Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Convenient synthesis of spiroindolenines from tryptamine-derived isocyanides and organic azides by cobalt catalysis in pure water

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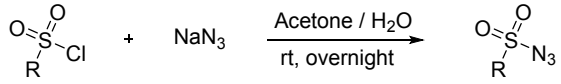
1. General information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Reactions were monitored through thin layer chromatography (TLC) on silica gel–precoated glass plates. Chromatograms were visualized by fluorescence quenching with UV-light at 254 nm. Flash column chromatography was performed using Yantai Yinlong flash silica gel (200–300 mesh). Concentration of cobalt-ions in water was detected by Inductively Coupled Plasma spectrometer. Melting points were recorded on an Electrothermal digital melting point apparatus. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker 400 MHz spectrometer in $CDCl_3$ or DMSO-d_6 with tetramethylsilane (TMS) as internal standard. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet; d = doublet; t = triplet; q = quarter; p = pentet; m = multiplet; br = broad), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). High resolution mass spectroscopy (HRMS) analyses were obtained using a commercial apparatus (ESI or EI Source).

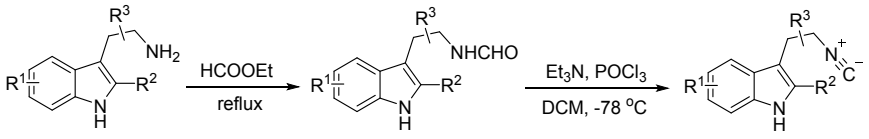
2. Synthesis of the starting materials

2.1. General procedure for the preparation of sulfonyl azides



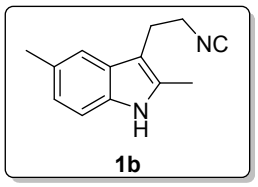
Sulfonyl azides were prepared following the literature procedures. [1,2] To a solution of sodium azide (0.5 g, 7.5 mmol) in water (2.5 mL) was added dropwise over 1 h a solution of sulfonyl chloride (5 mmol) in acetone (5 mL) at 0 °C. The reaction mixture was warmed up to room temperature and stirred for 11 h. Acetone was removed under reduced pressure and the reaction mixture was extracted with EtOAc. The combined organic layers were dried over Na_2SO_4 and solvent was removed under reduced pressure. Crude products were used without further purification.

2.2. Preparation of tryptamine-derived isocyanides



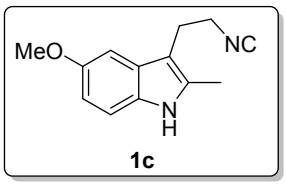
Tryptamine-derived isocyanides were prepared following the literature procedures. [3-5] tryptamine (3.2 g, 20 mmol, 1.0 equiv) was added to ethyl formate (16 mL) and refluxed for 10 h. The solvent was removed in vacuo. To a solution of the crude *N*-(2-(1*H*-indol-3-

yl)ethyl)formamide in anhydrous CH_2Cl_2 (20 mL) was added triethylamine (13 mL, 100 mmol, 5.0 equiv). The solution was cooled to -78 °C and $POCl_3$ (2.6 mL, 30 mmol, 1.5 equiv) was added dropwise. The reaction mixture was stirred for 4 hours at -78 °C. After completion, the reaction was quenched with H_2O and the aqueous layer was extracted with CH_2Cl_2. The collected organic layers were washed with H_2O and brine and dried over Na_2SO_4 followed by concentration in vacuo and purification by flash chromatography using CH_2Cl_2 as eluent to obtain the product as white solid. The characterization data matched the data reported in literature.



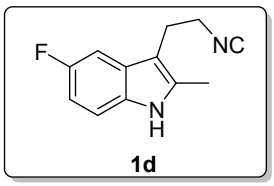
1b

1b was obtained in 71% overall yield, white solid, **mp** = 142.5 – 143.8 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.8 (s, 1H), 7.2 (s, 1H), 7.2 (d, *J* = 8.2 Hz, 1H), 7.0 – 7.0 (m, 1H), 3.6 (t, *J* = 7.1 Hz, 2H), 3.1 (t, *J* = 7.1 Hz, 2H), 2.5 (s, 3H), 2.4 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 155.9, 155.9, 155.8, 133.6, 133.0, 128.8, 128.2, 122.9, 117.1, 110.3, 106.2, 42.1, 42.1, 42.0, 25.0, 21.6, 11.8. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{13}H_{14}N_2Na^+$, m/z: 221.1049, found: 221.1046. **IR (thin film):** ν_{max} 3375, 1447, 1303, 1028, 804, 600, 515 cm^{-1}.



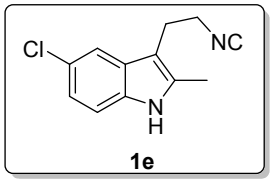
1c

1c was obtained in 73% overall yield, white solid, **mp** = 94.4 – 95.8 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.83 (s, 1H), 7.21 – 7.10 (m, 1H), 6.90 (s, 1H), 6.85 – 6.74 (m, 1H), 3.87 (s, 3H), 3.57 (t, *J* = 6.6 Hz, 2H), 3.09 (t, *J* = 6.6 Hz, 2H), 2.41 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 156.1, 156.1, 156.0, 154.2, 133.8, 130.4, 128.5, 111.3, 110.9, 106.5, 100.0, 56.1, 42.1, 42.0, 41.9, 25.0, 11.9. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{13}H_{15}N_2O^+$, m/z: 215.1173, found: 215.1177. **IR (thin film):** ν_{max} 3380, 1588, 1484, 1216, 813, 521 cm^{-1}.



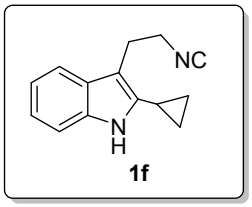
1d

1d was obtained in 75% overall yield, white solid, **mp** = 68.5 – 69.7 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.00 (s, 1H), 7.21 – 7.15 (m, 1H), 7.10 – 7.05 (m, 1H), 6.92 – 6.85 (m, 1H), 3.57 (t, *J* = 6.9 Hz, 2H), 3.06 (t, *J* = 6.8 Hz, 2H), 2.42 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.0 (d, J_{C-F} = 233 Hz), 156.1, 156.1, 156.0, 135.0, 131.8, 128.4 (d, J_{C-F} = 9.5 Hz), 111.1 (d, J_{C-F} = 9.6 Hz), 109.4 (d, J_{C-F} = 25.9 Hz), 106.9 (d, J_{C-F} = 4.3 Hz), 102.5 (d, J_{C-F} = 23.5 Hz), 42.0, 42.0, 41.9, 24.8, 11.9. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -126.43. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{12}H_{12}FN_2^+$, m/z: 203.0979, found: 203.0975. **IR (thin film):** ν_{max} 3385, 1583, 1447, 1174, 853, 609, 513 cm^{-1}.



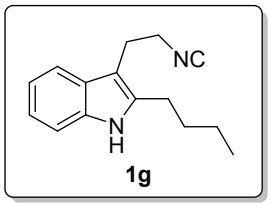
1e

1e was obtained in 73% overall yield, white solid, **mp** = 109.5 – 110.8 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.03 (s, 1H), 7.38 (s, 1H), 7.17 (d, *J* = 8.5 Hz, 1H), 7.08 (d, *J* = 8.5 Hz, 1H), 3.57 (t, *J* = 6.5 Hz, 2H), 3.05 (t, *J* = 6.3 Hz, 2H), 2.41 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 156.2, 156.1, 156.1, 134.7, 133.7, 129.1, 125.3, 121.6, 116.9, 111.6, 106.5, 42.1, 42.0, 42.0, 24.7, 11.9. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{12}H_{12}ClN_2^+$, m/z: 219.0684, found: 219.0679. **IR (thin film):** ν_{max} 3386, 1649, 1469, 866, 803, 515 cm^{-1}.



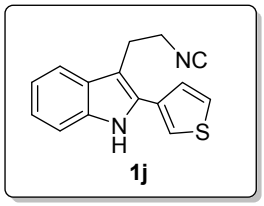
1f

1f was obtained in 68% overall yield, yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.95 (s, 1H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.15 – 6.99 (m, 2H), 3.57 (t, *J* = 7.7 Hz, 2H), 3.19 (t, *J* = 7.5 Hz, 2H), 2.09 – 1.92 (m, 1H), 0.97 (d, *J* = 8.2 Hz, 2H), 0.72 (d, *J* = 5.7 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 155.6, 155.6, 155.5, 137.7, 134.7, 128.1, 121.5, 119.6, 117.2, 110.7, 107.6, 42.0, 42.0, 41.9, 7.3, 6.7. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{14}H_{15}N_2^+$, m/z: 211.1230, found: 211.1232. **IR (thin film):** ν_{max} 3315, 1672, 1577, 1464, 1334, 740 cm^{-1}.



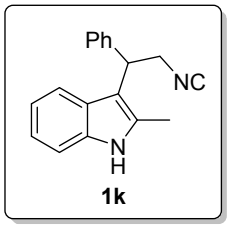
1g

1g was obtained in 68% overall yield, yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.99 (s, 1H), 7.41 (d, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 7.7 Hz, 1H), 7.16 – 7.02 (m, 2H), 3.51 (t, *J* = 6.9 Hz, 2H), 3.07 (t, *J* = 6.8 Hz, 2H), 2.68 (t, *J* = 7.7 Hz, 2H), 1.67 – 1.52 (m, 2H), 1.42 – 1.28 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 155.6, 155.6, 155.5, 137.4, 135.3, 127.8, 121.2, 119.4, 117.4, 110.7, 106.0, 42.2, 42.1, 42.0, 32.0, 25.7, 24.9, 22.5, 13.9. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{15}H_{18}N_2Na^+$, m/z: 249.1362, found: 249.1361. **IR (thin film):** ν_{max} 3404, 2929, 1461, 1310, 739, 490 cm^{-1}.



1j

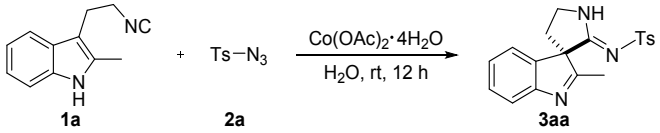
1j was obtained in 80% overall yield, white solid, **mp** = 169.6 – 170.6 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.20 (s, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.53 – 7.41 (m, 2H), 7.39 – 7.31 (m, 2H), 7.26 – 7.22 (m, 1H), 7.21 – 7.15 (m, 1H), 3.65 (t, *J* = 7.5 Hz, 2H), 3.34 (t, *J* = 7.5 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 156.4, 156.3, 156.2, 135.7, 133.0, 131.6, 128.4, 127.0, 126.9, 122.8, 122.6, 120.2, 118.3, 111.1, 107.6, 41.8, 41.8, 41.7, 25.5. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{15}H_{13}N_2S^+$, m/z: 253.0794, found: 253.0796. **IR (thin film):** ν_{max} 3299, 1454, 1342, 932, 740, 624, 624 cm^{-1}.



1k

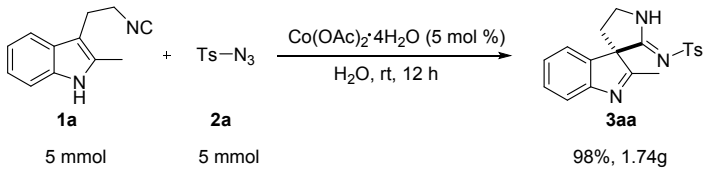
1k was obtained in 78% overall yield, white solid, **mp** = 128.4 – 129.7 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.89 (s, 1H), 7.34 – 7.18 (m, 7H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 4.61 (t, *J* = 7.6 Hz, 1H), 4.19 (dd, *J* = 14.6, 7.1 Hz, 1H), 4.06 (dd, *J* = 14.6, 8.3 Hz, 1H), 2.36 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 156.8, 140.1, 135.4, 132.9, 128.7, 127.6, 127.0, 127.0, 121.2, 119.6, 118.6, 110.7, 110.0, 45.4, 45.3, 45.3, 45.3, 42.2, 12.3. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{18}H_{17}N_2^+$, m/z: 261.1386, found: 261.1390. **IR (thin film):** ν_{max} 3416, 1564, 704, 537, 491 cm^{-1}.

3. Typical procedure for the synthesis of 3aa

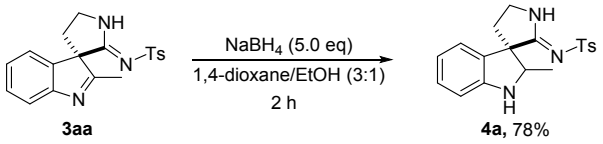


To a 15 mL reaction tube was sequentially added 3-(2-isocyanoethyl)-2-methyl-1H-indole **1a** (0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl azide **2a** (0.2 mmol, 1.0 equiv), $Co(OAc)_2 \cdot 4H_2O$ (5 mol%) and H_2O (4 mL). The reaction mixture was stirred at room temperature for 12 h. Afterwards, the reaction mixture was poured into water and extracted with CH_2Cl_2, the organic layer was combined and dried over Na_2SO_4, the solution was concentrated by rotary evaporation under reduced pressure. The final white solid was obtained by filtration and washed with EtOAc/PE (1: 6).

4. Gram-scale synthesis and further transformation



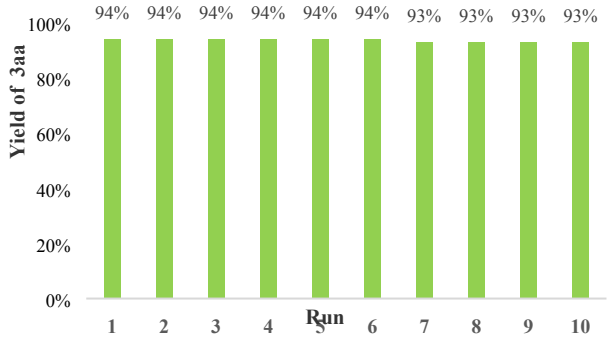
To a 250 mL reaction tube was sequentially added 3-(2-isocyanoethyl)-2-methyl-1H-indole **1a** (5 mmol, 1.0 equiv), 4-methylbenzenesulfonyl azide **2a** (5 mmol, 1.0 equiv), $Co(OAc)_2 \cdot 4H_2O$ (5 mol%) and H_2O (60 mL). The reaction mixture was stirred at room temperature for 12 h. Afterwards, the reaction mixture was poured into water and extracted with CH_2Cl_2, the organic layer was dried over Na_2SO_4, the solution was concentrated by rotary evaporation under reduced pressure. The final white solid (1.745 g) was obtained by filtration and washed with EtOAc/PE (1: 6).



3aa **4a,** 78%

To a solution of the spiroindolenine **3aa** (0.2 mmol) in 1,4-dioxane (1.5 mL) and EtOH (0.5 mL) under air at 25 °C was added $NaBH_4$ (1 mmol). After 2 h, the reaction mixture was quenched with saturated $NaHCO_3$ solution and extracted with CH_2Cl_2. The organic layer was washed with brine and dried over anhydrous Na_2SO_4. After removal of solvent, the crude residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (V_{PE} : V_{EA} = 3 : 1) to afford the desired product **4a** as a white solid.

5. Recycling study of aqueous catalytic system



To a 15 mL reaction tube was sequentially added 3-(2-isocyanoethyl)-2-methyl-1H-indole **1a** (0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl azide **2a** (0.2 mmol, 1.0 equiv), $Co(OAc)_2 \cdot 4H_2O$ (5 mol%) and H_2O (4 mL). The reaction mixture was stirred at room temperature for 12 hours. Afterwards, the reaction mixture was extracted with CH_2Cl_2 in reaction tube. The organic layer was dried over anhydrous Na_2SO_4, the reaction mixture was concentrated by rotary evaporation under reduced pressure. The final white solid (1.745 g) was obtained by filtration and washing with EtOAc/PE (1: 6).

The aqueous catalytic system in reaction tube could be recovered and reused in the next process. 3-(2-isocyanoethyl)-2-methyl-1H-indole **1a** (0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl azide **2a** (0.2 mmol, 1.0 equiv) was added in reaction tube. The reaction mixture was stirred at room temperature for 12 h. Afterwards, the reaction mixture was extracted with CH_2Cl_2 in reaction tube. The organic layer was dried over anhydrous Na_2SO_4, the solution was concentrated by rotary evaporation under reduced pressure. The final white solid (1.745 g) was obtained by filtration and washed with EtOAc/PE (1: 6). This process is repeated for the next nine times.

6. References

[1] Z.-Y. Gu, Y. Liu, F. Wang, X.-G. Bao, S.-Y. Wang and S.-J. Ji, *ACS Catal.*, 2017, **7**, 3893.

[2] F. Wang, P. Xu, B.-B. Liu, S.-Y. Wang and S.-J. Ji, *Org. Chem. Front.*, 2019, **6**, 3754–3758.

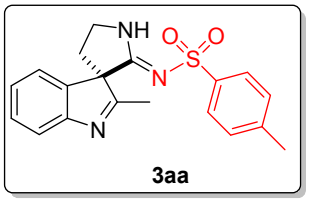
[3] X.-H. Zhao, X.-H. Liu, H.-J. Mei, J. Guo, L.-L. Lin and X.-M. Feng, *Angew. Chem. Int. Ed.,* 2015, **54**, 4032.

[4] J. M. Saya, T. R. Roose, J. J. Peek, B. Weijers, T. J. S. Waal, C. M. L. Velde, R. V. A. Orru and E. Ruijter, *Angew. Chem. Int. Ed.,* 2018, **57**, 15232.

[5] J.-X. Liu, H.-L. Li, L.-Z. Yu, L.-S. Tang, Q. Chen and M. Shi, *Adv. Synth. Catal.,* 2018, **360**, 2959.

7. Analytic and characterization data for the products

4-methyl-*N*-(2-methylspiro[indole-3,3'-pyrrolidin]-2'-ylidene)benzenesulfonamide (3aa)

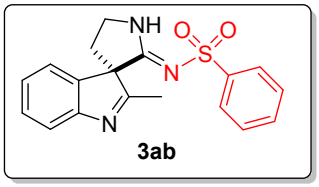


3aa

According to the general procedure, **3aa** was obtained in 94% yield (66 mg). White solid, **mp** = 193.1 – 194.3 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.56 (s, 1H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.36 – 7.29 (m, 1H), 7.20 – 7.10 (m, 4H), 3.98 – 3.99 (m, 1H), 3.89 – 3.81 (m, 1H), 2.52 – 2.43 (m, 1H), 2.36 (s, 3H), 2.26 – 2.18 (m, 1H), 2.17 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 179.1, 168.7, 155.3, 143.0, 140.5, 138.9, 129.3, 129.3, 126.2, 126.1, 121.5, 120.6, 68.3, 45.4, 29.5, 21.6, 16.4. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{19}H_{19}N_3NaO_2S^+$, m/z: 376.1090, found: 376.1103. **IR (thin film):** ν_{max} 1606, 1267, 1142, 853, 818, 719, 665, 552 cm^{-1}

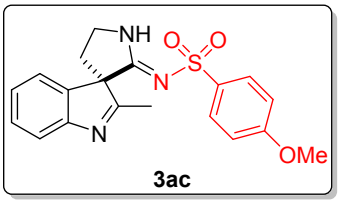
N-(2-methylspiro[indole-3,3'-pyrrolidin]-2'-ylidene)benzenesulfonamide (3ab)

According to the general procedure, **3ab** was obtained in 90% yield (61 mg). White solid, mp = 184.3 – 185.8 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.57 (s, 1H), 7.70 (d, *J* = 7.8 Hz, 2H), 7.53 – 7.44 (m, 2H), 7.40 – 7.30 (m, 3H), 7.15 (q, *J* = 7.2 Hz, 2H), 4.00 – 3.83 (m, 2H), 2.54 – 2.44 (m, 1H), 2.28 – 2.21 (m, 1H), 2.17 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 179.0, 168.9, 155.3, 141.8, 140.4, 132.3, 129.4, 128.7, 126.2, 126.1, 121.5, 120.7, 68.3,



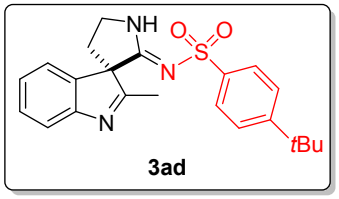
45.4, 29.4, 16.4. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{18}H_{18}N_3O_2S^+$, m/z: 340.1114, found: 340.1109. **IR (thin film):** ν_{max} 1605, 1289, 1141, 1085, 818, 718, 588, 556 cm^{-1}.

4-methoxy-*N*-(2-methylspiro[indole-3,3'-pyrrolidin]-2'-ylidene)benzenesulfonamide (3ac)



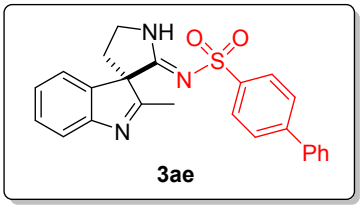
According to the general procedure, **3ac** was obtained in 96% yield (71 mg). White solid, **mp** = 169.3 – 170.5 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.50 (s, 1H), 7.64 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.36 – 7.30 (m, 1H), 7.20 – 7.11 (m, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 3.99 – 3.91 (m, 1H), 3.90 – 3.83 (m, 1H), 3.81 (s, 3H), 2.54 – 2.44 (m, 1H), 2.28 – 2.21 (m, 1H), 2.19 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 179.1, 168.5, 162.6, 155.3, 140.5, 133.7, 129.3, 128.3, 126.1, 121.5, 120.7, 113.9, 68.2, 55.7, 45.3, 29.5, 16.4. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{19}H_{19}N_3NaO_3S^+$, m/z: 392.1039, found: 392.1034. **IR (thin film):** ν_{max} 3369, 1619, 1259, 1138, 1016, 835, 671, 560 cm^{-1}.

4-(tert-butyl)-*N*-(2-methylspiro[indole-3,3'-pyrrolidin]-2'-ylidene)benzenesulfonamide (3ad)



According to the general procedure, **3ad** was obtained in 86% yield (68 mg). White solid, mp = 178.5 – 179.8 °C. **^{1}H NMR (400 MHz,$CDCl_3$)** δ 8.55 (s, 1H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.41 – 7.30 (m, 3H), 7.21 – 7.10 (m, 2H), 4.00 – 3.82 (m, 2H), 2.57 – 2.42 (m, 1H), 2.29 – 2.21 (m, 1H), 2.18 (s, 3H), 1.29 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 179.1, 168.7, 156.0, 155.3, 140.5, 138.8, 129.3, 126.1, 126.0, 125.7, 121.5, 120.7, 68.3, 45.4, 35.1, 31.2, 29.5, 16.4. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{22}H_{25}N_3NaO_2S^+$, m/z: 418.1560, found: 418.1557. **IR (thin film):** ν_{max} 3369, 1603, 1399, 1282, 1107, 818, 779, 643, 566 cm^{-1}.

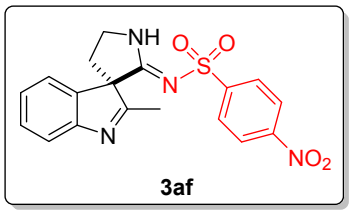
N-(2-methylspiro[indole-3,3'-pyrrolidin]-2'-ylidene)-[1,1'-biphenyl]-4-sulfonamide (3ae)



3ae

According to the general procedure, **3ae** was obtained in 60% yield (50 mg). White solid, mp = 246.3 – 247.8 °C. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 9.43 (s, 1H), 7.79 – 7.63 (m, 6H), 7.49 – 7.24 (m, 6H), 7.18 – 7.05 (m, 1H), 3.97 – 3.86 (m, 1H), 3.81 – 3.70 (m, 1H), 2.48 – 2.38 (m, 1H), 2.19 – 2.09 (m, 1H), 1.98 (s, 3H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 179.9, 167.7, 155.2, 143.7, 141.0, 140.7, 138.5, 129.1, 128.8, 128.5, 127.0, 127.0, 126.5, 125.8, 122.2, 119.6, 68.9, 46.1, 28.1, 15.8. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{24}H_{22}N_3O_2S^+$, m/z: 416.1427, found: 416.1429. **IR (thin film):** ν_{max} 3334, 1606, 1453, 1292, 1142, 854, 714, 675, 596 cm^{-1}.

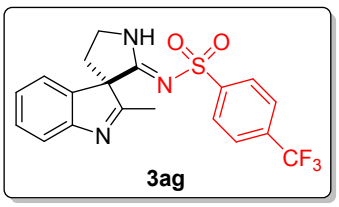
N-(2-methylspiro[indole-3,3'-pyrrolidin]-2'-ylidene)-4-nitrobenzenesulfonamide (3af)



3af

According to the general procedure, **3af** was obtained in 96% yield (74 mg). Light yellow solid, **mp** = 222.3 – 223.8 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.51 (s, 1H), 8.18 (d, J = 7.6 Hz, 2H), 7.81 (d, J = 7.5 Hz, 2H), 7.54 (d, J = 7.7 Hz, 1H), 7.43 – 7.34 (m, 1H), 7.17 (d, J = 6.3 Hz, 2H), 4.10 – 3.95 (m, 2H), 2.64 – 2.53 (m, 1H), 2.34 (ddd, J = 12.2, 7.2, 3.9 Hz, 1H), 2.27 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 178.5, 169.8, 155.4, 149.8, 147.4, 140.2, 129.7, 127.5, 126.3, 124.0, 121.3, 121.0, 68.4, 45.7, 29.2, 16.5. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{18}H_{16}N_4NaO_4S^+$, m/z: 407.0784, found: 407.0785. **IR (thin film):** ν_{max} 1613, 1524, 1348, 1293, 1148, 821, 743, 604 cm^{-1}.

N-(2-methylspiro[indole-3,3'-pyrrolidin]-2'-ylidene)-4-(trifluoromethyl)benzenesulfonamide (3ag)

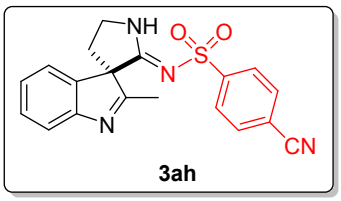


3ag

According to the general procedure, **3ag** was obtained in 83% yield (67 mg). White solid, mp = 190.5 – 192.1 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.54 (s, 1H), 7.78 (d, J = 8.2 Hz, 2H), 7.61 (d, J = 8.3 Hz, 2H), 7.53 (d, J = 7.7 Hz, 1H), 7.39 – 7.33 (m, 1H), 7.15 (d, J = 6.5 Hz, 2H), 4.04 – 3.89 (m, 2H), 2.60 – 2.50 (m, 1H), 2.34 –2.26 (m, 1H), 2.24(s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 178.7, 169.5, 155.3, 145.2 (d, J_{C-F} =1.1 Hz), 140.2, 134.1, 133.8, 129.6, 126.8, 126.2, 125.9 (q, J_{C-F} = 3.7 Hz), 124.8, 121.1 (d, J_{C-F}

= 50.8 Hz), 68.4, 45.6, 29.3, 16.4. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -63.06. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{19}H_{16}F_3N_3NaO_2S^+$, m/z: 430.0808, found: 430.0816. **IR (thin film):** ν_{max} 1614, 1400, 1294, 1122, 823, 714, 600, 550 cm^{-1}.

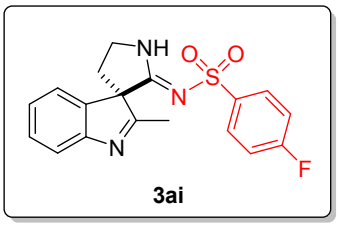
4-cyano-*N*-(2-methylspiro[indole-3,3'-pyrrolidin]-2'-ylidene)benzenesulfonamide (3ah)



3ah

According to the general procedure, **3ah** was obtained in 75% yield (55 mg). White solid, mp = 215.1 – 216.9 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.53 (s, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.40 – 7.33 (m, 1H), 7.21 – 7.11 (m, 2H), 4.05 – 3.89 (m, 2H), 2.61 – 2.51 (m, 1H), 2.35 – 2.27 (m, 1H), 2.24 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 178.6, 169.7, 155.3, 145.9, 140.2, 132.6, 129.6, 126.9, 126.2, 121.3, 120.9, 117.6, 115.9, 68.4, 45.7, 29.2, 16.4. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{19}H_{16}N_4NaO_2S^+$, m/z: 387.0886, found: 387.0882. **IR (thin film):** ν_{max} 3346, 1626, 1295, 1151, 871, 733, 651, 568 cm^{-1}.

4-fluoro-*N*-(2-methylspiro[indole-3,3'-pyrrolidin]-2'-ylidene)benzenesulfonamide (3ai)

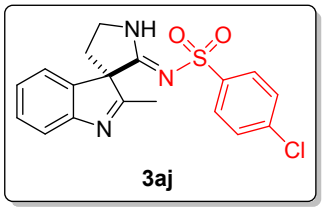


3ai

According to the general procedure, **3ai** was obtained in 84% yield (60 mg). White solid, **mp** = 160.3 – 161.7 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.54 (s, 1H), 7.75 – 7.63 (m, 2H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.37 – 7.31 (m, 1H), 7.15 (q, *J* = 7.4 Hz, 2H), 7.03 (t, *J* = 8.5 Hz, 2H), 4.00 – 3.85 (m, 2H), 2.56 – 2.46 (m, 1H), 2.30 – 2.23(m, 1H), 2.20 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 178.9, 168.9, 164.9 (d, J_{C-F} = 252 Hz), 155.3, 140.4, 137.9 (d, J_{C-F} = 3.2 Hz), 129.4, 128.9 (d, J_{C-F} = 9.2 Hz), 126.2, 121.4, 120.7, 115.9 (d, J_{C-F} = 22.4 Hz), 68.3, 45.5, 29.3, 16.4. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -63.06. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{18}H_{16}FN_3NaO_2S^+$, m/z: 380.0839, found:380.0839. **IR (thin film):** ν_{max} 1611, 1492, 1277, 1234, 1137, 841, 671, 558, 517 cm^{-1}.

4-chloro-*N*-(2-methylspiro[indole-3,3'-pyrrolidin]-2'-

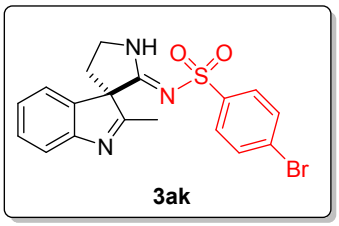
ylidene)benzenesulfonamide (3aj)



3aj

According to the general procedure, **3aj** was obtained in 85% yield (63 mg). White solid, mp = 174.5 – 175.8 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.49 (s, 1H), 7.68 – 7.56 (m, 2H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.41 – 7.29 (m, 3H), 7.16 (d, *J* = 6.5 Hz, 2H), 4.04 – 3.87 (m, 2H), 2.59 – 2.47 (m, 1H), 2.32 – 2.25 (m, 1H), 2.22 (s, 3H). **^{13}C NMR (100 MHz, CDCl3)** δ 178.8, 169.2, 155.3, 140.3, 138.7, 129.5, 129.0, 127.7, 126.2, 121.4, 120.8, 68.3, 45.5, 29.4, 16.4, one C(Ar) missing. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{18}H_{16}ClN_3NaO_2S^+$, m/z: 396.0554, found: 396.0552. **IR (thin film):** ν_{max} 3304, 1609, 1390, 1275, 1153, 822, 756, 556 cm^{-1}.

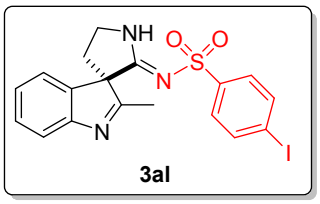
4-bromo-*N*-(2-methylspiro[indole-3,3'-pyrrolidin]-2'-ylidene)benzenesulfonamide (3ak)



3ak

According to the general procedure, **3ak** was obtained in 90% yield (75 mg). White solid, **mp** = 161.2 – 162.8 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.51 (s, 1H), 7.64 – 7.45 (m, 5H), 7.40 – 7.32 (m, 1H), 7.20 – 7.10 (m, 2H), 4.03 – 3.85 (m, 2H), 2.57 – 2.47 (m, 1H), 2.32 – 2.24(m, 1H), 2.22(s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 178.8, 169.2, 155.3, 140.8, 140.3, 132.0, 129.5, 127.8, 127.1, 126.2, 121.4, 120.8, 68.3, 45.5, 29.3, 16.4. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{18}H_{17}BrN_3O_2S^+$, m/z: 418.0219, found: 418.0218. **IR (thin film):** ν_{max} 3345, 1611, 1290, 1269, 1143, 857, 757, 554 cm^{-1}.

4-iodo-*N*-(2-methylspiro[indole-3,3'-pyrrolidin]-2'-ylidene)benzenesulfonamide (3al)

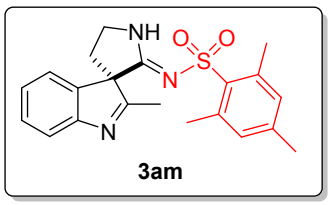


3al

According to the general procedure, **3al** was obtained in 75% yield (70 mg). White solid, mp = 205.3 – 206.4 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.53 (s, 1H), 7.76 – 7.66 (m, 2H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.42 – 7.31 (m, 3H), 7.15 (s, 2H), 4.00 – 3.83 (m, 2H), 2.56 – 2.45 (m, 1H), 2.30 – 2.23 (m, 1H), 2.21(s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 178.8, 169.1, 155.3, 141.5, 140.3, 137.9, 129.5, 127.7, 126.2, 121.4, 120.7, 99.5,

68.3, 45.6, 29.3, 16.4. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{18}H_{17}IN_3O_2S^+$, m/z: 466.0081, found: 466.0086. **IR (thin film):** ν_{max} 3345, 1609, 1453, 1265, 858, 739, 598, 553 cm^{-1}.

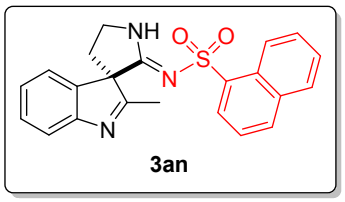
2,4,6-trimethyl-*N*-(2-methylspiro[indole-3,3'-pyrrolidin]-2'-ylidene)benzenesulfonamide (3am)



3am

According to the general procedure, **3am** was obtained in 90% yield (68 mg). White solid, mp = 179.3 – 180.5 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.23 (s, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.37 – 7.29 (m, 1H), 7.24 – 7.12 (m, 2H), 6.78 (s, 2H), 4.01 – 3.84 (m, 2H), 2.58 – 2.49 (m, 1H), 2.41 (s, 6H), 2.28(s, 3H), 2.27-2.22(m, 1H), 2.21(s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 179.5, 167.4, 155.3, 141.6, 140.5, 138.6, 135.8, 131.4, 129.3, 126.0, 121.6, 120.6, 68.1, 45.3, 29.6, 22.6, 21.0, 16.5. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{21}H_{23}N_3NaO_2S^+$, m/z: 404.1403, found: 404.1409. **IR (thin film):** ν_{max} 3352, 2072, 1606, 1287, 1144, 847, 753, 655, 581 cm^{-1}.

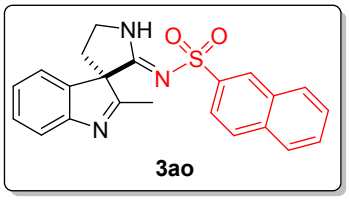
N-(2-methylspiro[indole-3,3'-pyrrolidin]-2'-ylidene)naphthalene-1-sulfonamide (3an)



3an

According to the general procedure, **3an** was obtained in 84% yield (65 mg). White solid, mp = 243.2 – 244.5 °C. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 9.29 (s, 1H), 8.17 (d, *J* = 8.6 Hz, 1H), 8.08 (d, *J* = 7.7 Hz, 2H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.55 – 7.47 (m, 2H), 7.46 – 7.40 (m, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.26 – 7.17 (m, 2H), 7.02 (t, *J* = 7.3 Hz, 1H), 3.88 – 3.79 (m, 1H), 3.73 – 3.64 (m, 1H), 2.41 – 2.31 (m, 1H), 2.11 – 2.01 (m, 1H), 1.76 (s, 3H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 179.8, 167.6, 155.0, 141.0, 136.8, 133.7, 133.4, 128.7, 128.5, 127.7, 127.3, 127.2, 126.6, 125.6, 125.5, 124.2, 122.0, 119.5, 68.8, 46.2, 28.1, 15.7. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{22}H_{20}N_3O_2S^+$, m/z: 390.1271, found: 390.1273. **IR (thin film):** ν_{max} 3264, 1615, 1404, 1114, 859, 807, 759, 587, 510 cm^{-1}.

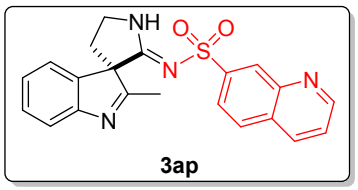
N-(2-methylspiro[indole-3,3'-pyrrolidin]-2'-ylidene)naphthalene-2-sulfonamide (3ao)



3ao

According to the general procedure, **3ao** was obtained in 85% yield (66 mg). White solid, mp = 190.1 – 191.6 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.65 (s, 1H), 8.26 (s, 1H), 7.82 (t, *J* = 8.8 Hz, 3H), 7.68 (d, *J* = 8.7 Hz, 1H), 7.61 – 7.48 (m, 3H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.17 – 7.06 (m, 2H), 4.00 – 3.83 (m, 2H), 2.54 – 2.43 (m, 1H), 2.27 – 2.19 (m, 1H), 2.18(s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 179.0, 169.1, 155.3, 140.4, 138.7, 134.7, 132.0, 129.4, 129.3, 129.0, 128.6, 127.9, 127.4, 126.9, 126.1, 122.1, 121.5, 120.7, 68.4, 45.5, 29.4, 16.4. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{22}H_{20}N_3O_2S^+$, m/z: 390.1271, found: 390.1274. **IR (thin film):** ν_{max} 3337, 1992, 1607, 1266, 1127, 865, 754, 664, 556 cm^{-1}.

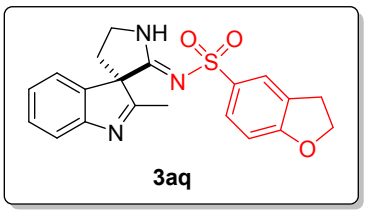
N-(2-methylspiro[indole-3,3'-pyrrolidin]-2'-ylidene)quinoline-7-sulfonamide (3ap)



3ap

According to the general procedure, **3ap** was obtained in 95% yield (74 mg). Light yellow solid, mp = 156.1 – 157.5 °C. **^{1}H NMR (400 MHz,$CDCl_3$)** δ 9.23 (s, 1H), 9.08 – 8.95 (m, 1H), 8.38 (d, *J* = 7.1 Hz, 1H), 8.24 – 8.16 (m, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.54 – 7.47 (m, 2H), 7.38 (d, *J* = 7.7 Hz, 1H), 7.25 – 7.13 (m, 2H), 7.02 (t, *J* = 7.4 Hz, 1H), 4.17 – 3.99 (m, 2H), 2.62 – 2.50 (m, 1H), 2.34 – 2.24 (m, 1H), 2.12 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 179.5, 169.4, 155.2, 150.7, 144.5, 140.5, 138.4, 136.8, 133.2, 131.5, 129.1, 128.8, 125.9, 125.8, 121.8, 121.8, 120.5, 68.4, 45.5, 30.0, 16.4. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{21}H_{18}NaN_4O_2S^+$, m/z: 413.1043, found: 413.1041. **IR (thin film):** ν_{max} 2021, 1619, 1457, 1291, 866, 758, 597, 519 cm^{-1}.

N-(2-methylspiro[indole-3,3'-pyrrolidin]-2'-ylidene)-2,3-dihydrobenzofuran-5-sulfonamide (3aq)

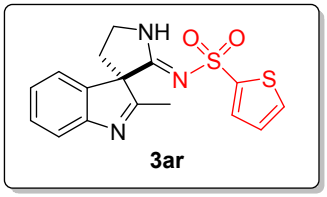


3aq

According to the general procedure, **3aq** was obtained in 91% yield (69 mg). White solid, mp = 182.0 – 183.5 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.47 (s, 1H), 7.58 – 7.43 (m, 3H), 7.37 – 7.31 (m, 1H), 7.21 – 7.10 (m, 2H), 6.70 (d, *J* = 9.0 Hz, 1H), 4.61 (t, *J* = 8.8 Hz, 2H), 4.00 – 3.84 (m, 2H), 3.14 (t, *J* = 8.8 Hz, 2H), 2.55 – 2.46 (m, 1H),

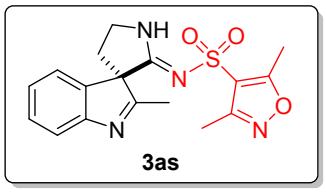
2.29 – 2.22 (m, 1H), 2.21 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 179.2, 168.3, 163.5, 155.3, 140.6, 133.7, 129.3, 127.9, 127.5, 126.1, 123.7, 121.5, 120.7, 109.0, 72.3, 68.2, 45.3, 29.6, 29.2, 16.4. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{20}H_{20}N_3O_3S^+$, m/z: 380.1220, found: 380.1224. **IR (thin film):** ν_{max} 3357, 2052, 1617, 1242, 1067, 896, 753, 557cm^{-1}.

N-(2-methylspiro[indole-3,3'-pyrrolidin]-2'-ylidene)thiophene-2-sulfonamide (3ar)



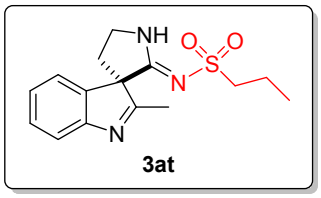
According to the general procedure, **3ar** was obtained in 71% yield (49 mg). White solid, mp = 165.3 – 166.7 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.54 (s, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 4.2 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.21 – 7.11 (m, 2H), 6.96 (t, *J* = 4.3 Hz, 1H), 4.03 – 3.86 (m, 2H), 2.57 – 2.45 (m, 1H), 2.32 – 2.24 (m, 1H), 2.22 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 178.8, 169.1, 155.3, 142.7, 140.3, 131.1, 131.0, 129.4, 127.0, 126.2, 121.6, 120.7, 68.3, 45.6, 29.4, 16.4. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{16}H_{15}N_3NaO_2S_2^+$, m/z: 368.0498, found: 368.0500. **IR (thin film):** ν_{max} 3361, 1605, 1302, 1136, 843, 736, 672, 578 cm^{-1}.

3,5-dimethyl-*N*-(2-methylspiro[indole-3,3'-pyrrolidin]-2'-ylidene)isoxazole-4-sulfonamide (3as)



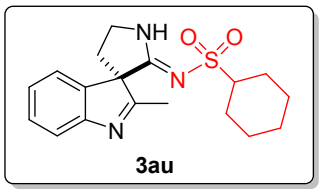
According to the general procedure, **3as** was obtained in 88% yield (63 mg). White solid, mp = 188.8 – 189.7 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.33 (s, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.24 – 7.12 (m, 2H), 4.04 – 3.90 (m, 2H), 2.62 – 2.52 (m, 1H), 2.39 (s, 3H), 2.36 – 2.32 (m, 1H), 2.31 (s, 3H), 2.03 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 178.9, 171.2, 168.6, 157.6, 155.3, 140.2, 129.6, 126.3, 121.3, 120.7, 118.1, 68.2, 45.7, 29.0, 16.5, 12.5, 10.6. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{17}H_{18}N_4NaO_3S^+$, m/z: 381.0992, found: 381.0995. **IR (thin film):** ν_{max} 3390, 1613, 1588, 1115, 863, 648, 549 cm^{-1}.

