Oxazoline/Copper Catalyzed Alkoxyl Radical Generation: Solvent-Switched to Access 3a,3a'-Bisfuroindoline and 3-Alkoxyl Furoindoline

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Supporting Information

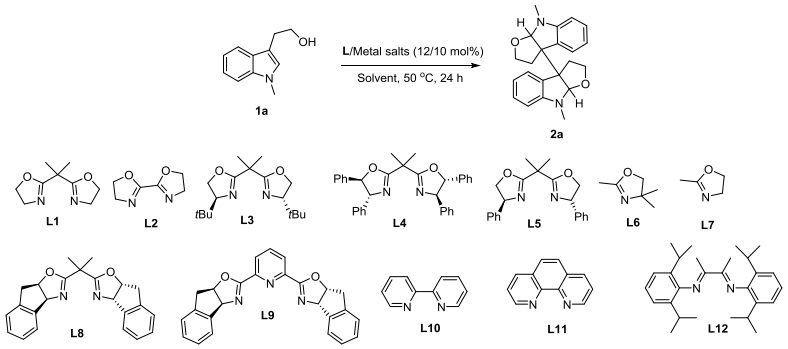
Content

1. General information

Unless stated, otherwise all reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. All 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 (^{1}H: 400 MHz, ^{13}C: 100 MHz) in chloroform-d or 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 40.5 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). 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[a]

Table S1: Ligand screening



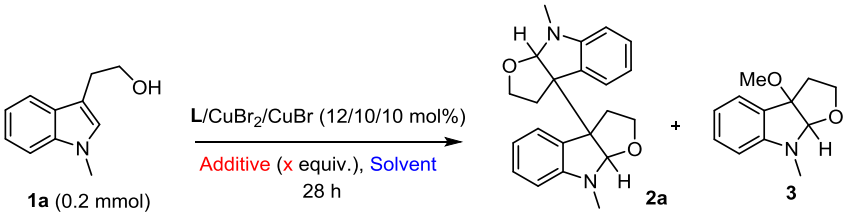
Entry	L	Metal salts	*t* (h)	Yield (%) [b]	Dr [c]
1	**L1**	$CuBr_2$/CuBr	24	15	3/1
2	**L2**	$CuBr_2$/CuBr	24	<10	--
3	**L3**	$CuBr_2$/CuBr	48	60	2.4/1
4	**L4**	$CuBr_2$/CuBr	24	76(75)[d]	2.6/1
5	**L5**	$CuBr_2$/CuBr	24	68	2.4/1
6	**L6**	$CuBr_2$/CuBr	24	42	2/1
7	**L7**	$CuBr_2$/CuBr	24	17	2.3/1
8	**L8**	$CuBr_2$/CuBr	24	28	2.5/1
9	**L9**	$CuBr_2$/CuBr	24	trace	--
10	**L10**	$CuBr_2$/CuBr	24	nr	--
11	**L11**	$CuBr_2$/CuBr	24	nr	--
22	**L12**	$CuBr_2$/CuBr	24	nr	--

[a] The reactions were carried out under Ar atmosphere: Metal salts (0.02 mmol), **L** (0.024 mmol), THF (2.0 mL), **1a** (0.20 mmol). [b] Yield was determined by ^{1}**H** NMR with TTCE as internal standard, in parentheses is isolated yield. [c] Dr was determined by ^{1}H NMR of the crude product. [d] The enantioinduction of the current catalyst for the reaction was, however, found to be problematic (6% ee), remaining an interesting and challenging subject for further investigation.

Procedure for eliminating the oxygen dissolved in THF: A mixture of $CuBr_2$ (4.5 mg, 0.02 mmol), CuBr (2.9 mg, 0.02 mmol), **L4** (11.7 mg, 0.024 mmol) and **2a** (35.0 mg) in dry THF (2 mL) was stirred at room temperature for 1 minute under the atmosphere of nitrogen and frozen in liqulid nitrogen under reduced pressure of oil-pump for another 30 minutes, then the mixture was warmed to 50 °C for 24 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, yield and dr were determined by ^{1}H NMR with TTCE as internal standard.

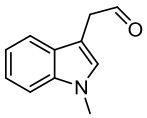
3. Mechanistic Studies

3.1 Controlled experiments with different radical scavengers



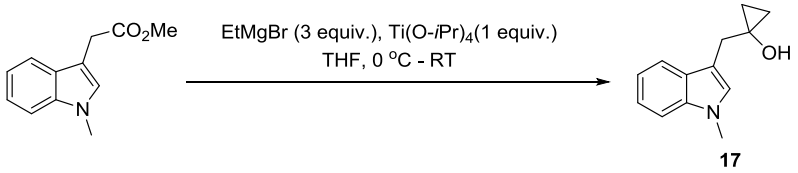
1a (0.2 mmol) **2a** **3**

Entry	Additive (x equiv.)	Solvent	Yield	dr
1	TEMPO (1)	THF	<10% (**2a**), 46% (**16**)	--
2	BHT (1)	THF	42% (**2a**)	2.4/1
3	TEMPO (1)	MeOH	trace (**3**)	--



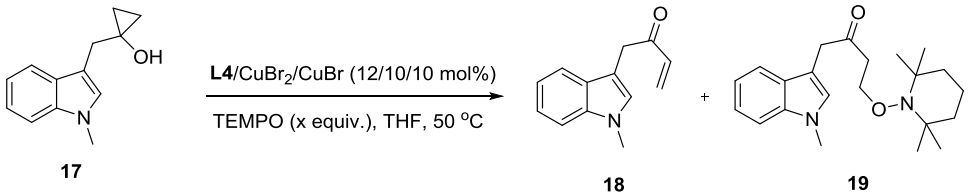
16

3.2 Radical clock experiments



Following theliteratureprocedure[1], ester (3 mmol, 1.0 eq.), titanium isopropoxide (3 mmol, 1 eq.) and THF (10 mL) were added to a 100 mL round-bottomed flask under the atmosphere of Ar. 9 mL of ethylmagnesium bromide (1 M in THF, 3.0 eq.) was added dropwise by syringe under Ar atmosphere at 0 ℃, then the mixture was warmed to room temperature for 20 mins. The mixture was then quenched with ammonium chloride solution and the precipitate was removed by filtration. The filtrate was extracted with ethyl acetate (3 x 30 mL), washed with sodium chloride solution, and dried over Na_2SO_4. After filtration and concentration, the residue was purified by column chromatography.

17 white solid, 543.0 mg, 90% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.23 (dd, *J* = 8.2, 7.0 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.00 (s, 1H), 3.77 (s, 3H), 3.03 (s, 2H), 0.83 (q, *J* = 5.2 Hz, 2H), 0.67 (q, *J* = 5.0 Hz, 2H).. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 137.0, 128.2, 127.6, 121.6, 119.4, 119.0, 111.0, 109.2, 77.2, 55.9, 33.9, 32.7, 13.6. IR (KBr): 3369.3, 2984.5, 2832.9, 1741.5, 1375.1, 1244.4, 1024.0 cm^{-1}; HRMS-ESI: Exact mass calcd. for $C_{13}H_{16}NO^+$ $[M+H]^+$: 202.1226; Found: 202.1230.



Procedure: A mixture of $CuBr_2$ (4.5 mg, 0.02 mmol), CuBr (2.9 mg, 0.02 mmol), **L4** (11.7 mg, 0.024 mmol) and **17** (35.0 mg) in THF (2 mL) was stirred at 50 °C for 12 h under the atmosphere of Ar. Then, 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

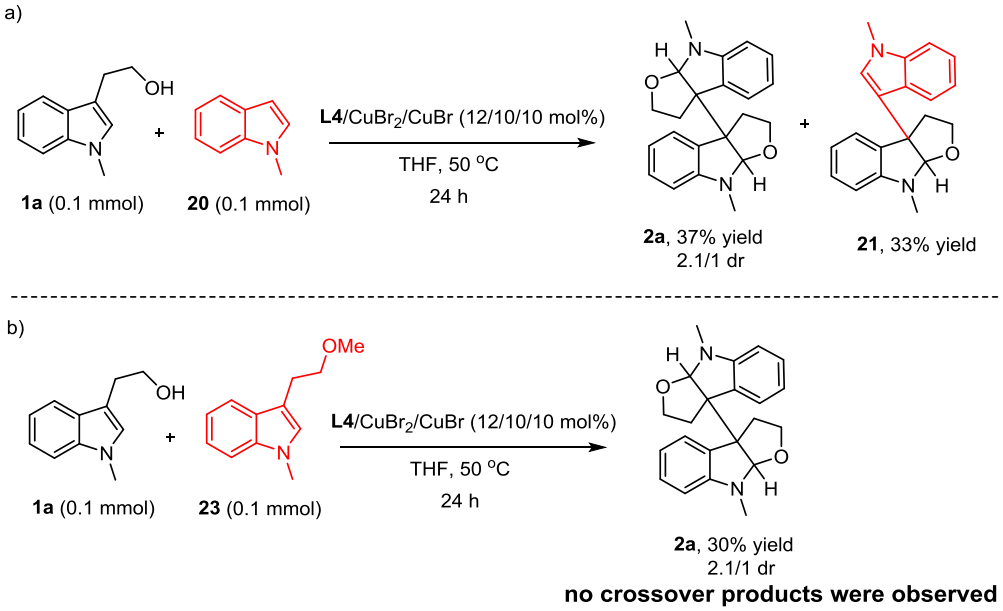
chromatography (hexane/ethyl acetate = 10/1) to afford the product **18**, which is unstable in air.

18 yellow liquid, 9.1 mg, 23% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.9 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.25 - 7.22 (m, 1H), 7.12 (dd, *J* = 11.3, 4.2 Hz, 1H), 6.98 (s, 1H), 6.46 (dd, *J* = 17.5, 10.5 Hz, 1H), 6.33 (dd, *J* = 17.5, 1.1 Hz, 1H), 5.74 (dd, *J* = 10.5, 1.2 Hz, 1H), 3.96 (s, 2H), 3.75 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 198.0, 136.9, 135.1, 128.5, 127.9, 127.7, 121.7, 119.2, 118.7, 109.3, 106.5, 37.3, 32.7. IR (KBr): 2984.7, 2942.8, 1742.2, 1373.9, 1242.2, 1047.1 cm^{-1}; HRMS-ESI: Exact mass calcd. for $C_{13}H_{14}NO^{+}$ $[M+H]^{+}$: 200.1070; Found: 200.1074.

Procedure: A mixture of $CuBr_2$ (4.5 mg, 0.02 mmol), CuBr (2.9 mg, 0.02 mmol), **L4** (11.7 mg, 0.024 mmol), TEMPO (31.2 mg, 0.2 mmol) and **17** (35.0 mg) in THF (2 mL) was stirred at 50 ºC for 2 h under the atmosphere of Ar. Then, 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 (hexane/ethyl acetate = 12/1) to afford the product **18** and **19**, the product **19** is unstable in the reaction system and air.

19 oil, 14.1 mg, 20% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.26 - 7.20 (m, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.01 (s, 1H), 3.98 (t, *J* = 6.3 Hz, 2H), 3.87 (s, 2H), 3.76 (s, 3H), 2.66 (t, *J* = 6.2 Hz, 2H), 1.42 - 1.41 (m, 4H), 1.30 - 1.25 (m, 2H), 1.13 (s, 6H), 1.04 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 207.5, 136.7, 127.7, 127.6, 121.6, 119.0, 118.6, 109.1, 106.7, 71.8, 59.6, 40.5, 40.2, 39.4, 32.7, 32.5, 19.9, 16.9. IR (KBr): 2985.2, 1738.1, 1374.3, 1244.2, 1047.1 cm^{-1}; HRMS-ESI: Exact mass calcd. for $C_{22}H_{33}N_2O_2^{+}$ $[M+H]^{+}$: 357.2537; Found: 357.2539.

3.3. Crossover experiments

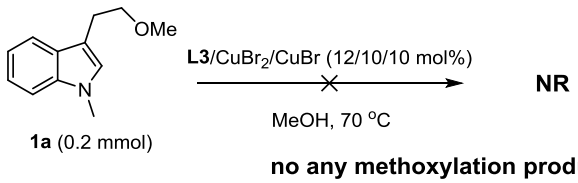


Procedure: A mixture of $CuBr_2$ (4.5 mg, 0.02 mmol), CuBr (2.9 mg, 0.02 mmol), **L4** (12.7 mg, 0.024 mmol) and **two substrates** in THF (2 mL) was stirred at 50 °C under the atmosphere of Ar. After the reaction was completed (monitored by TLC), the reaction was filtered through a glass funnel with 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 to afford the product.

21 white solid, 10.0 mg, 33% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.57 (t, *J* = 8.0 Hz, 1H), 7.31 - 7.27 (m, 1H), 7.24 - 7.20 (m, 1H), 7.19 - 7.14 (m, 2H), 7.10 - 7.03 (m, 1H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.49 - 6.43 (m, 1H), 5.63 (s, 1H), 4.20 (t, *J* = 7.9 Hz, 1H), 3.69 (d, *J* = 9.5 Hz, 3H), 3.65 - 3.56 (m, 1H), 3.01 - 2.90 (m, 4H), 2.38 (dt, *J* = 17.7, 8.8 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 150.9, 137.9, 132.5, 128.5, 126.7, 125.9, 124.2, 121.7, 120.0, 119.0, 117.3, 117.0, 109.5, 105.1, 104.0, 67.8, 55.9, 40.8, 32.6, 30.8. IR (KBr): 2984.9, 2946.7, 1742.5, 1374.0, 1241.9, 1047.3 cm^{-1}; HRMS-ESI: Exact mass calcd. for $C_{20}H_{21}N_2O^+$ $[M+H]^+$: 305.1648; Found: 305.1654.

3.4. Controlled experiments with hydroxyl group protected substrates

a)



1a (0.2 mmol)

no any methoxylation products were observed

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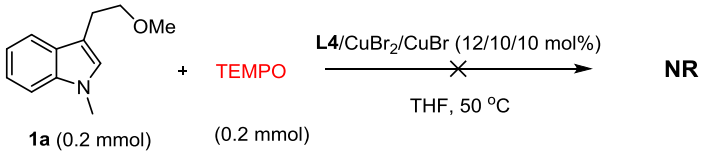
b)



1a (0.2 mmol) (0.2 mmol)

no any TEMPO-adduct products were observed

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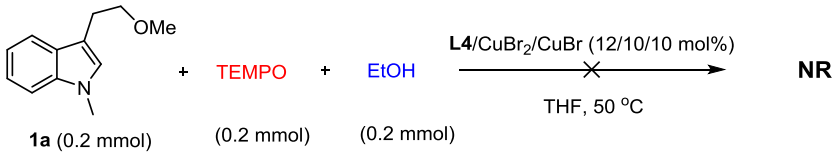
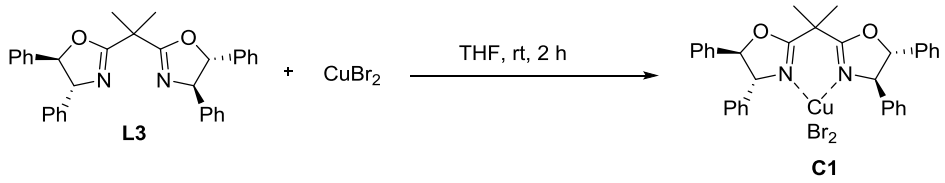
c)



1a (0.2 mmol) (0.2 mmol) (0.2 mmol)

no any TEMPO-adduct products were observed

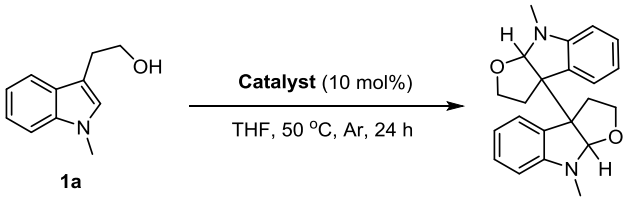
3.5 Mechanistic Investigations of the Catalyst



Procedure for preparing L4/CuBr2 complex C1:[2] A mixture of $CuBr_2$ (44.6 mg, 0.2 mmol) and **L4** (97.2 mg, 0.2 mmol) in THF (2 mL) was stirred at room temperature for 2 h under the atmosphere of Ar until the cupric salts disappeared. The reaction solution was concentrated under reduced pressure, affording the product **C1** as a reddish brown solide, which is stable in Air. However, we failed to get the X-Ray crystal structure of the **C1** after many tries.

Results: When chose previously prepared **L4**/$CuBr_2$ complex **C1** as the catalyst, the reaction procced smoothly (Table S2, entry 1). In combination with CuBr as a co catalyst, the reaction efficiency improved significantly to give **2a** in 75% yield and 2.4/1 dr (entry 2). However, a lower yield was obtained with $CuBr_2$ (entry 3). Notably, when CuBr was used as the single metal catalyst, trace amounts of product were observed (entries 4-5), suggesting that the Cu^{II}-active species formed directly from CuBr oxidated with O_2 is impossible in the catalytic cycle.

Table S2. **Mechanistic Investigations of the Catalyst**



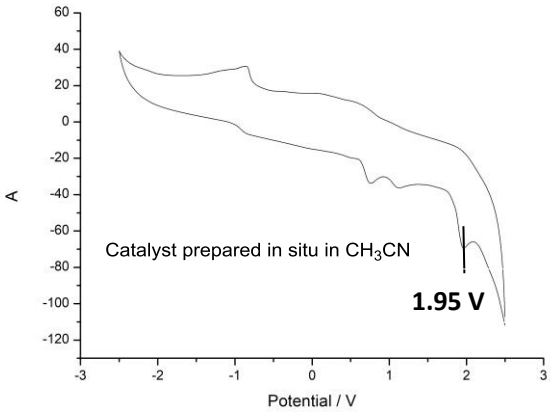
Entry	Catalyst	Yield	dr
1	$CuBr_2$	nr	--
2	**C1**	52%	2.4/1
3	**C1**/CuBr	75%	2.4/1
4	**C1**/$CuBr_2$	46%	2.5/1
5	**L4**/$CuBr_2$	42%	2.4/1
6	**L4**/CuBr	trace	--
7*	**L4**/CuBr	<5	--

* Carried out under the atmosphere of O_2.

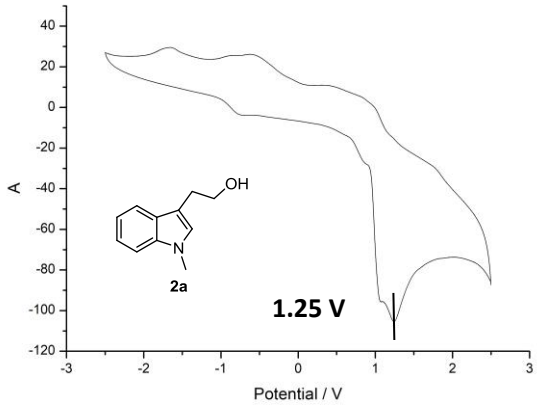
Procedure for reaction with C1 as catalyst: A mixture of **C1** (14.1 mg, 0.02 mmol) and **1a** (35.0 mg, 0.2 mmol) in THF (2 mL) was stirred at 50 ^{o}C under the atmosphere of Ar. After the reaction was completed (monitored by TLC), the reaction was filtered through a glass funnel with thin layer (30 mm) of silica gel (100-200 mesh) and eluted with DCM/Ethyl Acetate. The filtrate was concentrated under reduced pressure, the yields and dr of **2a** were determined by ^{1}H NMR with TTCE as internal standard.

3.6 The Cyclic Voltammetry Experiments

Cyclic Voltammetry was performed on a GU Instruments Electrochemical Workstation model CH/1660D. CV measurement were carried out in 0.1 M CH_3CN solution of **Catalyst (L4**/$CuBr_2$ = 1/1 prepared in situ in CH_3CN) or **2a** was prepared with 0.1 M n-Bu_4NPF_6 at a scan rate of 100 mV/s with the protection of Ar. The working electrode is a glassy carbon, the counter electrode is a Pt wire, and the reference electrode is saturated calomel electrode.

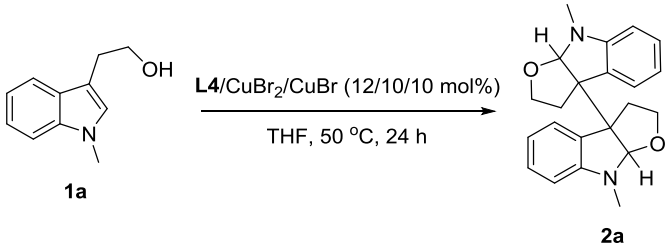


Scheme S1: The Cyclic Voltammetry Experiment of complex (**L3**/$CuBr_2$ = 1/1) prepared in situ in CH_3CN

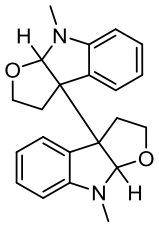


Scheme S2: The Cyclic Voltammetry Experiment of substrate **2a**

4. General Procedure for Dimerization and Product Characterizations



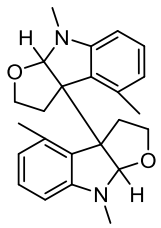
Procedure: A mixture of $CuBr_2$ (4.5 mg, 0.02 mmol), CuBr (2.9 mg, 0.02 mmol), **L4** (11.7 mg, 0.024 mmol) and **1a** (35.0 mg) in THF (2 mL) was stirred at 50 °C for 24 h under the atmosphere of Ar. After the reaction was completed (monitored by TLC), the reaction was filtered through a glass funnel 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 (hexane/ethyl acetate = 8/1) to afford the product **2a**.



8,8'-dimethyl-2,2',3,3',8,8a,8',8'a-octahydro-3a,3'a-bifuro[2,3-*b*]indole

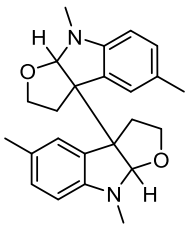
2a white solid, 24 h, 26.0 mg, 75% yield. 2.6 dr; for the mixture of the two diastereomers: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.13 - 7.06 (m, 2.4H), 6.61 (t, *J* = 7.4 Hz, 1H), 6.51 (br, 0.4H), 6.33 (d, *J* = 7.8 Hz, 1H), 6.29 (d, *J* = 7.8 Hz, 0.4H), 5.22 (s, 1H), 5.11 (s, 0.4H), 4.04 - 4.01 (m, 0.4H), 3.92 (t, *J* = 7.9 Hz, 1H), 3.43 (ddd, *J* = 11.9, 8.8, 4.8 Hz, 0.4H), 3.34 (ddd, *J* = 11.5, 8.6, 4.8 Hz, 1H), 2.93 (s, 3H), 2.72 (s, 1.2H), 2.46 - 2.41 (m, 1+0.4H), 2.23 (dd, *J* = 11.8, 4.7 Hz, 0.4H), 2.07 (dd, *J* = 12.0, 4.7 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 151.9, 151.8, 130.3, 128.7, 124.1, 123.9, 117.0, 117.0, 105.0, 105.0, 105.0, 101.3, 100.7, 66.9, 66.8, 61.4, 60.9, 37.8, 36.8, 31.0, 30.6.

IR (KBr): 3435.0, 2925.1, 2854.1, 1606.6, 1498.1, 1302.8, 1261.7, 1038.7, 911.9 cm^{-1}; HRMS-ESI: Exact mass calcd. for $C_{22}H_{25}N_2O_2^+$ $[M+H]^+$: 349.1911; Found: 349.1909.



4,4',8,8'-tetramethyl-2,2',3,3',8,8a,8',8'a-octahydro-3a,3'a-bifuro[2,3-*b*]indole

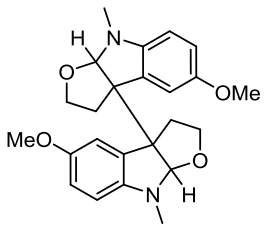
2b white solid, 28 h, 11.2 mg, 30% yield. the spectral data of the isolated isomer: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.98 (t, *J* = 7.7 Hz, 1H), 6.35 (d, *J* = 7.6 Hz, 1H), 6.15 (d, *J* = 7.7 Hz, 1H), 5.16 (s, 1H), 3.99 (ddd, *J* = 8.6, 7.2, 1.4 Hz, 1H), 3.45 (ddd, *J* = 10.8, 8.6, 4.9 Hz, 1H), 2.70 (s, 3H), 2.51 - 2.50 (m, 1H), 2.47 - 2.40 (m, 1H), 1.92 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 152.6, 135.5, 128.6, 127.5, 121.0, 103.3, 101.5, 67.7, 63.0, 35.7, 31.3, 19.3. IR (KBr): 3447.3, 2922.6, 2848.4, 2359.4, 2342.6, 1587.1, 1475.7, 1283.7, 1045.7, 924.0 cm^{-1}; HRMS-ESI: Exact mass calcd. for $C_{24}H_{29}N_2O_2^+$ $[M+H]^+$: 377.2224; Found: 377.2221.



5,5',8,8'-tetramethyl-2,2',3,3',8,8a,8',8'a-octahydro-3a,3'a-bifuro[2,3-*b*]indole

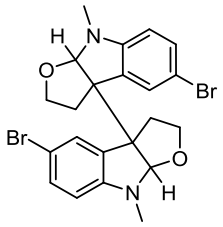
2c oil, 18 h, 31.3 mg, 83% yield. 2/1 dr; for the mixture of the two diastereomers: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.98 (s, 1H), 6.91 - 6.88 (m, 1+1.5H), 6.26 (d, *J* = 7.9 Hz, 1H), 6.20 (d, *J* = 7.9 Hz, 0.5H), 5.10 - 5.10 (s, 1+0.5H), 4.01 (t, *J* = 8.0 Hz, 0.5H), 3.89 (t, *J* = 7.8 Hz, 1H), 3.44 (ddd, *J* = 12.0, 8.7, 4.7 Hz, 0.5H), 3.33 (ddd, *J* = 11.4, 8.5, 4.8 Hz, 1H), 2.89 (s, 3H), 2.67 (s, 1.5H), 2.46 - 2.36 (m, 1+0.5H), 2.26 - 2.20 (m, 3+0.5H), 2.13 (s, 1.5H), 2.04 (dd, *J* = 12.0, 4.6 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 150.0, 130.7, 130.4, 129.0, 129.0, 126.1, 126.0, 125.5, 124.8, 105.0, 104.9, 101.5, 101.2, 67.1, 66.9, 61.4, 60.6, 37.5, 36.5, 31.5, 30.9, 20.9, 20.8. IR (KBr): 3456.6, 2925.5, 2865.0, 1738.6, 1616.2, 1504.9, 1288.5, 1039.4, 1006.0, 913.8 cm^{-1};

HRMS-ESI: Exact mass calcd. for $C_{24}H_{28}N_2O_2Na^+$ $[M+Na]^+$: 399.2048; Found: 399.2040.



5,5'-dimethoxy-8,8'-dimethyl-2,2',3,3',8,8a,8',8'a-octahydro-3a,3'a-bifuro[2,3-*b*]indole

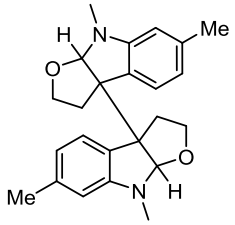
2d yellow solid, 18 h, 24.2 mg, 59% yield. 1.3/1 dr; for the mixture of the two diastereomers: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.79 (s, 1H), 6.68 - 6.64 (m, 1+0.8H), 6.25 - 6.23 (m, 1+1.6H), 5.19 (s, 1H), 5.08 (s, 0.8H), 4.02 (t, *J* = 8.0 Hz, 0.8H), 3.91 (t, *J* = 7.8 Hz, 1H), 3.71 (s, 3H), 3.59 (s, 2.4H), 3.47 - 3.43 (m, 0.8H), 3.34 (ddd, *J* = 11.4, 8.6, 4.9 Hz, 1H), 2.89 (s, 3H), 2.68 (s, 2.4H), 2.47 - 2.39 (m, 1.8H), 2.23 (dd, *J* = 11.7, 4.6 Hz, 0.8H), 2.05 (dd, *J* = 12.2, 4.5 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 152.2, 152.2, 146.6, 146.4, 131.6, 114.0, 113.1, 112.2, 111.0, 105.7, 105.3, 101.9, 101.5, 66.9, 66.8, 61.5, 60.9, 56.1, 56.0, 37.5, 36.6, 32.0, 31.3. IR (KBr): 3455.8, 2940.5, 2825.2, 2356.6, 1595.6, 1498.9, 1281.3, 1215.2, 1036.6, 915.2 cm^{-1}; HRMS-ESI: Exact mass calcd. for $C_{24}H_{28}N_2O_4Na^+$ $[M+Na]^+$: 431.1941; Found: 431.1937.



