Supplementary Information

Catalyst-free direct arylsulfonylation of N-arylacrylamides with sulfinic acids: A convenient and efficient route to sulfonated oxindoles

Wei Wei[a], Jiangwei Wen[a], Daoshan Yang[a], Juan Du[a], Jinmao You[a], Hua Wang[a*]

[a] *The Key Laboratory of Life-Organic Analysis and Key Laboratory of Pharmaceutical Intermediates and Analysis of Natural Medicine, School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu 273165, Shandong, China.*

[*] *Phone: +86 537 4458317; Fax: +86 537 4458317.* E-mail: huawang_qfnu@126.com

Contents

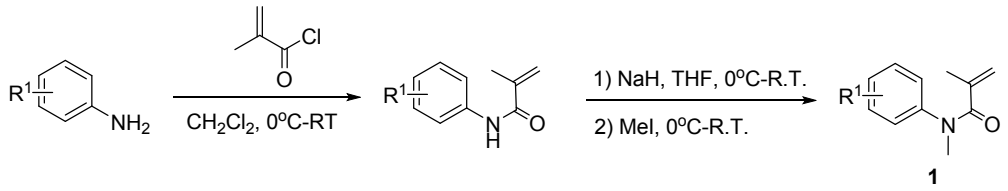
1. General information

All commercially available reagent grade chemicals were purchased from Aldrich, Acros, Alfa Aesar and Beijing Ouhe Chemical Company and used as received without further purification unless otherwise stated. All solvents were dried according to standard procedures. ^{1}H NMR and ^{13}C NMR were recorded in $CDCl_3$ on a Bruker Avance III 400 spectrometer with TMS as internal standard (400 MHz ^{1}H, 100 MHz ^{13}C) at room temperature, the chemical shifts (δ) were expressed in ppm and J values were given in Hz. The following abbreviations are used to indicate the multiplicity: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). All first order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted were designated as multiplet (m). Mass analyses and HRMS were obtained on a Finnigan-LCQDECA mass spectrometer and a Bruker Daltonics Bio-TOF-Q mass spectrometer by the ESI method, respectively. Column chromatography was performed on silica gel (200-300 mesh).

2. Typical procedures for the synthesis of substrates

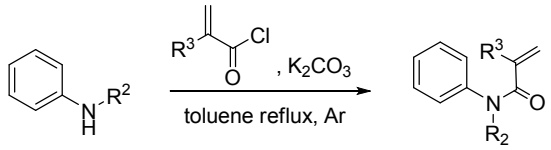
N-arylacrylamides **1** were prepared according to previous literatures[S1,2].

Method A: substrate **1** was prepared according to previous literature.[S1]



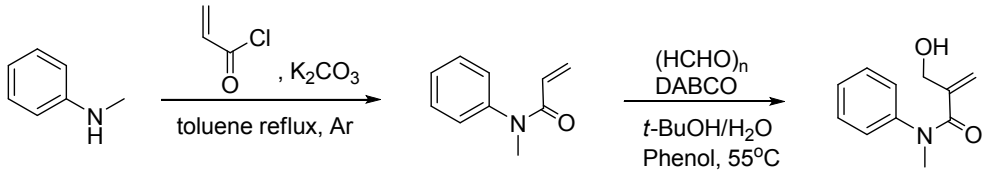
1

Method B: Substrate **1** was prepared according to previous literature.[S2]



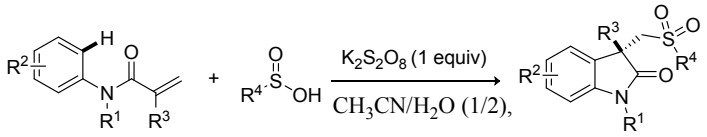
1l,1n

Substrate **1m** were prepared according to literature.[S1]



1m

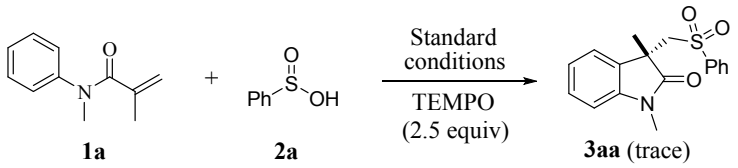
3. General procedure for catalyst-free direct arylsulfonylation of N-arylacrylamides with the sulfinic acids.



To a mixture of N-arylacrylamide **1** (0.25 mmol), sulfinic acids **2** (0.75 mmol), and $K_2S_2O_8$ (0.25 mmol) in a 25 mL round-bottomed flack at room temperature, was added the CH_3CN/H_2O (1/2, 3 mL). The reaction vessel was allowed to stir at 80 °C for 12-24h. After the reaction, the resulting mixture was extracted with EtOAc. The combined

organic phase was dried over anhydrous Na_2SO_4 and the solvent was then removed under vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **3**.

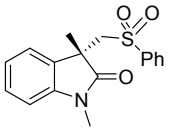
4. Preliminary mechanistic studies with TEMPO.



1a **2a** **3aa** (trace)

To a mixture of N-aryl acrylamide **1a** (0.25 mmol), benzenesulfinic acid **2a** (0.75 mmol), TEMPO (0.625 mmol), $K_2S_2O_8$ (0.25 mmol), and CH_3CN/H_2O (1/2) 3 mL at room temperature. The reaction vessel was allowed to stir for 12 h at 80 °C. After the reaction, the solution was concentrated in vacuum, only a trace amount of desired product was detected.

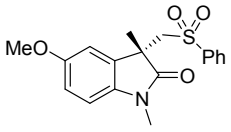
5. Characterization data of products 3aa-3aj



(3aa)

Compound **3aa** was obtained in 87% yield according to the general procedure (12h)[S3].

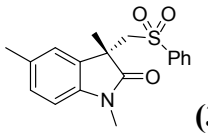
^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.58-7.52 (m, 3H), 7.40 (t, J = 8.0 Hz, 2H), 7.31 (d, J = 7.7 Hz, 1H), 7.08 (d, J = 7.4 Hz, 1H), 6.92 (t, J = 7.5 Hz, 1H), 6.87 (d, J = 7.8 Hz, 1H), 3.90 (d, J = 14.6 Hz, 1H), 3.70 (d, J = 14.6 Hz, 1H), 3.19 (s, 3H), 1.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 177.7, 144.3, 140.0, 133.4, 129.5, 128.9, 128.6, 127.8, 124.1, 122.6, 108.4, 61.9, 45.6, 26.6, 25.5. HRMS (ESI) calcd for $C_{17}H_{18}NO_3S$ $(M + H)^+$ 316.1007, found 316.1006.



(3ba)

Compound **3ba** was obtained in 86% yield according to the general procedure (12h)[S3].

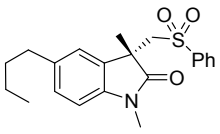
^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.56-7.52 (m, 1H), 7.50-7.47 (m, 2H), 7.31 (t, J = 7.4 Hz, 2H), 6.82-6.75 (m, 2H), 6.56 (t, J = 2.4 Hz, 1H), 3.89 (d, J = 14.7 Hz, 1H), 3.68 (d, J = 14.6 Hz, 1H), 3.66 (s, 3H), 3.17 (s, 3H), 1.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 177.3, 155.8, 140.1, 136.8, 133.3, 130.7, 128.8, 127.8, 113.4, 111.2, 108.7, 61.9, 55.6, 46.1, 26.6, 25.4. MS (ESI$^+$): $[M+H]^+$ 346.04.



(3ca)

Compound **3ca** was obtained in 84% yield according to the general procedure (12h)[S3].

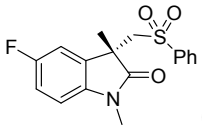
^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.53 (t, J = 6.9 Hz, 1H), 7.43 (d, J = 8.0 Hz, 2H), 7.35 (t, J = 7.7 Hz, 2H), 7.05 (d, J = 7.8 Hz, 1H), 6.75 (d, J = 7.9 Hz, 1H), 6.65 (s, 1H), 3.91 (d, J = 14.7 Hz, 1H), 3.70 (d, J = 14.7 Hz, 1H), 3.19 (s, 3H), 2.13 (s, 3H), 1.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 177.6, 141.1, 140.0, 133.1, 131.8, 129.4, 129.0, 128.7, 127.8, 124.8, 108.1, 61.9, 45.6, 26.6, 25.4, 20.9. MS (ESI$^+$): $[M+H]^+$ 330.08.



(3da)

Compound **3da** was obtained in 90% yield according to the general procedure (12h).

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.53 (t, J = 7.3 Hz, 1H), 7.50 (d, J = 1.0 Hz, 2H), 7.37 (t, J = 7.6 Hz, 2H), 7.09 (d, J_1 = 1.3 Hz, J_2 = 8.0 Hz, 1H), 6.84 (d, J = 1.2 Hz, 1H), 6.76 (d, J = 7.9 Hz, 1H), 3.89 (d, J = 14.6 Hz, 1H), 3.69 (d, J = 14.6 Hz, 1H), 3.17 (s, 3H), 2.52-2.37 (m, 2H), 1.56-1.49 (m, 2H), 1.40 (s, 3H), 1.39-1.31 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 177.6, 141.2, 140.1, 137.2, 133.2, 129.4, 128.7, 128.3, 127.8, 124.3, 108.1, 62.0, 45.7, 35.2, 33.7, 26.6, 25.5, 22.4, 13.9; MS (ESI$^+$): $[M+H]^+$ 372.09.

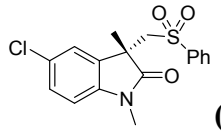


(3ea)

Compound **3ea** was obtained in 71% yield according to the general procedure (12h)[S3].

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.59-7.55 (m, 3H), 7.43 (t, J = 7.4 Hz, 2H), 7.00 (td, J_1 = 1.3 Hz, J_2 = 8.6 Hz, 1H), 6.81-6.77 (m, 2H), 3.88 (d, J = 14.6 Hz, 1H), 3.67 (d, J =

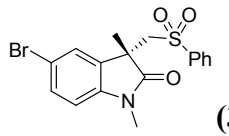
14.6 Hz, 1H), 3.20 (s, 3H), 1.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 177.3, 159.1 (d, J = 239.2 Hz), 140.0, 139.3 (d, J = 2.0 Hz), 133.6, 131.2 (d, J = 8.1 Hz), 129.0, 127.7, 115.0 (d, J = 23.4 Hz), 112.2 (d, J = 25.0 Hz), 108.8 (d, J = 8.1 Hz), 61.7, 46.0 (d, J = 1.8 Hz), 26.7, 25.3; MS (ESI$^+$): $[M+H]^+$ 334.09.



(3fa)

Compound **3fa** was obtained in 76% yield according to the general procedure (12h)[S3].

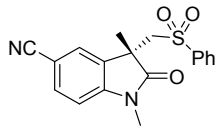
^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.59 (dt, J_1 = 1.3 Hz, J_2 = 7.0 Hz, 1H), 7.50-7.48 (m, 2H), 7.43-7.39 (m, 2H), 7.24 (dd, J_1 = 2.1 Hz, J_2 = 8.3 Hz, 1H), 6.83 (d, J = 2.0 Hz, 1H), 6.80 (d, J = 8.3 Hz, 1H), 3.90 (d, J = 14.7 Hz, 1H), 3.68 (d, J = 14.7 Hz, 1H), 3.23 (s, 3H), 1.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 177.2, 142.1, 139.8, 133.6, 131.1, 129.0, 128.7, 127.9, 127.6, 124.5, 109.3, 61.7, 45.8, 26.7, 25.2; MS (ESI$^+$): $[M+H]^+$ 350.0.



(3ga)

Compound **3ga** was obtained in 85% yield according to the general procedure (12h)[S3].

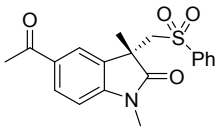
^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.60 (dt, J_1 = 1.3 Hz, J_2 = 7.3 Hz, 1H), 7.49-7.46 (m, 2H), 7.43-7.37 (m, 3H), 6.93 (d, J = 1.9 Hz, 1H), 6.76 (d, J = 8.3 Hz, 1H), 3.90 (d, J = 14.7 Hz, 1H), 3.68 (d, J = 14.7 Hz, 1H), 3.23 (s, 3H), 1.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 177.1, 142.6, 139.8, 133.6, 131.6, 131.5, 129.0, 127.6, 127.2, 115.2, 109.8, 61.8, 45.7, 26.7, 25.3; MS (ESI$^+$): $[M+H]^+$ 394.0.



(3ha)

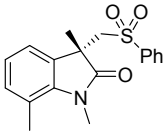
Compound **3ha** was obtained in 58% yield according to the general procedure (14h).

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.67-7.60 (m, 2H), 7.53 (d, J = 7.2 Hz, 2H), 7.45 (t, J = 7.4 Hz, 2H), 7.16 (d, J = 1.4 Hz, 1H), 6.96 (d, J = 8.2 Hz, 1H), 3.92 (d, J = 14.7 Hz, 1H), 3.74 (d, J = 14.7 Hz, 1H), 3.29 (s, 3H), 1.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 177.5, 147.3, 139.8, 133.9, 133.9, 130.6, 129.2, 127.5, 127.4, 118.7, 108.9, 106.8, 61.6, 45.3, 26.9, 25.1; MS (ESI$^+$): $[M+H]^+$ 341.0.



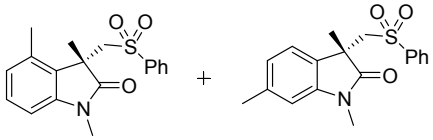
(3ia)

Compound **3ia** was obtained in 70% yield according to the general procedure (12h). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.94 (dd, J_1 = 1.7 Hz, J_2 = 8.2 Hz, 1H), 7.51-7.46 (m, 4H), 7.36 (d, J = 7.5 Hz, 2H), 6.94 (d, J = 8.4 Hz, 1H), 3.94 (d, J = 14.7 Hz, 1H), 3.78 (d, J = 14.7 Hz, 1H), 3.30 (s, 3H), 2.48 (s, 3H), 1.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 196.2, 178.1, 147.8, 140.0, 133.3, 131.9, 130.5, 129.6, 129.0, 127.5, 123.9, 108.0, 61.8, 45.4, 26.9, 26.3, 25.2; MS (ESI$^+$): $[M+H]^+$ 358.0.



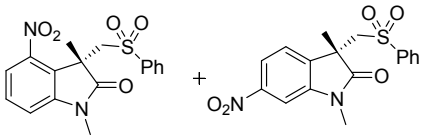
(3ja)

Compound **3ja** was obtained in 71% yield according to the general procedure (12h). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.56-7.54 (m, 3H), 7.41 (t, J = 7.6 Hz, 2H), 7.02 (d, J = 7.5 Hz, 1H), 6.92 (d, J = 7.2 Hz, 1H), 6.81 (d, J = 7.5 Hz, 1H), 3.91 (d, J = 14.6 Hz, 1H), 3.67 (d, J = 14.6 Hz, 1H), 3.46 (s, 3H), 2.60 (s, 3H), 1.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 178.4, 141.1, 140.1, 133.3, 132.3, 130.1, 128.8, 127.9, 122.4, 122.0, 120.0, 62.2, 45.1, 30.0, 25.9, 19.1; HRMS (ESI) calcd for $C_{18}H_{20}NO_3S$ $(M + H)^+$ 330.1164, found 330.1161.



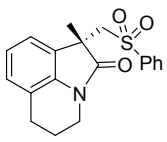
3ka **3ka'**

Compounds **3ka** and 3**ka'** were obtained in 60% yield according to the general procedure (12h)[S3]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58−7.53 (m, 2.5H), 7.47−7.44 (m, 2H), 7.42−7.36 (m, 3H), 7.23 (t, J = 7.8 Hz, 1H), 6.96 (d, J = 7.8 Hz, 0.5H), 6.74−7.68 (m, 3H), 3.99 (d, J = 14.7 Hz, 1H), 3.88−3.83 (m, 1.5H), 3.68 (d, J = 14.5 Hz, 0.5H), 3.17 (s, 1.5H), 3.15 (s, 3H), 2.41 (s, 1.5H), 2.10 (s, 3H), 1.42 (s, 3H), 1.39 (s, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.9, 177.6, 143.8, 143.4, 140.2, 139.5, 138.8, 135.4, 133.4, 133.3, 128.8, 128.8, 128.7, 128.2, 127.8, 126.7, 125.1, 123.8, 123.1, 109.3, 106.2, 62.0, 61.0, 45.9, 45.4, 26.6, 26.5, 25.4, 23.2, 21.8, 18.2; HRMS (ESI) calcd for $C_{18}H_{20}NO_3S$ $(M + H)^+$ 330.1164, found 330.1162.



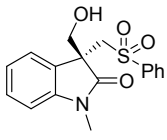
3la **3la'**

Compounds **3la** and **3la'** were obtained in 83% yield according to the general procedure (16h). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, J_1 = 2.1 Hz, J_2 = 8.2 Hz, 0.7H), 7.80 (dd, J_1 = 0.9 Hz, J_2 = 8.4 Hz, 1H), 7.72 (d, J = 2.0 Hz, 0.7H), 7.64−7.59 (m, 2.3H), 7.58−7.51 (m, 3.8H), 7.46 (t, J = 8 Hz, 1.4H), 7.41 (t, J = 7.5 Hz, 2H), 7.32 (d, J = 8.2 Hz, 0.7H), 7.23 (dd, J_1 = 0.8 Hz, J_2 = 7.8 Hz, 1H), 4.39 (d, J = 14.2 Hz, 1H), 3.96−3.89 (m, 1.7H), 3.74 (d, J = 14.5 Hz, 0.7H), 3.30 (s, 2.9H), 3.29 (s, 2H), 1.59 (s, 3H), 1.45 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 177.2, 148.7, 146.2, 144.6, 139.8, 139.2, 136.8, 133.9, 133.7, 129.9, 129.2, 129.0, 127.8, 127.7, 124.8, 124.6, 118.4, 118.0, 114.1, 103.4, 61.6, 59.3, 47.4, 45.8, 27.3, 27.0, 25.1, 23.0; HRMS (ESI) calcd for $C_{17}H_{17}N_2O_5S$ $(M + H)^+$ 361.0858, found 361.0854.



(3ma)

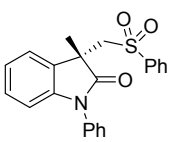
Compound **3ma** was obtained in 76% yield according to the general procedure (12h)[S3]. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.58-7.54 (m, 3H), 7.41 (t, J = 7.4 Hz, 2H), 7.05 (d, J = 7.6 Hz, 1H), 6.96 (d, J = 7.3 Hz, 1H), 6.83 (d, J = 7.6 Hz, 1H), 3.86 (d, J = 14.5 Hz, 1H), 3.75-3.61(m, 3H), 2.83-2.79 (m, 2H), 2.07-1.99 (m, 2H), 1.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 176.5, 140.2, 139.1, 133.3, 128.9, 128.3, 127.8, 127.3, 122.1, 122.0, 120.4, 61.9, 46.8, 39.1, 25.1, 24.6, 21.1; MS (ESI^+): $[M+H]^+$ 342.0.



