Supporting Information

# An unexpected cascade reaction of 3-hydroxyoxindoles with coumarin-3-carboxylates to construct 2,3-dihydrobenzofuran spirooxindoles

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## 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. Selected bioactive compounds containing spirooxindole scaffolds

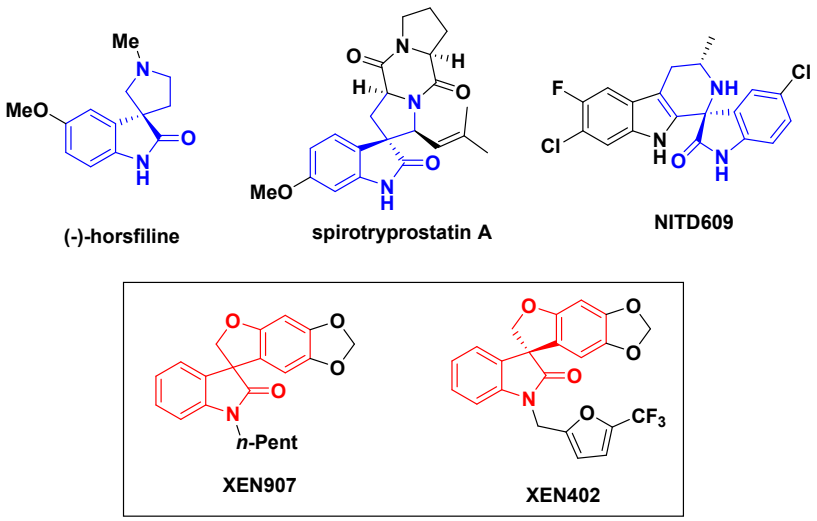
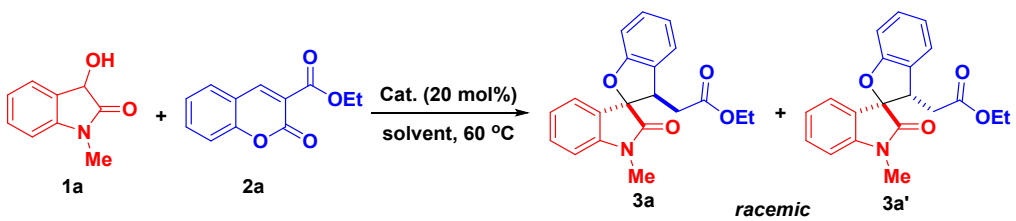



**Figure S1** Selected biologically active compounds containing spirooxindole scaffold

## 3. Optimizationof reaction conditions

Table S1 Optimization of reaction conditions[a]



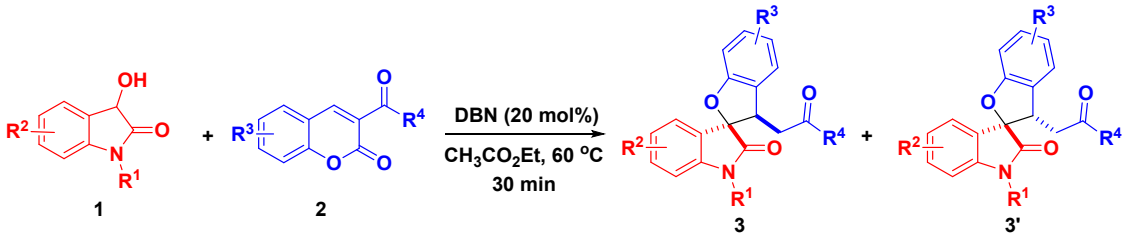
| entry | Cat. | Solvent | time (h) | yield[b] (%) | **3a**/**3a'**[c] |
|---|---|---|---|---|---|
| 1 | $Et_3N$ | $CH_3CN$ | 5 | 98 | 1:1.1 |
| 2 | DBU | $CH_3CN$ | 5 | 99 | 1.1:1 |
| 3 | DABCO·$6H_2O$ | $CH_3CN$ | 5 | 99 | 1:1 |
| 4 | DBN | $CH_3CN$ | 2 | 99 | 1:1 |
| 5 | $K_2CO_3$ | $CH_3CN$ | 4 | 91 | 1:1.3 |
| 6 | $Cs_2CO_3$ | $CH_3CN$ | 4 | 91 | 1:1 |
| 7 | DBN | 1,4-dioxane | 1 | 89 | 1:1.5 |
| 8 | DBN | DCE | 1 | 85 | 1:1.5 |
| 9 | DBN | $CHCl_3$ | 0.5 | 72 | 1:1.4 |
| 10 | DBN | EtOAc | 0.5 | 99 (95)[d] | 1:1 |
| 11[e] | DBN | EtOAc | 12 | trace | --- |
| 12[f] | DBN | EtOAc | 12 | 35 | 1:1 |
| 13[g] | DBN | EtOAc | 1 | 90 | 1:1 |

[a] Unless otherwise noted, the reactions were conducted with 0.25 mmol of **1a** and **2a** in the presence of 20 mol% of catalyst in 1.0 mL of specified solvent at 60 °C. [b] $^1$H NMR yield with 1,3,5-trimethoxybenzene as the internal standard. [c] The dr value was determined by $^1$H NMR analysis of the crude reaction mixture. [d] Isolated yield obtained by silica gel column chromatography. [e] At 0 °C. [f] At 25 °C. [g] At 40 °C. DBN = 1,5-diazabicyclo[4.3.0]non-5-ene; DCE = 1,2-dichloroethane.

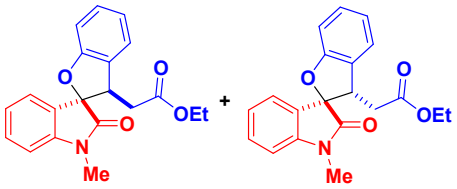
To improve the synthetic efficiency, initially, some bases including organic bases and inorganic bases were evaluated (Table S1). Among them, 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) proved to be the best in terms of yield and reaction time, in which the reaction time was shorten to 2 h (Table S1, entry 4). The reaction media optimization indicated that the reaction could not only be performed in $CH_3CN$, it also proceeded smoothly in other solvents, such as 1,4-dioxane, 1,2-dichloroethane, $CHCl_3$ and EtOAc. To our delight, the reaction went to completion within 30 min in EtOAc with the formation of **3a/3a'** in 95% isolated yield, which was chosen as the optimal solvent to evaluate other parameters. The reaction was quite sensitive to temperatures. When the temperature was decreased to 0 °C, the reaction proceeded very sluggishly, and only a trace

amount of products were generated after 12 h (Table S1, entry 11). The NMR yield was enhanced to 35% when the reaction was conducted at 25 °C for 12 h (Table S1, entry 12). Further increasing the temperature to 40 °C, 90% NMR yield of **3a**/**3a'** was obtained (Table S1, entry 13). As a consequence, the optimized reaction condition for the construction of **3a** and **3a'** was found to be 0.25 mmol of **1a** and **2a** with 20 mol% of DBN as catalyst in 1.0 mL of EtOAc at 60 °C for 30 min (Table S1, entry 10).

## 4. Experimental data for dihydrobenzofuran spirooxindoles 3



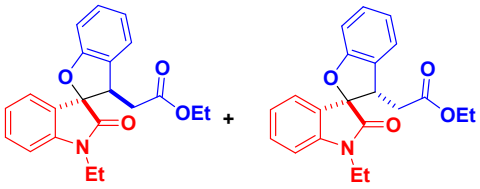

**General procedure:** To a 5.0 mL vial were successively added 3-hydroxyoxindoles **1** (0.25 mmol), coumarin-3-carboxylates **2** (0.25 mmol), DBN (0.05 mmol) and 1.0 mL EtOAc. The resulting mixture was stirred at 60 °C for 30 min, and then the reaction mixture was directly subjected to flash column chromatography on silica gel (petroleum ether/ ethyl acetate) to afford the corresponding dihydrobenzofuran spirooxindoles **3** and **3'**.




Ethyl 2-(1'-methyl-2'-oxo-3*H*-spiro[benzofuran-2,3'-indolin]-3-yl)acetate (**3a**/**3a'**)

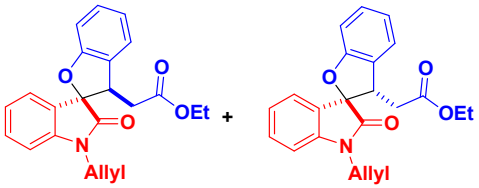
White solids for **3a** and **3a'**, 79.8 mg, 95% isolated yield obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1-8:1); Reaction time = 0.5 h; dr = 1:1 (**3a**/**3a'**, separable isomers); m. p. 109.8-110.1 °C (**3a**), 158.2-158.6 °C (**3a'**); $^{1}$H NMR (400 MHz, $CDCl_3$) for **3a** δ 7.36 (t, $J$ = 12.0 Hz, 1H), 7.30-7.17 (m, 3H), 7.06 (t, $J$ = 8.0 Hz, 1H), 6.97 (t, $J$ = 8.0 Hz, 1H), 6.87 (dd, $J_1 = J_2$ = 12.0 Hz, 2H), 4.27 (t, $J$ = 8.0 Hz, 1H), 4.03-3.97 (m, 2H), 3.18 (s, 3H), 3.02 (dd, $J_1 = J_2$ = 12.0 Hz, 1H), 2.85 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 1.15 (t, $J$ = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3a** δ 172.6, 171.5, 158.6, 143.6, 130.5, 129.3, 129.0, 128.5, 124.0, 123.5, 123.3, 121.4, 110.1, 108.3, 87.7, 60.6, 46.8, 35.5, 26.0, 14.0. $^{1}$H NMR (400 MHz, $CDCl_3$)

for **3a'** δ 7.34 (t, $J$ = 12.0 Hz, 1H), 7.24-7.12 (m, 3H), 6.97 (q, $J$ = 8.0 Hz, 2H), 6.85 (dd, $J_1$ = 8.0 Hz, $J_2$ = 12.0 Hz, 2H), 4.42 (dd, $J_1$ = $J_2$ = 8.0 Hz, 1H), 3.85 (q, $J$ = 8.0 Hz, 2H), 3.25 (s, 3H), 2.88 (dd, $J_1$ = $J_2$ = 8.0 Hz, 1H), 2.59 (dd, $J_1$ = $J_2$ = 12.0 Hz, 1H), 1.04 (t, $J$ = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3a'** δ 175.1, 170.7, 158.5, 144.3, 130.7, 128.9, 128.2, 125.1, 125.0, 123.8, 122.5, 121.3, 110.0, 108.5, 88.6, 60.6, 44.5, 36.1, 26.4, 13.9. IR (KBr) for **3a** $v$ 3441, 2991, 1732, 1607, 1476, 1178, 756 cm$^{-1}$; IR (KBr) for **3a'** $v$ 3443, 2985, 1728, 1607, 1468, 1187, 753 cm$^{-1}$. HRMS (ESI) calcd. for $C_{20}H_{20}NO_4$ $[M+H]^+$: 338.1387, found: 338.1390.



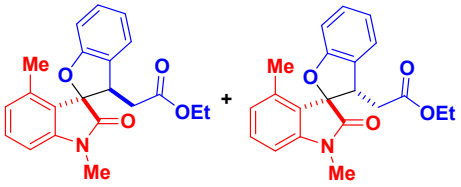

Ethyl 2-(1'-ethyl-2'-oxo-3*H*-spiro[benzofuran-2,3'-indolin]-3-yl)acetate (**3b**/**3b'**)

White solids for **3b**and **3b'**, 80.8 mg, 92% isolated yield obtained by silica gel column chromatography (petroleum ether/ethylacetate = 10:1-8:1); Reaction time = 0.5 h; dr = 1:1.2 (**3b**/**3b'**, separable isomers); m. p. 94.7-95.1 °C (**3b**), 135.4-136.2 °C (**3b'**); $^1$H NMR (400 MHz, $CDCl_3$) for **3b** δ 7.34 (t, $J$ = 8.0 Hz, 1H), 7.28 (d, $J$ = 8.0 Hz, 1H), 7.21 (dd, $J_1$ = $J_2$ = 8.0 Hz, 2H), 7.04 (t, $J$ = 8.0 Hz, 1H), 6.96 (t, $J$ = 8.0 Hz, 1H), 6.87 (t, $J$ = 8.0 Hz, 2H), 4.27 (dd, $J_1$ = $J_2$ = 4.0 Hz, 1H), 4.04-3.98 (m, 2H), 3.81-3.64 (m, 2H), 3.04 (dd, $J_1$ = $J_2$ = 8.0 Hz, 1H), 2.85 (dd, $J_1$ = $J_2$ = 8.0 Hz, 1H), 1.28 (t, $J$ = 8.0 Hz, 3H), 1.15 (t, $J$ = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3b** δ 172.2, 171.5, 158.6, 142.7, 130.4, 129.6, 129.0, 128.5, 124.0, 123.7, 123.1, 121.4, 110.1, 108.4, 87.6, 60.6, 46.7, 35.5, 34.6, 14.0, 12.4. $^1$H NMR (400 MHz, $CDCl_3$) for **3b'** δ 7.32 (t, $J$ = 8.0 Hz, 1H), 7.20 (t, $J$ = 8.0 Hz, 1H), 7.16 (d, $J$ = 8.0 Hz, 1H), 7.12 (d, $J$ = 8.0 Hz, 1H), 6.98-6.94 (m, 2H), 6.85 (t, $J$ = 8.0 Hz, 2H), 4.42 (dd, $J_1$ = $J_2$ = 4.0 Hz, 1H), 3.87-3.73 (m, 4H), 2.86 (dd, $J_1$ = $J_2$ = 4.0 Hz, 1H), 2.59 (dd, $J_1$ = $J_2$ = 4.0 Hz, 1H), 1.32 (t, $J$ = 8.0 Hz, 3H), 1.03 (t, $J$ = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3b'** δ 174.7, 170.7, 158.6, 143.5, 130.6, 128.9, 128.3, 125.3, 125.3, 123.8, 122.3, 121.3, 110.0, 108.7, 88.6, 60.5, 44.5, 36.0, 34.9, 13.9, 12.3. IR (KBr) for **3b** $v$ 3450, 2984, 1730, 1620, 1475, 753 cm$^{-1}$; IR (KBr) for **3b'** $v$ 3442, 2983, 1727, 1608, 1475, 1373, 1188, 750 cm$^{-1}$. HRMS (ESI) calcd. for $C_{21}H_{22}NO_4$ $[M+H]^+$: 352.1543, found: 352.1542.




Ethyl 2-(1'-allyl-2'-oxo-3*H*-spiro[benzofuran-2,3'-indolin]-3-yl)acetate (**3c**/**3c'**)

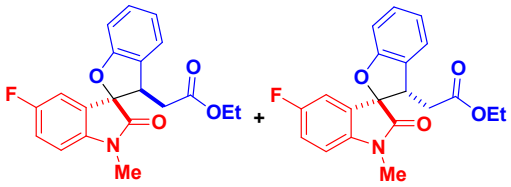
Colorless oilfor **3c** and white solid for **3c'**, 87.0 mg, 96% isolated yield obtained by silica gel column chromatography (petroleum ether/ethylacetate = 10:1-8:1); Reaction time = 0.5 h; dr = 1:1.2 (**3c**/**3c'**, separable isomers); m. p. 113.8-114.1 °C (**3c'**); $^{1}$H NMR (400 MHz, $CDCl_3$) for **3c** δ 7.36-7.28 (m, 2H), 7.23 (dd, $J_1 = J_2 = 4.0$ Hz, 2H), 7.07 (t, $J = 8.0$ Hz, 1H), 6.99 (t, $J = 8.0$ Hz, 1H), 6.90 (dd, $J_1 = J_2 = 8.0$ Hz, 2H), 5.93-5.83 (m, 1H), 5.31 (dd, $J_1 = J_2 = 8.0$ Hz, 2H), 4.44-4.23 (m, 3H), 4.10-3.98 (m, 2H), 3.08 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 2.89 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 1.18 (t, $J = 8.0$ Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3c** δ 172.3, 171.5, 158.5, 142.8, 131.1, 130.3, 129.3, 129.0, 128.5, 124.0, 123.5, 123.2, 121.4, 117.9, 110.1, 109.3, 87.6, 60.6, 46.7, 42.3, 35.5, 13.9. $^{1}$H NMR (400 MHz, $CDCl_3$) for **3c'** δ 7.28 (t, $J = 8.0$ Hz, 1H), 7.22-7.11 (m, 3H), 6.98-6.93 (m, 2H), 6.84 (dd, $J_1 = J_2 = 8.0$ Hz, 2H), 5.94-5.84 (m, 1H), 5.35 (d, $J = 20.0$ Hz, 1H), 5.26 (d, $J = 12.0$ Hz, 1H), 4.45-4.29 (m, 3H), 3.84 (q, $J = 8.0$ Hz, 2H), 2.87 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 2.61 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 1.02 (t, $J = 8.0$ Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3c'** δ 174.8, 170.7, 158.5, 143.6, 131.3, 130.5, 128.9, 128.1, 125.1, 125.0, 123.8, 122.4, 121.3, 117.8, 110.0, 109.5, 88.5, 60.5, 44.5, 42.7, 36.0, 13.9. IR (KBr) for **3c** *v* 3450, 2983, 1731, 1615, 1475, 1181, 753 cm$^{-1}$; IR (KBr) for **3c'** *v* 3448, 2976, 1730, 1610, 1477, 1372, 1186, 747 cm$^{-1}$. HRMS (ESI) calcd. for $C_{22}H_{22}NO_4$ $[M+H]^+$: 364.1543, found: 364.1548.




Ethyl 2-(1',4'-dimethyl-2'-oxo-3*H*-spiro[benzofuran-2,3'-indolin]-3-yl)acetate (**3d**/**3d'**)

White solids for **3d** and **3d'**, 78.8 mg, 90% isolated yield obtained by silica gel column chromatography (petroleum ether/ethylacetate = 10:1-8:1); Reaction time = 0.5 h; dr = 2:1 (**3d**/**3d'**, separable isomers); m. p. 114.2-114.8 °C (**3d**), 147.3-147.9 °C (**3d'**); $^{1}$H NMR (400 MHz, $CDCl_3$) for **3d** δ 7.24-7.21 (m, 2H), 7.16 (d, $J = 8.0$ Hz, 1H), 6.95 (t, $J = 8.0$ Hz, 1H), 6.88 (dd, $J_1 = J_2 = 4.0$ Hz, 2H), 6.66 (d, $J = 8.0$ Hz, 1H), 4.46 (t, $J = 8.0$ Hz, 1H), 4.05-3.91 (m, 2H), 3.14 (s, 3H),

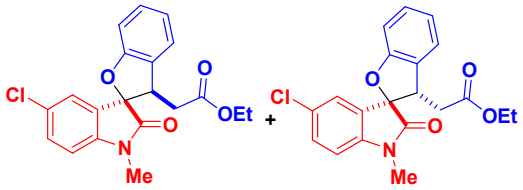
2.91 (dd, $J_1 = J_2 = 4.0$ Hz, 2H), 2.22 (s, 3H), 1.13 (t, $J = 8.0$ Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3d** δ 172.7, 171.4, 159.14, 144.0, 136.0, 130.1, 129.0, 128.3, 126.3, 125.7, 123.8, 121.3, 109.7, 105.9, 89.1, 60.7, 44.6, 35.6, 26.0, 17.7, 13.9. $^1$H NMR (400 MHz, $CDCl_3$) for **3d'** δ 7.21 (t, $J$ = 8.0 Hz, 2H),7.13 (d, $J = 8.0$ Hz, 1H), 6.95 (t, $J = 8.0$ Hz, 1H), 6.86 (d, $J = 8.0$ Hz, 1H), 6.81 (d, $J$ = 8.0 Hz, 1H), 6.64 (d, $J = 8.0$ Hz, 1H), 4.47 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 3.84 (q, $J = 8.0$ Hz, 2H), 3.22 (s, 3H), 2.85 (dd, $J_1 = J_2 = 4.0$ Hz, 1H), 2.44 (dd, $J_1 = 8.0$ Hz, $J_2 = 12.0$ Hz, 1H), 1.93 (s, 3H), 1.07 (t, $J = 8.0$ Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3d'** δ 176.0, 170.8, 158.8, 144.7, 136.6, 130.3, 129.2, 128.3, 125.4, 124.0, 123.0, 121.3, 109.7, 105.9, 89.6, 60.6, 46.1, 35.2, 26.5, 19.7, 14.0. IR (KBr) for **3d** $\nu$ 3444, 2929, 1729, 1623, 750 cm$^{-1}$; IR (KBr) for **3d'** $\nu$ 3446, 1725, 1632, 1048, 748 cm$^{-1}$. HRMS (ESI) calcd. for $C_{21}H_{22}NO_4$ $[M+H]^+$: 352.1543, found: 352.1548.




Ethyl 2-(5'-fluoro-1'-methyl-2'-oxo-3*H*-spiro[benzofuran-2,3'-indolin]-3-yl)acetate (**3e**/**3e'**)

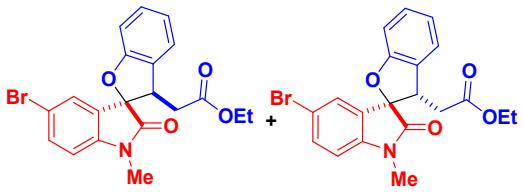
Colorless oilfor **3e** and white solid for **3e'**, 76.4 mg, 86% isolated yield obtained by silica gel column chromatography (petroleum ether/ethylacetate = 10:1-8:1); Reaction time = 0.5 h; dr = 1:1.4 (**3e**/**3e'**, separable isomers); m. p. 158.2-158.8 °C (**3e**), 152.5-153.4 °C (**3e'**); $^1$H NMR (400 MHz, $CDCl_3$) for **3e** δ 7.20 (q, $J = 8.0$ Hz, 2H), 7.06-6.99 (m, 3H), 6.88 (d, $J = 8.0$ Hz, 1H), 6.77 (dd, $J_1 = J_2 = 4.0$ Hz, 1H), 4.20 (t, $J = 8.0$ Hz, 1H), 4.05-3.95 (m, 2H), 3.15 (s, 3H), 3.07 (dd, $J_1$ = 12.0 Hz, $J_2 = 8.0$ Hz, 1H), 2.83 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 1.15 (t, $J = 8.0$ Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3e** δ 172.5, 171.6, 159.5 (d, $J = 241.0$ Hz, 1C), 158.5, 139.6 (d, $J = 2.0$ Hz, 1C), 131.1 (d, $J = 8.0$ Hz, 1C), 129.3, 128.2, 124.2, 121.8, 116.7 (d, $J = 13.0$ Hz, 1C), 111.7 (d, $J$ = 25.0 Hz, 1C), 110.3, 109.1 (d, $J = 8.0$ Hz, 1C), 87.6, 60.8, 47.0, 35.7, 26.3, 14.1. $^1$H NMR (400 MHz, $CDCl_3$) for **3e'** δ 7.20 (t, $J = 8.0$ Hz, 1H), 7.15 (d, $J = 8.0$ Hz, 1H), 7.06-6.94 (m, 2H), 6.86 (d, $J = 8.0$ Hz, 2H), 6.76 (dd, $J_1 = J_2 = 4.0$ Hz, 1H), 4.41 (dd, $J_1 = J_2 = 4.0$ Hz, 1H), 3.90-3.84 (m, 2H), 3.22 (s, 3H), 2.89 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 2.56 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 1.06 (tt, $J_1 = J_2$ = 4.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3e'** δ 174.9, 170.6, 158.8 (d, $J = 241.0$ Hz, 1C), 158.3, 140.4, 129.1, 127.8, 126.5 (d, $J = 8.0$ Hz, 1C), 123.9, 121.6, 116.9 (d, $J = 23.0$ Hz, 1C), 113.1 (d, $J = 25.0$ Hz, 1C), 110.1, 109.1 (d, $J = 8.0$ Hz, 1C), 88.5, 60.7, 44.7, 35.8, 26.5, 13.9. IR

(KBr) for **3e** *v* 3436, 2981, 1728, 1468, 1234, 747 $cm^{-1}$; IR (KBr) for **3e'** *v* 3446, 2922, 1733, 1474, 1243, 1179, 749 $cm^{-1}$. HRMS (ESI) calcd. for $C_{20}H_{19}FNO_4$ $[M+H]^+$: 356.1293, found: 356.1299.



Ethyl 2-(5'-chloro-1'-methyl-2'-oxo-3*H*-spiro[benzofuran-2,3'-indolin]-3-yl)acetate (**3f**/**3f'**)

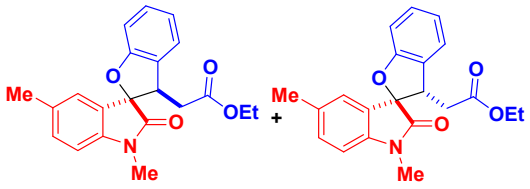
White solidsfor **3f** and **3f'**, 78.4 mg, 84% isolated yield obtained by silica gel column chromatography (petroleum ether/ethylacetate = 10:1-8:1); Reaction time = 0.5 h; dr = 1:1.5 (**3f**/**3f'**, separable isomers); m. p. 100.3-101.1 °C (**3f**), 141.5-142.1 °C (**3f'**); $^1$H NMR (400 MHz, $CDCl_3$) for **3f** δ 7.31 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 7.24-7.17 (m, 3H), 6.97 (t, $J$ = 8.0 Hz, 1H), 6.88 (d, $J$ = 8.0 Hz, 1H), 6.77 (d, $J$ = 8.0 Hz, 1H), 4.20 (t, $J$ = 4.0 Hz, 1H), 4.05-3.95 (m, 2H), 3.15 (s, 3H), 3.08 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 2.83 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 1.15 (t, $J$ = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3f** δ 172.2, 171.5, 158.3, 142.1, 131.2, 130.2, 129.2, 128.5, 127.9, 124.1, 123.9, 121.7, 110.2, 109.4, 87.2, 60.7, 46.8, 35.6, 26.1, 13.9. $^1$H NMR (400 MHz, $CDCl_3$) for **3f'** δ 7.31 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 7.22 (t, $J$ = 8.0 Hz, 1H), 7.16 (d, $J$ = 8.0 Hz, 1H), 7.09 (d, $J$ = 4.0 Hz, 1H), 6.98 (t, $J$ = 8.0 Hz, 1H), 6.87 (d, $J$ = 8.0 Hz, 1H), 6.76 (d, $J$ = 8.0 Hz, 1H), 4.40 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.87 (q, $J$ = 8.0 Hz, 2H), 3.22 (s, 3H), 2.90 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 2.58 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 1.07 (t, $J$ = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3f'** δ 174.7, 170.7, 158.3, 143.0, 130.5, 129.1, 127.9, 127.7, 126.7, 125.3, 123.8, 121.6, 110.1, 109.5, 88.3, 60.8, 44.7, 35.9, 26.5, 13.9. IR (KBr) for **3f** *v* 3443, 2931, 1733, 1480, 1239, 751 $cm^{-1}$; IR (KBr) for **3f'** *v* 3436, 3066, 1727, 1488, 1361, 1249, 748 $cm^{-1}$. HRMS (ESI) calcd. for $C_{20}H_{19}ClNO_4$ $[M+H]^+$: 372.0997, found: 372.0998.



Ethyl 2-(5'-bromo-1'-methyl-2'-oxo-3*H*-spiro[benzofuran-2,3'-indolin]-3-yl)acetate (**3g**/**3g'**)

White solids for **3g** and **3g'**, 98.9 mg, 95% isolated yield obtained by silica gel column chromatography (petroleum ether/ethylacetate = 10:1-8:1); Reaction time = 0.5 h; dr = 1:1.6 (**3g**/**3g'**, separable isomers); m. p. 121.6-122.6 °C (**3g**), 139.1-139.7 °C (**3g'**); $^1$H NMR (400 MHz,

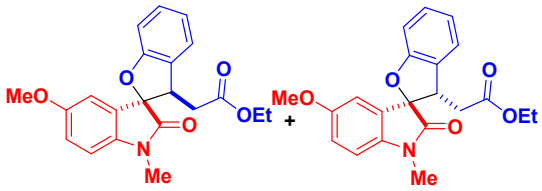
$CDCl_3$) for **3g** δ 7.47 (dd, $J_1 = J_2 = 4.0$ Hz, 1H), 7.36 (d, $J = 4.0$ Hz, 1H), 7.24-7.17 (m, 2H), 6.98 (t, $J = 8.0$ Hz, 1H), 6.88 (d, $J = 8.0$ Hz, 1H), 6.73 (d, $J = 8.0$ Hz, 1H), 4.21 (dd, $J_1 = J_2 = 4.0$ Hz, 1H), 4.07-3.94 (m, 2H), 3.15 (s, 3H), 3.08 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 2.83 (dd, $J_1 = 4.0$ Hz, $J_2 = 8.0$ Hz, 1H), 1.16 (t, $J = 8.0$ Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3g**δ 172.2, 171.6, 158.3, 142.6, 133.2, 131.6, 129.2, 128.0, 126.7, 124.1, 121.7, 115.8, 110.3, 109.9, 87.2, 60.8, 46.9, 35.7, 26.2, 14.0. $^1$H NMR (400 MHz, $CDCl_3$) for **3g'** δ 7.47-7.44 (m, 1H), 7.22 (t, $J = 8.0$ Hz, 2H), 6.97 (t, $J = 8.0$ Hz, 1H), 6.86 (d, $J = 8.0$ Hz, 1H), 6.71 (d, $J = 8.0$ Hz, 1H), 4.40 (dd, $J_1 = 4.0$ Hz, $J_2 = 8.0$ Hz, 1H), 3.90-3.84 (m, 2H), 3.21 (s, 3H), 2.90 (dd, $J_1 = 8.0$ Hz, $J_2 = 4.0$ Hz, 1H), 2.59 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 1.07 (t, $J = 8.0$ Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3g'** δ 174.6, 170.7, 158.3, 143.5, 133.4, 129.1, 128.0, 127.7, 127.1, 123.9, 121.6, 115.0, 110.1, 110.0, 88.3, 60.8, 44.7, 35.9, 26.5, 13.9. IR (KBr) for **3g** $\nu$ 3441, 2948, 1734, 1477, 1181, 747 cm$^{-1}$; IR (KBr) for **3g'** $\nu$ 3443, 2983, 1727, 1474, 1248, 750 cm$^{-1}$. HRMS (ESI) calcd. for $C_{20}H_{19}BrNO_4$ $[M+H]^+$: 416.0492, found: 416.0496.




Ethyl 2-(1',5'-dimethyl-2'-oxo-3*H*-spiro[benzofuran-2,3'-indolin]-3-yl)acetate (**3h**/**3h'**)

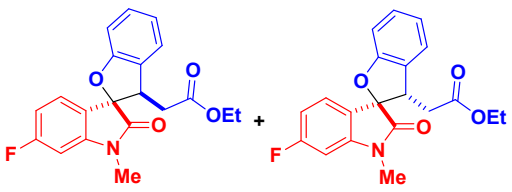
White solids for **3h** and **3h'**, 77.7 mg, 89% isolated yield obtained by silica gel column chromatography (petroleum ether/ethylacetate = 10:1-8:1); Reaction time = 0.5 h; dr = 1:1.3 (**3h**/**3h'**, separable isomers); m. p. 95.3-96.2 °C (**3h**), 98.6-99.5 °C (**3h'**); $^1$H NMR (400 MHz, $CDCl_3$) for **3h** δ 7.23-7.12 (m, 4H), 6.96 (t, $J = 8.0$ Hz, 1H), 6.88 (d, $J = 8.0$ Hz, 1H), 6.73 (d, $J = 8.0$ Hz, 1H), 4.27 (t, $J = 8.0$ Hz, 1H), 4.05-3.96 (m, 2H), 3.15 (s, 3H), 3.00 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 2.85 (dd, $J_1 = 8.0$ Hz, $J_2 = 4.0$ Hz, 1H), 2.28 (s, 3H), 1.15 (t, $J = 8.0$ Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3h** δ 172.5, 171.5, 158.6, 141.2, 132.9, 130.6, 129.2, 128.9, 128.5, 124.2, 124.0, 121.3, 110.0, 108.1, 87.8, 60.5, 46.7, 35.5, 26.0, 20.8, 13.9. $^1$H NMR (400 MHz, $CDCl_3$) for **3h'** δ 7.23-7.12 (m, 3H), 6.98-6.93 (m, 2H), 6.87 (d, $J = 8.0$ Hz, 1H), 6.71 (d, $J = 8.0$ Hz, 1H), 4.40 (dd, $J_1 = 8.0$ Hz, $J_2 = 4.0$ Hz, 1H), 3.89-3.84 (m, 2H), 3.21 (s, 3H), 2.86 (dd, $J_1 = 4.0$ Hz, $J_2 = 8.0$ Hz, 1H), 2.59 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 2.26 (s, 3H), 1.06 (t, $J = 8.0$ Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3h'** δ 175.1, 170.7, 158.6, 142.0, 132.2, 130.9, 128.9, 128.3, 125.8, 125.1, 123.9, 121.3,

110.0, 108.3, 88.7, 60.6, 44.5, 36.2, 26.4, 20.9, 13.9. IR (KBr) for **3h** *v* 3437, 1723, 1467, 1182, 743 $cm^{-1}$; IR (KBr) for **3h'** *v* 3442, 1728, 1472, 1192, 749 $cm^{-1}$. HRMS (ESI) calcd. for $C_{21}H_{22}NO_4$ $[M+H]^+$: 352.1543, found: 352.1535.




Ethyl 2-(5'-methoxy-1'-methyl-2'-oxo-3*H*-spiro[benzofuran-2,3'-indolin]-3-yl)acetate (**3i**/**3i'**)

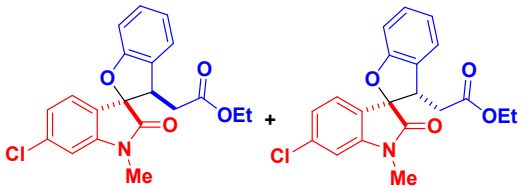
White solid for **3i** and **3i'**, 77.8 mg, 85% isolated yield obtained by silica gel column chromatography (petroleum ether/ethylacetate = 10:1-8:1); Reaction time = 0.5 h; dr = 1:1 (**3i**/**3i'**, separable isomers); m. p. 82.9-83.9 °C (**3i**), 125.1-126.1 °C (**3i'**); $^1$H NMR (400 MHz, $CDCl_3$) for **3i** δ 7.19 (q, *J* = 8.0 Hz, 2H), 6.95 (t, *J* = 8.0 Hz, 1H), 6.90-6.85 (m, 3H), 6.74 (d, *J* = 8.0 Hz, 1H), 4.25 (t, *J* = 4.0 Hz, 1H), 4.04-3.98 (m, 2H), 3.73 (s, 3H), 3.14 (s, 3H), 2.99 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 2.84 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 1.15 (t, *J* = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3i** δ 172.4, 171.5, 158.6, 156.5, 136.9, 130.3, 129.0, 128.4, 124.0, 121.4, 114.9, 110.7, 110.0, 108.8, 88.0, 60.6, 55.7, 46.9, 35.5, 26.1, 13.9. $^1$H NMR (400 MHz, $CDCl_3$) for **3i'** δ 7.21-7.14 (m, 2H), 6.95 (t, *J* = 8.0 Hz, 1H), 6.85 (dd, $J_1 = J_2$ = 4.0 Hz, 2H), 6.72 (t, *J* = 8.0 Hz, 2H), 4.40 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.87 (q, *J* = 8.0 Hz, 2H), 3.70 (s, 3H), 3.20 (s, 3H), 2.85 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 2.59 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 1.06 (t, *J* = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3i'** δ 174.8, 170.6, 158.5, 155.8, 137.7, 128.9, 128.1, 126.1, 123.8, 121.4, 114.8, 112.5, 110.0, 108.9, 88.8, 60.6, 55.8, 44.5, 36.0, 26.4, 13.9. IR (KBr) for **3i** *v* 3449, 2938, 1728, 1471, 1239, 750 $cm^{-1}$; IR (KBr) for **3i'** *v* 3429, 2948, 1726, 1490, 1246, 1030, 759 $cm^{-1}$. HRMS (ESI) calcd. for $C_{21}H_{21}NO_5$ $[M+H]^+$: 368.1492, found: 368.1486.




Ethyl 2-(6'-fluoro-1'-methyl-2'-oxo-3*H*-spiro[benzofuran-2,3'-indolin]-3-yl)acetate (**3j**/**3j'**)

White solids for **3j** and **3j'**, 82.8 mg, 93% isolated yield obtained by silica gel column chromatography (petroleum ether/ethylacetate = 10:1-8:1); Reaction time = 0.5 h; dr = 1:1.1 (**3j**/**3j'**, separable isomers); m. p. 88.4-89.2 °C (**3j**), 108.1-109.1 °C (**3j'**); $^1$H NMR (400 MHz,

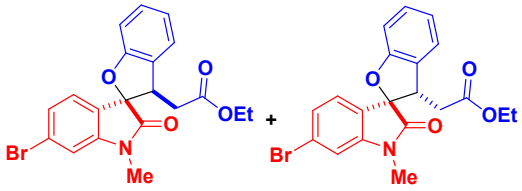
$CDCl_3$) for **3j** δ 7.24-7.17 (m, 3H), 6.96 (t, $J$ = 8.0 Hz, 1H), 6.87 (d, $J$ = 8.0 Hz, 1H), 6.74-6.69 (m, 1H), 6.59 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 4.21 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 4.05-3.96 (m, 2H), 3.15 (s, 3H), 3.03 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 2.83 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 1.16 (t, $J$ = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3j** δ 172.9, 171.6, 164.3 (d, $J$ = 247.0 Hz, 1C), 158.4, 145.5 (d, $J$ = 11.0 Hz, 1C), 129.1, 128.2, 124.9 (d, $J$ = 10.0 Hz, 1C), 124.8 (d, $J$ = 3.0 Hz, 1C), 124.0, 121.5, 110.1, 109.2 (d, $J$ = 23.0 Hz, 1C), 97.3 (d, $J$ = 28.0 Hz, 1C), 87.2, 60.7, 46.8, 35.5, 26.1, 14.0. $^1$H NMR (400 MHz, $CDCl_3$) for **3j'** δ 7.21-7.13 (m, 2H), 7.05 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 6.95 (t, $J$ = 8.0 Hz, 1H), 6.84 (d, $J$ = 8.0 Hz, 1H), 6.66-6.61 (m, 1H), 6.56 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 4.37 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.86 (q, $J$ = 8.0 Hz, 2H), 3.20 (s, 3H), 2.89 (dd, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 1H), 2.56 (dd, $J_1 = J_2$ = 12.0 Hz, 1H), 1.05 (t, $J$ = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3j'** δ 175.3, 170.6, 164.4 (d, $J$ = 247.0 Hz, 1C), 158.3, 146.3 (d, $J$ = 12.0 Hz, 1C), 129.0, 127.8, 126.3 (d, $J$ = 10.0 Hz, 1C), 123.7, 121.4, 120.6 (d, $J$ = 3.0 Hz, 1C), 109.9, 108.4 (d, $J$ = 22.0 Hz, 1C), 97.4 (d, $J$ = 27.0 Hz, 1C), 88.0, 60.6, 44.5, 35.9, 26.4, 13.8. IR (KBr) for **3j** $v$ 3446, 2973, 1732, 1613, 1468, 1231, 749 cm$^{-1}$; IR (KBr) for **3j'** $v$ 3459, 1741, 1617, 1469, 1244, 751 cm$^{-1}$. HRMS (ESI) calcd. for $C_{20}H_{19}FNO_4$ $[M+H]^+$: 356.1293, found: 356.1297.




Ethyl 2-(6'-chloro-1'-methyl-2'-oxo-3*H*-spiro[benzofuran-2,3'-indolin]-3-yl)acetate (**3k**/**3k'**)

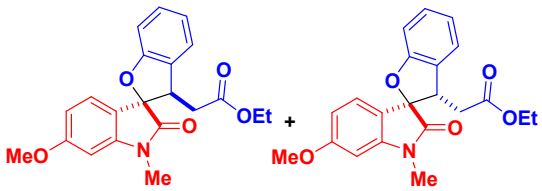
White solid for **3k** and **3k'**, 83.5 mg, 90% isolated yield obtained by silica gel column chromatography (petroleum ether/ethylacetate = 10:1-8:1); Reaction time = 0.5 h; dr = 1:1.4 (**3k**/**3k'**, separable isomers); m. p. 110.1-110.7 °C (**3k**), 141.7-142.1 °C (**3k'**); $^1$H NMR (400 MHz, $CDCl_3$) for **3k** δ 7.22 (d, $J$ = 8.0 Hz, 1H), 7.18 (d, $J$ = 8.0 Hz, 2H), 7.01 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 6.96 (t, $J$ = 8.0 Hz, 1H), 6.87 (d, $J$ = 8.0 Hz, 1H), 6.85 (d, $J$ = 4.0 Hz, 1H), 4.21 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 4.07-3.94 (m, 2H), 3.15 (s, 3H), 3.05 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 2.82 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 1.16 (t, $J$ = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3k** δ 172.5, 171.6, 158.3, 144.8, 136.2, 129.1, 128.1, 127.9, 124.4, 124.0, 123.0, 121.5, 110.1, 109.2, 87.1, 60.7, 46.8, 35.5, 26.1, 14.0. $^1$H NMR (400 MHz, $CDCl_3$) for **3k'** δ 7.19 (t, $J$ = 8.0 Hz, 1H), 7.14 (d, $J$ = 8.0 Hz, 1H), 7.02 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 6.97-6.93 (m, 2H), 6.86-6.83 (m, 2H), 4.38 (dd, $J_1 = J_2$ = 4.0 Hz, 1H),

3.89-3.83 (m, 2H), 3.20 (s, 3H), 2.89 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 2.55 (dd, $J_1 = J_2 = 4.0$ Hz, 1H), 1.05 (t, $J = 8.0$ Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3k'** δ 175.0, 170.6, 158.3, 145.7, 136.5, 129.0, 127.8, 125.9, 123.8, 123.4, 122.2, 121.5, 110.0, 109.3, 88.0, 60.7, 44.6, 35.9, 26.5, 13.9. IR (KBr) for **3k** *v* 3451, 2934, 1734, 1613, 1239, 747 cm$^{-1}$; IR (KBr) for **3k'** *v* 3442, 2973, 1731, 1608, 1473, 1373, 1245, 751 cm$^{-1}$. HRMS (ESI) calcd. for $C_{20}H_{19}ClNO_4$ $[M+H]^+$: 372.0997, found: 372.1002.



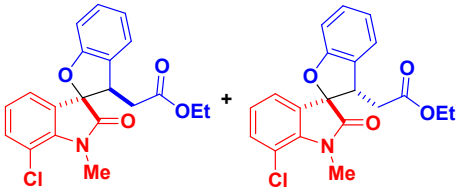

Ethyl 2-(6'-bromo-1'-methyl-2'-oxo-3*H*-spiro[benzofuran-2,3'-indolin]-3-yl)acetate (**3l**/**3l'**)

White solids for **3l** and **3l'**, 95.5 mg, 92% isolated yield obtained by silica gel column chromatography (petroleum ether/ethylacetate = 10:1-8:1); Reaction time = 0.5 h; dr = 1:1.6 (**3l**/**3l'**, separable isomers); m. p. 92.3-93.3 °C (**3l**), 166.3-166.8 °C (**3l'**); $^1$H NMR (400 MHz, $CDCl_3$) for **3l** δ 7.23-7.16 (m, 3H), 7.11 (d, $J = 8.0$ Hz, 1H), 7.00 (d, $J = 4.0$ Hz, 1H), 6.96 (t, $J = 8.0$ Hz, 1H), 6.87 (d, $J = 8.0$ Hz, 1H), 4.19 (dd, $J_1 = J_2 = 4.0$ Hz, 1H), 4.07-3.94 (m, 2H), 3.15 (s, 3H), 3.05 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 2.83 (dd, $J_1 = J_2 = 4.0$ Hz, 1H), 1.16 (t, $J = 8.0$ Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3l** δ 172.4, 171.5, 158.3, 144.9, 129.1, 128.4, 128.0, 126.0, 124.7, 124.1, 124.0, 121.5, 111.9, 110.1, 87.1, 60.7, 46.7, 35.5, 26.1, 14.0. $^1$H NMR (400 MHz, $CDCl_3$) for **3l'** δ 7.20 (t, $J = 8.0$ Hz, 1H),7.15-7.11 (m, 2H), 6.96 (t, $J = 8.0$ Hz, 3H), 6.85 (d, $J = 8.0$ Hz, 1H), 4.38 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 3.87 (q, $J = 8.0$ Hz, 2H), 3.22 (s, 3H), 2.89 (dd, $J_1 = 4.0$ Hz, $J_2 = 8.0$ Hz, 1H), 2.55 (dd, $J_1 = J_2 = 12.0$ Hz, 1H), 1.07 (t, $J = 8.0$ Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3l'** δ 175.0, 170.7, 158.3, 145.8, 129.1, 127.8, 126.2, 125.2, 124.5, 124.0, 123.8, 121.5, 112.1, 110.1, 88.1, 60.8, 44.6, 35.9, 26.5, 13.9. IR (KBr) for **3l** *v* 3451, 2966, 1735, 1601, 1469, 1373, 1175, 988, 750 cm$^{-1}$; IR (KBr) for **3l'** *v* 3442, 2929, 1729, 1606, 1475, 1246, 752 cm$^{-1}$. HRMS (ESI) calcd. for $C_{20}H_{19}BrNO_4$ $[M+H]^+$: 416.0492, found: 416.0500.




Ethyl 2-(6'-methoxy-1'-methyl-2'-oxo-3*H*-spiro[benzofuran-2,3'-indolin]-3-yl)acetate (**3m**/**3m'**)

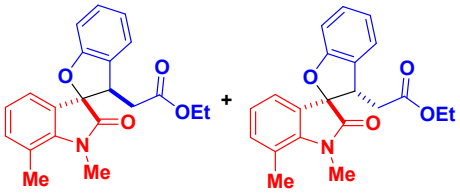
Colorless oilsfor **3m** and **3m'**, 85.3 mg, 93% isolated yield obtained by silica gel column chromatography (petroleum ether/ethylacetate = 10:1-8:1); Reaction time = 0.5 h; dr = 1.6:1 (**3m**/**3m'**, separable isomers); m. p. 99.1-100.0 °C (**3m'**); $^1$H NMR (400 MHz, $CDCl_3$) for **3m** δ 7.20-7.15 (m, 3H), 6.93 (t, $J$ = 8.0 Hz, 1H), 6.85 (d, $J$ = 8.0 Hz, 1H), 6.52 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 6.41 (d, $J$ = 4.0 Hz, 1H), 4.24 (t, $J$ = 4.0 Hz, 1H), 4.05-3.93 (m, 2H), 3.79 (s, 3H), 3.12 (s, 3H), 2.94 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 2.84 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 1.14 (t, $J$ = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3m** δ 172.9, 171.4, 161.8, 158.4, 145.1, 128.7, 128.5, 124.5, 123.8, 121.1, 120.7, 109.8, 106.7, 96.3, 87.6, 60.4, 55.3, 46.5, 35.2, 25.8, 13.8. $^1$H NMR (400 MHz, $CDCl_3$) for **3m'** δ 7.18 (t, $J$ = 8.0 Hz, 1H), 7.14 (d, $J$ = 8.0 Hz, 1H), 7.02 (d, $J$ = 8.0 Hz, 1H), 6.93 (t, $J$ = 8.0 Hz, 1H), 6.84 (d, $J$ = 8.0 Hz, 1H), 6.45 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 6.39 (d, $J$ = 4.0 Hz, 1H), 4.37 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.91-3.83 (m, 2H), 3.80 (s, 3H), 3.20 (s, 3H), 2.85 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 2.58 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 1.05 (t, $J$ = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3m'** δ 175.6, 170.7, 162.0, 158.4, 145.9, 128.8, 128.2, 126.0, 123.8, 121.2, 116.9, 109.9, 106.0, 96.5, 88.5, 60.5, 55.4, 44.3, 36.1, 26.3, 13.9. IR (KBr) for **3m** $v$ 3450, 2975, 1731, 1625, 1241, 1088, 750 cm$^{-1}$; IR (KBr) for **3m'** $v$ 3446, 2969, 1732, 1622, 1243, 1086, 753 cm$^{-1}$. HRMS (ESI) calcd. for $C_{21}H_{22}NO_5$ $[M+H]^+$: 368.1492, found: 368.1495.




Ethyl 2-(7'-chloro-1'-methyl-2'-oxo-3*H*-spiro[benzofuran-2,3'-indolin]-3-yl)acetate (**3n**/**3n'**)

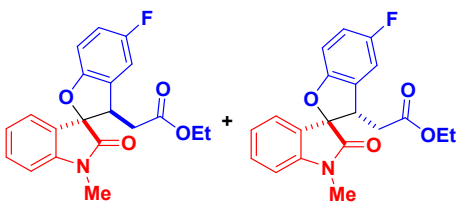
White solids for **3n** and **3n'**, 88.8 mg, 96% isolated yield obtained by silica gel column chromatography (petroleum ether/ethylacetate = 10:1-8:1); Reaction time = 0.5 h; dr = 1:1.7 (**3n**/**3n'**, separable isomers); m. p. 101.5-102.1 °C (**3n**), 150.1-150.7 °C (**3n'**); $^1$H NMR (400 MHz, $CDCl_3$) for **3n** δ 7.29 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 7.24-7.17 (m, 3H), 7.01-6.96 (m, 2H), 6.90 (d, $J$ = 8.0 Hz, 1H), 4.22 (dd, $J_1$ = 8.0 Hz, $J_2$ = 4.0 Hz, 1H), 4.12-3.99 (m, 2H), 3.57 (s, 3H), 3.07 (dd, $J_1$= $J_2$ = 8.0 Hz, 1H), 2.86 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 1.20 (t, $J$ = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3n** δ 173.0, 171.6, 158.4, 139.5, 132.6, 132.4, 129.2, 128.1, 124.2, 124.1, 122.0, 121.6, 115.7, 110.2, 87.0, 60.8, 47.3, 35.6, 29.5, 14.0. $^1$H NMR (400 MHz, $CDCl_3$) for **3n'** δ 7.25 (dd, $J_1$ = $J_2$ = 4.0 Hz, 1H),7.20 (t, $J$ = 8.0 Hz, 1H), 7.14 (d, $J$ = 8.0 Hz, 1H), 6.99-6.94 (m, 2H), 6.87 (dd,

$J_1 = J_2 = 8.0$ Hz, 2H), 4.41 (dd, $J_1 = J_2 = 4.0$ Hz, 1H), 3.92-3.86 (m, 2H), 3.61 (s, 3H), 2.88 (dd, $J_1$ = 8.0 Hz, $J_2$ = 4.0 Hz, 1H), 2.54 (dd, $J_1 = J_2$ = 12.0 Hz, 1H), 1.07 (t, $J$ = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3n'** δ 175.5, 170.5, 158.3, 140.1, 132.8, 129.0, 127.9, 127.7, 123.7, 123.4, 123.3, 121.5, 115.9, 110.0, 87.8, 60.7, 45.0, 35.7, 29.8, 13.9. IR (KBr) for **3n** *v* 3443, 2925, 1733, 1623, 1469, 746 cm$^{-1}$; IR (KBr) for **3n'** *v* 3450, 1731, 1637, 745 cm$^{-1}$. HRMS (ESI) calcd. for $C_{20}H_{19}ClNO_4$ $[M+H]^+$: 372.0997, found: 372.1001.



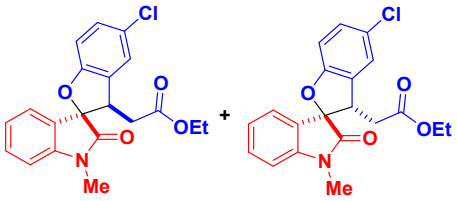

Ethyl 2-(1',7'-dimethyl-2'-oxo-3*H*-spiro[benzofuran-2,3'-indolin]-3-yl)acetate (**3o**/**3o'**)

White solids for **3o** and **3o'**, 79.2 mg, 90% isolated yield obtained by silica gel column chromatography (petroleum ether/ethylacetate = 10:1-8:1); Reaction time = 0.5 h; dr = 1:1 (**3o**/**3o'**, separable isomers); m. p. 117.6-118.3 °C (**3o**), 180.6-181.4 °C (**3o'**); $^1$H NMR (400 MHz, $CDCl_3$) for **3o** δ 7.19 (q, $J$ = 8.0 Hz, 2H), 7.13 (d, $J$ = 8.0 Hz, 1H), 7.08 (d, $J$ = 8.0 Hz, 1H), 6.94 (q, $J$ = 8.0 Hz, 2H), 6.87 (d, $J$= 8.0 Hz, 1H), 4.23 (t, $J$ = 8.0 Hz, 1H), 4.06-3.97 (m, 2H), 3.44 (s, 3H), 2.98 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 2.84 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 2.56 (s, 3H), 1.16 (t, $J$ = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3o** δ 173.4, 171.6, 158.6, 141.2, 134.2, 129.9, 128.9, 128.6, 124.0, 123.3, 121.5, 121.3, 120.0, 110.0, 87.2, 60.6, 47.0, 35.5, 29.6, 18.8, 13.9. $^1$H NMR (400 MHz, $CDCl_3$) for **3o'** δ 7.19 (t, $J$ = 8.0 Hz, 1H),7.14 (d, $J$ = 8.0 Hz, 1H), 7.05 (d, $J$ = 8.0 Hz, 1H), 6.94 (t, $J$ = 8.0 Hz, 2H), 6.86 (dd, $J_1 = J_2$ = 4.0 Hz, 2H), 4.40 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 3.92-3.86 (m, 2H), 3.51 (s, 3H), 2.83 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 2.58-2.51 (m, 4H), 1.06 (t, $J$ = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3o'** δ 176.0, 170.7, 158.6, 141.8, 134.3, 128.8, 128.2, 125.7, 123.8, 122.9, 122.5, 121.2, 120.2, 110.0, 88.0, 60.5, 44.8, 35.9, 29.8, 18.9, 13.9. IR (KBr) for **3o** *v* 3443, 2980, 2929, 1727, 1607, 748 cm$^{-1}$; IR (KBr) for **3o'** *v* 3445, 2928, 2860, 1721, 1635, 755 cm$^{-1}$. HRMS (ESI) calcd. for $C_{21}H_{22}NO_4$ $[M+H]^+$: 352.1543, found: 352.1542.




Ethyl 2-(5-fluoro-1'-methyl-2'-oxo-3*H*-spiro[benzofuran-2,3'-indolin]-3-yl)acetate (**3p**/**3p'**)

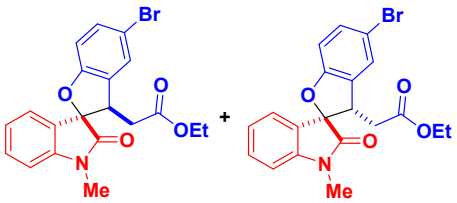
White solids for **3p** and **3p'**, 80.5 mg, 91% isolated yield obtained by silica gel column chromatography (petroleum ether/ethylacetate = 10:1-8:1); Reaction time = 0.5 h; dr = 1:1.1 (**3p**/**3p'**, separable isomers); m. p. 118.7-119.3 °C (**3p**), 176.8-177.6 °C (**3p'**); $^1$H NMR (400 MHz, $CDCl_3$) for **3p** δ 7.36 (tt, $J_1 = J_2 = 8.0$ Hz, 1H), 7.31 (d, $J = 8.0$ Hz, 1H), 7.07 (tt, $J_1 = J_2 = 8.0$ Hz, 1H), 6.92-6.86 (m, 2H), 6.84 (d, $J = 8.0$ Hz, 1H), 6.78 (dd, $J_1 = J_2 = 4.0$ Hz, 1H), 4.25 (t, $J = 8.0$ Hz, 1H), 4.04-3.93 (m, 2H), 3.17 (s, 3H), 2.92 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 2.82 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 1.15 (t, $J = 8.0$ Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3p** δ 172.4, 171.3, 158.0 (d, $J = 237.0$ Hz, 1C), 154.5, 143.7, 130.7, 130.0 (d, $J = 8.0$ Hz, 1C), 128.6, 123.6, 123.4, 115.2 (d, $J = 24.0$ Hz, 1C), 111.5 (d, $J = 25.0$ Hz, 1C), 110.2 (d, $J = 8.0$ Hz, 1C), 108.5, 88.4, 60.8, 46.8 (d, $J = 2.0$ Hz, 1C), 35.1, 26.0, 13.9. $^1$H NMR (400 MHz, $CDCl_3$) for **3p'** δ 7.34 (t, $J = 8.0$ Hz, 1H), 7.12 (d, $J = 8.0$ Hz, 1H), 6.99 (t, $J = 8.0$ Hz, 1H), 6.88-6.82 (m, 3H), 6.76 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 4.38 (dd, $J_1 = 4.0$ Hz, $J_2 = 8.0$ Hz, 1H), 3.86 (q, $J = 8.0$ Hz, 2H), 3.22 (s, 3H), 2.89 (dd, $J_1 = 8.0$ Hz, $J_2 = 4.0$ Hz, 1H), 2.57 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 1.04 (t, $J = 8.0$ Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3p'** δ 174.8, 170.4, 158.0 (d, $J = 237.0$ Hz, 1C), 154.5, 144.3, 130.8, 129.7 (d, $J = 9.0$ Hz, 1C), 125.0, 124.8, 122.6, 115.2 (d, $J = 24.0$ Hz, 1C), 111.3 (d, $J = 25.0$ Hz, 1C), 110.2 (d, $J = 7.0$ Hz, 1C), 108.7, 89.2, 60.7, 44.6, 35.9, 26.4, 13.9. IR (KBr) for **3p** *v* 3433, 2937, 1729, 1478, 1187, 772 cm$^{-1}$; IR (KBr) for **3p'** *v* 3441, 2927, 1729, 1483, 1188, 750 cm$^{-1}$. HRMS (ESI) calcd. for $C_{20}H_{19}FNO_4$ $[M+H]^+$: 356.1293, found: 356.1299.




Ethyl 2-(5-chloro-1'-methyl-2'-oxo-3*H*-spiro[benzofuran-2,3'-indolin]-3-yl)acetate (**3q**/**3q'**)

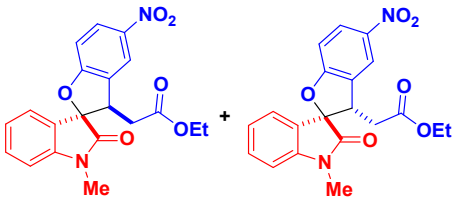
White solid for **3q** and colorless oil for **3q'**, 91.0 mg, 98% isolated yield obtained by silica gel column chromatography (petroleum ether/ethylacetate = 10:1-8:1); Reaction time = 0.5 h; dr = 1.5:1 (**3q**/**3q'**, separable isomers); m. p. 104.9-105.1 °C (**3q**); $^1$H NMR (400 MHz, $CDCl_3$) for **3q** δ 7.37 (t, $J = 8.0$ Hz, 1H), 7.30 (d, $J = 8.0$ Hz, 1H), 7.17 (dd, $J_1 = J_2 = 4.0$ Hz, 2H), 7.08 (t, $J = 8.0$ Hz, 1H), 6.85 (d, $J = 8.0$ Hz, 1H), 6.79 (d, $J = 8.0$ Hz, 1H), 4.25 (t, $J = 8.0$ Hz, 1H), 4.04-3.97 (m, 2H), 3.18 (s, 3H), 2.93 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 2.82 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 1.16 (t, $J = 8.0$ Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3q** δ 172.3, 171.3, 157.4, 143.7, 130.8, 130.5, 129.0,

128.6, 126.3, 124.4, 123.7, 123.5, 111.0, 108.5, 88.5, 60.9, 46.7, 35.2, 26.1, 14.0. $^{1}$H NMR (400 MHz, $CDCl_3$) for **3q'** δ 7.35 (t, $J$ = 8.0 Hz, 1H), 7.18-7.12 (m, 3H), 7.01 (t, $J$ = 8.0 Hz, 1H), 6.84 (d, $J$ = 8.0 Hz, 1H), 6.79 (d, $J$ = 12.0 Hz, 1H), 4.39 (dd, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 1H), 3.86 (q, $J$ = 8.0 Hz, 2H), 3.24 (s, 3H), 2.82 (dd, $J_1$ = $J_2$ = 8.0 Hz, 1H), 2.58 (dd, $J_1$ = $J_2$ = 8.0 Hz, 1H), 1.05 (t, $J$ = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3q'** δ 174.6, 170.4, 157.2, 144.3, 130.9, 130.2, 128.8, 126.2, 125.0, 124.6, 124.2, 122.6, 110.9, 108.7, 89.1, 60.7, 44.4, 35.9, 26.4, 13.9. IR (KBr) for **3q** $v$ 3436, 2970, 1728, 1607, 1474, 1173, 763 cm$^{-1}$; IR (KBr) for **3q'** $v$ 3445, 2969, 1730, 1613, 1472, 1245, 1174, 752 cm$^{-1}$. HRMS (ESI) calcd. for $C_{20}H_{19}ClNO_4$ $[M+H]^+$: 372.0997, found: 372.0995.



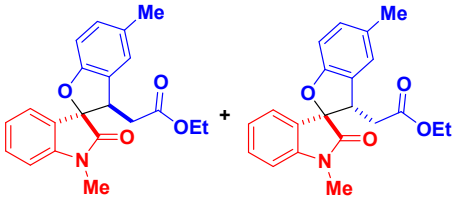

Ethyl 2-(5-bromo-1'-methyl-2'-oxo-3*H*-spiro[benzofuran-2,3'-indolin]-3-yl)acetate (**3r**/**3r'**)

White solids for **3r** and **3r'**, 83.6 mg, 80% isolated yield obtained by silica gel column chromatography (petroleum ether/ethylacetate = 10:1-8:1); Reaction time = 0.5 h; dr = 1.5:1 (**3r**/**3r'**, separable isomers); m. p. 106.8-107.5 °C (**3r**), 114.4-114.6 °C (**3r'**); $^{1}$H NMR (400 MHz, $CDCl_3$) for **3r** δ 7.37 (t, $J$ = 8.0 Hz, 1H), 7.31 (dd, $J_1$ = $J_2$ = 4.0 Hz, 3H), 7.08 (t, $J$ = 8.0 Hz, 1H), 6.85 (d, $J$ = 8.0 Hz, 1H), 6.76 (d, $J$ = 8.0 Hz, 1H), 4.25 (t, $J$ = 8.0 Hz, 1H), 4.05-3.96 (m, 2H), 3.18 (s, 3H), 2.94 (dd, $J_1$ = $J_2$ = 8.0 Hz, 1H), 2.82 (dd, $J_1$ = $J_2$ = 8.0 Hz, 1H), 1.16 (t, $J$ = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3r** δ 172.2, 171.2, 157.9, 143.7, 131.8, 131.0, 130.8, 128.5, 127.2, 123.7, 123.4, 113.3, 111.6, 108.5, 88.4, 60.8, 46.6, 35.2, 26.1, 14.0. $^{1}$H NMR (400 MHz, $CDCl_3$) for **3r'** δ 7.37-7.28 (m, 3H), 7.13 (d, $J$ = 8.0 Hz, 1H), 7.01 (t, $J$ = 8.0 Hz, 1H), 6.84 (d, $J$ = 8.0 Hz, 1H), 6.75 (d, $J$ = 8.0 Hz, 1H), 4.39 (dd, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 1H), 3.86 (q, $J$ = 8.0 Hz, 2H), 3.24 (s, 3H), 2.82 (dd, $J_1$ = $J_2$ = 8.0 Hz, 1H), 2.58 (dd, $J_1$ = $J_2$ = 8.0 Hz, 1H), 1.05 (t, $J$ = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3r'** δ 174.6, 170.4, 157.8, 144.3, 131.8, 130.9, 130.7, 127.0, 125.0, 124.5, 122.6, 113.2, 111.6, 108.7, 89.1, 60.8, 44.3, 35.9, 26.4, 13.9. IR (KBr) for **3r** $v$ 3439, 2971, 1733, 1607, 1469, 1239, 1174, 758 cm$^{-1}$; IR (KBr) for **3r'** $v$ 3453, 2973, 1734, 1613, 1469, 1243, 1177, 747 cm$^{-1}$. $C_{20}H_{19}BrNO_4$ $[M+H]^+$: 416.0492, found: 416.0492.



Ethyl 2-(1'-methyl-5-nitro-2'-oxo-3*H*-spiro[benzofuran-2,3'-indolin]-3-yl)acetate (**3s**/**3s'**)

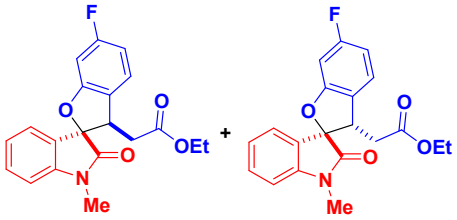
White solids for **3s** and **3s'**, 81.0 mg, 85% isolated yield obtained by silica gel column chromatography (petroleum ether/ethylacetate = 10:1-8:1); Reaction time = 0.5 h; dr = 1:1.6 (**3s**/**3s'**, separable isomers); m. p. 114.5-115.2 °C (**3s**), 118.5-119.1 °C (**3s'**); $^1$H NMR (400 MHz, $CDCl_3$) for **3s** δ 8.16 (dd, $J_1 = J_2 = 4.0$ Hz, 1H), 8.10 (t, $J = 4.0$ Hz, 1H), 7.40 (t, $J = 8.0$ Hz, 1H), 7.34 (d, $J = 8.0$ Hz, 1H), 7.11 (t, $J = 8.0$ Hz, 1H), 6.90 (d, $J = 8.0$ Hz, 1H), 6.87 (d, $J = 8.0$ Hz, 1H), 4.33 (t, $J = 8.0$ Hz, 1H), 4.07-3.96 (m, 2H), 3.17 (s, 3H), 2.91 (d, $J = 8.0$ Hz, 2H), 1.15 (t, $J = 8.0$ Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3s** δ 171.5, 170.8, 163.9, 143.9, 142.7, 131.3, 130.3, 127.2, 126.4, 123.9, 123.6, 120.6, 109.9, 108.7, 89.9, 61.0, 45.7, 34.8, 26.1, 13.9. $^1$H NMR (400 MHz, $CDCl_3$) for **3s'** δ 8.18 (dd, $J_1 = J_2 = 4.0$ Hz, 1H), 8.10 (s, 1H), 7.38 (t, $J = 8.0$ Hz, 1H), 7.12 (d, $J = 8.0$ Hz, 1H), 7.03 (t, $J = 8.0$ Hz, 1H), 6.92 (d, $J = 8.0$ Hz, 1H), 6.86 (d, $J = 4.0$ Hz, 1H), 4.43 (dd, $J_1 = 4.0$ Hz, $J_2 = 8.0$ Hz, 1H), 3.87 (q, $J = 8.0$ Hz, 2H), 3.25 (s, 3H), 2.92 (dd, $J_1 = J_2 = 4.0$ Hz, 1H), 2.65 (dd, $J_1 = J_2 = 12.0$ Hz, 1H), 1.04 (t, $J = 8.0$ Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3s'** δ 174.0, 170.1, 163.7, 144.5, 142.7, 131.4, 130.1, 126.4, 125.2, 123.7, 122.8, 120.5, 109.9, 108.9, 90.4, 61.0, 43.6, 35.9, 26.5, 13.9. IR (KBr) for **3s** *v* 3433, 2973, 1730, 1607, 1472, 1256, 758 cm$^{-1}$; IR (KBr) for **3s'** *v* 3439, 2928, 1728, 1334, 1262, 756 cm$^{-1}$. HRMS (ESI) calcd. for $C_{20}H_{19}N_2O_6$ $[M+H]^+$: 383.1238, found: 383.1242.



Ethyl 2-(1',5-dimethyl-2'-oxo-3*H*-spiro[benzofuran-2,3'-indolin]-3-yl)acetate (**3t**/**3t'**)

Colorless oilfor **3t** and white solid for **3t'**, 75.0 mg, 85% isolated yield obtained by silica gel column chromatography (petroleum ether/ethylacetate = 10:1-8:1); Reaction time = 0.5 h; dr = 1:1.3 (**3t**/**3t'**, separable isomers); m. p. 136.0-136.9 °C (**3t'**); $^1$H NMR (400 MHz, $CDCl_3$) for **3t** δ 7.34 (t, $J = 8.0$ Hz, 1H), 7.28 (d, $J = 8.0$ Hz, 1H), 7.07-6.99 (m, 3H), 6.83 (d, $J = 8.0$ Hz, 1H), 6.77 (d, $J = 8.0$ Hz, 1H), 4.23 (t, $J = 8.0$ Hz, 1H), 4.03-3.94 (m, 2H), 3.16 (s, 3H), 2.99 (dd, $J_1 = J_2 =$

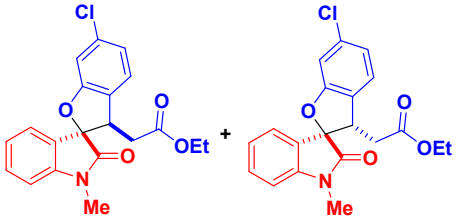
8.0 Hz, 1H), 2.84 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 2.32 (s, 3H), 1.14 (t, $J = 8.0$ Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3t** δ 172.6, 171.5, 156.5, 143.5, 130.6, 130.4, 129.3, 129.3, 128.4, 124.5, 123.4, 123.2, 109.5, 108.3, 87.8, 60.5, 46.8, 35.4, 25.9, 20.7, 13.9. $^1$H NMR (400 MHz, $CDCl_3$) for **3t'** δ 7.32 (t, $J = 8.0$ Hz, 1H), 7.12 (d, $J = 8.0$ Hz, 1H), 7.00-6.96 (m, 3H), 6.82 (d, $J = 8.0$ Hz, 1H), 6.74 (d, $J = 8.0$ Hz, 1H), 4.38 (dd, $J_1 = 4.0$ Hz, $J_2 = 8.0$ Hz, 1H), 3.85 (q, $J = 8.0$ Hz, 2H), 3.22 (s, 3H), 2.84 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 2.57 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 2.31 (s, 3H), 1.04 (t, $J = 8.0$ Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3t'** δ 175.2, 170.7, 156.5, 144.3, 130.7, 130.6, 129.3, 128.1, 125.2, 125.0, 124.4, 122.5, 109.5, 108.5, 88.6, 60.5, 44.5, 36.1, 26.3, 20.8, 13.9. IR (KBr) for **3t** *v* 3432, 2978, 1730, 1617, 1484, 1248, 753 cm$^{-1}$; IR (KBr) for **3t'** *v* 3439, 2927, 1727, 1611, 1484, 1246, 1178, 756 cm$^{-1}$. HRMS (ESI) calcd. for $C_{21}H_{22}NO_4$ $[M+H]^+$: 352.1543, found: 352.1549.