N-(2-methylspiro[indole-3,3'-pyrrolidin]-2'-ylidene)propane-1-sulfonamide (3at)



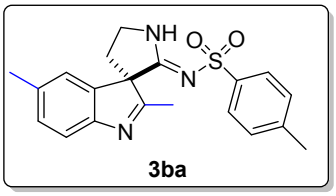
According to the general procedure, **3at** was obtained in 90% yield (55 mg). White solid, mp = 138.5 – 139.8 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.34 (s, 1H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.29 (t, *J* = 6.1 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 4.01 – 3.85 (m, 2H), 2.83 (t, *J* = 7.8 Hz, 2H), 2.60 – 2.50 (m, 1H), 2.36 (s, 3H), 2.33 – 2.25 (m, 1H), 1.68 – 1.52 (m, 2H), 0.87 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 179.3, 168.6, 155.3, 140.7, 129.3, 126.2, 121.5, 120.6, 68.2, 55.7, 45.3, 29.4, 17.2, 16.5, 12.9. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{15}H_{19}N_3NaO_2S^+$, m/z: 328.1090, found: 328.1089. **IR (thin film):** ν_{max} 3332, 1613, 1452, 1267, 1126, 860, 755, 592 cm^{-1}.

N-(2-methylspiro[indole-3,3'-pyrrolidin]-2'-ylidene)cyclohexanesulfonamide (3au)



According to the general procedure, **3au** was obtained in 96% yield (66 mg). White solid, mp = 211.2 – 212.7 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.39 (s, 1H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.42 – 7.34 (m, 1H), 7.32 – 7.27 (m, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 4.00 – 3.85 (m, 2H), 2.73 – 2.63 (m, 1H), 2.60 – 2.51 (m, 1H), 2.37 (s, 3H), 2.33 – 2.26 (m, 1H), 2.01 – 1.87 (m, 2H), 1.78 – 1.67 (m, 2H), 1.59 (d, *J* = 12.6 Hz, 1H), 1.29 – 1.19 (m, 2H), 1.18 – 1.07 (m, 2H), 1.06 – 0.93 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 179.4, 168.9, 155.3, 140.9, 129.3, 126.0, 121.5, 120.6, 68.4, 62.0, 45.2, 29.3, 26.1, 25.9, 25.2, 25.1, 25.1, 16.6. **HRMS (ESI)** calcd for $[M+Na]^+$ $C_{18}H_{23}N_3NaO_2S^+$, m/z: 368.1403, found: 368.1406. **IR (thin film):** ν_{max} 3384, 1627, 1254, 1107, 864, 666, 591, 539 cm^{-1}.

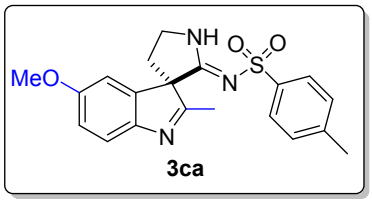
N-(2,5-dimethylspiro[indole-3,3'-pyrrolidin]-2'-ylidene)-4-methylbenzenesulfonamide (3ba)



According to the general procedure, **3ba** was obtained in 89% yield (65 mg). White solid, mp = 211.3 – 212.7 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.56 (s, 1H), 7.59 (d, *J* = 6.7 Hz, 2H), 7.36 (d, *J* = 6.8 Hz, 1H), 7.21 – 7.07 (m, 3H), 6.95 (s, 1H), 3.98 – 3.78 (m, 2H), 2.50 – 2.42 (m, 1H), 2.36 (s, 3H), 2.30 (s, 3H), 2.20 (s, 1H), 2.13 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 178.0, 168.9, 153.0, 142.9, 140.6, 138.9, 136.0, 129.7,

129.2, 126.2, 122.3, 120.1, 68.1, 45.4, 29.5, 21.6, 21.4, 16.3. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{20}H_{22}N_3O_2S^+$, m/z: 368.1427, found: 368.1428. **IR (thin film):** ν_{max} 1611, 1295, 1273, 1139, 814, 706, 617, 555 cm^{-1}.

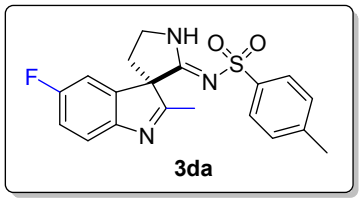
N-(5-methoxy-2-methylspiro[indole-3,3'-pyrrolidin]-2'-ylidene)-4-methylbenzenesulfonamide (3ca)



3ca

According to the general procedure, **3ca** was obtained in 91% yield (70 mg). White solid, mp = 165.4 – 166.8 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.58 (s, 1H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.86 – 6.78 (m, 1H), 6.72 (d, *J* = 2.2 Hz, 1H), 3.94 – 3.86 (m, 1H), 3.85 – 3.78 (m, 1H), 3.72 (s, 3H), 2.48 – 2.38 (m, 1H), 2.35 (s, 3H), 2.25 – 2.16 (m, 1H), 2.10 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.8, 168.7, 158.5, 148.8, 143.0, 141.9, 138.9, 129.3, 126.2, 120.8, 113.7, 108.5, 68.4, 55.8, 45.3, 29.5, 21.5, 16.2. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{20}H_{22}N_3O_3S^+$, m/z: 384.1376, found: 384.1378. **IR (thin film):** ν_{max} 3351, 1614, 1469, 1276, 1137, 817, 666, 568 cm^{-1}.

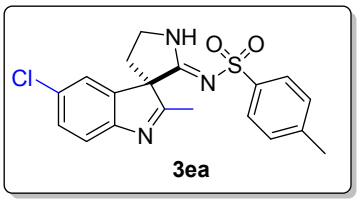
N-(5-fluoro-2-methylspiro[indole-3,3'-pyrrolidin]-2'-ylidene)-4-methylbenzenesulfonamide (3da)



3da

According to the general procedure, **3da** was obtained in 92% yield (62 mg). White solid, mp = 196.5 – 197.8 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.61 (s, 1H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.45 – 7.38 (m, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.04 – 6.96 (m, 1H), 6.89 – 6.80 (m, 1H), 3.93 – 3.81 (m, 2H), 2.50 – 2.41 (m, 1H), 2.36 (s, 3H), 2.25 – 2.18 (m, 1H), 2.14 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 179.0 (d, $J_{C\text{-}F}$ = 2.9 Hz), 168.0, 161.3 (d, $J_{C\text{-}F}$ = 244 Hz), 151.4, 143.2, 142.0 (d, $J_{C\text{-}F}$ = 8.8 Hz), 138.7, 129.4, 126.2, 121.2 (d, $J_{C\text{-}F}$ = 8.8 Hz), 115.7 (d, $J_{C\text{-}F}$ = 23.3 Hz), 109.6 (d, $J_{C\text{-}F}$ = 25.2 Hz), 68.7, 45.4, 29.2, 21.6, 16.3. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -115.87. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{19}H_{19}FN_3O_2S^+$, m/z: 372.1177, found: 372.1180. **IR (thin film):** ν_{max} 1609, 1470, 1267, 1147, 830, 737, 666, 564 cm^{-1}.

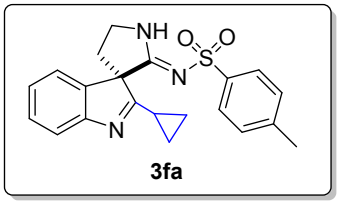
N-(5-chloro-2-methylspiro[indole-3,3'-pyrrolidin]-2'-ylidene)-4-methylbenzenesulfonamide (3ea)



3ea

According to the general procedure, **3ea** was obtained in 98% yield (76 mg). White solid, mp = 186.1 – 187.5 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.59 (s, 1H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 2H), 7.08 (s, 1H), 3.94 – 3.82 (m, 2H), 2.52 – 2.42 (m, 1H), 2.37 (s, 3H), 2.26 – 2.18 (m, 1H), 2.16 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 179.7, 167.8, 153.9, 143.2, 142.0, 138.6, 131.7, 129.4, 126.2, 122.1, 121.4, 68.6, 45.4, 29.1, 21.6, 16.4, one C(Ar) missing. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{19}H_{19}ClN_3O_2S^+$, m/z: 388.0881, found: 388.0881. **IR (thin film):** ν_{max} 3039, 1605, 1396, 1146, 866, 806, 674, 558 cm^{-1}.

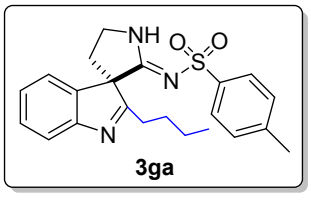
N-(2-cyclopropylspiro[indole-3,3'-pyrrolidin]-2'-ylidene)-4-methylbenzenesulfonamide (3fa)



3fa

According to the general procedure, **3fa** was obtained in 87% yield (66 mg). White solid, mp = 169.5 – 171.0 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.63 (s, 1H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 7.7 Hz, 1H), 7.32 – 7.26 (m, 1H), 7.16 (d, *J* = 8.7 Hz, 3H), 7.12 – 7.06 (m, 1H), 3.98 – 3.83 (m, 2H), 2.71 – 2.59 (m, 1H), 2.35 (s, 3H), 2.30 – 2.21 (m, 1H), 1.51 – 1.42 (m, 1H), 1.18 – 1.09 (m, 2H), 1.03 – 0.94 (m, 1H), 0.82 – 0.72 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 184.9, 168.8, 155.4, 142.8, 140.2, 139.1, 129.2, 126.3, 125.5, 121.5, 120.2, 68.7, 45.6, 29.6, 21.6, 10.9, 10.9, 10.8. **HRMS (ESI)** cacd for $[M+H]^+$ $C_{21}H_{22}N_3O_2S^+$, m/z: 380.1427, found: 380.1424. **IR (thin film):** ν_{max} 3363, 1612, 1390, 1138, 864, 730, 673, 559 cm^{-1}.

N-(2-butylspiro[indole-3,3'-pyrrolidin]-2'-ylidene)-4-methylbenzenesulfonamide (3ga)

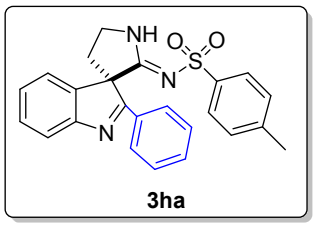


3ga

According to the general procedure, **3ga** was obtained in 86% yield (68 mg). White solid, mp = 137.6 – 138.8 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.57 (s, 1H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.37 – 7.29 (m, 1H), 7.23 – 7.10 (m, 4H),

3.98 – 3.80 (m, 2H), 2.52 – 2.38 (m, 2H), 2.36 (s, 3H), 2.30 – 2.18 (m, 2H), 1.76 – 1.62 (m, 2H), 1.32 – 1.20 (m, 2H), 0.86 (t, J = 7.3 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 182.5, 168.8, 155.4, 143.0, 140.3, 139.0, 129.3, 129.2, 126.3, 126.0, 121.5, 120.7, 68.4, 45.4, 29.9, 29.5, 28.0, 22.7, 21.6, 13.9. **HRMS (ESI)** cacd for $[M+H]^+$ $C_{22}H_{26}N_3O_2S^+$, m/z: 396.1740, found: 396.1743. **IR (thin film):** ν_{max} 1598, 1286, 1151, 832, 769, 668, 556 cm^{-1}.

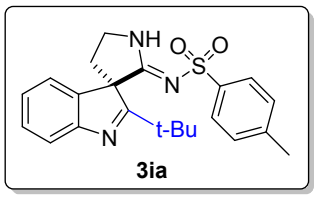
4-methyl-*N*-(2-phenylspiro[indole-3,3'-pyrrolidin]-2'-ylidene)benzenesulfonamide (3ha)



3ha

According to the general procedure, **3ha** was obtained in 90% yield (75 mg). White solid, mp > 250 °C. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 9.39 (s, 1H), 7.57 (d, J = 7.6 Hz, 1H), 7.46 (d, J = 7.6 Hz, 2H), 7.42 – 7.34 (m, 5H), 7.20 (t, J = 7.2 Hz, 3H), 7.13 (d, J = 7.8 Hz, 2H), 4.07 – 3.97 (m, 1H), 3.86 (t, J = 10.2 Hz, 1H), 2.53 – 2.42 (m, 1H), 2.27 (s, 3H), 2.08 – 1.99 (m, 1H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 176.2, 168.1, 153.9, 142.6, 142.3, 138.4, 136.9, 131.0, 131.0, 129.2, 128.8, 127.8, 126.7, 126.0, 121.5, 120.9, 67.4, 46.2, 30.1, 21.0. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{24}H_{22}N_3O_2S^+$, m/z: 416.1427, found: 416.1428. **IR (thin film):** ν_{max} 1593, 1529, 1297, 1146, 812, 772, 661, 560 cm^{-1}.

N-(2-(tert-butyl)spiro[indole-3,3'-pyrrolidin]-2'-ylidene)-4-methylbenzenesulfonamide (3ia)

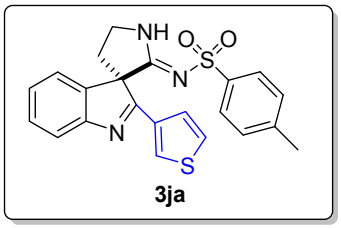


3ia

According to the general procedure, **3ia** was obtained in 98% yield (78 mg). White solid, mp > 250 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.46 (s, 1H), 7.66 – 7.42 (m, 3H), 7.35 – 7.29 (m, 1H), 7.20 – 7.04 (m, 4H), 4.05 – 3.90 (m, 2H), 3.01 – 2.91 (m, 1H), 2.36 (s, 3H), 2.25 – 2.17 (m, 1H), 1.28 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 188.2, 169.2, 154.2, 142.9, 142.0, 138.7, 129.2, 129.1, 126.4, 126.2, 120.7, 120.3, 68.4, 45.4, 37.7, 29.9, 28.2, 21.6. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{22}H_{26}N_3O_2S^+$, m/z: 396.1740, found: 396.1742. **IR (thin film):** ν_{max} 3360, 1600, 1289, 1141, 831, 671, 564, 542 cm^{-1}.

4-methyl-*N*-(2-(thiophen-3-yl)spiro[indole-3,3'-pyrrolidin]-2'-

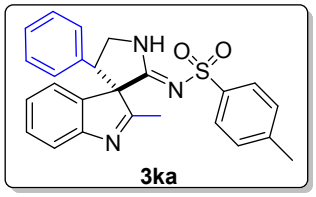
ylidene)benzenesulfonamide (3ja)



3ja

According to the general procedure, **3ja** was obtained in 90% yield (76 mg). White solid, mp > 250 °C. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 9.34 (s, 1H), 7.52 – 7.46 (m, 2H), 7.37 – 7.28 (m, 6H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 4.03 – 3.92 (m, 1H), 3.86 (t, *J* = 10.1 Hz, 1H), 2.54 – 2.43 (m, 1H), 2.25 (s, 3H), 2.09 – 2.01 (m, 1H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 172.5, 167.9, 154.4, 142.5, 141.9, 138.6, 133.8, 129.3, 128.6, 127.4, 126.7, 126.4, 125.9, 121.6, 120.6, 67.6, 46.2, 30.4, 21.1, one C(Ar) missing. **HRMS (ESI)** cacd for $[M+H]^+$ $C_{22}H_{20}N_3O_2S_2^+$, m/z: 422.0991, found: 422.0987. **IR (thin film):** ν_{max} 1612, 1563, 1138, 1095, 730, 673, 559 cm^{-1}.

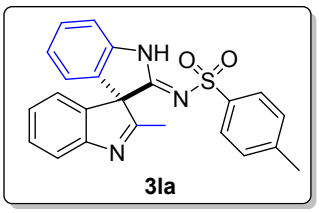
4-methyl-*N*-(2-methyl-4'-phenylspiro[indole-3,3'-pyrrolidin]-2'-ylidene)benzenesulfonamide (3ka, 2:1 dr)



3ka

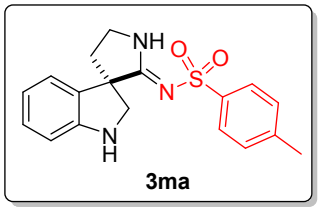
According to the general procedure, **3ka** was obtained in 95% yield (81 mg). White solid, mp = 110.2 – 111.5 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.80 (s, 0.33H, minor), 8.71 (s, 0.65H, major), 7.65 (d, *J* = 8.1 Hz, 0.65H, minor), 7.62 (d, *J* = 8.1 Hz, 1.30H, major), 7.49 – 7.27 (m, 2H, minor + major), 7.22 – 6.93 (m, 7H, minor + major), 6.84 – 6.76 (d, *J* = 7.4 Hz, 1.33H, major), 6.65 (d, *J* = 7.4 Hz, 0.66H, minor), 4.37 – 4.08 (m, 3H), 2.40 (s, 2H, major), 1.86 (s, 1H, minor), 2.36 (s, 3H). 2.36 (s, 3H). **^{13}C NMR (100 MHz,$CDCl_3$)** δ 178.4, 177.0, 168.5, 168.5, 156.2, 155.3, 143.1, 143.0, 140.1, 138.9, 138.8, 136.3, 134.5, 133.6, 129.5, 129.4, 129.3, 129.2, 128.9, 128.4, 128.1, 127.9, 127.2, 126.6, 126.3, 126.3, 126.2, 125.3, 123.0, 122.3, 120.6, 120.6, 73.1, 72.9, 49.0, 48.4, 47.5, 47.0, 21.6, 18.7, 16.9, 14.2. **HRMS (ESI)** cacd for $[M+H]^+$ $C_{25}H_{24}N_3O_2S^+$, m/z: 430.1584, found: 430.1585. **IR (thin film):** ν_{max} 1611, 1275, 1142, 828, 675, 555 cm^{-1}.

4-methyl-*N*-(2-methylspiro[indole-3,3'-indolin]-2'-ylidene)benzenesulfonamide (3la)



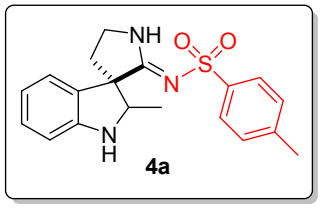
According to the general procedure, **3la** was obtained in 95% yield (76 mg). White solid, mp = 191.2 – 192.5 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.41 (s, 1H), 7.72 (d, *J* = 6.8 Hz, 2H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.39 – 7.28 (m, 2H), 7.20 (t, *J* = 8.4 Hz, 3H), 7.10 (t, *J* = 7.3 Hz, 1H), 7.01 (t, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 7.4 Hz, 1H), 6.66 (d, *J* = 7.5 Hz, 1H), 2.38 (s, 3H), 1.87 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.8, 166.8, 157.2, 143.6, 142.9, 138.9, 138.2, 129.9, 129.6, 129.5, 126.6, 126.5, 126.5, 124.7, 123.5, 122.9, 120.7, 111.9, 73.2, 21.7, 16.1. **HRMS (ESI)** calcd for $[M+H]^+$ $C_{23}H_{20}N_3O_2S^+$, m/z: 402.1271, found: 402.1275. **IR (thin film):** ν_{max} 1627, 1607, 1273, 1142, 1088, 790, 749, 564 cm^{-1}.

4-methyl-*N*-(spiro[indoline-3,3'-pyrrolidin]-2'-ylidene)benzenesulfonamide (3ma)



According to the general procedure, **3ma** was obtained in 83% yield (55 mg). White solid, mp = 128.3 – 129.9 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.34 (s, 1H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.07 – 7.00 (m, 1H), 6.76 (d, *J* = 7.2 Hz, 1H), 6.64 (t, *J* = 7.5 Hz, 2H), 3.97 (d, *J* = 9.5 Hz, 1H), 3.66 – 3.53 (m, 2H), 3.35 (d, *J* = 9.5 Hz, 1H), 2.36 (s, 3H), 2.25 – 2.15 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 172.3, 150.8, 142.7, 139.3, 131.5, 129.3, 129.0, 126.2, 122.6, 119.2, 110.6, 58.1, 56.8, 44.2, 35.6, 21.5. **HRMS (ESI)** cacd for $[M+H]^+$ $C_{18}H_{20}N_3O_2S^+$, m/z: 342.1271, found: 342.1279. **IR (thin film):** ν_{max} 3320, 1603, 1485, 1247, 1137, 1084, 875, 738, 558 cm^{-1}.

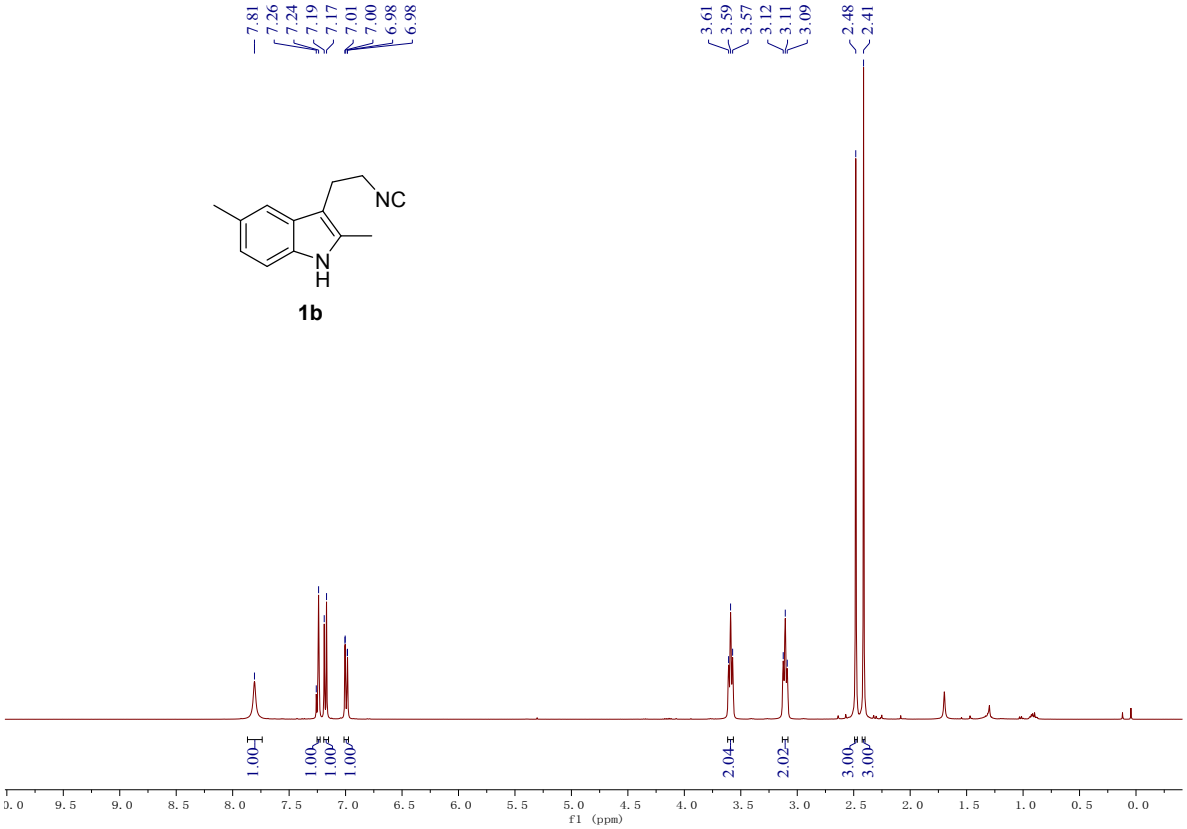
4-methyl-*N*-2-methylspiro[indoline-3,3'-pyrrolidin]-2'-ylidene)benzenesulfonamide (4a)

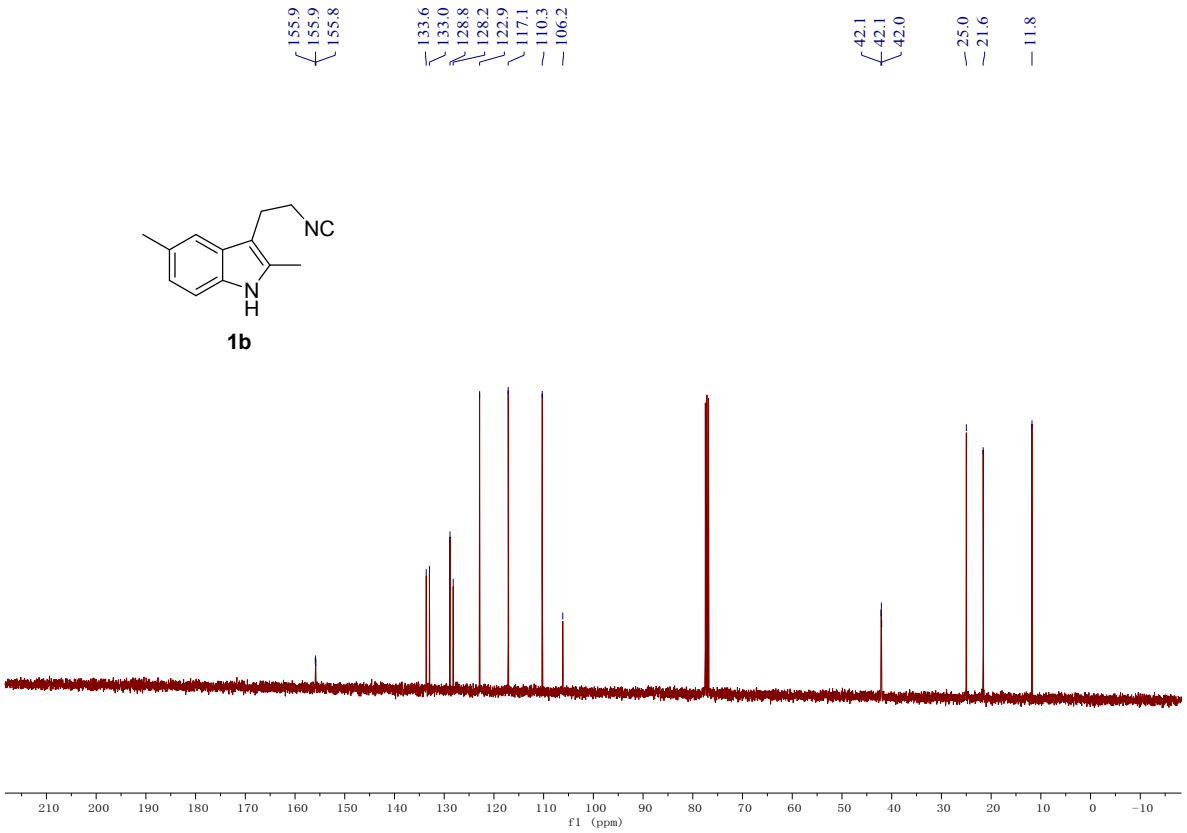


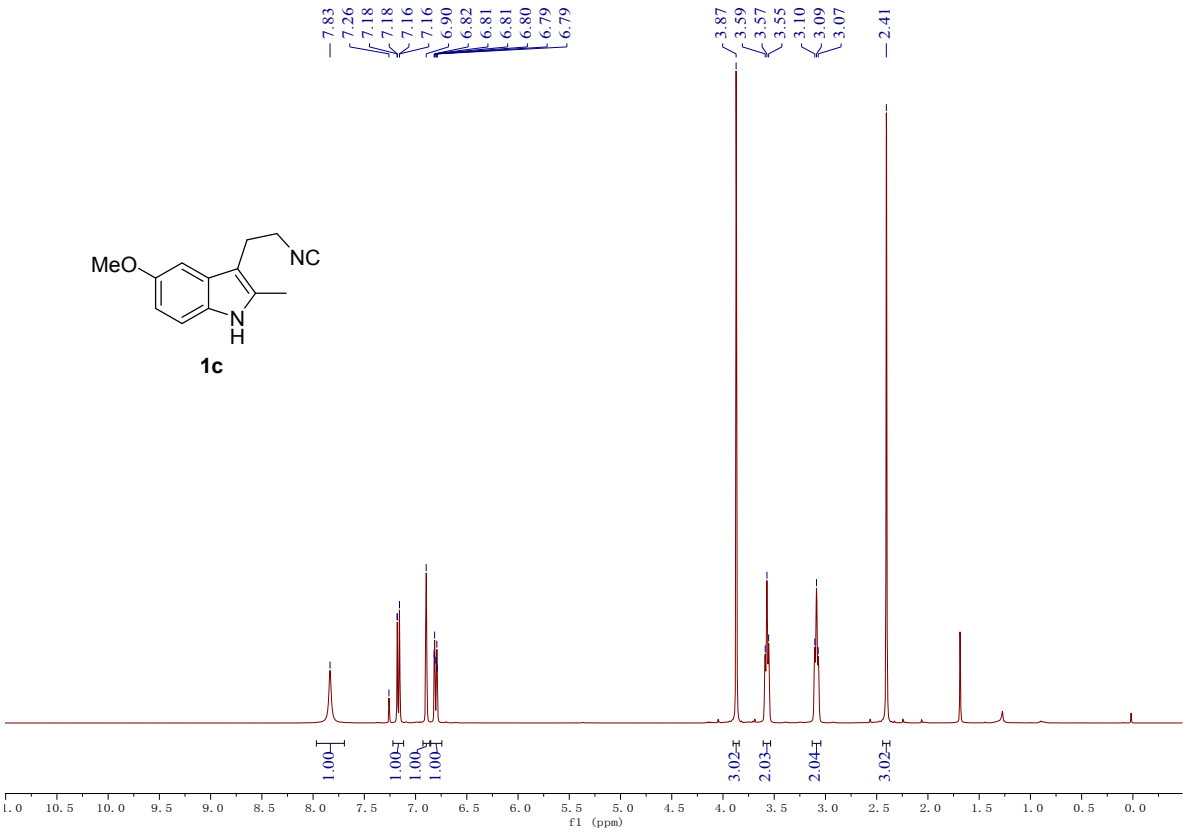
According to the general procedure, **4a** was obtained in 78% yield (55 mg). White solid, mp = 226.5 – 227.8 °C. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 8.73 (s, 1H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.90 – 6.83 (m, 1H), 6.77 (d, *J* = 7.2 Hz, 1H), 6.44 (t, *J* = 7.3 Hz, 1H), 6.36 (d, *J* = 7.7 Hz, 1H), 5.42 (s, 1H), 3.75 – 3.64 (m, 1H), 3.48 – 3.37 (m, 2H), 2.23 (s, 3H), 2.21 – 2.11 (m, 1H), 2.01 – 1.92 (m, 1H), 0.79 (d, *J*

= 6.5 Hz, 3H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 169.5, 152.0, 142.1, 140.0, 130.9, 129.2, 128.4, 126.1, 123.8, 117.3, 108.8, 64.5, 60.4, 44.4, 35.1, 21.0, 16.3. **HRMS (ESI)** cacd for $[M+Na]^+$ $C_{19}H_{21}N_3NaO_2S^+$, m/z: 378.1245, found: 378.1247. **IR (thin film):** ν_{max} 1586, 1258, 1143, 1081, 866, 724, 631, 540 cm^{-1}.

8. ^{1}H, ^{13}C and ^{19}F NMR spectra of new substrates and all products



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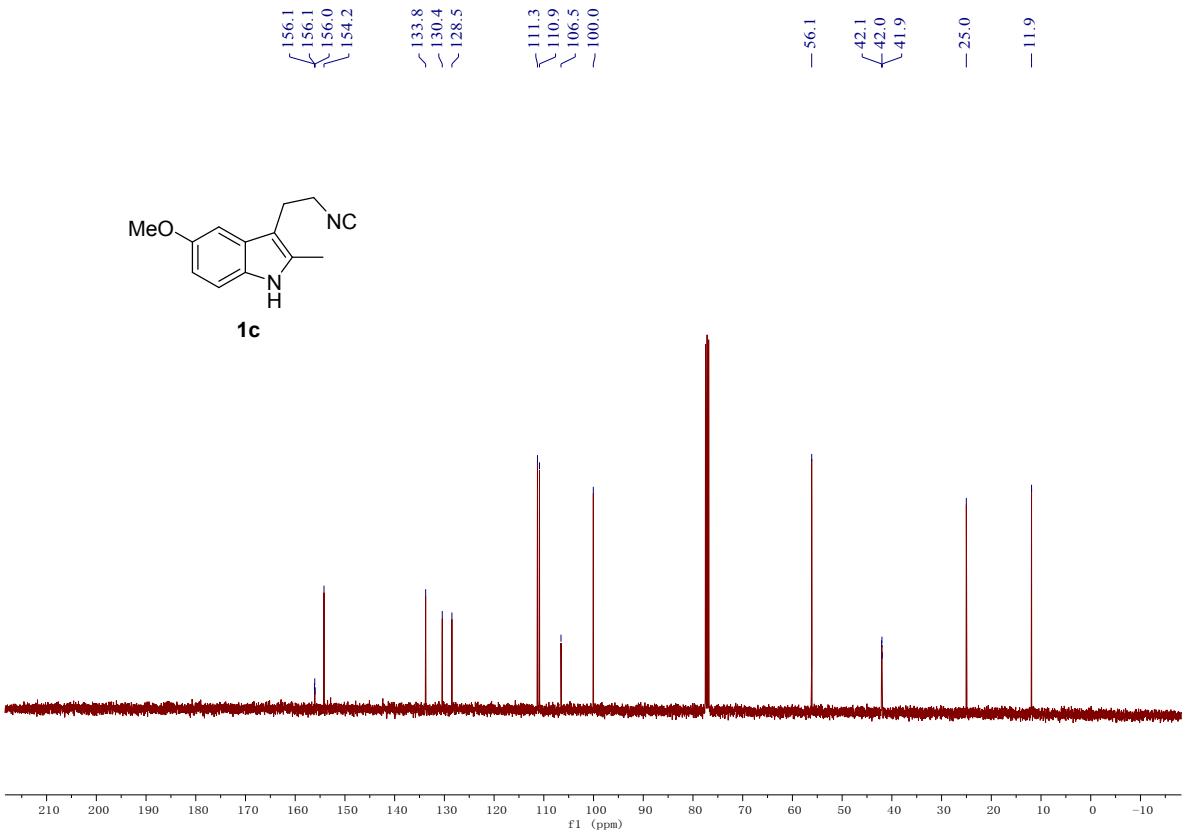
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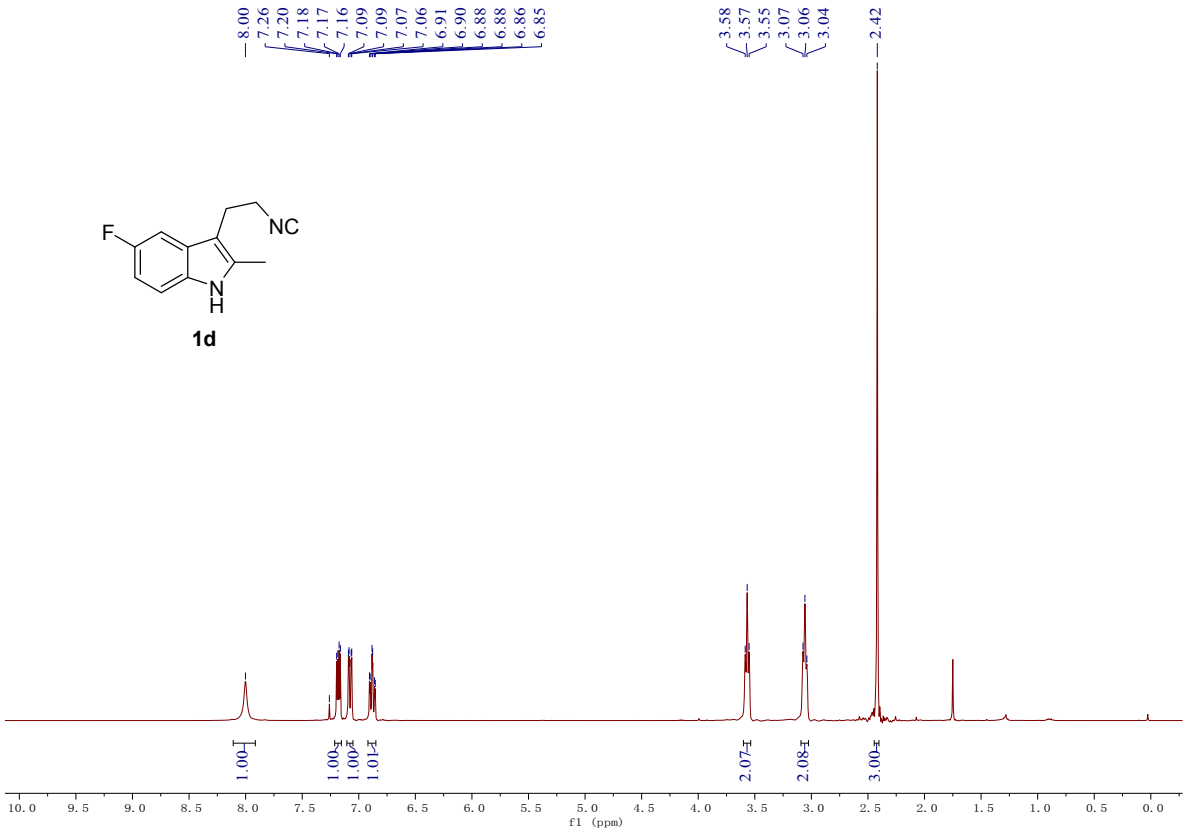
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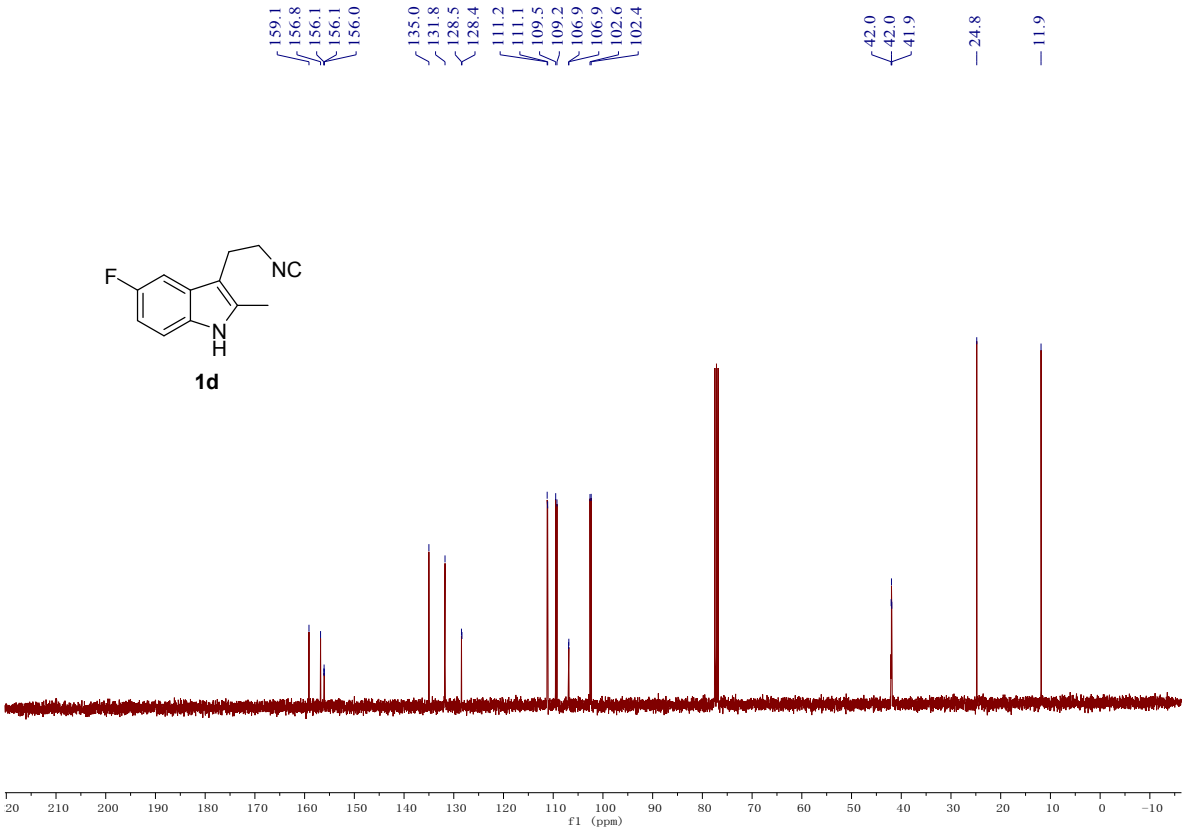
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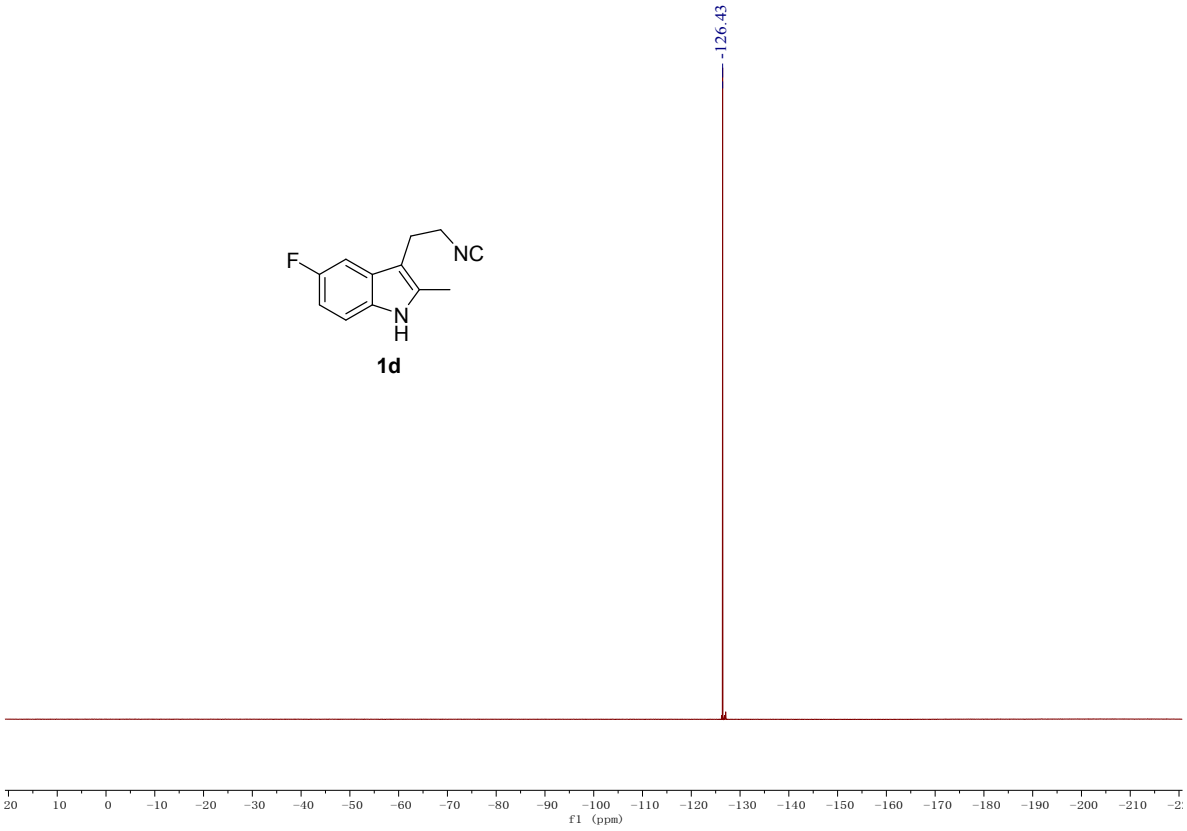
f1 (ppm)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N
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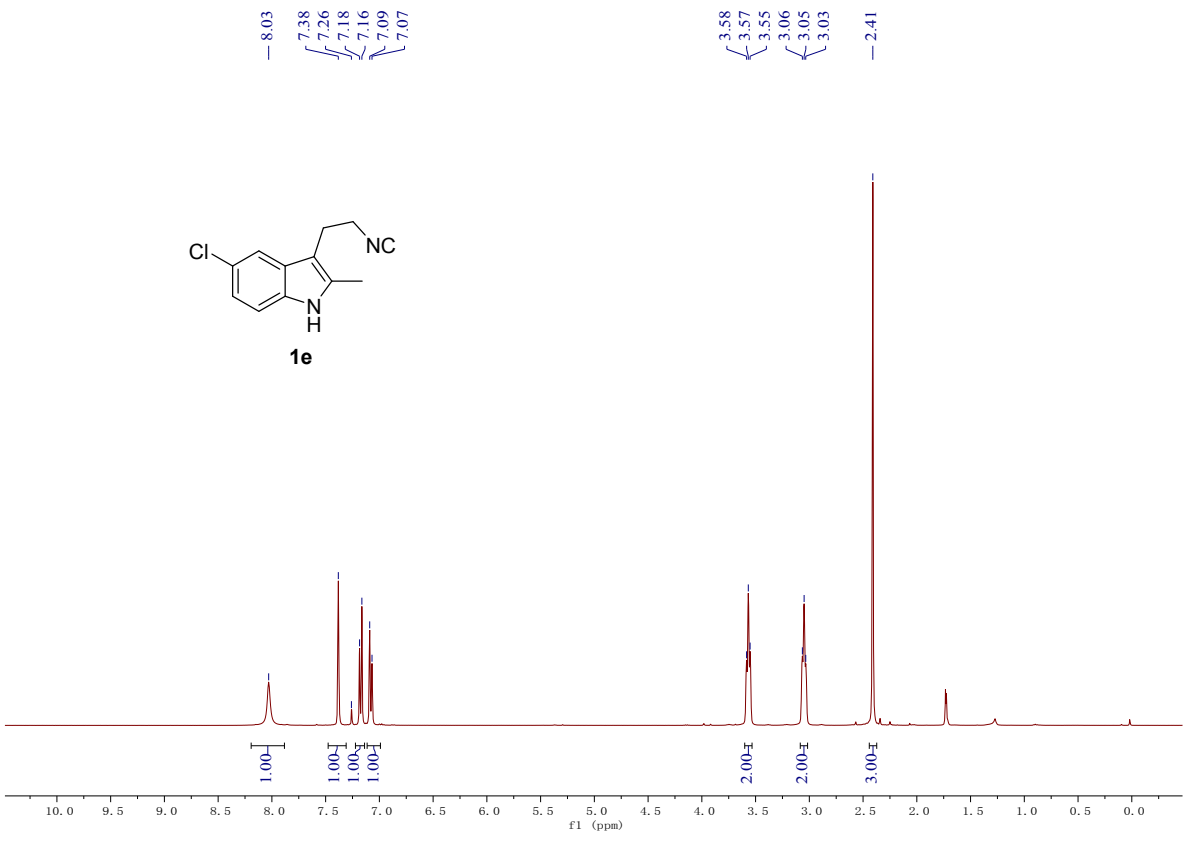
f1 (ppm)

