

Copper-catalyzed aerobic oxidative radical alkoxycyclization of tryptamines to access 3-alkoxypyrroloindolines

Wei Wang,[†] Jun-Rong Song,[†] Zhi-Yao Li, Ting Zhong, Qin Chi, Hai Ren* and Wei-Dong Pan*

School of Pharmaceutical Sciences, Guizhou University, Guizhou University, Huaxi Avenue South, Guiyang 550025, (China);

State Key Laboratory of Functions and Applications of Medicinal Plants, Guizhou Medical University, Guiyang 550014, (China); The Key Laboratory of Chemistry for Natural Products of Guizhou Province and Chinese Academy of Sciences, Guiyang 550014, (China).

E-mail: renh@gzcnpcn.cn; wdpan@163.com

Supporting Information

Content

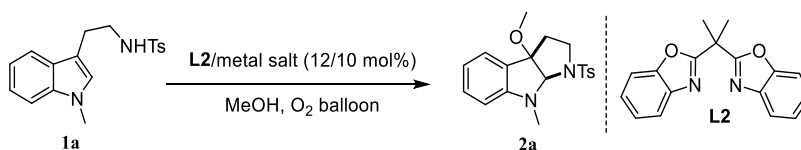
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1. General information

Unless stated, otherwise all reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. 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 a Varian Mercury 400 MHz or Agilent Mercury 400 MHz spectrometer (^1H : 400 MHz, ^{13}C : 100 MHz) in chloroform-d or Agilent Mercury 600 MHz spectrometer (^1H : 600 MHz and ^{13}C : 150 MHz) in chloroform-d. ^1H and ^{13}C NMR spectra were internally referenced to the proton (^1H) 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 40.5 ppm, respectively. Data for ^1H 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). IR spectra were recorded using a FTIR spectrometer (IR 200) and the KBr disk method was adopted; High resolution mass spectra were obtained using Bruker ESI-QTOF mass spectrometry.

2. Optimization of the reaction conditions

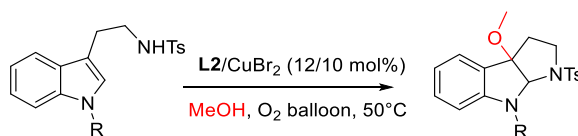
2.1 Metal salt and volume of solvent screening^a



Entry	T (°C)	Metal salts	MeOH (mL)	t (h)	Yield (%) ^b	Dr ^c
1	30	CuBr ₂	2	48	trace	-
2	50	CuBr ₂	2	48	45	-
3	50	CuBr ₂	4	42	71	>20/1
4	50	CuBr ₂	8	48	49	-
5	70	CuBr ₂	2	48	31	11/1

^a Carried out under oxygen atmosphere: Metal salt (0.02 mmol, 10 mol%), **1a** (0.2 mmol); ^b Isolated yields. ^c dr was determined by ¹H-NMR of the crude product.

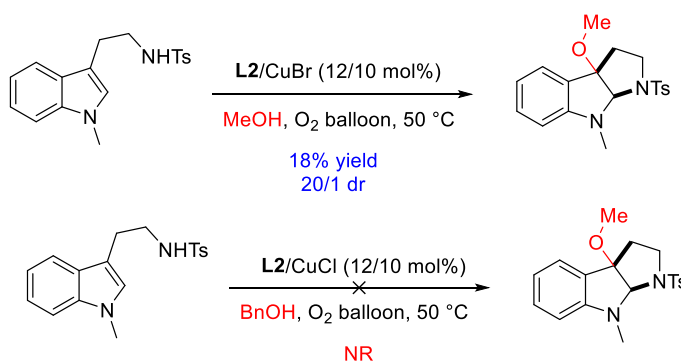
2.2 The influence of *N*-protecting group^a



Entry	R	t (h)	Yield (%)	dr
1	Me	48	71	20/1
2	Bn	60	79	20/1
3	PMB	60	70	20/1
4	Boc	42	NR	-
5	Ac	48	NR	-
6	Ts	48	NR	-

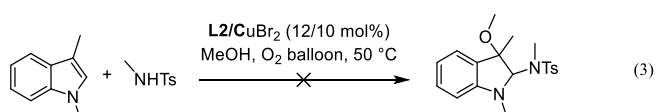
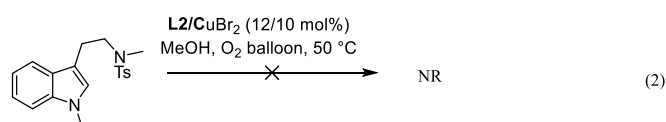
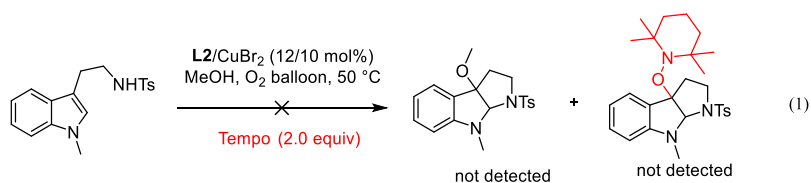
^a Carried out under oxygen atmosphere: Metal salt (0.02 mmol, 10 mol%), **1a** (0.2 mmol); ^bYields were isolated yields.

2.3 Investigation of Cu (I) metal salts



3. Mechanistic studies

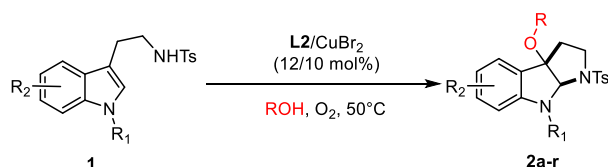
3.1 Control experiments of 3-alkoxylation reaction



A 50 mL reaction tube was charged with CuBr_2 (4.46 mg, 0.02mmol, 10 mol%), tryptamine substrates (0.2 mmol, 1.0 equiv.), **L2** (6.67 mg, 0.024 mmol, 12 mol%) and 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) (0.4 mmol, 2.0 equiv) before O_2 replacement operation, then alcohol (4mL) was added. The reaction mixture was stirred vigorously at 50 °C and monitored by TLC.

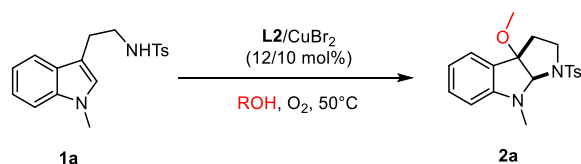
4. General Procedure for Alkoxylation and Product Characterizations

4.1 Synthesis of alkoxy pyrroloindolines



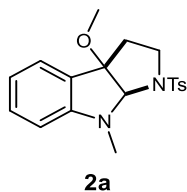
A 50 mL reaction tube was charged with CuBr_2 (4.46 mg, 0.02 mmol, 10 mol%), tryptamine substrates (0.2 mmol, 1.0 equiv) and ligand (0.024 mmol, 12 mol%) before O_2 replacement operation, then alcohol (4 mL) was added. Then the reaction mixture was heat to 50°C . After the reaction completed, the reaction mixture was filtered with short silica gel column, concentrated under reduced pressure and the residue was purified by chromatography on silica gel (PE/EA, 10:1) to afford alkoxy pyrroloindoline.

4.2 Scale experiments



A 200 mL reaction tube was charged with CuBr_2 (89.4 mg, 0.4 mmol, 10 mol%), tryptamine substrates **1a** (1.31 g, 4 mmol, 1.0 equiv) and ligand (133.6 mg, 0.48 mmol, 12 mol%) before O_2 replacement operation, then alcohol (80 mL) was added. Then the reaction mixture was heat to 50°C . After 72 h, the reaction mixture was filtered with short silica gel column, concentrated under reduced pressure and the residue was purified by chromatography on silica gel (PE/EA, 10:1) to afford alkoxy pyrroloindoline **2a** 0.813 g.

4.3 Product Characterizations



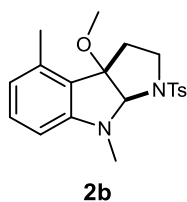
2a White solid, 51.0 mg, 71% yield, 20/1 dr.

For the mixture of the two diastereomers: $^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.79 - 7.76 (m, 2 + 0.32 H), 7.34 - 7.33 (m, 2 + 0.32 H), 7.28 (dd, $J = 12.0, 6.0$ Hz, 0.16 H), 7.22 (td, $J = 7.8, 1.2$ Hz, 1 H), 7.15 (d, $J = 6.0$ Hz, 0.16 H), 7.06 (d, $J = 6.0$ Hz, 1 H), 6.71 (td, $J = 7.8, 1.2$ Hz, 1 H), 6.47 (d, $J = 12.0$ Hz, 1 H), 6.34 (d, $J = 6.0$ Hz, 0.16 H), 5.36 (s, 1 H), 5.36 (s, 0.16 H), 3.58 - 3.55 (m, 1 + 0.16 H), 3.12 - 3.08 (m, 1 + 0.16 H), 3.02 (s, 3 H), 2.99 (s, 0.48 H), 2.97 (s, 0.48 H), 2.97 (s, 3 H), 2.44 - 2.44 (m, 3 + 0.48 H), 2.09 - 2.04 (m, 1 + 0.16 H), 1.84 - 1.79 (m, 1 + 0.16 H);

$^{13}\text{C NMR}$ (150 MHz, Chloroform-*d*) δ 151.9, 143.7, 136.2, 130.6, 129.7, 127.3, 124.8, 123.9, 117.8, 106.7, 93.7, 86.1, 52.7, 47.4, 38.6, 31.4, 21.5;

HRMS-ESI: Exact mass calcd. for $\text{C}_{19}\text{H}_{23}\text{O}_3\text{N}_2\text{S}$ $[\text{M}+\text{H}]^+$: 359.1424; Found: 359.1421;

IR (KBr): 2880.75, 2358.79, 1612.40, 1489.14, 1342.07, 1276.23, 1162.10, 1101.82, 1072.04, 1028.07, 1014.24, 931.01, 819.27, 735.84, 609.51, 545.47.



2b White solid, 31.7 mg, 43% yield, 2.5/1 dr;

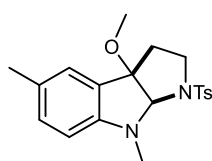
For the mixture of the two diastereomers: $^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.80 - 2.78 (m, 2 + 0.74 H), 7.34 (d, $J = 6.0$ Hz, 2 + 0.74 H), 7.10 (t, $J = 6.0$ Hz, 1 H), 6.48 (d, $J = 6.0$ Hz, 1 H), 6.30 (d, $J = 6.0$ Hz, 1 H), 6.19 (d, $J = 12.0$ Hz, 0.37 H), 5.37 (s, 0.37 H), 5.37 (s, 1 H), 3.59 - 3.55 (m, 1 + 0.37 H), 3.22 - 3.18 (m, 1 + 0.37 H), 2.99 (s, 3 H), 2.97 (s, 1.11 H), 2.92 (s, 3 + 1.11 H), 2.44 - 2.45 (m, 3 + 1.11 H), 2.24 (s, 1.11 H),

2.20 (s, 3 H), 2.18 - 2.15 (m, 1 H), 2.14 - 2.11 (m, 0.37 H), 1.89 - 1.84 (m, 1 + 0.37 H);

¹³C NMR (150 MHz, Chloroform-*d*) δ 151.8, 150.9, 143.8, 143.7, 136.3, 135.1, 134.7, 134.0, 130.4, 129.8, 129.7, 127.4, 121.9, 120.0, 105.8, 104.3, 94.8, 86.3, 52.8, 52.6, 47.4, 47.3, 38.3, 38.0, 31.7, 31.5, 21.6, 17.2, 17.0;

HRMS-ESI: Exact mass calcd. for C₂₀H₂₅O₃N₂S [M+H]⁺: 373.1580; Found: 373.1578;

IR (KBr): 2979.44, 1598.24, 1472.99, 1340.75, 1281.00, 1234.87, 1161.33, 1094.36, 1074.00, 1014.25, 943.90, 873.57, 818.52, 664.29, 599.49.



2c

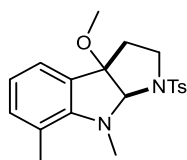
2c White solid, 34.9 mg, 47% yield, 20/1 dr;

¹H NMR (600 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 12.0 Hz, 2 H), 7.33 (d, *J* = 12.0 Hz, 2 H), 7.02 (d, *J* = 6.0 Hz, 1 H), 6.87 (s, 1 H), 6.39 (d, *J* = 6.0 Hz, 1 H), 5.32 (s, 1 H), 3.57 - 3.53 (m, 1 H), 3.13 - 3.09 (m, 1 H), 2.99 (s, 3 H), 2.92 (s, 3 H), 2.44 (s, 3 H), 2.25 (s, 3 H), 2.08 - 2.04 (m, 1 H), 1.85 - 1.80 (m, 1 H);

¹³C NMR (150 MHz, Chloroform-*d*) δ 149.9, 143.6, 136.3, 131.0, 129.7, 127.3, 127.2, 125.0, 124.4, 106.9, 93.8, 86.5, 52.7, 47.5, 38.5, 32.0, 21.5, 20.7;

HRMS-ESI: Exact mass calcd. for C₂₀H₂₅O₃N₂S [M+H]⁺: 373.1580; Found: 373.1578;

IR (KBr): 2884.84, 2358.58, 1621.28, 1497.65, 1341.77, 1288.09, 1163.25, 1102.67, 1071.64, 1029.72, 1014.90, 936.22, 818.49, 674.85, 662.16, 599.34.



2d

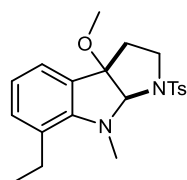
2d White solid, 60.0 mg, 80% yield, 20/1 dr;

¹H NMR (600 MHz, Chloroform-*d*) δ 7.78 (d, $J = 12.0$ Hz, 2 H), 7.29 - 7.26 (m, 2 H), 6.98 - 6.97 (m, 2 H), 6.77 (t, $J = 7.4$ Hz, 1 H), 5.20 (s, 1 H), 3.61 - 3.58 (m, 1 H), 3.14 (s, 3 H), 2.99 (s, 3 H), 2.92 - 2.88 (m, 1 H), 2.41 (s, 3 H), 2.21 (s, 3 H), 2.19 - 2.16 (m, 2 H);

¹³C NMR (150 MHz, Chloroform-*d*) δ 151.3, 143.2, 137.1, 133.3, 129.4, 127.3, 127.3, 121.9, 121.7, 120.6, 93.3, 88.6, 52.8, 46.4, 38.3, 38.1, 21.4, 18.8;

HRMS-ESI: Exact mass calcd. for C₂₀H₂₅O₃N₂S [M+H]⁺: 373.1580; Found: 373.1579;

IR (KBr): 2907.15, 1604.08, 1465.41, 1411.50, 1237.62, 1092.30, 944.15, 851.78, 836.64, 813.72, 784.69, 752.36, 734.77, 708.41, 573.90.



2e

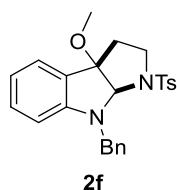
2e White solid, 50.0 mg, 65% yield, 20/1 dr;

For the mixture of the two diastereomers: **¹H NMR** (600 MHz, Chloroform-*d*) δ 7.78 - 7.76 (m, 2 + 0.26 H), 7.28 - 7.26 (m, 2 + 0.26 H), 7.13 (d, $J = 1.8$ Hz, 0.13 H), 7.06 (d, $J = 1.8$ Hz, 0.13 H), 7.03 (d, $J = 7.4$ Hz, 1H), 6.98 (d, $J = 6.0$ Hz, 1H), 6.83 (t, $J = 6.0$ Hz, 1 H), 5.21 (s, 1 H), 5.20 (s, 0.13 H), 3.63 - 3.59 (m, 1 + 0.13 H), 3.12 (s, 3 H), 3.11 (s, 0.39 H), 3.01 (s, 0.39 H), 3.00 (s, 3H), 2.92 - 2.88 (m, 1 + 0.13 H), 2.56 - 2.51 (m, 2 + 0.26 H), 3.41 (s, 0.39 H), 2.40 (s, 3 H), 2.22 - 2.17 (m, 2 + 0.26 H), 1.12 - 1.10 (m, 3 + 0.39 H);

¹³C NMR (150 MHz, Chloroform-*d*) δ 150.8, 143.1, 137.3, 131.2, 129.4, 128.2, 127.6, 127.2, 121.8, 120.8, 93.3, 88.8, 52.9, 46.3, 38.9, 38.2, 24.5, 21.4, 14.3;

HRMS-ESI: Exact mass calcd. for C₂₁H₂₇O₃N₂S [M+H]⁺: 387.1737; Found: 387.1735;

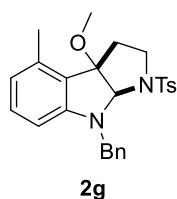
IR (KBr): 2964.05, 1600.63, 1454.82, 1340.92, 1159.35, 1118.51, 1079.94, 944.08, 812.27, 752.10, 707.52, 687.68, 659.60, 580.25, 546.82.



2f White solid, 68.7 mg, 79% yield, 20/1 dr;

¹H NMR (600 MHz, Chloroform-*d*) δ 7.21 (d, $J = 6.0$ Hz, 2 H), 7.37 (d, $J = 12.0$ Hz, 2 H), 7.31 - 7.28 (m, 4 H), 7.25 - 7.23 (m, 1 H), 7.15 (t, $J = 6.0$ Hz, 1 H), 7.07 (d, $J = 6.0$ Hz, 1 H), 6.71 (t, $J = 6.0$ Hz, 1 H), 6.47 (d, $J = 6.0$ Hz, 1 H), 5.54 (s, 1 H), 4.69 (ABd, $J = 24.0, 12.0$ Hz, 2 H), 3.64 - 3.60 (m, 1 H), 3.20 - 3.15 (td, $J = 12.0, 6.0$ Hz, 1 H), 2.82 (s, 3 H), 2.42 (s, 3 H), 2.10 - 2.07 (m, 1 H), 1.81 - 1.75 (m, 1 H).

HRMS-ESI: Exact mass calcd. for C₂₅H₂₇O₃N₂S [M+H]⁺: 435.1737; Found: 435.1734. All analytical data are consistent with literature (*Org. Biomol. Chem.* 2020, **18**, 32-35).



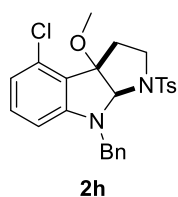
2g yellow liquid, 60.0 mg, 67% yield, 20/1 dr;

¹H NMR (600 MHz, Chloroform-*d*) δ 7.71 (d, $J = 12.0$ Hz, 2 H), 7.37 (d, $J = 6.0$ Hz, 2 H), 7.30 - 7.22 (m, 5 H), 7.05 (t, $J = 6.0$ Hz, 1 H), 6.48 (d, $J = 6.0$ Hz, 1 H), 6.34 (d, $J = 6.0$ Hz, 1 H), 5.56 (s, 1 H), 4.69 (ABd, $J = 18.0, 12.0$ Hz, 2 H), 3.65 - 3.61 (m, 1 H), 3.27 - 3.22 (m, 1 H), 2.77 (s, 3 H), 2.41 (s, 3 H), 2.23 - 2.18 (m, 4 H), 1.84 - 1.79 (m, 1 H);

¹³C NMR (150 MHz, Chloroform-*d*) δ 151.1, 143.6, 138.1, 136.3, 135.5, 130.4, 129.7, 128.4, 127.6, 127.3, 127.0, 121.7, 119.9, 104.7, 95.0, 84.4, 52.5, 48.1, 47.1, 38.5, 21.5, 17.0;

HRMS-ESI: Exact mass calcd. for C₂₆H₂₉O₃N₂S [M+H]⁺: 449.1893; Found: 449.1892;

IR (KBr): 2358.54, 1653.13, 1595.80, 1455.25, 1344.46, 1157.41, 1091.55, 927.47, 811.25, 764.71, 743.95, 704.46, 658.85, 582.11, 543.61.



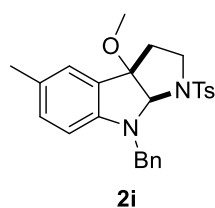
2h white solid, 67.4 mg, 72% yield, >20/1 dr.

