Highly diastereoselective synthesis of cyclopropane-fused spiropseudoindoxyl derivatives through [2 + 1] annulation of 2-ylideneoxindoles and sulfonium bromides

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Supporting Information

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1. General Information

NMR data were obtained for 1H at 400 MHz and 600 MHz, and for 13C at 100 MHz and 150 MHz. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance in $CDCl_3$ solution as the internal standard. Mass spectra were recorded using ESI as the ionization method. ESI-HRMS spectra were meacsured with a QTOF instrument. UV detection was performed at 254 nm. Column chromatography was performed on silica gel (200-300 mesh) using an eluent of ethyl acetate and petroleum ether. TLC was performed on glass-backed silica plates; products were visualized using UV light. All reagents and solvents were obtained from commercial sources and used without further purification. 2-Ylideneoxindole **1**[1-2] and sulfonium bromide **2**[3] were prepared according to the literature procedures.

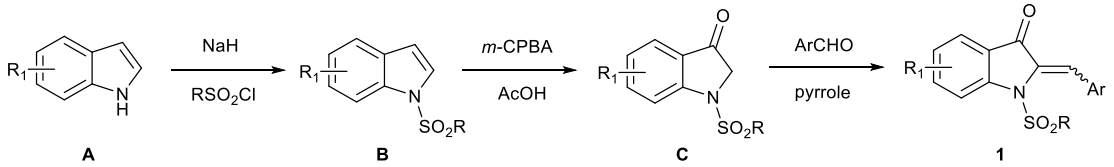
Reference:

[1] T. Noguchi-yachide, M. Tetsuhashi, H. Aoyama and Y. Hashimoto, *Chem. Pharm. Bull.*, 2009, **57**, 536-540.

[2] S. C. Conway and G. W. Gribble, *Heterocycles*, 1990, **30**, 627-633.

[3] S. K. Chittimalla and C. Bandi, *RSC Adv.*, 2013, **3**, 13663-13667.

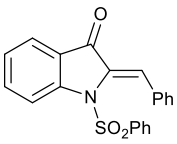
2. General Procedure for the Synthesis of (*Z*)-2-ylideneoxindoles 1



Sodium hydride (1.5 equiv) was added to indole **A** (1.0 equive) in THF while cooing with an ice bath and the mixture was stirred for 0.5 h at this temperature. Then benzenesulfonyl chloride or methanesulfonyl chloride (1.35 equiv) was added and the mixture was stirred at RT. After indole **A** was consumed (monitored by TLC), the reaction mixture was combined with water and extracted three times with EtOAc. The combined organic phase was dried on sodium sulphate and evaporated down. the residue was purified by flash chromatography (PE:EtOAc = 35:1) on silica gel to give sulfonyl-protected intermediate **B**.[1]

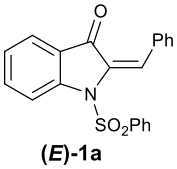
The protected indole **B** (1.0 equiv) and *m*-CPBA (1.05 equiv) were dissolved in glacial acetic acid, and the solution was refluxed for 2.5 h at 125 °C. After cooling, the bulk of the solvent was removed by vacuum distillation, then methylene dichloride and water were added. The resulting suspension was treated with solid sodium bicarbonate until gas evolution ceased. The mixture was extracted three times with methylene dichloride. The combined organic phase was dried on sodium sulphate and evaporated down. The residue was purified by flash chromatography (PE:EtOAc = 17:1 to 15:1) on silica gel to give sulfonyl-protected-indolin-3-one **C**.[2]

The indolin-3-one **C** (1.0 mmol, 1 equiv) and aromatic aldehyde (1.2 mmol, 1.2 equiv) were stirred at 60 °C with pyrrole (0.4 mmol, 0.4 equiv) in toluene. After compound **C** was consumed (monitored by TLC), the reaction mixture was purified by flash chromatography (PE:EtOAc = 18:1) on silica gel to give the corresponding compound **1**, which was further analyzed by ^{1}H-NMR, ^{13}C-HMR, and HRMS. The major isomer with *Z* configuration and minor isomer with *E* configuration were obtained respectively.



(*Z*)-1a

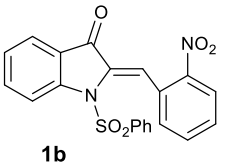
(*Z*)-2-benzylidene-1-(phenylsulfonyl)indolin-3-one ((*Z*)-1a). Yellow oil, 243.3 mg, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 8.4 Hz, 1H), 7.92 (s, 1H), 7.80-7.77 (m, 2H), 7.61-7.57 (m, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.49-7.47 (m, 2H), 7.45-7.42 (m, 1H), 7.35-7.33 (m, 3H), 7.28-7.24 (m, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 4.0 Hz, 1H) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.9, 148.4, 136.0, 136.0, 134.1, 133.5, 133.2, 132.2, 131.4, 130.6, 129.1, 128.1, 127.4, 126.6, 125.7, 124.3, 118.9 ppm. HRMS (ESI): *m/z* calculated for $C_{21}H_{15}NO_3S^{+}Na$: 384.0665, found: 384.0667.



(*E*)-1a

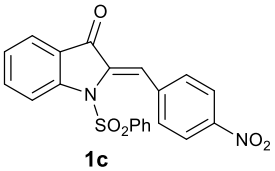
(*E*)-2-benzylidene-1-(phenylsulfonyl)indolin-3-one ((*E*)-1a). Yellow solid, 50.1 mg, 14% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 8.0 Hz, 1H), 7.96-7.94 (m, 2H), 7.64-7.60 (m, 1H),

7.49 (d, *J* = 7.2 Hz, 1H), 7.42-7.33 (m, 5H), 7.28-7.26 (m, 2H), 7.23-7.14 (m, 3H), ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.3, 150.6, 135.7, 134.0, 133.8, 133.8, 133.2, 132.6, 130.7, 129.6, 128.7, 128.3, 128.0, 127.6, 126.9, 124.3, 121.1 ppm. HRMS (ESI): *m/z* calculated for $C_{21}H_{15}NO_3S^+Na$: 384.0665, found: 384.0674.



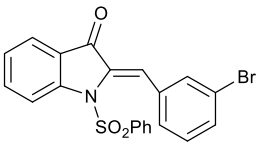
1b

(*Z*)-2-(2-nitrobenzylidene)-1-(phenylsulfonyl)indolin-3-one (1b). Yellow solid, 296.4 mg, 73% yield. ^{1}H NMR (600 MHz, DMSO-d6): δ = 8.18 (d, *J* = 8.4 Hz, 1H), 8.13 (s, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.83-7.80 (m, 3H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 7..8 Hz, 2H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 7.8 Hz, 1H) ppm.^{13}C NMR (150 MHz, DMSO-d6): δ = 182.9, 148.2, 147.6, 138.1, 135.8, 135.6, 134.2, 132.9, 132.8, 130.6, 130.3, 129.4, 127.7, 126.6, 126.2, 125.0, 124.9, 117.9 ppm. HRMS (ESI): *m/z* calculated for $C_{21}H_{14}N_2O_5S^+Na$: 429.0516, found: 429.0518.



1c

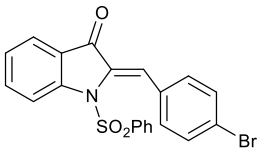
(*Z*)-2-(4-nitrobenzylidene)-1-(phenylsulfonyl)indolin-3-one (1c). Yellow solid, 285.2 mg, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25-8.23 (m, 2H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.97 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.74-7.70 (m, 1H), 7.65-7.61 (m, 3H), 7.61-7.57 (m, 1H), 7.43-7.39 (m, 2H), 7.31-7.27 (m, 1H) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.9, 148.7, 148.1, 138.8, 136.9, 136.1, 135.2, 134.5, 131.5, 129.3, 128.0, 127.3, 126.0, 125.6, 124.7, 123.3, 118.4 ppm. HRMS (ESI): *m/z* calculated for $C_{21}H_{14}N_2O_5S^+Na$: 429.0516, found: 429.0519.



1d

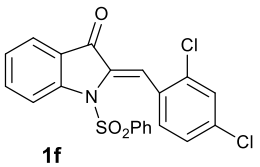
(*Z*)-2-(3-bromobenzylidene)-1-(phenylsulfonyl)indolin-3-one (1d). Yellow solid, 299.5 mg, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 8.4 Hz, 1H), 8.05-8.03 (m, 1H), 7.90 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.71-7.67 (m, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.59-7.56 (m, 2H), 7.56-7.53 (m, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.30-7.28 (m, 1H), 7.27-7.25 (m, 1H) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ =

182.9, 148.5, 136.3, 136.0, 134.2, 134.2, 133.7, 133.2, 130.5, 129.7, 129.6, 129.2, 127.3, 126.2, 125.8, 124.5, 122.1, 118.7 ppm. HRMS (ESI): *m/z* calculated for $C_{21}H_{14}BrNO_3S^+Na$: 461.9770, found: 461.9778.



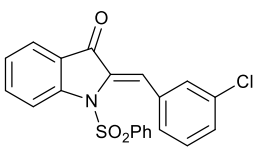
1e

(*Z*)-2-(4-bromobenzylidene)-1-(phenylsulfonyl)indolin-3-one (1e). Yellow solid, 315.9 mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 8.4 Hz, 1H), 7.90 (s, 1H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.71-7.66 (m, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.57-7.51 (m, 5H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.27 (t, *J* = 7.2 Hz, 1H) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ = 183.0, 148.4, 136.2, 136.0, 134.2, 133.8, 132.8, 131.4, 131.4, 131.1, 129.1, 127.4, 126.4, 125.8, 125.1, 124.4, 118.8 ppm. HRMS (ESI): *m/z* calculated for $C_{21}H_{14}BrNO_3S^+Na$: 461.9770, found: 461.9777.



1f

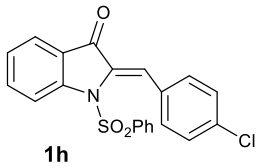
(*Z*)-2-(2,4-dichlorobenzylidene)-1-(phenylsulfonyl)indolin-3-one (1f). Yellow solid, 303.3 mg, 70% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 8.4 Hz, 1H), 7.97 (s, 1H), 7.72-7.69 (m, 3H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.59-7.56 (m, 2H), 7.45 (d, *J* = 1.8 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.27 (t, *J* = 7.8 Hz, 1H)7.24 (dd, *J* = 8.4, 2.4 Hz, 1H) ppm.^{13}C NMR (150 MHz, $CDCl_3$): δ = 183.0, 148.7, 136.8, 136.3, 136.1, 135.2, 134.4, 134.1, 132.7, 129.6, 129.3, 129.3, 127.5, 126.6, 125.8, 125.7, 124.7, 118.2 ppm. HRMS (ESI): *m/z* calculated for $C_{21}H_{13}Cl_2NO_3S^+Na$: 451.9885, found: 451.9890.



1g

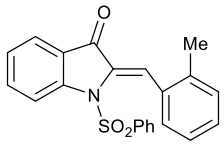
(*Z*)-2-(3-chlorobenzylidene)-1-(phenylsulfonyl)indolin-3-one (1g). Yellow solid, 276.5 mg, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 8.4 Hz, 1H), 7.91 (s, 1H), 7.89 (t, *J* = 1.6 Hz, 1H), 7.71-7.67 (m, 2H), 7.63 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.58 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.57-7.52 (m, 1H), 7.41-7.32 (m, 4H), 7.29-7.25 (m, 1H), ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.9, 148.5, 136.3, 136.0, 134.2, 134.1, 133.9, 130.8, 130.6, 130.3, 129.3, 129.2, 127.3, 125.8, 124.5, 118.7 ppm.

HRMS (ESI): *m/z* calculated for $C_{21}H_{14}ClNO_3S^+Na$: 418.0275, found: 418.0278.



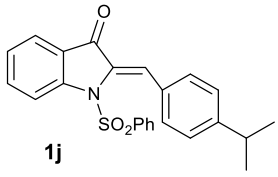
1h

(*Z*)-2-(4-chlorobenzylidene)-1-(phenylsulfonyl)indolin-3-one (1h). Yellow solid, 266.7 mg, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 8.4 Hz, 1H), 7.93 (s, 1H), 7.84 (d, *J* = 8.8 Hz, 2H), 7.70-7.66 (m, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.57-7.51 (m, 3H), 7.39-7.33 (m, 4H), 7.27 (t, *J* = 7.6 Hz, 1H) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ = 183.0, 148.4, 136.6, 136.2, 136.0, 134.2, 133.8, 132.7, 131.5, 130.7, 129.1, 128.4, 127.4, 126.4, 125.8, 124.4, 118.8 ppm. HRMS (ESI): *m/z* calculated for $C_{21}H_{14}ClNO_3S^+Na$: 418.0275, found: 418.0278.



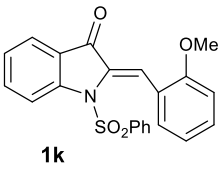
1i

(*Z*)-2-(2-methylbenzylidene)-1-(phenylsulfonyl)indolin-3-one (1i). Yellow solid, 243.8 mg, 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 8.4 Hz, 1H), 8.06 (s, 1H), 7.71-7.66 (m, 1H), 7.64 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.61-7.59 (m, 1H), 7.58-7.54 (m, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.41-7.31 (m, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.27-7.23 (m, 2H), 7.19 (t, *J* = 7.6 Hz, 1H), 2.34 (s, 3H) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.9, 148.5, 137.7, 136.2, 136.2, 134.2, 133.3, 131.5, 130.6, 130.4, 130.1, 130.0, 129.1, 127.4, 126.4, 125.6, 125.3, 124.4, 118.5, 20.3 ppm. HRMS (ESI): *m/z* calculated for $C_{22}H_{17}NO_3S^+Na$: 398.0821, found: 398.0826.



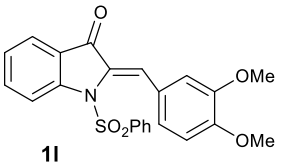
1j

(*Z*)-2-(4-isopropylbenzylidene)-1-(phenylsulfonyl)indolin-3-one (1j). Yellow solid, 288.2 mg, 71% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 8.4 Hz, 1H), 8.00 (s, 1H), 7.90 (d, *J* = 7.8 Hz, 2H), 7.67-7.65 (m, 1H), 7.62 (d, *J* = 7.2 Hz, 1H), 7.55-7.54 (m, 2H), 7.52-7.50 (m, 1H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.27 (t, *J* = .8 Hz, 1H), 2.97 (dq, *J* = 21.0, 7.2 Hz, 1H), 1.29 (s, 3H), 1.28 (s, 3H) ppm.^{13}C NMR (150 MHz, $CDCl_3$): δ = 182.9, 152.5, 148.3, 135.9, 135.9, 134.1, 134.0, 133.1, 132.0, 129.9, 129.1, 127.5, 126.9, 126.4, 125.8, 124.3, 119.1, 34.4, 23.8 ppm. HRMS (ESI): *m/z* calculated for $C_{24}H_{21}NO_3S^+Na$: 426.1134, found: 426.1137.



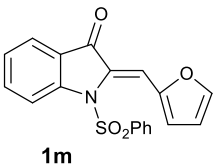
1k

(*Z*)-2-(2-methoxybenzylidene)-1-(phenylsulfonyl)indolin-3-one (1k). Yellow solid, 279.1 mg, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.22 (s, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.81 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.68-7.59 (m, 4H), 7.54-7.50 (m, 1H), 7.43-7.38 (m, 1H), 7.37-7.33 (m, 2H), 7.26-7.22 (m, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 3.89 (s, 3H) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.8, 158.3, 148.3, 136.1, 135.8, 133.9, 133.0, 132.3, 132.0, 128.9, 128.5, 127.5, 126.7, 125.5, 124.2, 121.2, 119.7, 118.7, 110.3, 55.6 ppm. HRMS (ESI): *m/z* calculated for $C_{22}H_{17}NO_4S^+Na$: 414.0770, found: 414.0772.



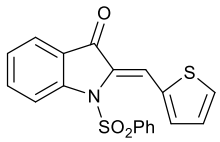
1l

(*Z*)-2-(3,4-dimethoxybenzylidene)-1-(phenylsulfonyl)indolin-3-one (1l). Yellow solid, 291.1 mg, 69% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 1.8 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.97 (s, 1H), 7.67-7.64 (m, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.54 (dd, *J* = 8.4, 1,8 Hz, 1H), 7.51-7.47 (m, 3H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.27-7.25 (m, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 3.98 (s, 3H), 3.95 (s, 3H) ppm.^{13}C NMR (150 MHz, $CDCl_3$): δ = 183.2, 152.0, 148.4, 148.1, 135.8, 135.7, 135.1, 134.0, 132.1, 129.0, 127.8, 127.5, 127.3, 125.8, 125.7, 124.2, 119.3, 114.3, 110.5, 56.1, 56.1 ppm. HRMS (ESI): *m/z* calculated for $C_{23}H_{19}NO_5S^+Na$: 444.0876, found: 444.0890.



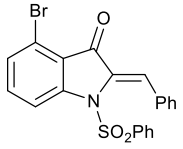
1m

(*Z*)-2-(furan-2-ylmethylene)-1-(phenylsulfonyl)indolin-3-one (1m). Yellow solid, 255.6 mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (d, *J* = 3.6 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 8.02 (s, 1H), 7.71-7.64 (m, 3H), 7.61-7.58 (m, 2H), 7.50-7.47 (m, 1H), 7.34-7.30 (m, 2H), 7.29-7.25 (m, 1H), 6.62-6.61 (m, 1H) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.5, 149.8, 147.8, 146.3, 136.1, 135.6, 134.0, 130.3, 129.1, 127.3, 126.3, 125.5, 124.0, 119.5, 118.3, 118.0, 113.5 ppm. HRMS (ESI): *m/z* calculated for $C_{19}H_{13}NO_4S^+Na$: 374.0457, found: 374.0459.



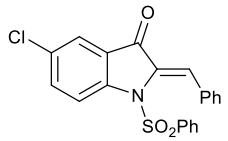
1n

(*Z*)-1-(phenylsulfonyl)-2-(thiophen-2-ylmethylene)indolin-3-one (1n). Yellow solid, 267.8 mg, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (s, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 3.6 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.69-7.66 (m, 1H), 7.65-7.64 (m, 1H), 7.56 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.50-7.45 (m, 1H), 7.32-7.26 (m, 3H), 7.21 (dd, *J* = 5.2, 4.0 Hz, 1H) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.9, 147.9, 138.7, 136.2, 135.9, 135.6, 134.0, 133.8, 130.0, 129.1, 127.6, 127.3, 126.4, 125.6, 124.8, 124.1, 118.6 ppm. HRMS (ESI): *m/z* calculated for $C_{19}H_{13}NO_3S_2^+Na$: 390.0229, found: 290.0236.



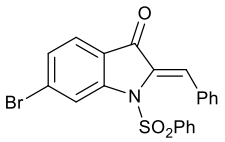
1o

(*Z*)-2-benzylidene-4-bromo-1-(phenylsulfonyl)indolin-3-one (1o). Yellow solid, 283.4 mg, 64% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 8.4 Hz, 1H), 8.03 (s, 1H), 7.88-7.87 (m, 2H), 7.58-7.55 (m, 3H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.45-7.40 (m, 4H), 7.38 (t, *J* = 7.8 Hz, 2H) ppm.^{13}C NMR (150 MHz, $CDCl_3$): δ = 180.7, 150.1, 136.1, 135.8, 134.5, 134.0, 133.1, 132.0, 131.6, 131.0, 130.8, 129.3, 128.3, 127.5, 123.9, 120.1, 117.9 ppm. HRMS (ESI): *m/z* calculated for $C_{21}H_{14}BrNO_3S^+Na$: 461.9770, found: 461.9773.



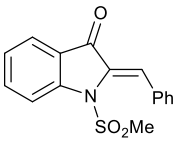
1p

(*Z*)-2-benzylidene-5-chloro-1-(phenylsulfonyl)indolin-3-one (1p). Yellow solid, 265.5 mg, 67% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 8.4 Hz, 1H), 8.03 (s, 1H), 7.88-7.87 (m, 2H), 7.63 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.57-7.55 (m, 4H), 7.46-7.44 (m, 3H), 7.40-7.37 (m, 2H) ppm.^{13}C NMR (150 MHz, $CDCl_3$): δ = 181.7, 146.7, 136.0, 135.7, 134.3, 134.3, 133.4, 132.0, 131.9, 131.6, 131.1, 130.3, 129.3, 128.3, 127.5, 124.0, 120.3 ppm. HRMS (ESI): *m/z* calculated for $C_{21}H_{14}ClNO_3S^+Na$: 418.0275, found: 418.0279.



1q

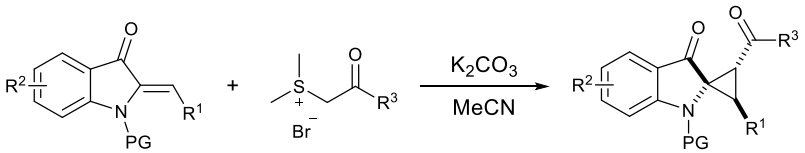
(*Z*)-2-benzylidene-6-bromo-1-(phenylsulfonyl)indolin-3-one (1q). Yellow solid, 269.9 mg, 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.38 (d, *J* = 1.2 Hz, 1H), 8.02 (s, 1H), 7.86-7.85 (m, 2H), 7.62-7.58 (m, 2H), 7.58-7.55 (m, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.47-7.44 (m, 2H), 7.42 (d, *J* = 1.6 Hz, 1H), 7.41 (d, *J* = 1.6 Hz, 1H), 7.40-7.38 (m, 2H) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ = 181.7, 148.9, 135.9, 134.4, 133.6, 133.2, 132.0, 131.4, 131.0, 130.9, 129.3, 128.2, 127.4, 125.3, 125.3, 121.9 ppm. HRMS (ESI): *m/z* calculated for $C_{21}H_{14}BrNO_3S^+Na$: 461.9770, found: 461.9776.



1r

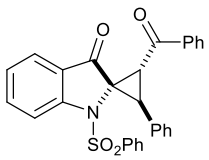
(*Z*)-2-benzylidene-1-(methylsulfonyl)indolin-3-one (1r). Yellow solid, 201.6 mg, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00-7.97 (m, 3H), 7.89 (s, 1H), 7.82 (dd, *J* = 7.6 Hz, 1H), 7.69-7.65 (m, 1H), 7.44-7.43 (m, 3H), 7.33 (t, *J* = 7.2 Hz, 1H), 2.92 (s, 3H) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.7, 148.1, 136.4, 133.3, 132.4, 132.2, 132.2, 131.5, 130.7, 128.2, 125.6, 124.7, 117.7, 36.5 ppm. HRMS (ESI): *m/z* calculated for $C_{16}H_{13}NO_3S^+Na$: 322.0508, found: 322.0509.

3. General Procedure for the Synthesis of Cyclopropane-fused Spiro-pseudo-indoxyl Derivatives 3



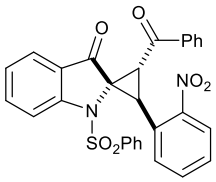
1 2 3

A mixture of (*Z*)-2-ylideneoxindole **1** (0.1 mmol), sulfonium bromide **2** (0.15 mmol), K_2CO_3 (0.15 mmol) and MeCN (1.0 mL) was stirred at room temperature without exclusion of air. Upon the consumption of (*Z*)-2-ylideneoxindole **1** (monitored by TLC), the reaction mixture was concentrated and the residue was purified by flash chromatography on silica gel to give compound **3** which was dried under vacuum and further analyzed by ^{1}H-NMR, ^{13}C-HMR, IR, and HRMS.



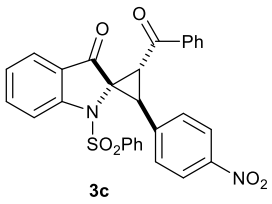
3a

2-benzoyl-3-phenyl-1'-(phenylsulfonyl)spiro[cyclopropane-1,2'-indolin]-3'-one (**3a**). The residue was purified by a silica gel flash chromatography (PE:EtOAc = 12:1 to PE:EtOAc = 3:1) giving the product **3a** as a white solid in 88% yield (42 mg, >20:1 dr), m.p. 194-196 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 8.0 Hz, 1H), 7.76 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.70-7.65 (m, 2H), 7.61-7.56 (m, 3H), 7.52-7.47 (m, 1H), 7.40-7.30 (m, 5H), 7.25-7.20 (m, 3H), 6.79 (dd, *J* = 6.8, 1.2 Hz, 2H), 5.23 (d, *J* = 8.4 Hz, 1H), 3.44 (d, *J* = 8.4 Hz, 1H) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.8, 190.5, 153.3, 137.0, 136.9, 136.3, 134.0, 133.5, 132.6, 129.5, 129.1, 128.7, 128.4, 128.0, 127.6, 127.5, 126.5, 126.1, 123.8, 120.7, 59.9, 43.4, 34.7 ppm. IR (CH_2Cl_2, cm^{-1}): 1707, 1680, 1599, 1473, 1457, 1447, 1367, 1158. HRMS (ESI): *m/z* calculated for $C_{29}H_{21}NO_4S^+Na$: 502.1083, found: 502.1088.



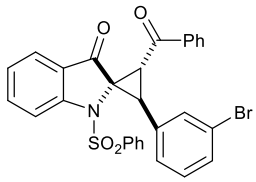
3b

2-benzoyl-3-(2-nitrophenyl)-1'-(phenylsulfonyl)spiro[cyclopropane-1,2'-indolin]-3'-one (**3b**). The residue was purified by a silica gel flash chromatography (PE:EtOAc = 12:1 to PE:EtOAc = 1:1) giving the product **3b** as a yellow solid in 74% yield (39 mg, >20:1 dr), m.p. 202-204 °C. ^{1}H NMR (400 MHz, $CDCl_3$) : δ = 8.04 (d, *J* = 8.4 Hz, 1H), 7.95 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.78-7.76 (m, 2H), 7.74-7.67 (m, 4H), 7.60-7.57 (m, 1H), 7.53-7.44 (m, 3H), 7.42-7.38 (m, 2H), 7.37-7.31 (m, 3H), 6.96 (d, *J* = 7.6 Hz, 1H), 5.07 (d, *J* = 8.4 Hz, 1H), 3.32 (d, *J* = 8.4 Hz, 1H) ppm.^{13}C NMR (100 MHz, $CDCl_3$) δ = 192.1, 190.1, 153.1, 148.8, 137.9, 136.8, 136.7, 134.1, 133.6, 133.0, 132.9, 129.4, 129.1, 128.8 128.7, 128.5, 127.7, 125.3, 124.9, 124.5, 124.1, 118.5, 61.3, 43.1, 31.9 ppm. IR (CH_2Cl_2, cm^{-1}): 1717, 1694, 1598, 1530, 1518, 1474, 1458, 1446, 1369, 1344, 1159. HRMS (ESI): *m/z* calculated for $C_{29}H_{20}N_2O_6S^+Na$: 547.0934, found: 547.0941.



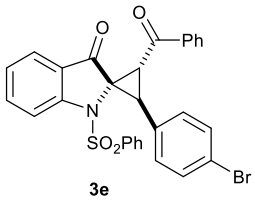
3c

2-benzoyl-3-(4-nitrophenyl)-1'-(phenylsulfonyl)spiro[cyclopropane-1,2'-indolin]-3'-one (**3c**). The residue was purified by a silica gel flash chromatography (PE:EtOAc = 12:1 to PE:EtOAc = 1:1) giving the product **3c** as a white solid in 72% yield (38 mg, >20:1 dr), m.p. 190-192 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08-8.05 (m, 3H), 7.75-7.71 (m, 4H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.56-7.50 (m, 3H), 7.41 (q, *J* = 7.6 Hz, 3H), 7.33 (t, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 5.21 (d, *J* = 8.4 Hz, 1H), 3.42 (d, *J* = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.6, 189.7, 153.5, 147.2, 140.4, 136.9, 136.8, 136.5, 134.3, 133.8, 130.0, 129.7, 128.8, 128.4, 127.5, 126.4, 126.1, 123.9, 123.2, 120.7, 59.4, 43.1, 33.5 ppm. IR (CH_2Cl_2, cm^{-1}): 1699, 1678, 1601, 1521, 1473, 1456, 1445, 1370, 1347, 1158. HRMS (ESI): *m/z* calculated for $C_{29}H_{20}N_2O_6S^+Na$: 547.0934, found: 547.0942.



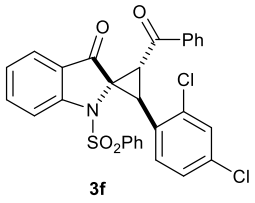
3d

2-benzoyl-3-(3-bromophenyl)-1'-(phenylsulfonyl)spiro[cyclopropane-1,2'-indolin]-3'-one (**3d**). The residue was purified by a silica gel flash chromatography (PE:EtOAc = 12:1 to PE:EtOAc = 3:1) giving the product **3d** as a white solid in 77% yield (43 mg, >20:1 dr), m.p. 206-208 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 8.4 Hz, 1H), 7.73-7.62 (m, 5H), 7.54 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.52-7.48 (m, 1H), 7.44-7.35 (m, 4H), 7.32 (t, *J* = 8.0 Hz, 2H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.81-6.79 (m, 1H), 6.64 (s, 1H), 5.13 (d, *J* = 8.4 Hz, 1H), 3.38 (d, *J* = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.5, 190.1, 153.5, 136.9, 136.7, 136.5, 134.9, 134.4, 133.7, 132.0, 130.6, 129.6, 129.6, 128.7, 128.4, 127.7, 127.5, 126.3, 126.3, 123.9, 122.0, 120.8, 59.5, 43.1, 33.7 ppm. IR (CH_2Cl_2, cm^{-1}): 1702, 1674, 1591, 1473, 1458, 1448, 1366, 1156. HRMS (ESI): *m/z* calculated for $C_{29}H_{20}BrNO_4S^+Na$: 580.0189, found: 580.0193.



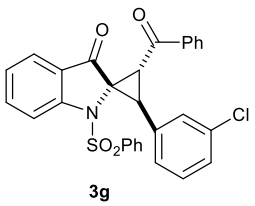
3e

2-benzoyl-3-(4-bromophenyl)-1'-(phenylsulfonyl)spiro[cyclopropane-1,2'-indolin]-3'-one (**3e**). The residue was purified by a silica gel flash chromatography (PE:EtOAc = 12:1 to PE:EtOAc = 3:1) giving the product **3e** as a white solid in 72% yield (40 mg, >20:1 dr), m.p. 186-188 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 8.0 Hz, 1H), 7.73-7.66 (m, 4H), 7.61-7.58 (m, 1H), 7.55-7.48 (m, 3H), 7.40-7.35 (m, 3H), 7.34-7.30 (m, 4H), 6.62 (d, *J* = 8.0 Hz, 2H), 5.12 (d, *J* = 8.0 Hz, 1H), 3.38 (d, *J* = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.7, 190.1, 153.4, 136.9, 136.7, 136.4, 134.0, 133.6, 131.7, 131.2, 130.7, 129.5, 128.7, 128.3, 127.5, 126.3, 126.2, 123.8, 121.5, 120.7, 59.6, 43.3, 33.8 ppm. IR (CH_2Cl_2, cm^{-1}): 1708, 1688, 1602, 1490, 1470, 1457, 1445, 1364, 1152. HRMS (ESI): *m/z* calculated for $C_{29}H_{20}BrNO_4S^+Na$: 580.0189, found: 580.0196.



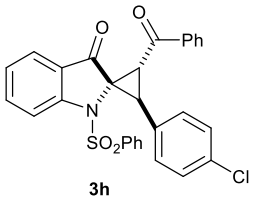
3f

2-benzoyl-3-(2,4-dichlorophenyl)-1'-(phenylsulfonyl)spiro[cyclopropane-1,2'-indolin]-3'-one (**3f**). The residue was purified by a silica gel flash chromatography (PE:EtOAc = 12:1 to PE:EtOAc = 3:1) giving the product **3f** as a white solid in 80% yield (44 mg, >20:1 dr), m.p. >220 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 8.4 Hz, 1H), 7.78-7.74 (m, 3H), 7.71 (td, *J* = 7.2, 1.2 Hz, 1H), 7.64 (dd, *J* = 8.0, 0.8 Hz, 2H), 7.60-7.56 (m, 1H), 7.53-7.49 (m, 1H), 7.40-7.33 (m, 5H), 7.29 (d, *J* = 2.0 Hz, 1H), 7.07 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.51 (dd, *J* = 8.4, 0.8 Hz, 1H), 4.88 (d, *J* = 8.4 Hz, 1H), 3.29 (d, *J* = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.9, 190.0, 153.2, 137.7, 136.7, 136.7, 135.4, 134.1, 134.1, 133.6, 132.4, 129.5, 129.5, 129.3, 128.7, 128.4, 127.7, 126.5, 125.7, 125.2, 124.0, 119.4, 60.4, 43.8, 32.1 ppm. IR (CH_2Cl_2, cm^{-1}): 1710, 1684, 1603, 1588, 1474, 1458, 1447, 1376, 1160. HRMS (ESI): *m/z* calculated for $C_{29}H_{19}Cl_2NO_4S^+Na$: 570.0304, found: 570.0312.



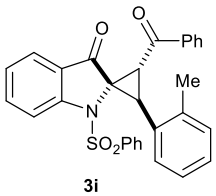
3g

2-benzoyl-3-(3-chlorophenyl)-1'-(phenylsulfonyl)spiro[cyclopropane-1,2'-indolin]-3'-one (**3g**). The residue was purified by a silica gel flash chromatography (PE:EtOAc = 12:1 to PE:EtOAc = 3:1) giving the product **3g** as a white solid in 80% yield (41 mg, >20:1 dr), m.p. 201-203 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08-8.06 (m, 1H), 7.74-7.68 (m, 4H), 7.65-7.61 (m, 1H), 7.54 (dd, *J* = 8.4, 0.8 Hz, 2H), 7.52-7.47 (m, 1H), 7.43-7.36 (m, 3H), 7.32 (t, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 1H), 7.16 (t, *J* = 8.4 Hz, 1H), 6.74 (d, *J* = 7.6 Hz, 1H), 6.50 (s, 1H), 5.13 (d, *J* = 8.4 Hz, 1H), 3.39 (d, *J* = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.6, 190.1, 153.5, 136.9, 136.7, 136.5, 134.7, 134.3, 133.9, 133.7, 129.6, 129.3, 129.2, 128.7, 128.4, 127.7, 127.5, 127.2, 126.4, 126.3, 123.9, 120.8, 59.5, 43.2, 33.8 ppm. IR (CH_2Cl_2, cm^{-1}): 1706, 1674, 1593, 1473, 1458, 1448, 1369, 1155. HRMS (ESI): *m/z* calculated for $C_{29}H_{20}ClNO_4S^+Na$: 536.0694, found: 536.0698.



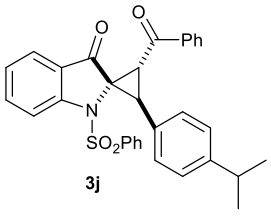
3h

2-benzoyl-3-(4-chlorophenyl)-1'-(phenylsulfonyl)spiro[cyclopropane-1,2'-indolin]-3'-one (**3h**). The residue was purified by a silica gel flash chromatography (PE:EtOAc = 12:1 to PE:EtOAc = 3:1) giving the product **3h** as a white solid in 74% yield (38 mg, >20:1 dr), m.p. 187-189 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 8.0 Hz, 1H), 7.74-7.67 (m, 4H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.41-7.35 (m, 3H), 7.32 (t, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.68 (d, *J* = 8.4 Hz, 2H), 5.14 (d, *J* = 8.4 Hz, 1H), 3.38 (d, *J* = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.8, 190.2, 153.4, 136.9, 136.7, 136.4, 134.0, 133.6, 133.4, 131.2, 130.4, 129.5, 128.7, 128.4, 128.2, 127.6, 126.4, 126.2, 123.8, 120.7, 59.7, 43.4, 33.8 ppm. IR (CH_2Cl_2, cm^{-1}): 1707, 1686, 1602, 1580, 1494, 1474, 1458, 1446, 1364, 1152. HRMS (ESI): *m/z* calculated for $C_{29}H_{20}ClNO_4S^+$ Na: 536.0694, found: 536.0700.



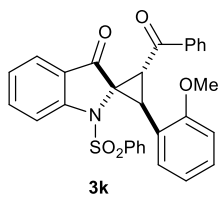
3i

2-benzoyl-1'-(phenylsulfonyl)-3-(o-tolyl)spiro[cyclopropane-1, 2'-indolin]-3'-one (**3i**). The residue was purified by a silica gel flash chromatography (PE:EtOAc = 12:1 to PE:EtOAc = 3:1) giving the product **3i** as a white solid in 81% yield (40 mg, >20:1 dr), m.p. 196-198 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 8.4 Hz, 1H), 7.76-7.72 (m, 3H), 7.68 (td, *J* = 7.6, 1.2 Hz, 1H), 7.58-7.46 (m, 4H), 7.39-7.29 (m, 5H), 7.19-7.16 (m, 2H), 6.94-6.89 (m, 1H), 6.08 (d, *J* = 8.0 Hz, 1H), 5.18 (d, *J* = 8.8 Hz, 1H), 3.28 (d, *J* = 8.4 Hz, 1H), 2.19 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.8, 190.1, 153.3, 137.6, 136.8, 136.7, 136.2, 134.0, 133.5, 130.4, 130.3, 129.9, 129.4, 128.6, 128.3, 127.8, 127.5, 126.4, 126.0, 124.7, 123.9, 120.7, 60.8, 45.2, 34.0, 19.6 ppm. IR (CH_2Cl_2, cm^{-1}): 1715, 1699, 1690, 1678, 1599, 1472, 1457, 1446, 1365, 1154. HRMS (ESI): *m/z* calculated for $C_{30}H_{23}NO_4S^+Na$: 516.1240, found: 516.1246.



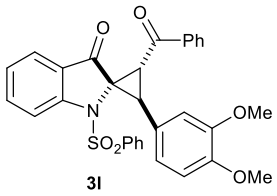
3j

2-benzoyl-3-(4-isopropylphenyl)-1'-(phenylsulfonyl)spiro[cyclopropane-1,2'-indolin]-3'-one (**3j**). The residue was purified by a silica gel flash chromatography (PE:EtOAc = 12:1 to PE:EtOAc = 3:1) giving the product **3j** as a white solid in 82% yield (43 mg, >20:1 dr), m.p. 188-190 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 8.4 Hz, 1H), 7.76 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.69-7.64 (m, 2H), 7.60-7.56 (m, 3H), 7.50-7.47 (m, 1H), 7.40-7.29 (m, 5H), 7.09 (d, *J* = 8.0 Hz, 2H) , 6.74 (d, *J* = 7.6 Hz, 2H), 5.21 (d, *J* = 8.4 Hz, 1H), 3.43 (d, *J* = 8.4 Hz, 1H), 2.88 (dq, *J* =20.4 Hz, 6.8 Hz, 1H), 1.24 (d , *J* = 1.6 Hz, 3H), 1.23 (d , *J* = 1.6 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.9, 190.6, 153.3, 148.0, 137.0, 136.9, 136.2, 133.9, 133.5, 129.8, 129.4, 129.0, 128.7, 128.4, 127.7, 126.6, 126.1, 126.1, 123.8, 120.7, 60.0, 43.5, 34.6, 33.8, 23.9, 23.9 ppm. IR (CH_2Cl_2, cm^{-1}): 1706, 1677, 1601, 1513, 1473, 1450, 1443, 1383, 1363, 1154. HRMS (ESI): *m/z* calculated for $C_{32}H_{27}NO_4S^+Na$: 544.1553, found: 544.1560.



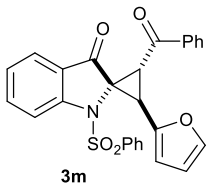
3k

2-benzoyl-3-(2-methoxyphenyl)-1'-(phenylsulfonyl)spiro[cyclopropane-1,2'-indolin]-3'-one (**3k**). The residue was purified by a silica gel flash chromatography (PE:EtOAc = 12:1 to PE:EtOAc = 1:1) giving the product **3k** as a white solid in 88% yield (45 mg, >20:1 dr), m.p. 168-170 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 8.4 Hz, 1H), 7.86 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.78 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.69 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.66-7.62 (m, 1H), 7.56-7.49 (m, 2H), 7.38-7.34 (m, 4H), 7.29-7.23 (m, 2H), 7.02 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.92 (td, *J* = 7.6, 0.8 Hz, 1H), 672 (d, *J* = 8.0 Hz, 1H), 4.82 (d, *J* = 8.8 Hz, 1H), 3.31 (d, *J* = 8.8 Hz, 1H), 3.16 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.6, 191.5, 157.3, 152.5, 138.0, 137.1, 136.0, 133.6, 133.4, 130.7, 129.1, 128.8, 128.6, 128.6, 127.9, 125.0, 125.0, 123.7, 121,3, 120.4, 118.5, 110.0, 60.6, 54.6, 43.2, 29.8 ppm. IR (CH_2Cl_2, cm^{-1}): 1707, 1679, 1598, 1496, 1477, 1460, 1447, 1360, 1164. HRMS (ESI): *m/z* calculated for $C_{30}H_{23}NO_5S^+Na$: 532.1189, found: 532.1193.



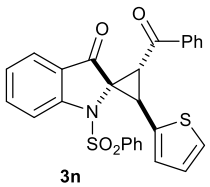
3l

2-benzoyl-3-(3,4-dimethoxyphenyl)-1'-(phenylsulfonyl)spiro[cyclopropane-1,2'-indolin]-3'-one (**3l**). The residue was purified by a silica gel flash chromatography (PE:EtOAc = 12:1 to PE:EtOAc = 1:1) giving the product **3l** as a white solid in 85% yield (46 mg, >20:1 dr)White solid, m.p. 189-191 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 2H), 7.71-7.65 (m, 2H), 7.60-7.55 (m, 3H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.40-7.31 (m, 5H), 6.71 (d, *J* = 8.4 Hz, 1H), 6.50 (d, *J* = 1.2 Hz, 1H), 6.34-6.32 (m, 1H), 5.17 (d, *J* = 8.4 Hz, 1H), 3.86 (s, 3H), 3.75 (s, 3H), 3.43 (d, *J* = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.8, 190.6, 153.2, 148.6, 148.4, 137.0, 136.9, 136.2, 133.9, 133.5, 129.4, 128.7, 128.4, 127.6, 126.5, 126.1, 124.8, 123.8, 121.5, 120.6, 112.2, 110.4, 60.1, 56.0, 55.8, 43.5, 34.6 ppm. IR (CH_2Cl_2, cm^{-1}): 1709, 1673, 1591, 1514, 1458, 1446, 1366, 1152. HRMS (ESI): *m/z* calculated for $C_{31}H_{25}NO_6S^+Na$: 562.1295, found: 562.1299.



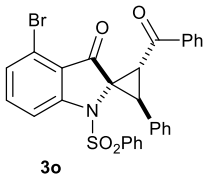
3m

2-benzoyl-3-(furan-2-yl)-1'-(phenylsulfonyl)spiro[cyclopropane-1,2'-indolin]-3'-one (**3m**). The residue was purified by a silica gel flash chromatography (PE:EtOAc = 12:1 to PE:EtOAc = 3:1) giving the product **3m** as a yellow solid in 87% yield (41 mg, >20:1 dr), m.p. 132-134 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 8.0 Hz, 1H), 7.77-7.74 (m, 2H), 7.65-7.61 (m, 4H), 7.53-7.47 (m, 2H), 7.36-7.29 (m, 6H), 6.38 (dd, *J* = 3.2, 2.0 Hz, 1H), 621-6.20 (m, 1H), 5.25 (d, *J* = 8.0 Hz, 1H), 3.55 (d, *J* = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.5, 189.7, 153.1, 146.9, 142.1, 136.8, 136.1, 135.7, 134.0, 133.6, 129.1, 128.7, 128.4, 127.8, 126.8, 126.4, 123.6, 121.2, 110.7, 109.2, 59.3, 41.3, 27.3 ppm. IR (CH_2Cl_2, cm^{-1}): 1711, 1676, 1600, 1504, 1472, 1457, 1447, 1367, 1157. HRMS (ESI): *m/z* calculated for $C_{27}H_{19}NO_5S^+Na$: 492.0876, found: 492.0884.



3n

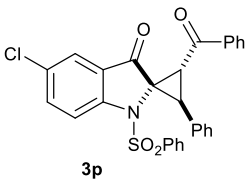
2-benzoyl-1'-(phenylsulfonyl)-3-(thiophen-2-yl)spiro[cyclopropane-1,2'-indolin]-3'-one (**3n**). The residue was purified by a silica gel flash chromatography (PE:EtOAc = 12:1 to PE:EtOAc = 3:1) giving the product **3n** as a pale yellow solid in 78% yield (38 mg, >20:1 dr). 155-157 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 8.0 Hz, 1H), 7.76 (dd, *J* = 8.4, 0.8 Hz, 2H), 7.68-7.64 (m, 2H), 7.59-7.54 (m, 3H), 7.52-7.48 (m, 1H), 7.40-7.36 (m, 2H), 7.33 (t, *J* = 7.6 Hz, 3H), 7.22-7.20 (m, 1H), 6.94 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.78-6.77 (m, 1H), 5.27 (d, *J* = 8.0 Hz, 1H), 3.53 (d, *J* = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.2, 189.9, 153.1, 136.8, 136.5, 136.2, 135.4, 134.0, 133.6, 129.5, 128.7, 128.4, 127.8, 127.6, 126.6, 126.5, 126.2, 125.3, 123.8, 120.7, 60.0, 43.7, 29.6 ppm. IR (CH_2Cl_2, cm^{-1}): 1705, 1681, 1590, 1473, 1459, 1442, 1365, 1154. HRMS (ESI): *m/z* calculated for $C_{27}H_{19}NO_4S_2^+Na$: 508.0648, found: 508.0652.



3o

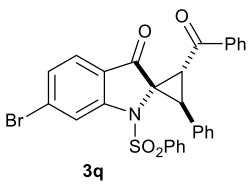
2-benzoyl-4'-bromo-3-phenyl-1'-(phenylsulfonyl)spiro[cyclopropane-1,2'-indolin]-3'-one (**3o**). The residue was purified by a silica gel flash chromatography (PE:EtOAc = 12:1 to PE:EtOAc = 3:1)

giving the product **3o** as a white solid in 79% yield (44 mg, >20:1 dr), m.p. 178-180 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.79-7.77 (m, 2H), 7.63-7.59 (m, 3H), 7.53-7.40 (m, 5H), 7.35 (t, *J* = 8.0 Hz, 2H), 7.27-7.22 (m, 3H), 6.91-6.88 (m, 2H), 5.21 (d, *J* = 8.4 Hz, 1H), 3.48 (d, *J* = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.4, 190.2, 154.8, 136.9, 136.8, 136.1, 134.2, 133.6, 132.1, 130.9, 129.6, 129.1, 128.7, 128.4, 128.2, 127.6, 127.6, 124.3, 119.5, 119.0, 60.3, 43.3, 35.0 ppm. IR (CH_2Cl_2, cm^{-1}): 1714, 1671, 1589, 1577, 1498, 1460, 1445, 1362, 1162. HRMS (ESI): *m/z* calculated for $C_{29}H_{20}BrNO_4S^+Na$: 580.0189, found: 580.0201.



