Electronic Supplementary Material (ESI) for ChemComm.

Cooperative catalysis of N-heterocyclic carbene and Brønsted acid for a highly enantioselective route to unprotected spiro-indoline-pyrans

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General Information: Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with basic solution of potassium permanganate or acidic solution of ceric molybdate.

Flash column chromatography was performed using Merck aluminium oxide 90 active neutral with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use.

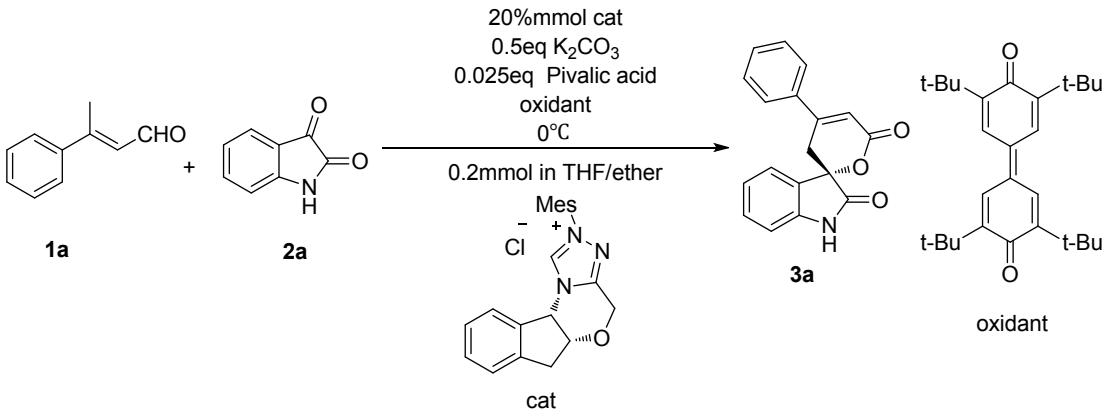
Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on Bruker AMX 400 spectrophotometer ($CDCl_3$ as solvent). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 7.2600, singlet). Multiplicities were given as: s (singlet), d (doublet), t (triplet), dd (doublets of doublet) or m (multiplets). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 77.0, triplet).

Enantiomeric excesses were determined by high performance liquid chromatography (HPLC) analysis on a chiral stationary phase, CHIRALPAK AD-H or CHIRALCEL OD-H. Optical rotations were measured in $CHCl_3$ on a Schmidt + Haensdch polarimeter (Polartronic MH8) with a 10 cm cell (*c* given in g/100 mL). Absolute configuration of the products was determined by X-ray crystallography.

High resolution mass spectrometry (HRMS) was recorded on QTOF perimer for ESI^+.

The racemic products used to determine the e.e. values were synthesized using *cis*-mixture catalyst.

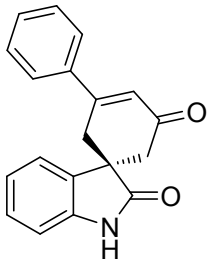
Typical procedure for the NHC catalyzed synthesis of unprotected spiro-indoline-pyrans.



Scheme 39 General procedure for the preparation of spiro products

To an oven dried 5 mL vial was added enal (**1a**, 43.8 mg, 0.3 mmol, 1.5 equiv), isatin (**2a**, 29.4 mg, 0.2 mmol, 1.0 equiv), cat. (14.7 mg, 0.04 mmol, 20 mol %), K_2CO_3 (13.8 mg，0.1 mmol，0.5 equiv) and oxidant (81.6 mg，0.2 mmol，1.0 equiv) was added 2 mL solvent (THF/ether 1:1), followed by addition of pivalic acid (0.51 mg，0.005 mmol，0.025 equiv). The resulting solution was stirred under Ar at 0 ℃until the limited reactants was fully consumed monitored by TLC. After the reaction was complete, reaction mixture was concentrated under reduced pressure. The resulting residue was purified by flash chromatography (EtOAc/PE = 1:5) to provide **3a**.

(S)-4'-(phenyl)spiro[indoline-3,2'-pyran]-2,6'(3'H)-dione (3a):



3a

The title compound was prepared according to the typical procedure, as described above, in 85% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.76 (s, 1H), 7.81 – 7.75 (m, 2H), 7.52 (t, *J* = 6.3 Hz, 1H), 7.50 – 7.43 (m, 3H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.66 (s, 1H), 3.41 (d, *J* = 18.2 Hz, 1H), 3.31 (d, *J* = 18.4 Hz, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 179.33 , 168.54 , 157.22 , 146.97 , 140.72 , 136.10 , 134.11 , 133.35 , 131.85 , 131.72 , 129.70 , 127.67 , 118.87 , 115.73 , 85.15 , 36.30 .

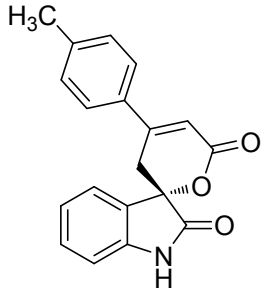
HRMS (ESI+) calcd for $C_{18}H_{13}NaNO_3$, m/z 314.0793, found 314.0789

HPLC: Chiralcel AD-H (n-hexane/i-PrOH, 90/10, flow rate 1 mL/min, λ= 254 nm), t_R(major) = 83.9 min, t_R (minor) = 75.0 min; 83% ee.

$[\alpha]_D^{20}$ = +16.5(*c* = 0.5, acetone)

Melting point：94.3℃~95.7℃

(S)-4'-(p-tolyl)spiro[indoline-3,2'-pyran]-2,6'(3'H)-dione (3b):



The title compound was prepared according to the typical procedure, as described above, in 80% yield.

^{1}H NMR (500 MHz, DMSO) δ 10.73 (s, 1H), 7.67 (d, *J* = 7.9 Hz, 2H), 7.51 (d, *J* = 7.4 Hz, 1H), 7.40 – 7.31 (m, 1H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.94

(d, *J* = 7.7 Hz, 1H), 6.61 (s, 1H), 3.36 (d, *J* = 20.4 Hz, 1H), 3.27 (d, *J* = 18.3 Hz, 1H), 2.35 (s, 3H).^{13}C NMR (126 MHz, DMSO) δ 174.58 , 163.85 , 152.35 , 142.21 , 141.39 , 133.09 , 131.36 , 129.95 , 128.68 , 126.98 , 124.88 , 122.89 , 113.12 , 110.98 , 80.35 , 31.55 , 21.35 .

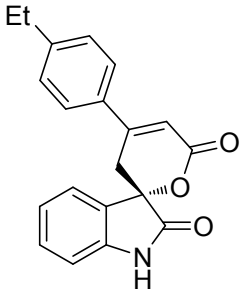
HRMS (ESI+) calcd for $C_{19}H_{16}NO_3$, m/z 306.1130, found 306.1125

HPLC: Chiralcel AD-H (n-hexane/i-PrOH, 85/15, flow rate 1 mL/min, λ= 254 nm), t_R(major) = 47.3 min, t_R (minor) = 38.3 min; 80% ee.

$[\alpha]_D^{20}$ = +22.0(*c* = 0.5, acetone)

Melting point：219.4℃~220.9℃

(S)-4'-(4-ethylphenyl)spiro[indoline-3,2'-pyran]-2,6'(3'H)-dione (3c):



The title compound was prepared according to the typical procedure, as described above, in 85% yield.

^{1}H NMR (500 MHz, DMSO) δ 10.77 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 7.4 Hz, 1H), 7.34 (dd, *J* = 14.4, 6.7 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 6.63 (s, 1H), 3.37 (d, *J* = 18.5 Hz, 1H), 3.28 (d, *J* = 18.2 Hz, 1H), 2.64 (q, *J* = 7.5 Hz, 2H), 1.18 (t, *J* = 7.5 Hz, 3H).^{13}C NMR (126 MHz, DMSO) δ 174.57 , 163.87 , 152.41 , 147.59 , 142.21 , 133.35 , 131.37 , 128.78 , 128.68 , 127.11 , 124.89 , 122.90 , 113.18 , 110.98 , 80.36 , 31.52 , 28.44 , 15.78 .

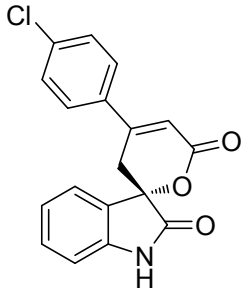
HRMS (ESI+) calcd for $C_{20}H_{17}NaNO_3$, m/z 342.1106, found 342.1099

HPLC: Chiralcel IC (n-hexane/i-PrOH, 60/40, flow rate 1 mL/min, λ= 254 nm), t_R(major) = 31.9 min, t_R (minor) = 22.8 min; 83% ee.

$[\alpha]_D^{20}$ = +25.2 (*c* = 0.5, acetone)

Melting point：199.2℃~121.0℃

(S)-4'-(4-chlorophenyl)spiro[indoline-3,2'-pyran]-2,6'(3'H)-dione (3d):



The title compound was prepared according to the typical procedure, as described above, in 93% yield.

^{1}H NMR (500 MHz, DMSO) δ 10.77 (s, 1H), 7.81 (d, *J* = 8.6 Hz, 2H), 7.57 – 7.48 (m, 3H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 6.70 (s, 1H), 3.41 (d, *J* = 18.5 Hz, 1H), 3.31 (d, *J* = 18.4 Hz, 1H).^{13}C NMR (126 MHz, DMSO) δ 174.57 , 163.70 , 151.14 , 142.23 , 136.02 , 134.82 , 131.44 , 129.35 , 128.92 , 128.49 , 124.97 , 122.93 , 114.71 , 110.98 , 80.37 , 31.44 .

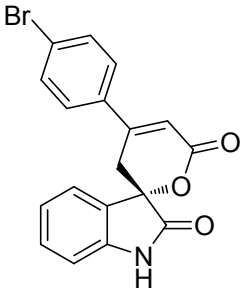
HRMS (ESI+) calcd for $C_{18}H_{12}ClNaNO_3$, m/z 348.0403, found 348.0397

HPLC: Chiralcel AD-H (n-hexane/i-PrOH, 60/40, flow rate 1 mL/min, λ= 254 nm), t_R(major) = 15.9 min, t_R (minor) = 12.9 min; 81% ee.

$[\alpha]_D^{20}$ = +27.2 (*c* = 0.5, acetone)

Melting point：204.3℃~205.8℃

(S)-4'-(4-bromophenyl)spiro[indoline-3,2'-pyran]-2,6'(3'H)-dione (3e)



The title compound was prepared according to the typical procedure, as described above, in 83% yield.

^{1}H NMR (500 MHz, DMSO) δ 10.77 (s, 1H), 7.74 (d, *J* = 8.7 Hz, 2H), 7.66 (d, *J* = 8.7 Hz, 2H), 7.52 (dd, *J* = 11.2, 4.7 Hz, 1H), 7.35 (td, *J* = 7.8, 1.1 Hz, 1H), 7.04 (td, *J* =

7.6, 0.7 Hz, 1H), 6.93 (d, *J* = 7.7 Hz, 1H), 6.70 (s, 1H), 3.41 (dd, *J* = 18.3, 1.4 Hz, 1H), 3.31 (dd, *J* = 18.3, 0.8 Hz, 1H).^{13}C NMR (126 MHz, DMSO) δ 174.56 , 163.69 , 151.25 , 142.22 , 135.19 , 132.28 , 131.44 , 129.12 , 128.48 , 124.98 , 124.86 , 122.93 , 114.71 , 110.98 , 80.37 , 31.39 .

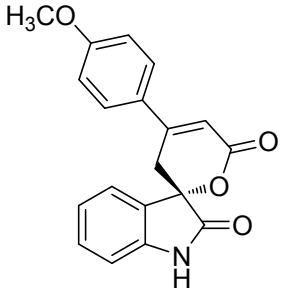
HRMS (ESI+) calcd for $C_{18}H_{12}BrNaNO_3$, m/z 391.9898, found 391.9899

HPLC: Chiralcel AD-H (n-hexane/i-PrOH, 85/15, flow rate 1 mL/min, λ= 254 nm), t_R(major) = 62.4 min, t_R (minor) = 49.1 min; 83% ee.

$[\alpha]_D^{20}$ = +27.2 (*c* = 0.5, acetone)

Melting point：218.5℃~220℃

(S)-4'-(4-methoxyphenyl)spiro[indoline-3,2'-pyran]-2,6'(3'H)-dione (3f)



The title compound was prepared according to the typical procedure, as described above, in 95% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.76 (s, 1H), 7.76 (d, *J* = 8.6 Hz, 2H), 7.51 (t, *J* = 10.1 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 3H), 6.93 (d, *J* = 7.7 Hz, 1H), 6.58 (s, 1H), 3.81 (s, 3H), 3.35 (d, *J* = 16.3 Hz, 2H), 3.27 (d, *J* = 18.2 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 179.36 , 168.75 , 166.72 , 156.72 , 146.95 , 136.09 , 133.66 , 133.52 , 132.77 , 129.63 , 127.64 , 119.52 , 116.48 , 115.72 , 85.03 , 60.64 , 36.16 .

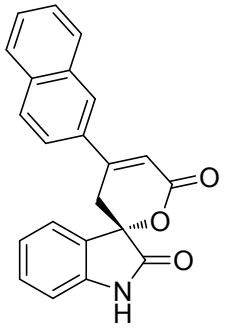
HRMS (ESI+) calcd for $C_{19}H_{15}NaNO_4$, m/z 344.0899, found 344.0898

HPLC: Chiralcel AJ-H (n-hexane/i-PrOH, 80/20, flow rate 1 mL/min, λ= 254 nm), t_R(major) = 79.1 min, t_R (minor) = 61.5 min; 81% ee.

$[\alpha]_D^{20}$ = +26.2 (*c* = 0.5, acetone)

Melting point：219.2℃~220.9℃

(S)-4'-(naphthalen-2-yl)spiro[indoline-3,2'-pyran]-2,6'(3'H)-dione (3g)



The title compound was prepared according to the typical procedure, as described above, in 85% yield.

^{1}H NMR (500 MHz, DMSO) δ 10.81 (s, 1H), 8.37 (s, 1H), 8.03 – 7.93 (m, 4H), 7.64 – 7.53 (m, 3H), 7.37 (td, *J* = 7.8, 0.9 Hz, 1H), 7.05 (dd, *J* = 11.1, 4.0 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 1H), 6.86 (s, 1H), 3.56 (dd, *J* = 18.2, 1.0 Hz, 1H), 3.46 (d, *J* = 18.4 Hz, 1H).^{13}C NMR (126 MHz, DMSO) δ 174.73 , 163.94 , 151.88 , 142.23 , 134.29 , 133.15 , 133.03 , 131.43 , 129.33 , 128.88 , 128.64 , 128.16 , 128.01 , 127.80 , 127.31 , 125.05 , 123.70 , 122.97 , 114.36 , 110.99 , 80.43 , 31.55 .

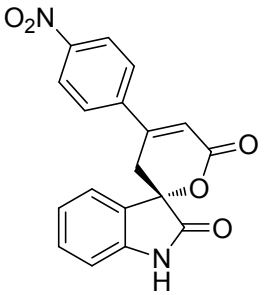
HRMS (ESI+) calcd for $C_{22}H_{15}NaNO_3$, m/z 364.0950, found 364.0946

HPLC: Chiralcel AD-H (n-hexane/i-PrOH, 90/10, flow rate 1 mL/min, λ= 254 nm), t_R(major) = 92.5 min, t_R (minor) = 75.9 min; 85% ee.

$[\alpha]_D^{20}$ = +50.6 (*c* = 0.5, acetone)

Melting point：218.1℃~219.7℃

(S)-4'-(4-nitrophenyl)spiro[indoline-3,2'-pyran]-2,6'(3'H)-dione (3h)



The title compound was prepared according to the typical procedure, as described above, in 67% yield.