¹H NMR (600 MHz, Chloroform-*d*) δ 7.72 (d, $J = 12.0$ Hz, 2 H), 7.37 (d, $J = 6.0$ Hz, 2 H), 7.33 - 7.25 (m, 5 H), 7.08 (t, $J = 6.0$ Hz, 1 H), 6.63 (d, $J = 6.0$ Hz, 1 H), 6.38 (d, $J = 6.0$ Hz, 1 H), 5.56 (s, 1 H), 4.69 (ABd, $J = 18.0, 12.0$ Hz, 2 H), 3.65 (dd, $J = 12.0, 6.0$ Hz, 1 H), 3.23 - 3.18 (m, 1 H), 2.85 (s, 3 H), 2.46 - 2.42 (m, 4 H), 1.74 - 1.69 (m, 1 H);

¹³C NMR (150 MHz, Chloroform-*d*) δ 152.6, 143.9, 137.6, 136.1, 131.9, 131.5, 129.8, 128.6, 127.5, 127.3, 127.3, 120.4, 118.5, 105.3, 94.7, 84.6, 53.0, 47.9, 47.1, 37.7, 21.6;

HRMS-ESI: Exact mass calcd. for C₂₅H₂₆O₃N₂ClS [M+H]⁺: 469.1347; Found: 469.1348;

IR (KBr): 2925.38, 1596.26, 1493.43, 1330.72, 1236.96, 1005.30, 925.74, 856.22, 811.51, 757.62, 704.35, 670.11, 574.04, 543.72.



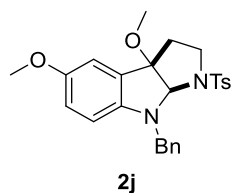
2i yellow liquid, 70.7 mg, 79% yield, 20/1 dr;

¹H NMR (600 MHz, Chloroform-*d*) δ 7.72 (d, $J = 6.0$ Hz, 2 H), 7.37 (d, $J = 6.0$ Hz, 2 H), 7.30 - 7.22 (m, 5 H), 6.96 (d, $J = 6.0$ Hz, 1 H), 6.88 (s, 1 H), 6.37 (d, $J = 6.0$ Hz, 1 H), 5.52 (s, 1 H), 4.66 (ABd, $J = 12.0, 6.0$ Hz, 2 H), 3.62 - 3.59 (m, 1 H), 3.20 - 3.15 (m, 1 H), 2.81 (s, 3 H), 2.42 (s, 3 H), 2.24 (s, 3 H), 2.08 - 2.05 (m, 1 H), 1.81 - 1.76 (m, 1 H);

¹³C NMR (150 MHz, Chloroform-*d*) δ 149.1, 143.6, 138.3, 136.4, 131.0, 129.7, 128.4, 127.6, 127.3, 127.2, 127.0, 124.7, 107.1, 94.1, 84.6, 52.6, 48.4, 47.3, 39.3, 21.5, 20.7;

HRMS-ESI: Exact mass calcd. for $C_{26}H_{28}O_3N_2NaS$ $[M+Na]^+$: 471.1713; Found: 471.1707;

IR (KBr): 2918.56, 1496.48, 1453.59, 1347.55, 1288.79, 1166.58, 1117.59, 1068.30, 1028.90, 807.79, 744.49, 701.32, 663.39, 582.09, 546.93.



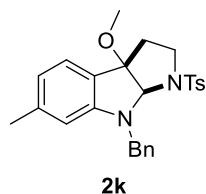
2j yellow liquid, 56.2 mg, 61% yield, 20/1 dr;

¹H NMR (600 MHz, Chloroform-*d*) δ 7.72 (d, $J = 6.0$ Hz, 2 H), 7.37 (d, $J = 6.0$ Hz, 2 H), 7.30 - 7.23 (m, 5 H), 6.73 (dd, $J = 12.0, 6.0$ Hz, 1 H), 6.69 (d, $J = 3.0$ Hz, 1 H), 6.37 (d, $J = 6.0$ Hz, 1 H), 5.53 (s, 1 H), 4.64 (ABd, $J = 22.0, 15.0$ Hz, 2 H), 3.72 (s, 3 H), 3.63 - 3.59 (m, 1 H), 3.22 - 3.17 (m, 1 H), 2.81 (s, 3 H), 2.42 (s, 3 H), 2.10 - 2.06 (m, 1 H), 1.84 - 1.78 (m, 1 H);

¹³C NMR (150 MHz, Chloroform-*d*) 152.8, 145.4, 143.6, 138.3, 136.4, 129.7, 128.4, 127.6, 127.3, 127.0, 126.1, 115.8, 110.5, 108.1, 94.1, 84.9, 56.0, 52.7, 49.1, 47.3, 39.4, 21.5;

HRMS-ESI: Exact mass calcd. for $C_{26}H_{29}O_3N_2S$ $[M+H]^+$: 465.1843; Found: 465.1843;

IR (KBr): 2882.38, 1492.03, 1338.51, 1273.37, 1157.22, 1037.03, 982.62, 939.48, 878.32, 804.29, 757.53, 667.19, 574.71 22.48.



2k yellow liquid, 56.2 mg, 63% yield, 5/1 dr;

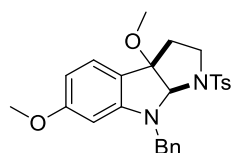
¹H NMR (600 MHz, Chloroform-*d*) δ 7.71 (d, $J = 6.0$ Hz, 2 H), 7.38 (d, $J = 6.0$ Hz, 2 H), 7.31 - 7.23 (m, 5 H), 6.96 (d, $J = 6.0$ Hz, 1 H), 6.54 (d, $J = 6.0$ Hz, 1 H), 6.31 (s, 1 H), 5.52 (s, 1 H), 4.67 (ABd, $J = 12.0, 6.0$ Hz, 2 H), 3.63 - 3.59 (m, 1 H), 3.19 - 3.14

(m, 1 H), 2.82 (s, 3 H), 2.41 (s, 3 H), 2.26 (s, 3 H), 2.07 - 2.04 (m, 1 H), 1.77 - 1.72 (m, 1 H);

¹³C NMR (150 MHz, Chloroform-*d*) δ 151.5, 143.6, 140.9, 138.3, 136.4, 129.7, 128.4, 127.5, 127.3, 127.0, 124.1, 121.7, 118.6, 107.6, 93.9, 84.6, 52.6, 47.8, 47.3, 39.4, 21.9, 21.5;

HRMS-ESI: Exact mass calcd. for C₂₆H₂₉O₃N₂S [M+H]⁺: 449.1893; Found: 449.1893;

IR (KBr): 2827.13, 1615.20, 1494.88, 1453.06, 1346.71, 1159.88, 1072.47, 933.36, 807.37, 743.79, 709.21, 661.59, 600.84, 566.55, 544.12.



21

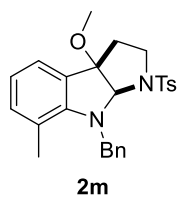
21 yellow liquid, 56.1 mg, 56% yield, 4/1 dr;

For the mixture of the two diastereomers: ¹H NMR (600 MHz, Chloroform-*d*) δ 7.72 - 7.70(m, 2 + 0.5 H), 7.39 - 7.37 (m, 2 + 0.5 H), 7.32 - 7.23 (m, 5 + 1.75 H), 6.96 (d, *J* = 12.0 Hz, 1 H), 6.24 (dd, *J* = 6.0, 3.0 Hz, 1 H), 6.03 (s, 1 H), 6.02 (s, 0.25 H), 5.52 (s, 1 H), 5.51 (s, 0.25 H), 4.73 - 4.61 (m, 2 + 0.5 H), 3.74 (s, 0.75 H), 3.71 (s, 3 H), 3.63 - 3.60 (m, 1 + 0.25 H), 3.18 - 3.13 (m, 1 + 0.25 H), 2.85 (s, 0.75 H), 2.83 (s, 3 H), 2.43 (s, 0.75 H), 2.42 (s, 3 H), 2.05 - 2.02 (m, 1 + 0.25 H), 1.74 - 1.68 (m, 1 + 0.25 H);

¹³C NMR (150 MHz, Chloroform-*d*) δ 162.5, 152.8, 143.7, 138.1, 136.4, 129.8, 128.5, 127.6, 127.3, 127.1, 125.0, 116.9, 102.8, 93.7, 93.6, 84.9, 55.3, 52.5, 47.9, 47.3, 39.4, 21.5;

HRMS-ESI: Exact mass calcd. for C₂₆H₂₉O₄N₂S [M+H]⁺: 465.1843; Found: 465.1843;

IR (KBr): 2880.46, 1612.19, 1489.16, 1430.79, 1342.02, 1161.81, 1101.52, 1071.75, 1027.78, 841.22, 818.98, 735.51, 574.15, 545.13.



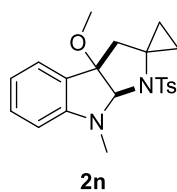
2m yellow liquid, 81.1 mg, 88% yield, >20/1 dr;

¹H NMR (600 MHz, Chloroform-*d*) δ 7.72 (d, $J = 12.0$ Hz, 2 H), 7.28 - 7.22 (m, 7 H), 7.00 (d, $J = 6.0$ Hz, 1 H), 6.93 (d, $J = 6.0$ Hz, 1 H), 6.74 (t, $J = 6.0$ Hz, 1 H), 5.43 (s, 1 H), 4.98 (d, $J = 18.0$ Hz, 1 H), 4.74 (d, $J = 12.0$ Hz, 1 H), 3.61 - 3.57 (m, 1 H), 3.09 - 3.04 (m, 1 H), 2.50 (s, 3 H), 2.41 (s, 3 H), 2.36 (s, 3 H), 2.04 - 2.01 (m, 1 H), 1.91 - 1.87 (m, 1 H);

¹³C NMR (150 MHz, Chloroform-*d*) δ 149.1, 143.4, 138.7, 136.8, 133.7, 129.6, 128.5, 128.1, 127.2, 126.8, 122.4, 119.6, 119.4, 93.2, 84.3, 52.1, 50.6, 46.6, 39.5, 21.5, 19.6;

HRMS-ESI: Exact mass calcd. for C₂₆H₂₉O₃N₂S [M+H]⁺: 449.1893; Found: 449.1891;

IR(KBr): 2937.15, 1602.29, 1451.44, 1422.90, 1383.56, 1343.02, 1301.19, 1255.38, 1153.58, 945.69, 807.65, 744.32, 696.87, 581.36, 543.11.



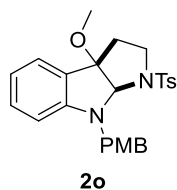
2n yellow liquid, 29.2 mg, 76% yield, 4/1 dr;

For the mixture of the two diastereomers: **¹H NMR** (600 MHz, Chloroform-*d*) δ 7.83 - 7.80 (m, 2 + 0.42 H), 7.35 (d, $J = 6.0$ Hz, 2 + 0.42 H), 7.29 (dd, $J = 6.0, 2.64$ Hz, 0.21 H), 7.20 (td, $J = 12.0, 6.0$ Hz, 1 H), 7.08 (d, $J = 6.0$ Hz, 0.21 H), 7.01 (d, $J = 6.0$ Hz, 1 H), 6.66 (t, $J = 18.0, 6.0$ Hz, 1 H), 6.43 (d, $J = 12.0$ Hz, 1 H), 6.30 (d, $J = 6.0$ Hz, 0.21 H), 5.66 (s, 1 H), 5.65 (s, 0.21 H), 3.05 (s, 0.63 H), 3.04 (s, 3 H), 2.97 (s, 3 H), 2.95 (s, 0.63 H), 2.46 (s, 3 + 0.63 H), 1.95 - 1.91 (m, 1 + 0.21 H), 1.79 - 1.77 (m, 1 + 0.21 H), 1.40 - 1.38 (m, 1 + 0.21 H), 0.57 - 0.53 (m, 1 + 0.21 H), 0.37 - 0.33 (m, 1 + 0.21 H), 0.15 - 0.12 (m, 0.21 H), 0.19 - 0.22 (m, 1 H);

¹³C NMR (150 MHz, Chloroform-*d*) δ 152.5, 151.5, 143.9, 143.8, 137.0, 136.8, 133.2, 130.5, 129.8, 129.7, 127.8, 127.8, 126.9, 126.2, 124.0, 117.2, 108.5, 107.1, 105.6, 92.4, 92.1, 88.1, 88.0, 52.6, 52.5, 46.8, 46.7, 41.8, 30.0, 29.7, 21.6, 14.5, 5.8;

HRMS-ESI: Exact mass calcd. for C₂₁H₂₅O₃N₂S [M+H]⁺: 385.1580; Found: 385.1579;

IR (KBr): 2928.29, 1609.97, 1492.70, 1351.52, 1165.27, 1092.20, 1041.62, 1006.66, 913.52, 812.99, 724.58, 662.07, 549.52.



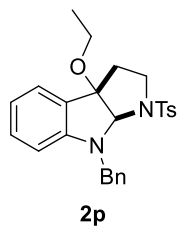
2o White solid, 65.2 mg, 70% yield, 20/1 dr;

¹H NMR (600 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 6.0 Hz, 2 H), 7.32 - 7.29 (m, 4 H), 7.15 (t, *J* = 6.0 Hz, 1H), 7.06 (d, *J* = 6.0 Hz, 1 H), 6.84 (d, *J* = 6.0 Hz, 2 H), 6.70 (t, *J* = 6.0 Hz, 1 H), 6.51 (d, *J* = 6.0 Hz, 1 H), 5.52 (s, 1 H), 4.62 (s, 2 H), 3.78 (s, 3 H), 3.60-3.63 (m, 1 H), 3.19 -3.14 (m, 1 H), 2.78 (s, 3 H), 2.42 (s, 3 H), 2.09-2.04 (m, 1 H), 1.80-1.74 (m, 1 H);

¹³C NMR (150 MHz, Chloroform-*d*) δ 158.7, 151.2, 143.7, 136.4, 130.5, 130.1, 129.7, 128.9, 127.3, 124.7, 124.3, 117.7, 113.8, 107.0, 94.0, 84.1, 55.2, 52.6, 47.4, 47.2, 39.5, 21.5;

HRMS-ESI: Exact mass calcd. for C₂₆H₂₉O₄N₂S [M+H]⁺: 465.1843; Found: 465.1843;

IR (KBr): 2932.38, 2358.87, 1733.91, 1609.39, 1512.36, 1488.34, 1346.85, 1245.74.



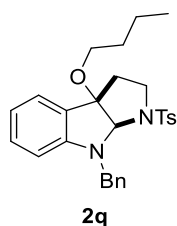
2p yellow solid, 77.8 mg, 87% yield, 6/1 dr;

¹H NMR (600 MHz, Chloroform-*d*) δ 7.72 (d, $J = 12.0$ Hz, 2 H), 7.35 (d, $J = 6.0$ Hz, 2 H), 7.32 - 7.25 (m, 5 H), 7.15 - 7.12 (m, 1 H), 7.07 (d, $J = 12.0$ Hz, 1 H), 6.69 (t, $J = 6.0$ Hz, 1 H), 6.45 (d, $J = 12.0$ Hz, 1 H), 5.53 (s, 1 H), 4.68 (s, 2 H), 3.66 - 3.62 (m, 1 H), 3.21 - 3.16 (m, 1 H), 3.05 - 2.99 (m, 1 H), 2.85 - 2.80 (m, 1 H), 2.43 (s, 3 H), 2.10 - 2.06 (m, 1 H), 1.81 - 1.76 (m, 1 H), 0.94 (t, 6.0 Hz, 3 H);

¹³C NMR (150 MHz, Chloroform-*d*) δ 150.9, 143.7, 138.2, 136.3, 130.4, 129.7, 128.5, 127.5, 127.3, 127.1, 125.6, 124.1, 117.8, 107.0, 93.6, 84.9, 60.6, 48.1, 47.2, 39.8, 21.5, 15.4;

HRMS-ESI: Exact mass calcd. for C₂₆H₂₉O₃N₂S [M+H]⁺: 449.1893; Found: 449.1892;

IR (KBr): 2979.81, 1609.32, 1492.74, 1454.41, 1344.71, 1328.59, 1294.23, 1160.55, 1101.10, 1052.40, 939.41, 746.44, 729.94, 671.28, 571.19.



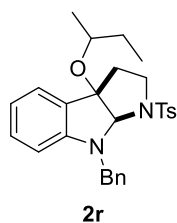
2q yellow liquid, 79.0 mg, 83% yield, 12/1 dr;

¹H NMR (600 MHz, Chloroform-*d*) δ 7.72 (d, $J = 6.0$ Hz, 2 H), 7.38 (d, $J = 6.0$ Hz, 2 H), 7.31 - 7.24 (m, 5 H), 7.14 (t, $J = 6.0$ Hz, 1 H), 7.06 (d, $J = 6.0$ Hz, 1 H), 6.69 (t, $J = 6.0$ Hz, 1 H), 6.47 (d, $J = 12.0$ Hz, 1 H), 5.48 (s, 1 H), 4.69 (ABd, $J = 18.0, 24.0$ Hz, 2 H), 3.66 - 3.62 (m, 1 H), 3.20 - 3.15 (m, 1 H), 2.95 - 2.91 (m, 1 H), 2.73 - 2.69 (m, 1 H), 2.41 (s, 3 H), 2.07 - 2.05 (m, 1 H), 1.79 - 1.74 (m, 1 H), 1.28 - 1.23 (m, 2 H), 1.17 - 1.11 (m, 2 H), 0.80 (t, $J = 6.0$ Hz, 3 H);

¹³C NMR (150 MHz, Chloroform-*d*) δ 151.0, 143.6, 138.2, 136.4, 130.4, 129.7, 128.4, 127.6, 127.3, 127.1, 125.6, 124.2, 117.7, 107.0, 93.5, 84.7, 64.8, 48.0, 47.3, 39.6, 31.9, 21.5, 19.2, 13.8;

HRMS-ESI: Exact mass calcd. for C₂₈H₃₃O₃N₂S [M+H]⁺: 477.2206; Found: 477.2212;

IR (KBr): 3137.42, 1608.94, 1401.44, 1161.39, 1082.63, 741.62, 661.36, 543.48.



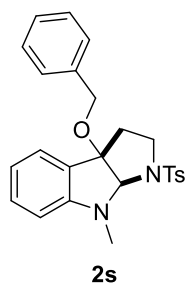
2r yellow liquid, 46.2 mg, 49% yield, 1/1 dr;

For the mixture of the two diastereomers: $^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.75 - 7.73 (m, 2 + 1.14 H), 7.41 - 7.39 (m, 2 + 1.14 H), 7.32 - 7.25 (m, 5 + 2.85 H), 7.16 - 7.08 (m, 2 + 1.14 H), 6.70 - 6.68 (m, 1 + 0.57 H), 6.50 - 6.48 (m, 1 + 0.57 H), 5.47 (s, 0.57 H), 5.45 (s, 1 H), 4.79 - 4.74 (m, 1 + 0.57 H), 4.64 - 4.60 (m, 1 + 0.57 H), 3.63 - 3.60 (m, 1 + 0.57 H), 3.06-3.00 (m, 2 + 1.14 H), 2.43 - 2.42 (m, 3 + 1.71 H), 2.07 - 2.04 (m, 1 + 0.57H), 1.73 - 1.71 (m, 1 + 0.57H), 1.21 - 1.17 (m, 2 + 1.14H), 0.78 - 0.76 (m, 3 + 1.71H), 0.64 -0.59 (m, 3 + 1.71H);

$^{13}\text{C NMR}$ (150 MHz, Chloroform-*d*) δ 151.3, 143.7, 138.4, 138.3, 136.6, 136.5, 130.5, 130.4, 129.8, 129.8, 128.5, 127.7, 127.6, 127.3, 127.3, 127.1, 126.3, 125.0, 117.5, 106.9, 106.8, 93.3, 93.2, 85.5, 85.1, 72.3, 72.0, 47.8, 47.5, 47.0, 46.8, 40.1, 39.8, 30.6, 30.3, 21.5, 20.9, 20.6, 9.6, 9.3;

HRMS-ESI: Exact mass calcd. for $\text{C}_{28}\text{H}_{33}\text{O}_3\text{N}_2\text{S}$ $[\text{M}+\text{H}]^+$: 477.2206; Found: 477.2205;

IR (KBr): 2942.90, 2359.04, 1653.84, 1595.22, 1452.17, 1344.10, 1224.03, 1201.37, 1156.61, 1091.72, 1024.58, 811.49, 764.92, 744.10, 704.67, 679.44, 656.88, 582.38.