3p

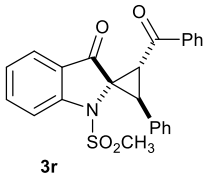
2-benzoyl-5'-chloro-3-phenyl-1'-(phenylsulfonyl)spiro[cyclopropane-1,2'-indolin]-3'-one (**3p**). The residue was purified by a silica gel flash chromatography (PE:EtOAc = 12:1 to PE:EtOAc = 3:1) giving the product **3p** as a white solid in 72% yield (37 mg, >20:1 dr), m.p. 150-152 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 9.0 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 2H), 7.64-7.62 (m, 3H), 7.58 (d, *J* = 7.8 Hz, 2H), 7.54-7.51 (m, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.27-7.21 (m, 3H), 6.76 (d, *J* = 7.2 Hz, 2H), 5.22 (d, *J* = 8.4 Hz, 1H), 3.44 (d, *J* = 8.4 Hz, 1H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 191.6, 190.1, 151.5, 136.7, 136.6, 136.0, 134.1, 133.6, 132.2, 132.1, 129.6, 129.0, 128.7, 128.3, 128.1, 127.6, 123.3, 121.8, 60.3, 43.7, 34.9 ppm. IR (CH_2Cl_2, cm^{-1}): 1715, 1683, 1598, 1497, 1457, 1446, 1377, 1151. HRMS (ESI): *m/z* calculated for $C_{29}H_{20}ClNO_4S^+Na$: 536.0694, found: 536.0697.



3q

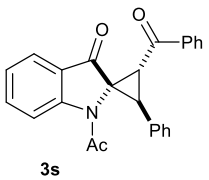
2-benzoyl-6'-bromo-3-phenyl-1'-(phenylsulfonyl)spiro[cyclopropane-1,2'-indolin]-3'-one (**3q**). The residue was purified by a silica gel flash chromatography (PE:EtOAc = 12:1 to PE:EtOAc = 3:1) giving the product **3q** as a white solid in 70% yield (39 mg, >20:1 dr), m.p. 194-196 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30 (d, *J* = 1.2 Hz, 1H), 7.77 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.65-7.61 (m, 3H), 7.55-7.51 (m, 2H), 7.48 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.45-7.41 (m, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.27-7.19 (m, 3H), 6.76 (d, *J* = 7.2 Hz, 2H), 5.18 (d, *J* = 8.4 Hz, 1H), 3.44 (d, *J* = 8.4 Hz, 1H)

ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.6, 190.2, 153.8, 136.9, 136.8, 134.2, 133.7, 132.3, 131.7, 129.7, 129.7, 129.0, 128.8, 128.4, 128.1, 127.6, 127.6, 125.0, 124.7, 123.5, 60.2, 43.4, 34.8 ppm. IR (CH_2Cl_2, cm^{-1}): 1705, 1676, 1594, 1574, 1498, 1472, 1443, 1368, 1161. HRMS (ESI): *m/z* calculated for $C_{29}H_{20}BrNO_4S^+Na$ 580.0189, found: 580.0198.



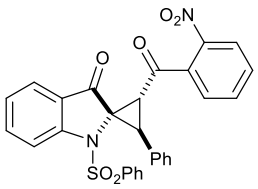
3r

2-benzoyl-1'-(methylsulfonyl)-3-phenylspiro[cyclopropane-1,2'-indolin]-3'-one (**3r**). The residue was purified by a silica gel flash chromatography (PE:EtOAc = 12:1 to PE:EtOAc = 3:1) giving the product **3r** as a white solid in 86% yield (36 mg, >20:1 dr). 206-208 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86-7.84 (m, 2H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.75 (dd, *J* = 11.6, 0.4 Hz, 1H), 7.67-7.62 (m, 1H), 7.55-7.51 (m, 1H), 7.43-7.36 (m, 6H), 7.35-7.30 (m, 2H), 5.07 (d, *J* = 8.8 Hz, 1H), 3.70 (d, *J* = 8.8 Hz, 1H), 3.10 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.3, 191.7, 152.6, 136.9, 136.3, 133.7, 132.2, 129.0, 128.8, 128.5, 128.4, 127.9, 125.5, 125.3, 124.1, 119.1, 61.2, 41.7, 39.1, 35.9 ppm. IR (CH_2Cl_2, cm^{-1}): 1707, 1679, 1594, 1496, 1472, 1447, 1360, 1150. HRMS (ESI): *m/z* calculated for $C_{24}H_{19}NO_4S^+Na$: 440.0927, found: 440.0927.



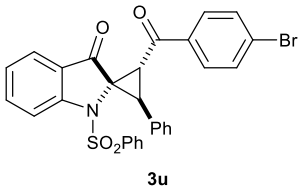
3s

1'-acetyl-2-benzoyl-3-phenylspiro[cyclopropane-1,2'-indolin]-3'-one (**3s**)**.** The residue was purified by a silica gel flash chromatography (PE:EtOAc = 12:1 to PE:EtOAc = 3:1) giving the product **3s** as a white solid in 84% yield (32 mg, >20:1 dr), m.p. 176-178 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96-7.94 (m, 2H), 7.77-7.75 (m, 1H), 7.70-7.65 (m, 1H), 7.58 (d, *J* = 8.8 Hz, 1H), 7.55-7.51 (m, 1H), 7.43-7.34 (m, 6H), 7.32-7.24 (m, 2H), 5.05 (d, *J* = 9.2 Hz, 1H), 3.57 (d, *J* = 9.2 Hz, 1H), 2.49 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.7, 191.6, 168.6, 151.2, 136.9, 136.0, 133.1, 133.0, 129.3, 128.7, 128.4, 128.2, 127.6, 124.6, 124.3, 124.0, 115.9, 60.1, 39.8, 36.2, 27.2 ppm. IR (CH_2Cl_2, cm^{-1}): 1709, 1672, 1595, 1469, 1447, 1430, 1371, 1152. HRMS (ESI): *m/z* calculated for $C_{25}H_{19}NO_3S^+Na$: 404.1257, found: 404.1262.



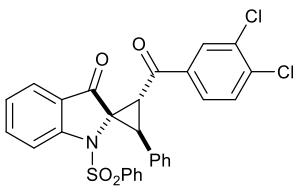
3t

2-(2-nitrobenzoyl)-3-phenyl-1'-(phenylsulfonyl)spiro[cyclopropane-1,2'-indolin]-3'-one (**3t**). The residue was purified by a silica gel flash chromatography (PE:EtOAc = 12:1 to PE:EtOAc = 3:1) giving the product **3t** as a white solid in 71% yield (37 mg, >20:1 dr), m.p. 190-192 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (d, *J* = 8.4 Hz, 1H), 8.11 (dd, *J* = 8.0, 0.4 Hz, 1H), 7.78-7.74 (m, 1H), 7.62 (td, *J* = 7.6, 1.2 Hz, 1H), 7.59-7.54 (m, 3H), 7.53-7.50 (m, 2H), 7.37-7.33 (m, 3H), 7.30 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.28-7.21 (m, 3H), 6.89-6.87 (m, 2H), 5.37 (d, *J* = 8.0 Hz, 1H), 3.13 (d, *J* = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.6, 192.4, 153.2, 145.5, 137.2, 136.2, 136.0, 134.7, 134.2, 132.0, 131.0, 129.4, 129.1, 128.1, 127.9, 127.7, 127.7, 127.1, 126.8, 124.4, 124.0, 121.5, 60.5, 47.6, 35.4 ppm. IR (CH_2Cl_2, cm^{-1}): 1698, 1602, 1573, 1526, 1496, 1472, 1459, 1444, 1377, 1154. HRMS (ESI): *m/z* calculated for $C_{29}H_{20}N_2O_6S^+Na$: 547.0934, found: 547.0936.



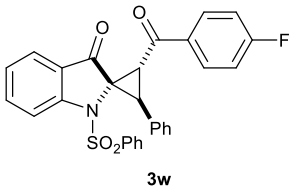
3u

2-(4-bromobenzoyl)-3-phenyl-1'-(phenylsulfonyl)spiro[cyclopropane-1,2'-indolin]-3'-one (**3u**). The residue was purified by a silica gel flash chromatography (PE:EtOAc = 12:1 to PE:EtOAc = 3:1) giving the product **3u** as a white solid in 75% yield (42 mg, >20:1 dr), m.p. 200-202 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10-8.08 (m, 1H), 7.72-7.68 (m, 2H), 7.62-7.56 (m, 5H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.41-7.34 (m, 3H), 7.27-7.19 (m, 3H), 6.77-6.76 (m, 2H), 5.18 (d, *J* = 8.4 Hz, 1H), 3.37 (d, *J* = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.5, 189.7, 153.2, 136.9, 136.5, 135.6, 134.0, 132.3, 132.0, 129.8, 129.5, 129.0, 128.9, 128.1, 127.6, 126.3, 126.2, 123.9, 120.5, 59.8, 43.0, 34.6 ppm. IR (CH_2Cl_2, cm^{-1}): 1704, 1677, 1583, 1475, 1458, 1446, 1369, 1162. HRMS (ESI): *m/z* calculated for $C_{29}H_{20}BrNO_4S^+Na$: 580.0189, found: 580.0187.



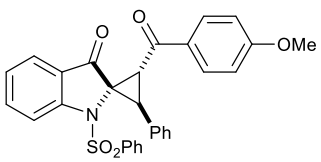
3v

2-(3,4-dichlorobenzoyl)-3-phenyl-1'-(phenylsulfonyl)spiro[cyclopropane-1,2'-indolin]-3'-one (**3v**). The residue was purified by a silica gel flash chromatography (PE:EtOAc = 12:1 to PE:EtOAc = 3:1) giving the product **3v** as a white solid in 75% yield (41 mg, >20:1 dr), m.p. 182-184 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 2.0 Hz, 1H), 7.74-7.69 (m, 2H), 7.62-7.57 (m, 3H), 7.54 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.42-7.35 (m, 4H), 7.27-7.19 (m, 3H), 6.76 (d, *J* = 7.2 Hz, 2H), 5.16 (d, *J* = 8.4 Hz, 1H), 3.33 (d, *J* = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.4, 188.7, 153.1, 138.2, 136.9, 136.6, 136.3, 134.1, 133.5, 132.1, 130.8, 130.4, 129.6, 129.0, 128.1, 127.7, 127.6, 127.3, 126.3, 126.3, 123.9, 120.5, 59.6, 42.7, 34.6 ppm. IR (CH_2Cl_2, cm^{-1}): 1711, 1683, 1598, 1474, 1459, 1446, 1369, 1162. HRMS (ESI): *m/z* calculated for $C_{29}H_{19}Cl_2NO_4S^+Na$: 570.0304, found: 570.0311



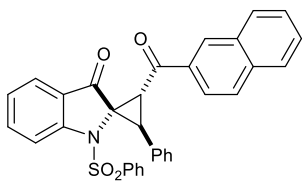
3w

2-(4-fluorobenzoyl)-3-phenyl-1'-(phenylsulfonyl)spiro[cyclopropane-1,2'-indolin]-3'-one (**3w**). The residue was purified by a silica gel flash chromatography (PE:EtOAc = 12:1 to PE:EtOAc = 3:1) giving the product **3w** as a white solid in 84% yield (42 mg, >20:1 dr), m.p. 199-201 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 8.8 Hz, 1H), 7.80-7.76 (m, 2H), 7.71-7.67 (m, 2H), 7.61-7.57 (m, 3H), 7.41-7.34 (m, 3H), 7.26-7.19 (m, 3H), 6.99 (t, *J* = 8.4 Hz, 2H), 6.78-6.76 (m, 2H), 5.18 (d, *J* = 8.4 Hz, 1H), 3.39 (d, *J* = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.6, 189.0, 166.0 (d, J_{CF} = 254.2 Hz), 153.3, 136.9, 136.4, 134.0, 133.4 (d, J_{CF} = 2.9 Hz), 132.4, 131.0 (d, J_{CF} = 9.4 Hz), 129.5, 129.0, 128.1, 127.6, 127.6, 126.3, 126.1, 123.9, 120.5, 115.9 (d, J_{CF} = 21.9 Hz), 59.8, 43.1, 34.6 ppm. IR (CH_2Cl_2, cm^{-1}): 1708, 1670, 1596, 1505, 1472, 1457, 1449, 1367, 1154. HRMS (ESI): *m/z* calculated for $C_{29}H_{20}FNO_4S^+Na$: 520.0989, found: 520.0992.



3x

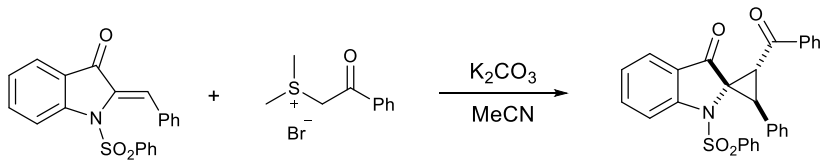
2-(4-methoxybenzoyl)-3-phenyl-1'-(phenylsulfonyl)spiro[cyclopropane-1,2'-indolin]-3'-one (**3x**). The residue was purified by a silica gel flash chromatography (PE:EtOAc = 12:1 to PE:EtOAc = 2:1) giving the product **3x** as a white solid in 65% yield (33 mg, >20:1 dr), m.p. 188-190 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 2H), 7.69-7.65 (m, 2H), 7.60-7.56 (m, 3H), 7.39-7.33 (m, 3H), 7.26-7.18 (m, 3H), 6.79-6.77 (m, 4H), 5.20 (d, *J* = 8.4 Hz, 1H), 3.79 (s, 3H), 3.39 (d, *J* = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.9, 188.8, 163.8, 153.3, 137.0, 136.2, 133.9, 132.8, 130.7, 130.1, 129.5, 129.1, 128.0, 127.6, 127.4, 126.5, 126.0, 123.7, 120.6, 113.9, 59.9, 55.5, 43.4, 34.6 ppm. IR (CH_2Cl_2, cm^{-1}): 1709, 1669, 1603, 1575, 1511, 1474, 1458, 1445, 1366, 1164. HRMS (ESI): *m/z* calculated for $C_{30}H_{23}NO_5S^{+}Na$: 532.1189, found: 532.1198.



3y

2-(2-naphthoyl)-3-phenyl-1'-(phenylsulfonyl)spiro[cyclopropane-1,2'-indolin]-3'-one (**3y**). The residue was purified by a silica gel flash chromatography (PE:EtOAc = 12:1 to PE:EtOAc = 3:1) giving the product **3y** as a white solid in 32% yield (18 mg, >20:1 dr), m.p. 208-210 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.09 (s, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.96-7.95 (m, 1H), 7.82 (q, *J* = 4.2 Hz, 2H) 7.75 (d, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.62-7.54 (m, 5H), 7.46-7.43 (m, 1H), 7.40-7.36 (m, 3H), 7.28-7.23 (m, 3H), 6.84 (d, J = 6.6 Hz, 2H), 5.29(d, *J* = 8.4 Hz, 1H), 3.56 (d, *J* = 8.4 Hz, 1H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 192.9, 190.3, 153.3, 136.9, 136.2, 135.7, 134.2, 133.9, 132.6, 132.2, 130.3, 130.3, 129.4, 129.0, 128.6, 128.6, 128.0, 127.7, 127.6, 127.5, 126.7, 126.6, 126.1, 123.9, 123.7, 120.7, 59.8, 43.6, 34.7 ppm. IR (CH_2Cl_2, cm^{-1}): 1704, 1679, 1624, 1598, 1502, 1474, 1461, 1445, 1367, 1159. HRMS (ESI): *m/z* calculated for $C_{33}H_{23}NO_4S^{+}Na$: 552.1240, found: 552.1246.

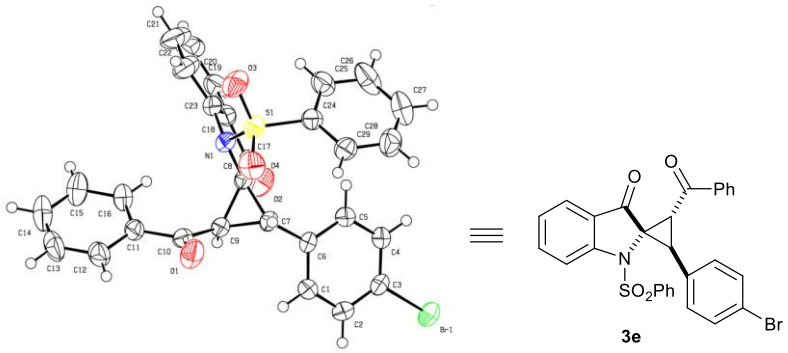
4. Gram-scale Reaction



1a, 2.8 mmol　　**2a**, 4.2 mmol　　**3a**, 1.09 g, 81%, >20:1 dr

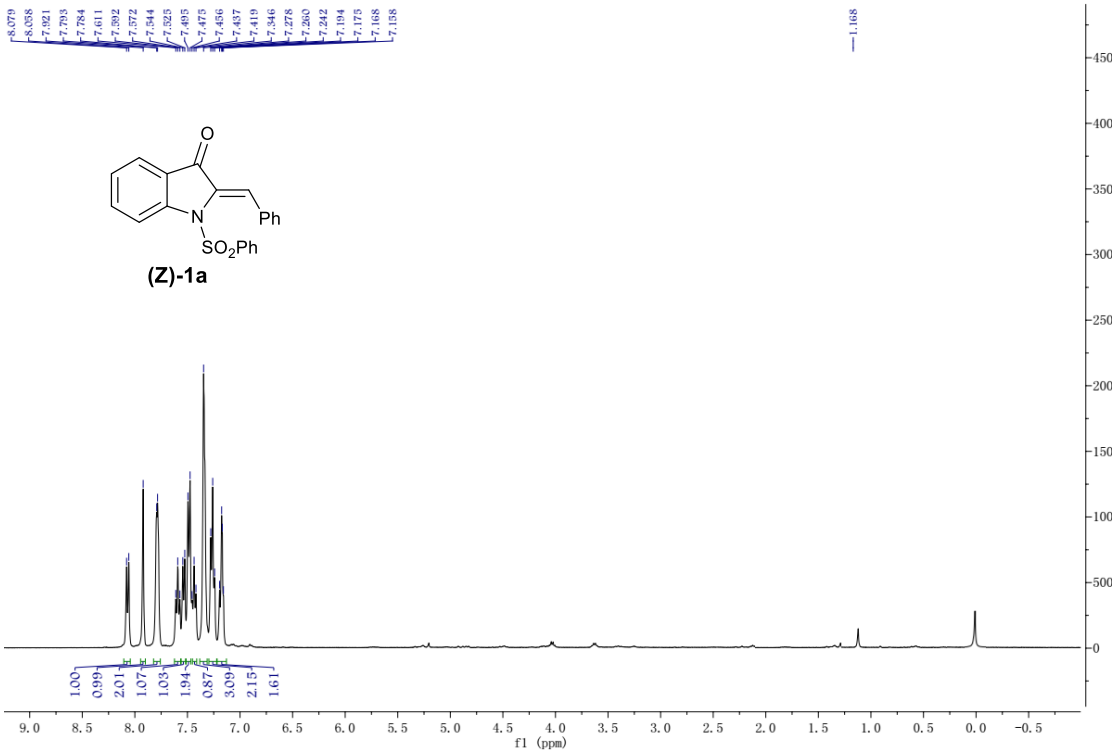
A mixture of (*Z*)-2-ylideneoxindole **1a** (1.01 g, 2.8 mmol), sulfonium bromide **2a** (1.10 g, 4.2 mmol), K_2CO_3 (0.58 g, 4.2 mmol) and MeCN (28.0 mL) was stirred at room temperature without exclusion of air. After (*Z*)-2-ylideneoxindoles **1a** was consumed (monitored by TLC), the reaction mixture was concentrated and the residue was purified by flash chromatography on silica gel (PE:EtOAc = 3:1) to give compound **3a** as red solid**.** Then the solid was recrystallized from 5.0 mL EtOAc and 30.0 mL PE to afford pure compound **3a** as white solid (1.09 g, 81% yield, >20:1 dr).

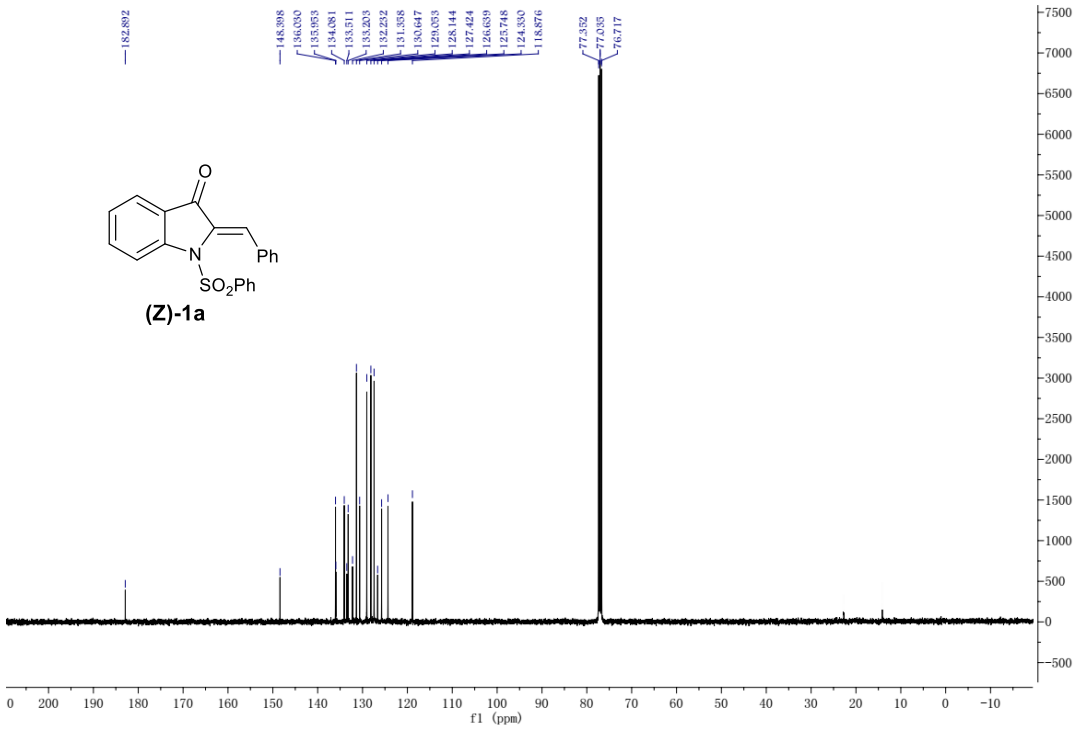
5. Crystal Data of 3e

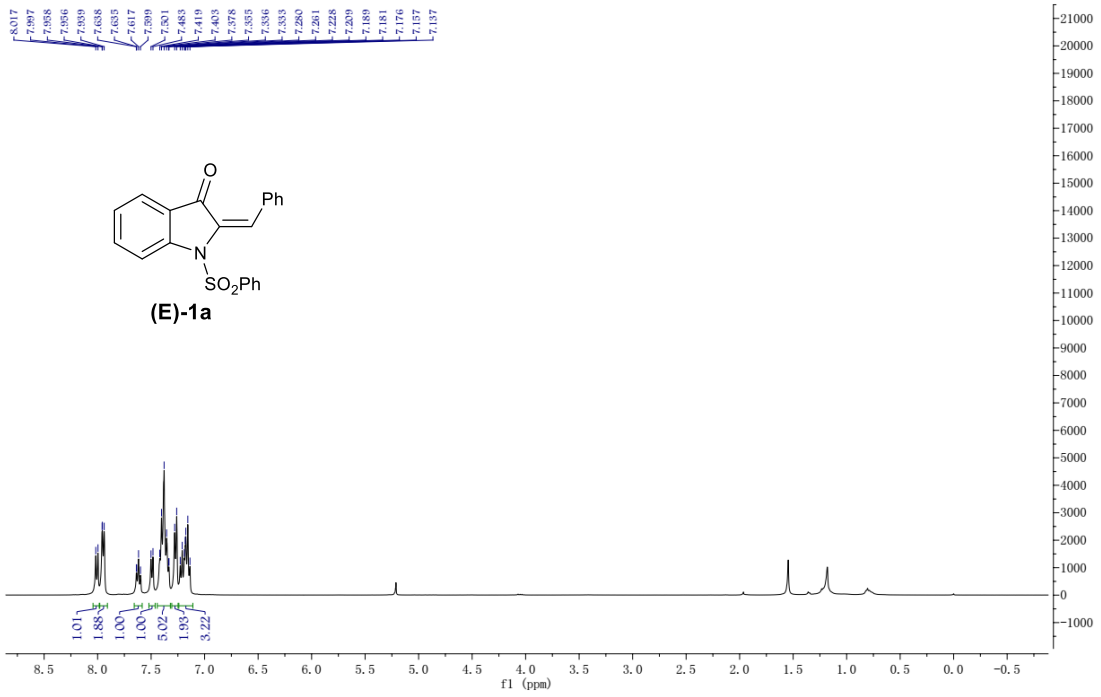


Empirical formula	$C_{29}H_{20}BrNO_4S$
Formula weight	558.43
Temperature/K	266(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.8247(5)
b/Å	11.5260(6)
c/Å	11.6543(5)
α/°	86.407(4)
β/°	74.525(4)
γ/°	72.819(5)
Volume/Å^3	1214.94(11)
Z	2
ρ_{calc}g/cm^3	1.526
μ/mm^{-1}	3.421
F(000)	568.0
Crystal size/mm^3	0.7 × 0.4 × 0.3
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.76 to 145.602
Index ranges	-11 ≤ h ≤ 9, -14 ≤ k ≤ 13, -14 ≤ l ≤ 10
Reflections collected	13326
Independent reflections	4725 [R_{int} = 0.0434, R_{sigma} = 0.0336]
Data/restraints/parameters	4725/0/325
Goodness-of-fit on F^2	1.086
Final R indexes [I>=2σ (I)]	R_1 = 0.0578, wR_2 = 0.1459
Final R indexes [all data]	R_1 = 0.0612, wR_2 = 0.1505
Largest diff. pEtOAck/hole / e Å^{-3}	0.43/-1.21

6. NMR Spectra of NMR Spectra of (*Z*)-2-ylideneoxindoles 1



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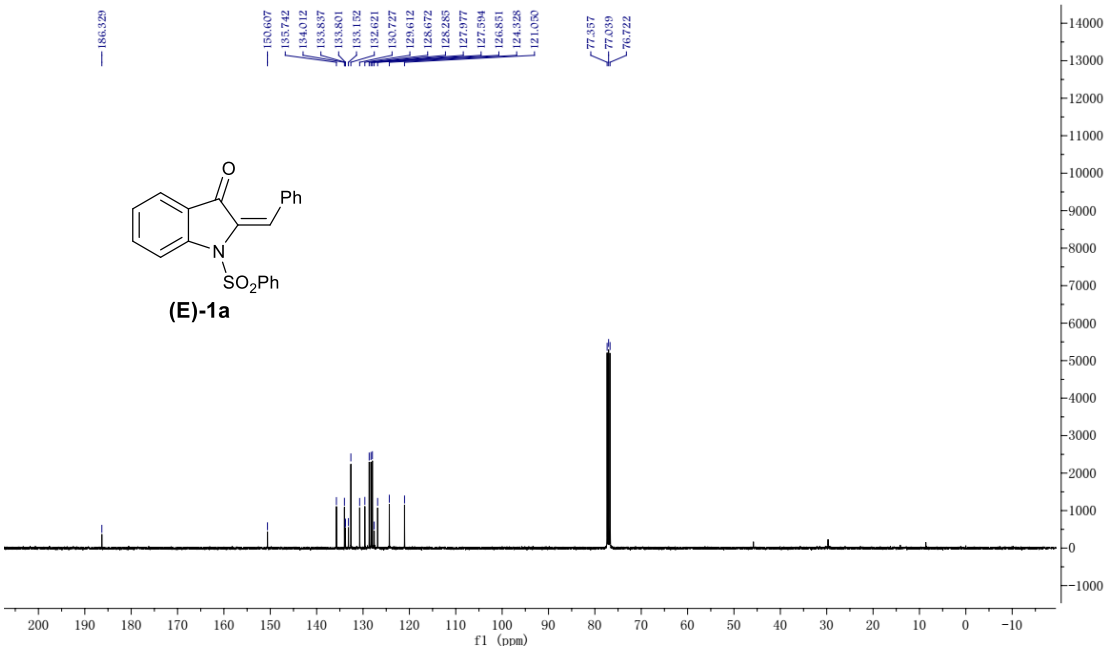
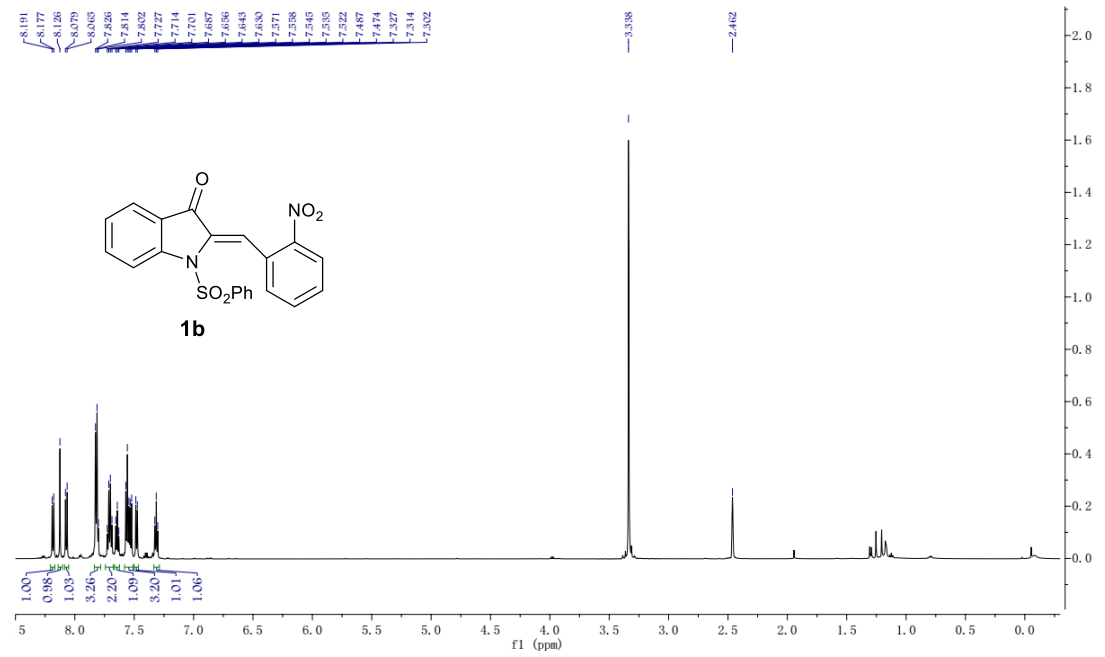
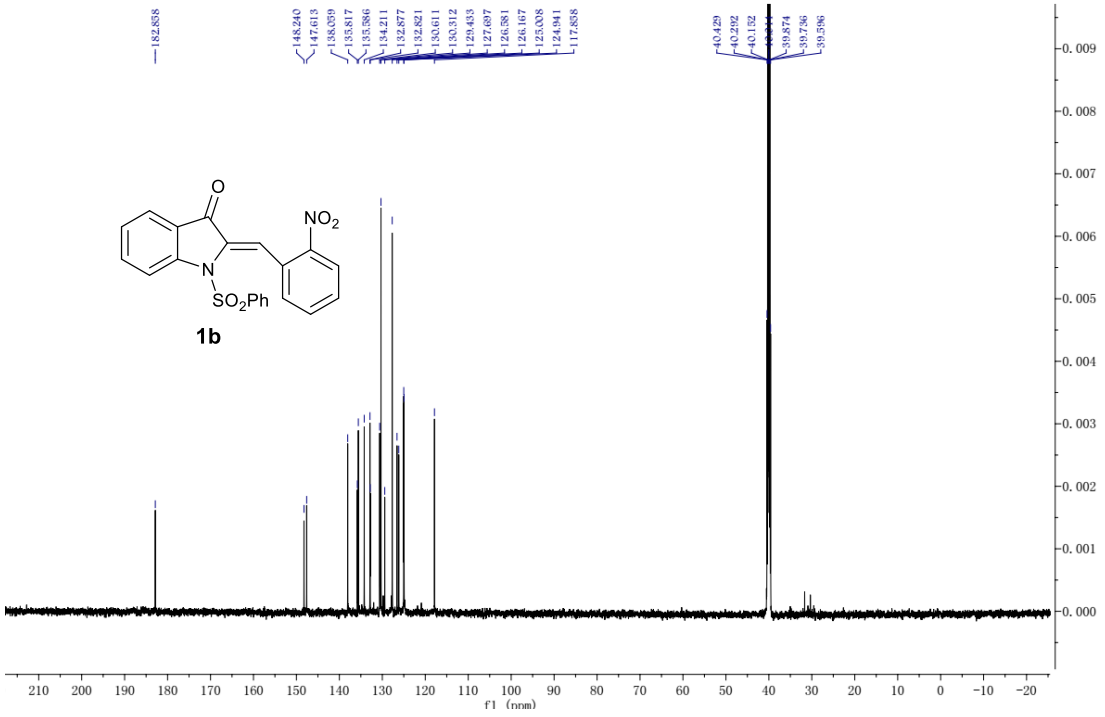
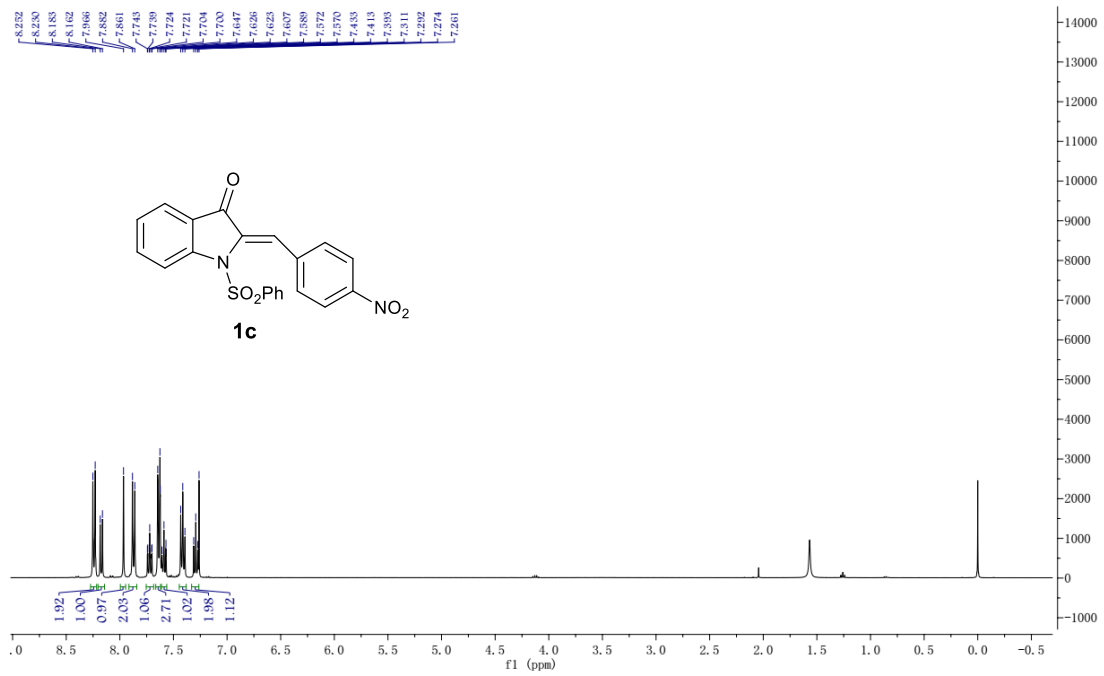
7.997
7.958
7.956
7.939
7.638
7.635
7.617
7.599
7.501
7.483
7.419
7.403
7.378
7.355
7.336
7.333
7.280
7.261
7.228
7.209
7.189
7.181
7.176
7.157
7.137
O
Ph
N
SO2Ph
(E)-1a
1.01
1.88
1.00
1.00
5.02
1.93
3.22
f1 (ppm)


186.329
152.607
135.742
134.012
133.837
133.801
133.152
132.621
130.727
129.612
128.672
128.285
127.977
127.594
126.851
124.328
121.050
77.357
77.039
76.722
O
Ph
N
SO2Ph
(E)-1a
f1 (ppm)


O
NO2
N
SO2Ph
1b
f1 (ppm)


O
NO2
N
SO2Ph
1b
f1 (ppm)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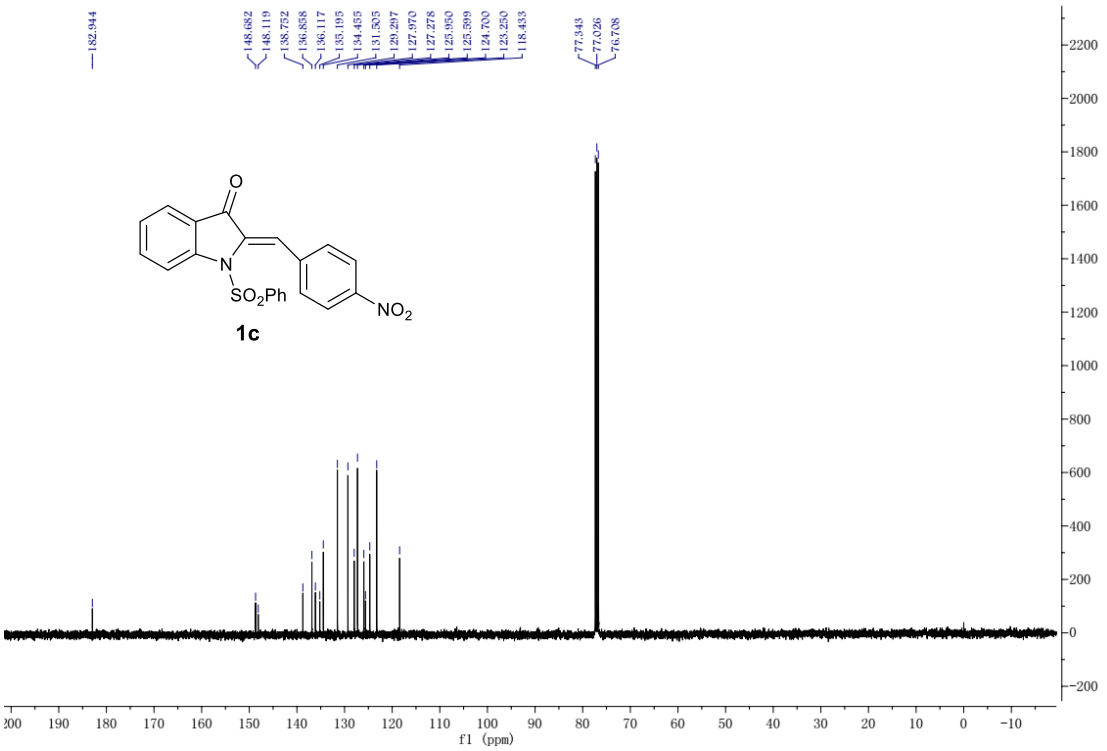
8.230
8.183
8.162
7.966
7.882
7.861
7.743
7.730
7.724
7.721
7.704
7.700
7.647
7.626
7.625
7.607
7.589
7.572
7.570
7.433
7.413
7.393
7.311
7.292
7.274
7.261
O
N
SO2Ph
NO2
1c
1.92
1.00
0.97
2.03
1.06
2.71
1.02
1.98
1.12
f1 (ppm)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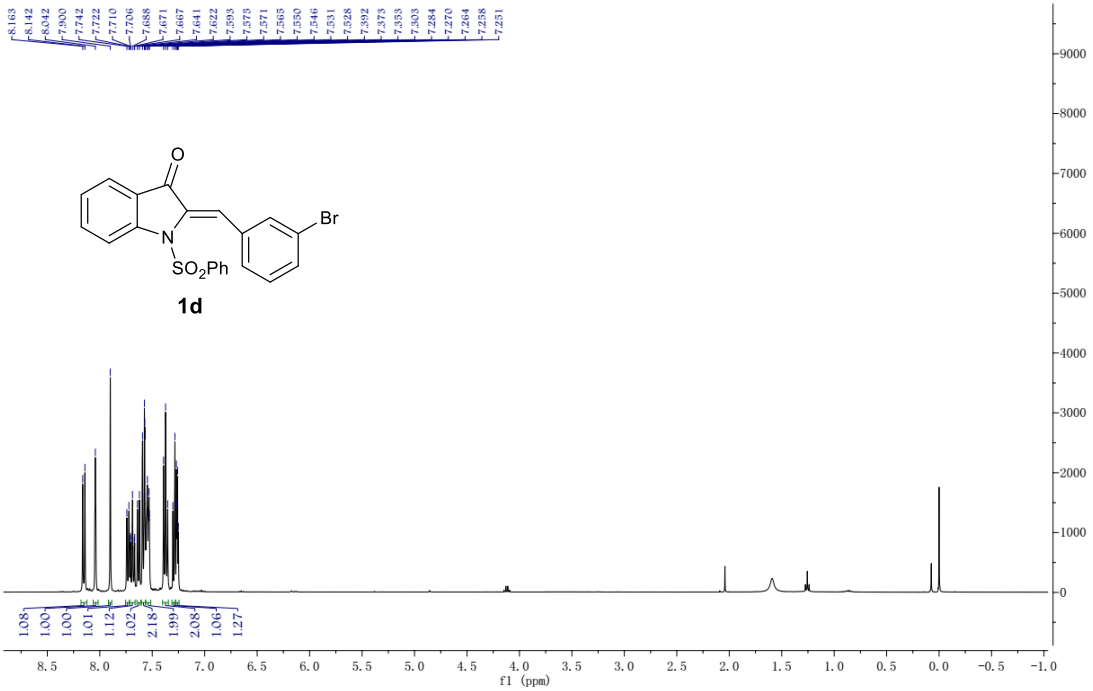
148.682
148.119
138.752
136.858
136.117
135.195
134.435
131.505
129.297
127.970
127.278
125.950
125.599
124.700
123.250
118.433
77.343
77.026
76.708
O
N
SO2Ph
NO2
1c
f1 (ppm)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8.142
8.042
7.900
7.742
7.722
7.710
7.706
7.688
7.671
7.667
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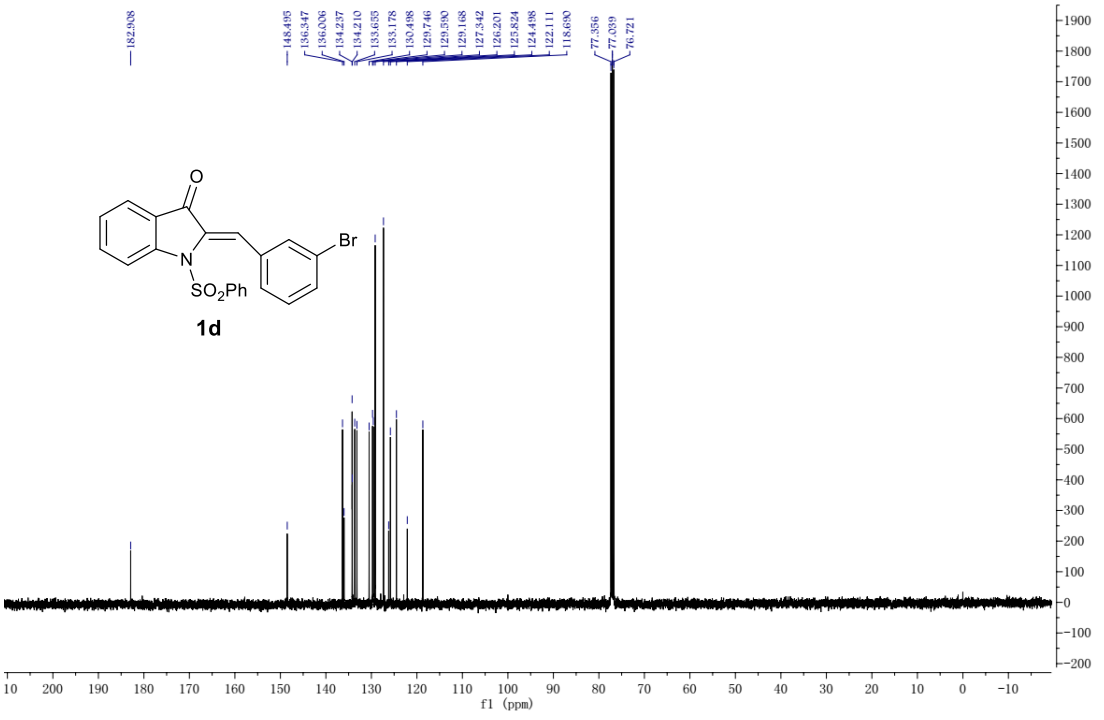
7.622
7.593
7.575
7.571
7.565
7.550
7.546
7.531
7.528
7.392
7.373
7.353
7.303
7.284
7.270
7.264
7.258
7.251
O
N
SO2Ph
Br
1d
1.08
1.00
1.00
1.01
1.12
1.02
2.18
1.99
2.08
1.06
1.27
f1 (ppm)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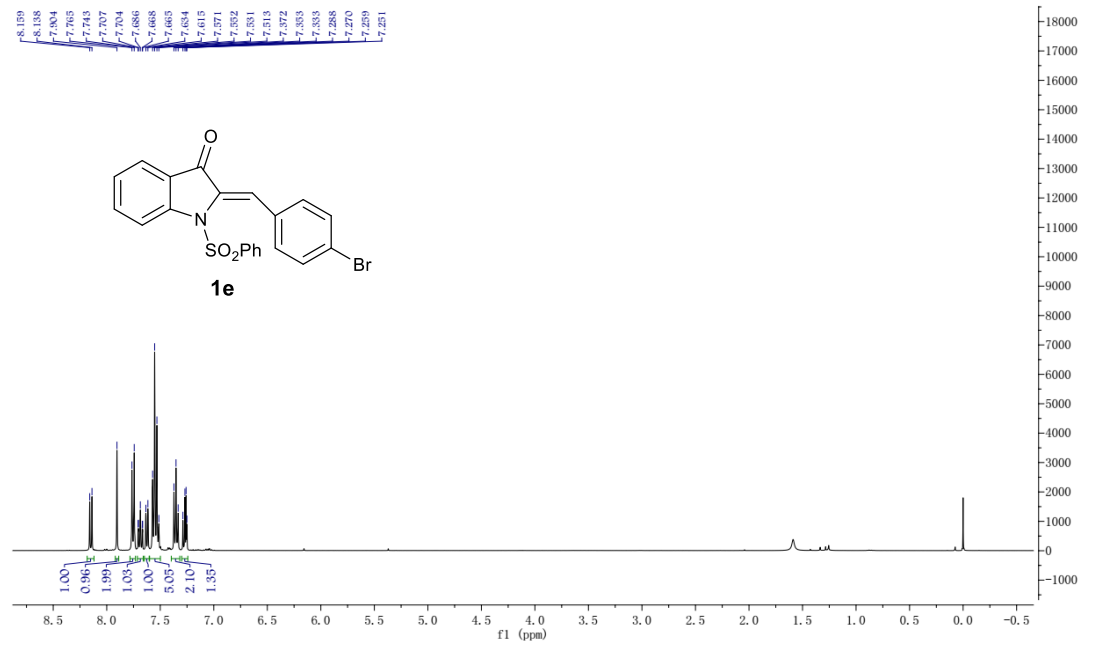
148.495
136.347
136.026
134.237
134.210
133.655
133.178
130.498
129.746
129.590
129.168
127.542
126.201
125.824
124.498
122.111
118.690
77.356
77.039
76.721
O
N
SO2Ph
Br
1d
f1 (ppm)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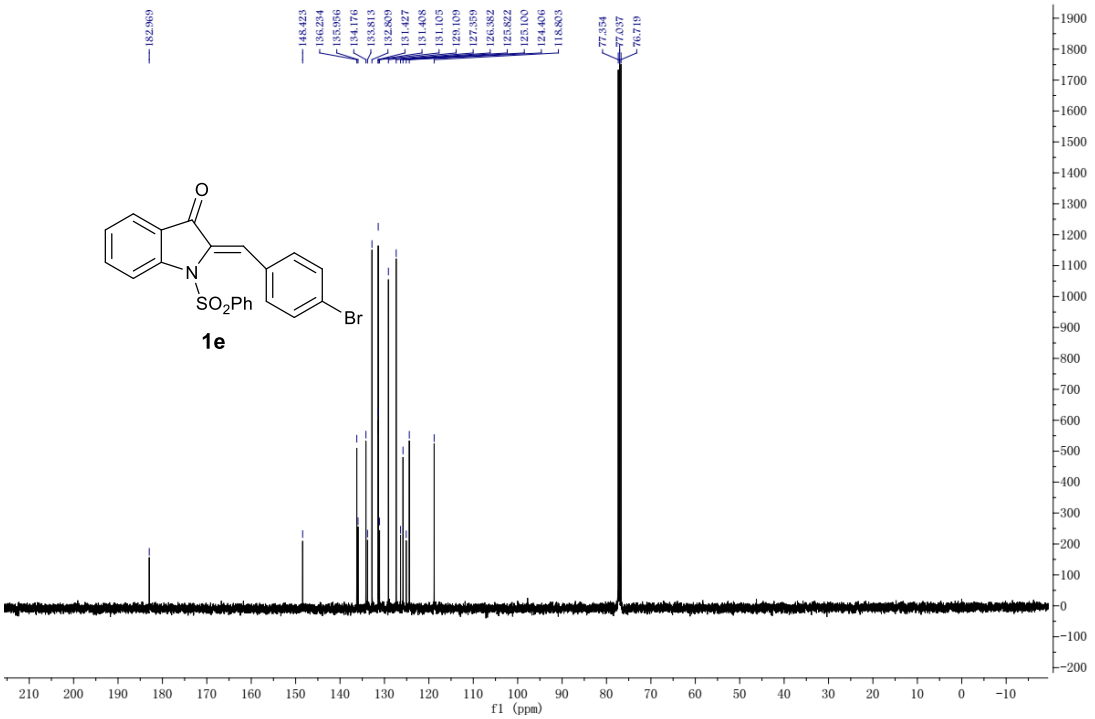
8.138
7.804
7.765
7.743
7.707
7.704
7.686
7.668
7.665
7.634
7.615
7.571
7.552
7.531
7.513
7.372
7.353
7.333
7.288
7.270
7.239
7.251
O
N
SO2Ph
Br
1e
1.00
0.96
1.99
1.03
1.00
5.05
2.10
1.35
f1 (ppm)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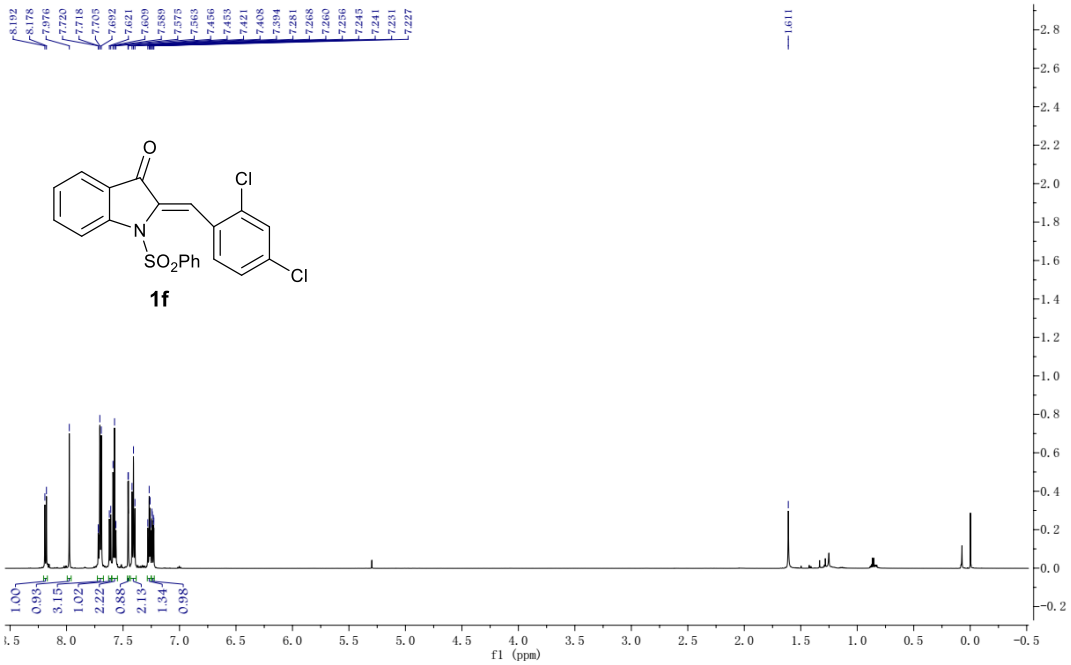
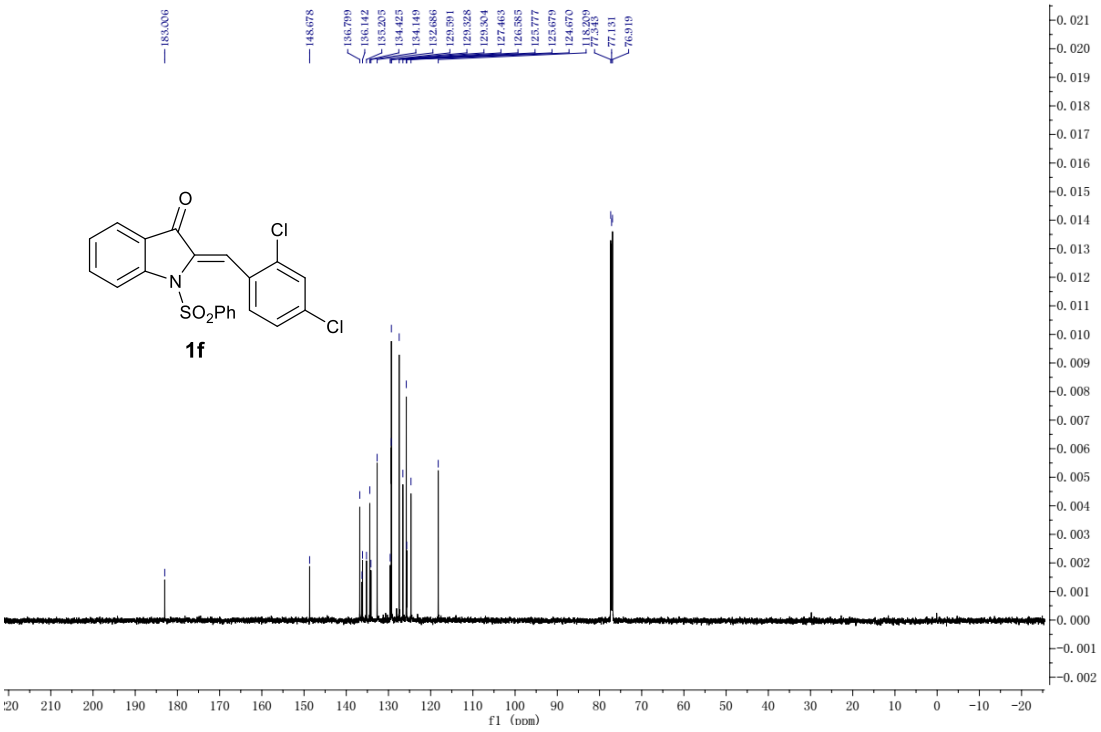
136.234
135.956
134.176
133.813
132.809
131.427
131.408
131.105
129.109
127.359
126.382
125.822
123.100
124.406
118.803
77.354
77.037
76.719
O
N
SO2Ph
Br
1e
f1 (ppm)