(3na)

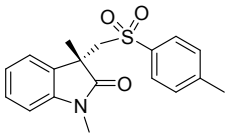
Compound **3na** was obtained in 92% yield according to the general procedure (12h)[S3]. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.58-7.53 (m, 3H), 7.40 (t, J = 7.3 Hz, 2H), 7.34 (dt, J_1 = 1.2 Hz, J_2 = 7.8 Hz, 1H), 7.10 (d, J = 7.4 Hz, 1H), 6.94 (dt, J_1 = 0.7 Hz, J_2 = 7.6 Hz, 1H), 6.89 (d, J = 7.9 Hz, 1H), 4.07 (d, J = 14.7 Hz, 1H), 3.90 (d, J = 14.7 Hz, 1H), 3.72 (d, J = 11.2 Hz, 1H), 3.65 (d, J = 11.2 Hz, 1H), 3.20 (s, 3H), 2.68 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 176.3, 143.9, 140.1, 133.4, 129.2, 129.0, 127.7, 125.7, 124.8,

122.8, 108.6, 67.5, 58.3, 51.0, 26.6; MS (ESI$^+$): $[M+H]^+$ 332.0.



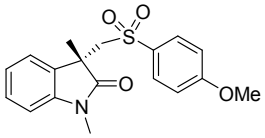
(3oa)

Compound **3oa** was obtained in 93% yield according to the general procedure (24h). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.60-7.53 (m, 7H), 7.47-7.44 (m, 1H), 7.39 (t, J = 7.7 Hz, 2H), 7.21 (d, J = 7.8 Hz, 1H), 7.01 (d, J = 7.4 Hz, 1H), 6.90-6.84 (m, 2H), 4.02 (d, J = 14.5 Hz, 1H), 3.80 (d, J = 14.5 Hz, 1H), 1.53 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 177.4, 143.7, 140.5, 134.6, 133.3, 129.6, 129.3, 129.1, 128.5, 128.2, 127.6, 126.9, 123.9, 122.9, 109.8, 62.4, 45.8, 25.7; MS (ESI$^+$): $[M+H]^+$ 378.2.



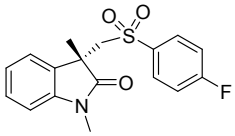
(3ab)

Compound **3ab** was obtained in 72% yield according to the general procedure (12h)[S3]. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.41 (d, J = 8.2 Hz, 2H), 7.30 (t, J = 7.7 Hz, 1H), 7.19 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 7.4 Hz, 1H), 6.94 (t, J = 7.5 Hz, 1H), 6.86 (d, J = 7.8 Hz, 1H), 3.86 (d, J = 14.5 Hz, 1H), 3.68 (d, J = 14.5 Hz, 1H), 3.17 (s, 3H), 2.42 (s, 3H), 1.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 177.7, 144.3, 143.3, 137.1, 129.7, 129.5, 128.6, 127.9, 124.2, 122.5, 108.4, 61.9, 45.7, 26.5, 25.5, 21.6; MS (ESI$^+$): $[M+H]^+$ 330.04.



(3ac)

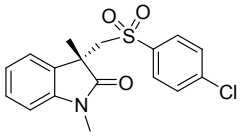
Compound **3ac** was obtained in 54% yield according to the general procedure (24h). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.44-7.40 (m, 2H), 7.30 (dt, J_1 = 1.2 Hz, J_2 = 7.7 Hz, 1H), 7.11 (dd, J_1 = 0.7 Hz, J_2 = 7.4 Hz,, 1H), 7.96 (dt, J_1 = 1.0 Hz, J_2 = 7.6 Hz, 1H), 6.87-6.83 (m, 3H), 3.88 (d, J = 14.5 Hz, 1H), 3.86 (s, 3H), 3.67 (d, J = 14.5 Hz, 1H), 3.17 (s, 3H), 1.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 177.7, 163.5, 143.3, 131.6, 130.1, 129.7, 128.6, 124.2, 122.5, 114.1, 108.4, 62.1, 55.7, 45.7, 26.5, 25.6; MS (ESI$^+$): $[M+H]^+$ 346.0.



(3ad)

Compound **3ad** was obtained in 81% yield according to the general procedure (24h).

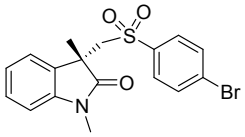
^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.51-7.48 (m, 2H), 7.31 (dt, J_1 = 1.2 Hz, J_2 = 7.7 Hz, 1H), 7.08-7.03 (m, 3H), 6.94 (dt, J_1 = 0.9 Hz, J_2 = 7.6 Hz, 1H), 6.87 (d, J = 7.5 Hz, 1H), 6.87 (d, J = 7.8 Hz, 1H), 3.92 (d, J = 14.6 Hz, 1H), 3.70 (d, J = 14.6 Hz, 1H), 3.20 (s, 3H), 1.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 177.5, 165.6 (d, J = 254 Hz), 143.3, 136.0 (d, J = 3 Hz), 130.6 (d, J = 10 Hz), 129.4, 128.8, 124.0, 122.5, 116.1 (d, J = 22 Hz), 108.5, 62.0, 45.6, 26.6, 25.5; MS (ESI$^+$): $[M+H]^+$ 334.0.



(3ae)

Compound **3ae** was obtained in 80% yield according to the general procedure (12h).

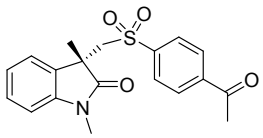
^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.39 (d, J = 8.6 Hz, 2H), 7.32 (t, J = 8.5 Hz, 3H), 7.01 (d, J = 7.3 Hz, 1H), 6.92 (t, J = 7.6 Hz, 1H), 6.86 (d, J = 7.8 Hz, 1H), 3.91 (d, J = 14.6 Hz, 1H), 3.70 (d, J = 14.6 Hz, 1H), 3.18 (s, 3H), 1.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 177.4, 143.3, 140.1, 138.3, 129.3, 129.1, 128.8, 124.0, 122.5, 108.5, 62.0, 45.6, 26.5, 25.5; MS (ESI$^+$): $[M+H]^+$ 350.0.



(3af)

Compound **3af** was obtained in 84% yield according to the general procedure (12h).

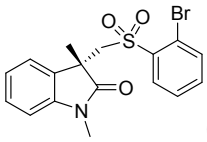
^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.51 (d, J = 8.6 Hz, 2H), 7.34-7.30 (m, 3H), 7.03 (d, J = 7.2 Hz, 1H), 6.94 (t, J = 7.6 Hz, 1H), 6.86 (d, J = 7.8 Hz, 1H), 3.92 (d, J = 14.6 Hz, 1H), 3.69 (d, J = 14.6 Hz, 1H), 3.18 (s, 3H), 1.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 177.4, 143.3, 138.8, 132.1, 129.4, 129.3, 128.8, 128.7, 124.0, 122.6, 108.5, 62.0, 45.6, 26.6, 25.6; MS (ESI$^+$): $[M+H]^+$ 394.0.



(3ag)

Compound **3ag** was obtained in 60% yield according to the general procedure (24h).

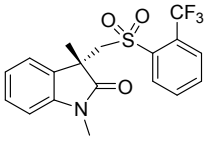
^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.93 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.30 (t, J = 7.8 Hz, 1H), 7.00 (d, J = 7.3 Hz, 1H), 6.89-6.85 (m, 2H), 3.92 (d, J = 14.6 Hz, 1H), 3.73 (d, J = 14.6 Hz, 1H), 3.20 (s, 3H), 2.65 (s, 3H), 1.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 196.7, 177.4, 143.7, 143.4, 140.5, 129.4, 128.8, 128.6, 128.2, 123.9, 122.5, 108.5, 61.9, 45.6, 26.9, 26.6, 25.4; MS (ESI$^+$): $[M+H]^+$ 358.0.



(3ah)

Compound **3ah** was obtained in 65% yield according to the general procedure (24h).

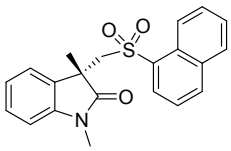
^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.93 (dd, J_1 = 0.9 Hz, J_2 = 7.9 Hz, 1H), 7.36-7.30 (m, 2H), 7.20-7.13 (m, 2H), 6.88 (d, J = 7.4 Hz, 1H), 6.83 (d, J = 7.8 Hz, 1H), 6.67 (dt, J_1 = 0.8 Hz, J_2 = 7.6 Hz, 1H), 4.32 (d, J = 14.9 Hz, 1H), 4.01 (d, J = 14.9 Hz, 1H), 3.25 (s, 3H), 1.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 177.8, 143.3, 139.2, 135.0, 134.1, 131.2, 129.3, 128.7, 127.8, 123.3, 122.4, 120.4, 108.4, 59.3, 45.6, 26.7, 25.1; MS (ESI$^+$): $[M+H]^+$ 394.0.



(3ai)

Compound **3ai** was obtained in 81% yield according to the general procedure (24h).

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.84 (d, J = 7.8 Hz, 1H), 7.66 (t, J = 7.6 Hz, 1H), 7.57 (d, J = 7.8 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.28 (dt, J_1 = 1.1 Hz, J_2 = 6.8 Hz, 1H), 7.04 (d, J = 7.4 Hz, 1H), 6.90-6.84 (m, 2H), 3.97 (s, 2H), 3.27 (s, 3H), 1.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 177.7, 143.4, 139.0, 133.4, 132.3, 129.7, 128.1(q, J = 6.1 Hz), 123.7, 122.7 (d, J = 272 Hz), 122.5, 108.5, 62.2 (d, J = 3.3 Hz), 45.8, 26.6, 25.4; MS (ESI$^+$): $[M+H]^+$ 384.0.



(3aj)

Compound **3aj** was obtained in 70% yield according to the general procedure (12h).

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.91-7.86 (m, 3H), 7.78 (d, J = 8.1 Hz, 1H), 7.69-7.58 (m, 3H), 7.23 (dt, J_1 = 1.1 Hz, J_2 = 7.8 Hz, 1H), 7.06 (d, J = 7.0 Hz, 1H), 6.79 (d, J = 7.8 Hz, 1H), 3.99 (d, J = 14.6 Hz, 1H), 3.76 (d, J = 14.6 Hz, 1H), 2.99 (s, 3H), 1.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 177.5, 143.3, 136.4, 135.2, 131.9, 130.0, 129.6, 129.3, 129.2, 128.2, 128.7, 127.8, 127.4, 124.2, 122.6, 122.4, 108.4, 61.7, 45.6, 26.4, 25.7. MS (ESI$^+$): $[M+H]^+$ 366.0.

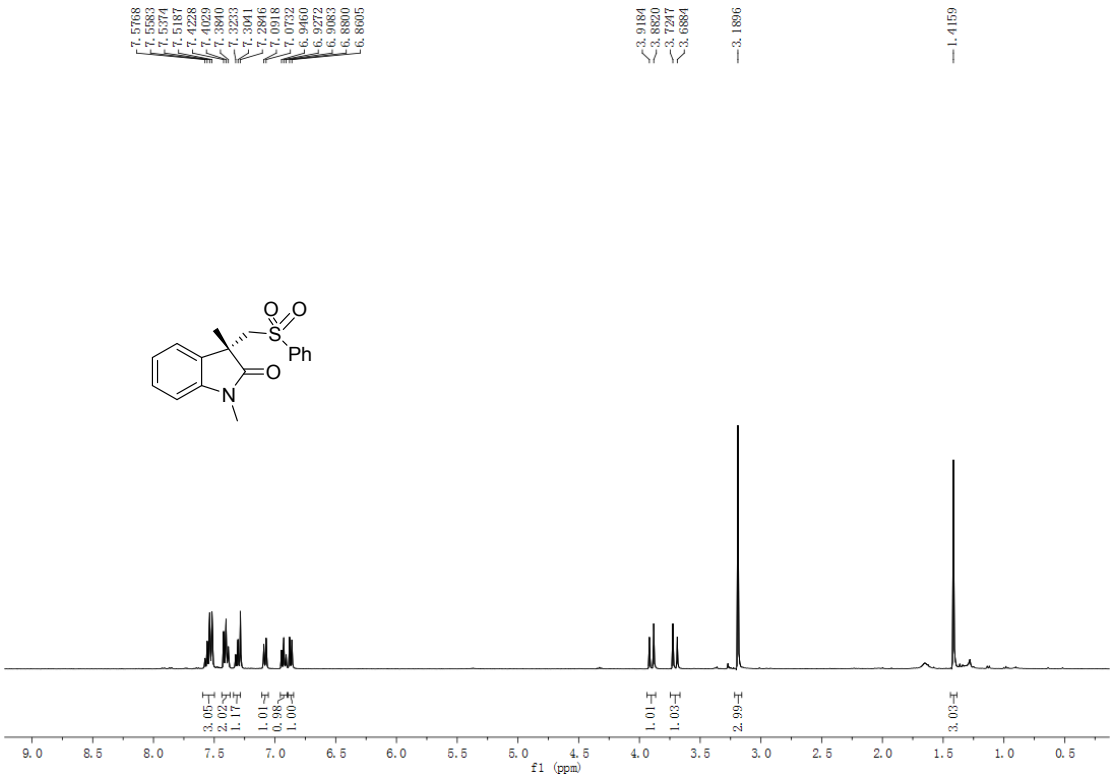
6. Reference

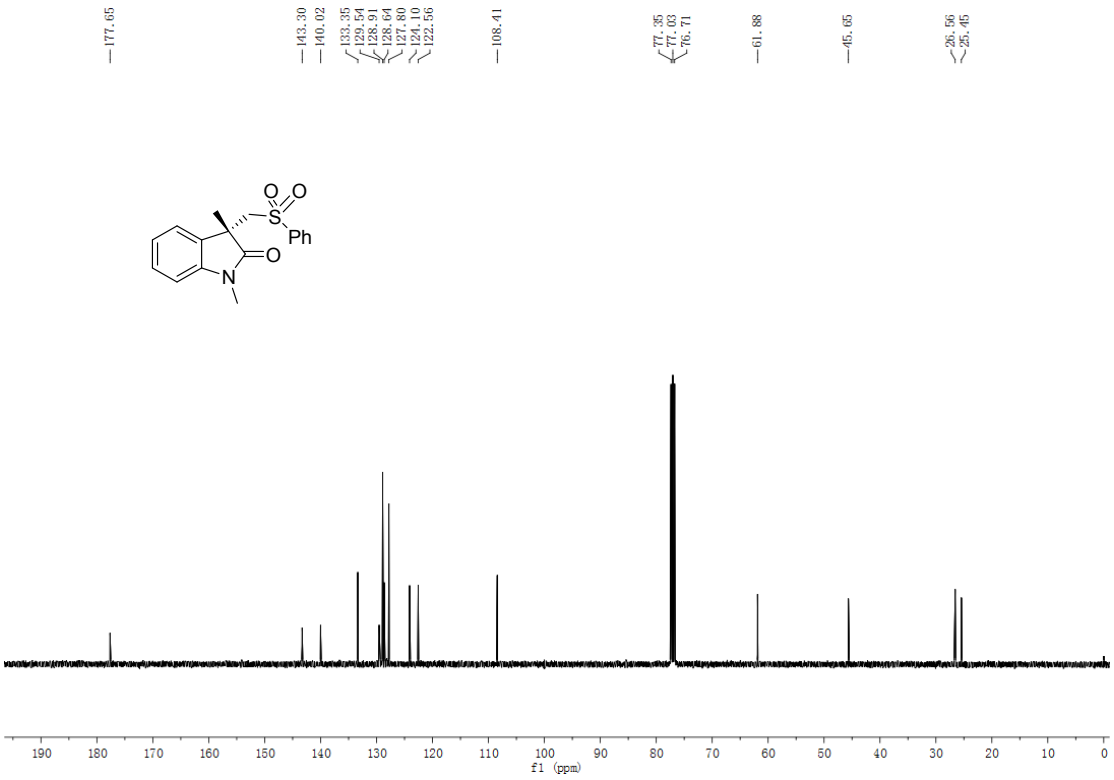
[S1] A. Pinto, Y. Jia, L. Neuville, J. Zhu, *Chem. Eur. J.* **2007**, *13*, 961.

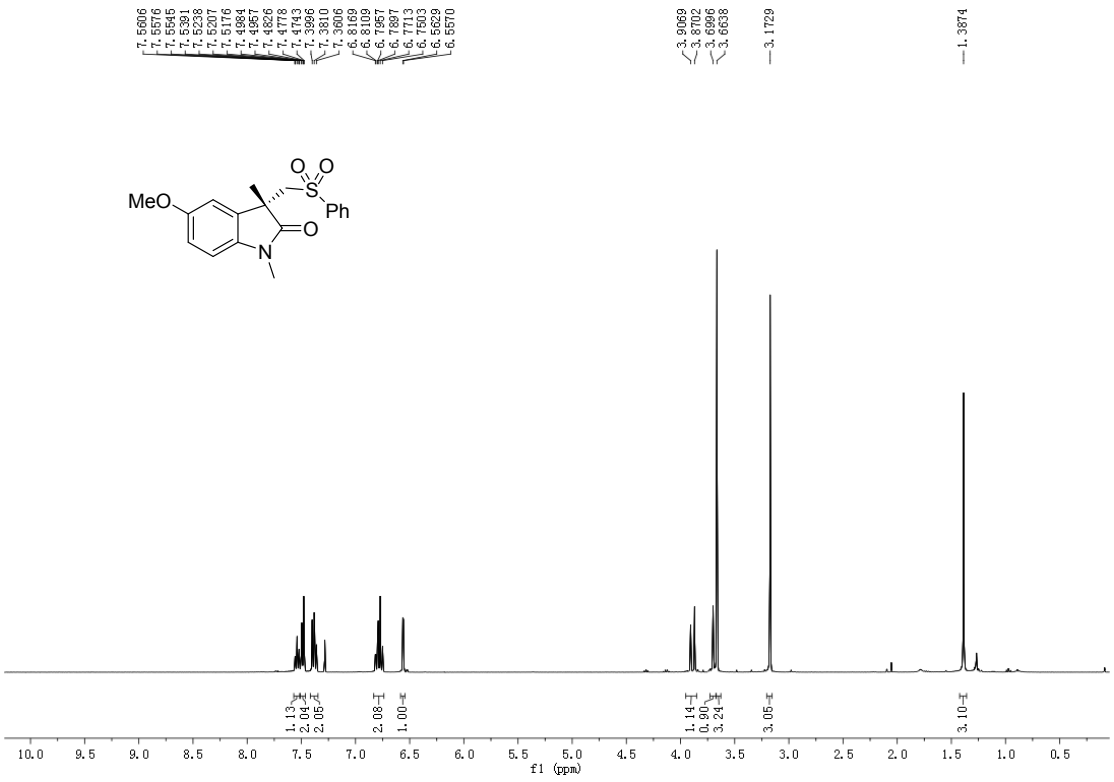
[S2] A. A.-L. Ayitou, J. Sivaguru, *Chem. Commun.* **2011**, *47*, 2568.

[S3] X. Li, X. Xu, P. Hu, X. Xiao, C. Zhou, *J. Org. Chem.,* 2013, **78**, 7343–7348.