Ethyl 2-(6-fluoro-1'-methyl-2'-oxo-3*H*-spiro[benzofuran-2,3'-indolin]-3-yl)acetate (**3u**/**3u'**)

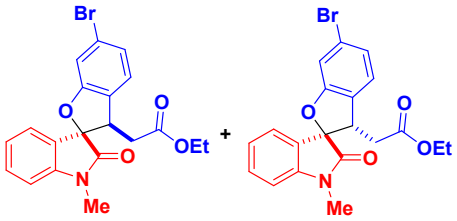
White solid for **3u** and yellow solid for **3u'**, 81.9 mg, 92% isolated yield obtained by silica gel column chromatography (petroleum ether/ethylacetate = 10:1-8:1); Reaction time = 0.5 h; dr = 2:1 (**3u**/**3u'**, separable isomers); m. p. 124.7-124.5 °C (**3u**), 124.6-125.1 °C (**3u'**); $^1$H NMR (400 MHz, $CDCl_3$) for **3u** δ 7.36 (tt, $J_1 = J_2 = 8.0$ Hz, 1H), 7.30 (d, $J = 8.0$ Hz, 1H), 7.12-7.05 (m, 2H), 6.84 (d, $J = 8.0$ Hz, 1H), 6.68-6.58 (m, 2H), 4.21 (t, $J = 8.0$ Hz, 1H), 4.05-3.92 (m, 2H), 3.17 (s, 3H), 2.94 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 2.82 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 1.14 (t, $J = 8.0$ Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3u** δ 172.2, 171.4, 163.6 (d, $J = 243.0$ Hz, 1C), 159.7 (d, $J = 13.0$ Hz, 1C), 143.7, 130.7, 128.7, 124.4 (d, $J = 10.0$ Hz, 1C), 124.2 (d, $J = 3.0$ Hz, 1C), 123.6, 123.4, 108.5, 108.1 (d, $J = 23.0$ Hz, 1C), 98.7 (d, $J = 27.0$ Hz, 1C), 88.9, 60.7, 46.1, 35.5, 26.0, 14.0. $^1$H NMR (400 MHz, $CDCl_3$) for **3u'** δ 7.35 (t, $J = 8.0$ Hz, 1H), 7.13 (d, $J = 8.0$ Hz, 1H), 7.08 (t, $J = 8.0$ Hz, 1H), 7.00 (t, $J = 8.0$ Hz, 1H), 6.83 (d, $J = 8.0$ Hz, 1H), 6.68-6.63 (m, 1H), 6.60-6.57 (m, 1H), 4.35 (dd, $J_1 = 4.0$ Hz, $J_2 = 8.0$ Hz, 1H), 3.87-3.81 (m, 2H), 3.23 (s, 3H), 2.82 (dd, $J_1 = J_2 = 4.0$ Hz, 1H), 2.57 (dd, $J_1 = J_2 = 4.0$ Hz, 1H), 1.04 (t, $J = 8.0$ Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3u'** δ 174.6, 170.5, 163.5 (d, $J = 244.0$ Hz, 1C), 159.6 (d, $J = 13.0$ Hz, 1C), 144.3, 130.9, 125.1, 124.6, 124.2 (d, $J = 10.0$ Hz, 1C), 123.8 (d, $J = 4.0$ Hz, 1C), 122.6, 108.6, 108.0 (d, $J = 22.0$ Hz, 1C),

98.6 (d, $J$ = 26.0 Hz, 1C), 89.6, 60.7, 44.6, 35.9, 26.4, 13.9. IR (KBr) for **3u** $\nu$ 3441, 2976, 1732, 1612, 1487, 1182, 751 $cm^{-1}$; IR (KBr) for **3u'** $\nu$ 3446, 2948, 1730, 1613, 1490, 753 $cm^{-1}$. HRMS (ESI) calcd. for $C_{20}H_{19}FNO_4$ $[M+H]^+$: 356.1293, found: 356.1299.




Ethyl 2-(6-chloro-1'-methyl-2'-oxo-3*H*-spiro[benzofuran-2,3'-indolin]-3-yl)acetate (**3v**/**3v'**)

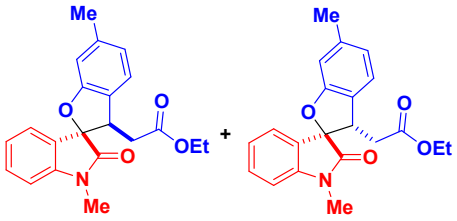
White solids for **3v** and **3v'**, 88.6 mg, 95% isolated yield obtained by silica gel column chromatography (petroleum ether/ethylacetate = 10:1-8:1); Reaction time = 0.5 h; dr = 2:1 (**3v**/**3v'**, separable isomers); m. p. 113.8-114.3 °C (**3v**), 126.3-127.2 °C (**3v'**); $^1$H NMR (400 MHz, $CDCl_3$) for **3v** δ 7.35 (t, $J$ = 8.0 Hz, 1H), 7.28 (d, $J$ = 4.0 Hz, 1H), 7.07 (q, $J$ = 8.0 Hz, 2H), 6.92 (d, $J$ = 8.0 Hz, 1H), 6.84 (t, $J$ = 8.0 Hz, 2H), 4.22 (t, $J$ = 8.0 Hz, 1H), 4.03-3.94 (m, 2H), 3.14 (s, 3H), 2.93 (dd, $J_1$ = $J_2$ = 8.0 Hz, 1H), 2.82 (dd, $J_1$ = $J_2$ = 8.0 Hz, 1H), 1.12 (t, $J$ = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3v** δ 172.0, 171.1, 159.3, 143.6, 134.2, 130.7, 128.4, 127.3, 124.6, 123.5, 123.3, 121.4, 110.7, 108.4, 88.6, 60.6, 46.1, 35.1, 25.9, 13.9. $^1$H NMR (400 MHz, $CDCl_3$) for **3v'** δ 7.34 (tt, $J_1$ = $J_2$ = 8.0 Hz, 1H), 7.12 (d, $J$ = 8.0 Hz, 1H), 7.07 (d, $J$ = 8.0 Hz, 1H), 7.00 (t, $J$ = 8.0 Hz, 1H), 6.93 (dd, $J_1$ = $J_2$ = 4.0 Hz, 1H), 6.85 (d, $J$ = 4.0 Hz, 1H), 6.83 (d, $J$ = 8.0 Hz, 1H), 4.33 (dd, $J_1$ = 8.0 Hz, $J_2$ = 4.0 Hz, 1H), 3.84 (q, $J$ = 8.0 Hz, 2H), 3.22 (s, 3H), 2.81 (dd, $J_1$ = 8.0 Hz, $J_2$ = 4.0 Hz, 1H), 2.56 (dd, $J_1$ = $J_2$ = 12.0 Hz, 1H), 1.03 (t, $J$ = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3v'**δ 174.6, 170.4, 159.3, 144.3, 134.3, 130.9, 127.1, 125.1, 124.5, 124.4, 122.6, 121.5, 110.7, 108.7, 89.3, 60.7, 43.9, 36.0, 26.4, 13.9. IR (KBr) for **3v** $\nu$ 3441, 2975, 1729, 1605, 1470, 1181, 744 $cm^{-1}$; IR (KBr) for **3v'** $\nu$ 3442, 2926, 1728, 1477, 1185, 755 $cm^{-1}$. HRMS (ESI) calcd. for $C_{20}H_{19}ClNO_4$ $[M+H]^+$: 372.0997, found: 372.0994.




Ethyl 2-(6-bromo-1'-methyl-2'-oxo-3*H*-spiro[benzofuran-2,3'-indolin]-3-yl)acetate (**3w**/**3w'**)

White solids for **3w** and **3w'**, 102.1 mg, 98% isolated yield obtained by silica gel column

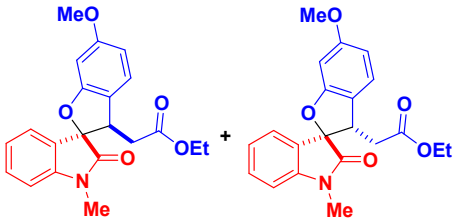
chromatography (petroleum ether/ethylacetate = 10:1-8:1); Reaction time = 0.5 h; dr = 2:1 (**3w**/**3w'**, separable isomers); m. p. 107.1-107.5 °C (**3w**), 135.9-136.9 °C (**3w'**); $^1$H NMR (400 MHz, $CDCl_3$) for **3w** δ 7.37 (t, $J$ = 8.0 Hz, 1H), 7.29 (d, $J$ = 4.0 Hz, 1H), 7.10-7.03 (m, 4H), 6.84 (d, $J$ = 8.0 Hz, 1H), 4.20 (t, $J$ = 8.0 Hz, 1H), 4.04-3.92 (m, 2H), 3.17 (s, 3H), 2.93 (dd, $J_1$ = $J_2$ = 8.0 Hz, 1H), 2.82 (dd, $J_1$ = $J_2$ = 8.0 Hz, 1H), 1.14 (t, $J$ = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3w** δ 172.1, 171.3, 159.5, 143.7, 130.8, 128.5, 128.0, 125.1, 124.5, 123.7, 123.4, 122.1, 113.7, 108.5, 88.6, 60.8, 46.3, 35.2, 26.1, 14.0. $^1$H NMR (400 MHz, $CDCl_3$) for **3w'** δ 7.35 (t, $J$ = 8.0 Hz, 1H), 7.10 (dd, $J_1$ = $J_2$ = 8.0 Hz, 2H), 7.00 (dd, $J_1$ = $J_2$ = 8.0 Hz, 3H), 6.83 (d, $J$ = 8.0 Hz, 1H), 4.32 (dd, $J_1$ = 8.0 Hz, $J_2$ = 4.0 Hz, 1H), 3.84 (q, $J$ = 8.0 Hz, 2H), 3.23 (s, 3H), 2.81 (dd, $J_1$ = 8.0 Hz, $J_2$ = 4.0 Hz, 1H), 2.57 (dd, $J_1$ = 8.0 Hz, $J_2$ = 12.0 Hz, 1H), 1.03 (t, $J$ = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3w'** δ 174.6, 170.4, 159.5, 144.4, 130.9, 127.7, 125.1, 124.9, 124.5, 124.4, 122.6, 122.0, 113.6, 108.7, 89.2, 60.7, 44.0, 36.0, 26.4, 13.9. IR (KBr) for **3w** $v$ 3433, 2983, 1729, 1604, 1468, 1228, 762 cm$^{-1}$; IR (KBr) for **3w'** $v$ 3442, 2983, 1729, 1474, 1186, 756 cm$^{-1}$. HRMS (ESI) calcd. for $C_{20}H_{19}BrNO_4$ $[M+H]^+$: 416.0492, found: 416.0496.




Ethyl 2-(1',6-dimethyl-2'-oxo-3*H*-spiro[benzofuran-2,3'-indolin]-3-yl)acetate (**3x**/**3x'**)

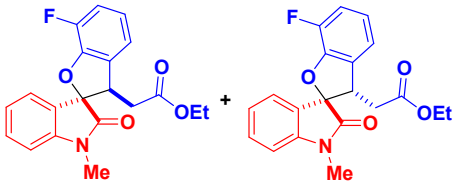
White solids for **3x** and **3x'**, 82.4 mg, 94% isolated yield obtained by silica gel column chromatography (petroleum ether/ethylacetate = 10:1-8:1); Reaction time = 0.5 h; dr = 1:1.5 (**3x**/**3x'**, separable isomers); m. p. 107.5-108.2 °C (**3x**), 109.0-110.0 °C (**3x'**); $^1$H NMR (400 MHz, $CDCl_3$) for **3x** δ 7.34 (tt, $J_1$ = $J_2$ = 8.0 Hz, 2H), 7.28 (d, $J$ = 8.0 Hz, 1H), 7.05 (t, $J$ = 8.0 Hz, 1H), 6.81 (dd, $J_1$ = $J_2$ = 8.0 Hz, 2H), 6.71 (s, 1H), 4.22 (t, $J$ = 8.0 Hz, 1H), 4.03-3.93 (m, 2H), 3.17 (s, 3H), 2.98 (dd, $J_1$ = $J_2$ = 8.0 Hz, 1H), 2.83 (dd, $J_1$ = $J_2$ = 8.0 Hz, 1H), 2.33 (s, 3H), 1.14 (t, $J$ = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3x** δ 172.6, 171.5, 158.8, 143.6, 139.2, 130.4, 129.3, 125.5, 123.5, 123.5, 123.2, 122.1, 110.7, 108.3, 87.9, 60.5, 46.6, 35.6, 25.9, 21.4, 13.9. $^1$H NMR (400 MHz, $CDCl_3$) for **3x'** δ 7.32 (t, $J$ = 8.0 Hz, 1H), 7.12 (d, $J$ = 8.0 Hz, 1H), 7.02 (d, $J$ = 8.0 Hz, 1H), 6.97 (t, $J$ = 8.0 Hz, 1H), 6.82 (d, $J$ = 8.0 Hz, 1H), 6.76 (d, $J$ = 8.0 Hz, 1H), 6.68 (s, 1H), 4.35 (dd, $J_1$ = 8.0 Hz, $J_2$ = 4.0 Hz, 1H), 3.83 (q, $J$ = 8.0 Hz, 2H), 3.22 (s, 3H), 2.83 (dd, $J_1$ = 8.0 Hz, $J_2$

= 4.0 Hz, 1H), 2.56 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 2.32 (s, 3H), 1.03 (t, $J$ = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3x'** δ 175.1, 170.7, 158.7, 144.3, 139.1, 130.5, 125.2, 125.1, 125.0, 123.3, 122.4, 122.0, 110.6, 108.4, 88.6, 60.5, 44.3, 36.2, 26.3, 21.4, 13.8. IR (KBr) for **3x** *v* 3448, 2987, 1718, 1611, 1465, 1370, 762 cm$^{-1}$; IR (KBr) for **3x'** *v* 3445, 2981, 1729, 1609, 1253, 1187, 753 cm$^{-1}$. HRMS (ESI) calcd. for $C_{21}H_{22}NO_4$ $[M+H]^+$: 352.1543, found: 352.1539.



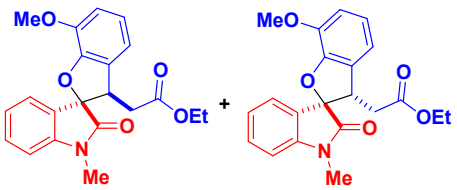

Ethyl 2-(6-methoxy-1'-methyl-2'-oxo-3*H*-spiro[benzofuran-2,3'-indolin]-3-yl)acetate (**3y**/**3y'**)

White solid for **3y**and **3y'**, 71.6 mg, 78% isolated yield obtained by silica gel column chromatography (petroleum ether/ethylacetate = 10:1-8:1); Reaction time = 0.5 h; dr = 1:1.4 (**3y**/**3y'**, separable isomers); m. p. 107.3-108.1 °C (**3y**), 145.5-146.5 °C (**3y'**); $^1$H NMR (400 MHz, $CDCl_3$) for **3y** δ 7.34 (t, $J$ = 8.0 Hz, 1H), 7.28 (d, $J$ = 8.0 Hz, 1H), 7.04 (t, $J$ = 8.0 Hz, 2H), 6.83 (d, $J$ = 8.0 Hz, 1H), 6.50 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 6.47 (d, $J$ = 4.0 Hz, 1H), 4.18 (t, $J$ = 8.0 Hz, 1H), 4.04-3.91 (m, 2H), 3.76 (s, 3H), 3.16 (s, 3H), 2.96 (dd, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 1H), 2.81 (dd, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 1H), 1.13 (t, $J$ = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3y** δ 172.5, 171.5, 160.9, 159.8, 143.5, 130.4, 129.2, 124.1, 123.4, 123.2, 120.3, 108.3, 107.1, 96.6, 88.4, 60.5, 55.4, 46.2, 35.6, 25.9, 13.9. $^1$H NMR (400 MHz, $CDCl_3$) for **3y'** δ 7.32 (tt, $J_1 = J_2$ = 8.0 Hz, 1H), 7.14 (d, $J$ = 4.0 Hz, 1H), 7.03-6.96 (m, 2H), 6.82 (d, $J$ = 8.0 Hz, 1H), 6.49 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 6.45 (d, $J$ = 4.0 Hz, 1H), 4.32 (dd, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 1H), 3.83 (q, $J$ = 8.0 Hz, 2H), 3.76 (s, 3H), 3.22 (s, 3H), 2.82 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 2.54 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 1.03 (t, $J$ = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3y'** δ 175.0, 170.7, 160.9, 159.8, 144.3, 130.6, 125.1, 123.9, 122.5, 120.1, 108.5, 107.0, 96.6, one carbon missing in the aromatic region, 89.2, 60.5, 55.5, 43.9, 36.3, 26.3, 13.9. IR (KBr) for **3y** *v* 3437, 2982, 1727, 1617, 1479, 1266, 757 cm$^{-1}$; IR (KBr) for **3y'** *v* 3442, 2973, 1732, 1614, 1477, 1208, 761 cm$^{-1}$. HRMS (ESI) calcd. for $C_{21}H_{22}NO_5$ $[M+H]^+$: 368.1492, found: 368.1496.




Ethyl 2-(7-fluoro-1'-methyl-2'-oxo-3*H*-spiro[benzofuran-2,3'-indolin]-3-yl)acetate (**3z**/**3z'**)

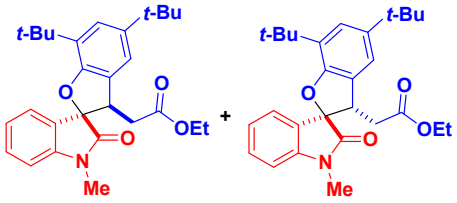
White solids for **3z** and **3z'**, 82.0 mg, 92% isolated yield obtained by silica gel column chromatography (petroleum ether/ethylacetate = 10:1-8:1); Reaction time = 0.5 h; dr = 2.5:1 (**3z**/**3z'**, separable isomers); m. p. 110.0-110.9 °C (**3z**), 147.6-148.5 °C (**3z'**); $^1$H NMR (400 MHz, $CDCl_3$) for **3z** δ 7.20 (dd, $J_1 = J_2 = 12.0$ Hz, 2H), 6.95 (t, $J = 8.0$ Hz, 1H), 6.87 (dd, $J_1 = 8.0$ Hz, $J_2 = 4.0$ Hz, 2H), 6.80-6.77 (m, 1H), 6.73 (d, $J = 8.0$ Hz, 1H), 4.21 (t, $J = 8.0$ Hz, 1H), 3.93-3.79 (m, 2H), 3.04 (s, 3H), 2.88 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 2.75 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 1.01 (t, $J = 8.0$ Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3z** δ 171.8, 171.1, 147.2 (d, $J = 246.0$ Hz, 1C), 145.1 (d, $J = 11.0$ Hz, 1C), 143.7, 132.0, 130.7, 128.2, 123.6, 123.3, 122.0 (d, $J = 5.0$ Hz, 1C), 119.2 (d, $J = 4.0$ Hz, 1C), 116.1 (d, $J = 17.0$ Hz, 1C), 108.4, 88.9, 60.6, 46.7 (d, $J = 2.0$ Hz, 1C), 35.1, 25.9, 13.8. $^1$H NMR (400 MHz, $CDCl_3$) for **3z'** δ 7.33 (t, $J = 8.0$ Hz, 1H), 7.13 (d, $J = 8.0$ Hz, 1H), 7.00-6.86 (m, 4H), 6.82 (d, $J = 8.0$ Hz, 1H), 4.43 (dd, $J_1 = 4.0$ Hz, $J_2 = 8.0$ Hz, 1H), 3.83 (q, $J = 8.0$ Hz, 2H), 3.22 (s, 3H), 2.86 (dd, $J_1 = 4.0$ Hz, $J_2 = 8.0$ Hz, 1H), 2.61 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 1.02 (t, $J = 8.0$ Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3z'** δ 174.4, 170.4, 147.3 (d, $J = 254.0$ Hz, 1C), 145.1 (d, $J = 11.0$ Hz, 1C), 144.4, 131.8 (d, $J = 3.0$ Hz, 1C), 131.0, 125.2, 124.4, 122.6, 122.0 (d, $J = 6.0$ Hz, 1C), 119.1 (d, $J = 4.0$ Hz, 1C), 116.2 (d, $J = 16.0$ Hz, 1C), 108.6, 89.7, 60.7, 44.6 (d, $J = 2.0$ Hz, 1C), 36.0, 26.4, 13.8. IR (KBr) for **3z** *v* 3438, 2983, 1727, 1617, 1479, 1266, 757 cm$^{-1}$; IR (KBr) for **3z'** *v* 3452, 2970, 1733, 1620, 763 cm$^{-1}$. HRMS (ESI) calcd. for $C_{20}H_{19}FNO_4$ $[M+H]^+$: 356.1293, found: 356.1292.




Ethyl 2-(7-methoxy-1'-methyl-2'-oxo-3*H*-spiro[benzofuran-2,3'-indolin]-3-yl)acetate (**3za**/**3za'**)

Colorless oilfor **3za** and white solid for **3za'**, 86.0 mg, 94% isolated yield obtained by silica gel column chromatography (petroleum ether/ethylacetate = 10:1-8:1); Reaction time = 0.5 h; dr = 1.4:1 (**3za**/**3za'**, separable isomers); m. p. 124.1-124.7 °C (**3za'**); $^1$H NMR (400 MHz, $CDCl_3$) for

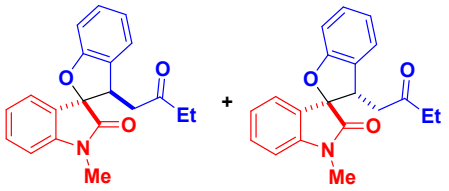
**3za** δ 7.24-7.21 (m, 2H), 6.95 (t, $J$ = 8.0 Hz, 1H), 6.83 (t, $J$ = 8.0 Hz, 1H), 6.75-6.72 (m, 3H), 4.23 (t, $J$ = 8.0 Hz, 1H), 3.96-3.82 (m, 2H), 3.74 (s, 3H), 3.06 (s, 3H), 2.95 (dd, $J_1$ = $J_2$ = 8.0 Hz, 1H), 2.79 (dd, $J_1$ = $J_2$ = 8.0 Hz, 1H), 1.04 (t, $J$ = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3za** δ 172.0, 171.2, 146.5, 144.3, 143.5, 130.3, 129.4, 128.8, 123.4, 122.9, 121.9, 115.7, 111.9, 108.0, 87.9, 60.3, 55.6, 46.7, 35.1, 25.7, 13.7. $^1$H NMR (400 MHz, $CDCl_3$) for **3za'** δ 7.30 (t, $J$ = 8.0 Hz, 1H), 7.14 (d, $J$ = 8.0 Hz, 1H), 6.95 (t, $J$ = 8.0 Hz, 1H), 6.90 (t, $J$ = 8.0 Hz, 1H), 6.78 (q, $J$ = 8.0 Hz, 3H), 4.42 (dd, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 1H), 3.85-3.79 (m, 5H), 3.20 (s, 3H), 2.86 (dd, $J_1$ = $J_2$ = 8.0 Hz, 1H), 2.62 (dd, $J_1$ = $J_2$ = 8.0 Hz, 1H), 1.01 (t, $J$ = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3za'** δ 174.8, 170.6, 146.7, 144.5, 144.5, 130.6, 129.3, 125.2, 124.9, 122.4, 122.0, 115.8, 112.1, 108.3, 88.8, 60.5, 55.9, 44.7, 36.1, 26.3, 13.8. IR (KBr) for **3za** $v$ 3448, 2976, 1730, 1619, 1485, 1279, 756 cm$^{-1}$; IR (KBr) for **3za'** $v$ 3445, 2930, 1732, 1616, 1463, 1380, 752 cm$^{-1}$. HRMS (ESI) calcd. for $C_{21}H_{22}NO_5$ $[M+H]^+$: 368.1492, found: 368.1489.




Ethyl 2-(5,7-di-tert-butyl-1'-methyl-2'-oxo-3*H*-spiro[benzofuran-2,3'-indolin]-3-yl)acetate (**3zb**/**3zb'**)

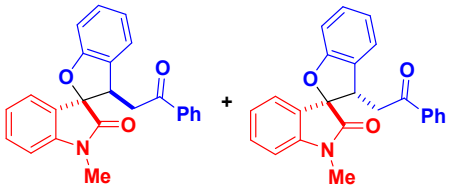
White solids for **3zb** and **3zb'**, 103.0 mg, 92% isolated yield obtained by silica gel column chromatography (petroleum ether/ethylacetate = 10:1-8:1); Reaction time = 0.5 h; dr = 1:2.3 (**3zb**/**3zb'**, separable isomers); m. p. 143.4-144.1 °C (**3zb**), 165.4-165.9 °C (**3zb'**); $^1$H NMR (400 MHz, $CDCl_3$) for **3zb** δ 7.34 (tt, $J_1$ = $J_2$ = 8.0 Hz, 1H), 7.28 (d, $J$ = 8.0 Hz, 1H), 7.20 (d, $J$ = 4.0 Hz, 1H), 7.07-7.03 (m, 2H), 6.85 (d, $J$ = 8.0 Hz, 1H), 4.20 (dd, $J_1$ = $J_2$ = 8.0 Hz, 1H), 4.05-3.91 (m, 2H), 3.19 (s, 3H), 3.00 (dd, $J_1$ = $J_2$ = 8.0 Hz, 1H), 2.86 (dd, $J_1$ = $J_2$ = 8.0 Hz, 1H), 1.34 (s, 18H), 1.15 (t, $J$ = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3zb** δ 173.0, 171.7, 154.4, 143.9, 143.6, 132.5, 130.2, 130.1, 128.1, 123.4, 123.1, 122.7, 118.3, 108.2, 87.6, 60.5, 47.1, 35.8, 34.5, 34.2, 31.8, 29.3, 26.0, 14.0. $^1$H NMR (400 MHz, $CDCl_3$) for **3zb'** δ 7.32 (tt, $J_1$ = $J_2$ = 4.0 Hz, 1H), 7.18 (s, 1H), 7.12 (d, $J$ = 8.0 Hz, 1H), 7.01 (s, 1H), 6.97 (t, $J$ = 8.0 Hz, 1H), 6.83 (d, $J$ = 8.0 Hz, 1H), 4.37 (dd, $J_1$ = 8.0 Hz, $J_2$ = 4.0 Hz, 1H), 3.85 (q, $J$ = 8.0 Hz, 2H), 3.25 (s, 3H), 2.87 (dd, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 1H), 2.57 (dd, $J_1$ = $J_2$ = 12.0 Hz, 1H), 1.32 (s, 18H), 1.05 (t, $J$ = 8.0 Hz, 3H); $^{13}$C

NMR (100 MHz, $CDCl_3$) for **3zb'** δ 175.6, 170.8, 154.3, 144.2, 143.9, 132.3, 130.2, 127.8, 125.8, 124.8, 122.5, 122.3, 118.1, 108.3, 88.3, 60.4, 44.7, 36.3, 34.5, 34.1, 31.7, 29.3, 26.3, 13.9. IR (KBr) for **3zb** *v* 3445, 2958, 1733, 1612, 1249, 763 $cm^{-1}$; IR (KBr) for **3zb'** *v* 3452, 2960, 1733, 1469, 1362, 1168, 759 $cm^{-1}$. HRMS (ESI) calcd. for $C_{28}H_{36}NO_4$ $[M+H]^+$: 450.2639, found: 450.2635.




1'-Methyl-3-(2-oxobutyl)-3*H*-spiro[benzofuran-2,3'-indolin]-2'-one (**3zc**/**3zc'**)

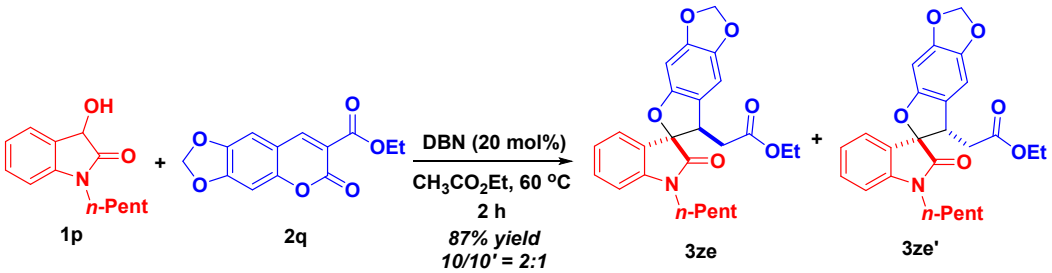
White solids for **3zc** and **3zc'**, 76.5 mg, 95% isolated yield obtained by silica gel column chromatography (petroleum ether/ethylacetate = 10:1-8:1); Reaction time = 0.5 h; dr = 1:1.8 (**3zc**/**3zc'**, separable isomers); m. p. 119.4-120.3 °C (**3zc**), 168.1-168.9 °C (**3zc'**); $^1H$ NMR (400 MHz, $CDCl_3$) for **3zc** δ 7.34 (t, $J$ = 8.0 Hz, 1H), 7.20 (t, $J$ = 8.0 Hz, 2H), 7.13 (d, $J$ = 8.0 Hz, 1H), 7.02 (t, $J$ = 8.0 Hz, 1H), 6.95 (t, $J$ = 8.0 Hz, 1H), 6.87 (dd, $J_1$ = $J_2$ = 8.0 Hz, 2H), 4.45 (dd, $J_1$ = $J_2$ = 8.0 Hz, 1H), 3.32 (dd, $J_1$ = 8.0 Hz, $J_2$ = 12.0 Hz, 1H), 3.15 (s, 3H), 2.85 (dd, $J_1$ = $J_2$ = 4.0 Hz, 1H), 2.48-2.34 (m, 2H), 1.01 (t, $J$ = 8.0 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) for **3zc** δ 209.7, 173.1, 158.6, 143.1, 130.3, 130.1, 129.0, 128.9, 124.2, 123.3, 123.0, 121.4, 110.2, 108.5, 87.4, 45.8, 44.4, 35.7, 26.0, 7.65. $^1H$ NMR (400 MHz, $CDCl_3$) for **3zc'** δ 7.29 (tt, $J_1$ = $J_2$ = 8.0 Hz, 1H), 7.17 (t, $J$ = 8.0 Hz, 1H), 7.09 (d, $J$ = 4.0 Hz, 1H), 7.05 (d, $J$ = 8.0 Hz, 1H), 6.96-6.92 (m, 2H), 6.84 (d, $J$ = 8.0 Hz, 1H), 6.78 (d, $J$ = 8.0 Hz, 1H), 4.43 (dd, $J_1$ = 8.0 Hz, $J_2$ = 4.0 Hz, 1H), 3.24 (s, 3H), 2.94 (dd, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 1H), 2.81 (dd, $J_1$ = $J_2$ = 8.0 Hz, 1H), 2.15-2.05 (m, 1H), 1.85-1.71 (m, 1H), 0.69 (t, $J$ = 8.0 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) for **3zc'** δ 208.2, 175.3, 158.6, 144.4, 130.6, 128.7, 128.3, 125.4, 124.6, 123.6, 122.1, 121.2, 109.9, 108.6, 88.6, 44.0, 43.6, 35.4, 26.3, 7.5. IR (KBr) for **3zc** *v* 3421, 1723, 1619, 1473, 754 $cm^{-1}$; IR (KBr) for **3zc'** *v* 3444, 2974, 1725, 1611, 1476, 1246, 755 $cm^{-1}$. HRMS (ESI) calcd. for $C_{20}H_{20}NO_3$ $[M+H]^+$: 322.1438, found: 322.1432.



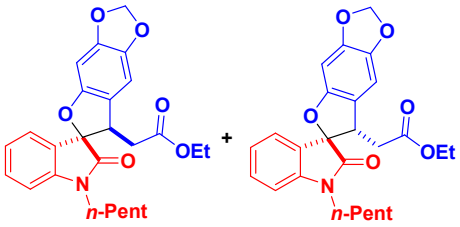
1'-Methyl-3-(2-oxo-2-phenylethyl)-3*H*-spiro[benzofuran-2,3'-indolin]-2'-one (**3zd**/**3zd'**)

White solids for **3zd** and **3zd'**, 77.8 mg, 84% isolated yield obtained by silica gel column chromatography (petroleum ether/ethylacetate = 10:1-8:1); Reaction time = 0.5 h; dr = 1:1.6 (**3zd**/**3zd'**, separable isomers); m. p. 148.7-149.6 °C (**3zd**), 194.9-195.8 °C (**3zd'**); $^{1}$H NMR (400 MHz, $CDCl_3$) for **3zd** δ 7.86 (d, $J$ = 8.0 Hz, 2H), 7.52 (t, $J$ = 8.0 Hz, 1H), 7.40 (t, $J$ = 8.0 Hz, 2H), 7.34 (tt, $J_1 = J_2$ = 8.0 Hz, 1H), 7.25-7.19 (m, 3H), 7.03 (t, $J$ = 8.0 Hz, 1H), 6.95 (t, $J$ = 8.0 Hz, 1H), 6.90 (d, $J$ = 8.0 Hz, 1H), 6.83 (d, $J$ = 8.0 Hz, 1H), 4.45 (dd, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 1H), 3.90 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 3.39 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 3.06 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3zd** δ 198.3, 173.0, 158.6, 143.3, 136.4, 133.2, 130.3, 130.0, 129.0, 128.9, 128.5, 127.9, 124.3, 123.3, 123.1, 121.4, 110.2, 108.4, 87.5, 46.1, 40.9, 26.0. $^{1}$H NMR (400 MHz, $CDCl_3$) for **3zd'** δ 7.62 (d, $J$ = 4.0 Hz, 2H), 7.47 (t, $J$ = 8.0 Hz, 1H), 7.33 (t, $J$ = 8.0 Hz, 2H), 7.21 (t, $J$ = 8.0 Hz, 2H), 7.14 (t, $J$ = 8.0 Hz, 1H), 7.06 (d, $J$ = 4.0 Hz, 1H), 6.97 (t, $J$ = 8.0 Hz, 1H), 6.88 (d, $J$ = 8.0 Hz, 1H), 6.79 (t, $J$ = 8.0 Hz, 1H), 6.71 (d, $J$ = 8.0 Hz, 1H), 4.62 (dd, $J_1$ = 8.0 Hz, $J_2$ = 4.0 Hz, 1H), 3.51-3.39 (m, 2H), 3.28 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3zd'** δ 197.1, 175.3, 158.7, 144.3, 136.1, 133.0, 130.5, 128.8, 128.5, 128.3, 127.5, 125.4, 124.5, 123.8, 122.1, 121.2, 110.0, 108.6, 88.8, 44.3, 40.4, 26.4. IR (KBr) for **3zd** $v$ 3443, 2923, 1728, 1679, 1605, 1467, 1233, 761 cm$^{-1}$; IR (KBr) for **3zd'** $v$ 3448, 2923, 1730, 1186, 747 cm$^{-1}$. HRMS (ESI) calcd. for $C_{24}H_{20}NO_3$ $[M+H]^+$: 370.1438, found: 370.1433.

## 5. Experimental data for XEN907 analogue 3ze and 3ze'



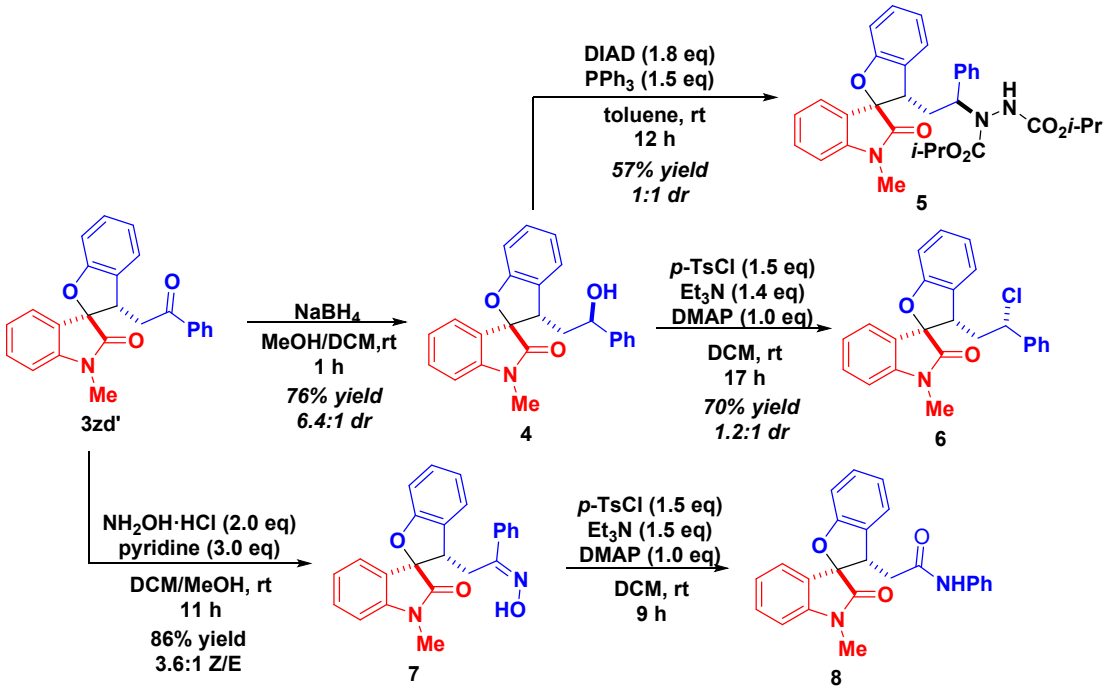

**General procedure:** To a 5.0 mL vial were successively added 3-hydroxyoxindole **1p** (0.25 mmol), coumarin-3-carboxylate **2q** (0.25 mmol), DBN (0.05 mmol) and 1.0 mL EtOAc. The resulting mixture was stirred at 60 °C for 2 h, and then the reaction mixture was directly subjected to flash column chromatography on silica gel (petroleum ether/ ethyl acetate) to afford the corresponding XEN907 analogues **3ze** and **3ze'** in 87% yield with 2:1 dr.



Ethyl 2-(2-oxo-1-pentyl-7'*H*-spiro[indoline-3,6'-[1,3]dioxolo[4,5-*f*]benzofuran]-7'-yl)acetate (**3ze**/**3ze'**)

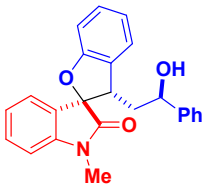
White solids for **3ze** and **3ze'**, 95.1 mg, 87% isolated yield obtained by silica gel column chromatography (petroleum ether/ethylacetate = 10:1-8:1); Reaction time = 0.5 h; dr = 2:1 (**3ze**/**3ze'**, separable isomers); m. p. 102.1-102.8 °C (**3ze**), 118.2-118.6 °C (**3ze'**); $^{1}$H NMR (400 MHz, $CDCl_3$) for **3ze** δ 7.35-7.29 (m, 2H), 7.03 (t, $J$ = 8.0 Hz, 1H), 6.83 (d, $J$ = 4.0 Hz, 1H), 6.65 (s, 1H), 6.45 (s, 1H), 5.92 (dd, $J_1$ = $J_2$ = 4.0 Hz, 2H), 4.14 (t, $J$ = 8.0 Hz, 1H), 4.01 (q, $J$ = 8.0 Hz, 2H), 3.71-3.56 (m, 2H), 2.94 (dd, $J_1$ = $J_2$ = 8.0 Hz, 1H), 2.76 (dd, $J_1$ = $J_2$ = 8.0 Hz, 1H), 1.74-1.66 (m, 2H), 1.38-1.34 (m, 4H), 1.16 (t, $J$ = 8.0 Hz, 3H), 0.90 (t, $J$ = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3ze** δ 172.4, 171.6, 153.2, 148.0, 143.1, 142.3, 130.5, 129.4, 123.7, 123.1, 119.5, 108.6, 104.3, 101.4, 93.7, 88.4, 60.7, 46.7, 40.1, 35.7, 29.0, 26.9, 22.3, 14.0, 13.9. $^{1}$H NMR (400 MHz, $CDCl_3$) for **3ze'** δ 7.29 (q, $J$ = 8.0 Hz, 1H), 7.16 (d, $J$ = 8.0 Hz, 1H), 6.96 (t, $J$ = 4.0 Hz, 1H), 6.81 (d, $J$ = 8.0 Hz, 1H), 6.61 (s, 1H), 6.42 (s, 1H), 5.90 (d, $J$ = 12.0 Hz, 2H), 4.28 (dd, $J_1$ = 8.0 Hz, $J_2$ = 4.0 Hz, 1H), 3.84 (q, $J$ = 8.0 Hz, 2H), 3.67 (t, $J$ = 8.0 Hz, 2H), 2.73 (dd, $J_1$ = $J_2$ = 8.0 Hz, 1H), 2.52 (dd, $J_1$ = $J_2$ = 8.0 Hz, 1H), 1.72-1.68 (m, 2H), 1.39-1.36 (m, 4H), 1.02 (t, $J$ = 8.0 Hz, 3H), 0.89 (t, $J$ = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **3ze'** δ 174.7, 170.5, 153.1, 147.9, 143.8, 142.2, 130.5, 125.2, 125.1, 122.2, 119.1, 108.8, 104.0, 101.3, 93.4, 89.1, 60.5, 44.4, 40.2, 36.3, 28.9, 26.8, 22.2, 13.9, 13.8. IR (KBr) for **3ze** *v*3429, 2929, 1728, 1466, 1151, 1035, 751 cm$^{-1}$; IR (KBr) for **3ze'** *v*3431, 2933, 1729, 1467, 1155, 910, 735 cm$^{-1}$. HRMS (ESI) calcd. for $C_{25}H_{28}NO_6$ $[M+H]^+$: 438.1911, found: 438.1900.

## 6. Experimental data for derivations of 3zd'




**Scheme S1** Chemical transformations of **3zd'**

**General procedure for the formation of 4:** A solution of **3zd'** (111.0 mg, 0.30 mmol) in 4.0 mL MeOH and 2.0 mL DCM was cooled to 0 °C, and then $NaBH_4$ (22.8 mg, 0.6 mmol) was added successively. The reaction mixture was stirred at 0 °C for 1 h until the complete consumption of **3zd'** as monitored by thin layer chromatography. Then, saturated aq. $NH_4Cl$ solution was added.The mixture was extracted with $CH_2Cl_2$. The combined organic phase was dried over $MgSO_4$, filtered, concentrated and purified with silica gel column chromatography to obtain **4** in 76% yield with 6.4:1 dr.

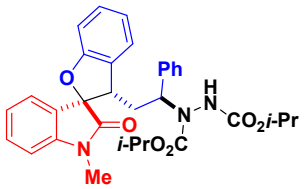


3-(2-Hydroxy-2-phenylethyl)-1'-methyl-3*H*-spiro[benzofuran-2,3'-indolin]-2'-one (**4**)

White solid, 85.1mg, 76% isolated yield obtained by silica gel column chromatography (petroleum ether/ethylacetate = 3:1); Reaction time = 1 h; dr = 6.4:1 (inseparable isomers); m. p. 166.1-166.5 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, *J* = 8.0 Hz, 1H), 7.29-7.16 (m, 5H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 1H), 7.00-6.91 (m, 2H), 6.85 (t, *J* = 8.0 Hz, 2H), 4.61-4.57 (m, 1H), 4.08 (t, *J* = 8.0 Hz, 1H), 3.20 (s, 3H), 2.22-2.16 (m, 1H), 2.02-1.91 (m, 2H); $^{13}$C NMR

(100 MHz, $CDCl_3$) δ 175.2, 158.2, 144.0, 143.9, 130.4, 129.9, 128.4, 127.6, 126.0, 125.6, 124.9, 124.8, 124.1, 122.6, 121.1, 109.8, 108.7, 89.8, 72.5, 45.6, 39.5, 26.2. IR (KBr) *v* 2922, 1720, 1609, 1469, 1375, 753$cm^{-1}$. HRMS (ESI) calcd. for $C_{24}H_{22}NO_3$ $[M+H]^+$: 372.1594, found: 372.1598.

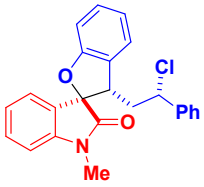
**General procedure for the formation of 5:** To a solution of **4** (94.2 mg, 0.25 mmol) in 1.0 mL toluene, $PPh_3$ (98.4 mg, 0.38mmol) and DIAD (91.0 mg, 0.45 mmol) were successively added. The resulting mixture was stirred at room temperature for 17 h until complete consumption of **4** as monitored by thin layer chromatography. Afterward, the reaction mixture was concentrated and purified by silica gel column chromatography (petroleum ether/ ethyl acetate) to form **5** as a white solid in 57% yield with 2:1 dr.




Diisopropyl 1-(1'-methyl-2'-oxo-3*H*-spiro[benzofuran-2,3'-indolin]-3-yl)-1-phenylethyl)hydrazine-1,2-dicarboxylate (**5**)

White solid, 79.6mg, 57% isolated yield obtained by silica gel column chromatography (petroleum ether/ethylacetate = 25:1-15:1); Reaction time = 12 h; dr = 2:1 (inseparable isomers); m. p. 141.6-142.5°C; $^1H$ NMR (400 MHz, DMSO-$d_6$) δ 9.49-8.81 (m, 1H), 7.59-6.84 (m, 13H), 4.90-4.70 (m, 2H), 4.52-3.88 (m, 2H), 3.21 (s, 3H), 2.65-2.35 (m, 1H), 2.04-1.86 (m, 1H), 1.23-1.13 (m, 12H); $^{13}C$ NMR (100 MHz, DMSO-$d_6$) δ 174.5, 158.1, 156.2, 155.1, 144.3, 139.1, 138.6, 130.7, 128.4, 128.1, 127.8, 127.4, 127.2, 125.3, 124.9, 124.7, 122.4, 120.9, 109.3, 88.1, 79.2, 69.1, 67.9, 57.2, 44.8, 26.4, 21.9, 21.4. IR (KBr) *v* 3449, 3306, 2981, 1729, 1246, 1105, 754 $cm^{-1}$. HRMS (ESI) calcd. for $C_{32}H_{36}N_3O_6$ $[M+H]^+$: 558.2599, found: 558.2582.

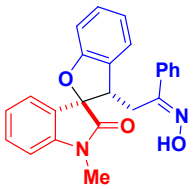
**General procedure for the formation of 6:** To a solution of **4** (110.0 mg, 0.3 mmol) in 2.0 mL DCM, *p*-TsCl (85.8 mg, 0.45 mmol), DMAP (36.6 mg, 0.30 mmol) and $Et_3N$ (42.5 mg, 0.42 mmol) were successively added. The resulting mixture was stirred at room temperature for 17 h. After completion of the reaction, the reaction mixture was concentrated and purified by silica gel column chromatography (petroleum ether/ ethyl acetate) to afford **6** as a white solid in 70% yield.




3-(2-Chloro-2-phenylethyl)-1'-methyl-3*H*-spiro[benzofuran-2,3'-indolin]-2'-one (**6**)

White solid, 82.1 mg, 70% isolated yield obtained by silica gel column chromatography (petroleum ether/ethylacetate = 35:1-20:1); Reaction time = 17 h; dr = 2:1 (inseparable isomers); m. p. 162.5-163.1°C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.43 (t, $J$ = 8.0 Hz, 1H), 7.30-7.10 (m, 7H), 7.03-6.78 (m, 5H), 4.40 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 4.10 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.24 (s, 3H), 2.58-2.51 (m, 1H), 2.26-2.18 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 175.1, 158.4, 143.9, 134.1, 130.9, 128.8, 128.7, 128.5, 128.2, 126.1, 125.3, 125.1, 124.9, 123.7, 123.0, 121.3, 109.9, 108.9, 88.4, 60.9, 46.3, 26.5. IR (KBr) $v$ 3450, 2921, 1733, 1609, 1467, 1235, 752cm$^{-1}$. HRMS (ESI) calcd. for $C_{24}H_{21}ClNO_2$ $[M+H]^+$: 390.1255, found: 390.1258.

**General procedure for the synthesis of 7：** To a 5.0 mL vial were successively added dihydeobenzofuran spirooxindole **3zd'** (92.5 mg, 0.25 mmol), hydroxylamine hydrochloride (34.8 mg, 0.50 mmol) and 1.0 mL EtOAc and 1.0 mL $CH_2Cl_2$. Then, pyridine (59.5 mg, 0.73 mmol) was added by syringe. The resulting mixture was stirred at 50 °C for 11 h until almost full consumption of **3zd'** as 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 oxime **7** in 86% yield with a E/Z ratio of 3.6:1.

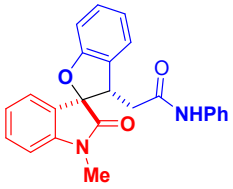



3-(2-(Hydroxyimino)-2-phenylethyl)-1'-methyl-3*H*-spiro[benzofuran-2,3'-indolin]-2'-one (**7**)

White solid, 82.5 mg, 86% isolated yield obtained by silica gel column chromatography (petroleum ether/ethylacetate = 5:1-3:1); Reaction time = 11 h; dr = 3.6:1 (inseparable isomers); m. p. 187.2-188.0°C; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 11.39 (s, 1H), 7.41-7.00 (m, 9H), 6.98-6.91 (m, 4H), 4.33 (t, $J$ = 8.0 Hz, 1H), 3.41 (d, $J$ = 4.0 Hz, 1H), 2.98 (s, 3H), 2.75 (dd, $J_1 = J_2$ = 8.0 Hz, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 173.7, 158.0, 154.3, 143.6, 135.6, 130.8, 129.3, 128.7, 128.4, 128.2, 127.2, 125.9, 124.8, 124.3, 122.5, 121.3, 109.4, 109.3, 88.8, 44.9, 26.1, 26.1. IR

(KBr) *v* 3448, 1627, 1469, 752cm$^{-1}$. HRMS (ESI) calcd. for $C_{24}H_{21}N_2O_3$ $[M+H]^+$: 385.1547, found: 385.1544.

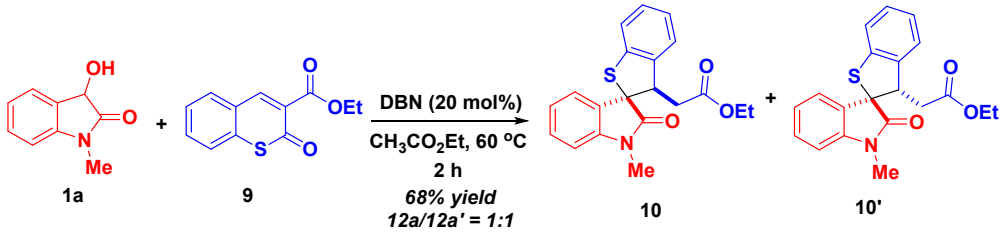
**General procedure for the synthesis of 8：** To a solution of **7** (56.5 mg, 0.15 mmol) in 1.0 mL DCM, *p*-TsCl (43.8 mg, 0.23 mmol), DMAP (18.3 mg, 0.15 mmol) and $Et_3N$ (21.2 mg, 0.21 mmol) were successively added. The resulting mixture was stirred at room temperature for 9 h. After completion of the reaction, the reaction mixture was concentrated and purified by silica gel column chromatography (petroleum ether/ ethyl acetate) to afford **8** as a white solid in 52% yield.



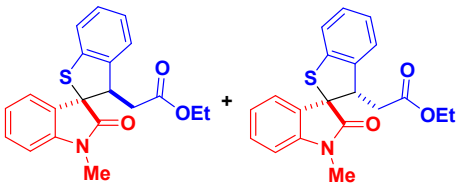

2-(1'-Methyl-2'-oxo-3*H*-spiro[benzofuran-2,3'-indolin]-3-yl)-*N*-phenylacetamide (**8**)

White solid, 30.2mg, 52% isolated yield obtained by silica gel column chromatography (petroleum ether/ethylacetate = 15:1-3:1); Reaction time = 9 h; m. p. 104.6-105.5$^o$C; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.23-7.05 (m, 10H), 6.95-6.90 (m, 2H), 6.83 (d, $J$ = 12.0 Hz, 1H), 6.67 (d, $J$ = 6.0 Hz, 1H), 4.51 (dd, $J_1 = J_2$ = 6.0 Hz, 1H), 3.08 (s, 3H), 2.91 (dd, $J_1 = J_2$ = 6.0 Hz, 1H), 2.50 (dd, $J_1 = J_2$ = 12.0 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 175.3, 167.8, 158.7, 144.3, 137.5, 130.8, 128.9, 128.7, 128.2, 125.3, 124.7, 124.1, 123.9, 122.4, 121.4, 119.6, 110.0, 108.9, 88.7, 45.2, 38.7, 26.4. IR (KBr) *v* 3430, 2924, 1511, 1017, 754cm$^{-1}$. HRMS (ESI) calcd. for $C_{24}H_{21}N_2O_3$ $[M+H]^+$: 385.1547, found: 385.1549.

## 7. Experimental data for dihydrobenzothiophene spirooxindoles 10 and 10'




**General procedure：** To a 5.0 mL vial were successively added 3-hydroxyoxindole **1a** (0.25mmol), coumarin-3-carboxylate **9** (0.25 mmol), DBN (0.05 mmol) and 1.0 mL EtOAc. The resulting mixture was stirred at 60 $^o$C for 2 h, and then the reaction mixture was directly subjected to flash column chromatography on silica gel (petroleum ether/ ethyl acetate) to afford the corresponding dihydrobenzothiophene spirooxindoles **10** and **10'** in 68% yield with 1:1 dr.

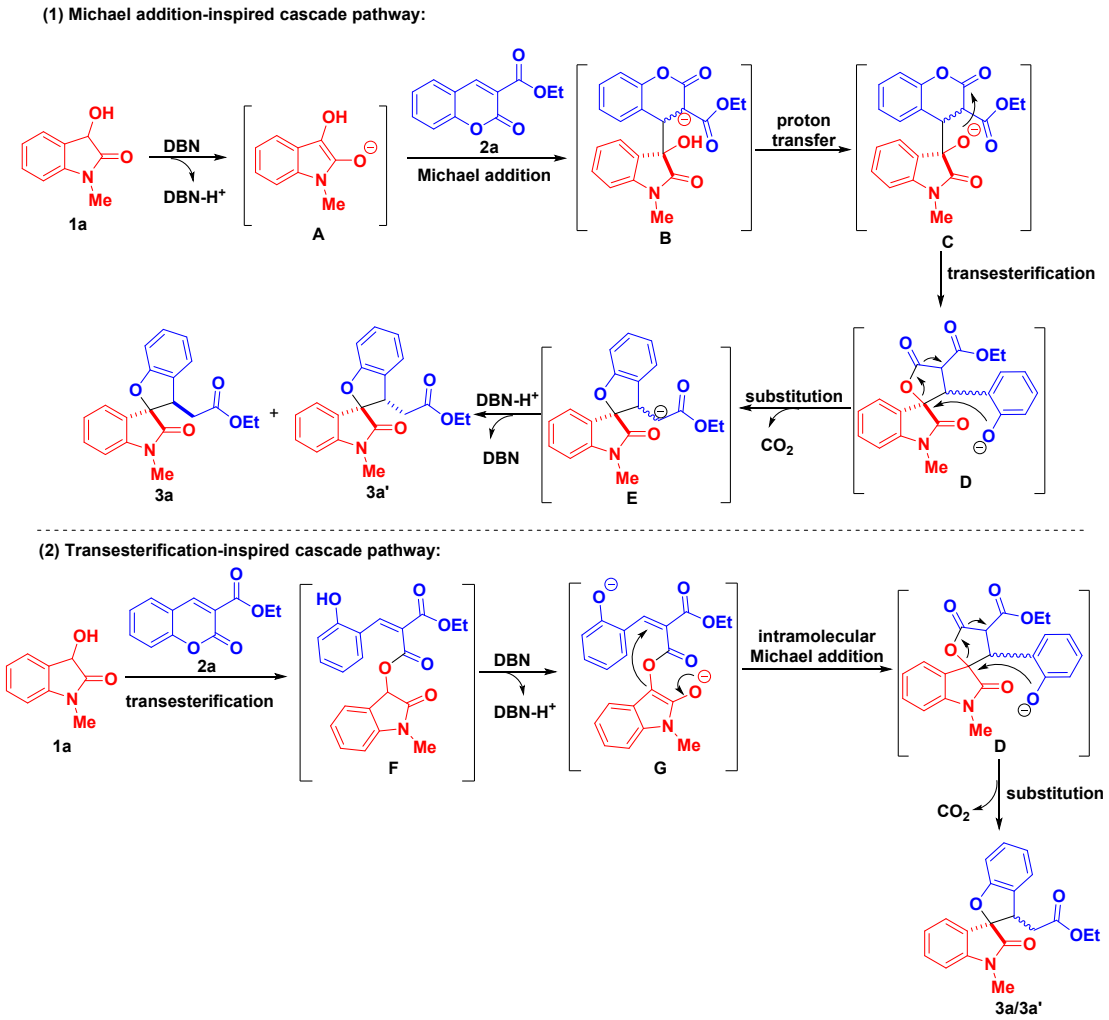



ethyl 2-(1'-methyl-2'-oxo-3*H*-spiro[benzo[*b*]thiophene-2,3'-indolin]-3-yl)acetate (**10**/**10'**)

White solids for **10** and **10'**, 59.8mg, 68% isolated yield obtained by silica gel column chromatography (petroleum ether/ethylacetate = 35:1-15:1); Reaction time = 2 h; dr = 1:1 (**10**/**10'**, separable isomers); m. p. 121.2-121.5°C (**10**), 152.0-152.2°C (**10'**); $^{1}$H NMR (400 MHz, $CDCl_3$) for **10** δ 7.43 (d, $J$ = 12.0 Hz, 1H), 7.32 (t, $J$ = 8.0 Hz, 1H), 7.23-7.04 (m, 5H), 6.83 (d, $J$ = 8.0 Hz, 1H), 4.43 (t, $J$ = 8.0 Hz, 1H), 3.87 (q, $J$ = 8.0 Hz, 2H), 3.20 (s, 3H), 2.80 (dd, $J_1$ = $J_2$ = 8.0 Hz, 1H), 2.67 (dd, $J_1$ =$J_2$ = 8.0 Hz, 1H), 1.15 (t, $J$ = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **10** δ 174.8, 171.5, 143.3, 139.9, 138.8, 129.6, 128.6, 128.4, 128.3, 125.4, 123.9, 123.1, 122.3, 108.2, 62.9, 60.7, 52.0, 34.4, 26.3, 14.0. $^{1}$H NMR (400 MHz, $CDCl_3$) for **10'** δ 7.32-7.23(m, 3H), 7.14-7.05 (m, 3H), 6.95 (t, $J$ = 8.0 Hz, 1H), 6.84 (d, $J$ = 8.0 Hz, 1H), 4.52 (t, $J$ = 8.0 Hz, 1H), 3.96 (q, $J$ = 8.0 Hz, 2H), 3.25 (s, 3H), 2.73 (dd, $J_1$ =$J_2$ = 8.0 Hz, 1H), 2.47 (dd, $J_1$ =$J_2$ = 8.0 Hz, 1H), 1.13 (t, $J$ = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for **10'** δ 175.8, 170.8, 142.6, 139.4, 139.1, 129.6, 128.6, 128.4, 125.2, 124.2, 124.1, 122.8, 122.2, 108.5, 63.9, 60.8, 50.7, 35.6, 26.8, 14.0. IR (KBr) for **10** $v$ 3428, 1717, 1611, 1468, 758cm$^{-1}$; IR (KBr) for **10'** $v$ 3425, 1730, 1715, 1609, 1469, 766 cm$^{-1}$. HRMS (ESI) calcd. for $C_{20}H_{20}NO_3S$ $[M+H]^+$: 354.1158, found: 354.1162.

## 8. Details about theoretical studies.

### (1) Proposed reaction mechanism




**Scheme S2**. Possible transesterification-inspired cascade pathway

Based on the experimental results, a plausible reaction mechanism was proposed to explain the possible pathway (Scheme S3, taking the formation of **3a** and **3a'** for example). Initially, a Michael addition between **1a** and **2a** occurred with the catalysis of DBN to generate intermediate **B**. After sequential proton transfer and transesterification, the coumarin ring was opened to afford intermediate **D** with a pedant nucleophilic phenolic anion. Next, an intramolecular nucleophilic substitution of **D** took place respectively with the emission of one molecule of $CO_2$ to furnish intermediate **E**. Finally, a protonation proceeded to afford the dihydrobenzofuran spirooxindole **3a** and **3a'** with the release of DBN to participate in next catalytic cycle. Also, there was another possible pathway, in

which transesterification proceeded first, followed by intramoleular Michael addition and sequential substitution.

**(2) Computational results**

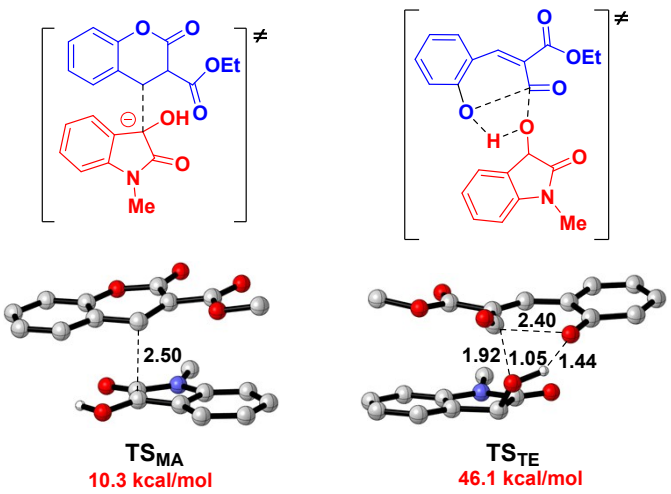



**Figure S2**. Optimized geometry parameters of all involved transition states. Bond lengths in Å.

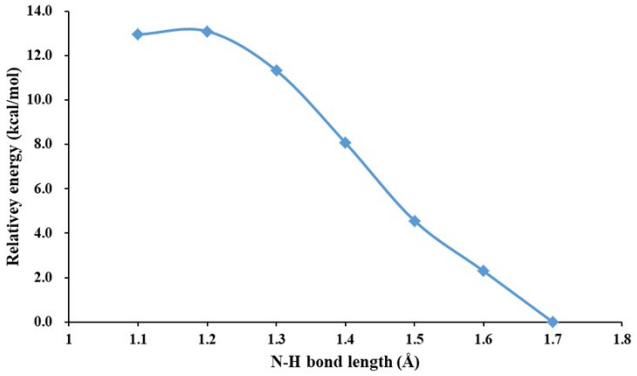



**Figure S3**. The flexible scanning curve to the N–H bond.

To differentiate these two pathways, DFT calculations were conducted. It is revealed that free energy barrier of the direct transesterification of **1a** and **2a** via **TS$_{TE}$** is 46.1 kcal/mol, which is too high to be overcome under mild experimental conditions. This should be mainly due to the strain of the four-membered ring structure in **TS$_{TE}$**. As for the Michael addition-inspired cascade mechanism, the deprotonation of **1a** with assistance of DBN was verified to be feasible by a flexible scanning of the N-H bond (Figure S3). The subsequent Michael addition was predicted to be with a free energy barrier of 10.3 kcal/mol only. All these results demonstrated the reaction went through the Michael addition-inspired cascade process.

