Copper-Catalyzed Oxidative Selective Cyclization/C-N Cross-Coupling of Two Tryptamines to Access 3a-Tryptamine-Pyrroloindolines

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Supporting Information

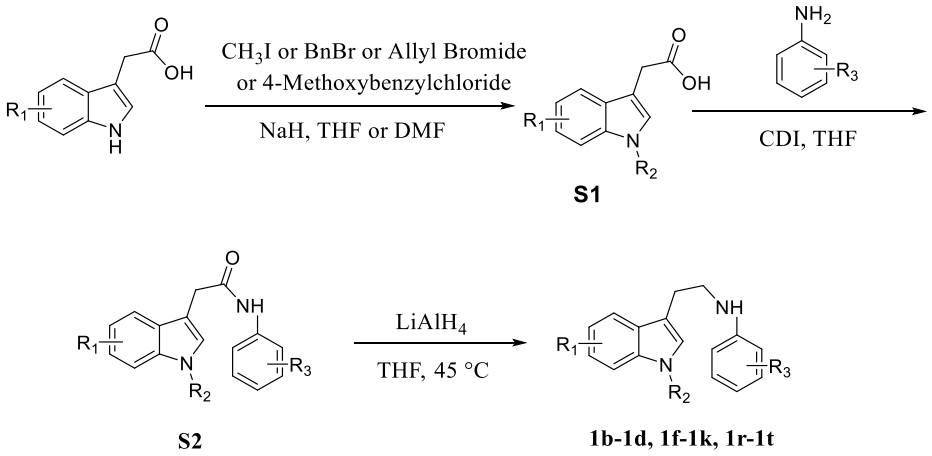
Content

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 tryptamine substrates

Substrates **1a**, **1e** are known compounds, the general procedure for synthesis of these substrates according to the reported method of the literatures [1,2].



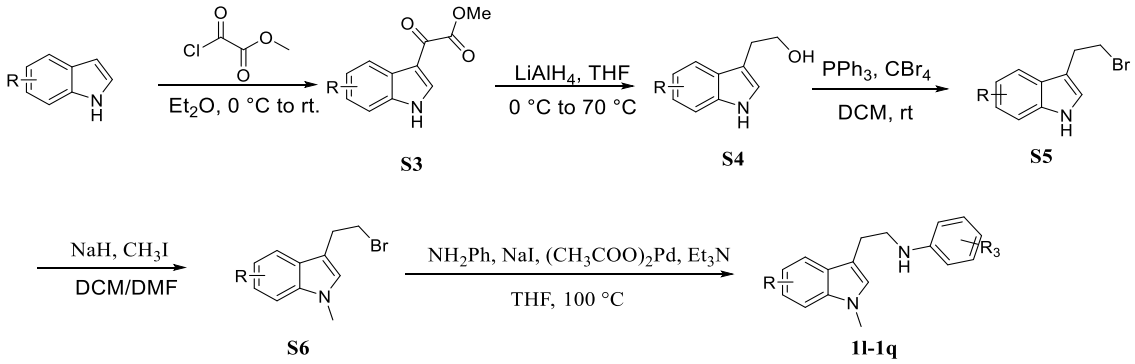
General Procedures for **1b-1d, 1f-1k, 1r-1t:**

To a solution of indole-3-acetic acid (15.0 mmol, 1.0 equiv.) in THF (90 mL), NaH (3.0 g, 75.0 mmol, 5.0 equiv.) was added portionwise at 0 ℃ under argon atmosphere. The mixture was stirred for 30 minutes and then iodomethane (2.8 mL, 45.0 mmol, 3.0 equiv.) was added dropwise. The reaction was moved to room temperature and after completion as detected by TLC. The reaction mixture was then cooled to 0 ℃ and the excess hydride was destroyed by the dropwise addition of ice-cold water. Then the mixture was acidified with 6 N HCl and extracted with EtOAc. The combined organic phase was dried and concentrated. The crude solid was recrystallised from EtOAc/ Petroleum ether to give the desired compounds **S1**.

Compounds **S1** (1.0 equiv.) and carbonyl dimidazole (CDI) (1.0 equiv.) were dissolved in THF (3 mL/mmol of **S1**) and stirred at room temperature. After 0.5 h, amine (1.2 equiv.) was added and the reaction mixture stirred overnight (monitored by TLC). Then the mixture was poured into water, extracted by ethyl acetate and the combined organic solvent was dried over Na_2SO_4, filtered and concentrated in vacumn. The crude solid was recrystallised from EtOAc/ Petroleum ether to give the desired compounds **S2**.

Under argon atmosphere, the THF solution (10 mL/mmol of **S2**) of **S2** (1.0

equiv.) was added to a stirred slurry of $LiAlH_4$ (3.0 equiv.) in THF at 0 ℃. The solution was stirred at 45 ℃ and after completion as detected by TLC. The solution was quenched carefully by H_2O (1.5 mL), 10% aqueous NaOH (3.0 mL), H_2O (4.5 mL) at 0 ℃. After being stirred at room temperature for 12 hours. 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 residue was purified by flash column chromatography (Petroleum ether/Ethyl acetate = 20/1) to give the tryptophan derivative **1b-1d, 1f-1k, 1r-1t.**



General Procedures for **1l-1q**:

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) under argon atmosphere. The ice bath was removed and the resultant slurry was stirred at room temperature for 48 h. The crude reaction mixture was filtered and washed with cold Et_2O. The solid **S3** was used directly for the next step without further purification. A solution of **S3** in THF (20 mL) was added dropwise to a suspension of $LiAlH_4$ (1.52 g, 40.0 mmol) in THF (40 mL) at 0 °C. The solution was stirred at 70 ℃ for 3 h and quenched carefully by H_2O (1.5 mL), 10% aqueous NaOH (3.0 mL), H_2O (4.5 mL) at 0 ℃. After being stirred at room temperature for 12 hours. 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 flash column chromatography (Petroleum ether/Ethyl acetate = 3/1) to give the compounds **S4.**

Compounds **S4** (1.0 equiv.) and triphenyl phosphine (1.3 equiv.) was dissolved in dry CH_2Cl_2 (2 mL/mmol of **S4**). In an addition funnel, carbon tetrabromide (1.3 equiv.)

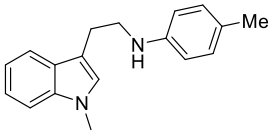
dissolved in dry CH_2Cl_2 was added dropwise under argon atmosphere at 0 ℃, until the addition was complete. The reaction was allowed to stir at room temperature and when the reaction was completed as monitored by TLC. Solvent was removed under reduced pressure and the residue was purified by flash column chromatography (Petroleum ether/ Ethyl acetate = 10/1) to give the compounds **S5**.

Compounds **S5** (1.0 equiv.) were dissolved in a mixture of anhydrous DCM/DMF (2/1 v/v, 1.5 mL/mmol of **S5**) under magnetic stirring and the temperature was set to 0 ℃. To this solution, 1.5 equivalents of NaH were added portion wise and the mixture was allowed to react for 30 min. Then, 1.5 equivalents of methyl iodide in DCM were added dropwise and the reaction was warmed to room temperature and when the reaction was completed as monitored by TLC. The reaction was then quenched by a 10% aqueous solution of citric acid and washed with brine. The organic layer was separated, dried over anhydrous Na_2SO_4, filtered and evaporated in vacuo. Crude products were purified by flash column chromatography (Petroleum ether/Ethyl acetate = 30/1) to give the compounds **S6**.

Compounds **S6** (1.0 equiv.) was dissolved in THF (3 mL/mmol of **S6**) and 1.5 equivalents of the proper amine, 1.5 equivalents of TEA, 1.5 equivalents of NaI and 0.3 equivalents of $Pd(OAc)_2$ were added to this solution 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. 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 = 60/1-40/1) to give the tryptophan derivative **1l- 1q**.

The physical data for new compounds were provided below:

4-Methyl-N-(2-(1-methyl-1*H*-indol-3-yl)ethyl)aniline (1b)

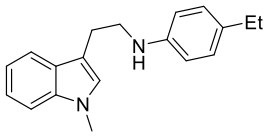


1b

Following the general procedure for preparations of tryptophan derivative **1b-1d, 1f-1k, 1r-1t**. The procedure was performed on indole-3-acetic acid (0.70 g, 4.0 mmol) to afford **1b**. Brown solid, 0.47 g, 44% yield; **^{1}H NMR** (600

MHz, $CDCl_3$) δ 7.73 – 7.65 (m, 1 H), 7.37 (d, *J* = 7.0 Hz, 1 H), 7.34 – 7.29 (m, 1 H), 7.22 – 7.16 (m, 1 H), 7.10 – 7.04 (m, 2 H), 6.95 (s, 1 H), 6.66 – 6.59 (m, 2 H), 3.80 (s, 3 H), 3.53 – 3.48 (m, 2 H), 3.17 – 3.10 (m, 2 H), 2.32 (d, *J* = 3.0 Hz, 3 H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 145.9, 137.1, 129.7, 127.8, 126.8, 126.4, 121.6, 118.9, 118.8, 113.2, 111.8, 109.2, 44.5, 32.5, 25.0, 20.4 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{21}N_2$ 265.1699; Found 265.1697.

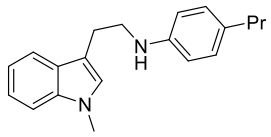
4-Ethyl-N-(2-(1-methyl-1*H*-indol-3-yl)ethyl)aniline (1c)



1c

Following the general procedure for preparations of tryptophan derivative **1b-1d, 1f-1k, 1r-1t**. The procedure was performed on indole-3-acetic acid (0.70 g, 4.0 mmol) to afford **1c**. Brown oil, 0.57 g, 51% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.8 Hz, 1 H), 7.25 (d, *J* = 8.2 Hz, 1 H), 7.23 – 7.19 (m, 1 H), 7.12 – 7.06 (m, 1 H), 6.99 (d, *J* = 8.4 Hz, 2 H), 6.82 (s, 1 H), 6.53 (d, *J* = 8.4 Hz, 2 H), 3.66 (s, 3 H), 3.39 (t, *J* = 6.8 Hz, 2 H), 3.02 (t, *J* = 6.8 Hz, 2 H), 2.52 (q, *J* = 7.6 Hz, 2 H), 1.17 (t, *J* = 7.6 Hz, 3 H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 146.2, 137.0, 133.0, 128.5, 127.8, 126.7, 121.6, 118.8, 118.8, 113.1, 111.8, 109.2, 44.4, 32.4, 27.9, 25.0, 15.9 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{23}N_2$ 279.1856; Found 279.1853.

N-(2-(1-methyl-1*H*-indol-3-yl)ethyl)-4-propylaniline (1d)

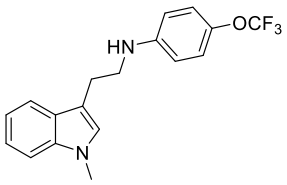


1d

Following the general procedure for preparations of tryptophan derivative **1b-1d, 1f-1k, 1r-1t**. The procedure was performed on indole-3-acetic acid (0.70 g, 4.0 mmol) to afford **1d**. Brown oil, 0.57 g, 49% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.8 Hz, 1 H), 7.26 (d, *J* = 8.2 Hz, 1 H), 7.21 (t, *J* = 7.4 Hz, 1 H), 7.09 (t, *J* = 7.4 Hz, 1 H), 6.97 (d, *J* = 8.4 Hz, 2 H), 6.84 (s, 1 H), 6.53 (d, *J* = 8.4 Hz, 2 H), 3.68 (s, 3 H), 3.40 (t, *J* = 6.8 Hz, 2 H), 3.03 (t, *J* = 6.8 Hz, 2 H), 2.46 (t, *J* = 7.6 Hz, 2 H), 1.61 – 1.54 (m, 2 H), 0.91 (t, *J* = 7.3 Hz, 3 H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 146.4, 137.2, 131.7, 129.29, 128.0, 126.9, 121.8, 119.1, 119.0, 113.2, 112.1, 109.4, 44.6, 37.3, 32.7, 25.2, 25.0, 14.0 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{25}N_2$

293.2012; Found 293.2011.

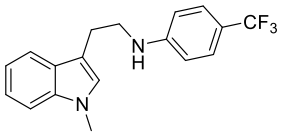
N-(2-(1-methyl-1*H*-indol-3-yl)ethyl)-4-(trifluoromethoxy)aniline (1f)



1f

Following the general procedure for preparations of tryptophan derivative **1b-1d, 1f-1k, 1r-1t**. The procedure was performed on indole-3-acetic acid (0.70 g, 4.0 mmol) to afford **1f**. Brown oil, 0.79 g, 59% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.8 Hz, 1 H), 7.30 (d, *J* = 8.2 Hz, 1 H), 7.24 (t, *J* = 8.4 Hz, 1 H), 7.11 (t, *J* = 7.6 Hz, 1 H), 7.01 (d, *J* = 8.4 Hz, 2 H), 6.88 (s, 1 H), 6.53 (d, *J* = 7.2 Hz, 2 H), 3.74 (s, 3 H), 3.42 (t, *J* = 6.8 Hz, 2 H), 3.06 (t, *J* = 6.6 Hz, 2 H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 147.0, 140.3, 137.1, 127.8, 126.8, 122.4, 121.8, 120.7(q, $^{1}J_{C\text{-}F}$ = 253.5 Hz), 118.9, 118.8, 113.1, 111.5, 109.3, 44.3, 32.6, 24.9 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -58.43 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{18}ON_2F_3$ 335.1366; Found 335.1356.

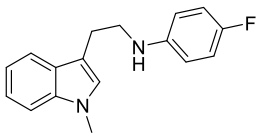
N-(2-(1-methyl-1*H*-indol-3-yl)ethyl)-4-(trifluoromethyl)aniline (1g)



1g

Following the general procedure for preparations of tryptophan derivative **1b-1d, 1f-1k, 1r-1t**. The procedure was performed on indole-3-acetic acid (0.52 g, 3.0 mmol) to afford **1g**. Light yellow solid, 0.32 g, 34% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.8 Hz, 1 H), 7.38 (d, *J* = 8.4 Hz, 2 H), 7.32 (d, *J* = 8.2 Hz, 1 H), 7.27 – 7.22 (m, 1 H), 7.15 – 7.10 (m, 1 H), 6.89 (s, 1H), 6.58 (d, *J* = 8.6 Hz, 2 H), 4.08 (s, 1 H), 3.76 (s, 3 H), 3.49 – 3.46 (m, 2 H), 3.07 (t, *J* = 6.7 Hz, 2 H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 150.6, 137.1, 127.7, 126.9, 126.5 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz), 125.0 (q, $^{1}J_{C\text{-}F}$ = 268.6 Hz), 121.8, 119.0, 118.8, 118.6 (q, $^{2}J_{C\text{-}F}$ = 31.6 Hz), 111.9, 111.3, 109.4, 43.6, 32.6, 24.8 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -60.90 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{18}N_2F_3$ 319.1417; Found 319.1416.

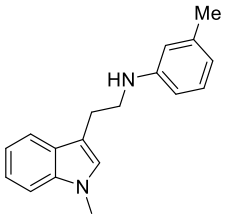
4-Fluoro-N-(2-(1-methyl-1*H*-indol-3-yl)ethyl)aniline (1h)



1h

Following the general procedure for preparations of tryptophan derivative **1b-1d, 1f-1k, 1r-1t**. The procedure was performed on indole-3-acetic acid (0.70 g, 4.0 mmol) to afford **1h**. Brown oil, 0.54 g, 50 % yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.8 Hz, 1 H), 7.25 (d, *J* = 8.2 Hz, 1 H), 7.21 (t, *J* = 7.4 Hz, 1 H), 7.09 (t, *J* = 7.4 Hz, 1 H), 6.85 – 6.80 (m, 3 H), 6.49 – 6.46 (m, 2 H), 3.65 (s, 3 H), 3.48 (br, 1 H), 3.34 (t, *J* = 6.8 Hz, 2 H), 3.00 (t, *J* = 6.8 Hz, 2 H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 155.7 (d, $^{1}J_{C\text{-}F}$ = 232.6 Hz), 144.4, 137.0, 127.7, 126.8, 121.6, 118.8, 118.7, 115.6 (d, $^{2}J_{C\text{-}F}$ = 22.6 Hz), 113.8 (d, $^{3}J_{C\text{-}F}$ = 7.6 Hz), 111.5, 109.2, 44.8, 32.4, 24.8 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -127.81 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{18}N_2F$ 269.1448; Found 269.1447.

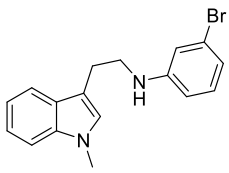
3-methyl-N-(2-(1-methyl-1*H*-indol-3-yl)ethyl)aniline (1i)



1i

Following the general procedure for preparations of tryptophan derivative **1b-1d, 1f-1k, 1r-1t**. The procedure was performed on indole-3-acetic acid (0.35 g, 2.0 mmol) to afford **1i**. Brown oil, 0.28 g, 53 % yield;**^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 1 H), 7.30 (d, *J* = 8.2 Hz, 1 H), 7.25 – 7.21 (m, 1 H), 7.13 – 7.09 (m, 1 H), 7.08 – 7.03 (m, 1 H), 6.89 (s, 1 H), 6.52 (d, *J* = 7.6 Hz, 1 H), 6.45 – 6.41 (m, 2 H), 3.74 (s, 3 H), 3.44 (t, *J* = 6.8 Hz, 2 H), 3.06 (t, *J* = 6.8 Hz, 2 H), 2.26 (s, 3 H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.3, 138.9, 137.1, 129.1, 127.8, 126.8, 121.7, 118.9, 118.8, 118.2, 113.8, 111.8, 110.2, 109.2, 44.2, 32.6, 25.0, 21.6 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{21}N_2$ 265.1699; Found 265.1692.

3-Bromo-N-(2-(1-methyl-1*H*-indol-3-yl)ethyl)aniline (1j)

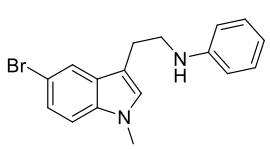


1j

Following the general procedure for preparations of tryptophan derivative **1b-1d, 1f-1k, 1r-1t**. The procedure was performed on indole-3-acetic acid (1.05 g, 6.0 mmol) to afford **1j**. Brown oil,

1.17 g, 59 % yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.9 Hz, 1 H), 7.36 (d, *J* = 8.2 Hz, 1 H), 7.30 (t, *J* = 7.6 Hz, 1 H), 7.19 – 7.15 (m, 1 H), 7.03 (t, *J* = 8.0 Hz, 1 H), 6.92 (s, 1 H), 6.85 – 6.82 (m, 1 H), 6.78 – 6.76 (m, 1 H), 6.53 (dd, *J* = 8.4, 2.2 Hz, 1 H), 3.85 (s, 1 H), 3.79 (s, 3 H), 3.45 (t, *J* = 6.8 Hz, 2 H), 3.09 (t, *J* = 6.8 Hz, 2 H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.5, 137.1, 130.4, 127.7, 126.8, 123.2, 121.7, 119.8, 118.9, 118.8, 115.3, 111.6, 111.4, 109.3, 43.8, 32.6, 24.8 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{18}N_2Br$ 329.0648; Found 329.0646.

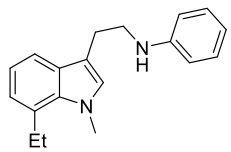
N-(2-(5-bromo-1-methyl-1*H*-indol-3-yl)ethyl)aniline (1k)



1k

Following the general procedure for preparations of tryptophan derivative **1b-1d, 1f-1k, 1r-1t**. The procedure was performed on 5-bromo-3-indoleacetic acid (0.76 g, 3.0 mmol) to afford **1k**. Brown oil, 0.30 g, 29 % yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.68 (s, 1 H), 7.28 (d, *J* = 8.8 Hz, 1 H), 7.16 (t, *J* = 7.8 Hz, 2 H), 7.12 (d, *J* = 8.8 Hz, 1 H), 6.86 (s, 1 H), 6.69 (t, *J* = 7.2 Hz, 1 H), 6.59 (d, *J* = 8.0 Hz, 2 H), 3.68 (s, 3 H), 3.39 (t, *J* = 6.8 Hz, 2 H), 2.97 (t, *J* = 6.8 Hz, 2 H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.0, 135.7, 129.5, 129.2, 127.9, 124.4, 121.4, 117.3, 112.9, 112.2, 111.5, 110.8, 44.0, 32.7, 24.8 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{18}N_2Br$ 329.0648; Found 329.0647.

N-(2-(7-ethyl-1-methyl-1*H*-indol-3-yl)ethyl)aniline (1l)

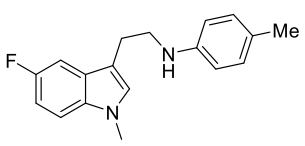


1l

Following the general procedure for preparations of tryptophan derivative **1l-1q**. The procedure was performed on 7-ethyl tryptophol (1.14 g, 6.0 mmol) to afford **1l**. Brown oil, 0.34 g, 20 % yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.8 Hz, 1 H), 7.15 (t, *J* = 7.6 Hz, 2 H), 7.01 (t, *J* = 7.5 Hz, 1 H), 6.99 – 6.95 (m, 1 H), 6.73 (s, 1 H), 6.67 (t, *J* = 7.2 Hz, 1 H), 6.58 (d, *J* = 7.8 Hz, 2 H), 3.92 (s, 3 H), 3.40 (t, *J* = 6.8 Hz, 2 H), 3.07 (q, *J* = 7.6 Hz, 2 H), 3.00 (t, *J* = 6.8 Hz, 2 H), 1.33 (t, *J* = 7.4 Hz, 3 H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.2, 134.9, 129.3, 129.1, 128.6, 127.9, 122.6, 119.2,

117.1, 116.8, 112.9, 111.5, 43.9, 36.4, 25.4, 24.8, 16.6 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{23}N_2$ 279.1856; Found 279.1855.

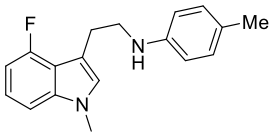
N-(2-(5-fluoro-1-methyl-1*H*-indol-3-yl)ethyl)-4-methylaniline (1m)



1m

Following the general procedure for preparations of tryptophan derivative **1l-1q**. The procedure was performed on 5-fluoroindole (1.35 g, 10.0 mmol) to afford **1m**. Brown oil, 0.36 g, 13 % yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.21 (dd, *J* = 9.8, 2.4 Hz, 1 H), 7.16 (dd, *J* = 8.8, 4.2 Hz, 1 H), 6.98 (d, *J* = 8.2 Hz, 2 H), 6.94 (dd, *J* = 9.0, 2.4Hz, 1 H), 6.90 (s, 1 H), 6.53 (d, *J* = 8.4 Hz, 2 H), 3.69 (s, 3 H), 3.38 (t, *J* = 6.8 Hz, 2 H), 2.97 (t, *J* = 6.8 Hz, 2 H), 2.23 (s, 3 H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.5 (d, $^1J_{C\text{-}F}$ = 232.4 Hz), 145.8, 133.7, 129.7, 128.4, 128.0 (d, $^3J_{C\text{-}F}$ = 9.0 Hz), 126.5, 113.2, 111.8 (d, $^4J_{C\text{-}F}$ = 4.5 Hz), 109.9 (d, $^2J_{C\text{-}F}$ = 27.0 Hz), 109.8 (d, $^3J_{C\text{-}F}$ = 10.6 Hz), 103.8 (d, $^2J_{C\text{-}F}$ = 24.0 Hz), 44.4, 32.8, 24.9, 20.3 ppm.. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -125.36 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{20}N_2F$ 283.1605; Found 283.1606.

N-(2-(4-fluoro-1-methyl-1*H*-indol-3-yl)ethyl)-4-methylaniline (1n)

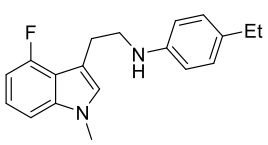


1n

Following the general procedure for preparations of tryptophan derivative **1l-1q**. The procedure was performed on 4-fluoroindole (1.35 g, 10.0 mmol) to afford **1n**. Brown oil, 0.33 g, 11 % yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.16 – 7.12 (m, 1 H), 7.08 (d, *J* = 8.2 Hz, 1 H), 7.02 (d, *J* = 8.0 Hz, 2 H), 6.85 (s, 1 H), 6.78 (dd, *J* = 11.2, 7.8 Hz, 1 H), 6.60 (d, *J* = 8.2 Hz, 2 H), 3.75 (s, 3 H), 3.47 (t, *J* = 6.8 Hz, 2 H), 3.16 (t, *J* = 6.8 Hz, 2 H), 2.27 (s, 3 H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.2 (d, $^1J_{C\text{-}F}$ = 244.8 Hz), 146.0, 140.0 (d, $^3J_{C\text{-}F}$ = 10.6 Hz), 129.7, 127.1, 126.4, 122.1 (d, $^3J_{C\text{-}F}$ = 7.6 Hz), 116.4 (d, $^2J_{C\text{-}F}$ = 19.6 Hz), 113.2, 110.7 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 105.4 (d, $^3J_{C\text{-}F}$ = 4.6 Hz), 104.1 (d, $^2J_{C\text{-}F}$ = 19.6 Hz), 45.0 (d, $^4J_{C\text{-}F}$ = 1.6 Hz), 32.9, 26.2, 20.4 ppm.**^{19}F NMR** (565 MHz, $CDCl_3$) δ -123.36 ppm. **HRMS (ESI)** *m/z*: [M +

H]$^+$ Calcd for $C_{18}H_{20}N_2F$ 283.1605; Found 283.1603.

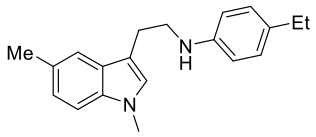
4-Ethyl-N-(2-(4-fluoro-1-methyl-1*H*-indol-3-yl)ethyl)aniline (1o)



1o

Following the general procedure for preparations of tryptophan derivative **1l-1q**. The procedure was performed on 4-fluoroindole (1.35 g, 10.0 mmol) to afford **1o**. yellow oil, 0.17 g, 6 % yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.14 – 7.09 (m, 1 H), 7.06 (d, *J* = 8.2 Hz, 1 H), 7.02 (d, *J* = 7.8 Hz, 2 H), 6.84 (s, 1 H), 6.77 – 6.73 (m, 1 H), 6.59 (d, *J* = 7.4 Hz, 2 H), 3.74 (s, 3 H), 3.44 (t, *J* = 6.8 Hz, 2 H), 3.13 (t, *J* = 6.8 Hz, 2 H), 2.54 (q, *J* = 7.6 Hz, 2 H), 1.19 (t, *J* = 7.6 Hz, 3 H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.2(d, $^1J_{C\text{-}F}$ = 244.6 Hz), 146.3, 140.0 (d, $^3J_{C\text{-}F}$ = 10.5 Hz), 133.1, 128.5, 127.1, 122.1(d, $^3J_{C\text{-}F}$ = 7.6 Hz), 116.3(d, ^2J = 19.5 Hz), 113.1, 110.8 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 105.4 (d, $^3J_{C\text{-}F}$ = 3.0 Hz), 104.1(d, ^2J = 19.5 Hz), 45.0 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 32.9, 27.9, 26.3, 16.0 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -123.39 ppm. **HRMS (ESI)** *m/z*: [M + H]$^+$ Calcd for $C_{19}H_{22}N_2F$ 297.1762; Found 297.1761.

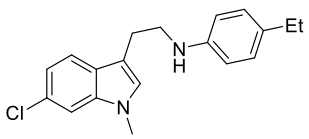
N-(2-(1,5-dimethyl-1*H*-indol-3-yl)ethyl)-4-ethylaniline (1p)



1p

Following the general procedure for preparations of tryptophan derivative **1l-1q**. The procedure was performed on 5-methylindole (1.57 g, 12.0 mmol) to afford **1p**. Brown oil, 0.35 g, 10 % yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.36 (s, 1 H), 7.16 (d, *J* = 8.4 Hz, 1 H), 7.04 (dd, *J* = 8.4, 1.6 Hz, 1 H), 7.00 (d, *J* = 8.4 Hz, 2 H), 6.82 (s, 1 H), 6.55 (d, *J* = 8.4 Hz, 2 H), 3.67 (s, 3 H), 3.40 (t, *J* = 6.8 Hz, 2 H), 3.01 (t, *J* = 6.8 Hz, 2 H), 2.53 (q, *J* = 7.6 Hz, 2 H), 2.45 (s, 3 H), 1.18 (t, *J* = 7.6 Hz, 3 H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 146.2, 135.5, 133.1, 128.5, 128.0, 128.0, 126.8, 123.2, 118.6, 113.1, 111.2, 108.9, 44.5, 32.5, 27.9, 25.0, 21.4, 16.0 ppm. **HRMS (ESI)** *m/z*: [M + H]$^+$ Calcd for $C_{20}H_{25}N_2$ 293.2012; Found 293.2012.

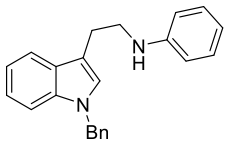
N-(2-(6-chloro-1-methyl-1*H*-indol-3-yl)ethyl)-4-ethylaniline (1q)



1q

Following the general procedure for preparations of tryptophan derivative **1l-1q**. The procedure was performed on 6-chloroindole (1.82 g, 12.0 mmol) to afford **1q**. Brown oil, 0.34 g, 9 % yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 1 H), 7.25 (s, 1 H), 7.05 (d, *J* = 8.4 Hz, 1 H), 7.00 (d, *J* = 8.4 Hz, 2 H), 6.84 (s, 1 H), 6.54 (d, *J* = 8.4 Hz, 2 H), 3.64 (s, 3 H), 3.38 (t, *J* = 6.8 Hz, 2 H), 2.99 (t, *J* = 6.8 Hz, 2 H), 2.53 (q, *J* = 7.6 Hz, 2 H), 1.18 (t, *J* = 7.6 Hz, 3 H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 146.0, 137.4, 133.2, 128.5, 127.7, 127.4, 126.4, 119.7, 119.4, 113.1, 112.2, 109.2, 44.4, 32.6, 27.9, 24.9, 15.9 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{22}N_2Cl$ 313.1466; Found 313.1466.

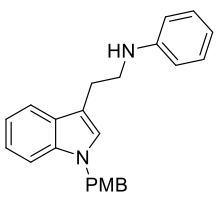
N-(2-(1-benzyl-1*H*-indol-3-yl)ethyl)aniline (1r)



1r

Following the general procedure for preparations of tryptophan derivative **1b-1d, 1f-1k, 1r-1t**. The procedure was performed on indole-3-acetic acid (1.05 g, 6.0 mmol) and benzyl bromide (3.08 g, 18.0 mmol) to afford **1r**. Brown oil, 0.58 g, 29 % yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.8 Hz, 1 H), 7.27 – 7.19 (m, 4 H), 7.18 – 7.12 (m, 3 H), 7.10 (t, *J* = 7.6 Hz, 1 H), 7.06 (d, *J* = 7.2 Hz, 2 H), 6.90 (s, 1 H), 6.67 (t, *J* = 7.3 Hz, 1 H), 6.56 (d, *J* = 7.4 Hz, 2 H), 5.20 (s, 2 H), 3.42 (t, *J* = 6.8 Hz, 2 H), 3.04 (t, *J* = 6.8 Hz, 2 H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.1, 137.6, 136.8, 129.2, 128.7, 128.0, 127.5, 126.7, 126.1, 121.9, 119.1, 119.0, 117.2, 113.0, 112.5, 109.7, 49.8, 44.0, 25.0 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{23}N_2$ 327.1856; Found 327.1857.

N-(2-(1-(4-methoxybenzyl)-1*H*-indol-3-yl)ethyl)aniline (1s)

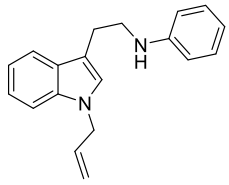


1s

Following the general procedure for preparations of tryptophan derivative **1b-1d, 1f-1k, 1r-1t**. The procedure was performed on indole-3-acetic acid (1.0 g, 5.71 mmol) to afford **1s**. Brown oil, 0.83 g, 41% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.8

Hz, 1 H), 7.32 (d, *J* = 8.4 Hz, 1 H), 7.23 – 7.15 (m, 3 H), 7.13 (t, *J* = 7.5 Hz, 1 H), 7.08 (d, *J* = 8.5 Hz, 2 H), 6.95 (s, 1 H), 6.87 – 6.81 (m, 2 H), 6.71 (t, *J* = 7.3 Hz, 1 H), 6.61 (d, *J* = 7.7 Hz, 2 H), 5.21 (s, 2 H), 3.78 (s, 3 H), 3.47 (t, *J* = 6.8 Hz, 2 H), 3.11 – 3.05 (m, 2 H) ppm.**^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.1, 148.2, 136.7, 129.6, 129.2, 128.2, 128.1, 126.0, 121.8, 119.1, 119.0, 117.3, 114.1, 113.0, 112.4, 109.7, 55.2, 49.4, 44.0, 25.1 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{25}ON_2$ 357.1961; Found 357.1952.

N-(2-(1-allyl-1*H*-indol-3-yl)ethyl)aniline (1t)

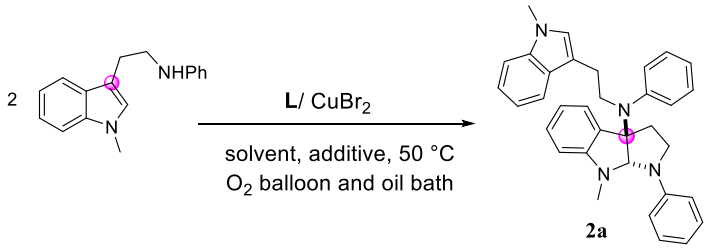


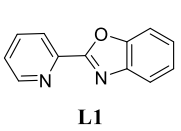
1t

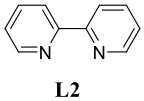
Following the general procedure for preparations of tryptophan derivative **1b-1d, 1f-1k, 1r-1t**. The procedure was performed on indole-3-acetic acid (1.05 g, 6.0 mmol) and allyl bromide (2.1776 g, 18.0 mmol) to afford **1t**. Brown oil, 0.26 g, 16% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.8 Hz, 1 H), 7.27 (d, *J* = 8.2 Hz, 1 H), 7.22 – 7.18 (m, 1 H), 7.15 (t, *J* = 7.9 Hz, 2 H), 7.13 – 7.08 (m, 1 H), 6.89 (s, 1 H), 6.68 (t, *J* = 7.4 Hz, 1 H), 6.58 (d, *J* = 8.6 Hz, 2 H), 5.98 – 5.90 (m, 1 H), 5.16 (d, *J* = 10.2 Hz, 1 H), 5.05 (d, *J* = 17.0 Hz, 1 H), 4.62 (d, *J* = 5.4 Hz, 2 H), 3.42 (t, *J* = 6.8 Hz, 2 H), 3.04 (t, *J* = 6.8 Hz, 2 H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.2, 136.5, 133.5, 129.3, 128.0, 125.7, 121.7, 119.0, 118.9, 117.2, 117.1, 112.9, 112.2, 109.6, 48.6, 44.0, 25.0 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{21}N_2$ 277.1699; Found 277.1700.

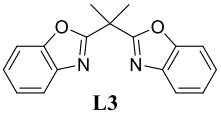
3. Optimization of the reaction conditions

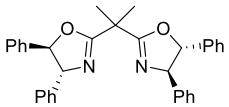
3.1 Ligands screening [a]

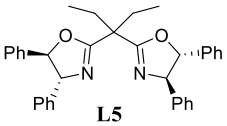


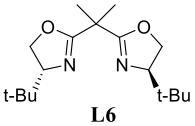

L1

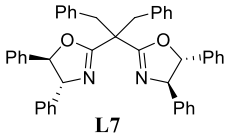

L2

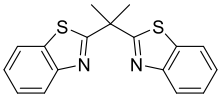

L3

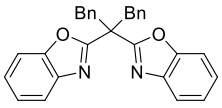

L4

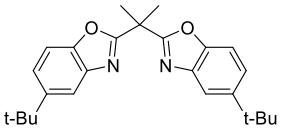

L5

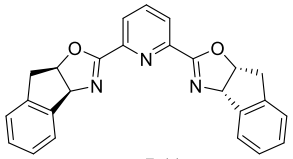

L6


L7


L8


L9

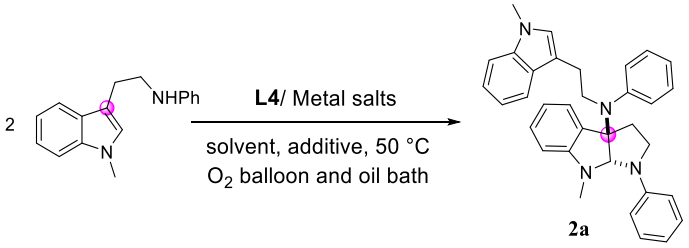

L10


L11

Entry	L	Solvent	Additives	T (h)	Yields (%)[a]
1	-	PhCl	-	48	trace
2	**L1**	PhCl	-	48	13
3	**L2**	PhCl	-	48	NR
4	**L3**	PhCl	-	48	NR
5	**L4**	PhCl	-	22	16
6	**L5**	PhCl	-	48	Trace
7	**L6**	PhCl	-	48	Trace
8	**L7**	PhCl	-	48	8
9	**L8**	PhCl	-	48	NR
10	**L9**	PhCl	-	48	NR
11	**L10**	PhCl	-	48	NR
12	**L11**	PhCl	-	48	NR

[a] The reactions were carried out under O_2 balloon: Metal salts (0.02 mmol), **L** (0.024 mmol), Solvent (2.0 mL), **1a** (0.20 mmol). Yields were determined by ^{1}H NMR with TTCE as the internal standard.

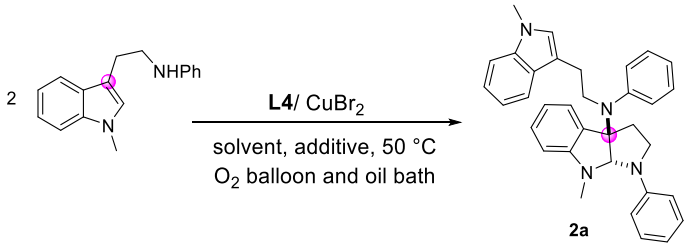
3.2 Metal salts screening [a]



Entry	L	Solvent	Metal salts	Additives	T (h)	Yields (%)[a]
1	**L4**	PhCl	$CuBr_2$	-	22	16
2	**L4**	PhCl	CuBr	-	48	7
3	**L4**	PhCl	CuCl	-	47	9
4	**L4**	PhCl	Cu_2O	-	48	Nr
5	**L4**	PhCl	CuI	-	48	Nr
6	**L4**	PhCl	$Cu(OTf)_2$	-	48	6
7	**L4**	PhCl	CuOAc	-	48	Nr
8	**L4**	PhCl	$Cu(ClO_4)_2 \cdot 6H_2O$	-	48	11
9	**L4**	PhCl	$CuBr_2/Cu(OTf)_2$	-	6	13

[a] The reactions were carried out under O_2 balloon: Metal salts (0.02 mmol), **L** (0.024 mmol), Solvent (2.0 mL), **1a** (0.20 mmol). Yields were determined by ^1H NMR with TTCE as the internal standard.

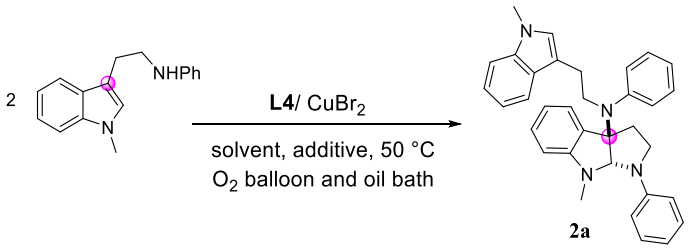
3.3 Solvent screening [a]



Entry	L	Solvent	Additives	T (h)	Yields (%)[a]
1	**L4**	PhCl	-	22	16
2	**L4**	$PhCF_3$	-	27	27
3	**L4**	PhMe	-	22	26
4	**L4**	Mesitylene	-	48	34
5	**L4**	EA	-	48	22
6	**L4**	MeOH	-	4	20
7	**L4**	1,4-dioxane	-	22	21
8	**L4**	ACN	-	48	15

[a] The reactions were carried out under O_2 balloon: Metal salts (0.02 mmol), **L4** (0.024 mmol), Solvent (2.0 mL), **1a** (0.20 mmol). Yields were determined by ^{1}H NMR with TTCE as the internal standard.