^{1}H NMR (500 MHz, DMSO) δ 10.76 (s, 1H), 8.27 (t, *J* = 7.8 Hz, 2H), 8.05 (d, *J* = 8.9

Hz, 2H), 7.56 (d, *J* = 7.4 Hz, 1H), 7.41 – 7.32 (m, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 6.84 (d, *J* = 7.5 Hz, 1H), 3.51 (dd, *J* = 18.4, 1.5 Hz, 1H), 3.39 (d, *J* = 18.4 Hz, 1H).^{13}C NMR (126 MHz, DMSO) δ 174.52 , 163.40 , 150.24 , 148.87 , 142.34 , 142.26 , 131.53 , 128.48 , 128.27 , 125.07 , 124.24 , 122.98 , 117.47 , 111.01 , 80.46 , 31.53 .

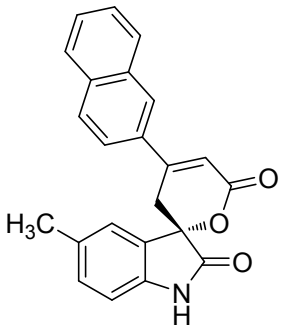
HRMS (ESI+) calcd for $C_{18}H_{12}NaNO_5$, m/z 359.0644, found 359.0641

HPLC: Chiralcel AD-H (n-hexane/i-PrOH, 60/40, flow rate 1 mL/min, λ= 254 nm), t_R(major) = 25.1 min, t_R (minor) = 17.7 min; 90% ee.

$[\alpha]_D^{20}$ = +74.4(*c* = 0.5, acetone)

Melting point：208.7℃~210.3℃

(S)-5-methyl-4'-(naphthalen-2-yl)spiro[indoline-3,2'-pyran]-2,6'(3'H)-dione (3i)



The title compound was prepared according to the typical procedure, as described above, in 83% yield.

^{1}H NMR (500 MHz, DMSO) δ 10.68 (s, 1H), 8.37 (s, 1H), 8.03 – 7.93 (m, 4H), 7.64 – 7.53 (m, 2H), 7.40 (s, 1H), 7.17 (d, *J* = 7.9 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.84 – 6.83 (m, 1H), 3.54 (d, *J* = 18.2 Hz, 1H), 3.46 – 3.39 (m, 1H), 2.26 (s, 3H).^{13}C NMR (126 MHz, DMSO) δ 174.74 , 163.93 , 151.77 , 139.71 , 134.29 , 133.18 , 133.05 , 132.03 , 131.57 , 129.33 , 128.88 , 128.71 , 128.14 , 127.99 , 127.76 , 127.29 , 125.54 , 123.68 , 114.37 , 110.75 , 80.53 , 31.65 , 21.07 .

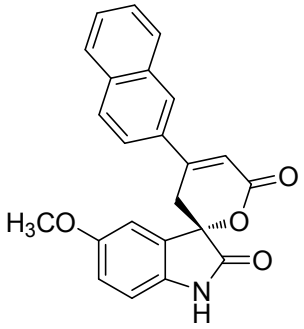
HRMS (ESI+) calcd for $C_{23}H_{17}NaNO_3$, m/z 378.1106, found 378.1099

HPLC: Chiralcel AD-H (n-hexane/i-PrOH, 60/40, flow rate 1 mL/min, λ= 254 nm), t_R(major) = 11.2 min, t_R (minor) = 8.2 min; 81% ee.

$[\alpha]_D^{20}$ = +114.4 (*c* = 0.5, acetone)

Melting point：219.2℃~220.6℃

(S)-5-methoxy-4'-(naphthalen-2-yl)spiro[indoline-3,2'-pyran]-2,6'(3'H)-dione (3j)



The title compound was prepared according to the typical procedure, as described above, in 83% yield.

^{1}H NMR (500 MHz, DMSO) δ 10.60 (s, 1H), 8.37 (s, 1H), 8.02 – 7.93 (m, 4H), 7.63 – 7.53 (m, 2H), 7.26 (d, *J* = 2.5 Hz, 1H), 6.95 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.88 (d, *J* = 8.5 Hz, 1H), 6.83 (s, 1H), 3.73 (s, 3H), 3.59 (dd, *J* = 18.2, 1.4 Hz, 1H), 3.49 – 3.38 (m, 1H).^{13}C NMR (126 MHz, DMSO) δ 174.81 , 163.93 , 155.85 , 151.67 , 135.29 , 134.28 , 133.18 , 133.07 , 129.64 , 129.32 , 128.89 , 128.13 , 128.00 , 127.72 , 127.30 , 123.66 , 116.20 , 114.35 , 112.02 , 111.54 , 80.74 , 56.13 , 31.65 .

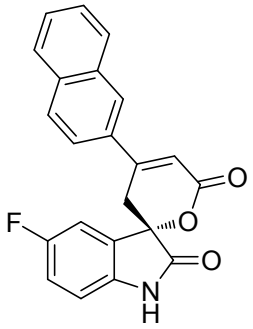
HRMS (ESI+) calcd for $C_{23}H_{17}NaNO_4$, m/z 394.1055, found 394.1049

HPLC: Chiralcel AD-H (n-hexane/i-PrOH, 85/15, flow rate 1 mL/min, λ= 254 nm), t_R(major) = 88.4 min, t_R (minor) = 41.2 min; 88% ee.

$[\alpha]_D^{20}$ = +133.2 (*c* = 0.5, acetone)

Melting point：208.2℃~220℃

(S)-5-fluoro-4'-(naphthalen-2-yl)spiro[indoline-3,2'-pyran]-2,6'(3'H)-dione (3k)



The title compound was prepared according to the typical procedure, as described

above, in 83% yield.

^{1}H NMR (500 MHz, DMSO) δ 10.81 (s, 1H), 8.37 (s, 1H), 8.08 – 7.90 (m, 4H), 7.58 (dt, *J* = 15.9, 7.3 Hz, 3H), 7.23 (dd, *J* = 12.4, 5.3 Hz, 1H), 6.97 (dd, *J* = 8.4, 4.1 Hz, 1H), 6.84 (s, 1H), 3.62 (d, *J* = 18.2 Hz, 1H), 3.49 (d, *J* = 18.2 Hz, 1H).^{13}C NMR (126 MHz, DMSO) δ 174.84 , 163.67 , 159.61 , 157.72 , 151.62 , 138.48 , 134.31 , 133.16 , 133.00 , 129.98 (d, *J* = 8.2 Hz), 129.31 , 128.90 , 128.08 (d, *J* = 18.7 Hz), 127.75 , 127.31 , 123.67 , 117.80 (d, *J* = 23.3 Hz), 114.34 , 113.11 (d, *J* = 25.2 Hz), 112.02 (d, *J* = 7.8 Hz), 80.52 , 31.37 .

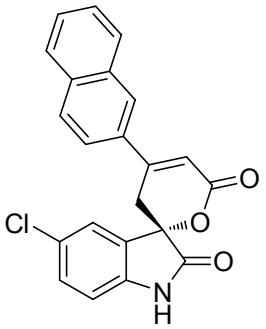
HRMS (ESI+) calcd for $C_{22}H_{14}FNaNO_3$, m/z 382.0855, found 382.0851

HPLC: Chiralcel AD-H (n-hexane/i-PrOH, 90/10, flow rate 1 mL/min, λ= 254 nm), t_R(major) = 59.2 min, t_R (minor) = 49.9 min; 93% ee.

$[\alpha]_D^{20}$ = +45.8 (*c* = 0.5, acetone)

Melting point:209.8℃~211.1℃

(S)-5-chloro-4'-(naphthalen-2-yl)spiro[indoline-3,2'-pyran]-2,6'(3'H)-dione (3l)



The title compound was prepared according to the typical procedure, as described above, in 93% yield.

^{1}H NMR (500 MHz, DMSO) δ 10.92 (s, 1H), 8.36 (s, 1H), 7.96 (dd, *J* = 21.7, 13.3 Hz, 4H), 7.70 (t, *J* = 9.3 Hz, 1H), 7.63 – 7.51 (m, 2H), 7.43 (dd, *J* = 8.3, 1.9 Hz, 1H), 6.98 (d, *J* = 8.3 Hz, 1H), 6.85 (s, 1H), 3.65 (d, *J* = 18.2 Hz, 1H), 3.49 (d, *J* = 18.2 Hz, 1H).

^{13}C NMR (126 MHz, DMSO) δ 174.59 , 163.64 , 151.65 , 141.22 , 134.31 , 133.16 , 132.97 , 131.27 , 130.39 , 129.31 , 128.91 , 128.17 , 128.01 , 127.77 , 127.32 , 126.94 , 125.41 , 123.65 , 114.28 , 112.53 , 80.30 , 31.28 .

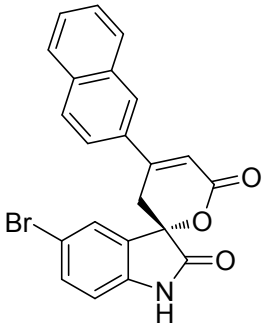
HRMS (ESI+) calcd for $C_{22}H_{14}ClNaNO_3$, m/z 398.0560, found 398.0556

HPLC: Chiralcel AD-H (n-hexane/i-PrOH, 90/10, flow rate 1 mL/min, λ= 254 nm), t_R(major) = 65.8 min, t_R (minor) = 47.1 min; 86% ee.

$[\alpha]_D^{20}$ = +156.2 (*c* = 0.5, acetone)

Melting point：139.1℃~140.0℃

(S)-5-bromo-4'-(naphthalen-2-yl)spiro[indoline-3,2'-pyran]-2,6'(3'H)-dione (3m)



The title compound was prepared according to the typical procedure, as described above, in 83% yield.

^{1}H NMR (500 MHz, DMSO) δ 10.92 (s, 1H), 8.36 (s, 1H), 7.99 (s, 4H), 7.82 (s, 1H), 7.66 – 7.50 (m, 3H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.84 (s, 1H), 3.66 (d, *J* = 18.0 Hz, 1H), 3.48 (d, *J* = 18.3 Hz, 1H).^{13}C NMR (126 MHz, DMSO) δ 174.47, 163.64 , 151.65 , 141.64 , 134.31 , 134.13 , 133.16 , 132.97 , 130.76 , 129.31 , 128.90 , 128.17 , 128.13 , 128.02 , 127.77 , 127.33 , 123.66 , 114.48 , 114.24 (s), 113.01 , 80.24 , 31.25 .

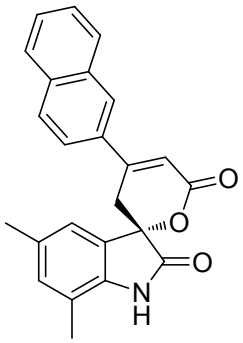
HRMS (ESI+) calcd for $C_{22}H_{14}BrNaNO_3$, m/z 442.0055, found 442.0053

HPLC: Chiralcel AD-H (n-hexane/i-PrOH, 85/15, flow rate 1 mL/min, λ= 254 nm), t_R(major) = 37.8 min, t_R (minor) = 26.8 min; 79% ee.

$[\alpha]_D^{20}$ = +140.8 (*c* = 0.5, acetone)

Melting point：219.5℃~220.3℃

(S)-5,7-dimethyl-4'-(naphthalen-2-yl)spiro[indoline-3,2'-pyran]-2,6'(3'H)-dione (3n)



The title compound was prepared according to the typical procedure, as described above, in 52% yield.

^{1}H NMR (500 MHz, DMSO) δ 10.77 (d, *J* = 54.0 Hz, 1H), 8.37 (s, 1H), 8.04 – 7.90 (m, 5H), 7.64 – 7.51 (m, 3H), 7.24 – 7.17 (m, 1H), 7.02 (d, *J* = 14.7 Hz, 1H), 6.83 (s, 1H), 3.51 (dd, *J* = 18.2, 1.1 Hz, 1H), 3.42 (d, *J* = 18.2 Hz, 1H), 2.22 (s, 3H), 2.21 (s, 3H).^{13}C NMR (126 MHz, DMSO) δ 175.23 , 163.99 , 151.70 , 138.21 , 134.28 , 133.18 , 133.03 , 132.91 , 131.96 , 129.34 , 128.88 , 128.45 , 128.13 , 127.99 , 127.77 , 127.28 , 123.67 , 122.76 , 120.19 , 114.37 , 80.76 , 31.75 , 20.99 , 16.67 .

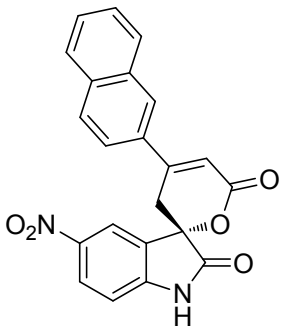
HRMS (ESI+) calcd for $C_{24}H_{19}NaNO_3$, m/z 392.1263, found 392.1261

HPLC: Chiralcel OD-H (n-hexane/i-PrOH, 60/40, flow rate 1 mL/min, λ= 254 nm), t_R(major) = 15.0 min, t_R (minor) = 11.6 min;81% ee.

$[\alpha]_D^{20}$ = +51.2 (*c* = 0.5, acetone)

Melting point：251.2℃~253.2℃

(S)-4'-(naphthalen-2-yl)-5-nitrospiro[indoline-3,2'-pyran]-2,6'(3'H)-dione (3o)



The title compound was prepared according to the typical procedure, as described above, in 87% yield.

^{1}H NMR (500 MHz, DMSO) δ 11.49 (s, 1H), 8.54 (d, *J* = 2.3 Hz, 1H), 8.40 – 8.30 (m,

2H), 8.03 – 7.93 (m, 4H), 7.63 – 7.54 (m, 2H), 7.17 (d, *J* = 8.7 Hz, 1H), 6.89 (s, 1H), 3.81 (dd, *J* = 18.3, 1.6 Hz, 1H), 3.67 – 3.50 (m, 1H).^{13}C NMR (126 MHz, DMSO) δ 175.24 , 163.42 , 151.83 , 148.73 , 143.20 , 134.33 , 133.13 , 132.95 , 129.29 , 129.26 , 128.94 , 128.43 , 128.20 , 128.03 , 127.76 , 127.36 , 123.65 , 121.21 , 114.08 , 111.34 , 79.82 , 30.95

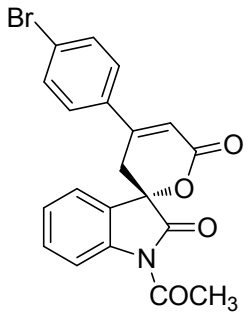
HRMS (ESI+) calcd for $C_{22}H_{14}NaN_2O_5$, m/z 409.0800, found 409.0797

HPLC: Chiralcel AD-H (n-hexane/i-PrOH, 60/40, flow rate 1 mL/min, λ= 254 nm), t_R(major) = 14.1 min, t_R (minor) = 11.7 min; 46% ee.

$[\alpha]_D^{20}$ = +74.4 (*c*= 0.5, acetone)

Melting point：221.1℃~222.6℃

(S)-1-acetyl-4'-(4-bromophenyl)spiro[indoline-3,2'-pyran]-2,6'(3'H)-dione(3P)



The title compound was prepared according to the typical procedure, as described above, in 25% yield.

^{1}H NMR (500 MHz, DMSO) δ 8.18 (d, *J* = 8.2 Hz, 1H), 7.74 (dd, *J* = 11.9, 8.2 Hz, 3H), 7.68 (d, *J* = 8.7 Hz, 2H), 7.54 (dt, *J* = 15.7, 4.0 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 6.73 (s, 1H), 3.59 (d, *J* = 18.5 Hz, 1H), 3.55 (d, *J* = 1.7 Hz, 1H), 2.55 (s, 3H).^{13}C NMR (126 MHz, DMSO) δ 174.16 , 170.84 , 163.27 , 150.87 , 140.12 , 135.13 , 132.33 , 131.59 , 129.13 , 127.37 , 126.21 , 125.12 , 124.94 , 116.60 , 114.44 , 80.22 , 32.14 , 26.67 .

