

*Supporting Information For:*

## **Enantioselective Synthesis of Benzazepinoindoles Bearing Trifluoromethylated Quaternary Stereocenters Catalyzed by Chiral Spirocyclic Phosphoric Acids**

*Xuejian Li, Di Chen, Haorui Gu, and Xufeng Lin \**

Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China

Email: [lxfok@zju.edu.cn](mailto:lxfok@zju.edu.cn)

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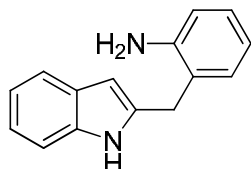
## 1. General Information

All reactions were carried out in oven-dried glassware with magnetic stirring under dry argon atmosphere unless otherwise mentioned. Powdered 4Å molecular sieves were activated at 200 °C for 2 h under vacuum (<0.2 Torr). Catalysts **4a-4d** were prepared according to the methods reported by our group<sup>[1]</sup>. <sup>1</sup>H NMR spectra were recorded on 400 MHz or 500 MHz spectrometer. The chemical shifts were reported relative to internal standard TMS (0) in CDCl<sub>3</sub> or 2.5 in DMSO-d<sub>6</sub>. The following abbreviations were used to describe peak patterns where appropriate: br=broad, s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet. Coupling constants were reported in Hertz (Hz). <sup>13</sup>C NMR spectra were recorded on 100 MHz or 125 MHz spectrometer, referred to the internal solvent signals (77.0 for CDCl<sub>3</sub> or 40.0 for DMSO-d<sub>6</sub>). Infrared spectra were recorded on an ATR-FTIR spectrometer. Optical rotations were determined using a Perkin Elmer Model 341 polarimeter at 20 °C. The enantiomeric excesses (*ee*) were determined by chiral HPLC analysis on Daicel Chiralpak AD-H and Chiralcel OD-H columns. HRMS were obtained using EI ionization.

## 2. Preparation of substrates 1

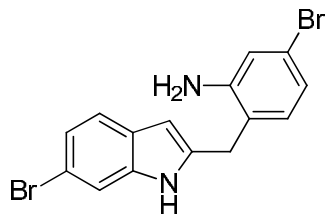
Compounds **1a-1e** were prepared followed by the reported procedures.<sup>[2,3]</sup>

### 2-((1H-indol-2-yl)methyl)aniline (**1a**)



m.p.112-114°C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 8.03 (s, 1H), 7.52 (d, *J*=7.5 Hz, 1H), 7.21 (d, *J*=8.0 Hz, 1H), 7.18-7.00 (m, 4H), 6.76-6.82 (m, 1H), 6.69 (d, *J*=7.9 Hz, 1H), 6.35 (s, 1H), 4.04 (s, 2H), 3.65 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 144.95, 136.62, 136.21, 130.56, 128.46, 128.27, 123.09, 121.36, 119.89, 119.72, 119.06, 116.34, 110.57, 100.59, 31.45; IR (film): γ = 3396, 2959, 2920, 1617, 1458, 1587, 1456, 1329, 1284, 1163, 1096, 1043, 799, 748cm<sup>-1</sup>; HRMS (EI-TOF): calcd for C<sub>15</sub>H<sub>14</sub>N<sub>2</sub> 222.1157, found 222.1159.

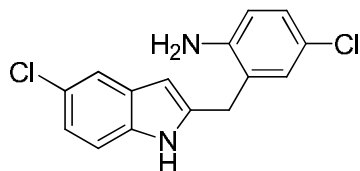
### 5-bromo-2-((6-bromo-1H-indol-2-yl)methyl)aniline (**1b**)



m.p. 89-91°C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 8.03 (s, 1H), 7.40-7.29 (m, 2H), 7.14-7.18 (m, 1H), 6.97 (d, *J*=8.0 Hz, 1H), 6.93-6.86 (m, 1H), 6.83 (d, *J*=1.9 Hz, 1H), 6.30 (s, 1H), 3.94 (s, 2H), 3.71 (s,

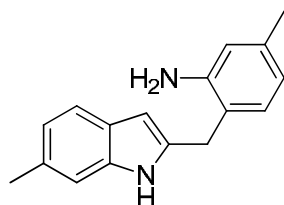
2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 146.18, 137.02, 136.62, 131.85, 127.26, 123.11, 121.80, 121.49, 121.48, 121.15, 118.89, 114.91, 113.56, 100.93, 30.87; IR (film):  $\gamma$  = 3409, 2962, 2926, 1617, 1612, 1491, 1452, 1412, 1260, 1090, 1049, 805, 733  $\text{cm}^{-1}$ ; HRMS (EI-TOF): calcd for  $\text{C}_{15}\text{H}_{14}\text{N}_2$  377.9367, found 377.9374.

**4-chloro-2-((5-chloro-1H-indol-2-yl)methyl)aniline (1c)**



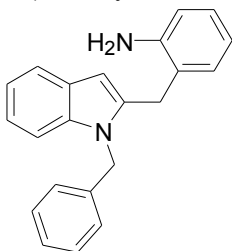
m.p. 30-32°C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.15 (s, 1H), 7.46 (d,  $J$ =1.8 Hz, 1H), 7.14-6.99 (m, 4H), 6.60 (d,  $J$ =8.2 Hz, 1H), 6.27 (s, 1H), 3.94 (s, 2H), 3.68 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 143.35, 137.28, 134.59, 130.07, 129.43, 128.13, 125.40, 124.38, 123.60, 121.78, 119.36, 117.55, 111.57, 100.59, 31.16; IR (film):  $\gamma$  = 3415, 2929, 2855, 1618, 1575, 1492, 1466, 1447, 1414, 1310, 1061, 876, 736  $\text{cm}^{-1}$ ; HRMS (EI-TOF): calcd for  $\text{C}_{15}\text{H}_{12}\text{Cl}_2\text{N}_2$  290.0378, found 290.0377.

**5-methyl-2-((6-methyl-1H-indol-2-yl)methyl)aniline (1d)**



m.p. 97-100°C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.88 (s, 1H), 7.37-7.42 (m, 1H), 7.01 (d,  $J$ =7.6 Hz, 1H), 6.95 (s, 1H), 6.89 (d,  $J$ =8.0 Hz, 1H), 6.60 (d,  $J$ =7.5 Hz, 1H), 6.49 (s, 1H), 6.28 (s, 1H), 3.95 (s, 2H), 3.60 (s, 2H), 2.40 (s, 3H), 2.26 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 144.79, 138.04, 136.67, 136.18, 131.06, 130.47, 126.27, 121.36, 120.25, 119.83, 119.49, 117.05, 110.61, 100.25, 31.12, 21.63, 21.07; IR (film):  $\gamma$  = 3410, 2962, 2925, 1617, 1490, 1453, 1413, 1261, 1091, 1051, 809  $\text{cm}^{-1}$ ; HRMS (EI-TOF): calcd for  $\text{C}_{17}\text{H}_{18}\text{N}_2$  250.1470, found 250.1476.

**2-(1-Benzyl-1H-indol-2-ylmethyl)-phenylamine (1e)**



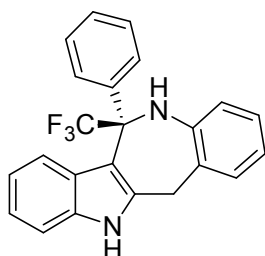
m.p. 28-30 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.54 (d,  $J$ =7.5 Hz, 1H), 7.29-7.17 (m, 4H), 7.10-7.14 (m, 3H), 6.99-6.90 (m, 3H), 6.70-6.74 (m, 1H), 6.65 (d,  $J$ =7.9 Hz, 1H), 6.25 (s, 1H), 5.29 (s, 2H), 3.88 (s, 2H), 3.55 (s, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 144.83, 137.71, 137.79, 130.40, 128.79, 127.94, 127.82, 127.32, 125.92, 122.49, 121.33, 120.11, 119.69, 118.91, 116.12, 109.30, 101.48, 46.57, 30.11; IR (film):  $\gamma$  = 3438, 3360, 3057, 3024, 1617, 1621, 1584, 1495, 1454, 1407, 1355, 1316, 910, 749, 730, 696  $\text{cm}^{-1}$ ; HRMS (EI-TOF): calcd for  $\text{C}_{22}\text{H}_{20}\text{N}_2$  312.1626, found 312.1628.

### 3. General procedure for synthesis of benzazepinoindoles 3.

To a solution of indoles **1** (0.1 mmol), trifluoromethyl ketones **2** (0.12 mmol) in 1,2-dichloroethane (0.6 mL) was added powdered 4Å molecular sieves (0.1 g) and the catalyst **4b** (0.005 mmol). The resulting mixture was stirred under an argon atmosphere at the definitized temperature until complete conversion was indicated by TLC. The crude product was then subjected to a silica gel column (petroleum ether/ethyl acetate) to afford the desired product **3**.

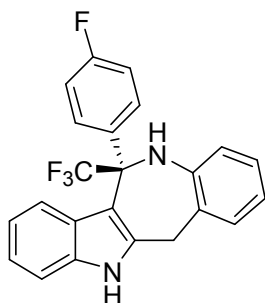
The racemates were prepared by heating a 1:1 mixture of the corresponding **1** and **2** to 80 °C in dichloroethane for 24 h in the presence of TFA (0.2 eq). The crude reaction mixture was directly subjected to a silica gel column (petroleum ether/ethyl acetate) to afford the desired racemate.

#### (S)-12-phenyl-12-(trifluoromethyl)-5,6,11,12-tetrahydro-benzo[6,7]azepino[4,3-b]indole (**3aa**)



According to general procedure: the product was obtained as yellow solid; m.p. 172-174°C; from flash chromatography (hexane/EtOAc = 10:1 to 6:1), 93% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 95/5, 0.8 mL/min),  $t_R$  (minor) 17.5 min,  $t_R$  (major) 20.7 min;  $[\alpha]_D^{20} = -24.5$  (c = 0.45, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.08 (s, 1H), 7.47-7.26 (m, 5H), 7.24 (s, 1H), 7.18 (d,  $J=7.6$  Hz, 1H), 7.10-6.93 (m, 3H), 6.71-6.75 (m, 1H), 6.59 (d,  $J=8.2$  Hz, 1H), 6.47 (d,  $J=7.6$  Hz, 1H), 4.50 (d,  $J=15.1$  Hz, 1H), 3.90 (d,  $J=15.1$  Hz, 1H), 3.82 (s, 1H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ = -69.59 (s, 3F); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 142.51, 139.30, 136.93, 134.84, 134.39, 128.22, 127.90, 127.72, 127.43, 127.23, 125.34, 124.30, 123.49, 121.30, 120.81, 120.79, 119.75, 110.31, 106.03, 68.88 (q,  $J=26.1$  Hz), 32.55; IR (film): γ = 3406, 3058, 2926, 2855, 1620, 1596, 1560, 1495, 1474, 1459, 1058, 958, 746 cm<sup>-1</sup>; HRMS (EI-TOF): calcd for C<sub>23</sub>H<sub>17</sub>F<sub>3</sub>N<sub>2</sub> 378.1344, found 378.1344.

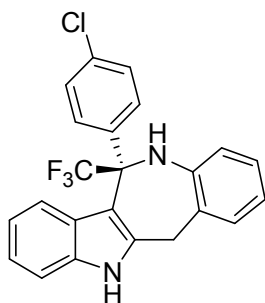
#### (S)-12-(4-fluorophenyl)-12-(trifluoromethyl)-5,6,11,12-tetrahydro-benzo[6,7]azepino[4,3-b]indole (**3ab**)



According to general procedure: the product was obtained as yellow solid; m.p. 147-149°C; from flash chromatography (hexane/EtOAc = 10:1 to 6:1), 94% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 95/5, 0.8 mL/min),  $t_R$  (minor) 16.6 min,  $t_R$  (major) 22.5 min;  $[\alpha]_D^{20} = -14$  (c = 0.39, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.10 (s, 1H), 7.27 (s, 1H), 7.23-7.24 (m, 2H), 7.18 (d,  $J=6$  Hz, 1H),

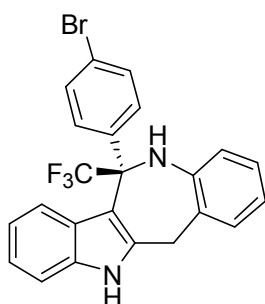
7.04-7.06 (m, 2H), 6.92-7.00 (m,  $J=8.2$  Hz, 3H), 6.80-6.78 (m, 1H), 6.59 (d,  $J=8$  Hz, 1H), 6.46 (d,  $J=7.2$  Hz, 1H), 4.51 (d,  $J=15.1$  Hz, 1H), 3.87 (d,  $J=15.1$  Hz, 1H), 3.77 (s, 1H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta = -69.89$  (s, 3F),  $-114.01$  (s, 1F);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 163.32, 160.86, 142.19, 137.05, 135.14, 134.40, 129.19$ (d,  $J=5.7$  Hz),  $127.62, 127.32, 124.37, 123.69, 121.42, 120.68, 119.86, 115.19, 114.98, 110.39, 105.79, 68.34$ (q,  $J=26.5$  Hz),  $32.49$ ; IR (film):  $\gamma = 3401, 3057, 2955, 2926, 2853, 1727, 1605, 1510, 1458, 1287, 1166, 960, 831, 746$   $\text{cm}^{-1}$ ; HRMS (EI-TOF): calcd for  $\text{C}_{23}\text{H}_{16}\text{F}_4\text{N}_2$  396.1250, found 396.1250.

**(S)-12-(4-chlorophenyl)-12-(trifluoromethyl)-5,6,11,12-tetrahydro-benzo[6,7]azepino[4,3-b]indole (3ac)**



According to general procedure: the product was obtained as yellow solid; m.p. 98-100°C; from flash chromatography (hexane/EtOAc = 10:1 to 6:1), 96% ee; HPLC analysis: Chiralpak AD-H (hexane/*i*-PrOH = 95/5, 0.8 mL/min),  $t_R$  (minor) 15.9 min,  $t_R$  (major) 19.3min;  $[\alpha]_D^{20} = -36.8$  ( $c = 5.4, \text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.12$  (s, 1H), 7.18-7.27 (m, 7H), 7.02-7.07 (m, 2H), 6.99-6.97 (m, 1H), 6.81 (d,  $J=7.6$  Hz, 1H), 6.59 (d,  $J=8$  Hz, 1H), 6.45 (d,  $J=7.6$  Hz, 1H), 4.54 (d,  $J=14.8$  Hz, 1H), 3.85 (d,  $J=14.8$  Hz, 1H), 3.76 (s, 1H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta = -70.01$ (s, 3F);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 142.02, 137.71, 137.18, 135.13, 134.39, 133.82, 129.59, 128.68, 128.41, 127.64, 127.26, 125.16, 124.43, 123.76, 121.47, 120.63, 119.93, 110.40, 105.44, 68.54$ (q,  $J=27$  Hz),  $32.47$ ; IR (film):  $\gamma = 3405, 3057, 2923, 1723, 1614, 1494, 1475, 1459, 1336, 1161, 960, 746$   $\text{cm}^{-1}$ ; HRMS (EI-TOF): calcd for  $\text{C}_{23}\text{H}_{16}\text{ClF}_3\text{N}_2$  412.0954, found 412.0946.

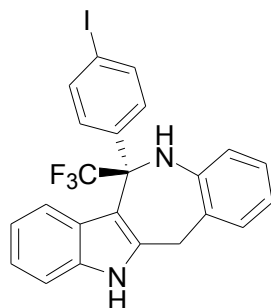
**(S)-12-(4-bromophenyl)-12-(trifluoromethyl)-5,6,11,12-tetrahydro-benzo[6,7]azepino[4,3-b]indole (3ad)**



According to general procedure: the product was obtained as yellow solid; m.p. 85-87°C; from flash chromatography (hexane/EtOAc = 10:1 to 6:1), 95% ee; HPLC analysis: Chiralpak AD-H (hexane/*i*-PrOH = 95/5, 0.8 mL/min),  $t_R$  (minor) 16.9 min,  $t_R$  (major) 20.9 min;  $[\alpha]_D^{20} = -41.5$  ( $c = 0.19, \text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta=8.12$  (s, 1H), 7.93 (d,  $J=8.4$  Hz, 1H), 7.71 (d,  $J=8.4$  Hz, 1H), 7.38 (d,  $J=8.4$  Hz, 2H), 7.20(d,  $J=8.4$  Hz, 1H) 7.12 (d,  $J=8.4$  Hz, 2H), 6.97-7.04(m, 2H), 6.81-6.83 (m, 1H), 6.59 (d,  $J=8$  Hz, 1H), 6.45 (d,  $J=7.6$ , 1H), 4.54 (d,  $J=15.2$  Hz, 1H), 3.84 (d,  $J=15.2$  Hz, 1H), 3.76 (s, 1H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta = -69.59$  (s, 3F);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 141.96$ ,

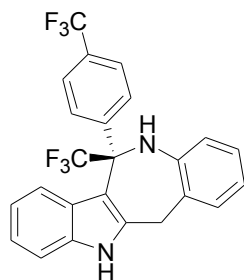
138.19, 137.21, 135.11, 134.37, 132.56, 131.35, 128.98, 128.55, 127.63, 127.19, 124.40, 123.75, 122.08, 121.42, 120.59, 119.91, 110.48, 105.25, 68.57 (q,  $J=26.45$  Hz), 32.33; IR (film):  $\gamma=3407, 3351, 3057, 1721, 1585, 1475, 1458, 1497, 1011, 924, 822, 748$   $\text{cm}^{-1}$ ; HRMS (EI-TOF): calcd for  $\text{C}_{23}\text{H}_{16}\text{BrF}_3\text{N}_2$  456.0449, found 456.0440.

**(S)-12-(4-Iodo-phenyl)-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3ae)**



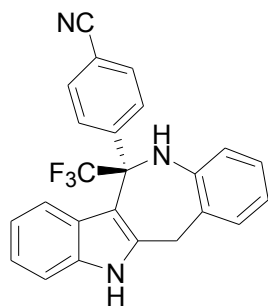
According to general procedure: the product was obtained as yellow solid; m.p. 68-70 °C; from flash chromatography (hexane/EtOAc = 10:1 to 6:1); 92% ee; HPLC analysis: Chiralpak AD-H (hexane/*i*-PrOH = 95/5, 0.8 mL/min),  $t_R$  (minor) 19.5 min,  $t_R$  (major) 22.5 min;  $[\alpha]_D^{20} = -28.2$  ( $c = 1.8, \text{CH}_2\text{Cl}_2$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.12$  (s, 1H), 7.66-7.50 (m, 2H), 7.26 (d,  $J=4.6$  Hz, 1H), 7.18 (dd,  $J=7.2, 1.2$  Hz, 1H), 7.11-6.93 (m, 5H), 6.82-6.84 (m, 1H), 6.59 (d,  $J=8.1$  Hz, 1H), 6.45 (d,  $J=7.6$  Hz, 1H), 4.53 (d,  $J=15.0$  Hz, 1H), 3.83 (d,  $J=15.1$  Hz, 1H), 3.76 (s, 1H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta = -70.00$  (s, 3F);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 141.94, 138.83, 137.33, 137.19, 135.10, 134.32, 129.13, 129.11, 127.63, 127.59, 127.19, 124.42, 123.74, 121.45, 120.60, 119.93, 110.39, 105.22, 94.00, 68.53$ (q,  $J = 10$  Hz), 32.44 (s); IR (film):  $\gamma = 3403, 3048, 2918, 2849, 1724, 1474, 1458, 1249, 1190, 1140, 1105, 1062, 923, 908, 746$   $\text{cm}^{-1}$ ; HRMS (EI-TOF): calcd for  $\text{C}_{23}\text{H}_{16}\text{F}_3\text{IN}_2$  504.0310, found 504.0315.

**(S)-12-Trifluoromethyl-12-(4-trifluoromethyl-phenyl)-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3af)**



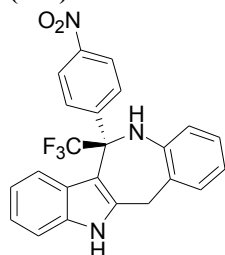
According to general procedure: the product was obtained as white solid; m.p. 88-90°C, from flash chromatography (hexane/EtOAc = 10:1 to 6:1); 93% ee; HPLC analysis: Chiralpak AD-H (hexane/*i*-PrOH = 95/5, 0.8 mL/min),  $t_R$  (minor) 10.1 min,  $t_R$  (major) 12.4 min;  $[\alpha]_D^{20} = -24.59$  ( $c = 4.1, \text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.10$  (s, 1H), 7.19-7.15 (m, 3H), 7.12-6.94 (m, 6H), 6.89-6.76 (m, 1H), 6.63 (d,  $J=7.5$  Hz, 1H), 6.46 (d,  $J=7.6$  Hz, 1H), 4.49 (d,  $J=15.1$  Hz, 1H), 3.82 (d,  $J=15.1$  Hz, 1H), 3.81 (s, 1H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta = -69.98$  (s, 3F),  $-62.63$  (s, 3F);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 142.84, 141.79, 137.33, 135.17, 134.40, 129.98$ , (q,  $J=26.6$  Hz), 127.74, 127.68, 127.62, 127.60, 127.12, 125.26, 125.22, 124.42, 123.91, 121.55, 120.45, 120.03, 110.48, 105.10, 68.99 (q,  $J=26.6$  Hz), 32.45; IR (film):  $\gamma = 3404, 3457, 2920, 1617, 1562, 1475, 1459, 1323, 1122, 1072, 745$   $\text{cm}^{-1}$ ; HRMS (EI-TOF): calcd for  $\text{C}_{24}\text{H}_{16}\text{F}_6\text{N}_2$  446.1218, found 446.1213.

**(S)-4-(12-Trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indol-12-yl)-benzonitrile (3ag)**



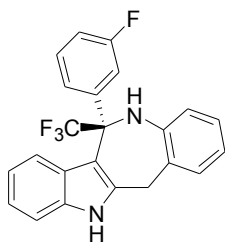
According to general procedure: the product was obtained as yellow solid; m.p. 258-260°C; from flash chromatography (hexane/EtOAc = 10:1 to 6:1); 93% ee; HPLC analysis: Chiralpak AS-H (hexane/i-PrOH = 85/15, 0.8 mL/min),  $t_R$  (major) 19.6 min,  $t_R$  (minor) 28.3 min;  $[\alpha]_D^{20} = -7.2$  (c = 1.2, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.23$  (s, 1H), 7.55 (d,  $J=8.6$  Hz, 2H), 7.34 (d,  $J=8.3$  Hz, 2H), 7.28 (d,  $J=8.1$  Hz, 1H), 7.20 (d,  $J=7.1$  Hz, 1H), 7.03-7.06 (m, 3H), 6.81-6.83 (m, 1H), 6.49 (d,  $J=8.1$  Hz, 1H), 6.36 (d,  $J=7.3$  Hz, 1H), 4.61 (d,  $J=15.0$  Hz, 1H), 3.80 (d,  $J=15.0$  Hz, 1H), 3.76 (s, 1H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta = -70.22$  (s, 3F); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 143.75, 141.33, 137.57, 135.37, 134.33, 132.10, 127.92, 127.90, 127.76, 127.70, 126.88, 124.45, 124.10, 121.63, 120.10, 118.49, 111.76, 110.58, 104.46, 68.78$  (q,  $J=27$  Hz), 32.31; IR (film):  $\gamma = 3397, 3060, 1475, 1459, 1286, 1251, 1159, 1127, 1075, 1059, 1011, 961, 909, 734$  cm<sup>-1</sup>; HRMS (EI-TOF): calcd for C<sub>24</sub>H<sub>16</sub>N<sub>3</sub>F<sub>3</sub> 403.1296, found 403.1298.

**(S)-12-(4-Nitro-phenyl)-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3ah)**



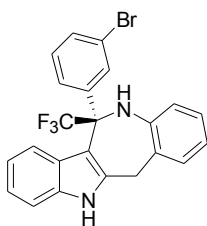
According to general procedure: the product was obtained as yellow solid; m.p. 240-242°C; from flash chromatography (hexane/EtOAc = 10:1 to 6:1); >99.5% ee; HPLC analysis: Chiralpak AS-H (hexane/i-PrOH = 90/10, 0.7 mL/min),  $t_R$  (minor) 43.7 min,  $t_R$  (major) 62.1 min;  $[\alpha]_D^{20} = -96.2$  (c = 2.0, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.19$  (s, 1H), 8.11 (d,  $J=9.0$  Hz, 2H), 7.39 (d,  $J=8.7$  Hz, 2H), 7.29 (d,  $J=8.1$  Hz, 1H), 7.24-7.19 (m, 1H), 7.09-6.98 (m, 3H), 6.80-6.82 (m, 1H), 6.49 (d,  $J=8.2$  Hz, 1H), 6.39-6.32 (m, 1H), 4.64 (d,  $J=15.0$  Hz, 1H), 3.81 (d,  $J=15.0$ , 1H), 3.77 (s, 1H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta = -70.34$  (s, 3F); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 147.19, 145.60, 141.23, 137.56, 135.45, 134.39, 128.21, 128.19, 127.83, 127.75, 126.88, 124.49, 124.21, 123.48, 121.71, 120.19, 119.77, 110.63, 104.49, 68.69$  (q,  $J=26.6$  Hz), 32.34; IR (KBr):  $\gamma = 3401, 2920, 1520, 1459, 1349, 1251, 1162, 1140, 1066, 956, 742$  cm<sup>-1</sup>; HRMS (EI-TOF): calcd for C<sub>23</sub>H<sub>16</sub>F<sub>3</sub>N<sub>3</sub>O<sub>2</sub> 423.1195, found 423.1199.

**(S)-12-(3-Fluoro-phenyl)-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3ai)**



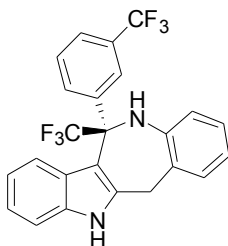
According to general procedure: the product was obtained as yellow solid; m.p. 184-186°C; from flash chromatography (hexane/EtOAc = 10:1 to 6:1); 96% ee; HPLC analysis: Chiralpak AS-H (hexane/*i*-PrOH = 95/5, 0.8 mL/min),  $t_R$  (minor) 16.9 min,  $t_R$  (major) 19.9 min;  $[\alpha]_D^{20} = -13.2$  ( $c = 0.93$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.16$  (s, 1H), 7.52 (d,  $J=8.4$  Hz, 2H), 7.38 (d,  $J=8.3$  Hz, 2H), 7.31 (m, 1H), 7.20 (m, 1H), 7.03-7.06 (m, 3H), 6.85-6.76 (m, 1H), 6.53 (d,  $J=8.2$  Hz, 1H), 6.41 (d,  $J=7.5$  Hz, 1H), 4.57 (d,  $J=15.0$  Hz, 1H), 3.86 (d,  $J=15.0$  Hz, 1H), 3.78 (s, 1H);  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta = -69.84$  (s, 3F),  $-112.02$  (s, 1F);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 163.68$ , 161.23, 142.04, 141.56 (d,  $J=6.6$  Hz), 137.16, 135.04, 134.39, 129.71 (d,  $J=8.0$  Hz), 127.65, 127.26, 124.35, 123.77, 122.92, 121.43, 120.59 (d,  $J=2.5$  Hz), 119.90, 115.01, 114.74 (d,  $J=12.6$ ), 114.44, 110.43, 105.34, 68.67 (q,  $J=26.6$  Hz), 32.49; IR (film):  $\gamma = 3404$ , 3060, 2926, 1718, 1614, 1589, 1475, 1444, 1141, 1055, 746  $\text{cm}^{-1}$ ; HRMS (EI-TOF): calcd for  $\text{C}_{23}\text{H}_{16}\text{F}_4\text{N}_2$  396.1250, found 396.1256.

**(S)-12-(3-Bromo-phenyl)-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3aj)**



According to general procedure: the product was obtained as yellow solid; m.p. 184-186°C; from flash chromatography (hexane/EtOAc = 10:1 to 6:1); 93% ee; HPLC analysis: Chiralpak AD-H (hexane/*i*-PrOH = 95/5, 0.8 mL/min),  $t_R$  (minor) 23.7 min,  $t_R$  (major) 30.1 min;  $[\alpha]_D^{20} = -47$  ( $c = 0.06$ ,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.11$  (s, 1H), 7.58-7.52 (m, 1H), 7.52-7.31 (m, 1H), 7.31-7.24 (m, 1H), 7.24-7.13 (m, 1H), 7.13-6.92 (m, 5H), 6.82-6.84 (m, 1H), 6.69-6.56 (m, 1H), 6.52-6.41 (m, 1H), 4.50 (d,  $J=15.1$  Hz, 1H), 3.87 (d,  $J=15.1$  Hz, 1H), 3.78 (s, 1H);  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta = -69.74$  (s, 3F);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 141.97$ , 141.36, 137.14, 135.02, 134.41, 131.09, 129.85, 129.83, 129.79, 127.68, 127.66, 127.18, 126.35, 126.34, 124.45, 123.83, 122.33, 121.48, 119.97, 110.43, 105.29, 68.50 (q,  $J=26.6$  Hz), 31.48; IR (film):  $\gamma = 3405$ , 3348, 2962, 1563, 1474, 1459, 1331, 1263, 1162, 1061, 746  $\text{cm}^{-1}$ ; HRMS (EI-TOF): calcd for  $\text{C}_{23}\text{H}_{16}\text{BrF}_3\text{N}_2$  456.0449, found 456.0452.

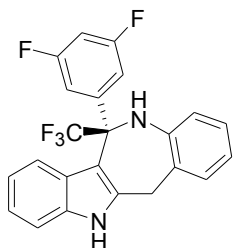
**(S)-12-Trifluoromethyl-12-(3-trifluoromethyl-phenyl)-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3ak)**





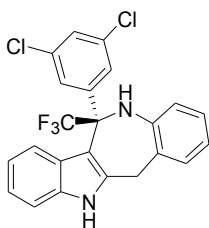
According to general procedure: the product was obtained as white solid; m.p. 162-164°C, from flash chromatography (hexane/EtOAc = 10:1 to 6:1); 93% ee; HPLC analysis: Chiralpak AD-H (hexane/*i*-PrOH = 90/10, 0.8 mL/min),  $t_R$  (minor) 6.5 min,  $t_R$  (major) 8.1 min;  $[\alpha]_D^{20} = -11.2$  ( $c = 0.71$ , CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.14$  (s, 1H), 7.64 (s, 1H), 7.54 (d,  $J=7.1$  Hz, 1H), 7.31-7.24 (m, 2H), 7.22-7.17 (m, 1H), 7.15 (d,  $J=7.2$  Hz, 1H), 7.06-6.94 (m, 3H), 6.85-6.74 (m, 1H), 6.54 (d,  $J=8.2$  Hz, 1H), 6.39 (d,  $J=7.5$  Hz, 1H), 4.48 (d,  $J=15.1$  Hz, 1H), 3.87 (d,  $J=15.1$  Hz, 1H), 3.78 (s, 1H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta = -69.67$  (s, 3F); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta^{13}C$  NMR (101 MHz, CDCl<sub>3</sub>)  $\delta = 141.80, 140.13, 137.32, 135.16, 134.43, 131.20, 130.64$  (q,  $J=32$  Hz), 128.71, 127.72, 127.68, 127.07, 125.07, 124.85, 124.44, 123.95, 121.52, 120.37, 120.35, 120.01, 110.51, 105.10, 69.76 (q,  $J=26$  Hz), 32.44; IR (film):  $\gamma = 3467, 3402, 2920, 1611, 1510, 1462, 1270, 1181, 1166, 1126, 734$  cm<sup>-1</sup>; HRMS (EI-TOF): calcd for C<sub>25</sub>H<sub>20</sub>ClF<sub>3</sub>N<sub>2</sub> 446.1267, found 446.1219.

**(S)-12-(3,5-Difluoro-phenyl)-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3al)**



According to general procedure: the product was obtained as yellow solid; m.p. 158-162°C, from flash chromatography (hexane/EtOAc = 10:1 to 6:1); 93% ee; HPLC analysis: Chiralpak AD-H (hexane/*i*-PrOH = 90/10, 0.8 mL/min),  $t_R$  (minor) 6.5 min,  $t_R$  (major) 8.1 min;  $[\alpha]_D^{20} = -26.3$  ( $c = 2.9$ , CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.09$  (s, 1H), 7.23-7.13 (m, 3H), 7.00-7.05 (m, 6H), 6.81-6.83 (m, 1H), 6.63 (d,  $J=6.7$  Hz, 1H), 6.45 (d,  $J=7.5$  Hz, 1H), 4.49 (d,  $J=15.1$  Hz, 1H), 3.84 (d,  $J=15.1$  Hz, 1H), 3.80 (s, 1H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta = -69.67$  (s, 3F); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 163.87$  (d,  $J=13$  Hz), 161.40 (d,  $J=14$  Hz), 141.60, 137.40, 135.20, 134.40, 127.77, 127.70, 127.04, 124.39, 124.07, 121.61, 120.42, 120.39, 120.12, 110.68 (d,  $J=23$  Hz), 110.53, 110.42 (d,  $J=21$  Hz), 104.70, 103.53, 65.93 (q,  $J=12.6$  Hz), 32.42; IR (film):  $\gamma = 3467, 3402, 2920, 1611, 1510, 1462, 1270, 1181, 1166, 1126, 734$  cm<sup>-1</sup>; HRMS (EI-TOF): calcd for C<sub>25</sub>H<sub>20</sub>ClF<sub>3</sub>N<sub>2</sub> 440.1267, found 414.1152.

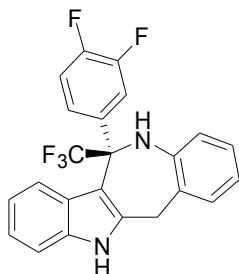
**(S)-12-(3,5-Dichloro-phenyl)-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3am)**



According to general procedure: the product was obtained as yellow solid; m.p. 166-168°C, from flash chromatography (hexane/EtOAc = 10:1 to 6:1); 96% ee; HPLC analysis: Chiralpak AD-H (hexane/*i*-PrOH = 95/5, 0.8 mL/min),  $t_R$  (minor) 16.9 min,  $t_R$  (major) 21.2 min;  $[\alpha]_D^{20} = -16.9$  ( $c = 3.9$ , CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.15$  (s, 1H), 7.31 (s, 1H), 7.27 (s, 1H), 7.23-7.17 (m, 1H), 7.14 (d,  $J=0.8$  Hz, 2H), 7.13-6.96 (m, 3H), 6.90-6.81 (m, 1H), 6.66 (d,  $J=8.1$  Hz, 1H), 6.48 (d,  $J=7.6$  Hz, 1H), 4.52 (d,  $J=15.1$  Hz, 1H), 3.87 (d,  $J=15.1$  Hz, 1H), 3.75 (s, 1H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta = -69.85$  (s, 3F); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 142.30, 141.53, 137.32, 135.13, 134.80, 134.43,$

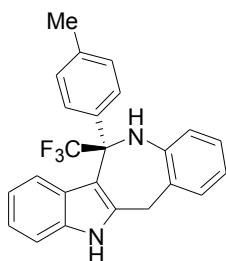
128.23, 127.79, 127.75, 126.91, 125.83, 125.81, 124.51, 124.14, 121.64, 120.35, 120.19, 110.57, 104.61, 68.57 (q,  $J=26.9$  Hz), 32.45; IR (film):  $\gamma = 3399, 2950, 2852, 1561, 1458, 1277, 1173, 1141, 977, 745$   $\text{cm}^{-1}$ ; HRMS (EI-TOF): calcd for  $\text{C}_{28}\text{H}_{15}\text{Cl}_2\text{F}_3\text{N}_2$  446.0564, found 446.0564.

**(S)-12-(3,4-Difluoro-phenyl)-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3an)**



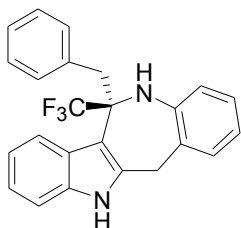
According to general procedure: the product was obtained as yellow solid; m.p. 165-167°C, from flash chromatography (hexane/EtOAc = 10:1 to 6:1); 96% ee; HPLC analysis: Chiralpak AS-H (hexane/*i*-PrOH = 85/15, 0.8 mL/min),  $t_R$  (minor) 7.5 min,  $t_R$  (major) 8.7 min;  $[\alpha]_D^{20} = -16$  ( $c = 0.24$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.09$  (s, 1H), 7.25 (s, 1H), 7.17 (d,  $J=7.2$  Hz, 1H), 7.14-6.94 (m, 6H), 6.83-6.85 (m, 1H), 6.62 (d,  $J=8.1$  Hz, 1H), 6.45 (d,  $J=7.5$  Hz, 1H), 4.50 (d,  $J=15.1$  Hz, 1H), 3.81 (d,  $J=15.1$  Hz, 1H), 3.76 (s, 1H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta = -70.09$  (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 151.00$  (dd,  $J=7.0, 6.9$  Hz), 148.53 (dd,  $J=9.0, 8.9$  Hz), 141.77, 137.29, 135.19, 134.41, 127.70, 127.68, 127.09, 124.39, 123.97, 121.56, 120.49, 120.47 (q,  $J=26$  Hz), 120.03, 117.02, 116.85, 116.83 (ddd,  $J=2.2, 2.1, 27$  Hz), 110.52, 105.13, 68.41 (q,  $J=27$  Hz), 32.40; IR (film):  $\gamma = 3461, 3402, 3057, 1608, 1518, 1459, 1278, 1141, 912, 775, 746, 736$   $\text{cm}^{-1}$ ; HRMS (EI-TOF): calcd for  $\text{C}_{23}\text{H}_{15}\text{F}_5\text{N}_2$  414.1155, found 414.1151.

**(S)-12-*p*-Tolyl-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3ao)**



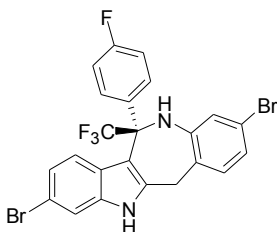
According to general procedure: the product was obtained as yellow solid; m.p. 45-47°C, from flash chromatography (hexane/EtOAc = 10:1 to 6:1); 87% ee; HPLC analysis: Chiralpak AD-H (hexane/*i*-PrOH = 90/10, 0.8 mL/min),  $t_R$  (minor) 8.7 min,  $t_R$  (major) 10.5 min;  $[\alpha]_D^{20} = -18.3$  ( $c = 4.4$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.07$  (s, 1H), 7.30-7.23 (m, 1H), 7.23-7.13 (m, 3H), 7.10-6.92 (m, 3H), 6.83-6.74 (m, 2H), 6.62 (d,  $J=8.2$  Hz, 1H), 6.50 (d,  $J=7.6$  Hz, 1H), 4.45 (d,  $J=15.1$  Hz, 1H), 3.93 (d,  $J=15.1$  Hz, 1H), 3.80 (s, 1H), 2.32 (s, 3H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta = -70.01$  (s, 3F);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 142.67, 137.57, 136.81, 136.45, 134.77, 134.39, 128.29, 127.59, 127.55, 127.15, 127.13, 124.26, 123.40, 121.25, 120.89, 120.92, 119.68, 110.30, 106.19, 68.69$  (q,  $J=25.1$  Hz), 32.53, 20.99; IR (film):  $\gamma = 3406, 3354, 3051, 2917, 2863, 1474, 1460, 1286, 1265, 1158, 1114, 745$   $\text{cm}^{-1}$ ; HRMS (EI-TOF): calcd for  $\text{C}_{24}\text{H}_{19}\text{F}_3\text{N}_2$  392.1500, found 392.1492.

**(S)-12-Benzyl-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole 3ap**



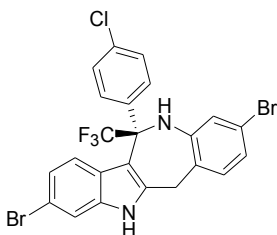
According to general procedure: the product was obtained as yellow solid; m.p. 68-70°C, from flash chromatography (hexane/EtOAc = 10:1 to 6:1); 55% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 90/10, 0.8 mL/min),  $t_R$  (minor) 20.8 min,  $t_R$  (major) 26.8 min;  $[\alpha]_D^{20} = -119.9 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$  ( $c = 0.0164 \text{ g cm}^{-3}$  in  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.02\text{-}7.92$  (m, 1H), 7.92-7.78 (m, 1H), 7.34-7.24 (m, 1H), 7.24-7.02 (m, 6H), 7.02-6.89 (m, 5H), 4.20-4.10 (m, 1H), 3.85 (d,  $J=13.9$  Hz, 1H), 3.78-3.67 (m, 1H), 3.43-3.30 (m, 2H);  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta = -70.77$  (s, 3F);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 144.03, 135.74, 135.11, 134.75, 133.75, 130.72, 128.48, 127.63, 126.75, 125.57, 123.60, 123.31, 121.44, 120.74, 120.14, 110.80, 105.47, 68.95$  (q,  $J=24.9$  Hz), 41.27, 32.78; IR (film):  $\gamma = 3410, 3355, 2926, 1605, 1480, 1287, 1261, 1181, 1163, 1117, 942, 746, 700 \text{ cm}^{-1}$ ; MS (ESI):  $m/z$  ( $[\text{M}+\text{H}]$ ): 393.

**(S)-3,9-Dibromo-12-(4-fluoro-phenyl)-12-trifluoromethyl-5,6,11,12-tetrahydrobenzo[2,3]azepino[5,6-b]indole (3bb)**



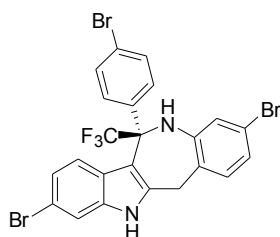
According to general procedure: the product was obtained as yellow solid; m.p. 64-67°C; from flash chromatography (hexane/EtOAc = 10:1 to 6:1), 88% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 90/10, 0.8 mL/min),  $t_R$  (minor) 13.5 min,  $t_R$  (major) 11.5 min,  $[\alpha]_D^{20} = +15.1$  ( $c = 0.5, \text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.10$  (s, 1H), 7.41 (d,  $J=1.5$  Hz, 1H), 7.27 (s, 1H), 7.24 (s, 1H), 7.14 (d,  $J=8.0$  Hz, 1H), 7.06 (d,  $J=8.0$  Hz, 1H), 6.99-7.01 (m, 2H), 6.91 (d,  $J=8.7$  Hz, 1H), 6.69 (d,  $J=1.5$  Hz, 1H), 6.42 (d,  $J=8.6$  Hz, 1H), 4.36 (d,  $J=15.3$  Hz, 1H), 3.90 (d,  $J=15.3$  Hz, 1H), 3.76 (s, 1H);  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta = -69.63$  (s, 3F), -112.97 (s, 1F);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 163.51, 161.04, 143.65, 136.78, 135.24, 133.36, 129.06, 126.96, 126.69, 126.08, 123.39, 121.86$  (d,  $J=26$  Hz), 120.57, 115.52, 115.31, 115.14, 113.41, 113.50, 106.27, 100.98, 68.31 (q,  $J=26.8$  Hz), 31.98; IR (film):  $\gamma = 3414, 3348, 3054, 1606, 1594, 1510, 1492, 1166, 959, 809, 732 \text{ cm}^{-1}$ ; HRMS (EI-TOF): calcd for  $\text{C}_{23}\text{H}_{14}\text{Br}_2\text{F}_2\text{N}_2$  551.9640, found 551.9470.

**(S)-3,9-Dibromo-12-(4-chloro-phenyl)-12-trifluoromethyl-5,6,11,12-tetrahydrobenzo[2,3]azepino[5,6-b]indole (3bc)**



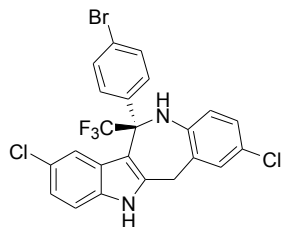
According to general procedure: the product was obtained as yellow solid; mp 231-233°C; from flash chromatography (hexane/EtOAc = 10:1 to 6:1), 90% ee; HPLC analysis: Chiralpak AS-H (hexane/*i*-PrOH = 90/10, 0.7 mL/min),  $t_R$  (minor) 13.0 min,  $t_R$  (major) 19.2 min;  $[\alpha]_D^{20} = +16$  ( $c = 0.2$ , CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.11$  (s, 1H), 7.41 (d,  $J=1.5$  Hz, 1H), 7.27 (d,  $J=8.8$  Hz, 2H), 7.20 (d,  $J=8.5$  Hz, 2H), 7.14 (d,  $J=8.0$  Hz, 1H), 7.05 (d,  $J=8.0$  Hz, 1H), 6.92 (d,  $J=8.7$  Hz, 1H), 6.69 (d,  $J=1.7$  Hz, 1H), 6.42 (d,  $J=8.6$  Hz, 1H), 4.37 (d,  $J=15.3$  Hz, 1H), 3.88 (d,  $J=15.3$  Hz, 1H), 3.78 (s, 1H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta = -69.77$  (s, 3F); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 143.51, 137.14, 136.89, 135.23, 134.37, 133.38, 129.07, 128.72, 128.60, 128.58, 126.95, 126.75, 126.02, 123.47, 121.80, 120.61, 115.19, 113.43, 105.95, 68.35$ (q,  $J=27$  Hz), 31.96; IR (film):  $\gamma = 3367, 3060, 2953, 1660, 1591, 1493, 1446, 1372, 1324, 1072$  cm<sup>-1</sup>; HRMS (EI-TOF): calcd for C<sub>23</sub>H<sub>14</sub>Br<sub>2</sub>ClF<sub>3</sub>N<sub>2</sub> 567.9164, found 576.9164.