3.4 Additives screening [a]

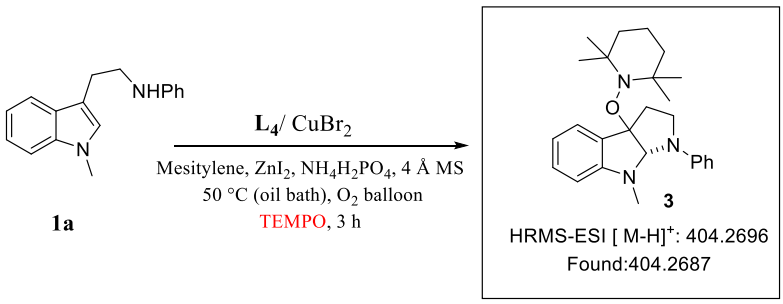


Entry	L	Solvent	Additives	*t* (h)	Yields (%)[a]
1	**L4**	Mesitylene	-	48	34
2	**L4**	Mesitylene	4 Å MS	48	54
3 [c]	**L4**	Mesitylene	$HClO_4$	49	51
4 [c]	**L4**	Mesitylene	AcOH	48	49
5 [c]	**L4**	Mesitylene	H_3BO_3	36	49
6 [c]	**L4**	Mesitylene	t-BuOK	48	46
7 [c]	**L4**	Mesitylene	Na_2CO_3	48	44
8 [c]	**L4**	Mesitylene	KH_2PO_4	48	50
9 [c]	**L4**	Mesitylene	$NH_4H_2PO_4$	47	62
10 [c]	**L4**	Mesitylene	NaH_2PO_4	47	52 [b]
11 [c]	**L4**	Mesitylene	ZnI_2 [d]	27	63 [b]
12[c]	**L4**	Mesitylene	$NH_4H_2PO_4/ZnI_2$ [d]	16	68[b]
13 [c]	**L1**	PhCl	$NH_4H_2PO_4/ZnI_2$ [d]	22	62[b]

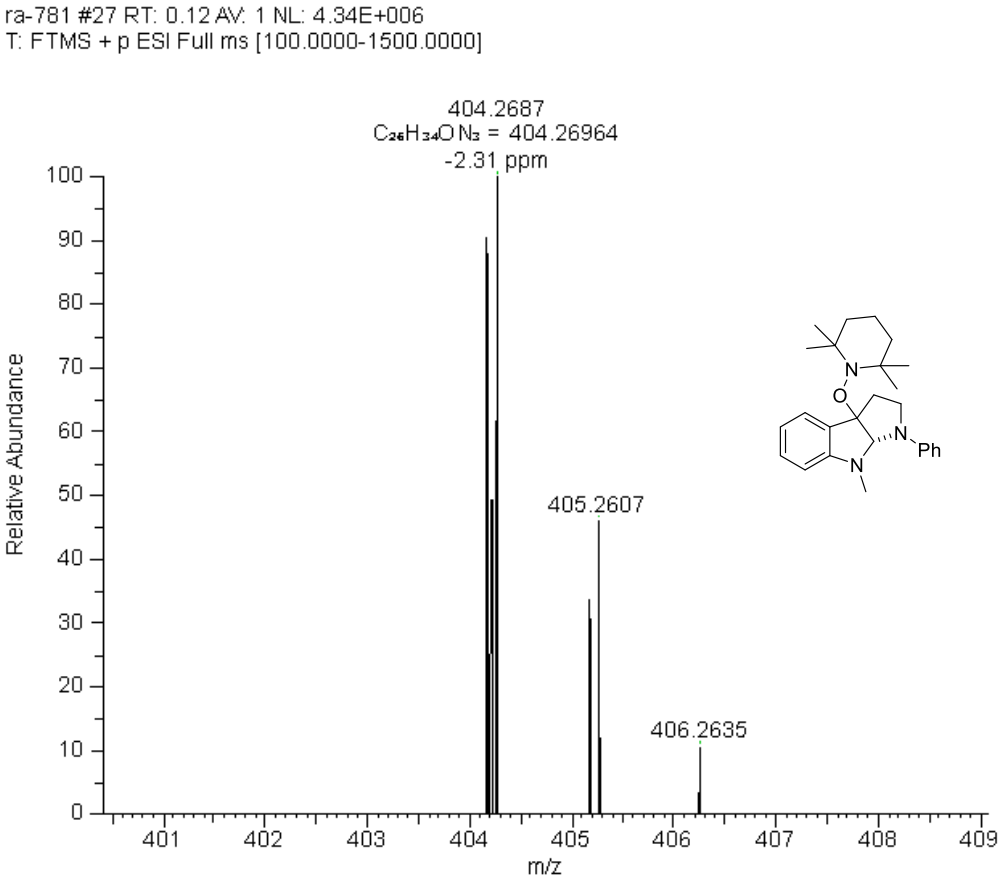
[a] The reactions were carried out under O_2 balloon: Metal salts (0.02 mmol), **L4** (0.024 mmol), Solvent (2.0 mL), **1a** (0.20 mmol). Yields were determined by ^{1}H NMR with TTCE as the internal standard. [b] Isolated yield. [c] 4ÅMSs (200 mg). [d] ZnI_2(0.03 mmol).

4. Mechanistic studies

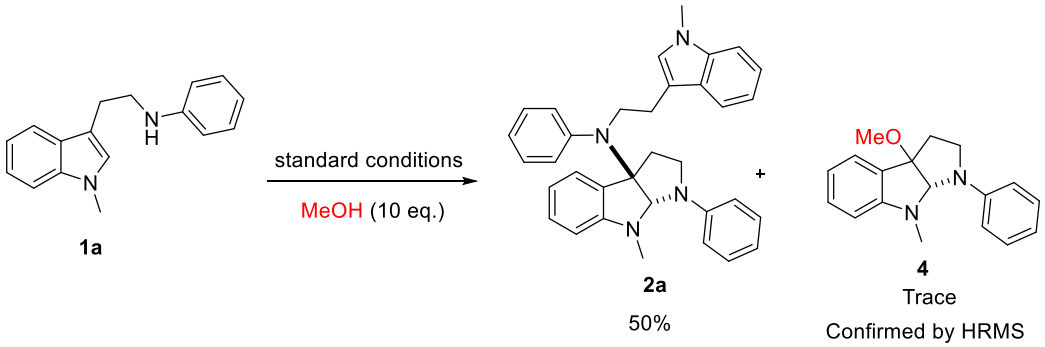
4.1 Radical trapping experiments



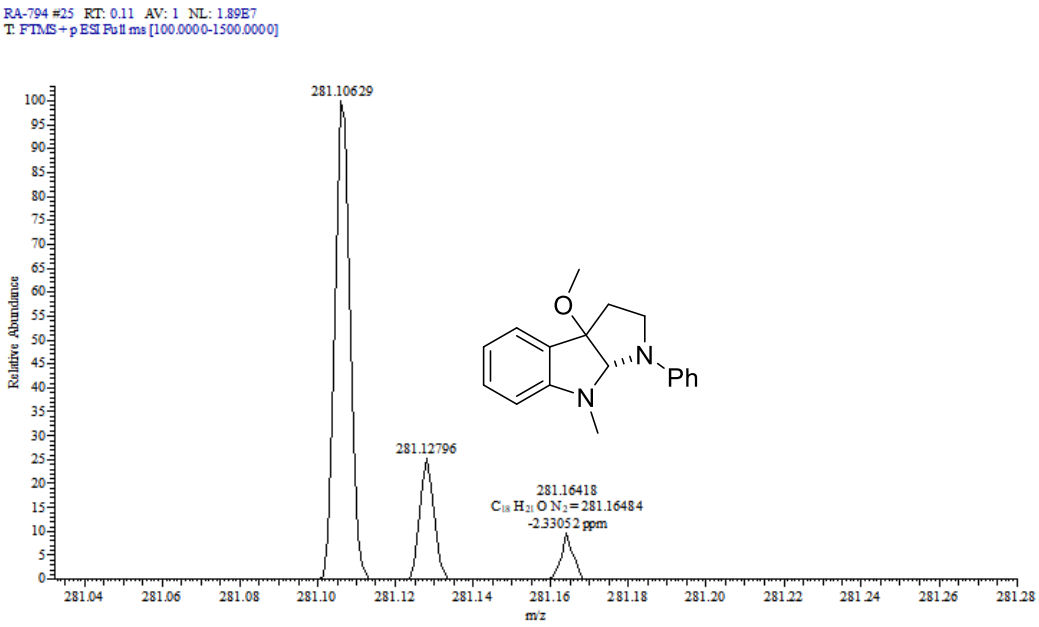
Procedure: A mixture of **1a** (50.1 mg, 0.2 mmol), $CuBr_2$ (4.5 mg, 0.02 mmol), **L4** (11.7 mg, 0.024 mmol), ZnI_2 (9.6mg, 0.03 mmol), $NH_4H_2PO_4$ (2.3 mg, 0.02 mmol) , TEMPO (62.5 mg, 0.4 mmol) and 4 Å MS (200 mg) in Mesitylene (2 mL) was stirred at 50 ℃ under O_2 balloon. After 3 hours of reaction, send it to HRMS-ESI for monitoring.

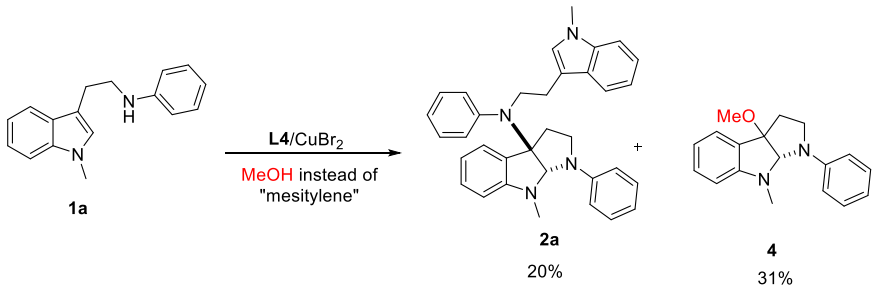


4.2 C3a-cation-pyrroloindoline intermediate investigations



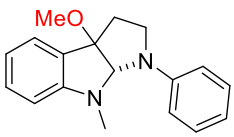
Procedure: A mixture of **1a** (50.1 mg, 0.2 mmol), MeOH (64.1mg, 2 mmol), $CuBr_2$ (4.5 mg, 0.02 mmol), **L4** (11.7 mg, 0.024 mmol), ZnI_2 (9.6mg, 0.03 mmol), $NH_4H_2PO_4$ (2.3mg, 0.02 mmol) and 4 Å MS (200 mg) in Mesitylene (2 mL) was stirred at 50 ℃ under O_2 balloon. After 17 hours of reaction, we stopped the reaction. The Yield of **2a** was determined by ^1H NMR with TTCE as the internal standard and compound **4** was confirmed by HRMS analysis.





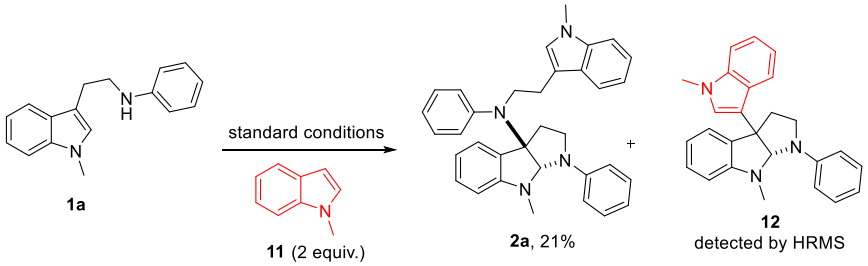
Procedure: A mixture of **1a** (50.1 mg, 0.2 mmol), $CuBr_2$ (4.5 mg, 0.02 mmol), **L4** (11.7 mg, 0.024 mmol), ZnI_2 (9.6mg, 0.03 mmol), $NH_4H_2PO_4$ (2.3mg, 0.02 mmol) and 4 Å MS (200 mg) in MeOH (2 mL) was stirred at 50 ℃ under O_2 balloon. After 4 h, the reaction was filtered through a glass funnel with thin layer (30 mm) of silica gel (100-200 mesh) and eluted with DCM/Ethyl Acetate. The filtrate was concentrated under reduced pressure, purified by flash chromatography (Petroleum ether/Ethyl acetate = 60/1) to afford the product **2a** and **4**.

3a-Methoxy-8-methyl-1-phenyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indole (4)

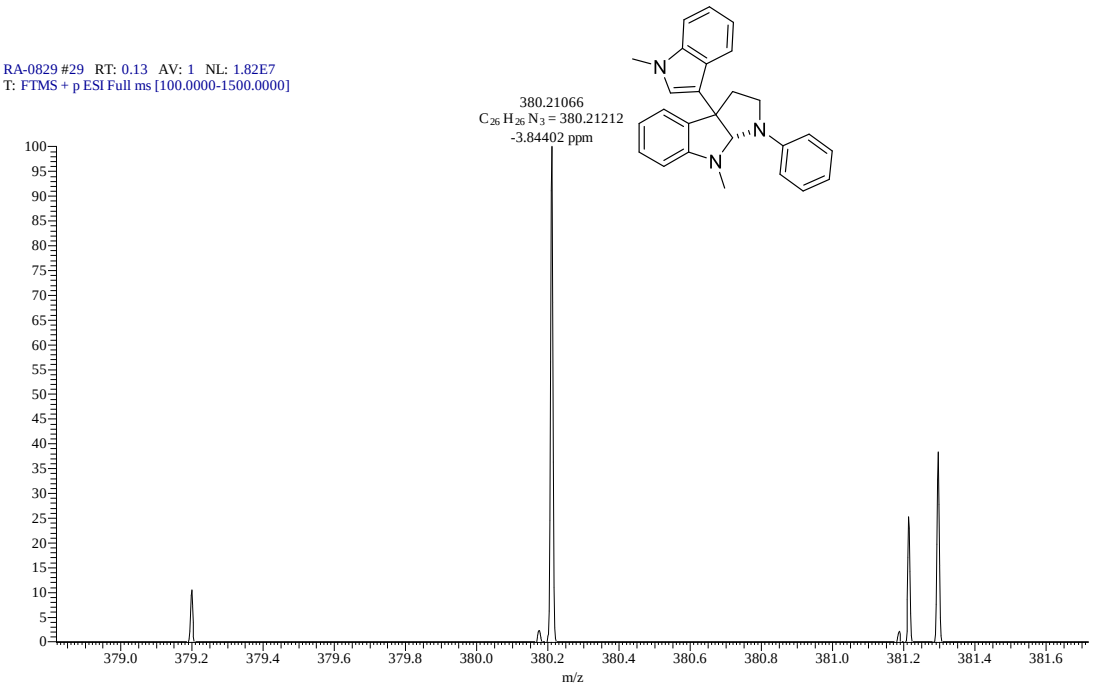


4

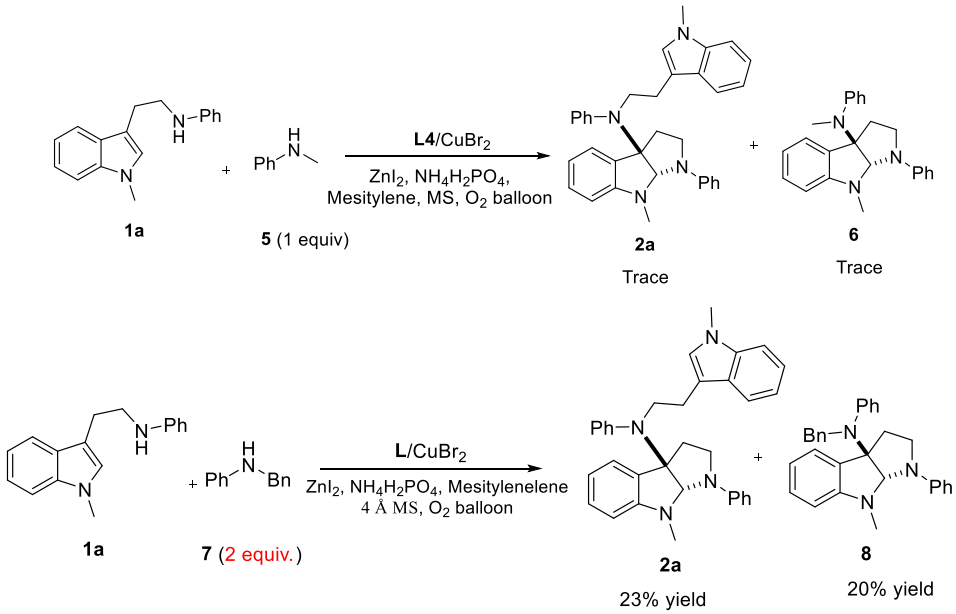
Light oil, 4 h, 17.2 mg, 31% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 2 H), 7.22 – 7.17 (m, 2 H), 6.90 (d, *J* = 7.6 Hz, 2 H), 6.81 – 6.74 (m, 2 H), 6.46 (d, *J* = 7.8 Hz, 1 H), 5.58 (s, 1 H), 3.52 (ddd, *J* = 9.4, 7.6, 4.8 Hz, 1 H), 3.34 (dt, *J* = 9.4, 7.2 Hz, 1 H), 3.17 (s, 3H), 2.90 (s, 3H), 2.44 – 2.38 (m, 1H), 2.37 – 2.32 (m, 1H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 152.0, 147.5, 129.9, 129.1, 126.7, 123.6, 117.8, 117.8, 113.8, 107.3, 93.5, 85.7, 52.9, 47.7, 38.2, 35.2 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{21}ON_2$ 281.1648; Found 281.1642.



Procedure: A mixture of **1a** (50.1 mg, 0.2 mmol), **11** (52.5 mg, 0.4 mmol), $CuBr_2$ (4.5 mg, 0.02 mmol), **L4** (11.7 mg, 0.024 mmol), ZnI_2 (9.6 mg, 0.03 mmol), $NH_4H_2PO_4$ (2.3 mg, 0.02 mmol) and 4ÅMS (200 mg) in Mesitylene (2 mL) was stirred at 50 °C under O_2 balloon. After 48 hours of reaction, we stopped the reaction, The Yield of **2a** was isolated yield and compound **12** was confirmed by HRMS analysis.

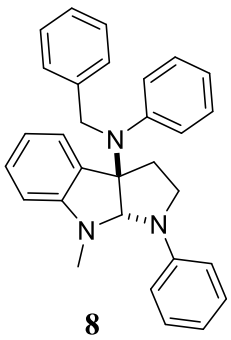


4.3 Control experiments



A mixture of $CuBr_2$ (4.5 mg, 0.02 mmol), **L4** (11.7 mg, 0.024 mmol), **1a** (50.1 mg, 0.2 mmol), **7** (73.2 mg, 0.4 mmol), ZnI_2 (9.6 mg, 0.03 mmol), $NH_4H_2PO_4$ (2.3 mg, 0.02 mmol) and 4Å MS (200 mg) in Mesitylene (2 mL) was stirred at 50 ℃ under O_2 balloon. After 13 h, the reaction was filtered through a glass funnel with thin layer (30 mm) of silica gel (100-200 mesh) and eluted with DCM/Ethyl Acetate. The filtrate was concentrated under reduced pressure, purified by flash chromatography (Petroleum ether/Ethyl acetate = 60/1) to afford the product **2a** and **8**.

N-Benzyl-8-methyl-N,1-diphenyl-2,3,8,8a-tetrahydropyrrolo[2,3-b]indol-3a(1*H*)-amine (8)



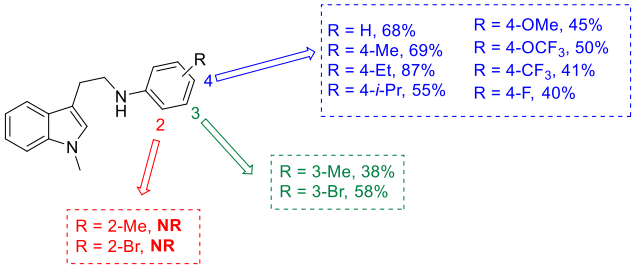
8

Light yellow oil, 13 h, 17.5 mg, 20% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.2 Hz, 1 H), 7.23 – 7.15 (m, 7 H), 7.13 – 7.10 (m, 1 H), 7.08 – 7.03 (m, 2 H), 6.97 – 6.90 (m, 3 H), 6.71 – 6.78 (m, 4 H), 6.40 (d, *J* = 7.8 Hz, 1 H), 5.84 (s, 1 H), 4.41 (d, *J* = 15.2 Hz, 1 H), 4.28 (d, *J* = 15.2 Hz, 1 H), 3.15 (q, *J* = 7.6 Hz, 1 H), 3.10 – 3.04 (m, 1 H), 2.76 (s, 3 H), 2.68 (dt, *J* = 12.6, 7.7 Hz, 1H), 2.32 – 2.25 (m, 1 H) ppm. **^{13}C NMR** (150MHz, $CDCl_3$) δ 151.6, 148.2, 147.2, 140.1, 130.9, 129.2, 129.1, 128.3, 128.0, 127.8, 126.5,

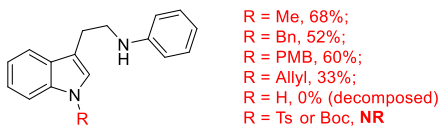
126.1, 123.6, 123.5, 117.6, 117.4, 113.7, 106.9, 86.4,78.6, 56.1, 47.2, 37.6, 35.0 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{30}H_{30}N_3$ 432.2434; Found 432.2439.

4.4 The influence of substitutents of substrates

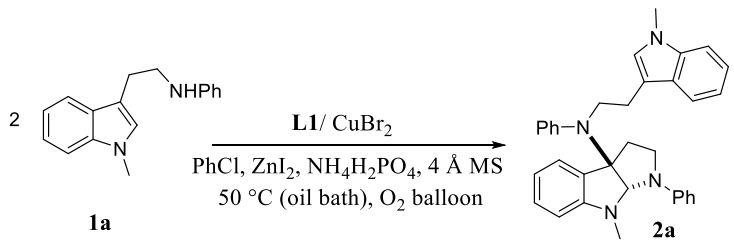
As showed below, substrates bearing side-chain moieties with *para*-substituted phenzyl group, regardless of electron-donating, electron-withdrawing or highly steric groups, were well tolerated under this catalytic system. It was noted that the *meta*-substituted phenzyl substrates were also found to be compatible, providing the desired products smoothly. However, when the *ortho*- (vicinal position) substituted subtrates were employed in the conditions, the reaction did not take place. These results suggested that except the electronic property, the steric effect of the vicinal position on the aniline group also has great influence for the reaction.



Furthermore, the influence of indole moiety of substrate was further studied. As showed below, the *N*-benzyl-, *N*-PMB- and *N*-allyl-substituted tryptamines were also found to be compatible, providing the desired products smoothly. However, when the indole *N*-free tryptamine was exposed to the optimal conditions, none of the desired product was detected. We speculate that the *N*-H moiety combined with the large aromatic indole system is unstable under the current oxidative conditions. It should be noted that when the electron-withdrawing group Ts or Boc substituted substrates were conducted in the standard conditions, the reaction did not happen. These results indicated that the electron property of indole moiety has great influence for the reaction.

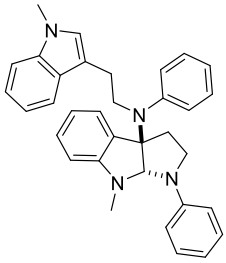


5. General Procedure for 3a-tryptamine-pyrroloindolines and product characterizations



General Procedure for 3a-tryptamine-pyrroloindolines: A mixture of $CuBr_2$ (4.5 mg, 0.02 mmol), **L1** (4.7 mg, 0.024 mmol), **1a** (50.1 mg, 0.2 mmol) , ZnI_2(9.6 mg, 0.03 mmol), $NH_4H_2PO_4$ (2.3 mg, 0.02 mmol) and 4Å MS (200 mg) in PhCl (2 mL) was stirred at 50 ℃ under O_2 balloon. After the reaction was completed (monitored by TLC), the reaction was filtered through a glass funnel with thin layer (30 mm) of silica gel (100-200 mesh) and eluted with DCM/Ethyl Acetate. The filtrate was concentrated under reduced pressure, purified by flash chromatography (Petroleum ether/Ethyl acetate = 60/1) to afford the product **2a**.

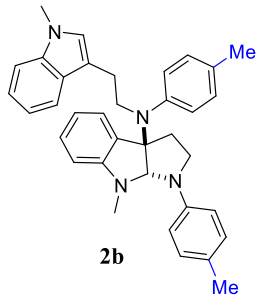
8-Methyl-N-(2-(1-methyl-1*H*-indol-3-yl)ethyl)-N,1-diphenyl-2,3,8,8a-tetrahydropyrrolo[2,3-b]indol-3a(1*H*)-amine (2a)



Following the general procedure for 3a-tryptamine-pyrroloindolines. The procedure was performed on **1a** (0.2 mmol), $CuBr_2$ (0.02 mmol), **L4** (0.024 mmol), Mesitylene (2.0 mL), ZnI_2 (0.03 mmol), $NH_4H_2PO_4$ (0.02 mmol) to afford **2a**. White foam, 16 h, 33.9 mg, 68% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 2 H), 7.23 – 7.16 (m, 6 H), 7.15 – 7.12 (m, 4 H), 7.01 (t, *J* = 7.4 Hz, 1 H), 6.73 – 6.69 (m, 3 H), 6.65 (d, *J* = 8.2 Hz, 2 H), 6.36 (d, *J* = 7.8 Hz, 1 H), 5.58 (s, 1 H), 3.68 (s, 3 H), 3.40 – 3.35 (m, 1 H), 3.34 – 3.28 (m, 1 H), 3.11–3.06 (m, 1 H), 2.94 – 2.88 (m, 1 H), 2.74 – 2.69 (m, 1H), 2.66 (s, 3 H), 2.64–2.59 (m, 1 H), 2.47 (dt, *J* = 12.4, 7.6 Hz, 1H), 2.17 (ddd, *J* = 12.0, 6.8, 4.8 Hz, 1H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 151.6, 147.8, 147.3, 136.9, 131.0, 129.0, 129.0, 128.5, 127.8, 126.6, 125.2, 123.6, 121.3, 119.0, 118.5, 117.4, 117.0, 113.3, 112.7,

109.0, 107.1, 86.5, 78.7, 52.4, 47.6, 37.1, 35.0, 32.5, 25.2 ppm. **HRMS (ESI)** *m/z*: [M + H]$^+$ Calcd for $C_{34}H_{35}N_4$ 499.2856; Found 499.2854.

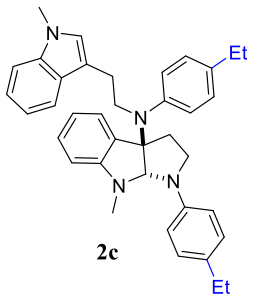
8-Methyl-N-(2-(1-methyl-1*H*-indol-3-yl)ethyl)-N,1-di-p-tolyl-2,3,8,8a-tetrahydropyrrolo[2,3-b]indol-3a(1*H*)-amine (2b)



2b

Yellow oil, 17 h, 36.6 mg, 69% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 2 H), 7.22 – 7.16 (m, 2 H), 7.13 (td, *J* = 7.8, 1.2 Hz, 1 H), 7.02 (s, 4 H), 7.01 – 6.97 (m, 3 H), 6.72 – 6.67 (m, 2 H), 6.58 (d, *J* = 8.5 Hz, 2 H), 6.33 (d, *J* = 7.8 Hz, 1 H), 5.52 (s, 1 H), 3.68 (s, 3 H), 3.35 – 3.30 (m, 1 H), 3.28 – 3.23 (m, 1 H), 3.08 – 3.03 (m, 1 H), 2.95 – 2.91 (m, 1 H), 2.72 – 2.66 (m, 1 H), 2.64 (s, 3 H), 2.62 – 2.57 (m, 1 H), 2.42 (dt, *J* = 12.4, 7.8 Hz, 1 H), 2.32 (s, 3 H), 2.26 (s, 3 H), 2.14 – 2.09 (m, 1 H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 151.9, 145.2, 145.1, 136.9, 134.9, 131.2, 129.5, 129.1, 129.1 128.9, 127.9, 126.6, 126.1, 123.7, 121.3, 119.0, 118.5, 117.2, 113.5, 112.9, 109.0, 107.0, 86.8, 78.8, 52.5, 47.7, 37.2, 35.2, 32.5, 25.2, 21.0, 20.3 ppm. **HRMS (ESI)** *m/z*: [M + H]$^+$ Calcd for $C_{36}H_{39}N_4$ 527.3169; Found 527.3168.

N,1-bis(4-ethylphenyl)-8-methyl-N-(2-(1-methyl-1*H*-indol-3-yl)ethyl)-2,3,8,8a-tetrahydropyrrolo[2,3-b]indol-3a(1*H*)-amine (2c)

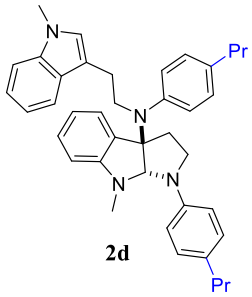


2c

Light yellow oil, 9 h, 48.5 mg, 87% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 2 H), 7.22 – 7.16 (m, 2 H), 7.14 (td, *J* = 7.8, 1.2 Hz, 1 H), 7.04 – 6.99 (m, 7 H), 6.72 – 6.67 (m, 2 H), 6.59 (d, *J* = 8.6 Hz, 2 H), 6.34 (d, *J* = 7.8 Hz, 1 H), 5.53 (s, 1 H), 3.67 (s, 3 H), 3.36 – 3.31 (m, 1 H), 3.29 – 3.23 (m, 1 H), 3.08 – 3.02 (m, 1 H), 2.95 – 2.91 (m, 1 H), 2.72 – 2.67 (m, 1 H), 2.64 (s, 3 H), 2.63 – 2.59 (m, 3 H), 2.56 (q, *J* = 7.6 Hz, 2 H), 2.43 (dt, *J* = 12.4, 7.8 Hz, 1 H), 2.13 (ddd, *J* = 12.2, 6.6, 4.2 Hz, 1 H), 1.22 (dt, *J* = 10.8, 7.6 Hz, 6 H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 151.9, 145.4, 145.3, 141.2, 136.9, 132.7, 131.2, 128.9, 128.9, 128.3, 127.9,

127.8, 126.6, 123.7, 121.3, 119.0, 118.5, 117.2, 113.5, 112.9, 109.0, 107.0, 86.8, 78.8, 52.4, 47.6, 37.2, 35.2, 32.5, 28.3, 27.8, 25.2, 15.9, 15.6 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{38}H_{43}N_4$ 555.3482; Found 555.3483.

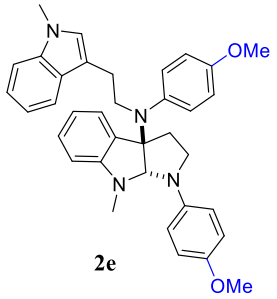
8-Methyl-N-(2-(1-methyl-1*H*-indol-3-yl)ethyl)-N,1-bis(4-propylphenyl)-2,3,8,8a-tetrahydropyrrolo[2,3-b]indol-3a(1*H*)-amine (2d)



2d

Light brown oil, 22 h, 32.2 mg, 55% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 2 H), 7.21 – 7.16 (m, 2 H), 7.15 – 7.12 (m, 1 H), 7.03 – 6.97 (m, 7 H), 6.71 – 6.68 (m, 2 H), 6.58 (d, *J* = 8.4 Hz, 2 H), 6.34 (d, *J* = 7.8 Hz, 1H), 5.53 (s, 1H), 3.67 (s, 3H), 3.37 – 3.31 (m, 1 H), 3.29 – 3.23 (m, 1 H), 3.05 (q, *J* = 7.6 Hz, 1 H), 2.90 – 2.85 (m, 1 H), 2.72 – 2.67 (m, 1 H), 2.64 (s, 3H), 2.62 – 2.58 (m, 1 H), 2.57 – 2.52 (m, 2 H), 2.51 – 2.47 (m, 2 H), 2.43 (dt, *J* = 12.4, 7.6 Hz, 1 H), 2.14 (ddd, *J* = 11.8, 6.6, 4.4 Hz, 1 H), 1.65 – 1.57 (m, 4 H), 0.93 (td, *J* = 7.4, 2.8 Hz, 6 H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 151.8, 145.4, 145.3, 139.7, 136.8, 131.2, 131.1, 128.9, 128.9, 128.4, 127.9, 126.6, 123.6, 121.3, 119.0, 118.5, 117.3, 113.3, 112.9, 109.0, 107.1, 86.8, 78.8, 52.5, 47.7, 37.5, 37.2, 37.1, 35.2, 32.5, 25.2, 24.8, 24.5, 13.8, 13.8 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{40}H_{47}N_4$ 583.3795; Found 583.3793.

N,1-bis(4-methoxyphenyl)-8-methyl-N-(2-(1-methyl-1*H*-indol-3-yl)ethyl)-2,3,8,8a-tetrahydropyrrolo[2,3-b]indol-3a(1*H*)-amine (2e)

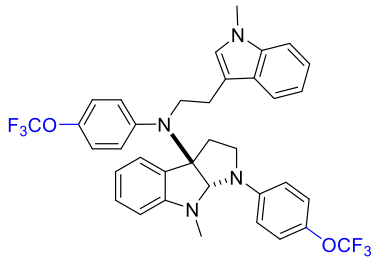


2e

Following the general procedure for 3a-tryptamine-pyrroloindolines. The procedure was performed on **1e** (0.2 mmol), $CuBr_2$ (0.03 mmol), **L1** (0.024 mmol), PhCl (2.0 mL), ZnI_2 (0.03 mmol), $NH_4H_2PO_4$ (0.02 mmol) to afford **2e**. Yellow oil, 48 h, 25.5 mg, 45% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 2 H), 7.21 – 7.16 (m, 2 H), 7.15 – 7.11 (m, 1 H), 7.06 – 7.00 (m, 3 H), 6.80 – 6.74 (m, 4 H), 6.72 – 6.67 (m, 2 H), 6.62 (d, *J* =

9.0 Hz, 2 H), 6.33 (d, *J* = 7.8 Hz, 1 H), 5.43 (s, 1 H), 3.79 (s, 3 H), 3.76 (s, 3 H), 3.69 (s, 3H), 3.34 – 3.28 (m, 1 H), 3.23 – 3.18 (m, 1 H), 3.04 (q, *J* = 8.4 Hz, 1 H), 2.89 – 2.83 (m, 1 H), 2.72 – 2.66 (m, 1 H), 2.63 – 2.56 (m, 4 H), 2.40 (dt, *J* = 12.2, 7.8 Hz, 1 H), 2.16 – 2.11 (m, 1 H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.4, 152.0, 151.8, 141.7, 140.7, 136.9, 131.2, 130.7, 128.8, 127.9, 126.6, 123.6, 121.3, 119.0, 118.5, 117.2, 115.0, 114.6, 113.5, 112.9, 109.0, 107.0, 87.7, 79.0, 55.7, 55.4, 52.8, 47.9, 37.5, 35.4, 32.5, 25.2 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{36}H_{39}O_2N_4$ 559.3068; Found 559.3068.

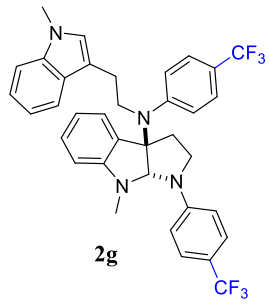
8-Methyl-N-(2-(1-methyl-1*H*-indol-3-yl)ethyl)-N,1-bis(4-(trifluoromethoxy)phenyl)-2,3,8,8a-tetrahydropyrrolo[2,3-b]indol-3a(1*H*)-amine (2f)



2f

Following the general procedure for 3a-tryptamine-pyrroloindolines. The procedure was performed on **1f** (0.2 mmol), $CuBr_2$ (0.02 mmol), **L4** (0.024 mmol), Mesitylene (2.0 mL), ZnI_2 (0.03 mmol), $NH_4H_2PO_4$ (0.02 mmol) to afford **2f**. Light oil, 17 h, 33.6 mg, 50% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2 H), 7.22 – 7.15 (m, 3 H), 7.10 – 7.02 (m, 7 H), 6.73 (t, *J* = 7.4 Hz, 1 H), 6.70 (s, 1 H), 6.54 (d, *J* = 9.2 Hz, 2 H), 6.37 (d, *J* = 7.8 Hz, 1H), 5.40 (s, 1 H), 3.68 (s, 3 H), 3.44 – 3.36 (m, 1 H), 3.31 – 3.24 (m, 1 H), 3.07 (q, *J* = 7.5 Hz, 1 H), 2.91 – 2.84 (m, 1 H), 2.75 – 2.66 (m, 1 H), 2.66 – 2.56 (m, 4 H), 2.44 (dt, *J* = 12.4, 7.7 Hz, 1 H), 2.20 (ddd, *J* = 12.0, 6.8, 4.4 Hz, 1 H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 151.5, 146.5, 146.4, 145.8, 140.3, 136.9, 130.1, 130.0, 129.3, 127.7, 126.7, 123.6, 122.2, 121.5, 121.0, 120.7(q, $^1J_{C\text{-}F}$ = 254.0 Hz), 120.4(q, $^1J_{C\text{-}F}$ = 255.2 Hz), 118.8, 118.6, 117.7, 113.5, 112.3, 109.2, 107.4, 86.9, 78.8, 52.3, 47.9, 36.9, 35.1, 32.5, 25.1 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -57.93, -58.39 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{36}H_{33}O_2N_4F_6$ 667.2502; Found 667.2485.

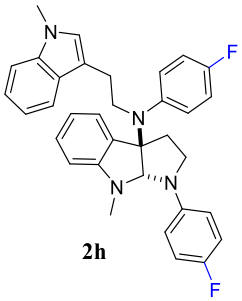
8-Methyl-N-(2-(1-methyl-1*H*-indol-3-yl)ethyl)-N,1-bis(4-(trifluoromethyl)phenyl)-2,3,8,8a-tetrahydropyrrolo[2,3-b]indol-3a(1*H*)-amine (2g)



2g

Following the general procedure for 3a-tryptamine-pyrroloindolines. The procedure was performed on **1g** (0.2 mmol), $CuBr_2$ (0.02 mmol), **L1** (0.024 mmol), PhCl (2.0 mL), ZnI_2 (0.03 mmol), $NH_4H_2PO_4$ (0.02 mmol) to afford **2g**. Brown oil, 48 h, 26.3 mg, 41% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.4 Hz, 2 H), 7.42 (d, *J* = 8.4 Hz, 2 H), 7.29 – 7.24 (m, 2 H), 7.23 – 7.18 (m, 2 H), 7.17 – 7.11 (m, 3 H), 7.05 (t, *J* = 7.2 Hz, 1H), 6.75 (t, *J* = 7.4 Hz, 1 H), 6.67 – 6.63 (m, 3 H), 6.42 (d, *J* = 7.8 Hz, 1 H), 5.57 (s, 1 H), 3.69 (s, 3 H), 3.56 – 3.49 (m, 1 H), 3.49 – 3.43 (m, 1 H), 3.22 – 3.13 (m, 2 H), 2.80 – 2.74 (m, 1 H), 2.70 (s, 3 H), 2.68 – 2.60 (m, 2 H), 2.22 (ddd, *J* = 12.6, 6.6, 4.2 Hz, 1 H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 151.2, 150.8, 149.4, 136.9, 129.8, 129.6, 129.2, 127.6, 126.7, 126.5, 125.7, 123.9, 121.6, 118.9, 118.8, 117.9, 113.0, 112.5, 111.9, 109.2, 107.3, 85.9, 78.3, 51.5, 47.5, 36.6, 34.7, 32.5, 25.0 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -61.05, -61.88 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{36}H_{33}N_4F_6$ 635.2604; Found 635.2597

N,1-bis(4-fluorophenyl)-8-methyl-N-(2-(1-methyl-1*H*-indol-3-yl)ethyl)-2,3,8,8a-tetrahydropyrrolo[2,3-b]indol-3a(1*H*)-amine (2h)

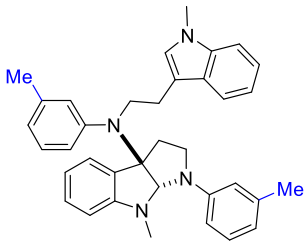


2h

Following the general procedure for 3a-tryptamine-pyrroloindolines. The procedure was performed on **1h** (0.2 mmol), $CuBr_2$ (0.02 mmol), **L4** (0.024 mmol), Mesitylene (2.0 mL), ZnI_2 (0.03 mmol), $NH_4H_2PO_4$ (0.02 mmol) to afford **2h**. Brown oil, 17 h, 21.2 mg, 40% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 2 H), 7.21 – 7.12 (m, 3 H), 7.08 – 7.00 (m, 3 H), 6.94 – 6.87 (m, 4 H), 6.74 – 6.67 (m, 2 H), 6.57 – 6.52 (m, 2 H), 6.34 (d, *J* = 7.8 Hz, 1 H), 5.39 (s, 1 H), 3.69 (s, 3 H), 3.39 – 3.32 (m, 1 H), 3.26 – 3.20 (m, 1 H), 3.05 (q, *J* = 8.2 Hz, 1 H), 2.85 (td, *J* =

8.8, 8.2, 4.4 Hz, 1 H), 2.72 – 2.66 (m, 1 H), 2.62 – 2.54 (m, 4 H), 2.40 (dt, *J* = 12.4, 7.8 Hz, 1 H), 2.21 – 2.13 (m, 1 H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.6 (d, $^1J_{C\text{-}F}$ = 243.0 Hz), 155.7 (d, $^1J_{C\text{-}F}$ = 235.6 Hz), 151.8, 143.8(d, $^4J_{C\text{-}F}$ = 3.0 Hz), 143.6 (d, $^4J_{C\text{-}F}$ = 1.6 Hz), 136.9, 131.0 (d, $^3J_{C\text{-}F}$ = 9.0 Hz), 130.6, 129.1, 127.8, 126.6, 123.6, 121.4, 118.9, 118.6, 117.5, 115.4 (d, $^2J_{C\text{-}F}$ = 22.5 Hz), 115.1 (d, $^2J_{C\text{-}F}$ = 22.5 Hz), 114.4 (d, $^3J_{C\text{-}F}$ = 6.0 Hz), 112.5, 109.1, 107.3, 87.4, 79.0, 52.7, 48.0, 37.2, 35.3, 32.5, 25.1 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -116.53, -128.01 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{34}H_{33}N_4F_2$ 535.2668; Found 535.2666.

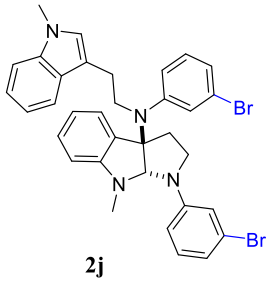
8-Methyl-N-(2-(1-methyl-1*H*-indol-3-yl)ethyl)-N,1-di-m-tolyl-2,3,8,8a-tetrahydro pyrrolo[2,3-b]indol-3a(1*H*)-amine (2i)



2i

Following the general procedure for 3a-tryptamine-pyrroloindolines. The procedure was performed on **1i** (0.2 mmol), $CuBr_2$ (0.02 mmol), **L4** (0.024 mmol), Mesitylene (2.0 mL), ZnI_2 (0.03 mmol), $NH_4H_2PO_4$ (0.02 mmol) to afford **2i**. Light yellow oil, 27 h, 20.1 mg, 38% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.25 – 7.21 (m, 3 H), 7.19 – 7.06 (m, 4 H), 7.02 – 6.96 (m, 2 H), 6.94 (d, *J* = 7.6 Hz, 1 H), 6.86 (s, 1 H), 6.72 (t, *J* = 7.2 Hz, 1 H), 6.69 (s, 1 H), 6.55 (d, *J* = 7.4 Hz, 1 H), 6.49 (d, *J* = 8.6 Hz, 1H), 6.46 (s, 1 H), 6.36 (d, *J* = 7.8 Hz, 1 H), 5.63 (s, 1 H), 3.67 (s, 3 H), 3.37 – 3.29 (m, 1H), 3.29 – 3.19 (m, 1 H), 3.07 (q, *J* = 7.2 Hz, 1 H), 2.75 – 2.66 (m, 5 H), 2.65 – 2.58 (m, 1 H), 2.47 – 2.40 (m, 1 H), 2.29 (s, 3 H), 2.20 – 2.13 (m, 1 H), 2.09 (s, 3 H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 151.1, 147.6, 147.4, 138.7, 138.2, 136.8, 131.5, 129.5, 128.9, 128.8, 128.0, 127.8, 126.5, 126.5, 126.1, 123.3, 121.3, 119.0, 118.5, 117.8, 117.4, 113.7, 112.8, 110.2, 109.0, 106.9, 86.4, 78.7, 52.7, 47.9, 37.0, 34.7, 32.5, 25.2, 21.8, 21.1 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{36}H_{39}N_4$ 527.3169; Found 527.3156.