5,5'-dibromo-8,8'-dimethyl-2,2',3,3',8,8a,8',8'a-octahydro-3a,3'a-bifuro[2,3-*b*]indole

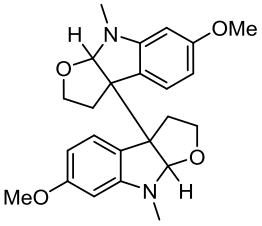
2e white solid, 72 h, 12.0 mg (recycle **1e**, 13.1 mg), 24% yield (brsm, 49%). 2/1 dr; for the mixture of the two diastereomers: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.21 - 7.20 (m, 1H), 7.14 - 7.10 (m, 2 H), 6.20 - 6.17 (m, 1+0.5H), 5.22 (s, 1H), 5.07 (s, 0.5H), 4.06 - 4.03 (m, 0.5H), 3.96 (t, *J* = 7.9 Hz, 1H), 3.45 - 3.41 (m, 0.5H), 3.37 (ddd, *J* = 11.4, 8.8, 4.8 Hz, 1H), 2.92 (s, 3H), 2.72 (s, 1.5H), 2.42 - 2.35 (m, 1.5H), 2.22 (dd, *J* = 11.8, 4.7 Hz, 0.5H), 2.06 (dd, *J* = 12.1, 4.7 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 150.8, 150.7, 132.1, 131.7, 131.5, 126.8, 126.7, 108.5, 108.5, 106.4, 106.3, 101.3,

100.6, 66.9, 66.8, 61.2, 60.8, 37.4, 36.3, 30.9, 30.7. The purified major isomer **2e'** was recrystallized from cold DCM/hexane. Major isomer **2e'**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.19 - 7.06 (m, 2H), 6.18 (d, *J* = 8.3 Hz, 1H), 5.22 (s, 1H), 3.97 (t, *J* = 8.0 Hz, 1H), 3.37 (ddd, *J* = 11.5, 8.8, 4.8 Hz, 1H), 2.92 (s, 3H), 2.40 (td, *J* = 11.7, 7.4 Hz, 1H), 2.06 (dd, *J* = 12.2, 4.7 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 150.6, 132.1, 131.5, 126.7, 108.5, 106.4, 101.3, 66.8, 60.8, 36.3, 30.7. IR (KBr): 3435.2, 2928.6, 2866.4, 2359.5, 1710.6, 1599.3, 1492.8, 1271.6, 1036.1, 1003.2, 912.4 cm^{-1}; HRMS-ESI: Exact mass calcd. for $C_{22}H_{23}N_2O_2Br_2$ $[M+H]^+$: 505.0121; Found: 505.0104.



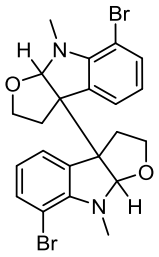
6,6',8,8'-tetramethyl-2,2',3,3',8,8a,8',8'a-octahydro-3a,3'a-bifuro[2,3-*b*]indole

2f white solid, 20 h, 29.0 mg, 77% yield. 3.5/1 dr; for the mixture of the two diastereomers: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.06 - 7.05 (m, 1+0.3H), 6.46 (d, *J* = 7.3 Hz, 1H), 6.34 (br, 0.3H), 6.18 (s, 1H), 6.12 (s, 0.3H), 5.11 (s, 1+0.3H), 4.01 (t, *J* = 9.0 Hz, 0.3H), 3.88 (t, *J* = 7.9 Hz, 1H), 3.45 - 3.41 (m, 0.3H), 3.32 (ddd, *J* = 11.5, 8.6, 4.8 Hz, 1H), 2.89 (s, 3H), 2.72 (s, 0.9H), 2.42 - 2.37 (m, 1+0.3H), 2.28 (s, 3H), 2.26 (s, 0.9H), 2.18 (dd, *J* = 11.7, 4.7 Hz, 0.3H), 2.01 (dd, *J* = 11.9, 4.6 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 152.2, 152.0, 138.7, 138.5, 127.8, 127.6, 124.1, 123.6, 117.8, 117.7, 106.1, 105.8, 101.5, 101.1, 67.0, 66.7, 61.1, 60.6, 37.9, 36.8, 31.0, 30.6, 23.2, 21.7. IR (KBr): 3447.3, 2922.6, 2848.4, 2359.4, 2342.6, 1587.1, 1475.7, 1422.5, 1287.7, 1045.7, 924.0 cm^{-1}; HRMS-ESI: Exact mass calcd. for $C_{24}H_{29}N_2O_2^+$ $[M+H]^+$: 377.2224; Found: 377.2222.



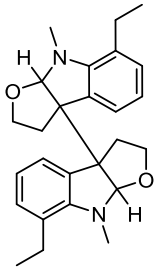
6,6'-dimethoxy-8,8'-dimethyl-2,2',3,3',8,8a,8',8'a-octahydro-3a,3'a-bifuro[2,3-*b*]indole

2g white solid, 24 h, 18.5 mg, 45% yield. 3.5/1 dr; for the mixture of the two diastereomers: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.05 - 7.04 (m, 1.3H), 6.17 (d, *J* = 7.4 Hz, 1H), 6.06 (br, 0.3H), 5.93 (d, *J* = 1.5 Hz, 1H), 5.87 (d, *J* = 2.2 Hz, 0.3H), 5.12 (s, 1+0.3H), 4.01 (t, *J* = 9.0 Hz, 0.3H), 3.90 (t, *J* = 7.9 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 0.9H), 3.46 - 3.42 (m, 0.3H), 3.34 (ddd, *J* = 11.6, 8.6, 4.7 Hz, 1H), 2.89 (s, 3H), 2.73 (s, 0.9H), 2.39 - 2.34 (m, 1+0.3H), 2.16 (dd, *J* = 11.6, 4.5 Hz, 0.3H), 2.00 (dd, *J* = 11.9, 4.5 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 161.0, 161.0, 153.4, 124.6, 124.2, 122.9, 101.7, 101.1, 92.4, 92.0, 67.1, 66.8, 60.9, 60.4, 55.2, 36.9, 30.9, 30.6. IR (KBr): 3445.7, 2925.6, 2859.9, 2358.5, 2342.7, 1618.7, 1499.9, 1259.9, 1094.0, 1031.1 cm^{-1}; Exact mass calcd. for $C_{24}H_{29}N_2O_4^+$ $[M+H]^+$: 409.2122; Found: 409.2117.



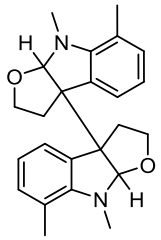
7,7'-dibromo-8,8'-dimethyl-2,2',3,3',8,8a,8',8'a-octahydro-3a,3'a-bifuro[2,3-*b*]indole

2h white solid, 48 h, 14.8 mg (recycle, 21.2 mg), 29% yield (brsm, 71%). 2.4/1 dr; for the mixture of the two diastereomers: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.0 Hz, 0.4H), 7.17 (d, *J* = 8.0 Hz, 1H), 6.94 - 6.93 (m, 1+0.4H), 6.48 - 6.45 (m, 1+0.4H), 5.18 (s, 1H), 4.98 (s, 0.4H), 4.04 (t, *J* = 9.0 Hz, 0.4H), 3.95 (t, *J* = 8.0 Hz, 1H), 3.50 - 3.46 (m, 0.4H), 3.41 (ddd, *J* = 11.6, 8.7, 4.8 Hz, 1H), 3.34 (s, 3H), 3.03 (br, 1.2H), 2.44 - 2.38 (m, 1+0.4H), 2.20 (dd, *J* = 11.8, 4.5 Hz, 0.4H), 2.06 (dd, *J* = 12.0, 4.7 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.0, 134.3, 134.2, 133.6, 123.0, 122.9, 119.6, 119.0, 103.2, 100.5, 66.7, 66.2, 60.8, 60.2, 37.0, 35.0. IR (KBr): 3444.4, 2962.1, 2852.2, 1598.2, 1260.9, 1026.3 cm^{-1}; HRMS-ESI: Exact mass calcd. for $C_{22}H_{23}N_2O_2Br_2$ $[M+H]^+$: 505.0121; Found: 505.0108.



7,7'-diethyl-8,8'-dimethyl-2,2',3,3',8,8a,8',8'a-octahydro-3a,3'a-bifuro[2,3-*b*]indole

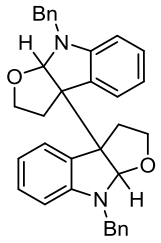
2i white solid, 48 h, 29.0 mg, 71% yield. 2/1 dr; for the major isomer: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.91 (d, *J* = 7.3 Hz, 1H), 6.80 (d, *J* = 7.5 Hz, 1H), 6.54 (t, *J* = 7.5 Hz, 1H), 4.92 (s, 1H), 3.82 (t, *J* = 7.8 Hz, 1H), 3.31 (ddd, *J* = 11.3, 8.5, 4.9 Hz, 1H), 3.09 (s, 3H), 2.68 (dt, *J* = 15.0, 7.5 Hz, 1H), 2.59 (dd, *J* = 14.7, 7.4 Hz, 1H), 2.40 (td, *J* = 11.6, 7.5 Hz, 1H), 2.02 (dd, *J* = 11.9, 4.6 Hz, 1H), 1.10 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.2, 131.7, 130.2, 124.7, 122.1, 118.4, 103.7, 66.5, 60.0, 36.8, 35.8, 25.2, 15.4. for the minor isomer: **^{1}H NMR** (600 MHz, d-DMSO, 80 ^{o}C) 6.90 (d, *J* = 7.5 Hz, 1H), 6.54 (t, *J* = 7.5 Hz, 1H), 6.43 (br, 1H), 4.92 (s, 1H), 3.95 (t, *J* = 7.7 Hz, 1H), 3.31 (ddd, *J* = 11.2, 8.6, 5.0 Hz, 1H), 2.79 (s, 3H), 2.65 (ddt, *J* = 22.1, 14.6, 7.3 Hz, 2H), 2.40 (td, *J* = 11.5, 7.5 Hz, 1H), 2.18 (dd, *J* = 12.0, 4.8 Hz, 1H), 1.14 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, d-DMSO, 80 ^{o}C) δ 149.9, 132.9, 130.4, 125.1, 122.2, 119.0, 103.6, 66.5, 60.9, 37.7, 36.2, 25.0, 15.7. IR (KBr): 3446.8, 2965.7, 2860.6, 2364.3, 1464.9, 1261.4, 1018.2, 919.8 cm^{-1}; Exact mass calcd. for $C_{26}H_{33}N_2O_4^+$ $[M+H]^+$: 405.2537; Found: 405.2531.



7,7',8,8'-tetramethyl-2,2',3,3',8,8a,8',8'a-octahydro-3a,3'a-bifuro[2,3-*b*]indole

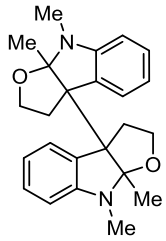
2j white solid, 17 h, 35.0 mg, 93% yield. 1.5/1 dr; for the major isomer: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.99 (d, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 7.5 Hz, 1H), 6.60 (t, *J* = 7.5 Hz, 1H), 5.00 (s, 1H), 3.90 (t, *J* = 7.8 Hz, 1H), 3.38 (ddd, *J* = 11.3, 8.6, 4.9 Hz, 1H), 3.19 (s, 3H), 2.44 (td, *J* = 11.6, 7.5 Hz, 1H), 2.38 (s, 3H), 2.06 (dd, *J* = 12.0, 4.7 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 150.1, 131.9, 131.3, 122.3, 118.4, 118.2, 103.6, 66.5, 60.2, 37.0, 36.0, 19.4. for the minor isomer: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.85 (br, 1H), 6.54 (br, 2H), 4.95 (s, 1H), 4.02 (t, *J* = 8.0 Hz, 1H), 3.47 (ddd, *J* = 12.0, 8.8, 4.7 Hz, 1H), 2.79 (s, 3H), 2.43 (dd, *J* = 19.0, 11.3 Hz, 1H), 2.31 (s, 3H), 2.22 (dd, *J* = 11.7, 4.6 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 150.7, 132.1, 131.8, 121.9, 119.0, 103.8, 66.7, 61.2, 37.5, 36.7, 19.2. IR (KBr): 3419.8, 2924.3, 2360.1, 1595.7, 1465.9,

1261.0, 1093.4 cm^{-1}. HRMS-ESI: Exact mass calcd. for $C_{24}H_{28}N_2O_2Na^+$ $[M+Na]^+$: 399.2048; Found: 399.2042.



8,8'-dibenzyl-2,2',3,3',8,8a,8',8'a-octahydro-3a,3'a-bifuro[2,3-*b*]indole

2k white solid, 48 h, 22.6 mg, 45% yield. 1.5/1 dr; A purified mixture isomers of 5/1 dr were determined by NMR: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.34 (dt, *J* = 12.9, 7.4 Hz, 4H), 7.27 - 7.25 (m, 1H), 6.99 - 6.95 (m, 1H), 6.54 (t, *J* = 7.4 Hz, 1H), 6.26 (d, *J* = 7.8 Hz, 1H), 5.46 (s, 1H), 4.49 (s, 2H), 4.35 (s, 0.4H), 4.04 - 4.01 (m, 0.2H), 3.96 (t, *J* = 7.9 Hz, 1H), 3.54 - 3.49 (m, 0.2H), 3.44 (ddd, *J* = 11.6, 8.7, 4.9 Hz, 1H), 2.49 - 2.44 (m, 1.2H), 2.33 - 2.26 (m, 0.2H), 2.08 (dd, *J* = 11.9, 4.7 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 151.1, 138.3, 130.2, 128.5, 128.5, 127.5, 127.1, 124.1, 117.2, 105.4, 100.2, 66.4, 61.4, 48.6, 37.2. IR (KBr): 3446.0, 2934.3, 2873.7, 2358.2, 2337.3, 1608.9, 1473.7, 1368.6, 1109.5, 1031.5, 913.6 cm^{-1}. HRMS-ESI: Exact mass calcd. for $C_{34}H_{33}N_2O_2^+$ $[M+H]^+$: 501.2537; Found: 501.2535.



8,8a,8',8'a-tetramethyl-2,2',3,3',8,8a,8',8'a-octahydro-3a,3'a-bifuro[2,3-*b*]indole

2l white solid, 48 h, 12.0 mg, 32% yield. 1/1 dr; for the mixture of the two diastereomers: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.8 Hz, 1H), 7.20 - 7.16 (m, 3H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.70 (t, *J* = 7.4 Hz, 1H), 6.39 (d, *J* = 7.9 Hz, 1H), 3.88 (t, *J* = 8.1 Hz, 1H), 3.60 (s, 3H), 3.39 - 3.31 (m, 3H), 2.95 - 2.90 (m, 2H), 2.77 (s, 3H), 2.44 (td, *J* = 11.8, 7.7 Hz, 1H), 2.34 (dd, *J* = 11.7, 4.7 Hz, 1H), 2.24 (s, 3H), 1.48 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.2, 136.4, 133.6, 130.2, 127.7, 126.3, 124.7, 120.4, 118.6, 117.8, 117.4, 108.4, 107.0, 106.1, 91.7, 65.8, 65.5, 40.0, 29.4, 27.8, 25.8, 19.2, 10.1. IR (KBr): 3439.4, 2934.5, 2867.7, 1608.7, 1371.9,

1110.0, 1031.7, 913.8 cm^{-1}. HRMS-ESI: Exact mass calcd. for $C_{24}H_{29}N_2O_2^+$ $[M+H]^+$: 377.2221; Found: 377.2224.

5. X-ray Dates

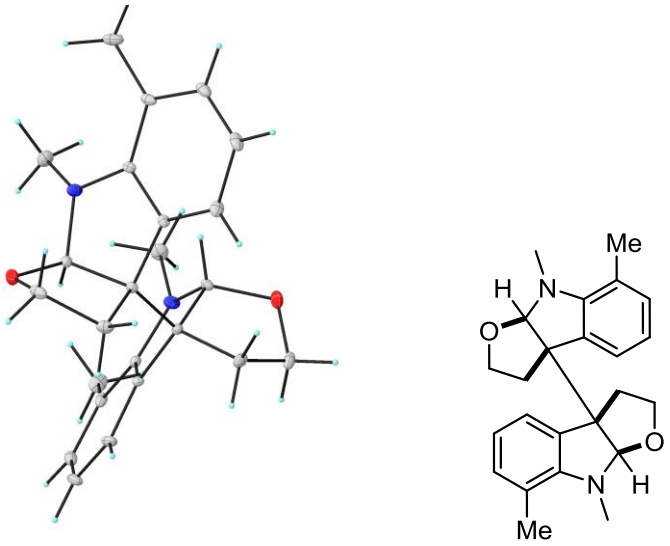


Figure S1. Crystal structure of major isomer **2j'** (CCDC number：1915998)

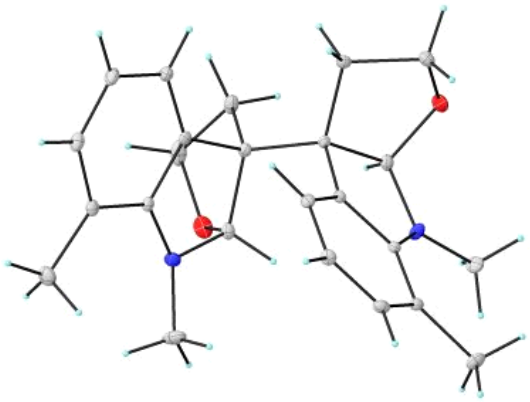
Bond precision:	C-C = 0.0044 A	Wavelength=1.54184	
Cell:	a=38.8350(15)	b=12.1246(6)	c=8.3689(4)
	alpha=90	beta=90	amma=90
Temperature:	293 K		
	Calculated	Reported	
Volume	3940.6(3)	3940.6(3)	
Space group	F d d 2	F d d 2	
Hall group	F 2 -2d	F 2 -2d	
Moiety formula	C24 H28 N2 O2	C24 H28 N2 O2	
Sum formula	C24 H28 N2 O2	C24 H28 N2 O2	
Mr	376.48	376.48	
Dx,g cm-3	1.269	1.269	
Z	8	8	
Mu (mm-1)	0.635	0.635	
F000	1616.0	1616.0	
F000'	1620.50		
h,k,lmax	45,14,9	45,14,9	

Nref	1681[904]	1659
Tmin,Tmax	0.892,0.927	0.650,1.000
Tmin’	0.892	

Correction method= # Reported T Limits: Tmin=0.650 Tmax=1.000

AbsCorr = MULTI-SCAN

Data completeness= 1.84/0.99	Theta(max)= 64.920
R(reflections)= 0.0404(1548)	wR2(reflections)= 0.1132(1659)
S = 1.068	Npar= 130



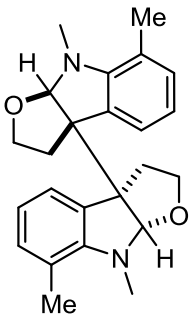


Figure S2. Crystal structure of minor isomer **2j”** (CCDC number：1915999)

Bond precision:	C-C = 0.0047 A	Wavelength=0.71073	
Cell:	a=30.916(2)	b=30.916(2)	c=8.2746(14)
	alpha=90	beta=90	gamma=90
Temperature:	293 K		
	Calculated	Reported	
Volume	7908.9(17)	7908.9(17)	
Space group	I 41/a	I 41/a	
Hall group	-I 4ad	-I 4ad	
Moiety formula	$C_{24}H_{28}N_2O_2$	$C_{24}H_{28}N_2O_2$	
Sum formula	$C_{24}H_{28}N_2O_2$	$C_{24}H_{28}N_2O_2$	

Mr	376.48	376.48
Dx,g cm^{-3}	1.265	1.265
Z	16	16
Mu (mm-1)	0.080	0.080
F000	3232.0	3232.0
F000’	3233.28	
h,k,lmax	39,39,10	39,38,10
Nref	4321	4281
Tmin,Tmax	0.986,0.991	0.301,1.000

Tmin’ 0.979

Correction method= # Reported T Limits: Tmin=0.301 Tmax=1.000

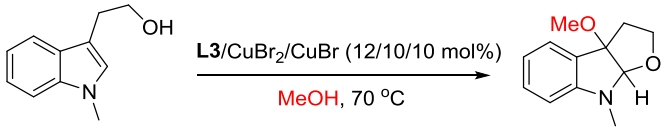
AbsCorr = MULTI-SCAN

Data completeness= 0.991 Theta(max)= 26.995

R(reflections)= 0.0808(1975) wR2(reflections)= 0.1752(4281)

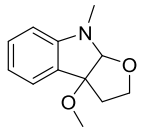
S = 1.033 Npar= 257

6. General procedure for alkoxylation and Product Characterizations



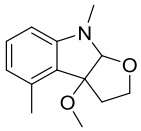
1a **3**

Procedure: A mixture of $CuBr_2$ (4.5 mg, 0.02 mmol), CuBr (2.9 mg, 0.02 mmol), **L3** (7.0 mg, 0.024 mmol) and **1a** (35.0 mg) in dry MeOH (10 mL) was stirred at 70 °C under the atmosphere of Ar. 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 (hexane/ethyl acetate = 8/1) to afford the product **3**.



3a-methoxy-8-methyl-3,3a,8,8a-tetrahydro-2*H*-furo[2,3-*b*]indole

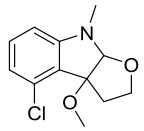
3 Light yellow oil, 23 h, 25.5 mg, 62% yield. 20/1 dr; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.03 (d, *J* = 7.8 Hz, 2 H), 6.84 (dd, *J* = 7.8, 1.6 Hz, 1 H), 6.55 (d, *J* = 1.2 Hz, 1 H), 5.31 (s, 1 H), 4.05 - 4.02 (m, 1H), 3.56 - 3.55 (m, 1 H), 3.11 (s, 3 H), 2.90 (s, 3 H), 2.42 (td, *J* = 11.4, 7.8 Hz, 1H), 2.22 (ddd, *J* = 11.4, 5.0, 1.1 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 152.0, 130.2, 126.2, 124.4, 117.5, 105.8, 100.0, 93.5, 70.0, 53.1, 40.5, 30.8. **IR** (KBr): 3441.8, 2945.3, 2823.2, 1709.7, 1422.3, 1224.3, 1033.6 cm^{-1}; HRMS-ESI: Exact mass calcd. for $C_{12}H_{16}NO_2^+$ $[M+H]^+$: 206.1176; Found: 206.1176.



3a-methoxy-4,8-dimethyl-3,3a,8,8a-tetrahydro-2*H*-furo[2,3-*b*]indole

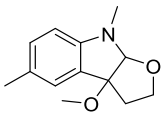
4 Light yellow oil, 17 h, 39.4 mg, 90% yield. 3/1 dr; for the mixture of the two diastereomers: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.4 Hz, 0.33 H), 7.11 (t, *J* =

7.8 Hz, 1H), 6.51 (d, *J* = 7.8 Hz, 1 H), 6.27 (d, *J* = 7.8 Hz, 1 H), 6.16 (d, *J* = 8.4 Hz, 0.33 H), 5.33 (s, 1+0.33H), 4.04 - 4.01 (m, 1+0.33H), 3.61 - 3.56 (m, 1+0.33H), 3.04 (s, 3+1H), 2.91 (s, 3H), 2.88 (s, 1 H), 2.42 - 2.38 (m, 1+0.33H), 2.35 (s, 1H), 2.34 (d, J = 2.6 Hz, 0.33H), 2.31 (s, 3+1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 152.0, 151.1, 135.6, 135.1, 133.7, 130.1, 125.2, 123.2, 119.5, 112.8, 104.7, 103.2, 100.2, 100.0, 94.2, 66.4, 66.3, 53.0, 52.9, 40.1, 39.8, 31.0, 30.9, 17.4, 17.1. **IR** (KBr): 3419.0, 2945.5, 1709.8, 1422.2, 1364.3, 1224.4, 1030.9. HRMS-ESI: Exact mass calcd. for $C_{13}H_{18}NO_2^+$ $[M+H]^+$: 220.1332; Found: 220.1331.



4-chloro-3a-methoxy-8-methyl-3,3a,8,8a-tetrahydro-2*H*-furo[2,3-*b*]indole

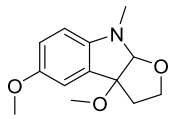
5 Light yellow oil, 23 h, 22.9 mg, 48% yield. 6/1 dr; for the mixture of the two diastereomers: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.21 - 7.19 (m, 0.18H), 7.13 (t, *J* = 8.0 Hz, 1H), 6.74 (t, *J* = 7.4 Hz, 0.18H), 6.66 (d, *J* = 8.0 Hz, 1H), 6.44 (d, *J* = 7.8 Hz, 0.18H), 6.31 (d, *J* = 7.9 Hz, 1H), 5.32 (d, *J* = 6.0 Hz, 1+0.18H), 4.07 - 4.03 (m, 1+0.18H), 3.56 - 3.55 (m, 1+0.18H), 3.11 (s, 3+0.54H), 2.92 (s, 3+0.54H), 2.60 - 2.57 (m, 1H), 2.43 - 2.38 (m, 1+0.18H), 2.28 - 2.25 (m, 0.18H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 153.4, 131.6, 131.6, 130.2, 126.6, 124.4, 122.0, 118.1, 117.5, 105.8, 103.9, 100.0, 99.8, 93.9, 67.0, 66.7, 53.3, 53.1, 40.5, 39.0, 30.8, 30.7. **IR** (KBr): 3418.8, 2946.3, 2832.2, 1704.6, 1422.9, 1365.0, 1228.7, 1093.4, 1031.7. HRMS-ESI: Exact mass calcd. for $C_{12}H_{15}ClNO_2^+$ $[M+H]^+$: 240.0786; Found: 240.0785.



3a-methoxy-5,8-dimethyl-3,3a,8,8a-tetrahydro-2*H*-furo[2,3-*b*]indole

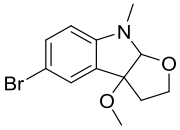
6 Light yellow oil, 24 h, 24.1 mg, 55% yield. >20/1 dr; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.02 (d, *J* = 6.8 Hz, 2H), 6.36 (d, *J* = 8.6 Hz, 1H), 5.29 (s, 1H), 4.03 (ddd, *J* = 9.2, 7.8, 1.8 Hz, 1H), 3.56 (ddd, *J* = 11.2, 8.9, 5.2 Hz, 1H), 3.12 (s, 3H), 2.90 (s, 3H), 2.43 (td, *J* = 11.5, 7.8 Hz, 1H), 2.29 (s, 3H), 2.26 (ddd, *J* = 11.9, 5.2, 1.8 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 150.0, 130.6, 126.9, 126.4, 125.0, 105.8, 100.4, 93.5, 67.0, 53.0, 40.4, 31.2, 20.7. **IR** (KBr): 3441.9, 3002.6, 2945.6, 2827.1, 1709.5, 1422.1,

1364.4, 1224.6, 1031.7. HRMS-ESI: Exact mass calcd. for $C_{13}H_{18}NO_2^+$ $[M+H]^+$: 220.1332; Found: 220.1331.



