Supporting Information

# Metal-Free Diastereoselective Construction of Bridged Ketal Spirooxindoles via Michael Addition-Inspired Sequence

Yanshuo Zhu,[a] Jing Zhou,[b] Shaojing Jin,[a] Huahui Dong,[a] Jiaomei Guo,[a] Xuguan Bai,[a] Qilin Wang,*[a] and Zhanwei Bu*[a]

[a] College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, China

[b] School of Pharmaceutical Science, Chongqing Research Center for Pharmaceutical Engineering, Chongqing Medical University, Chongqing 400016, China

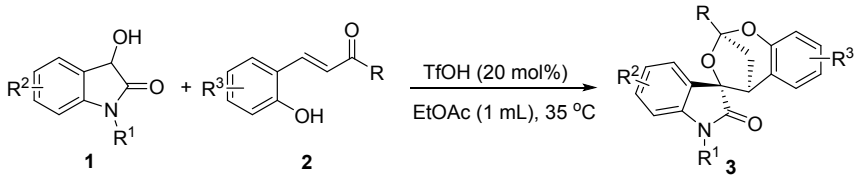
E-mail: wangqilin@henu.edu.cn; buzhanwei@henu.edu.cn

Table of Contents

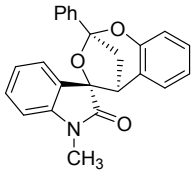
## 1. General methods

NMR spectra were recorded with tetramethylsilane as the internal standard. $^{1}H$ NMR spectra were recorded at 400 MHz, and $^{13}C$ NMR spectra were recorded at 100 MHz (Bruker Avance). $^{1}H$ NMR chemical shifts (δ) are reported in ppm relative to tetramethylsilane (TMS) with the solvent signal as the internal standard ($CDCl_3$ at 7.26 ppm, $(CD_3)_2SO$ at 2.50 ppm). $^{13}C$ NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ at 77.00 ppm, $(CD_3)_2SO$ at 39.52 ppm). Data are given as: s (singlet), d (doublet), t (triplet), q (quartet), dd (double of doublet), br (broad) or m (multiplets), coupling constants (Hz) and integration. Flash column chromatography was carried out using silica gel eluting with ethyl acetate and petroleum ether. High resolution mass spectra were obtained with the Q-TOF-Premier mass spectrometer. Reactions were monitored by TLC and visualized with ultraviolet light. IR spectra were recorded on a Thermo Fisher Nicolet Avatar 360 FTIR spectrometer on a KBr beam splitter. All the solvents were used directly without any purification.

## 2. Experimental data for bridged ketal spirooxindoles 3



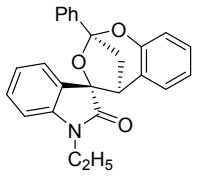

**General procedure：** To a dried tube were successively added 3-hydrooxindoles **1** (0.24 mmol), *ortho*-hydroxychalcone **2** (0.20 mmol) and 1.0 mL EtOAc, followed by adding TfOH (3.5 μL, 0.04 mmol) by syringe. The resulting mixture was stirred at 35 °C till almost full consumption of **2** monitored by thin layer chromatography, and then the reaction mixture was directly subjected to flash column chromatography on silica gel (petroleum ether/ ethyl acetate) to afford the corresponding products **3**. For products **3a**, **3f**, **3k**, **3n**, **3p-r**, **3t**, **3v-w** and **3y-zb**, the precipitate was generated, and only a simple filtration was needed to purify the product.




1-methyl-2'-phenyl-5'*H*-spiro[indoline-3,4'-[2,5]methanobenzo[*d*][1,3]dioxepin]-2-one (**3a**)

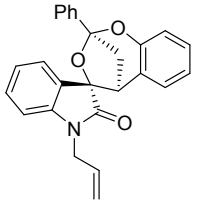
White solid obtained by filtration of the precipitate; 71.0 mg, 96% yield; reaction time = 24 h; mp

261.7-262.4 °C; $^1$H NMR (400 MHz, $CDCl_3$), δ 7.92 (d, $J$ = 8.0 Hz, 2H), 7.44 (t, $J$ = 8.0 Hz, 2H), 7.38 (t, $J$ = 8.0 Hz, 1H), 7.30 (t, $J$ = 8.0 Hz, 1H), 7.22 (t, $J$ = 8.0 Hz, 1H), 7.10 (d, $J$ = 8.0 Hz, 1H), 6.83 (t, $J$ = 8.0 Hz, 1H), 6.77 (d, $J$ = 8.0 Hz, 1H), 6.72-6.65 (m, 2H), 5.92 (d, $J$ = 8.0 Hz, 1H), 3.93 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.41 (d, $J$ = 4.0 Hz, 1H), 3.21 (s, 3H), 2.58 (d, $J$ = 12.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.4, 152.8, 143.8, 138.5, 130.1, 129.5, 128.8, 128.7, 128.2, 126.4, 125.9, 125.7, 125.1, 122.5, 120.7, 116.7, 108.9, 108.0, 90.9, 46.8, 37.7, 26.2. IR (KBr) $v$ 3407, 3055, 2951, 1712, 1613, 1478, 1346, 1236, 1112, 1046, 1008, 869, 764 cm$^{-1}$. HRMS (ESI) calcd for $C_{24}H_{19}NNaO_3$ $[M+Na]^+$ 392.1257, found 392.1251.




1-ethyl-2'-phenyl-5'*H*-spiro[indoline-3,4'-[2,5]methanobenzo[*d*][1,3]dioxepin]-2-one (**3b**)

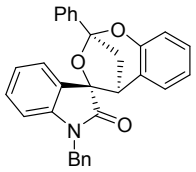
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 70:1 to 50:1); 50.7 mg, 66% yield; reaction time = 24 h; mp 138.7-139.5 °C; $^1$H NMR (400 MHz, $CDCl_3$), δ 7.93 (d, $J$ = 8.0 Hz, 2H), 7.45-7.36 (m, 3H), 7.29 (t, $J$ = 8.0 Hz, 1H), 7.20 (t, $J$ = 8.0 Hz, 1H), 7.10 (d, $J$ = 8.0 Hz, 1H), 6.82 (d, $J$ = 8.0 Hz, 1H), 6.78 (d, $J$ = 8.0 Hz, 1H), 6.70-6.65 (m, 2H), 5.93 (d, $J$ = 8.0 Hz, 1H), 3.93 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.83-3.67 (m, 2H), 3.39 (d, $J$ = 4.0 Hz, 1H), 2.57 (d, $J$ = 12.0 Hz, 1H), 1.30 (t, J = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.0, 152.8, 142.9, 138.5, 130.0, 129.4, 128.8, 128.2, 126.5, 126.1, 125.9, 125.2, 122.2, 120.7, 116.6, 109.0, 108.1, 90.9, 46.9, 37.7, 34.8, 12.6, one carbon missing in the aromatic region. IR (KBr) $v$ 3422, 3054, 2934, 1714, 1612, 1487, 1465, 1370, 1242, 1113, 1040, 896, 756, 697 cm$^{-1}$. HRMS (ESI) calcd for $C_{25}H_{22}NO_3$ $[M+H]^+$ 384.1594, found 384.1581.




1-allyl-2'-phenyl-5'*H*-spiro[indoline-3,4'-[2,5]methanobenzo[*d*][1,3]dioxepin]-2-one (**3c**)

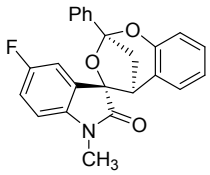
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 70:1); 44.4 mg, 56% yield; reaction time = 24 h; mp 167.4-167.8 °C; $^1$H NMR (400 MHz, $CDCl_3$), δ 7.92 (d, $J$ = 8.0 Hz, 2H), 7.45-7.35 (m, 3H), 7.29 (t, $J$ = 8.0 Hz, 1H), 7.17 (t, $J$ = 8.0 Hz, 1H), 7.10 (d, $J$ = 8.0

Hz, 1H), 6.83 (t, $J$ = 8.0 Hz, 1H), 6.76 (d, $J$ = 8.0 Hz, 1H), 6.70-6.65 (m, 2H), 5.93 (d, $J$ = 4.0 Hz, 1H), 5.90-5.82 (m, 1H), 5.30-5.24 (m, 2H), 4.41 (dd, $J_1$ = 8.0 Hz, $J_2$ = 4.0 Hz, 1H), 4.23 (dd, $J_1$ = $J_2$ = 4.0 Hz, 1H), 3.92 (dd, $J_1$ = $J_2$ = 4.0 Hz, 1H), 3.41 (d, $J$ = 4.0 Hz, 1H), 2.58 (d, $J$ = 12.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.2, 152.8, 143.0, 138.5, 131.3, 130.0, 129.5, 128.8, 128.2, 126.5, 126.0, 125.7, 125.1, 122.4, 120.7, 118.0, 116.6, 109.0, 108.8, 90.8, 47.1, 42.4, 37.7, one carbon missing in the aromatic region. IR (KBr) $v$ 3427, 3058, 2921, 1721, 1614, 1480, 1462, 1240, 1187, 1113, 1036, 897, 753, 698 cm$^{-1}$. HRMS (ESI) calcd for $C_{26}H_{22}NO_3$ $[M+H]^+$ 396.1594, found 396.1592.




1-benzyl-2'-phenyl-5'*H*-spiro[indoline-3,4'-[2,5]methanobenzo[*d*][1,3]dioxepin]-2-one (**3d**)

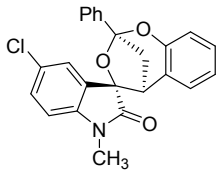
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 70:1 to 50:1); 27.7 mg, 31% yield; reaction time = 24 h; mp 202.9-203.7 °C; $^1$H NMR (400 MHz, $CDCl_3$), δ 7.86 (d, $J$ = 4.0 Hz, 2H), 7.37 (t, $J$ = 8.0 Hz, 2H), 7.32-7.16 (m, 7H), 7.02 (t, $J$ = 8.0 Hz, 2H), 6.75 (t, $J$ = 8.0 Hz, 1H), 6.58 (t, $J$ = 8.0 Hz, 3H), 5.86 (d, $J$ = 8.0 Hz, 1H), 4.95 (d, $J$ = 16.0 Hz, 1H), 4.68 (d, $J$ = 16.0 Hz, 1H), 3.90 (dd, $J_1$ = $J_2$ = 4.0 Hz, 1H), 3.37 (d, $J$ = 4.0 Hz, 1H), 2.54 (d, $J$ = 12.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.6, 152.8, 142.9, 138.5, 135.6, 130.0, 129.5, 128.9, 128.8, 128.7, 128.3, 127.8, 127.3, 126.5, 126.0, 125.7, 125.1, 122.5, 120.7, 116.7, 109.0, 108.9, 90.9, 47.2, 43.8, 37.7. IR (KBr) $v$ 3427, 3059, 2923, 1716, 1612, 1484, 1460, 1367, 1241, 1178, 1114, 1036, 896, 755, 697 cm$^{-1}$. HRMS (ESI) calcd for $C_{30}H_{24}NO_3$ $[M+H]^+$ 446.1751, found 446.1737.




5-fluoro-1-methyl-2'-phenyl-5'*H*-spiro[indoline-3,4'-[2,5]methanobenzo[*d*][1,3]dioxepin]-2-one (**3e**)

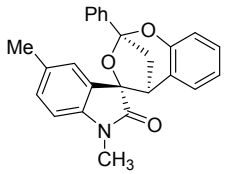
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 30:1); 68.4 mg, 88% yield; reaction time = 24 h; mp 249.2-249.8 °C; $^1$H NMR (400 MHz, $CDCl_3$), δ 7.90 (d, $J$ =

4.0 Hz, 2H), 7.45-7.30 (m, 4H), 7.11 (d, $J$ = 8.0 Hz, 1H), 6.94-6.85 (m, 2H), 6.67 (t, $J$ = 8.0 Hz, 2H), 5.61 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.91 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.41 (d, $J$ = 4.0 Hz, 1H), 3.18 (s, 3H), 2.59 (d, $J$ = 12.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.2, 158.8 (d, $J$ = 239.0 Hz, 1C), 152.6, 139.7, 138.2, 129.8, 128.9, 128.7, 128.3, 127.4 (d, $J$ = 8.0 Hz, 1C), 126.4, 124.6, 121.0, 116.8, 116.3 (d, $J$ = 23.0 Hz, 1C), 114.0 (d, $J$ = 26.0 Hz, 1C), 109.1, 108.4 (d, $J$ = 8.0 Hz, 1C), 90.7, 46.9, 37.6, 26.3. IR (KBr) $v$ 3422, 3076, 2957, 1715, 1620, 1491, 1460, 1358, 1270, 1238, 1157, 1115, 1043, 868, 759, 667 cm$^{-1}$. HRMS (ESI) calcd for $C_{24}H_{19}FNO_3$ $[M+H]^+$ 388.1343, found 388.1330.




5-chloro-1-methyl-2'-phenyl-5'*H*-spiro[indoline-3,4'-[2,5]methanobenzo[*d*][1,3]dioxepin]-2-one (**3f**)

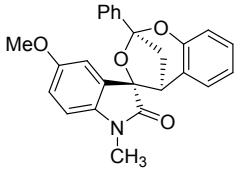
White solid obtained by filtration of the precipitate; 64.2 mg, 80% yield; reaction time = 24 h; mp 278.3-278.6 °C; $^1$H NMR (400 MHz, $CDCl_3$), δ 7.90 (d, $J$ = 8.0 Hz, 2H), 7.46-7.32 (m, 4H), 7.19 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 7.12 (d, $J$ = 8.0 Hz, 1H), 6.89 (t, $J$ = 8.0 Hz, 1H), 6.67 (t, $J$ = 8.0 Hz, 2H), 5.79 (d, $J$ = 4.0 Hz, 1H), 3.89 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.41 (d, $J$ = 4.0 Hz, 1H), 3.19 (s, 3H), 2.61 (d, $J$ = 12.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.0, 152.6, 142.2, 138.2, 129.9, 129.8, 128.9, 128.7, 128.3, 128.0, 127.4, 126.5, 126.4, 124.6, 120.9, 116.9, 109.1, 108.8, 90.7, 46.9, 37.5, 26.3. IR (KBr) $v$ 3419, 3069, 2926, 2857, 1716, 1610, 1487, 1460, 1354, 1238, 1115, 1042, 866, 760, 701 cm$^{-1}$. HRMS (ESI) calcd for $C_{24}H_{19}ClNO_3$ $[M+H]^+$ 404.1048 and 406.1018, found 404.1033 and 406.1020.




1,5-dimethyl-2'-phenyl-5'H-spiro[indoline-3,4'-[2,5]methanobenzo[d][1,3]dioxepin]-2-one (**3g**)

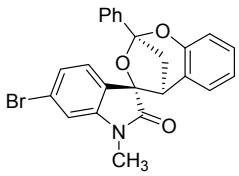
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 40:1 to 30:1); 54.7 mg, 71% yield; reaction time = 24 h; mp 177.6-178.2 °C; $^1$H NMR (400 MHz, $CDCl_3$), δ 7.92 (d, $J$ = 8.0 Hz, 2H), 7.45-7.35 (m, 3H), 7.30 (t, $J$ = 8.0 Hz, 1H), 7.10 (d, $J$ = 8.0 Hz, 1H), 7.00

(d, $J$ = 8.0 Hz, 1H), 6.83 (t, $J$ = 8.0 Hz, 1H), 6.64 (d, $J$ = 8.0 Hz, 2H), 5.66 (s, 1H), 3.91 (dd, $J_1$ = $J_2$ = 4.0 Hz, 1H), 3.39 (d, $J$ = 4.0 Hz, 1H), 3.18 (s, 3H), 2.59 (d, $J$ = 12.0 Hz, 1H), 1.98 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.4, 152.9, 141.3, 138.5, 131.9, 130.1, 129.3, 128.9, 128.7, 128.2, 126.9, 126.5, 125.6, 125.2, 120.5, 116.7, 109.0, 107.6, 91.0, 46.9, 37.6, 26.2, 20.8. IR (KBr) $v$ 3427, 3035, 2923, 2859, 1716, 1617, 1492, 1455, 1354, 1241, 1113, 1040, 869, 758 cm$^{-1}$. HRMS (ESI) calcd for $C_{25}H_{22}NO_3$ $[M+H]^+$ 384.1594, found 384.1590.




5-methoxy-1-methyl-2'-phenyl-5'H-spiro[indoline-3,4'-[2,5]methanobenzo[d][1,3]dioxepin]-2-one (**3h**)

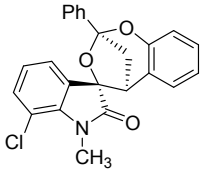
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 15:1 to 10:1); 63.8 mg, 80% yield; reaction time = 24 h; mp 117.2-117.6 °C; $^1$H NMR (400 MHz, $CDCl_3$), δ 7.92 (d, $J$ = 8.0 Hz, 2H), 7.45-7.35 (m, 3H), 7.29 (t, $J$ = 8.0 Hz, 1H), 7.11 (d, $J$ = 8.0 Hz, 1H), 6.85 (t, $J$ = 8.0 Hz, 1H), 6.75 (dd, $J_1$ = $J_2$ = 4.0 Hz, 1H), 6.69-6.64 (m, 2H), 5.55 (d, $J$ = 4.0 Hz, 1H), 3.92 (dd, $J_1$ = $J_2$ = 4.0 Hz, 1H), 3.41 (d, $J$ = 4.0 Hz, 1H), 3.35 (s, 3H), 3.16 (s, 3H), 2.59 (d, $J$ = 12.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.2, 155.5, 152.9, 138.4, 137.1, 129.4, 129.0, 128.8, 128.3, 126.6, 126.5, 125.1, 120.8, 116.7, 116.5, 112.3, 109.1, 108.6, 91.0, 55.4, 47.0, 37.7, 26.3. IR (KBr) $v$ 3428, 3058, 3004, 2927, 1711, 1608, 1492, 1363, 1332, 1285, 1238, 1113, 1037, 896, 760 cm$^{-1}$. HRMS (ESI) calcd for $C_{25}H_{22}NO_4$ $[M+H]^+$ 400.1543, found 400.1541.




6-bromo-1-methyl-2'-phenyl-5'*H*-spiro[indoline-3,4'-[2,5]methanobenzo[*d*][1,3]dioxepin]-2-one (**3i**)

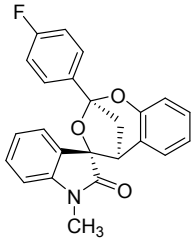
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 40:1 to 30:1); 67.0 mg, 75% yield; reaction time = 24 h; mp 192.5-193.0 °C; $^1$H NMR (400 MHz, $CDCl_3$), δ 7.81 (d, $J$ = 4.0 Hz, 2H), 7.38-7.29 (m, 3H), 7.22 (t, $J$ = 8.0 Hz, 1H), 7.01 (d, $J$ = 8.0 Hz, 1H), 6.84 (s, 1H), 6.78-6.75 (m, 2H), 6.58 (d, $J$ = 8.0 Hz, 1H), 5.66 (d, $J$ = 8.0 Hz, 1H), 3.80 (dd, $J_1$ = $J_2$ =

4.0 Hz, 1H), 3.31 (d, $J$ = 4.0 Hz, 1H), 3.10 (s, 3H), 2.51 (d, $J$ = 12.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.2, 152.7, 145.0, 138.2, 129.7, 128.9, 128.7, 128.3, 127.1, 126.4, 125.3, 124.8, 124.6, 124.0, 120.9, 116.7, 111.6, 109.0, 90.5, 46.8, 37.6, 26.4. IR (KBr) $v$ 3440, 3064, 3032, 2933, 1729, 1603, 1486, 1367, 1333, 1239, 1163, 1108, 1038, 991, 895, 752, 701 cm$^{-1}$. HRMS (ESI) calcd for $C_{24}H_{19}BrNO_3$ $[M+H]^+$ 448.0543 and 450.0522, found 448.0561 and 450.0528.




7-chloro-1-methyl-2'-phenyl-5'*H*-spiro[indoline-3,4'-[2,5]methanobenzo[*d*][1,3]dioxepin]-2-one (**3j**)

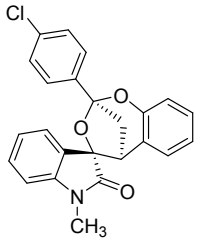
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 70:1 to 50:1); 61.8 mg, 77% yield; reaction time = 24 h; mp 161.4-162.7 °C; $^1$H NMR (400 MHz, $CDCl_3$), δ 7.90 (d, $J$ = 8.0 Hz, 2H), 7.45-7.34 (m, 3H), 7.28 (t, $J$ = 8.0 Hz, 1H), 7.13 (d, $J$ = 8.0 Hz, 1H), 7.08 (d, $J$ = 8.0 Hz, 1H), 6.81 (t, $J$ = 8.0 Hz, 1H), 6.63-6.56 (m, 2H), 5.86 (d, $J$ = 8.0 Hz, 1H), 3.90 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.58 (s, 3H), 3.39 (d, $J$ = 4.0 Hz, 1H), 2.56 (d, $J$ = 12.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.8, 152.7, 139.5, 138.3, 132.3, 129.7, 128.9, 128.8, 128.6, 128.3, 126.4, 124.8, 124.4, 123.1, 120.8, 116.7, 115.3, 109.1, 90.3, 47.2, 37.6, 29.8. IR (KBr) $v$ 3430, 3060, 3020, 2926, 1728, 1605, 1459, 1363, 1335, 1243, 1118, 1046, 892, 757, 699 cm$^{-1}$. HRMS (ESI) calcd for $C_{24}H_{19}ClNO_3$ $[M+H]^+$ 404.1048 and 406.1018, found 404.1052 and 406.1040.




2'-(4-fluorophenyl)-1-methyl-5'*H*-spiro[indoline-3,4'-[2,5]methanobenzo[*d*][1,3]dioxepin]-2-one (**3k**)

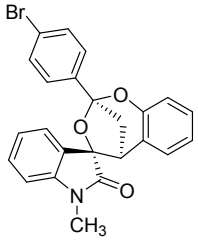
White solid obtained by filtration of the precipitate; 70.0 mg, 90% yield; reaction time = 24 h; mp 189.5-190.3 °C; $^1$H NMR (400 MHz, $CDCl_3$), δ 7.84-7.81 (m, 2H), 7.23 (t, $J$ = 8.0 Hz, 1H), 7.15 (t, $J$ = 8.0 Hz, 1H), 7.03 (t, $J$ = 8.0 Hz, 3H), 6.76 (t, $J$ = 8.0 Hz, 1H), 6.69 (d, $J$ = 8.0 Hz, 1H), 6.63 (t, $J$ = 8.0 Hz, 1H), 6.58 (d, $J$ = 8.0 Hz, 1H), 5.82 (d, $J$ = 8.0 Hz, 1H), 3.82 (dd, $J_1 = J_2$ = 4.0 Hz, 1H),

3.34 (d, $J$ = 4.0 Hz, 1H), 3.13 (s, 3H), 2.47 (d, $J$ = 12.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 174.4, 162.0 (d, $J$ = 245.0 Hz, 1C), 151.5, 142.7, 133.4, 129.1, 128.5, 127.8, 127.5 (d, $J$ = 8.0 Hz, 1C), 124.8, 124.4, 124.0, 121.5, 119.8, 115.6, 114.0 (d, $J$ = 22.0 Hz, 1C), 107.5, 107.0, 89.8, 45.7, 36.7, 25.2. IR (KBr) $v$ 3408, 3072, 2950, 1712, 1612, 1467, 1378, 1349, 1233, 1116, 1046, 1006, 876, 846, 752 cm$^{-1}$. HRMS (ESI) calcd for $C_{24}H_{18}FNNaO_3$ $[M+Na]^+$ 410.1163, found 410.1156.




2'-(4-chlorophenyl)-1-methyl-5'*H*-spiro[indoline-3,4'-[2,5]methanobenzo[*d*][1,3]dioxepin]-2-one (**3l**)

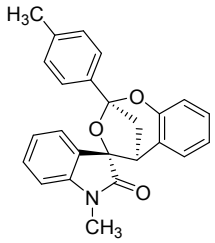
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 30:1 to 25:1); 77.7 mg, 96% yield; reaction time = 24 h; mp 190.1-190.8 $^o$C; $^1$H NMR (400 MHz, $CDCl_3$), δ 7.85 (d, $J$ = 12.0 Hz, 2H), 7.39 (d, $J$ = 8.0 Hz, 2H), 7.30 (t, $J$ = 8.0 Hz, 1H), 7.22 (t, $J$ = 8.0 Hz, 1H), 7.08 (d, $J$ = 8.0 Hz, 1H), 6.84 (t, $J$ = 8.0 Hz, 1H), 6.76 (d, $J$ = 8.0 Hz, 1H), 6.70 (d, $J$ = 8.0 Hz, 1H), 6.65 (d, $J$ = 8.0 Hz, 1H), 5.89 (d, $J$ = 8.0 Hz, 1H), 3.88 (dd, $J_1$ = 8.0 Hz, $J_2$ = 4.0 Hz, 1H), 3.40 (d, $J$ = 4.0 Hz, 1H), 3.19 (s, 3H), 2.54 (d, $J$ = 12.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.4, 152.5, 143.8, 137.2, 134.7, 130.2, 129.6, 128.9, 128.4, 128.1, 125.8, 125.4, 125.0, 122.6, 120.9, 116.7, 108.5, 108.1, 91.0, 46.8, 37.7, 26.3. IR (KBr) $v$ 3425, 3056, 2962, 1722, 1613, 1487, 1376, 1347, 1239, 1162, 1042, 1007, 900, 828, 755 cm$^{-1}$. HRMS (ESI) calcd for $C_{24}H_{18}ClNNaO_3$ $[M+Na]^+$ 426.0867 and 428.0838, found 426.0857 and 428.0831.




2'-(4-bromophenyl)-1-methyl-5'*H*-spiro[indoline-3,4'-[2,5]methanobenzo[*d*][1,3]dioxepin]-2-one (**3m**)

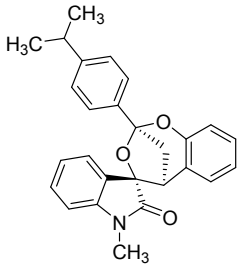
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 30:1 to 25:1); 88.7 mg, 99% yield; reaction time = 24 h; mp 115.2-116.3 $^o$C; $^1$H NMR (400 MHz, $CDCl_3$), δ 7.79 (d, $J$ = 8.0 Hz, 2H), 7.54 (d, $J$ = 8.0 Hz, 2H), 7.30 (t, $J$ = 8.0 Hz, 1H), 7.22 (t, $J$ = 8.0 Hz, 1H),

7.08 (d, $J$ = 8.0 Hz, 1H), 6.83 (t, $J$ = 8.0 Hz, 1H), 6.76 (d, $J$ = 8.0 Hz, 1H), 6.69 (t, $J$ = 8.0 Hz, 1H), 6.64 (d, $J$ = 4.0 Hz, 1H), 5.88 (d, $J$ = 4.0 Hz, 1H), 3.87 (dd, $J_1$ = 8.0 Hz, $J_2$ = 4.0 Hz, 1H), 3.40 (d, $J$ = 4.0 Hz, 1H), 3.19 (s, 3H), 2.54 (d, $J$ = 12.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.4, 152.5, 143.8, 137.7, 131.4, 130.2, 129.6, 128.9, 128.4, 125.8, 125.4, 125.0, 123.1, 122.6, 120.9, 116.7, 108.5, 108.1, 91.0, 46.8, 37.7, 26.3. IR (KBr) $v$ 3428, 3055, 2932, 1721, 1613, 1486, 1373, 1349, 1240, 1162, 1113, 1042, 1004, 898, 825, 754 cm$^{-1}$. HRMS (ESI) calcd for $C_{24}H_{18}BrNNaO_3$ $[M+Na]^+$ 470.0386 and 472.0342, found 470.0371 and 472.0327.




1-methyl-2'-(p-tolyl)-5'*H*-spiro[indoline-3,4'-[2,5]methanobenzo[*d*][1,3]dioxepin]-2-one (**3n**)

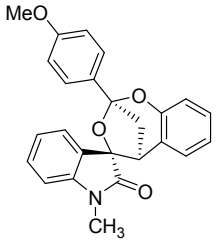
White solid obtained by filtration of the precipitate; 63.1 mg, 82% yield; reaction time = 24 h; mp 223.2-224.5 °C; $^1$H NMR (400 MHz, $CDCl_3$), δ 7.79 (d, $J$ = 8.0 Hz, 2H), 7.29 (t, $J$ = 8.0 Hz, 1H), 7.24-7.19 (m, 3H), 7.09 (d, $J$ = 8.0 Hz, 1H), 6.82 (t, $J$ = 8.0 Hz, 1H), 6.75 (d, $J$ = 8.0 Hz, 1H), 6.69 (t, $J$ = 8.0 Hz, 1H), 6.64 (d, $J$ = 4.0 Hz, 1H), 5.91 (d, $J$ = 8.0 Hz, 1H), 3.90 (dd, $J_1$ = $J_2$ = 4.0 Hz, 1H), 3.39 (d, $J$ = 4.0 Hz, 1H), 3.19 (s, 3H), 2.54 (d, $J$ = 12.0 Hz, 1H), 2.37 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.5, 152.9, 143.8, 138.5, 135.6, 130.1, 129.4, 128.9, 128.8, 126.3, 125.9, 125.7, 125.2, 122.5, 120.6, 116.6, 109.1, 108.0, 90.8, 46.8, 37.7, 26.2, 21.3. IR (KBr) $v$ 3428, 3057, 2926, 1721, 1614, 1480, 1375, 1345, 1240, 1112, 1043, 1010, 897, 818, 755 cm$^{-1}$. HRMS (ESI) calcd for $C_{25}H_{21}NNaO_3$ $[M+Na]^+$ 406.1414, found 406.1419.




2'-(4-isopropylphenyl)-1-methyl-5'*H*-spiro[indoline-3,4'-[2,5]methanobenzo[*d*][1,3]dioxepin]-2-one (**3o**)

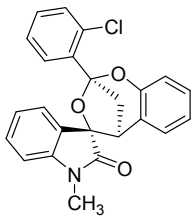
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 30:1); 71.4 mg, 87% yield; reaction time = 24 h; mp 93.7-94.8 °C; $^1$H NMR (400 MHz, $CDCl_3$), δ 7.82 (d, $J$ = 8.0

Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 3H), 7.23-7.18 (m, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.81 (t, *J* = 8.0 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 6.68 (t, *J* = 8.0 Hz, 1H), 6.64 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 5.91 (d, *J* = 8.0 Hz, 1H), 3.93 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.39 (d, *J* = 4.0 Hz, 1H), 3.18 (s, 3H), 2.97-2.90 (m, 1H), 2.57 (d, *J* = 12.0 Hz, 1H), 1.25 (d, J = 8.0 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.5, 152.9, 149.5, 143.8, 135.9, 130.1, 129.4, 128.8, 126.4, 126.3, 125.9, 125.8, 125.2, 122.5, 120.6, 116.6, 109.1, 107.9, 90.8, 46.9, 37.4, 34.0, 26.2, 24.0. IR (KBr) *v* 3418, 3055, 2960, 2927, 1722, 1613, 1467, 1372, 1348, 1240, 1112, 1043, 895, 834, 752 cm$^{-1}$. HRMS (ESI) calcd for $C_{27}H_{25}NNaO_3$ $[M+Na]^+$ 434.1727, found 434.1729.




2'-(4-methoxyphenyl)-1-methyl-5'*H*-spiro[indoline-3,4'-[2,5]methanobenzo[*d*][1,3]dioxepin]-2-one (**3p**)

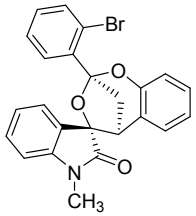
Light yellow solid obtained by filtration of the precipitate; 66.1 mg, 83% yield; reaction time = 24 h; mp 182.6-183.5 $^{o}$C; $^{1}$H NMR (400 MHz, $CDCl_3$), δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.83 (t, *J* = 8.0 Hz, 1H), 6.76 (d, *J* = 4.0 Hz, 1H), 6.70 (t, *J* = 8.0 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 5.91 (d, *J* = 8.0 Hz, 1H), 3.90 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.83 (s, 3H), 3.40 (d, *J* = 4.0 Hz, 1H), 3.20 (s, 3H), 2.56 (d, *J* = 12.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.5, 159.9, 152.8, 143.8, 130.8, 130.1, 129.4, 128.8, 127.8, 125.9, 125.7, 125.2, 122.5, 120.6, 116.6, 113.5, 109.0, 108.0, 90.7, 55.4, 46.8, 37.6, 26.2. IR (KBr) *v* 3429, 3054, 2954, 1711, 1613, 1466, 1374, 1349, 1240, 1181, 1107, 1029, 871, 835, 754 cm$^{-1}$. HRMS (ESI) calcd for $C_{25}H_{21}NNaO_4$ $[M+Na]^+$ 422.1363, found 422.1373.