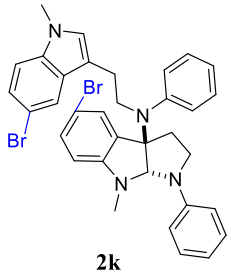
N,1-bis(3-bromophenyl)-8-methyl-N-(2-(1-methyl-1*H*-indol-3-yl)ethyl)-2,3,8,8a-tetrahydropyrrolo[2,3-b]indol-3a(1*H*)-amine (2j)



2j

Following the general procedure for 3a-tryptamine-pyrroloindolines. The procedure was performed on **1j** (0.2 mmol), $CuBr_2$ (0.02 mmol), **L4** (0.024 mmol), Mesitylene (2.0 mL), ZnI_2 (0.03 mmol), $NH_4H_2PO_4$ (0.02 mmol) to afford **2j**. Light yellow oil, 39 h, 38.4 mg, 58% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 3 H), 7.25 – 7.17 (m, 4 H), 7.13 (t, *J* = 7.8 Hz, 1 H), 7.06 (t, *J* = 7.8 Hz, 3 H), 6.87 (d, *J* = 8.0 Hz, 1 H), 6.81 (s, 1 H), 6.76 (t, *J* = 7.4 Hz, 1 H), 6.72 (s, 1 H), 6.59 (d, *J* = 8.2 Hz, 1 H), 6.41 (d, *J* = 7.8 Hz, 1 H), 5.49 (s, 1 H), 3.73 (s, 3 H), 3.44 – 3.37 (m, 1 H), 3.34 – 3.28 (m, 1 H), 3.10 (q, *J* = 7.8 Hz, 1 H), 2.95 – 2.90 (m, 1 H), 2.78 – 2.63 (m, 5 H), 2.52 – 2.46 (m, 1 H), 2.25 – 2.18 (m, 1 H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 151.3, 149.3, 148.3, 136.9, 131.5, 130.3, 130.2, 129.7, 129.3, 128.1, 127.7, 127.1, 126.7, 123.5, 123.4, 122.1, 121.5, 120.1, 118.8, 118.7, 117.8, 116.1, 112.2, 111.9, 109.2, 107.3, 86.4,78.7, 52.2, 47.7, 36.7, 35.0, 32.5, 25.1 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{34}H_{33}N_4Br_2$ 655.1066; Found 655.1079.

5-Bromo-N-(2-(5-bromo-1-methyl-1*H*-indol-3-yl)ethyl)-8-methyl-N,1-diphenyl-2,3,8,8a-tetrahydropyrrolo[2,3-b]indol-3a(1*H*)-amine (2k)

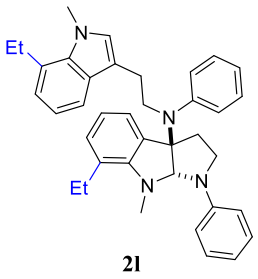


2k

Following the general procedure for 3a-tryptamine-pyrroloindolines. The procedure was performed on **1k** (0.2 mmol), $CuBr_2$ (0.03 mmol), **L1** (0.024 mmol), PhCl (2.0 mL), ZnI_2 (0.03 mmol), $NH_4H_2PO_4$ (0.02 mmol) to afford **2k**. Light yellow oil, 17 h, 40.8 mg, 62% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.38 (d, *J* = 1.9 Hz, 1 H), 7.28 – 7.16 (m, 8 H), 7.15 – 7.09 (m, 3 H), 6.73 (t, *J* = 7.4 Hz, 1 H), 6.71 (s, 1 H), 6.63 (d, *J* = 8.0 Hz, 2 H), 6.24 (d, *J* = 8.2 Hz, 1 H), 5.58 (s, 1 H), 3.68 (s, 3 H), 3.28 (t, *J* = 7.4 Hz, 2 H), 3.10 – 3.02 (m, 1 H), 2.90 – 2.84 (m, 1 H), 2.67 (s, 3 H), 2.66 – 2.59 (m, 1 H), 2.59 – 2.52 (m, 1 H), 2.38 (dt, *J* = 12.6, 7.6 Hz, 1 H), 2.06 (ddd, *J* = 11.4, 6.4, 4.4 Hz, 1 H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 150.4, 147.1, 147.0, 135.5, 133.2, 131.8, 129.2,

129.1, 128.6, 127.9, 126.9, 126.4, 125.7, 124.2, 121.4, 117.3, 113.2, 112.3, 112.1, 110.7, 108.8, 108.3, 86.3, 78.5, 52.1, 47.5, 37.0, 34.6, 32.7, 24.7 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{34}H_{33}N_4Br_2$ 655.1066; Found 655.1070.

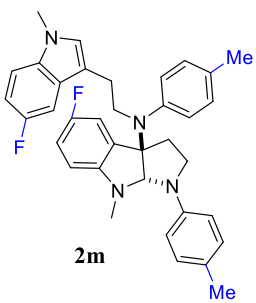
7-Ethyl-N-(2-(7-ethyl-1-methyl-1*H*-indol-3-yl)ethyl)-8-methyl-N,1-diphenyl-2,3,8,8a-tetrahydropyrrolo[2,3-b]indol-3a(1*H*)-amine (2l)



2l

Following the general procedure for 3a-tryptamine-pyrroloindolines. The procedure was performed on **1l** (0.2 mmol), $CuBr_2$ (0.02 mmol), **L4** (0.024 mmol), Mesitylene (2.0 mL), ZnI_2 (0.03 mmol), $NH_4H_2PO_4$ (0.02 mmol) to afford **2l**. Light yellow oil, 19 h, 24.7 mg, 44% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 2 H), 7.22 – 7.17 (m, 2 H), 7.15 – 7.11 (m, 2 H), 7.06 – 7.02 (m, 3 H), 6.99 (d, *J* = 7.6 Hz, 1 H), 6.94 (d, *J* = 4.8 Hz, 2 H), 6.82 (t, *J* = 7.6 Hz, 1 H), 6.70 (t, *J* = 7.4 Hz, 1 H), 6.64 (s, 1 H), 6.61 (d, *J* = 8.0 Hz, 2 H), 5.20 (s, 1 H), 3.93 (s, 3 H), 3.49 – 3.42 (m, 1 H), 3.40 – 3.30 (m, 1 H), 3.29 (t, *J* = 8.4 Hz, 1 H), 3.07 (q, *J* = 7.4 Hz, 2 H), 2.90 (td, *J* = 10.0, 9.4, 5.8 Hz, 1 H), 2.72 – 2.65 (m, 1 H), 2.61 – 2.53 (m, 2 H), 2.50 – 2.44 (m, 4 H), 2.44 – 2.36 (m, 1 H), 2.33 (dd, *J* = 12.0, 4.8 Hz, 1 H), 1.33 (t, *J* = 7.4 Hz, 3 H), 1.01 (t, *J* = 7.4 Hz, 3 H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 152.1, 148.5, 146.6, 134.9, 132.6, 129.6, 129.4, 129.2, 128.8, 128.7, 128.6, 128.5, 127.7, 125.4, 122.3, 121.9, 120.4, 119.0, 116.9, 116.6, 114.0, 112.6, 89.7, 78.7, 52.0, 46.4, 40.9, 36.4, 35.8, 25.4, 25.1, 24.7, 16.7, 13.8 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{38}H_{43}N_4$ 555.3482; Found 555.3482.

5-Fluoro-N-(2-(5-fluoro-1-methyl-1*H*-indol-3-yl)ethyl)-8-methyl-N,1-di-p-tolyl-2,3,8,8a-tetrahydropyrrolo[2,3-b]indol-3a(1*H*)-amine (2m)

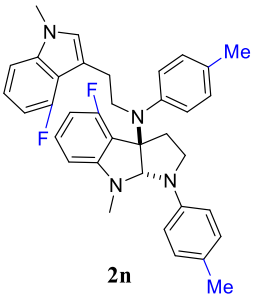


2m

Following the general procedure for 3a-tryptamine-pyrroloindolines. The procedure was performed on **1m** (0.2 mmol), $CuBr_2$ (0.02 mmol), **L4** (0.024 mmol), Mesitylene (2.0 mL), ZnI_2 (0.03 mmol), $NH_4H_2PO_4$ (0.02 mmol) to afford **2m**. Light yellow oil, 24 h, 31.6

mg, 56% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.15 (dd, *J* = 8.7, 4.2 Hz, 1 H), 7.07 – 6.97 (m, 6 H), 6.95 – 6.88 (m, 2 H), 6.87 (dd, *J* = 8.4, 2.8 Hz, 1 H), 6.82 (td, *J* = 8.8, 2.8 Hz, 1 H), 6.74 (s, 1 H), 6.57 (d, *J* = 8.4 Hz, 2 H), 6.24 (dd, *J* = 8.5, 4.1 Hz, 1 H), 5.53 (s, 1 H), 3.68 (s, 3 H), 3.24 (t, *J* = 7.4 Hz, 2 H), 3.03 (q, *J* = 7.4 Hz, 1 H), 2.92 – 2.85 (m, 1 H), 2.65 – 2.58 (m, 4 H), 2.58 – 2.51 (m, 1 H), 2.39 – 2.31 (m, 4 H), 2.26 (s, 3 H), 2.11 – 2.03 (m, 1 H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.4 (d, $^{1}J_{C\text{-}F}$ = 232.4 Hz), 156.3 (d, $^{1}J_{C\text{-}F}$ = 234.0 Hz), 148.0, 144.9, 144.6, 135.4, 133.5, 132.7 (d, $^{3}J_{C\text{-}F}$ = 6.0 Hz), 129.6, 129.2, 129.2, 128.3, 128.0 (d, $^{3}J_{C\text{-}F}$ = 10.5 Hz), 126.3, 115.4 (d, $^{2}J_{C\text{-}F}$ = 24.0 Hz), 113.5, 112.7 (d, $^{4}J_{C\text{-}F}$ = 4.6 Hz), 110.8 (d, $^{2}J_{C\text{-}F}$ = 22.6 Hz), 109.7 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 109.6 (d, $^{2}J_{C\text{-}F}$ = 15.0 Hz), 107.5 (d, $^{3}J_{C\text{-}F}$ = 7.4 Hz), 103.7 (d, $^{2}J_{C\text{-}F}$ = 22.6 Hz), 87.3,78.6, 52.3, 47.6, 37.0, 35.9, 32.8, 25.0, 21.0, 20.3 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -125.91, -127.38. ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{36}H_{37}N_4F_2$ 563.2981; Found 563.2977.

4-Fluoro-N-(2-(4-fluoro-1-methyl-1*H*-indol-3-yl)ethyl)-8-methyl-N,1-di-p-tolyl-2,3,8,8a-tetrahydropyrrolo[2,3-b]indol-3a(1*H*)-amine (2n)

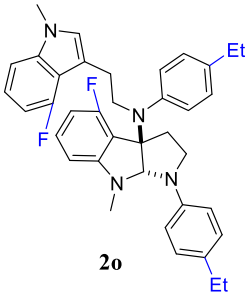


2n

Following the general procedure for 3a-tryptamine-pyrroloindolines. The procedure was performed on **1n** (0.2 mmol), $CuBr_2$ (0.02 mmol), **L4** (0.024 mmol), Mesitylene (2.0 mL), ZnI_2 (0.03 mmol), $NH_4H_2PO_4$ (0.02 mmol) to afford **2n**. Light yellow oil, 22 h, 34.1 mg, 60% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.09 – 7.04 (m, 1 H), 7.04 – 6.96 (m, 8 H), 6.71 – 6.63 (m, 2 H), 6.58 (d, *J* = 8.2 Hz, 2 H), 6.30 (t, *J* = 8.8 Hz, 1 H), 6.01 (d, *J* = 7.8 Hz, 1 H), 5.42 (s, 1 H), 3.66 (s, 3 H), 3.55 – 3.48 (m, 1 H), 3.40 – 3.33 (m, 1 H), 3.28 – 3.22 (m, 1 H), 3.14 – 3.07 (m, 1 H), 2.79 – 2.72 (m, 1 H), 2.72 – 2.65 (m, 1 H), 2.52 (s, 3 H), 2.47 – 2.39 (m, 2 H), 2.29 (s, 3 H), 2.24 (s, 3 H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.4 (d, $^{1}J_{C\text{-}F}$ = 224.6 Hz), 157.2 (d, $^{1}J_{C\text{-}F}$ = 246.0 Hz), 154.9 (d, $^{3}J_{C\text{-}F}$ = 9 Hz), 145.1, 144.8, 139.8 (d, $^{2}J_{C\text{-}F}$ = 12.0 Hz), 134.6, 130.6, 130.5 (d, $^{3}J_{C\text{-}F}$ = 9 Hz), 129.0, 128.6, 127.1, 126.4, 121.6 (d, $^{3}J_{C\text{-}F}$ = 6 Hz), 116.4 (d, $^{2}J_{C\text{-}F}$ = 19.6 Hz), 115.4 (d, $^{2}J_{C\text{-}F}$ = 18.0 Hz), 114.0, 111.7 (d, $^{3}J_{C\text{-}F}$ = 7.5 Hz), 105.2 (d, $^{4}J_{C\text{-}F}$ = 4.6 Hz),

104.6 (d, $^{3}J_{C\text{-}F}$ = 7.6 Hz), 103.8 (d, $^{2}J_{C\text{-}F}$ = 19.5 Hz), 103.0 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 87.3, 78.8, 52.6, 47.8, 35.4, 32.8, 26.3, 20.9, 20.3 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -116.38, -123.25 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{36}H_{37}N_4F_2$ 563.2981; Found 563.2985.

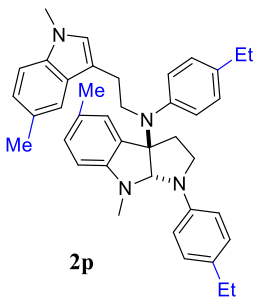
N,1-bis(4-ethylphenyl)-4-fluoro-N-(2-(4-fluoro-1-methyl-1*H*-indol-3-yl)ethyl)-8-methyl-2,3,8,8a-tetrahydropyrrolo[2,3-b]indol-3a(1*H*)-amine (2o)



2o

Following the general procedure for 3a-tryptamine-pyrroloindolines. The procedure was performed on **1o** (0.2 mmol), $CuBr_2$ (0.03 mmol), **L1** (0.024 mmol), PhCl (2.0 mL), ZnI_2 (0.03 mmol), $NH_4H_2PO_4$ (0.02 mmol) to afford **2o**. Light yellow oil, 48 h, 17.5 mg, 30 % yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.12 – 6.97 (m, 9 H), 6.73 – 6.67 (m, 2 H), 6.62 (d, *J* = 8.0 Hz, 2 H), 6.33 (t, *J* = 8.8 Hz, 1 H), 6.04 (d, *J* = 7.8 Hz, 1 H), 5.44 (s, 1 H), 3.69 (s, 3 H), 3.59 – 3.49 (m, 1 H), 3.43 – 3.35 (m, 1 H), 3.32 – 3.24 (m, 1 H), 3.13 (q, *J* = 8.2 Hz, 1 H), 2.82 – 2.74 (m, 1 H), 2.75 – 2.68 (m, 1 H), 2.61 (q, *J* = 7.6 Hz, 2 H), 2.57 (q, *J* = 7.8 Hz, 2 H), 2.53 (s, 3 H), 2.49 – 2.43 (m, 2 H), 1.26 – 1.18 (m, 6 H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.4 (d, $^{1}J_{C\text{-}F}$ = 244.6 Hz), 157.2 (d, $^{1}J_{C\text{-}F}$ = 244.6 Hz), 155.0, 145.3, 145.0, 140.9, 139.8 (d, $^{2}J_{C\text{-}F}$ = 12.0 Hz), 133.0, 130.5 (d, $^{3}J_{C\text{-}F}$ = 9.0 Hz) , 128.5, 128.3, 127.7, 127.1, 121.6 (d, $^{3}J_{C\text{-}F}$ = 7.6 Hz), 116.5 (d, $^{2}J_{C\text{-}F}$ = 21 Hz), 115.5 (d, $^{2}J_{C\text{-}F}$ = 18.0 Hz), 113.8, 111.7, 105.2 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 104.6 (d, $^{2}J_{C\text{-}F}$ = 22.6 Hz), 103.8 (d, $^{2}J_{C\text{-}F}$ = 19.5 Hz), 103.0, 87.2, 78.9, 52.6, 47.8, 35.4, 35.3, 32.8, 28.3, 27.8, 26.3, 15.9, 15.5.**^{19}F NMR** (565 MHz, $CDCl_3$) δ -116.47, -123.28 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{38}H_{41}N_4F_2$ 591.3294; Found 591.3298.

N-(2-(1,5-dimethyl-1*H*-indol-3-yl)ethyl)-N,1-bis(4-ethylphenyl)-5,8-dimethyl-2,3,8,8a-tetrahydropyrrolo[2,3-b]indol-3a(1*H*)-amine (2p)

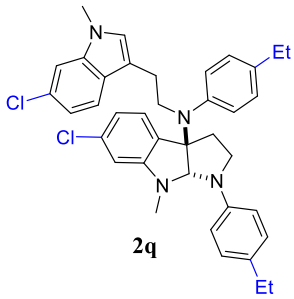


2p

Following the general procedure for 3a-tryptamine-pyrroloindolines. The procedure was performed on **1p**(0.2 mmol), $CuBr_2$ (0.02 mmol), **L4** (0.024 mmol), Mesitylene

(2.0 mL), ZnI_2 (0.03 mmol), $NH_4H_2PO_4$ (0.02 mmol) to afford **2p**. Brown oil, 26 h, 36.0 mg, 62% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.8 Hz, 1 H), 7.06 – 6.98 (m, 9 H), 6.96 (d, *J* = 7.8 Hz, 1 H), 6.65 (s, 1 H), 6.59 (d, *J* = 8.6 Hz, 2 H), 6.28 (d, *J* = 7.8 Hz, 1 H), 5.53 (s, 1 H), 3.64 (s, 3 H), 3.38 – 3.30 (m, 1 H), 3.25 – 3.18 (m, 1 H), 3.08 – 3.01 (m, 1 H), 2.88 – 2.82 (m, 1 H), 2.72 – 2.63 (m, 4 H), 2.63 – 2.57 (m, 3 H), 2.57 – 2.53 (m, 2 H), 2.47 – 2.40 (m, 1 H), 2.39 (s, 3 H), 2.29 (s, 3 H), 2.15 – 2.09 (m, 1 H), 1.22 (dt, *J* = 12.8, 7.6 Hz, 6 H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.8, 145.4, 145.4, 141.1, 135.3, 132.6, 131.7, 129.3, 129.0, 128.3, 128.1, 127.8, 127.6, 126.7, 126.6, 124.3, 122.9, 118.7, 113.4, 112.2, 108.7, 107.2, 87.2, 78.9, 52.6, 47.6, 37.0, 35.8, 32.5, 28.3, 27.8, 25.4, 21.3, 20.9, 15.9, 15.6 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{40}H_{47}N_4$ 583.3795; Found 583.3790.

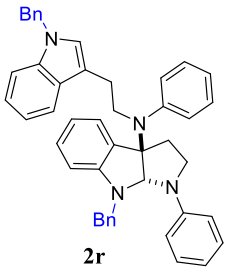
6-Chloro-N-(2-(6-chloro-1-methyl-1*H*-indol-3-yl)ethyl)-N,1-bis(4-ethylphenyl)-8-methyl-2,3,8,8a-tetrahydropyrrolo[2,3-b]indol-3a(1*H*)-amine (2q)



2q

Following the general procedure for 3a-tryptamine-pyrroloindolines. The procedure was performed on **1q** (0.2 mmol), $CuBr_2$ (0.03 mmol), **L1** (0.024 mmol), PhCl (2.0 mL), ZnI_2 (0.03 mmol), $NH_4H_2PO_4$ (0.02 mmol) to afford **2q**. Light yellow oil, 5 h, 22.6 mg, 36% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.25 – 7.24 (m, 1 H), 7.14 (d, *J* = 8.4 Hz, 1 H), 7.07 – 6.98 (m, 8 H), 6.68 (s, 1 H), 6.61 (dd, *J* = 7.8, 1.8 Hz, 1 H), 6.56 (d, *J* = 8.6 Hz, 2 H), 6.28 (d, *J* = 1.8 Hz, 1 H), 5.52 (s, 1 H), 3.64 (s, 3 H), 3.27 – 3.19 (m, 2 H), 3.05 – 2.99 (m, 1 H), 2.95 – 2.90 (m, 1 H), 2.66 – 2.59 (m, 6 H), 2.56 (q, *J* = 7.4 Hz, 3 H), 2.36 (dt, *J* = 12.4, 7.8 Hz, 1 H), 2.05 – 1.99 (m, 1 H), 1.22 (dt, *J* = 13.4, 7.6 Hz, 6 H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 152.8, 145.0, 144.9, 141.6, 137.3, 134.6, 133.2, 129.6, 129.0, 128.4, 127.9, 127.5, 127.3, 126.4, 124.4, 119.8, 119.2, 116.7, 113.5, 113.1, 109.1, 106.7, 86.6, 78.4, 52.1, 47.6 37.2, 34.4, 32.6, 28.3, 27.8, 24.9, 15.9, 15.6 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{38}H_{41}N_4Cl_2$ 623.2703; Found 623.2697.

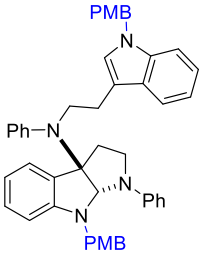
8-Benzyl-N-(2-(1-benzyl-1*H*-indol-3-yl)ethyl)-N,1-diphenyl-2,3,8,8a-tetrahydropyrrolo[2,3-b]indol-3a(1*H*)-amine (2r)



2r

Following the general procedure for 3a-tryptamine-pyrroloindolines. The procedure was performed on **1r** (0.2 mmol), $CuBr_2$ (0.02 mmol), **L4** (0.024 mmol), Mesitylene (2.0 mL), ZnI_2 (0.03 mmol), $NH_4H_2PO_4$ (0.02 mmol) to afford **2r**. Yellow oil, 70 h, 34.1 mg, 52% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 5 H), 7.22 – 7.17 (m, 3 H), 7.17 – 7.12 (m, 2 H), 7.12 – 7.08 (m, 2 H), 7.06 (s, 5 H), 7.04 – 6.97 (m, 4 H), 6.91 (d, *J* = 7.6 Hz, 2 H), 6.75 (s, 1 H), 6.69 (t, *J* = 7.6 Hz, 1 H), 6.64 (t, *J* = 7.4 Hz, 1 H), 6.54 (d, *J* = 8.0 Hz, 2 H), 6.23 (d, *J* = 7.8 Hz, 1 H), 5.88 (s, 1 H), 5.20 (s, 2 H), 4.37 (d, *J* = 17.0 Hz, 1 H), 4.11 (d, *J* = 16.8 Hz, 1 H), 3.51 – 3.43 (m, 1 H), 3.37 – 3.28 (m, 1 H), 3.16 (q, *J* = 7.8 Hz, 1 H, 3.06 – 2.99 (m, 1H), 2.78 – 2.69 (m, 1 H), 2.68 – 2.58 (m, 1 H), 2.51 – 2.42 (m, 1 H), 2.26 – 2.18 (m, 1 H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 151.2, 147.9, 147.4, 138.8, 137.8, 136.6, 130.7, 129.2, 129.0, 129.0, 128.7, 128.6, 128.2, 128.1, 127.5, 126.8, 126.7, 126.5, 125.9, 125.4, 123.9, 121.5, 119.1, 118.8, 117.2, 117.2, 113.4, 113.3, 109.5, 106.5, 84.4, 79.2, 52.5, 50.0, 49.8, 47.5, 38.0, 25.4 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{46}H_{43}N_4$ 651.3482; Found 651.3475

8-(4-Methoxybenzyl)-N-(2-(1-(4-methoxybenzyl)-1*H*-indol-3-yl)ethyl)-N,1-diphenyl-2,3,8,8a-tetrahydropyrrolo[2,3-b]indol-3a(1*H*)-amine (2s)

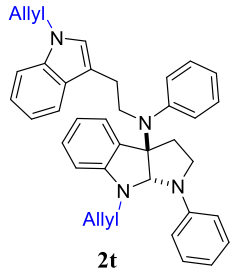


2s

Following the general procedure for 3a-tryptamine-pyrroloindolines. The procedure was performed on **1s** (0.2 mmol), $CuBr_2$ (0.02 mmol), **L4** (0.024 mmol), Mesitylene (2.0 mL), ZnI_2 (0.03 mmol), $NH_4H_2PO_4$ (0.02 mmol) to afford **2s**. Brown oil, 24 h, 42.6 mg, 60% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.26 (d, *J* = 7.4 Hz, 1 H), 7.24 –7.17(m, 4 H),

7.16 – 7.12 (m, 2 H), 7.12 – 7.04 (m, 5 H), 7.02 – 6.94 (m, 3 H), 6.83 (d, *J* = 8.2 Hz, 2 H), 6.78 (d, *J* = 8.6 Hz, 2 H), 6.73 (s, 1H), 6.69 (t, *J* = 7.2 Hz, 1 H), 6.66 (t, *J* = 7.4 Hz, 1 H), 6.55 (t, *J* = 7.6 Hz, 4 H), 6.26 (d, *J* = 7.8 Hz, 1 H), 5.87 (s, 1 H), 5.13 (s, 2 H), 4.34 (d, *J* = 16.6 Hz, 1 H), 4.04 (d, *J* = 16.6 Hz, 1 H), 3.73 (s, 3 H), 3.66 (s, 3 H), 3.52 – 3.39 (m, 1 H), 3.33 – 3.22 (m, 1 H), 3.15 (q, *J* = 8.1 Hz, 1 H), 3.04 – 2.95 (m, 1 H), 2.77 – 2.66 (m, 1 H), 2.65 – 2.54 (m, 1 H), 2.51 – 2.41 (m, 1 H), 2.24 – 2.14 (m, 1 H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 158.9, 158.2, 151.2, 147.9, 147.4, 136.5, 130.8, 130.7, 129.7, 129.2, 129.0, 129.0, 128.6, 128.1, 127.8, 125.8, 125.3, 123.8, 121.4, 119.1, 118.8, 117.2, 117.1, 114.0, 113.6, 113.4, 113.2, 109.5, 106.5, 84.2, 79.2, 55.2, 55.1, 52.6, 49.3, 49.2, 47.4, 38.0, 25.4 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ Calcd for $C_{48}H_{47}O_2N_4$ 711.3694; Found 711.3672.

8-Allyl-N-(2-(1-allyl-1*H*-indol-3-yl)ethyl)-N,1-diphenyl-2,3,8,8a-tetrahydropyrrolo[2,3-b]indol-3a(1*H*)-amine (2t)

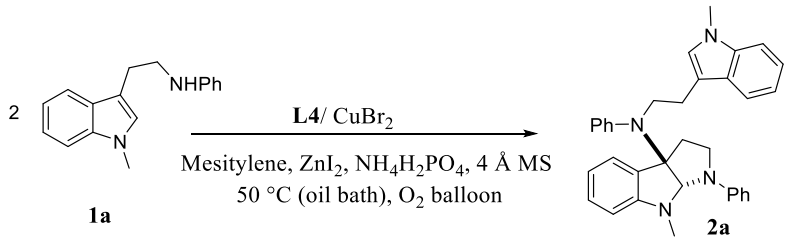


2t

Following the general procedure for 3a-tryptamine-pyrroloindolines. The procedure was performed on **1t** (0.2 mmol), $CuBr_2$ (0.02 mmol), **L4** (0.024 mmol), Mesitylene (2.0 mL), ZnI_2 (0.03 mmol), $NH_4H_2PO_4$ (0.02 mmol) to afford **2t**. Light yellow oil, 75 h, 18.5 mg, 33% yield; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.28 – 7.09 (m, 12 H), 7.01 (t, *J* = 7.6 Hz, 1 H), 6.78 – 6.61 (m, 5 H), 6.34 (d, *J* = 7.8 Hz, 1 H), 5.97 – 5.90 (m, 1 H), 5.84 (s, 1 H), 5.53 – 5.45 (m, 1 H), 5.17 – 5.13 (m, 1 H), 5.08 – 4.94 (m, 3 H), 4.61 (d, *J* = 5.4 Hz, 2 H), 3.80 – 3.74 (m, 1 H), 3.55 (dd, *J* = 17.2, 6.4 Hz, 1 H), 3.46 – 3.39 (m, 1 H), 3.37 – 3.30 (m, 1 H), 3.14 – 3.08 (m, 1 H), 2.94 – 2.88 (m, 1 H), 2.77 – 2.70 (m, 1 H), 2.66 – 2.60 (m, 1 H), 2.48 (dt, *J* = 12.6, 7.6 Hz, 1H), 2.23 – 2.16 (m, 1 H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 150.4, 147.9, 147.4, 136.3, 134.1, 133.7, 131.0, 129.1, 129.0, 128.9, 128.5, 128.1, 125.5, 125.3, 123.7, 121.4, 119.0, 118.7, 117.3, 117.1, 117.1, 116.2, 113.5, 113.1, 109.4, 106.7, 84.5, 79.0, 52.5, 49.1, 48.6, 47.4, 37.8, 25.3 ppm.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{38}H_{39}N_4$ 551.3169; Found 551.3166.

6 Scale-up experiments



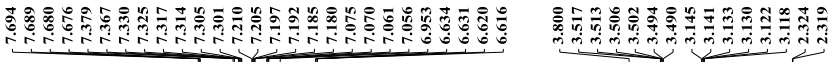
Procedure: A mixture of **1a** (250.3 mg, 1.0 mmol), $CuBr_2$ (22.3 mg, 0.1 mmol), **L4** (58.4 mg, 0.12 mmol), ZnI_2 (47.9 mg, 0.15 mmol), $NH_4H_2PO_4$ (11.5 mg, 0.1 mmol) and 4ÅMS (1.0 g) in Mesitylene (10 mL) was stirred at 50 ℃ under O_2 balloon. After the reaction was completed (monitored by TLC), the reaction was filtered through a glass funnel with thin layer (30 mm) of silica gel (100-200 mesh) and eluted with DCM/Ethyl Acetate. The filtrate was concentrated under reduced pressure, purified by flash chromatography (Petroleum ether/Ethyl acetate = 60/1) to afford the product **2a** (14 h, 161.9 mg, 65%).

7 References

[1] W.-D. Li, J. Chen, D.-Y. Zhu and J.-B. Xia, *Chin. J. Chem*, 2020, **39**, 614-620.

[2] L. Serusi, M. Bonnans, A. Luridiana, F. Secci, P. Caboni, T. Boddaert, D.-J. Aitken and A. Frongia, *Adv. Synth. Catal*, 2019, **361**, 1908-1912.

8 ^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectra of compounds



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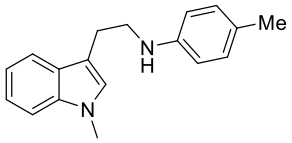
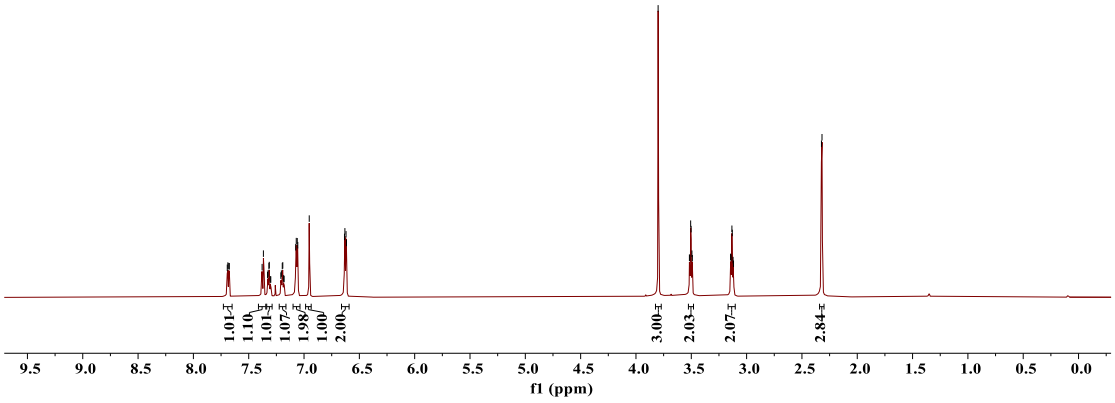
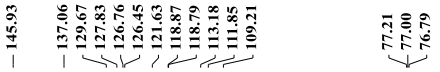


1b





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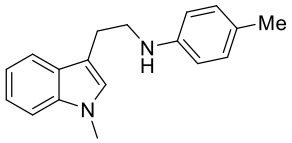
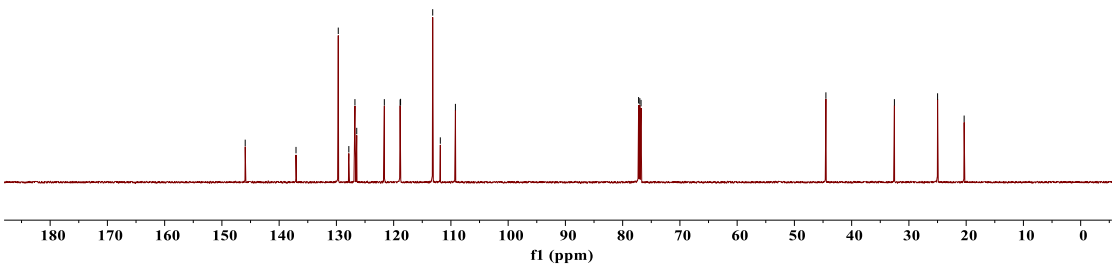
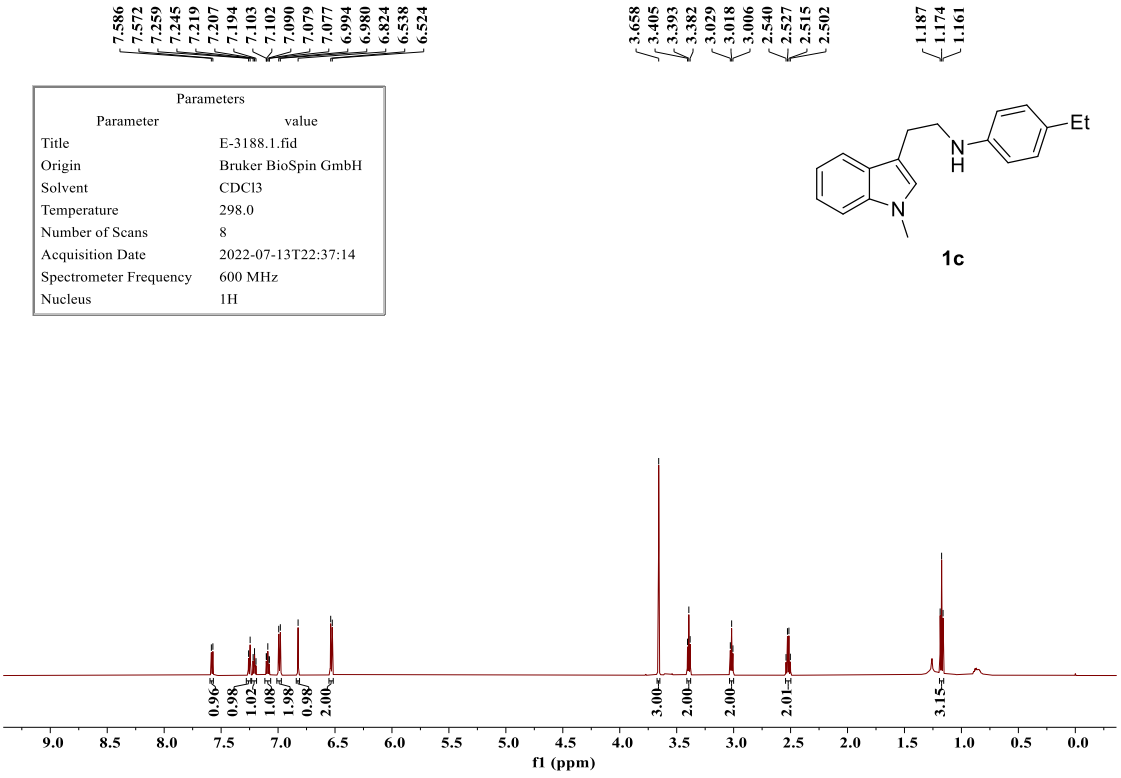


1b

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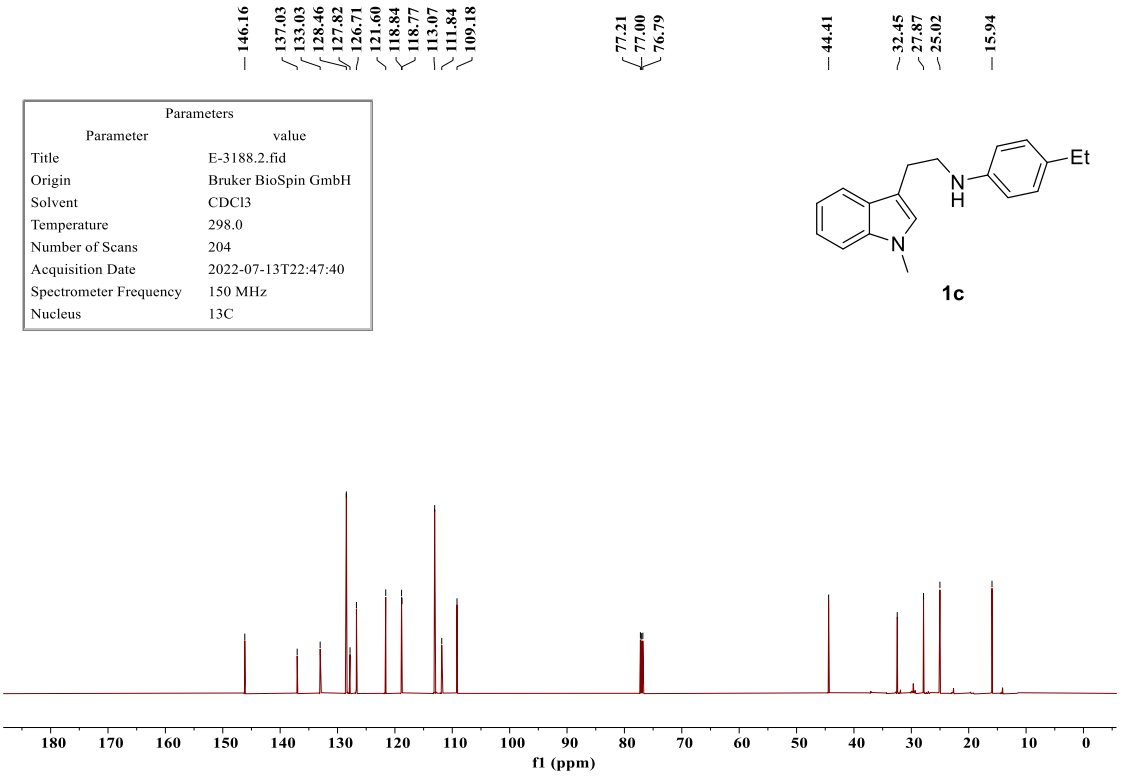
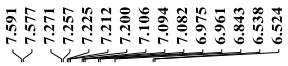
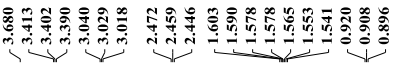
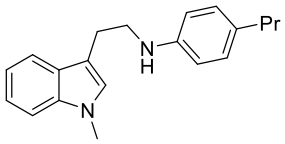
Number of Scans 8
Acquisition Date 2022-07-13T22:37:14
Spectrometer Frequency 600 MHz
Nucleus 1H
Et
N
H
N
1c
0.96
0.98
1.02
1.08
1.98
0.98
2.00
3.00
2.00
2.00
2.01
3.15
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


146.16
137.03
133.03
128.46
127.82
126.71
121.60
118.84
118.77
113.07
111.84
109.18
77.21
77.00
76.79
44.41
32.45
27.87
25.02
15.94
Parameters
Parameter value
Title E-3188.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 204
Acquisition Date 2022-07-13T22:47:40
Spectrometer Frequency 150 MHz
Nucleus 13C
Et
N
H
N
1c
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

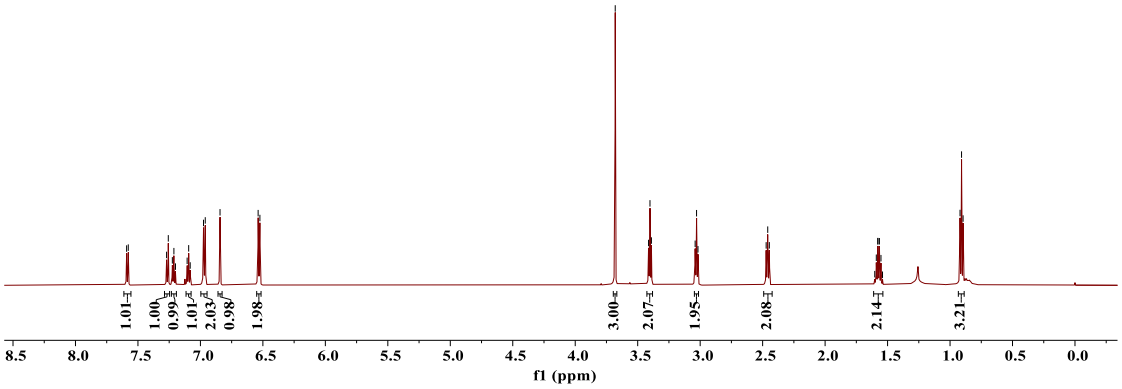


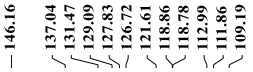


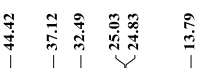
Parameters	
Parameter	value
Title	E-3185.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	8
Acquisition Date	2022-07-14T10:01:02
Spectrometer Frequency	600 MHz
Nucleus	1H



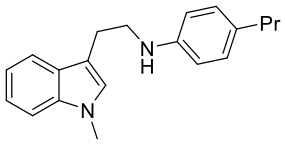
1d



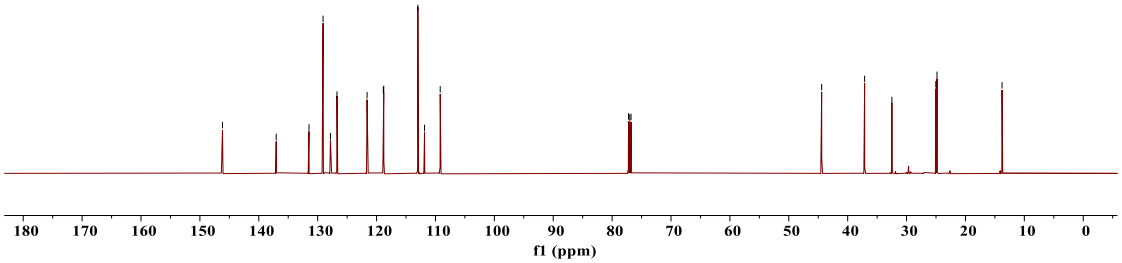


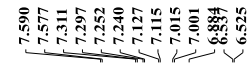


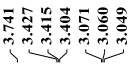
Parameters	
Parameter	value
Title	E-3185.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	364
Acquisition Date	2022-07-14T10:19:16
Spectrometer Frequency	150 MHz
Nucleus	13C