8.192
8.178
7.976
7.720
7.718
7.705
7.692
7.621
7.609
7.589
7.575
7.563
7.456
7.453
7.421
7.408
7.394
7.281
7.268
7.260
7.256
7.243
7.241
7.231
7.227
1.611
O
N
SO2Ph
Cl
Cl
1f
1.00
0.93
3.15
1.02
2.22
0.88
2.13
1.34
0.98
f1 (ppm)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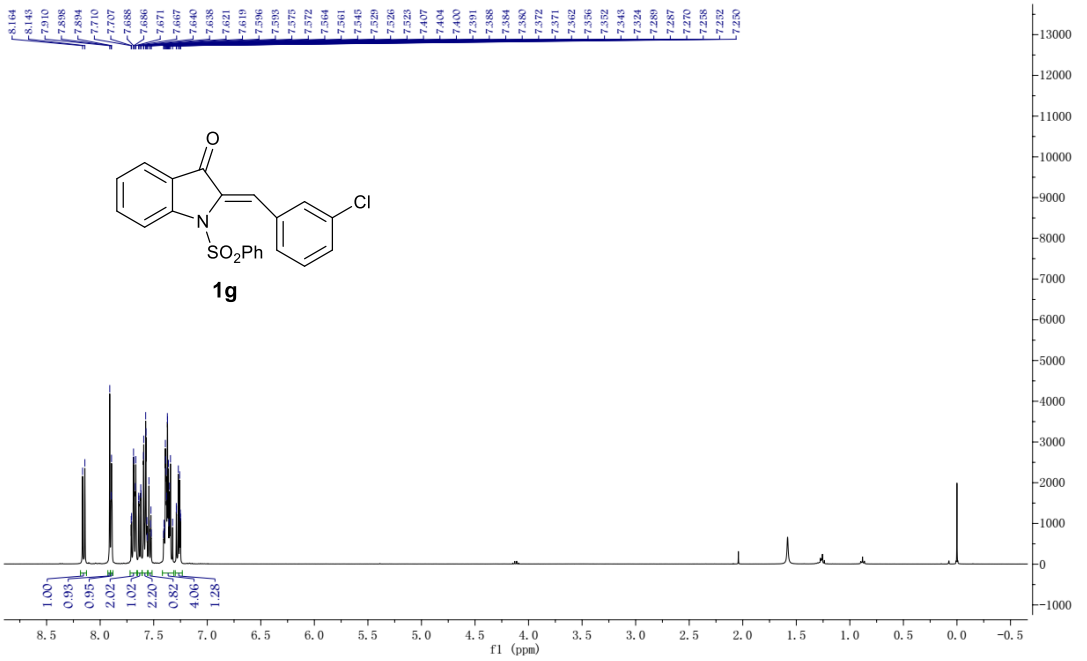
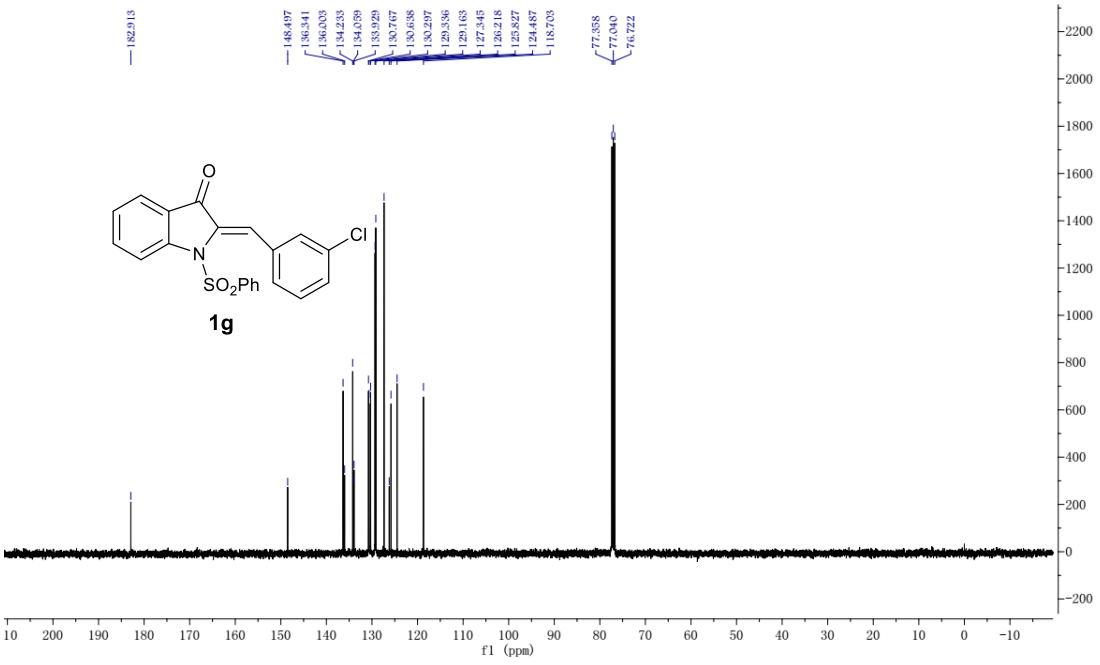
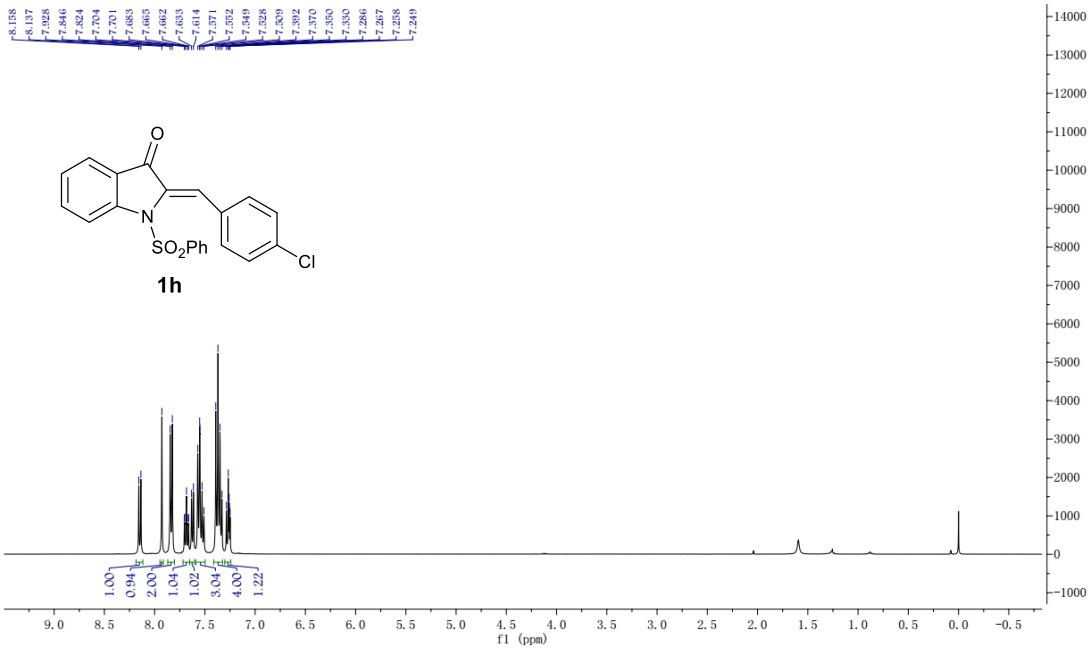
136.142
135.205
134.425
134.149
132.686
129.891
129.328
129.304
127.463
126.585
125.777
125.679
124.670
118.209
77.343
77.131
76.919
O
N
SO2Ph
Cl
Cl
1f
f1 (ppm)


O
N
SO2Ph
Cl
1g
f1 (ppm)


O
N
SO2Ph
Cl
1g
f1 (ppm)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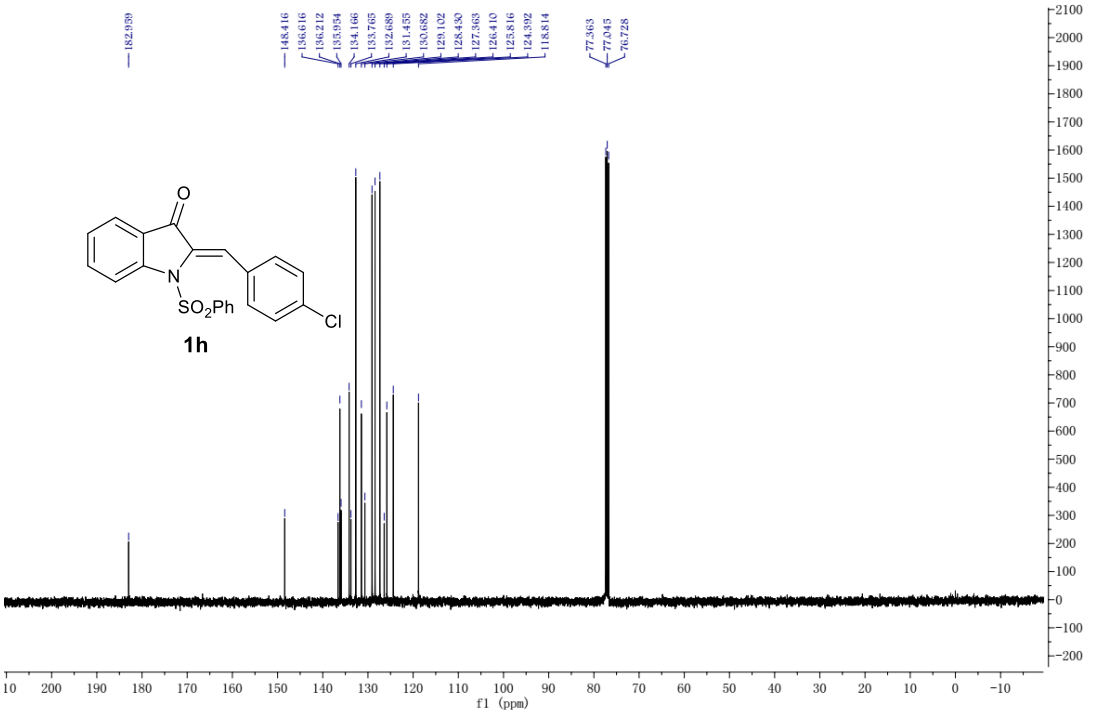
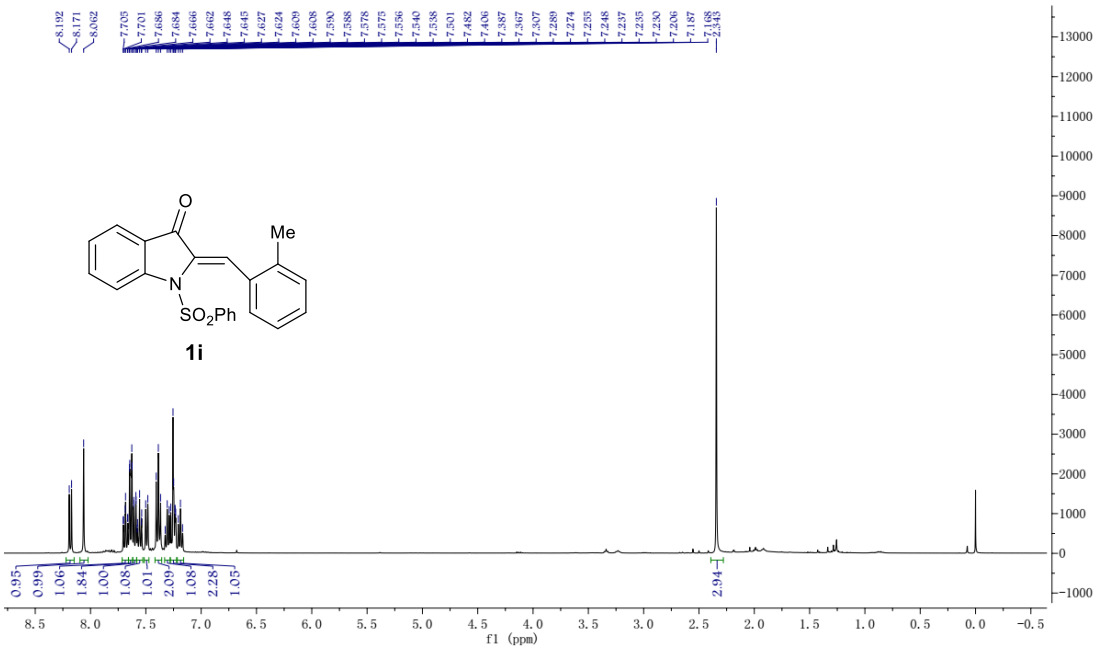
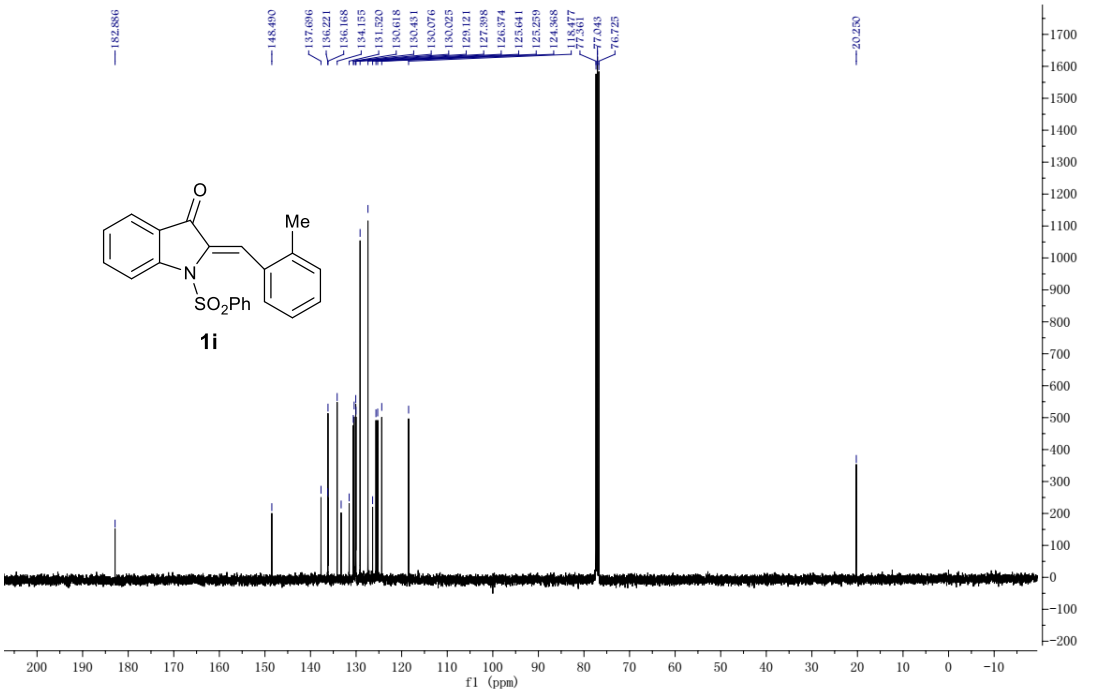
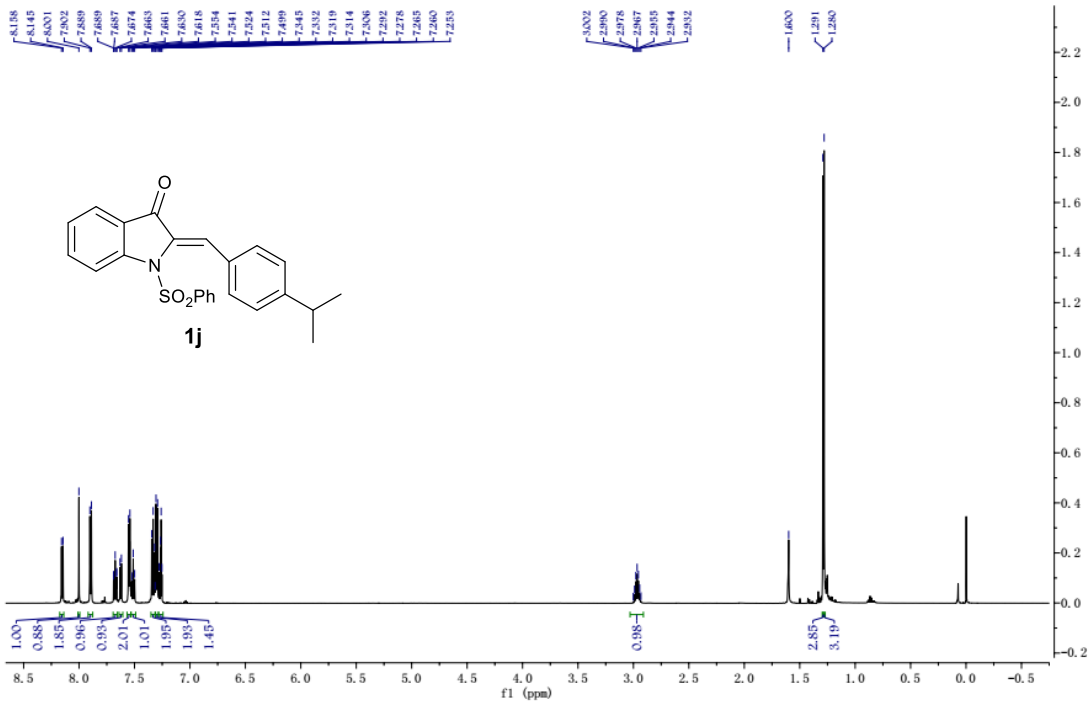
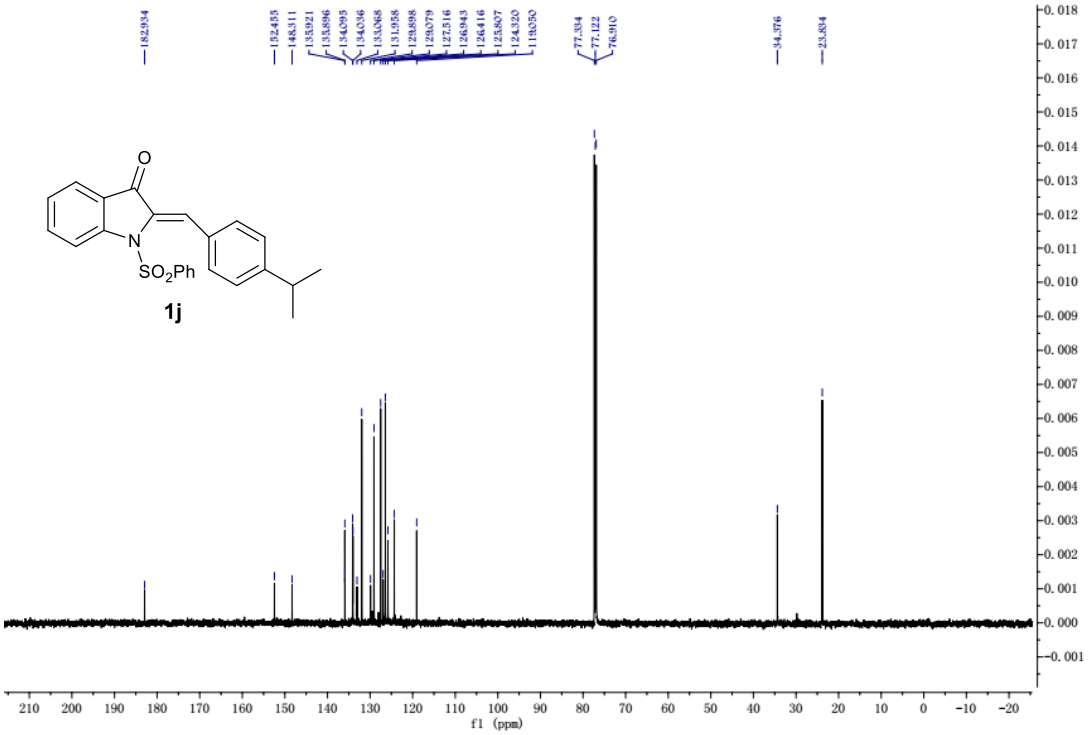
7.928
7.846
7.824
7.704
7.701
7.683
7.665
7.662
7.633
7.614
7.371
7.352
7.549
7.528
7.509
7.392
7.370
7.350
7.330
7.286
7.267
7.258
7.249
O
N
SO2Ph
Cl
1h
1.00
0.94
2.00
1.04
1.02
3.04
4.00
1.22
f1 (ppm)

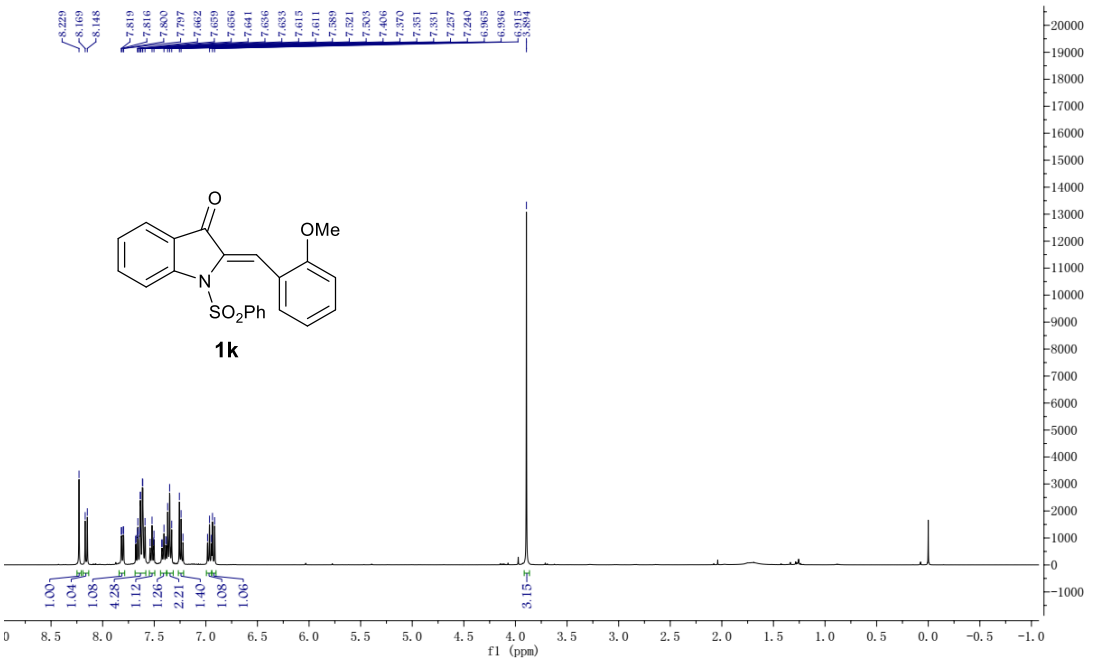

182.939
148.416
136.616
136.212
135.954
134.166
133.765
132.689
131.435
130.682
129.102
128.430
127.363
126.410
125.816
124.392
118.814
77.363
77.043
76.728
O
N
SO2Ph
Cl
1h
f1 (ppm)

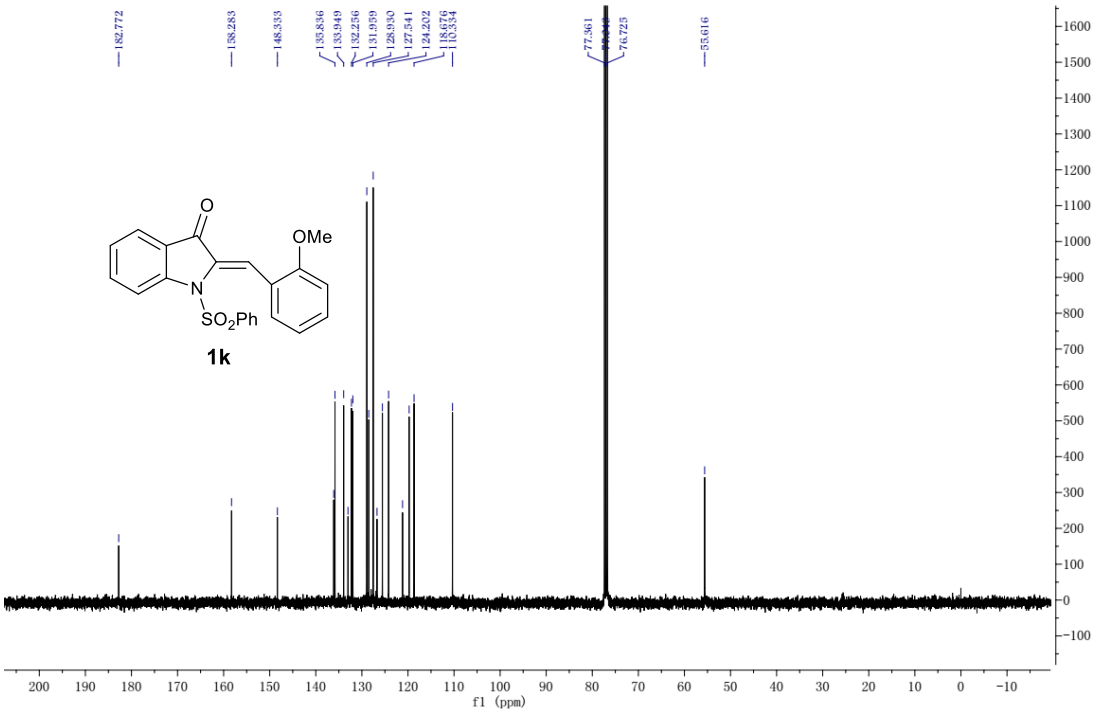

8.192
8.171
8.062
7.705
7.701
7.686
7.684
7.666
7.662
7.648
7.645
7.627
7.624
7.620
7.608
7.590
7.588
7.578
7.575
7.556
7.540
7.538
7.501
7.482
7.406
7.387
7.367
7.307
7.289
7.274
7.255
7.248
7.237
7.235
7.230
7.206
7.187
7.168
2.543
O
Me
N
SO2Ph
1i
0.95
0.99
1.06
1.84
1.00
1.08
1.01
2.09
1.08
2.28
1.05
2.94
f1 (ppm)

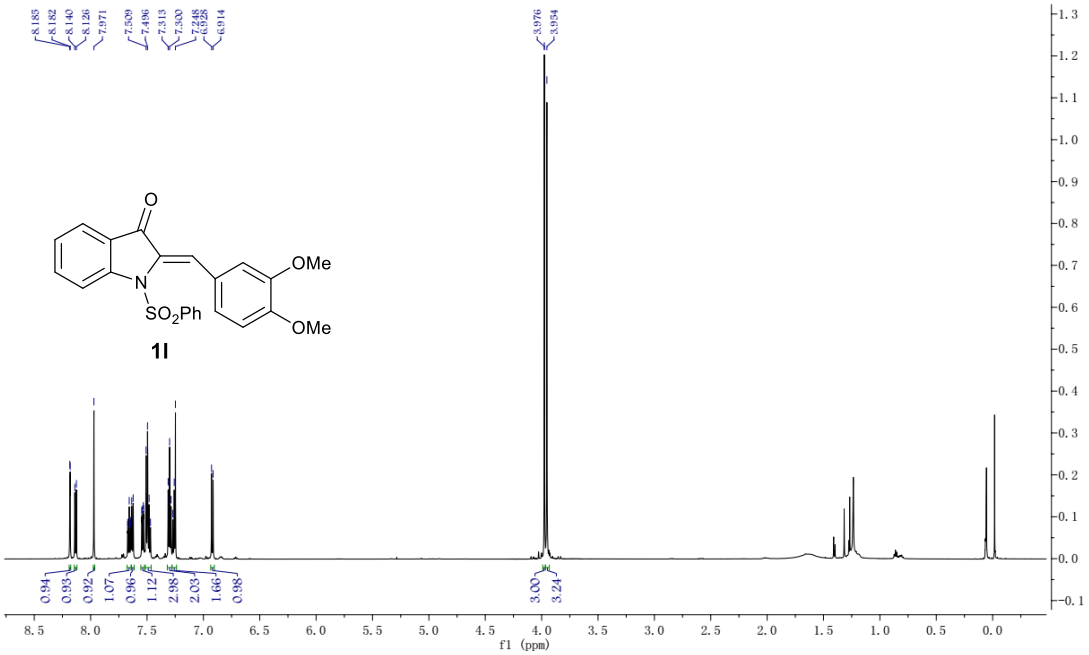

182.886
148.490
137.696
136.221
136.168
134.155
131.820
130.618
130.431
130.076
130.025
129.121
127.398
126.374
123.641
125.259
124.368
118.477
77.361
77.043
76.725
20.250
O
Me
N
SO2Ph
1i
f1 (ppm)

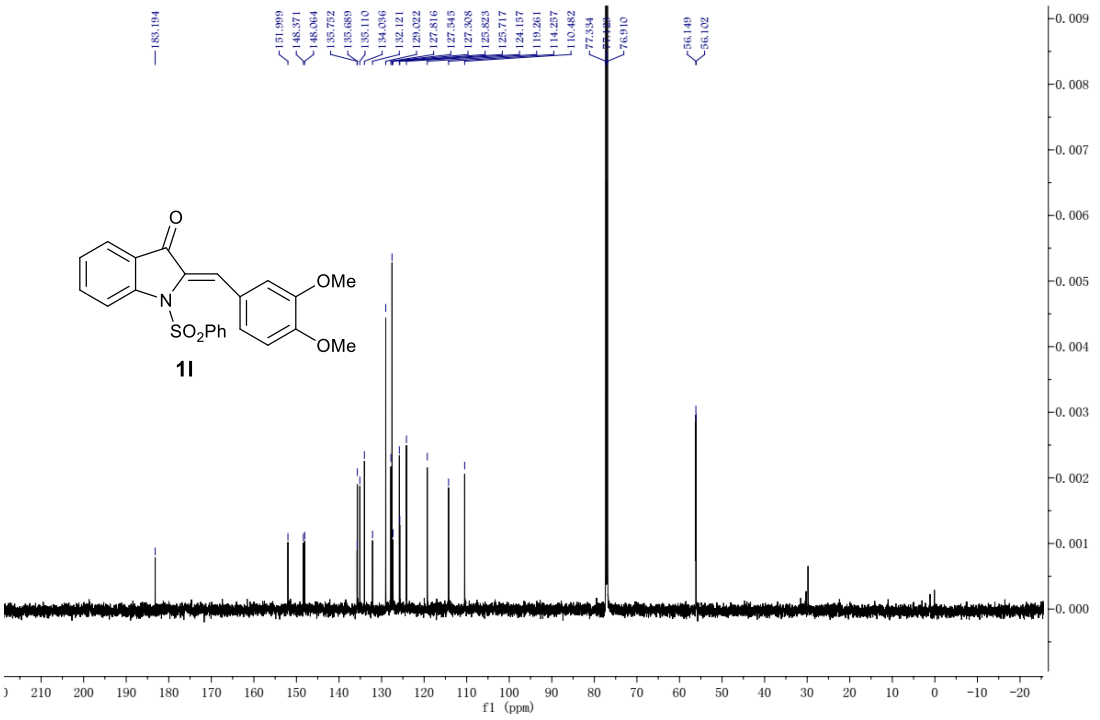

O
N
SO2Ph
1j
f1 (ppm)

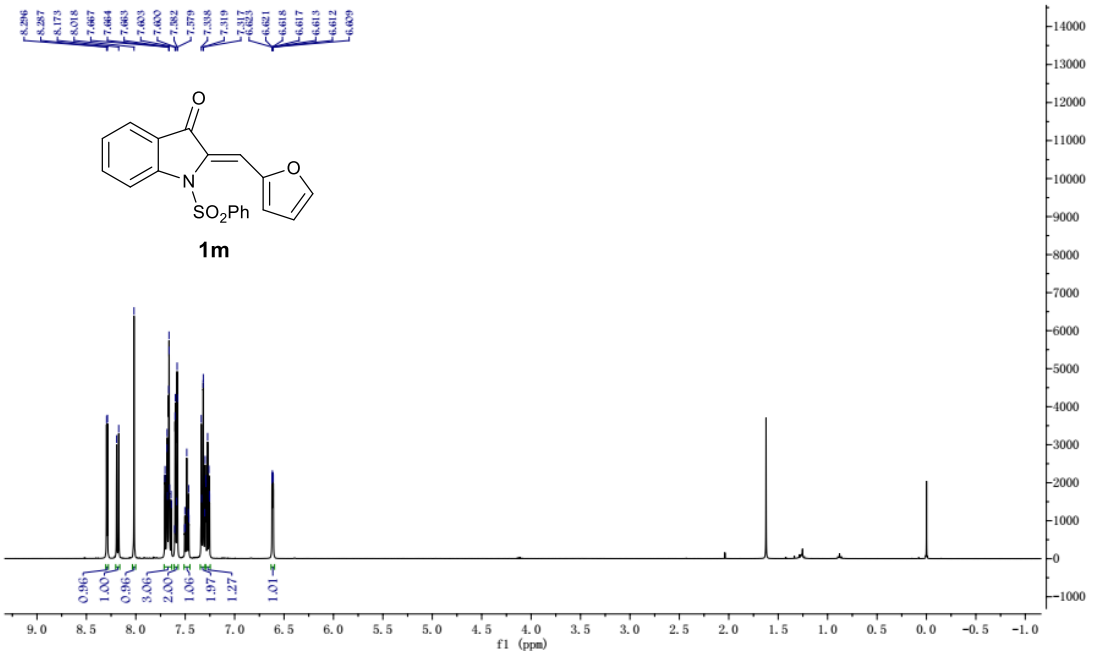

O
N
SO2Ph
1j
f1 (ppm)

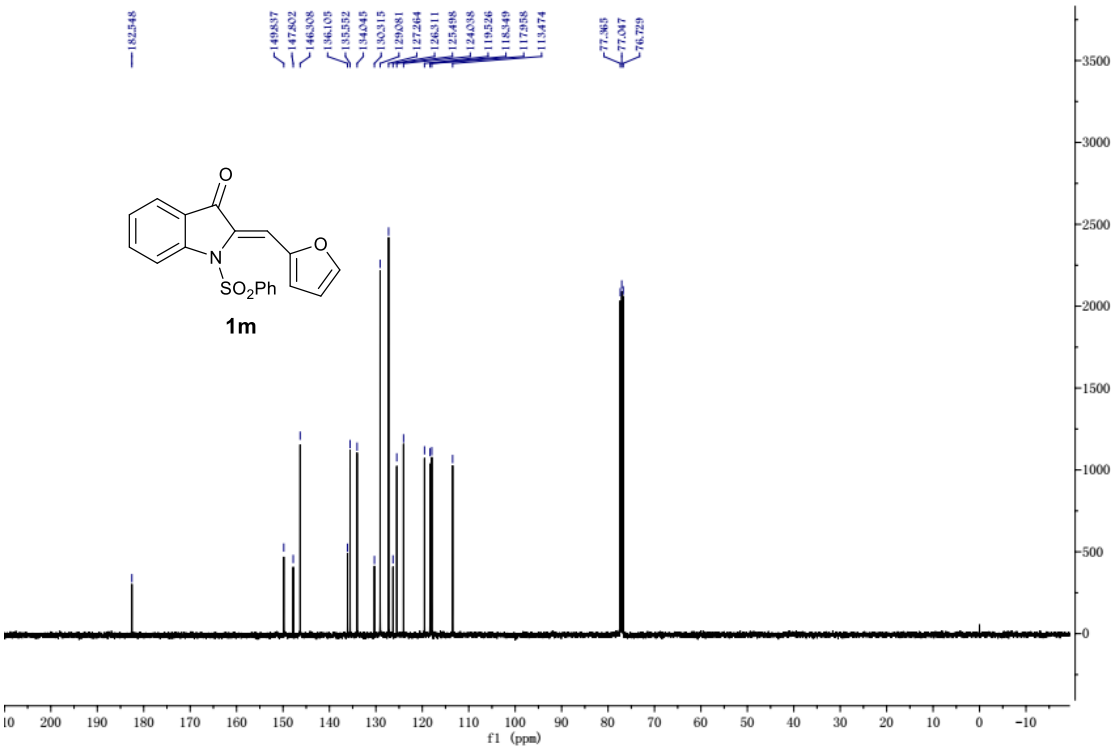

8.229
8.169
8.148
7.819
7.816
7.800
7.797
7.662
7.659
7.656
7.641
7.636
7.633
7.615
7.611
7.589
7.521
7.503
7.406
7.370
7.351
7.331
7.257
7.240
6.965
6.936
6.915
3.884
O
OMe
N
SO2Ph
1k
1.00
1.04
1.08
4.28
1.12
1.26
2.21
1.40
1.08
1.06
3.15
f1 (ppm)