1d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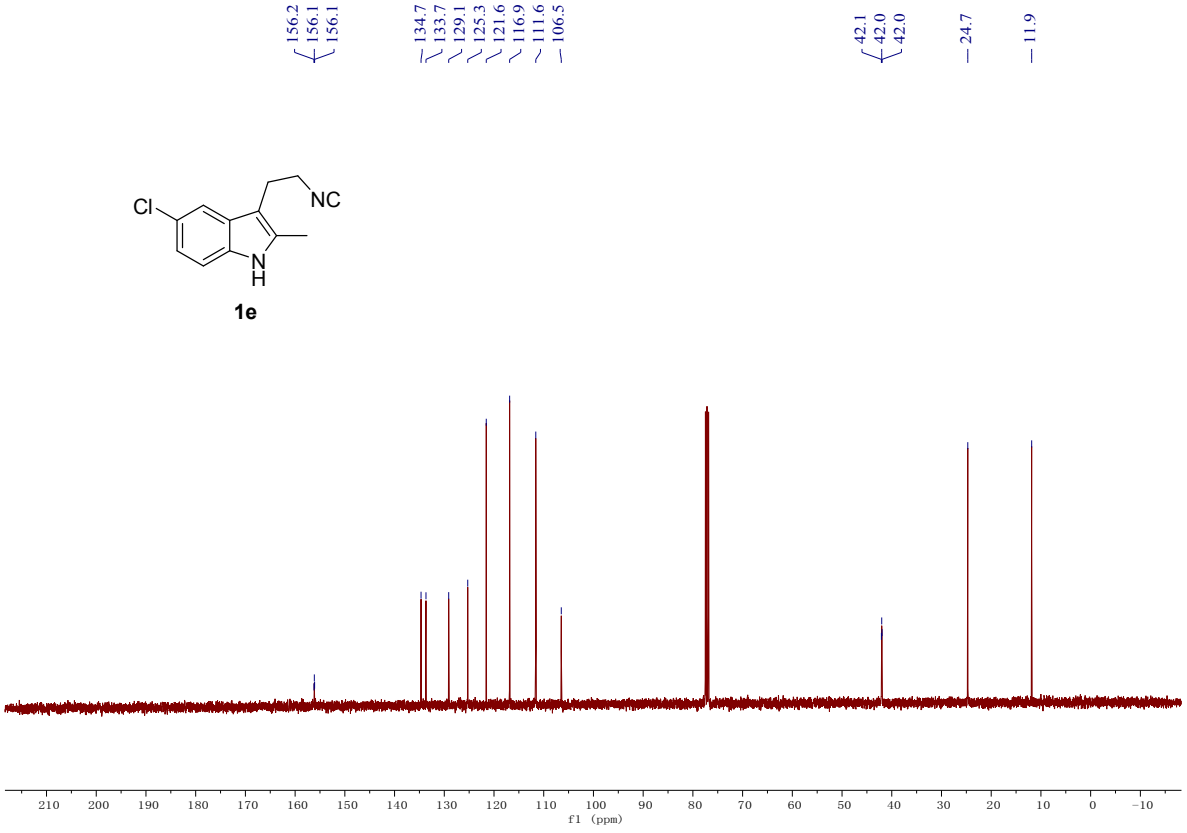
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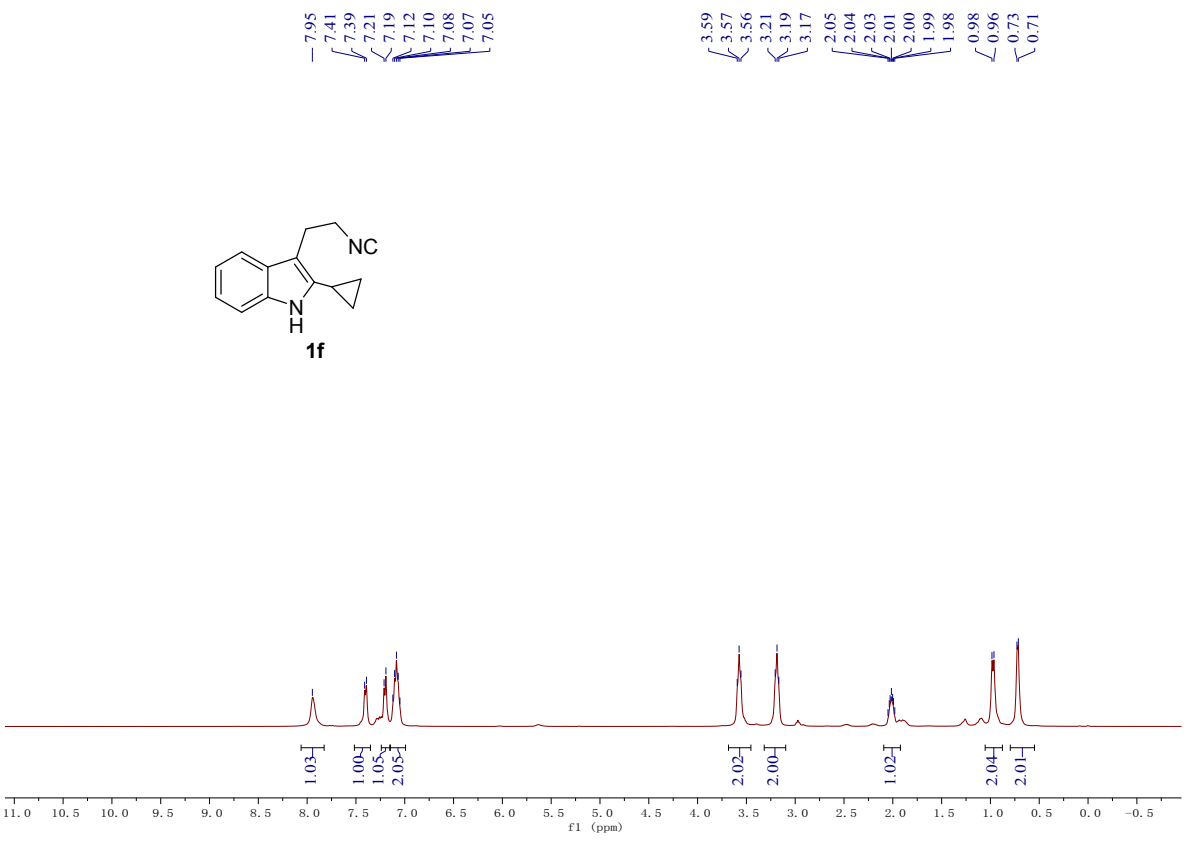
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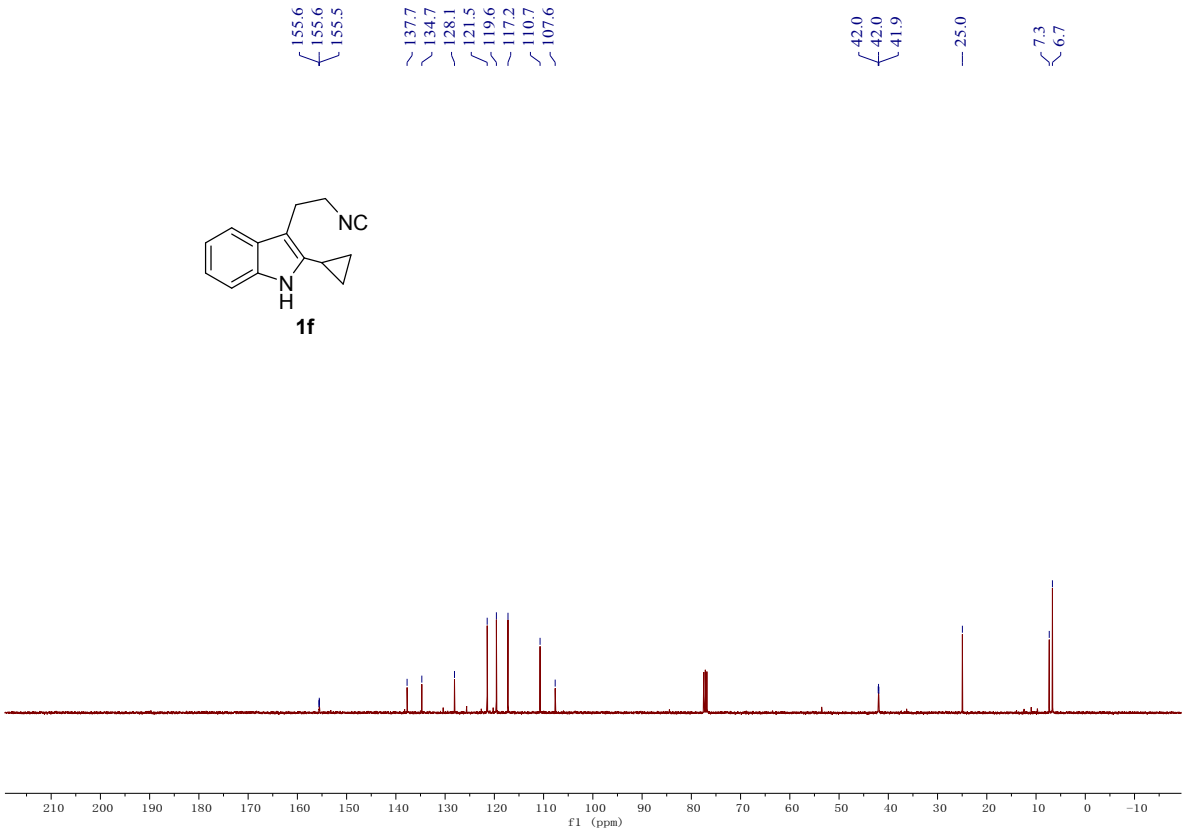
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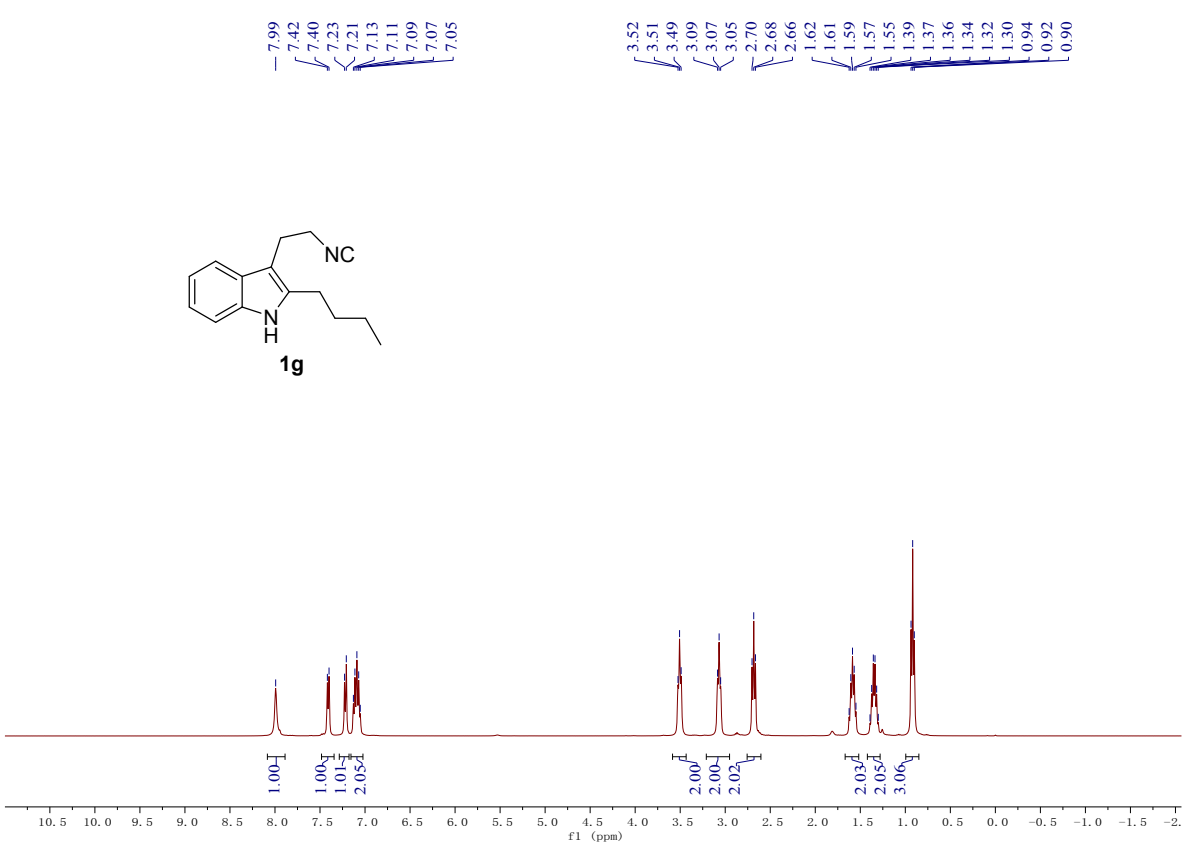
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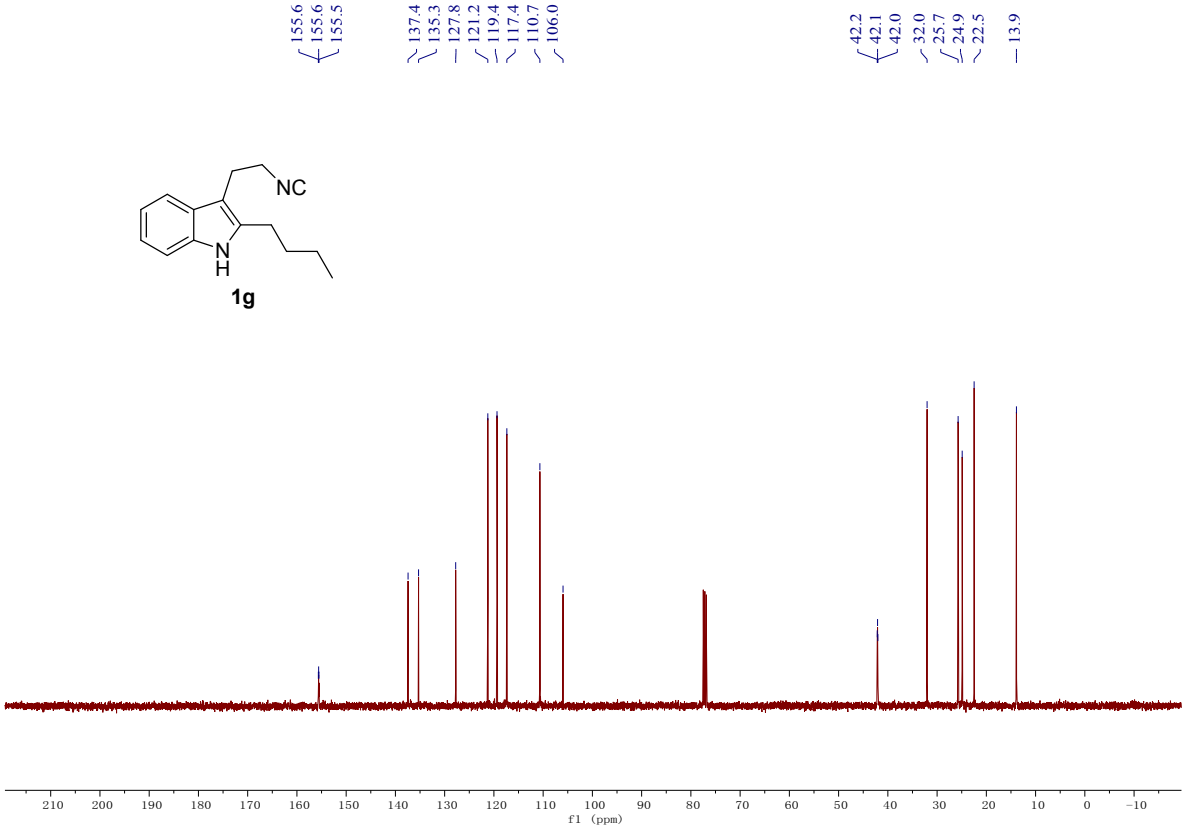
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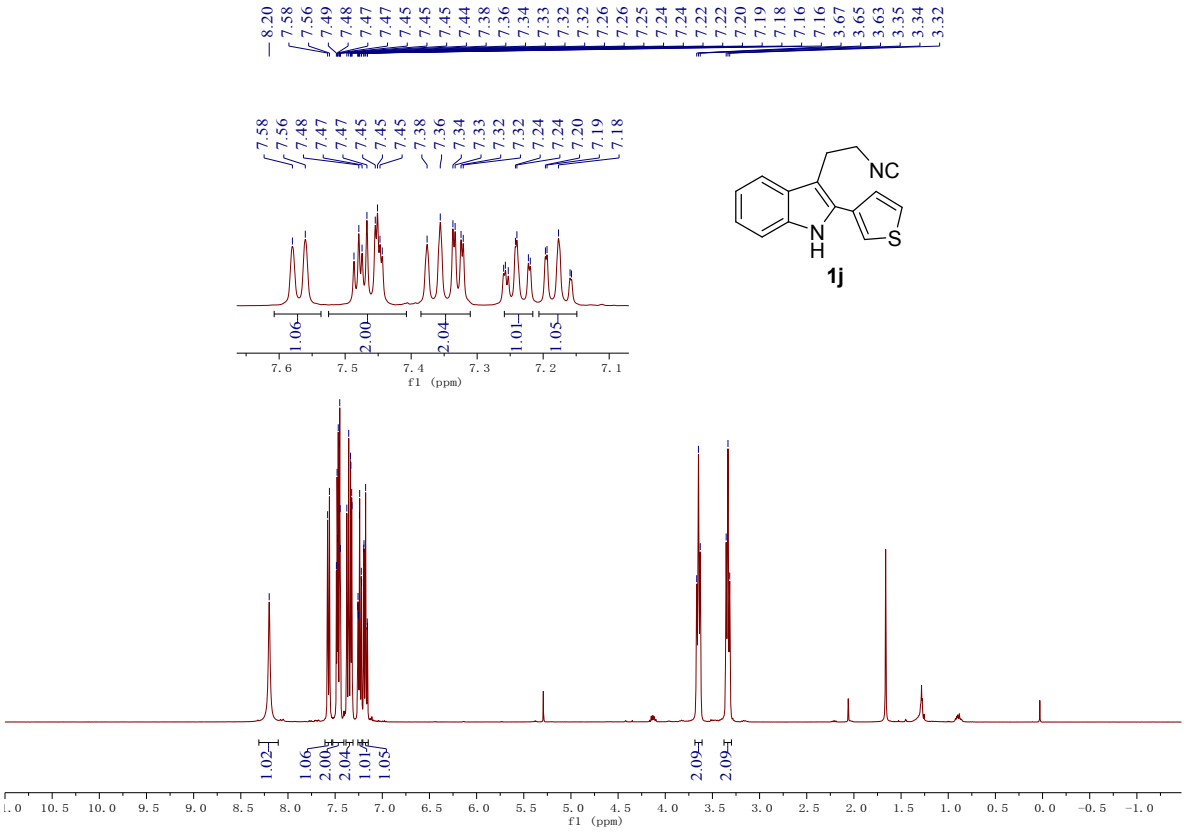
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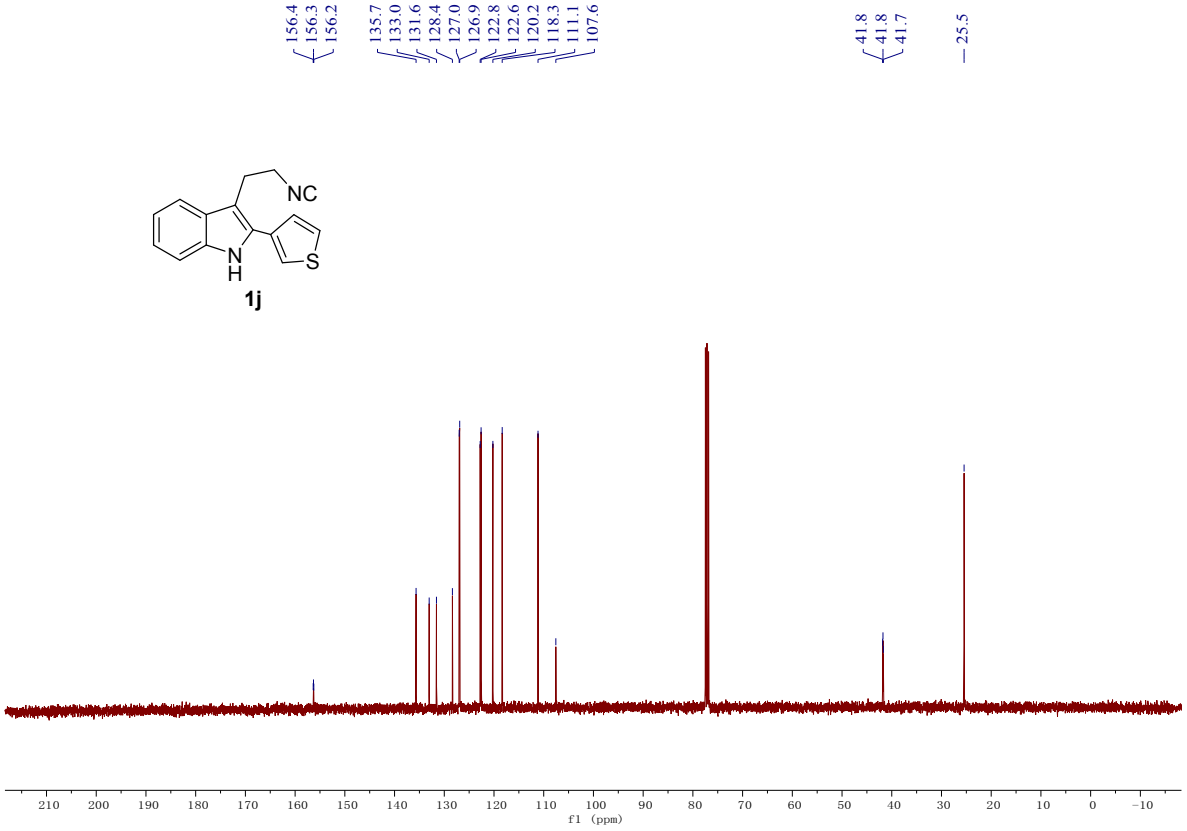
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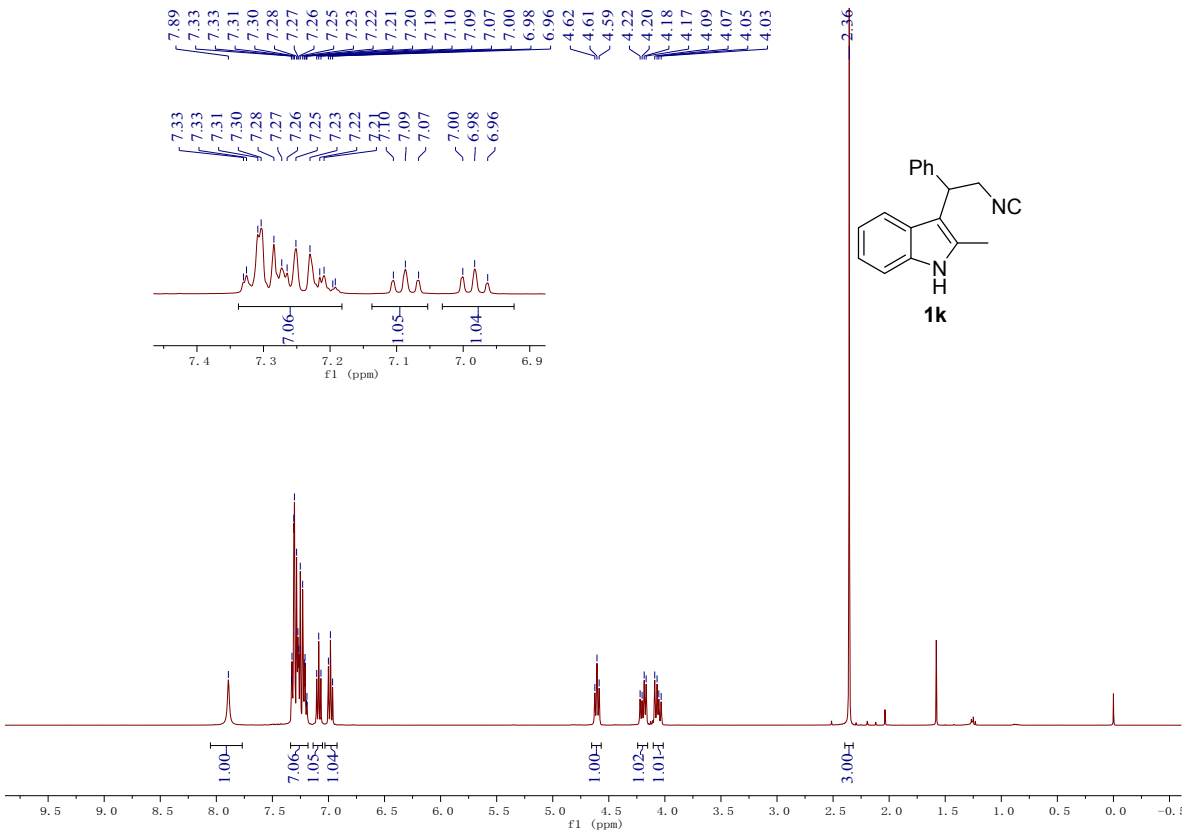
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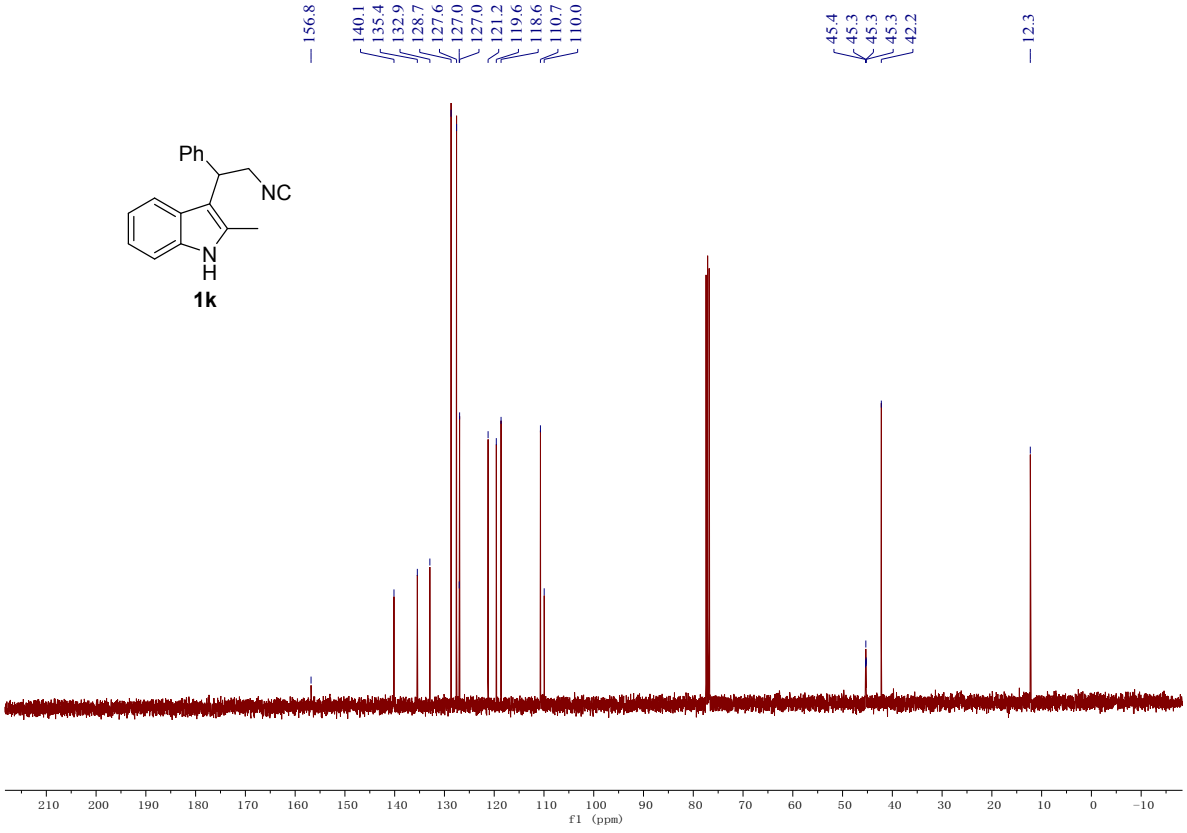
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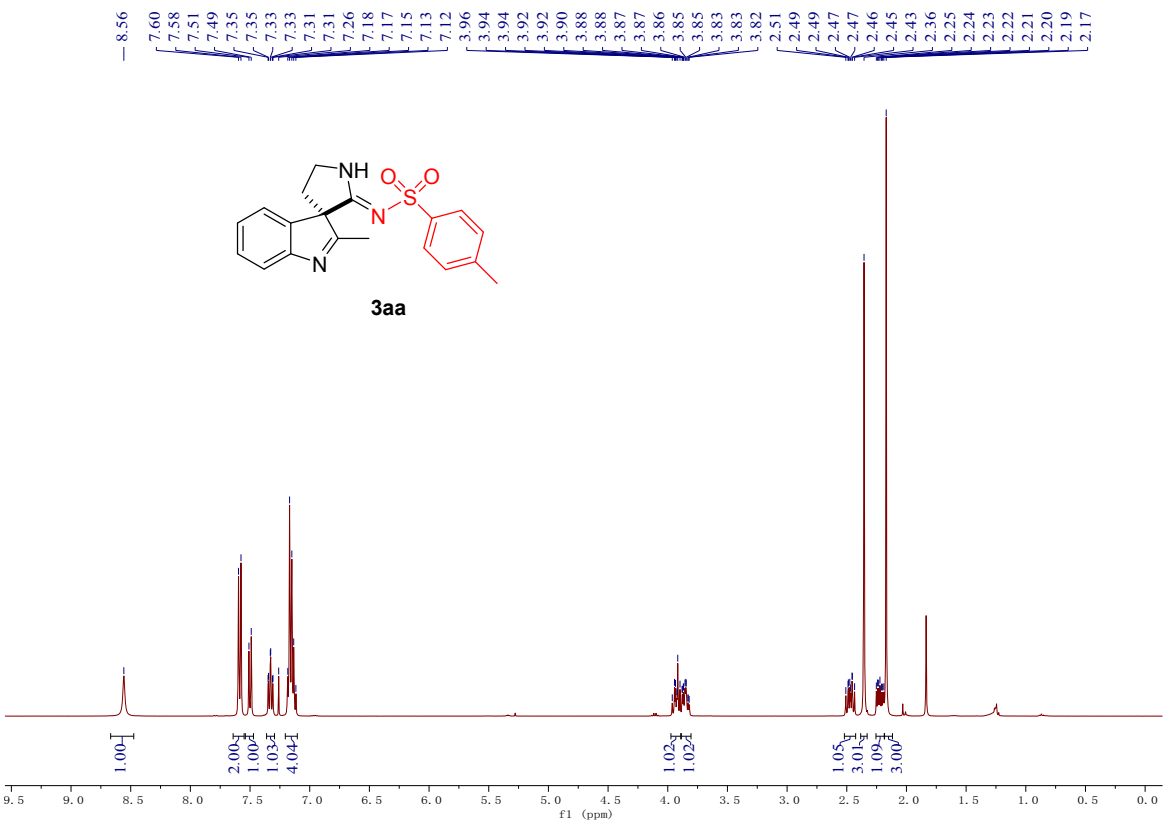
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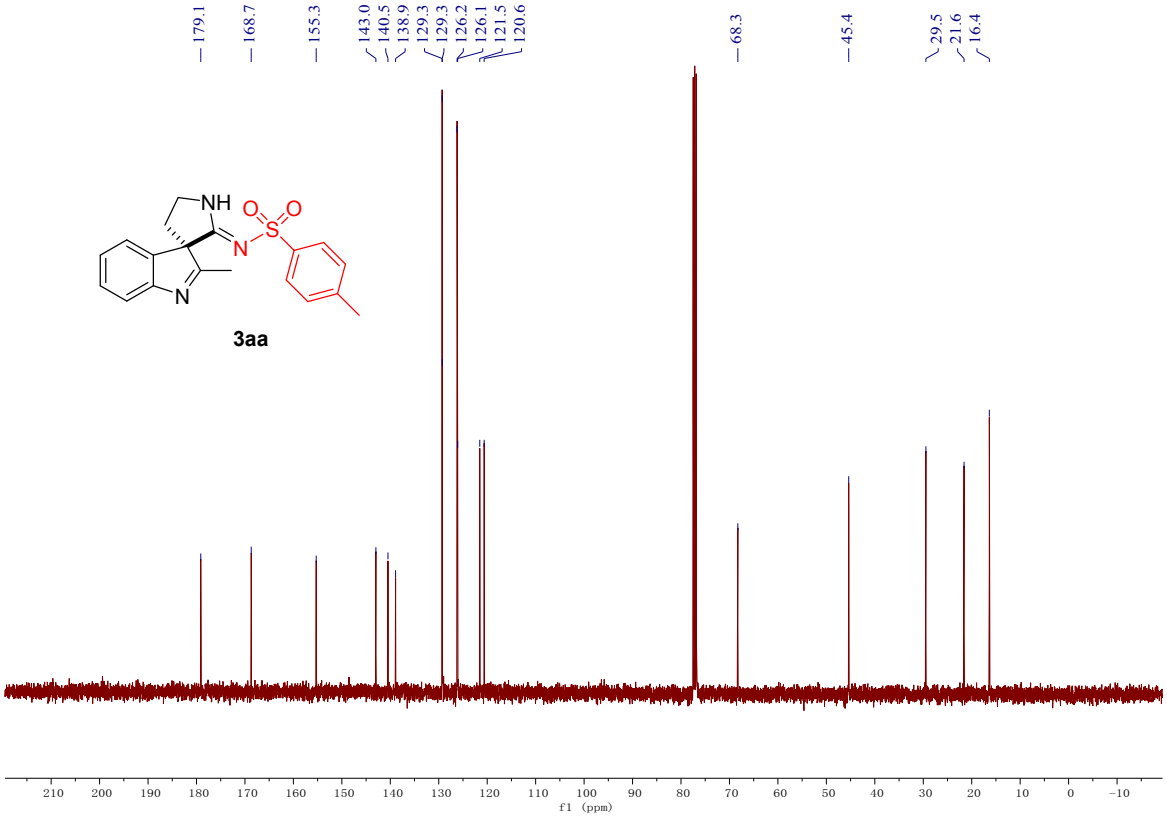
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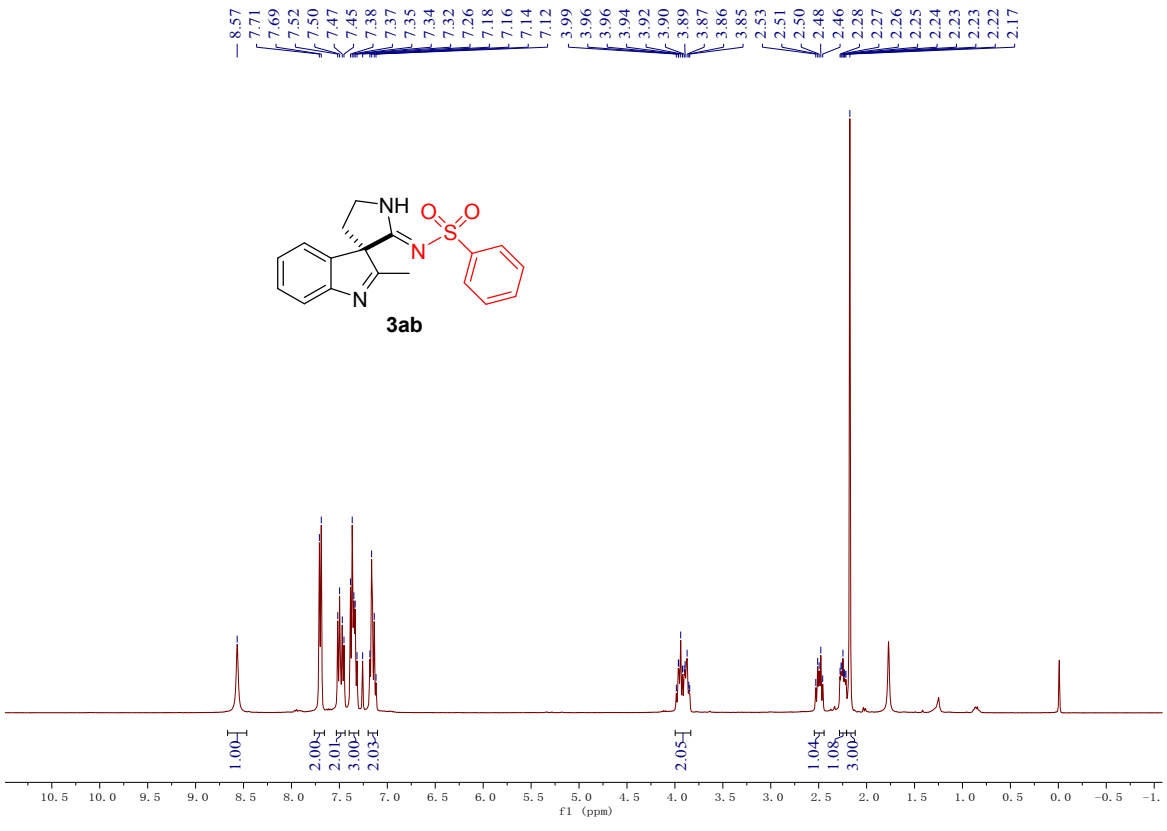
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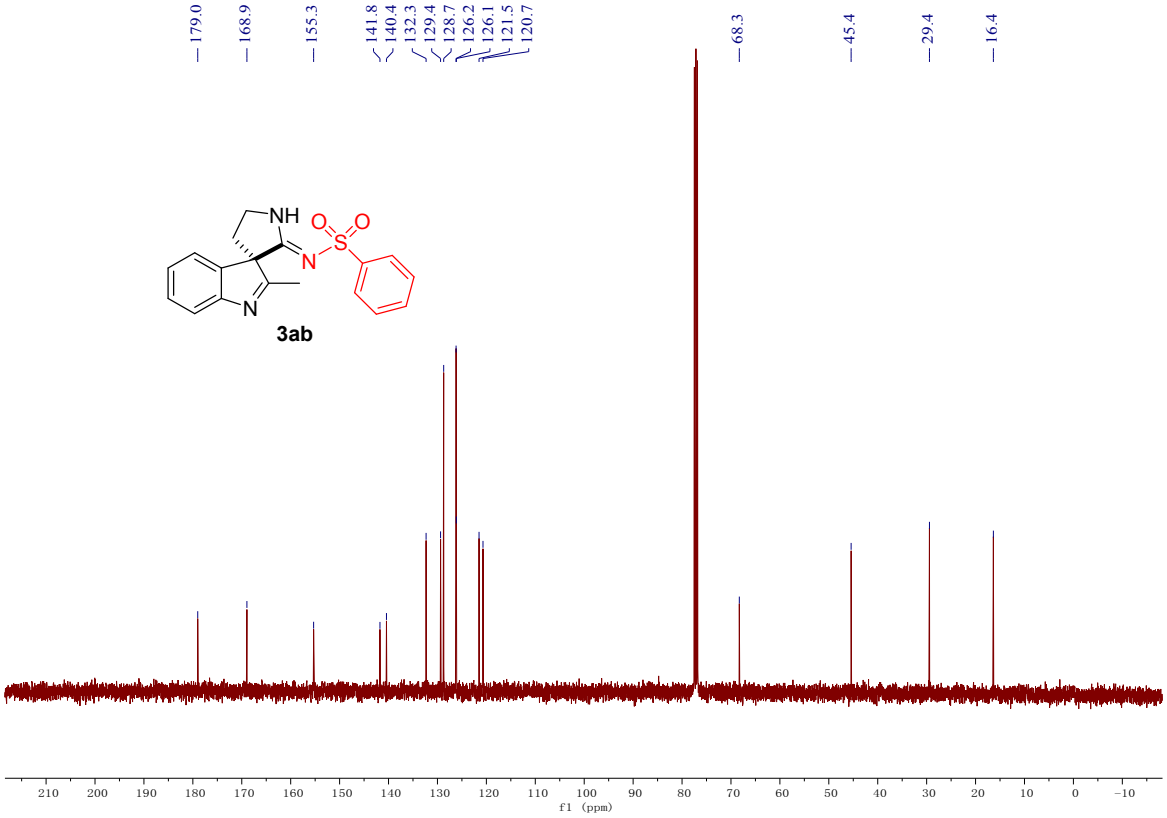
f1 (ppm)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168.9
155.3
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140.4
132.3
129.4
128.7
126.2
126.1
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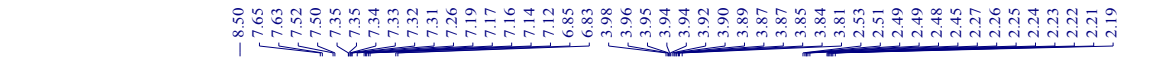
68.3
45.4
29.4
16.4
NH
O
O
S
N
N
3ab
f1 (ppm)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7.32
7.31
7.26
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7.17
7.16
7.14
7.12
6.85
6.83
3.98
3.96
3.95
3.94
3.94
3.92
3.90
3.89
3.87
3.87
3.85
3.84
3.81
2.53
2.51
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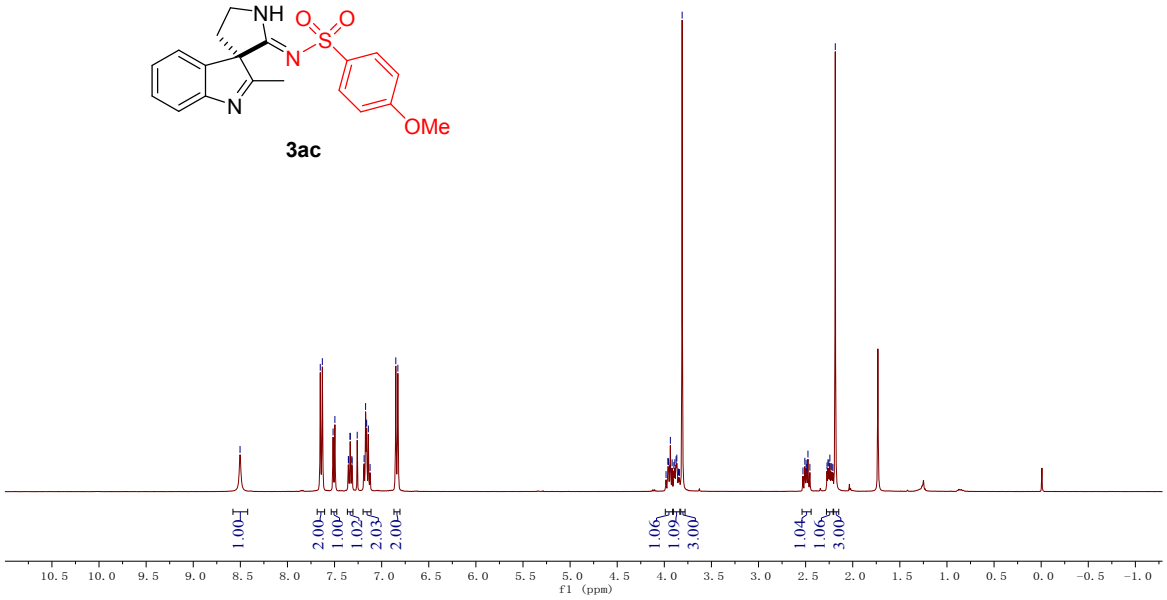
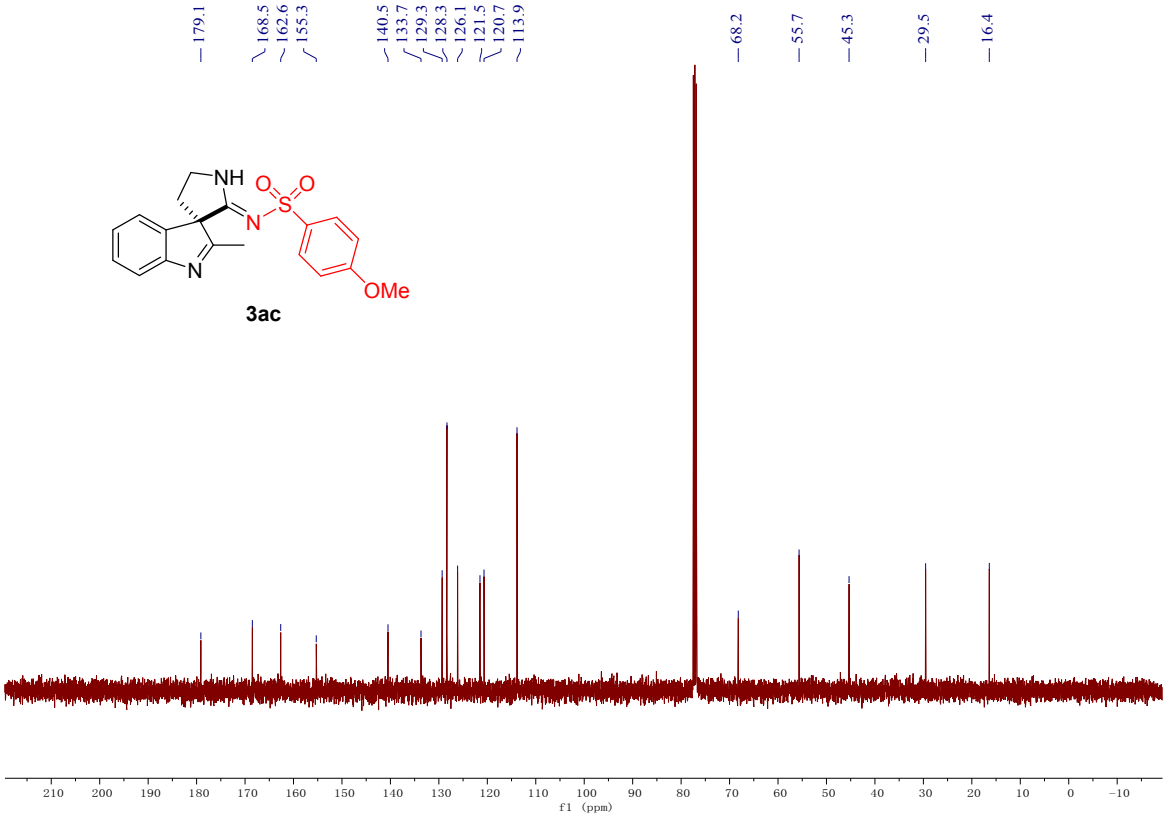
2.26
2.25
2.24
2.23
2.22
2.21
2.19