2'-(2-chlorophenyl)-1-methyl-5'*H*-spiro[indoline-3,4'-[2,5]methanobenzo[*d*][1,3]dioxepin]-2-one (**3q**)

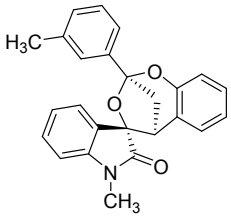
White solid obtained by filtration of the precipitate; 79.2 mg, 98% yield; reaction time = 24 h; mp

274.6-275.5 °C; $^1$H NMR (400 MHz, $CDCl_3$), δ 7.95 (dd, $J_1 = J_2 = 4.0$ Hz, 1H), 7.45 (dd, $J_1 = J_2 = 4.0$ Hz, 1H), 7.33-7.24 (m, 4H), 7.02 (d, $J = 8.0$ Hz, 1H), 6.82 (q, $J = 8.0$ Hz, 2H), 6.73 (t, $J = 8.0$ Hz, 1H), 6.66 (d, $J = 4.0$ Hz, 1H), 5.99 (d, $J = 8.0$ Hz, 1H), 3.66 (dd, $J_1 = J_2 = 4.0$ Hz, 1H), 3.42 (d, $J = 4.0$ Hz, 1H), 3.33 (d, $J = 12.0$ Hz, 1H), 3.20 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.1, 152.8, 143.9, 135.8, 132.5, 130.9, 130.2, 130.1, 129.6, 128.9, 128.7, 126.8, 125.9, 125.6, 125.2, 122.6, 120.7, 116.5, 108.4, 108.1, 90.2, 46.6, 34.0, 26.3. IR (KBr) *v* 3396, 3052, 2983, 2955, 1723, 1695, 1611, 1467, 1375, 1350, 1329, 1234, 1161, 1134, 1109, 1027, 996, 881, 763 cm$^{-1}$. HRMS (ESI) calcd for $C_{24}H_{18}ClNNaO_3$ $[M+Na]^+$ 426.0867 and 428.0838, found 426.0881 and 428.0864.




2'-(2-bromophenyl)-1-methyl-5'*H*-spiro[indoline-3,4'-[2,5]methanobenzo[*d*][1,3]dioxepin]-2-one (**3r**)

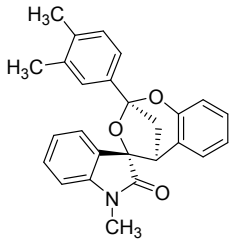
White solid obtained by filtration of the precipitate; 85.5 mg, 95% yield; reaction time = 24 h; mp 265.5-266.5 °C; $^1$H NMR (400 MHz, $CDCl_3$), δ 7.96 (d, $J = 8.0$ Hz, 1H), 7.67 (d, $J = 8.0$ Hz, 1H), 7.34-7.20 (m, 4H), 7.04 (d, $J = 8.0$ Hz, 1H), 6.82 (q, $J = 8.0$ Hz, 2H), 6.73 (t, $J = 8.0$ Hz, 1H), 6.66 (d, $J = 4.0$ Hz, 1H), 6.00 (d, $J = 8.0$ Hz, 1H), 3.62 (dd, $J_1 = J_2 = 4.0$ Hz, 1H), 3.42 (d, $J = 4.0$ Hz, 1H), 3.38 (d, $J = 12.0$ Hz, 1H), 3.20 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.2, 152.6, 143.8, 137.4, 134.5, 130.4, 130.2, 129.6, 129.1, 128.7, 127.4, 125.8, 125.6, 125.2, 122.6, 121.2, 120.7, 116.5, 108.8, 108.1, 90.2, 46.6, 33.9, 26.3. IR (KBr) *v* 3401, 3053, 2957, 1709, 1611, 1467, 1374, 1350, 1235, 1161, 1114, 1055, 1027, 997, 884, 759 cm$^{-1}$. HRMS (ESI) calcd for $C_{24}H_{18}BrNNaO_3$ $[M+Na]^+$ 470.0362 and 472.0342, found 470.0373 and 472.0328.




1-methyl-2'-(m-tolyl)-5'*H*-spiro[indoline-3,4'-[2,5]methanobenzo[*d*][1,3]dioxepin]-2-one (**3s**)

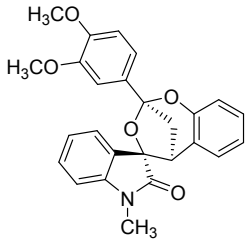
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 40:1 to 30:1); 64.3 mg, 84% yield; reaction time = 24 h; mp 172.3-173.5 °C; $^1$H NMR (400 MHz, $CDCl_3$), δ

7.71 (d, $J$ = 8.0 Hz, 2H), 7.34-7.27 (m, 2H), 7.21 (dd, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 2H), 7.09 (d, $J$ = 8.0 Hz, 1H), 6.82 (t, $J$ = 8.0 Hz, 1H), 6.73 (d, $J$ = 8.0 Hz, 1H), 6.69 (t, $J$ = 8.0 Hz, 1H), 6.64 (d, $J$ = 8.0 Hz, 1H), 5.91 (d, $J$ = 4.0 Hz, 1H), 3.90 (dd, $J_1$ = $J_2$ = 4.0 Hz, 1H), 3.40 (d, $J$ = 4.0 Hz, 1H), 3.18 (s, 3H), 2.57 (d, $J$ = 12.0 Hz, 1H), 2.41 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.4, 152.8, 143.8, 138.4, 137.9, 130.1, 129.6, 129.5, 128.8, 128.2, 127.0, 125.9, 125.7, 125.2, 123.6, 122.5, 120.7, 116.6, 109.0, 108.0, 90.8, 46.8, 37.5, 26.3, 21.7. IR (KBr) $v$ 3419, 2925, 2856, 1718, 1614, 1466, 1376, 1348, 1239, 1113, 1046, 756 cm$^{-1}$. HRMS (ESI) calcd for $C_{25}H_{21}NNaO_3$ $[M+Na]^+$ 406.1414, found 406.1416.



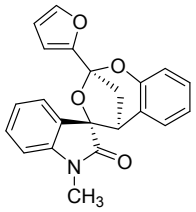
2'-(3,4-dimethylphenyl)-1-methyl-5'*H*-spiro[indoline-3,4'-[2,5]methanobenzo[*d*][1,3]dioxepin]-2-one (**3t**)

White solid obtained by filtration of the precipitate; 74.0 mg, 93% yield; reaction time = 24 h; mp 189.5-190.2 $^o$C; $^1$H NMR (400 MHz, $CDCl_3$), δ 7.66 (s, 1H), 7.62 (d, $J$ = 8.0 Hz, 1H), 7.29 (t, $J$ = 8.0 Hz, 1H), 7.24-7.18 (m, 2H), 7.09 (d, $J$ = 8.0 Hz, 1H), 6.82 (t, $J$ = 8.0 Hz, 1H), 6.75 (d, $J$ = 8.0 Hz, 1H), 6.69 (t, $J$ = 8.0 Hz, 1H), 6.64 (d, $J$ = 4.0 Hz, 1H), 5.92 (d, $J$ = 8.0 Hz, 1H), 3.91 (dd, $J_1$ = $J_2$ = 4.0 Hz, 1H), 3.39 (d, $J$ = 4.0 Hz, 1H), 3.19 (s, 3H), 2.57 (d, $J$ = 8.0 Hz, 1H), 2.30 (d, $J$ = 16.0 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.4, 152.9, 143.8, 137.2, 136.4, 135.9, 130.0, 129.5, 129.4, 128.7, 127.4, 125.9, 125.8, 125.2, 123.8, 122.5, 120.6, 116.6, 109.1, 107.9, 90.8, 46.8, 37.5, 26.2, 20.0, 19.7. IR (KBr) $v$ 3423, 2963, 1722, 1612, 1484, 1375, 1344, 1240, 1160, 1112, 1046, 990, 910, 882, 754 cm$^{-1}$. HRMS (ESI) calcd for $C_{26}H_{23}NNaO_3$ $[M+Na]^+$ 420.1570, found 420.1567.



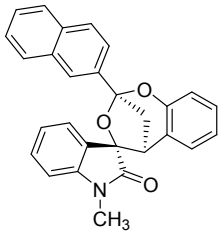
2'-(3,4-dimethoxyphenyl)-1-methyl-5'*H*-spiro[indoline-3,4'-[2,5]methanobenzo[*d*][1,3]dioxepin]-2-one (**3u**)

Light yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 15:1 to 5:1); 36.8 mg, 43% yield; reaction time = 24 h; mp 171.3-172.1 °C; $^1$H NMR (400 MHz, $CDCl_3$), δ 7.42 (d, $J$ = 4.0 Hz, 1H), 7.39 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 7.23 (t, $J$ = 8.0 Hz, 1H), 7.15 (t, $J$ = 8.0 Hz, 1H), 7.03 (d, $J$ = 8.0 Hz, 1H), 6.84 (d, $J$ = 8.0 Hz, 1H), 6.76 (t, $J$ = 8.0 Hz, 1H), 6.69 (d, $J$ = 8.0 Hz, 1H), 6.63 (t, $J$ = 8.0 Hz, 1H), 6.58 (d, $J$ = 8.0 Hz, 1H), 5.84 (d, $J$ = 8.0 Hz, 1H), 3.88 (s, 3H), 3.85 (d, $J$ = 4.0 Hz, 1H), 3.83 (s, 3H), 3.33 (d, $J$ = 4.0 Hz, 1H), 3.13 (s, 3H), 2.49 (d, $J$ = 12.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.6, 152.8, 149.3, 148.7, 143.8, 131.1, 130.1, 129.4, 128.8, 125.9, 125.7, 125.2, 122.4, 120.7, 118.8, 116.6, 110.6, 109.9, 109.0, 107.9, 90.8, 56.0, 55.9, 46.9, 37.6, 26.2. IR (KBr) $v$ 3427, 2958, 2929, 2840, 1719, 1613, 1518, 1465, 1415, 1350, 1241, 1111, 1034, 878, 757 cm$^{-1}$. HRMS (ESI) calcd for $C_{26}H_{23}NNaO_5$ $[M+Na]^+$ 452.1468, found 452.1462.



2'-(furan-2-yl)-1-methyl-5'*H*-spiro[indoline-3,4'-[2,5]methanobenzo[*d*][1,3]dioxepin]-2-one (**3v**)

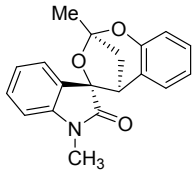
White solid obtained by filtration of the precipitate; 56.7 mg, 79% yield; reaction time = 24 h; mp 202.2-203.4 °C; $^1$H NMR (400 MHz, $CDCl_3$), δ 7.44 (s, 1H), 7.19 (s, 3H), 7.09 (d, $J$ = 8.0 Hz, 1H), 6.96-6.83 (m, 4H), 6.73 (d, $J$ = 4.0 Hz, 1H), 6.41 (s, 1H), 4.57 (s, 1H), 3.37-3.26 (m, 5H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 185.9, 175.3, 158.7, 152.0, 146.3, 144.4, 130.6, 129.0, 128.5, 125.4, 124.8, 123.9, 122.2, 121.4, 116.8, 112.1, 110.1, 108.7, 88.8, 43.9, 40.0, 26.5. IR (KBr) $v$ 3432, 3219, 2932, 1726, 1673, 1611, 1471, 1377, 1237, 1020, 989, 755 cm$^{-1}$. HRMS (ESI) calcd for $C_{22}H_{18}NO_4$ $[M+H]^+$ 360.1230, found 360.1246.



1-methyl-2'-(naphthalen-2-yl)-5'*H*-spiro[indoline-3,4'-[2,5]methanobenzo[*d*][1,3]dioxepin]-2-one (**3w**)

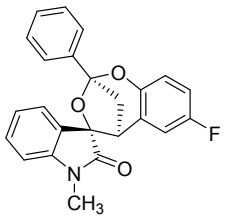
White solid obtained by filtration of the precipitate; 79.7 mg, 95% yield; reaction time = 24 h; mp

227.1-227.8 °C; $^1$H NMR (400 MHz, $CDCl_3$), δ 8.31 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.86-7.76 (m, 3H), 7.42-7.40 (m, 2H), 7.24 (t, *J* = 8.0 Hz, 1H), 7.15-7.07 (m, 2H), 6.76 (t, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 6.61 (q, *J* = 8.0 Hz, 2H), 5.87 (d, *J* = 8.0 Hz, 1H), 3.94 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.37 (d, *J* = 4.0 Hz, 1H), 3.13 (s, 3H), 2.55 (d, *J* = 12.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.4, 152.8, 143.8, 135.9, 133.5, 133.0, 130.2, 129.5, 128.8, 128.7, 128.1, 127.7, 126.4, 126.1, 125.9, 125.7, 125.6, 125.2, 124.4, 122.5, 120.8, 116.7, 109.1, 108.0, 91.0, 46.9, 37.7, 26.3. IR (KBr) *v* 3427, 2958, 1715, 1612, 1466, 1350, 1235, 1159, 1110, 1046, 995, 865, 752 cm$^{-1}$. HRMS (ESI) calcd for $C_{28}H_{21}NNaO_3$ $[M+Na]^+$ 442.1414, found 442.1403.




1,2'-dimethyl-5'*H*-spiro[indoline-3,4'-[2,5]methanobenzo[*d*][1,3]dioxepin]-2-one (**3x**)

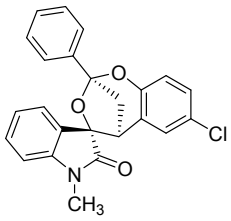
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 20:1); 46.0 mg, 75% yield; reaction time = 24 h; mp 163.1-163.5 °C; $^1$H NMR (400 MHz, $CDCl_3$), δ 7.25-7.18 (m, 2H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.78-6.72 (m, 2H), 6.68 (t, *J* = 8.0 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 1H), 5.83 (d, *J* = 4.0 Hz, 1H), 3.63 (dd, $J_1$ = 8.0 Hz, $J_2$ = 4.0 Hz, 1H), 3.25 (d, *J* = 4.0 Hz, 1H), 3.15 (s, 3H), 2.36 (d, *J* = 12.0 Hz, 1H), 1.86 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.5, 152.9, 143.8, 130.0, 129.3, 128.7, 125.8, 125.7, 125.1, 122.4, 120.3, 116.2, 108.5, 107.9, 90.6, 46.7, 35.3, 26.1, 23.3. IR (KBr) *v* 3409, 2995, 2935, 1711, 1611, 1488, 1465, 1380, 1348, 1248, 1165, 1133, 1085, 1038, 998, 874, 753 cm$^{-1}$. HRMS (ESI) calcd for $C_{19}H_{18}NO_3$ $[M+H]^+$ 308.1281, found 308.1294.




7'-fluoro-1-methyl-2'-phenyl-5'*H*-spiro[indoline-3,4'-[2,5]methanobenzo[*d*][1,3]dioxepin]-2-one (**3y**)

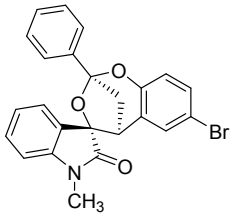
White solid obtained by filtration of the precipitate; 72.8 mg, 94% yield; reaction time = 24 h; mp 214.3-214.9 °C; $^1$H NMR (400 MHz, $CDCl_3$), δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.45-7.38 (m, 3H), 7.26-7.22 (m, 1H), 7.06-6.97 (m, 2H), 6.79-6.74 (m, 2H), 6.41 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 6.00 (d, *J* =

4.0 Hz, 1H), 3.93 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.36 (d, $J$ = 4.0 Hz, 1H), 3.20 (s, 3H), 2.54 (d, $J$ = 12.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.2, 156.8 (d, $J$ = 239.0 Hz, 1C), 148.8, 143.8, 138.2, 130.3, 128.9, 128.3, 126.4, 126.2 (d, $J$ = 8.0 Hz, 1C), 125.6, 125.3, 122.7, 117.5 (d, $J$ = 8.0 Hz, 1C), 115.8 (d, $J$ = 23.0 Hz, 1C), 115.2 (d, $J$ = 23.0 Hz, 1C), 109.0, 108.2, 90.7, 46.7, 37.4, 26.2. IR (KBr) *v* 3423, 3063, 2967, 1721, 1613, 1487, 1448, 1341, 1217, 1165, 1111, 1043, 1018, 898, 760 cm$^{-1}$. HRMS (ESI) calcd for $C_{24}H_{19}FNO_3$ $[M+H]^+$ 388.1343, found 388.1360.




7'-chloro-1-methyl-2'-phenyl-5'*H*-spiro[indoline-3,4'-[2,5]methanobenzo[*d*][1,3]dioxepin]-2-one (**3z**)

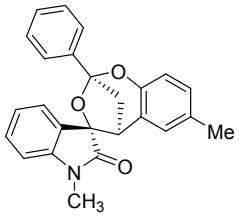
White solid obtained by filtration of the precipitate; 71.2 mg, 88% yield; reaction time = 24 h; mp 261.6-262.0 °C; $^1$H NMR (400 MHz, $CDCl_3$), δ 7.88 (d, $J$ = 8.0 Hz, 2H), 7.45-7.36 (m, 3H), 7.27-7.24 (m, 2H), 7.03 (d, $J$ = 8.0 Hz, 1H), 6.76 (t, $J$ = 8.0 Hz, 2H), 6.67 (s, 1H), 6.02 (d, $J$ = 8.0 Hz, 1H), 3.94 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.37 (d, $J$ = 4.0 Hz, 1H), 3.20 (s, 3H), 2.54 (d, $J$ = 12.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.1, 151.4, 143.8, 138.0, 130.4, 129.3, 128.9, 128.4, 128.3, 126.7, 126.4, 125.7, 125.6, 125.2, 122.7, 117.9, 109.1, 108.2, 90.7, 46.6, 37.4, 26.3. IR (KBr) *v* 3424, 2931, 1722, 1612, 1474, 1340, 1242, 1162, 1116, 1044, 1013, 898, 754 cm$^{-1}$. HRMS (ESI) calcd for $C_{24}H_{18}ClNaNO_3$ $[M+Na]^+$ 426.0891 and 428.0838, found 426.0884 and 428.0827.




7'-bromo-1-methyl-2'-phenyl-5'*H*-spiro[indoline-3,4'-[2,5]methanobenzo[*d*][1,3]dioxepin]-2-one (**3za**)

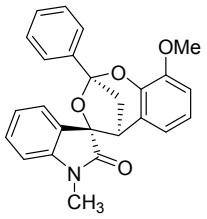
White solid obtained by filtration of the precipitate; 75.6 mg, 84% yield; reaction time = 24 h; mp 284.2-285.4 °C; $^1$H NMR (400 MHz, $CDCl_3$), δ 7.88 (d, $J$ = 8.0 Hz, 2H), 7.45-7.25 (m, 4H), 7.28-7.25 (m, 1H), 6.98 (d, $J$ = 8.0 Hz, 1H), 6.78 (t, $J$ = 8.0 Hz, 3H), 6.02 (d, $J$ = 8.0 Hz, 1H), 3.93 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.37 (d, $J$ = 4.0 Hz, 1H), 3.20 (s, 3H), 2.54 (d, $J$ = 12.0 Hz, 1H); $^{13}$C NMR

(100 MHz, $CDCl_3$) δ 175.1, 152.0, 143.8, 138.0, 132.3, 131.2, 130.4, 128.9, 128.3, 127.2, 126.4, 125.7, 125.2, 122.7, 118.4, 112.8, 109.1, 108.2, 90.7, 46.6, 37.4, 26.3. IR (KBr) *v* 3425, 3060, 2934, 1721, 1611, 1473, 1373, 1339, 1242, 1161, 1117, 1044, 1013, 897, 755 $cm^{-1}$. HRMS (ESI) calcd for $C_{24}H_{19}BrNO_3$ $[M+H]^+$ 448.0543 and 450.0522, found 448.0523 and 450.0520.




1,7'-dimethyl-2'-phenyl-5'*H*-spiro[indoline-3,4'-[2,5]methanobenzo[*d*][1,3]dioxepin]-2-one (**3zb**)

White solid obtained by filtration of the precipitate; 69.5 mg, 91% yield; reaction time = 24 h; mp 256.2-256.9 °C; $^1H$ NMR (400 MHz, $CDCl_3$), δ 7.91 (d, $J$ = 8.0 Hz, 2H), 7.44-7.34 (m, 3H), 7.22 (t, $J$ = 8.0 Hz, 1H), 7.09 (d, $J$ = 8.0 Hz, 1H), 6.99 (d, $J$ = 8.0 Hz, 1H), 6.76 (d, $J$ = 8.0 Hz, 1H), 6.71 (t, $J$ = 8.0 Hz, 1H), 6.47 (s, 1H), 5.94 (d, $J$ = 4.0 Hz, 1H), 3.90 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.35 (d, $J$ = 4.0 Hz, 1H), 3.19 (s, 3H), 2.56 (d, $J$ = 12.0 Hz, 1H), 2.19 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 175.5, 150.5, 143.8, 138.6, 130.1, 130.0, 129.8, 129.2, 128.7, 128.2, 126.5, 126.0, 125.8, 124.8, 122.4, 116.3, 108.9, 107.9, 90.8, 46.9, 37.8, 26.2, 20.4. IR (KBr) *v* 3426, 3028, 2923, 1721, 1613, 1491, 1376, 1341, 1245, 1119, 1044, 896, 753, 699 $cm^{-1}$. HRMS (ESI) calcd for $C_{25}H_{22}NO_3$ $[M+H]^+$ 384.1594, found 384.1608.

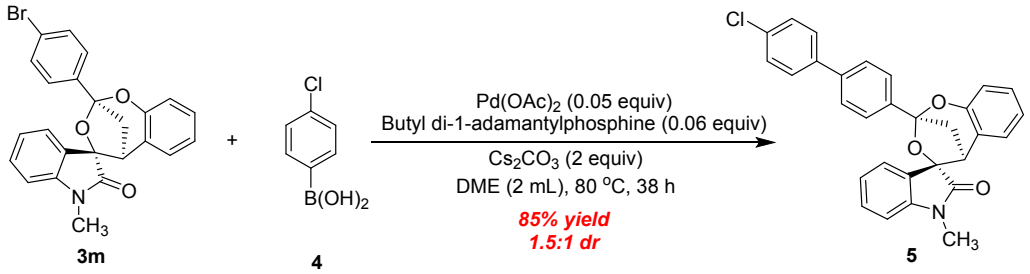



9'-methoxy-1-methyl-2'-phenyl-5'*H*-spiro[indoline-3,4'-[2,5]methanobenzo[*d*][1,3]dioxepin]-2-one (**3zc**)

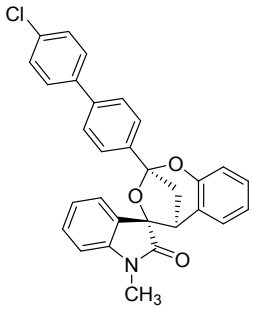
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 30:1 to 10:1); 68.8 mg, 86% yield; reaction time = 24 h; mp 259.1-260.2 °C; $^1H$ NMR (400 MHz, $CDCl_3$), δ 7.87 (d, $J$ = 4.0 Hz, 2H), 7.37-7.27 (m, 3H), 7.14 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 6.85 (d, $J$ = 8.0 Hz, 1H), 6.72-6.60 (m, 3H), 6.20 (d, $J$ = 8.0 Hz, 1H), 5.91 (d, $J$ = 8.0 Hz, 1H), 3.87-3.84 (m, 4H), 3.31 (d, $J$ = 4.0 Hz, 1H), 3.11 (s, 3H), 2.49 (d, $J$ = 12.0 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 175.4, 148.6, 143.8, 142.1, 138.6, 130.1, 128.7, 128.2, 126.6, 126.0, 125.9, 125.6, 122.4, 120.9, 120.6,

112.5, 108.9, 107.9, 90.9, 56.3, 46.8, 37.6, 26.2. IR (KBr) *v* 3423, 2964, 1713, 1614, 1586, 1483, 1350, 1261, 1216, 1168, 1105, 1082, 1043, 880, 753, 703 $cm^{-1}$. HRMS (ESI) calcd for $C_{25}H_{22}NO_4$ $[M+H]^+$ 400.1543, found 400.1560.

### 3. Experimental data for functionalization of 3m




**General procedure:** Under nitrogen atmosphere, compound **3m** (109.4 mg, 0.244 mmol), 4-chlorophenylboronic acid (1.5 equiv), $Cs_2CO_3$ (2.0 equiv), $Pd(OAc)_2$ (0.05 equiv) and butyl di-1-adamantylphosphine (0.06 equiv) were successively added to a 15 mL dried tube, followed by adding 2.0 mL DME. The resulting mixture was stirred at 80 °C for 38 h till almost full consumption of **3m** monitored by thin layer chromatography, and then the reaction mixture was directly subjected to flash column chromatography on silica gel (petroleum ether/ ethyl acetate) to afford the corresponding products **5**. The dr value was determined by $^{13}C$ NMR.

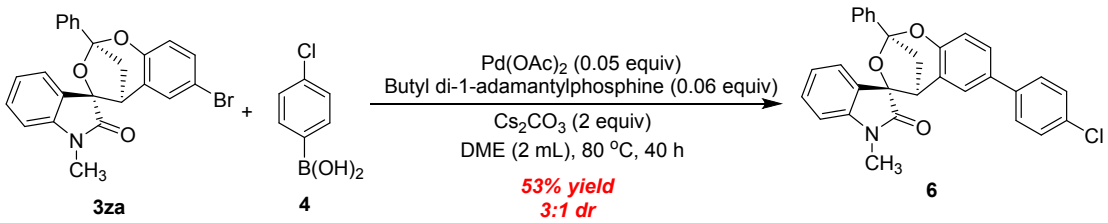



2'-(4'-chloro-[1,1'-biphenyl]-4-yl)-1-methyl-5'*H*-spiro[indoline-3,4'-[2,5]methanobenzo[*d*][1,3]dioxepin]-2-one (**5**)

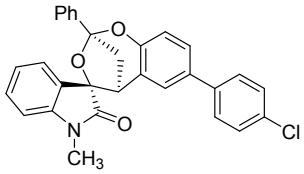
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 40:1 to 20:1); 99.4 mg, 85% yield, 1.5:1 dr; reaction time = 38 h; mp 125.4-126.1 °C; $^1H$ NMR (400 MHz, $CDCl_3$), δ 7.90 (d, $J$ = 8.0 Hz, 2H), 7.57 (d, $J$ = 8.0 Hz, 1H), 7.52 (d, $J$ = 8.0 Hz, 2H), 7.44 (d, $J$ = 8.0 Hz, 1H), 7.37-7.30 (m, 2H), 7.22 (t, $J$ = 8.0 Hz, 1H), 7.13 (t, $J$ = 8.0 Hz, 1H), 7.03 (d, $J$ = 8.0 Hz, 1H), 6.75 (d, $J$ = 8.0 Hz, 1H), 6.67 (d, $J$ = 4.0 Hz, 1H), 6.63-6.56 (m, 2H), 5.84 (d, $J$ = 8.0 Hz, 1H), 3.90-3.85 (m, 1H), 3.33 (d, $J$ = 4.0 Hz, 1H), 3.11 (s, 3H), 2.52 (dd, $J_1 = J_2$ = 4.0 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 175.5, 152.8, 143.8, 141.7, 140.9, 139.4,138.0, 133.6, 130.1, 129.5,

129.0, 128.8, 128.5, 127.1, 126.9, 125.9, 125.1, 122.5, 120.7, 116.7, 108.9, 108.0, 90.0, 46.9, 37.6, 26.3. IR (KBr) *v* 3428, 3053, 2957, 1721, 1612, 1481, 1344, 1240, 1107, 1042, 1006, 895, 817, 754 $cm^{-1}$. HRMS (ESI) calcd for $C_{30}H_{23}ClNO_3$ $[M+H]^+$ 480.1361 and 481.1395, found 480.1361 and 481.1394.

## 4. Experimental data for functionalization of 3za




**General procedure：** Under nitrogen atmosphere, compound **3za** (89.7 mg, 0.20 mmol), 4-chlorophenylboronic acid (1.5 equiv), $Cs_2CO_3$ (2.0 equiv), $Pd(OAc)_2$ (0.05 equiv) and butyl di-1-adamantylphosphine (0.06 equiv) were successively added to a 15 mL dried tube, followed by adding 2.0 mL DME. The resulting mixture was stirred at 80 °C for 40 h till almost full consumption of **3za** monitored by thin layer chromatography, and then the reaction mixture was directly subjected to flash column chromatography on silica gel (petroleum ether/ ethyl acetate) to afford the corresponding products **6**. The dr value was determined by $^{13}C$ NMR.

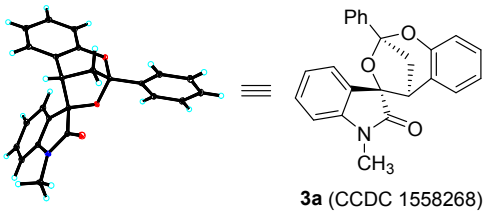



7'-(4-chlorophenyl)-1-methyl-2'-phenyl-5'*H*-spiro[indoline-3,4'-[2,5]methanobenzo[*d*][1,3]dioxepin]-2-one (**6**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 40:1 to 20:1); 50.7 mg, 53% yield, 3:1 dr; reaction time = 40 h; mp 227.7-228.1 °C; $^1H$ NMR (400 MHz, $CDCl_3$), δ 7.83 (d, $J$ = 8.0 Hz, 2H), 7.36-7.25 (m, 5H), 7.18 (s, 3H), 7.07 (dd, $J_1$ = 8.0 Hz, $J_2$ = 12.0 Hz, 2H), 6.70 (s, 1H), 6.63 (d, $J$ = 8.0 Hz, 1H), 6.55 (t, $J$ = 8.0 Hz, 1H), 5.87 (d, $J$ = 8.0 Hz, 1H), 3.85 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.33 (d, $J$ = 4.0 Hz, 1H), 3.07 (s, 3H), 2.48 (d, $J$ = 12.0 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 175.3, 152.6, 143.8, 139.1, 138.4, 132.9, 132.8, 130.3, 128.9, 128.8, 128.3, 128.0, 127.4, 126.8, 126.5, 125.9, 125.7, 125.5, 122.4, 117.2, 109.2, 108.2, 90.9, 47.0, 37.7,

26.3. IR (KBr) *v* 3428, 3058, 2959, 2928, 2856, 1722, 1613, 1478, 1373, 1343, 1243, 1122, 1042, 1012, 895, 819, 750, 698 $cm^{-1}$. HRMS (ESI) calcd for $C_{30}H_{22}ClNNaO_3$ $[M+Na]^+$ 502.1180 and 503.1214, found 502.1188 and 503.1210.

## 5. Crystal data for 3a




**3a** (CCDC 1558268)

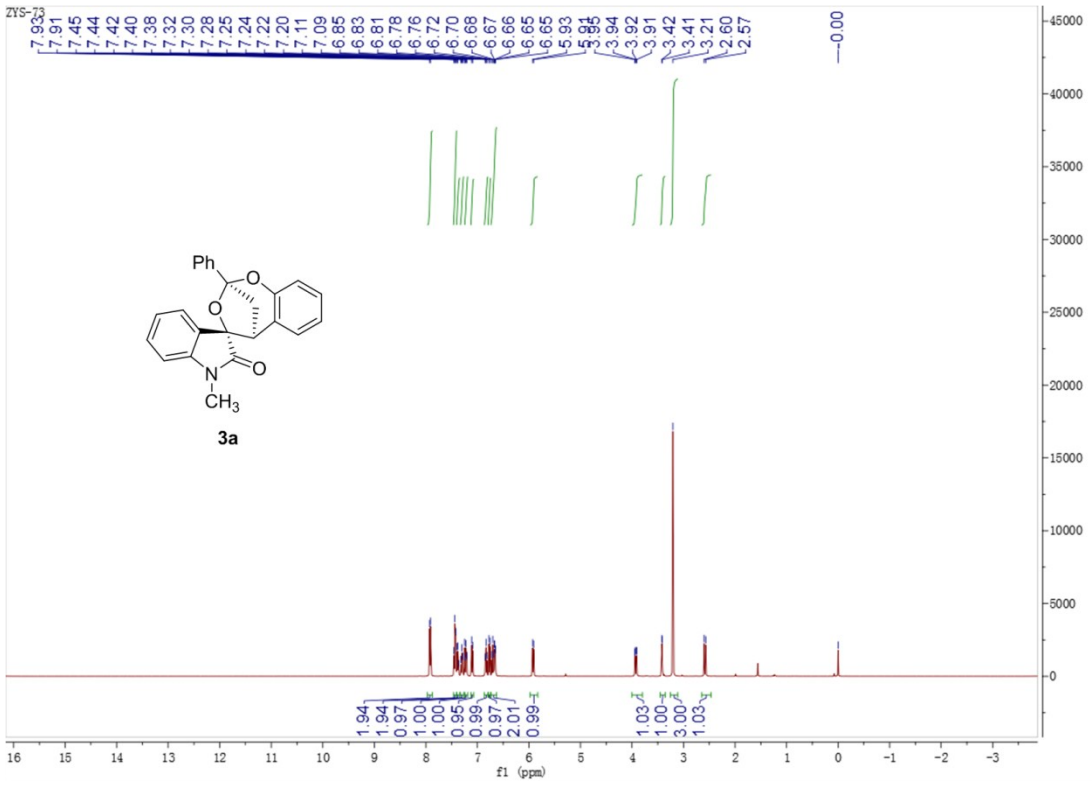
Displacement ellipsoids are drawn at the 30% probability level.