**(S)-3,9-Dibromo-12-(4-bromo-phenyl)-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3bd)**



According to general procedure: the product was obtained as yellow solid; m.p. 243-245°C; from flash chromatography (hexane/EtOAc = 10:1 to 6:1), 96% ee; HPLC analysis: Chiralpak AD-H (hexane/*i*-PrOH = 90/10, 0.8 mL/min),  $t_R$  (minor) 12.6 min,  $t_R$  (major) 19.7 min;  $[\alpha]_D^{20} = +2.5$  ( $c = 2.5$ , CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.17$  (s, 1H), 7.94 (d,  $J=7.9$  Hz, 1H), 7.71 (d,  $J=8.8$  Hz, 1H), 7.43-7.45 (m, 2H), 7.17-7.12 (m, 2H), 7.06 (d,  $J=8.0$  Hz, 1H), 6.92 (d,  $J=8.7$  Hz, 1H), 6.69 (d,  $J=1.8$  Hz, 1H), 6.42 (d,  $J=8.6$  Hz, 1H), 4.37 (d,  $J=15.3$  Hz, 1H), 3.89 (d,  $J=15.3$  Hz, 1H), 3.78 (s, 1H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta = -69.59$  (s, 3F); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 143.49, 136.90, 135.22, 133.37, 131.67, 129.08, 128.87, 127.67, 126.94, 126.76, 126.01, 123.49, 122.65, 121.79, 120.63, 115.20, 113.43, 105.87, 99.96, 53.34$ (q,  $J=15.3$  Hz), 31.96; IR (film):  $\gamma = 3421, 3354, 2926, 1719, 1585, 1458, 1191, 1375, 1176, 1154, 756$  cm<sup>-1</sup>; HRMS (EI-TOF): calcd for C<sub>23</sub>H<sub>14</sub>F<sub>2</sub>Br<sub>3</sub>N<sub>2</sub> 611.8659, found 611.8661.

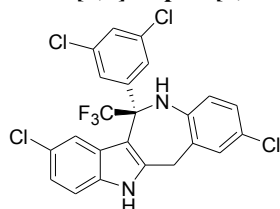
**(S)-12-(4-Bromo-phenyl)-2,8-dichloro-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3cd)**



According to general procedure: the product was obtained as yellow solid, m.p. 59-62°C, from flash chromatography (hexane/EtOAc = 10:1 to 6:1), 90% ee; HPLC analysis: Chiralpak AD-H (hexane/*i*-PrOH = 90/10, 0.8 mL/min),  $t_R$  (major) 9.4 min,  $t_R$  (minor) 11.6 min;  $[\alpha]_D^{20} = -62.1$  ( $c = 7.0$ , CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.16$  (s, 1H), 7.40 (d,  $J=8.7$  Hz, 2H), 7.16 (d,  $J=5.4$  Hz, 2H), 7.09 (d,  $J=8.4$  Hz, 2H), 7.06-6.97 (m, 2H), 6.58 (s, 1H), 6.37 (d,  $J=8.3$  Hz, 1H), 4.45 (d,  $J=15.1$  Hz, 1H), 3.80 (d,  $J=15.1$  Hz, 1H), 3.73 (s, 1H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta = -69.74$  (s, 3F); <sup>13</sup>C NMR (100 MHz,

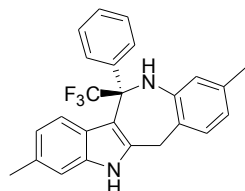
CDCl<sub>3</sub>):  $\delta$  = 140.46, 137.64, 137.34, 136.38, 132.81, 131.68, 129.01, 128.77, 128.10, 127.68, 125.87, 125.60, 122.59, 122.19, 120.00, 111.53, 105.35, 68.44 (q,  $J$  = 15.1 Hz), 32.18; IR (film):  $\gamma$  = 3425, 3352, 3078, 1576, 1492, 1465, 1278, 1189, 1159, 1246, 1011, 907, 731 cm<sup>-1</sup>; HRMS (EI-TOF): calcd for C<sub>23</sub>H<sub>14</sub>BrCl<sub>2</sub>F<sub>3</sub>N<sub>2</sub> 523.9669, found 523.9662.

**(S)-2,8-Dichloro-12-(3,5-dichloro-phenyl)-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3ck)**



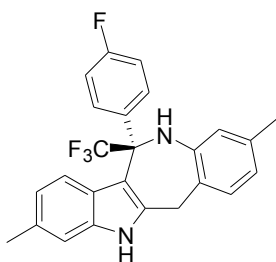
According to general procedure: the product was obtained as white solid; m.p. 239-240°C; from flash chromatography (hexane/EtOAc = 10:1 to 6:1), 90% ee; HPLC analysis: Chiralpak AD-H (hexane/*i*-PrOH = 80/20, 0.8 mL/min),  $t_R$  (minor) 5.2 min,  $t_R$  (major) 11.9 min;  $[\alpha]_D^{20}$  = -47 ( $c$  = 1.7, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.24 (s, 1H), 7.35 (s, 1H), 7.20 (d,  $J$ =8.5 Hz, 2H), 7.12 (s, 2H), 7.05-7.08 (m, 2H), 6.64 (s, 1H), 6.42 (d,  $J$ =8.3 Hz, 1H), 4.43 (d,  $J$ =15.1 Hz, 1H), 3.86 (d,  $J$ =15.1 Hz, 1H), 3.73 (s, 1H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  = -69.53 (s, 3F); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 141.49, 140.04, 137.80, 136.37, 135.14, 132.86, 129.40, 128.73, 127.93, 127.75, 127.72, 126.11, 125.66, 125.63, 122.41, 119.70, 119.68, 111.72, 104.59, 68.42 (q,  $J$ =26.5 Hz), 32.19; IR (film):  $\gamma$  = 3406, 3369, 22953, 2925, 1584, 1493, 1466, 1173, 1144, 1122, 803 cm<sup>-1</sup>; HRMS (EI-TOF): calcd for C<sub>23</sub>H<sub>13</sub>Cl<sub>2</sub>F<sub>3</sub>N<sub>2</sub> 513.9785, found 513.9777.

**(S)-3,9-Dimethyl-12-phenyl-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3da)**



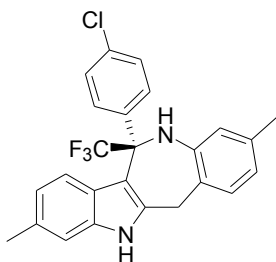
According to general procedure: the product was obtained as yellow solid, m.p. 228-230°C, from flash chromatography (hexane/EtOAc = 10:1 to 6:1), 81% ee; HPLC analysis: Chiralpak AD-H (hexane/*i*-PrOH = 90/10, 0.8 mL/min),  $t_R$  (minor) 8.8 min,  $t_R$  (major) 11.2 min;  $[\alpha]_D^{20}$  = +2.2 ( $c$  = 2.4, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.93 (s, 1H), 7.26-7.34 (m, 5H), 7.05 (d,  $J$ =7.4 Hz, 2H), 6.77 (d,  $J$ =6.9 Hz, 1H), 6.61 (d,  $J$ =8.3 Hz, 1H), 6.46 (d,  $J$ =8.4 Hz, 1H), 6.32 (s, 1H), 4.37 (d,  $J$ =15.2 Hz, 1H), 3.88 (d,  $J$ =15.2 Hz, 1H), 3.75 (s, 1H), 2.33 (s, 3H), 2.18 (s, 3H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  = -69.41 (s, 3F); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 142.50, 139.56, 137.25, 136.43, 134.80, 131.58, 131.00, 128.16, 127.82, 127.43, 127.29, 127.27, 125.37, 124.84, 123.92, 121.40, 120.35, 110.31, 105.97, 68.816 (q,  $J$ =26.2 Hz), 32.19, 21.41, 20.86; IR (KBr):  $\gamma$  = 3401, 2917, 2849, 1462, 1265, 1180, 1158, 1061, 940, 721 cm<sup>-1</sup>; HRMS (EI-TOF): calcd for C<sub>25</sub>H<sub>21</sub>F<sub>3</sub>N<sub>2</sub> 406.1657, found 406.1662.

**(S)-12-(4-Fluoro-phenyl)-3,9-dimethyl-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3db)**



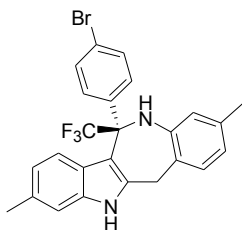
According to general procedure: the product was obtained as yellow solid; m.p. 105-108°C; from flash chromatography (hexane/EtOAc = 10:1 to 6:1); 84% ee; HPLC analysis: Chiralpak OD-H (hexane/i-PrOH = 97.5/2.5, 0.8 mL/min),  $t_R$  (major) 6.5 min,  $t_R$  (minor) 8.0 min;  $[\alpha]_D^{20} = +16.5$  (c = 1.0, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.92 (s, 1H), 7.22 (m, 4H), 7.04 (d,  $J=7.9$  Hz, 2H), 6.78 (d,  $J=7.4$  Hz, 1H), 6.64 (d,  $J=8.3$  Hz, 1H), 6.46 (d,  $J=8.2$  Hz, 1H), 6.29 (s, 1H), 4.39 (d,  $J=15.2$  Hz, 1H), 3.80 (d,  $J=15.2$  Hz, 1H), 3.69 (s, 1H), 2.33 (s, 3H), 2.18 (s, 3H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  = -69.78 (s, 3F), 114.16 (s, 1F); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 142.02, 138.00, 137.39, 136.66, 134.80, 133.73, 131.82, 131.21, 128.76, 128.74, 128.35, 127.46, 125.12, 124.90, 124.18, 121.57, 120.21(q,  $J=25$  Hz), 110.41, 105.37, 68.46 (q,  $J=26.6$  Hz), 32.09, 21.41, 20.87; IR (film):  $\gamma$  = 3403, 2922, 1462, 1280, 1181, 1159, 1127, 1096, 1015, 821, 732 cm<sup>-1</sup>; HRMS (EI-TOF): calcd for C<sub>25</sub>H<sub>20</sub>F<sub>4</sub>N<sub>2</sub> 424.1563, found 424.1563.

**(S)-12-(4-Chloro-phenyl)-3,9-dimethyl-12-trifluoromethyl-5,6,11,12-tetrahydrobenzo[2,3]azepino[5,6-b]indole (3dc)**



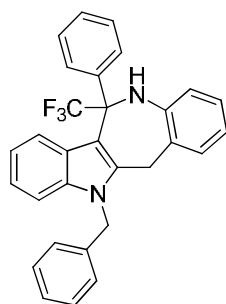
According to general procedure: the product was obtained as white solid; m.p. 158-162°C, from flash chromatography (hexane/EtOAc = 10:1 to 6:1); 93% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 90/10, 0.8 mL/min),  $t_R$  (minor) 6.5 min,  $t_R$  (major) 8.1min;  $[\alpha]_D^{20} = -3.7$  (c = 2.3, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.92 (s, 1H), 7.27-7.29 (m, 2H), 7.04 (d,  $J=7.5$  Hz, 2H), 6.94-6.97 (m, 2H), 6.78 (d,  $J=7.4$  Hz, 1H), 6.69-6.59 (m, 1H), 6.46 (d,  $J=8.2$  Hz, 1H), 6.30 (s, 1H), 4.38 (d,  $J=15.2$  Hz, 1H), 3.83 (d,  $J=15.2$  Hz, 1H), 3.53 (s, 1H), 2.33 (s, 3H), 2.18 (s, 3H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  = -69.67 (s, 3F); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 142.17, 137.35, 136.55, 134.82, 134.79, 131.79, 131.17, 129.27(q,  $J=8.3$  Hz), 129.19 (q,  $J=2.2$  Hz), 127.45, 125.19, 124.91, 124.13, 121.51, 120.25, 115.12, 114.90, 110.39, 105.72, 68.42(q,  $J=24$  Hz), 32.14, 21.41, 20.87. IR (film):  $\gamma$  = 3467, 3402, 2920, 1611, 1510, 1462, 1270, 1181, 1166, 1126, 734 cm<sup>-1</sup>; HRMS (EI-TOF): calcd for C<sub>25</sub>H<sub>20</sub>ClF<sub>3</sub>N<sub>2</sub> 440.1267, found 440.1265.

**(S)-12-(4-Bromo-phenyl)-3,9-dimethyl-12-trifluoromethyl-5,6,11,12-tetrahydrobenzo[2,3]azepino[5,6-b]indole (3dd)**



According to general procedure: the product was obtained as yellow solid; m.p. 80°C; from flash chromatography (hexane/EtOAc = 10:1 to 6:1); 90% ee; HPLC analysis: Chiralpak AD-H (hexane/*i*-PrOH = 90/10, 0.8 mL/min),  $t_R$  (minor) 8.7 min,  $t_R$  (major) 11.7 min; 90% ee;  $[\alpha]_D^{20} = -9.1$  ( $c = 2.1$ ,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.94$  (s, 1H), 7.42-7.35 (m, 2H), 7.16 (d,  $J=8.3$  Hz, 2H), 7.04 (d,  $J=7.2$  Hz, 2H), 6.78 (d,  $J=6.8$  Hz, 1H), 6.64 (d,  $J=8.3$  Hz, 1H), 6.46 (d,  $J=8.2$  Hz, 1H), 6.29 (s, 1H), 4.40 (d,  $J=15.2$  Hz, 1H), 3.81 (d,  $J=15.2$  Hz, 1H), 3.69 (s, 1H), 2.34 (s, 3H), 2.19 (s, 3H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta = -69.82$  (s, 3F);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 142.00$ , 138.52, 137.41, 136.68, 134.80, 131.82, 131.31, 131.22, 129.05, 127.46, 125.11, 124.90, 124.18, 122.02, 121.59, 120.21, 120.19, 110.40, 105.29, 68.52 (q,  $J=26.6$  Hz), 32.10, 21.41, 20.88; IR (film):  $\gamma = 3401$ , 3030, 2919, 2860, 1724, 1488, 1461, 1290, 1264, 1158, 1127, 1075, 1011, 819, 730  $\text{cm}^{-1}$ ; HRMS (EI-TOF): calcd for  $\text{C}_{25}\text{H}_{20}\text{BrF}_3\text{N}_2$  484.0762, found 484.0762.

#### 5-Benzyl-12-phenyl-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3ea)



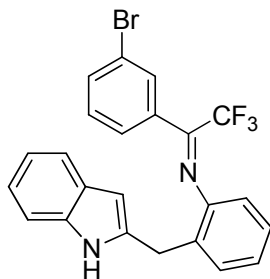
According to general procedure for racemate: the product was obtained as yellow solid; m.p. 56°C  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.33$ -7.26 (m, 8H), 7.22 (d,  $J=8.3$  Hz, 1H), 7.06-6.94 (m, 4H), 6.84-6.86 (m, 1H), 6.81-6.74 (m, 1H), 6.68 (d,  $J=7.4$  Hz, 1H), 6.57 (d,  $J=8.1$  Hz, 1H), 6.38 (d,  $J=7.7$  Hz, 1H), 5.53 (d,  $J=8.7$  Hz, 2H), 4.47 (d,  $J=15.0$  Hz, 1H), 3.80 (d,  $J=15.0$  Hz, 1H), 3.71 (s, 1H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta = -70.06$  (s, 3F);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 142.40$ , 138.88, 137.65, 136.23, 135.12, 128.97, 128.26, 127.82, 127.57, 127.54, 127.35, 127.12, 127.10, 126.67, 125.85, 124.03, 123.28, 121.19, 120.98, 119.68, 109.09, 106.00, 68.99 (q,  $J=18$  Hz), 47.50, 27.34; IR (film):  $\gamma = 3414$ , 3352, 2926, 1617, 1592, 1458, 1587, 1459, 1329, 1164, 1094, 1032, 907, 732  $\text{cm}^{-1}$ ; HRMS (EI-TOF): calcd for  $\text{C}_{24}\text{H}_{17}\text{Br}_2\text{F}_3\text{N}_2$  547.9411, found 547.9709.

## 4. Synthesis of the intermediate ketoimine

To a solution of indoles **1a** (0.1 mmol), trifluoromethyl ketones **2h** (0.12 mmol) in 1,2-dichloroethane (0.6 mL) was added powdered 4Å molecular sieves (0.1 g) and the catalyst **4b** (0.005 mmol). The resulting mixture was stirred under an argon atmosphere at room temperature

for 2 h. The crude product was then subjected to a silica gel column (petroleum ether/ethyl acetate) to afford the desired product intermediate ketoimine **3ahi** in 30% yield.

### 2-((1H-indol-2-yl)methyl)-N-(1-(3-bromophenyl)-2,2,2-trifluoroethylidene)aniline (**3ahi**)



The product was obtained as yellow liquid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.57 (s, 1H), 7.51 (d,  $J=7.8$  Hz, 1H), 7.47-7.39 (m, 1H), 7.32 (d,  $J=7.5$  Hz, 1H), 7.27 (d,  $J=8.1$  Hz, 1H), 7.15 (s, 1H), 7.11 (d,  $J=7.1$  Hz, 1H), 7.08-7.00 (m, 3H), 7.00-6.94 (m, 1H), 6.80 (d,  $J=7.7$  Hz, 1H), 6.32-6.35 (m, 2H), 4.12 (s, 2H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  = -69.71 (s, 3F);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 144.68, 137.21, 136.20, 133.64, 131.65, 131.31, 131.08, 130.23, 130.07, 128.38, 127.38, 126.93, 126.70, 122.64, 121.46, 121.35, 120.00, 119.63, 119.32, 110.62, 100.59, 68.81(q,  $J=20$  Hz), 31.29; IR (film):  $\gamma$  = 3401, 3058, 2927, 1724, 1588, 1475, 1587, 1459, 1333, 1162, 1140, 1059, 779, 747 $\text{cm}^{-1}$ ; HRMS (EI-TOF): calcd for  $\text{C}_{23}\text{H}_{16}\text{BrF}_3\text{N}_2$  456.0449, found 456.0447.

## 5. Gram-scale preparation of **3ad**

To a solution of indoles **1a** (3 mmol, 0.67 g), trifluoromethyl ketones **2d** (3.6 mmol, 0.91 g) in 1,2-dichloroethane (18 mL) was added powdered 4Å molecular sieves (3 g) and the catalyst **4b** (0.15 mmol). The resulting mixture was stirred under an argon atmosphere at 35 °C until complete conversion was indicated by TLC. The reaction mixture was then filtered and the residue washed thoroughly with 1,2-dichloroethane. The filtrate was concentrated in vacuo to give the crude product. The crude product was then subjected to a silica gel column eluting with hexane: EtOAc (4:1) then  $\text{CH}_2\text{Cl}_2$ : MeOH (10:1). From this, the desired product **3ad** (1.23 g) was obtained in 90% yield. Spectroscopic data was in accordance with that reported above. Additionally recovery of catalyst **4b** was achieved after acidification of the relevant fractions as described previously (99 mg, 90%). The above reaction was repeated with the recovered catalyst **4b** to give the desired product **3ad** (1.20 g) in 87% yield, and this reaction proceeded without compromising the enantioselectivity.

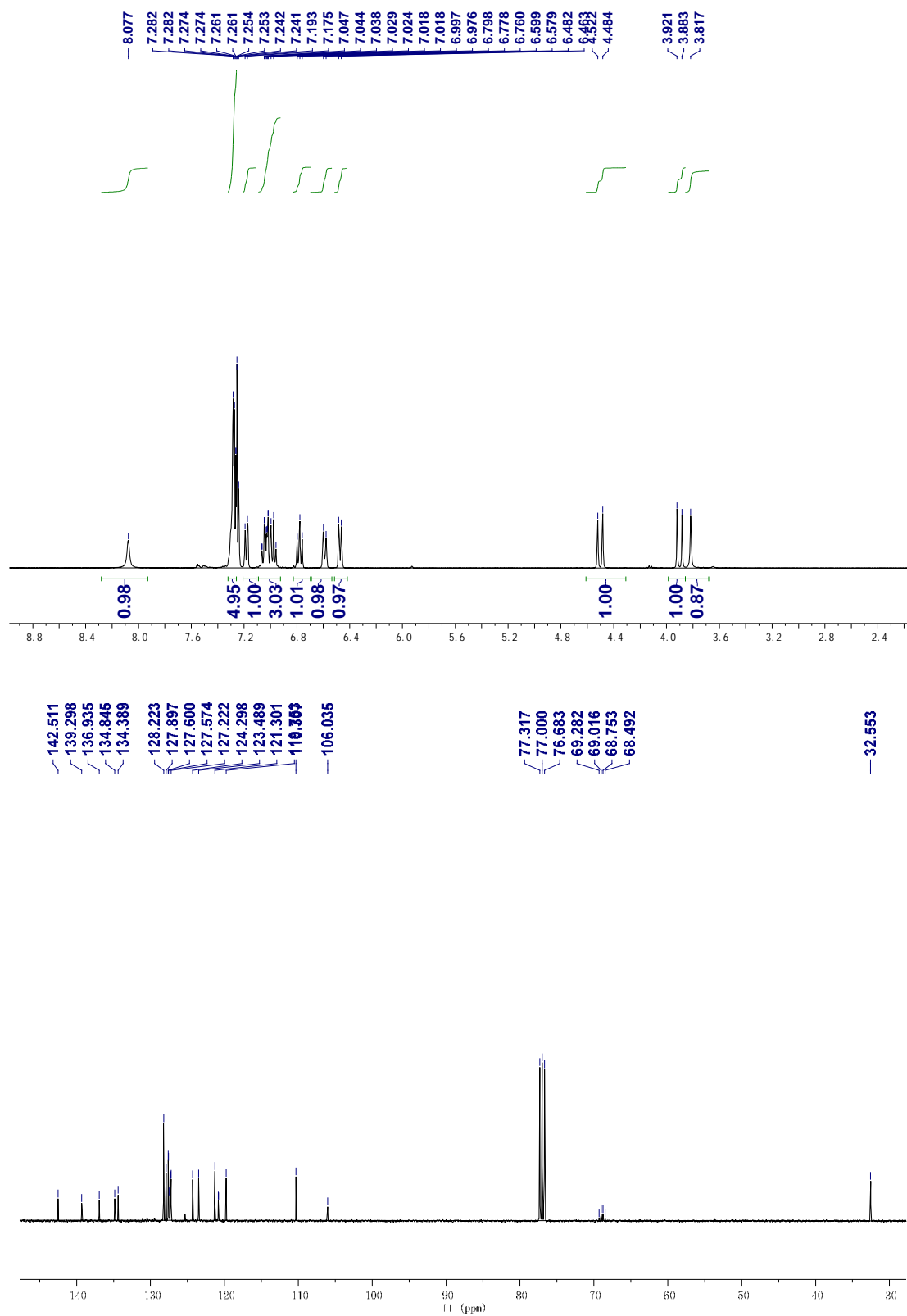
## 6. References

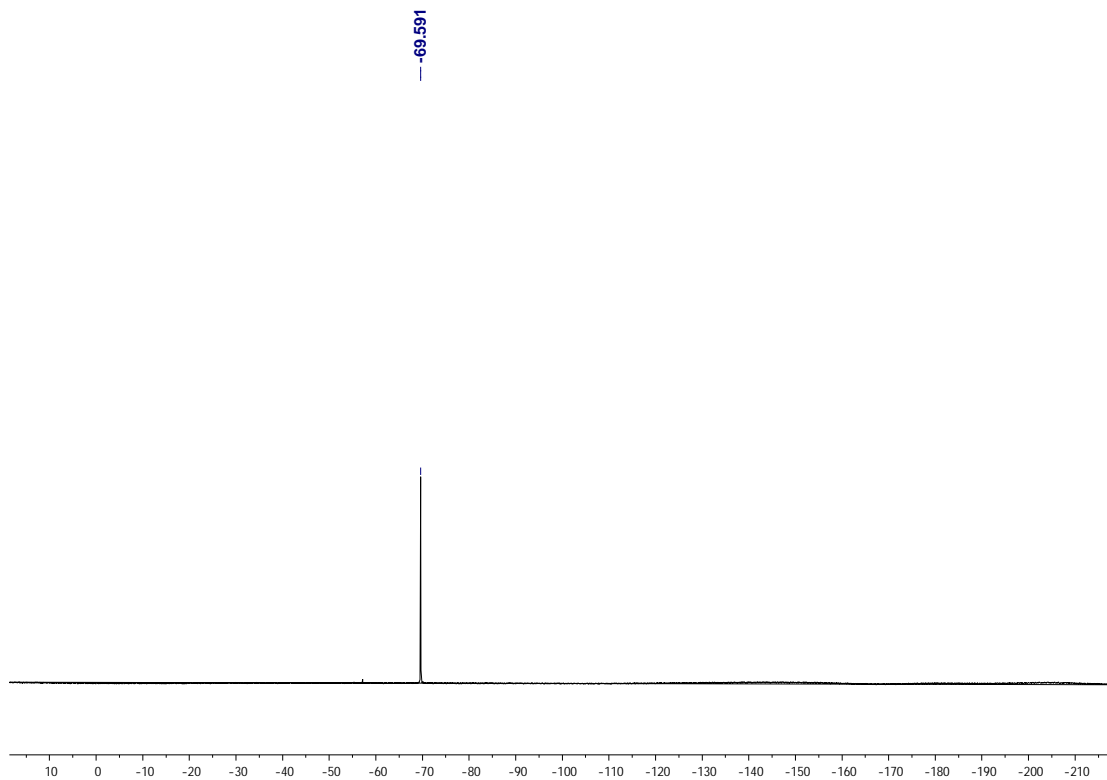
- [1] F. X. Xu, D. Huang, C. Han, W. Shen, X. F. Lin, Y. G. Wang, *J. Org. Chem.* **2010**, *75*, 8677-8680.
- [2] S. K. Sharma, S. Sharma, P. K. Agarwal, B. Kundu, *Eur. J. Org. Chem.* **2009**, 1309-1312.
- [3] P. Albaugh, Y. Fan, Y. Mi, *ACS Med. Chem. Lett.* **2012**, *3*, 140-145.



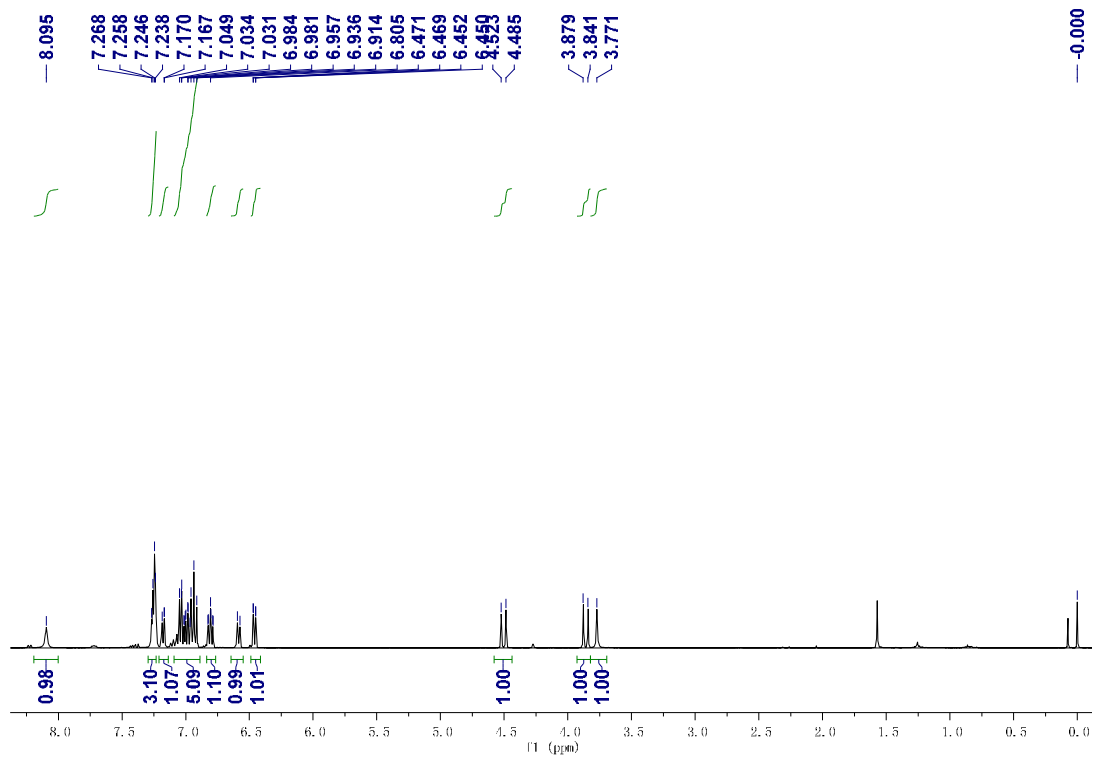
## 7. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra

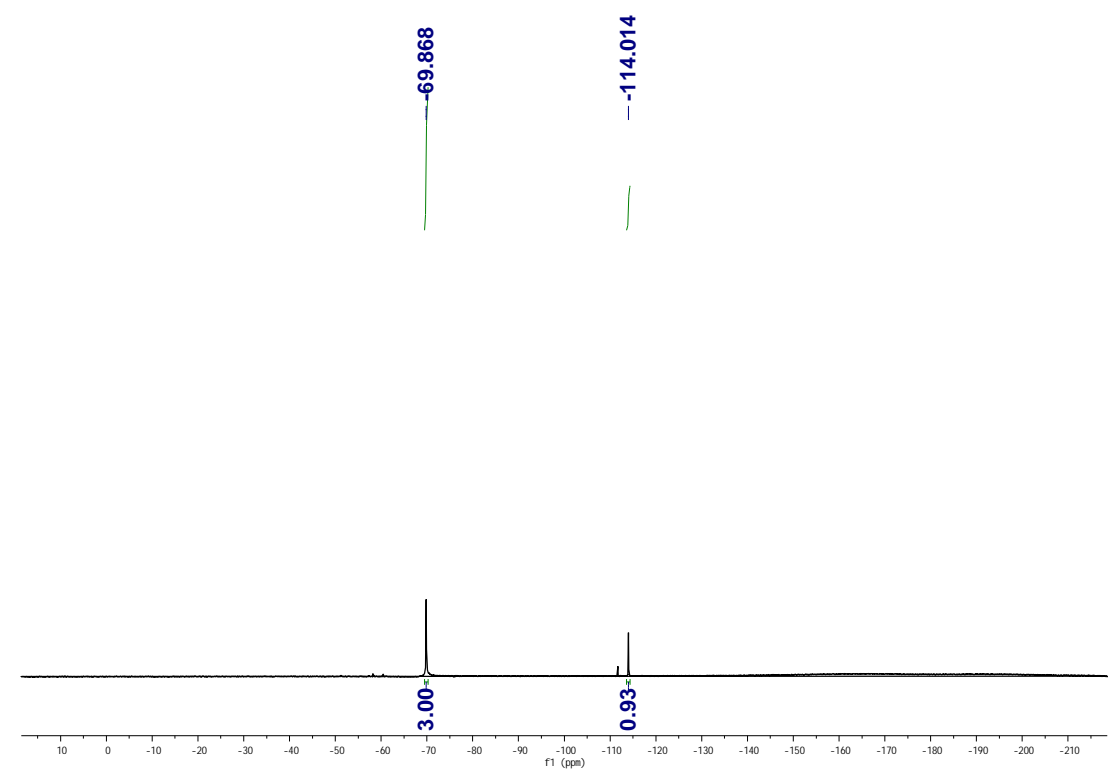
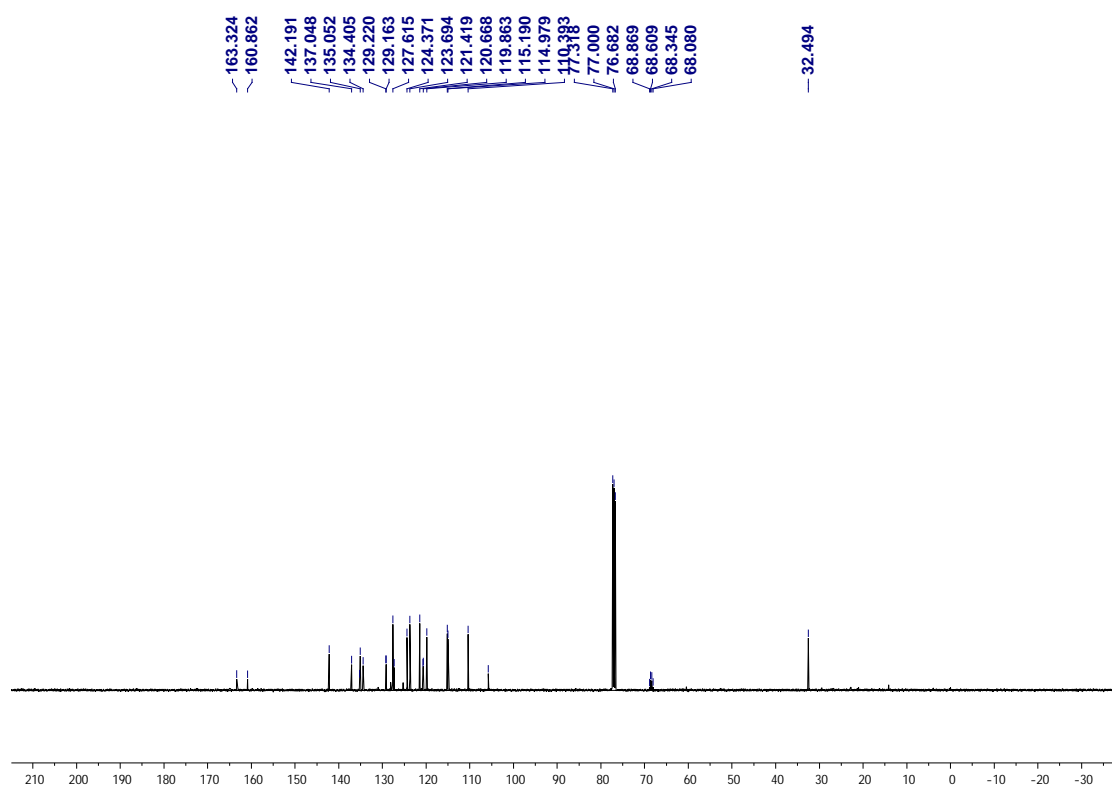
### (*S*)-12-phenyl-12-(trifluoromethyl)-5,6,11,12-tetrahydrobenzo[6,7]azepino[4,3-b]indole (3aa)



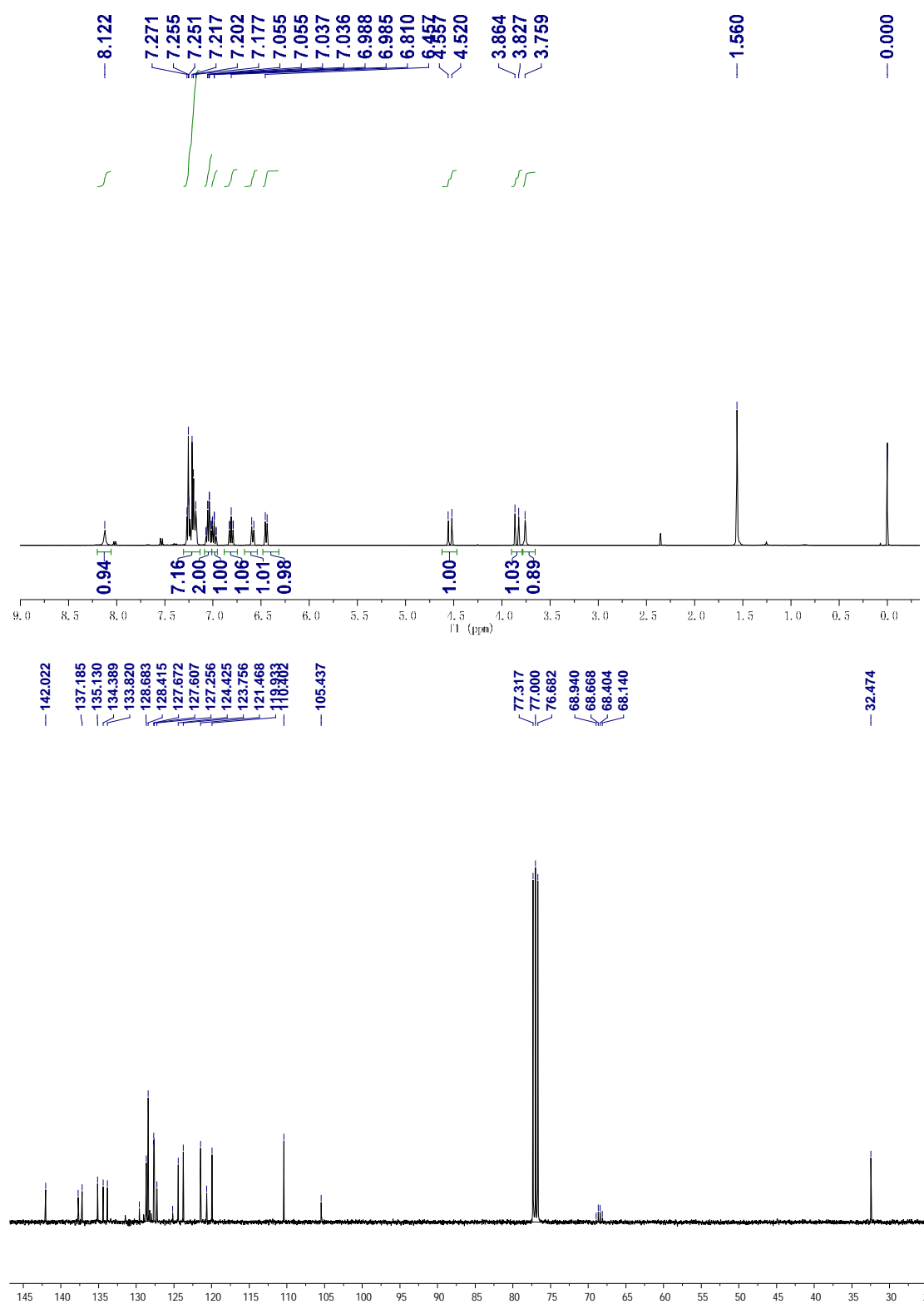


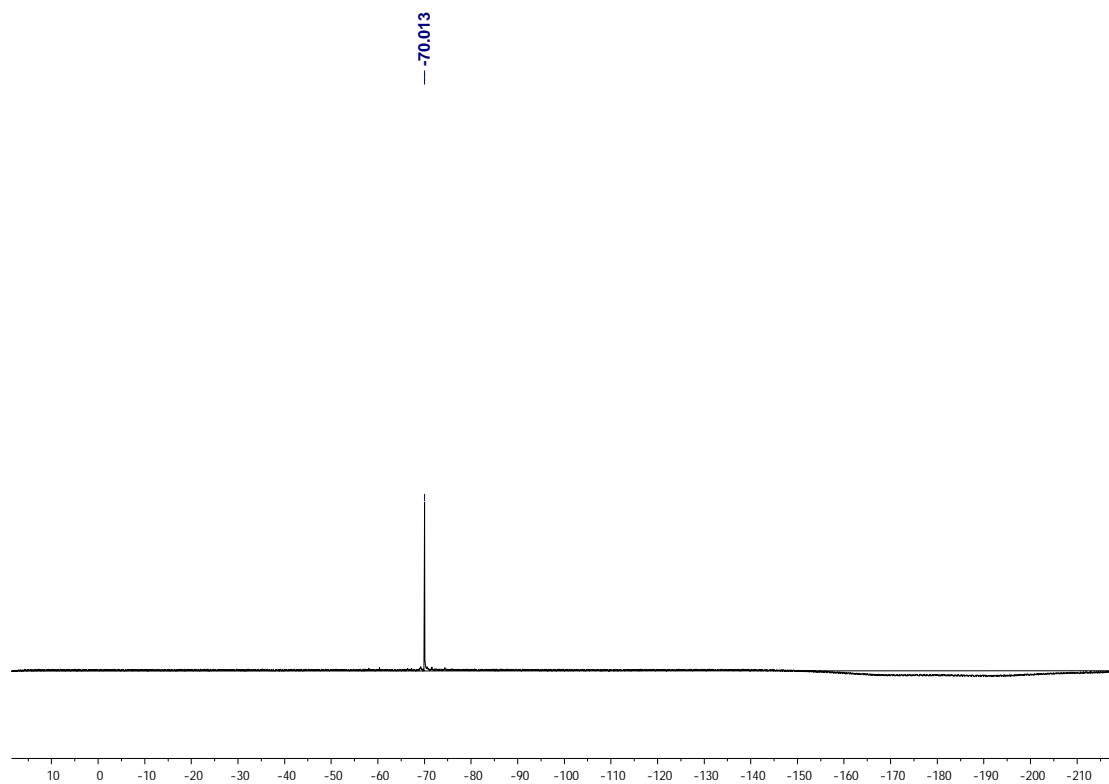
**(S)-12-(4-fluorophenyl)-12-(trifluoromethyl)-5,6,11,12-tetrahydrobenzo[6,7]azepino[4,3-b]indole (3ab)**



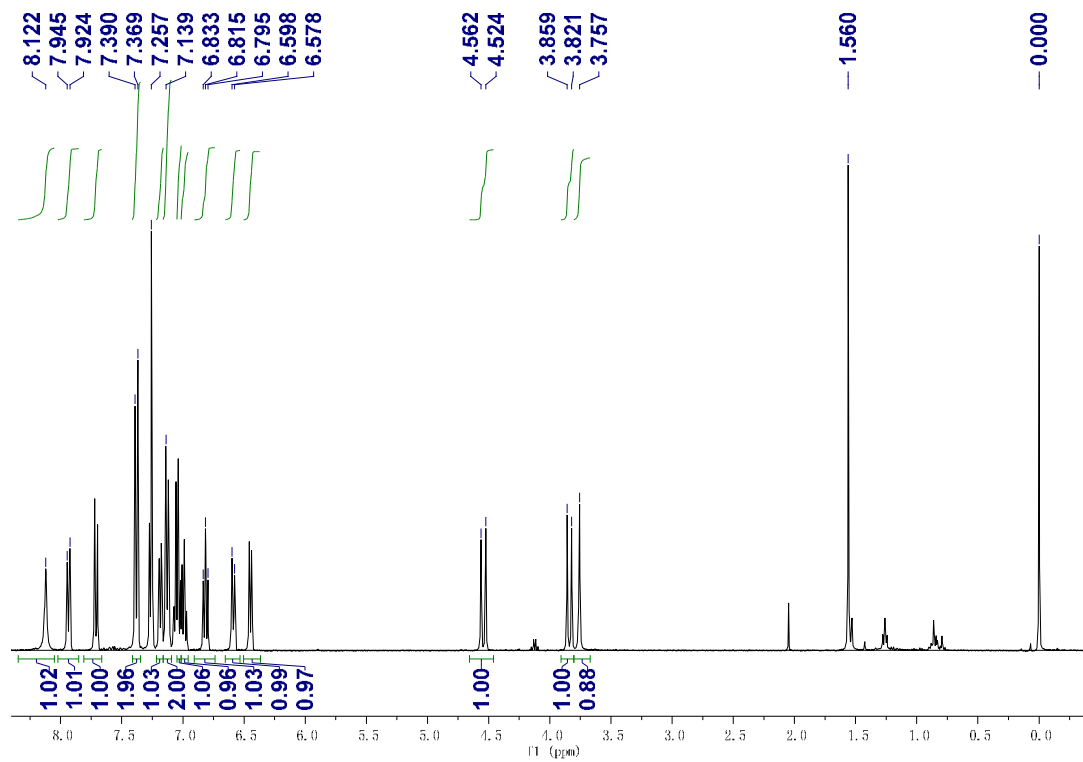


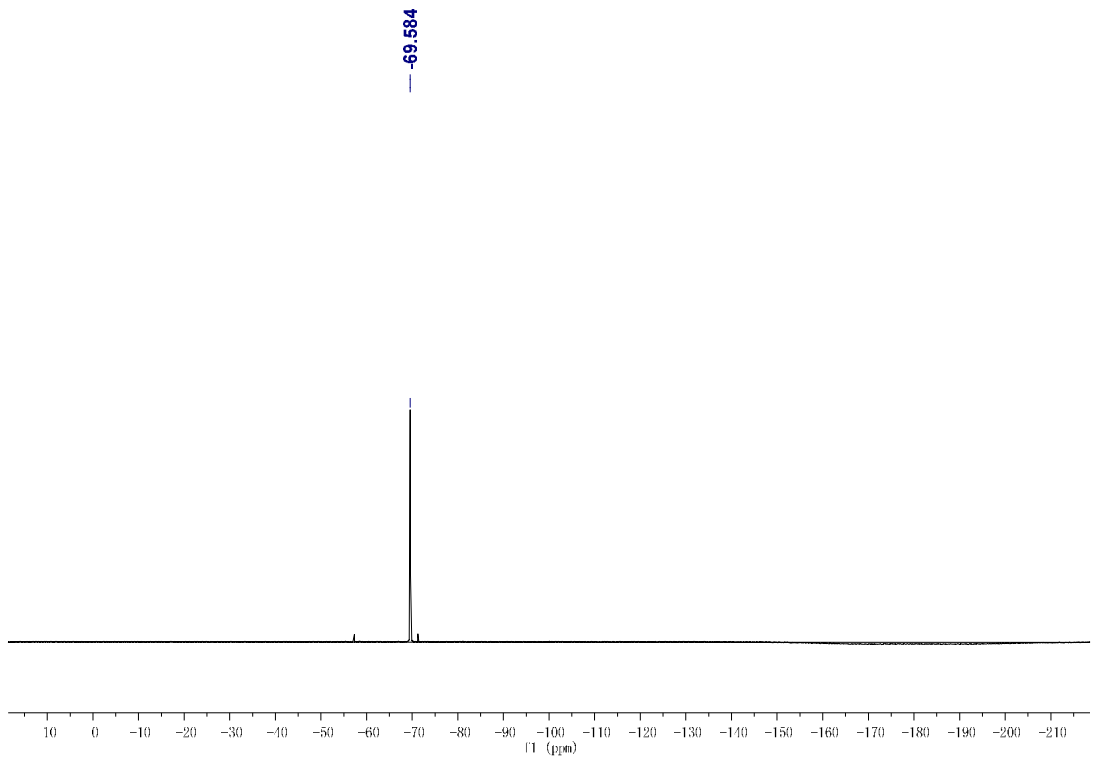
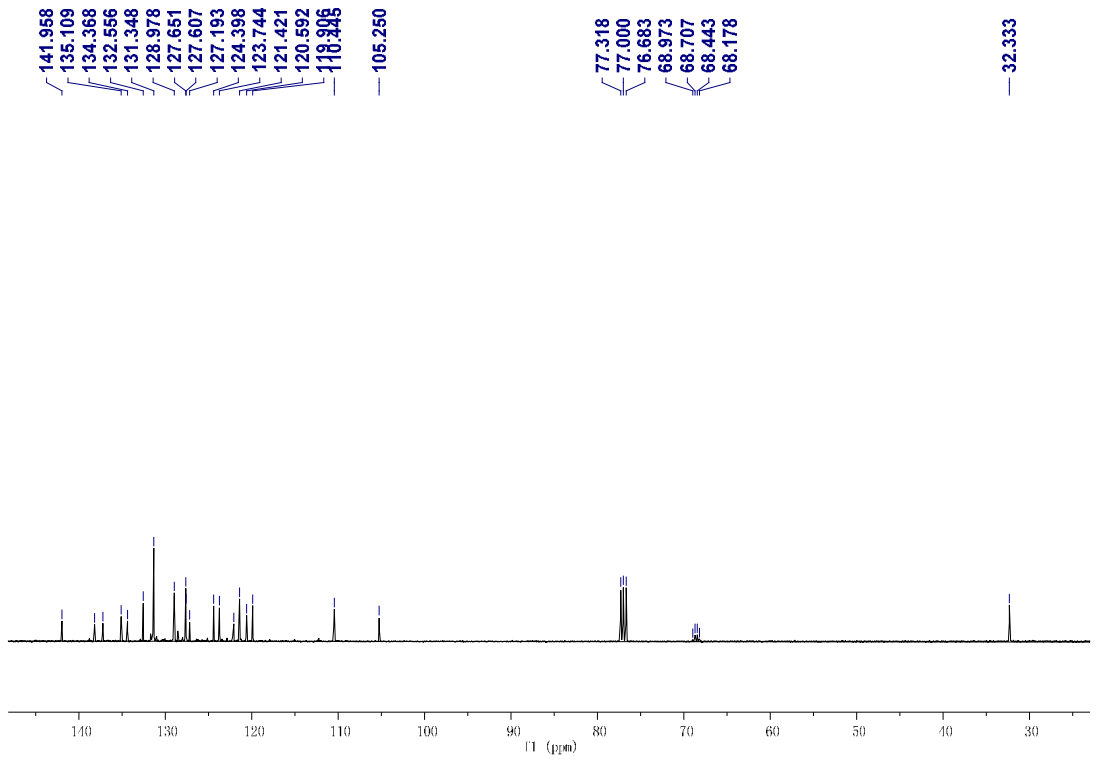
(S)-12-(4-chlorophenyl)-12-(trifluoromethyl)-5,6,11,12-tetrahydrobenzo[6,7]azepino[4,3-b]indole  
(3ac)