NH
O
O
S
N
N
OMe
3ac
1.00
2.00
1.00
1.02
2.03
2.00
1.06
1.09
3.00
1.04
1.06
3.00
f1 (ppm)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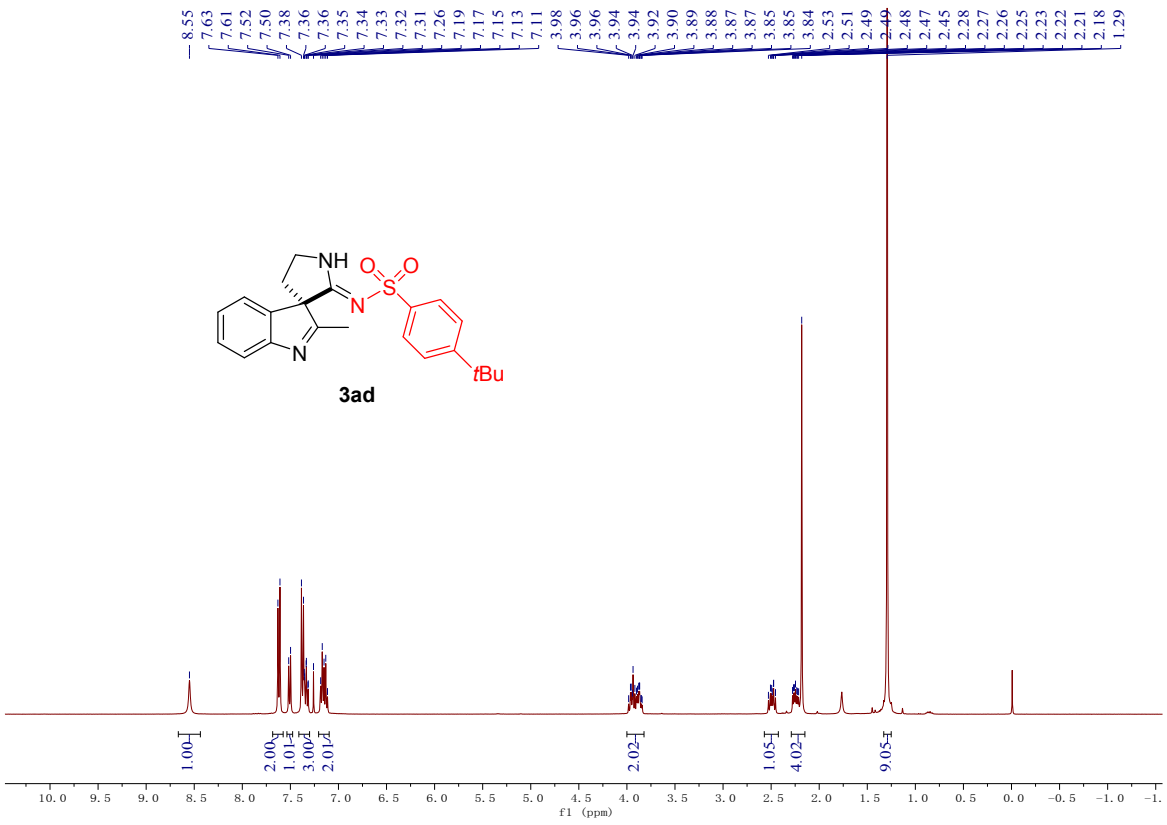
140.5
133.7
129.3
128.3
126.1
121.5
120.7
113.9
68.2
55.7
45.3
29.5
16.4
NH
O
O
N
S
N
OMe
f1 (ppm)

3ac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7.33
7.32
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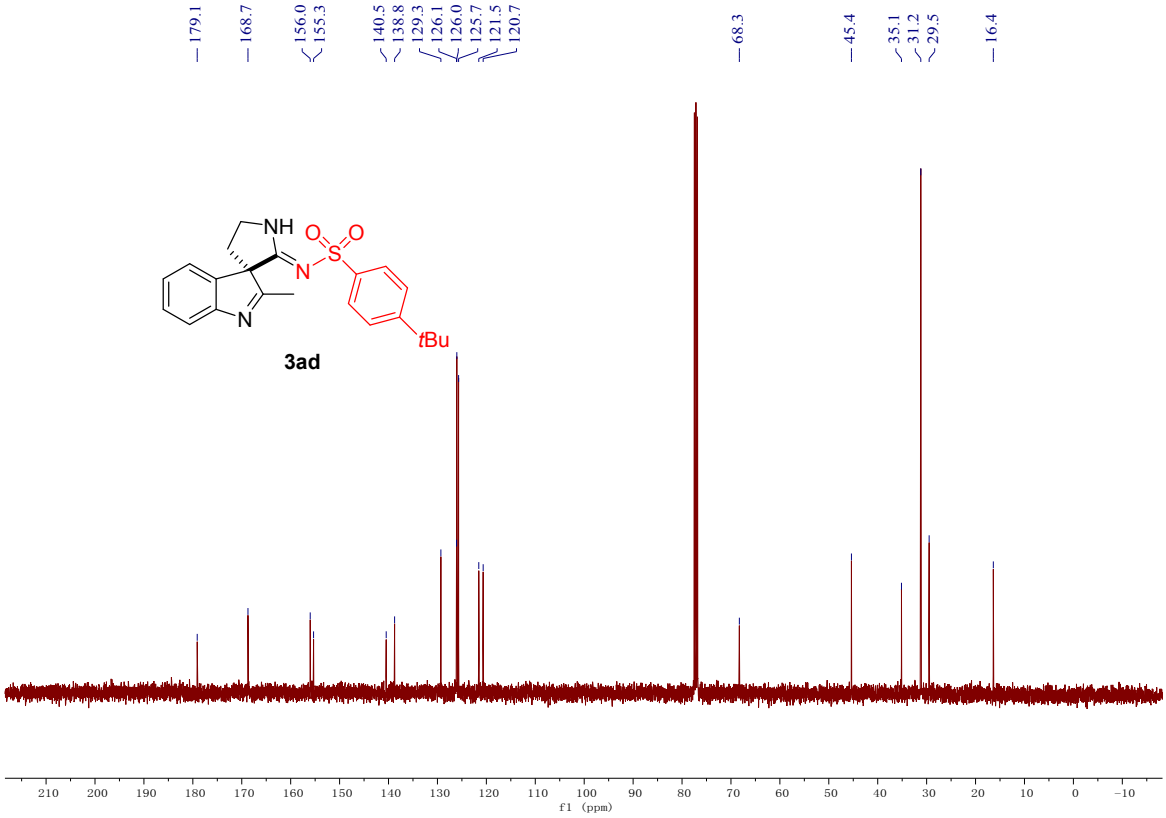
7.26
7.19
7.17
7.15
7.13
7.11
3.98
3.96
3.96
3.94
3.94
3.92
3.90
3.89
3.88
3.87
3.87
3.85
3.85
3.84
2.53
2.51
2.49
2.49
2.48
2.47
2.45
2.28
2.27
2.26
2.25
2.23
2.22
2.21
2.18
1.29
NH
O
O
N
S
N
tBu
1.00
2.00
1.01
3.00
2.01
2.02
1.05
4.02
9.05
f1 (ppm)

3ad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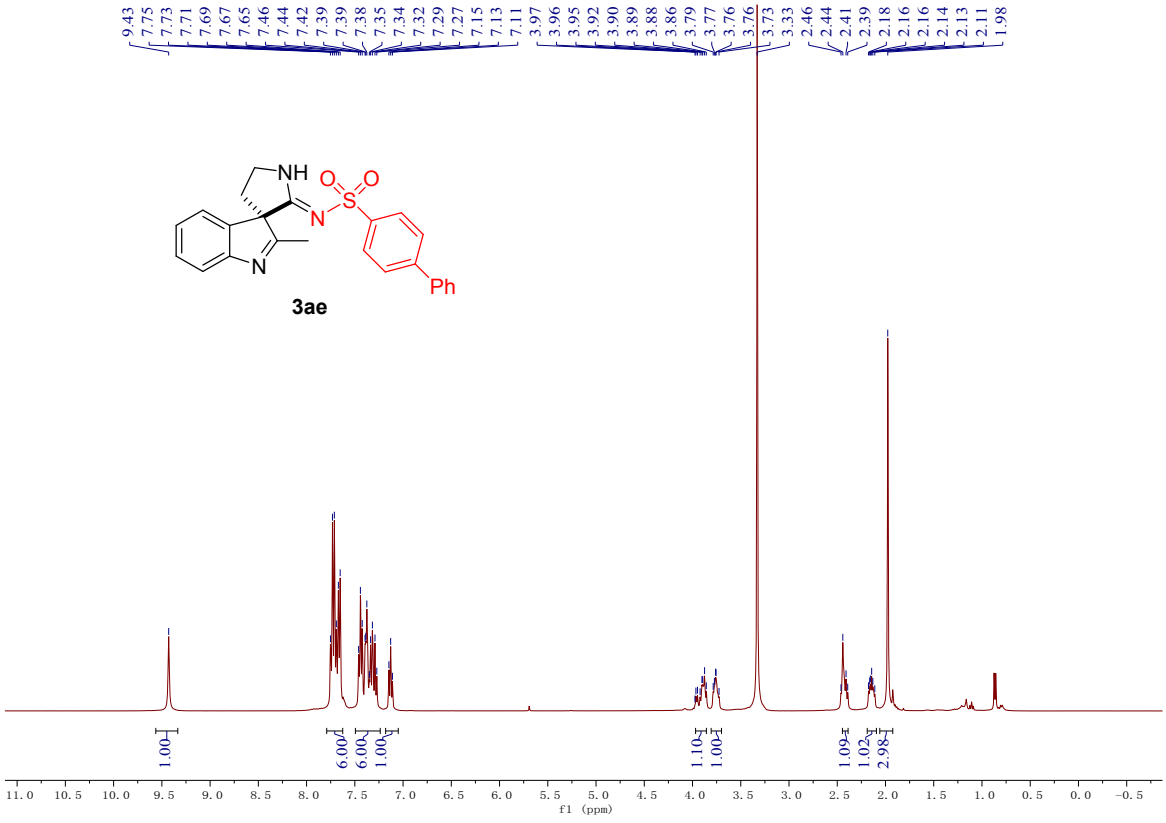
155.3
140.5
138.8
129.3
126.1
126.0
125.7
121.5
120.7
68.3
45.4
35.1
31.2
29.5
16.4
NH
O
S
O
N
N
tBu
3ad
f1 (ppm)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7.42
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7.39
7.38
7.35
7.34
7.32
7.29
7.27
7.15
7.13
7.11
3.97
3.96
3.95
3.92
3.90
3.89
3.88
3.86
3.79
3.77
3.76
3.76
3.73
3.33
2.46
2.44
2.41
2.39
2.18
2.16
2.16
2.14
2.13
2.11
1.98
NH
O
S
O
N
N
Ph
3ae
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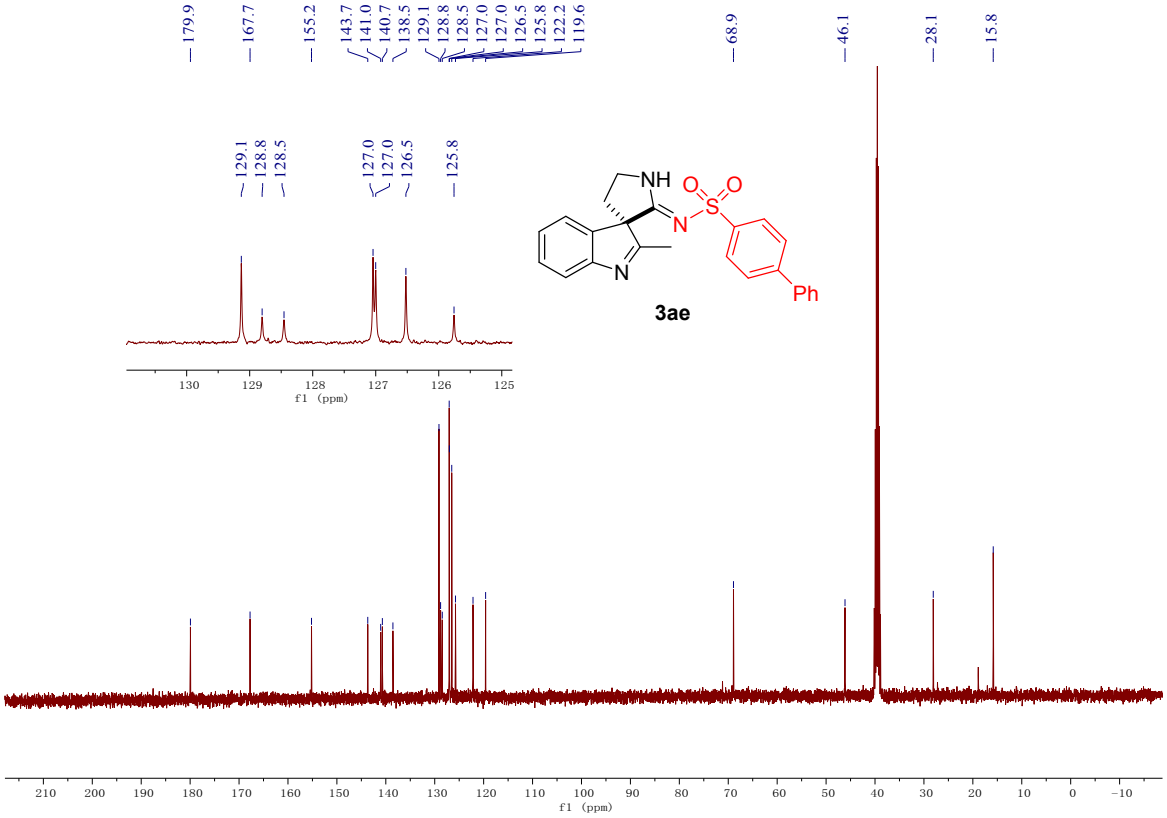
6.00
6.00
1.00
1.10
1.00
1.09
1.02
2.98
f1 (ppm)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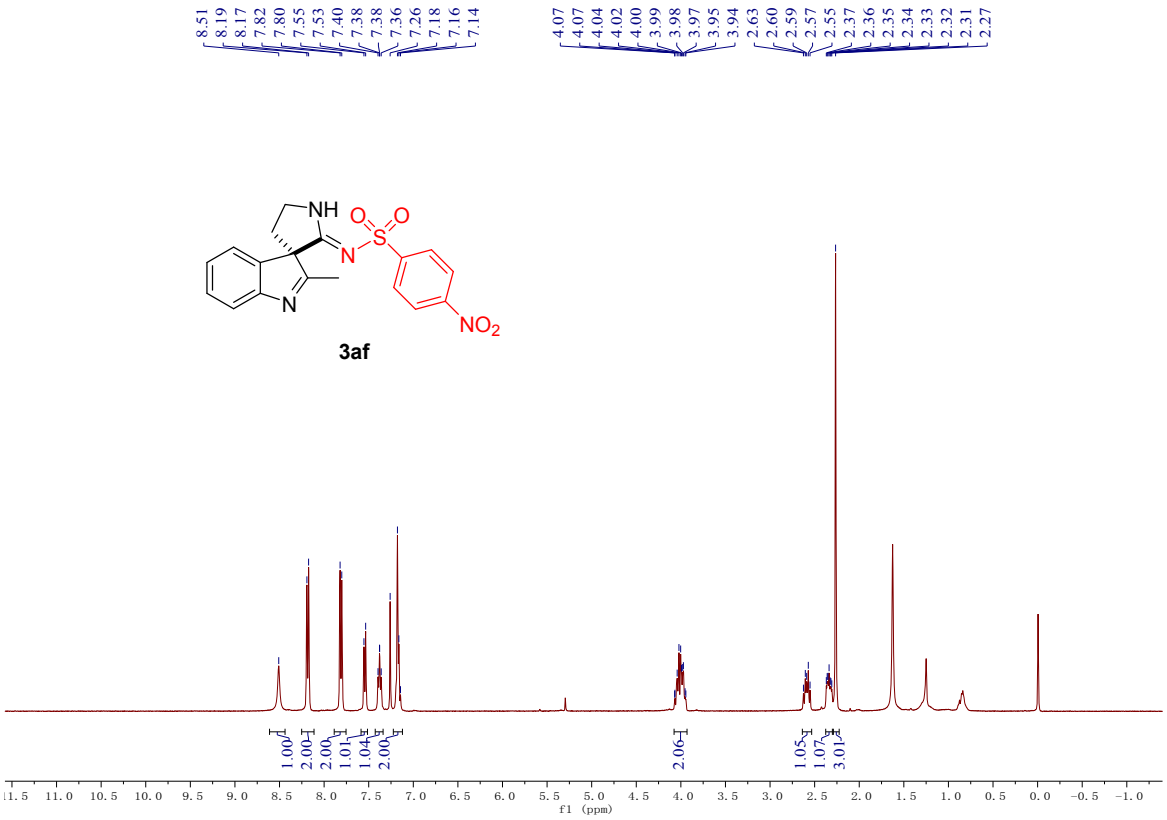
167.7
155.2
143.7
141.0
140.7
138.5
129.1
128.8
128.5
127.0
127.0
126.5
125.8
122.2
119.6
68.9
46.1
28.1
15.8
129.1
128.8
128.5
127.0
127.0
126.5
125.8
NH
O
O
S
N
N
Ph
3ae
f1 (ppm)
f1 (ppm)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8.17
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7.80
7.55
7.53
7.40
7.38
7.38
7.36
7.26
7.18
7.16
7.14
4.07
4.07
4.04
4.02
4.00
3.99
3.98
3.97
3.95
3.94
2.63
2.60
2.59
2.57
2.55
2.37
2.36
2.35
2.34
2.33
2.32
2.31
2.27
NH
O
O
S
N
N
NO2
3af
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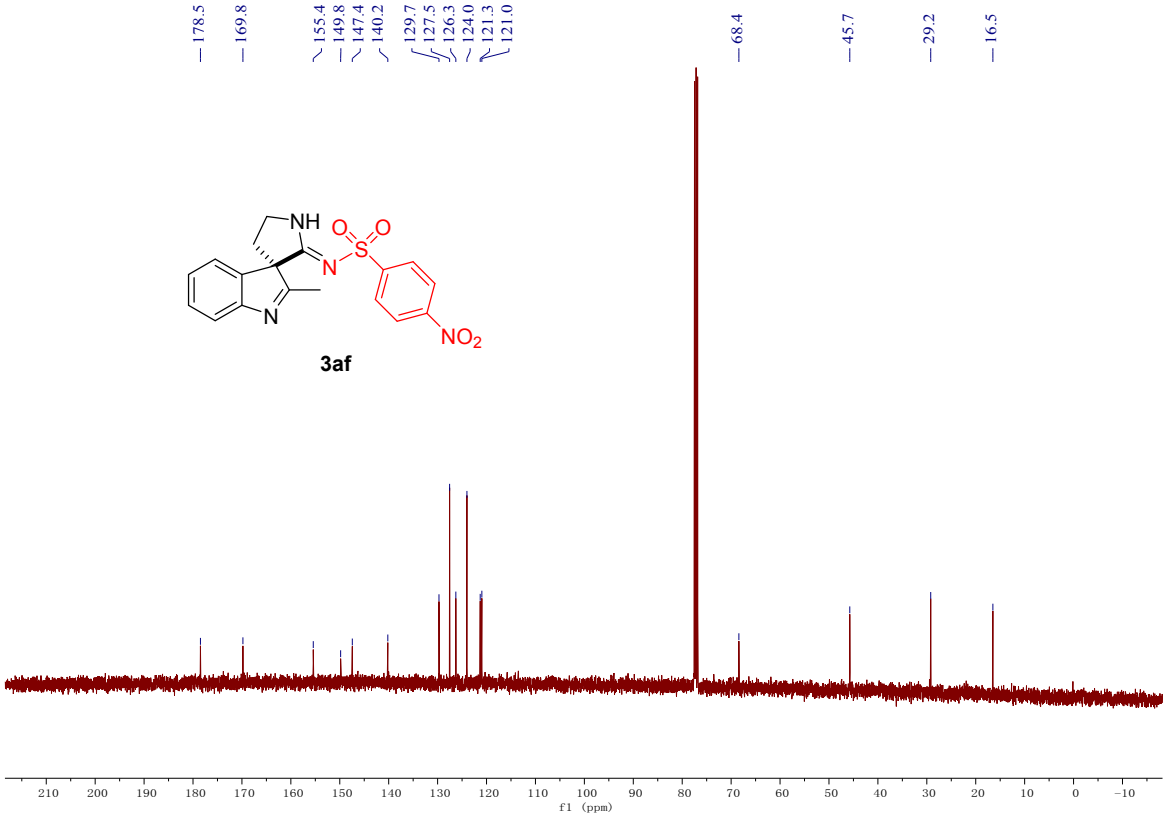
2.00
2.00
1.01
1.04
2.00
2.06
1.05
1.07
3.01
f1 (ppm)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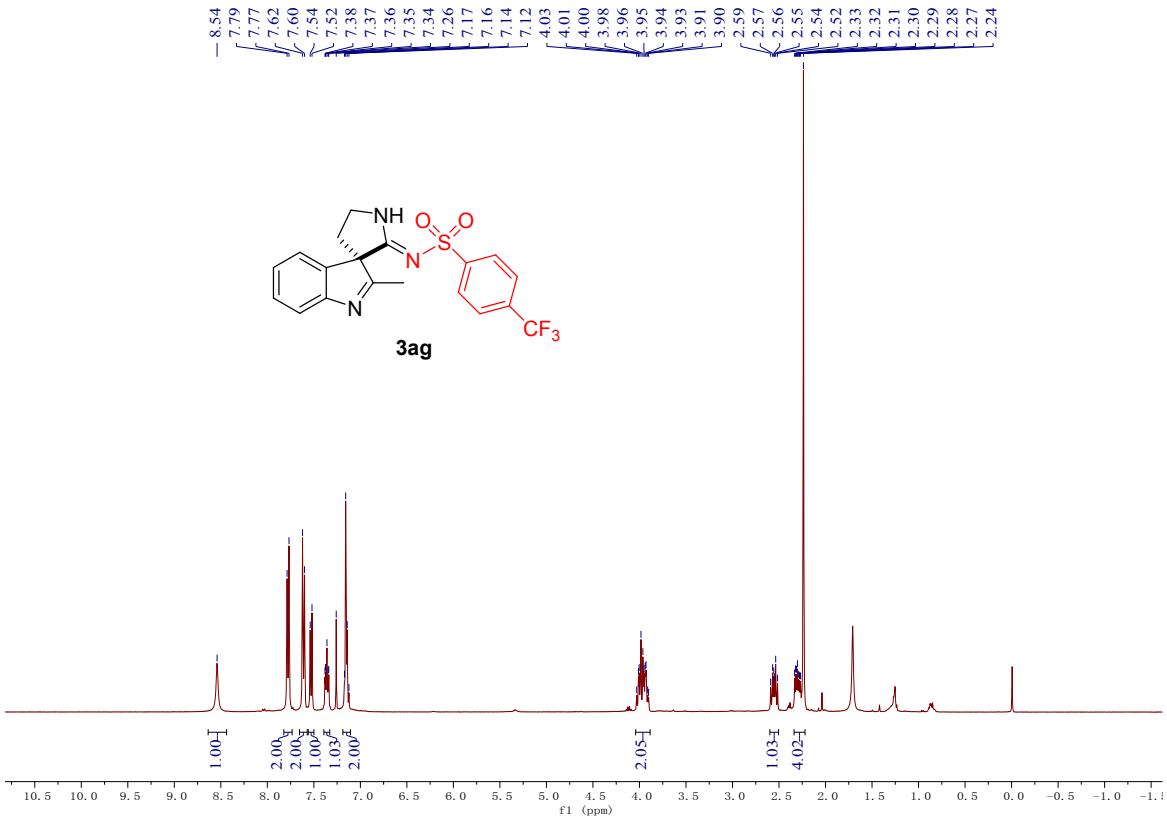
169.8
155.4
149.8
147.4
140.2
129.7
127.5
126.3
124.0
121.3
121.0
68.4
45.7
29.2
16.5
NH
O
O
S
N
N
NO2
f1 (ppm)

3af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7.54
7.52
7.38
7.37
7.36
7.35
7.34
7.26
7.17
7.16
7.14
7.12
4.03
4.01
4.00
3.98
3.96
3.95
3.94
3.93
3.91
3.90
2.59
2.57
2.56
2.55
2.54
2.52
2.33
2.32
2.31
2.30
2.29
2.28
2.27
2.24
NH
O
O
S
N
N
CF3
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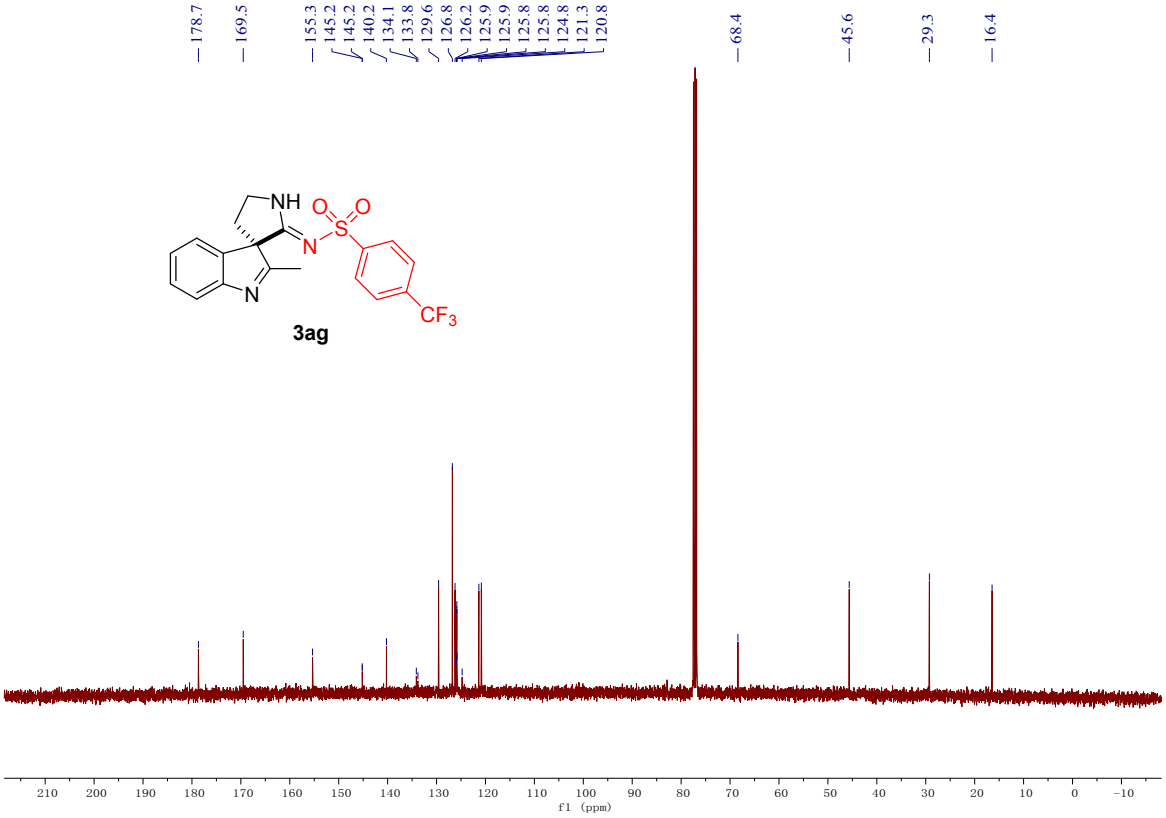
2.00
2.00
1.00
1.03
2.00
2.05
1.03
4.02
f1 (ppm)

3ag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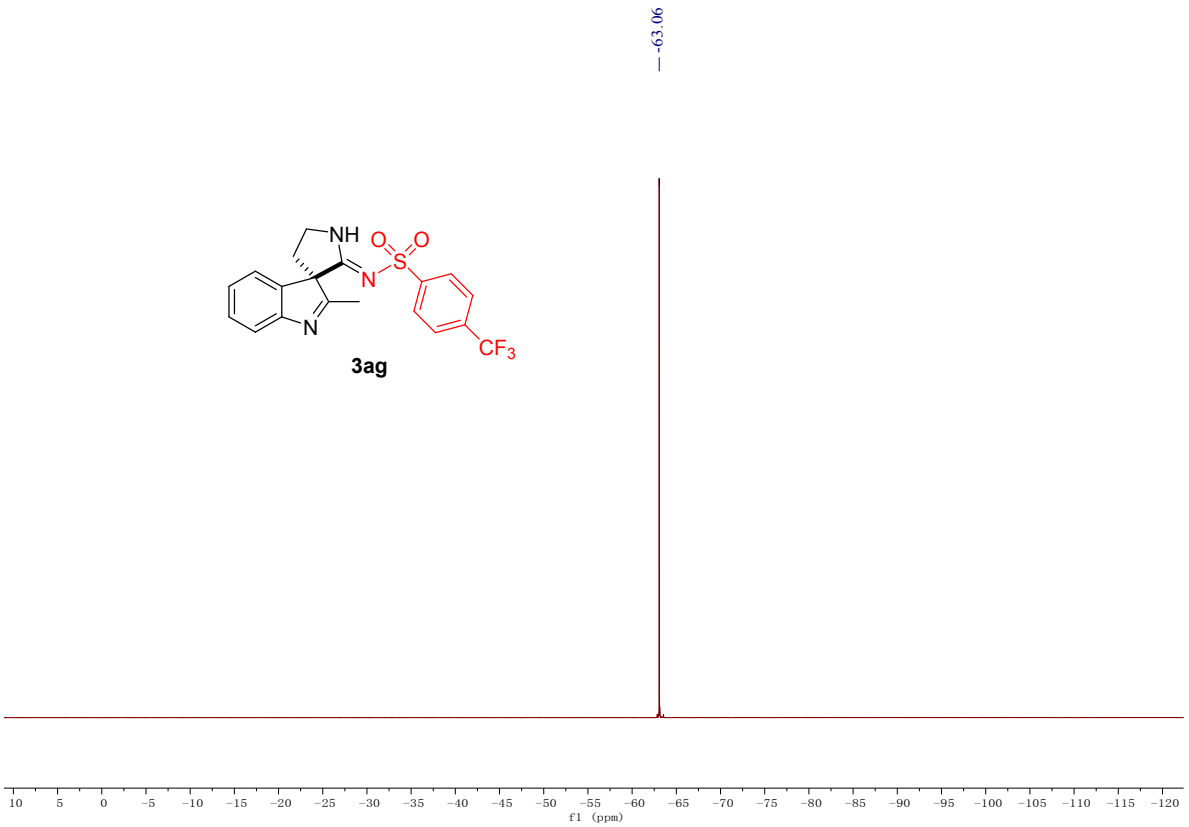
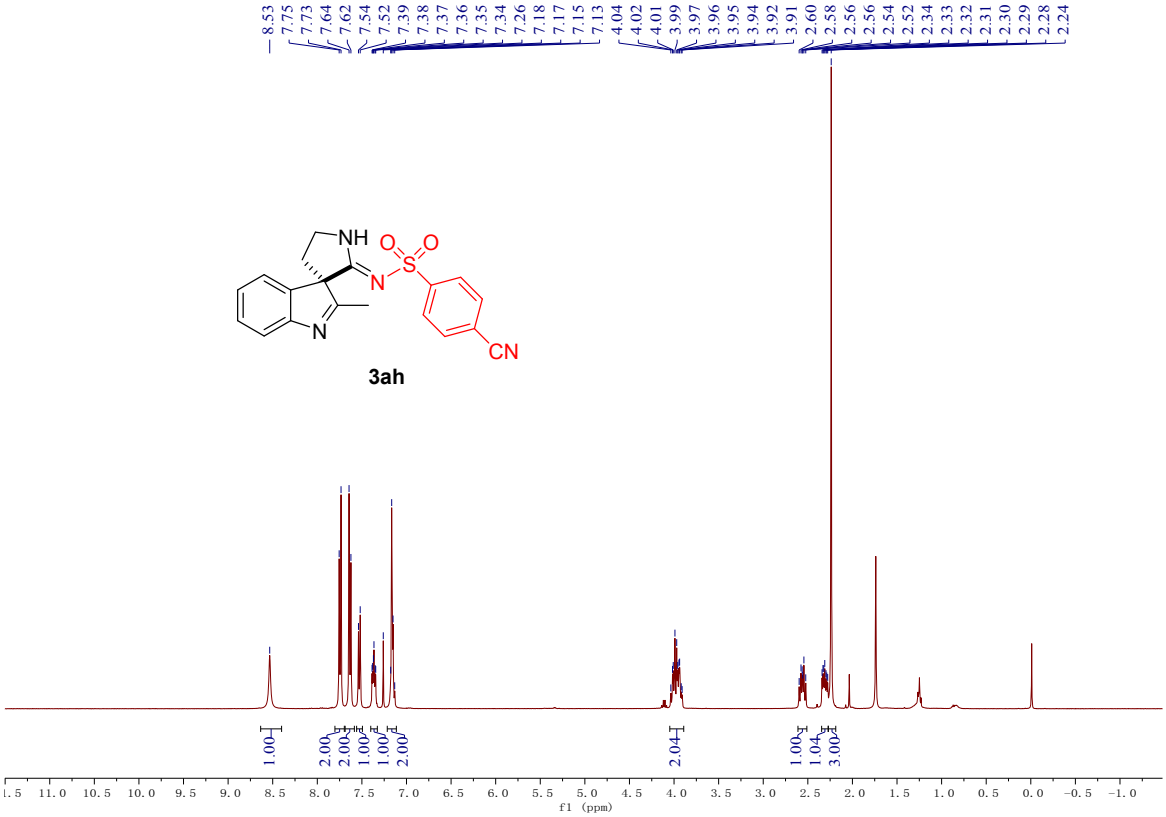
169.5
155.3
145.2
145.2
140.2
134.1
133.8
129.6
126.8
126.2
125.9
125.9
125.8
125.8
124.8
121.3
120.8
68.4
45.6
29.3
16.4
NH
O
O
S
N
N
CF3
3ag
f1 (ppm)