7. Copies of NMR Spectra for 3aa−3aj



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6.7697
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6.5510
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3.6996
3.6638
3.1729
1.3874
MeO
Ph
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2.05
2.08
1.00
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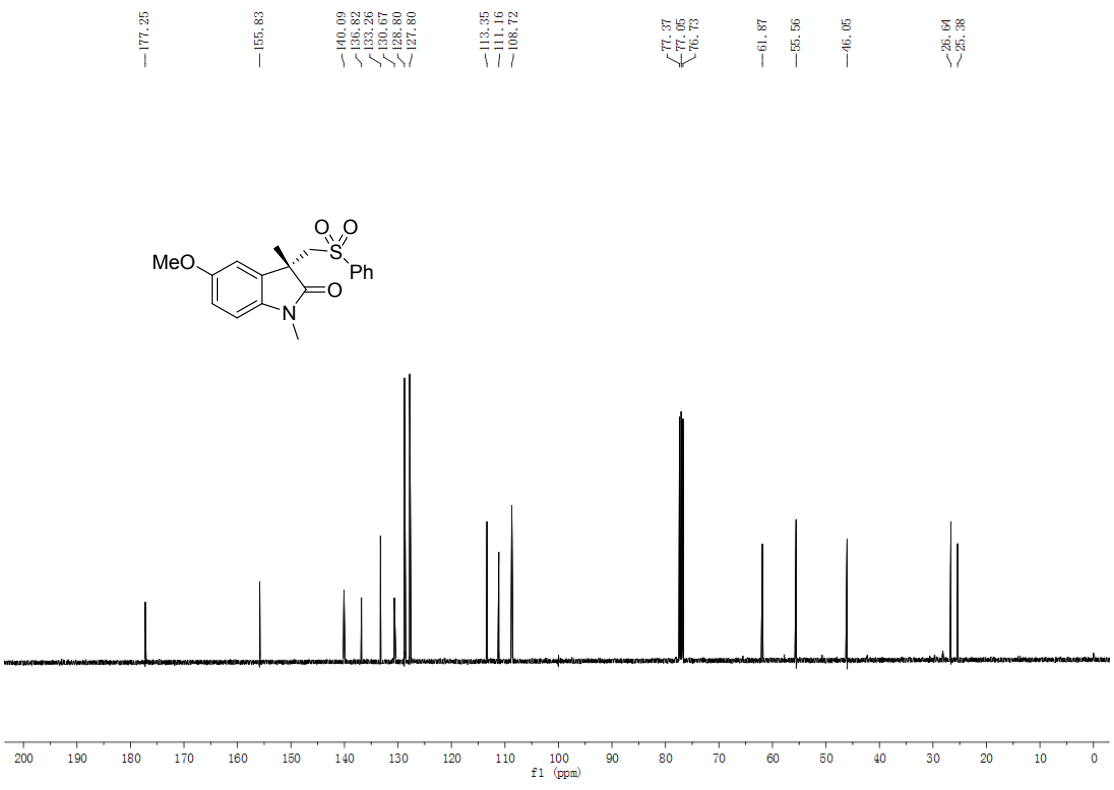
3.05
3.10
f1 (ppm)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26.64
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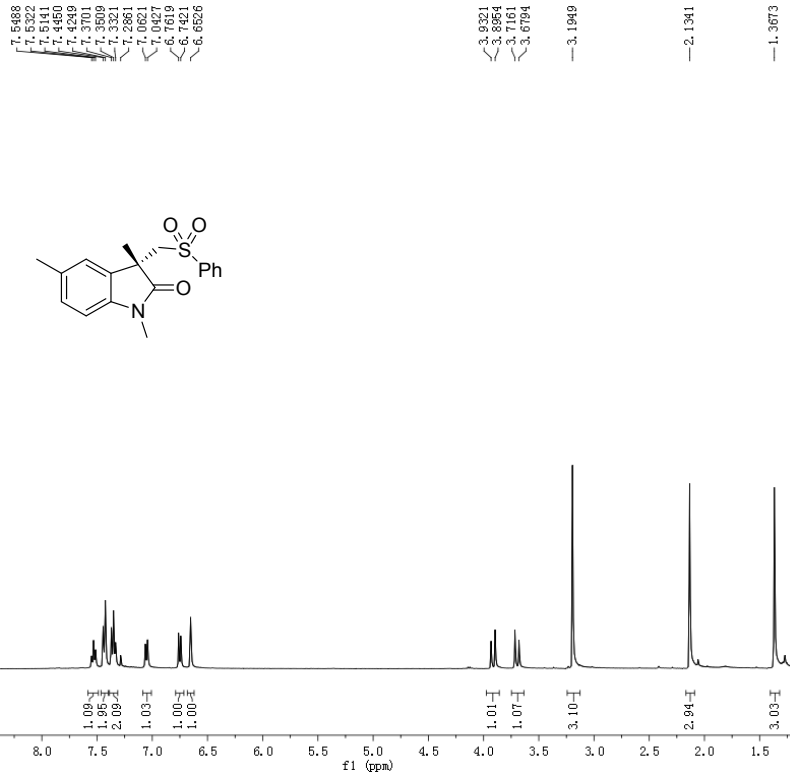
MeO
Ph
f1 (ppm)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6.7421
6.6526
3.9321
3.8954
3.7161
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O
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O
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1.00
1.00
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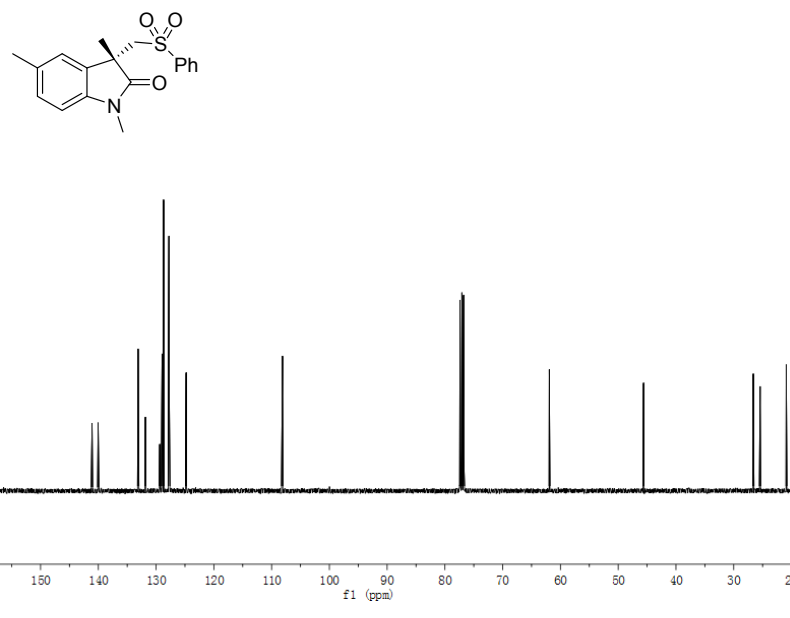
3.10
2.94
3.03
f1 (ppm)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128.70
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61.93
45.60
26.61
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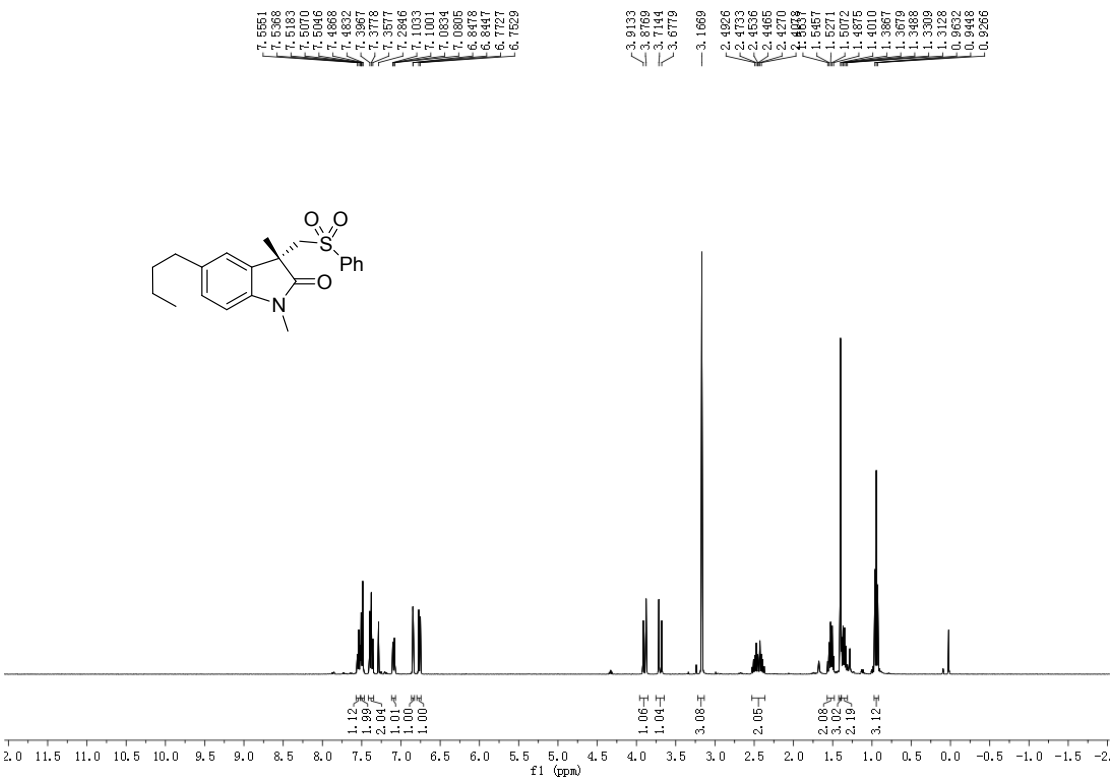
20.91
O
O
S
Ph
O
N
f1 (ppm)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7.1033
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6.7529
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3.7144
3.6779
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2.4270
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O
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3.02
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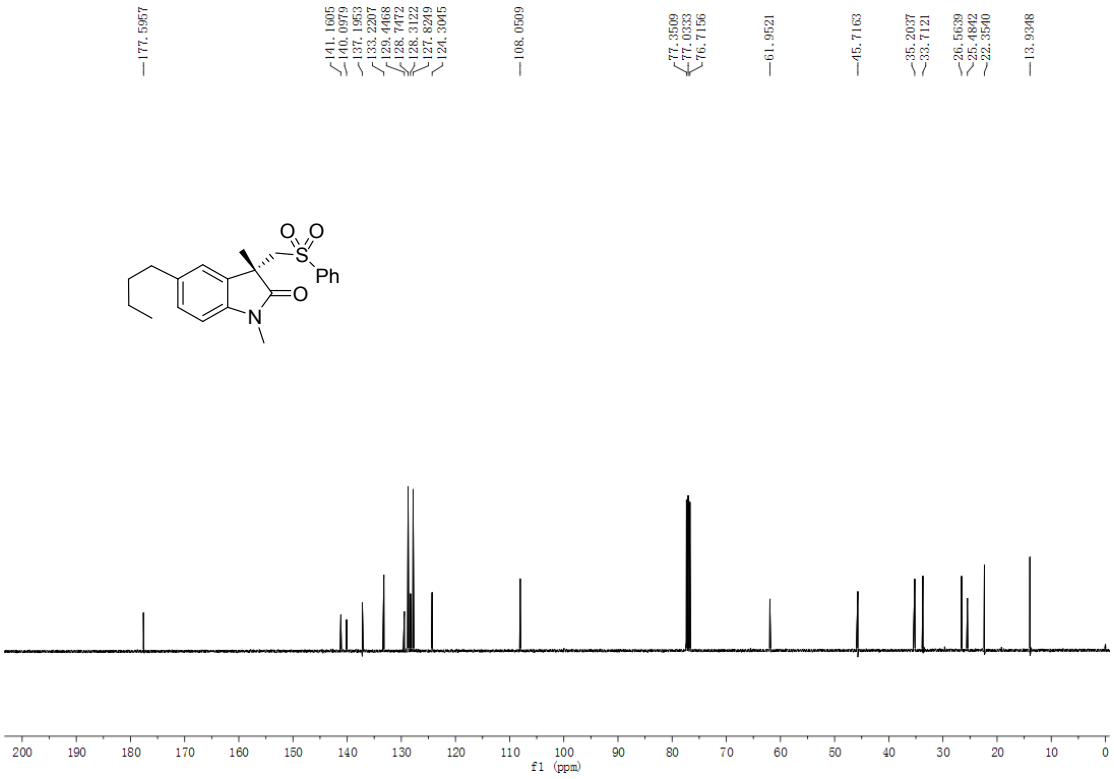
3.12
f1 (ppm)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61.9521
45.7163
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S
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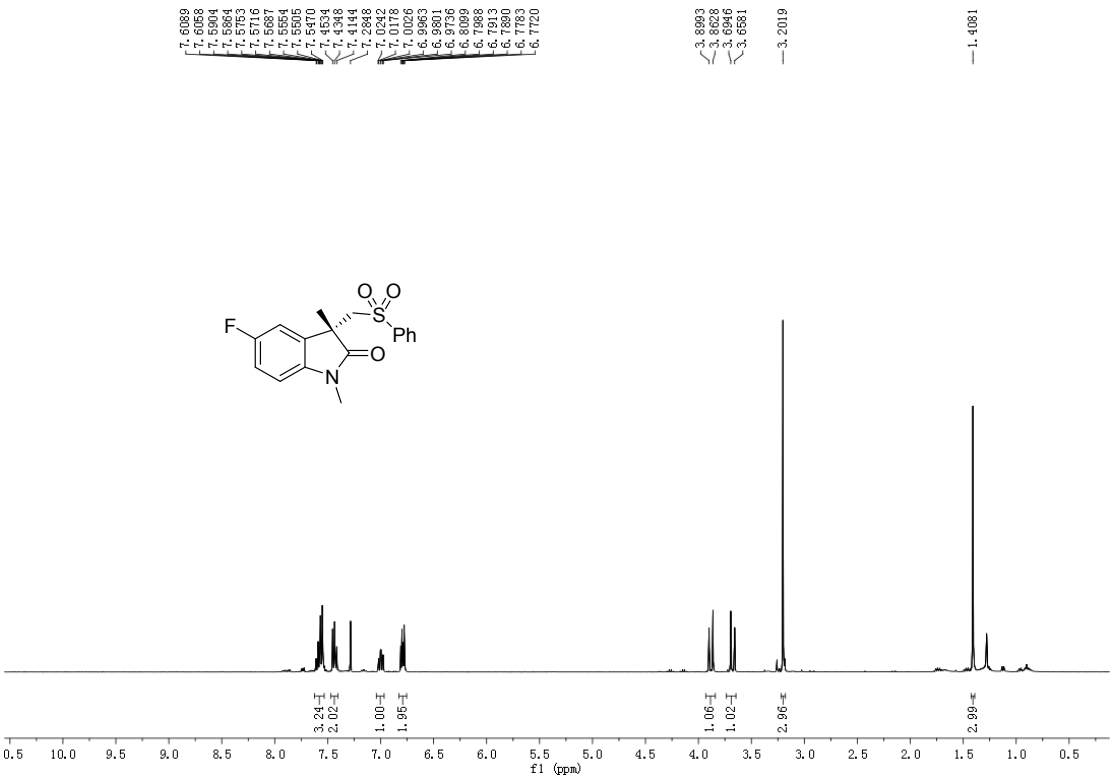
O
N
f1 (ppm)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1.02
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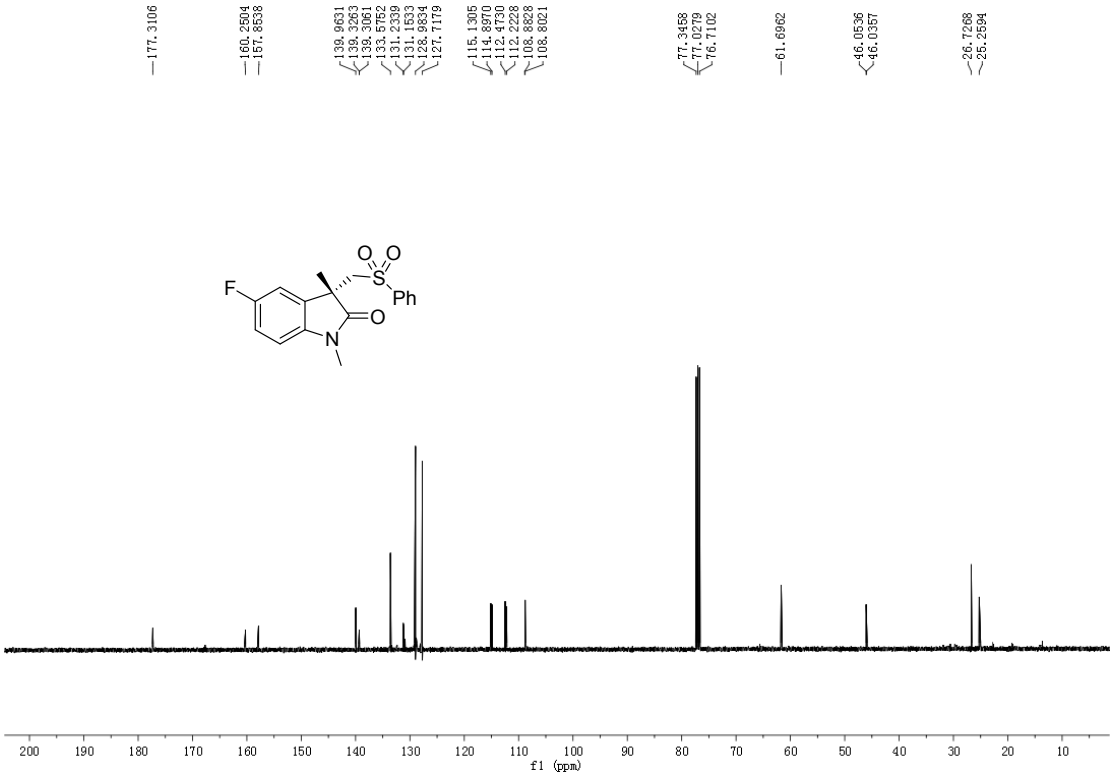