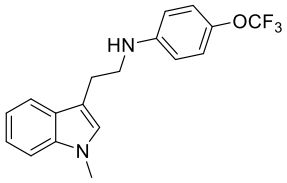
1d



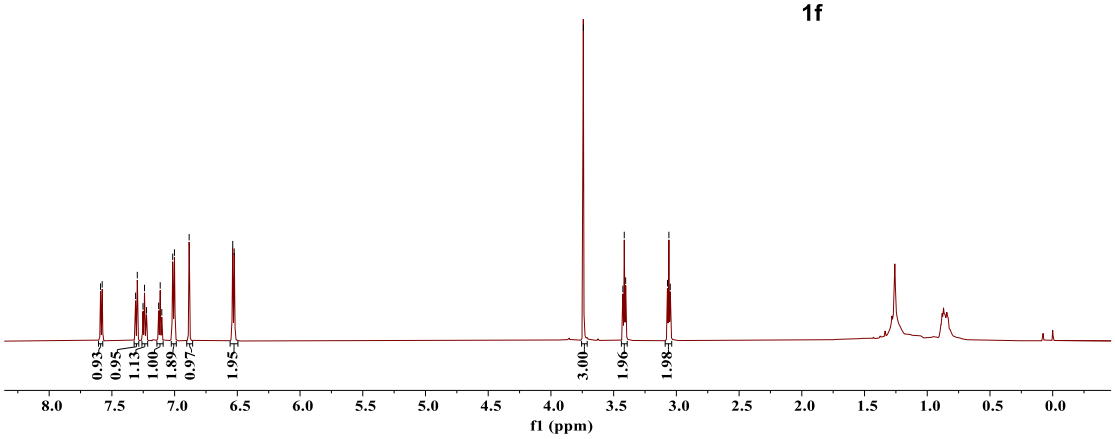


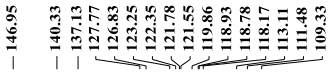


Parameter	value
Title	Ra-3184-1.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	4
Acquisition Date	2022-11-19T11:06:37
Spectrometer Frequency	600 MHz
Nucleus	1H

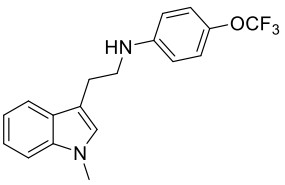


1f

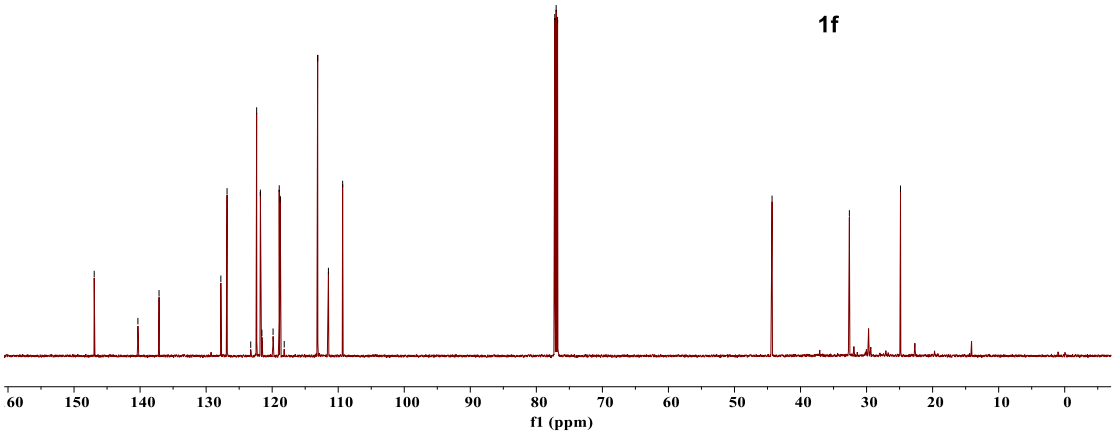




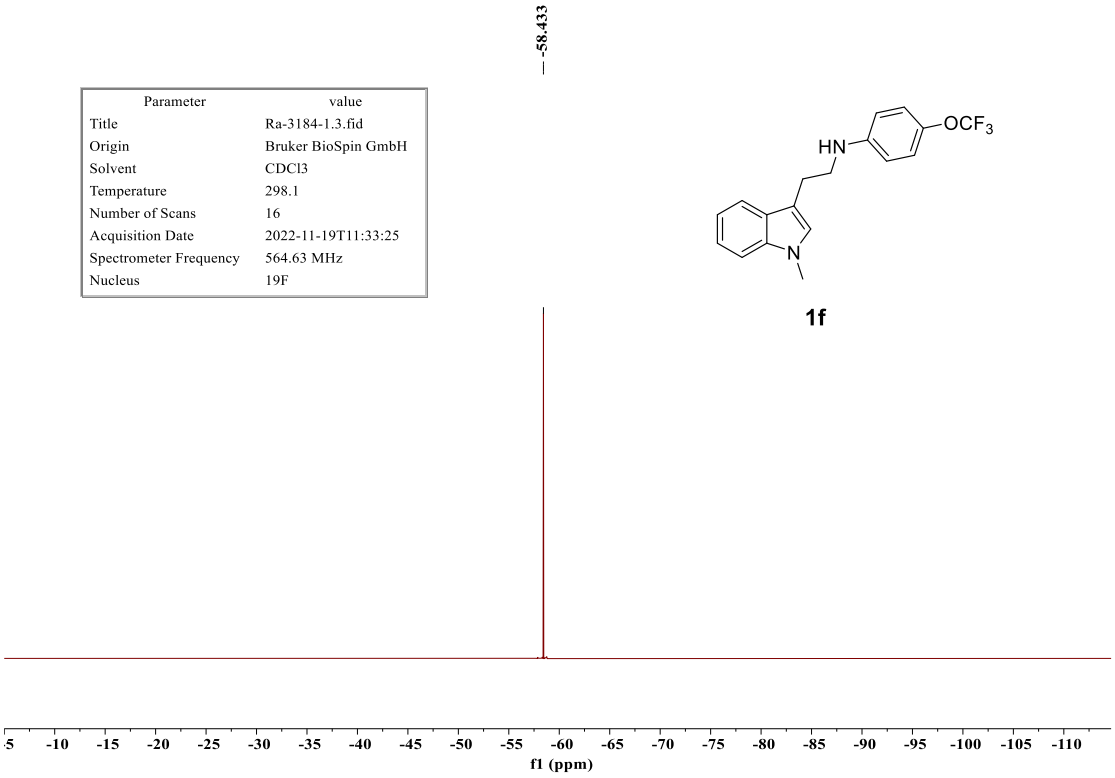
Parameter	value
Title	Ra-3184-1.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	512
Acquisition Date	2022-11-19T11:31:45
Spectrometer Frequency	150 MHz
Nucleus	13C

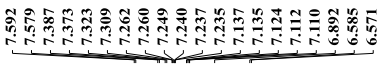


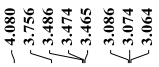
1f



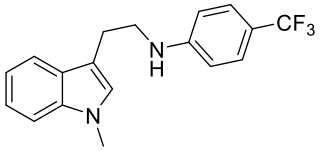
Parameter	value
Title	Ra-3184-1.3.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.1
Number of Scans	16
Acquisition Date	2022-11-19T11:33:25
Spectrometer Frequency	564.63 MHz
Nucleus	19F



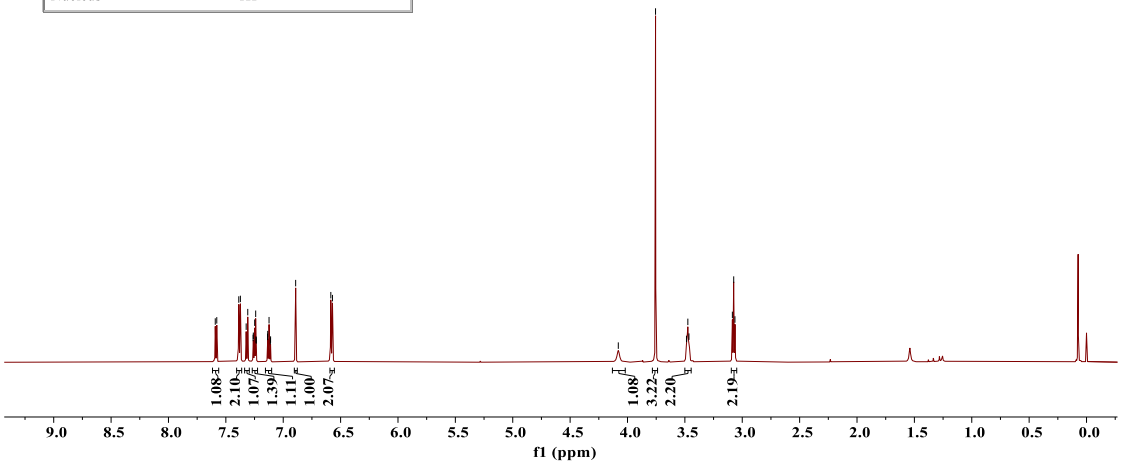




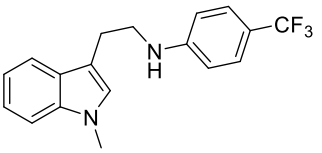
Parameters	
Parameter	value
Title	E-282-2.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	8
Acquisition Date	2022-07-19T01:29:58
Spectrometer Frequency	600 MHz
Nucleus	1H



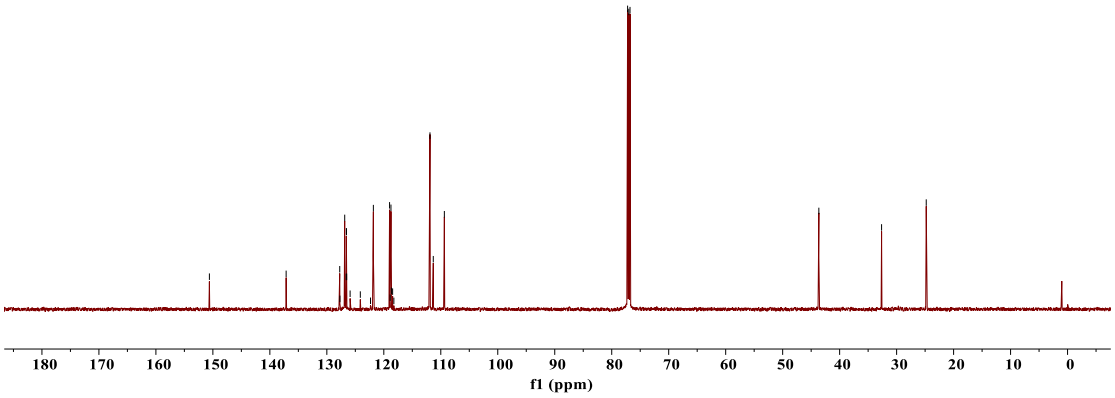
1g



Parameter	value
Title	E-282-2.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	512
Acquisition Date	2022-07-20T13:37:10
Spectrometer Frequency	150 MHz
Nucleus	13C

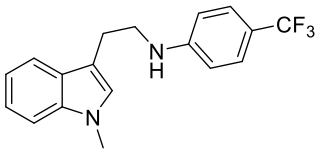


1g

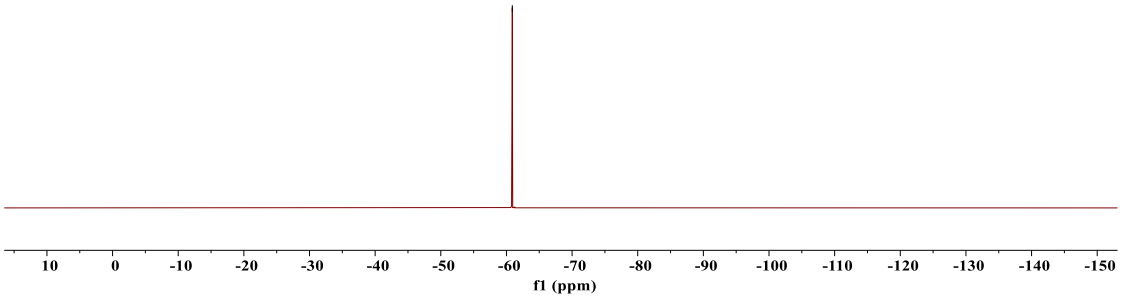


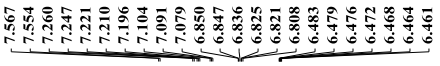
-60.895

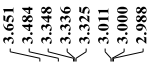
Parameters	
Parameter	value
Title	E-282-2.3.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	16
Acquisition Date	2022-07-20T13:38:38
Spectrometer Frequency	565 MHz
Nucleus	19F



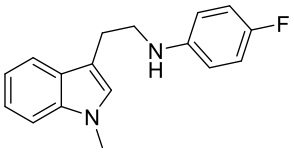
1g



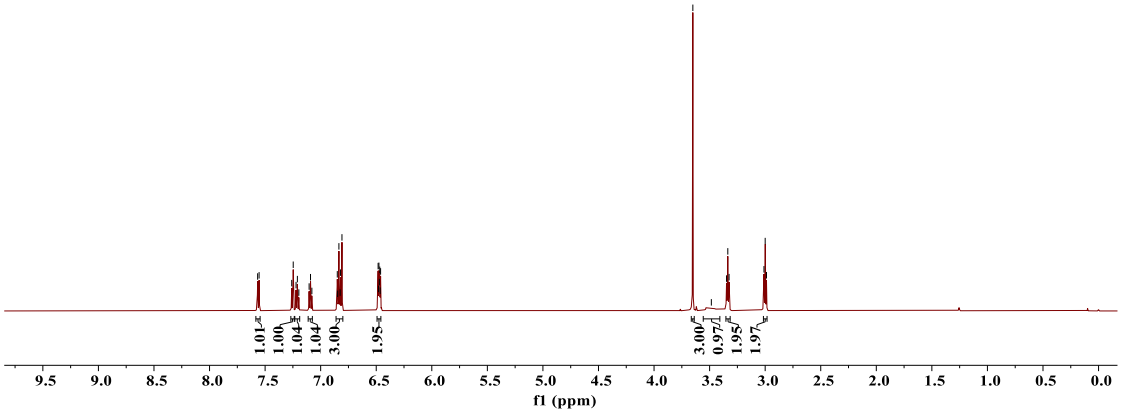


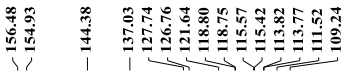


Parameters	
Parameter	value
Title	E-3180.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	8
Acquisition Date	2022-06-20T23:38:26
Spectrometer Frequency	600 MHz
Nucleus	1H

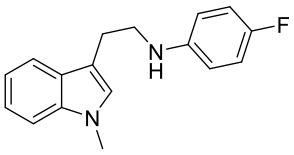


1h

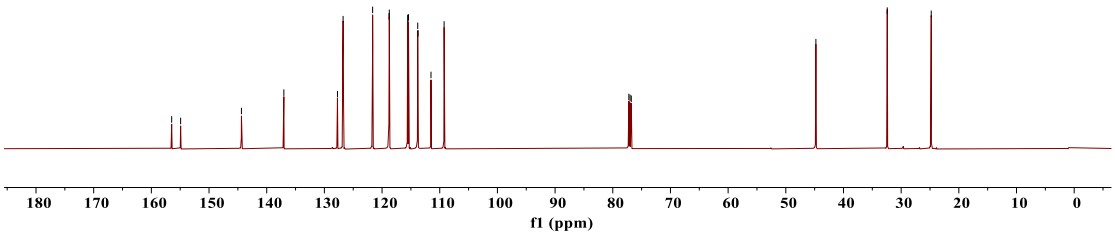




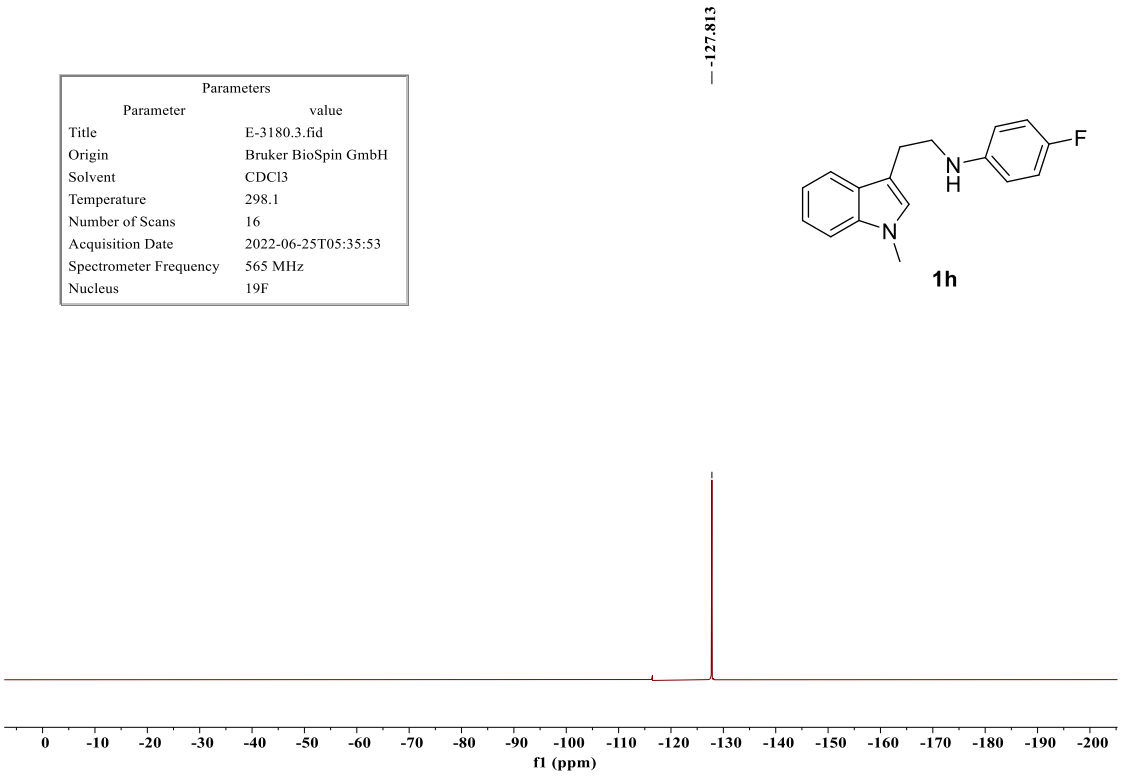
Parameter	value
Title	E-3180.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	512
Acquisition Date	2022-06-25T05:34:28
Spectrometer Frequency	150 MHz
Nucleus	13C

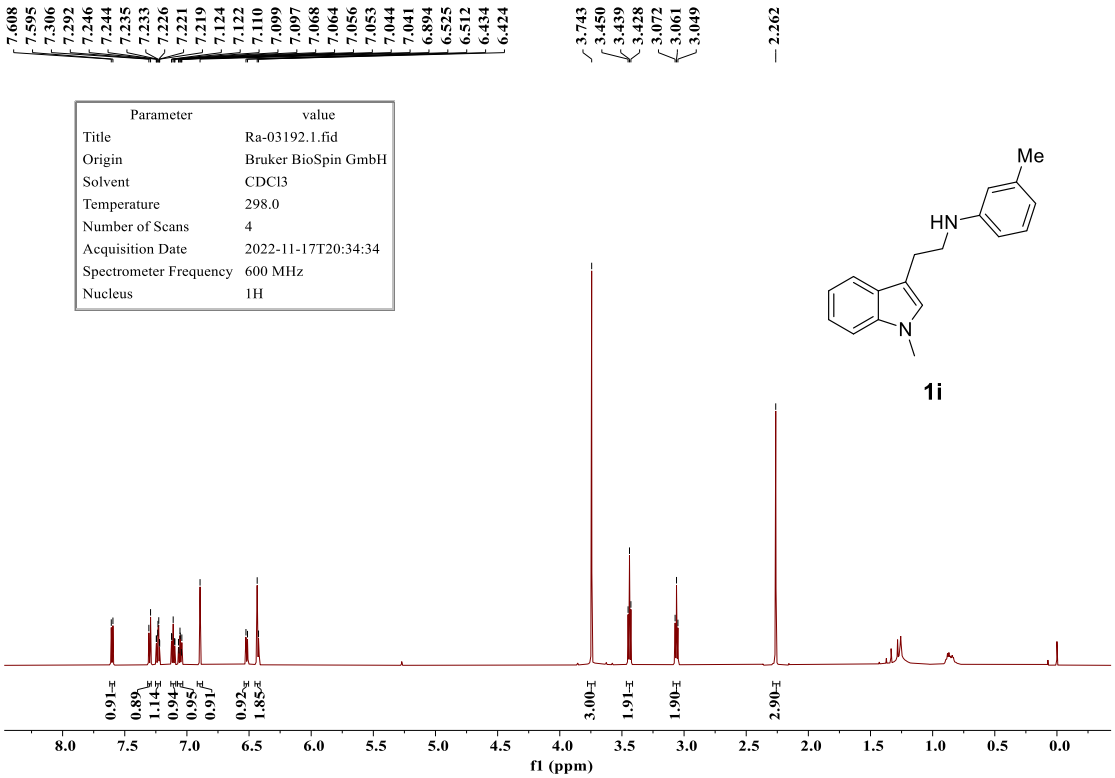


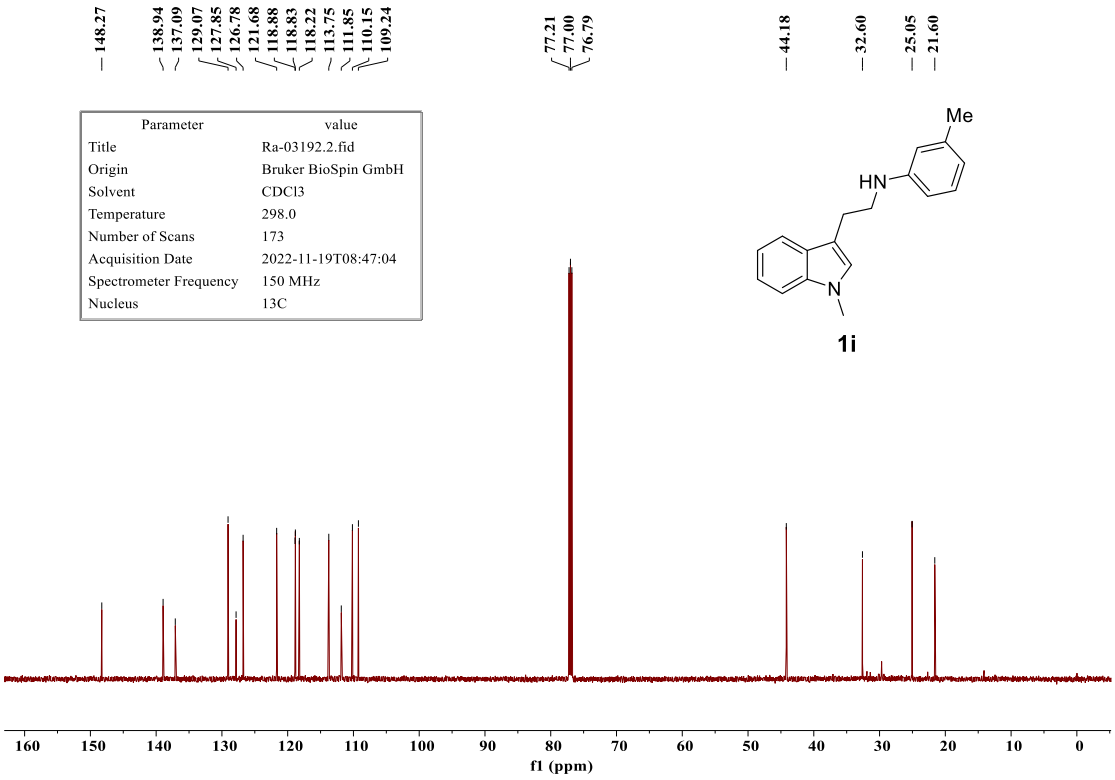
1h

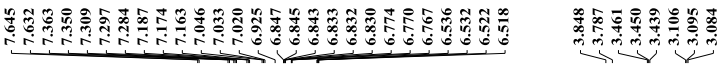


Parameters	
Parameter	value
Title	E-3180.3.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.1
Number of Scans	16
Acquisition Date	2022-06-25T05:35:53
Spectrometer Frequency	565 MHz
Nucleus	19F

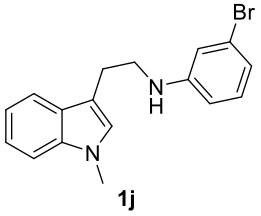



7.608
7.595
7.306
7.292
7.246
7.244
7.235
7.233
7.226
7.221
7.219
7.124
7.122
7.110
7.099
7.097
7.068
7.064
7.056
7.053
7.044
7.041
6.894
6.525
6.512
6.434
6.424
3.743
3.450
3.439
3.428
3.072
3.061
3.049
2.262
Parameter value
Title Ra-03192.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 4
Acquisition Date 2022-11-17T20:34:34
Spectrometer Frequency 600 MHz
Nucleus 1H
Me
HN
N
1i
0.91
0.89
1.14
0.94
0.95
0.91
0.92
1.85
3.00
1.91
1.90
2.90
f1 (ppm)

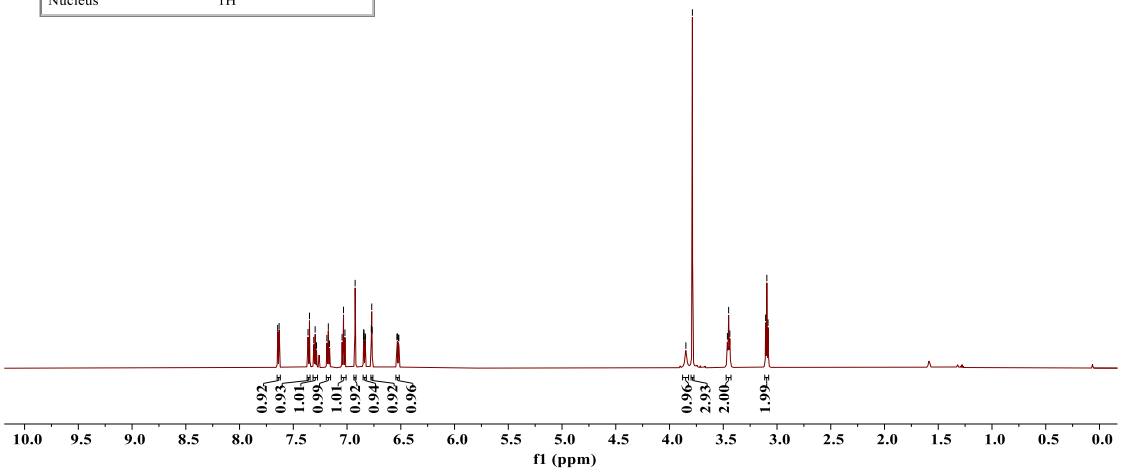

148.27
138.94
137.09
129.07
127.85
126.78
121.68
118.88
118.83
118.22
113.75
111.85
110.15
109.24
77.21
77.00
76.79
44.18
32.60
25.05
21.60
Parameter value
Title Ra-03192.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 173
Acquisition Date 2022-11-19T08:47:04
Spectrometer Frequency 150 MHz
Nucleus 13C
Me
HN
N
1i
f1 (ppm)

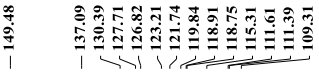


Parameters	
Parameter	value
Title	E-3173-2.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	8
Acquisition Date	2022-07-21T00:09:36
Spectrometer Frequency	600 MHz
Nucleus	1H

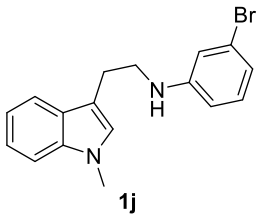


1j

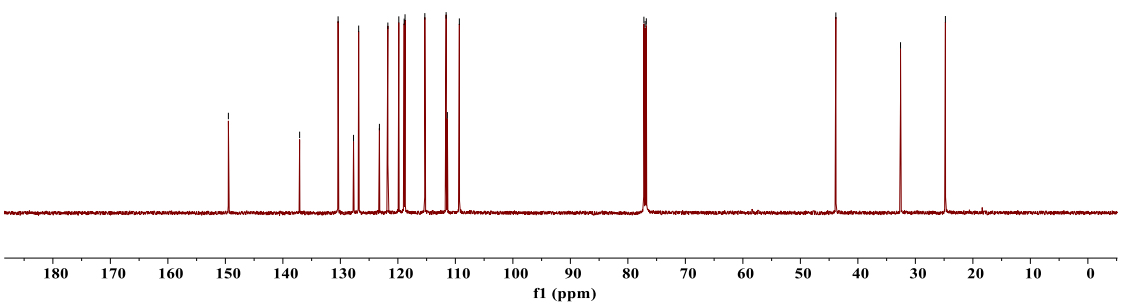


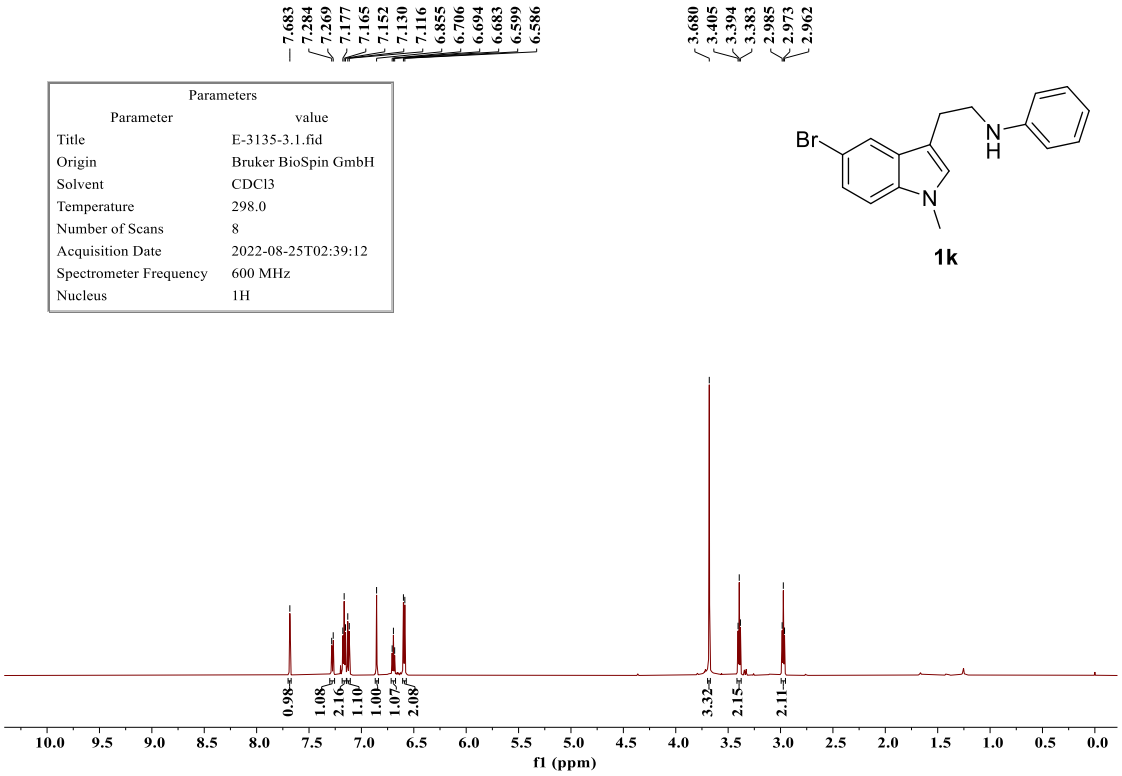


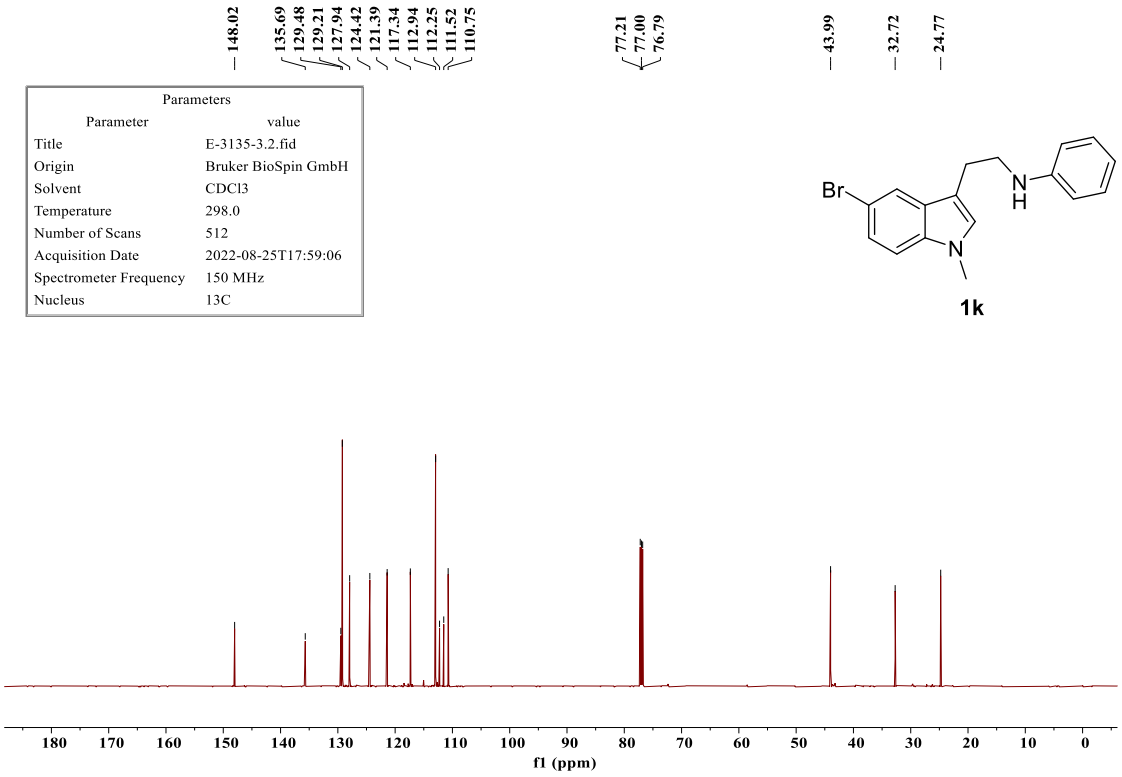
Parameters	
Parameter	value
Title	E-3173-2.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	264
Acquisition Date	2022-07-22T09:07:50
Spectrometer Frequency	150 MHz
Nucleus	13C

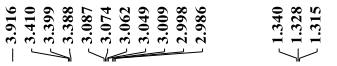


1j

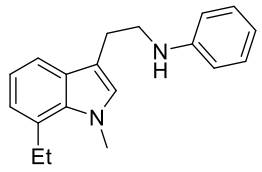



7.683
7.284
7.269
7.177
7.165
7.152
7.130
7.116
6.855
6.706
6.694
6.683
6.599
6.586
3.680
3.405
3.394
3.383
2.985
2.973
2.962
Parameters
Parameter value
Title E-3135-3.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-08-25T02:39:12
Spectrometer Frequency 600 MHz
Nucleus 1H
Br
N
H
N
1k
0.98
1.08
2.16
1.10
1.00
1.07
2.08
3.32
2.15
2.11
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
f1 (ppm)

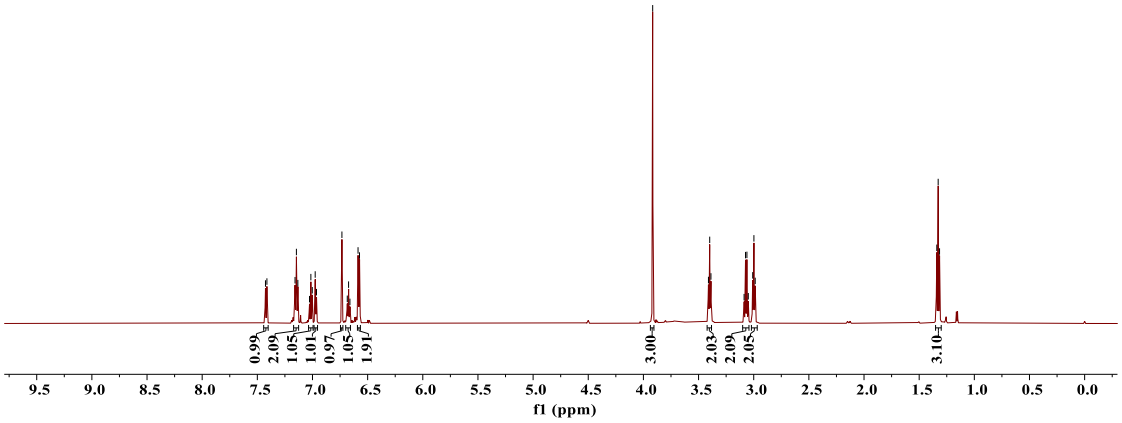

148.02
135.69
129.48
129.21
127.94
124.42
121.39
117.34
112.94
112.25
111.52
110.75
77.21
77.00
76.79
43.99
32.72
24.77
Parameters
Parameter value
Title E-3135-3.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 512
Acquisition Date 2022-08-25T17:59:06
Spectrometer Frequency 150 MHz
Nucleus 13C
Br
N
H
N
1k
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

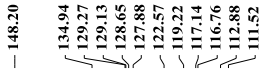


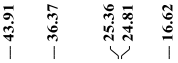
Parameters	
Parameter	value
Title	E-407.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	8
Acquisition Date	2022-06-23T03:14:34
Spectrometer Frequency	600 MHz
Nucleus	1H



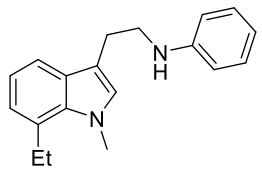
1l



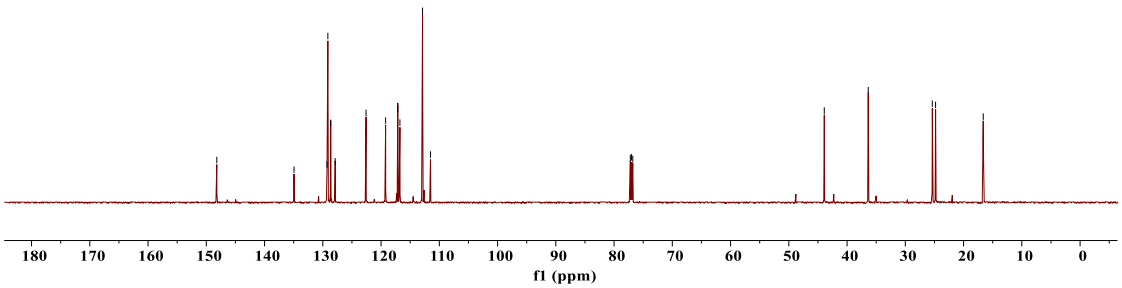


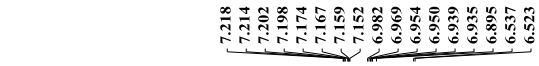


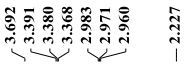
Parameters	
Parameter	value
Title	E-407.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	256
Acquisition Date	2022-06-25T12:11:38
Spectrometer Frequency	150 MHz
Nucleus	13C



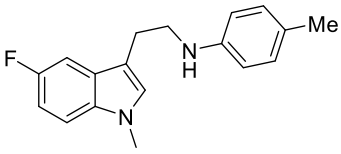
1l



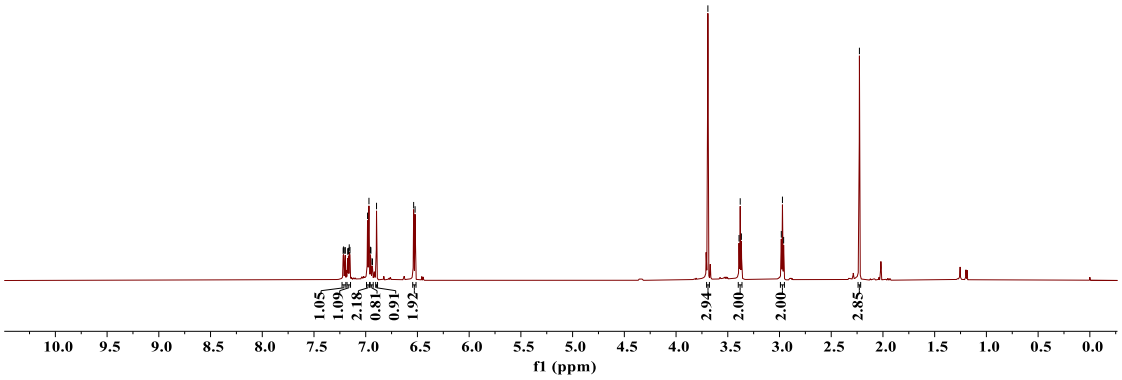




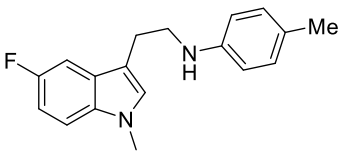
Parameters	
Parameter	value
Title	E-448.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	8
Acquisition Date	2022-06-22T00:25:08
Spectrometer Frequency	600 MHz
Nucleus	1H