-63.06
NH
O
O
S
N
N
CF3
3ag
f1 (ppm)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7.39
7.38
7.37
7.36
7.35
7.34
7.26
7.18
7.17
7.15
7.13
4.04
4.02
4.01
3.99
3.97
3.96
3.95
3.94
3.92
3.91
2.60
2.58
2.56
2.56
2.54
2.52
2.34
2.33
2.32
2.31
2.30
2.29
2.28
2.24
NH
O
O
S
N
N
CN
3ah
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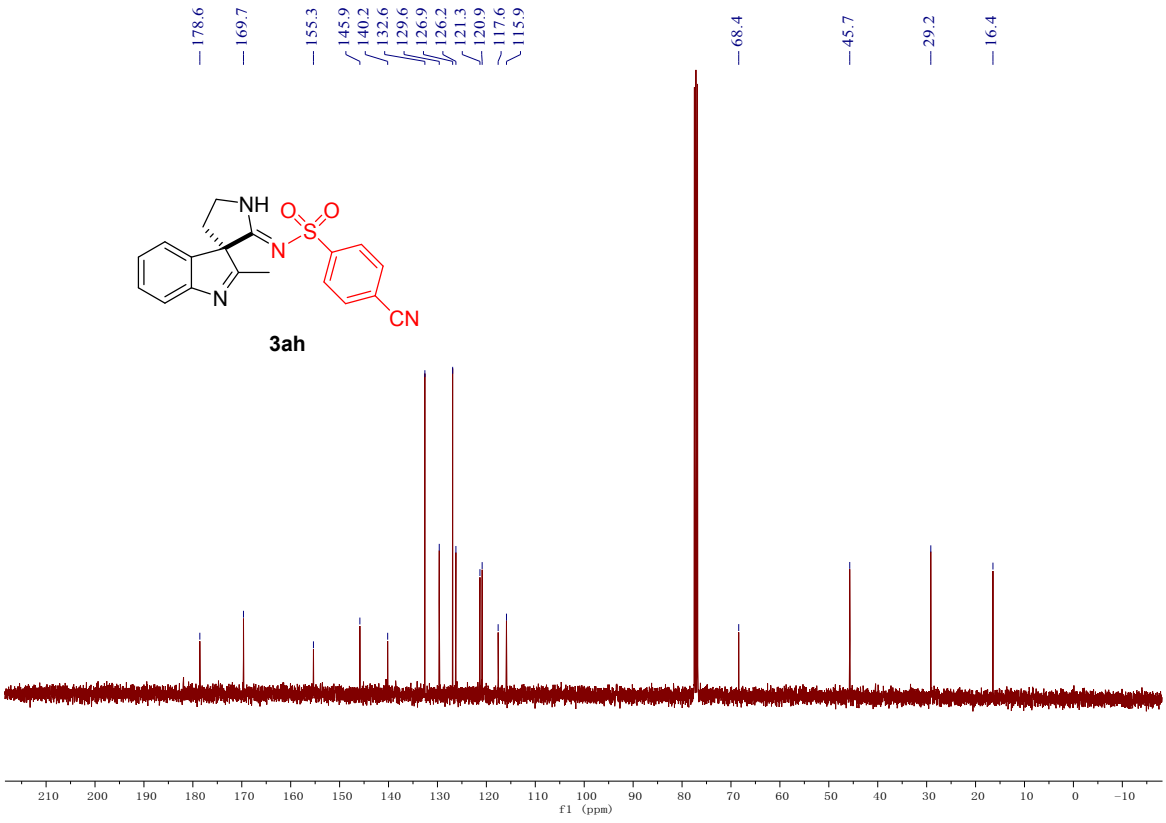
2.00
1.00
1.00
2.00
2.04
1.00
1.04
3.00
f1 (ppm)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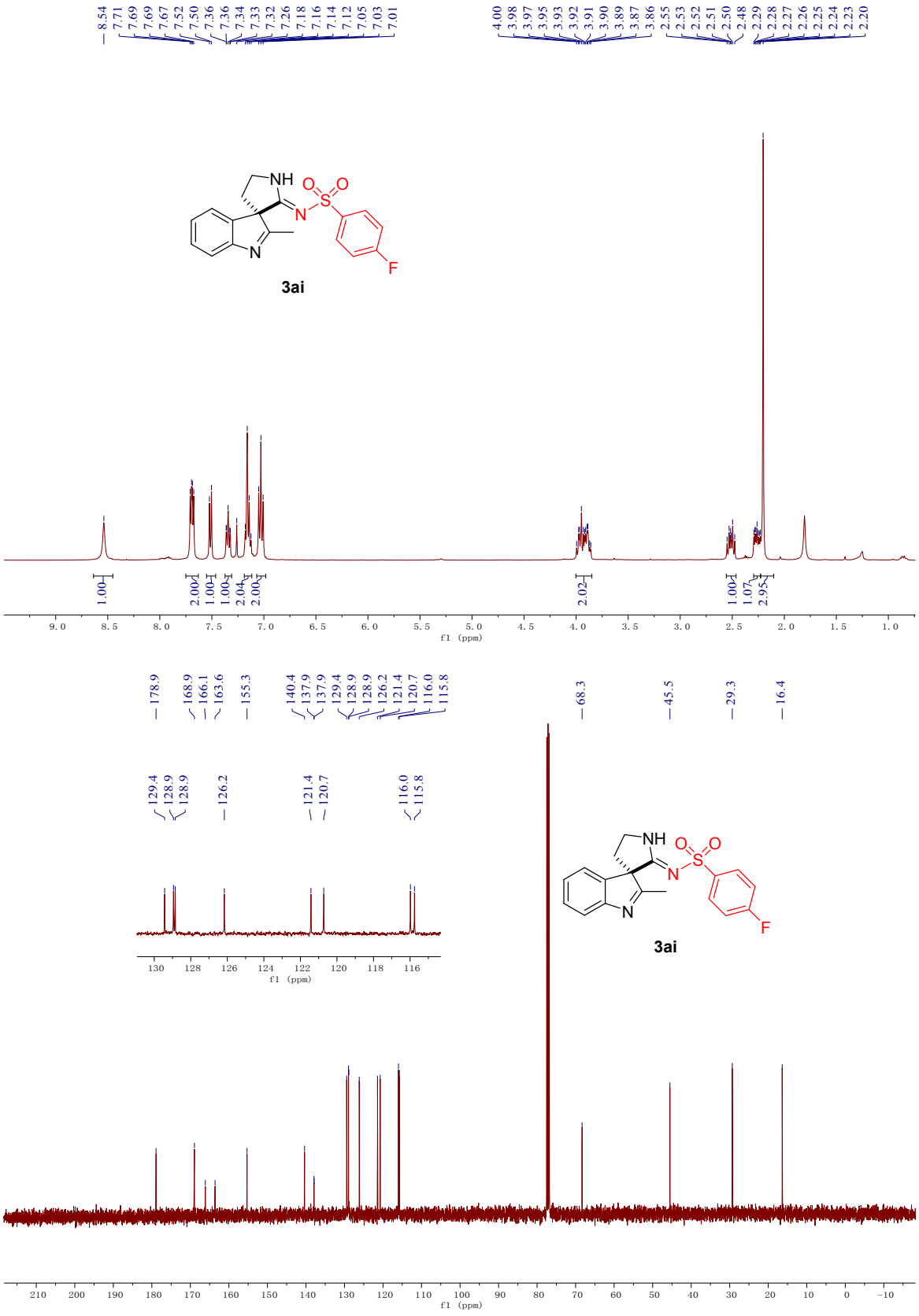
169.7
155.3
145.9
140.2
132.6
129.6
126.9
126.2
121.3
120.9
117.6
115.9
68.4
45.7
29.2
16.4
NH
O
O
S
N
N
CN
3ah
f1 (ppm)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7.36
7.36
7.34
7.33
7.32
7.26
7.18
7.16
7.14
7.12
7.05
7.03
7.01
4.00
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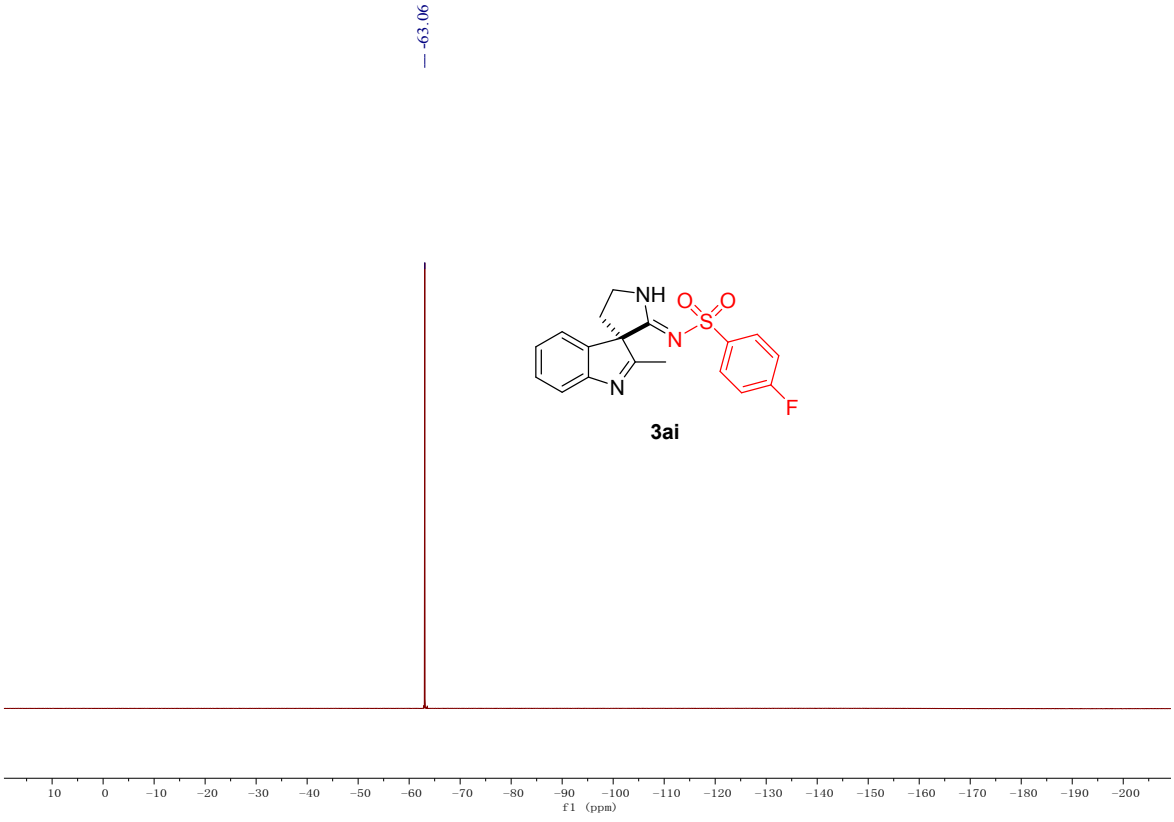
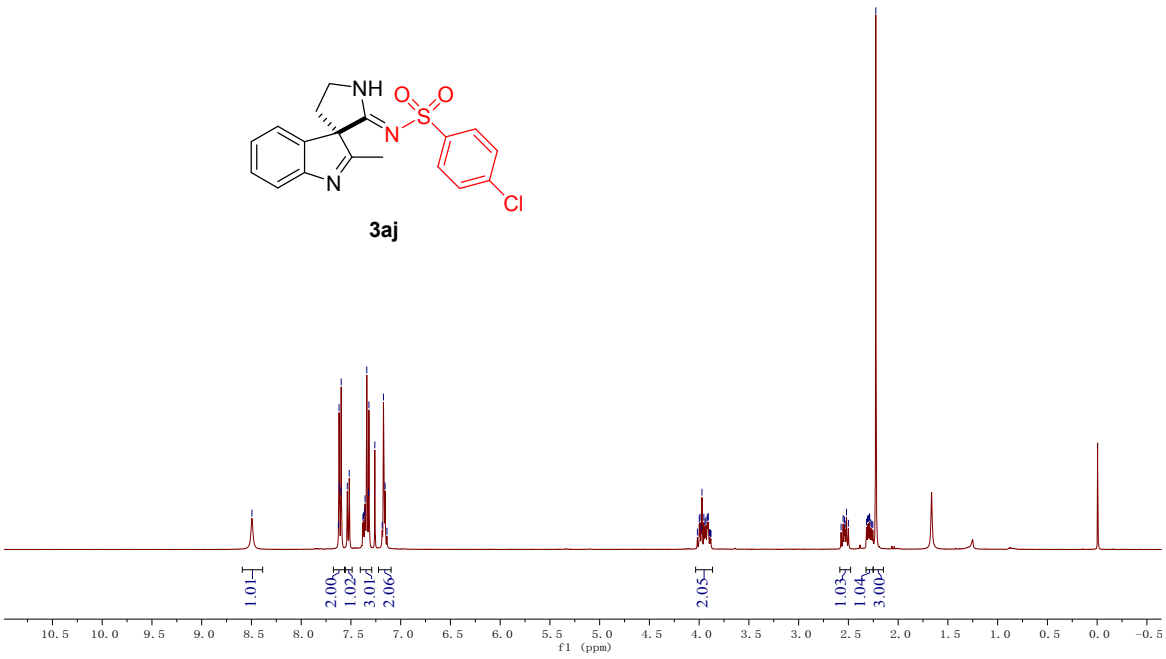
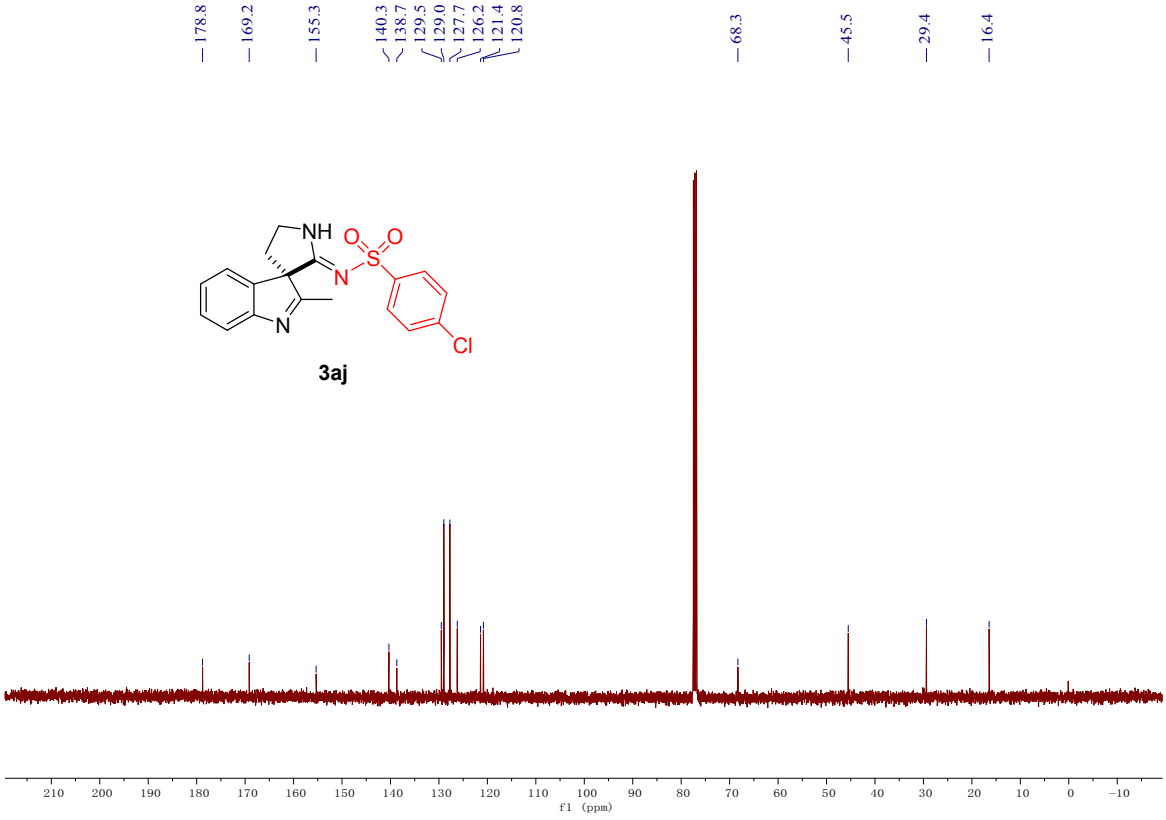
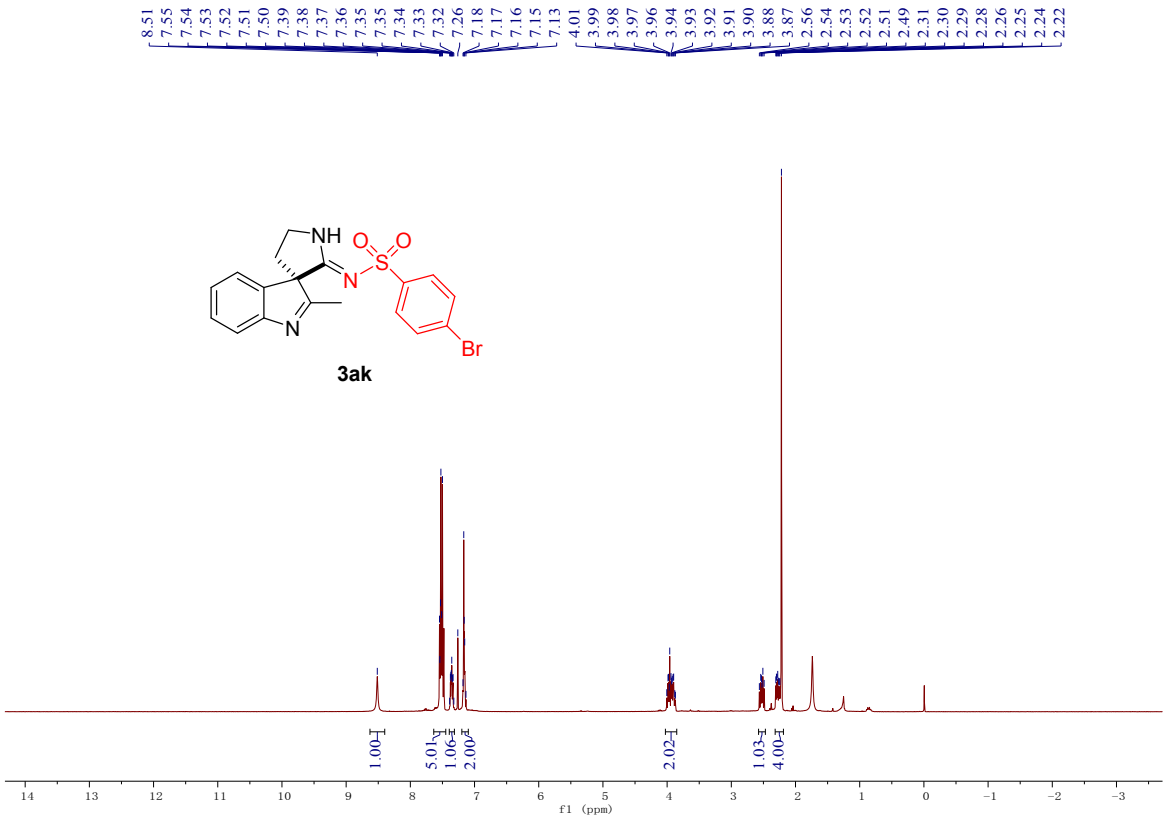
3.97
3.95
3.93
3.92
3.91
3.90
3.89
3.87
3.86
2.55
2.53
2.52
2.51
2.50
2.48
2.29
2.28
2.27
2.26
2.25
2.24
2.23
2.20
NH
O
O
S
N
N
F
3ai
1.00
2.00
1.00
1.00
2.04
2.00
2.02
1.00
1.07
2.95
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)
178.9
168.9
166.1
163.6
155.3
140.4
137.9
137.9
129.4
128.9
128.9
126.2
121.4
120.7
116.0
115.8
68.3
45.5
29.3
16.4
129.4
128.9
128.9
126.2
121.4
120.7
116.0
115.8
130
128
126
124
122
120
118
116
f1 (ppm)
NH
O
O
S
N
N
F
3ai
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


— -63.06
NH
O
O
S
N
N
F
3ai
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200
f1 (ppm)


8.49 7.63 7.62 7.61 7.60 7.60 7.54 7.52 7.38 7.37 7.36 7.36 7.34 7.32 7.32 7.26 7.19 7.17 7.16 7.14
4.02 4.00 3.99 3.98 3.97 3.95 3.94 3.93 3.92 3.91 3.91 3.89 3.89 3.88 3.88
2.57 2.55 2.54 2.53 2.52 2.50 2.32 2.31 2.30 2.29 2.29 2.27 2.27 2.25 2.22


NH
O
O
S
N
N
Cl
3aj
1.01 2.00 1.02 3.01 2.06 2.05 1.03 1.04 3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


178.8
169.2
155.3
140.3
138.7
129.5
129.0
127.7
126.2
121.4
120.8
68.3
45.5
29.4
16.4
NH
O
O
S
N
N
Cl
3aj
f1 (ppm)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7.36
7.35
7.35
7.34
7.33
7.32
7.26
7.18
7.17
7.16
7.15
7.13
4.01
3.99
3.98
3.97
3.96
3.94
3.93
3.92
3.91
3.90
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3.87
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2.52
2.51
2.49
2.31
2.30
2.29
2.28
2.26
2.25
2.24
2.22
NH
O
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S
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N
Br
3ak
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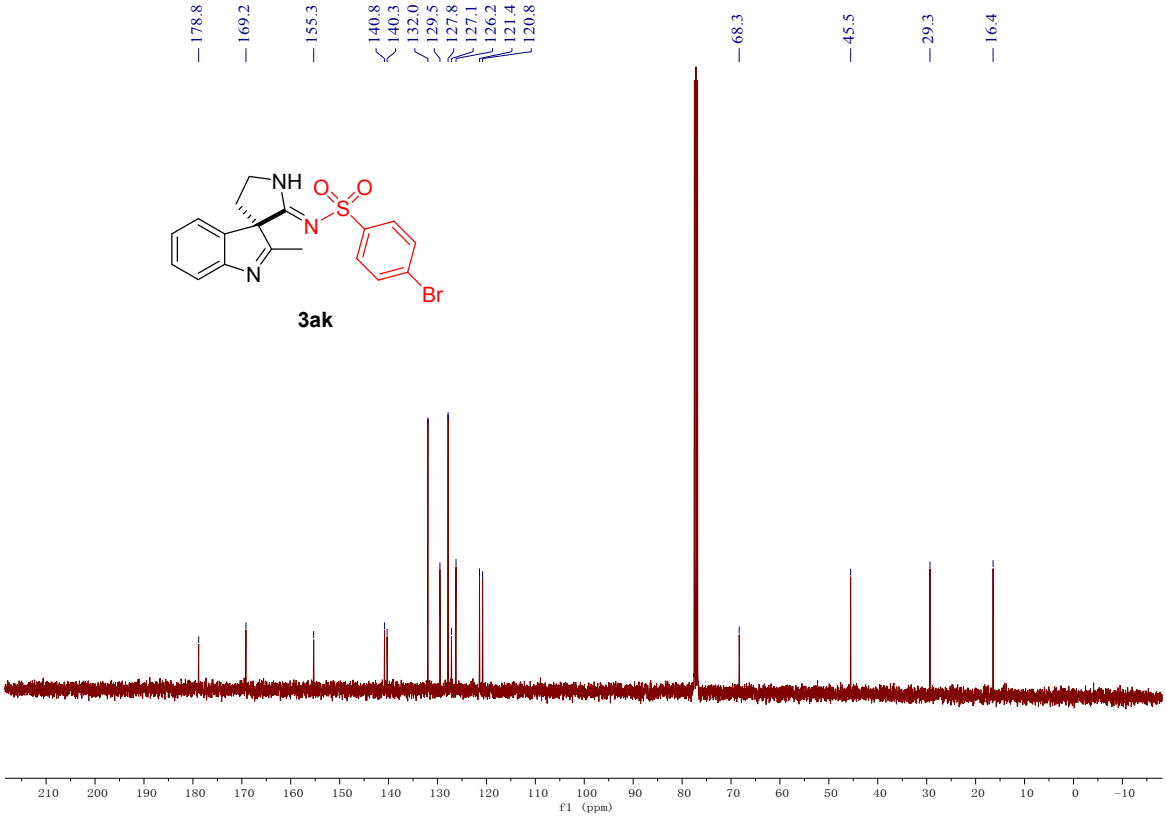
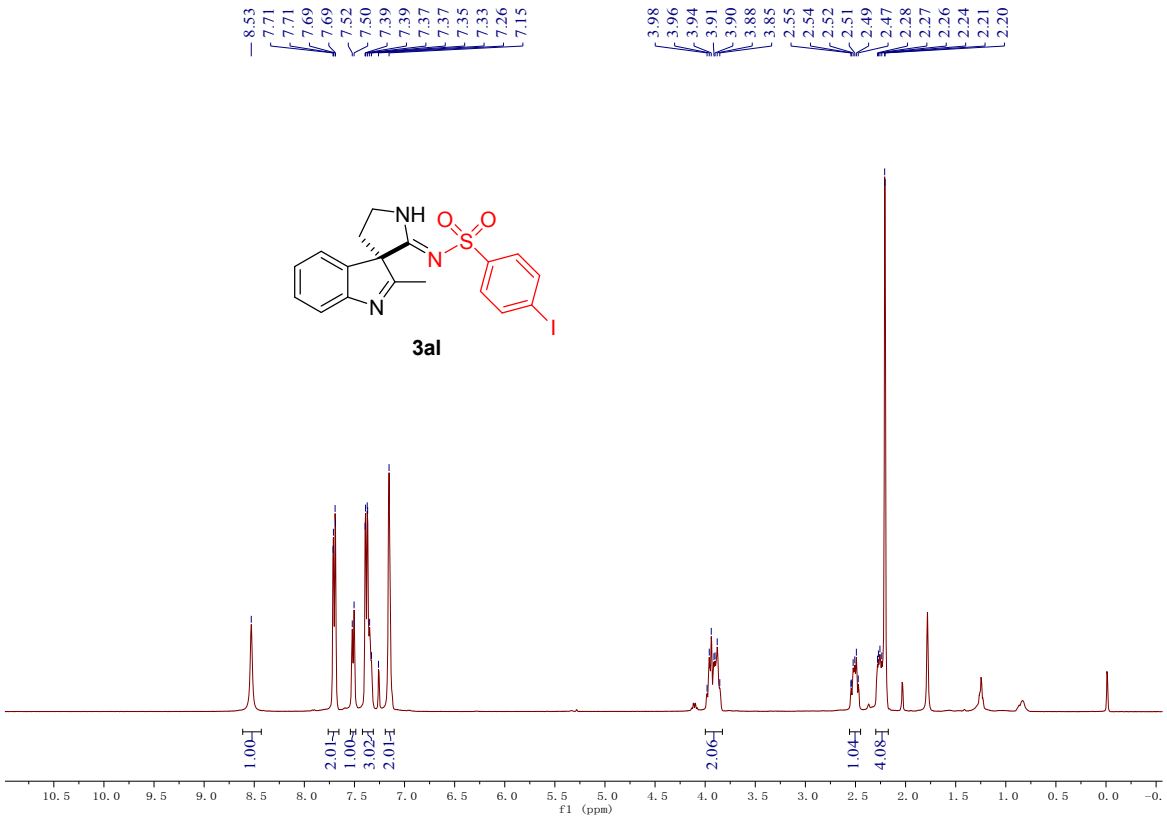
1.06
2.00
2.02
1.03
4.00
f1 (ppm)


178.8
169.2
155.3
140.8
140.3
132.0
129.5
127.8
127.1
126.2
121.4
120.8
68.3
45.5
29.3
16.4
NH
O
O
S
N
N
Br
3ak
f1 (ppm)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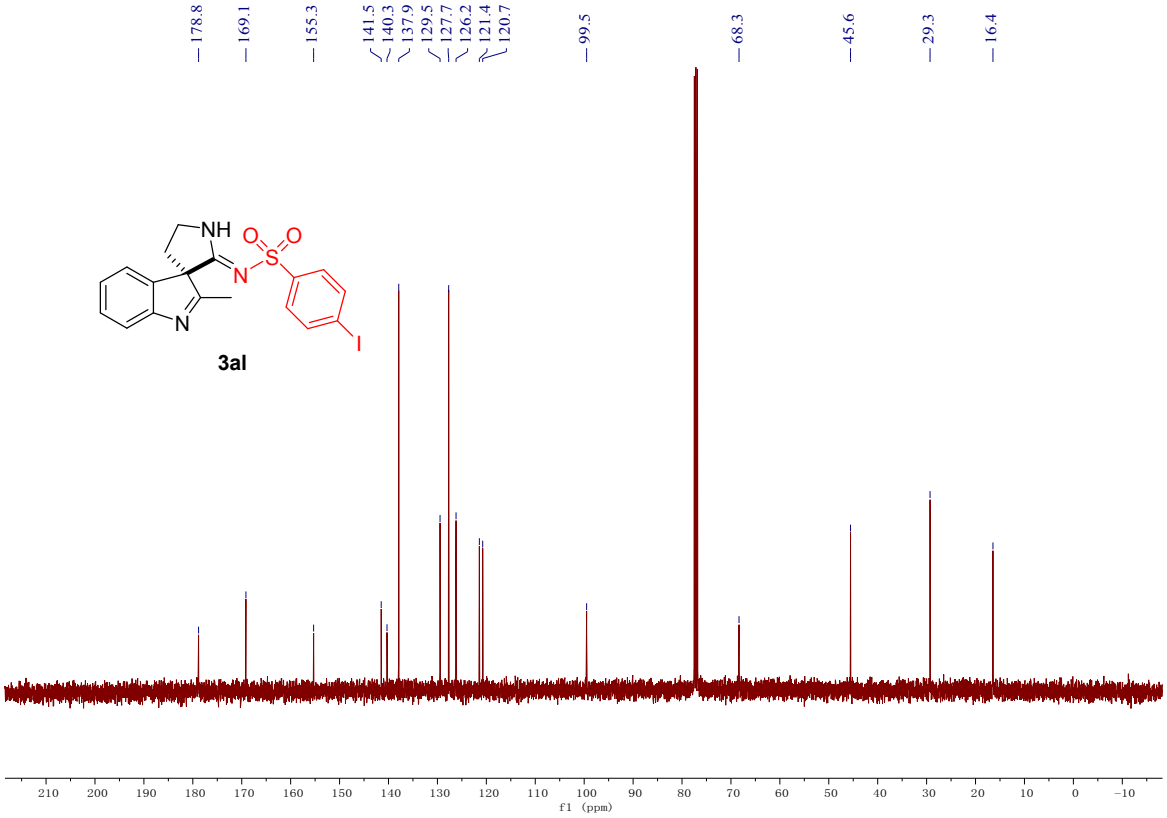
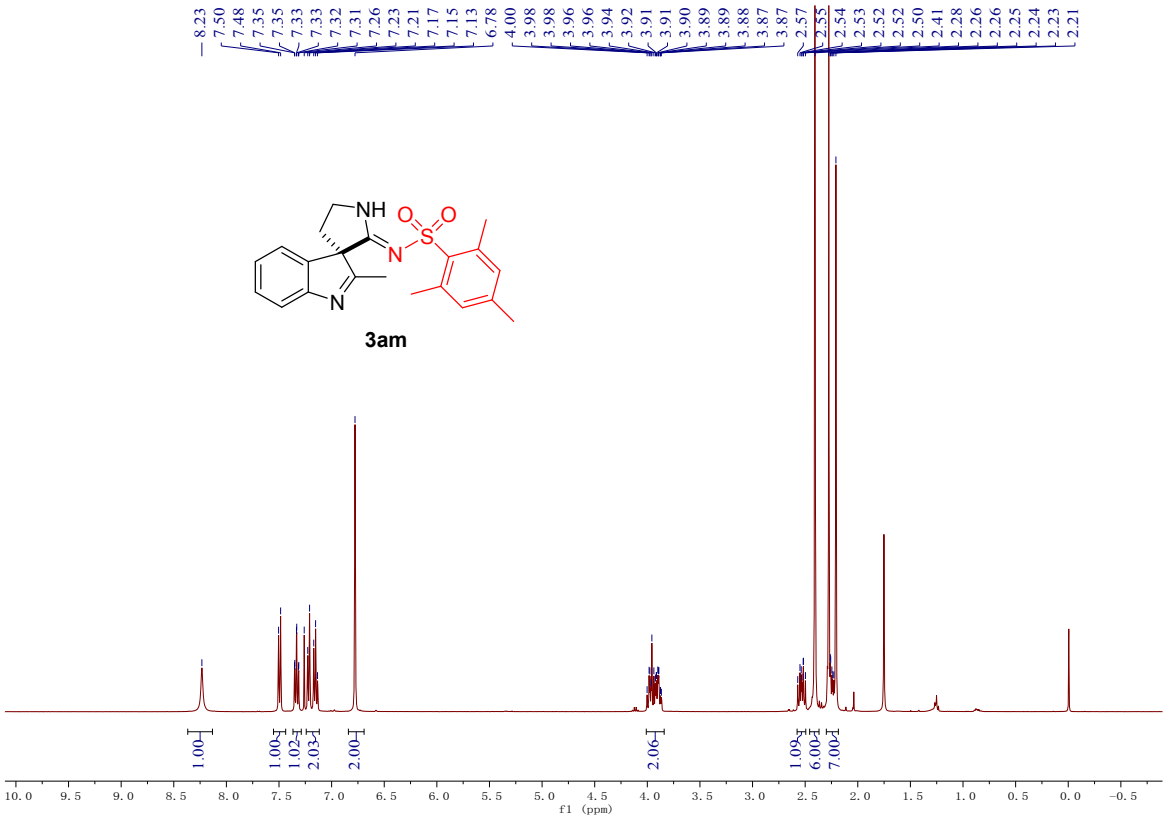
7.52
7.50
7.39
7.39
7.37
7.37
7.35
7.33
7.26
7.15
3.98
3.96
3.94
3.91
3.90
3.88
3.85
2.55
2.54
2.52
2.51
2.49
2.47
2.28
2.27
2.26
2.24
2.21
2.20
NH
O
O
S
N
N
I
3al
1.00
2.01
1.00
3.02
2.01
2.06
1.04
4.08
f1 (ppm)