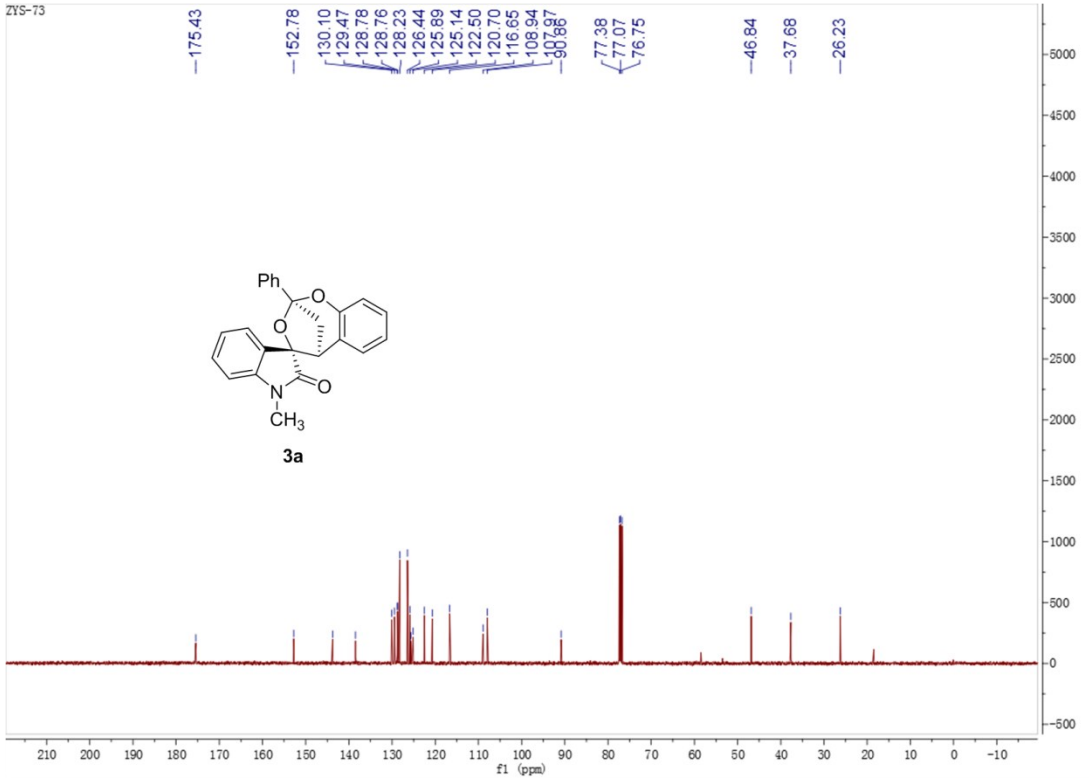
Table S1. Crystal data and structure refinement for **3a**.

| | | |
|---|---|---|
| Identification code | **3a** | |
| Empirical formula | $C_{24}H_{19}NO_3$ | |
| Formula weight | 369.40 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | P-1 | |
| Unit cell dimensions | a = 9.5595(9) Å | α= 84.7530(10)°. |
| | b = 9.7636(9) Å | β= 79.2070(10)°. |
| | c = 10.1483(10) Å | γ= 72.8890(10)°. |
| Volume | 888.59(15) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.381 $Mg/m^3$ | |
| Absorption coefficient | 0.091 $mm^{-1}$ | |
| F(000) | 388 | |
| Crystal size | 0.840 x 0.700 x 0.480 $mm^3$ | |
| Theta range for data collection | 2.044 to 30.981°. | |
| Index ranges | -13<=h<=13, -13<=k<=13, -14<=l<=14 | |
| Reflections collected | 13221 | |
| Independent reflections | 5188 [R(int) = 0.0217] | |
| Completeness to theta = 25.242° | 99.8 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 5188 / 0 / 254 | |
| Goodness-of-fit on $F^2$ | 1.059 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0387, wR2 = 0.1042 | |

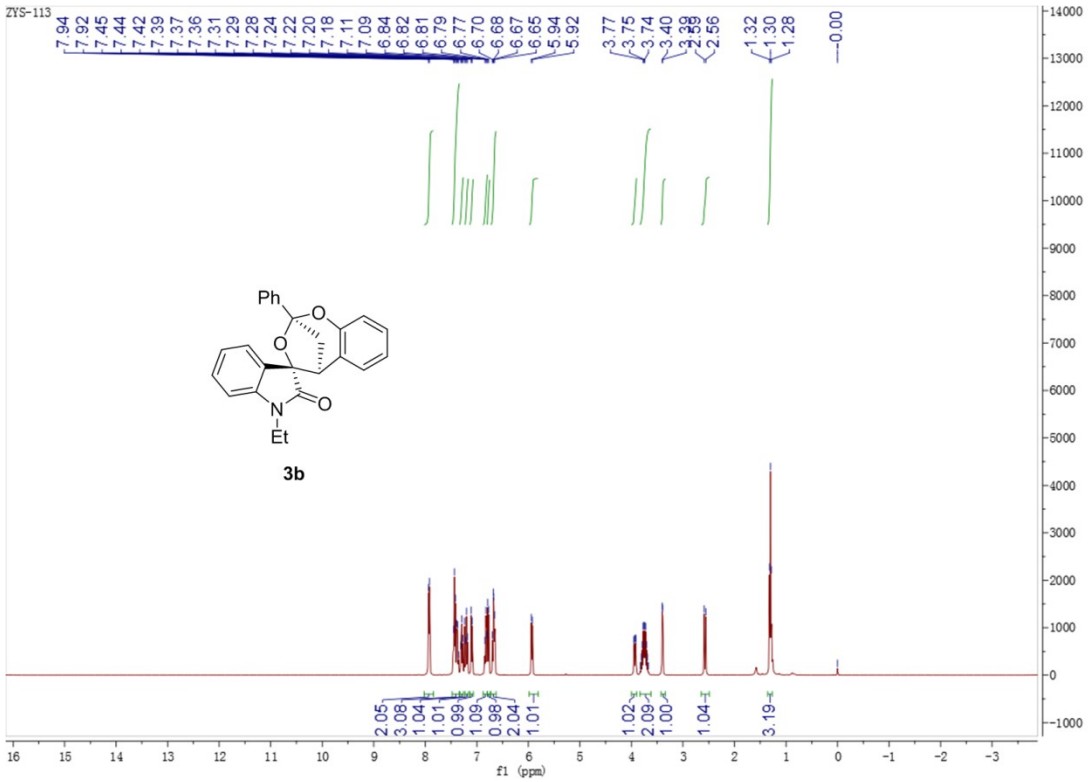
| | |
|---|---|
| R indices (all data) | R1 = 0.0420, wR2 = 0.1066 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.415 and -0.379 e.Å$^{-3}$ |

## 6. $^{1}$H NMR and $^{13}$C NMR spectra

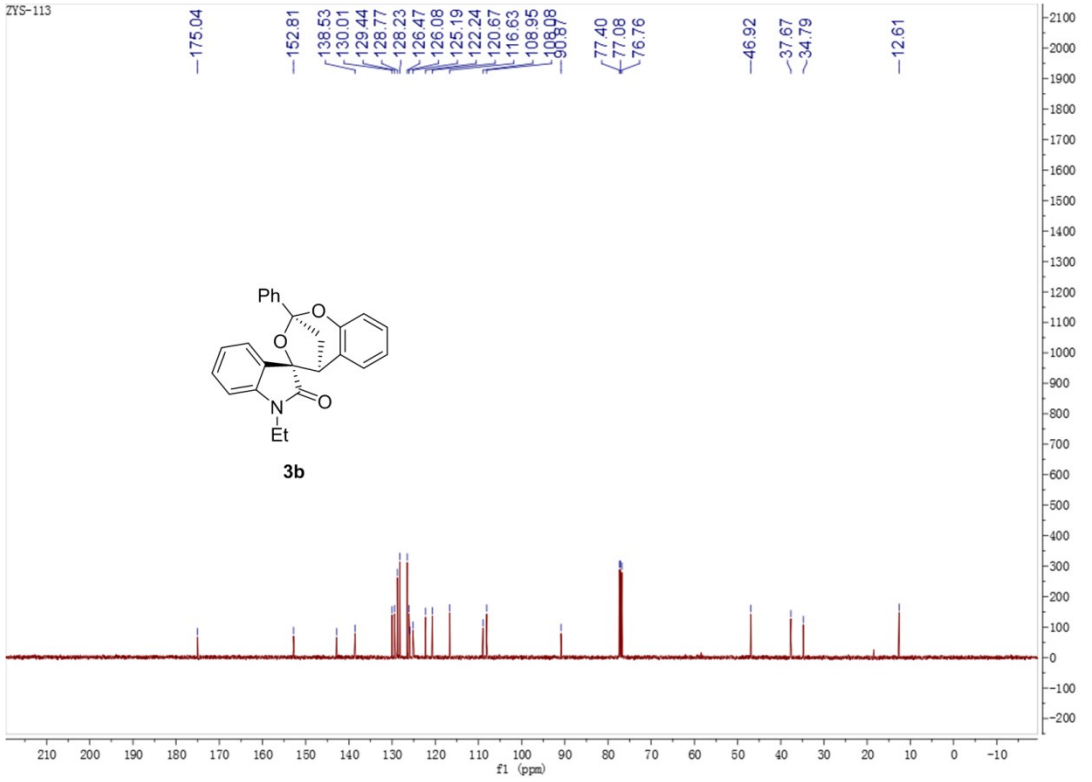



ZYS-73
175.43
152.78
130.10
129.47
128.78
128.76
128.23
126.44
125.89
125.14
122.50
120.70
116.65
108.94
90.86
77.38
77.07
76.75
46.84
37.68
26.23
Ph
O
O
N
CH3
O
f1 (ppm)

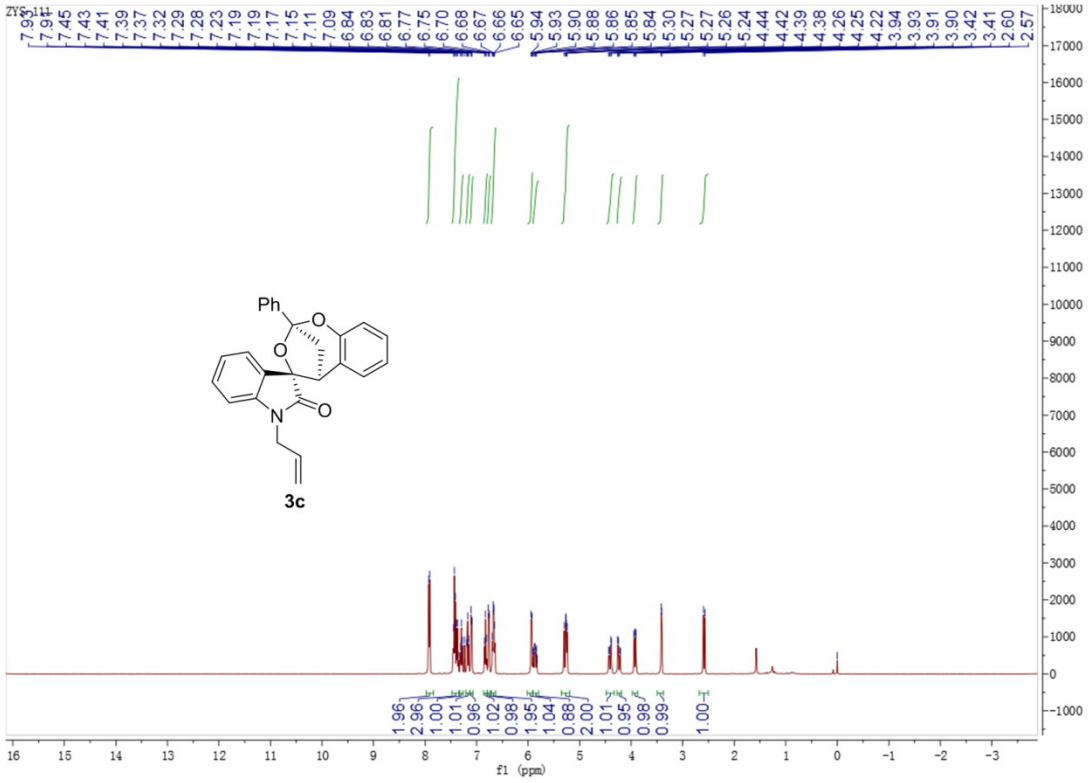
**3a**


ZYS-113
7.94
7.92
7.45
7.44
7.42
7.39
7.37
7.36
7.31
7.29
7.28
7.24
7.22
7.20
7.18
7.11
7.09
6.84
6.82
6.81
6.79
6.77
6.70
6.68
6.67
6.65
5.94
5.92
3.77
3.75
3.74
3.40
2.56
1.32
1.30
1.28
0.00
Ph
O
O
N
Et
O
2.05
3.08
1.04
1.01
0.99
1.09
0.98
2.04
1.01
1.02
2.09
1.00
1.04
3.19
f1 (ppm)

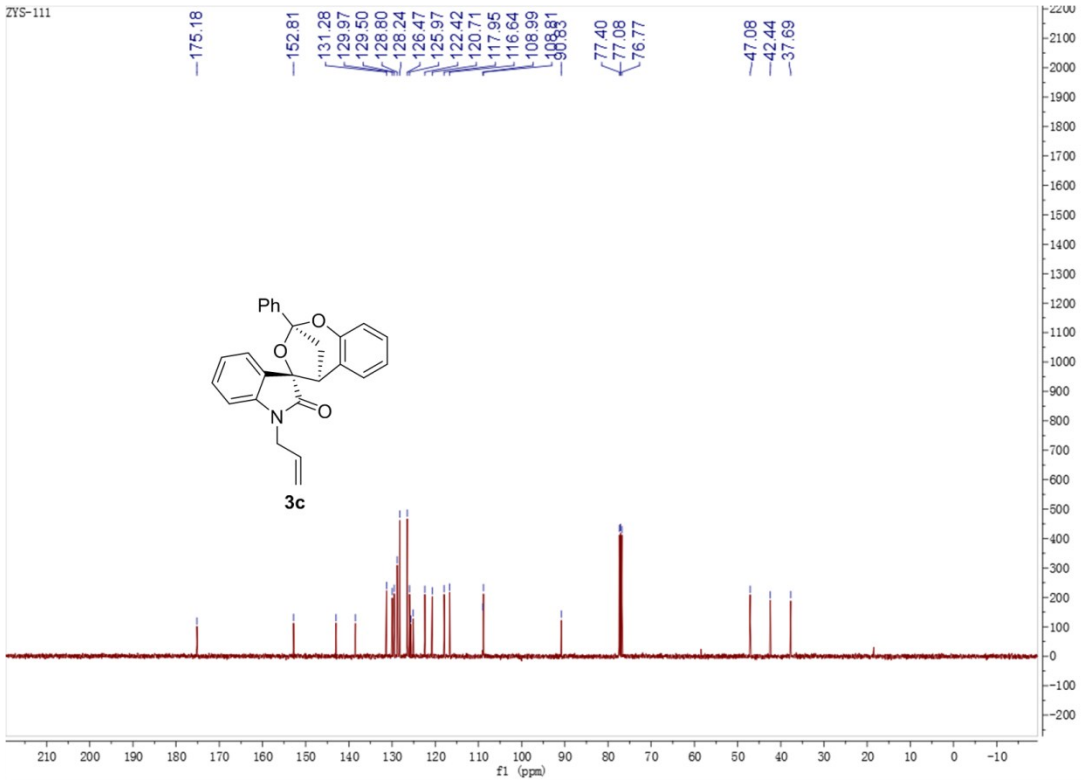
**3b**

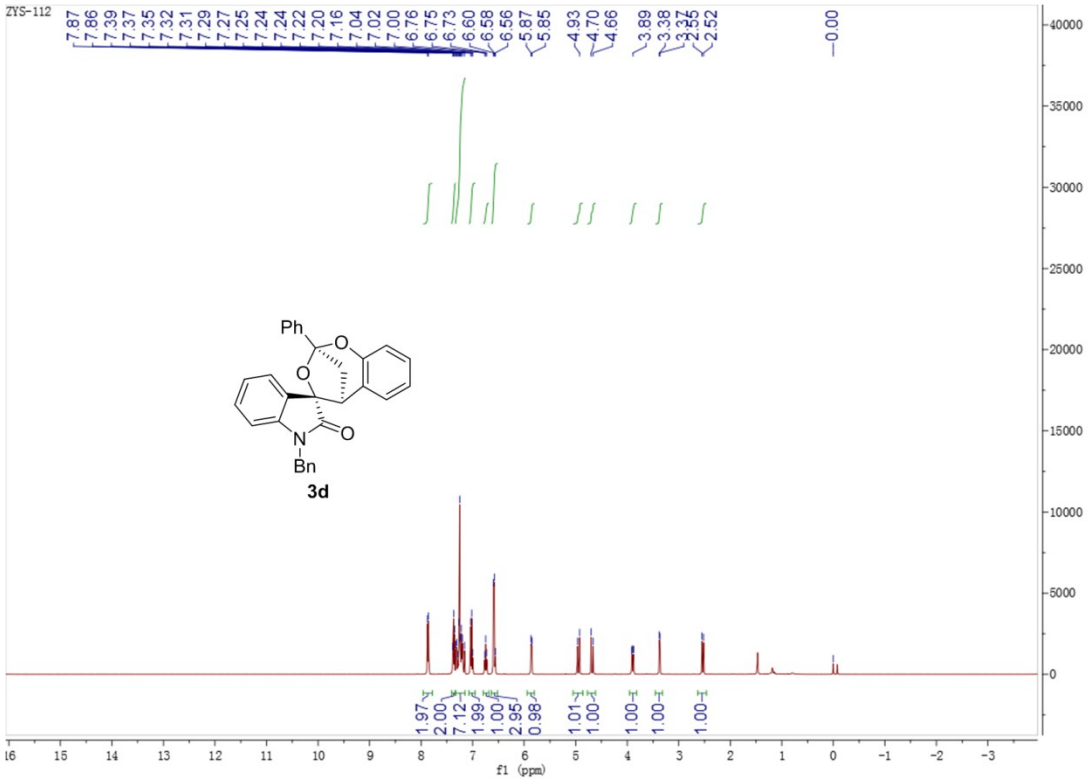

ZYS-113
175.04
152.81
138.53
130.01
129.44
128.77
128.23
126.47
126.08
125.19
122.24
120.67
116.63
108.95
108.08
90.87
77.40
77.08
76.76
46.92
37.67
34.79
12.61
Ph
O
O
N
O
Et
f1 (ppm)

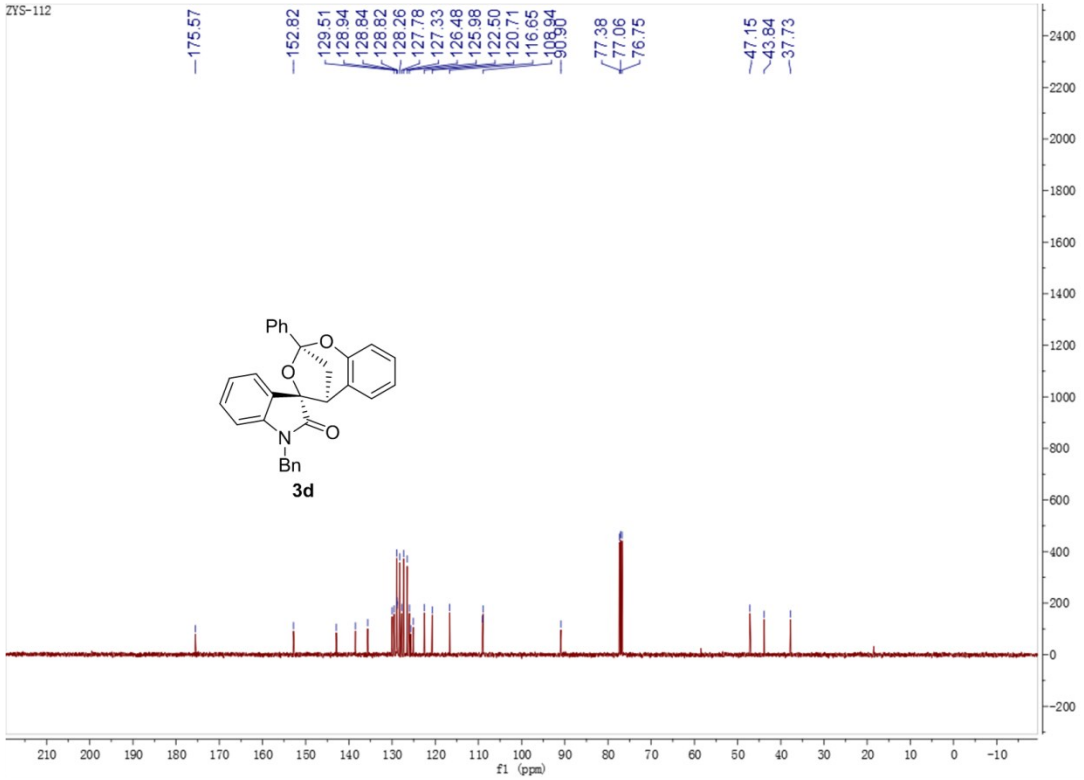
**3b**

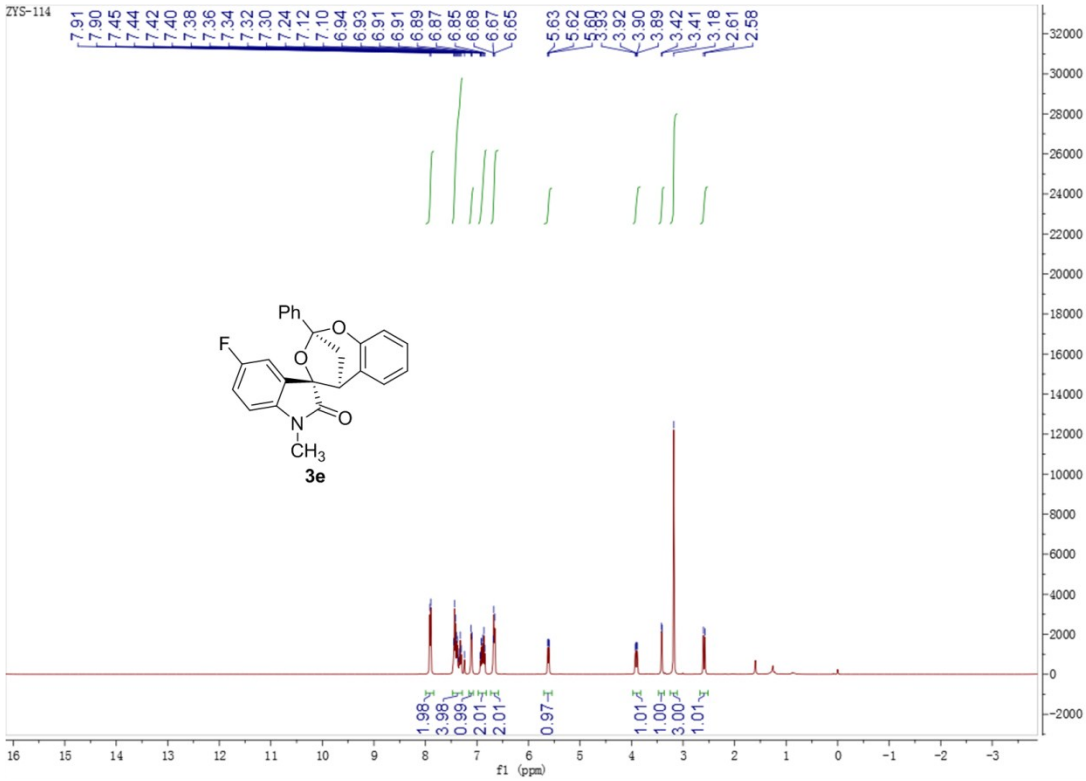

7.95
7.94
7.45
7.43
7.41
7.39
7.37
7.32
7.29
7.28
7.23
7.19
7.19
7.17
7.15
7.11
7.09
6.84
6.83
6.81
6.77
6.75
6.70
6.68
6.67
6.66
6.65
5.94
5.93
5.90
5.88
5.86
5.85
5.84
5.30
5.27
5.27
5.26
5.24
4.44
4.42
4.39
4.38
4.26
4.25
4.22
3.94
3.93
3.91
3.90
3.42
3.41
2.60
2.57
Ph
O
O
N
O
1.96
2.96
1.00
1.01
0.96
1.02
0.98
1.95
1.04
0.88
2.00
1.01
0.95
0.98
0.99
1.00
f1 (ppm)

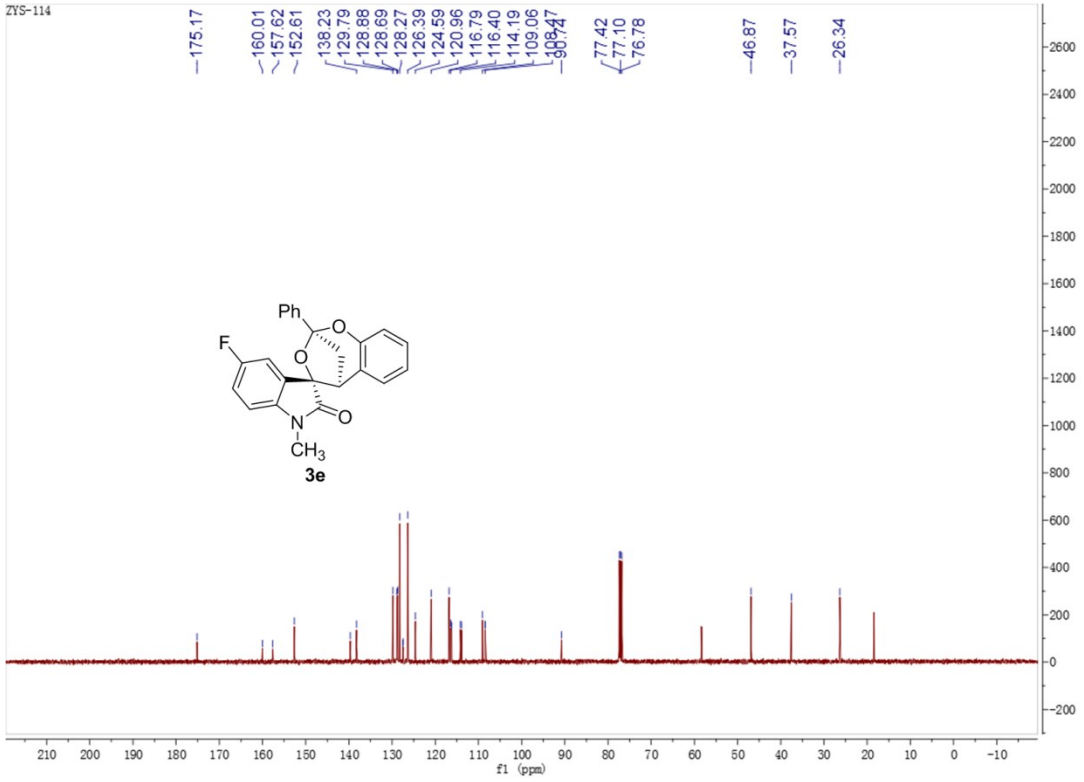
**3c**

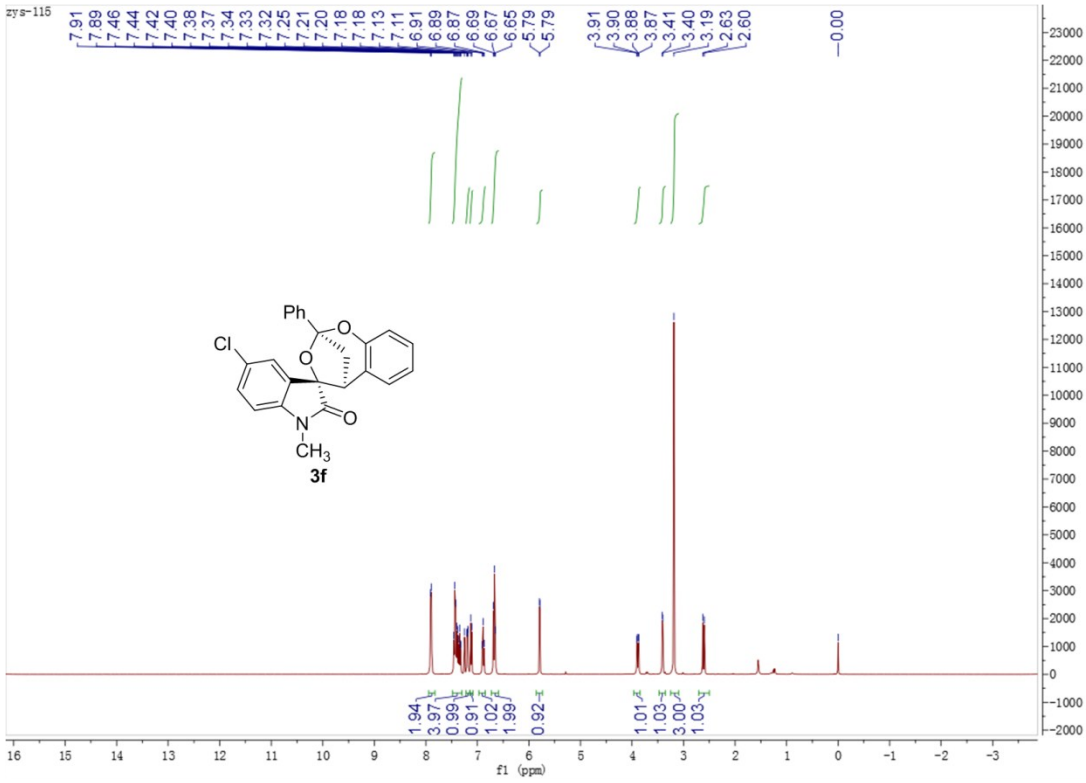

ZYS-111
175.18
152.81
131.28
129.97
129.50
128.80
128.24
126.47
125.97
122.42
120.71
117.95
116.64
108.99
90.83
77.40
77.08
76.77
47.08
42.44
37.69
Ph
O
O
N
O
3c
f1 (ppm)