**(3) Computational details**

The density functional theory (DFT)[1-2] calculations were performed by using the *Gaussian 09* program.[3] The geometric structures of all involved transition states were optimized by using the M06-2X[4-5] density functional, combined with the 6-31G(d, p)[6-7] basis set. The harmonic frequency calculations were conducted at the same level to corroborate each transition state has one and only one imaginary frequency and other structures have no imaginary frequency.Based on the optimized structures, all energies were refined by conducting single point energy calculations at the M06-2X/6-31++G(2df, 2pd)[8] level of theory, with the solvent effects of $CH_3CO_2Et$ simulated by the IEFPCM[9-10]model. The optimized geometries were illustrated by using the CYLview program.[11]

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**(4) Cartesian coordinates of all structures involved.**

**1a**

| | | | |
|---|---|---|---|
| C | -0.42243600 | 0.64834000 | -0.06534000 |
| C | -0.52810600 | -0.74242400 | -0.18950100 |
| C | -1.76555000 | -1.35409100 | -0.14942300 |
| C | -2.90661400 | -0.55780900 | 0.00765400 |
| C | -2.78801000 | 0.82456200 | 0.11415600 |
| C | -1.53971700 | 1.45567200 | 0.08101700 |
| C | 1.75849300 | -0.07192800 | -0.14148400 |
| C | 0.85800000 | -1.31523100 | -0.35331600 |
| H | -1.84218500 | -2.43437600 | -0.22990600 |
| H | -3.88748900 | -1.01880000 | 0.04636700 |
| H | -3.68144100 | 1.42998500 | 0.23039000 |
| H | -1.45160200 | 2.53304400 | 0.17406700 |
| N | 0.92499900 | 1.03086600 | -0.08465900 |
| O | 2.96250800 | -0.05104100 | -0.04446200 |
| C | 1.40448300 | 2.37639700 | 0.12008800 |
| H | 1.04285100 | 2.77736400 | 1.07275200 |
| H | 2.49388500 | 2.33123700 | 0.13461600 |
| H | 1.07486600 | 3.03236700 | -0.69115100 |
| O | 1.19111400 | -2.40668500 | 0.45909100 |
| H | 1.10553700 | -2.13506200 | 1.38038600 |
| H | 1.01834500 | -1.65094500 | -1.38504600 |

**2a**

| | | | |
|---|---|---|---|
| C | -3.07764400 | 1.12495300 | -0.00105400 |
| C | -1.75867300 | 0.67260200 | -0.00001000 |
| C | -1.46246700 | -0.69639900 | 0.00082700 |
| C | -2.51834500 | -1.62218000 | 0.00059600 |
| C | -3.82946500 | -1.18374000 | -0.00039500 |
| C | -4.10253500 | 0.19183900 | -0.00121000 |
| H | -3.26664300 | 2.19217600 | -0.00165700 |
| H | -2.28440700 | -2.68270500 | 0.00116100 |
| H | -4.64492600 | -1.89802800 | -0.00058100 |
| H | -5.13194300 | 0.53510100 | -0.00199100 |
| C | -0.07535900 | -1.06455700 | 0.00162700 |
| H | 0.21057400 | -2.11355800 | 0.00187500 |
| C | 0.90828400 | -0.13557900 | 0.00197200 |
| O | -0.77505800 | 1.60442500 | 0.00021600 |
| C | 0.58182300 | 1.30525100 | 0.00187900 |

| | | | |
|---|---|---|---|
| O | 1.34209500 | 2.22926300 | -0.00168600 |
| C | 2.31266000 | -0.65333000 | 0.00239400 |
| O | 3.24209900 | 0.29697300 | 0.00222800 |
| C | 4.58522400 | -0.18609300 | -0.00154900 |
| H | 4.76826500 | -0.79414000 | -0.89012400 |
| H | 5.21400000 | 0.70162200 | -0.00316300 |
| H | 4.77304800 | -0.79419100 | 0.88602600 |
| O | 2.56349200 | -1.83852100 | -0.00350900 |

**$TS_{MA}$**

| | | | |
|---|---|---|---|
| C | -1.70113400 | -0.63735300 | 1.18411500 |
| C | -1.30604800 | -1.71111900 | 0.32989500 |
| C | -2.27422000 | -2.35190000 | -0.44960100 |
| C | -3.59602000 | -1.92030300 | -0.37589100 |
| C | -3.96422400 | -0.85391300 | 0.45233800 |
| C | -3.01516000 | -0.19979500 | 1.24400000 |
| C | 0.53138700 | -0.95059000 | 1.53324300 |
| C | 0.10035700 | -1.81868800 | 0.47967000 |
| H | -1.99130100 | -3.17703400 | -1.09636700 |
| H | -4.35552400 | -2.41695600 | -0.97450500 |
| H | -4.99929100 | -0.52540500 | 0.48146900 |
| H | -3.29205400 | 0.63669400 | 1.87853900 |
| N | -0.59651600 | -0.20719400 | 1.89964700 |
| O | 1.67741700 | -0.81368900 | 1.99363200 |
| C | -0.55719600 | 0.92395000 | 2.79029500 |
| H | -0.94791700 | 1.81914900 | 2.29489900 |
| H | -1.12776000 | 0.72885300 | 3.70687100 |
| H | 0.49241900 | 1.08796500 | 3.04460900 |
| O | 0.91427300 | -2.80935700 | 0.00092000 |
| C | 4.03812500 | 0.67907700 | 0.03313300 |
| C | 2.66870700 | 0.80511000 | -0.18782000 |
| C | 1.97356500 | -0.11734100 | -0.98120600 |
| C | 2.69233800 | -1.17477100 | -1.56157300 |
| C | 4.05652000 | -1.30769800 | -1.34580500 |
| C | 4.72597900 | -0.37979100 | -0.54200100 |
| H | 4.52963100 | 1.41284400 | 0.66194500 |
| H | 2.15051000 | -1.89233700 | -2.16909100 |
| H | 4.60090500 | -2.12971200 | -1.80005400 |
| H | 5.79247000 | -0.48438600 | -0.36562100 |
| C | 0.55020400 | 0.05691100 | -1.10805600 |
| H | 0.00199300 | -0.59131400 | -1.78194900 |
| C | -0.04541000 | 1.23933800 | -0.68113500 |
| O | 2.04379800 | 1.86942300 | 0.36839000 |
| C | 0.69944100 | 2.18161000 | 0.13616200 |
| O | 0.31640600 | 3.20747400 | 0.64281000 |

| | | | |
|---|---|---|---|
| C | -1.43660500 | 1.56208800 | -1.01442800 |
| O | -1.96154700 | 0.64448500 | -1.87879300 |
| C | -3.28687300 | 0.91959400 | -2.29262000 |
| H | -3.30912300 | 1.78107800 | -2.97007900 |
| H | -3.63265700 | 0.02117600 | -2.80590400 |
| H | -3.92434000 | 1.12840400 | -1.43265200 |
| O | -2.08095900 | 2.52211500 | -0.64940400 |
| H | 1.79014900 | -2.57877200 | 0.35362300 |

**$TS_{TE}$**

| | | | |
|---|---|---|---|
| C | 4.47607900 | -0.72347900 | -0.75440100 |
| C | 3.09431300 | -0.78620100 | -0.40567800 |
| C | 2.65615000 | 0.00779000 | 0.70996300 |
| C | 3.58230900 | 0.86087200 | 1.37665200 |
| C | 4.89507100 | 0.91625800 | 0.99950700 |
| C | 5.33437100 | 0.10316500 | -0.07714300 |
| H | 4.80605100 | -1.33958400 | -1.58322400 |
| H | 3.22055100 | 1.46578600 | 2.20472100 |
| H | 5.59490900 | 1.56538800 | 1.51254900 |
| H | 6.37903000 | 0.14136500 | -0.37406700 |
| C | 1.33747400 | -0.04212600 | 1.19188000 |
| H | 1.12102600 | 0.62725300 | 2.02548700 |
| C | 0.22304400 | -0.80239100 | 0.88149200 |
| O | 2.28269200 | -1.53685000 | -1.05357600 |
| C | 0.11241800 | -1.85658800 | -0.07654800 |
| O | -0.14706100 | -2.95846600 | -0.27398200 |
| C | -0.99058800 | -0.58388400 | 1.71039600 |
| O | -1.96074100 | -1.46416600 | 1.43926100 |
| C | -3.12921700 | -1.35223300 | 2.25376800 |
| H | -3.48405700 | -0.32156100 | 2.26372000 |
| H | -3.86783900 | -2.00939500 | 1.79860900 |
| H | -2.90197000 | -1.67111700 | 3.27377700 |
| O | -1.09315100 | 0.29861400 | 2.53458600 |
| C | -2.09130500 | 1.27959200 | -0.57642900 |
| C | -1.96356700 | 0.19945800 | -1.45918300 |
| C | -3.01977000 | -0.66354800 | -1.67426300 |
| C | -4.22804300 | -0.42082000 | -1.01158900 |
| C | -4.35117300 | 0.66907700 | -0.15377400 |
| C | -3.28020600 | 1.53562900 | 0.08974500 |
| C | 0.09356600 | 1.37952000 | -1.25832000 |
| C | -0.56545000 | 0.20140500 | -2.00858400 |
| H | -2.90513100 | -1.51493700 | -2.33808500 |
| H | -5.07333100 | -1.08170700 | -1.16977700 |
| H | -5.29629500 | 0.84761500 | 0.35015500 |
| H | -3.37330200 | 2.36753300 | 0.77951400 |

| | | | |
|---|---|---|---|
| N | -0.88074100 | 1.97595200 | -0.48556900 |
| O | 1.25226100 | 1.71743200 | -1.34138700 |
| C | -0.59871600 | 3.01986800 | 0.47430300 |
| H | -0.81112200 | 2.65912900 | 1.48638700 |
| H | 0.46116400 | 3.26193400 | 0.38062100 |
| H | -1.19499400 | 3.91273300 | 0.26508100 |
| O | 0.08890400 | -1.03265800 | -1.81146000 |
| H | 1.13092400 | -1.01569400 | -1.73319400 |
| H | -0.54419400 | 0.43417300 | -3.08160800 |

**Pre-TS$_{MA}$**

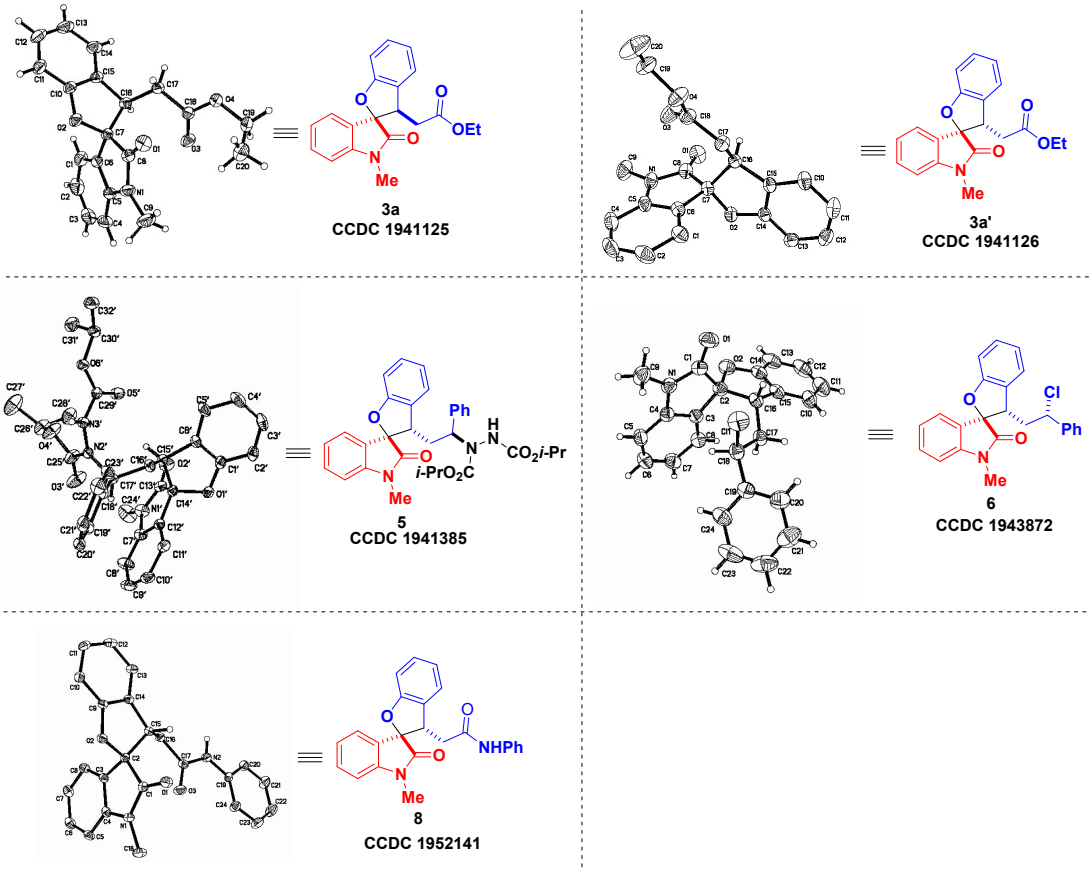
| | | | |
|---|---|---|---|
| C | -1.74838700 | -0.65897800 | 1.14217100 |
| C | -1.29572800 | -1.75930300 | 0.34791300 |
| C | -2.22136400 | -2.44276800 | -0.44973000 |
| C | -3.55245700 | -2.03281500 | -0.44688400 |
| C | -3.97778600 | -0.95201600 | 0.33374000 |
| C | -3.07254900 | -0.25138200 | 1.13839000 |
| C | 0.48064600 | -0.89452400 | 1.56790600 |
| C | 0.09940500 | -1.84009000 | 0.57020900 |
| H | -1.89893600 | -3.28328500 | -1.05705700 |
| H | -4.27561500 | -2.56342800 | -1.06113300 |
| H | -5.02005800 | -0.64635900 | 0.31182200 |
| H | -3.38945800 | 0.59981000 | 1.73391700 |
| N | -0.68014000 | -0.16895400 | 1.87107500 |
| O | 1.61415700 | -0.68399100 | 2.03894800 |
| C | -0.69442700 | 1.01799000 | 2.68693700 |
| H | -1.11341300 | 1.86415200 | 2.13114100 |
| H | -1.26879800 | 0.86159600 | 3.60863200 |
| H | 0.34436500 | 1.23884700 | 2.94230000 |
| O | 0.96360100 | -2.81099300 | 0.13935100 |
| C | 4.06328400 | 0.61375500 | 0.01809800 |
| C | 2.69964600 | 0.78302800 | -0.20958900 |
| C | 1.97319500 | -0.13247300 | -0.98323100 |
| C | 2.65420400 | -1.22885400 | -1.53784600 |
| C | 4.01241200 | -1.40289900 | -1.31799200 |
| C | 4.71297500 | -0.48101700 | -0.53291200 |
| H | 4.57960800 | 1.34310600 | 0.63172300 |
| H | 2.08790300 | -1.94205500 | -2.12749500 |
| H | 4.52839000 | -2.25360000 | -1.75159000 |
| H | 5.77474900 | -0.61985100 | -0.35216300 |
| C | 0.56157100 | 0.09200600 | -1.12320900 |
| H | -0.01911000 | -0.56782700 | -1.75725100 |
| C | -0.00781000 | 1.27235600 | -0.67943100 |
| O | 2.11463300 | 1.88651100 | 0.31213200 |
| C | 0.77244300 | 2.21288300 | 0.11443000 |

| | | | |
|---|---|---|---|
| O | 0.41251500 | 3.25015300 | 0.61205400 |
| C | -1.41040000 | 1.60384600 | -0.97017300 |
| O | -1.94660200 | 0.72868100 | -1.86606700 |
| C | -3.28441100 | 1.01135700 | -2.23661600 |
| H | -3.90479600 | 1.16115900 | -1.35269100 |
| H | -3.32839800 | 1.90914400 | -2.86322700 |
| H | -3.63061600 | 0.13869600 | -2.79174800 |
| O | -2.04731000 | 2.54158900 | -0.54148400 |
| H | 1.82044400 | -2.53363600 | 0.50475300 |

**DBN**

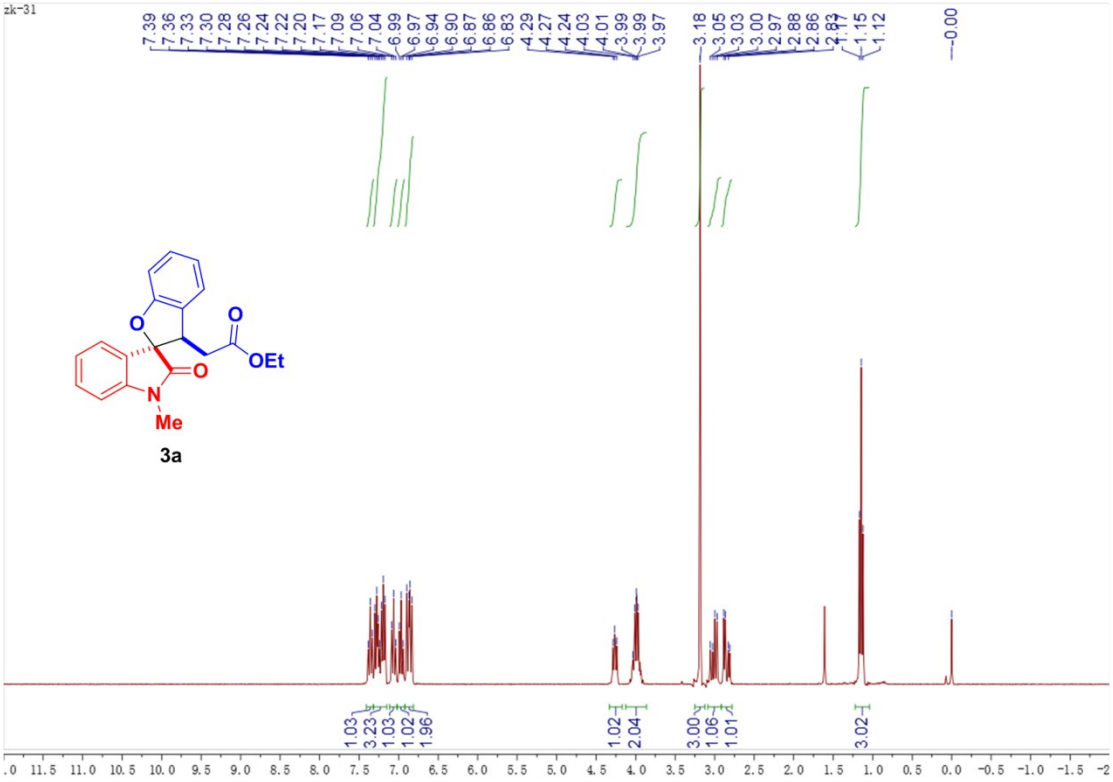
| | | | |
|---|---|---|---|
| C | 0.19428200 | -0.73454700 | 0.01448800 |
| C | -2.13036200 | -0.82438900 | 0.12955800 |
| C | -2.14000700 | 0.61633400 | -0.39191700 |
| C | -0.97372200 | 1.39997700 | 0.20734000 |
| C | 1.55921800 | 1.17143100 | 0.19765000 |
| C | 2.45635700 | 0.02092200 | -0.28069100 |
| C | 1.62700300 | -1.22806600 | 0.05005000 |
| H | -2.84436300 | -1.42594100 | -0.44265400 |
| H | -2.02749500 | 0.61123000 | -1.48119000 |
| H | -1.12176800 | 1.54690300 | 1.28993200 |
| H | 1.72199300 | 2.10243300 | -0.35567000 |
| H | 3.43765200 | 0.03030500 | 0.19633300 |
| H | 2.59805600 | 0.10269100 | -1.36173800 |
| N | 0.23146800 | 0.64841400 | -0.05524900 |
| N | -0.83010100 | -1.48881300 | 0.07453100 |
| H | 1.71514700 | 1.38252000 | 1.26879500 |
| H | -0.88430500 | 2.39137400 | -0.25100300 |
| H | -3.08909600 | 1.10613000 | -0.15606500 |
| H | -2.48208600 | -0.84384000 | 1.17051500 |
| H | 1.83517500 | -1.58731100 | 1.06368300 |
| H | 1.77490600 | -2.06367600 | -0.63477400 |

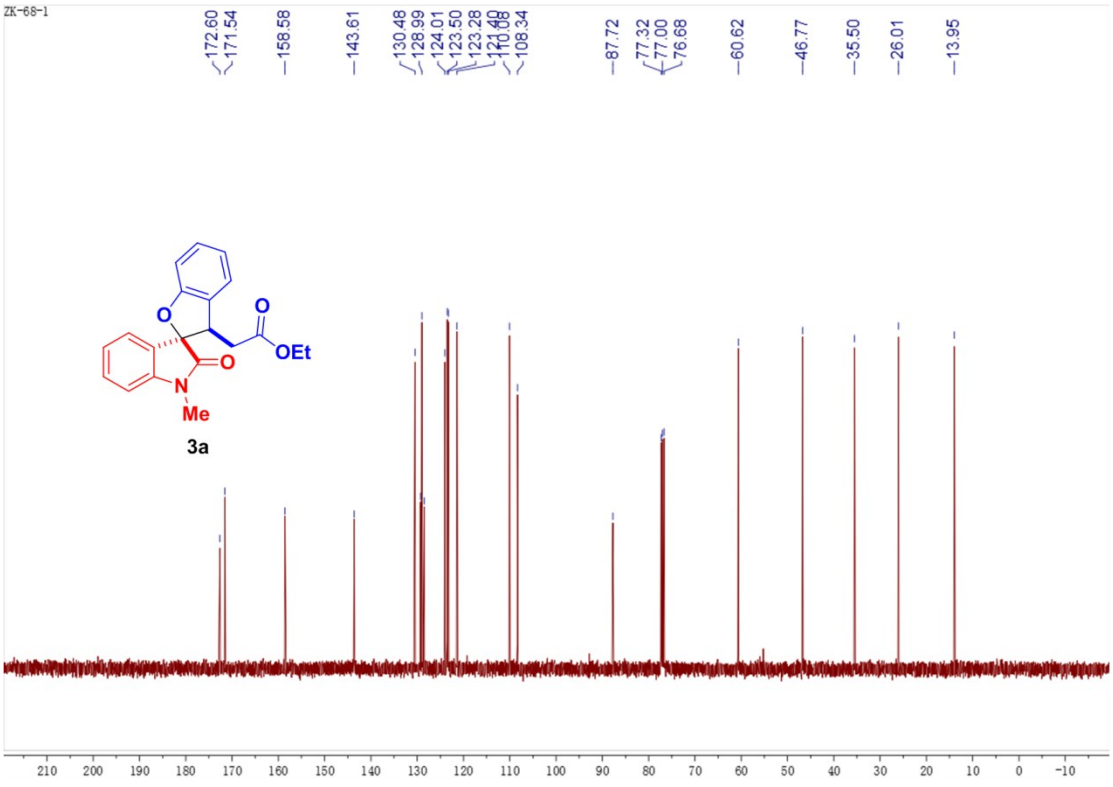
## 9. Crystal structure of 3a, 3a', 3s, 5, 6 and 8

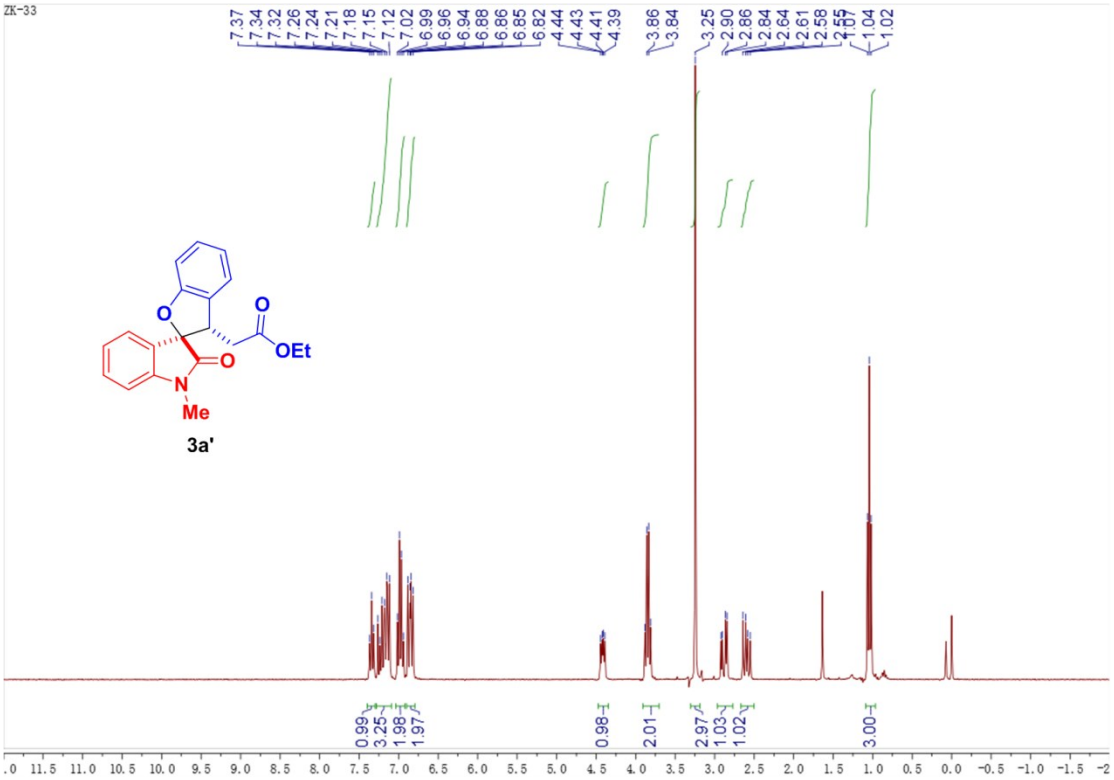


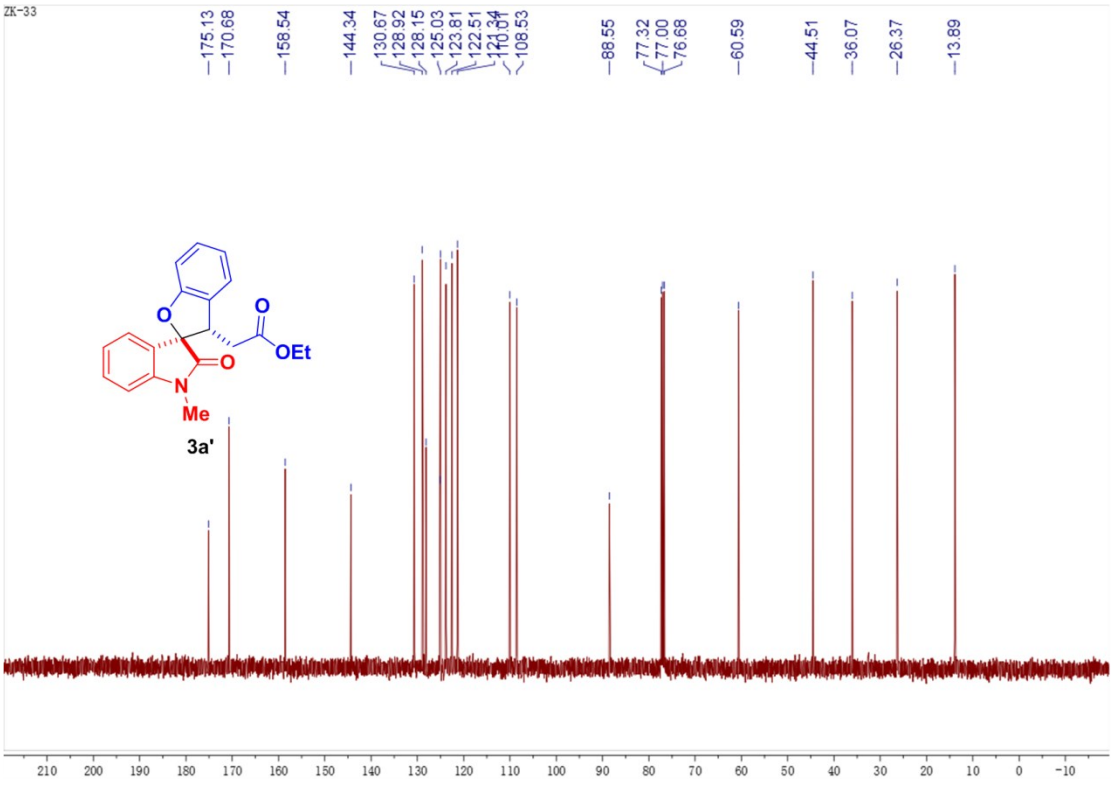

Displacement ellipsoids are drawn at the 30% probability level.

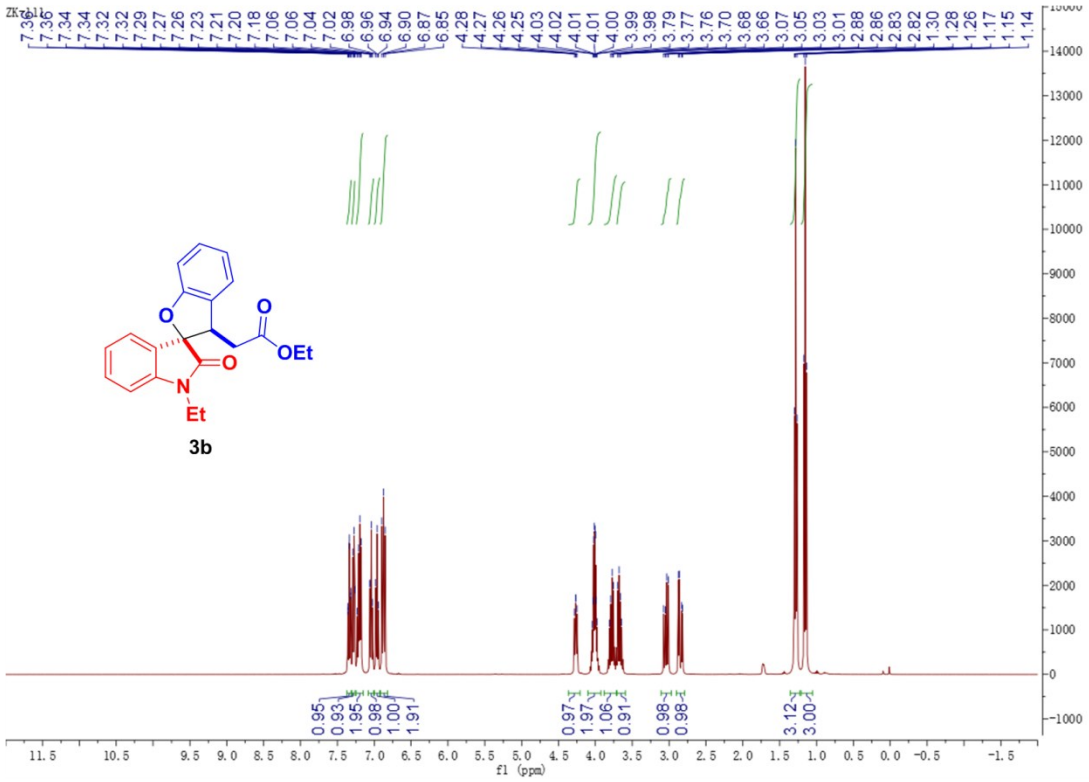
## 10. $^{1}$H NMR and $^{13}$C NMR spectra

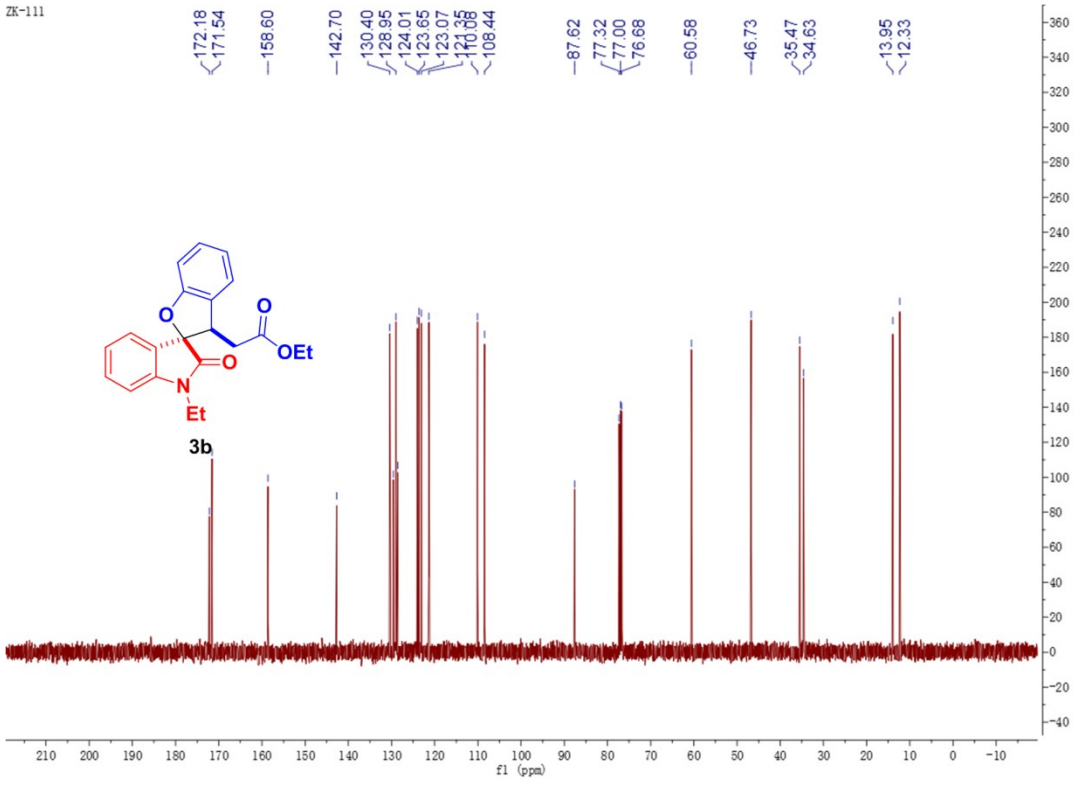


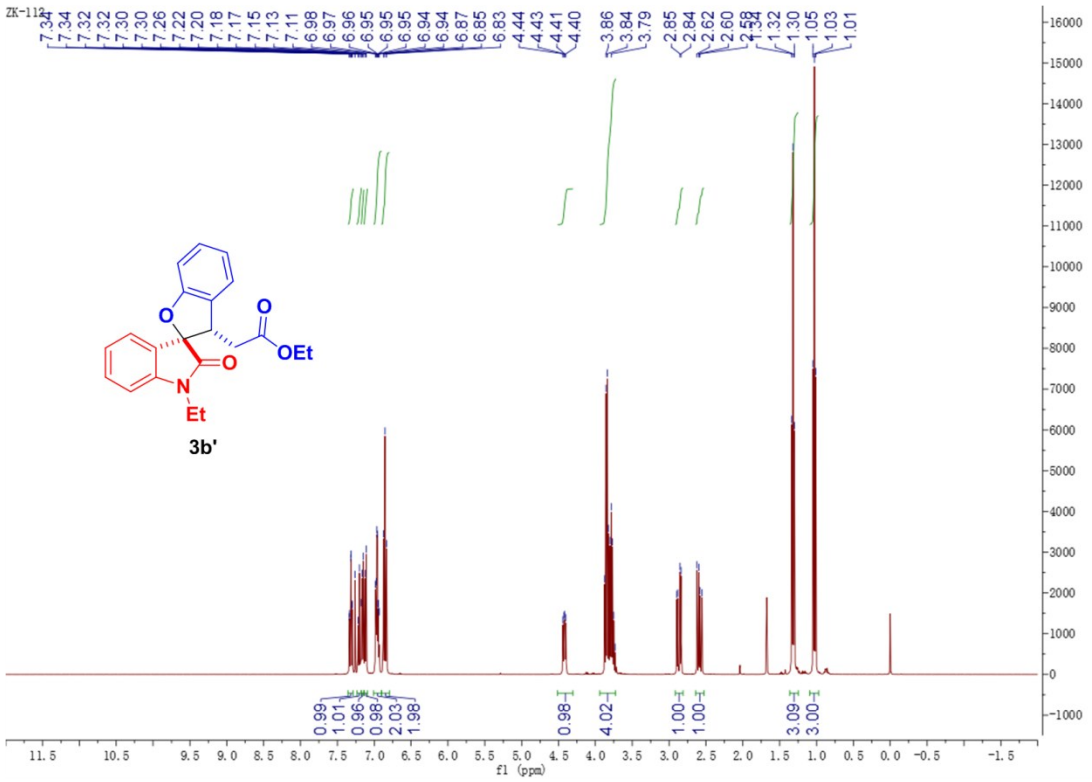



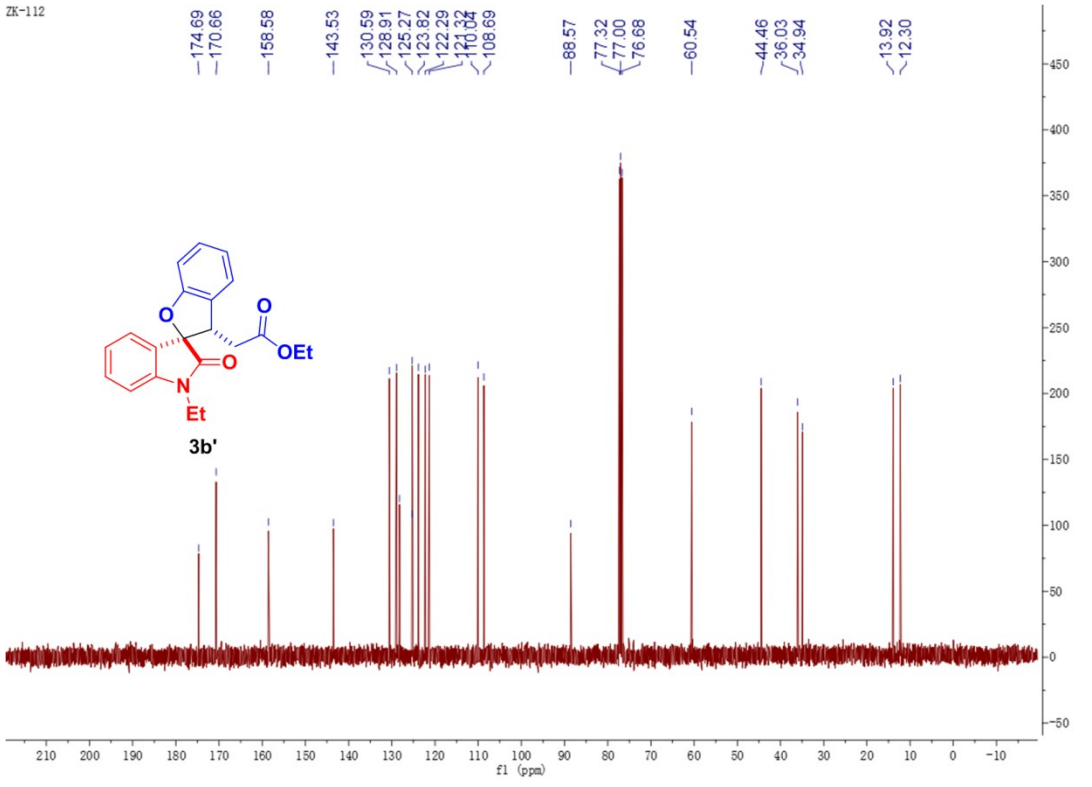

ZK-33
7.37
7.34
7.32
7.26
7.24
7.21
7.18
7.15
7.12
7.02
6.99
6.96
6.94
6.88
6.86
6.85
6.82
4.44
4.43
4.41
4.39
3.86
3.84
3.25
2.90
2.86
2.84
2.64
2.61
2.58
1.07
1.04
1.02
O
O
OEt
O
N
Me
3a'
0.99
3.25
1.98
1.97
0.98
2.01
2.97
1.03
1.02
3.00

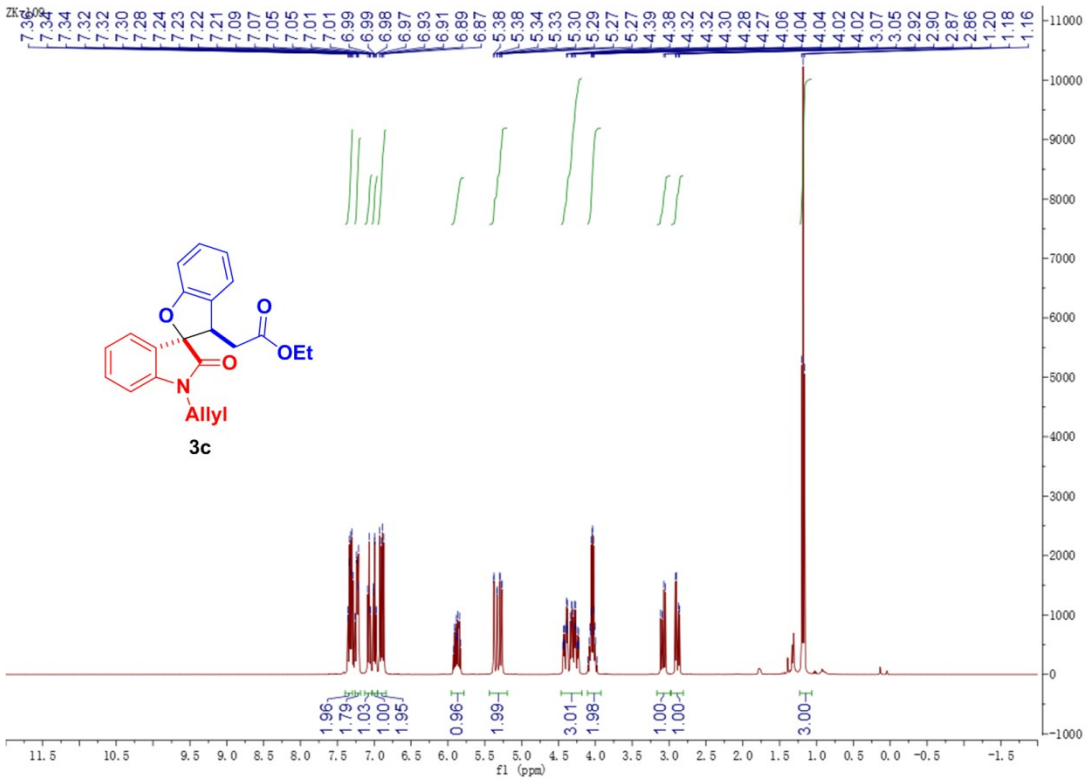

ZK-33
175.13
170.68
158.54
144.34
130.67
128.92
128.15
125.03
123.81
122.51
111.34
110.01
108.53
88.55
77.32
77.00
76.68
60.59
44.51
36.07
26.37
13.89
O
O
OEt
O
N
Me
3a'

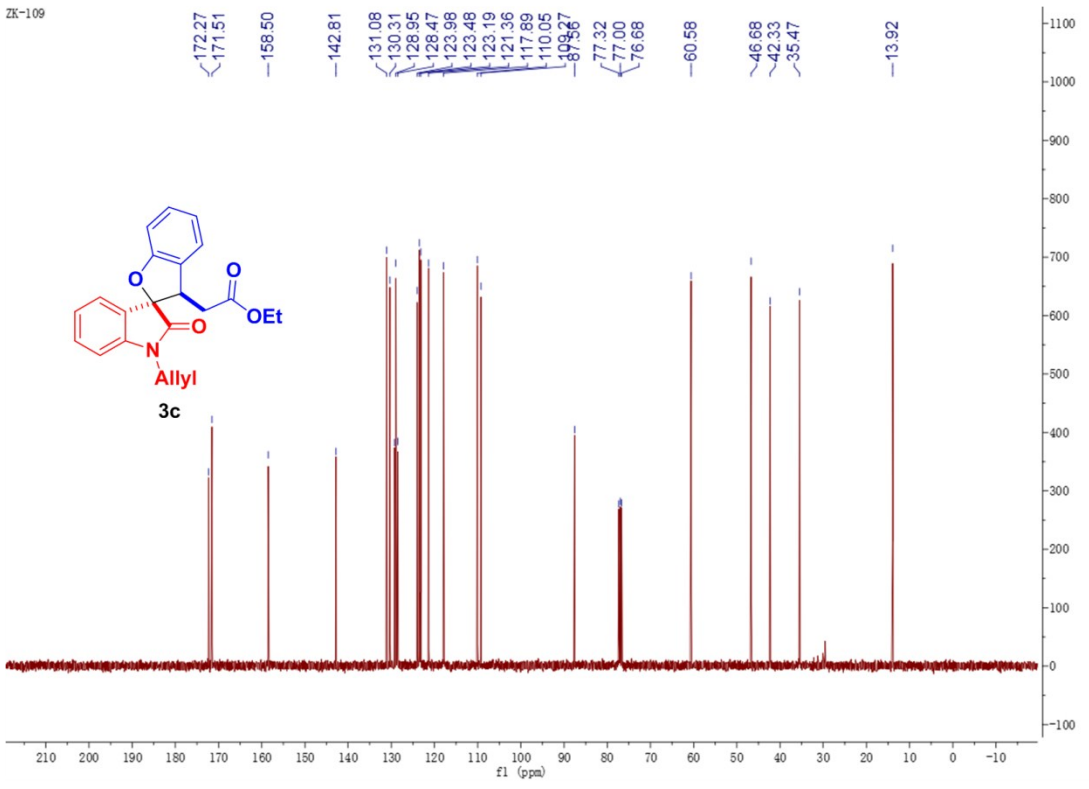

ZK-111
7.36
7.36
7.34
7.34
7.32
7.32
7.29
7.27
7.26
7.23
7.21
7.20
7.18
7.06
7.06
7.04
7.02
6.98
6.96
6.94
6.90
6.87
6.85
4.28
4.27
4.26
4.25
4.03
4.02
4.01
4.01
4.00
3.99
3.98
3.79
3.77
3.76
3.70
3.68
3.66
3.07
3.05
3.03
3.01
2.88
2.86
2.83
2.82
1.30
1.28
1.26
1.17
1.15
1.14
O
O
OEt
O
N
Et
3b
0.95
0.93
1.95
0.98
1.00
1.91
0.97
1.97
1.06
0.91
0.98
0.98
3.12
3.00
f1 (ppm)

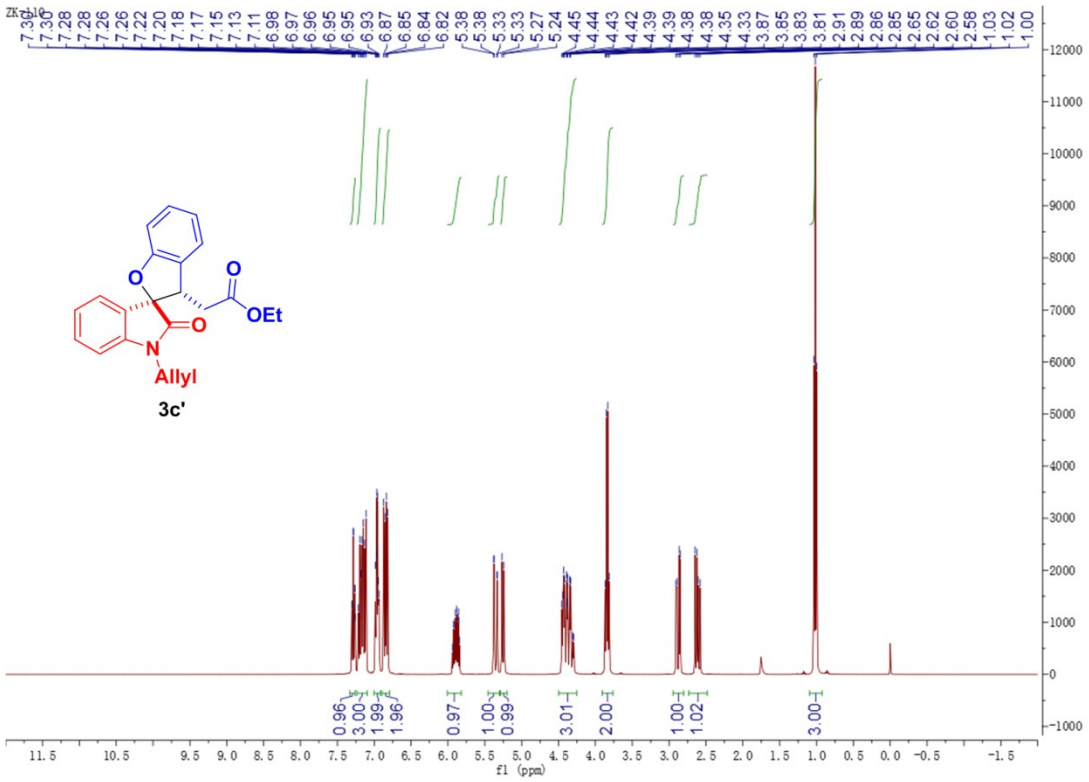

ZK-111
172.18
171.54
158.60
142.70
130.40
128.95
124.01
123.65
123.07
121.35
110.08
108.44
87.62
77.32
77.00
76.68
60.58
46.73
35.47
34.63
13.95
12.33
O
O
OEt
O
N
Et
3b
f1 (ppm)

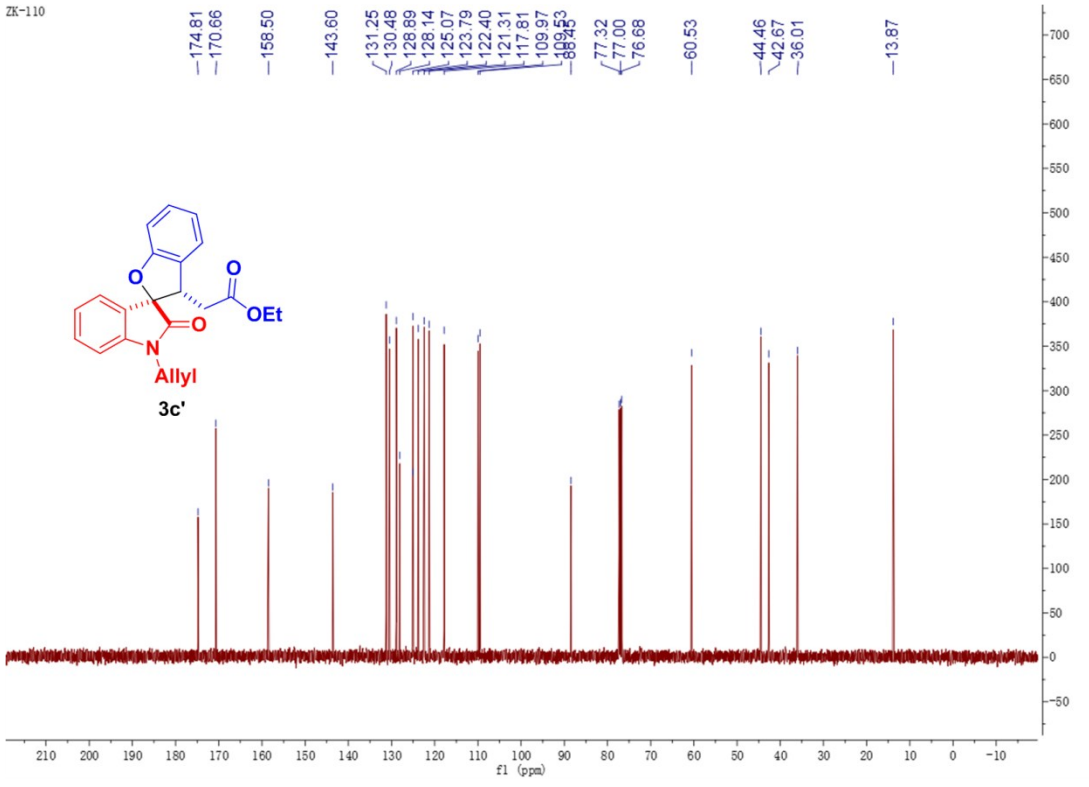

ZK-112
7.34
7.34
7.32
7.32
7.30
7.30
7.26
7.22
7.20
7.18
7.17
7.15
7.13
7.11
6.98
6.97
6.96
6.95
6.95
6.95
6.94
6.94
6.87
6.85
6.83
4.44
4.43
4.41
4.40
3.86
3.84
3.79
2.85
2.84
2.62
2.60
2.58
2.54
1.32
1.30
1.05
1.03
1.01
O
O
OEt
O
N
Et
3b'
0.99
1.01
0.96
0.98
2.03
1.98
0.98
4.02
1.00
1.00
3.09
3.00
f1 (ppm)

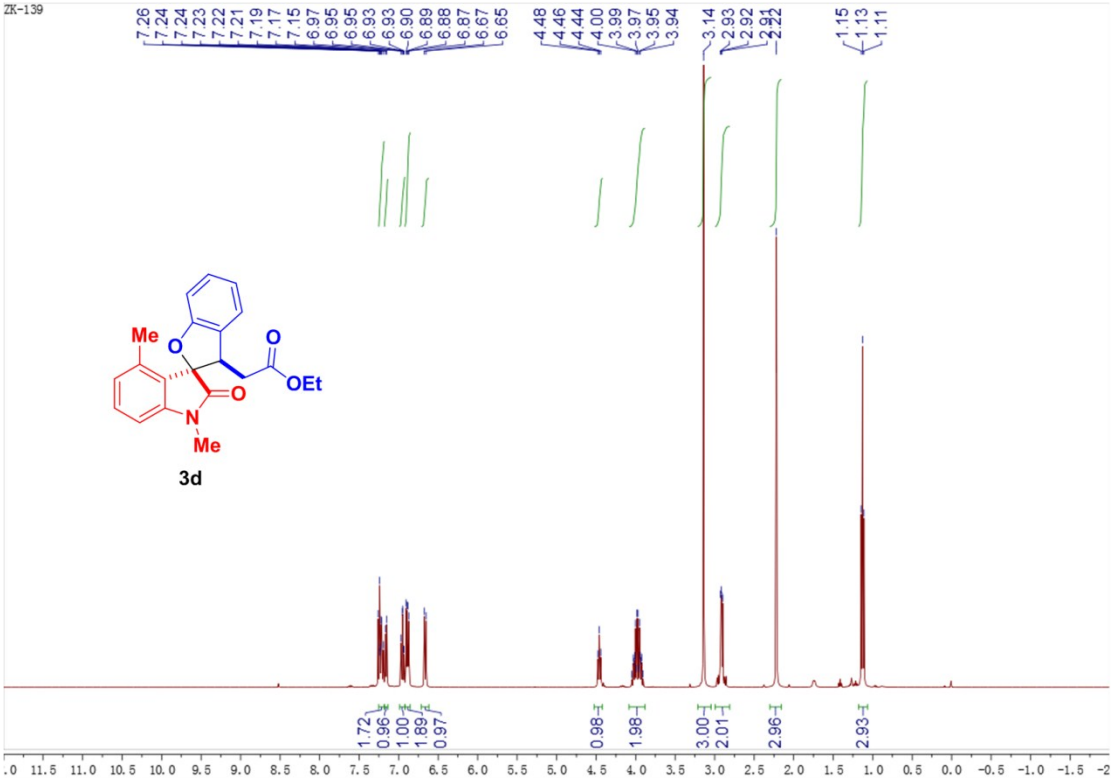

ZK-112
174.69
170.66
158.58
143.53
130.59
128.91
125.27
123.82
122.29
121.32
110.04
108.69
88.57
77.32
77.00
76.68
60.54
44.46
36.03
34.94
13.92
12.30
O
O
OEt
O
N
Et
3b'
f1 (ppm)

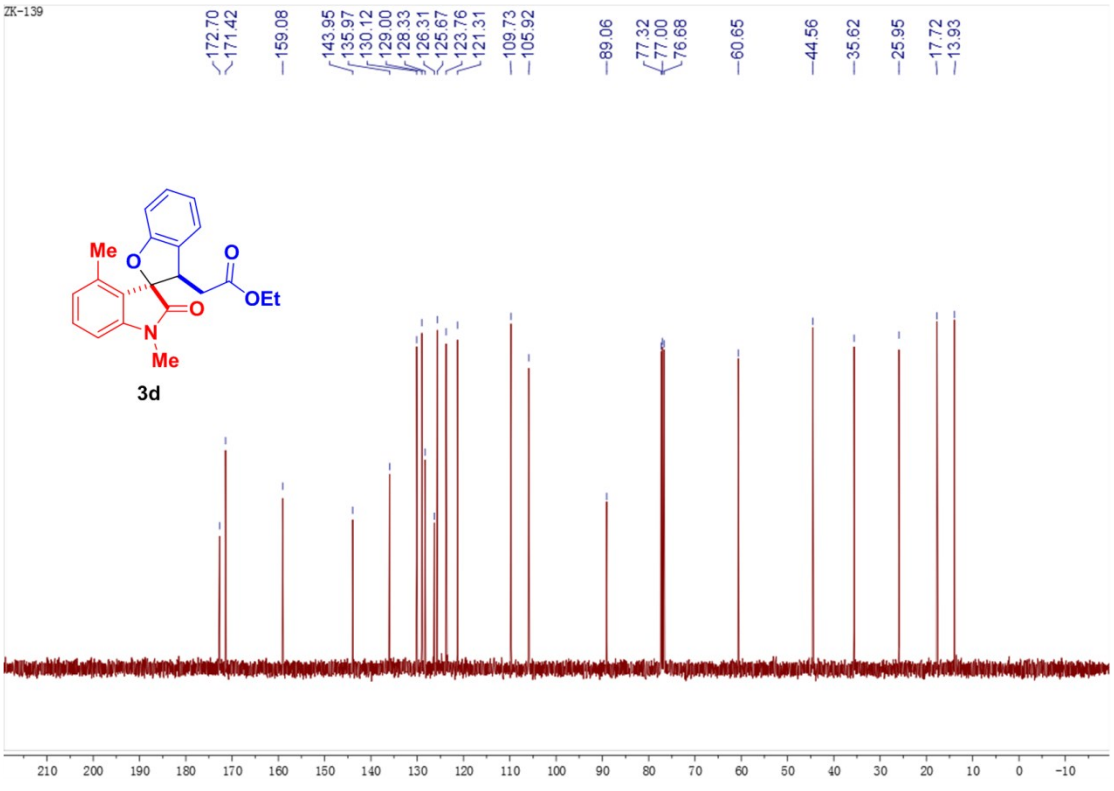

ZK-109
7.36
7.34
7.34
7.32
7.32
7.30
7.28
7.24
7.23
7.22
7.21
7.09
7.07
7.05
7.05
7.01
7.01
6.99
6.99
6.98
6.97
6.93
6.91
6.89
6.87
5.38
5.38
5.34
5.33
5.30
5.29
5.27
5.27
4.39
4.38
4.32
4.30
4.28
4.27
4.06
4.04
4.04
4.02
4.02
3.07
3.05
2.92
2.90
2.87
2.86
1.20
1.18
1.16
O
O
OEt
O
N
Allyl
3c
1.96
1.79
1.03
1.00
1.95
0.96
1.99
3.01
1.98
1.00
1.00
3.00
f1 (ppm)

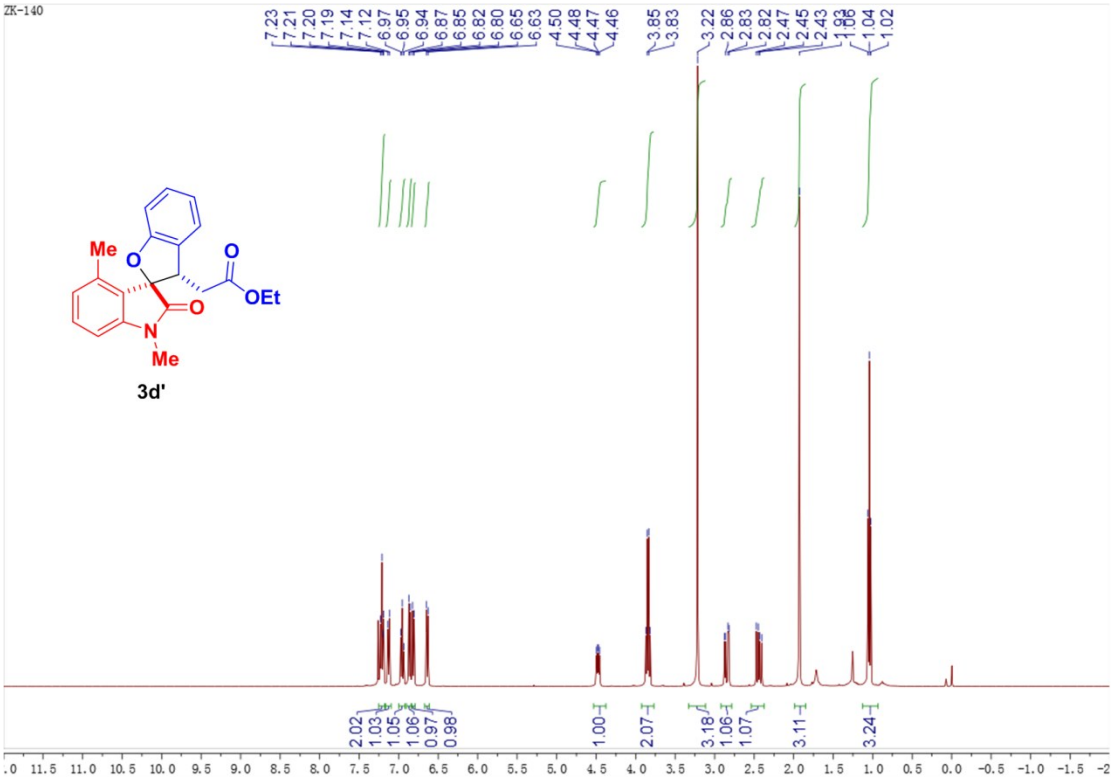

ZK-109
172.27
171.51
158.50
142.81
131.08
130.31
128.95
128.47
123.98
123.48
123.19
121.36
117.89
110.05
109.27
97.56
77.32
77.00
76.68
60.58
46.68
42.33
35.47
13.92
O
O
OEt
O
N
Allyl
3c
f1 (ppm)


ZK-110
O
O
OEt
O
N
Allyl
3c'
f1 (ppm)


ZK-110
O
O
OEt
O
N
Allyl
3c'
f1 (ppm)


ZK-139
Me
O
O
OEt
N
Me
3d


ZK-139
Me
O
O
OEt
N
Me
3d


ZK-140
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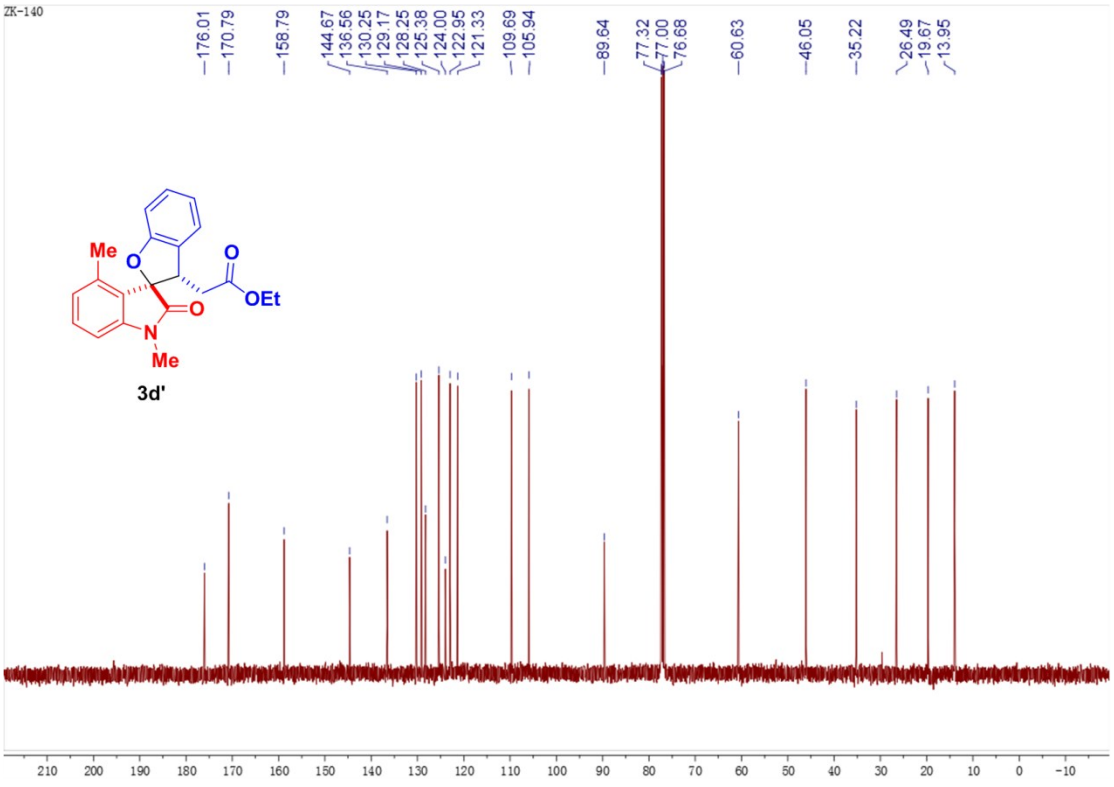
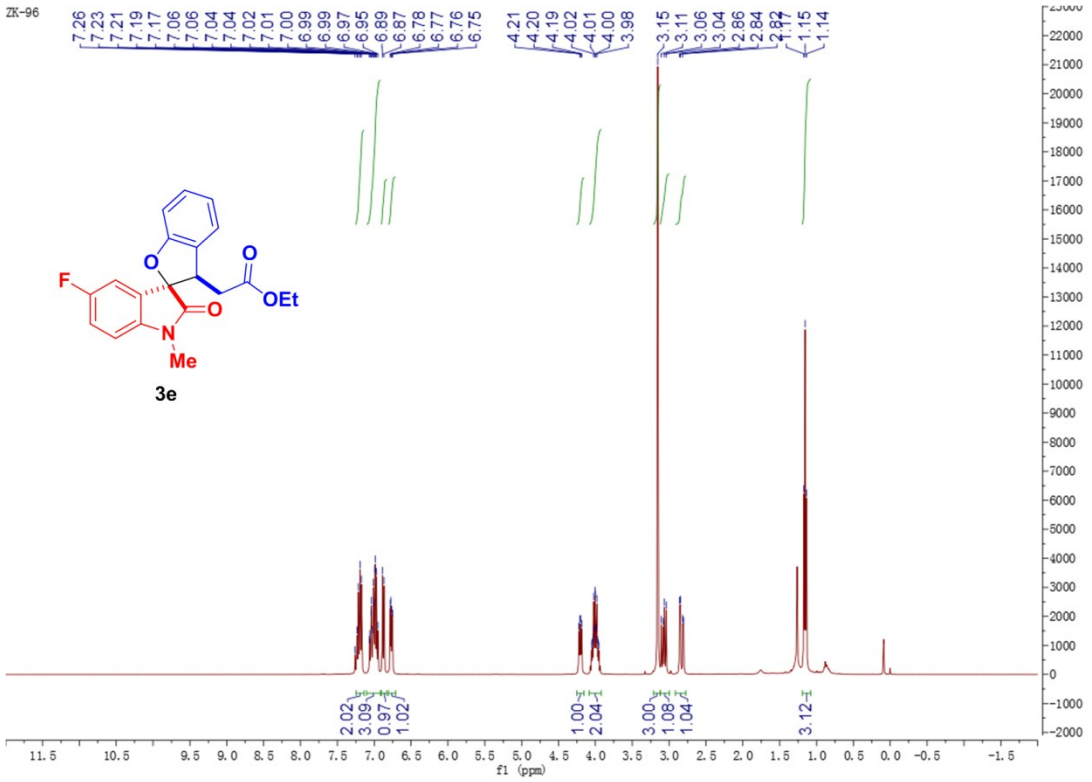
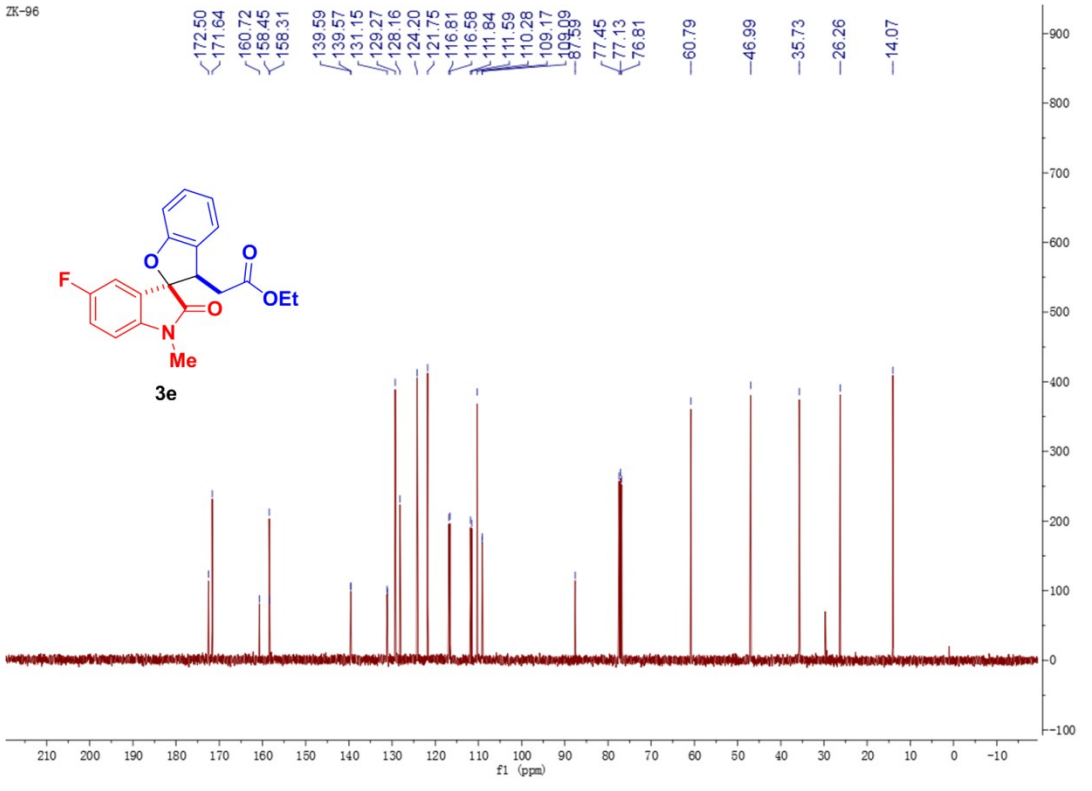
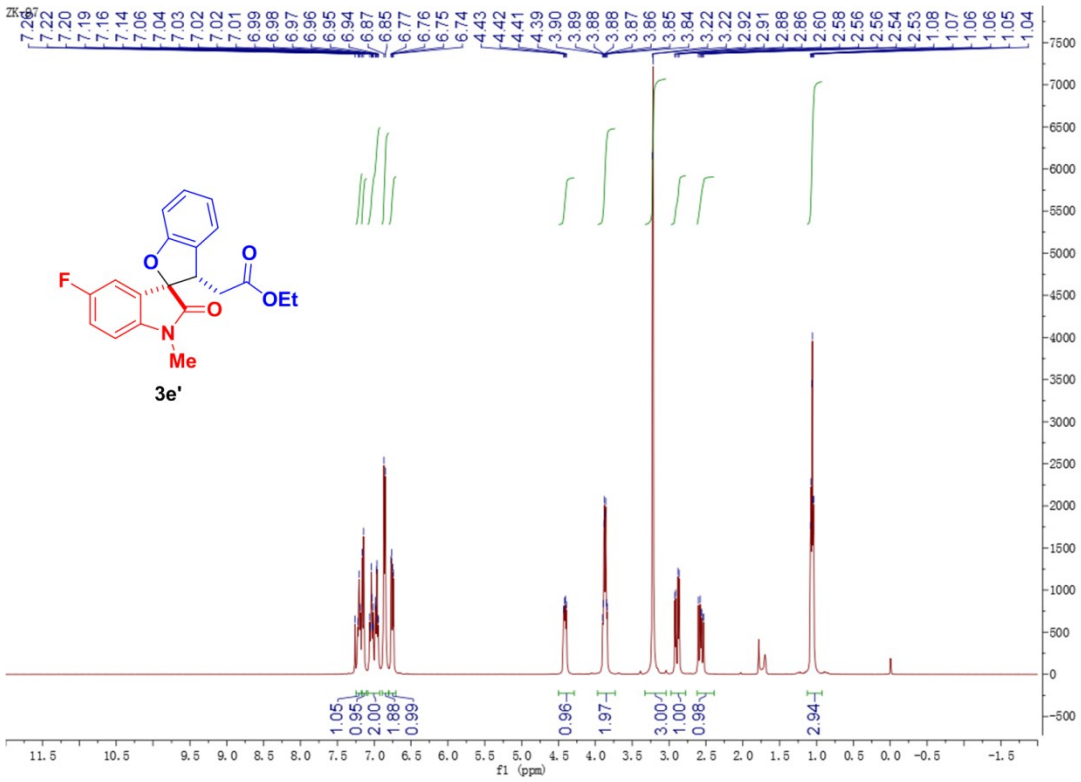
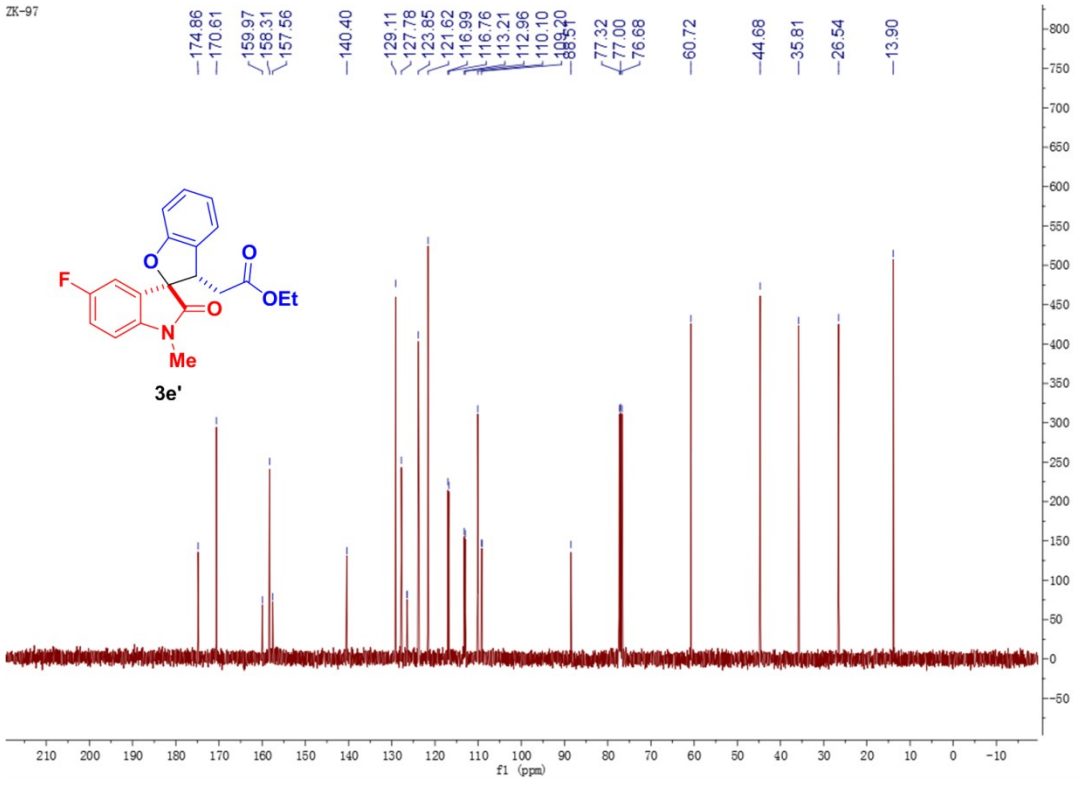
7.21
7.20
7.19
7.14
7.12
6.97
6.95
6.94
6.87
6.85
6.82
6.80
6.65
6.63
4.50
4.48
4.47
4.46
3.85
3.83
3.22
2.86
2.83
2.82
2.47
2.45
2.43
1.06
1.04
1.02
Me
O
O
OEt
O
N
Me
3d'
2.02
1.03
1.05
1.06
0.97
0.98
1.00
2.07
3.18
1.06
1.07
3.11
3.24

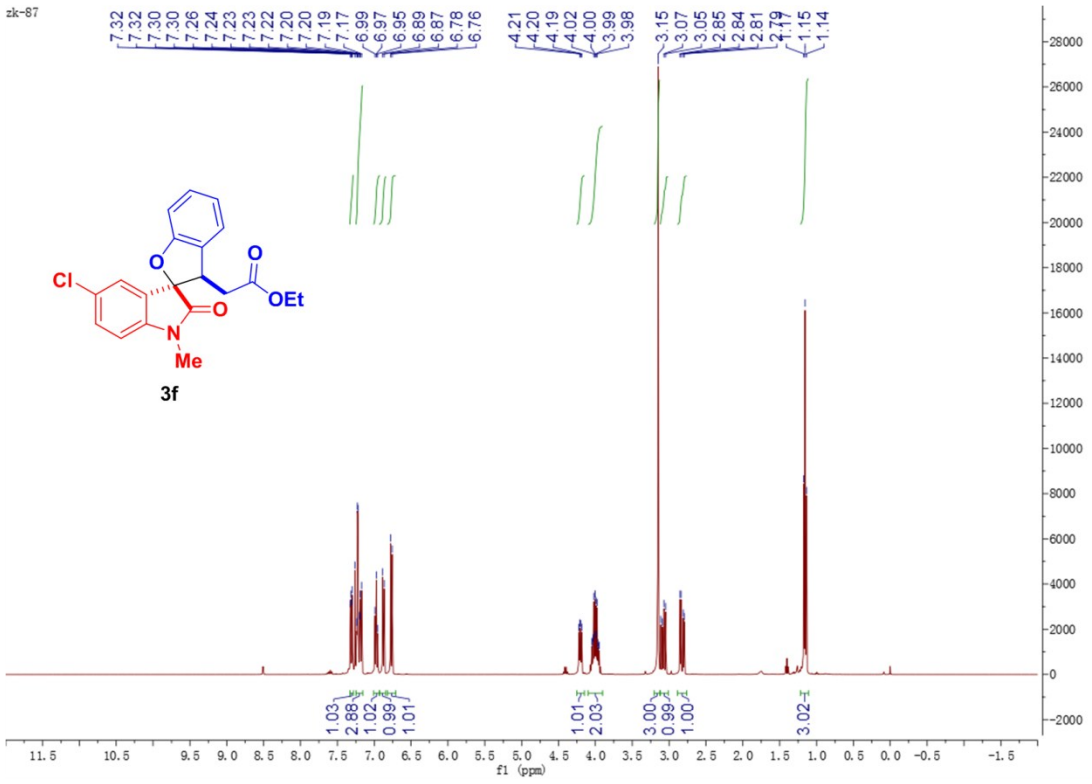

ZK-140
176.01
170.79
158.79
144.67
136.56
130.25
129.17
128.25
125.38
124.00
122.95
121.33
109.69
105.94
89.64
77.32
77.00
76.68
60.63
46.05
35.22
26.49
19.67
13.95
Me
O
O
OEt
O
N
Me
3d'