178.8
169.1
155.3
141.5
140.3
137.9
129.5
127.7
126.2
121.4
120.7
99.5
68.3
45.6
29.3
16.4
NH
O
O
S
N
N
I
3al
f1 (ppm)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7.33
7.32
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7.26
7.23
7.21
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7.15
7.13
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4.00
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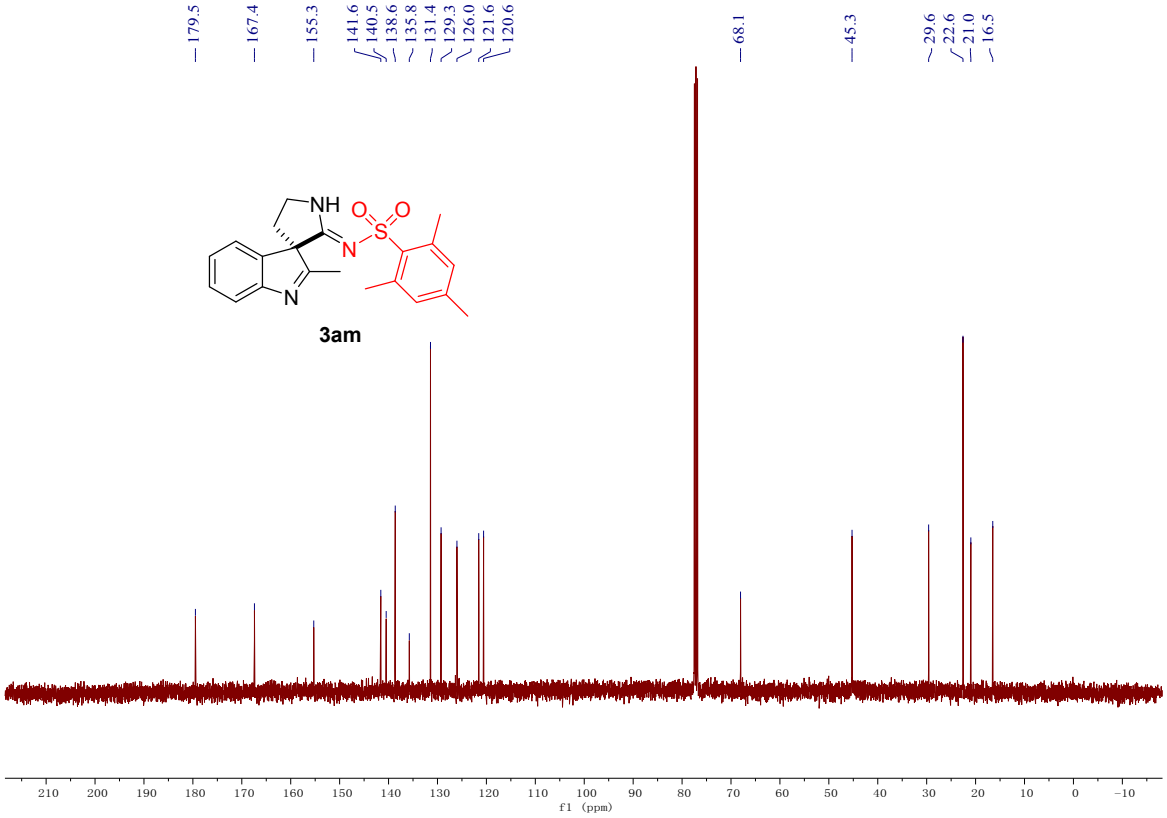
3.98
3.96
3.96
3.94
3.92
3.91
3.91
3.90
3.89
3.89
3.88
3.87
3.87
2.57
2.55
2.54
2.53
2.52
2.52
2.50
2.41
2.28
2.26
2.26
2.25
2.24
2.23
2.21
NH
O
O
S
N
N
3am
1.00
1.00
1.02
2.03
2.00
2.06
1.09
6.00
7.00
f1 (ppm)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155.3
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138.6
135.8
131.4
129.3
126.0
121.6
120.6
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29.6
22.6
21.0
16.5
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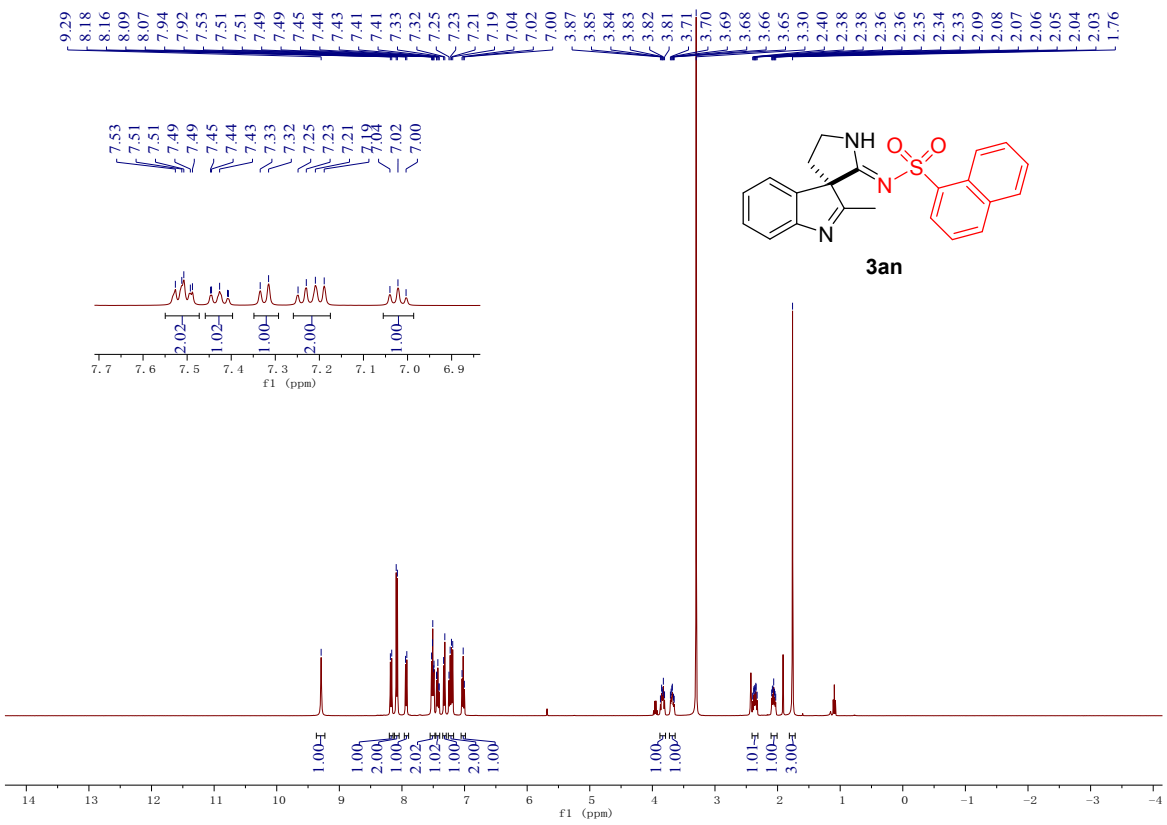
O
O
S
N
N
3am
f1 (ppm)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7.53
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7.51
7.49
7.49
7.45
7.44
7.43
7.41
7.41
7.33
7.32
7.25
7.23
7.21
7.19
7.04
7.02
7.00
3.87
3.85
3.84
3.83
3.82
3.81
3.71
3.70
3.69
3.68
3.66
3.65
3.30
2.40
2.38
2.38
2.36
2.36
2.35
2.34
2.33
2.09
2.08
2.07
2.06
2.05
2.04
2.03
1.76
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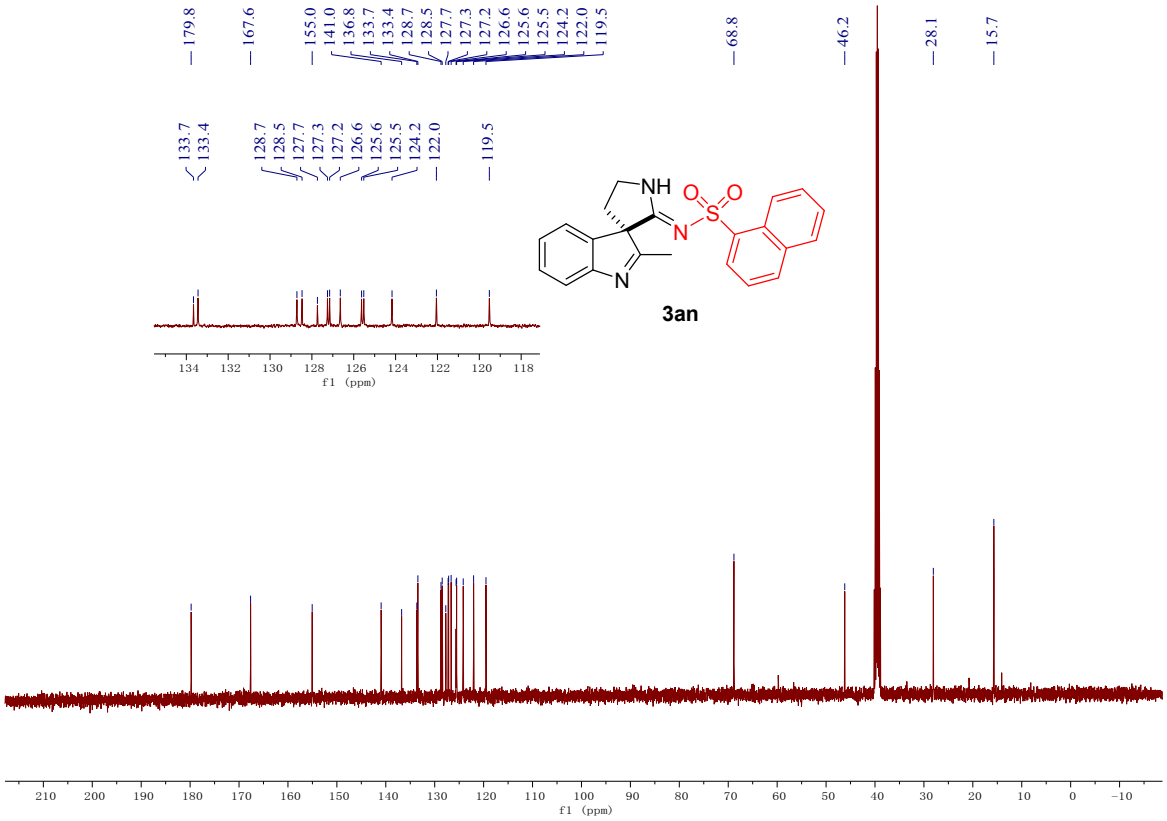
O
S
N
N
3an
f1 (ppm)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127.7
127.3
127.2
126.6
125.6
125.5
124.2
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46.2
28.1
15.7
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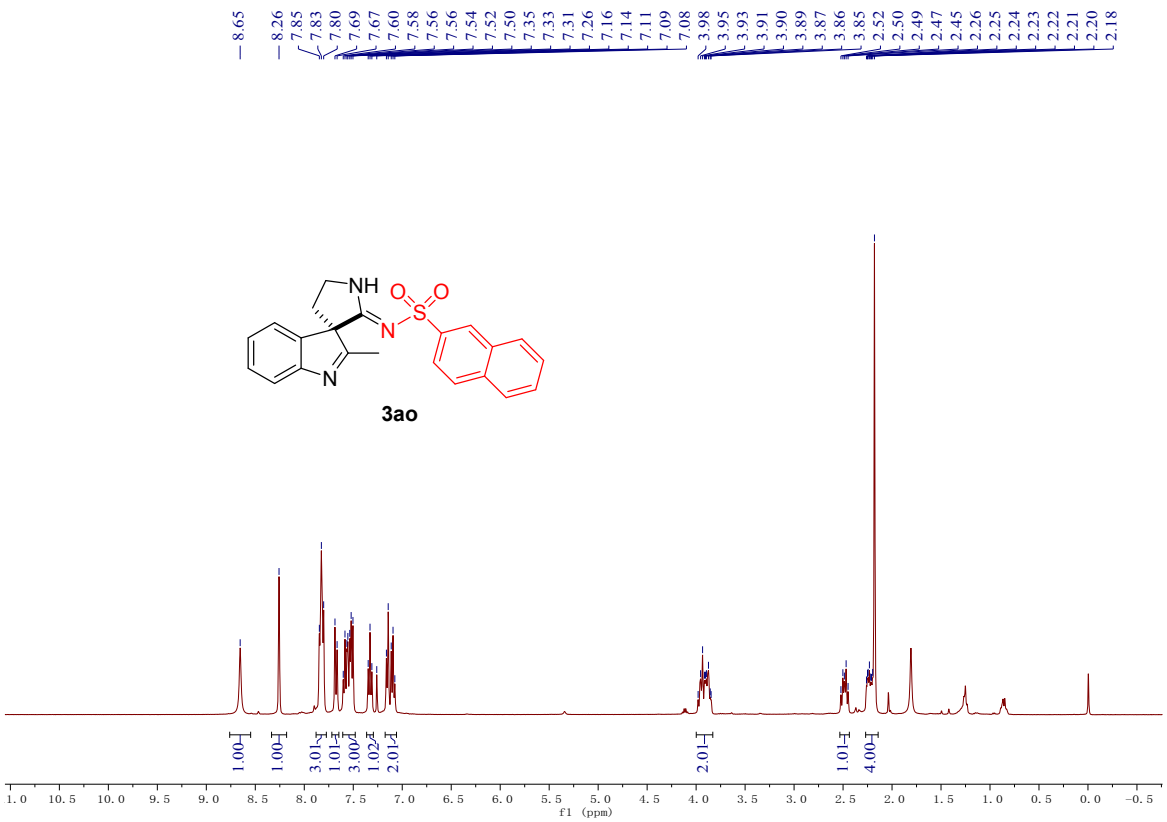
O
O
S
N
N
3an
f1 (ppm)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7.56
7.56
7.54
7.52
7.50
7.35
7.33
7.31
7.26
7.16
7.14
7.11
7.09
7.08
3.98
3.95
3.93
3.91
3.90
3.89
3.87
3.86
3.85
2.52
2.50
2.49
2.47
2.45
2.26
2.25
2.24
2.23
2.22
2.21
2.20
2.18
NH
O
O
S
N
N
3ao
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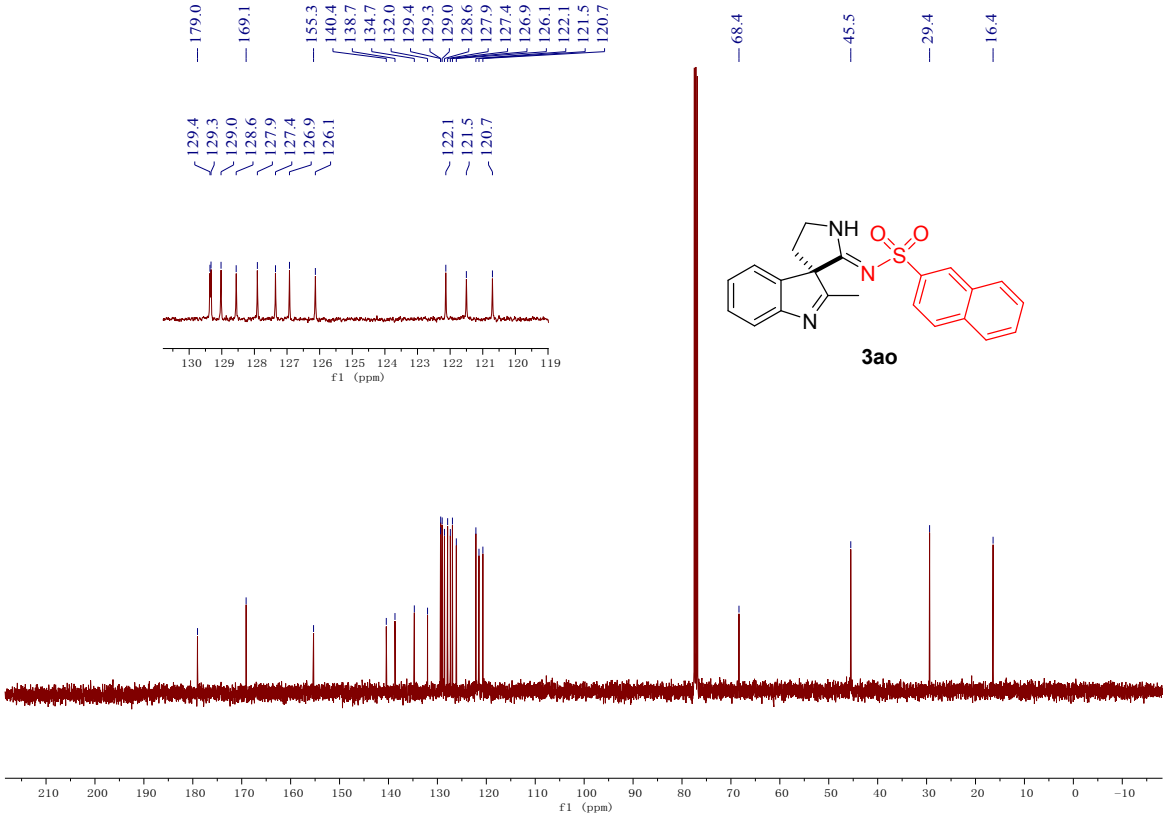
3.01
1.01
3.00
1.02
2.01
2.01
1.01
4.00
f1 (ppm)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169.1
155.3
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132.0
129.4
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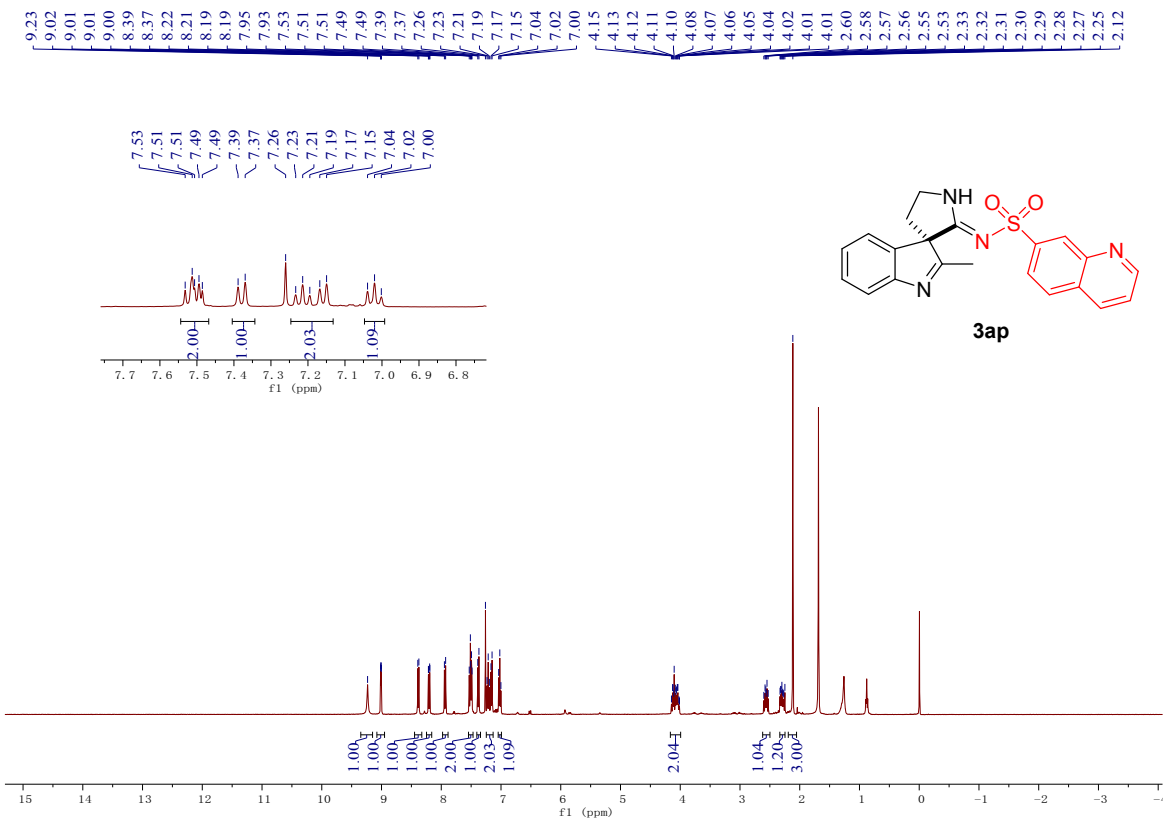
129.0
128.6
127.9
127.4
126.9
126.1
122.1
121.5
120.7
68.4
45.5
29.4
16.4
NH
O
O
S
N
N
3ao
f1 (ppm)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9.01
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8.19
8.19
7.95
7.93
7.53
7.51
7.51
7.49
7.49
7.39
7.37
7.26
7.23
7.21
7.19
7.17
7.15
7.04
7.02
7.00
4.15
4.13
4.12
4.11
4.10
4.08
4.07
4.06
4.05
4.04
4.02
4.01
4.01
2.60
2.58
2.57
2.56
2.55
2.53
2.33
2.32
2.31
2.30
2.29
2.28
2.27
2.25
2.12
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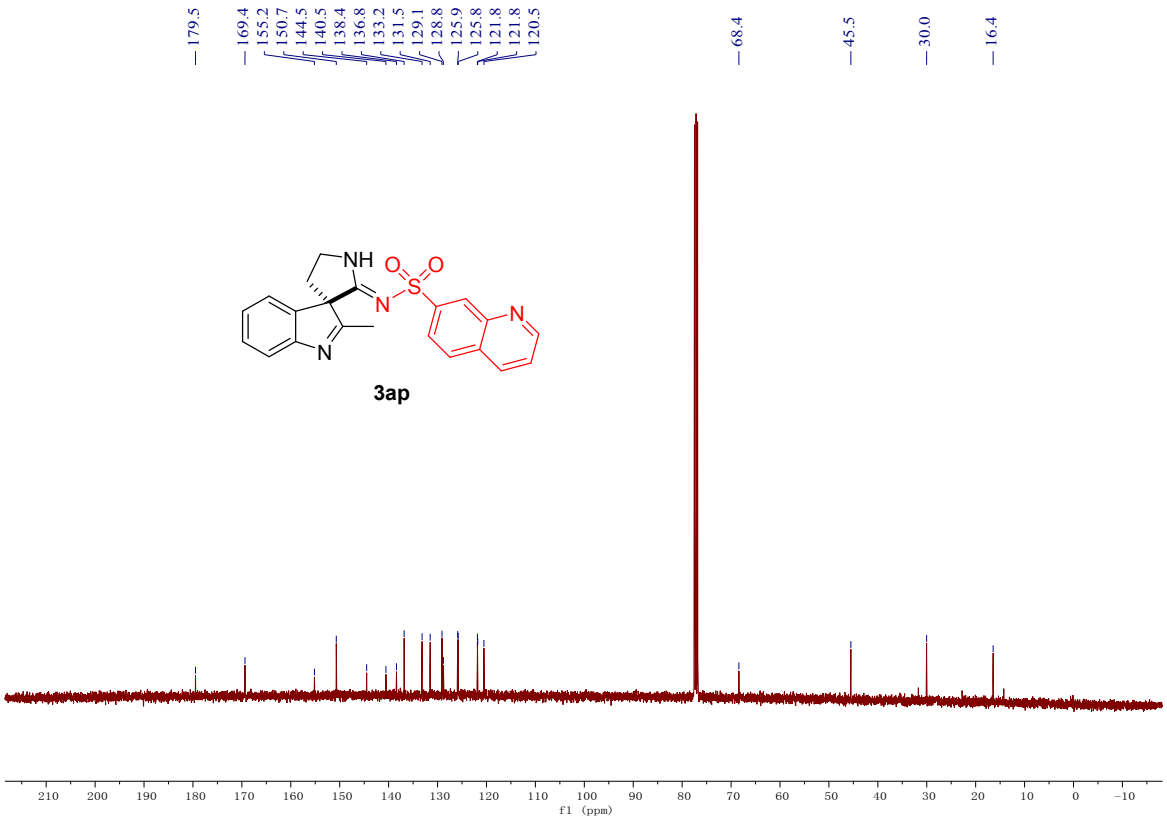
O
S
N
N
N
3ap
f1 (ppm)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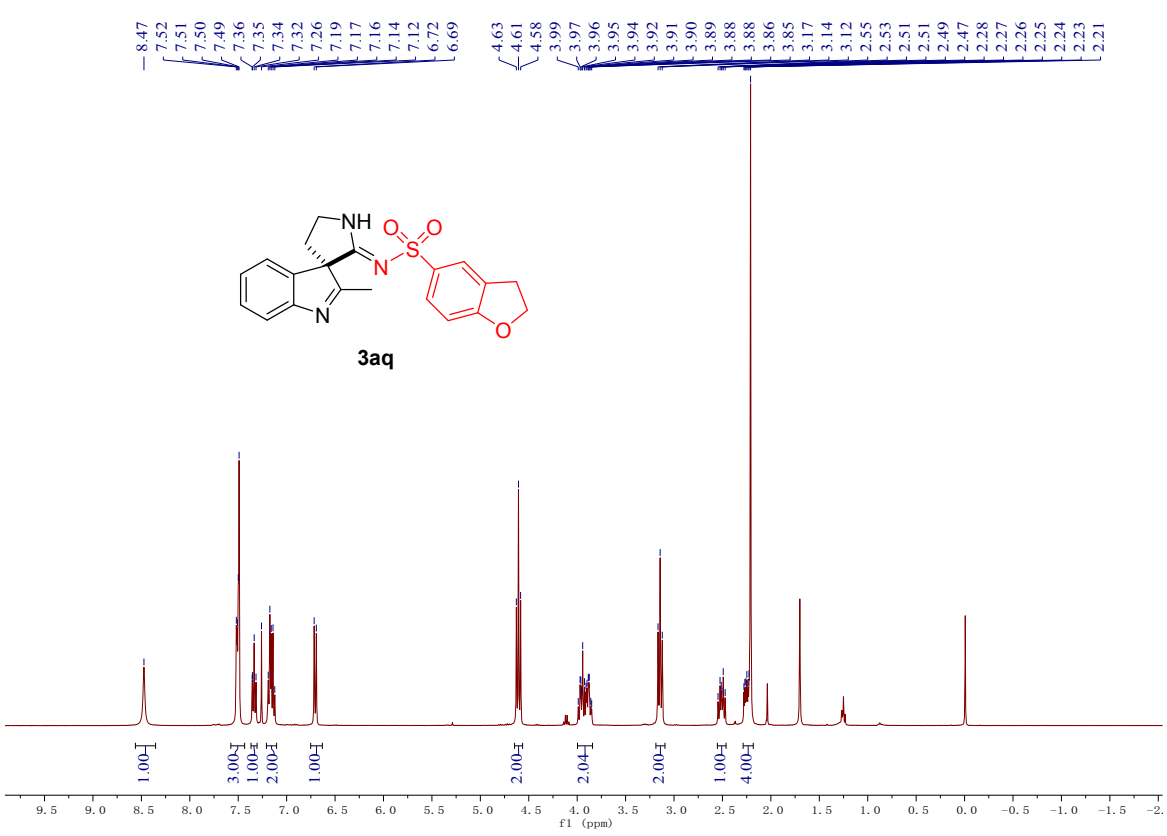
150.7
144.5
140.5
138.4
136.8
133.2
131.5
129.1
128.8
125.9
125.8
121.8
121.8
120.5
68.4
45.5
30.0
16.4
NH
O
O
S
N
N
N
f1 (ppm)

3ap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7.52
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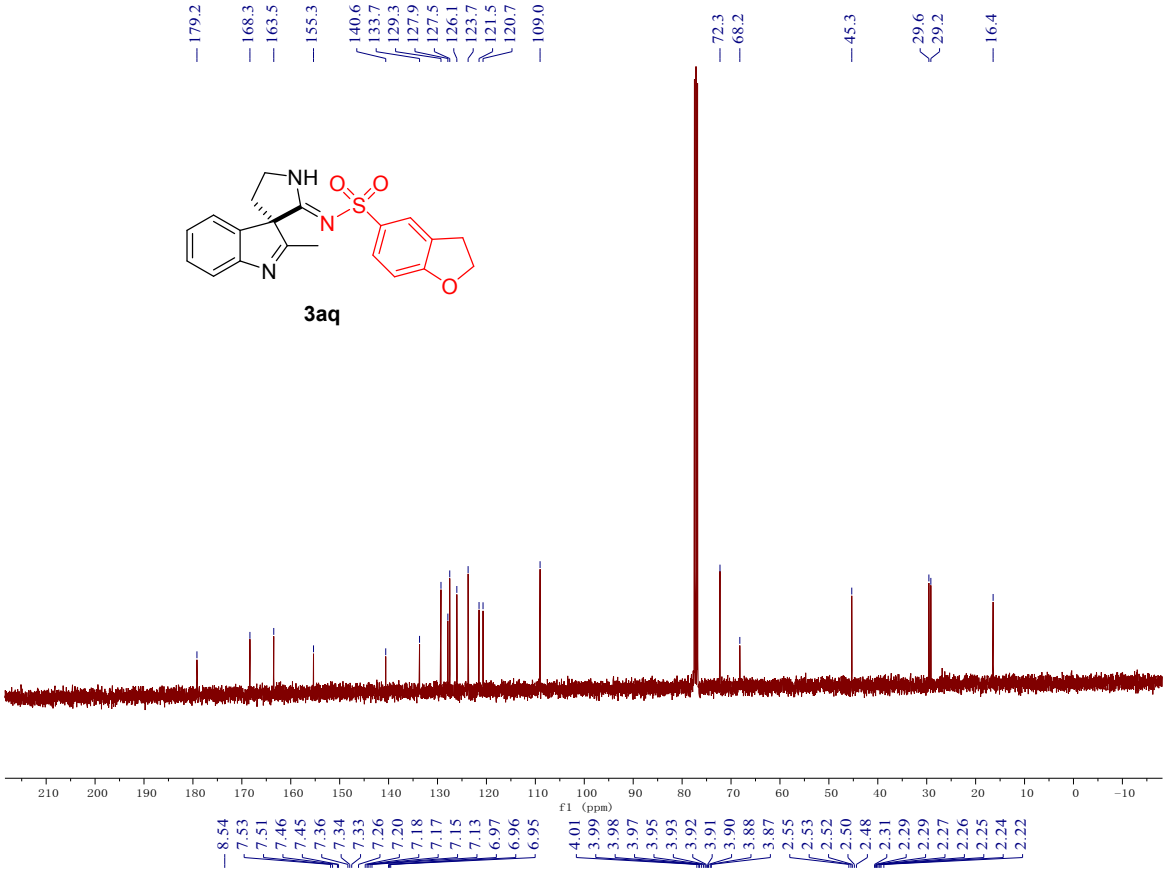
7.49
7.36
7.35
7.34
7.32
7.26
7.19
7.17
7.16
7.14
7.12
6.72
6.69
4.63
4.61
4.58
3.99
3.97
3.96
3.95
3.94
3.92
3.91
3.90
3.89
3.88
3.88
3.86
3.85
3.17
3.14
3.12
2.55
2.53
2.51
2.51
2.49
2.47
2.28
2.27
2.26
2.25
2.24
2.23
2.21
NH
O
O
S
N
N
O
1.00
3.00
1.00
2.00
1.00
2.00
2.04
2.00
1.00
4.00
f1 (ppm)

3aq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168.3
163.5
155.3
140.6
133.7
129.3
127.9
127.5
126.1
123.7
121.5
120.7
109.0
72.3
68.2
45.3
29.6
29.2
16.4
NH
O
O
N
S
N
O
f1 (ppm)
8.54
7.53
7.51
7.46
7.45
7.36
7.34
7.33
7.26
7.20
7.18
7.17
7.15
7.13
6.97
6.96
6.95
4.01
3.99
3.98
3.97
3.95
3.93
3.92
3.91
3.90
3.88
3.87
2.55
2.53
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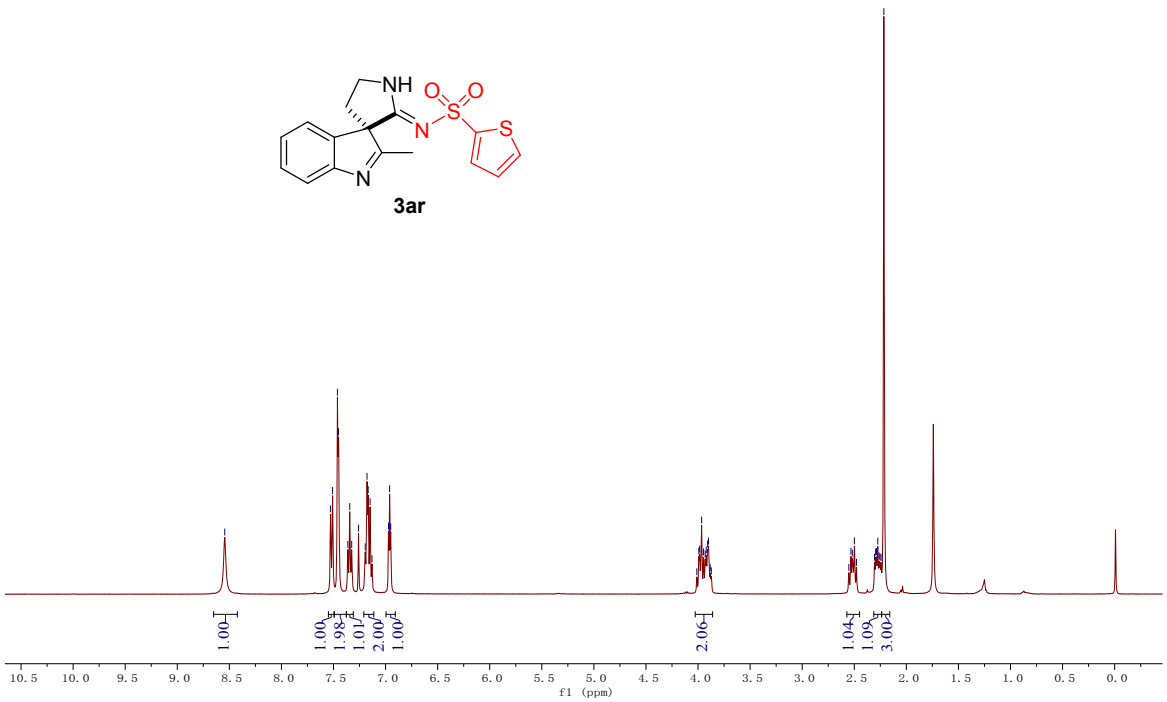
2.29
2.27
2.26
2.25
2.24
2.22

3aq


NH
O
O
N
S
S
N
f1 (ppm)
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1.00
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1.01
2.00
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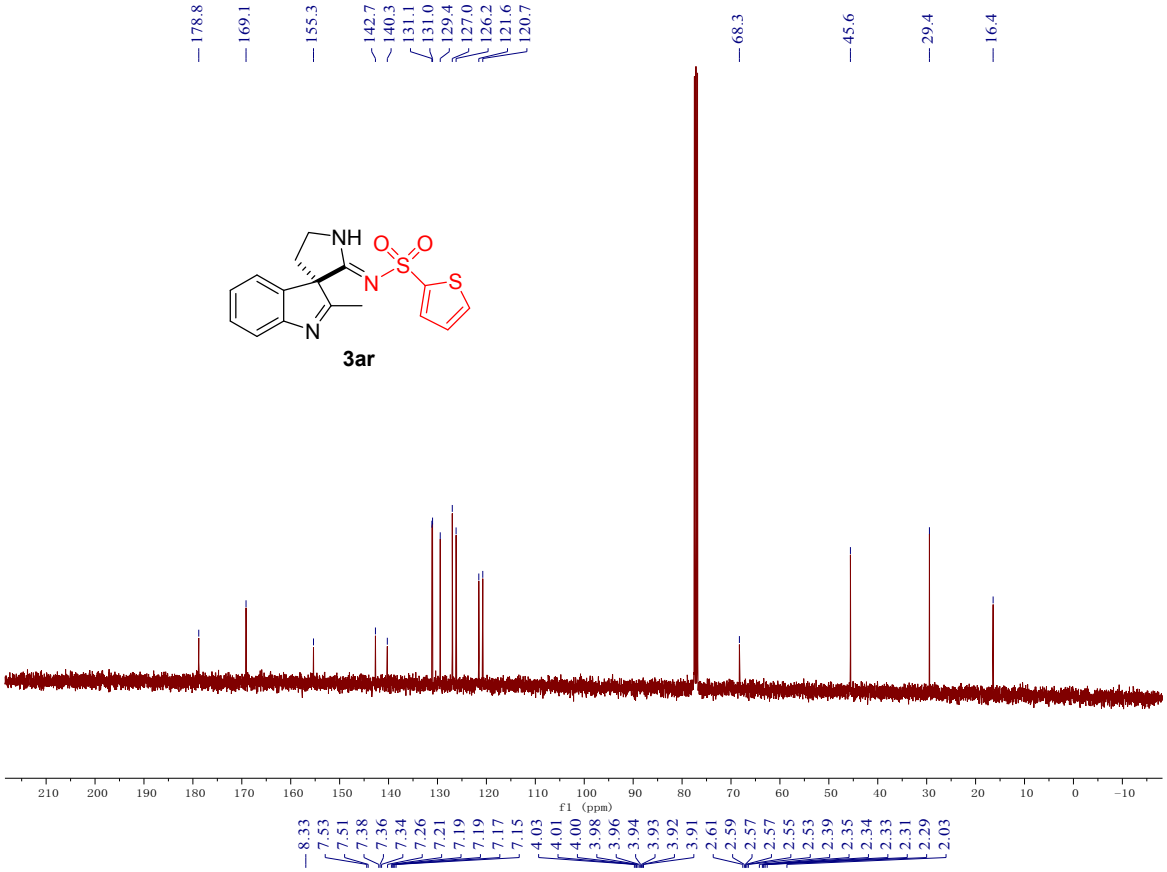
2.06
1.04
1.09
3.00

3ar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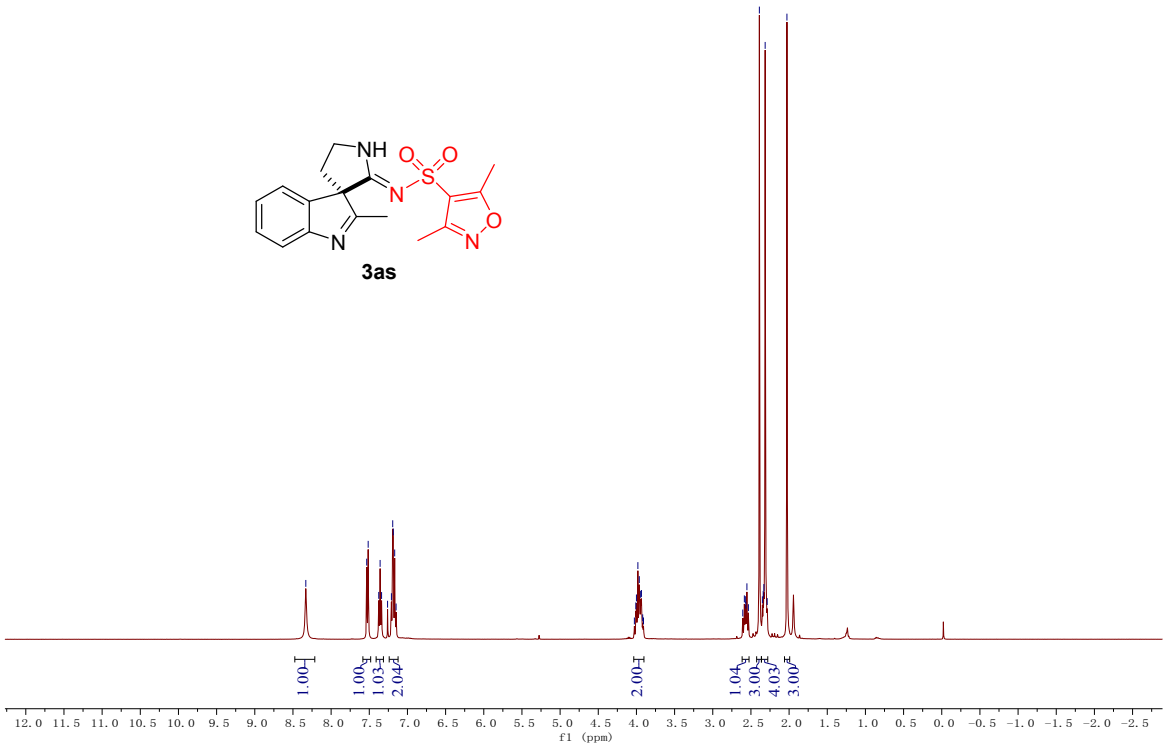
169.1
155.3
142.7
140.3
131.1
131.0
129.4
127.0
126.2
121.6
120.7
68.3
45.6
29.4
16.4
NH
O
O
S
N
S
N
f1 (ppm)

3ar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7.53
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7.36
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7.21
7.19
7.19
7.17
7.15
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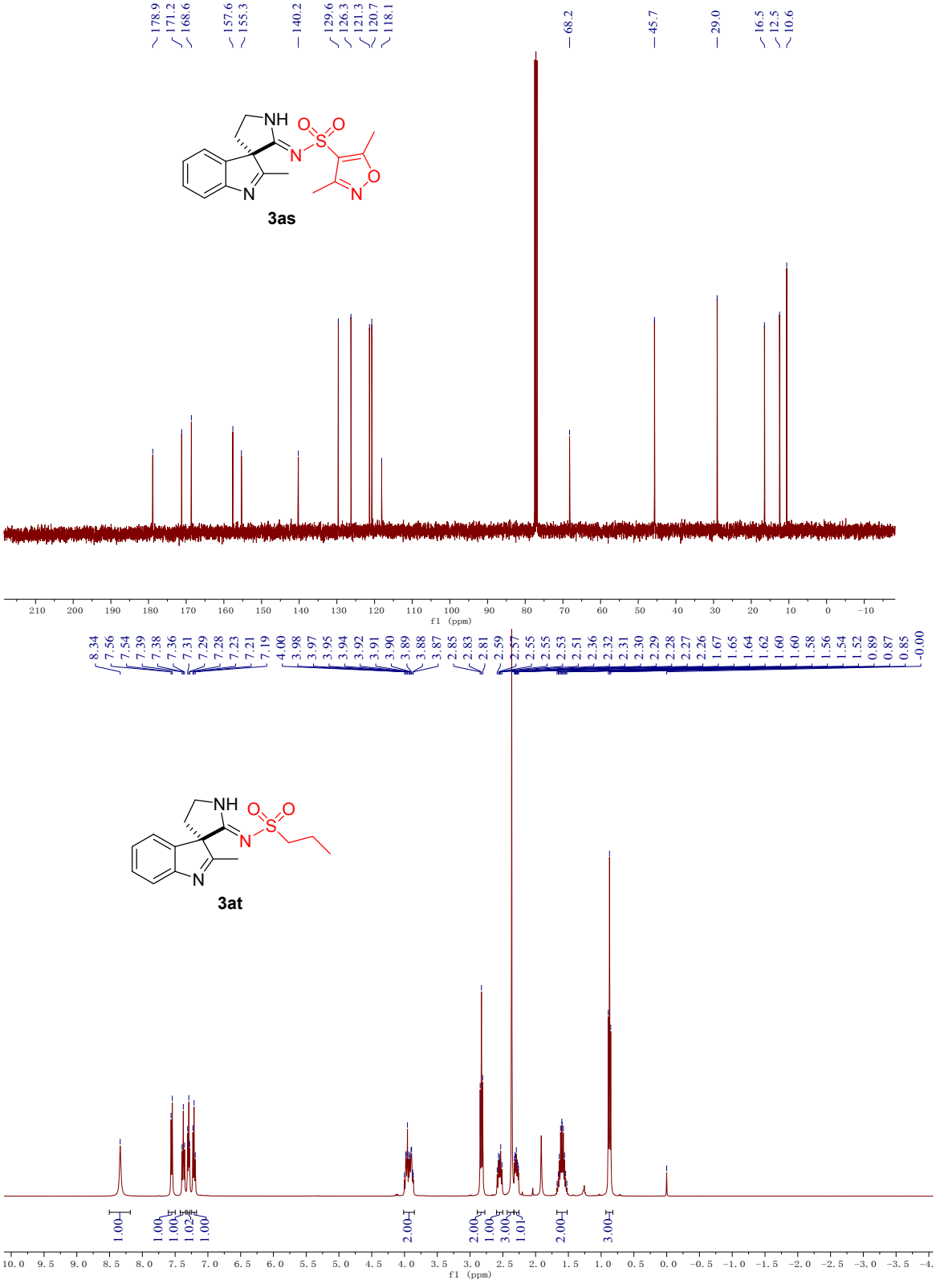
4.01
4.00
3.98
3.96
3.94
3.93
3.92
3.91
2.61
2.59
2.57
2.57
2.55
2.53
2.39
2.35
2.34
2.33
2.31
2.29
2.03
NH
O
O
S
N
O
N
1.00
1.00
1.03
2.04
2.00
1.04
3.00
4.03
3.00
f1 (ppm)

3as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171.2
168.6
157.6
155.3
140.2
129.6
126.3
121.3
120.7
118.1
68.2
45.7
29.0
16.5
12.5
10.6
NH
O
O
S
N
O
N
3as
f1 (ppm)
8.34
7.56
7.54
7.39
7.38
7.36
7.31
7.29
7.28
7.23
7.21
7.19
4.00
3.98
3.97
3.95
3.94
3.92
3.91
3.90
3.89
3.88
3.87
2.85
2.83
2.81
2.59
2.57
2.55
2.55
2.53
2.51
2.36
2.32
2.31
2.30
2.29
2.28
2.27
2.26
1.67
1.65
1.64
1.62
1.60
1.60
1.58
1.56
1.54
1.52
0.89
0.87
0.85
0.00
NH
O
O
S
N
N
3at
1.00
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1.00
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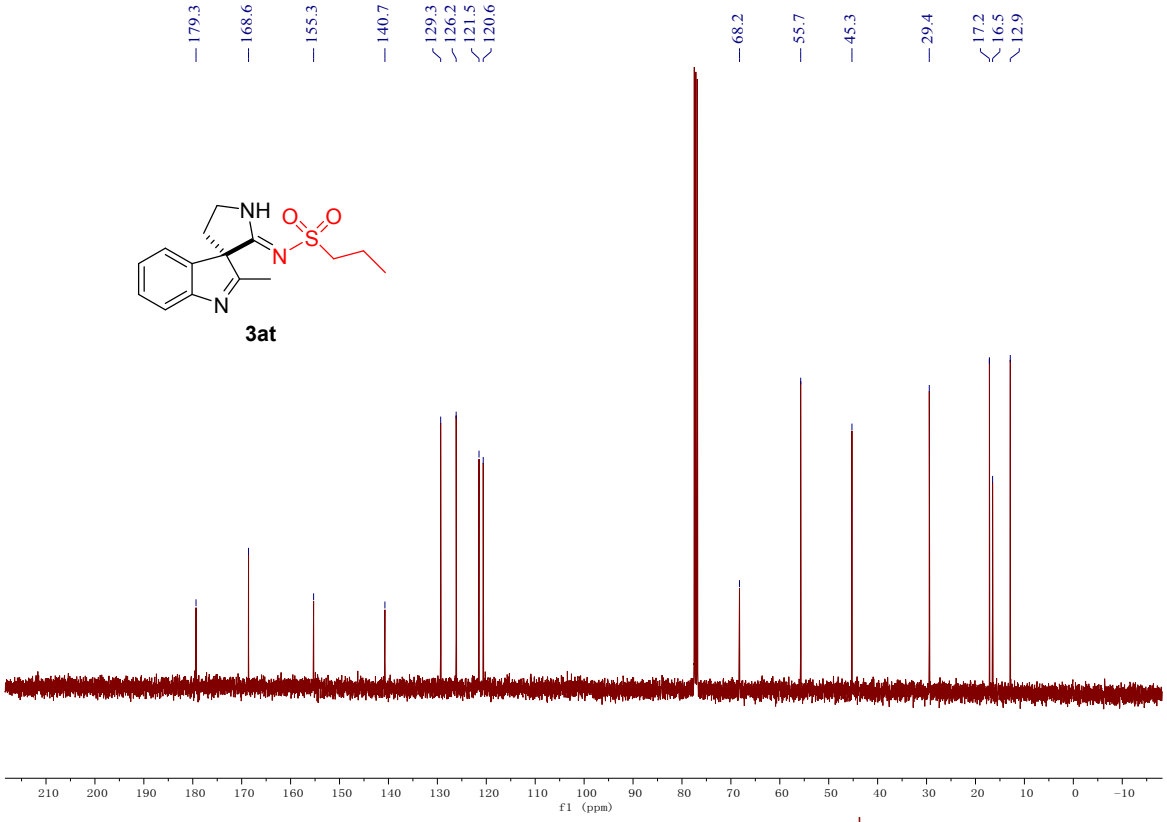
1.00
2.00
2.00
1.00
3.00
1.01
2.00
3.00
f1 (ppm)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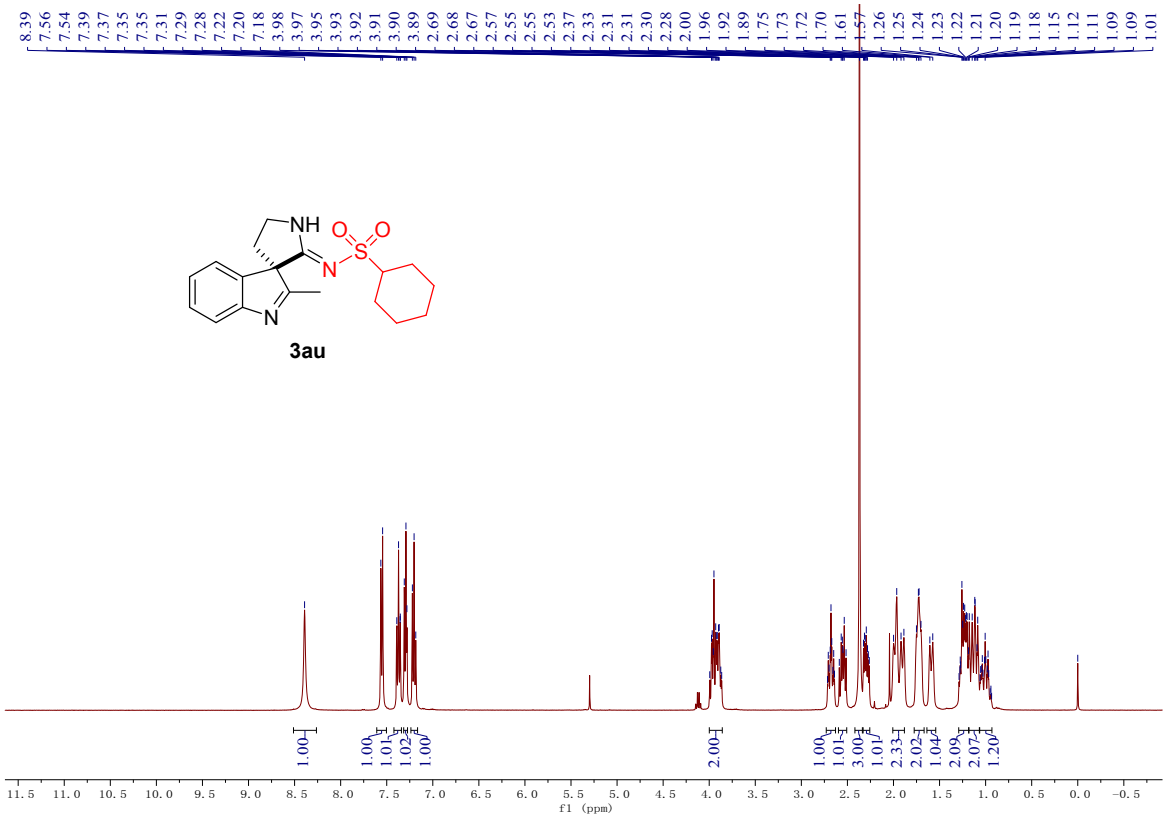
155.3
140.7
129.3
126.2
121.5
120.6
68.2
55.7
45.3
29.4
17.2
16.5
12.9
NH
O
O
S
N
N
3at
f1 (ppm)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7.22
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7.18
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3.97
3.95
3.93
3.92
3.91
3.90
3.89
2.69
2.68
2.67
2.57
2.55
2.55
2.53
2.37
2.33
2.31
2.31
2.30
2.28
2.00
1.96
1.92
1.89
1.75
1.73
1.72
1.70
1.61
1.57
1.26
1.25
1.24
1.23
1.22
1.21
1.20
1.19
1.18
1.15
1.12
1.11
1.09
1.09
1.01
NH
O
O
S
N
N
3au
1.00
1.00
1.01
1.02
1.00
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3.00
1.01
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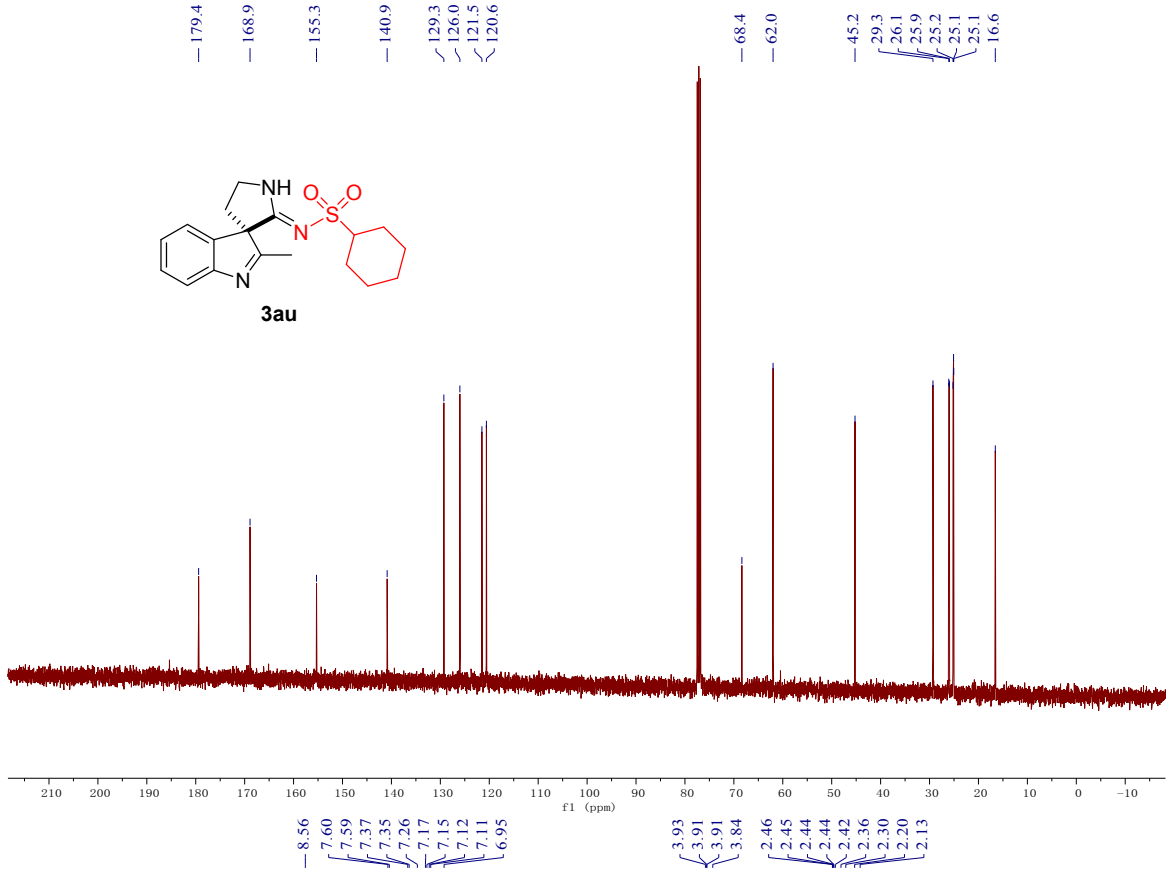
2.02
1.04
2.09
2.07
1.20
f1 (ppm)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121.5
120.6
68.4
62.0
45.2
29.3
26.1
25.9
25.2
25.1
25.1
16.6
NH
O
S
O
N
N
3au
f1 (ppm)
8.56
7.60
7.59
7.37
7.35
7.26
7.17
7.15
7.12
7.11
6.95
3.93
3.91
3.91
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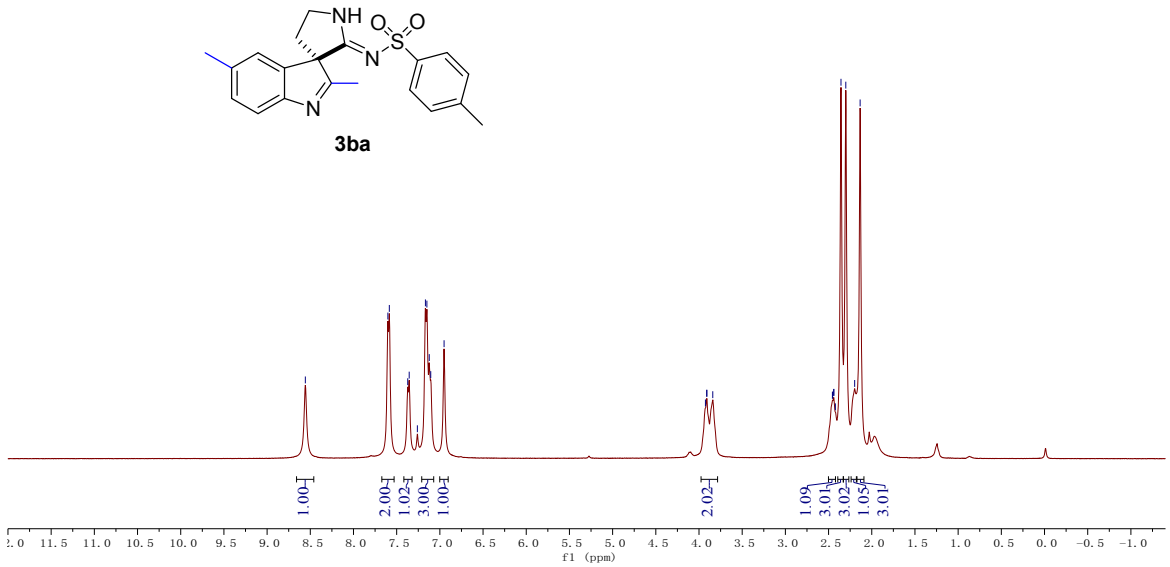
2.44
2.44
2.42
2.36
2.30
2.20
2.13