2s Yellow solid, 29.4 mg, 34% yield, 14/1 dr;

For the mixture of the two diastereomers: $^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.76 (d, $J = 8.0$ Hz, 2 H), 7.73 (s, 0.07 H), 7.37 (s, 0.07 H), 7.33 - 7.22 (m, 6 + 0.56 H), 7.20 (d, $J = 2.0$ Hz, 0.07 H), 7.15 - 7.09 (m, 3 + 0.07 H), 6.73 (t, $J = 7.4$ Hz, 1 H), 6.50 (d, $J = 8.0$ Hz, 0.07 H), 6.37 (d, $J = 8.4$ Hz, 1 H), 5.38 (s, 1 H), 5.36 (s, 0.07 H), 4.18

– 4.14 (m, 1 + 0.07 H), 4.06 - 4.04 (m, 1 + 0.07 H), 3.64 - 3.60 (m, 1 + 0.07 H), 3.16 - 3.11 (m, 1 + 0.07 H), 3.02 (s, 3 H), 2.99 (s, 0.21 H), 2.40 (s, 3 + 0.21 H), 2.14 - 2.10 (m, 1 + 0.07 H), 1.90 - 1.85 (m, 1 + 0.07 H);

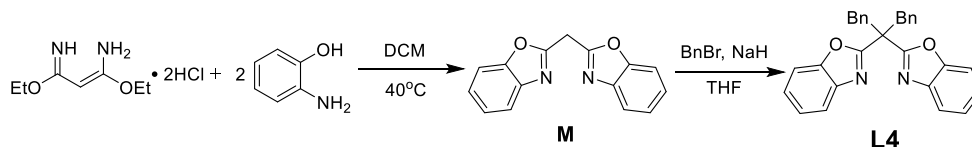
¹³C NMR (150 MHz, Chloroform-*d*) δ 151.9, 143.7, 137.9, 136.2, 130.8, 129.8, 128.2, 127.62, 127.5, 127.3, 125.2, 124.0, 117.8, 108.1, 106.7, 93.8, 93.4, 86.3, 86.3, 67.6, 67.4, 47.5, 39.2, 31.2, 21.5;

HRMS-ESI: Exact mass calcd. for C₂₅H₂₆O₃N₂NaS [M+Na⁺]: 457.1556; Found: 457.1548;

IR(KBr): 2890.77, 2358.52, 1608.79, 1481.94, 1349.52, 1166.11, 1045.23, 1029.40, 1012.45, 983.52, 943.02, 844.94, 813.85, 755.47, 697.62, 661.00, 627.00, 594.40, 573.09, 546.75, 466.69.

5. Ligand and substrate preparation

5.1 Synthesis of the parent ligand L4



2-Aminophenol (5.6 g, 50.0 mmol, 2.5 eq.) and ethylbisimidate dihydrochloride (4.62 g, 20 mmol, 1.0 eq.) were dissolved in DCM (50 mL). Then the reaction mixture was heated to 40°C over night, after cooling to rt, stirred at -32 °C in a fridge. The resulting crystalline material was filtered off, washed subsequently with saturated aq. NaHCO₃ solution (2 × 50 mL). Then extracted with CH₂Cl₂ (3 × 20 mL), dried over anhydrous NaSO₄ and concentrated under reduced pressure to afford **M**.

The crude of **M** (1.0 g, 4.0 mmol, 1 eq.) was dissolved in THF (50 mL). NaH (0.64 g, 16.0 mmol, 4 eq.) was added in portions at 0 °C and stirred for 15 min. Then a solution of Benzyl bromide (2.74 g, 16.0 mmol, 4 eq.) was added dropwise at 0 °C. The reaction mixture was then allowed to warm up to room temperature and monitored by TLC. Upon completion, the reaction mixture was quenched with H₂O, extracted with ethyl acetate (3 × 20 mL), dried over anhydrous NaSO₄ and concentrated under reduced pressure. The crude material was purified by chromatography on silica gel (ethyl acetate /Petroleum ether 10/1 v/v) to afford **L4**.

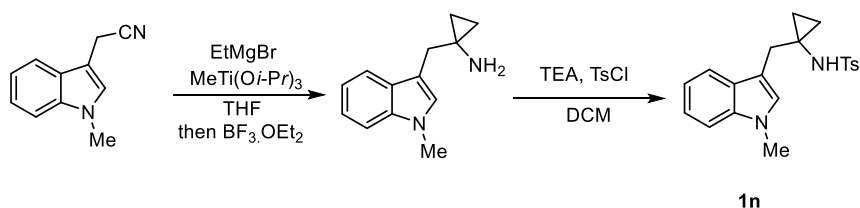
¹H NMR (600 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 12.0 Hz, 2 H), 7.46 (d, *J* = 6.0 Hz, 2 H), 7.40 -7.36 (m, 4 H), 7.16 (t, *J* = 6.0 Hz, 2 H), 7.10 (t, *J* = 6.0 Hz, 4 H), 6.88 (d, *J* = 12.0 Hz, 4 H), 3.91 (s, 4 H);

¹³C NMR (150 MHz, Chloroform-*d*) δ 165.5, 150.6, 140.7, 135.5, 130.0, 128.2, 127.0, 125.3, 124.5, 120.3, 110.8, 50.5, 41.7;

HRMS-ESI: Exact mass calcd. for C₂₉H₂₃O₂N₂ [M+H]⁺: 431.1754; Found: 431.1749;

IR (KBr): 2919.70, 1354.79, 1166.75, 1083.65, 1058.73, 995.09, 912.07, 865.88, 726.73, 659.13, 597.82, 549.61.

5.2 Preparation of cyclopropyl substituted tryptamines



To a solution of nitrile (508.0 mg, 2.95 mmol) and $\text{MeTi}(\text{O}i\text{-Pr})_3$ (1.33 mL, 1.5 eq.) in THF (30 mL) was dropwise added under argon EtMgBr (ca 2M in Et₂O, 1.5 eq.). The yellow solution darkened gradually within 5 minutes. After stirring for 1.5 h, $\text{BF}_3 \cdot \text{OEt}_2$ was added (750 μL , 2.0 eq.). After 30 min, the dark mixture was quenched with HCl 1 M (10 mL). EtOAc (20 mL) was added, followed by NaOH 3M (10 mL). The mixture was stirred until the blue aqueous solution becomes white. The aqueous phase was extracted twice with ethyl acetate. After drying by NaSO_4 and evaporation of the solvents, the crude material was purified by flash-chromatography ethyl acetate.

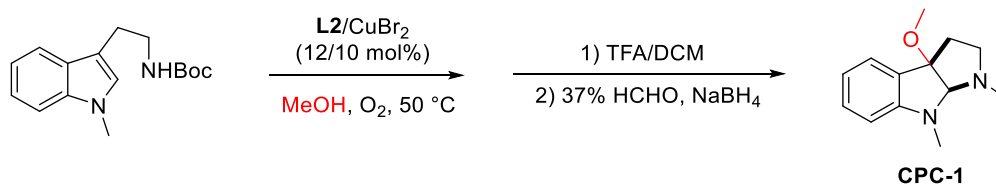
¹H NMR (600 MHz, Chloroform-*d*) δ 7.76 (d, $J = 6.0$ Hz, 2 H), 7.46 (d, $J = 6.0$ Hz, 1 H), 7.33-7.29 (m, 1 H), 7.25 (t, $J = 6.0$ Hz, 1 H), 7.12 (t, $J = 6.0$ Hz, 1 H), 6.87 (s, 1 H), 3.78 (s, 3 H), 2.86 (s, 2 H), 2.46 (s, 3 H), 0.90 (t, $J = 6.0$ Hz, 2 H), 0.75 (t, $J = 6.0$ Hz, 2 H);

¹³C NMR (150 MHz, Chloroform-*d*) δ 143.3, 139.3, 137.0, 129.6, 128.0, 127.2, 121.6, 119.3, 118.9, 110.2, 109.2, 35.8, 32.8, 32.7, 21.5, 13.0;

HRMS-ESI: Exact mass calcd. for $\text{C}_{20}\text{H}_{23}\text{O}_2\text{N}_2\text{S}$ $[\text{M}+\text{H}]^+$: 355.1475; Found: 355.1466;

IR (KBr): 3137.56, 1654.50, 1401.77, 1151.60, 813.44, 731.90, 664.52, 555.15.

6. Synthesis of CPC-1 and Product Characterizations



A mixture of CuBr_2 (4.46 mg, 0.02 mmol), **L2** (6.68 mg, 0.024 mmol), and **1s** (54.9 mg, 0.2 mmol) were added in a dried Schlenk tube before oxygen replacement operation, then MeOH (2 ml) was added under O_2 atmosphere, and the reaction system was stirred at 50 °C for 36 h. After completion as detected by TLC, the reaction was filtered through a glass funnel with thin layer (30 mm) of silica gel (300-400 mesh) and eluted with DCM/Ethyl Acetate. The filtrate was concentrated under reduced pressure, purified by flash chromatography (Petroleum ether/ethyl acetate = 10/1) to afford cycloadduct intermediate as white solid (44.4 mg, 73% yield).

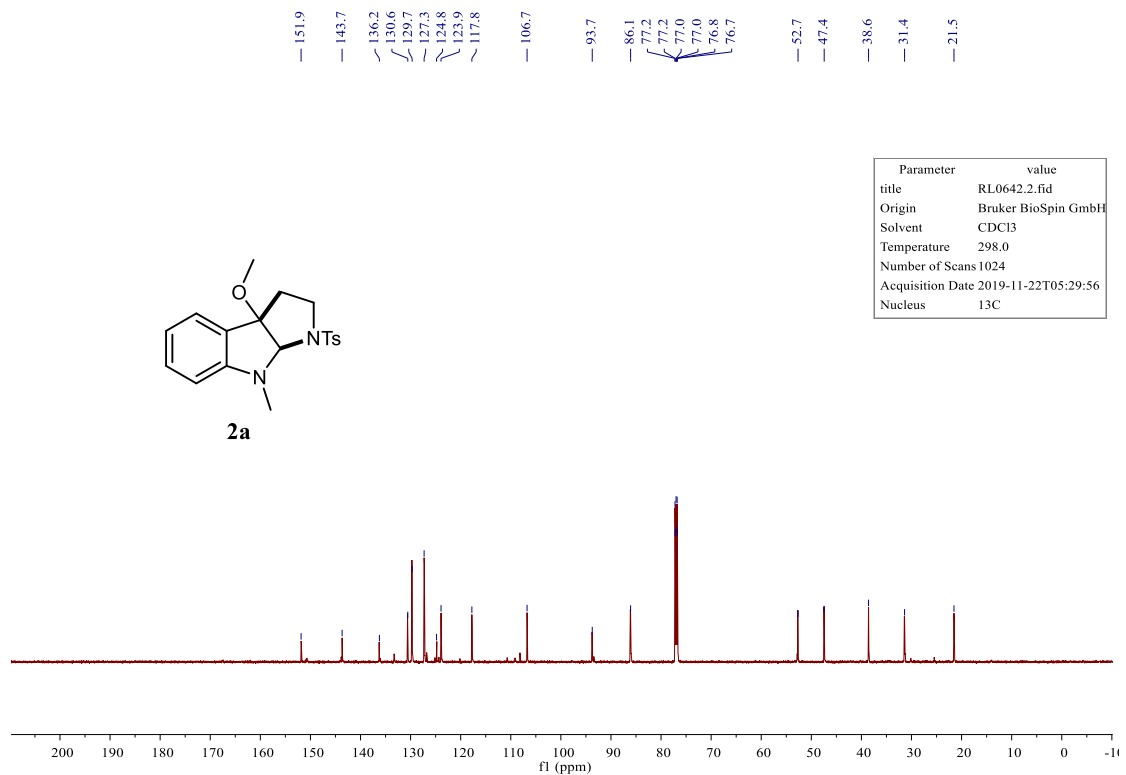
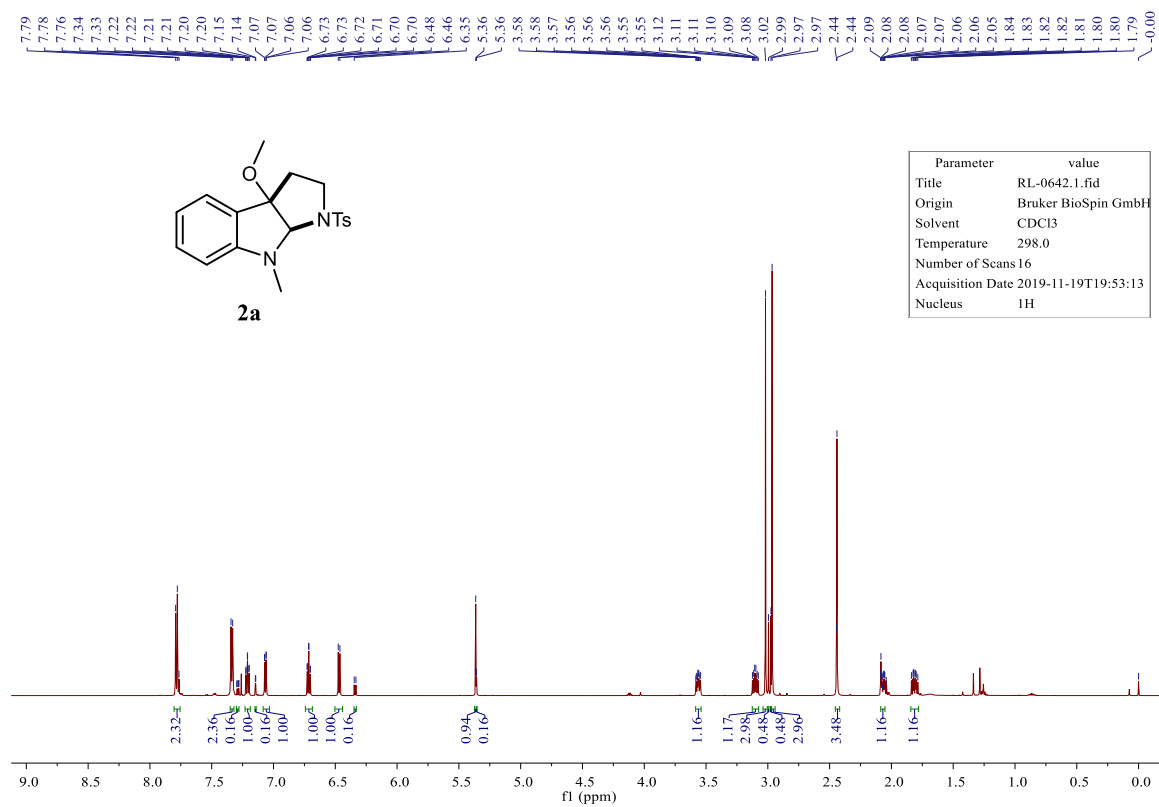
Chargecycloadduct intermediate (60.1 mg, 0.2 mmol) dissolved in anhydrous CH_2Cl_2 (2.5 mL) after raw material accumulation, TFA (2.5 mL) was added before stirred at room temperature for 4.5 hours. The mixture was concentrated under reduced pressure without further purified. The crude residue was dissolved in anhydrous MeOH after dried, and Formalin (26.0 mg, 0.32 mmol) were added under argon atmosphere, then sodium borohydride (22.7 mg, 0.6 mmol) were added before reaction mixture was stirred for 10 minutes at room temperature. After 30 min, the reaction mixture was quenched with H_2O (50 mL), extracted with EtOAc. The organic layers were combined and dried over Na_2SO_4 , filtered, concentrated in vacuum. The residue was purified by chromatography on silica gel ($\text{CH}_2\text{Cl}_2/\text{MeOH}$, 20:1) to afford (\pm)-CPC-1 as an oil (32.2 mg, 74% yield).

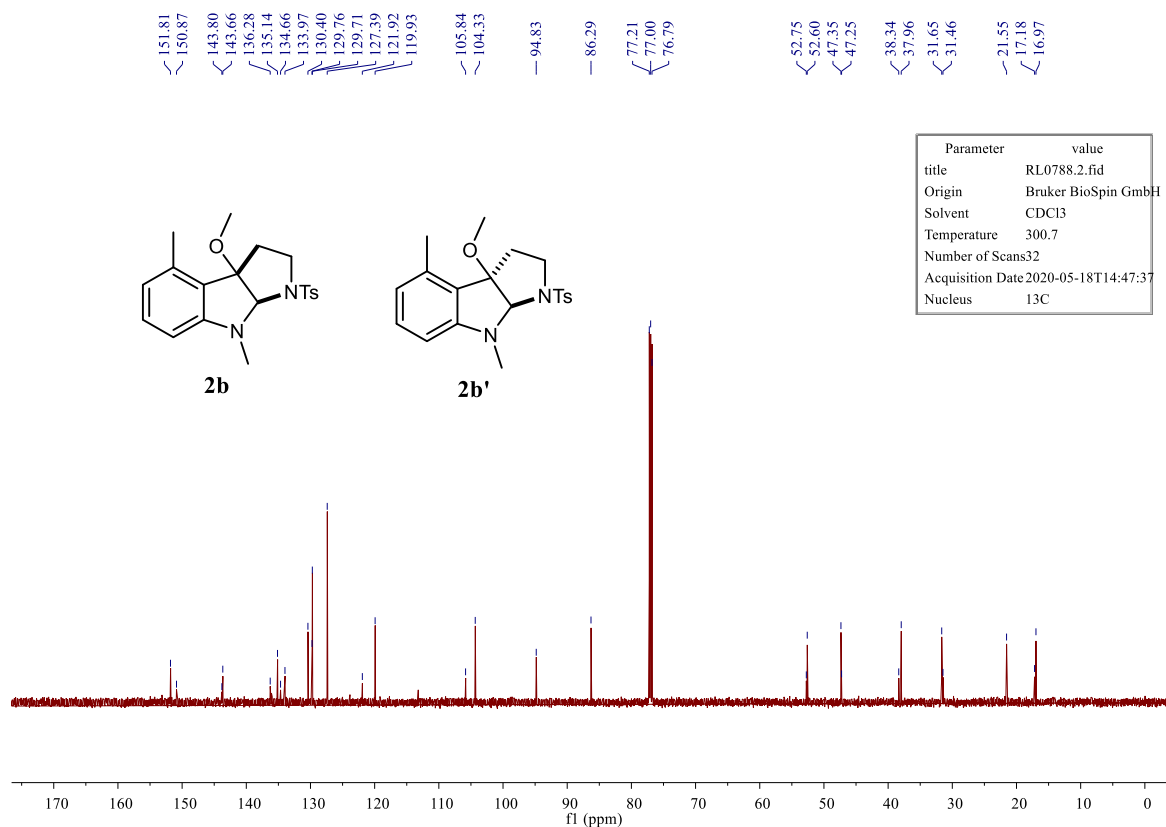
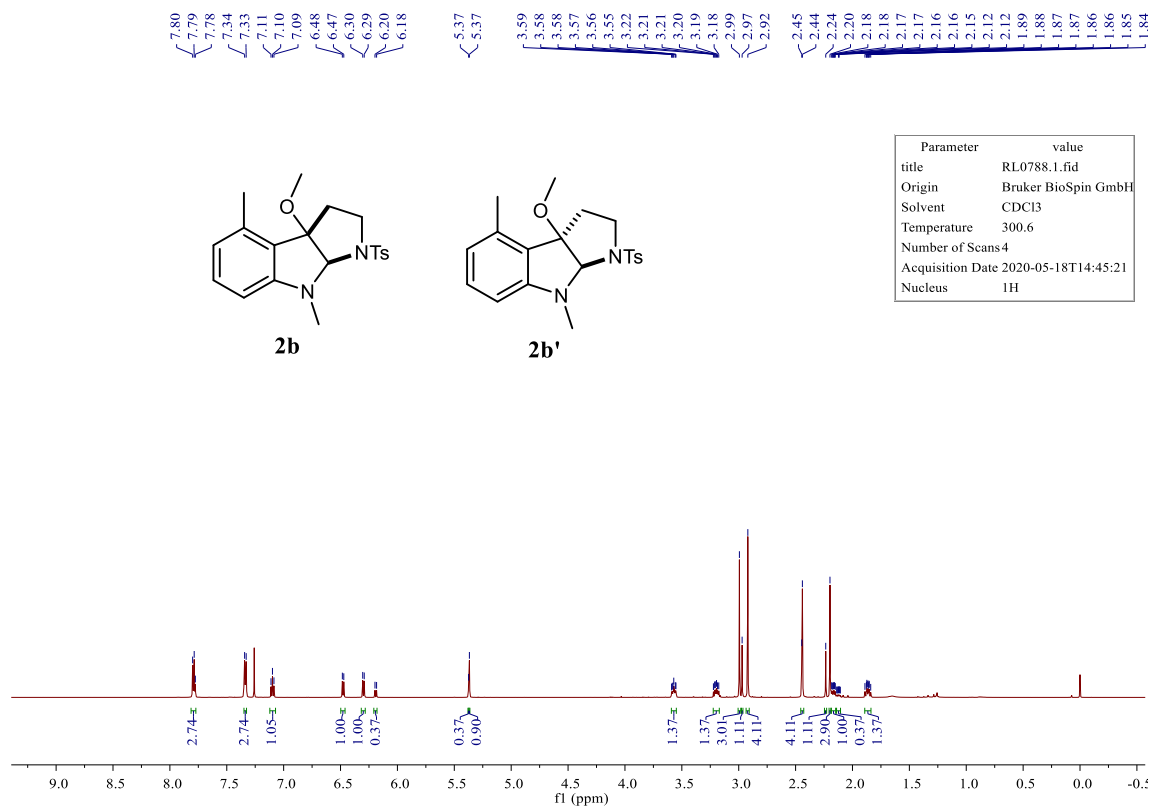
(\pm)-CPC-1: $^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.27 - 7.26 (m, 0.26 H), 7.23 (d, $J = 2.4$ Hz, 0.13 H), 7.21 - 7.18 (m, 1 H), 7.15 (d, $J = 6.0$ Hz, 1 H), 6.74 (t, $J = 6.0$ Hz, 1 H), 6.50 (d, $J = 6.0$ Hz, 1 H), 6.35 (d, $J = 12.0$ Hz, 0.13 H), 4.36 (s, 1 H), 3.05 (s, 0.39 H), 3.04 (s, 3 H), 2.94 (s, 0.39 H), 2.97 (s, 3 H), 2.81 - 2.78 (m, 1 + 0.13 H), 2.64 - 2.61 (m, 1 + 0.13 H), 2.57 - 2.56 (m, 3 + 0.39 H), 2.37 - 2.33 (m, 1 + 0.13 H), 2.15 -

