2) to afford the desired product **1**.

The physical datas for new compounds were provided below:

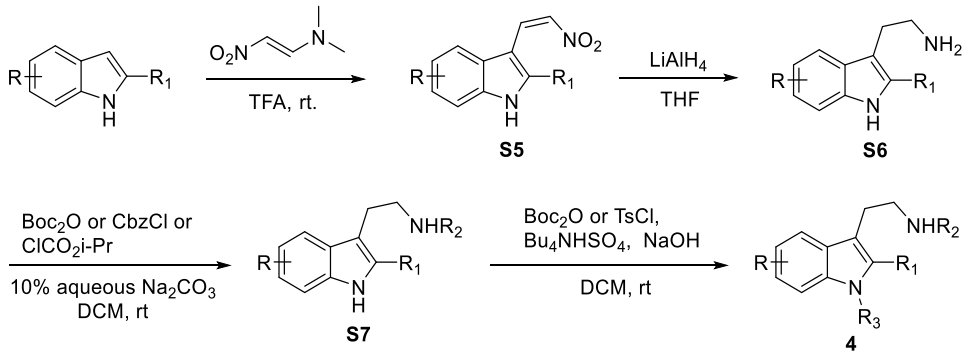
2-(1-(ethylsulfonyl)-1H-indol-3-yl)ethan-1-ol (**1e**)



1e

Following the general procedure for preparations of tryptophol substrates. The procedure was performed on tryptophol (0.4836 g, 2 mmol) to afford **1e,** Light yellow oil, 290.6 mg, 57% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.2 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.26–7.17(m, 3H), 3.79 (t, *J* = 6.6 Hz, 2H), 3.16 (q, *J* = 7.4 Hz, 2H), 2.84 (t, *J* = 6.6 Hz, 2H), 1.09 (t, *J* = 7.4 Hz, 3H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 135.2, 130.5, 124.7, 124.0, 123.0, 119.5, 118.3, 113.0, 61.5, 48.3, 28.1, 7.8 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{12}H_{15}NO_3SNa$ 276.0665; Found 276.0654.

2.2 Preparations of tryptamine substrates



Substrates **4a**, **4b**, **4c**, **4f**, **4g**, **4h**, **4i**, **4j**, **4l**, **4m** were prepared according to the published procedures[1, 5].

General procedures: To a solution of 1-dimethylamino-2-nitroethylene (20.0 mmol) in trifluoroacetic acid (15 mL) was added indole (20.0 mmol) at 0 ℃. The mixture was allowed to warm to room temperature and stirred for 0.5 hours. The reaction mixture was basified to pH 9~10 using saturated $NaHCO_3$ in aqueous solution and extracted with DCM. The combined organic layers were washed with saturated brine, dried over Na_2SO_4, filtered and concentrated in vacuo to furnish the desired crude nitroolefin. The crude nitroolefin was purified by flash column chromatography (Petroleum ether/ EtOAc = 3/1) to give the tryptophan derivative **S5**.

Under a nitrogen atmosphere, the THF solution (10 mL/mmol of **S5**) of **S5** (1.0 equiv.) was added to a stirred slurry of $LiAlH_4$ (6.0 equiv.) in THF at 0 ℃. The mixture was allowed to warm to room temperature and after completion as detected by TLC. After the reaction mixture was cooled to 0℃, the reaction was quenched by dropwise addition of H_2O until effervescence ceased and followed by three times the amount of H_2O of 15% aqueous sodium hydroxide. After being stirred at room temperature for 12 hours, the solid was removed by filtration (or the mixture was filtered through Celite pad to remove by-product). The filtrate was concentrated to dryness to give crude product **S6**.

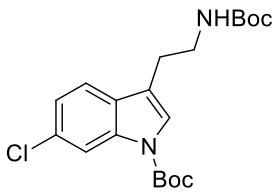
The tryptamine derivative **S6** was dissolved in CH_2Cl_2 (2 mL/mmol of **S6**) and 10% aqueous Na_2CO_3 (1 mL/mmol of **S6**), and then to the reaction mixture was added Boc_2O or CbzCl or isobutyl chlorocarbonate (2 equiv.). After completion as detected by TLC, the reaction mixture was diluted with water. The organic layer was collected

and the aqueous phase was extracted with EtOAc. The combined extracts were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo* to give the desired tryptamine derivative **S7**, which was used for the next step without further purification.

To a stirred solution of tryptamine derivative **S7** in CH_2Cl_2 (3 mL/mmol of **S6**) were sequentially added Bu_4NHSO_4 (0.1 equiv.) and NaOH (4.5 equiv.) at 0 ℃. The resulting mixture was stirred at room temperature for 5 minutes before addition of TsCl or Boc_2O (2 equiv.). The reaction mixture was allowed to stir at room temperature and after completion as detected by TLC. Water was added, and the mixture was extracted with EtOAc. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (Petroleum ether/EtOAc = 10/1) to give the tryptophan derivative **4.**

The physical datas for new compounds were provided below:

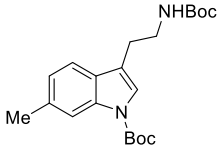
***tert*-butyl-3-(2-((tert-butoxycarbonyl)amino)ethyl)-6-chloro-1*H*-indole-1-carboxy late (4d)**



4d

Following the general procedure for synthesis of the tryptophan derivative. The procedure was performed on 6-Chloroindole (1.51 g, 10 mmol) to afford **4d**. Yellow solid, 2.12 g, 54% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.17 (s, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.39 (s, 1H), 7.21 (dd, *J* = 8.2, 1.8 Hz, 1H), 4.63 (s, 1H), 3.45–3.41 (m, 2H), 2.86 (t, *J* = 7.0 Hz, 2H), 1.67 (s, 9H), 1.44 (s, 9H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 155.8, 149.3, 130.5, 128.9, 123.6, 123.0, 119.7, 117.6, 115.6, 84.1, 79.4, 40.2, 28.4, 28.1, 25.5 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{27}N_2O_4ClNa$ 417.1552; Found 417.1551.

***tert*-butyl-3-(2-((tert-butoxycarbonyl)amino)ethyl)-6-methyl-1H-indole-1-carboxy late(4e)**

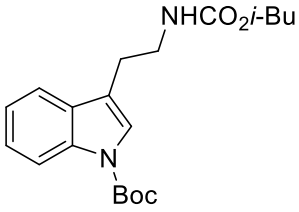


4e

Following the general procedure for synthesis of the tryptophan derivative. The procedure was performed on 6-Methylindole (1.31 g, 10 mmol) to afford **4e**. Brown oil, 717.9 mg, 19% yield; **^{1}H NMR**

(600 MHz, Chloroform-*d*) δ 8.00 (s, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.33 (s, 1H), 7.07 (d, *J* = 7.8 Hz, 1H), 4.69 (s, 1H), 3.46–3.43 (m, 2H), 2.87 (t, *J* = 7.0 Hz, 2H), 2.48 (s, 3H), 1.66 (s, 9H), 1.44 (s, 9H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 155.9, 149.7, 136.0, 134.4, 128.1, 123.8, 122.4, 118.5, 117.7, 115.5, 83.2, 79.1, 40.2, 28.3, 28.1, 25.6, 21.9 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{21}H_{30}N_2O_4Na$ 397.2098; Found 397.2095.

***tert*-Butyl 3-(2-((isopropoxycarbonyl)amino)ethyl)-1H-indole-1-carboxylate (4k)**



4k

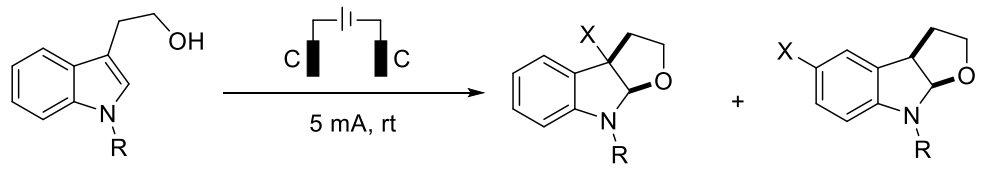
Following the general procedure for synthesis of the tryptophan derivative. The procedure was performed on Indole (0.80 g, 5 mmol) to afford **4k**. Light yellow oil, 441.8 mg, 25% yield. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.14 (s, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.42 (s, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 1H), 4.84 (s, *J* = 6.0 Hz, 1H), 3.85 (d, *J* = 6.8 Hz, 2H), 3.53–3.49 (m, 2H), 2.91 (t, *J* = 7.0 Hz, 2H), 1.91–1.87 (m, 1H), 1.67 (s, 9H), 0.91 (d, *J* = 6.8 Hz, 6H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 156.7, 149.6, 135.5, 130.3, 124.4, 123.1, 122.5, 118.9, 117.6, 115.3, 83.5, 70.9, 40.5, 28.2, 28.0, 25.6, 19.0 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{28}N_2O_4Na$ 383.1941; Found 383.1938.

3. Optimization of the reaction conditions

3.1 Electrolysis general informations

Electrochemical reactions were performed with ElectraSyn 2.0 package (IKA) using the constant current or constant voltage modes. The reactions were conducted in a 10 mL vial for 4 mL of solvent with a stir bar and a carbon graphite-SK-50 (5.0 × 0.8 × 0.2 cm) working electrode (anode and cathode) with a distance of 0.6 cm between the two electrodes.

3.2 Screening of protecting group, solvent and electrolyte [a]

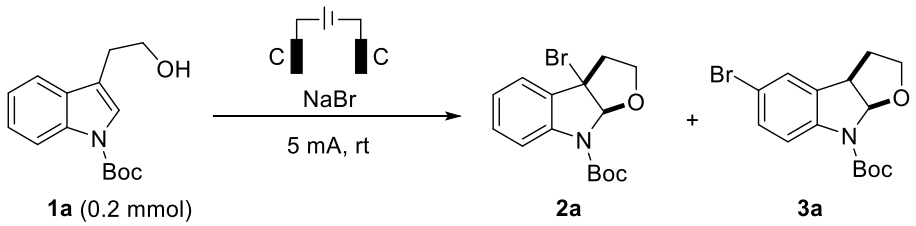


1 (0.2 mmol) **2** X = Br or Cl **3**

Entry	R	Electrolyte	Solvent (mL)	*t* (h)	Yield **2** (%)	Yield **3** (%)
1	H	NaBr	MeCN (4)	24	0	0
2	Boc	NaBr	MeCN (4)	24	69	0
3	Boc	NaBr	MeCN/EtOH (4/0.1)	24	NR	NR
4	Boc	NaBr	MeCN/H_2O (4/0.1)	4	83	0
5	Boc	NaCl	MeCN (4)	24	Trace	NR
6	Boc	NH_4Cl	MeCN (4)	24	NR	NR

[a] Reaction conditions: undivided cell, carbon cloth anode and cathode, **1** (0.2 mmol), electrolyte (0.4 mmol), CH_3CN (4 mL), CCE = 5.0 mA, 4 h, rt, under air. Yields were isolated yields. CCE = constant current electrolysis.

3.3 Screening of the amounts of water [a]

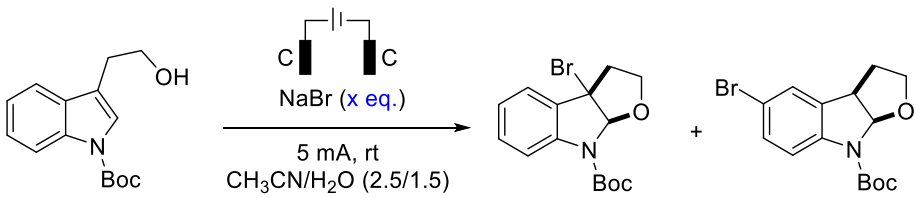


1a (0.2 mmol) **2a** **3a**

Entry	Solvent (mL)	*t* (h)	Yield **2a** (%)	Yield **3a** (%)
1	MeCN/H_2O (4/0.1)	4	83	0
2	MeCN/H_2O (4/0.3)	7	77	0
3	MeCN/H_2O (4/0.5)	7	68	0
4	MeCN/H_2O (3/1)	12	39	31
5	MeCN/H_2O (2.5/1.5)	12	trace	75
6	MeCN/H_2O (2/2)	12	trace	34
7	MeCN/H_2O (1/3)	12	trace	trace
8	H_2O (4)	12	trace	0

[a] Reaction conditions: undivided cell, carbon cloth anode and cathode, **1a** (0.2 mmol), electrolyte (0.4 mmol), CCE = 5.0 mA, rt, under air. Yields were isolated yields. CCE = constant current electrolysis.

3.4 Screening of the amounts of NaBr [a]



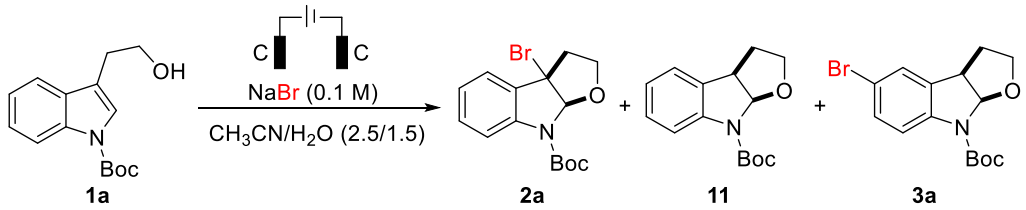
1a (0.2 mmol) **2a** **3a**

Entry	x	Yield **2a** (%)	Yield **3a** (%)
1	1.5	trace	64
2	2	trace	75
3	3	10	67

[a] Reaction conditions: undivided cell, carbon cloth anode and cathode, **1a** (0.2 mmol), CH_3CN/H_2O (2.5/1.5), CCE = 5.0 mA, 12 h, rt, under air. Yields were isolated yields. CCE = constant current electrolysis.

4. Mechanistic studies

4.1 Kinetic experiments



Reaction procedure: A mixture of **1a** (0.2 mmol) and NaBr (41.2 mg, 0.4 mmol) were added in a 10 mL vial with a stir bar, then CH_3CN/H_2O (2.5/1.5 mL) were added under air atmosphere. The vial was covered with the electrode holder. The electrolysis was carried out at RT using a constant current of 5.0 mA between a carbon graphite anode and carbon graphite cathode (1.4 × 0.8 × 0.2 cm submerged in solution) with stirring. The reactions were stopped respectively at 0.5 h, 1 h, 1.5 h, 2 h, 2.5 h, 3 h, 4 h, 5 h, 8 h and 12 h. The reaction mixture was diluted with EtOAc. The organic phase was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. Yields were determined by ^1H NMR with TTCE as internal standard. The plots of the percentage yield of the product displayed in Figure S1.

Entry	*t* (h)	Yield **2a** (%)	Yield **11** (%)	Yield **3a** (%)	Recoved yield **1a** (%)
1	0	0	0	0	100
2	0.5	13	6	0	80
3	1	18	10	3	65
4	1.5	28	13	5	53
5	2	36	20	7	42
6	2.5	28	25	13	33
7	3	22	28	18	27
8	4	18	40	24	15
9	5	14	31	30	8
10	6.5	10	23	43	0
11	8	8	18	55	0
12	10	4	9	68	0
13	12	2	4	75	0

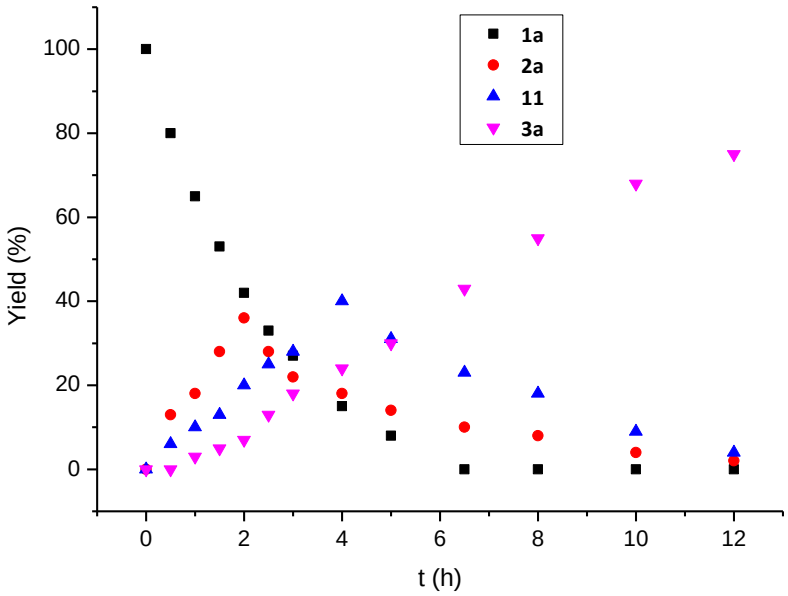
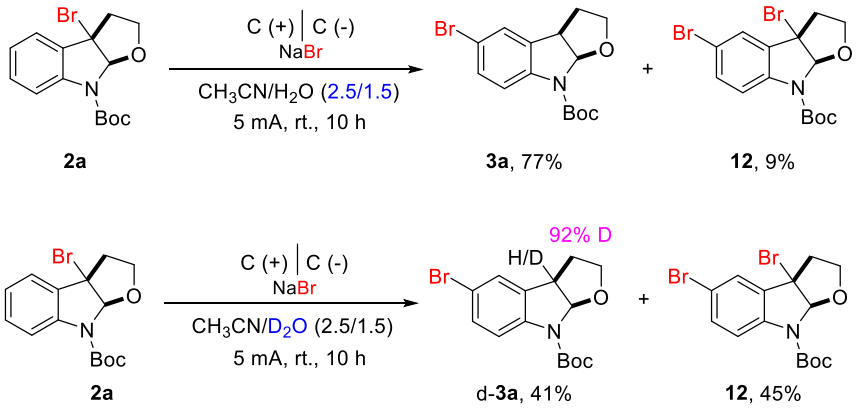
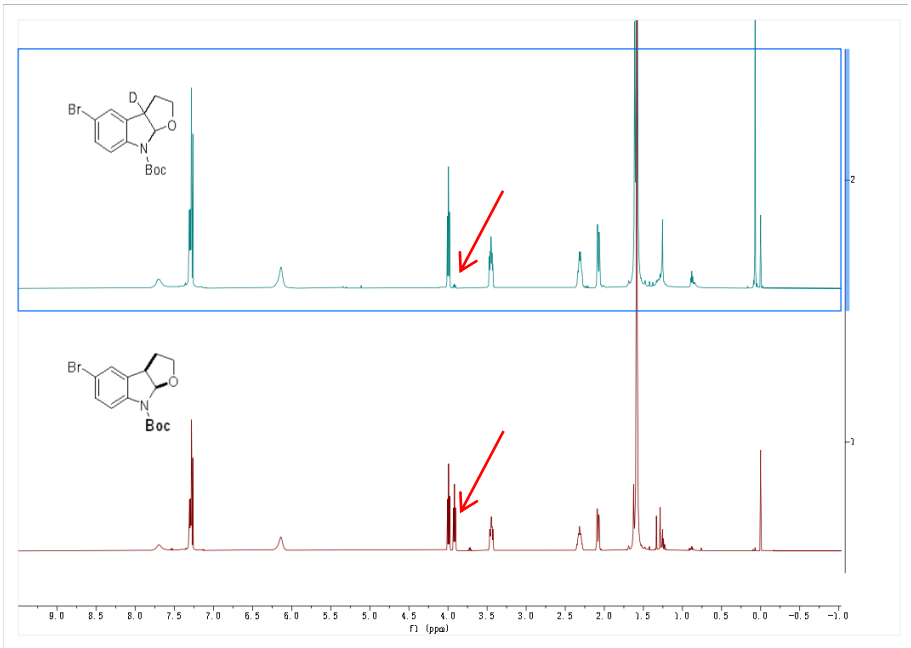


Figure S1 Results of kinetic experiments

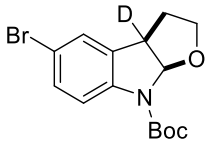
4.2 Investigation of the hydrodebromination process and isotopic experiment using D_2O





General Procedure for deuterium labelling experiments: A mixture of **2a** (0.2 mmol) and NaBr (41.2 mg, 0.4 mmol) were added in a 10 mL vial with a stir bar, then CH_3CN/H_2O (2.5/1.5mL) were added under air atmosphere. The vial was covered with the electrode holder. The electrolysis was carried out at RT using a constant current of 5.0 mA a carbon graphite anode and carbon graphite cathode (1.4 × 0.8 × 0.2 cm submerged in solution) with stirring for 10 h. After completion as detected by TLC. The reaction mixture was diluted with EtOAc. The organic phase was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure, purified by flash column chromatography (Petroleum ether/Ethyl acetate = 10/1) to give compound **3a** and **12**.

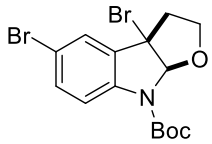
***tert*-Butyl-5-bromo-2,3,3a,8a-tetrahydro-8H-furo[2,3-*b*]indole-8-carboxylate-3a-d (d-3a)**



d-3a

Light brown solid, m.p. 81.1 – 82.8 °C, 28.0 mg, 41% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.70 (s, 1H), 7.31–7.28 (m, 2H), 6.14 (s, 1H), 3.99 (t, *J* = 8.2 Hz, 1H), 3.47–3.42 (m, 1H), 2.34–2.29 (m, 1H), 2.09–2.06 (m, 1H), 1.58 (s, 9H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 152.2, 131.0, 127.4, 115.8, 115.1, 93.5, 66.4, 33.6, 28.3 ppm. **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{17}DBrNO_3Na$ 363.0425; Found 363.0418.

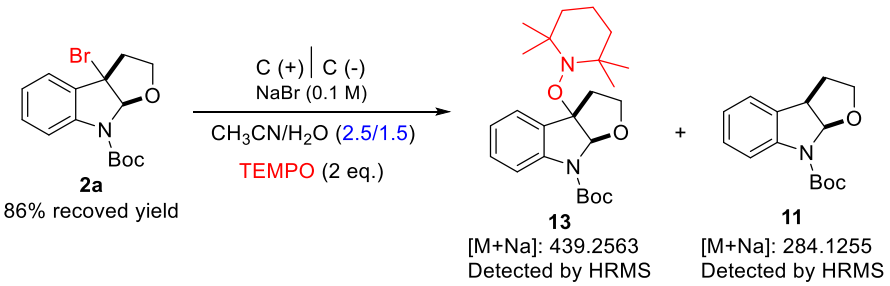
***tert*-Butyl-3a,5-dibromo-2,3,3a,8a-tetrahydro-8H-furo[2,3-b]indole-8-carboxylate (12)**



12

Light brown oil, 10 h, 38.0 mg, 45% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.73 (s, 1H), 7.51 (d, *J* = 2.0 Hz, 1H), 7.38 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.15 (s, 1H), 4.01 (t, *J* = 7.8 Hz, 1H), 3.52–3.48 (m, 1H), 2.90 – 2.85 (m, 1H), 2.78 – 2.75 (m, 1H), 1.59 (s, 9H) ppm. All spectral data were in agreement with the literature [1].

4.3 TEMPO trapping experiments and HRMS-ESI analysis

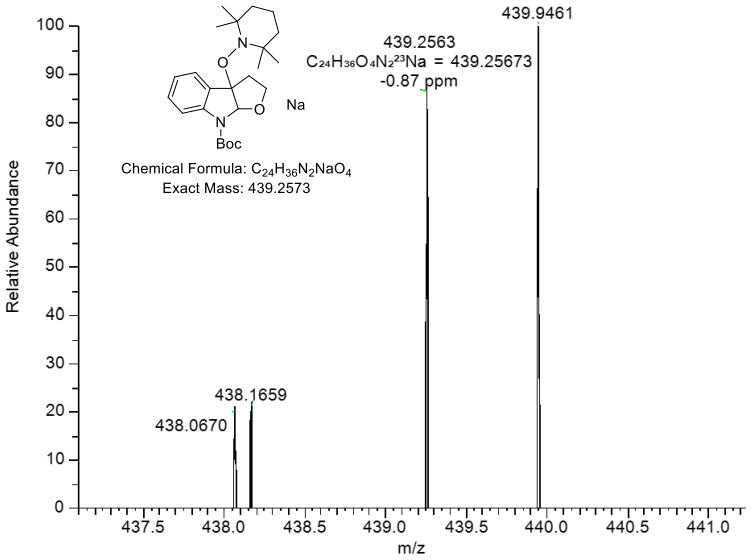


2a
86% recoved yield

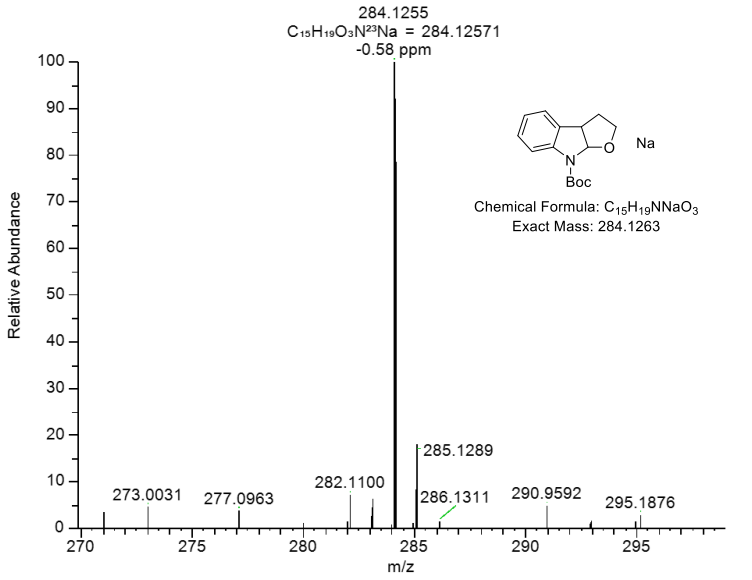
13
[M+Na]: 439.2563
Detected by HRMS

11
[M+Na]: 284.1255
Detected by HRMS

ra-612 #25 RT: 0.11 AV: 1 NL: 3.97E+006
T: FTMS + p ESI Full ms [100.0000-1500.0000]



ra-613 #124 RT: 0.55 AV: 1 NL: 4.49E+007
T: FTMS + p ESI Full ms [100.0000-1500.0000]

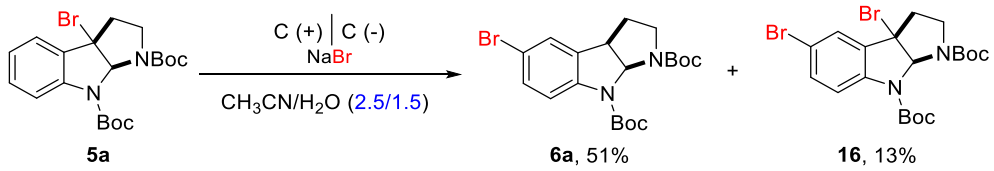


Procedure for HRMS-ESI analysis: A mixture of **2a** (0.2 mmol), NaBr (41.2 mg,

0.4 mmol) and TEMPO (62.5 mg, 0.4 mmol) were added in a 10 mL vial with a stir bar, then CH_3CN/H_2O (2.5/1.5 mL) were added under air atmosphere. The vial was covered with the electrode holder. The electrolysis was carried out at RT using a constant current of 5.0 mA between a carbon graphite anode and carbon graphite cathode (1.4 × 0.8 × 0.2 cm submerged in solution) with stirring. After 4 hours of reaction, send it to HRMS-ESI for monitoring.

4.4 Investigation of 3-bromopyrroloindoline

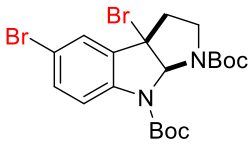
The reaction activities of 3-bromopyrroloindoline **5a** were also investigated. When the 3-bromopyrroloindoline **5a** was employed in the standard conditions, 51% yield of 5-bromopyrroloindoline **6a** and 13% yield of 3,5-dibromopyrroloindoline were obtained, providing further evidence for the formation of 5-bromoindoline via key 3-bromoindoline intermediate.



5a **6a**, 51% **16**, 13%

General Procedures: A mixture of **5a** (0.2 mmol) and NaBr (41.2 mg, 0.4 mmol) were added in a 10 mL vial with a stir bar, then CH_3CN/H_2O (2.5/1.5 mL) were added under air atmosphere. The vial was covered with the electrode holder. The electrolysis was carried out at RT using a constant current of 5.0 mA a carbon graphite anode and carbon graphite cathode (1.4 × 0.8 × 0.2 cm submerged in solution) with stirring. After completion as detected by TLC. The reaction mixture was diluted with EtOAc. The organic phase was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure, purified by flash column chromatography (Petroleum ether/ EtOAc = 10/1) to give compound **6a** and **16**.

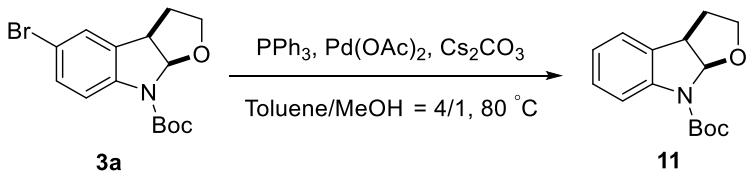
Di-*tert*-Butyl-3a,5-dibromo-2,3,3a,8a-tetrahydropyrrolo[2,3-b]indole-1,8-dicarboxylate (16)



16

Yellow oil, 6 h, 13.7 mg, 13% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.50–7.47 (m, 2H), 7.39 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.42 (s, 1H), 3.78–3.75 (m, 1H), 2.85–3.80 (m, 1H), 2.75–2.67 (m, 2H), 1.58 (s, 9H), 1.48 (s, 9H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 153.3, 151.8, 141.2, 134.7, 133.2, 126.9, 118.7, 116.2, 84.2, 82.5, 80.9, 61.0, 46.2, 28.3, 28.2 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{26}N_2O_4Br_2Na$ 539.0152; Found 539.0142.

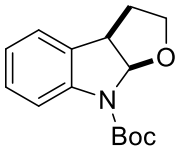
4.5 Investigation of 5-bromonation of indolines



3a **11**

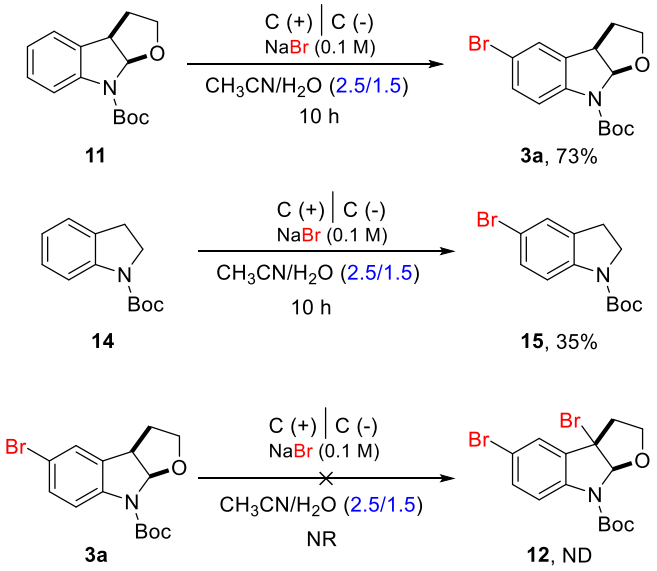
Procedures for substrate 11: A mixture of **3a** (68.9 mg, 0.2 mmol), Triphenylphosphine (5.3 mg, 0.02 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), Cs_2CO_3 (97.8 mg, 0.3 mmol) was dissolved in Toluene/MeOH (4:1) under argon atmosphere. Then, the mixture was stirred at 80 ℃ and when the reaction was completed as monitored by TLC. The reaction was cooled to room temperature. The resulting solid was filtered off and the solvent was concentrated under reduced pressure, purified by flash column chromatography (Petroleum ether/Ethyl acetate = 10/1) to obtain **11**.

***tert*-butyl -2, 3, 3a, 8a-tetrahydro-8H-furo[2, 3-b]indole-8-carboxylate (11)**



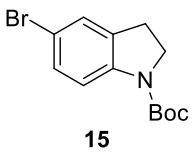
11

Colorless oil, 16 h, 39.2 mg, 75%; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.81 (s, 1H), 7.20–7.15 (m, 2H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.15 (br, 1H), 3.97 (t, *J* = 8.0 Hz, 1H), 3.93 (t, *J* = 7.4 Hz, 1H), 3.46–3.41 (m, 1H), 3.35–2.28 (m, 1H), 2.10–2.07 (m, 1H), 1.59 (s, 9H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 152.4, 142.9, 131.1, 128.1, 124.3, 122.7, 114.3, 93.3, 81.2, 66.3, 44.8, 33.8, 28.3 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{19}O_3NNa$ 284.1257; Found 284.1255.



Procedures for 5-bromination of 11: A mixture of **11** (0.2 mmol) and NaBr (41.2 mg, 0.4 mmol) were added in a 10 mL vial with a stir bar, then CH_3CN/H_2O (2.5/1.5 mL) were added under air atmosphere. The vial was covered with the electrode holder. The electrolysis was carried out at RT using a constant current of 5.0 mA between a carbon graphite anode and carbon graphite cathode (1.4 × 0.8 × 0.2 cm submerged in solution) with stirring. After completion as detected by TLC. The reaction mixture was diluted with EtOAc. The organic phase was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure, purified by flash column chromatography (Petroleum ether/Ethyl acetate = 10/1) to give compound **3a**.

***tert*-Butyl 5-bromoindoline-1-carboxylate (15)**

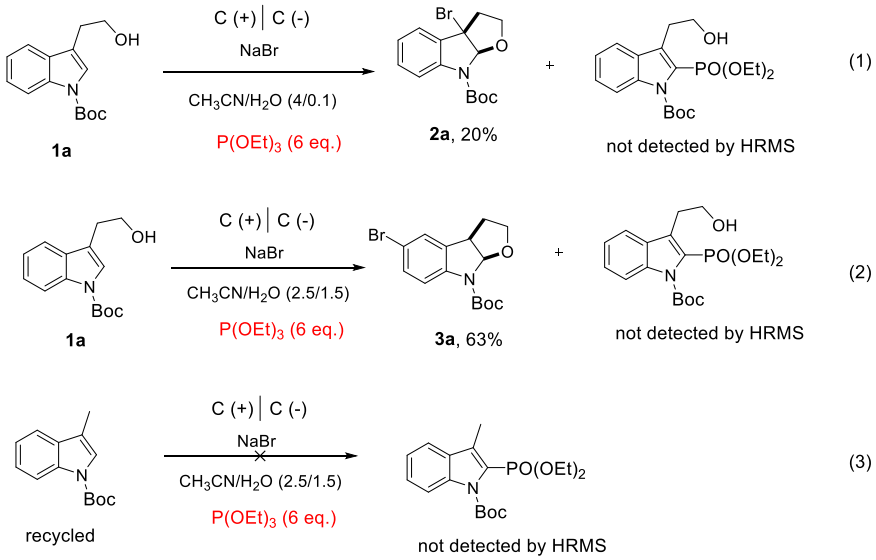


15

White solid, m.p. 102.7 – 103.9 °C, 10 h, 21.0 mg, 35% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.71 (br, 1H), 7.25–7.23 (m, 2H), 3.97 (t, *J* = 8.8, 2H), 3.06 (t, *J* = 8.6 Hz, 2H), 1.55 (s, 9H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 152.4, 142.3, 130.2, 127.6, 116.0, 114.4, 47.7, 28.4 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{13}H_{16}O_2NBrNa$ 320.0257; Found 320.0249.

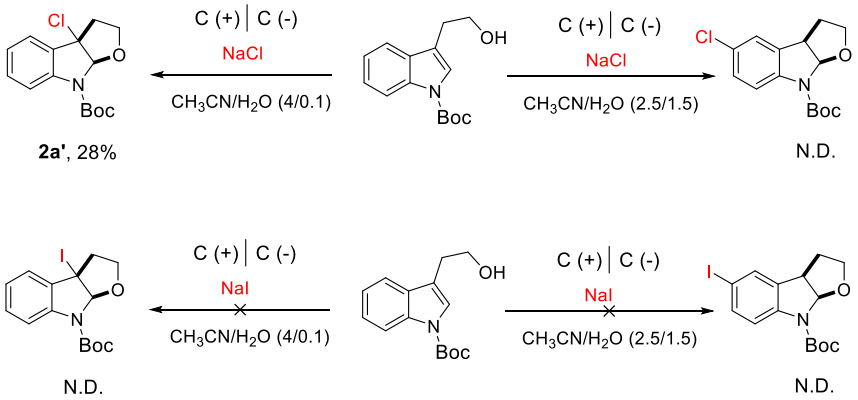
4.6 $P(OEt)_3$ trapping experiments

In order to explore the oxidative activities between bromide and **1a** in the current conditions, several control experiments have been performed. The electrochemical indole radical cation intermediate could be trapped by $P(EtO)_3$ have been frequently identified.[8] According to Lei's work[8a], when 6 equivalent of $P(EtO)_3$ was added in the reaction, 20% yield of 3a-bromoindoline **2a** and 63% yield of 5a-bromoindoline **3a** was obtained, but none of indole-phosphorylation adduct was detected by HRMS analysis. Besides, when 3-methyl indole was employed in the standard condition, the reaction did not take place and none of indole-phosphorylation product was detected. These results suggested the preferred oxidation of **1a** to indole radical cation intermediate may not involve in this reaction.

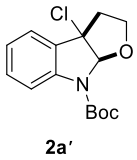


4.7 Investigation of NaCl and NaI

When NaCl was used in the standard conditions instead of NaBr, only 28% yield of 3a-chloroindolines was obtained in the less water conditions, and none of 5a-chloroindoline was isolated, and most substrates decomposed. When the NaI was used in the standard conditions instead of NaBr, none of any 3a- or 5a-chloroindoline was detected, and part of substrates decomposed. We assumed that the reactivity of Br^- is the key to the reaction.



***tert*-butyl-3a-chloro-2,3,3a,8a-tetrahydro-8*H*-furo[2,3-*b*]indole-8-carboxylate (2a′)**

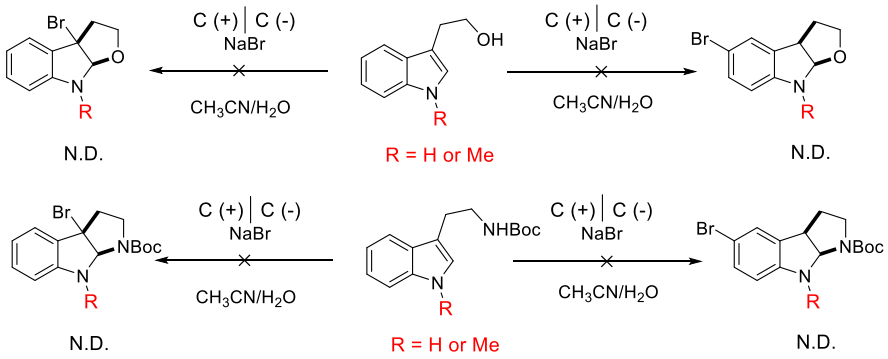


2a′

Light yellow oil, 3.5 h, 16.7 mg, 28% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.87 (br, 1H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.08 (s, 1H), 4.09 (t, *J* = 8.2 Hz, 1H), 3.60–3.49 (m, 1H), 2.82–2.77 (m, 1H), 2.71–2.68 (m, 1H), 1.60 (s, 9H) ppm. All spectral data were in agreement with the literature [3].

4.8 Investigation N-H/Me substrate

When the N-Me and N-H substituted tryptophol and tryptamine substrates were employed in the standard conditions, none of 3a-bromoindolines or 5a-bromoindolines was obtained, and the substrates decomposed after a period of time. We assumed that the electron-rich of indole was unstable under the current electronic oxidative conditions, an electron-withdrawing group is necessary for the reaction.



5. Cyclic voltammetry studies

Cyclic voltammetry were performed with CORRTEST potentiostat/galvanostat CS310H. A glassy carbon disc (diameter 3 mm) working electrode, a platinum wire counter electrode and a saturated silver chloride electrode as reference electrode were used at scan rate of 100 mV/s. The experiments were conducted in a 50 mL vial without stirring in CH_3CN/H_2O (10 mL/0.25 mL) or CH_3CN/H_2O (6.25 mL/3.73 mL) with **1a** (5 mmol/L) and/or NaBr (5 mmol/L) and *n*Bu_4NBF_4 (0.05 M).

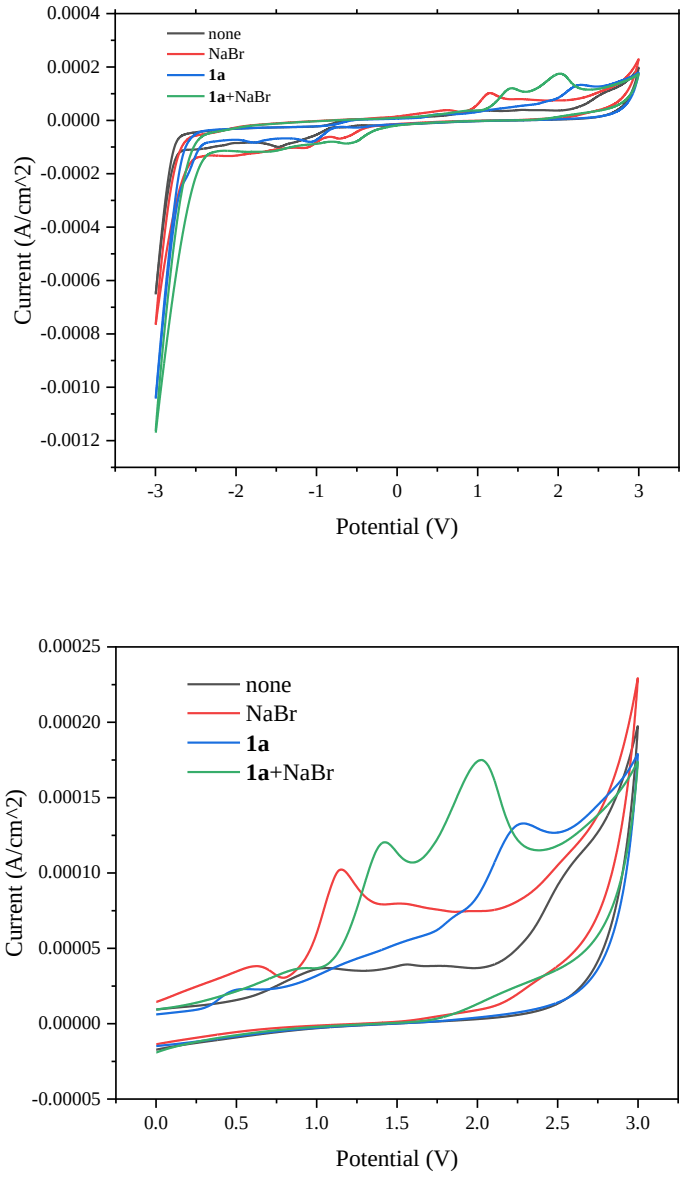


Figure S2 Cyclic voltammograms of *n*-Bu_4NBF_4 (0.05 M) in CH_3CN/H_2O (4/0.1)

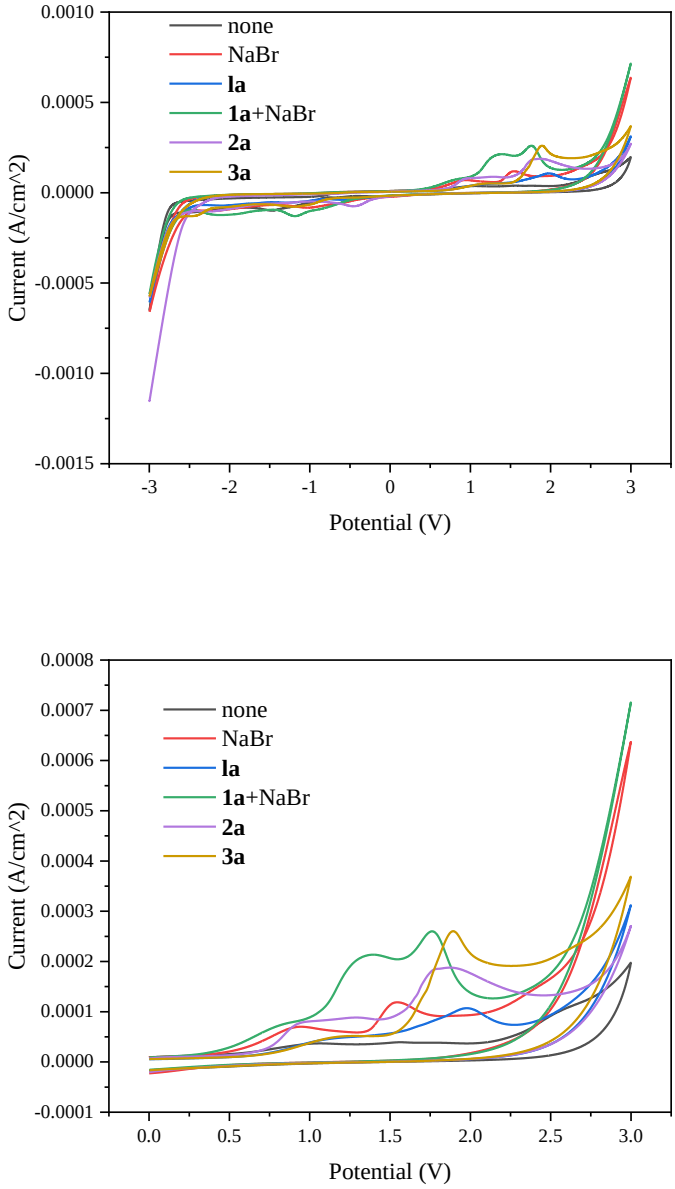
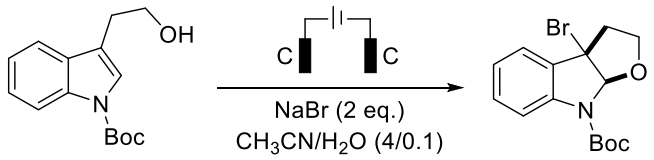


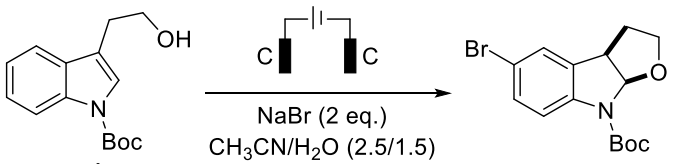
Figure S3 Cyclic voltammograms of *n*-Bu_4NBF_4 (0.05 M) in CH_3CN/H_2O (2.5/1.5)

6. General Procedure for cyclic 3a- and 5a-bromoindolins and product characterizations



1a **2a**

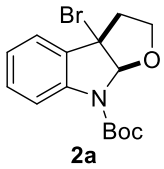
General Procedure for cyclic 3a-bromoindolins: A mixture of **1a** (0.2 mmol) and NaBr (41.2 mg, 0.4 mmol) were added in a 10 mL vial with a stir bar, then CH_3CN/H_2O (4/0.1 mL) were added under air atmosphere. The vial was covered with the electrode holder. The electrolysis was carried out at RT using a constant current of 5.0 mA a carbon graphite anode and carbon graphite cathode (1.4 × 0.8 × 0.2 cm submerged in solution) with stirring. After completion as detected by TLC. The reaction mixture was diluted with EtOAc. The organic phase was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure, purified by flash column chromatography (Petroleum ether/Ethyl acetate = 10/1) to give compound **2a**.



1a **3a**

General Procedure for cyclic 5a-bromoindolins: A mixture of **1a** (0.2 mmol) and NaBr (41.2 mg, 0.4 mmol) were added in a 10 mL vial with a stir bar, then CH_3CN/H_2O (2.5/1.5 mL) were added under air atmosphere. The vial was covered with the electrode holder. The electrolysis was carried out at RT using a constant current of 5.0 mA between a carbon graphite anode and carbon graphite cathode (1.4 × 0.8 × 0.2 cm submerged in solution) with stirring. After completion as detected by TLC. The reaction mixture was diluted with EtOAc. The organic phase was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure, purified by flash column chromatography (Petroleum ether/Ethyl acetate = 10/1) to give compound **3a**.

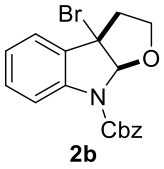
***tert*-Butyl-3a-bromo-2,3,3a,8a-tetrahydro-8H-furo[2,3-*b*]indole-8-carboxylate (2a)**



2a

White solid, 4 h, 56.3 mg, 83% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.83 (br, 1H), 7.40 (d, *J* = 7.4 Hz, 1H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.07 (td, *J* = 7.6, 0.9 Hz, 1H), 6.19 (br, 1H), 3.99 (t, *J* = 8.6 Hz, 1H), 3.50–3.46 (m, 1H), 2.87–2.92(m, 1H), 2.81–2.78 (m, 1H), 1.60 (s, 9H) ppm. All spectral data were in agreement with the literature [1].

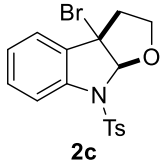
Benzyl-3a-bromo-2,3, 3a, 8a-tetrahydro-8H-furo[2, 3-b]indole-8-carboxylate (2b)



2b

Colorless oil, 5 h, 58.4 mg, 79% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.88 (br, 1H), 7.46–7.31 (m, 7H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.29 (s, 1H), 5.39–5.29 (m, 2H), 4.01 (t, *J* = 8.0 Hz, 1H), 3.53–3.48 (m, 1H), 2.92–2.87 (m, 1H), 2.82–2.79 (m, 1H) ppm. All spectral data were in agreement with the literature [1].

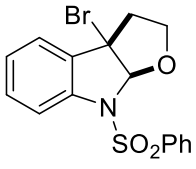
3a-Bromo-8-tosyl-3, 3a, 8, 8a-tetrahydro-2H-furo[2,3-b]indole (2c)



2c

Light yellow foam, 8 h, 71.1 mg, 90% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.34 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.27 (td, *J* = 7.8, 1.2 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 1H)., 7.10 (td, *J* = 7.6, 1.0 Hz, 1H), 6.24 (s, 1H), 4.02–3.99 (m, 1H), 3.46–3.41 (m, 1H), 2.87–2.81 (m, 1H), 2.74–2.71 (m, 1H), 2.37 (s, 3H) ppm. All spectral data were in agreement with the literature [1].

3a-Bromo-8-(phenylsulfonyl)-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indole (2d)

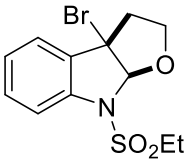


2d

Light yellow oil, 6 h, 54.8 mg, 72% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 7.4 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.51 – 7.42 (m, 3H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.23 (s, 1H), 3.99 (t, *J* = 8.2 Hz, 1H), 3.44 – 3.37 (m, 1H), 2.85 – 2.80 (m, 1H), 2.73 (dd, *J* = 12.7, 4.1 Hz, 1H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 140.3, 138.5, 133.4, 132.4, 130.6, 129.0, 127.2, 125.2, 124.9, 114.2, 103.1, 68.0, 61.2, 44.5 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for

$C_{16}H_{14}NO_3BrSNa$ 401.9770; Found 401.9755.

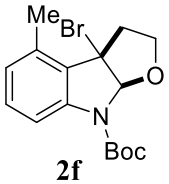
3a-Bromo-8-(ethylsulfonyl)-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indole (2e)



2e

white solid, m.p. 97.3 – 98.5 °C, 6 h, 43.8 mg, 66% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.45 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.30 (td, *J* = 7.8, 1.4 Hz, 1H), 7.14 (td, *J* = 7.6, 1.0 Hz, 1H), 6.19 (s, *J* = 0.4 Hz, 1H), 4.07–4.04 (m, 1H), 3.56 –3.52 (m, 1H), 3.34 – 3.21 (m, 2H), 2.94 –2.89 (m, 1H), 2.86 – 2.80 (m, 1H), 1.42 (t, *J* = 7.4 Hz, 3H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 140.8, 131.8, 130.8, 125.4, 124.5, 113.1, 102.7, 68.1, 61.4, 47.8, 44.4, 7.8 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{12}H_{14}NO_3BrSNa$ 353.9770; Found 353.9757.

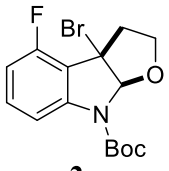
***Tert*-butyl-3a-bromo-4-methyl-2,3,3a,8a-tetrahydro-8*H*-furo[2,3-*b*]indole-8-carbo xylate (2f)**



2f

Colorless oil, 3.5 h, 43.2 mg, 61% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.71 (br, 1H), 7.20 (t, *J* = 7.8 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 6.21 (s, 1H), 4.04–3.96 (m, 1H), 3.61–3.57 (m, 1H), 2.91–2.83 (m, 2H), 2.49 (s, 3H), 1.60 (s, 9H) ppm. All spectral data were in agreement with the literature [4].

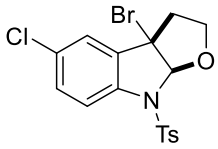
***Tert*-butyl-3a-bromo-4-fluoro-2,3,3a,8a-tetrahydro-8*H*-furo[2,3-*b*]indole-8-carbo xylate (2g)**



2g

Colorless oil, 3 h, 54.0 mg, 75% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.64 (s, 1H), 7.32–7.24 (m, 2H), 6.73 (t, *J* = 8.8 Hz, 2H), 6.18 (s, 1H), 4.03 (t, *J* = 7.8 Hz, 2H), 3.58–3.54 (m, 2H), 3.02–2.98 (m, 2H), 2.87–2.82 (m, 2H), 1.60 (s, 9H) ppm. All spectral data were in agreement with the literature[3].

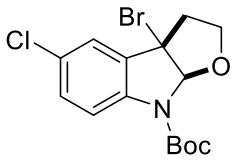
3a-Bromo-5-chloro-8-tosyl-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indole (2h)



2h

Yellow solid, 7 h, 52.6 mg, 61% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 1H), 7.30 (d, *J* = 2.2 Hz, 1H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.24 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.21 (s, 1H), 4.04–4.01 (m, 1H), 3.47–3.43 (m, 1H), 2.85–2.79 (m, 1H), 2.71–2.68 (m, 1H), 2.38 (s, 3H) ppm. All spectral data were in agreement with the literature [3].

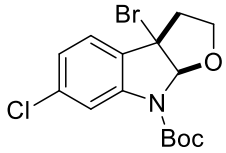
***tert*-Butyl-3a-bromo-5-chloro-2,3,3a,8a-tetrahydro-8H-furo[2,3-b]indole-8-carboxylate (2i)**



2i

Light yellow oil, 6 h, 49.2 mg, 66% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.78 (s, 1H), 7.36 (s, 1H), 7.24 (d, *J* = 8.2 Hz, 1H), 6.16 (s, 1H), 4.01 (t, *J* = 8.4 Hz, 1H), 3.51–3.47 (m, 1H), 2.90–2.85 (m, 1H), 2.77–2.75 (m, 1H), 1.59 (s, 9H) ppm. All spectral data were in agreement with the literature [3].

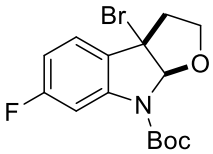
***Tert*-butyl-3a-bromo-6-chloro-2,3,3a,8a-tetrahydro-8*H*-furo[2,3-*b*]indole-8-carboxylate (2j)**



2j

Colorless oil, 3 h, 42.8 mg, 57% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.90 (s, 1H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.05 (dd, *J* = 8.2, 1.8 Hz, 2H), 6.17 (s, 1H), 4.01 (t, *J* = 8.2 Hz, 2H), 3.51–3.47 (m, 2H), 2.90–2.85 (m, 2H), 2.77–2.74 (m, 2H), 1.60 (s, 9H) ppm. All spectral data were in agreement with the literature[3].

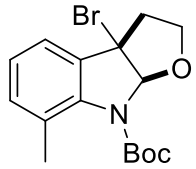
***tert*-butyl-3a-bromo-6-fluoro-2,3,3a,8a-tetrahydro-8*H*-furo[2,3-*b*]indole-8-carboxylate (2k)**



2k

Colorless oil, 2.5 h, 37.4 mg, 52% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.59 (s, 1H), 7.34 (dd, *J* = 8.4, 5.4 Hz, 1H), 6.77 (td, *J* = 8.4, 2.2 Hz, 1H), 6.19 (s, 1H), 4.01 (t, *J* = 8.2 Hz, 1H), 3.54–3.46 (m, 1H), 2.91–2.85 (m, 1H), 2.78–2.75 (m, 1H), 1.60 (s, 9H). All spectral data were in agreement with the literature [4].