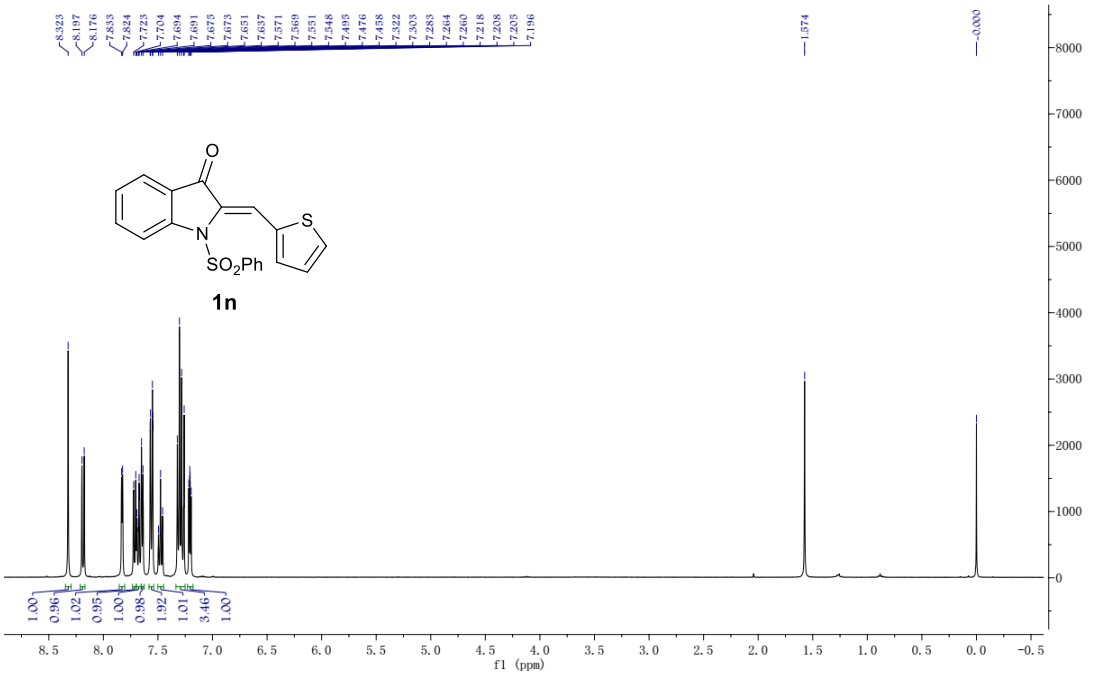

182.772
158.283
148.333
135.836
133.949
132.256
131.959
128.930
127.541
124.202
118.676
110.334
77.361
76.723
55.616
O
OMe
N
SO2Ph
1k
f1 (ppm)

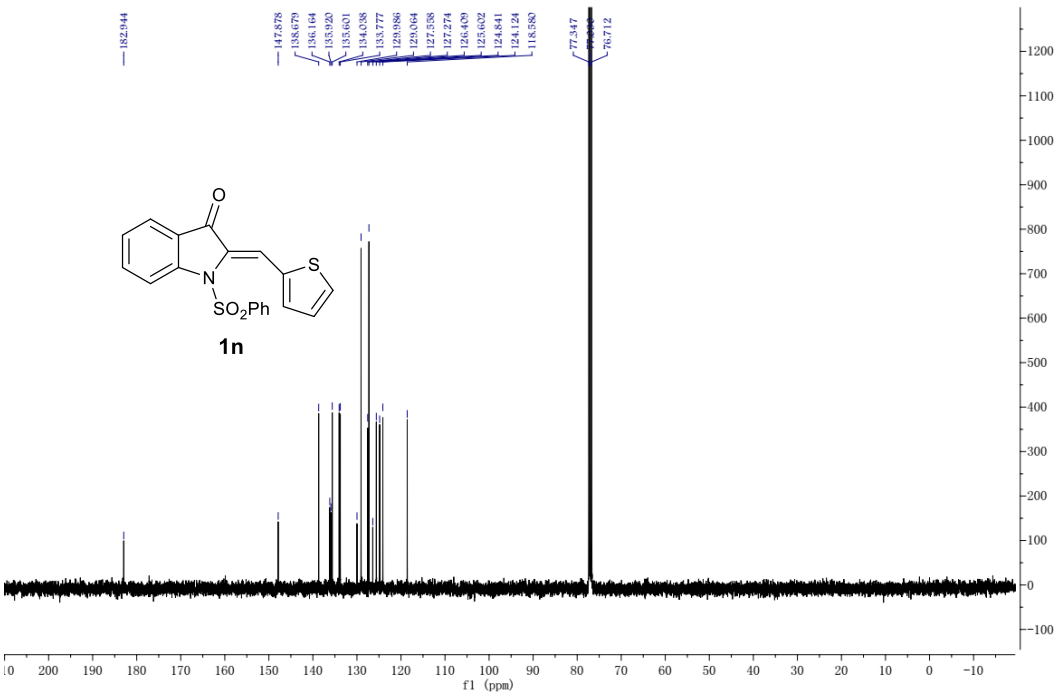

8.183
8.182
8.140
8.126
7.971
7.529
7.496
7.313
7.300
7.248
6.928
6.914
3.976
3.954
O
N
SO2Ph
OMe
OMe
1l
0.94
0.93
0.92
1.07
0.96
1.12
2.98
2.03
1.66
0.98
3.00
3.24
f1 (ppm)

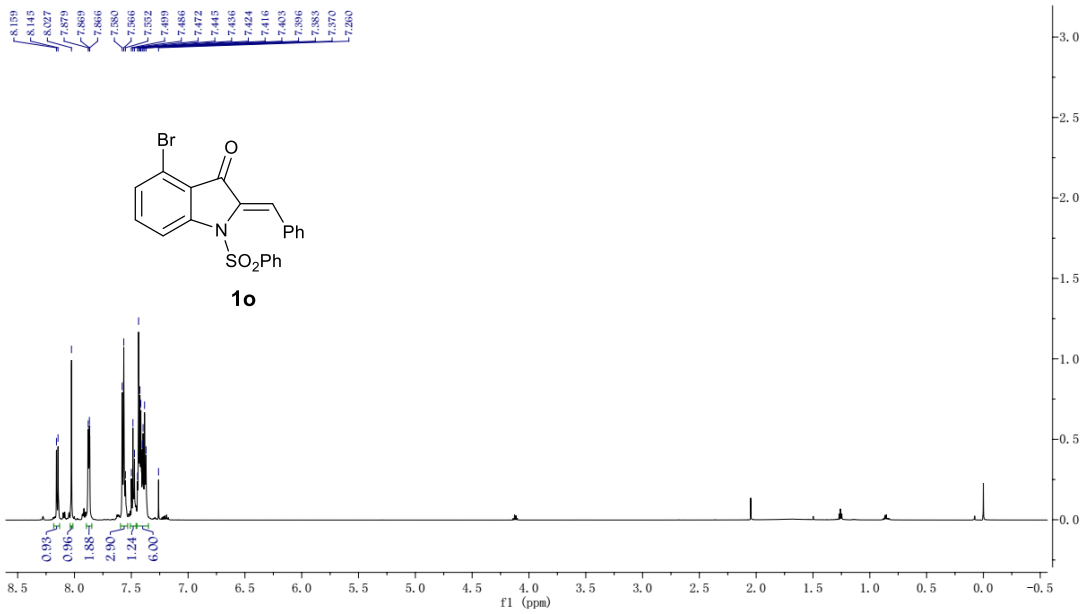

183.194
151.999
148.371
148.064
135.752
135.689
135.110
134.036
132.121
129.022
127.816
127.545
127.308
125.823
125.717
124.157
119.261
114.257
110.482
77.334
76.910
56.149
56.102
O
N
SO2Ph
OMe
OMe
1l
f1 (ppm)

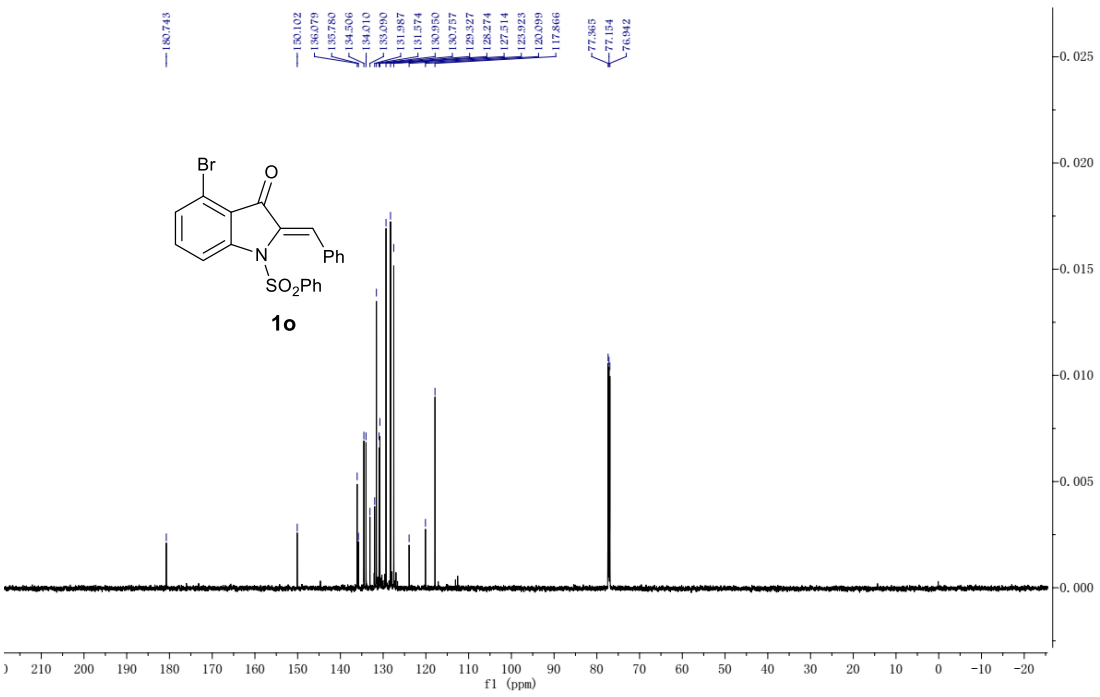

8.296
8.287
8.173
8.018
7.667
7.664
7.663
7.603
7.600
7.582
7.579
7.338
7.319
6.621
6.618
6.617
6.613
6.612
6.609
O
N
SO2Ph
O
1m
0.96
1.00
0.96
3.06
2.00
1.06
1.97
1.27
1.01
f1 (ppm)

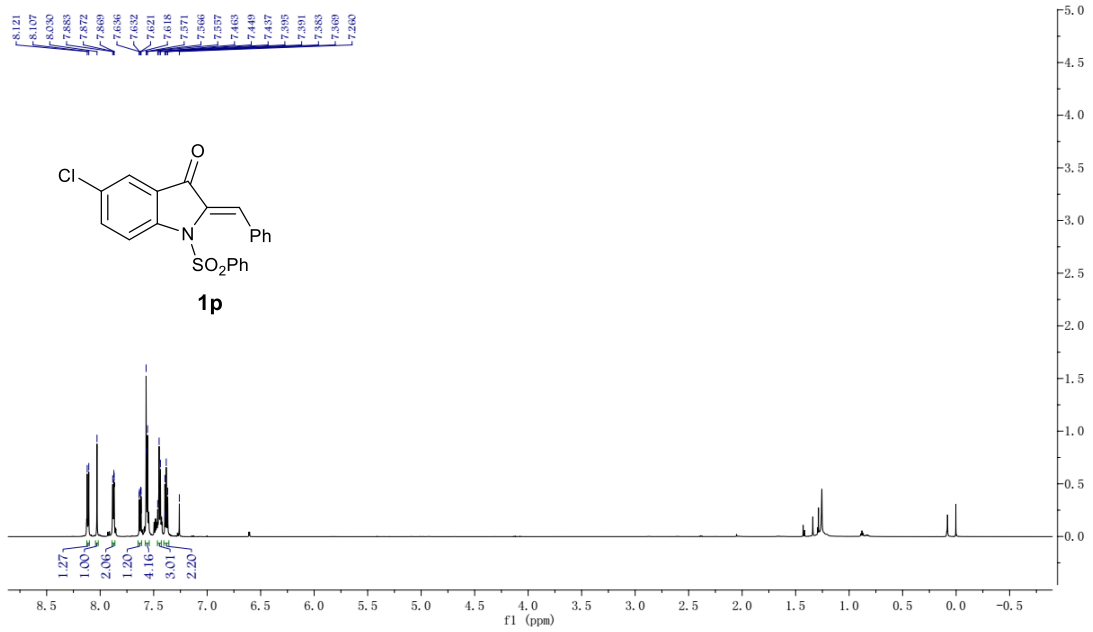

182.548
149.837
147.802
146.308
136.105
135.552
134.045
130.315
129.081
127.264
126.311
125.498
124.038
119.526
118.349
117.958
113.474
77.365
77.047
76.729
O
N
SO2Ph
O
1m
f1 (ppm)

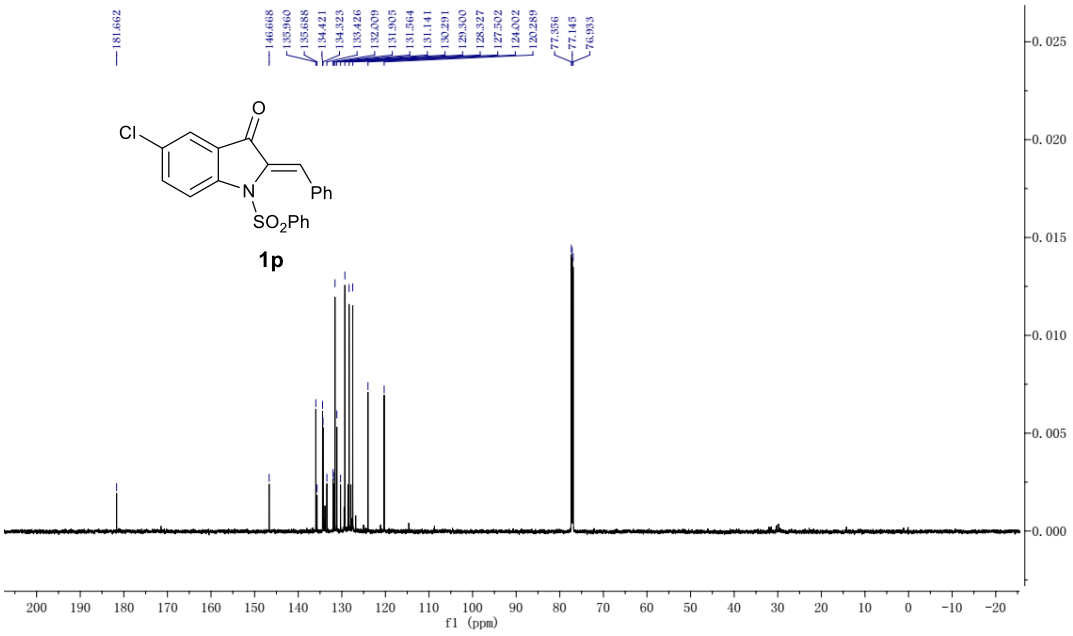

8.323
8.197
8.176
7.833
7.824
7.723
7.704
7.694
7.691
7.675
7.673
7.651
7.637
7.571
7.569
7.551
7.548
7.495
7.476
7.458
7.322
7.303
7.283
7.264
7.260
7.218
7.208
7.205
7.196
1.574
0.000
O
N
S
SO2Ph
1n
1.00
0.96
1.02
0.95
1.00
0.98
1.92
1.01
3.46
1.00
f1 (ppm)

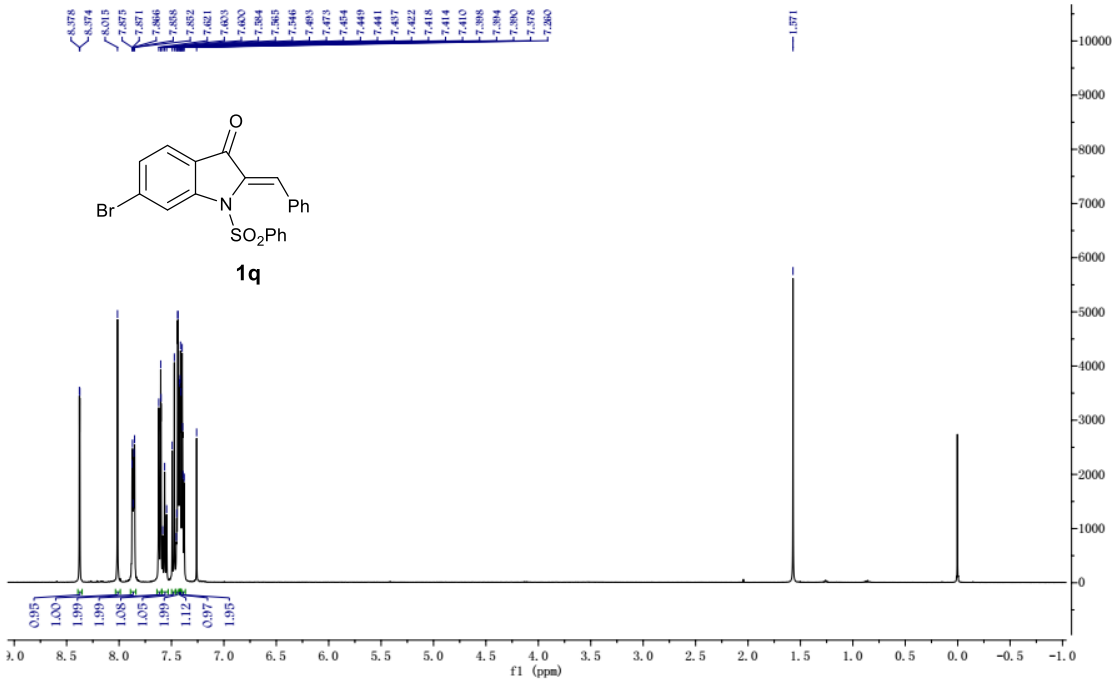

182.944
147.878
138.679
136.164
135.920
135.601
134.038
133.777
129.986
129.064
127.538
127.274
126.409
123.602
124.841
124.124
118.580
77.347
76.712
O
N
S
SO2Ph
1n
f1 (ppm)


8.159
8.143
8.027
7.879
7.869
7.866
7.580
7.566
7.532
7.499
7.486
7.472
7.445
7.436
7.424
7.416
7.403
7.396
7.383
7.370
7.260
Br
O
N
Ph
SO2Ph
1o
0.93
0.96
1.88
2.90
1.24
6.00
f1 (ppm)

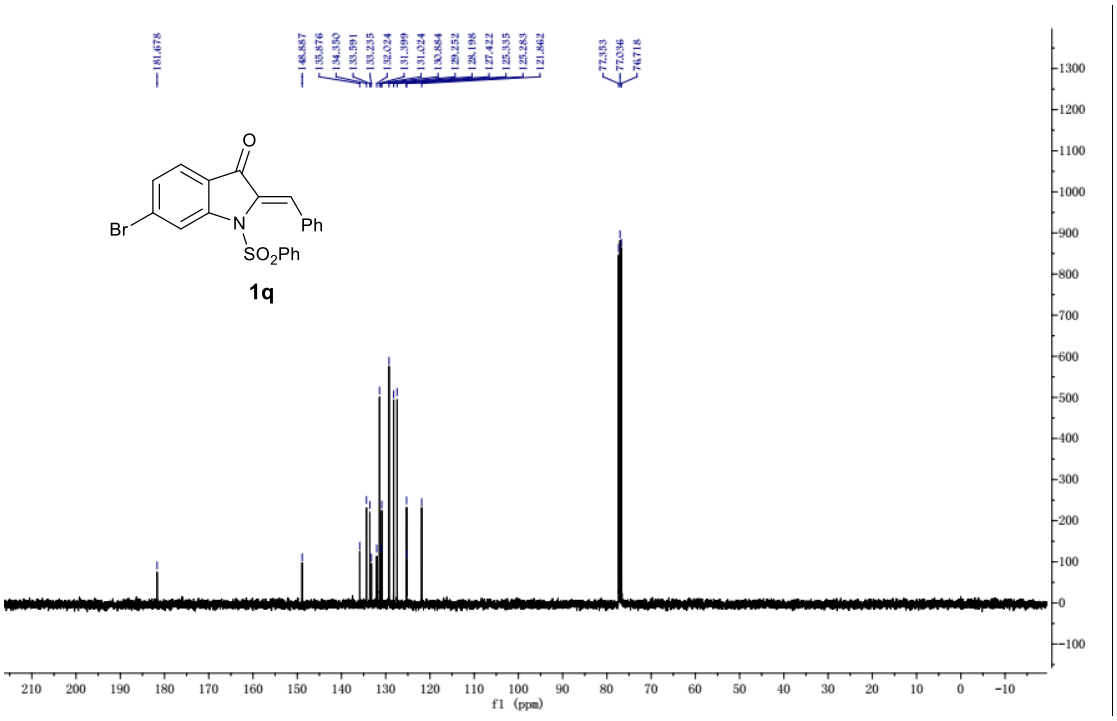

180.743
150.102
136.079
135.780
134.506
134.010
133.090
131.987
131.574
130.950
130.757
129.327
128.274
127.514
123.923
120.099
117.866
77.365
77.154
76.942
Br
O
N
Ph
SO2Ph
1o
f1 (ppm)


8.121
8.107
8.030
7.883
7.872
7.869
7.636
7.632
7.621
7.618
7.571
7.566
7.557
7.463
7.449
7.437
7.395
7.391
7.383
7.369
7.260
Cl
O
N
Ph
SO2Ph
1p
1.27
1.00
2.06
1.20
4.16
3.01
2.20
f1 (ppm)

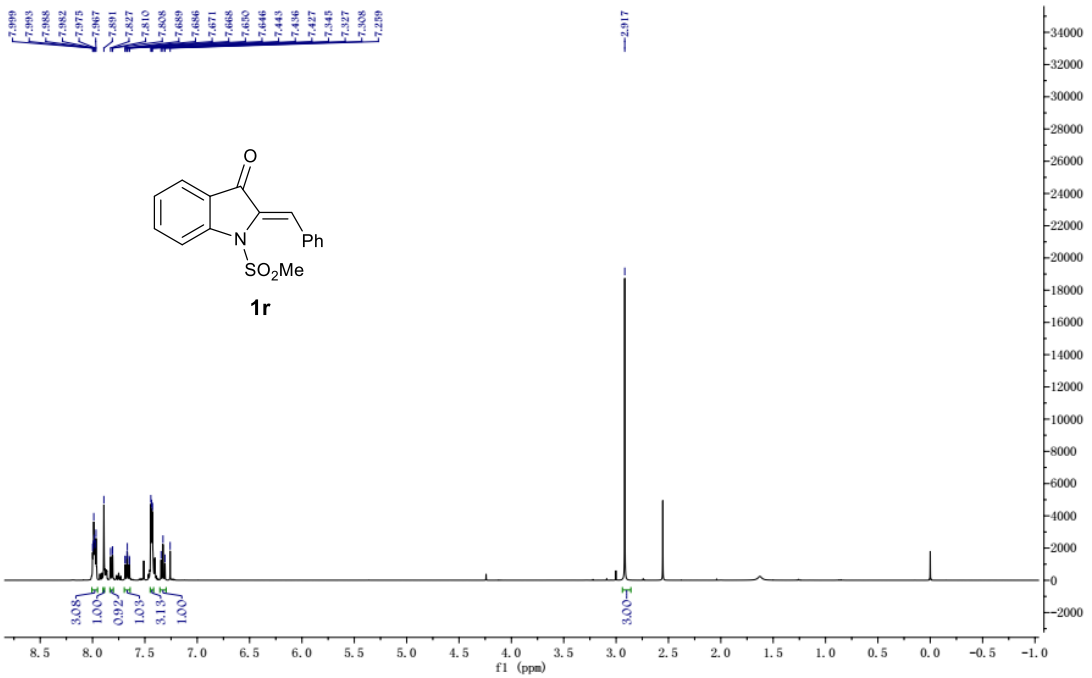

181.662
146.668
135.960
135.688
134.421
134.323
133.426
132.009
131.935
131.564
131.141
130.291
129.300
128.327
127.502
124.002
120.289
77.356
77.145
76.933
Cl
O
N
Ph
SO2Ph
1p
f1 (ppm)

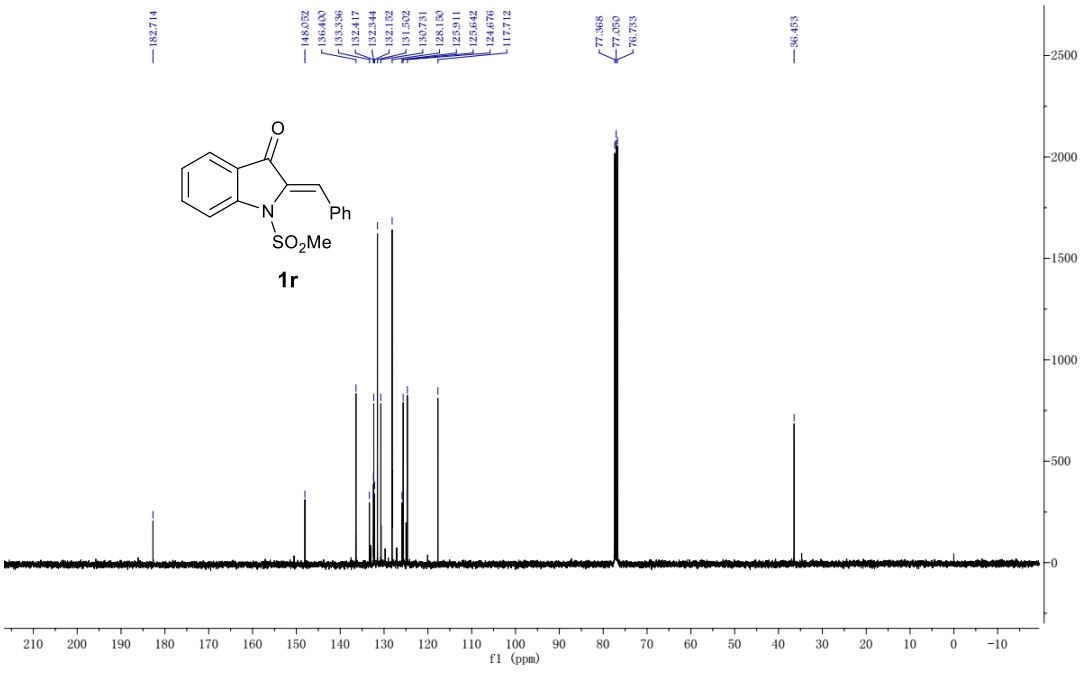


1q

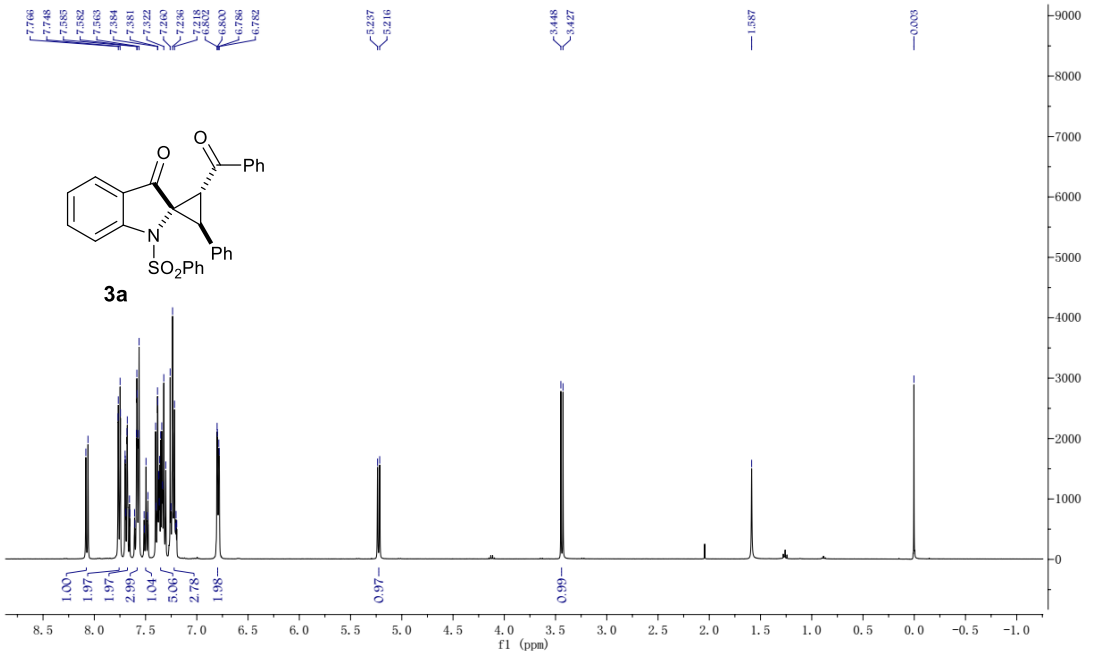


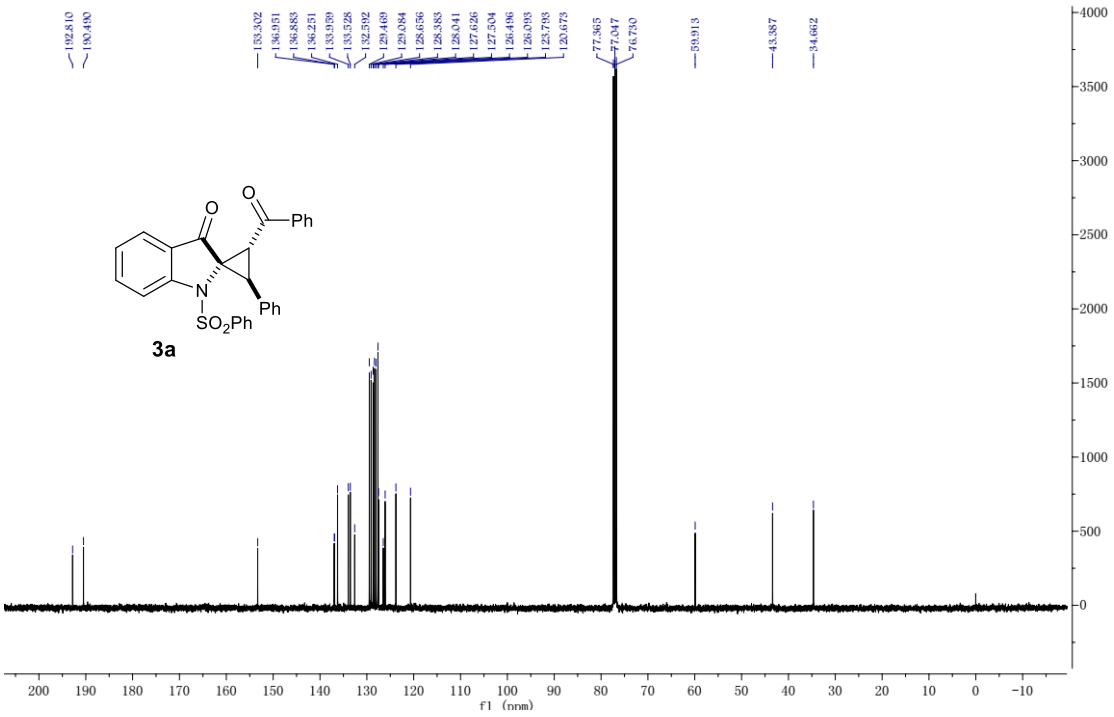
1q

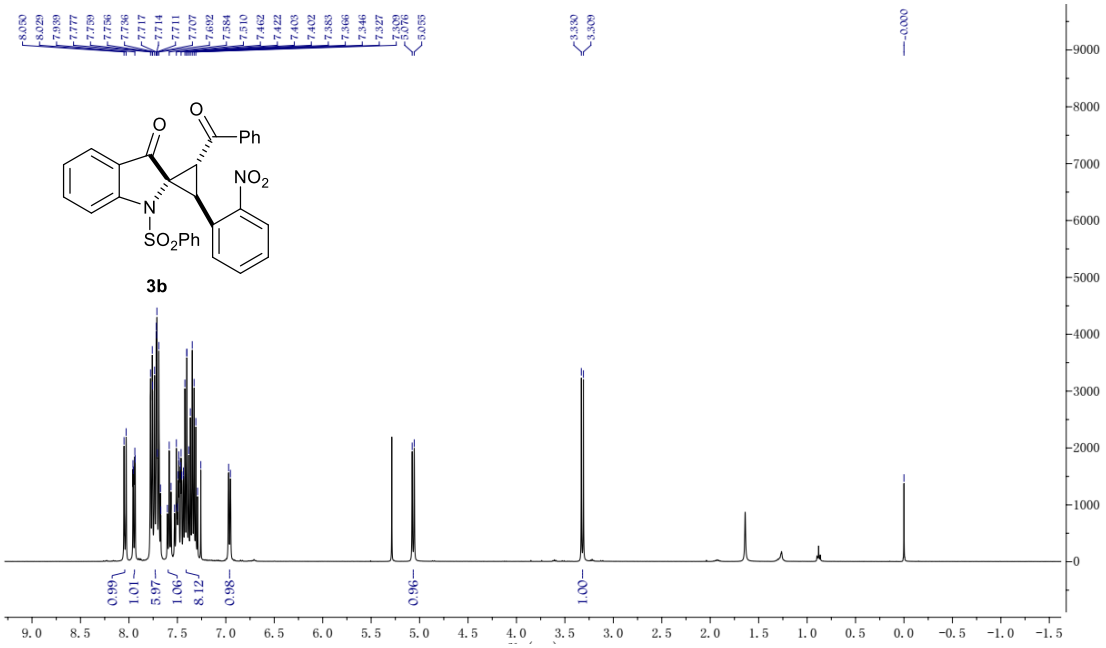

7.999
7.993
7.988
7.982
7.975
7.967
7.891
7.827
7.810
7.808
7.689
7.686
7.671
7.668
7.650
7.646
7.443
7.436
7.427
7.345
7.327
7.308
7.259
2.917
O
N
Ph
SO2Me
1r
3.08
1.00
0.92
1.03
3.13
1.00
3.00
f1 (ppm)

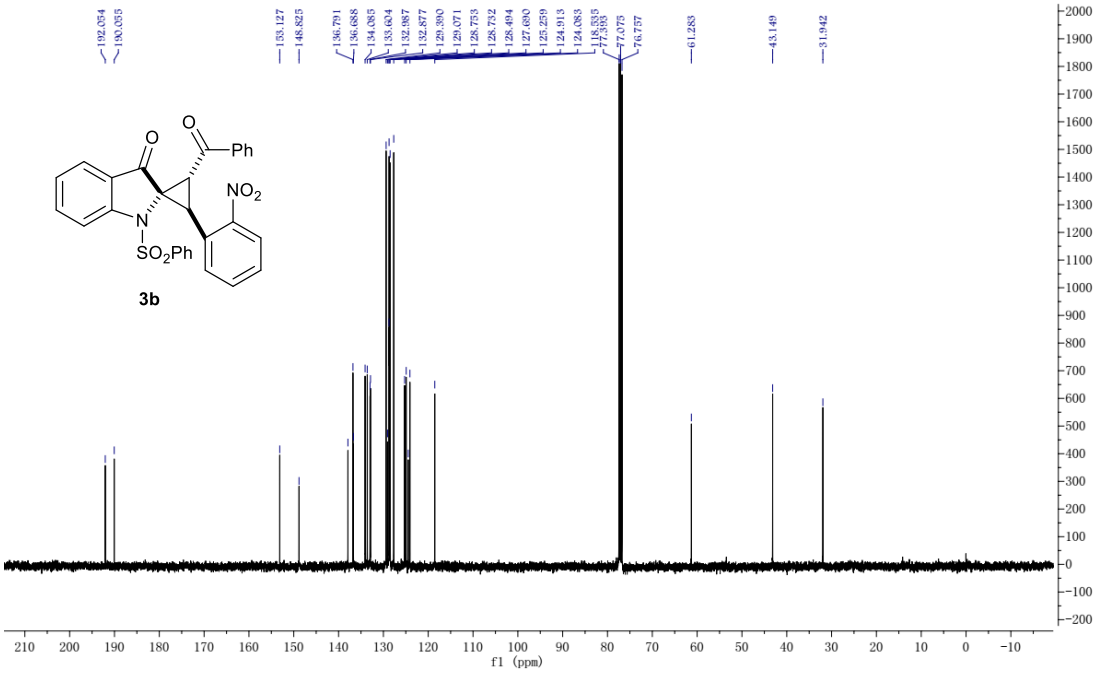

182.714
148.032
136.400
133.336
132.417
132.344
132.152
131.502
130.731
128.150
125.911
125.642
124.676
117.712
77.368
77.050
76.733
36.453
O
N
Ph
SO2Me
1r
f1 (ppm)

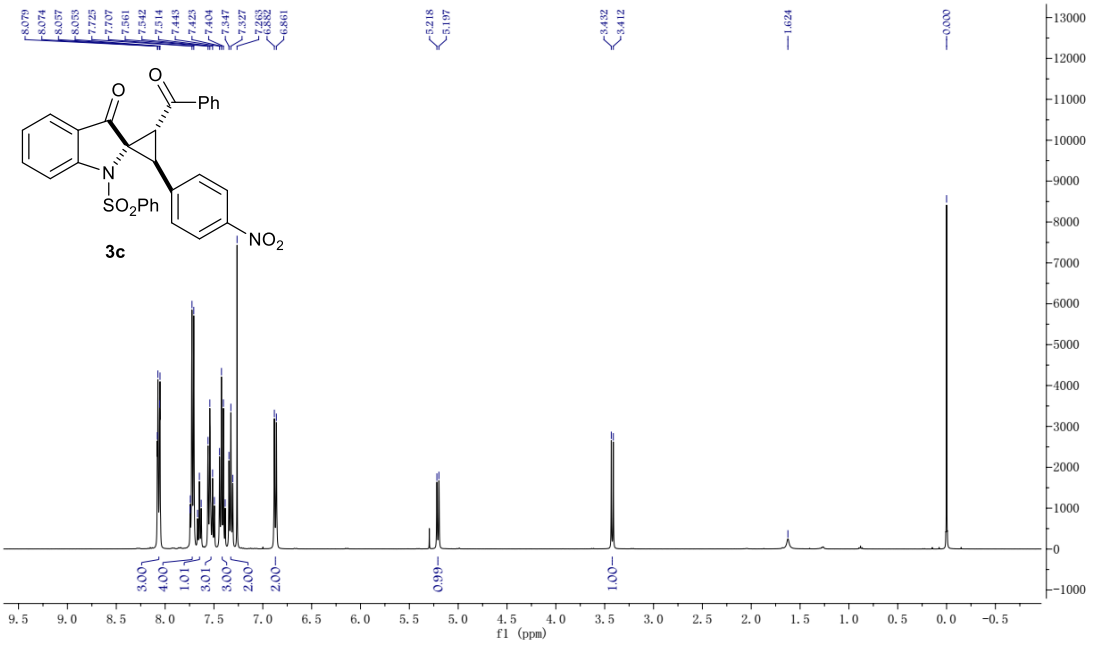
7. NMR Spectra of NMR Spectra of the Spiro-pseudoindoxyl Derivatives 3

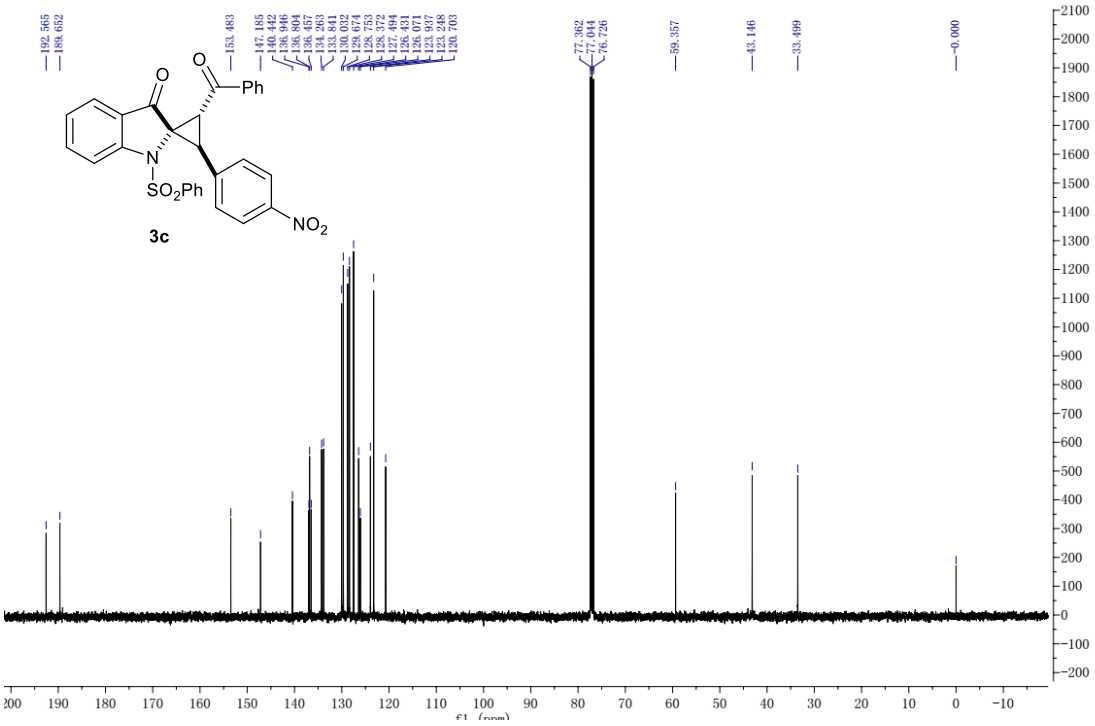


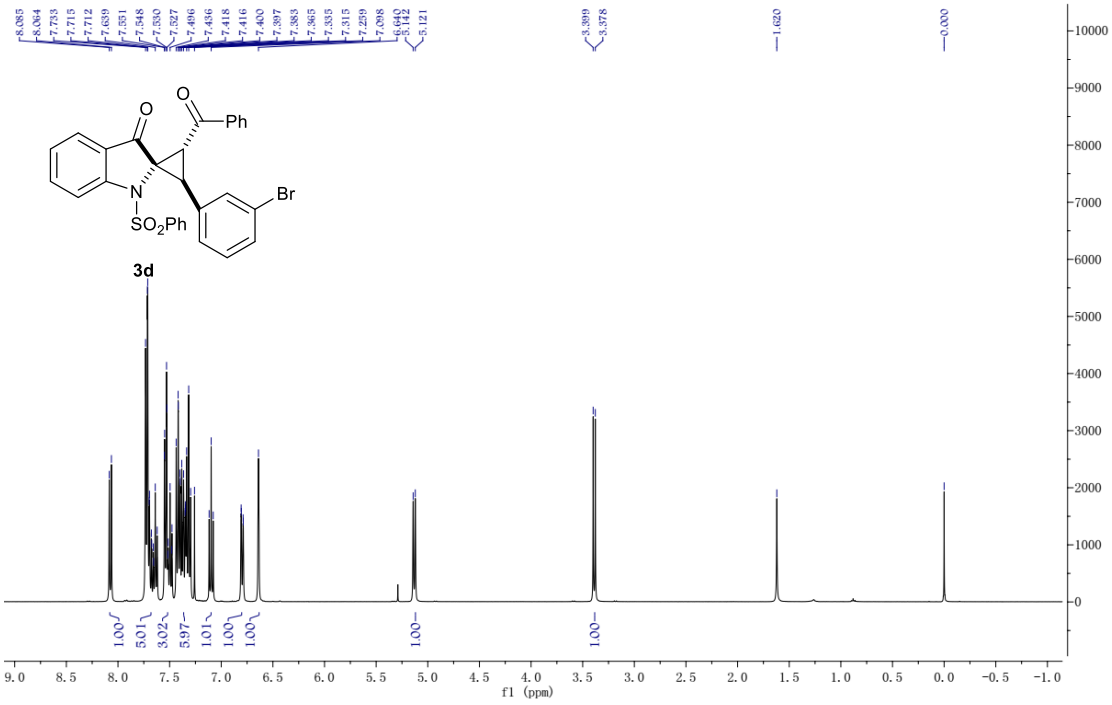


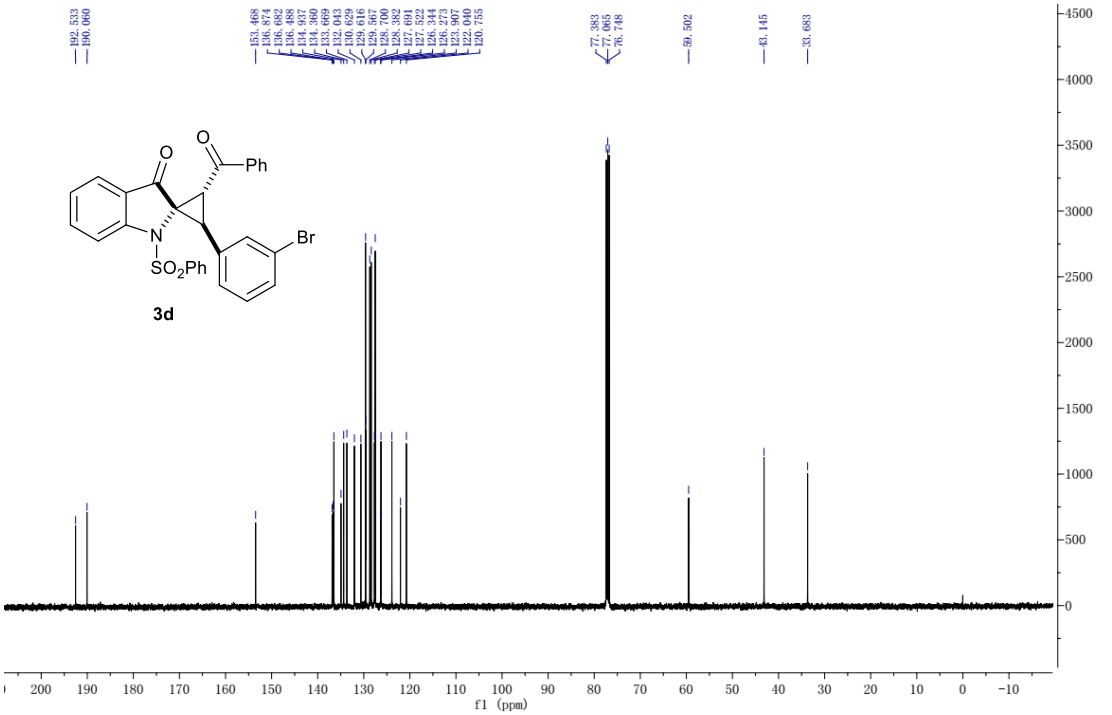

3b
0.99
1.01
5.97
1.06
8.12
0.98
0.96
1.00

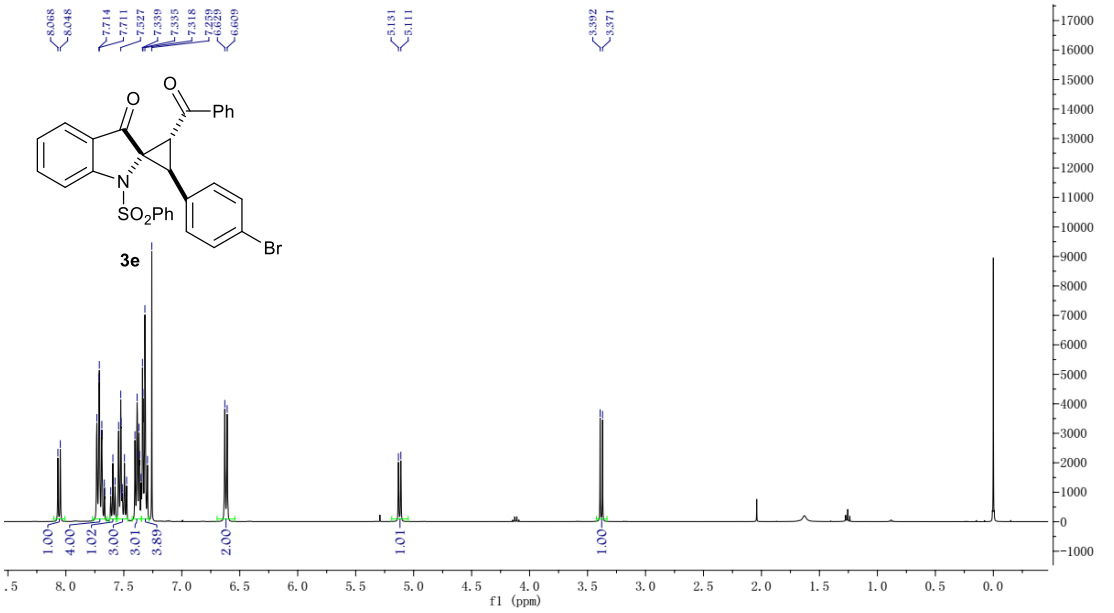

3b
f1 (ppm)