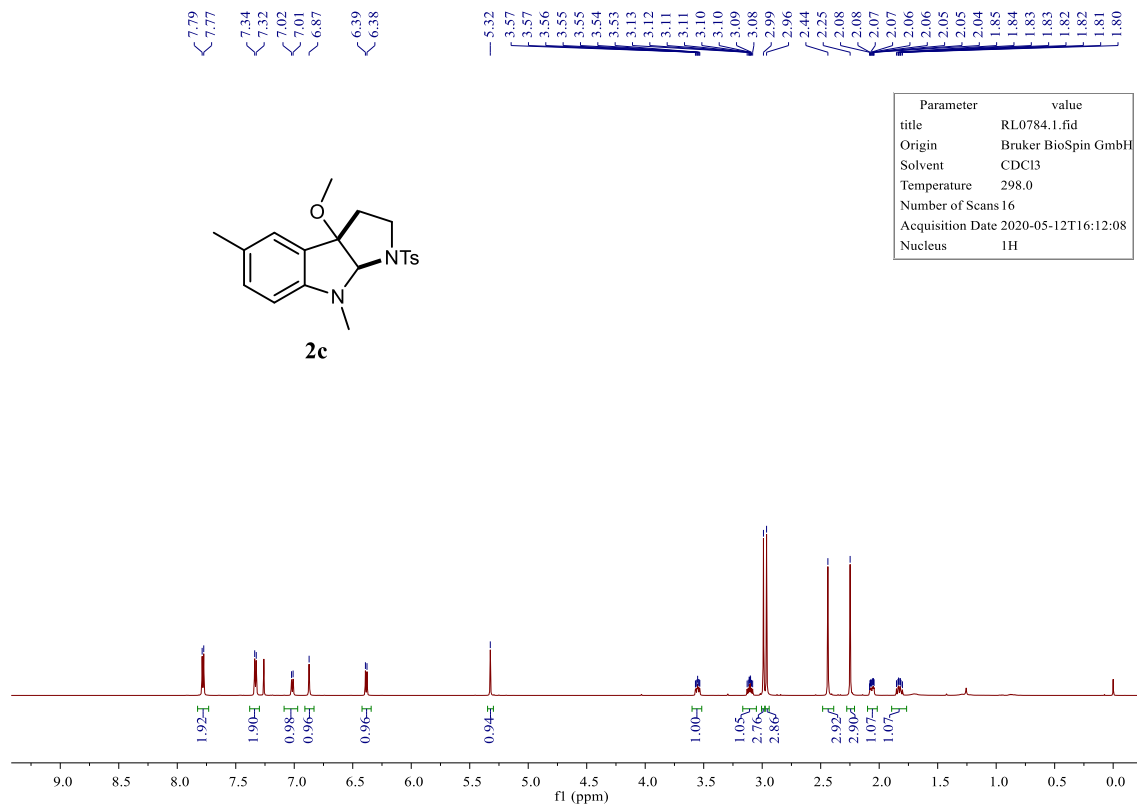
2.11 (m, 1 + 0.13 H).

¹³C NMR (150 MHz, Chloroform-*d*) δ 153.1, 129.7, 128.0, 124.1, 117.9, 107.8, 94.0, 91.7, 52.5, 39.3, 38.6, 36.3. All spectral data were in agreement with the literature (*Org. Biomol. Chem.* 2020, **18**, 32-35).

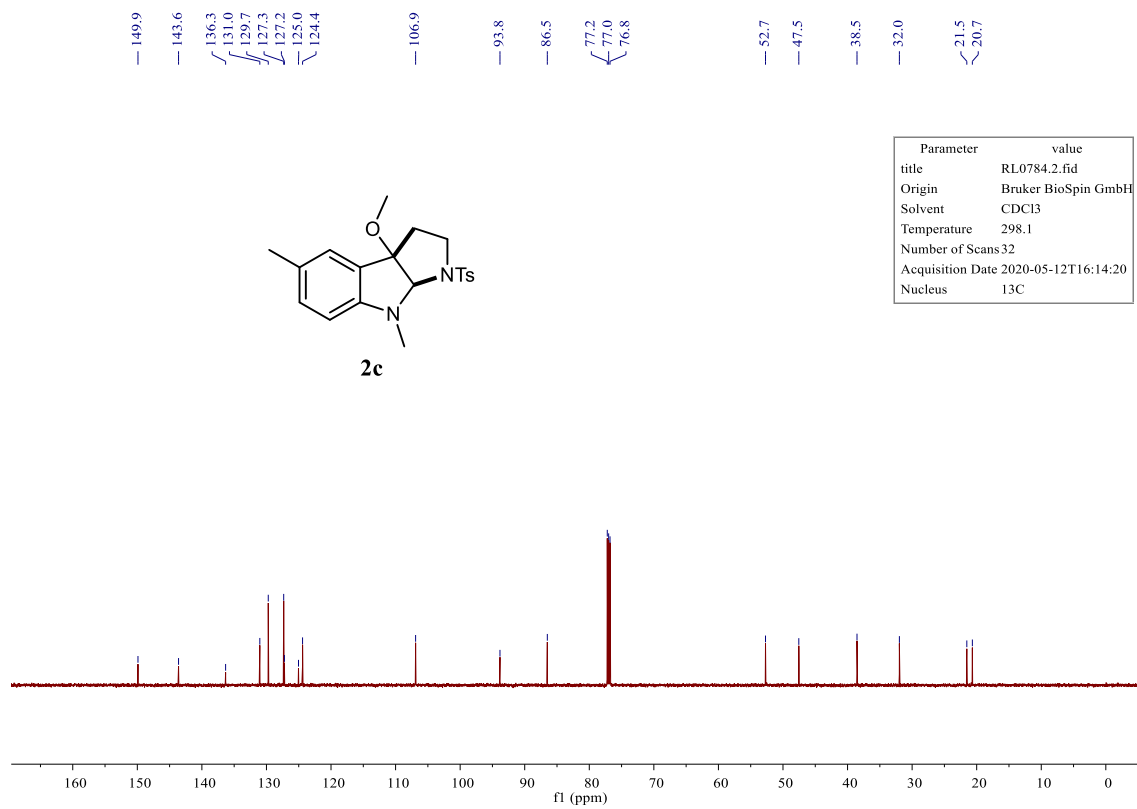
7. ^1H NMR and ^{13}C NMR Spectra of compounds



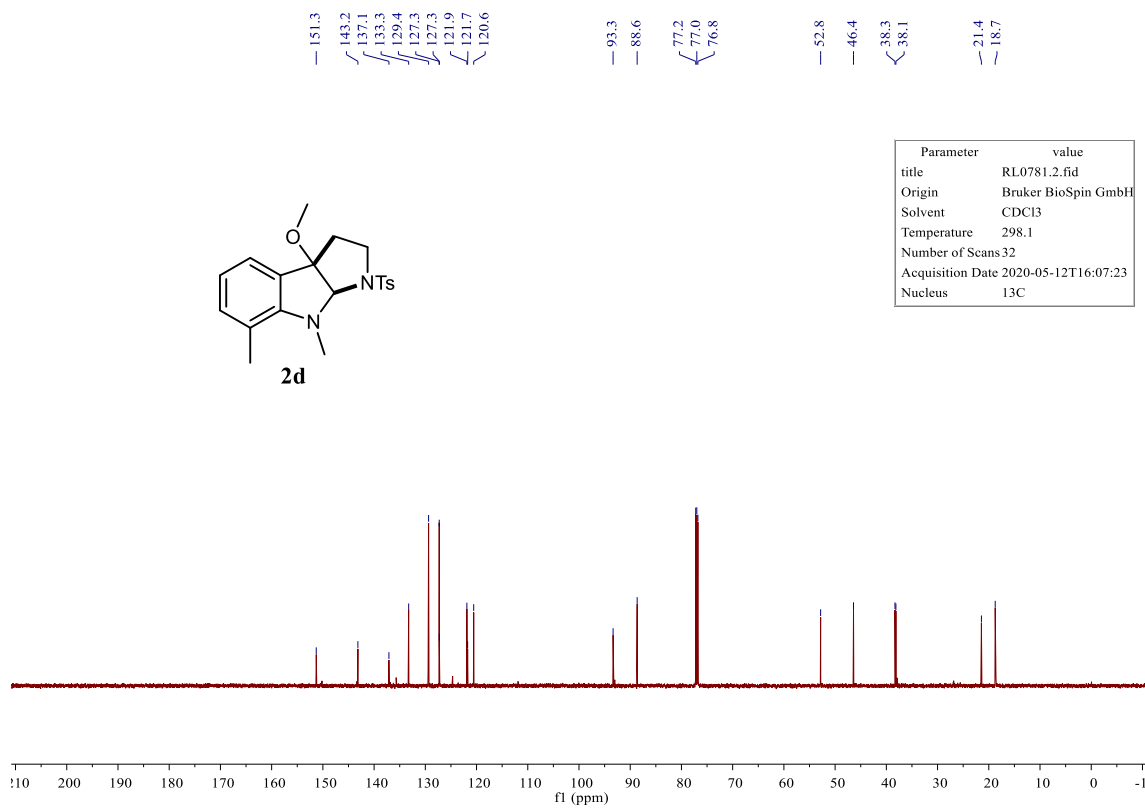
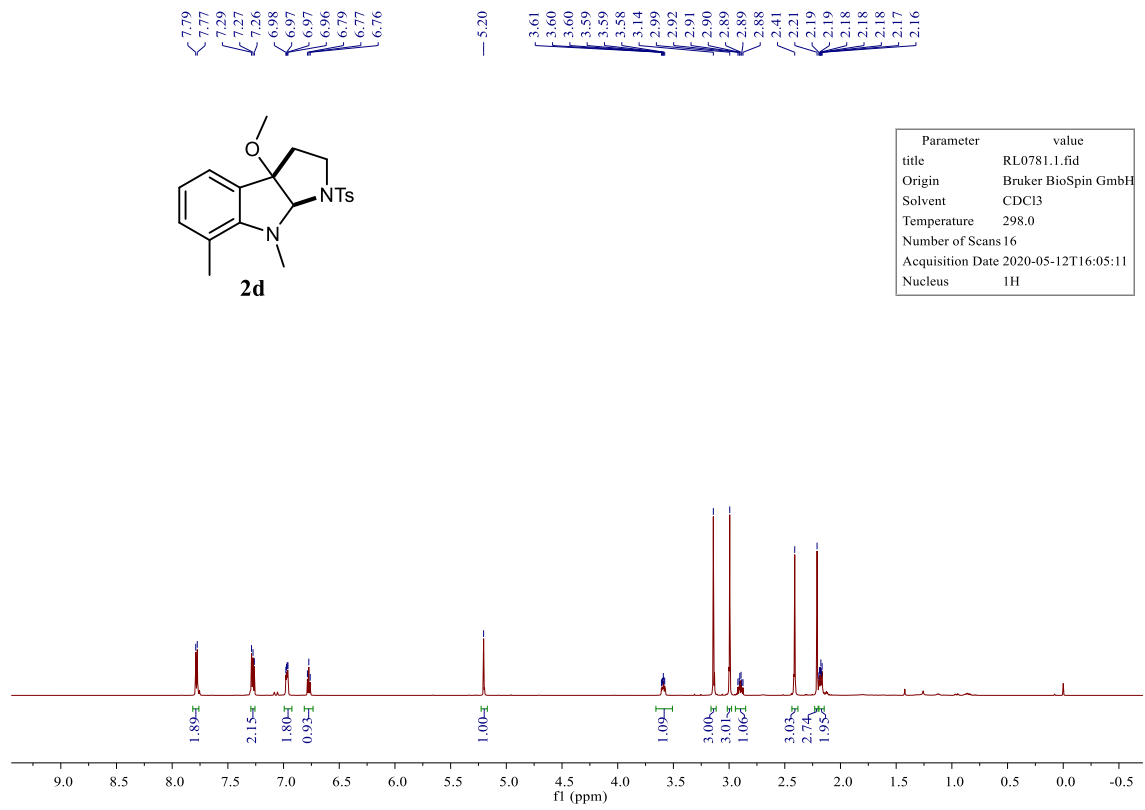


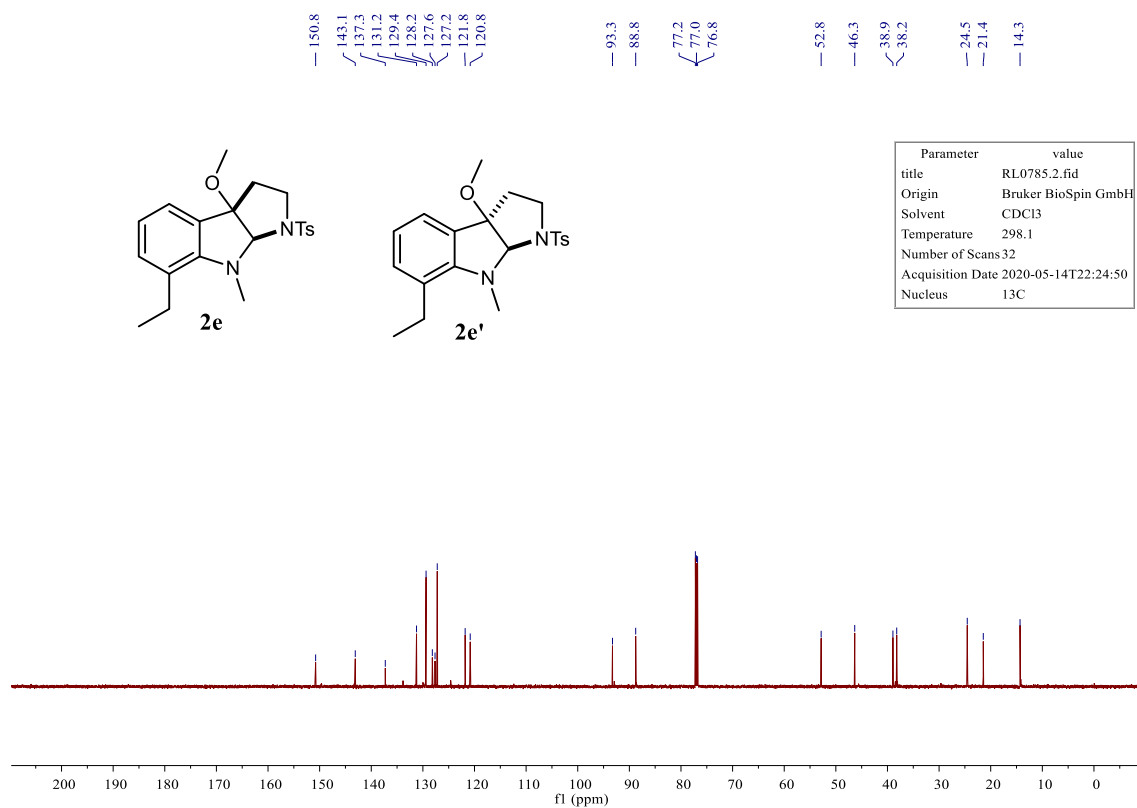
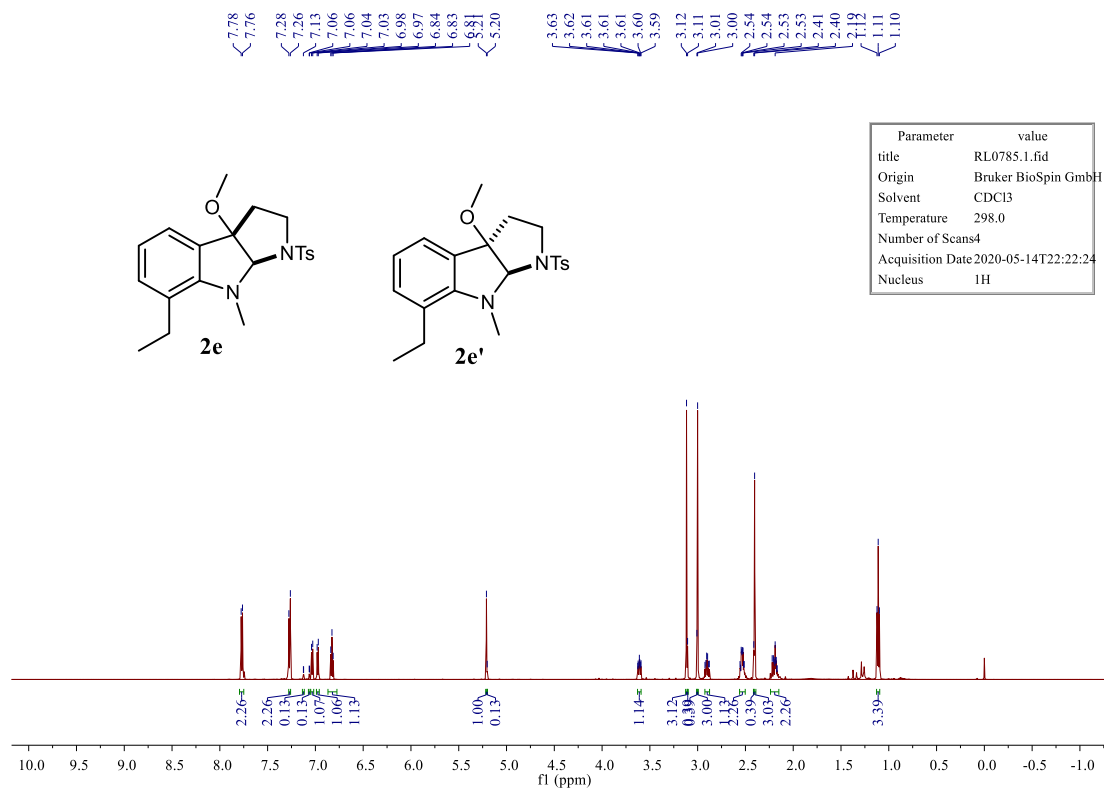


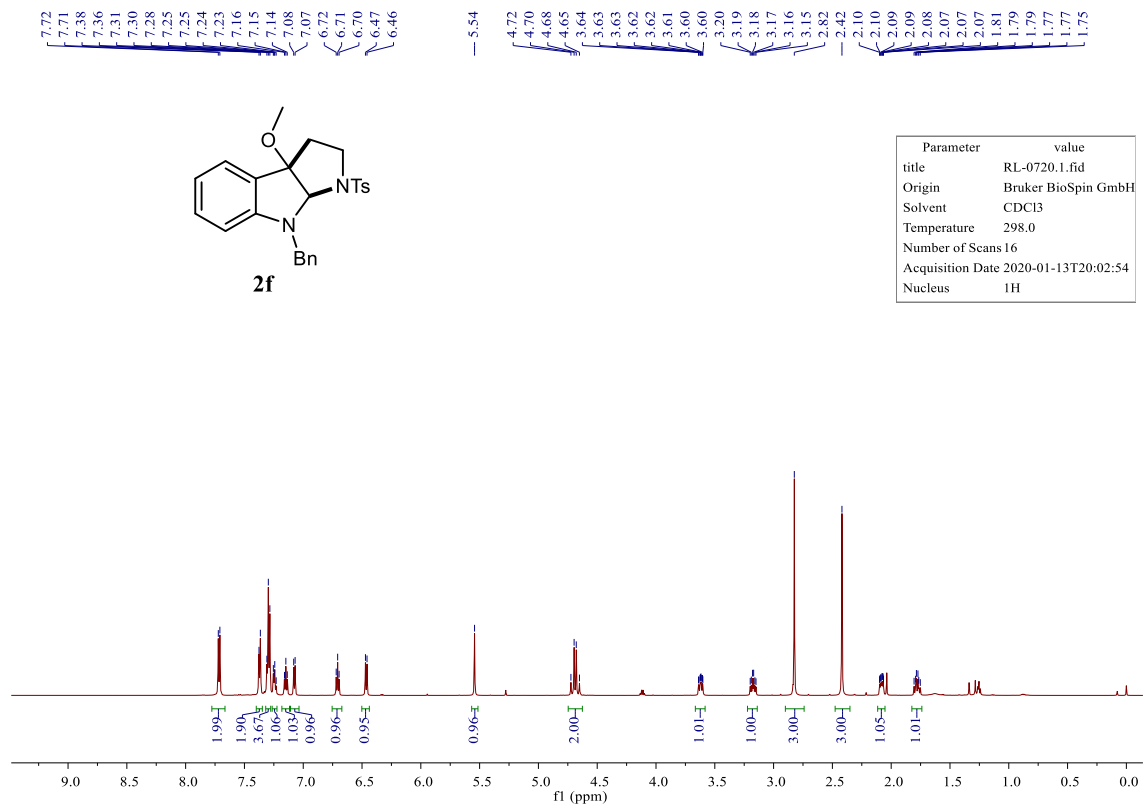
Parameter	value
title	RL0784.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	16
Acquisition Date	2020-05-12T16:12:08
Nucleus	1H