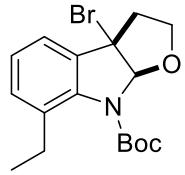
***tert*-Butyl-3a-bromo-7-methyl-2,3,3a,8a-tetrahydro-8H-furo[2,3-b]indole-8-carboxylate (2l)**



2l

White solid, 9 h, 65.6 mg, 93% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.25 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.14–7.09 (m, 2H), 6.18 (s, 1H), 3.97–3.94 (m, 1H), 3.43–3.39 (m, 1H), 2.89–2.84 (m, 1H), 2.80–2.76 (m, 1H), 2.32 (s, 3H), 1.57 (s, 9H) ppm. All spectral data were in agreement with the literature [2].

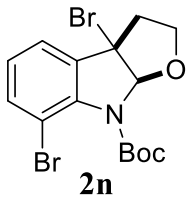
***tert*-Butyl-3a-bromo-7-ethyl-2,3,3a,8a-tetrahydro-8H-furo[2,3-b]indole-8-carboxylate (2m)**



2m

Yellow oil, 6 h, 68.5 mg, 93% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.25 (d, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 7.4 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 6.18 (s, 1H), 3.96–3.93 (m, 1H), 3.42–3.38 (m, 1H), 2.89–2.84 (m, 1H), 2.80–2.60 (m, 3H), 1.57 (s, 9H), 1.18 (t, *J* = 7.4 Hz, 3H) ppm. All spectral data were in agreement with the literature [2].

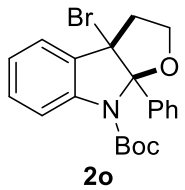
tert-butyl-3a,7-dibromo-2,3,3a,8a-tetrahydro-8*H*-furo[2,3-*b*]indole-8-carboxylate (2n)



2n

Colorless oil, 4 h, 38.3 mg, 46% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.51 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.37 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.06 (t, *J* = 7.8 Hz, 1H), 6.15 (s, 1H), 4.00–3.98 (m, 1H), 3.48–3.44 (m, 1H), 2.89–2.84 (m, 1H), 2.78–2.75 (m, 1H), 1.58 (s, 9H) ppm. All spectral data were in agreement with the literature[3].

***Tert*-Butyl-3a-bromo-8a-phenyl-2,3,3a,8a-tetrahydro-8H-furo[2,3-b]indole-8-carboxylate (2o)**

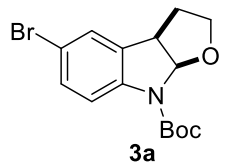


2o

Colorless oil, 9 h, 75.0 mg, 90% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.97–7.87 (m, 1H), 7.65–7.30 (m, 6H), 7.20–7.08 (m, 2H), 4.21 (t, *J* = 8.0 Hz, 1H), 3.69–3,65 (m, 1H), 2.93–2.86 (m, 1H), 2.83–2.77 (m, 1H), 1.16 (s, 9H) ppm. All spectral data were in

agreement with the literature [1].

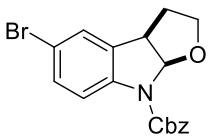
tert-Butyl -5-bromo-2,3,3a,8a-tetrahydro-8H-furo[2,3-b]indole-8-carboxylate (3a)



3a

Light yellow oil, 12 h, 50.8 mg, 75% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.70 (br, 1H), 7.31–7.28 (m, 2H), 6.14 (br, 1H), 3.99 (t, *J* = 8.0 Hz, 1H), 3.92 (t, *J* = 7.6 Hz, 1H), 3.47–3.43 (m, 1H), 2.35–2.28 (m, 1H), 2.10–2.07 (m, 1H), 1.58 (s, 9H) ppm.**^{13}C NMR** (150 MHz, Chloroform-*d*) δ 152.2, 131.0, 127.3, 115.8, 115.1, 93.5, 66.3, 58.4, 33.7, 28.3, 18.4 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{18}O_3NBrNa$ 362.0362; Found 362.0357.

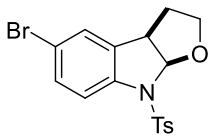
Benzyl-5-bromo-2,3,3a,8a-tetrahydro-8H-furo[2,3-b]indole-8-carboxylate (3b)



3b

Colorless oil, 20 h, 64.5 mg, 86% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.74 (br, 1H), 7.45–7.29 (m, 7H), 6.23 (s, 1H), 5.41–5.25 (m, 2H), 4.01 (t, *J* = 8.2 Hz, 1H), 3.94 (t, *J* = 7.6 Hz, 1H), 3.49–3.45 (m, 1H), 2.36–2.29 (m, 1H), 2.11–2.08 (m, 1H) ppm; **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 152.7, 141.8, 136.0, 133.4, 131.2, 128.6, 128.2, 127.9, 127.4, 115.8, 115.6, 93.35, 67.36, 66.52, 44.99, 33.67 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{16}O_3NBrNa$ 396.0206; Found 396.0205.

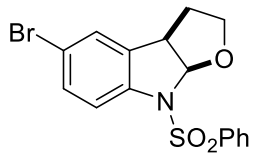
5-Bromo-8-tosyl-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indole (3c)



3c

White solid, m.p. 88.0 – 89.2 ^{o}C, 20 h, 40.2 mg, 51% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.29–7.25 (m, 6H), 6.24 (d, *J* = 6.6 Hz, 1H), 3.98 (t, *J* = 8.2 Hz, 1H), 3.88 (t, *J* = 7.6 Hz, 1H), 3.33–2.28 (m, 1H), 2.39 (s, 3H), 2.32–2.26 (m, 1H), 2.02–1.99 (m, 1H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 144.2, 140.8, 136.2, 133.7, 131.3, 129.7, 128.0, 127.4, 116.0, 114.3, 96.0, 66.4, 45.3, 33.5, 21.5 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{16}O_3NBrNaS$ 415.9926; Found 415.9916.

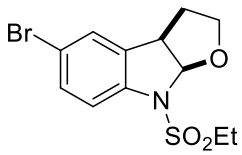
5-Bromo-8-(phenylsulfonyl)-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indole (3d)



3d

colorless oil, 12 h, 36.3 mg, 48% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.98 – 7.95 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.29 – 7.25 (m, 3H), 6.26 (d, *J* = 6.6 Hz, 1H), 4.00 – 3.95 (m, 1H), 3.90 (t, *J* = 7.6 Hz, 1H), 3.26 – 3.30 (m, 1H), 2.34 – 2.25 (m, 1H), 2.00 (dd, *J* = 12.2, 4.8 Hz, 1H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 140.6, 139.2, 133.7, 133.2, 131.3, 129.0, 128.0, 127.3, 116.1, 114.21, 96.0, 66.4, 45.3, 33.5 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{14}NO_3BrSNa$ 401.9770; Found 401.9757.

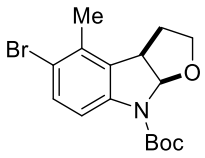
5-Bromo-8-(ethylsulfonyl)-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indole (3e)



3e

white solid, m.p. 93.0 – 94.1 °C, 15 h, 34.4 mg, 52% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.33 – 7.29 (m, 2H), 7.22 (d, *J* = 8.5 Hz, 1H), 6.18 (d, *J* = 6.4 Hz, 1H), 4.06 (t, *J* = 7.8 Hz, 1H), 4.02 (t, *J* = 7.4 Hz, 1H), 3.51 – 3.47 (m, 1H), 3.33 – 3.23 (m, 2H), 2.40 – 2.32 (m, 1H), 2.12 (dd, *J* = 12.4, 4.7 Hz, 1H), 1.41 (t, *J* = 7.4 Hz, 3H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 141.5, 133.0, 131.4, 128.1, 115.6, 113.6, 95.7, 66.8, 48.7, 45.4, 33.4, 7.6 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{12}H_{14}NO_3BrSNa$ 353.9770; Found 353.9757.

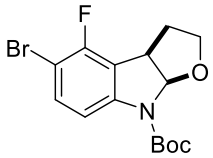
***Tert*-butyl-5-bromo-4-methyl-2,3,3a,8a-tetrahydro-8*H*-furo[2,3-*b*]indole-8-carboxylate (3f)**



3f

Colorless oil, 10.5 h, 25.2 mg, 36% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.53 (br, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 6.19 (s, 1H), 4.00–3.96 (m, 1H), 3.92 (t, *J* = 8.0 Hz, 1H), 3.51–3.46 (m, 1H), 2.35 (s, 3H), 2.34–2.29 (m, 1H), 2.03–2.01 (m, 1H), 1.59 (s, 9H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 152.3, 142.5, 133.5, 131.8, 118.2, 113.1, 93.6, 81.7, 65.7, 44.6, 32.8, 28.3, 19.2 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{20}O_3NBrNa$ 376.0519; Found 376.0515.

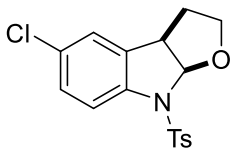
***tert*-butyl-5-bromo-4-fluoro-2,3,3a,8a-tetrahydro-8*H*-furo[2,3-*b*]indole-8-carboxylate (3g)**



3g

Colorless oil, 24 h, 50.3 mg, 70% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.51 (s, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 6.18 (s, 1H), 4.06–4.02 (m, 2H), 3.50–3.46 (m, 1H), 2.33–2.18 (m, 2H), 1.58 (s, 9H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 155.0 (d, $^{1}J_{C\text{-}F}$ = 244.6 Hz) , 151.9, 136.8, 133.1, 111.2 (d, $^{3}J_{C\text{-}F}$ = 3.0 Hz), 101.4 (d, $^{2}J_{C\text{-}F}$ = 19.6 Hz), 96.6, 93.9, 83.0, 66.5, 42.4, 31.9, 28.3 ppm; **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -115.49 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{17}O_3NFBrNa$ 380.0268; Found 380.0260.

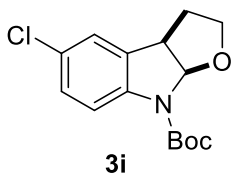
5-Chloro-8-tosyl-3,3a,8,8a-tetrahydro-2H-furo[2,3-*b*]indole (3h)



3h

Solid, m.p. 106.6 – 107.0 °C, 20 h, 37.7 mg, 54% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.14 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.10 (s, 1H), 6.25 (d, *J* = 6.6 Hz, 1H), 3.98 (t, *J* = 8.0 Hz, 1H), 3.87 (t, *J* = 7.6 Hz, 1H), 3.33–3.29 (m, 1H), 2.39 (s, 3H), 2.32–2.26 (m, 1H), 2.01–1.99 (m, 1H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 144.2, 140.3, 136.2, 133.3, 129.7, 128.7, 128.4, 127.4, 113.9, 96.1, 66.4, 45.4, 33.6, 21.5 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{16}O_3NClNaS$ 372.0432; Found 372.0428.

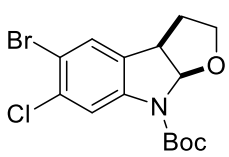
***tert*-Butyl-5-Chloro-2,3,3a,8a-tetrahydro-8H-furo[2,3-b]indole-8-carboxylate (3i)**



3i

Yellow solid, m.p. 66.3 – 67.5 °C, 8 h, 35.3 mg, 60% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.75 (br, 1H), 7.16–7.14 (m, 2H), 6.15 (br, 1H), 3.99 (t, *J* = 8.2 Hz, 1H), 3.91 (t, *J* = 7.4 Hz, 1H), 3.47–3.42 (m, 1H), 2.35–2.29 (m, 1H), 2.09–2.07 (m, 1H), 1.59 (s, 9H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 152.2, 141.7, 133.1, 128.1, 127.7, 124.4, 115.3, 93.5, 81.6, 66.3, 44.8, 33.7, 28.3 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{18}O_3NClNa$ 318.0867; Found 318.0865.

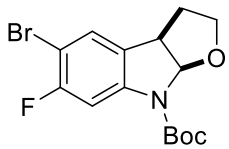
***tert*-Butyl-5-bromo-6-chloro-2,3,3a,8a-tetrahydro-8*H*-furo[2,3-*b*]indole-8-carboxylate (3j)**



3j

Colorless oil, 16 h, 42.8 mg, 57% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.97 (br, 1H), 7.37 (s, 1H), 6.15 (s, 1H), 4.00 (t, *J* = 8.2 Hz, 1H), 3.90 (t, *J* = 7.4 Hz, 1H), 3.47–3.43 (m, 1H), 2.35–2.28 (m, 1H), 2.08–2.05 (m, 1H), 1.59 (s, 9H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 151.9, 143.2, 133.8, 128.8, 127.3, 116.0, 114.8, 93.8, 82.1, 66.4, 44.4, 33.7, 28.3 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{17}O_3NClBrNa$ 395.9972; Found 395.9968.

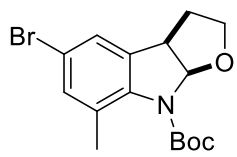
***tert*-Butyl-5-bromo-6-fluoro-2,3,3a,8a-tetrahydro-8*H*-furo[2,3-*b*]indole-8-carboxylate (3k)**



3k

Light yellow oil, 22 h, 31.2 mg, 44% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.66 (s, 1H), 7.28 (d, *J* = 6.8 Hz, 1H), 6.16 (s, 1H), 4.00 (t, *J* = 8.0 Hz, 1H), 3.90 (t, *J* = 7.6 Hz, 1H), 3.48–3.43 (m, 1H), 2.34–2.28 (m, 2H), 2.07–2.05 (m, 1H), 1.59 (s, 9H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 158.8 (d, $^{1}J_{C\text{-}F}$ = 241.5 Hz), 151.9, 128.1, 103.5 (d, $^{2}J_{C\text{-}F}$ = 29.8 Hz), 101.2 (d, $^{3}J_{C\text{-}F}$ = 22.5 Hz), 94.0, 66.4, 44.3, 33.8, 28.3 ppm; **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -106.65 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{17}O_3NFBrNa$ 380.0268; Found 380.0258.

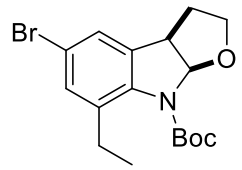
***tert*-Butyl-5-bromo-7-methyl-2,3,3a,8a-tetrahydro-8H-furo[2,3-b]indole-8-carboxylate (3l)**



3l

White solid, 14 h, 61.1 mg, 86% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.19 (s, 1H), 7.14 (s, 1H), 6.11 (d, *J* = 5.9 Hz, 1H), 4.02 (t, *J* = 7.0 Hz, 1H), 3.95 – 3.93 (m, 1H), 3.40 – 3.36 (m, 1H), 2.33 – 2.28 (m, 1H), 2.27 (s, 3H), 2.09 – 2.03 (m, 1H), 1.56 (s, 9H) ppm. **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 152.8, 140.6, 136.0, 133.4, 129.1, 124.4, 117.1, 95.7, 81.9, 66.7, 45.6, 33.0, 28.2, 20.2; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{20}O_3NBrNa$ 376.0519; Found 376.0508.

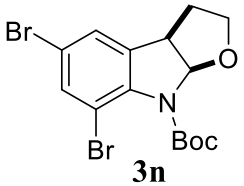
***tert*-Butyl-5-bromo-7-ethyl-2,3,3a,8a-tetrahydro-8H-furo[2,3-b]indole-8-carboxylate (3m)**



3m

Colorless oil, 13 h, 47.6 mg, 65% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.24 (s, 1H), 7.15 (s, 1H), 6.11 (d, *J* = 5.8 Hz, 1H), 4.01 (t, *J* = 7.0 Hz, 1H), 3.94 (t, *J* = 8.1 Hz, 1H), 3.39 – 3.35 (m, 1H), 2.75 – 2.65 (m, 2H), 2.32 – 2.26 (m, 1H), 2.07 – 2.04 (m, 1H), 1.55 (s, 9H), 1.16 (t, *J* = 7.5 Hz, 3H) ppm. **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 152.9, 139.8, 136.2, 135.1, 131.4, 124.4, 117.6, 95.7, 81.8, 66.6, 45.5, 33.1, 28.2, 26.0, 13.3 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{22}O_3NBrNa$ 390.0675; Found 390.0671.

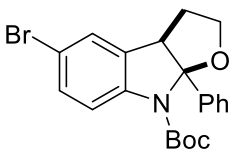
***tert*-Butyl-5,7-dibromo-2,3,3a,8a-tetrahydro-8*H*-furo[2,3-*b*]indole-8-carboxylate (3n)**



3n

Light yellow oil, 24 h, 17.6 mg, 20% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.58 (s, 1H), 7.27 (s, 1H), 6.10 (d, *J* = 5.8 Hz, 1H), 4.09–4.07 (m, 1H), 3.98–3.95 (m, 1H), 3.44–3.93 (m, 1H), 2.35–2.28 (m, 1H), 2.07–2.04 (m, 1H), 1.57 (s, 9H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 151.9, 141.2, 138.3, 135.2, 126.2, 117.3, 111.8, 96.3, 82.6, 66.7, 46.2, 32.9, 28.1 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{17}O_3NBr_2Na$ 439.9467; Found 439.9455.

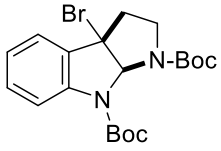
***tert*-Butyl-5-bromo-8a-phenyl-2,3,3a,8a-tetrahydro-8H-furo[2,3-b]indole-8-carboxylate (3o)**



3o

Colorless oil, 20 h, 56.2 mg, 68% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.83 (br, 1H), 7.38–7.36 (m, 3H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.28–7.25 (m, 2H), 4.27 (t, *J* = 8.0 Hz, 1H), 3.79–3.72 (m, 2H), 2.40–2.34 (m, 1H), 2.03 (dd, *J* = 12.4, 5.0 Hz, 1H), 1.16 (s, 9H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ135.3, 132.0, 131.2, 128.1, 127.4, 127.2, 125.3, 124.4, 115.8, 115.0, 104.7, 68.1, 58.5, 55.6, 33.7, 27.8, 27.5 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{21}H_{22}O_3NBrNa$ 438.0675; Found 438.0668.

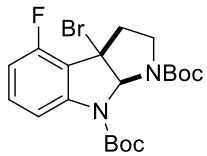
Di-*tert*-butyl-3a-bromo-2,3,3a,8a-tetrahydropyrrolo[2,3-b]indole-1,8-dicarboxylate (5a)



5a

White foam, 4 h, 80.9 mg, 92% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.59 (s, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.28 (td, *J* = 7.8, 1.4 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.44 (s, 1H), 3.75–3.72 (m, 1H), 2.83–2.77 (m, 2H), 2.74–2.69 (m, 1H), 1.59 (s, 9H), 1.49 (s, 9H) ppm. All spectral data were in agreement with the literature [1].

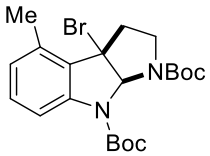
Di-*tert*-butyl-3a-bromo-4-fluoro-2,3,3a,8a-tetrahydropyrrolo[2,3-b]indole-1,8-dicarboxylate (5b)



5b

Light yellow oil, 12 h, 60.7 mg, 66% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.42 (s, 1H), 7.29–7.25 (m, 1H), 6.74 (t, *J* = 8.8 Hz, 1H), 6.44 (s, 1H), 3.79–3.76 (m, 1H), 3.07–3.04 (m, 1H), 2.92–2.87 (tm, 1H), 2.67–2.62 (m, 1H), 1.59 (s, 9H), 1.49 (s, 9H) ppm. All spectral data were in agreement with the literature [5].

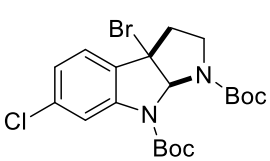
Di-*tert*-butyl-3a-bromo-4-methyl-2,3,3a,8a-tetrahydropyrrolo[2,3-b]indole-1,8-dicarboxylate (5c)



5c

Following the general Procedure for cyclic 3a-bromoindolins. The procedure was performed on **4c** (0.2 mmol) and NaBr (24.7 mg, 0.24 mmol) to afford **5c**. Light yellow oil, 3 h, 70.8 mg, 78 % yield. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 8.6 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 6.48 (s, 1H), 3.73 (dd, *J* = 11.2, 7.8 Hz, 1H), 3.00 (dd, *J* = 12.6, 4.8 Hz, 1H), 2.84 – 2.78 (m, 1H), 2.67-2.61 (m, *J* = 12.4, 7.8 Hz, 1H), 2.48 (s, 3H), 1.57 (s, 9H), 1.49 (s, 9H) ppm. All spectral data were in agreement with the literature [5].

Di-*tert*-butyl-3a-bromo-6-chloro-2,3,3a,8a-tetrahydropyrrolo[2,3-b]indole-1,8-dicarboxylate (5d)

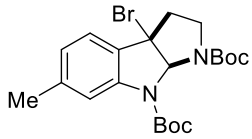


5d

Yellow oil, 9 h, 75.2 mg, 80% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.66 (s, 1H), 7.27 (d, *J* = 8.2 Hz, 1H), 7.07 (dd,

J = 8.2, 1.8 Hz, 1H), 6.44 (s, 1H), 3.77–3.74 (m, 1H), 2.84–2.79 (m, 1H), 2.75–2.67 (m, 2H), 1.59 (s, 9H), 1.48 (s, 9H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 153.2, 151.7, 143.0, 136.1, 131.1, 124.7, 124.1, 117.6, 84.4, 82.7, 80.9, 61.4, 46.2, 28.3, 28.2 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{26}O_4N_2BrClNa$ 495.0657; Found 495.0651.

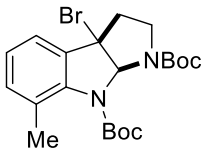
Di-*tert*-butyl-3a-bromo-6-methyl-2,3,3a,8a-tetrahydropyrrolo[2,3-b]indole-1,8-di carboxylate (5e)



5e

Following the general procedure for cyclic 3a-bromoindolines. The procedure was performed on **4e** (0.2 mmol) and NaBr (24.7 mg, 0.24 mmol) to afford **5e**. Colorless oil, 3 h, 47.3 mg, 58% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.46 (br, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 7.2 Hz, 1H), 6.42 (s, 1H), 3.71 (dd, *J* = 10.8, 7.6 Hz, 1H), 2.83 – 2.74 (m, 2H), 2.72– 2.67 (m, 1H), 2.35 (s, 3H), 1.59 (s, 9H), 1.48 (s, 9H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 153.4, 152.3, 142.2, 140.8, 129.8, 124.9, 123.4, 84.2, 82.0, 80.7, 62.5, 46.2, 28.4, 28.2, 21.9 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{21}H_{29}BrN_2O_4Na$ 475.1203; Found 475.1197.

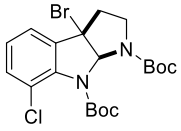
Di-*tert*-butyl-3a-bromo-7-methyl-2,3,3a,8a-tetrahydropyrrolo[2,3-b]indole-1,8-di carboxylate (5f)



5f

White solid, 9 h, 74.0 mg, 82% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.20 (dd, *J* = 6.6, 2.2 Hz, 1H), 7.14–7.11 (m, 2H), 6.24 (s, 1H), 3.55–3.52 (m, 1H), 2.82–2.81 (m, 1H), 2.76–2.67 (m, 2H), 2.30 (s, 3H), 1.54 (s, 9H), 1.50 (s, 9H) ppm; All spectral data were in agreement with the literature[3].

Di-*tert*-butyl-3a-bromo-7-chloro-2,3,3a,8a-tetrahydropyrrolo[2,3-*b*]indole-1,8-dic arboxylate (5g)

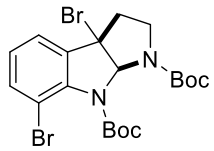


5g

Light yellow oil, 5.5 h, 71.5 mg, 75% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 1H),

7.14 (t, *J* = 7.8 Hz, 1H), 6.21 (s, 1H), 3.60–3.55 (m, 1H), 2.82–2.75 (m, 2H), 2.74–2.67 (m, 1H), 1.53 (s, 9H), 1.50 (s, 9H) ppm. All spectral data were in agreement with the literature [5].

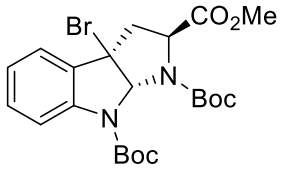
Di-*tert*-butyl-3a,7-dibromo-2,3,3a,8a-tetrahydropyrrolo[2,3-*b*]indole-1,8-dicarboxylate (5h)



5h

Colorless oil, 8 h, 73.5 mg, 71% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.8 Hz, 1H), 6.19 (s, 1H), 3.59–3.54 (m, 1H), 2.81–2.75 (m, 2H), 2.74–2.66 (m, 1H), 1.54 (s, 9H), 1.51 (s, 9H) ppm. All spectral data were in agreement with the literature [5].

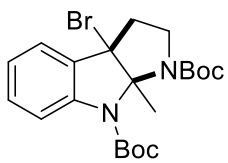
1,8-Di-*tert*-butyl-2-methyl-3a-bromo-2,3,3a,8a-tetrahydropyrrolo-[2,3-b]indole-1,2,8-tricarboxylate (5i)



5i

Following the general procedure for cyclic 3a-bromoindolins, the procedure was performed on **4i** (0.2 mmol) and NaBr (24.7 mg, 0.24 mmol); Colorless oil, 9 h, 82.1 mg, 83% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.55 (s, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.13 (t, *J* = 7.4 Hz, 1H), 6.40 (s, 1H), 3.91–3.88 (m, 1H), 3.75 (s, 3H), 3.23–3.20 (m, 1H), 2.84–2.81 (m, 1H), 1.59 (s, 9H), 1.40 (s, 9H) ppm. All spectral data were in agreement with the literature [1].

Di-*tert*-butyl-3a-bromo-8a-methyl-2,3,3a,8a-tetrahydropyrrolo[2,3-b]indole-1,8-dicarboxylate (5j)

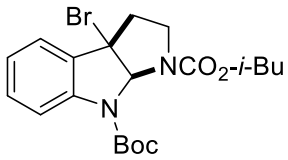


5j

Following the general procedure for cyclic 3a-bromoindolines. The procedure was performed on **4j** (0.2 mmol) and NaBr (24.7 mg, 0.24 mmol) to afford **5j**; Light yellow oil, 9 h, 44.5 mg, 49% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.67 (s, 1H), 7.35 (d, *J* = 7.6, 1.3 Hz, 1H), 7.26 (td, *J* = 7.4, 1.2 Hz, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 3.43 (t, *J* = 9.4 Hz, 1H), 2.91–2.81 (m, 2H), 2.69–2.61 (m, 1H), 2.16 (s, 3H), 1.59 (s, 9H), 1.42

(s, 9H) ppm. All spectral data were in agreement with the literature [6].

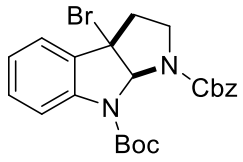
8-(*tert*-Butyl)-1-isopropyl-3a-bromo-2,3,3a,8a-tetrahydropyrrolo[2,3-b]indole-1,8-dicarboxylate (5k)



5k

Light brown oil, 9 h, 37.5 mg, 43%; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.62 (s, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.44 (s, 1H), 3.93–3.88 (m, 2H), 3.81–3.77 (m, 1H), 2.91–2.86 (m, 1H), 2.85–2.82 (m, 1H), 2.78–2.73 (m, 1H), 1.98 (s, 1H), 1.59 (s, 9H), 0.94 (t, *J* = 6.2 Hz, 6H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 154.3, 152.1, 142.0, 132.4, 130.4, 124.1, 123.7, 117.4, 84.0, 82.1, 71.9, 62.0, 46.2, 28.2, 27.8, 19.1, 19.0 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{27}BrN_2O_4Na$ 461.1046; Found 461.1034.

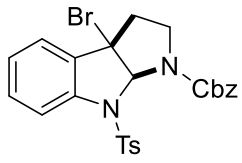
1-Benzyl-8-(*tert*-butyl)-3a-bromo-2,3,3a,8a-tetrahydropyrrolo[2,3-b]indole-1,8-dicarboxylate (5l)



5l

Following the general procedure for cyclic 3a-bromoindolins, the procedure was performed on **4l** (0.2 mmol) and NaBr (24.7 mg, 0.24 mmol); Light Coral oil, 4 h, 51.3 mg, 54% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.63 (s, 1H), 7.38–7.29 (m, 7H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.46 (s, 1H), 5.19–5.15 (m, 2H), 3.80–3.77 (m, 1H), 2.92–2.87 (m, 1H), 2.84–2.81 (m, 1H), 2.77–2.72 (m, 1H), 1.54 (s, 9H) ppm. All spectral data were in agreement with the literature [1].

Benzyl-3a-bromo-8-tosyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (5m)

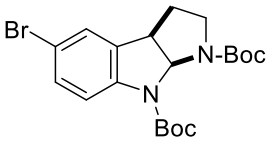


5m

Following the general procedure for cyclic 3a-bromoindolins, the procedure was performed on **4m** (0.2 mmol) and NaBr (24.7 mg, 0.24 mmol); Light yellow oil, 16 h, 45.4 mg, 43% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.65–7.46 (m, 5H), 7.38 (t, *J*

= 7.2 Hz, 2H), 7.34–7.31 (m, 2H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.17–7.12 (m, 3H), 6.30 (s, 1H), 5.30–5.18 (m, 2H), 3.82–3.79 (m, 1H), 2.84–2.80 (m, 1H), 2.71–2.63 (m, 2H), 2.32 (s, 3H) ppm. All spectral data were in agreement with the literature [1].

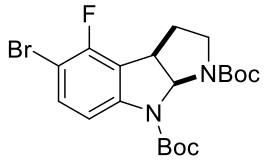
Di-*tert*-butyl-5-bromo-2,3,3a,8a-tetrahydropyrrolo[2,3-b]indole-1,8-dicarboxylate (6a)



6a

Light yellow oil, 8 h, 63.8 mg 73% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.52 (br, 1H), 7.29 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.25 (s, 1H), 6.44 (d, *J* = 7.4 Hz, 1H), 3.96 (t, *J* = 7.6 Hz, 1H), 3.85–3.82 (m, 1H), 2.86–2.81 (m, 1H), 2.13–2.06 (m, 1H), 1.99–1.96 (m, 1H), 1.56 (s, 9H), 1.48 (s, 9H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 153.9, 152.2, 142.3, 134.3, 130.9, 127.0, 117.1, 115.2, 81.8, 80.1, 76.3, 44.9, 31.9, 29.6, 28.3, 28.3 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{27}BrN_2O_4Na$ 461.1046; Found 461.1030.

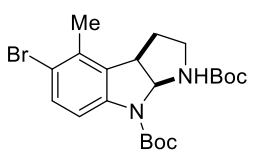
Di-*tert*-butyl-5-bromo-4-fluoro-2,3,3a,8a-tetrahydropyrrolo[2,3-b]indole-1,8-dicarboxylate (6b)



6b

White solid, m.p. 106.3 – 107.6 ^{o}C, 12 h, 60.4 mg, 66% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.37–7.31 (m, 2H), 6.51 (d, *J* = 7.6 Hz, 1H), 4.08 (t, *J* = 7.8 Hz, 1H), 3.91–3.88 (m, 1H), 2.88–2.83 (m, 1H), 2.13–2.10 (m, 1H), 2.05–1.99 (m, 1H), 1.54 (s, 9H), 1.48 (s, 9H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ **13C NMR** (150 MHz, Chloroform-*d*) δ154.9 (d, $^{1}J_{C\text{-}F}$ = 244.4 Hz), 153.7, 152.0, 144.6 (d, $^{3}J_{C\text{-}F}$ = 7.6 Hz), , 132.9, 119.3, 112.2, 101.4 (d, $^{2}J_{C\text{-}F}$= 19.6 Hz), 82.2, 81.8, 80.2, 76.9, 45.0, 42.5, 28.3, 28.3 ppm; **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -114.1 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{26}BrFN_2O_4Na$ 479.0952; Found 479.0942.

Di-*tert*-butyl-5-bromo-4-methyl-2,3,3a,8a-tetrahydropyrrolo[2,3-b]indole-1,8-dicarboxylate (6c)

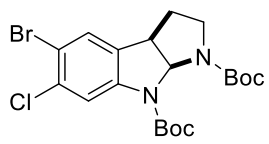


6c

White solid, m.p. 128.8 – 129.9 ^{o}C, 20.5 h, 48.6 mg, 54% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.45 (br, 1H), 7.34 (d, *J* =

8.6 Hz, 1H), 6.53 (d, *J* = 7.8 Hz, 1H), 3.98 – 3.88 (m, 2H), 2.85 (td, *J* = 12.2, 5.4 Hz, 1H), 2.31 (s, 3H), 2.12 – 2.04 (m, 1H), 1.87 (dd, *J* = 12.4, 5.4 Hz, 1H), 1.55 (s, 9H), 1.50 (s, 9H) ppm. **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 153.8, 152.4, 142.2, 133.2, 131.7, 118.1, 113.8, 81.7, 80.0, 76.6, 44.3, 32.4, 28.4, 28.3, 19.3 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{21}H_{29}BrN_2O_4Na$ 475.1203; Found 475.1193.

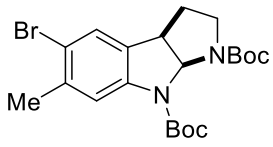
Di-*tert*-butyl-5-bromo-6-chloro-2,3,3a,8a-tetrahydropyrrolo[2,3-b]indole-1,8-dicarboxylate (6d)



6d

Light yellow oil, 9 h, 59.3 mg, 63% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.81 (br, 1H), 7.34 (s, 1H), 6.46 (d, *J* = 7.2 Hz, 1H), 3.94 (t, *J* = 7.6 Hz, 1H), 3.87–3.84 (m, 1H), 2.86–2.81 (m, 1H), 2.12–2.06 (m, 1H), 1.96–1.93 (m, 1H), 1.57 (s, 9H), 1.48 (s, 9H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 153.7, 151.9, 143.3, 133.6, 132.4, 128.4, 124.6, 114.9, 82.3, 81.9, 80.2, 76.8, 44.9, 44.3, 28.3, 28.2 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{26}O_4N_2BrClNa$ 495.0657; Found 495.0644.

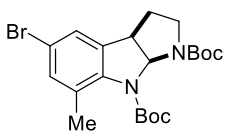
Di-tert-butyl-5-bromo-6-methyl-2,3,3a,8a-tetrahydropyrrolo[2,3-b]indole-1,8-dicarboxylate (6e)



6e

Light yellow oil, 9 h, 20.9 mg, 23% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.60 (br, 1H), 7.27 (s, 1H), 6.43 (d, *J* = 7.0 Hz, 1H), 3.93 (t, *J* = 7.6 Hz, 1H), 3.83–3.80 (m, 1H), 2.85–2,80 (m, 1H), 2.36 (s, 3H), 2.09–2.03 (m, 1H), 2.00–1.90 (m, 1H), 1.57 (s, 9H), 1.48 (s, 9H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 13C NMR (151 MHz, CDCl3) δ 153.9, 152.4, 142.6, 137.3, 131.5, 127.4, 117.7, 81.7, 80.0, 76.6, 44.9, 44.4, 29.7, 28.4, 28.3, 23.3 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{21}H_{29}BrN_2O_4Na$ 475.1203; Found 475.1195.

Di-tert-butyl-5-bromo-7-methyl-2,3,3a,8a-tetrahydropyrrolo[2,3-b]indole-1,8-dicarboxylate (6f)

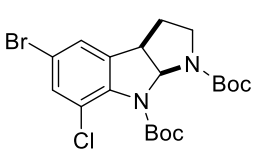


6f

Light yellow oil, 20.5 h, 46.5 mg, 51% yield; **^{1}H NMR** (600 MHz,

Chloroform-*d*) δ 7.16 (s, 1H), 7.11 (s, 1H), 6.20 (s, 1H), 3.95 (t, *J* = 5.8 Hz, 1H), 3.55 (dd, *J* = 10.6, 7.8 Hz, 1H), 2.80 – 2.75 (m, 1H), 2.24 (s, 3H), 2.15 – 2.04 (m, 2H), 1.48 (d, *J* = 7.0 Hz, 18H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 154.0, 153.2, 141.4, 137.2, 132.8, 131.8, 123.9, 117.9, 81.7, 80.0, 78.9, 46.4, 44.8, 28.5, 28.2, 19.5 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{21}H_{29}BrN_2O_4Na$ 475.1203; Found 475.1193.

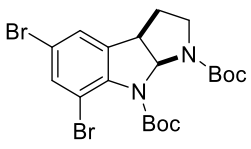
Di-*tert*-butyl-5-bromo-7-chloro-2,3,3a,8a-tetrahydropyrrolo[2,3-*b*]indole-1,8-dicarboxylate (6g)



6g

Colorless oil, 10.5 h, 9.5 mg, 10% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.38 (s, 1H), 7.21 (s, 1H), 6.18 (s, 1H), 4.03 (t, *J* = 6.0 Hz, 1H), 3.64–3.55 (m, 1H), 2.85–2.81 (m, 1H), 2.20–2.10 (m, 2H), 1.50 (s, 9H), 1.49 (s, 9H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 154.0, 152.3, 140.2, 139.3, 132.0, 125.2, 117.8, 115.5, 82.2, 80.5, 79.3, 47.1, 44.8, 28.5, 28.1 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{26}O_4N_2ClBrNa$ 495.0657; Found 495.0651.

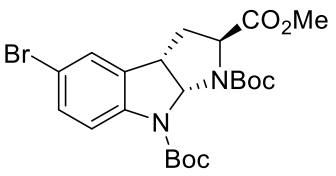
Di-*tert*-butyl-5,7-dibromo-2,3,3a,8a-tetrahydropyrrolo[2,3-*b*]indole-1,8-dicarboxylate (6h)



6h

Light yellow oil, 19 h, 21.2 mg, 20% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.55 (s, 1H), 7.26 (s, 1H), 6.16 (s, 1H), 4.04 (t, *J* = 6.0 Hz, 1H), 3.59 (t, *J* = 9.2 Hz, 1H), 2.86–2.80 (m, 1H), 2.17–2.08 (m, 2H), 1.51 (s, 9H), 1.50 (s, 9H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 153.9, 152.2, 142.0, 139.3, 134.7, 125.8, 118.1, 115.6, 82.4, 80.5, 79.4, 47.3, 44.8, 28.5, 28.1 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{26}O_4N_2Br_2Na$ 539.0152; Found 539.0145.

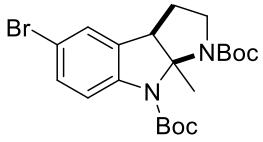
1,8-Di-*tert*-butyl-2-methyl-5-bromo-2,3,3a,8a-tetrahydropyrrolo[2,3-b]indole-1,2,8-tricarboxylate (6i)



6i

Colorless oil, 20 h, 47.5 mg, 48% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.44 (br, 1H), 7.34 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.28–7.27 (m, 1H), 6.35 (d, *J* = 5.9 Hz, 1H), 4.00–3.94 (m, 2H), 3.74 (s, 3H), 2.53–2.49 (m, 1H), 2.31–2.26 (m, 1H), 1.58/1.57 (s, 9H), 1.39 (s, 9H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 173.0, 152.1, 141.6, 134.4, 131.3, 126.8, 126.6, 119.0, 115.9, 81.9, 80.9, 58.9, 52.1, 44.6, 32.8, 29.7, 28.2, 28.1 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{22}H_{29}BrN_2O_6Na$ 519.1101; Found 519.1092.

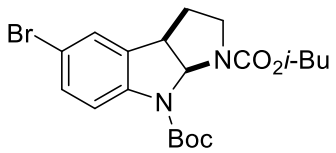
Di-*tert*-butyl-5-bromo-8a-methyl-2,3,3a,8a-tetrahydropyrrolo[2,3-b]indole-1,8-di carboxylate (6j)



6j

Light yellow oil, 9 h, 53.0 mg, 58% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 8.7 Hz, 1H), 7.29–7.26 (m, 1H), 7.22 (s, 1H), 3.73–3.70 (m, 1H), 3.49 (d, *J* = 7.8 Hz, 1H), 3.08–3.03 (m, 1H), 2.25–2.18 (m, 1H), 2.04 (s, 3H), 1.93–1.90 (m, 1H), 1.57 (s, 9H), 1.45 (s, 9H) ppm. For the mixture of two conformationl isomers: **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 155.8, 152.9, 151.8, 150.3, 142.4, 135.6, 134.5, 133.3, 130.8, 126.5, 126.1, 120.3, 118.0, 116.9, 115.8, 114.8, 87.8, 84.1, 81.6, 79.7, 54.6, 46.7, 28.5, 28.4, 28.2, 24.2, 14.0 ppm. **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{21}H_{29}BrN_2O_4Na$ 475.1203; Found 475.1194.

8-(*tert*-Butyl)-1-isopropyl-5-bromo-2,3,3a,8a-tetrahydropyrrolo[2,3-b]indole-1,8-dicarboxylate (6k)

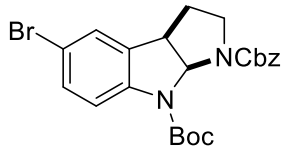


6k

Light yellow oil, 9 h, 38.2 mg, 43% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.53 (br, 1H), 7.30 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.26 (s, 1H), 6.44 (d, *J* = 6.8 Hz, 1H), 3.98 (t, *J* = 7.2 Hz, 1H), 3.93–3.84 (m, 3H), 2.94–2.89 (m, 1H), 2.17–2.11 (m, 1H), 2.04–2.02 (m, 1H), 1.99–1.95 (m, 1H), 1.57/1.56 (s, 9H), 0.94–0.92 (m, 6H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 154.8, 152.2, 142.2, 134.2, 130.9, 128.0, 126.9, 115.4, 81.9, 81.4, 76.6, 71.6, 44.8, 28.3, 28.3, 27.9, 19.1 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{27}BrN_2O_4Na$ 461.1046; Found

461.1034.

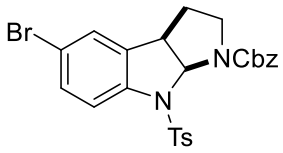
1-Benzyl-8-(tert-butyl)-5-bromo-2,3,3a,8a-tetrahydropyrrolo[2,3-b]indole-1,8-dicarboxylate (6l)



6l

Colorless oil, 12 h, 66.1 mg, 70% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.53 (s, 1H), 7.42–7.28 (m, 6H), 7.26 (s, 1H), 6.45 (d, *J* = 7.2 Hz, 1H), 5.20–5.13 (m, 2H), 3.97 (t, *J* = 7.2 Hz, 1H), 3.92–3.88 (m, 1H), 2.95–2.90 (m, 1H), 2.17–2.10 (m, 1H), 2.04–2.01 (m, 1H), 1.53/1.52 (s, 9H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 154.4, 152.2, 142.1, 136.7, 134.1, 131.0, 128.4, 127.9, 127.8, 126.9, 123.8, 115.4, 82.0, 76.7, 67.0, 66.9, 44.9, 28.3, 28.2 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{23}H_{25}O_4N_2BrNa$ 495.0890; Found 495.0885.

Benzyl-5-bromo-8-tosyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (6m)



6m

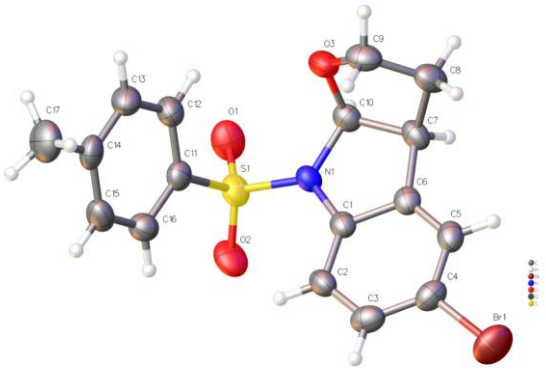
White solid, m.p. 112.9 – 114.2 ^{o}C, 12 h, 74.0 mg, 70% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.58–7.32 (m, 9H), 7.24–7.05 (m, 3H), 6.20 (br, 1H), 5.29–5.10 (m, 2H), 3.85–3.82 (m, 1H), 3.55 (t, *J* = 7.2 Hz, 1H), 2.89 (s, 1H), 2.35 (s, 3H), 2.11–2.04 (m, 1H), 1.97–1.91 (m, 1H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 13C NMR (151 MHz, CDCl3) δ 154.1, 144.1, 141.3, 136.3, 135.1, 131.5, 129.6, 129.4, 128.4, 128.4, 128.1, 128.0, 127.3, 127.1, 79.7, 67.5, 44.5, 29.6, 21.5 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{25}H_{23}O_4N_2BrNaS$ 549.0454; Found 549.0449.

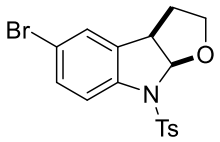
7. X-ray Dates

Single-crystal X-ray diffraction measurements were carried out on an Agilent Gemini E diffractometer using graphite monochromated Mo radiation (λ = 0.71073 Å, 50kV 40mA). The crystal data was collected on a Agilent Gemini E diffractometer (Mo, 50kV 40mA) and reducted by CrysAlisPro (Rigaku). The structures were solved by direct methods using SHELXS-97. Refinements were performed with SHELXL-2013 using fullmatrix least-squares calculations on F2, with anisotropic displacement parameters for all the nonhydrogen atoms.

The single crystals of compound **3c** suitable for X-ray diffraction analysis were obtained by slow evaporation of a mixed Dichloromethane/Petroleum ether solution of **3c** at room temperature.

Molecular structure of **3c**, ellipsoids shown at 35% probability.





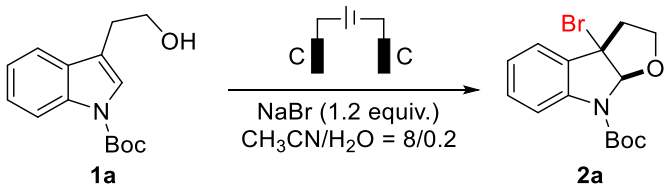
CCDC: 2173146

Crystal data and structure refinement for CCDC:2173146.

Identification code	exp_10608
Empirical formula	$C_{17}H_{16}BrNO_3S$
Formula weight	394.28
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	8.2932(10)
b/Å	8.8298(11)
c/Å	12.4718(14)

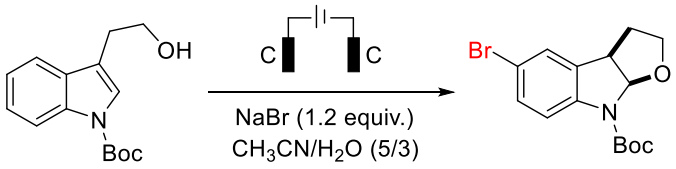
α/°	95.863(10)
β/°	90.752(10)
γ/°	116.824(12)
Volume/Å^3	808.94(18)
Z	2
ρ_{calc}g/cm^3	1.619
μ/mm^{-1}	2.684
F(000)	400.0
Crystal size/mm^3	0.22 × 0.18 × 0.09
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.208 to 48.994
Index ranges	$-9 \leq h \leq 9$, $-6 \leq k \leq 10$, $-13 \leq l \leq 14$
Reflections collected	5512
Independent reflections	2687 [R_{int} = 0.0339, R_{sigma} = 0.0567]
Data/restraints/parameters	2687/0/209
Goodness-of-fit on F^2	1.074
Final R indexes [I>=2σ (I)]	R_1 = 0.0572, wR_2 = 0.1393
Final R indexes [all data]	R_1 = 0.0813, wR_2 = 0.1524
Largest diff. peak/hole / e Å^{-3}	0.37/-0.64

8. Scale-up experiments



1a **2a**

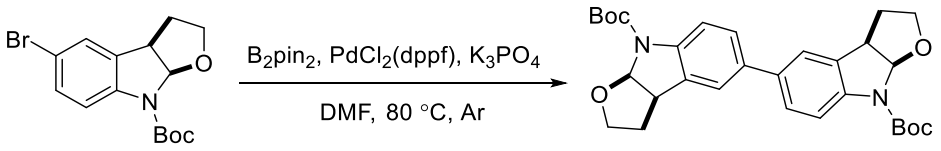
Procedure: A mixture of **1a** (261.1 mg, 1.0 mmol) and NaBr (123.5 mg, 1.2 mmol) were added in a 10 mL vial with a stir bar, then CH_3CN/H_2O (8/0.2ml) were added under air atmosphere. The vial was covered with the electrode holder. The electrolysis was carried out at rt using a constant current of 5.0 mA between a graphite anode and graphite cathode (1.4 × 0.8 × 0.2 cm submerged in solution) with stirring. After completion as detected by TLC. The reaction mixture was diluted with EtOAc. The organic phase was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure, purified by flash column chromatography (Petroleum ether/Ethyl acetate = 10/1) to give compound **2a** (15 h, 214.2 mg, 63% yield).



1a **3a**

Procedure: A mixture of **1a** (261.1 mg, 1.0 mmol) and NaBr (123.5 mg, 1.2 mmol) were added in a 10 mL vial with a stir bar, then CH_3CN/H_2O (5/3ml) were added under air atmosphere. The vial was covered with the electrode holder. The electrolysis was carried out at RT using a constant current of 5.0 mA between a graphite anode and graphite cathode (1.4 × 0.8 × 0.2 cm submerged in solution) with stirring. After completion as detected by TLC. The reaction mixture was diluted with EtOAc. The organic phase was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure, purified by flash column chromatography (Petroleum ether/Ethyl acetate = 10/1) to give compound **3a** (28 h, 223.2 mg, 66 %).

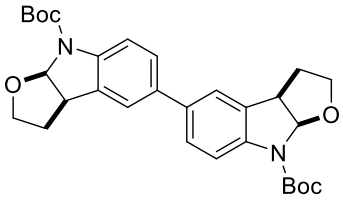
9. Transformation and applications



3a **7**

A mixture of **3a** (34.0 mg, 0.1 mmol), K_3PO_4 (64.1 mg, 0.30 mmol), $PdCl_2$ (dppf) (7.3 mg, 0.01 mmol), and B_2Pin_2 (28.2 mg, 0.11 mmol) was dissolved in DMF (3 mL) under argon atmosphere. Then, the mixture was stirred at 80 ℃ and when the reaction was completed as monitored by TLC. The reaction was cooled to room temperature. The resulting solid was filtered off and adsorbed onto the minimal amount of silica gel using CH_2Cl_2. the solvent was concentrated under reduced pressure, purified by flash column chromatography (Petroleum ether/Ethyl acetate = 4/1) to give **7**. The same procedure was performed on **6a** to afford **10**.

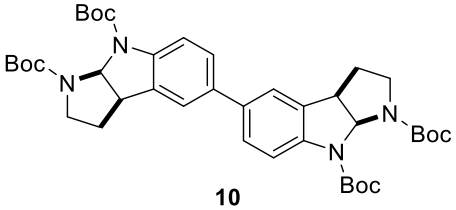
Di-*tert*-butyl-2,2',3,3a,3',3'a,8a,8'a-octahydro-8H,8'H-[5,5'-bifuro[2,3-b]indole]-8, 8'-dicarboxylate (7)



7

Colorless oil, 2.5 h, 18.1 mg, 70 % yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.85 (br, 1H), 7.41–7.37 (m, 5H), 6.19 (br, 2H), 4.02–3.94 (m, 4H), 3.52–3.47 (m, 2H), 2.39–2.33 (m, 2H), 2.18–2.15 (m, 2H), 1.63/1.61 (s, 18H); **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 152.4, 142.1, 135.8, 126.7, 122.6, 114.5, 93.6, 66.4, 33.9, 28.4, 24.8 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{30}H_{36}N_2O_6Na$ 543.2466; Found 543.2465.

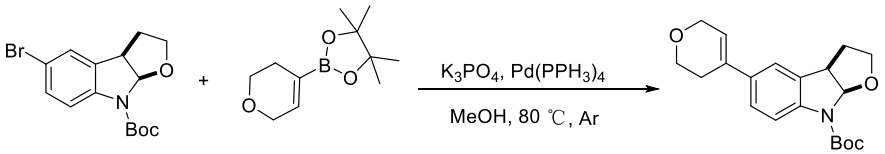
Di-*tert*-Butyl-2,2',3,3a,3',3'a,8a,8'a-octahydro-[5,5'-bipyrrolo[2,3-b]indole]-1,1',8, 8'-tetracarboxylate (10)



10

Reaction of **6a** (35.1 mg, 0.08 mmol) with K_3PO_4 (51.3 mg, 0.24 mmol), $PdCl_2$(dppf) (5.8 mg, 0.008 mmol), and B_2Pin_2 (22.5 mg, 0.089 mmol) provided **10.** Light yellow oil, 1 h, 18.9 mg, 66 % yield; **^{1}H NMR** (600 MHz,

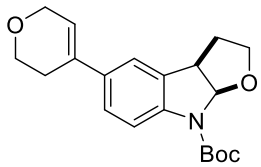
Chloroform-*d*) δ 7.66 (br, 2H), 7.39 (d, *J* = 7.0 Hz, 2H), 7.33 (d, *J* = 7.0 Hz, 2H), 6.48 (d, *J* = 7.2 Hz, 2H), 4.02 (t, *J* = 7.4 Hz, 2H), 3.85–3.81 (m, 2H), 2.93–2.86 (m, 2H), 2.17–2.05 (m, 4H), 1.58 (s, 18H), 1.50 (s, 18H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 144.7, 143.3, 134.3, 128.7, 126.0, 120.6, 120.5, 116.7, 81.0, 79.7, 76.5, 48.8, 34.3, 10.2 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{40}H_{54}N_4O_8Na$ 741.3834; Found 741.3836.



3a **8a**

General Procedures for **8a**：A mixture of **3a** (34.0 mg, 0.1 mmol), 3,6-dihydro-2H-pyran-4-boronic acid pinacol ester (23.1 mg, 0.11 mmol), K_3PO_4 (25.5 mg, 0.112 mmol) and $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol) dissolved in MeOH (0.8 mL) under argon atmosphere. Then, the mixture was stirred at 80 ℃ and when the reaction was completed as monitored by TLC. The reaction was cooled to room temperature. the solvent was concentrated under reduced pressure, purified by flash column chromatography (Petroleum ether/Ethyl acetate =40/1 to 10/1) to give **8a**.

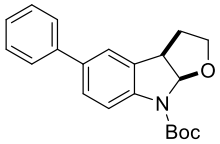
tert-butyl-5-(3,6-dihydro-2H-pyran-4-yl)-2,3,3a,8a-tetrahydro-8H-furo[2,3-b]indole-8-carboxylate (8a)



8a

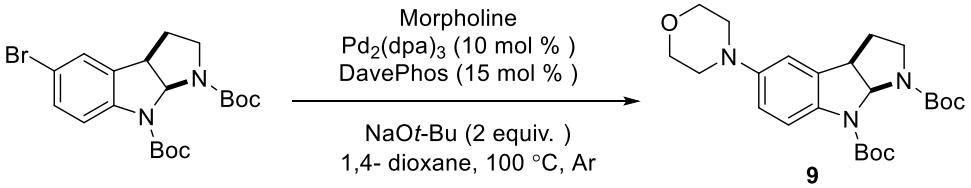
Light yellow oil, 22 h, 16.3 mg, 48 % yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.76 (br, 1H), 7.25 – 7.22 (m, 2H), 6.17 (br, 1H), 6.06 (s, 1H), 4.32 (d, *J* = 2.9 Hz, 2H), 3.99 (t, *J* = 8.1 Hz, 1H), 3.93 (q, *J* = 5.3 Hz, 3H), 3.95 – 3.92 (m, 1H), 2.57 – 2.44 (m, 2H), 2.38 – 2.28 (m, 1H), 2.11 (dd, *J* = 12.2, 4.7 Hz, 1H), 1.60 (s, 9H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 152.1, 141.7, 135.2, 133.6, 131.2, 124.7, 121.1, 120.6, 114.0, 93.6, 81.3, 66.3, 65.8, 64.4, 45.0, 33.8, 28.4, 27.3 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{25}NO_4Na$ 366.1676; Found 366.1661.