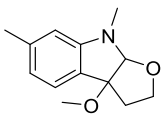
3a,5-dimethoxy-8-methyl-3,3a,8,8a-tetrahydro-2*H*-furo[2,3-*b*]indole

7 Light yellow oil, 23 h, 33.0 mg, 70% yield. >20/1 dr; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.84 - 6.79 (m, 2H), 6.38 (d, *J* = 8.5 Hz, 1H), 5.29 (s, 1H), 4.05 - 4.02 (m, 1H), 3.77 (s, 3H), 3.61 - 3.55 (m, 1H), 3.12 (s, 3H), 2.89 (s, 3H), 2.43 (td, *J* = 11.5, 7.7 Hz, 1H), 2.26 (ddd, *J* = 12.0, 5.2, 1.8 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 152.7, 146.5, 127.5, 115.4, 110.9, 106.6, 100.7, 93.5, 66.9, 56.0, 53.1, 40.4, 31.8. **IR** (KBr): 3424.9, 2945.8, 2831.0, 1709.5, 1422.4, 1364.9, 1226.5. HRMS-ESI: Exact mass calcd. for $C_{13}H_{18}NO_3^+$ $[M+H]^+$: 236.1281; Found: 236.1281.



5-bromo-3a-methoxy-8-methyl-3,3a,8,8a-tetrahydro-2*H*-furo[2,3-*b*]indole

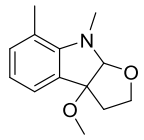
8 Light yellow oil, 41 h, 35.0 mg, 63% yield. 16/1 dr; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.03 (d, J = 7.8 Hz, 1H), 6.84 (dd, J = 7.8 Hz, 1.8 Hz, 1H), 6.55 (d, J = 1.4 Hz, 1H), 5.31 (s, 1H), 4.06 - 4.03 (m, 1H), 3.54 - 3.53 (m, 1H), 3.11 (s, 3H), 2.90 (s, 3H), 2.45-2.40 (m, 1H), 2.23 -2.20 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) 153.1, 125.6, 125.4, 124.3, 120.2, 108.8, 99.8, 93.1, 66.9, 53.1, 40.5, 30.5. **IR** (KBr): 3350.75, 2974.09, 2884.99, 1708.86, 1423.21, 1379.87. HRMS-ESI: Exact mass calcd. for $C_{12}H_{15}BrNO_2^+$ $[M+H]^+$: 284.0281; Found: 284.0278.



3a-methoxy-6,8-dimethyl-3,3a,8,8a-tetrahydro-2*H*-furo[2,3-*b*]indole

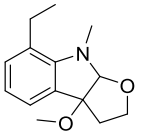
9 Light yellow oil, 29 h, 36.3 mg, 83% yield. 12/1 dr; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.10 (d, *J* = 7.4 Hz, 1H), 6.59 (d, *J* = 7.4 Hz, 1H), 6.29 (s, 1H), 5.32 (s, 1H), 4.07 - 4.04 (m, 1H), 3.60 - 3.55 (m, 1H), 3.13 (s, 3H), 2.93 (s, 3H), 2.47 - 2.42 (m, 1H), 2.35 (s, 3H), 2.27 (ddd, *J* = 11.8, 5.0, 1.2 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 152.3, 140.5, 124.2, 123.4, 118.3, 106.6, 100.3, 93.3, 67.0, 53.0, 40.5, 30.8, 21.9. **IR** (KBr): 3418.9, 2947.7, 2832.9,

1705.0, 1656.5, 1421.2, 1366.9, 1231.1, 1031.7. HRMS-ESI: Exact mass calcd. for $C_{13}H_{18}NO_2^+$ [M+H]$^+$: 220.1332; Found: 220.1331.



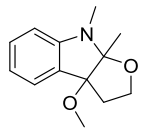
3a-methoxy-7,8-dimethyl-3,3a,8,8a-tetrahydro-2*H*-furo[2,3-*b*]indole

10 Light yellow oil, 23 h, 35.6 mg, 81% yield. >20/1 dr; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.99 (d, *J* = 7.3 Hz, 1H), 6.91 (d, *J* = 7.4 Hz, 1H), 6.67 (t, *J* = 7.4 Hz, 1H), 5.11 (s, 1H), 3.96 - 3.93 (m, 1H), 3.52 (ddd, *J* = 10.7, 9.1, 5.2 Hz, 1H), 3.09 (s, 3H), 3.03 (s, 3H), 2.38 - 2.34 (m, 1H), 2.33 (s, 3H), 2.16 (ddd, *J* = 11.9, 5.2, 1.9 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 150.5, 133.2, 127.6, 122.4, 119.5, 119.3, 102.7, 92.8, 66.6, 53.0, 40.5, 36.4, 19.2. **IR** (KBr): 3415.9, 2946.9, 2834.8, 1708.9, 1421.3, 1365.8, 1229.7, 1025.9. HRMS-ESI: Exact mass calcd. for $C_{13}H_{18}NO_2^+$ [M+H]$^+$: 220.1332; Found: 220.1331.



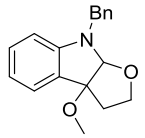
7-ethyl-3a-methoxy-8-methyl-3,3a,8,8a-tetrahydro-2*H*-furo[2,3-*b*]indole

11 Light yellow oil, 23 h, 42.6 mg, 92% yield. 14/1 dr; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.00 - 6.95 (m, 2H), 6.71 (t, *J* = 7.2 Hz, 1H), 5.12 (s, 1H), 3.93 (ddd, *J* = 9.4, 7.8, 2.0 Hz, 1H), 3.51 - 3.50 (m, 1H), 3.07 (s, 3H), 3.03 (s, 3H), 2.70 - 2.65 (m, 2H), 2.36 (td, *J* = 11.4, 7.6 Hz, 1H), 2.17 - 2.13 (m, 1H), 1.17 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (600 MHz, $CDCl_3$) δ 149.8, 131.4, 127.9, 125.9, 122.3, 119.4, 102.8, 92.6, 66.6, 53.0, 40.6, 36.5, 25.0, 15.2. **IR** (KBr): 3350.8, 2974.4, 2925.5, 2886.9, 1450.2, 1415.5, 1270.9, 1324.9, 1089.5. HRMS-ESI: Exact mass calcd. for $C_{14}H_{20}NO_2^+$ [M+H]$^+$: 234.1489; Found: 234.1483.



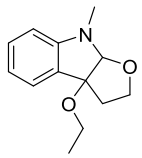
3a-methoxy-8,8a-dimethyl-3,3a,8,8a-tetrahydro-2*H*-furo[2,3-*b*]indole

12 Light yellow oil, 19 h, 86% yield. 5.5/1 dr; for the mixture of the two diastereomers: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.23 - 7.20 (m, 2.6H), 6.81 - 6.77 (m, 0.33H), 6.74 (dd, *J* = 10.8, 3.9 Hz, 1H), 6.52 (d, *J* = 7.8 Hz, 0.33H), 6.46 (d, *J* = 8.1 Hz, 1H), 4.09 (t, *J* = 8.3 Hz, 0.33H), 3.91 - 3.88 (m, 1H), 3.47 - 3.43 (m, 0.33H), 3.38 - 3.33 (m, 1H), 3.28 (s, 1H), 3.14 (s, 3H), 2.86 (s, 1H), 2.83 (s, 3H), 2.64 - 2.60 (m, 0.33H), 2.43 - 2.37 (m, 1+0.33H), 2.36 - 2.33 (m, 1H), 1.51 (s, 3+0.7H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 152.2, 130.5, 130.2, 125.5, 124.8, 124.7, 118.2, 117.3, 107.3, 106.1, 102.4, 92.7, 91.7, 67.4, 65.8, 53.3, 52.7, 39.2, 39.1, 31.6, 29.1, 27.7, 18.8. **IR** (KBr): 3350.9, 2974.2, 2883.0, 1708.9, 1378.9, 1230.3, 1093.44. HRMS-ESI: Exact mass calcd. for $C_{13}H_{18}NO_2^+$ $[M+H]^+$: 220.1332; Found: 220.1331.



8-benzyl-3a-methoxy-3,3a,8,8a-tetrahydro-2*H*-furo[2,3-*b*]indole

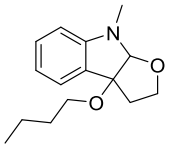
13 Light yellow oil, 18 h, 39.1 mg, 70% yield. >20/1 dr; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.32 - 7.28 (m, 4H), 7.24 (dt, *J* = 7.4, 2.7 Hz, 2H), 7.15 (td, *J* = 7.8, 1.2 Hz, 1H), 6.76 - 6.73 (m, 1H), 6.40 (d, *J* = 7.9 Hz, 1H), 5.42 (s, 1H), 4.55 (d, *J* = 16.0 Hz, 1H), 4.47 (d, *J* = 16.0 Hz, 1H), 4.06 - 4.05 (m, 1H), 3.63 (ddd, *J* = 11.6, 9.0, 5.0 Hz, 1H), 3.08 (s, 3H), 2.46 (td, *J* = 11.7, 7.7 Hz, 1H), 2.31 (ddd, *J* = 11.8, 4.9, 1.1 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 151.5, 138.0, 130.2, 128.5, 127.3, 127.1, 124.6, 117.8, 106.1, 98.5, 93.5, 66.8, 53.1, 48.5, 40.9. **IR (KBr)**: 3441.8, 2932.5, 2869.1, 2817.4, 2361.4, 1607.6, 1492.0, 1315.13, 1363.7, 1130.4, 1040.3, 946.1. HRMS-ESI: Exact mass calcd. for $C_{18}H_{20}NO_2^+$ $[M+H]^+$: 282.1489; Found: 282.1489.



3a-ethoxy-8-methyl-3,3a,8,8a-tetrahydro-2*H*-furo[2,3-*b*]indole

14 Light yellow oil, 23 h, 30.2 mg, 69% yield. 3/1 dr; A purified mixture isomers of 10/1 dr were determined by NMR: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.21 - 7.18 (m, 2H), 6.75 (ddd, *J* = 8.4, 5.4, 0.8 Hz, 1H), 6.46 (t, *J* = 8.0 Hz, 1H), 5.33 (d, *J* = 6.9 Hz, 1H), 4.06 (ddd, *J* = 9.0, 7.8, 1.8 Hz, 1H), 3.53 - 3.52 (m, 1H), 3.24 (qd, *J* = 7.0, 3.4

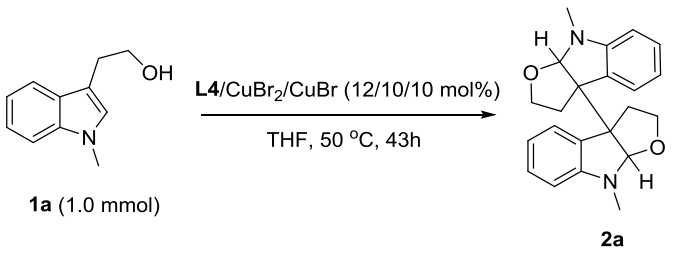
Hz, 2H), 2.94 (s, 3H), 2.85 (s, 0.26H), 2.47 - 2.44 (m, 1H), 2.33 - 2.27 (m, 1H), 1.15 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 151.9, 130.1, 127.1, 124.3, 117.4, 105.7, 100.3, 92.9, 66.8, 60.9, 40.9, 30.8, 15.6. **IR** (KBr): 3368.2, 2974.7, 1708.5, 1616.0, 1380.2, 1232.2, 1087.6, 1047.1, 946.1. HRMS-ESI: Exact mass calcd. for $C_{13}H_{18}NO_2^+$ [M+H]$^+$: 220.1332; Found: 220.1332.



3a-butoxy-8-methyl-3,3a,8,8a-tetrahydro-2*H*-furo[2,3-*b*]indole

15 Light yellow oil, 48 h, 16.7 mg, 34% yield. 3/1 dr; A purified mixture isomers of 5/1 dr were determined by NMR: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.21 – 7.16 (m, 2+0.4H), 6.75 - 6.71 (m, 1+0.2H), 6.44 - 6.42 (m, 1+0.2H), 5.30 (s, 1+0.2H), 4.08 (t, *J* = 8.3 Hz, 0.2H), 4.03 (ddd, *J* = 9.1, 7.7, 1.7 Hz, 1H), 3.53 (ddd, *J* = 11.4, 8.9, 5.1 Hz, 1H), 3.35 (ddd, *J* = 12.1, 8.9, 5.1 Hz, 0.2H), 3.20 – 3.13 (m, 2+0.4H), 2.92 (s, 3H), 2.82 (s, 0.6H), 2.53 - 2.49 (m, 0.2H), 2.45 (td, *J* = 11.6, 7.6 Hz, 1H), 2.34 (dd, *J* = 12.0, 4.9 Hz, 0.2H), 2.27 (ddd, *J* = 11.9, 5.1, 1.6 Hz, 1H), 1.51 - 1.47 (m, 2+0.4H), 1.34 -1.29 (m, 2+0.4H), 0.95 (t, *J* = 7.4 Hz, 0.6H), 0.87 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 151.9, 150.2, 130.3, 130.0, 127.2, 125.9, 124.5, 124.4, 117.9, 117.4, 106.0, 105.6, 100.2, 92.9, 87.8, 66.8, 65.2, 64.8, 64.0, 63.7, 40.9, 40.0, 32.5, 32.3, 32.2, 30.8, 19.3, 19.2, 14.0, 13.9. **IR** (KBr): 3367.8, 2974.4, 2923.5, 2883.0, 1656.5, 1612.2, 1452.1, 1087.6, 1048.8. HRMS-ESI: Exact mass calcd. for $C_{15}H_{22}NO_2^+$ [M+H]$^+$: 248.1645; Found: 248.1651.

7. 1.0 mmol Scale experiment



1a (1.0 mmol)

2a

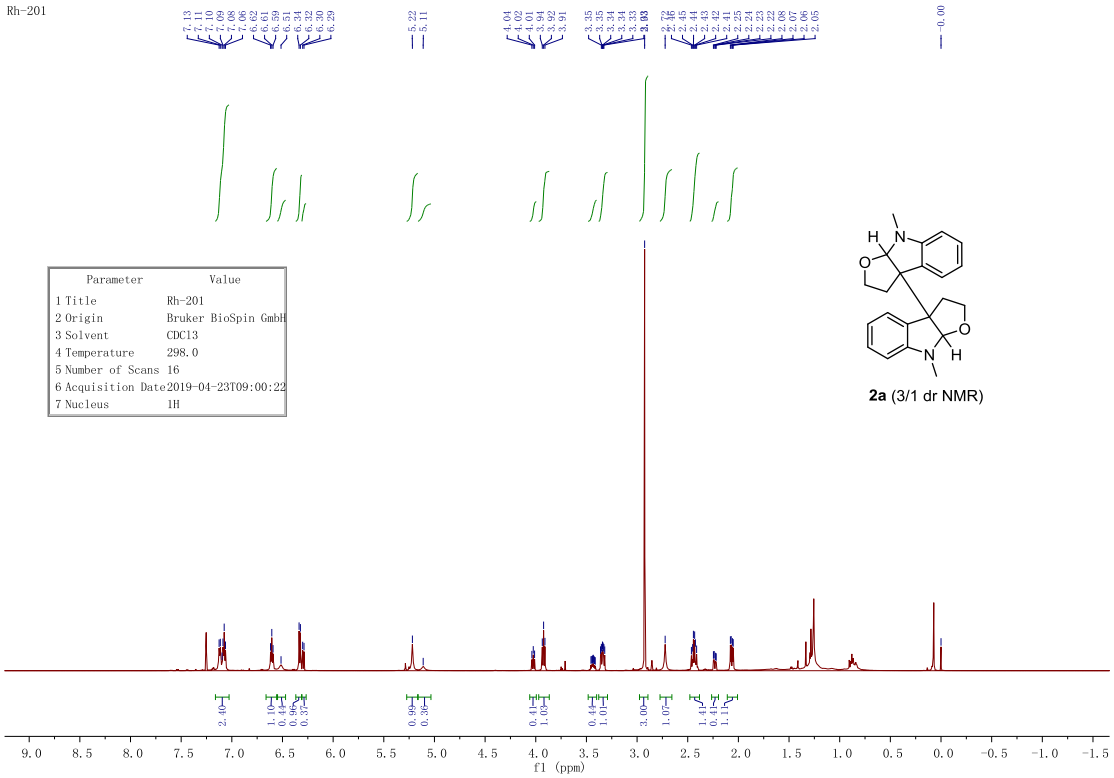
Procedure: A mixture of $CuBr_2$ (22.3 mg, 0.1 mmol), CuBr (14.3 mg, 0.1 mmol), **L4** (58.5 mg, 0.12 mmol) and **1a** (175 mg) in THF (10 mL) was stirred at 50 °C for 43 h under the atmosphere of Ar. The reaction was filtered through a glass funnel with thin layer (30 mm) of silica gel (100-200 mesh) and eluted with DCM/Ethyl Acetate. The filtrate was concentrated under reduced pressure, purified by flash chromatography (hexane/ethyl acetate = 8/1) to afford the product **2a** (73.8 mg, 42% yield**,** 2.3/1 dr).

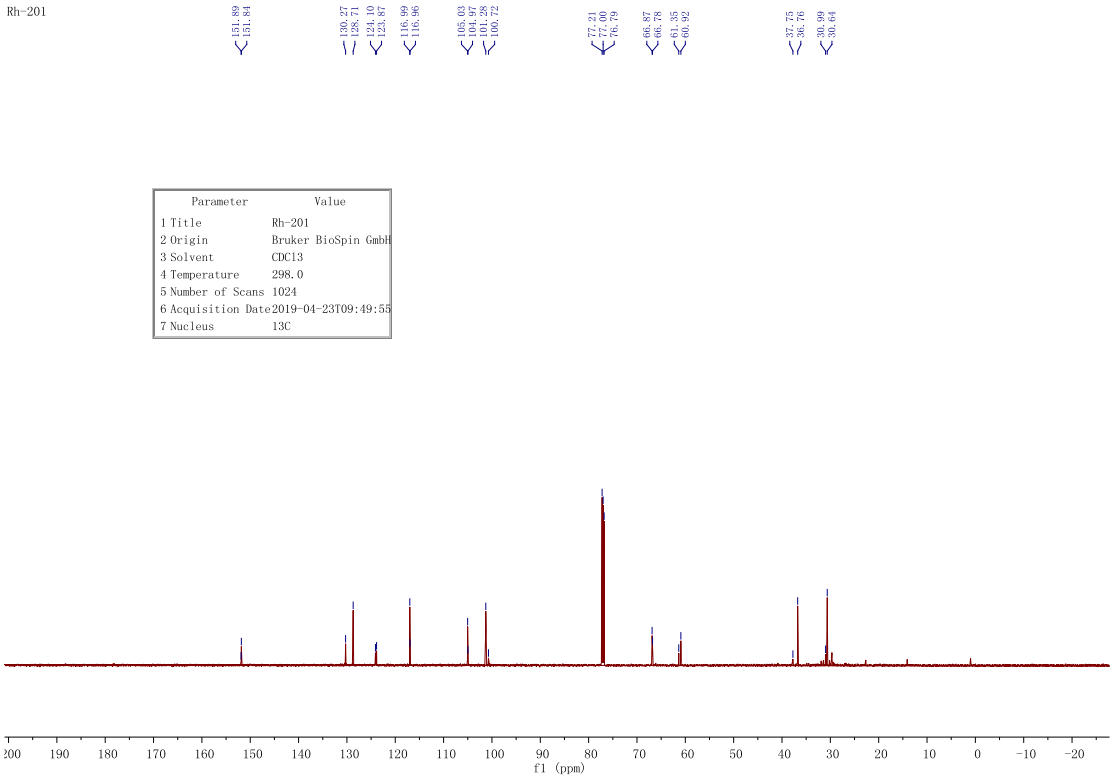
8. References

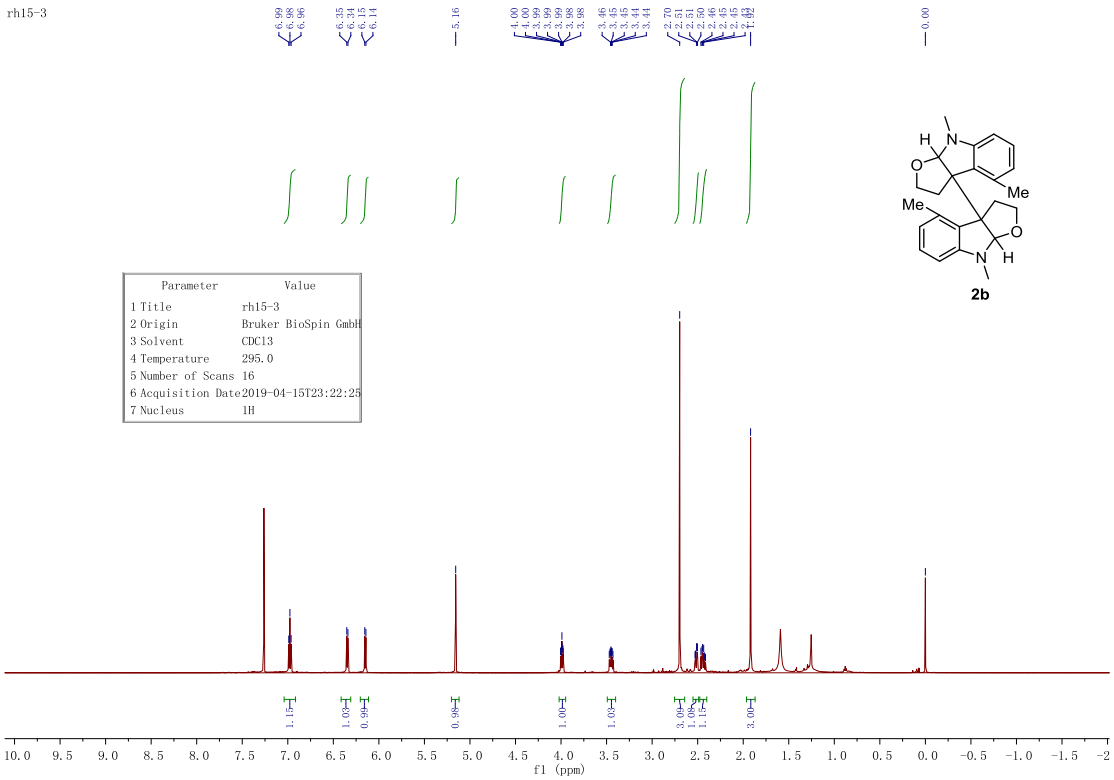
1. Jia, K.; Zhang, F.; Huang, H.; Chen, Y. *J. Am. Chem. Soc.* **2016**, *138*, 1514.

2. (a) Evans, D. A.; Olhava, E. J.; Johnson, J. S.; Janey, J. M. *Angew. Chem. Int. Ed.* **1998**, *37*, 3372. (b) Xiong, H.; Xu, H.; Liao, S.; Xie, Z.; Tang, Y. *J. Am. Chem. Soc.* **2013**, *135*, 7851.

9. ^{1}H NMR、and ^{13}C NMR Spectras After purification

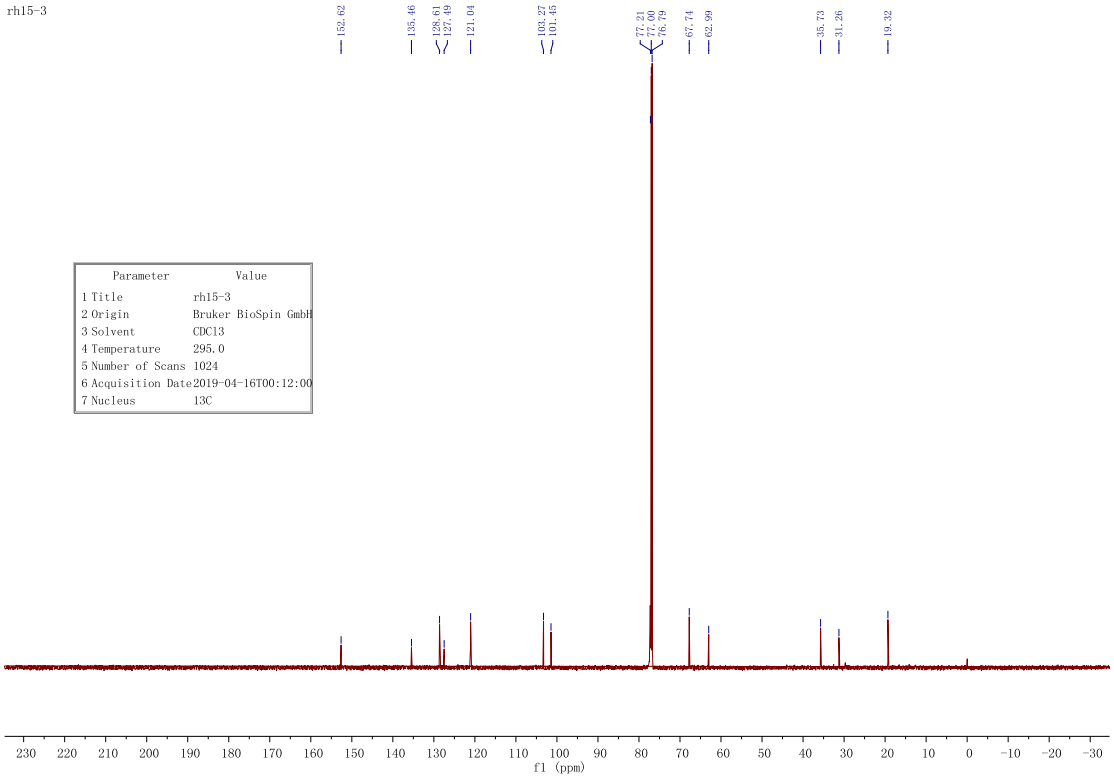


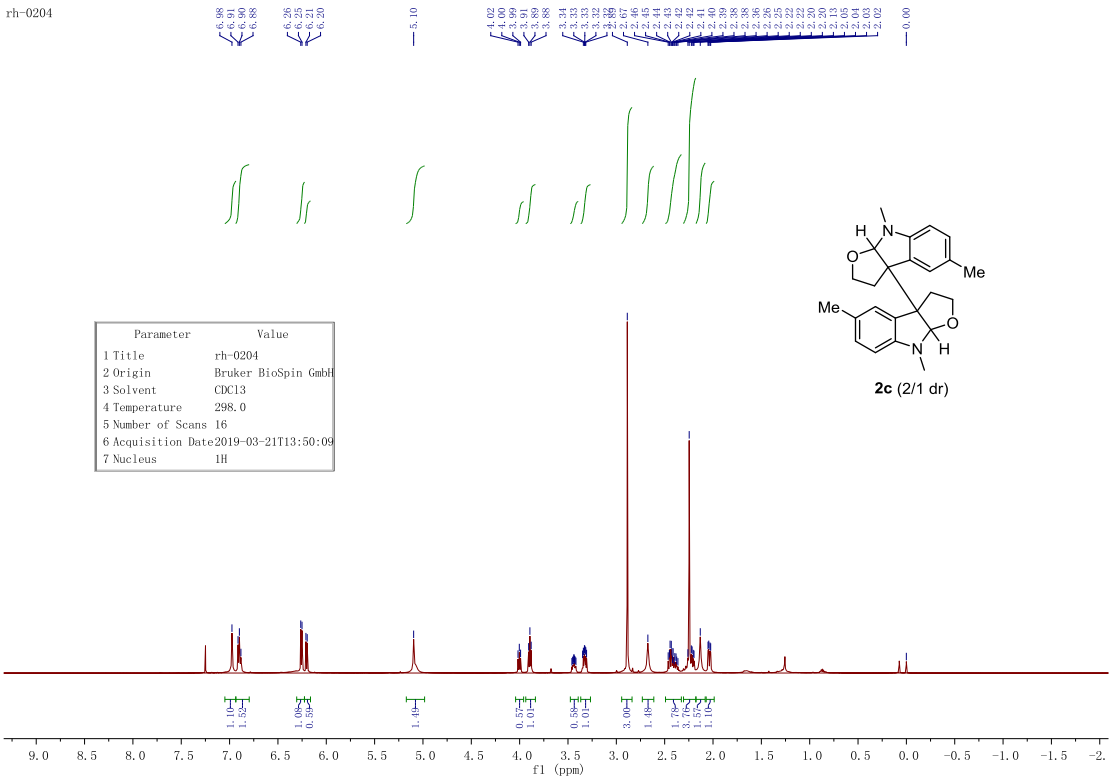



rh15-3
6.99
6.98
6.96
6.35
6.34
6.15
6.14
5.16
4.00
4.00
3.99
3.99
3.99
3.98
3.98
3.46
3.45
3.45
3.44
3.44
2.70
2.51
2.51
2.50
2.46
2.45
2.45
2.43
1.92
0.00
Parameter Value
1 Title rh15-3
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 295.0
5 Number of Scans 16
6 Acquisition Date 2019-04-15T23:22:25
7 Nucleus 1H
1.15
1.03
0.99
0.98
1.00
1.03
3.00
1.08
1.10
3.00
f1 (ppm)