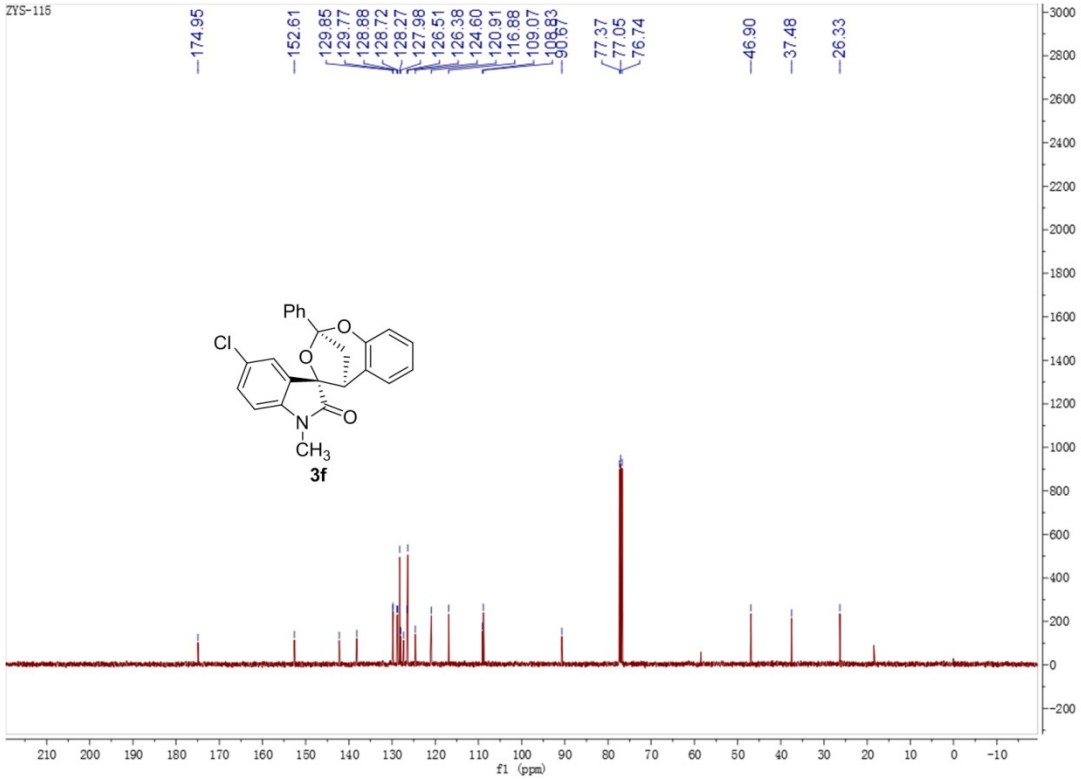

ZYS-112
7.87
7.86
7.39
7.37
7.35
7.32
7.31
7.29
7.27
7.25
7.24
7.24
7.22
7.20
7.16
7.04
7.02
7.00
6.76
6.75
6.73
6.60
6.58
6.56
5.87
5.85
4.93
4.70
4.66
3.89
3.38
2.52
0.00
Ph
O
O
N
O
Bn
3d
1.97
2.00
7.12
1.99
1.00
2.95
0.98
1.01
1.00
1.00
1.00
1.00
f1 (ppm)

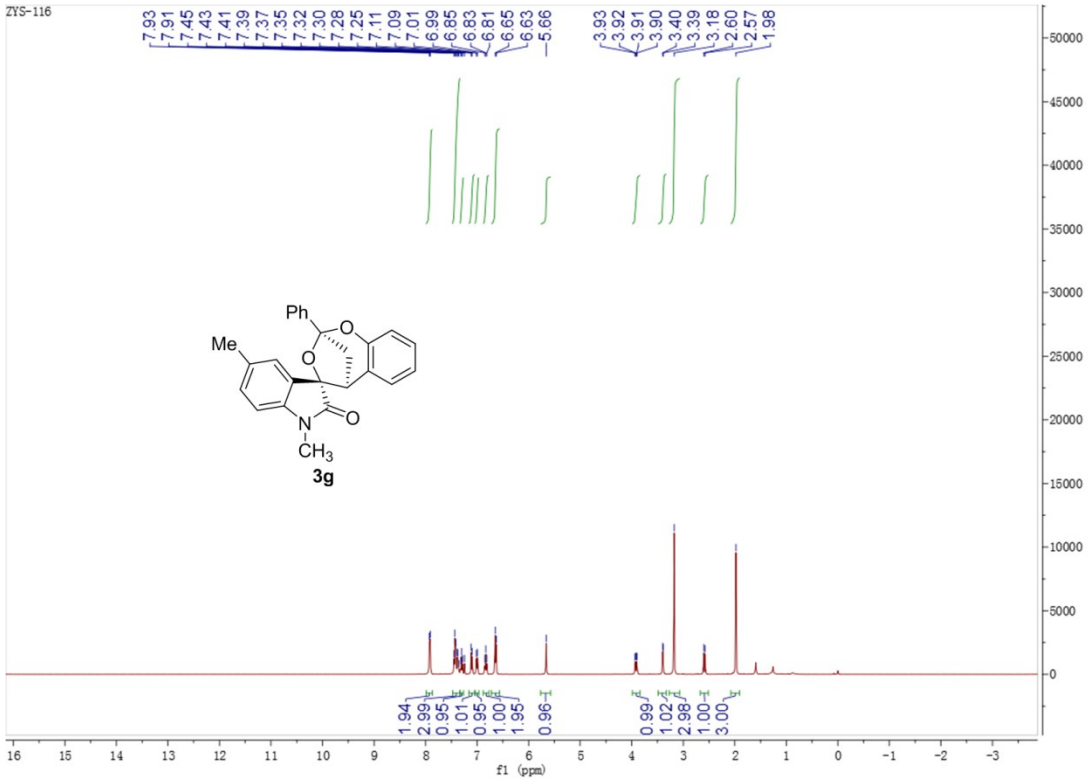

ZYS-112
175.57
152.82
129.51
128.94
128.84
128.82
128.26
127.78
127.33
126.48
125.98
122.50
120.71
116.65
90.90
77.38
77.06
76.75
47.15
43.84
37.73
Ph
O
O
N
O
Bn
3d
f1 (ppm)

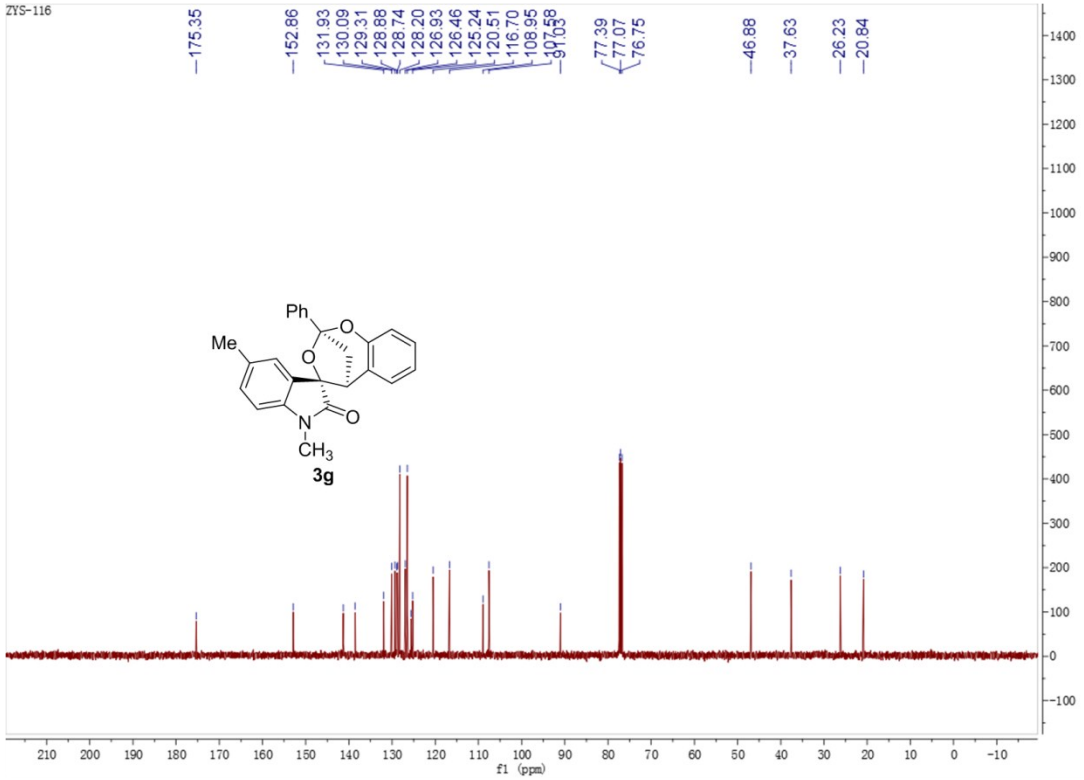

ZYS-114
7.91
7.90
7.45
7.44
7.42
7.40
7.38
7.36
7.34
7.32
7.30
7.24
7.12
7.10
6.94
6.93
6.91
6.91
6.89
6.87
6.85
6.68
6.67
6.65
5.63
5.62
3.92
3.90
3.89
3.42
3.41
3.18
2.61
2.58
Ph
O
O
F
N
O
CH3
3e
1.98
3.98
0.99
2.01
2.01
0.97
1.01
1.00
3.00
1.01
f1 (ppm)

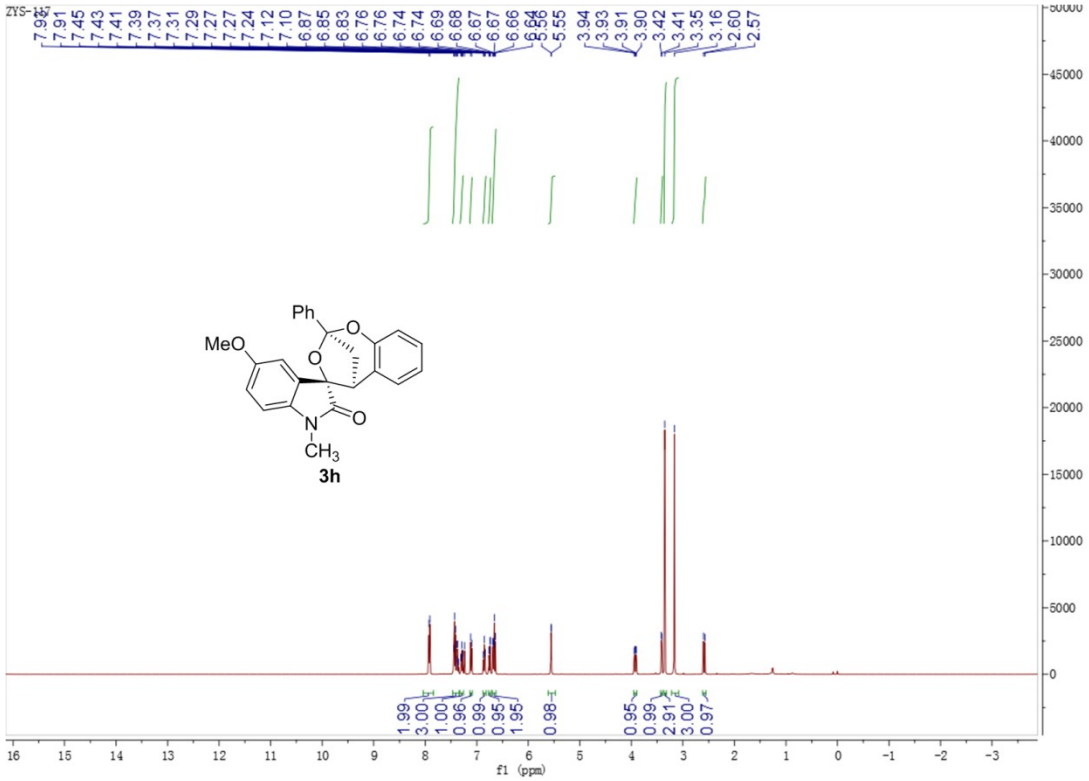

ZYS-114
175.17
160.01
157.62
152.61
138.23
129.79
128.88
128.69
128.27
126.39
124.59
120.96
116.79
116.40
114.19
109.06
90.47
77.42
77.10
76.78
46.87
37.57
26.34
Ph
O
F
O
O
N
CH3
3e
f1 (ppm)

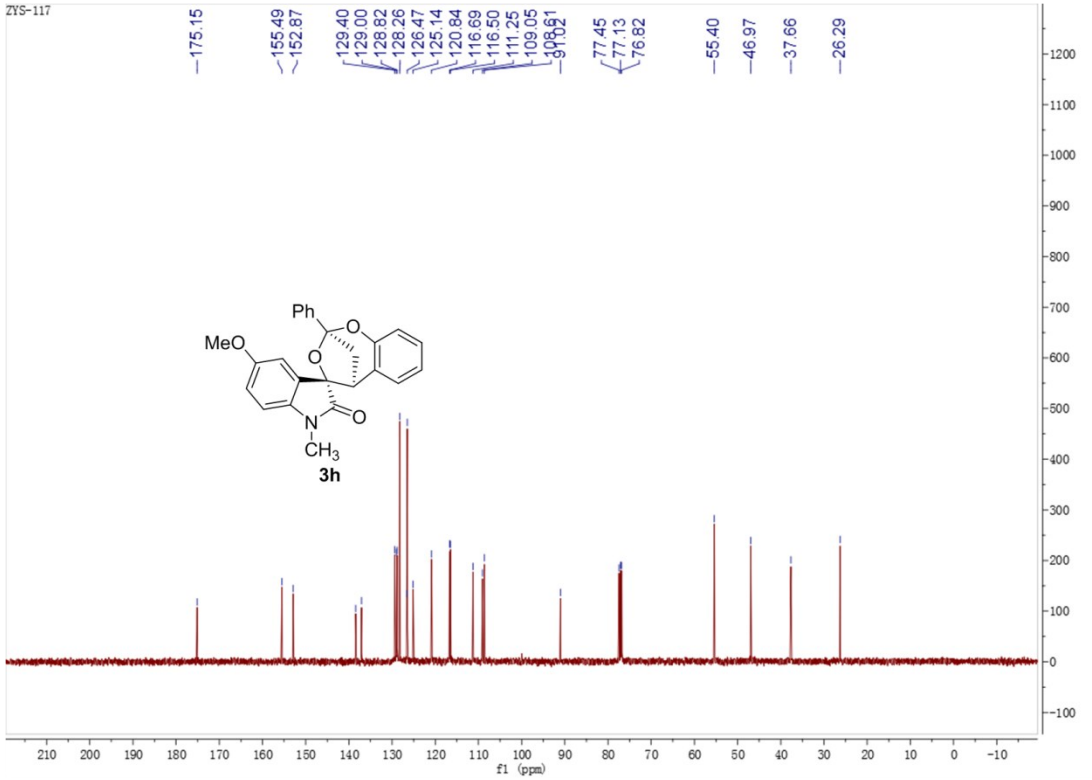

zys-115
7.91
7.89
7.46
7.44
7.42
7.40
7.38
7.37
7.34
7.33
7.32
7.25
7.21
7.20
7.18
7.13
7.11
6.91
6.89
6.87
6.69
6.67
6.65
5.79
5.79
3.91
3.90
3.88
3.87
3.41
3.40
3.19
2.63
2.60
0.00
Ph
O
Cl
O
O
N
CH3
3f
1.94
3.97
0.99
0.91
1.02
1.99
0.92
1.01
1.03
3.00
1.03
f1 (ppm)

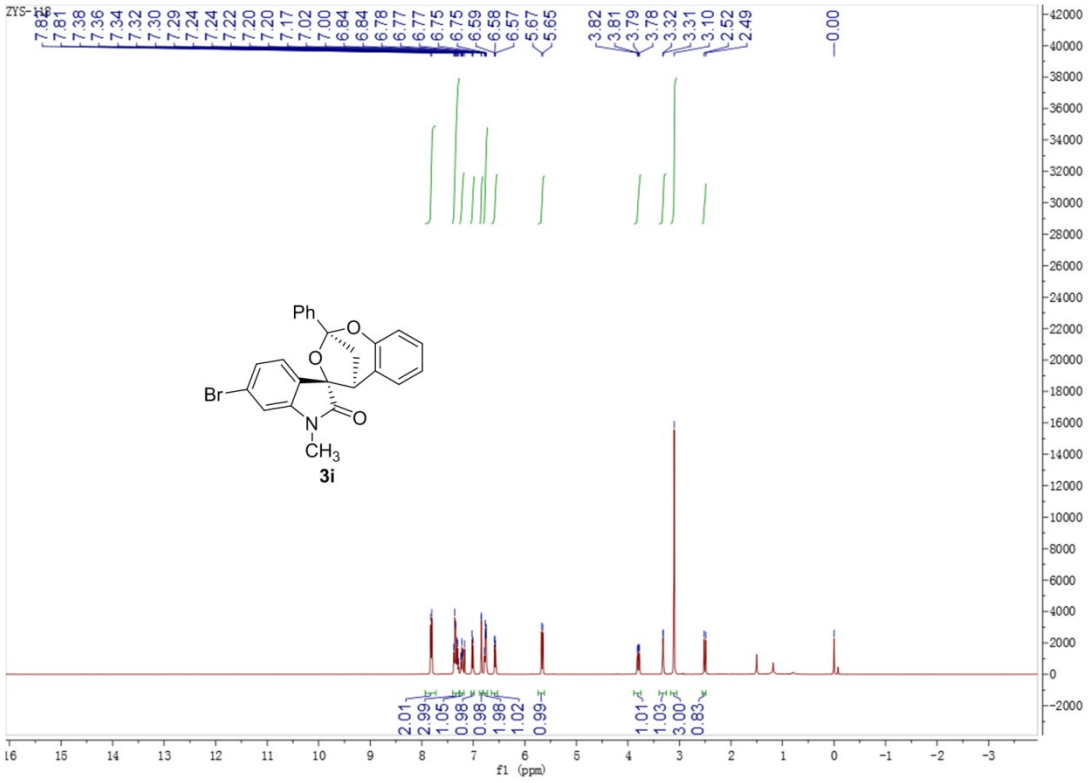

ZYS-115
174.95
152.61
129.85
129.77
128.88
128.72
128.27
127.98
126.51
126.38
124.60
120.91
116.88
109.07
90.67
77.37
77.05
76.74
46.90
37.48
26.33
Ph
O
O
Cl
N
O
CH3
3f
f1 (ppm)

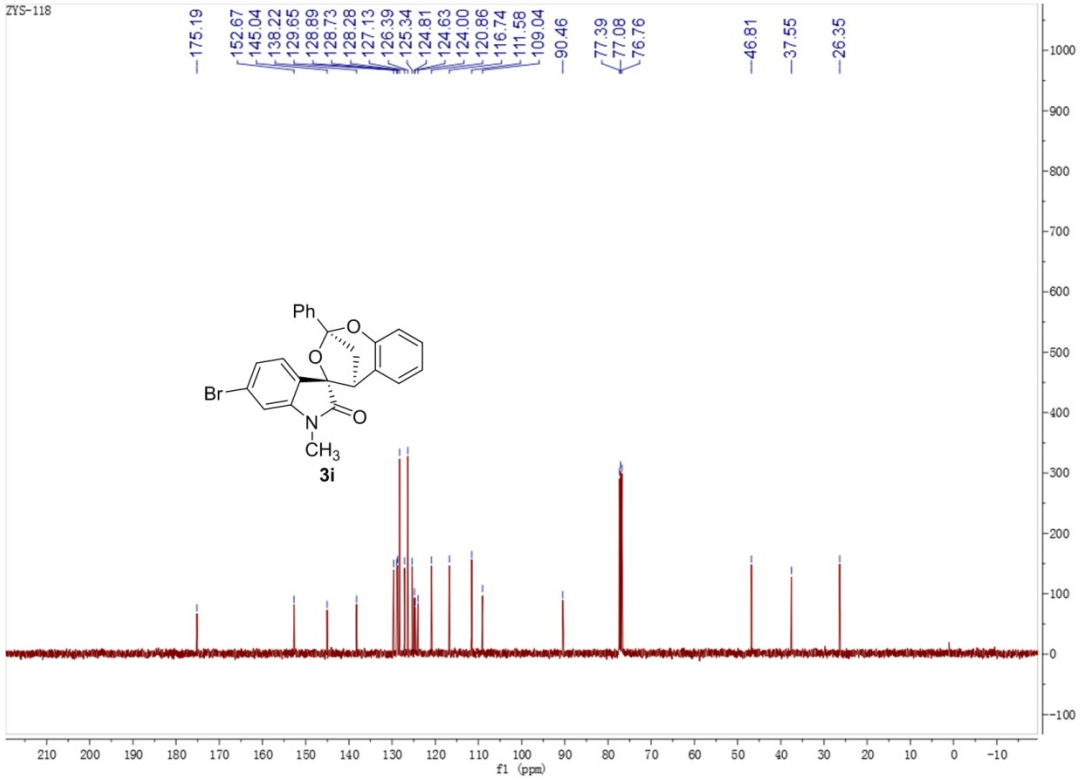

ZYS-116
7.93
7.91
7.45
7.43
7.41
7.39
7.37
7.35
7.32
7.30
7.28
7.25
7.11
7.09
7.01
6.99
6.85
6.83
6.81
6.65
6.63
5.66
3.93
3.92
3.91
3.90
3.40
3.39
3.18
2.60
2.57
1.98
Ph
O
O
Me
N
O
CH3
3g
1.94
2.99
0.95
1.01
0.95
1.00
1.95
0.96
0.99
1.02
2.98
1.00
3.00
f1 (ppm)

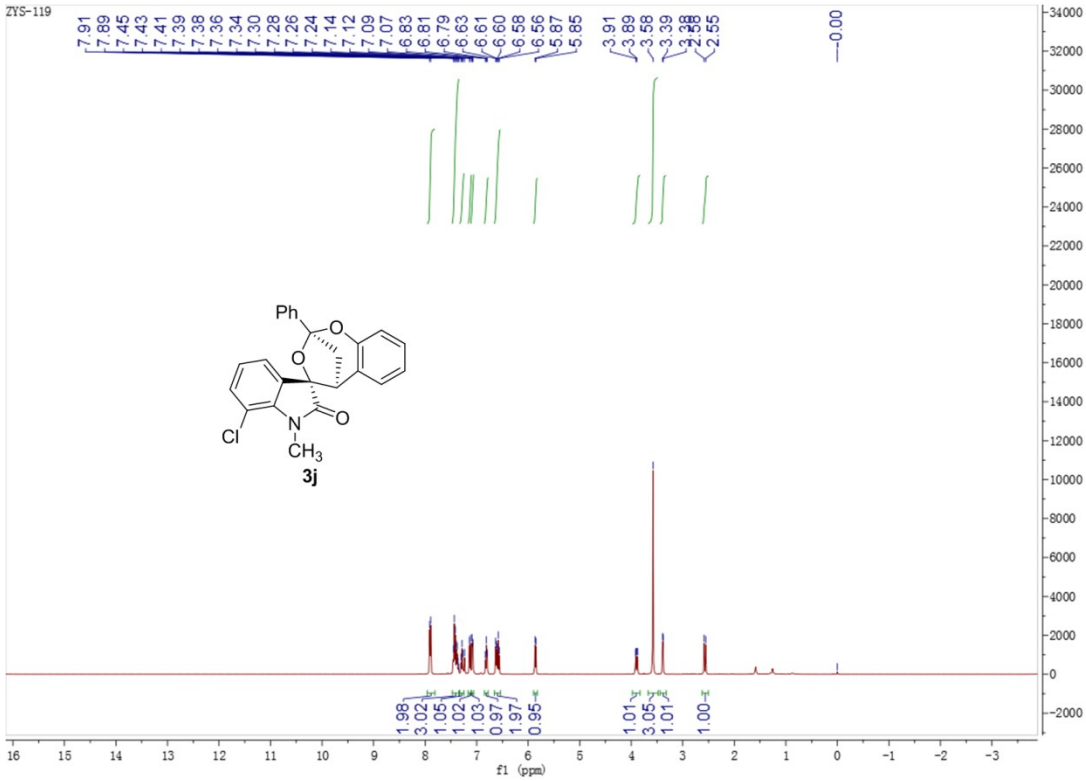

ZYS-116
175.35
152.86
131.93
130.09
129.31
128.88
128.74
128.20
126.93
126.46
125.24
120.51
116.70
108.95
91.03
77.39
77.07
76.75
46.88
37.63
26.23
20.84
Ph
Me
O
O
N
CH3
O
3g
f1 (ppm)

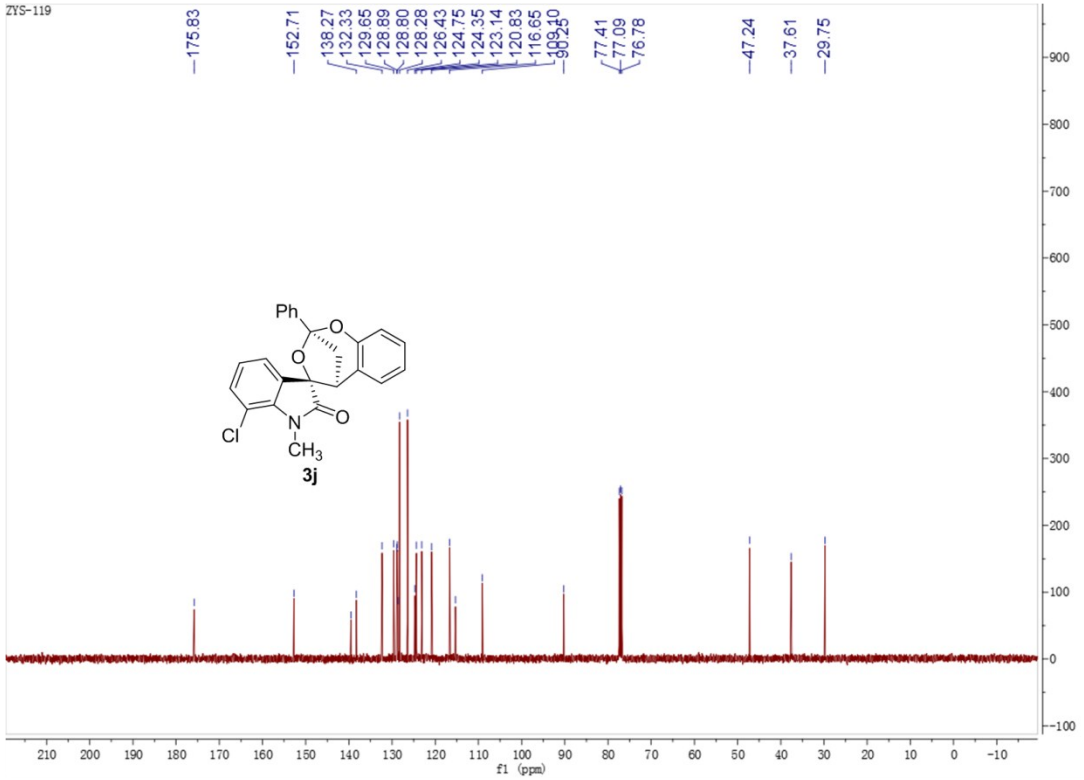

7.92
7.91
7.45
7.43
7.41
7.39
7.37
7.31
7.29
7.27
7.27
7.24
7.12
7.10
6.87
6.85
6.83
6.76
6.76
6.74
6.74
6.69
6.68
6.67
6.67
6.66
6.64
5.56
5.55
3.94
3.93
3.91
3.90
3.42
3.41
3.35
3.16
2.60
2.57
Ph
MeO
O
O
N
CH3
O
3h
1.99
3.00
1.00
0.96
0.99
0.95
1.95
0.98
0.95
0.99
2.91
3.00
0.97
f1 (ppm)

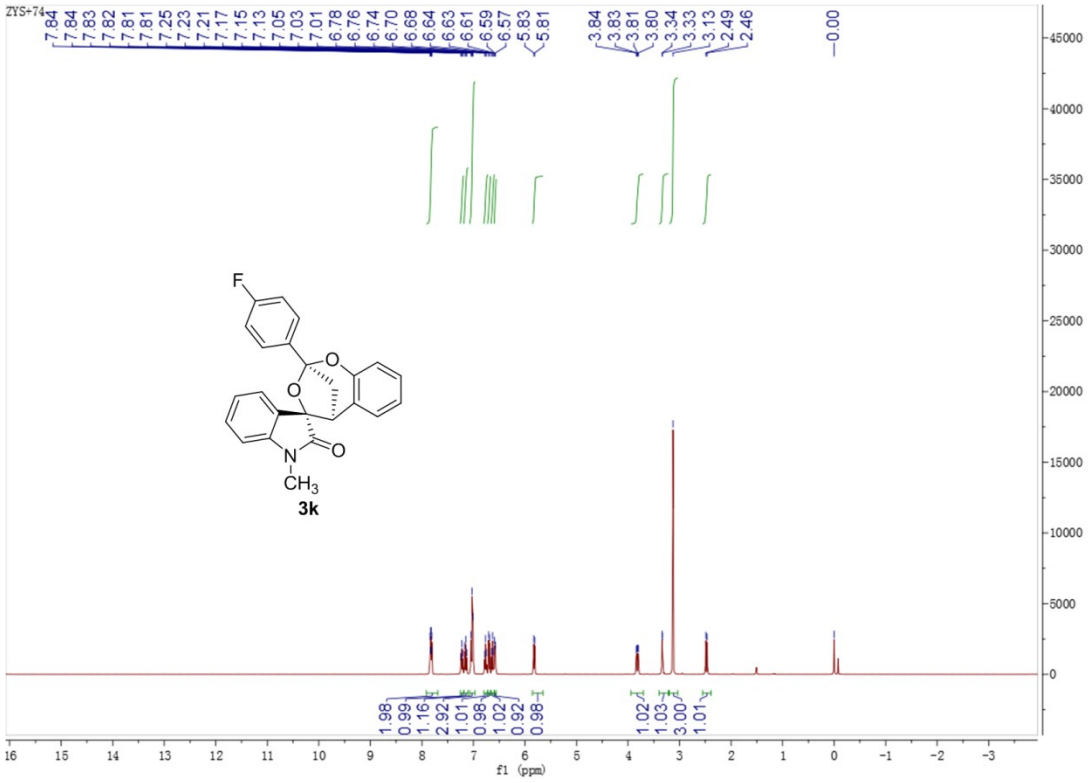

ZYS-117
175.15
155.49
152.87
129.40
129.00
128.82
128.26
126.47
125.14
120.84
116.69
116.50
111.25
109.05
91.02
77.45
77.13
76.82
55.40
46.97
37.66
26.29
Ph
MeO
O
O
N
O
CH3
3h
f1 (ppm)

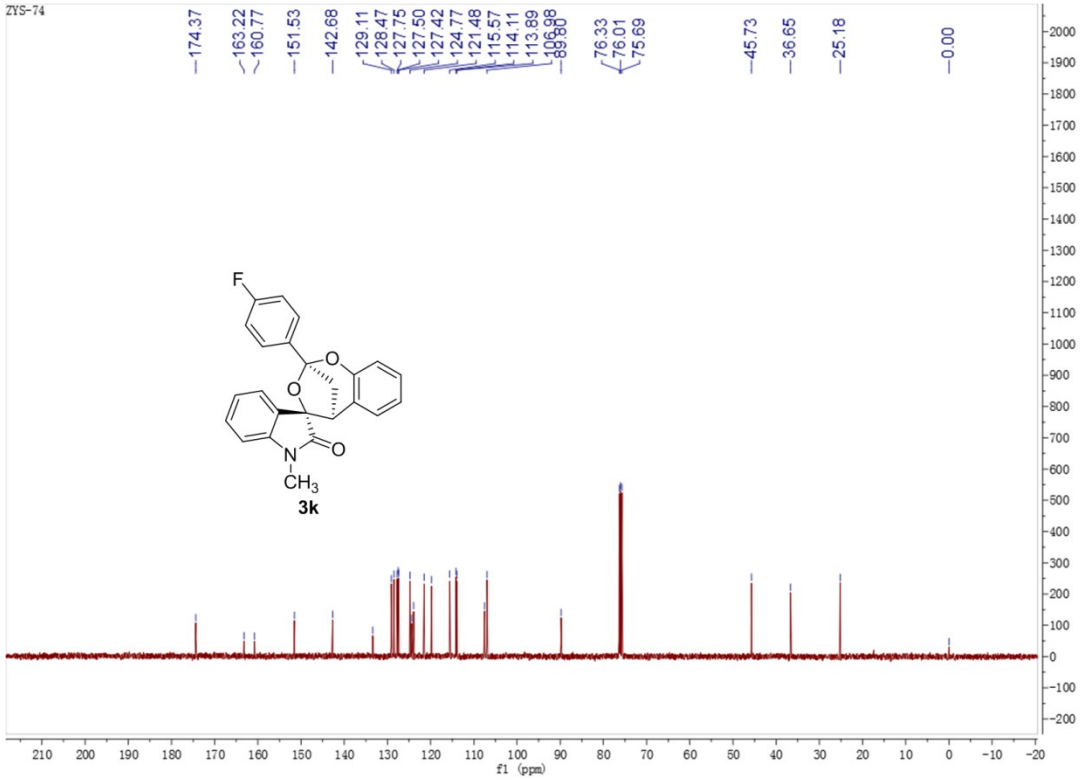

7.84
7.81
7.38
7.36
7.34
7.32
7.30
7.29
7.24
7.24
7.22
7.20
7.20
7.17
7.02
7.00
6.84
6.84
6.78
6.77
6.77
6.75
6.75
6.59
6.58
6.57
5.67
5.65
3.82
3.81
3.79
3.78
3.32
3.31
3.10
2.52
2.49
0.00
Ph
Br
O
O
N
O
CH3
3i
2.01
2.99
1.05
0.98
0.98
1.98
1.02
0.99
1.01
1.03
3.00
0.83
f1 (ppm)