***tert*-Butyl-5-phenyl-2,3,3a,8a-tetrahydro-8*H*-furo[2,3-*b*]indole-8-carboxylate (8b)**



8b

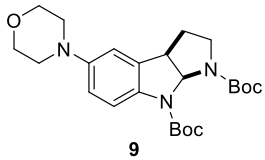
Following the general Procedure for **8a**. The procedure was performed on **3a** (68.0 mg, 0.2 mmol), phenylboronic acid (26.8 mg, 0.22 mmol), K_3PO_4 (50.9 mg, 0.24 mmol) and $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol) to afford **8b**. Light yellow oil, 22 h, 51.0 mg, 76% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.88 (br, 1H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.46–7.41 (m, 4H), 7.32 (t, *J* = 7.4 Hz, 1H), 6.20 (s, 1H), 4.00 (q, *J* = 9.4, 8.8 Hz, 2H), 3.53–3.49 (m, 1H), 2.41–2.31 (m, 1H), 2.17–2.14 (m, 1H), 1.62 (s, 9H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 152.4, 140.8, 136.0, 131.8, 128.7, 127.1, 126.8, 126.7, 114.5, 93.6, 81.5, 66.4, 44.9, 33.8, 28.4 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{21}H_{23}O_3NNa$ 360.1570; Found 360.1556.



6a **9**

A mixture of **6a** (17.56 mg, 40 μmol), DavePhos (2.3 mg, 6 μmol), $Pd_2(dba)_3$ (3.7 mg, 4 μmol), NaOt-Bu (7.7 mg, 80 μmol), and morpholine (10.5 μL, 120 μmol) was dissolved in 1,4-dioxane (315 μL) under argon atmosphere .Then, the mixture was stirred at 100 ℃ and when the reaction was completed as monitored by TLC. The reaction was cooled to room temperature and diluted with CH_2Cl_2 (2 mL). The solution was washed with water (2 mL) and the aqueous layer was extracted with CH_2Cl_2 (2 mL x 3). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated under reduced pressure, purified by flash column chromatography (Petroleum ether/Ethyl acetate = 3/1) to give **9.**

Di-*tert*-butyl-5-morpholino-2,3,3a,8a-tetrahydropyrrolo[2,3-*b*]indole-1,8-dicarbo xylate (9)



9

Yellow oil, 4.5 h, 14.4 mg, 81% yield; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.50 (br, 1H), 6.77–6.75 (m, 2H), 6.40 (d, *J* =

5.2 Hz, 1H), 3.94 (t, *J* = 7.3 Hz, 1H), 3.86 (t, *J* = 4.8 Hz, 4H), 3.79 (dd, *J* = 11.3, 7.4 Hz, 1H), 3.13–3.05 (m, 4H), 2.84 (td, *J* = 11.7, 5.2 Hz, 1H), 2.13–1.98 (m, 2H), 1.56 (s, 9H), 1.49 (s, 9H) ppm; **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 154.0, 152.6, 147.9, 136.7, 133.1, 116.6, 115.8, 112.3, 81.1, 76.2, 71.6, 71.1, 66.9, 61.8, 50.5, 44.9, 28.4, 28.4 ppm; **HRMS (ESI)** *m/z*: $[M + Na]^+$ Calcd for $C_{24}H_{35}O_5N_3Na$ 468.2469; Found 468.2467.

10. References

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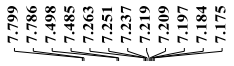
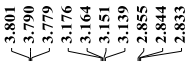
11 ^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectra of compounds





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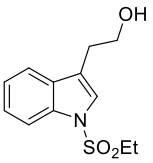

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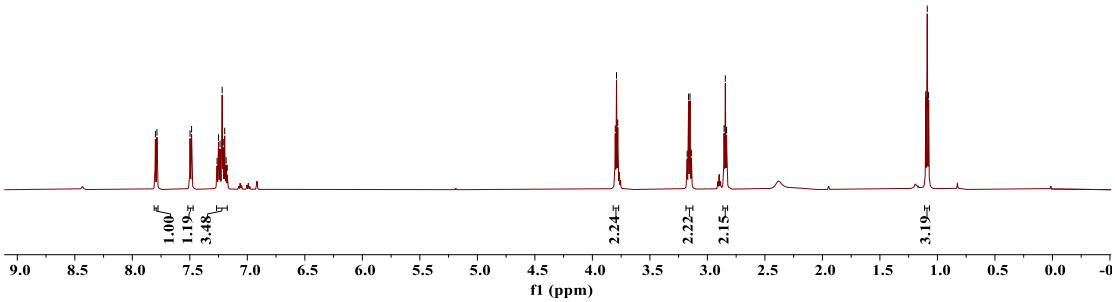

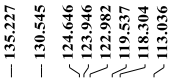

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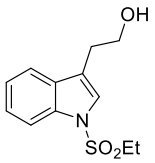

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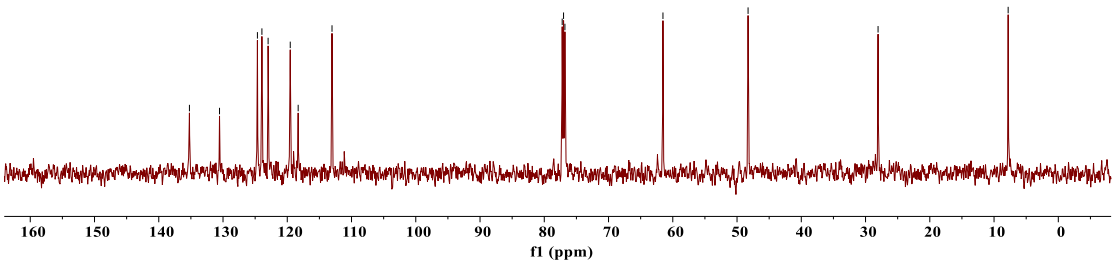

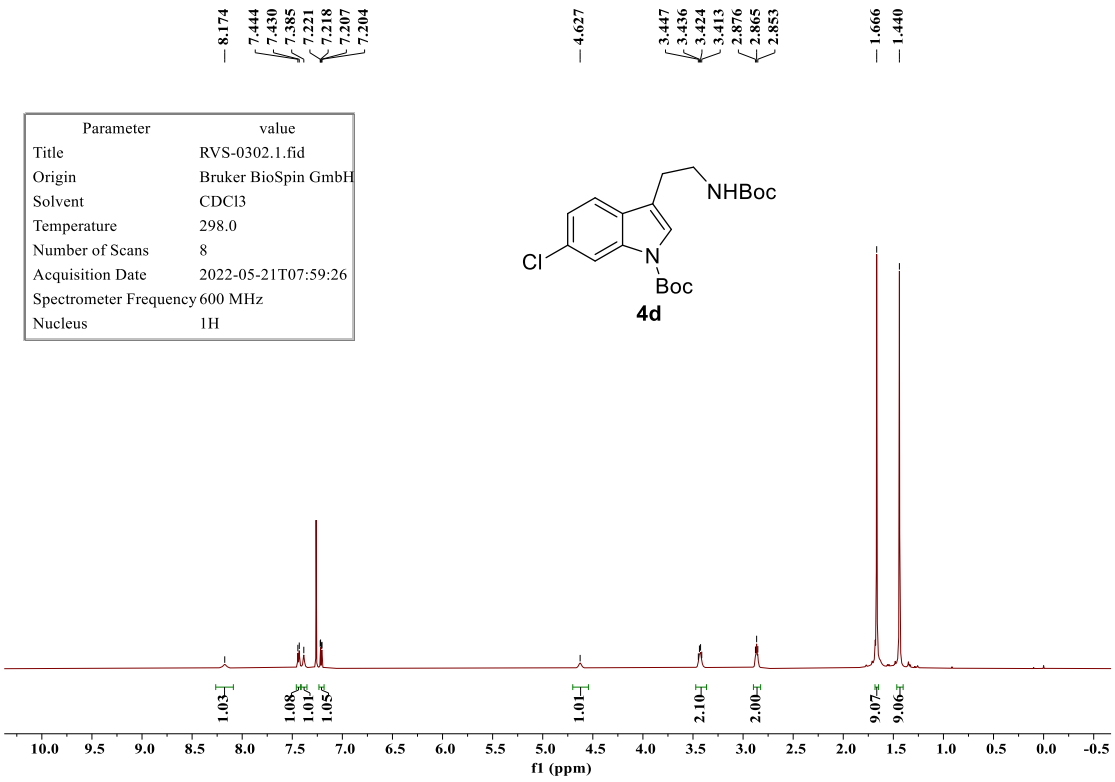
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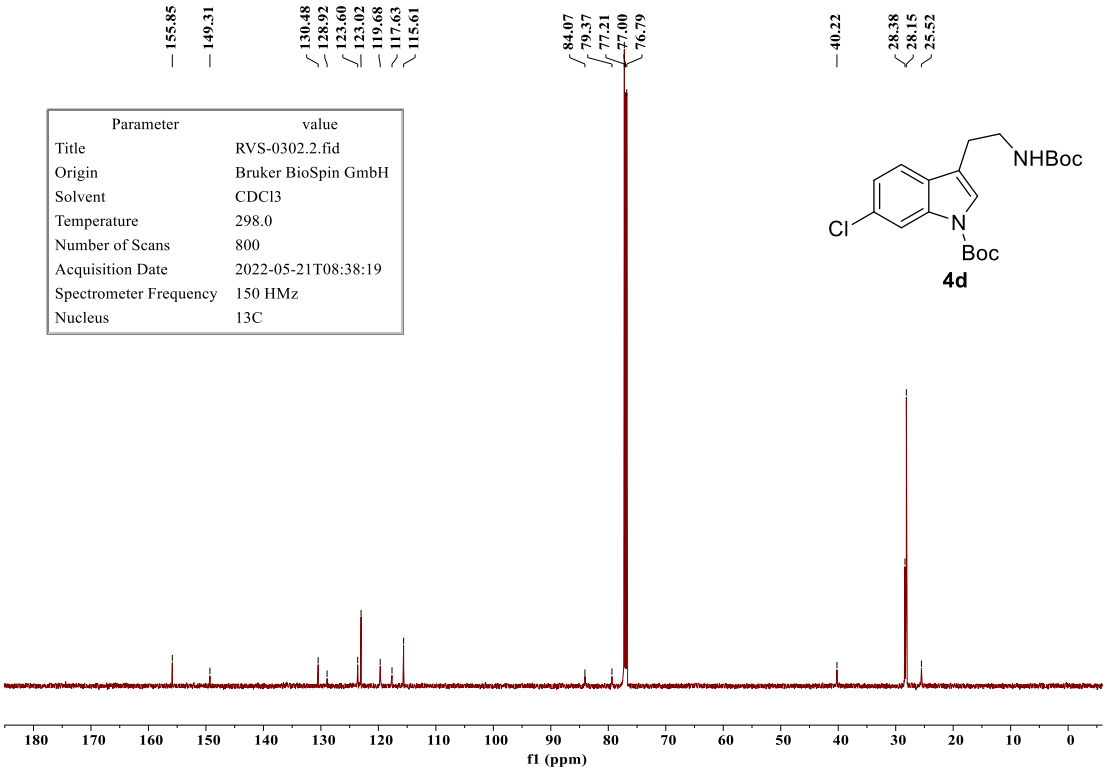
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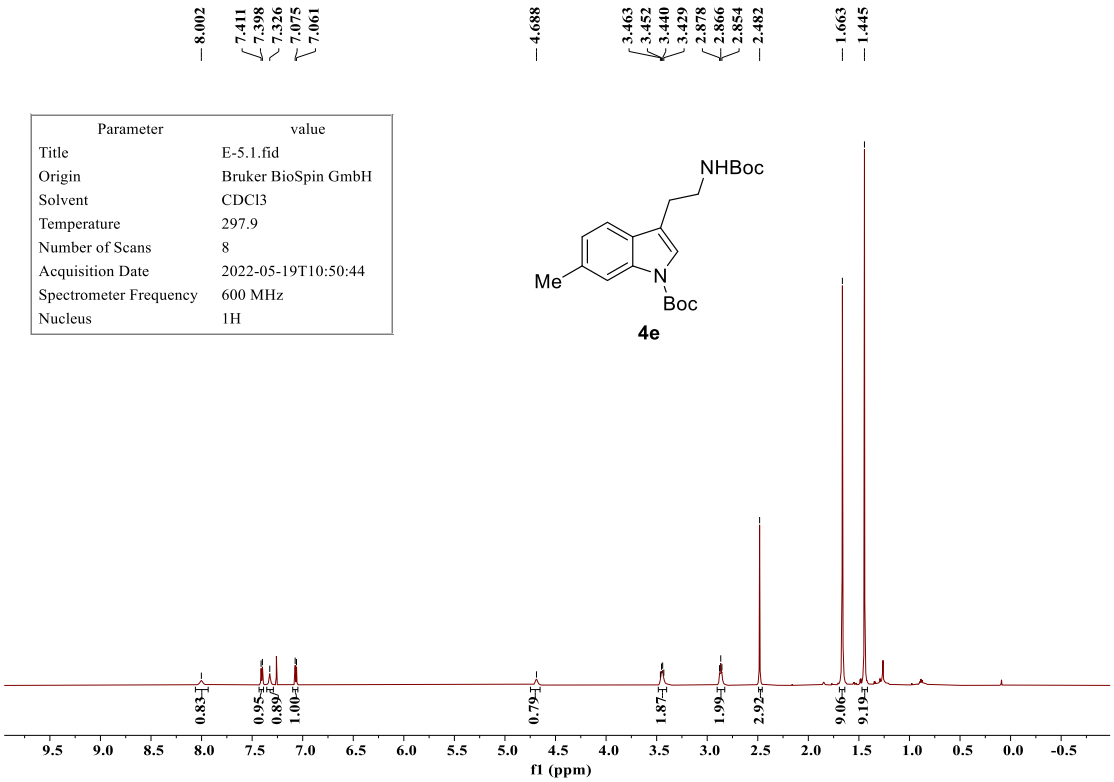
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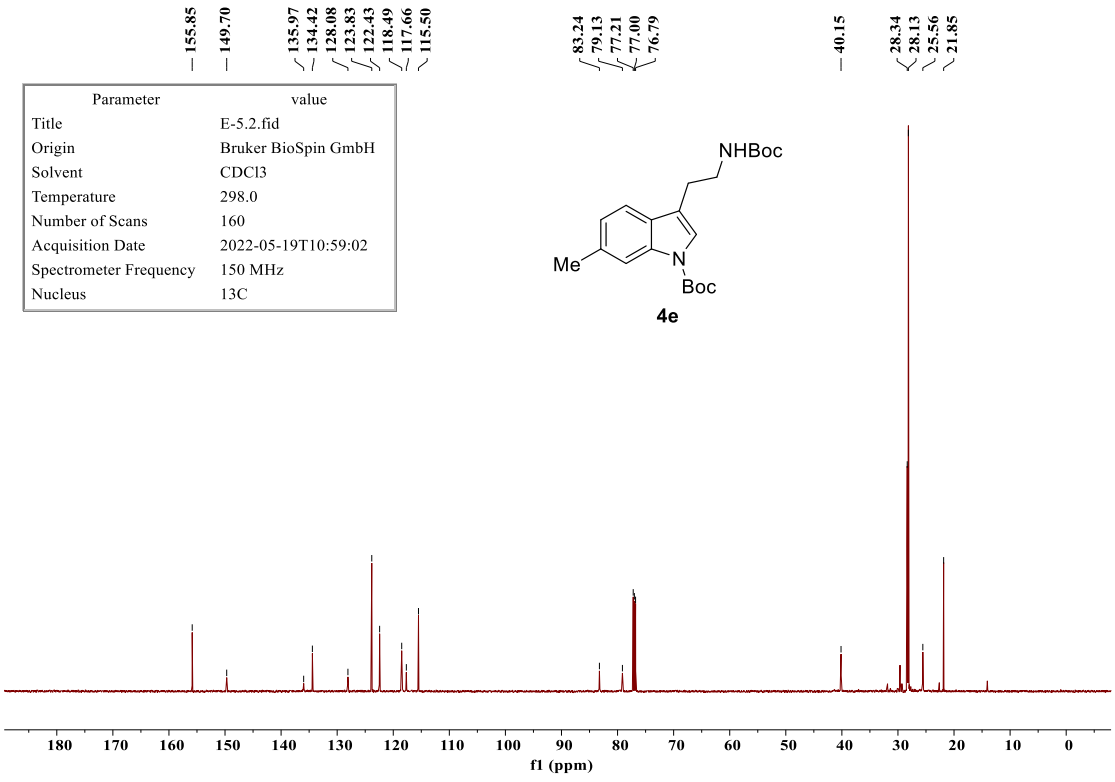
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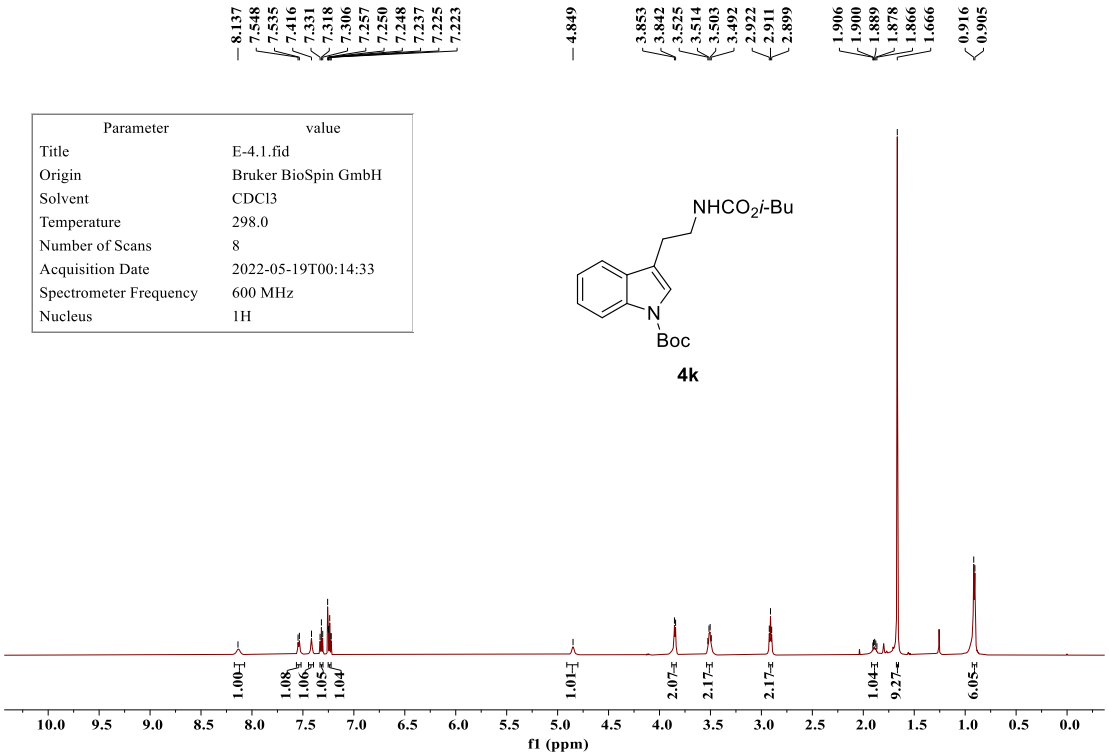
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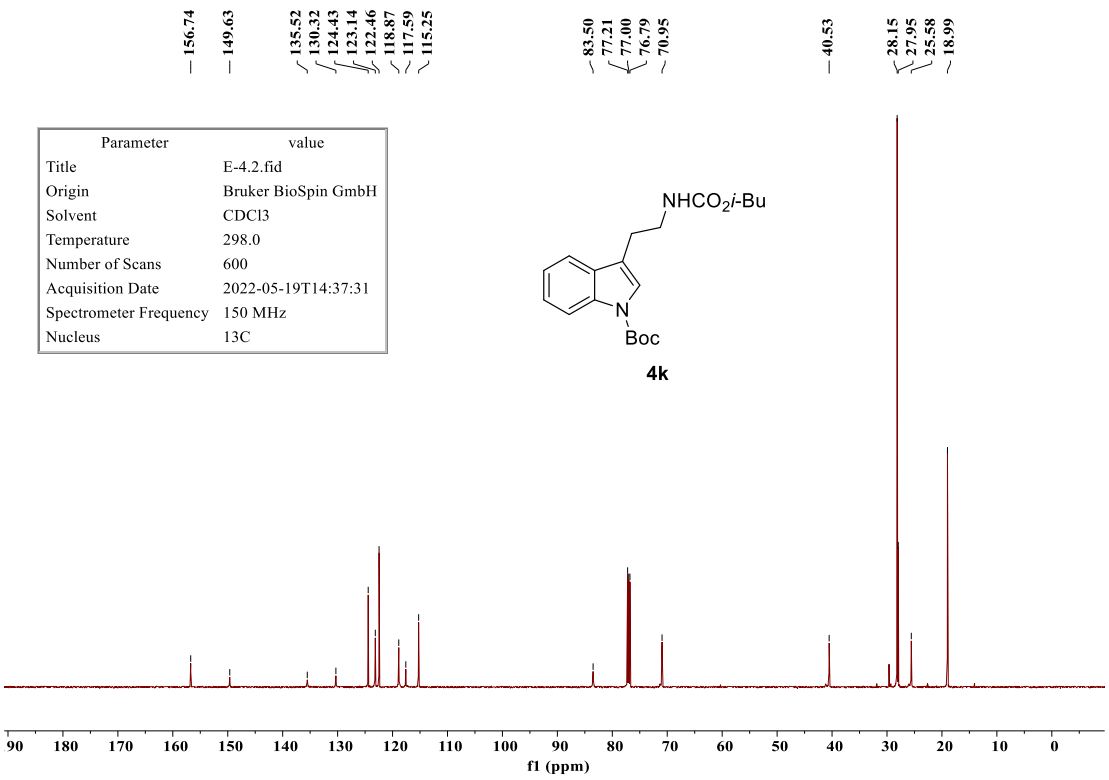
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83.50
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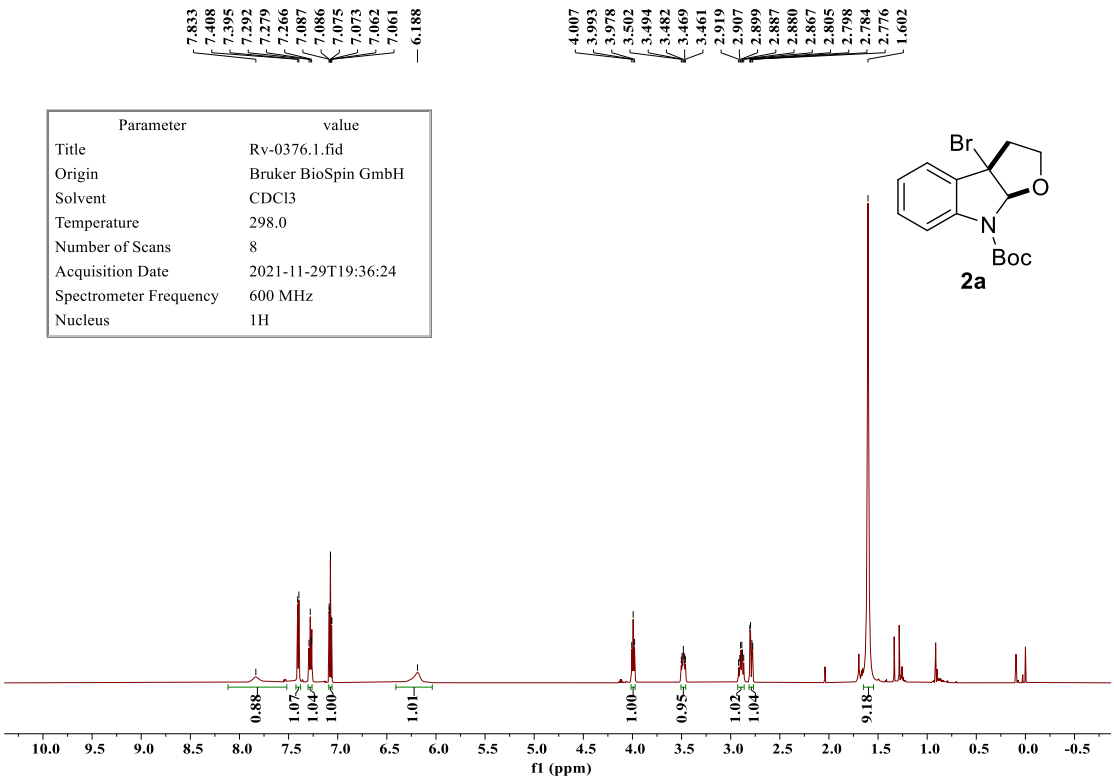
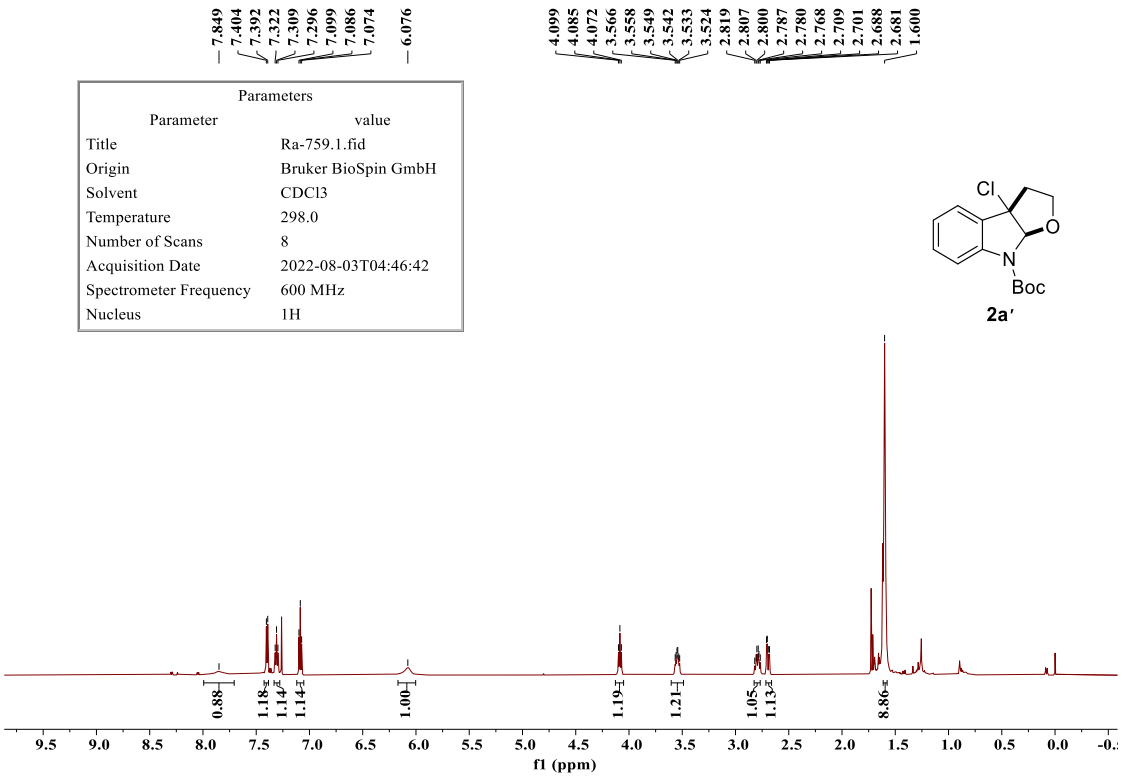
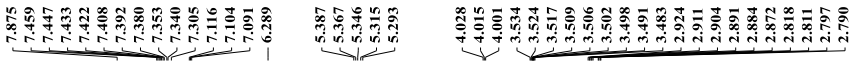
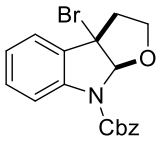
77.00
76.79
70.95
40.53
28.15
27.95
25.58
18.99
Parameter value
Title E-4.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 600
Acquisition Date 2022-05-19T14:37:31
Spectrometer Frequency 150 MHz
Nucleus 13C
NHCO2i-Bu
N
Boc
4k
f1 (ppm)


7.833
7.408
7.395
7.292
7.279
7.266
7.087
7.086
7.075
7.073
7.062
7.061
6.188
4.007
3.993
3.978
3.502
3.494
3.482
3.469
3.461
2.919
2.907
2.899
2.887
2.880
2.867
2.805
2.798
2.784
2.776
1.602
Parameter value
Title Rv-0376.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2021-11-29T19:36:24
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
O
N
Boc
2a
0.88
1.07
1.04
1.00
1.01
1.00
0.95
1.02
1.04
9.18
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

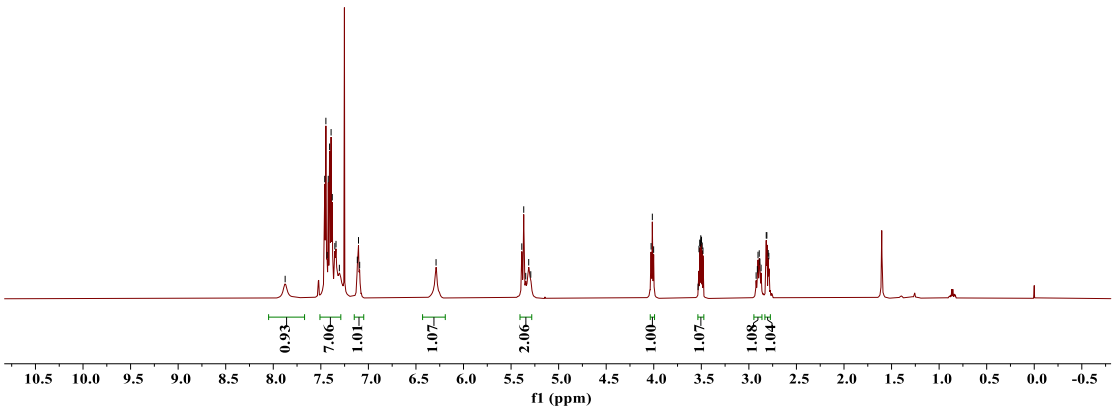

7.849
7.404
7.392
7.322
7.309
7.296
7.099
7.086
7.074
6.076
4.099
4.085
4.072
3.566
3.558
3.549
3.542
3.533
3.524
2.819
2.807
2.800
2.787
2.780
2.768
2.709
2.701
2.688
2.681
1.600
Parameters
Parameter value
Title Ra-759.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-08-03T04:46:42
Spectrometer Frequency 600 MHz
Nucleus 1H
Cl
O
N
Boc
2a′
0.88
1.18
1.14
1.14
1.00
1.19
1.21
1.05
1.13
8.86
f1 (ppm)

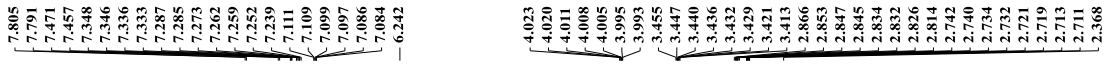


Parameter	value
Title	RV-0402-1.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	8
Acquisition Date	2022-05-12T23:03:40
Spectrometer Frequency	600 MHz
Nucleus	1H

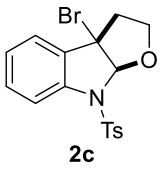


2b

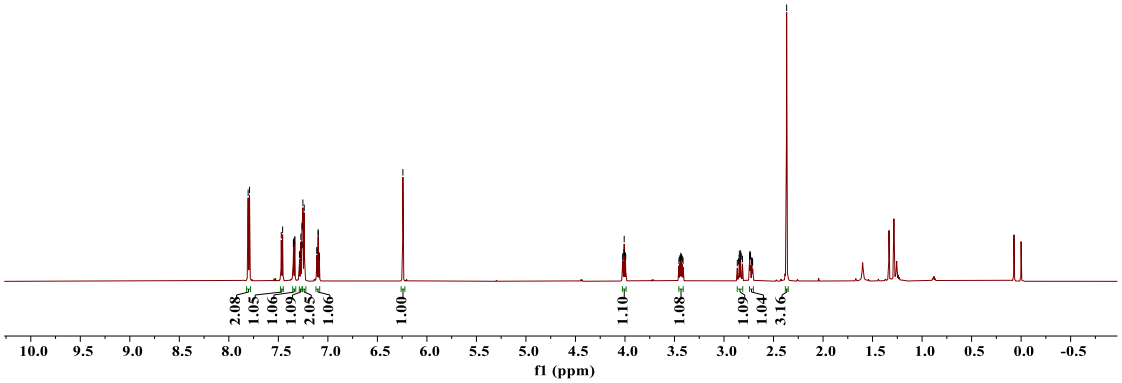


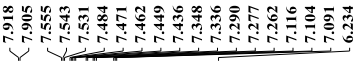


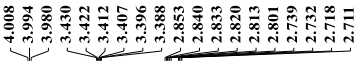
Parameter	value
Title	RV-0399-1.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	8
Acquisition Date	2021-12-13T23:50:45
Spectrometer Frequency	600 MHz
Nucleus	1H



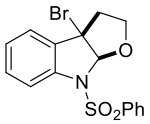
2c



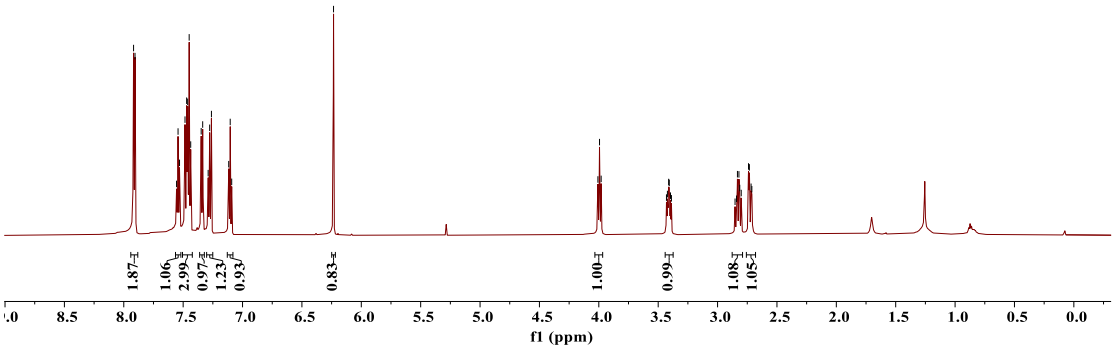




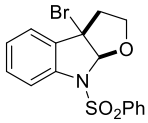
Parameters	
Parameter	value
Title	Ra-641.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	8
Acquisition Date	2022-05-31T00:34:19
Spectrometer Frequency	600 MHz
Nucleus	1H



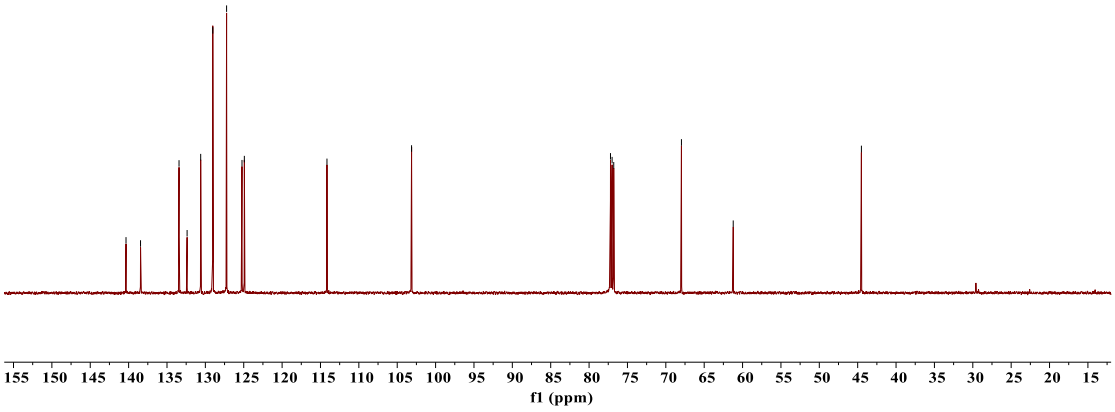
2d

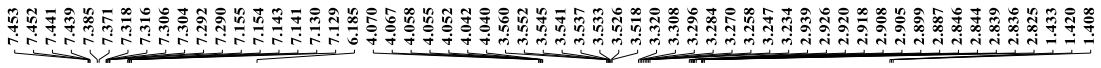


Parameters	
Parameter	value
Title	Ra-641.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	131
Acquisition Date	2022-05-31T11:01:44
Spectrometer Frequency	150 MHz
Nucleus	13C



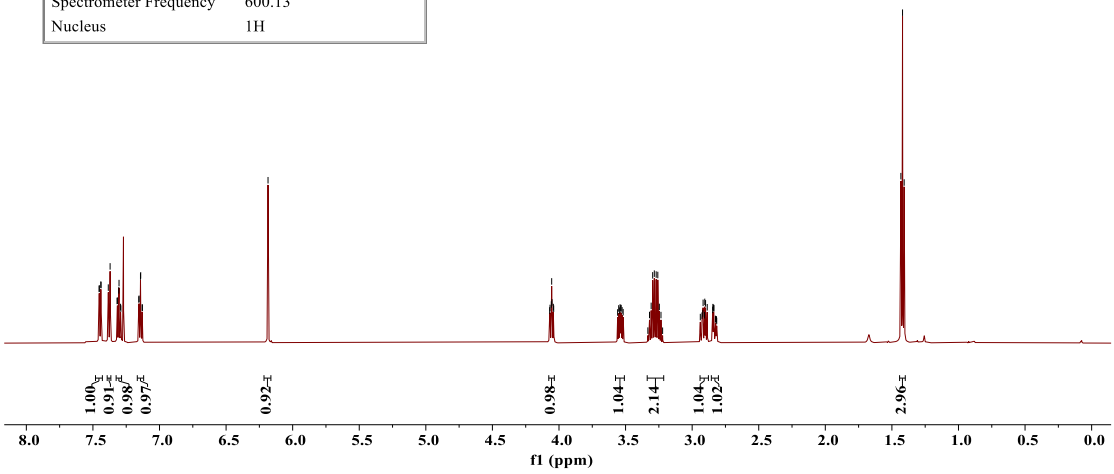
2d

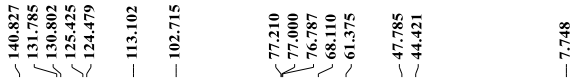




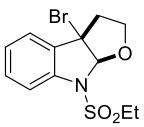
Parameters	
Parameter	value
Title	Ra-640.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	8
Acquisition Date	2022-05-31T01:12:18
Spectrometer Frequency	600.13
Nucleus	1H

2e

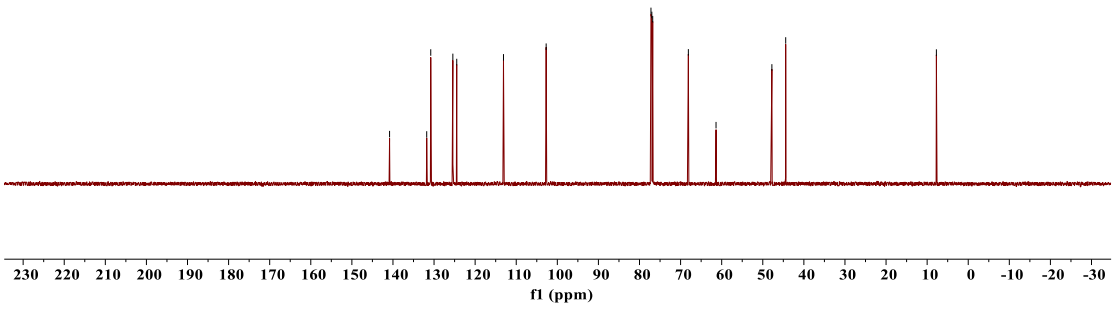


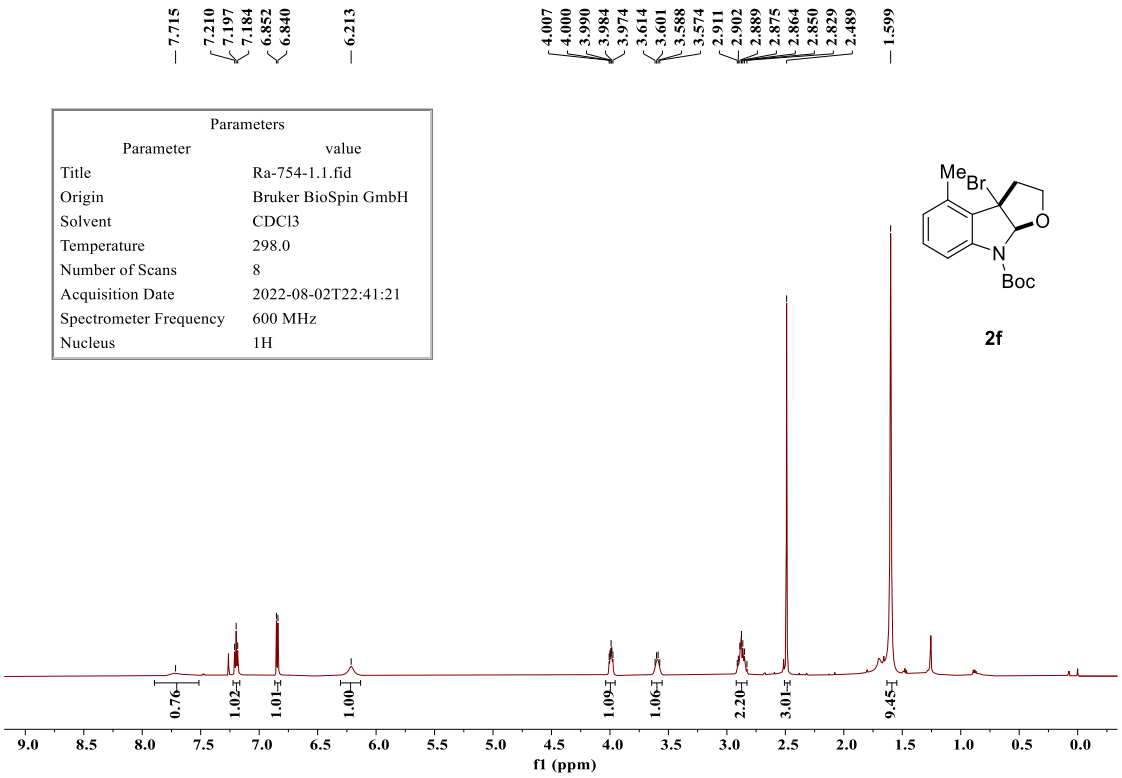


Parameters	
Parameter	value
Title	Ra-640.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.1
Number of Scans	60
Acquisition Date	2022-05-31T10:50:32
Spectrometer Frequency	150 MHz
Nucleus	13C



2e

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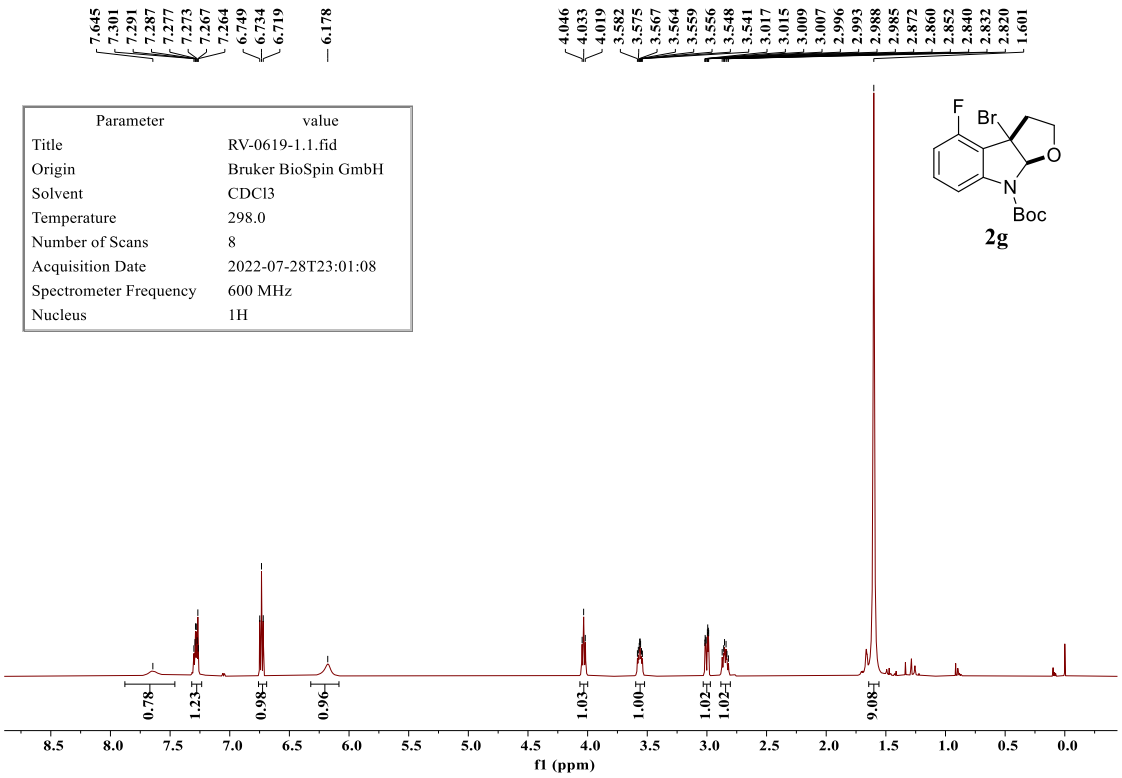
7.210
7.197
7.184
6.852
6.840
6.213
4.007
4.000
3.990
3.984
3.974
3.614
3.601
3.588
3.574
2.911
2.902
2.889
2.875
2.864
2.850
2.829
2.489
1.599
Parameters
Parameter value
Title Ra-754-1.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-08-02T22:41:21
Spectrometer Frequency 600 MHz
Nucleus 1H
Me
Br
O
N
Boc
2f
0.76
1.02
1.01
1.00
1.09
1.06
2.20
3.01
9.45
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


7.645
7.301
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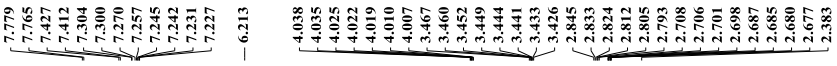
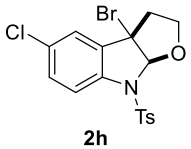
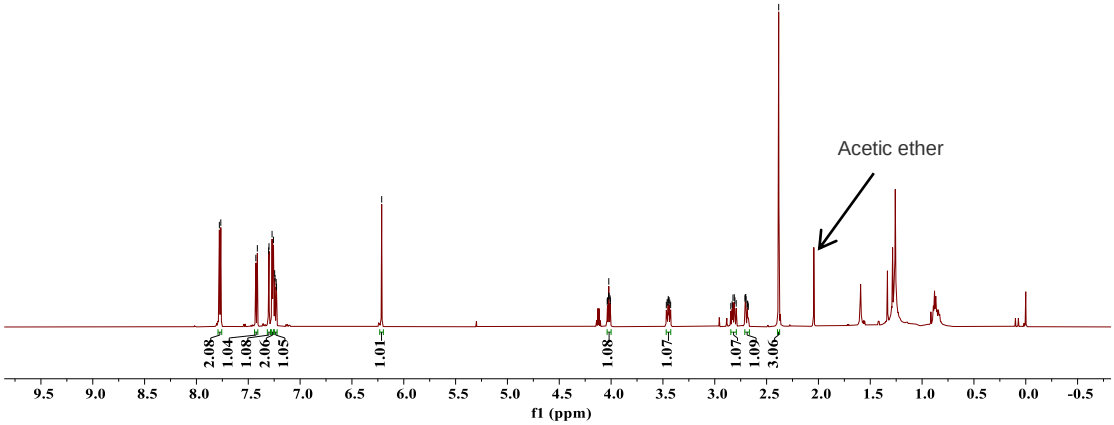
7.287
7.277
7.273
7.267
7.264
6.749
6.734
6.719
6.178
4.046
4.033
4.019
3.582
3.575
3.567
3.564
3.559
3.556
3.548
3.541
3.017
3.015
3.009
3.007
2.996
2.993
2.988
2.985
2.872
2.860
2.852
2.840
2.832
2.820
1.601
Parameter value
Title RV-0619-1.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-07-28T23:01:08
Spectrometer Frequency 600 MHz
Nucleus 1H
F
Br
O
N
Boc
2g
0.78
1.23
0.98
0.96
1.03
1.00
1.02
1.02
9.08
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

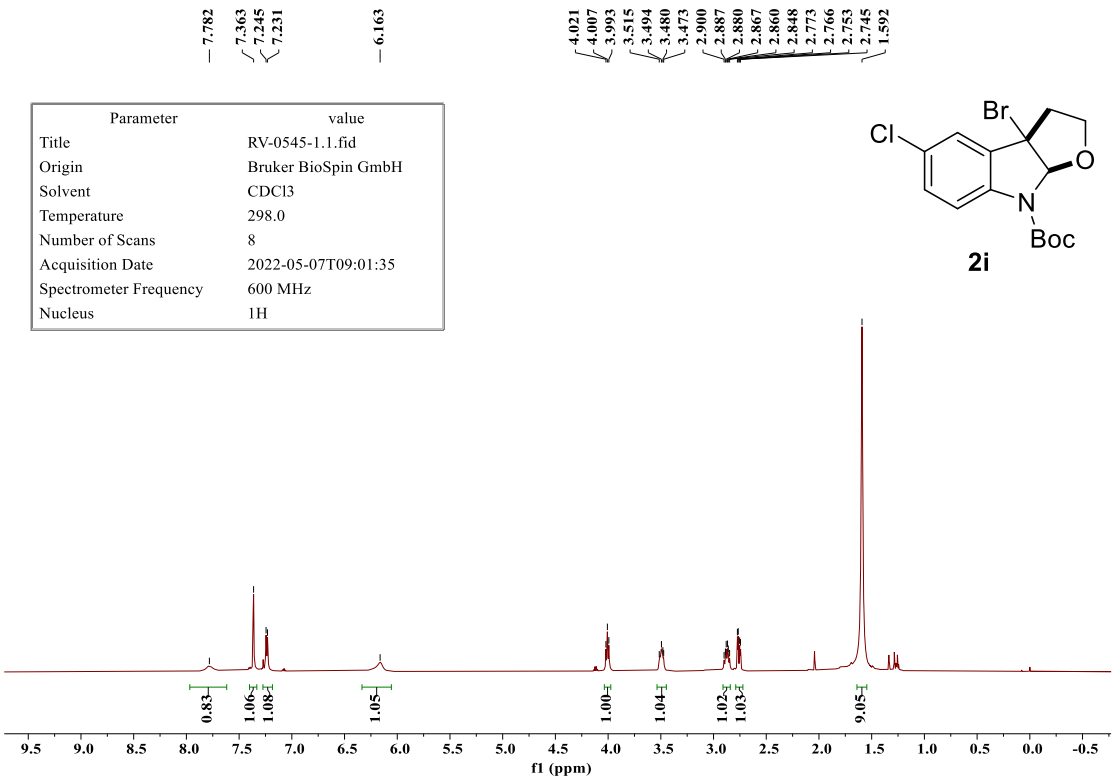


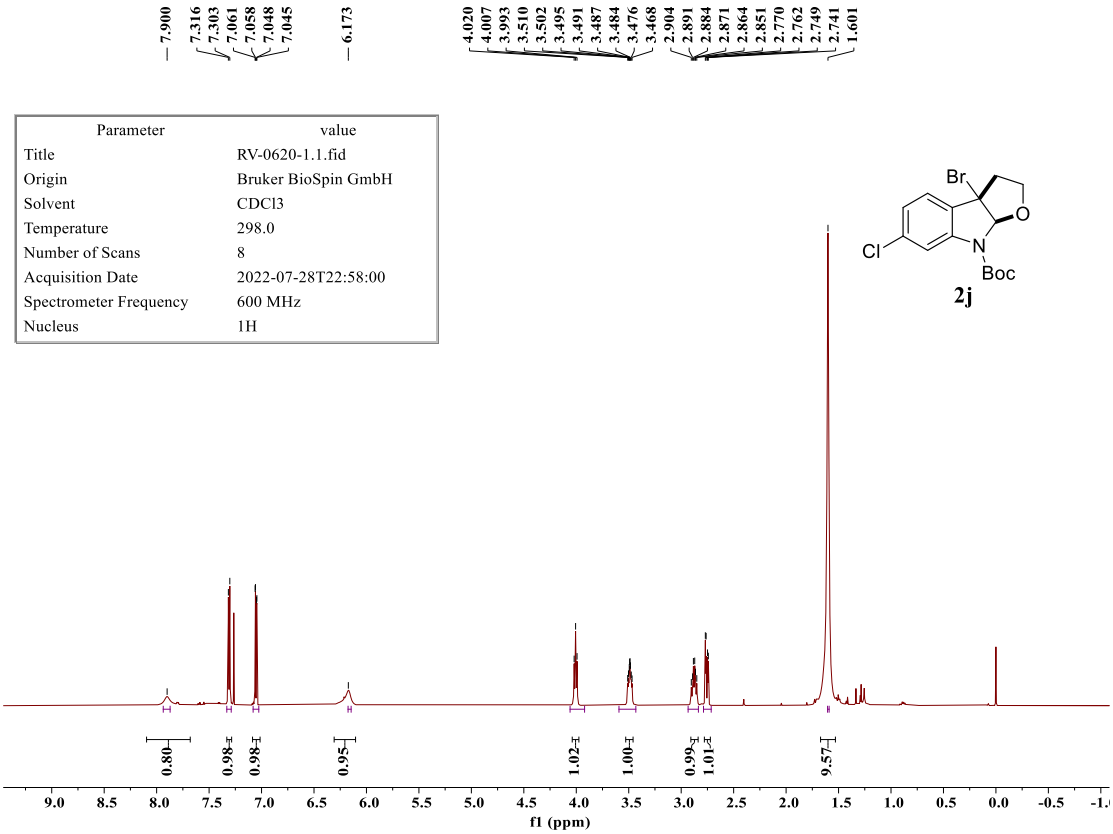
Parameter	value
Title	RV-0461.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.2
Number of Scans	8
Acquisition Date	2022-02-21T21:17:32
Spectrometer Frequency	600 MHz
Nucleus	1H