NH
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S
O
N
N
3ba
f1 (ppm)
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3.00
1.00
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1.09
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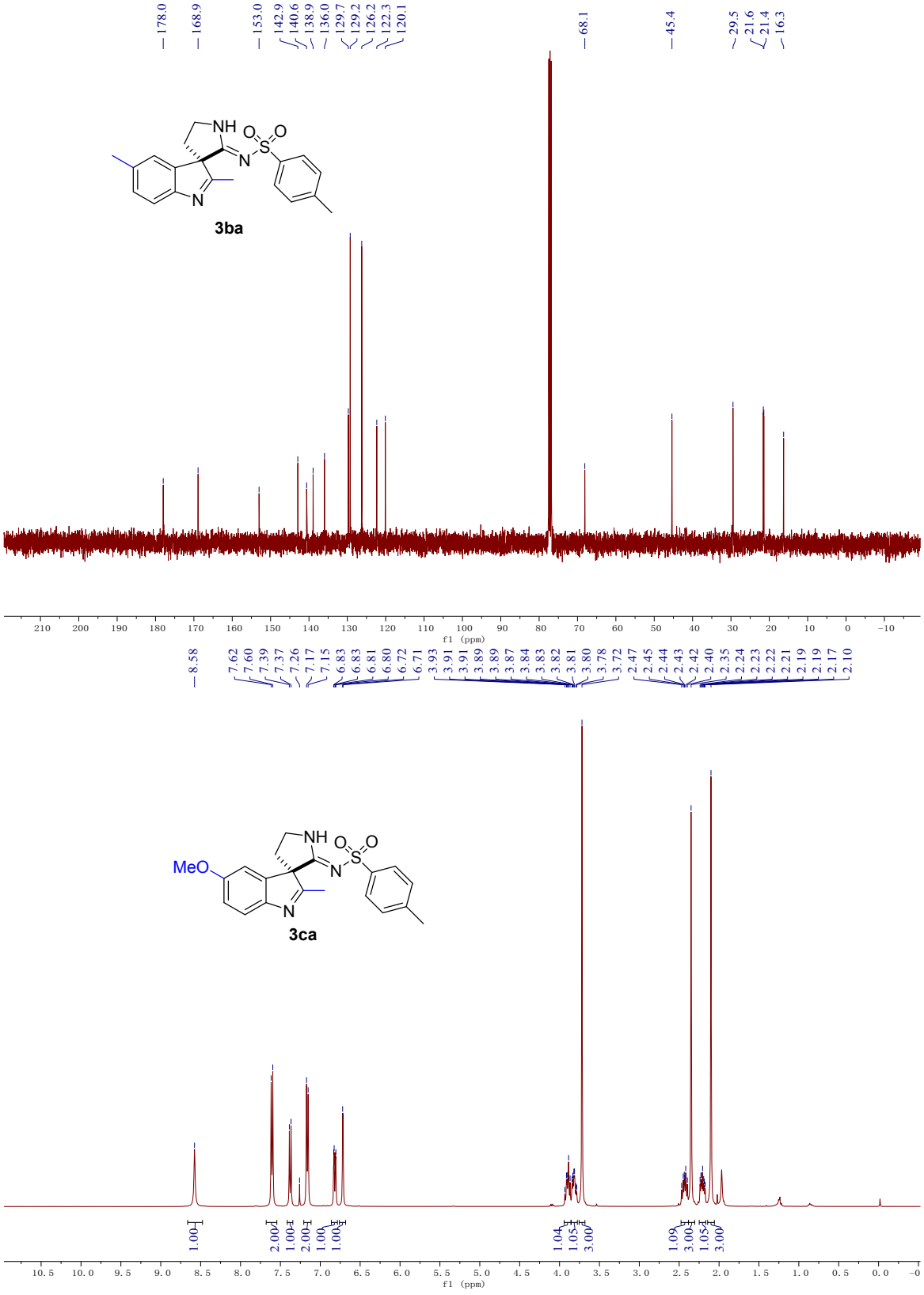
3.02
1.05
3.01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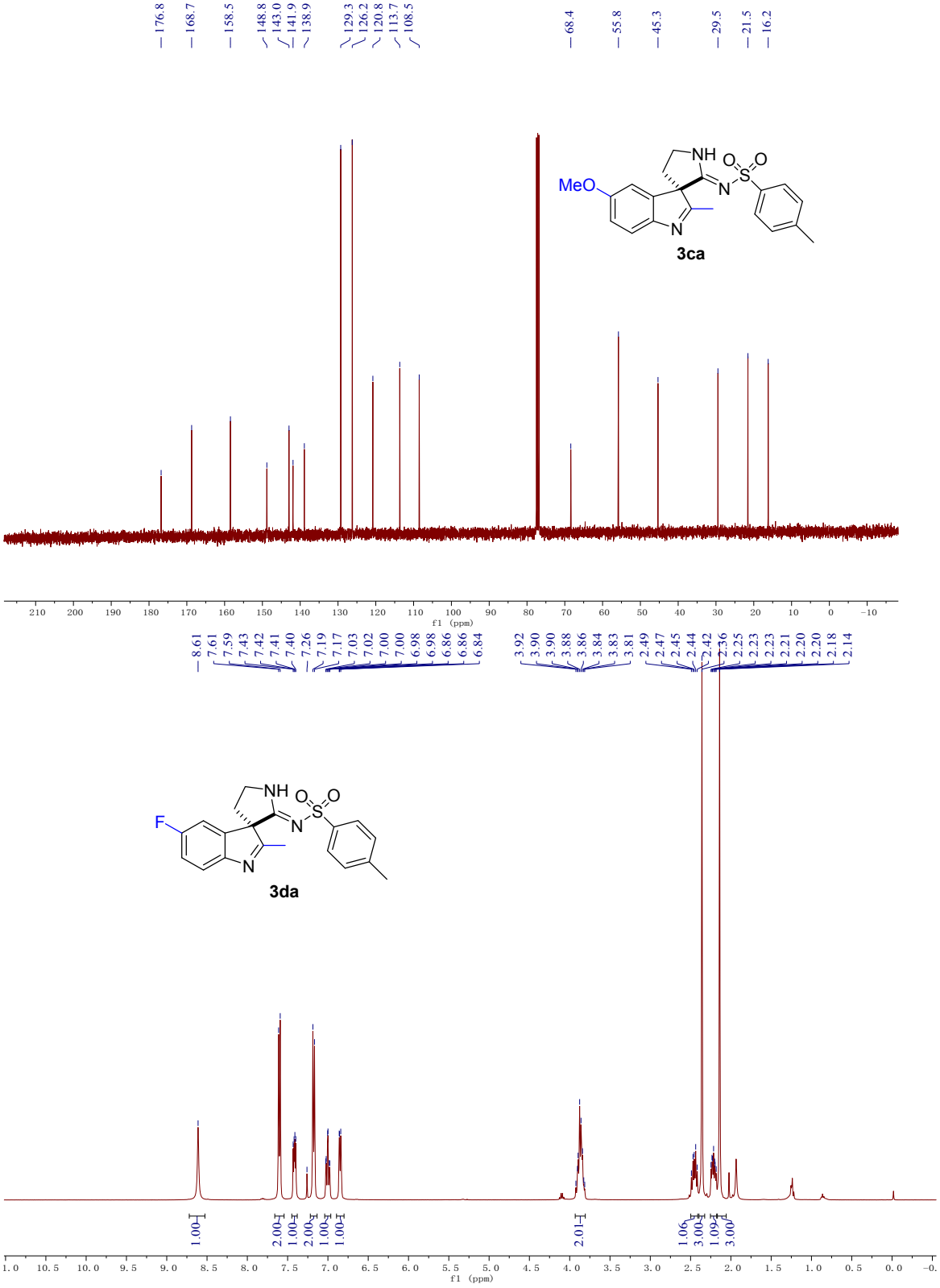
138.9
136.0
129.7
129.2
126.2
122.3
120.1
68.1
45.4
29.5
21.6
21.4
16.3
NH
O
S
O
N
N
3ba
f1 (ppm)
8.58
7.62
7.60
7.39
7.37
7.26
7.17
7.15
6.83
6.83
6.81
6.80
6.72
6.71
3.93
3.91
3.89
3.89
3.87
3.84
3.83
3.82
3.81
3.80
3.78
3.72
2.47
2.45
2.44
2.43
2.42
2.40
2.35
2.24
2.23
2.22
2.21
2.19
2.19
2.17
2.10
MeO
NH
O
S
O
N
N
3ca
1.00
2.00
1.00
2.00
1.00
1.00
1.04
1.05
3.00
1.09
3.00
1.05
3.00
f1 (ppm)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148.8
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141.9
138.9
129.3
126.2
120.8
113.7
108.5
68.4
55.8
45.3
29.5
21.5
16.2
MeO
NH
O
S
O
N
N
3ca
f1 (ppm)
8.61
7.61
7.59
7.43
7.42
7.41
7.40
7.26
7.19
7.17
7.03
7.02
7.00
7.00
6.98
6.98
6.86
6.86
6.84
3.92
3.90
3.90
3.88
3.86
3.84
3.83
3.81
2.49
2.47
2.45
2.44
2.42
2.36
2.25
2.23
2.23
2.21
2.20
2.20
2.18
2.14
F
NH
O
S
O
N
N
3da
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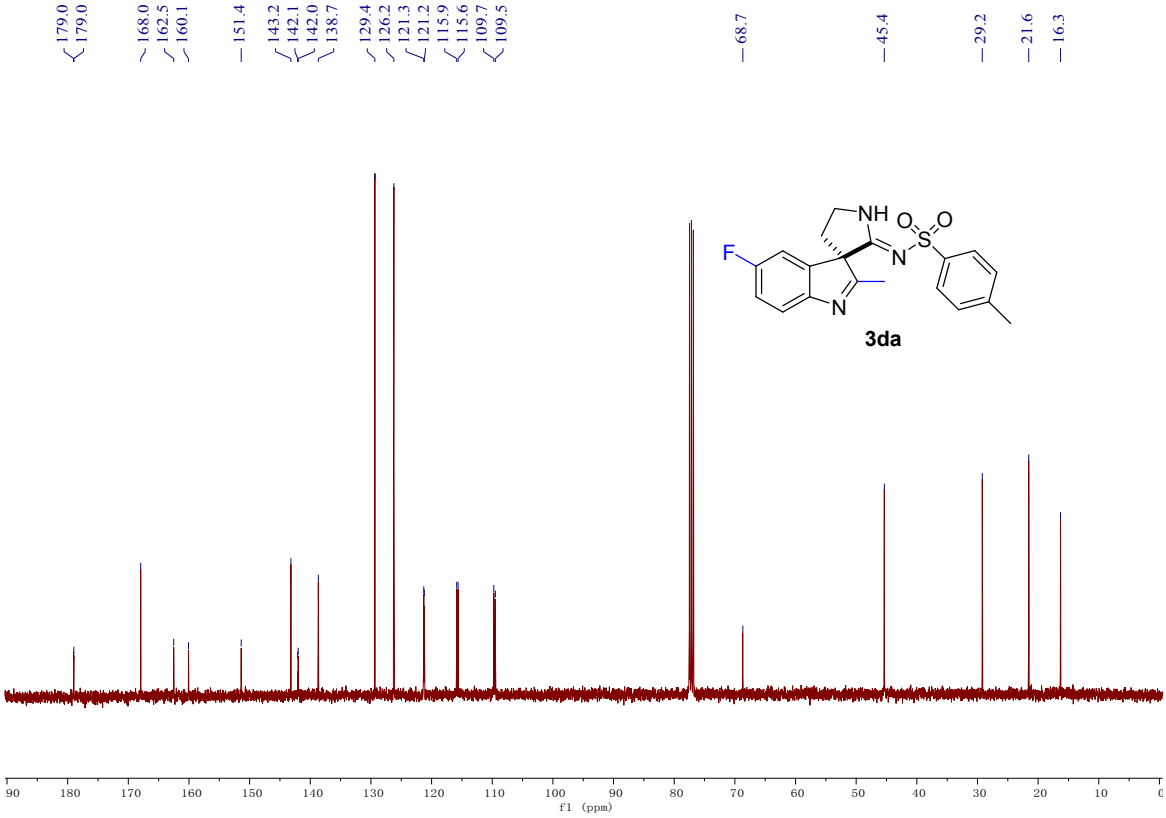
2.00
1.00
1.00
2.01
1.06
3.00
1.09
3.00
f1 (ppm)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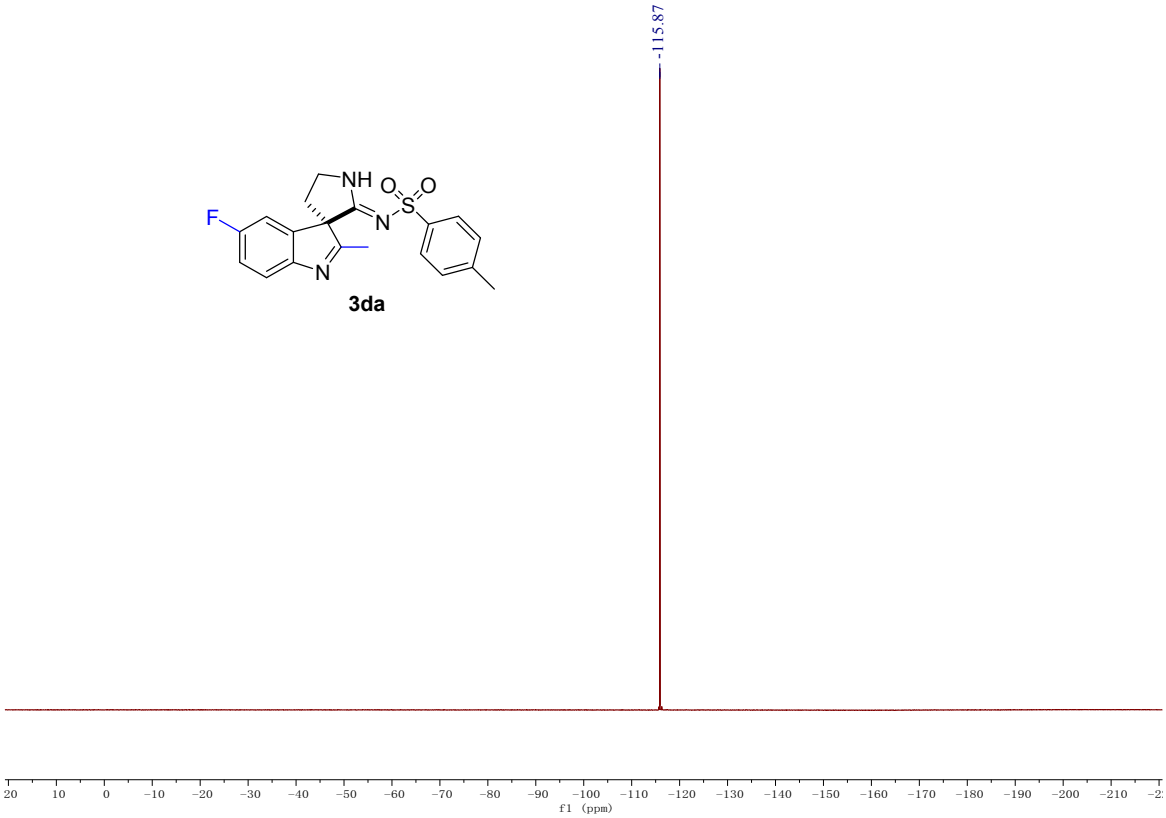
179.0
168.0
162.5
160.1
151.4
143.2
142.1
142.0
138.7
129.4
126.2
121.3
121.2
115.9
115.6
109.7
109.5
68.7
45.4
29.2
21.6
16.3
NH
O
O
S
N
F
N
3da
f1 (ppm)


-115.87
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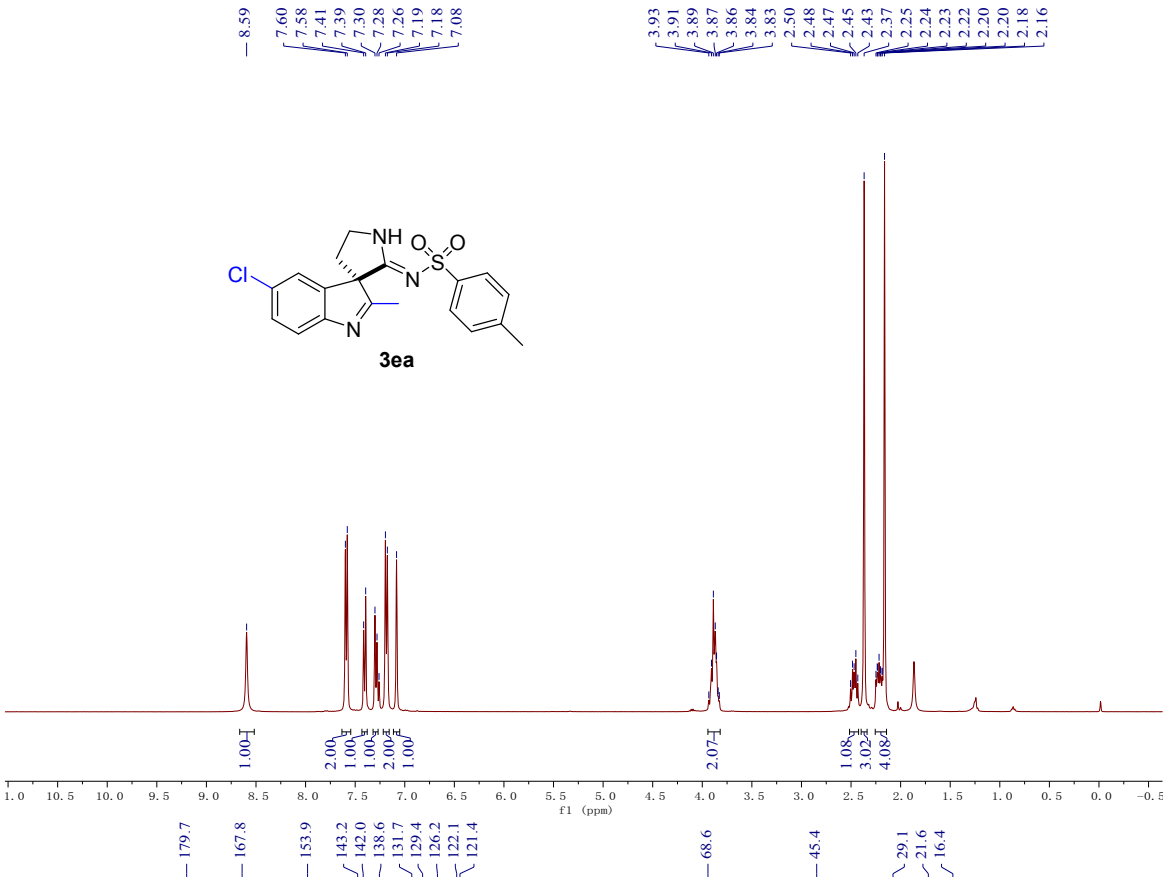
O
S
N
F
N
3da
f1 (ppm)


8.59
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7.41
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7.30
7.28
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7.19
7.18
7.08
3.93
3.91
3.89
3.87
3.86
3.84
3.83
2.50
2.48
2.47
2.45
2.43
2.37
2.25
2.24
2.23
2.22
2.20
2.20
2.18
2.16
NH
O
O
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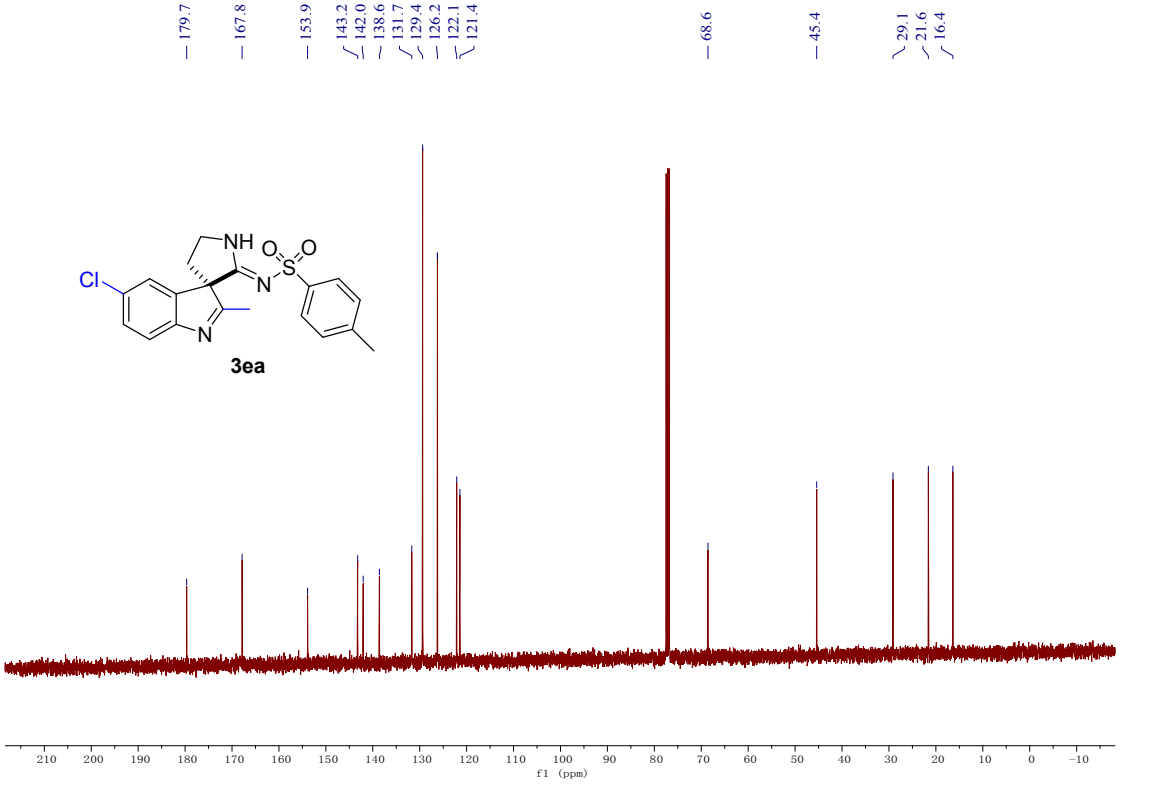
1.08
3.02
4.08
f1 (ppm)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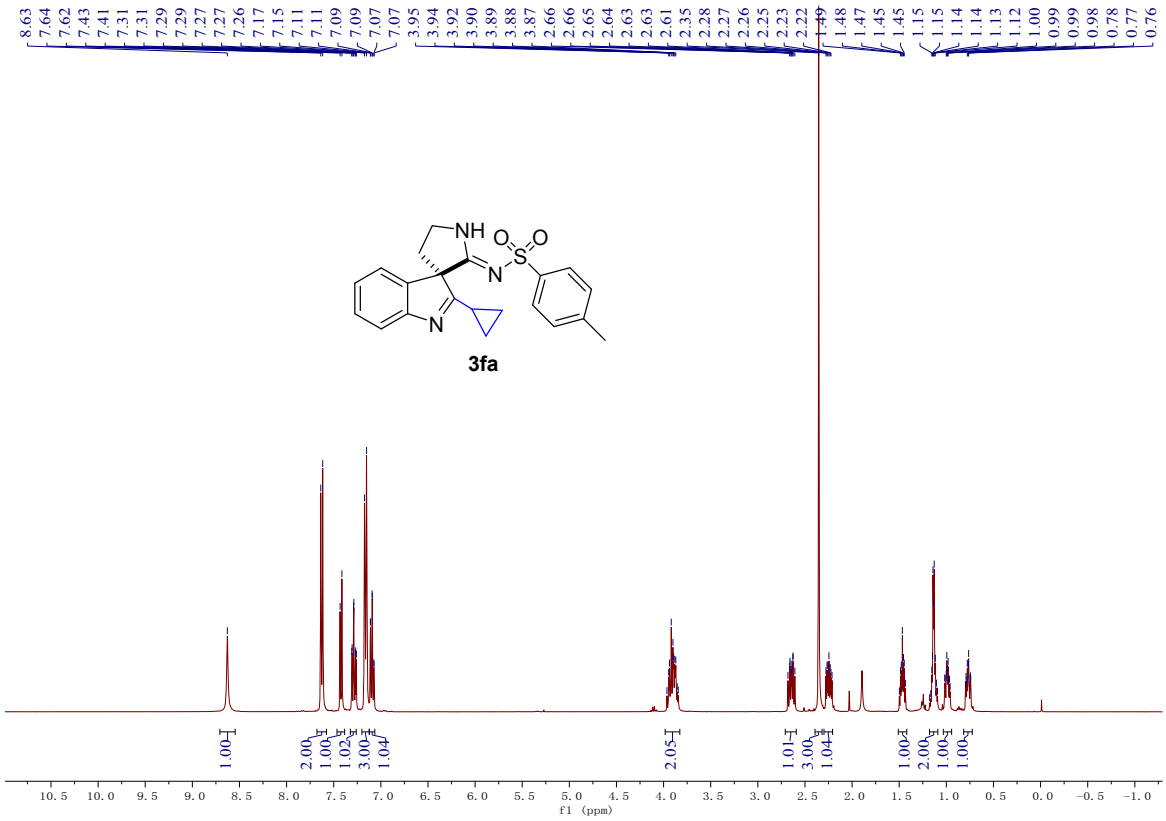
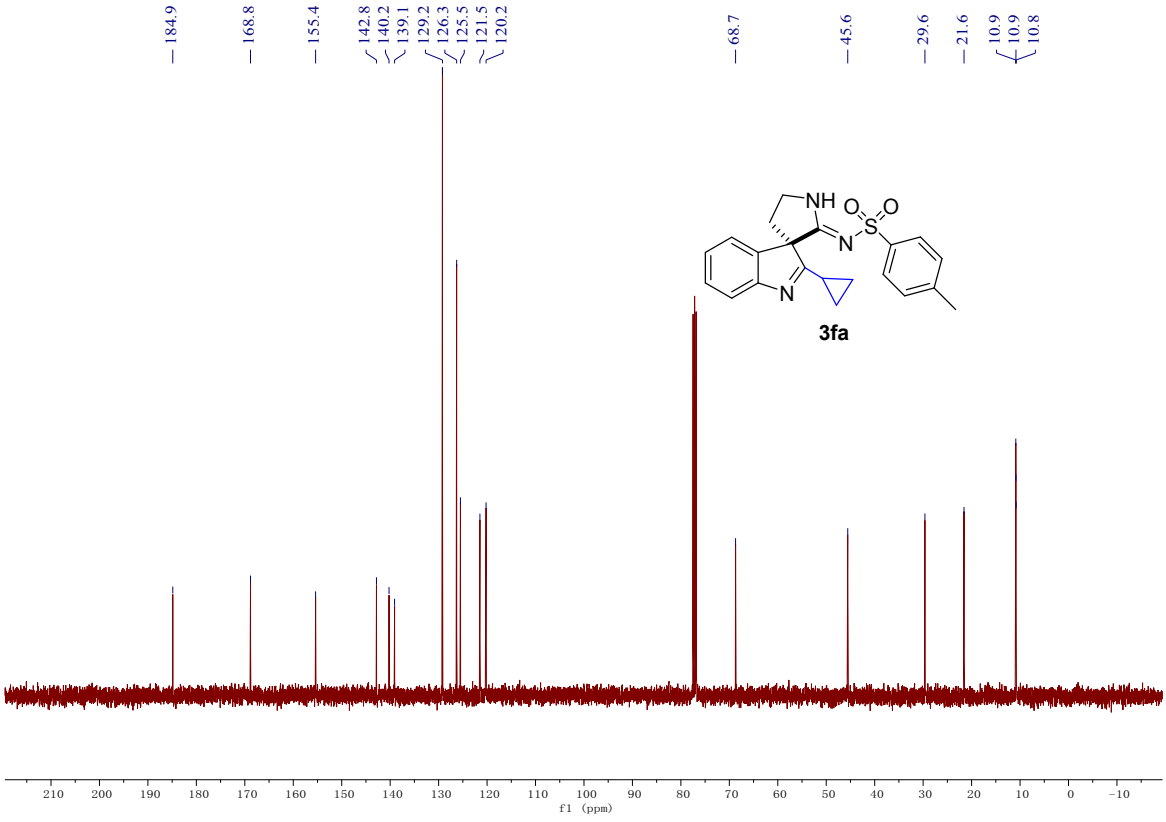
167.8
153.9
143.2
142.0
138.6
131.7
129.4
126.2
122.1
121.4
68.6
45.4
29.1
21.6
16.4
NH
O
O
S
N
Cl
N
3ea
f1 (ppm)


8.63 7.64 7.62 7.43 7.41 7.31 7.31 7.29 7.29 7.27 7.27 7.26 7.17 7.15 7.11 7.11 7.09 7.09 7.07 7.07 3.95 3.94 3.92 3.90 3.89 3.88 3.87 2.66 2.66 2.65 2.64 2.63 2.63 2.61 2.35 2.28 2.27 2.26 2.25 2.23 2.22 1.49 1.48 1.47 1.45 1.45 1.15 1.15 1.14 1.14 1.13 1.12 1.00 0.99 0.99 0.98 0.78 0.77 0.76
NH
O
O
S
N
N
3fa
1.00 2.00 1.00 1.02 3.00 1.04 2.05 1.01 3.00 1.04 1.00 2.00 1.00 1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)


184.9 168.8 155.4 142.8 140.2 139.1 129.2 126.3 125.5 121.5 120.2 68.7 45.6 29.6 21.6 10.9 10.9 10.8
NH
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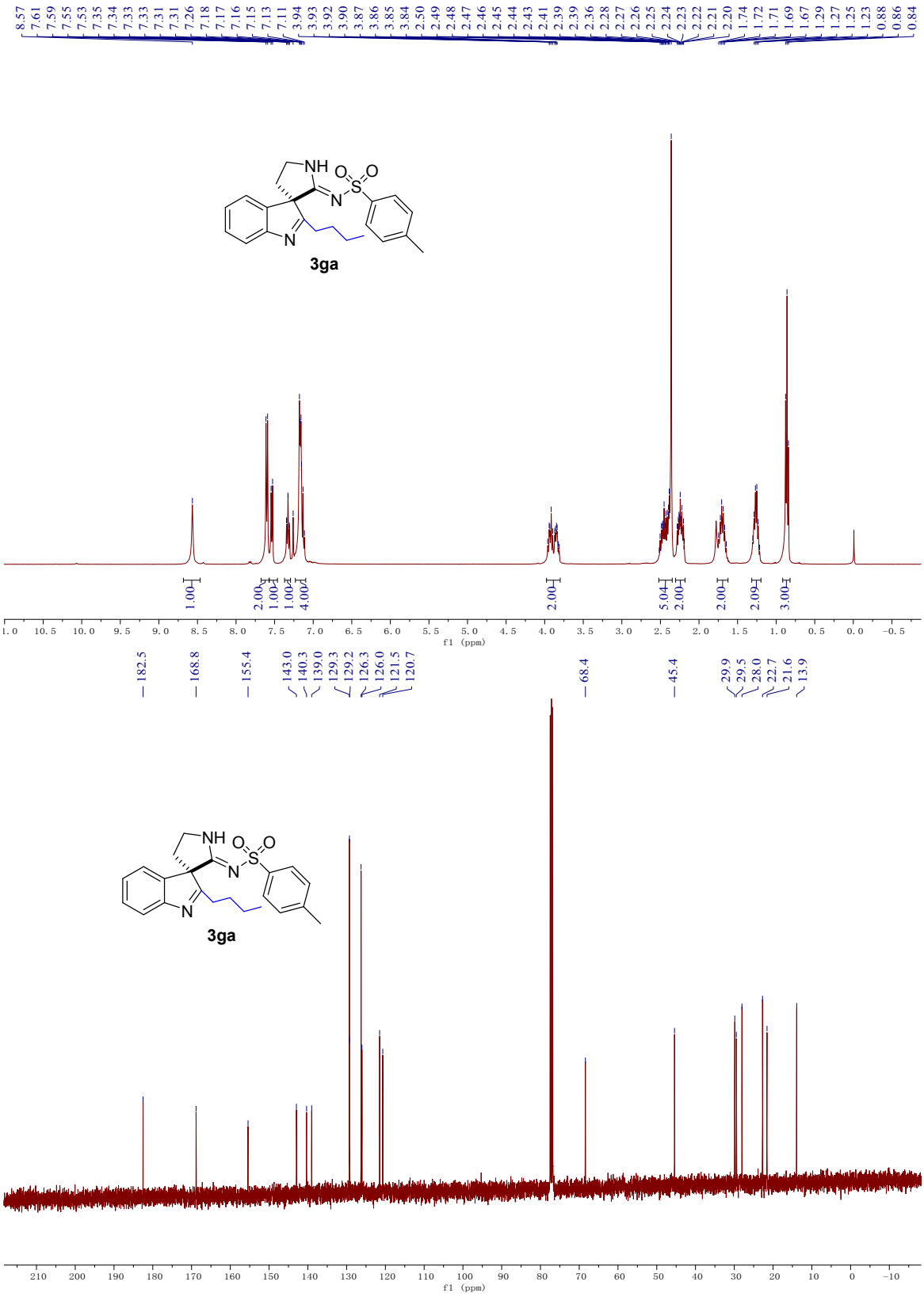
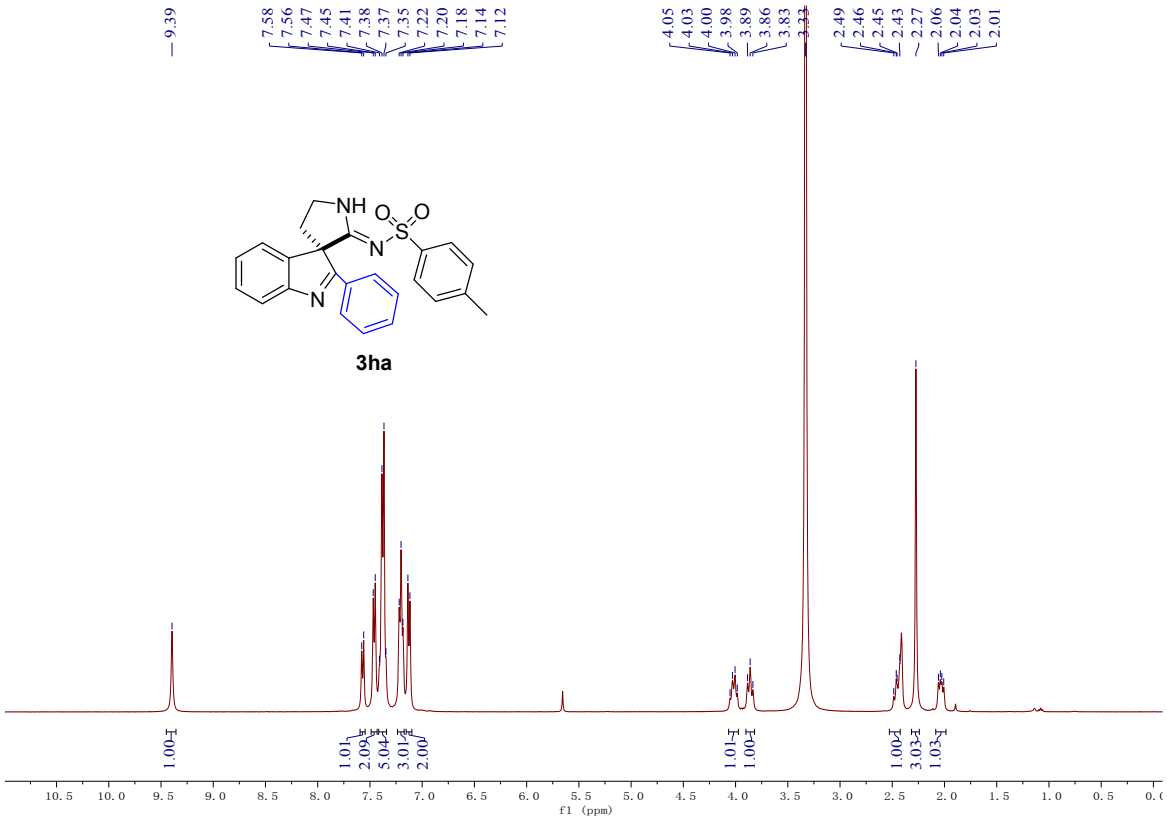
O
S
N
N
3fa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