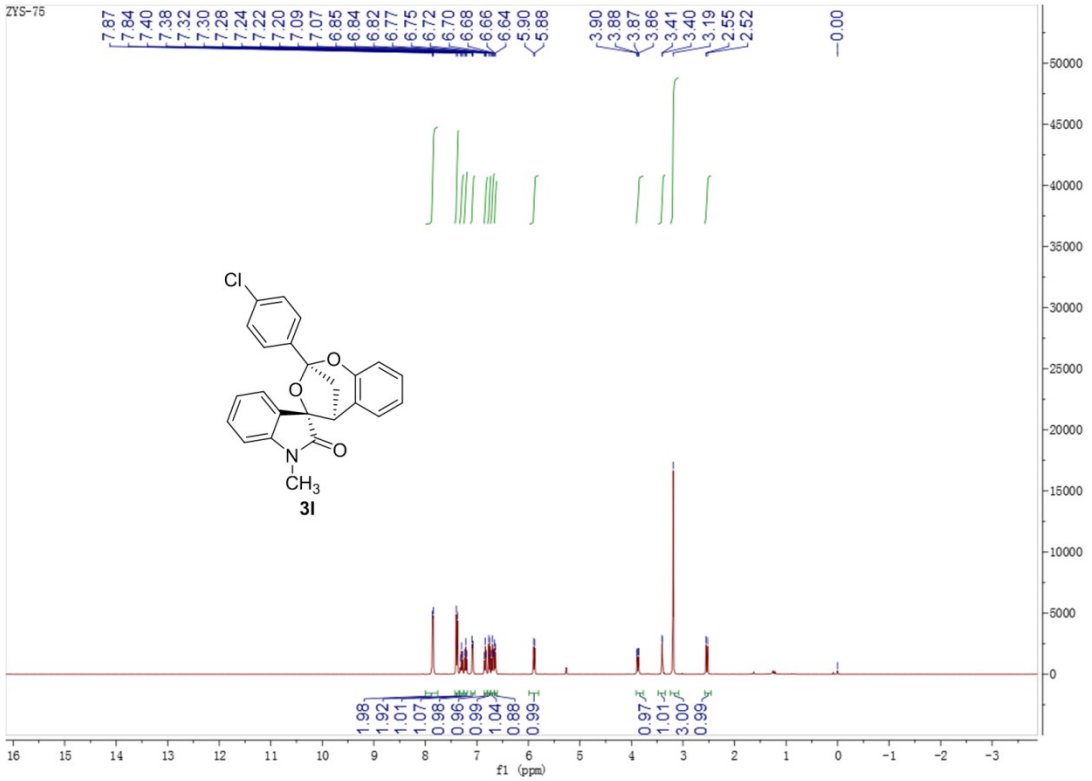

ZYS-118
175.19
152.67
145.04
138.22
129.65
128.89
128.73
128.28
127.13
126.39
125.34
124.81
124.63
124.00
120.86
116.74
111.58
109.04
90.46
77.39
77.08
76.76
46.81
37.55
26.35
Ph
O
O
Br
N
O
CH3
3i
f1 (ppm)

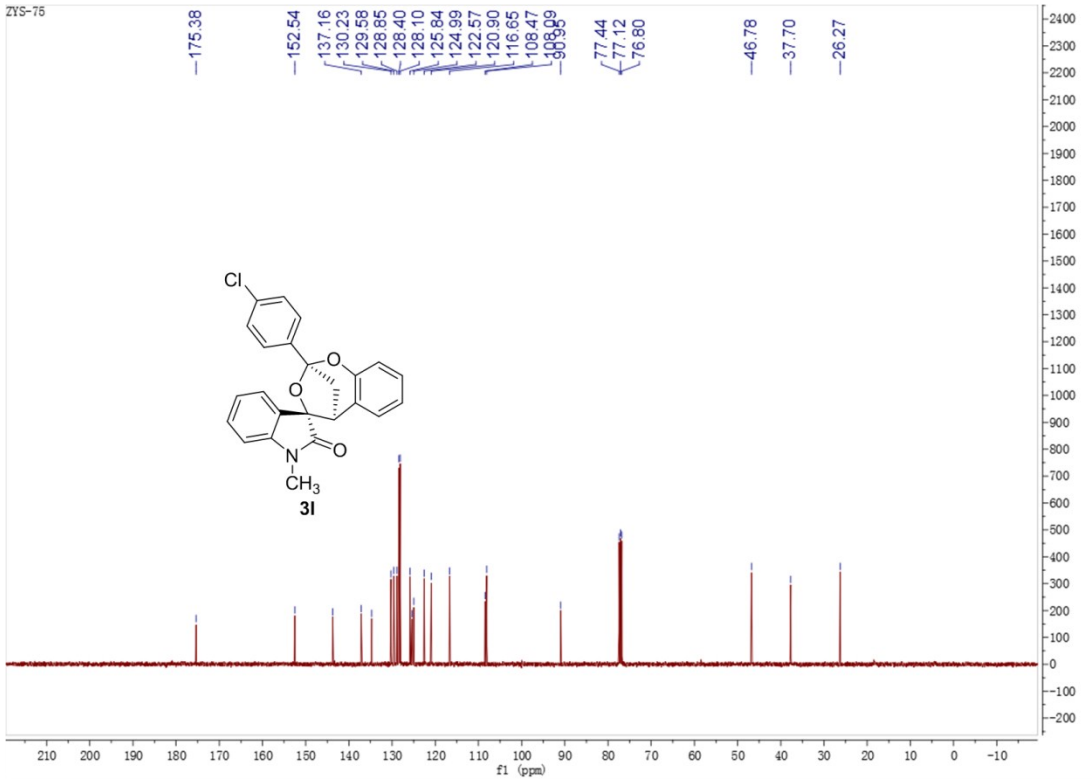

ZYS-119
7.91
7.89
7.45
7.43
7.41
7.39
7.38
7.36
7.34
7.30
7.28
7.26
7.24
7.14
7.12
7.09
7.07
6.83
6.81
6.79
6.63
6.61
6.60
6.58
6.56
5.87
5.85
3.91
3.89
3.58
3.39
2.55
0.00
Ph
O
O
Cl
N
O
CH3
3j
1.98
3.02
1.05
1.02
1.03
0.97
1.97
0.95
1.01
3.05
1.01
1.00
f1 (ppm)

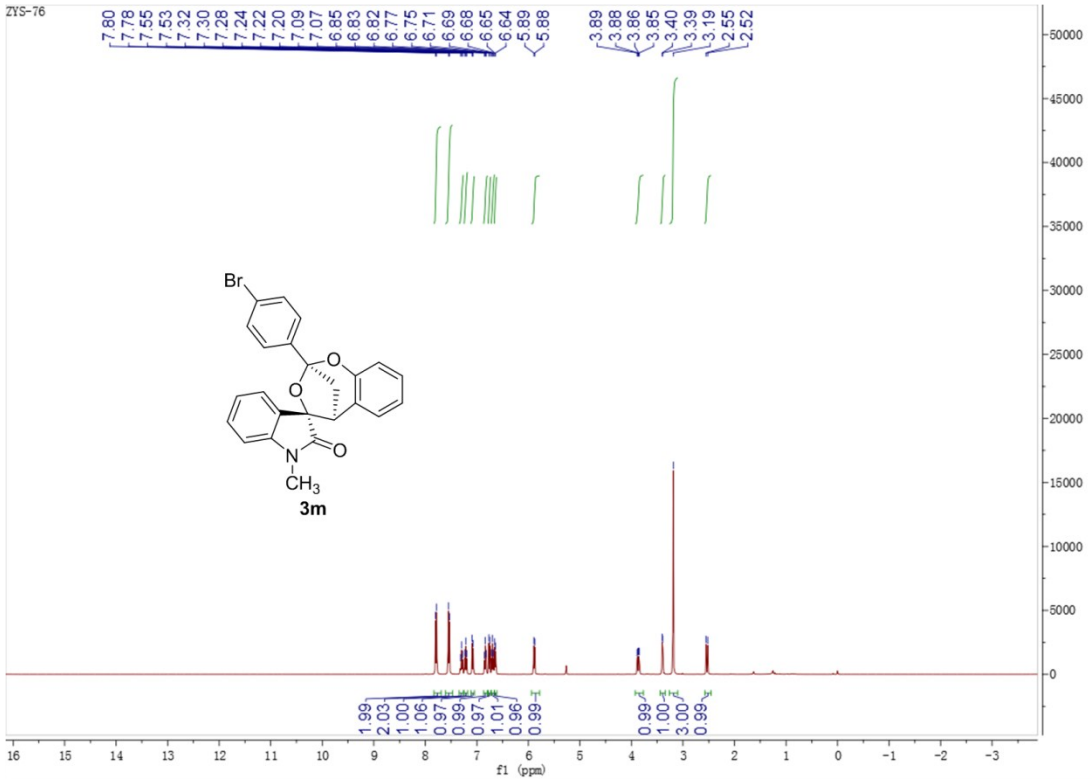

ZYS-119
175.83
152.71
138.27
132.33
129.65
128.89
128.80
128.28
126.43
124.75
124.35
123.14
120.83
116.65
109.10
90.25
77.41
77.09
76.78
47.24
37.61
29.75
Ph
O
O
Cl
N
O
CH3
3j
f1 (ppm)

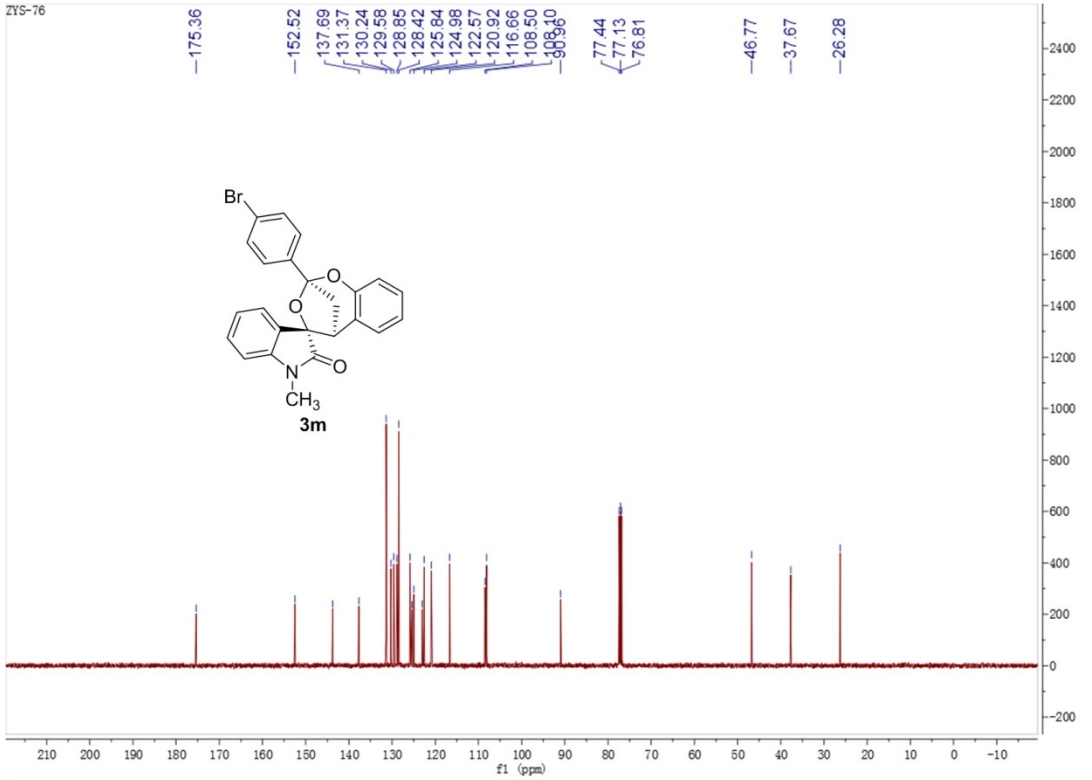

ZYS-74
7.84
7.84
7.83
7.82
7.81
7.81
7.25
7.23
7.21
7.17
7.15
7.13
7.05
7.03
7.01
6.78
6.76
6.74
6.70
6.68
6.64
6.63
6.61
6.59
6.57
5.83
5.81
3.84
3.83
3.81
3.80
3.34
3.33
3.13
2.49
2.46
0.00
F
O
O
N
O
CH3
3k
1.98
0.99
1.16
2.92
1.01
0.98
1.02
0.92
0.98
1.02
1.03
3.00
1.01
f1 (ppm)


ZYS-74
174.37
163.22
160.77
151.53
142.68
129.11
128.47
127.75
127.50
127.42
124.77
121.48
115.57
114.11
113.89
106.98
89.80
76.33
76.01
75.69
45.73
36.65
25.18
0.00
F
O
O
N
O
CH3
3k
f1 (ppm)

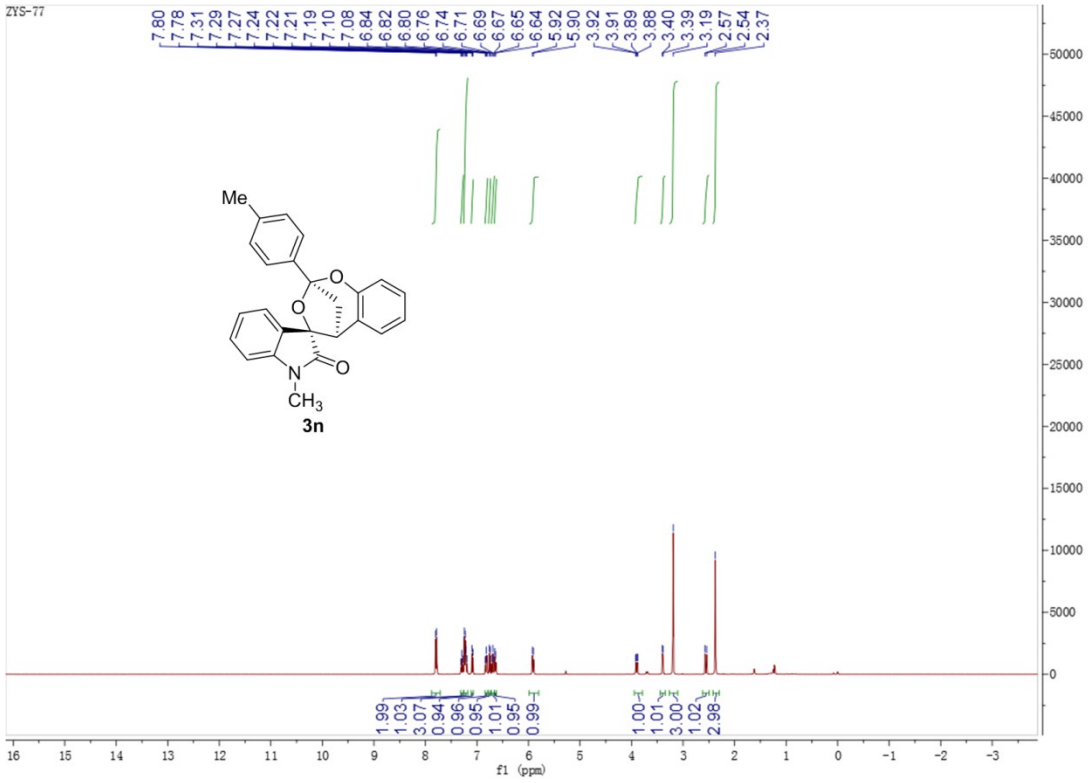

ZYS-75
7.87
7.84
7.40
7.38
7.32
7.30
7.28
7.24
7.22
7.20
7.09
7.07
6.85
6.84
6.82
6.77
6.75
6.72
6.70
6.68
6.66
6.64
5.90
5.88
3.90
3.88
3.87
3.86
3.41
3.40
3.19
2.55
2.52
0.00
Cl
O
O
N
O
CH3
3l
1.98
1.92
1.01
1.07
0.98
0.96
0.99
1.04
0.88
0.99
0.97
1.01
3.00
0.99
f1 (ppm)


ZYS-75
175.38
152.54
137.16
130.23
129.58
128.85
128.40
128.10
125.84
124.99
122.57
120.90
116.65
108.47
90.95
77.44
77.12
76.80
46.78
37.70
26.27
Cl
O
O
N
O
CH3
3l
f1 (ppm)

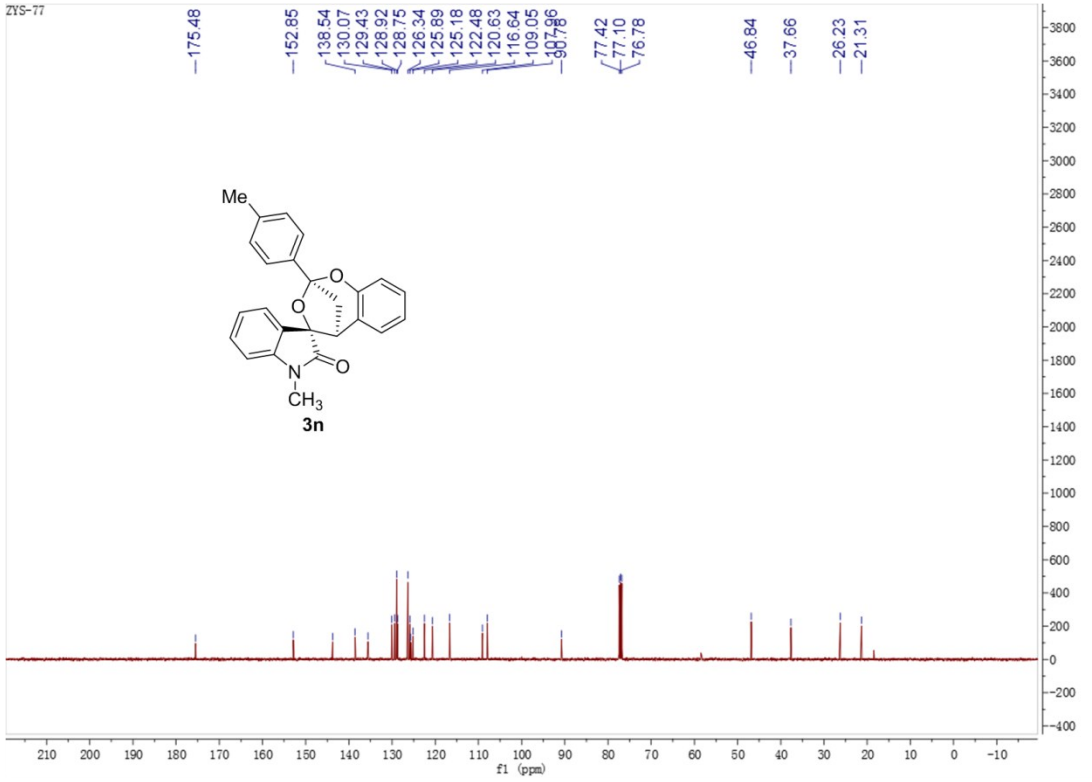

ZYS-76
7.80
7.78
7.55
7.53
7.32
7.30
7.28
7.24
7.22
7.20
7.09
7.07
6.85
6.83
6.82
6.77
6.75
6.71
6.69
6.68
6.65
6.64
5.89
5.88
3.89
3.88
3.86
3.85
3.40
3.39
3.19
2.55
2.52
Br
O
O
N
O
CH3
3m
1.99
2.03
1.00
1.06
0.97
0.99
0.97
1.01
0.96
0.99
0.99
1.00
3.00
0.99
f1 (ppm)


ZYS-76
175.36
152.52
137.69
131.37
130.24
129.58
128.85
128.42
125.84
124.98
122.57
120.92
116.66
108.50
90.96
77.44
77.13
76.81
46.77
37.67
26.28
Br
O
O
N
O
CH3
f1 (ppm)

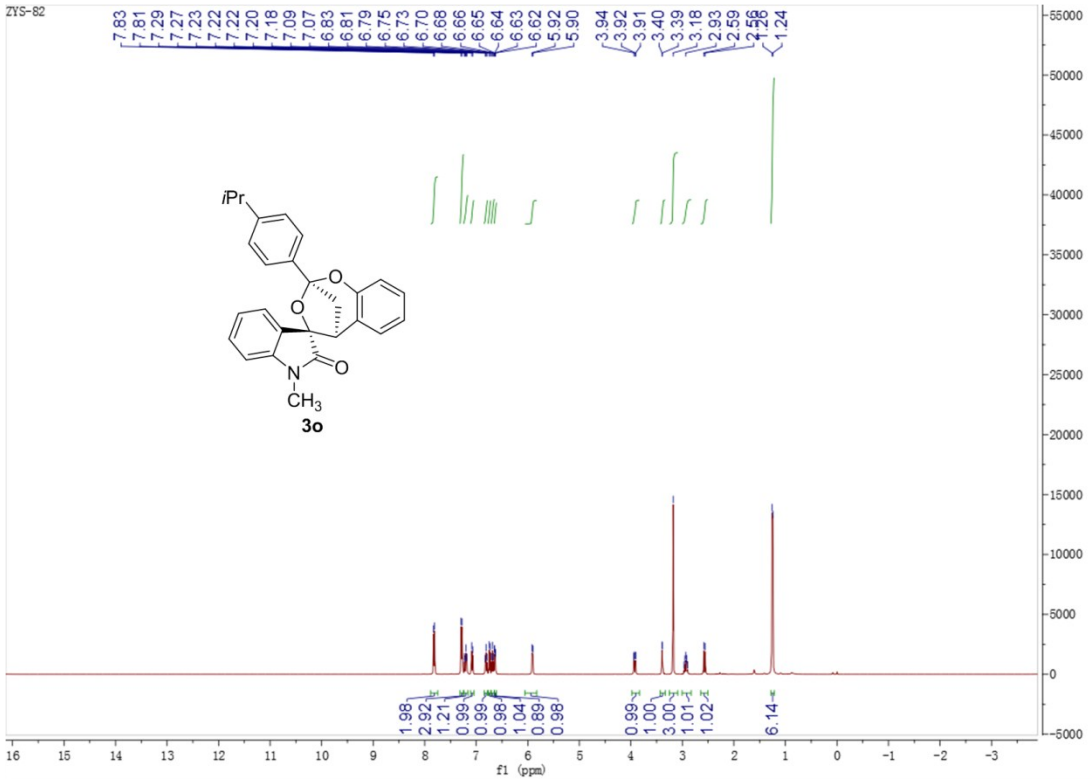
**3m**


ZYS-77
7.80
7.78
7.31
7.29
7.27
7.24
7.22
7.21
7.19
7.10
7.08
6.84
6.82
6.80
6.76
6.74
6.71
6.69
6.67
6.65
6.64
5.92
5.90
3.92
3.91
3.89
3.88
3.40
3.39
3.19
2.57
2.54
2.37
Me
O
O
N
O
CH3
1.99
1.03
3.07
0.94
0.96
0.95
1.01
0.95
0.99
1.00
1.01
3.00
1.02
2.98
f1 (ppm)

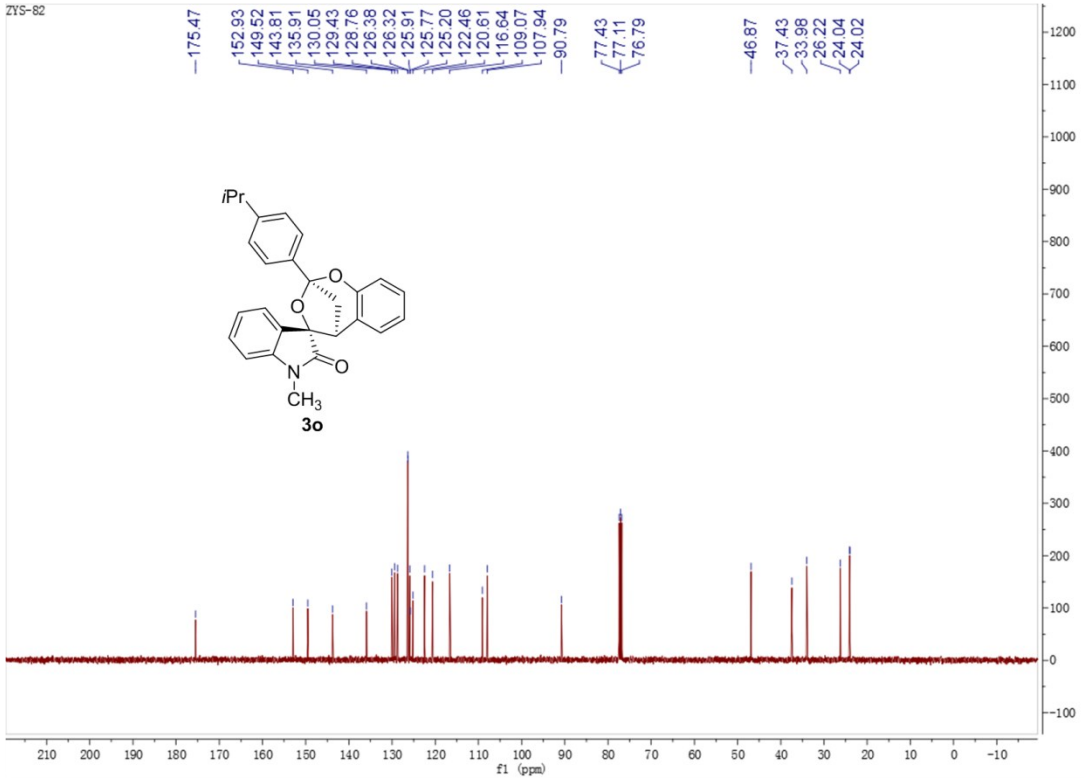
**3n**


ZYS-77
175.48
152.85
138.54
130.07
129.43
128.92
128.75
126.34
125.89
125.18
122.48
120.63
116.64
109.05
90.78
77.42
77.10
76.78
46.84
37.66
26.23
21.31
Me
O
O
N
O
CH3
f1 (ppm)

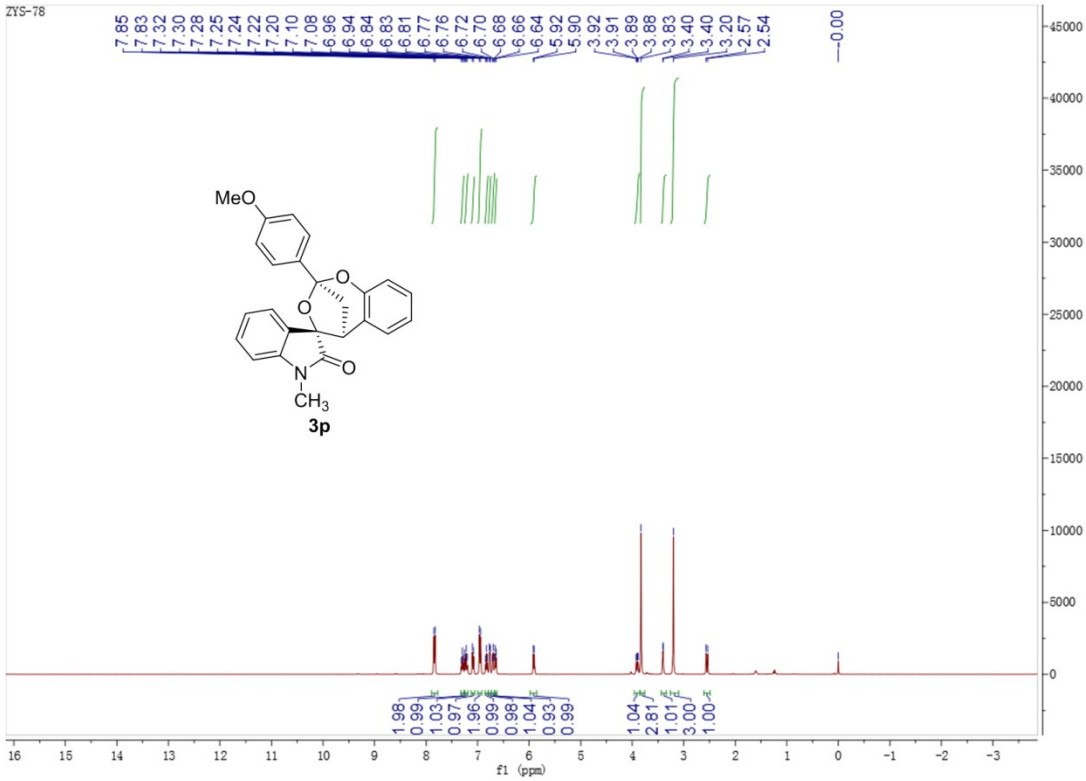
**3n**


ZYS-82
7.83
7.81
7.29
7.27
7.23
7.22
7.22
7.20
7.18
7.09
7.07
6.83
6.81
6.79
6.75
6.73
6.70
6.68
6.66
6.65
6.64
6.63
6.62
5.92
5.90
3.94
3.92
3.91
3.40
3.39
3.18
2.93
2.59
1.26
1.24
iPr
O
O
N
O
CH3
1.98
2.92
1.21
0.99
0.99
0.98
1.04
0.89
0.98
0.99
1.00
3.00
1.01
1.02
6.14
f1 (ppm)

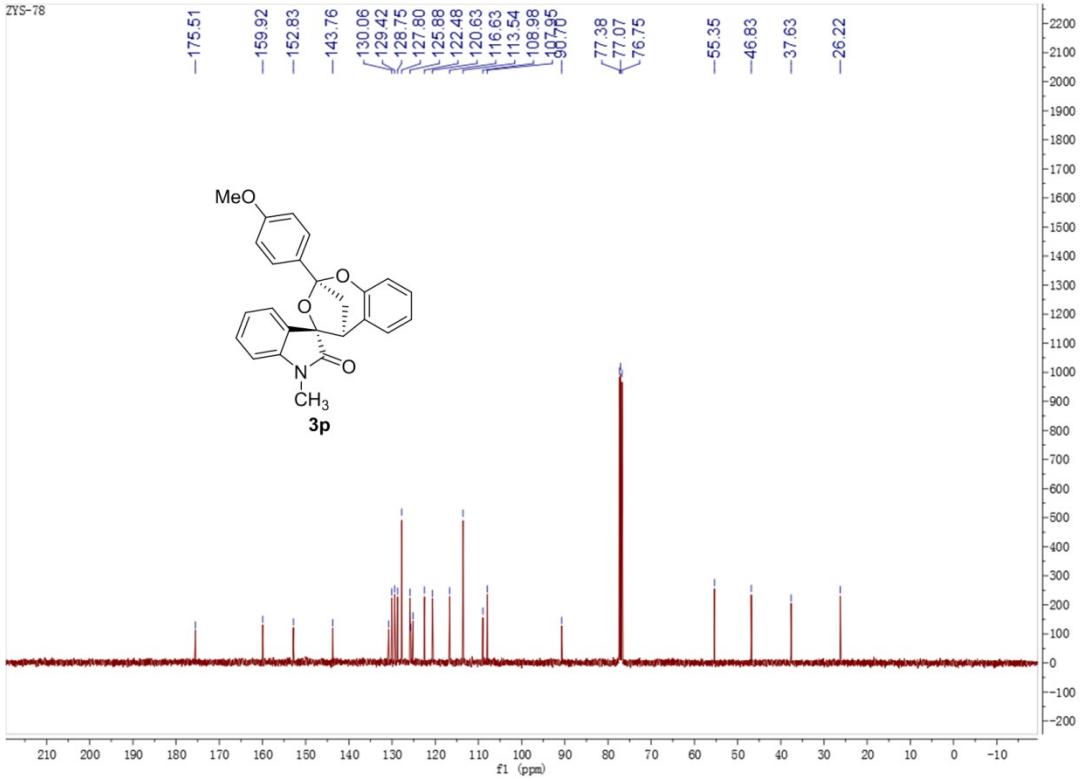
**3o**


ZYS-82
175.47
152.93
149.52
143.81
135.91
130.05
129.43
128.76
126.38
126.32
125.91
125.77
125.20
122.46
120.61
116.64
109.07
107.94
90.79
77.43
77.11
76.79
46.87
37.43
33.98
26.22
24.04
24.02
iPr
O
O
N
O
CH3
f1 (ppm)