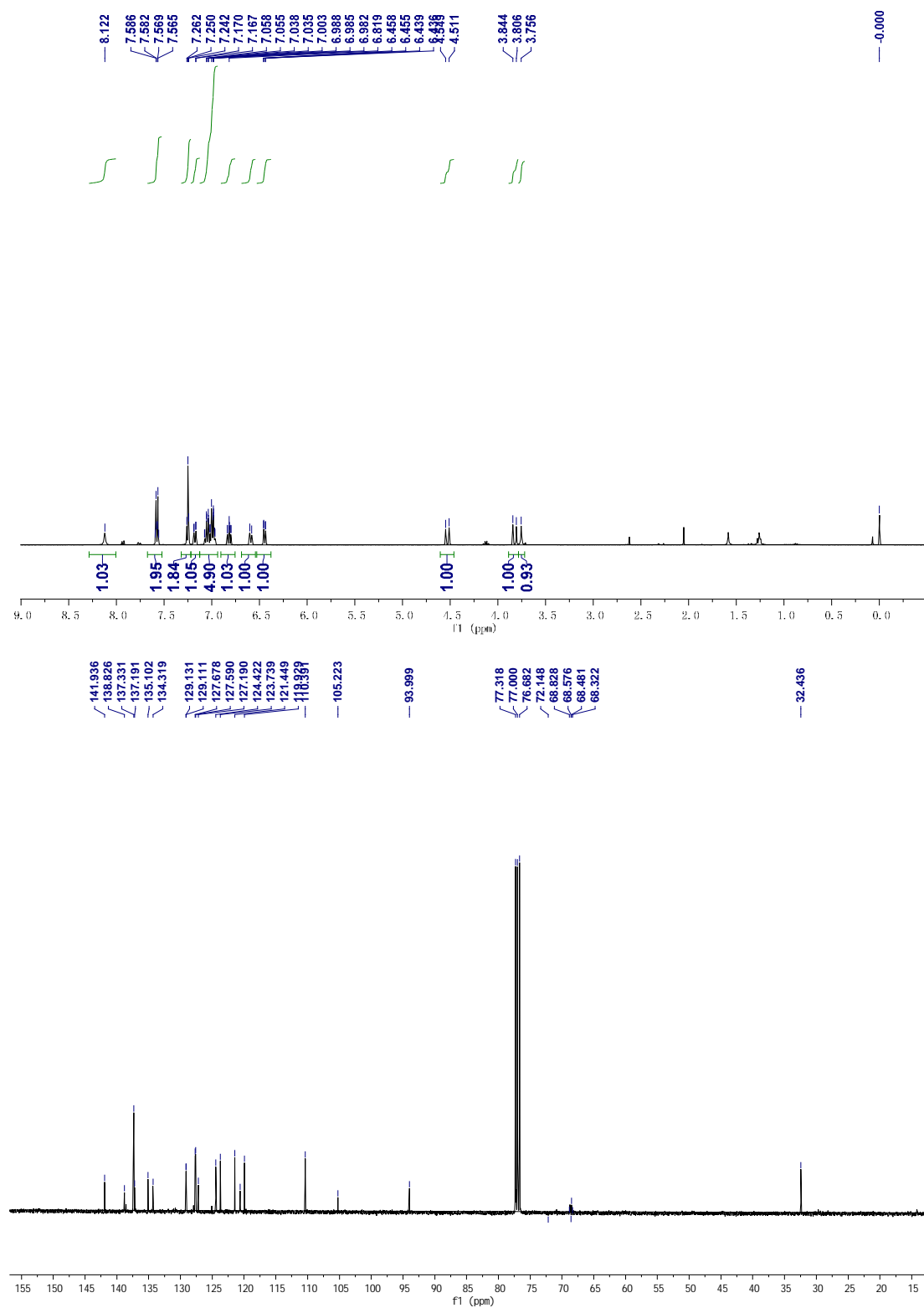


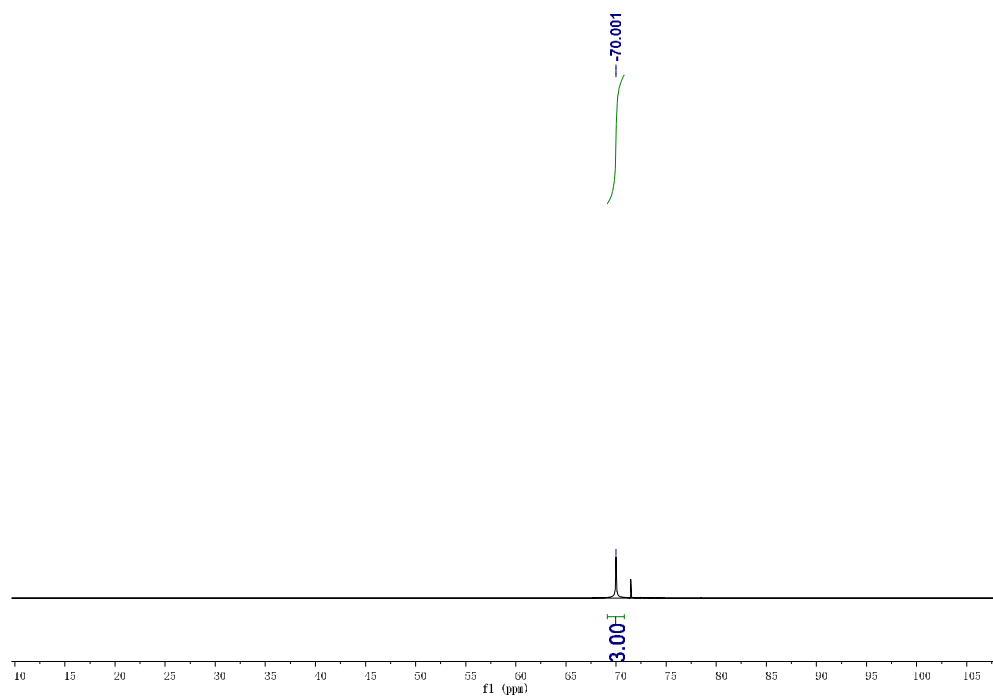
(S)-12-(4-bromophenyl)-12-(trifluoromethyl)-5,6,11,12-tetrahydrobenzo[6,7]azepino[4,3-b]indole (3ad)



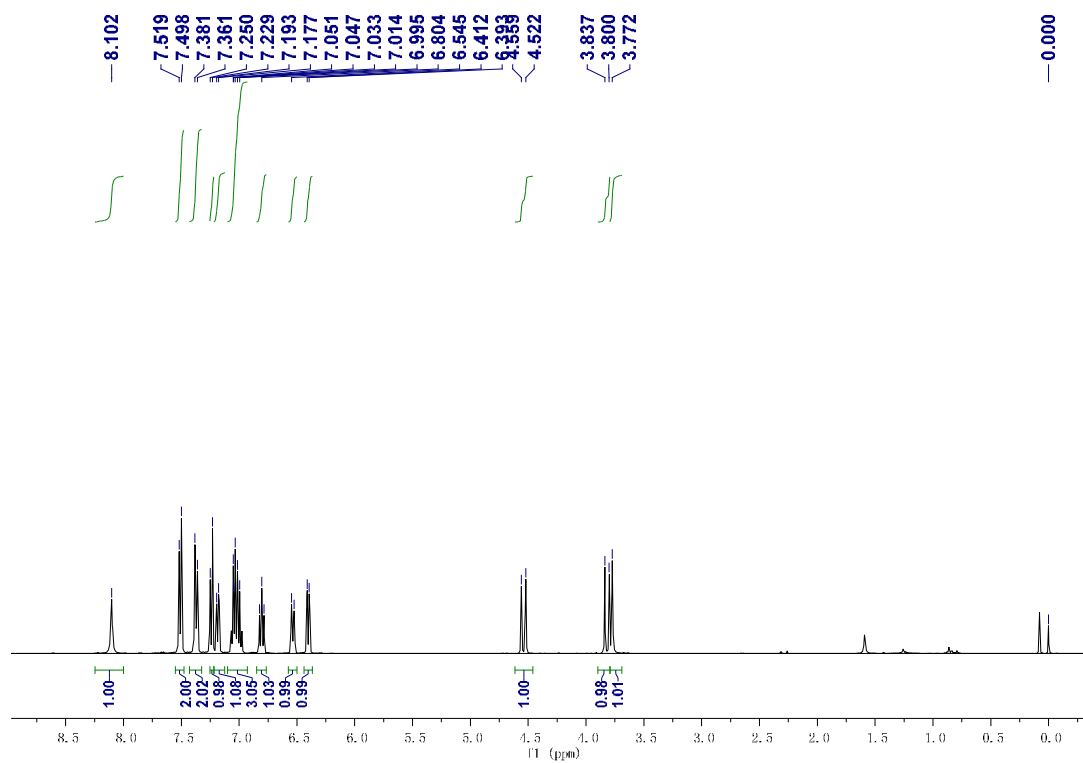


**(S)-12-(4-Iodo-phenyl)-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3ae)**

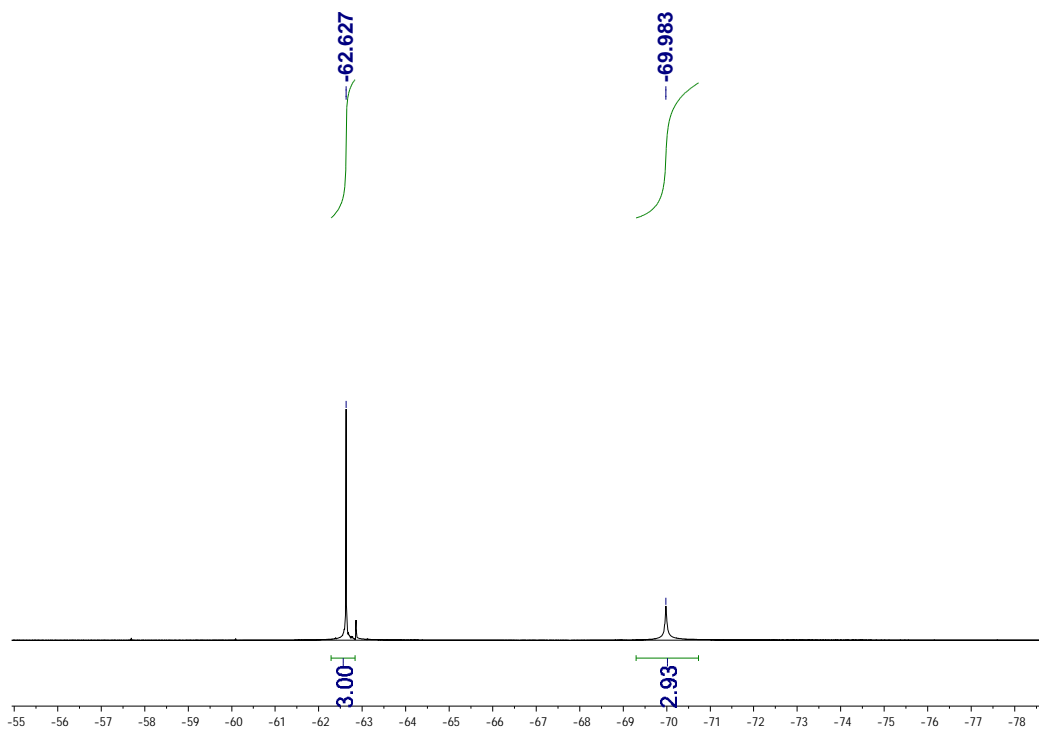
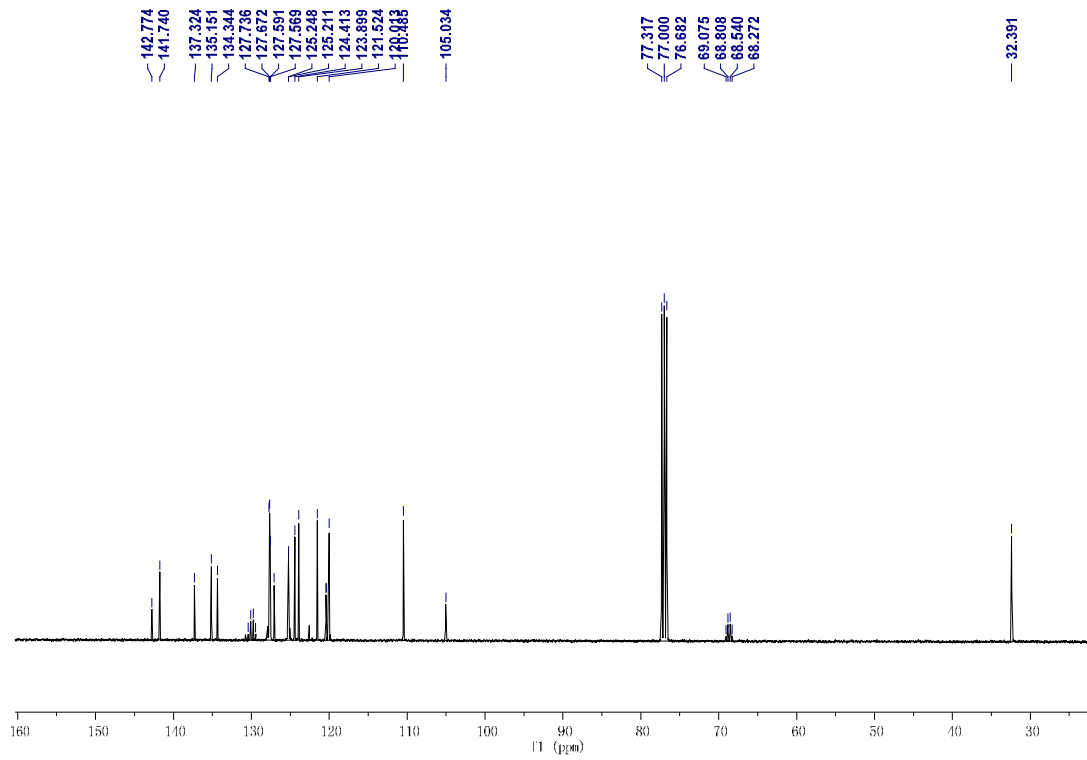




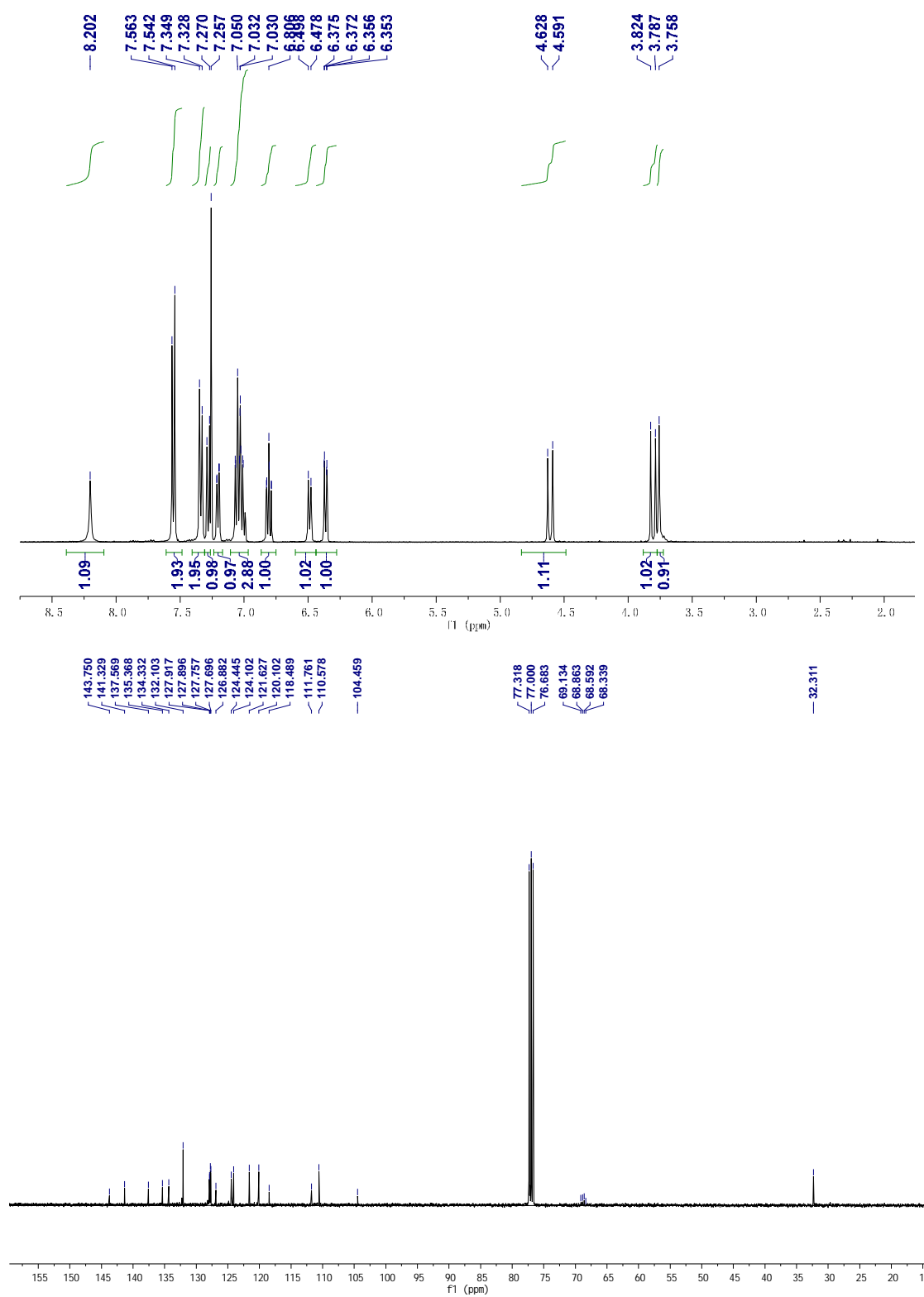
**(S)- 12-Trifluoromethyl-12-(4-trifluoromethyl-phenyl)-5,6,11,12-tetrahydrobenzo[2,3]azepino[5,6-b]indole (3af)**

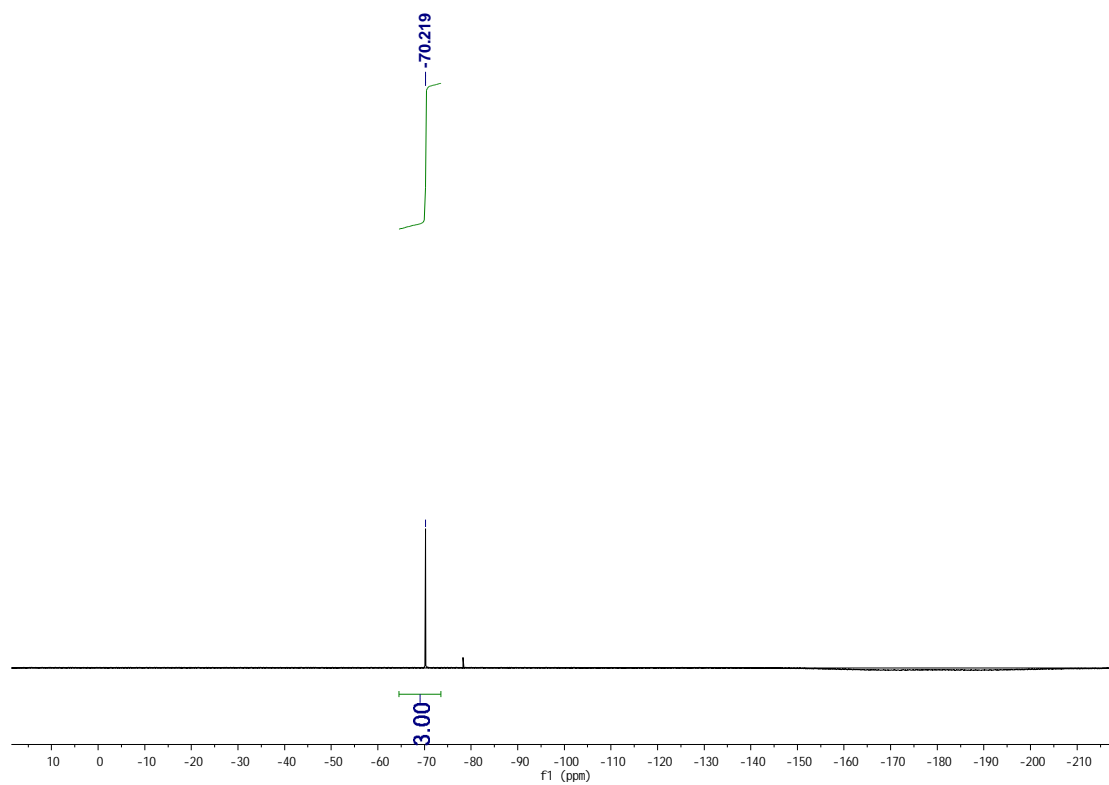




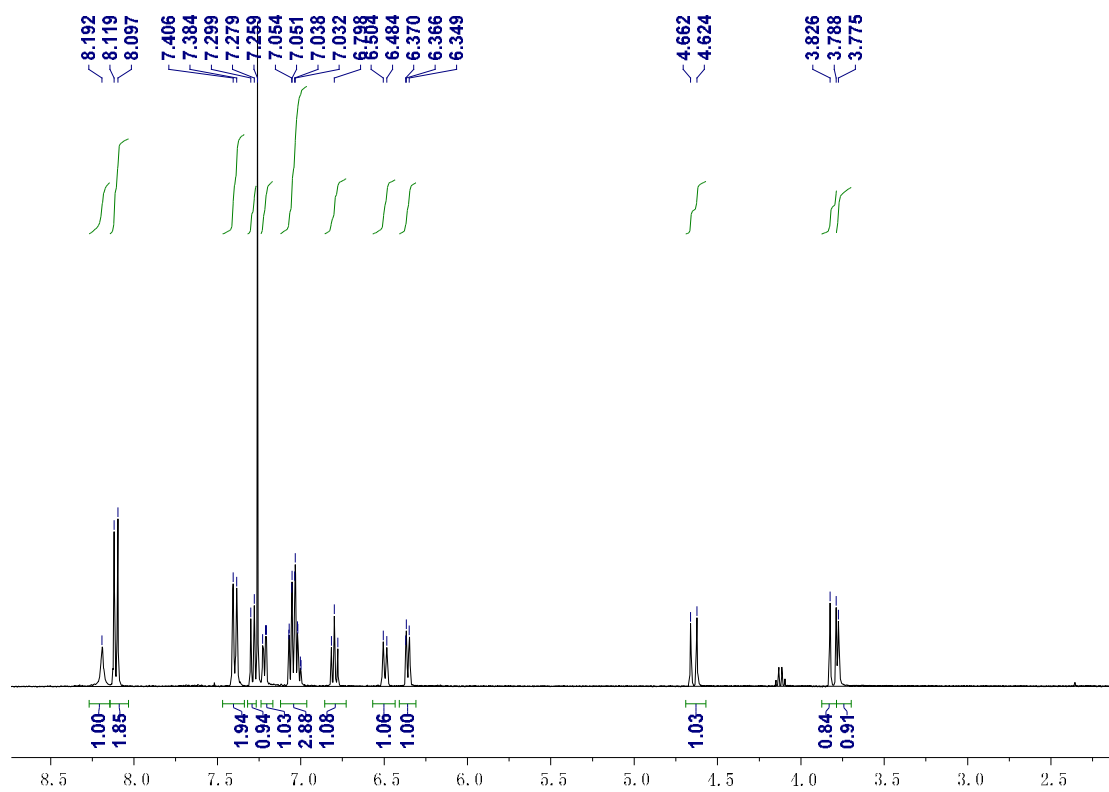


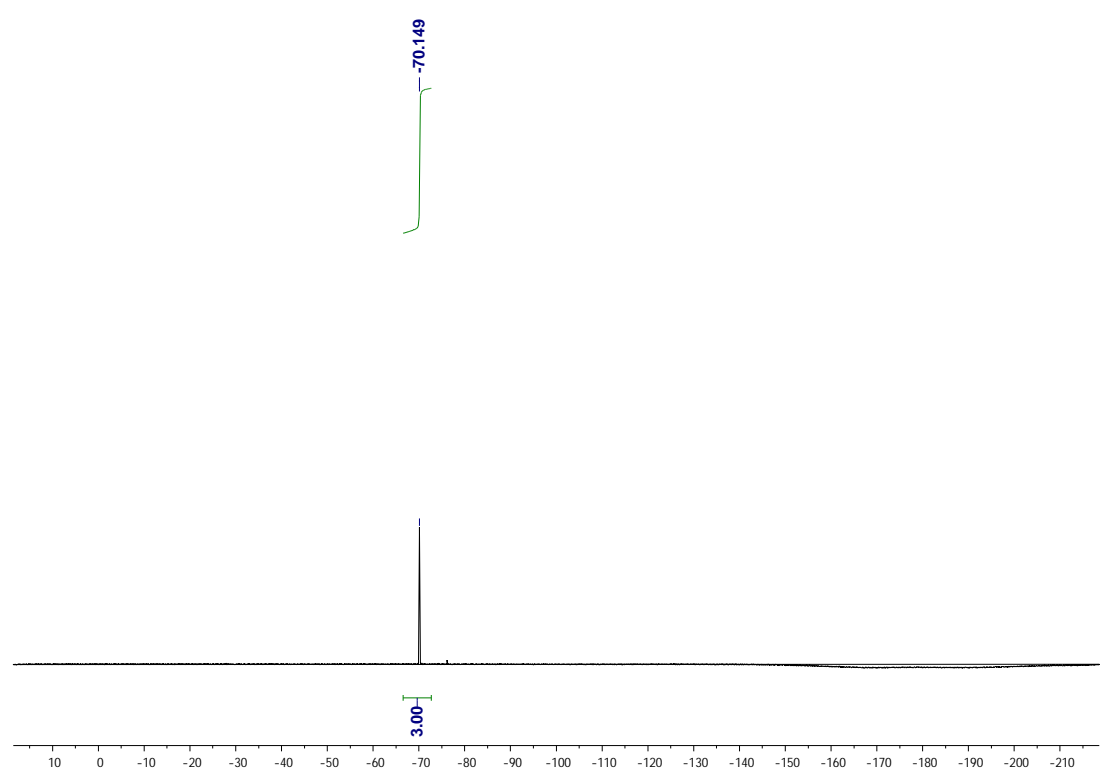
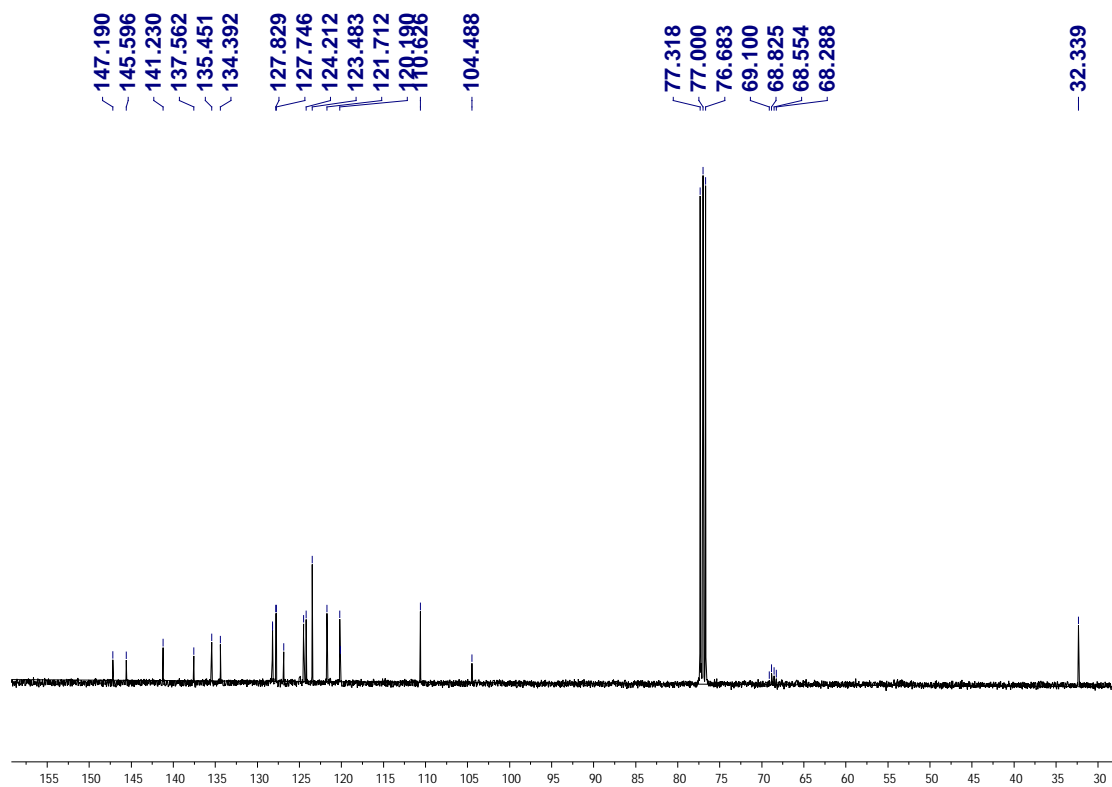
(S)-4-(12-Trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indol-12-yl)-benzonitrile  
(3ag)



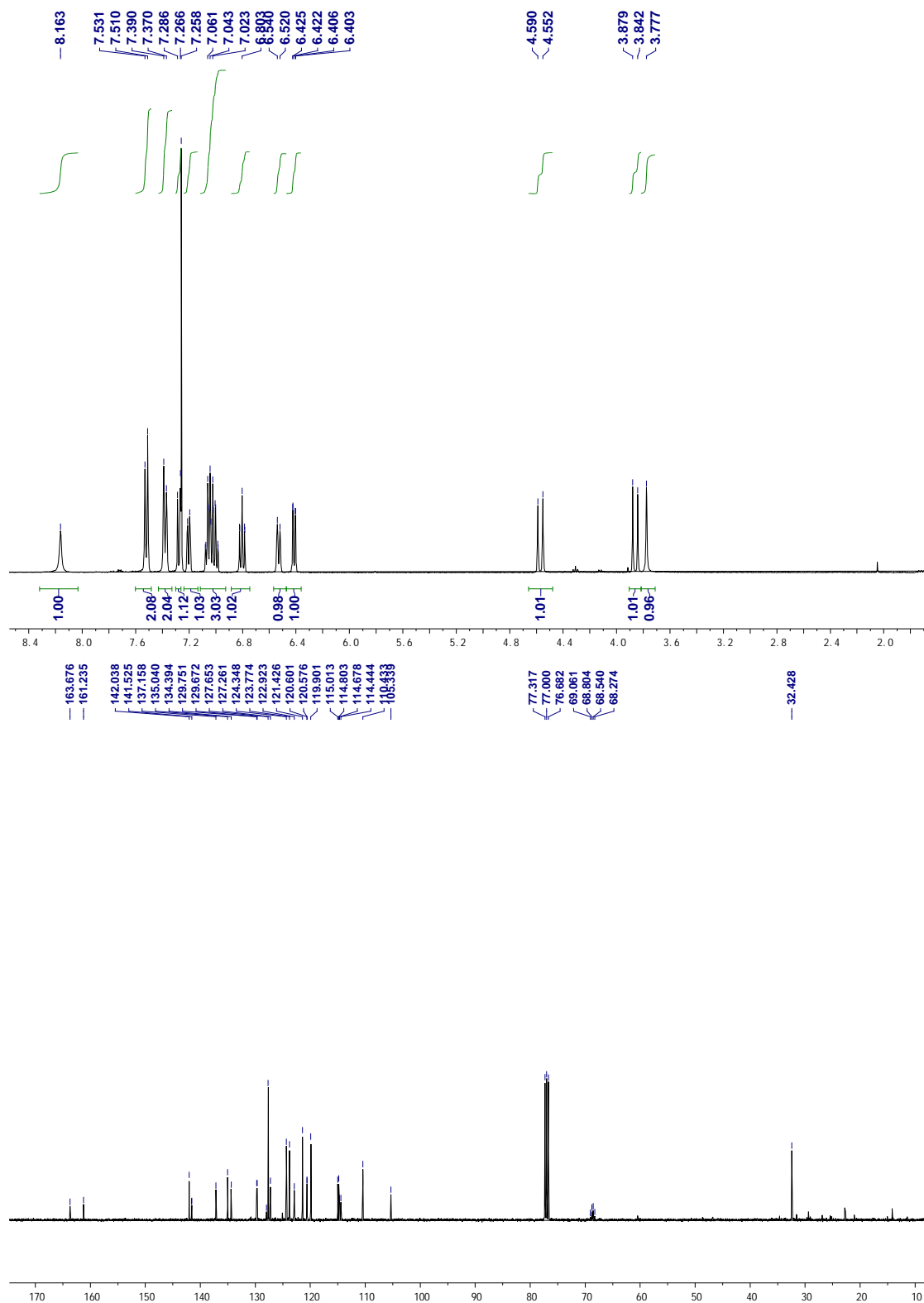


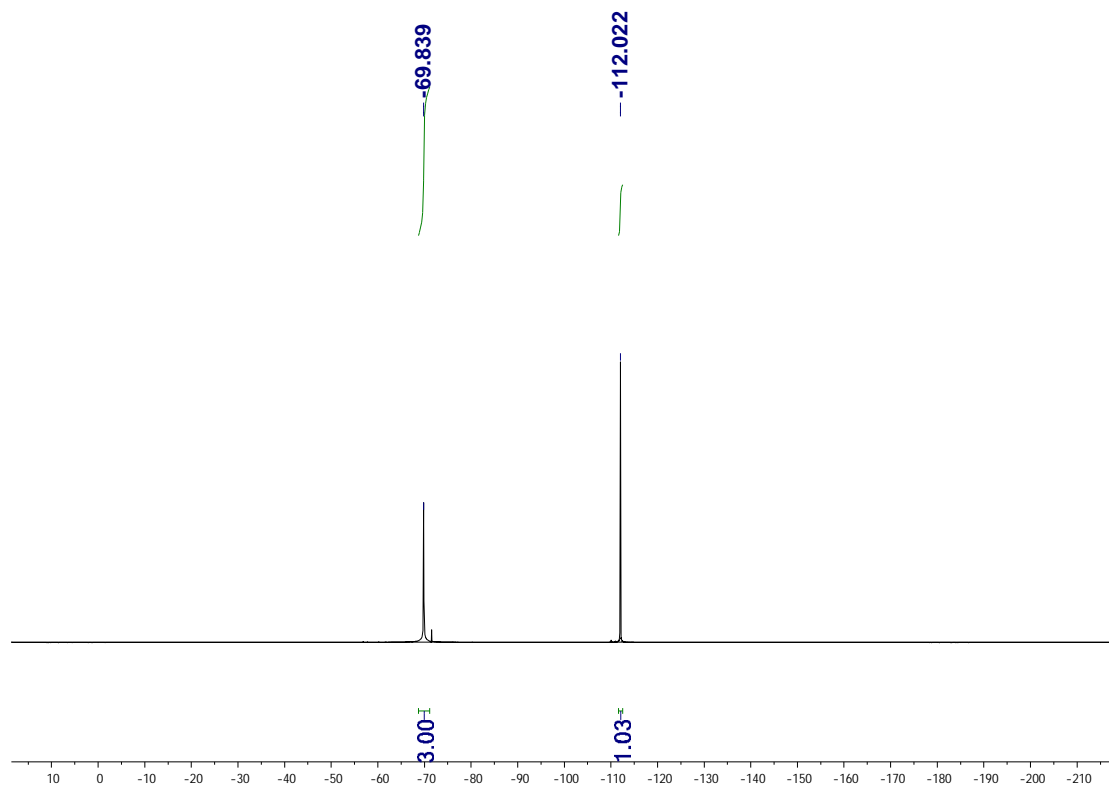
**(S)-12-(4-nitrophenyl)-12-(trifluoromethyl)-5,6,11,12-tetrahydrobenzo[6,7]azepino[4,3-b]indole (3ah)**



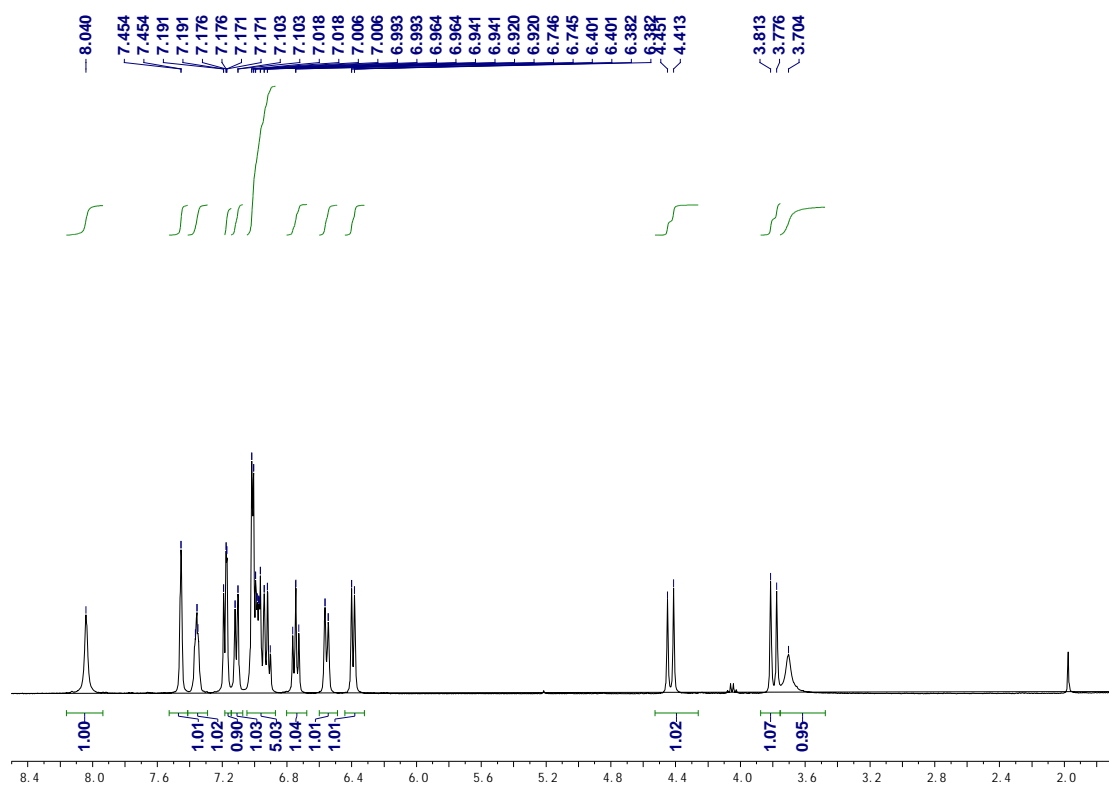


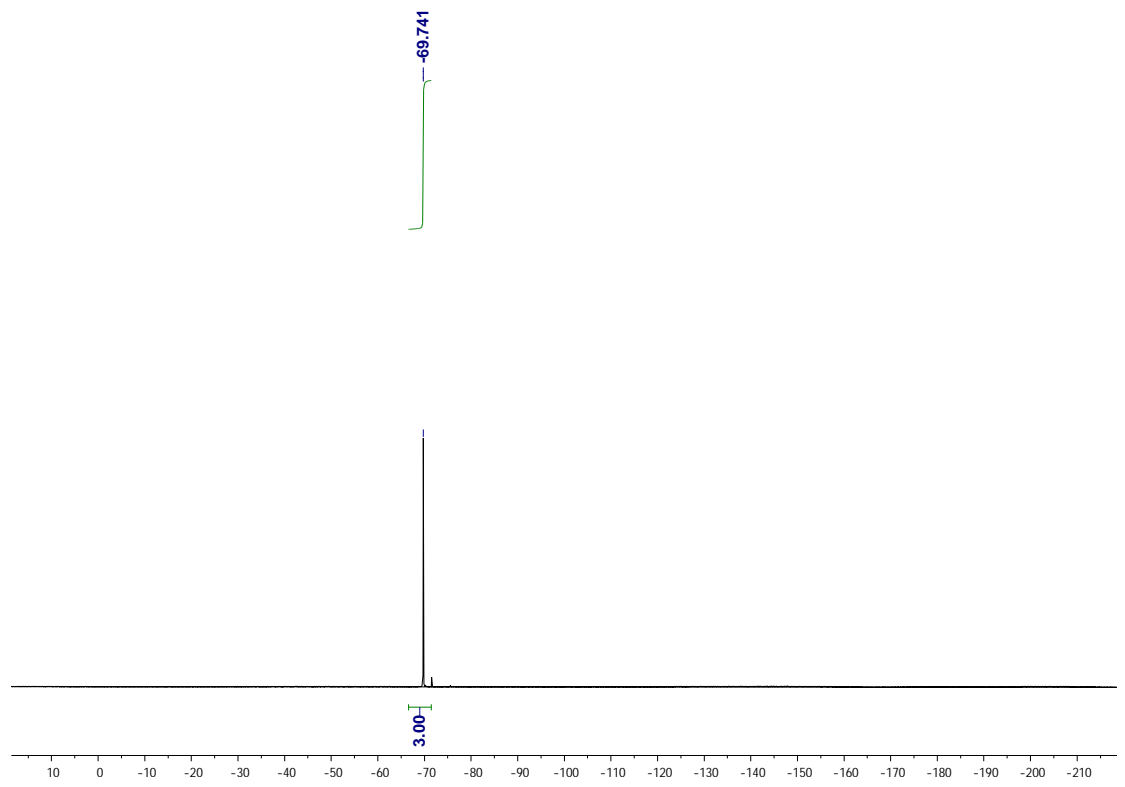
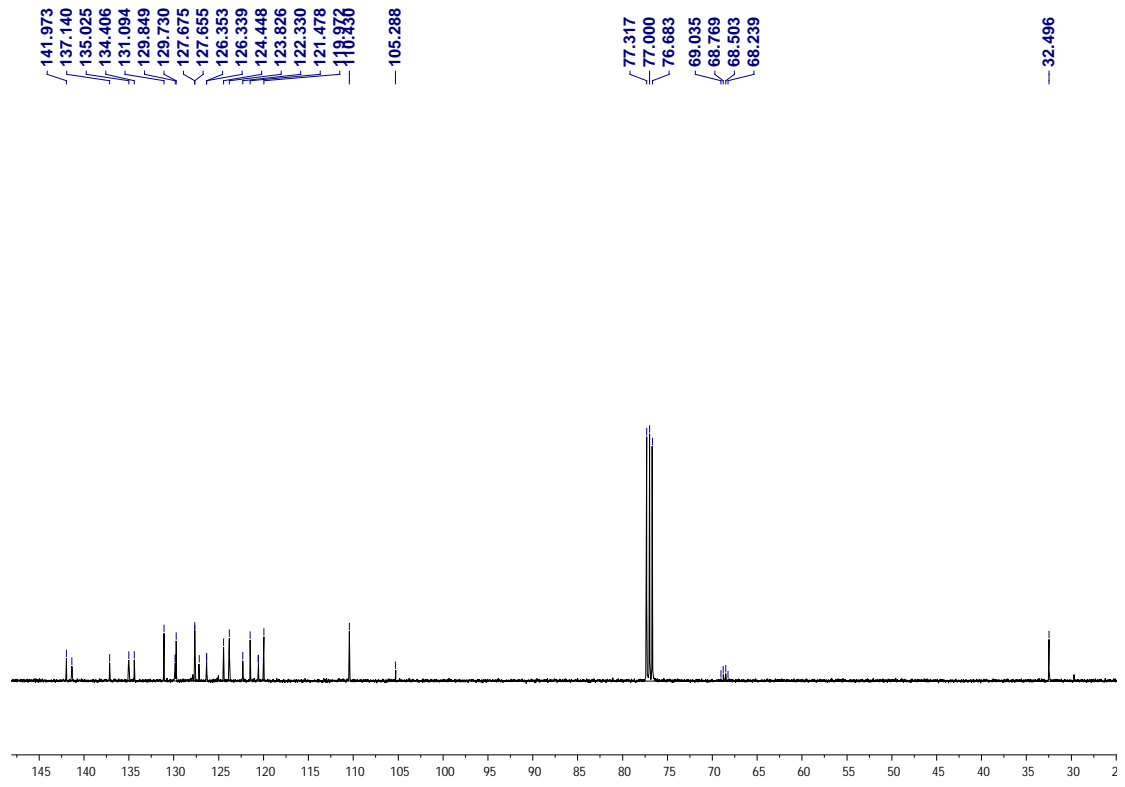
**(S)-12-(3-Fluoro-phenyl)-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole**  
**(3ai)**