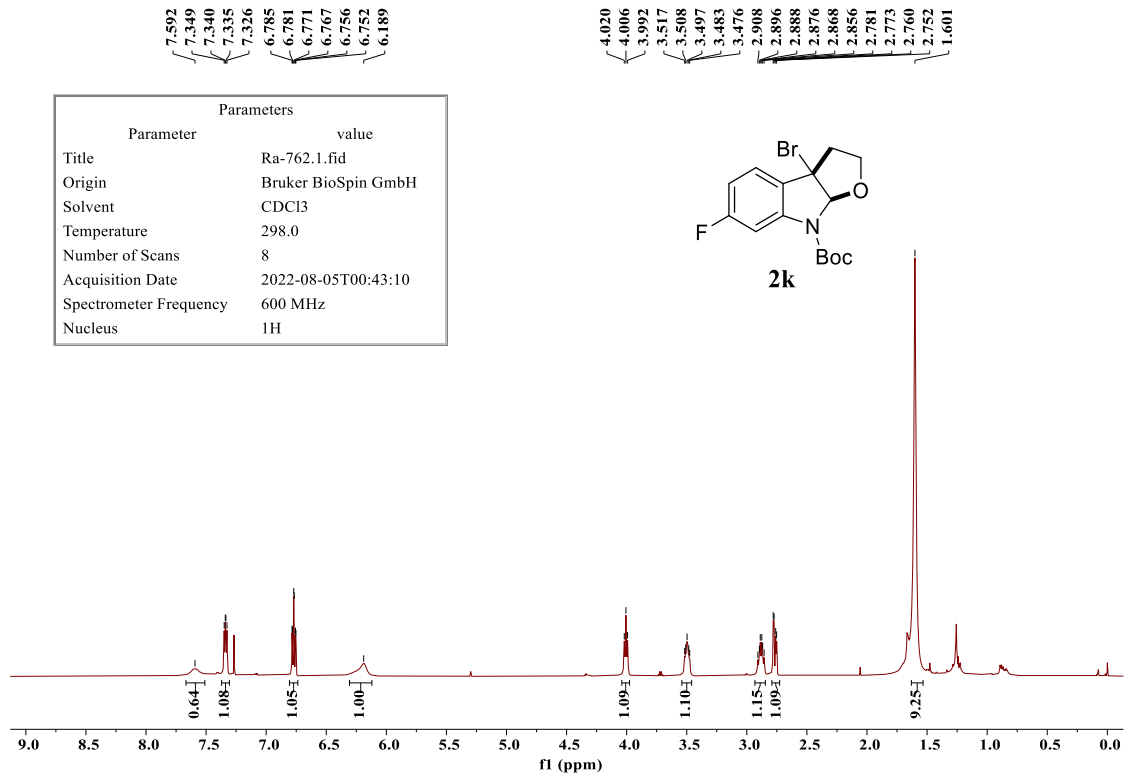


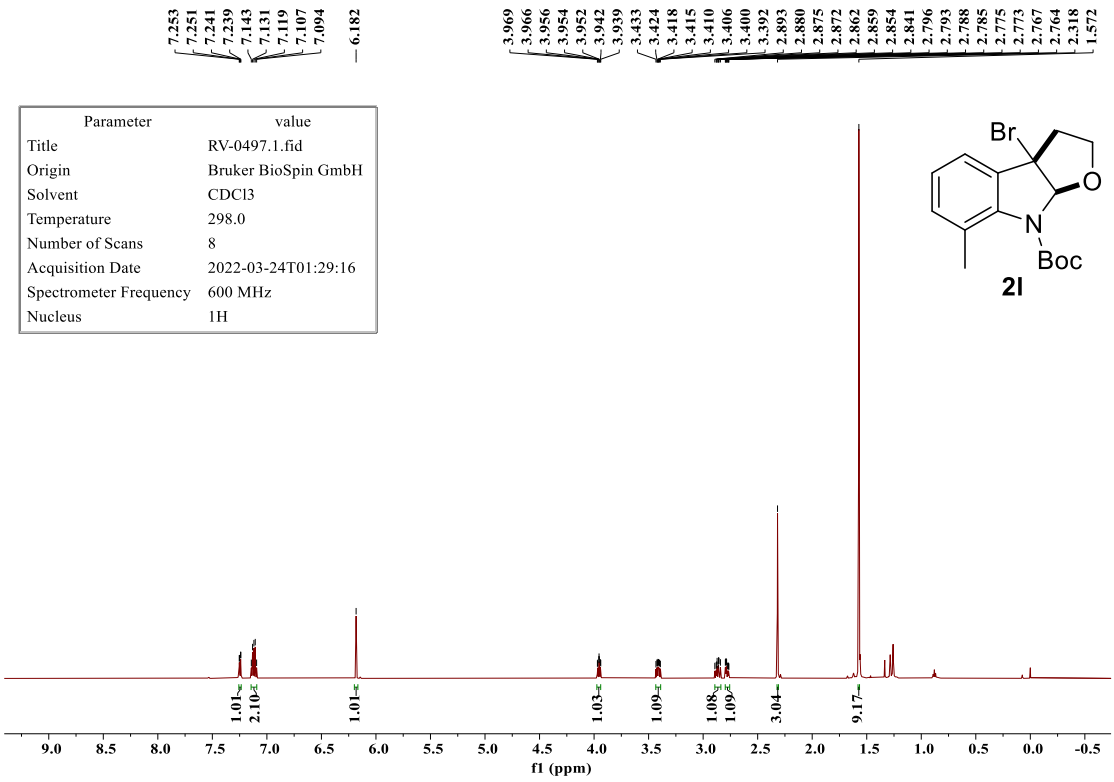
2h




7.782
7.363
7.345
7.231
6.163
4.021
4.007
3.993
3.515
3.494
3.480
3.473
2.900
2.887
2.880
2.867
2.860
2.848
2.773
2.766
2.753
2.745
1.592
Parameter value
Title RV-0545-1.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-05-07T09:01:35
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
Cl
O
N
Boc
2i
0.83
1.06
1.08
1.05
1.00
1.04
1.02
1.03
9.05
f1 (ppm)


7.900
7.316
7.303
7.061
7.058
7.048
7.045
6.173
4.020
4.007
3.993
3.510
3.502
3.495
3.491
3.487
3.484
3.476
3.468
2.904
2.891
2.884
2.871
2.864
2.851
2.770
2.762
2.749
2.741
1.601
Parameter value
Title RV-0620-1.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-07-28T22:58:00
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
O
Cl
N
Boc
2j
0.80
0.98
0.98
0.95
1.02
1.00
0.99
1.01
9.57
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


7.592
7.349
7.340
7.335
7.326
6.785
6.781
6.771
6.767
6.756
6.752
6.189
4.020
4.006
3.992
3.517
3.508
3.497
3.483
3.476
2.908
2.896
2.888
2.876
2.868
2.856
2.781
2.773
2.760
2.752
1.601
Parameters
Parameter value
Title Ra-762.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-08-05T00:43:10
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
O
F
N
Boc
2k
0.64
1.08
1.05
1.00
1.09
1.10
1.15
1.09
9.25
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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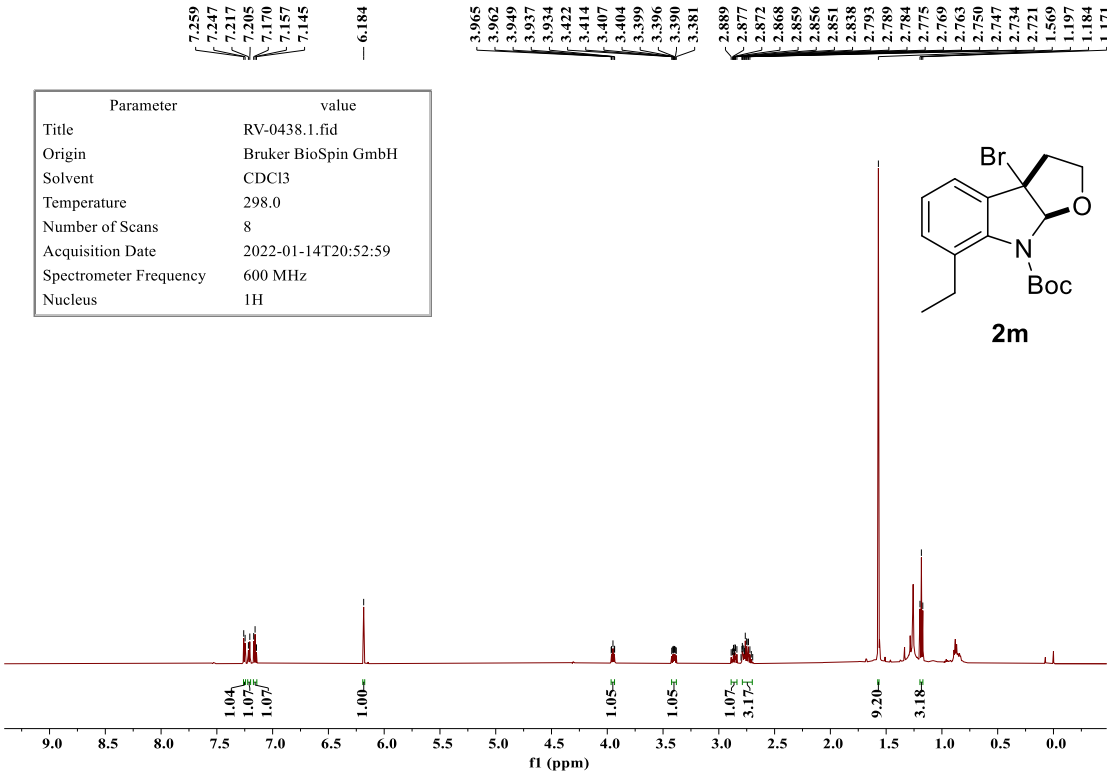
7.241
7.239
7.143
7.131
7.119
7.107
7.094
6.182
3.969
3.966
3.956
3.954
3.952
3.942
3.939
3.433
3.424
3.418
3.415
3.410
3.406
3.400
3.392
2.893
2.880
2.875
2.872
2.862
2.859
2.854
2.841
2.796
2.793
2.788
2.785
2.775
2.773
2.767
2.764
2.318
1.572
Parameter value
Title RV-0497.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-03-24T01:29:16
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
O
N
Boc
2l
1.01
2.10
1.01
1.03
1.09
1.08
1.09
3.04
9.17
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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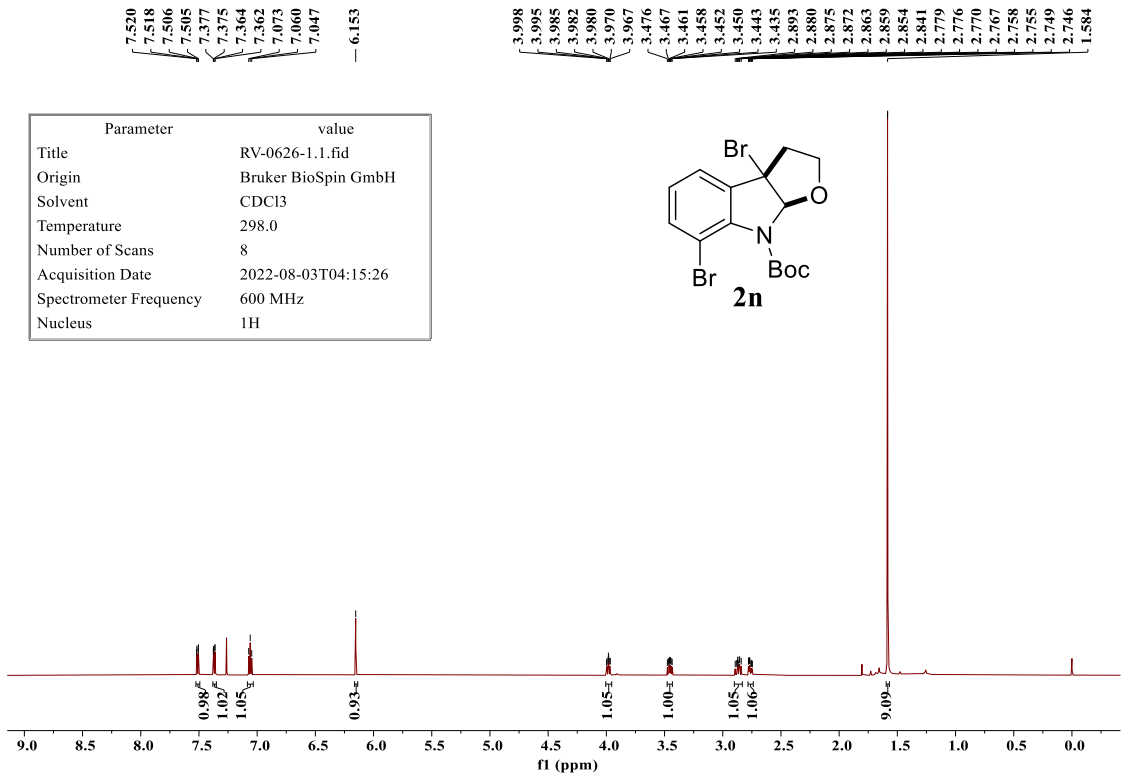
7.247
7.217
7.205
7.170
7.157
7.145
6.184
3.965
3.962
3.949
3.937
3.934
3.422
3.414
3.407
3.404
3.399
3.396
3.390
3.381
2.889
2.877
2.872
2.868
2.859
2.856
2.851
2.838
2.793
2.789
2.784
2.775
2.769
2.763
2.750
2.747
2.734
2.721
1.569
1.197
1.184
Parameter value
Title RV-0438.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-01-14T20:52:59
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
O
N
Boc
2m
1.04
1.07
1.07
1.00
1.05
1.05
1.07
3.17
9.20
3.18
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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7.506
7.505
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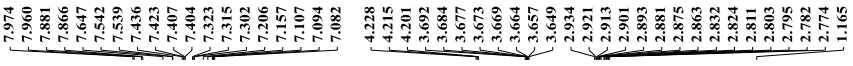
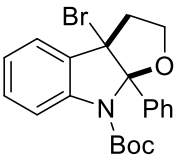
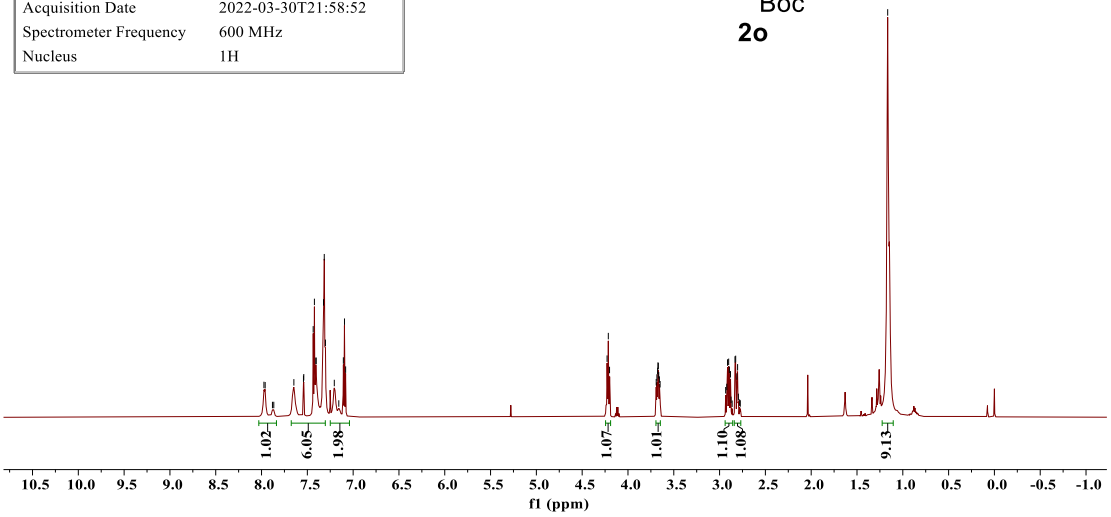
7.375
7.364
7.362
7.073
7.060
7.047
6.153
3.998
3.995
3.985
3.982
3.980
3.970
3.967
3.476
3.467
3.461
3.458
3.452
3.450
3.443
3.435
2.893
2.880
2.875
2.872
2.863
2.859
2.854
2.841
2.779
2.776
2.770
2.767
2.758
2.755
2.749
2.746
1.584
Parameter value
Title RV-0626-1.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-08-03T04:15:26
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
O
N
Boc
Br
2n
0.98
1.02
1.05
0.93
1.05
1.00
1.05
1.06
9.09
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

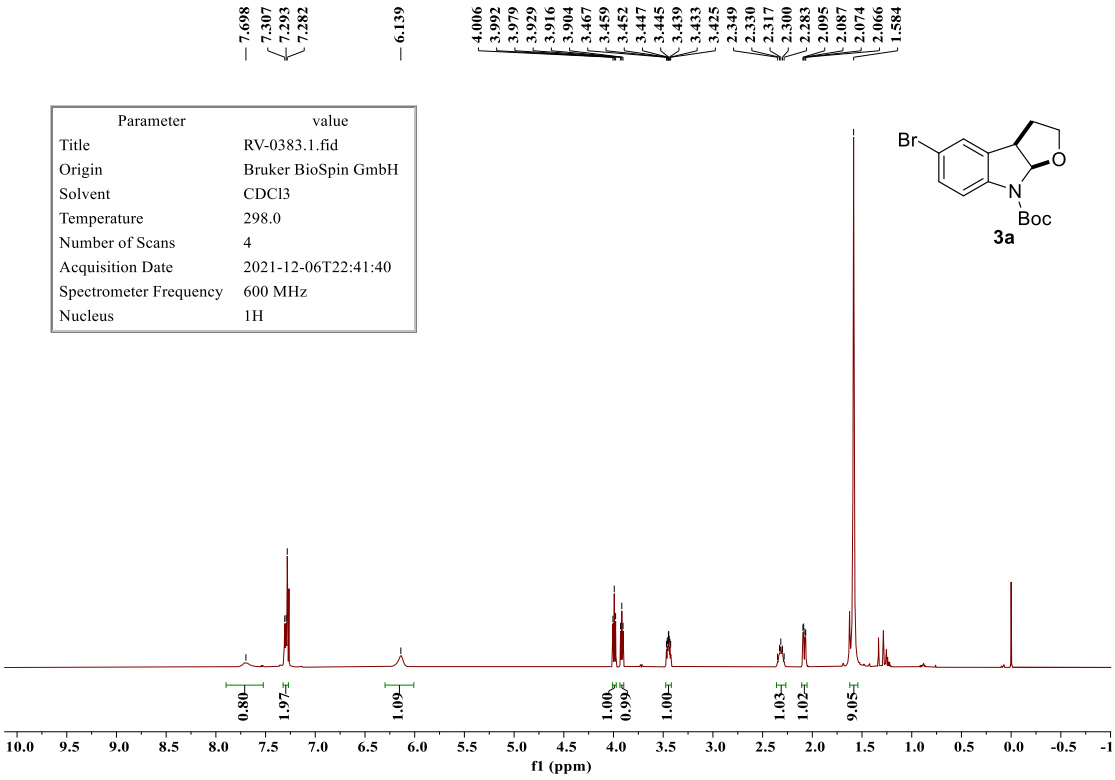


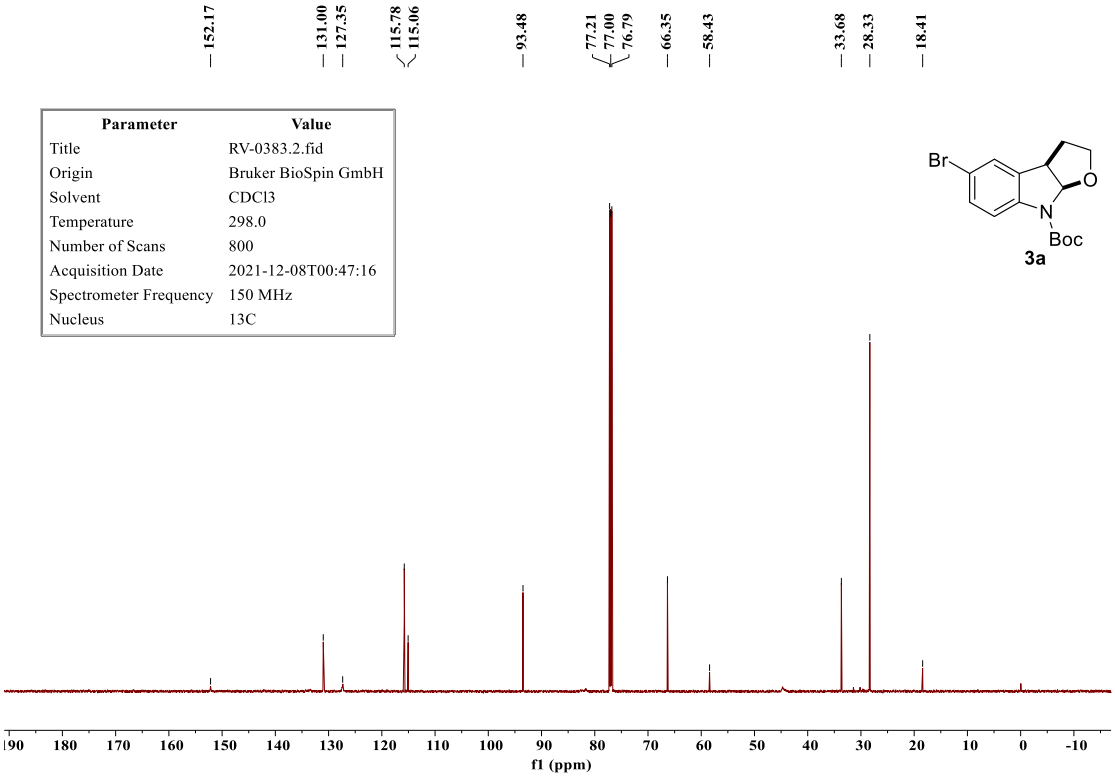
Parameter	value
Title	RV-0507.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	8
Acquisition Date	2022-03-30T21:58:52
Spectrometer Frequency	600 MHz
Nucleus	1H

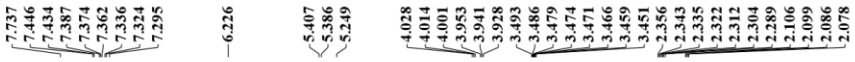


2o

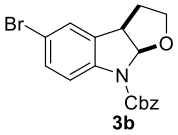



7.698
7.307
7.293
7.282
6.139
4.006
3.992
3.979
3.929
3.916
3.904
3.467
3.459
3.452
3.447
3.445
3.439
3.433
3.425
2.349
2.330
2.317
2.300
2.283
2.095
2.087
2.074
2.066
1.584
Parameter value
Title RV-0383.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 4
Acquisition Date 2021-12-06T22:41:40
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
O
N
Boc
3a
0.80
1.97
1.09
1.00
0.99
1.00
1.03
1.02
9.05
f1 (ppm)

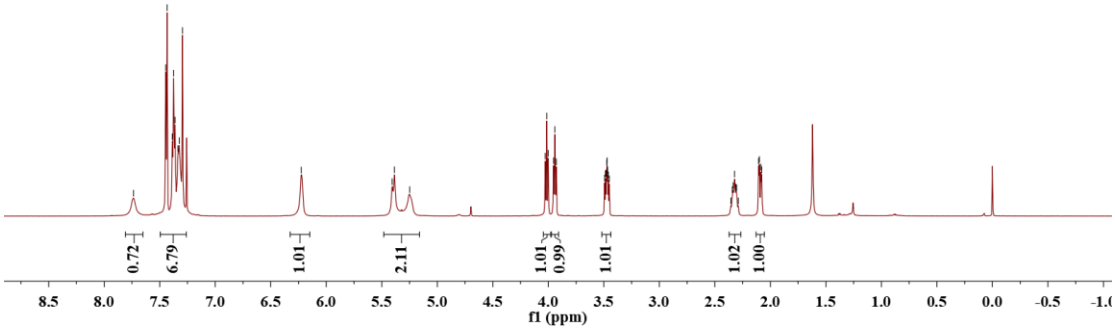

152.17
131.00
127.35
115.78
115.06
93.48
77.21
77.00
76.79
66.35
58.43
33.68
28.33
18.41
Parameter Value
Title RV-0383.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 800
Acquisition Date 2021-12-08T00:47:16
Spectrometer Frequency 150 MHz
Nucleus 13C
Br
O
N
Boc
3a
f1 (ppm)



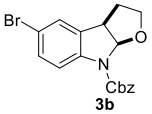
Parameter	value
Title	rv-0561-2.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	8
Acquisition Date	2022-06-02T14:30:32
Spectrometer Frequency	600 MHZ
Nucleus	1H



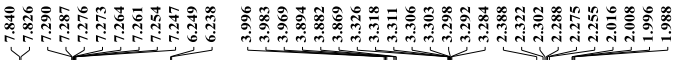
3b



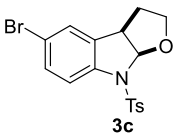
Parameter	value
Title	rv-0561-2.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	800
Acquisition Date	2022-06-02T15:32:29
Spectrometer Frequency	150 MHZ
Nucleus	13C



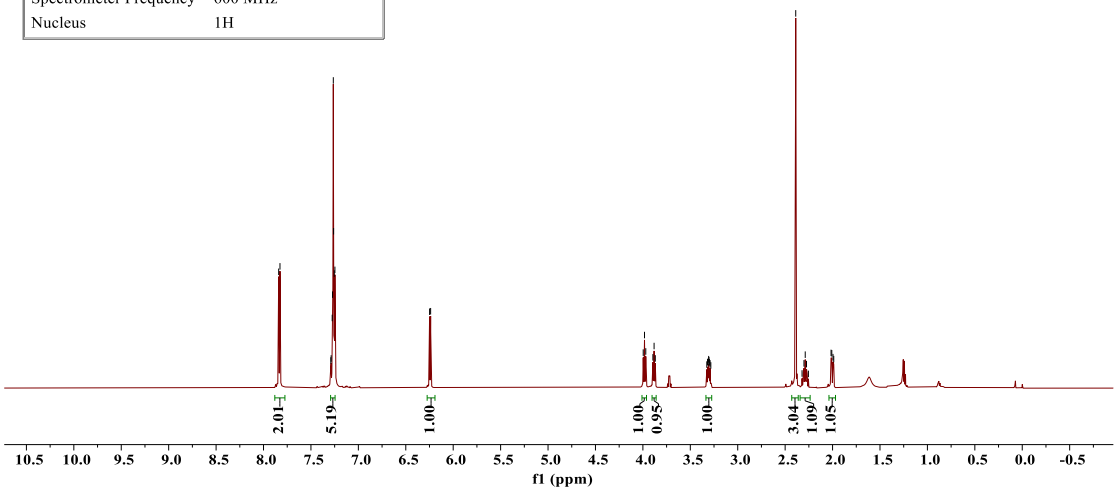
3b

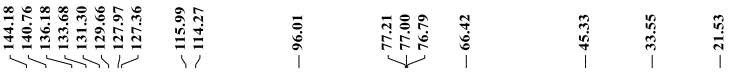


Parameter	value
Title	RV-0556-2.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	8
Acquisition Date	2022-05-24T04:18:22
Spectrometer Frequency	600 MHz
Nucleus	1H

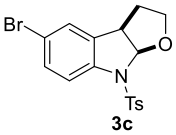


3c

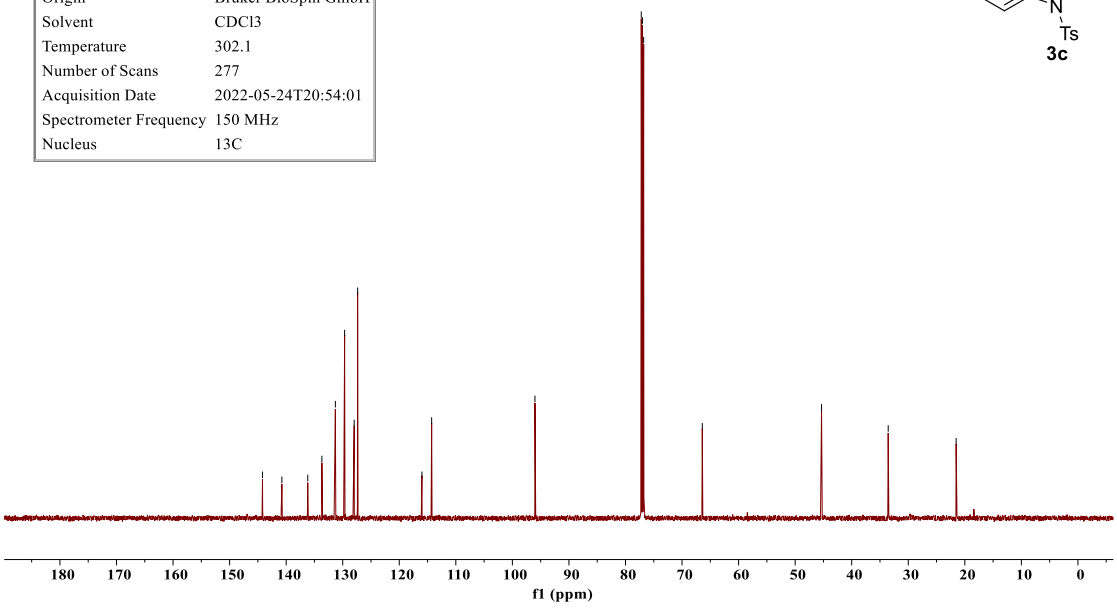


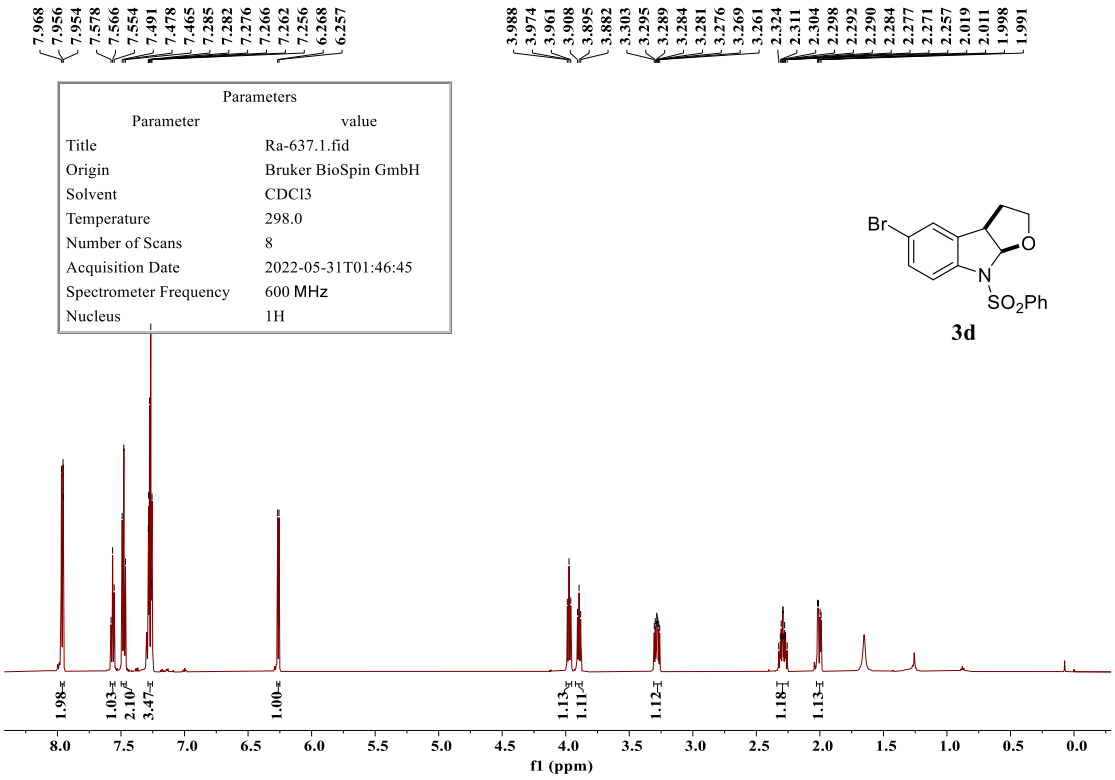


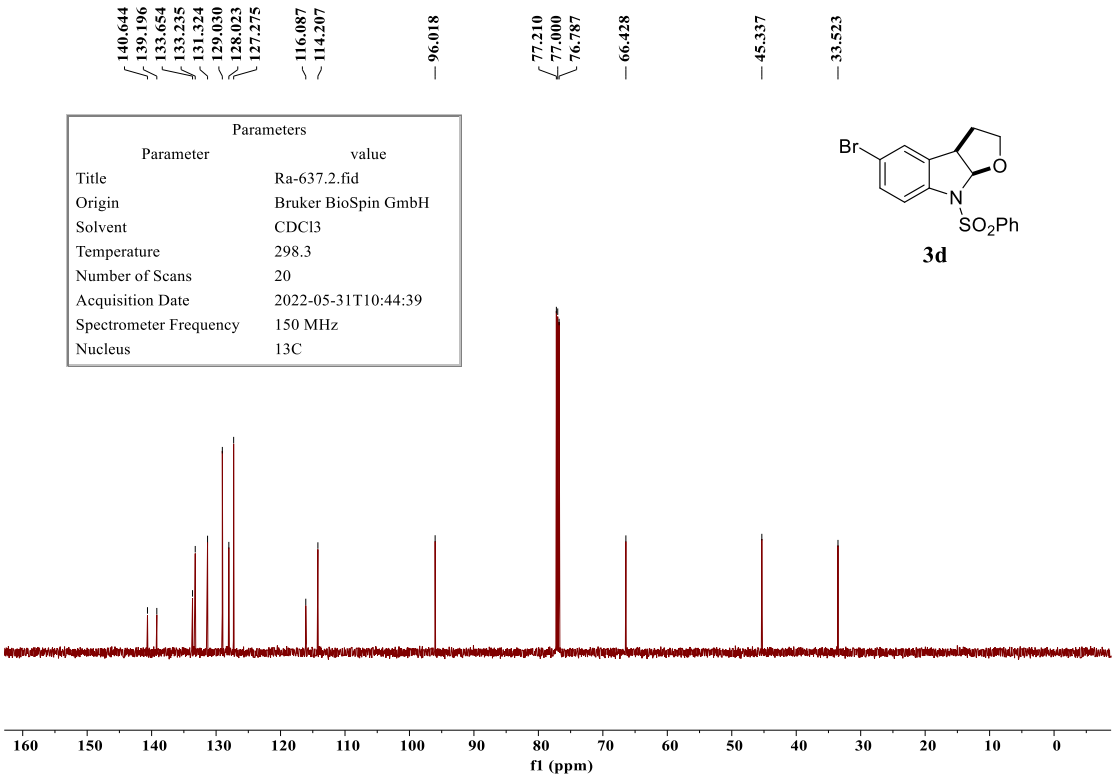
Parameter	value
Title	RV-0556-2.3.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	302.1
Number of Scans	277
Acquisition Date	2022-05-24T20:54:01
Spectrometer Frequency	150 MHz
Nucleus	13C

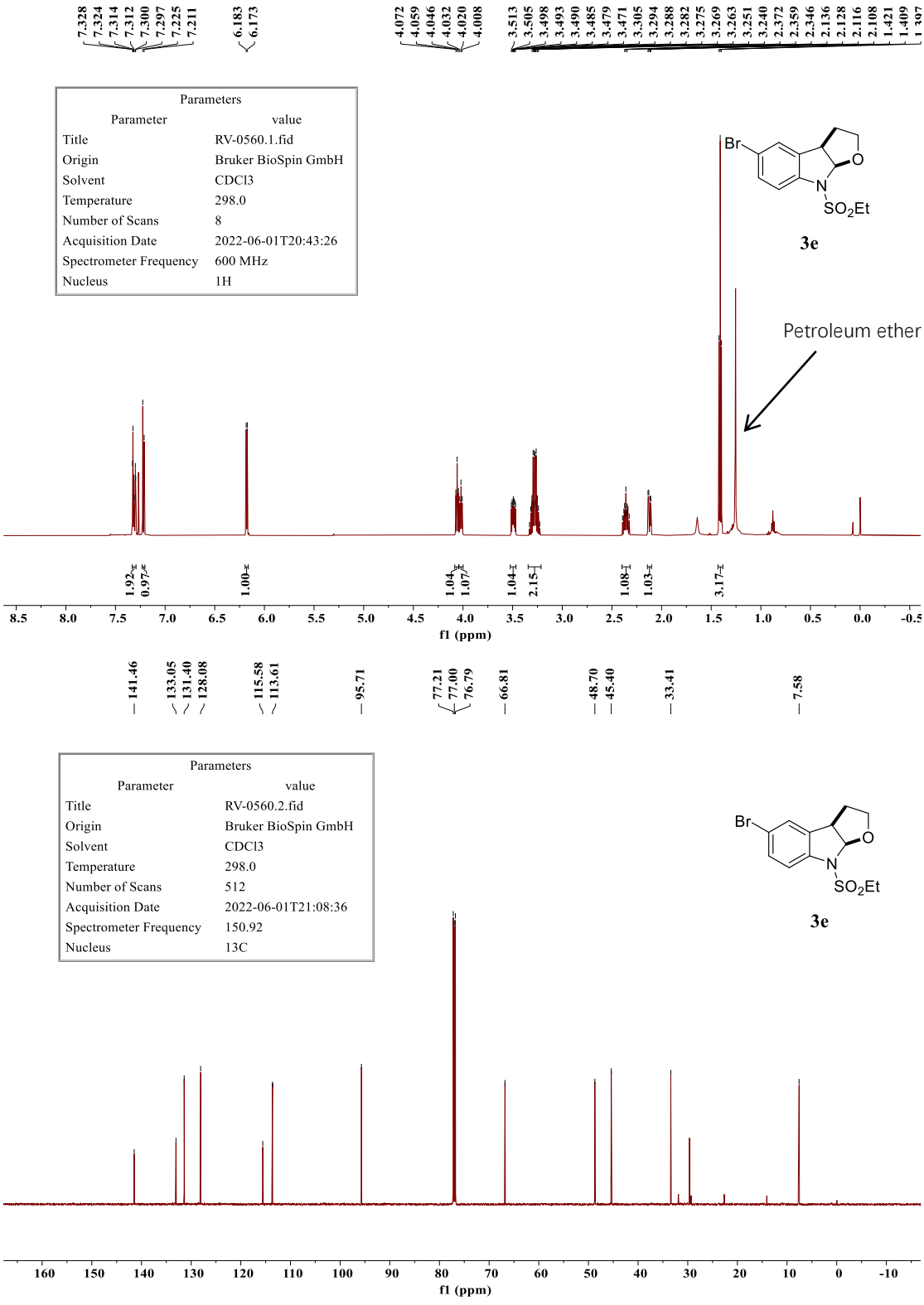


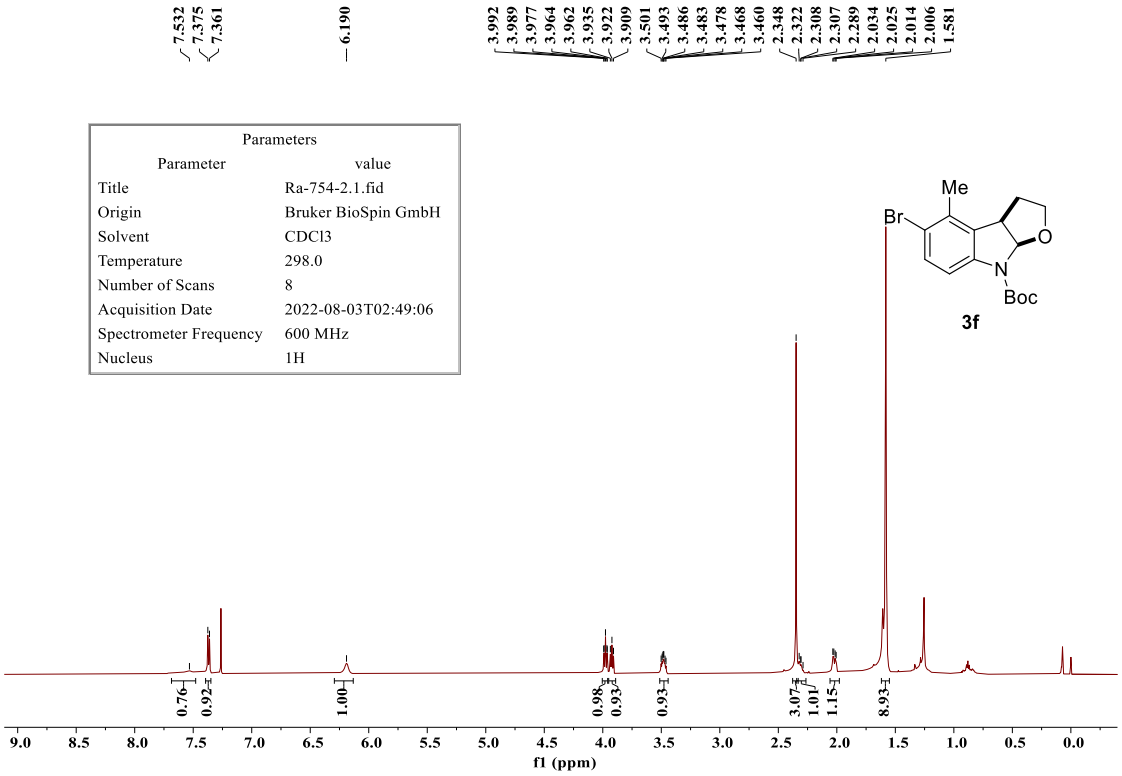
3c

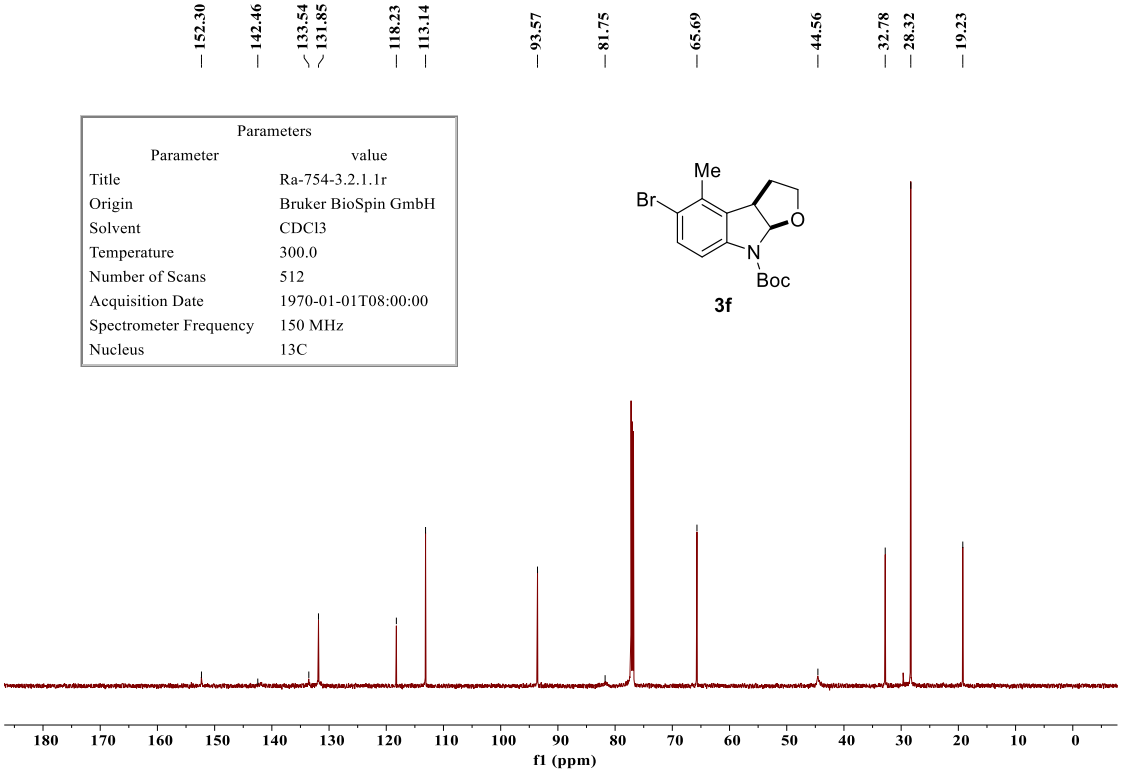


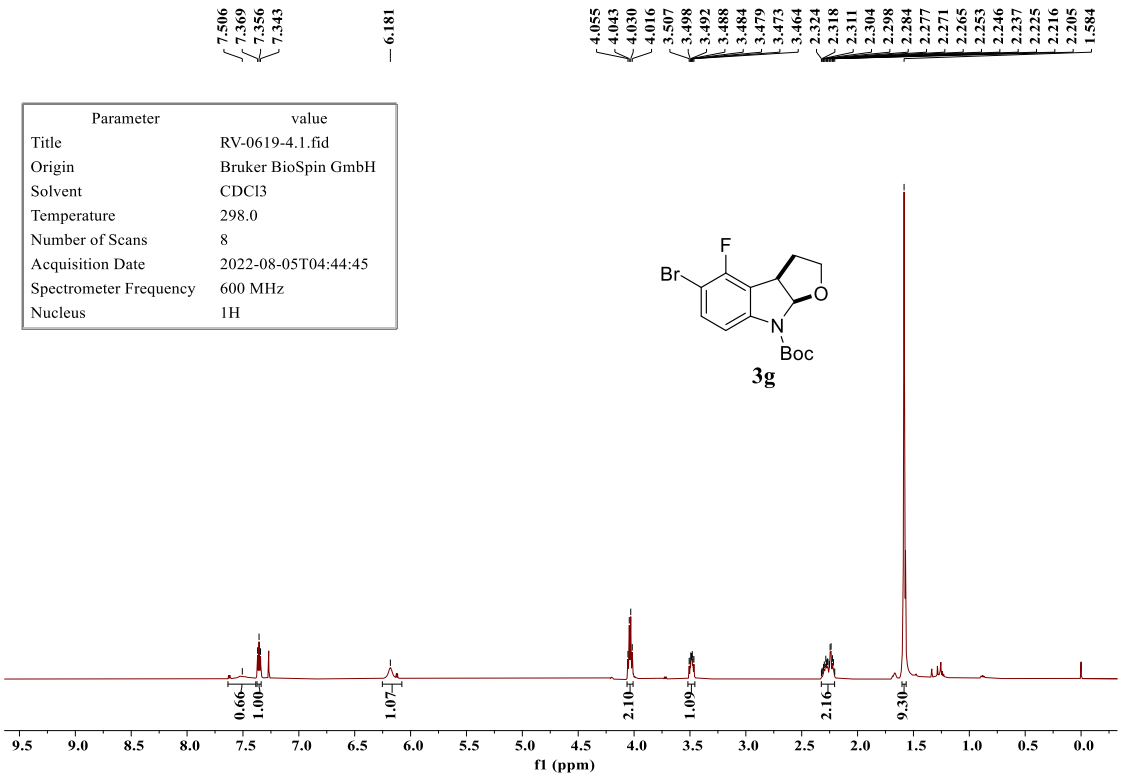

7.968
7.956
7.954
7.578
7.566
7.554
7.491
7.478
7.465
7.285
7.282
7.276
7.266
7.262
7.256
6.268
6.257
3.988
3.974
3.961
3.908
3.895
3.882
3.303
3.295
3.289
3.284
3.281
3.276
3.269
3.261
2.324
2.311
2.304
2.298
2.292
2.290
2.284
2.277
2.271
2.257
2.019
2.011
1.998
1.991
Parameters
Parameter value
Title Ra-637.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-05-31T01:46:45
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
O
N
SO2Ph
3d
1.98
1.03
2.10
3.47
1.00
1.13
1.11
1.12
1.18
1.13
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


140.644
139.196
133.654
133.235
131.324
129.030
128.023
127.275
116.087
114.207
96.018
77.210
77.000
76.787
66.428
45.337
33.523
Parameters
Parameter value
Title Ra-637.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.3
Number of Scans 20
Acquisition Date 2022-05-31T10:44:39
Spectrometer Frequency 150 MHz
Nucleus 13C
Br
O
N
SO2Ph
3d
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.328
7.324
7.314
7.312
7.300
7.297
7.225
7.211
6.183
6.173
4.072
4.059
4.046
4.032
4.020
4.008
3.513
3.505
3.498
3.493
3.490
3.485
3.479
3.471
3.305
3.294
3.288
3.282
3.275
3.269
3.263
3.251
3.240
2.372
2.359
2.346
2.136
2.128
2.116
2.108
1.421
1.409
Parameters
Parameter value
Title RV-0560.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-06-01T20:43:26
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
O
N
SO2Et
3e
Petroleum ether
1.92
0.97
1.00
1.04
1.07
1.04
2.15
1.08
1.03
3.17
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
141.46
133.05
131.40
128.08
115.58
113.61
95.71
77.21
77.00
76.79
66.81
48.70
45.40
33.41
7.58
Parameters
Parameter value
Title RV-0560.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 512
Acquisition Date 2022-06-01T21:08:36
Spectrometer Frequency 150.92
Nucleus 13C
Br
O
N
SO2Et
3e
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

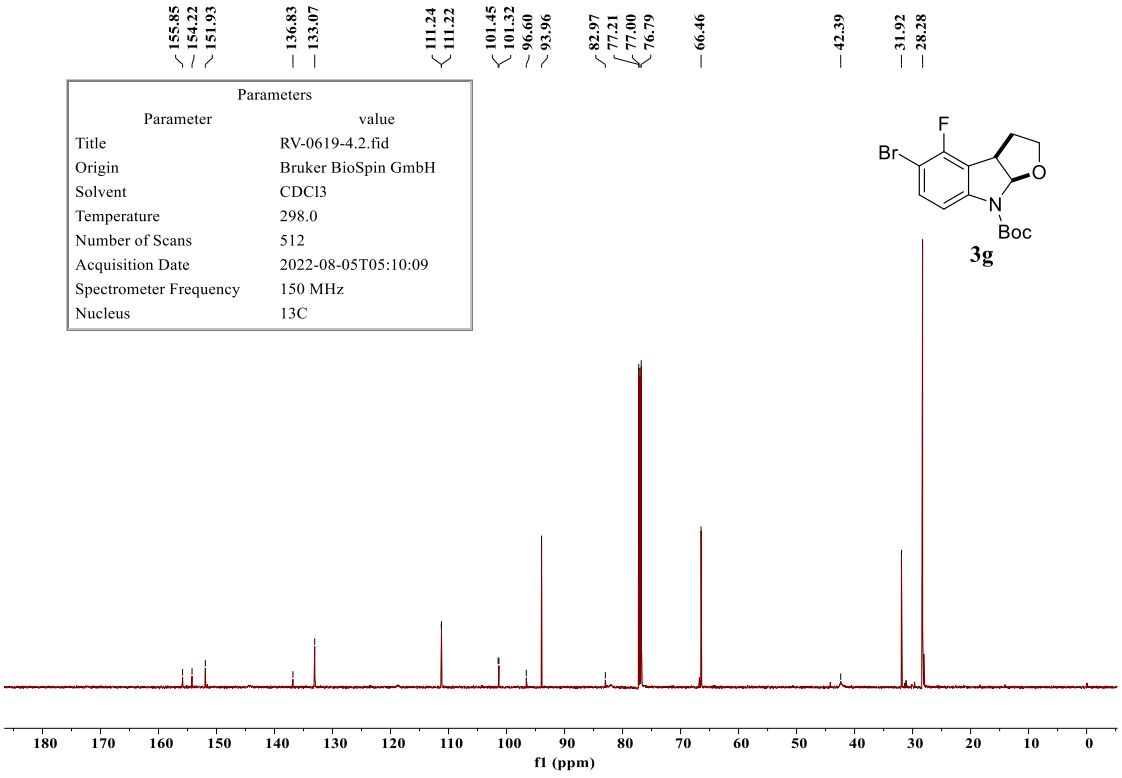

7.532
7.375
7.361
6.190
3.992
3.989
3.977
3.964
3.962
3.935
3.922
3.909
3.501
3.493
3.486
3.483
3.478
3.468
3.460
2.348
2.322
2.308
2.307
2.289
2.034
2.025
2.014
2.006
1.581
Parameters
Parameter value
Title Ra-754-2.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-08-03T02:49:06
Spectrometer Frequency 600 MHz
Nucleus 1H
Me
Br
O
N
Boc
3f
0.76
0.92
1.00
0.98
0.93
0.93
3.07
1.01
1.15
8.93
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


152.30
142.46
133.54
131.85
118.23
113.14
93.57
81.75
65.69
44.56
32.78
28.32
19.23
Parameters
Parameter value
Title Ra-754-3.2.1.1r
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 300.0
Number of Scans 512
Acquisition Date 1970-01-01T08:00:00
Spectrometer Frequency 150 MHz
Nucleus 13C
Me
Br
O
N
Boc
3f
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



Parameter	value
Title	RV-0619-4.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	8
Acquisition Date	2022-08-05T04:44:45
Spectrometer Frequency	600 MHz
Nucleus	1H

3g

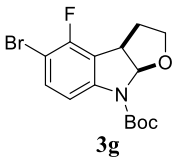


Parameters

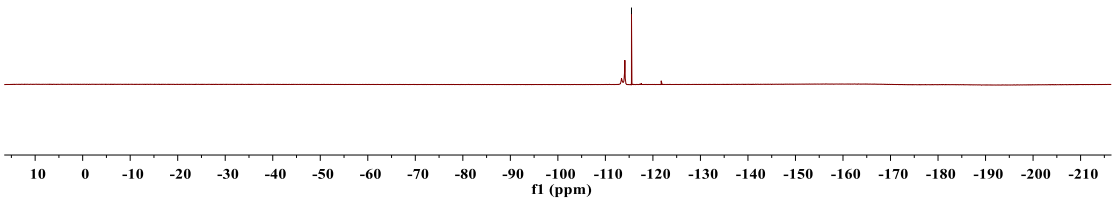
Parameter	value
Title	RV-0619-4.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	512
Acquisition Date	2022-08-05T05:10:09
Spectrometer Frequency	150 MHz
Nucleus	13C

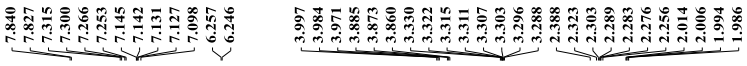
3g

Parameters	
Parameter	value
Title	RV-0619-4.3.fid
Origin	Bruker BioSpin GmbH
Instrument	Avance
Solvent	CDCl3
Number of Scans	16
Acquisition Time	0.4981
Spectrometer Frequency	565MHZ
Nucleus	19F

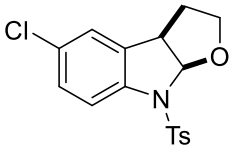


3g

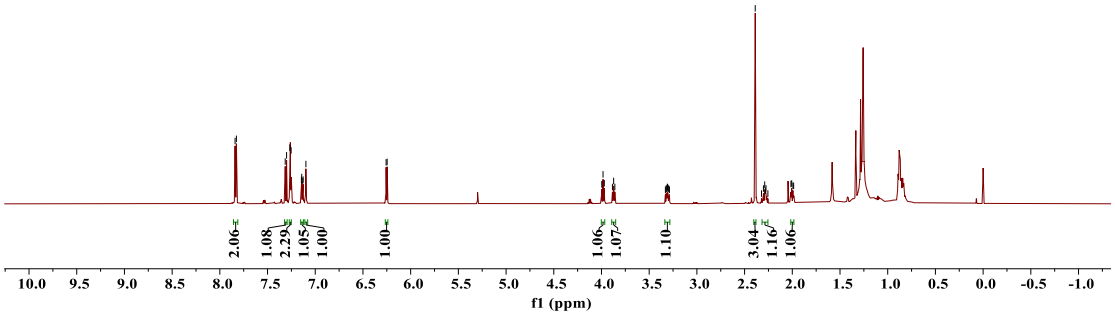


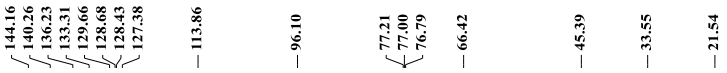


Parameter	value
Title	RV-0460.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.2
Number of Scans	8
Acquisition Date	2022-02-21T21:14:21
Spectrometer Frequency	600 MHz
Nucleus	1H