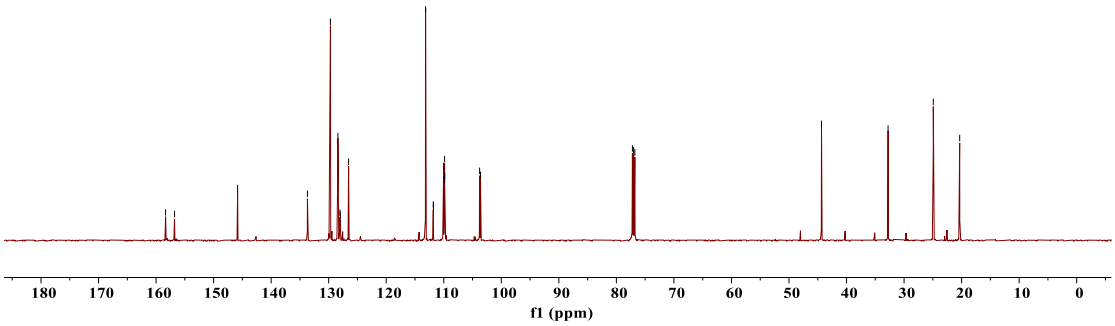
1m



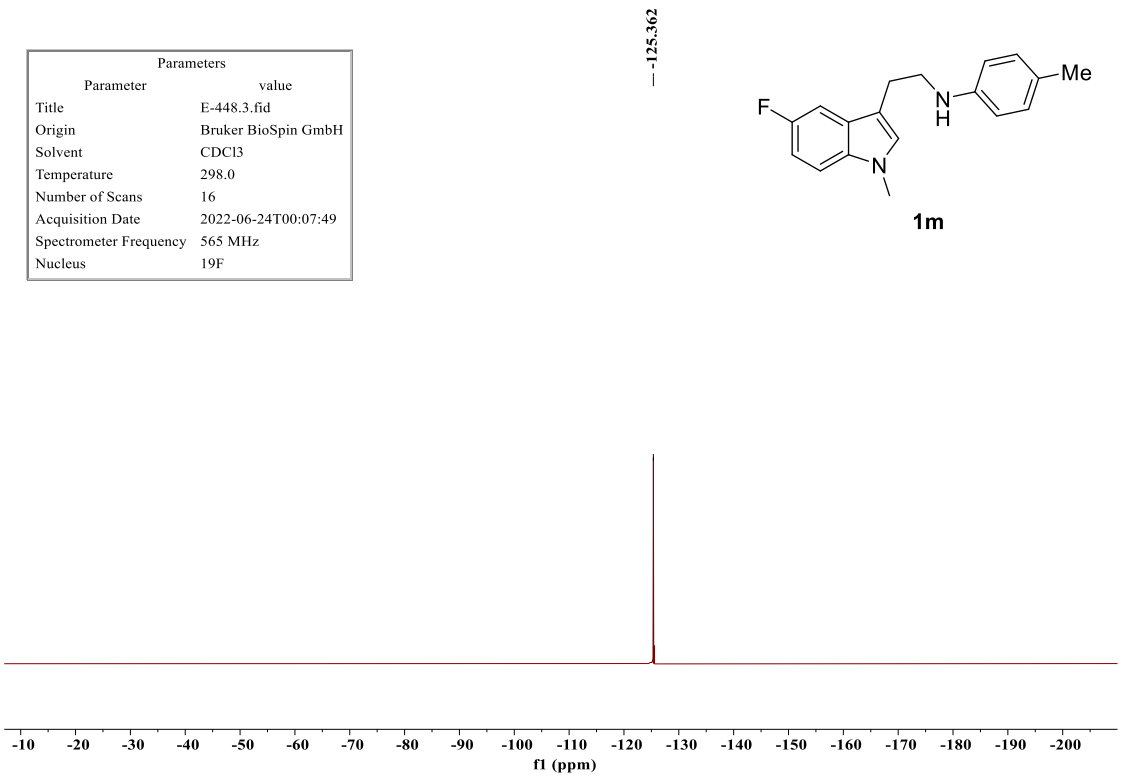
Parameter	value
Title	E-448.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	800
Acquisition Date	2022-06-24T00:06:21
Spectrometer Frequency	150 MHz
Nucleus	13C

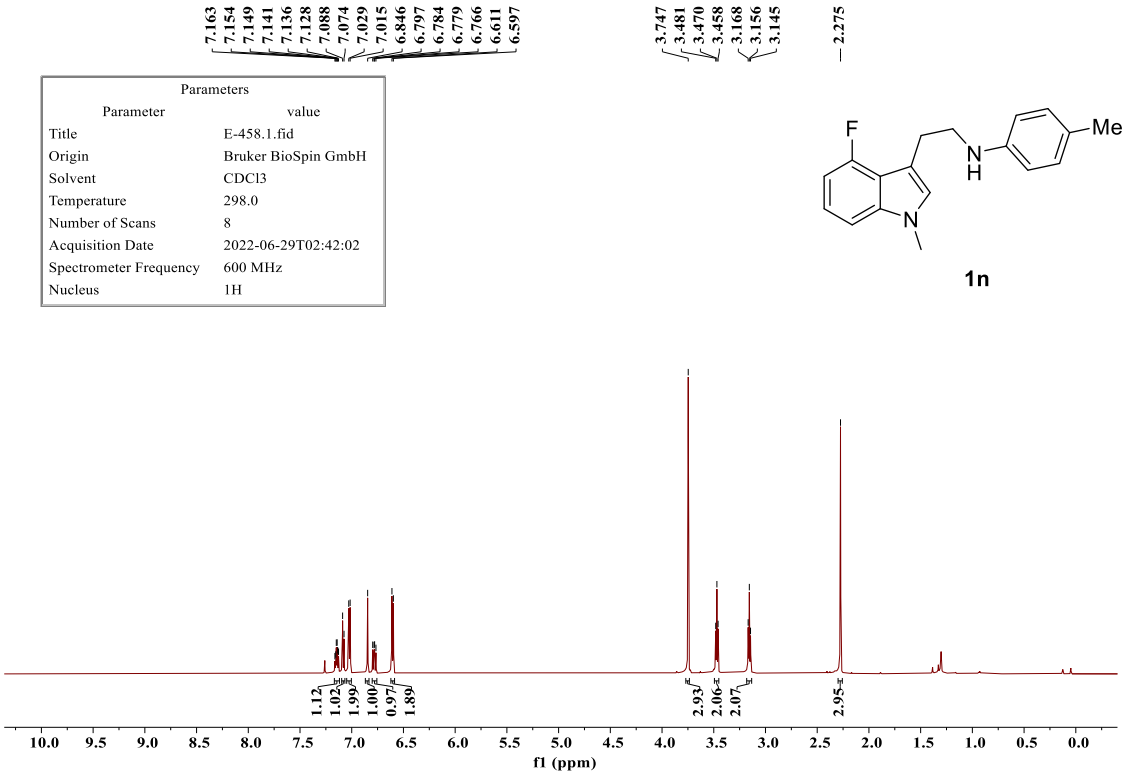


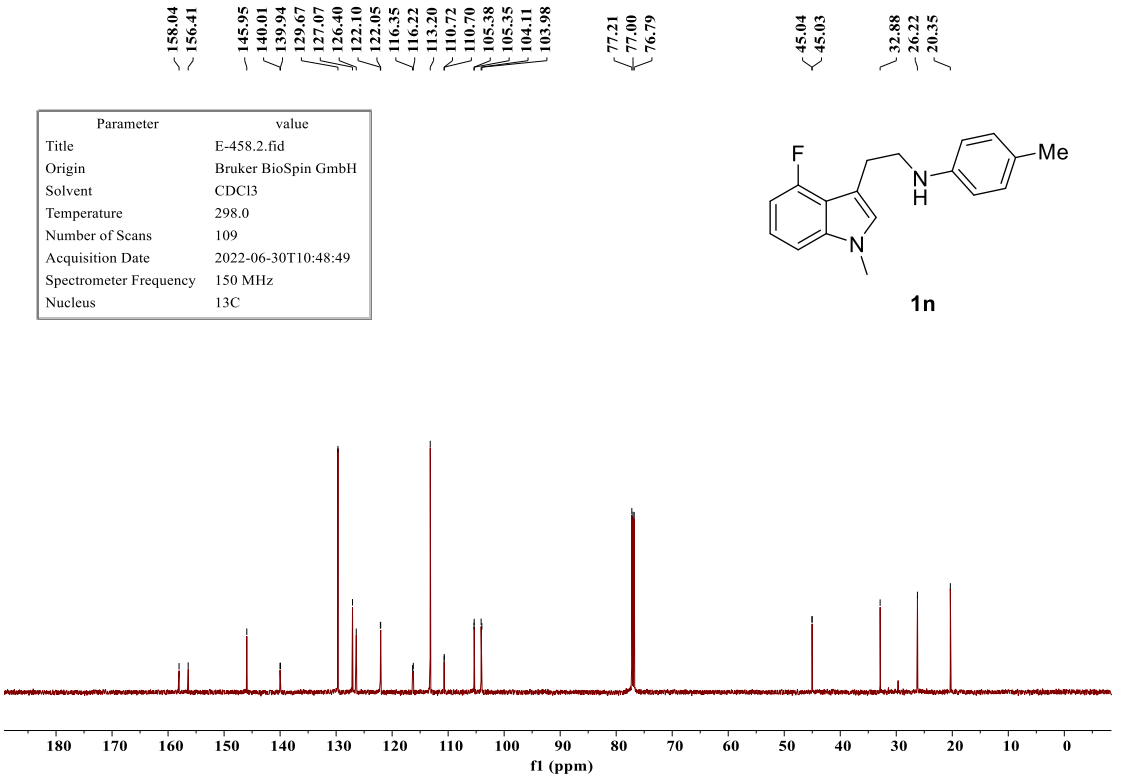
1m



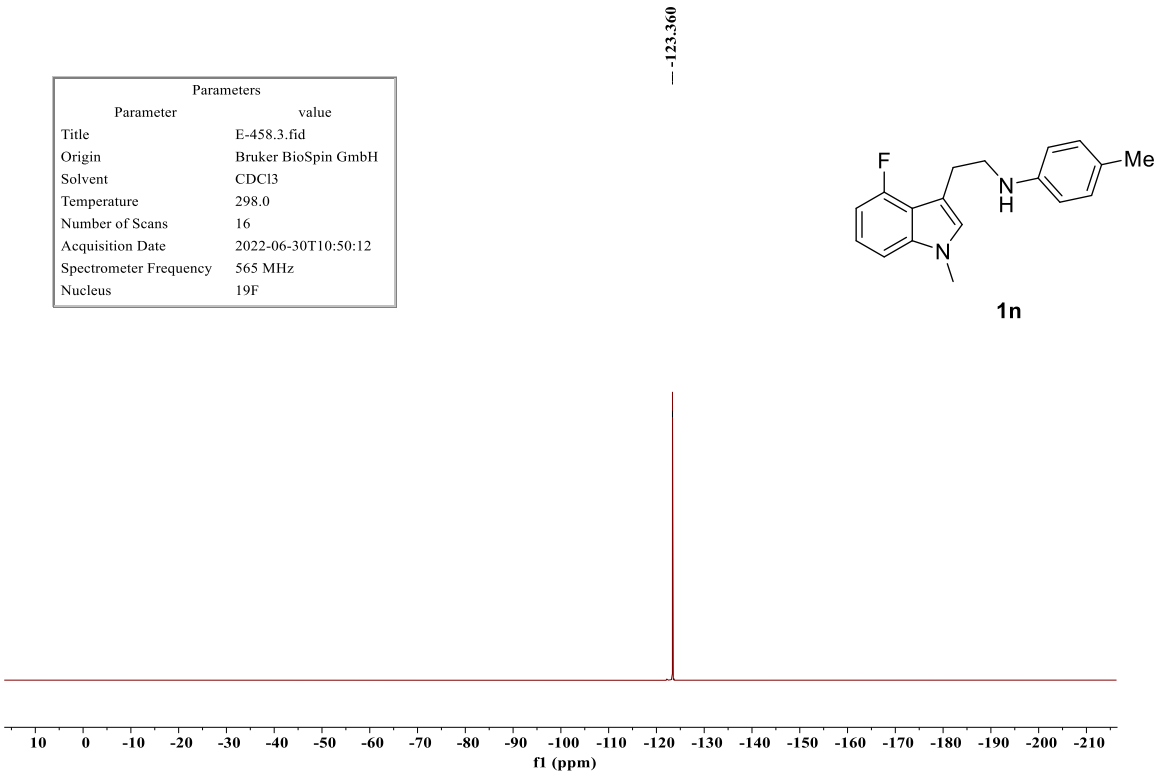
Parameters	
Parameter	value
Title	E-448.3.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	16
Acquisition Date	2022-06-24T00:07:49
Spectrometer Frequency	565 MHz
Nucleus	19F

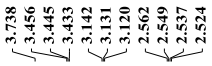



7.163
7.154
7.149
7.141
7.136
7.128
7.088
7.074
7.029
7.015
6.846
6.797
6.784
6.779
6.766
6.611
6.597
3.747
3.481
3.470
3.458
3.168
3.156
3.145
2.275
Parameters
Parameter value
Title E-458.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-06-29T02:42:02
Spectrometer Frequency 600 MHz
Nucleus 1H
F
N
H
N
Me
1n
1.12
1.02
1.99
1.00
0.97
1.89
2.93
2.06
2.07
2.95
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)

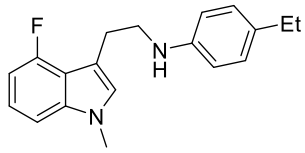

158.04
156.41
145.95
140.01
139.94
129.67
127.07
126.40
122.10
122.05
116.35
116.22
113.20
110.72
110.70
105.38
105.35
104.11
103.98
77.21
77.00
76.79
45.04
45.03
32.88
26.22
20.35
Parameter value
Title E-458.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 109
Acquisition Date 2022-06-30T10:48:49
Spectrometer Frequency 150 MHz
Nucleus 13C
F
N
H
N
Me
1n
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Parameters	
Parameter	value
Title	E-458.3.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	16
Acquisition Date	2022-06-30T10:50:12
Spectrometer Frequency	565 MHz
Nucleus	19F

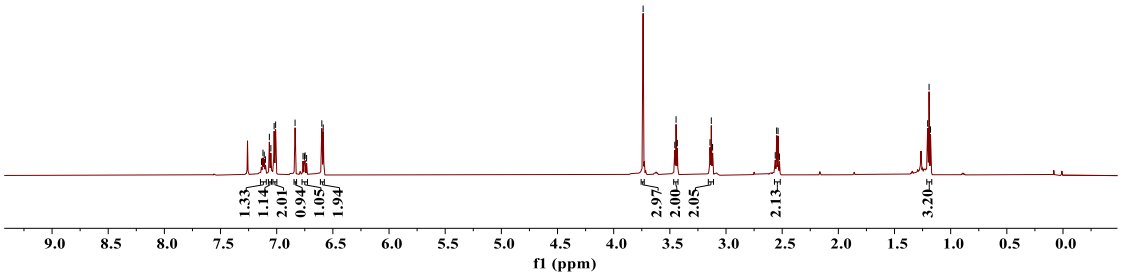


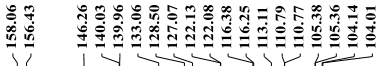


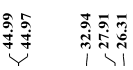
Parameters	
Parameter	value
Title	E-439.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	8
Acquisition Date	2022-09-09T12:03:18
Spectrometer Frequency	600 MHz
Nucleus	1H



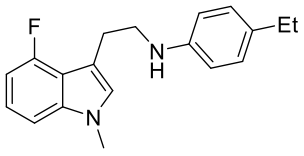
1o





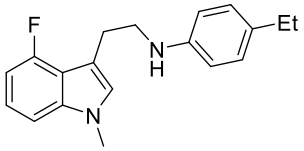


Parameters	
Parameter	value
Title	E-439.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	512
Acquisition Date	2022-09-13T14:30:05
Spectrometer Frequency	150 MHz
Nucleus	13C

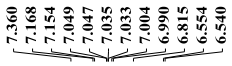


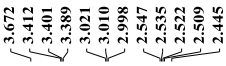
1o

Parameters	
Parameter	value
Title	E-439.3.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.1
Number of Scans	16
Acquisition Date	2022-09-13T14:31:44
Spectrometer Frequency	565 MHz
Nucleus	19F

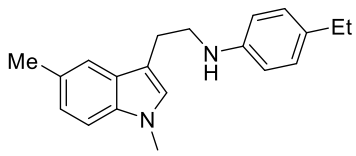


1o

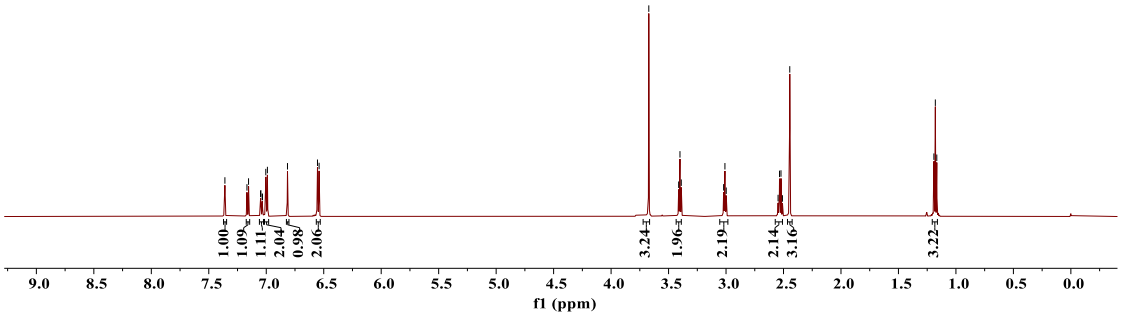


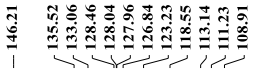


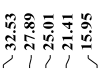
Parameters	
Parameter	value
Title	E-476.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	8
Acquisition Date	2022-06-23T02:53:08
Spectrometer Frequency	600 MHz
Nucleus	1H



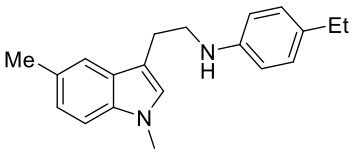
1p



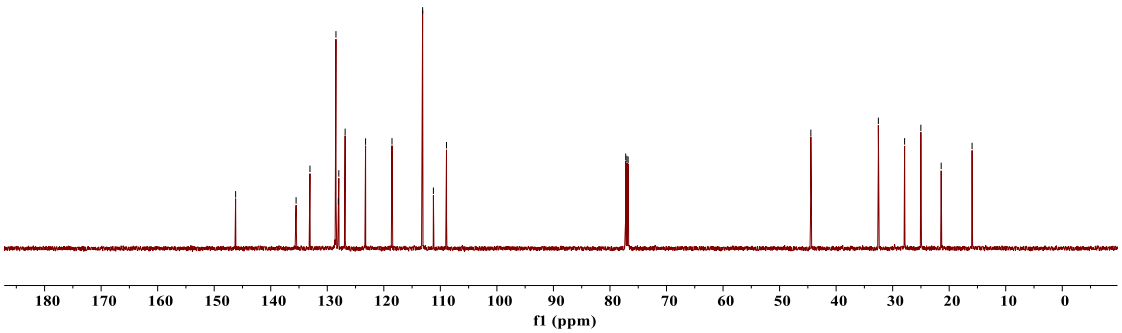


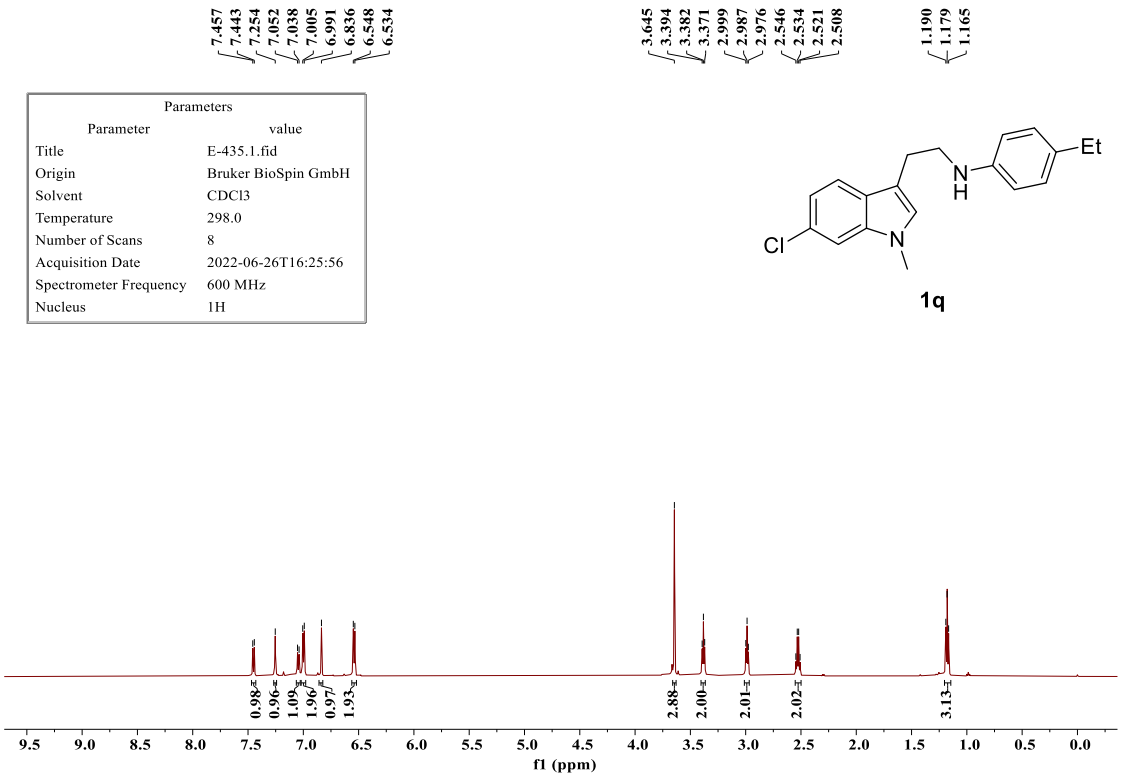


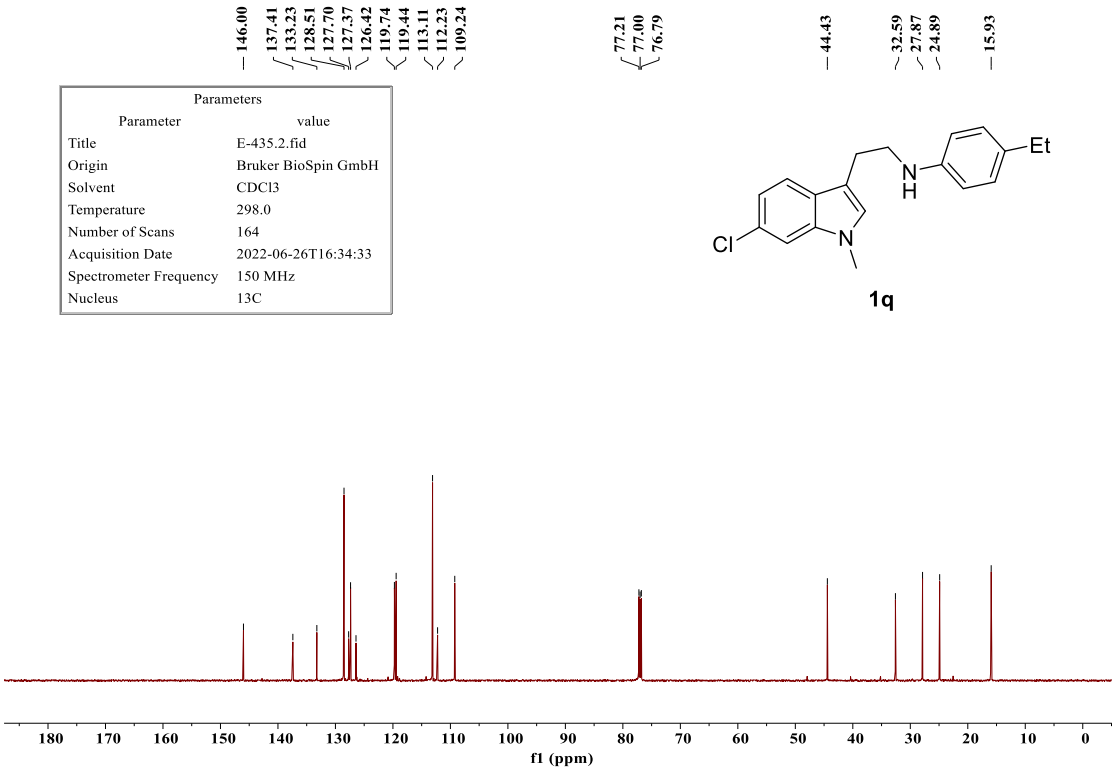
Parameters	
Parameter	value
Title	E-476.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	48
Acquisition Date	2022-06-25T02:29:36
Spectrometer Frequency	150 MHz
Nucleus	13C

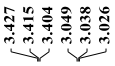


1p

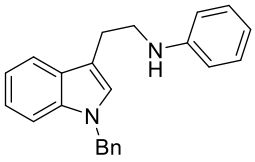



7.457
7.443
7.254
7.052
7.038
7.005
6.991
6.836
6.548
6.534
3.645
3.394
3.382
3.371
2.999
2.987
2.976
2.546
2.534
2.521
2.508
1.190
1.179
1.165
Parameters
Parameter value
Title E-435.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-06-26T16:25:56
Spectrometer Frequency 600 MHz
Nucleus 1H
Et
N
H
Cl
N
1q
0.98
0.96
1.09
1.96
0.97
1.93
2.88
2.00
2.01
2.02
3.13
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)

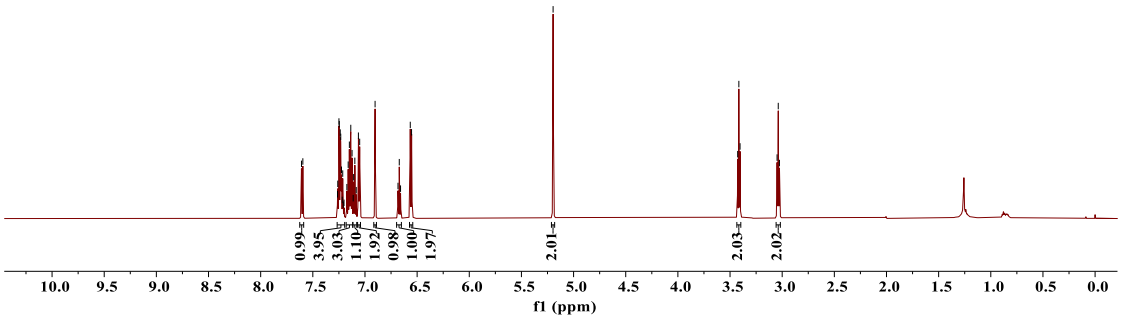

146.00
137.41
133.23
128.51
127.70
127.37
126.42
119.74
119.44
113.11
112.23
109.24
77.21
77.00
76.79
44.43
32.59
27.87
24.89
15.93
Parameters
Parameter value
Title E-435.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 164
Acquisition Date 2022-06-26T16:34:33
Spectrometer Frequency 150 MHz
Nucleus 13C
Et
N
H
Cl
N
1q
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



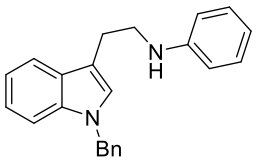
Parameters	
Parameter	value
Title	E-3073.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	8
Acquisition Date	2022-06-29T02:24:01
Spectrometer Frequency	600 MHz
Nucleus	1H



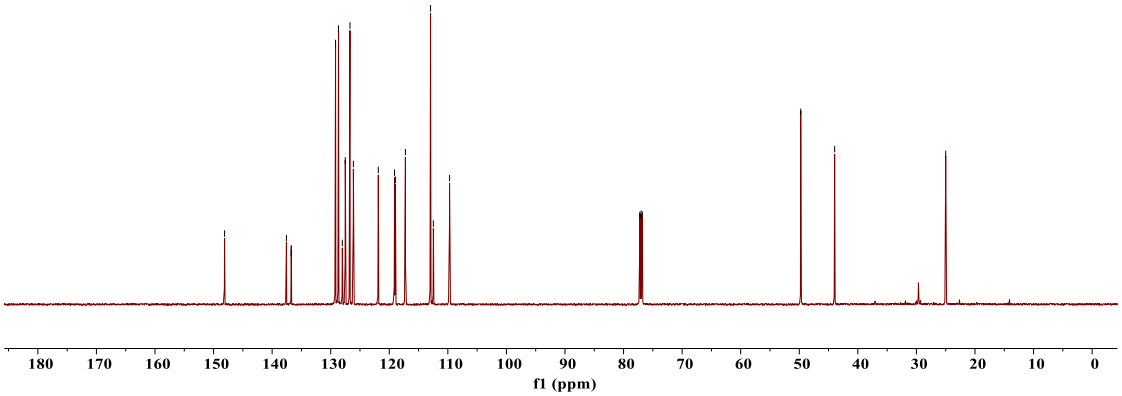
1r

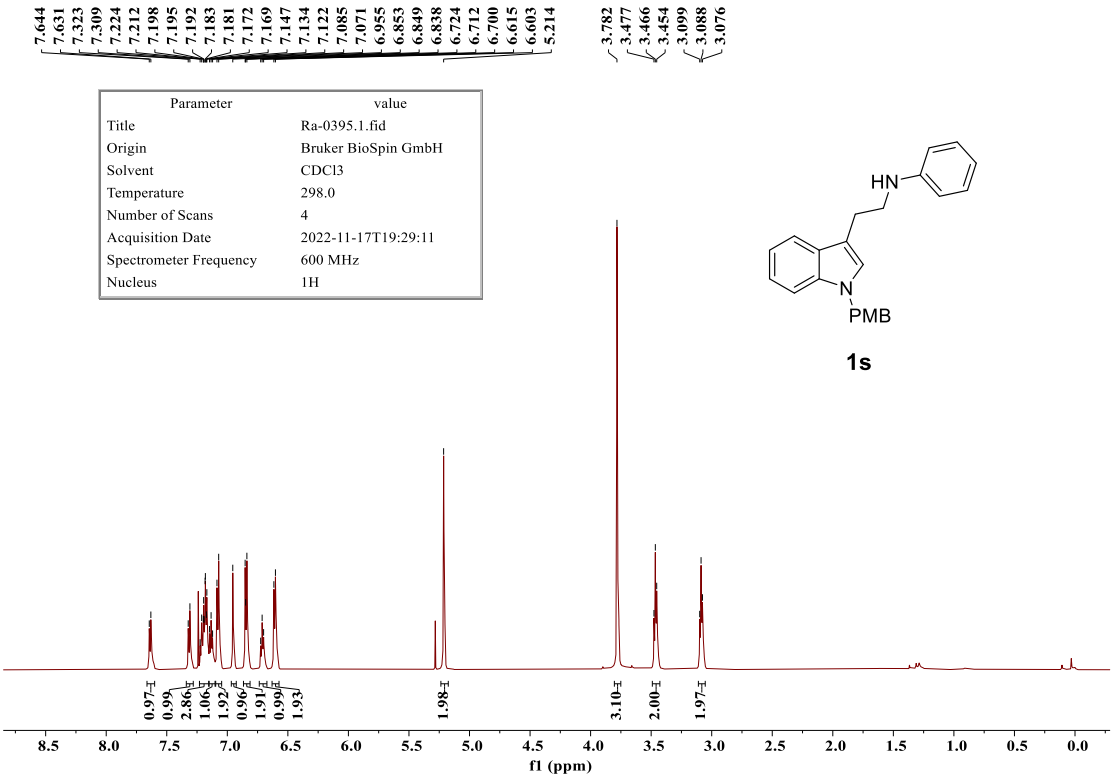


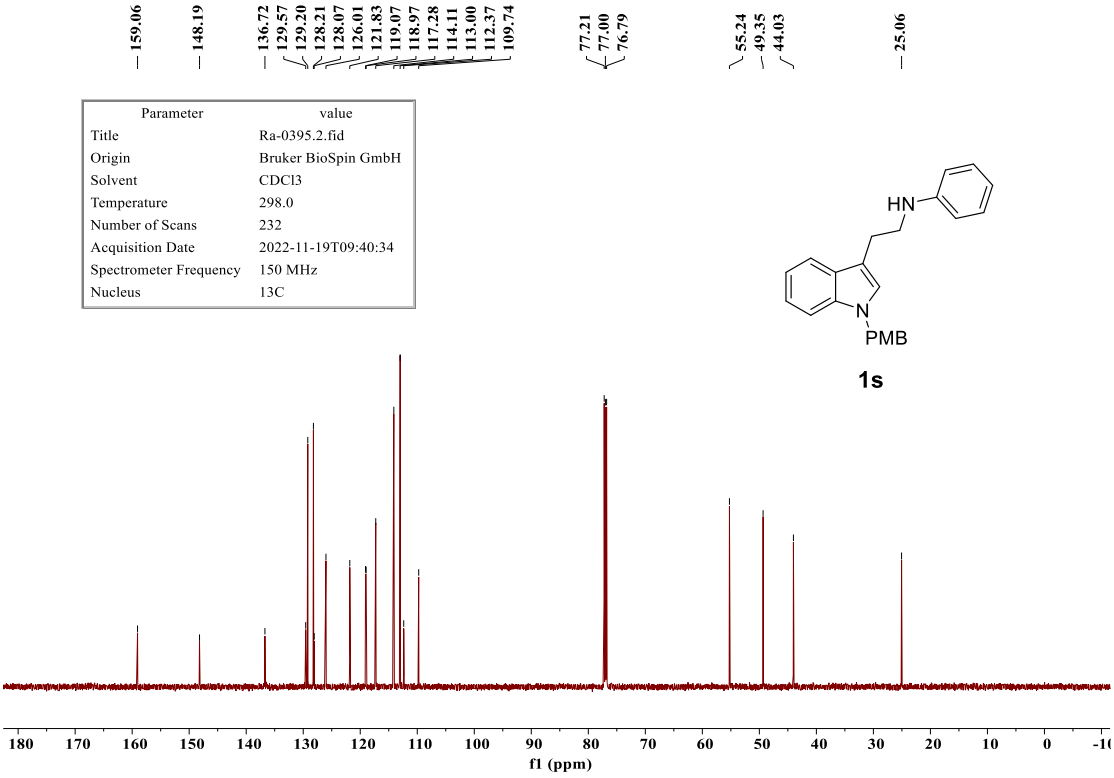
Parameters	
Parameter	value
Title	E-3073.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	512
Acquisition Date	2022-07-01T04:37:30
Spectrometer Frequency	150 MHz
Nucleus	13C

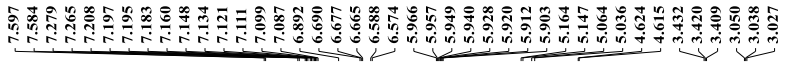


1r

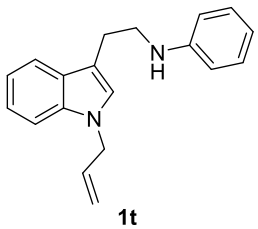



7.644
7.631
7.323
7.309
7.224
7.212
7.198
7.195
7.192
7.183
7.181
7.172
7.169
7.147
7.134
7.122
7.085
7.071
6.955
6.853
6.849
6.838
6.724
6.712
6.700
6.615
6.603
5.214
3.782
3.477
3.466
3.454
3.099
3.088
3.076
Parameter value
Title Ra-0395.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 4
Acquisition Date 2022-11-17T19:29:11
Spectrometer Frequency 600 MHz
Nucleus 1H
HN
N
PMB
1s
0.97
0.99
2.86
1.06
1.92
0.96
1.91
0.99
1.93
1.98
3.10
2.00
1.97
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)

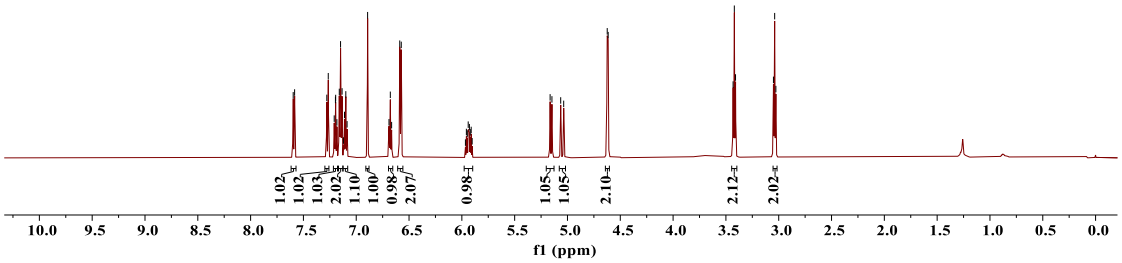

159.06
148.19
136.72
129.57
129.20
128.21
128.07
126.01
121.83
119.07
118.97
117.28
114.11
113.00
112.37
109.74
77.21
77.00
76.79
55.24
49.35
44.03
25.06
Parameter value
Title Ra-0395.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 232
Acquisition Date 2022-11-19T09:40:34
Spectrometer Frequency 150 MHz
Nucleus 13C
HN
N
PMB
1s
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

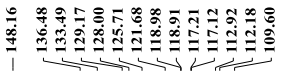


Parameters	
Parameter	value
Title	E-3071.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	8
Acquisition Date	2022-06-26T06:42:41
Spectrometer Frequency	600 MHz
Nucleus	1H

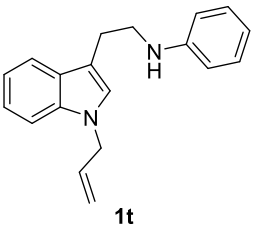


1t

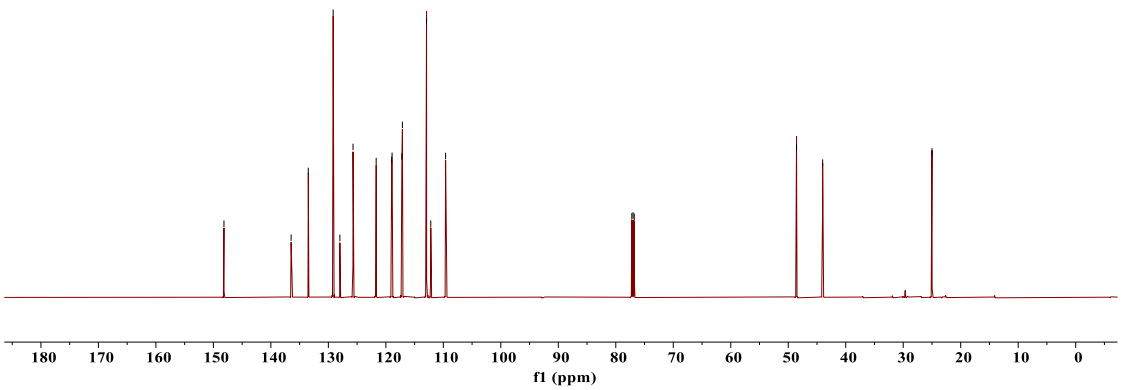


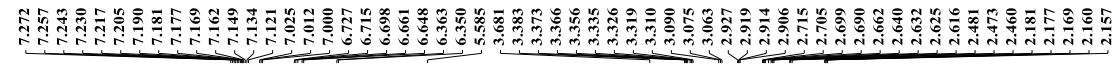


Parameters	
Parameter	value
Title	E-3071.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	512
Acquisition Date	2022-06-26T07:07:49
Spectrometer Frequency	150 MHz
Nucleus	13C

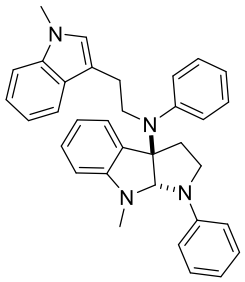


1t

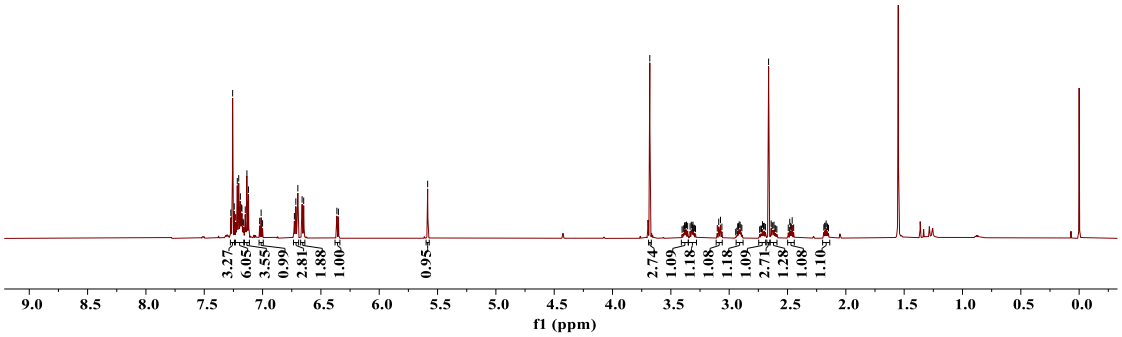




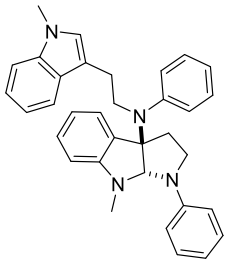
Parameters	
Parameter	value
Title	Ra-0307.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	8
Acquisition Date	2021-07-02T15:00:49
Spectrometer Frequency	600 MHz
Nucleus	1H