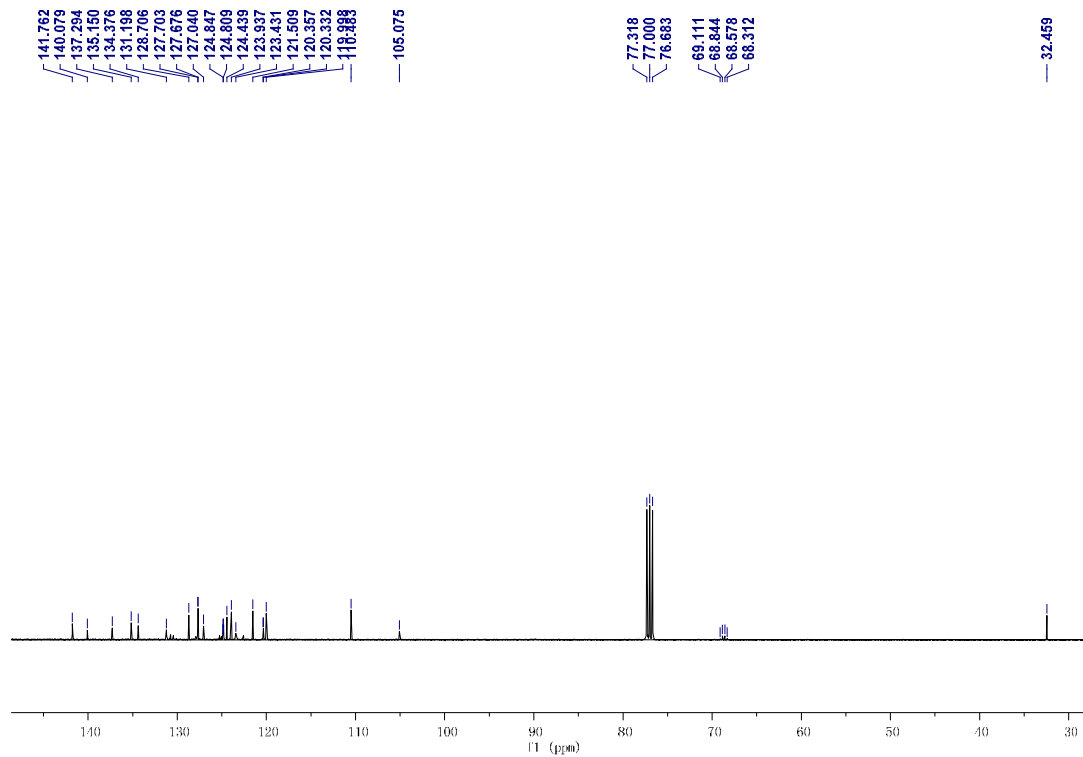
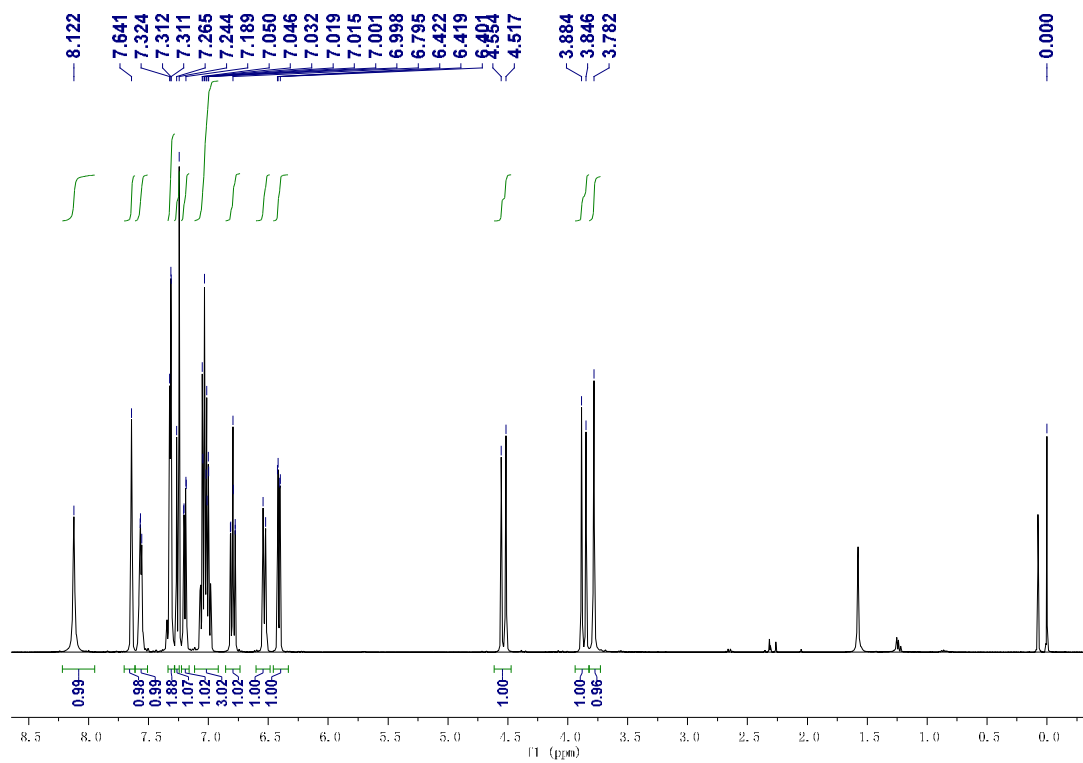


**(S)-12-(3-Bromo-phenyl)-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3aj)**

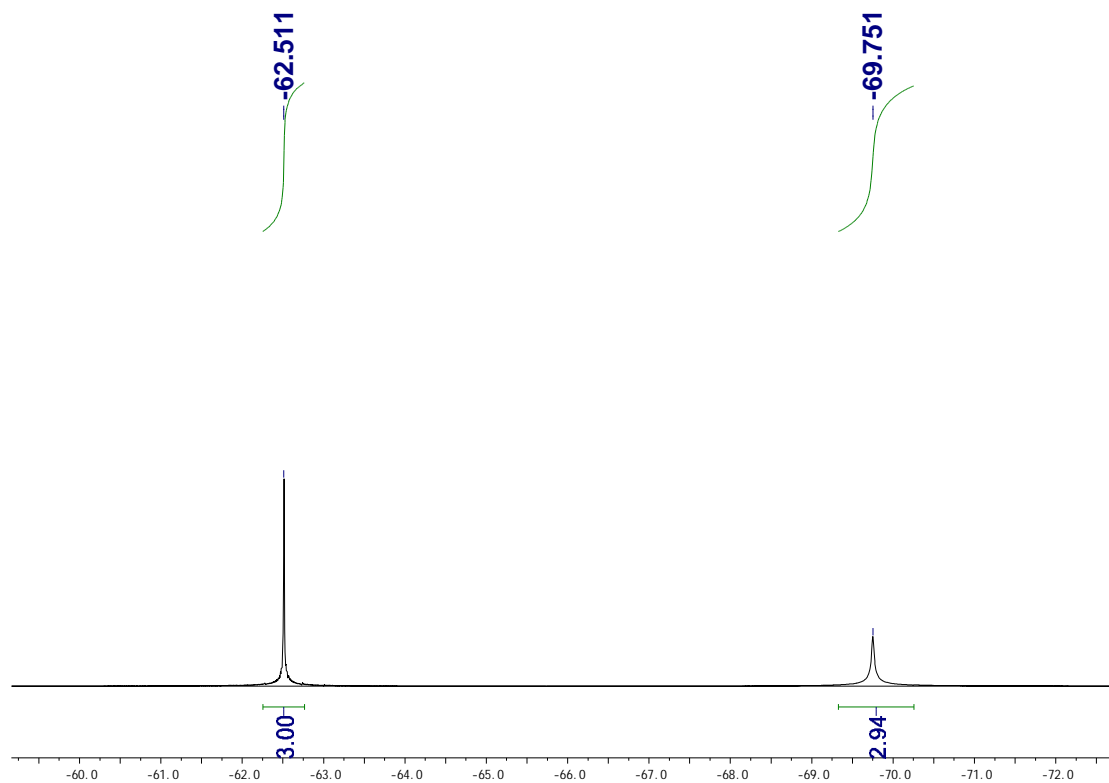




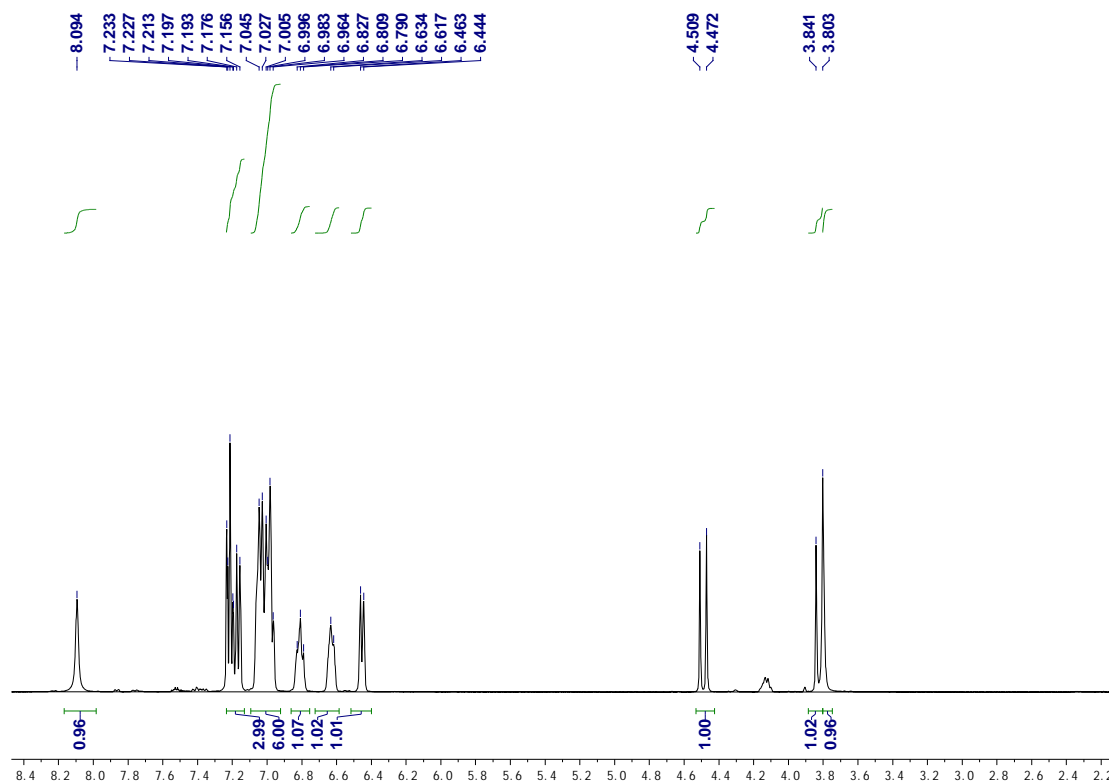
**(S)-12-Trifluoromethyl-12-(3-trifluoromethyl-phenyl)-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3ak)**

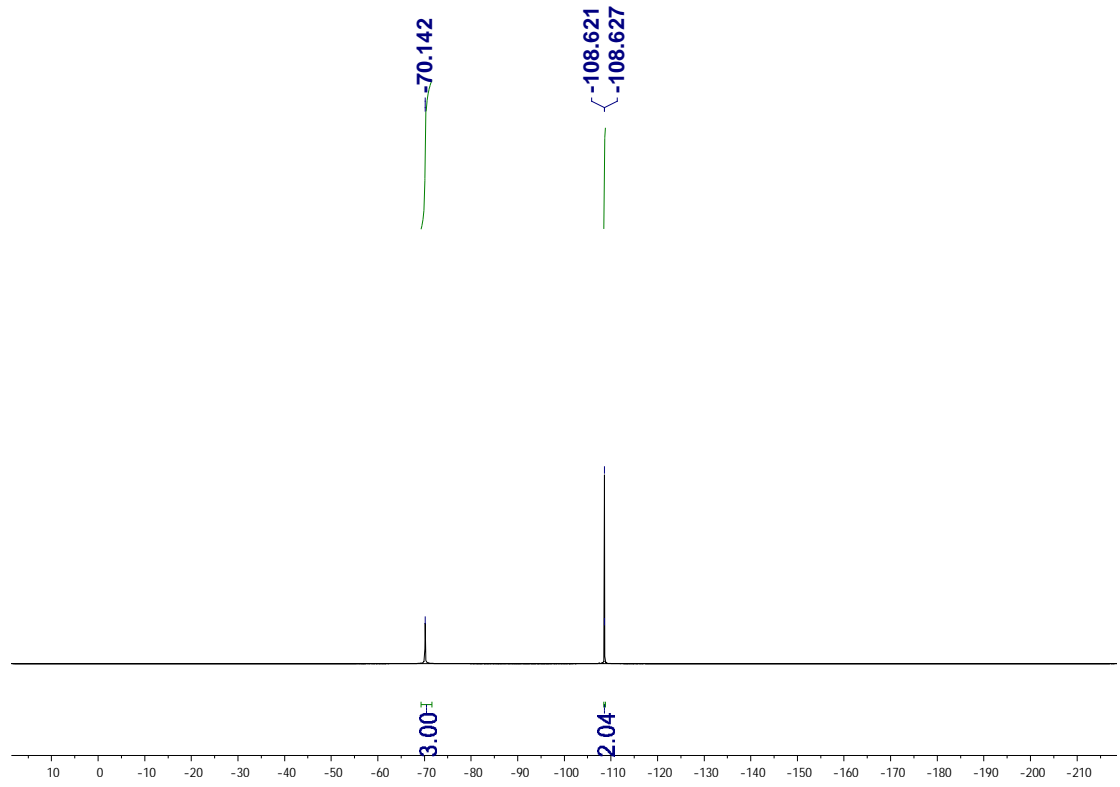
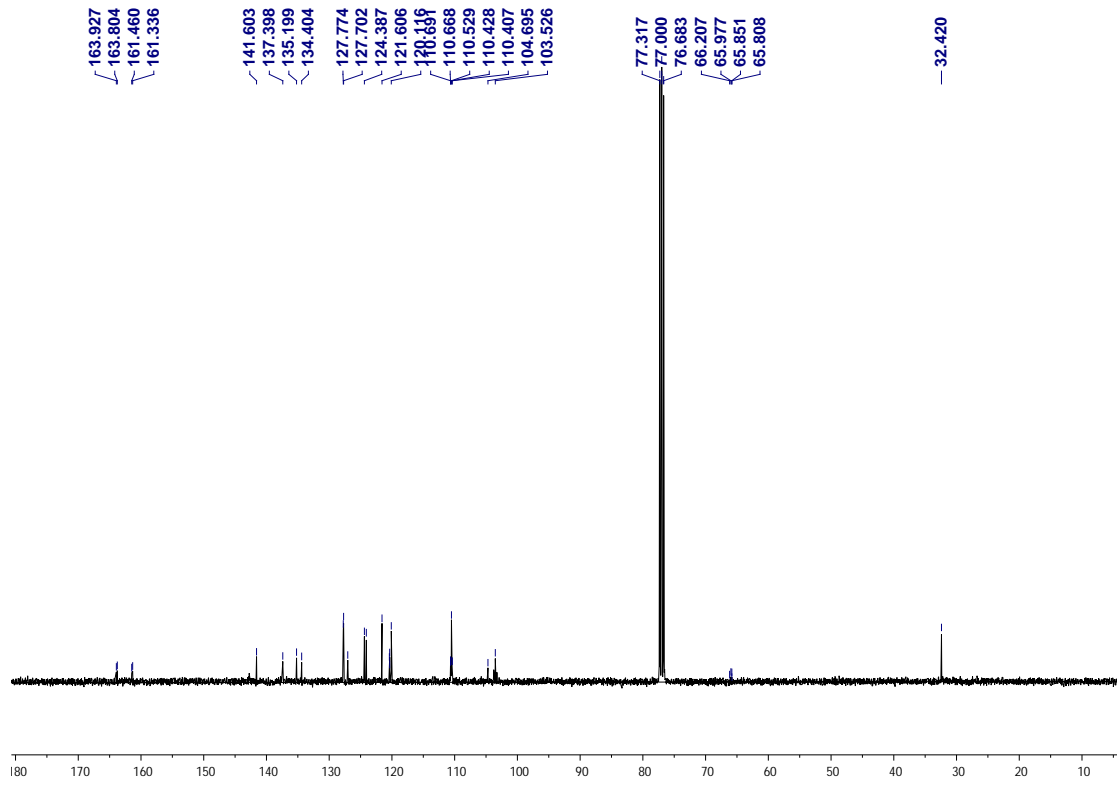




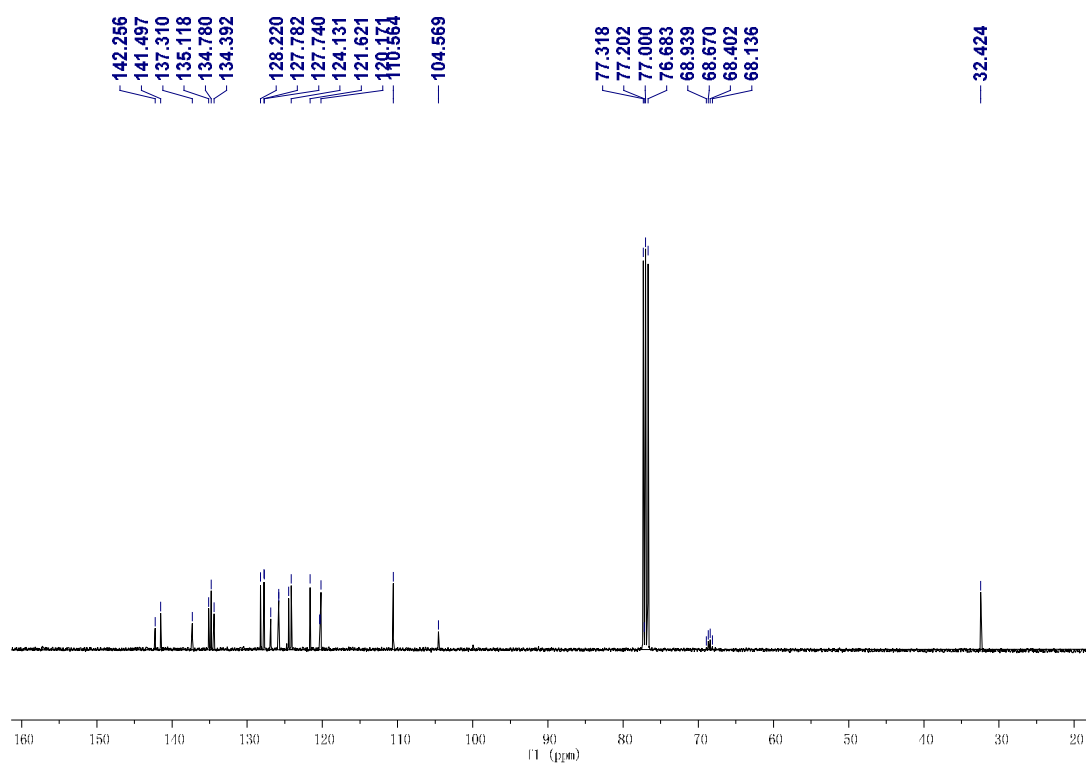
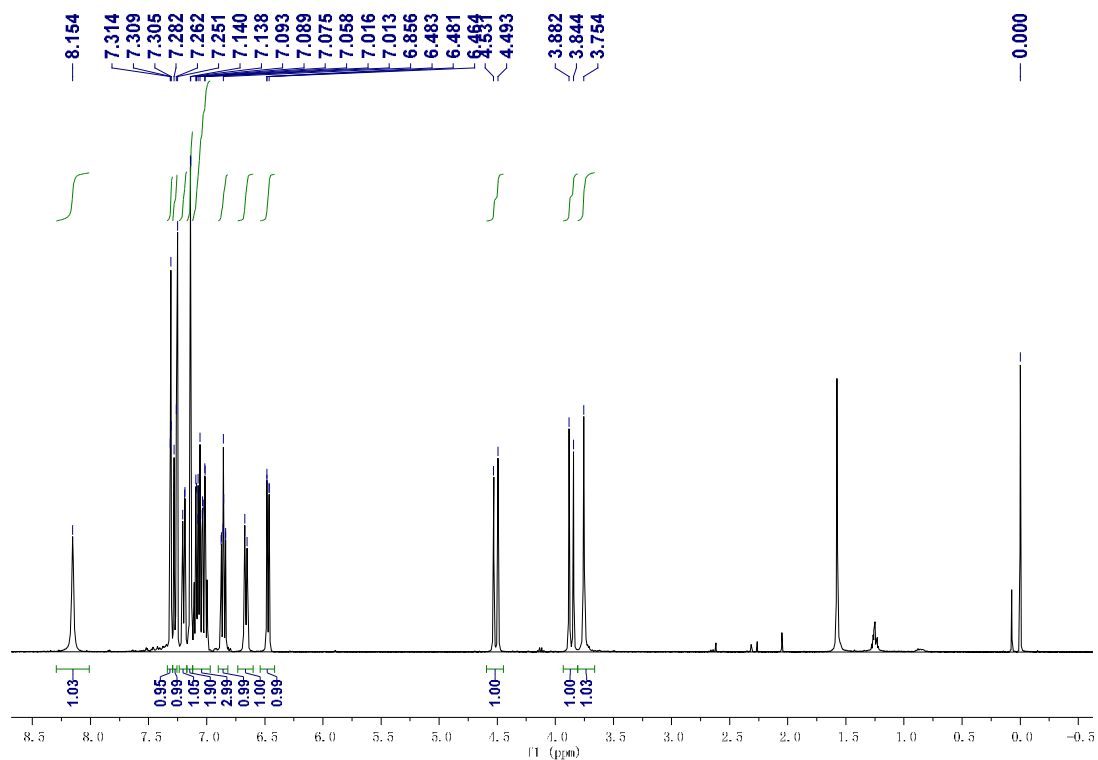


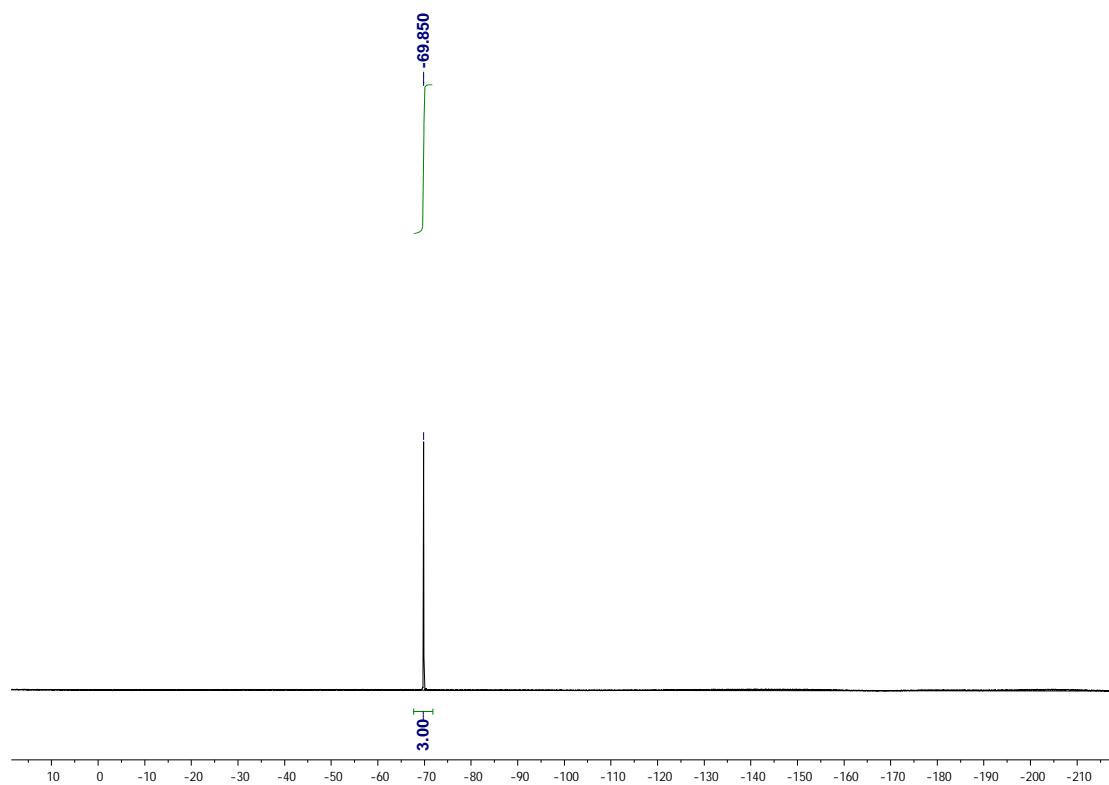
(S) 12-(3,5-Difluoro-phenyl)-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3a)



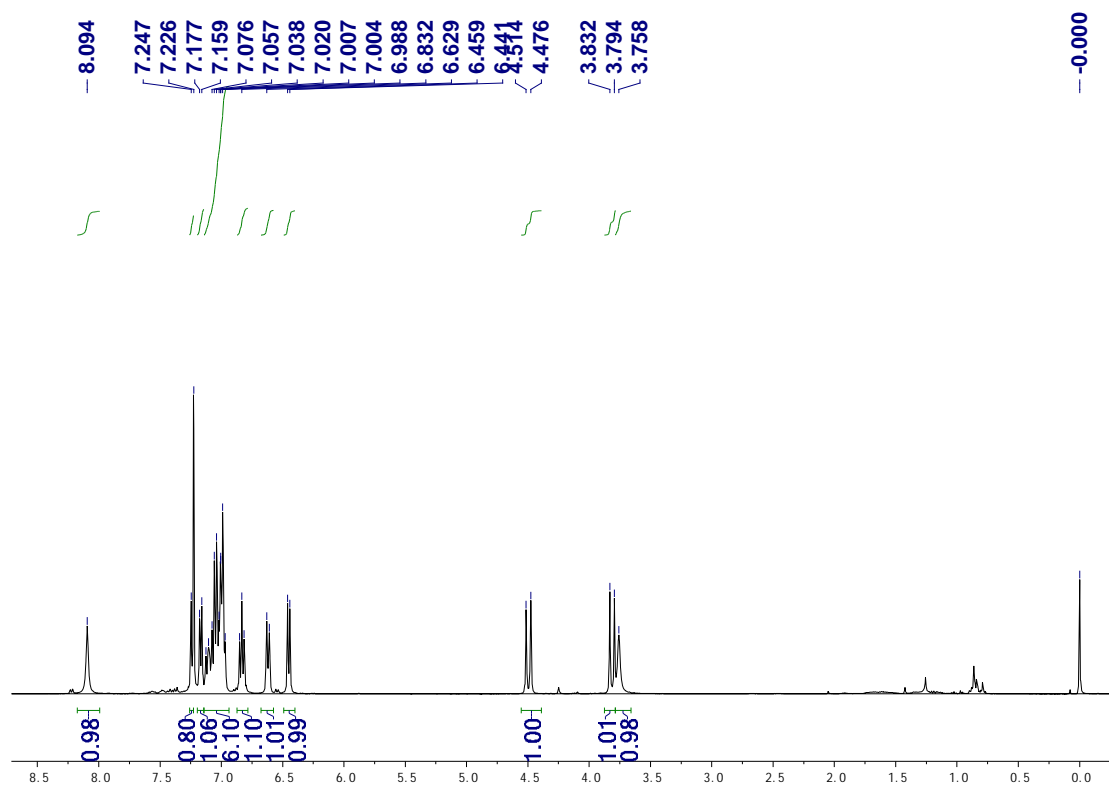


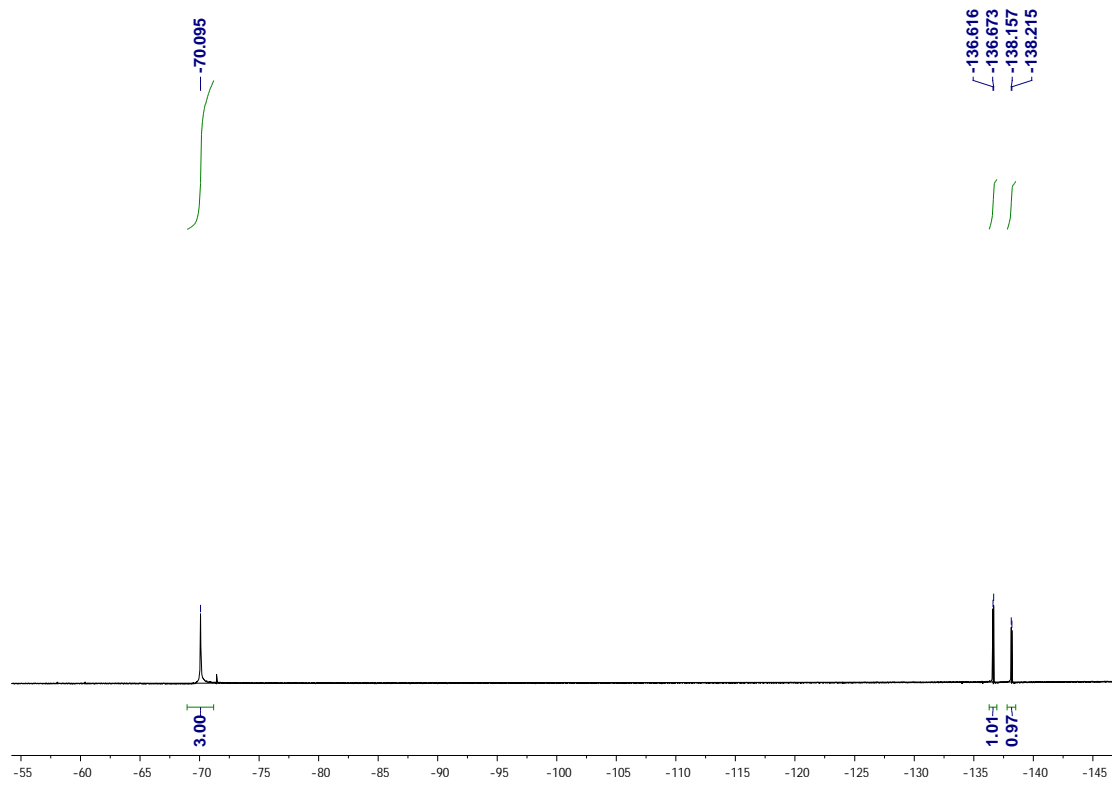
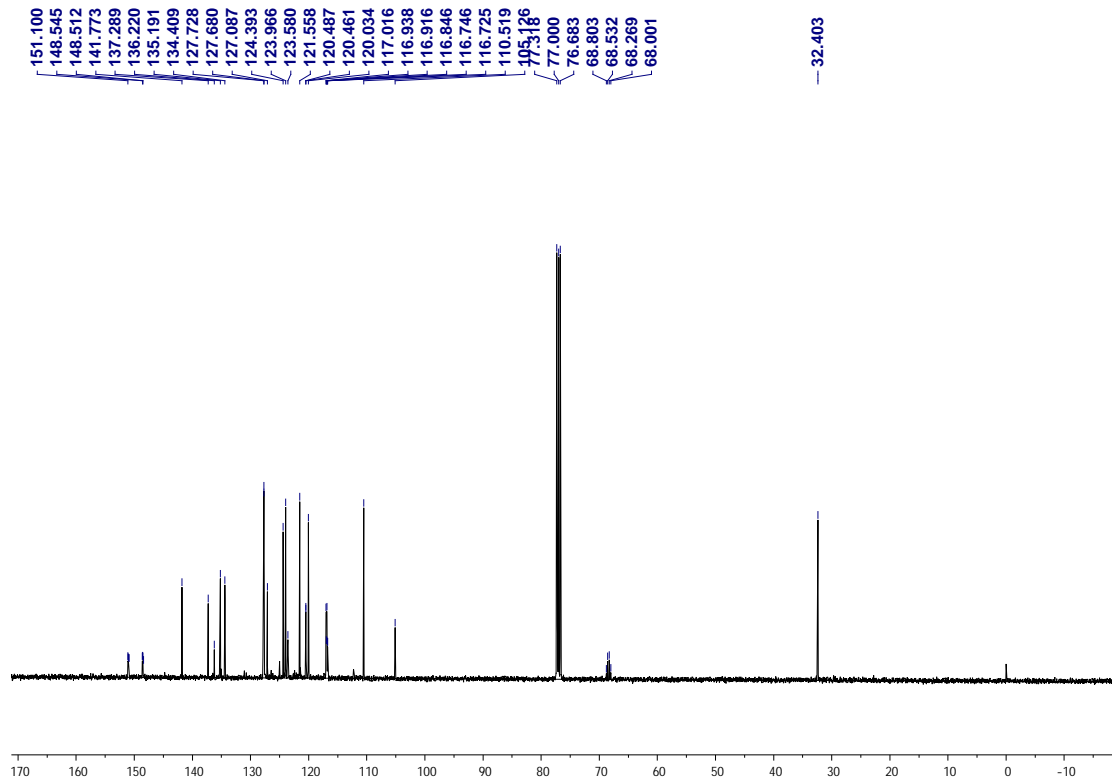
**(S)-12-(3,5-Dichloro-phenyl)-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3am)**





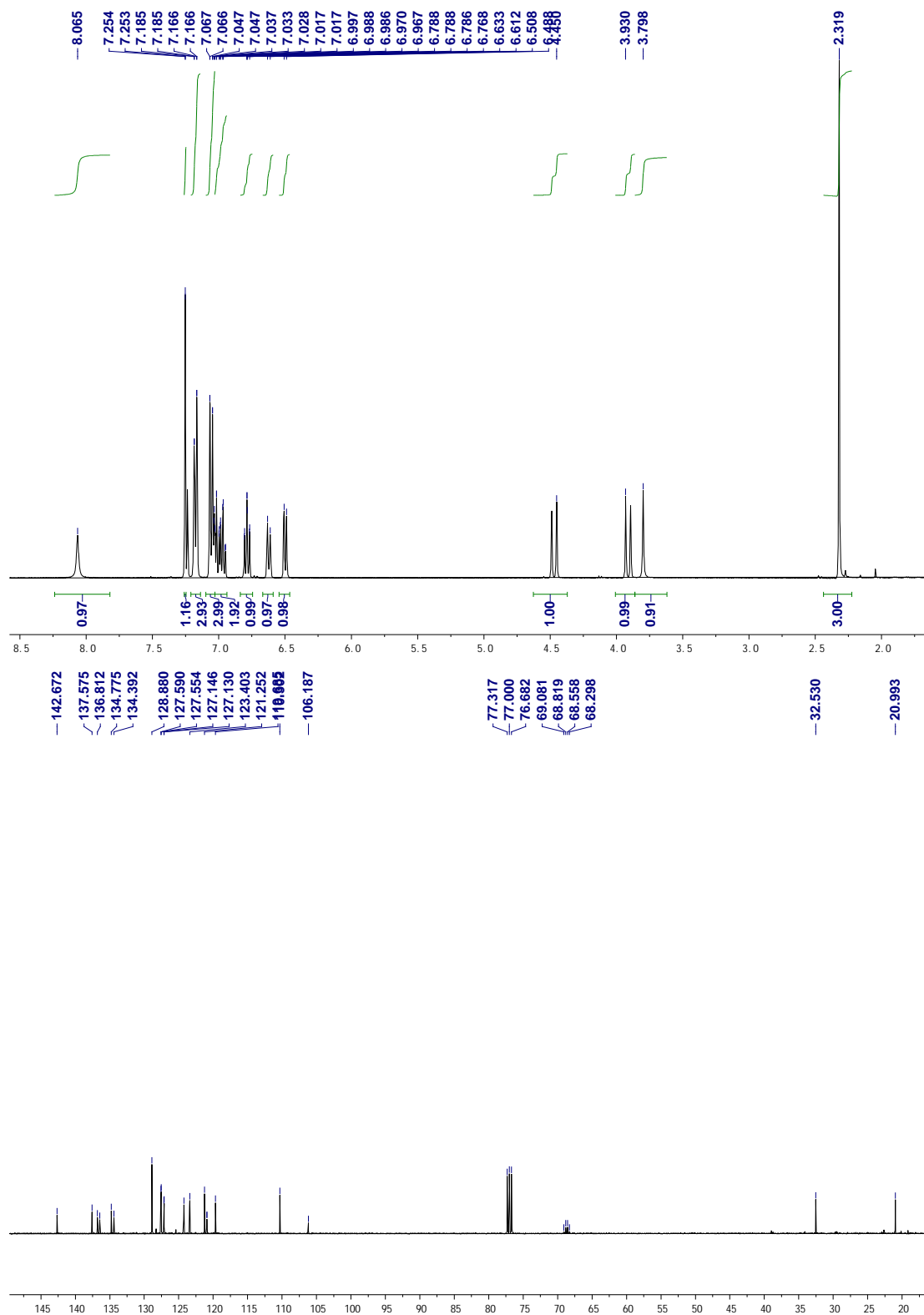
(S)-12-(3,4-difluorophenyl)-12-(trifluoromethyl)-5,6,11,12-tetrahydrobenzo[6,7]azepino[4,3-b]indole (3an)

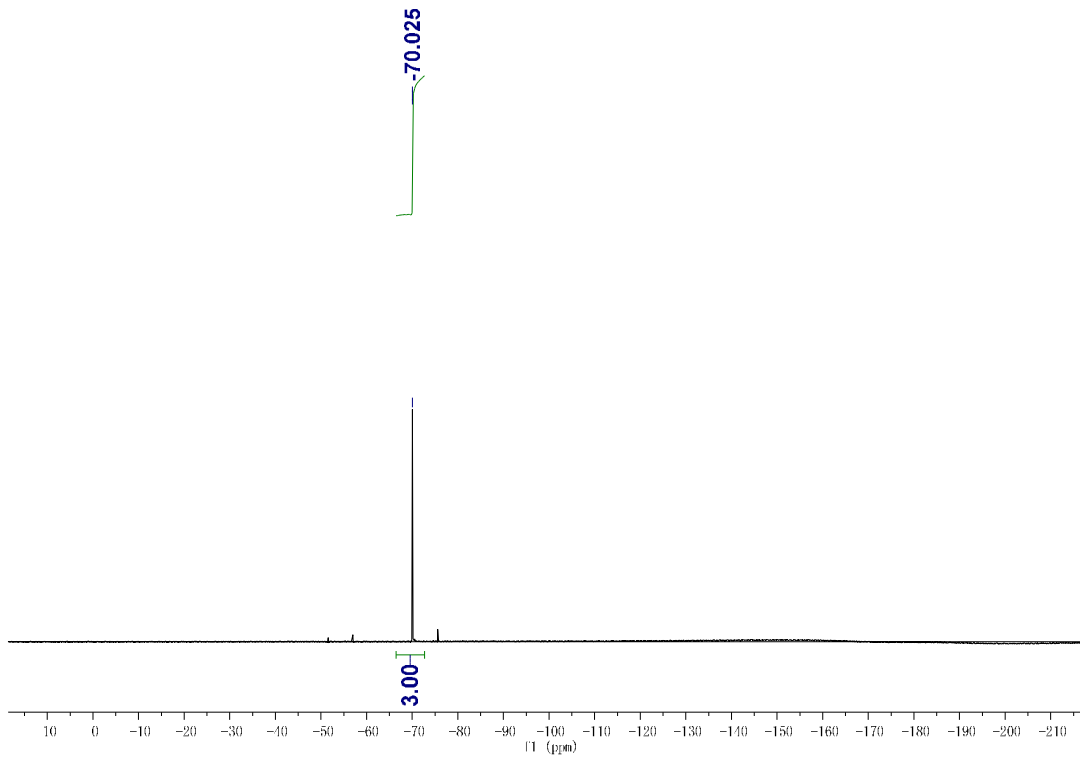




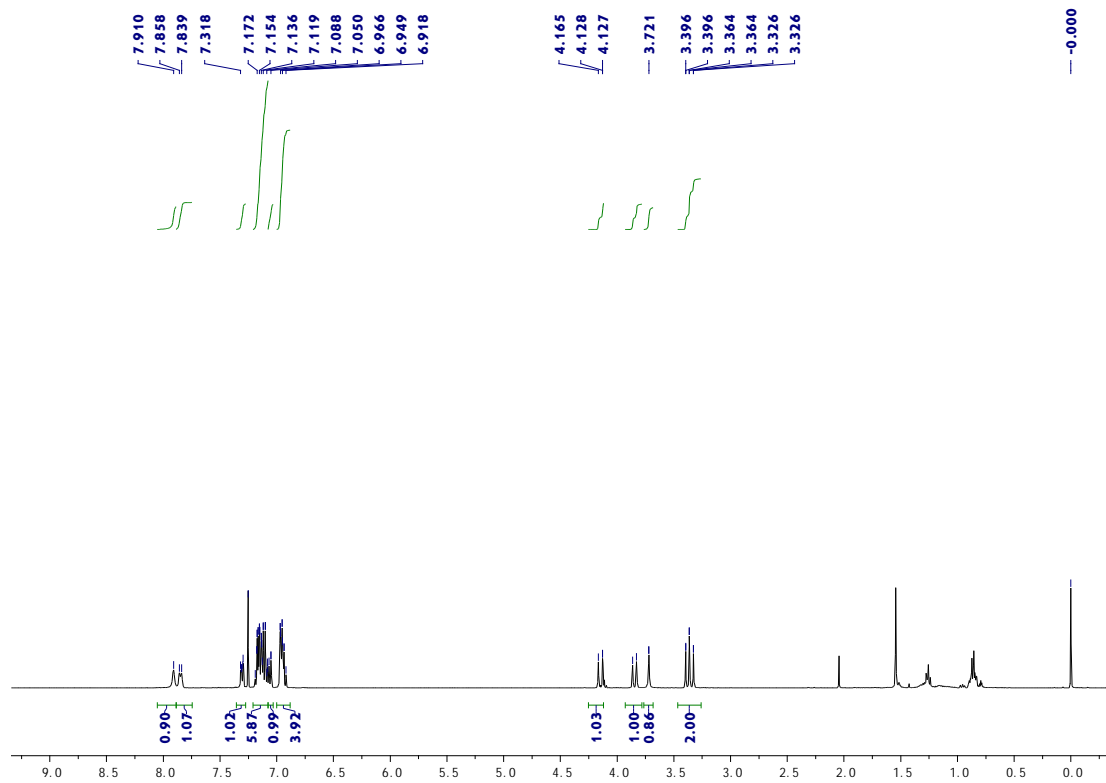
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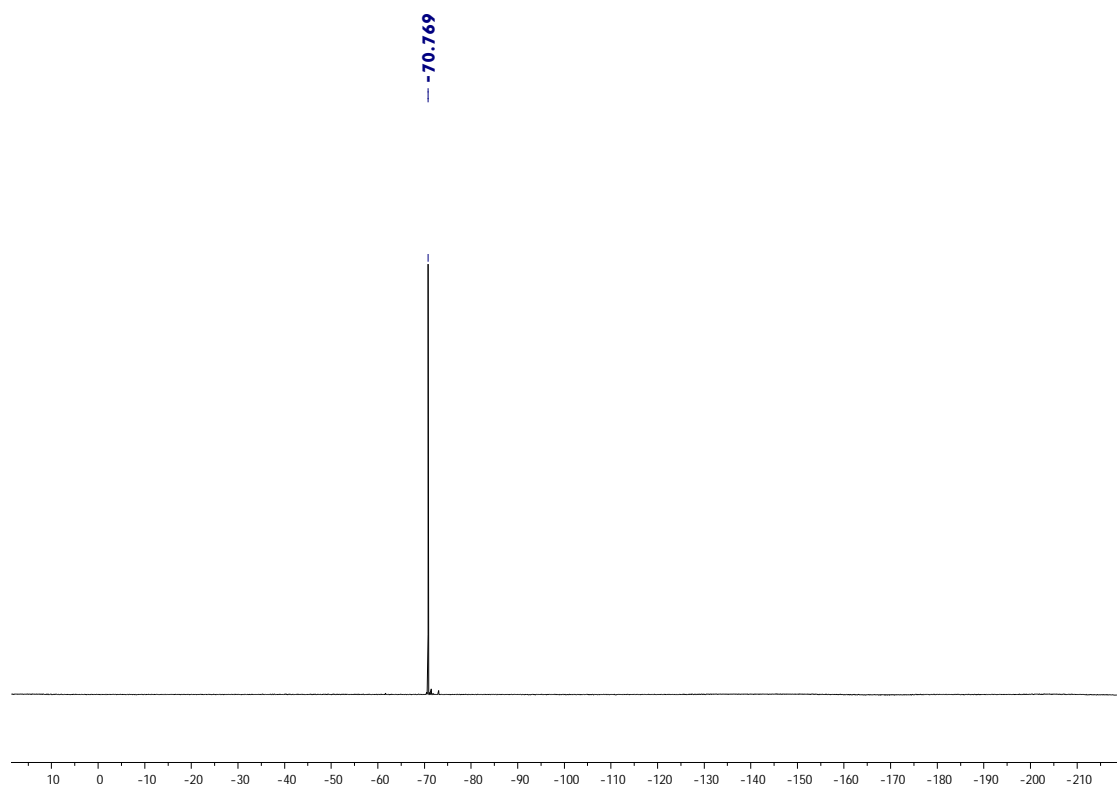
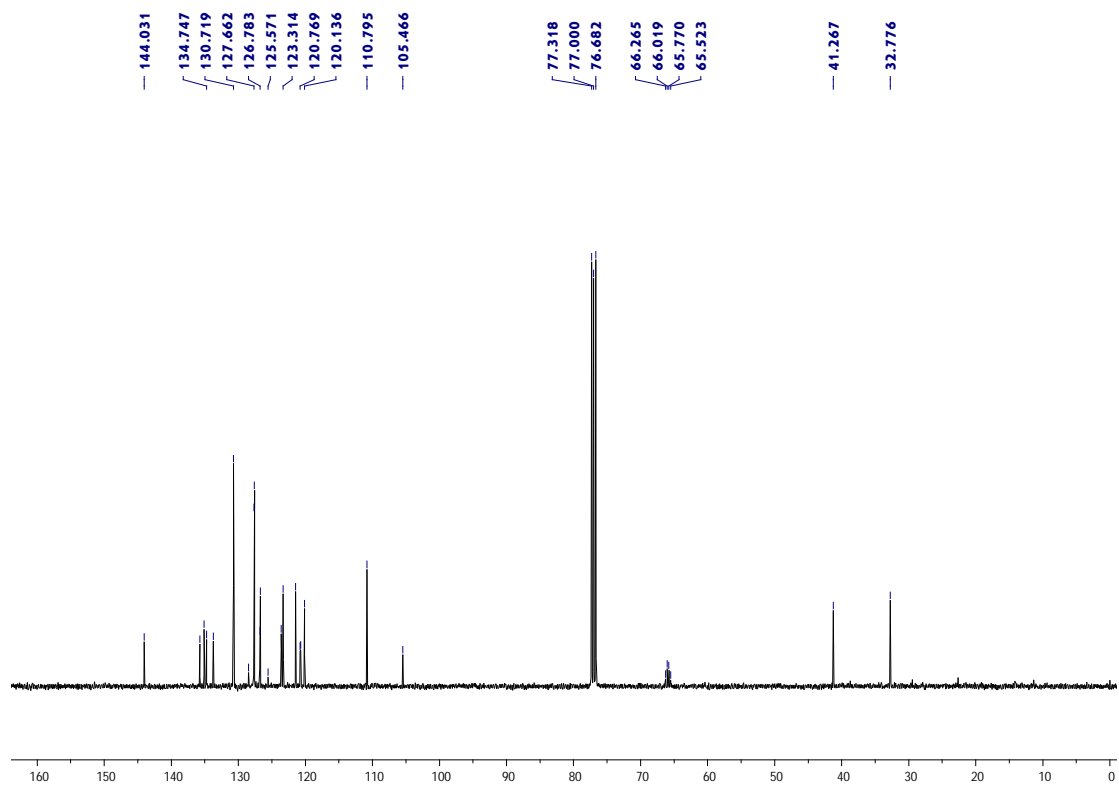
(3ao)