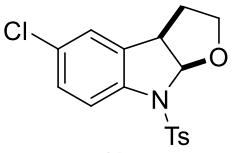


3h

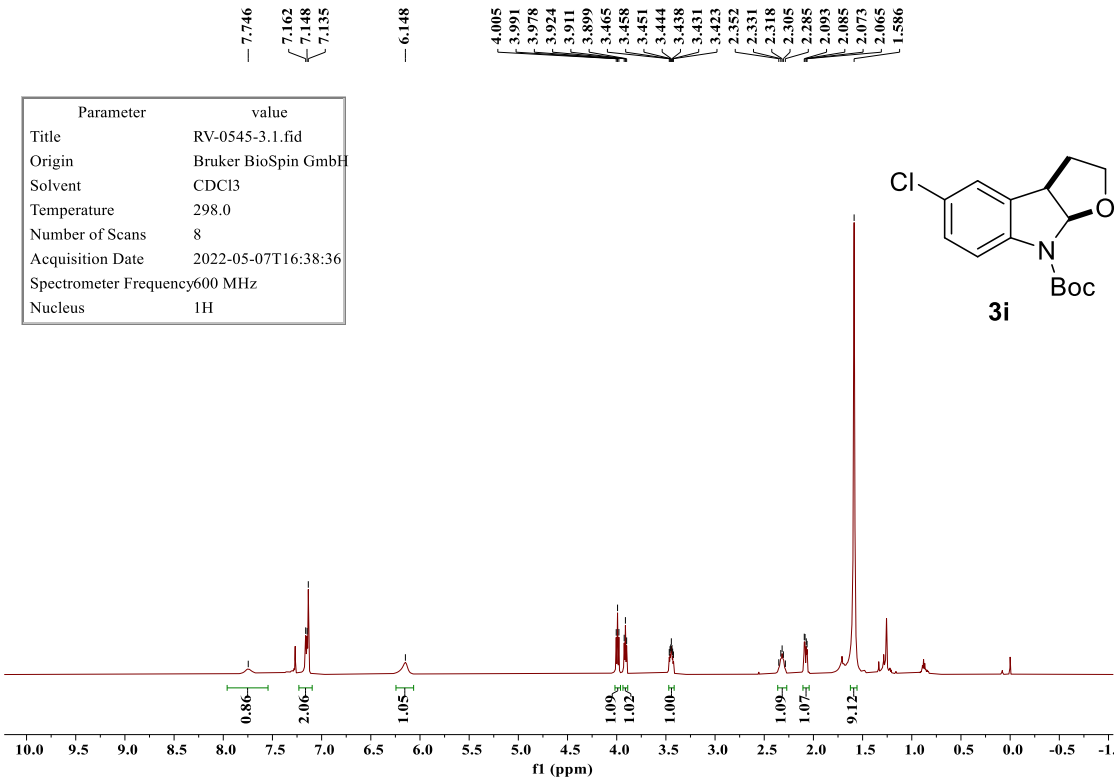


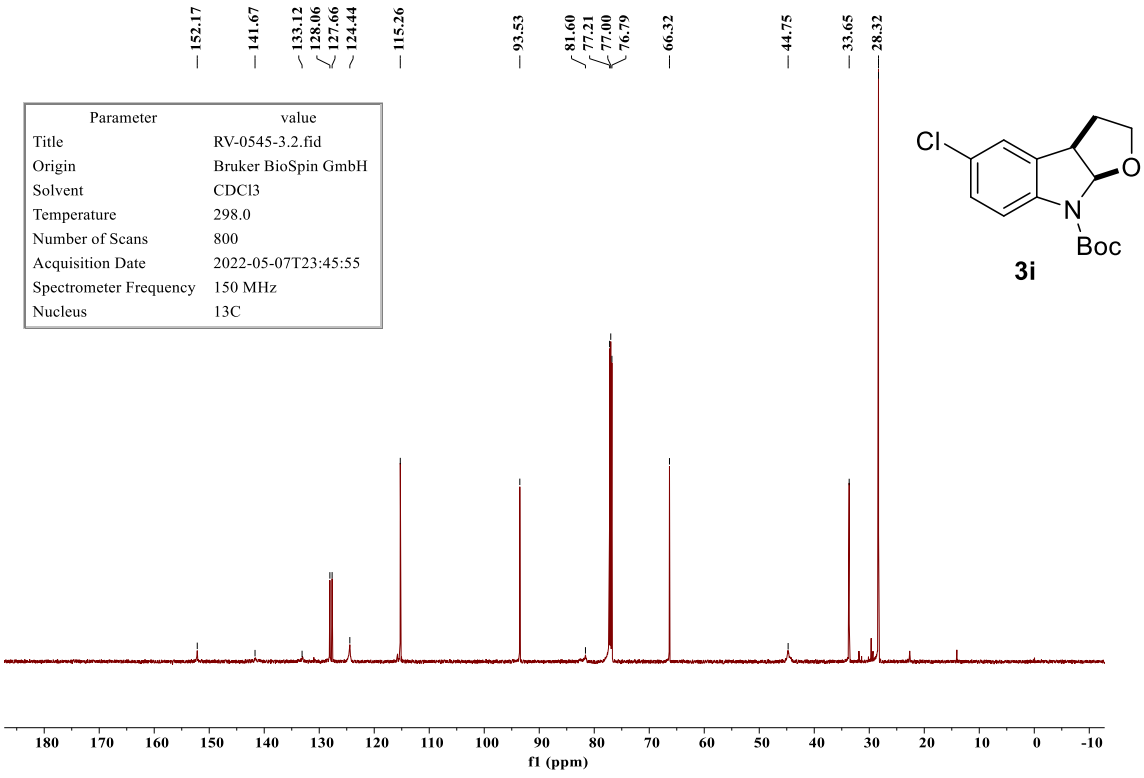


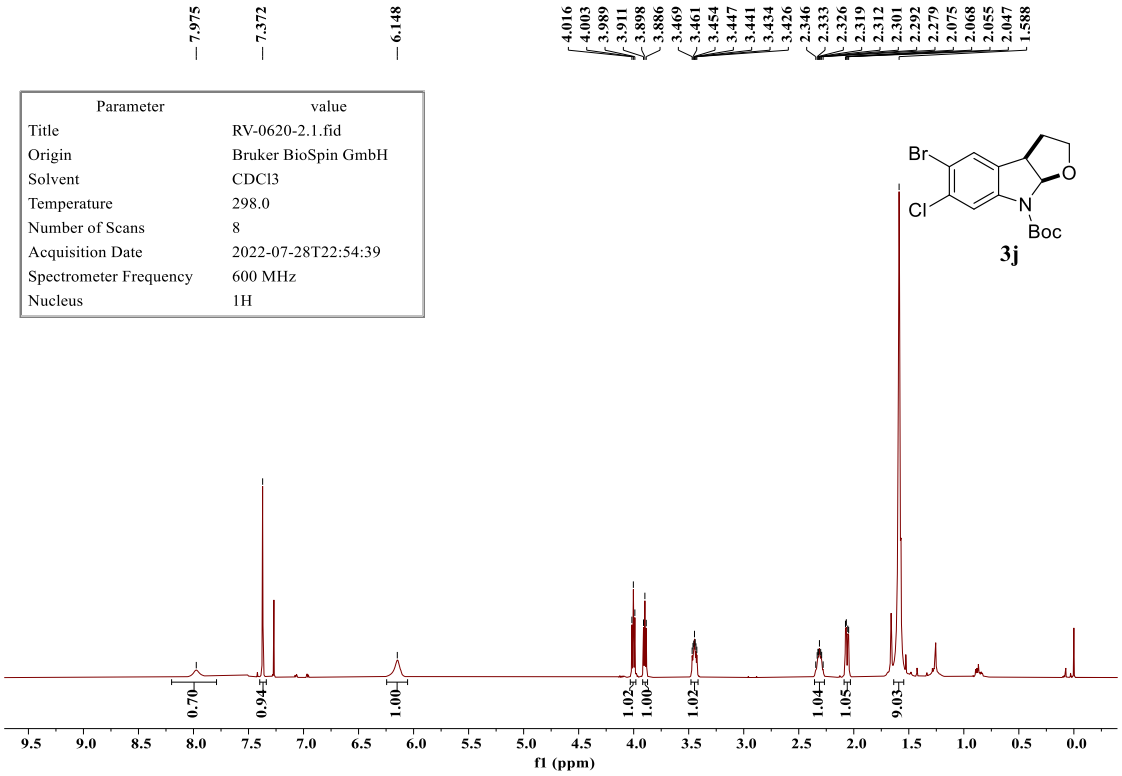
Parameter	value
Title	RV-0460.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.1
Number of Scans	800
Acquisition Date	2022-02-23T09:18:36
Spectrometer Frequency	150 MHz
Nucleus	13C

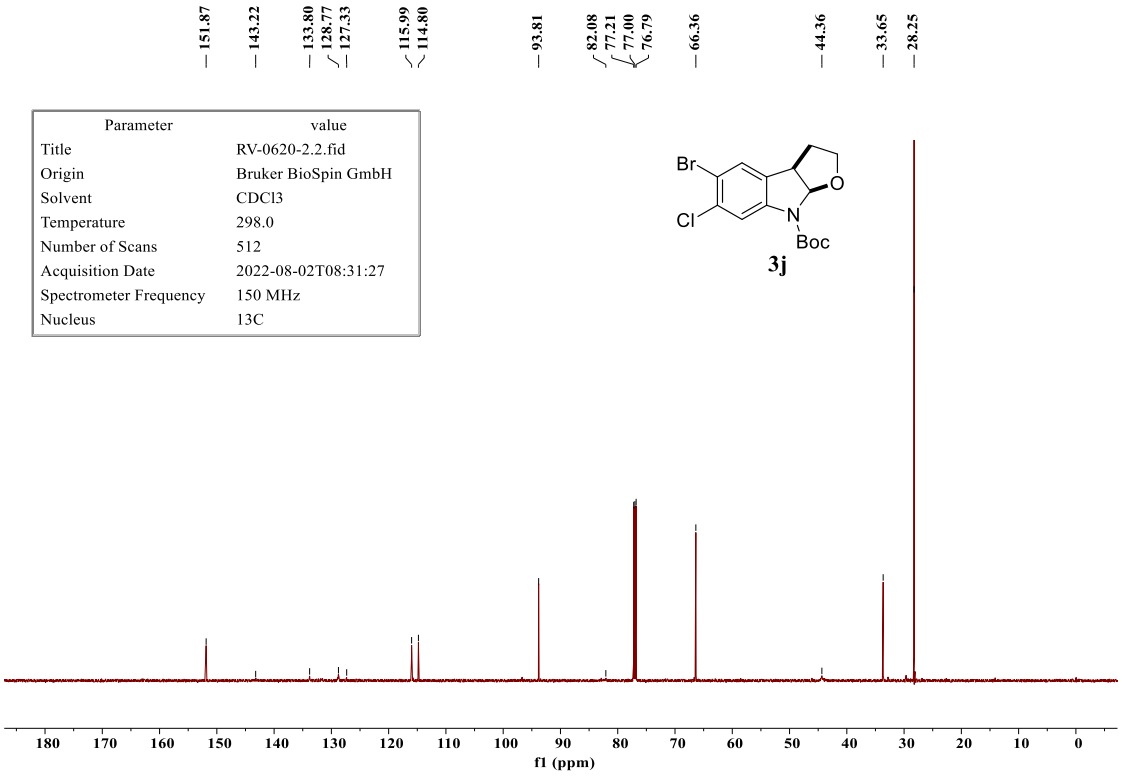


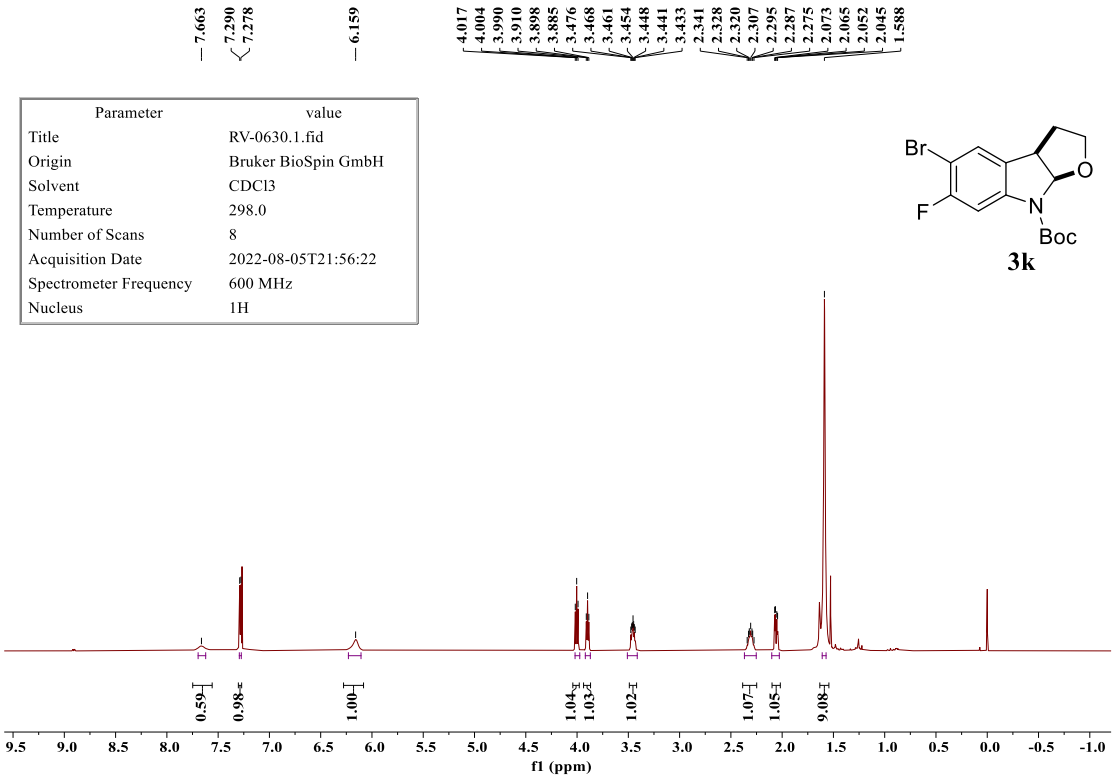
3h

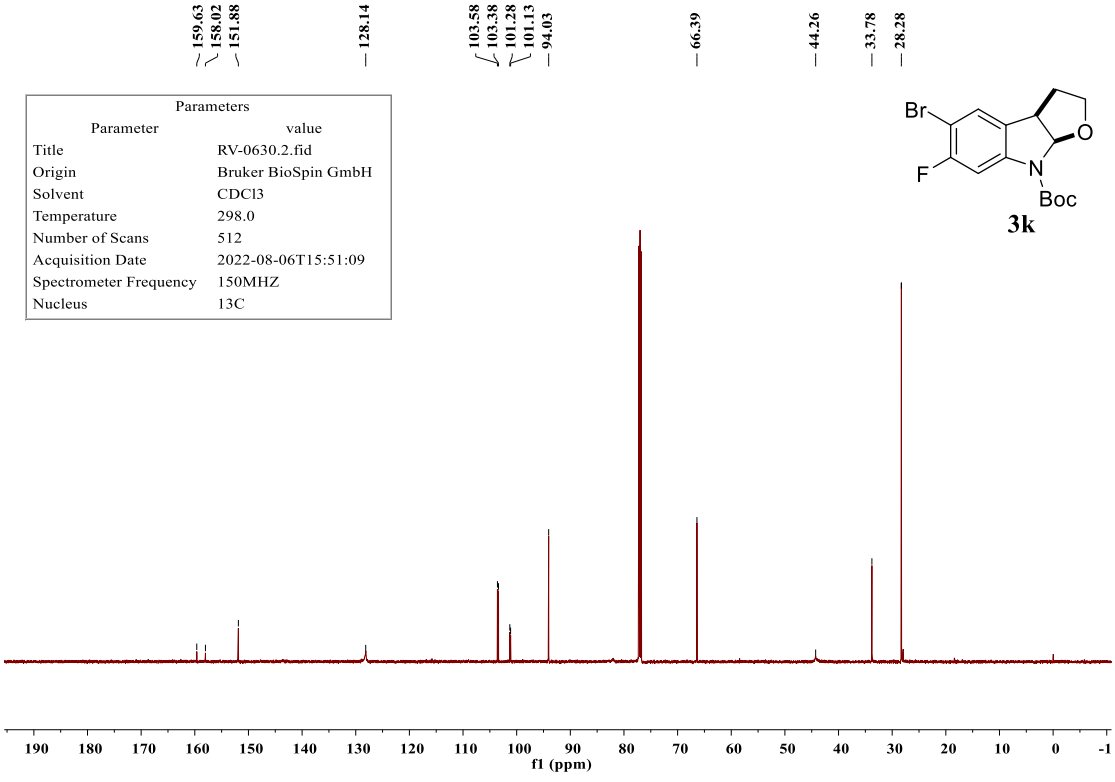

7.746
7.162
7.148
7.135
6.148
4.005
3.991
3.978
3.924
3.911
3.899
3.465
3.458
3.451
3.444
3.438
3.431
3.423
2.352
2.331
2.318
2.305
2.285
2.093
2.085
2.073
2.065
1.586
Parameter value
Title RV-0545-3.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-05-07T16:38:36
Spectrometer Frequency 600 MHz
Nucleus 1H
Cl
O
N
Boc
3i
0.86
2.06
1.05
1.09
1.02
1.00
1.09
1.07
9.12
f1 (ppm)


152.17
141.67
133.12
128.06
127.66
124.44
115.26
93.53
81.60
77.21
77.00
76.79
66.32
44.75
33.65
28.32
Parameter value
Title RV-0545-3.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 800
Acquisition Date 2022-05-07T23:45:55
Spectrometer Frequency 150 MHz
Nucleus 13C
Cl
O
N
Boc
3i
f1 (ppm)

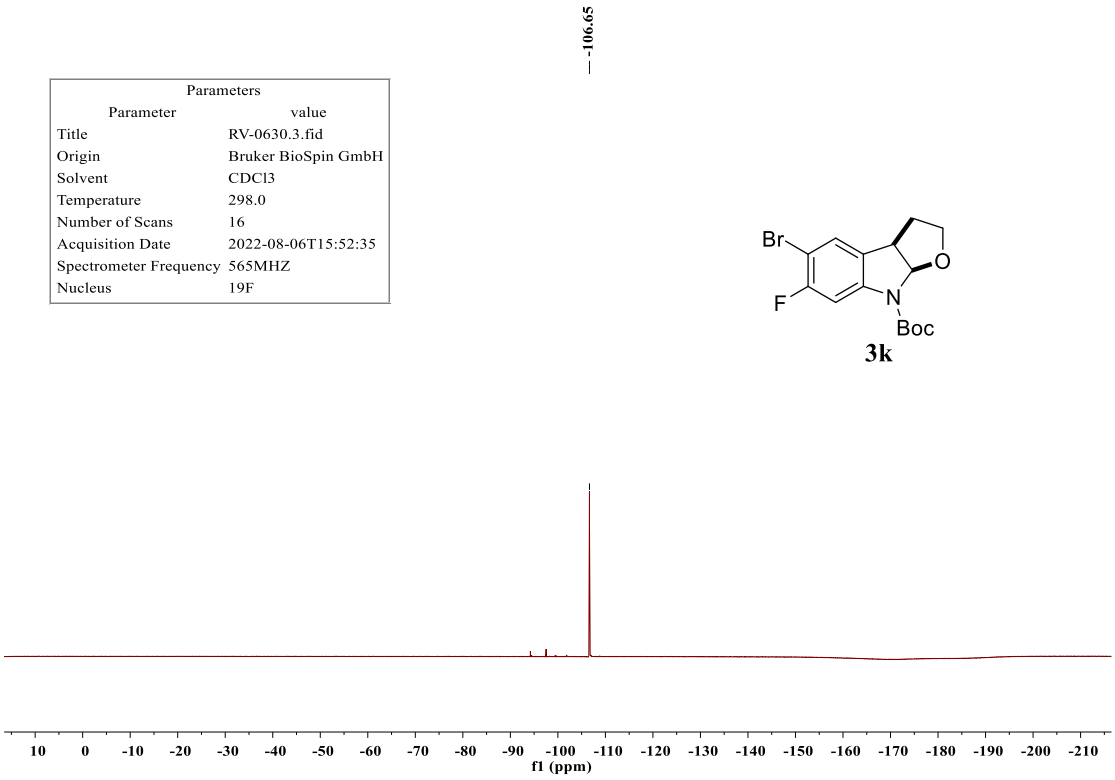

7.975
7.372
6.148
4.016
4.003
3.989
3.911
3.898
3.886
3.469
3.461
3.454
3.447
3.441
3.434
3.426
2.346
2.333
2.326
2.319
2.312
2.301
2.292
2.279
2.075
2.068
2.055
2.047
1.588
Parameter value
Title RV-0620-2.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-07-28T22:54:39
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
Cl
O
N
Boc
3j
0.70
0.94
1.00
1.02
1.00
1.02
1.04
1.05
9.03
f1 (ppm)


151.87
143.22
133.80
128.77
127.33
115.99
114.80
93.81
82.08
77.21
77.00
76.79
66.36
44.36
33.65
28.25
Parameter value
Title RV-0620-2.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 512
Acquisition Date 2022-08-02T08:31:27
Spectrometer Frequency 150 MHz
Nucleus 13C
Br
Cl
O
N
Boc
3j
f1 (ppm)


7.663
7.290
7.278
6.159
4.017
4.004
3.990
3.910
3.898
3.885
3.476
3.468
3.461
3.454
3.448
3.441
3.433
2.341
2.328
2.320
2.307
2.295
2.287
2.275
2.073
2.065
2.052
2.045
1.588
Parameter value
Title RV-0630.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-08-05T21:56:22
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
F
O
N
Boc
3k
0.59
0.98
1.00
1.04
1.03
1.02
1.07
1.05
9.08
f1 (ppm)

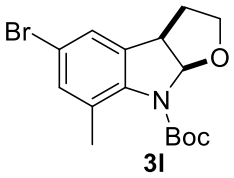

159.63
158.02
151.88
128.14
103.58
103.38
101.28
101.13
94.03
66.39
44.26
33.78
28.28
Parameters
Parameter value
Title RV-0630.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 512
Acquisition Date 2022-08-06T15:51:09
Spectrometer Frequency 150MHZ
Nucleus 13C
Br
F
O
N
Boc
3k
f1 (ppm)

Parameters	
Parameter	value
Title	RV-0630.3.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	16
Acquisition Date	2022-08-06T15:52:35
Spectrometer Frequency	565MHZ
Nucleus	19F



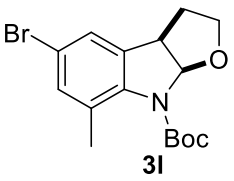
3k

Parameter	value
Title	RV-0558.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	8
Acquisition Date	2022-05-30T10:16:57
Spectrometer Frequency	600 MHZ
Nucleus	1H

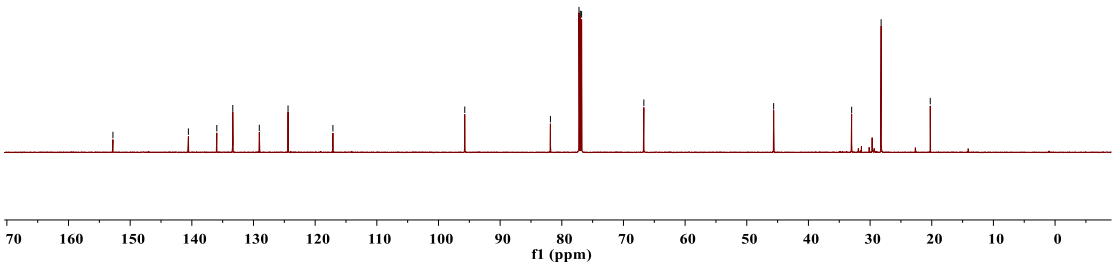


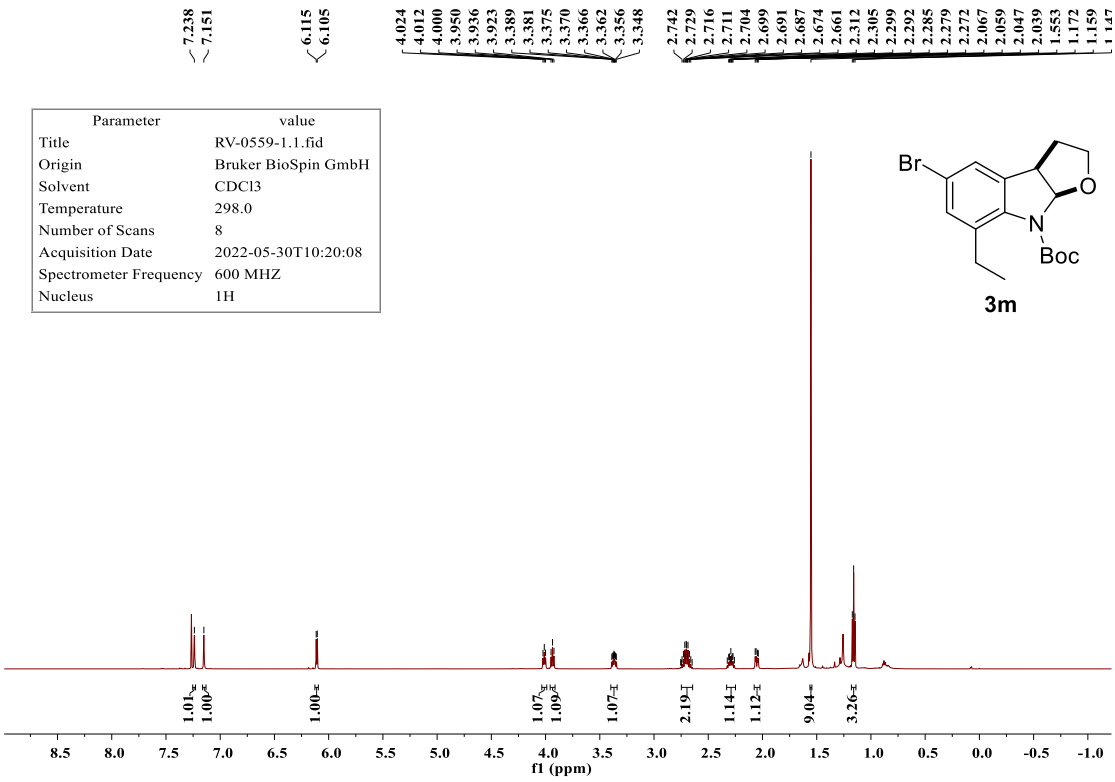
3l

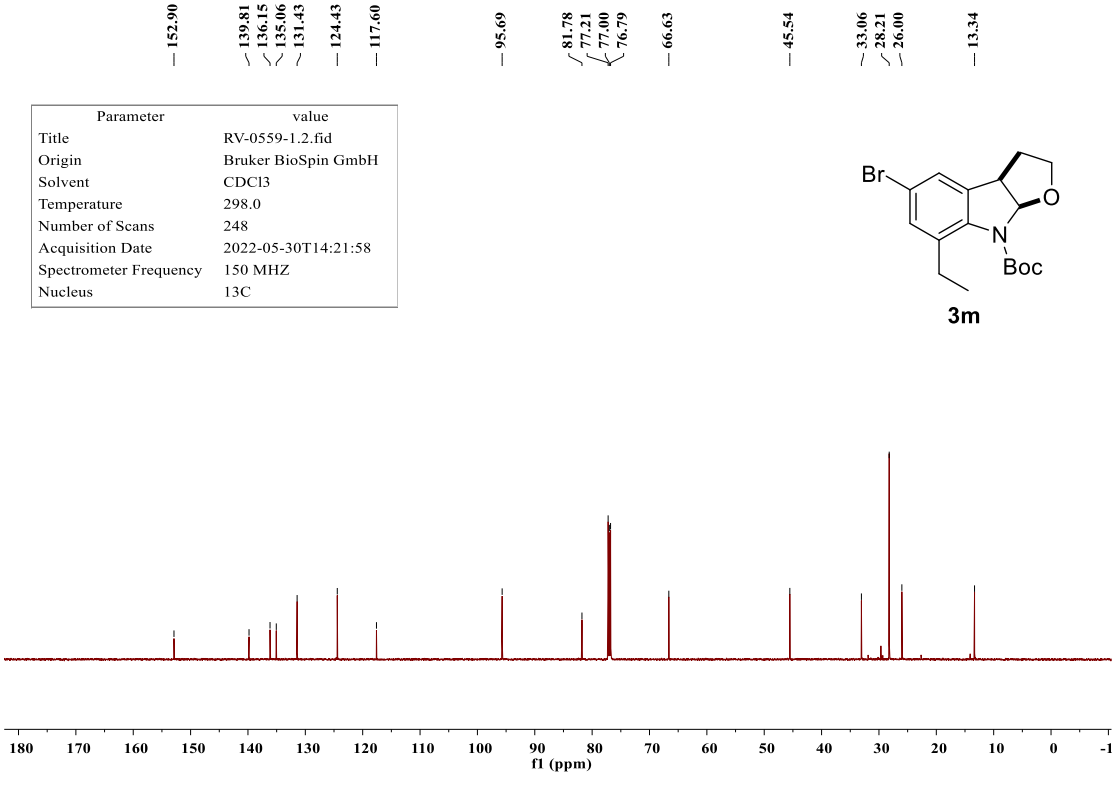
Parameter	value
Title	RV-0558.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	800
Acquisition Date	2022-05-30T14:06:56
Spectrometer Frequency	150 MHZ
Nucleus	13C

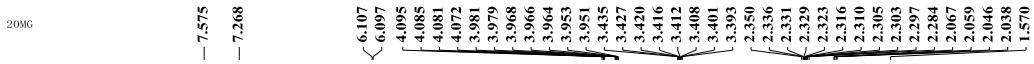


3l

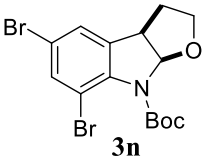



7.238
7.151
6.115
6.105
4.024
4.012
4.000
3.950
3.936
3.923
3.389
3.381
3.375
3.370
3.366
3.362
3.356
3.348
2.742
2.729
2.716
2.711
2.704
2.699
2.691
2.687
2.674
2.661
2.312
2.305
2.299
2.292
2.285
2.279
2.272
2.067
2.059
2.047
2.039
1.553
1.172
1.159
1.147
Parameter value
Title RV-0559-1.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-05-30T10:20:08
Spectrometer Frequency 600 MHZ
Nucleus 1H
Br
O
N
Boc
3m
1.01
1.00
1.00
1.07
1.09
1.07
2.19
1.14
1.12
9.04
3.26
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


152.90
139.81
136.15
135.06
131.43
124.43
117.60
95.69
81.78
77.21
77.00
76.79
66.63
45.54
33.06
28.21
26.00
13.34
Parameter value
Title RV-0559-1.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 248
Acquisition Date 2022-05-30T14:21:58
Spectrometer Frequency 150 MHZ
Nucleus 13C
Br
O
N
Boc
3m
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

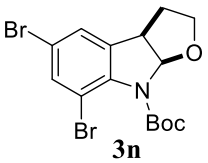


Parameter	value
Title	Rv-0626-3.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	8
Acquisition Date	2022-08-05T22:18:44
Spectrometer Frequency	600 MHz
Nucleus	1H

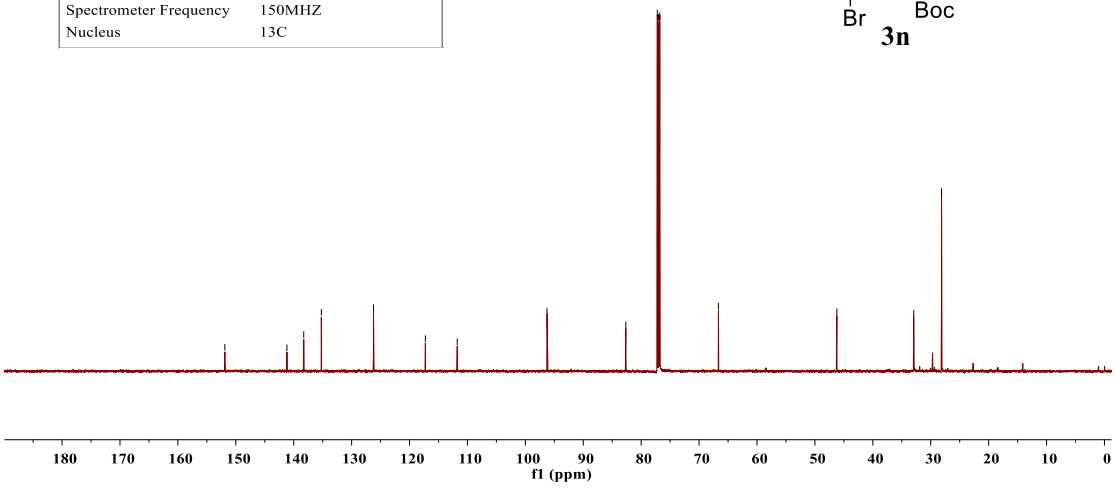


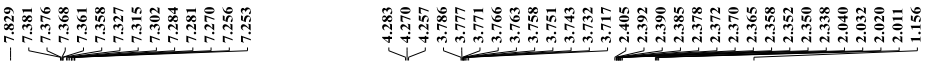
3n

Parameters	
Parameter	value
Title	Ra-0626-3.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	512
Acquisition Date	2022-08-06T16:19:56
Spectrometer Frequency	150MHZ
Nucleus	13C

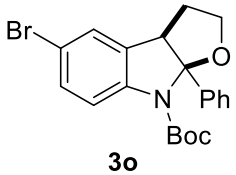


3n

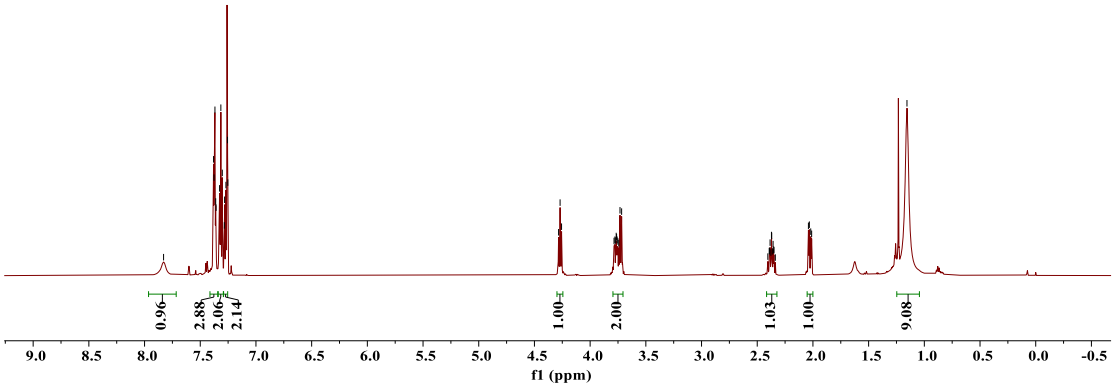




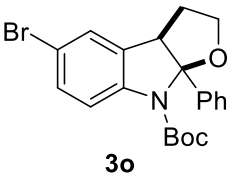
Parameter	value
Title	RV-0556-3.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	8
Acquisition Date	2022-05-24T04:21:43
Spectrometer Frequency	600 MHz
Nucleus	1H



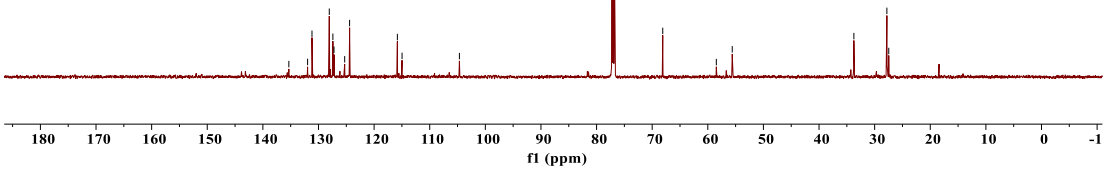
3o

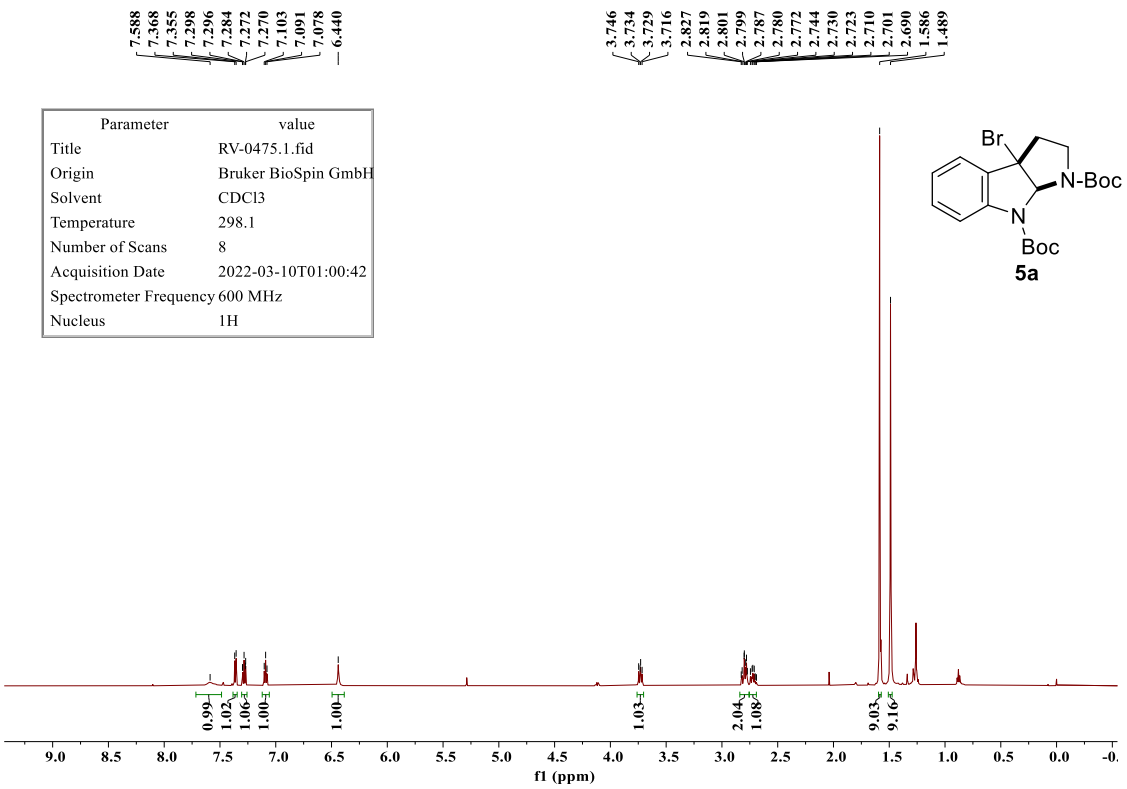


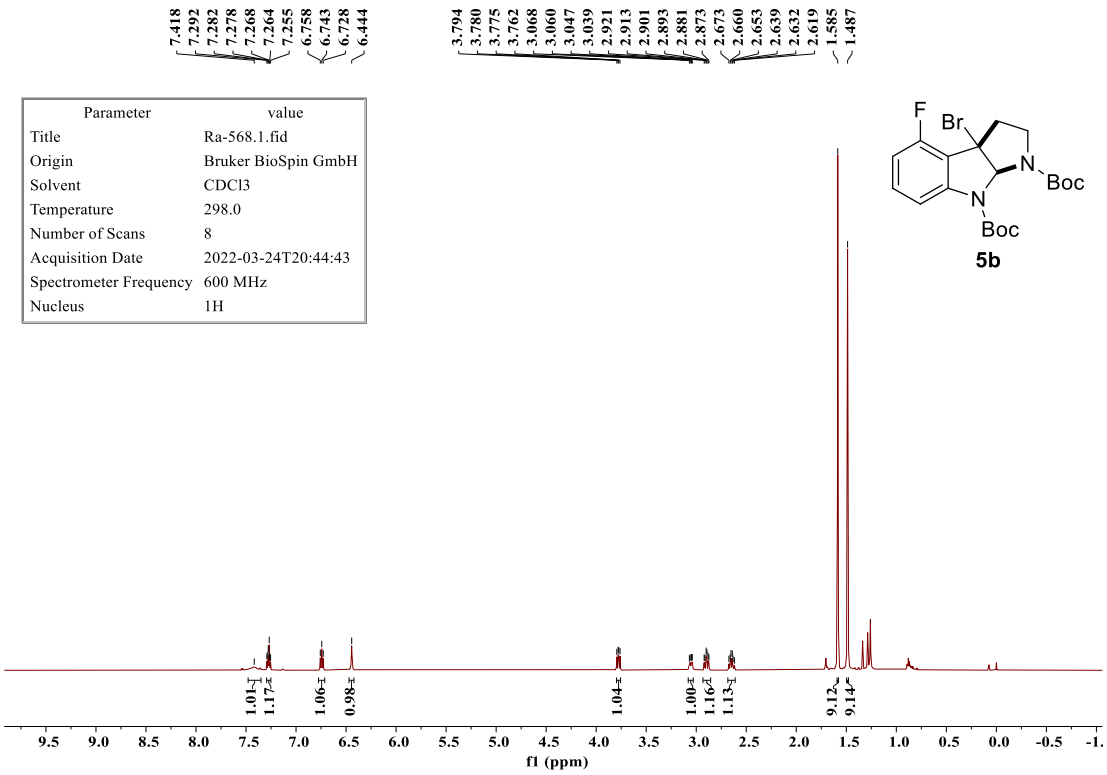
Parameter	value
Title	RV-0556-4.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	656
Acquisition Date	2022-05-25T00:02:48
Spectrometer Frequency	150 MHz
Nucleus	13C

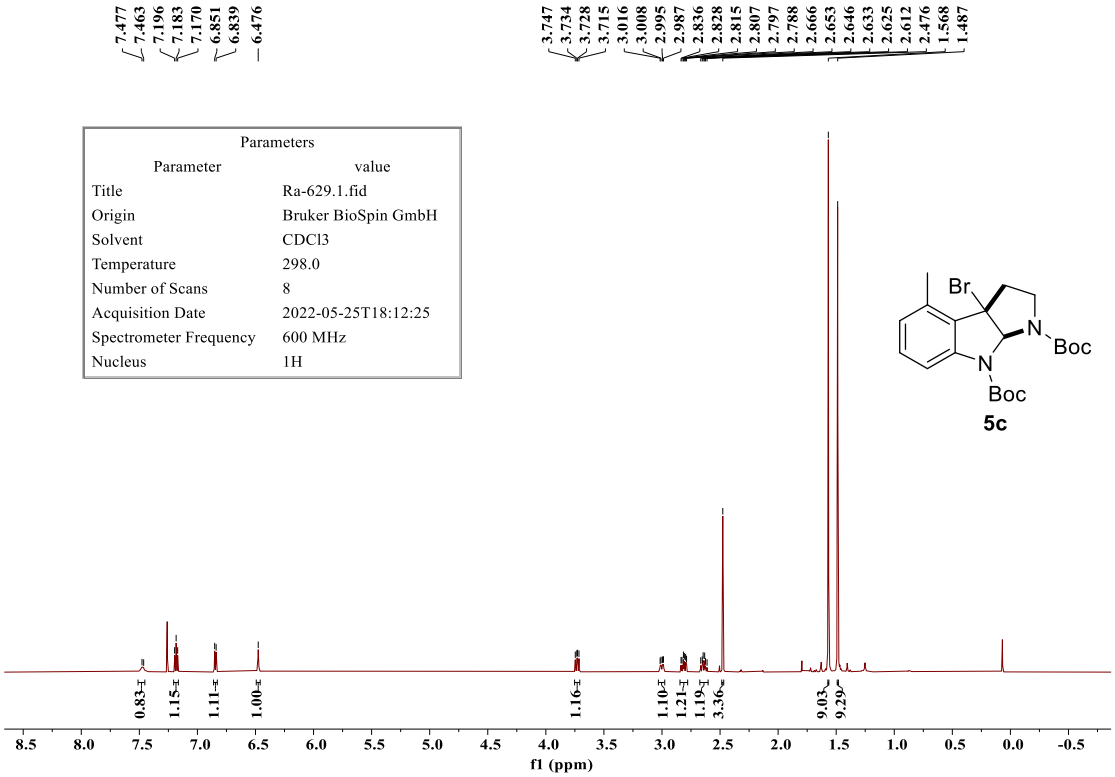


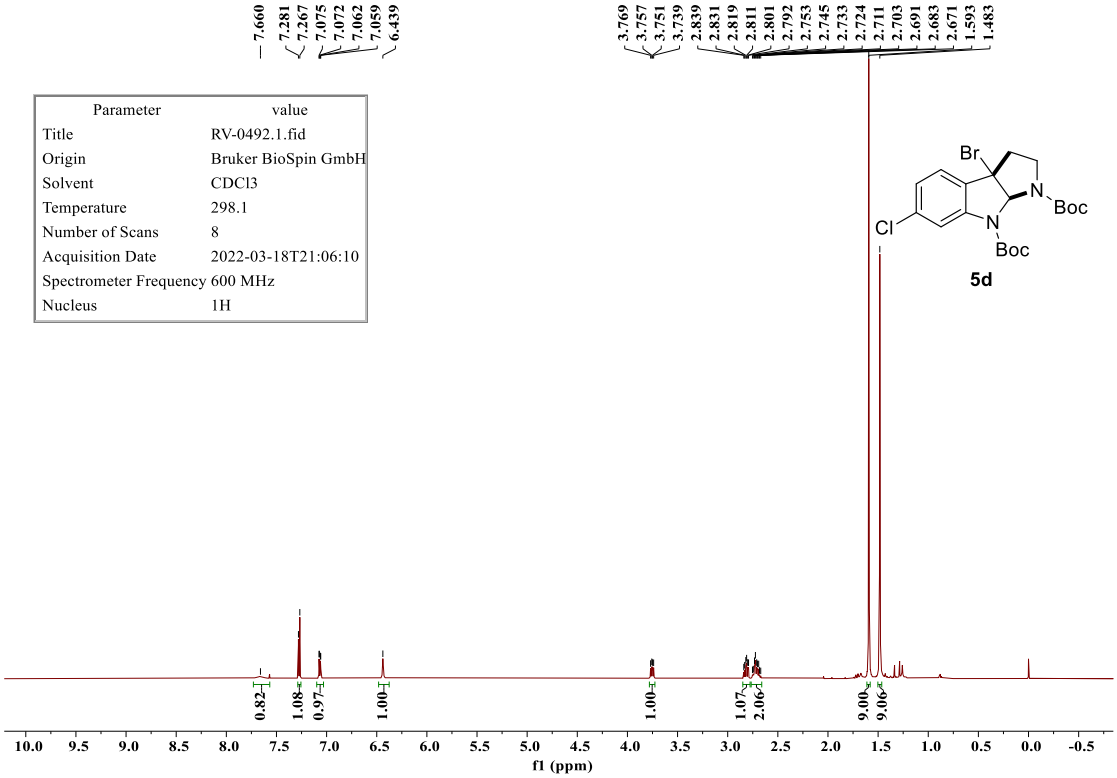
3o

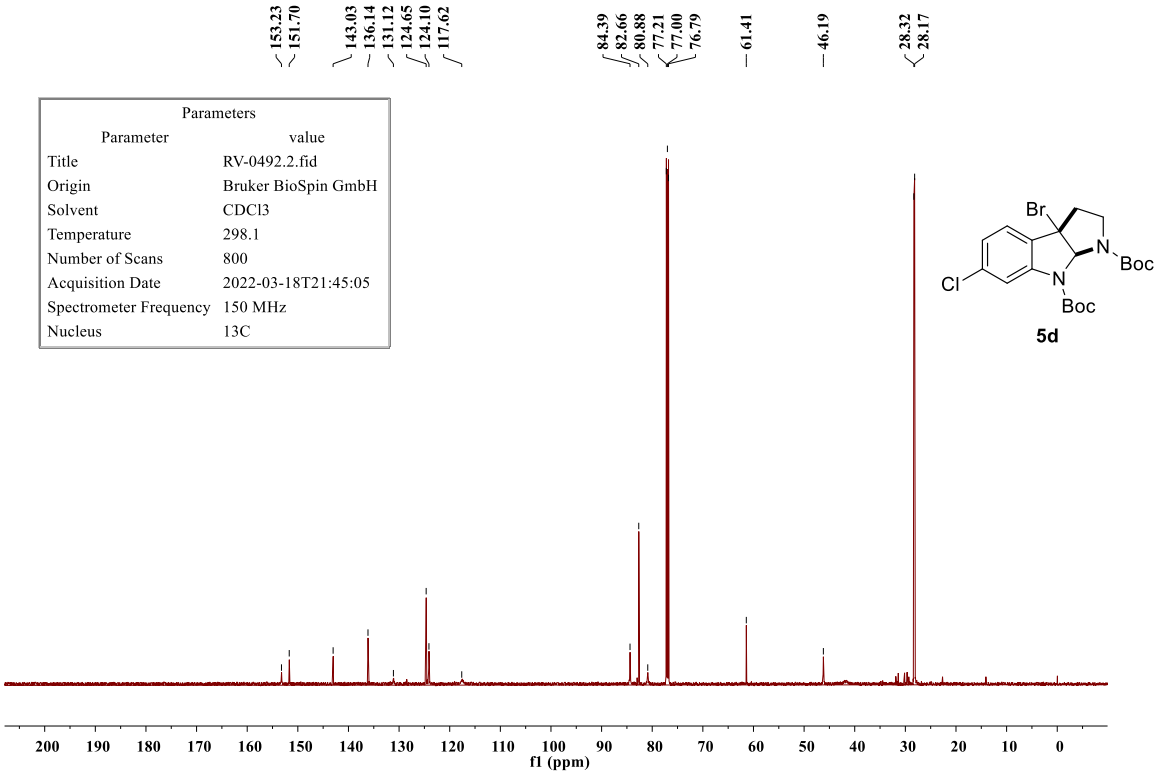


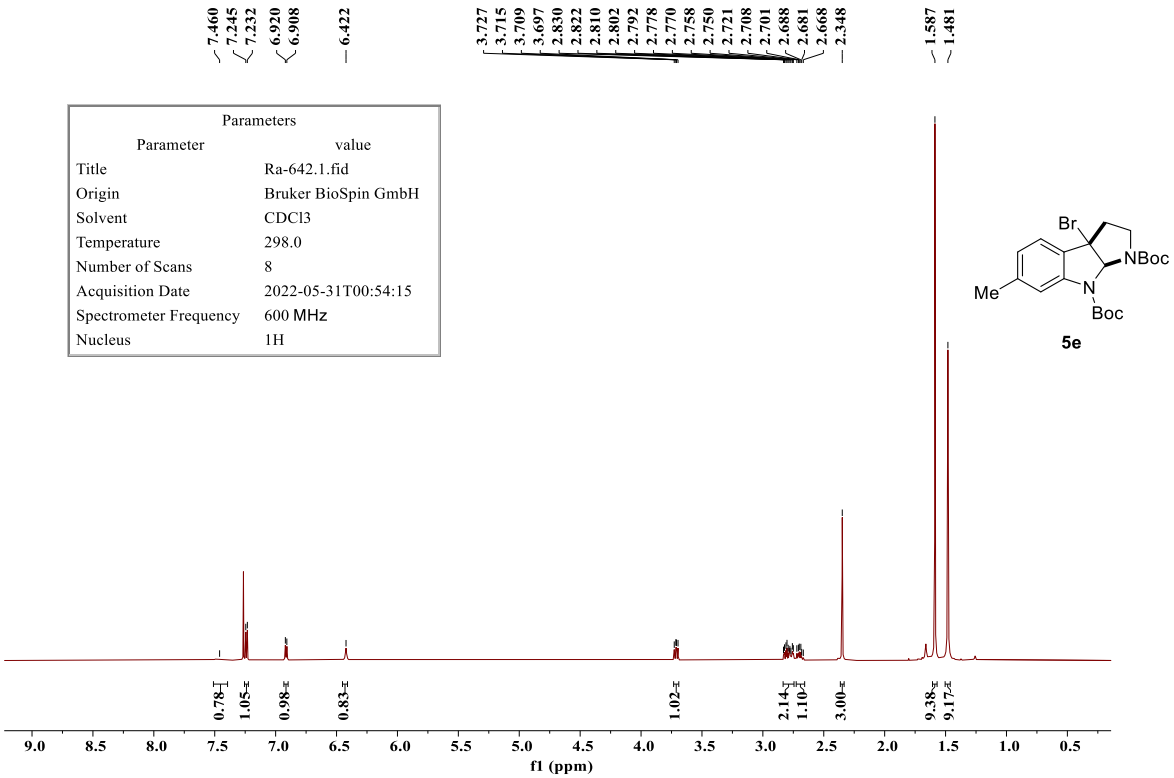

7.588
7.368
7.355
7.298
7.296
7.284
7.272
7.270
7.103
7.091
7.078
6.440
3.746
3.734
3.729
3.716
2.827
2.819
2.801
2.799
2.787
2.780
2.772
2.744
2.730
2.723
2.710
2.701
2.690
1.586
1.489
Parameter value
Title RV-0475.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.1
Number of Scans 8
Acquisition Date 2022-03-10T01:00:42
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
N-Boc
N
Boc
5a
0.99
1.02
1.06
1.00
1.00
1.03
2.04
1.08
9.03
9.16
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

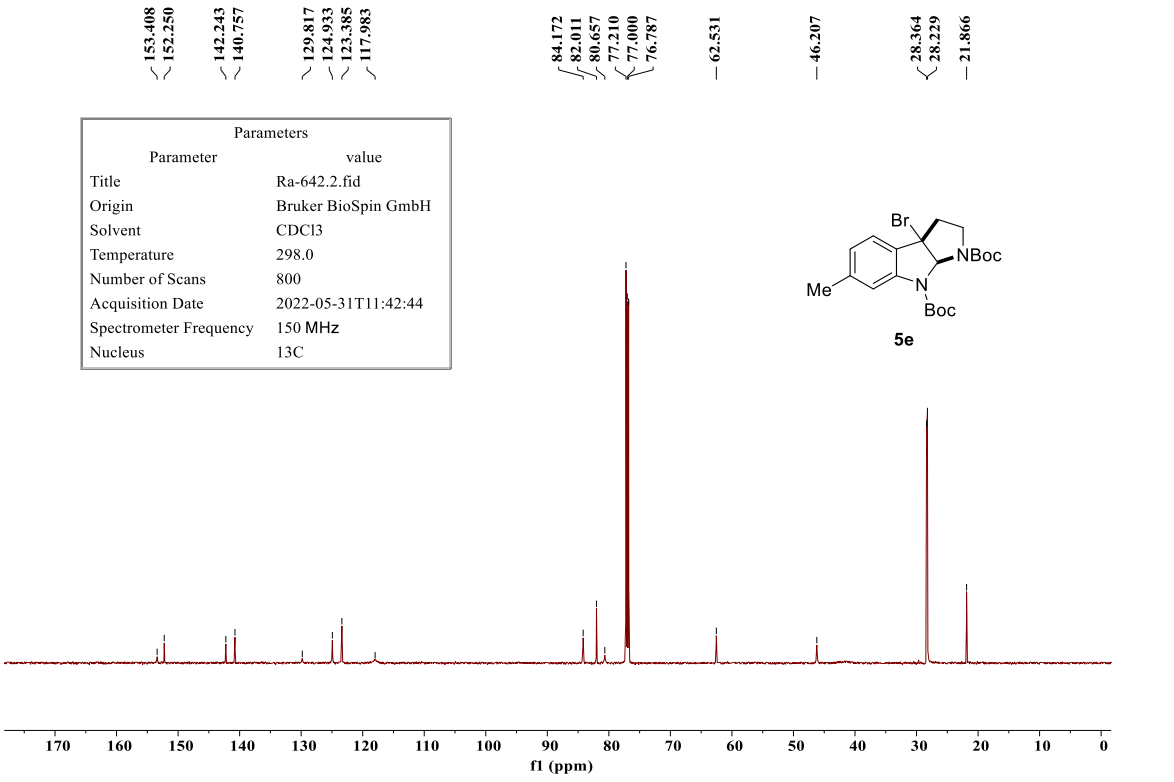

7.418
7.292
7.282
7.278
7.268
7.264
7.255
6.758
6.743
6.728
6.444
3.794
3.780
3.775
3.762
3.068
3.060
3.047
3.039
2.921
2.913
2.901
2.893
2.881
2.873
2.673
2.660
2.653
2.639
2.632
2.619
1.585
1.487
Parameter value
Title Ra-568.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-03-24T20:44:43
Spectrometer Frequency 600 MHz
Nucleus 1H
F
Br
N
Boc
N
Boc
5b
1.01
1.17
1.06
0.98
1.04
1.00
1.16
1.13
9.12
9.14
f1 (ppm)