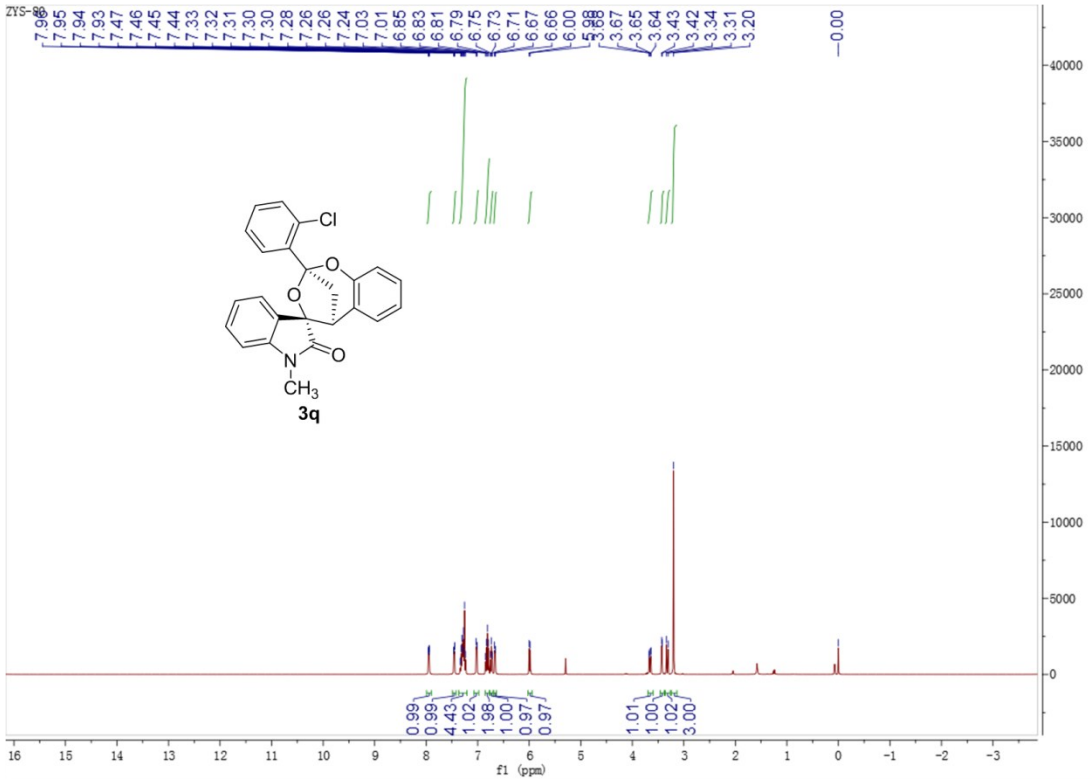
**3o**


ZYS-78
7.85
7.83
7.32
7.30
7.28
7.25
7.24
7.22
7.20
7.10
7.08
6.96
6.94
6.84
6.83
6.81
6.77
6.76
6.72
6.70
6.68
6.66
6.64
5.92
5.90
3.92
3.91
3.89
3.88
3.83
3.40
3.40
3.20
2.57
2.54
0.00
MeO
O
O
N
O
CH3
1.98
0.99
1.03
0.97
1.96
0.99
0.98
1.04
0.93
0.99
1.04
2.81
1.01
3.00
1.00
f1 (ppm)

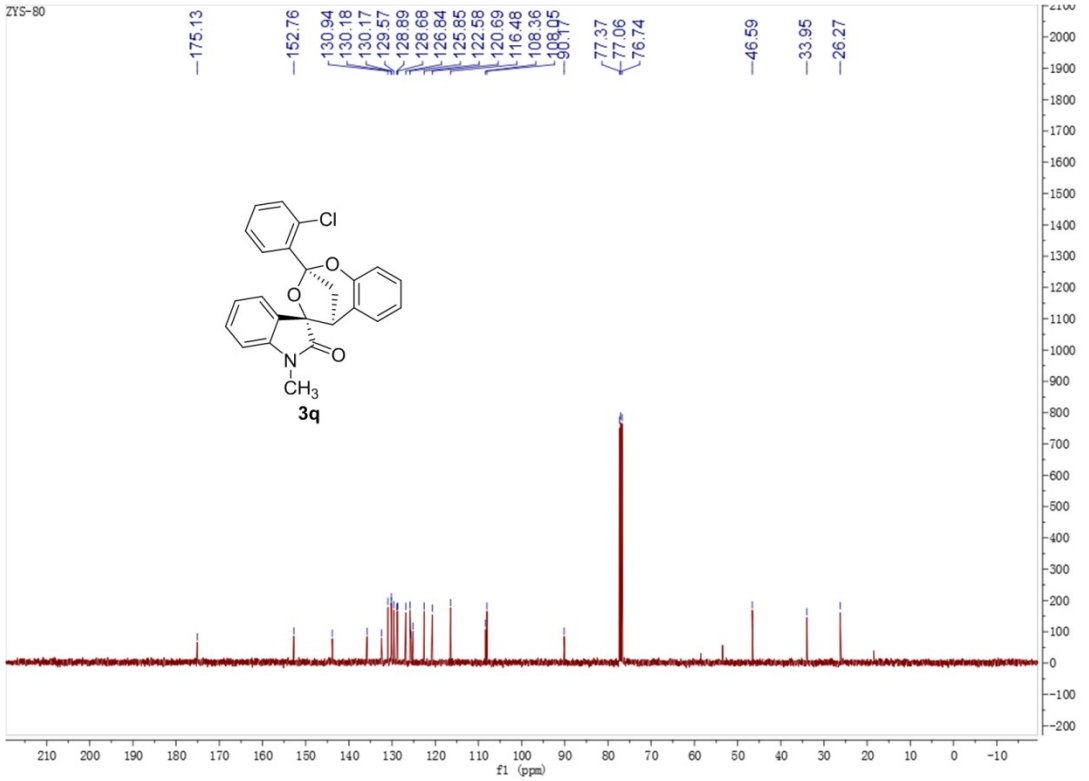
**3p**

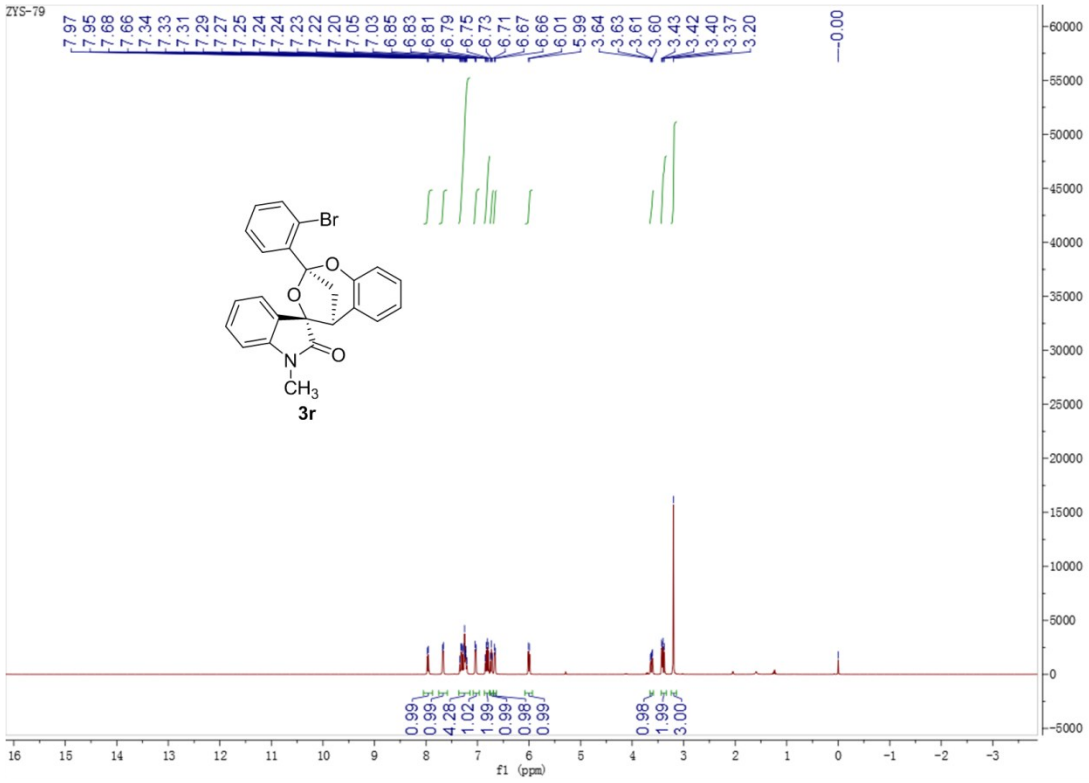

ZYS-78
175.51
159.92
152.83
143.76
130.06
129.42
128.75
127.80
125.88
122.48
120.63
116.63
113.54
108.98
90.70
77.38
77.07
76.75
55.35
46.83
37.63
26.22
MeO
O
O
N
O
CH3
f1 (ppm)

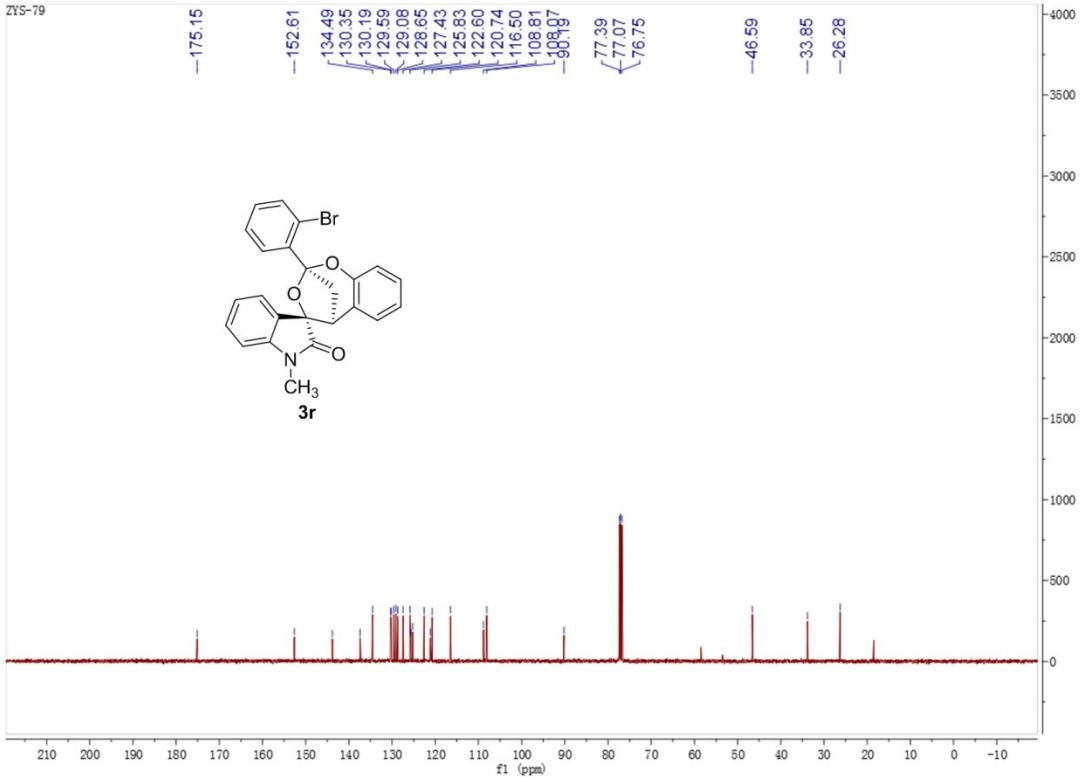
**3p**

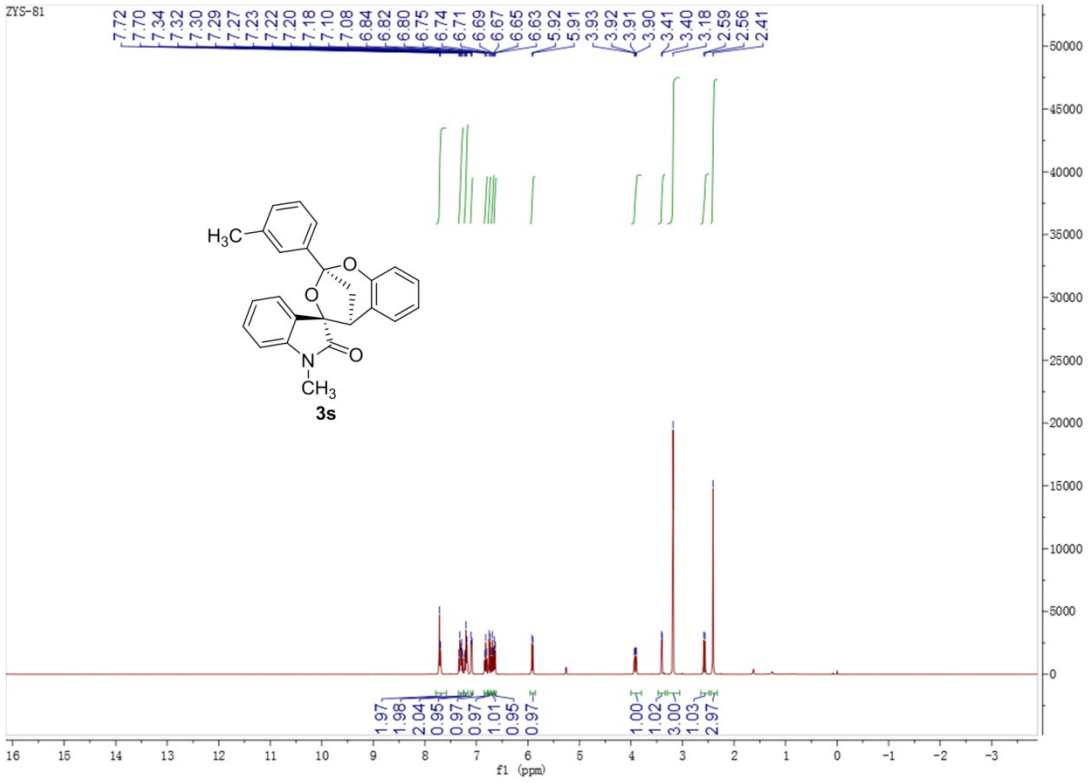

ZYS-80
7.96
7.95
7.94
7.93
7.47
7.46
7.45
7.44
7.33
7.32
7.31
7.30
7.30
7.28
7.26
7.26
7.24
7.03
7.01
6.85
6.83
6.81
6.79
6.75
6.73
6.71
6.67
6.66
6.00
3.67
3.65
3.64
3.43
3.42
3.34
3.31
3.20
0.00
Cl
O
O
N
O
CH3
0.99
0.99
4.43
1.02
1.98
1.00
0.97
0.97
1.01
1.00
1.02
3.00
f1 (ppm)

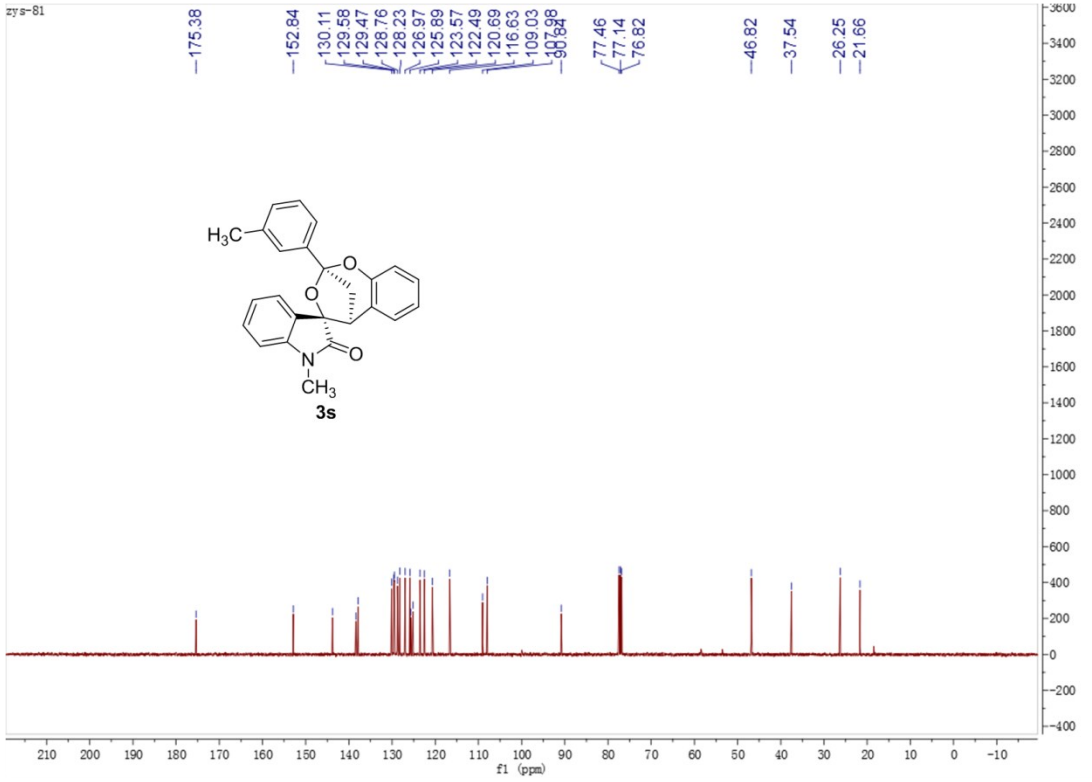
**3q**


ZYS-80
175.13
152.76
130.94
130.18
130.17
129.57
128.89
128.68
126.84
125.85
122.58
120.69
116.48
108.36
108.05
90.17
77.37
77.06
76.74
46.59
33.95
26.27
Cl
O
O
N
O
CH3
3q
f1 (ppm)

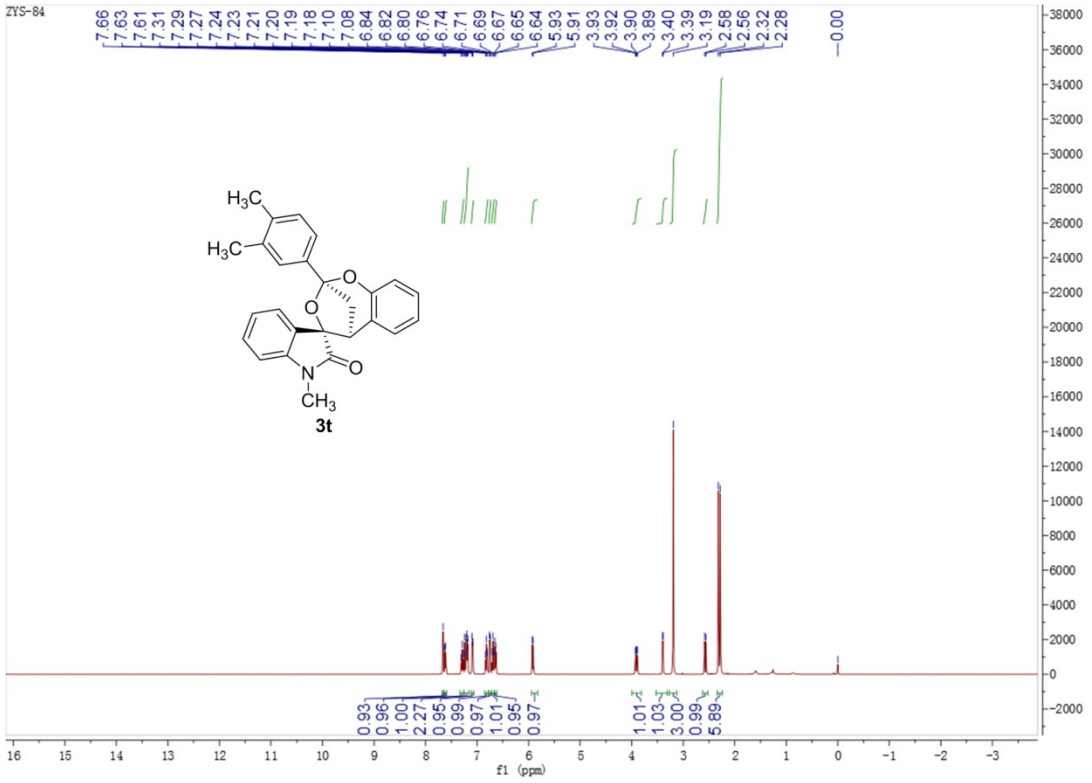

ZYS-79
7.97
7.95
7.68
7.66
7.34
7.33
7.31
7.29
7.27
7.25
7.24
7.24
7.23
7.22
7.20
7.05
7.03
6.85
6.83
6.81
6.79
6.75
6.73
6.71
6.67
6.66
6.01
5.99
3.64
3.63
3.61
3.60
3.43
3.42
3.40
3.37
3.20
0.00
Br
O
O
N
O
CH3
3r
0.99
0.99
4.28
1.02
1.99
0.99
0.98
0.99
0.98
1.99
3.00
f1 (ppm)


ZYS-79
175.15
152.61
134.49
130.35
130.19
129.59
129.08
128.65
127.43
125.83
122.60
120.74
116.50
108.81
108.07
90.19
77.39
77.07
76.75
46.59
33.85
26.28
Br
O
O
N
O
CH3
3r
f1 (ppm)

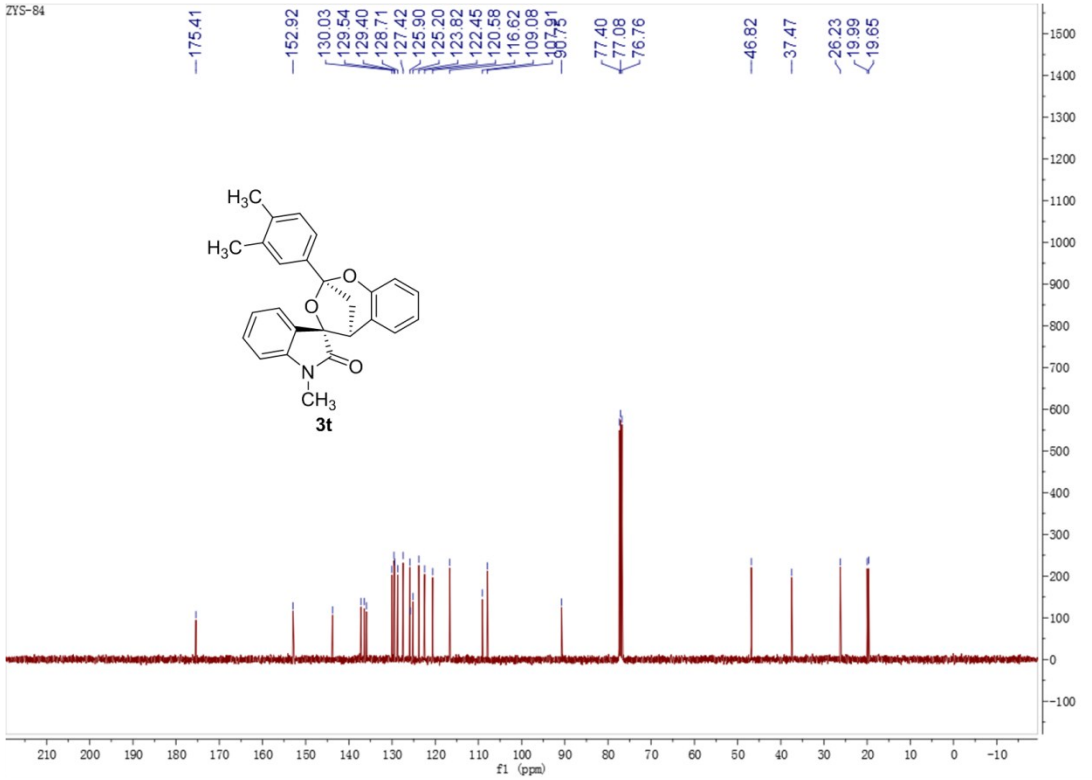

ZYS-81
7.72
7.70
7.34
7.32
7.30
7.29
7.27
7.23
7.22
7.20
7.18
7.10
7.08
6.84
6.82
6.80
6.75
6.74
6.71
6.69
6.67
6.65
6.63
5.92
5.91
3.93
3.92
3.91
3.90
3.41
3.40
3.18
2.59
2.56
2.41
H3C
O
O
N
O
CH3
3s
1.97
1.98
2.04
0.95
0.97
0.97
1.01
0.95
0.97
1.00
1.02
3.00
1.03
2.97
f1 (ppm)


zys-81
175.38
152.84
130.11
129.58
129.47
128.76
128.23
126.97
125.89
123.57
122.49
120.69
116.63
109.03
90.84
77.46
77.14
76.82
46.82
37.54
26.25
21.66
f1 (ppm)

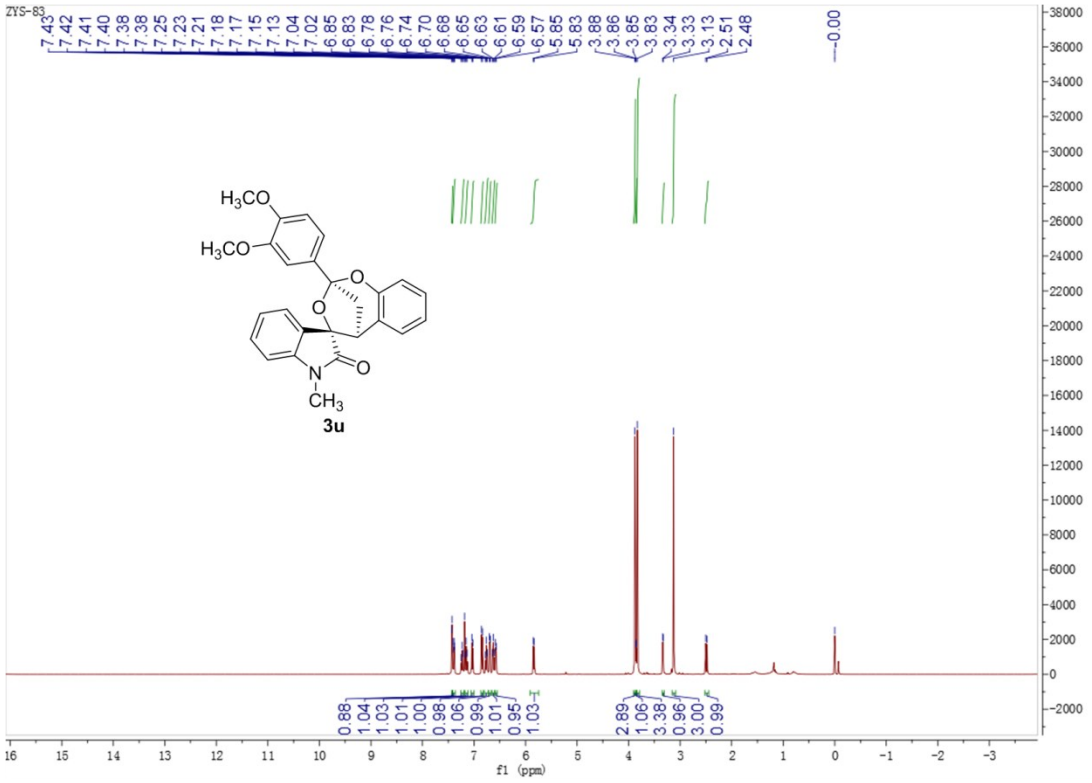
**3s**


ZYS-84
7.66
7.63
7.61
7.31
7.29
7.27
7.24
7.23
7.21
7.20
7.19
7.18
7.10
7.08
6.84
6.82
6.80
6.76
6.74
6.71
6.69
6.67
6.65
6.64
5.93
5.91
3.93
3.92
3.90
3.89
3.40
3.39
3.19
2.58
2.56
2.32
2.28
0.00
0.93
0.96
1.00
2.27
0.95
0.99
0.97
1.01
0.95
0.97
1.01
1.03
3.00
0.99
5.89
f1 (ppm)

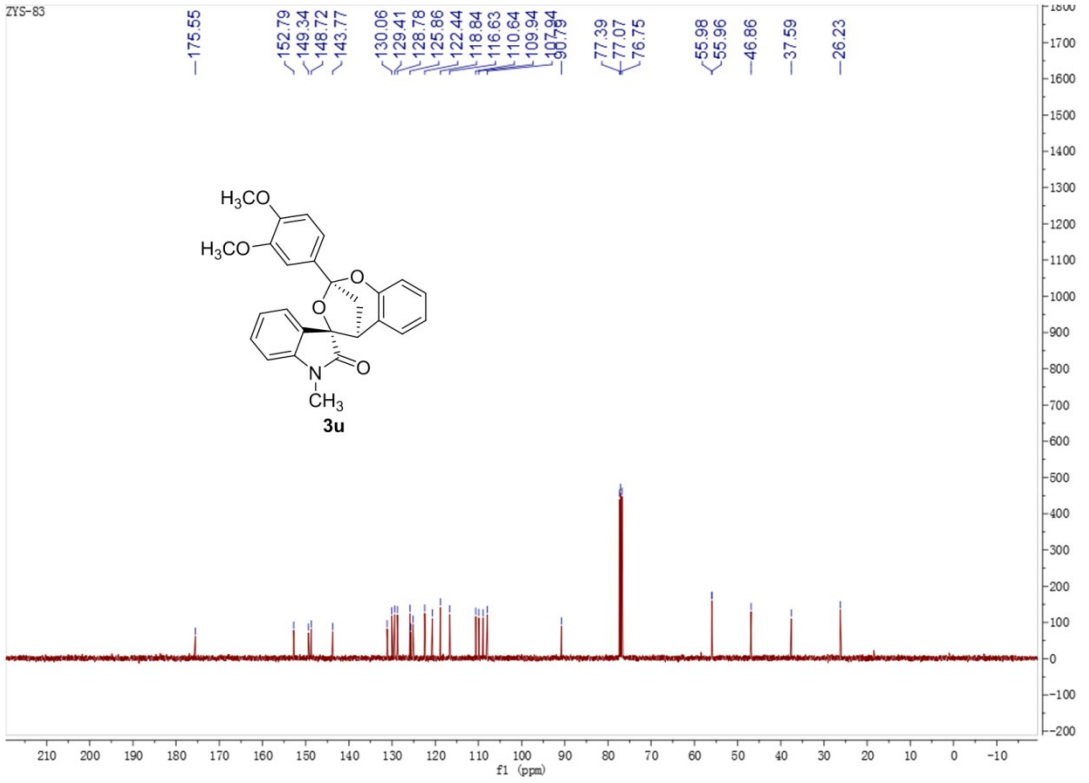
**3t**

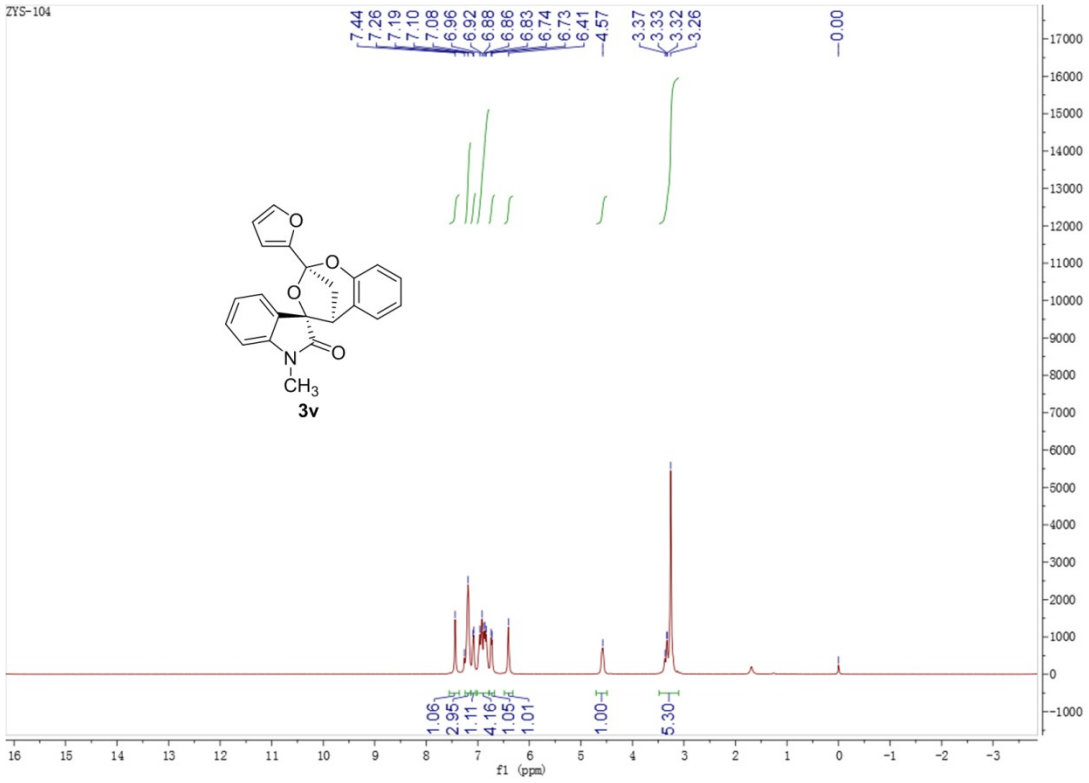

ZYS-84
175.41
152.92
130.03
129.54
129.40
128.71
127.42
125.90
125.20
123.82
122.45
120.58
116.62
109.08
77.40
77.08
76.76
46.82
37.47
26.23
19.99
19.65
f1 (ppm)