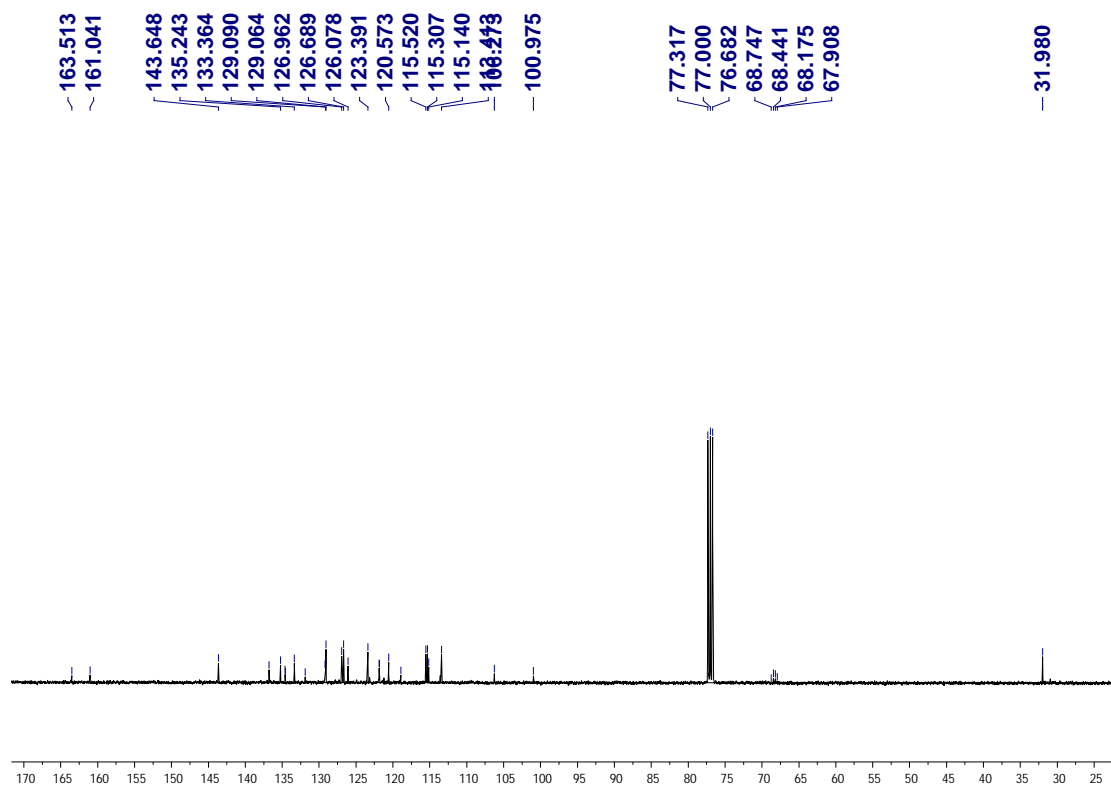
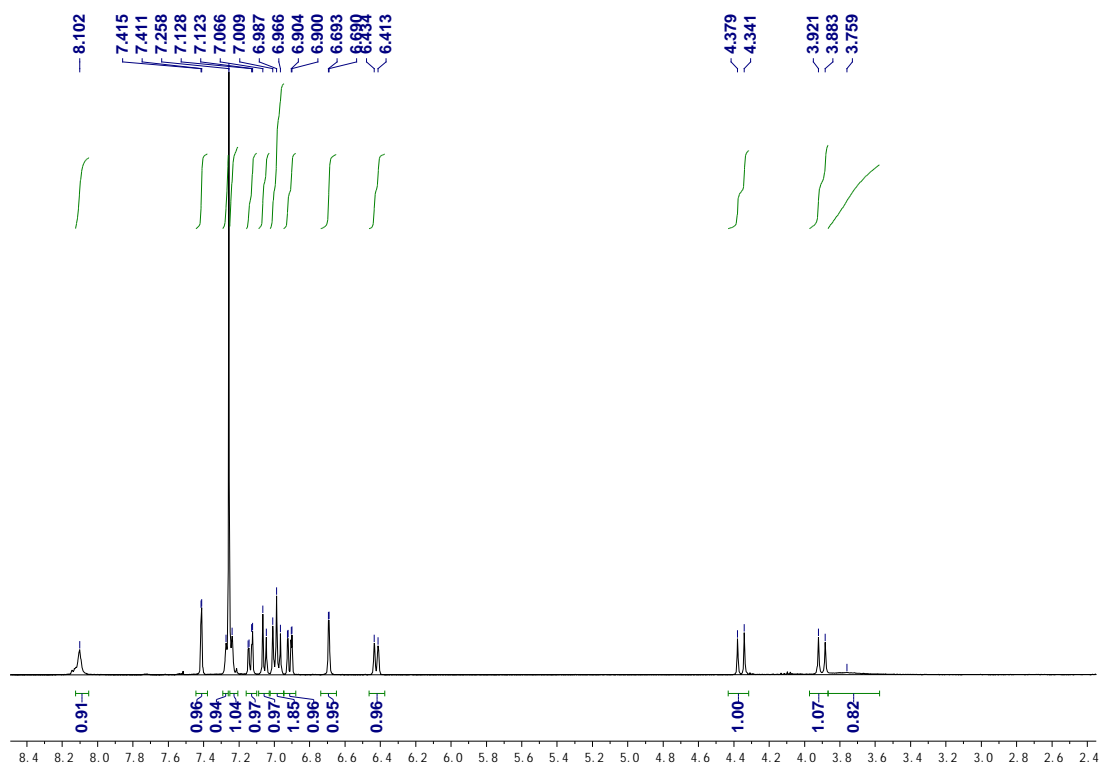
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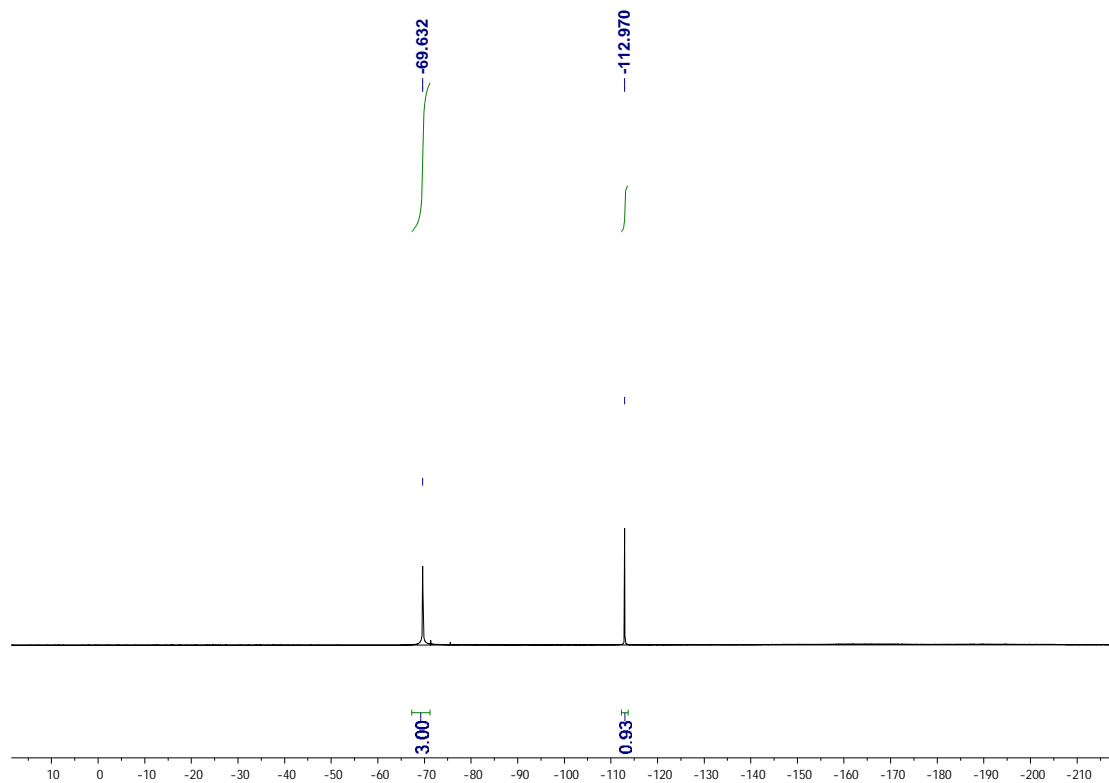




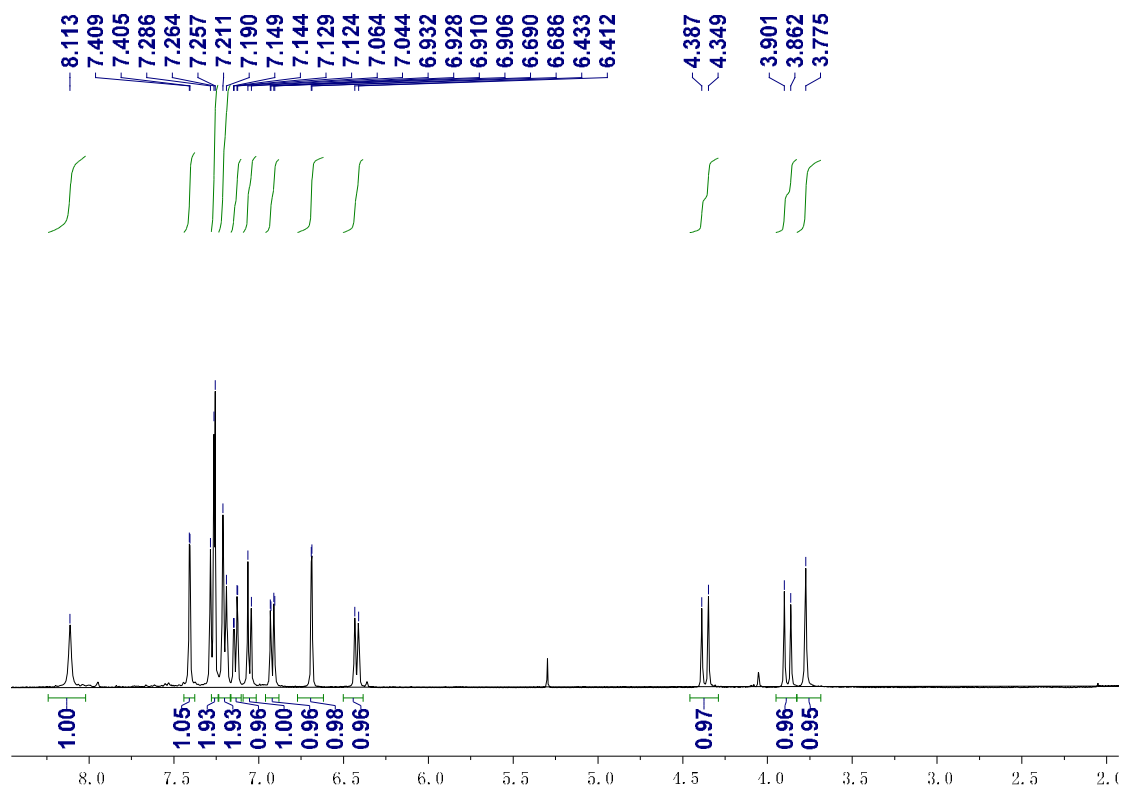


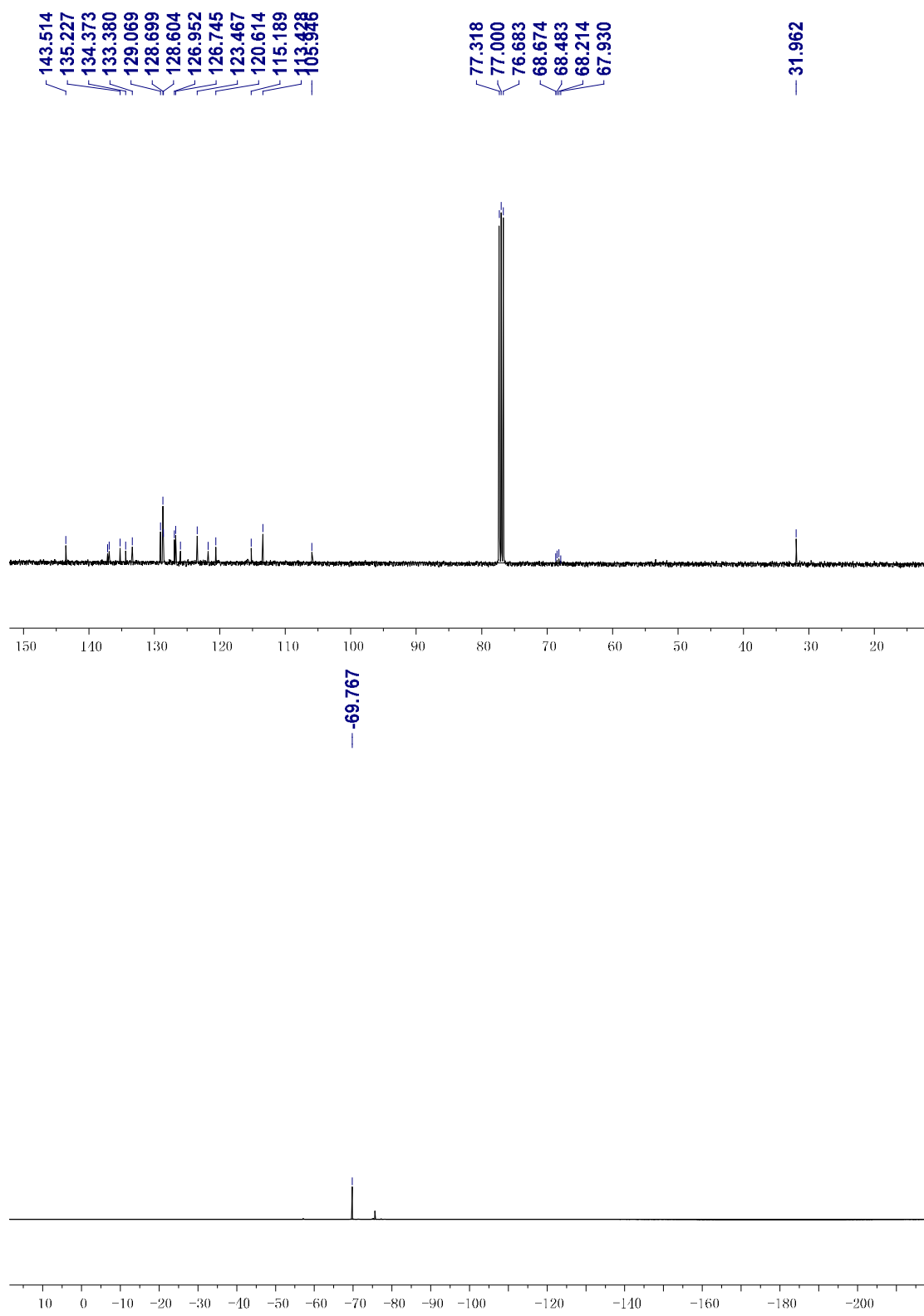
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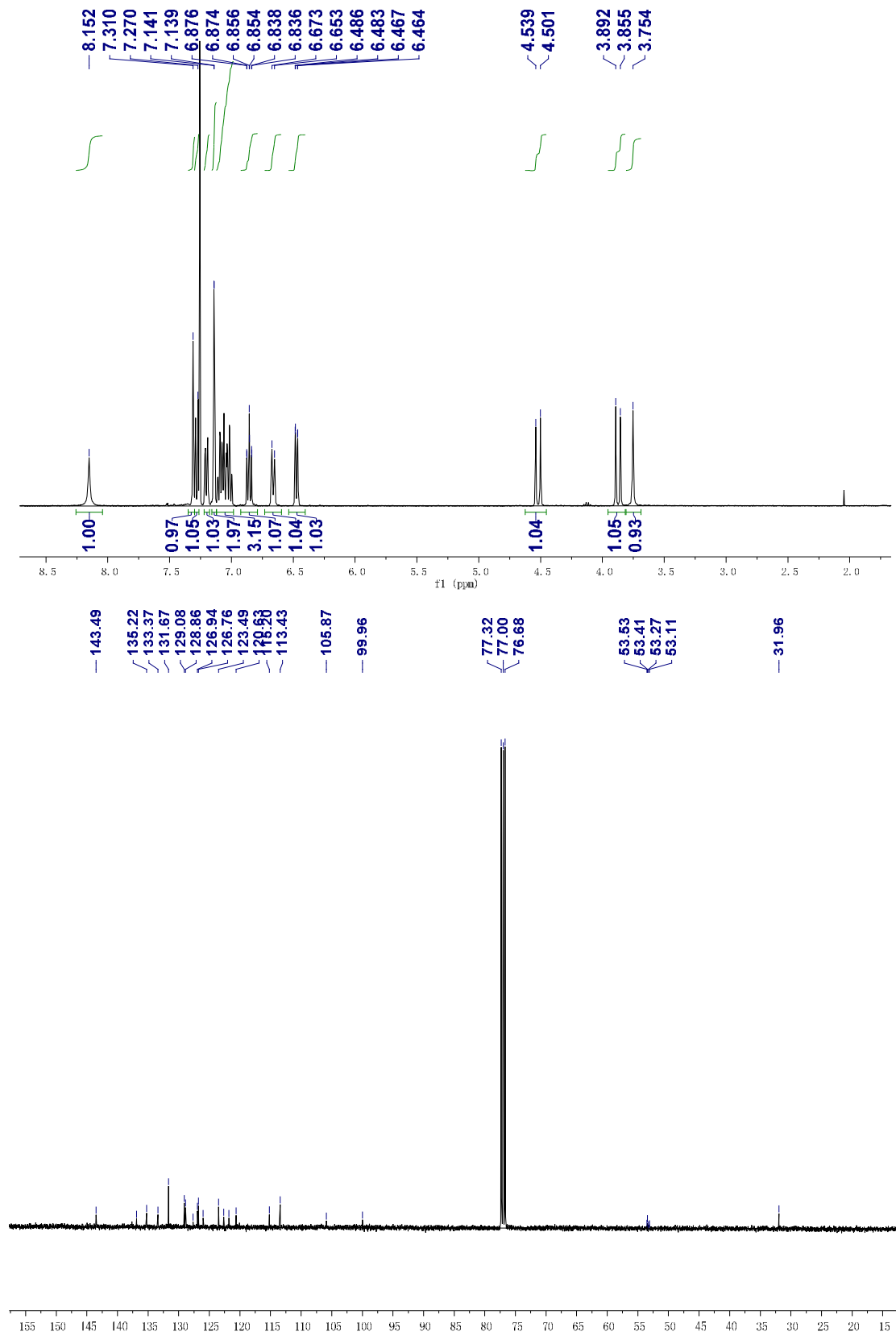


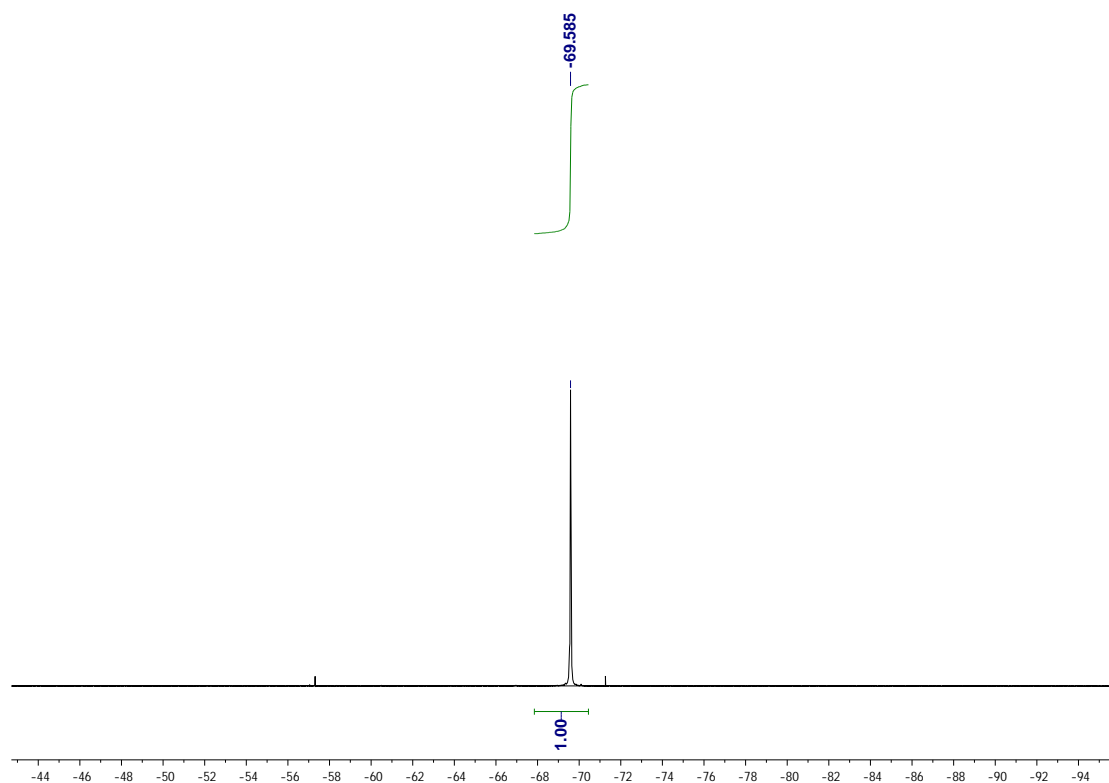
**(S)3,9-Dibromo-12-(4-chloro-phenyl)-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3bc)**



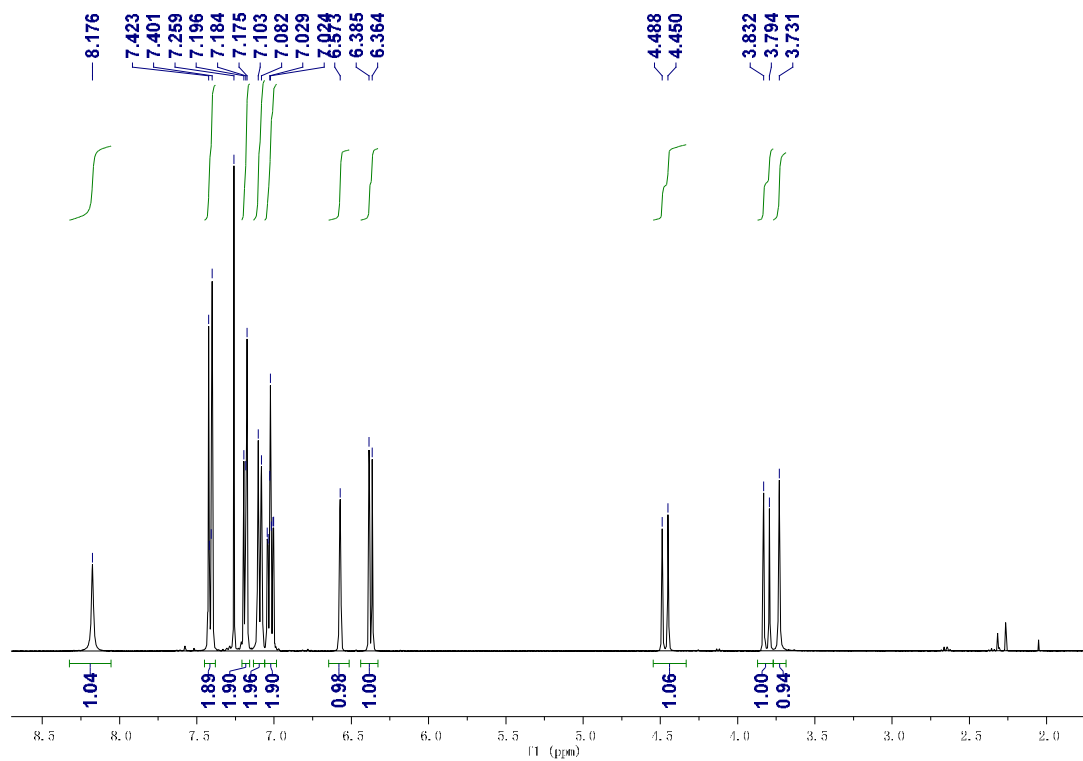


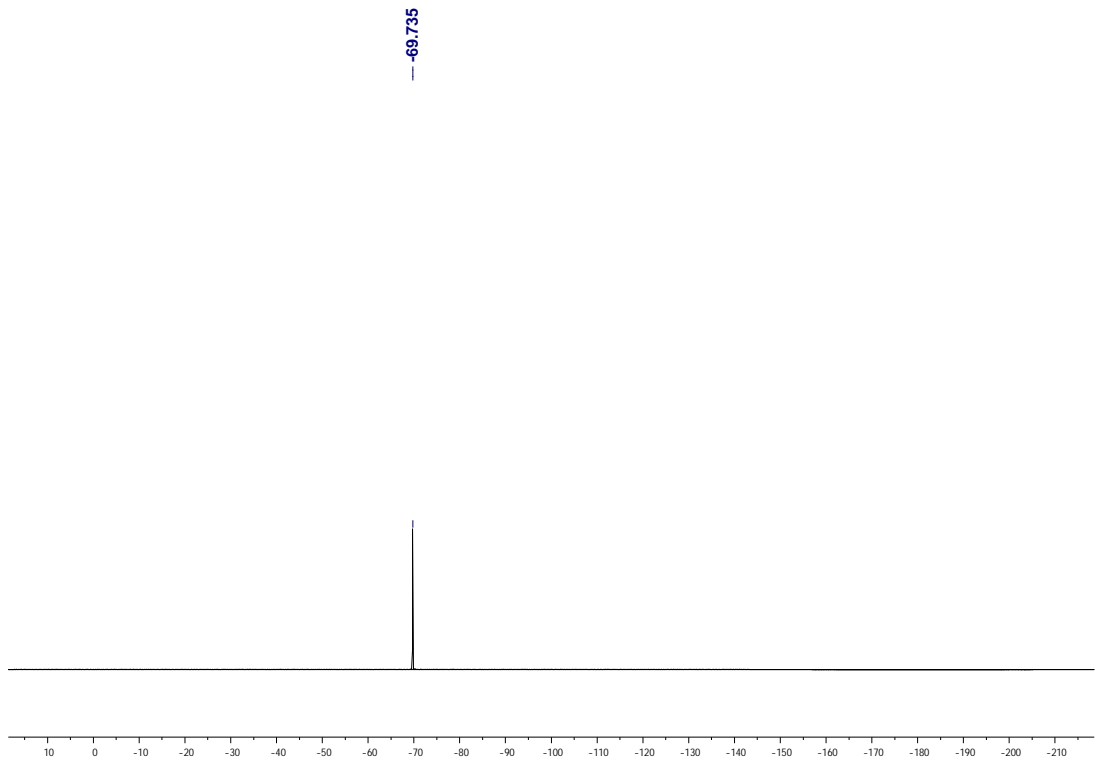
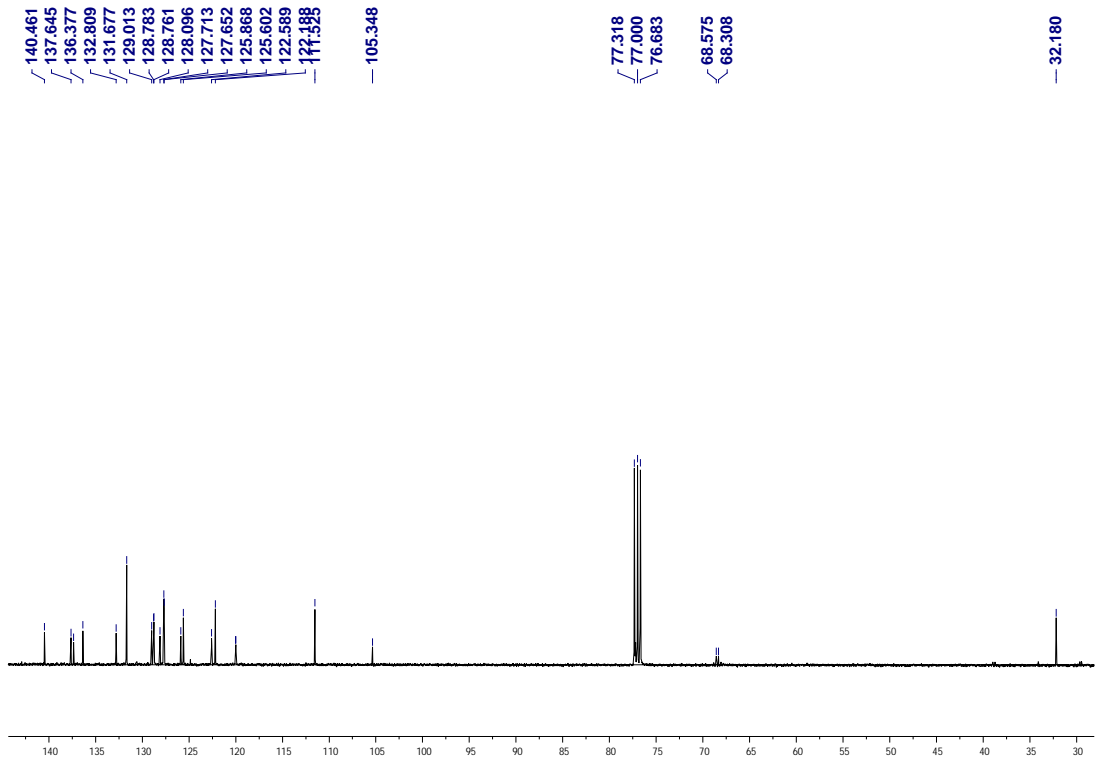
**(S)-3,9-Dibromo-12-(4-bromo-phenyl)-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole(3bd)**



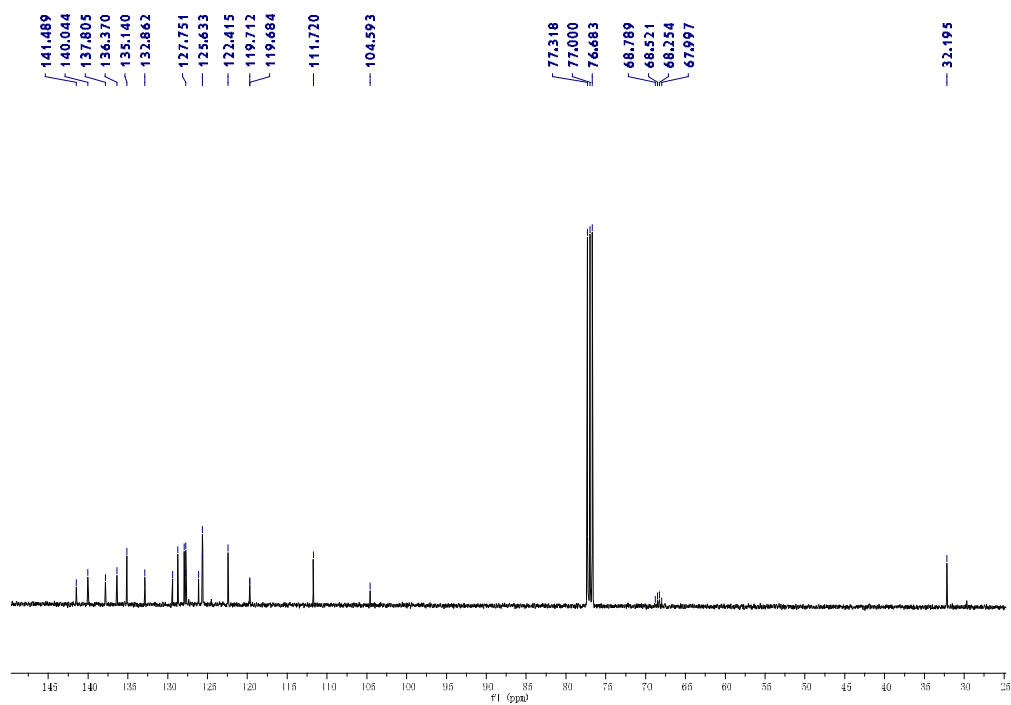
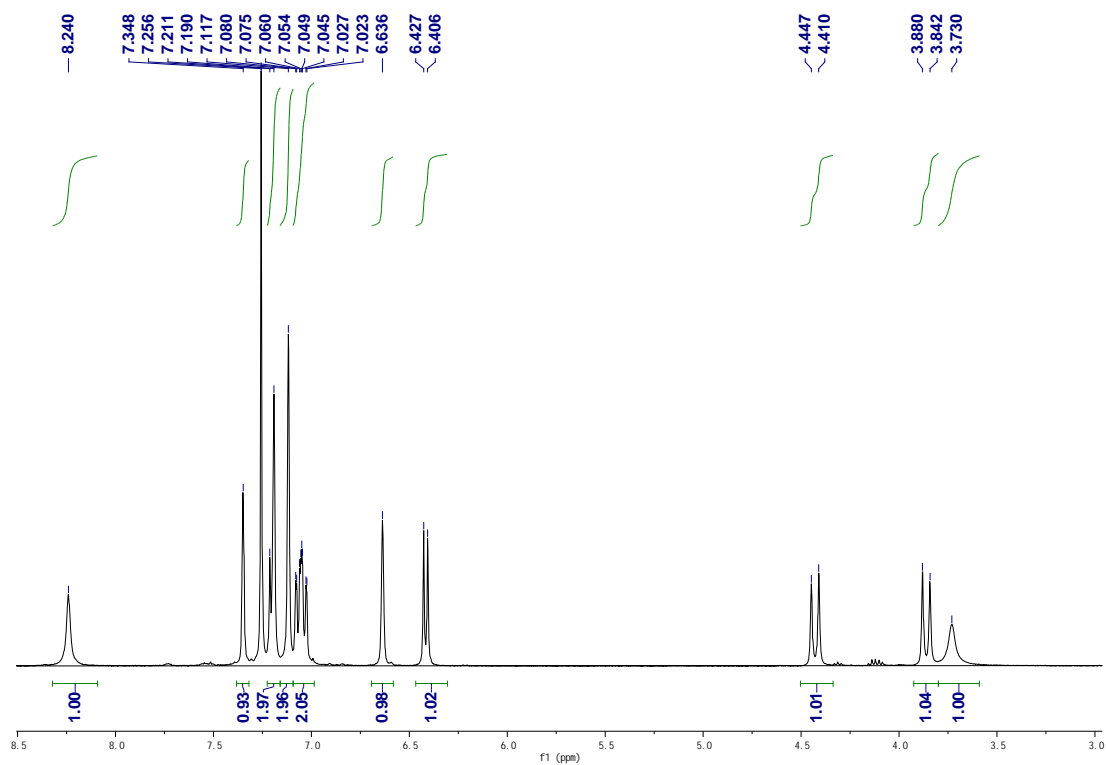


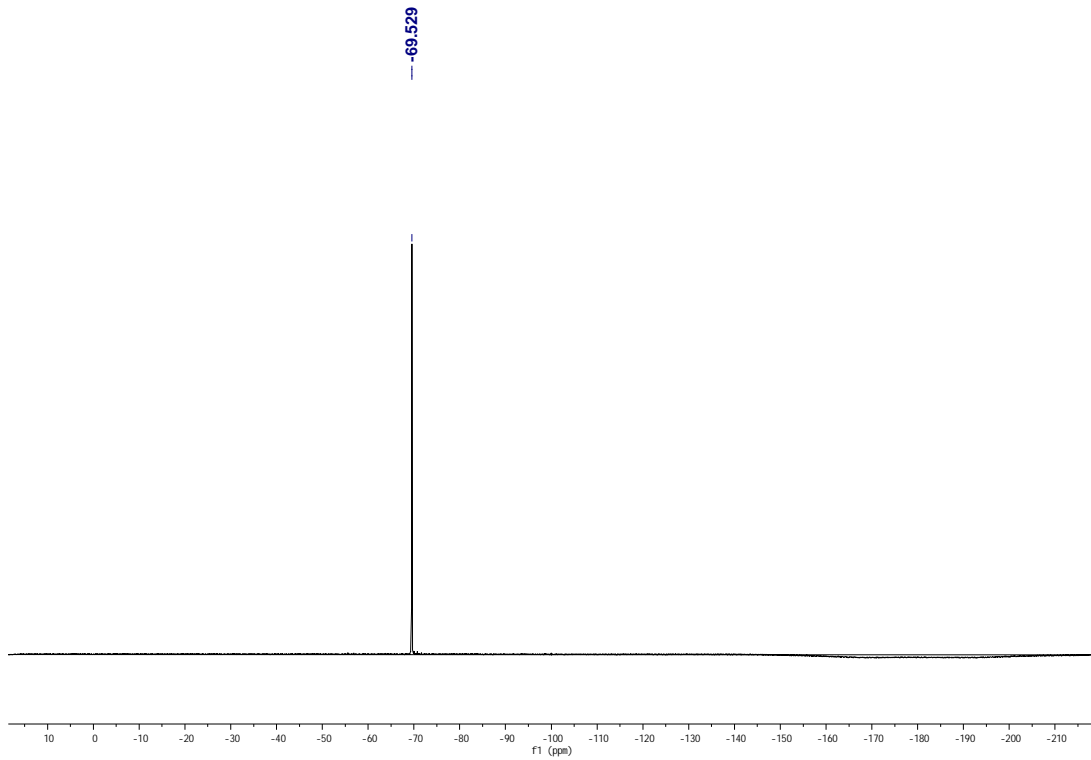
**(S)-12-(4-Bromo-phenyl)-2,8-dichloro-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3cd)**



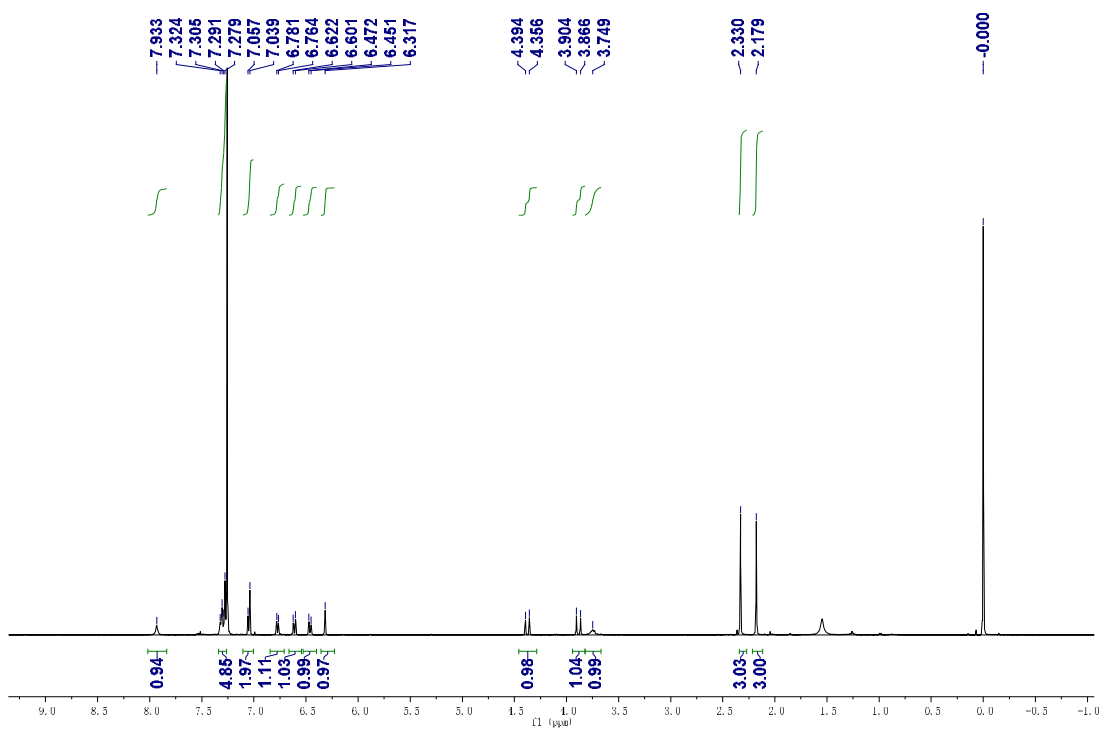


**(S)-2,8-Dichloro-12-(3,5-dichloro-phenyl)-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3ck)**

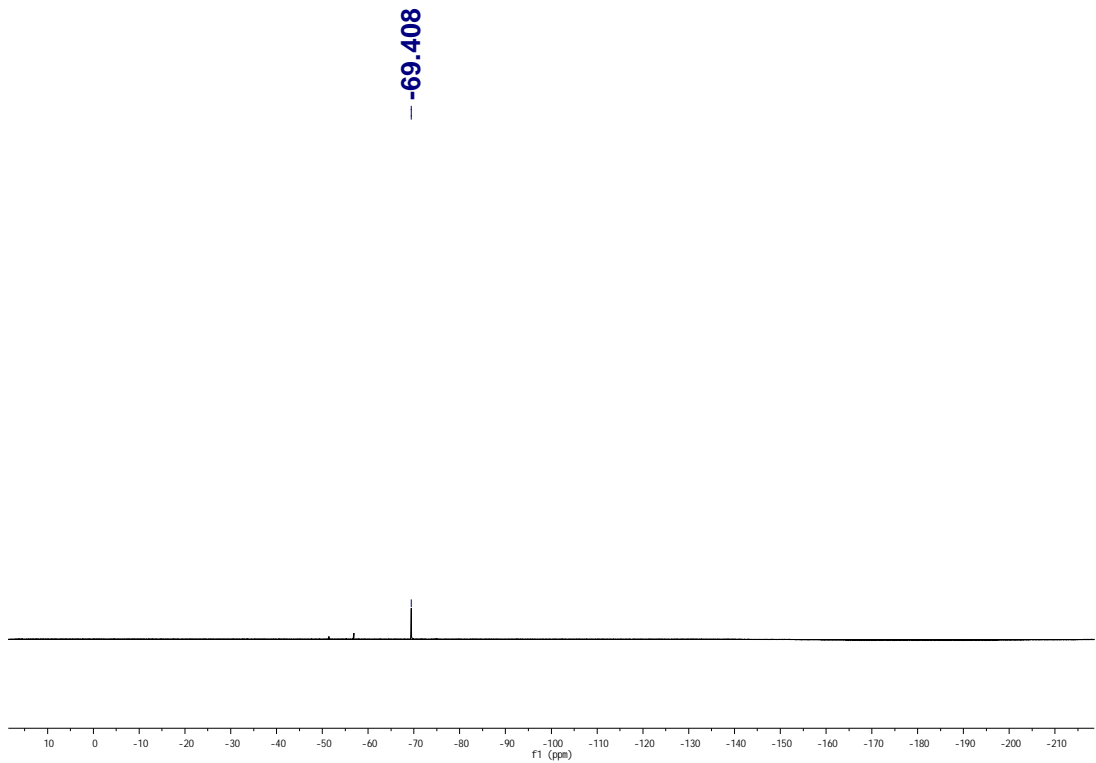
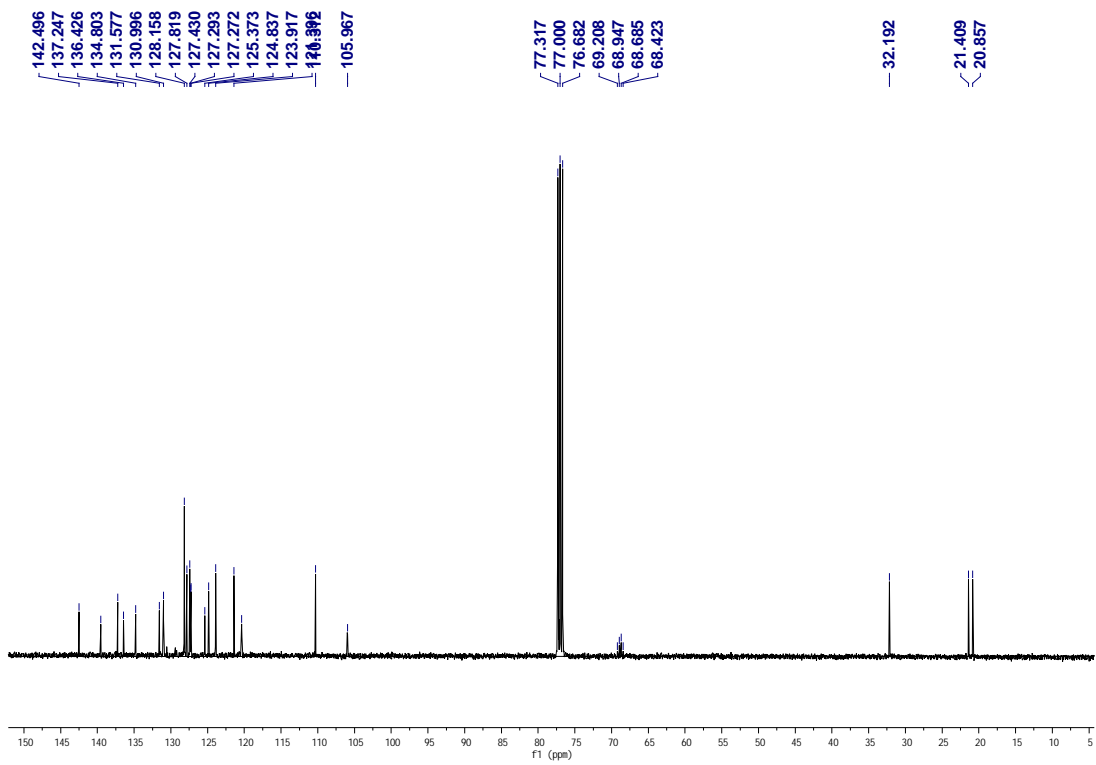