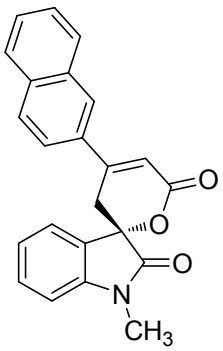
HRMS (ESI+) calcd for $C_{20}H_{14}BrNaNO_4$, m/z 434.0004, found 433.9999

HPLC: Chiralcel AD-H (n-hexane/i-PrOH, 60/40, flow rate 1 mL/min, λ= 254 nm), t_R(major) = 23.1 min, t_R (minor) = 43.0 min; 40% ee.

$[\alpha]_D^{20}$ = -2.7 (*c*= 0.5, acetone)

Melting point：187.2℃-188.6℃

(S)-1-methyl-4'-(naphthalen-2-yl)spiro[indoline-3,2'-pyran]-2,6'(3'H)-dione (3q)



The title compound was prepared according to the typical procedure, as described above, in 80% yield.

^{1}H NMR (500 MHz, DMSO) δ 8.34 (s, 1H), 8.04 – 7.92 (m, 4H), 7.69 – 7.53 (m, 3H), 7.51 – 7.41 (m, 1H), 7.14 (t, *J* = 7.4 Hz, 2H), 6.86 (s, 1H), 3.59 (dd, *J* = 18.2, 1.6 Hz, 1H), 3.46 (d, *J* = 0.8 Hz, 1H), 3.17 (s, 3H).^{13}C NMR (126 MHz, DMSO) δ 173.03 , 163.85 , 151.95 , 143.70 , 134.30 , 133.14 , 133.05 , 131.51 , 129.30 , 128.89 , 128.16 , 128.01 , 127.98 , 127.74 , 127.32 , 124.69 , 123.69 , 123.59 , 114.34 , 109.94 , 80.10 , 31.58 , 26.72 .

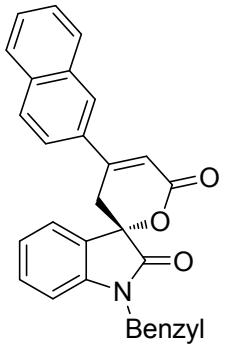
HRMS (ESI+) calcd for $C_{23}H_{18}NO_3$, m/z 356.1287, found 356.1285

HPLC: Chiralcel AD-H (n-hexane/i-PrOH, 60/40, flow rate 1 mL/min, λ= 254 nm), t_R(major) = 18.0 min, t_R (minor) = 15.1 min; 29% ee.

$[\alpha]_D^{20}$ = +10.4 (*c*= 0.5, acetone)

Melting point：204.6℃-206.1℃

(S)-1-benzyl-4'-(naphthalen-2-yl)spiro[indoline-3,2'-pyran]-2,6'(3'H)-dione (3r)



The title compound was prepared according to the typical procedure, as described above, in 87% yield.

^{1}H NMR (500 MHz, DMSO) δ 8.39 (s, 1H), 8.06 – 7.94 (m, 4H), 7.67 (d, *J* = 7.3 Hz, 1H), 7.59 (pd, *J* = 6.8, 1.4 Hz, 2H), 7.43 – 7.33 (m, 5H), 7.33 – 7.25 (m, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 7.9 Hz, 1H), 6.91 (s, 1H), 4.98 (d, *J* = 15.9 Hz, 1H), 4.92 (d, *J* = 15.9 Hz, 1H), 3.68 (dd, *J* = 18.2, 1.3 Hz, 1H), 3.56 (d, *J* = 18.4 Hz, 1H).

^{13}C NMR (126 MHz, DMSO) δ 173.27 , 163.77 , 152.07 , 142.70 , 136.15 , 134.34 , 133.16 , 133.03 , 131.46 , 129.35 , 129.25 , 128.92 , 128.19 , 128.07 , 128.03 , 127.84 , 127.71 , 127.33 , 124.96 , 123.80 , 123.71 , 114.36 , 110.60 , 80.16 , 43.46 , 31.62 .

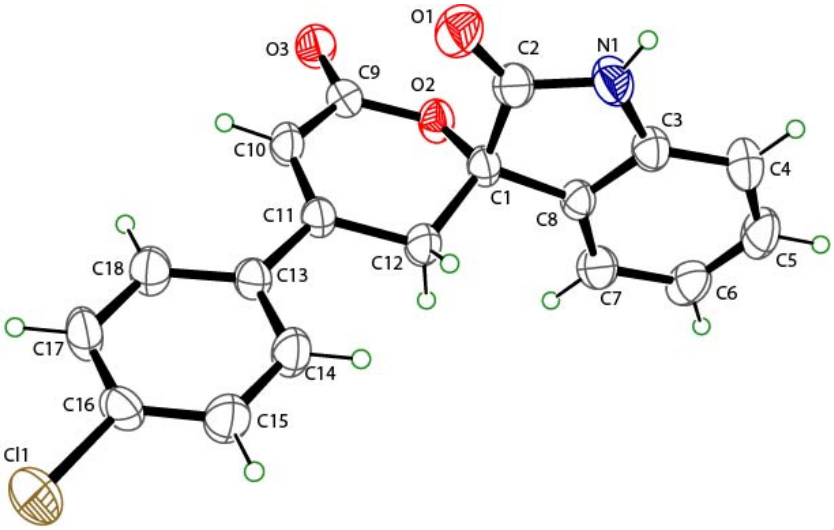
HRMS (ESI+) calcd for $C_{29}H_{22}NO_3$, m/z 432.1600, found 432.1596

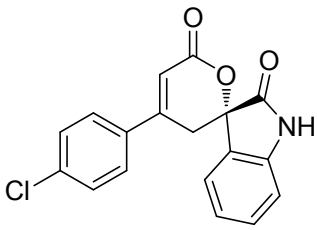
HPLC: Chiralcel AD-H (n-hexane/i-PrOH, 60/40, flow rate 1 mL/min, λ= 254 nm), t_R(major) = 27.9 min, t_R (minor) = 22.2 min; 11% ee.

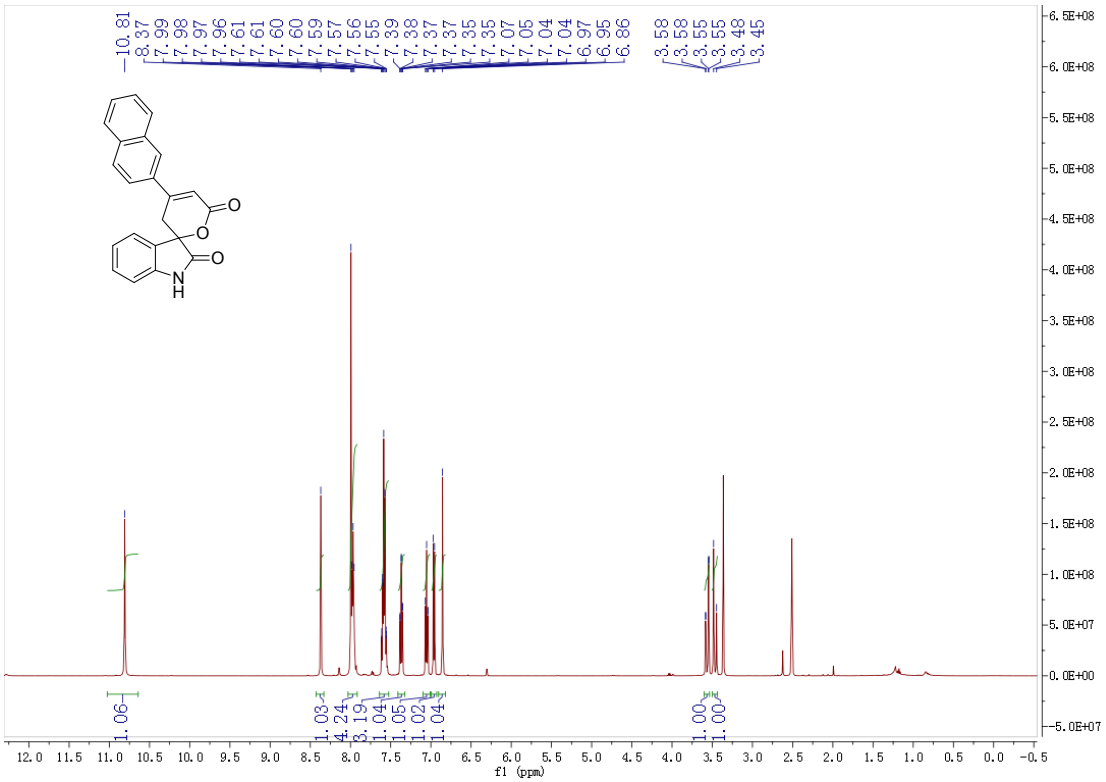
$[\alpha]_D^{20}$ = +3.6 (*c*= 0.5, acetone)

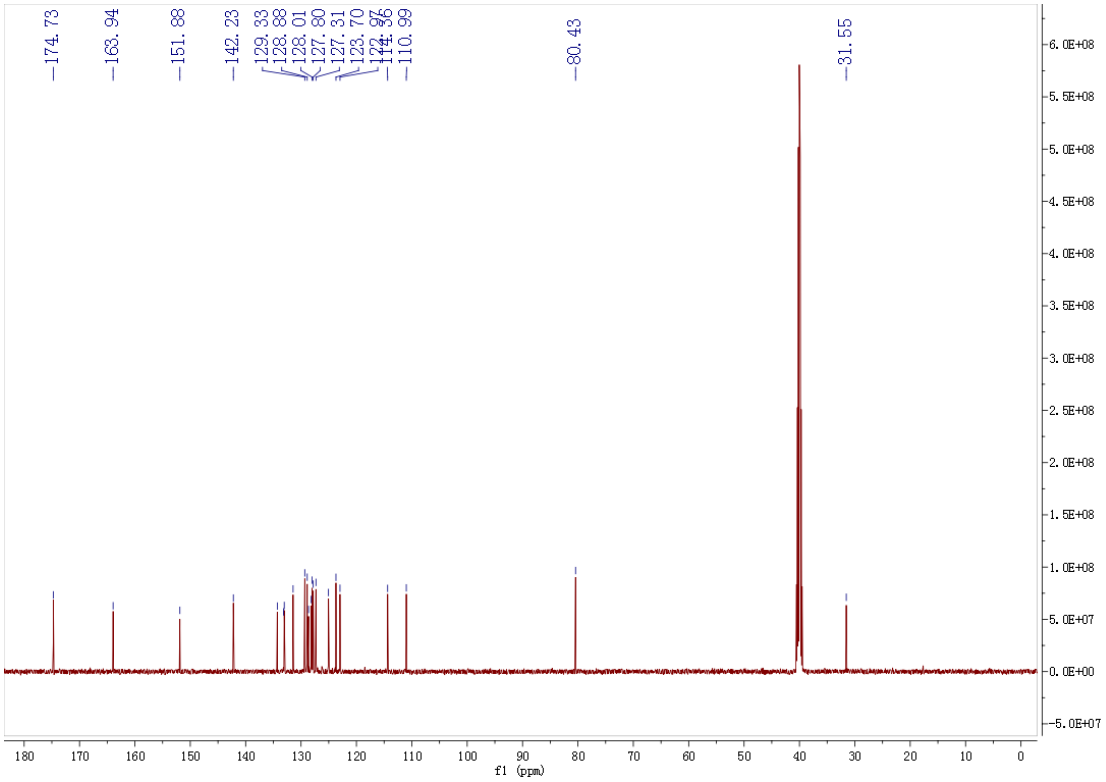
Melting point：173.1℃-174.3℃

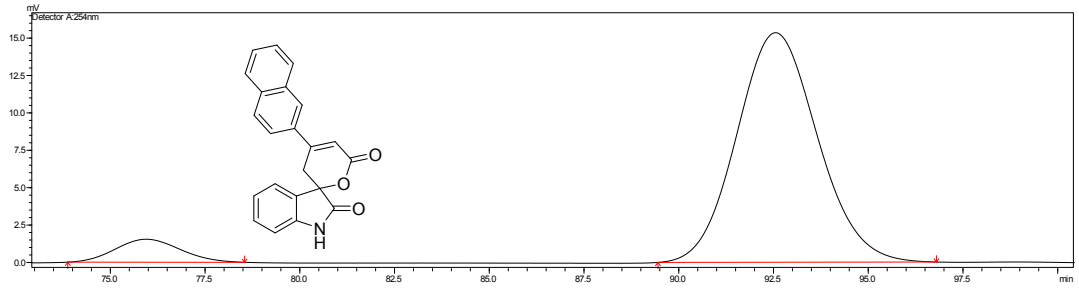
X-ray crystal structure of 3d



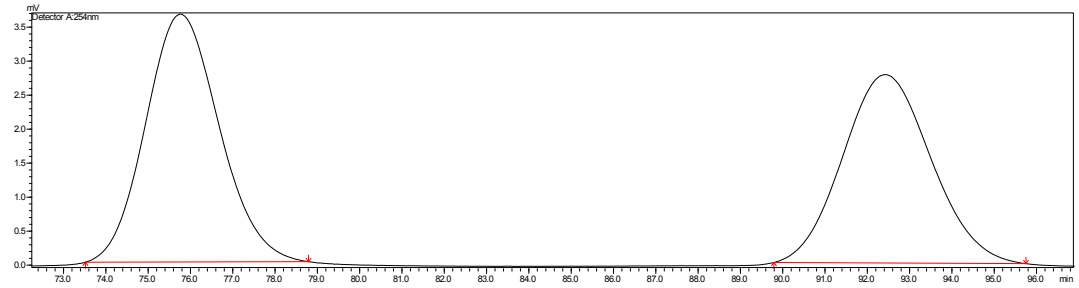



10.81
8.37
7.99
7.98
7.97
7.96
7.61
7.61
7.60
7.60
7.59
7.57
7.56
7.55
7.39
7.38
7.37
7.37
7.35
7.35
7.07
7.05
7.04
7.04
6.97
6.95
6.86
3.58
3.58
3.55
3.55
3.48
3.45
O
O
O
N
H
1.06
1.03
4.24
3.19
1.04
1.05
1.02
1.04
1.00
1.00
f1 (ppm)


174.73
163.94
151.88
142.23
129.33
128.88
128.01
127.80
127.31
123.70
122.97
114.36
110.99
80.43
31.55
f1 (ppm)



Peak	Ret .Time	Area	Height	Area%	Height%
1	75.952	183015	1537	7.447	9.102
2	92.547	2274618	15348	92.553	90.898
Total		2457633	16885	100.000	100.000