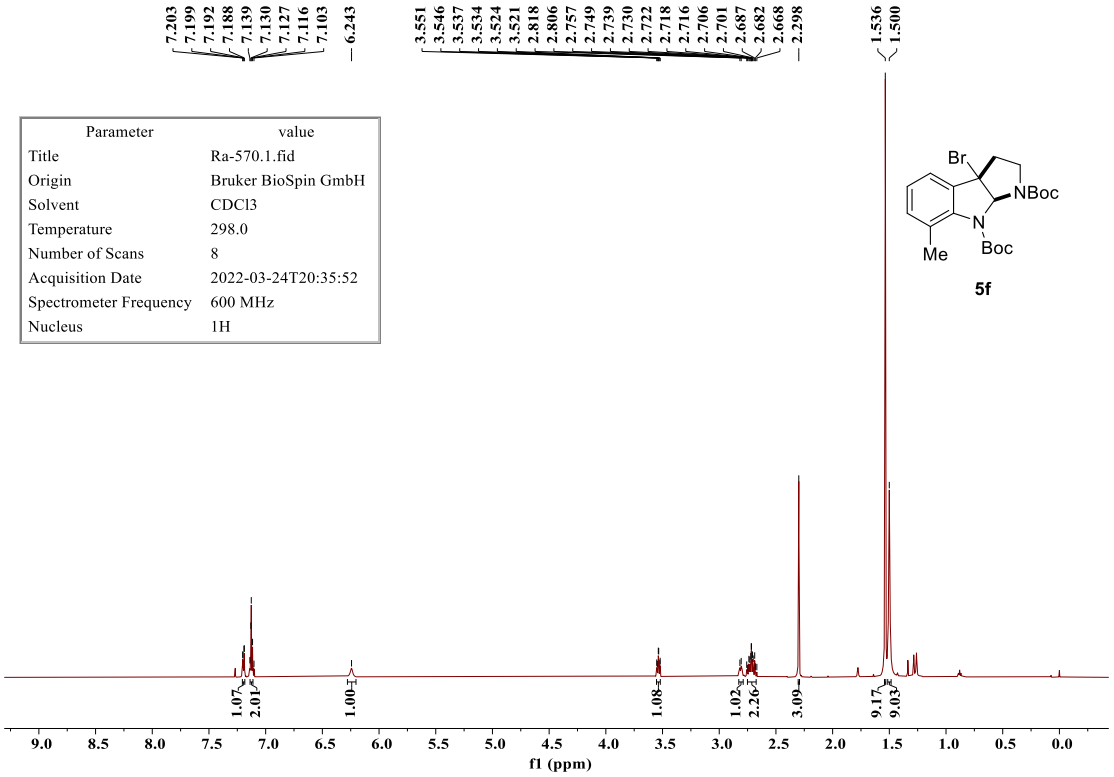

7.477
7.463
7.196
7.183
7.170
6.851
6.839
6.476
3.747
3.734
3.728
3.715
3.016
3.008
2.995
2.987
2.836
2.828
2.815
2.807
2.797
2.788
2.666
2.653
2.646
2.633
2.625
2.612
2.476
1.568
1.487
Parameters
Parameter value
Title Ra-629.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-05-25T18:12:25
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
N
Boc
N
Boc
5c
0.83
1.15
1.11
1.00
1.16
1.10
1.21
1.19
3.36
9.03
9.29
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

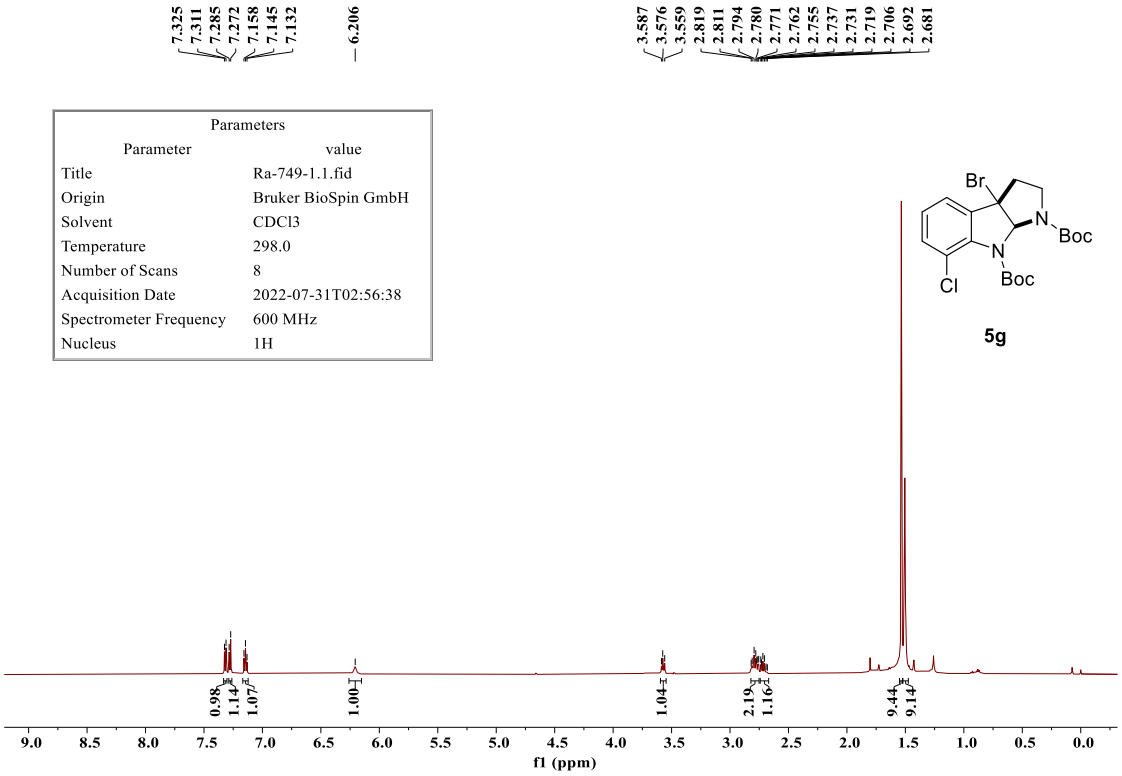

7.660
7.281
7.267
7.075
7.072
7.062
7.059
6.439
3.769
3.757
3.751
3.739
2.839
2.831
2.819
2.811
2.801
2.792
2.753
2.745
2.733
2.724
2.711
2.703
2.691
2.683
2.671
1.593
1.483
Parameter value
Title RV-0492.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.1
Number of Scans 8
Acquisition Date 2022-03-18T21:06:10
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
N
Boc
Cl
N
Boc
5d
0.82
1.08
0.97
1.00
1.00
1.07
2.06
9.00
9.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

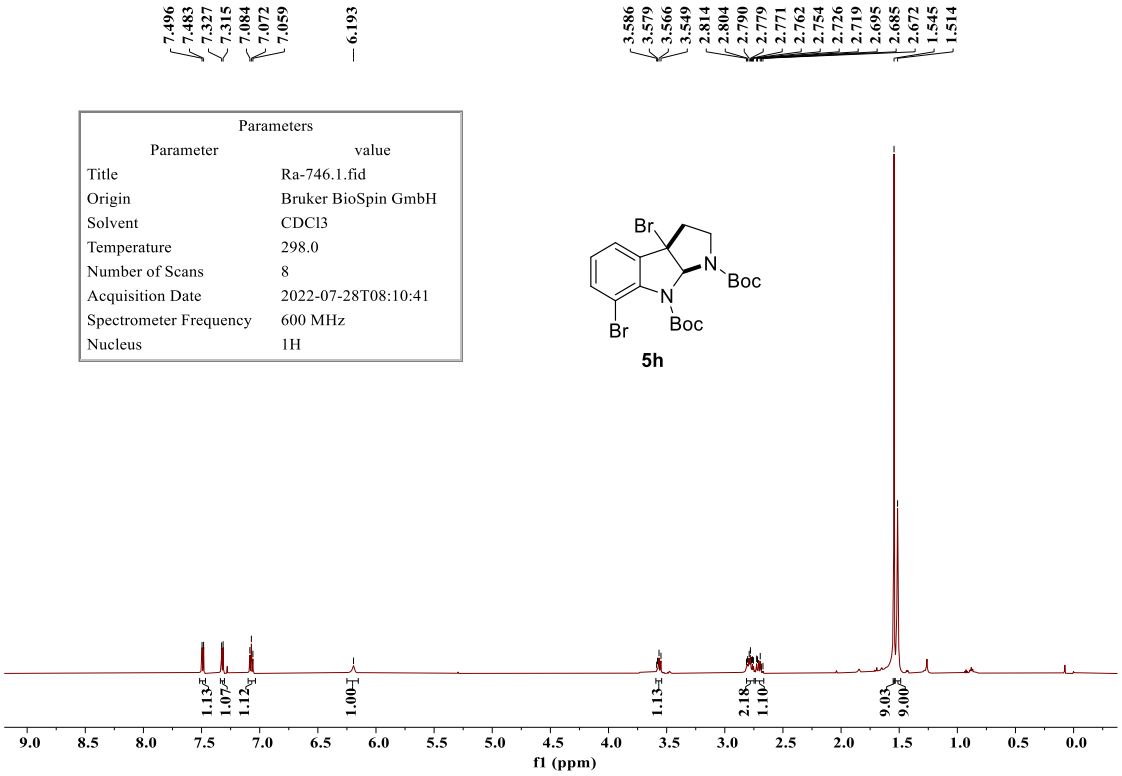

153.23
151.70
143.03
136.14
131.12
124.65
124.10
117.62
84.39
82.66
80.88
77.21
77.00
76.79
61.41
46.19
28.32
28.17
Parameters
Parameter value
Title RV-0492.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.1
Number of Scans 800
Acquisition Date 2022-03-18T21:45:05
Spectrometer Frequency 150 MHz
Nucleus 13C
Br
N
Boc
Cl
N
Boc
5d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

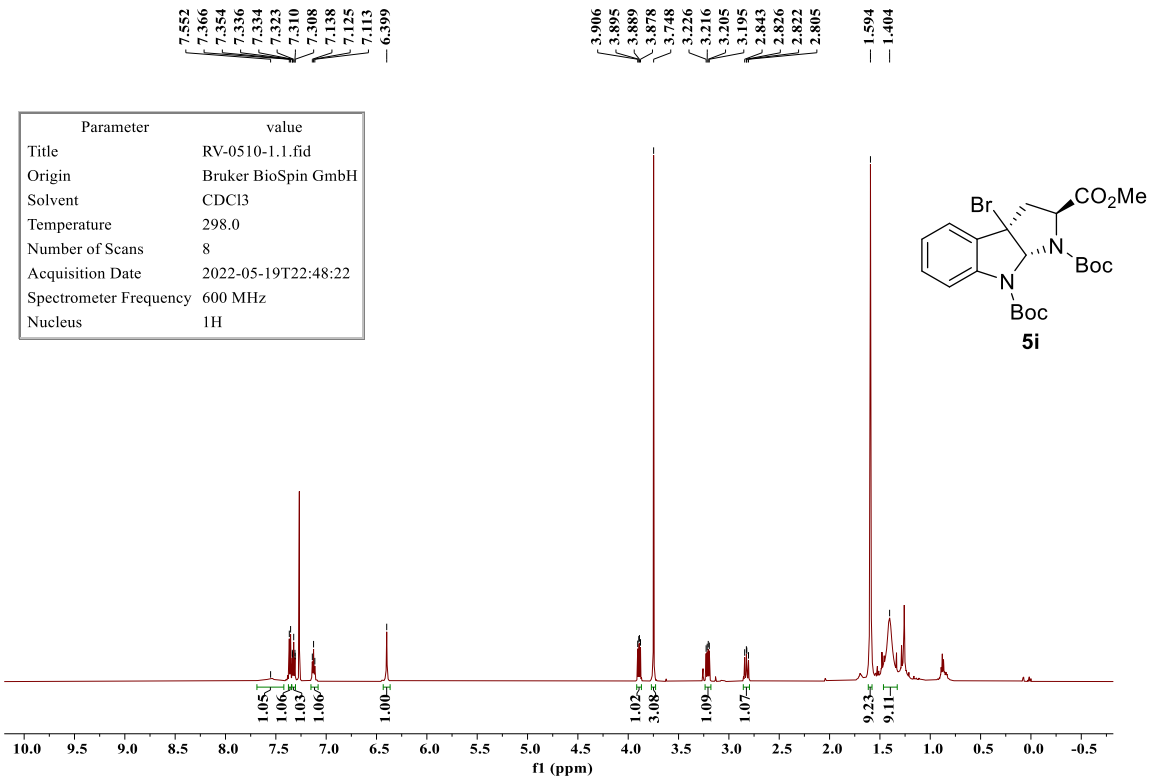

7.460
7.245
7.232
6.920
6.908
6.422
3.727
3.715
3.709
3.697
2.830
2.822
2.810
2.802
2.792
2.778
2.770
2.758
2.750
2.721
2.708
2.701
2.688
2.681
2.668
2.348
1.587
1.481
Parameters
Parameter value
Title Ra-642.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-05-31T00:54:15
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
NBoc
Me
N
Boc
5e
0.78
1.05
0.98
0.83
1.02
2.14
1.10
3.00
9.38
9.17
f1 (ppm)

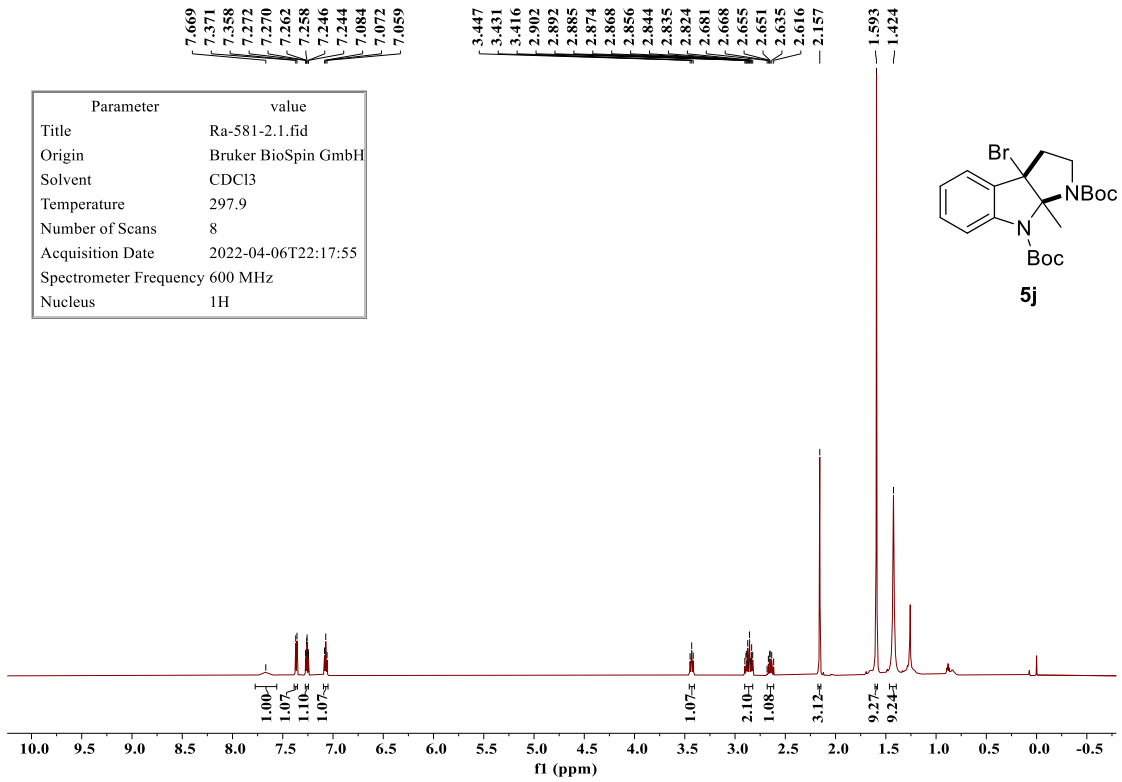

153.408
152.250
142.243
140.757
129.817
124.933
123.385
117.983
84.172
82.011
80.657
77.210
77.000
76.787
62.531
46.207
28.364
28.229
21.866
Parameters
Parameter value
Title Ra-642.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 800
Acquisition Date 2022-05-31T11:42:44
Spectrometer Frequency 150 MHz
Nucleus 13C
Br
NBoc
Me
N
Boc
5e
f1 (ppm)


7.203
7.199
7.192
7.188
7.139
7.130
7.127
7.116
7.103
6.243
3.551
3.546
3.537
3.534
3.524
3.521
2.818
2.806
2.757
2.749
2.739
2.730
2.722
2.718
2.716
2.706
2.701
2.687
2.682
2.668
2.298
1.536
1.500
Parameter value
Title Ra-570.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-03-24T20:35:52
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
NBoc
N
Boc
Me
5f
1.07
2.01
1.00
1.08
1.02
2.26
3.09
9.17
9.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


7.325
7.311
7.285
7.272
7.158
7.145
7.132
6.206
3.587
3.576
3.559
2.819
2.811
2.794
2.780
2.771
2.762
2.755
2.737
2.731
2.719
2.706
2.692
2.681
Parameters
Parameter value
Title Ra-749-1.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-07-31T02:56:38
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
N
Boc
N
Boc
Cl
5g
0.98
1.14
1.07
1.00
1.04
2.19
1.16
9.44
9.14
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


7.496
7.483
7.327
7.315
7.084
7.072
7.059
6.193
3.586
3.579
3.566
3.549
2.814
2.804
2.790
2.779
2.771
2.762
2.754
2.726
2.719
2.695
2.685
2.672
1.545
1.514
Parameters
Parameter value
Title Ra-746.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-07-28T08:10:41
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
N
Boc
N
Boc
Br
5h
1.13
1.07
1.12
1.00
1.13
2.18
1.10
9.03
9.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


7.552
7.366
7.354
7.336
7.334
7.323
7.310
7.308
7.138
7.125
7.113
6.399
3.906
3.895
3.889
3.878
3.748
3.226
3.216
3.205
3.195
2.843
2.826
2.822
2.805
1.594
1.404
Parameter value
Title RV-0510-1.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-05-19T22:48:22
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
CO2Me
N
Boc
N
Boc
5i
1.05
1.06
1.03
1.06
1.00
1.02
3.08
1.09
1.07
9.23
9.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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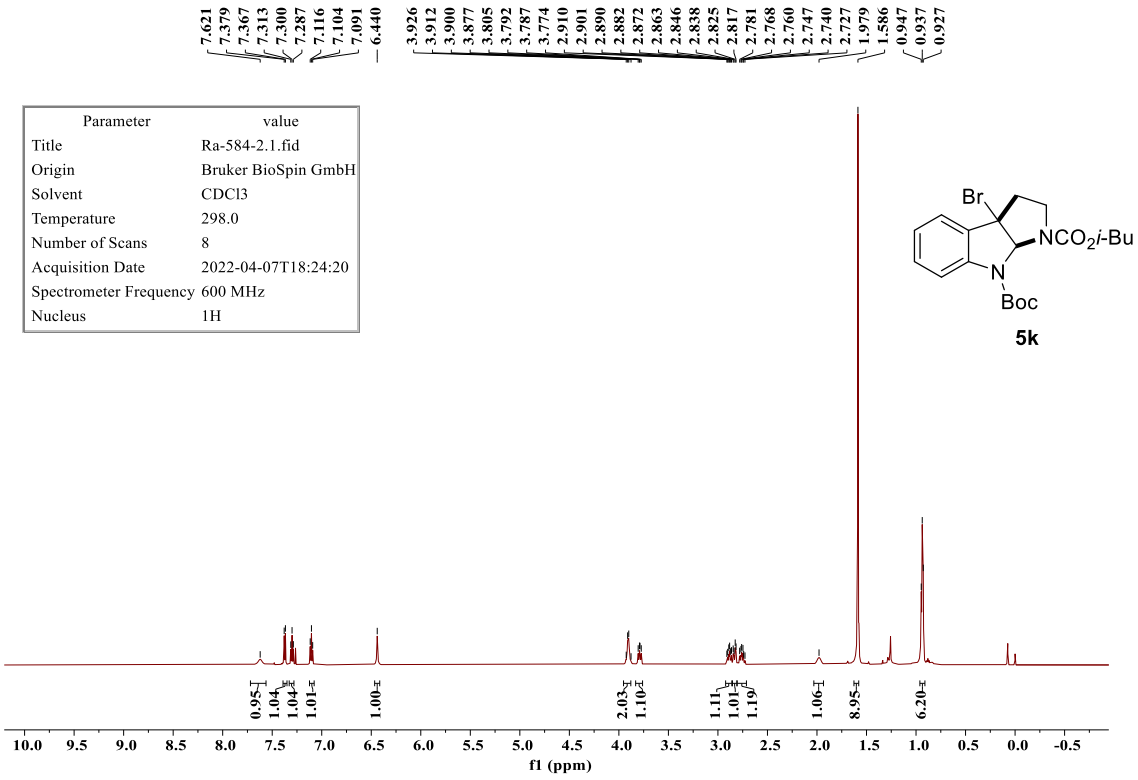
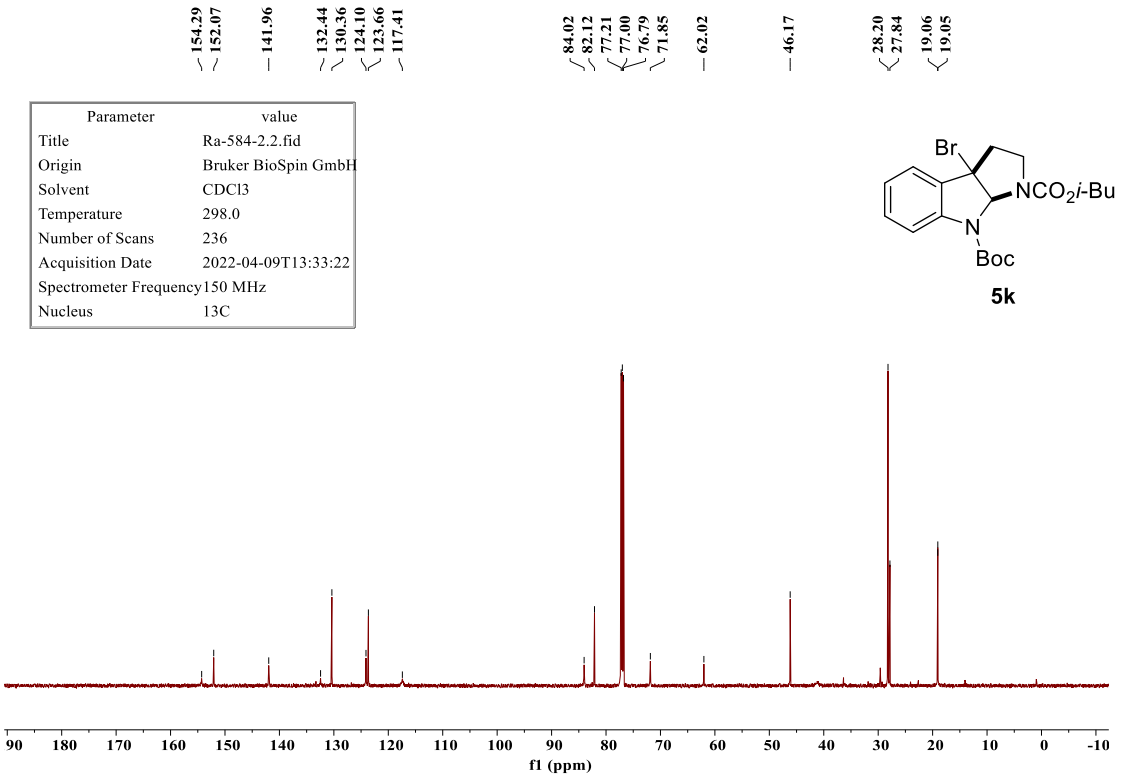
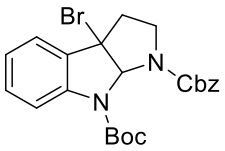
7.371
7.358
7.272
7.270
7.262
7.258
7.246
7.244
7.084
7.072
7.059
3.447
3.431
3.416
2.902
2.892
2.885
2.874
2.868
2.856
2.844
2.835
2.824
2.681
2.668
2.655
2.651
2.635
2.616
2.157
1.593
1.424
Parameter value
Title Ra-581-2.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.9
Number of Scans 8
Acquisition Date 2022-04-06T22:17:55
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
NBoc
N
Boc
5j
1.00
1.07
1.10
1.07
1.07
2.10
1.08
3.12
9.27
9.24
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

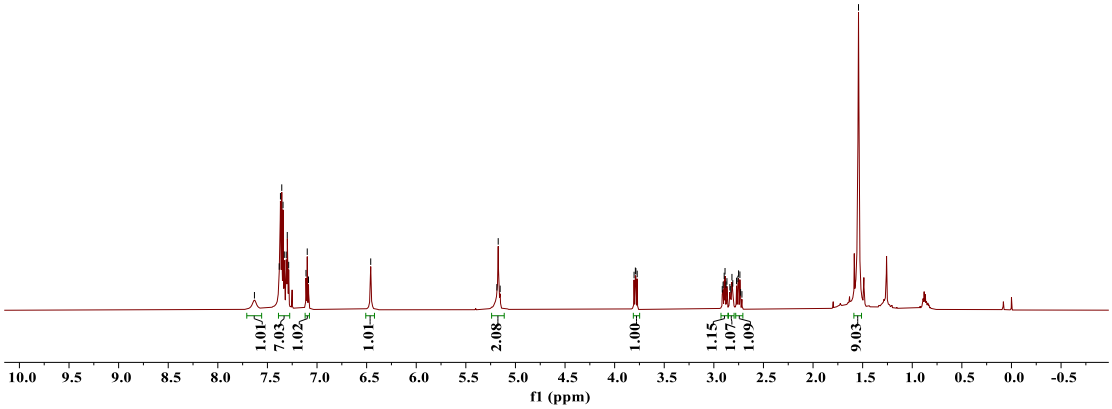

7.621
7.379
7.367
7.313
7.300
7.287
7.116
7.104
7.091
6.440
3.926
3.912
3.900
3.877
3.805
3.792
3.787
3.774
2.910
2.901
2.890
2.882
2.872
2.863
2.846
2.838
2.825
2.817
2.781
2.768
2.760
2.747
2.740
2.727
1.979
1.586
0.947
0.937
0.927
Parameter value
Title Ra-584-2.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-04-07T18:24:20
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
NCO2i-Bu
N
Boc
5k
0.95
1.04
1.04
1.01
1.00
2.03
1.10
1.11
1.01
1.19
1.06
8.95
6.20
f1 (ppm)

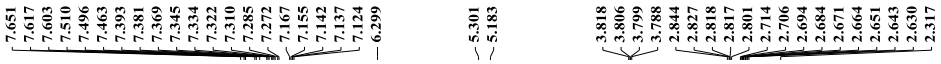

154.29
152.07
141.96
132.44
130.36
124.10
123.66
117.41
84.02
82.12
77.21
77.00
76.79
71.85
62.02
46.17
28.20
27.84
19.06
19.05
Parameter value
Title Ra-584-2.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 236
Acquisition Date 2022-04-09T13:33:22
Spectrometer Frequency 150 MHz
Nucleus 13C
Br
NCO2i-Bu
N
Boc
5k
f1 (ppm)

Parameter	value
Title	RV-0534-2.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	8
Acquisition Date	2022-04-25T22:25:29
Spectrometer Frequency	600 MHz
Nucleus	1H

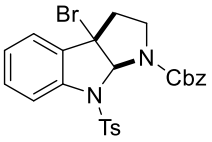


5l

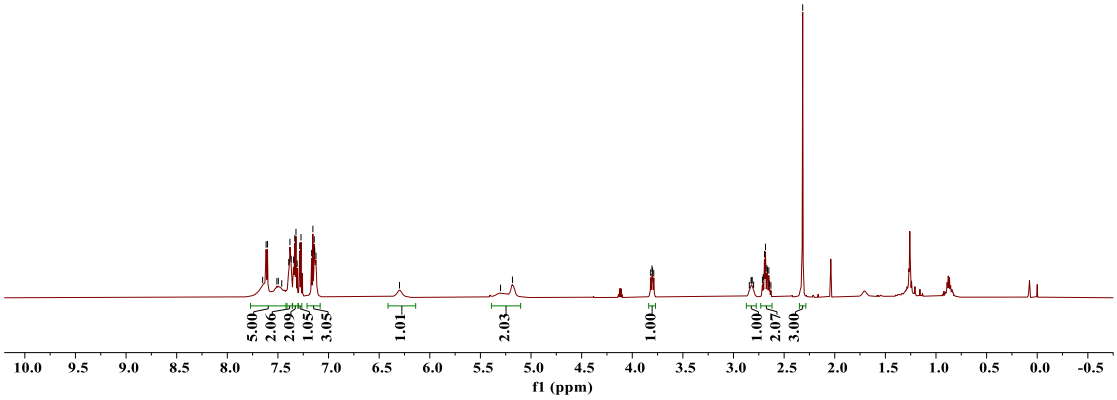


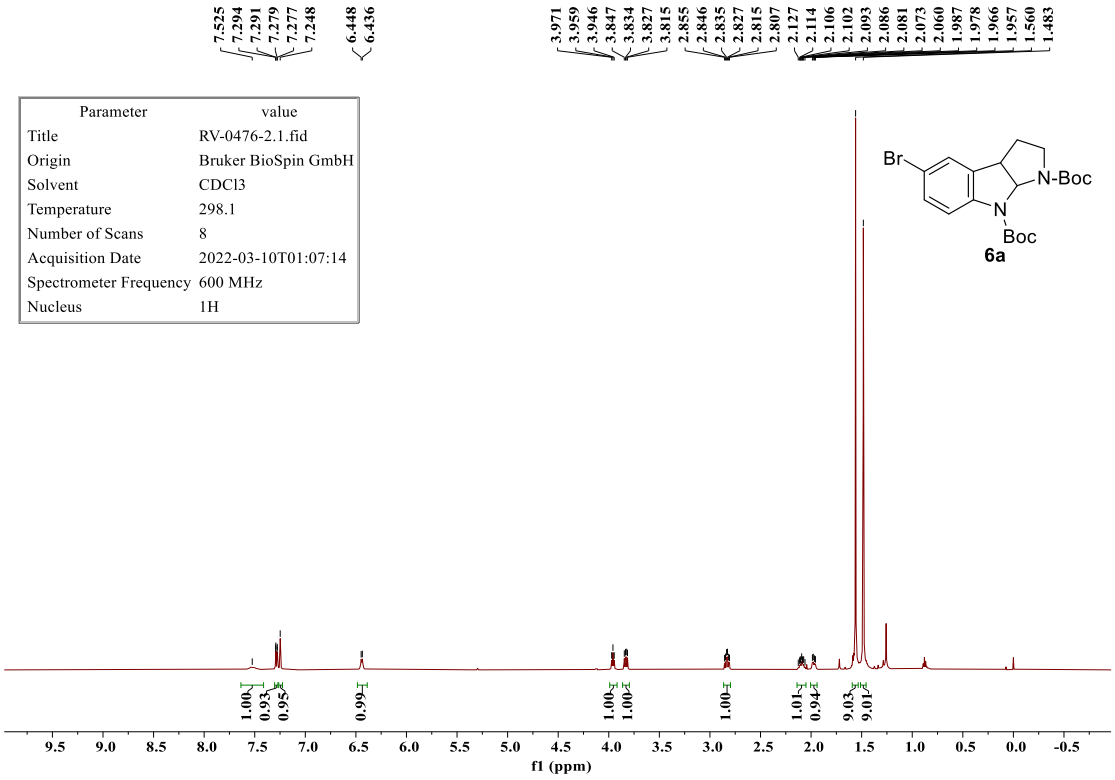


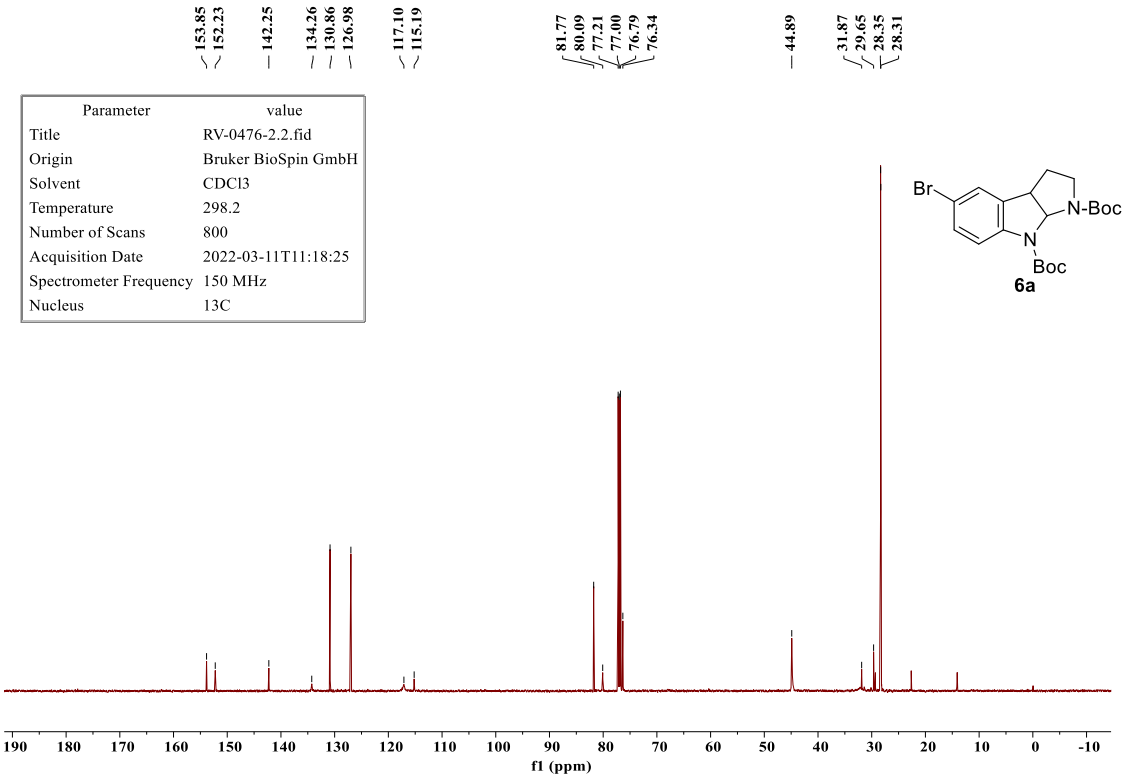
Parameter	value
Title	RV-0533.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	8
Acquisition Date	2022-04-25T22:14:21
Spectrometer Frequency	600 MHz
Nucleus	1H

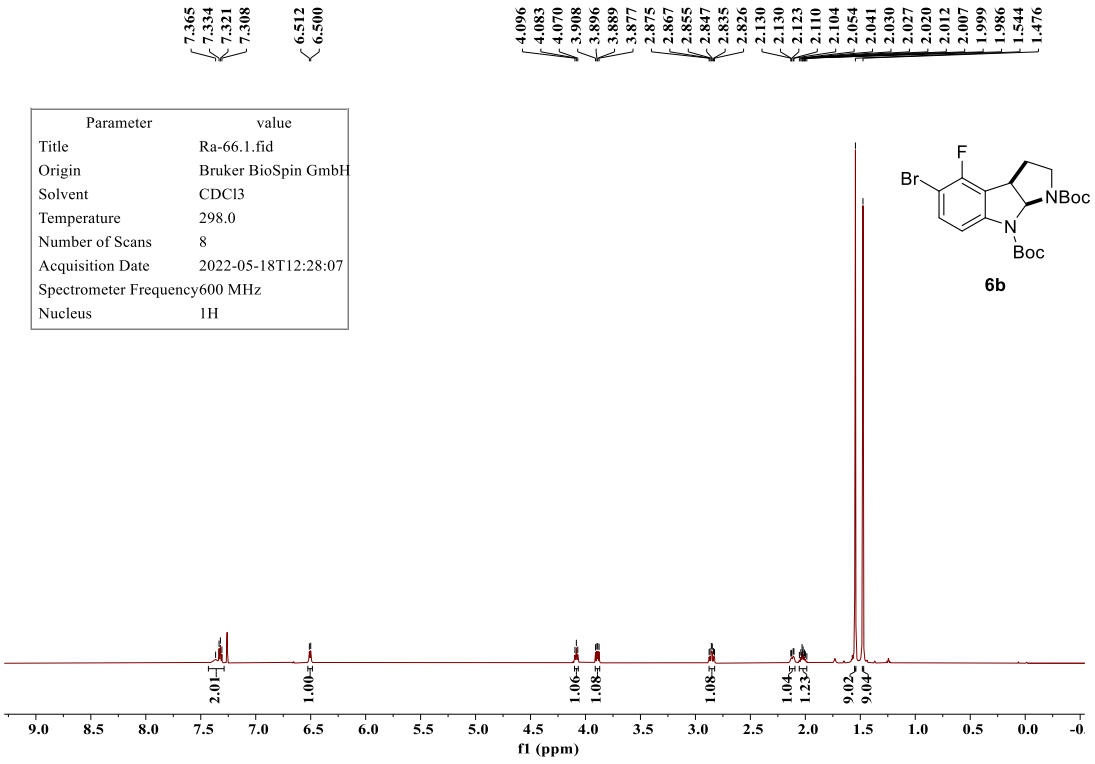


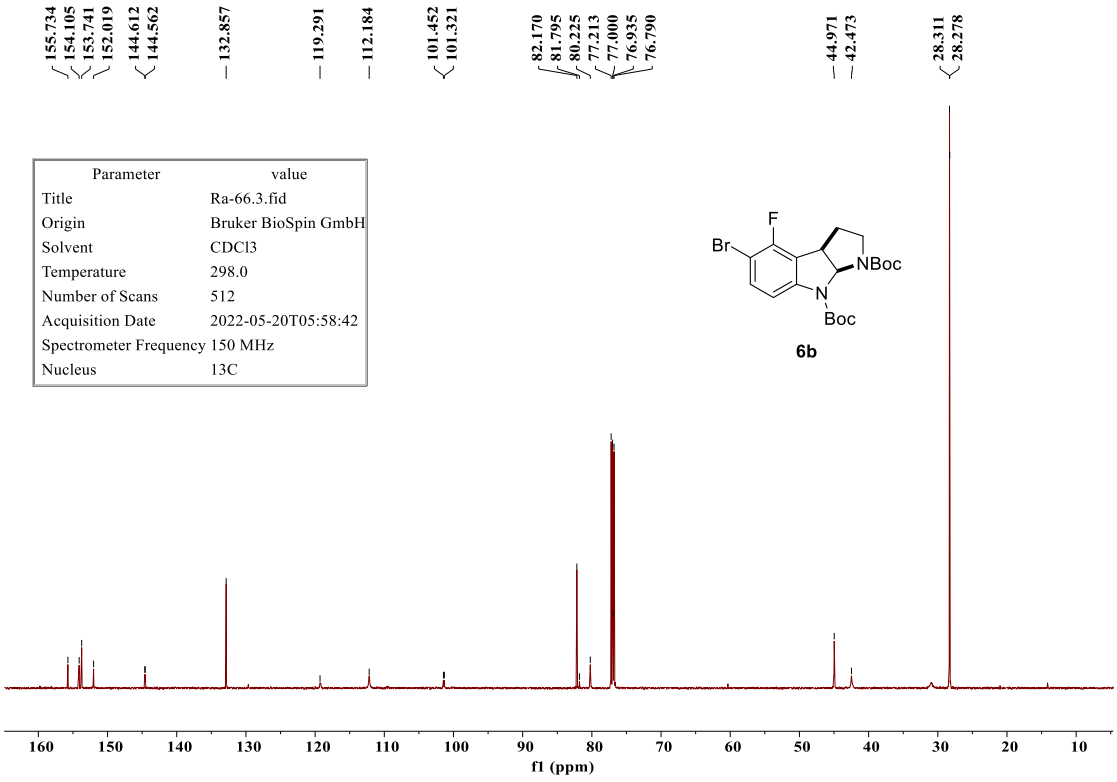
5m



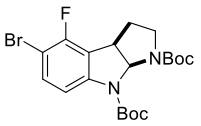

7.525
7.294
7.291
7.279
7.277
7.248
6.448
6.436
3.971
3.959
3.946
3.847
3.834
3.827
3.815
2.855
2.846
2.835
2.827
2.815
2.807
2.127
2.114
2.106
2.102
2.093
2.086
2.081
2.073
2.060
1.987
1.978
1.966
1.957
1.560
1.483
Parameter value
Title RV-0476-2.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.1
Number of Scans 8
Acquisition Date 2022-03-10T01:07:14
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
N-Boc
N
Boc
6a
1.00
0.93
0.95
0.99
1.00
1.00
1.00
1.01
0.94
9.03
9.01
f1 (ppm)


153.85
152.23
142.25
134.26
130.86
126.98
117.10
115.19
81.77
80.09
77.21
77.00
76.79
76.34
44.89
31.87
29.65
28.35
28.31
Parameter value
Title RV-0476-2.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.2
Number of Scans 800
Acquisition Date 2022-03-11T11:18:25
Spectrometer Frequency 150 MHz
Nucleus 13C
Br
N-Boc
N
Boc
6a
f1 (ppm)

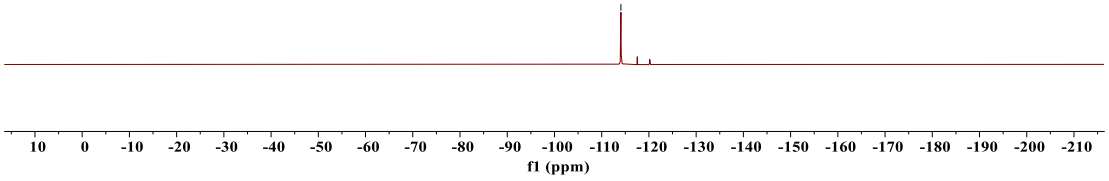

7.365
7.334
7.321
7.308
6.512
6.500
4.096
4.083
4.070
3.908
3.896
3.889
3.877
2.875
2.867
2.855
2.847
2.835
2.826
2.130
2.123
2.110
2.104
2.054
2.041
2.030
2.027
2.020
2.012
2.007
1.999
1.986
1.544
1.476
Parameter value
Title Ra-66.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-05-18T12:28:07
Spectrometer Frequency 600 MHz
Nucleus 1H
F
Br
NBoc
N
Boc
6b
2.01
1.00
1.06
1.08
1.08
1.04
1.23
9.02
9.04
f1 (ppm)

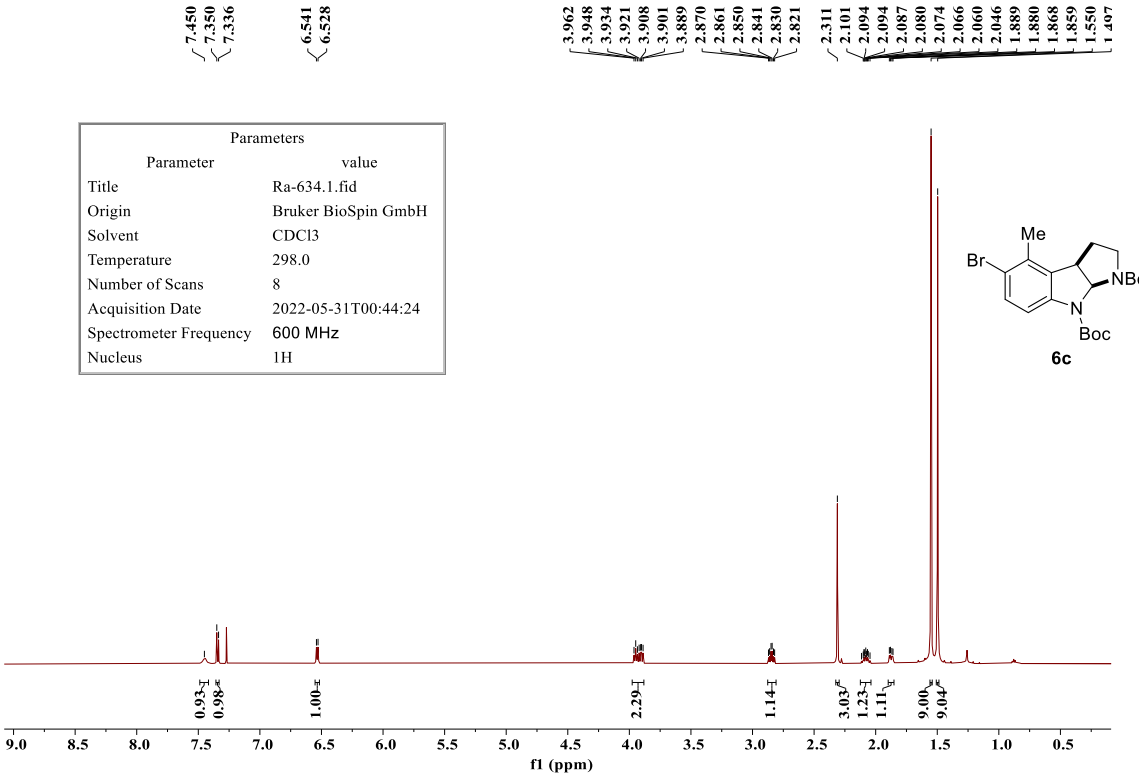

155.734
154.105
153.741
152.019
144.612
144.562
132.857
119.291
112.184
101.452
101.321
82.170
81.795
80.225
77.213
77.000
76.935
76.790
44.971
42.473
28.311
28.278
Parameter value
Title Ra-66.3.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 512
Acquisition Date 2022-05-20T05:58:42
Spectrometer Frequency 150 MHz
Nucleus 13C
F
Br
NBoc
N
Boc
6b
f1 (ppm)

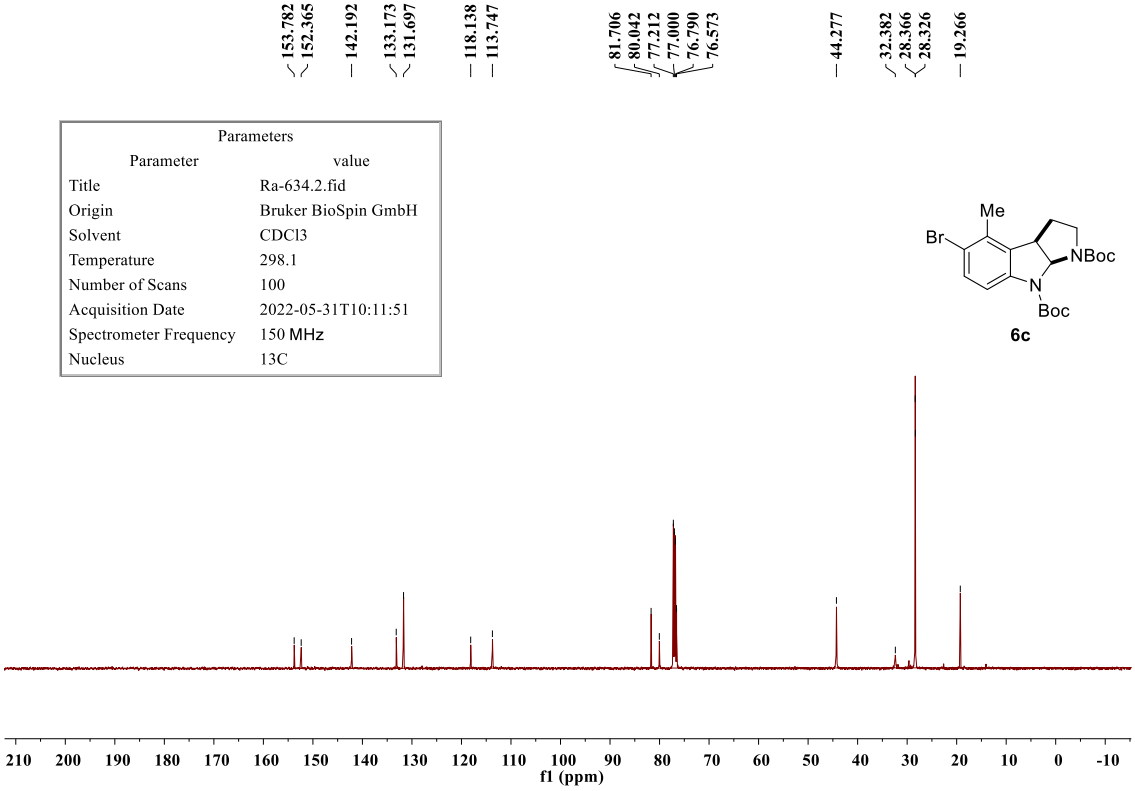
Parameter	value
Title	Ra-66.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.4
Number of Scans	16
Acquisition Date	2022-05-18T12:29:38
Spectrometer Frequency	565 MHz
Nucleus	19F

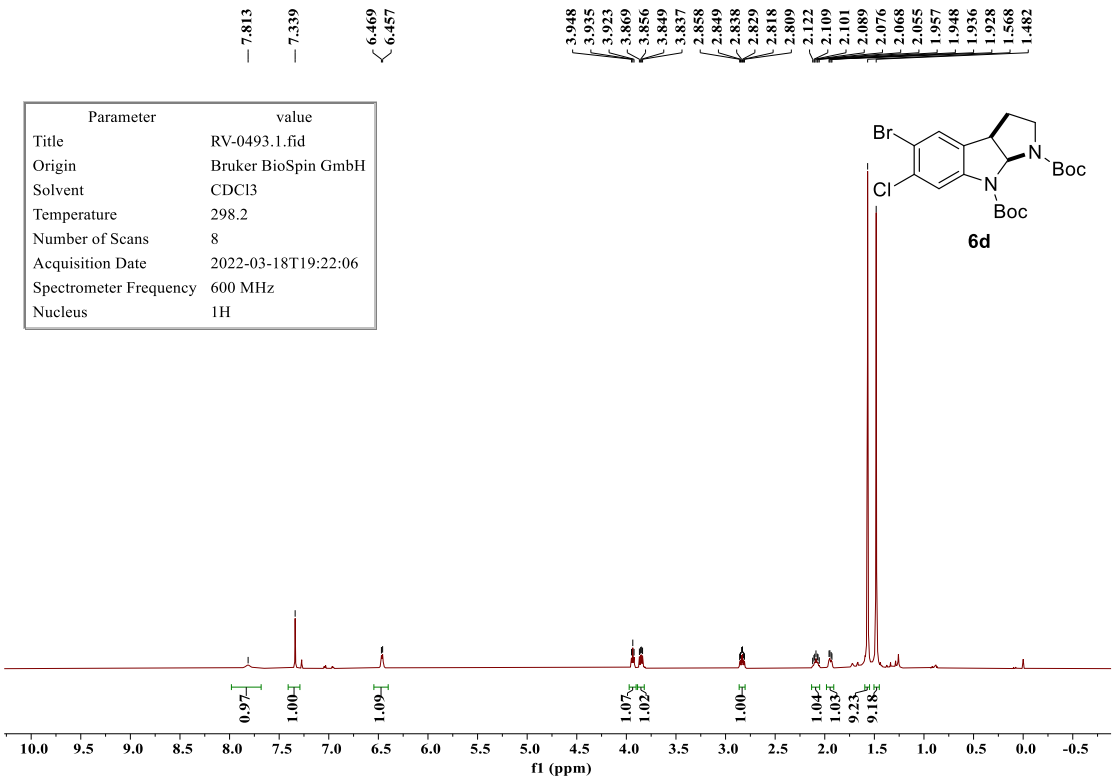


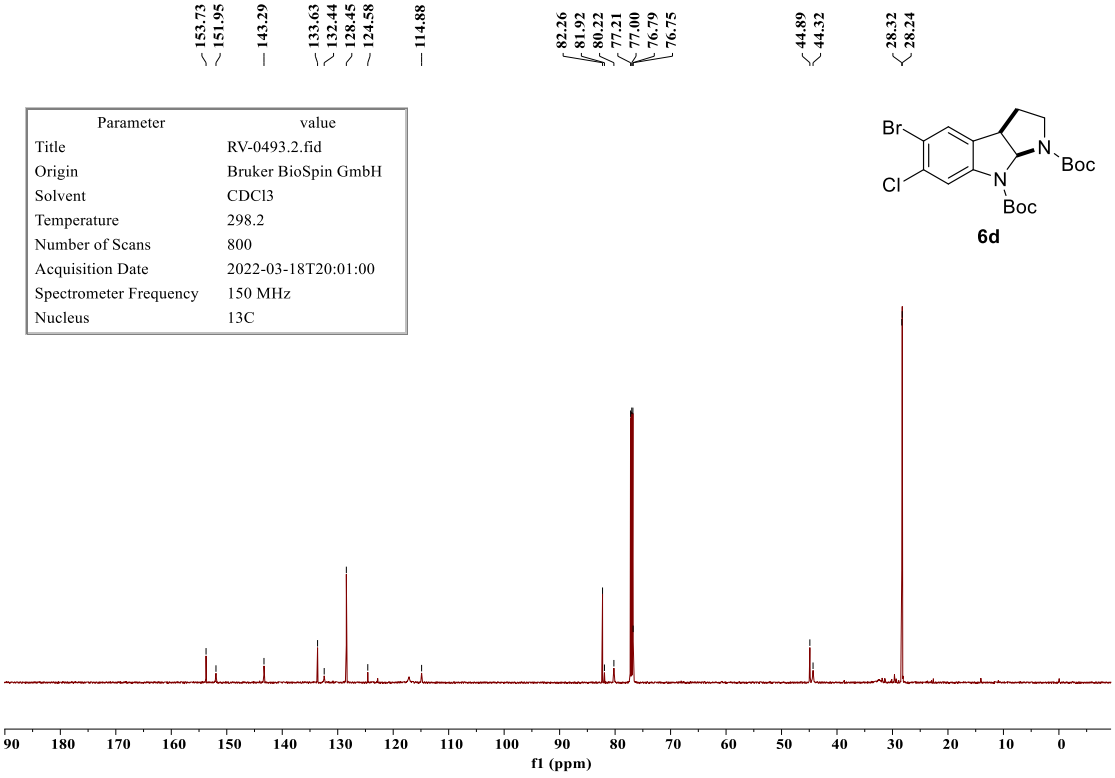
6b

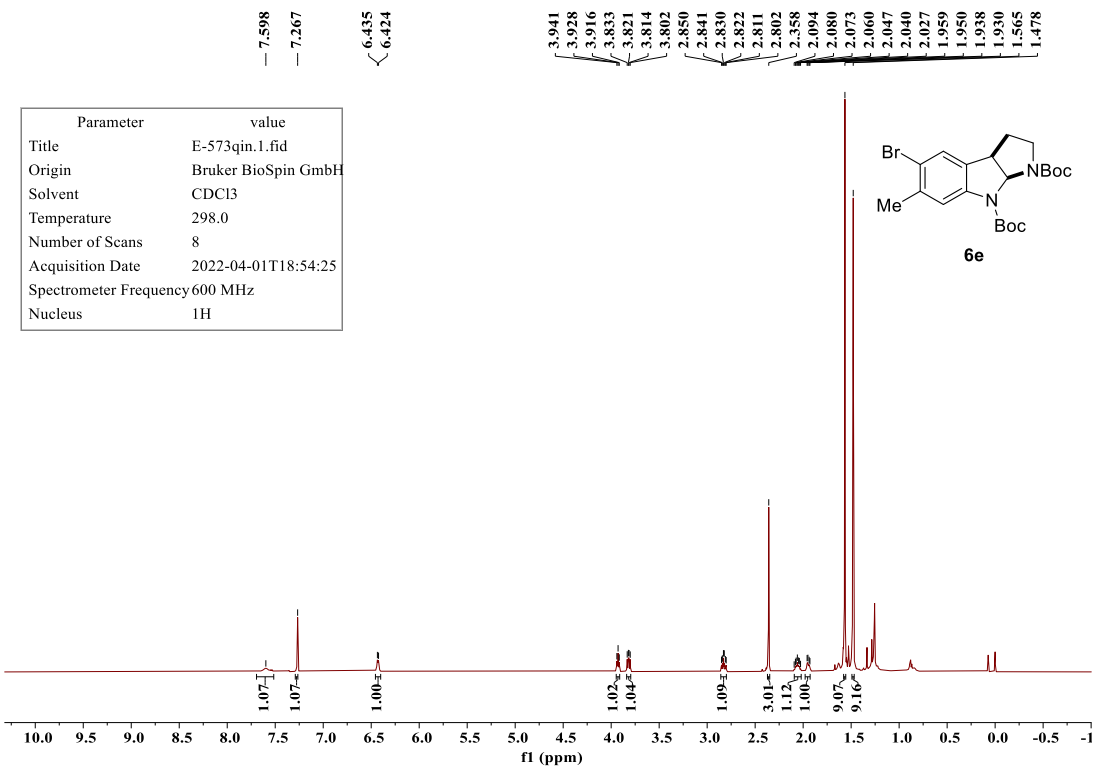


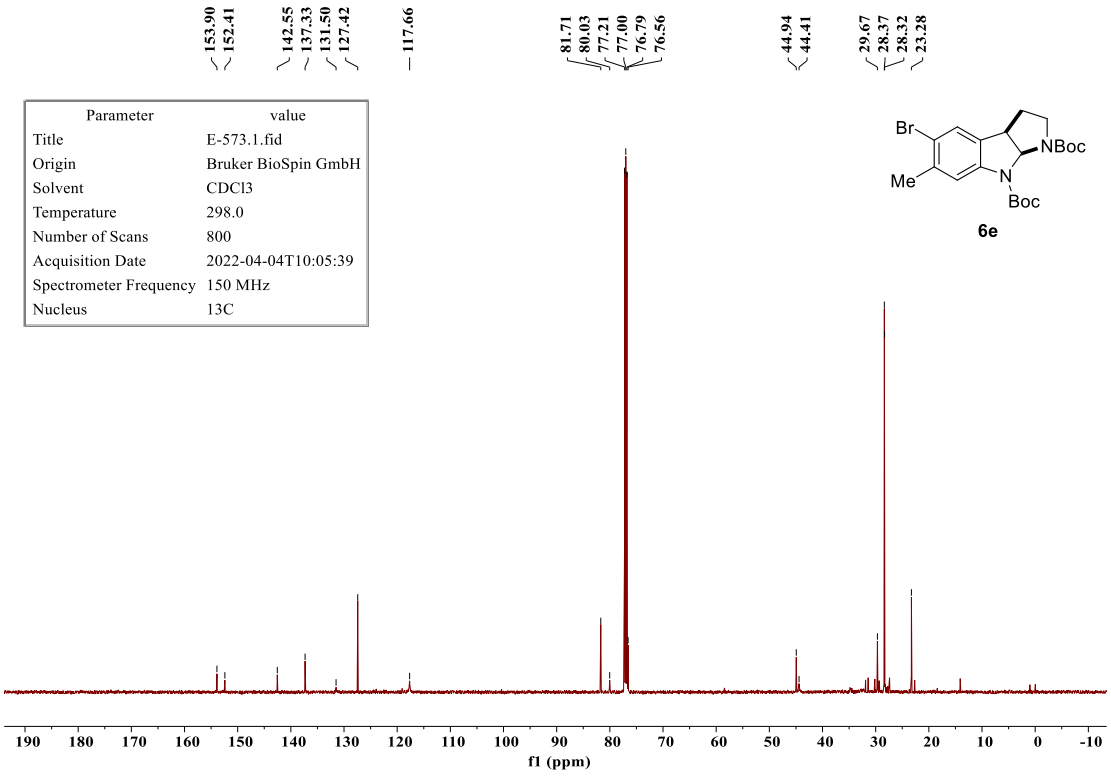

7.450
7.350
7.336
6.541
6.528
3.962
3.948
3.934
3.921
3.908
3.901
3.889
2.870
2.861
2.850
2.841
2.830
2.821
2.311
2.101
2.094
2.094
2.087
2.080
2.074
2.066
2.060
2.046
1.889
1.880
1.868
1.859
1.550
1.497
Parameters
Parameter value
Title Ra-634.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-05-31T00:44:24
Spectrometer Frequency 600 MHz
Nucleus 1H
Me
Br
NBoc
N
Boc
6c
0.93
0.98
1.00
2.29
1.14
3.03
1.23
1.11
9.00
9.04
f1 (ppm)