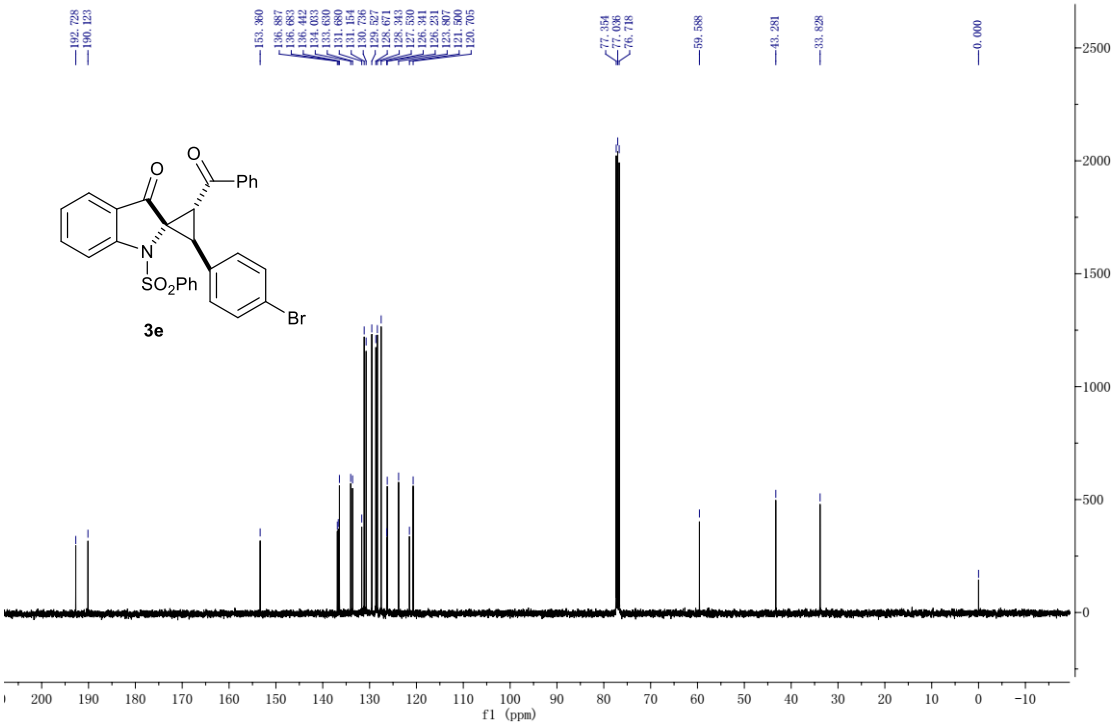

8.079
8.074
8.057
8.053
7.725
7.707
7.561
7.542
7.514
7.443
7.423
7.404
7.347
7.327
7.263
6.882
6.861
5.218
5.197
3.432
3.412
1.624
0.000
O
Ph
N
SO2Ph
NO2
3c
3.00
4.00
1.01
3.01
3.00
2.00
2.00
0.99
1.00
f1 (ppm)

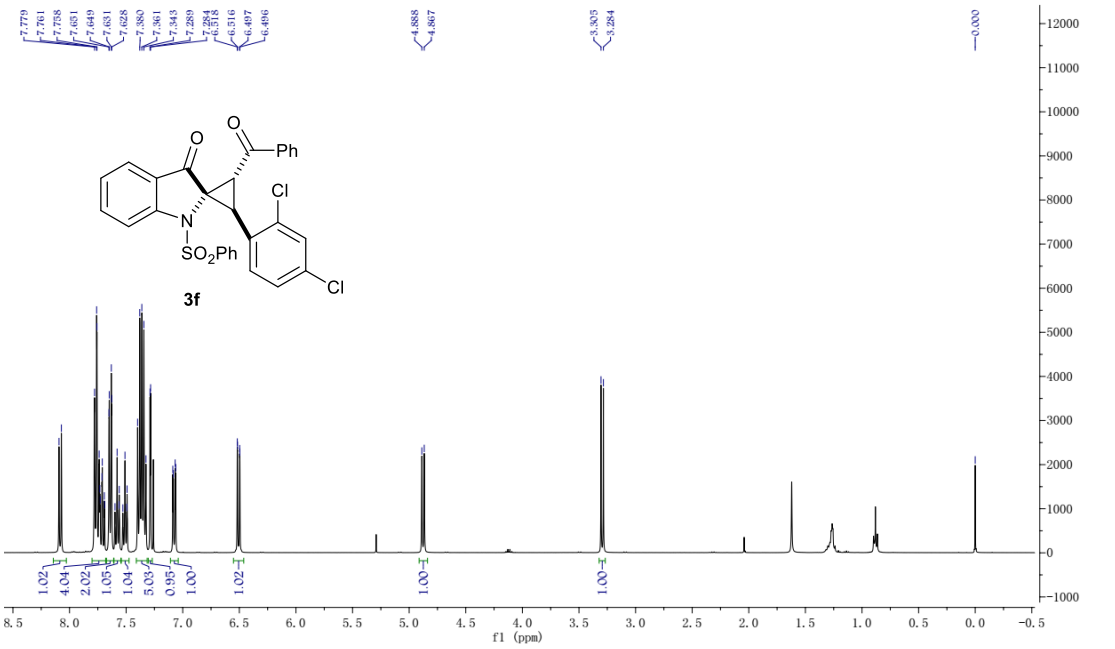

192.565
189.652
153.483
147.185
140.442
136.946
134.904
134.457
134.263
133.841
130.032
129.674
128.753
128.372
127.404
126.431
126.071
123.937
123.248
120.703
77.362
77.044
76.726
59.357
43.146
33.499
0.000
O
Ph
N
SO2Ph
NO2
3c
f1 (ppm)


8.085
8.064
7.733
7.715
7.712
7.639
7.551
7.548
7.530
7.527
7.496
7.436
7.418
7.416
7.400
7.397
7.383
7.365
7.335
7.315
7.259
7.208
6.642
6.142
5.121
3.399
3.378
1.620
0.000
O
Ph
O
N
SO2Ph
Br
3d
1.00
5.01
3.02
5.97
1.01
1.00
1.00
1.00
1.00
f1 (ppm)


192.533
190.060
153.468
136.874
136.682
136.488
134.937
134.360
133.669
132.616
130.629
129.616
129.567
128.700
128.382
127.691
127.522
126.344
126.273
123.907
122.040
120.755
77.383
77.065
76.748
60.502
43.145
33.683
O
Ph
O
N
SO2Ph
Br
3d
f1 (ppm)


8.068
8.048
7.714
7.711
7.527
7.339
7.335
7.318
7.259
6.629
6.609
5.131
5.111
3.392
3.371
O
Ph
O
N
SO2Ph
Br
3e
1.00
4.00
1.02
3.00
3.01
3.89
2.00
1.01
1.00
f1 (ppm)


192.728
190.123
153.360
136.887
136.883
136.442
134.033
133.630
131.690
131.154
130.736
129.527
128.671
128.343
127.530
126.544
126.251
123.807
121.500
120.705
77.354
77.036
76.718
59.588
43.281
33.828
0.000
O
Ph
O
N
SO2Ph
Br
3e
f1 (ppm)


7.779
7.761
7.758
7.651
7.649
7.631
7.628
7.380
7.361
7.343
7.289
7.284
6.518
6.516
6.497
6.496
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3.305
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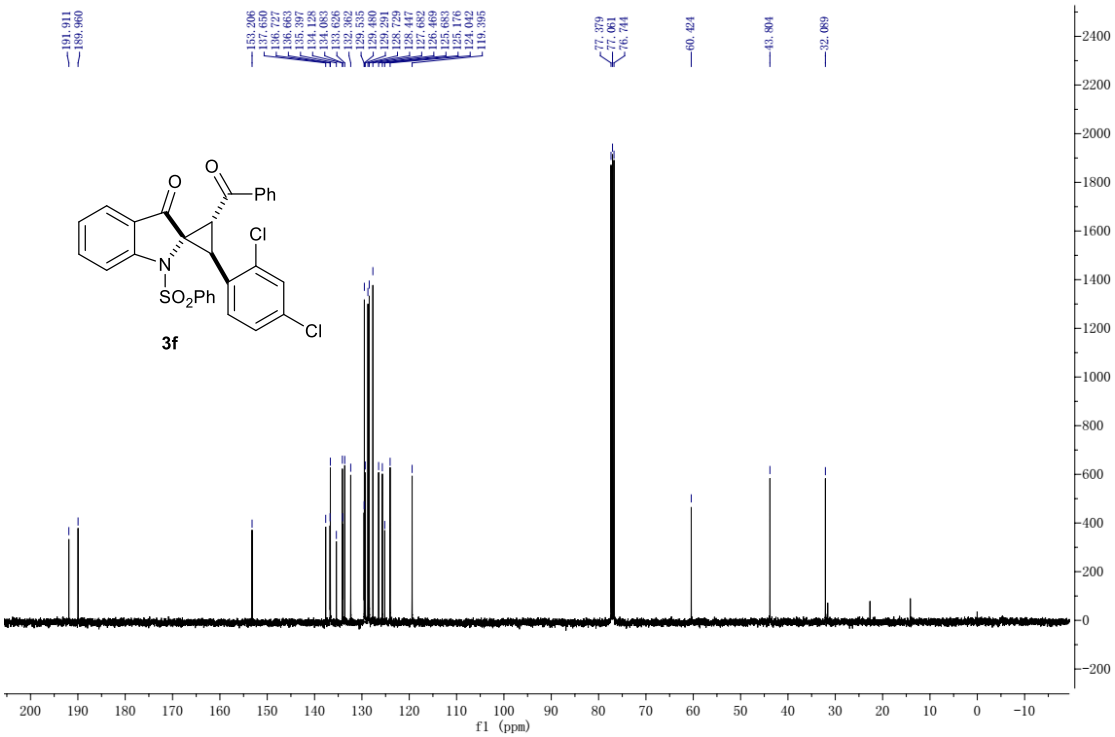
Cl
N
SO2Ph
Cl
3f
f1 (ppm)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128.447
127.468
126.469
125.683
125.176
124.042
119.395
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32.089
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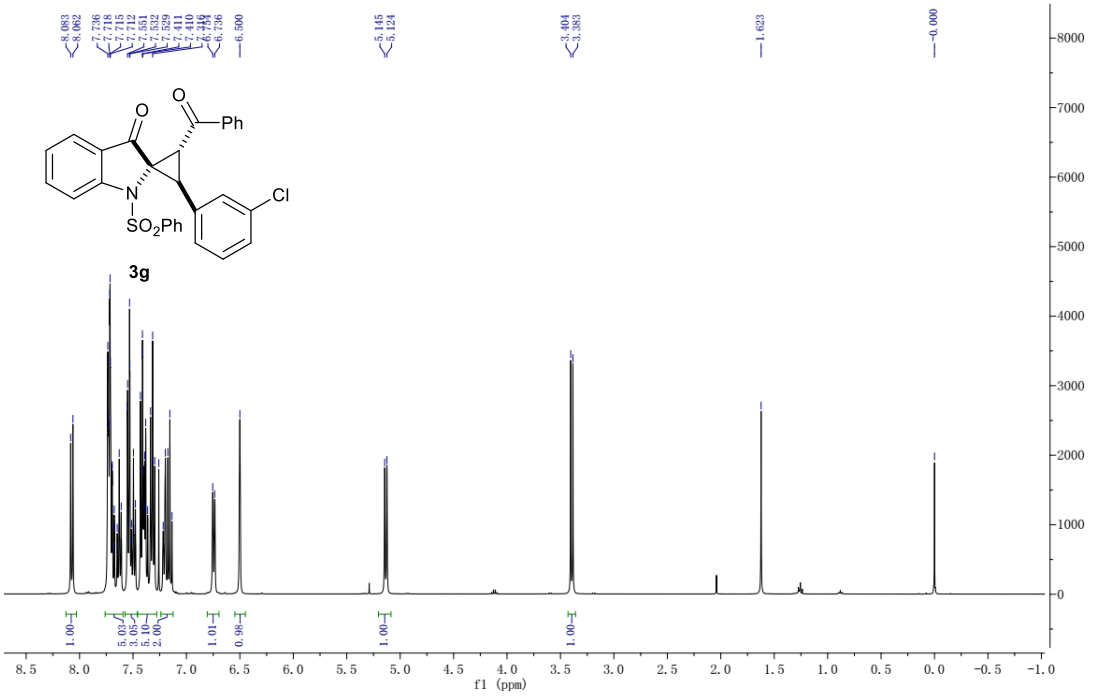
Ph
Cl
N
SO2Ph
Cl
3f
f1 (ppm)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7.532
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7.410
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6.500
5.145
5.124
3.404
3.383
1.623
0.000
O
O
Ph
N
SO2Ph
Cl
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3.05
5.10
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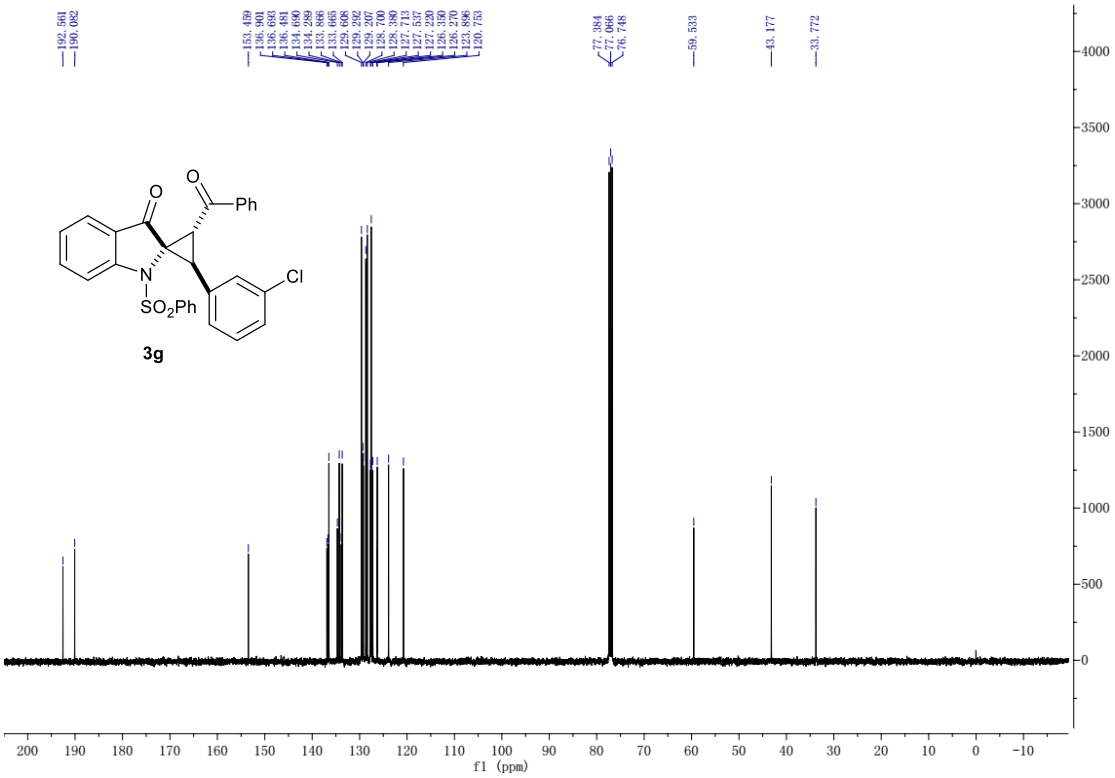
1.00
f1 (ppm)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128.369
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127.537
127.230
126.350
126.270
123.896
120.753
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33.772
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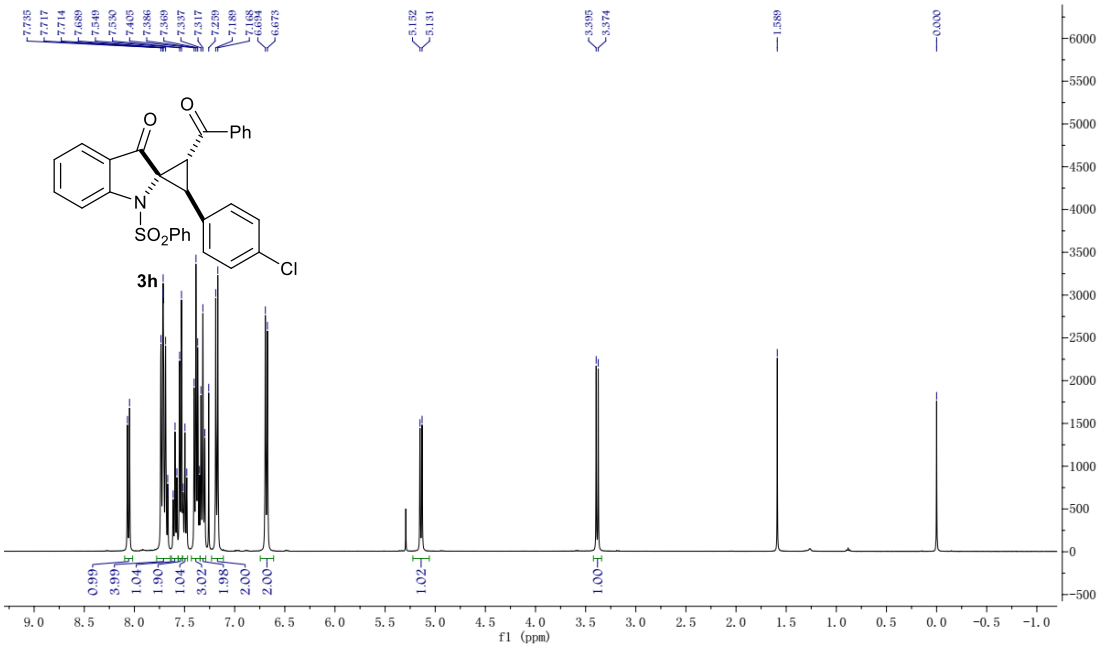
O
Ph
N
SO2Ph
Cl
3g
f1 (ppm)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6.694
6.673
5.132
5.131
3.395
3.374
1.589
0.000
O
Ph
O
N
SO2Ph
Cl
3h
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1.04
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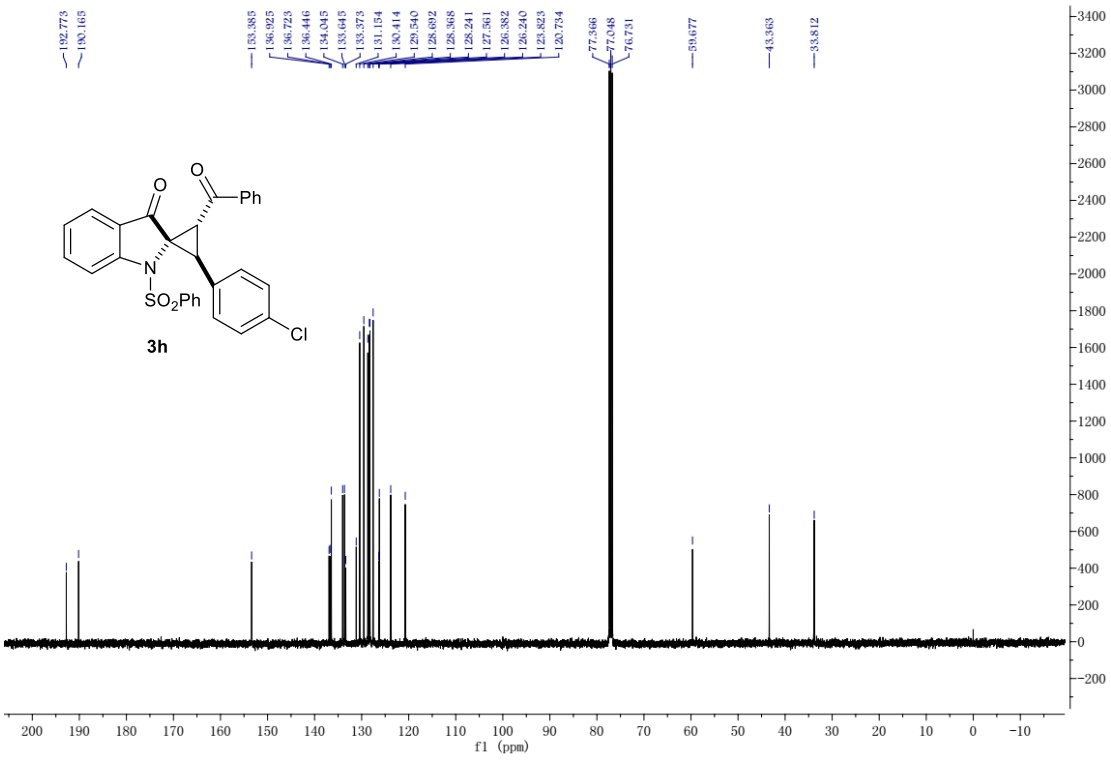
2.00
1.02
1.00
f1 (ppm)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128.241
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126.382
126.240
123.823
120.734
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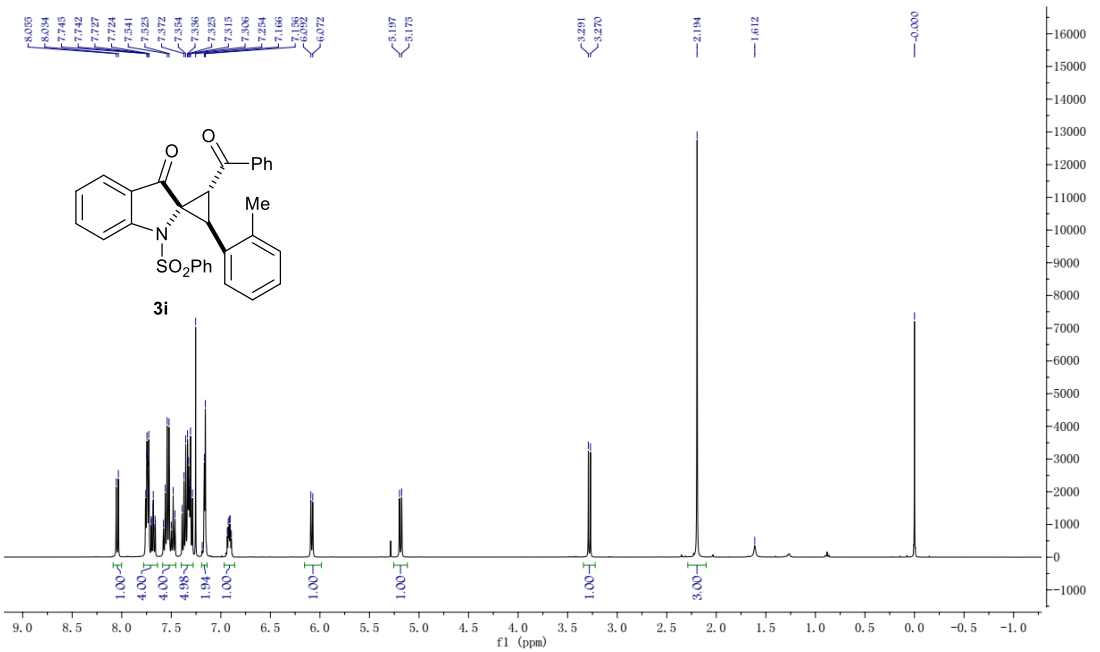
Ph
O
N
SO2Ph
Cl
3h
f1 (ppm)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7.306
7.254
7.166
7.156
6.092
6.072
5.197
5.175
3.291
3.270
2.194
1.612
-0.000
O
Ph
Me
N
SO2Ph
3i
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4.00
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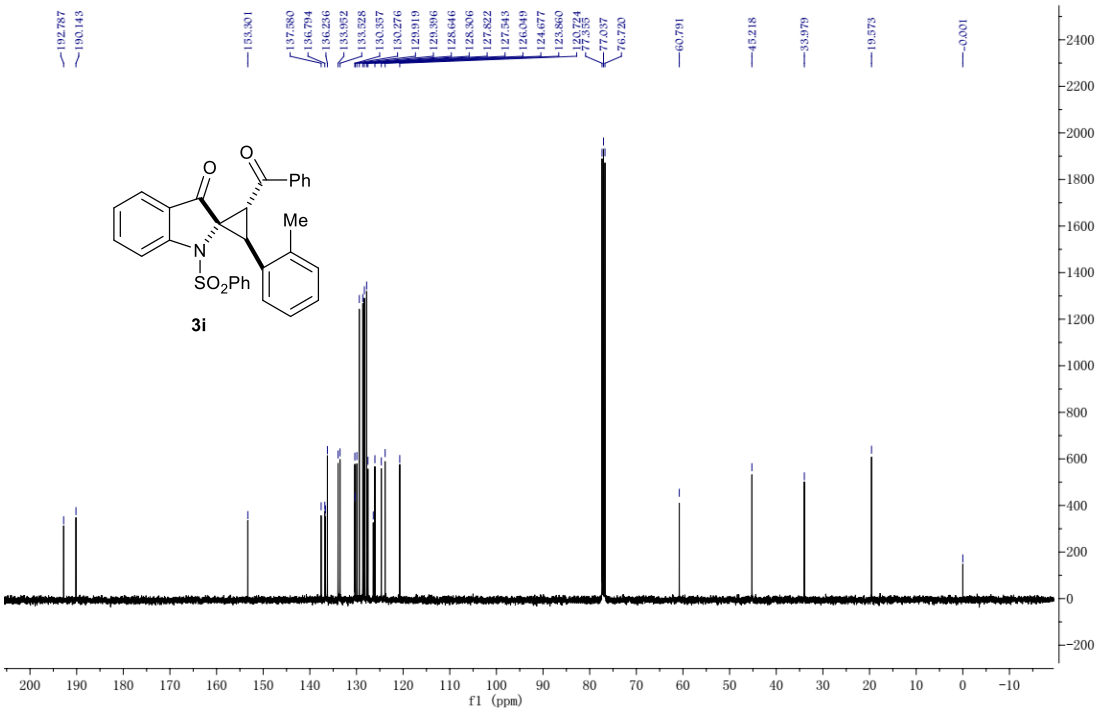
1.00
1.00
1.00
1.00
3.00
f1 (ppm)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128.306
127.822
127.543
126.049
124.677
123.860
77.355
77.037
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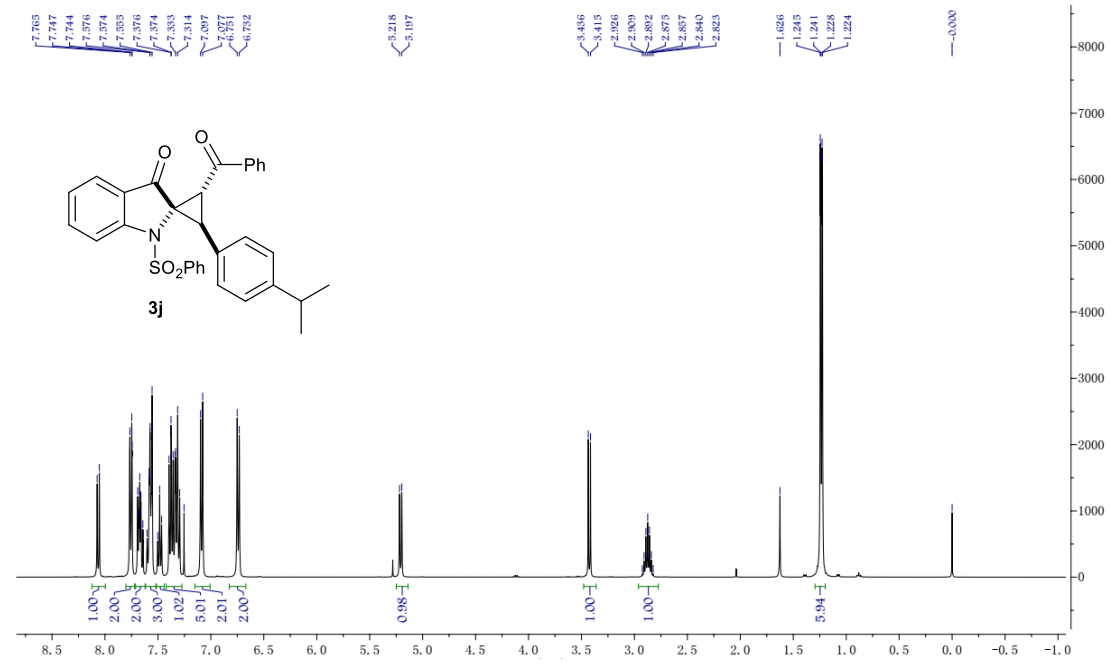
19.573
-0.001
O
Ph
Me
N
SO2Ph
3i
f1 (ppm)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7.374
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7.097
7.077
6.751
6.732
5.218
5.197
3.436
3.415
2.926
2.909
2.892
2.875
2.857
2.840
2.823
1.626
1.245
1.241
1.228
1.224
0.000
O
Ph
N
SO2Ph
3j
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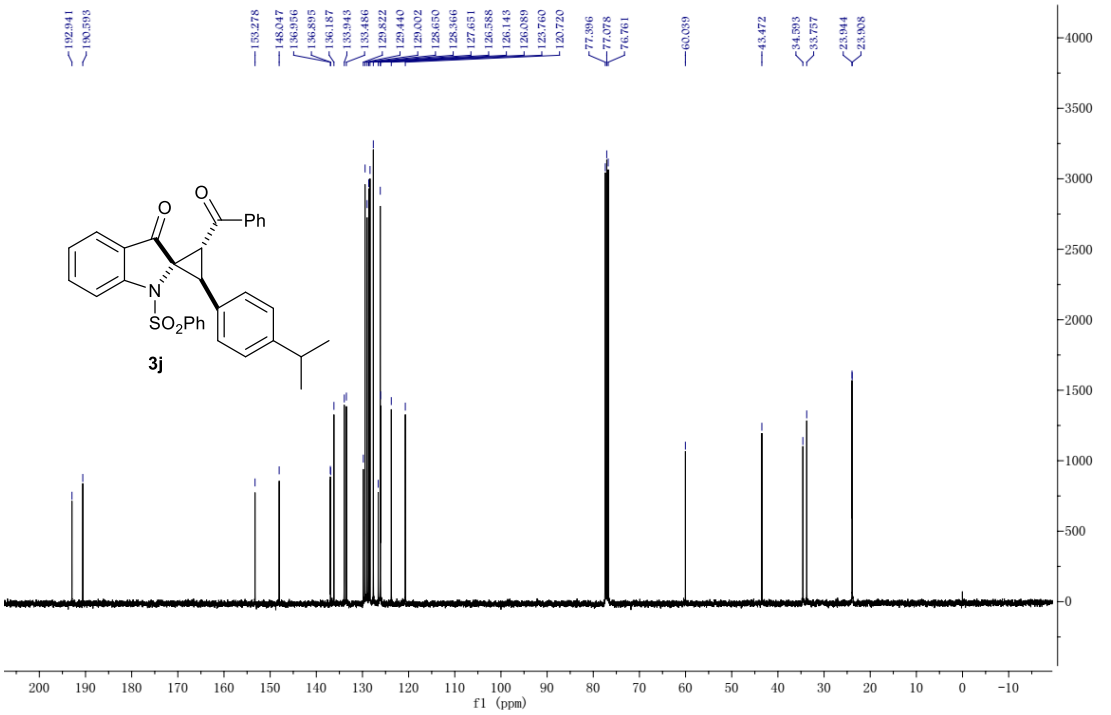
2.00
2.00
3.00
1.02
5.01
2.01
2.00
0.98
1.00
1.00
5.94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128.366
127.651
126.588
126.143
126.089
123.760
120.720
77.396
77.078
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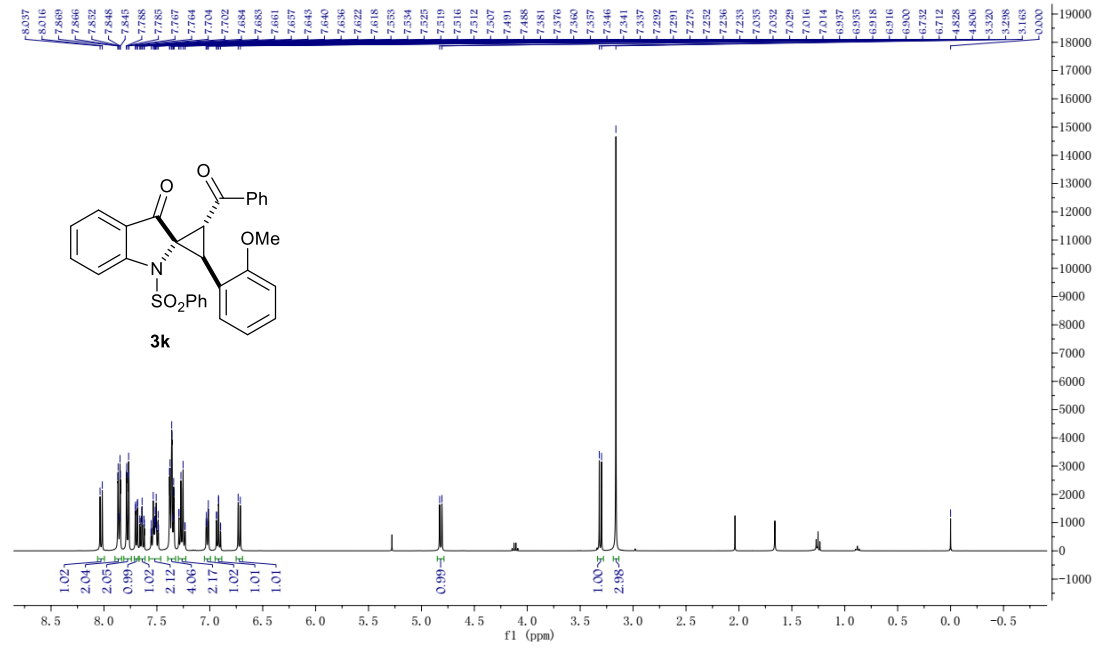
23.944
23.908
O
Ph
N
SO2Ph
3j
f1 (ppm)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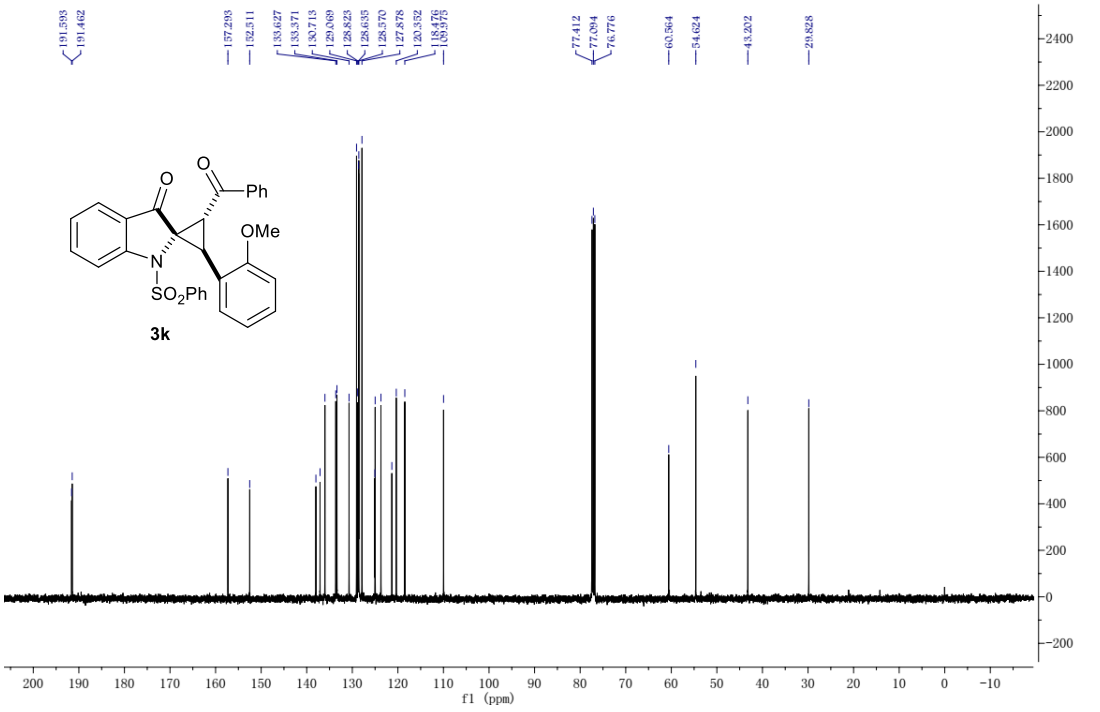
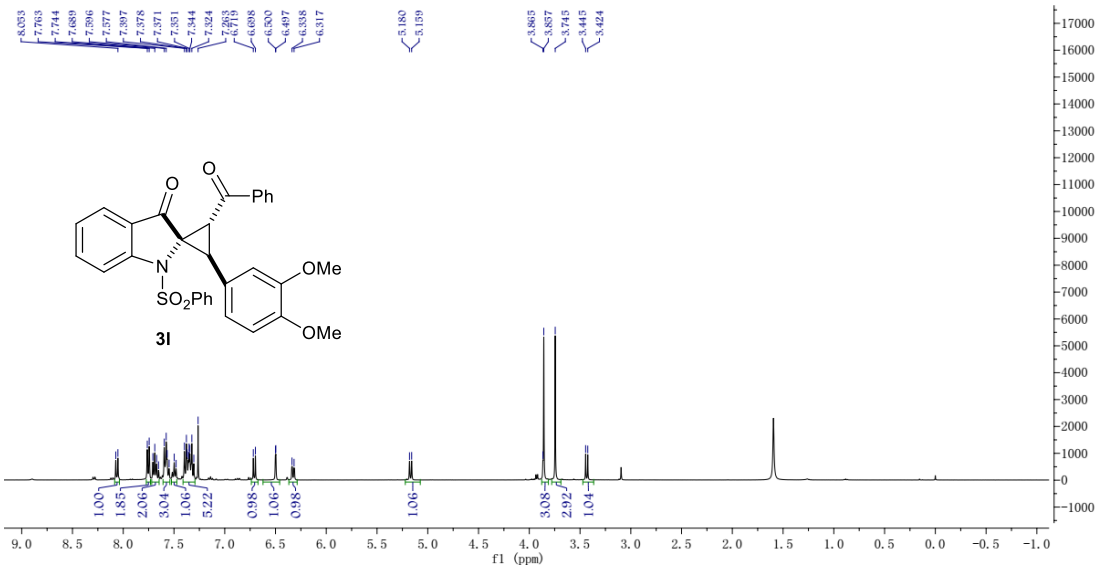
Ph
OMe
N
SO2Ph
3k
f1 (ppm)