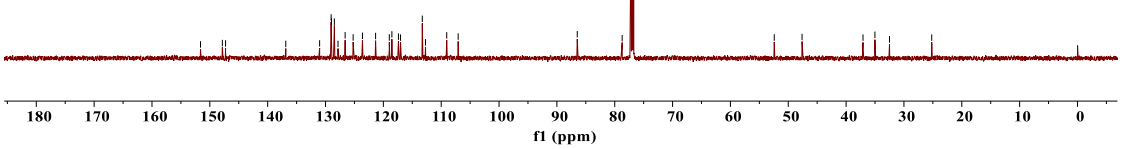
2a

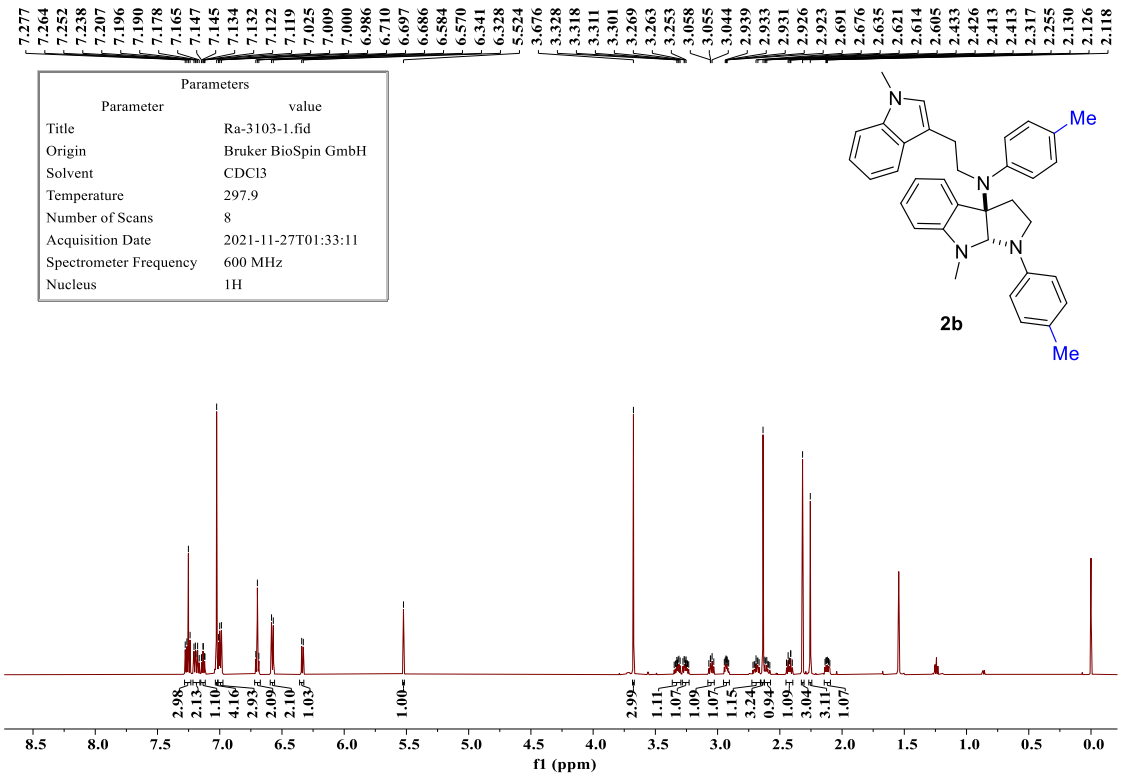


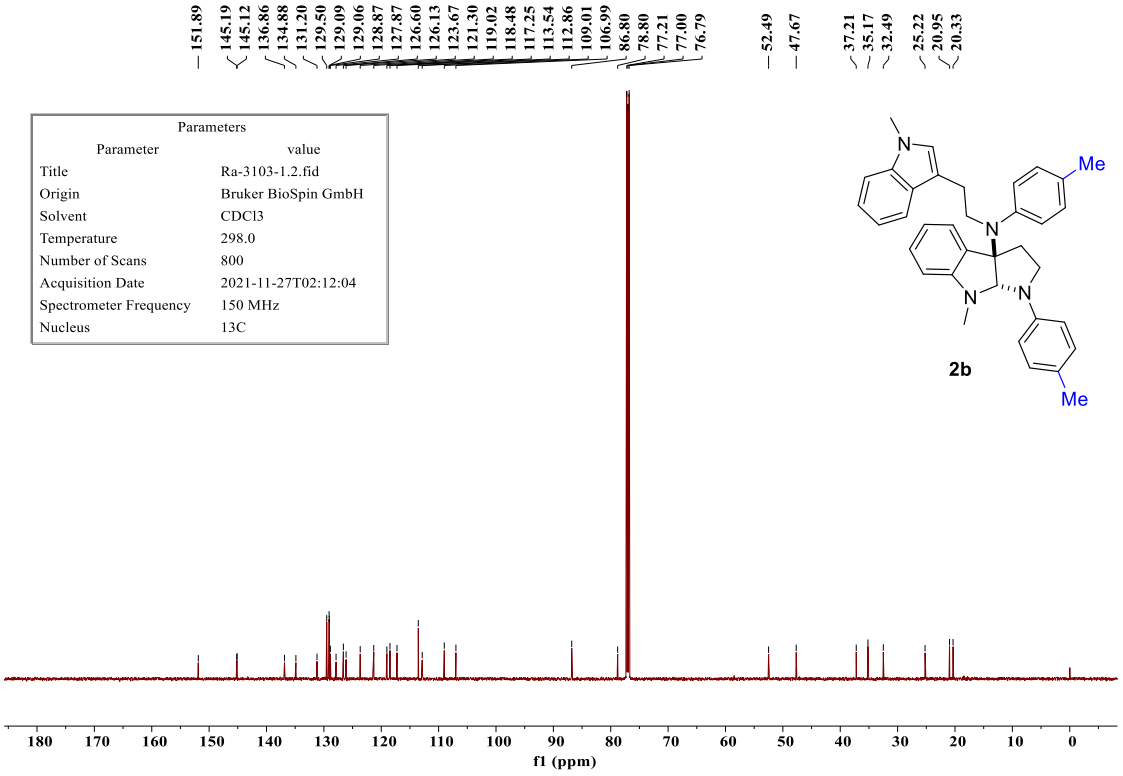
Parameters	
Parameter	value
Title	Ra-0307.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	622
Acquisition Date	2021-07-02T15:31:10
Spectrometer Frequency	150 MHz
Nucleus	13C

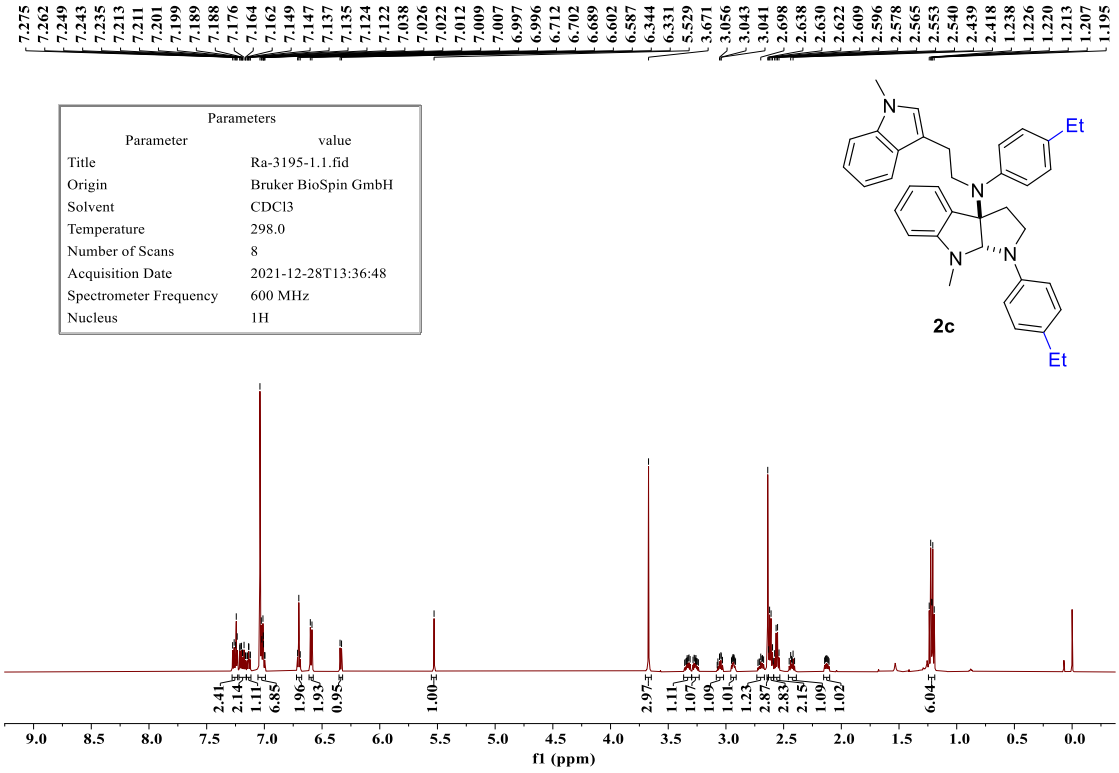


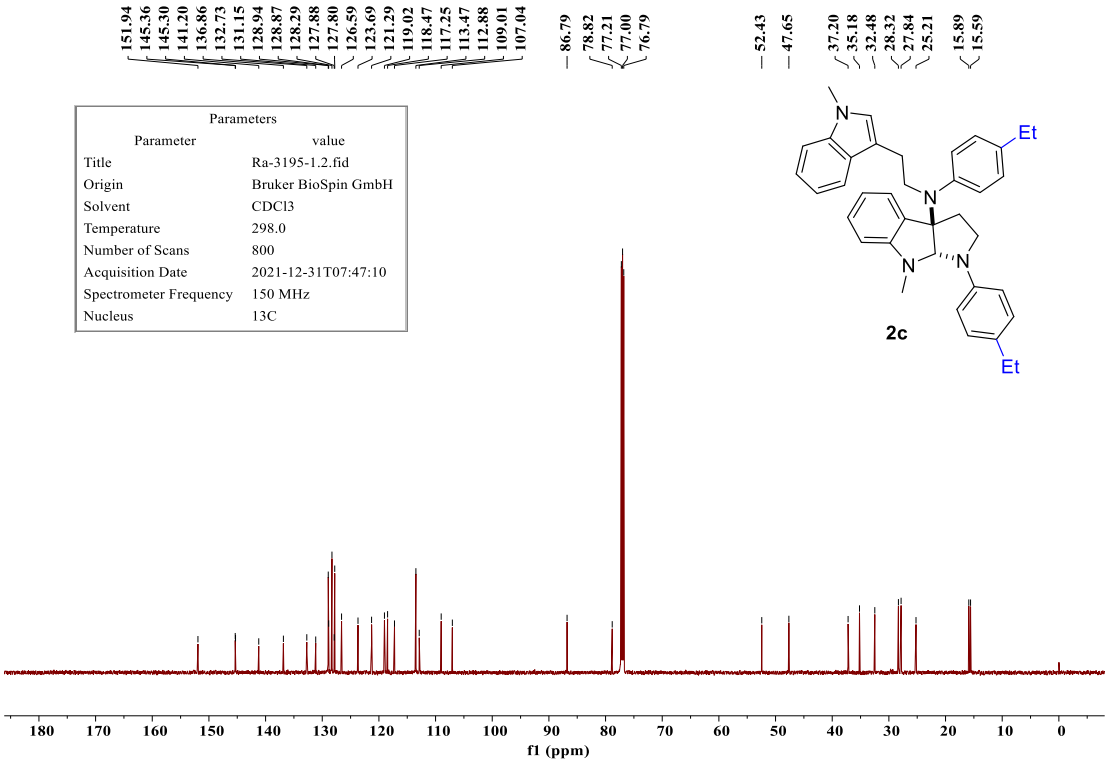
2a

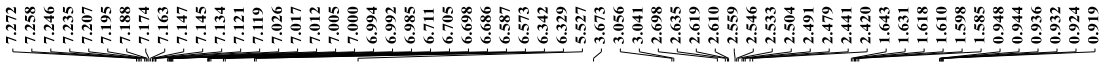



7.277 7.264 7.252 7.238 7.207 7.196 7.190 7.178 7.165 7.147 7.145 7.134 7.132 7.122 7.119 7.025 7.009 7.000 6.986 6.710 6.697 6.686 6.584 6.570 6.341 6.328 5.524
3.676 3.328 3.318 3.311 3.301 3.269 3.263 3.253 3.058 3.055 3.044 2.939 2.933 2.931 2.926 2.923 2.691 2.676 2.635 2.621 2.614 2.605 2.433 2.426 2.413 2.413 2.317 2.255 2.130 2.126 2.118
Parameters
Parameter value
Title Ra-3103-1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.9
Number of Scans 8
Acquisition Date 2021-11-27T01:33:11
Spectrometer Frequency 600 MHz
Nucleus 1H
Me
N
N
N
N
Me
2b
2.98 2.13 1.10 4.16 2.93 2.09 2.10 1.03 1.00 2.99 1.11 1.07 1.09 1.07 1.15 3.24 0.94 1.09 3.04 3.11 1.07
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)

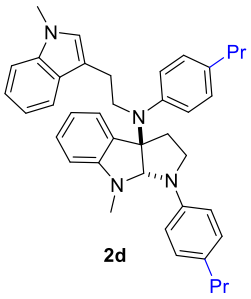

151.89 145.19 145.12 136.86 134.88 131.20 129.50 129.09 129.06 128.87 127.87 126.60 126.13 123.67 121.30 119.02 118.48 117.25 113.54 112.86 109.01 106.99 86.80 78.80 77.21 77.00 76.79
52.49 47.67 37.21 35.17 32.49 25.22 20.95 20.33
Parameters
Parameter value
Title Ra-3103-1.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 800
Acquisition Date 2021-11-27T02:12:04
Spectrometer Frequency 150 MHz
Nucleus 13C
Me
N
N
N
N
Me
2b
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.275 7.262 7.249 7.243 7.235 7.213 7.211 7.201 7.199 7.189 7.188 7.176 7.164 7.162 7.149 7.147 7.137 7.135 7.124 7.122 7.038 7.026 7.022 7.012 7.009 7.007 6.997 6.996 6.712 6.702 6.689 6.602 6.587 6.344 6.331 5.529 3.671 3.056 3.043 3.041 2.698 2.638 2.630 2.622 2.609 2.596 2.578 2.565 2.553 2.540 2.439 2.418 1.238 1.226 1.220 1.213 1.207 1.195
Parameters
Parameter value
Title Ra-3195-1.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2021-12-28T13:36:48
Spectrometer Frequency 600 MHz
Nucleus 1H
Et
N
N
N
N
Et
2c
2.41 2.14 1.11 6.85 1.96 1.93 0.95 1.00 2.97 1.11 1.07 1.09 1.01 1.23 2.87 2.83 2.15 1.09 1.02 6.04
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)

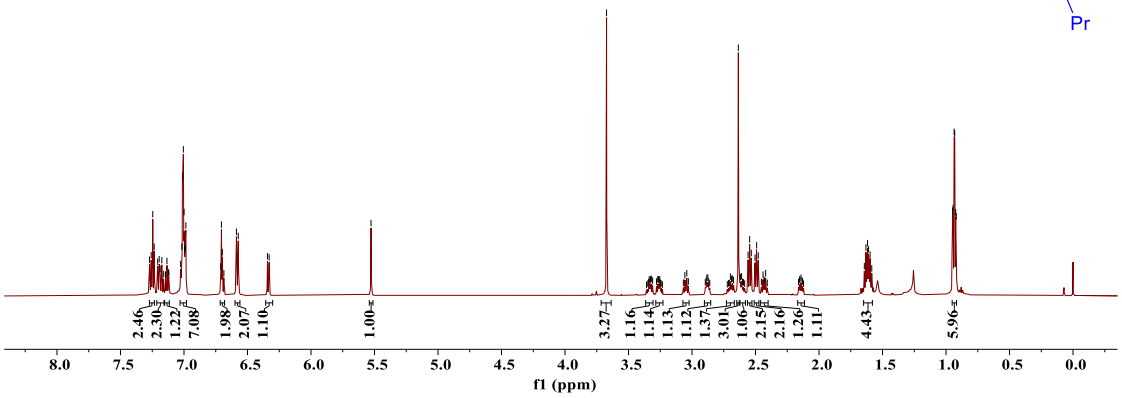

151.94 145.36 145.30 141.20 136.86 132.73 131.15 128.94 128.87 128.29 127.88 127.80 126.59 123.69 121.29 119.02 118.47 117.25 113.47 112.88 109.01 107.04 86.79 78.82 77.21 77.00 76.79 52.43 47.65 37.20 35.18 32.48 28.32 27.84 25.21 15.89 15.59
Parameters
Parameter value
Title Ra-3195-1.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 800
Acquisition Date 2021-12-31T07:47:10
Spectrometer Frequency 150 MHz
Nucleus 13C
Et
N
N
N
N
Et
2c
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

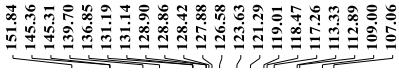


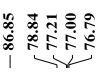
Parameters	
Parameter	value
Title	Ra-3187.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	8
Acquisition Date	2021-12-28T13:33:22
Spectrometer Frequency	600 MHz
Nucleus	1H

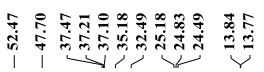


2d

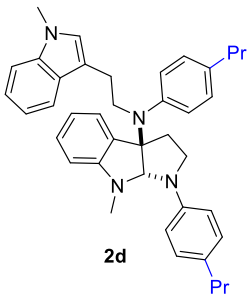




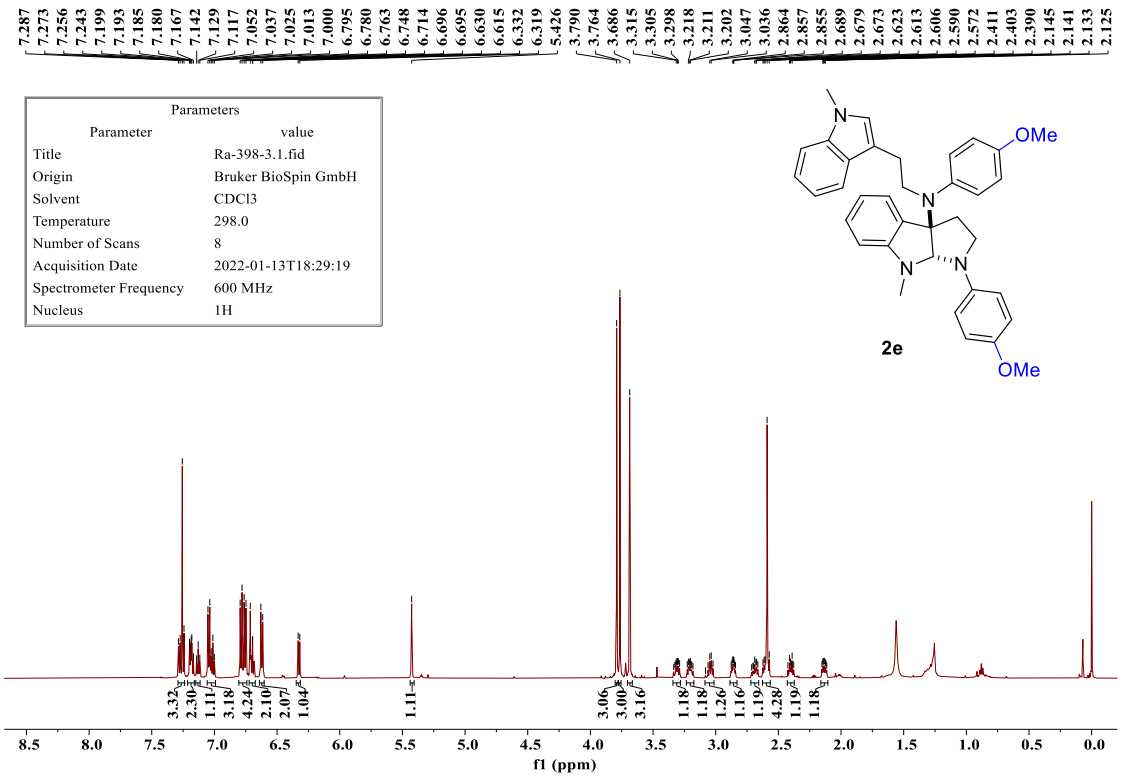


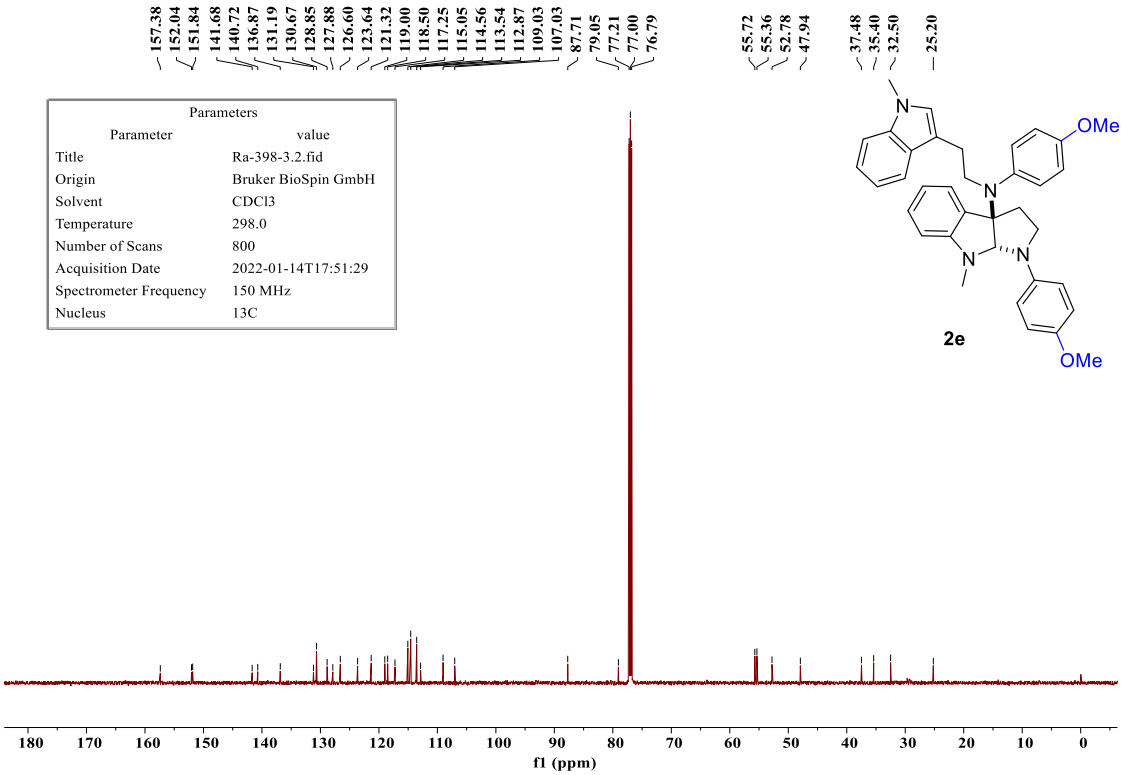


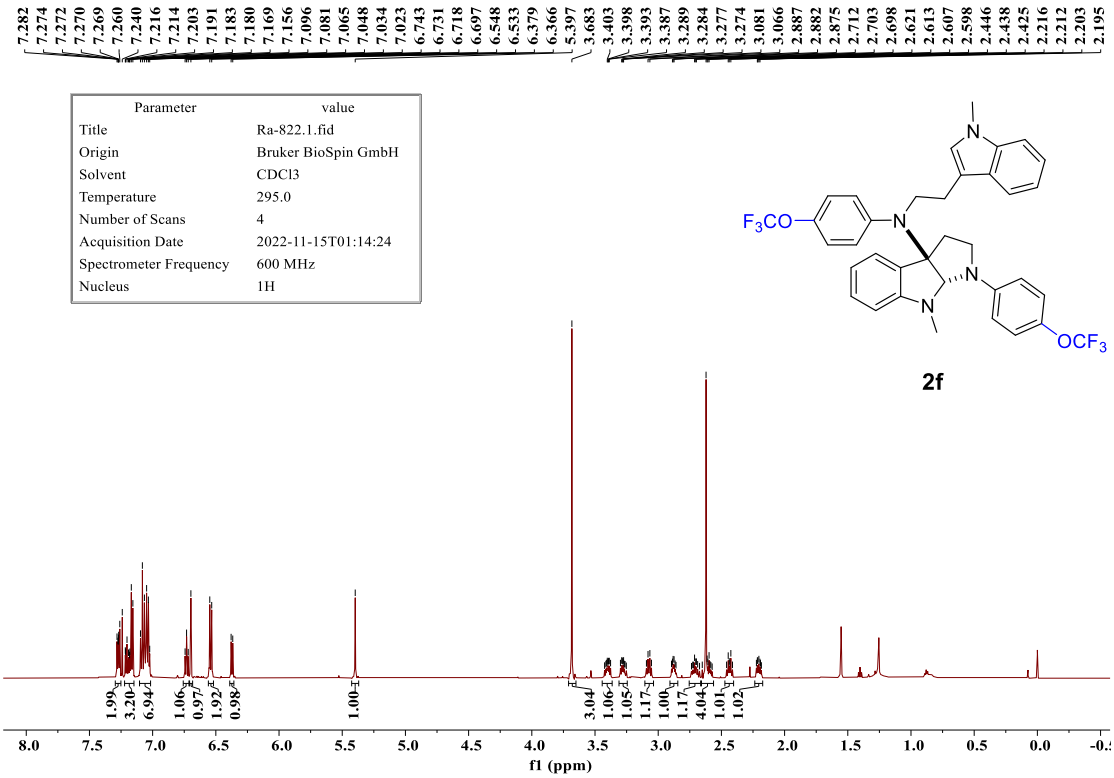
Parameters	
Parameter	value
Title	Ra-3187.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	800
Acquisition Date	2021-12-31T04:58:19
Spectrometer Frequency	150 MHz
Nucleus	13C

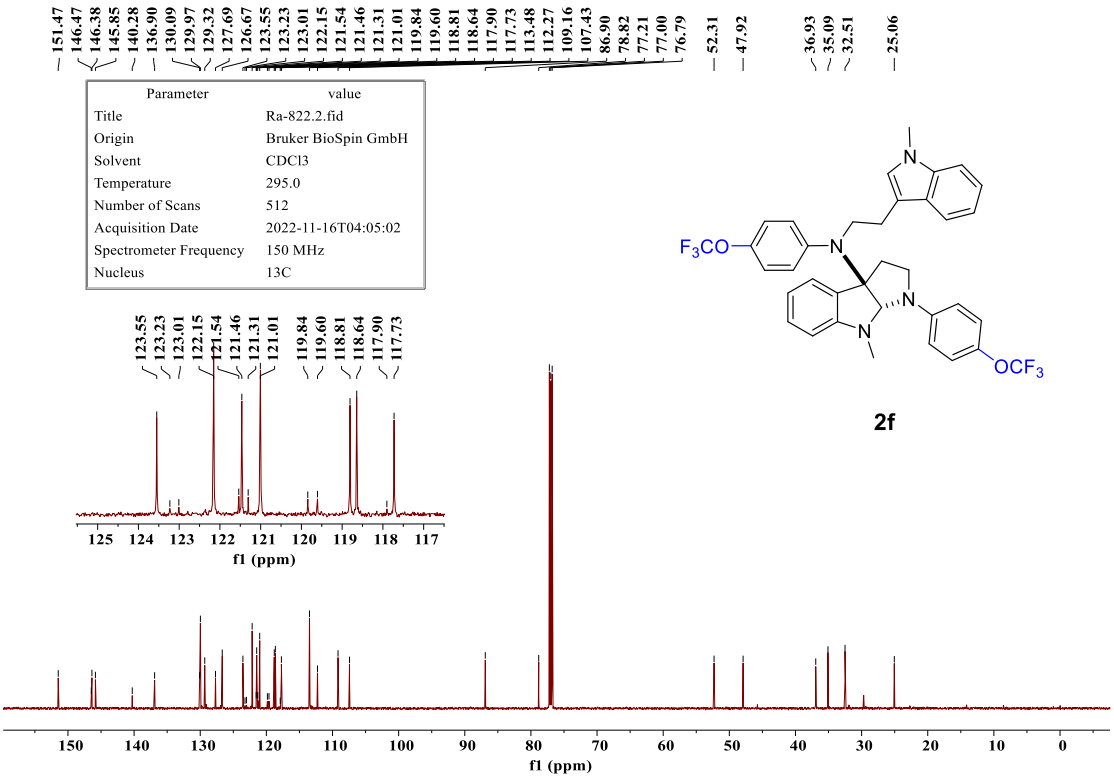


2d

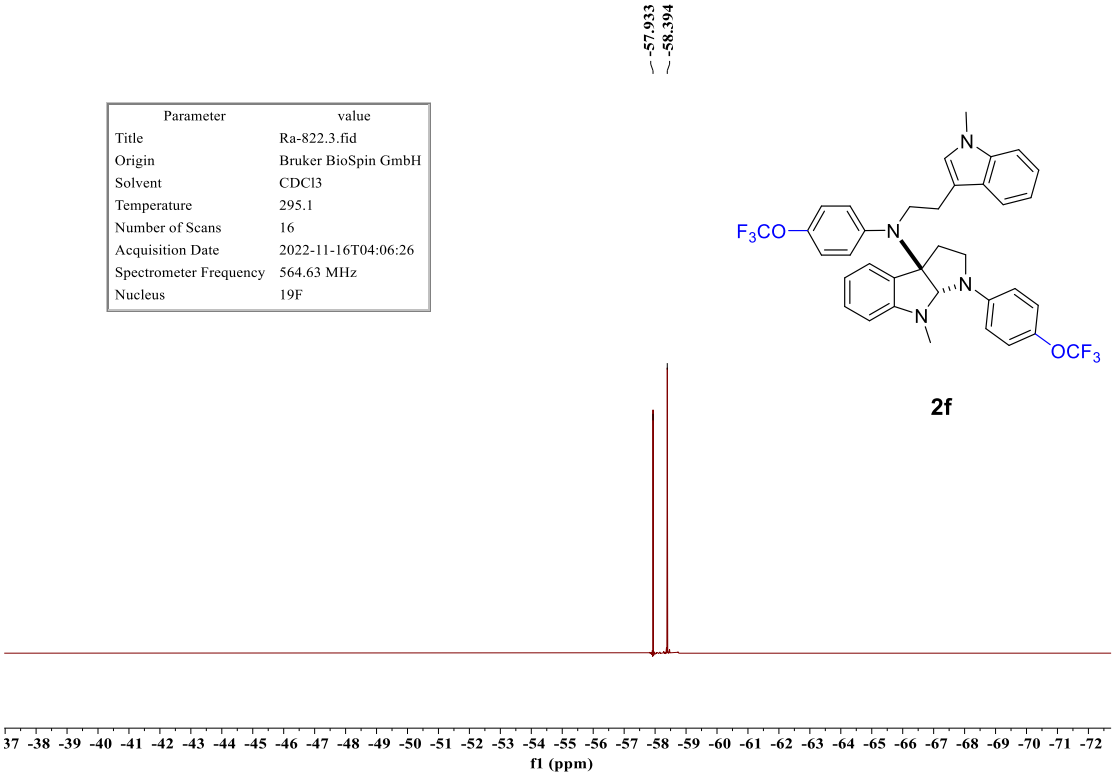

7.287 7.273 7.256 7.243 7.199 7.193 7.185 7.180 7.167 7.142 7.129 7.117 7.052 7.037 7.025 7.013 7.000 6.795 6.780 6.763 6.748 6.714 6.696 6.695 6.630 6.615 6.332 6.319 5.426 3.790 3.764 3.686 3.315 3.305 3.298 3.218 3.211 3.202 3.047 3.036 2.864 2.857 2.855 2.689 2.679 2.673 2.623 2.613 2.606 2.590 2.572 2.411 2.403 2.390 2.145 2.141 2.133 2.125
Parameters
Parameter value
Title Ra-398-3.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-01-13T18:29:19
Spectrometer Frequency 600 MHz
Nucleus 1H
OMe
N
N
N
OMe
2e
3.32 2.30 1.11 3.18 4.24 2.10 2.07 1.04 1.11 3.06 3.00 3.16 1.18 1.18 1.26 1.16 1.19 4.28 1.19 1.18
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)


157.38 152.04 151.84 141.68 140.72 136.87 131.19 130.67 128.85 127.88 126.60 123.64 121.32 119.00 118.50 117.25 115.05 114.56 113.54 112.87 109.03 107.03 87.71 79.05 77.21 77.00 76.79 55.72 55.36 52.78 47.94 37.48 35.40 32.50 25.20
Parameters
Parameter value
Title Ra-398-3.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 800
Acquisition Date 2022-01-14T17:51:29
Spectrometer Frequency 150 MHz
Nucleus 13C
OMe
N
N
N
OMe
2e
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

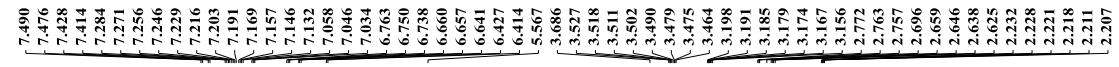

7.282 7.274 7.272 7.270 7.269 7.260 7.240 7.216 7.214 7.203 7.191 7.183 7.180 7.169 7.156 7.096 7.081 7.065 7.048 7.034 7.023 6.743 6.731 6.718 6.697 6.548 6.533 6.379 6.366 5.397 3.683 3.403 3.398 3.393 3.387 3.289 3.284 3.277 3.274 3.081 3.066 2.887 2.882 2.875 2.712 2.703 2.698 2.621 2.613 2.607 2.598 2.446 2.438 2.425 2.216 2.212 2.203 2.195
Parameter value
Title Ra-822.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 295.0
Number of Scans 4
Acquisition Date 2022-11-15T01:14:24
Spectrometer Frequency 600 MHz
Nucleus 1H
F3CO
OCF3
2f
1.99 3.20 6.94 1.06 0.97 1.92 0.98 1.00 3.04 1.06 1.05 1.17 1.00 1.17 4.04 1.01 1.02
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)


151.47 146.47 146.38 145.85 140.28 136.90 130.09 129.97 129.32 127.69 126.67 123.55 123.23 123.01 122.15 121.54 121.46 121.31 121.01 119.84 119.60 118.81 118.64 117.90 117.73 113.48 112.27 109.16 107.43 86.90 78.82 77.21 77.00 76.79 52.31 47.92 36.93 35.09 32.51 25.06
Parameter value
Title Ra-822.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 295.0
Number of Scans 512
Acquisition Date 2022-11-16T04:05:02
Spectrometer Frequency 150 MHz
Nucleus 13C
F3CO
OCF3
2f
123.55 123.23 123.01 122.15 121.54 121.46 121.31 121.01 119.84 119.60 118.81 118.64 117.90 117.73
125 124 123 122 121 120 119 118 117
f1 (ppm)
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

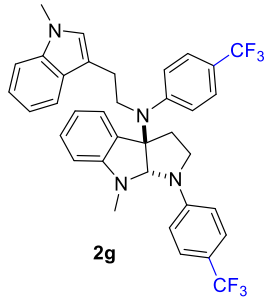
Parameter	value
Title	Ra-822.3.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.1
Number of Scans	16
Acquisition Date	2022-11-16T04:06:26
Spectrometer Frequency	564.63 MHz
Nucleus	19F



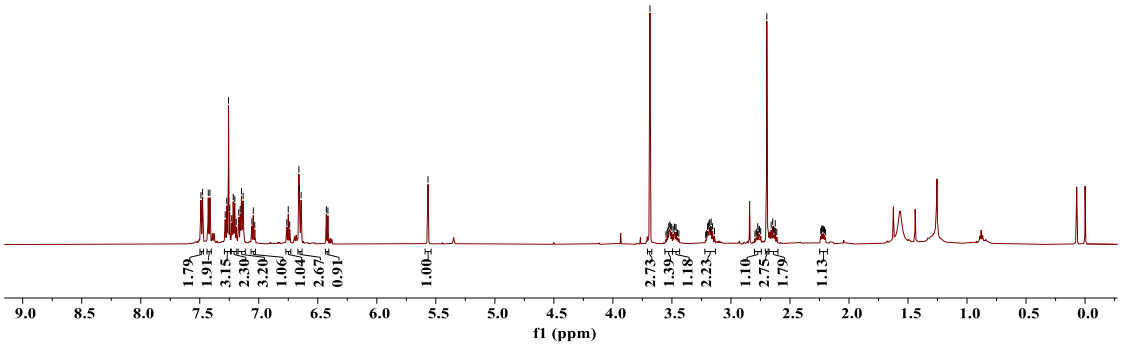
2f

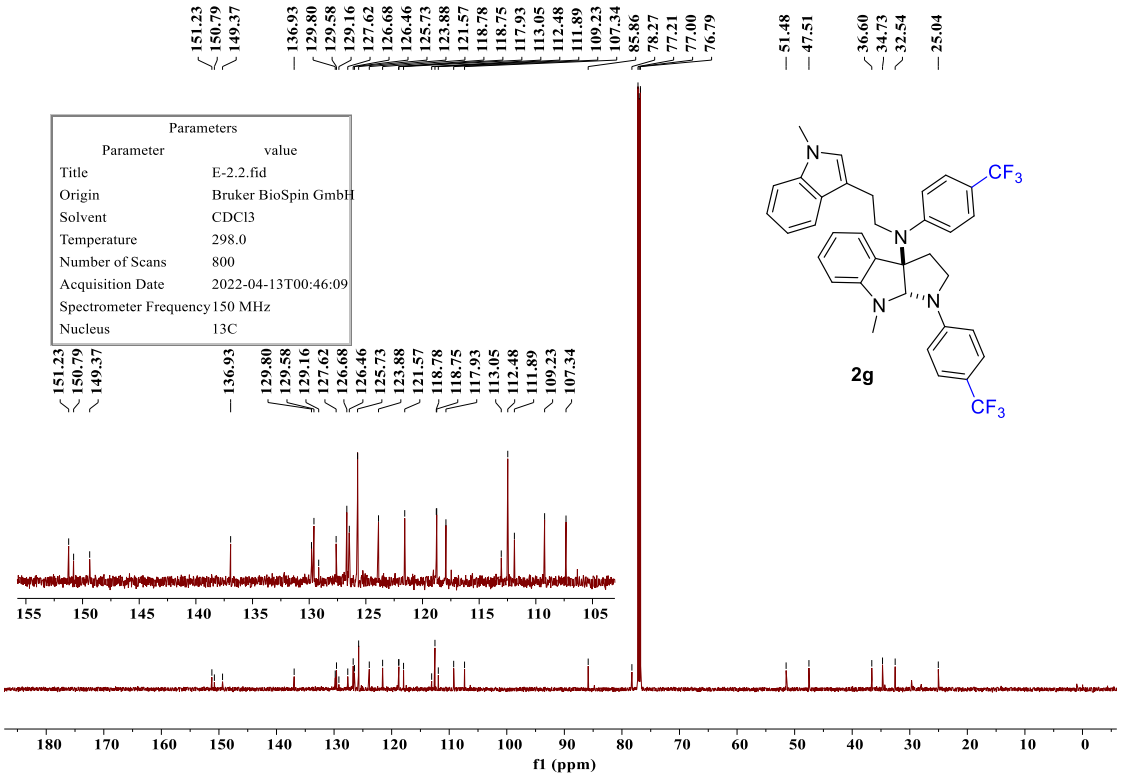


Parameters	
Parameter	value
Title	E-2.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	8
Acquisition Date	2022-04-11T20:47:52
Spectrometer Frequency	600 MHz
Nucleus	1H



2g

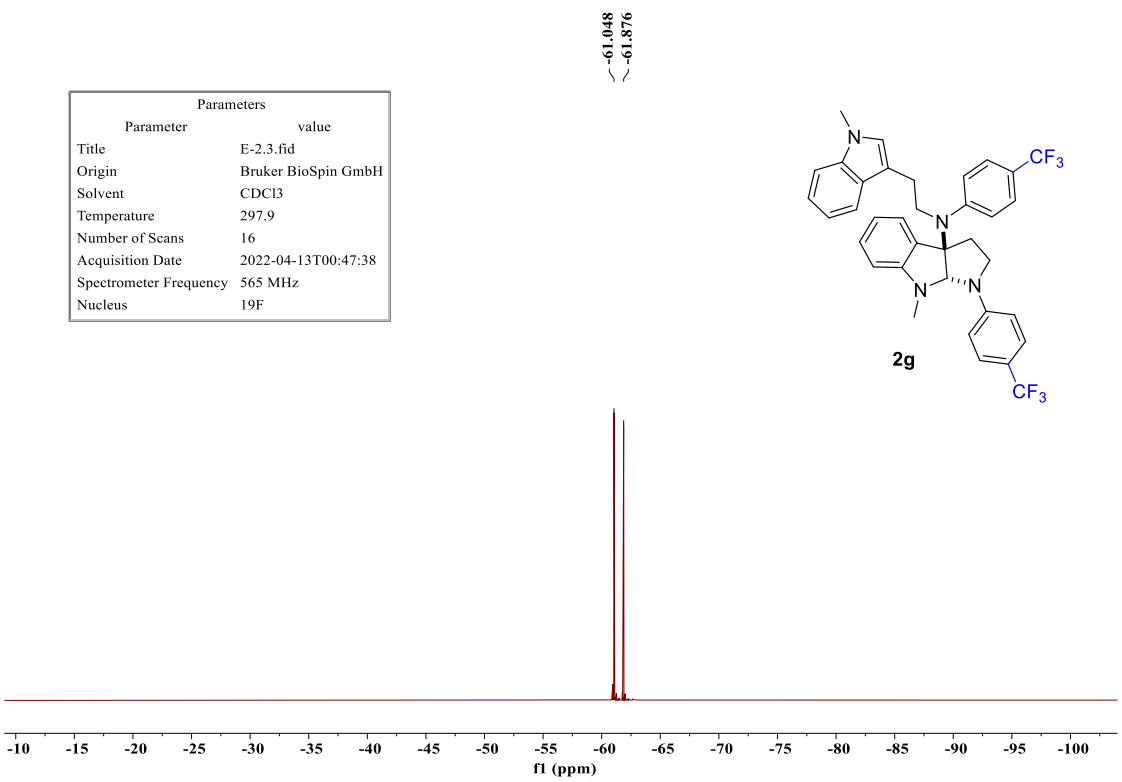


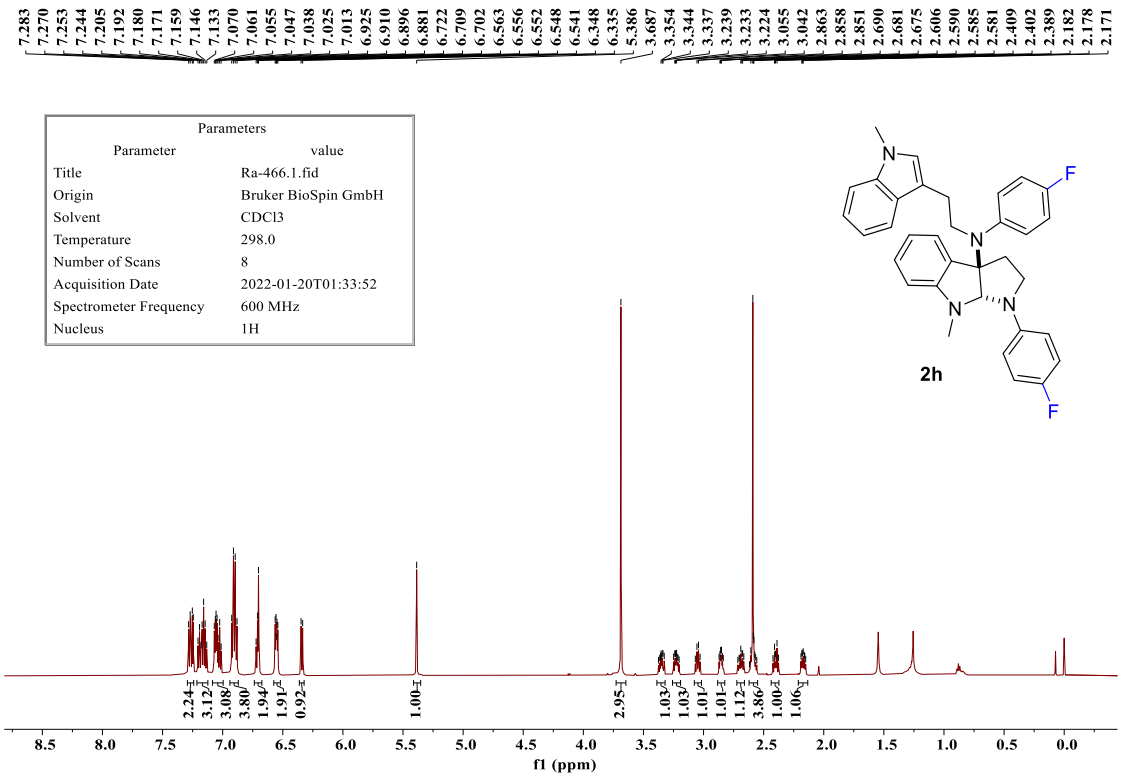


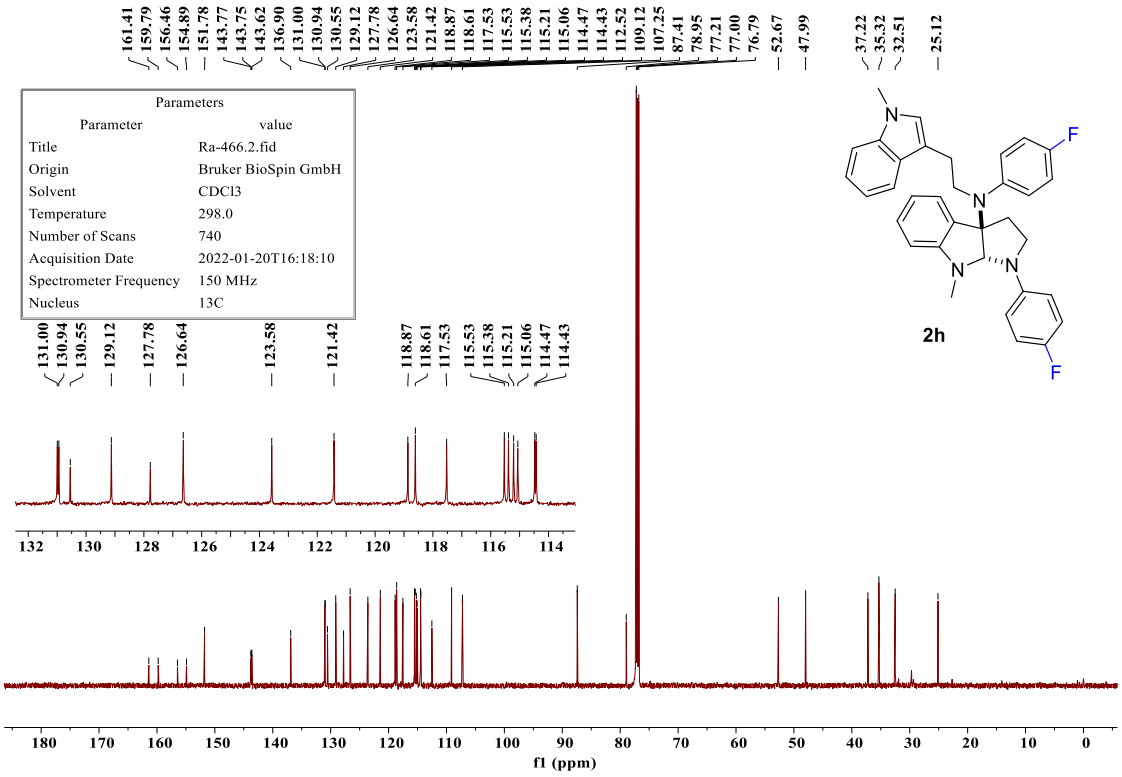
Parameters	
Parameter	value
Title	E-2.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	800
Acquisition Date	2022-04-13T00:46:09
Spectrometer Frequency	150 MHz
Nucleus	13C