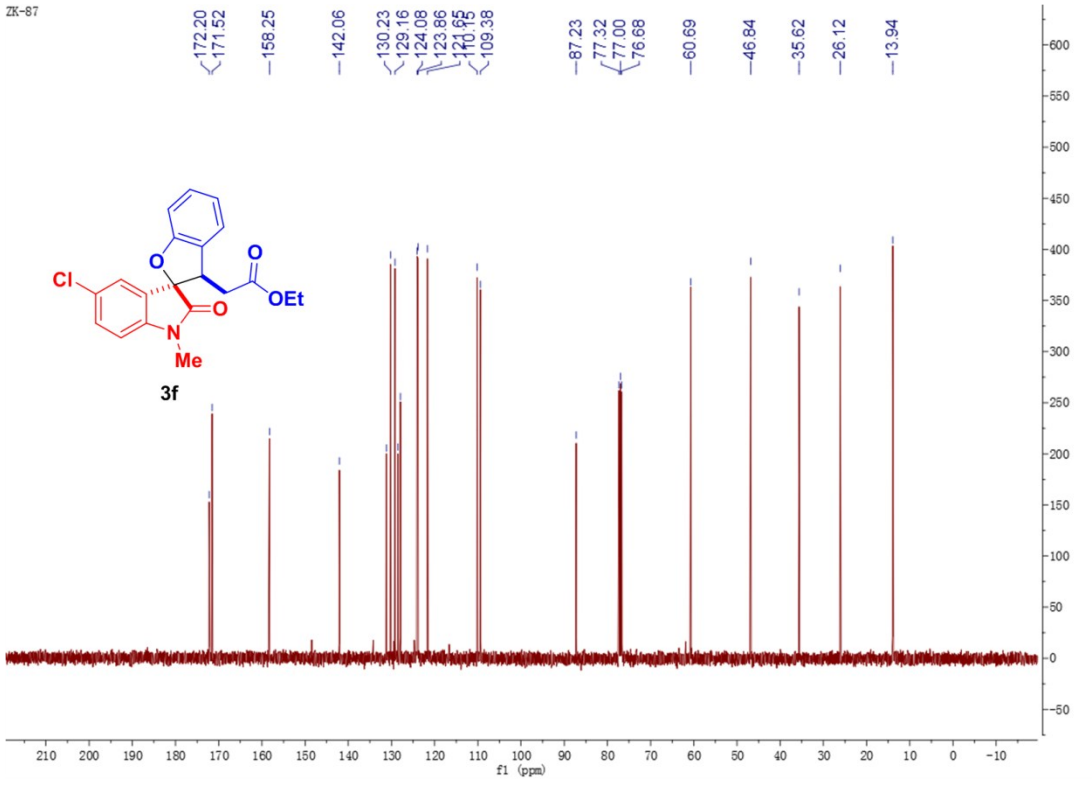

ZK-96
7.26
7.23
7.21
7.19
7.17
7.06
7.06
7.04
7.04
7.02
7.01
7.00
6.99
6.99
6.97
6.95
6.89
6.87
6.78
6.77
6.76
6.75
4.21
4.20
4.19
4.02
4.01
4.00
3.98
3.15
3.11
3.06
3.04
2.86
2.84
2.82
1.17
1.15
1.14
2.02
3.09
0.97
1.02
1.00
2.04
3.00
1.08
1.04
3.12
f1 (ppm)
F
O
O
OEt
O
N
Me
3e

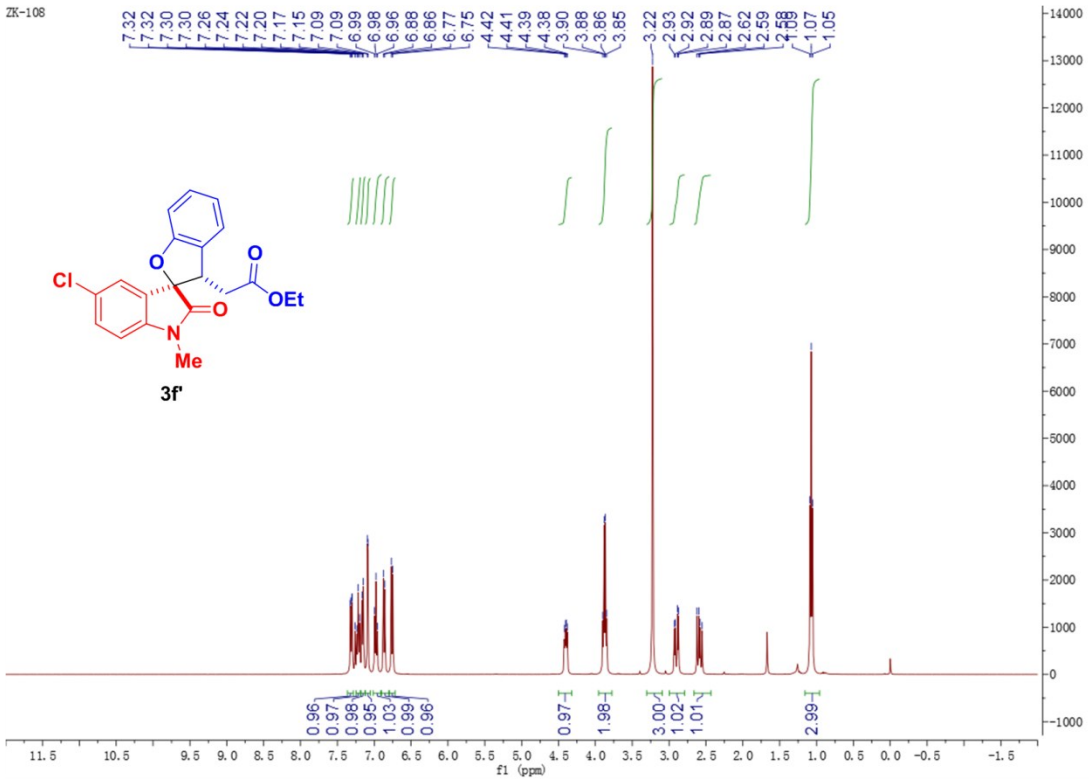

ZK-96
172.50
171.64
160.72
158.45
158.31
139.59
139.57
131.15
129.27
128.16
124.20
121.75
116.81
116.58
111.84
111.59
110.28
109.17
109.09
97.59
77.45
77.13
76.81
60.79
46.99
35.73
26.26
14.07
f1 (ppm)
F
O
O
OEt
O
N
Me
3e

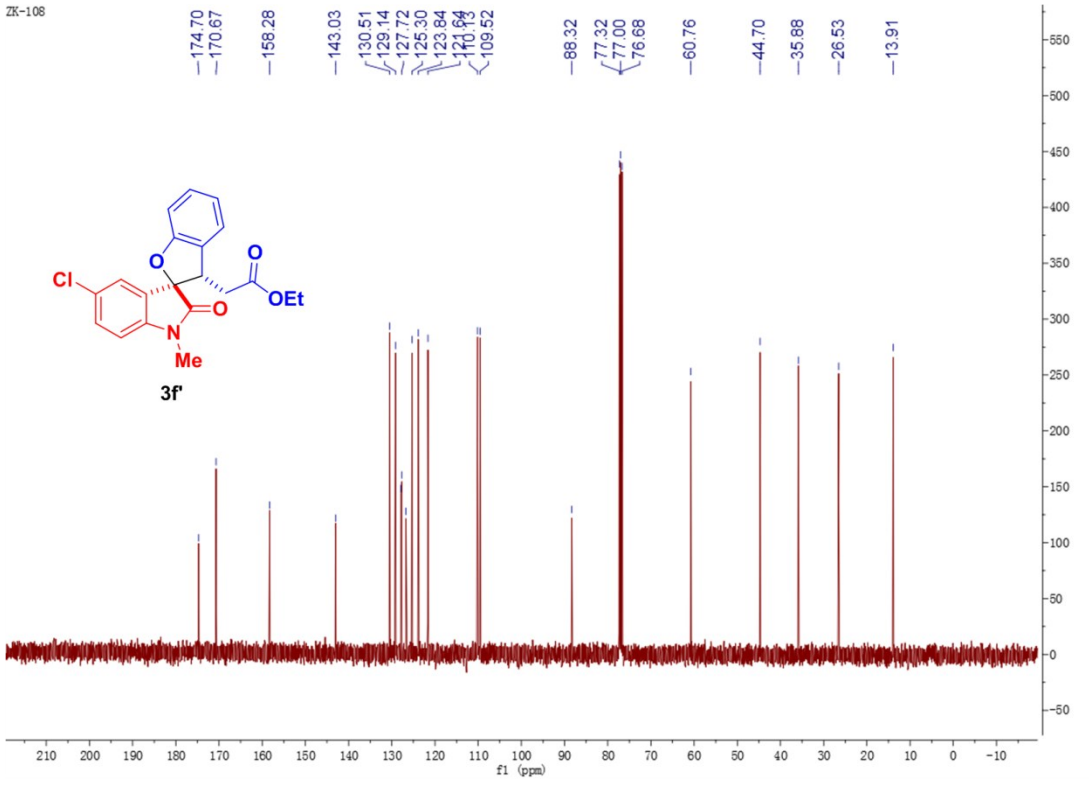

ZK-97
F
O
O
OEt
N
Me
3e'
f1 (ppm)

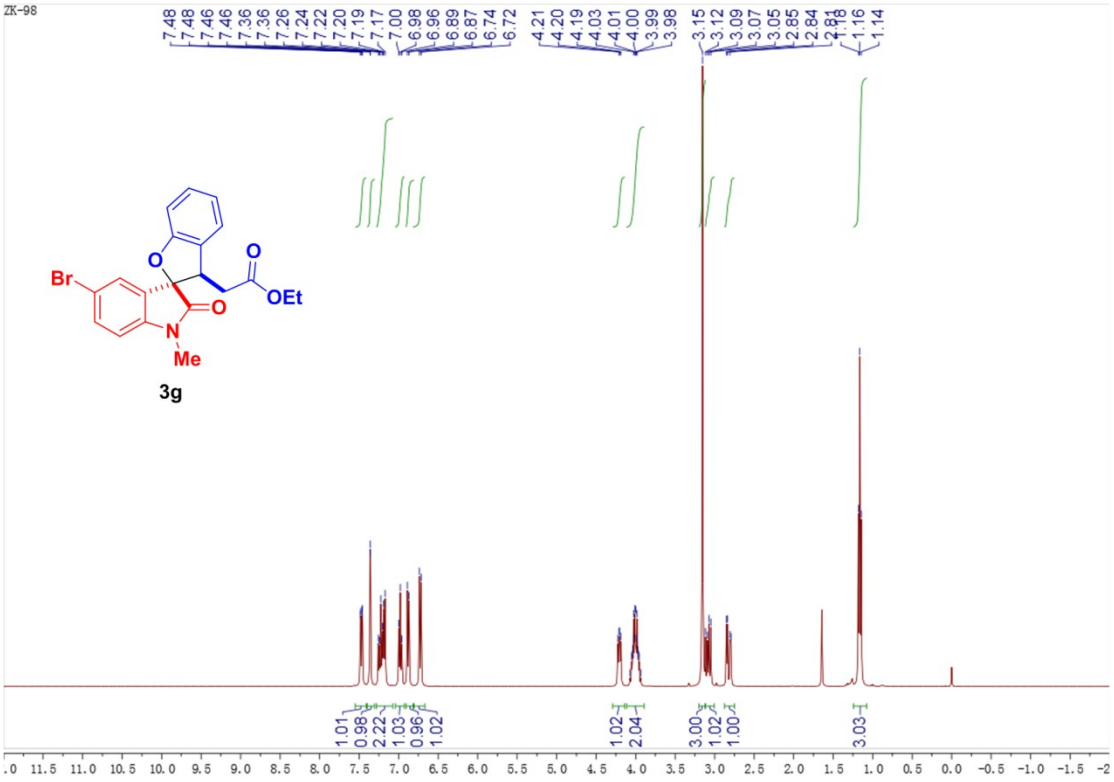

ZK-97
F
O
O
OEt
N
Me
3e'
f1 (ppm)


zk-87
7.32
7.32
7.30
7.30
7.26
7.24
7.23
7.23
7.22
7.20
7.20
7.19
7.17
6.99
6.97
6.95
6.89
6.87
6.78
6.76
4.21
4.20
4.19
4.02
4.00
3.99
3.98
3.15
3.07
3.05
2.85
2.84
2.81
2.79
1.17
1.15
1.14
Cl
O
O
OEt
O
N
Me
3f
1.03
2.88
1.02
0.99
1.01
1.01
2.03
3.00
0.99
1.00
3.02
f1 (ppm)

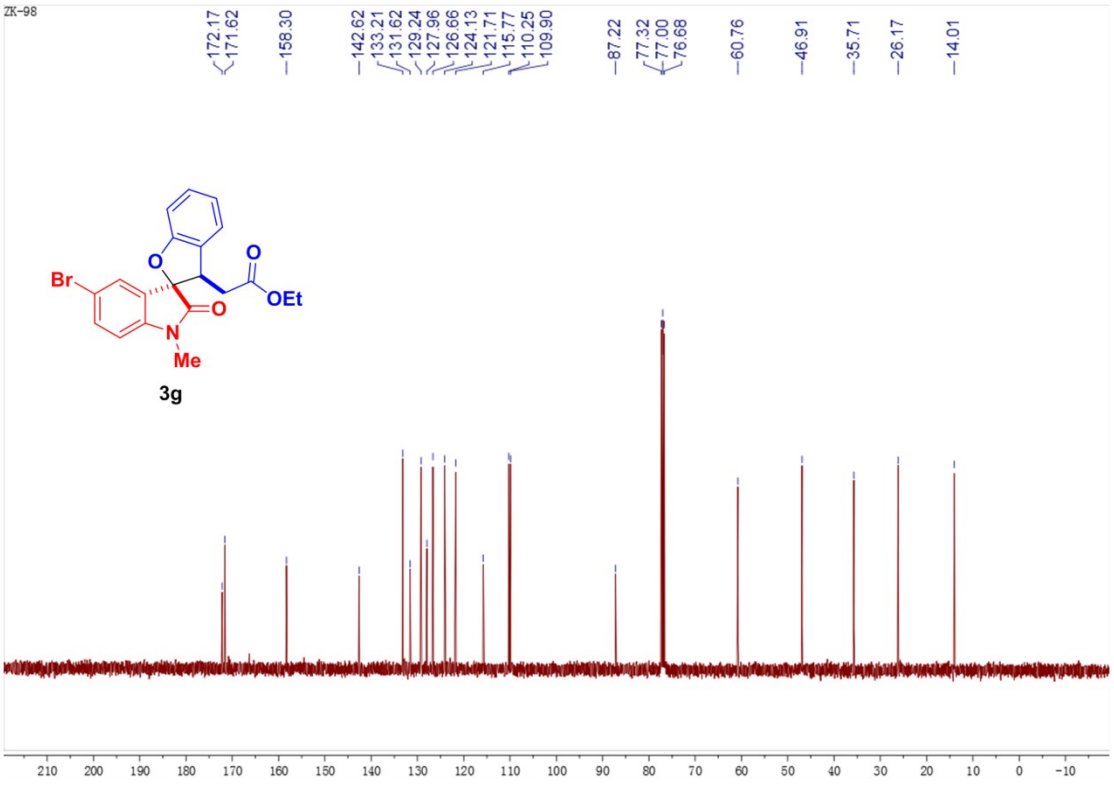

ZK-87
172.20
171.52
158.25
142.06
130.23
129.16
124.08
123.86
121.65
110.15
109.38
87.23
77.32
77.00
76.68
60.69
46.84
35.62
26.12
13.94
Cl
O
O
OEt
O
N
Me
3f
f1 (ppm)


ZK-108
7.32
7.32
7.30
7.30
7.26
7.24
7.22
7.20
7.17
7.15
7.09
7.09
6.99
6.98
6.96
6.88
6.86
6.77
6.75
4.42
4.41
4.39
4.38
3.90
3.88
3.86
3.85
3.22
2.93
2.92
2.89
2.87
2.62
2.59
2.58
1.08
1.07
1.05
Cl
O
O
OEt
O
N
Me
3f'
0.96
0.97
0.98
0.95
1.03
0.99
0.96
0.97
1.98
3.00
1.02
1.01
2.99
f1 (ppm)

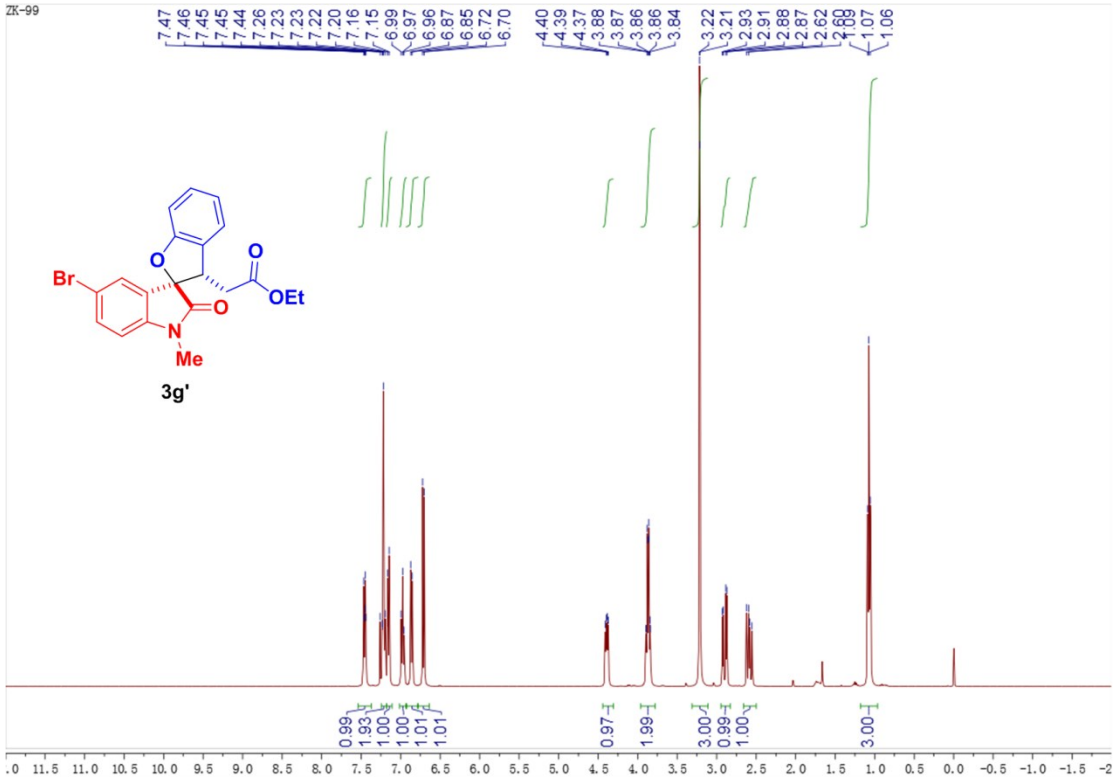

ZK-108
174.70
170.67
158.28
143.03
130.51
129.14
127.72
125.30
123.84
121.64
110.13
109.52
88.32
77.32
77.00
76.68
60.76
44.70
35.88
26.53
13.91
Cl
O
O
OEt
O
N
Me
3f'
f1 (ppm)

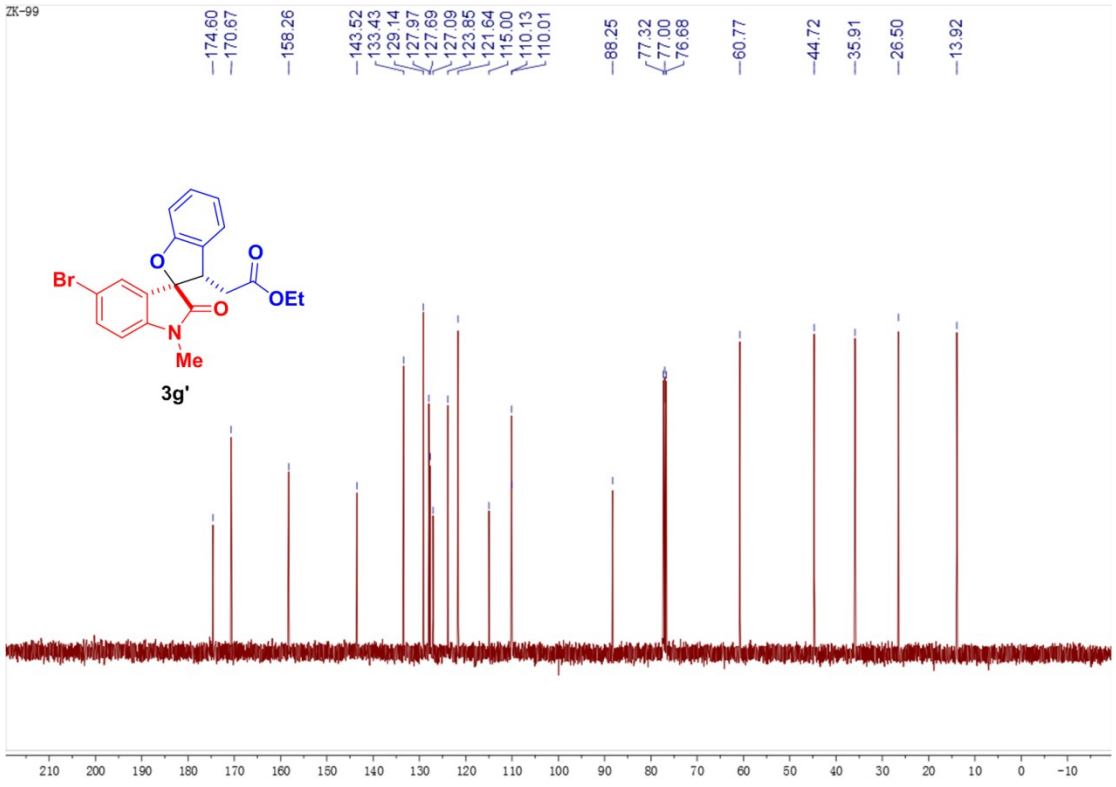

ZK-98
7.48
7.48
7.46
7.46
7.36
7.36
7.26
7.24
7.22
7.20
7.19
7.17
7.00
6.98
6.96
6.89
6.87
6.74
6.72
4.21
4.20
4.19
4.03
4.01
4.00
3.99
3.98
3.15
3.12
3.09
3.07
3.05
2.85
2.84
2.81
1.18
1.16
1.14
Br
O
O
OEt
O
N
Me
1.01
0.98
2.22
1.03
0.96
1.02
1.02
2.04
3.00
1.02
1.00
3.03

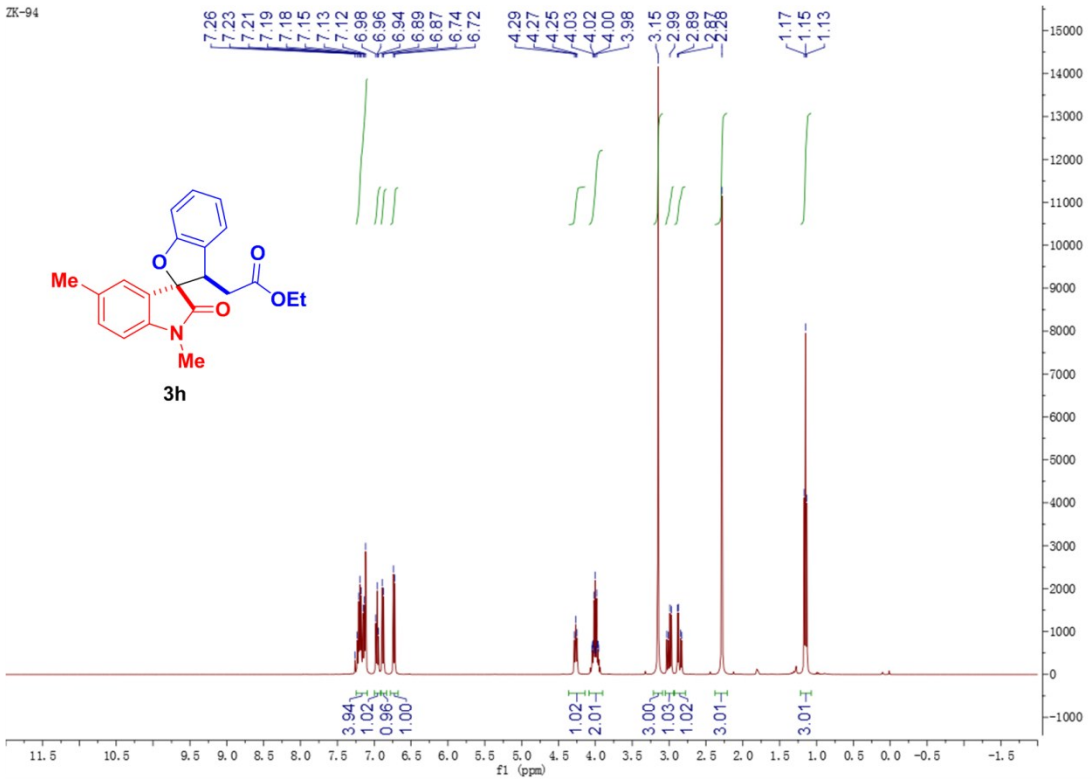
3g

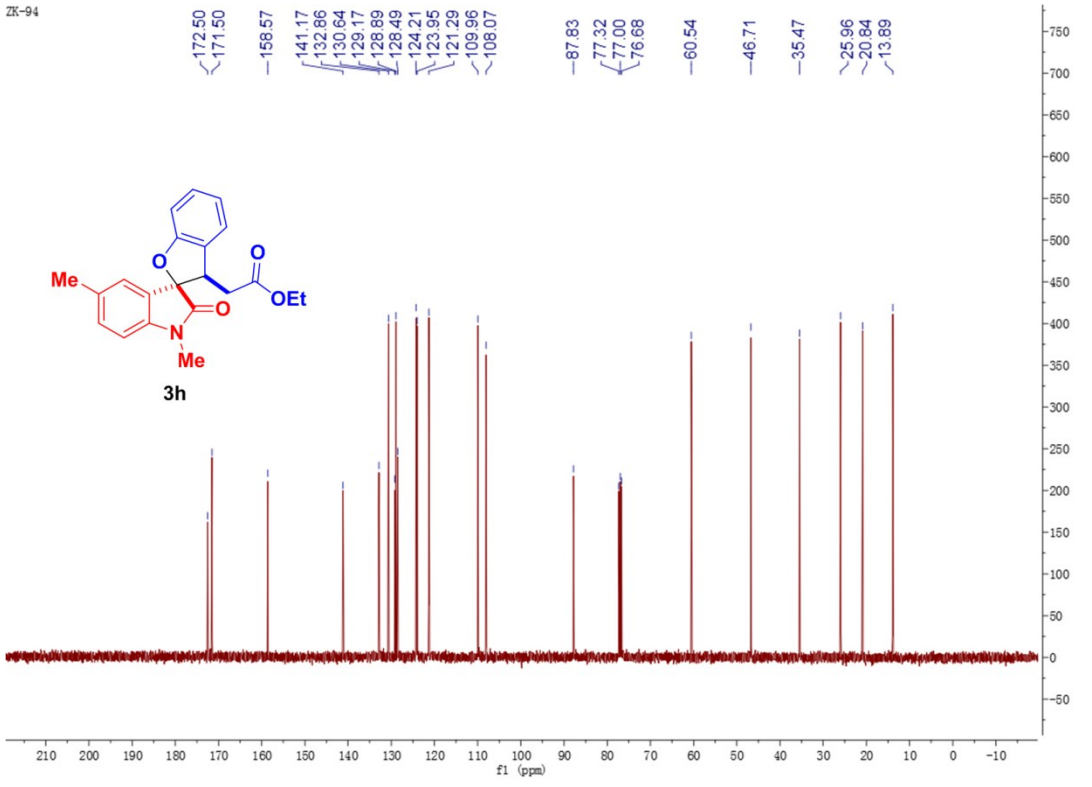

ZK-98
172.17
171.62
158.30
142.62
133.21
131.62
129.24
127.96
126.66
124.13
121.71
115.77
110.25
109.90
87.22
77.32
77.00
76.68
60.76
46.91
35.71
26.17
14.01
Br
O
O
OEt
O
N
Me

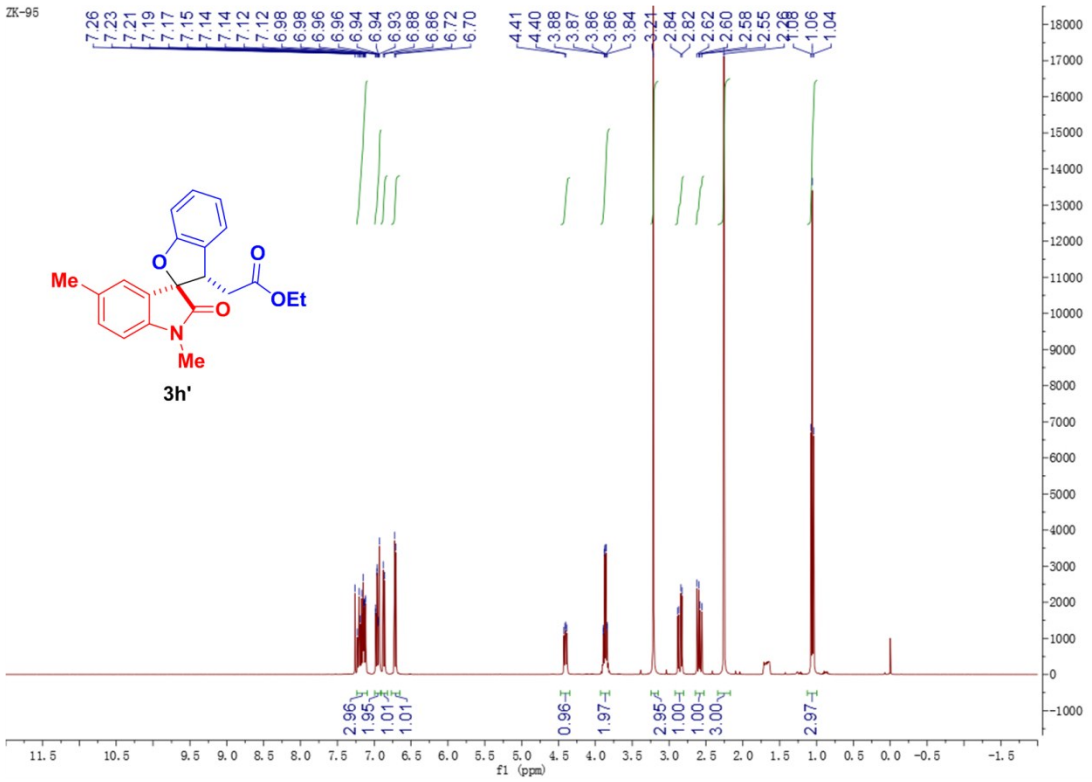
3g


ZK-99
7.47
7.46
7.45
7.45
7.44
7.26
7.23
7.23
7.22
7.20
7.16
7.15
6.99
6.97
6.96
6.87
6.85
6.72
6.70
4.40
4.39
4.37
3.88
3.87
3.86
3.86
3.84
3.22
3.21
2.93
2.91
2.88
2.87
2.62
2.60
1.07
1.06
Br
O
O
OEt
O
N
Me
3g'
0.99
1.93
1.00
1.00
1.01
1.01
0.97
1.99
3.00
0.99
1.00
3.00


ZK-99
174.60
170.67
158.26
143.52
133.43
129.14
127.97
127.69
127.09
123.85
121.64
115.00
110.13
110.01
88.25
77.32
77.00
76.68
60.77
44.72
35.91
26.50
13.92
Br
O
O
OEt
O
N
Me
3g'


ZK-94
7.26
7.23
7.21
7.19
7.18
7.15
7.13
7.12
6.98
6.96
6.94
6.89
6.87
6.74
6.72
4.29
4.27
4.25
4.03
4.02
4.00
3.98
3.15
2.99
2.89
2.87
2.28
1.17
1.15
1.13
Me
O
OEt
O
N
Me
3h
3.94
1.02
0.96
1.00
1.02
2.01
3.00
1.03
1.02
3.01
3.01
f1 (ppm)


ZK-94
172.50
171.50
158.57
141.17
132.86
130.64
129.17
128.89
128.49
124.21
123.95
121.29
109.96
108.07
87.83
77.32
77.00
76.68
60.54
46.71
35.47
25.96
20.84
13.89
Me
O
OEt
O
N
Me
3h
f1 (ppm)


ZK-95
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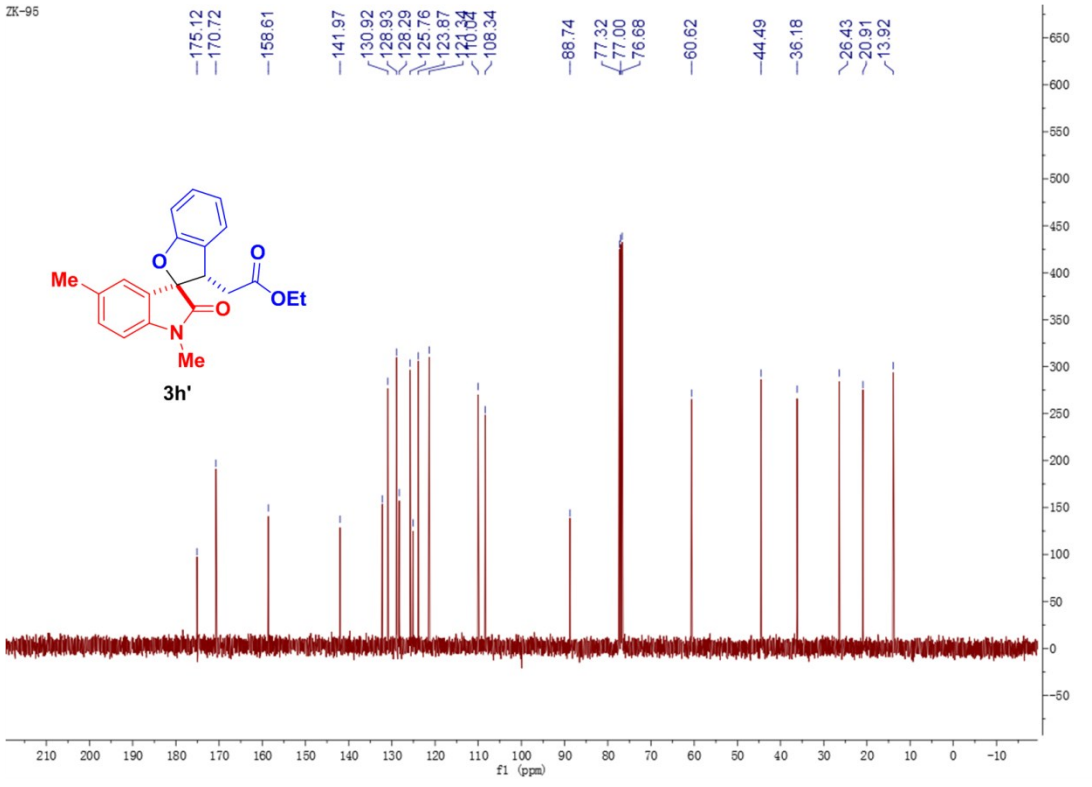
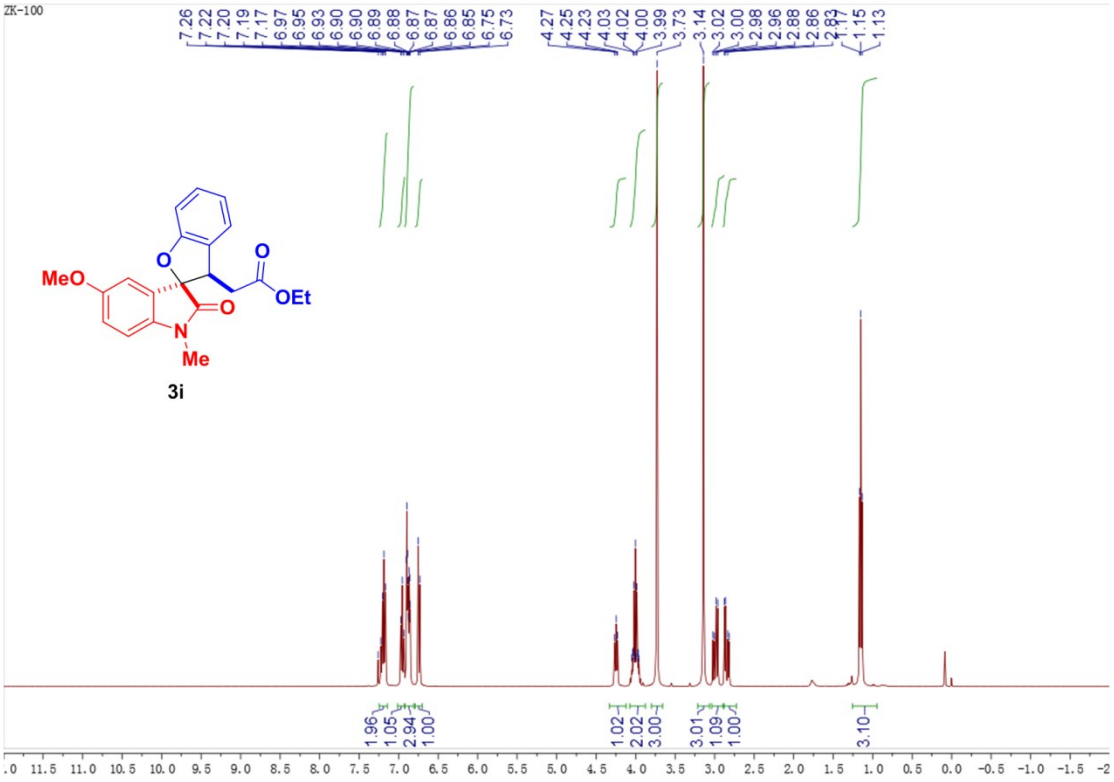
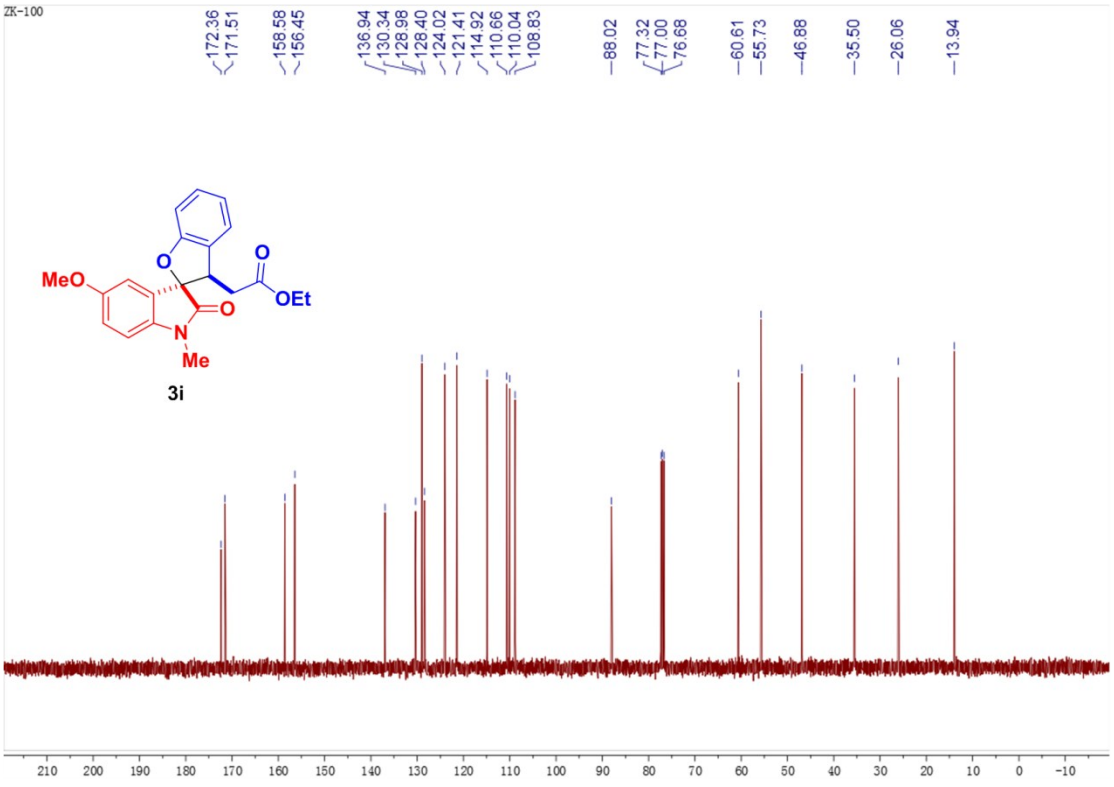
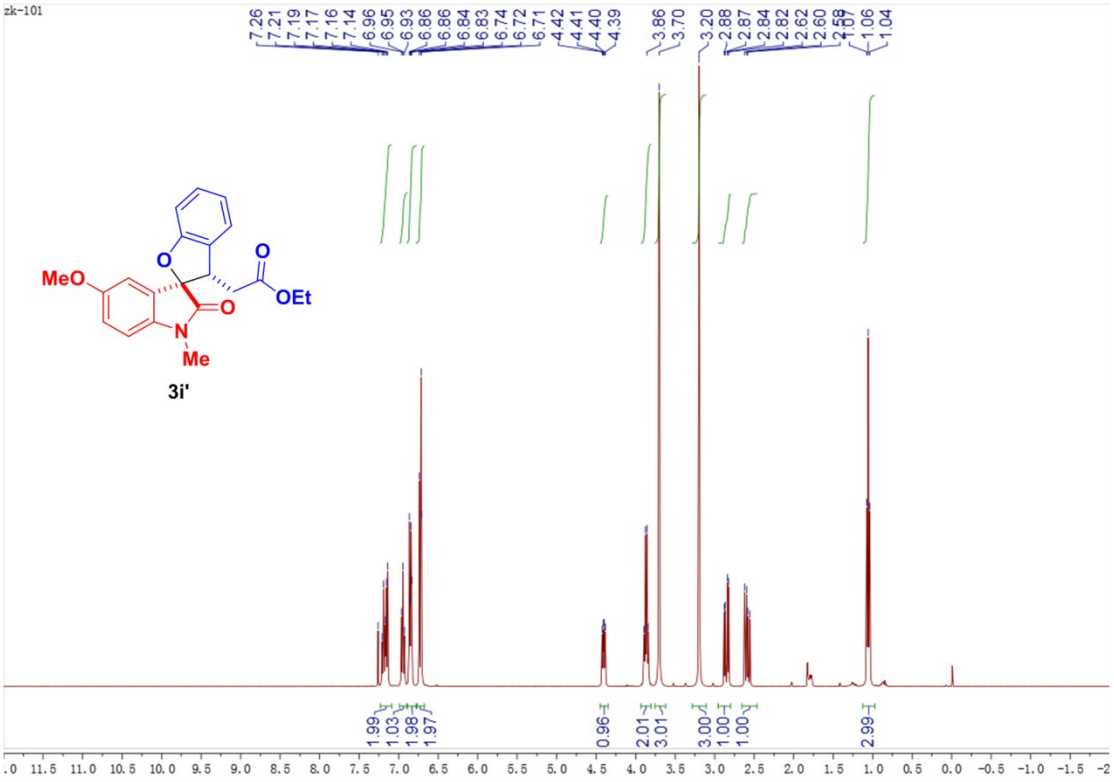
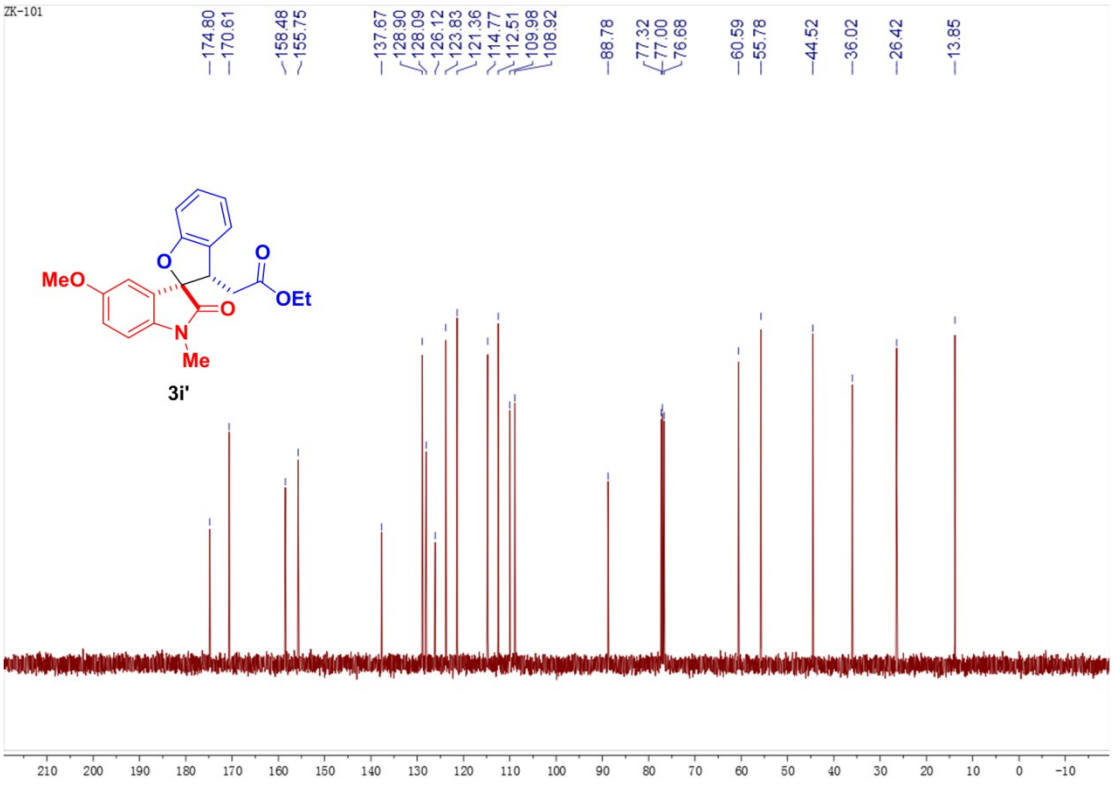
7.23
7.21
7.19
7.17
7.15
7.14
7.14
7.12
7.12
6.98
6.98
6.96
6.96
6.94
6.94
6.93
6.88
6.86
6.72
6.70
4.41
4.40
3.88
3.87
3.86
3.86
3.84
3.21
2.84
2.82
2.62
2.60
2.58
2.55
2.26
1.08
1.06
1.04
Me
O
O
OEt
N
O
Me
3h'
2.96
1.95
1.01
1.01
0.96
1.97
2.95
1.00
1.00
3.00
2.97
f1 (ppm)

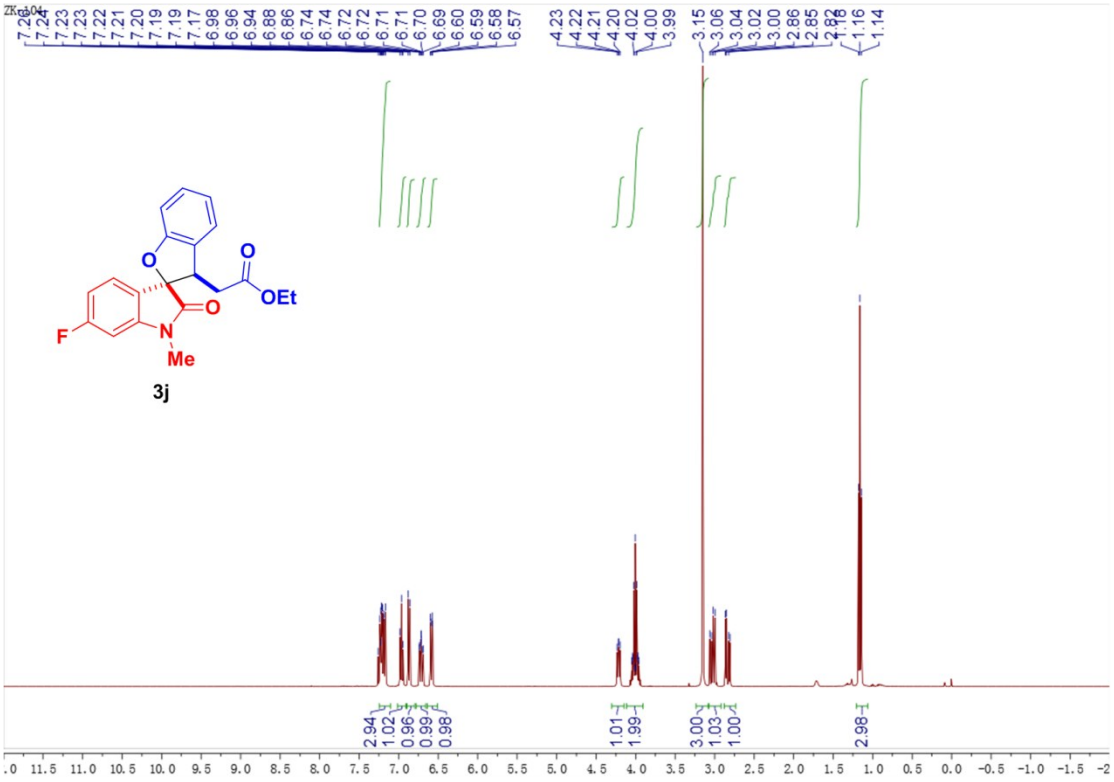

ZK-95
175.12
170.72
158.61
141.97
130.92
128.93
128.29
125.76
123.87
121.34
110.04
108.34
88.74
77.32
77.00
76.68
60.62
44.49
36.18
26.43
20.91
13.92
Me
O
O
OEt
N
O
Me
3h'
f1 (ppm)


ZK-100
MeO
O
OEt
O
N
Me
3i


ZK-100
MeO
O
OEt
O
N
Me
3i


zk-101
MeO
O
OEt
N
Me
3i'


ZK-101
MeO
O
OEt
N
Me
3i'


ZK-104
7.25
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7.23
7.23
7.22
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7.20
7.19
7.19
7.17
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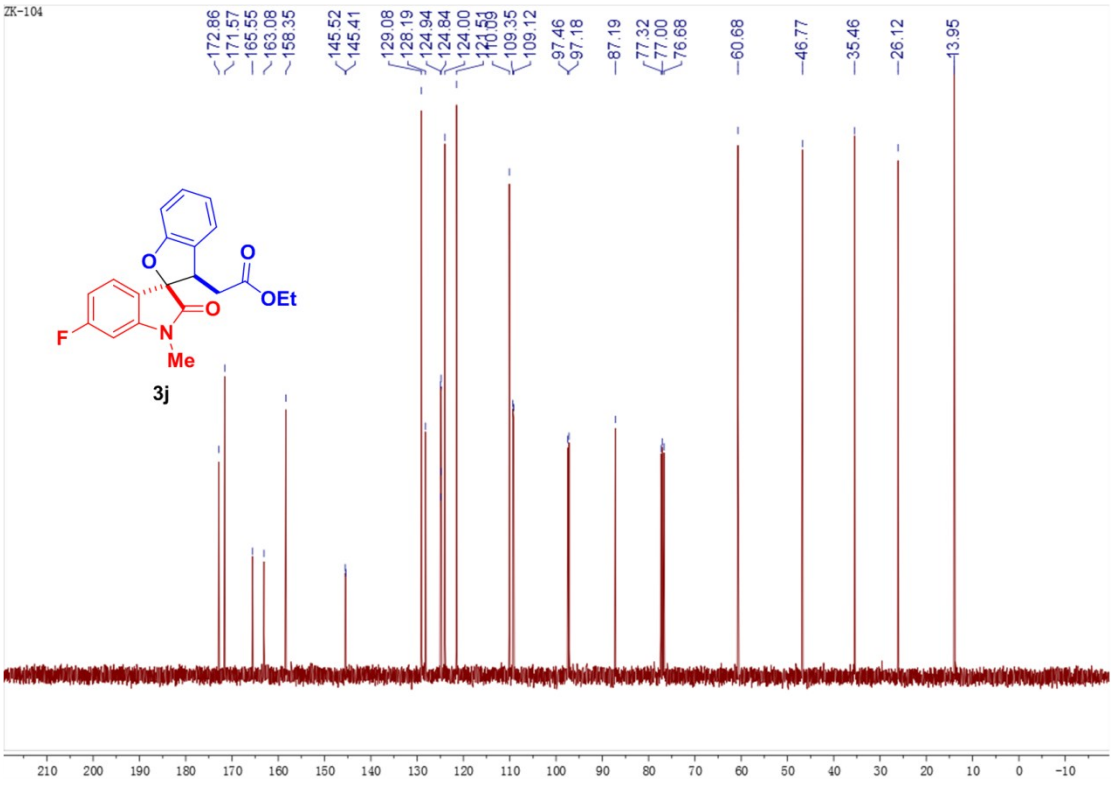
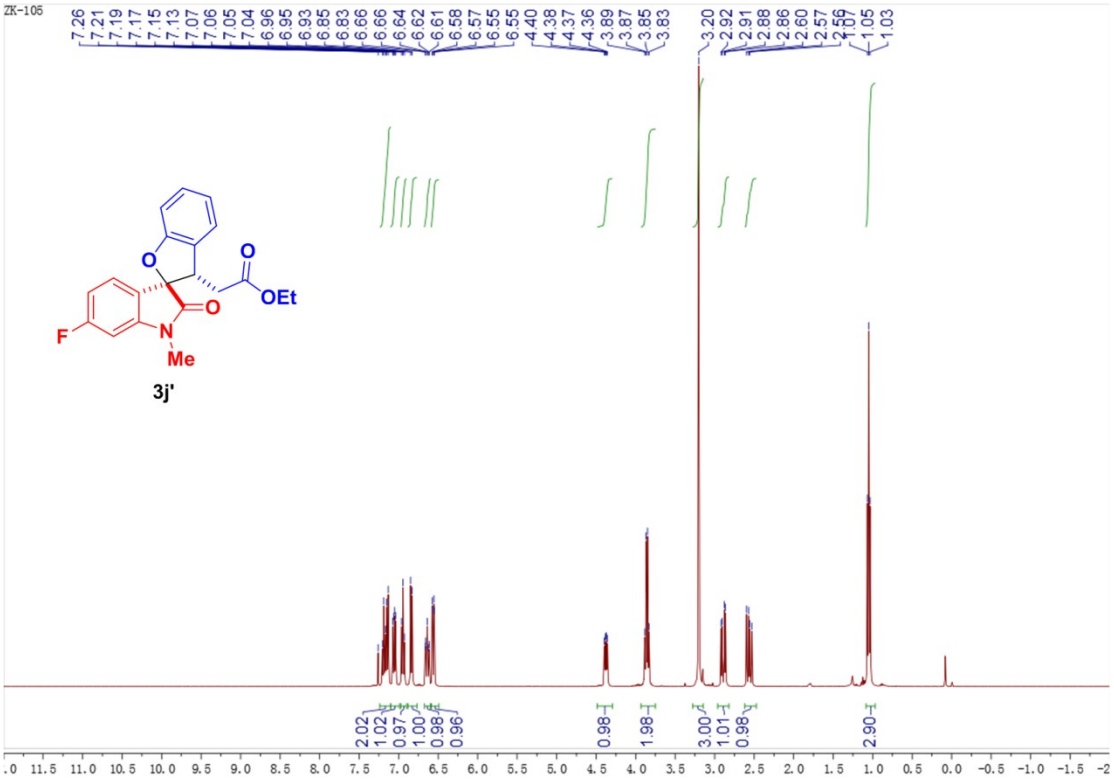
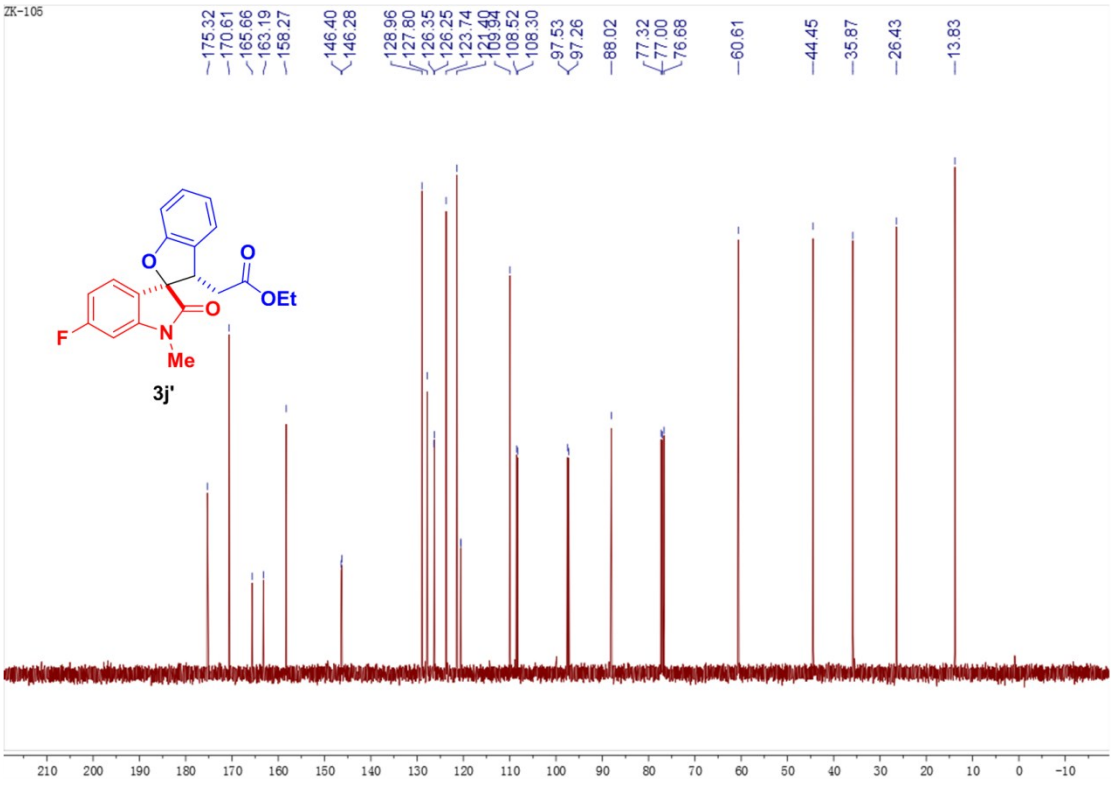
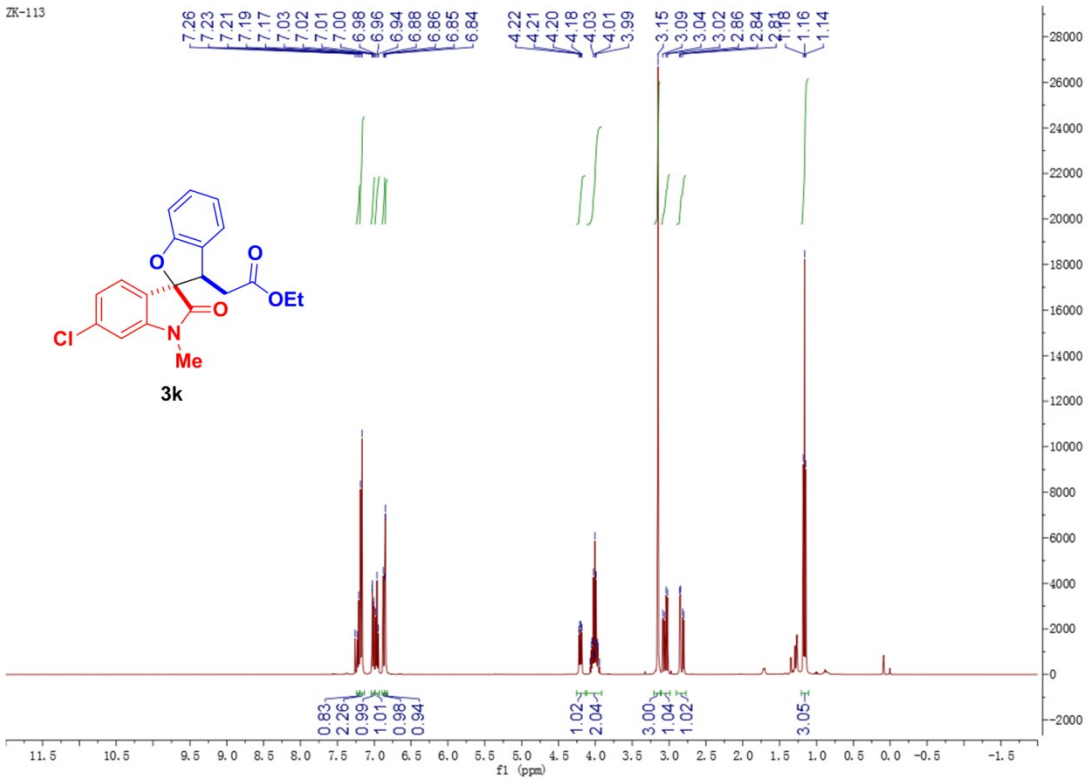
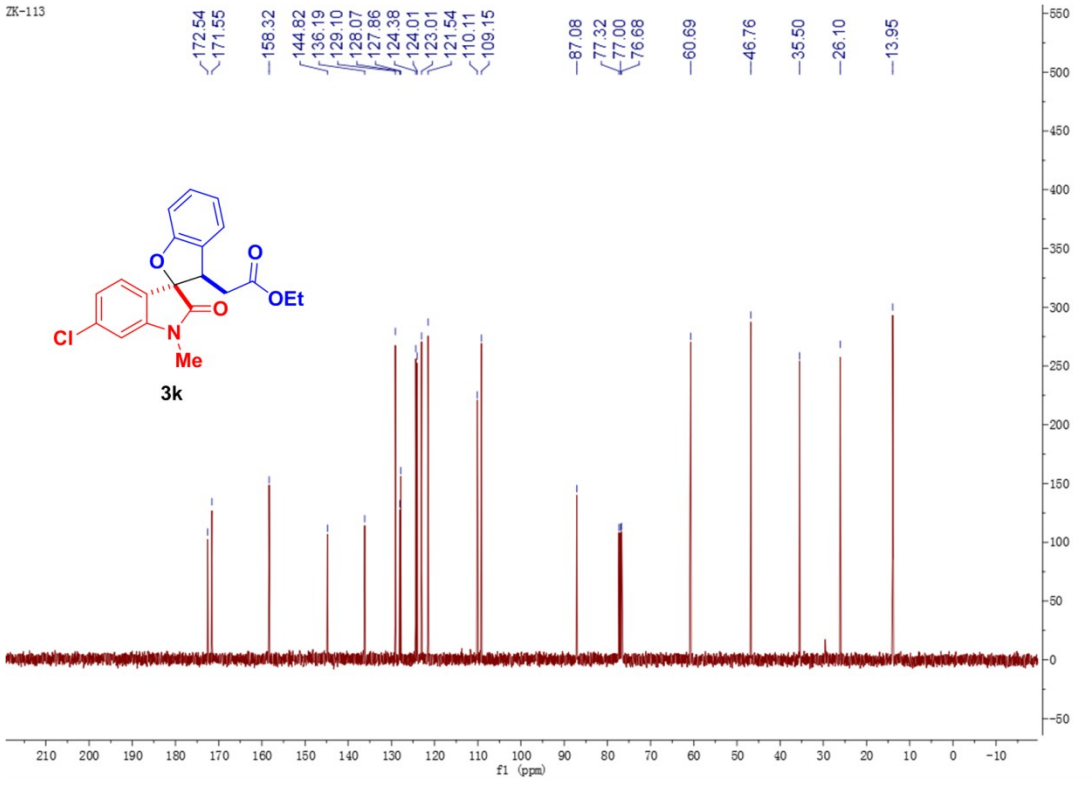
6.96
6.94
6.88
6.86
6.74
6.74
6.72
6.72
6.71
6.71
6.70
6.69
6.60
6.59
6.58
6.57
4.23
4.22
4.21
4.20
4.02
4.00
3.99
3.15
3.06
3.04
3.02
3.00
2.86
2.85
2.82
2.81
1.16
1.14
O
O
OEt
O
F
N
Me
3j
2.94
1.02
0.96
0.99
0.98
1.01
1.99
3.00
1.03
1.00
2.98
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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
-1.5

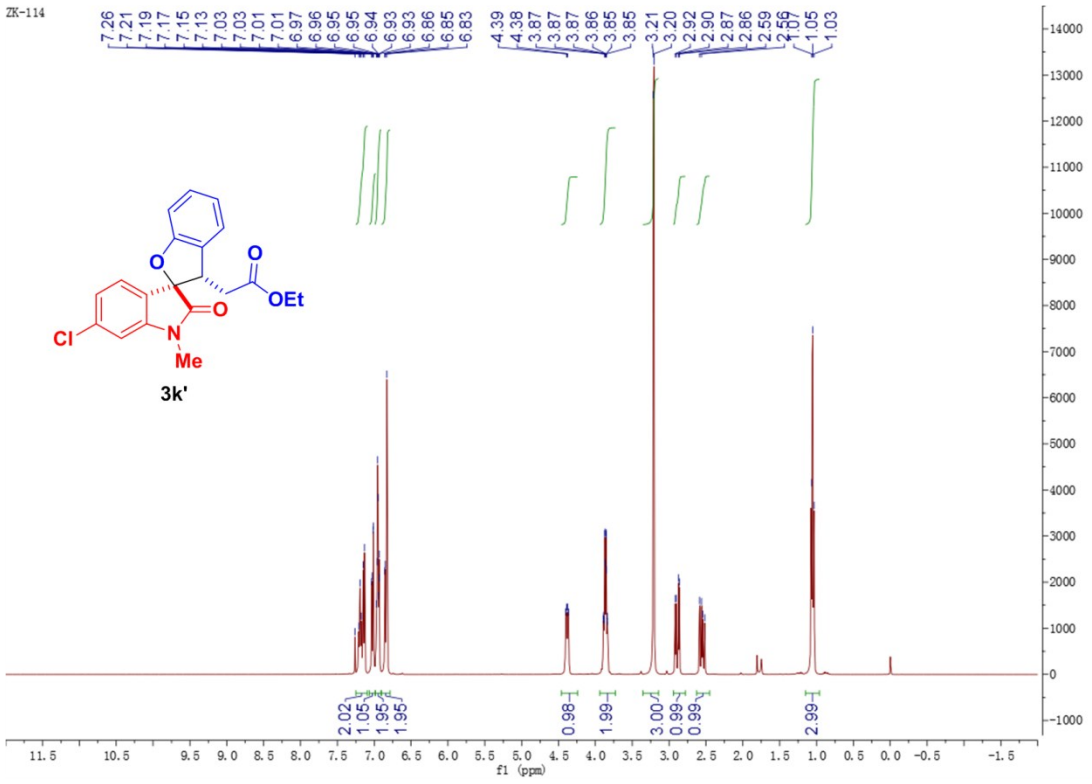

ZK-104
172.86
171.57
165.55
163.08
158.35
145.52
145.41
129.08
128.19
124.94
124.84
124.00
121.51
121.09
109.35
109.12
97.46
97.18
87.19
77.32
77.00
76.68
60.68
46.77
35.46
26.12
13.95
O
O
OEt
O
F
N
Me
3j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


ZK-105
7.26
7.21
7.19
7.17
7.15
7.13
7.07
7.06
7.05
7.04
6.96
6.95
6.93
6.85
6.83
6.66
6.64
6.62
6.61
6.58
6.57
6.55
4.40
4.38
4.37
4.36
3.89
3.87
3.85
3.83
3.20
2.92
2.91
2.88
2.86
2.60
2.57
1.07
1.05
1.03
O
O
OEt
O
F
N
Me
3j'
2.02
1.02
0.97
1.00
0.98
0.96
0.98
1.98
3.00
1.01
0.98
2.90


ZK-105
175.32
170.61
165.66
163.19
158.27
146.40
146.28
128.96
127.80
126.35
126.25
123.74
121.40
109.94
108.52
108.30
97.53
97.26
88.02
77.32
77.00
76.68
60.61
44.45
35.87
26.43
13.83
O
O
OEt
O
F
N
Me
3j'


ZK-113
7.26
7.23
7.21
7.19
7.17
7.03
7.02
7.01
7.00
6.98
6.96
6.94
6.88
6.86
6.85
6.84
4.22
4.21
4.20
4.18
4.03
4.01
3.99
3.15
3.09
3.04
3.02
2.86
2.84
2.81
1.18
1.16
1.14
O
O
OEt
O
N
Me
Cl
3k
0.83
2.26
0.99
1.01
0.98
0.94
1.02
2.04
3.00
1.04
1.02
3.05
f1 (ppm)


ZK-113
172.54
171.55
158.32
144.82
136.19
129.10
128.07
127.86
124.38
124.01
123.01
121.54
110.11
109.15
87.08
77.32
77.00
76.68
60.69
46.76
35.50
26.10
13.95
O
O
OEt
O
N
Me
Cl
3k
f1 (ppm)