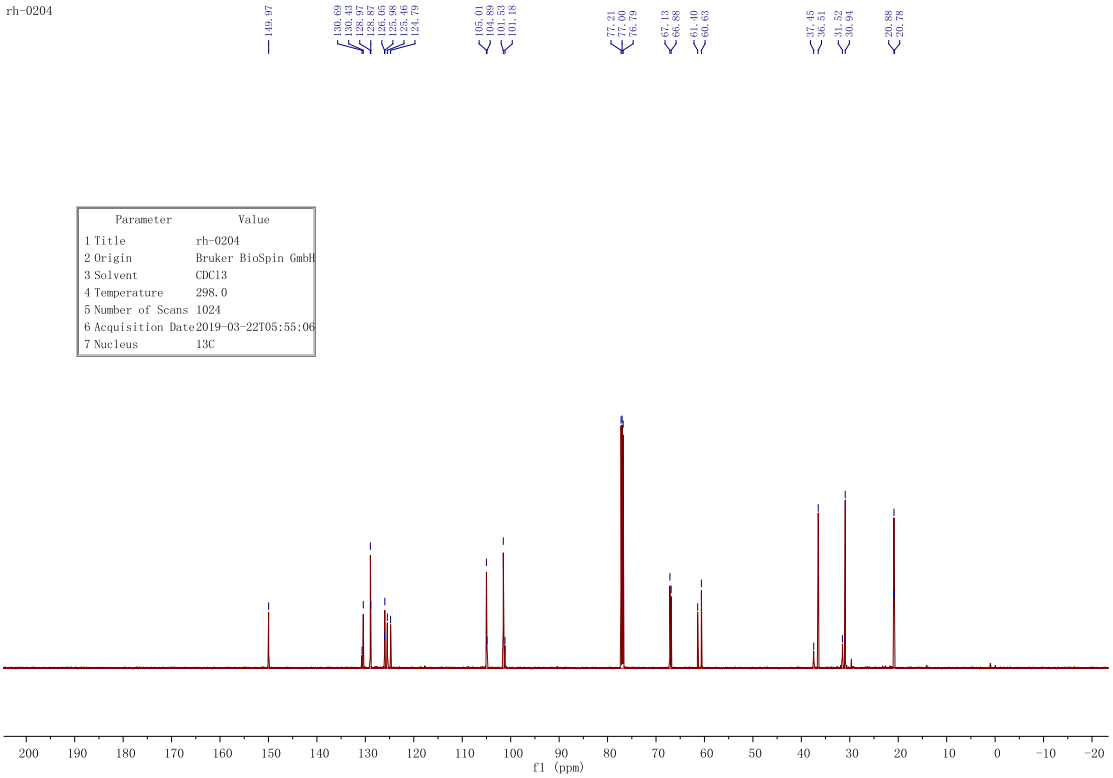
H
N
O
Me
Me
O
N
H

2b

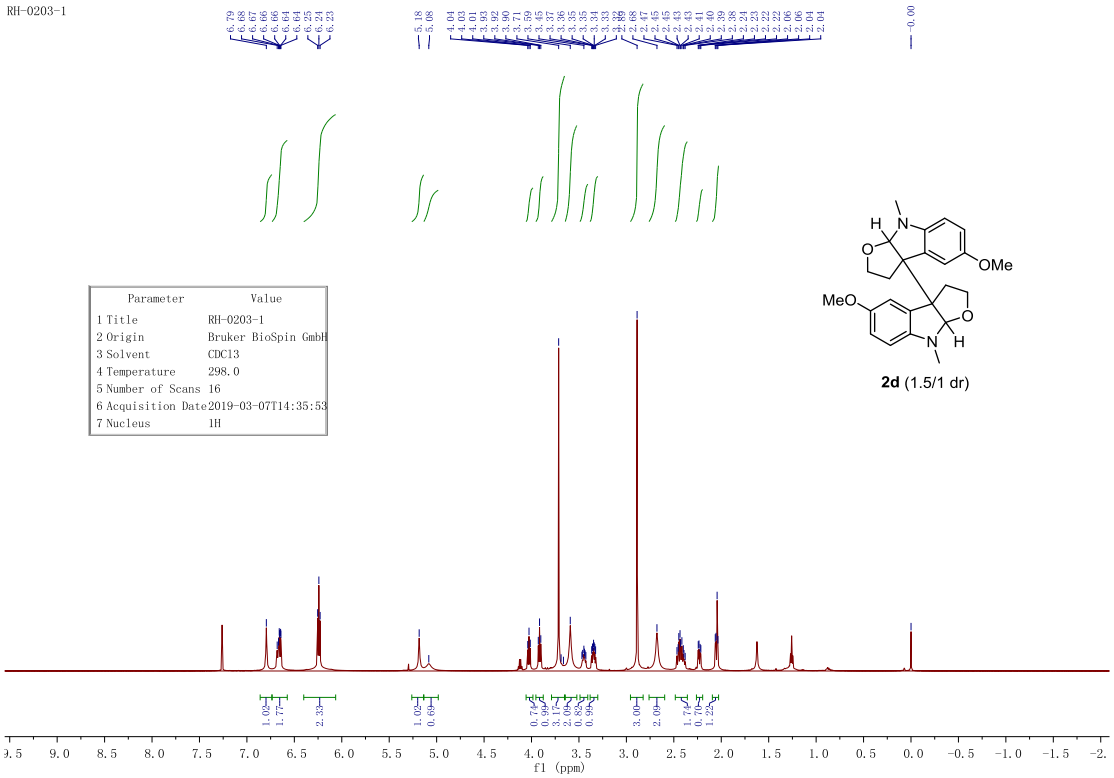

rh15-3
152.62
135.46
128.61
127.49
121.04
103.27
101.45
77.21
77.00
76.79
67.74
62.99
35.73
31.26
19.32
Parameter Value
1 Title rh15-3
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 295.0
5 Number of Scans 1024
6 Acquisition Date 2019-04-16T00:12:00
7 Nucleus 13C
f1 (ppm)


rh-0204
Parameter Value
1 Title rh-0204
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 298.0
5 Number of Scans 16
6 Acquisition Date 2019-03-21T13:50:09
7 Nucleus 1H
f1 (ppm)

2c (2/1 dr)


rh-0204
Parameter Value
1 Title rh-0204
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 298.0
5 Number of Scans 1024
6 Acquisition Date 2019-03-22T05:55:06
7 Nucleus 13C
f1 (ppm)

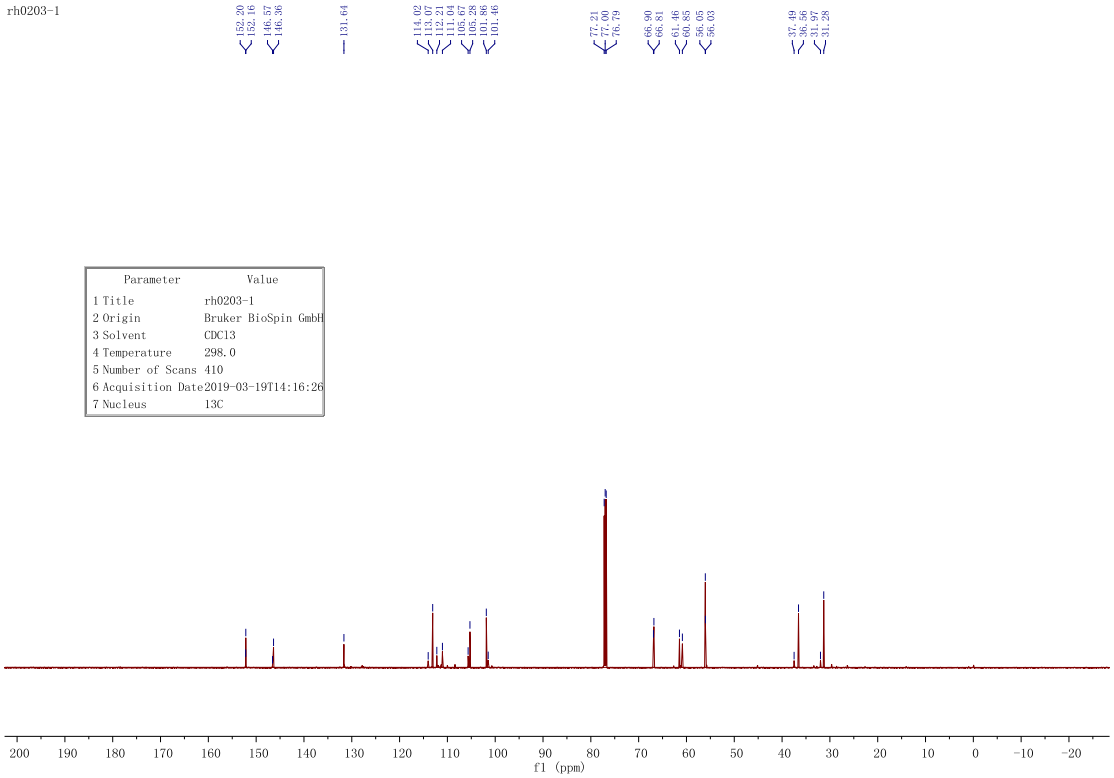
RH-0203-1



Parameter	Value
1 Title	RH-0203-1
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	16
6 Acquisition Date	2019-03-07T14:35:53
7 Nucleus	1H

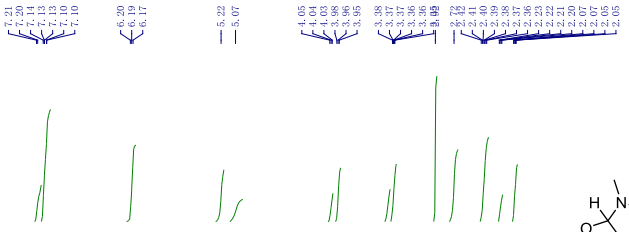
2d (1.5/1 dr)

rh0203-1

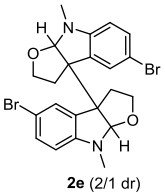


Parameter	Value
1 Title	rh0203-1
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	410
6 Acquisition Date	2019-03-19T14:16:26
7 Nucleus	13C

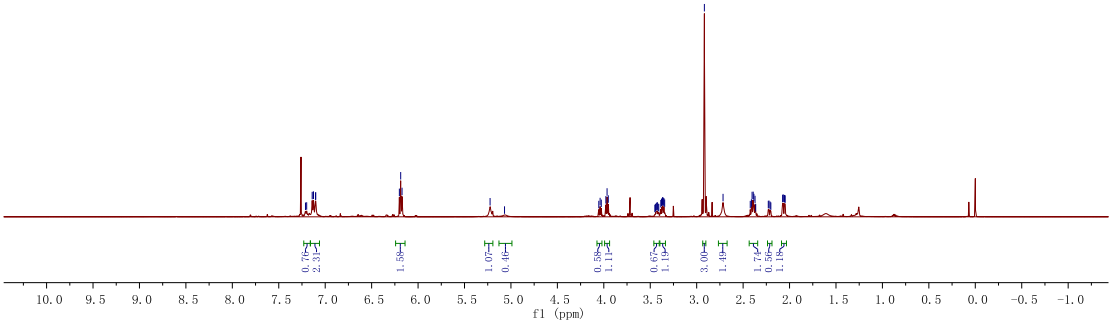
rh-0205-1



Parameter	Value
1 Title	rh-0205-1
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	16
6 Acquisition Date	2019-03-25T21:32:08
7 Spectrometer Frequency	600.13
8 Nucleus	1H

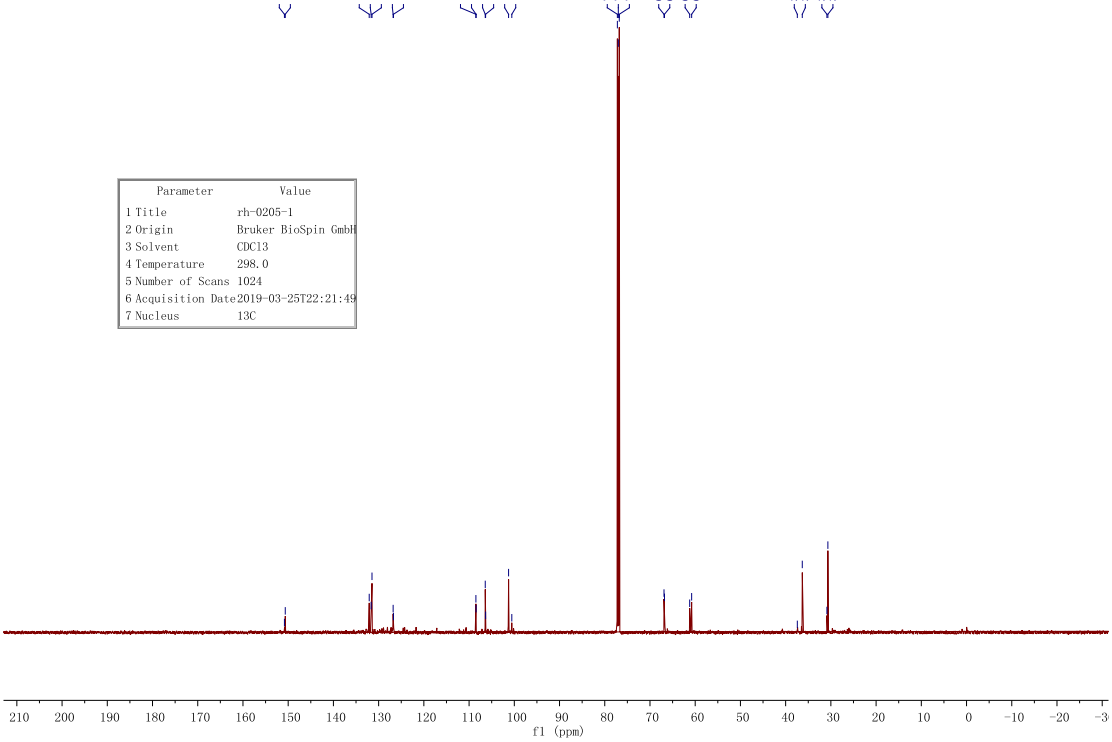


2e (2/1 dr)



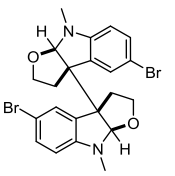
rh-0205-1

Parameter	Value
1 Title	rh-0205-1
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	1024
6 Acquisition Date	2019-03-25T22:21:49
7 Nucleus	13C



rh025

Parameter	Value
1 Title	rh025
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.0
5 Number of Scans	16
6 Acquisition Date	2019-05-22T18:27:06
7 Spectrometer Frequency	600.13
8 Nucleus	1H

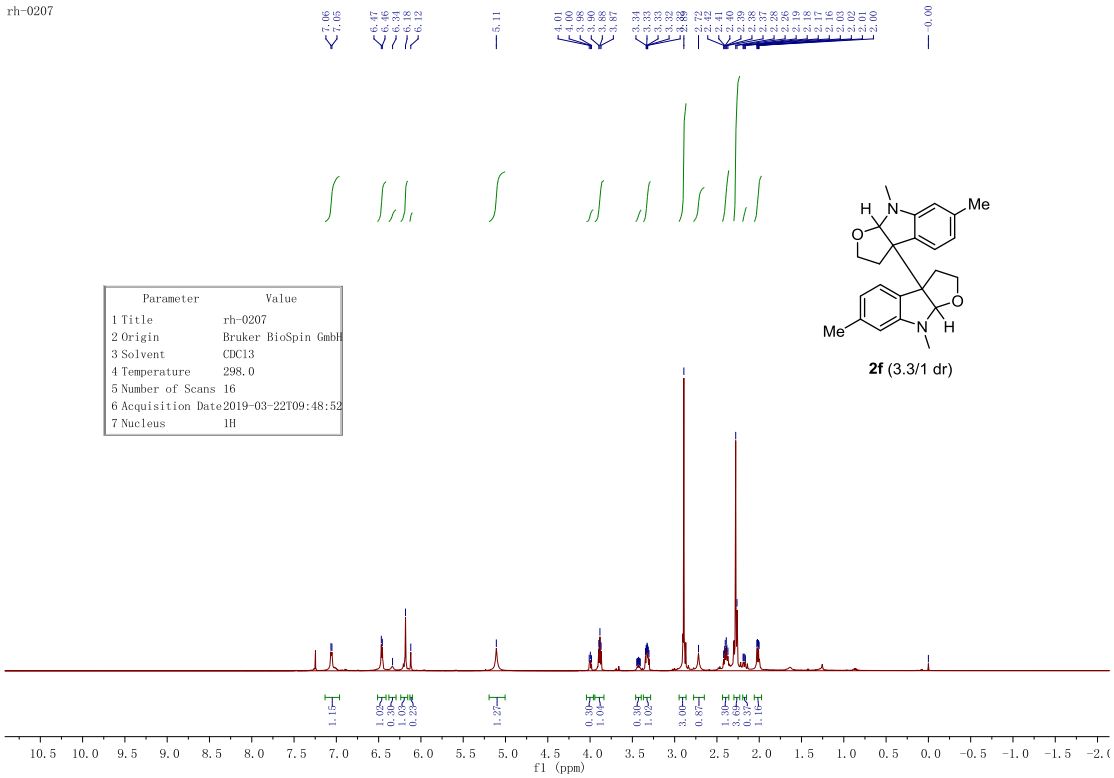


major isomer: 2e'

rh0205-C

Parameter	Value
1 Title	rh0205-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.0
5 Number of Scans	1024
6 Acquisition Date	2019-05-29T17:42:09
7 Spectrometer Frequency	150.90
8 Nucleus	13C

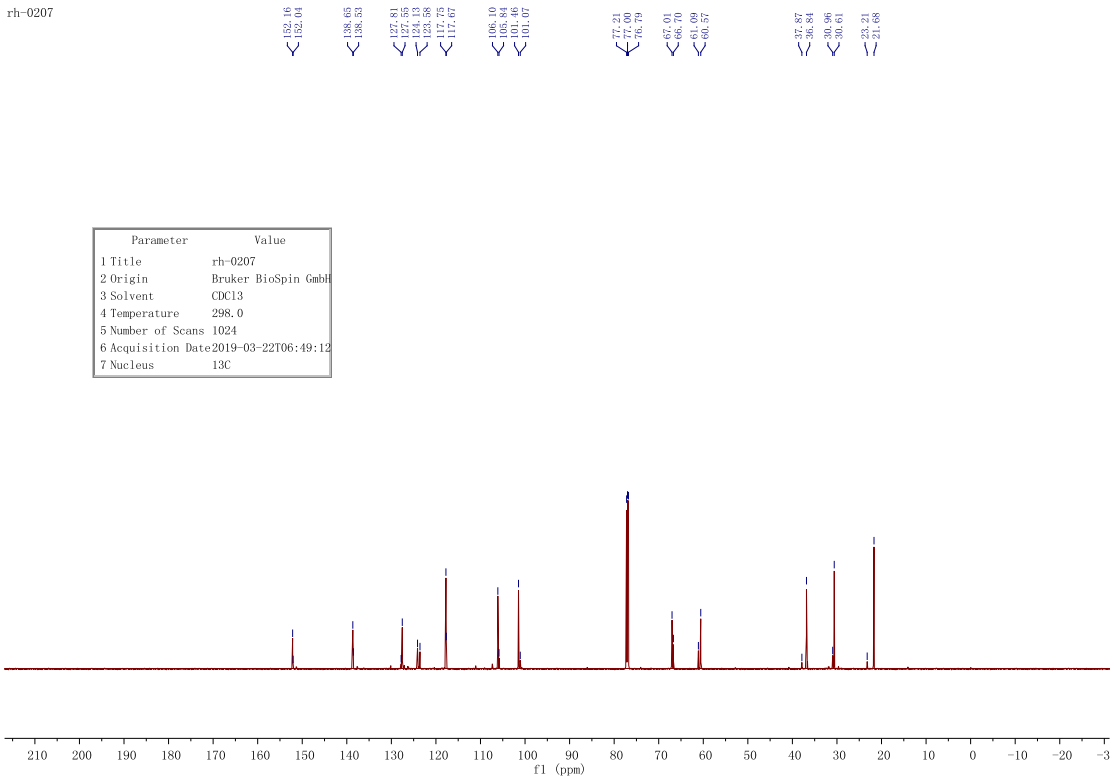
rh-0207



Parameter	Value
1 Title	rh-0207
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	16
6 Acquisition Date	2019-03-22T09:48:52
7 Nucleus	1H

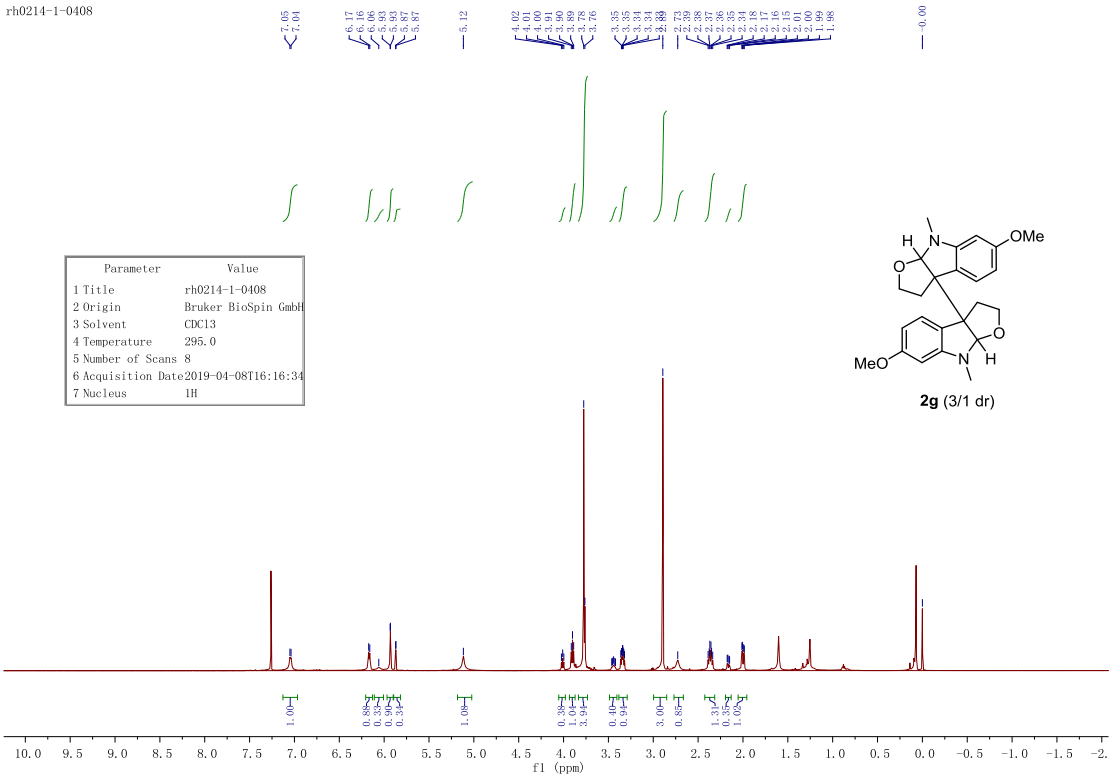
2f (3.3/1 dr)

rh-0207



Parameter	Value
1 Title	rh-0207
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	1024
6 Acquisition Date	2019-03-22T06:49:12
7 Nucleus	13C

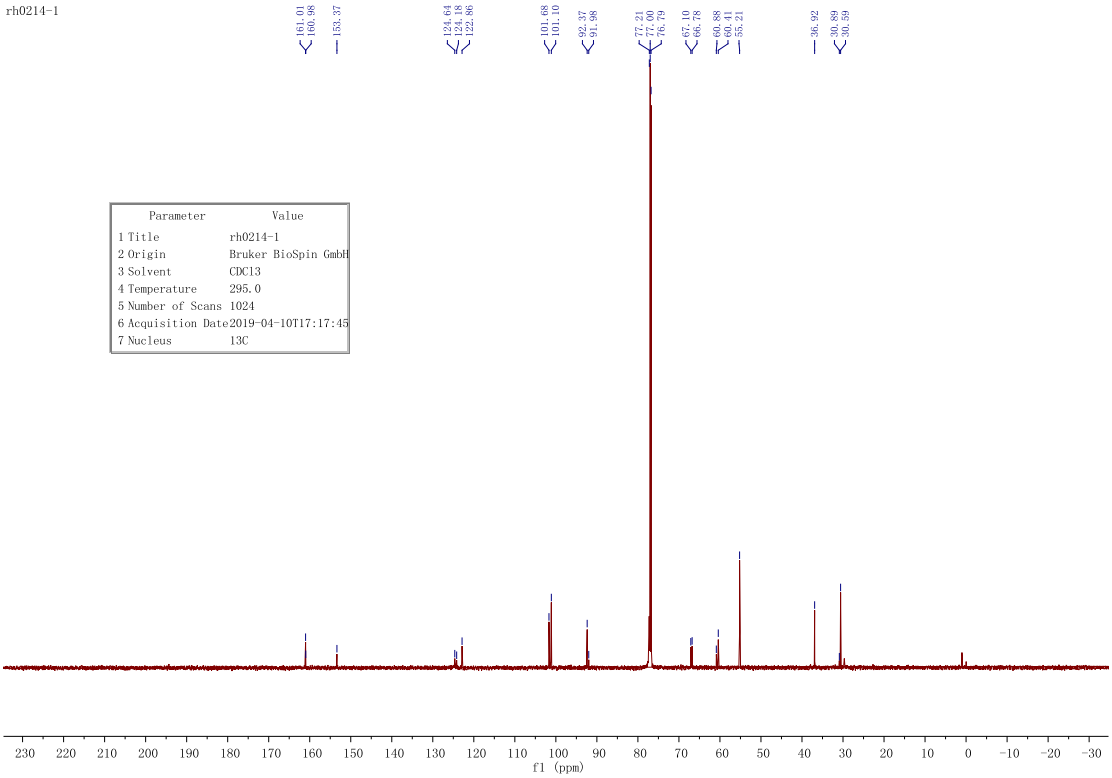
rh0214-1-0408



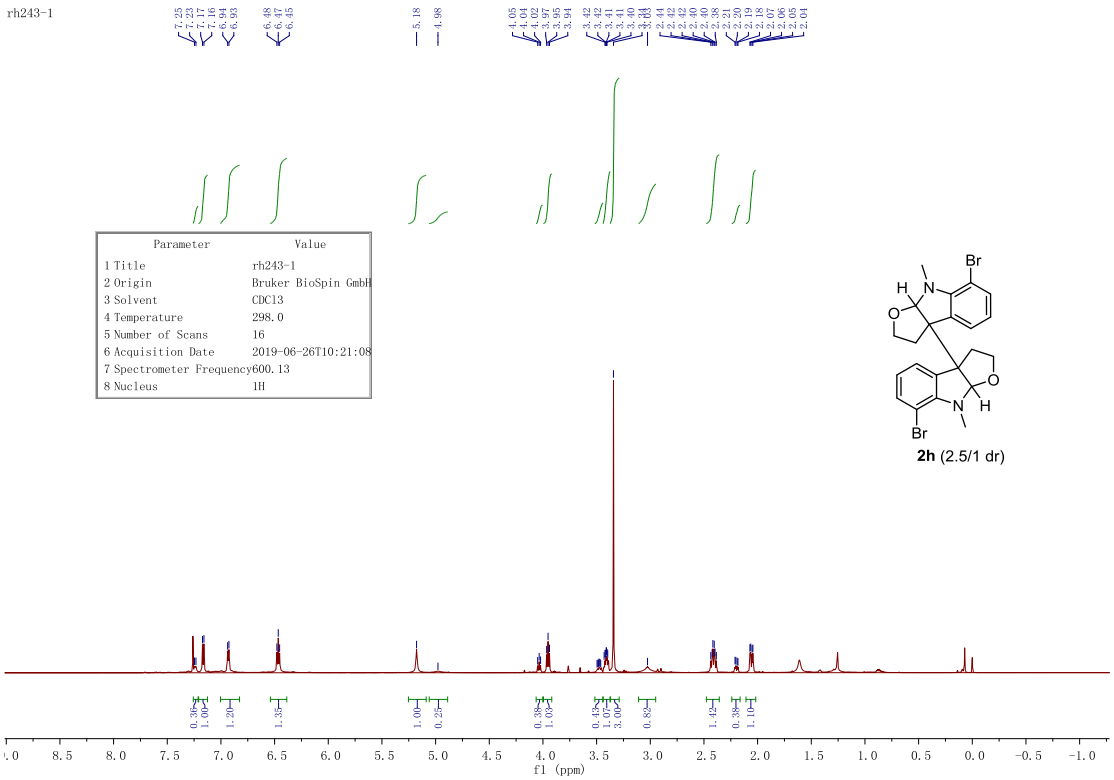
Parameter	Value
1 Title	rh0214-1-0408
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.0
5 Number of Scans	8
6 Acquisition Date	2019-04-08T16:16:34
7 Nucleus	1H