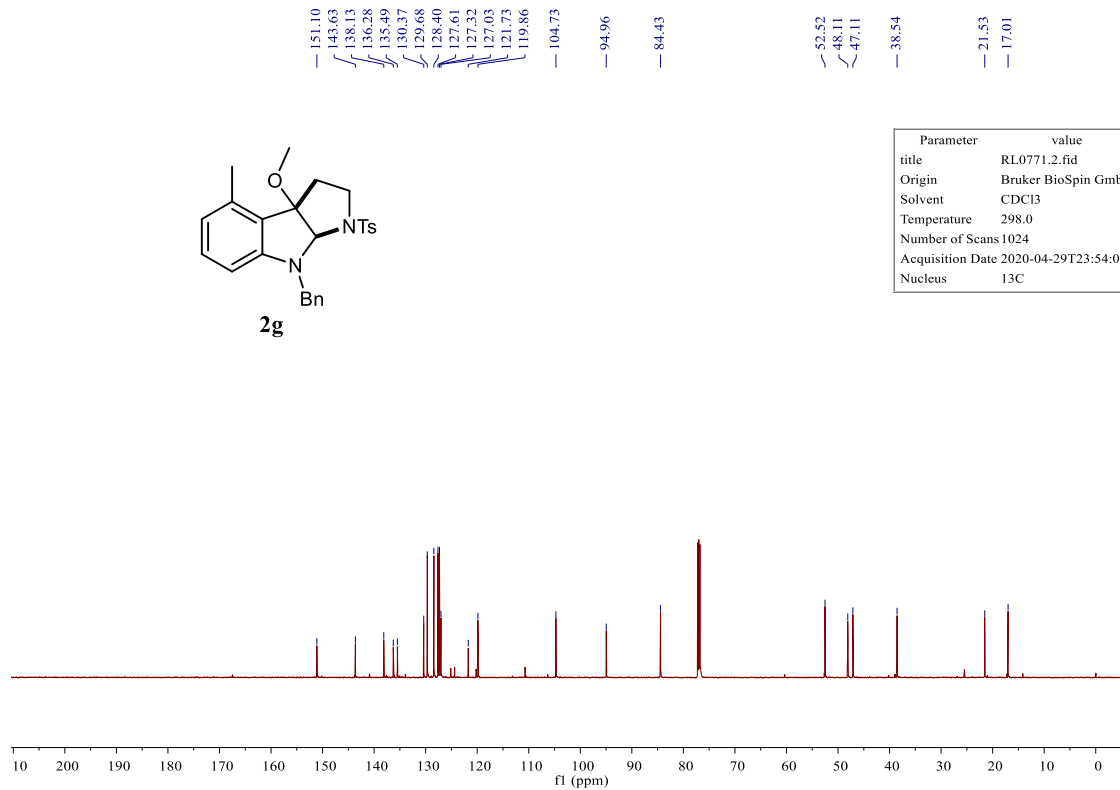
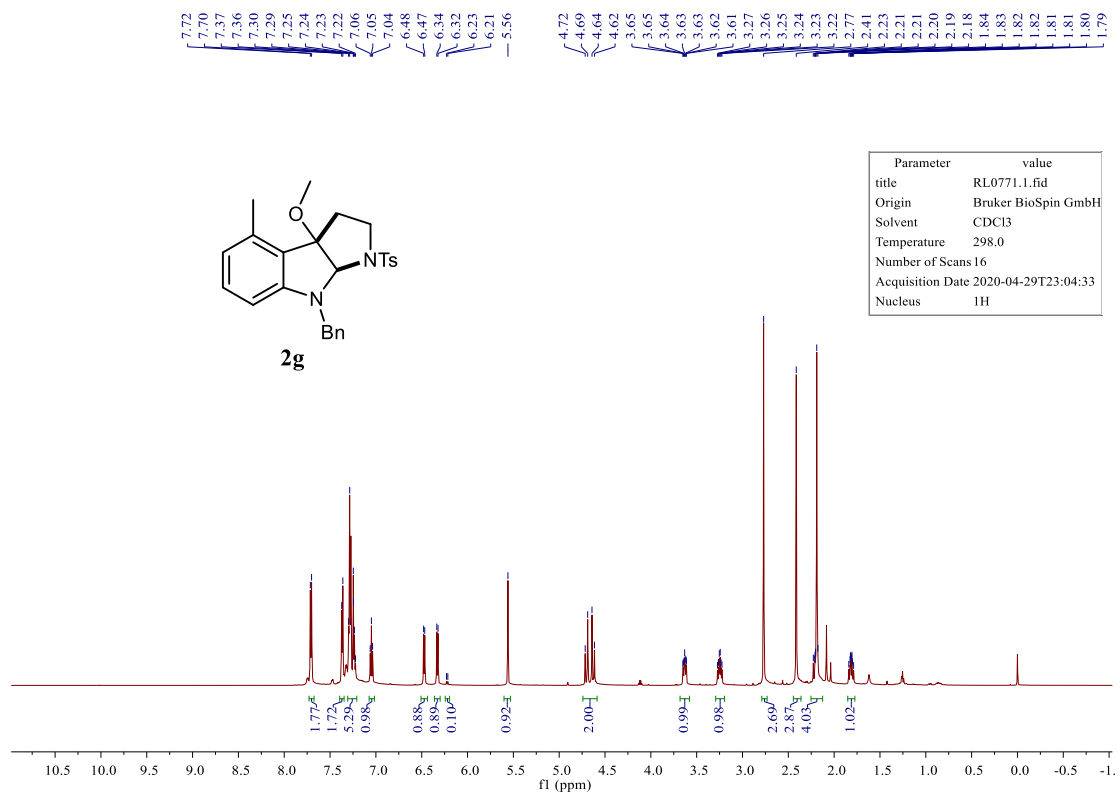


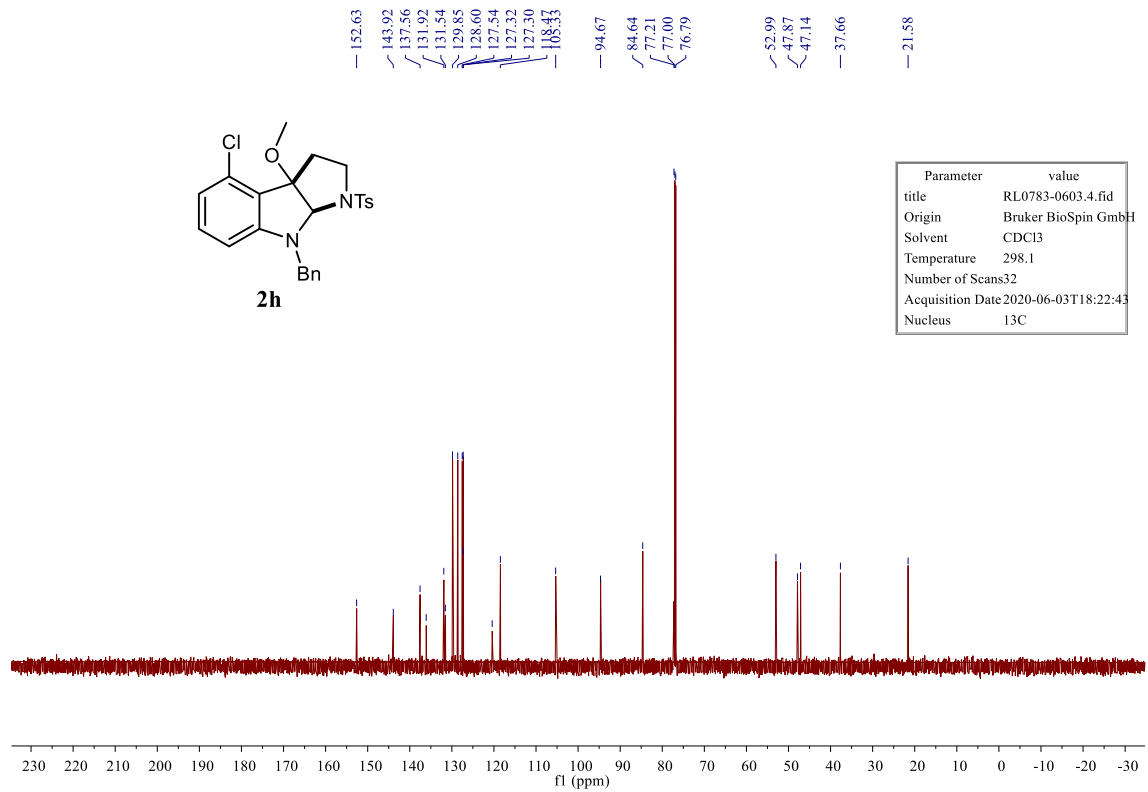
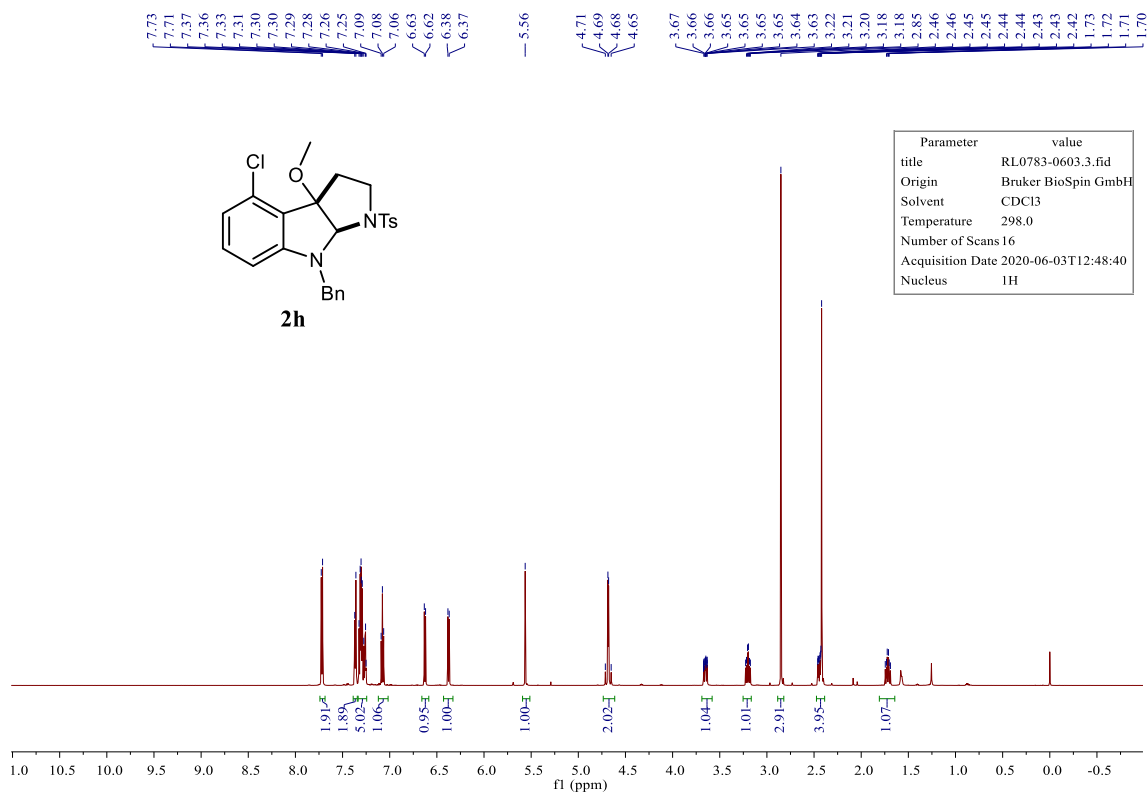
Parameter	value
title	RL0784.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.1
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Acquisition Date	2020-05-12T16:14:20
Nucleus	13C



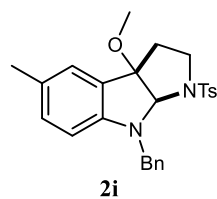




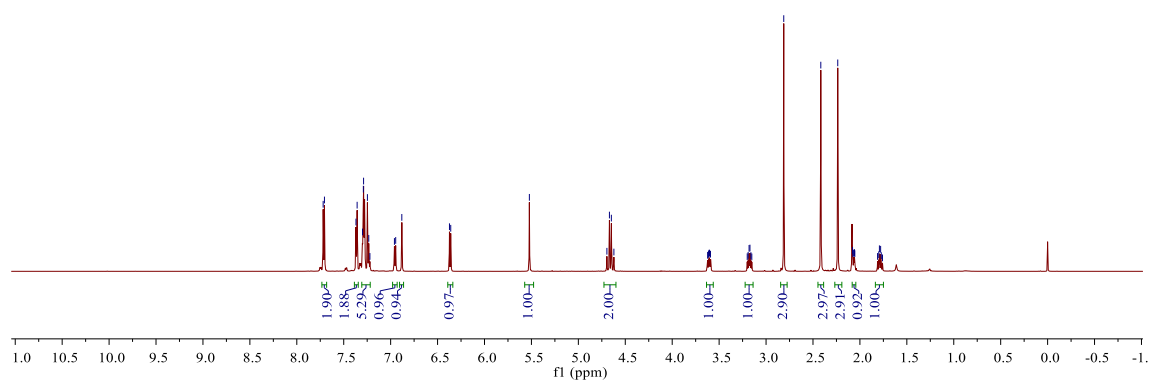




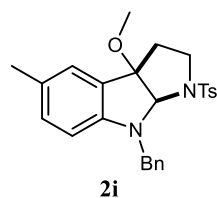
7.72, 7.71, 7.37, 7.36, 7.30, 7.29, 7.29, 7.25, 7.23, 7.22, 6.96, 6.88, 6.37, 6.36, — 5.52, 4.70, 4.67, 4.65, 4.62, 3.62, 3.61, 3.61, 3.60, 3.59, 3.20, 3.19, 3.18, 3.17, 3.16, 3.15, 2.81, 2.42, 2.24, 2.08, 2.07, 2.07, 2.06, 2.05, 1.81, 1.80, 1.79, 1.78, 1.77, 1.76



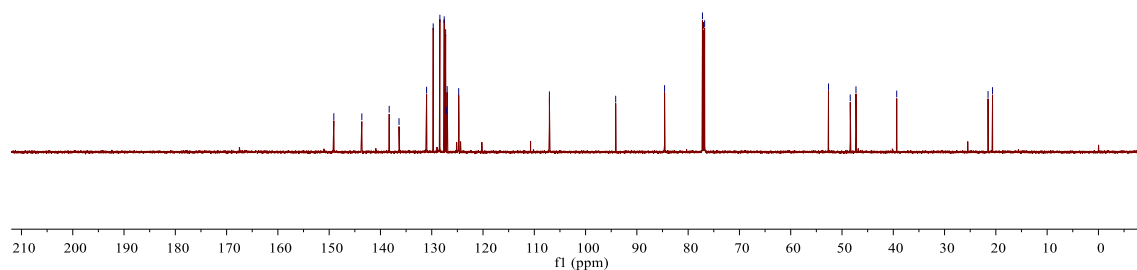
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Solvent	CDC13
Temperature	298.0
Number of Scans	16
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Nucleus	¹ H

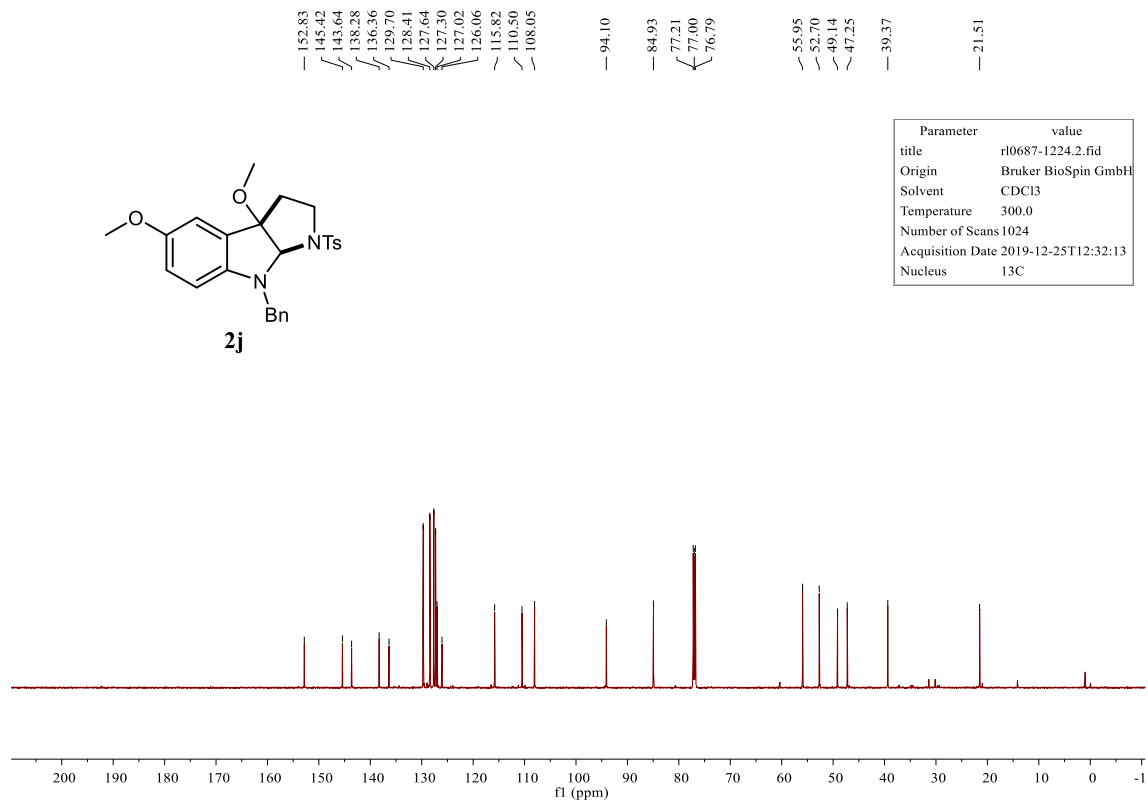
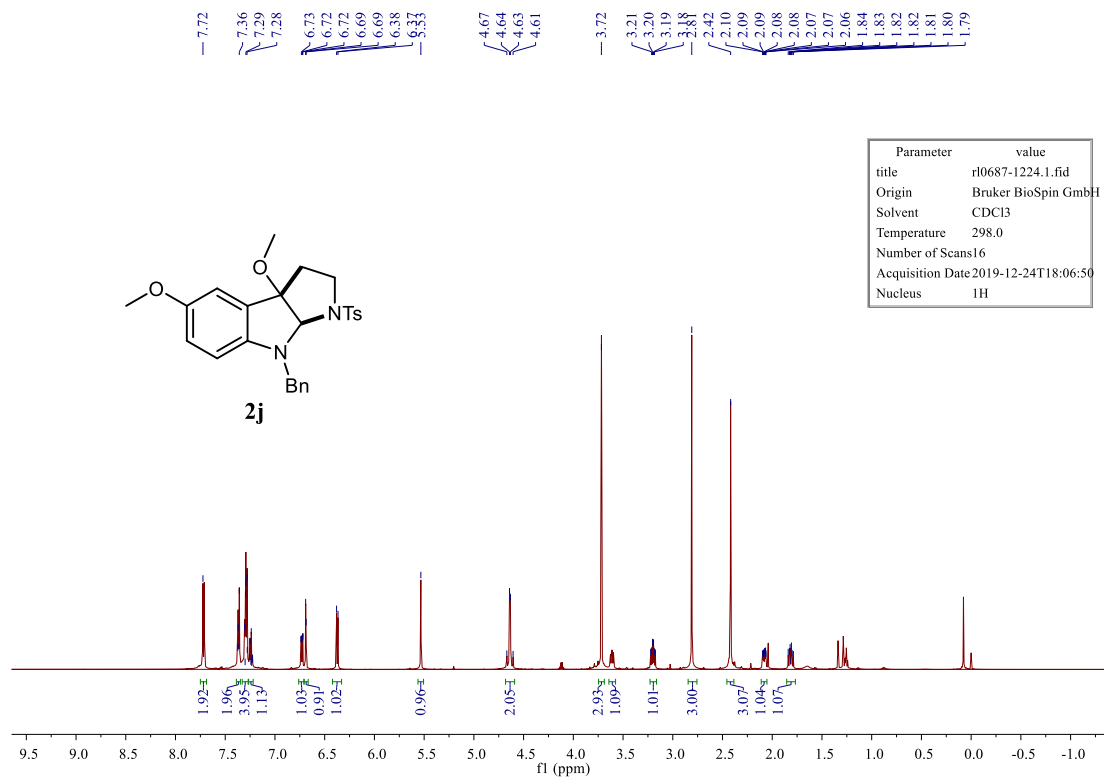