2.99
f1 (ppm)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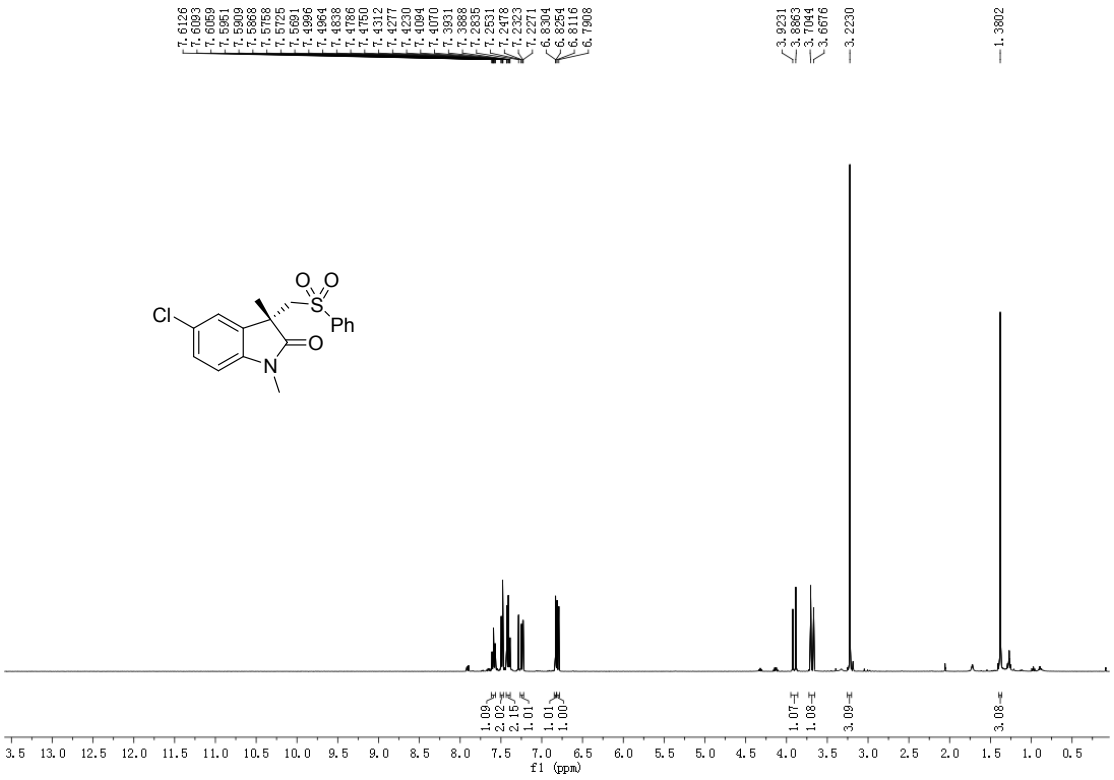
O
S
Ph
F
O
N
f1 (ppm)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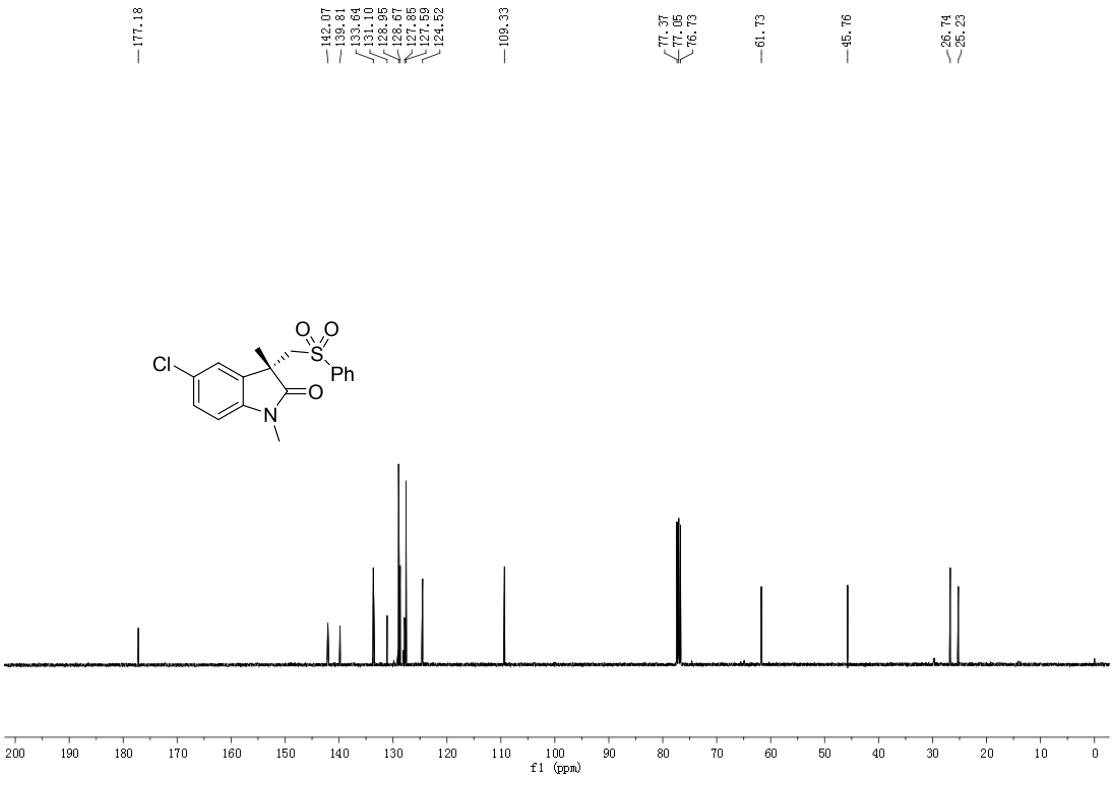
3.08
f1 (ppm)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O
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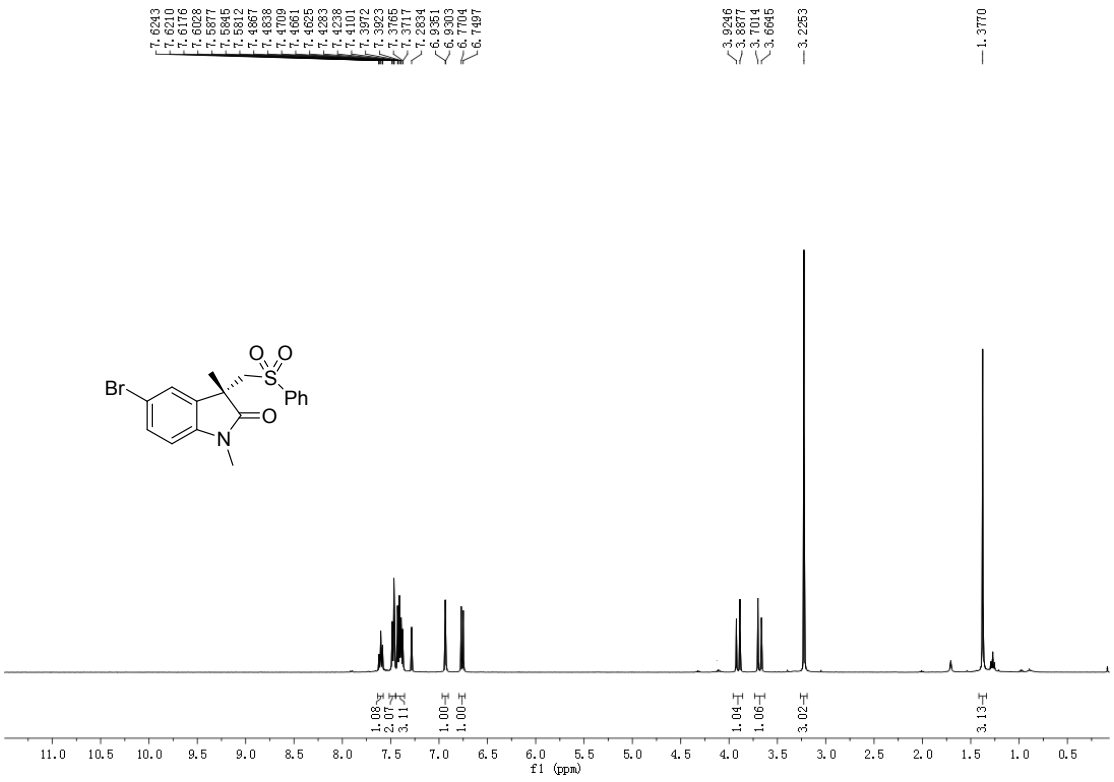
S
Ph
O
N
f1 (ppm)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6.9303
6.7704
6.7497
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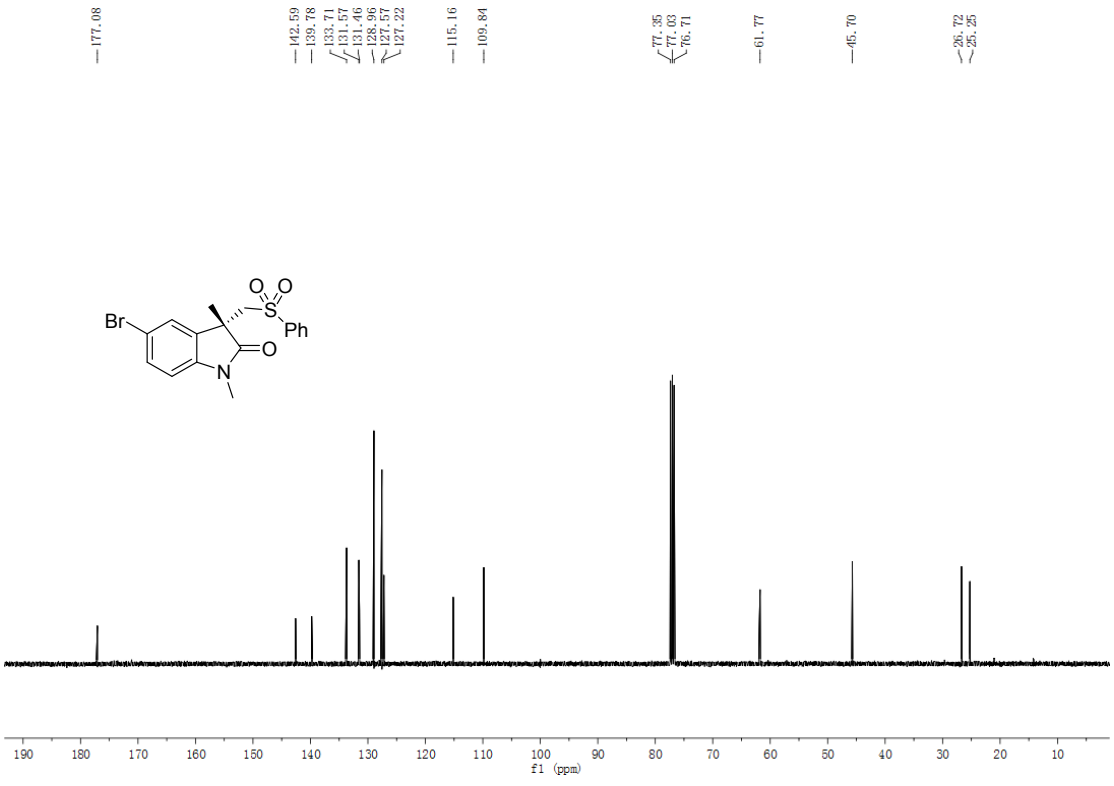
3.8877
3.7014
3.6645
3.2253
1.3770
Br
O
O
S
Ph
O
N
1.08
2.07
3.11
1.00
1.00
1.04
1.06
3.02
3.13
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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77.35
77.03
76.71
61.77
45.70
26.72
25.25
Br
O
O
S
Ph
O
N
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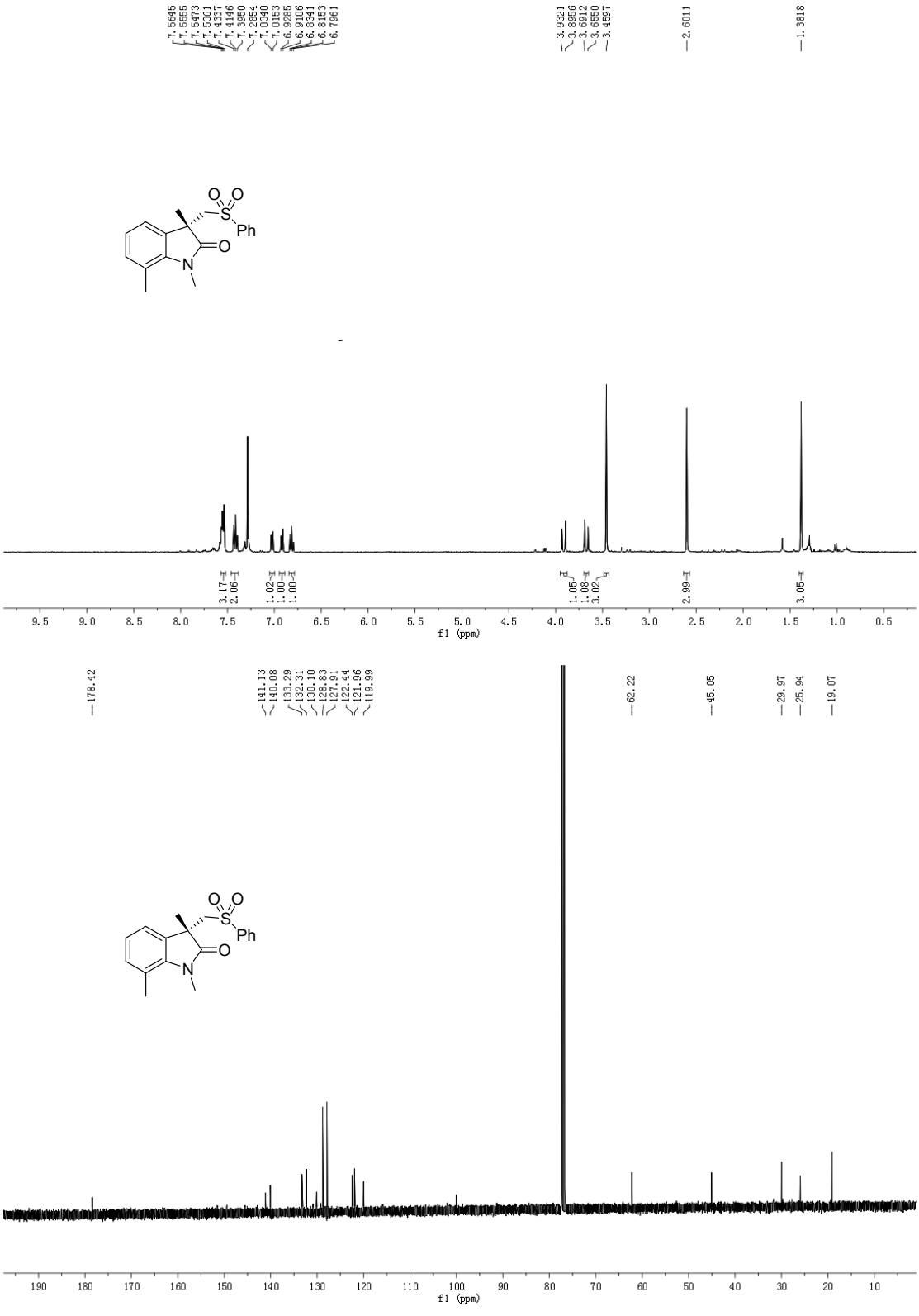
f1 (ppm)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3.4597
2.6011
1.3818
O
O
S
Ph
O
N
3.17
2.06
1.02
1.00
1.00
1.05
1.08
3.02
2.99
3.05
f1 (ppm)
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141.13
140.08
133.29
132.31
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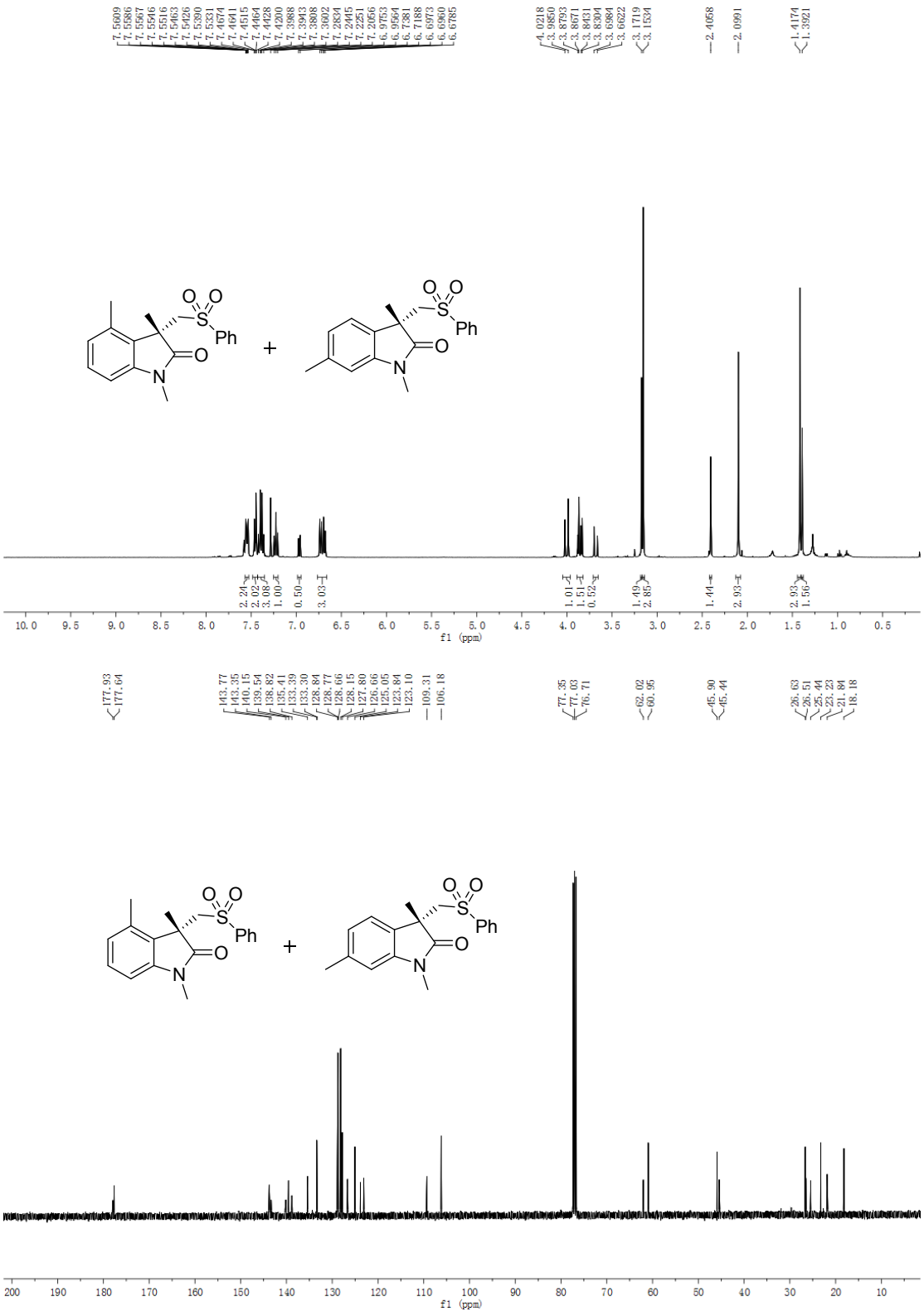
19.07
f1 (ppm)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1.3921
Ph
2.24
2.02
3.08
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0.52
1.49
2.85
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2.93
1.56
f1 (ppm)
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177.64
143.77
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140.15
139.54
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133.30
128.84
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123.84
123.10
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77.35
77.03
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23.23
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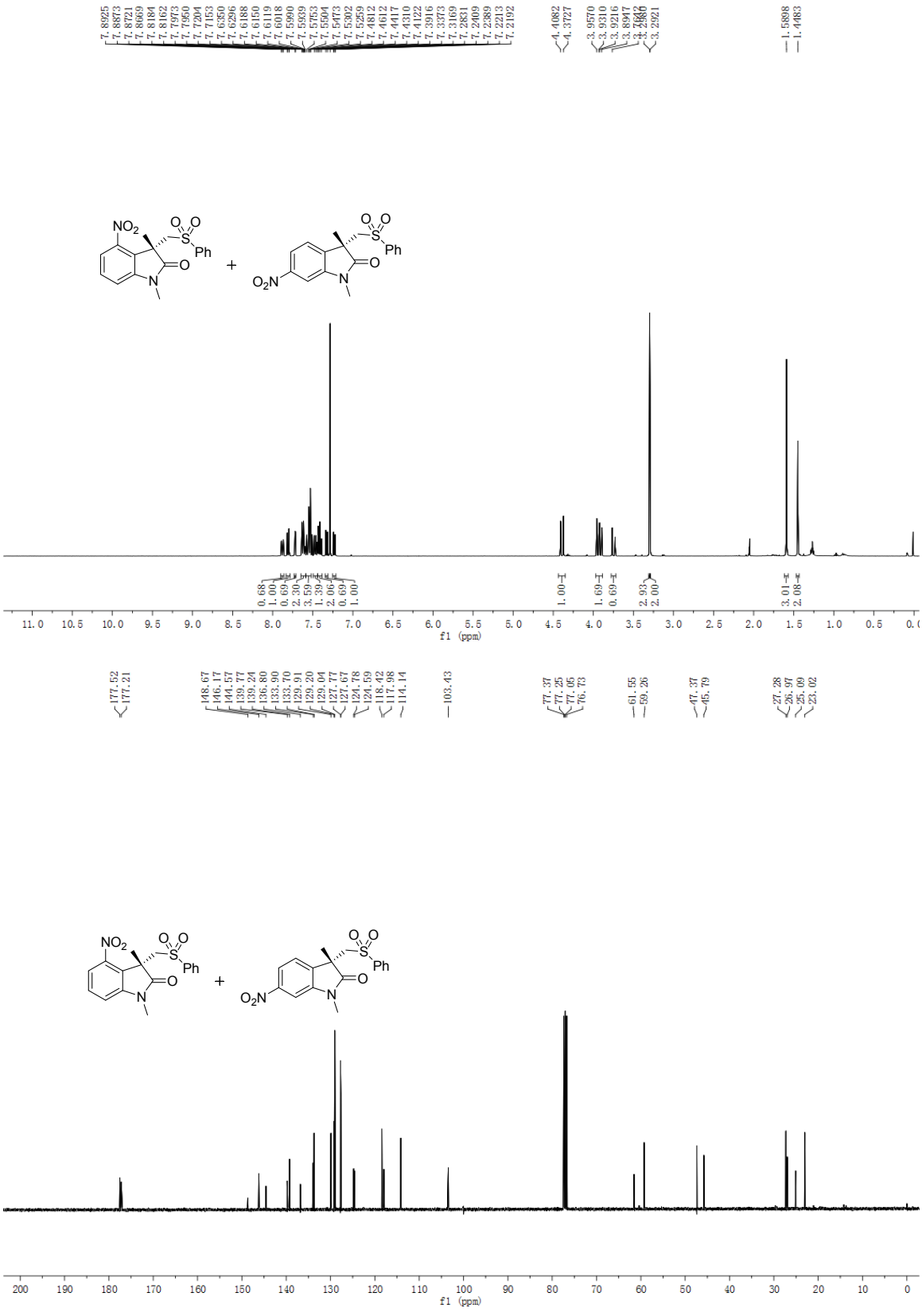
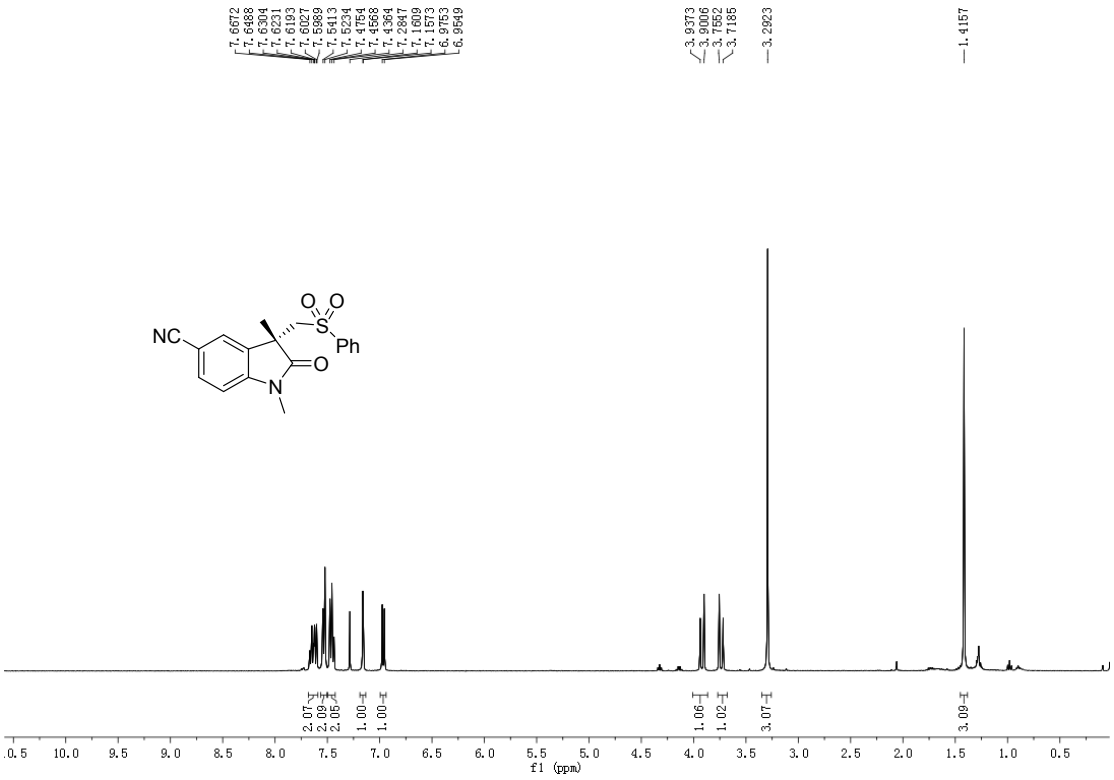
18.18
f1 (ppm)