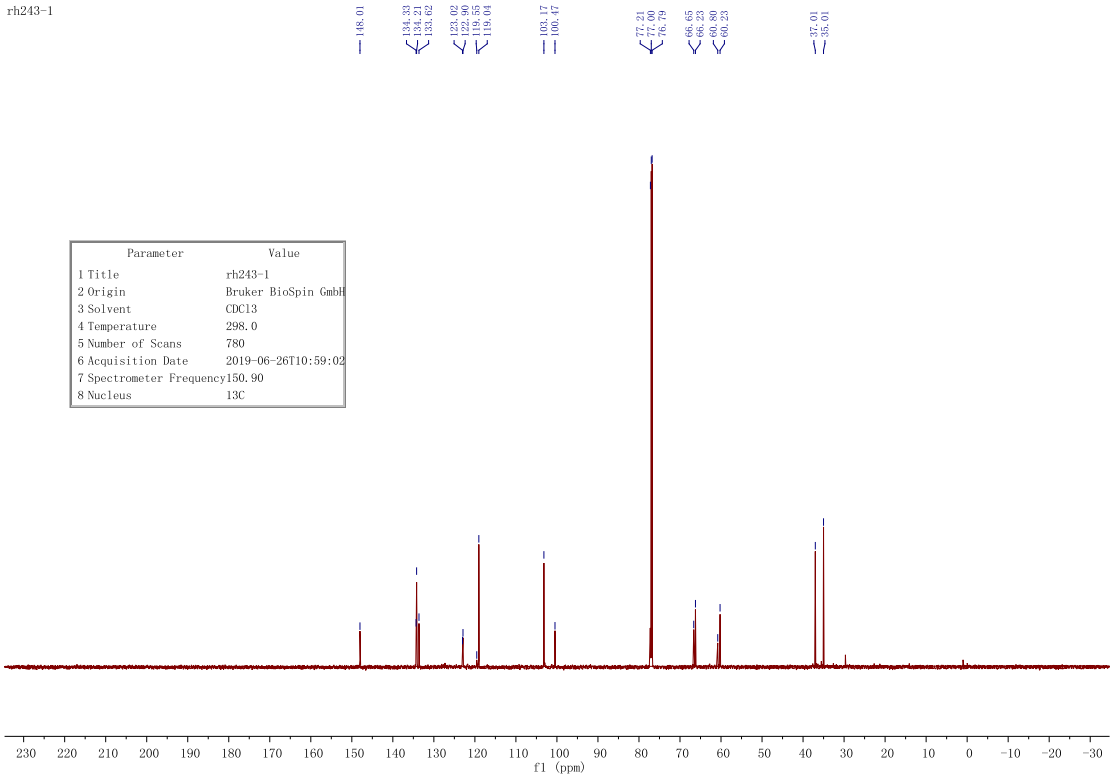
2g (3/1 dr)

rh0214-1

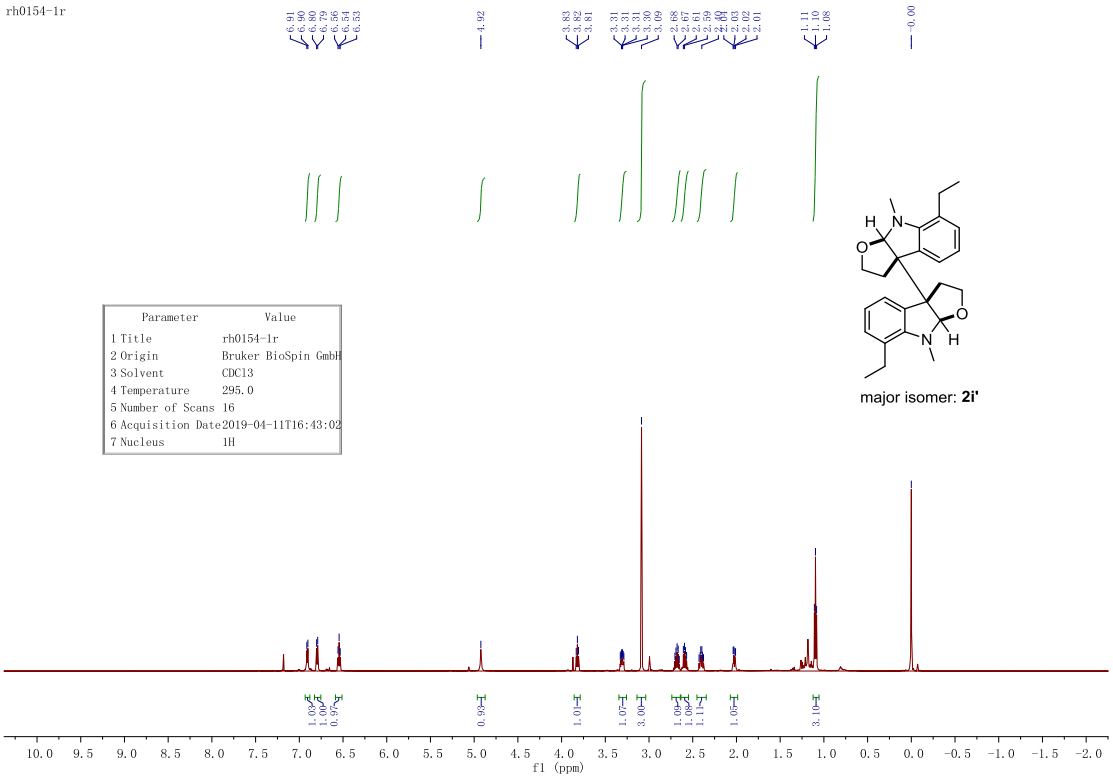


Parameter	Value
1 Title	rh0214-1
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.0
5 Number of Scans	1024
6 Acquisition Date	2019-04-10T17:17:45
7 Nucleus	13C


rh243-1
7.25
7.23
7.17
7.15
6.94
6.93
6.48
6.47
6.45
5.18
4.98
4.05
4.04
4.02
3.97
3.95
3.94
3.42
3.42
3.41
3.41
3.40
3.40
3.03
3.03
2.44
2.42
2.42
2.42
2.40
2.38
2.21
2.20
2.19
2.18
2.07
2.06
2.05
2.04
Parameter Value
1 Title rh243-1
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 298.0
5 Number of Scans 16
6 Acquisition Date 2019-06-26T10:21:08
7 Spectrometer Frequency 600.13
8 Nucleus 1H
Br
H
N
O
O
N
H
Br
2h (2.5/1 dr)
0.30
1.00
1.20
1.35
1.00
0.23
0.38
1.00
0.42
1.07
3.00
0.82
1.40
0.38
1.10
f1 (ppm)


rh243-1
148.01
134.33
134.21
133.62
123.02
122.90
119.55
119.04
103.17
100.47
77.21
77.00
76.79
66.65
66.33
60.80
60.23
37.01
35.01
Parameter Value
1 Title rh243-1
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 298.0
5 Number of Scans 780
6 Acquisition Date 2019-06-26T10:59:02
7 Spectrometer Frequency 150.90
8 Nucleus 13C
f1 (ppm)

rh0154-1r

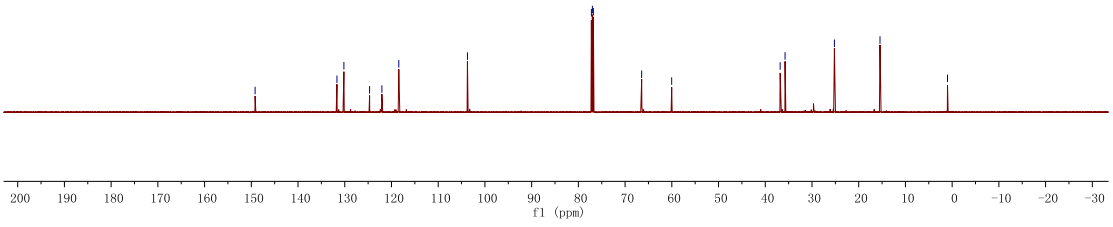


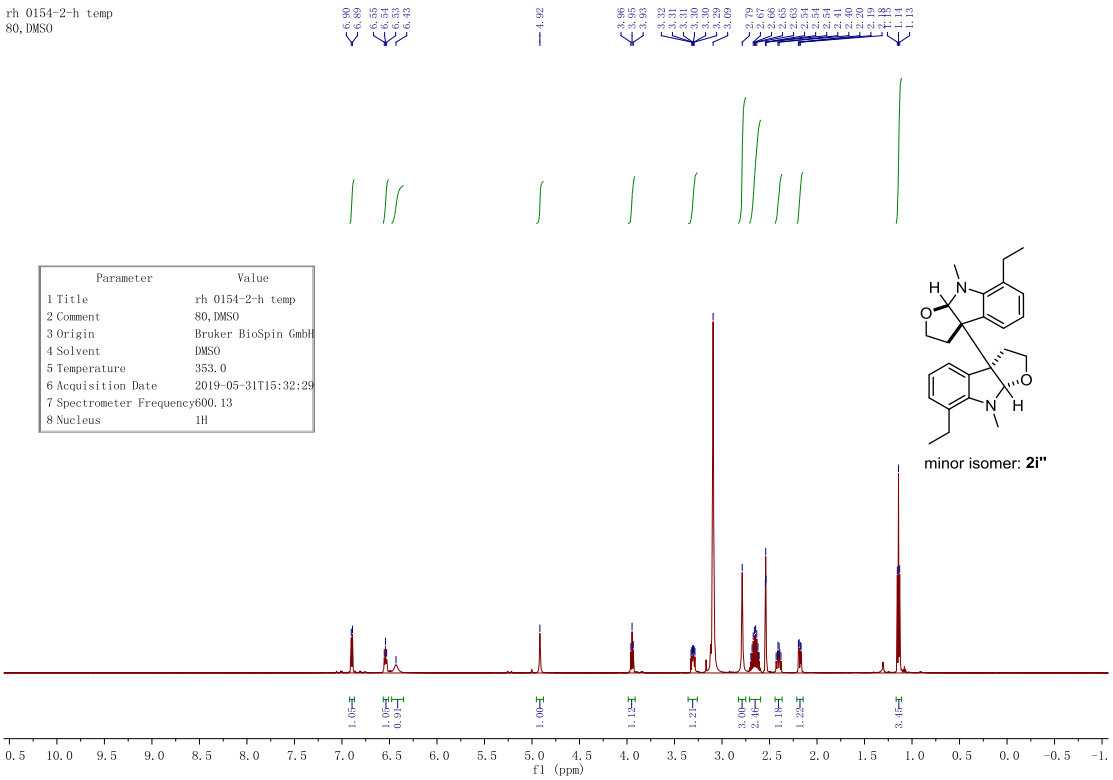
Parameter	Value
1 Title	rh0154-1r
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.0
5 Number of Scans	16
6 Acquisition Date	2019-04-11T16:43:02
7 Nucleus	1H

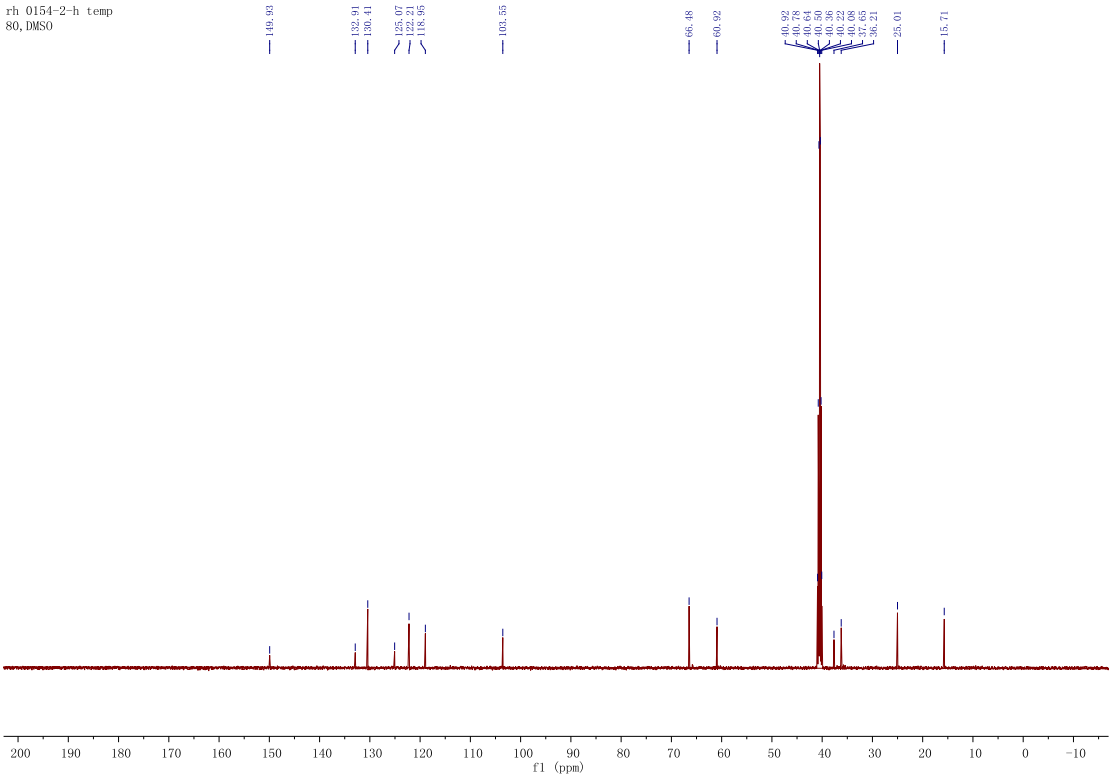
major isomer: **2i'**

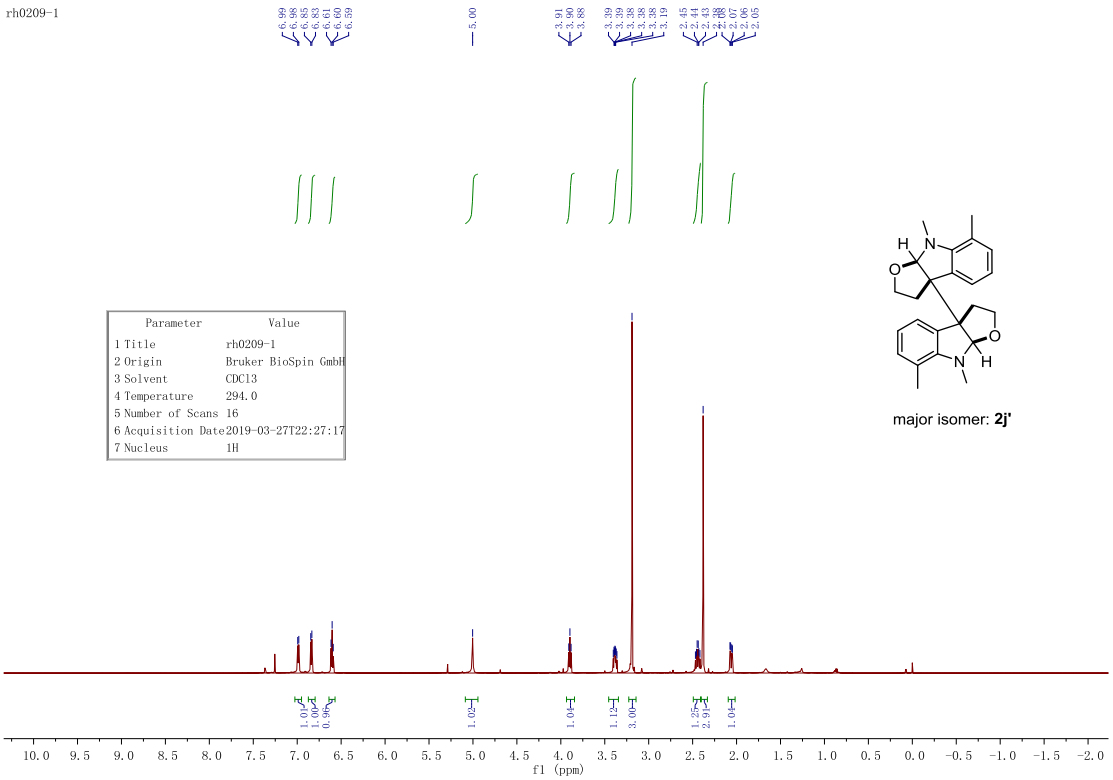
rh0154-1r

Parameter	Value
1 Title	rh0154-1r
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.0
5 Number of Scans	697
6 Acquisition Date	2019-04-11T17:16:58
7 Nucleus	13C

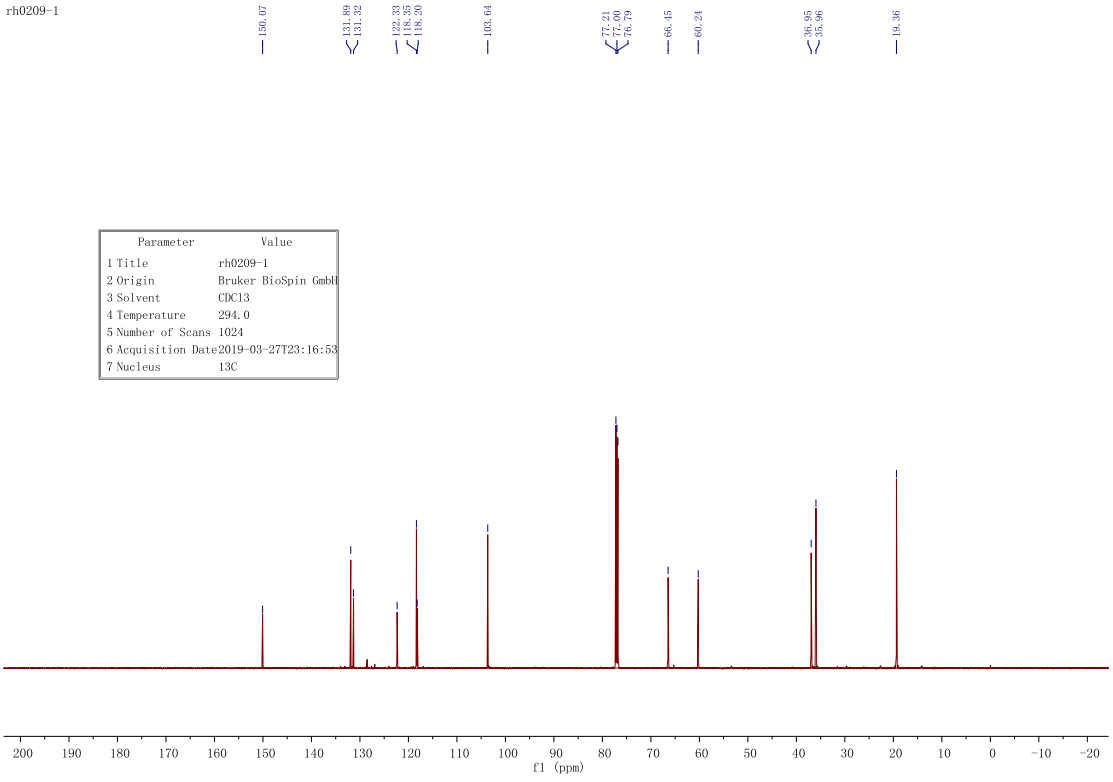



rh 0154-2-h temp
80, DMSO
Parameter Value
1 Title rh 0154-2-h temp
2 Comment 80, DMSO
3 Origin Bruker BioSpin GmbH
4 Solvent DMSO
5 Temperature 353.0
6 Acquisition Date 2019-05-31T15:32:29
7 Spectrometer Frequency 600.13
8 Nucleus 1H
minor isomer: 2i''
f1 (ppm)

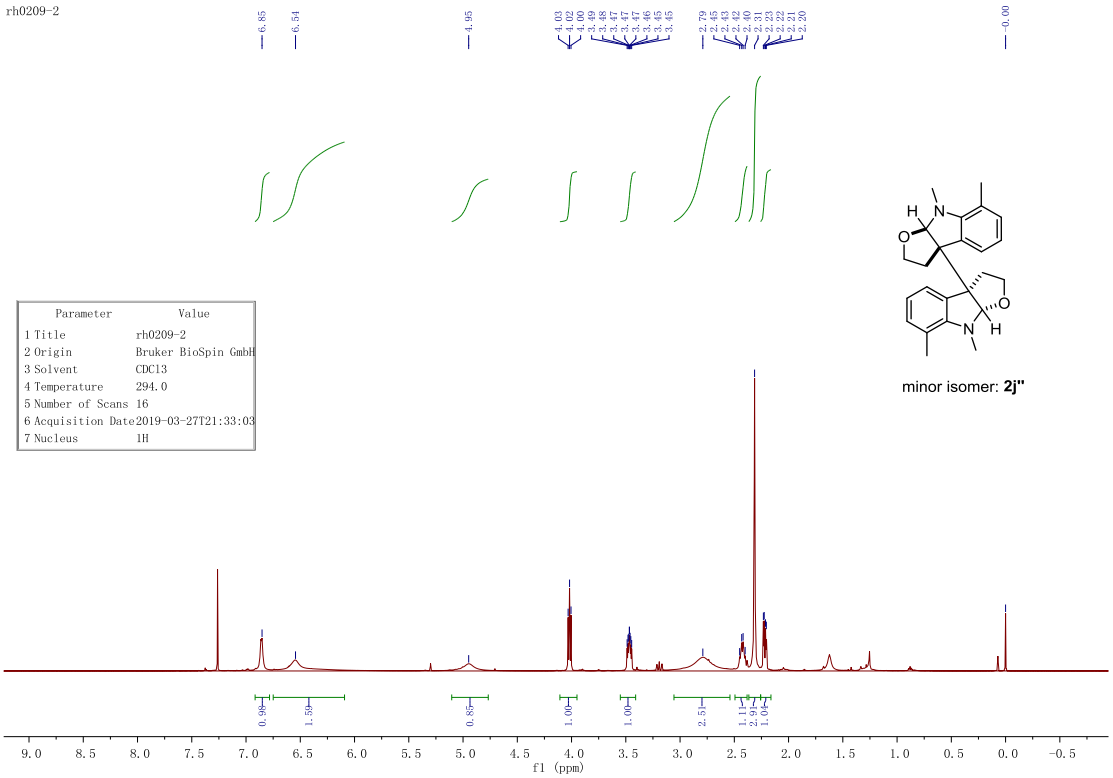

rh 0154-2-h temp
80, DMSO
f1 (ppm)



major isomer: **2j'**



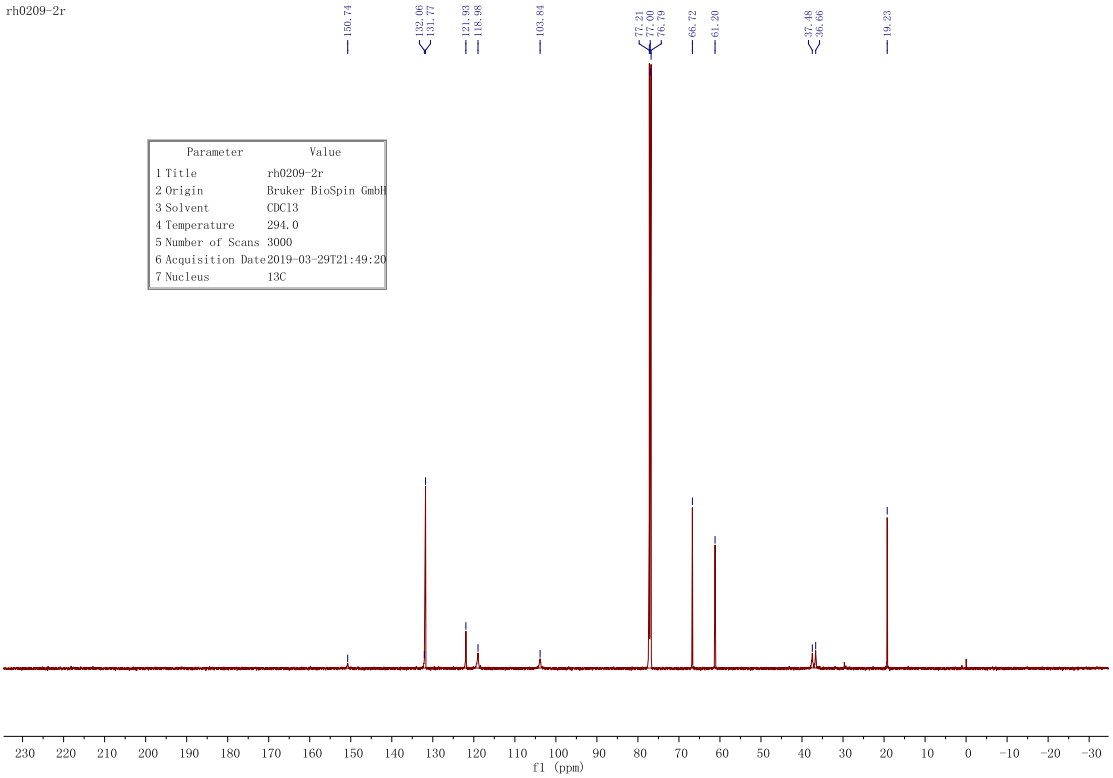
rh0209-2



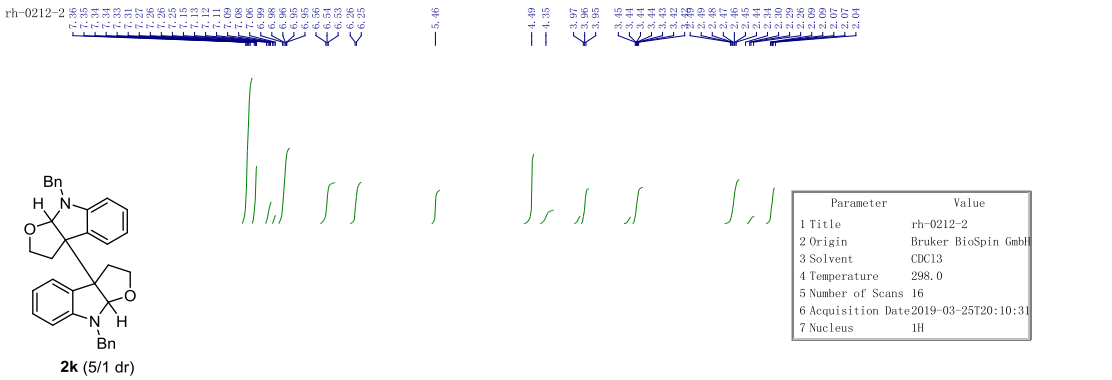
Parameter	Value
1 Title	rh0209-2
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	294.0
5 Number of Scans	16
6 Acquisition Date	2019-03-27T21:33:03
7 Nucleus	1H

minor isomer: **2j''**

rh0209-2r

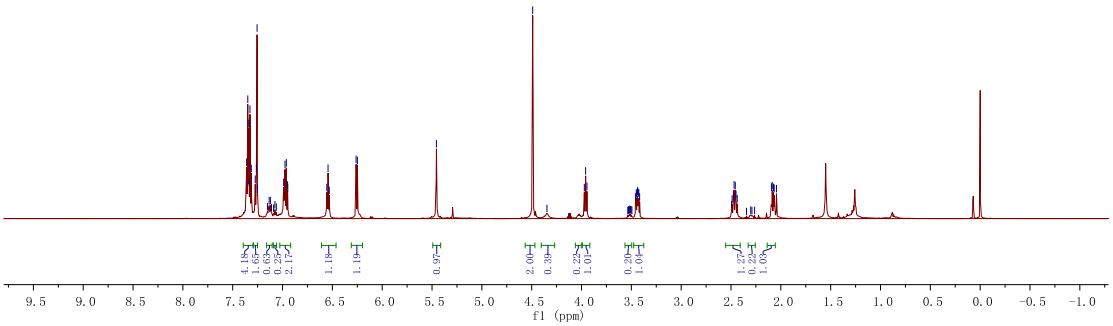


Parameter	Value
1 Title	rh0209-2r
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	294.0
5 Number of Scans	3000
6 Acquisition Date	2019-03-29T21:49:20
7 Nucleus	13C