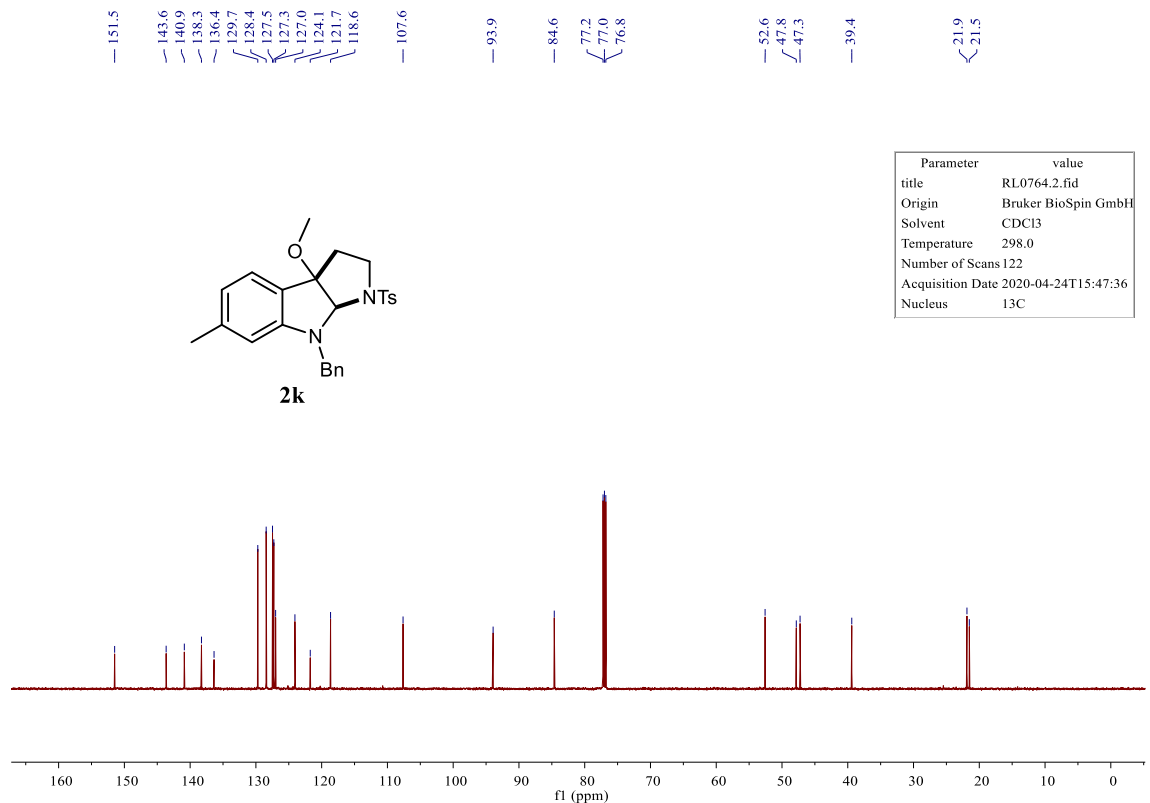
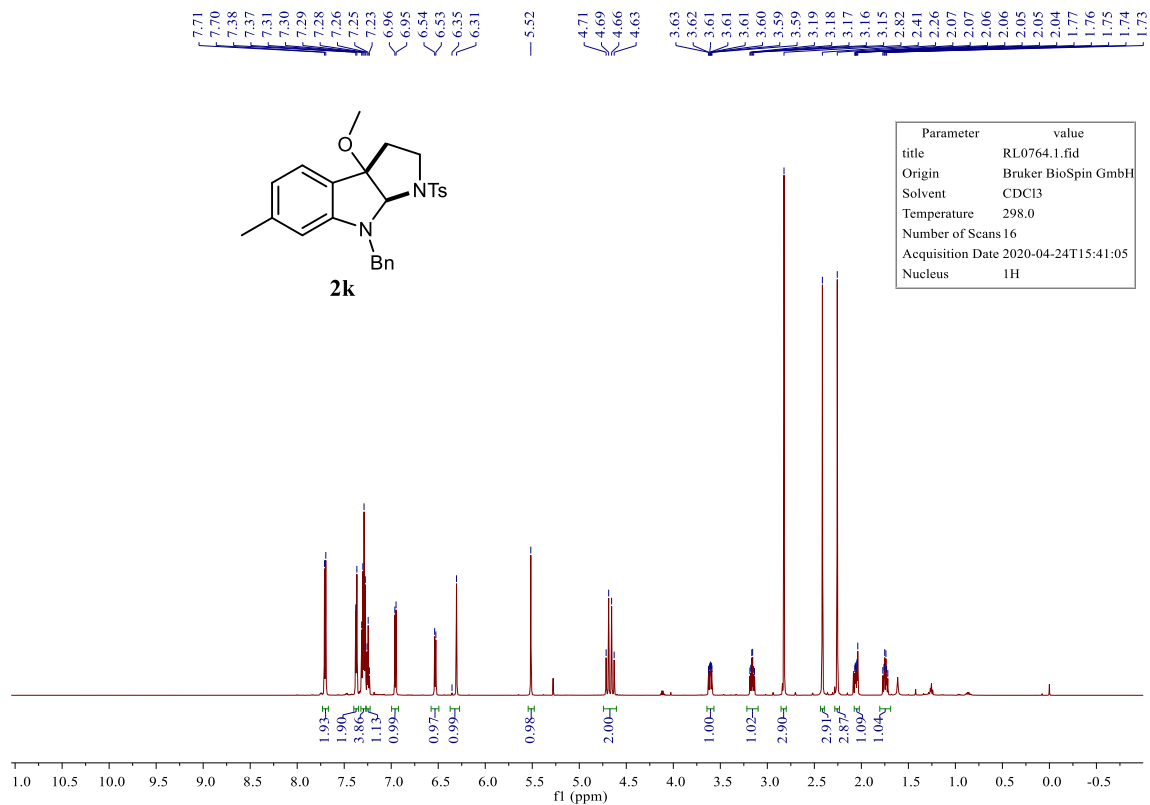
149.09, 143.63, 138.30, 136.38, 131.00, 129.71, 128.41, 127.57, 127.29, 127.15, 126.99, 124.74, — 107.06, — 94.13, — 84.60, 77.21, 77.00, 76.79, — 52.64, — 48.39, — 47.27, — 39.33, — 21.52, — 20.65

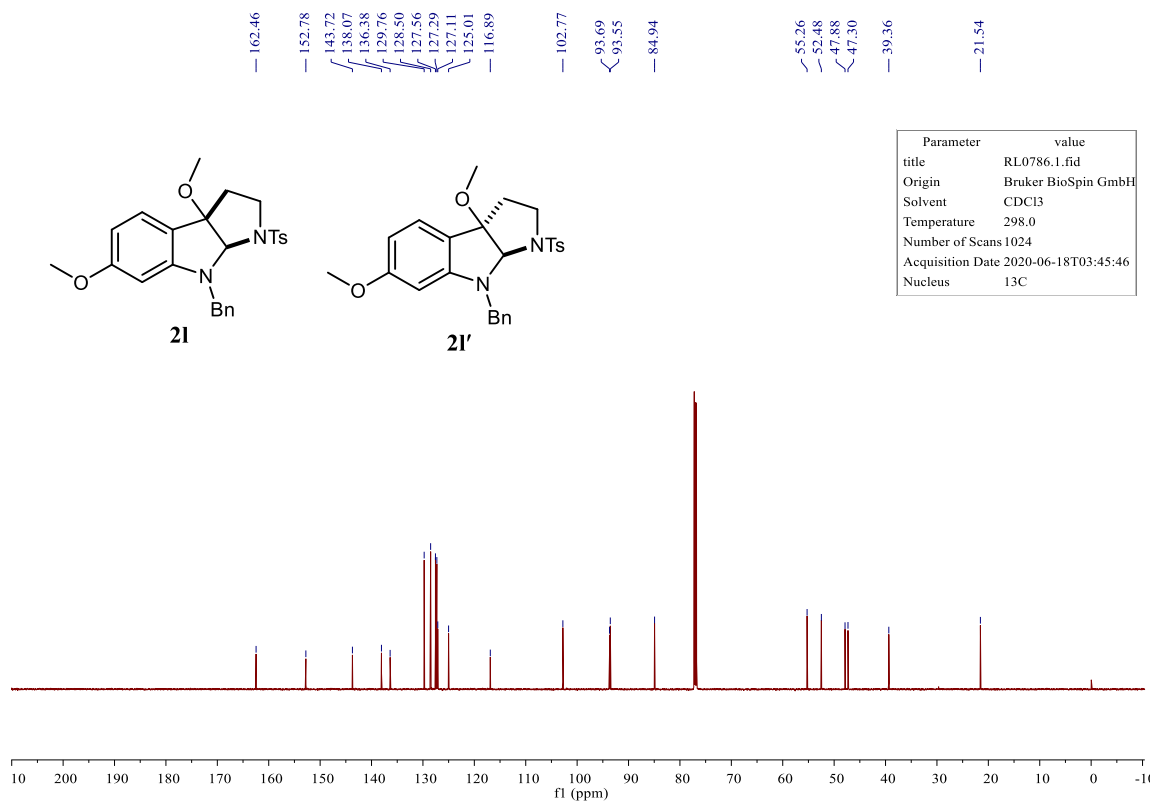
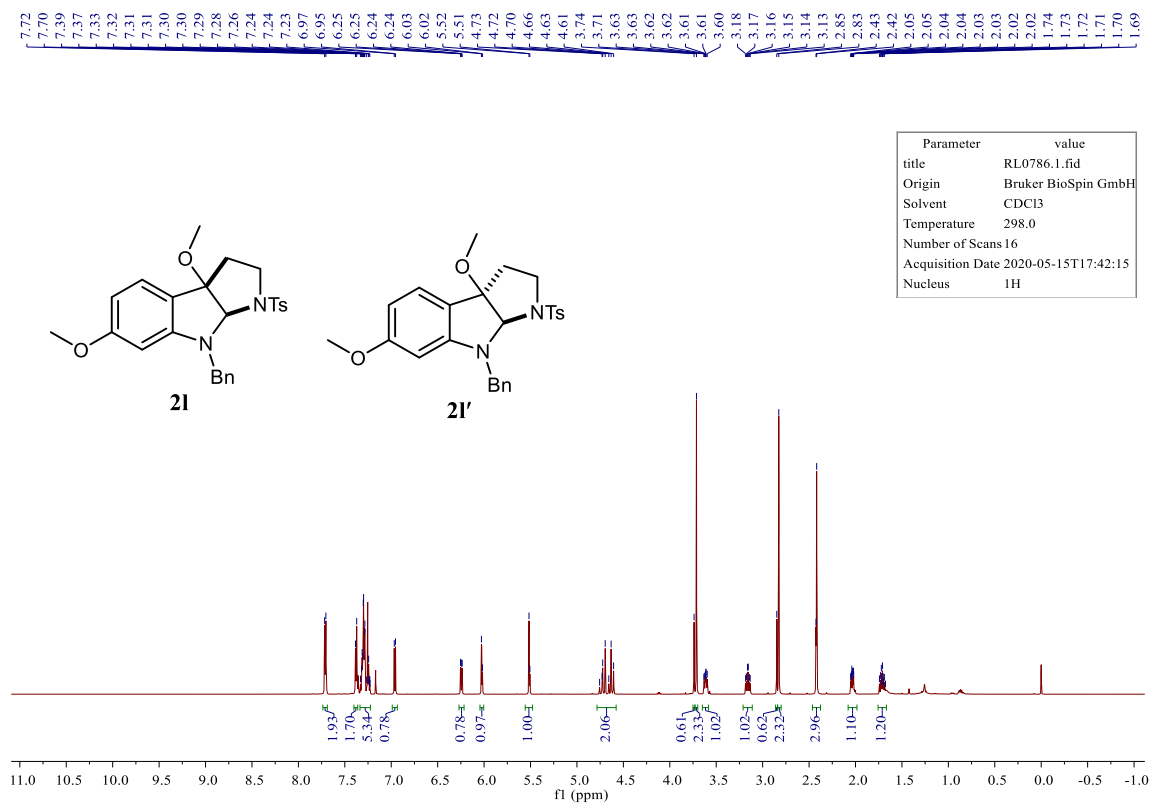


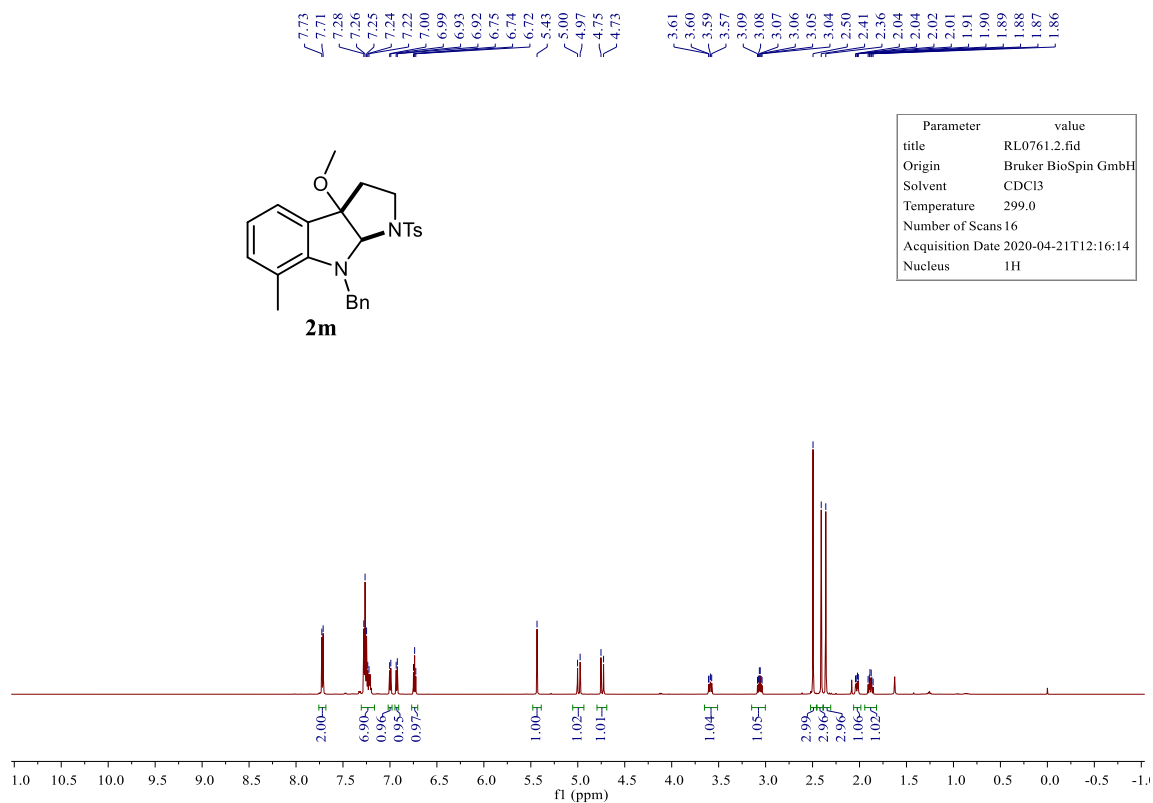
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title	RL-0773-20200509.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDC13
Temperature	298.0
Number of Scans	100
Acquisition Date	2020-05-08T18:05:12
Nucleus	¹³ C