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7.4364
7.2847
7.1609
7.1573
6.9753
6.9549
3.9373
3.9006
3.7552
3.7185
3.2923
1.4157
NC
O
O
S
Ph
O
N
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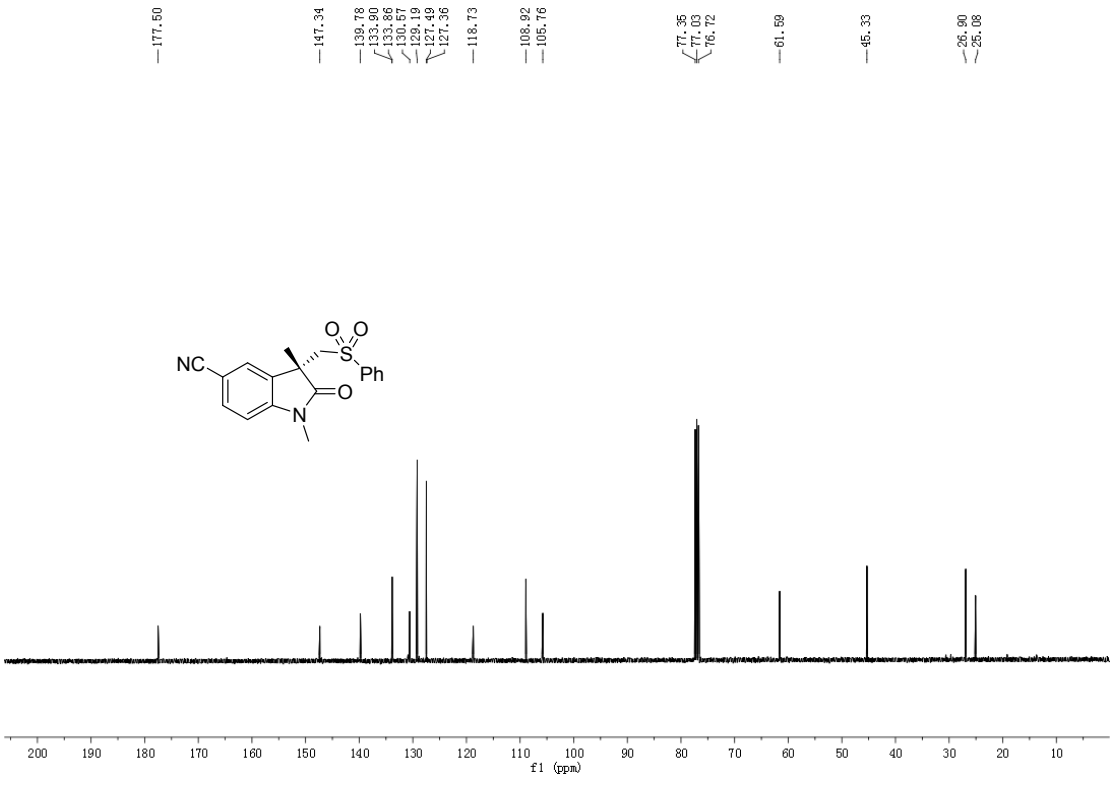
2.09
2.05
1.00
1.00
1.06
1.02
3.07
3.09
f1 (ppm)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127.49
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105.76
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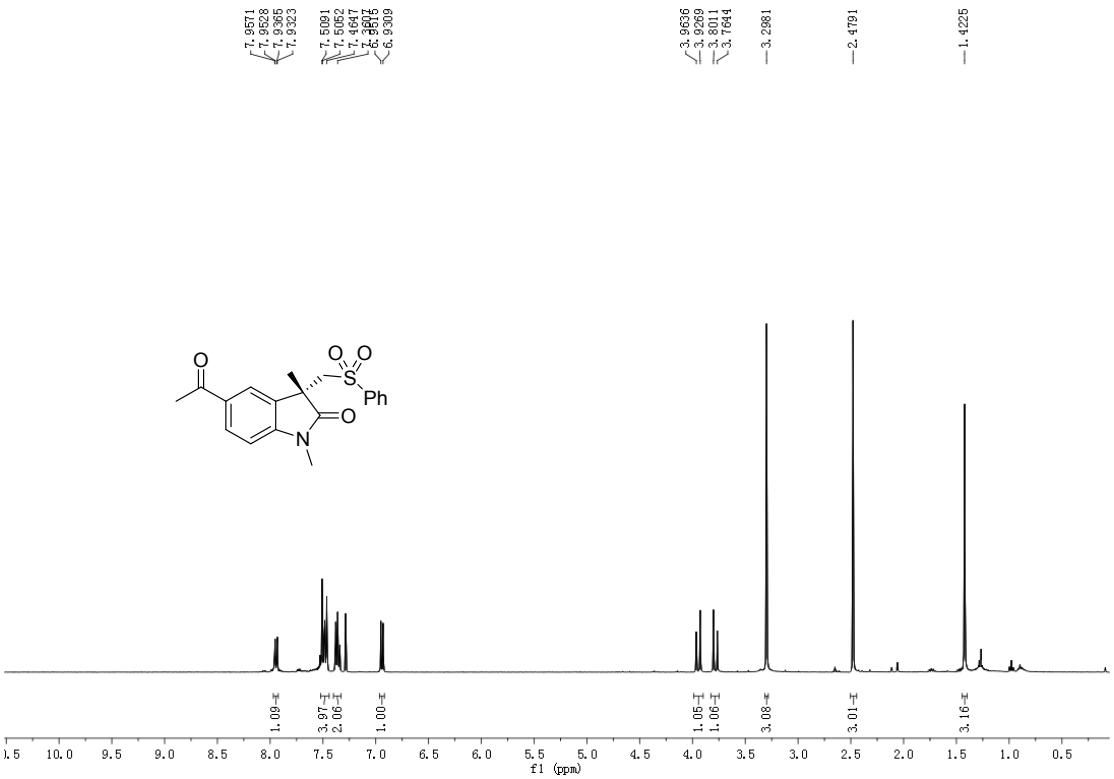
61.59
45.33
26.90
25.08
NC
O
O
S
Ph
O
N
f1 (ppm)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3.8011
3.7644
3.2981
2.4791
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3.97
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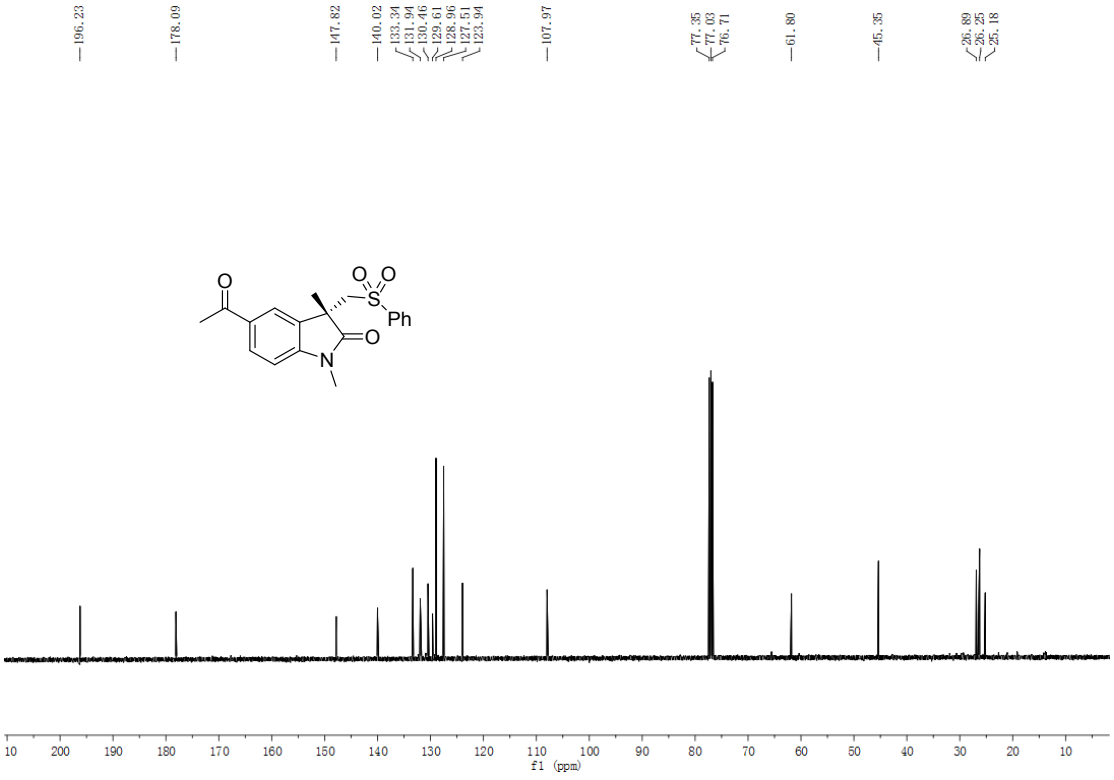
1.00
1.05
1.06
3.08
3.01
3.16
f1 (ppm)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131.94
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123.94
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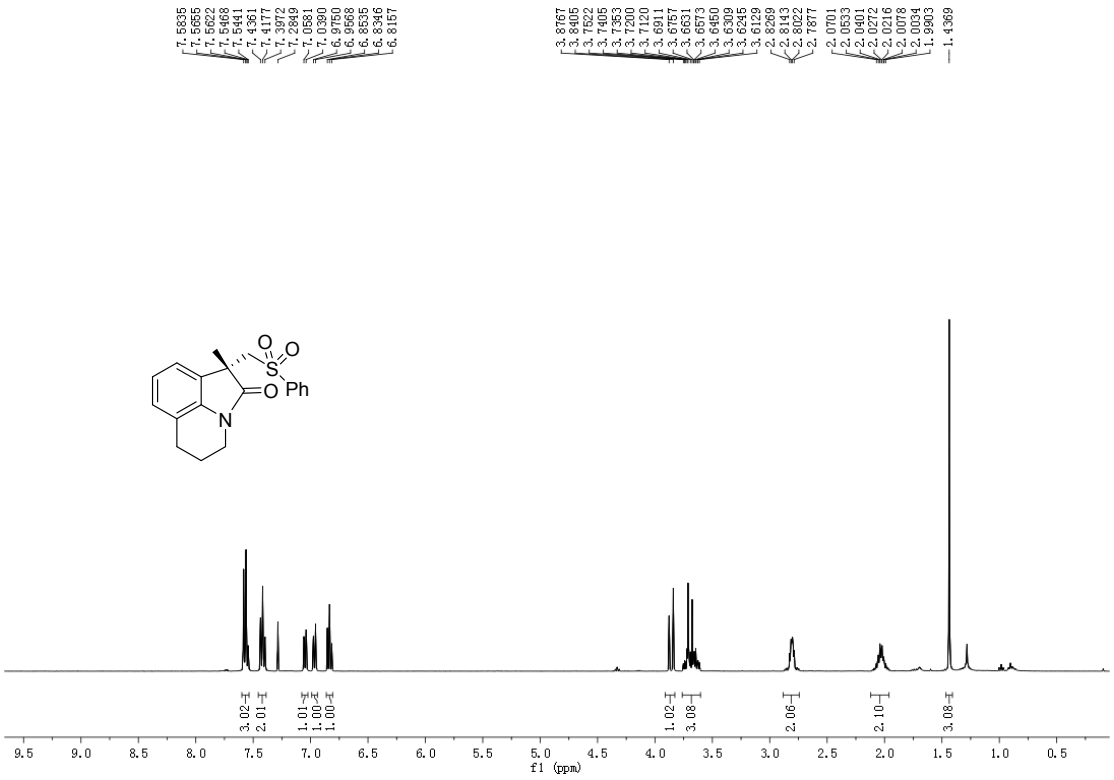
77.35
77.03
76.71
61.80
45.35
26.89
26.25
25.18
f1 (ppm)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2.0272
2.0216
2.0078
2.0034
1.9903
1.4369
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O
S
O Ph
N
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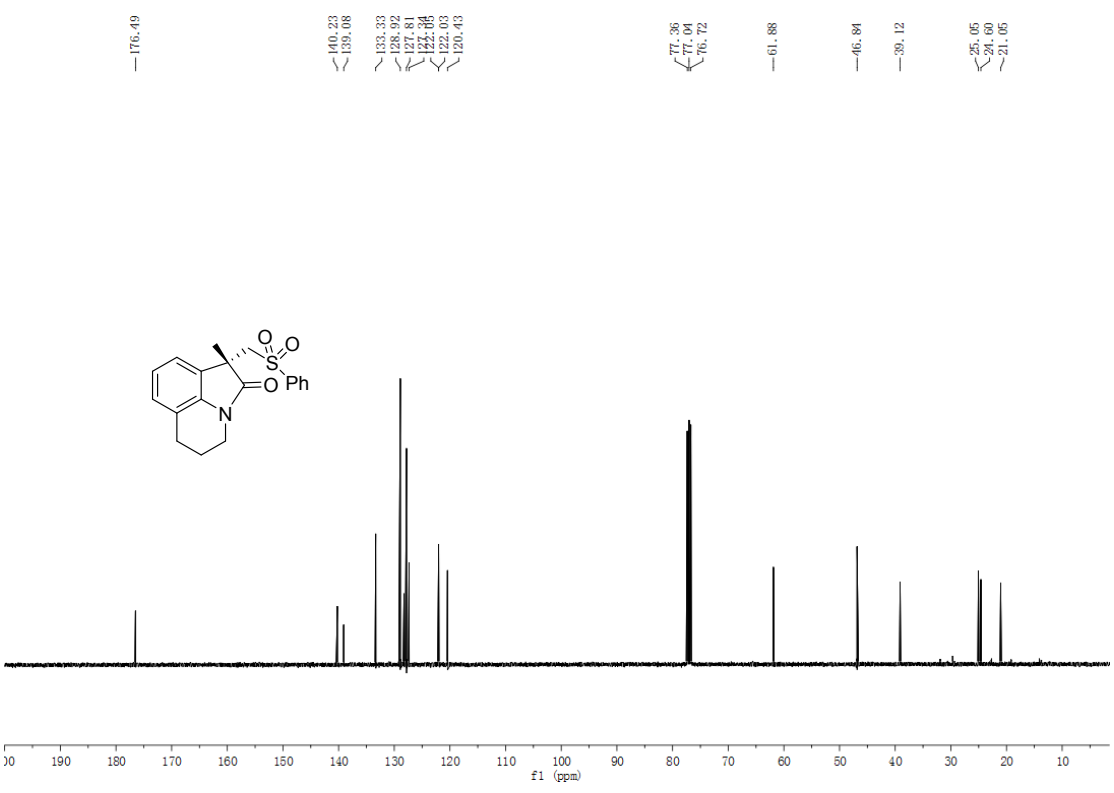
2.01
1.01
1.00
1.00
1.02
3.08
2.06
2.10
3.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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77.04
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46.84