ZK-114
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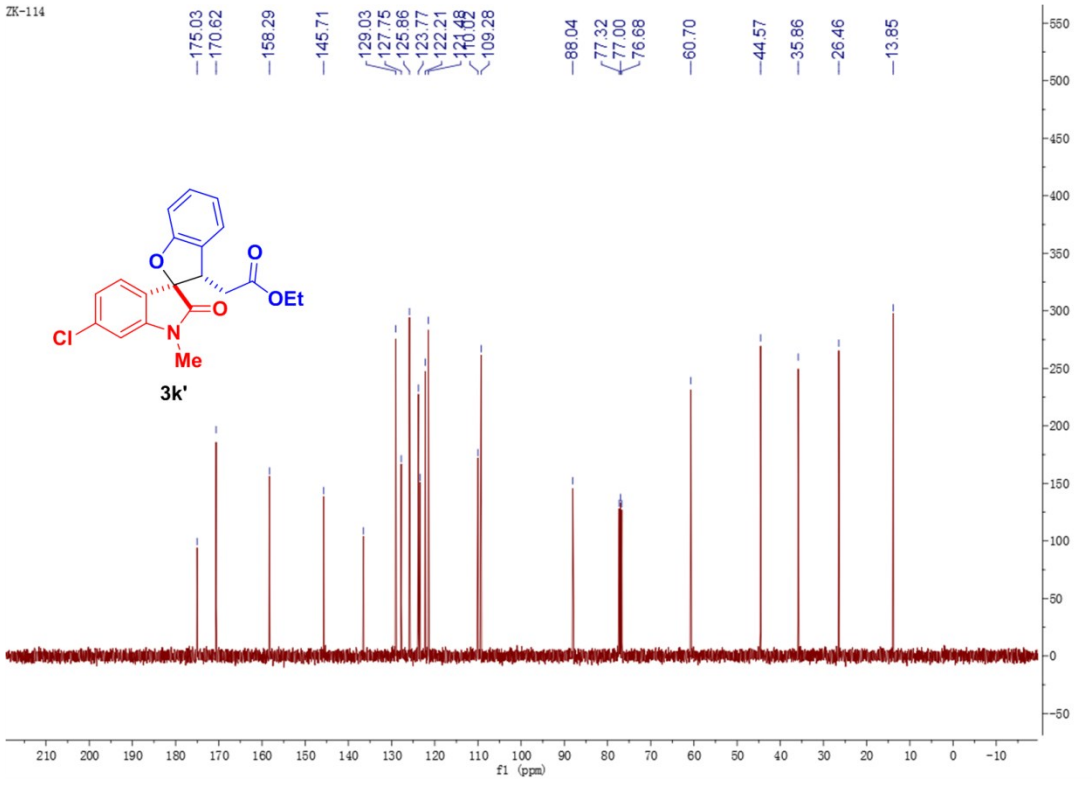
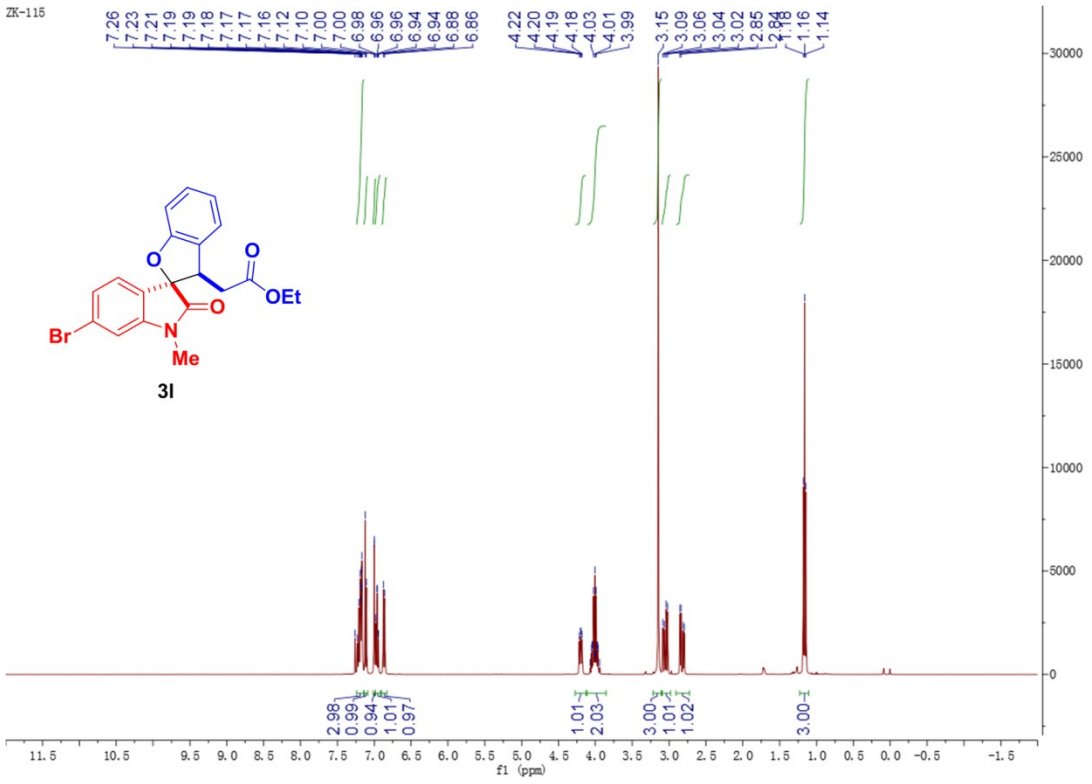
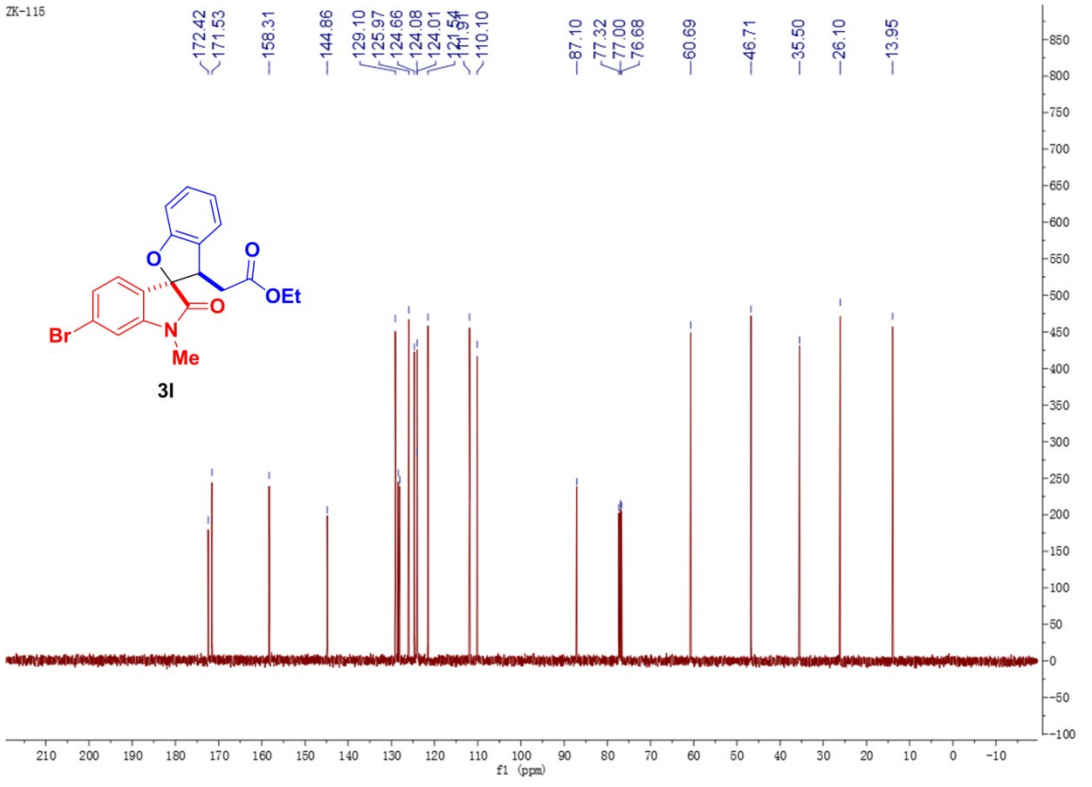
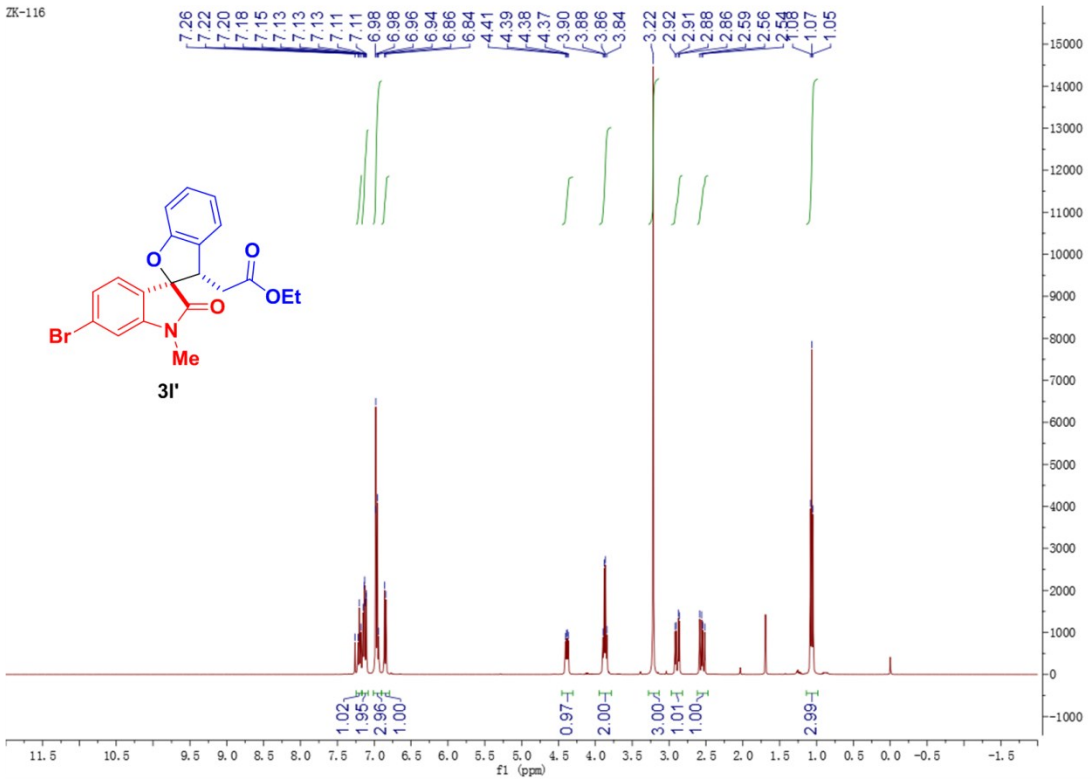
7.21
7.19
7.17
7.15
7.13
7.03
7.01
7.01
6.97
6.96
6.95
6.95
6.94
6.93
6.93
6.86
6.85
6.83
4.39
4.38
3.87
3.87
3.87
3.86
3.85
3.85
3.21
3.20
2.92
2.90
2.87
2.86
2.59
2.56
1.07
1.05
1.03
O
O
OEt
O
Cl
N
Me
3k'
2.02
1.05
1.95
1.95
0.98
1.99
3.00
0.99
0.99
2.99
f1 (ppm)


ZK-114
175.03
170.62
158.29
145.71
129.03
127.75
125.86
123.77
122.21
109.28
88.04
77.32
77.00
76.68
60.70
44.57
35.86
26.46
13.85
O
O
OEt
O
Cl
N
Me
3k'
f1 (ppm)


ZK-115
7.26
7.23
7.21
7.19
7.19
7.18
7.17
7.17
7.16
7.12
7.10
7.00
7.00
6.98
6.96
6.96
6.94
6.94
6.88
6.86
4.22
4.20
4.19
4.18
4.03
4.01
3.99
3.15
3.09
3.06
3.04
3.02
2.85
1.18
1.16
1.14
O
O
OEt
O
N
Me
Br
3l
2.98
0.99
0.94
1.01
0.97
1.01
2.03
3.00
1.01
1.02
3.00
f1 (ppm)


ZK-115
172.42
171.53
158.31
144.86
129.10
125.97
124.66
124.08
124.01
111.54
111.41
110.10
87.10
77.32
77.00
76.68
60.69
46.71
35.50
26.10
13.95
O
O
OEt
O
N
Me
Br
3l
f1 (ppm)


ZK-116
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7.22
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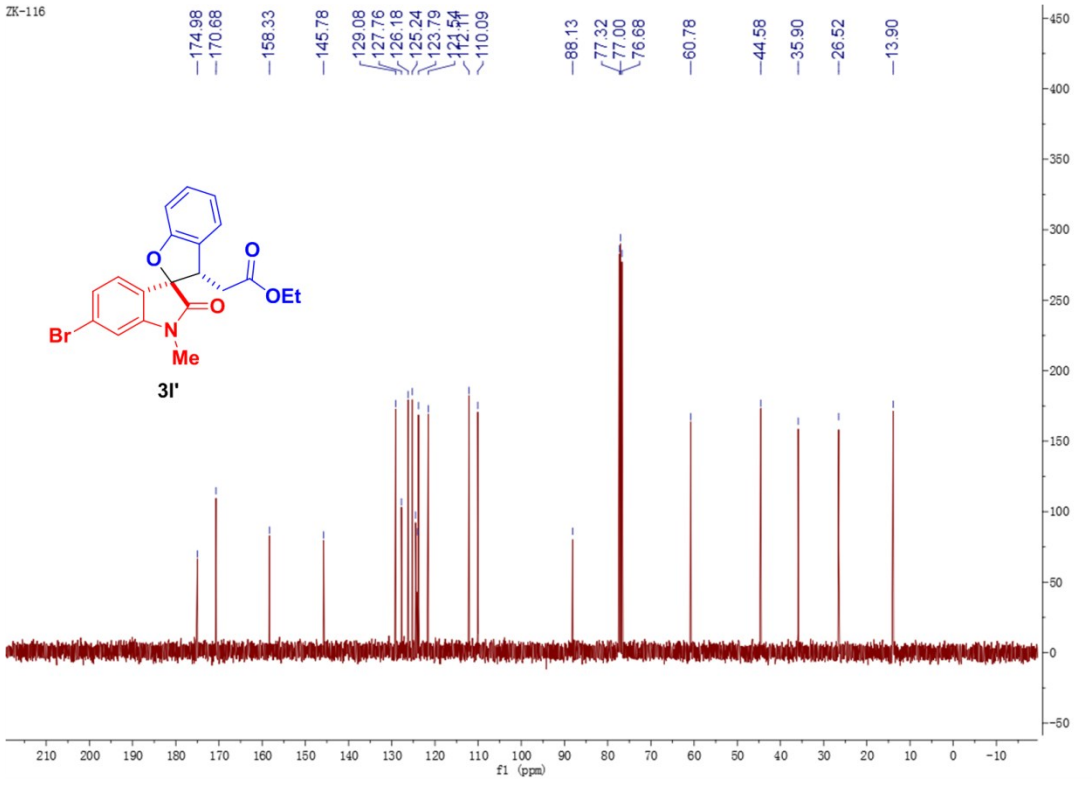
7.13
7.13
7.11
7.11
6.98
6.98
6.96
6.94
6.86
6.84
4.41
4.39
4.38
4.37
3.90
3.88
3.86
3.84
3.22
2.92
2.91
2.88
2.86
2.59
2.56
2.54
1.08
1.07
1.05
O
O
OEt
O
N
Me
Br
3l'
1.02
1.95
2.96
1.00
0.97
2.00
3.00
1.01
1.00
2.99
f1 (ppm)


ZK-116
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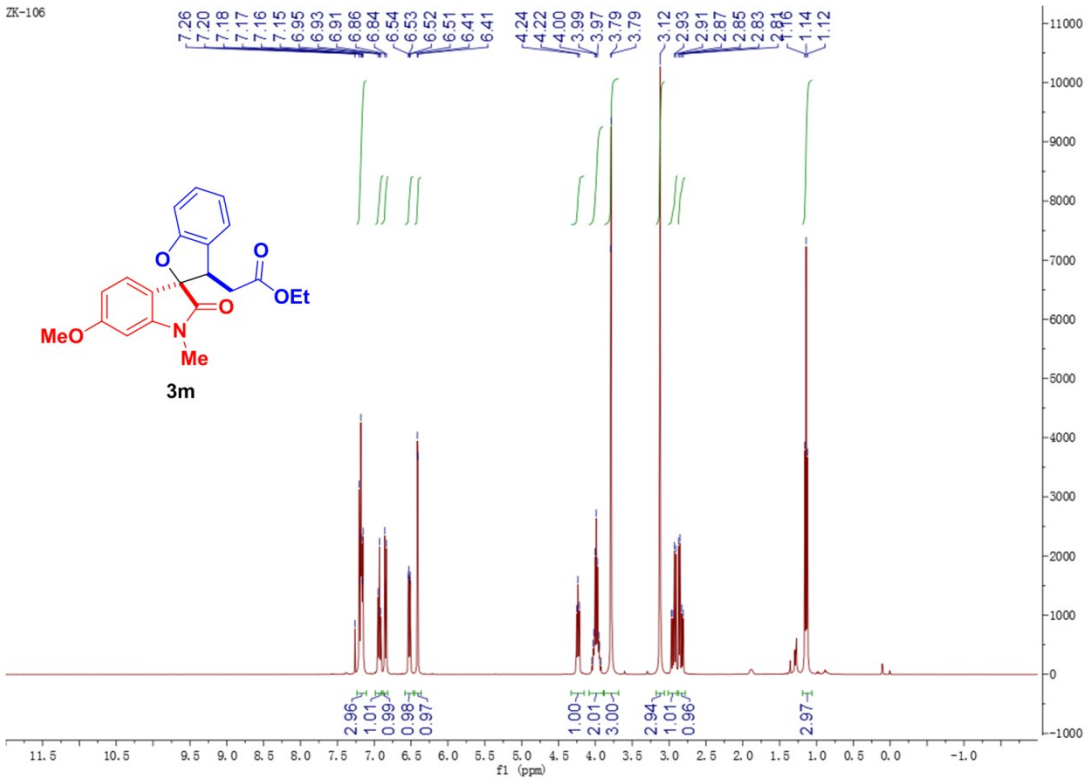
127.76
126.18
125.24
123.79
112.11
110.09
88.13
77.32
77.00
76.68
60.78
44.58
35.90
26.52
13.90
O
O
OEt
O
N
Me
Br
3l'
f1 (ppm)


ZK-106
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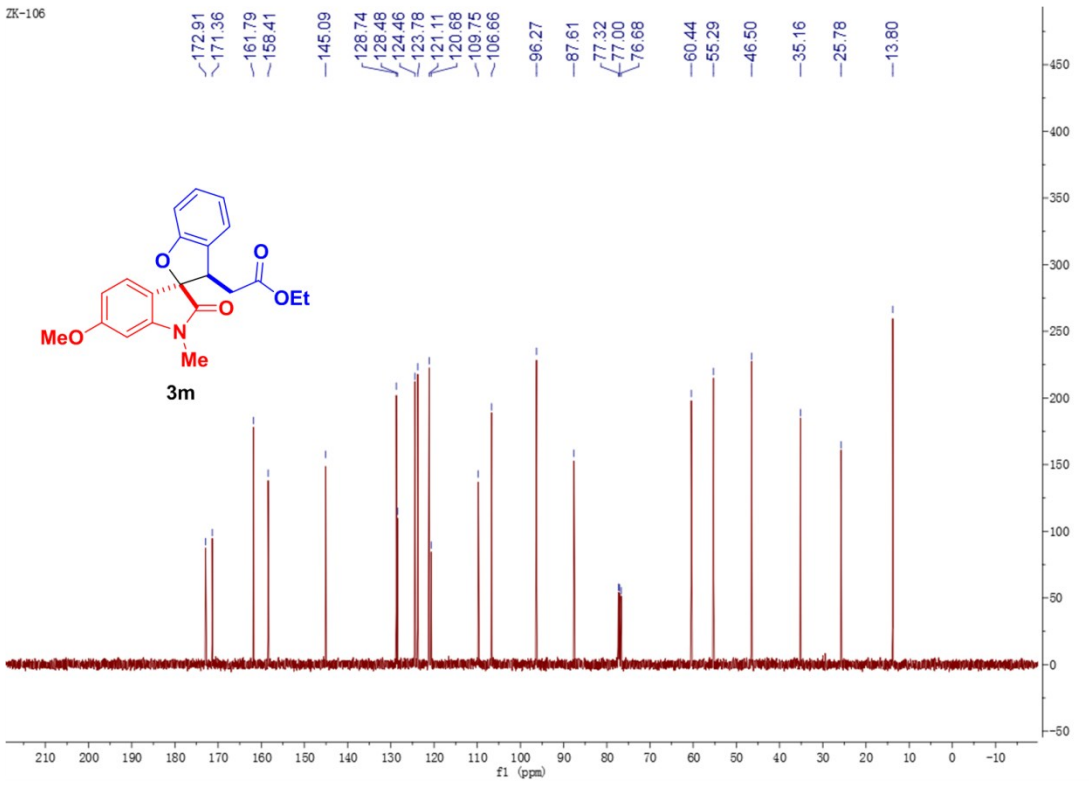
6.91
6.86
6.84
6.54
6.53
6.52
6.51
6.41
6.41
4.24
4.22
4.00
3.99
3.97
3.79
3.79
3.12
2.93
2.91
2.87
2.85
2.83
2.81
1.16
1.14
1.12
O
O
OEt
O
N
MeO
Me
3m
2.96
1.01
0.99
0.98
0.97
1.00
2.01
3.00
2.94
1.01
0.96
2.97
f1 (ppm)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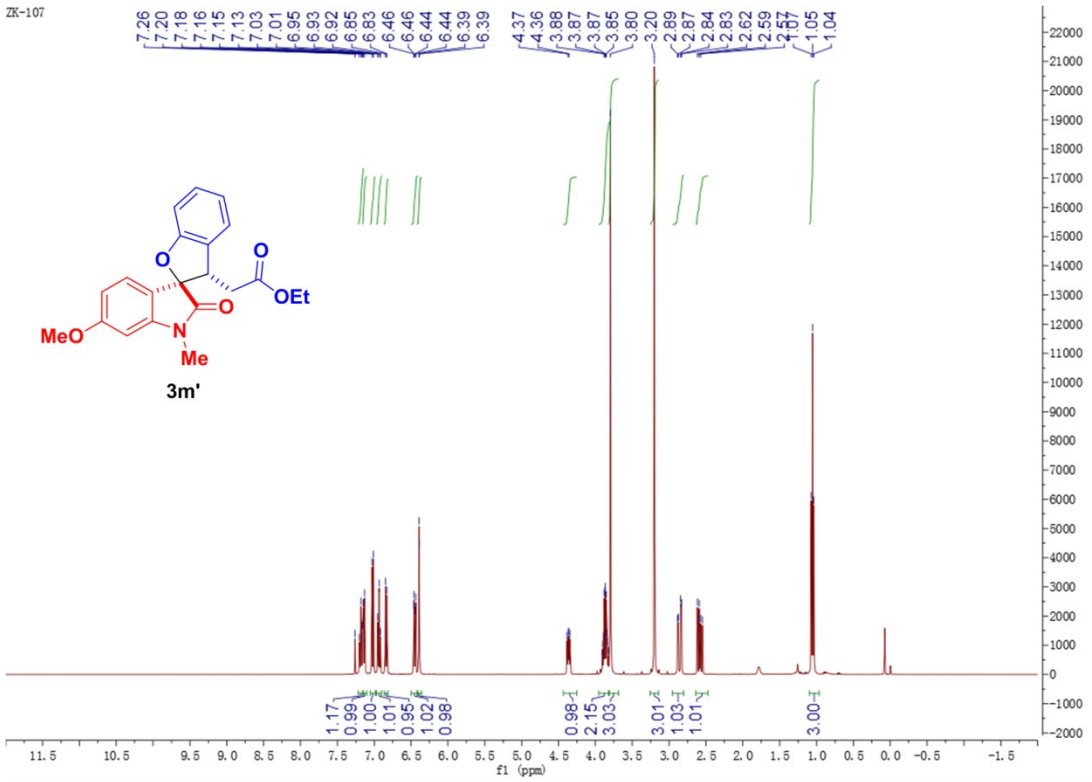
123.78
121.11
120.68
109.75
106.66
96.27
87.61
77.32
77.00
76.68
60.44
55.29
46.50
35.16
25.78
13.80
O
O
OEt
O
N
MeO
Me
3m
f1 (ppm)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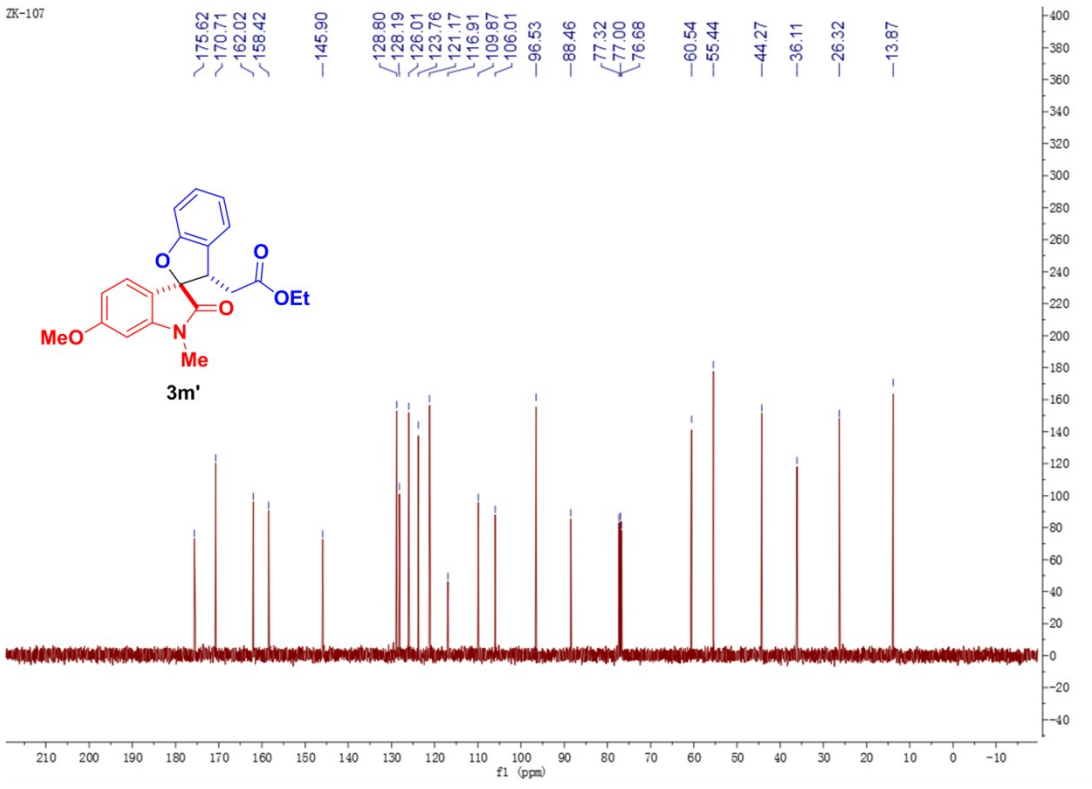
7.20
7.18
7.16
7.15
7.13
7.03
7.01
6.95
6.93
6.92
6.85
6.83
6.46
6.44
6.44
6.39
6.39
4.37
4.36
3.88
3.87
3.87
3.85
3.80
3.20
2.89
2.87
2.84
2.83
2.62
2.59
2.57
1.07
1.05
1.04
1.17
0.99
1.00
1.01
0.95
1.02
0.98
0.98
2.15
3.03
3.01
1.03
1.01
3.00
MeO
N
Me
O
O
OEt
3m'
f1 (ppm)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162.02
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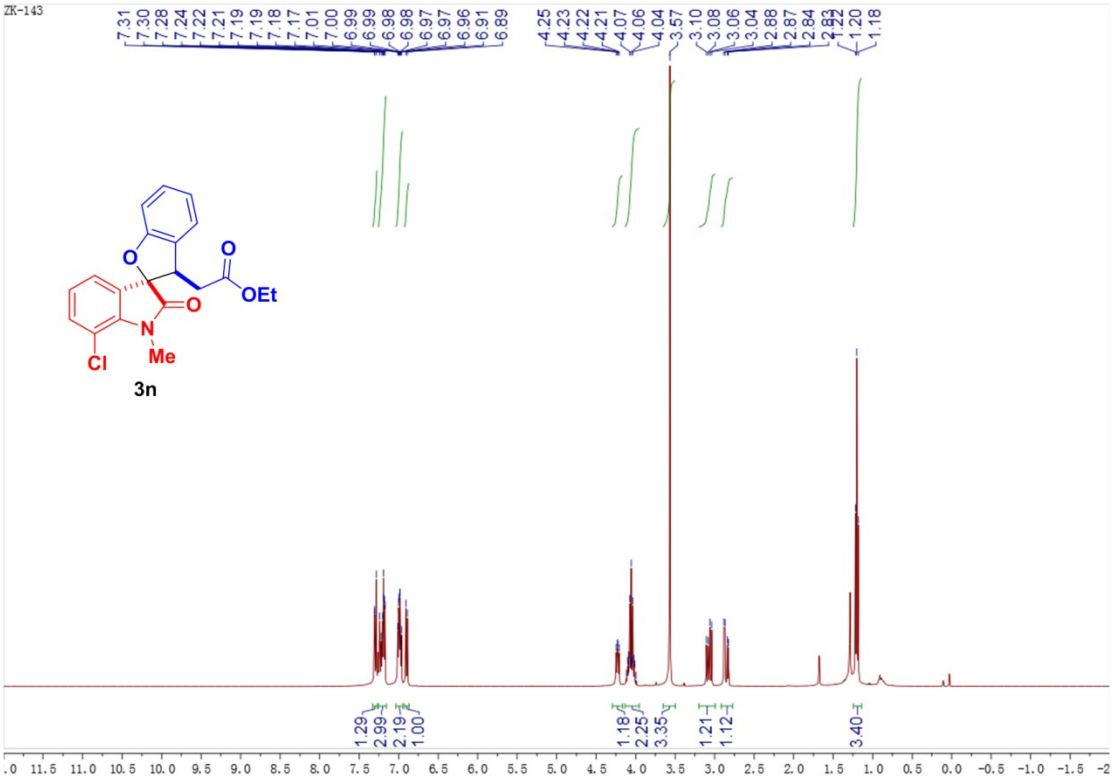
128.19
126.01
123.76
121.17
116.91
109.87
106.01
96.53
88.46
77.32
77.00
76.68
60.54
55.44
44.27
36.11
26.32
13.87
MeO
N
Me
O
O
OEt
3m'
f1 (ppm)


ZK-143
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7.30
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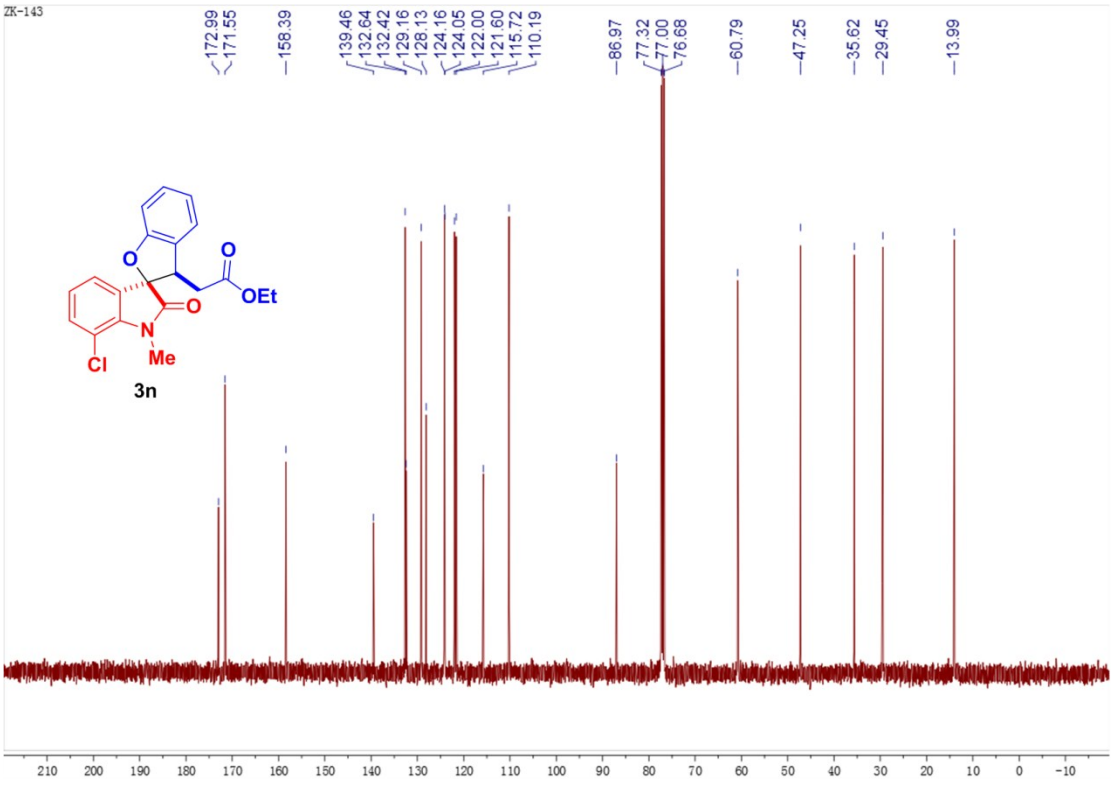
7.00
6.99
6.99
6.98
6.98
6.97
6.97
6.96
6.91
6.89
4.25
4.23
4.22
4.21
4.07
4.06
4.04
3.57
3.10
3.08
3.06
3.04
2.88
2.87
2.84
1.20
1.18
O
O
OEt
O
N
Me
Cl
3n
1.29
2.99
2.19
1.00
1.18
2.25
3.35
1.21
1.12
3.40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132.42
129.16
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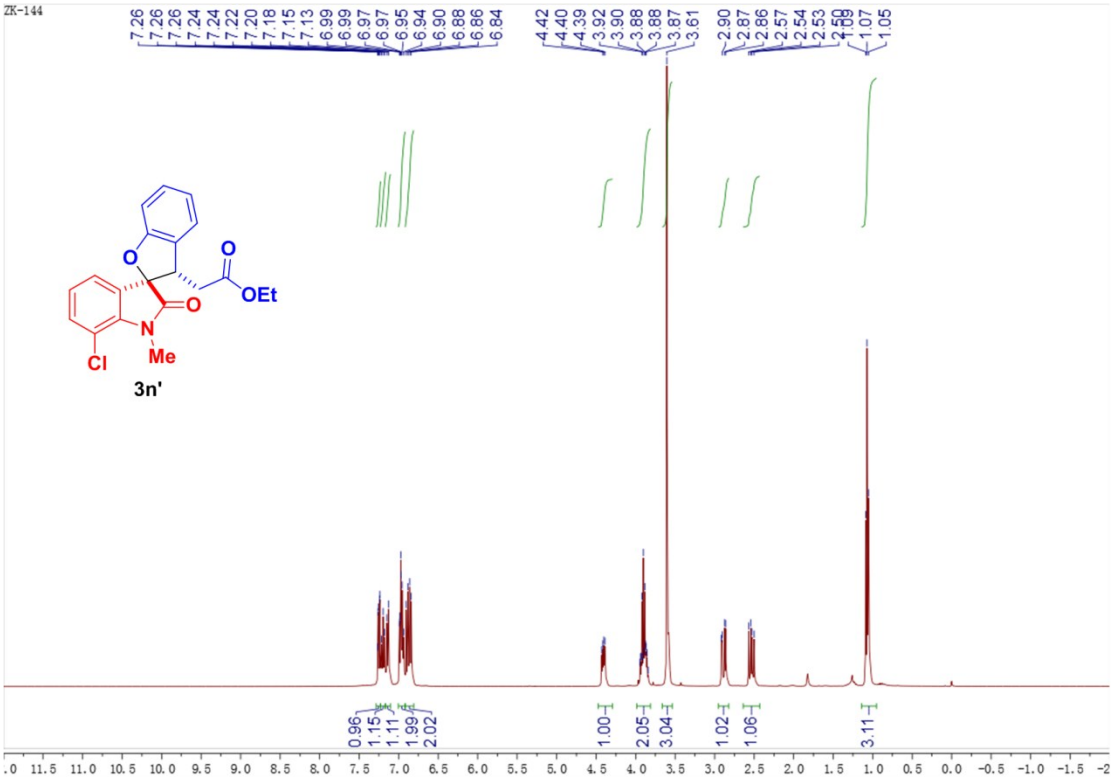
124.16
124.05
122.00
121.60
115.72
110.19
86.97
77.32
77.00
76.68
60.79
47.25
35.62
29.45
13.99
O
O
OEt
O
N
Me
Cl
3n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7.13
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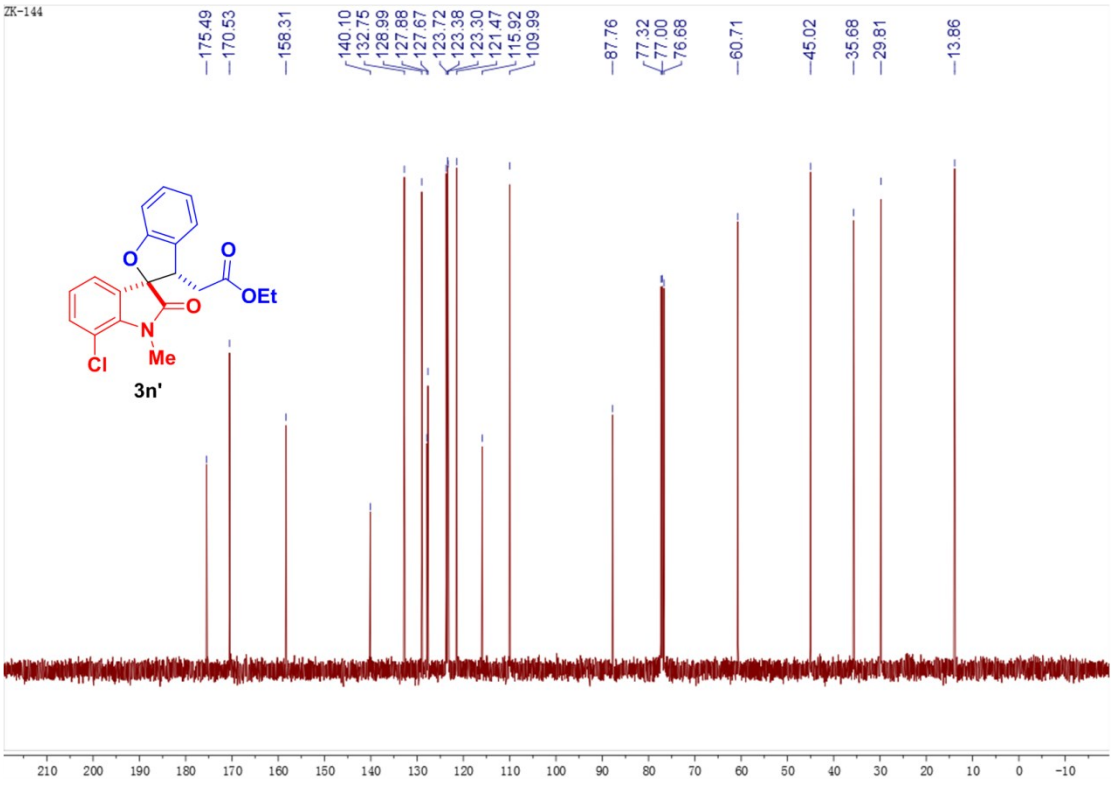
6.99
6.97
6.97
6.95
6.94
6.90
6.88
6.86
6.84
4.42
4.40
4.39
3.92
3.90
3.88
3.88
3.87
3.61
2.90
2.87
2.86
2.57
2.54
2.53
1.09
1.07
1.05
O
O
OEt
O
N
Me
Cl
3n'
0.96
1.15
1.11
1.99
2.02
1.00
2.05
3.04
1.02
1.06
3.11
.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2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158.31
140.10
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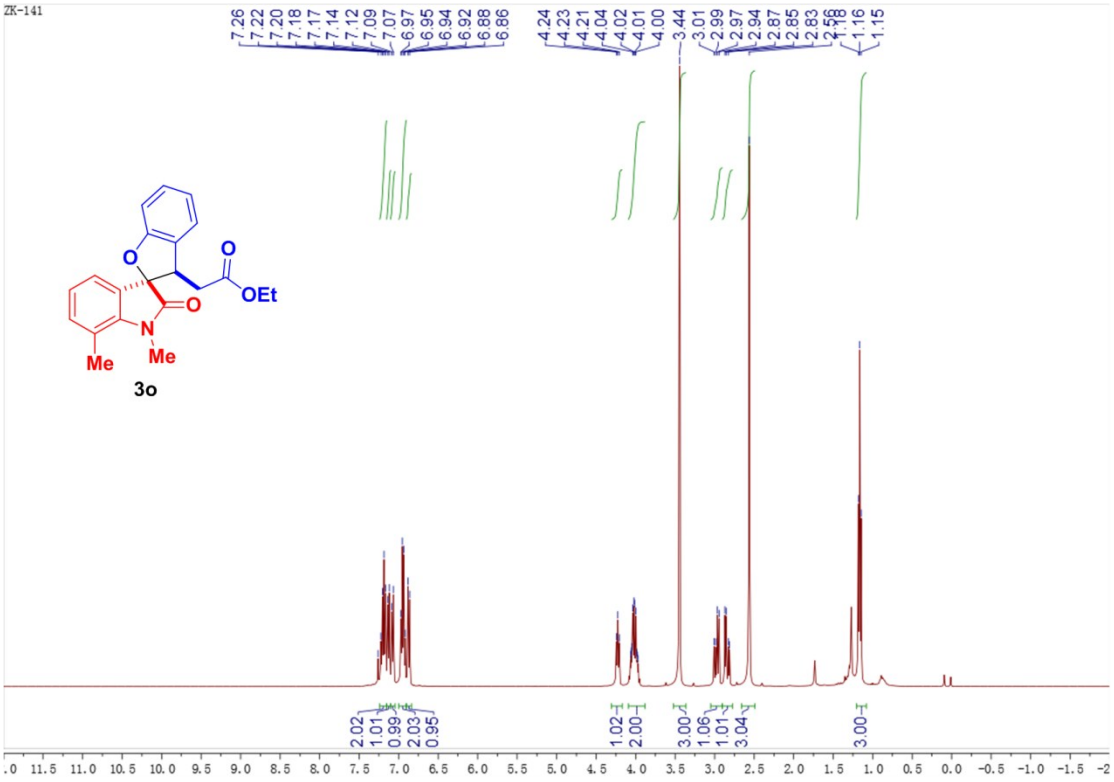
127.88
127.67
123.72
123.38
123.30
121.47
115.92
109.99
87.76
77.32
77.00
76.68
60.71
45.02
35.68
29.81
13.86
O
O
OEt
O
N
Me
Cl
3n'
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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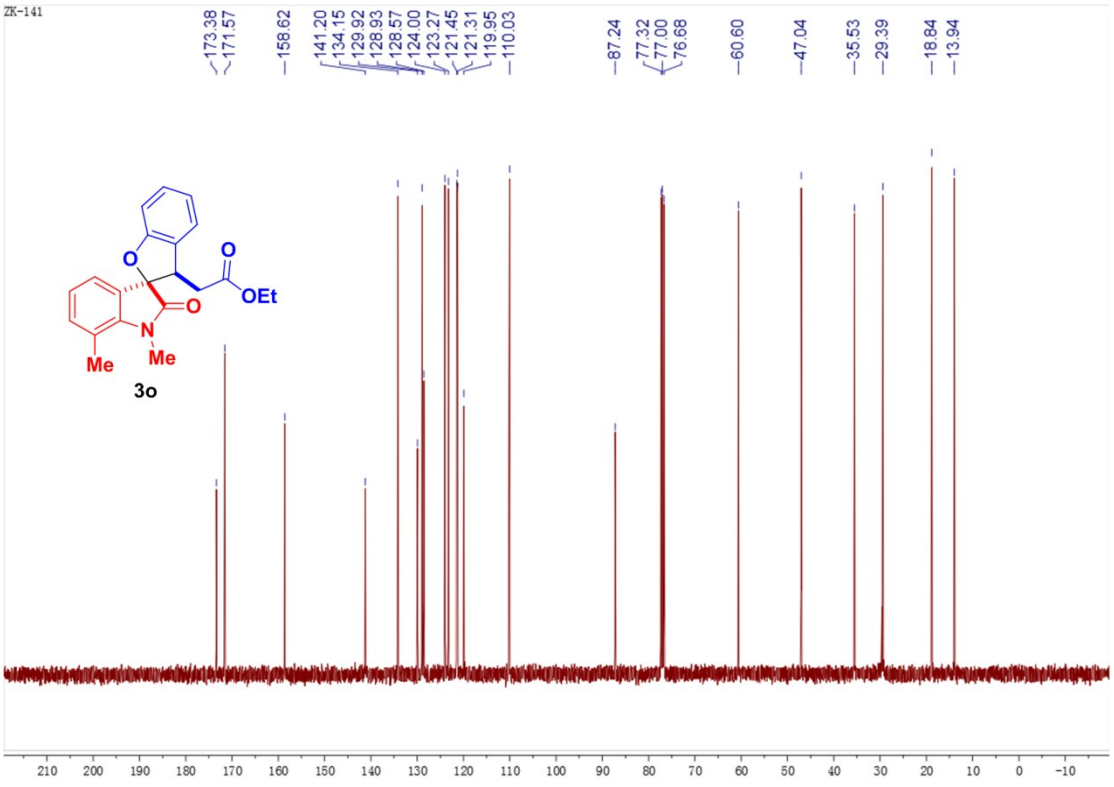
7.22
7.20
7.18
7.17
7.14
7.12
7.09
7.07
6.97
6.95
6.94
6.92
6.88
6.86
4.24
4.23
4.21
4.04
4.02
4.01
4.00
3.44
3.01
2.99
2.97
2.94
2.87
2.85
2.83
1.18
1.16
1.15
O
OEt
O
N
Me
Me
3o
2.02
1.01
0.99
2.03
0.95
1.02
2.00
3.00
1.06
1.01
3.04
3.00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123.27
121.45
121.31
119.95
110.03
87.24
77.32
77.00
76.68
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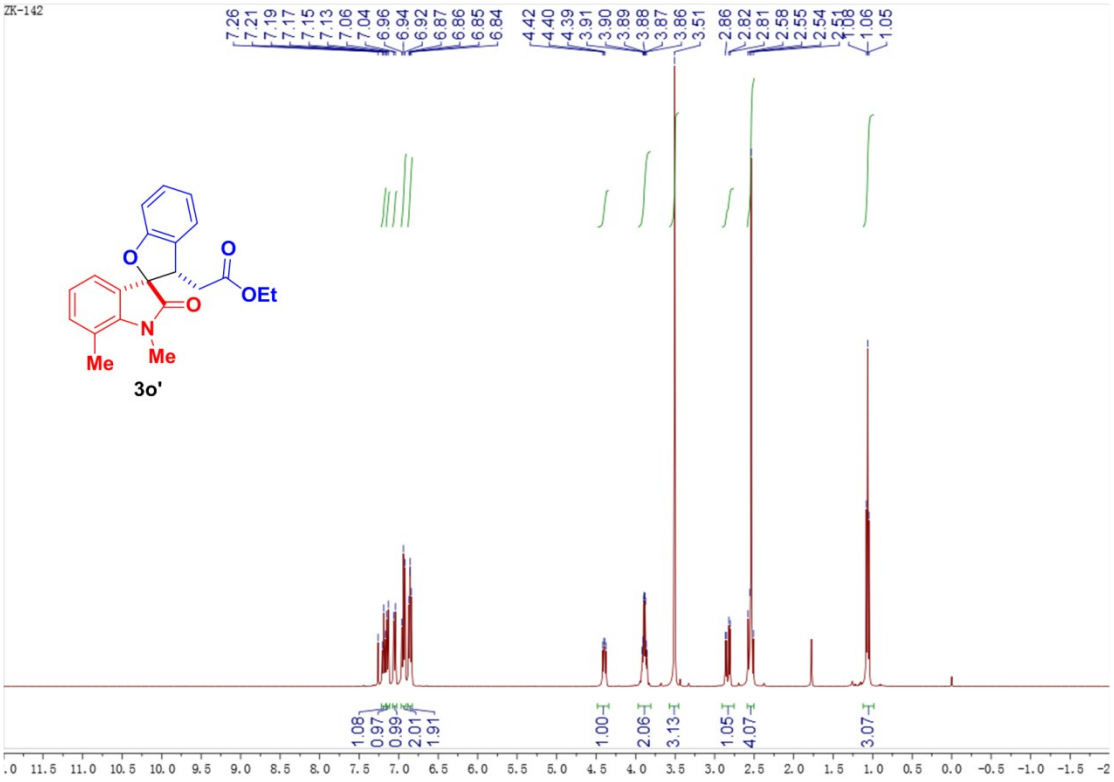
47.04
35.53
29.39
18.84
13.94
O
OEt
O
N
Me
Me
3o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7.13
7.06
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6.94
6.92
6.87
6.86
6.85
6.84
4.42
4.40
4.39
3.91
3.90
3.89
3.88
3.87
3.86
3.51
2.86
2.82
2.81
2.58
2.55
2.54
2.51
1.08
1.06
1.05
O
O
OEt
O
N
Me
Me
3o'
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0.99
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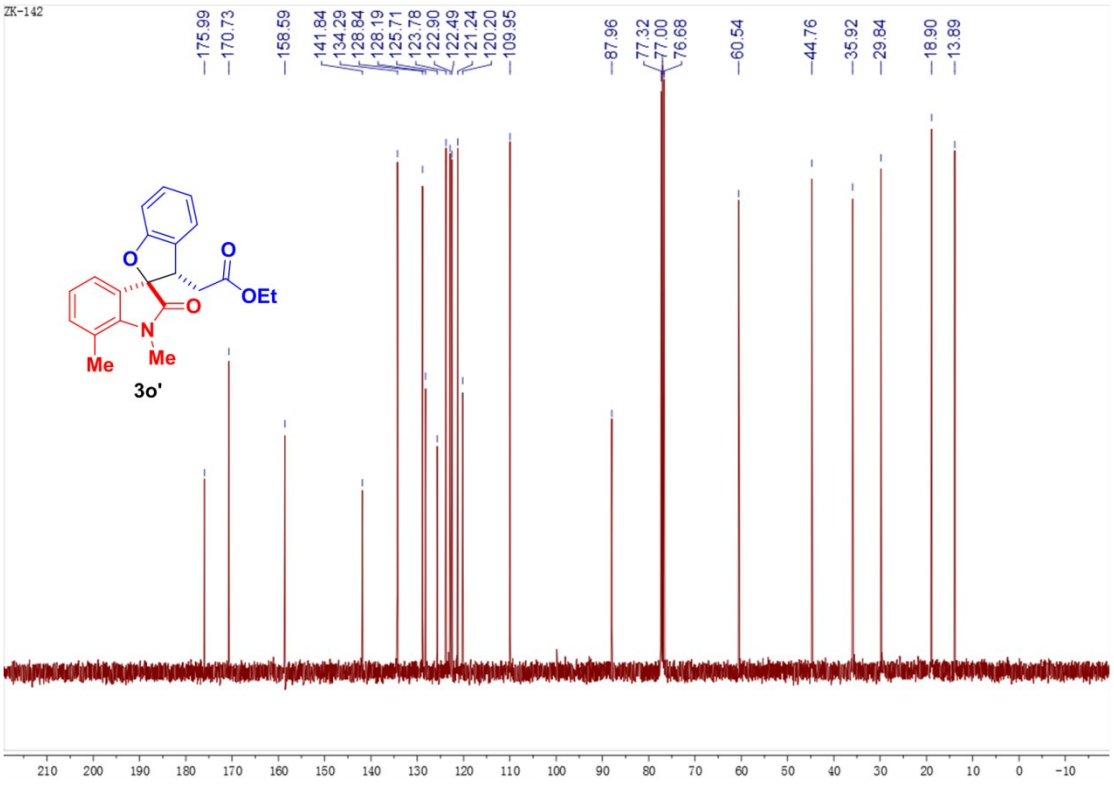
1.91
1.00
2.06
3.13
1.05
4.07
3.07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122.49
121.24
120.20
109.95
87.96
77.32
77.00
76.68
60.54
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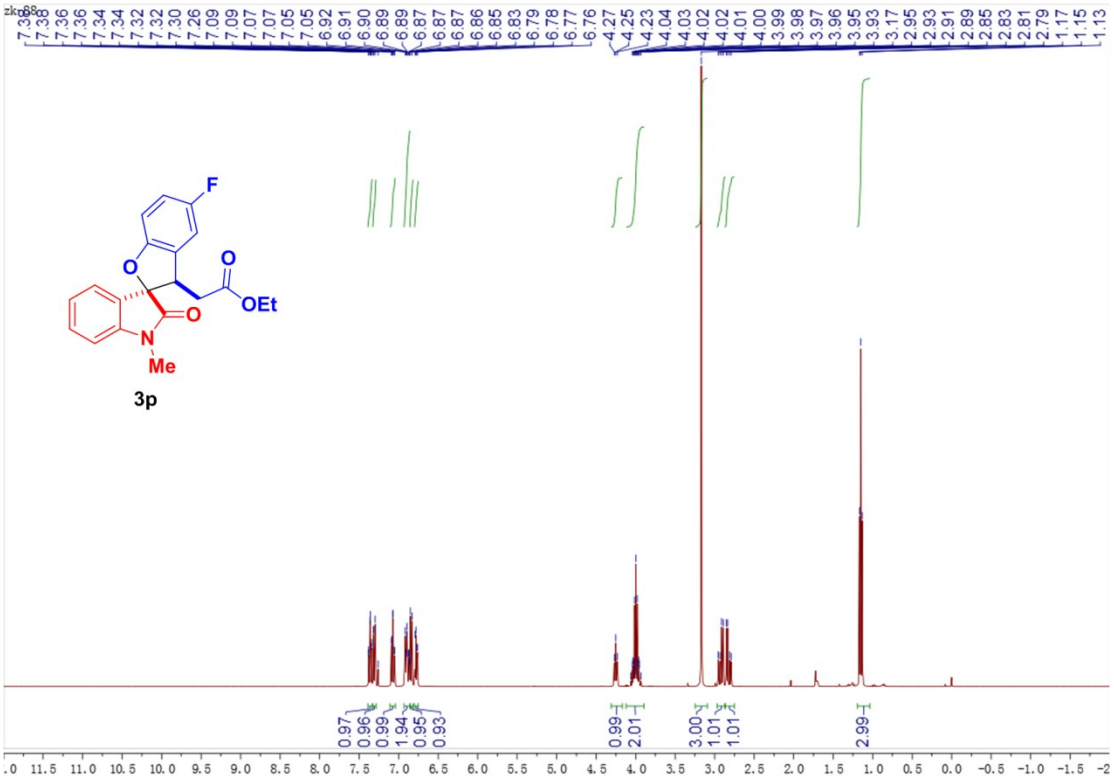
35.92
29.84
18.90
13.89
O
O
OEt
O
N
Me
Me
3o'


F
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O
OEt
O
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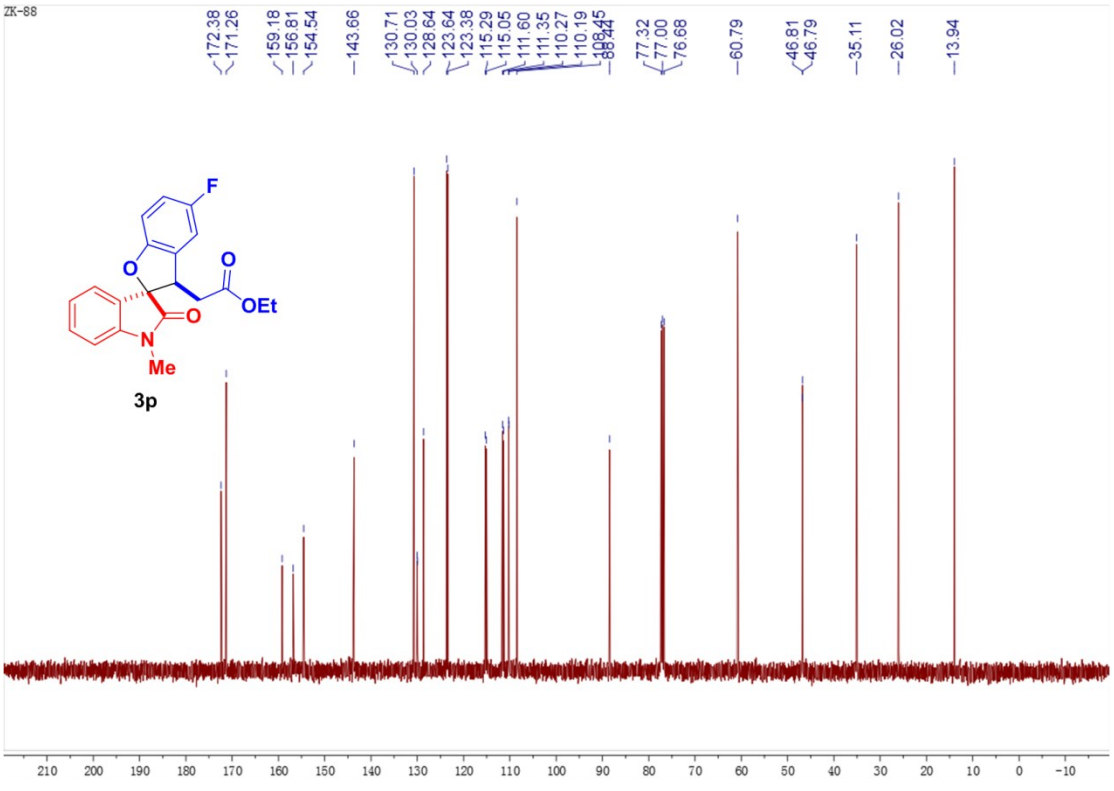
Me
3p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OEt
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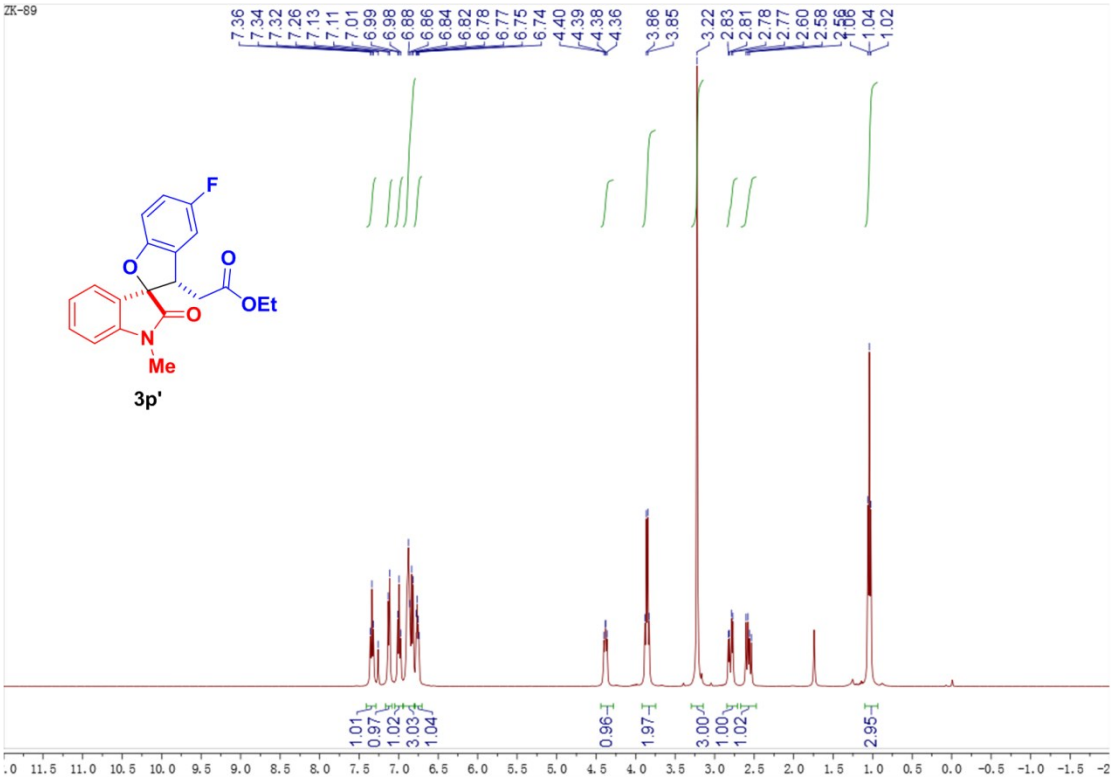
N
Me
3p


ZK-89
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6.82
6.78
6.77
6.75
6.74
4.40
4.39
4.38
4.36
3.86
3.85
3.22
2.83
2.81
2.78
2.77
2.60
2.58
1.06
1.04
1.02
F
O
O
OEt
O
N
Me
3p'
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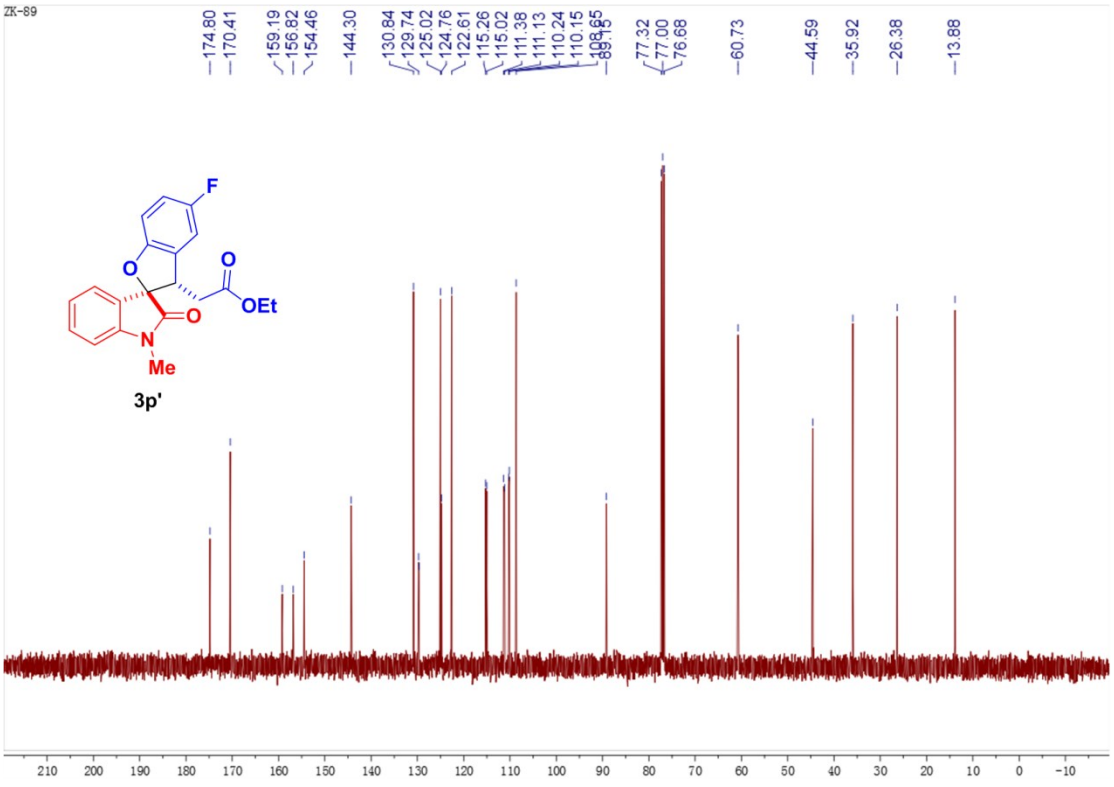
1.02
3.03
1.04
0.96
1.97
3.00
1.00
1.02
2.95


ZK-89
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144.30
130.84
129.74
125.02
124.76
122.61
115.26
115.02
111.38
111.13
110.24
110.15
77.32
77.00
76.68
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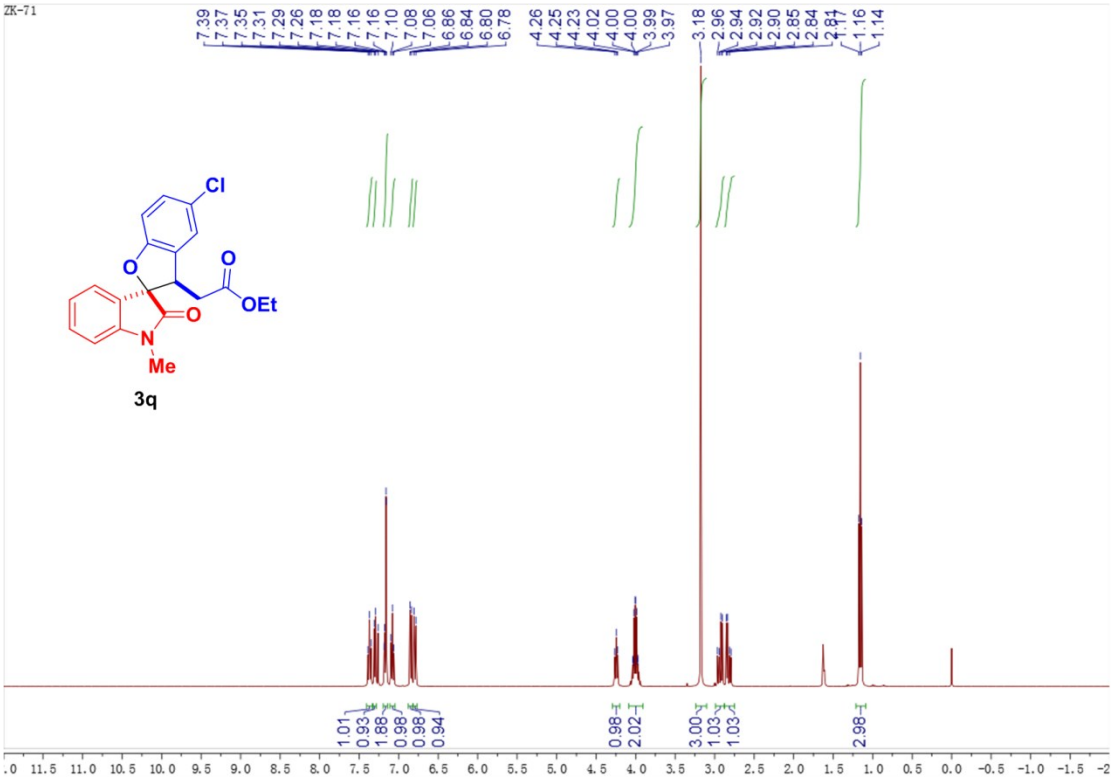
44.59
35.92
26.38
13.88
F
O
O
OEt
O
N
Me
3p'