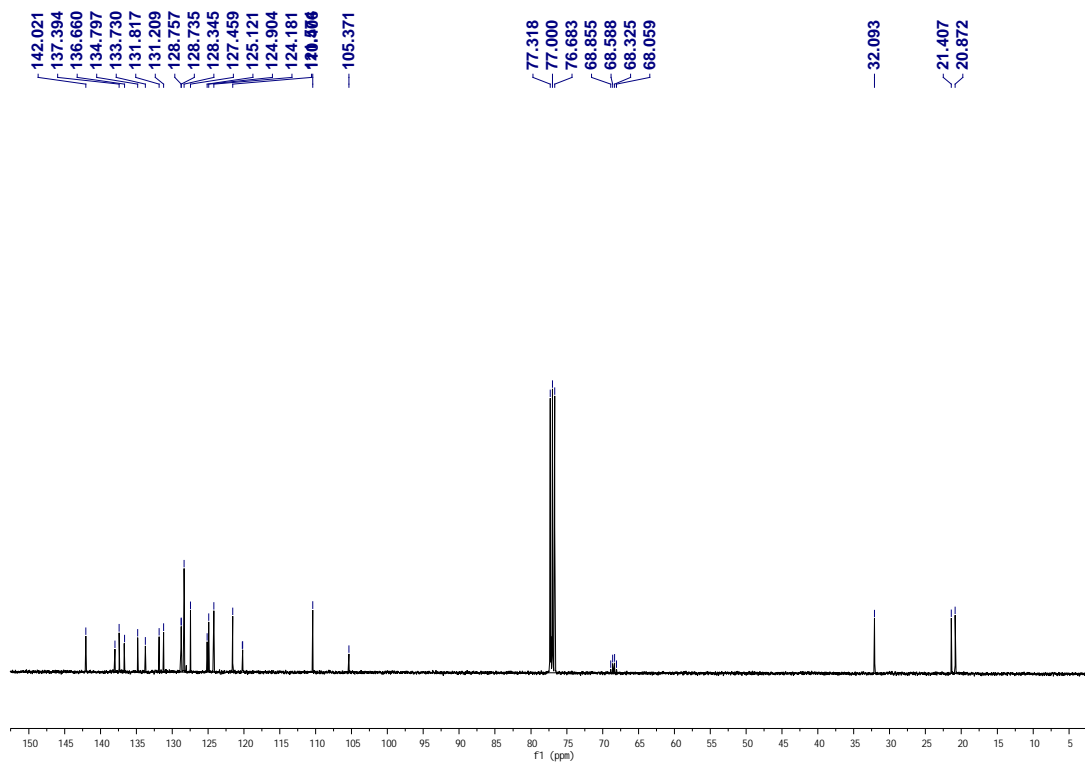
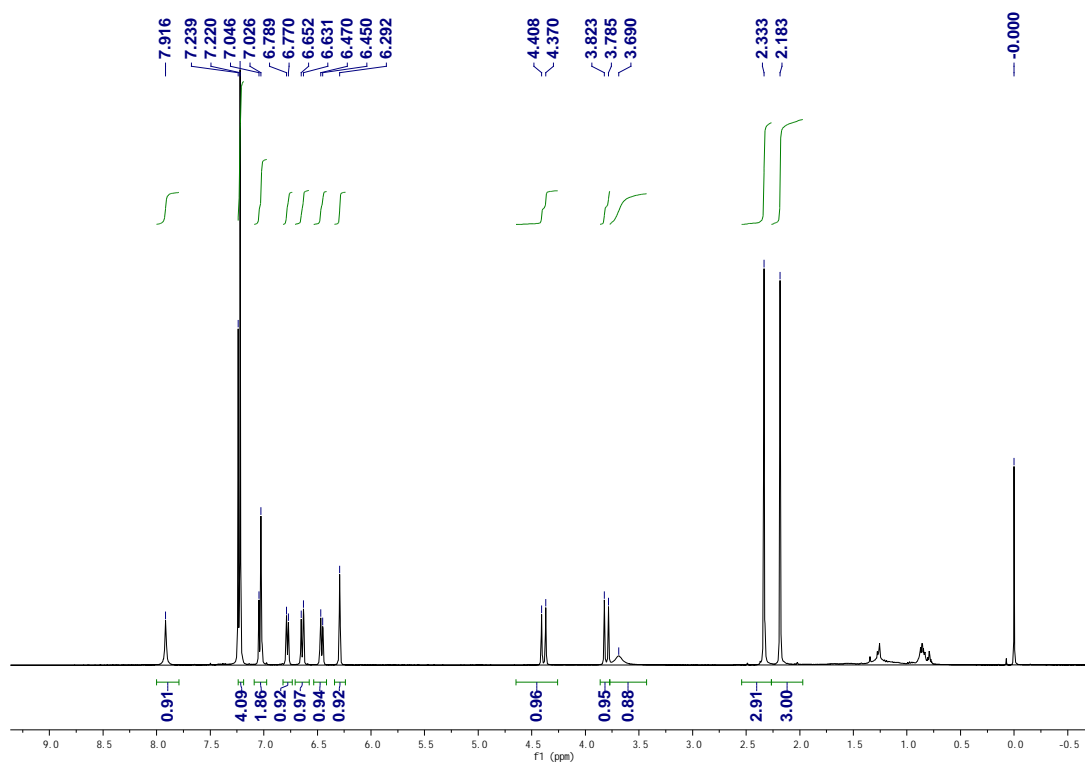
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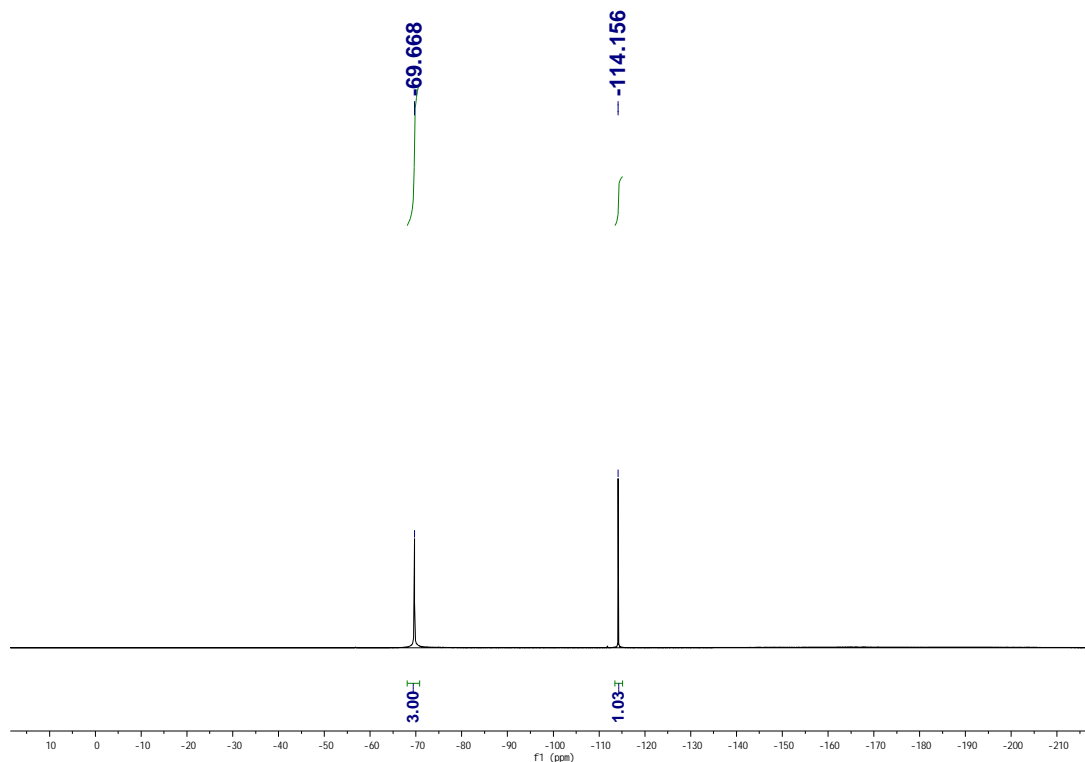




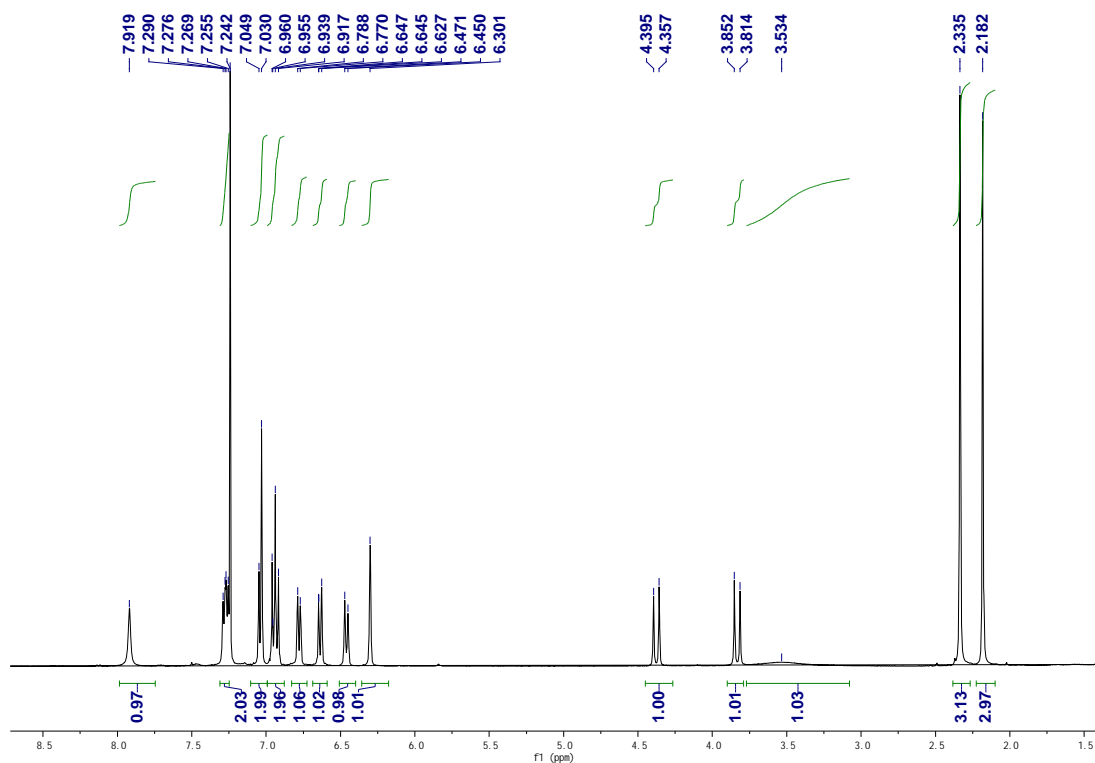


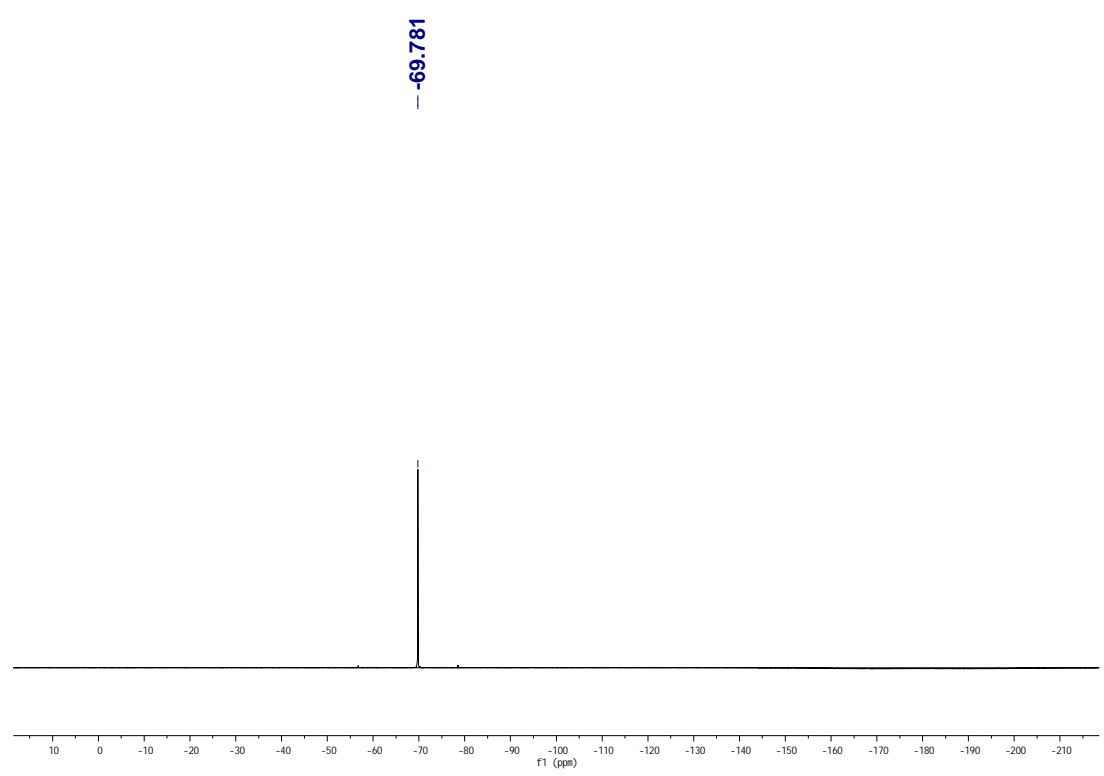
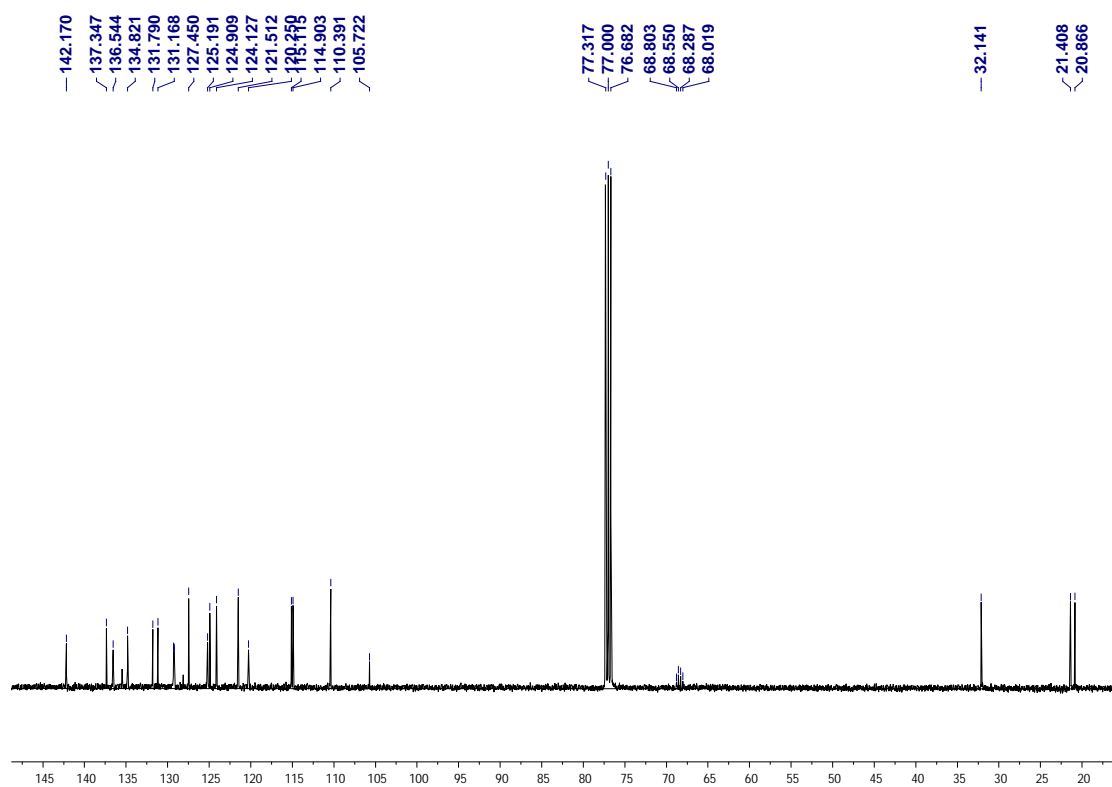
**(S)-12-(4-Fluoro-phenyl)-3,9-dimethyl-12-trifluoromethyl-5,6,11,12-tetrahydrobenzo[2,3]azepino[5,6-b]indole (3db)**



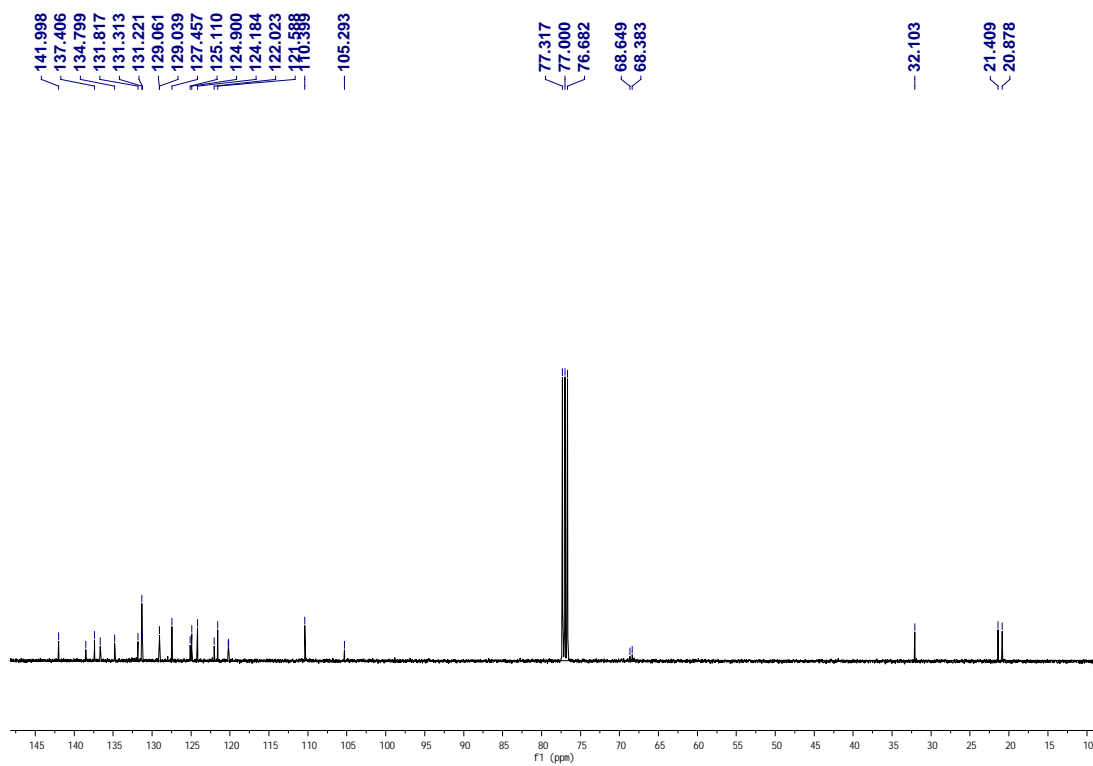
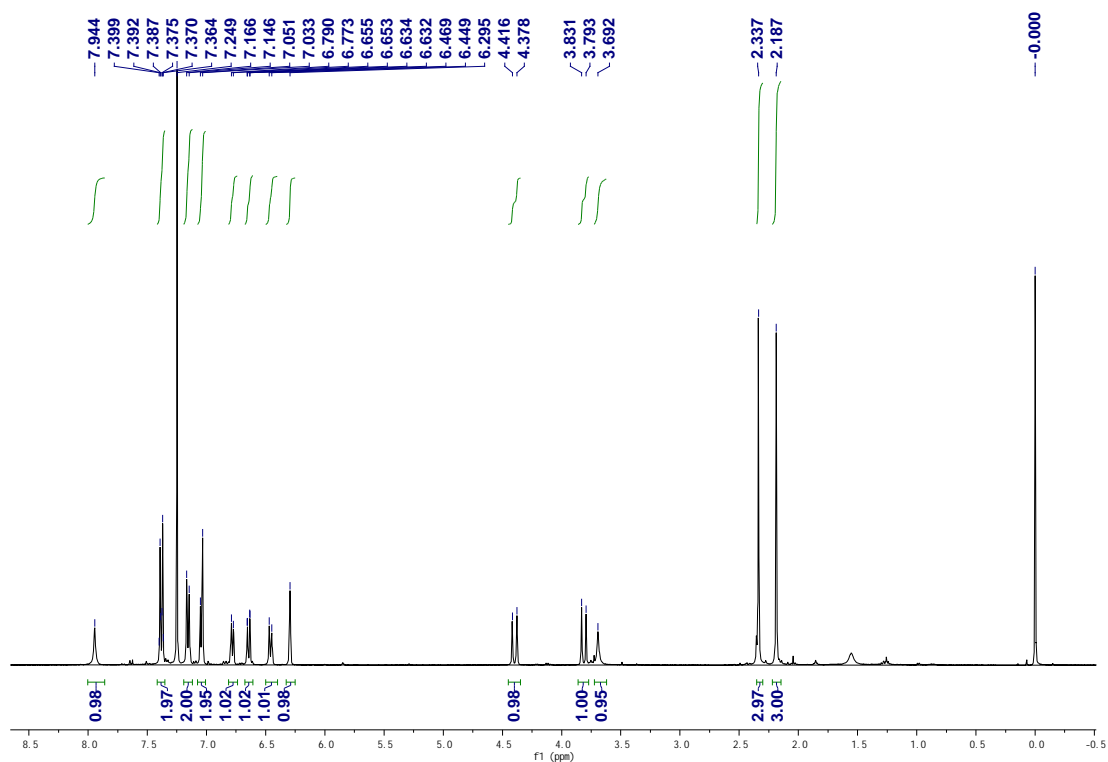


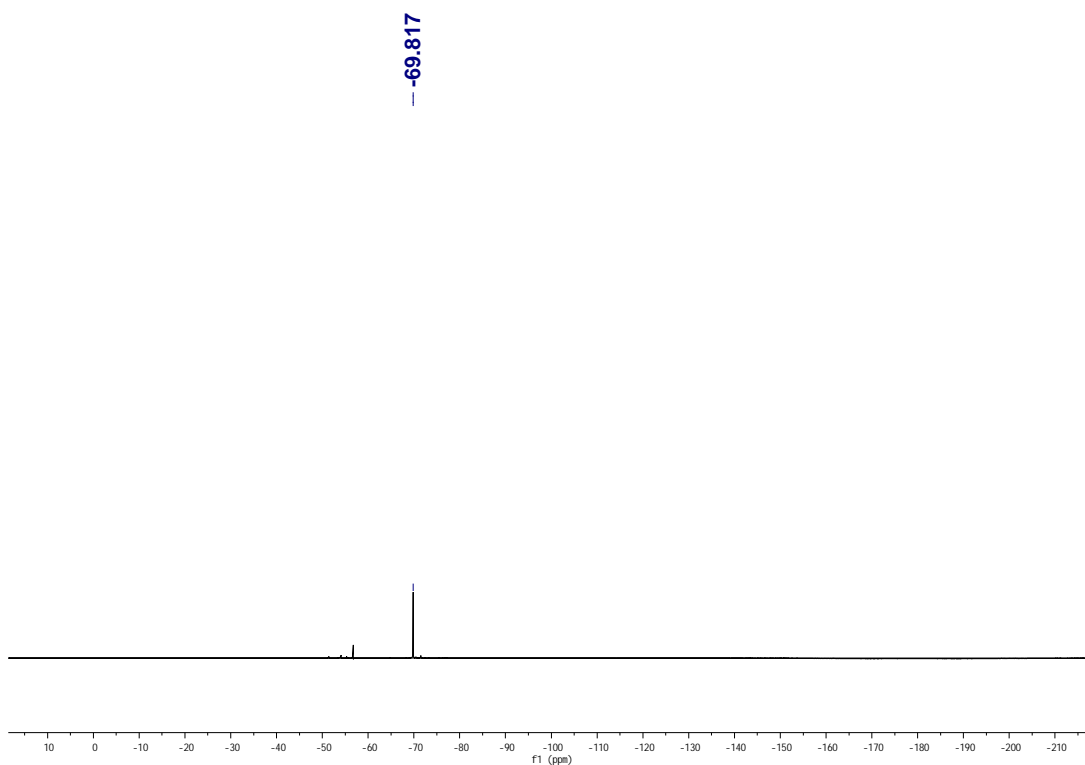
**(S)-12-(4-Chloro-phenyl)-3,9-dimethyl-12-trifluoromethyl-5,6,11,12-tetrahydrobenzo[2,3]azepino[5,6-b]indole (3dc)**



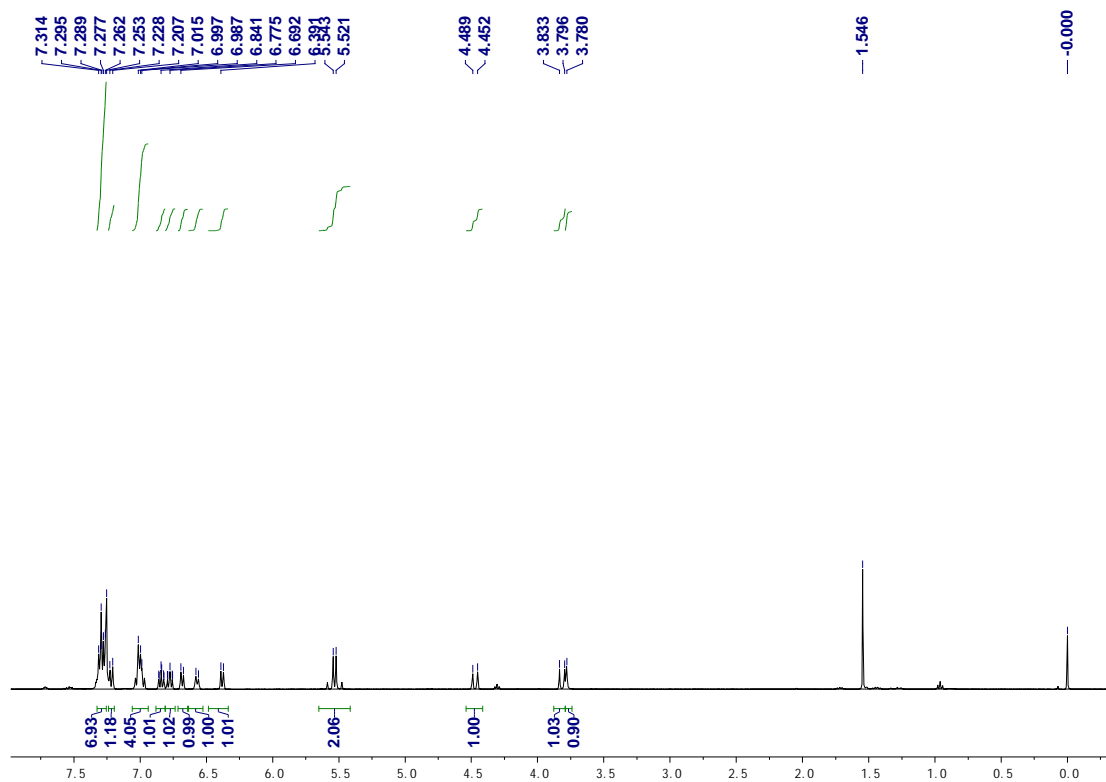


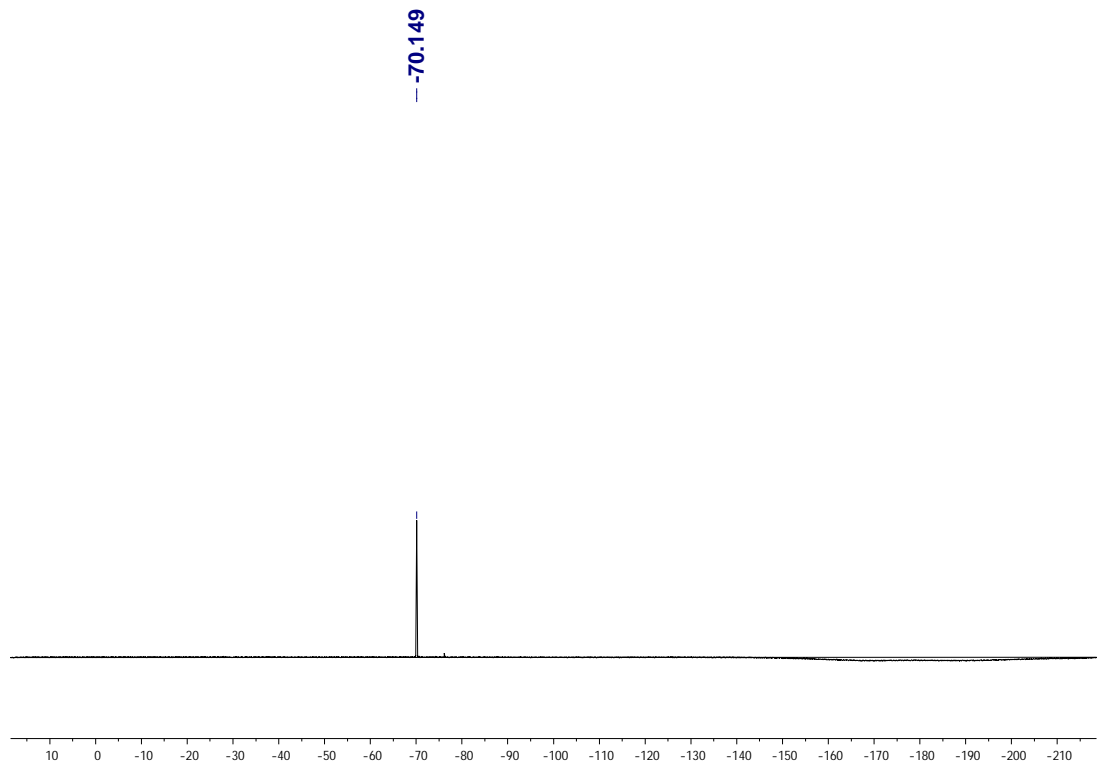
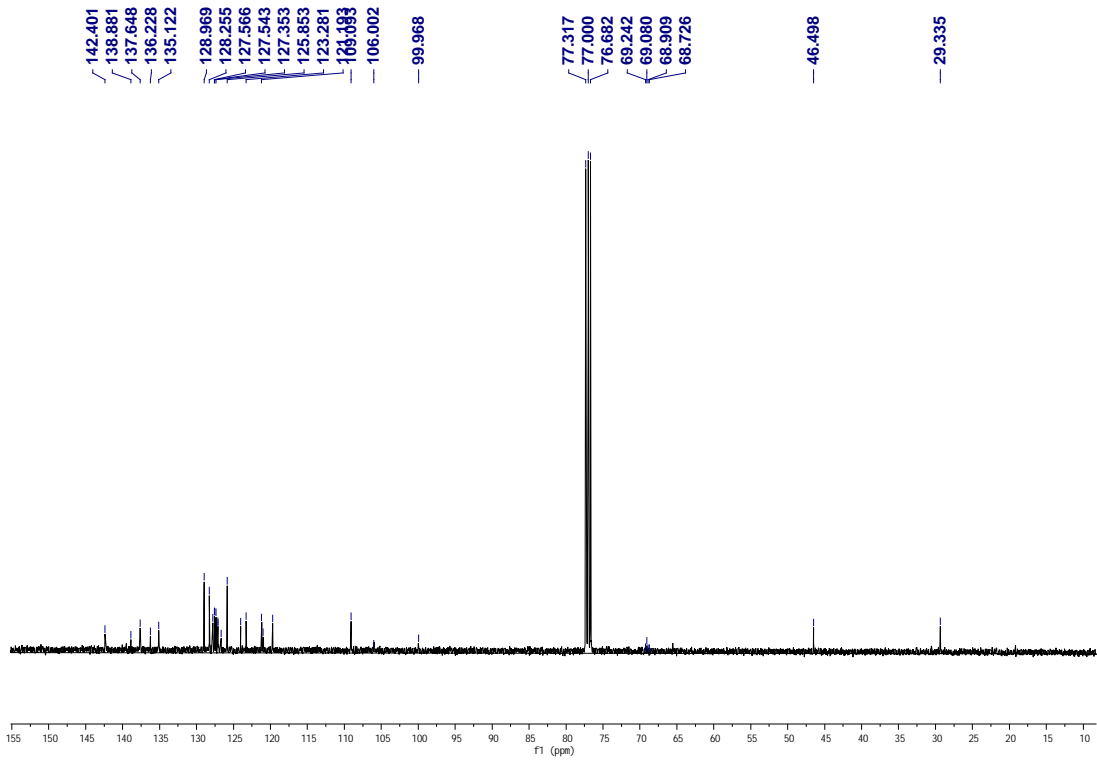
**(S)-12-(4-Bromo-phenyl)-3,9-dimethyl-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3dd)**



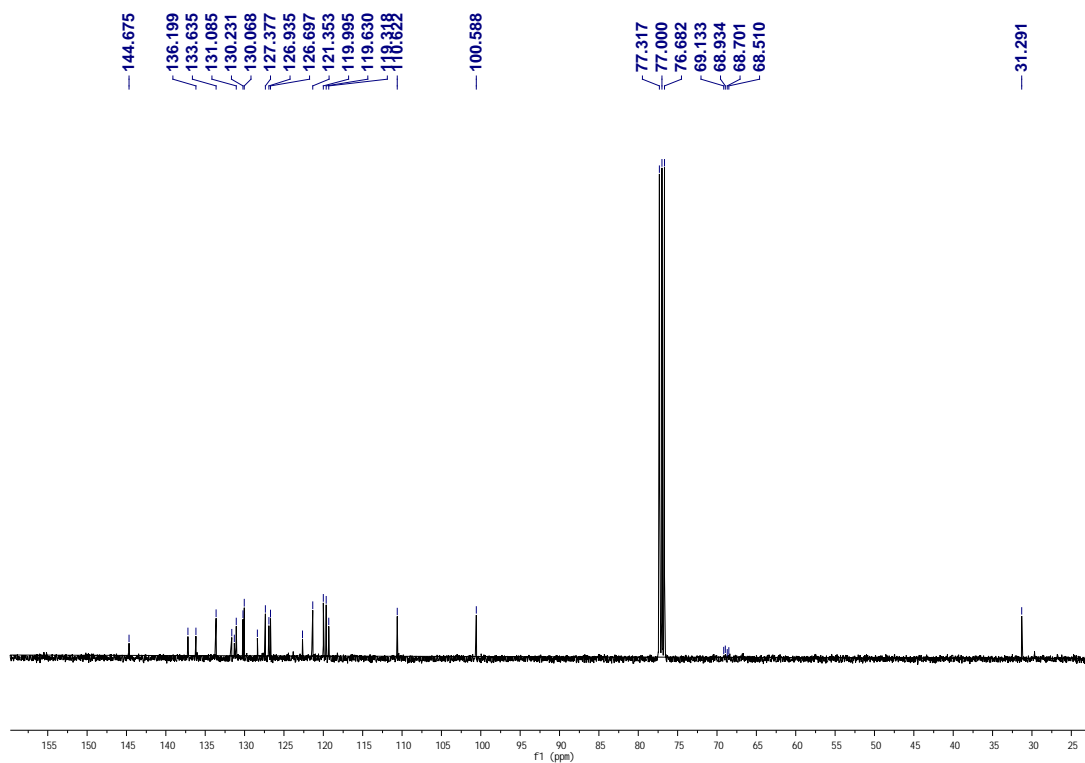
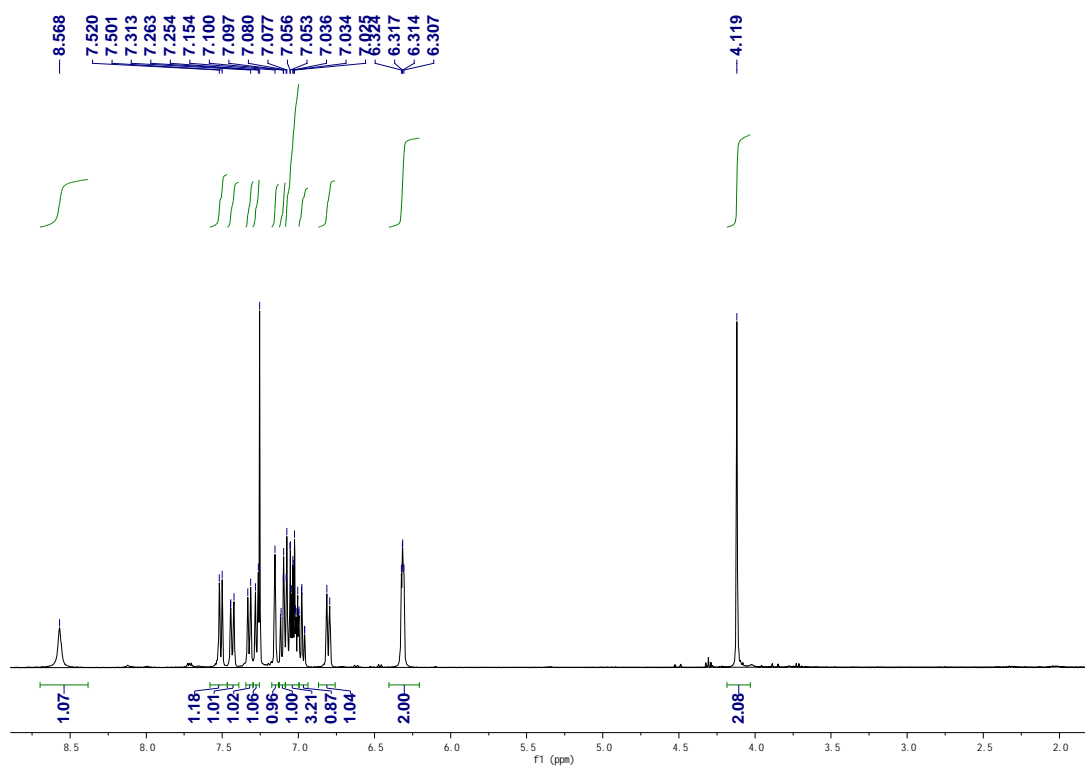


**(S)-5-Benzyl-12-phenyl-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3ea)**

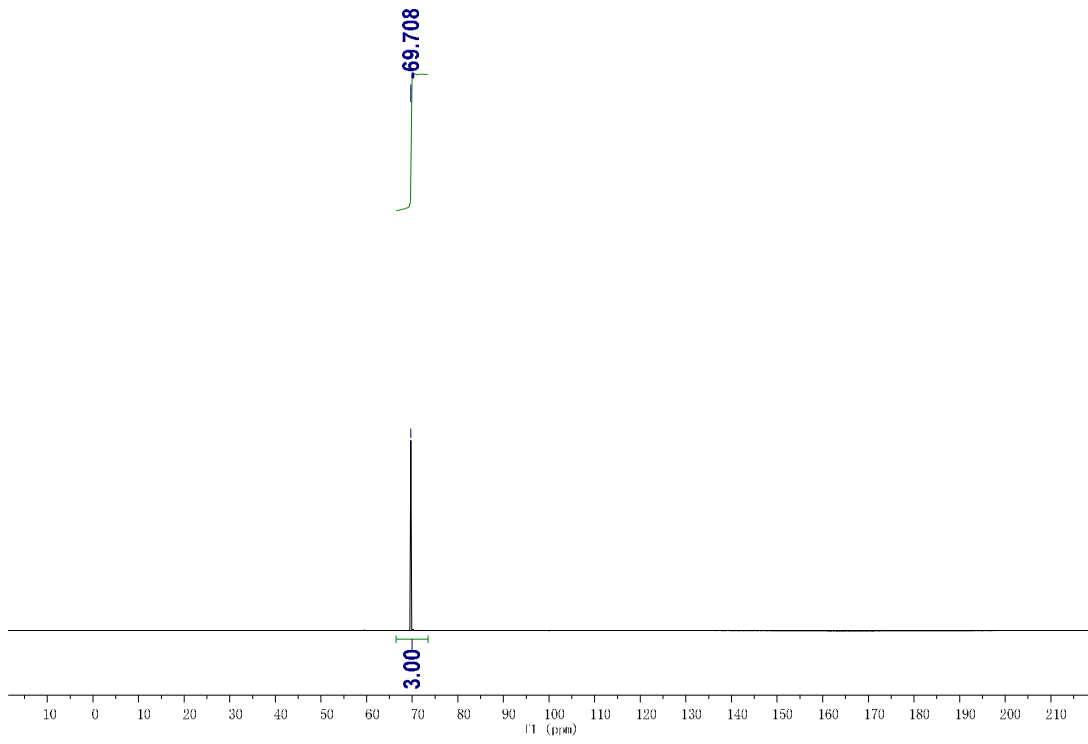




2((1Hindol2yl)methyl)N(1(3bromophenyl)2,2,2trifluoroethylidene)aniline (3ahi)







## 8. Absolute configuration assignments

The crystal structure of enantiopure **3aa** was obtained (Figure 1), and a single crystal X-ray analysis determined its configuration as (*S*). CCDC 953552 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

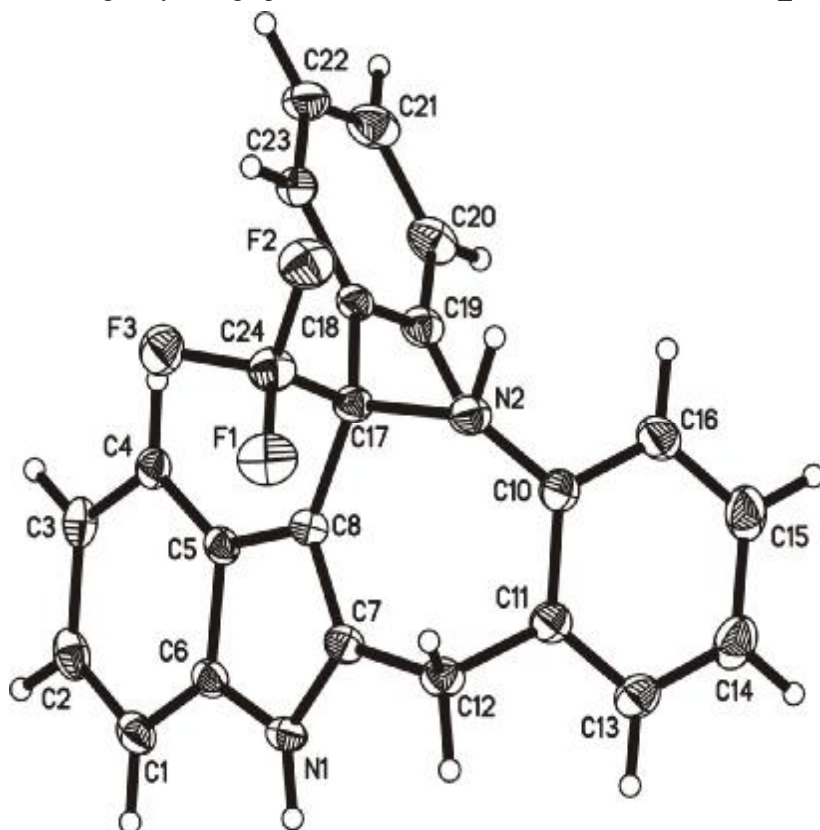
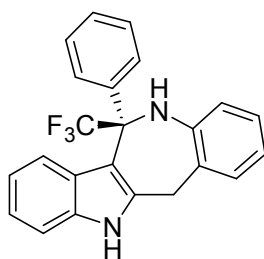


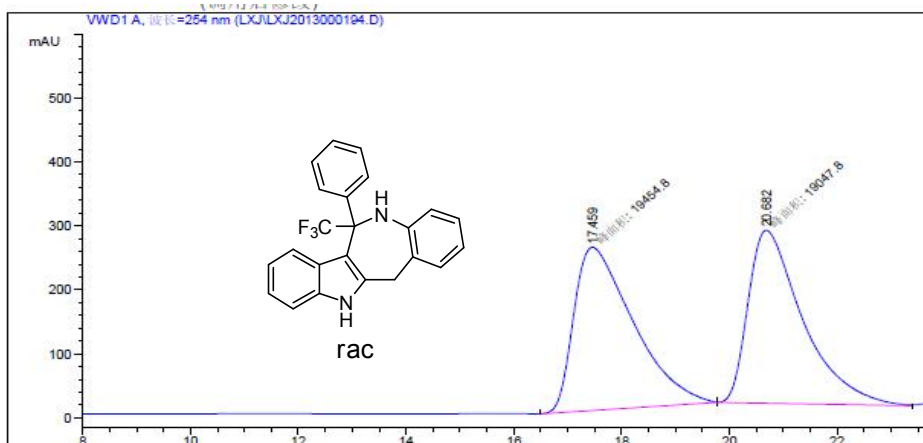
Figure 1. X-ray crystal structure of **3aa**  
(*S*)-12-phenyl-12-(trifluoromethyl)-5,6,11,12-tetrahydrobenzo[6,7]azepino[4,3-*b*]indole (**3aa**)



Molecular structure of **3aa**.