Peak	Ret .Time	Area	Height	Area%	Height%
1	75.760	440744	3646	52.280	56.817
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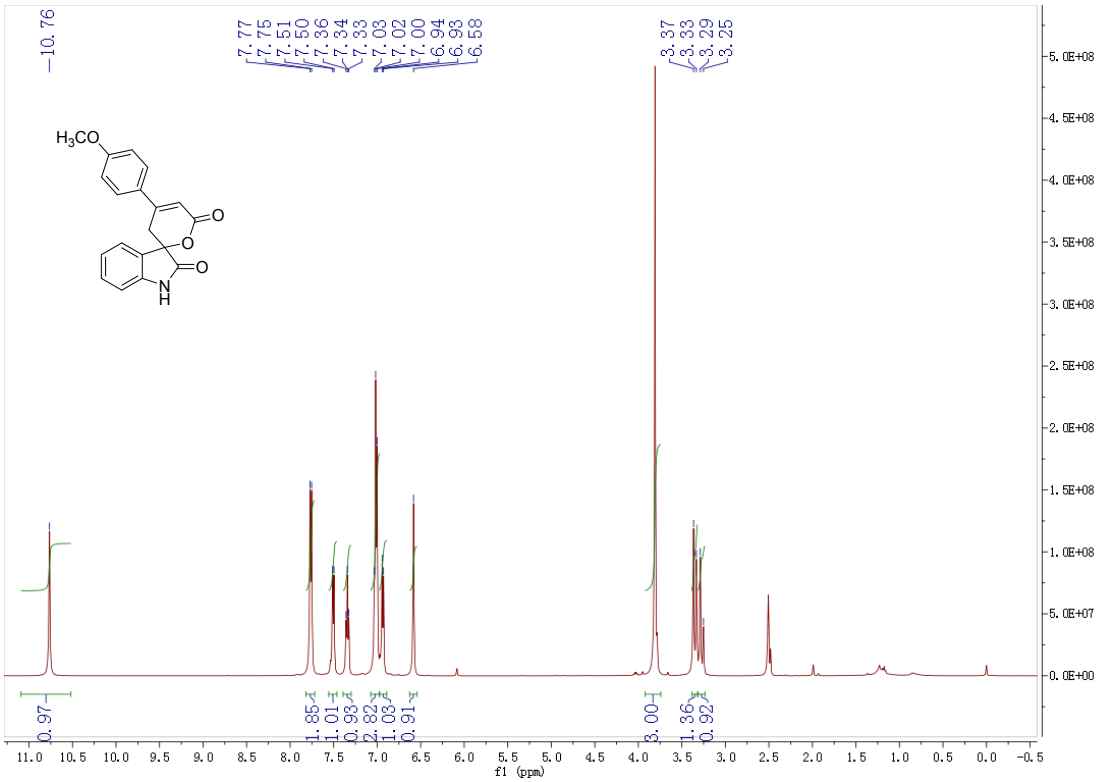
Total		843045	6417	100.000	100.000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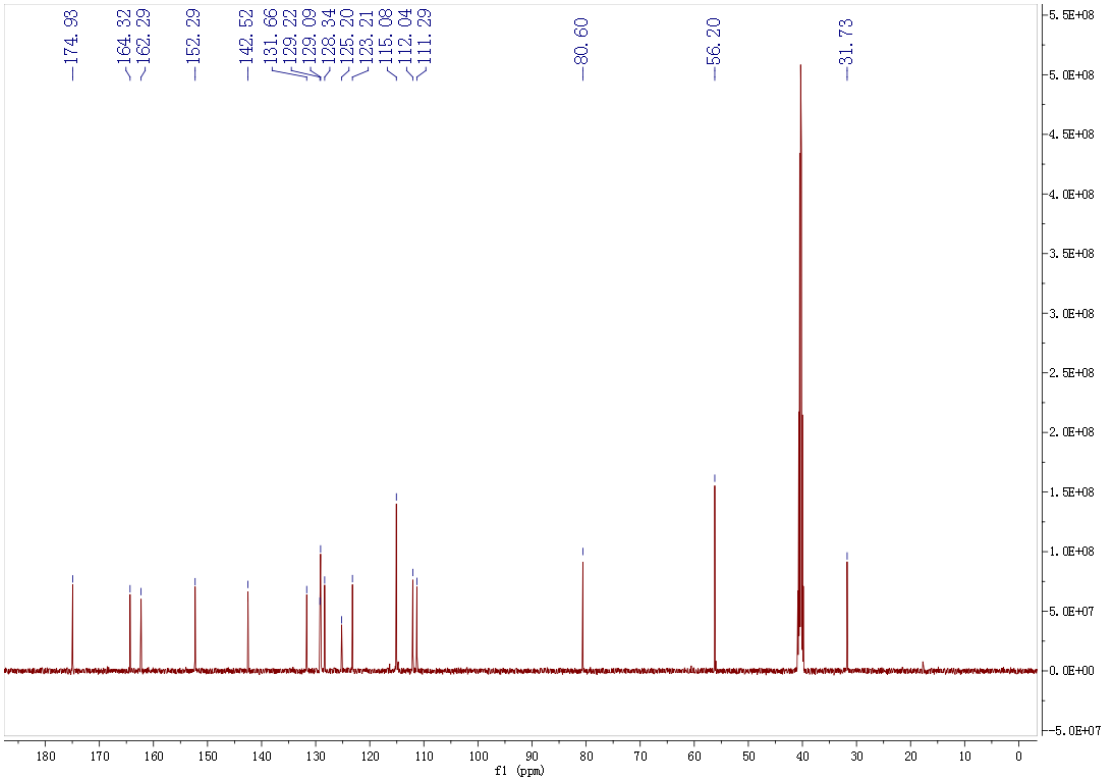
7.77
7.75
7.51
7.50
7.36
7.34
7.33
7.03
7.02
7.00
6.94
6.93
6.58
3.37
3.33
3.29
3.25
H3CO
O
O
O
N
H
0.97
1.85
1.01
0.93
2.82
1.03
0.91
3.00
1.36
0.92
f1 (ppm)


174.93
164.32
162.29
152.29
142.52
131.66
129.22
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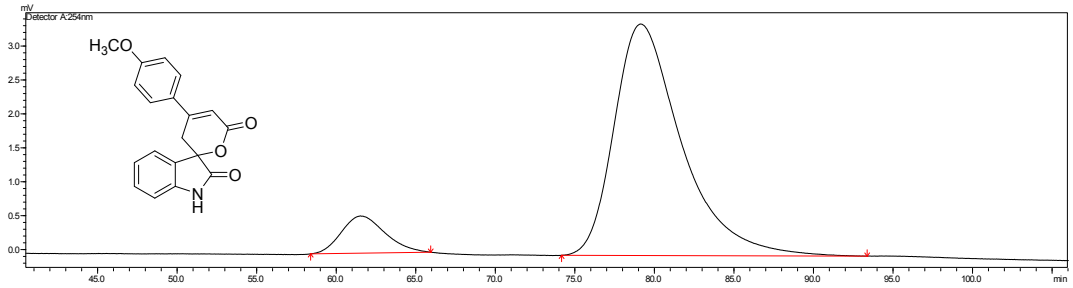
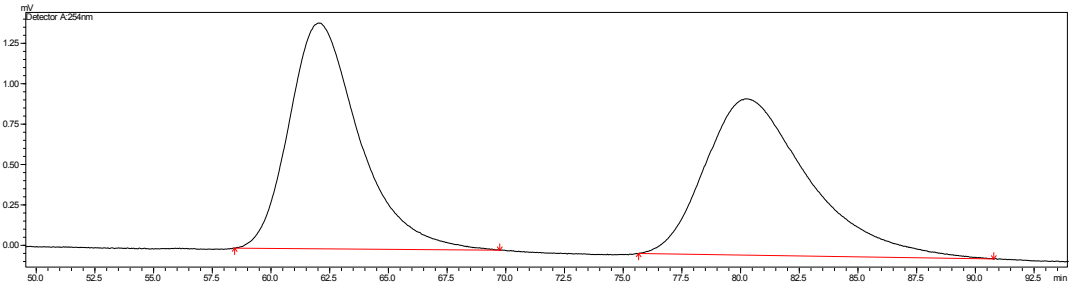
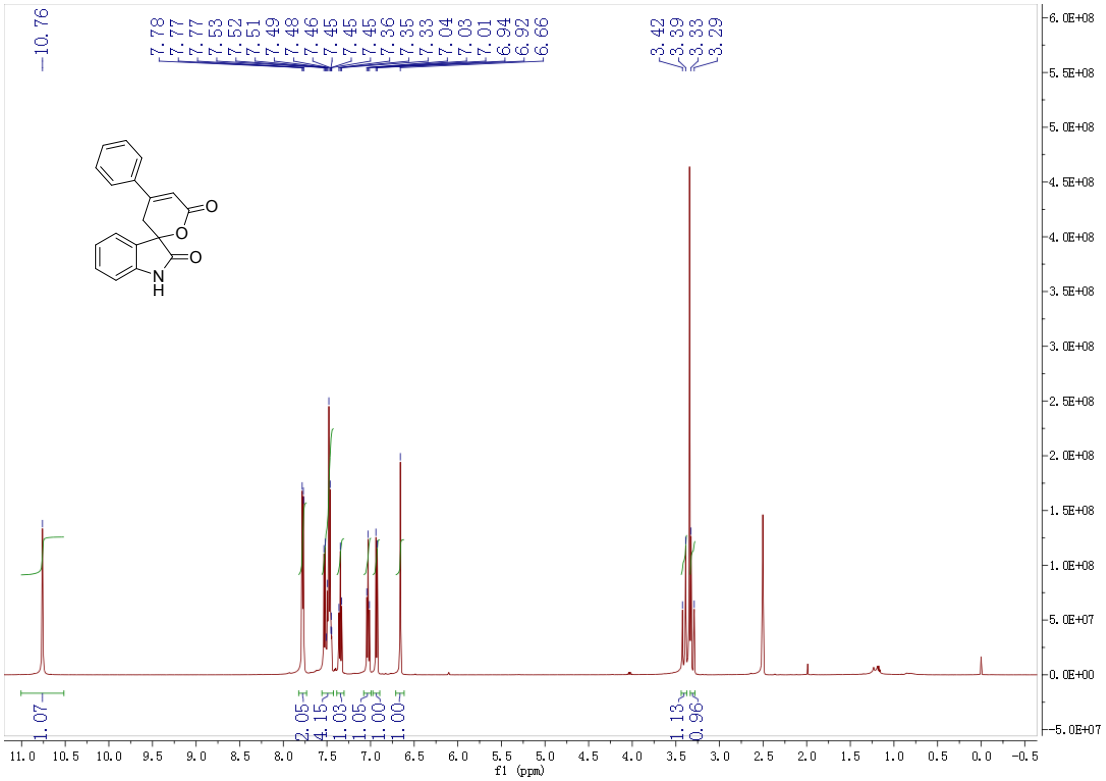
128.34
125.20
123.21
115.08
112.04
111.29
80.60
56.20
31.73
f1 (ppm)



Peak	Ret .Time	Area	Height	Area%	Height%
1	61.520	104499	550	9.415	13.879
2	79.114	1005396	3412	90.585	86.121
Total		1109895	3962	100.000	100.000



Peak	Ret .Time	Area	Height	Area%	Height%
1	62.035	291094	1398	49.479	59.093
2	80.238	297224	968	50.521	40.907
Total		588317	2366	100.000	100.000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7.78
7.77
7.77
7.53
7.52
7.51
7.49
7.48
7.46
7.45
7.45
7.45
7.36
7.35
7.33
7.04
7.03
7.01
6.94
6.92
6.66
3.42
3.39
3.33
3.29
O
O
O
N
H
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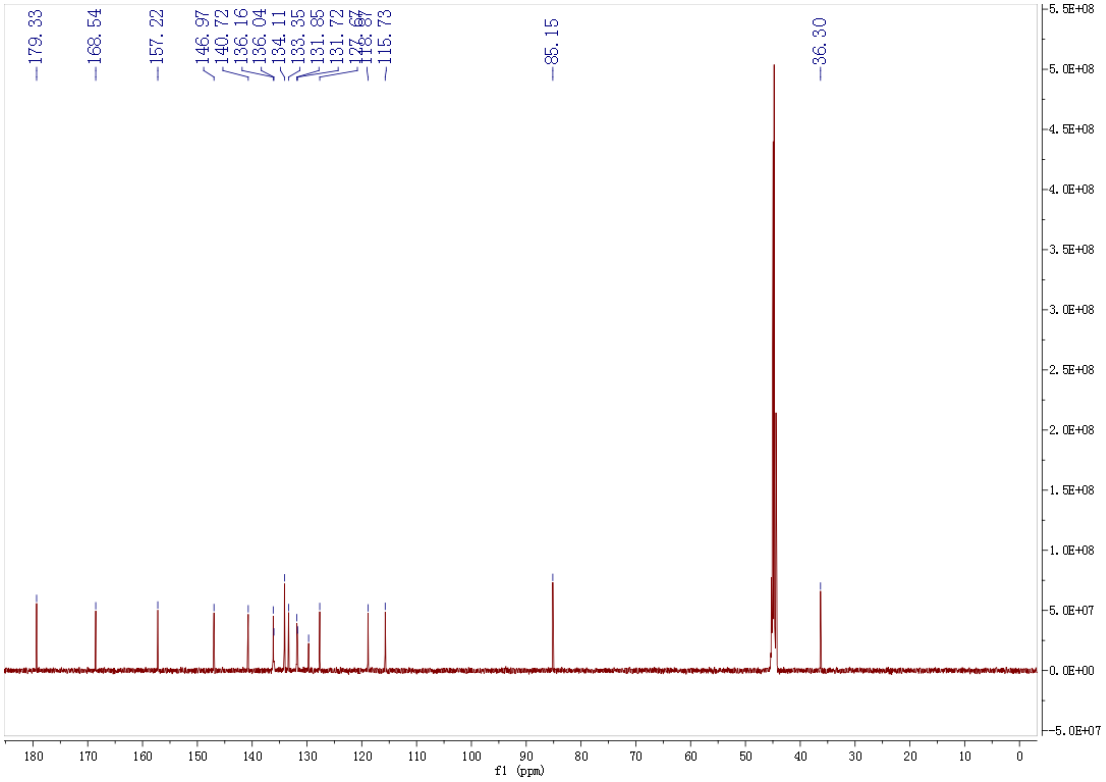
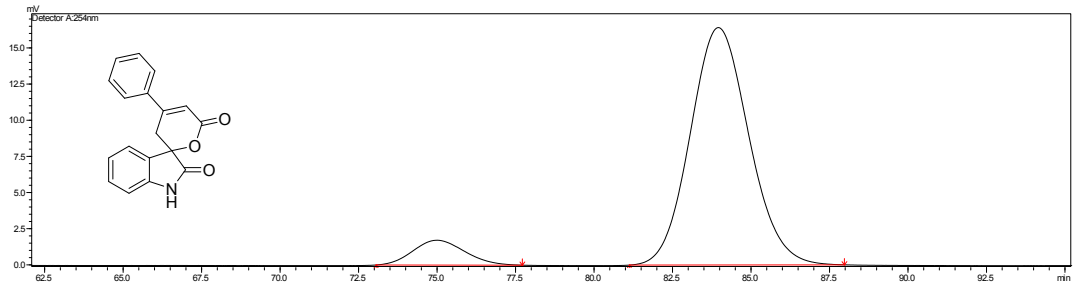
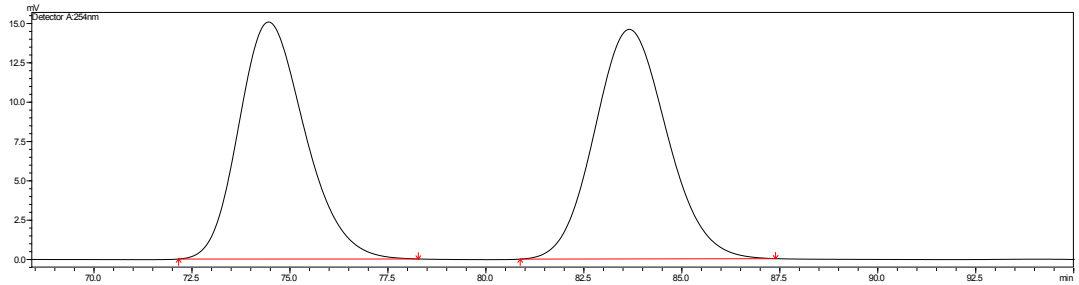
1.00
1.00
1.13
0.96
f1 (ppm)