8.57 7.61 7.59 7.55 7.53 7.35 7.34 7.33 7.33 7.31 7.31 7.26 7.18 7.17 7.16 7.15 7.13 7.11 3.94 3.93 3.92 3.90 3.87 3.86 3.85 3.84 2.50 2.49 2.48 2.47 2.46 2.45 2.44 2.43 2.41 2.39 2.39 2.36 2.28 2.27 2.26 2.25 2.24 2.23 2.22 2.21 2.20 1.74 1.72 1.71 1.69 1.67 1.29 1.27 1.25 1.23 0.88 0.86 0.84
NH
O
O
S
N
N
3ga
1.00 2.00 1.00 1.00 4.00 2.00 5.04 2.00 2.00 2.09 3.00
f1 (ppm)
182.5 168.8 155.4 143.0 140.3 139.0 129.3 129.2 126.3 126.0 121.5 120.7 68.4 45.4 29.9 29.5 28.0 22.7 21.6 13.9
f1 (ppm)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7.20
7.18
7.14
7.12
4.05
4.03
4.00
3.98
3.89
3.86
3.83
3.33
2.49
2.46
2.45
2.43
2.27
2.06
2.04
2.03
2.01
NH
O
S
O
N
N
3ha
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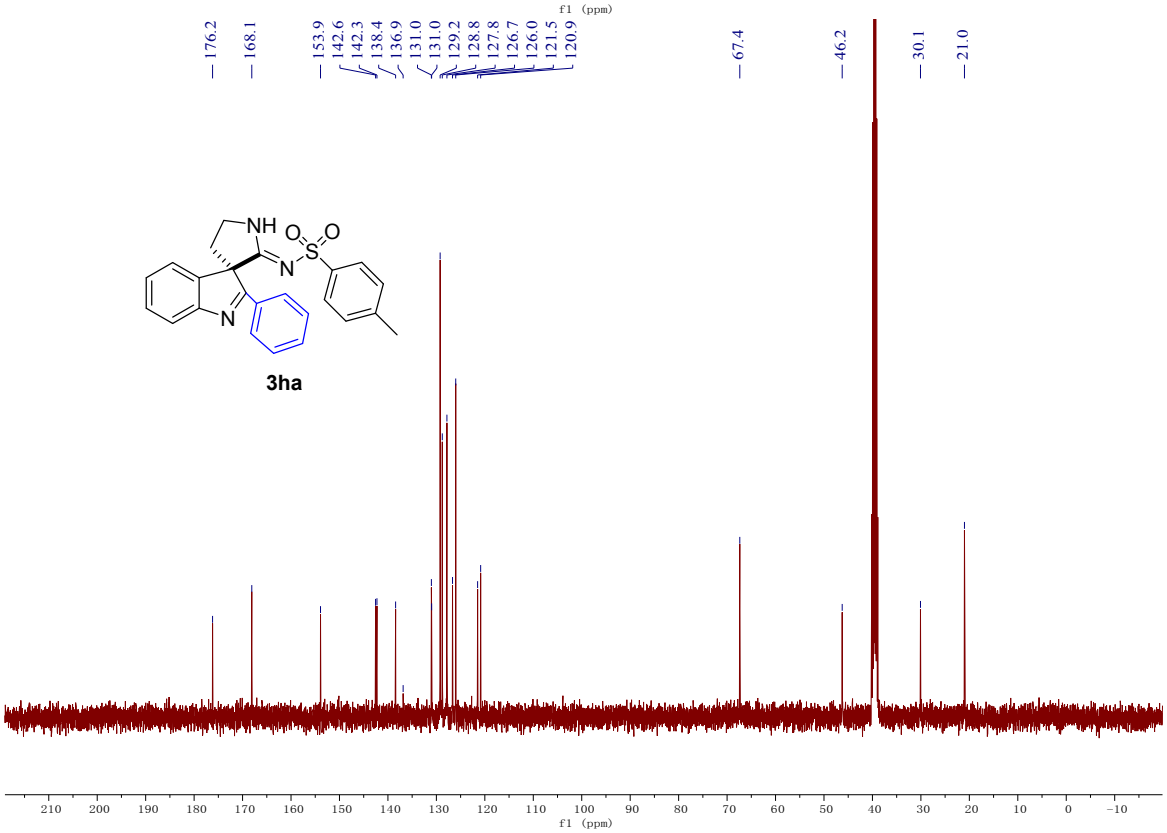
1.01
2.09
5.04
3.01
2.00
1.01
1.00
1.00
3.03
1.03
f1 (ppm)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153.9
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142.3
138.4
136.9
131.0
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129.2
128.8
127.8
126.7
126.0
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67.4
46.2
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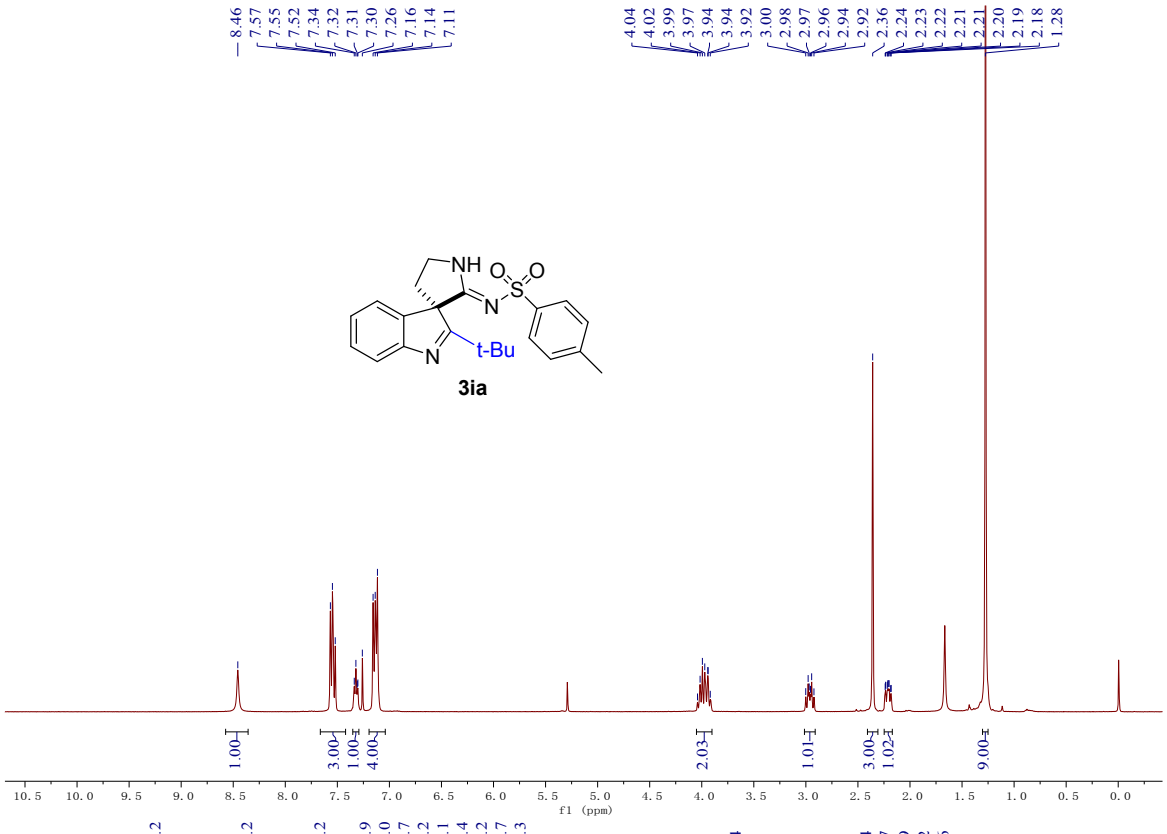
NH
O
S
O
N
N
3ha
f1 (ppm)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7.31
7.30
7.26
7.16
7.14
7.11
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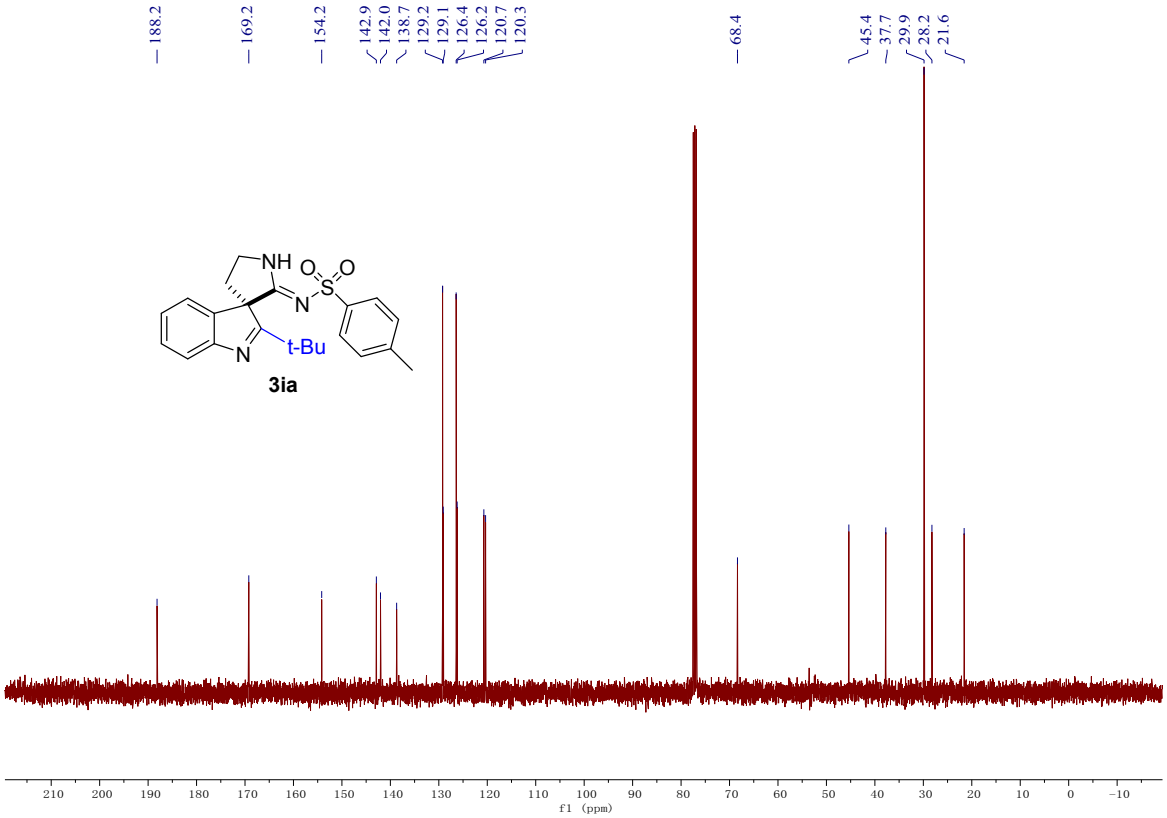
4.02
3.99
3.97
3.94
3.94
3.92
3.00
2.98
2.97
2.96
2.94
2.92
2.36
2.24
2.23
2.22
2.21
2.21
2.20
2.19
2.18
1.28
NH
O
O
S
N
N
t-Bu
3ia
1.00
3.00
1.00
4.00
2.03
1.01
3.00
1.02
9.00
f1 (ppm)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129.1
126.4
126.2
120.7
120.3
68.4
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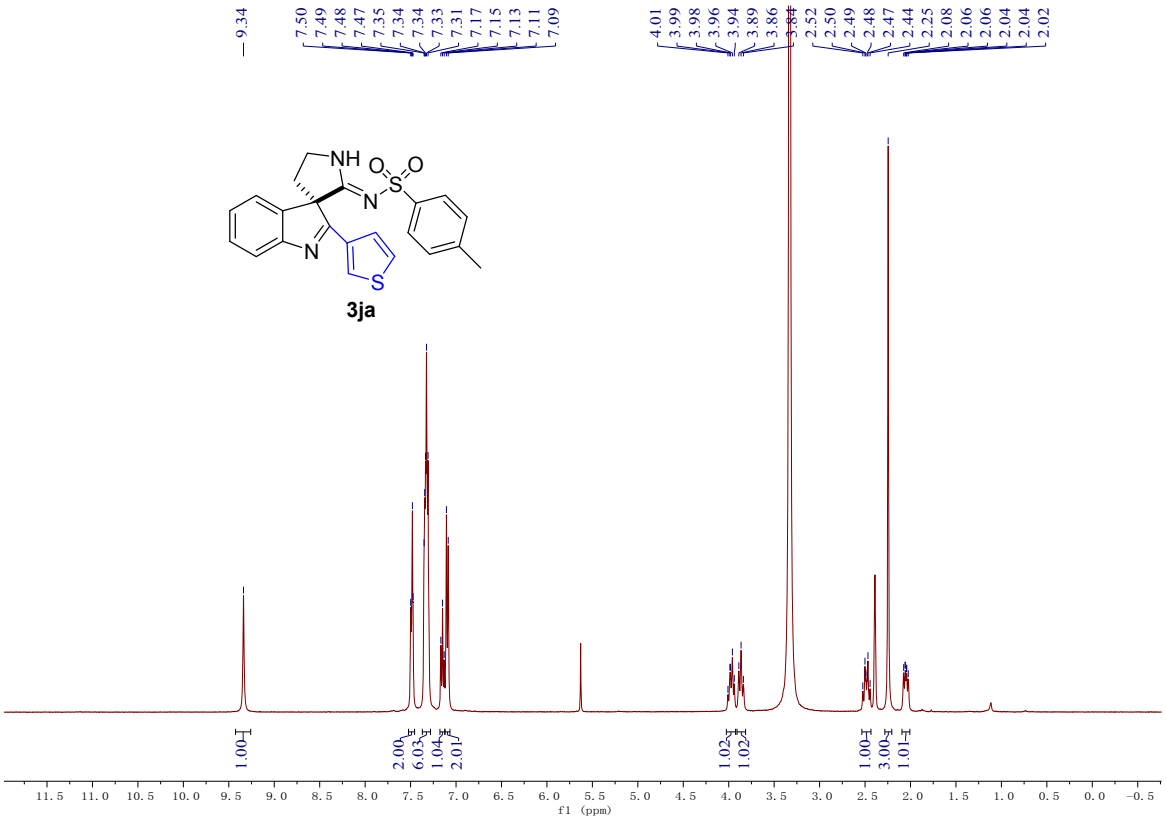
29.9
28.2
21.6
NH
O
O
S
N
N
t-Bu
3ia
f1 (ppm)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7.31
7.17
7.15
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2.49
2.48
2.47
2.44
2.25
2.08
2.06
2.06
2.04
2.04
2.02
NH
O
O
S
N
N
S
3ja
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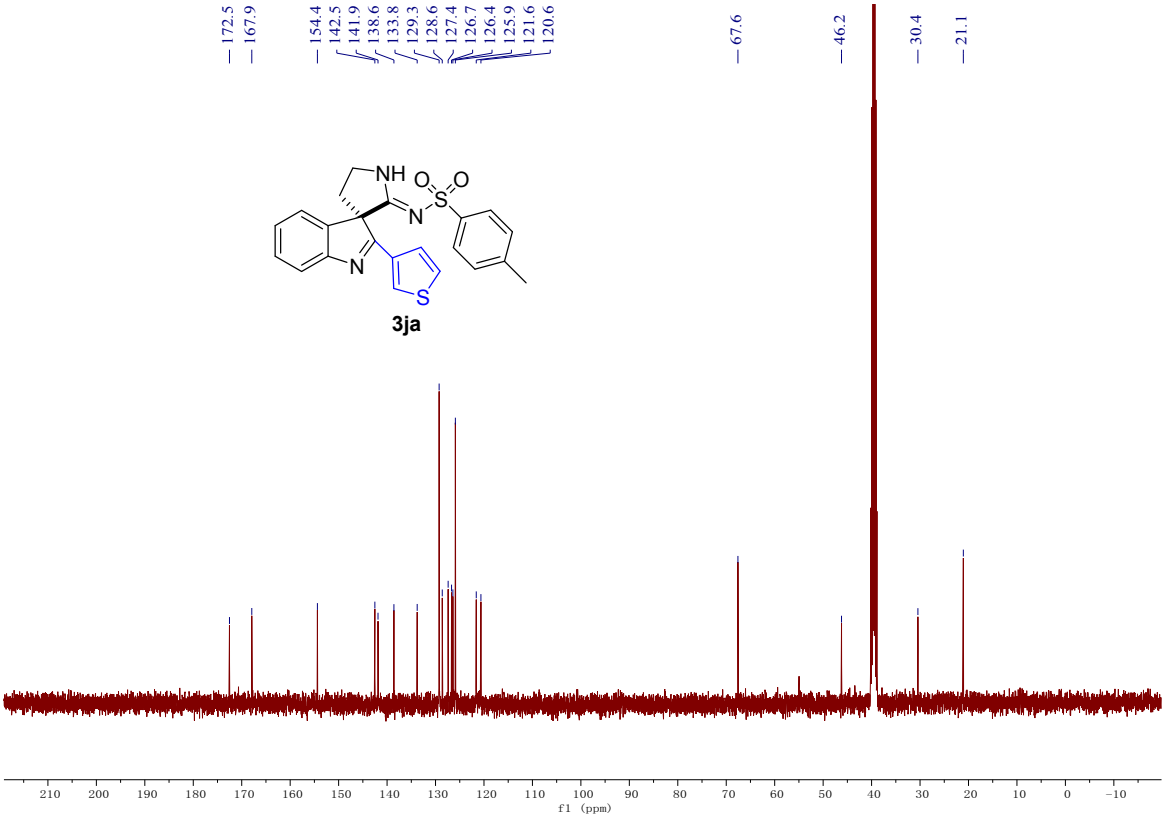
2.00
6.03
1.04
2.01
1.02
1.02
1.00
3.00
1.01
f1 (ppm)


172.5
167.9
154.4
142.5
141.9
138.6
133.8
129.3
128.6
127.4
126.7
126.4
125.9
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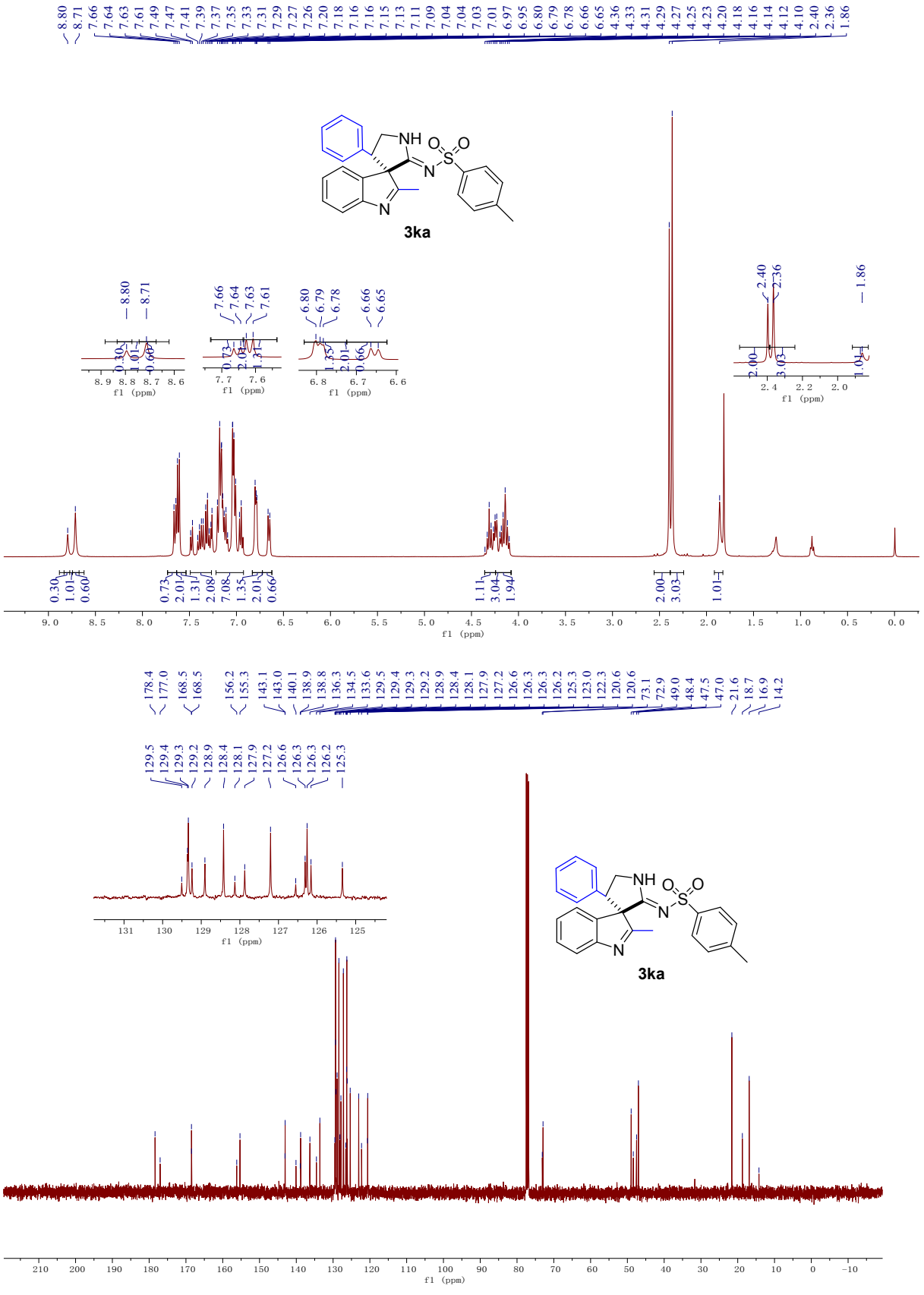
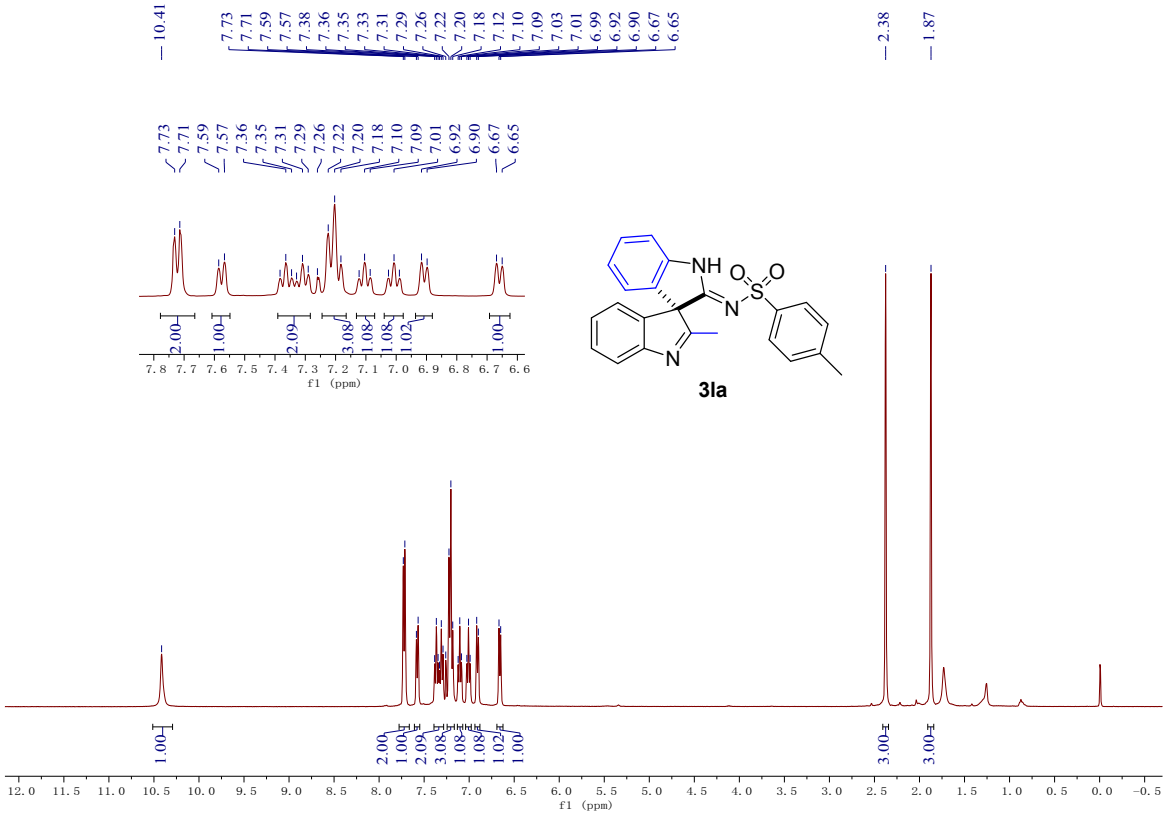
O
O
S
N
N
S
3ja
f1 (ppm)


3ka
f1 (ppm)
3ka
f1 (ppm)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7.59
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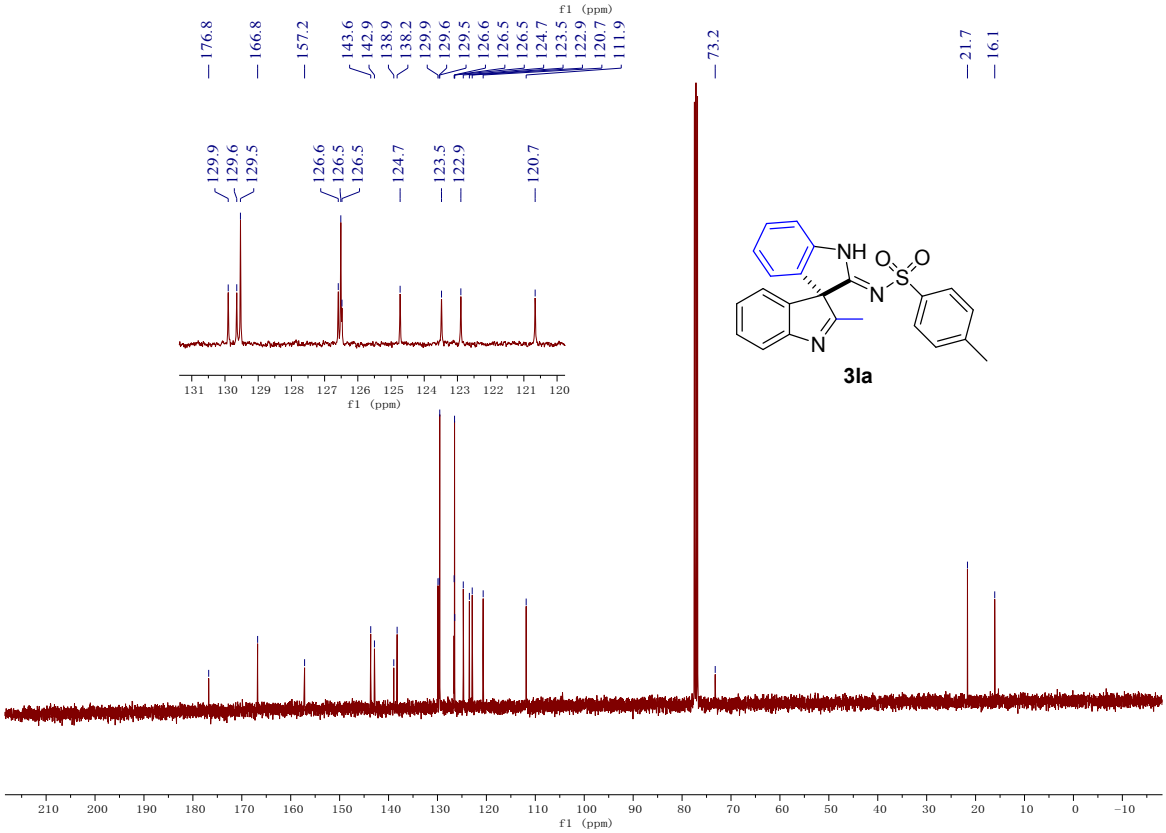
7.38
7.36
7.35
7.33
7.31
7.29
7.26
7.22
7.20
7.18
7.12
7.10
7.09
7.03
7.01
6.99
6.92
6.90
6.67
6.65
2.38
1.87
NH
O
O
S
N
N
3la
f1 (ppm)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157.2
143.6
142.9
138.9
138.2
129.9
129.6
129.5
126.6
126.5
126.5
124.7
123.5
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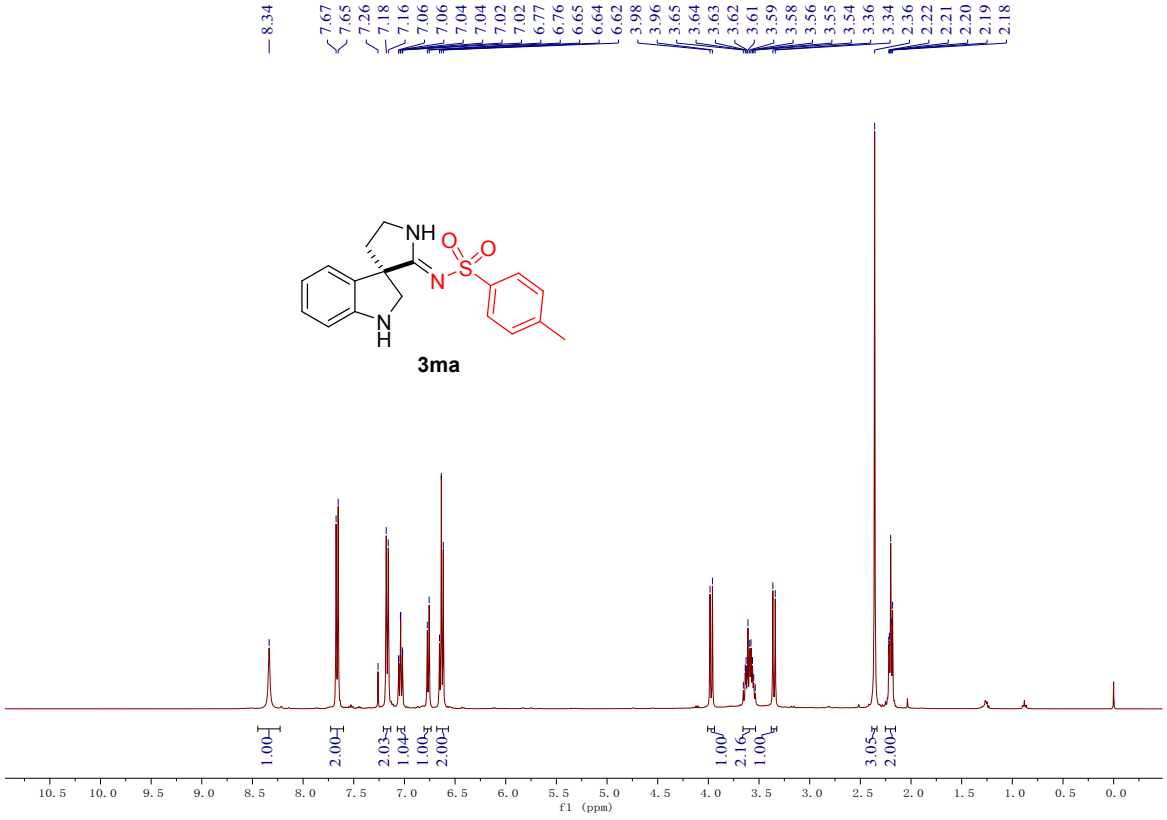
111.9
73.2
21.7
16.1
NH
O
O
S
N
N
3la
f1 (ppm)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7.06
7.06
7.04
7.04
7.02
7.02
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6.62
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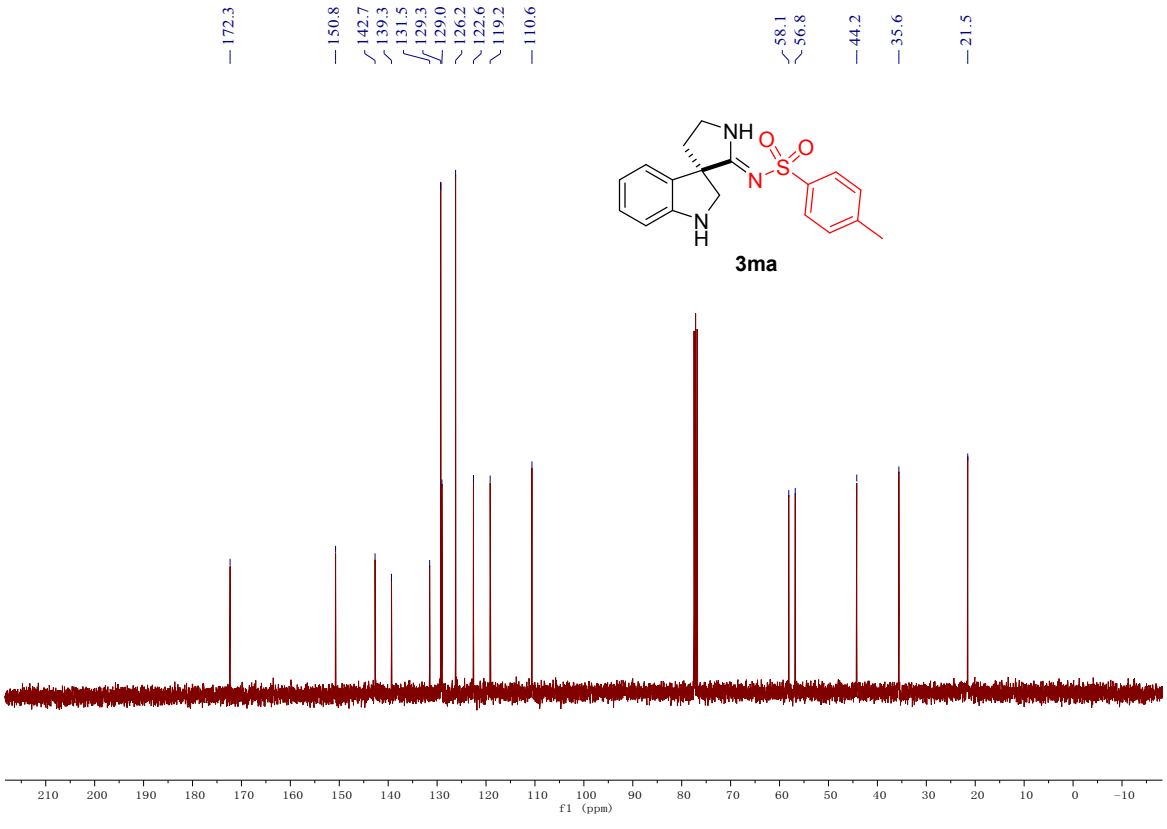
3.59
3.58
3.56
3.55
3.54
3.36
3.34
2.36
2.22
2.21
2.20
2.19
2.18
NH
O
O
N
S
N
H
3ma
1.00
2.00
2.03
1.04
1.00
2.00
1.00
2.16
1.00
3.05
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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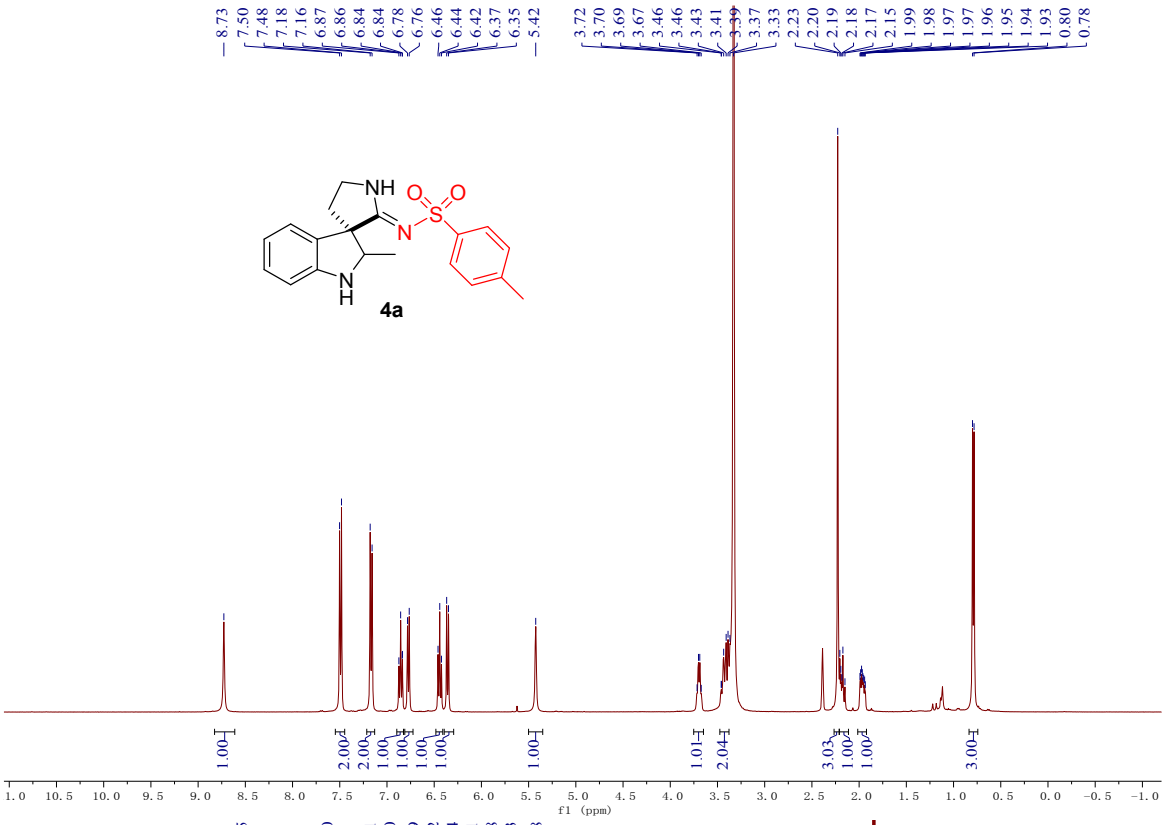
142.7
139.3
131.5
129.3
129.0
126.2
122.6
119.2
110.6
58.1
56.8
44.2
35.6
21.5
NH
O
O
N
S
N
H
3ma
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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6.84
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6.42
6.37
6.35
5.42
3.72
3.70
3.69
3.67
3.46
3.46
3.43
3.41
3.39
3.37
3.33
2.23
2.20
2.19
2.18
2.17
2.15
1.99
1.98
1.97
1.97
1.96
1.95
1.94
1.93
0.80
0.78
NH
O
O
S
N
N
H
4a
1.00
2.00
2.00
1.00
1.00
1.00
1.00
1.01
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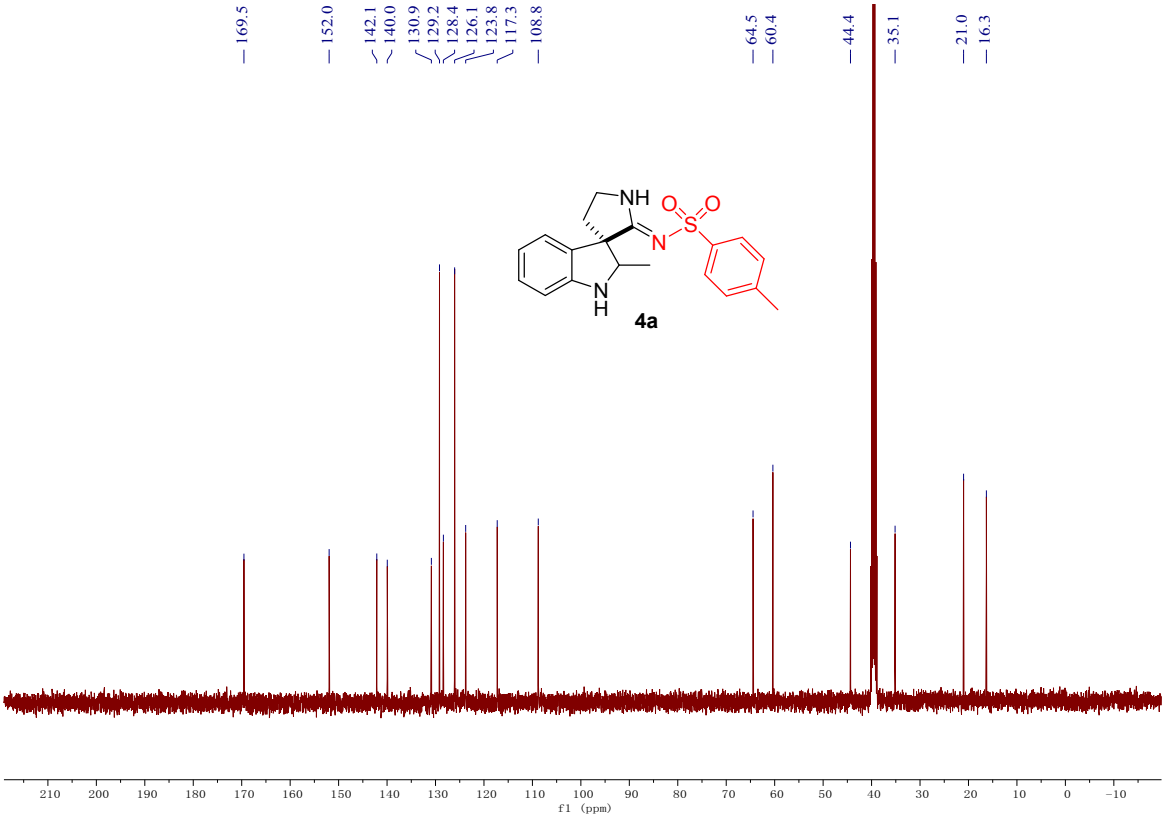
3.03
1.00
1.00
3.00
f1 (ppm)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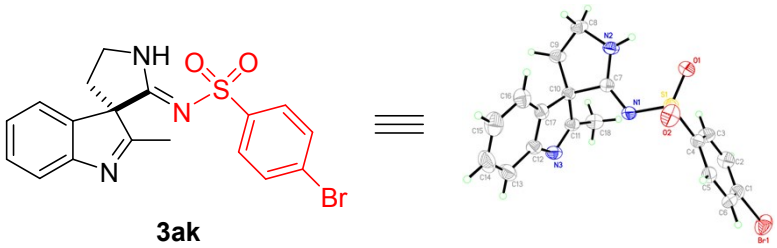
142.1
140.0
130.9
129.2
128.4
126.1
123.8
117.3
108.8
64.5
60.4
44.4
35.1
21.0
16.3
NH
O
O
S
N
N
H
4a
f1 (ppm)

9. Crystal data and structure refinement for 3ak.



3ak

Crystal data and structure refinement for **3ak**.

Crystal number: CCDC 2034492

Empirical formula: $C_{18}H_{16}BrN_3O_2S$

Formula weight: 418.30

Unit cell parameters: a = 15.138 (3) Å, b = 10.099 (2) Å, c = 22.516 (7) Å,

$\alpha = 90$, $\beta = 90$, $\gamma = 90$

Temperature: 296 K

Wavelength: 0.71073 Å

Crystal system: orthorhombic

Volume: 3442.2 (15) $Å^3$

Calculated density: 1.614 Mg/m^3

Absorption coefficient: 2.527 mm^{-1}

F (000): 1696

Crystal size: 0.50× 0.30 × 0.20 mm^3

Correction-type: multi-scan

h, k, l max: 19,13,29

Tmin, Tmax: 0.283/0.746

Data completeness: 0.989