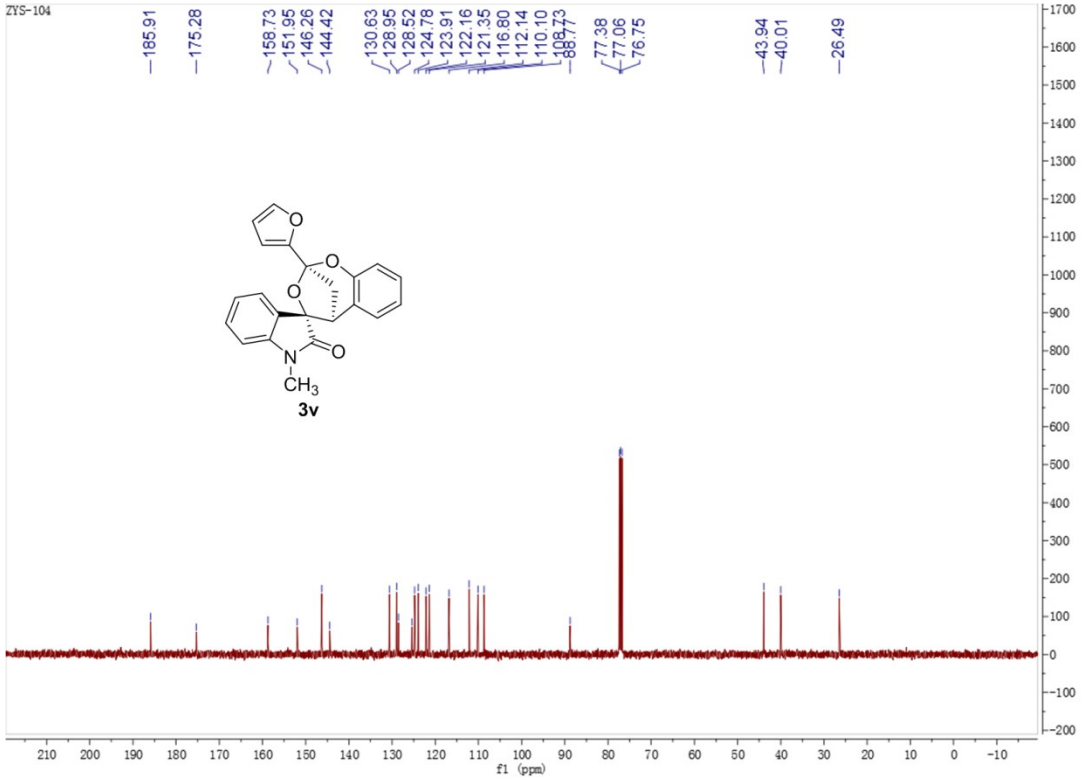
**3t**


ZYS-83
7.43
7.42
7.41
7.40
7.38
7.38
7.25
7.23
7.21
7.18
7.17
7.15
7.13
7.04
7.02
6.85
6.83
6.78
6.76
6.74
6.70
6.68
6.65
6.63
6.61
6.59
6.57
5.85
5.83
3.88
3.86
3.85
3.83
3.34
3.33
3.13
2.51
2.48
0.00
0.88
1.04
1.03
1.01
1.00
0.98
1.06
0.99
1.01
0.95
1.03
2.89
1.06
3.38
0.96
3.00
0.99
f1 (ppm)

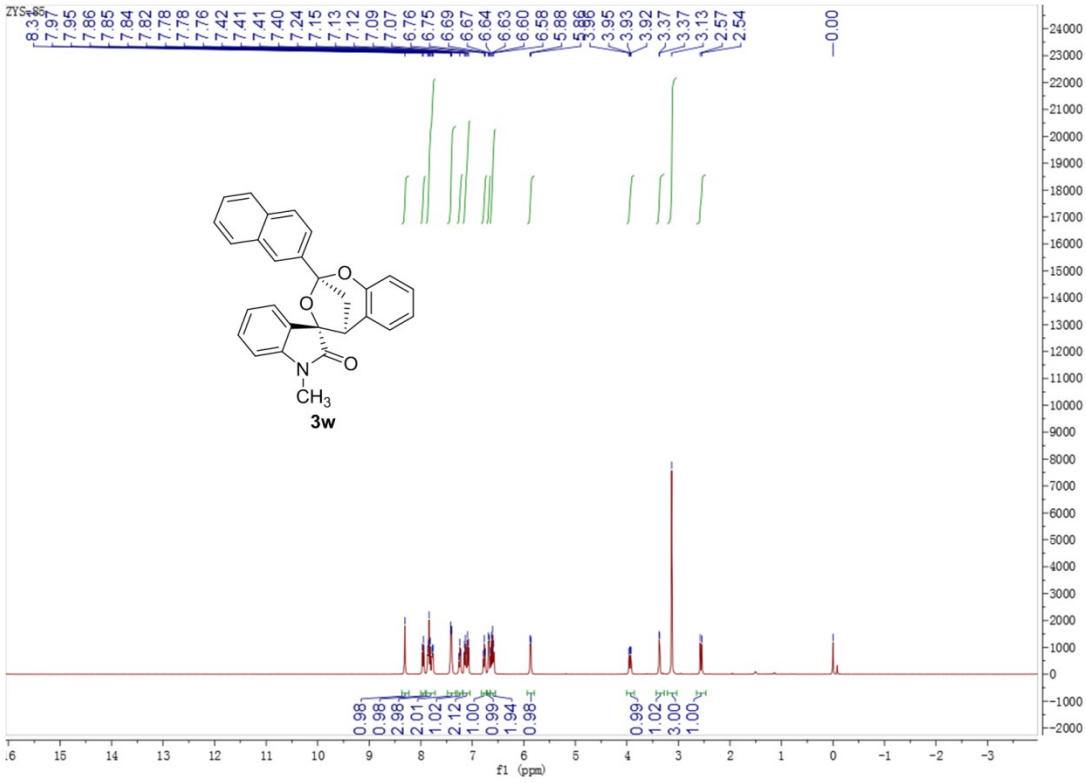
**3u**


ZYS-83
175.55
152.79
149.34
148.72
143.77
130.06
129.41
128.78
125.86
122.44
118.84
116.63
110.64
109.94
90.79
77.39
77.07
76.75
55.98
55.96
46.86
37.59
26.23
H3CO
H3CO
O
O
N
CH3
O
3u
f1 (ppm)

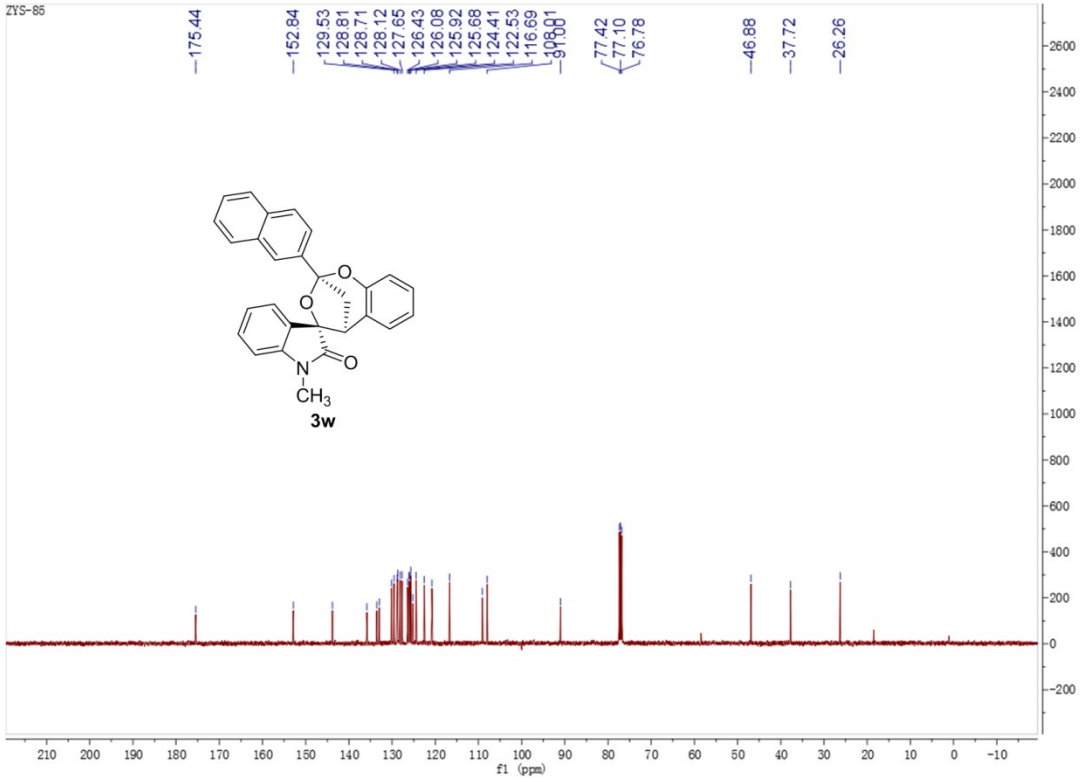

ZYS-104
7.44
7.26
7.19
7.10
7.08
6.96
6.92
6.88
6.86
6.83
6.74
6.73
6.41
4.57
3.37
3.33
3.32
3.26
0.00
O
O
O
N
CH3
O
3v
1.06
2.95
1.11
4.16
1.05
1.01
1.00
5.30
f1 (ppm)


ZYS-104
185.91
175.28
158.73
151.95
146.26
144.42
130.63
128.95
128.52
124.78
123.91
122.16
121.35
116.80
112.14
110.10
108.73
88.77
77.38
77.06
76.75
43.94
40.01
26.49
f1 (ppm)

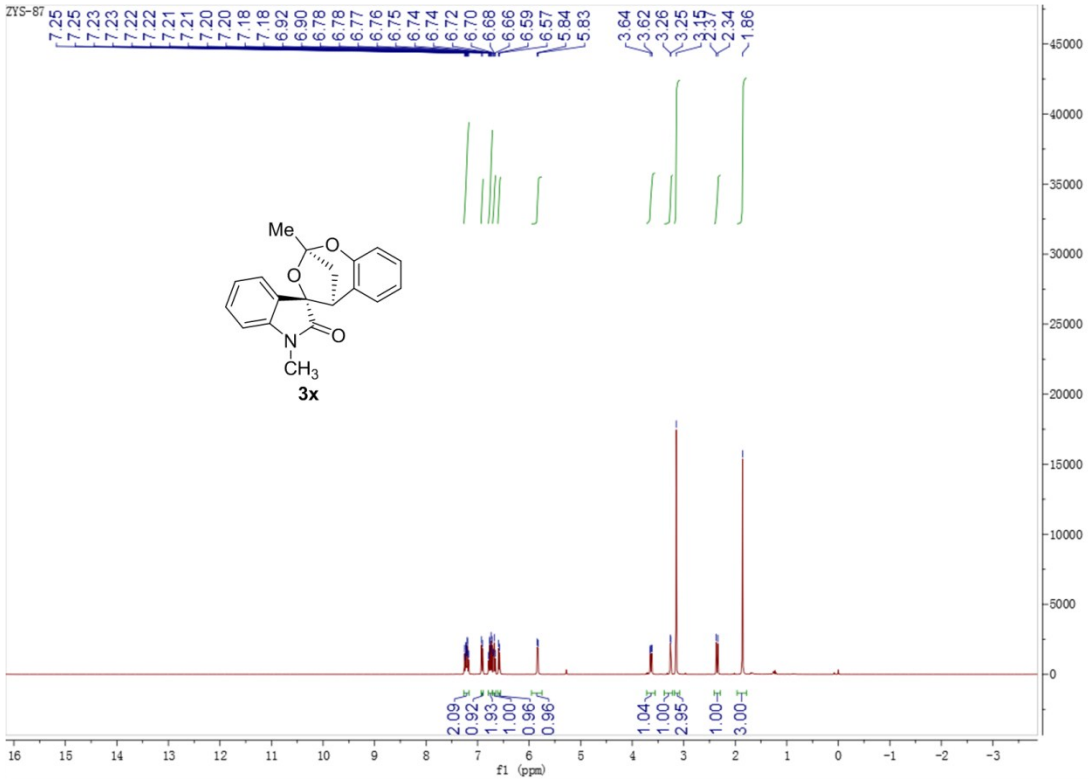
**3v**


ZYS-85
8.31
7.97
7.95
7.86
7.85
7.84
7.82
7.78
7.78
7.76
7.42
7.41
7.41
7.40
7.24
7.15
7.13
7.12
7.09
7.07
6.76
6.75
6.69
6.67
6.64
6.63
6.60
6.58
5.88
3.95
3.93
3.92
3.37
3.37
3.13
2.57
2.54
0.00
0.98
0.98
2.98
2.01
1.02
2.12
1.00
0.99
1.94
0.98
0.99
1.02
3.00
1.00
f1 (ppm)

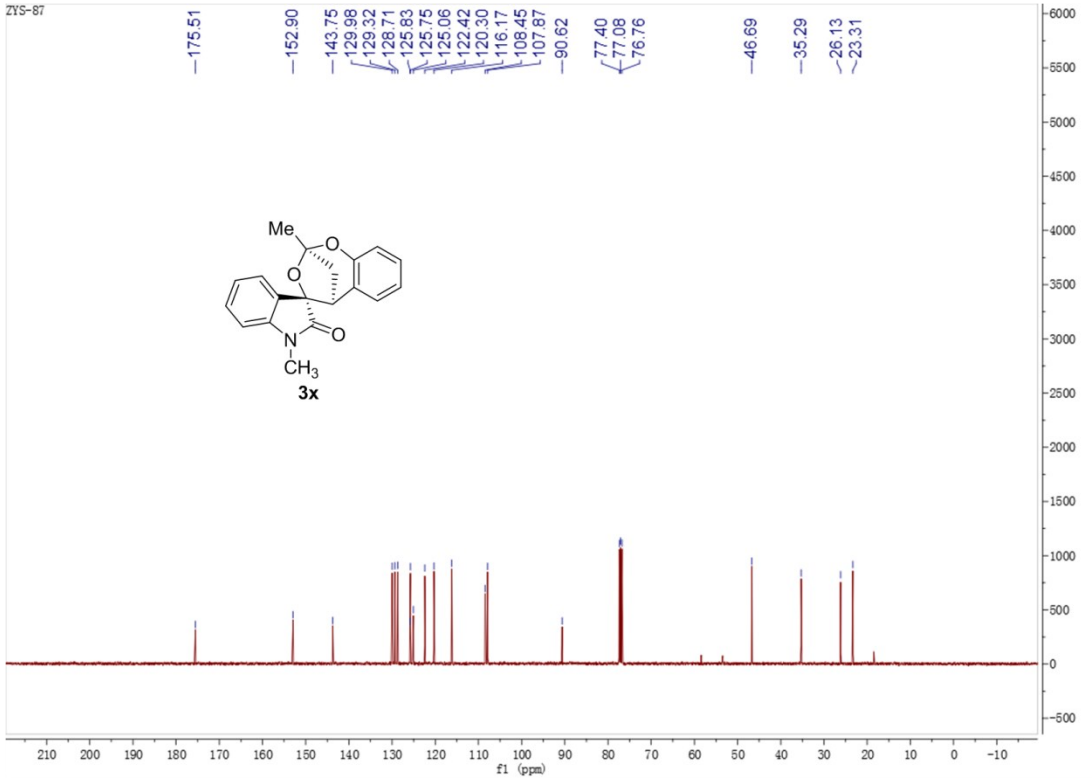
**3w**


ZYS-85
175.44
152.84
129.53
128.81
128.71
128.12
127.65
126.43
126.08
125.92
125.68
124.41
122.53
116.69
91.00
77.42
77.10
76.78
46.88
37.72
26.26
f1 (ppm)

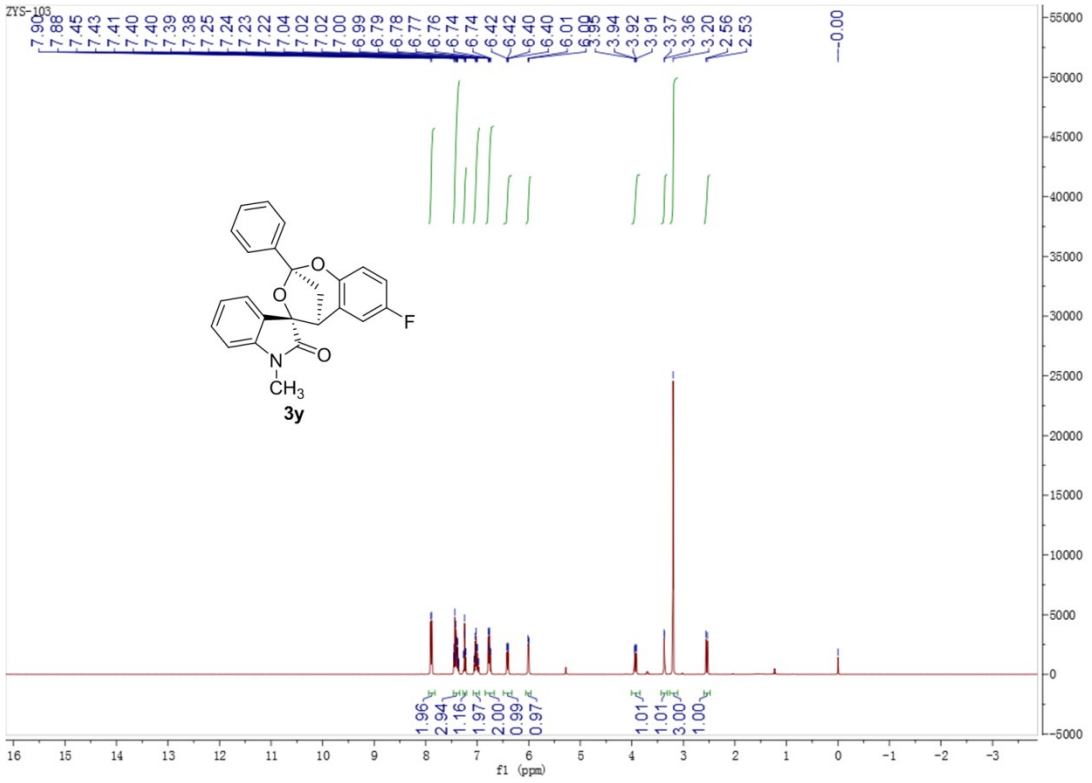
**3w**


ZYS-87
7.25
7.23
7.22
7.21
7.20
7.18
6.92
6.90
6.78
6.77
6.76
6.75
6.74
6.72
6.70
6.68
6.66
6.59
6.57
5.84
5.83
3.64
3.62
3.26
3.25
2.37
2.34
1.86
2.09
0.92
1.93
1.00
0.96
0.96
1.04
1.00
2.95
1.00
3.00
f1 (ppm)

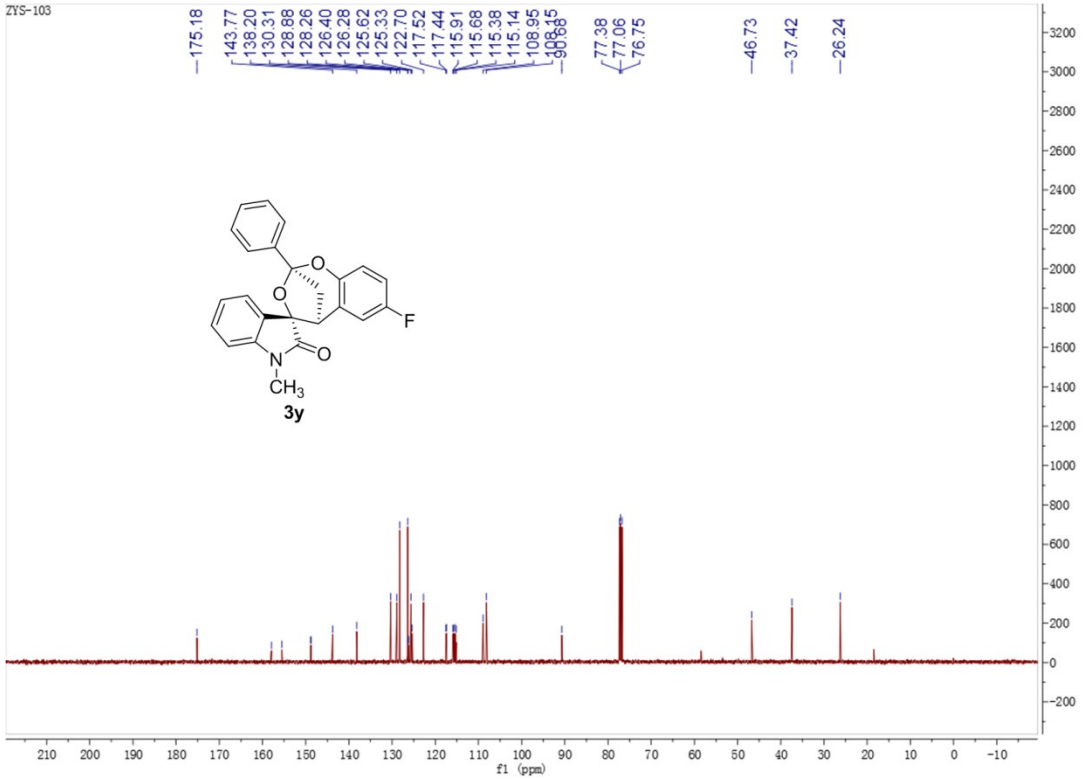
**3x**


ZYS-87
175.51
152.90
143.75
129.98
129.32
128.71
125.83
125.75
125.06
122.42
120.30
116.17
108.45
107.87
90.62
77.40
77.08
76.76
46.69
35.29
26.13
23.31
Me
O
O
N
O
CH3
f1 (ppm)

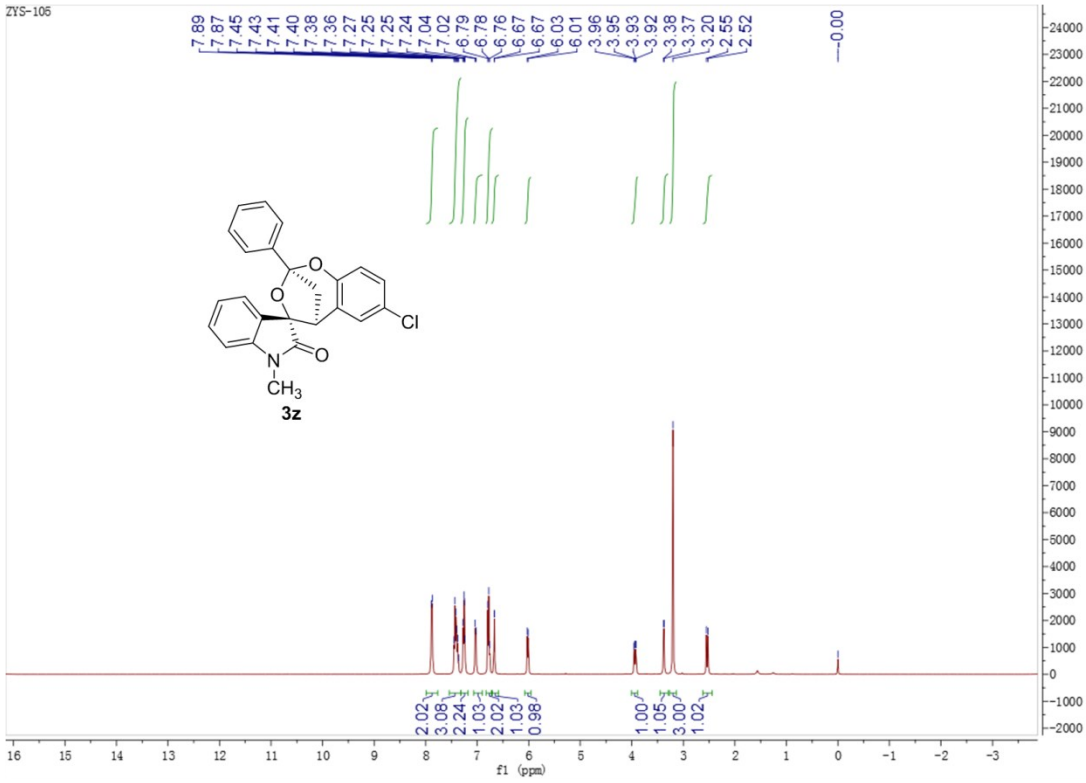
**3x**


ZYS-103
7.90
7.88
7.45
7.43
7.41
7.40
7.40
7.39
7.38
7.25
7.24
7.23
7.22
7.04
7.02
7.02
7.00
6.99
6.79
6.78
6.77
6.76
6.74
6.74
6.42
6.42
6.40
6.40
6.01
3.94
3.92
3.91
3.37
3.36
3.20
2.56
2.53
0.00
O
O
F
N
O
CH3
1.96
2.94
1.16
1.97
2.00
0.99
0.97
1.01
1.01
3.00
1.00
f1 (ppm)

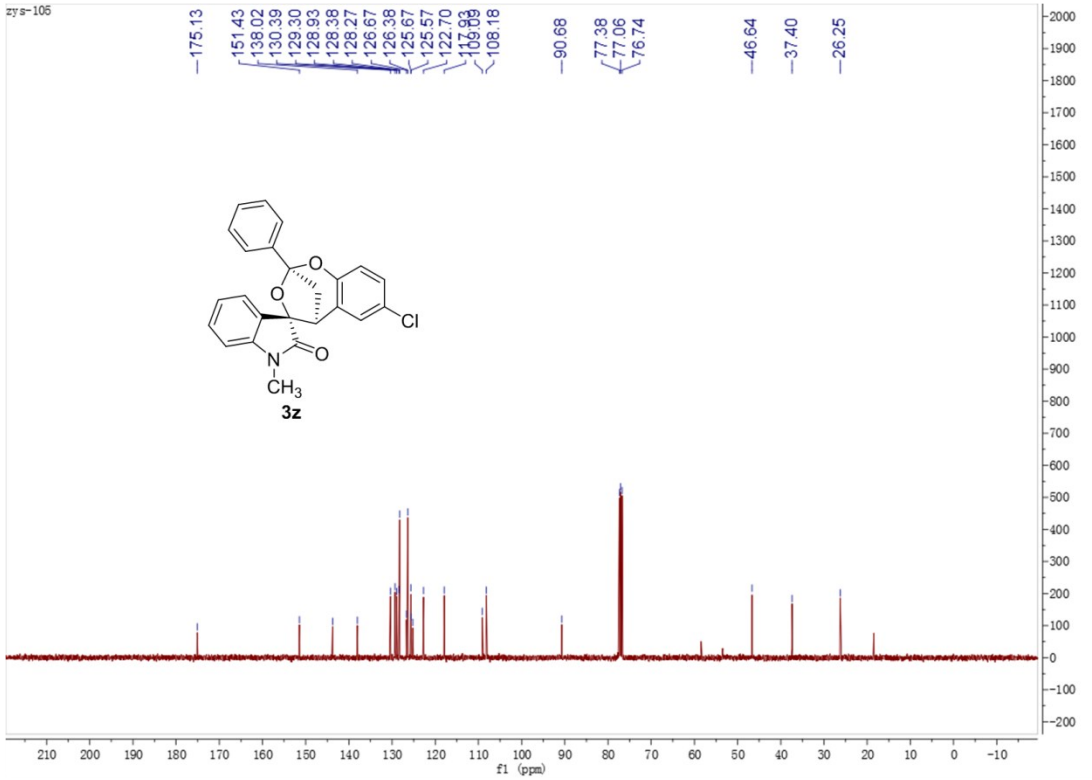
**3y**


ZYS-103
175.18
143.77
138.20
130.31
128.88
128.26
126.40
126.28
125.62
125.33
122.70
117.52
117.44
115.91
115.68
115.38
115.14
108.95
108.45
90.68
77.38
77.06
76.75
46.73
37.42
26.24
F
O
O
N
O
CH3
f1 (ppm)

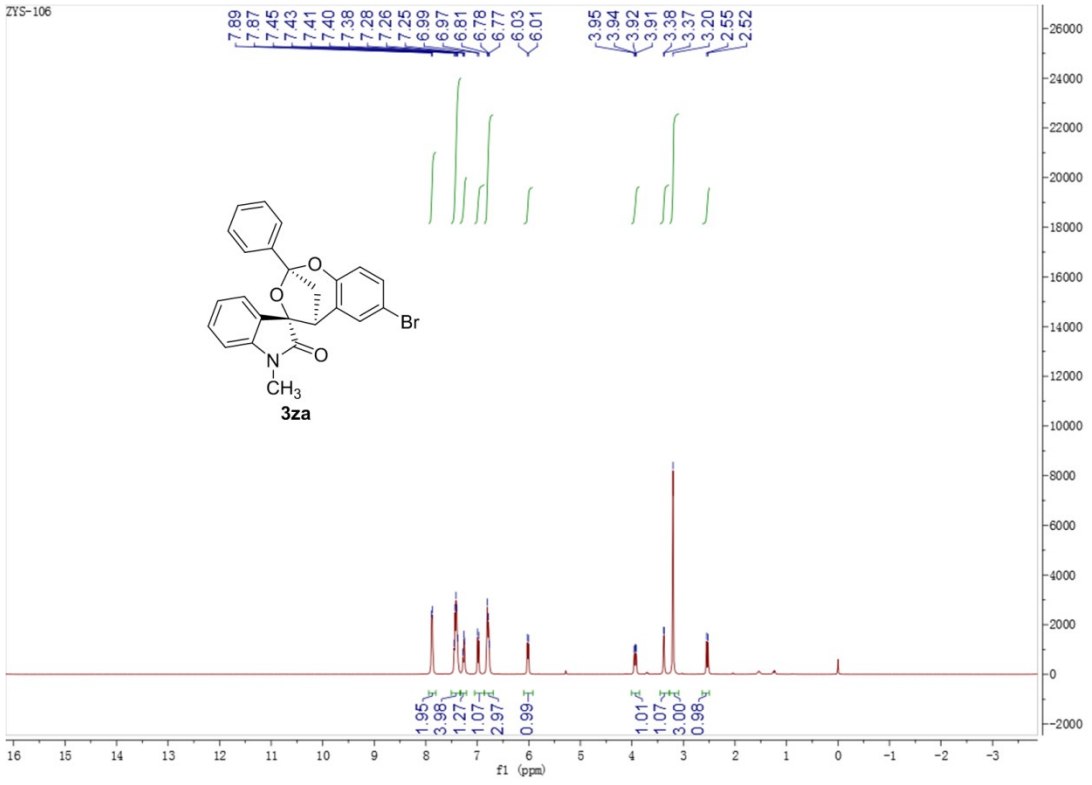
**3y**


ZYS-106
7.89
7.87
7.45
7.43
7.41
7.40
7.38
7.36
7.27
7.25
7.25
7.24
7.04
7.02
6.79
6.78
6.76
6.67
6.67
6.03
6.01
3.96
3.95
3.93
3.92
3.38
3.37
3.20
2.55
2.52
0.00
2.02
3.08
2.24
1.03
2.02
1.03
0.98
1.00
1.05
3.00
1.02
Cl
O
O
N
O
CH3
f1 (ppm)