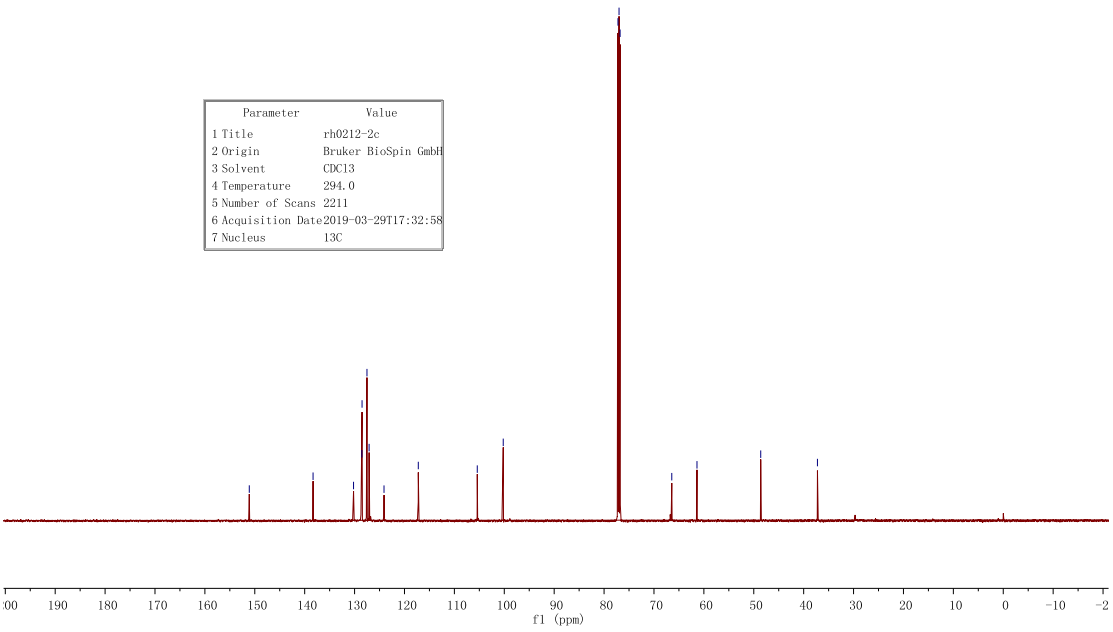


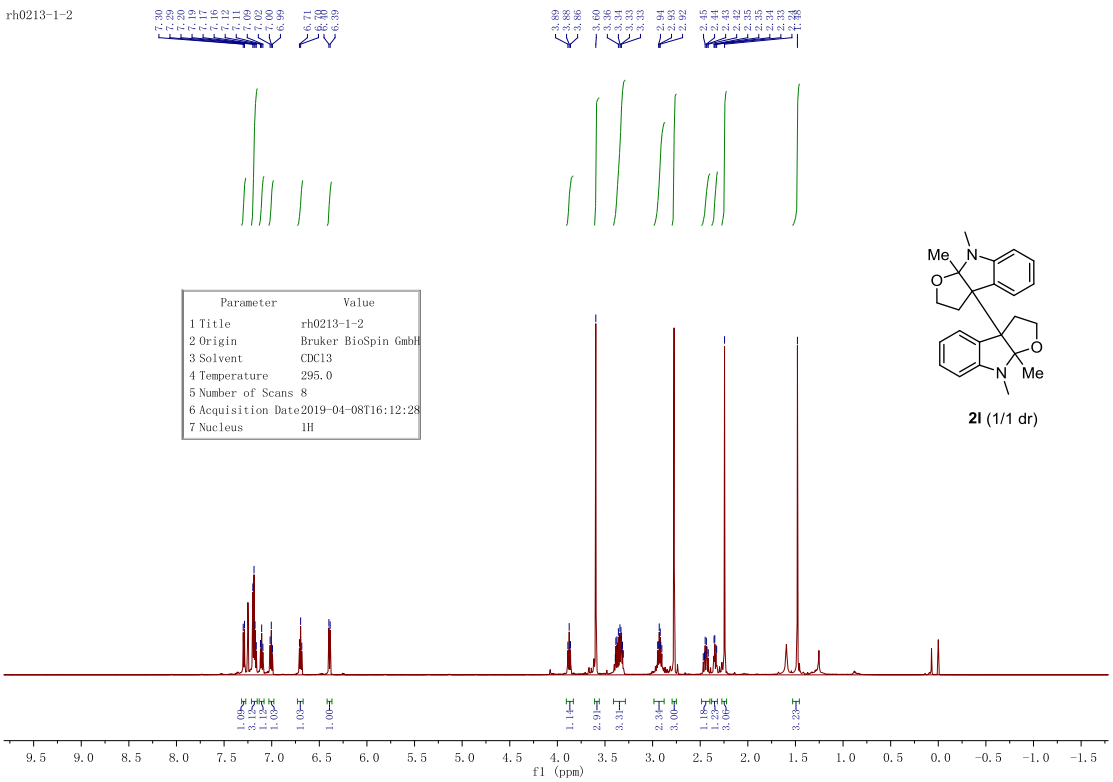
2k (5/1 dr)

Parameter	Value
1 Title	rh-0212-2
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	16
6 Acquisition Date	2019-03-25T20:10:31
7 Nucleus	1H

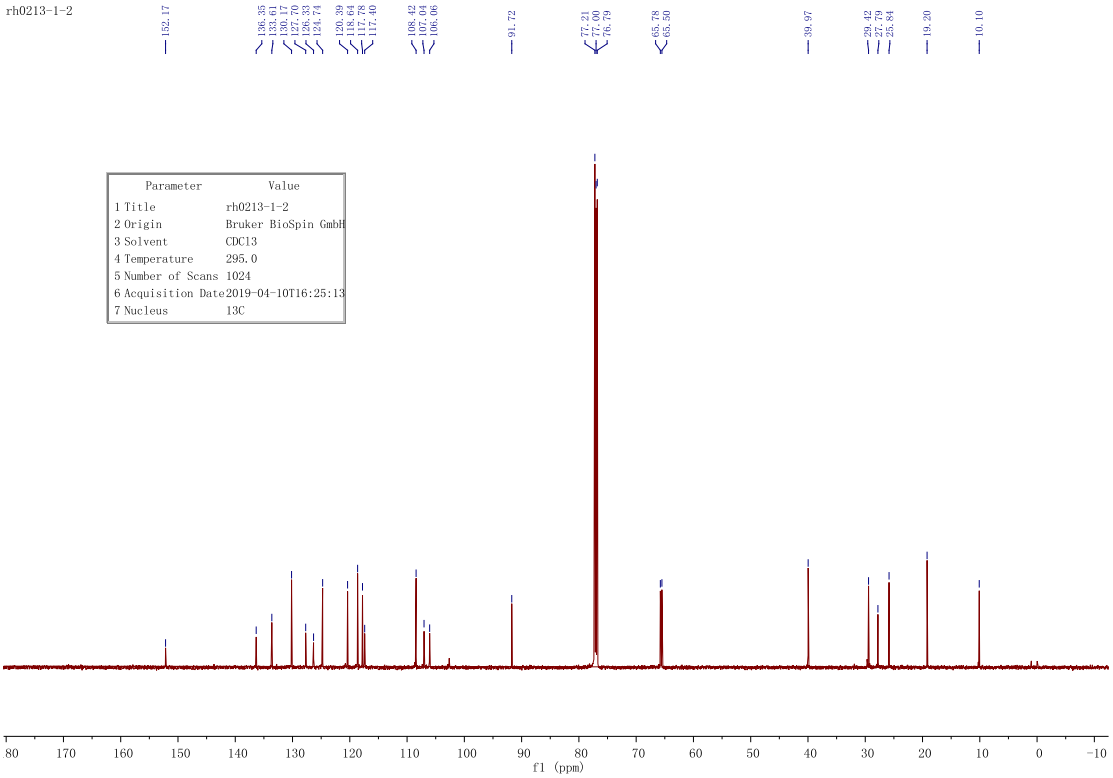


Parameter	Value
1 Title	rh0212-2c
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	294.0
5 Number of Scans	2211
6 Acquisition Date	2019-03-29T17:32:58
7 Nucleus	13C

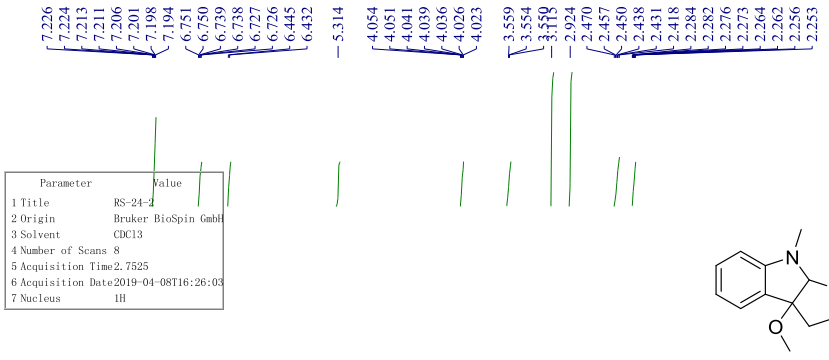



rh0213-1-2
Parameter Value
1 Title rh0213-1-2
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 295.0
5 Number of Scans 8
6 Acquisition Date 2019-04-08T16:12:28
7 Nucleus 1H
Me
N
O
O
N
Me
f1 (ppm)

2l (1/1 dr)

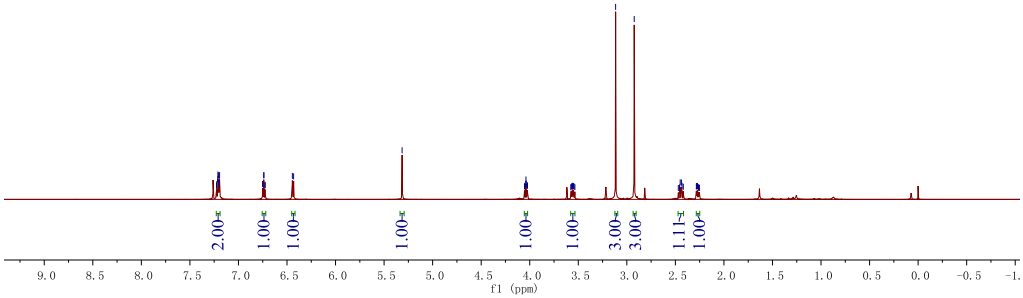

rh0213-1-2
Parameter Value
1 Title rh0213-1-2
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 295.0
5 Number of Scans 1024
6 Acquisition Date 2019-04-10T16:25:13
7 Nucleus 13C
f1 (ppm)

RS-24-2



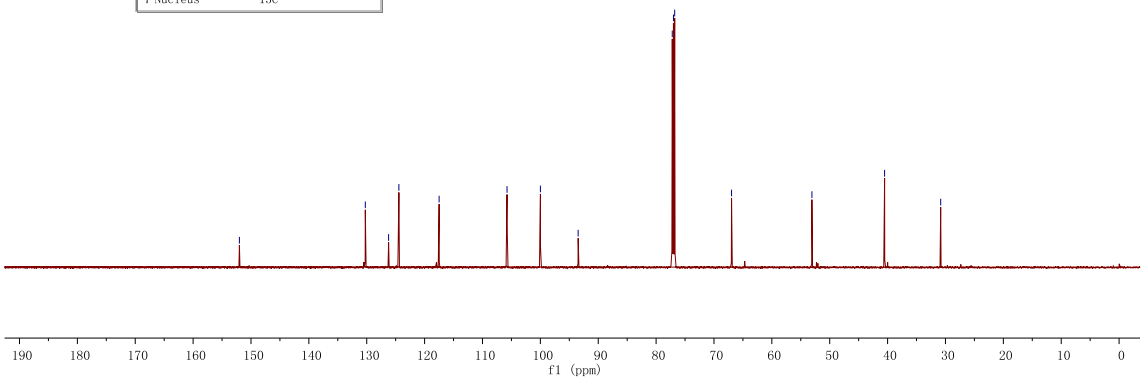
Parameter	Value
1 Title	RS-24-2
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Number of Scans	8
5 Acquisition Time	2.7525
6 Acquisition Date	2019-04-08T16:26:03
7 Nucleus	1H

3 (>20/1 dr)

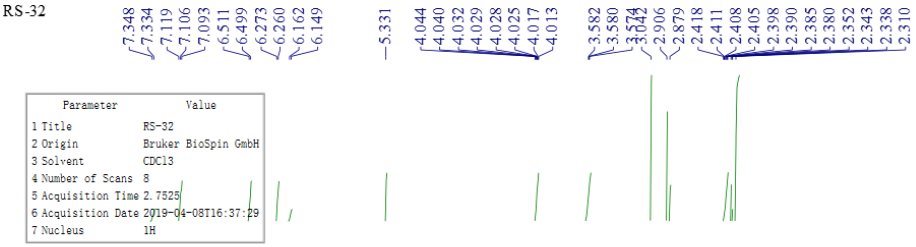


RS-24-2

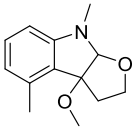
Parameter	Value
1 Title	RS-24-2
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Number of Scans	1024
5 Acquisition Time	0.8061
6 Acquisition Date	2019-04-10T13:01:27
7 Nucleus	13C



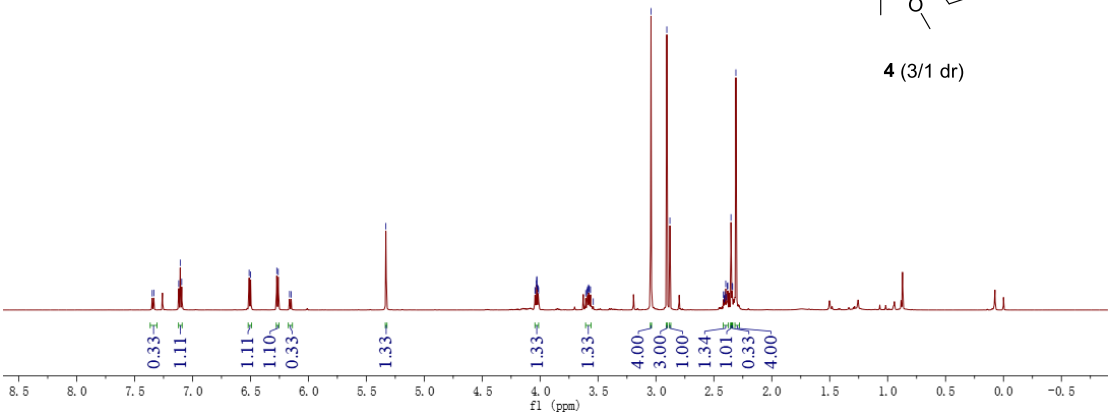
RS-32



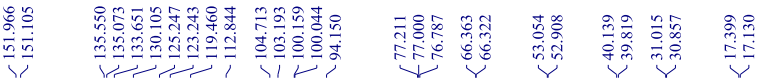
Parameter	Value
1 Title	RS-32
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Number of Scans	8
5 Acquisition Time	2.7525
6 Acquisition Date	2019-04-08T16:37:29
7 Nucleus	1H



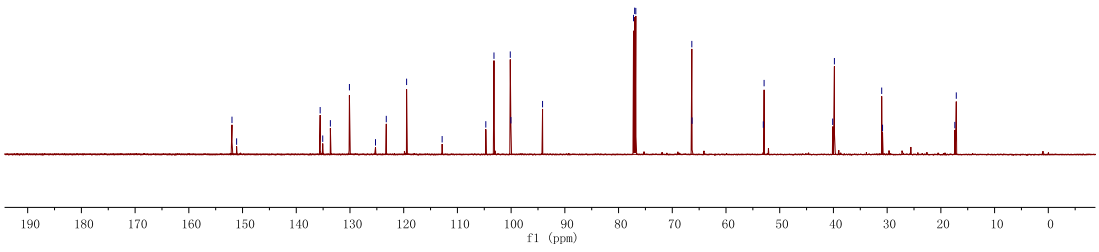
4 (3/1 dr)



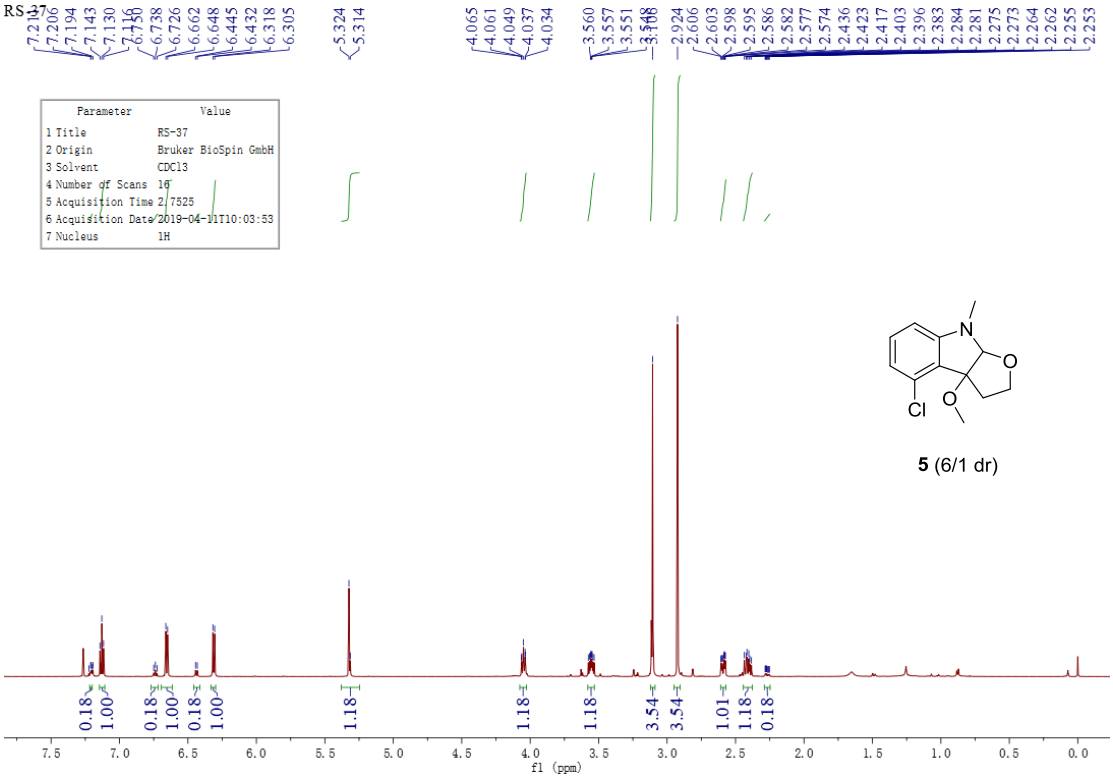
RS-32



Parameter	Value
1 Title	RS-32
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Number of Scans	569
5 Acquisition Time	0.8061
6 Acquisition Date	2019-04-10T13:55:39
7 Nucleus	13C

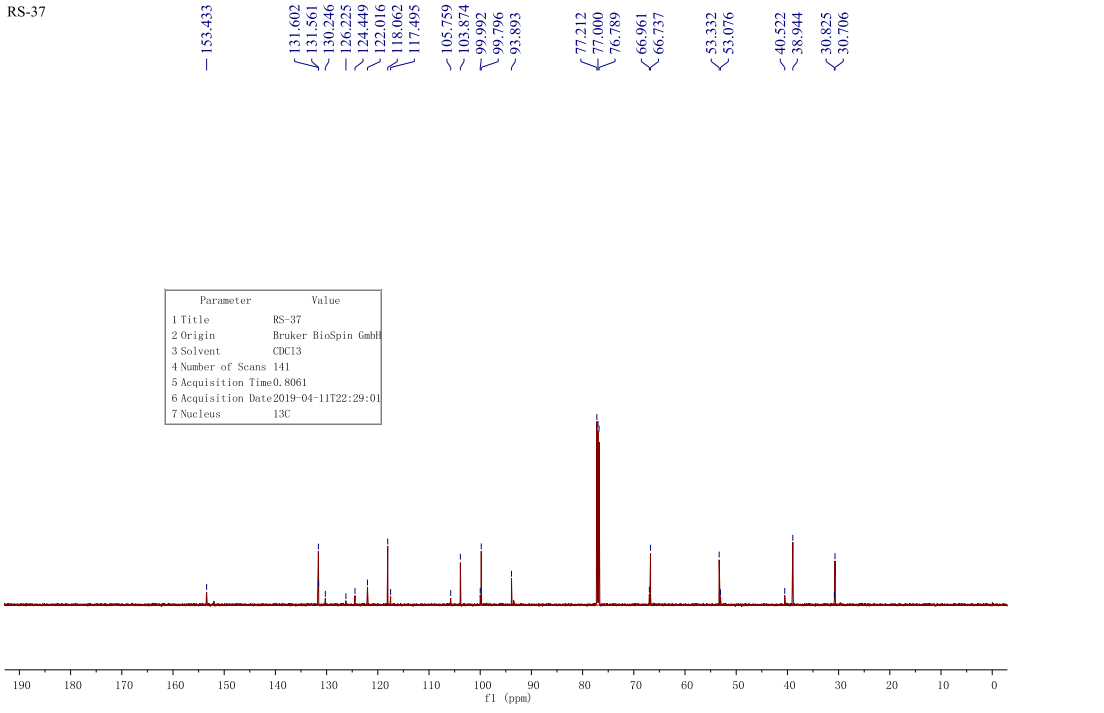


RS-37

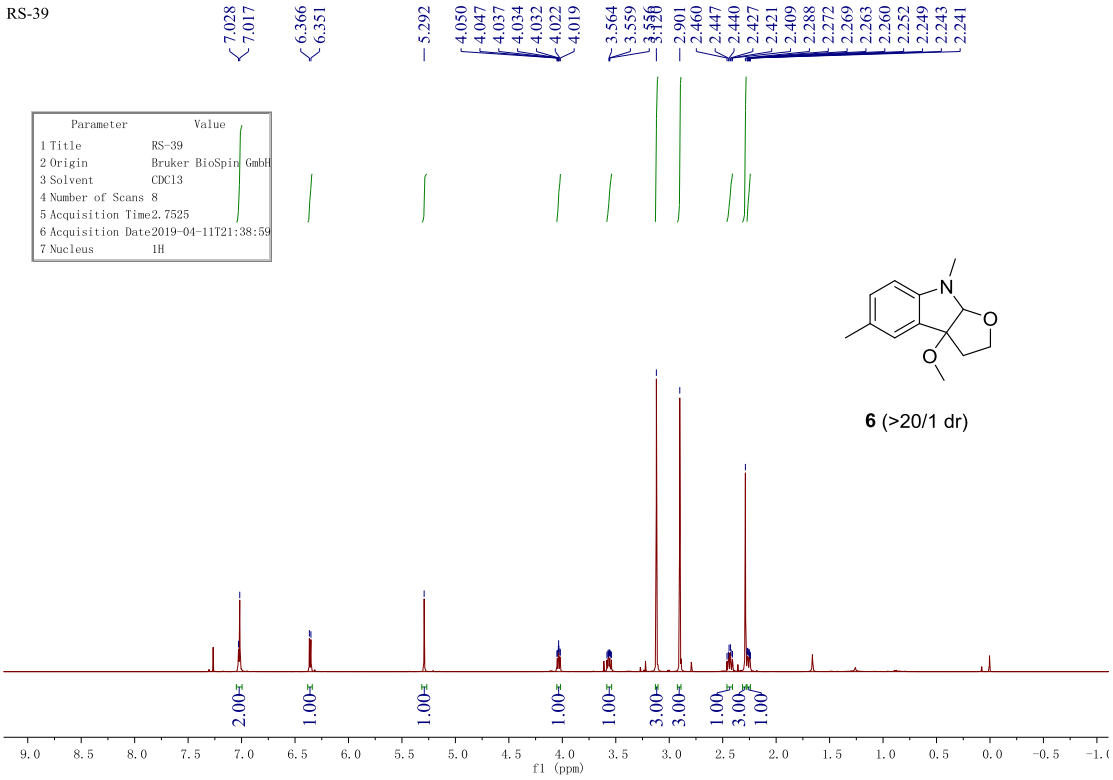


5 (6/1 dr)