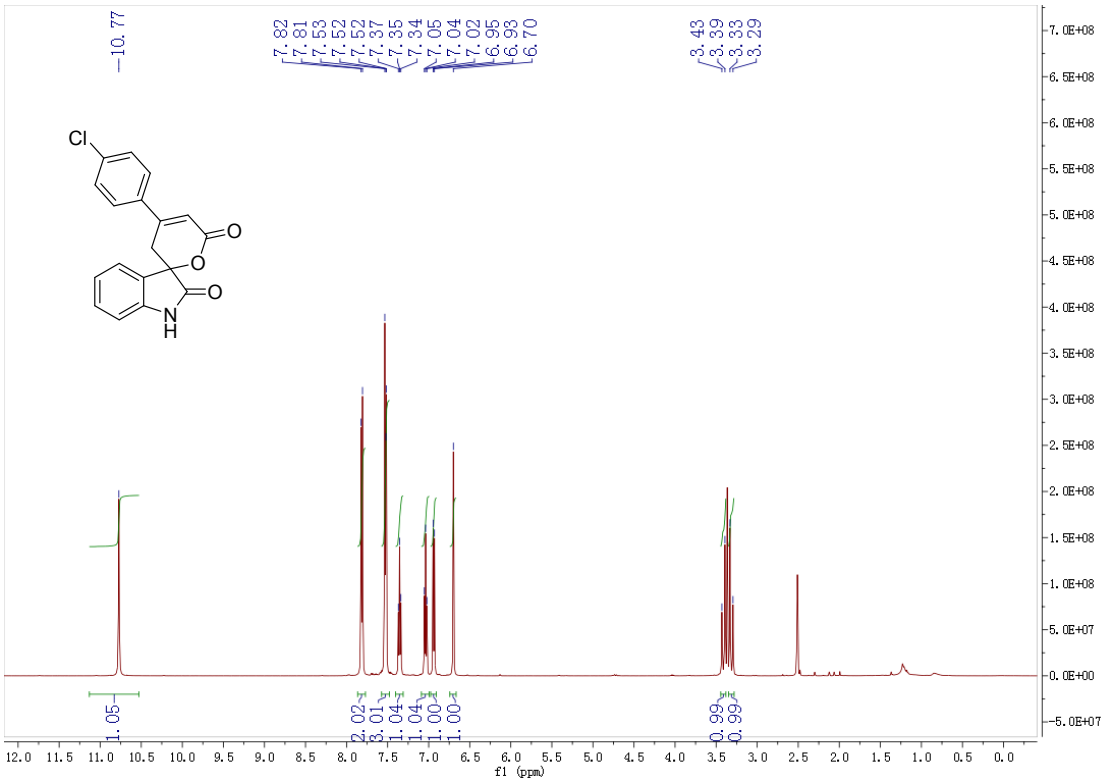

179.33
168.54
157.22
146.97
140.72
136.16
136.04
134.11
133.35
131.85
131.72
115.73
85.15
36.30
f1 (ppm)



Peak	Ret .Time	Area	Height	Area%	Height%
1	75.004	196194	1717	8.432	9.469
2	83.955	2130582	16416	91.568	90.531
Total		2326776	18133	100.000	100.000



Peak	Ret .Time	Area	Height	Area%	Height%
1	74.453	1772762	15063	48.534	50.797
2	83.654	1879869	14590	51.466	49.203
Total		3652631	29653	100.000	100.000


10.77
7.82
7.81
7.53
7.52
7.52
7.37
7.35
7.34
7.05
7.04
7.02
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6.93
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3.29
Cl
O
O
O
N
H
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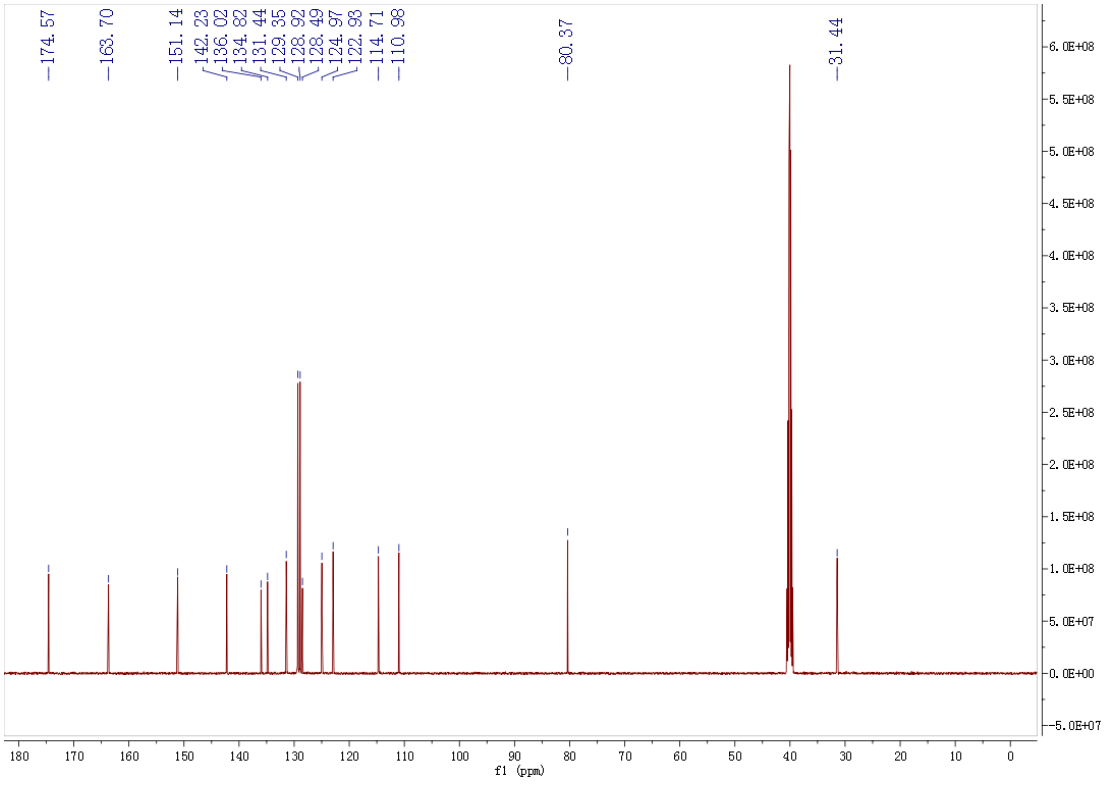
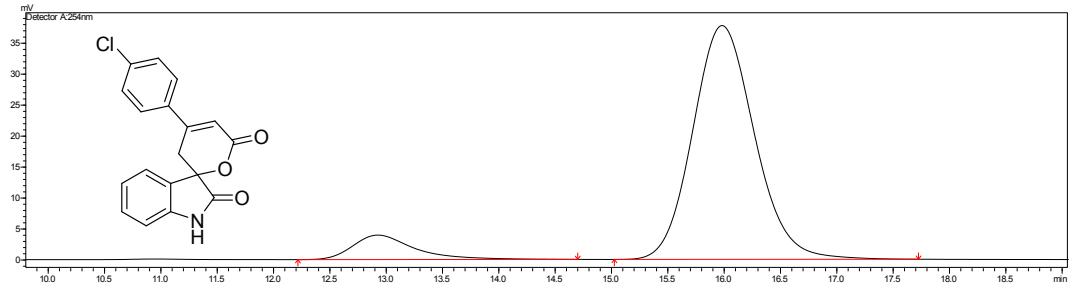
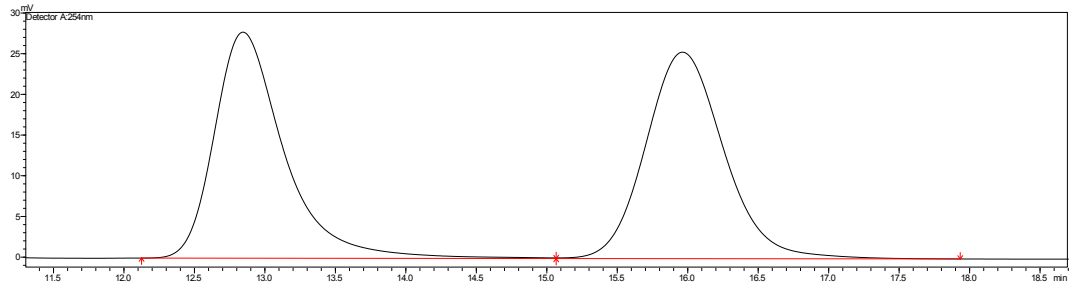
2.02
3.01
1.04
1.04
1.00
1.00
0.99
0.99
f1 (ppm)

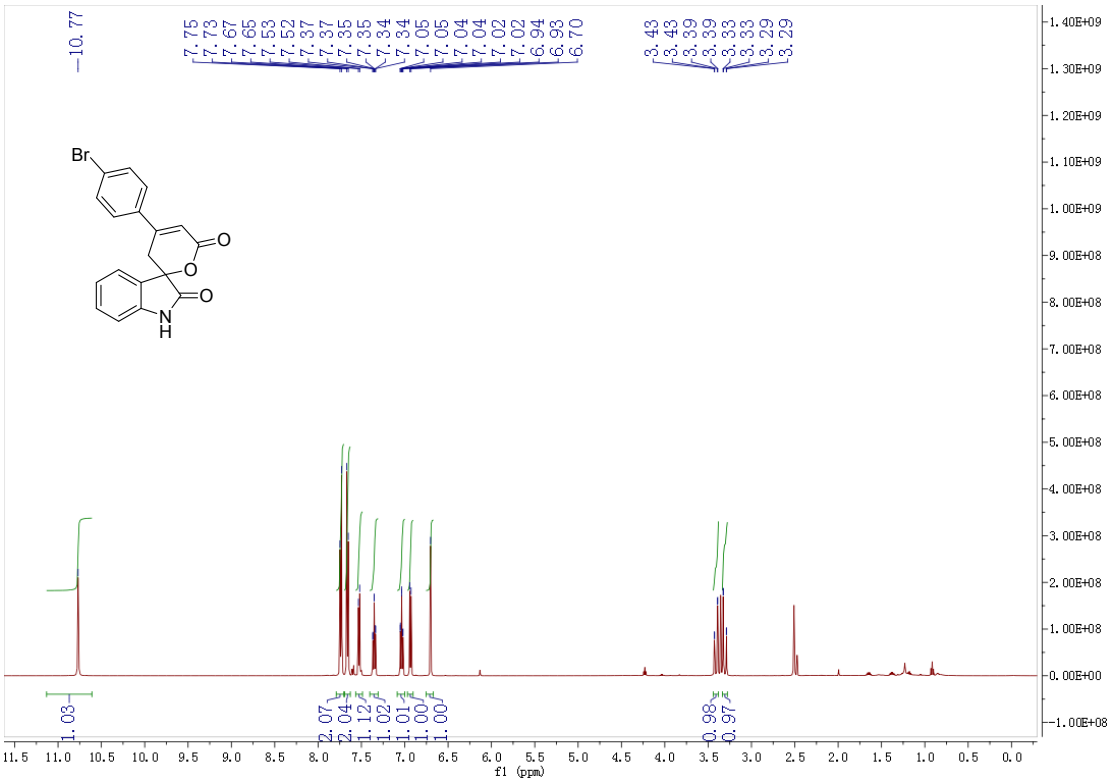

174.57
163.70
151.14
142.23
136.02
134.82
131.44
129.35
128.92
128.49
124.97
122.93
114.71
110.98
80.37
31.44
f1 (ppm)

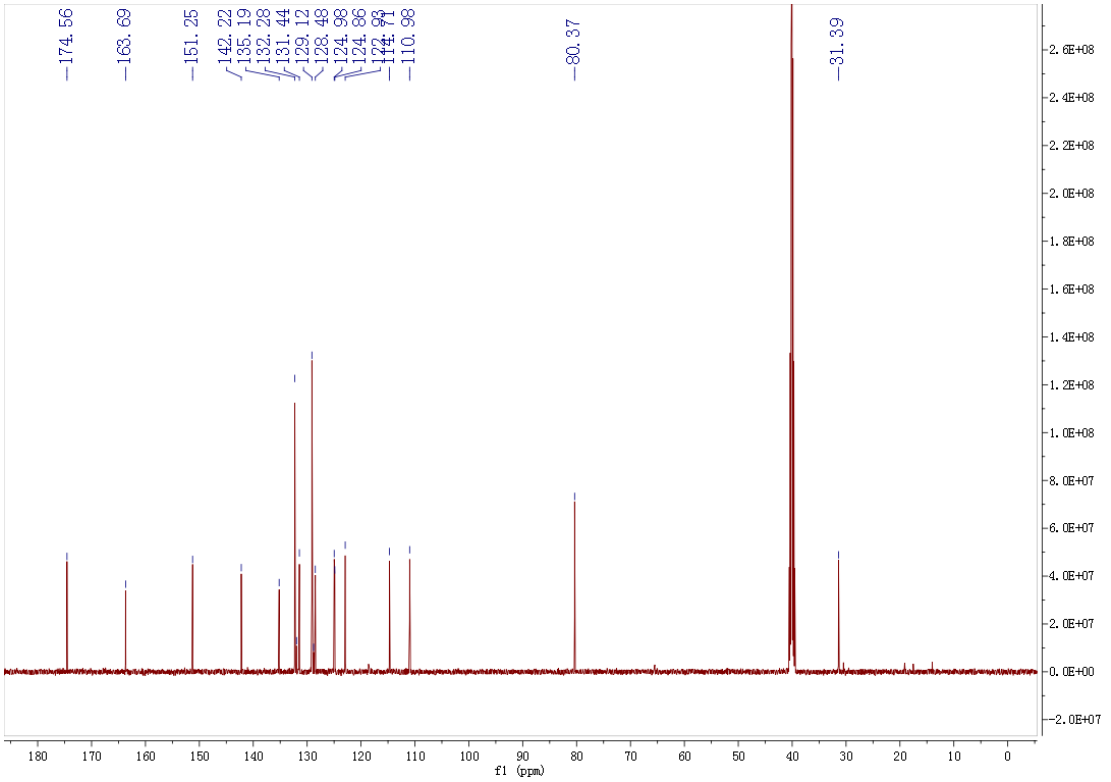


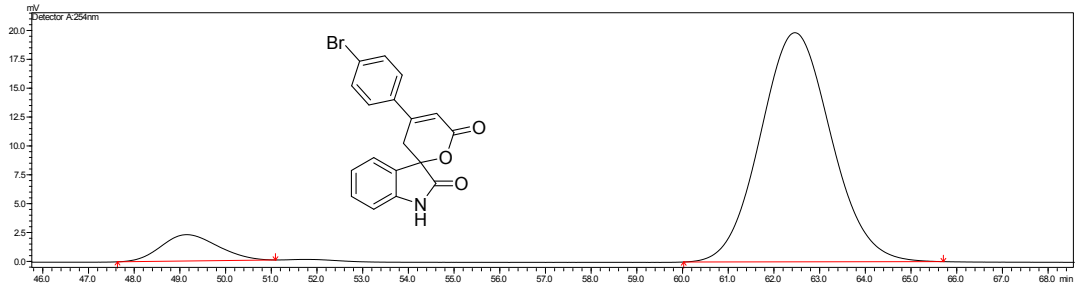
Peak	Ret .Time	Area	Height	Area%	Height%
1	12.922	149844	3948	9.436	9.468
2	15.977	1438234	37755	90.564	90.532
Total		1588079	41704	100.000	100.000



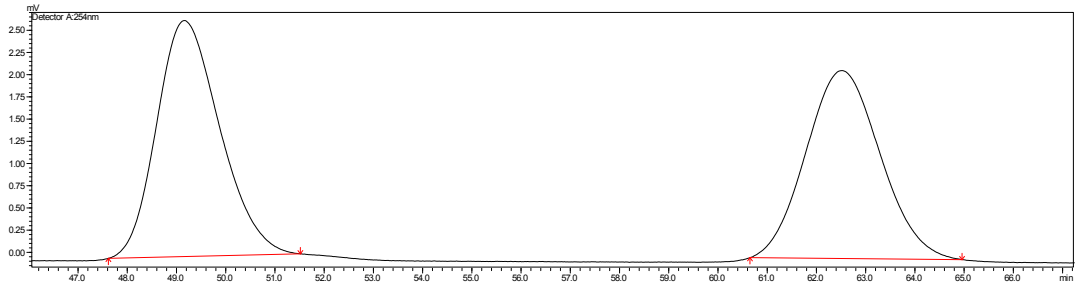
Peak	Ret .Time	Area	Height	Area%	Height%
1	12.840	954671	27773	49.395	52.258
2	15.959	978067	25373	50.605	47.742
Total		1932738	53146	100.000	100.000