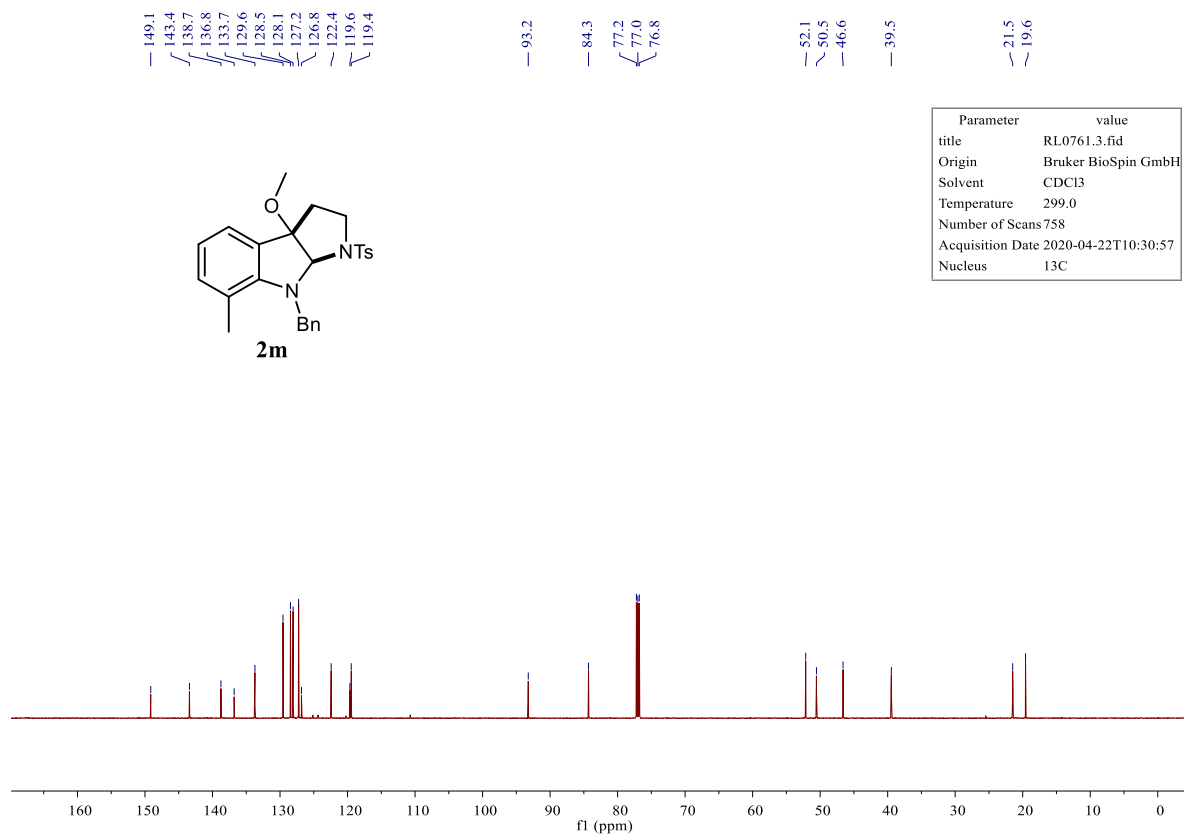




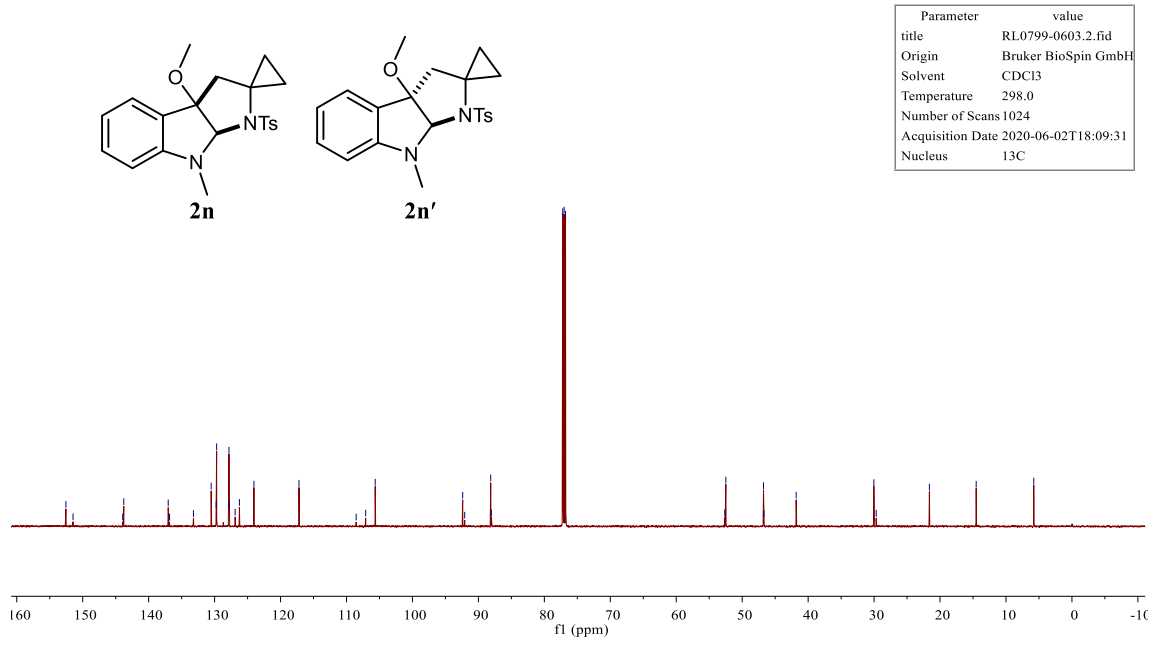
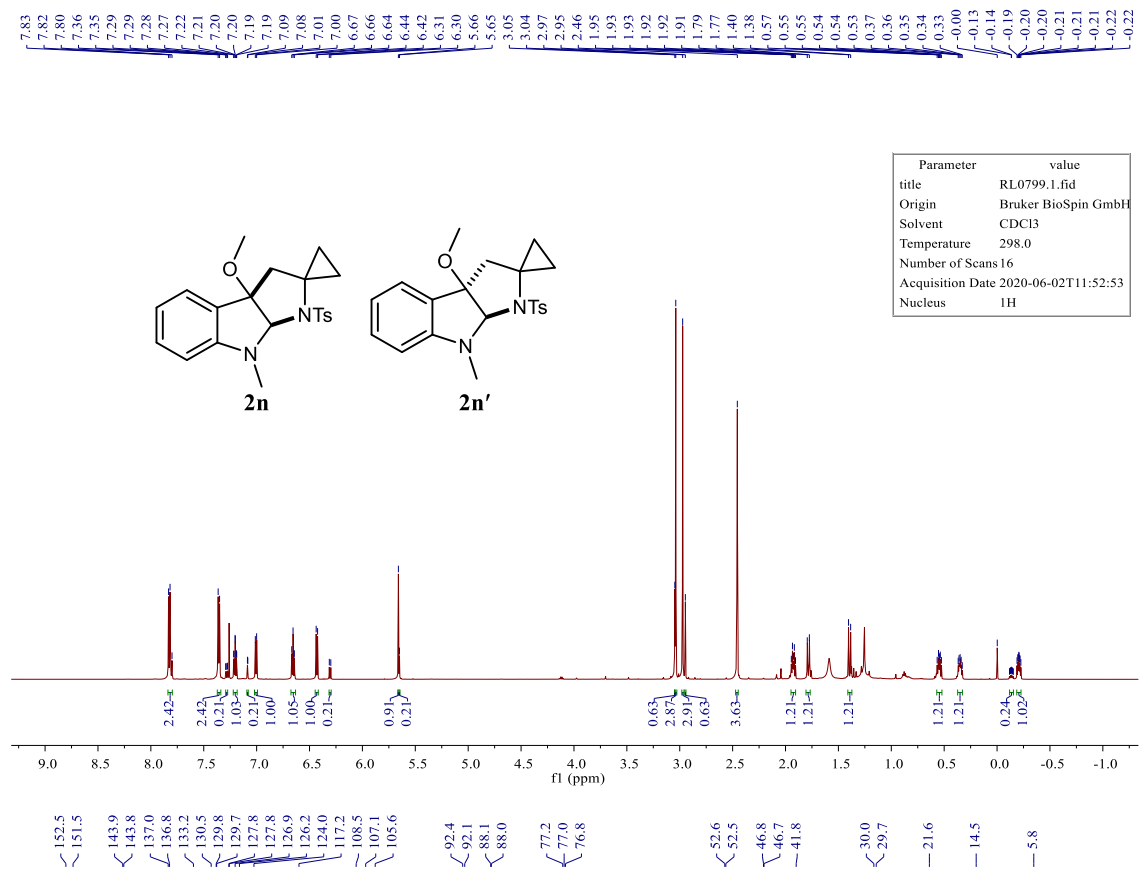


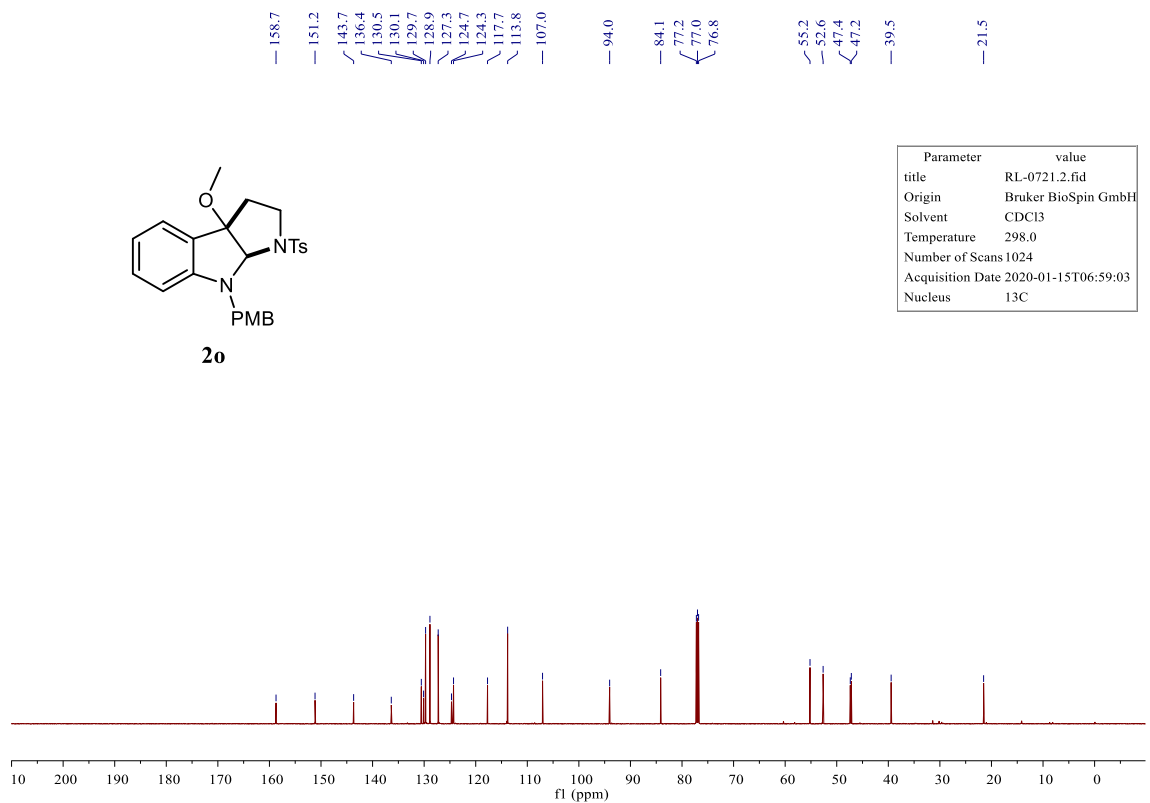
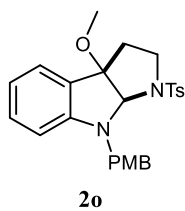
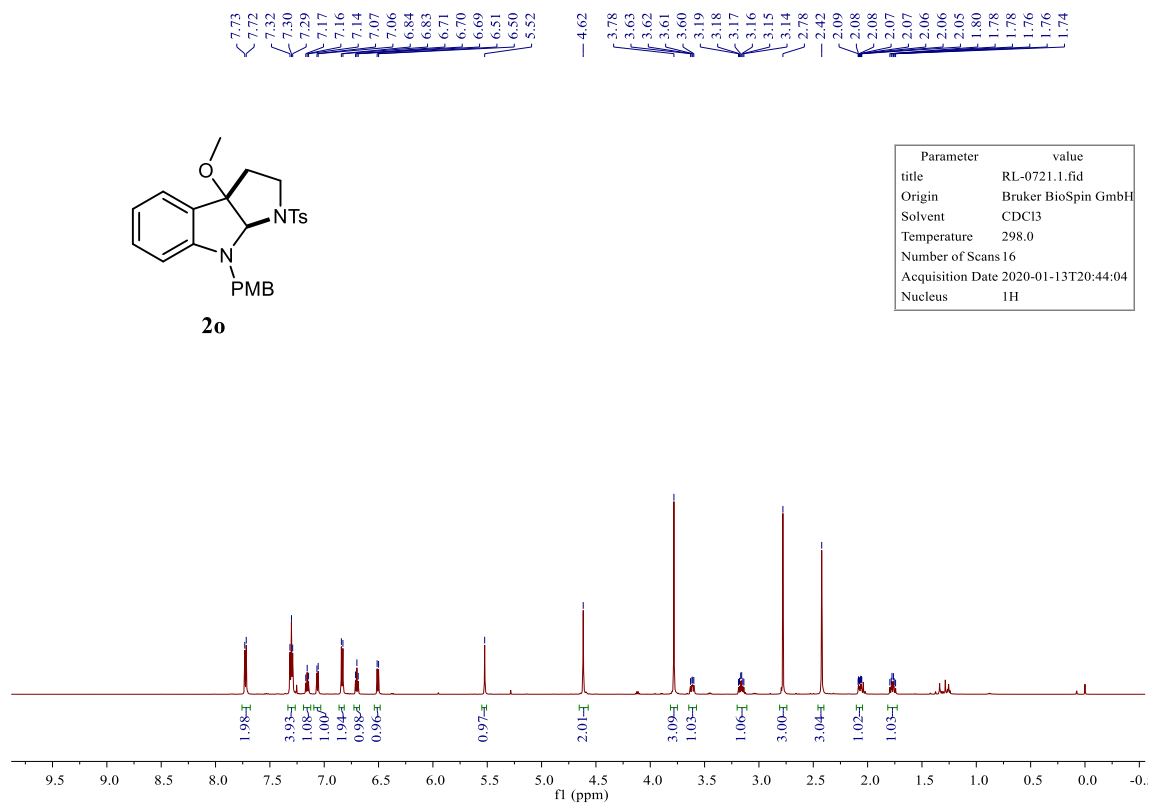
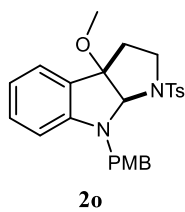


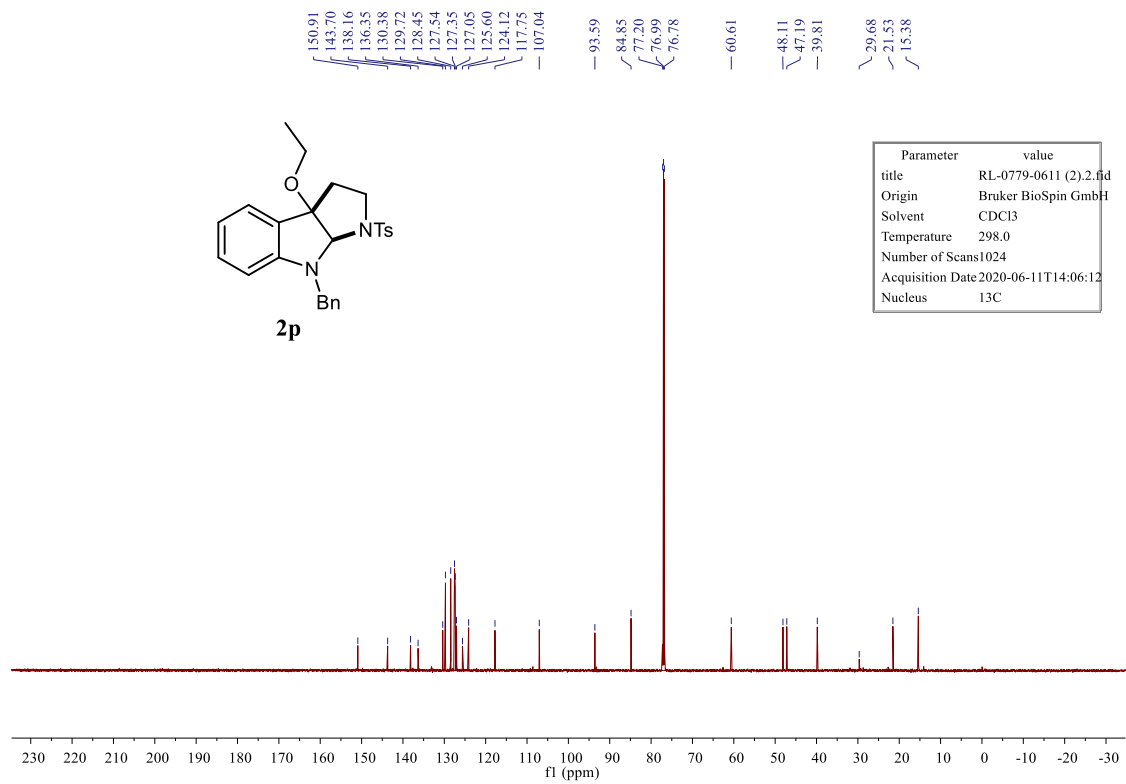
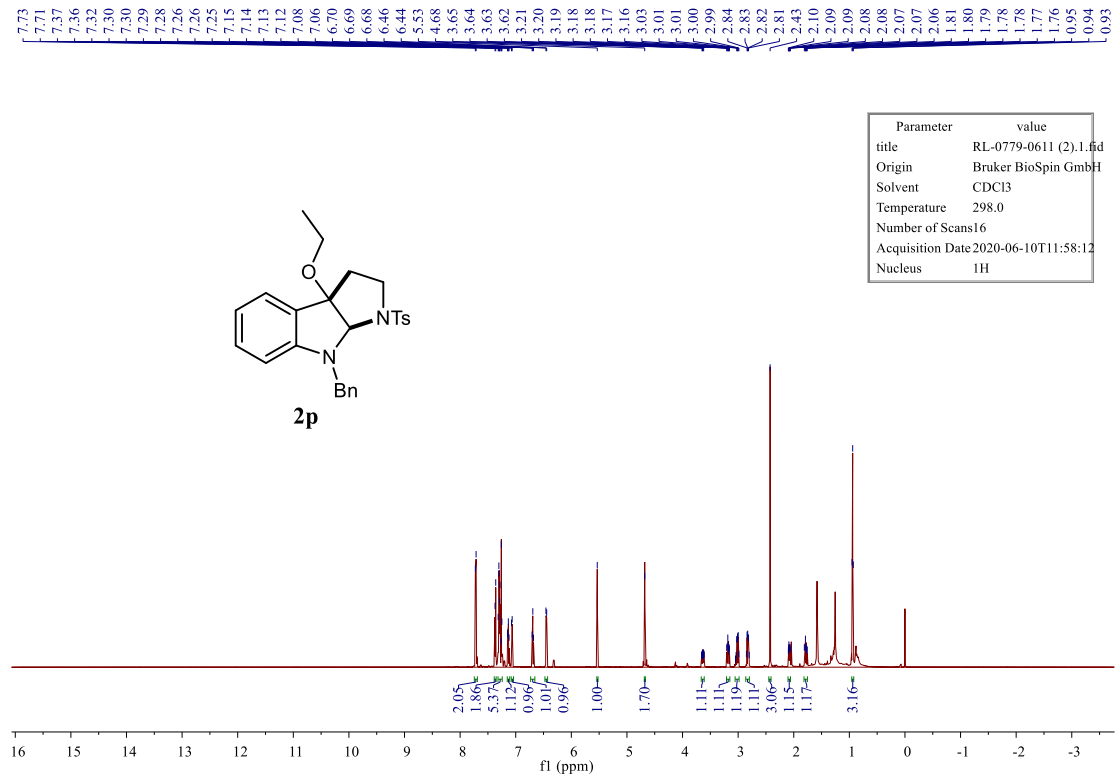
Parameter	value
title	RL0761.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl ₃
Temperature	299.0
Number of Scans	16
Acquisition Date	2020-04-21T12:16:14
Nucleus	¹ H



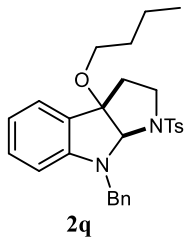
Parameter	value
title	RL0761.3.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl ₃
Temperature	299.0
Number of Scans	758
Acquisition Date	2020-04-22T10:30:57
Nucleus	¹³ C



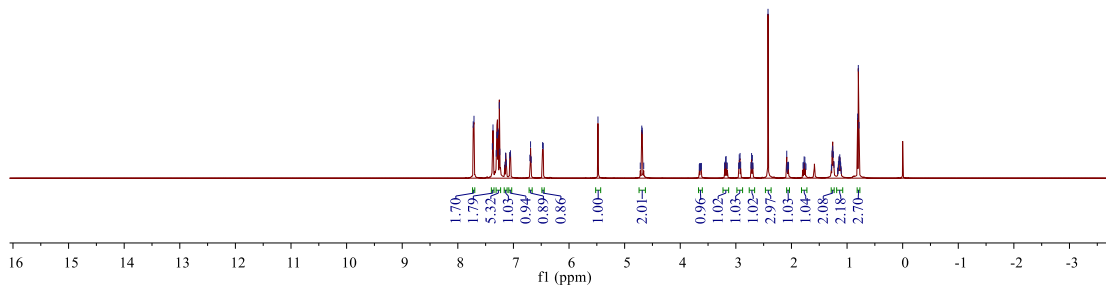




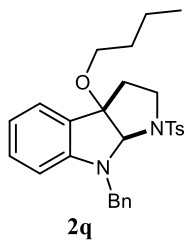
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7.71
7.38
7.37
7.31
7.30
7.29
7.27
7.25
7.24
7.15
7.14
7.13
7.07
7.05
6.70
6.69
6.68
6.48
6.46
5.48
4.72
4.69
4.68
4.66
3.19
3.18
3.17
3.16
2.95
2.94
2.93
2.92
2.91
2.73
2.72
2.71
2.70
2.42
2.08
2.08
2.07
2.06
2.06
1.79
1.78
1.77
1.76
1.75
1.27
1.26
1.25
1.23
1.16
1.14
1.13
1.13
1.12
1.11
0.81
0.80
0.79



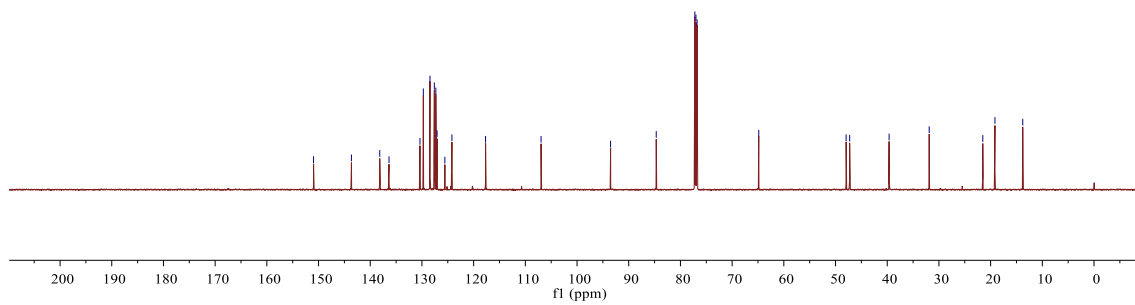
Parameter	value
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Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	16
Acquisition Date	2020-06-18T18:31:25
Nucleus	¹ H



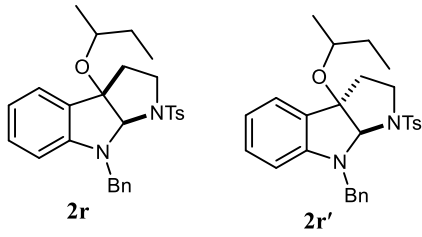
151.0
143.6
138.2
136.4
130.4
129.7
128.4
127.6
127.3
127.1
125.6
124.2
117.7
107.0
93.5
84.7
77.2
77.0
76.8
64.8
48.0
47.3
39.6
31.9
21.5
19.2
13.8



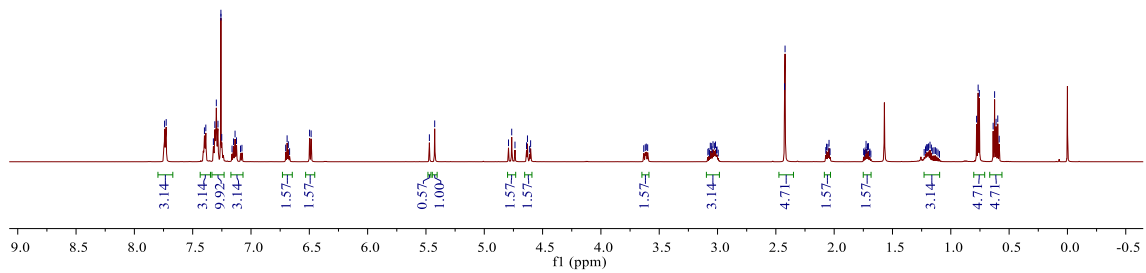
Parameter	value
title	RL-0780-0618.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	1024
Acquisition Date	2020-06-19T12:39:54
Nucleus	¹³ C