ZK-71
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7.16
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7.08
7.06
6.86
6.84
6.80
6.78
4.26
4.25
4.23
4.02
4.00
4.00
3.99
3.97
3.18
2.96
2.94
2.92
2.90
2.85
2.84
2.81
1.17
1.16
1.14
Cl
O
O
OEt
O
N
Me
3q
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0.94
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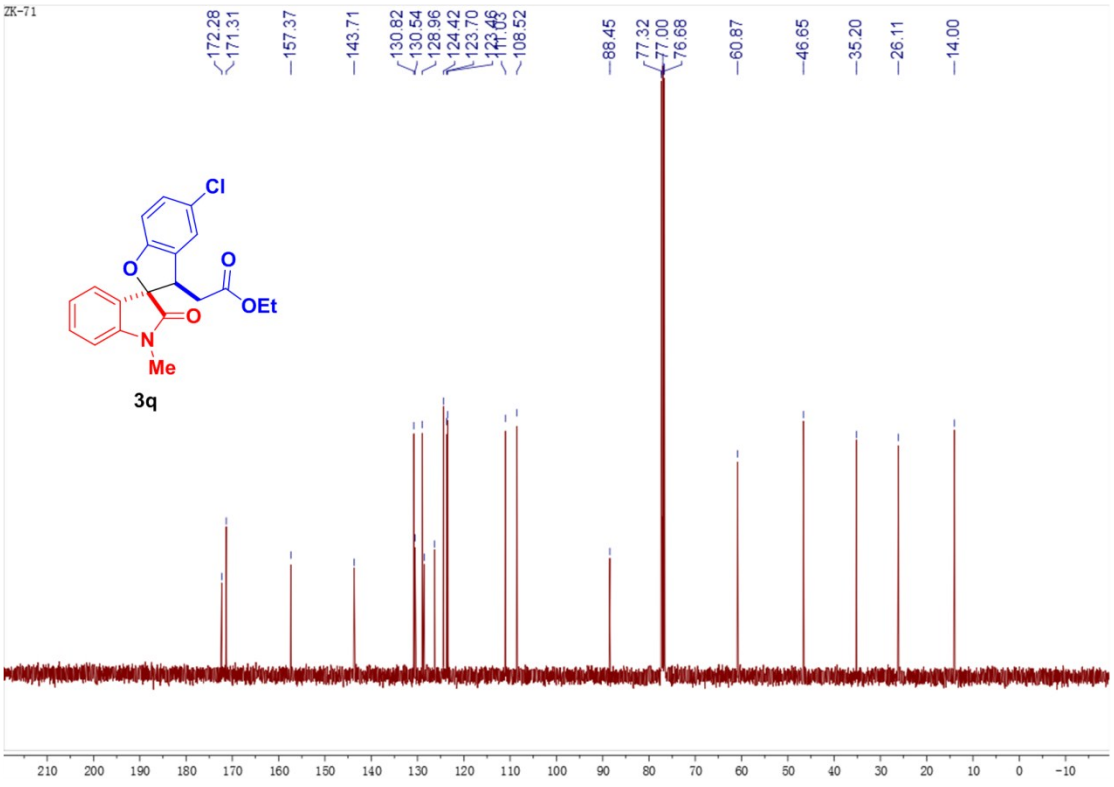
1.03
2.98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123.70
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88.45
77.32
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76.68
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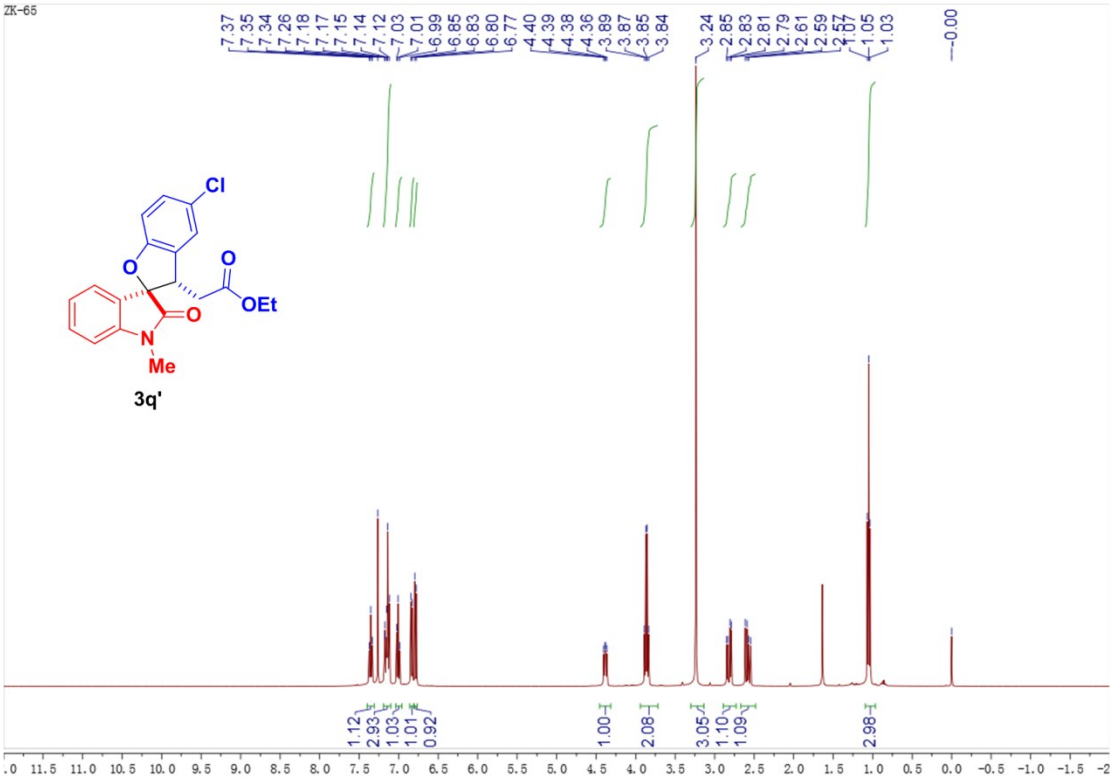
46.65
35.20
26.11
14.00
Cl
O
O
OEt
O
N
Me
3q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Cl
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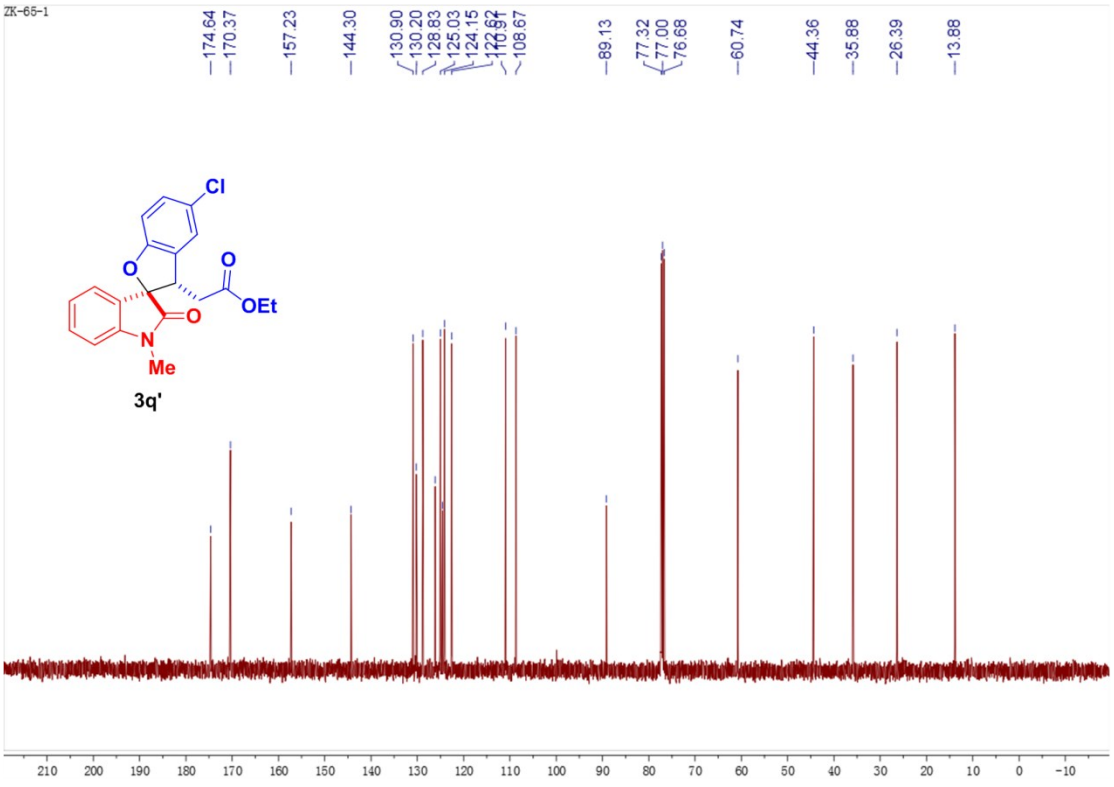
OEt
O
N
Me
3q'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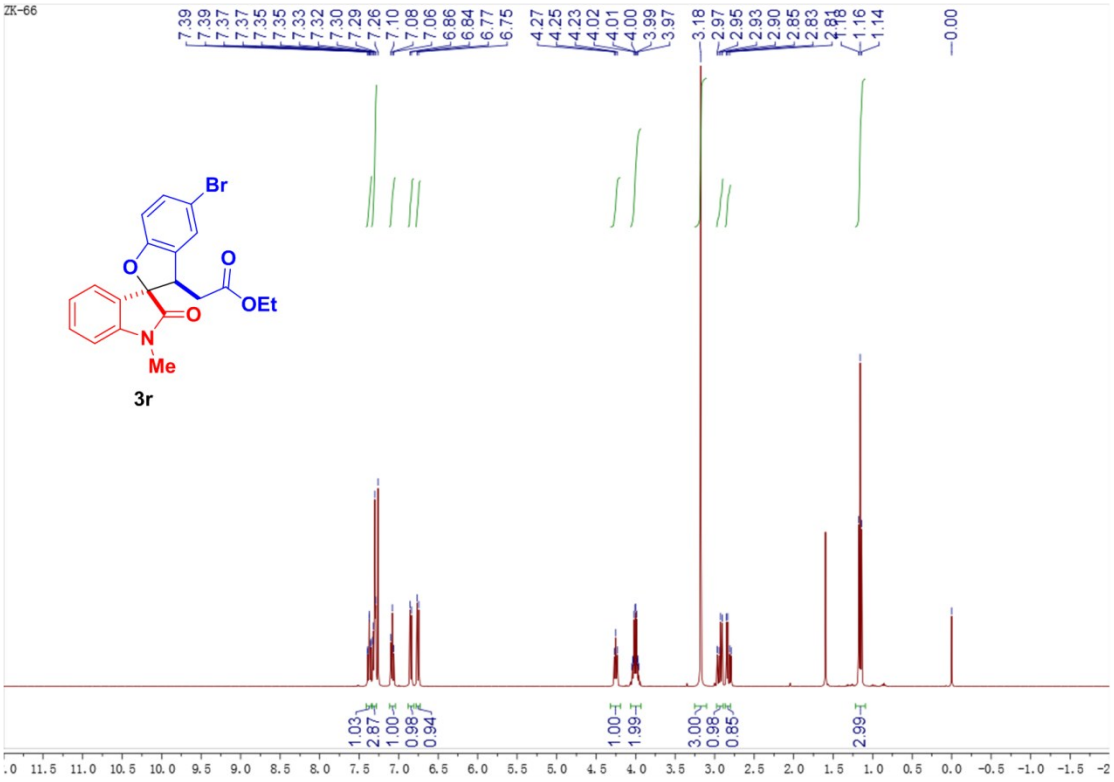
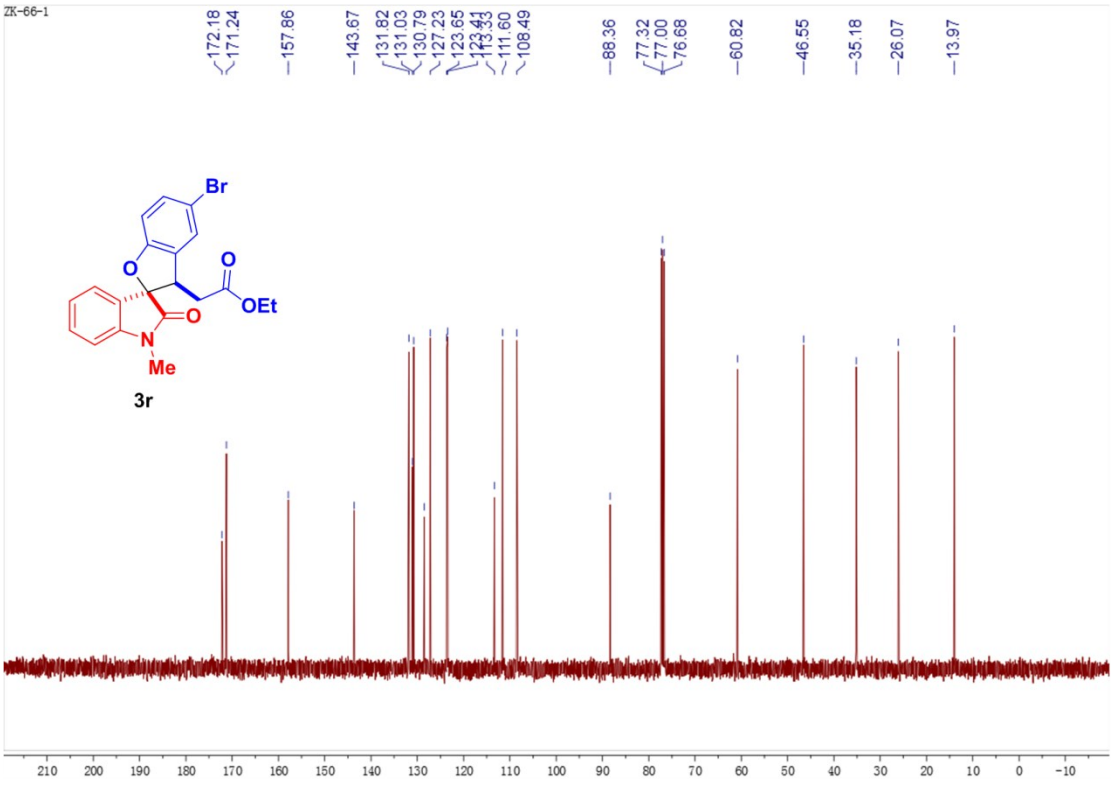
OEt
O
N
Me
3q'


ZK-66
Br
O
O
OEt
O
N
Me
3r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O
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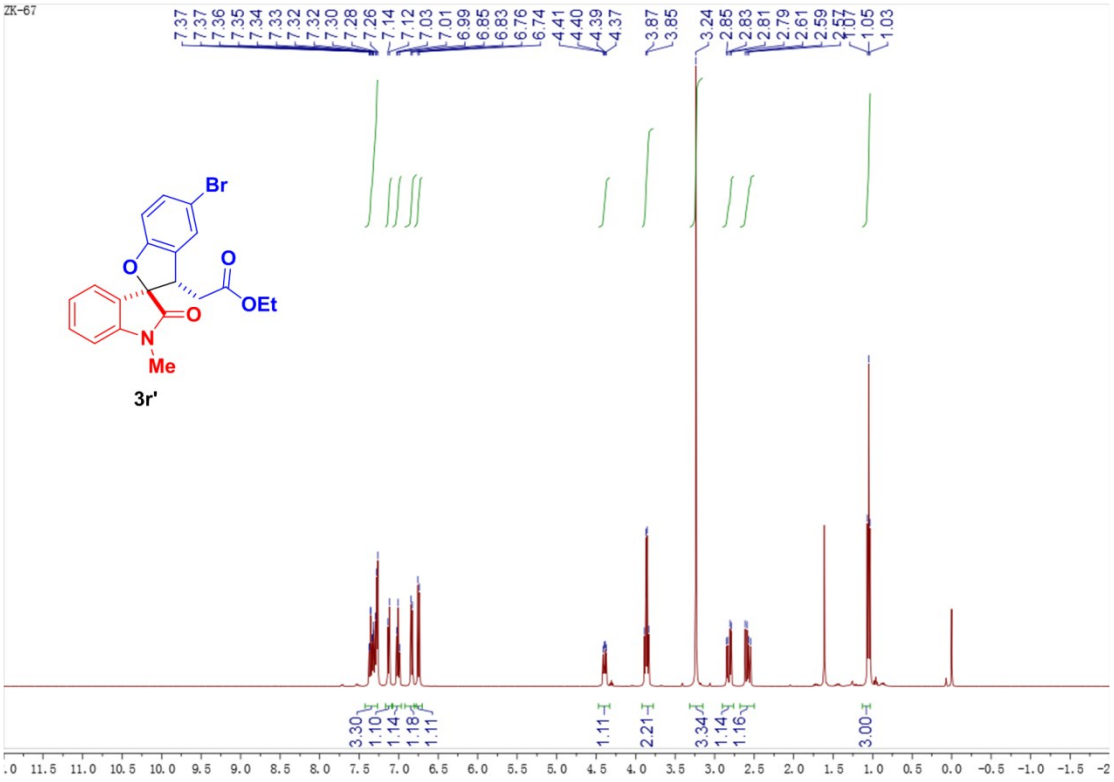
OEt
O
N
Me
3r


ZK-67
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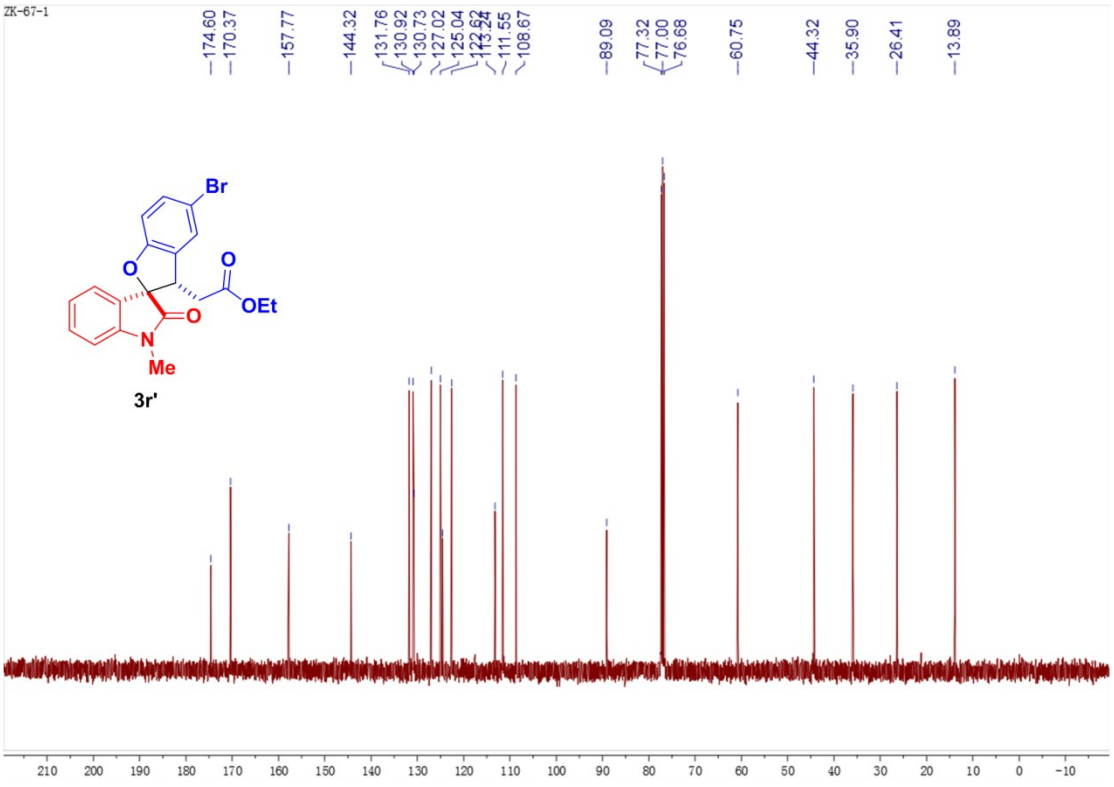
7.30
7.28
7.26
7.14
7.12
7.03
7.01
6.99
6.85
6.83
6.76
6.74
4.41
4.40
4.39
4.37
3.87
3.85
3.24
2.85
2.83
2.81
2.79
2.61
2.59
1.07
1.05
1.03
Br
O
O
OEt
O
N
Me
3r'
3.30
1.10
1.14
1.18
1.11
1.11
2.21
3.34
1.14
1.16
3.00


ZK-67-1
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157.77
144.32
131.76
130.92
130.73
127.02
125.04
111.55
108.67
89.09
77.32
77.00
76.68
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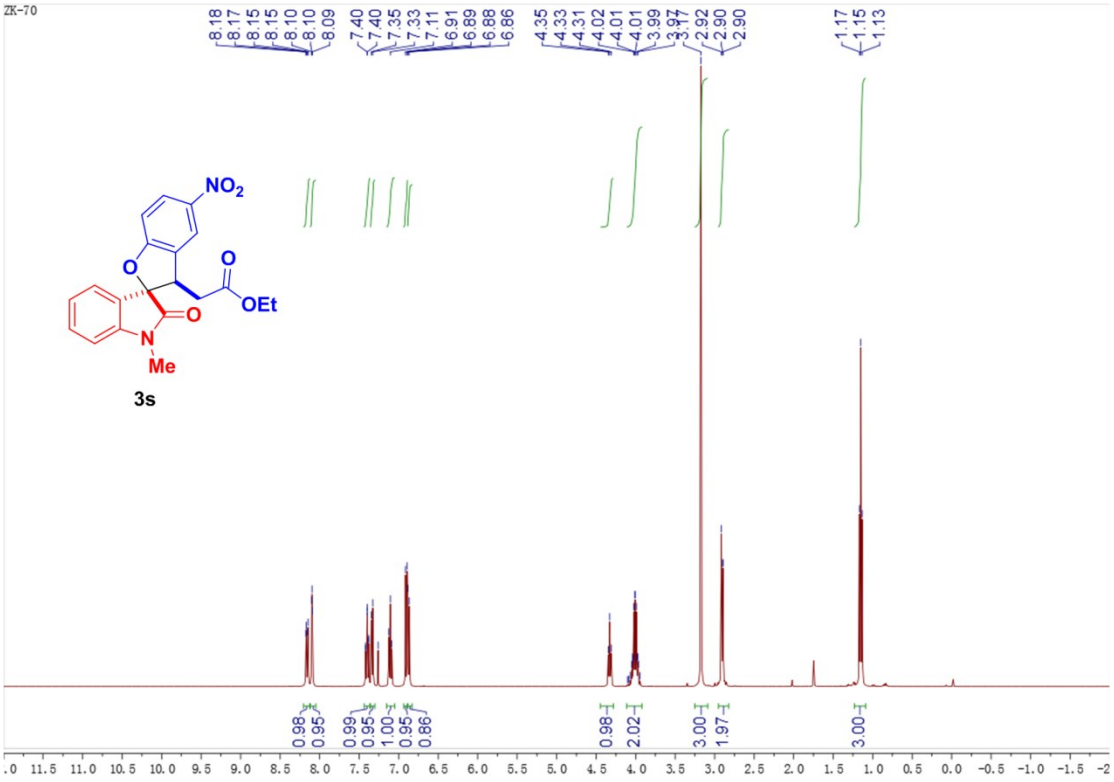
44.32
35.90
26.41
13.89
Br
O
O
OEt
O
N
Me
3r'


ZK-70
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8.15
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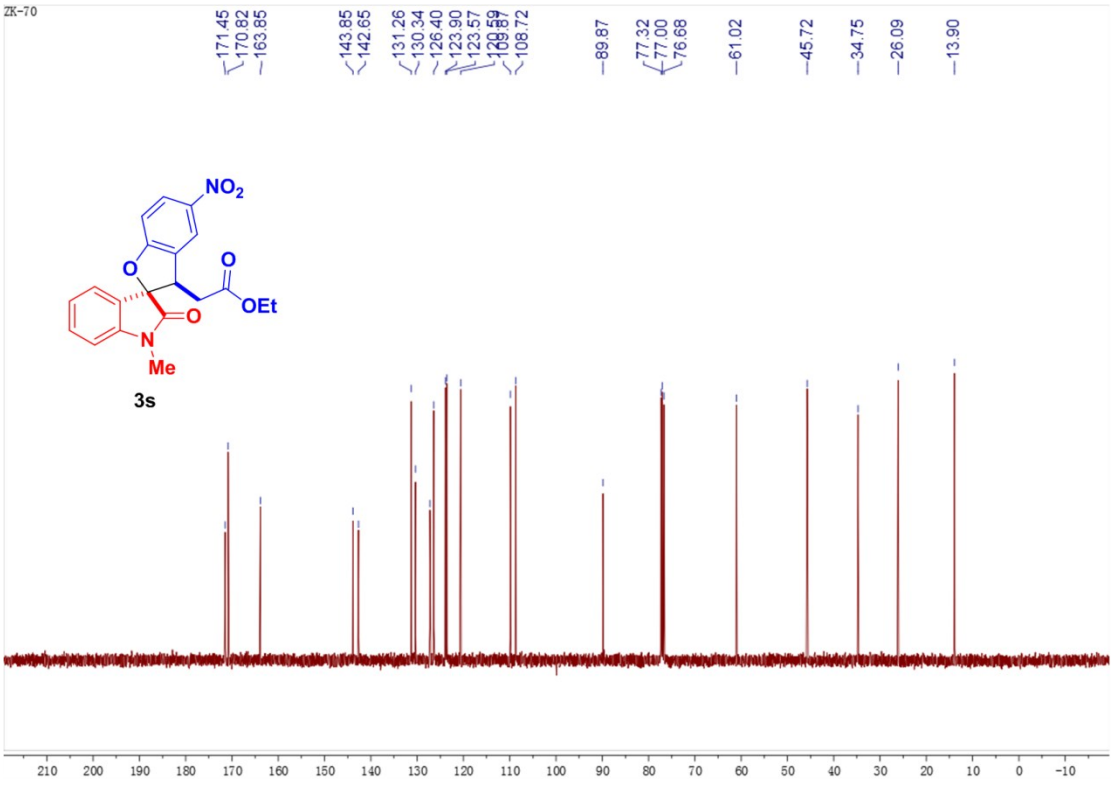
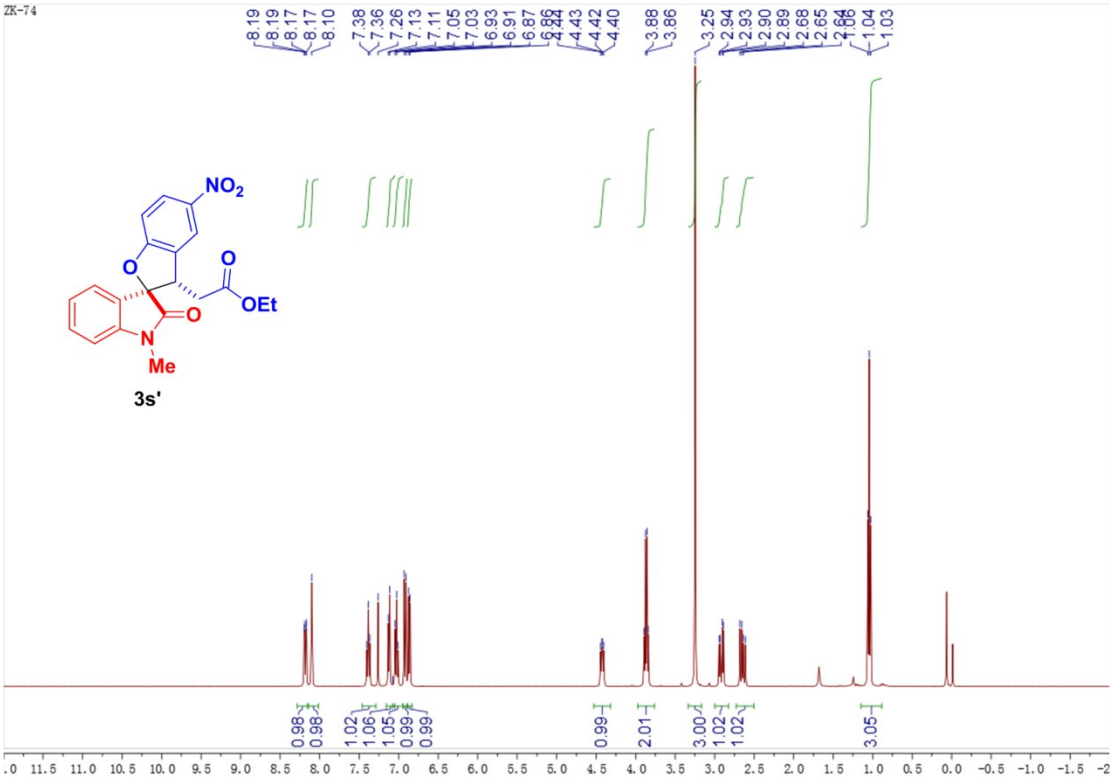
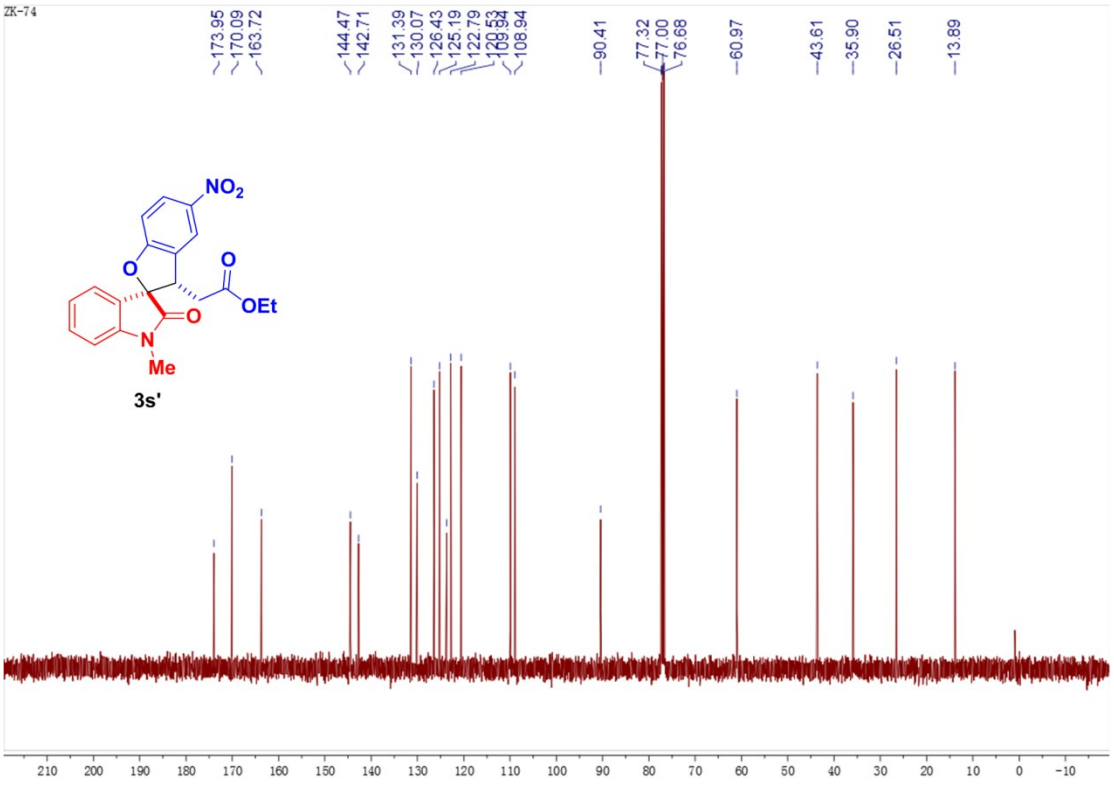
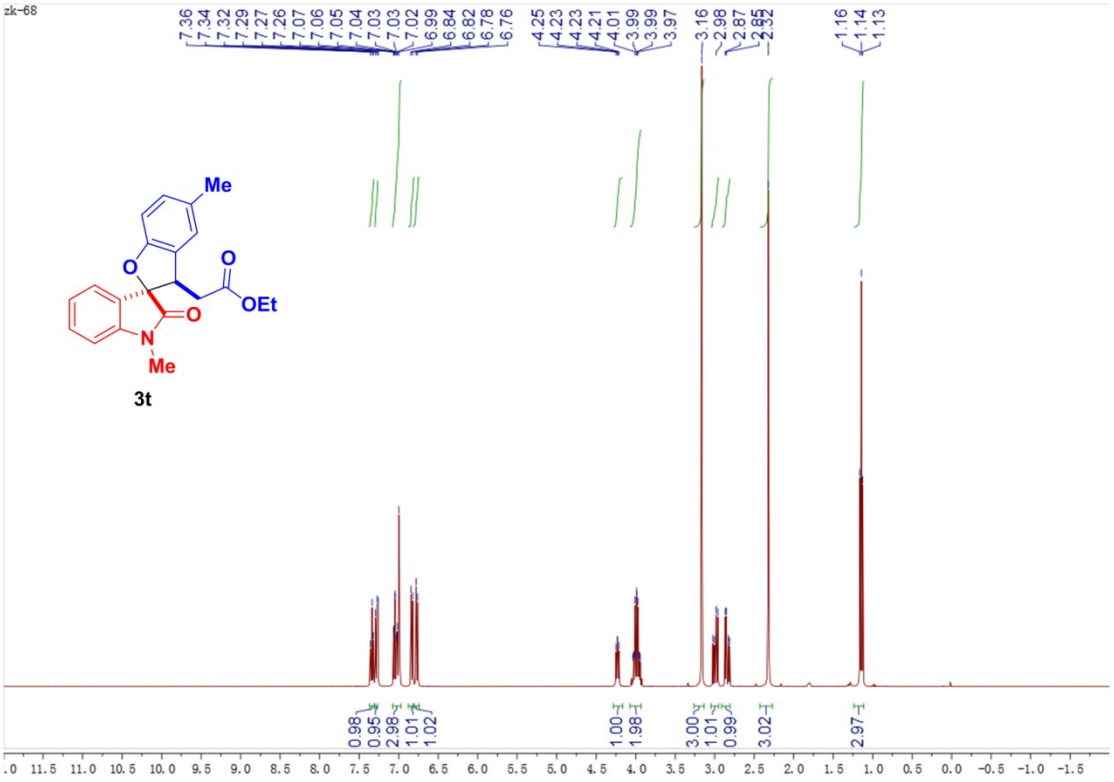
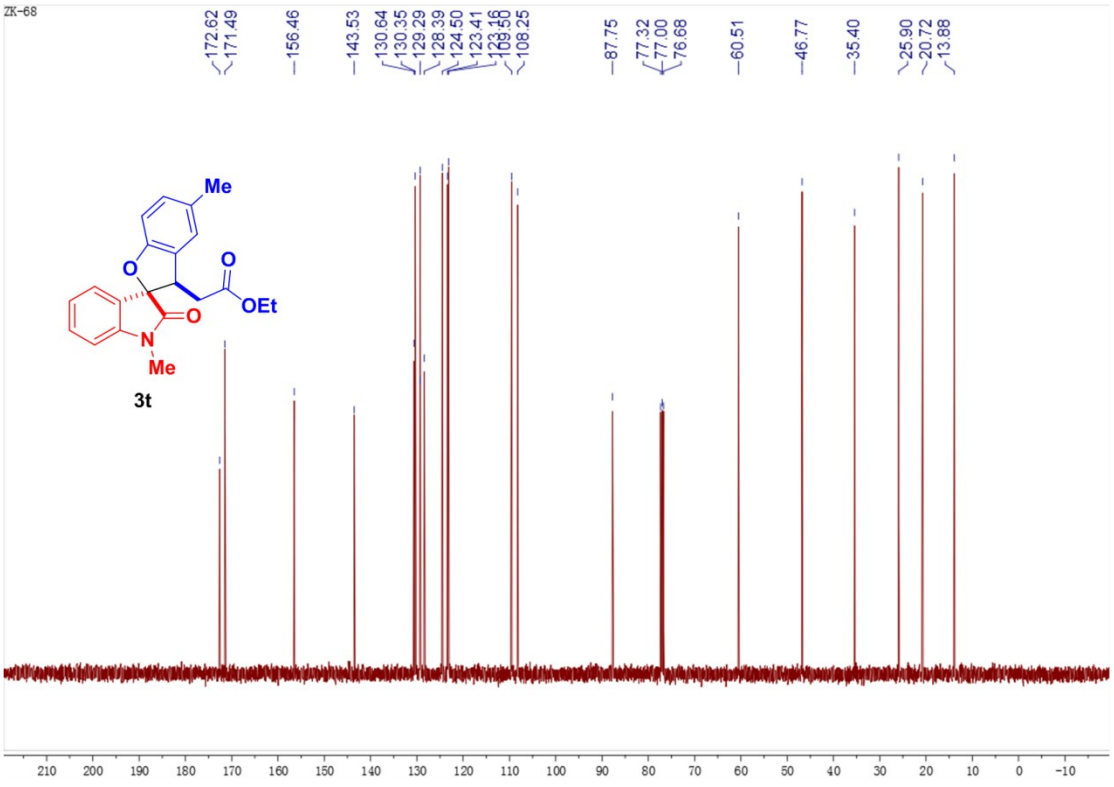
8.10
8.09
7.40
7.40
7.35
7.33
7.11
6.91
6.89
6.88
6.86
4.35
4.33
4.31
4.02
4.01
4.01
3.99
3.97
2.92
2.90
2.90
1.17
1.15
1.13
NO2
O
O
OEt
O
N
Me
3s
0.98
0.95
0.99
0.95
1.00
0.95
0.86
0.98
2.02
3.00
1.97
3.00

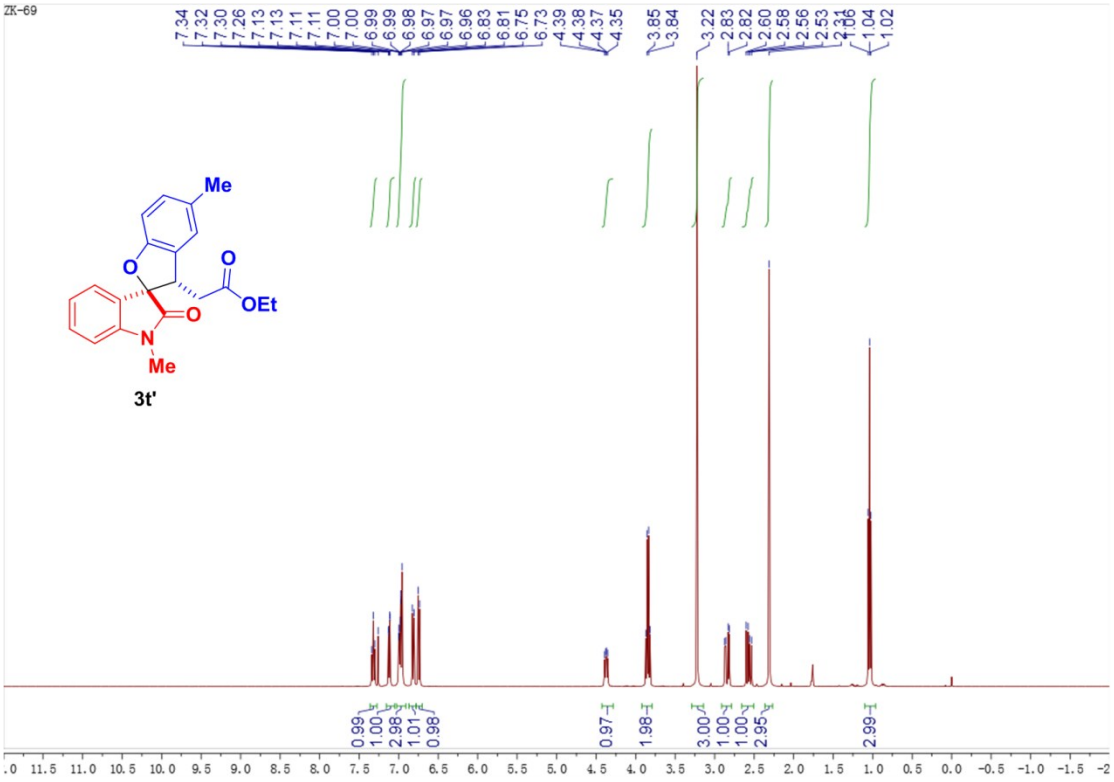

ZK-70
171.45
170.82
163.85
143.85
142.65
131.26
130.34
126.40
123.90
123.57
108.72
89.87
77.32
77.00
76.68
61.02
45.72
34.75
26.09
13.90
NO2
O
O
OEt
O
N
Me
3s

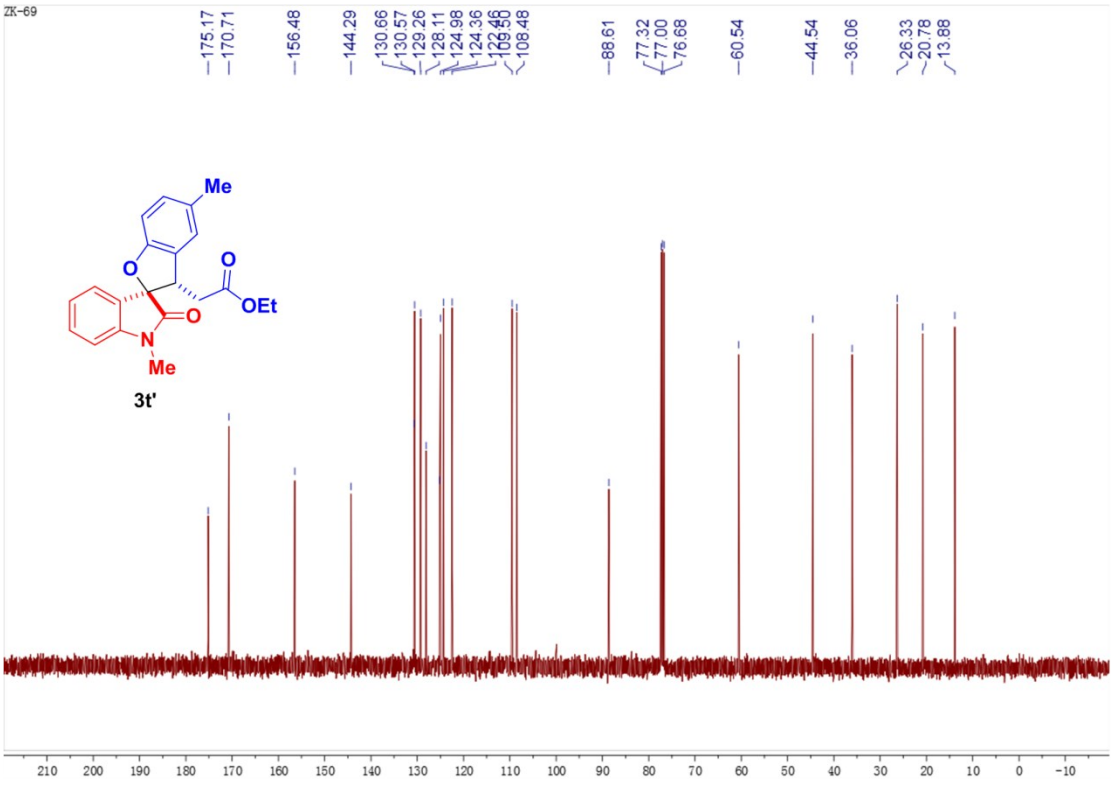

ZK-74
8.19
8.19
8.17
8.17
8.10
7.38
7.36
7.26
7.13
7.11
7.05
7.03
6.93
6.91
6.87
4.43
4.42
4.40
3.88
3.86
3.25
2.94
2.93
2.90
2.89
2.68
2.65
1.04
1.03
NO2
O
O
OEt
O
N
Me
3s'
0.98
0.98
1.02
1.06
1.05
0.99
0.99
0.99
2.01
3.00
1.02
1.02
3.05

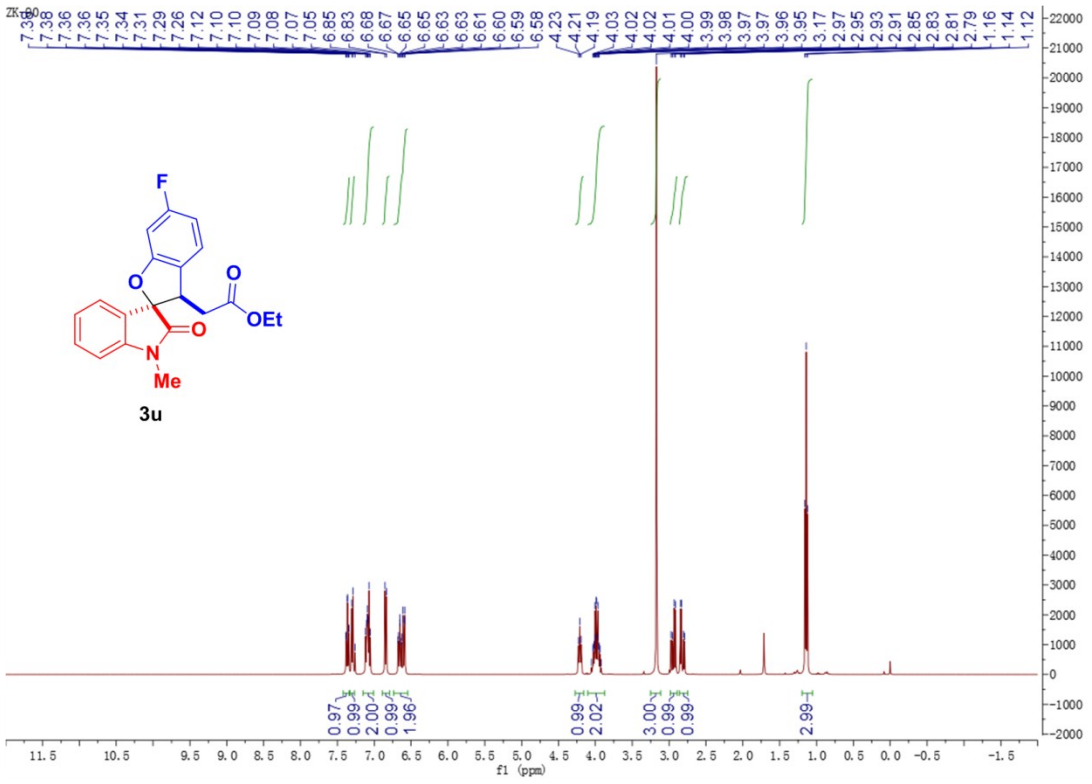

ZK-74
173.95
170.09
163.72
144.47
142.71
131.39
130.07
126.43
125.19
122.79
90.41
77.32
77.00
76.68
60.97
43.61
35.90
26.51
13.89
NO2
O
O
OEt
O
N
Me
3s'

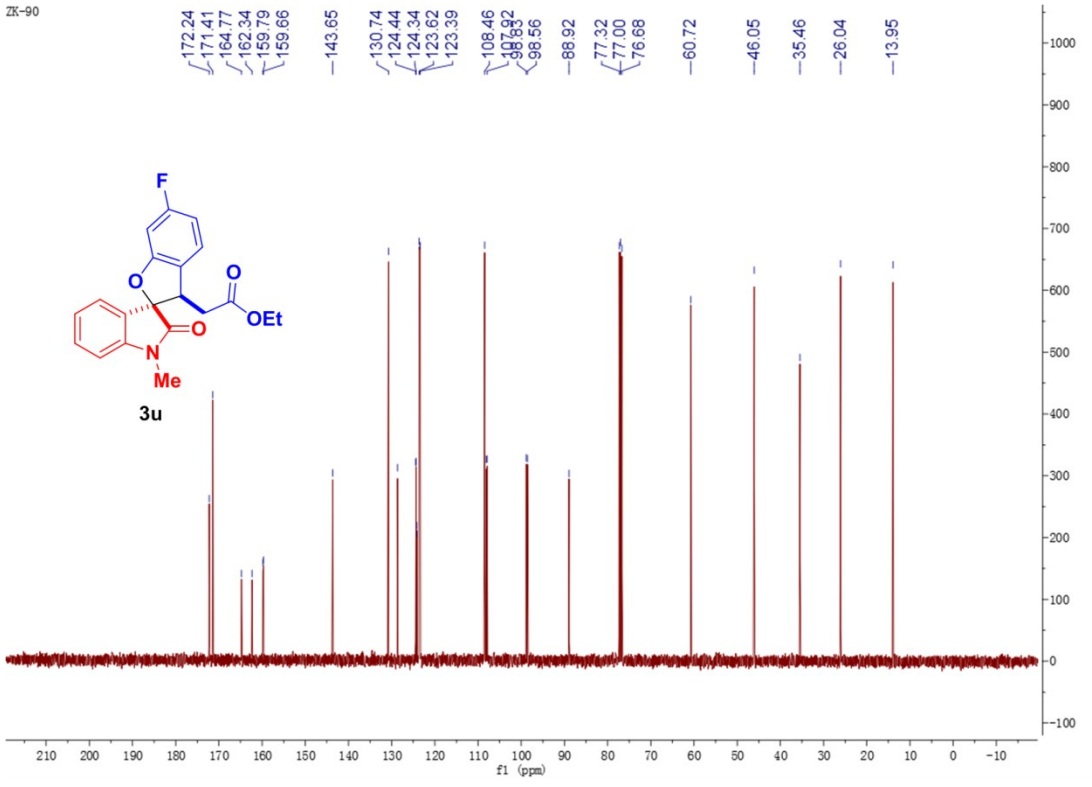

zk-68
Me
O
O
OEt
O
N
Me
3t

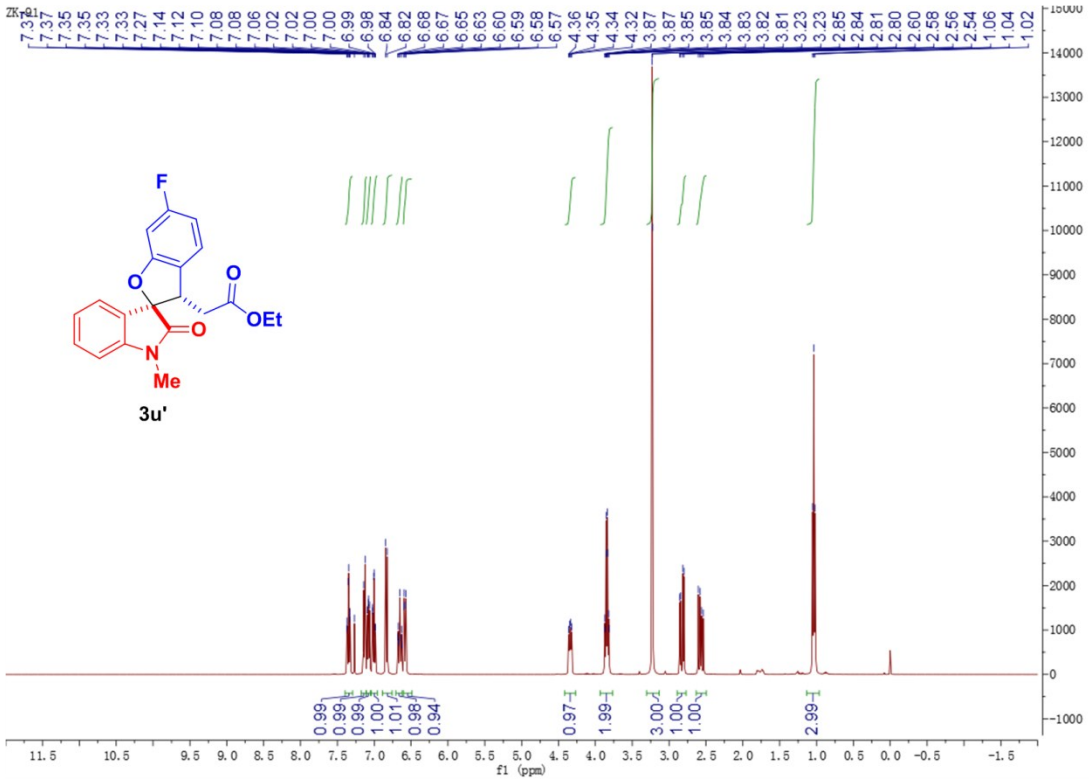

ZK-68
Me
O
O
OEt
O
N
Me
3t

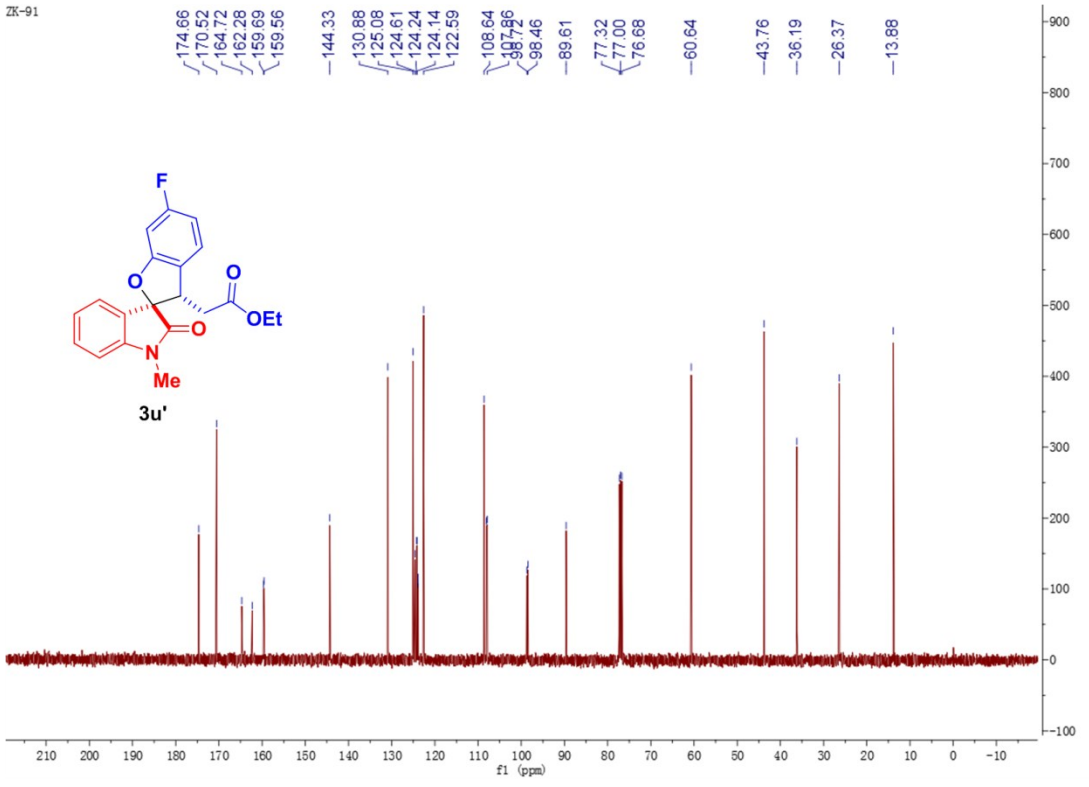

ZK-69
Me
O
O
OEt
O
N
Me
3t'

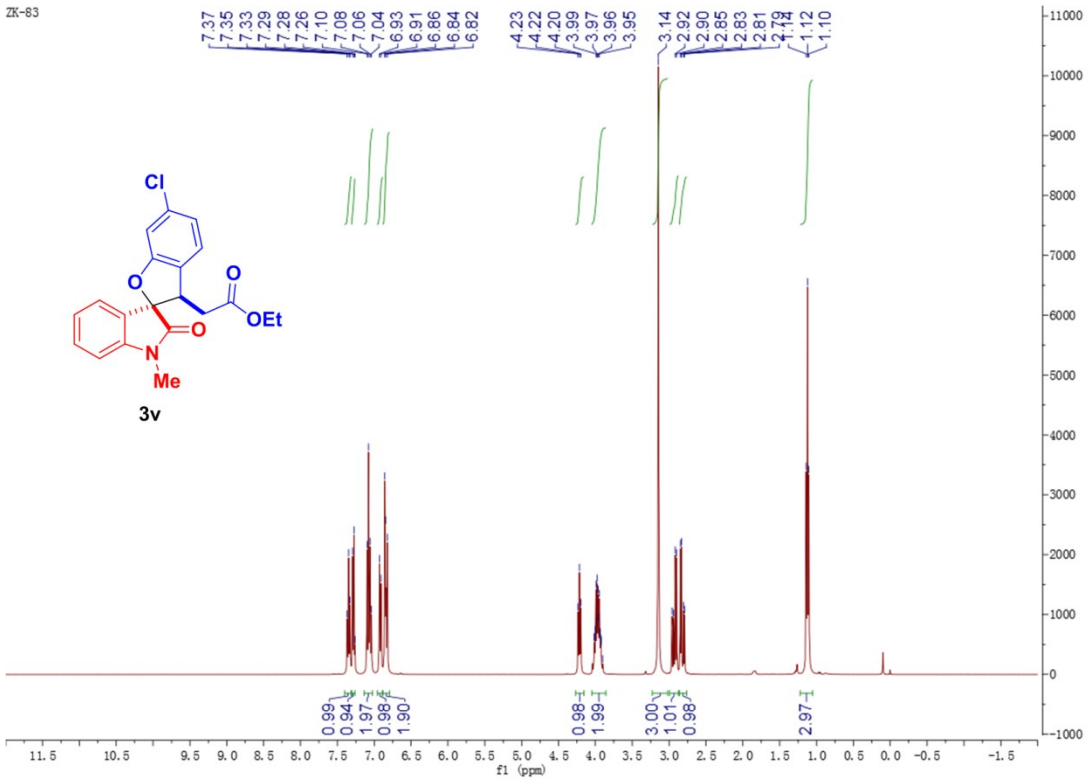

ZK-69
Me
O
O
OEt
O
N
Me
3t'

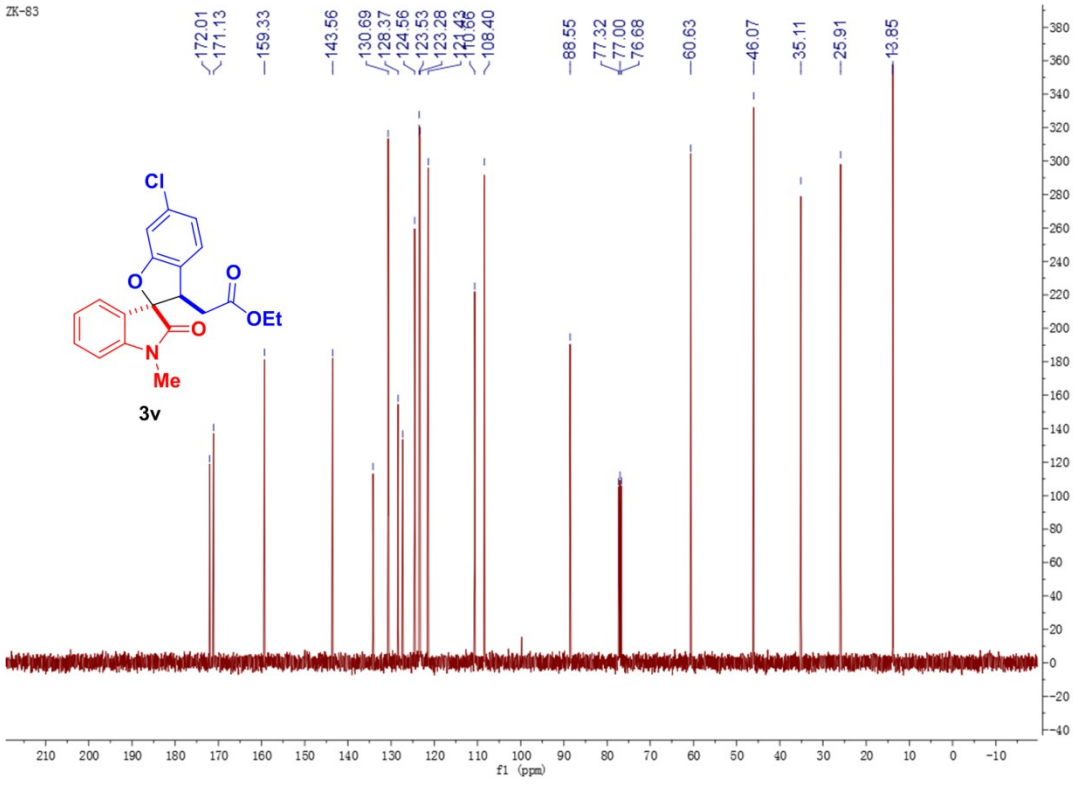

ZK-90
F
O
O
OEt
O
N
Me
3u
f1 (ppm)

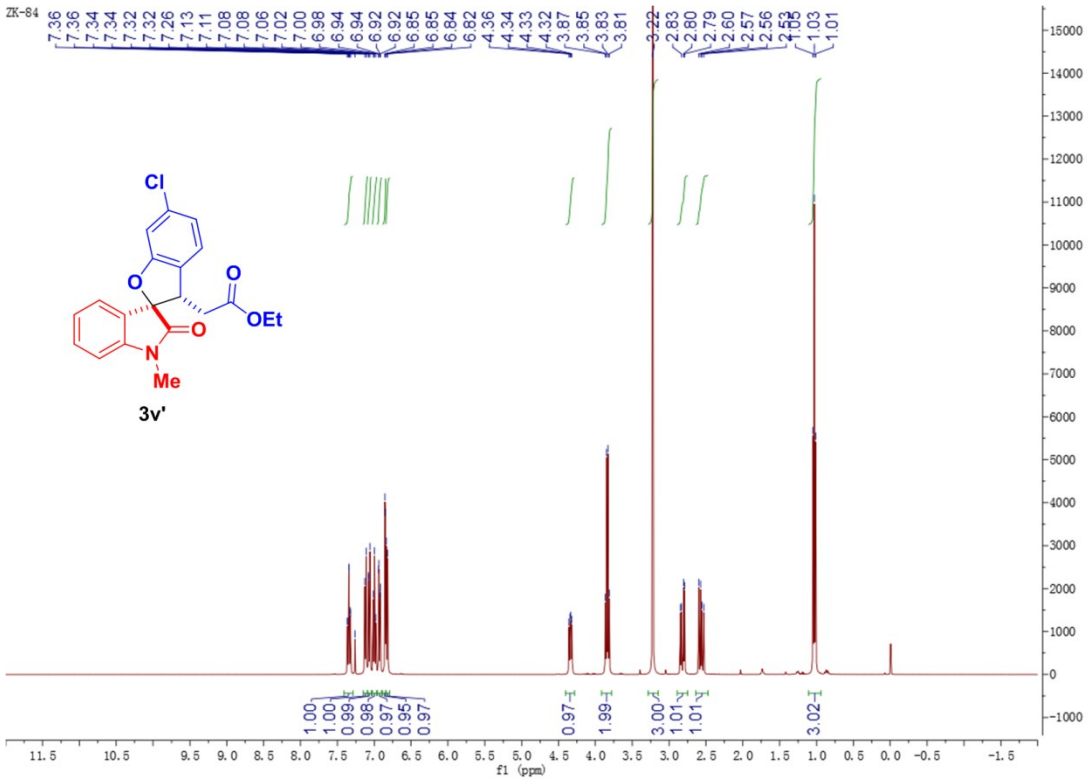

ZK-90
172.24
171.41
164.77
162.34
159.79
159.66
143.65
130.74
124.44
124.34
123.62
123.39
108.46
98.56
88.92
77.32
77.00
76.68
60.72
46.05
35.46
26.04
13.95
F
O
O
OEt
O
N
Me
3u
f1 (ppm)

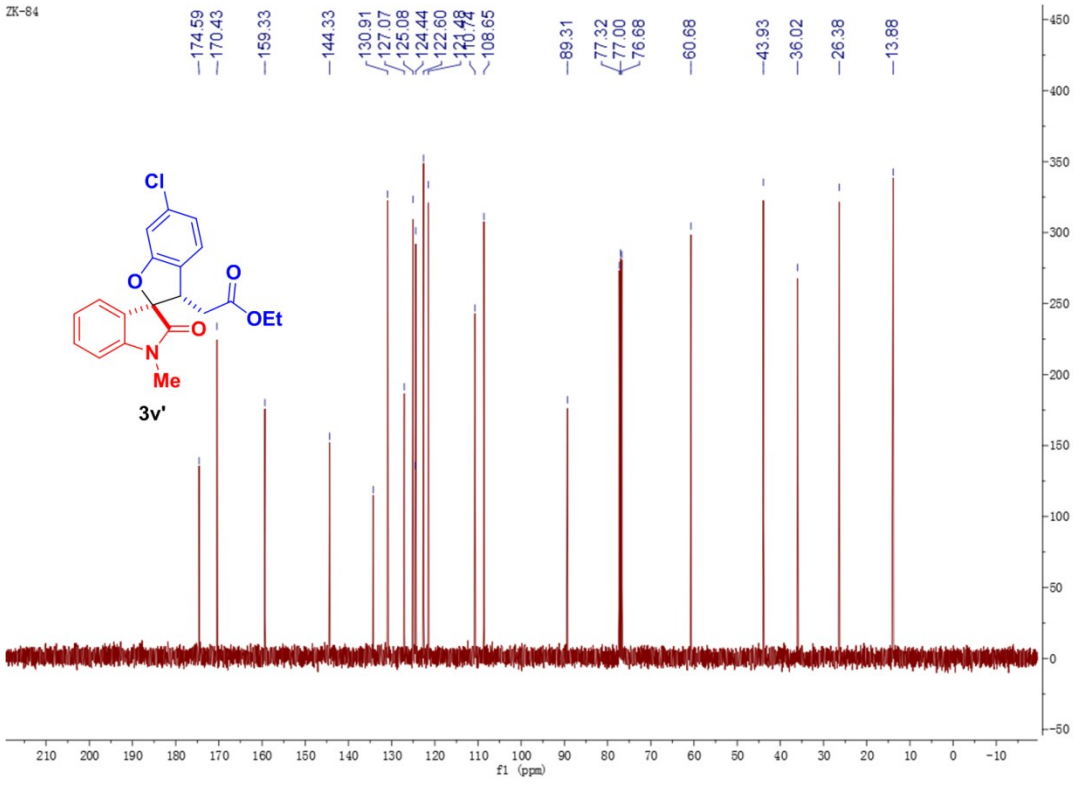

ZK-91
F
O
O
OEt
O
N
Me
3u'
f1 (ppm)

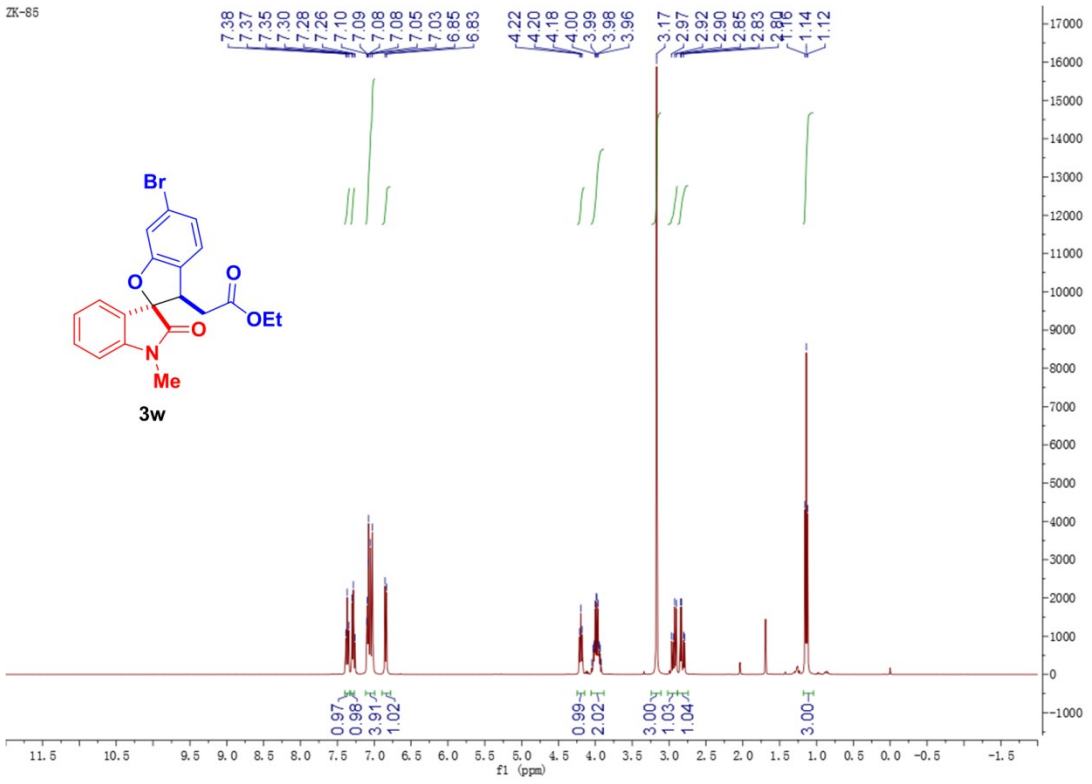

ZK-91
174.66
170.52
164.72
162.28
159.69
159.56
144.33
130.88
125.08
124.61
124.24
124.14
122.59
108.64
98.72
98.46
89.61
77.32
77.00
76.68
60.64
43.76
36.19
26.37
13.88
F
O
O
OEt
O
N
Me
3u'
f1 (ppm)

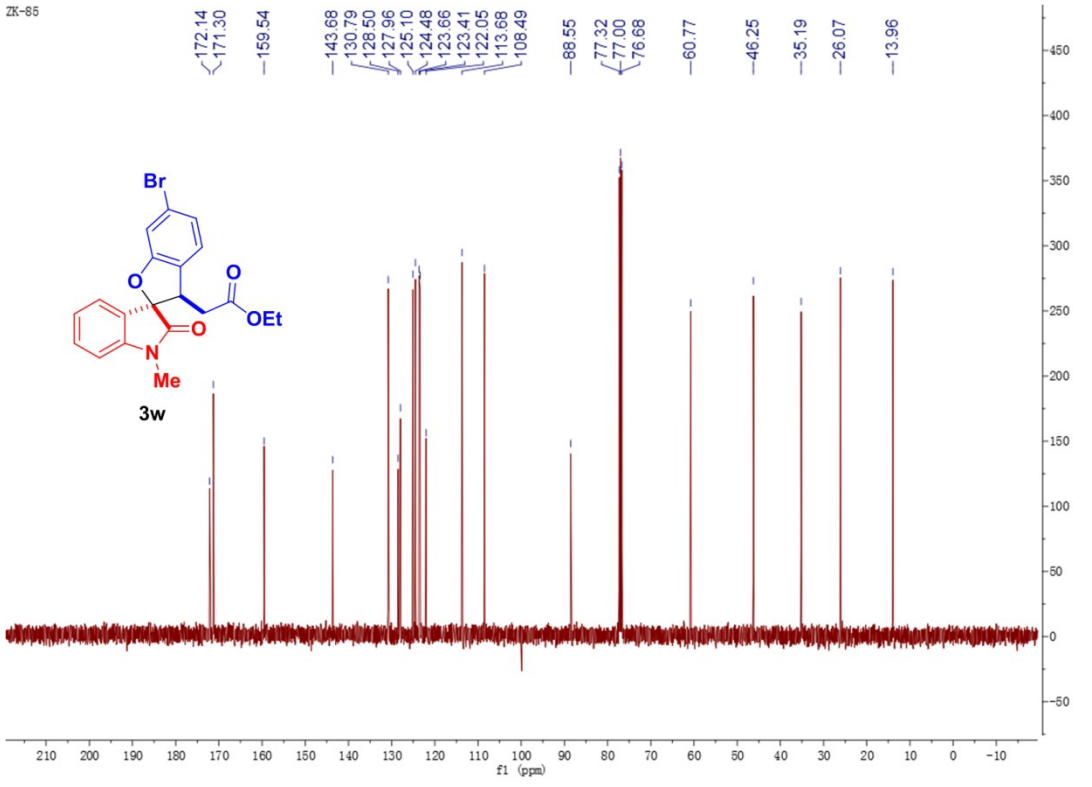

ZK-83
7.37
7.35
7.33
7.29
7.28
7.26
7.10
7.08
7.06
7.04
6.93
6.91
6.86
6.84
6.82
4.23
4.22
4.20
3.99
3.97
3.96
3.95
3.14
2.92
2.90
2.85
2.83
2.81
2.79
1.12
1.10
Cl
O
O
OEt
O
N
Me
3v
0.99
0.94
1.97
0.98
1.90
0.98
1.99
3.00
1.01
0.98
2.97
f1 (ppm)

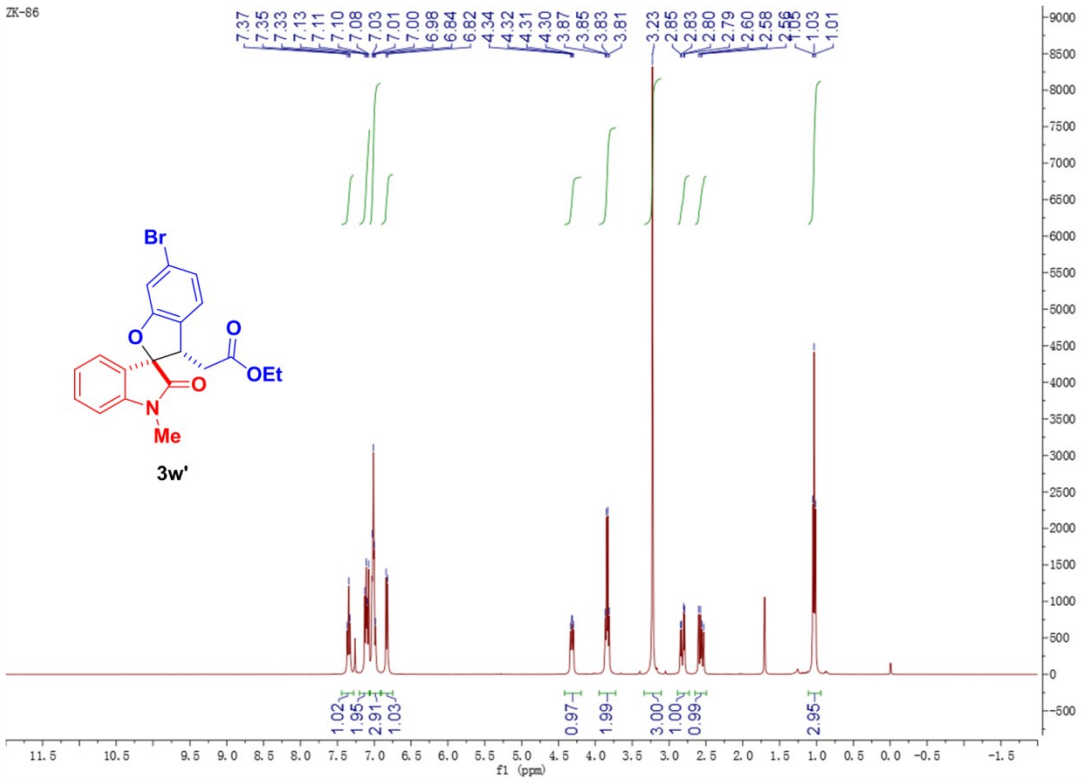

ZK-83
172.01
171.13
159.33
143.56
130.69
128.37
124.56
123.53
123.28
121.43
110.66
108.40
88.55
77.32
77.00
76.68
60.63
46.07
35.11
25.91
13.85
Cl
O
O
OEt
O
N
Me
3v
f1 (ppm)

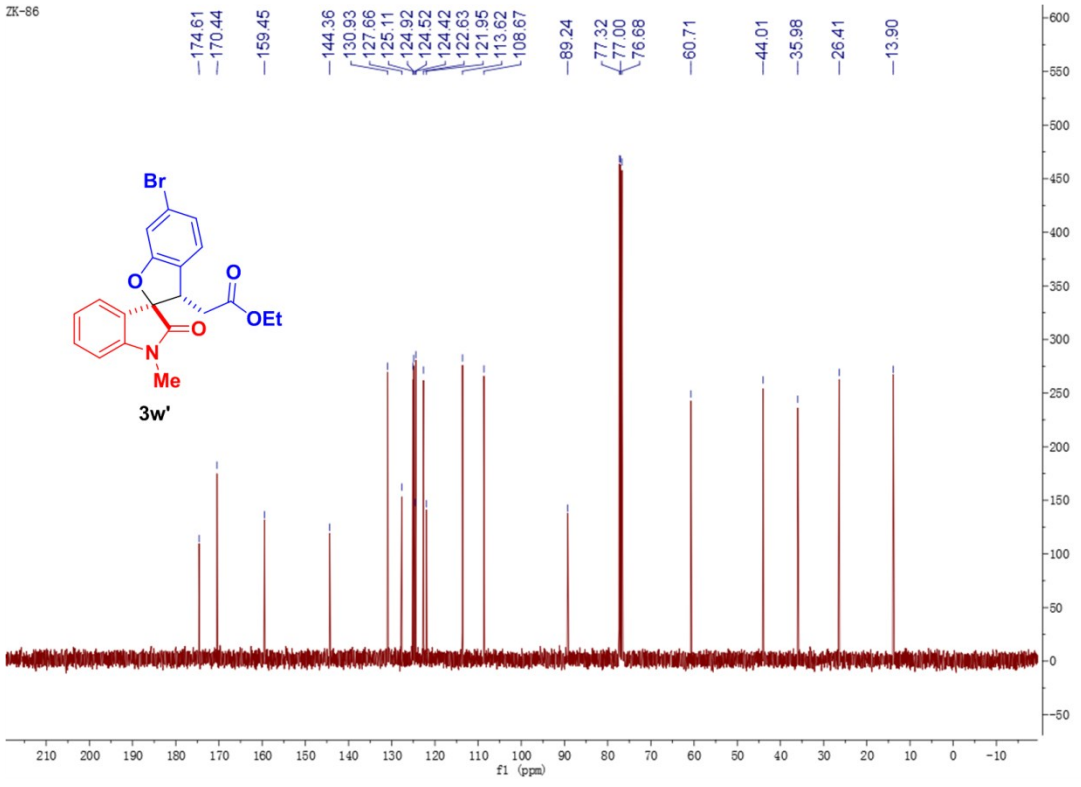

ZK-84
Cl
O
O
OEt
O
N
Me
3v'
f1 (ppm)