10.77
7.75
7.73
7.67
7.65
7.53
7.52
7.37
7.37
7.35
7.35
7.34
7.34
7.05
7.04
7.04
7.02
7.02
6.94
6.93
6.70
3.43
3.43
3.39
3.39
3.33
3.33
3.29
3.29
Br
O
O
O
N
H
1.03
2.07
2.04
1.12
1.02
1.01
1.00
1.00
0.98
0.97
f1 (ppm)

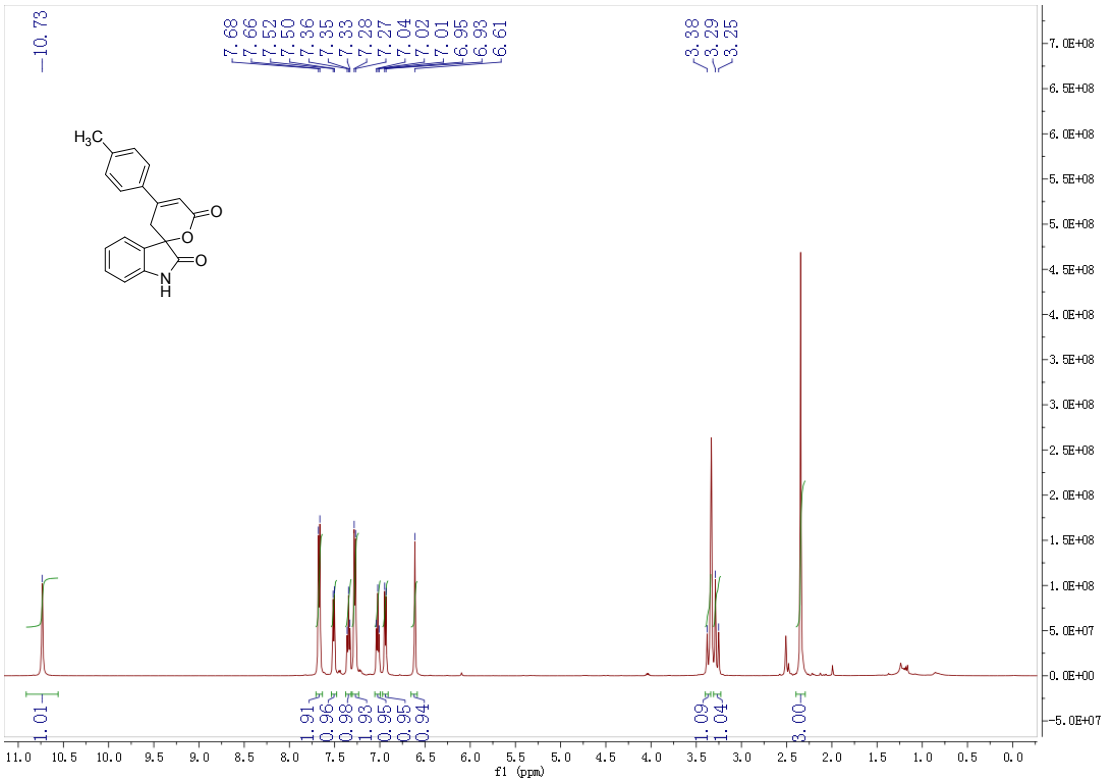

174.56
163.69
151.25
142.22
135.19
132.28
131.44
129.12
128.48
124.98
124.86
122.93
110.98
80.37
31.39
f1 (ppm)

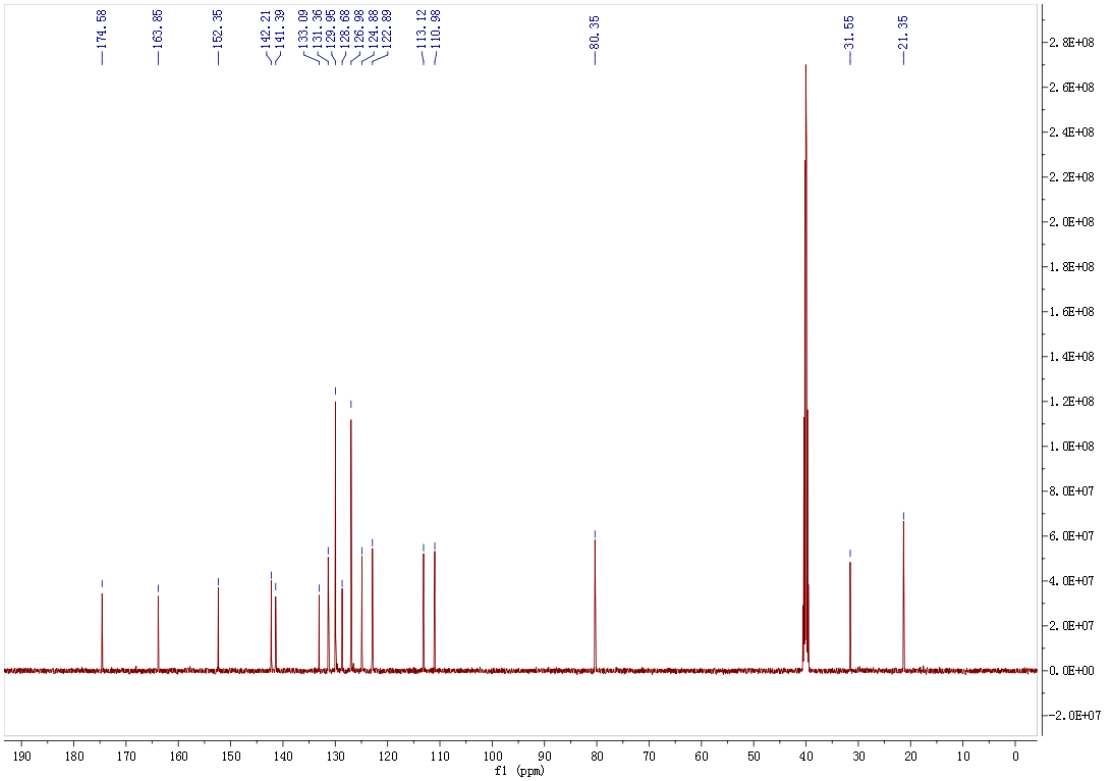


Peak	Ret .Time	Area	Height	Area%	Height%
1	49.143	195879	2281	8.398	10.309
2	62.454	2136480	19845	91.602	89.691
Total		2332359	22126	100.000	100.000



Peak	Ret .Time	Area	Height	Area%	Height%
1	49.158	236781	2657	51.602	55.674
2	62.519	222077	2115	48.398	44.326
Total		458858	4772	100.000	100.000


10.73
7.68
7.66
7.52
7.50
7.36
7.35
7.33
7.28
7.27
7.04
7.02
7.01
6.95
6.93
6.61
3.38
3.29
3.25
H3C
O
O
O
N
H
1.01
1.91
0.96
0.98
1.93
0.95
0.95
0.94
1.09
1.04
3.00
f1 (ppm)


174.58
163.85
152.35
142.21
141.39
133.09
131.36
129.96
128.68
126.98
124.88
122.89
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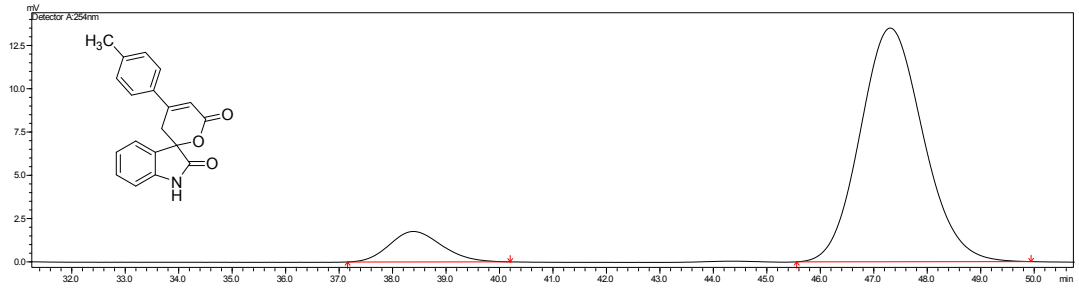
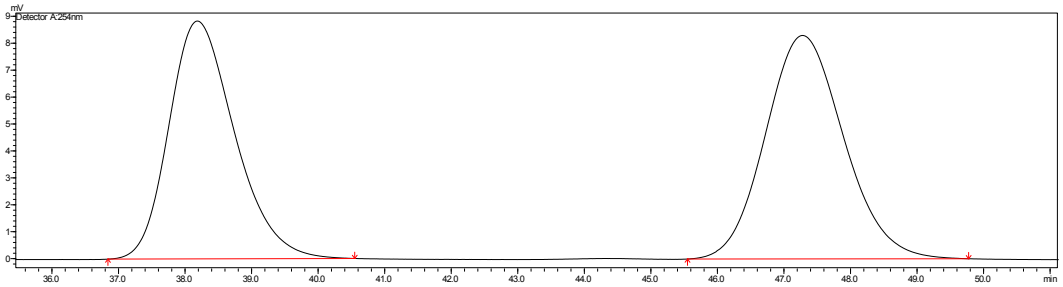
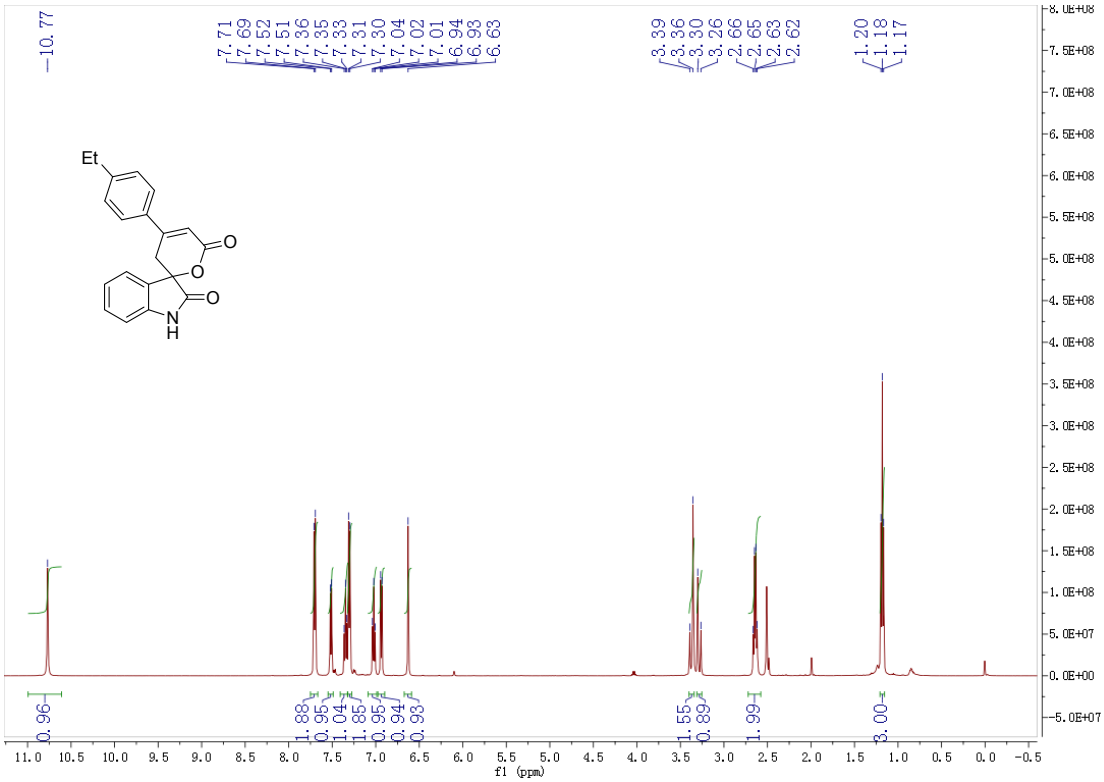
110.98
80.35
31.55
21.35
f1 (ppm)



Peak	Ret .Time	Area	Height	Area%	Height%
1	38.392	120089	1758	9.813	11.524
2	47.302	1103719	13497	90.187	88.476
Total		1223808	15255	100.000	100.000



Peak	Ret .Time	Area	Height	Area%	Height%
1	38.182	605766	8831	47.135	51.555
2	47.274	679396	8298	52.865	48.445
Total		1285162	17129	100.000	100.000


10.77
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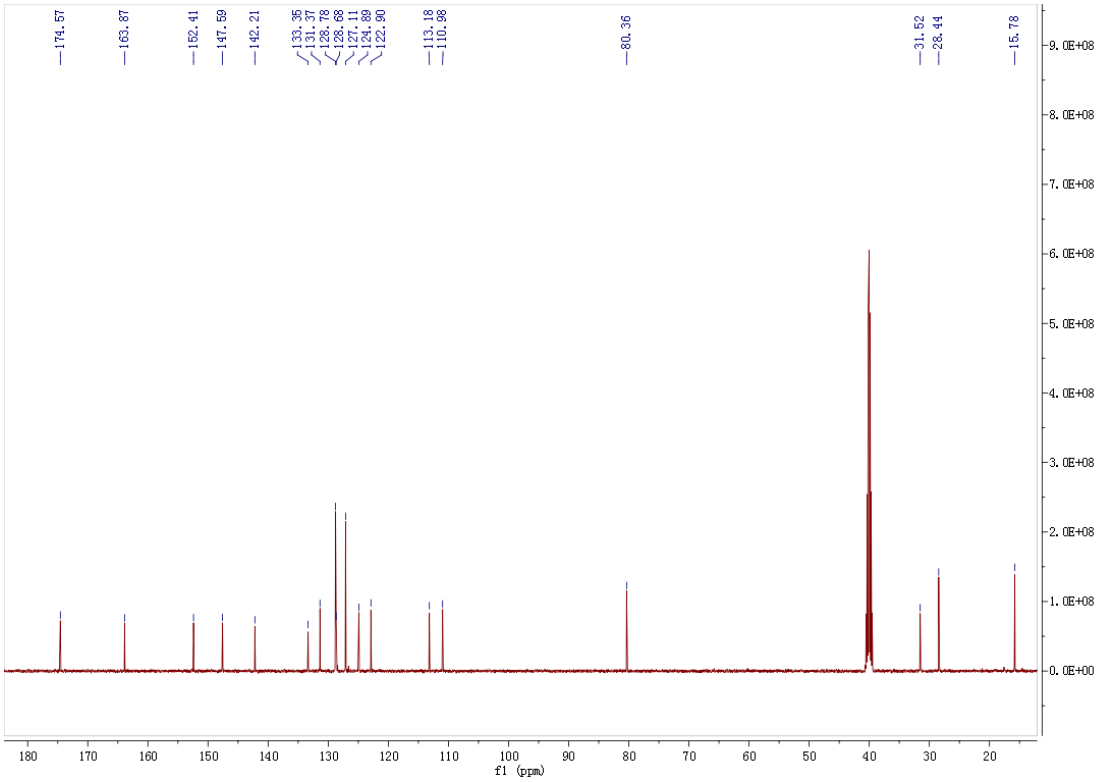
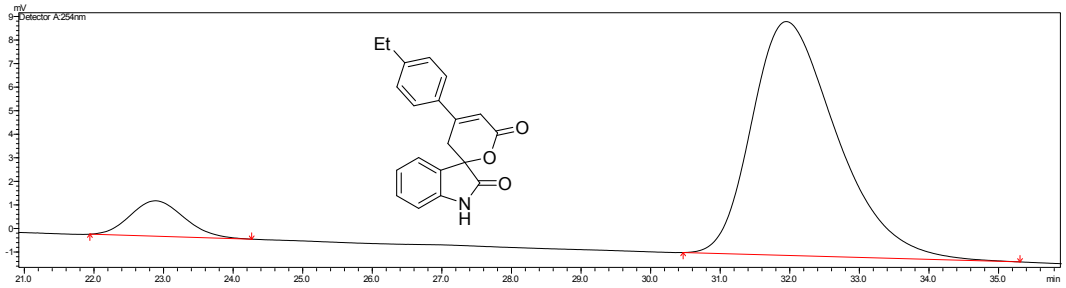
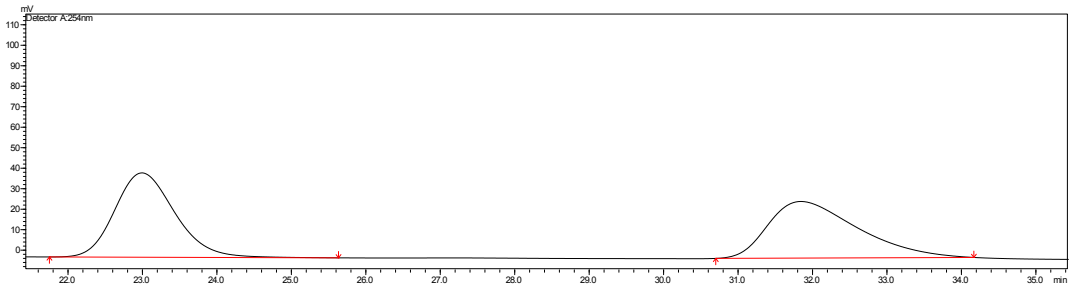
7.52
7.51
7.36
7.35
7.33
7.31
7.30
7.04
7.02
7.01
6.94
6.93
6.63
3.39
3.36
3.30
3.26
2.66
2.65
2.63
2.62
1.20
1.18
1.17
Et
O
O
O
N
H
0.96
1.88
0.95
1.04
1.85
0.95
0.94
0.93
1.55
0.89
1.99
3.00
f1 (ppm)