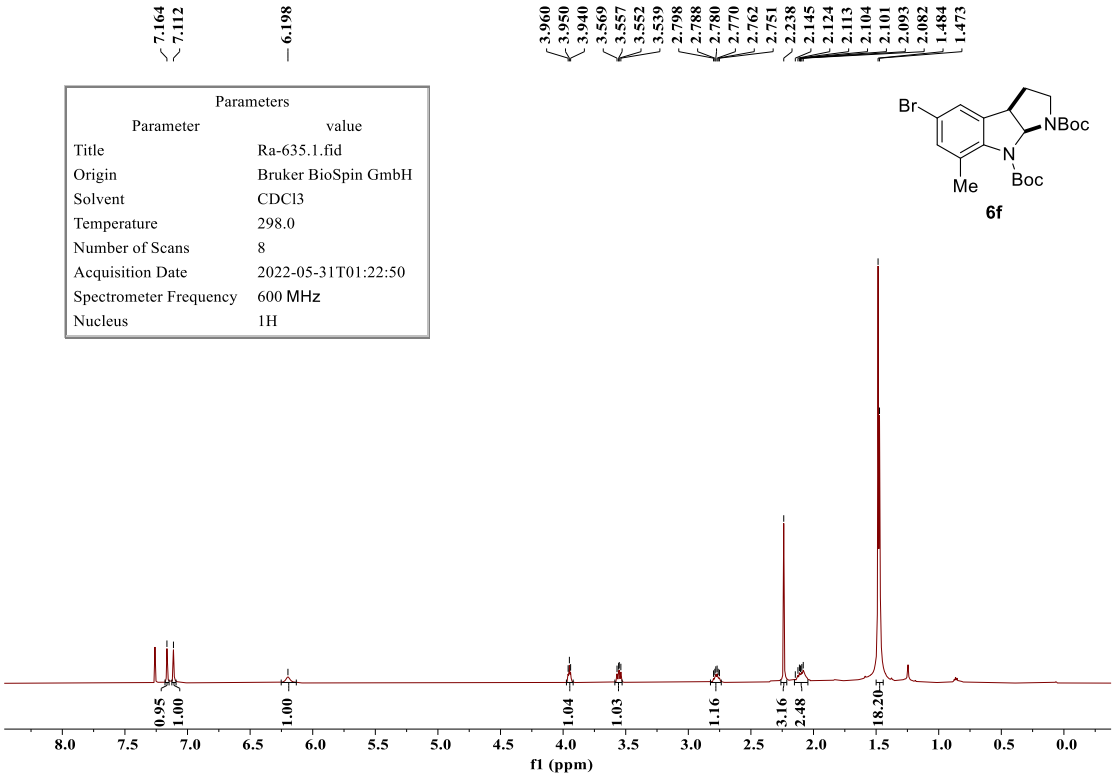

153.782
152.365
142.192
133.173
131.697
118.138
113.747
81.706
80.042
77.212
77.000
76.790
76.573
44.277
32.382
28.366
28.326
19.266
Parameters
Parameter value
Title Ra-634.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.1
Number of Scans 100
Acquisition Date 2022-05-31T10:11:51
Spectrometer Frequency 150 MHz
Nucleus 13C
Me
Br
NBoc
N
Boc
6c
f1 (ppm)

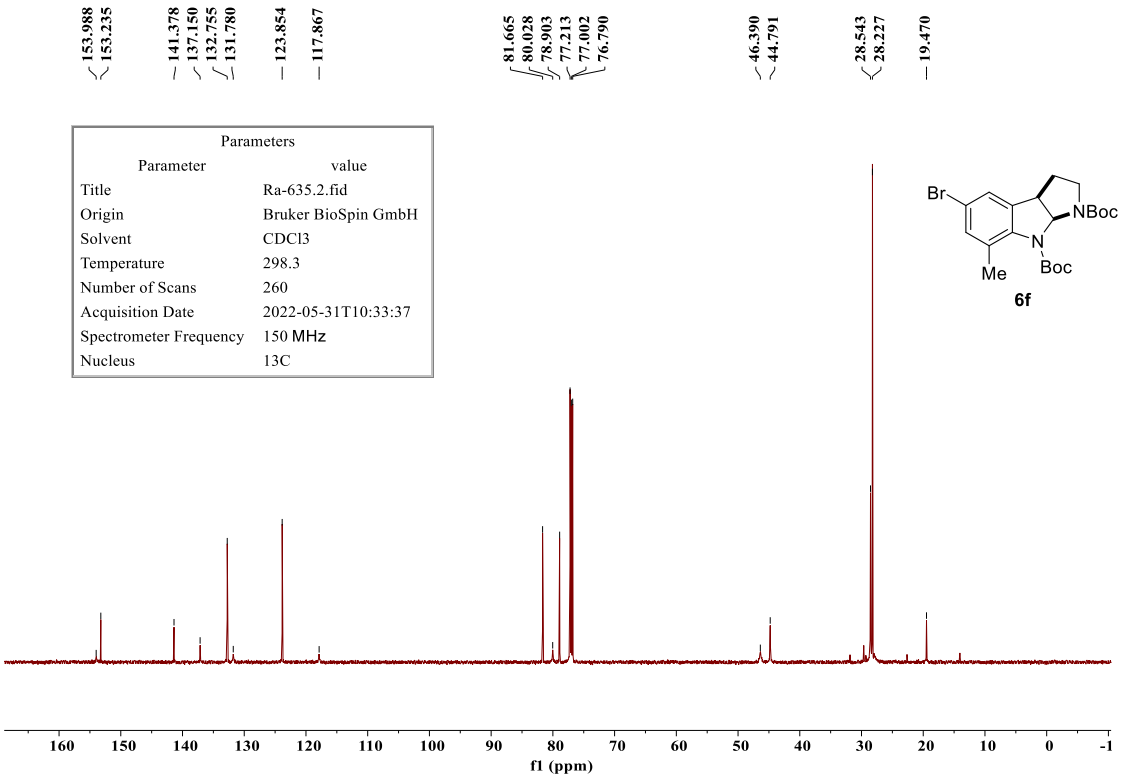

7.813
7.339
6.469
6.457
3.948
3.935
3.923
3.869
3.856
3.849
3.837
2.858
2.849
2.838
2.829
2.818
2.809
2.122
2.109
2.101
2.089
2.076
2.068
2.055
1.957
1.948
1.936
1.928
1.568
1.482
Parameter value
Title RV-0493.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.2
Number of Scans 8
Acquisition Date 2022-03-18T19:22:06
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
Cl
N
Boc
N
Boc
6d
0.97
1.00
1.09
1.07
1.02
1.00
1.04
1.03
9.23
9.18
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

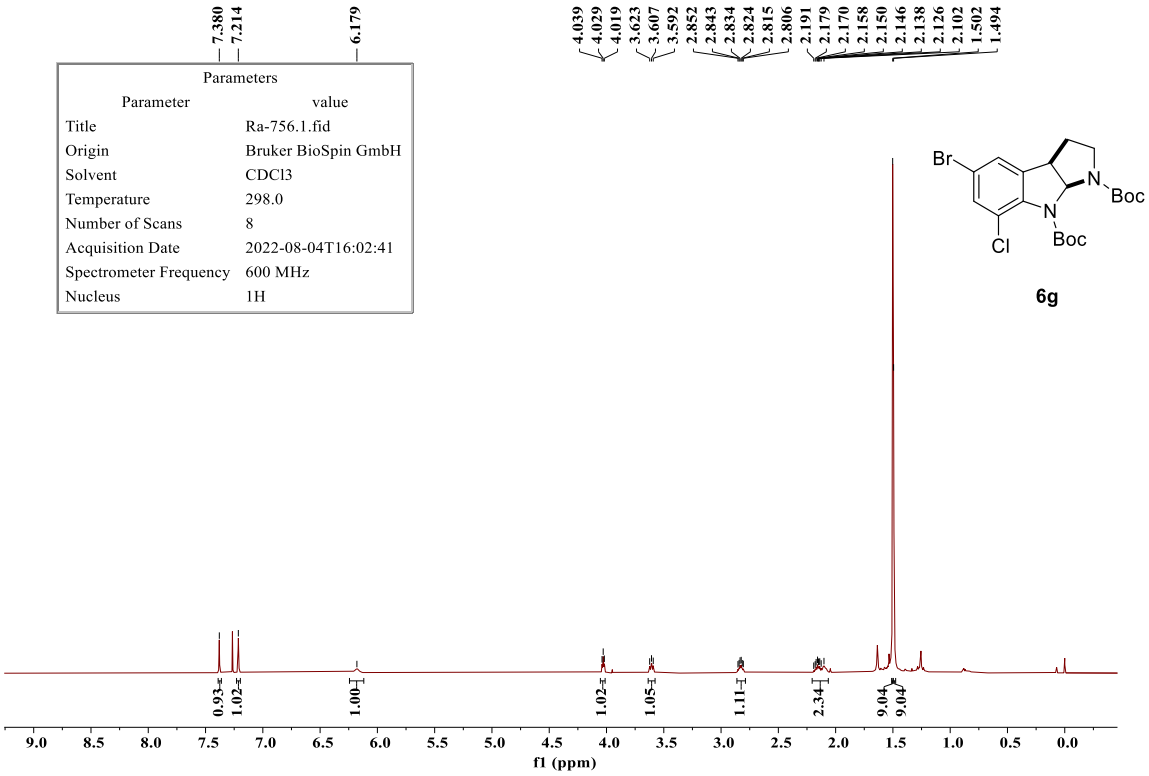

153.73
151.95
143.29
133.63
132.44
128.45
124.58
114.88
82.26
81.92
80.22
77.21
77.00
76.79
76.75
44.89
44.32
28.32
28.24
Parameter value
Title RV-0493.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.2
Number of Scans 800
Acquisition Date 2022-03-18T20:01:00
Spectrometer Frequency 150 MHz
Nucleus 13C
Br
Cl
N
Boc
N
Boc
6d
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

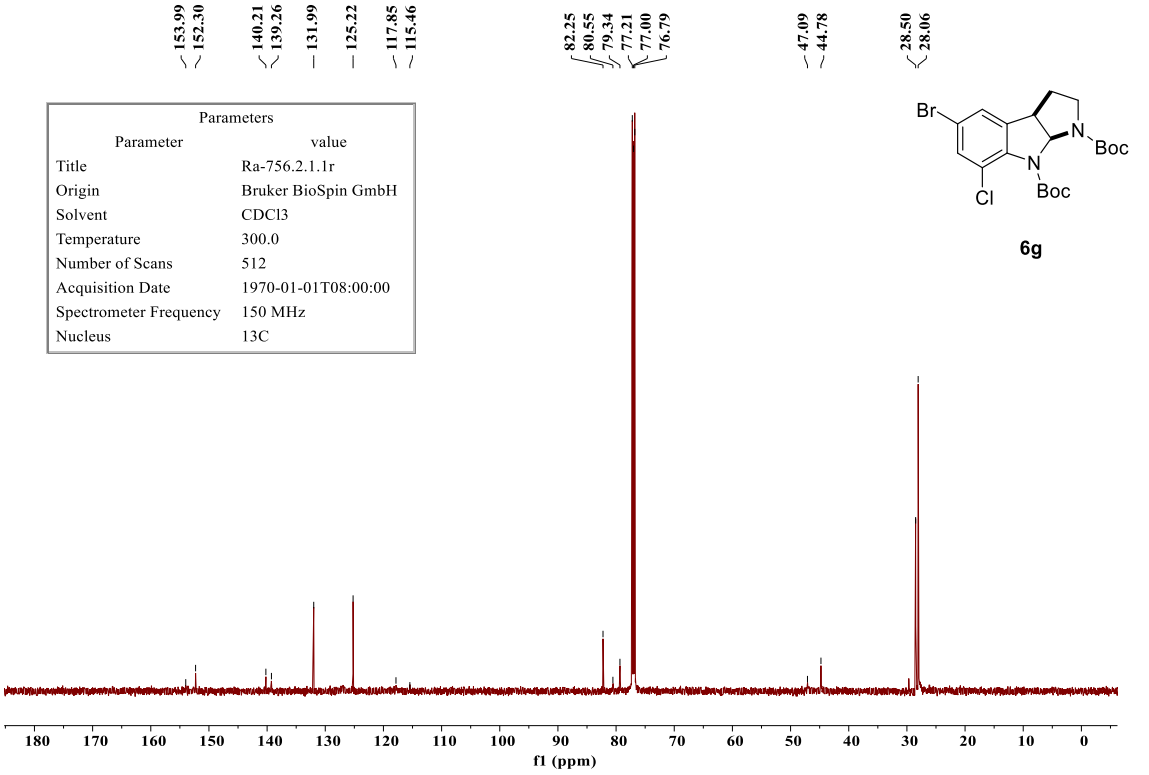

7.598
7.267
6.435
6.424
3.941
3.928
3.916
3.833
3.821
3.814
3.802
2.850
2.841
2.830
2.822
2.811
2.802
2.358
2.094
2.080
2.073
2.060
2.047
2.040
2.027
1.959
1.950
1.938
1.930
1.565
1.478
Parameter value
Title E-573qin.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-04-01T18:54:25
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
NBoc
Me
N
Boc
6e
1.07
1.07
1.00
1.02
1.04
1.09
3.01
1.12
1.00
9.07
9.16
f1 (ppm)

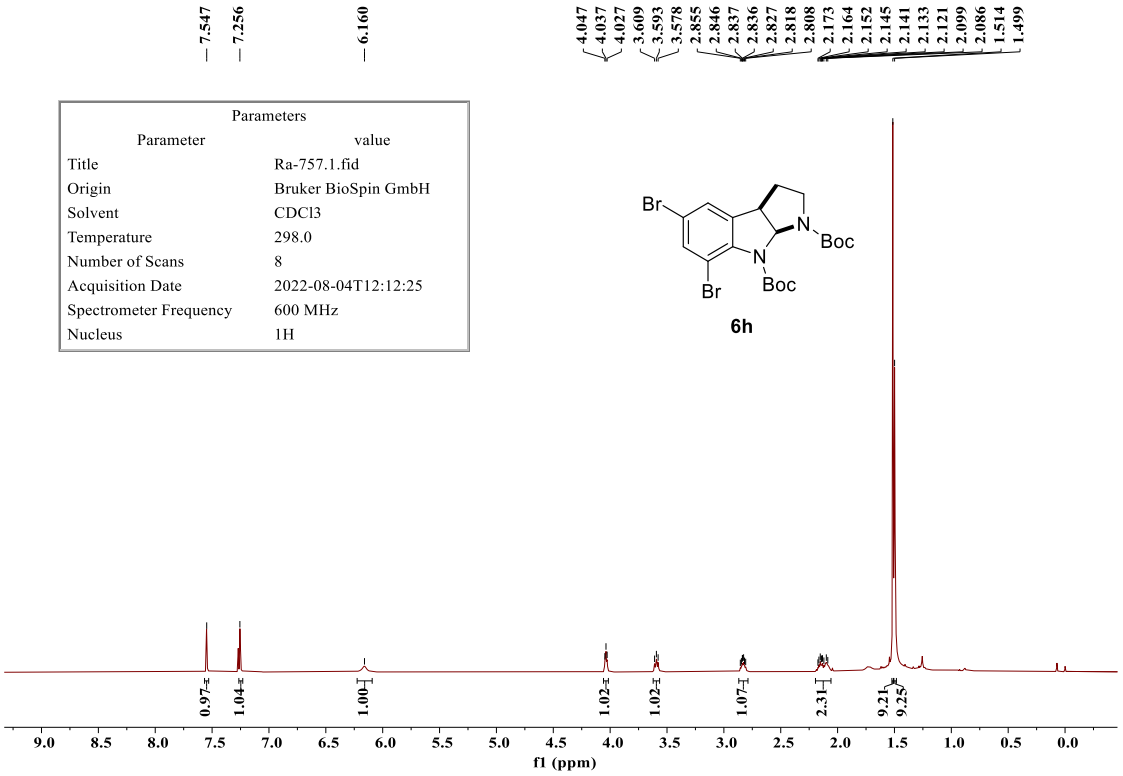

153.90
152.41
142.55
137.33
131.50
127.42
117.66
81.71
80.03
77.21
77.00
76.79
76.56
44.94
44.41
29.67
28.37
28.32
23.28
Parameter value
Title E-573.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 800
Acquisition Date 2022-04-04T10:05:39
Spectrometer Frequency 150 MHz
Nucleus 13C
Br
NBoc
Me
N
Boc
6e
f1 (ppm)

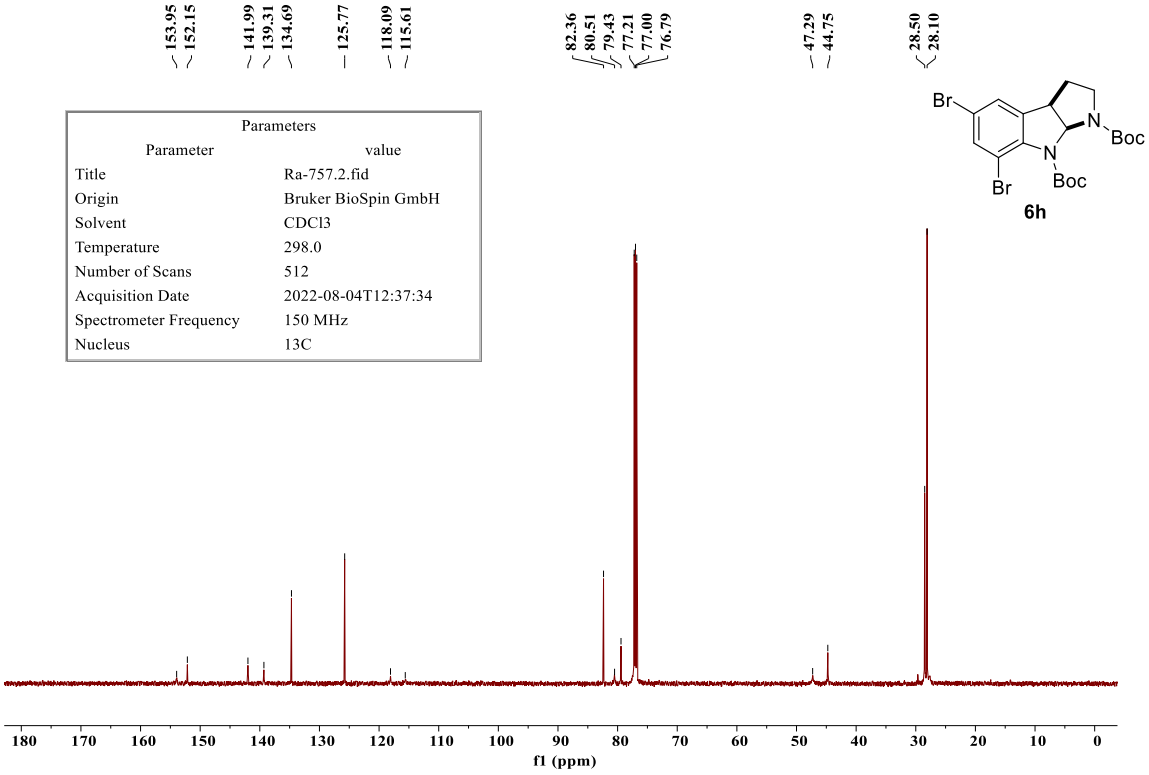

7.164
7.112
6.198
3.960
3.950
3.940
3.569
3.557
3.552
3.539
2.798
2.788
2.780
2.770
2.762
2.751
2.238
2.145
2.124
2.113
2.104
2.101
2.093
2.082
1.484
1.473
Parameters
Parameter value
Title Ra-635.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-05-31T01:22:50
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
NBoc
N
Me
Boc
6f
0.95
1.00
1.00
1.04
1.03
1.16
3.16
2.48
18.20
f1 (ppm)

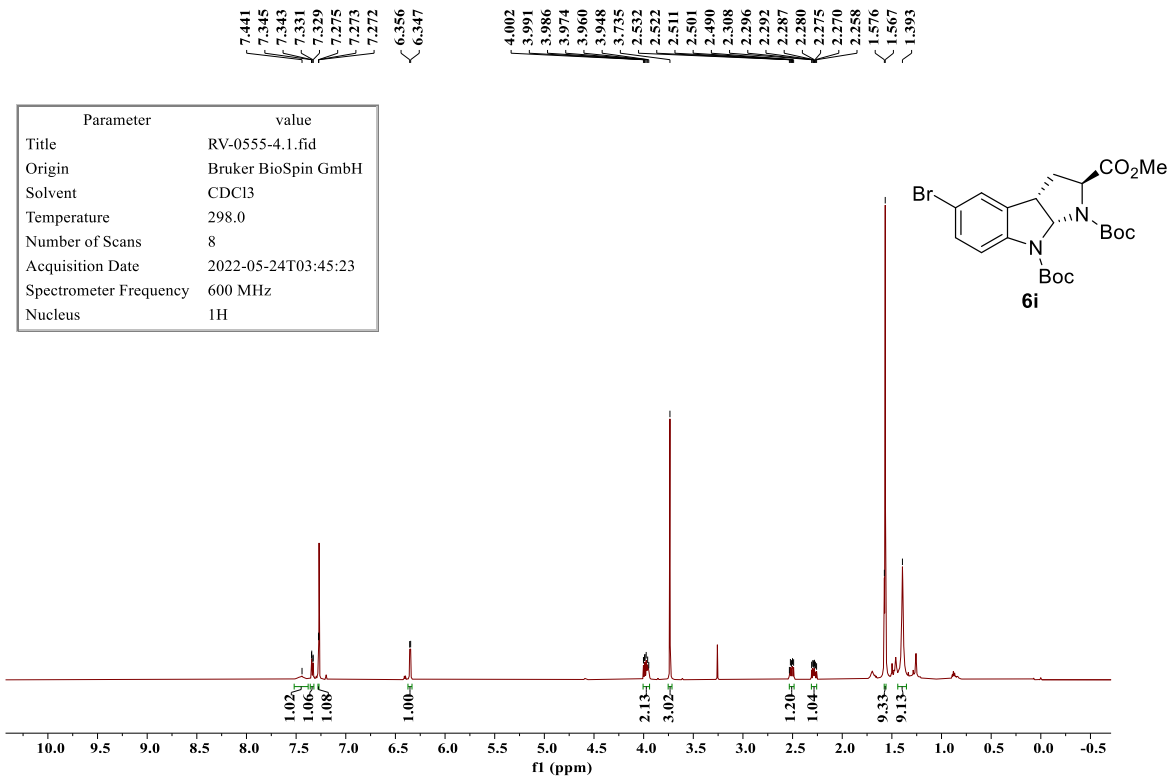

153.988
153.235
141.378
137.150
132.755
131.780
123.854
117.867
81.665
80.028
78.903
77.213
77.002
76.790
46.390
44.791
28.543
28.227
19.470
Parameters
Parameter value
Title Ra-635.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.3
Number of Scans 260
Acquisition Date 2022-05-31T10:33:37
Spectrometer Frequency 150 MHz
Nucleus 13C
Br
NBoc
N
Me
Boc
6f
f1 (ppm)

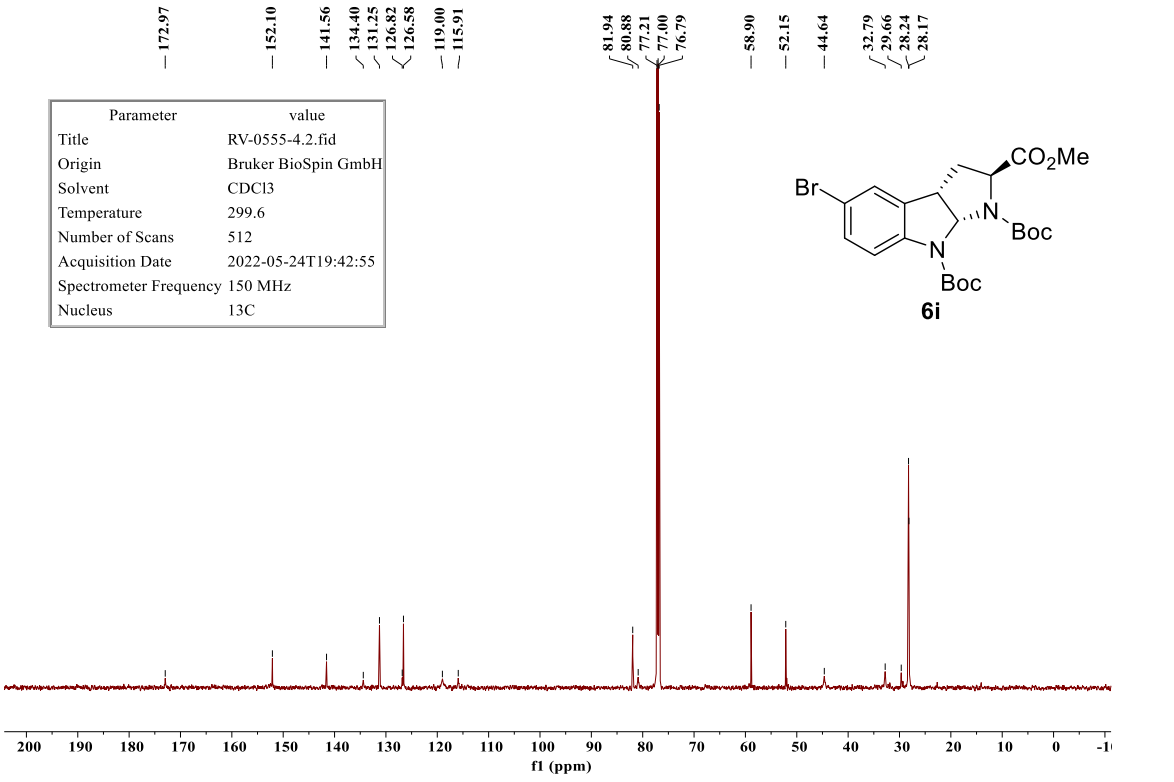

7.380
7.214
6.179
4.039
4.029
4.019
3.623
3.607
3.592
2.852
2.843
2.834
2.824
2.815
2.806
2.191
2.179
2.170
2.158
2.150
2.146
2.138
2.126
2.102
1.502
1.494
Parameters
Parameter value
Title Ra-756.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-08-04T16:02:41
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
N
Boc
N
Boc
Cl
6g
0.93
1.02
1.00
1.02
1.05
1.11
2.34
9.04
9.04
f1 (ppm)

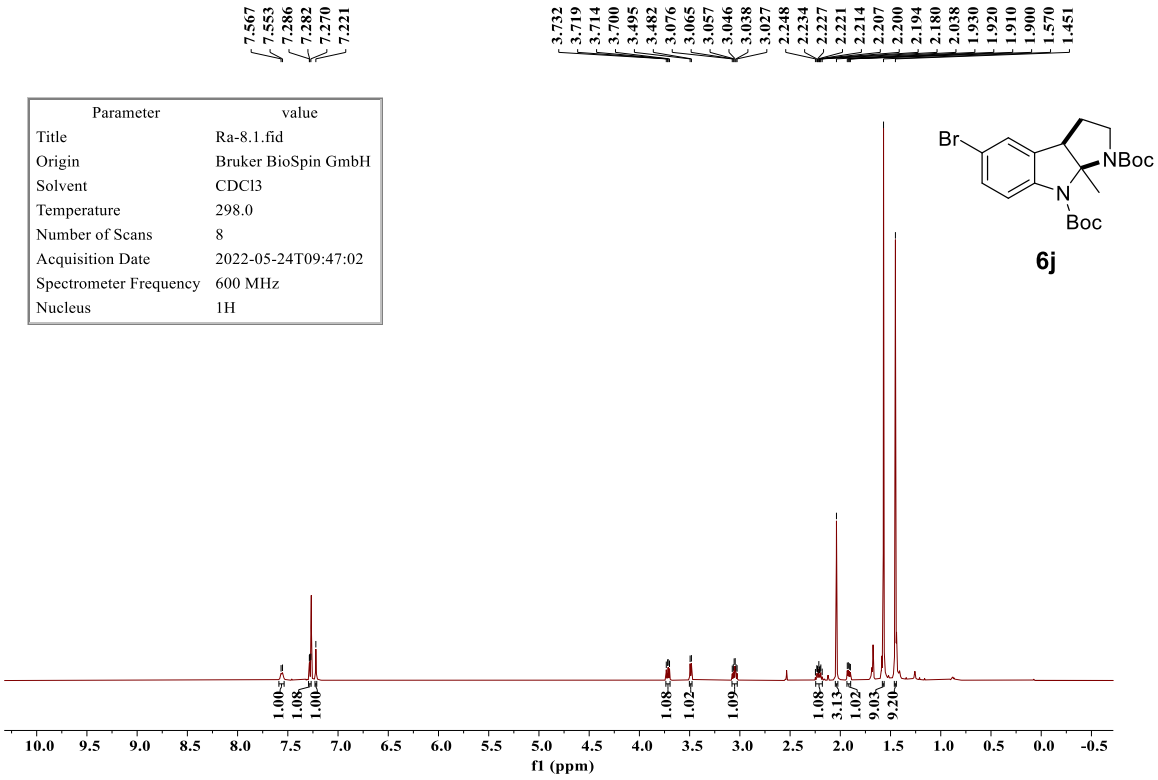

153.99
152.30
140.21
139.26
131.99
125.22
117.85
115.46
82.25
80.55
79.34
77.21
77.00
76.79
47.09
44.78
28.50
28.06
Parameters
Parameter value
Title Ra-756.2.1.1r
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 300.0
Number of Scans 512
Acquisition Date 1970-01-01T08:00:00
Spectrometer Frequency 150 MHz
Nucleus 13C
Br
N
Boc
N
Boc
Cl
6g
f1 (ppm)

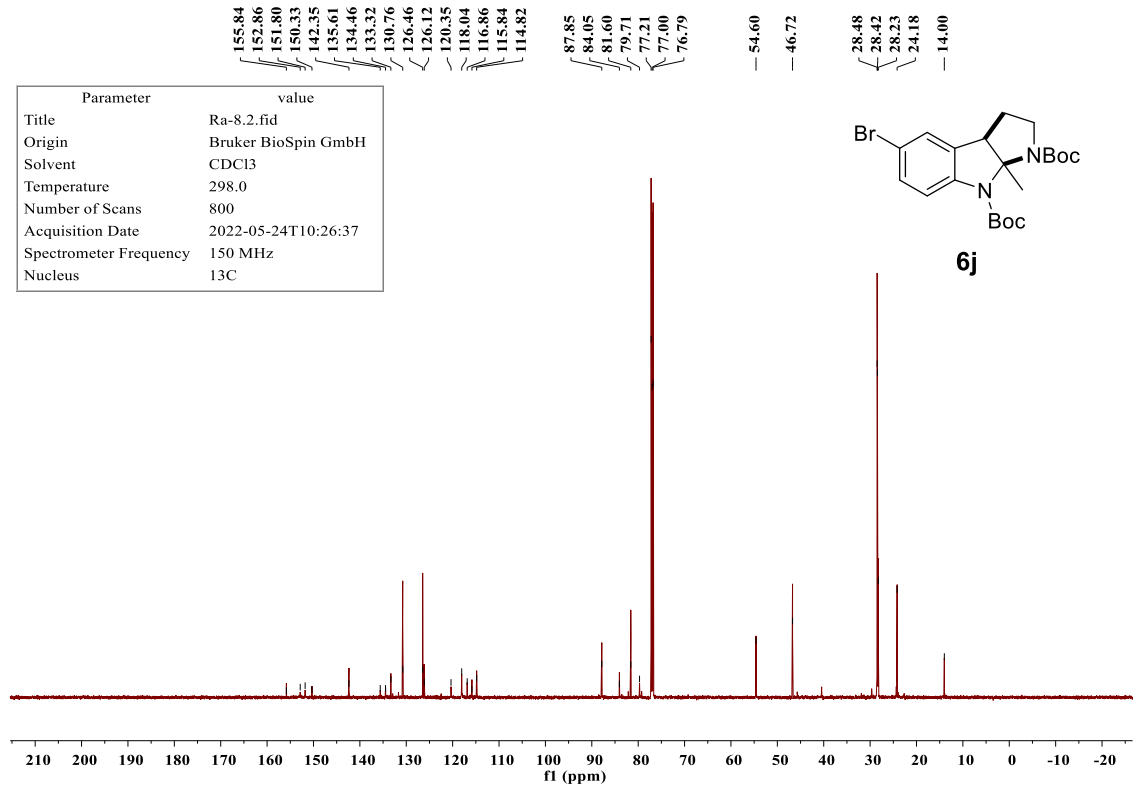

7.547
7.256
6.160
4.047
4.037
4.027
3.609
3.593
3.578
2.855
2.846
2.837
2.836
2.827
2.818
2.808
2.173
2.164
2.152
2.145
2.141
2.133
2.121
2.099
2.086
1.514
1.499
Parameters
Parameter value
Title Ra-757.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-08-04T12:12:25
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
N
Boc
N
Boc
Br
6h
0.97
1.04
1.00
1.02
1.02
1.07
2.31
9.21
9.25
f1 (ppm)

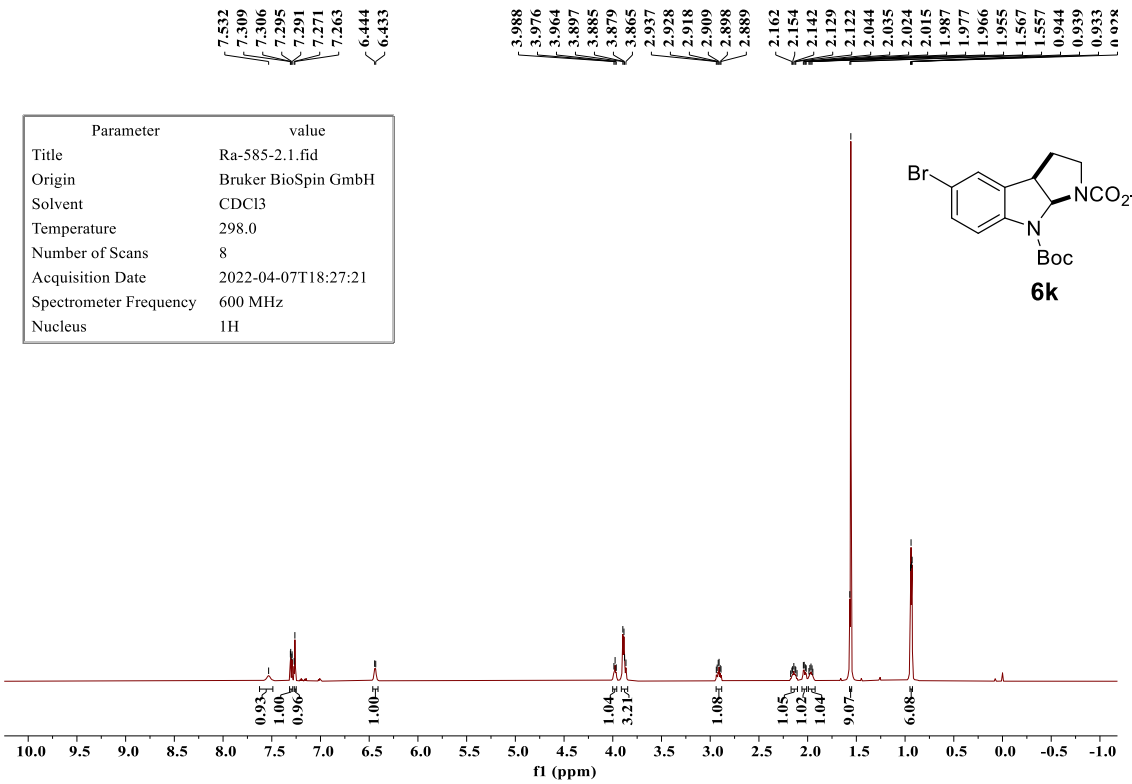

153.95
152.15
141.99
139.31
134.69
125.77
118.09
115.61
82.36
80.51
79.43
77.21
77.00
76.79
47.29
44.75
28.50
28.10
Parameters
Parameter value
Title Ra-757.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 512
Acquisition Date 2022-08-04T12:37:34
Spectrometer Frequency 150 MHz
Nucleus 13C
Br
N
Boc
N
Boc
Br
6h
f1 (ppm)

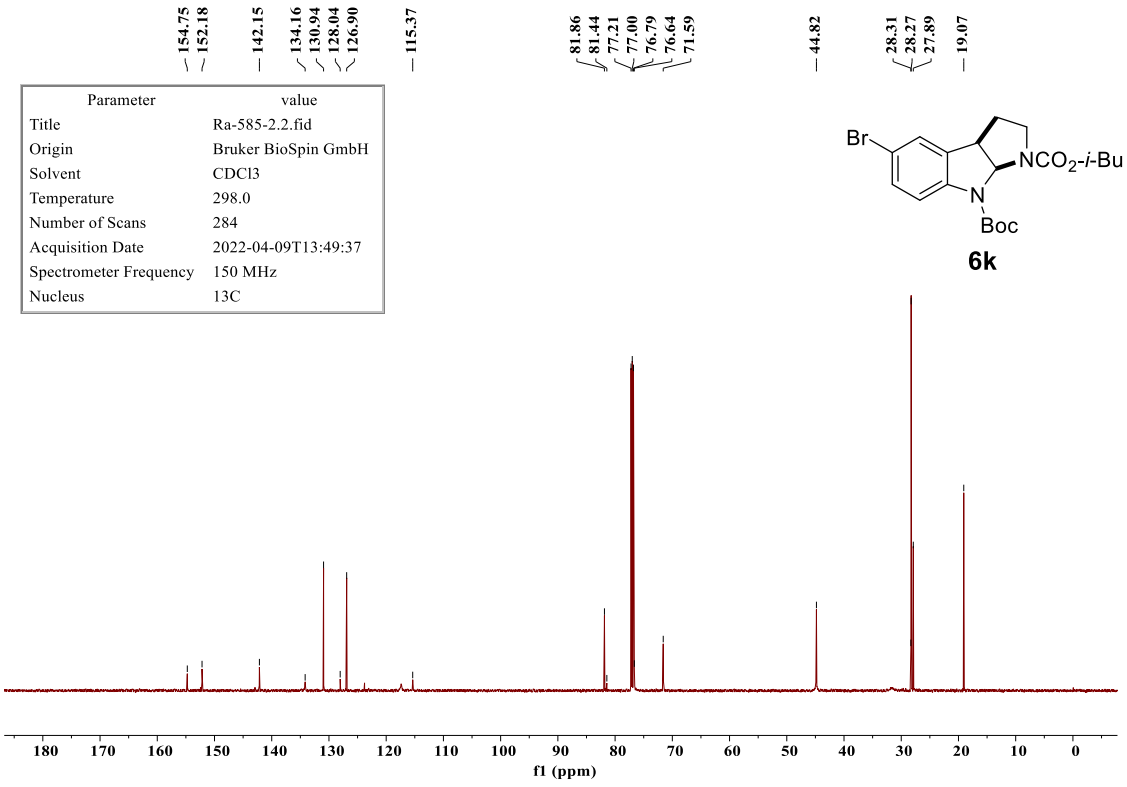

7.441
7.345
7.343
7.331
7.329
7.275
7.273
7.272
6.356
6.347
4.002
3.991
3.986
3.974
3.960
3.948
3.735
2.532
2.522
2.511
2.501
2.490
2.308
2.296
2.292
2.287
2.280
2.275
2.270
2.258
1.576
1.567
1.393
Parameter value
Title RV-0555-4.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-05-24T03:45:23
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
CO2Me
N
Boc
N
Boc
6i
1.02
1.06
1.08
1.00
2.13
3.02
1.20
1.04
9.33
9.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

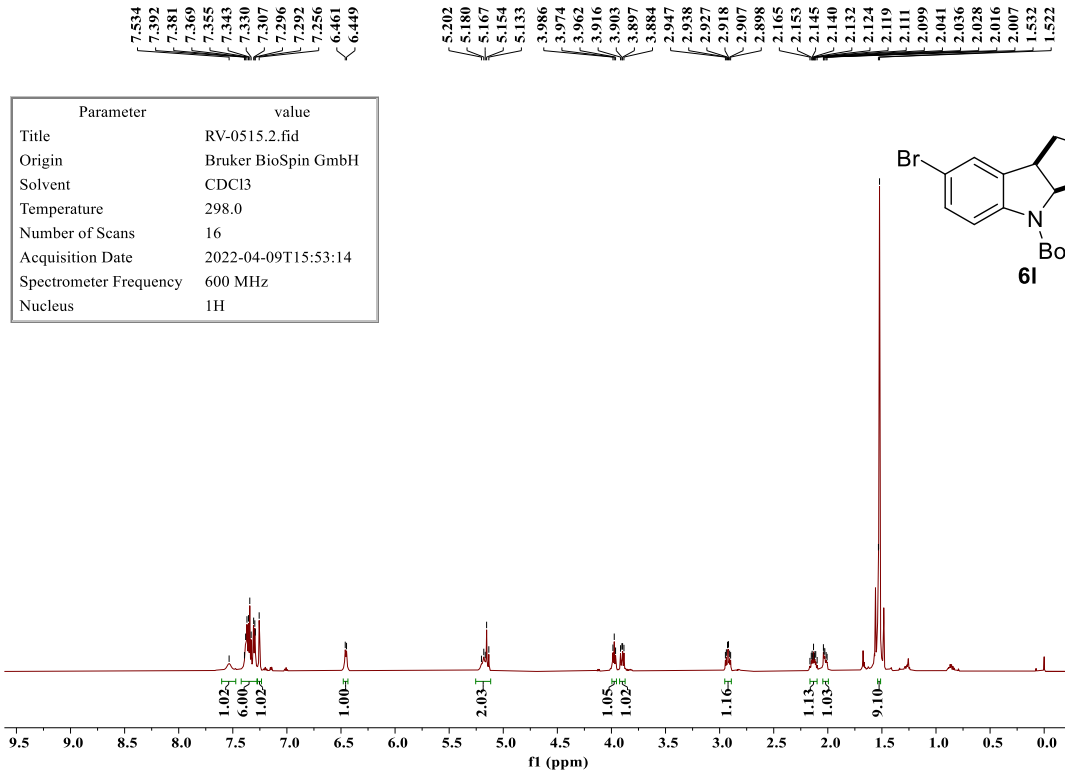

172.97
152.10
141.56
134.40
131.25
126.82
126.58
119.00
115.91
81.94
80.88
77.21
77.00
76.79
58.90
52.15
44.64
32.79
29.66
28.24
28.17
Parameter value
Title RV-0555-4.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 299.6
Number of Scans 512
Acquisition Date 2022-05-24T19:42:55
Spectrometer Frequency 150 MHz
Nucleus 13C
Br
CO2Me
N
Boc
N
Boc
6i
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

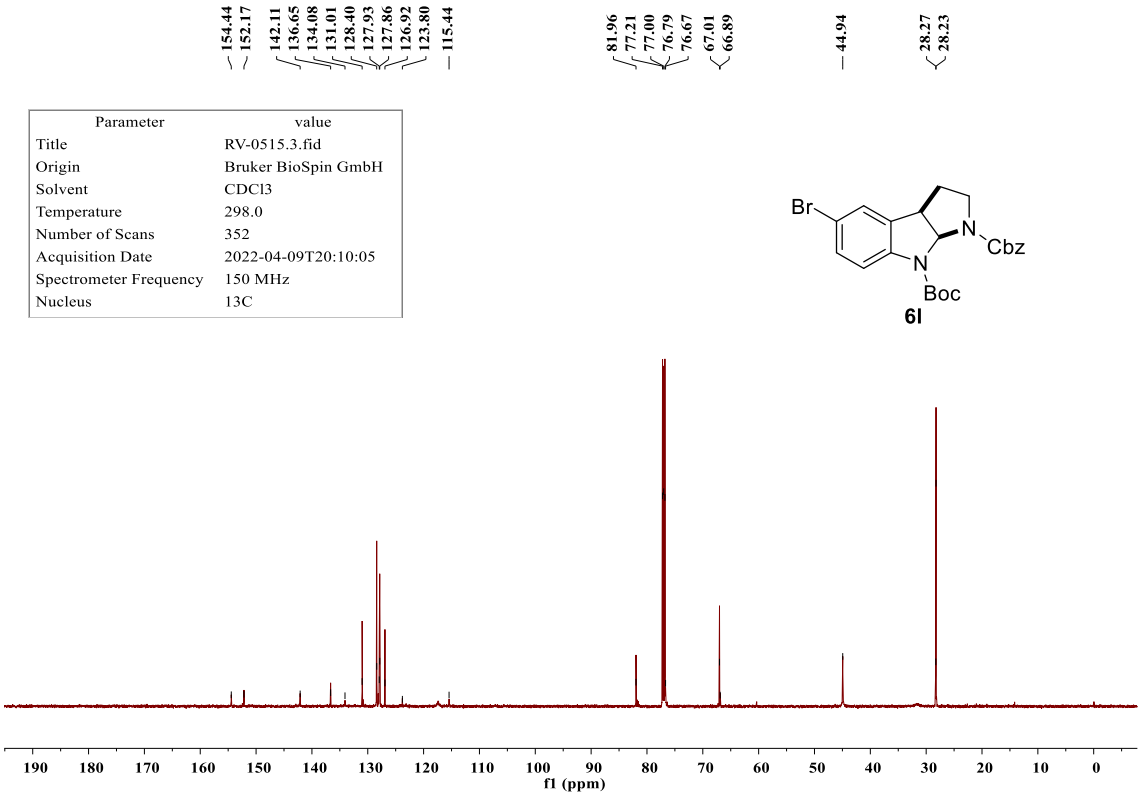

7.567
7.553
7.286
7.282
7.270
7.221
3.732
3.719
3.714
3.700
3.495
3.482
3.076
3.065
3.057
3.046
3.038
3.027
2.248
2.234
2.227
2.221
2.214
2.207
2.200
2.194
2.180
2.038
1.930
1.920
1.910
1.900
1.570
1.451
Parameter value
Title Ra-8.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-05-24T09:47:02
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
NBoc
N
Boc
6j
1.00
1.08
1.00
1.08
1.02
1.09
1.08
3.13
1.02
9.03
9.20
f1 (ppm)

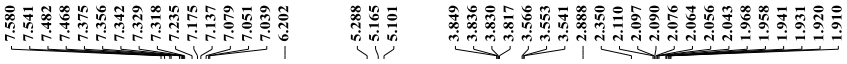

155.84
152.86
151.80
150.33
142.35
135.61
134.46
133.32
130.76
126.46
126.12
120.35
118.04
116.86
115.84
114.82
87.85
84.05
81.60
79.71
77.21
77.00
76.79
54.60
46.72
28.48
28.42
28.23
24.18
14.00
Parameter value
Title Ra-8.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 800
Acquisition Date 2022-05-24T10:26:37
Spectrometer Frequency 150 MHz
Nucleus 13C
Br
NBoc
N
Boc
6j
f1 (ppm)


7.532
7.309
7.306
7.295
7.291
7.271
7.263
6.444
6.433
3.988
3.976
3.964
3.897
3.885
3.879
3.865
2.937
2.928
2.918
2.909
2.898
2.889
2.162
2.154
2.142
2.129
2.122
2.044
2.035
2.024
2.015
1.987
1.977
1.966
1.955
1.567
1.557
0.944
0.939
0.933
0.928
Parameter value
Title Ra-585-2.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-04-07T18:27:21
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
NCO2-i-Bu
N
Boc
6k
0.93
1.00
0.96
1.00
1.04
3.21
1.08
1.05
1.02
1.04
9.07
6.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

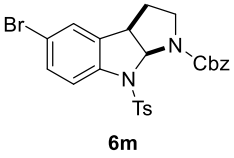

154.75
152.18
142.15
134.16
130.94
128.04
126.90
115.37
81.86
81.44
77.21
77.00
76.79
76.64
71.59
44.82
28.31
28.27
27.89
19.07
Parameter value
Title Ra-585-2.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 284
Acquisition Date 2022-04-09T13:49:37
Spectrometer Frequency 150 MHz
Nucleus 13C
Br
NCO2-i-Bu
N
Boc
6k
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.534
7.392
7.381
7.369
7.355
7.343
7.330
7.307
7.296
7.292
7.256
6.461
6.449
5.202
5.180
5.167
5.154
5.133
3.986
3.974
3.962
3.916
3.903
3.897
3.884
2.947
2.938
2.927
2.918
2.907
2.898
2.165
2.153
2.145
2.140
2.132
2.124
2.119
2.111
2.099
2.041
2.036
2.028
2.016
2.007
1.532
1.522
Parameter value
Title RV-0515.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 16
Acquisition Date 2022-04-09T15:53:14
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
N
Cbz
N
Boc
6l
1.02
6.00
1.02
1.00
2.03
1.05
1.02
1.16
1.13
1.03
9.10
f1 (ppm)

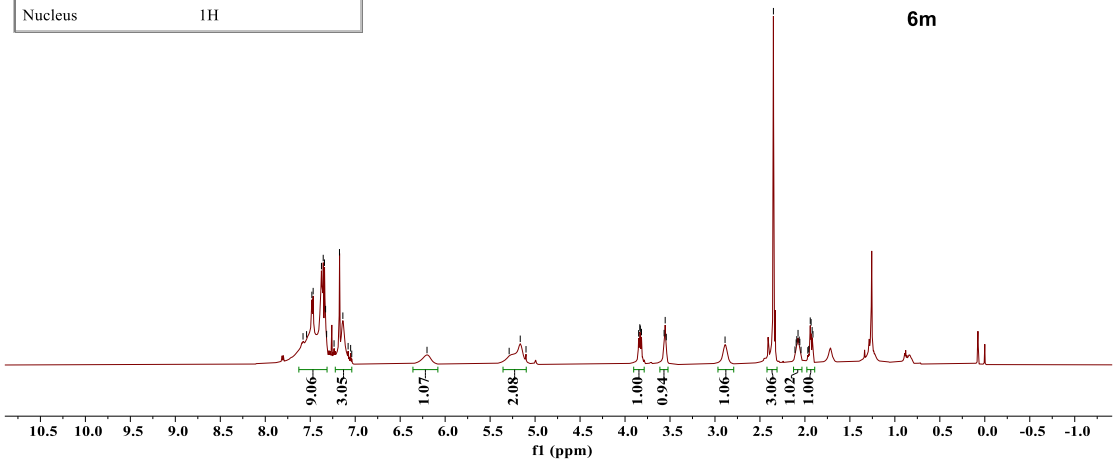

154.44
152.17
142.11
136.65
134.08
131.01
128.40
127.93
127.86
126.92
123.80
115.44
81.96
77.21
77.00
76.79
76.67
67.01
66.89
44.94
28.27
28.23
Parameter value
Title RV-0515.3.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 352
Acquisition Date 2022-04-09T20:10:05
Spectrometer Frequency 150 MHz
Nucleus 13C
Br
N
Cbz
N
Boc
6l
f1 (ppm)

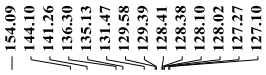


Parameter	value
Title	RV-0518-4.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	8
Acquisition Date	2022-05-01T05:45:12
Spectrometer Frequency	600 MHz
Nucleus	1H