2g

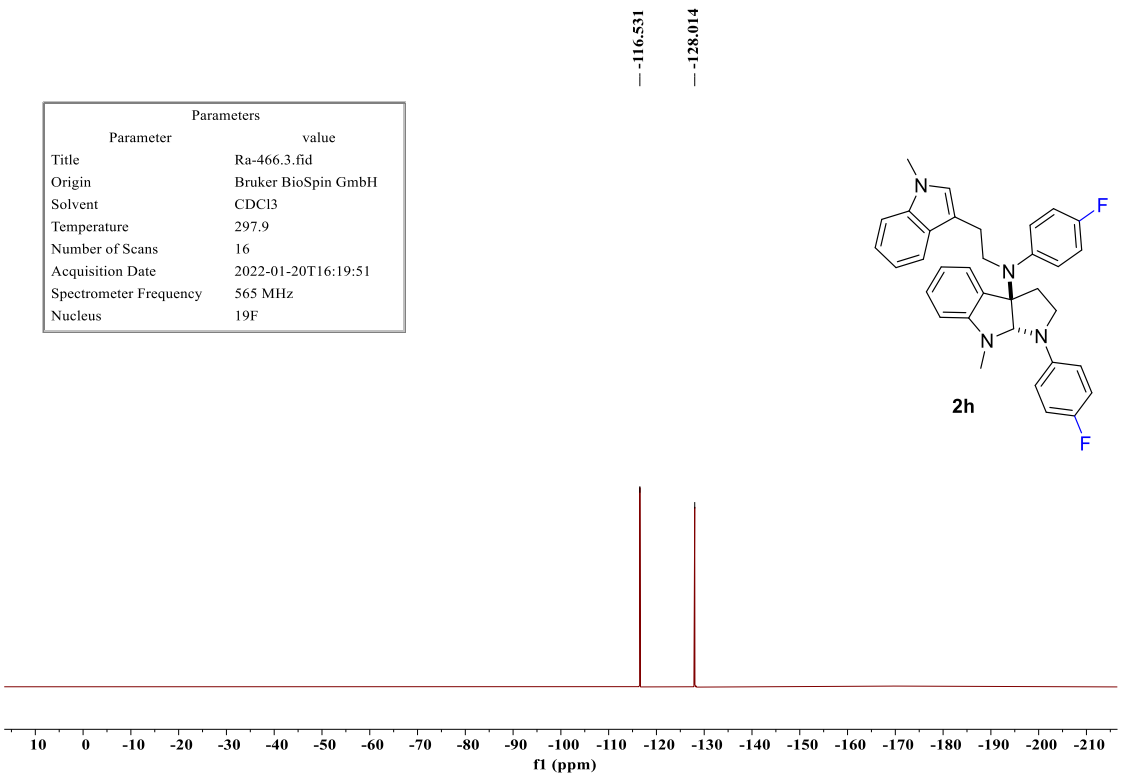
Parameters	
Parameter	value
Title	E-2.3.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.9
Number of Scans	16
Acquisition Date	2022-04-13T00:47:38
Spectrometer Frequency	565 MHz
Nucleus	19F

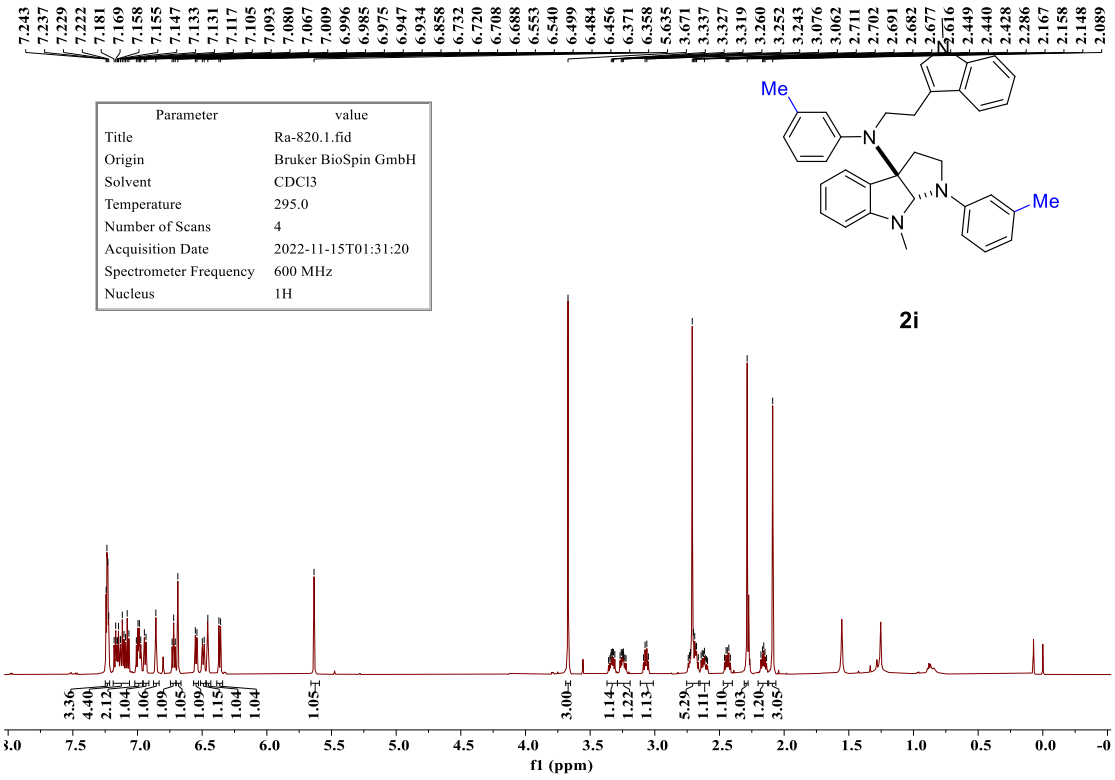


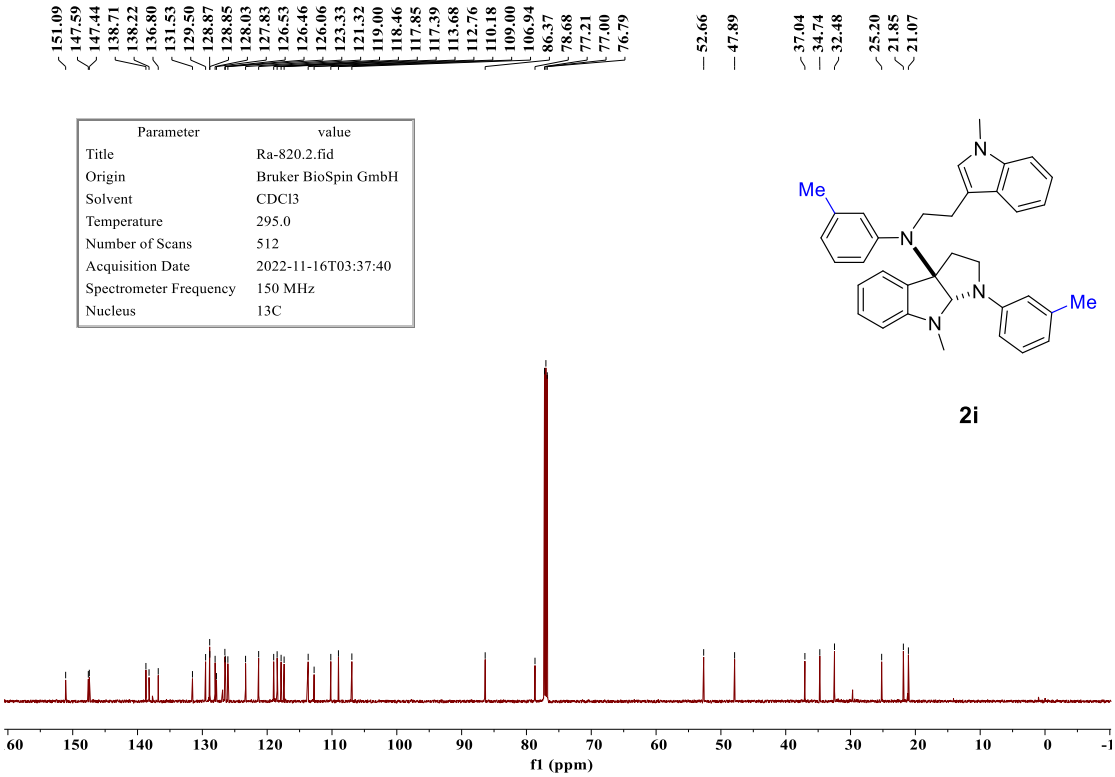

7.283 7.270 7.253 7.244 7.205 7.192 7.180 7.171 7.159 7.146 7.133 7.070 7.061 7.055 7.047 7.038 7.025 7.013 6.925 6.910 6.896 6.881 6.722 6.709 6.702 6.563 6.556 6.552 6.548 6.541 6.348 6.335 5.386 3.687 3.354 3.344 3.337 3.239 3.233 3.224 3.055 3.042 2.863 2.858 2.851 2.690 2.681 2.675 2.606 2.590 2.585 2.581 2.409 2.402 2.389 2.182 2.178 2.171
Parameters
Parameter value
Title Ra-466.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-01-20T01:33:52
Spectrometer Frequency 600 MHz
Nucleus 1H
2h
2.24 3.12 3.08 3.80 1.94 1.91 0.92 1.00 2.95 1.03 1.03 1.01 1.01 1.12 3.86 1.00 1.06
f1 (ppm)

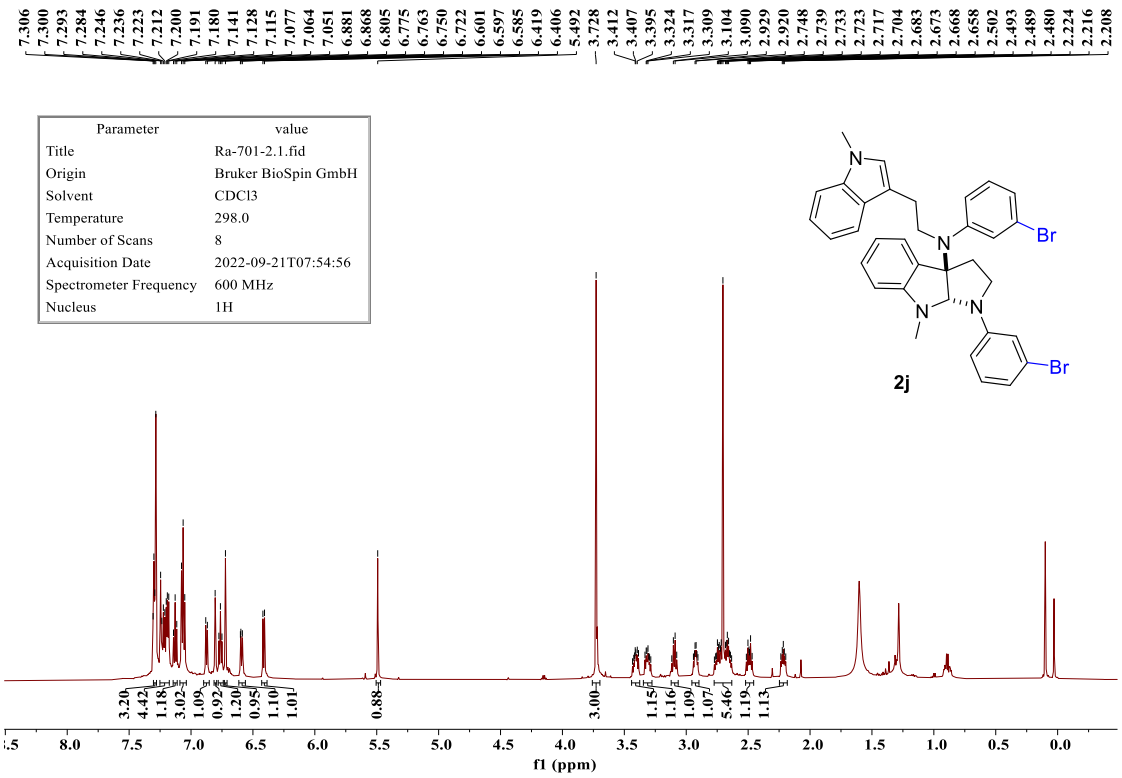

161.41 159.79 156.46 154.89 151.78 143.77 143.75 143.62 136.90 131.00 130.94 130.55 129.12 127.78 126.64 123.58 121.42 118.87 118.61 117.53 115.53 115.38 115.21 115.06 114.47 114.43 112.52 109.12 107.25 87.41 78.95 77.21 77.00 76.79 52.67 47.99 37.22 35.32 32.51 25.12
Parameters
Parameter value
Title Ra-466.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 740
Acquisition Date 2022-01-20T16:18:10
Spectrometer Frequency 150 MHz
Nucleus 13C
2h
f1 (ppm)

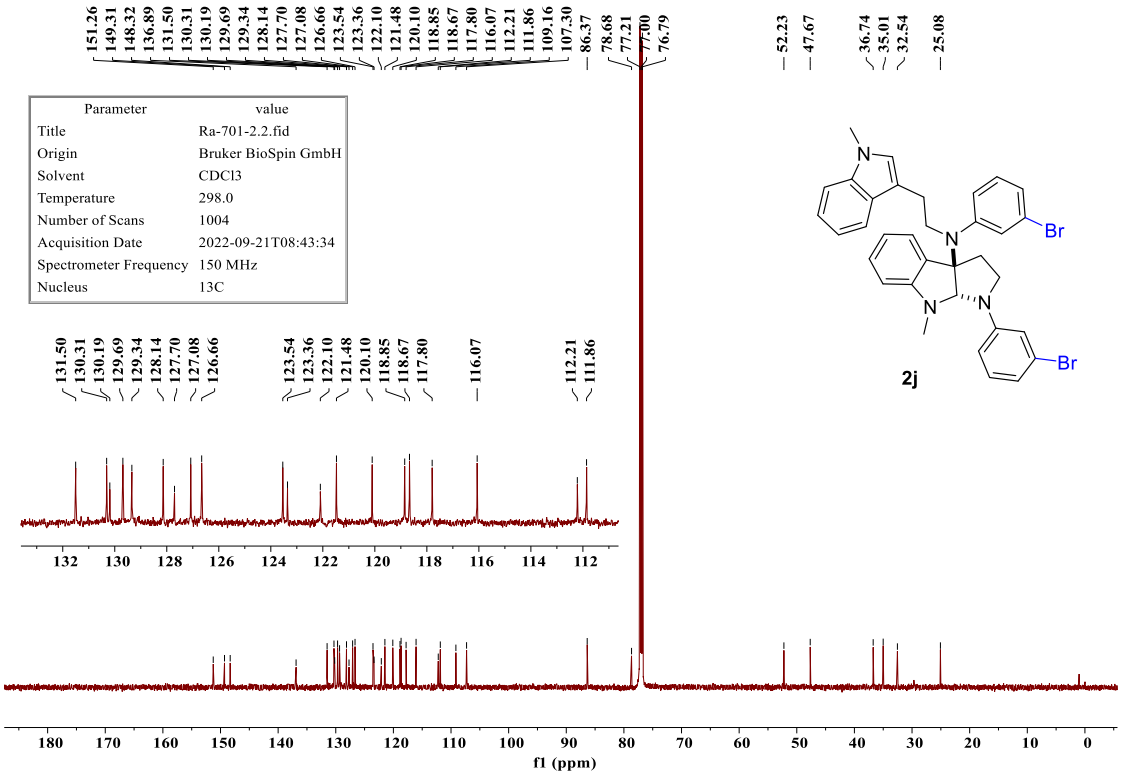
Parameters	
Parameter	value
Title	Ra-466.3.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.9
Number of Scans	16
Acquisition Date	2022-01-20T16:19:51
Spectrometer Frequency	565 MHz
Nucleus	19F

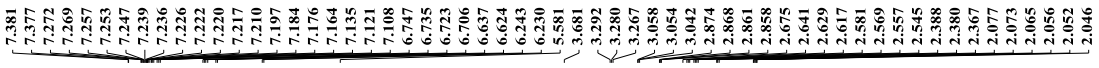



7.243 7.237 7.229 7.222 7.181 7.169 7.158 7.155 7.147 7.133 7.131 7.117 7.105 7.093 7.080 7.067 7.009 6.996 6.985 6.975 6.947 6.934 6.858 6.732 6.720 6.708 6.688 6.553 6.540 6.499 6.484 6.456 6.371 6.358 5.635 3.671 3.337 3.327 3.319 3.260 3.252 3.243 3.076 3.062 2.711 2.702 2.691 2.682 2.677 2.616 2.449 2.440 2.428 2.286 2.167 2.158 2.148 2.089
Parameter value
Title Ra-820.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 295.0
Number of Scans 4
Acquisition Date 2022-11-15T01:31:20
Spectrometer Frequency 600 MHz
Nucleus 1H
Me
N
N
N
Me
2i
3.36 4.40 2.12 1.04 1.06 1.09 1.05 1.09 1.15 1.04 1.04 1.05 3.00 1.14 1.22 1.13 5.29 1.11 1.10 3.03 1.20 3.05
f1 (ppm)

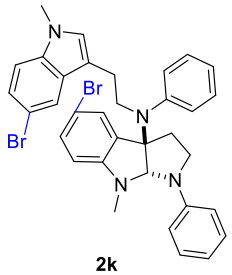

151.09 147.59 147.44 138.71 138.22 136.80 131.53 129.50 128.87 128.85 128.03 127.83 126.53 126.46 126.06 123.33 121.32 119.00 118.46 117.85 117.39 113.68 112.76 110.18 109.00 106.94 86.37 78.68 77.21 77.00 76.79 52.66 47.89 37.04 34.74 32.48 25.20 21.85 21.07
Parameter value
Title Ra-820.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 295.0
Number of Scans 512
Acquisition Date 2022-11-16T03:37:40
Spectrometer Frequency 150 MHz
Nucleus 13C
Me
N
N
N
Me
2i
f1 (ppm)


7.306 7.300 7.293 7.284 7.246 7.236 7.223 7.212 7.200 7.191 7.180 7.141 7.128 7.115 7.077 7.064 7.051 6.881 6.868 6.805 6.775 6.763 6.750 6.722 6.601 6.597 6.585 6.419 6.406 5.492 3.728 3.412 3.407 3.395 3.324 3.317 3.309 3.104 3.090 2.929 2.920 2.748 2.739 2.733 2.723 2.717 2.704 2.683 2.673 2.668 2.658 2.502 2.493 2.489 2.480 2.224 2.216 2.208
Parameter value
Title Ra-701-2.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-09-21T07:54:56
Spectrometer Frequency 600 MHz
Nucleus 1H
N
N
Br
N
N
Br
2j
3.20 4.42 1.18 3.02 1.09 0.92 1.20 0.95 1.10 1.01 0.88 3.00 1.15 1.16 1.09 1.07 5.46 1.19 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)

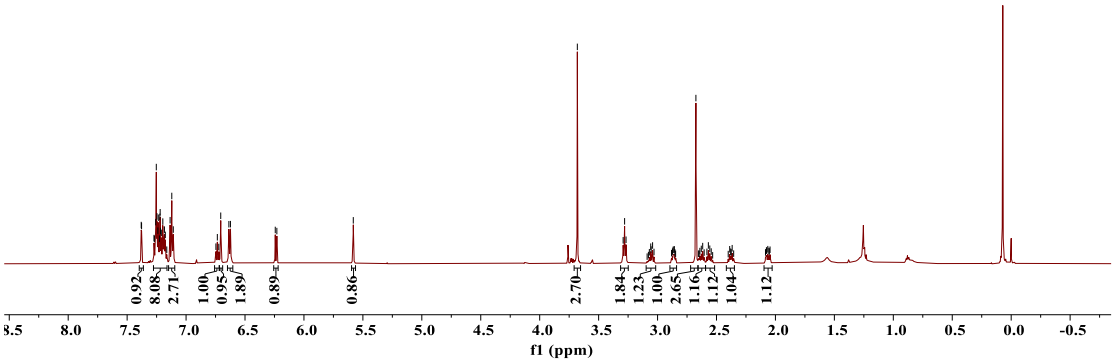

151.26 149.31 148.32 136.89 131.50 130.31 130.19 129.69 129.34 128.14 127.70 127.08 126.66 123.54 123.36 122.10 121.48 120.10 118.85 118.67 117.80 116.07 112.21 111.86 109.16 107.30 86.37 78.68 77.21 77.00 76.79 52.23 47.67 36.74 35.01 32.54 25.08
Parameter value
Title Ra-701-2.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 1004
Acquisition Date 2022-09-21T08:43:34
Spectrometer Frequency 150 MHz
Nucleus 13C
N
N
Br
N
N
Br
2j
131.50 130.31 130.19 129.69 129.34 128.14 127.70 127.08 126.66 123.54 123.36 122.10 121.48 120.10 118.85 118.67 117.80 116.07 112.21 111.86
132 130 128 126 124 122 120 118 116 114 112
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

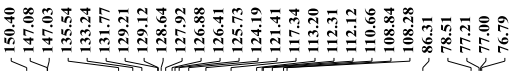


Parameter	value
Title	RA-2I.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Number of Scans	8
Acquisition Date	2022-10-13T11:42:33
Spectrometer Frequency	600 MHz
Nucleus	1H



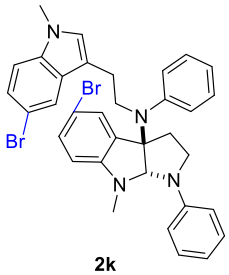
2k



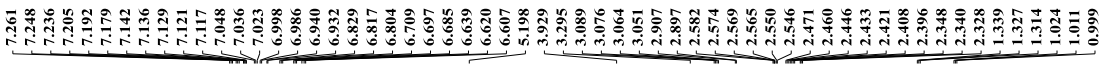


Parameters

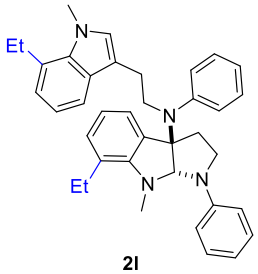
Parameter	value
Title	E-3196.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	512
Acquisition Date	2022-09-14T09:57:34
Spectrometer Frequency	150 MHz
Nucleus	13C



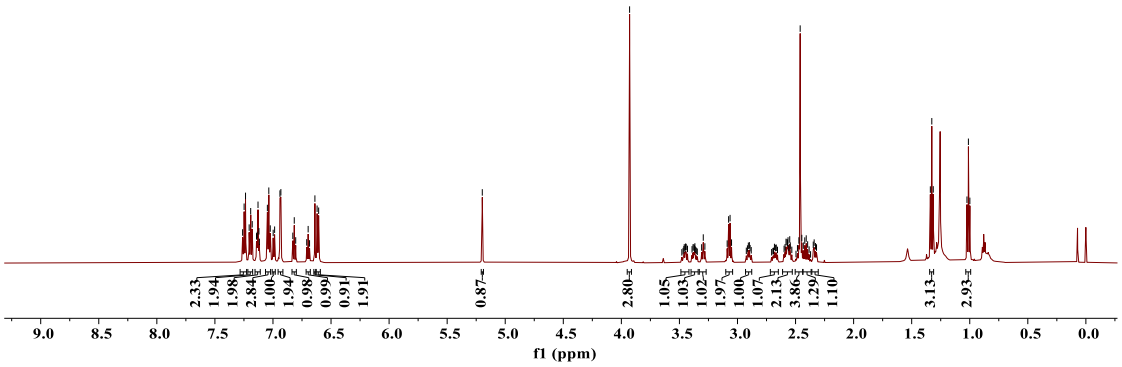
2k

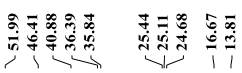


Parameters	
Parameter	value
Title	Ra-462.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	8
Acquisition Date	2022-01-10T22:02:14
Spectrometer Frequency	600 MHz
Nucleus	1H

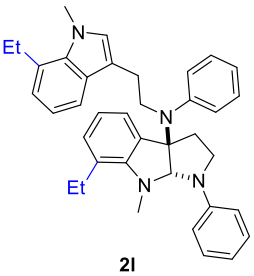


2l

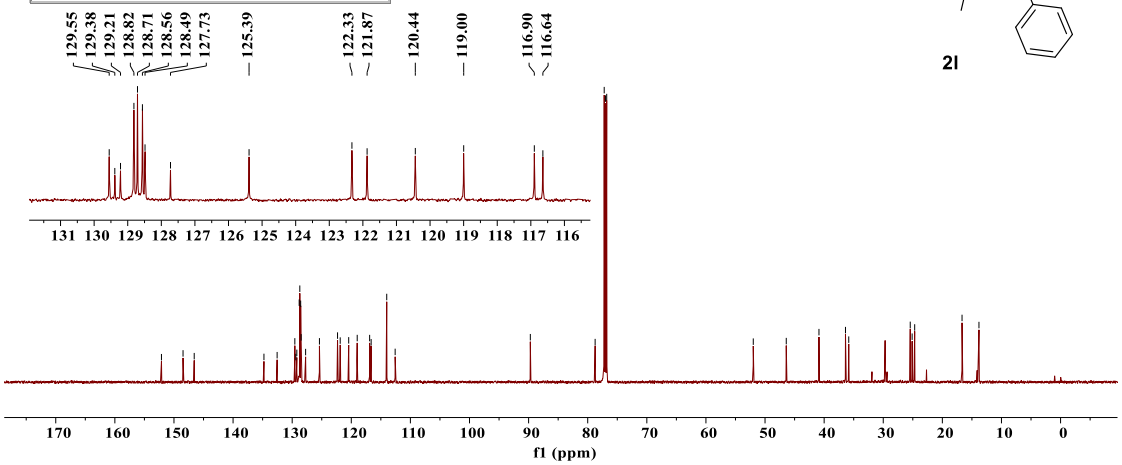


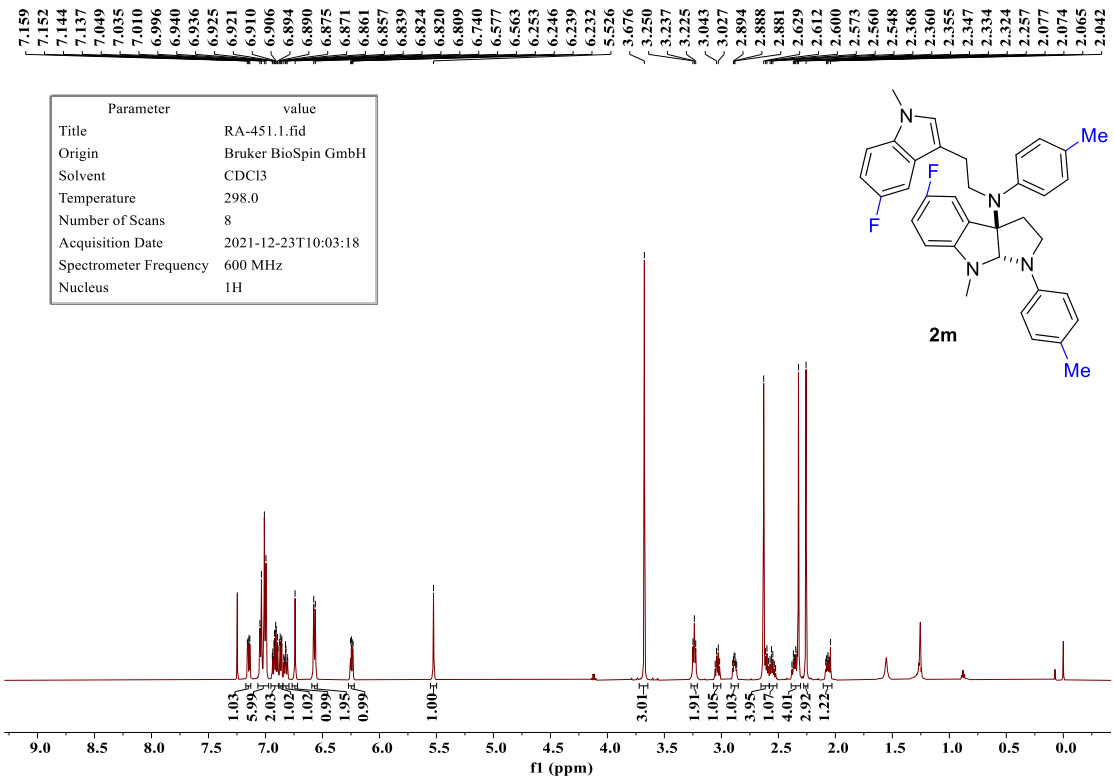


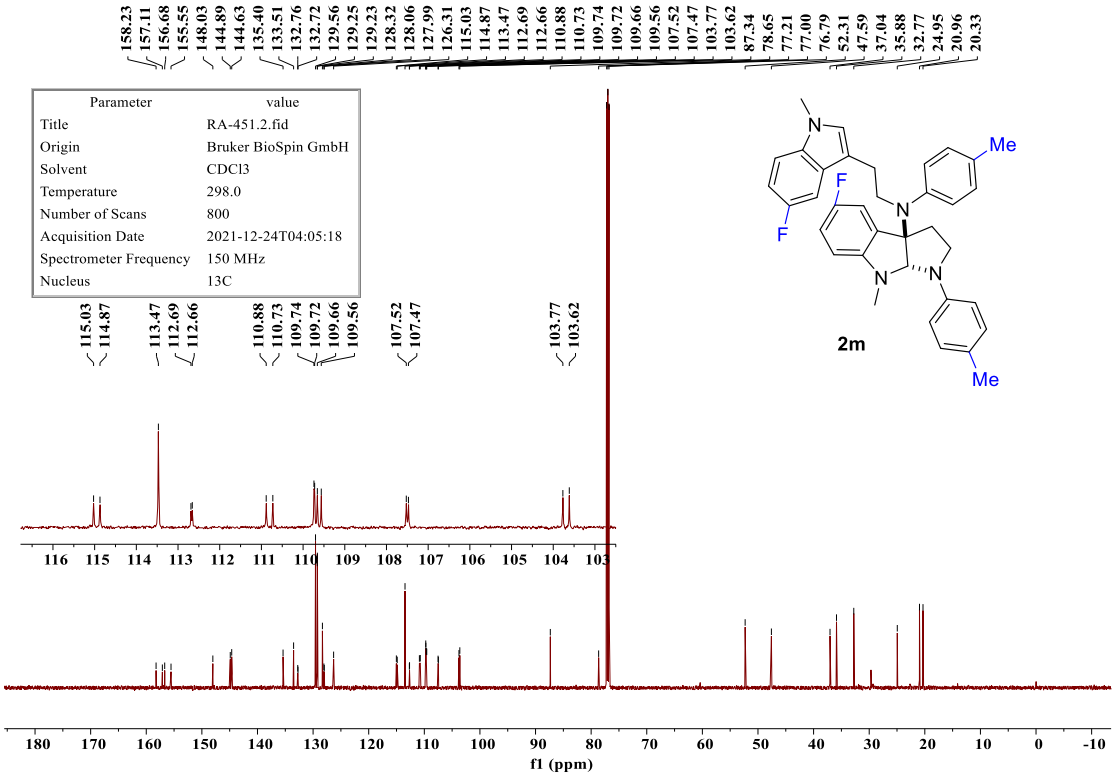
Parameters	
Parameter	value
Title	Ra-462.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	800
Acquisition Date	2022-01-12T18:03:35
Spectrometer Frequency	150 MHz
Nucleus	13C



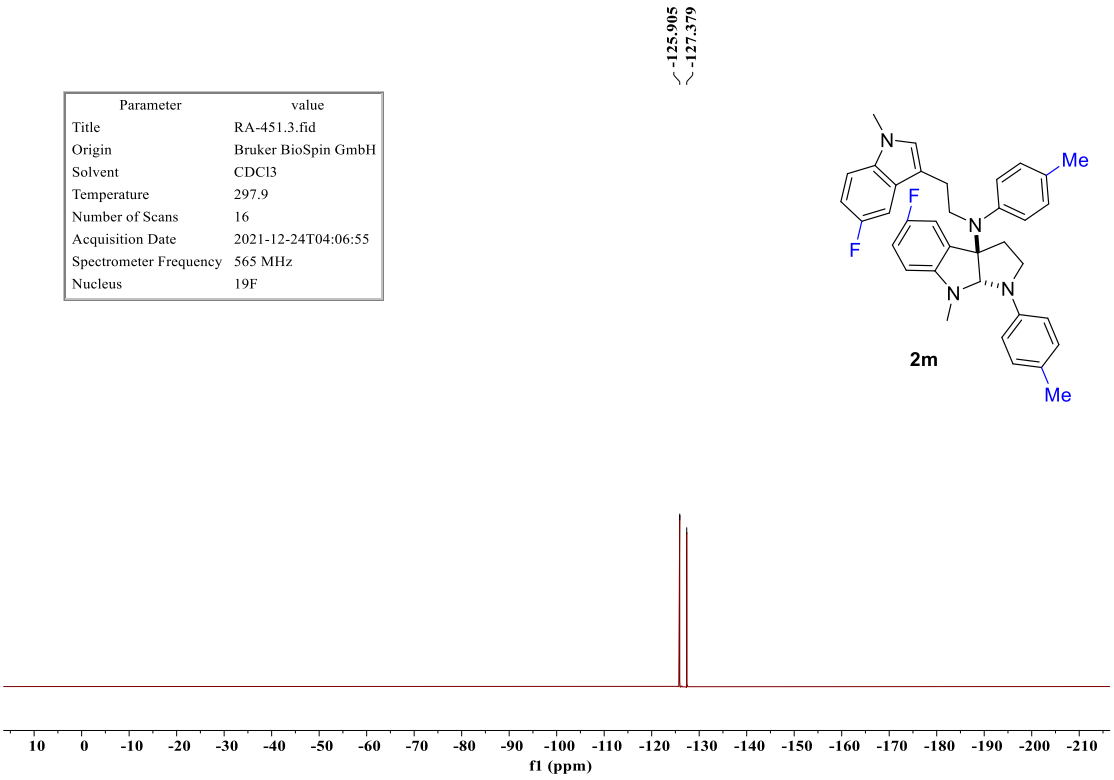
2l

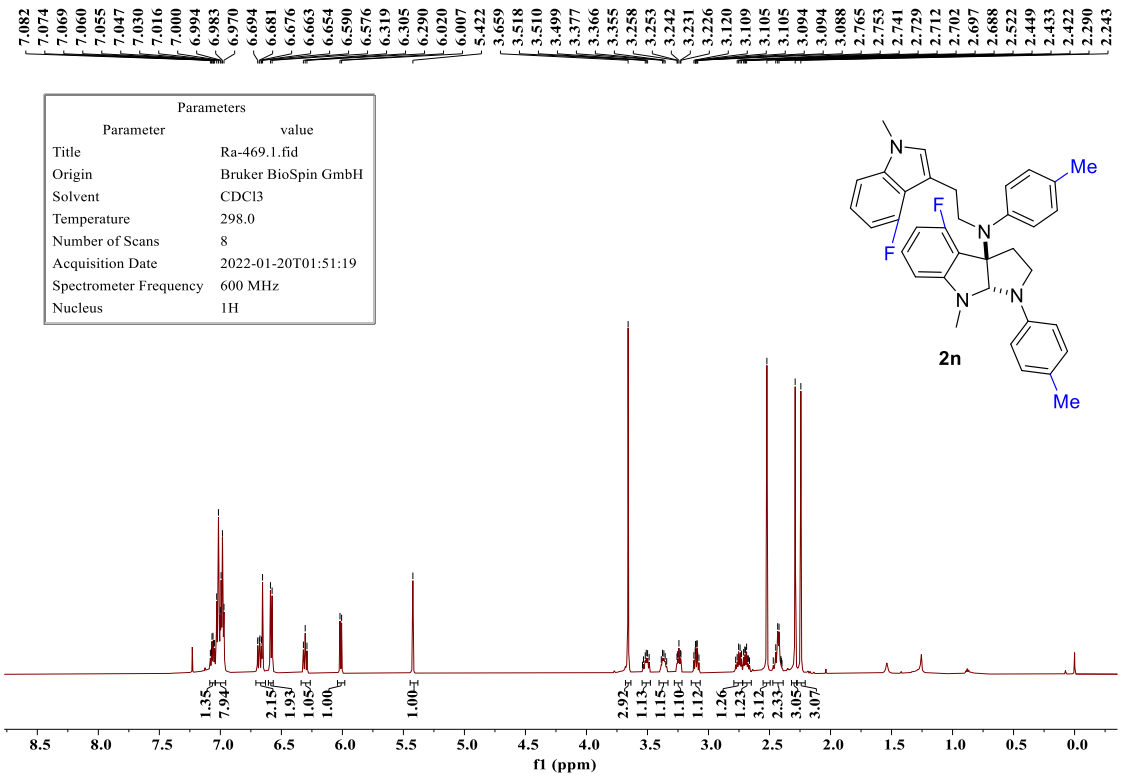


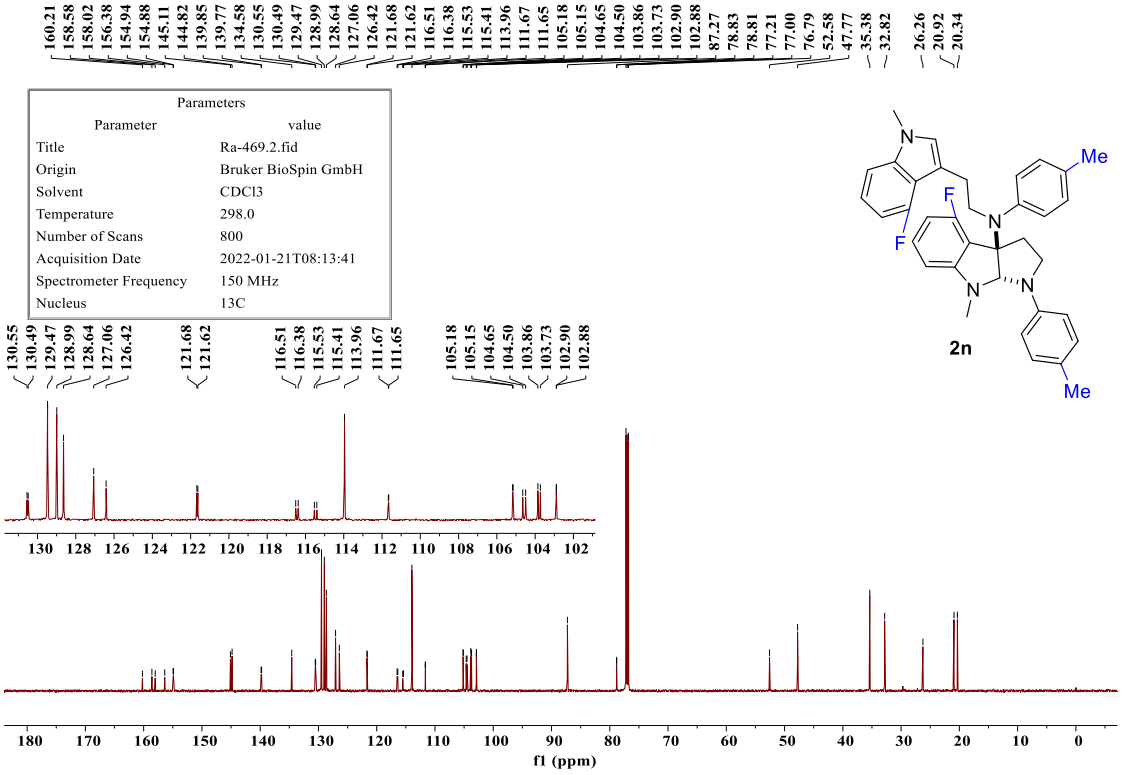

7.159 7.152 7.144 7.137 7.049 7.035 7.010 6.996 6.940 6.936 6.925 6.921 6.910 6.906 6.894 6.890 6.875 6.871 6.861 6.857 6.839 6.824 6.820 6.809 6.740 6.577 6.563 6.253 6.246 6.239 6.232 5.526 3.676 3.250 3.237 3.225 3.043 3.027 2.894 2.888 2.881 2.629 2.612 2.600 2.573 2.560 2.548 2.368 2.360 2.355 2.347 2.334 2.324 2.257 2.077 2.074 2.065 2.042
Parameter value
Title RA-451.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2021-12-23T10:03:18
Spectrometer Frequency 600 MHz
Nucleus 1H
Me
F
F
N
N
N
N
Me
2m
1.03 5.90 2.03 1.02 1.02 0.99 1.95 0.99 1.00 3.01 1.91 1.05 1.03 3.95 1.07 4.01 2.92 1.22
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)