O
Ph
OMe
N
SO2Ph
3k
f1 (ppm)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7.377
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7.378
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7.351
7.344
7.324
7.263
6.719
6.698
6.500
6.497
6.338
6.317
5.180
5.159
3.865
3.857
3.745
3.445
3.424
O
Ph
O
N
SO2Ph
OMe
OMe
3l
1.00
1.85
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1.06
5.22
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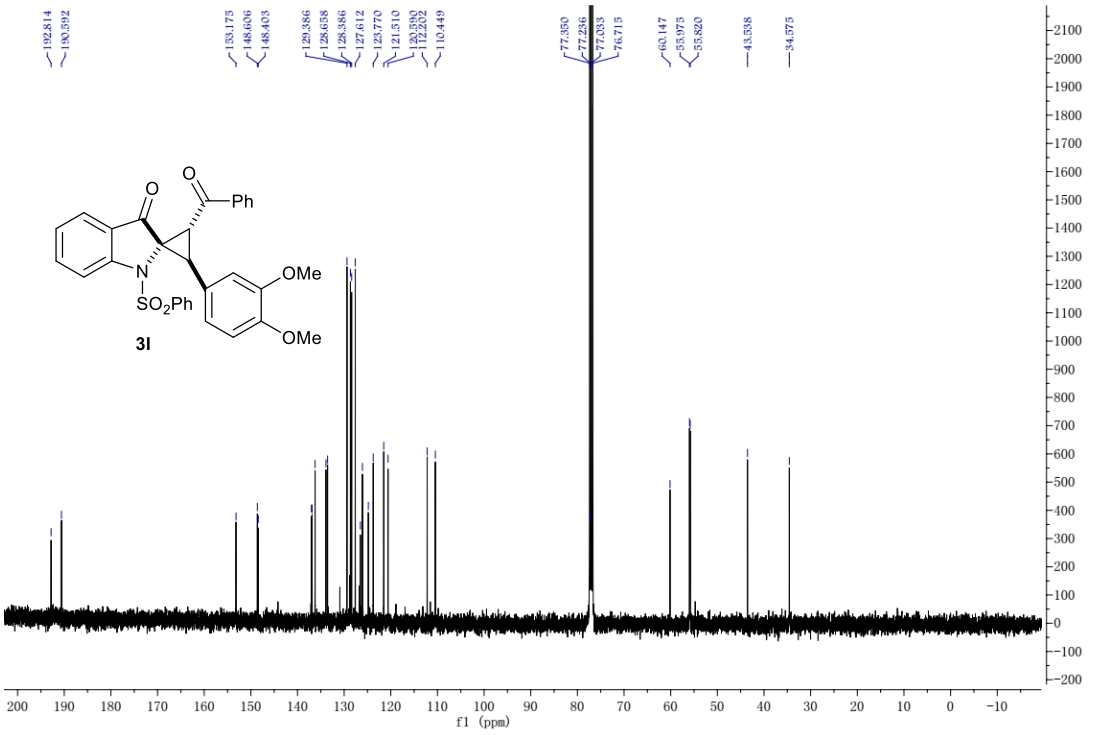
1.06
0.98
1.06
3.08
2.92
1.04
f1 (ppm)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128.386
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120.580
112.202
110.449
77.350
77.236
77.033
76.715
60.147
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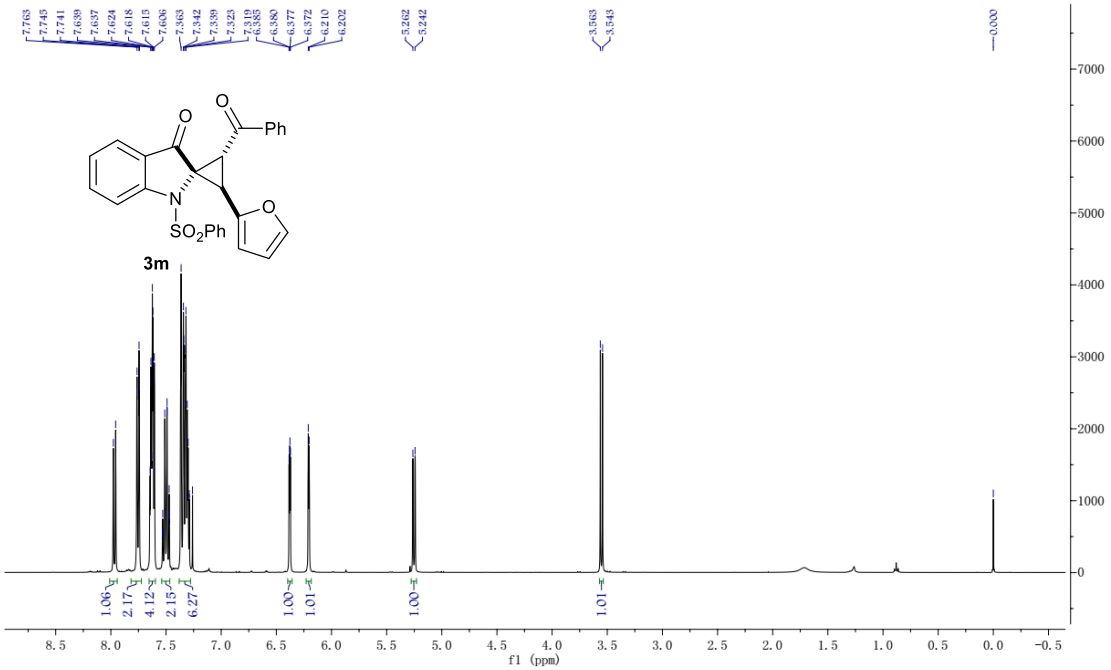
43.538
34.575
O
Ph
O
N
SO2Ph
OMe
OMe
3l
f1 (ppm)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7.615
7.606
7.363
7.342
7.339
7.323
7.319
6.385
6.380
6.377
6.372
6.210
6.202
5.262
5.242
3.563
3.543
0.000
O
Ph
O
N
SO2Ph
O
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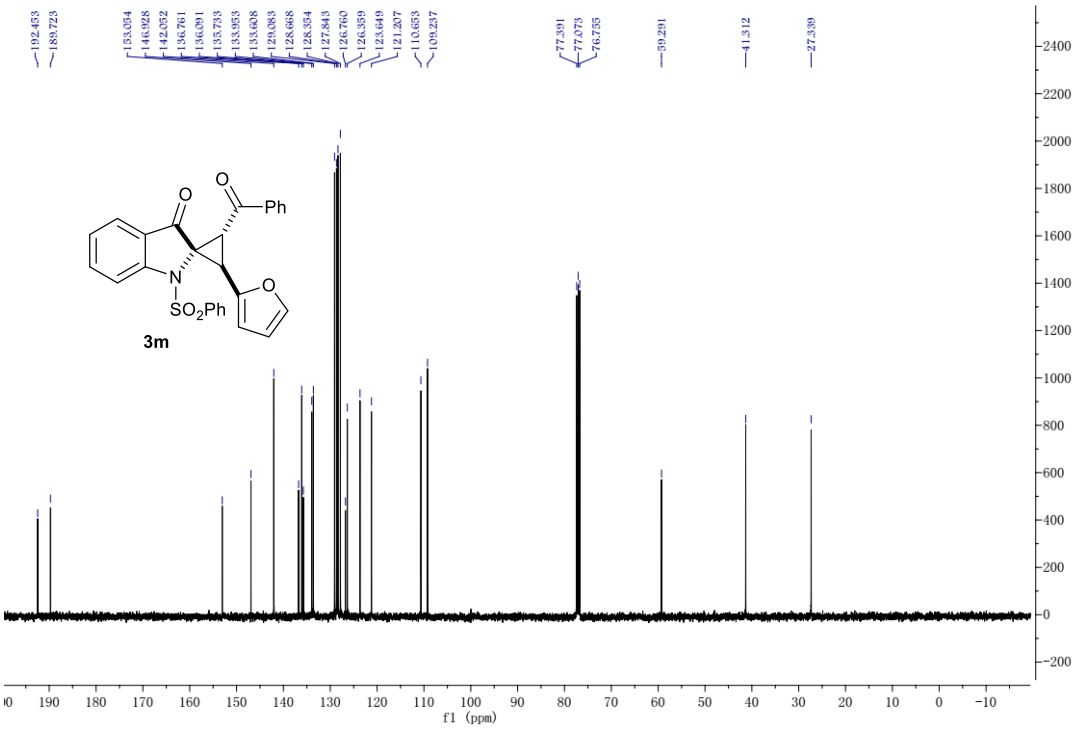
1.01
1.00
1.01
f1 (ppm)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129.085
128.668
128.354
127.843
126.760
126.359
123.649
121.207
110.653
109.237
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59.291
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27.339
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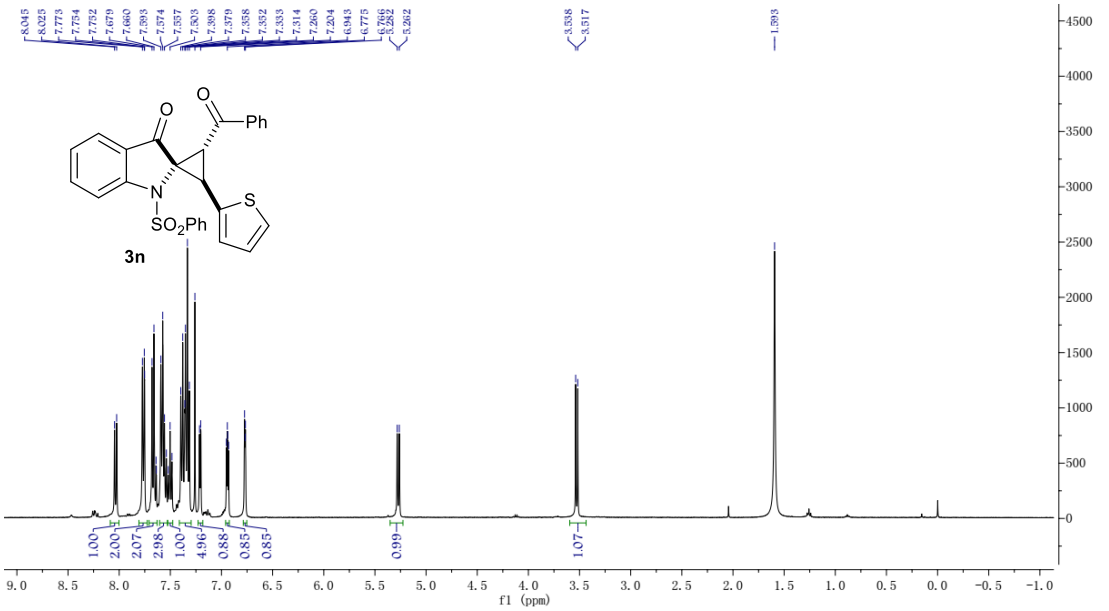
Ph
O
N
SO2Ph
O
3m
f1 (ppm)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7.379
7.358
7.352
7.333
7.314
7.260
7.204
6.943
6.775
6.766
6.282
6.262
3.538
3.517
1.593
O
Ph
O
N
S
SO2Ph
3n
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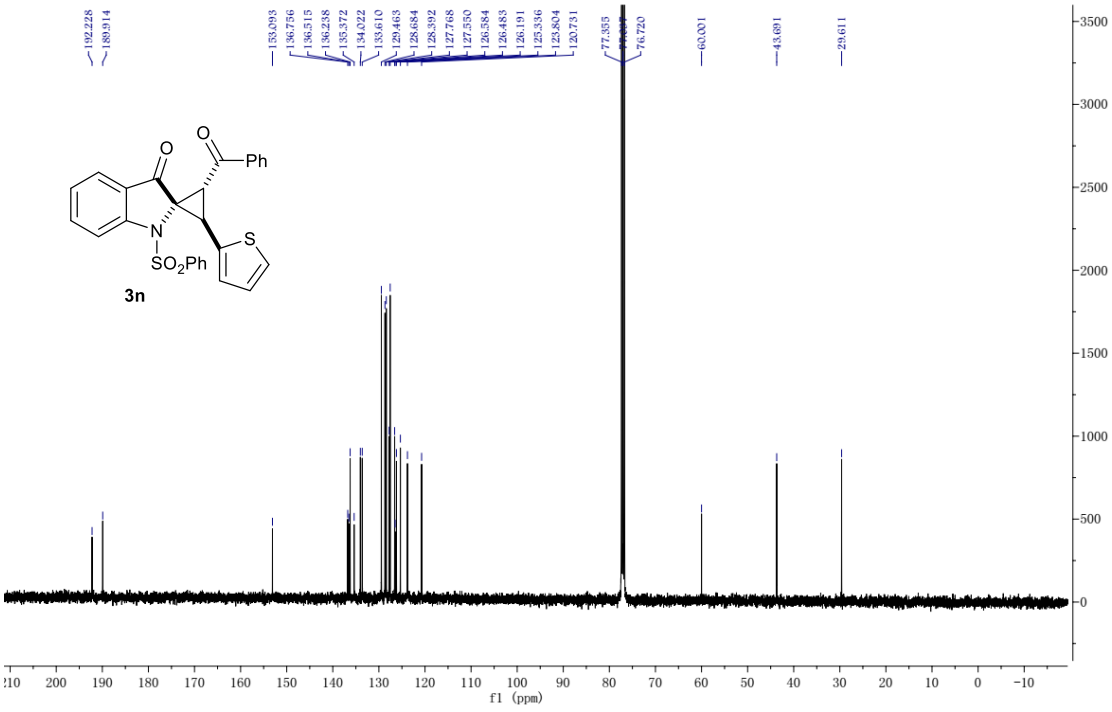
f1 (ppm)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127.768
127.550
126.584
126.483
126.191
125.336
123.804
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60.001
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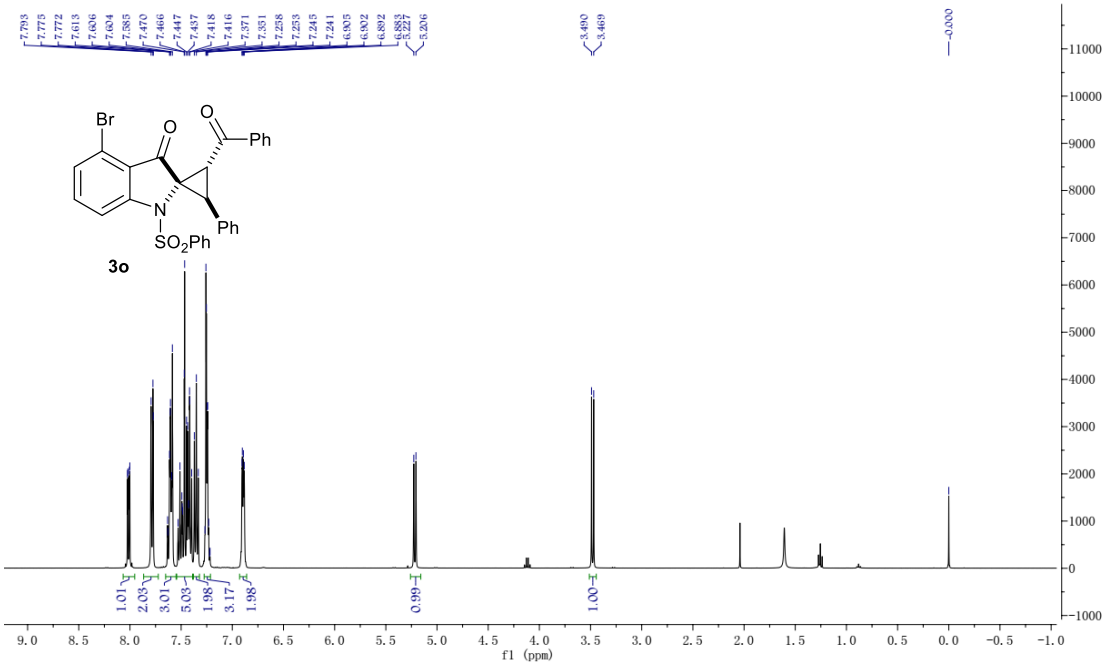
Ph
O
N
S
SO2Ph
3n
f1 (ppm)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7.371
7.351
7.258
7.253
7.245
7.241
6.905
6.902
6.892
5.227
5.206
3.490
3.469
0.000
Br
O
O
Ph
N
Ph
SO2Ph
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2.03
3.01
5.03
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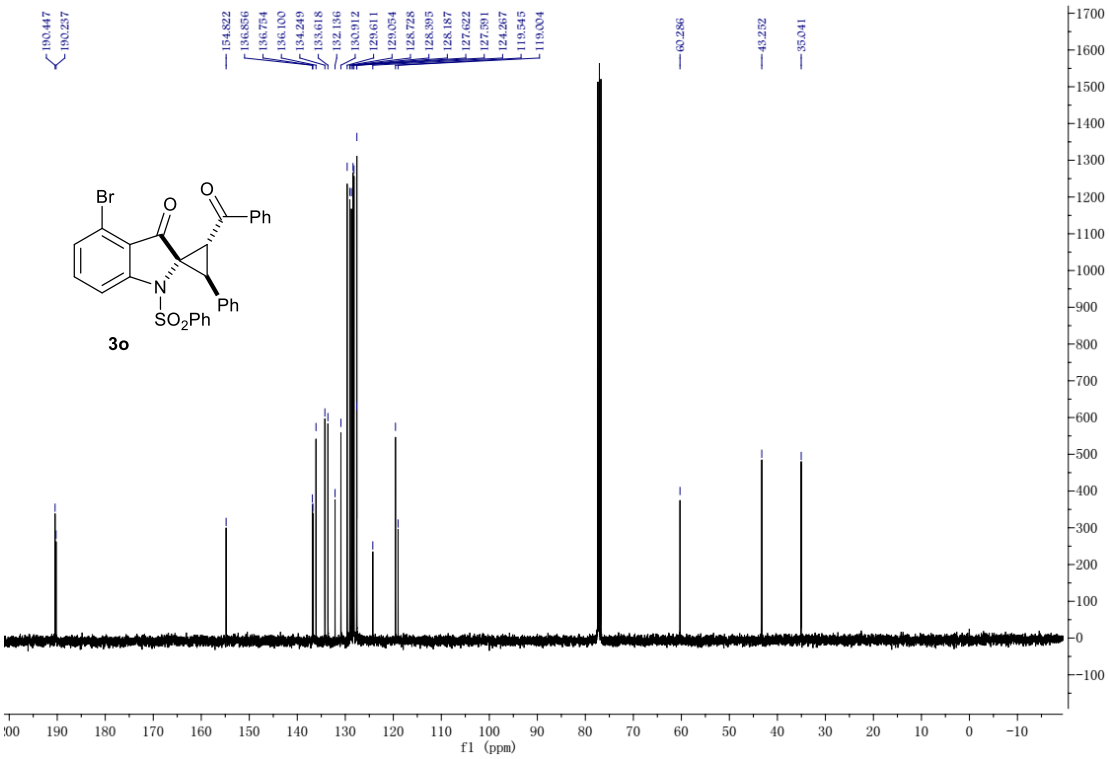
3.17
1.98
0.99
1.00
f1 (ppm)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128.728
128.395
128.187
127.622
127.391
124.267
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60.286
43.252
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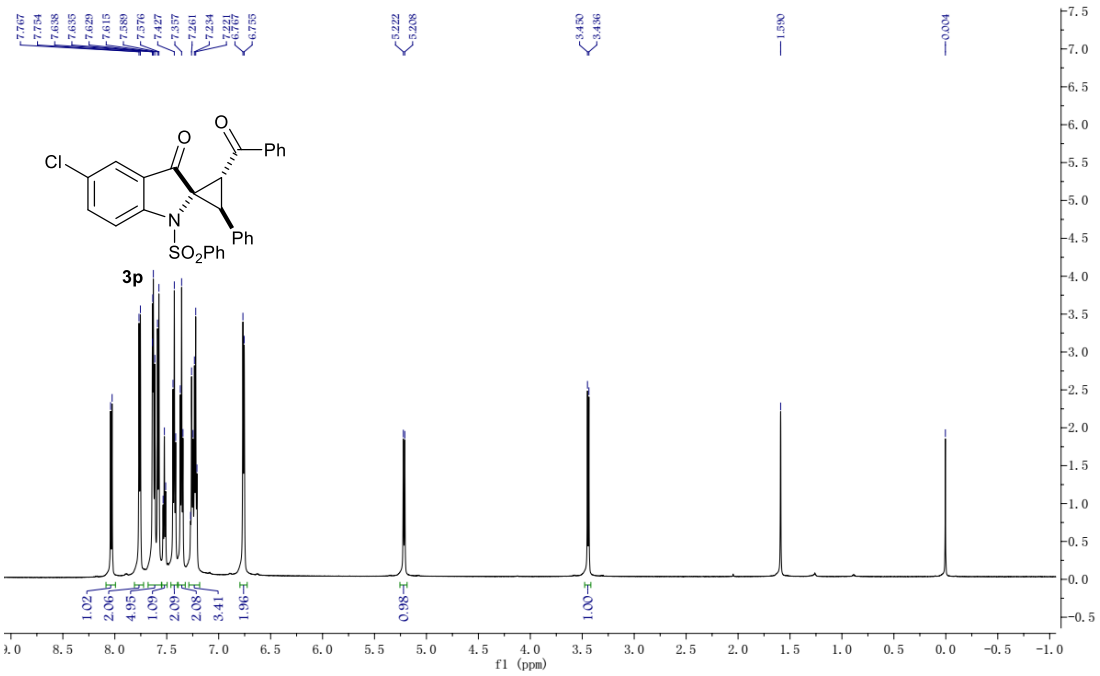
Br
O
O
Ph
N
Ph
SO2Ph
3o
f1 (ppm)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7.221
6.767
6.755
5.222
5.208
3.430
3.436
1.580
0.004
Cl
O
O
Ph
N
SO2Ph
Ph
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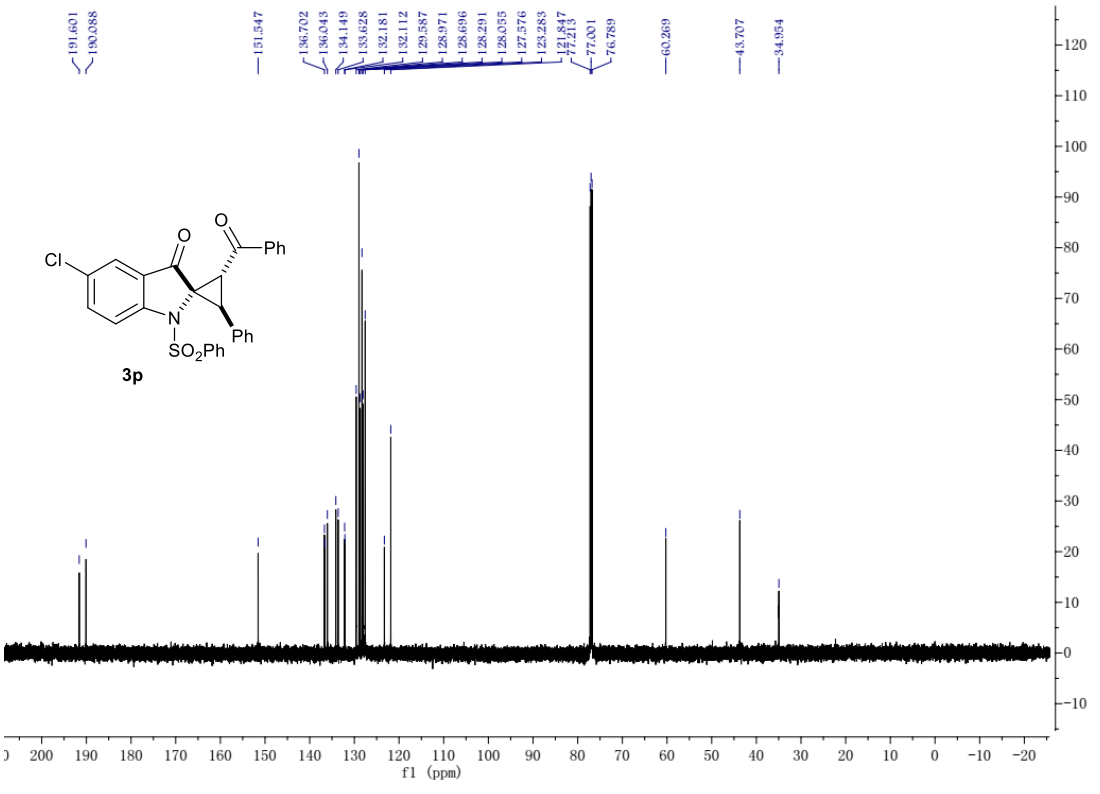
4.95
1.09
2.09
2.08
3.41
1.96
0.98
1.00
f1 (ppm)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123.283
121.847
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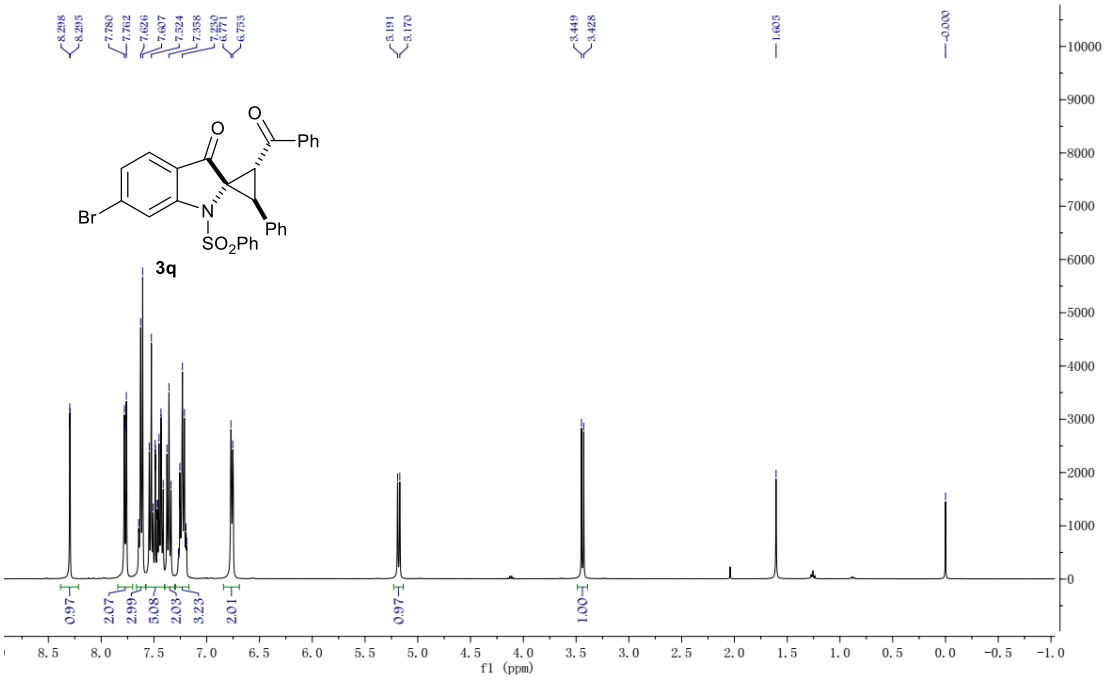
Ph
N
SO2Ph
Ph
3p
f1 (ppm)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5.170
3.449
3.428
1.605
0.000
O
O
Ph
Br
N
Ph
SO2Ph
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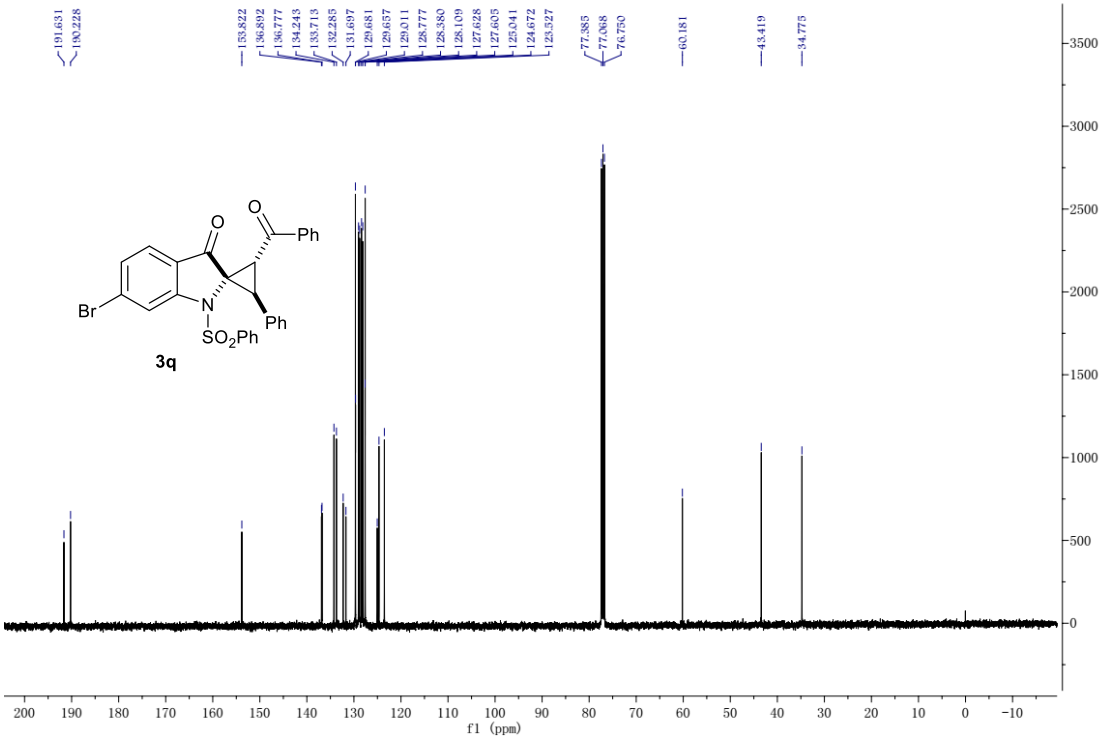
2.99
5.08
2.03
3.23
2.01
0.97
1.00
f1 (ppm)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128.380
128.109
127.628
127.605
125.041
124.672
123.527
77.385
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43.419
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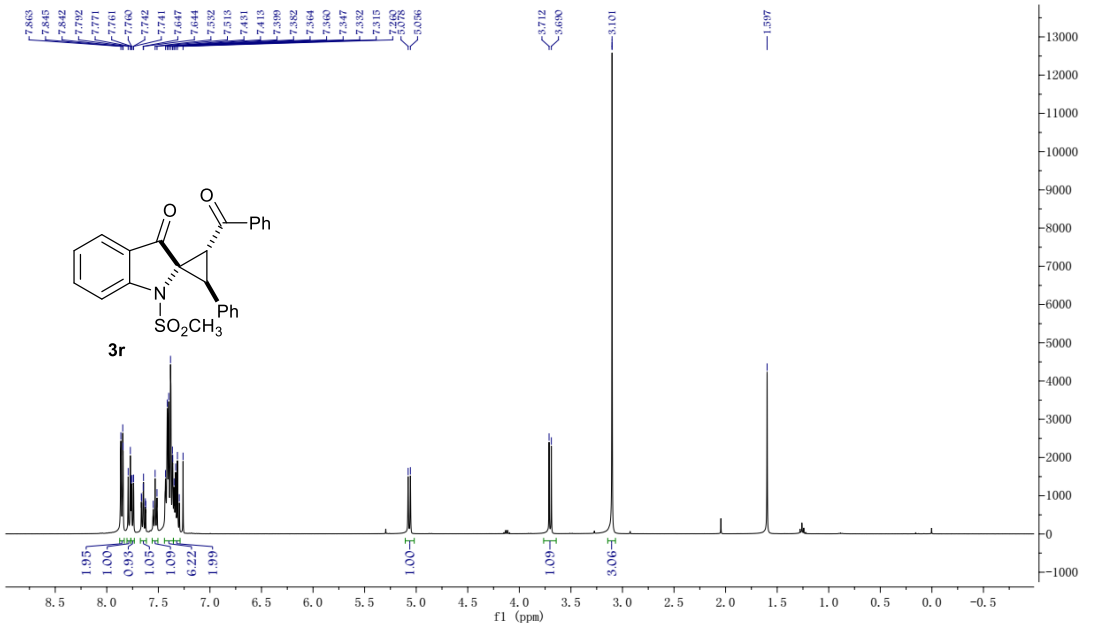
O
Ph
Br
N
Ph
SO2Ph
3q
f1 (ppm)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7.532
7.513
7.431
7.413
7.399
7.382
7.364
7.360
7.347
7.332
7.315
7.260
5.078
5.086
3.712
3.690
3.101
1.597
O
Ph
N
Ph
SO2CH3
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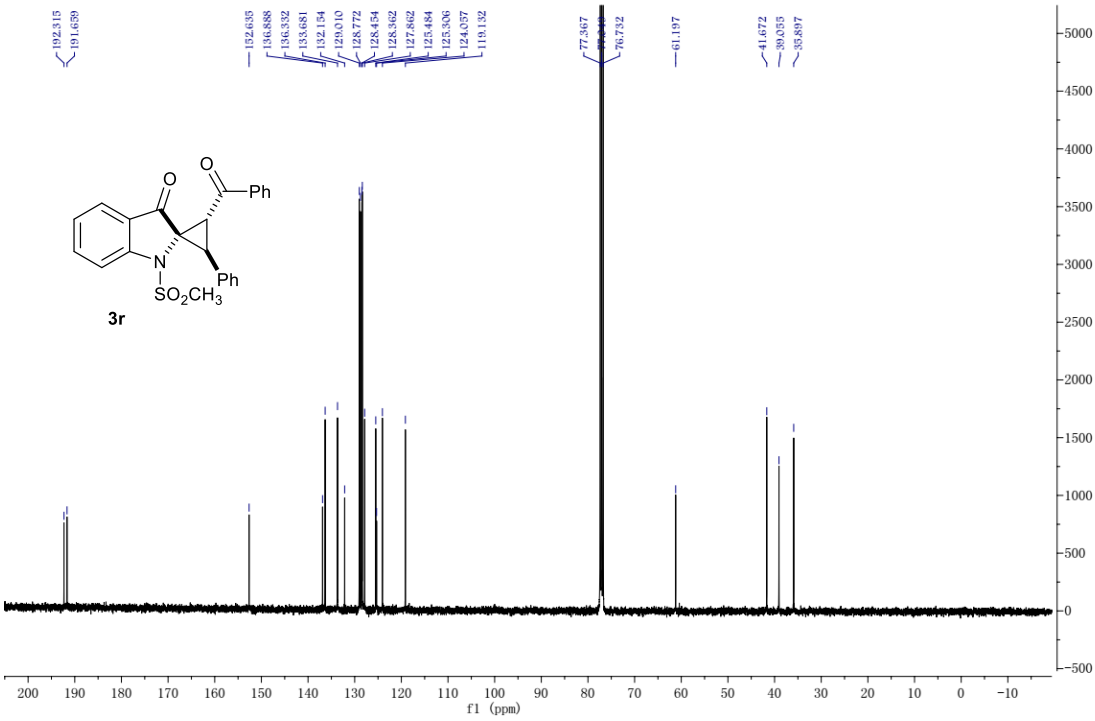
1.00
1.09
3.06
f1 (ppm)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125.306
124.057
119.132
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61.197
41.672
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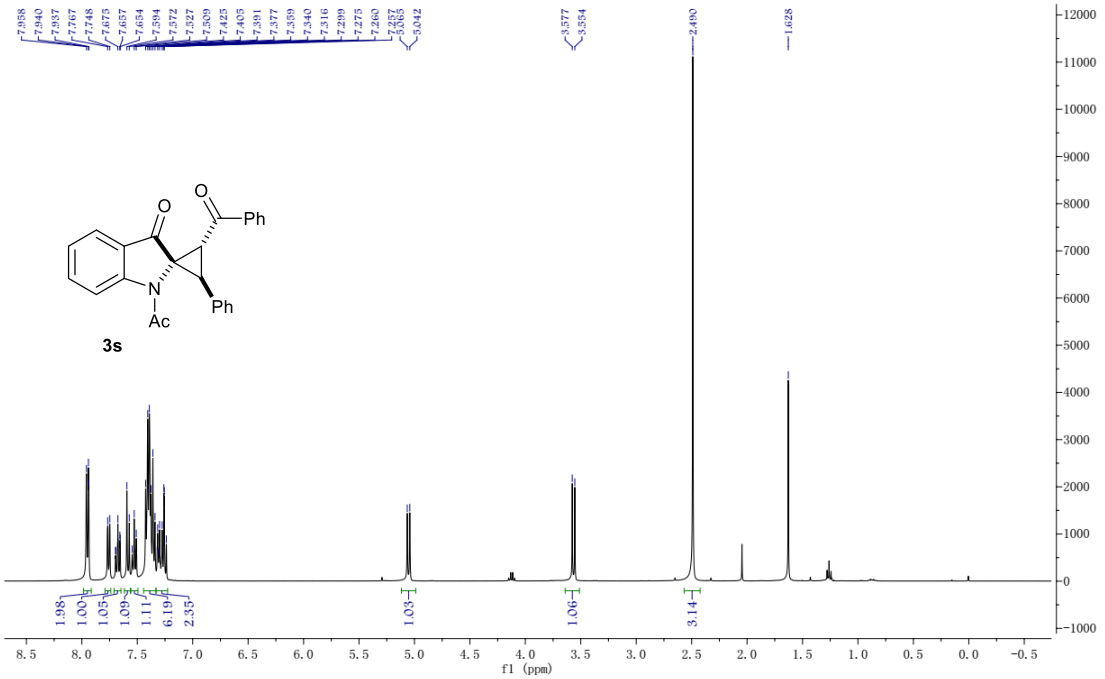
35.897
O
Ph
N
Ph
SO2CH3
3r
f1 (ppm)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7.391
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7.299
7.275
7.260
5.365
5.042
3.577
3.554
2.490
1.628
O
O
Ph
N
Ac
Ph
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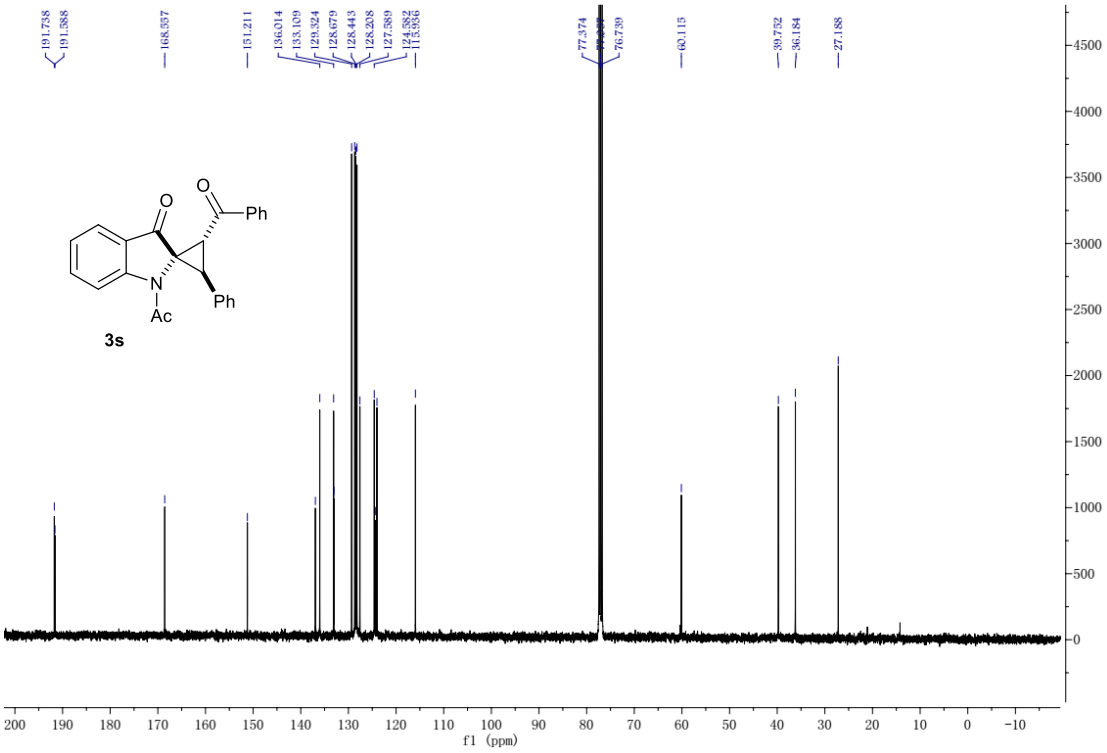
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128.679
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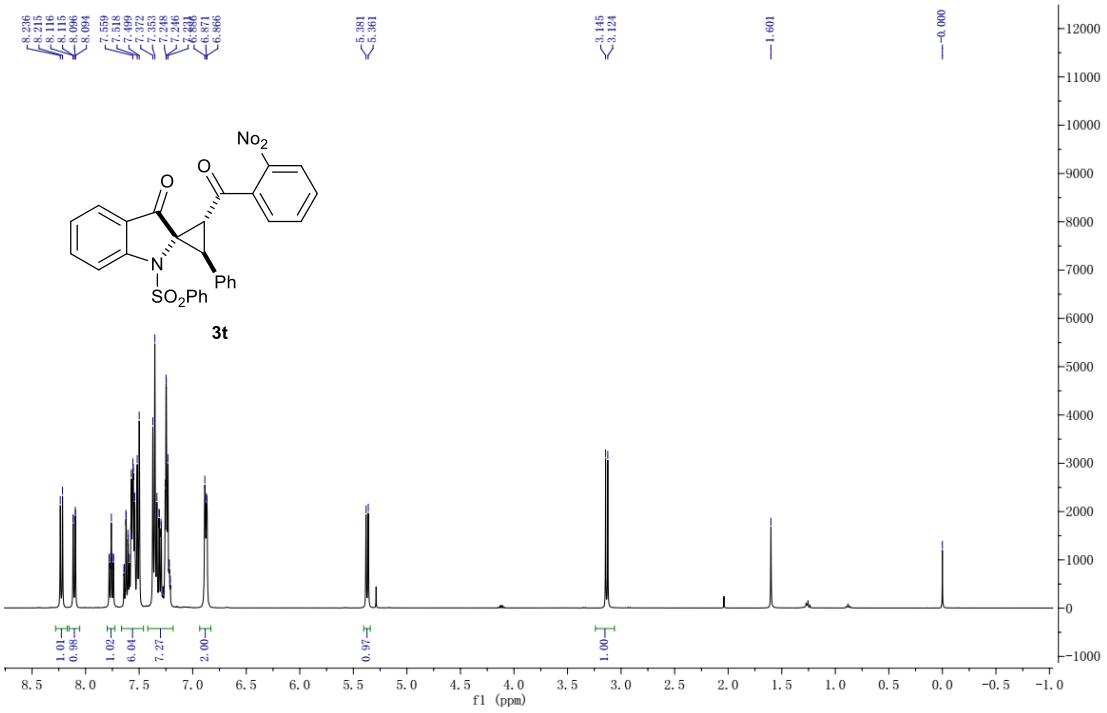
127.389
124.582
113.936
77.374
76.739
60.115
39.732
36.184
27.188
O
O
Ph
N
Ac
Ph
3s
f1 (ppm)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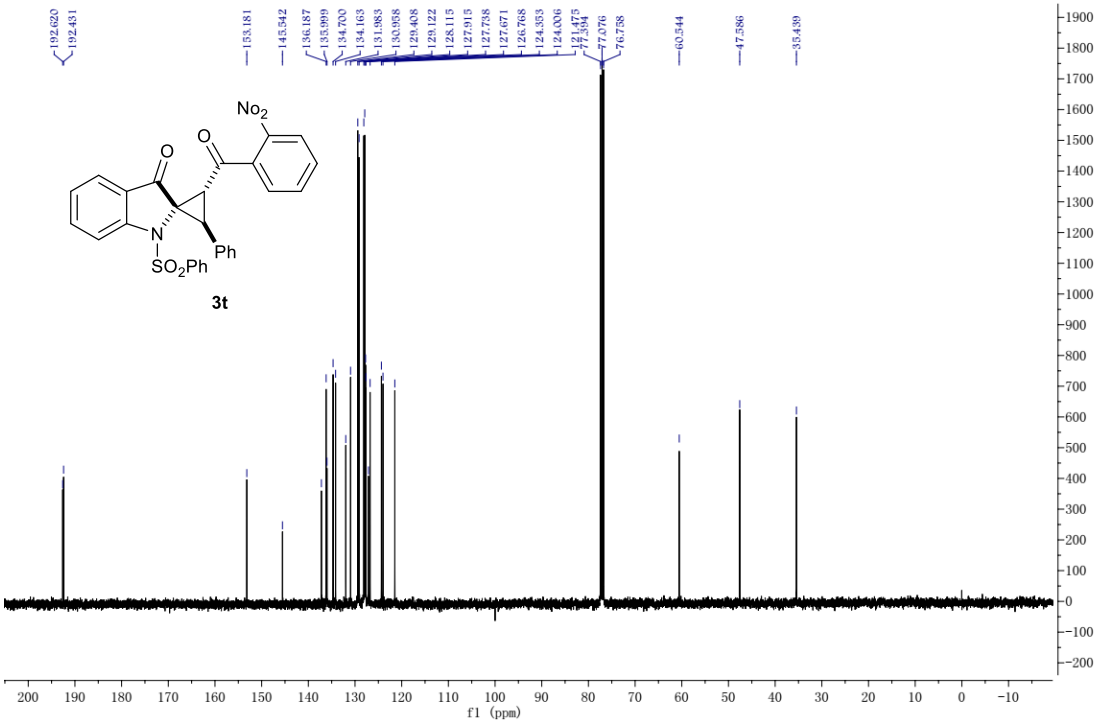
8.116
8.115
8.096
8.094
7.559
7.518
7.499
7.372
7.353
7.248
7.246
6.871
6.866
5.381
5.361
3.145
3.124
1.601
0.000
No2
O
O
N
Ph
SO2Ph
3t
1.01
0.98
1.02
6.04
7.27
2.00
0.97
1.00
f1 (ppm)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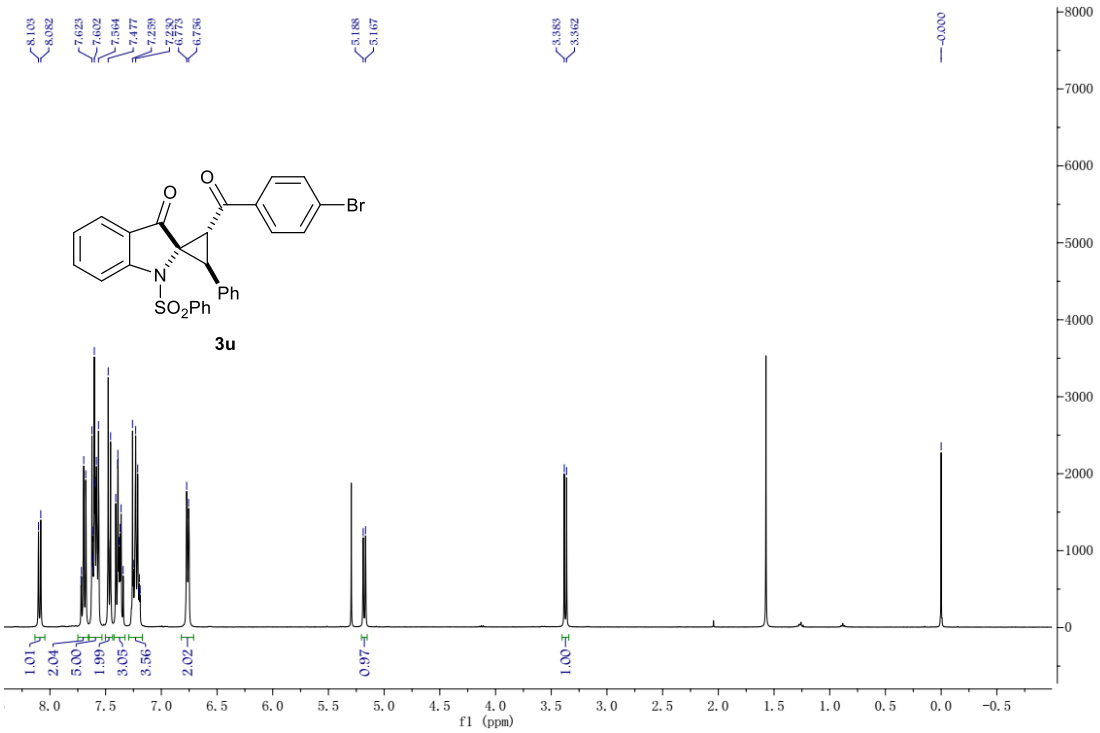
192.431
153.181
145.542
136.187
135.999
134.700
134.163
131.983
130.958
129.408
129.122
128.115
127.913
127.738
127.671
126.768
124.353
124.006
121.475
77.394
77.076
76.758
60.544
47.586
35.439
No2
O
O
N
Ph
SO2Ph
3t
f1 (ppm)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8.082
7.623
7.602
7.564
7.477
7.239
7.232
6.775
6.756
5.188
5.167
3.383
3.362
0.000
O
O
Br
N
Ph
SO2Ph
3u
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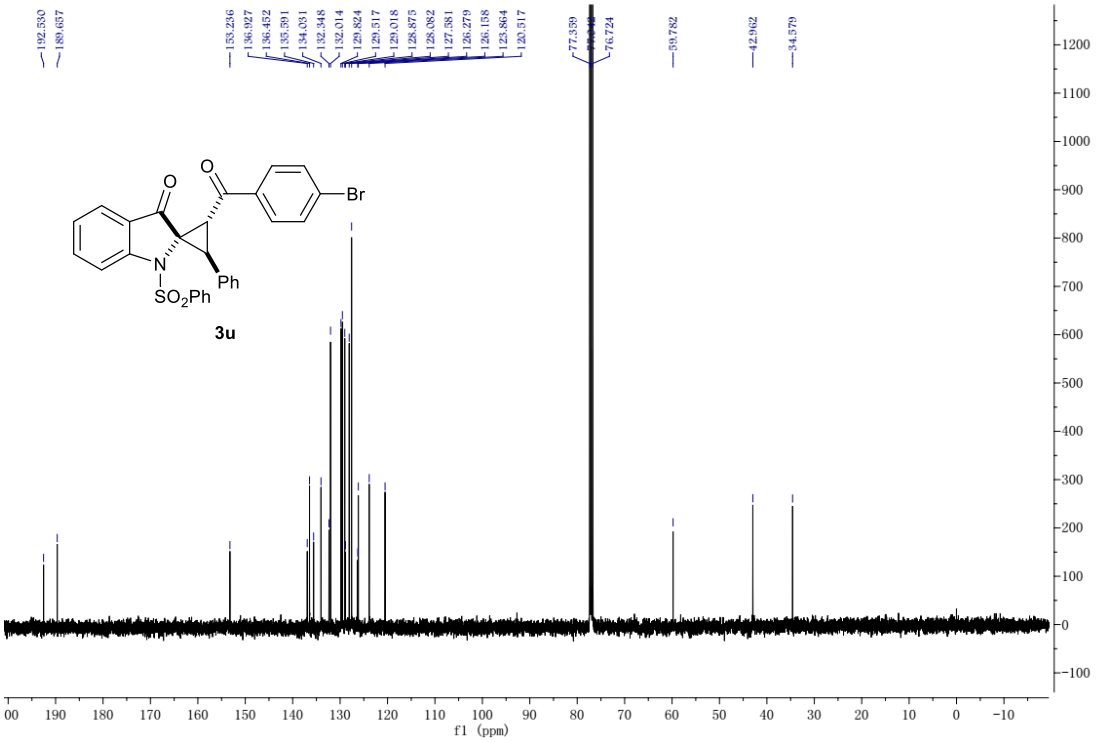
2.04
5.00
1.99
3.05
3.56
2.02
0.97
1.00
f1 (ppm)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132.348
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128.875
128.082
127.581
126.279
126.158
123.864
120.517
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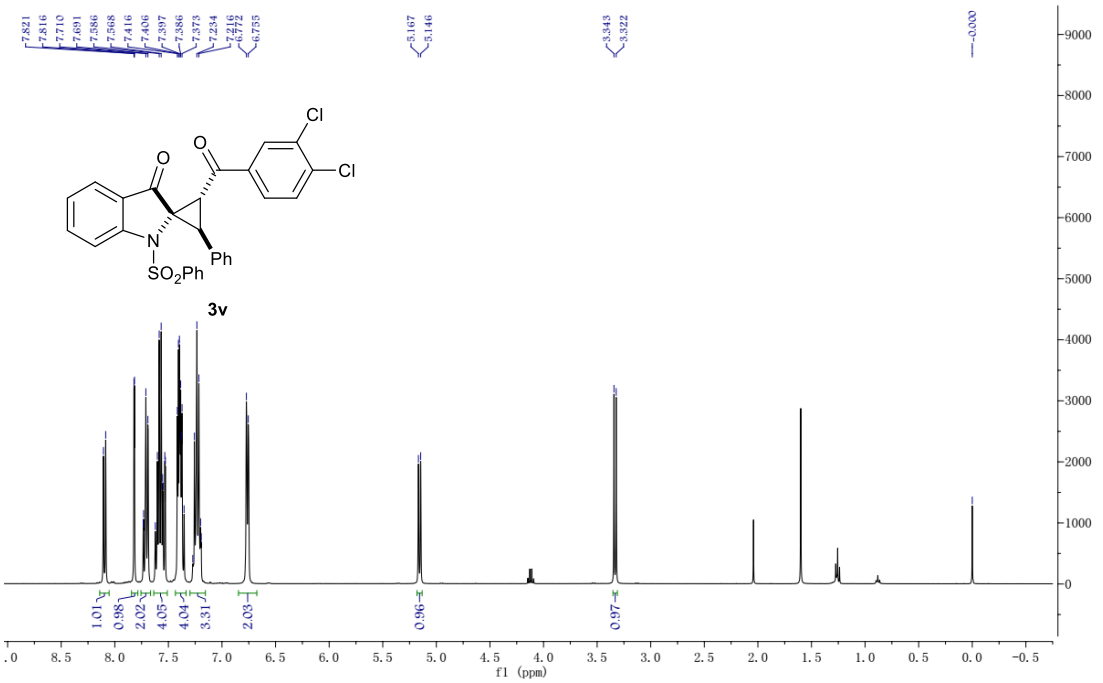
59.782
42.962
34.579
O
O
Br
N
Ph
SO2Ph
3u
f1 (ppm)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7.816
7.710
7.691
7.586
7.568
7.416
7.406
7.397
7.386
7.373
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6.772
6.755
5.167
5.146
3.343
3.322
0.000
Cl
Cl
O
O
N
Ph
SO2Ph
3v
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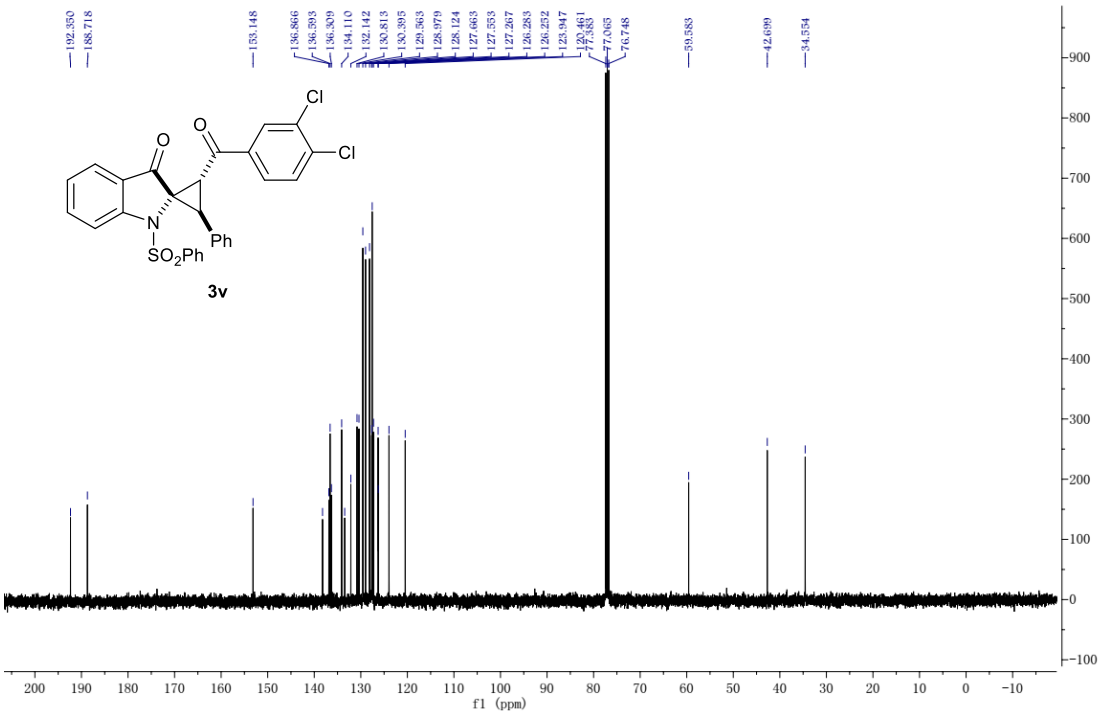
0.98
2.02
4.05
4.04
3.31
2.03
0.96
0.97
f1 (ppm)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153.148
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136.593
136.309
134.110
132.142
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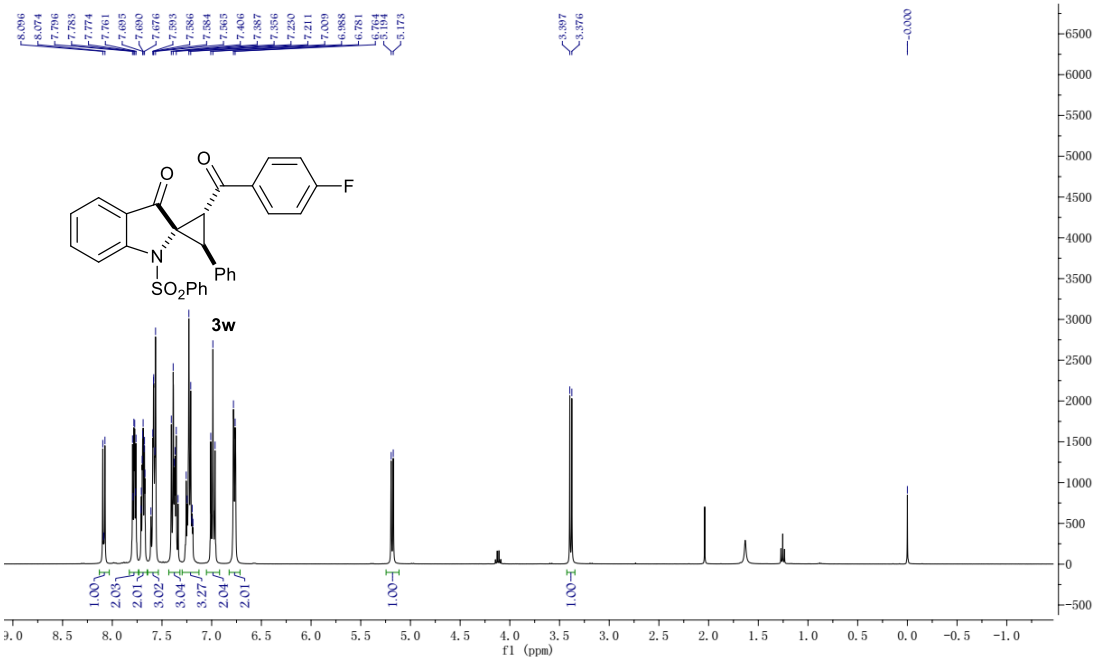
130.395
129.563
128.979
128.124
127.663
127.553
127.267
126.283
126.252
123.947
123.461
77.383
77.065
76.748
59.583
42.699
34.554
Cl
Cl
O
O
N
Ph
SO2Ph
3v
f1 (ppm)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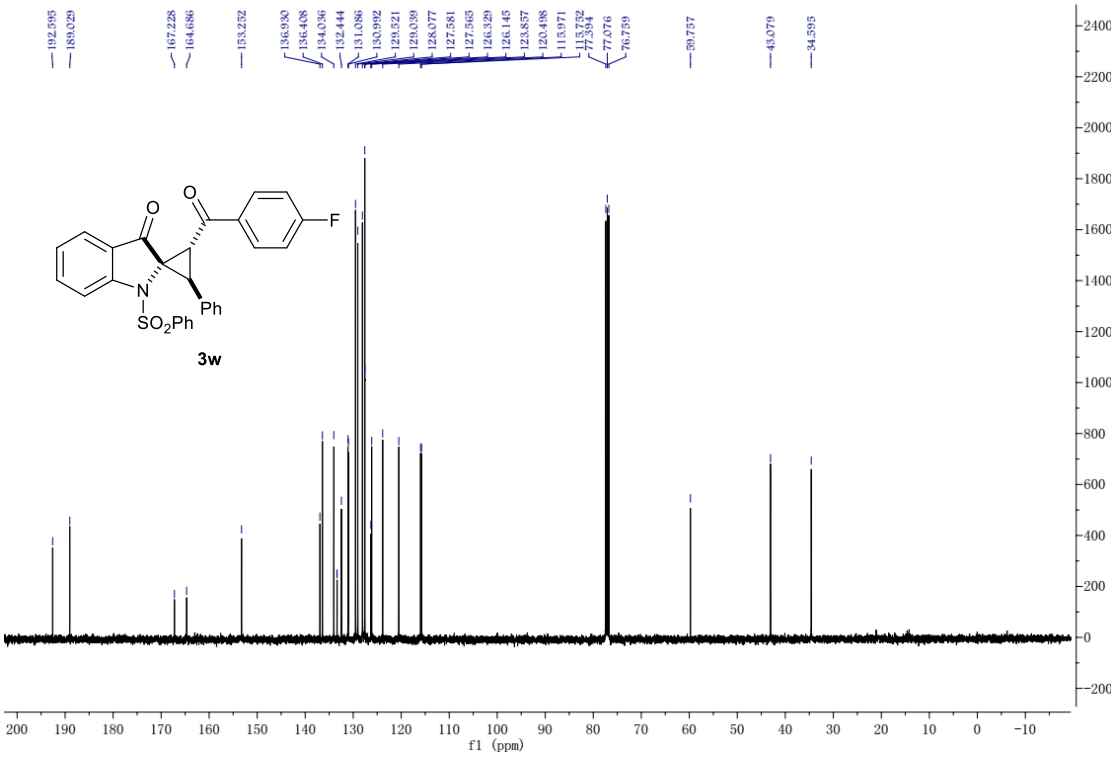
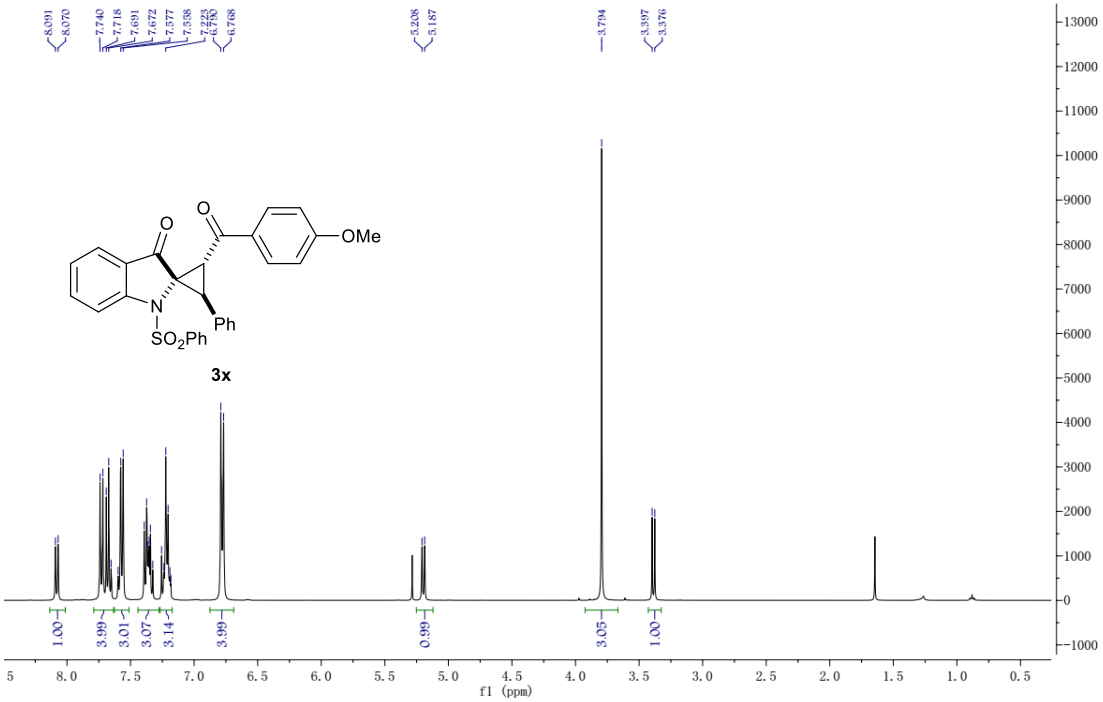
f1 (ppm)