39.12
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24.60
21.05
O
O
S
O Ph
N
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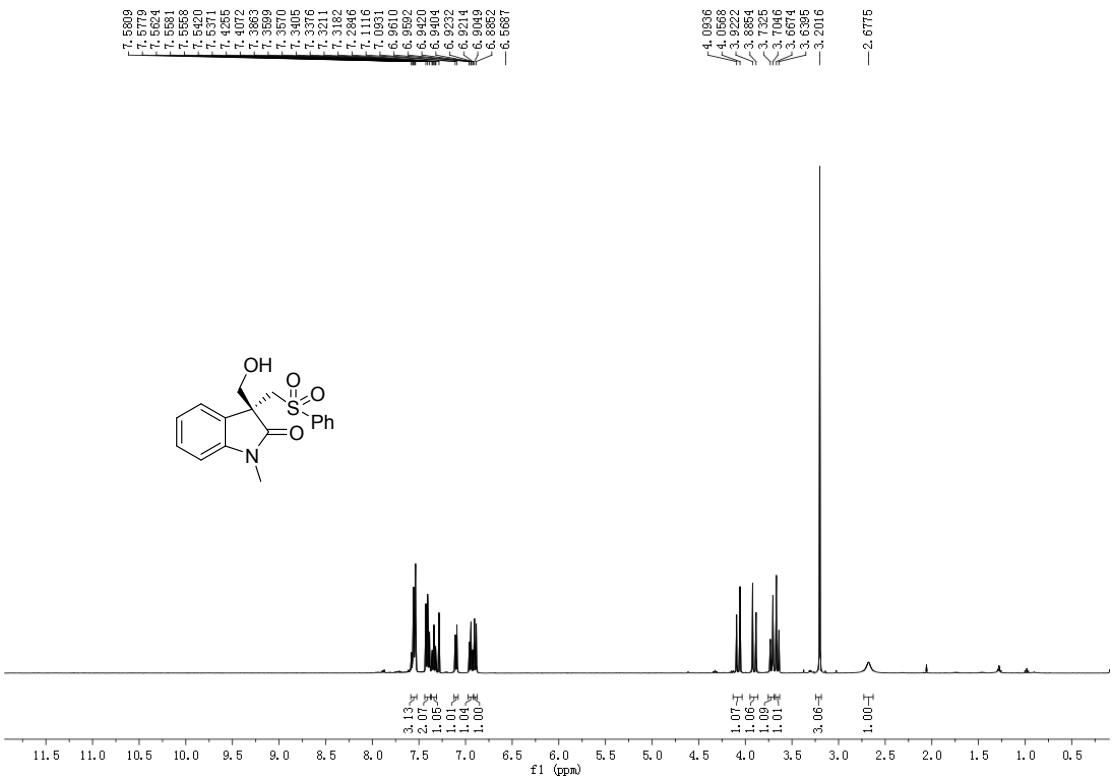
f1 (ppm)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3.6395
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OH
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S
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Ph
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N
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1.06
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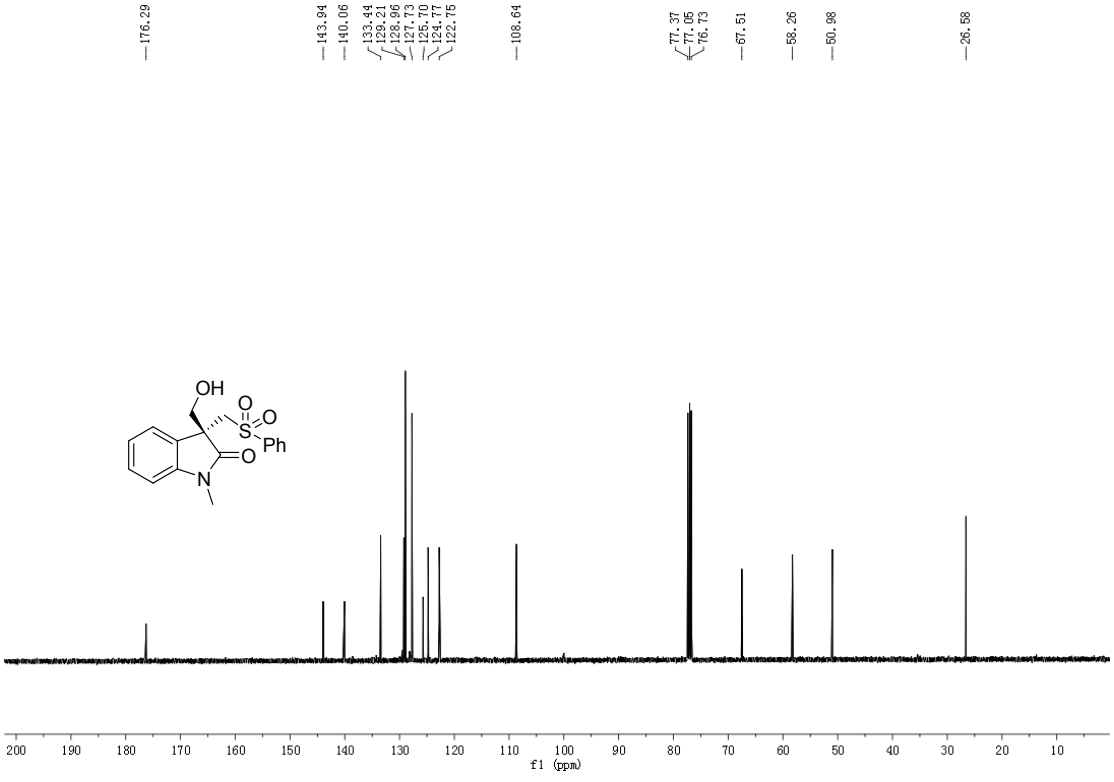
1.01
3.06
1.00
f1 (ppm)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67.51
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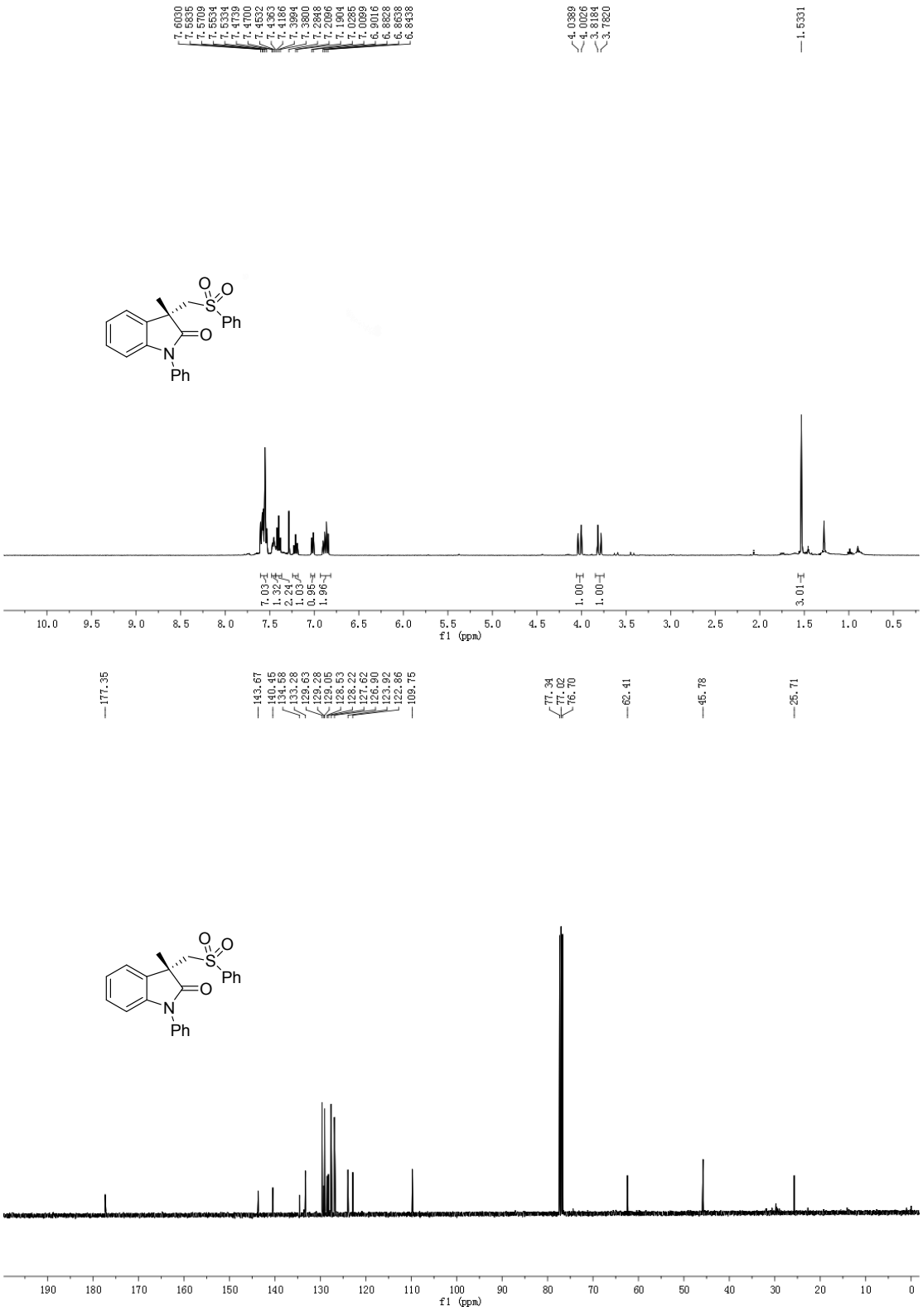
50.98
26.58
OH
O
S
O
Ph
O
N
f1 (ppm)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6.8638
6.8438
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3.7820
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f1 (ppm)
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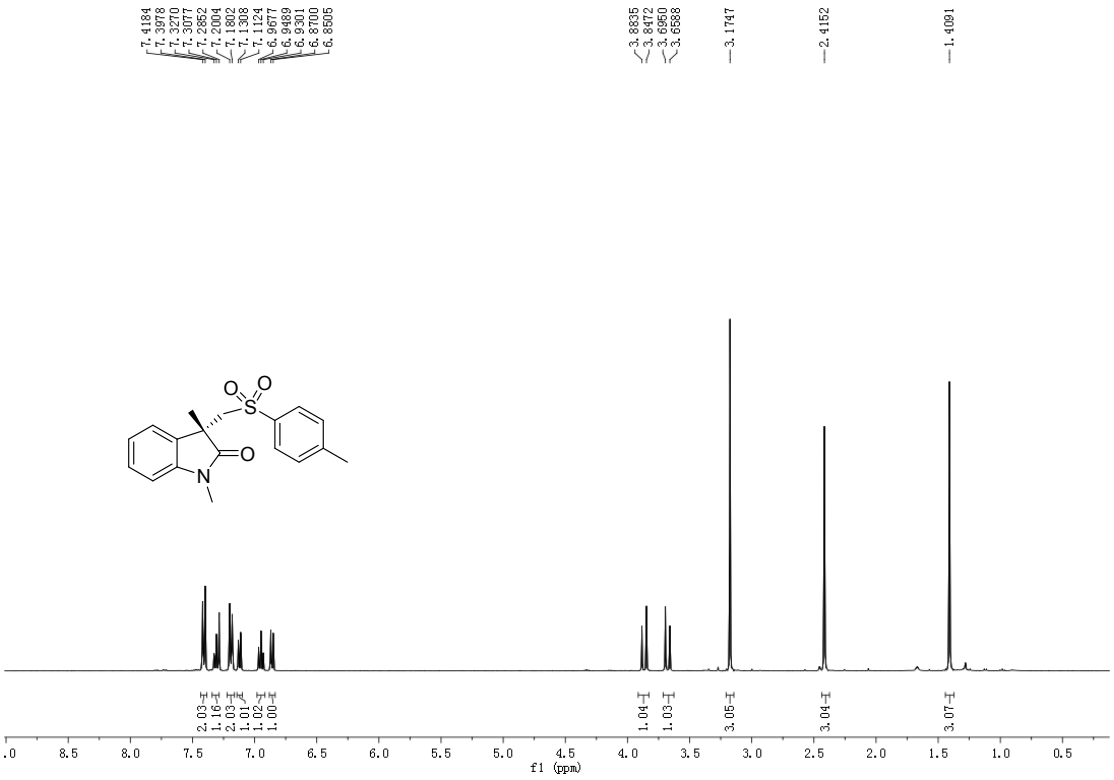
f1 (ppm)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3.05
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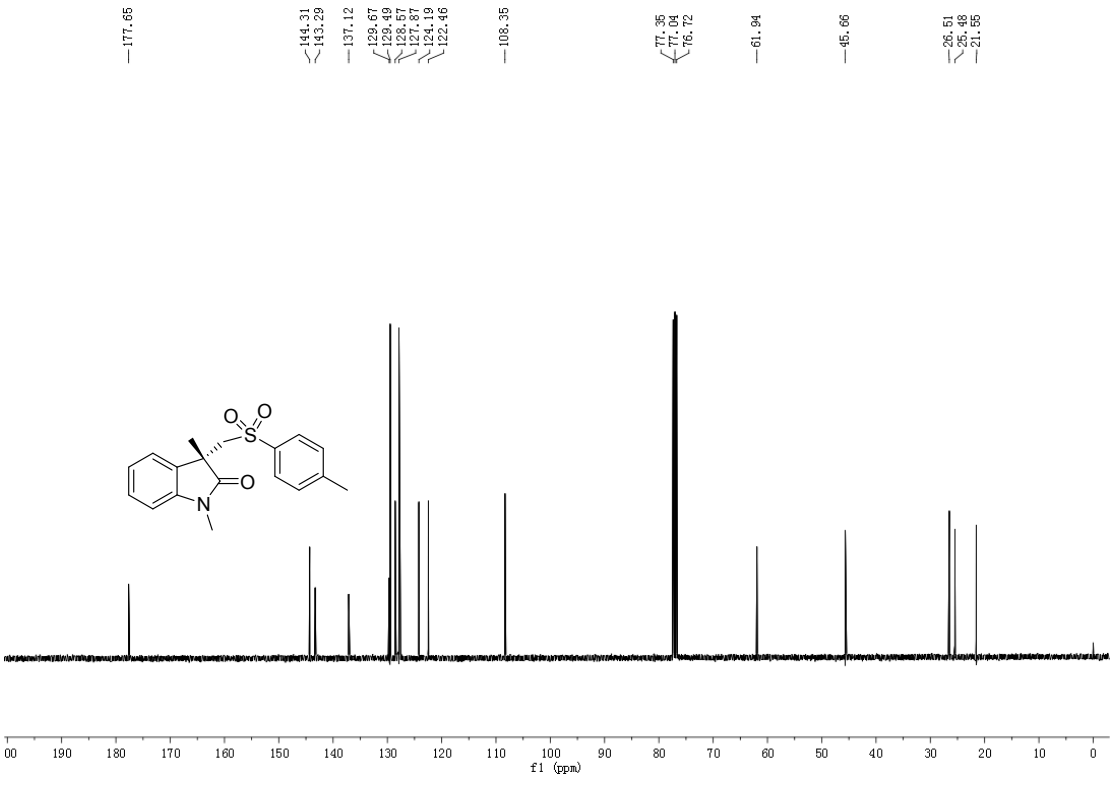
3.07
f1 (ppm)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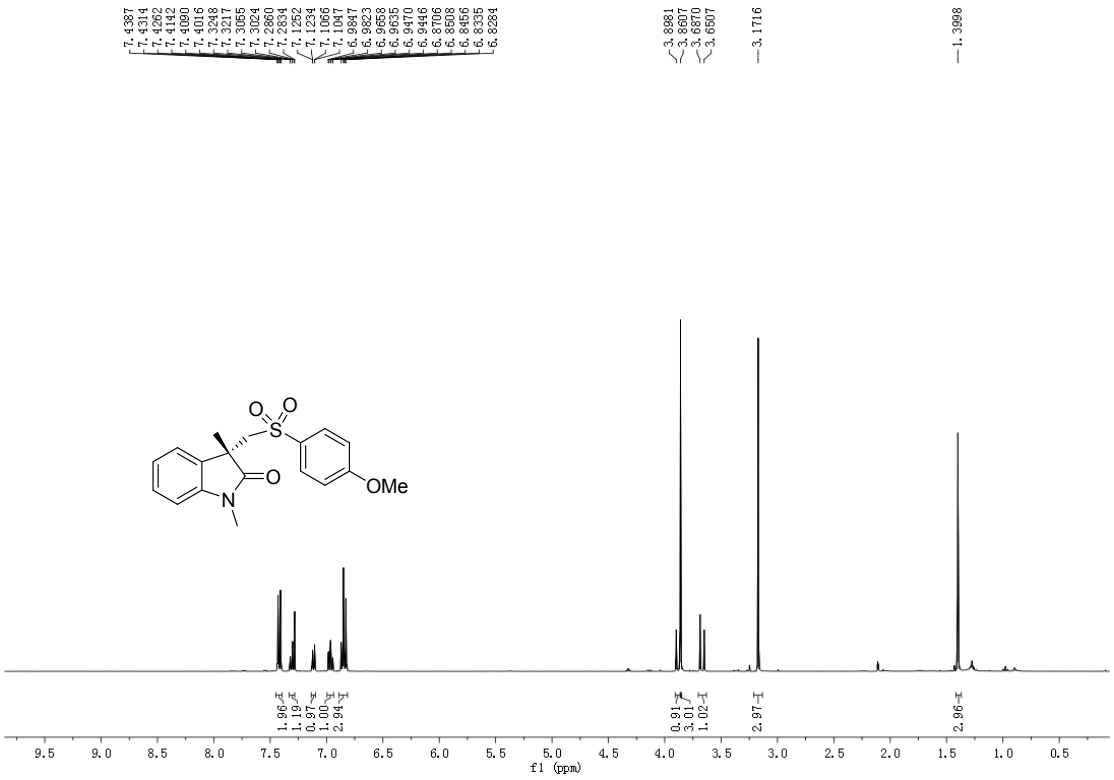
21.55
f1 (ppm)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2.96
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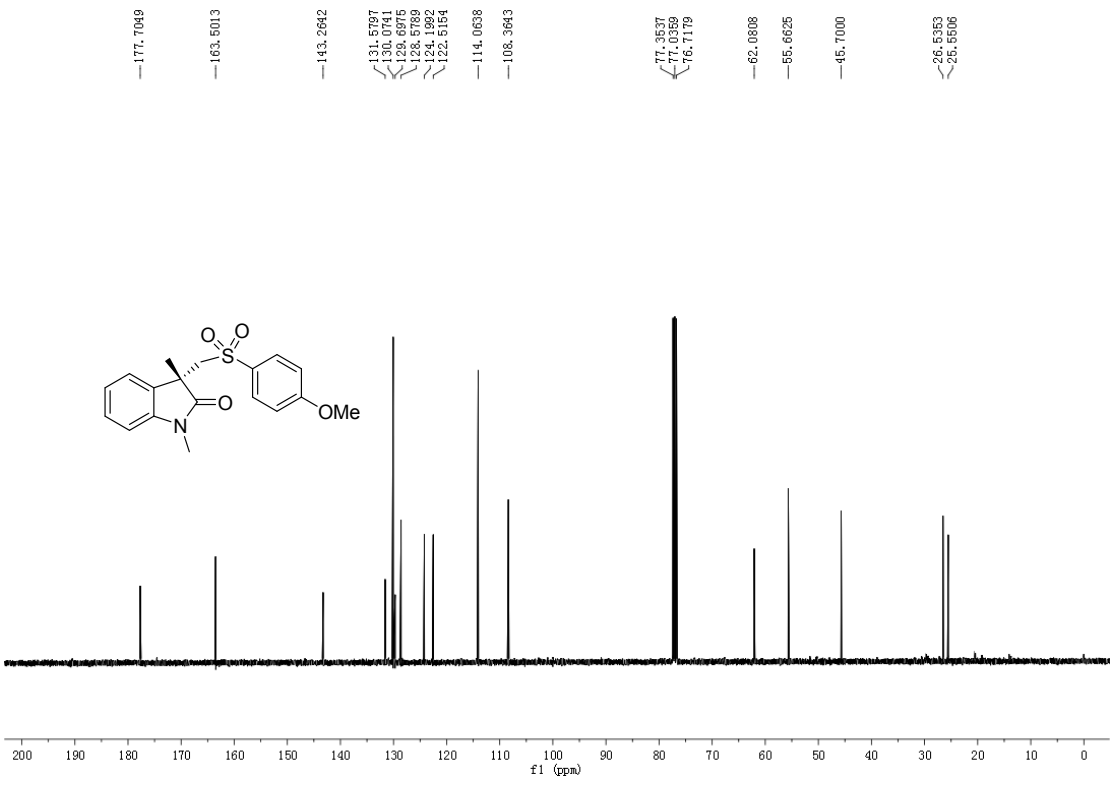