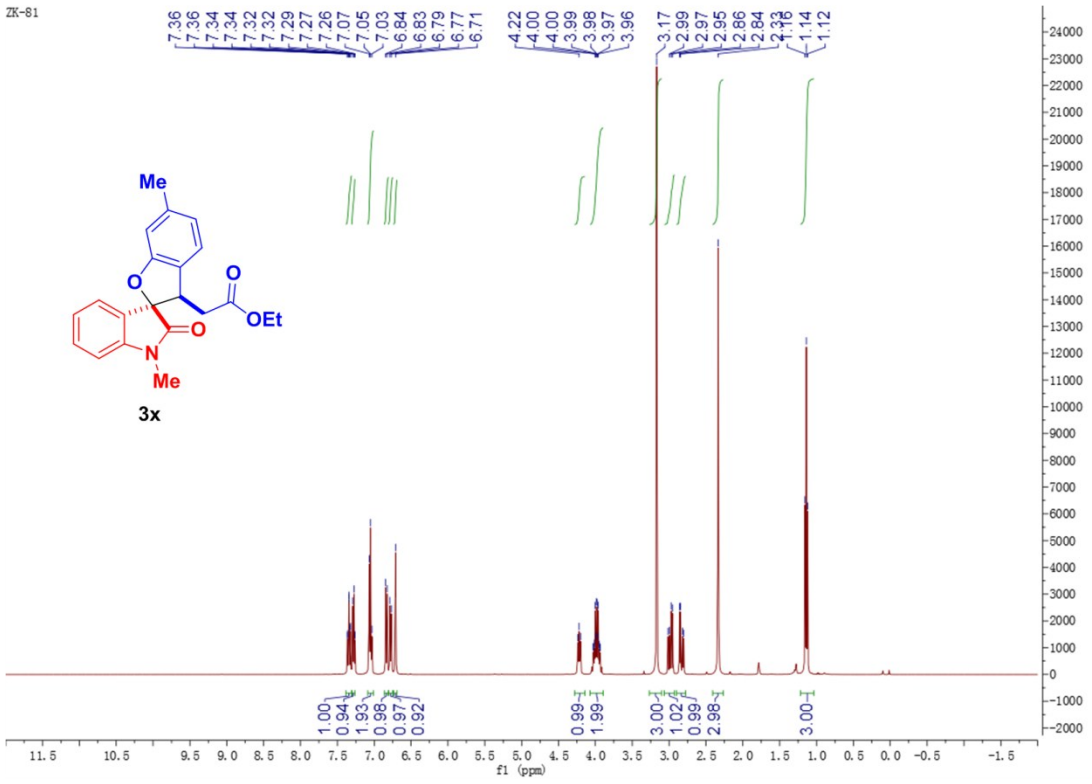

ZK-84
Cl
O
O
OEt
O
N
Me
3v'
f1 (ppm)

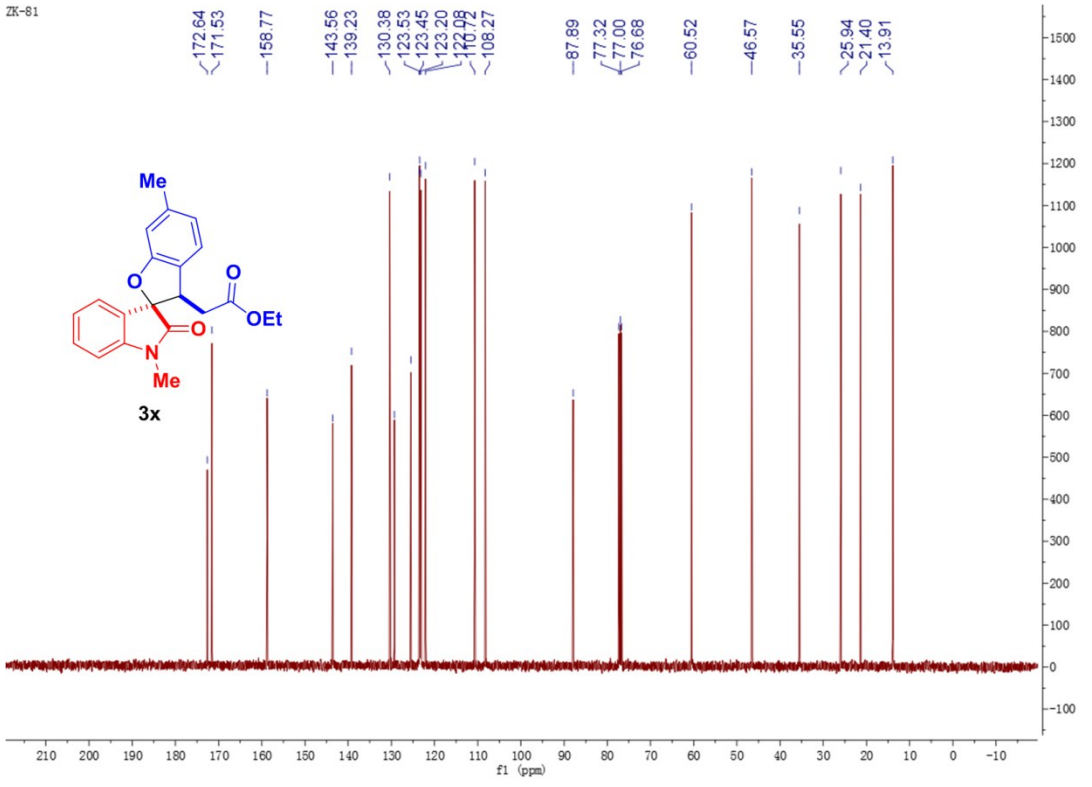

ZK-85
7.38
7.37
7.35
7.30
7.28
7.26
7.10
7.09
7.08
7.08
7.05
7.03
6.85
6.83
4.22
4.20
4.18
4.00
3.99
3.98
3.96
3.17
2.97
2.92
2.90
2.85
2.83
1.14
1.12
Br
O
O
OEt
O
N
Me
3w
0.97
0.98
3.91
1.02
0.99
2.02
3.00
1.03
1.04
3.00
f1 (ppm)

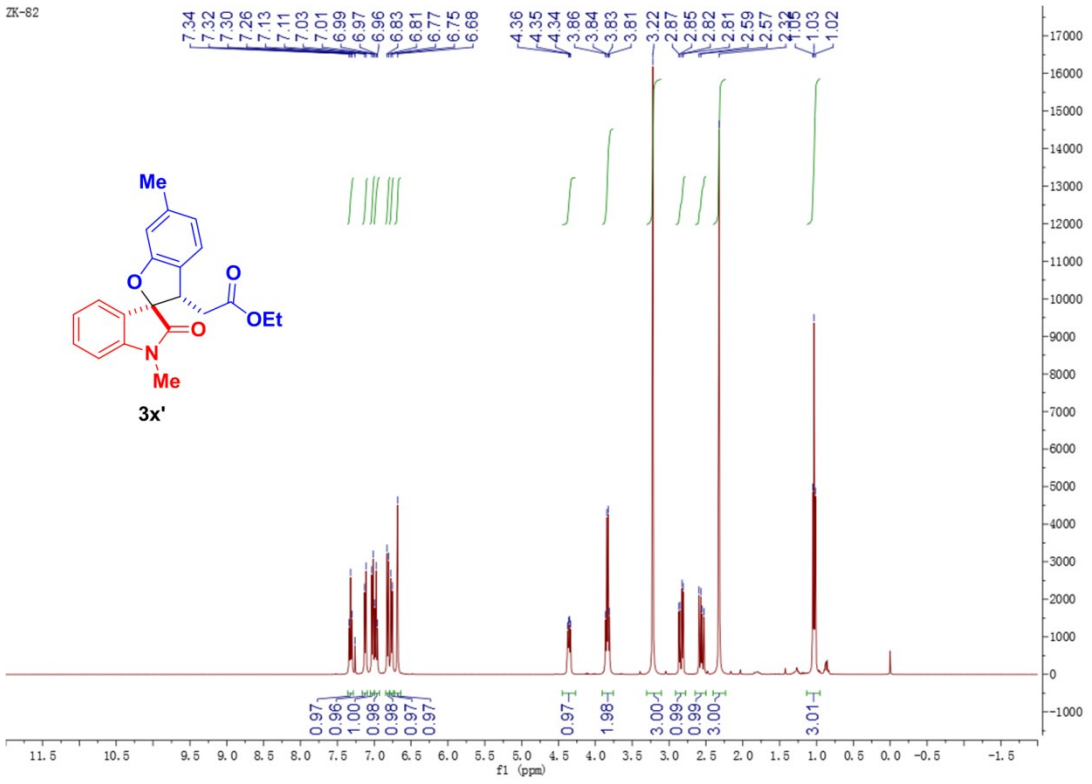

ZK-85
172.14
171.30
159.54
143.68
130.79
128.50
127.96
125.10
124.48
123.66
123.41
122.05
113.68
108.49
88.55
77.32
77.00
76.68
60.77
46.25
35.19
26.07
13.96
Br
O
O
OEt
O
N
Me
3w
f1 (ppm)

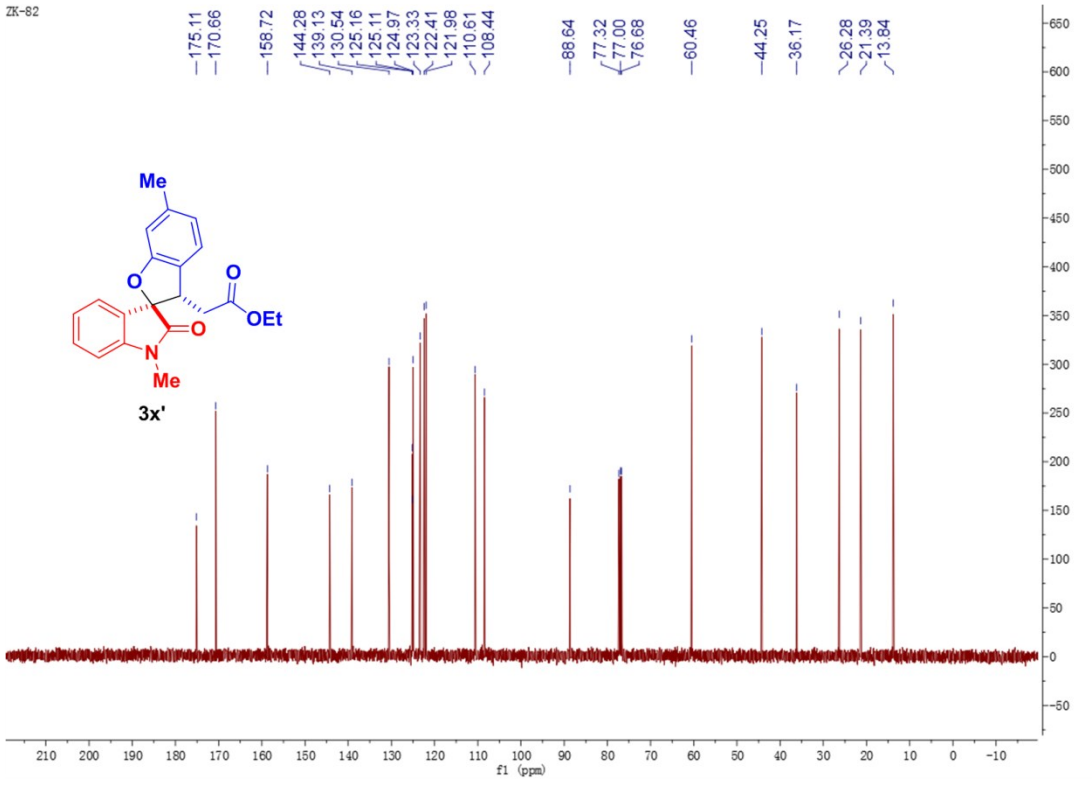

ZK-86
7.37
7.35
7.33
7.13
7.11
7.10
7.08
7.03
7.01
7.00
6.98
6.84
6.82
4.34
4.32
4.31
4.30
3.87
3.85
3.83
3.81
3.23
2.85
2.83
2.80
2.79
2.60
2.58
1.03
1.01
Br
O
O
OEt
O
N
Me
3w'
1.02
1.95
2.91
1.03
0.97
1.99
3.00
1.00
0.99
2.95
f1 (ppm)

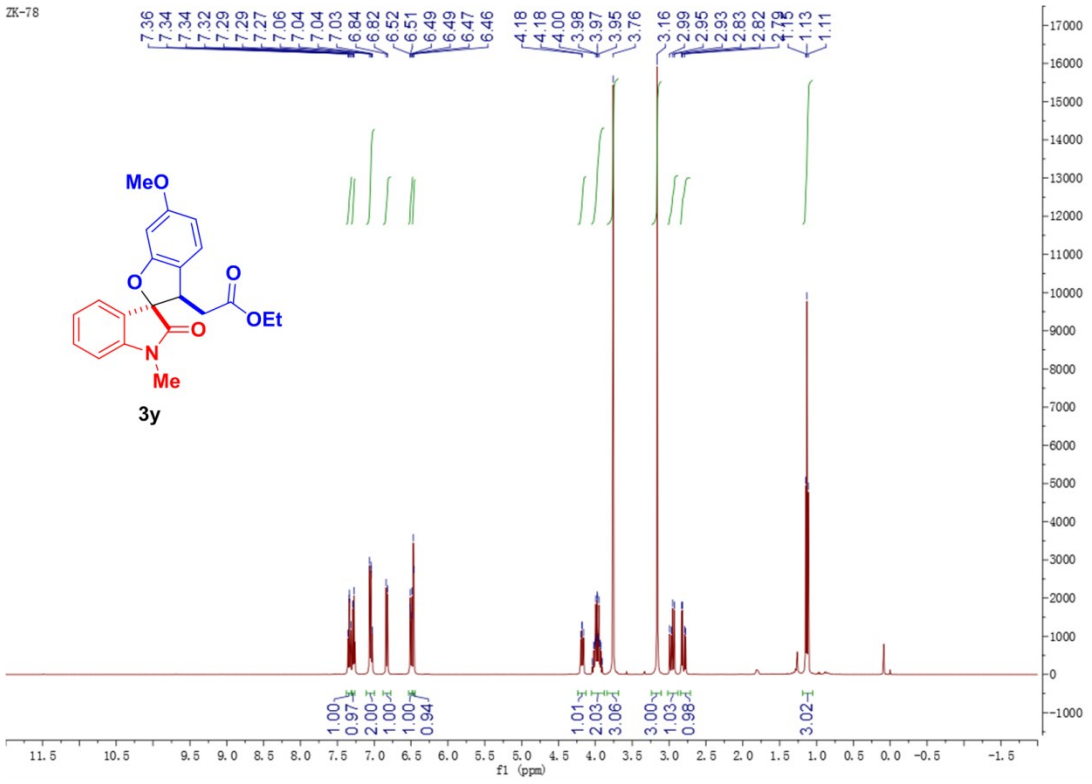

ZK-86
174.61
170.44
159.45
144.36
130.93
127.66
125.11
124.92
124.52
124.42
122.63
121.95
113.62
108.67
89.24
77.32
77.00
76.68
60.71
44.01
35.98
26.41
13.90
Br
O
O
OEt
O
N
Me
3w'
f1 (ppm)

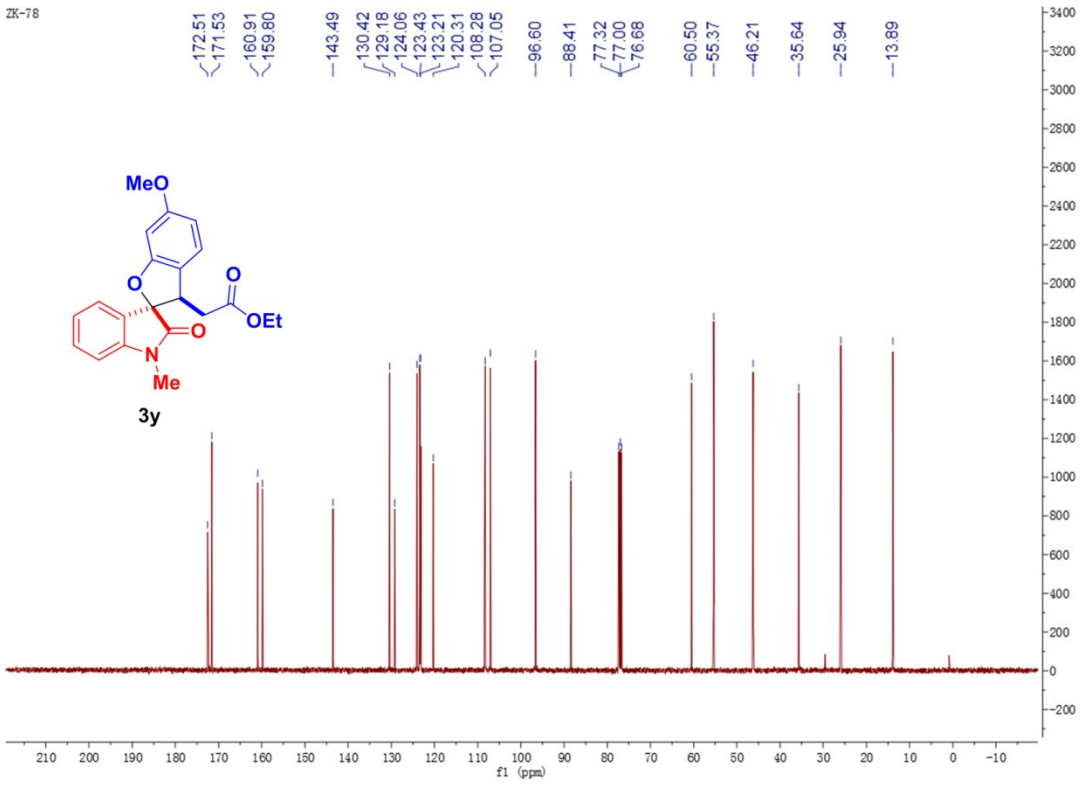

ZK-81
7.36
7.36
7.34
7.34
7.32
7.32
7.29
7.27
7.26
7.07
7.05
7.03
6.84
6.83
6.79
6.77
6.71
4.22
4.00
4.00
3.99
3.98
3.97
3.96
3.17
2.99
2.97
2.95
2.86
2.84
2.33
1.16
1.14
1.12
Me
O
O
OEt
O
N
Me
3x
1.00
0.94
1.93
0.98
0.97
0.92
0.99
1.99
3.00
1.02
0.99
2.98
3.00
f1 (ppm)

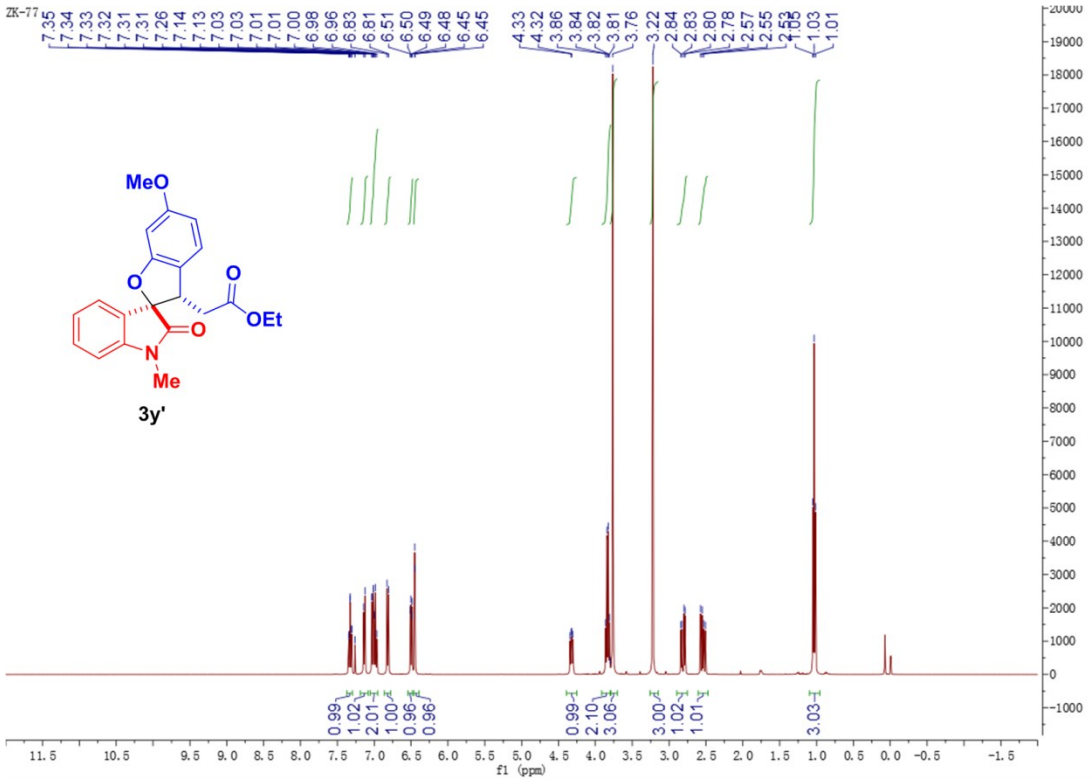

ZK-81
172.64
171.53
158.77
143.56
139.23
130.38
123.53
123.45
123.20
122.08
110.72
108.27
87.89
77.32
77.00
76.68
60.52
46.57
35.55
25.94
21.40
13.91
Me
O
O
OEt
O
N
Me
3x
f1 (ppm)

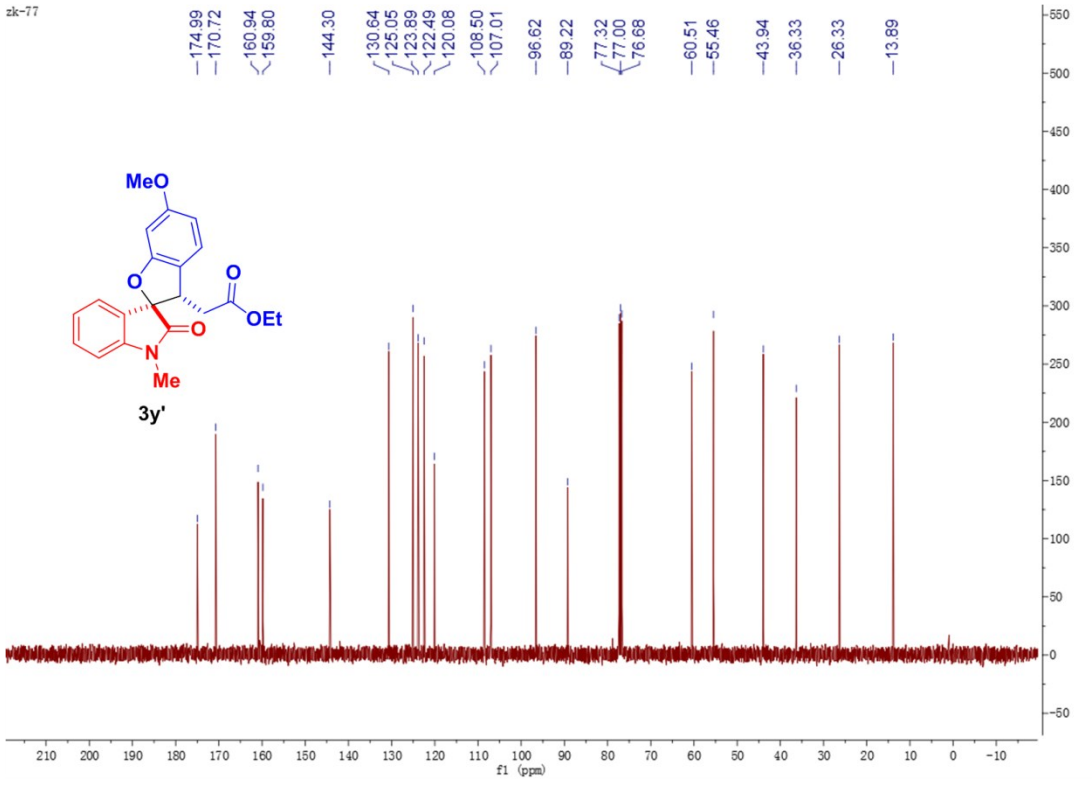

ZK-82
7.34
7.32
7.30
7.26
7.13
7.11
7.03
7.01
6.99
6.97
6.96
6.83
6.81
6.77
6.75
6.68
4.36
4.35
4.34
3.86
3.84
3.83
3.81
3.22
2.87
2.85
2.82
2.81
2.59
2.57
1.03
1.02
Me
O
OEt
O
N
Me
3x'
0.97
0.96
1.00
0.98
0.98
0.97
0.97
0.97
1.98
3.00
0.99
0.99
3.00
3.01
f1 (ppm)

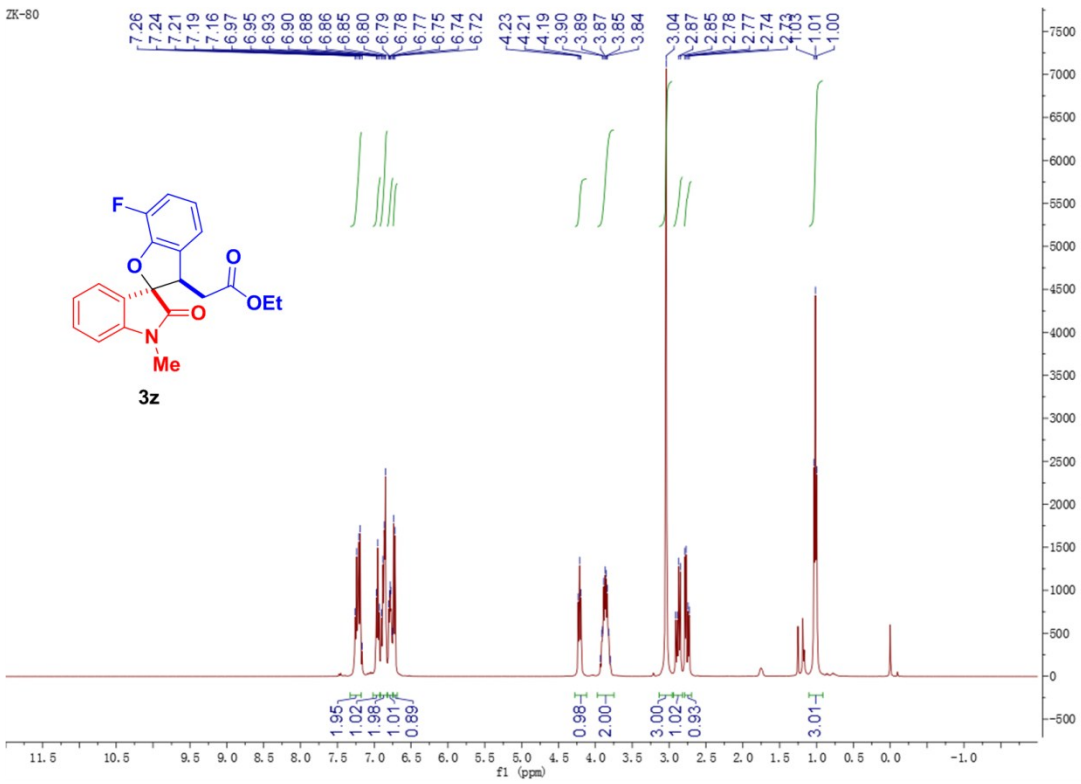

ZK-82
175.11
170.66
158.72
144.28
139.13
130.54
125.16
125.11
124.97
123.33
122.41
121.98
110.61
108.44
88.64
77.32
77.00
76.68
60.46
44.25
36.17
26.28
21.39
13.84
Me
O
OEt
O
N
Me
3x'
f1 (ppm)

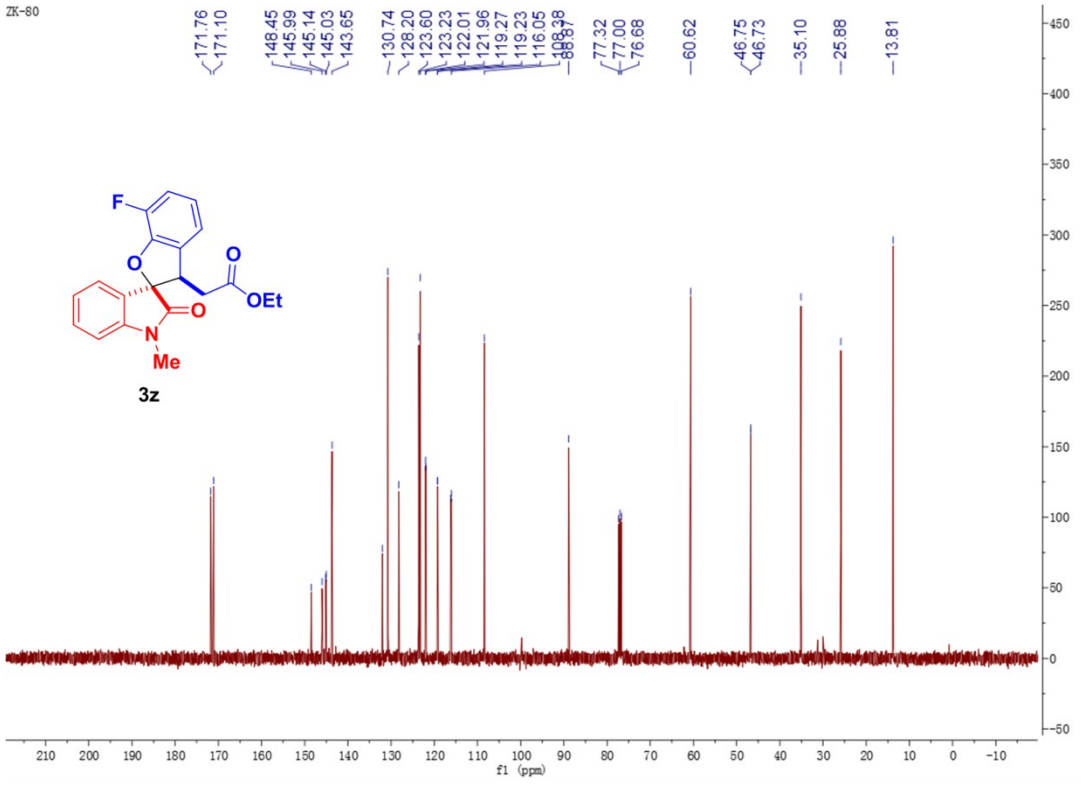

ZK-78
MeO
O
OEt
O
N
Me
3y
f1 (ppm)

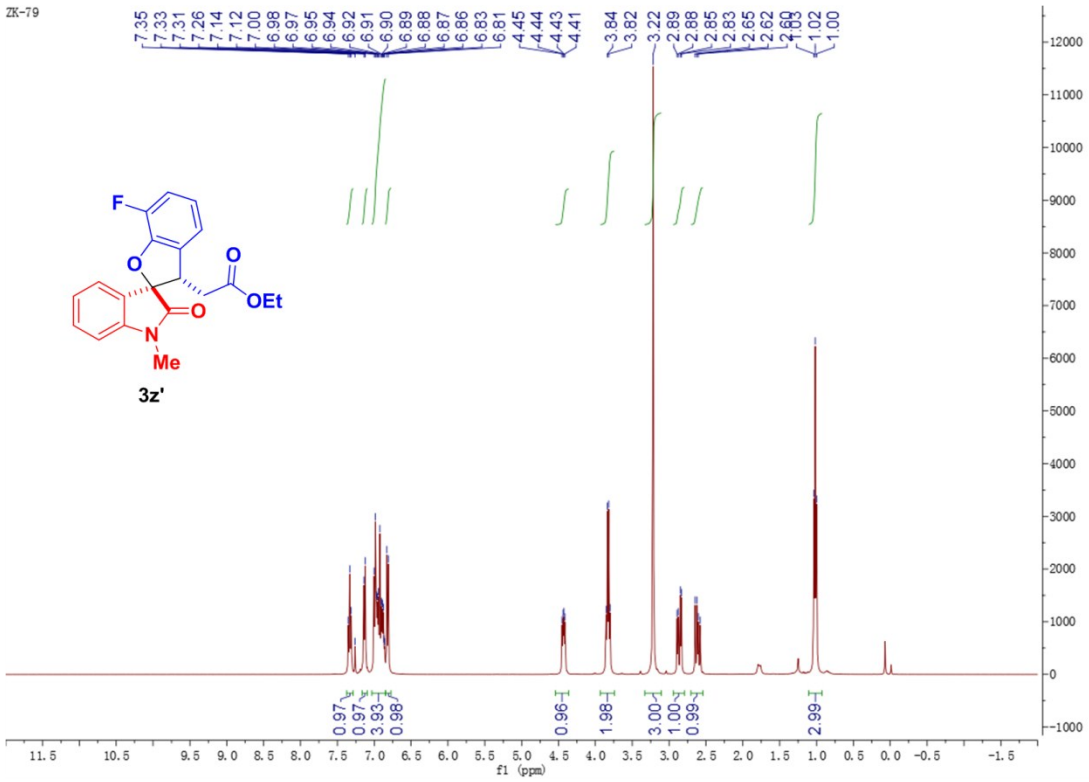

ZK-78
MeO
O
OEt
O
N
Me
3y
f1 (ppm)

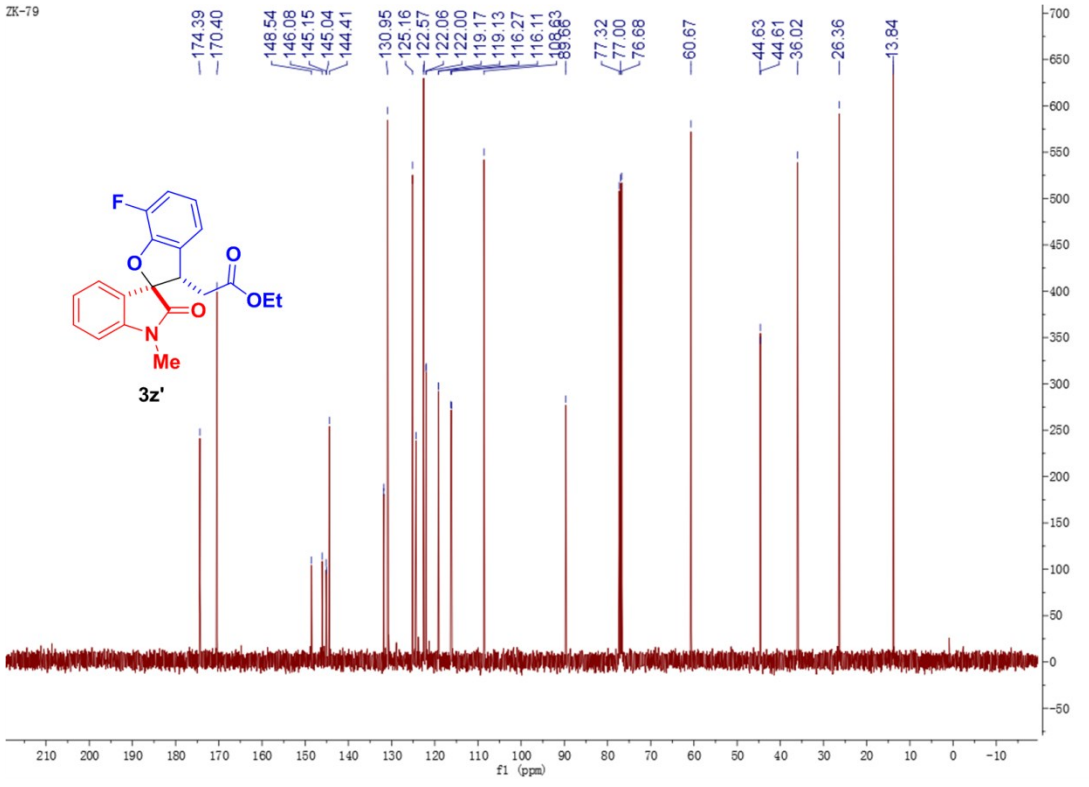

ZK-77
MeO
O
OEt
O
N
Me
3y'
f1 (ppm)

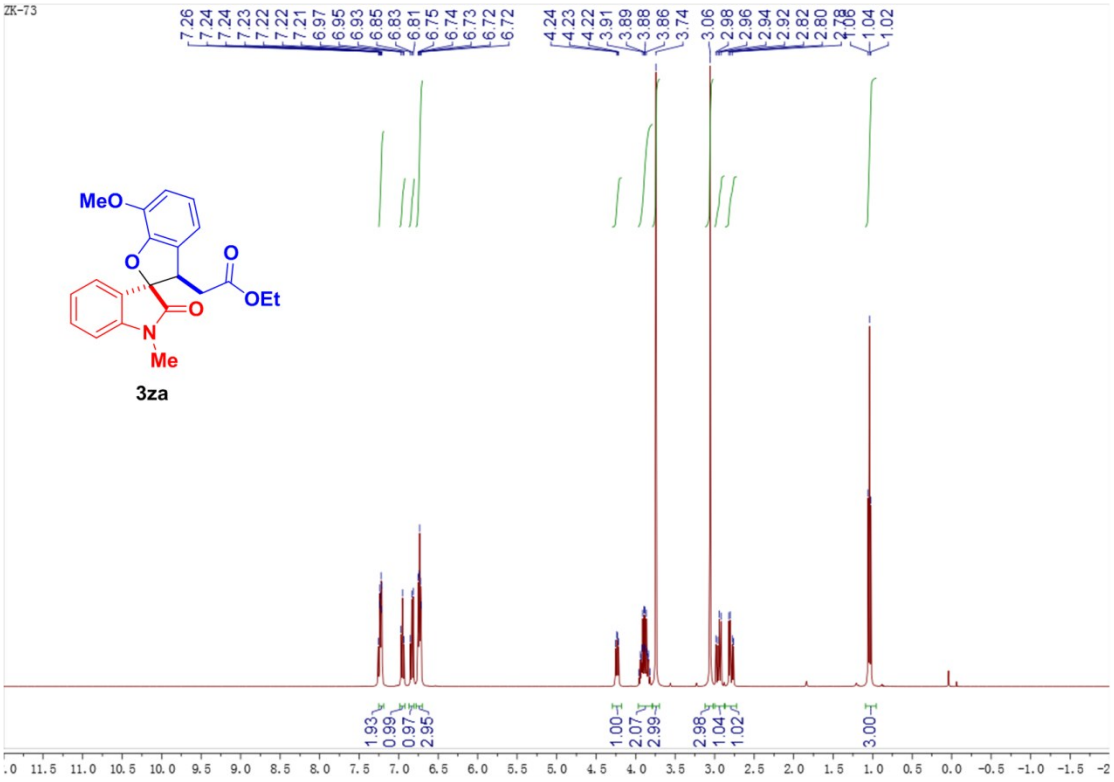

zk-77
MeO
O
OEt
O
N
Me
3y'
f1 (ppm)

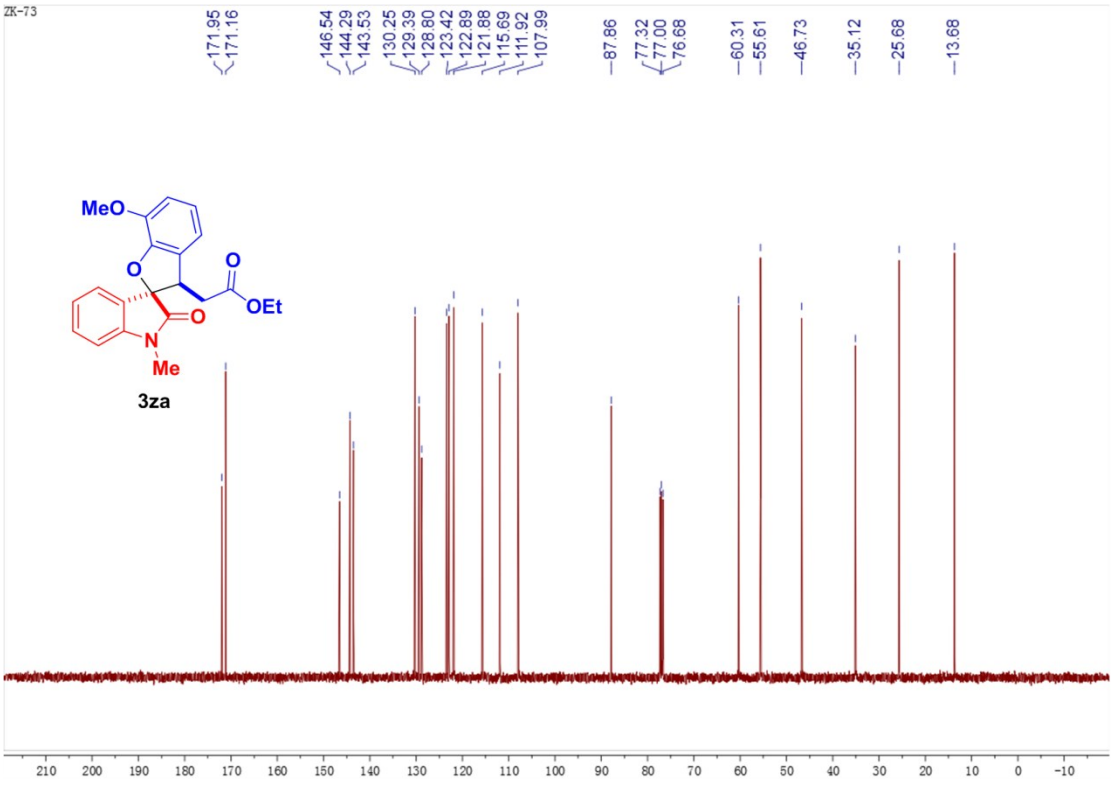

ZK-80
7.26
7.24
7.21
7.19
7.16
6.97
6.95
6.93
6.90
6.88
6.86
6.85
6.80
6.79
6.78
6.77
6.75
6.74
6.72
4.23
4.21
4.19
3.90
3.89
3.87
3.85
3.84
3.04
2.87
2.85
2.78
2.77
2.74
2.73
1.03
1.01
1.00
F
O
O
OEt
O
N
Me
3z
1.95
1.02
1.98
1.01
0.89
0.98
2.00
3.00
1.02
0.93
3.01
f1 (ppm)

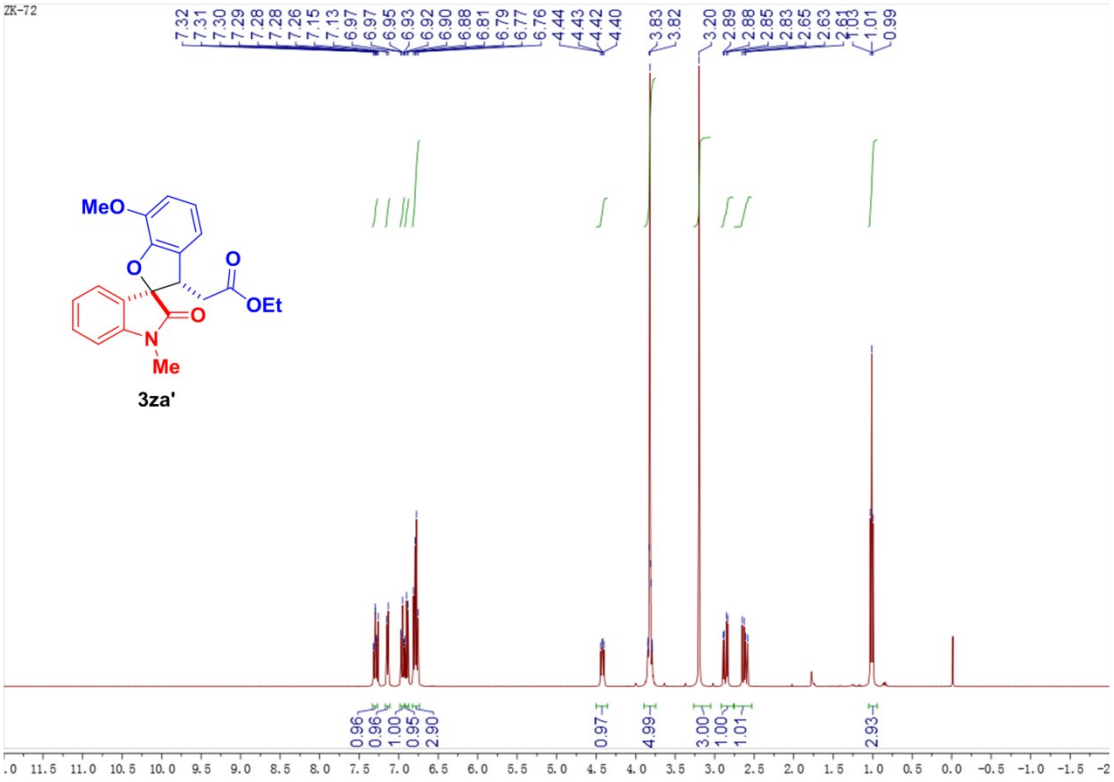

ZK-80
171.76
171.10
148.45
145.99
145.14
145.03
143.65
130.74
128.20
123.60
123.23
122.01
121.96
119.27
119.23
116.05
108.38
77.32
77.00
76.68
60.62
46.75
46.73
35.10
25.88
13.81
F
O
O
OEt
O
N
Me
3z
f1 (ppm)

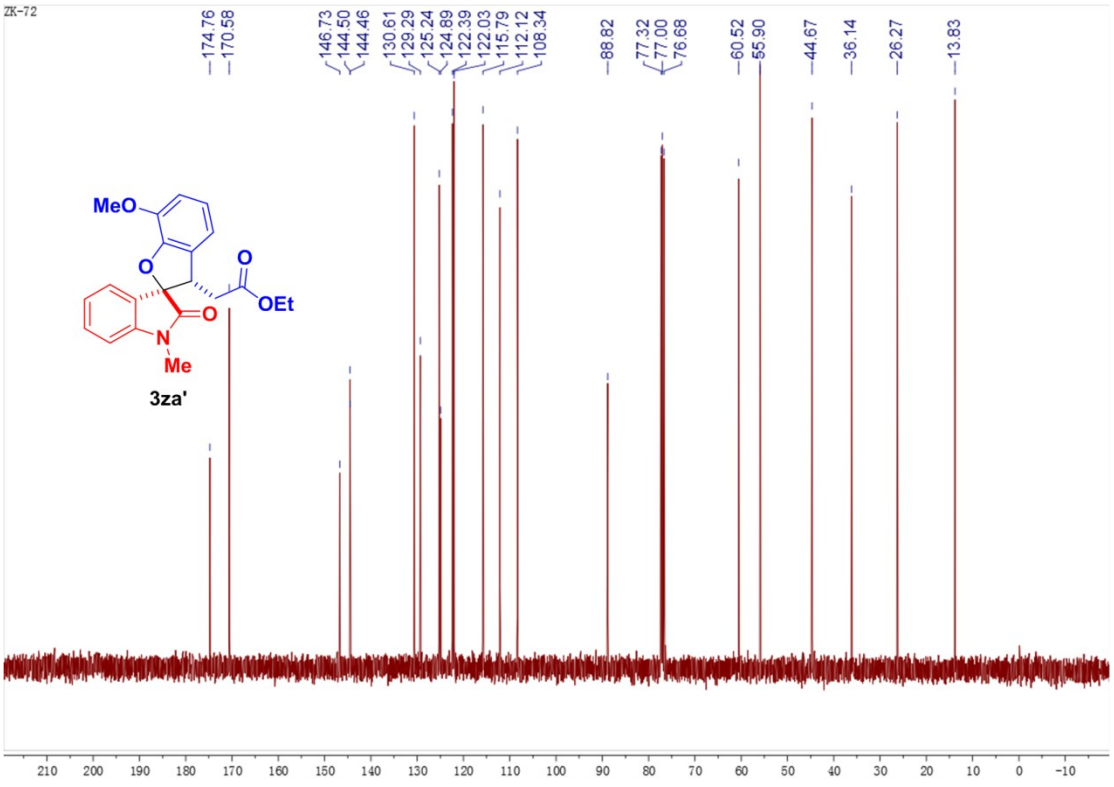

ZK-79
7.35
7.33
7.31
7.26
7.14
7.12
7.00
6.98
6.97
6.95
6.94
6.92
6.91
6.90
6.89
6.88
6.87
6.86
6.83
6.81
4.45
4.44
4.43
4.41
3.84
3.82
3.22
2.89
2.88
2.85
2.83
2.65
2.62
1.03
1.02
1.00
F
O
O
OEt
O
N
Me
3z'
0.97
0.97
3.93
0.98
0.96
1.98
3.00
1.00
0.99
2.99
f1 (ppm)

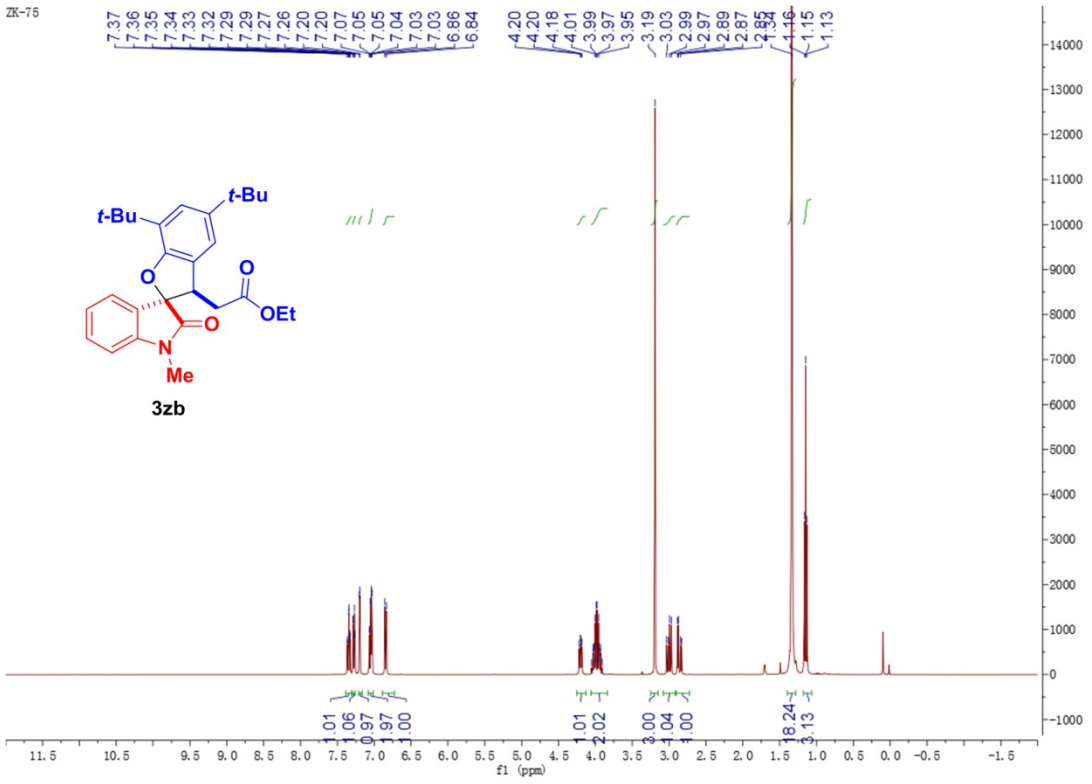

ZK-79
174.39
170.40
148.54
146.08
145.15
145.04
144.41
130.95
125.16
122.57
122.06
122.00
119.17
119.13
116.27
116.11
108.63
89.66
77.32
77.00
76.68
60.67
44.63
44.61
36.02
26.36
13.84
F
O
O
OEt
O
N
Me
3z'
f1 (ppm)

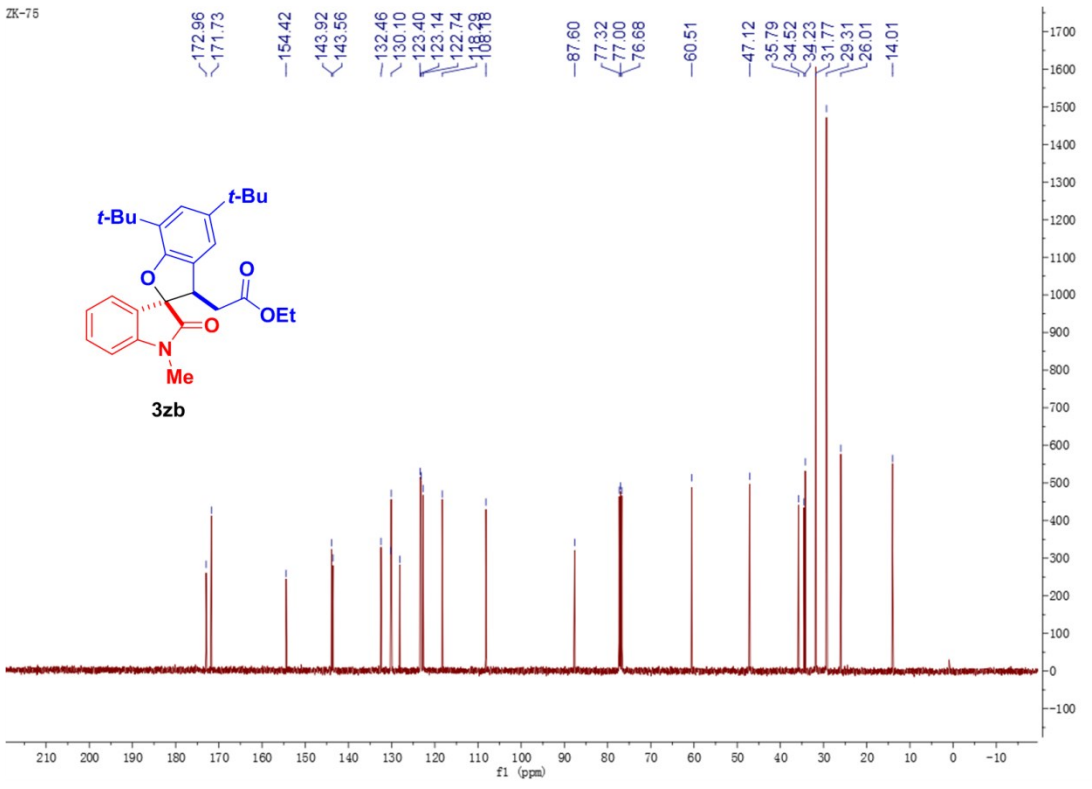

ZK-73
MeO
O
O
OEt
N
Me
3za

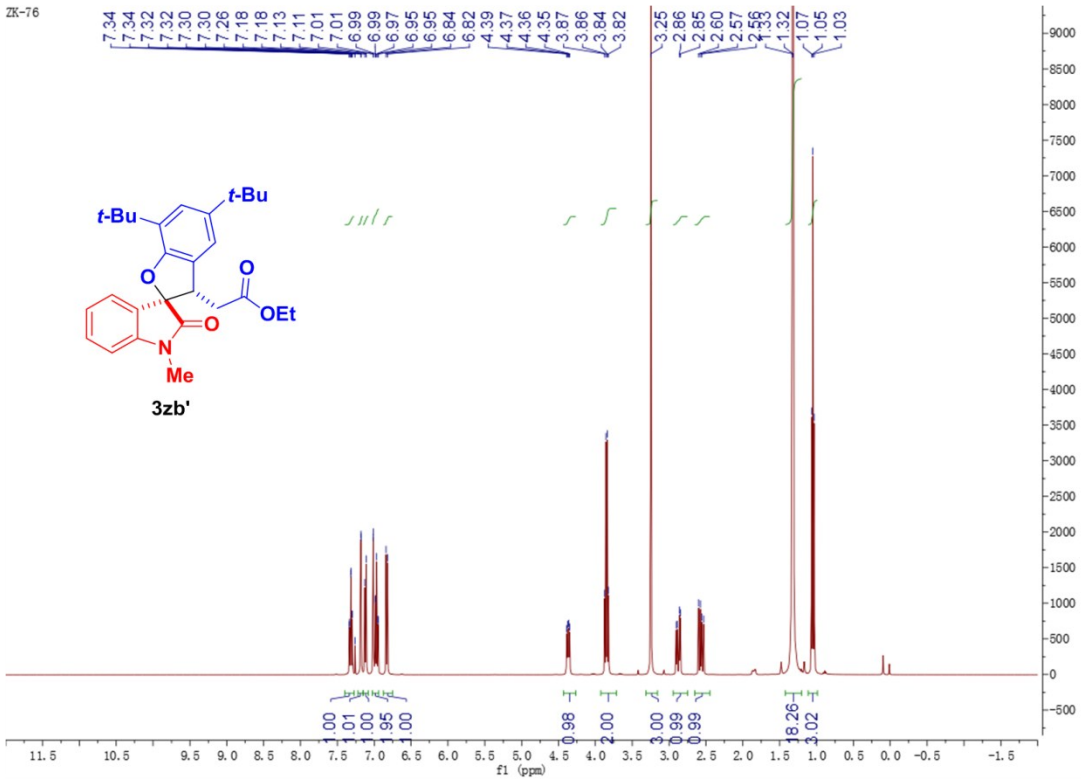

ZK-73
MeO
O
O
OEt
N
Me
3za

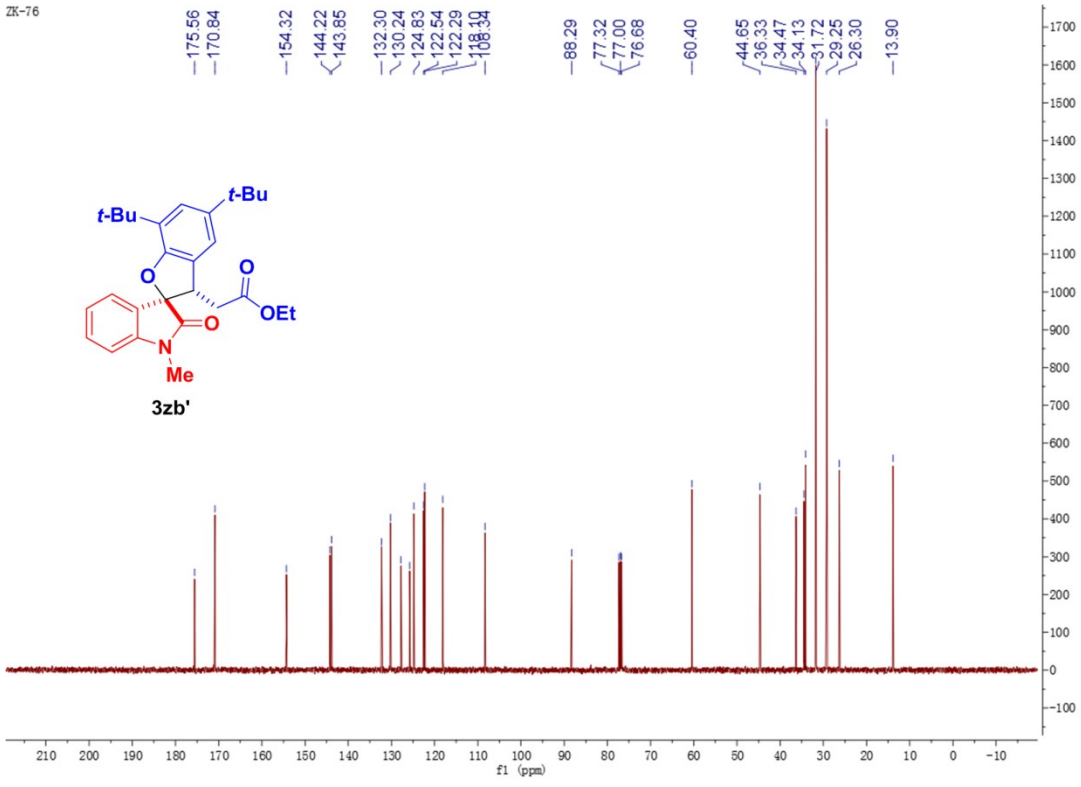

ZK-72
MeO
O
O
OEt
N
Me
3za'

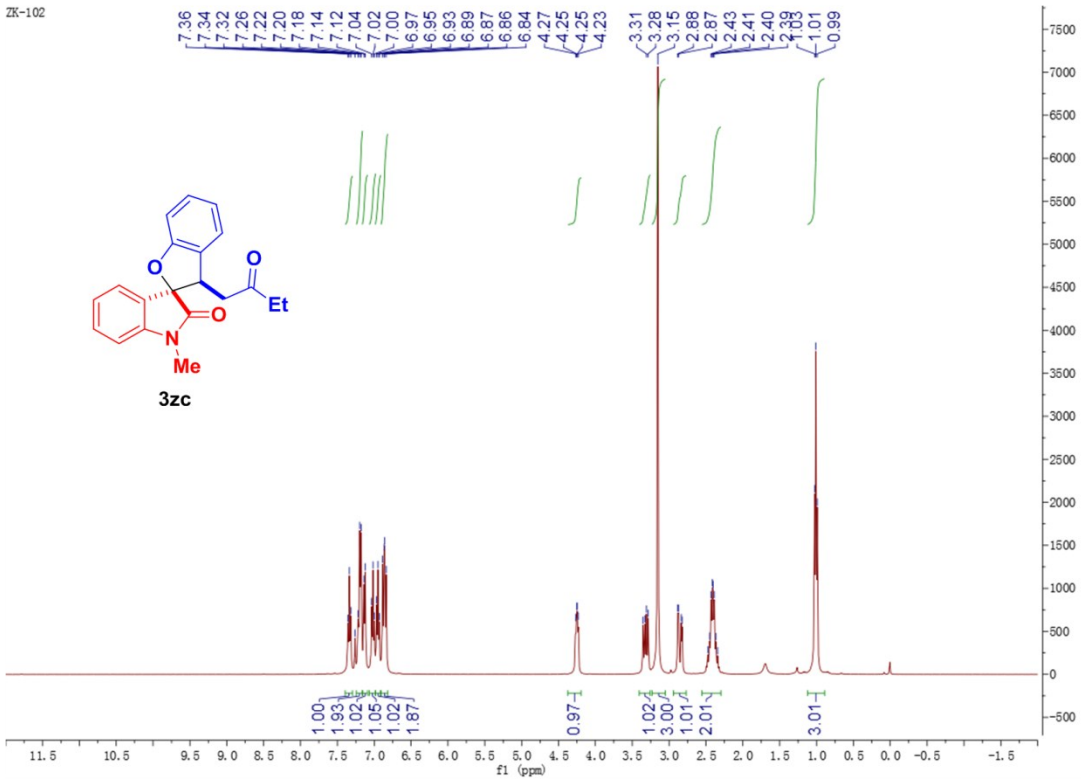

ZK-72
MeO
O
O
OEt
N
Me
3za'

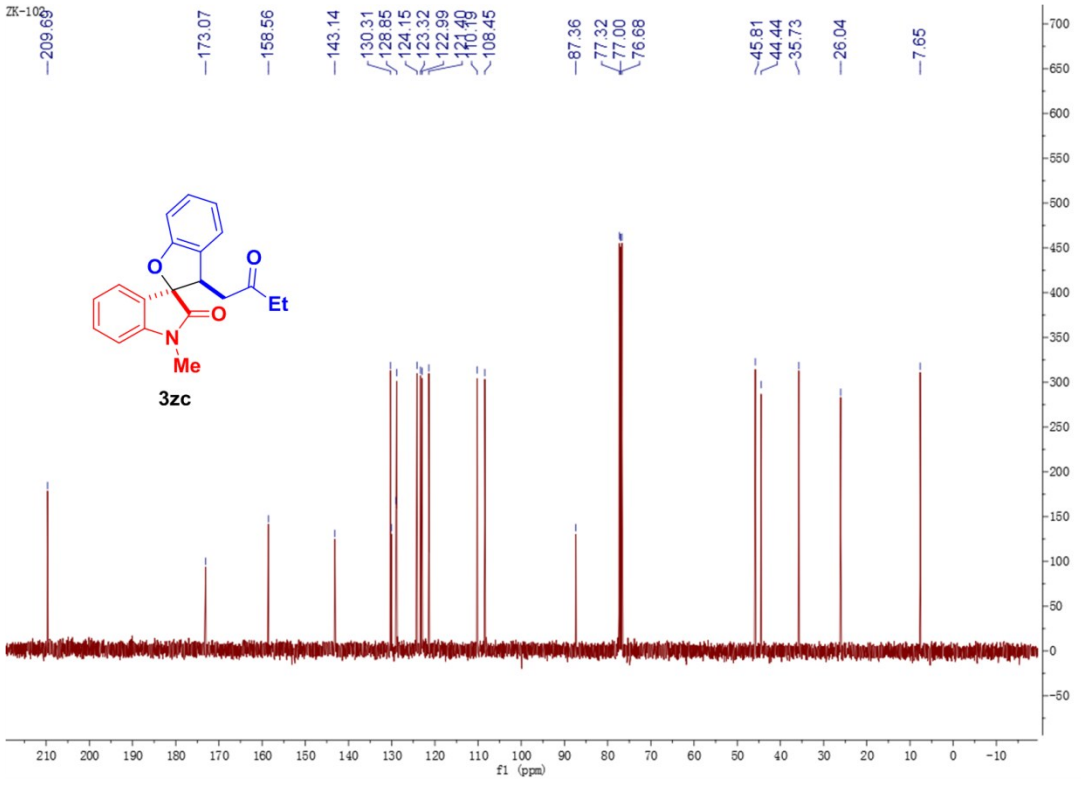

ZK-75
7.37
7.36
7.35
7.34
7.33
7.32
7.29
7.27
7.26
7.20
7.20
7.07
7.05
7.05
7.04
7.03
7.03
6.86
6.84
4.20
4.20
4.18
4.01
3.99
3.97
3.95
3.19
3.03
2.99
2.97
2.89
2.87
1.16
1.15
1.13
t-Bu
t-Bu
O
O
OEt
O
N
Me
3zb
1.01
1.06
0.97
1.97
1.00
1.01
2.02
3.00
1.04
1.00
18.24
3.13
f1 (ppm)

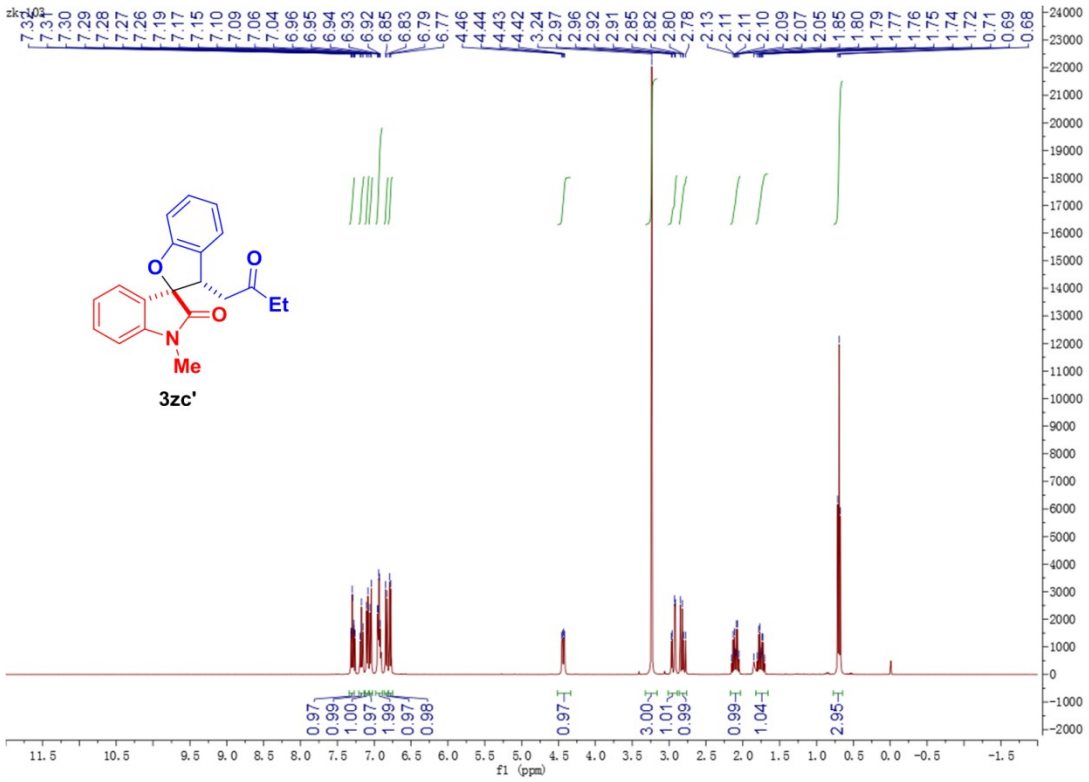

ZK-75
172.96
171.73
154.42
143.92
143.56
132.46
130.10
123.40
123.14
122.74
118.29
108.18
87.60
77.32
77.00
76.68
60.51
47.12
35.79
34.52
34.23
31.77
29.31
26.01
14.01
t-Bu
t-Bu
O
O
OEt
O
N
Me
3zb
f1 (ppm)

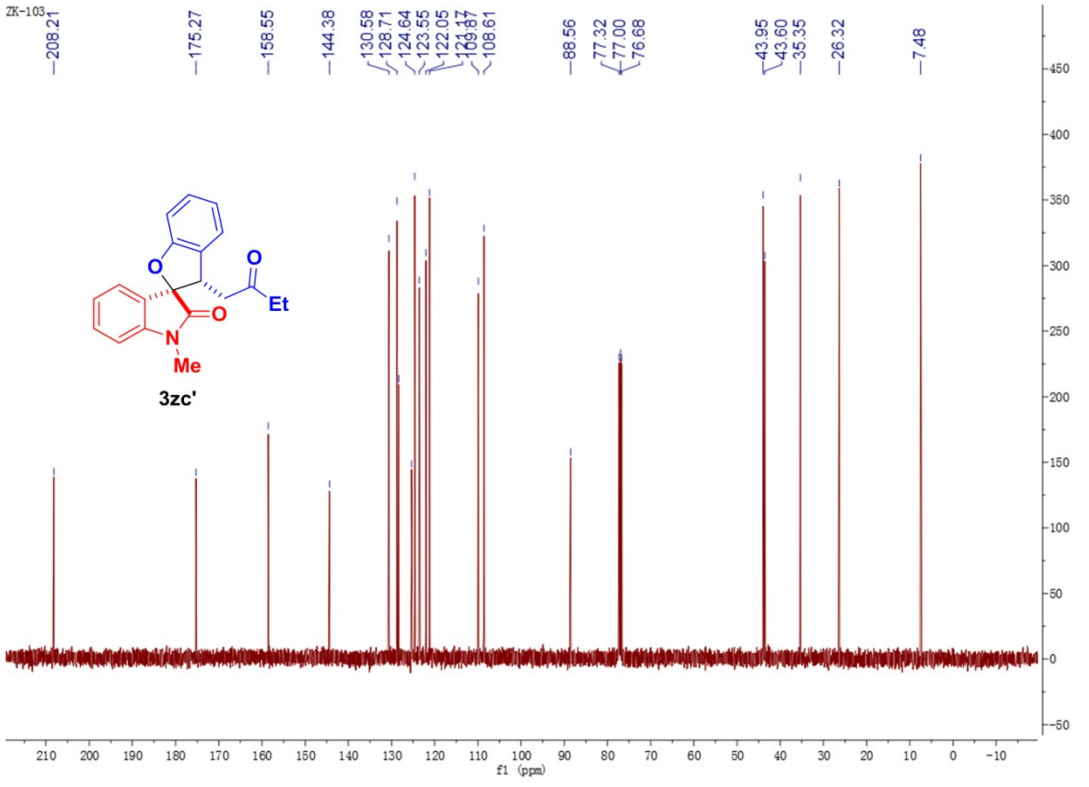

ZK-76
7.34
7.34
7.32
7.32
7.30
7.30
7.26
7.18
7.18
7.13
7.11
7.01
7.01
6.99
6.99
6.97
6.95
6.95
6.84
6.82
4.39
4.37
4.36
4.35
3.87
3.86
3.84
3.82
3.25
2.86
2.85
2.60
2.57
2.56
1.33
1.32
1.07
1.05
1.03
t-Bu
t-Bu
O
O
OEt
O
N
Me
3zb'
1.00
1.01
1.00
1.95
1.00
0.98
2.00
3.00
0.99
0.99
18.26
3.02
f1 (ppm)