3w
f1 (ppm)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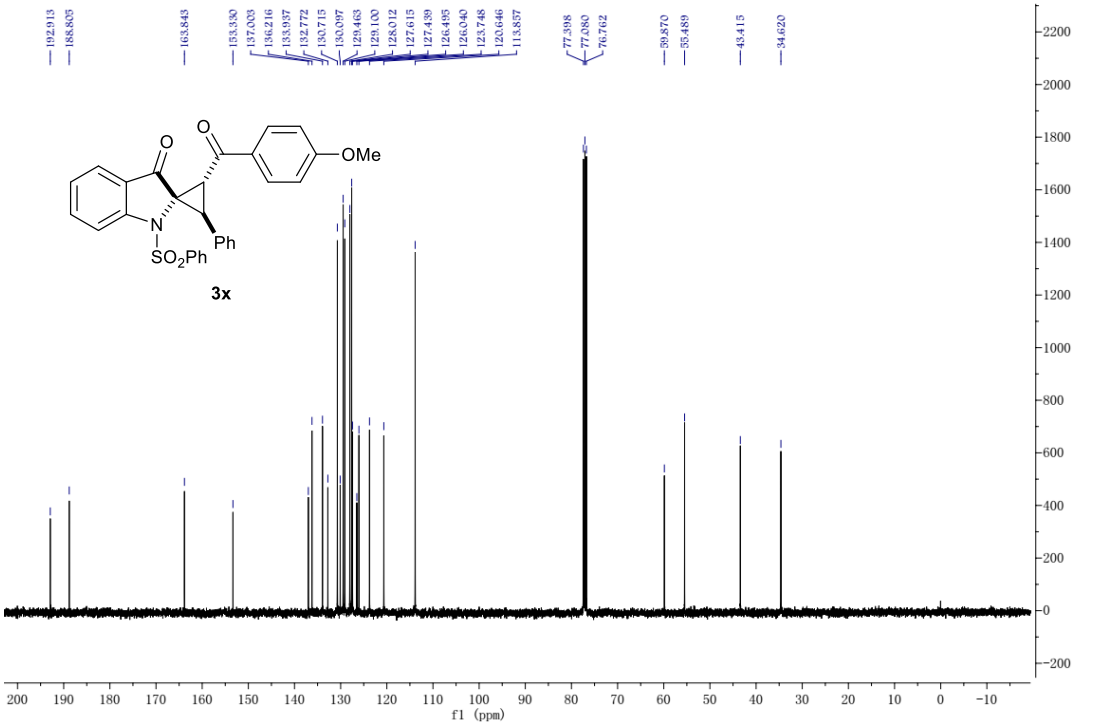
7.718
7.691
7.672
7.577
7.558
7.223
6.793
6.768
5.208
5.187
3.794
3.397
3.376
O
O
OMe
N
Ph
SO2Ph
3x
1.00
3.99
3.01
3.07
3.14
3.99
0.99
3.05
1.00
f1 (ppm)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163.843
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137.003
136.216
133.937
132.772
130.715
130.097
129.463
129.100
128.012
127.615
127.439
126.495
126.040
123.748
120.646
113.857
77.398
77.080
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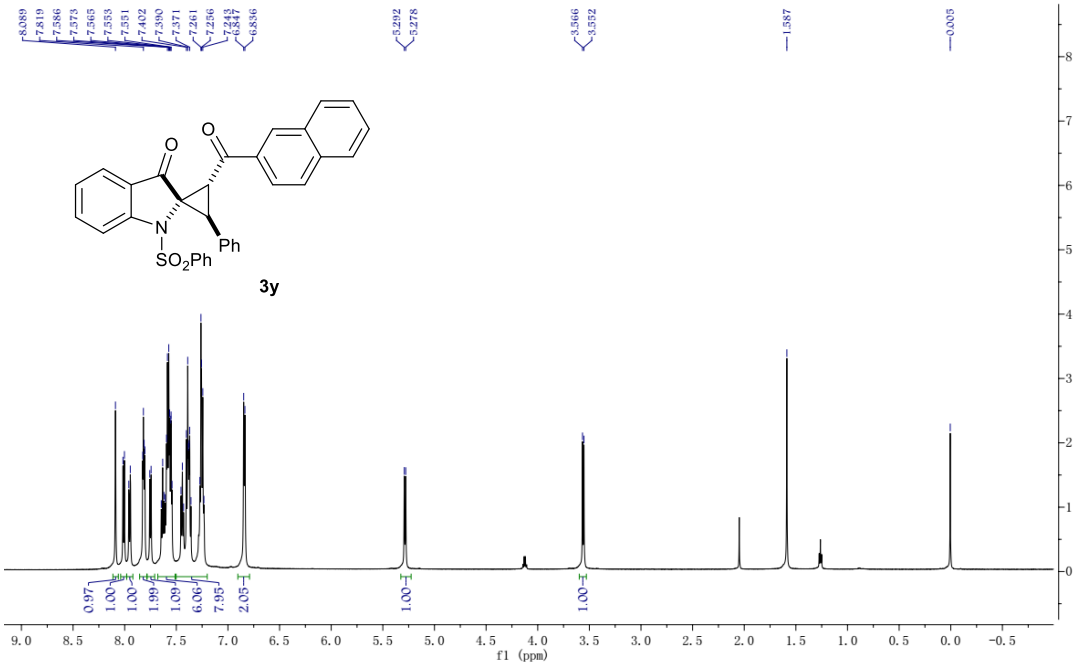
59.870
55.489
43.415
34.620
O
O
OMe
N
Ph
SO2Ph
3x
f1 (ppm)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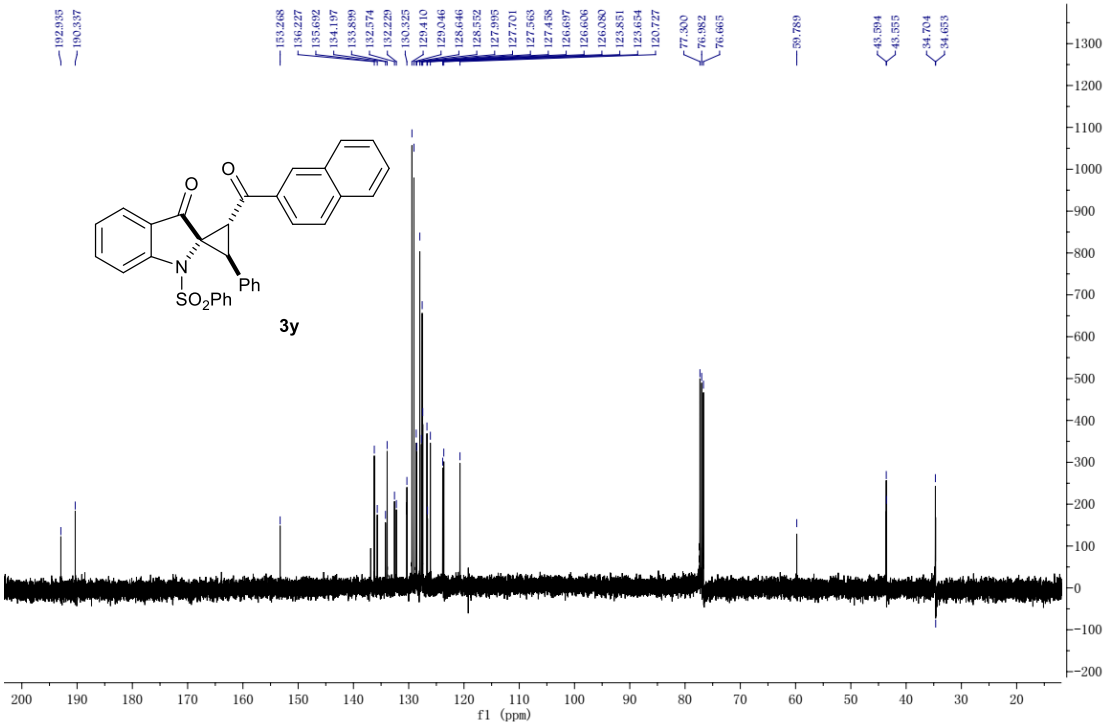
7.819
7.586
7.573
7.565
7.553
7.551
7.402
7.390
7.371
7.261
7.256
7.248
6.847
6.836
5.292
5.278
3.566
3.552
1.587
0.005
O
O
N
SO2Ph
Ph
3y
0.97
1.00
1.00
1.99
1.09
6.06
7.95
2.05
1.00
1.00
f1 (ppm)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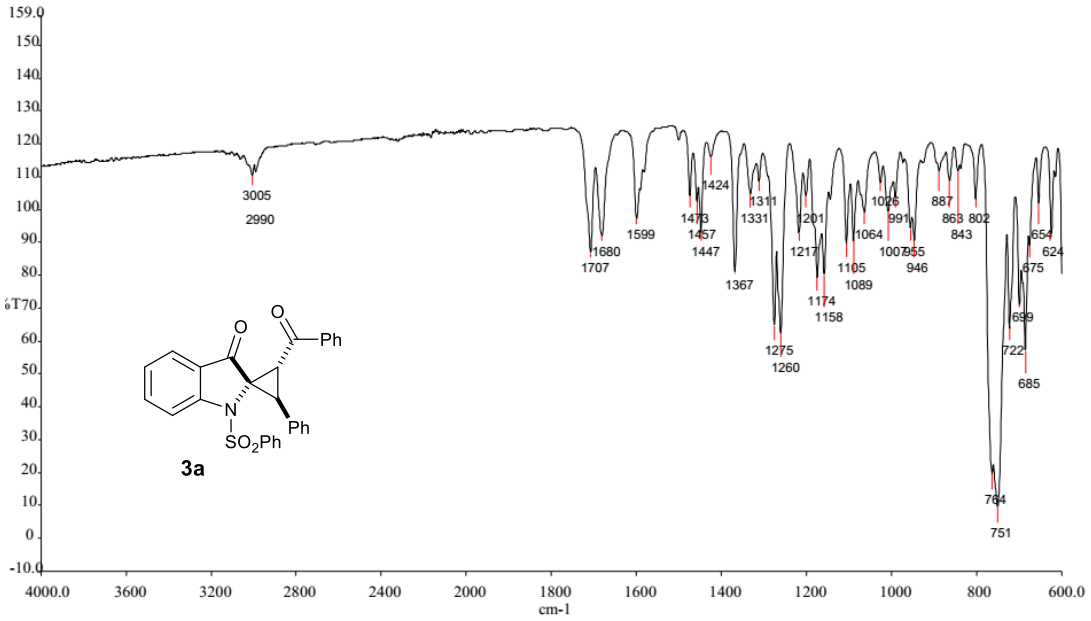
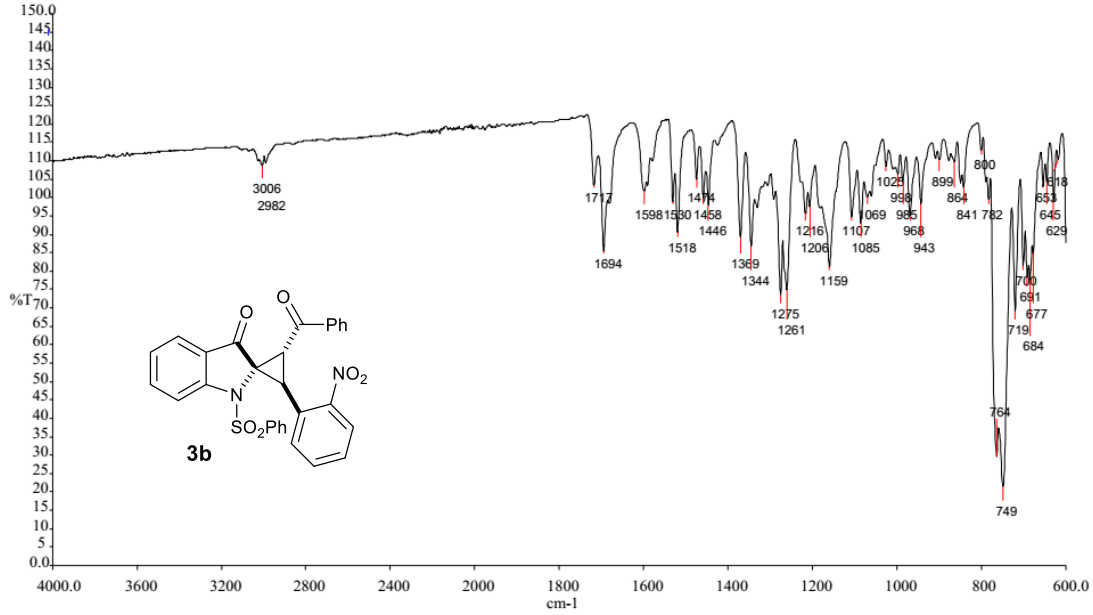
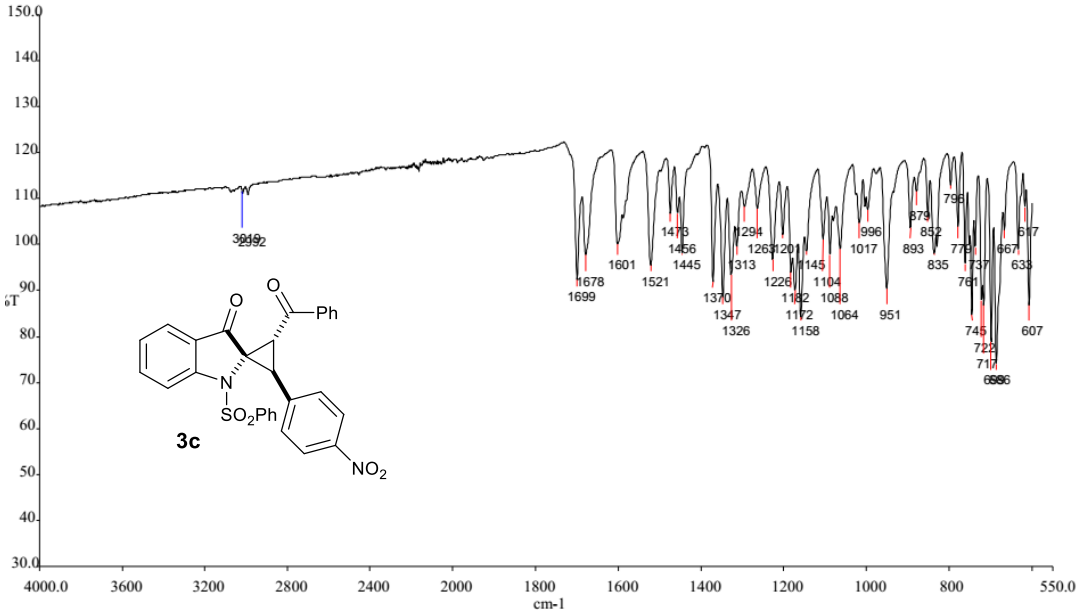
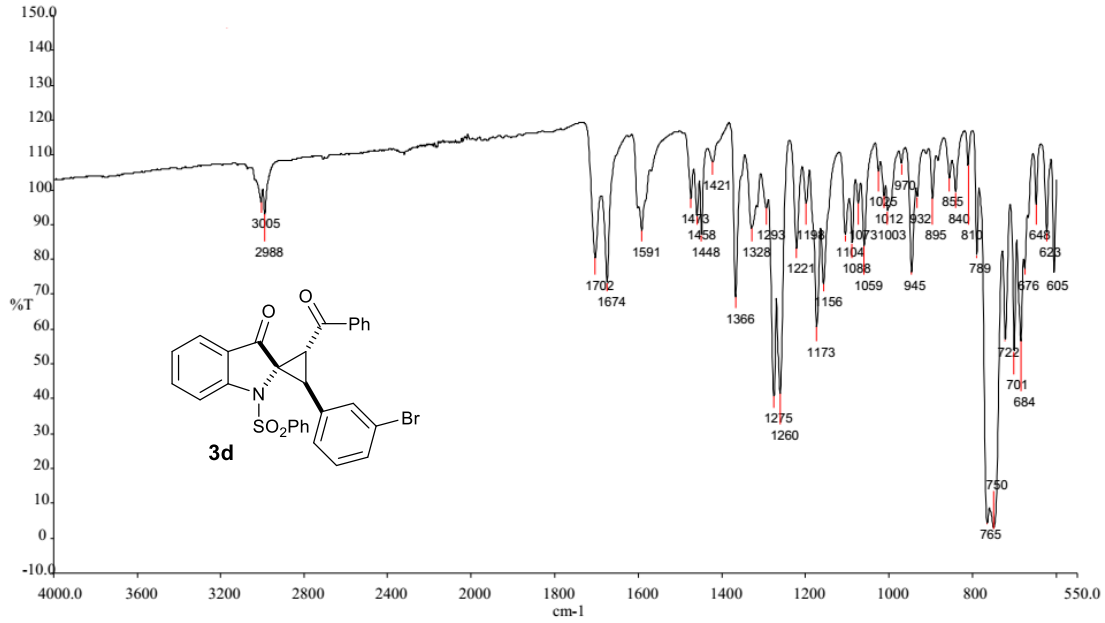
135.692
134.197
133.899
132.574
132.229
130.325
129.410
129.046
128.646
128.532
127.995
127.701
127.563
127.458
126.697
126.636
126.082
123.851
123.654
120.727
77.300
76.982
76.665
39.789
43.594
43.555
34.704
34.653
O
O
N
SO2Ph
Ph
3y
f1 (ppm)

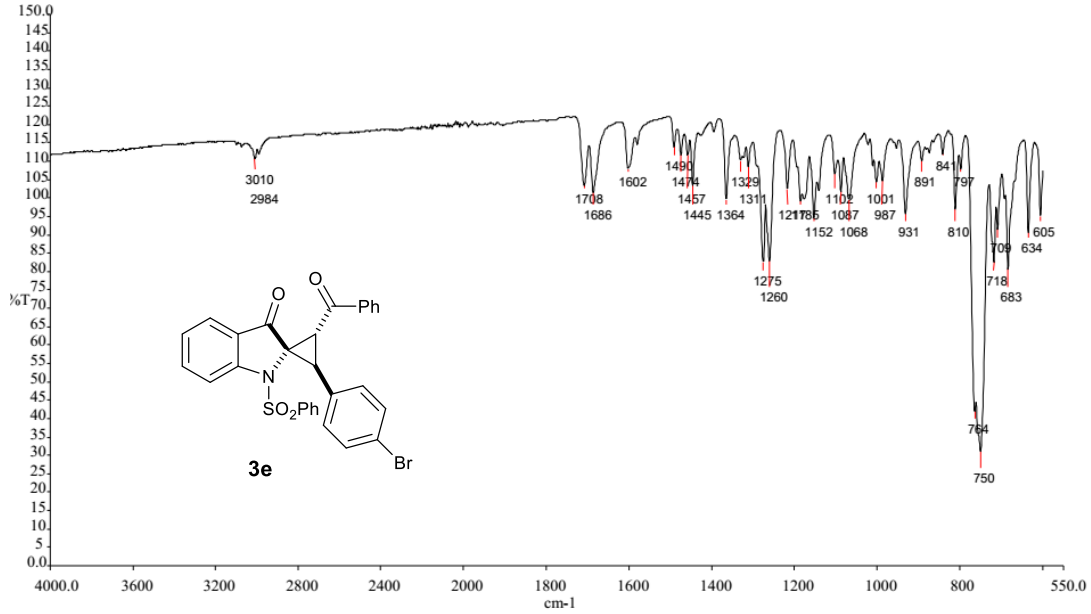
8. IR Spectra of the Spiro-pseudoindoxyl Derivatives 3






%T
cm-1
3c
SO2Ph
NO2
Ph
O
N


%T
cm-1
3d
SO2Ph
Br
Ph
O
N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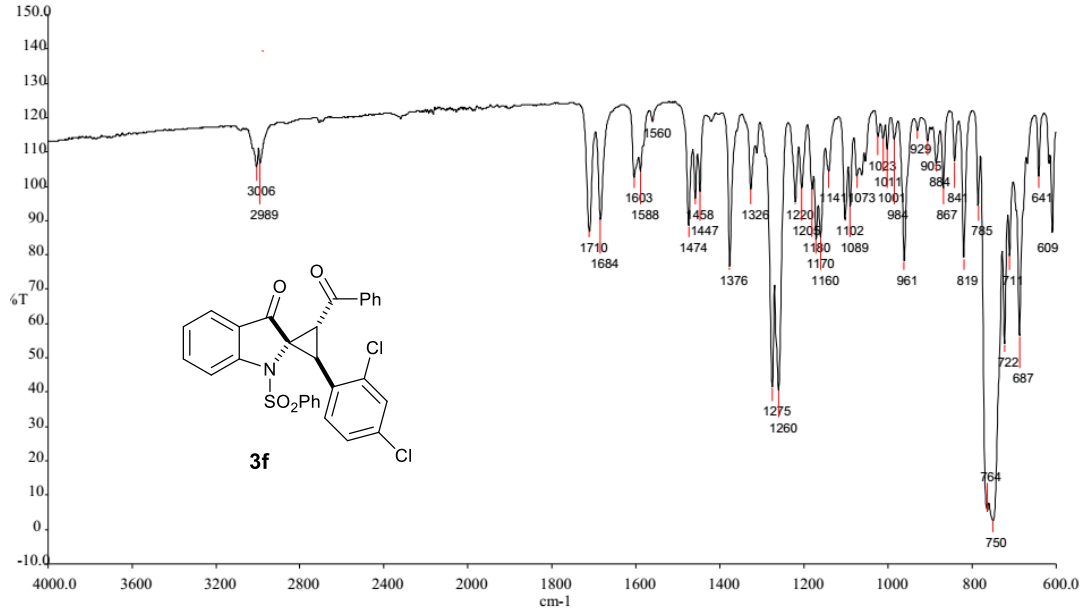
1708
1686
1602
1490
1474
1457
1445
1364
1329
1311
1275
1260
1102
1087
1068
1001
987
931
891
841
797
810
764
750
718
709
683
634
605
O
Ph
N
SO2Ph
Br
3e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1603
1588
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1458
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1376
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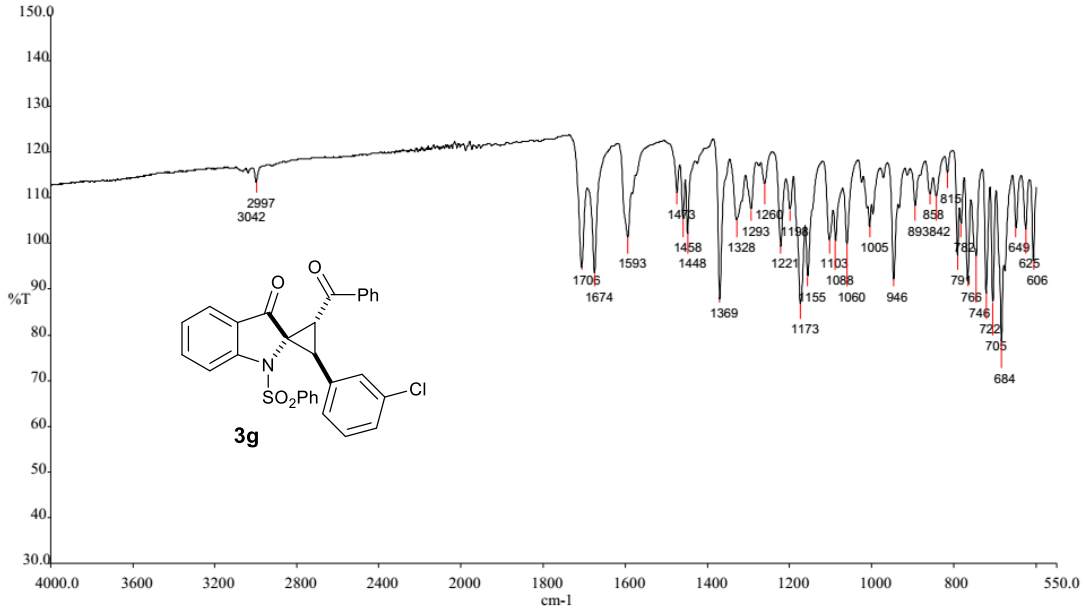
1260
1220
1205
1180
1170
1160
1141
1102
1089
1073
1023
1011
1001
984
961
929
905
884
867
841
819
785
764
750
722
711
687
641
609
O
Ph
N
SO2Ph
Cl
Cl
3f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cm-1
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1706
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1473
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1198
1173
1155
1103
1088
1060
1005
946
893842
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766
746
722
705
684
649
625
606
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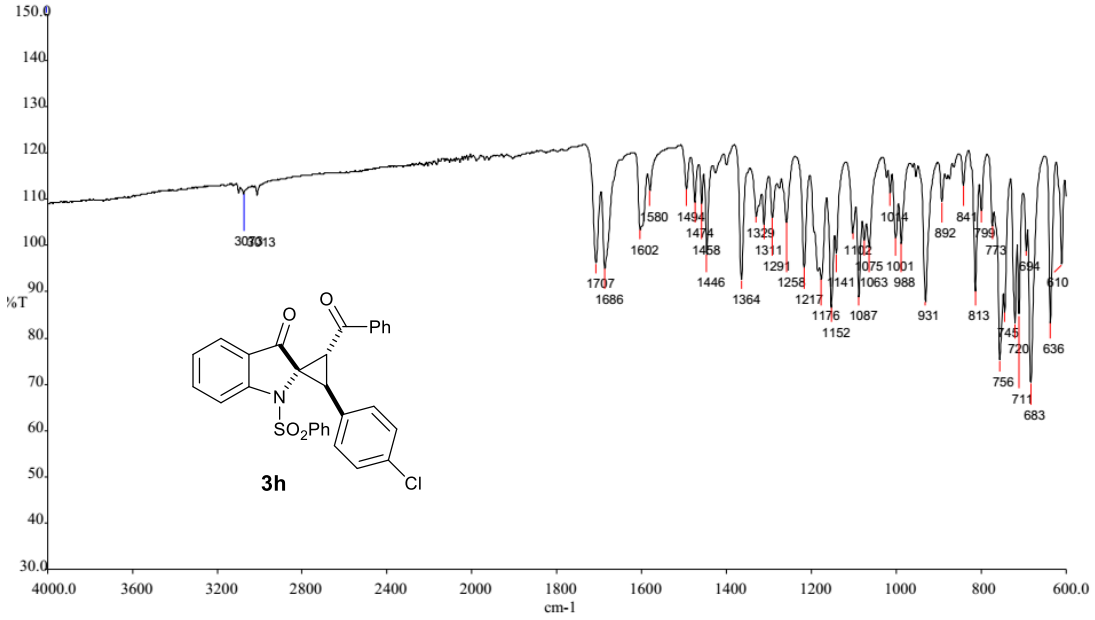
N
SO2Ph
Cl
3g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1311
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1075
1063
1044
1001
988
931
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813
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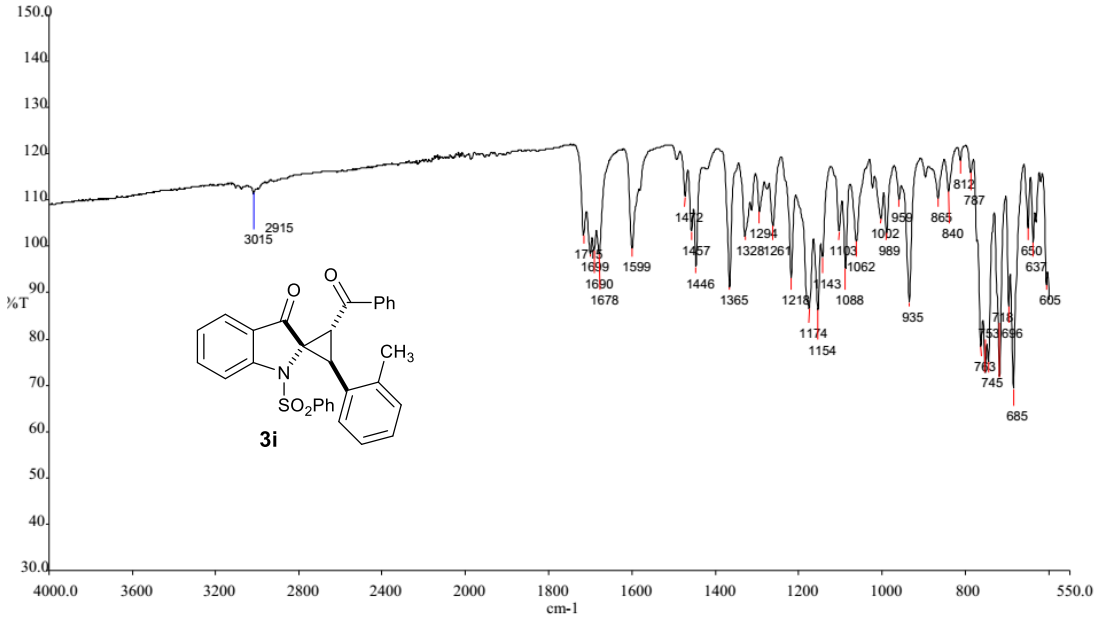
773
745
720
694
636
610
756
711
683
O
Ph
N
SO2Ph
Cl
3h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1472
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1446
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1328
1294
1261
1218
1174
1154
1143
1103
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650
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685
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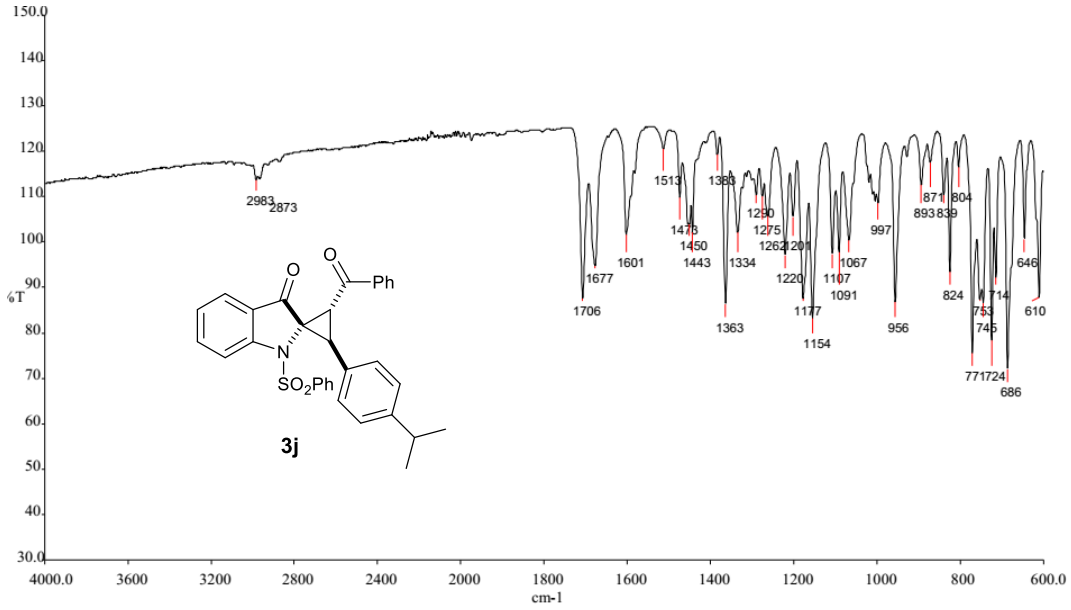
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1262
1220
1201
1177
1154
1107
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871
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824
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745
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646
610
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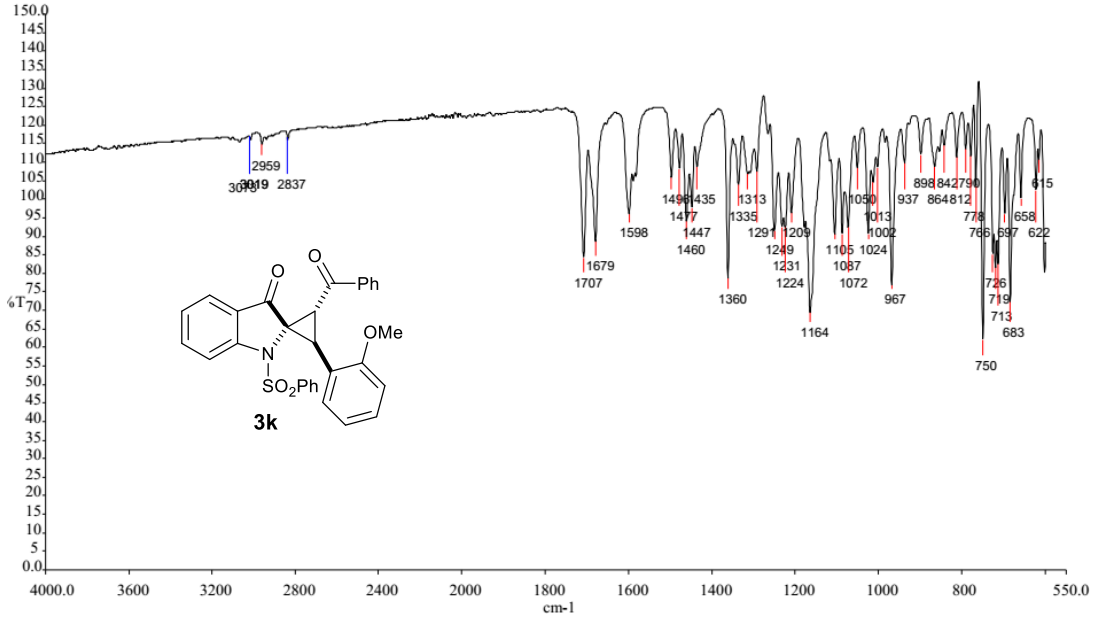
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1400
1200
1000
800
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1707
1598
1496
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1477
1447
1460
1360
1313
1335
1291
1209
1249
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937
898
864
842
812
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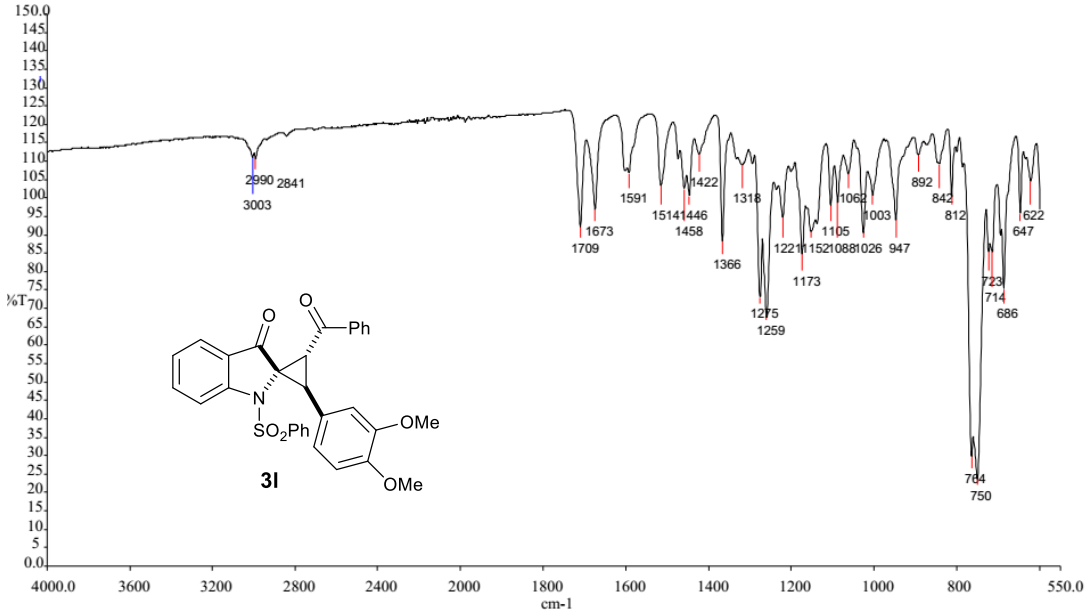
719
713
697
683
658
622
615
750
O
Ph
OMe
N
SO2Ph
3k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800
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1318
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1259
1221
1173
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1088
1062
1026
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784
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723
714
686
647
622
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Ph
OMe
N
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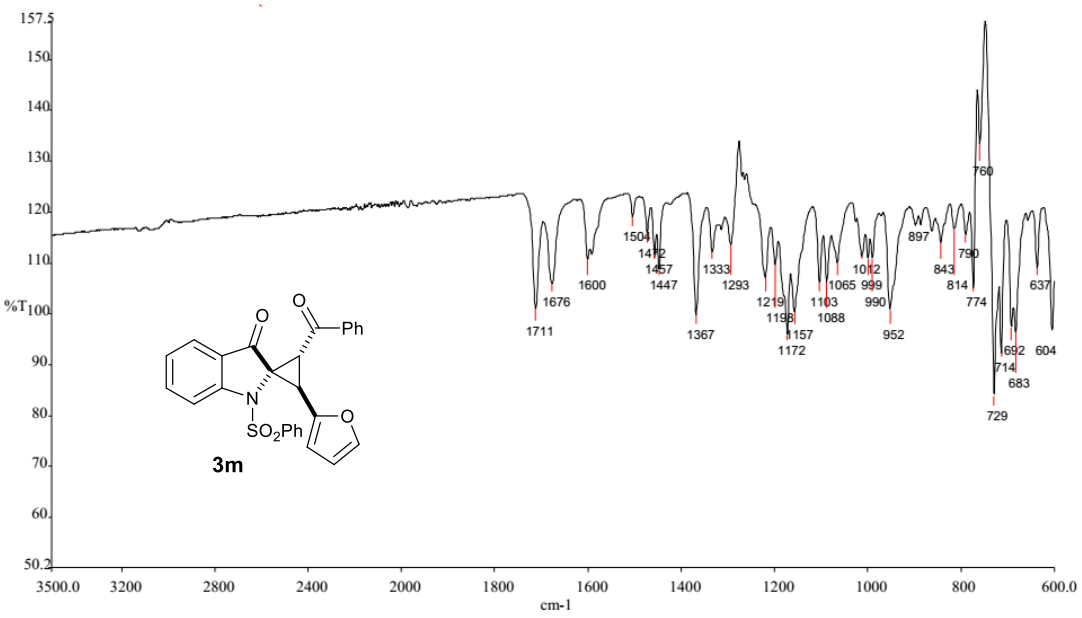
3l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1172
1103
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1065
1012
999
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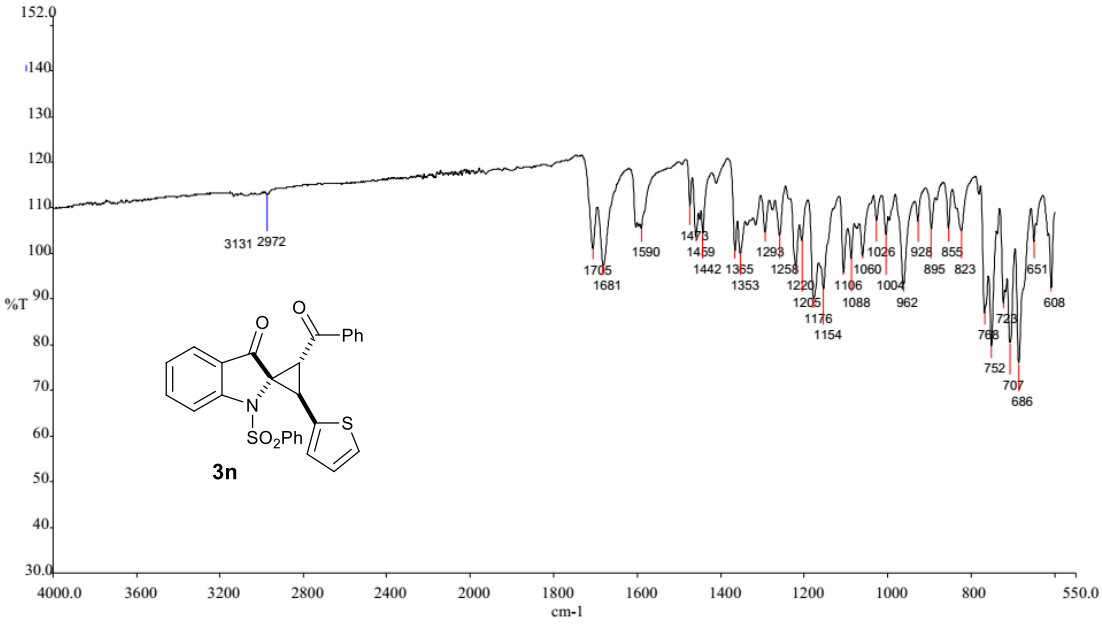
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1060
1026
1004
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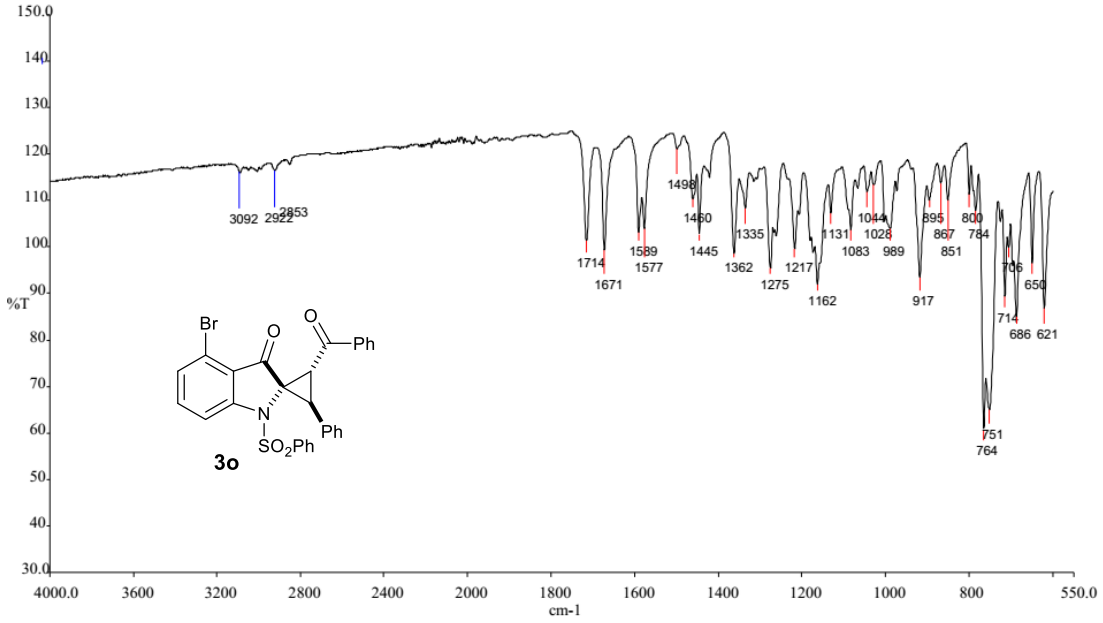
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1131
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989
917
895
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621
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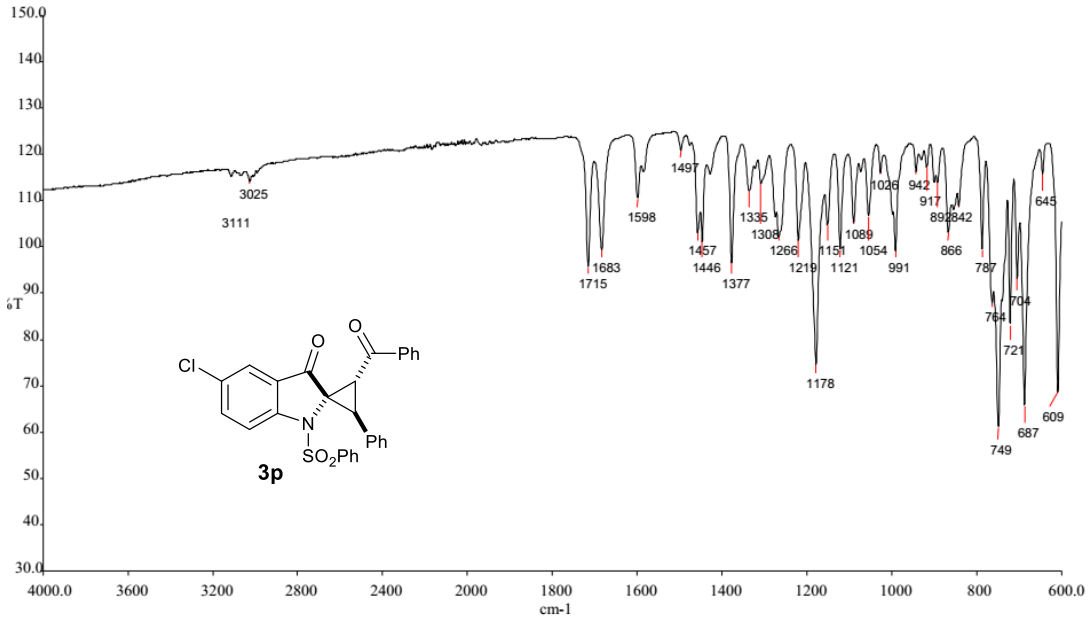
SO2Ph
Ph
3o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1151
1121
1089
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1026
991
942
917
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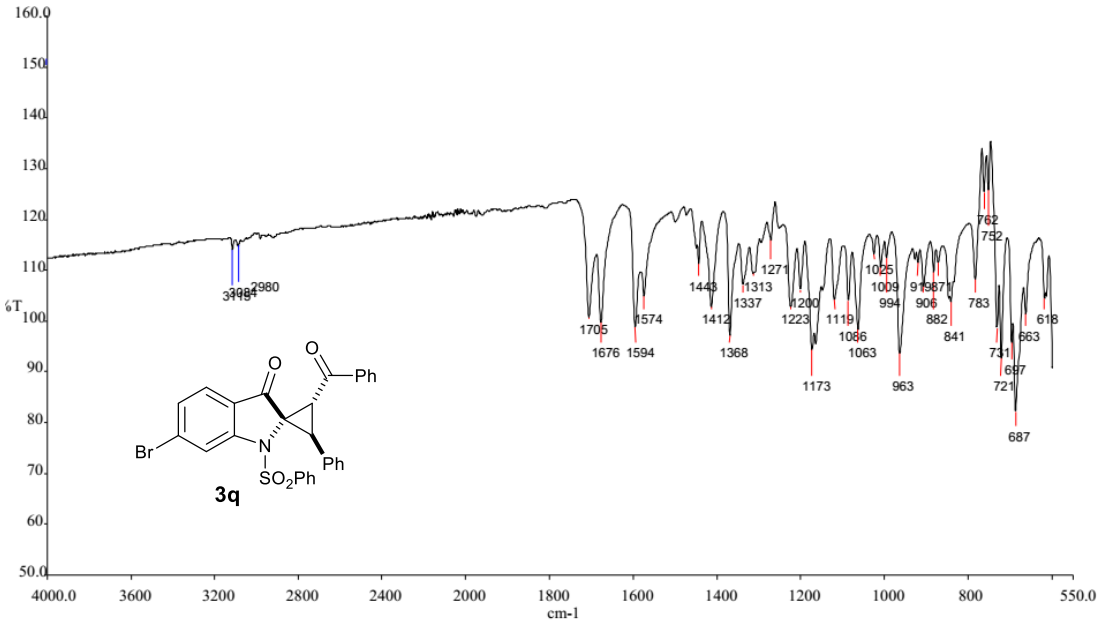
Cl
O
Ph
N
SO2Ph
Ph
3p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Ph
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1119
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752
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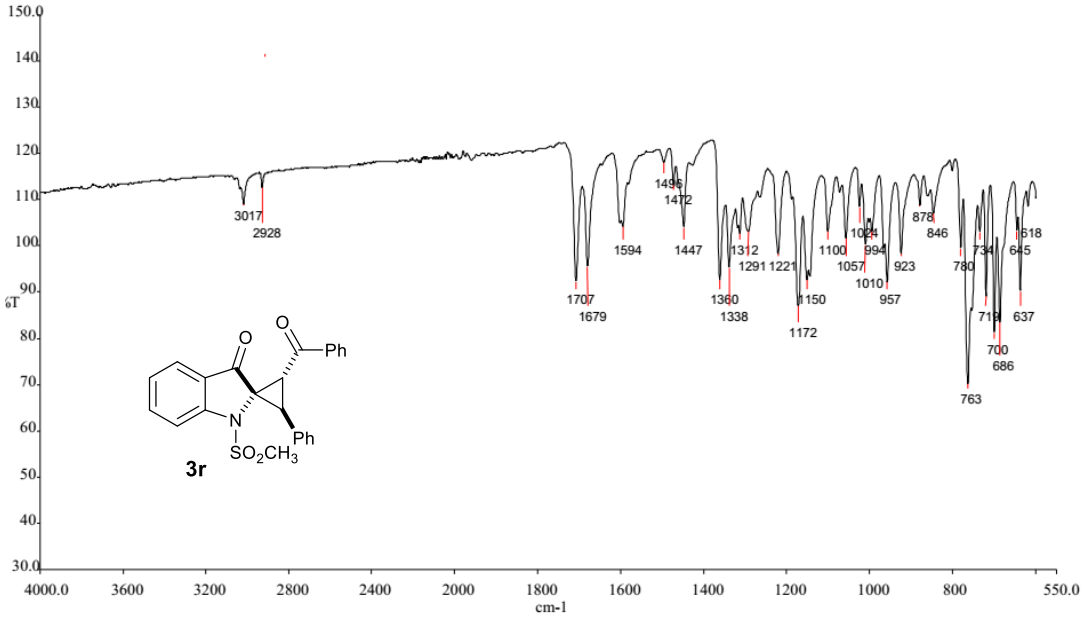
663
618