RS-37

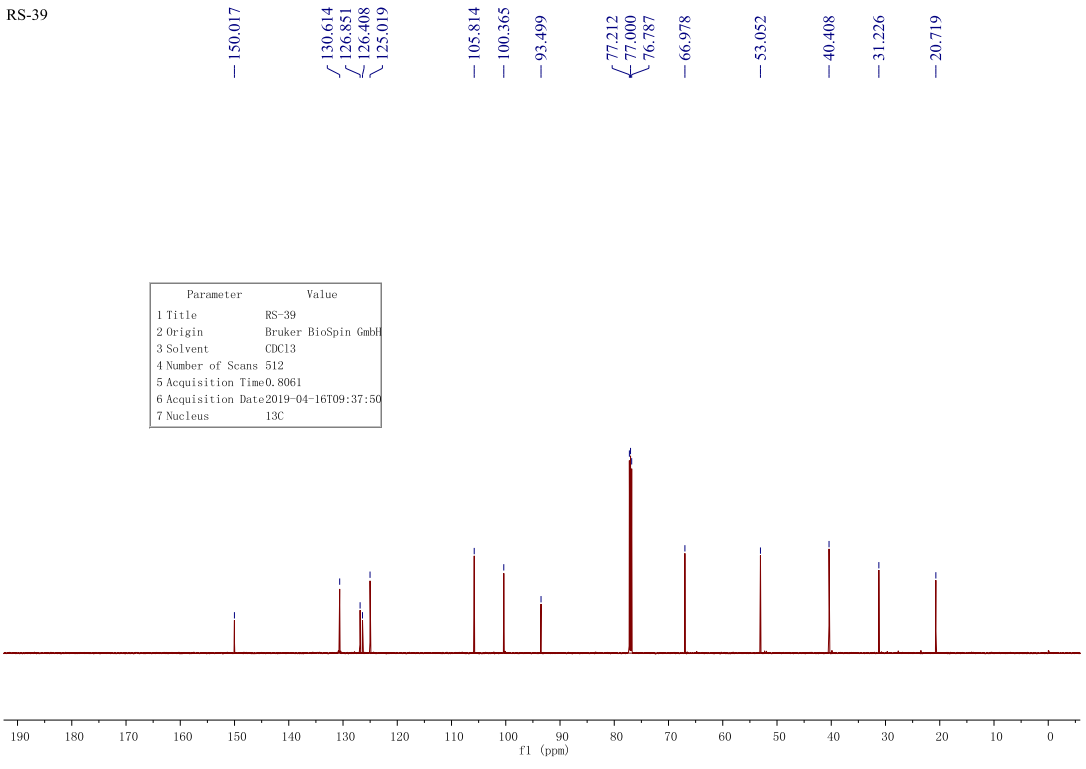


RS-39

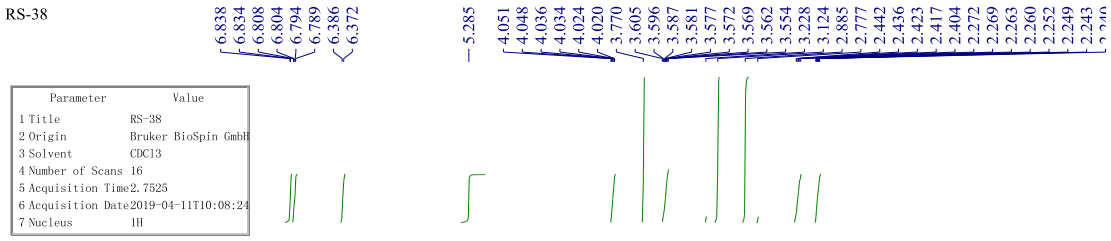


6 (>20/1 dr)

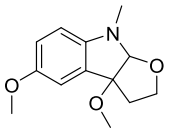
RS-39



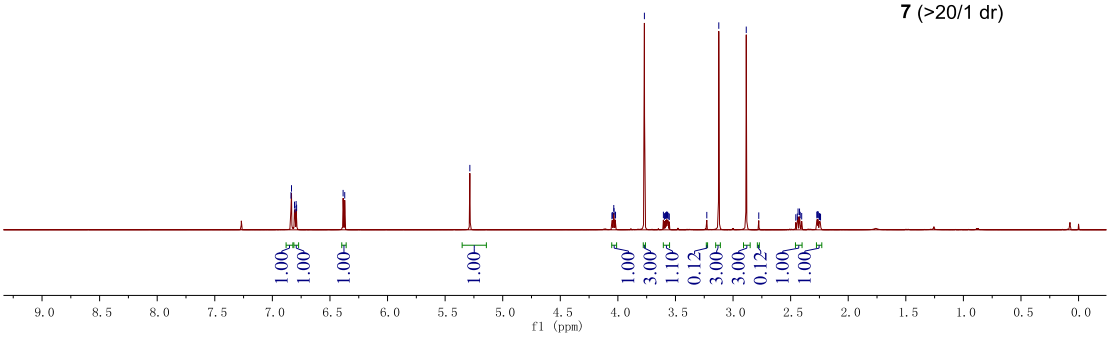
RS-38



Parameter	Value
1 Title	RS-38
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Number of Scans	16
5 Acquisition Time	2.7525
6 Acquisition Date	2019-04-11T10:08:24
7 Nucleus	1H

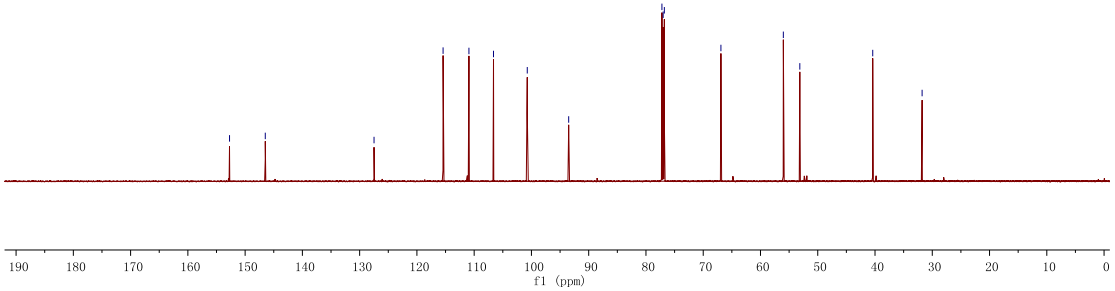


7 (>20/1 dr)

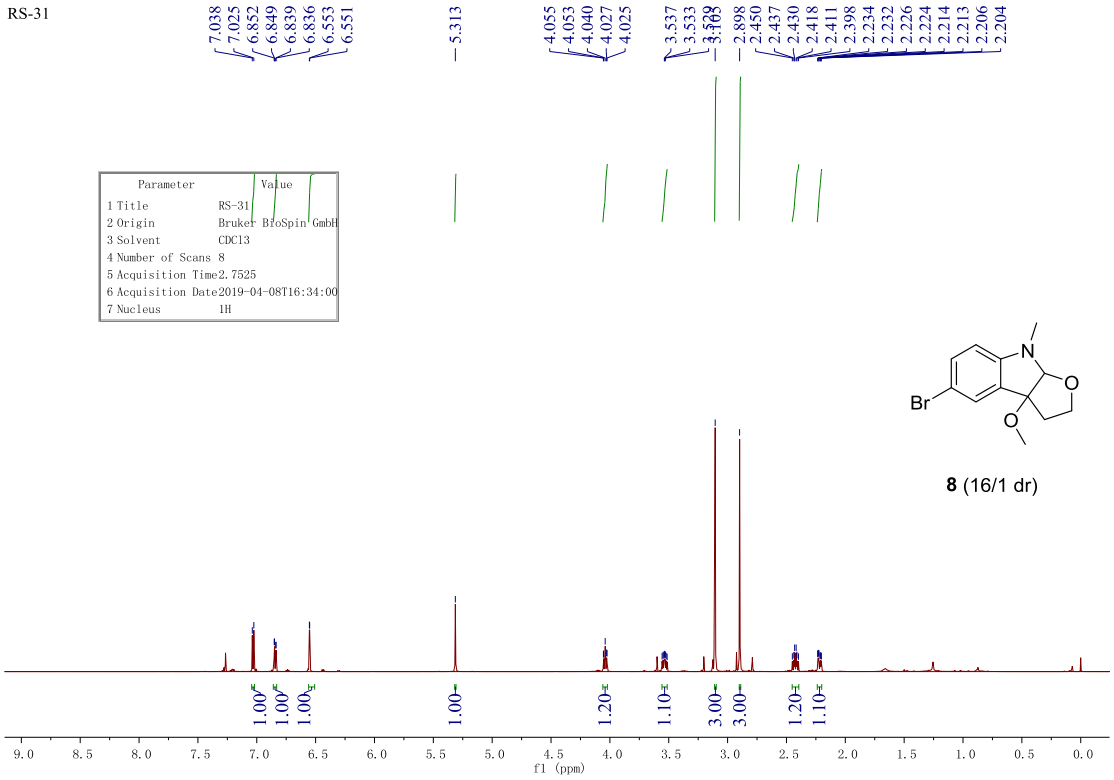


RS-38

Parameter	Value
1 Title	RS-38
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Receiver Gain	101
5 Acquisition Time	0.8061
6 Acquisition Date	2019-04-11T22:56:57
7 Nucleus	13C

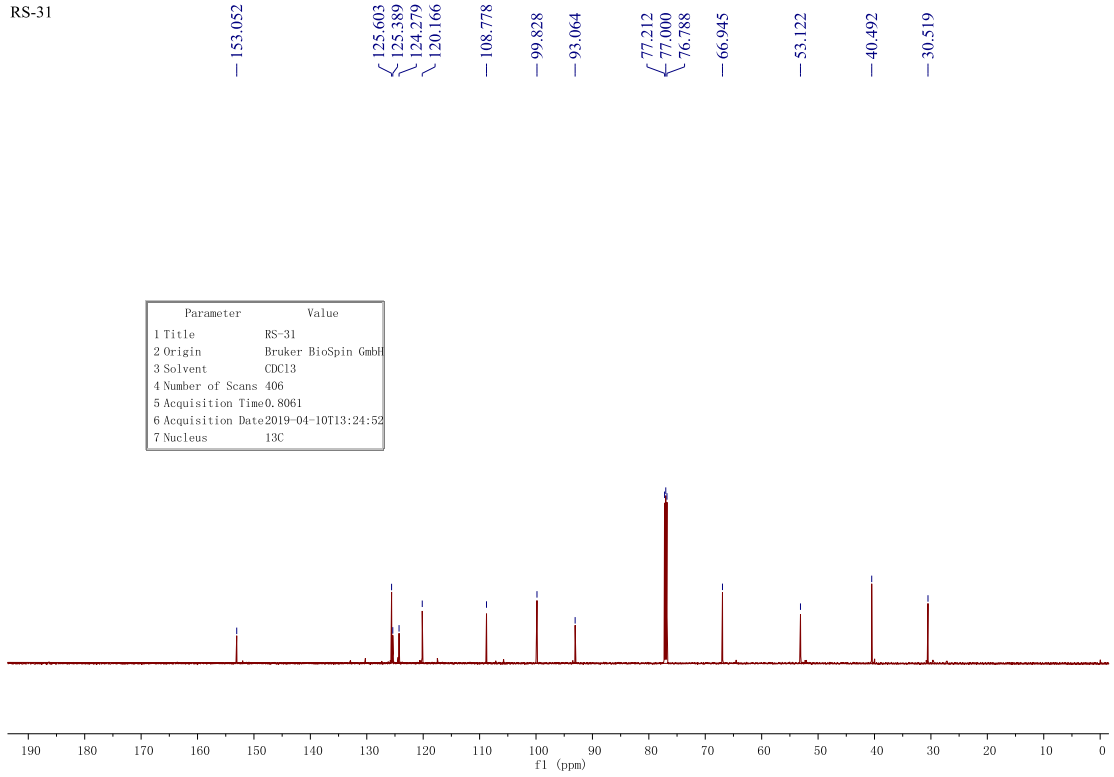


RS-31



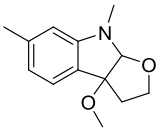
8 (16/1 dr)

RS-31

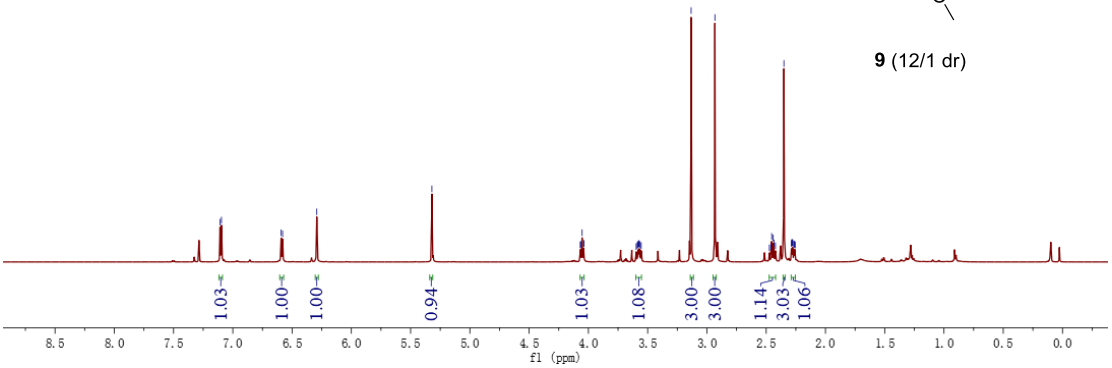


RS-41

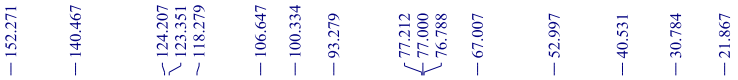
Parameter	Value
1 Title	RS-41
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Number of Scans	16
5 Acquisition Time	2.7525
6 Acquisition Date	2019-04-15T16:46:44
7 Nucleus	1H



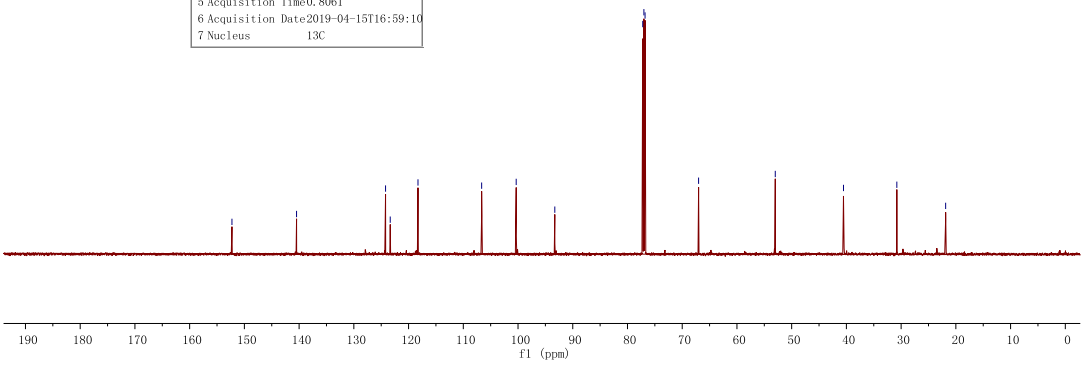
9 (12/1 dr)



RS-41

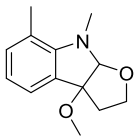


Parameter	Value
1 Title	RS-41
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Number of Scans	247
5 Acquisition Time	0.8061
6 Acquisition Date	2019-04-15T16:59:10
7 Nucleus	13C

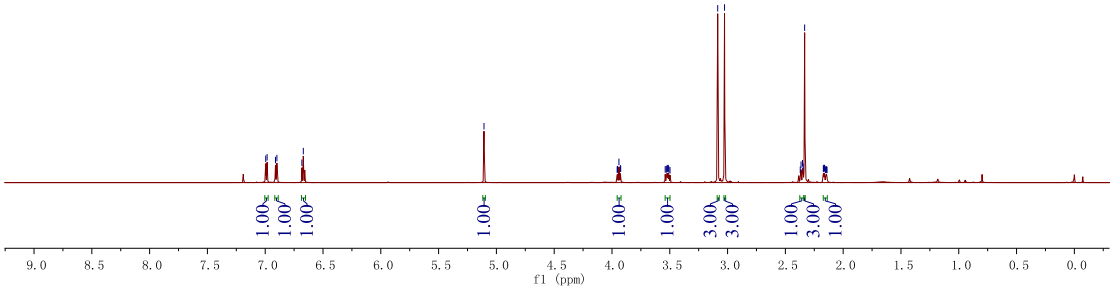


RS-36

Parameter	Value
1 Title	RS-36
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Number of Scans	16
5 Acquisition Time	2.7525
6 Acquisition Date	2019-04-11T09:59:18
7 Nucleus	1H

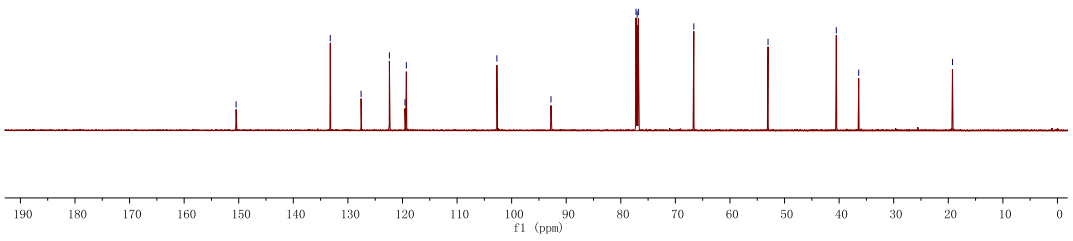


10 (>20/1 dr)

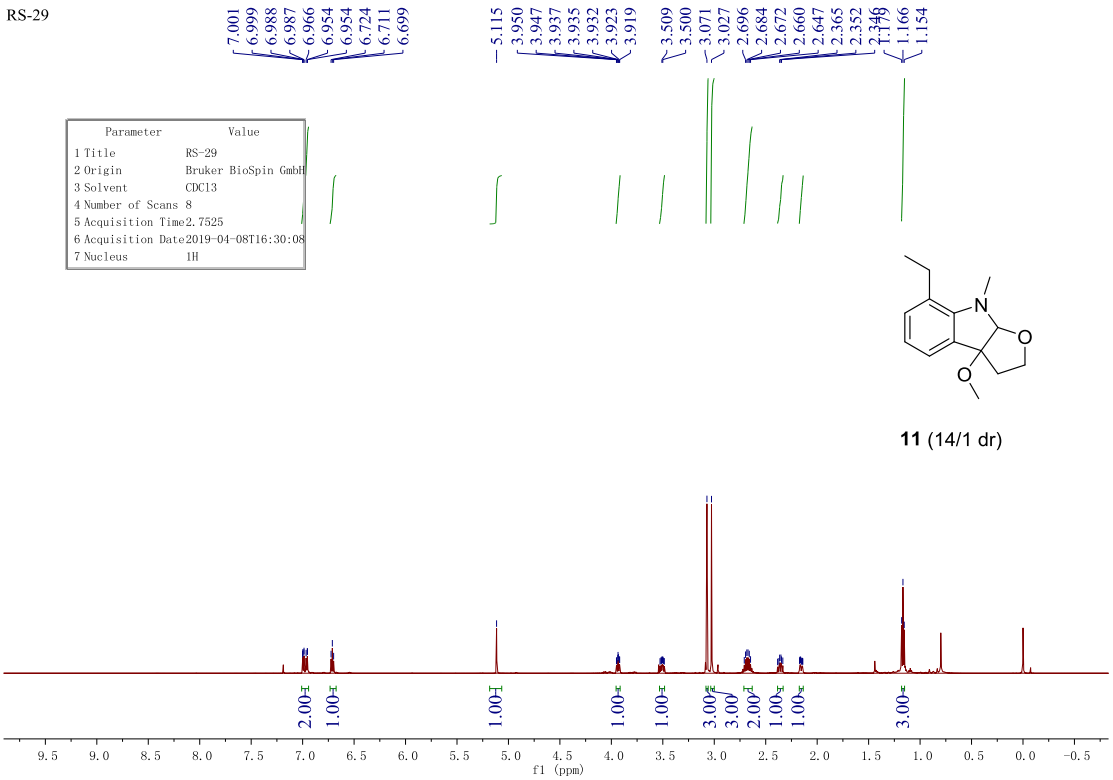


RS-36

Parameter	Value
1 Title	RS-36
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Number of Scans	512
5 Acquisition Time	0.8061
6 Acquisition Date	2019-04-11T22:18:51
7 Nucleus	13C

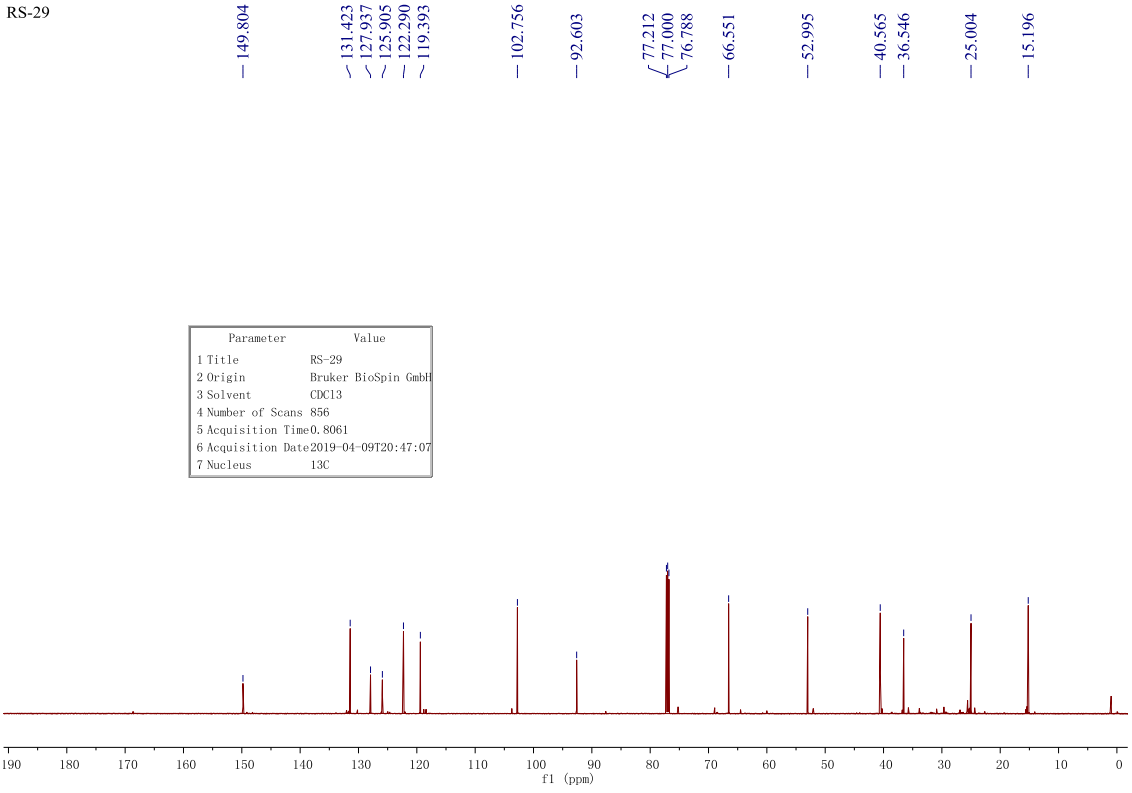


RS-29



11 (14/1 dr)

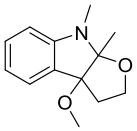
RS-29



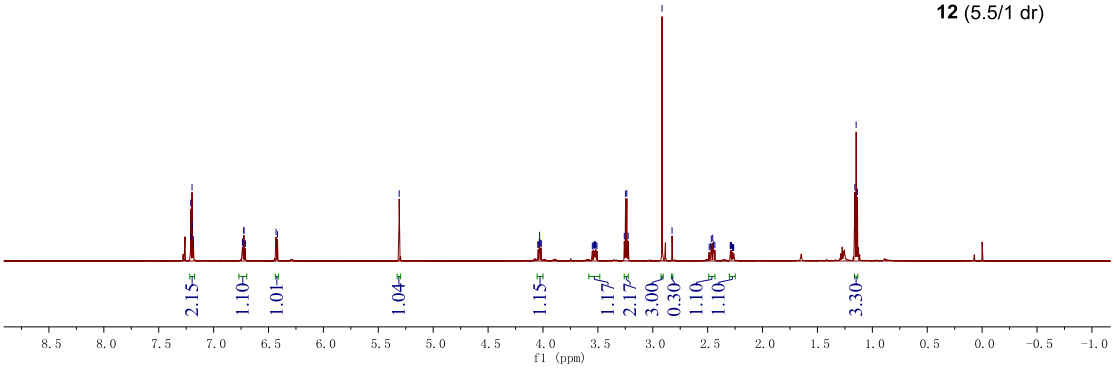
rs-54-2

Parameter	Value
1 Title	rs-54-2
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Number of Scans	16
5 Acquisition Time	2.7525
6 Acquisition Date	2019-05-22T00:54:48
7 Nucleus	1H

7.209, 7.207, 7.197, 7.195, 7.185, 7.183, 6.718, 6.716, 6.725, 6.724, 6.713, 6.712, 6.431, 6.418, 5.310, 4.046, 4.043, 4.033, 4.031, 4.029, 4.018, 4.016, 3.542, 3.532, 3.523, 3.259, 3.248, 3.236, 3.224, 2.915, 2.824, 2.467, 2.454, 2.447, 2.435, 1.159, 1.148, 1.136



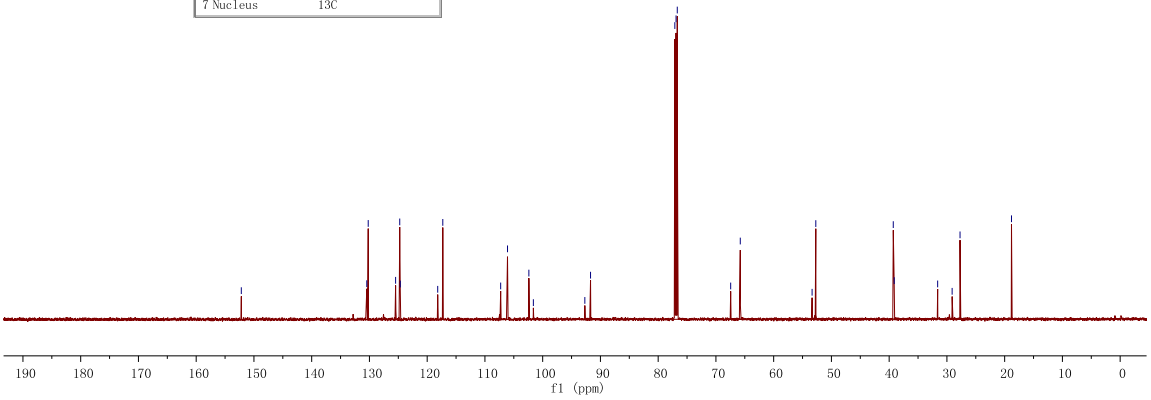
12 (5.5/1 dr)



RS-43-0416

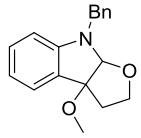
152.187, 130.457, 130.211, 125.467, 124.752, 124.661, 118.176, 117.295, 107.275, 106.088, 102.391, 101.611, 92.699, 91.712, 77.114, 76.904, 76.692, 67.443, 65.781, 53.347, 52.704, 39.288, 39.123, 31.602, 29.095, 27.729, 18.817

Parameter	Value
1 Title	RS-43-0416
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Number of Scans	1024
5 Acquisition Time	0.8061
6 Acquisition Date	2019-04-16T21:34:21
7 Nucleus	13C

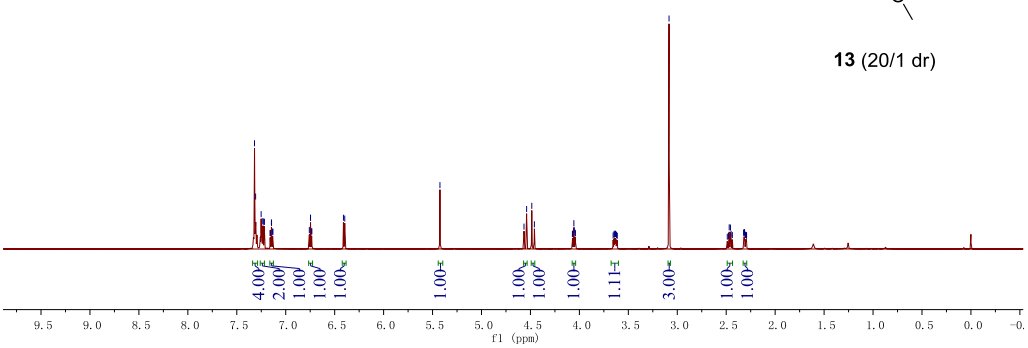


RS-42

Parameter	Value
1 Title	RS-42
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Number of Scans	8
5 Acquisition Time	2.7525
6 Acquisition Date	2019-04-11T21:46:26
7 Nucleus	1H