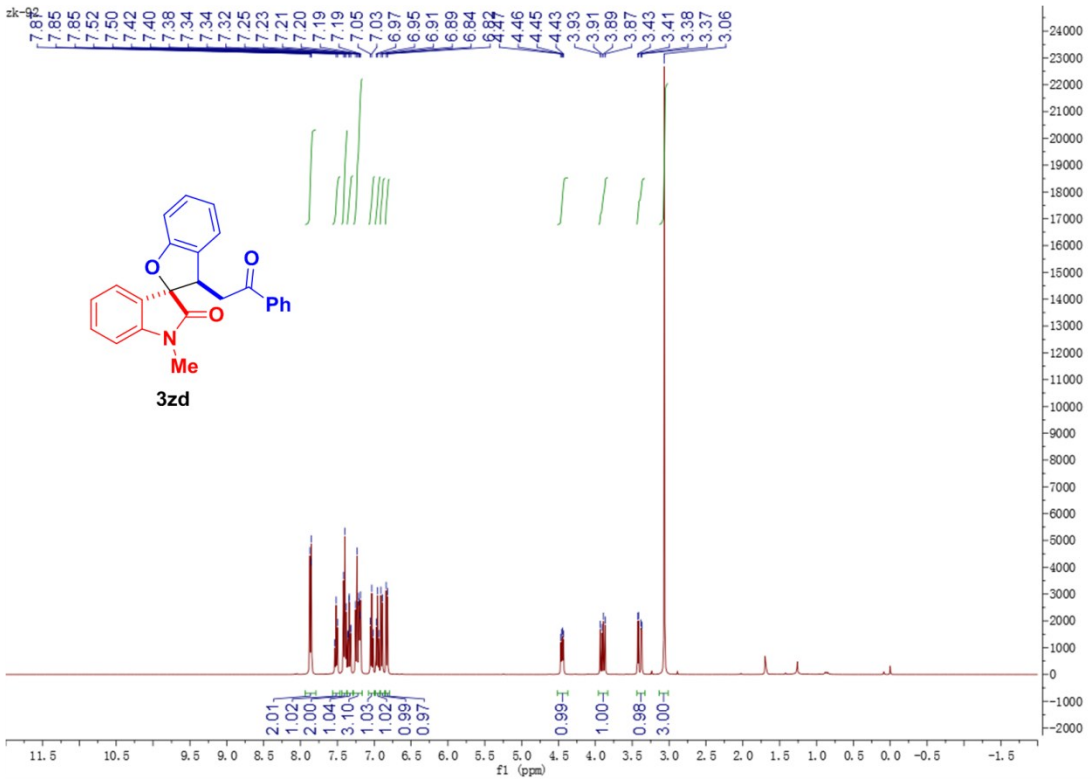

ZK-76
175.56
170.84
154.32
144.22
143.85
132.30
130.24
124.83
122.54
122.29
118.10
108.34
88.29
77.32
77.00
76.68
60.40
44.65
36.33
34.47
34.13
31.72
29.25
26.30
13.90
t-Bu
t-Bu
O
O
OEt
O
N
Me
3zb'
f1 (ppm)

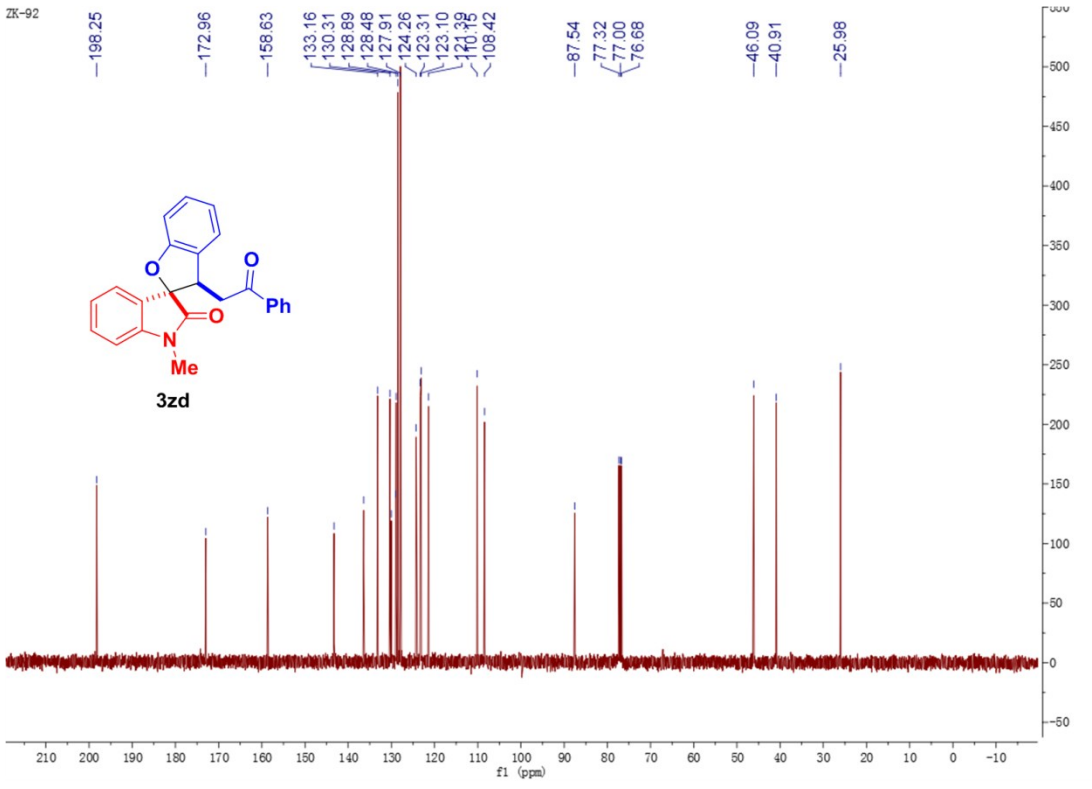

ZK-102
7.36
7.34
7.32
7.26
7.22
7.20
7.18
7.14
7.12
7.04
7.02
7.00
6.97
6.95
6.93
6.89
6.87
6.86
6.84
4.27
4.25
4.23
3.31
3.28
3.15
2.88
2.87
2.43
2.41
2.40
1.03
1.01
0.99
O
Et
O
O
N
Me
3zc
1.00
1.93
1.02
1.05
1.02
1.87
0.97
1.02
3.00
1.01
2.01
3.01
f1 (ppm)

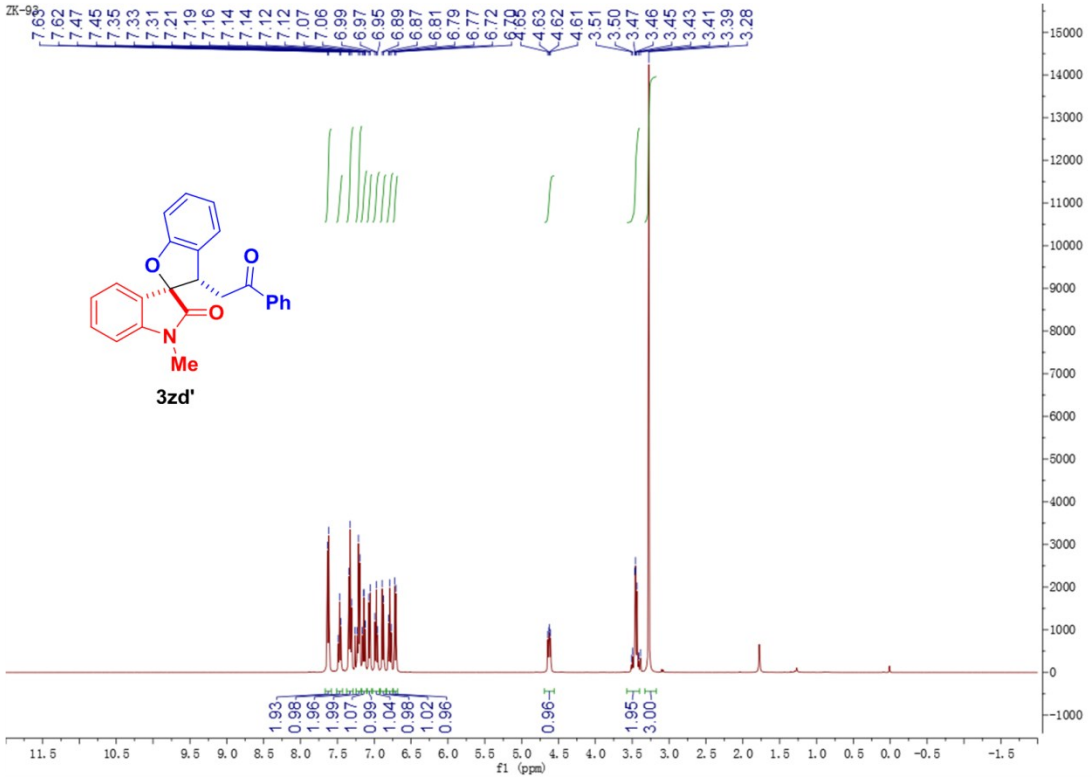

ZK-102
209.69
173.07
158.56
143.14
130.31
128.85
124.15
123.32
122.99
121.40
110.19
108.45
87.36
77.32
77.00
76.68
45.81
44.44
35.73
26.04
7.65
O
Et
O
O
N
Me
3zc
f1 (ppm)

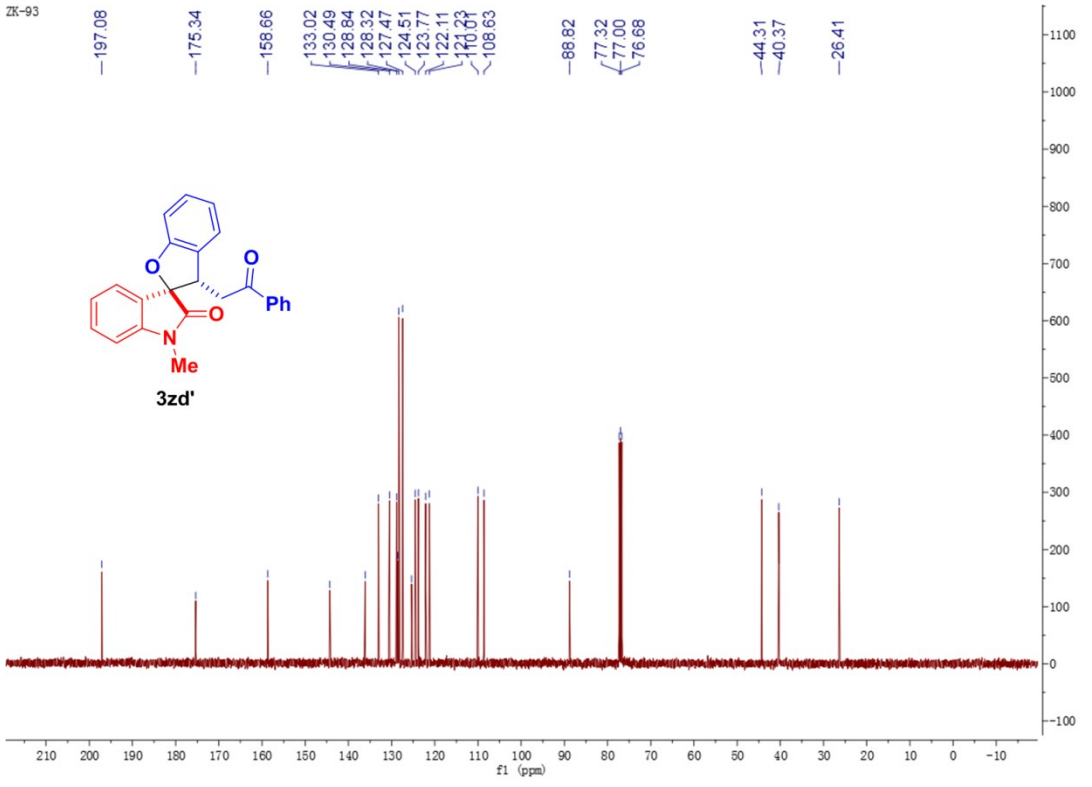

zk-103
7.34
7.31
7.30
7.29
7.28
7.27
7.26
7.19
7.17
7.15
7.10
7.09
7.06
7.04
6.96
6.95
6.94
6.93
6.92
6.85
6.83
6.79
6.77
4.46
4.44
4.43
4.42
3.24
2.97
2.96
2.92
2.91
2.85
2.82
2.80
2.78
2.13
2.11
2.11
2.10
2.09
2.07
2.05
1.85
1.80
1.79
1.77
1.76
1.75
1.74
1.72
0.71
0.69
0.68
O
O
Et
O
N
Me
3zc'
0.97
0.99
1.00
0.97
1.99
0.97
0.98
0.97
3.00
1.01
0.99
0.99
1.04
2.95
f1 (ppm)

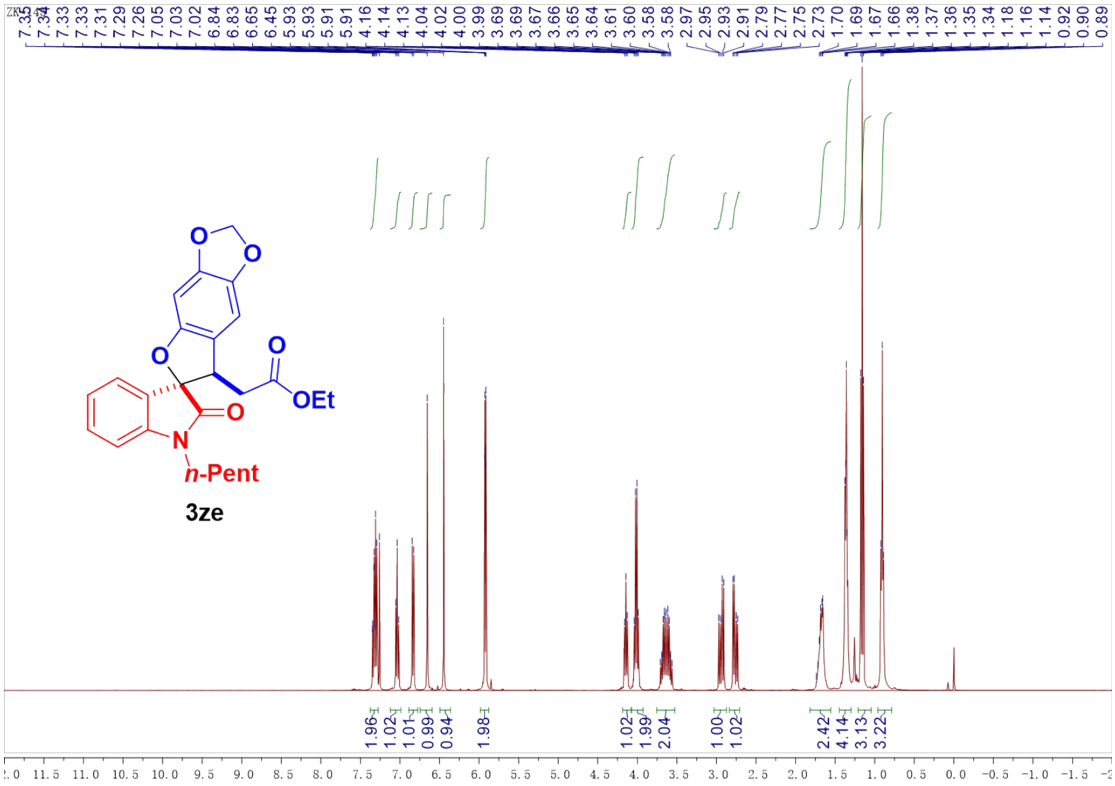

ZK-103
208.21
175.27
158.55
144.38
130.58
128.71
124.64
123.55
122.05
121.17
109.87
108.61
88.56
77.32
77.00
76.68
43.95
43.60
35.35
26.32
7.48
O
O
Et
O
N
Me
3zc'
f1 (ppm)

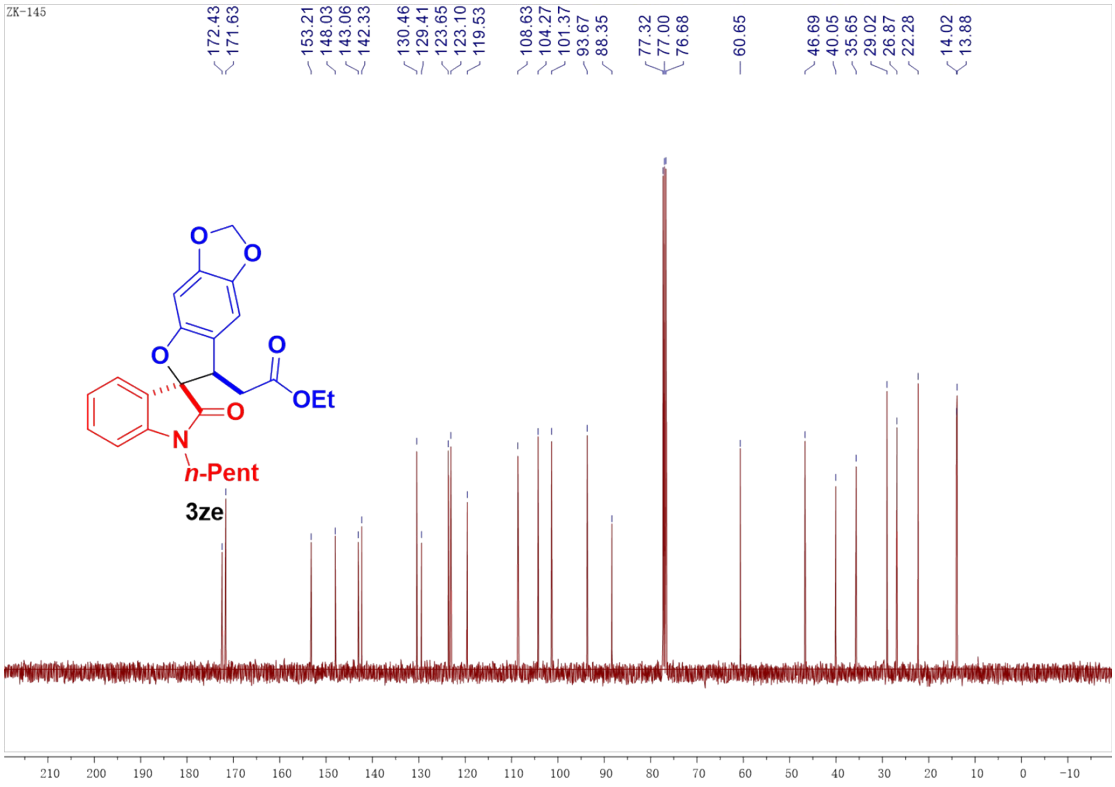

zk-92
7.87
7.85
7.85
7.52
7.50
7.42
7.40
7.38
7.34
7.34
7.32
7.25
7.23
7.21
7.20
7.19
7.19
7.05
7.03
6.97
6.95
6.91
6.89
6.84
6.82
4.47
4.46
4.45
4.43
3.93
3.91
3.89
3.87
3.43
3.41
3.38
3.37
3.06
O
O
Ph
O
N
Me
3zd
2.01
1.02
2.00
1.04
3.10
1.03
1.02
0.99
0.97
0.99
1.00
0.98
3.00
f1 (ppm)

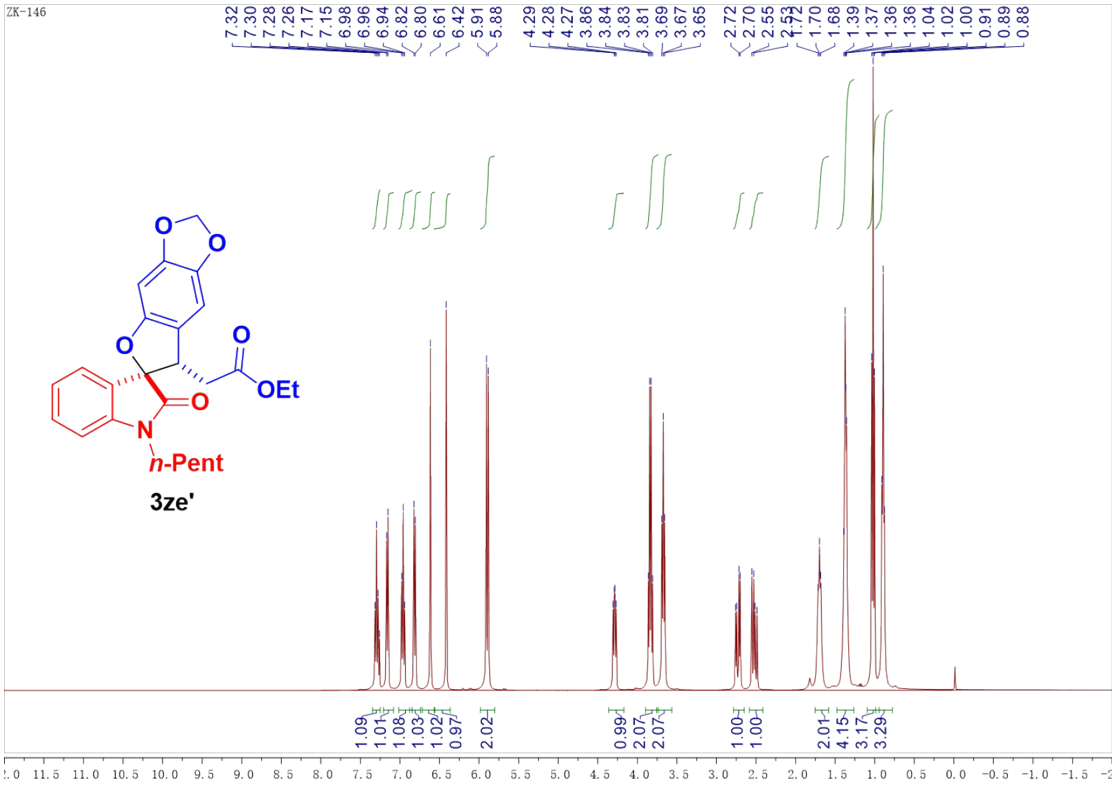

ZK-92
198.25
172.96
158.63
133.16
130.31
128.89
128.48
127.91
124.26
123.31
123.10
87.54
77.32
77.00
76.68
46.09
40.91
25.98
O
O
Ph
O
N
Me
3zd
f1 (ppm)

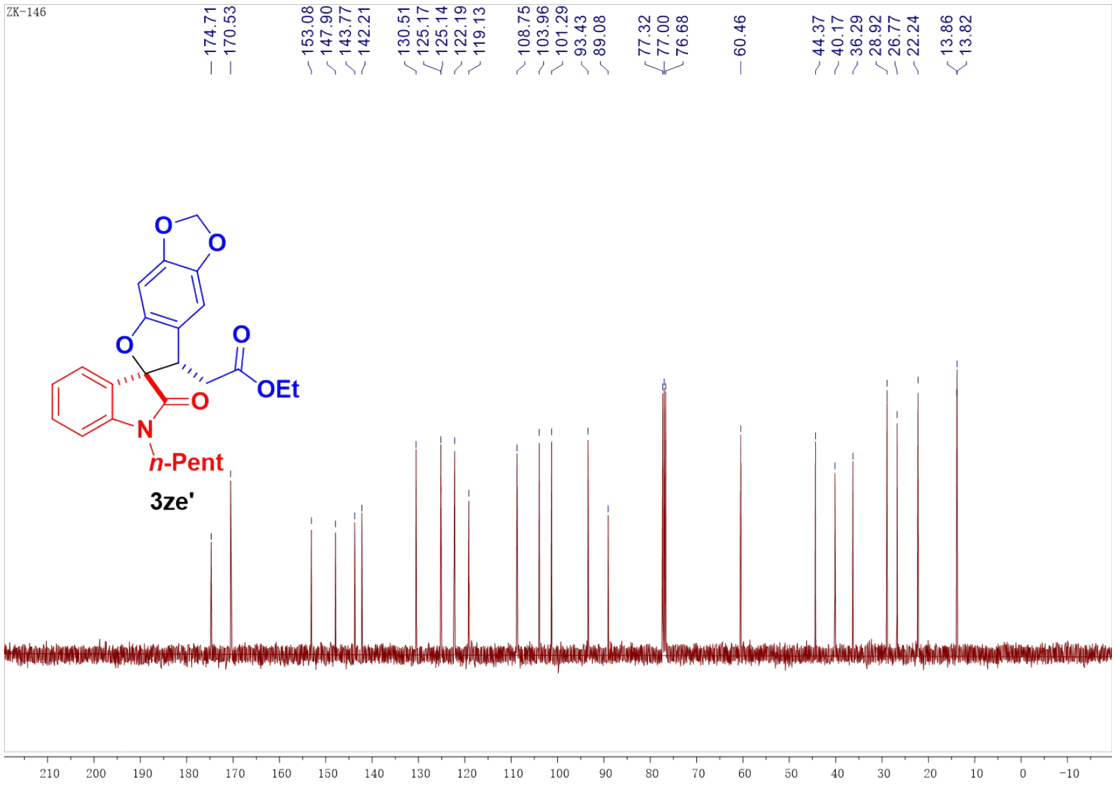

ZK-93
7.63
7.62
7.47
7.45
7.35
7.33
7.31
7.21
7.19
7.16
7.14
7.14
7.12
7.12
7.07
7.06
6.99
6.97
6.95
6.89
6.87
6.81
6.79
6.77
6.72
6.70
4.65
4.63
4.62
4.61
3.51
3.50
3.47
3.46
3.45
3.43
3.41
3.39
3.28
O
O
Ph
O
N
Me
3zd'
1.93
0.98
1.96
1.99
1.07
0.99
1.04
0.98
1.02
0.96
0.96
1.95
3.00
f1 (ppm)

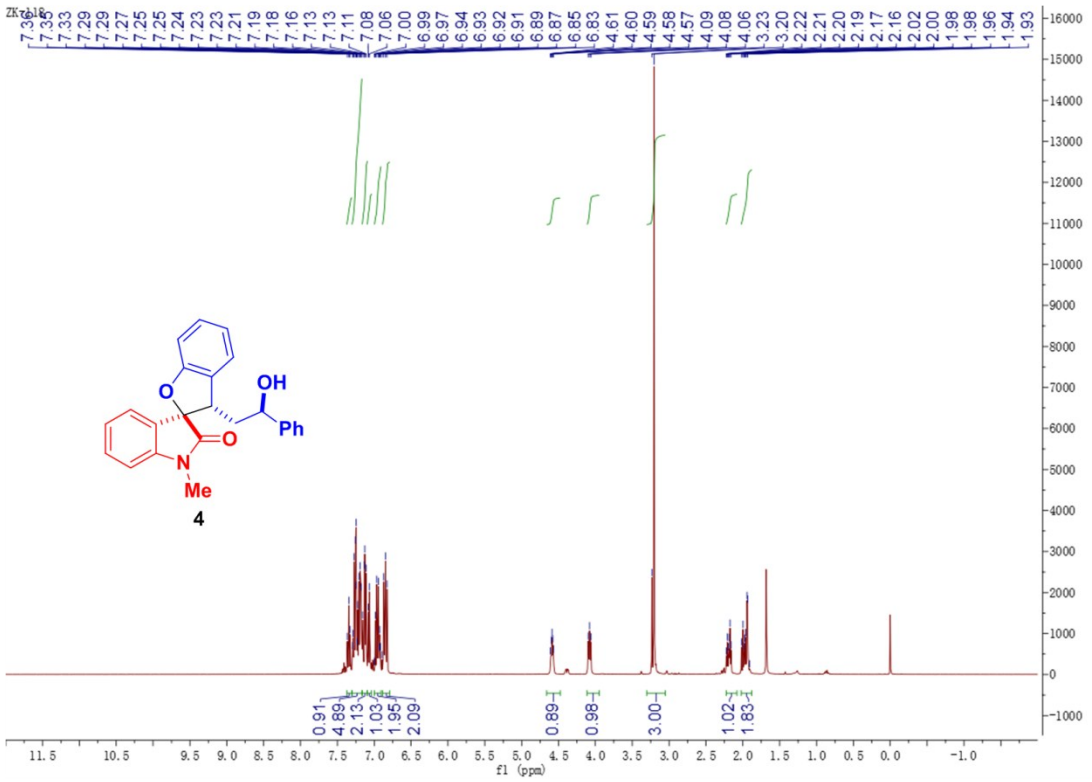

ZK-93
197.08
175.34
158.66
133.02
130.49
128.84
128.32
127.47
124.51
123.77
122.11
121.23
110.07
108.63
88.82
77.32
77.00
76.68
44.31
40.37
26.41
O
O
Ph
O
N
Me
3zd'
f1 (ppm)

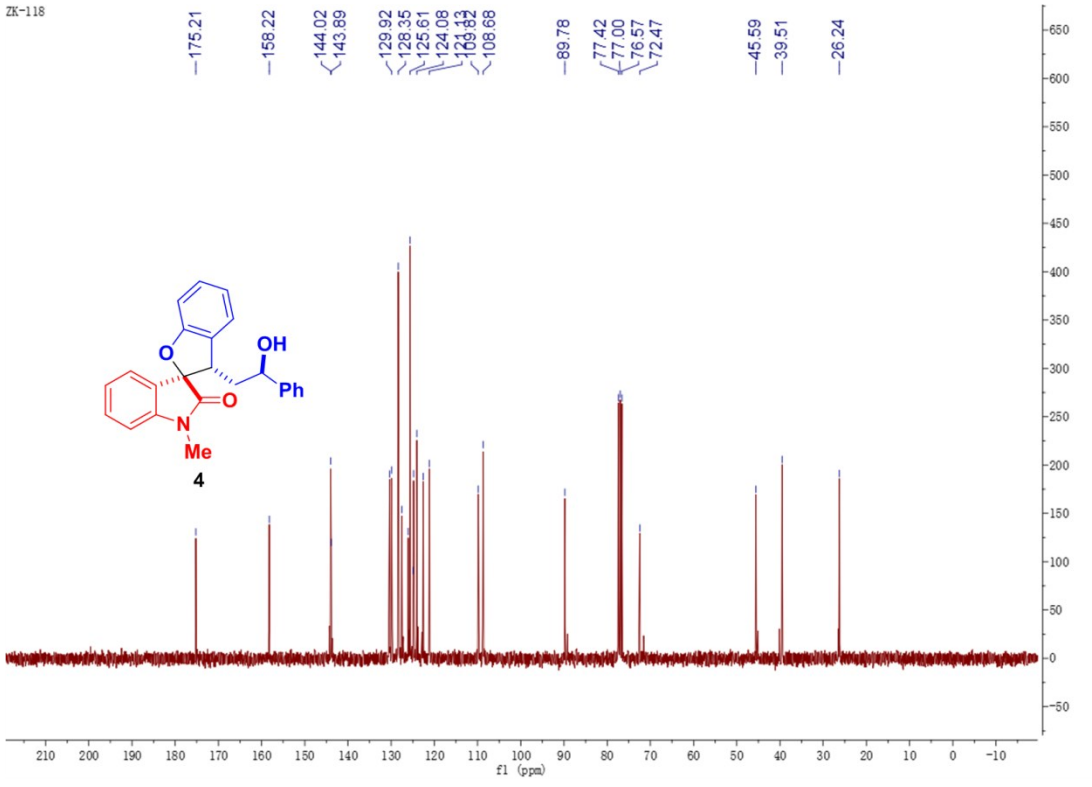

7.35 7.34 7.34 7.33 7.33 7.31 7.29 7.26 7.05 7.03 7.02 6.84 6.83 6.65 6.45 5.93 5.93 5.91 5.91 4.16 4.14 4.13 4.04 4.02 4.00 3.99 3.69 3.69 3.67 3.66 3.65 3.64 3.61 3.60 3.58 3.58 2.97 2.95 2.93 2.91 2.79 2.77 2.75 2.73 1.70 1.69 1.67 1.66 1.38 1.37 1.36 1.35 1.34 1.18 1.16 1.14 0.92 0.90 0.89
O
O
O
O
OEt
N
n-Pent
3ze
1.96 1.02 1.01 0.99 0.94 1.98 1.02 1.99 2.04 1.00 1.02 2.42 4.14 3.13 3.22
11.5 11.0 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 -1.5

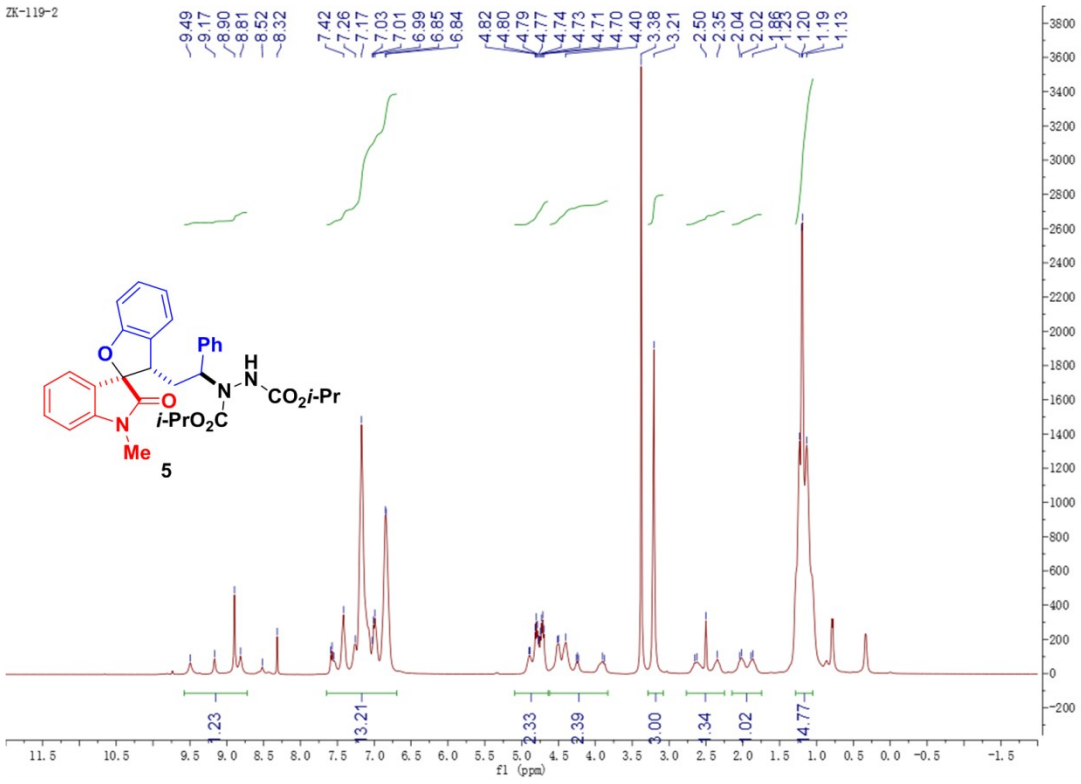

ZK-145
172.43 171.63 153.21 148.03 143.06 142.33 130.46 129.41 123.65 123.10 119.53 108.63 104.27 101.37 93.67 88.35 77.32 77.00 76.68 60.65 46.69 40.05 35.65 29.02 26.87 22.28 14.02 13.88
O
O
O
O
OEt
N
n-Pent
3ze
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

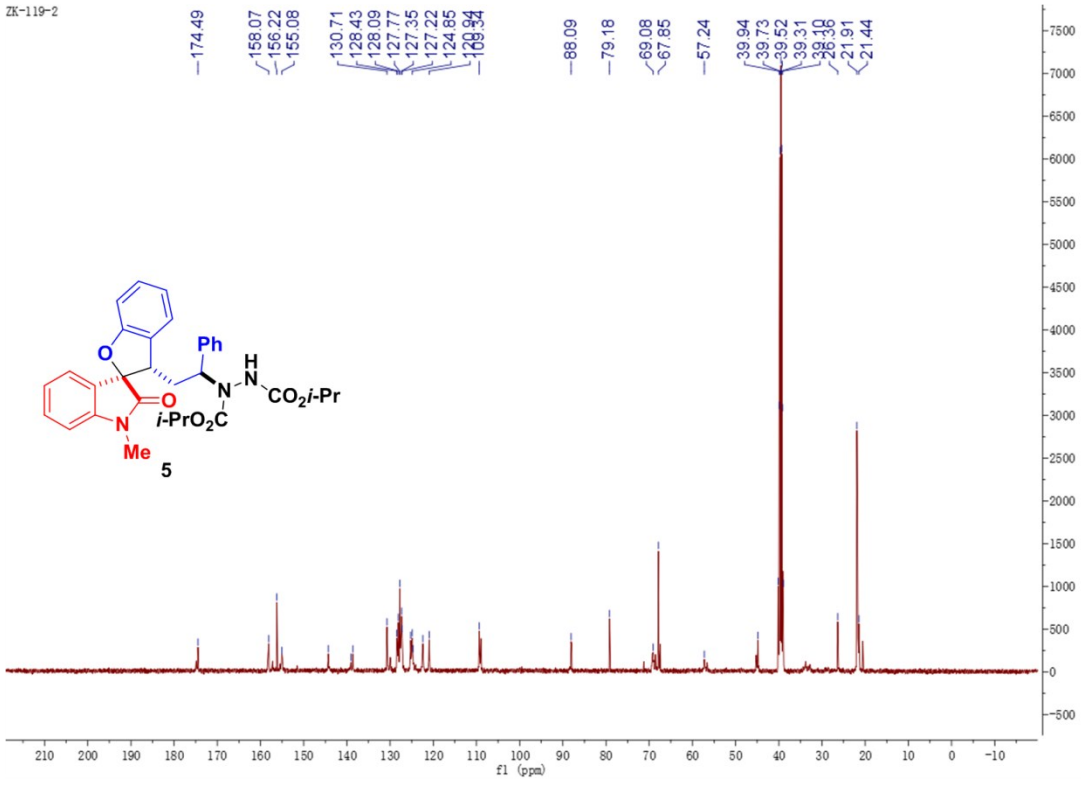

ZK-146
7.32
7.30
7.28
7.26
7.17
7.15
6.98
6.96
6.94
6.82
6.80
6.61
6.42
5.91
5.88
4.29
4.28
4.27
3.86
3.84
3.83
3.81
3.69
3.67
3.65
2.72
2.70
2.55
2.53
1.70
1.68
1.39
1.37
1.36
1.36
1.04
1.02
1.00
0.91
0.89
0.88
1.09
1.01
1.08
1.03
1.02
0.97
2.02
0.99
2.07
2.07
1.00
1.00
2.01
4.15
3.17
3.29
O
O
O
O
OEt
N
n-Pent
3ze'

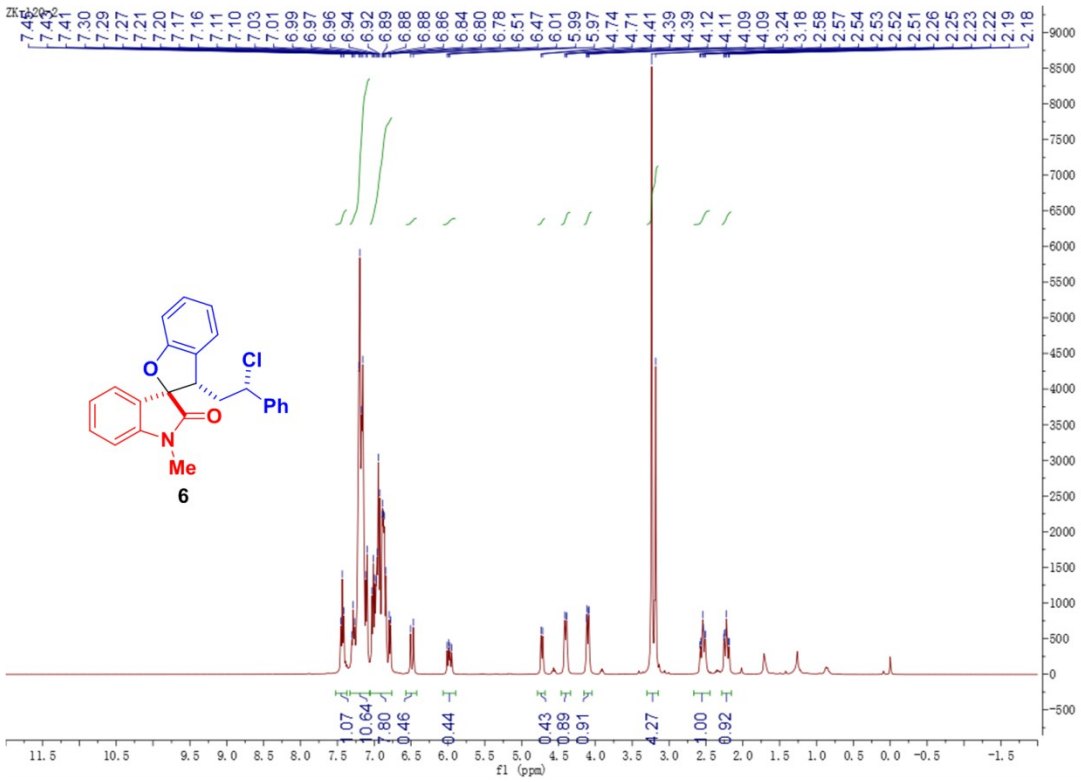

ZK-146
174.71
170.53
153.08
147.90
143.77
142.21
130.51
125.17
125.14
122.19
119.13
108.75
103.96
101.29
93.43
89.08
77.32
77.00
76.68
60.46
44.37
40.17
36.29
28.92
26.77
22.24
13.86
13.82
O
O
O
O
OEt
N
n-Pent
3ze'

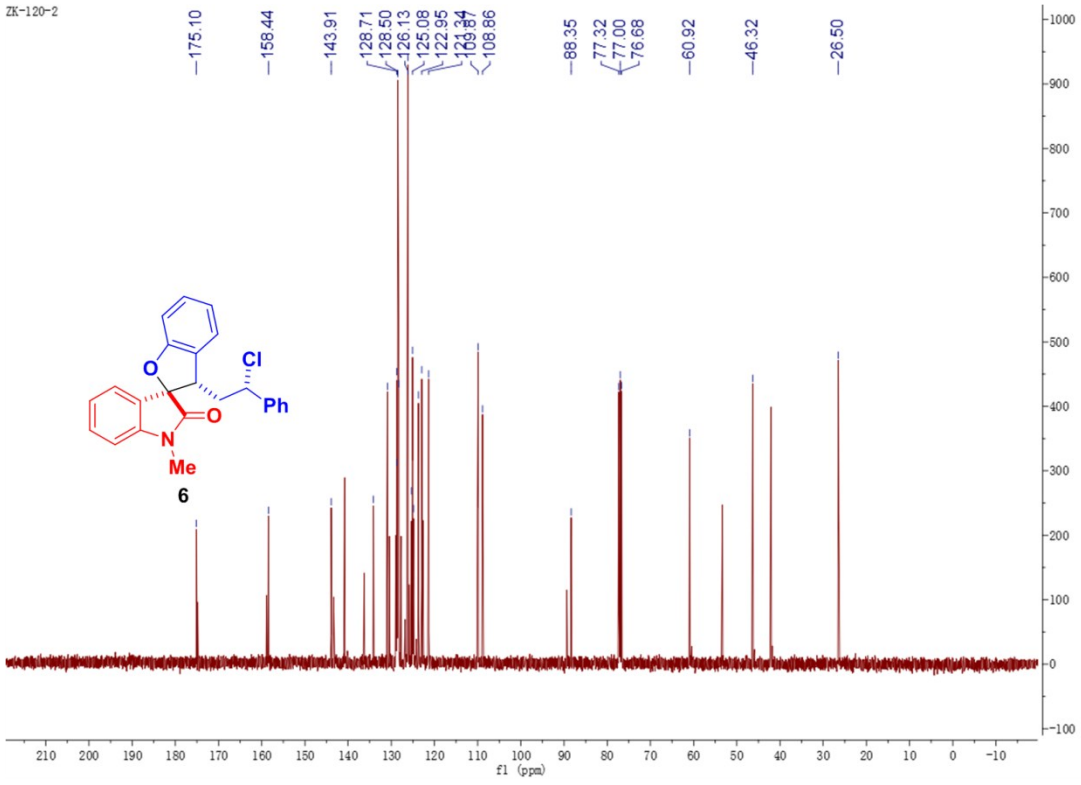

OH
Ph
O
O
N
Me
4
f1 (ppm)

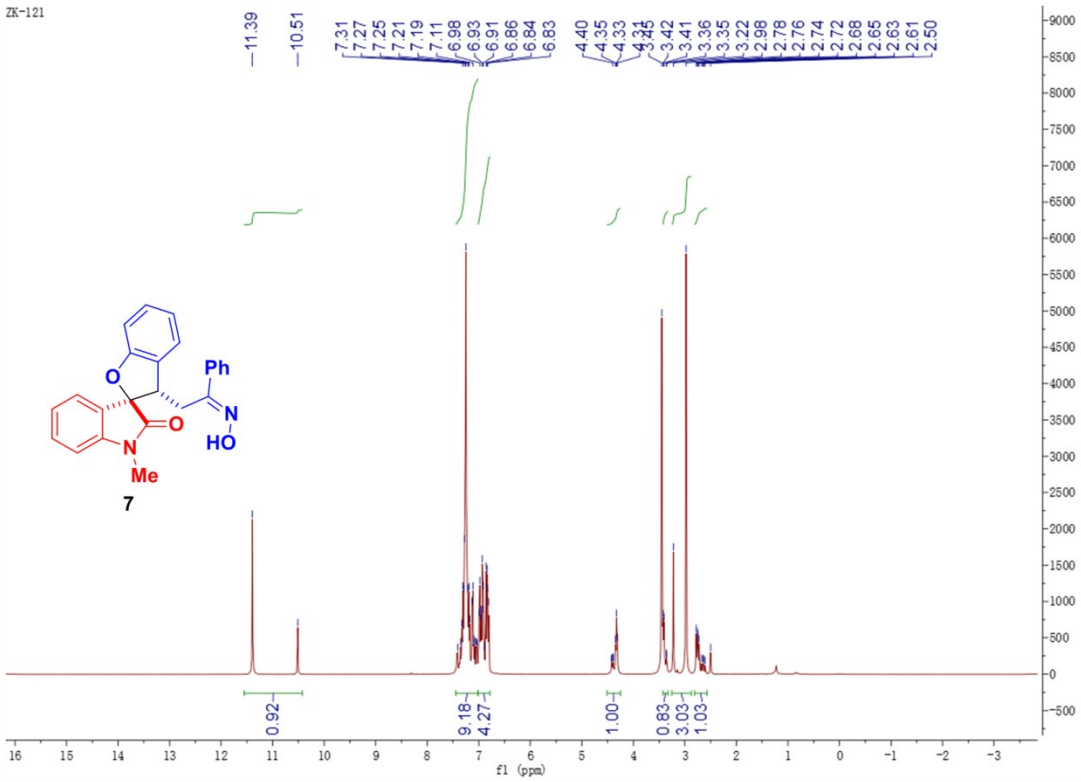

ZK-118
175.21
158.22
144.02
143.89
129.92
128.35
125.61
124.08
108.68
89.78
77.42
77.00
76.57
72.47
45.59
39.51
26.24
OH
Ph
O
O
N
Me
4
f1 (ppm)

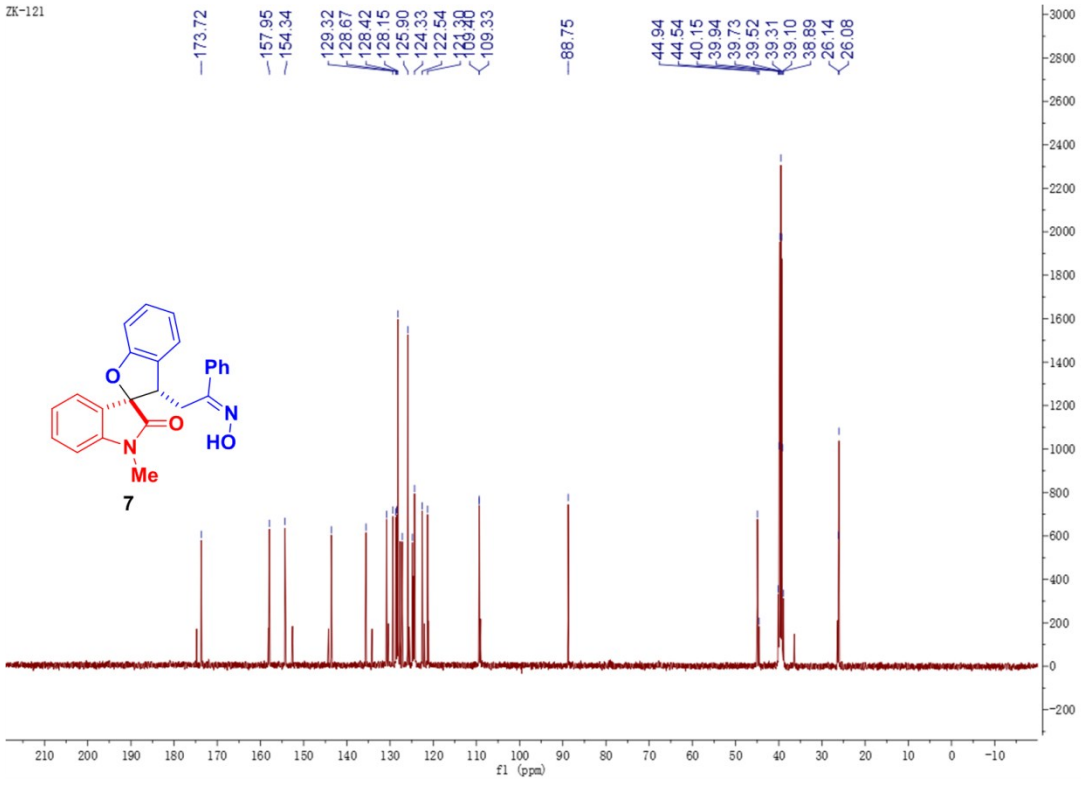

ZK-119-2
9.49
9.17
8.90
8.81
8.52
8.32
7.42
7.26
7.17
7.03
7.01
6.99
6.85
6.84
4.82
4.80
4.79
4.77
4.74
4.73
4.71
4.70
4.40
3.38
3.21
2.50
2.35
2.04
2.02
1.86
1.23
1.20
1.19
1.13
Ph
H
N
CO2i-Pr
O
N
i-PrO2C
Me
5
1.23
13.21
2.33
2.39
3.00
1.34
1.02
14.77
f1 (ppm)

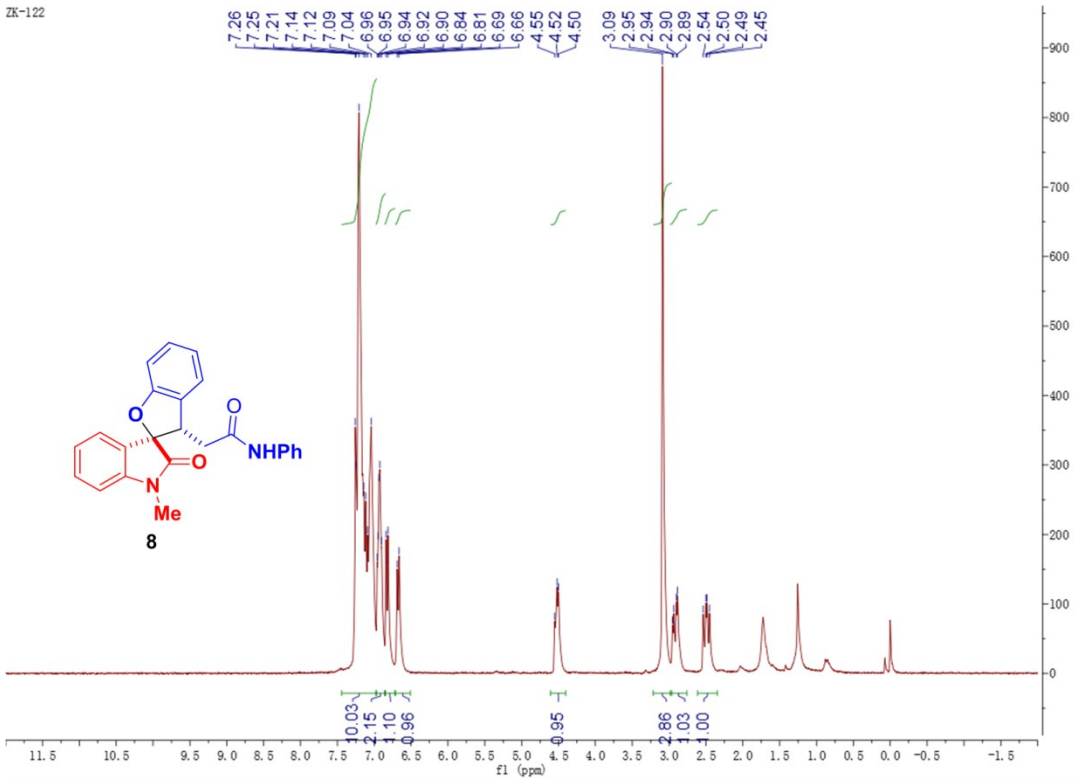

ZK-119-2
174.49
158.07
156.22
155.08
130.71
128.43
128.09
127.77
127.35
127.22
124.85
88.09
79.18
69.08
67.85
57.24
39.94
39.73
39.52
39.31
26.36
21.91
21.44
Ph
H
N
CO2i-Pr
O
N
i-PrO2C
Me
5
f1 (ppm)

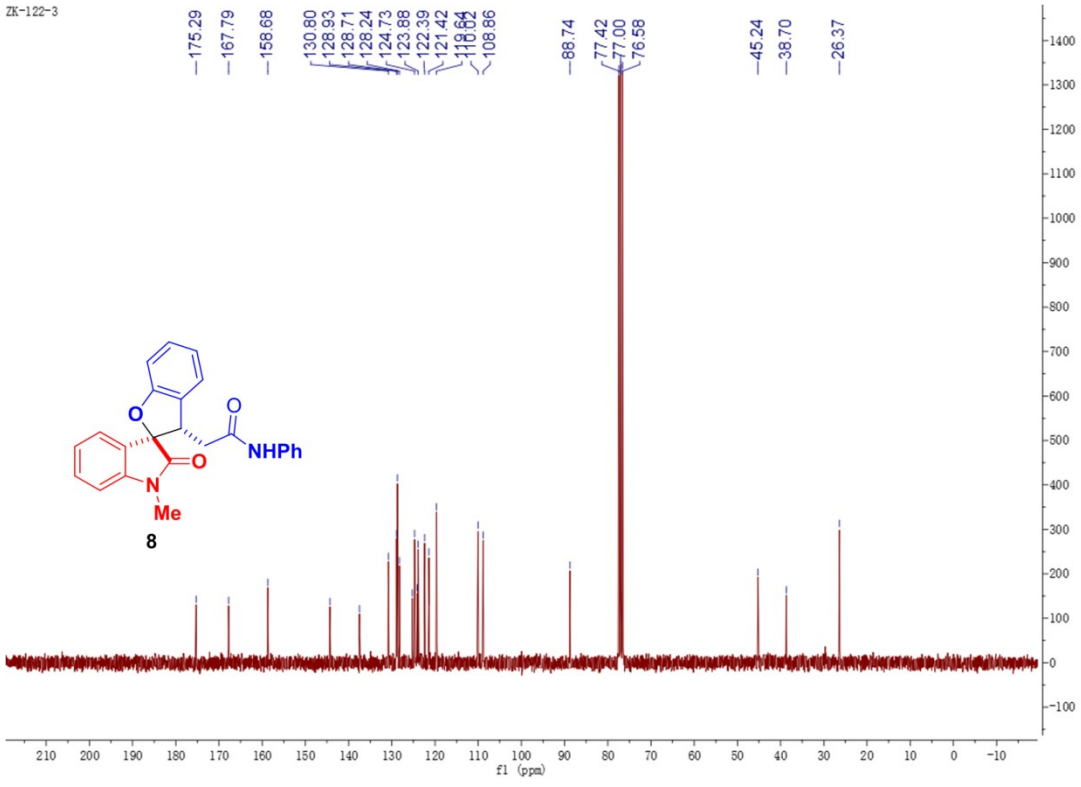

Cl
Ph
O
O
N
Me
6
f1 (ppm)

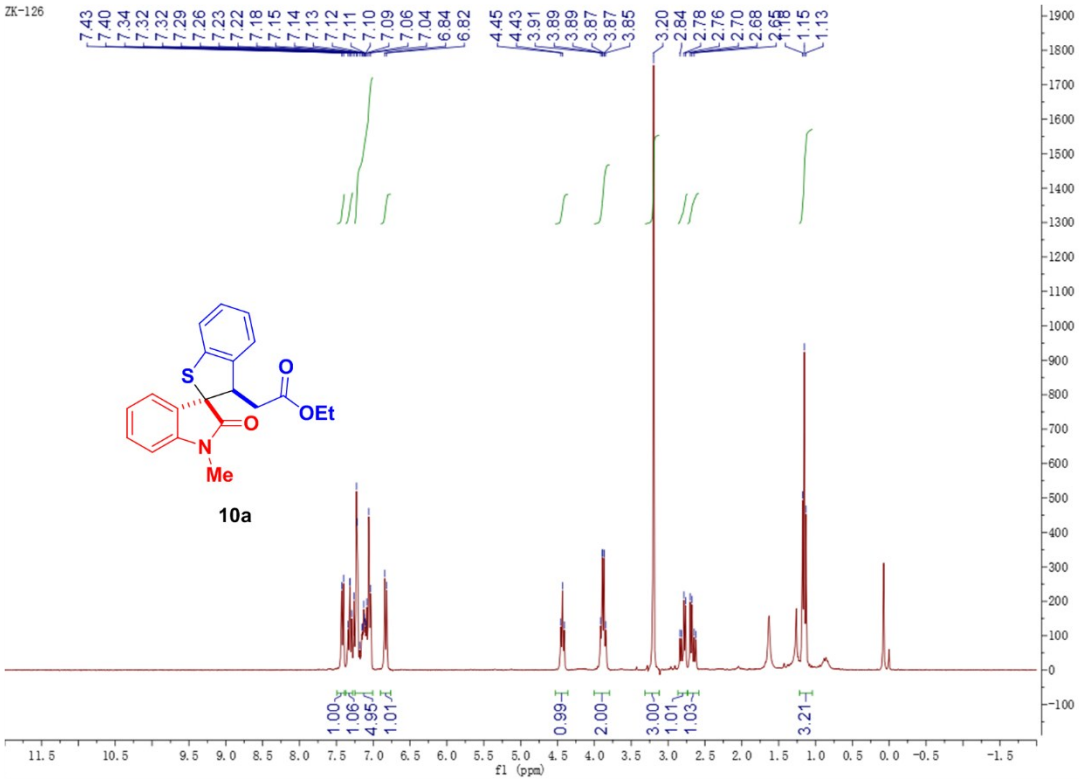

ZK-120-2
Cl
Ph
O
O
N
Me
6
f1 (ppm)

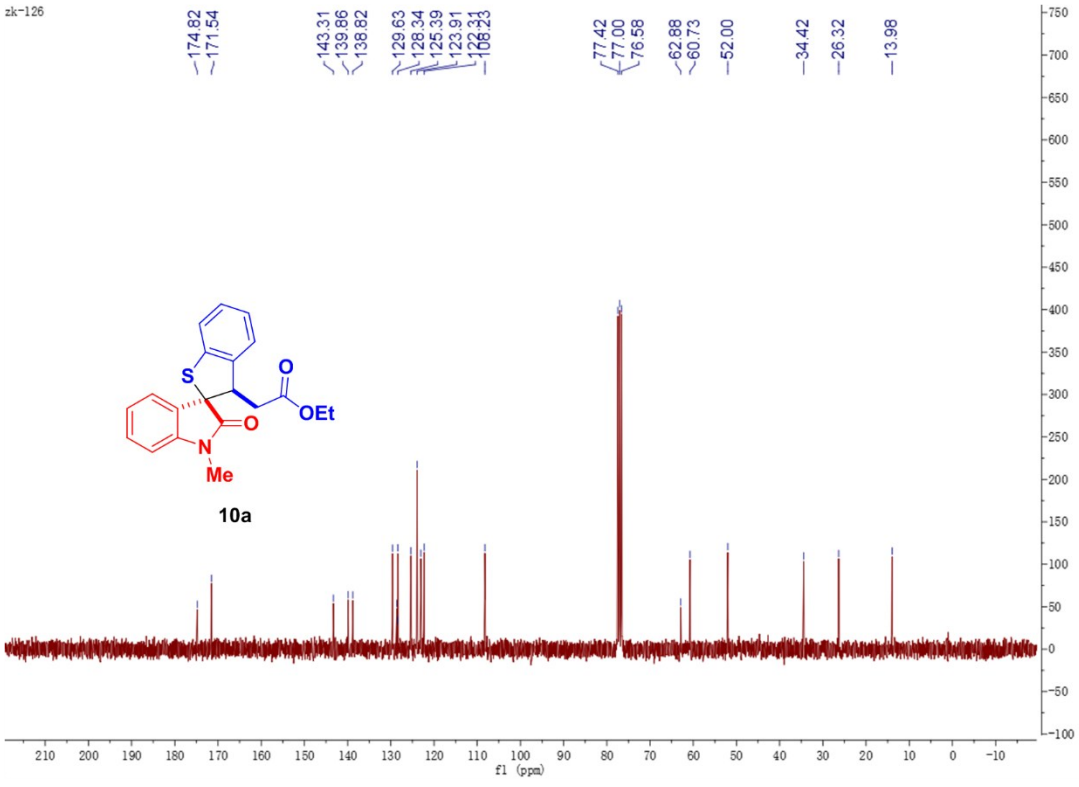

ZK-121
11.39
10.51
7.31
7.27
7.25
7.21
7.19
7.11
6.98
6.93
6.91
6.86
6.84
6.83
4.40
4.35
4.33
3.42
3.41
3.36
3.35
3.22
2.98
2.78
2.76
2.74
2.72
2.68
2.65
2.63
2.61
2.50
0.92
9.18
4.27
1.00
0.83
3.03
1.03
f1 (ppm)
Ph
N
HO
O
N
Me
7

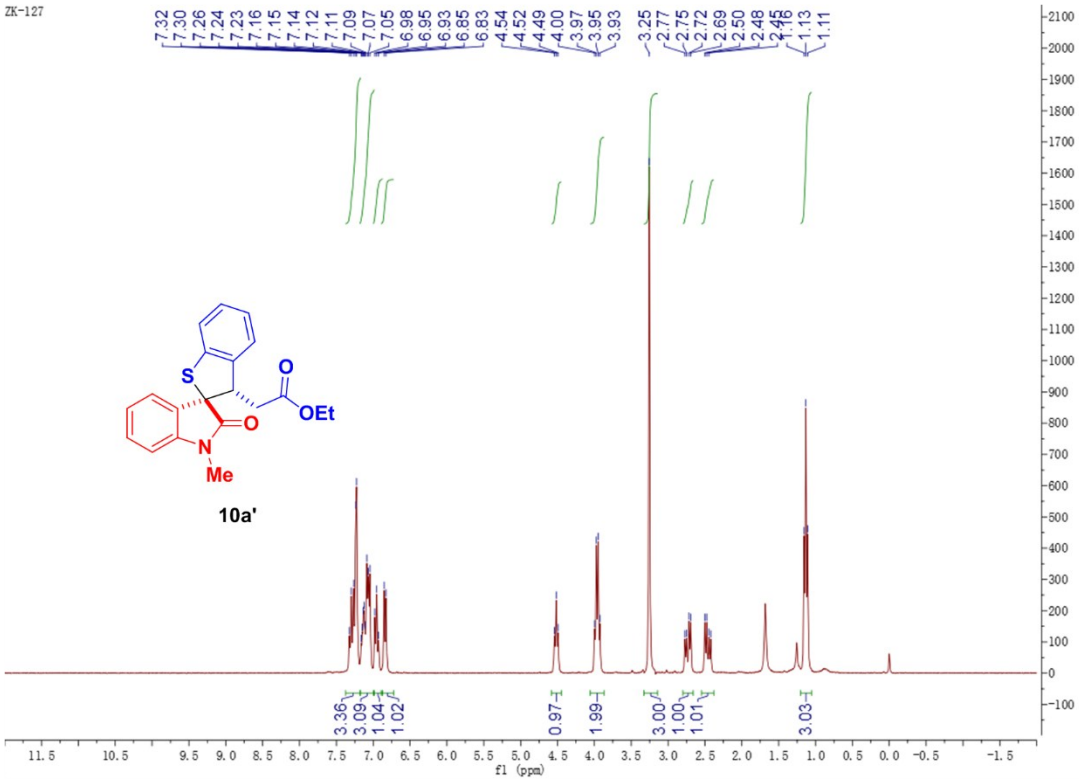

ZK-121
173.72
157.95
154.34
129.32
128.67
128.42
128.15
125.90
124.33
122.54
109.33
88.75
44.94
44.54
40.15
39.94
39.73
39.52
39.31
39.10
38.89
26.14
26.08
f1 (ppm)
Ph
N
HO
O
N
Me
7

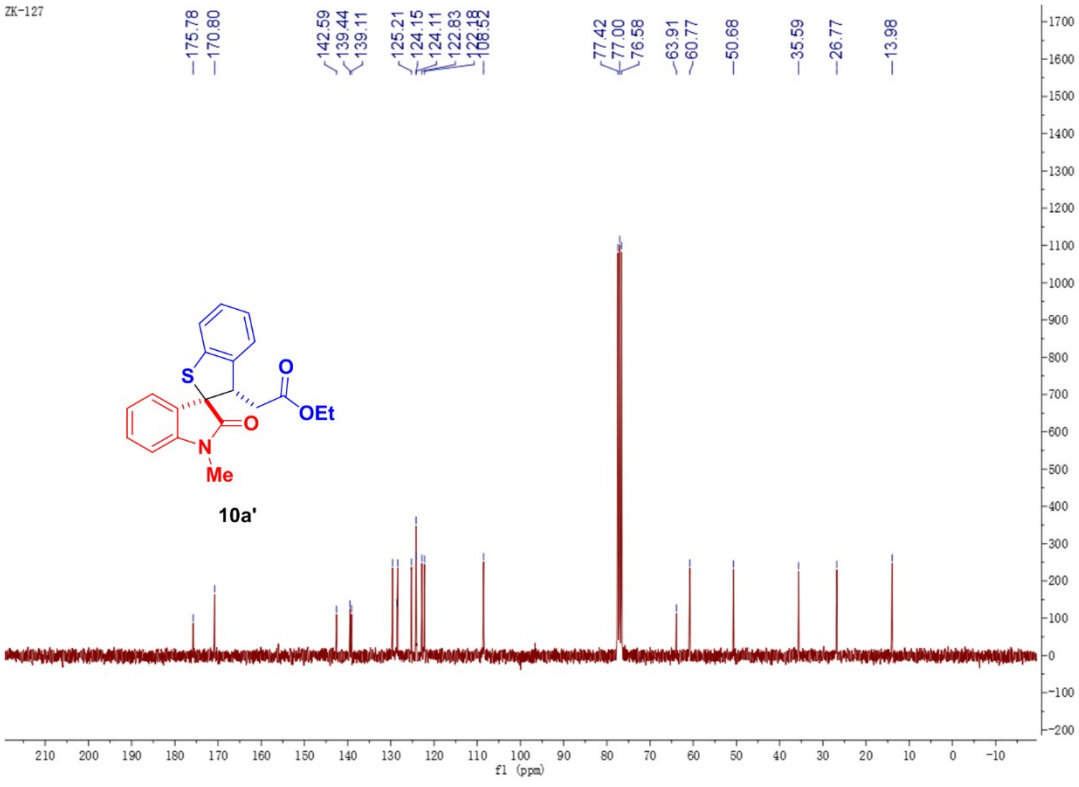

ZK-122
7.26
7.25
7.21
7.14
7.12
7.09
7.04
6.96
6.95
6.94
6.92
6.90
6.84
6.81
6.69
6.66
4.55
4.52
4.50
3.09
2.95
2.94
2.90
2.89
2.54
2.50
2.49
2.45
10.03
2.15
1.10
0.96
0.95
2.86
1.03
1.00
f1 (ppm)
O
NHPh
N
Me
8


ZK-122-3
175.29
167.79
158.68
130.80
128.93
128.71
128.24
124.73
123.88
122.39
121.42
88.74
77.42
77.00
76.58
45.24
38.70
26.37
f1 (ppm)
O
NHPh
N
Me
8


ZK-126
7.43
7.40
7.34
7.32
7.29
7.26
7.23
7.22
7.18
7.15
7.14
7.13
7.12
7.11
7.10
7.09
7.06
7.04
6.84
6.82
4.45
4.43
3.91
3.89
3.89
3.87
3.87
3.85
3.20
2.84
2.78
2.76
2.70
2.68
1.15
1.13
S
O
OEt
O
N
Me
10a
1.00
1.06
4.95
1.01
0.99
2.00
3.00
1.01
1.03
3.21
f1 (ppm)


zk-126
174.82
171.54
143.31
139.86
138.82
129.63
128.34
125.39
123.91
122.31
108.23
77.42
77.00
76.58
62.88
60.73
52.00
34.42
26.32
13.98
S
O
OEt
O
N
Me
10a
f1 (ppm)


ZK-127
7.32
7.30
7.26
7.24
7.23
7.16
7.15
7.14
7.12
7.11
7.09
7.07
7.05
6.98
6.95
6.93
6.85
6.83
4.54
4.52
4.49
4.00
3.97
3.95
3.93
3.25
2.77
2.75
2.72
2.69
2.50
2.48
1.13
1.11
S
O
OEt
O
N
Me
10a'
3.36
3.09
1.04
1.02
0.97
1.99
3.00
1.00
1.01
3.03
f1 (ppm)


ZK-127
175.78
170.80
142.59
139.44
139.11
125.21
124.15
124.11
122.83
122.18
108.52
77.42
77.00
76.58
63.91
60.77
50.68
35.59
26.77
13.98
S
O
OEt
O
N
Me
10a'
f1 (ppm)