%T
cm-1
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Ph
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1338
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1150
1100
1057
1024
1010
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957
923
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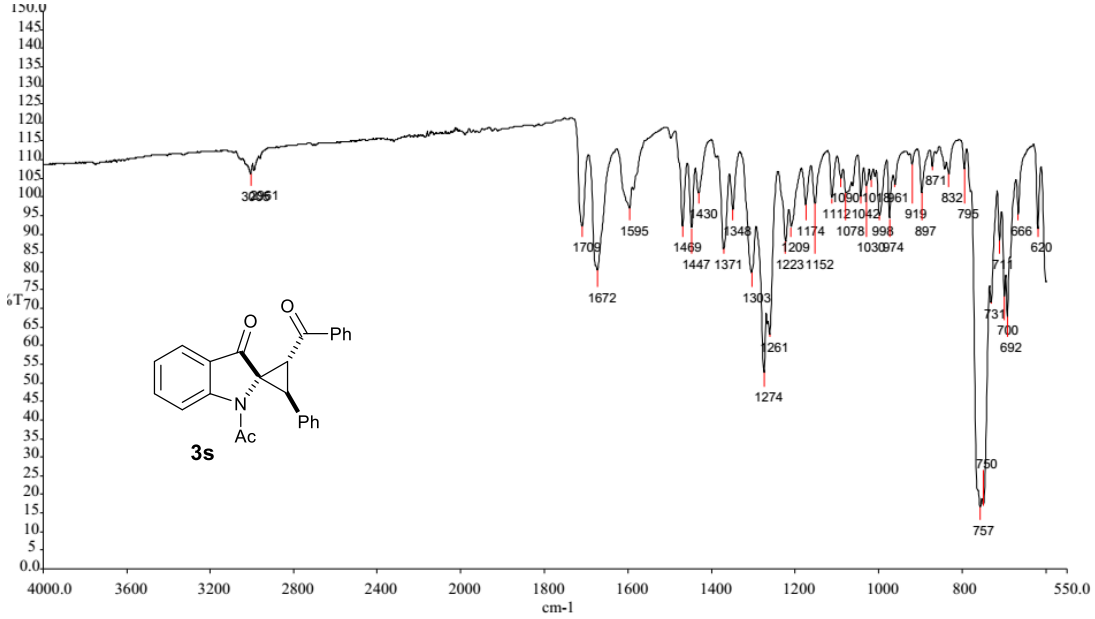
846
780
763
734
719
700
686
645
637
618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cm-1
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3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
550.0
3s
Ac
Ph
Ph
O
O
N
1709
1672
1595
1469
1447
1430
1371
1348
1303
1274
1261
1223
1209
1174
1152
1111
1090
1078
1042
1030
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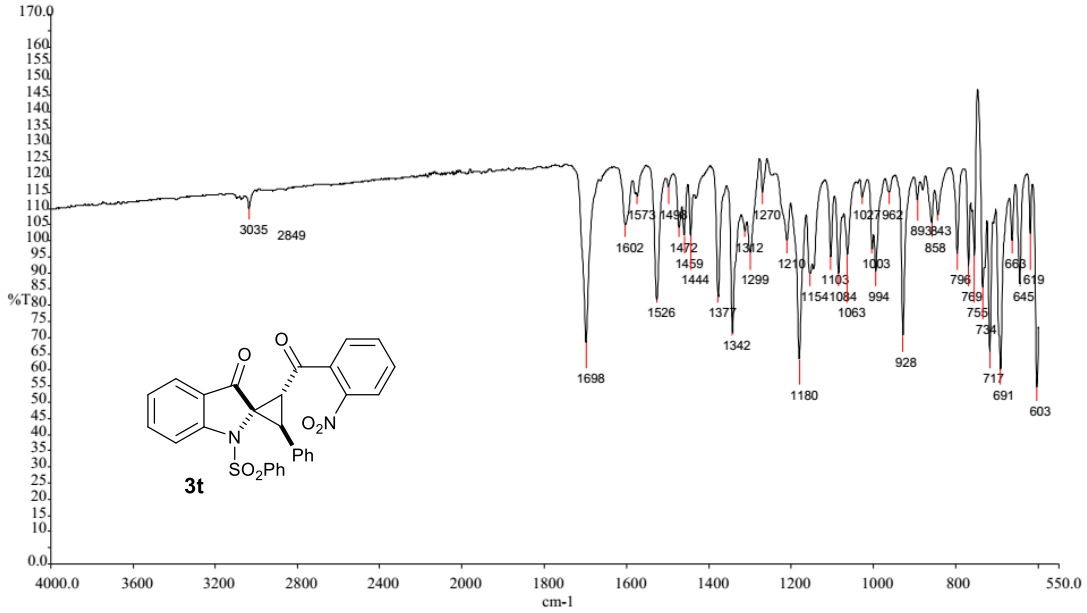
974
961
919
897
871
832
795
757
750
731
711
700
692
666
620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cm-1
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1600
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800
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3t
SO2Ph
O2N
Ph
O
O
N
3035
2849
1698
1602
1573
1526
1498
1472
1459
1444
1377
1342
1312
1299
1270
1210
1180
1154
1103
1084
1063
1027
1003
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928
893
858
843
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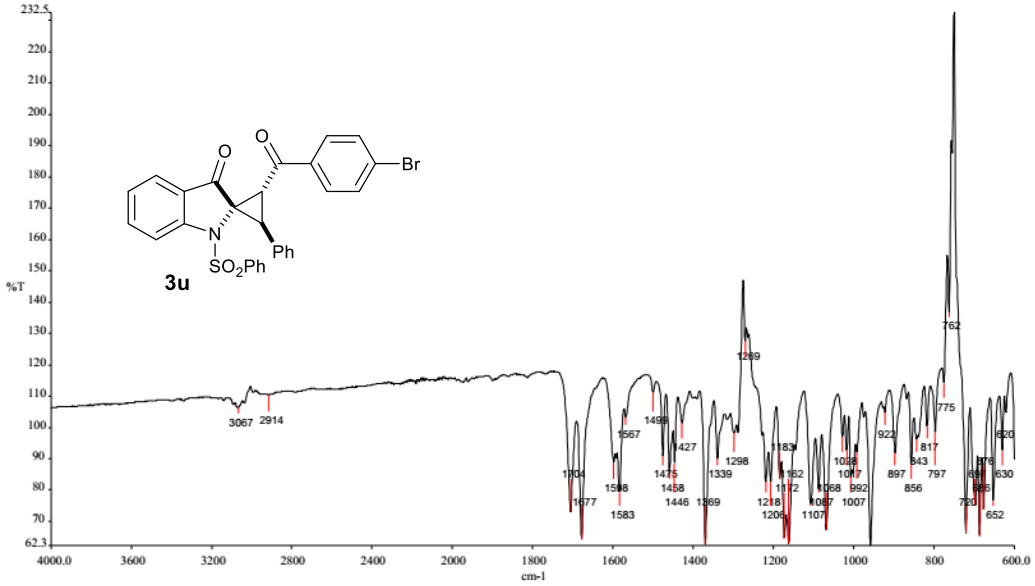
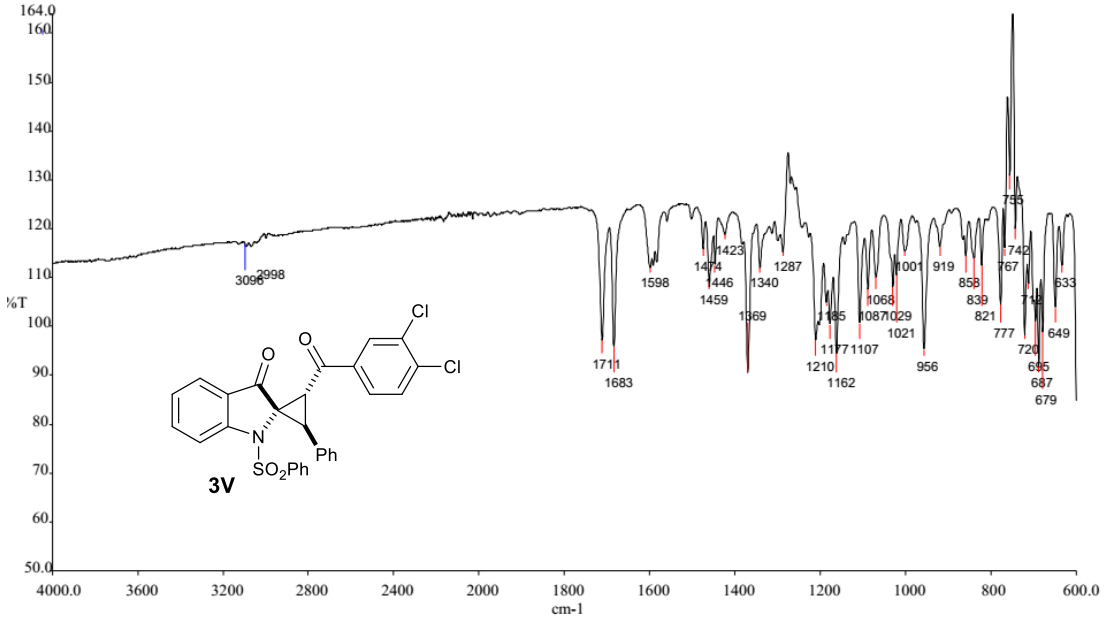
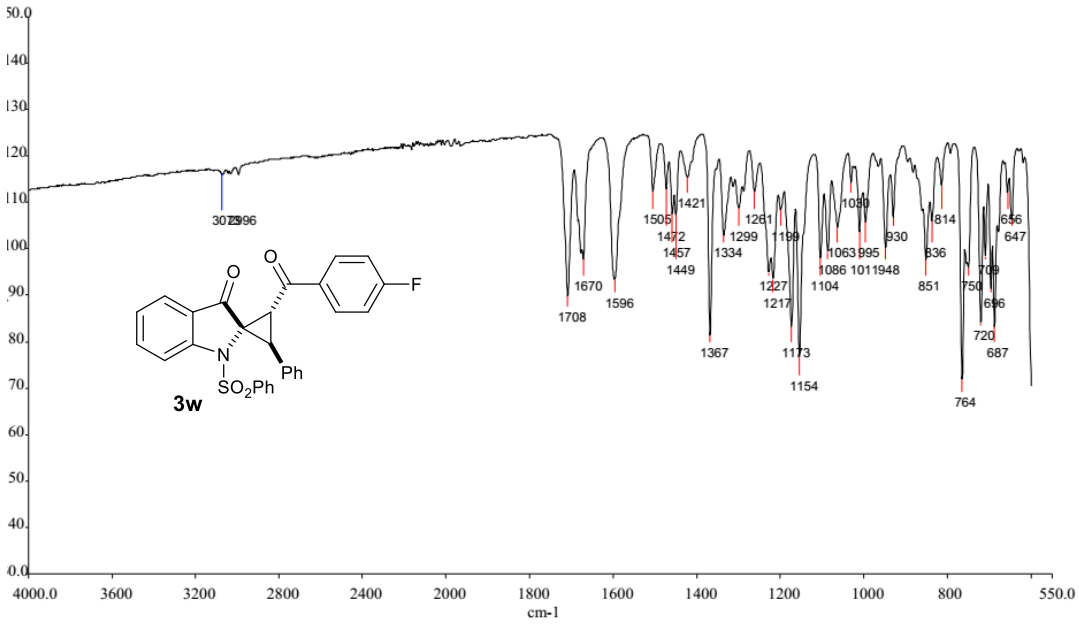
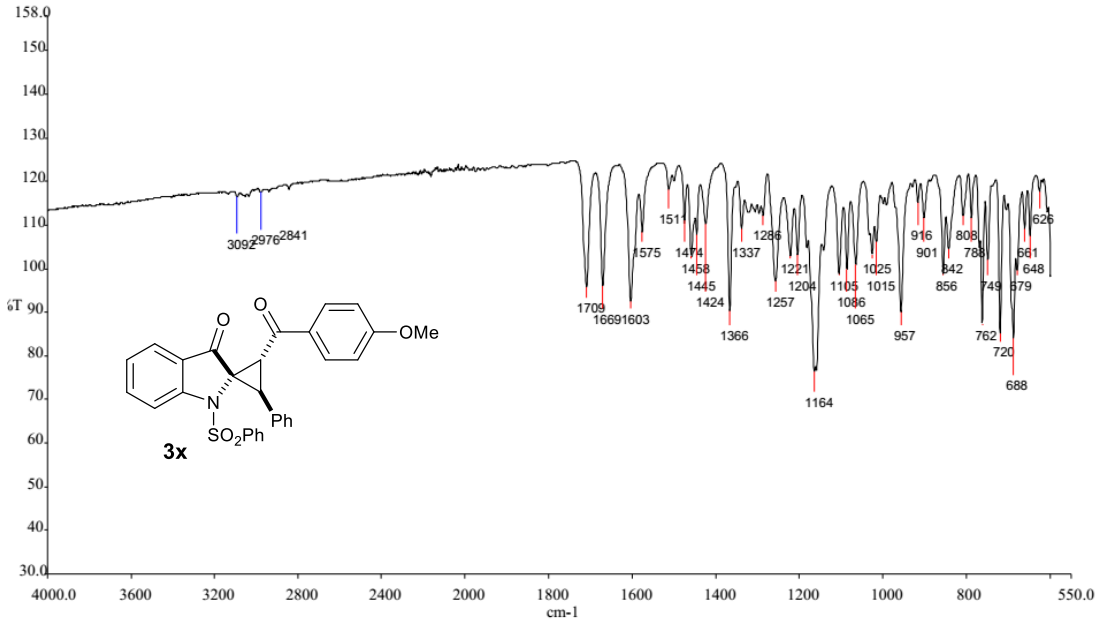
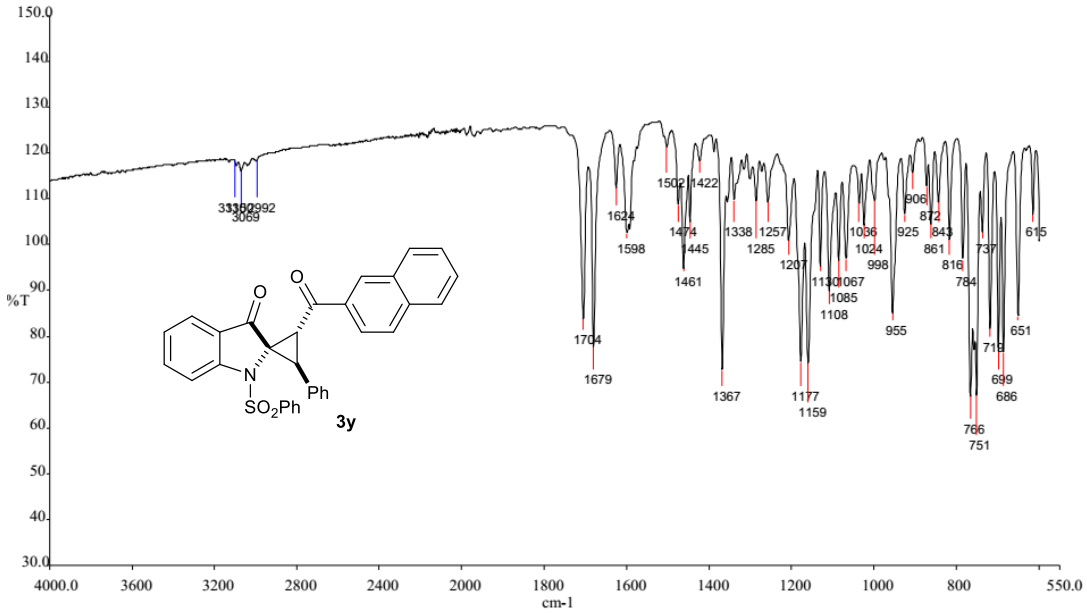
769
755
734
717
691
663
645
619
603


3u
%T
cm-1

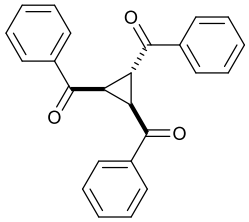

3V
%T
cm-1


3w
F
Ph
SO2Ph
cm-1

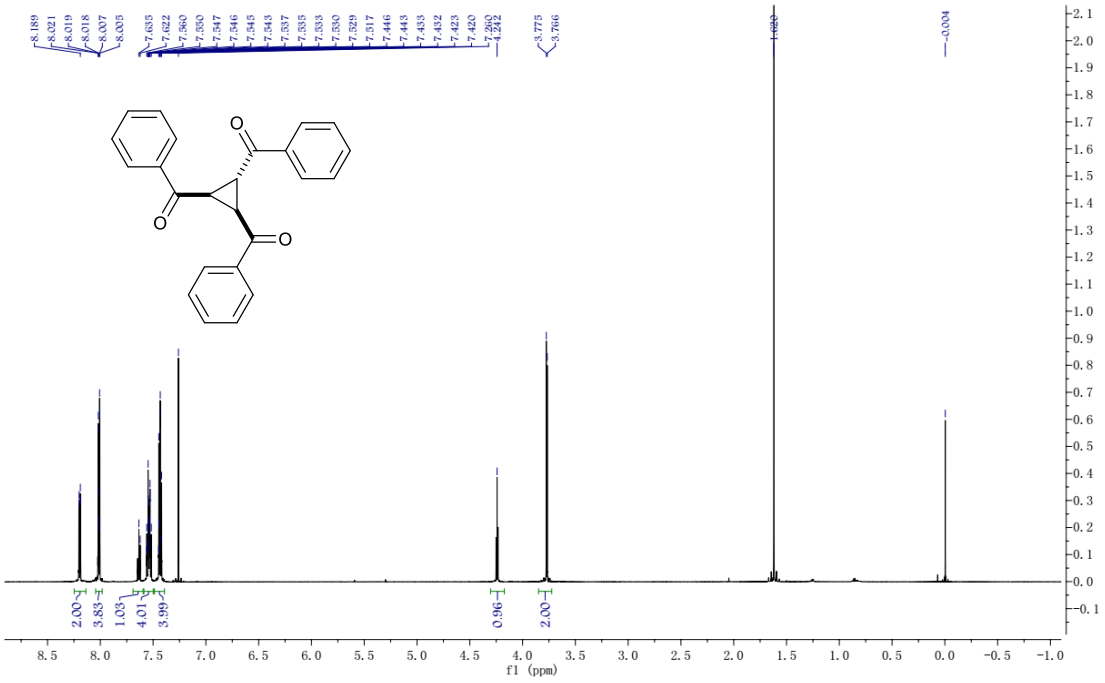

3x
OMe
Ph
SO2Ph
%T
cm-1

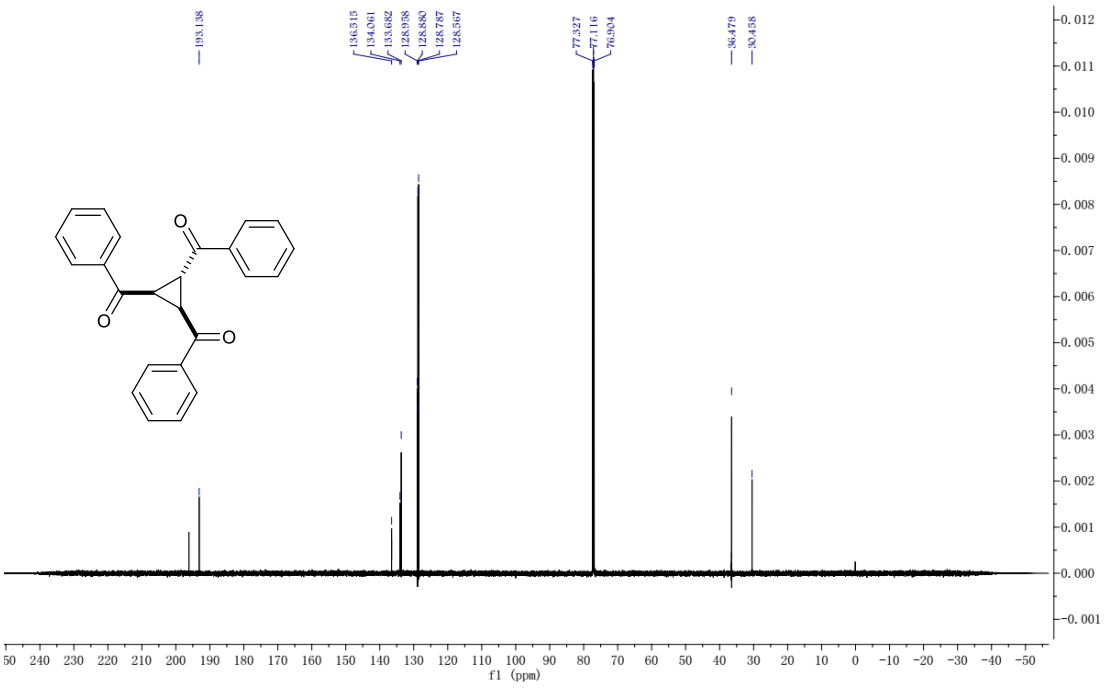

150.0
140
130
120
110
100
90
80
70
60
50
40
30.0
%T
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
550.0
cm-1
3069
1704
1679
1624
1598
1502
1474
1461
1445
1422
1367
1338
1285
1257
1207
1177
1159
1130
1108
1085
1067
1036
1024
998
955
925
906
872
861
843
816
784
766
751
737
719
699
686
651
615
O
O
N
SO2Ph
Ph
3y

9. **Spectra of the By-product**



White solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.20-8.19 (m, 2H), 8.02-8.01 (m, 4H), 7.65-7.62 (m, 1H), 7.56-7.52 (m, 4H), 7.45-7.42 (m, 4H), 4.24 (t, *J* = 5.4 Hz, 1H), 3.77 (d, *J* = 5.4 Hz, 1H), 7.35-7.33 (m, 3H), 7.28-7.24 (m, 1H), 7.18 (d, 7.6 Hz, 2H) ppm.^{13}C NMR (150 MHz, $CDCl_3$): δ = 196.2, 193.1, 136.5, 136.5, 134.1, 133.7, 129.0, 128.9, 128.8, 128.6, 36.5, 30.5 ppm. HRMS (ESI): *m/z* calculated for $C_{24}H_{18}O_3^{+}Na$: 377.1148, found: 377.1144.




193.138
136.515
134.061
133.682
128.958
128.880
128.787
128.567
77.327
77.116
76.904
36.479
30.458
O
O
O
0.012
0.011
0.010
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0.000
-0.001
f1 (ppm)

10. Computational Data and Details

All calculations and geometry optimizations were performed with the Gaussian 09 Rev. D01 program. Geometry optimizations of all the minima structures involved were carried out using the 6-31+G basis set for the optimization of all stationary points in gas phase without any constraints. Optimizations at different theoretical levels were completed to verify the influence of different methods, which came to the same conclusion. The wave functions of all stationary points have been computationally tested as stable ones. Frequency calculations were performed to confirm that each stationary point was a global minimum with the imaginary frequency as zero.

	major	Minor1	Minor2	Minor3
E_{ele} (singlet, a.u.)	-4441.58	-4441.58	-4441.57	-4441.57

Cartesian Coordinates of All Computed Structures

Major

Br	-6.33467	-1.41365	0.40946
C	-2.36813	-2.06016	-0.78089
C	1.90731	-2.12102	-0.9354
C	2.74372	-3.25696	-0.44665
C	3.76631	-3.69422	-1.30413
C	4.59494	-4.74833	-0.93753
C	4.41308	-5.38075	0.29747
C	3.40176	-4.95066	1.15927
C	2.56915	-3.89317	0.79034
C	0.52687	0.19152	1.67923
C	1.62525	1.10542	2.03881
C	1.98449	1.59695	3.28954
C	-3.73313	-2.21618	-0.54742
C	3.10713	2.41852	3.38232
C	3.8537	2.72453	2.23127
C	3.50846	2.224	0.97372
C	2.37522	1.41149	0.88966
C	0.39297	3.18374	-1.12543
C	0.89783	4.29792	-0.47425

C	-0.0066	5.2652	-0.03108
C	-1.376	5.09872	-0.26074
C	-1.85114	3.9751	-0.94469
C	-0.95518	3.00129	-1.39114
C	-4.44366	-1.19941	0.07922
C	-3.80209	-0.03197	0.47075
C	-2.43558	0.12301	0.23467
C	-1.70123	-0.89016	-0.39132
C	-0.25042	-0.7507	-0.73143
C	0.73959	-0.09023	0.2008
C	0.78547	-1.64294	-0.08372
H	-1.81434	-2.8535	-1.27015
H	3.88136	-3.18148	-2.25095
H	5.38064	-5.07934	-1.60639
H	5.05697	-6.20336	0.58658
H	3.26197	-5.43673	2.11761
H	1.79515	-3.57	1.47476
H	1.39654	1.33118	4.1604
H	-4.24303	-3.1209	-0.84952
H	3.41665	2.8126	4.34246
H	4.7324	3.35289	2.32096
H	4.0783	2.45069	0.08506
H	1.96525	4.40895	-0.33849
H	0.35713	6.14704	0.48181
H	-2.07369	5.85308	0.08285
H	-2.9103	3.86157	-1.14073
H	-1.2795	2.13532	-1.95402
H	-4.36446	0.74938	0.96393
H	-1.94245	1.03433	0.54532
H	-0.01098	-0.54842	-1.77462
H	0.4634	-2.21841	0.77243
N	1.845	0.74559	-0.25886
O	2.14276	-1.57688	-2.02712
O	-0.31947	-0.33013	2.41106
O	2.98223	2.56422	-1.96406
O	0.8134	1.09054	-2.87354
S	1.56748	1.88802	-1.72667

Minor1

Br	-6.64496	-0.47715	0.81019
C	-2.46573	-0.76527	0.59422
C	1.27999	-2.44986	-1.22379
C	2.37342	-3.06104	-0.41056

C	3.26267	-3.90727	-1.09344
C	4.30405	-4.53278	-0.41824
C	4.46798	-4.32285	0.95607
C	3.58691	-3.48616	1.64384
C	2.5367	-2.85692	0.96949
C	1.0255	0.60897	-2.1219
C	0.81392	2.06165	-1.92035
C	1.12291	3.12027	-2.76573
C	-3.77435	-0.6425	1.05621
C	0.80258	4.41398	-2.34962
C	0.18539	4.62656	-1.10589
C	-0.13267	3.56491	-0.25378
C	0.19128	2.27948	-0.684
C	2.56257	1.43026	1.42679
C	2.92833	2.72436	1.76904
C	4.25463	3.10937	1.57452
C	5.17446	2.19841	1.04682
C	4.77712	0.89903	0.71973
C	3.45144	0.50012	0.91156
C	-4.83472	-0.64212	0.15757
C	-4.60047	-0.76188	-1.20572
C	-3.29169	-0.88103	-1.66988
C	-2.20544	-0.88568	-0.78125
C	-0.84204	-1.03248	-1.33933
C	0.31052	-0.02864	-0.94502
C	0.33057	-1.50303	-0.53181
H	-1.65331	-0.75652	1.30959
H	3.10421	-4.05196	-2.15488
H	4.98571	-5.18312	-0.95368
H	5.27671	-4.81155	1.48725
H	3.70925	-3.32695	2.70879
H	1.8709	-2.20602	1.52602
H	1.59551	2.92699	-3.72166
H	-3.96974	-0.54775	2.1158
H	1.02163	5.26026	-2.98922
H	-0.06129	5.63696	-0.80125
H	-0.59792	3.71519	0.70907
H	2.18371	3.38816	2.18797
H	4.56734	4.11271	1.83633
H	6.20387	2.49992	0.89452
H	5.49214	0.19127	0.31917
H	3.14832	-0.51105	0.67747
H	-5.43189	-0.7636	-1.89753
H	-3.11166	-0.97542	-2.73507

H	-0.769	-1.31983	-2.38473
H	0.17438	-1.65591	0.52486
N	-0.05889	1.03779	-0.003
O	1.13779	-2.73571	-2.42024
O	1.57465	0.04585	-3.07001
O	0.13771	2.24952	2.47591
O	0.56714	-0.46058	2.25746
S	0.77086	1.02214	1.68921

Minor2

Br	-5.03713	3.10367	0.93367
C	-2.18163	0.03143	0.83896
C	-0.71453	-2.79563	0.28102
C	-1.85082	-3.28645	-0.55211
C	-2.68343	-4.26475	0.01214
C	-3.75859	-4.77467	-0.70702
C	-4.01183	-4.31046	-2.00282
C	-3.18717	-3.33654	-2.57136
C	-2.10932	-2.82396	-1.84912
C	0.9493	-0.70705	1.93456
C	2.32716	-0.54682	2.41745
C	2.77264	-0.41207	3.7276
C	-3.29727	0.81105	1.13897
C	4.1399	-0.27619	3.95993
C	5.03427	-0.29005	2.87753
C	4.6013	-0.43238	1.55666
C	3.22519	-0.55219	1.3339
C	2.95939	1.39423	-1.72289
C	3.4565	2.30362	-0.8019
C	3.27552	3.66425	-1.06092
C	2.62004	4.07629	-2.2256
C	2.14073	3.13471	-3.14088
C	2.31425	1.77201	-2.8906
C	-3.48808	2.03281	0.50679
C	-2.56948	2.48913	-0.42938
C	-1.45584	1.70923	-0.73347
C	-1.24093	0.46967	-0.10612
C	-0.04122	-0.3048	-0.5321
C	1.06224	-0.84612	0.41736
C	0.20937	-1.81206	-0.38091
H	-2.02498	-0.8911	1.37275
H	-2.45741	-4.60289	1.01605
H	-4.39861	-5.53003	-0.26644

H	-4.84923	-4.70572	-2.56629
H	-3.38604	-2.97536	-3.57341
H	-1.47899	-2.06164	-2.28884
H	2.04974	-0.418	4.53486
H	-4.01652	0.4674	1.86974
H	4.5167	-0.17167	4.96951
H	6.09817	-0.20261	3.06662
H	5.29585	-0.48484	0.73207
H	3.95943	1.97203	0.09815
H	3.64448	4.39733	-0.35442
H	2.48524	5.13344	-2.42013
H	1.63998	3.45697	-4.04561
H	1.96159	1.00433	-3.56787
H	-2.72478	3.4418	-0.91751
H	-0.74088	2.06775	-1.46652
H	0.37299	0.04809	-1.46985
H	0.73461	-2.20201	-1.25011
N	2.49456	-0.68465	0.13792
O	-0.53082	-3.21539	1.43205
O	-0.08455	-0.71636	2.60608
O	4.70233	-0.8622	-1.41611
O	2.2047	-1.12772	-2.5328
S	3.17732	-0.43147	-1.47527

Minor3

Br	-5.98243	-1.25833	-0.32876
C	-2.90181	0.24695	2.08042
C	0.20837	2.07716	0.24928
C	0.46155	3.54562	0.19138
C	-0.22893	4.26433	-0.797
C	-0.05823	5.63858	-0.92201
C	0.82308	6.31083	-0.06882
C	1.53052	5.60061	0.90395
C	1.34878	4.224	1.03806
C	1.8123	-0.55774	2.71429
C	2.29522	-1.89152	2.3125
C	2.96812	-2.85973	3.04758
C	-4.15658	-0.09317	1.57808
C	3.2746	-4.06892	2.41972
C	2.91039	-4.28703	1.08154
C	2.23626	-3.31138	0.34149
C	1.92704	-2.11433	0.9771
C	1.94197	-0.63999	-2.44811

C	0.74146	-0.13394	-2.9185
C	0.30607	-0.56487	-4.17538
C	1.07013	-1.47087	-4.91679
C	2.28075	-1.95539	-4.41268
C	2.72874	-1.53491	-3.1599
C	-4.24748	-0.77393	0.37121
C	-3.09873	-1.11438	-0.33211
C	-1.84422	-0.76419	0.16289
C	-1.7277	-0.07639	1.38009
C	-0.43618	0.29464	2.0179
C	0.98233	-0.09228	1.52991
C	0.56158	1.36184	1.50342
H	-2.83453	0.77104	3.0278
H	-0.8959	3.71578	-1.44991
H	-0.60408	6.18694	-1.6807
H	0.96182	7.38148	-0.16523
H	2.22683	6.11706	1.5539
H	1.92476	3.68254	1.77685
H	3.23694	-2.67054	4.08011
H	-5.0553	0.16388	2.12211
H	3.7927	-4.8478	2.96566
H	3.15655	-5.23182	0.61159
H	1.95833	-3.47914	-0.69058
H	0.1624	0.5614	-2.32155
H	-0.62997	-0.18986	-4.57128
H	0.72349	-1.79716	-5.89029
H	2.87528	-2.65169	-4.99164
H	3.66318	-1.87036	-2.72848
H	-3.18413	-1.65278	-1.26644
H	-0.94892	-1.02845	-0.377
H	-0.47256	0.28526	3.10442
H	1.03662	1.93527	2.28839
N	1.24813	-0.97686	0.3861
O	-0.37626	1.50171	-0.68787
O	1.92939	0.04332	3.78566
O	2.61968	1.42495	-0.5092
O	3.98951	-0.94366	-0.62205
S	2.625	-0.14187	-0.80145