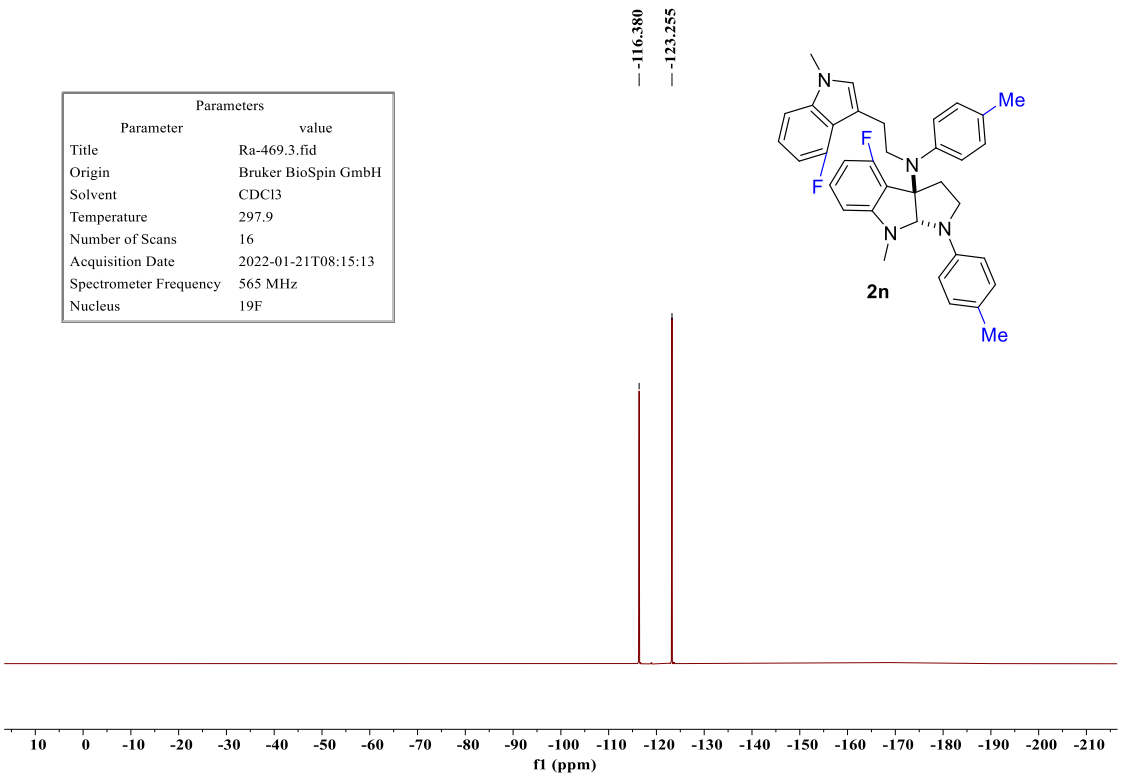

158.23 157.11 156.68 155.55 148.03 144.89 144.63 135.40 133.51 132.76 132.72 129.56 129.25 129.23 128.32 128.06 127.99 126.31 115.03 114.87 113.47 112.69 112.66 110.88 110.73 109.74 109.72 109.66 109.56 107.52 107.47 103.77 103.62 87.34 78.65 77.21 77.00 76.79 52.31 47.59 37.04 35.88 32.77 24.95 20.96 20.33
Parameter value
Title RA-451.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 800
Acquisition Date 2021-12-24T04:05:18
Spectrometer Frequency 150 MHz
Nucleus 13C
115.03 114.87 113.47 112.69 112.66 110.88 110.73 109.74 109.72 109.66 109.56 107.52 107.47 103.77 103.62
Me
F
F
N
N
N
N
Me
2m
116 115 114 113 112 111 110 109 108 107 106 105 104 103
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

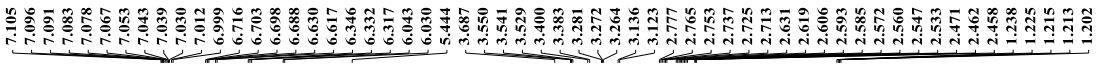
Parameter	value
Title	RA-451.3.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.9
Number of Scans	16
Acquisition Date	2021-12-24T04:06:55
Spectrometer Frequency	565 MHz
Nucleus	19F



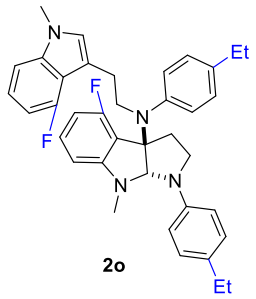

7.082 7.074 7.069 7.060 7.055 7.047 7.030 7.016 7.000 6.994 6.983 6.970 6.694 6.681 6.676 6.663 6.654 6.590 6.576 6.319 6.305 6.290 6.020 6.007 5.422 3.659 3.518 3.510 3.499 3.377 3.366 3.355 3.258 3.253 3.242 3.231 3.226 3.120 3.109 3.105 3.105 3.094 3.094 3.088 2.765 2.753 2.741 2.729 2.712 2.702 2.697 2.688 2.522 2.449 2.433 2.422 2.290 2.243
Parameters
Parameter value
Title Ra-469.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2022-01-20T01:51:19
Spectrometer Frequency 600 MHz
Nucleus 1H
N
Me
F
F
N
N
N
Me
2n
1.35 7.94 2.15 1.93 1.05 1.00 1.00 2.92 1.13 1.15 1.10 1.12 1.26 1.23 3.12 2.33 3.05 3.07
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)


160.21 158.58 158.02 156.38 154.94 154.88 145.11 144.82 139.85 139.77 134.58 130.55 130.49 129.47 128.99 128.64 127.06 126.42 121.68 121.62 116.51 116.38 115.53 115.41 113.96 111.67 111.65 105.18 105.15 104.65 104.50 103.86 103.73 102.90 102.88 87.27 78.83 78.81 77.21 77.00 76.79 52.58 47.77 35.38 32.82 26.26 20.92 20.34
Parameters
Parameter value
Title Ra-469.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 800
Acquisition Date 2022-01-21T08:13:41
Spectrometer Frequency 150 MHz
Nucleus 13C
N
Me
F
F
N
N
N
Me
2n
130.55 130.49 129.47 128.99 128.64 127.06 126.42 121.68 121.62 116.51 116.38 115.53 115.41 113.96 111.67 111.65 105.18 105.15 104.65 104.50 103.86 103.73 102.90 102.88
130 128 126 124 122 120 118 116 114 112 110 108 106 104 102
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

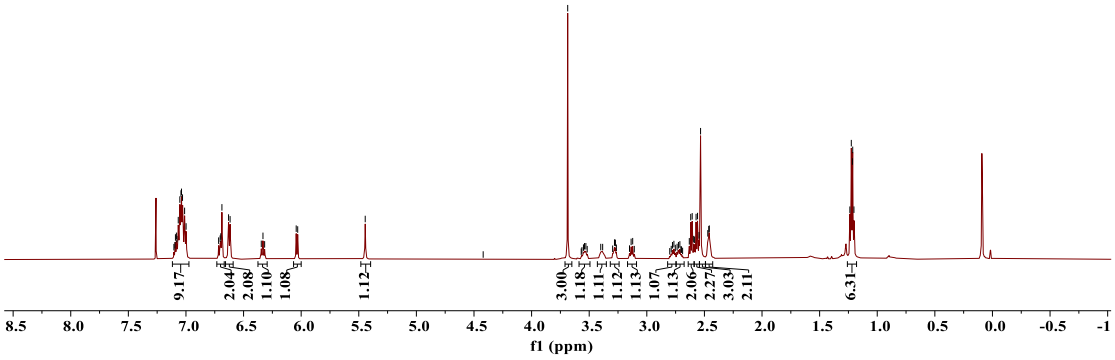

Parameters
Parameter value
Title Ra-469.3.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.9
Number of Scans 16
Acquisition Date 2022-01-21T08:15:13
Spectrometer Frequency 565 MHz
Nucleus 19F
-116.380
-123.255
N
Me
F
F
N
N
N
Me
2n
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

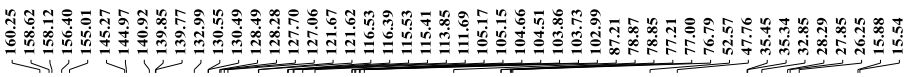


Parameter	value
Title	RA-2M.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Number of Scans	8
Acquisition Date	2022-10-13T11:45:55
Spectrometer Frequency	600 MHz
Nucleus	1H

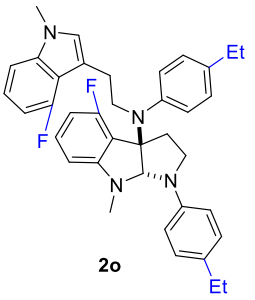


2o



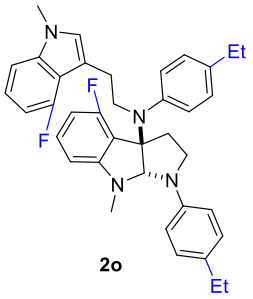


Parameter	value
Title	Ra-450-1.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.1
Number of Scans	4407
Acquisition Date	2022-03-18T14:46:23
Spectrometer Frequency	150 MHz
Nucleus	13C

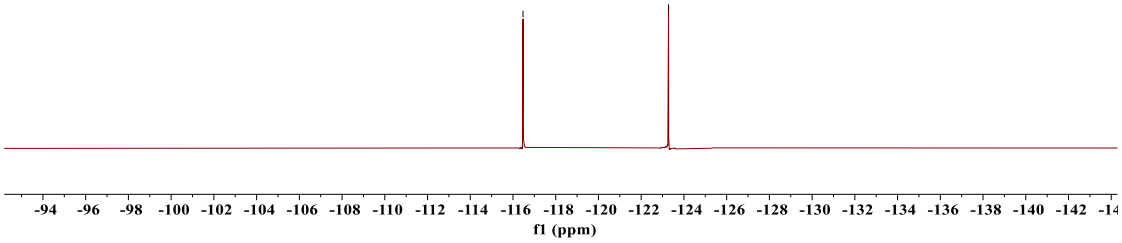


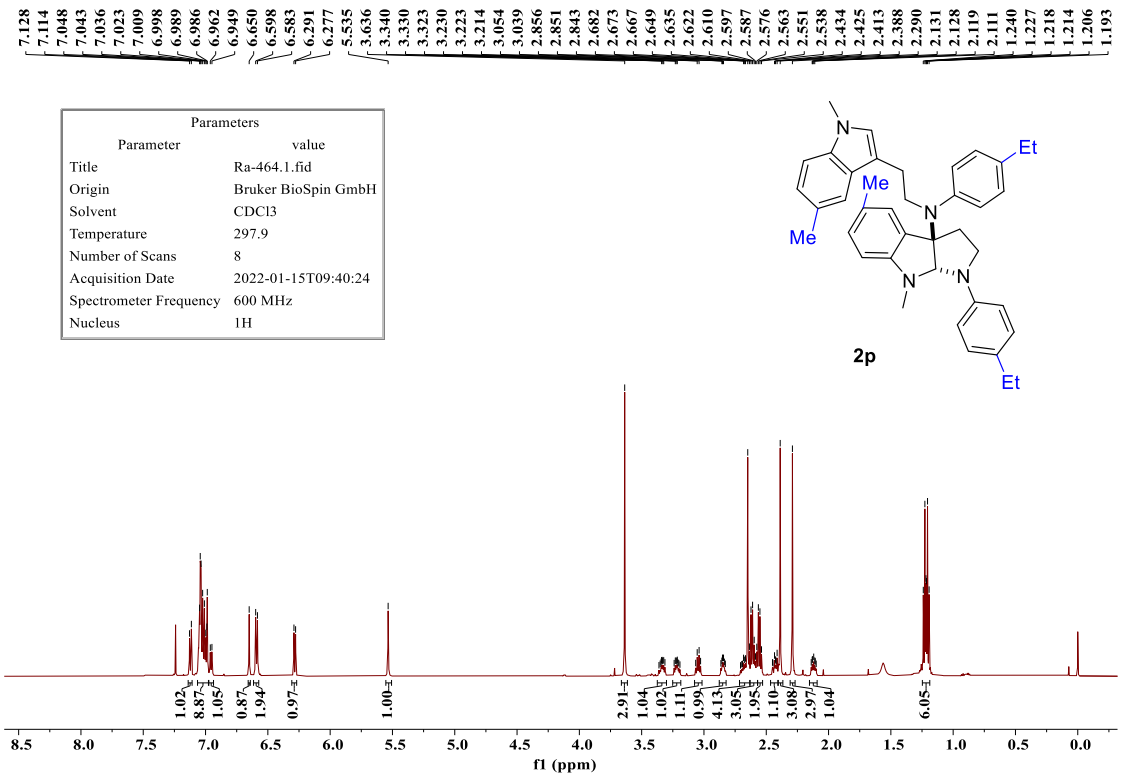
2o

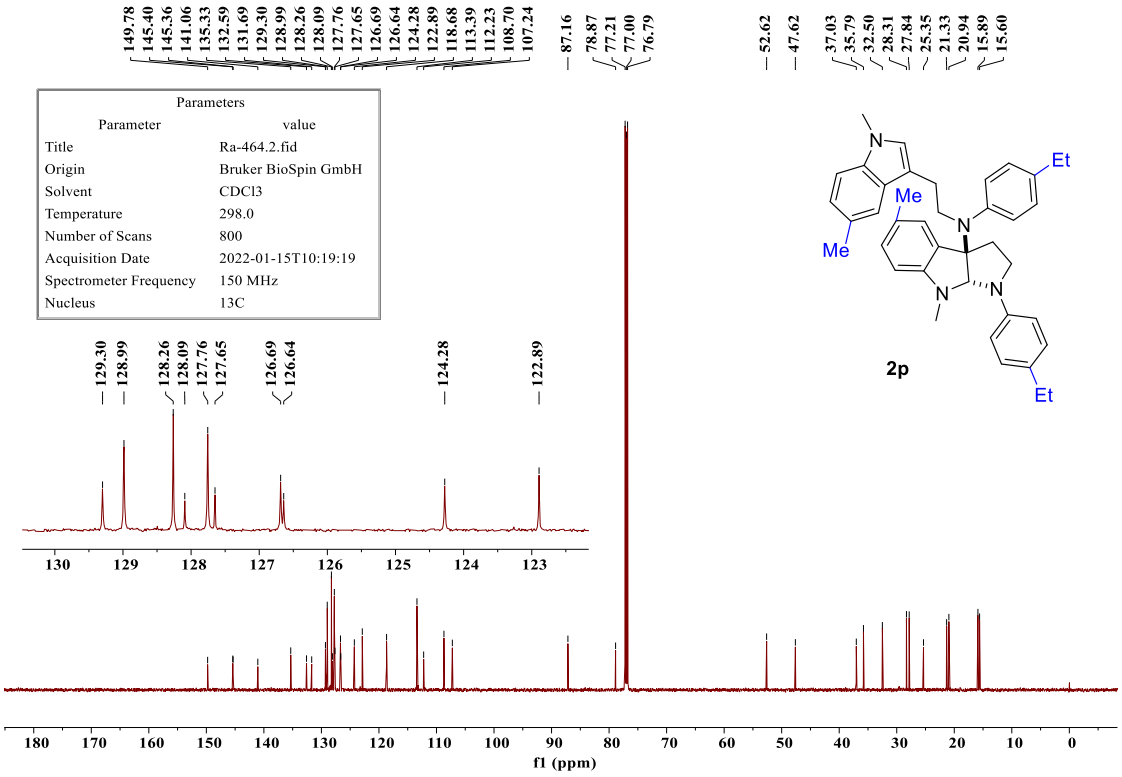
Parameters	
Parameter	value
Title	Ra-450-1-F.1.1.1r
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.2
Number of Scans	16
Acquisition Date	2022-03-11T23:05:27
Spectrometer Frequency	565 MHz
Nucleus	19F

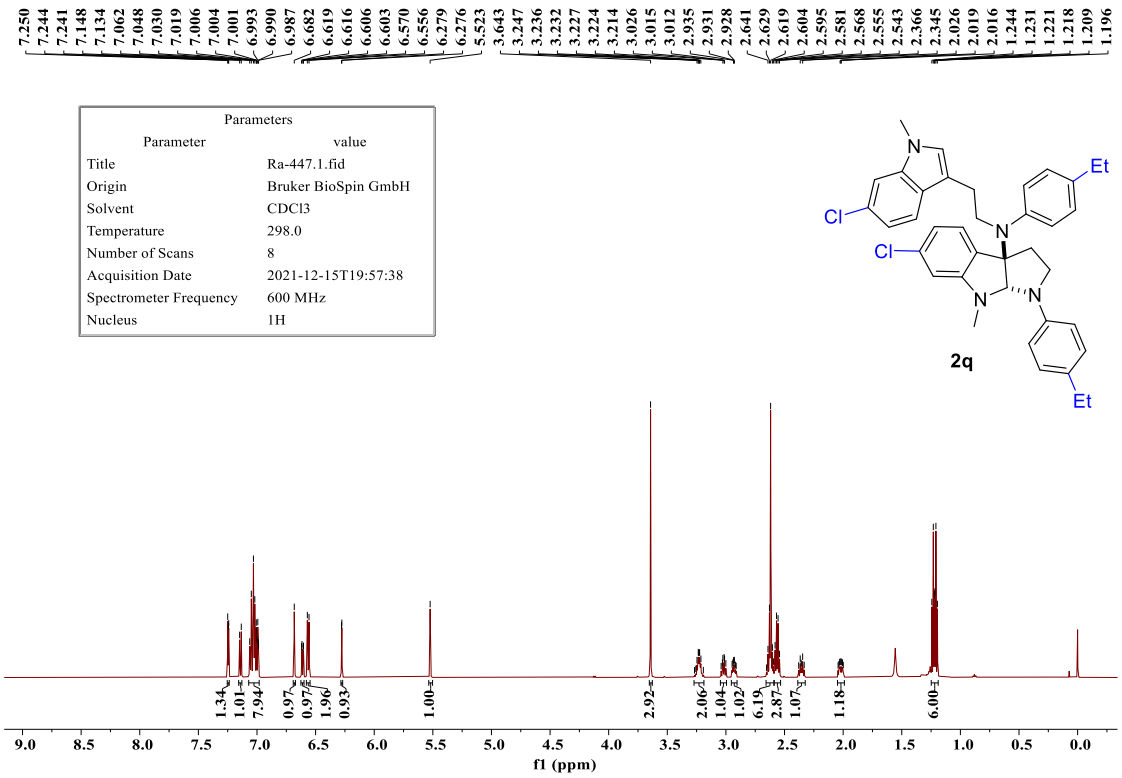


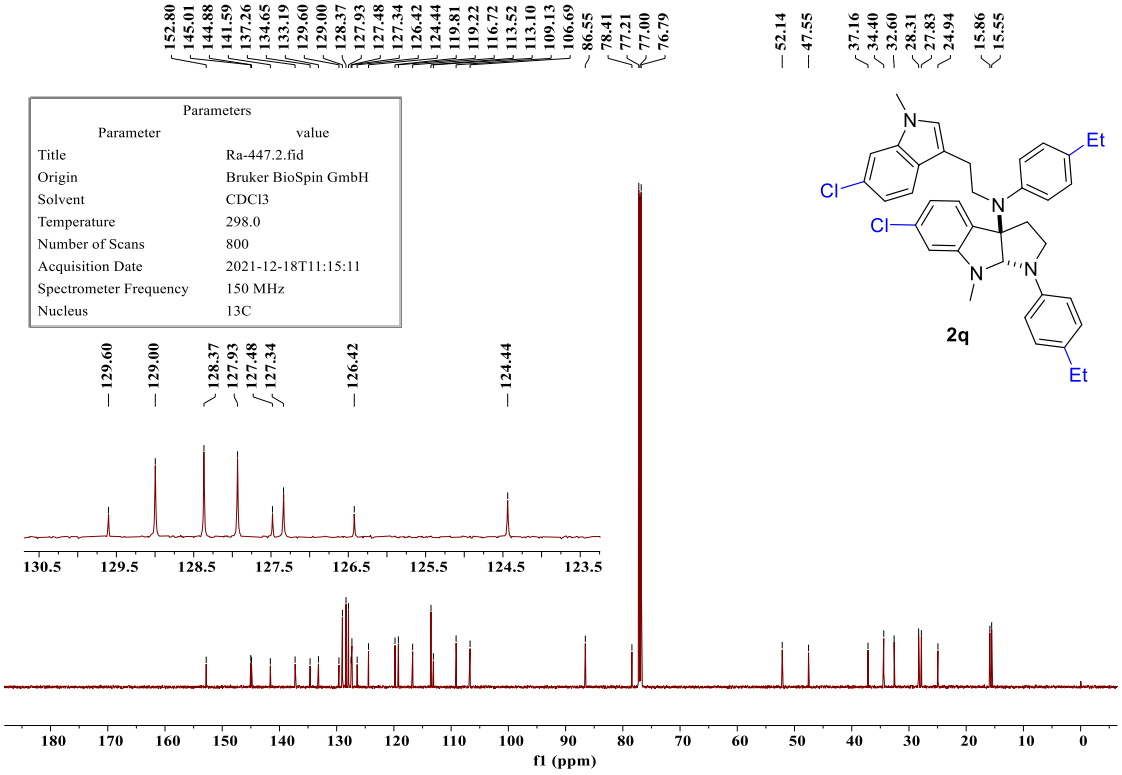
2o

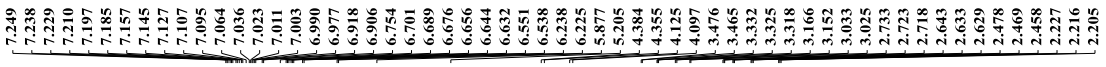



7.128 7.114 7.048 7.043 7.036 7.023 7.009 6.998 6.989 6.986 6.962 6.949 6.650 6.598 6.583 6.291 6.277 5.535 3.636 3.340 3.330 3.323 3.230 3.223 3.214 3.054 3.039 2.856 2.851 2.843 2.682 2.673 2.667 2.649 2.635 2.622 2.610 2.597 2.587 2.576 2.563 2.551 2.538 2.434 2.425 2.413 2.388 2.290 2.131 2.128 2.119 2.111 1.240 1.227 1.218 1.214 1.206 1.193
Parameters
Parameter value
Title Ra-464.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.9
Number of Scans 8
Acquisition Date 2022-01-15T09:40:24
Spectrometer Frequency 600 MHz
Nucleus 1H
N
Et
Me
Me
N
N
N
Et
2p
1.02 8.87 1.05 0.87 1.94 0.97 1.00 2.91 1.04 1.02 1.11 0.99 4.13 3.05 1.95 1.10 3.08 2.97 1.04 6.05
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)

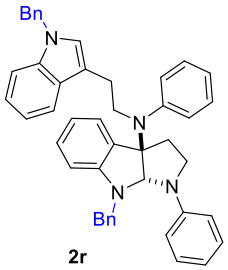

149.78 145.40 145.36 141.06 135.33 132.59 131.69 129.30 128.99 128.26 128.09 127.76 127.65 126.69 126.64 124.28 122.89 118.68 113.39 112.23 108.70 107.24
87.16 78.87 77.21 77.00 76.79
52.62 47.62 37.03 35.79 32.50 28.31 27.84 25.35 21.33 20.94 15.89 15.60
Parameters
Parameter value
Title Ra-464.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 800
Acquisition Date 2022-01-15T10:19:19
Spectrometer Frequency 150 MHz
Nucleus 13C
N
Et
Me
Me
N
N
N
Et
2p
129.30 128.99 128.26 128.09 127.76 127.65 126.69 126.64 124.28 122.89
130 129 128 127 126 125 124 123
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.250 7.244 7.241 7.148 7.134 7.062 7.048 7.030 7.019 7.006 7.004 7.001 6.993 6.990 6.987 6.682 6.619 6.616 6.606 6.603 6.570 6.556 6.279 6.276 5.523 3.643 3.247 3.236 3.232 3.227 3.224 3.214 3.026 3.015 3.012 2.935 2.931 2.928 2.641 2.629 2.619 2.604 2.595 2.581 2.568 2.555 2.543 2.366 2.345 2.026 2.019 2.016 1.244 1.231 1.221 1.218 1.209 1.196
Parameters
Parameter value
Title Ra-447.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 8
Acquisition Date 2021-12-15T19:57:38
Spectrometer Frequency 600 MHz
Nucleus 1H
N
Et
Cl
Cl
N
N
N
Et
2q
1.34 1.01 7.94 0.97 0.97 1.96 0.93 1.00 2.92 2.06 1.04 1.02 6.19 2.87 1.07 1.18 6.00
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)

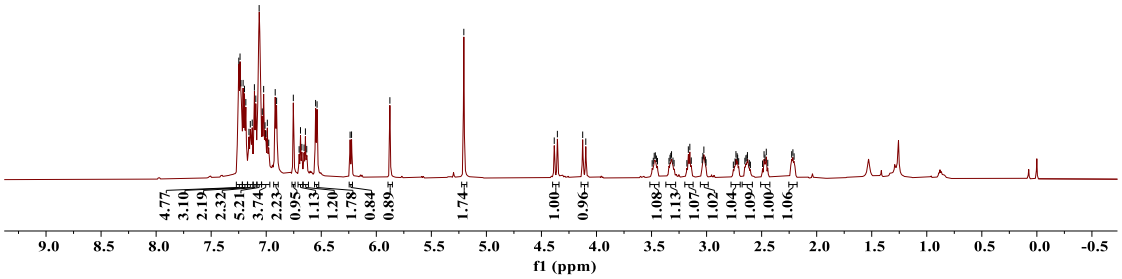

152.80 145.01 144.88 141.59 137.26 134.65 133.19 129.60 129.00 128.37 127.93 127.48 127.34 126.42 124.44 119.81 119.22 116.72 113.52 113.10 109.13 106.69 86.55 78.41 77.21 77.00 76.79 52.14 47.55 37.16 34.40 32.60 28.31 27.83 24.94 15.86 15.55
Parameters
Parameter value
Title Ra-447.2.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Number of Scans 800
Acquisition Date 2021-12-18T11:15:11
Spectrometer Frequency 150 MHz
Nucleus 13C
N
Et
Cl
Cl
N
N
N
Et
2q
129.60 129.00 128.37 127.93 127.48 127.34 126.42 124.44
130.5 129.5 128.5 127.5 126.5 125.5 124.5 123.5
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

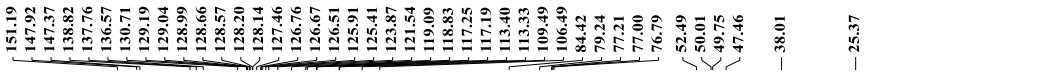


Parameters	
Parameter	value
Title	Ra-375.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	8
Acquisition Date	2022-01-24T00:27:46
Spectrometer Frequency	600 MHz
Nucleus	1H

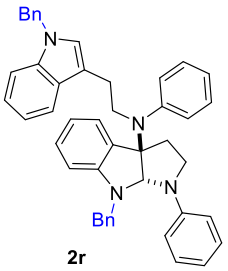


2r

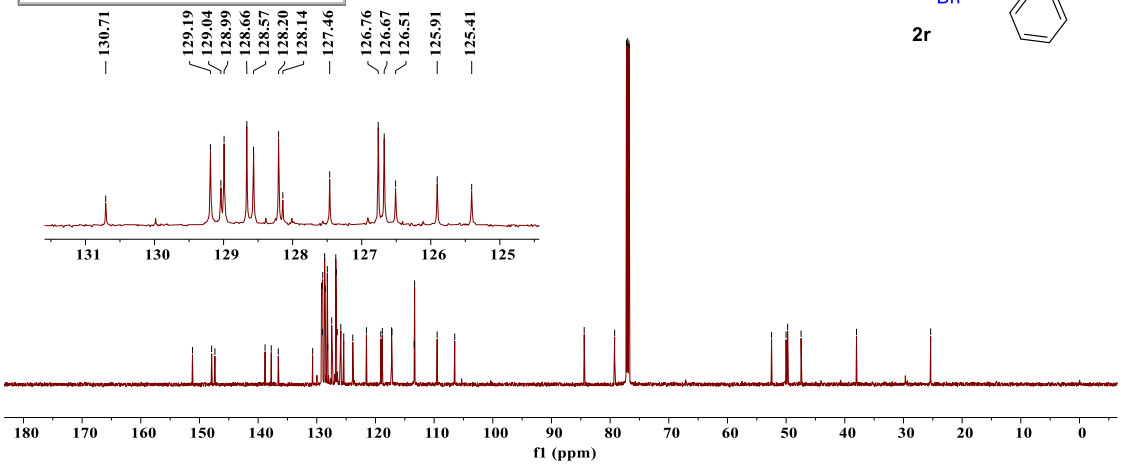


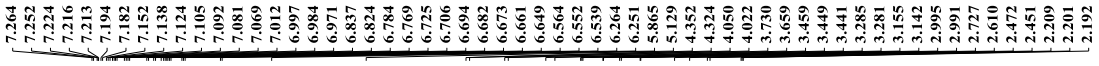


Parameters	
Parameter	value
Title	Ra-375.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	800
Acquisition Date	2022-01-24T01:06:50
Spectrometer Frequency	150 MHz
Nucleus	13C

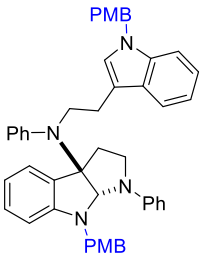


2r

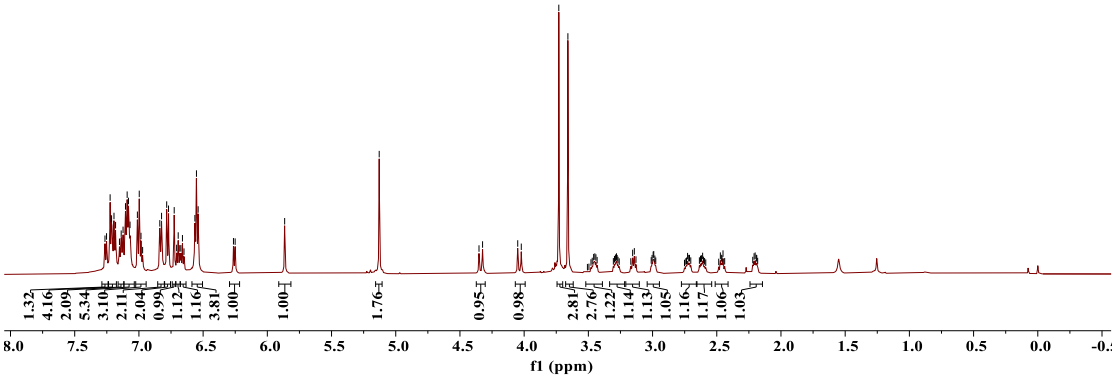


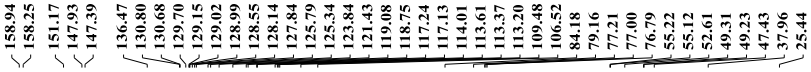


Parameter	value
Title	Ra-827.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Number of Scans	4
Acquisition Date	2022-11-15T01:40:57
Spectrometer Frequency	600 MHz
Nucleus	1H

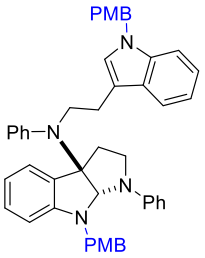


2s

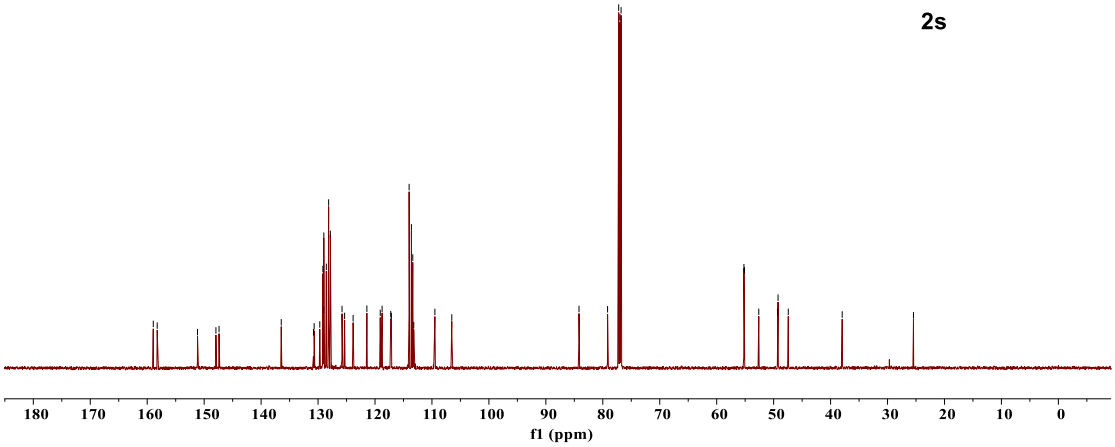


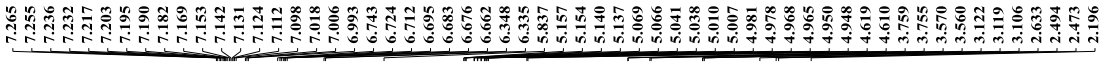


Parameter	value
Title	Ra-827.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Number of Scans	512
Acquisition Date	2022-11-16T02:13:42
Spectrometer Frequency	150 MHz
Nucleus	13C

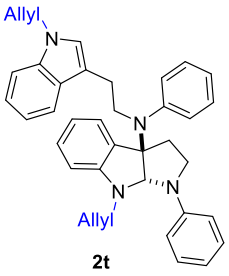


2s

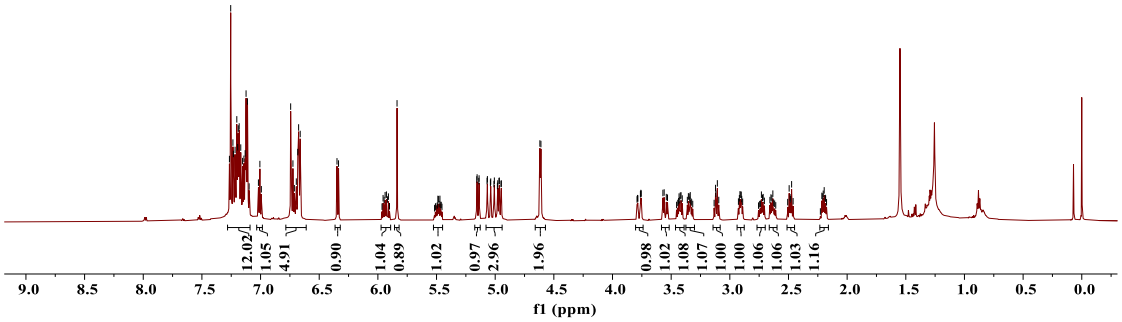


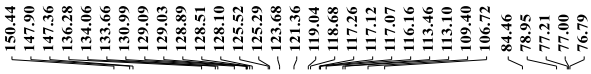


Parameters	
Parameter	value
Title	Ra-374.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	8
Acquisition Date	2022-01-24T02:00:28
Spectrometer Frequency	600 MHz
Nucleus	1H

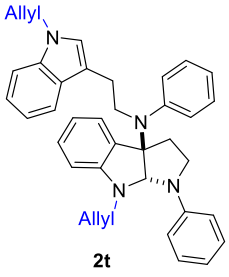


2t

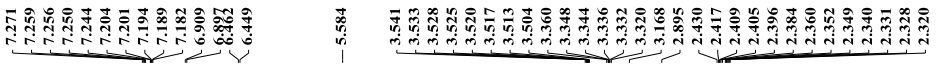




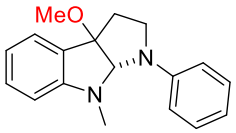
Parameters	
Parameter	value
Title	Ra-374.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	800
Acquisition Date	2022-01-24T02:39:23
Spectrometer Frequency	150 MHz
Nucleus	13C



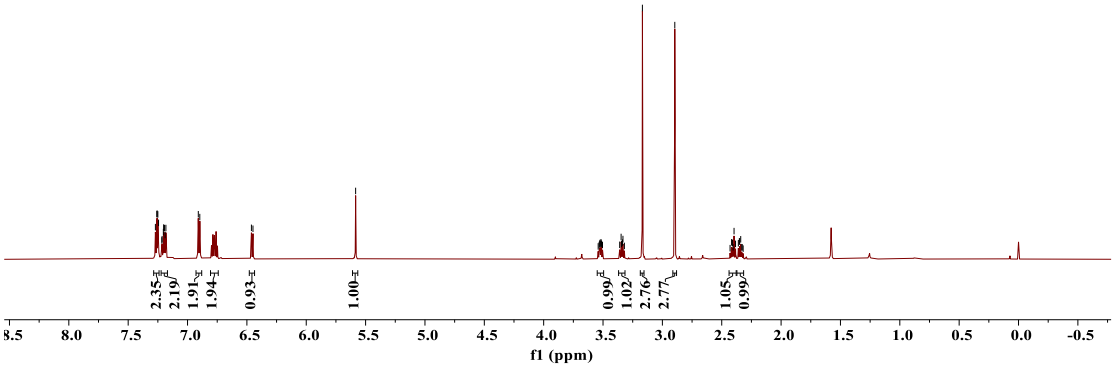
2t

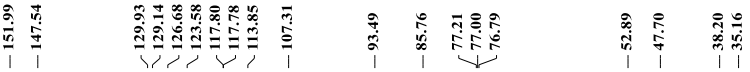


Parameter	value
Title	ra-847.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Number of Scans	4
Acquisition Date	2022-12-05T09:49:01
Spectrometer Frequency	600 MHz
Nucleus	1H

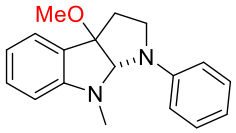


4

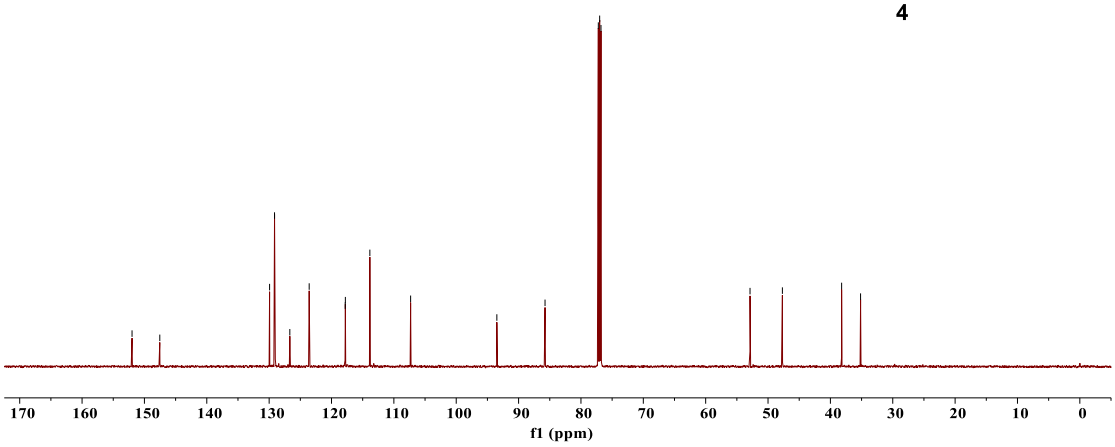


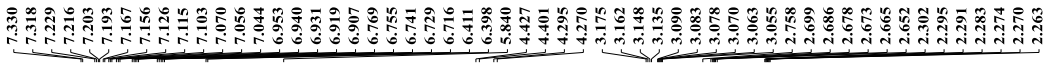


Parameter	value
Title	ra-847.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Number of Scans	800
Acquisition Date	2022-12-05T10:28:17
Spectrometer Frequency	150 MHz
Nucleus	13C

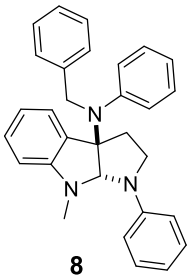


4

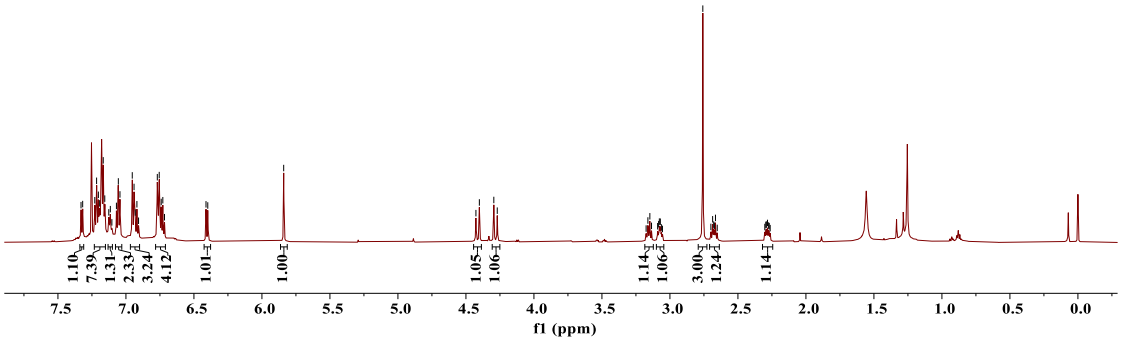




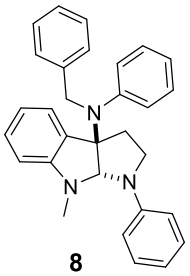
Parameter	value
Title	Ra-701-1.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	8
Acquisition Date	2022-09-21T08:47:48
Spectrometer Frequency	600 MHz
Nucleus	1H



8



Parameter	value
Title	Ra-701-1.2.1.1r
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	1004
Acquisition Date	2022-09-21T09:36:27
Spectrometer Frequency	150 MHz
Nucleus	13C



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