## 9. HPLC spectra of products

### (S)-12-phenyl-12-(trifluoromethyl)-5,6,11,12-tetrahydrobenzo[6,7]azepino[4,3-b]indole (3aa)

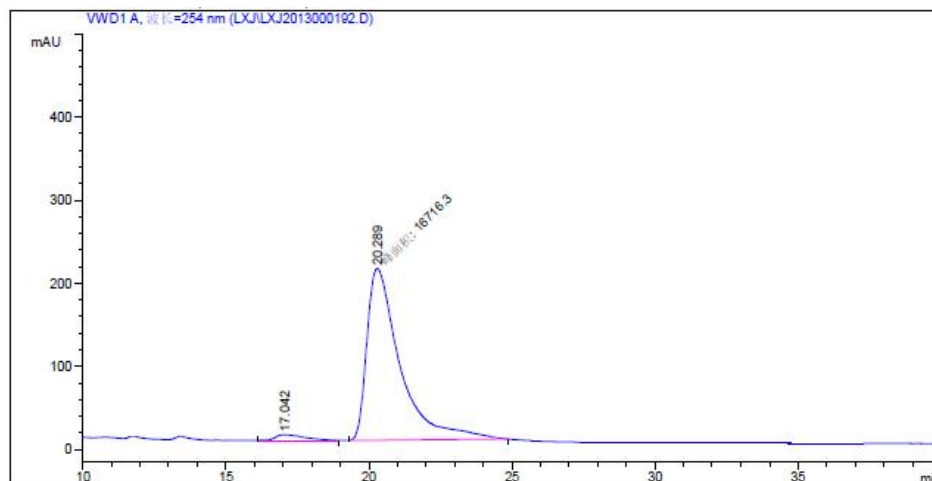


#### 面积百分比报告

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	17.459	MM	1.2722	1.94548e4	254.87125	50.5286
2	20.682	MM	1.1744	1.90478e4	270.31207	49.4714



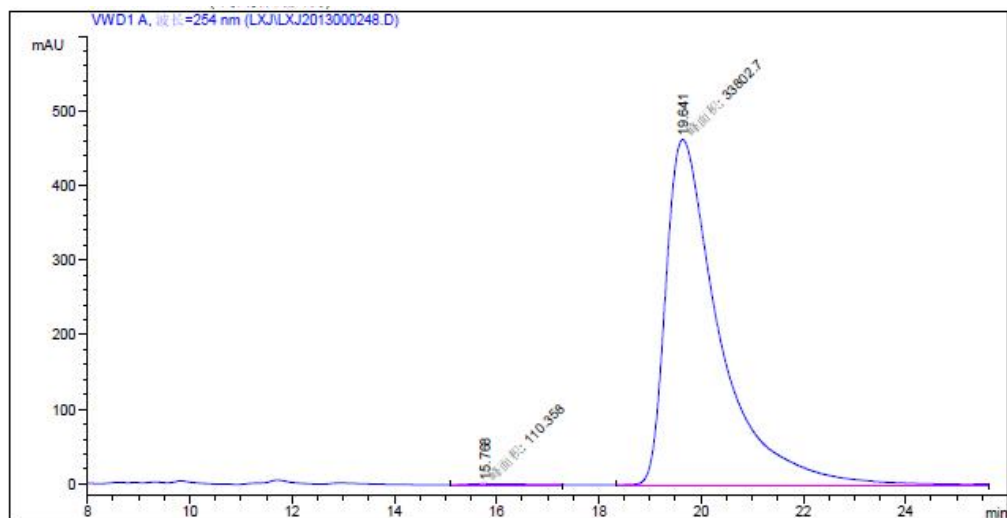
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乘积因子 : 1.0000  
稀释因子 : 1.0000  
内标使用乘积因子和稀释因子

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	17.042	BB	0.9243	522.53961	7.23386	3.0312
2	20.289	MM	1.3477	1.67163e4	206.71829	96.9688

After single recrystallization



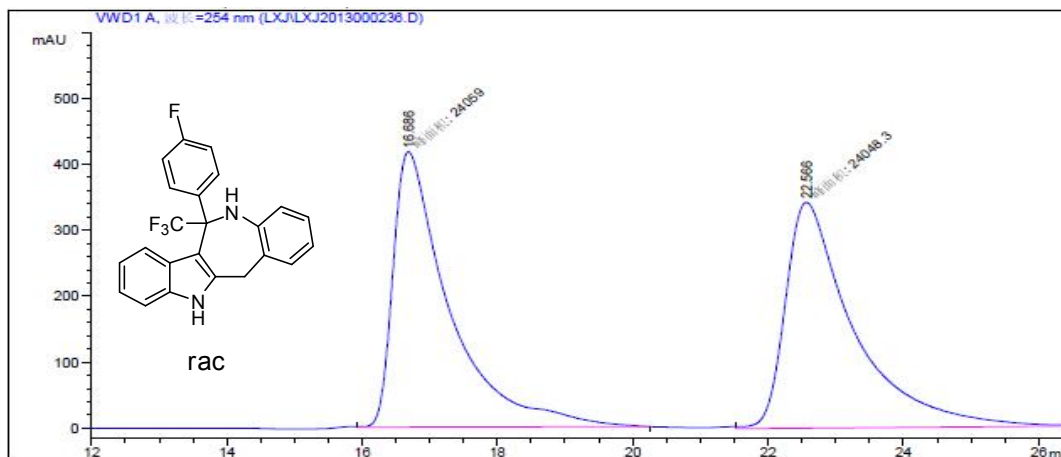
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 面积百分比报告  
 =====

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	15.768	MM	1.2790	110.35831	1.43813	0.3254
2	19.641	MM	1.2173	3.38027e4	462.80902	99.6746

**(S)-12-(4-fluorophenyl)-12-(trifluoromethyl)-5,6,11,12-tetrahydrobenzo[6,7]azepino[4,3-b]indole (3ab)**

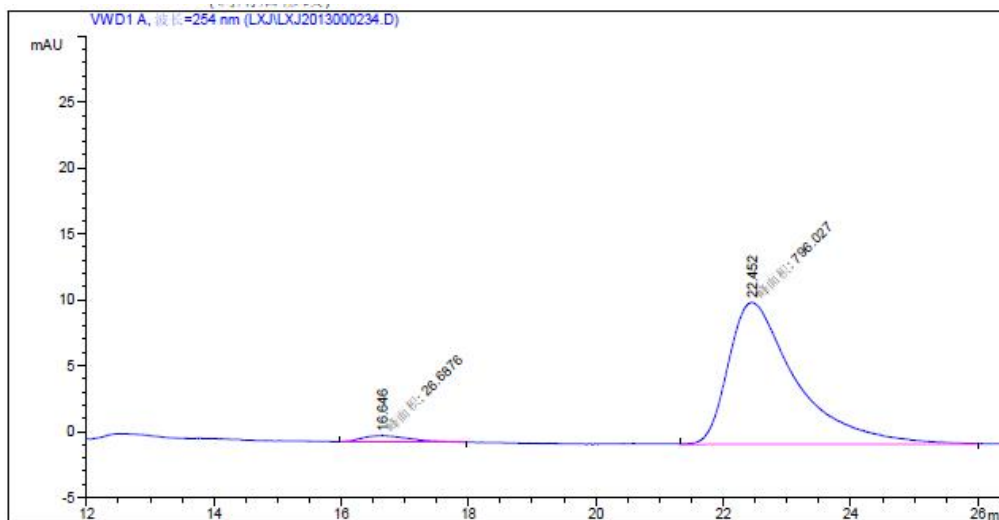


面积百分比报告

排序 : 信号  
 乘积因子 : 1.0000  
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 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	16.686	MM	0.9613	2.40590e4	417.14209	50.0111
2	22.566	MM	1.1711	2.40483e4	342.25894	49.9889



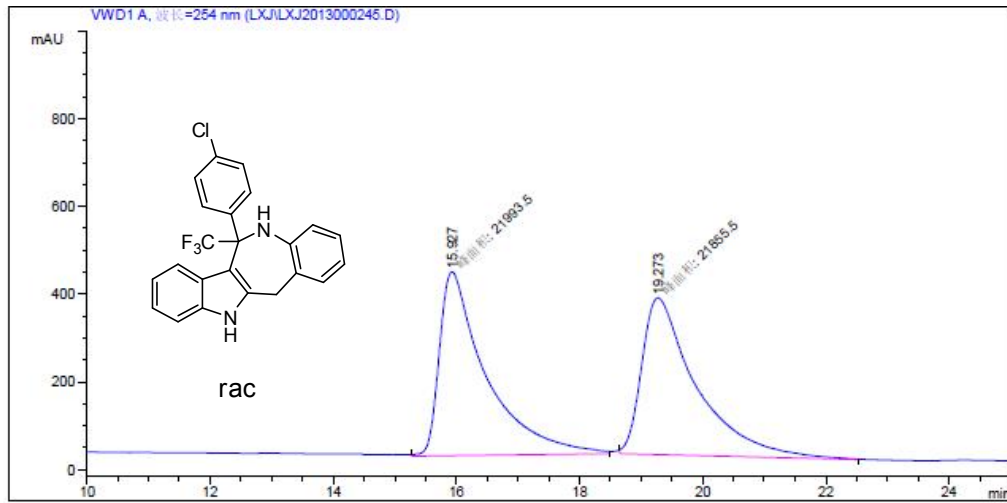
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 内标使用乘积因子和稀释因子

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	16.646	MM	0.8714	26.68762	5.10407e-1	3.2438
2	22.452	MM	1.2328	796.02692	10.76221	96.7562

**(S)-12-(4-chlorophenyl)-12-(trifluoromethyl)-5,6,11,12-tetrahydrobenzo[6,7]azepino[4,3-b]indole (3ac)**

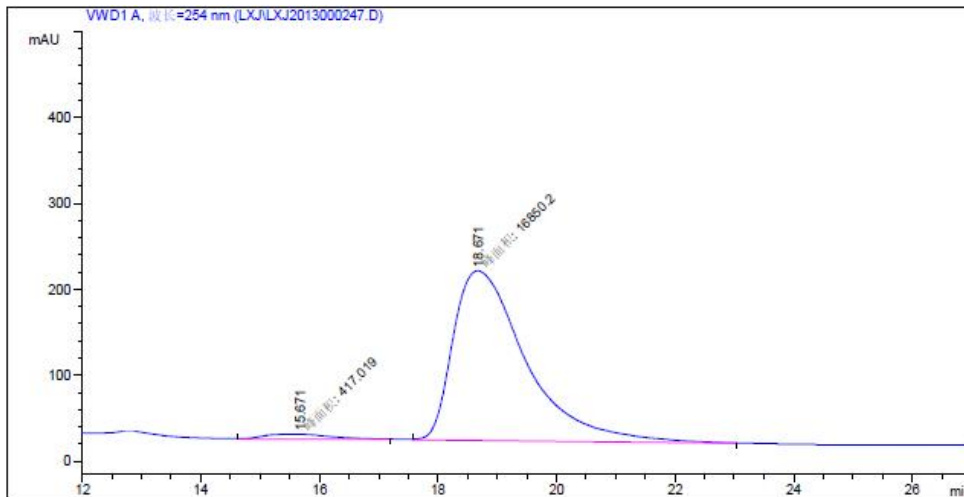


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面积百分比报告  
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排序 : 信号  
乘积因子 : 1.0000  
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内标使用乘积因子和稀释因子

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	15.927	MM	0.8753	2.19935e4	418.80261	50.1573
2	19.273	MM	1.0205	2.18555e4	356.94153	49.8427



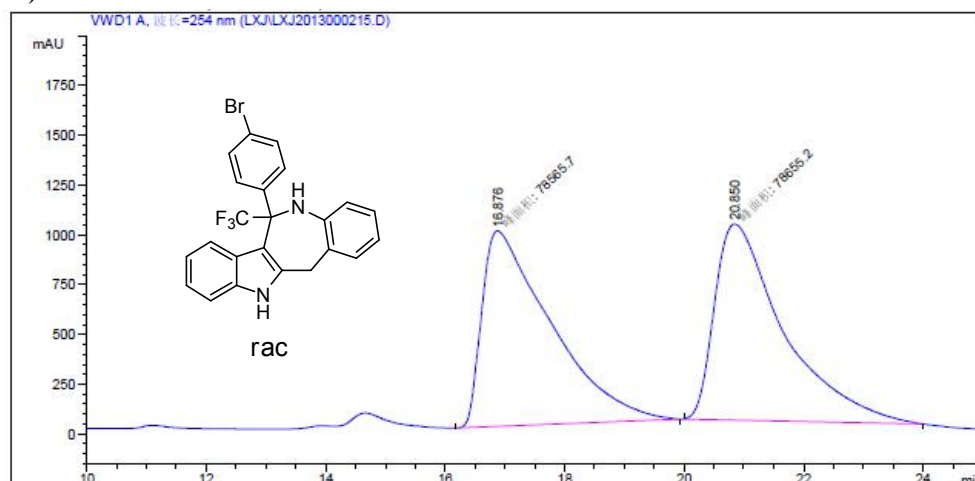
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排序 : 信号  
乘积因子 : 1.0000  
稀释因子 : 1.0000  
内标使用乘积因子和稀释因子

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	15.671	MM	1.3066	417.01874	5.31956	2.4151
2	18.671	MM	1.4244	1.68502e4	197.16277	97.5849

**(S)-12-(4-bromophenyl)-12-(trifluoromethyl)-5,6,11,12-tetrahydrobenzo[6,7]azepino[4,3-b]indole (3ad)**

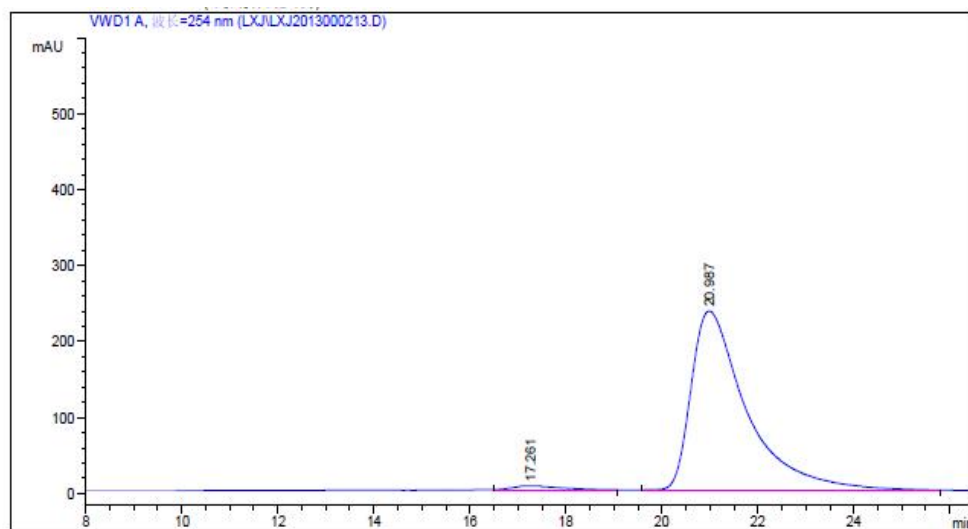


面积百分比报告

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	16.876	MM	1.3346	7.85657e4	981.16339	49.9715
2	20.850	MM	1.3319	7.86552e4	984.26453	50.0285



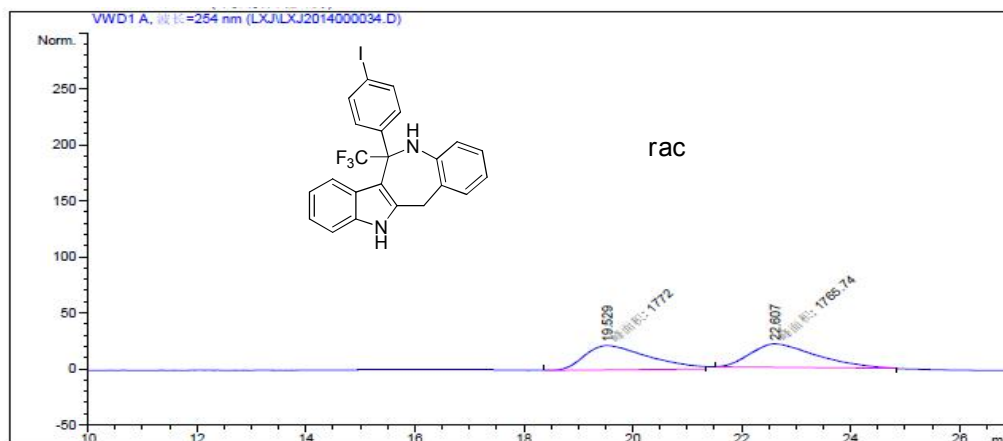
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 内标使用乘积因子和稀释因子

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	17.261	VB	0.8985	403.47394	5.53492	2.0826
2	20.987	BB	1.1840	1.89697e4	235.58955	97.9174

(S)-12-(4-Iodo-phenyl)-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole  
(3ae)

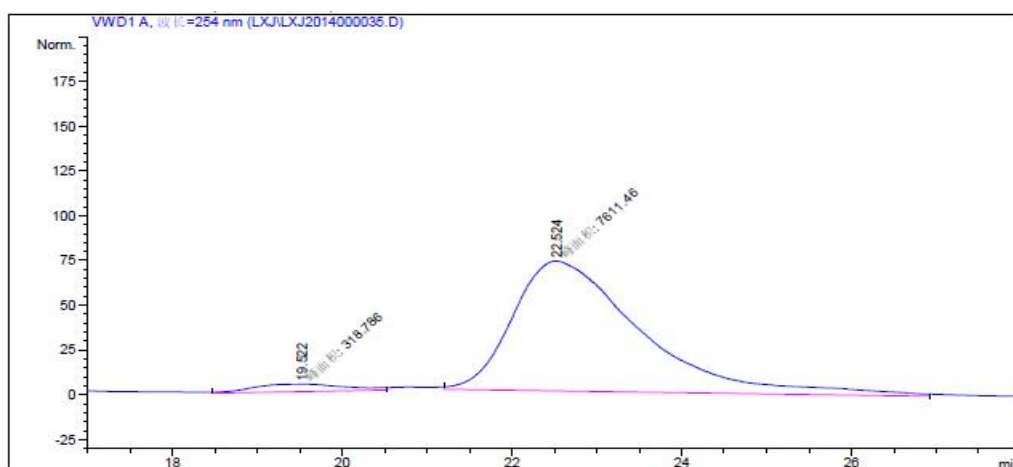


面积百分比报告

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	19.529	MM	1.3675	1772.00220	21.59696	50.0885
2	22.607	MM	1.4075	1765.74072	20.90832	49.9115



面积百分比报告

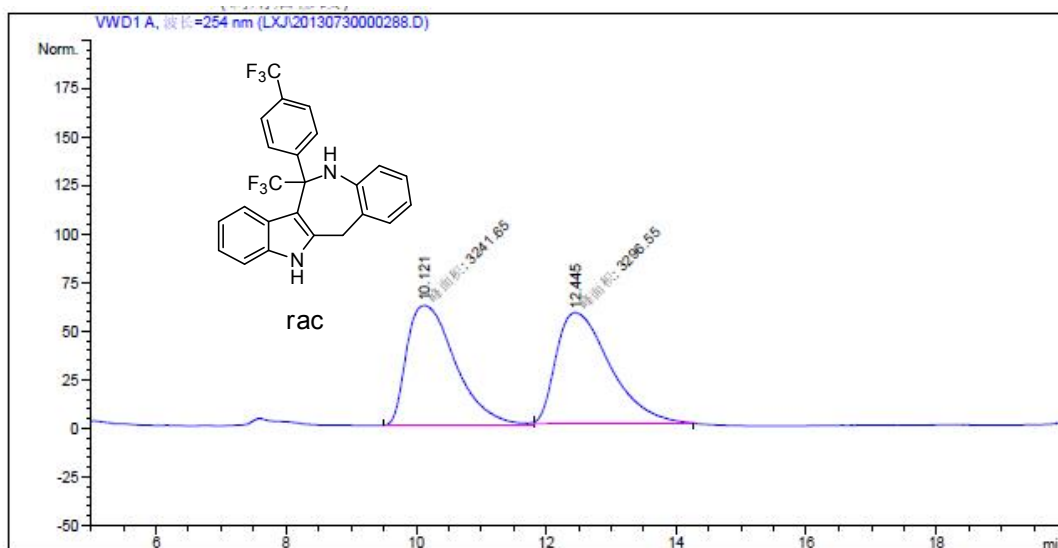
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稀释因子 : 1.0000  
内标使用乘积因子和稀释因子

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	19.522	MM	1.2686	318.78586	4.18821	4.0199
2	22.524	MM	1.7464	7611.46484	72.64082	95.9801



**(S)- 12-Trifluoromethyl-12-(4-trifluoromethyl-phenyl)-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3af)**

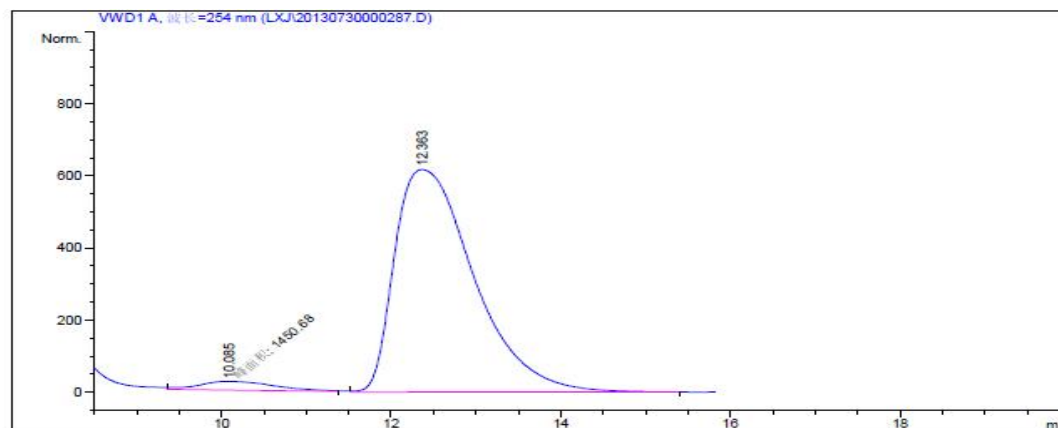


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面积百分比报告  
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排序 : 信号  
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内标使用乘积因子和稀释因子

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	10.121	MF	0.8748	3241.65161	61.76221	49.5802
2	12.445	MM	0.9639	3296.54517	56.99990	50.4198



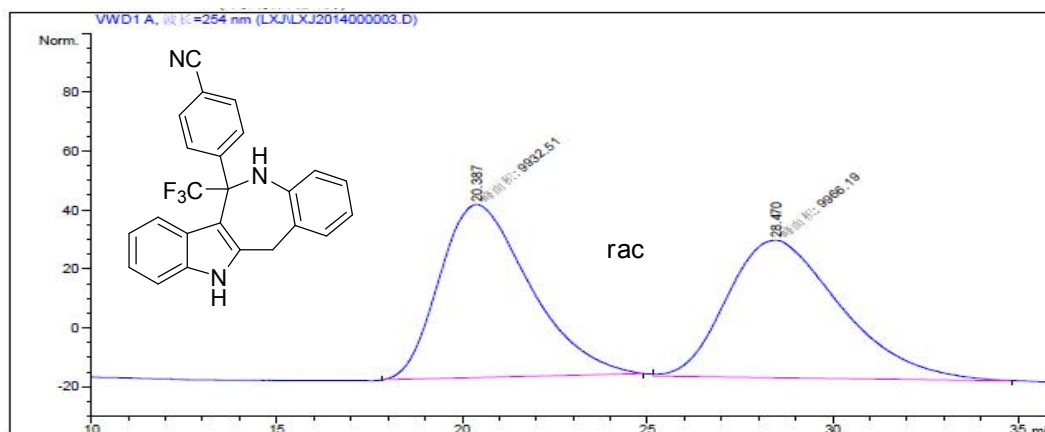
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稀释因子 : 1.0000  
内标使用乘积因子和稀释因子

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	10.085	MM	1.0136	1450.67798	23.85460	3.4933
2	12.363	VB	1.0129	4.00773e4	616.76947	96.5067

**(S)-4-(12-Trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indol-12-yl)-benzonitrile(3ag)**

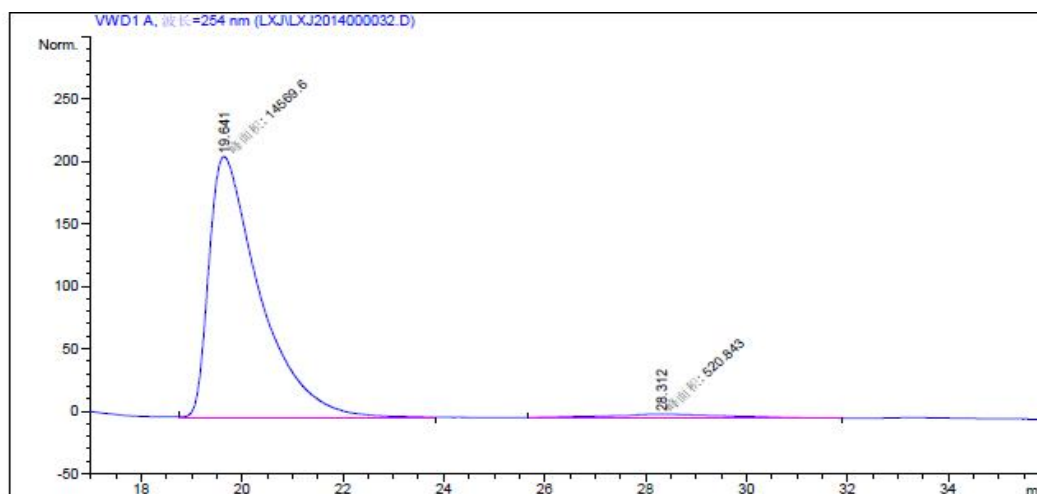


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面积百分比报告  
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排序 : 信号  
乘积因子 : 1.0000  
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内标使用乘积因子和稀释因子

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	20.387	MM	2.8203	9932.50694	58.69551	49.9154
2	28.470	MM	3.5644	9966.19043	46.60021	50.0846



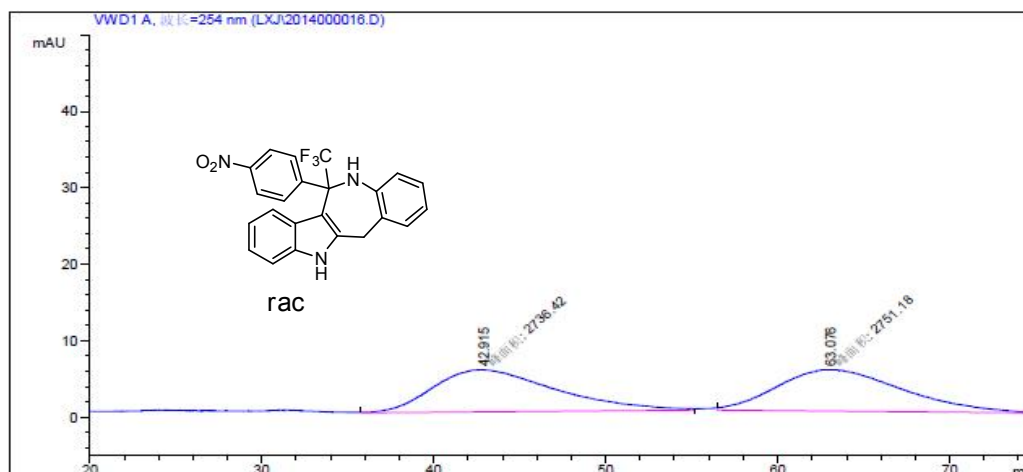
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排序 : 信号  
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稀释因子 : 1.0000  
内标使用乘积因子和稀释因子

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	19.641	MM	1.1647	1.45696e4	208.48674	96.5485
2	28.312	MM	2.8113	520.84290	3.08776	3.4515

(S)-12-(4-nitrophenyl)-12-(trifluoromethyl)-5,6,11,12-tetrahydrobenzo[6,7]azepino[4,3-b]indole  
(3ah)

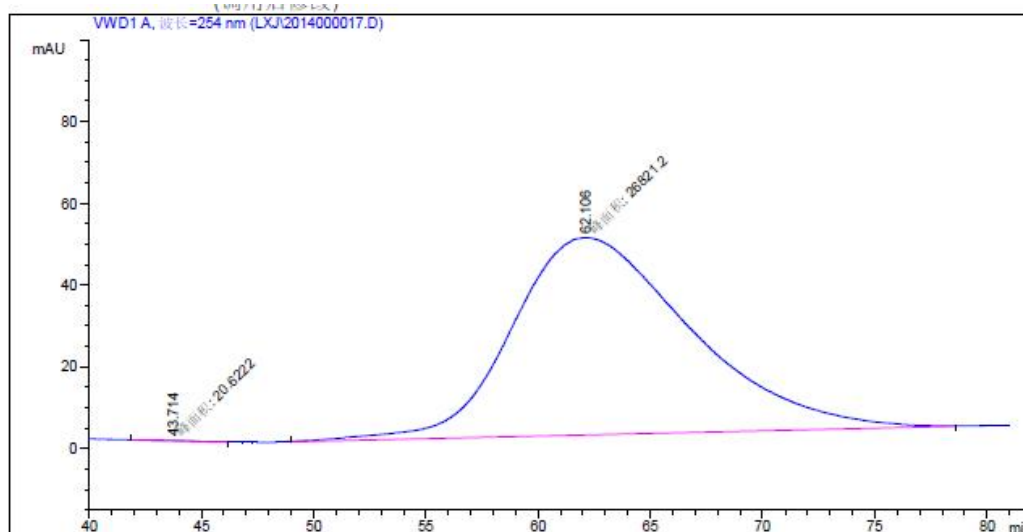


面积百分比报告

排序 : 信号  
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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	42.915	MM	8.2737	2736.42456	5.51226	49.8655
2	63.076	MM	8.4585	2751.18188	5.42092	50.1345



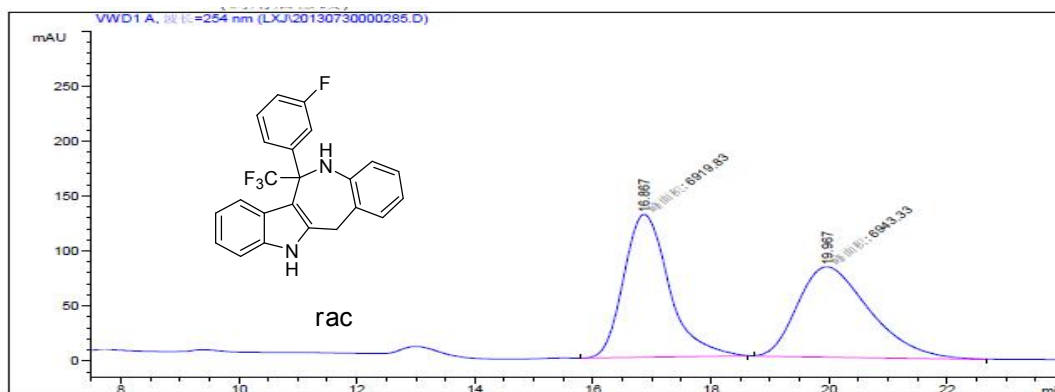
面积百分比报告

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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	43.714	MM	2.1933	20.62224	1.56703e-1	0.0768
2	62.106	MM	9.2496	2.68212e4	48.32857	99.9232

(S)-12-(3-Fluoro-phenyl)-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole  
(3ai)

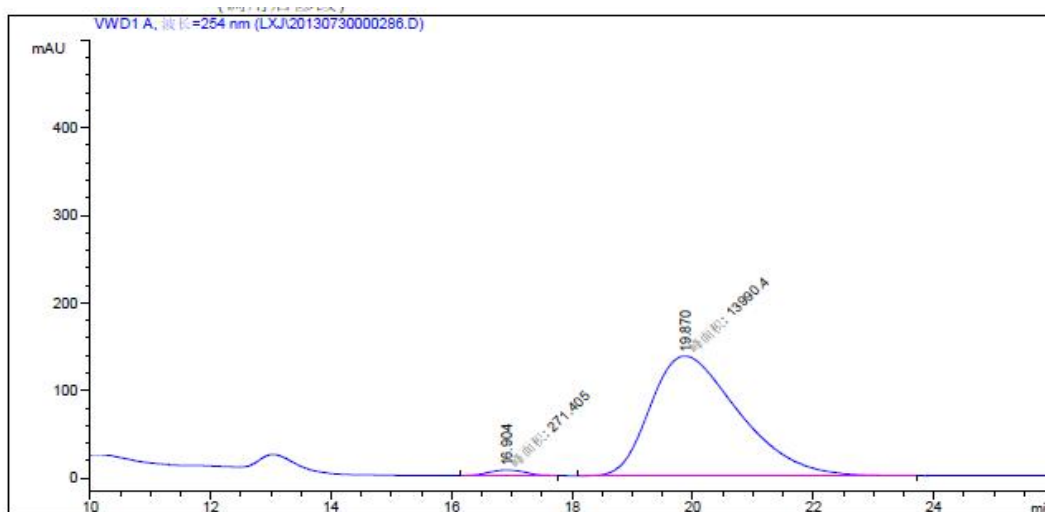


面积百分比报告

排序 : 信号  
乘积因子 : 1.0000  
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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	16.867	MM	0.8887	6919.83057	129.78127	49.9152
2	19.967	MM	1.4103	6943.32910	82.05376	50.0848



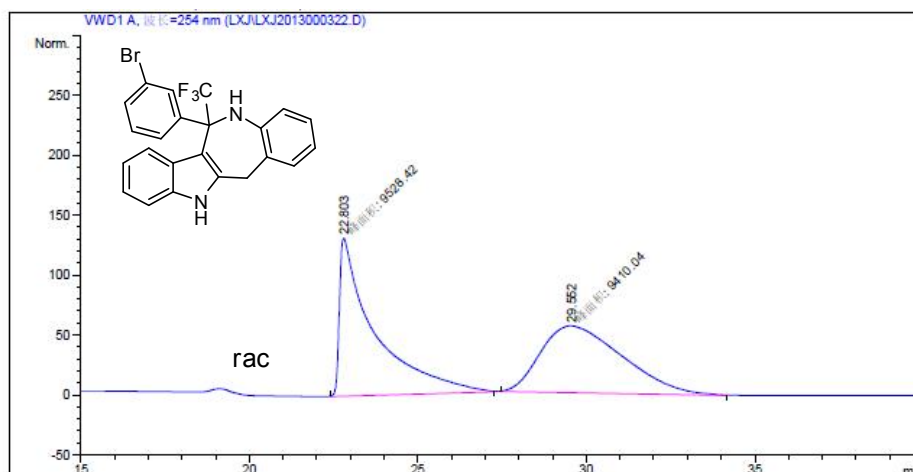
面积百分比报告

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	16.904	MM	0.7084	271.40518	6.38569	1.9030
2	19.870	MM	1.7064	1.39904e4	136.64641	98.0970

**(S)-12-(3-Bromo-phenyl)-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3aj)**

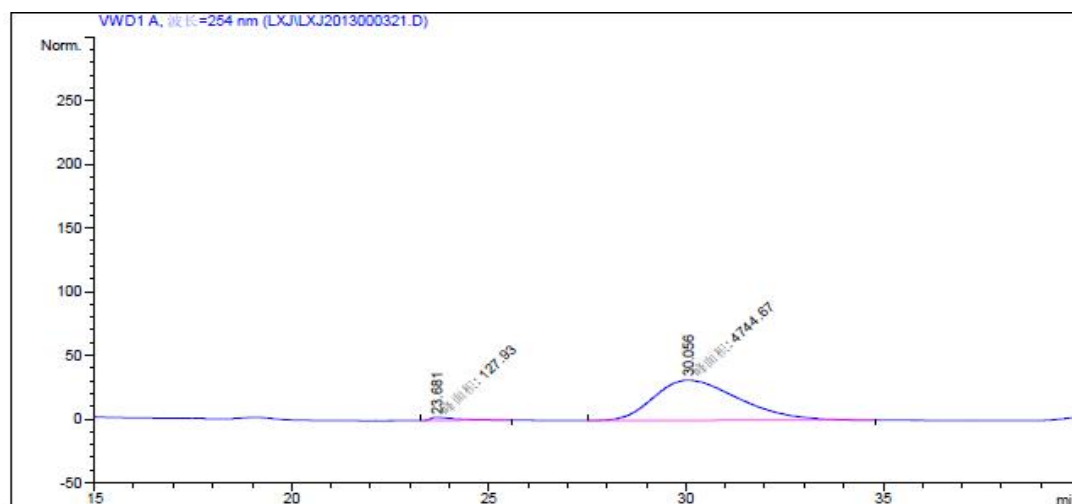


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 面积百分比报告  
 =====

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	22.803	MM	1.2058	9528.42285	131.69998	50.3126
2	29.552	MM	2.8173	9410.03516	55.66789	49.6874



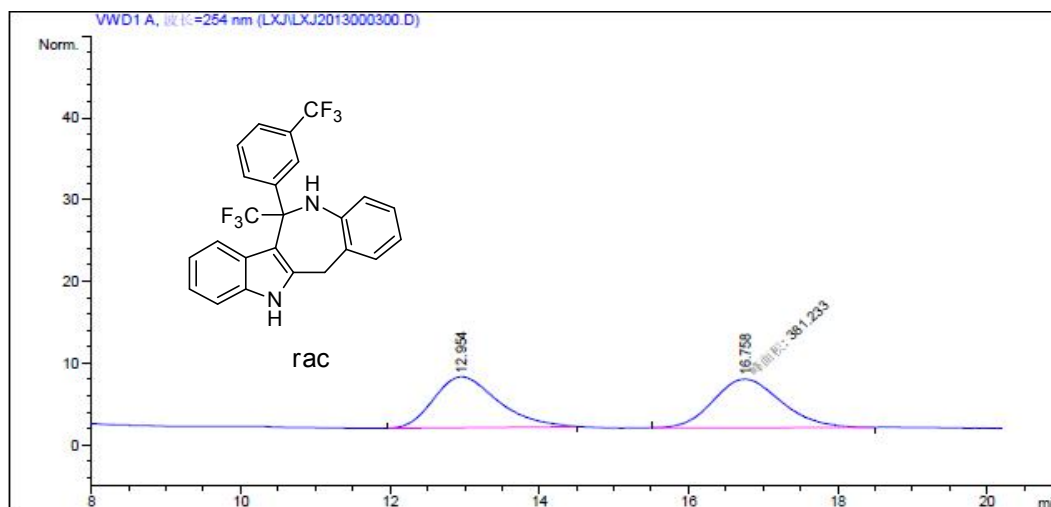
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 面积百分比报告  
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排序 : 信号  
 乘积因子 : 1.0000  
 稀释因子 : 1.0000  
 内标使用乘积因子和稀释因子

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	23.681	MM	0.8810	127.93026	2.42008	2.6255
2	30.056	MM	2.5043	4744.66504	31.57695	97.3745

**(S)-12-Trifluoromethyl-12-(3-trifluoromethyl-phenyl)-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3ak)**

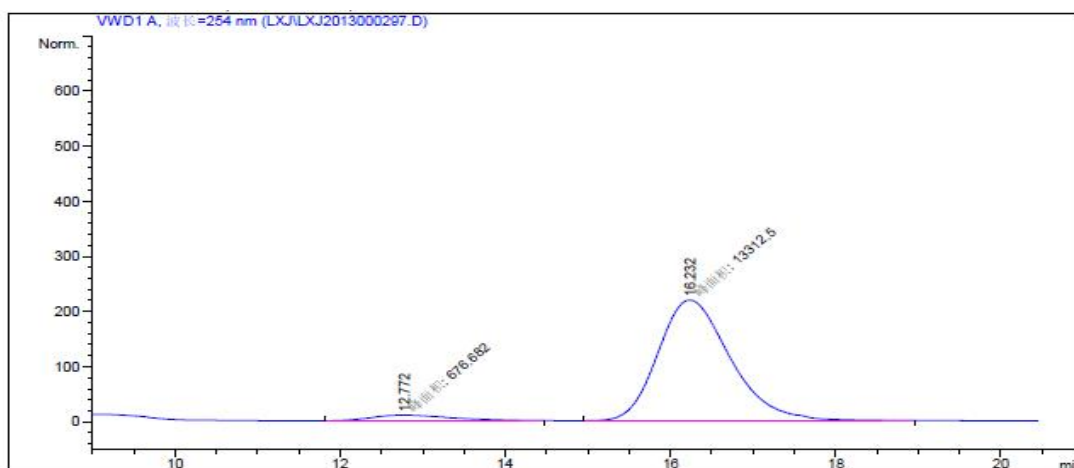


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 面积百分比报告  
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排序 : 信号  
 乘积因子 : 1.0000  
 稀释因子 : 1.0000  
 内标使用乘积因子和稀释因子

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	12.954	BB	0.8039	374.98508	6.23233	49.5869
2	16.758	MM	1.0629	381.23288	5.97798	50.4131



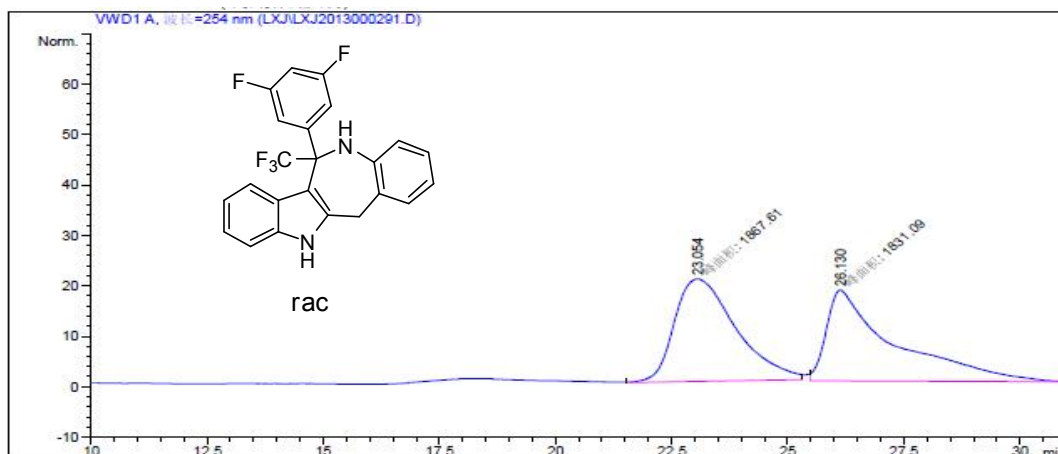
=====  
 面积百分比报告  
 =====

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	12.772	MM	1.1072	676.68152	10.18578	4.8372
2	16.232	MM	1.0132	1.33125e4	218.98650	95.1628

(S) 12-(3,5-Difluoro-phenyl)-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3a)

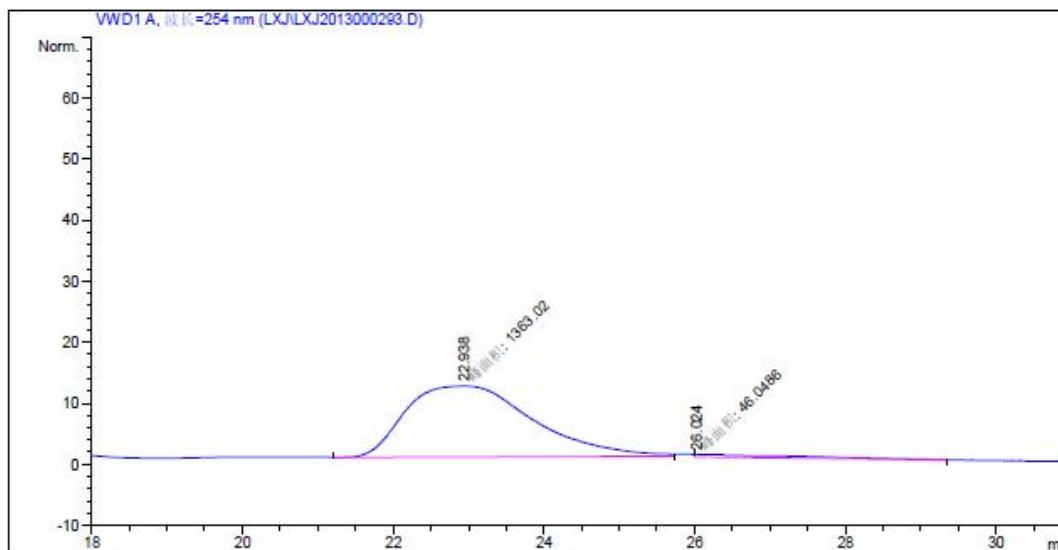


面积百分比报告

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	23.054	MM	1.5336	1867.61072	20.29638	50.4937
2	26.130	MM	1.6957	1831.08923	17.99780	49.5063



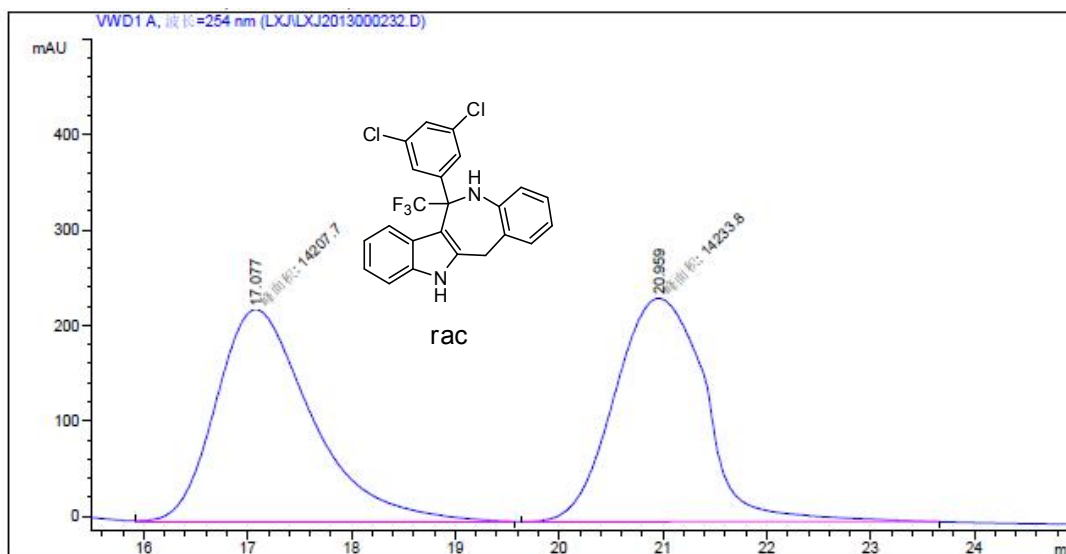
面积百分比报告

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	22.938	MM	1.9508	1363.01782	11.64481	96.7320
2	26.024	MM	1.8265	46.04865	4.20181e-1	3.2680