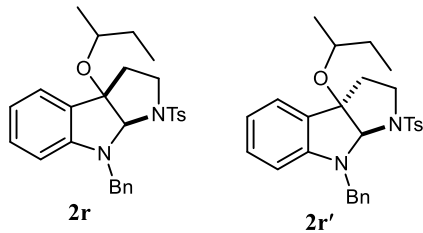
7.74
7.73
7.40
7.39
7.33
7.31
7.30
7.28
7.26
7.25
7.16
7.15
7.14
7.12
7.09
7.08
6.70
6.69
6.68
6.50
6.48
5.47
5.43
4.79
4.76
4.74
4.64
4.63
4.61
4.60
3.63
3.62
3.61
3.60
3.06
3.05
3.05
3.04
3.04
3.02
3.02
3.00
2.43
2.42
2.07
2.05
2.04
1.73
1.71
1.71
1.21
1.20
1.19
1.19
1.18
1.17
0.78
0.77
0.76
0.64
0.62
0.61
0.60
0.59



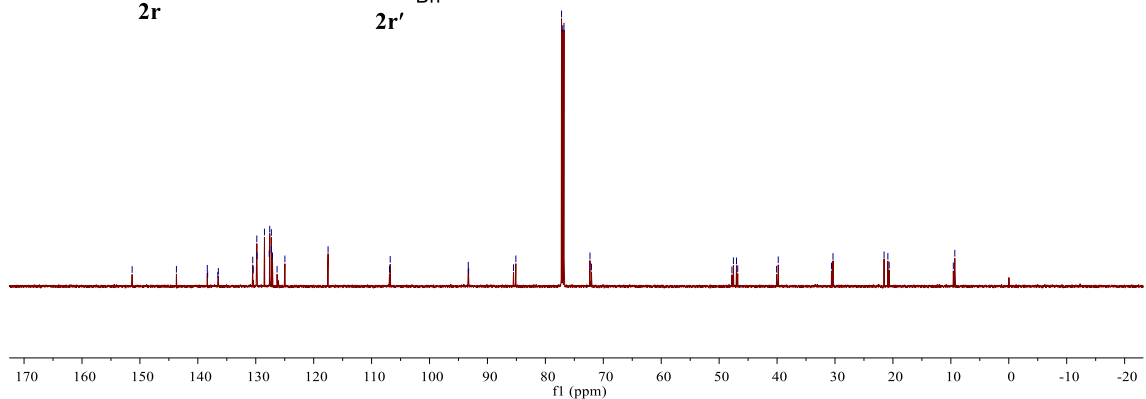
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title	RL-0766-0618.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	16
Acquisition Date	2020-06-18T18:35:20
Nucleus	1H



151.3
143.7
138.4
138.3
136.5
130.5
130.4
129.8
129.8
128.5
127.7
127.6
127.3
127.3
127.1
126.3
125.0
117.5
106.9
106.8
93.3
93.2
85.5
85.1
77.2
77.0
76.8
72.3
72.0
47.8
47.5
47.0
46.8
40.1
39.8
30.6
30.3
21.5
20.9
20.6
9.6
9.3

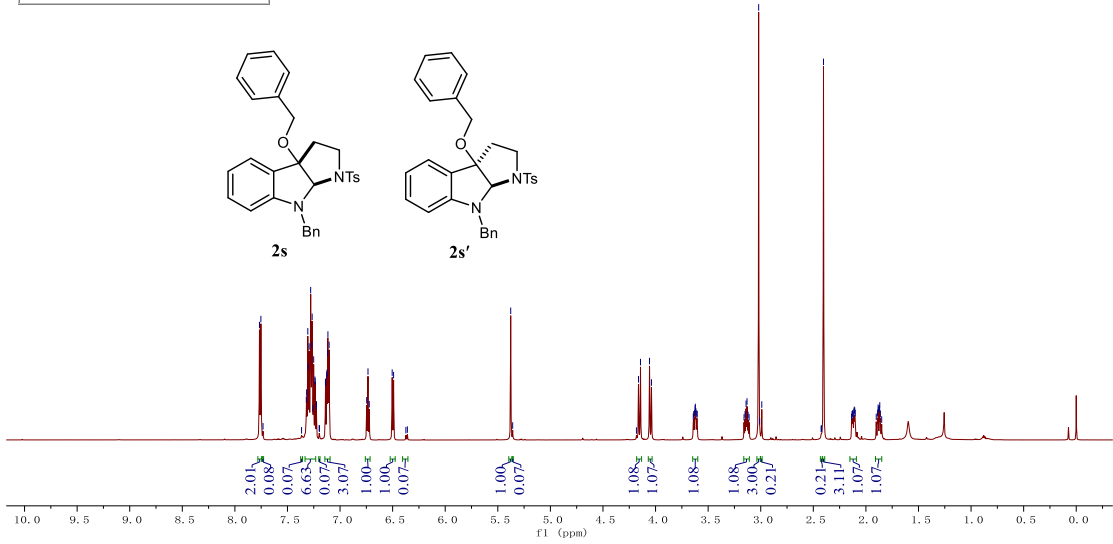
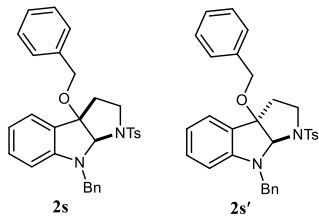


Parameter	value
title	RL-0766-0618.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	256
Acquisition Date	2020-06-19T12:56:07
Nucleus	13C



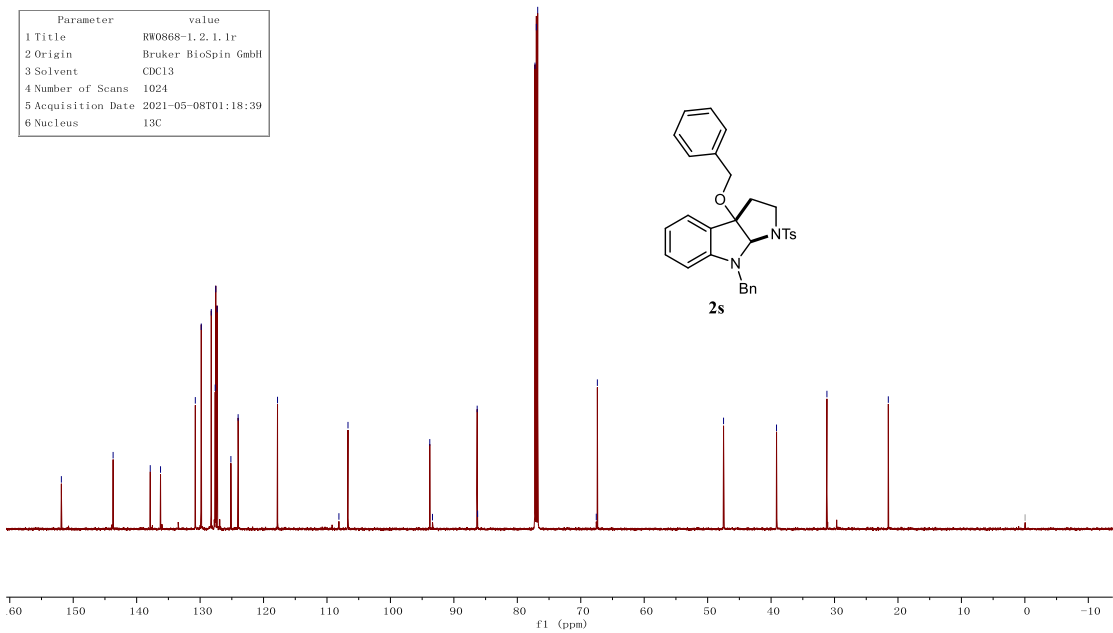
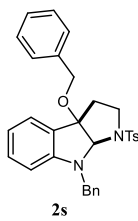
RW0868-1.1.1.1r
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Parameter	value
1 Title	RW0868-1.1.1.1r
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Number of Scans	8
5 Acquisition Date	2021-05-08T00:29:03
6 Nucleus	1H



RW0868-1.2.1.1r
 151.86, 143.71, 137.86, 136.24, 130.75, 129.82, 128.24, 127.62, 127.53, 127.32, 125.15, 124.01, 117.80, 108.12, 106.69, 93.80, 93.37, 86.33, 86.26, 77.21, 77.00, 76.79, 67.55, 67.38, 47.49, 39.15, 31.20, 21.52, -0.04

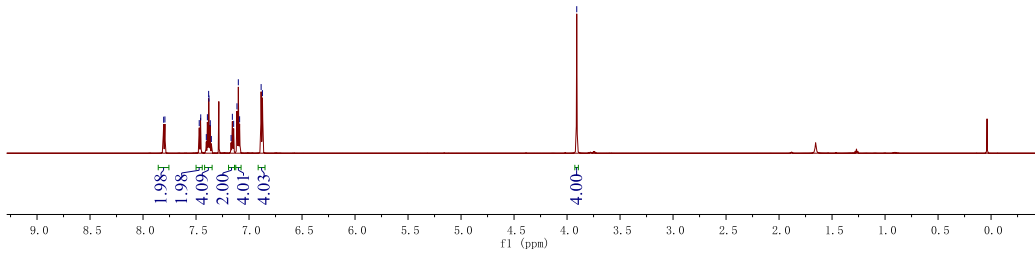
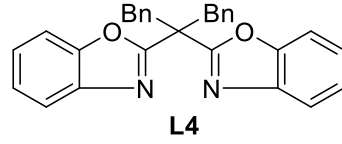
Parameter	value
1 Title	RW0868-1.2.1.1r
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Number of Scans	1024
5 Acquisition Date	2021-05-08T01:18:39
6 Nucleus	13C



L-Bn. 1. 1r
 7.84
 7.79
 7.47
 7.46
 7.40
 7.39
 7.38
 7.37
 7.36
 7.17
 7.16
 7.15
 7.11
 7.10
 7.09
 6.89
 6.87

- 3.91

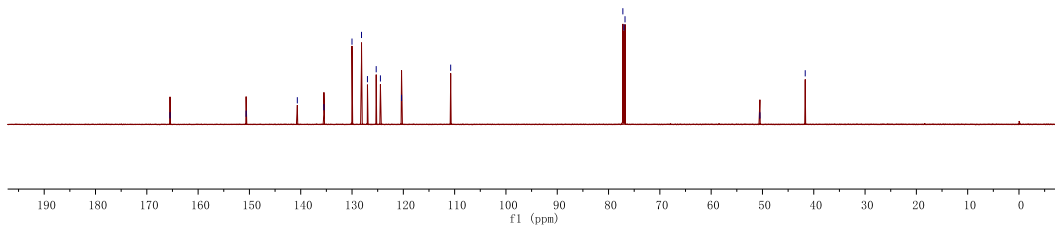
Parameter	Value
1 Title	L-Bn. 1. 1r
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	16
6 Acquisition Time	2.7525
7 Nucleus	1H



L-Bn. 2. 1. 1r

165.5
 150.6
 140.7
 135.5
 130.0
 128.2
 127.0
 125.3
 124.5
 120.3
 110.8
 77.2
 77.0
 76.8
 50.5
 41.7

Parameter	Value
1 Title	L-Bn. 2. 1. 1r
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	1024
6 Acquisition Time	0.8061
7 Nucleus	13C



Rs-0482.1.1.1r

7.77
7.76
7.47
7.46
7.33
7.31
7.30
7.29
7.26
7.25
7.24
7.13
7.12
7.10
6.87

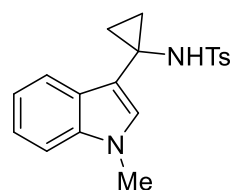
-3.78

-2.86

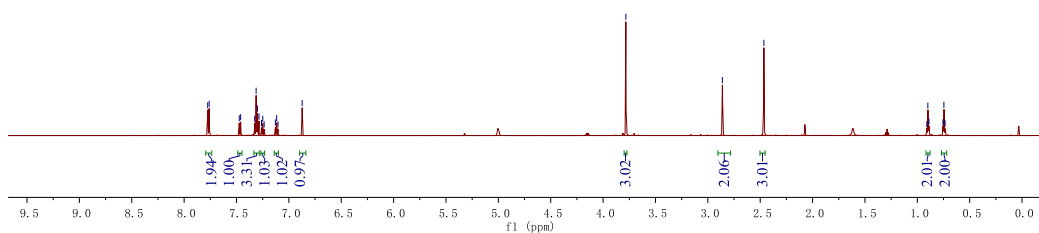
-2.46

0.91
0.90
0.89
0.76
0.75
0.73

Parameter	Value
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2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	16
6 Acquisition Date	2020-01-08T04:07:55
7 Nucleus	1H



1n



RS-0482.2.1.1r

143.3
139.3
137.0
129.6
128.0
127.2
121.6
119.3
118.9
110.2
109.2

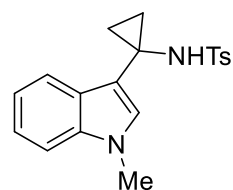
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77.0
76.8

35.8
32.8
32.7

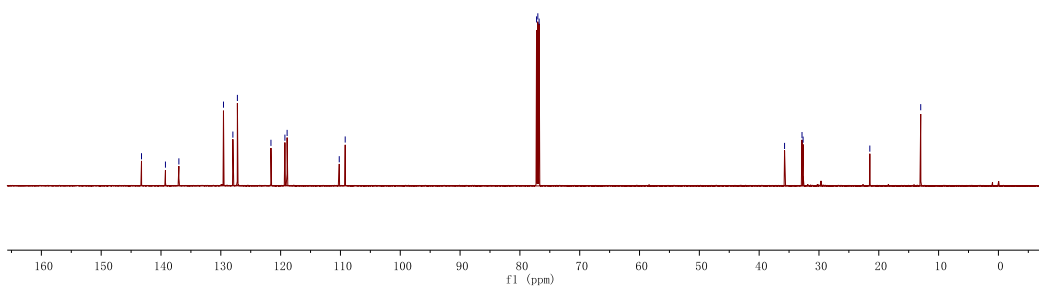
21.5

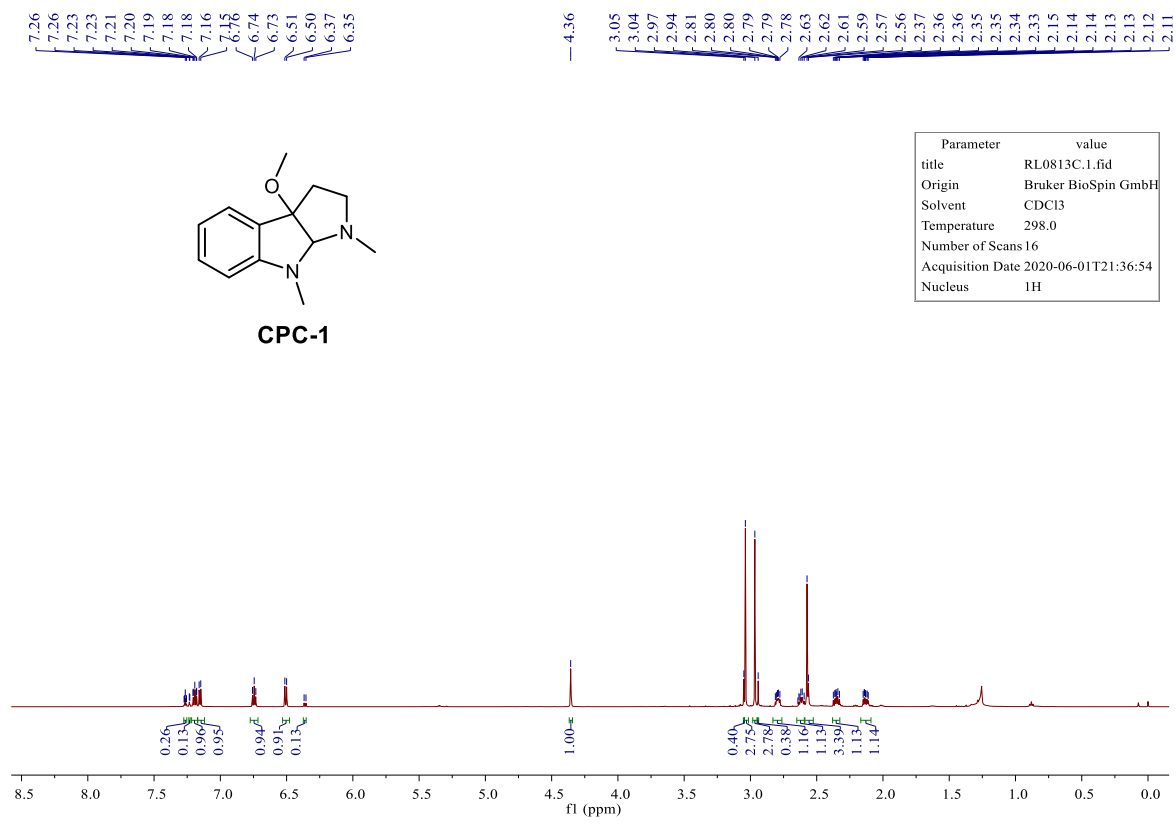
13.0

Parameter	Value
1 Title	RS-0482.2.1.1r
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	1024
6 Acquisition Date	2020-07-23T07:12:11
7 Nucleus	13C

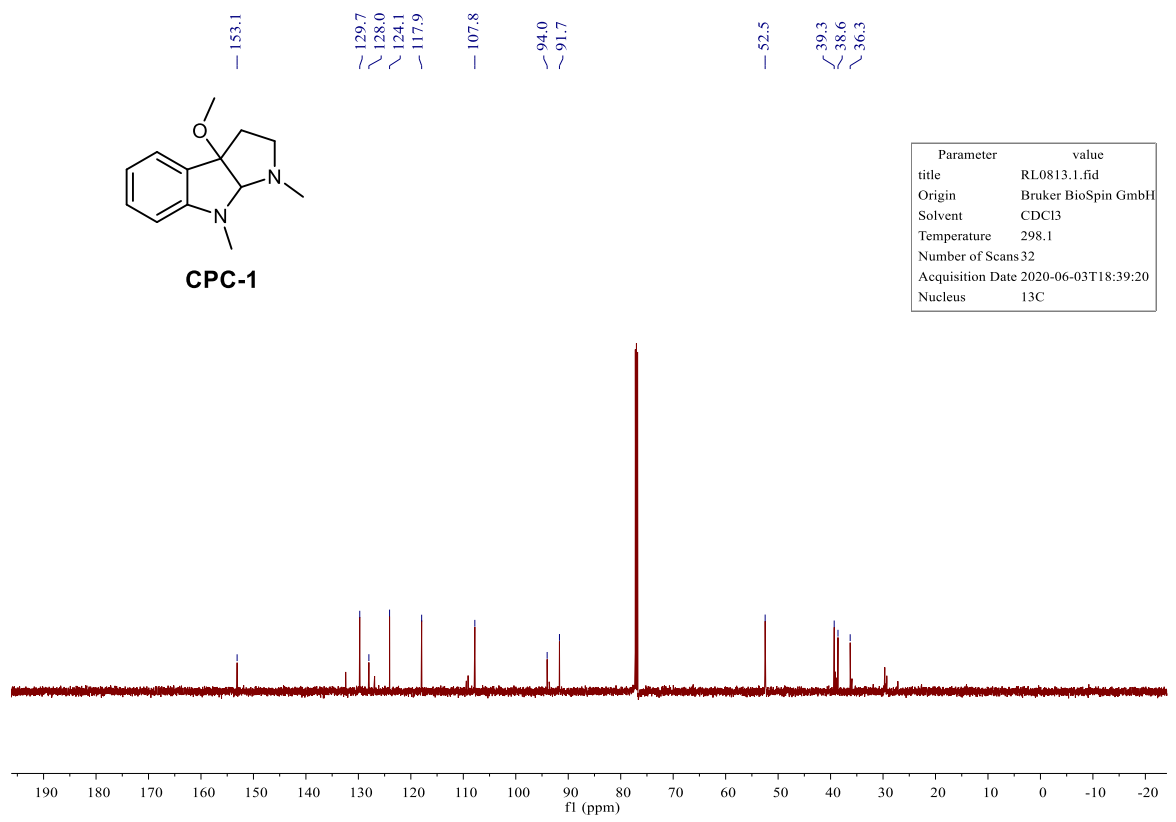


1n





Parameter	value
title	RL0813C.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Number of Scans	16
Acquisition Date	2020-06-01T21:36:54
Nucleus	1H



Parameter	value
title	RL0813.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.1
Number of Scans	32
Acquisition Date	2020-06-03T18:39:20
Nucleus	13C