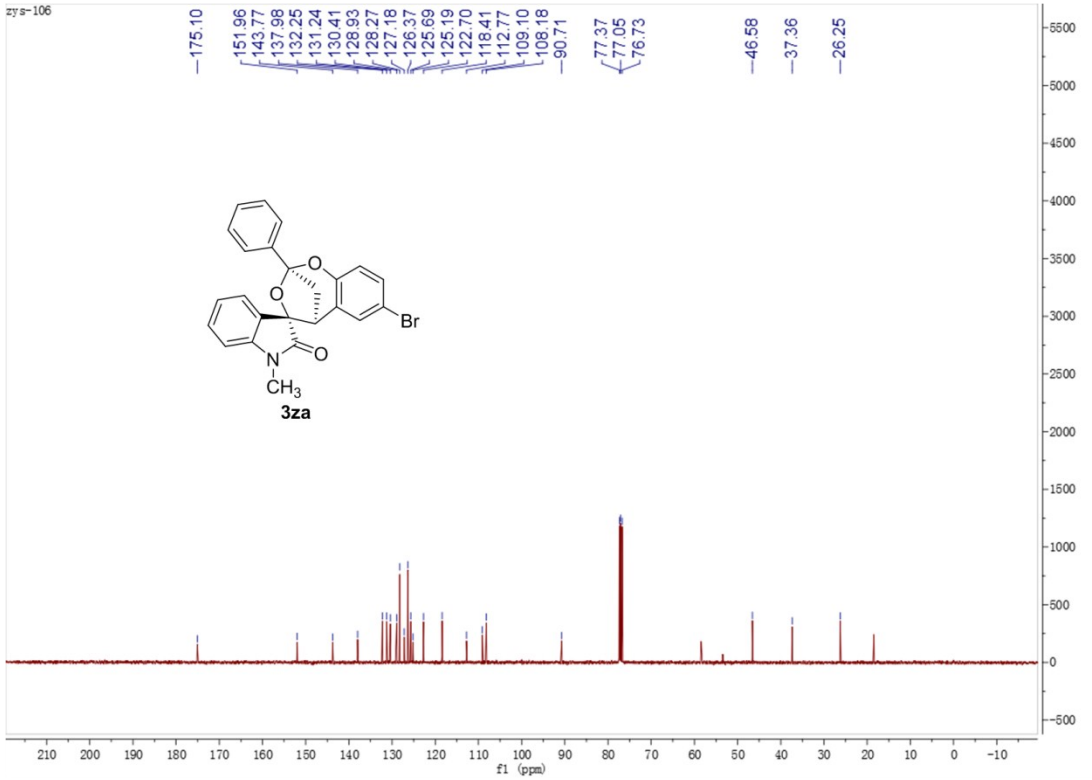
**3z**

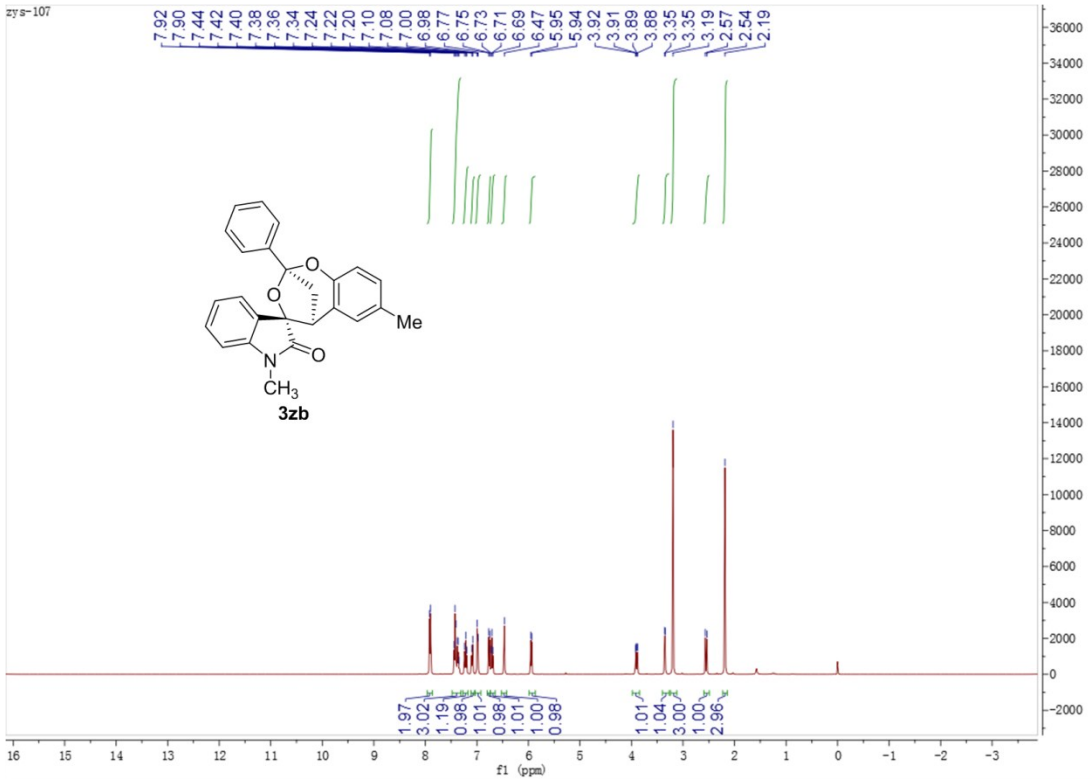

zys-105
175.13
151.43
138.02
130.39
129.30
128.93
128.38
128.27
126.67
126.38
125.67
125.57
122.70
90.68
77.38
77.06
76.74
46.64
37.40
26.25
Cl
O
O
N
O
CH3
f1 (ppm)

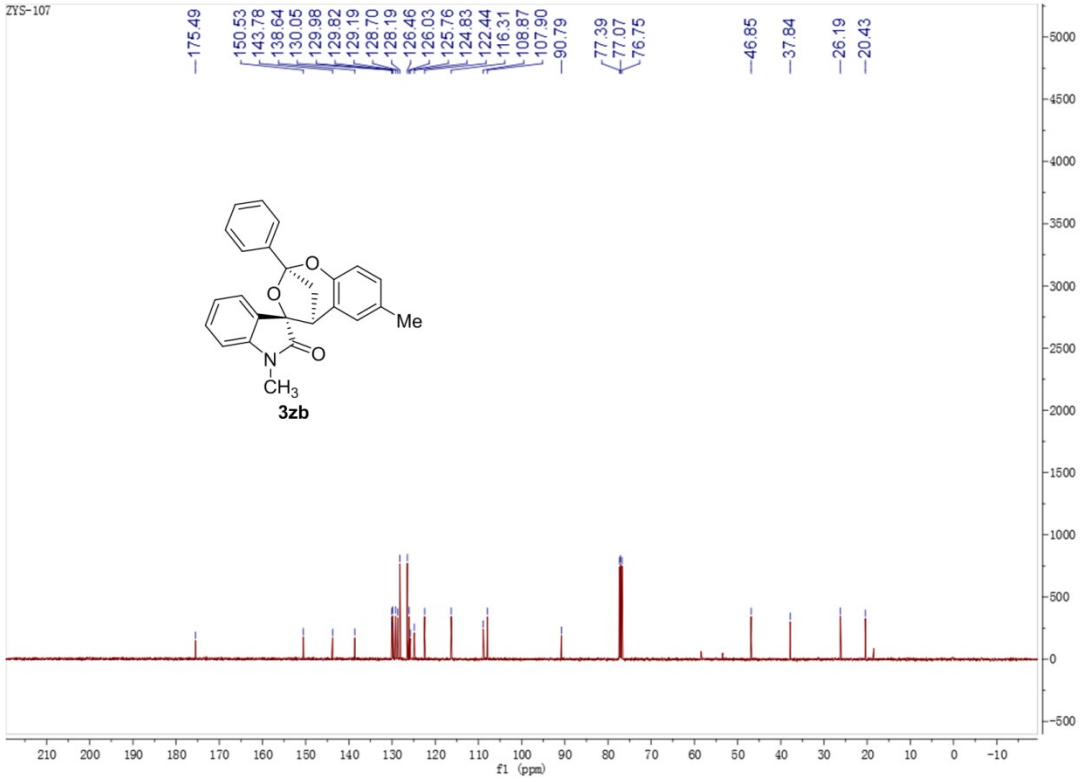
**3z**

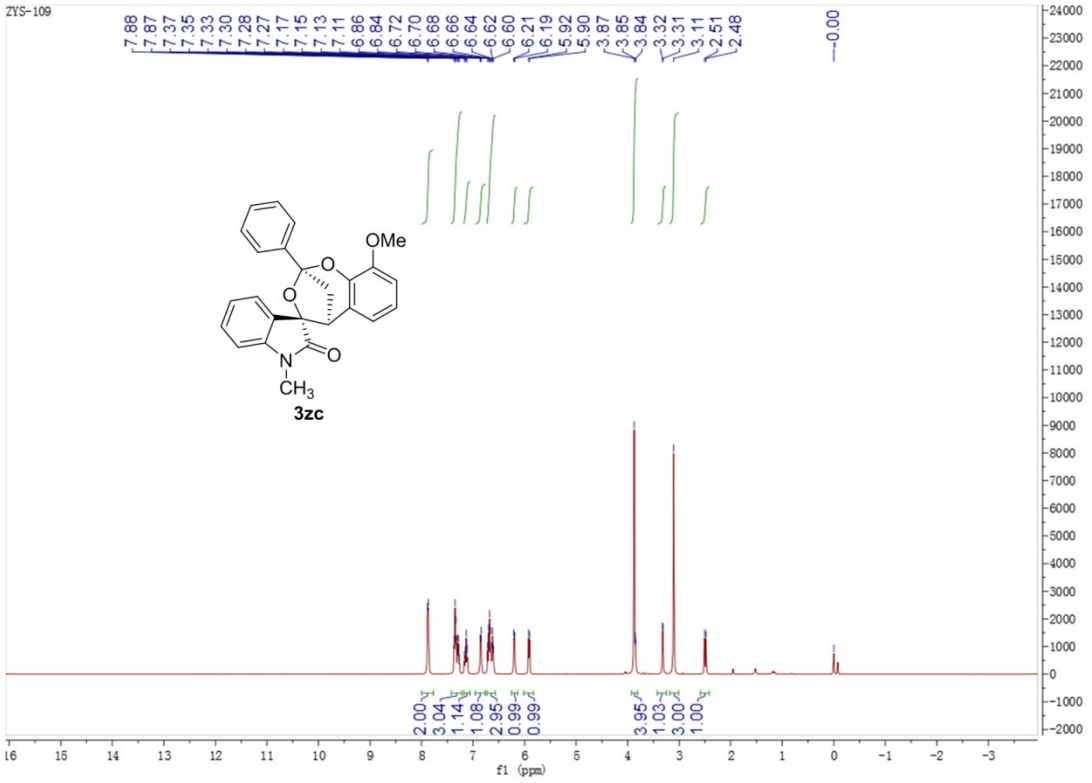

ZYS-106
7.89
7.87
7.45
7.43
7.41
7.40
7.38
7.28
7.26
7.25
6.99
6.97
6.81
6.78
6.77
6.03
6.01
3.95
3.94
3.92
3.91
3.38
3.37
3.20
2.55
2.52
Br
O
O
N
O
CH3
1.95
3.98
1.27
1.07
2.97
0.99
1.01
1.07
3.00
0.98
f1 (ppm)

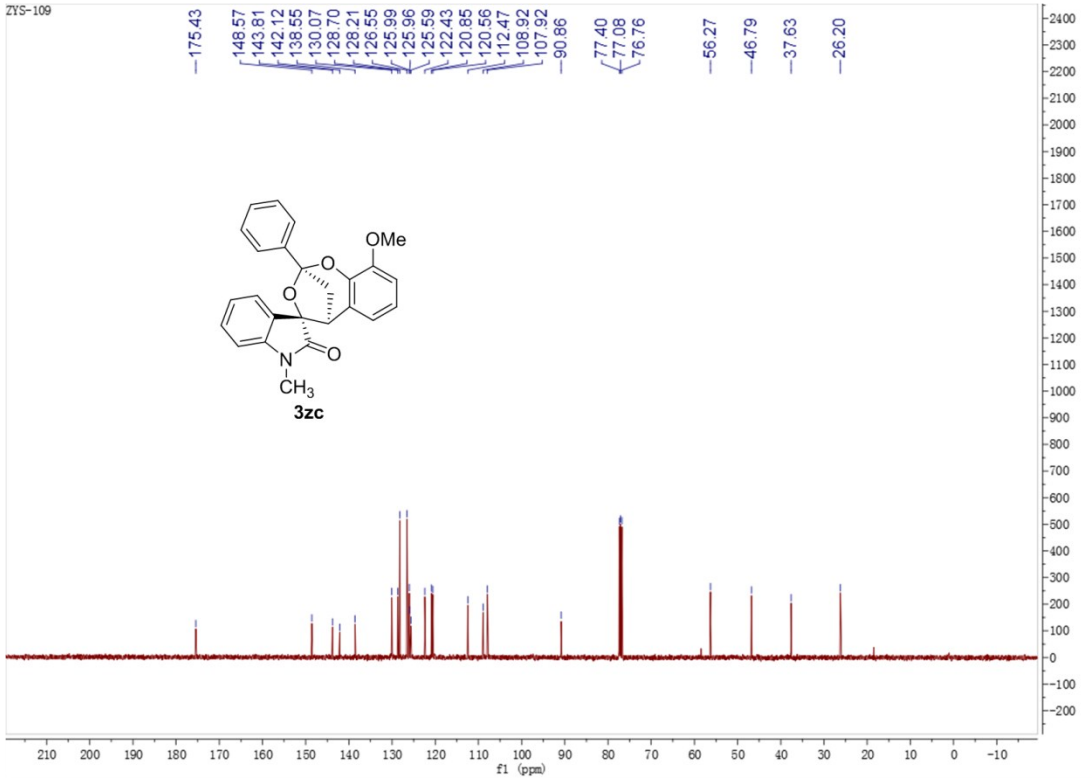
**3za**

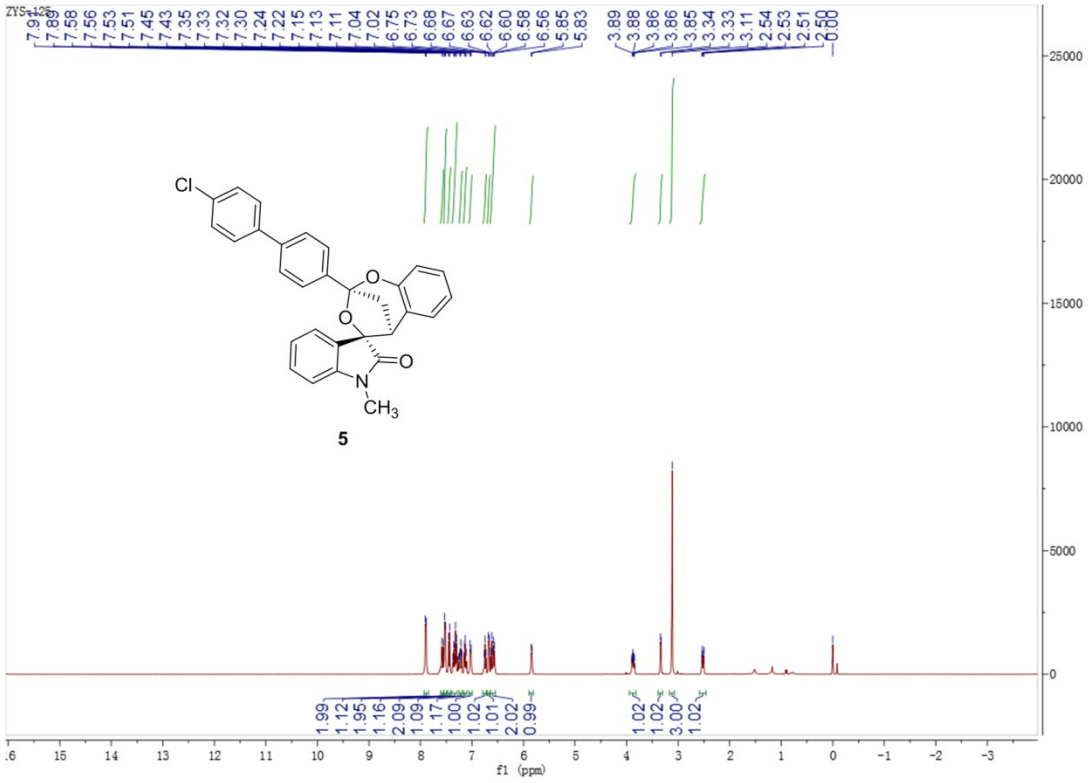

zys-106
175.10
151.96
143.77
137.98
132.25
131.24
130.41
128.93
128.27
127.18
126.37
125.69
125.19
122.70
118.41
112.77
109.10
108.18
90.71
77.37
77.05
76.73
46.58
37.36
26.25
Br
O
O
N
O
CH3
3za
f1 (ppm)

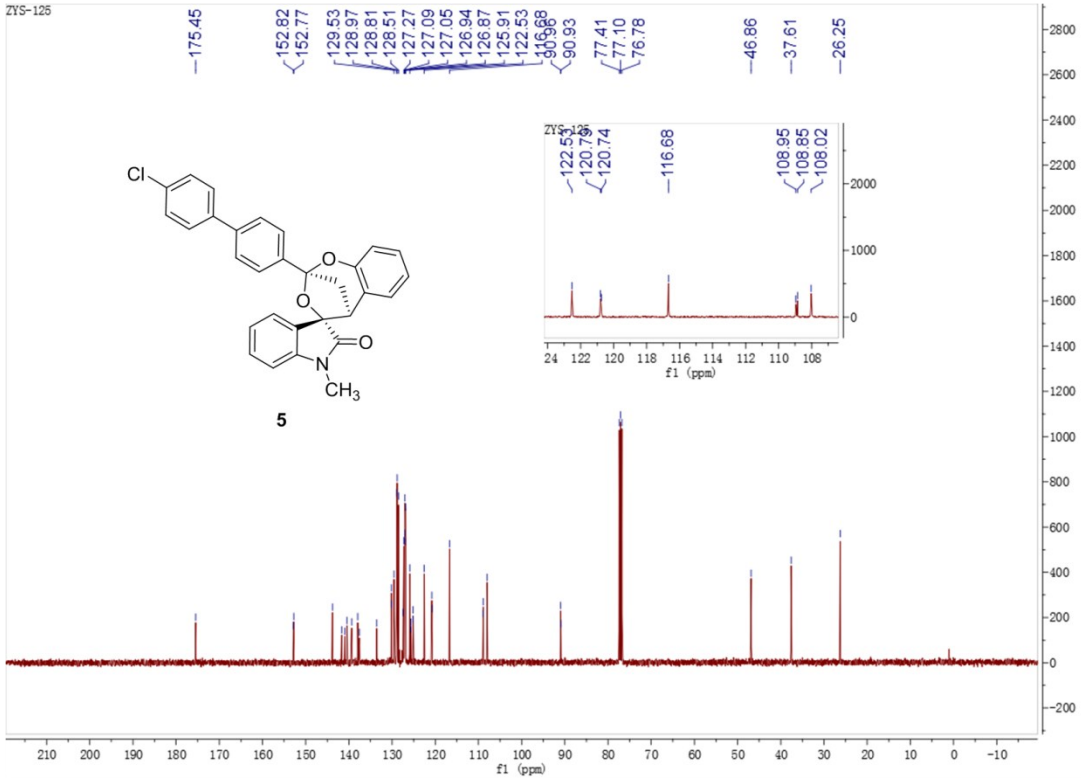

zys-107
7.92
7.90
7.44
7.42
7.40
7.38
7.36
7.34
7.24
7.22
7.20
7.10
7.08
7.00
6.98
6.77
6.75
6.73
6.71
6.69
6.47
5.95
5.94
3.92
3.91
3.89
3.88
3.35
3.35
3.19
2.57
2.54
2.19
Me
O
O
N
O
CH3
3zb
1.97
3.02
1.19
0.98
1.01
0.98
1.01
1.00
0.98
1.01
1.04
3.00
1.00
2.96
f1 (ppm)

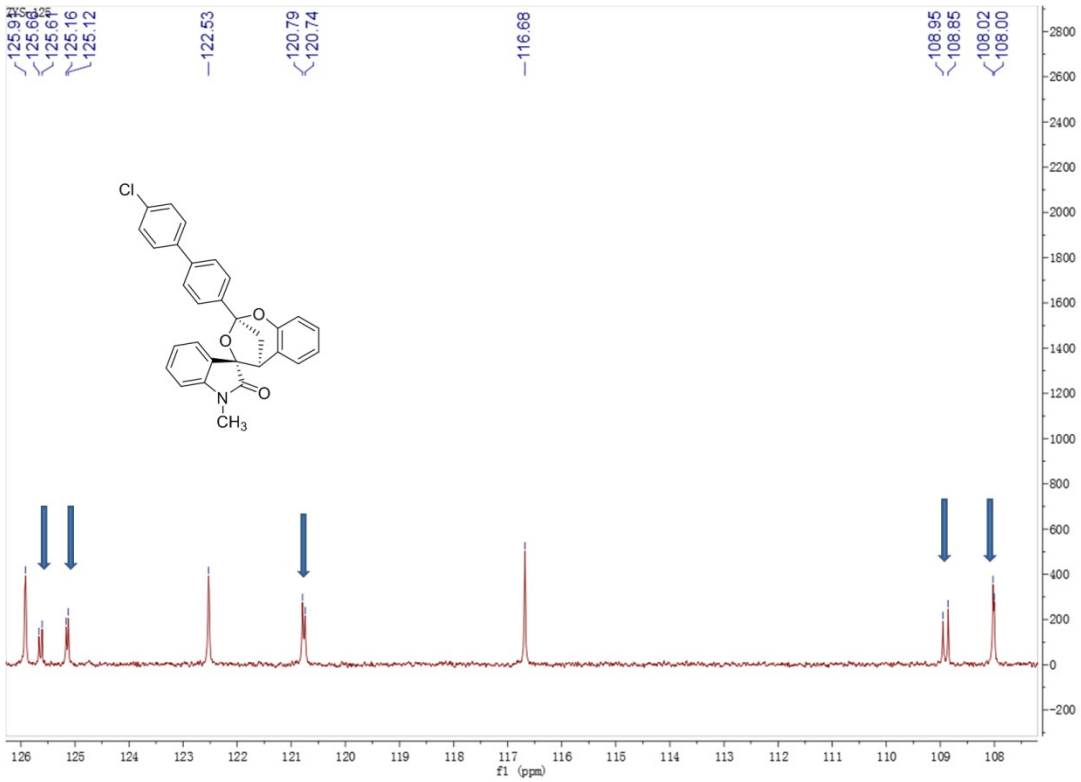

ZYS-107
175.49
150.53
143.78
138.64
130.05
129.98
129.82
129.19
128.70
128.19
126.46
126.03
125.76
124.83
122.44
116.31
108.87
107.90
90.79
77.39
77.07
76.75
46.85
37.84
26.19
20.43
Me
O
O
N
O
CH3
3zb
f1 (ppm)

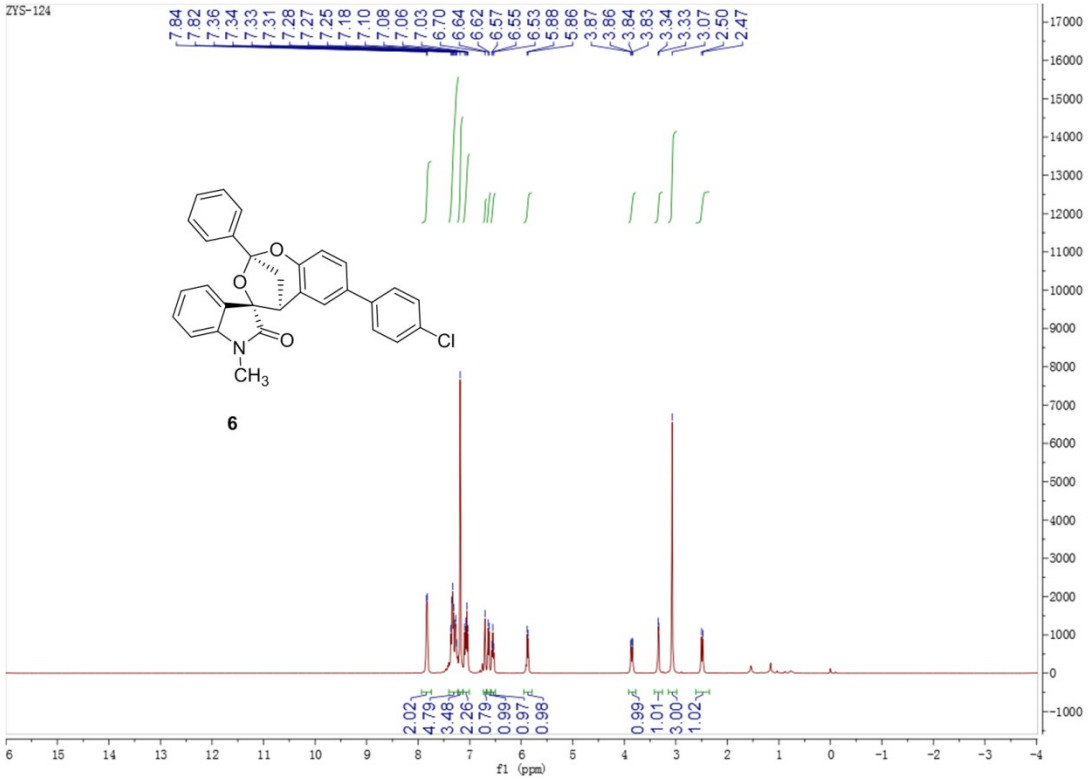

ZYS-109
7.88
7.87
7.37
7.35
7.33
7.30
7.28
7.27
7.17
7.15
7.13
7.11
6.86
6.84
6.72
6.70
6.68
6.66
6.64
6.62
6.60
6.21
6.19
5.92
5.90
3.87
3.85
3.84
3.32
3.31
3.11
2.51
2.48
0.00
OMe
O
O
N
O
CH3
3zc
2.00
3.04
1.14
1.08
2.95
0.99
0.99
3.95
1.03
3.00
1.00
f1 (ppm)

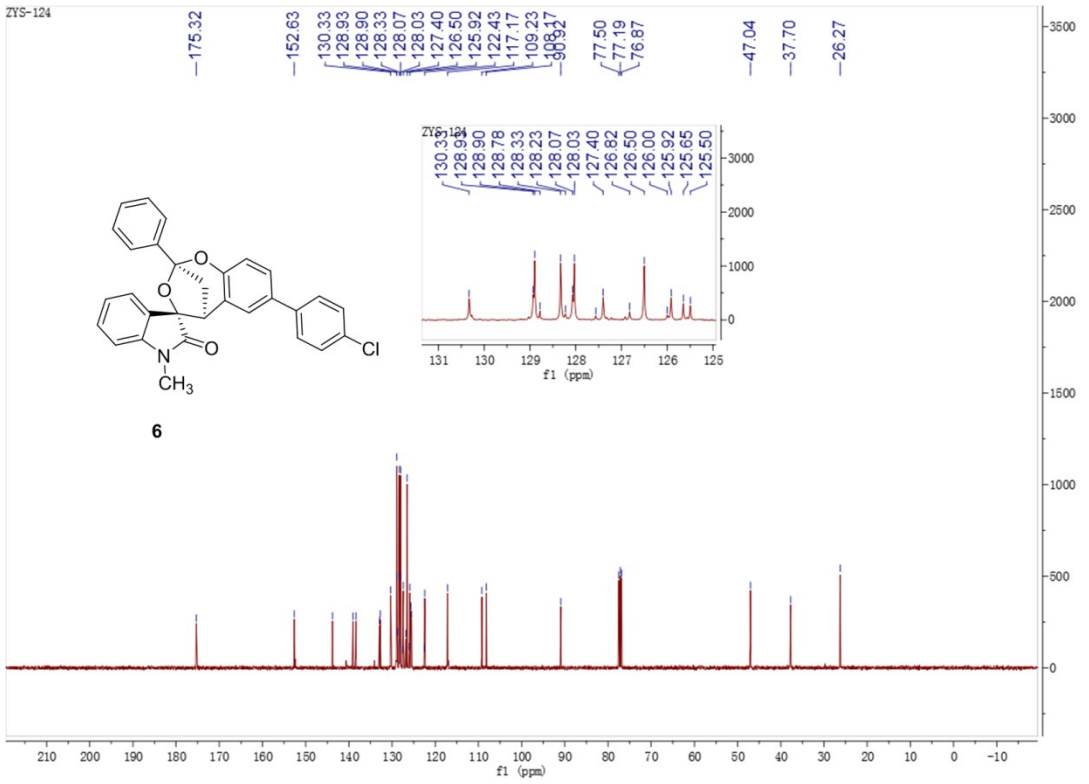

ZYS-109
175.43
148.57
143.81
142.12
138.55
130.07
128.70
128.21
126.55
125.99
125.96
125.59
122.43
120.85
120.56
112.47
108.92
107.92
90.86
77.40
77.08
76.76
56.27
46.79
37.63
26.20
OMe
O
O
N
O
CH3
3zc
f1 (ppm)

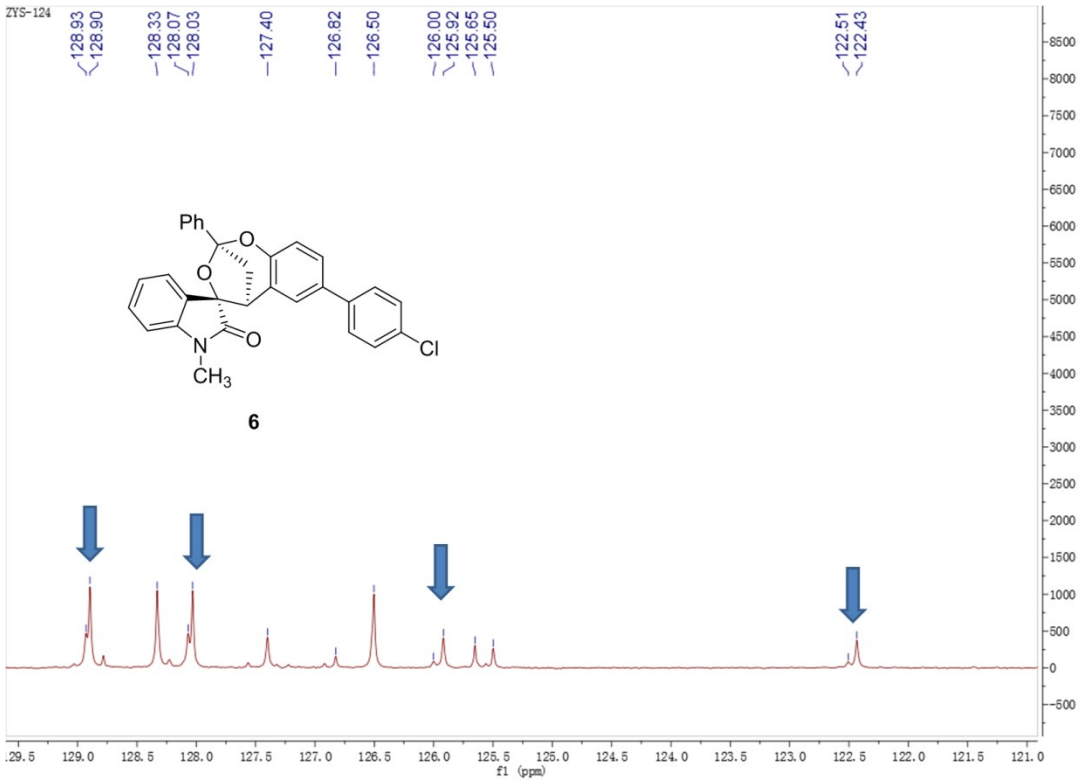

7.91
7.89
7.58
7.56
7.53
7.51
7.45
7.43
7.35
7.33
7.32
7.30
7.24
7.22
7.15
7.13
7.11
7.04
7.02
6.75
6.73
6.68
6.67
6.63
6.62
6.60
6.58
6.56
5.85
5.83
3.89
3.88
3.86
3.86
3.85
3.34
3.33
3.11
2.54
2.53
2.51
2.50
0.00
Cl
O
O
N
O
CH3
5
1.99
1.12
1.95
1.16
2.09
1.09
1.17
1.00
1.02
1.01
2.02
0.99
1.02
1.02
3.00
1.02
f1 (ppm)


ZYS-125
175.45
152.82
152.77
129.53
128.97
128.81
128.51
127.27
127.09
127.05
126.94
126.87
125.91
122.53
116.68
90.93
77.41
77.10
76.78
46.86
37.61
26.25
Cl
O
O
O
N
CH3
5
122.53
120.79
120.74
116.68
108.95
108.85
108.02
f1 (ppm)


125.16
125.12
122.53
120.79
120.74
116.68
108.95
108.85
108.02
108.00
Cl
O
O
O
N
CH3
f1 (ppm)


ZYS-124
7.84
7.82
7.36
7.34
7.33
7.31
7.28
7.27
7.25
7.18
7.10
7.08
7.06
7.03
6.70
6.64
6.62
6.57
6.55
6.53
5.88
5.86
3.87
3.86
3.84
3.83
3.34
3.33
3.07
2.50
2.47
O
O
N
O
CH3
Cl
6
2.02
4.79
3.48
2.26
0.79
0.99
0.97
0.98
0.99
1.01
3.00
1.02
f1 (ppm)


ZYS-124
175.32
152.63
130.33
128.93
128.90
128.33
128.07
128.03
127.40
126.50
125.92
122.43
117.17
109.23
90.92
77.50
77.19
76.87
47.04
37.70
26.27
O
O
N
O
CH3
Cl
6
f1 (ppm)


ZYS-124
128.93
128.90
128.33
128.07
128.03
127.40
126.82
126.50
126.00
125.92
125.65
125.50
122.51
122.43
Ph
O
O
N
O
CH3
Cl
f1 (ppm)

**6**