(S)-12-(3,5-Dichloro-phenyl)-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b  
(3am)

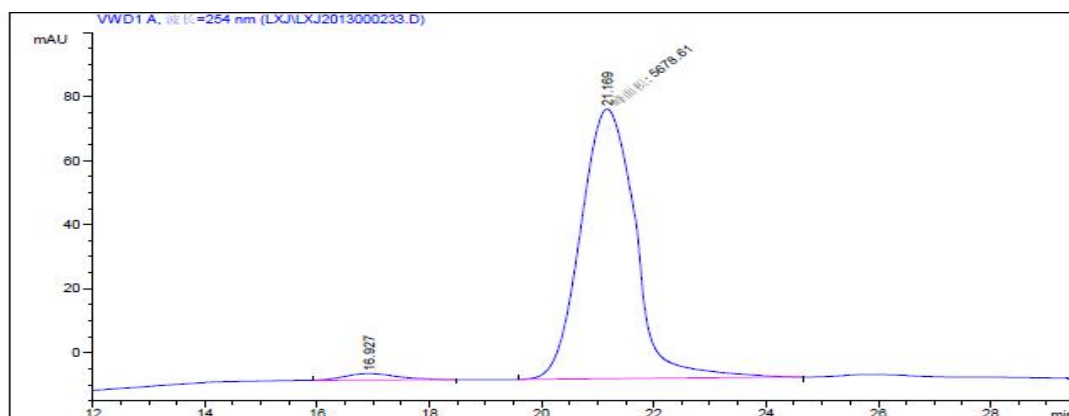


面积百分比报告

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	17.077	MM	1.0680	1.42077e4	221.71262	49.9540
2	20.959	MM	1.0143	1.42338e4	233.88942	50.0460



面积百分比报告

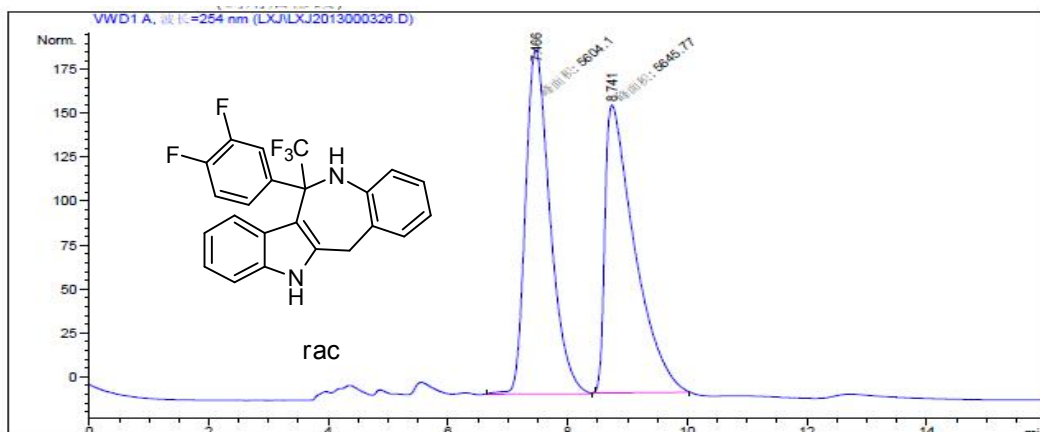
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乘积因子 : 1.0000  
稀释因子 : 1.0000  
内标使用乘积因子和稀释因子

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	16.927	BB	0.7564	124.52750	1.95467	2.1459
2	21.169	MM	1.1242	5678.60645	84.18747	97.8541



**(S)-12-(3,4-difluorophenyl)-12-(trifluoromethyl)-5,6,11,12-tetrahydrobenzo[6,7]azepino[4,3-b]indole (3an)**

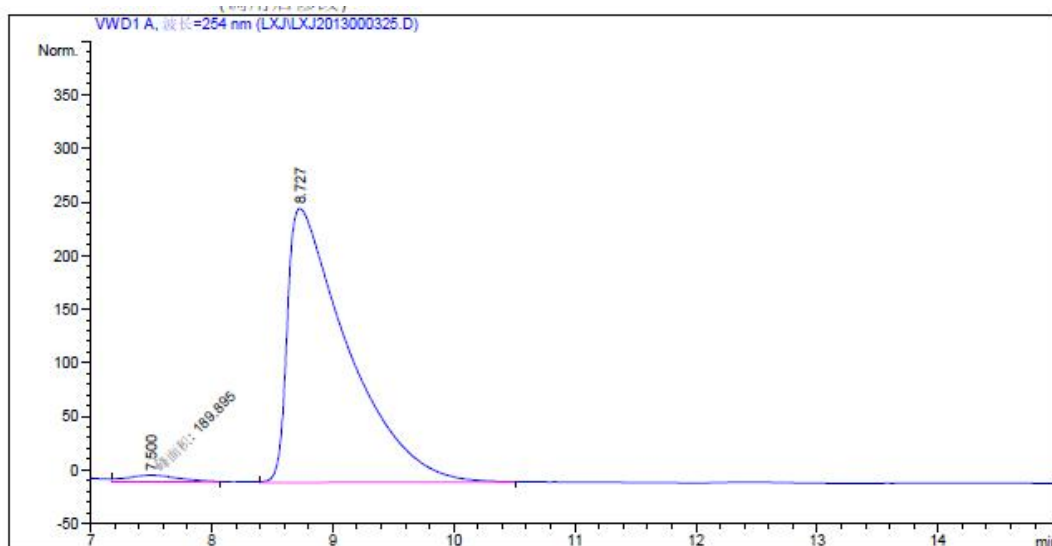


面积百分比报告

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	7.466	MM	0.4763	5604.09863	196.09146	49.8148
2	8.741	MM	0.5733	5645.77490	164.12943	50.1852



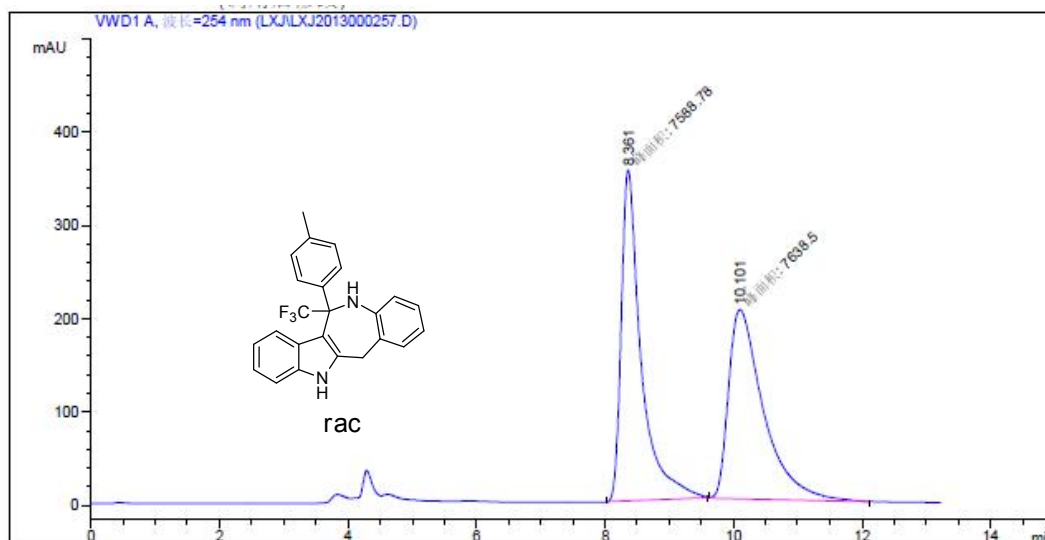
面积百分比报告

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	7.500	MM	0.5108	189.89465	6.19620	2.0978
2	8.727	VB	0.4875	8862.40430	255.61443	97.9022

(S)-12-p-Tolyl-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3a)

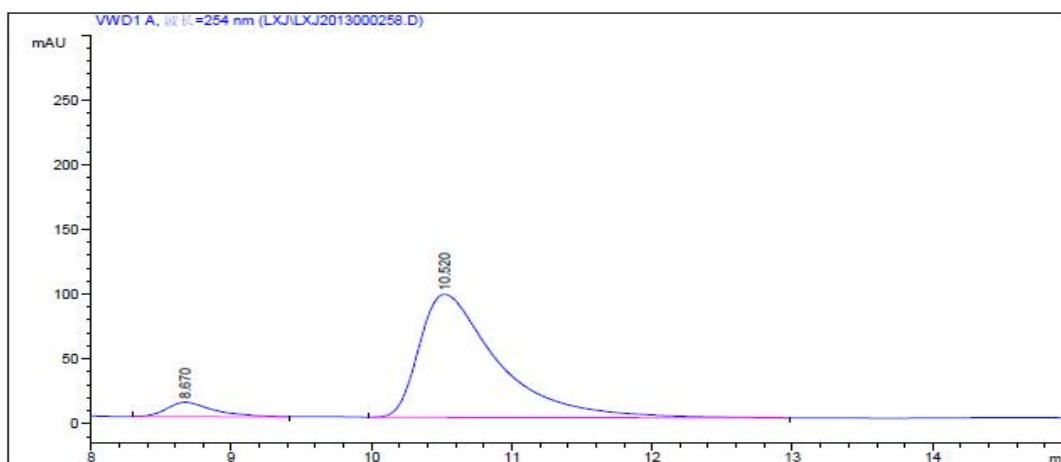


面积百分比报告

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	8.361	MM	0.3572	7588.77539	354.06784	49.8367
2	10.101	MM	0.6285	7638.49805	202.54819	50.1633



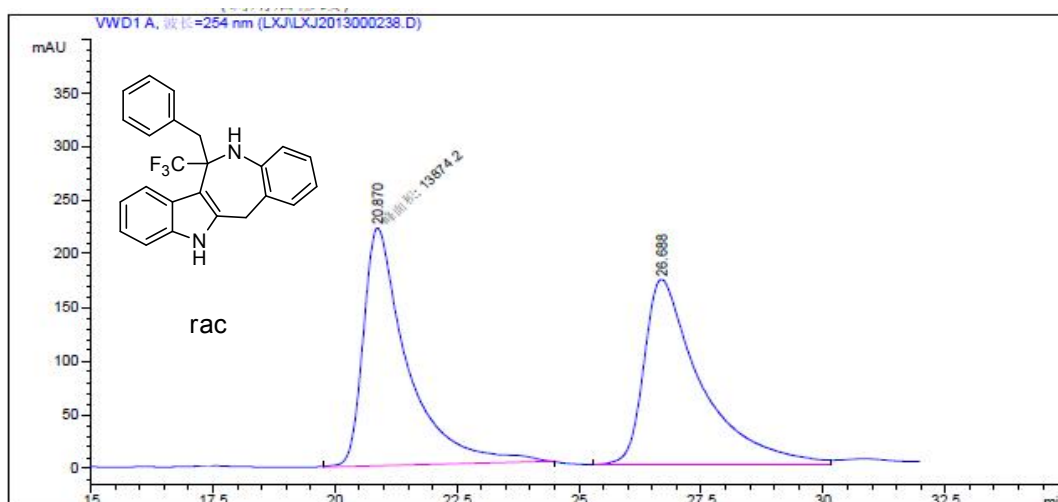
面积百分比报告

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	8.670	BB	0.3455	257.02408	10.99477	6.4973
2	10.520	VB	0.5737	3698.85425	94.99114	93.5027

(S)-12-Benzyl-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3ap)

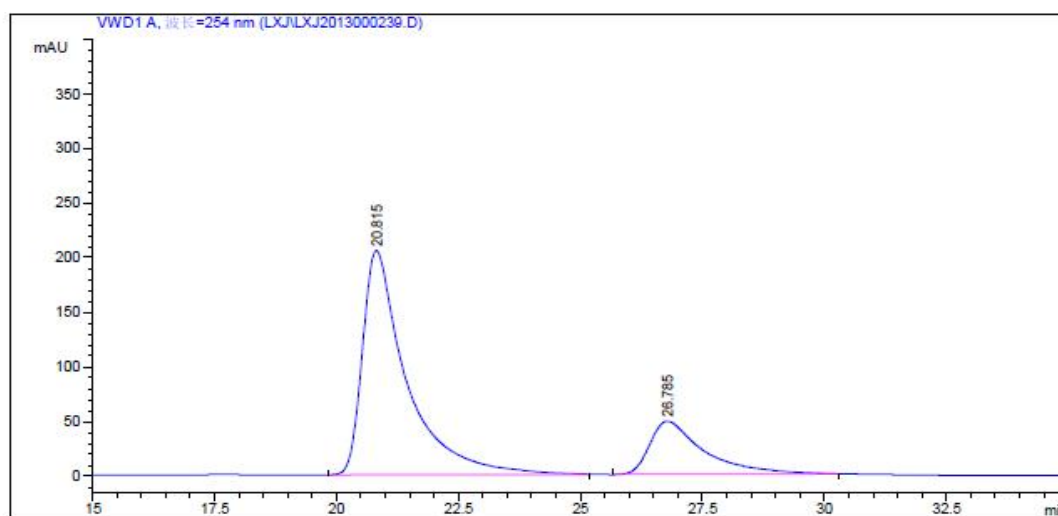


面积百分比报告

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	20.870	MM	1.0451	1.38742e4	221.24940	49.8100
2	26.688	BB	1.1637	1.39801e4	172.26900	50.1900



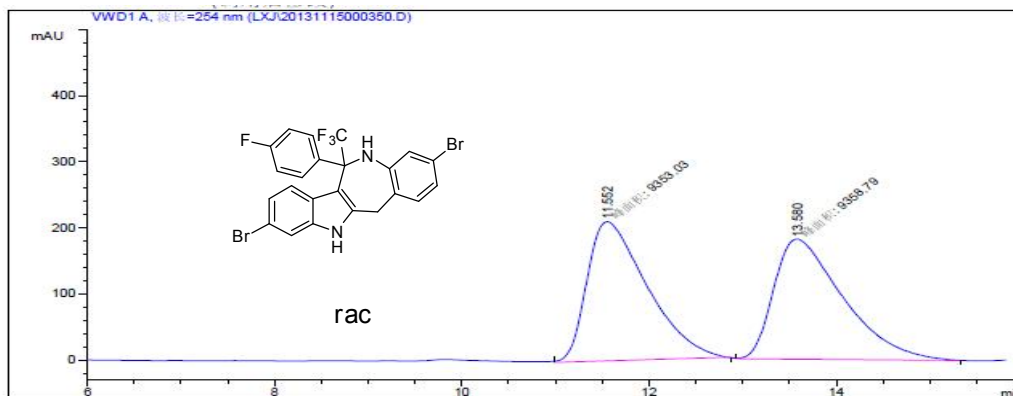
面积百分比报告

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	20.815	BB	0.8974	1.29070e4	205.04984	77.4323
2	26.785	BB	1.1145	3761.75366	48.58274	22.5677

**(S)-3,9-Dibromo-12-(4-fluoro-phenyl)-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3bb)**

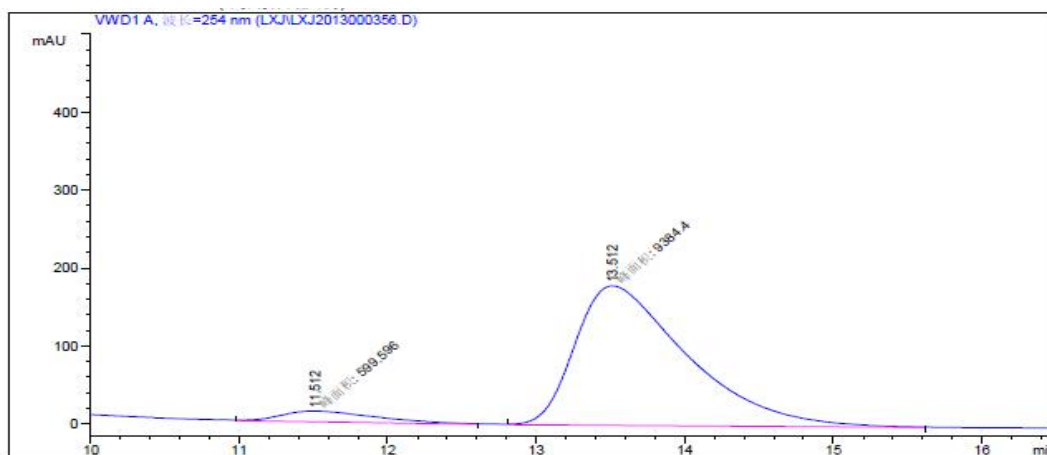


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面积百分比报告  
=====

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	11.552	MM	0.7414	9353.02832	210.24843	49.9846
2	13.580	MM	0.8581	9356.78809	181.76820	50.0154



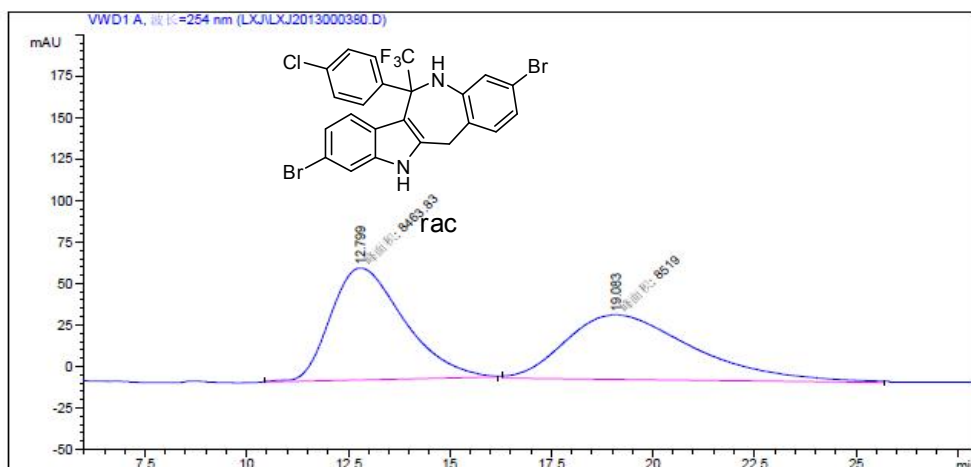
=====  
面积百分比报告  
=====

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	11.512	MM	0.7303	599.59583	13.68343	6.0056
2	13.512	MM	0.8743	9384.39746	178.89296	93.9944

**(S)3,9-Dibromo-12-(4-chloro-phenyl)-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3bc)**

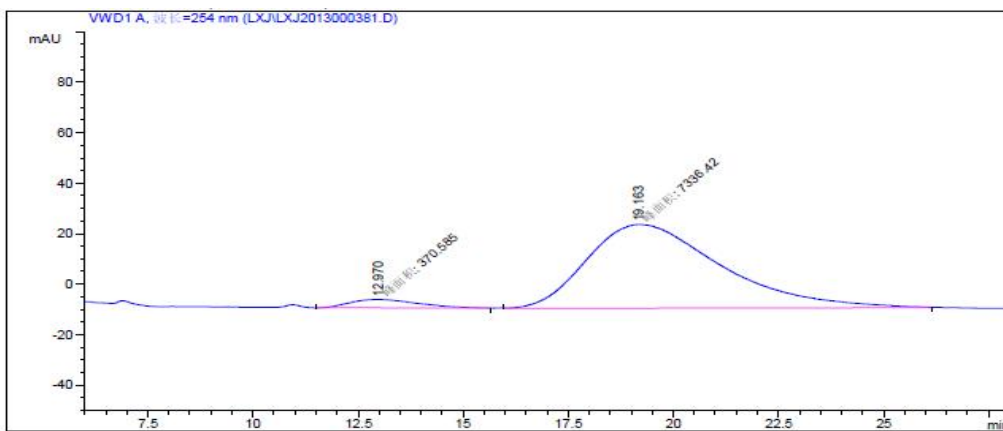


面积百分比报告

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	12.799	MM	2.0908	8463.83008	67.46748	49.8376
2	19.083	MM	3.6544	8518.99805	38.85303	50.1624



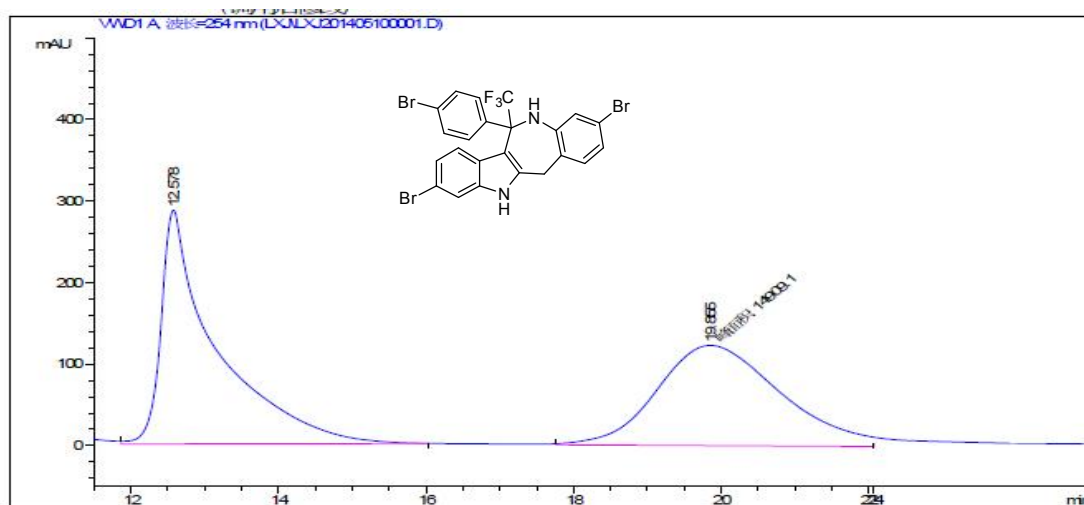
面积百分比报告

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	12.970	MM	1.8582	370.58511	3.32384	4.8084
2	19.163	MM	3.6923	7336.42334	33.11551	95.1916

**(S)-3,9-Dibromo-12-(4-bromo-phenyl)-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole(3bd)**

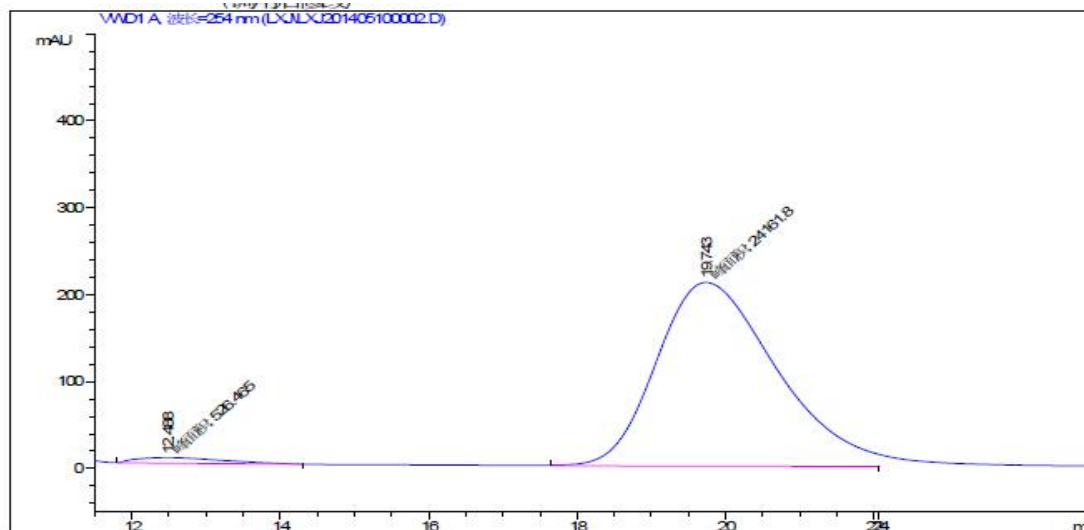


面积百分比报告

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: WVD1 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	12.578	VB	0.6750	1.49151e4	286.89767	50.0100
2	19.885	MM	2.0272	1.49091e4	122.57795	49.9900



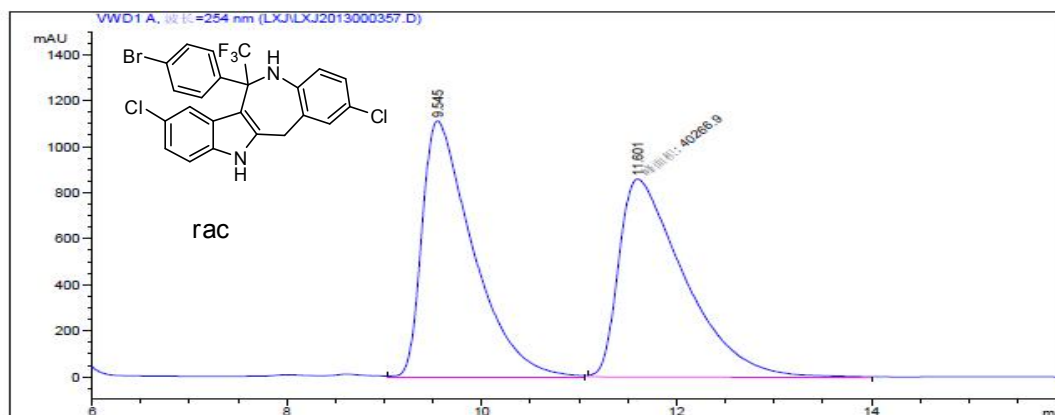
面积百分比报告

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: WVD1 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	12.488	MM	1.3360	526.46545	6.56778	2.1325
2	19.743	MM	1.9071	2.41618e4	211.15454	97.8675

**(S)-12-(4-Bromo-phenyl)-2,8-dichloro-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3cd)**

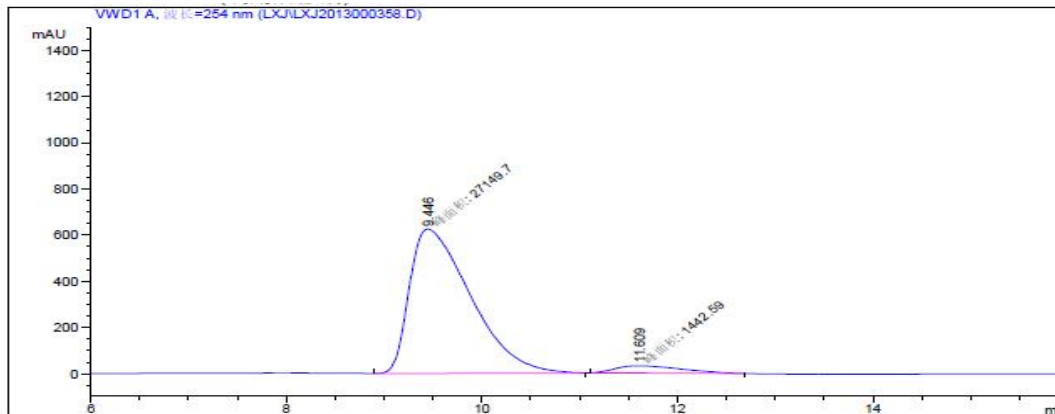


面积百分比报告

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	峰面积 %	峰高 [mAU]	峰面积 %
1	9.545	VV	0.5326	4.07903e4	50.3228	1116.23486	50.3228
2	11.601	MM	0.7813	4.02669e4	49.6772	858.98761	49.6772



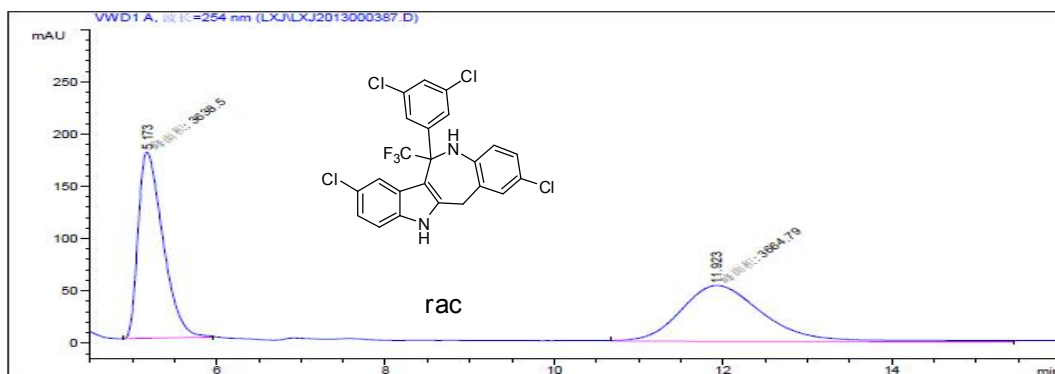
面积百分比报告

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	峰面积 %	峰高 [mAU]	峰面积 %
1	9.446	MM	0.7250	2.71497e4	94.9546	624.11548	94.9546
2	11.609	MM	0.7648	1442.58911	5.0454	31.43518	5.0454

**(S)-2,8-Dichloro-12-(3,5-dichloro-phenyl)-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3ck)**

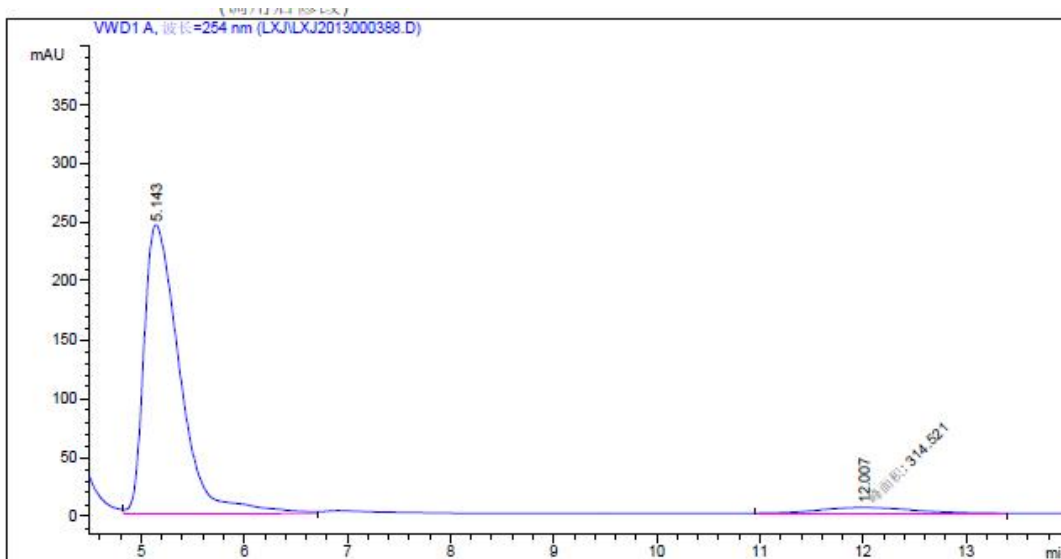


面积百分比报告

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	5.173	MM	0.3404	3638.49683	178.16745	49.8200
2	11.923	MM	1.1476	3664.79443	53.22231	50.1800



面积百分比报告

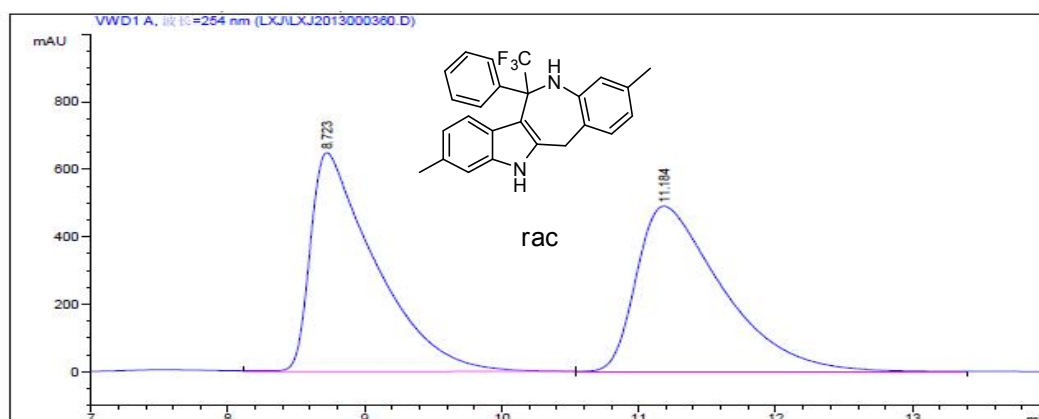
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乘积因子 : 1.0000  
稀释因子 : 1.0000  
内标使用乘积因子和稀释因子

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	5.143	VV	0.3774	5914.07813	245.24733	94.9504
2	12.007	MM	1.0569	314.52087	4.95990	5.0496



**(S)- 3,9-Dimethyl-12-phenyl-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3da)**

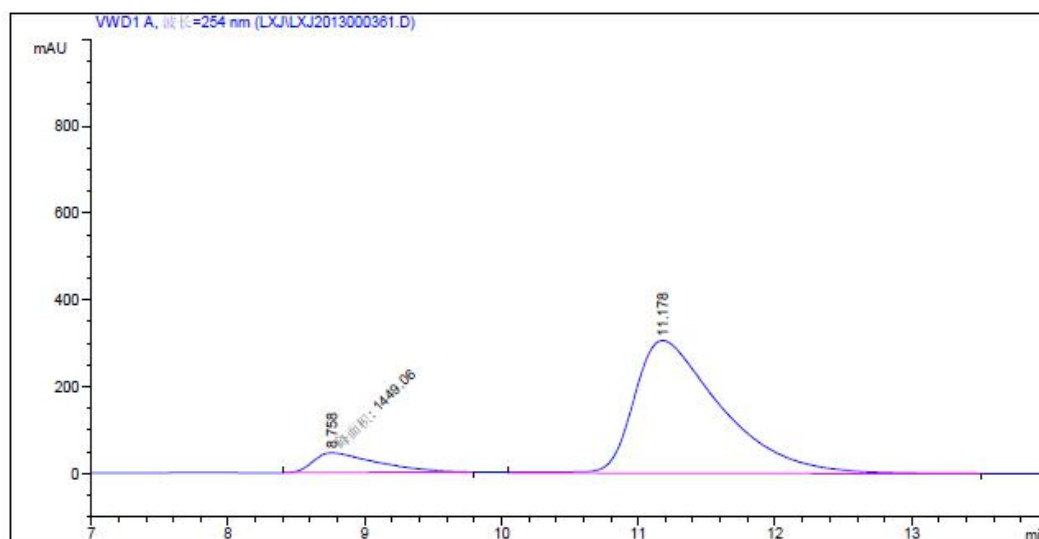


面积百分比报告

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	8.723	VV	0.4602	2.14649e4	648.81995	50.1108
2	11.184	VB	0.6472	2.13699e4	489.91684	49.8892



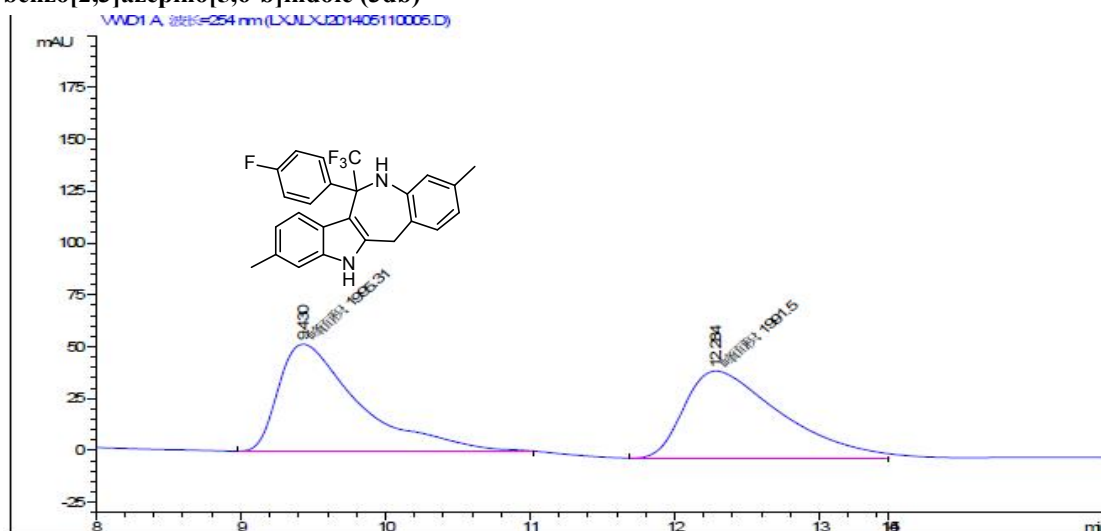
面积百分比报告

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	8.758	MM	0.5318	1449.06177	45.41173	9.6372
2	11.178	BB	0.6575	1.35871e4	306.16129	90.3628

**(S)-12-(4-Fluoro-phenyl)-3,9-dimethyl-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3db)**

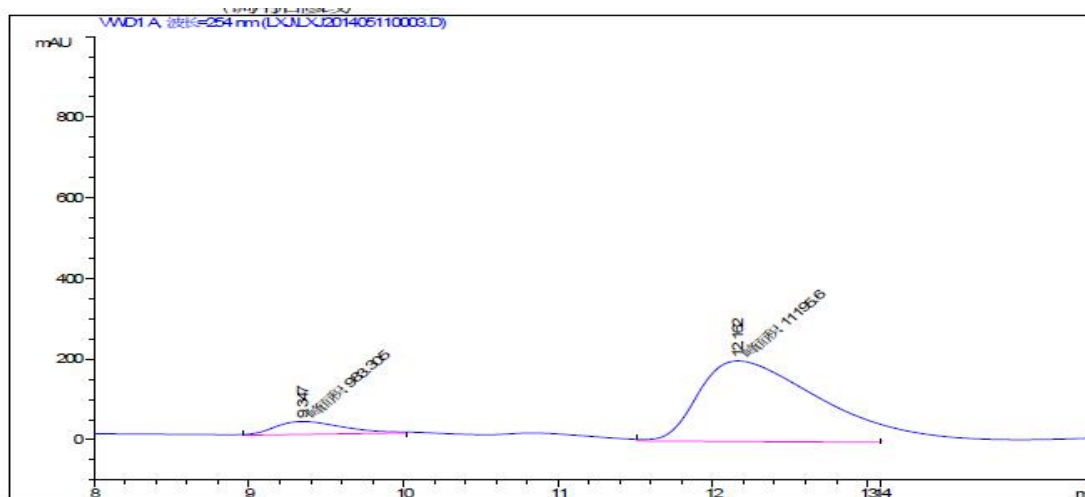


面积百分比报告

排序 : 信号  
 乘数因子 : 1.0000  
 稀释因子 : 1.0000  
 内标使用乘数因子和稀释因子

信号 1: WVD1 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	9.430	MM	0.6439	1995.30847	51.64572	50.0478
2	12.284	MM	0.7879	1991.49927	42.12440	49.9522



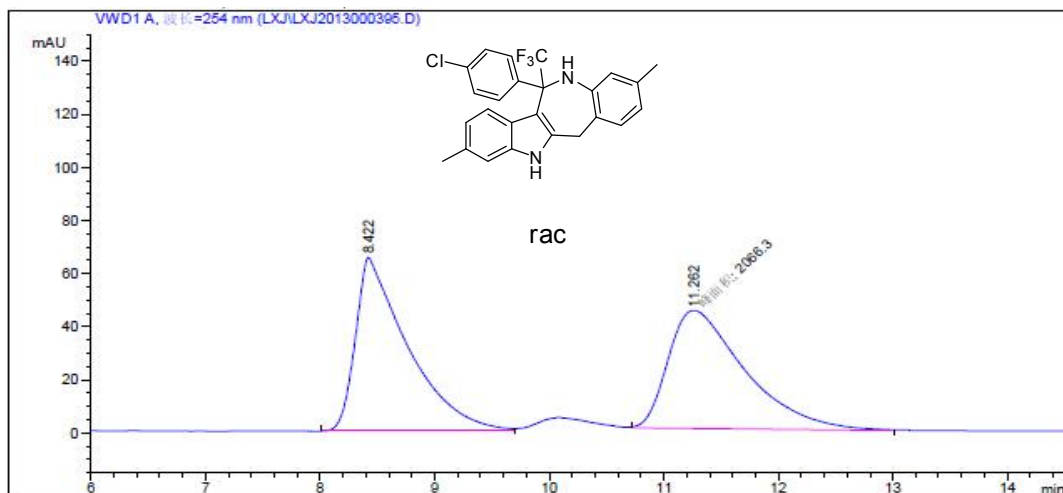
面积百分比报告

排序 : 信号  
 乘数因子 : 1.0000  
 稀释因子 : 1.0000  
 内标使用乘数因子和稀释因子

信号 1: WVD1 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	9.347	MM	0.5127	983.30475	31.96283	8.0739
2	12.162	MM	0.9359	1.11956e4	199.37914	91.9261

**(S)-12-(4-Chloro-phenyl)-3,9-dimethyl-12-trifluoromethyl-5,6,11,12-tetrahydro-benzo[2,3]azepino[5,6-b]indole (3dc)**

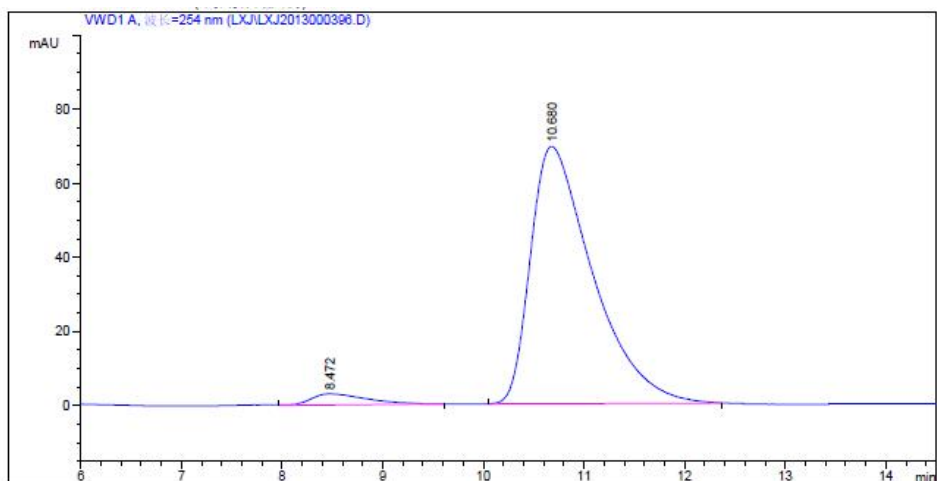


面积百分比报告

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	8.422	BV	0.4101	2059.60742	65.31741	49.9188
2	11.262	MM	0.7737	2066.30420	44.51122	50.0812



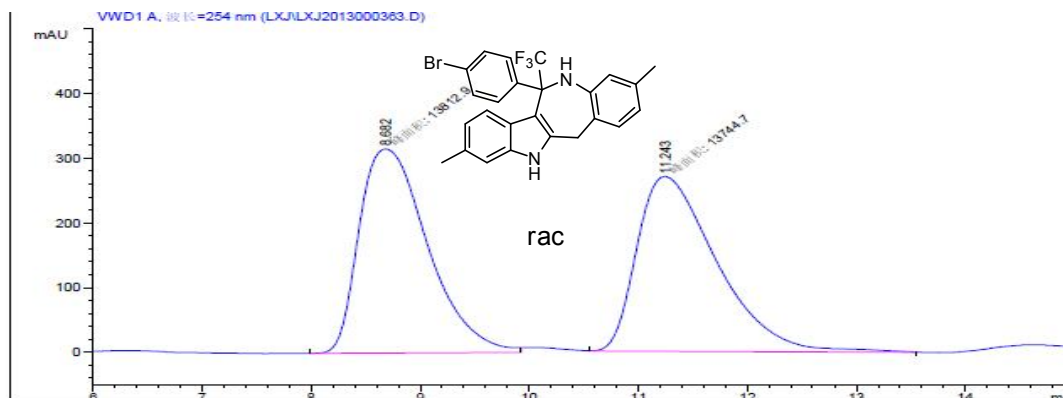
面积百分比报告

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	8.472	BB	0.5257	115.40557	2.98266	3.7230
2	10.680	BB	0.6409	2984.36182	69.47305	96.2770

**(S)-12-(4-Bromo-phenyl)-3,9-dimethyl-12-trifluoromethyl-5,6,11,12-tetrahydrobenzo[2,3]azepino[5,6-b]indole (3dd)**

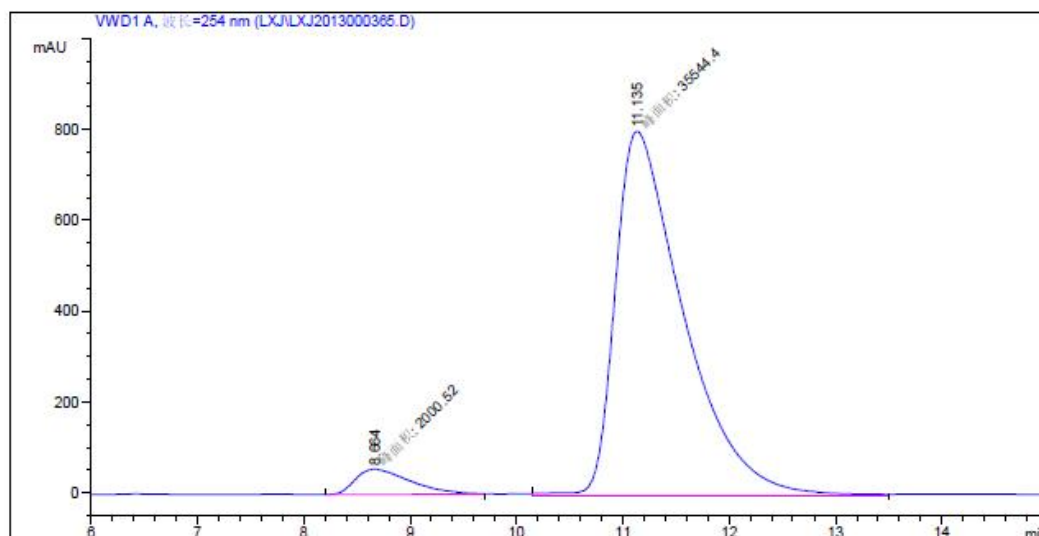


面积百分比报告

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	8.682	MM	0.7295	1.38129e4	315.56689	50.1238
2	11.243	MM	0.6472	1.37447e4	270.40216	49.8762



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	8.664	MM	0.6001	2000.52356	55.55849	5.3283
2	11.135	MM	0.7408	3.55444e4	799.65906	94.6717