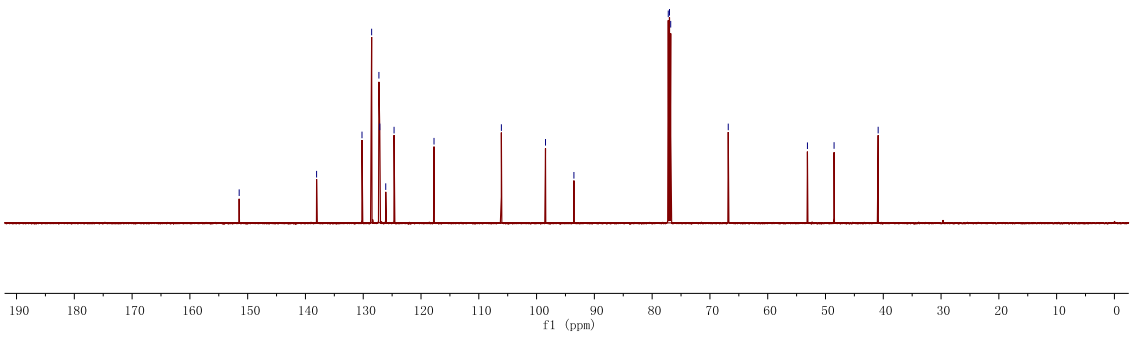


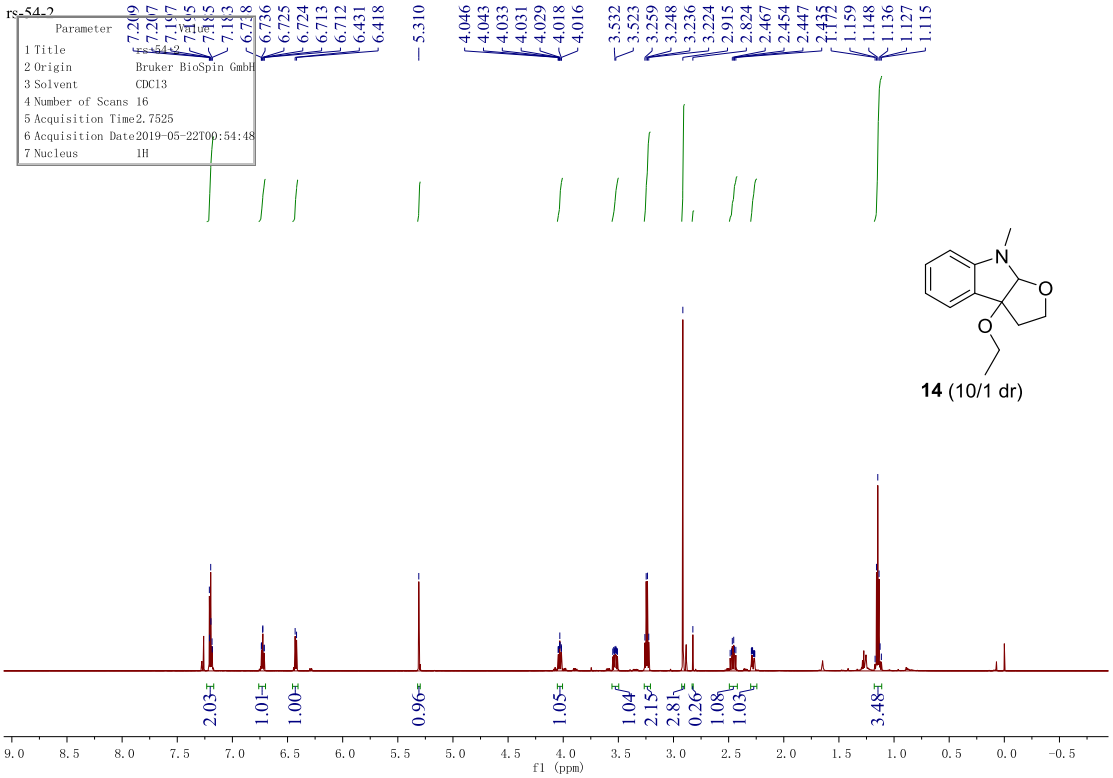
13 (20/1 dr)



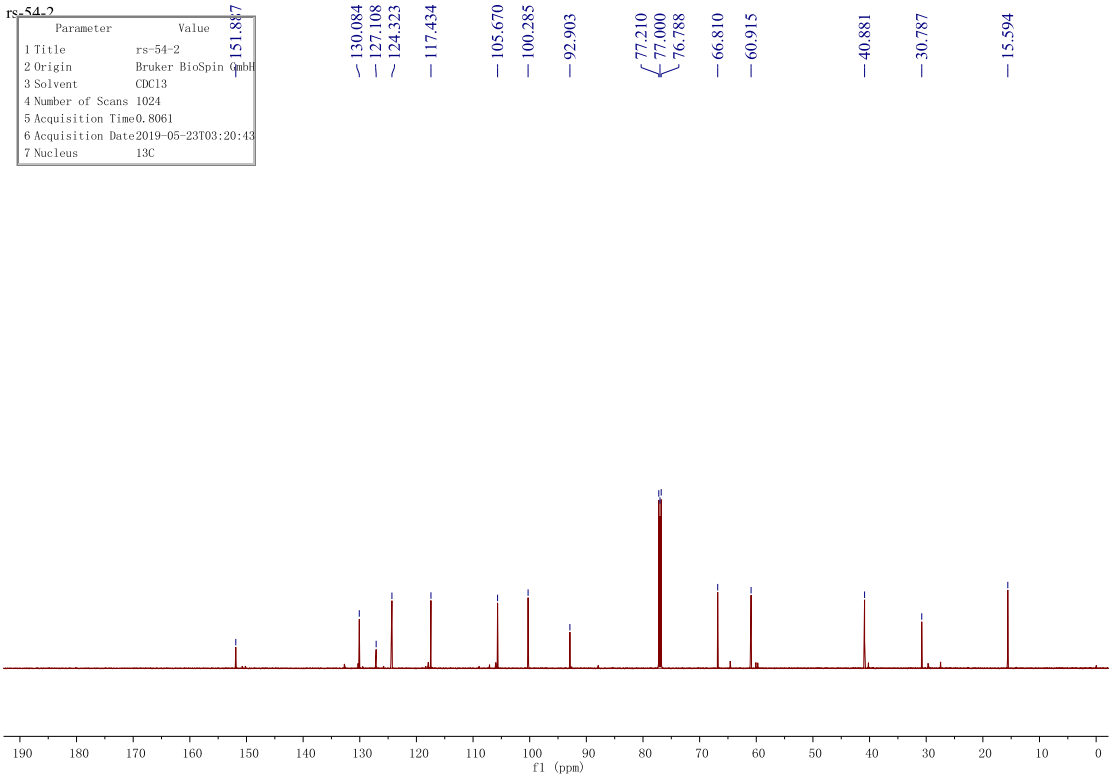
RS-42

Parameter	Value
1 Title	RS-42
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Number of Scans	512
5 Acquisition Time	0.8061
6 Acquisition Date	2019-04-15T23:16:47
7 Nucleus	13C

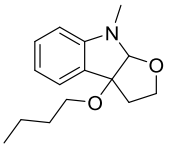



rs-54-2
Parameter
1 Title rs-54-2
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Number of Scans 16
5 Acquisition Time 2.7525
6 Acquisition Date 2019-05-22T09:54:48
7 Nucleus 1H
7.209
7.207
7.197
7.195
7.185
7.183
6.738
6.736
6.725
6.724
6.713
6.712
6.431
6.418
5.310
4.046
4.043
4.033
4.031
4.029
4.018
4.016
3.532
3.523
3.259
3.248
3.236
3.224
2.915
2.824
2.467
2.454
2.447
2.435
1.172
1.159
1.148
1.136
1.127
1.115
2.03
1.01
1.00
0.96
1.05
1.04
2.15
2.81
0.26
1.08
1.03
3.48
f1 (ppm)

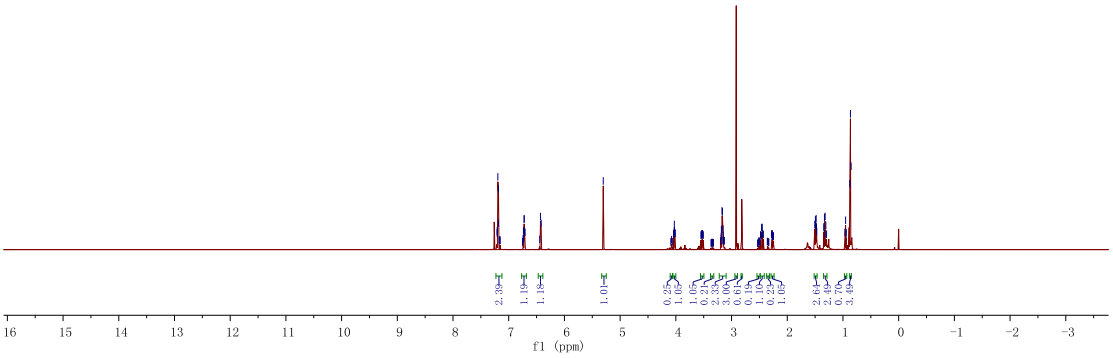
14 (10/1 dr)


rs-54-2
Parameter Value
1 Title rs-54-2
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Number of Scans 1024
5 Acquisition Time 0.8061
6 Acquisition Date 2019-05-23T03:20:43
7 Nucleus 13C
151.847
130.084
127.108
124.323
117.434
105.670
100.285
92.903
77.210
77.000
76.788
66.810
60.915
40.881
30.787
15.594
f1 (ppm)

Parameter	Value
1 Title	rs-62-20
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.0
5 Number of Scans	16
6 Acquisition Date	2019-05-23T03:24:52
7 Spectrometer Frequency	600.13
8 Nucleus	1H

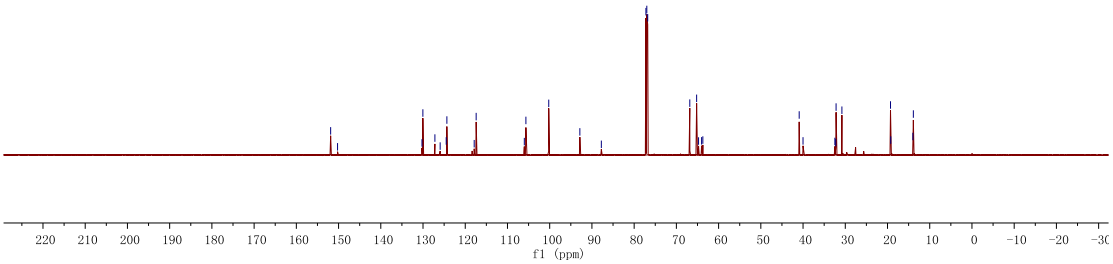


15 (5/1 dr)

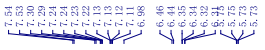


rs-62-20

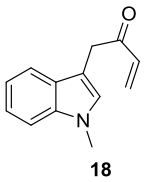
Parameter	Value
1 Title	rs-62-20
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.0
5 Number of Scans	1024
6 Acquisition Date	2019-05-23T04:14:31
7 Spectrometer Frequency	150.90
8 Nucleus	13C



rh0237-2

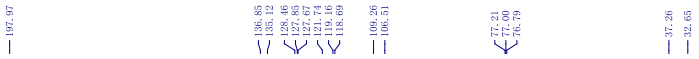


Parameter	Value
1 Title	rh0237-2
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.0
5 Number of Scans	16
6 Acquisition Date	2019-05-30T14:58:18
7 Nucleus	1H

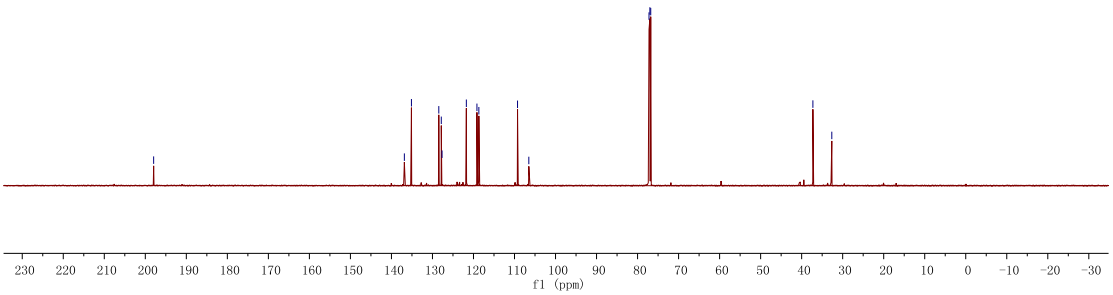


18

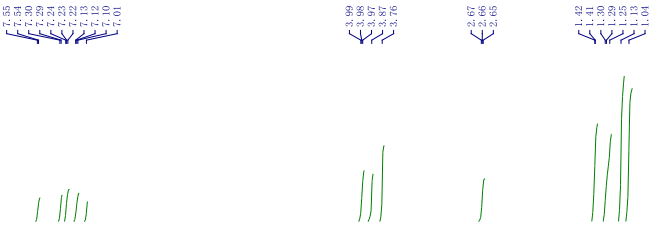
rh0237-2



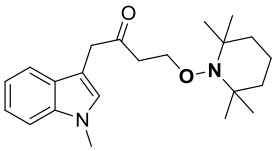
Parameter	Value
1 Title	rh0237-2
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.0
5 Number of Scans	1024
6 Acquisition Date	2019-05-30T18:37:43
7 Nucleus	13C



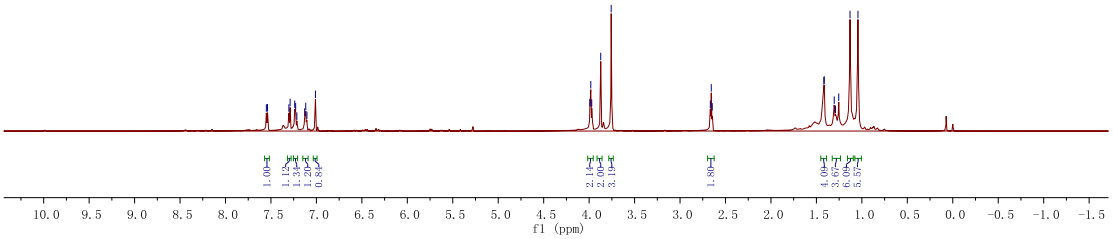
rh0238-3



Parameter	Value
1 Title	rh0238-3
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	16
6 Acquisition Date	2019-06-04T14:08:16
7 Spectrometer Frequency	600.13
8 Nucleus	1H

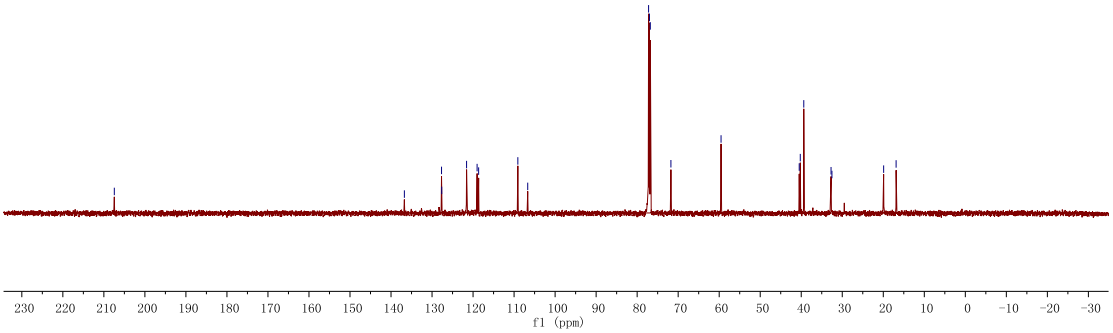


19

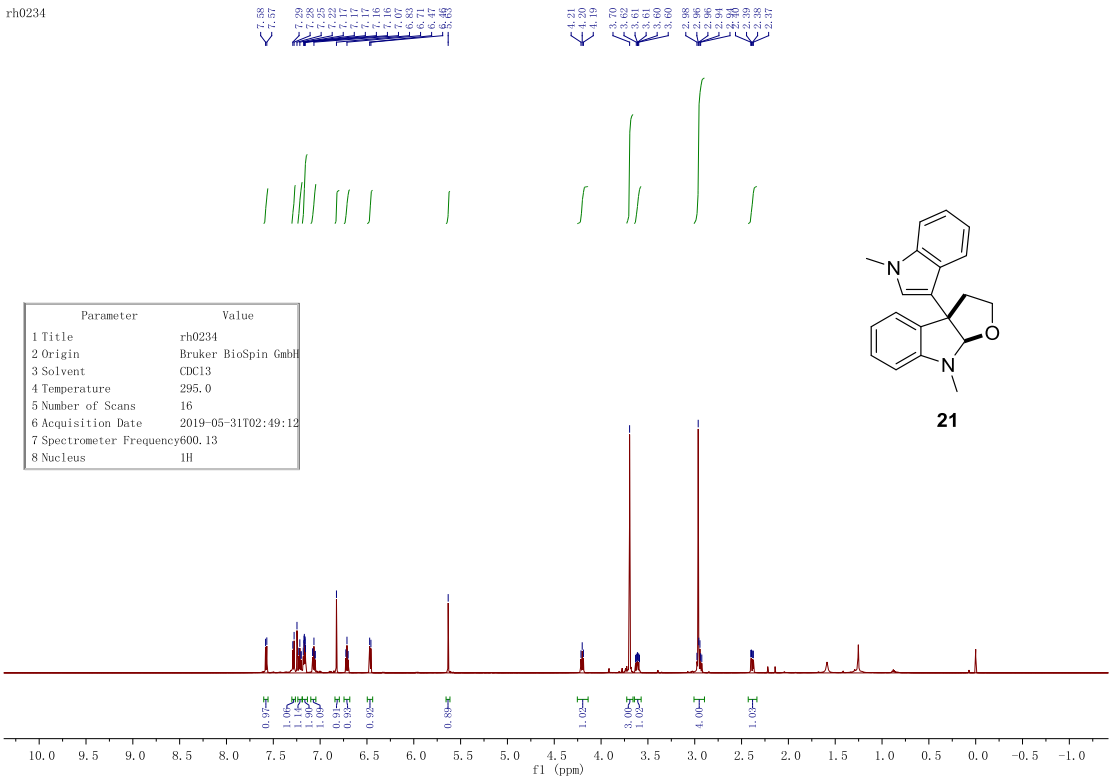


rh0238-3

Parameter	Value
1 Title	rh0238-3
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.3
5 Number of Scans	78
6 Acquisition Date	2019-06-04T14:12:40
7 Spectrometer Frequency	150.90
8 Nucleus	13C



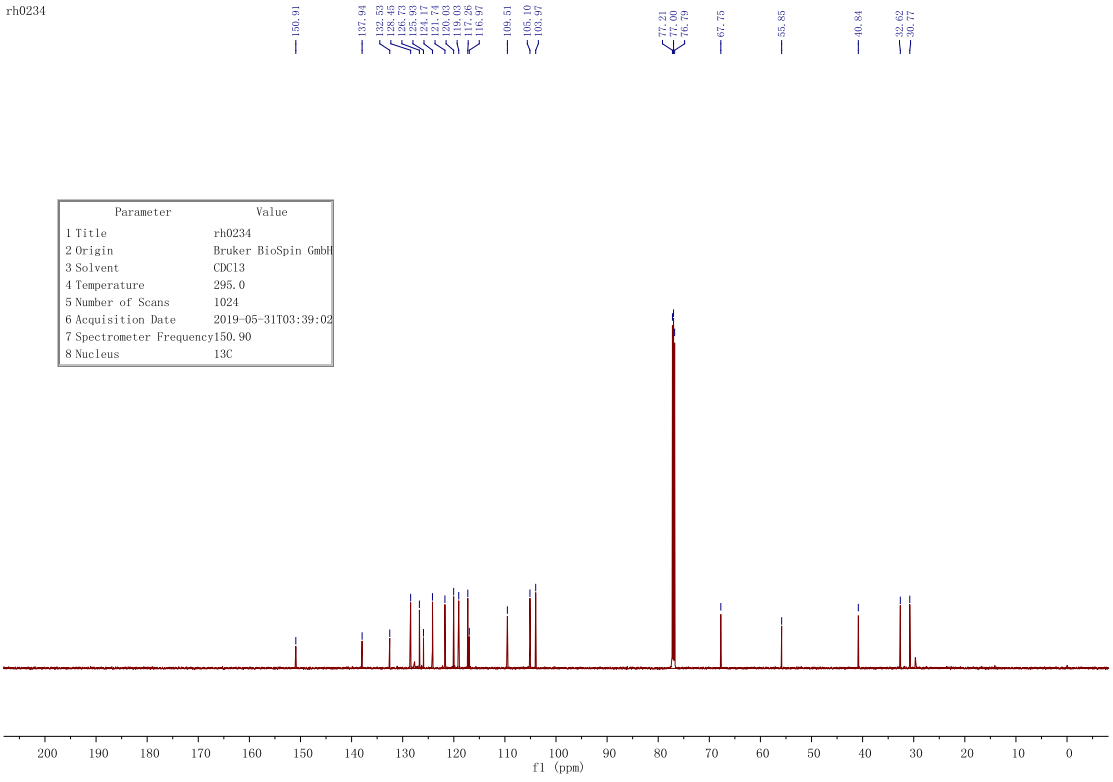
rh0234



Parameter	Value
1 Title	rh0234
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.0
5 Number of Scans	16
6 Acquisition Date	2019-05-31T02:49:12
7 Spectrometer Frequency	600.13
8 Nucleus	1H

21

rh0234



Parameter	Value
1 Title	rh0234
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.0
5 Number of Scans	1024
6 Acquisition Date	2019-05-31T03:39:02
7 Spectrometer Frequency	150.90
8 Nucleus	13C

10. HPLC Spectras of 2a’

数据文件: C:\CHEM32\1\DATA\SONGJUNRONG\RS-0299.D
样品名称: rs-0299(99-1)

```
======================================================================
操作者          : sjr
仪器            : 仪器 1                              位置 : 样品瓶 1
进样日期        : 2019/7/30 9:16:02
                                                      进样量 : 2.0 µl
采集方法        : C:\CHEM32\1\METHODS\SONGJUNRONG\DEF_LC.M (0.7-99-1-2019.07.30) .M
最后修改        : 2019/7/30 9:15:04 :  sjr
                  (调用后修改)
分析方法        : C:\CHEM32\1\METHODS\SONGJUNRONG\GZ.M(1.0-70-30).M
最后修改        : 2019/7/30 11:07:10 :  sjr
                  (调用后修改)
样品信息        : RS-0299 99-1-1
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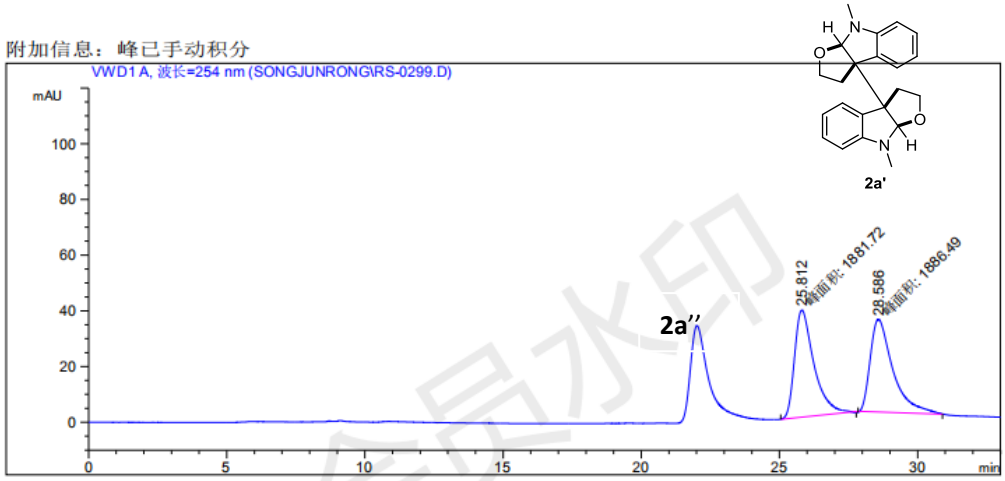
附加信息：峰已手动积分




```
======================================================================
                        面积百分比报告
======================================================================

排序                :      信号
乘积因子:           :      1.0000
稀释因子:           :      1.0000
内标中不使用乘积因子和稀释因子


信号 1: VWD1 A, 波长=254 nm

 峰  保留时间 类型  峰宽      峰面积       峰高      峰面积
  #    [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  25.812 MM    0.8151 1881.72437   38.47661  49.9367
   2  28.586 MM    0.9454 1886.49390   33.25739  50.0633

总量 :                   3768.21826   71.73400

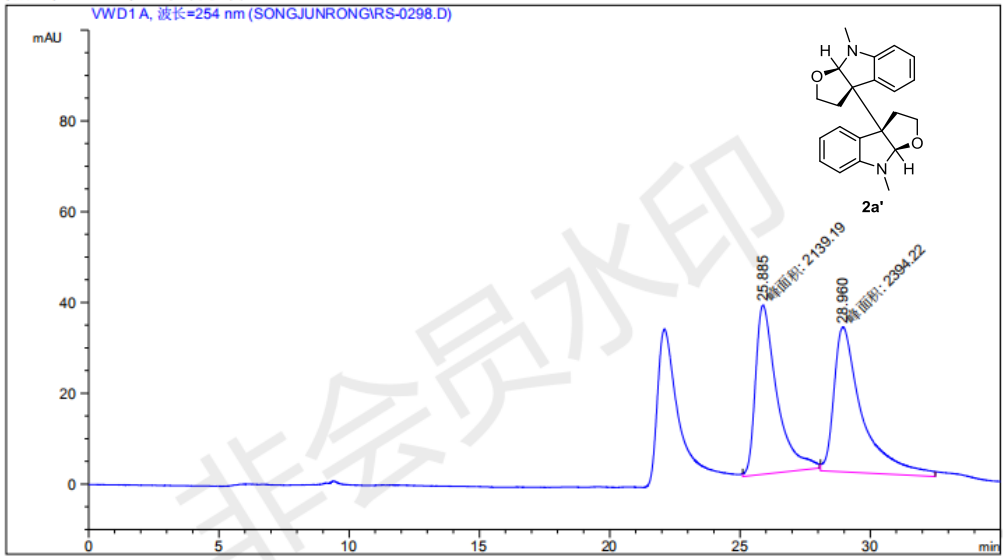

======================================================================
                        *** 报告结束 ***
```

仪器 1 2019/7/30 11:07:36 sjr　　页 1/1

数据文件: C:\CHEM32\1\DATA\SONGJUNRONG\RS-0298.D
样品名称: rs-0298(99-1)

操作者 : sjr
仪器 : 仪器 1 位置 : 样品瓶 2
进样日期 : 2019/7/30 9:54:04
进样量 : 2.0 µl
采集方法 : C:\CHEM32\1\METHODS\SONGJUNRONG\DEF_LC.M (0.7-99-1-2019.07.30) .M
最后修改 : 2019/7/30 9:50:05 : sjr
(调用后修改)
分析方法 : C:\CHEM32\1\METHODS\SONGJUNRONG\DEF_LC.M (1.0-95-5-2019.07.30) .M
最后修改 : 2019/7/30 11:17:49 : sjr
(调用后修改)
样品信息 : RS-0298 99-1-1

附加信息: 峰已手动积分



面积百分比报告

排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

信号 1: VWD1 A, 波长=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	25.885	MM	0.9577	2139.19189	37.22751	47.1872
2	28.960	MM	1.2497	2394.22363	31.93000	52.8128
总量 :				4533.41553	69.15751	