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OMe
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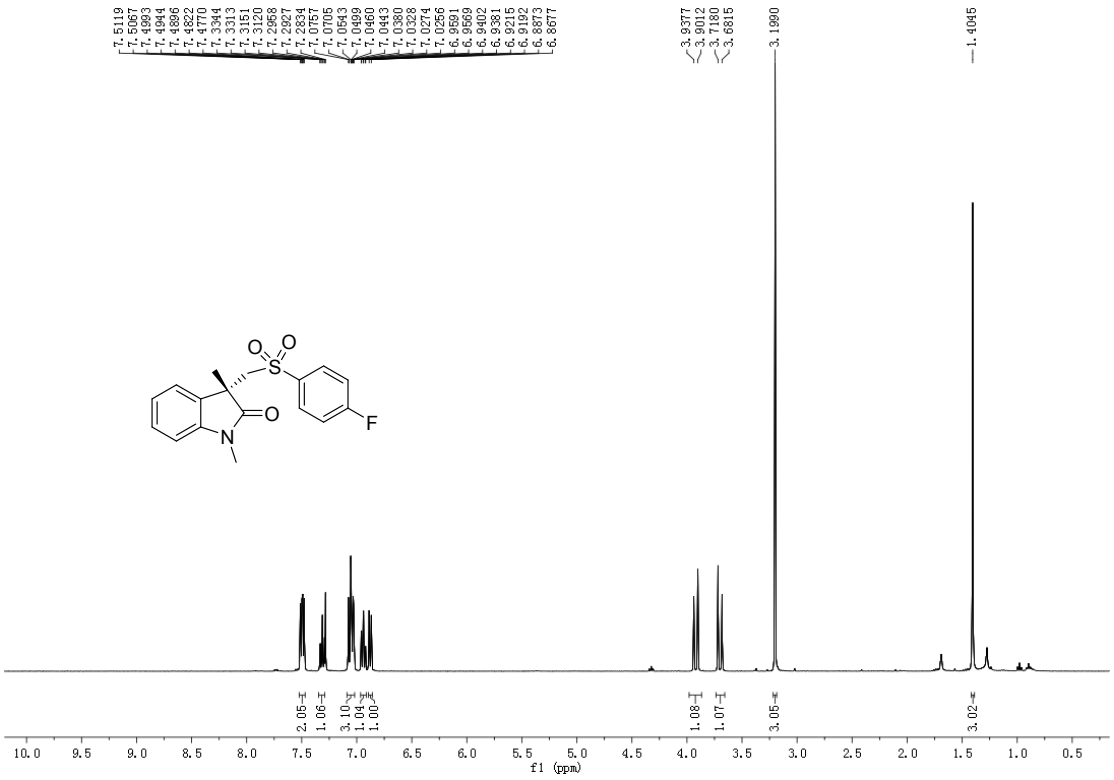
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O
S
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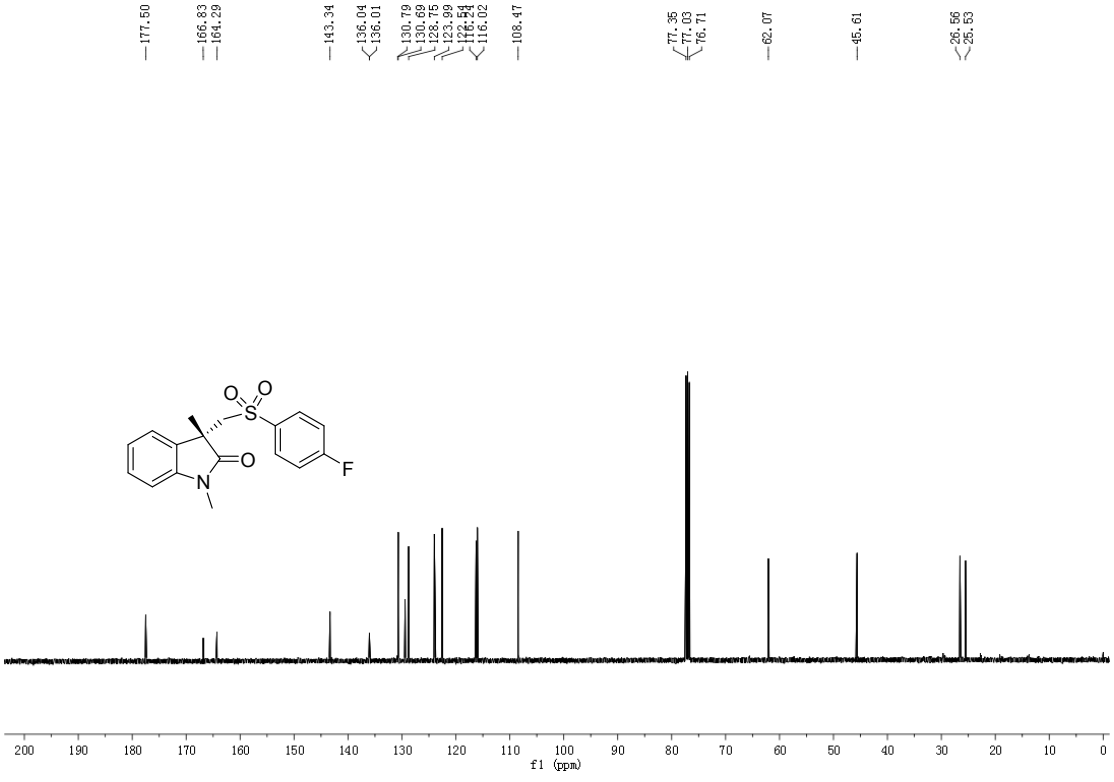
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116.02
108.47
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62.07
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25.53
O
O
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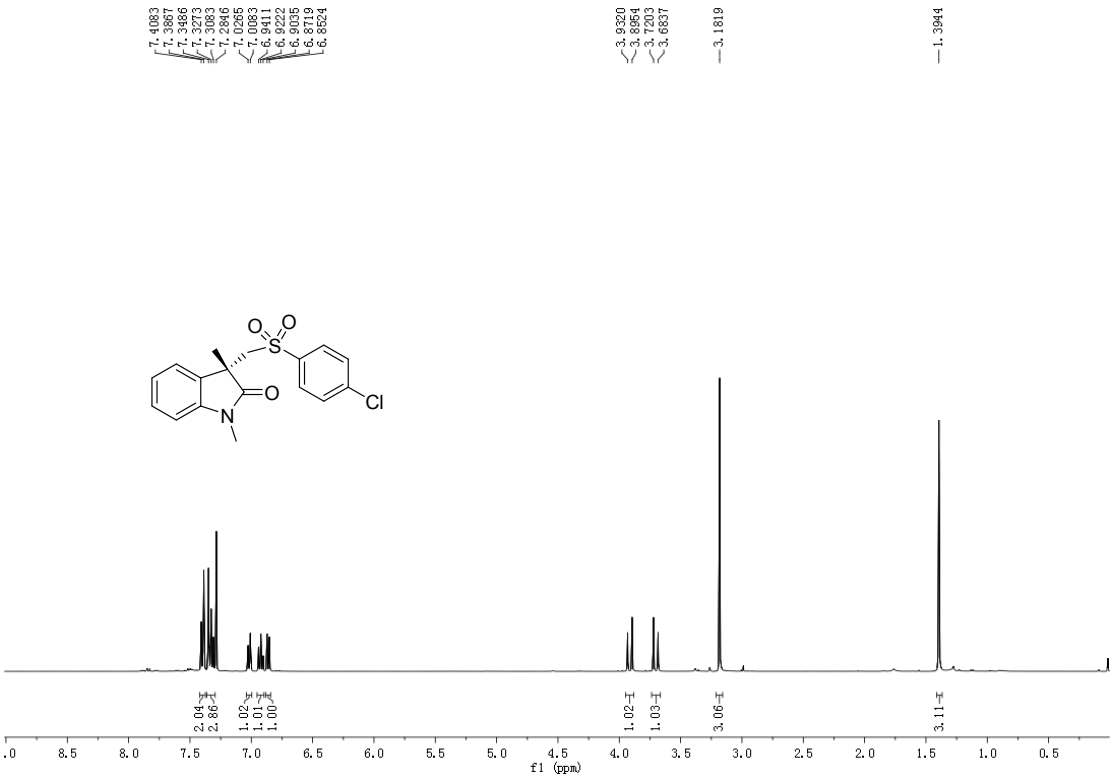
O
N
F
f1 (ppm)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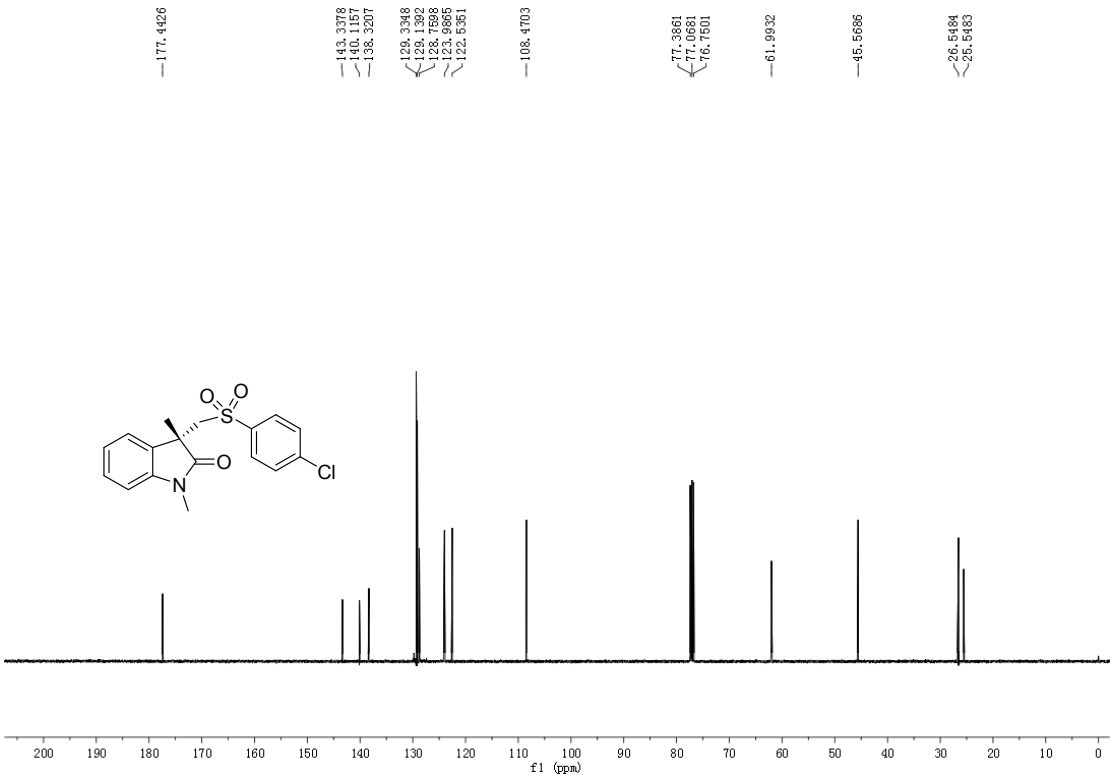
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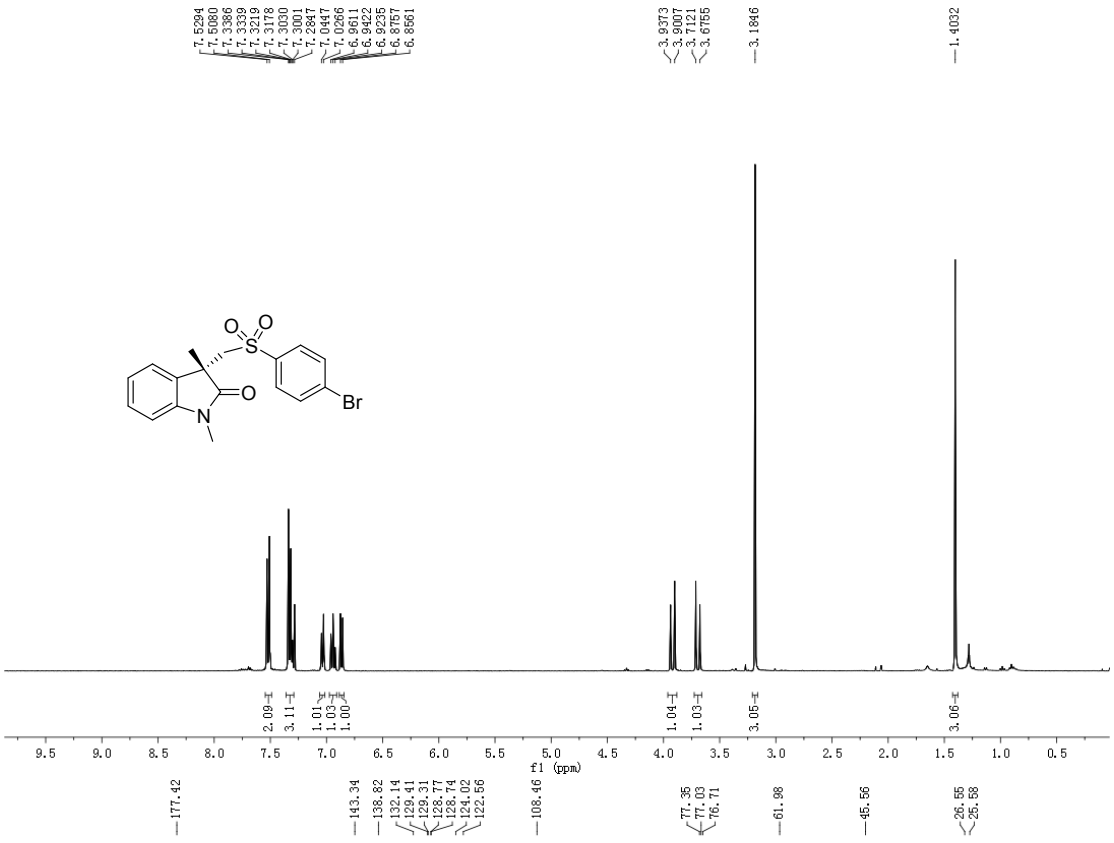
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O
O
S
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N
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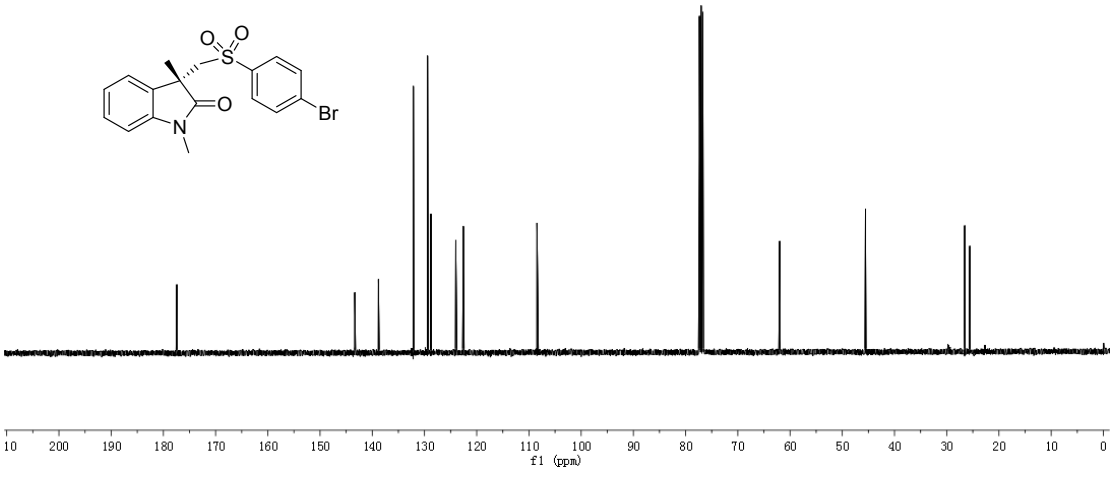
1.03
1.00
1.04
1.03
3.05
3.06
f1 (ppm)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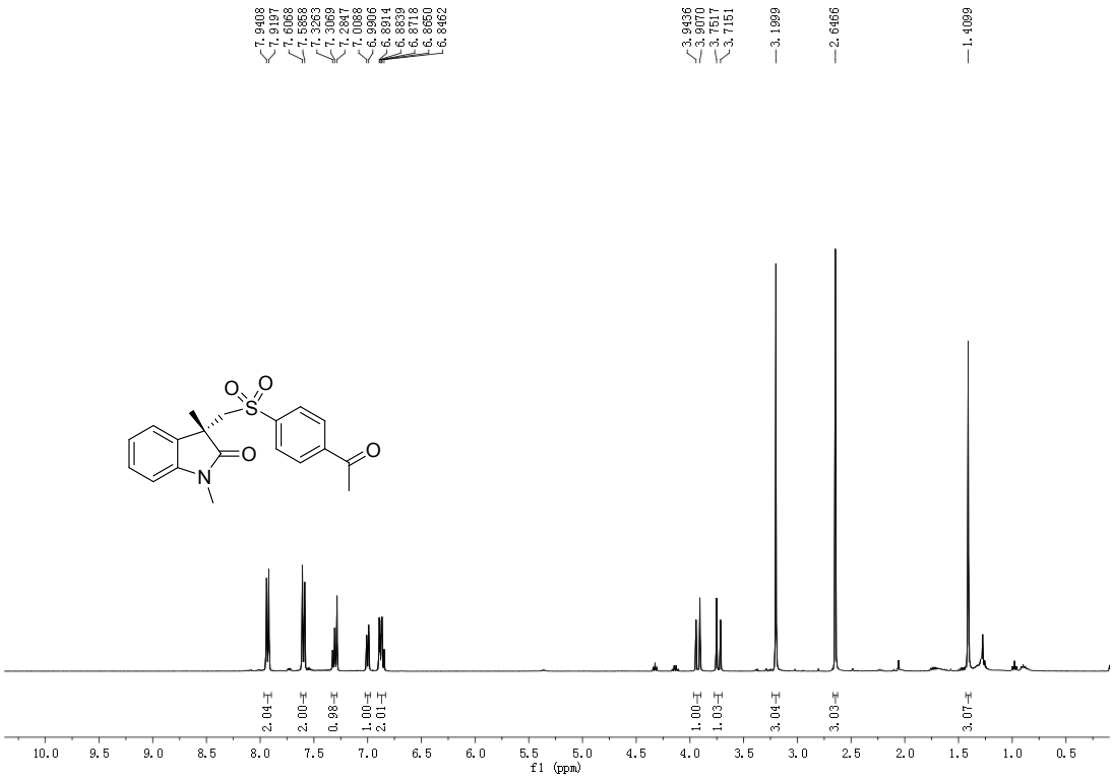
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6.8839
6.8718
6.8650
6.8462
3.9436
3.9070
3.7517
3.7151
3.1999
2.6466
1.4099
2.04
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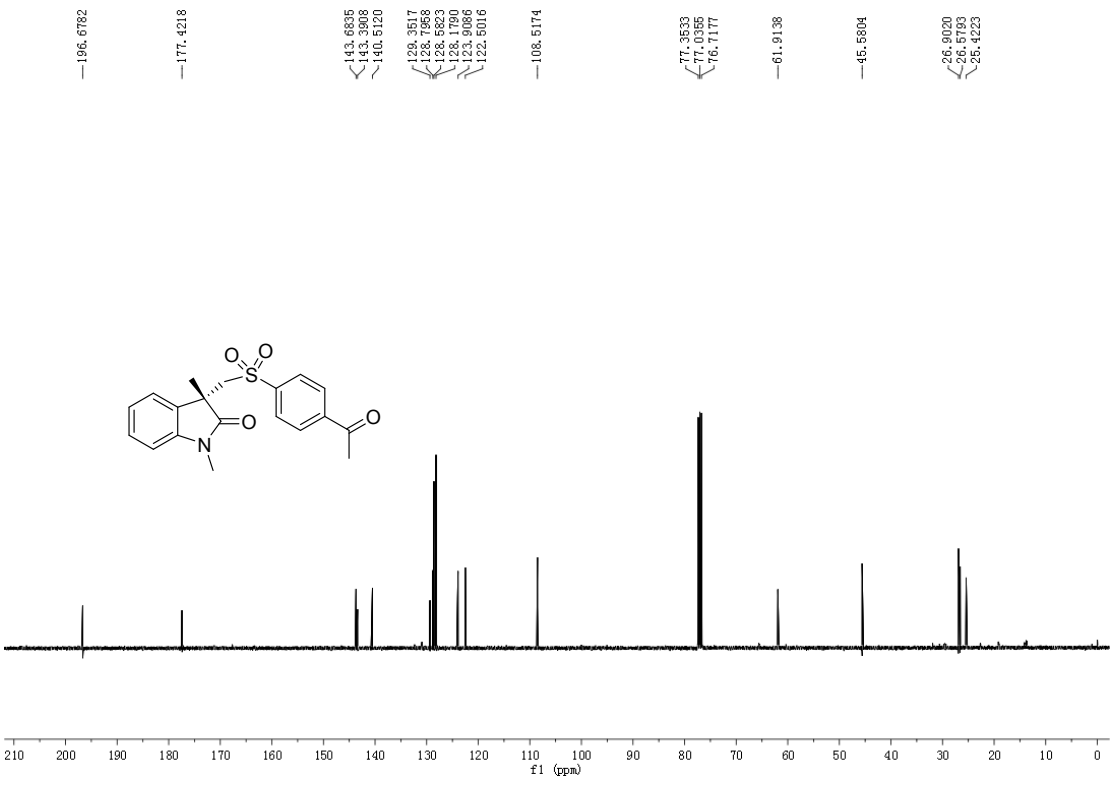
0.98
1.00
2.01
1.00
1.03
3.04
3.03
3.07
f1 (ppm)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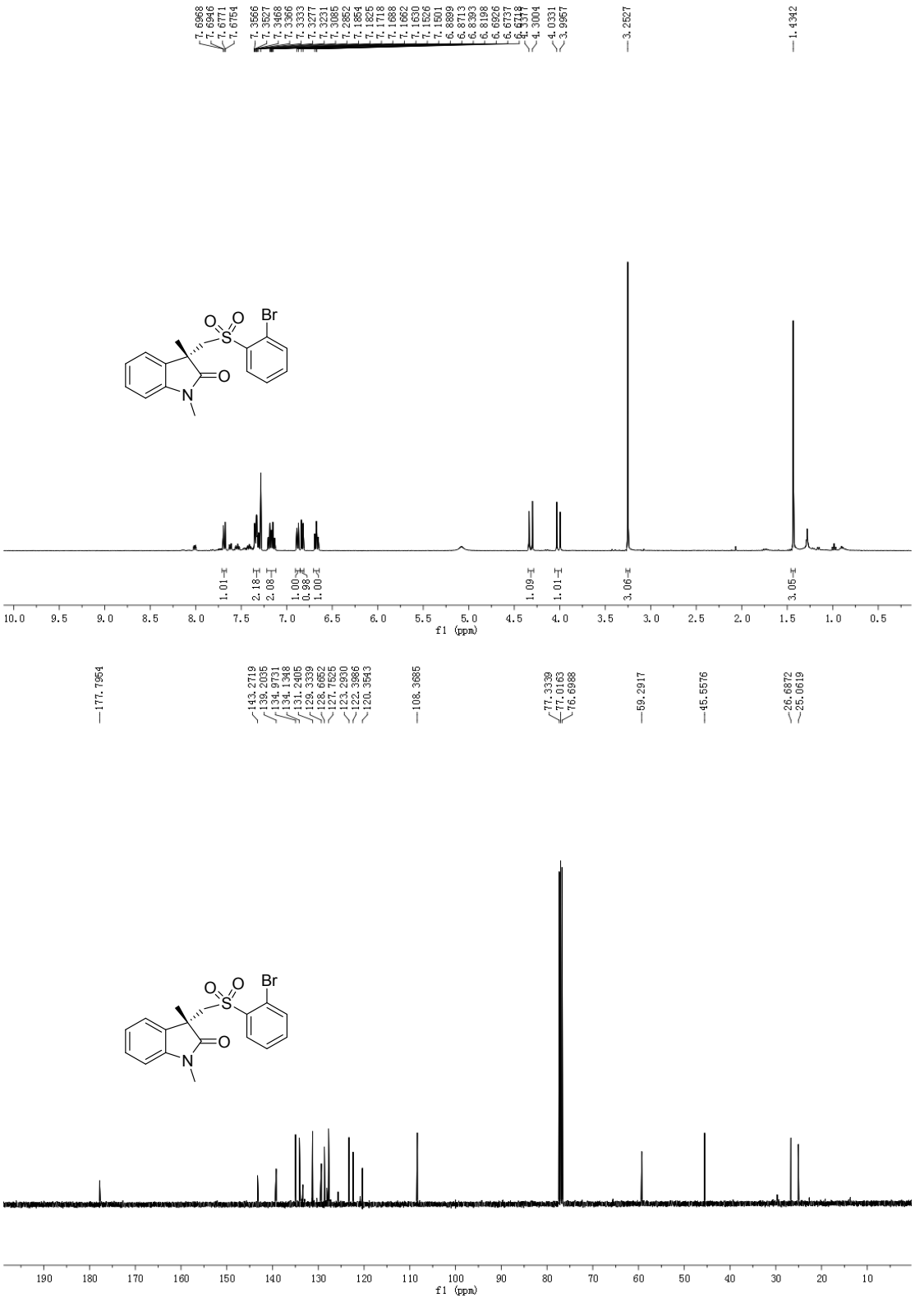
77.0355
76.7177
61.9138
45.5804
26.9020
26.5793
26.4223