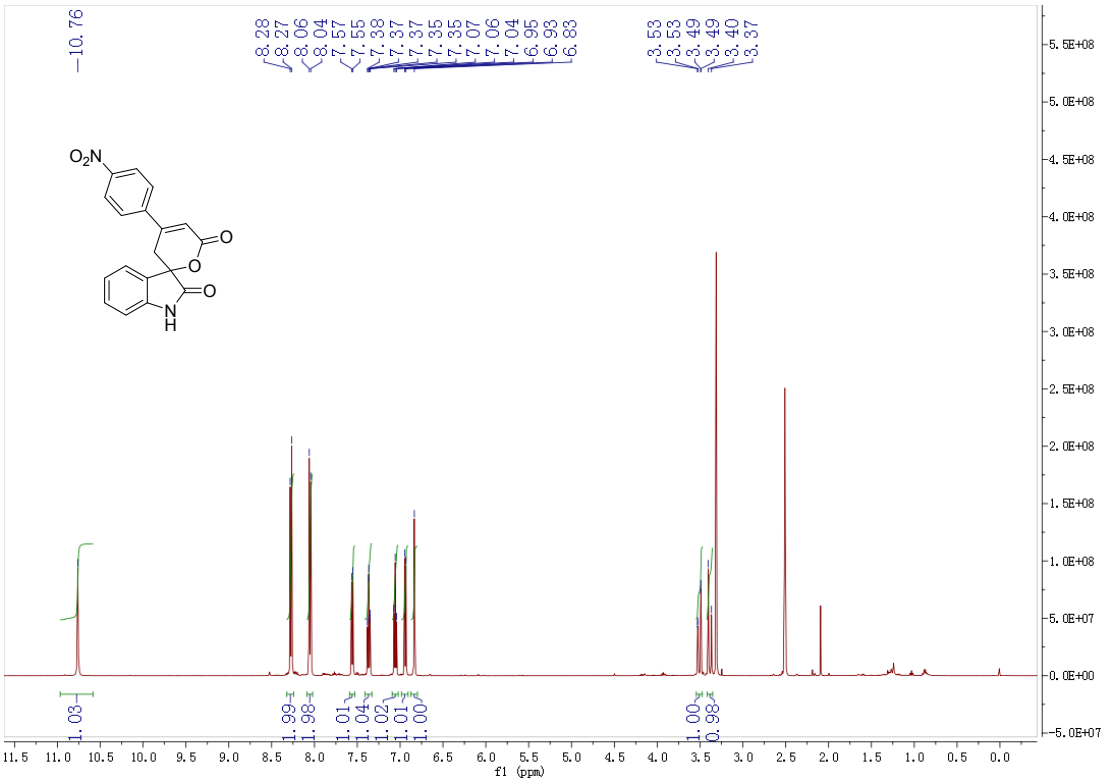

174.57
163.87
152.41
147.59
142.21
133.35
131.37
128.78
128.68
127.11
124.89
122.90
113.18
110.98
80.36
31.52
28.44
15.78
f1 (ppm)



Peak	Ret .Time	Area	Height	Area%	Height%
1	22.881	80912	1503	8.774	13.155
2	31.945	841322	9924	91.226	86.846
Total		922235	11428	100.000	100.000



Peak	Ret .Time	Area	Height	Area%	Height%
1	22.989	2310582	41151	50.040	59.836
2	31.840	2306876	27623	49.960	40.164
Total		4617457	68774	100.000	100.000


10.76
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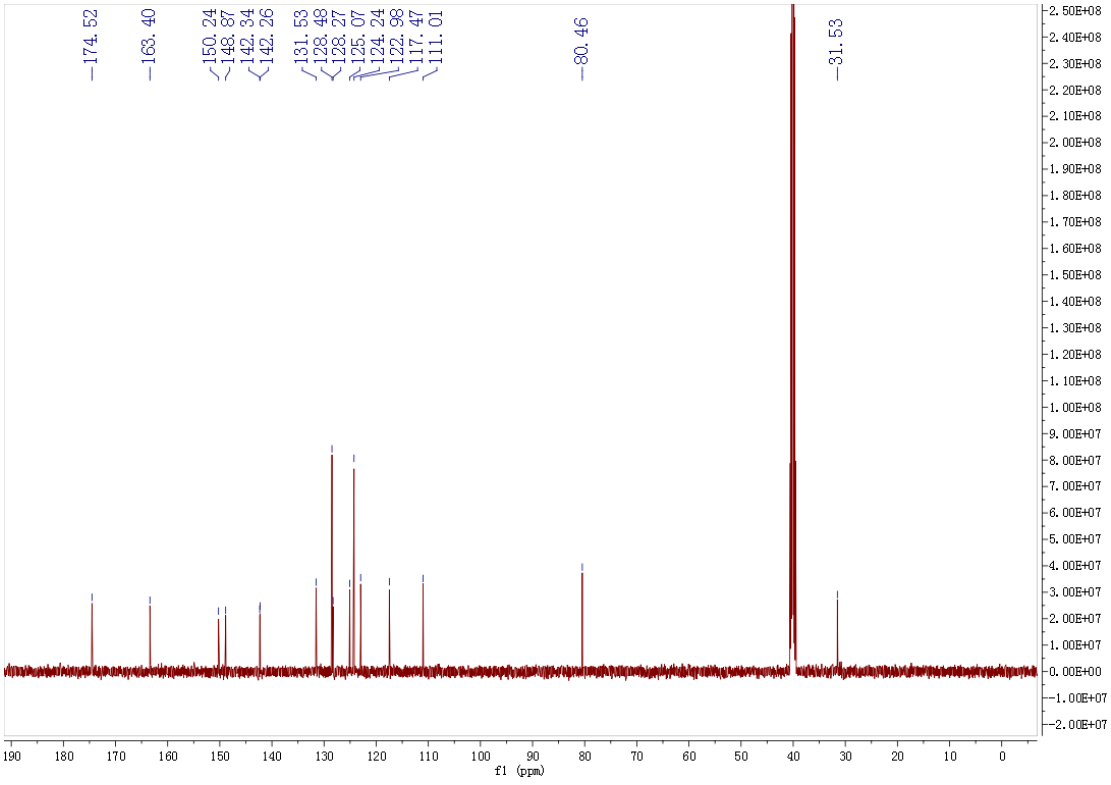
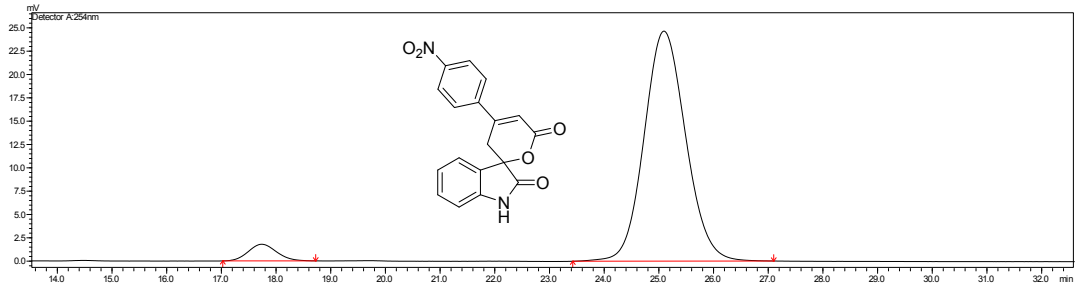
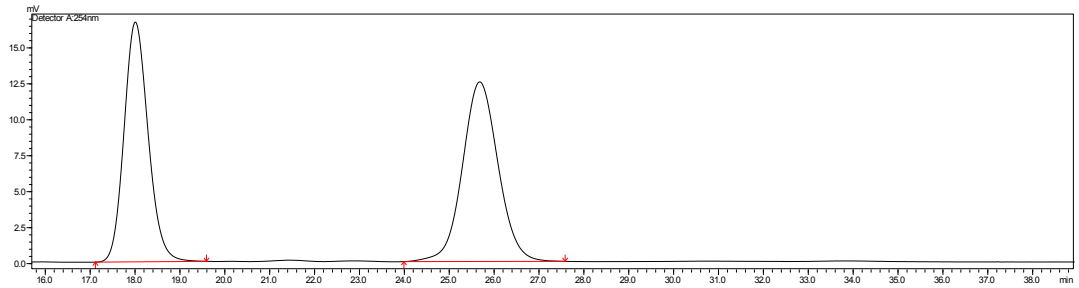
8.27
8.06
8.04
7.57
7.55
7.38
7.37
7.37
7.35
7.35
7.07
7.06
7.04
6.95
6.93
6.83
3.53
3.53
3.49
3.49
3.40
3.37
O2N
O
O
O
N
H
1.03
1.99
1.98
1.01
1.04
1.02
1.01
1.00
1.00
0.98
f1 (ppm)

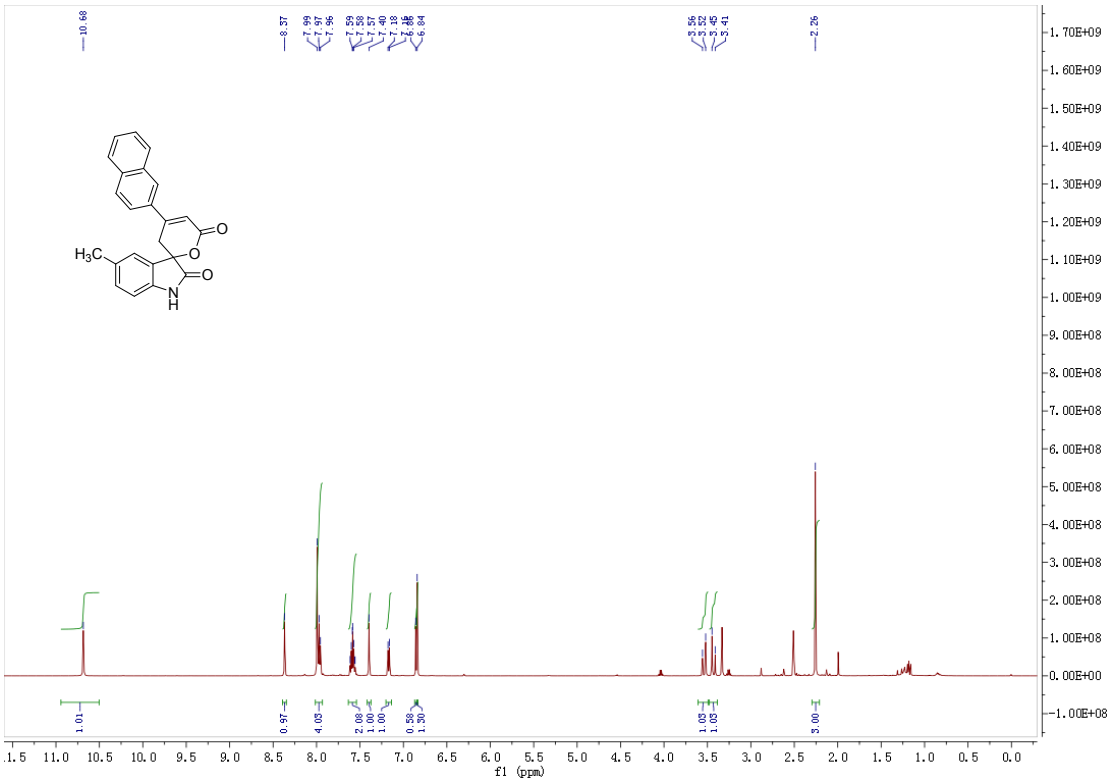

174.52
163.40
150.24
148.87
142.34
142.26
131.53
128.48
128.27
125.07
124.24
122.98
117.47
111.01
80.46
31.53
f1 (ppm)



Peak	Ret .Time	Area	Height	Area%	Height%
1	17.733	64251	1782	4.702	6.743
2	25.089	1302225	24650	95.298	93.257
Total		1366477	26432	100.000	100.000



Peak	Ret .Time	Area	Height	Area%	Height%
1	18.003	622253	16672	47.440	57.181
2	25.677	689419	12485	52.560	42.819
Total		1311672	29157	100.000	100.000


10.68
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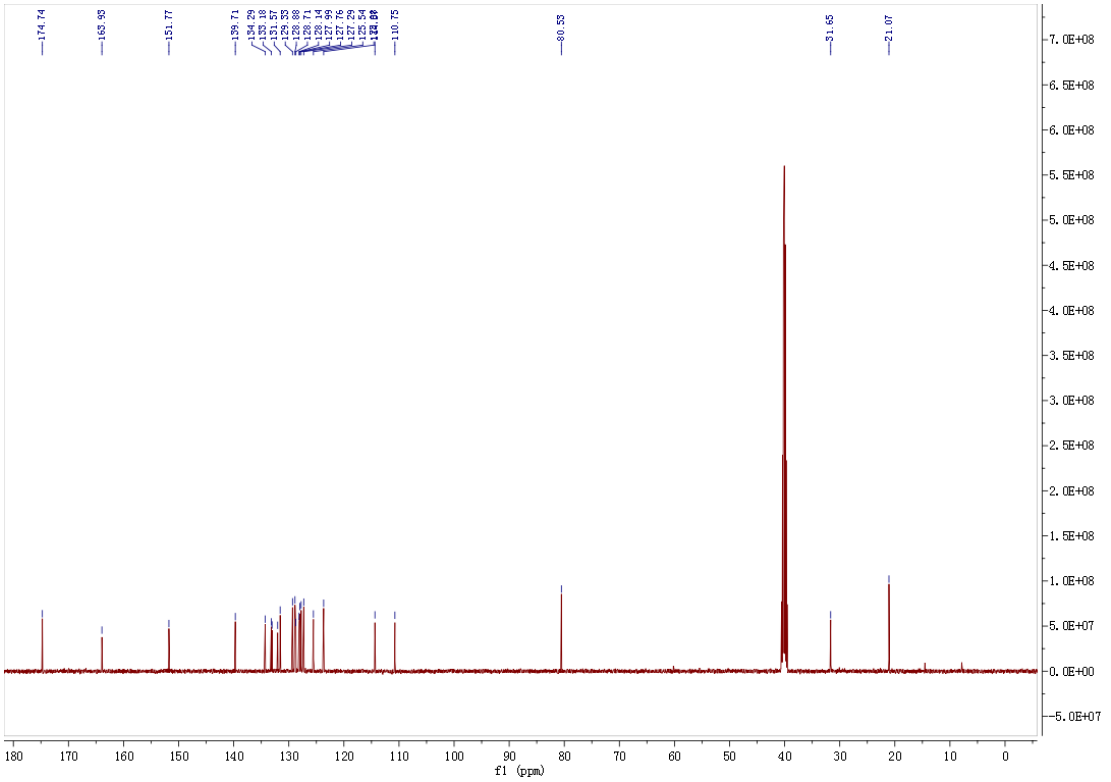
7.99
7.97
7.96
7.59
7.58
7.57
7.40
7.38
6.88
6.84
3.56
3.53
3.45
3.41
2.26
O
O
O
N
H
H3C
1.01
0.97
4.03
2.08
1.00
1.00
0.58
1.00
1.03
1.03
3.00
f1 (ppm)