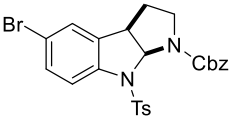


6m

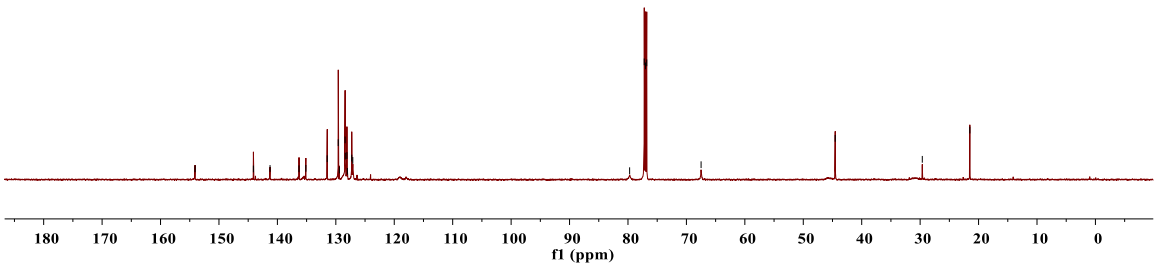


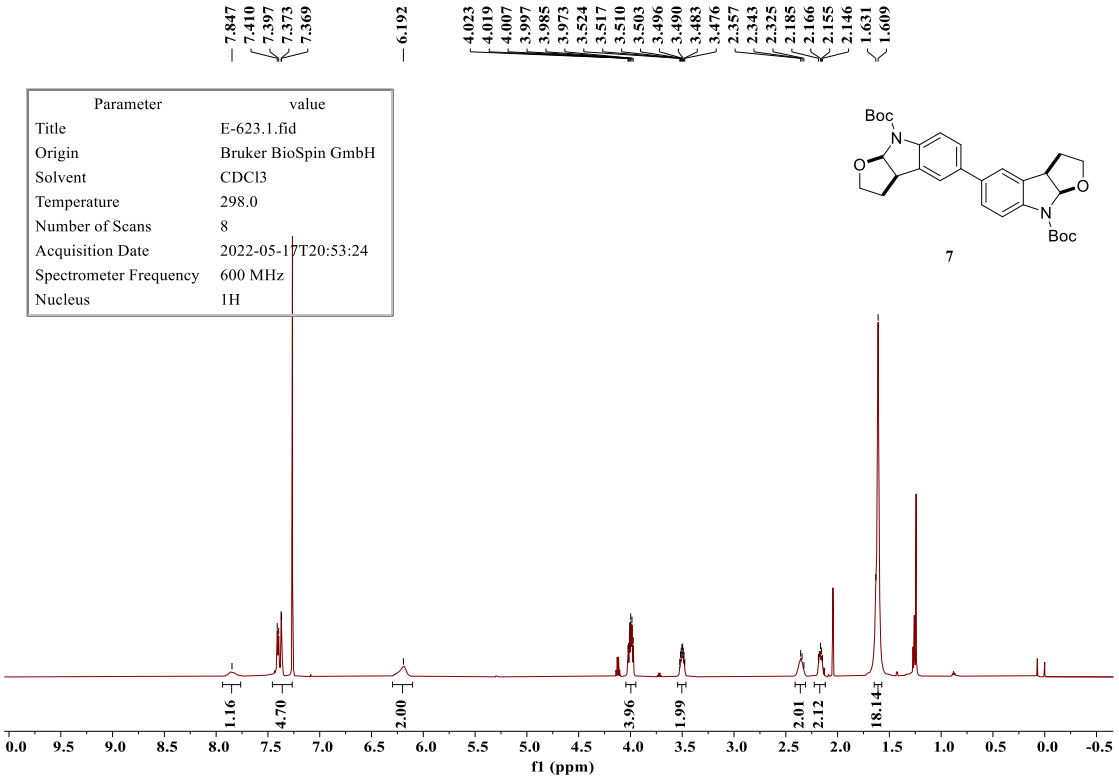


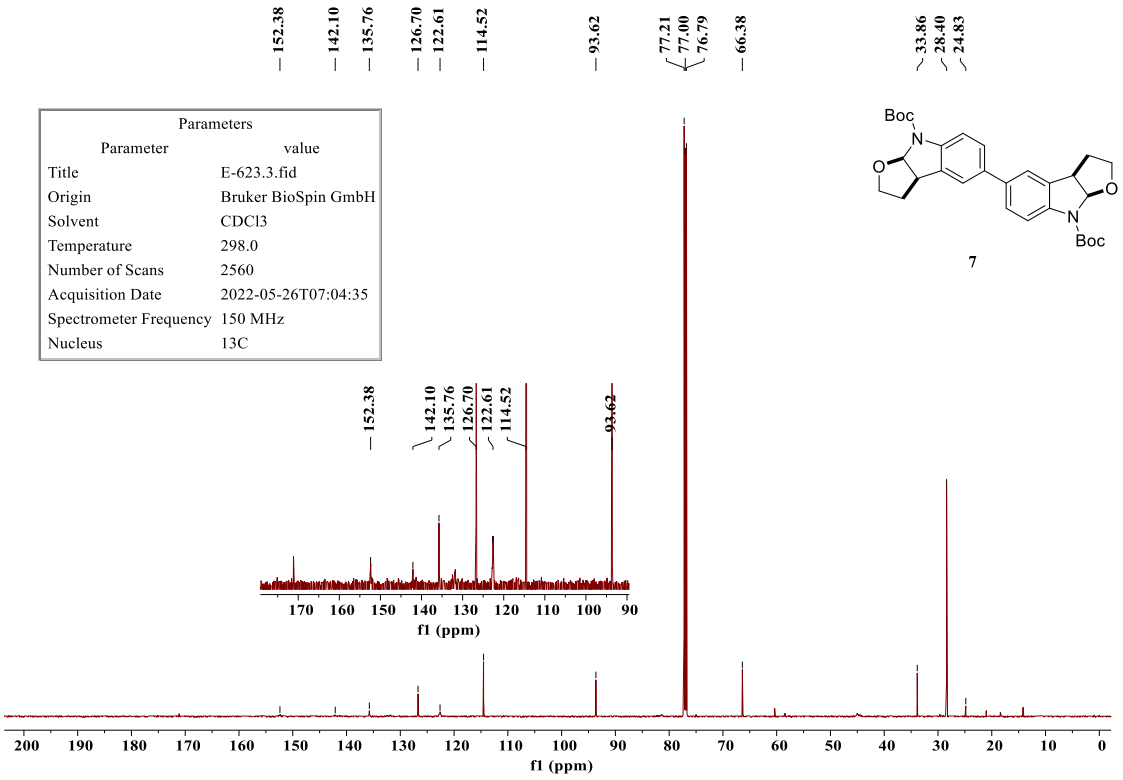
Parameter	value
Title	RV-0518-4.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	800
Acquisition Date	2022-05-01T06:24:07
Spectrometer Frequency	150 MHz
Nucleus	13C

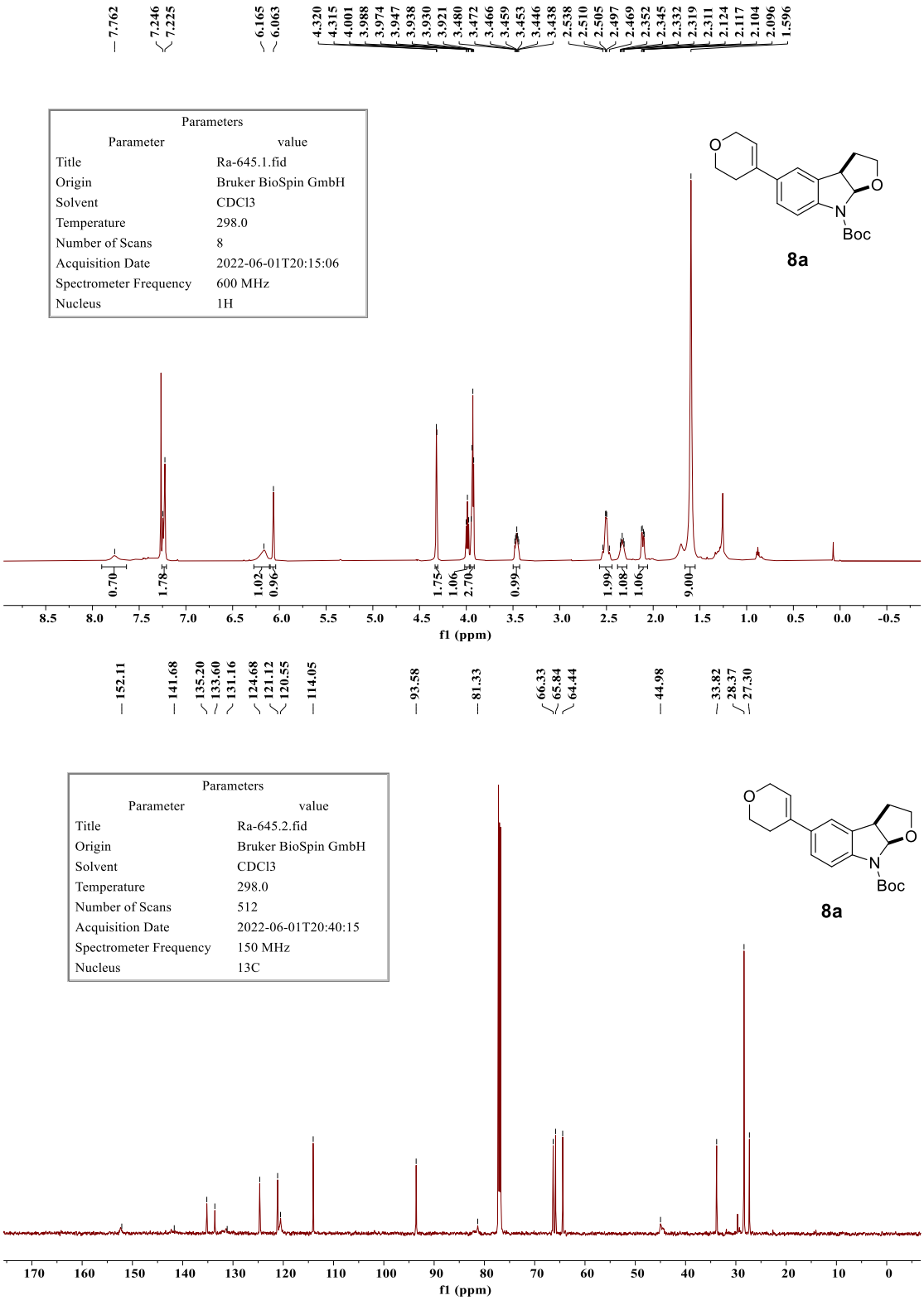


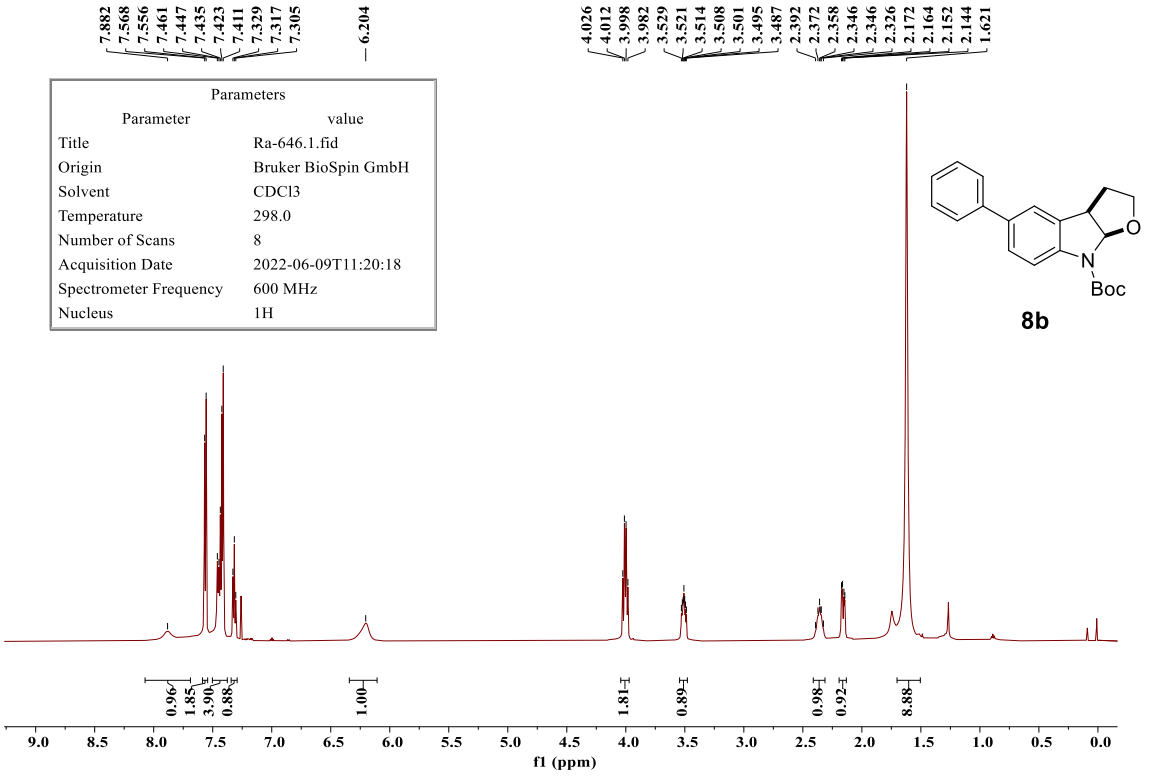
6m

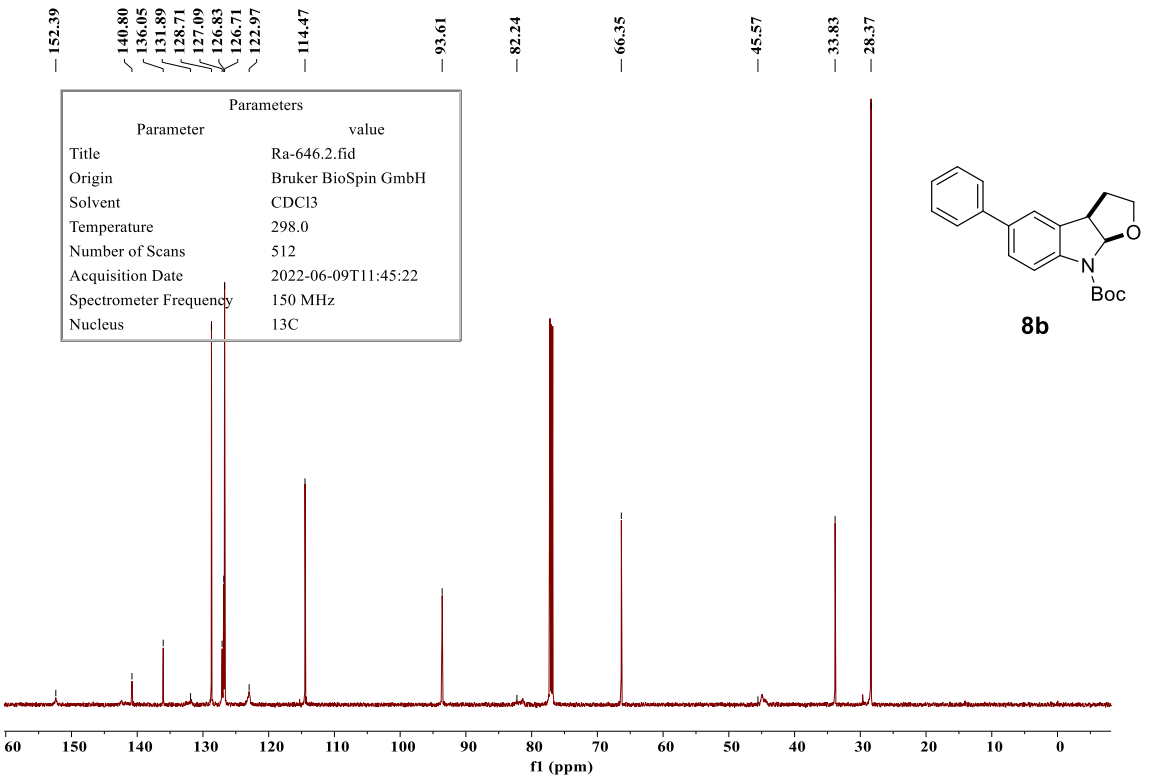


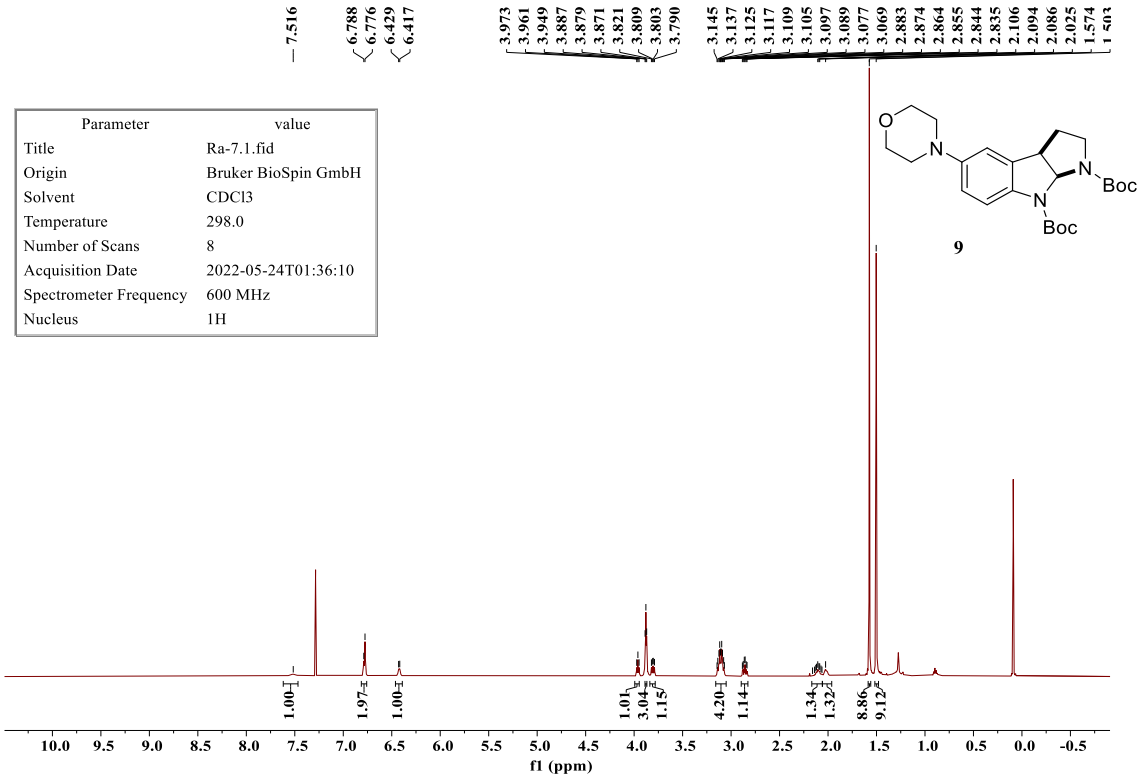

7.847
7.410
7.397
7.373
7.369
6.192
4.023
4.019
4.007
3.997
3.985
3.973
3.524
3.517
3.510
3.503
3.496
3.490
3.483
3.476
2.357
2.343
2.325
2.185
2.166
2.155
2.146
1.631
1.609
Parameter value
Title E-623.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-05-17T20:53:24
Spectrometer Frequency 600 MHz
Nucleus 1H
Boc
N
O
O
N
Boc
7
1.16
4.70
2.00
3.96
1.99
2.01
2.12
18.14
f1 (ppm)

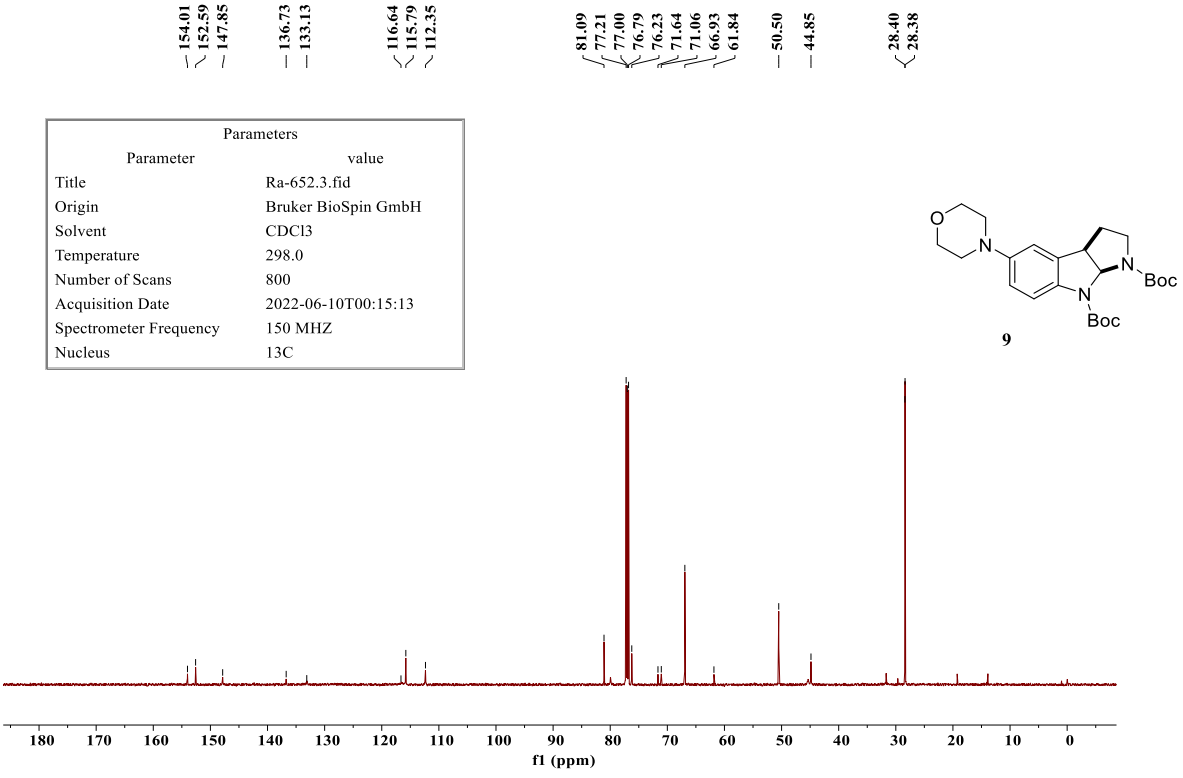

152.38
142.10
135.76
126.70
122.61
114.52
93.62
77.21
77.00
76.79
66.38
33.86
28.40
24.83
Parameters
Parameter value
Title E-623.3.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 2560
Acquisition Date 2022-05-26T07:04:35
Spectrometer Frequency 150 MHz
Nucleus 13C
Boc
N
O
O
N
Boc
7
f1 (ppm)

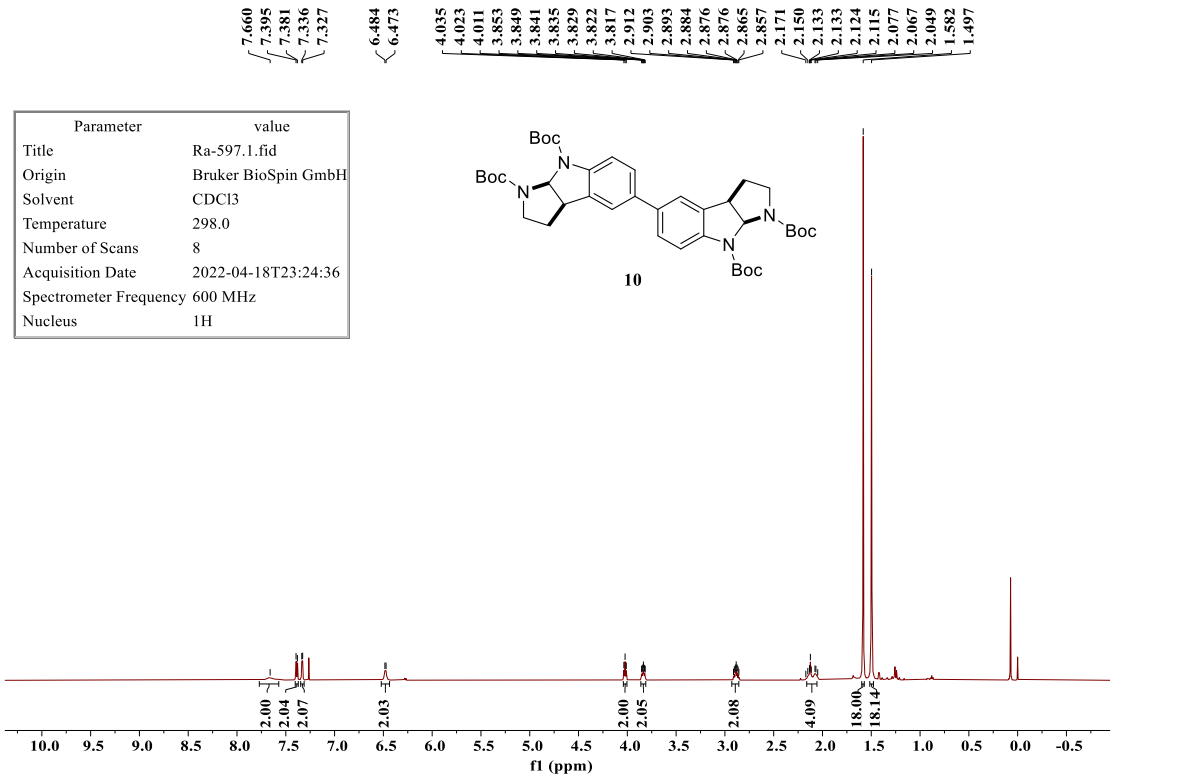

7.762
7.246
7.225
6.165
6.063
4.320
4.315
4.001
3.988
3.974
3.947
3.938
3.930
3.921
3.480
3.472
3.466
3.459
3.453
3.446
3.438
2.538
2.510
2.505
2.497
2.469
2.352
2.345
2.332
2.319
2.311
2.124
2.117
2.104
2.096
1.596
Parameters
Parameter value
Title Ra-645.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-06-01T20:15:06
Spectrometer Frequency 600 MHz
Nucleus 1H
O
O
N
Boc
8a
0.70
1.78
1.02
0.96
1.75
1.06
2.70
0.99
1.99
1.08
1.06
9.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
152.11
141.68
135.20
133.60
131.16
124.68
121.12
120.55
114.05
93.58
81.33
66.33
65.84
64.44
44.98
33.82
28.37
27.30
Parameters
Parameter value
Title Ra-645.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 512
Acquisition Date 2022-06-01T20:40:15
Spectrometer Frequency 150 MHz
Nucleus 13C
O
O
N
Boc
8a
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

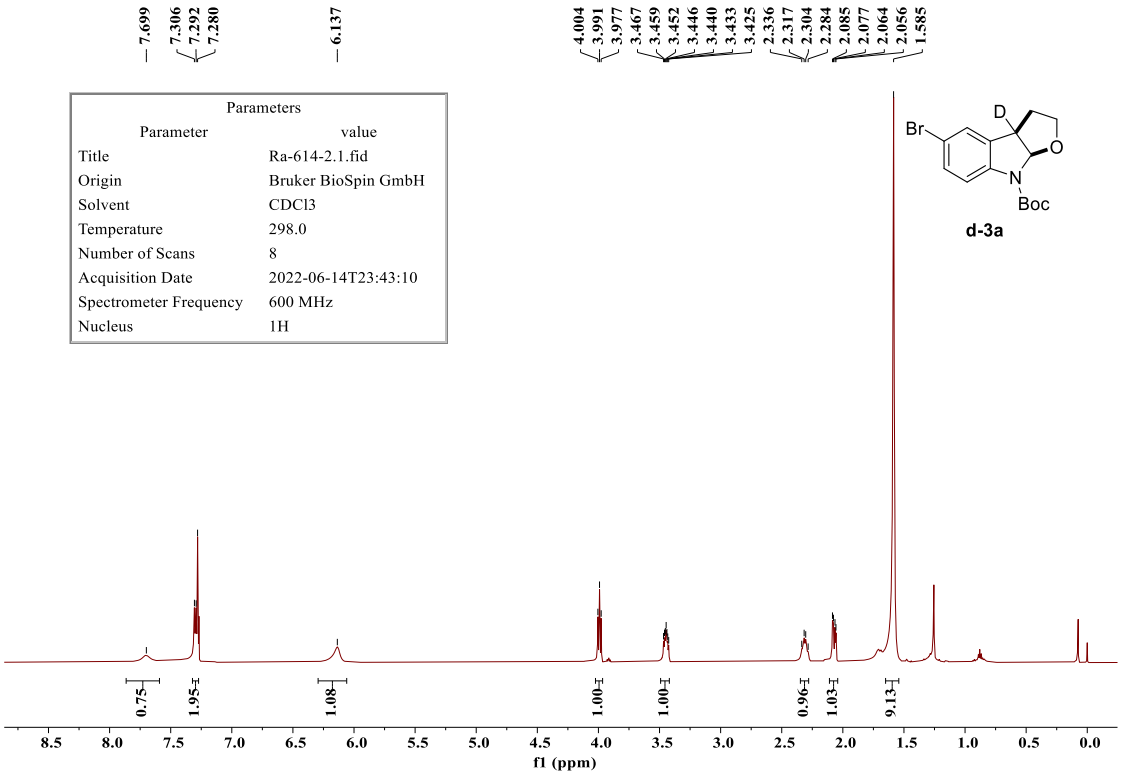

7.882
7.568
7.556
7.461
7.447
7.435
7.423
7.411
7.329
7.317
7.305
6.204
4.026
4.012
3.998
3.982
3.529
3.521
3.514
3.508
3.501
3.495
3.487
2.392
2.372
2.358
2.346
2.346
2.326
2.172
2.164
2.152
2.144
1.621
Parameters
Parameter value
Title Ra-646.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-06-09T11:20:18
Spectrometer Frequency 600 MHz
Nucleus 1H
O
N
Boc
8b
0.96
1.85
3.90
0.88
1.00
1.81
0.89
0.98
0.92
8.88
f1 (ppm)

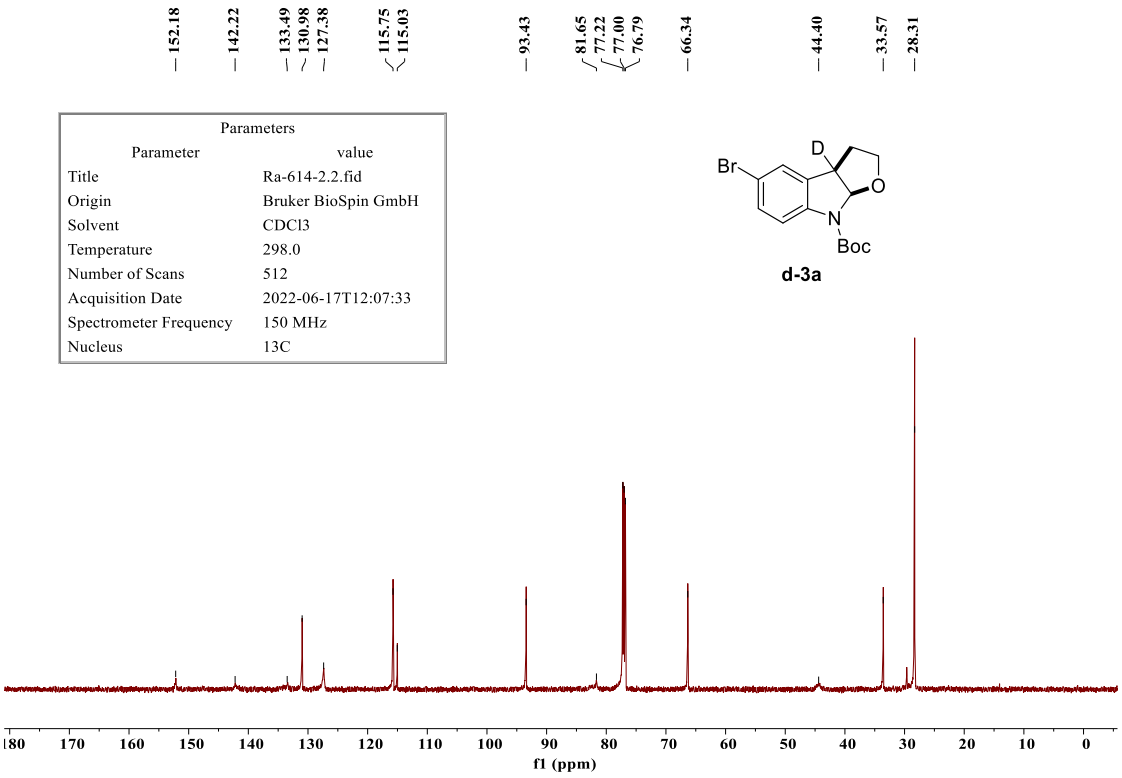

152.39
140.80
136.05
131.89
128.71
127.09
126.83
126.71
122.97
114.47
93.61
82.24
66.35
45.57
33.83
28.37
Parameters
Parameter value
Title Ra-646.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 512
Acquisition Date 2022-06-09T11:45:22
Spectrometer Frequency 150 MHz
Nucleus 13C
O
N
Boc
8b
f1 (ppm)

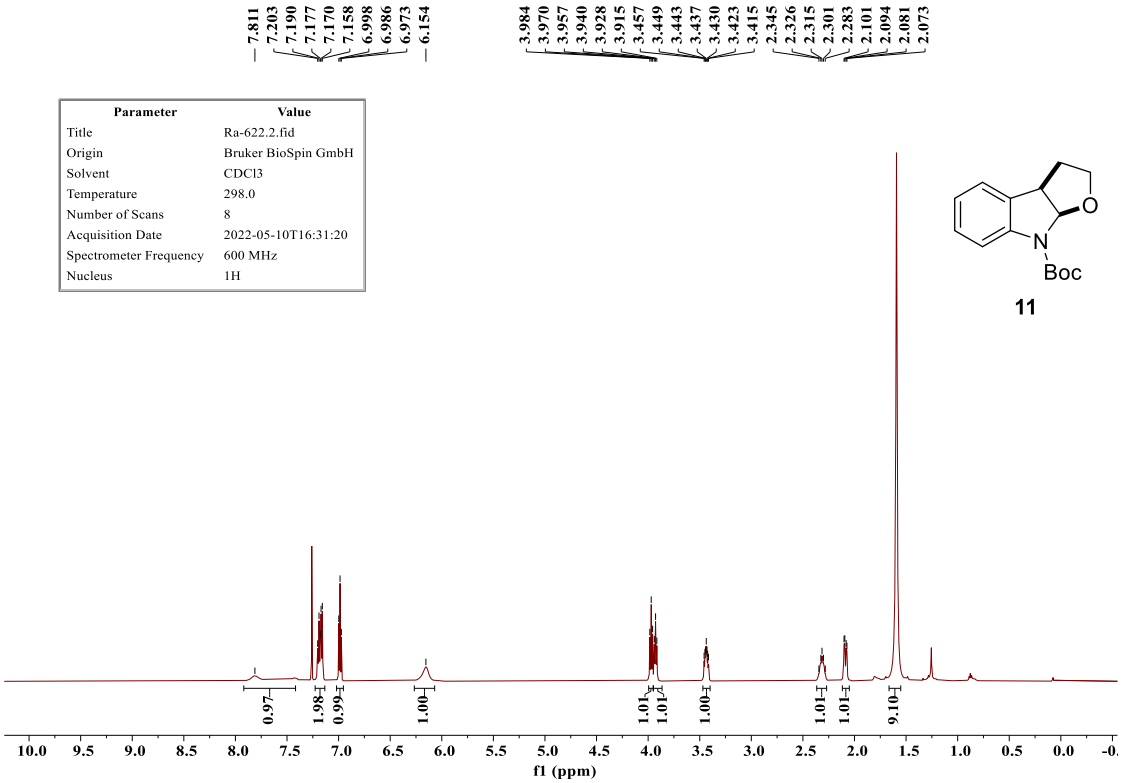

7.516
6.788
6.776
6.429
6.417
3.973
3.961
3.949
3.887
3.879
3.871
3.821
3.809
3.803
3.790
3.145
3.137
3.125
3.117
3.109
3.105
3.097
3.089
3.077
3.069
2.883
2.874
2.864
2.855
2.844
2.835
2.106
2.094
2.086
2.025
1.574
Parameter value
Title Ra-7.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-05-24T01:36:10
Spectrometer Frequency 600 MHz
Nucleus 1H
O
N
N
Boc
N
Boc
9
1.00
1.97
1.00
1.01
3.04
1.15
4.20
1.14
1.34
1.32
8.86
9.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

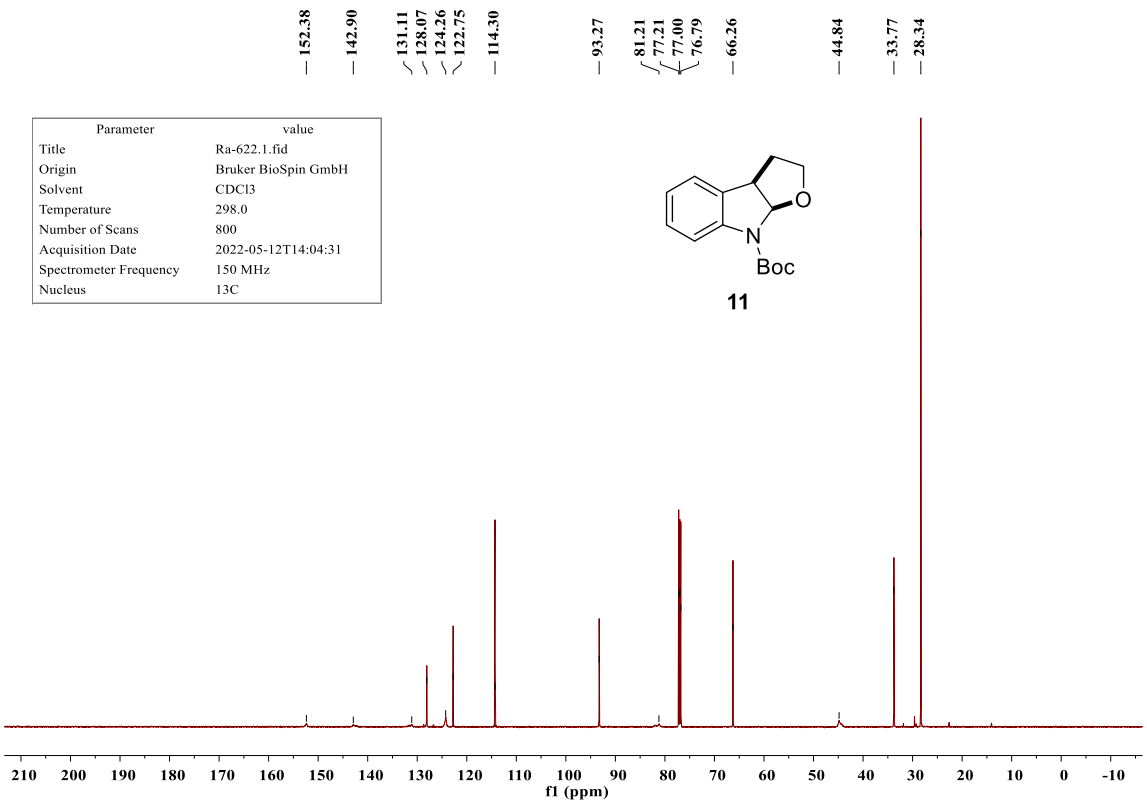

154.01
152.59
147.85
136.73
133.13
116.64
115.79
112.35
81.09
77.21
77.00
76.79
76.23
71.64
71.06
66.93
61.84
50.50
44.85
28.40
28.38
Parameters
Parameter value
Title Ra-652.3.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 800
Acquisition Date 2022-06-10T00:15:13
Spectrometer Frequency 150 MHZ
Nucleus 13C
O
N
N
Boc
N
Boc
9
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

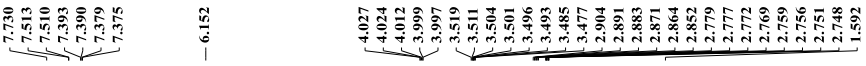

7.660
7.395
7.381
7.336
7.327
6.484
6.473
4.035
4.023
4.011
3.853
3.849
3.841
3.835
3.829
3.822
3.817
2.912
2.903
2.893
2.884
2.876
2.876
2.865
2.857
2.171
2.150
2.133
2.133
2.124
2.115
2.077
2.067
2.049
1.582
1.497
Parameter value
Title Ra-597.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-04-18T23:24:36
Spectrometer Frequency 600 MHz
Nucleus 1H
Boc
N
Boc
N
Boc
N
Boc
10
2.00
2.04
2.07
2.03
2.00
2.05
2.08
4.09
18.00
18.14
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
144.68
143.33
134.28
128.75
125.95
120.58
120.56
116.74
80.97
79.68
77.19
77.00
76.81
76.49
48.84
34.29
10.21
Parameter value
Title Ra-597.2.1.1r
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 300.0
Number of Scans 800
Acquisition Date 1970-01-01T08:00:00
Spectrometer Frequency 150 MHz
Nucleus 13C
Boc
N
Boc
N
Boc
N
Boc
10
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.699
7.306
7.292
7.280
6.137
4.004
3.991
3.977
3.467
3.459
3.452
3.446
3.440
3.433
3.425
2.336
2.317
2.304
2.284
2.085
2.077
2.064
2.056
1.585
Parameters
Parameter value
Title Ra-614-2.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-06-14T23:43:10
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
D
O
N
Boc
d-3a
0.75
1.95
1.08
1.00
1.00
0.96
1.03
9.13
f1 (ppm)

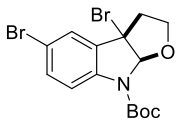

152.18
142.22
133.49
130.98
127.38
115.75
115.03
93.43
81.65
77.22
77.00
76.79
66.34
44.40
33.57
28.31
Parameters
Parameter value
Title Ra-614-2.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 512
Acquisition Date 2022-06-17T12:07:33
Spectrometer Frequency 150 MHz
Nucleus 13C
Br
D
O
N
Boc
d-3a
f1 (ppm)


7.811
7.203
7.190
7.177
7.170
7.158
6.998
6.986
6.973
6.154
3.984
3.970
3.957
3.940
3.928
3.915
3.457
3.449
3.443
3.437
3.430
3.423
3.415
2.345
2.326
2.315
2.301
2.283
2.101
2.094
2.081
2.073
Parameter Value
Title Ra-622.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-05-10T16:31:20
Spectrometer Frequency 600 MHz
Nucleus 1H
O
N
Boc
11
0.97
1.98
0.99
1.00
1.01
1.01
1.00
1.01
1.01
9.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

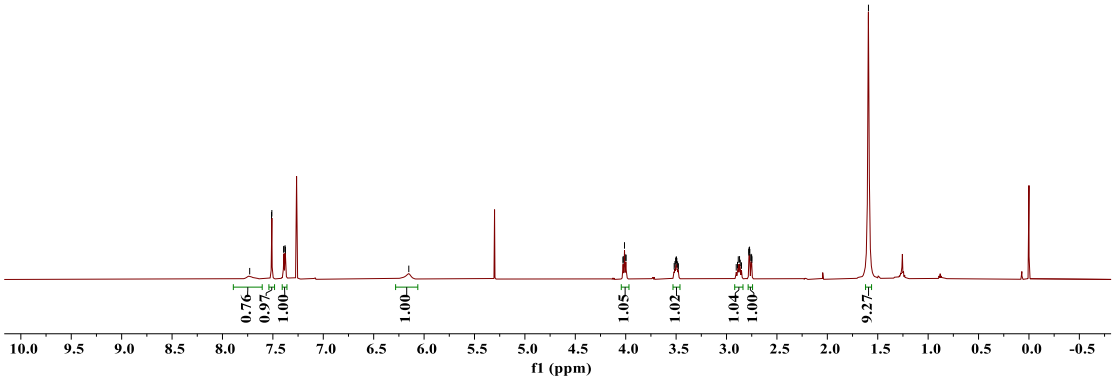

152.38
142.90
131.11
128.07
124.26
122.75
114.30
93.27
81.21
77.21
77.00
76.79
66.26
44.84
33.77
28.34
Parameter value
Title Ra-622.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 800
Acquisition Date 2022-05-12T14:04:31
Spectrometer Frequency 150 MHz
Nucleus 13C
O
N
Boc
11
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

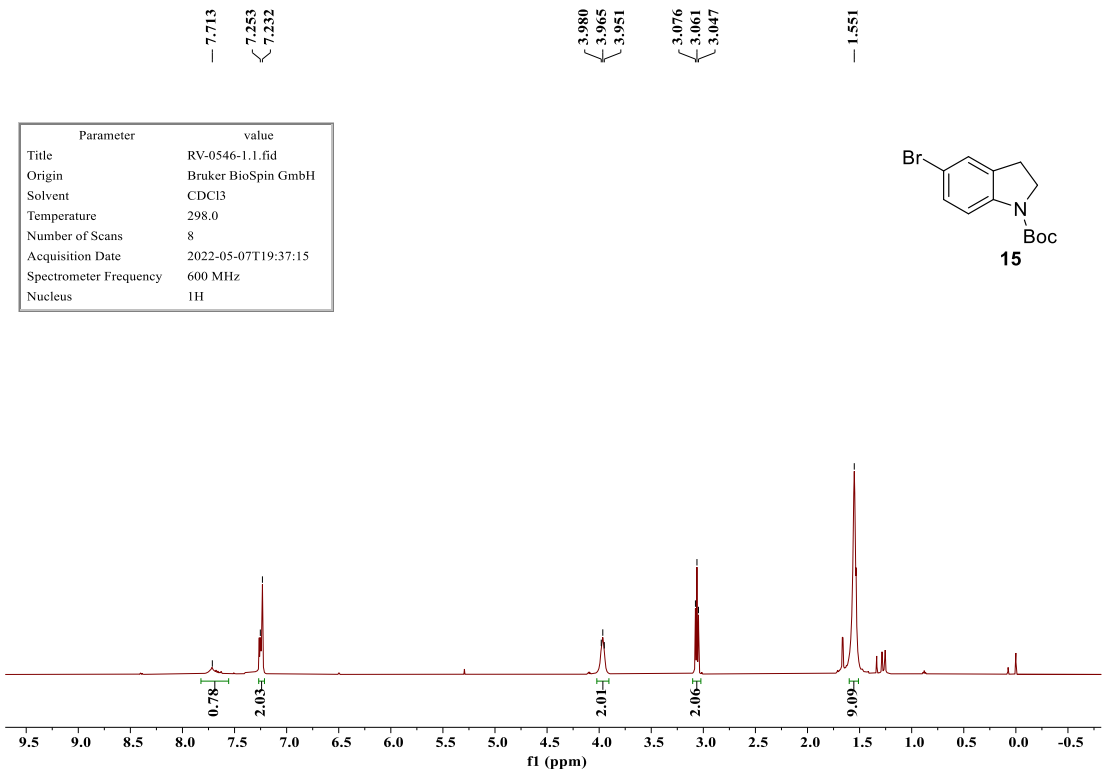


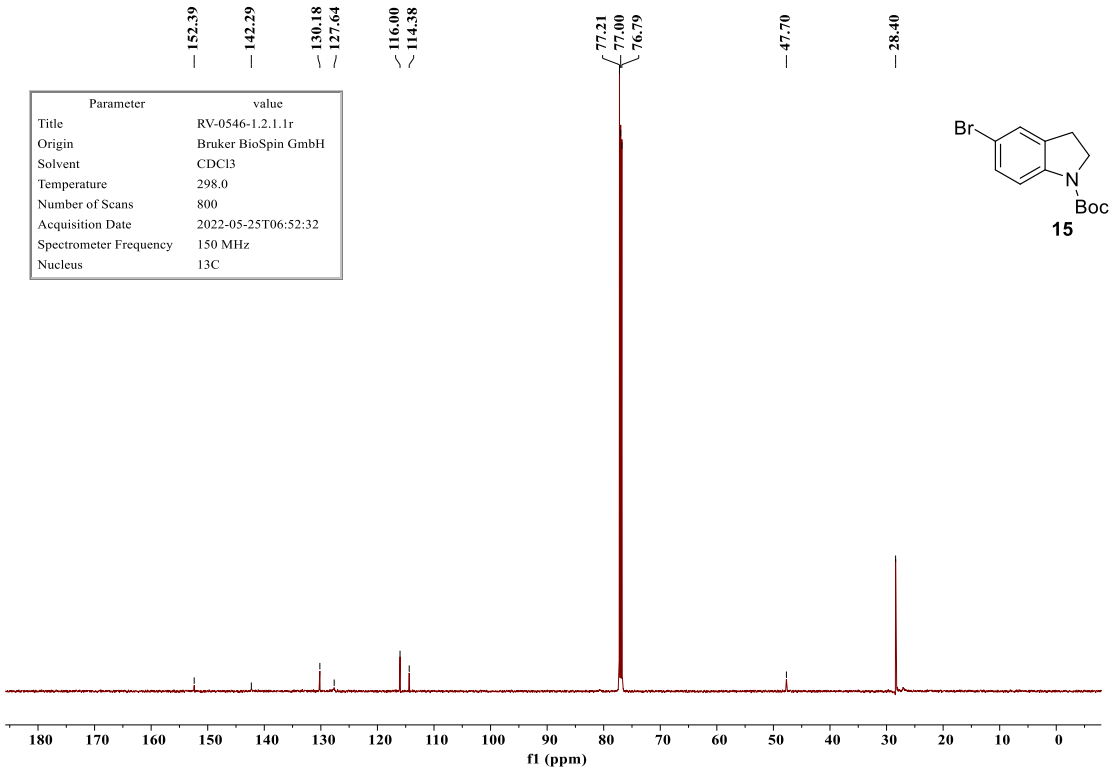
Parameter	Value
Title	E-614
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	8
Acquisition Date	2022-05-07T19:25:25
Spectrometer Frequency	600 MHz
Nucleus	1H

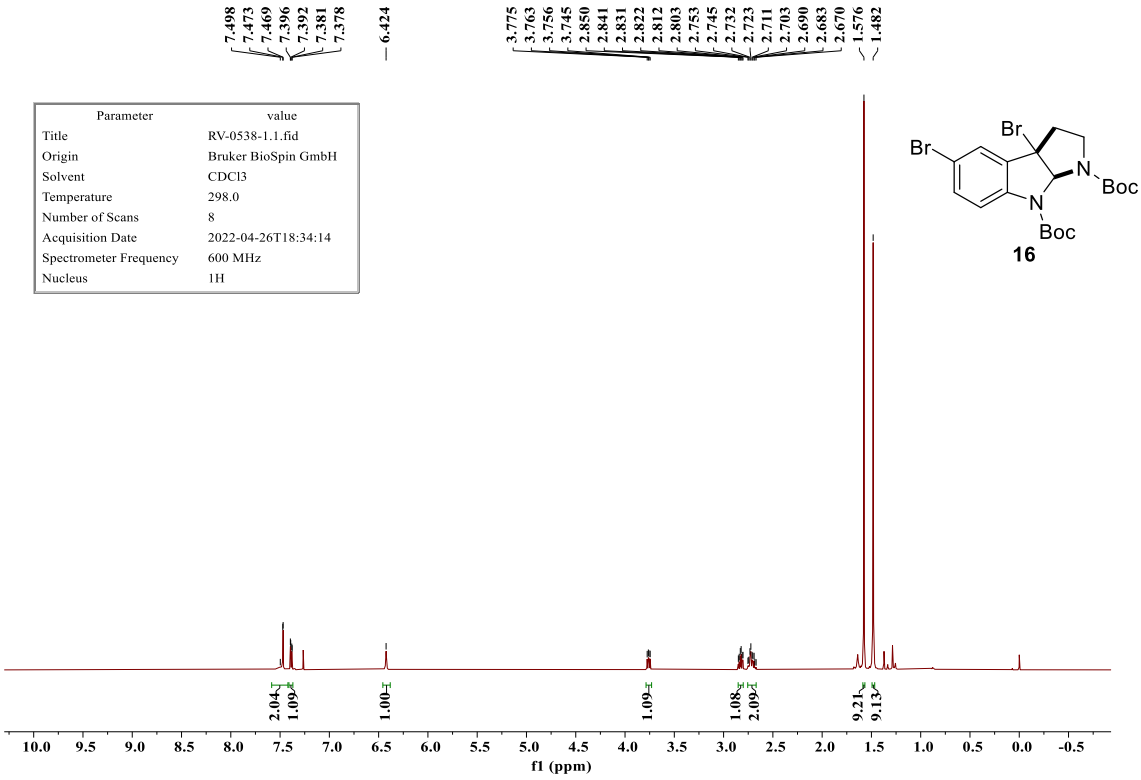


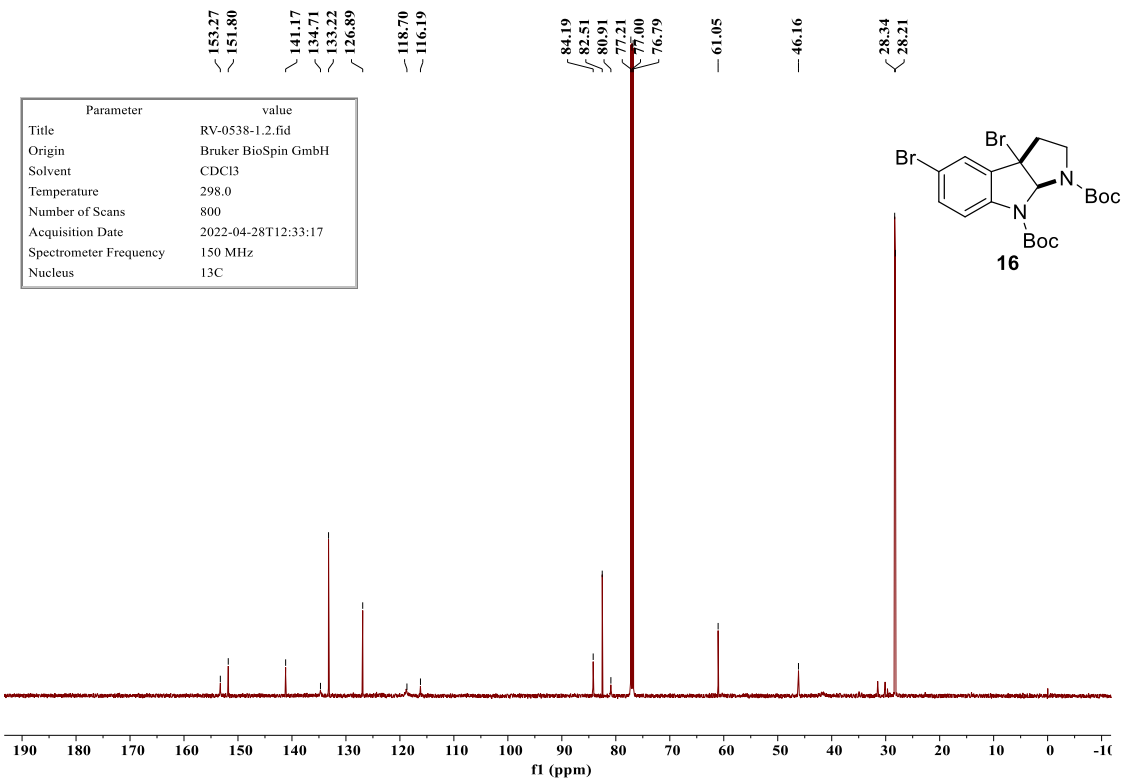
12




7.713
7.253
7.232
3.980
3.965
3.951
3.076
3.061
3.047
1.551
Parameter value
Title RV-0546-1.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-05-07T19:37:15
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
N
Boc
15
0.78
2.03
2.01
2.06
9.09
f1 (ppm)


152.39
142.29
130.18
127.64
116.00
114.38
77.21
77.00
76.79
47.70
28.40
Parameter value
Title RV-0546-1.2.1.1r
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 800
Acquisition Date 2022-05-25T06:52:32
Spectrometer Frequency 150 MHz
Nucleus 13C
Br
N
Boc
15
f1 (ppm)


7.498
7.473
7.469
7.396
7.392
7.381
7.378
6.424
3.775
3.763
3.756
3.745
2.850
2.841
2.831
2.822
2.812
2.803
2.753
2.745
2.732
2.723
2.711
2.703
2.690
2.683
2.670
1.576
1.482
Parameter value
Title RV-0538-1.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-04-26T18:34:14
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
Br
N
Boc
N
Boc
16
2.04
1.09
1.00
1.09
1.08
2.09
9.21
9.13
f1 (ppm)


153.27
151.80
141.17
134.71
133.22
126.89
118.70
116.19
84.19
82.51
80.91
77.21
77.00
76.79
61.05
46.16
28.34
28.21
Parameter value
Title RV-0538-1.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 800
Acquisition Date 2022-04-28T12:33:17
Spectrometer Frequency 150 MHz
Nucleus 13C
Br
Br
N
Boc
N
Boc
16
f1 (ppm)