f1 (ppm)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7.3085
7.2852
7.1854
7.1825
7.1718
7.1688
7.1662
7.1620
7.1501
6.8899
6.8713
6.8393
6.8198
6.6926
6.6737
6.6718
6.6317
4.3004
4.0331
3.9957
3.2627
1.4342
Br
O
S
O
N
1.01
2.18
2.08
1.00
0.98
1.00
1.09
1.01
3.06
3.05
f1 (ppm)
177.7954
143.2719
138.2035
134.9731
134.1348
131.2405
128.3339
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122.3986
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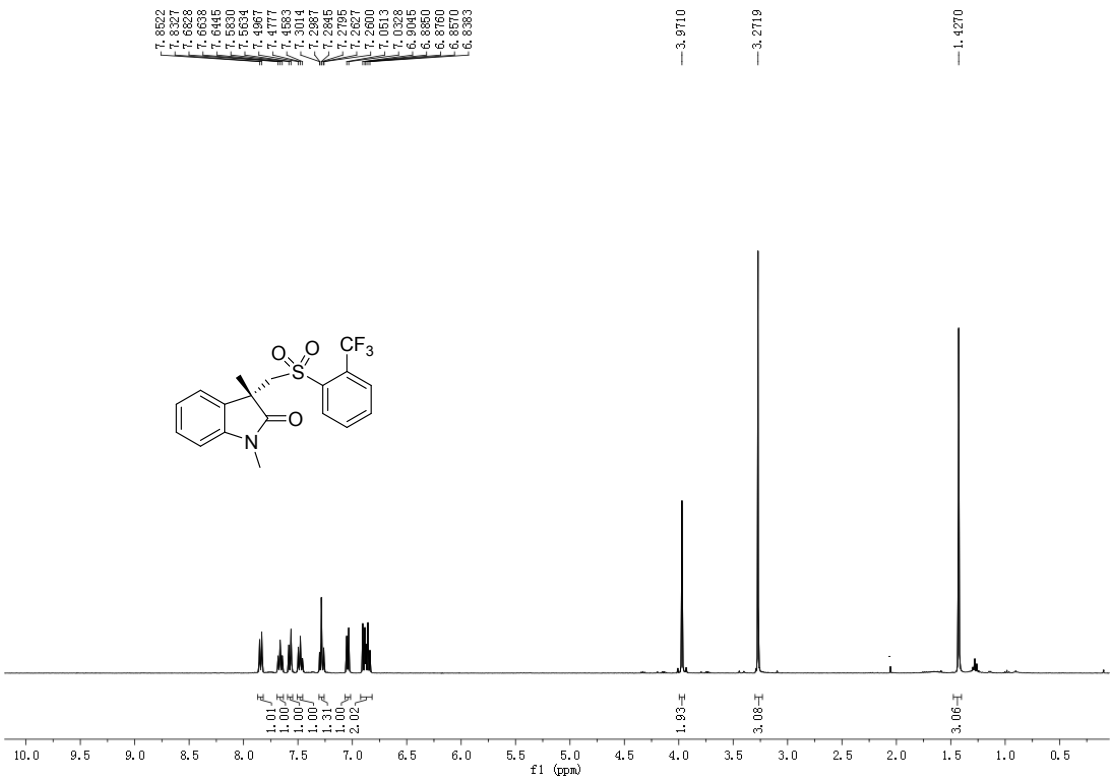
f1 (ppm)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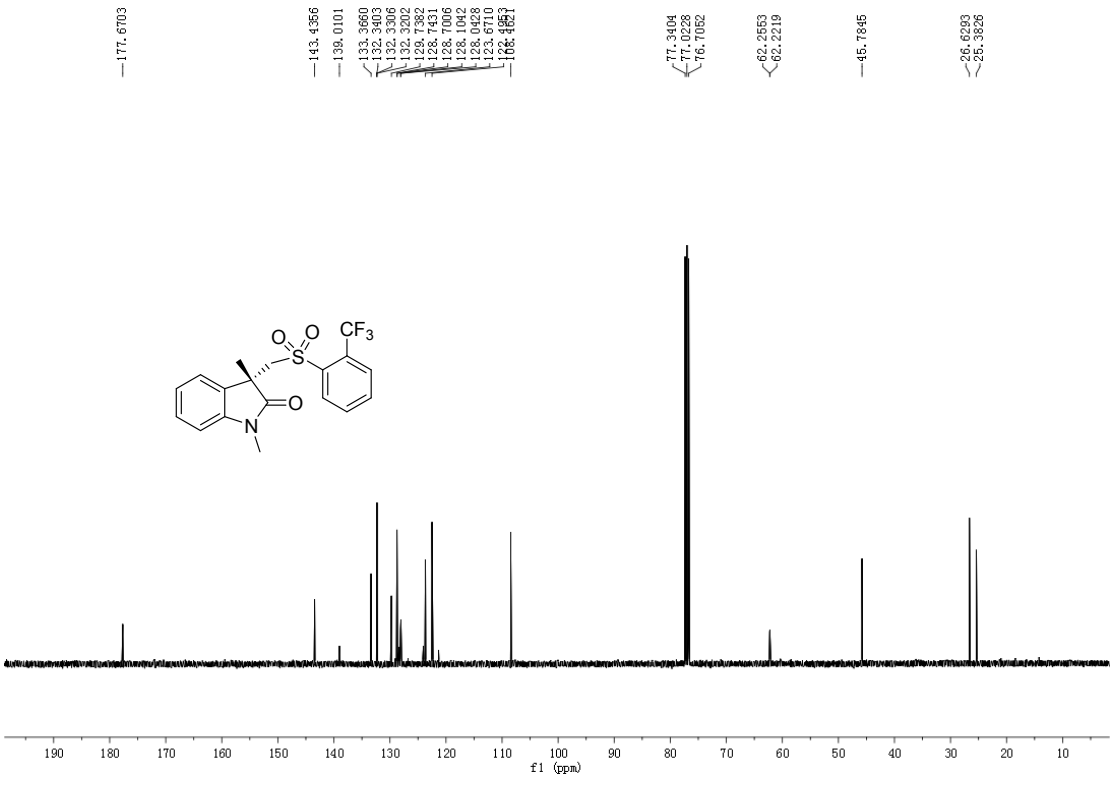
7.2627
7.2600
7.0513
7.0328
6.9045
6.8850
6.8760
6.8570
6.8383
3.9710
3.2719
1.4270
O
O
S
CF3
O
N
1.01
1.00
1.00
1.00
1.31
1.00
2.02
1.93
3.08
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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123.6710
122.4963
122.4621
77.3404
77.0228
76.7052
62.2563
62.2219
45.7845
26.6293
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O
O
S
CF3
O
N
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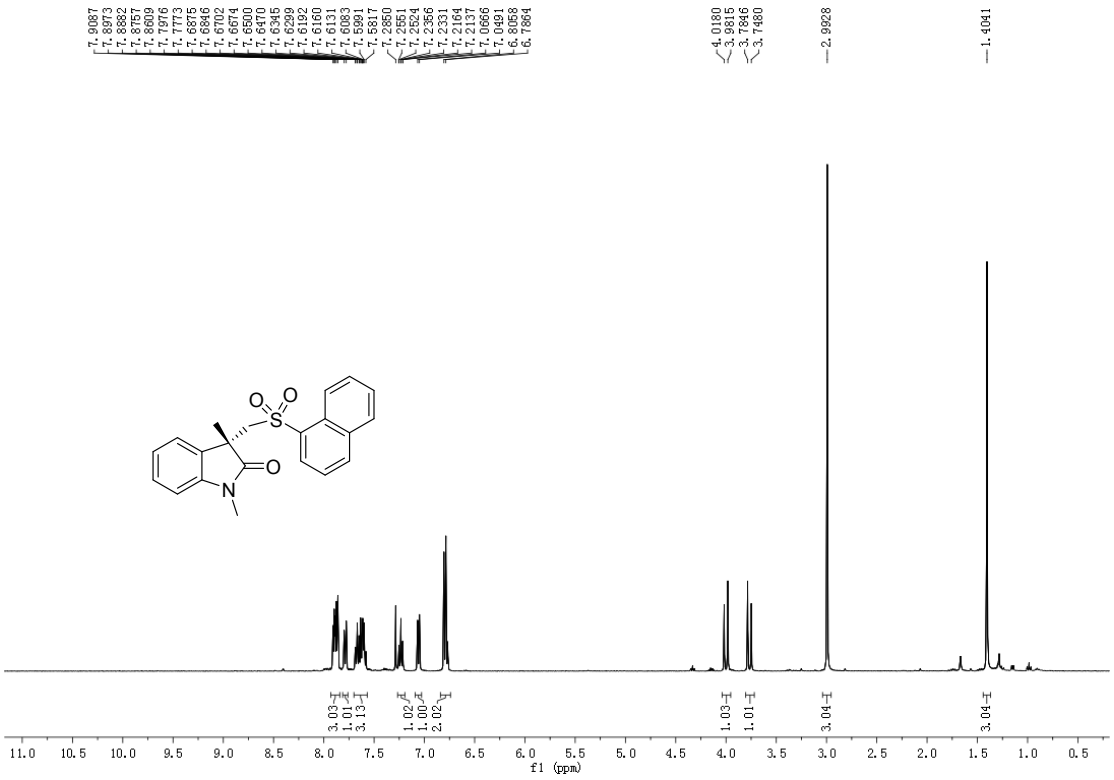
f1 (ppm)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7.6299
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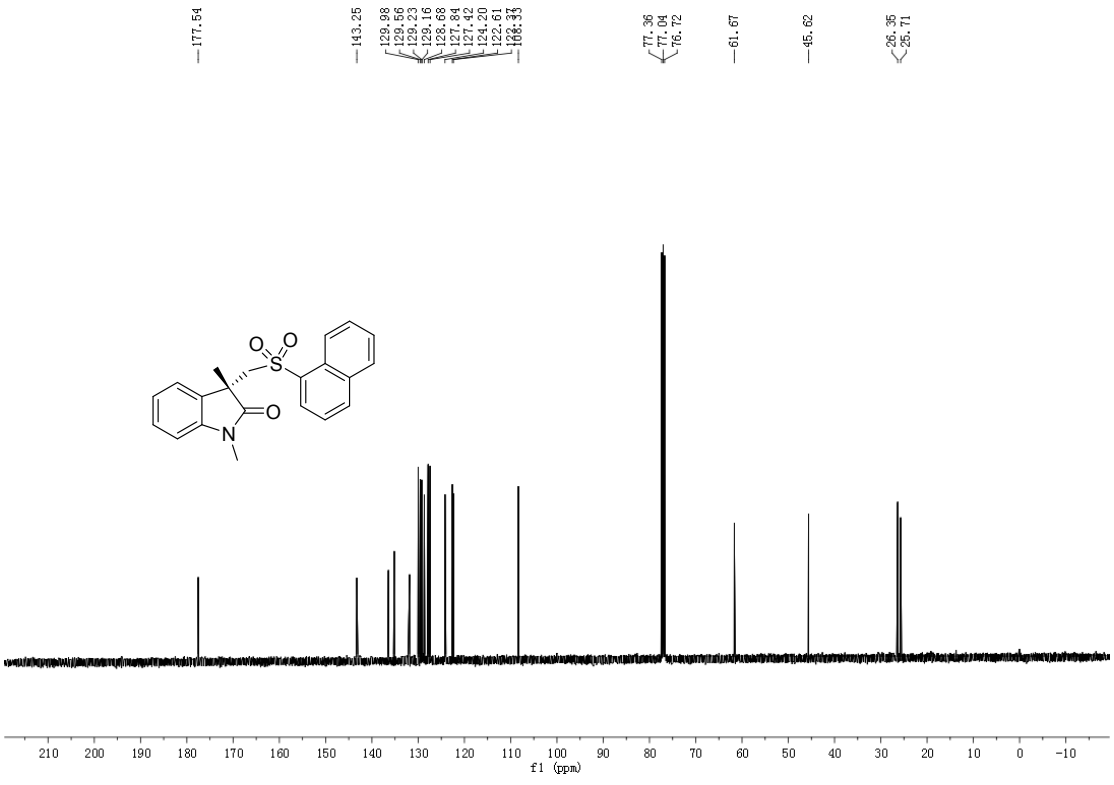
7.6160
7.6131
7.6083
7.5991
7.5817
7.2850
7.2551
7.2524
7.2356
7.2331
7.2164
7.2137
7.0666
7.0491
6.8058
6.7864
4.0180
3.9815
3.7946
3.7480
2.9928
1.4041
3.03
1.01
3.13
1.02
1.00
2.02
1.03
1.01
3.04
3.04
f1 (ppm)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127.42
124.20
122.61
77.36
77.04
76.72
61.67
45.62
26.36
25.71
f1 (ppm)