174.74
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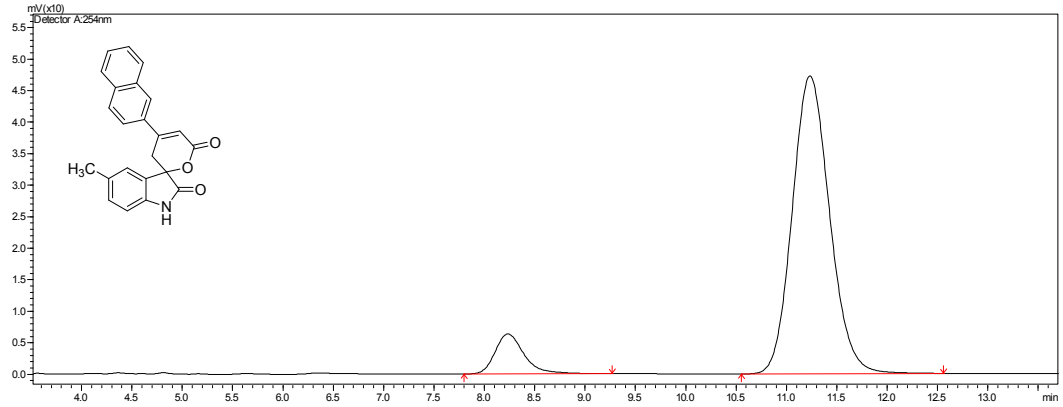
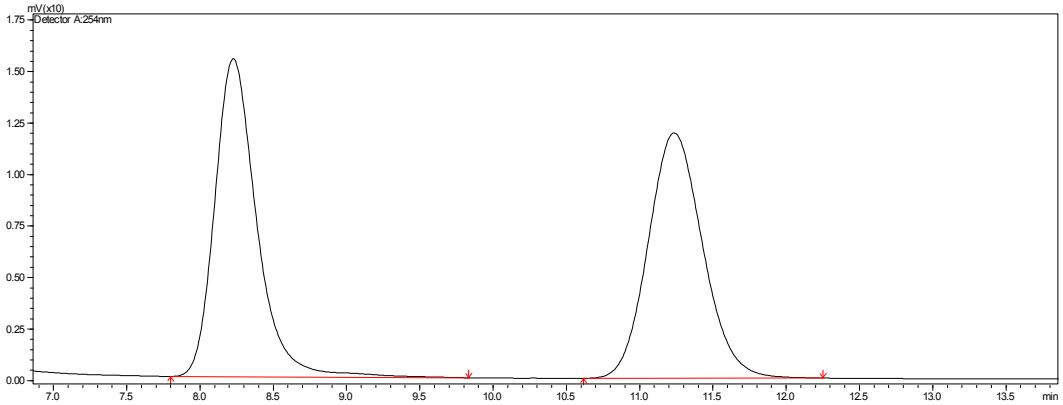
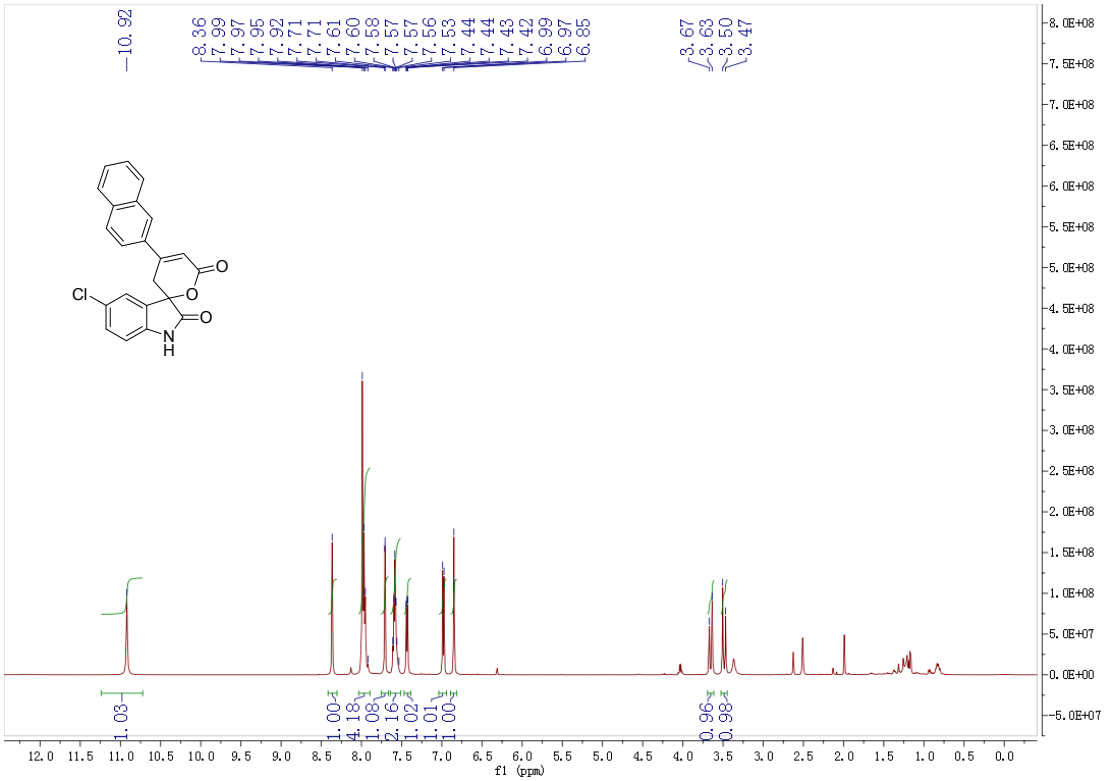
134.29
133.18
131.57
129.38
128.88
128.71
128.14
127.76
127.29
125.54
110.75
80.53
31.65
21.07
f1 (ppm)



Peak	Ret .Time	Area	Height	Area%	Height%
1	8.230	126661	6338	9.409	11.824
2	11.229	1219564	47264	90.591	88.176
Total		1346225	53602	100.000	100.000



Peak	Ret .Time	Area	Height	Area%	Height%
1	8.222	307547	15437	49.978	56.452
2	11.231	307819	11909	50.022	43.548
Total		615366	27346	100.000	100.000


10.92
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7.97
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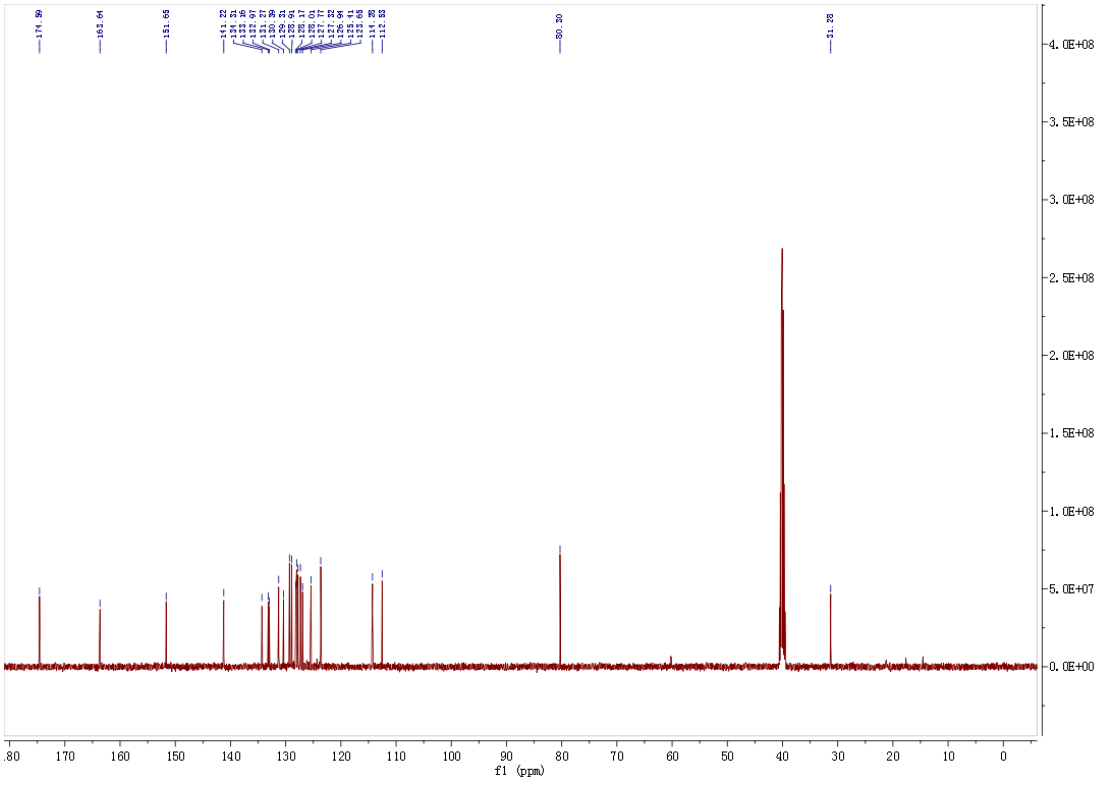
7.92
7.71
7.71
7.61
7.60
7.58
7.57
7.57
7.56
7.53
7.44
7.44
7.43
7.42
6.99
6.97
6.85
3.67
3.63
3.50
3.47
Cl
O
O
O
N
H
1.03
1.00
4.18
1.08
2.16
1.02
1.01
1.00
0.96
0.98
f1 (ppm)


174.99
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134.31
133.49
132.67
131.27
130.39
130.21
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128.17
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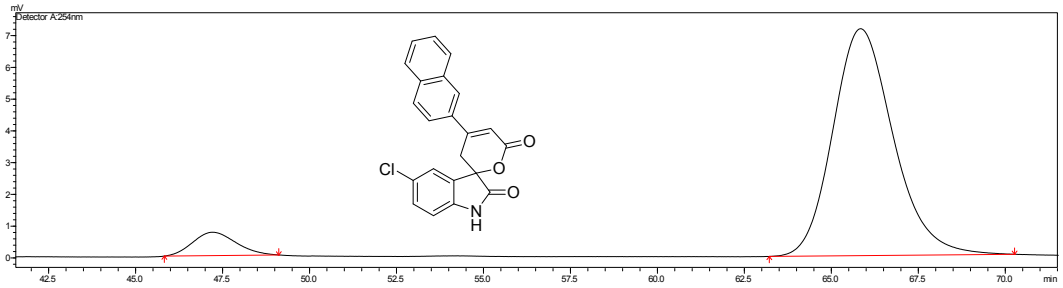
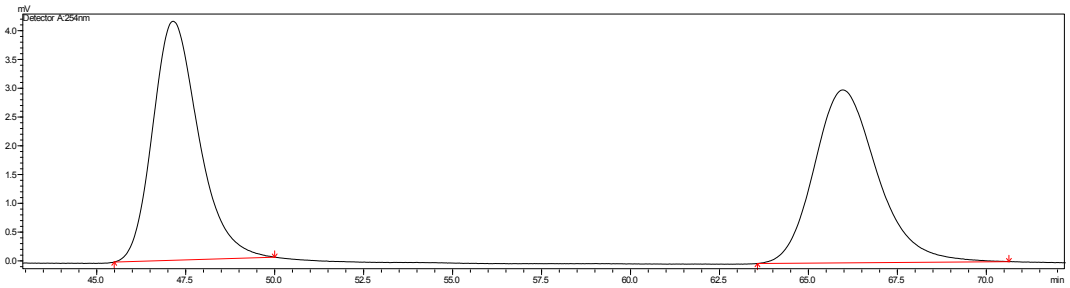
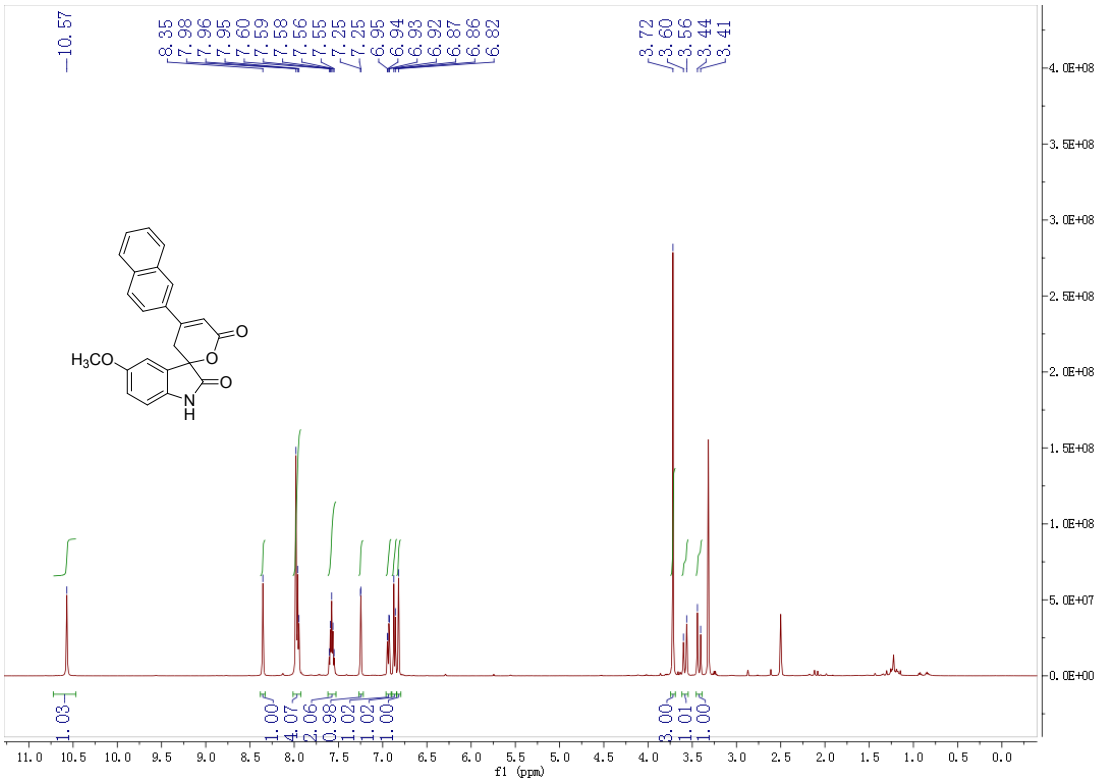
114.28
112.53
80.20
31.28
f1 (ppm)



Peak	Ret .Time	Area	Height	Area%	Height%
1	47.188	63699	737	6.868	9.344
2	65.845	863756	7147	93.132	90.656
Total		927455	7884	100.000	100.000



Peak	Ret .Time	Area	Height	Area%	Height%
1	47.144	374075	4152	50.172	58.015
2	65.965	371505	3005	49.828	41.985
Total		745580	7157	100.000	100.000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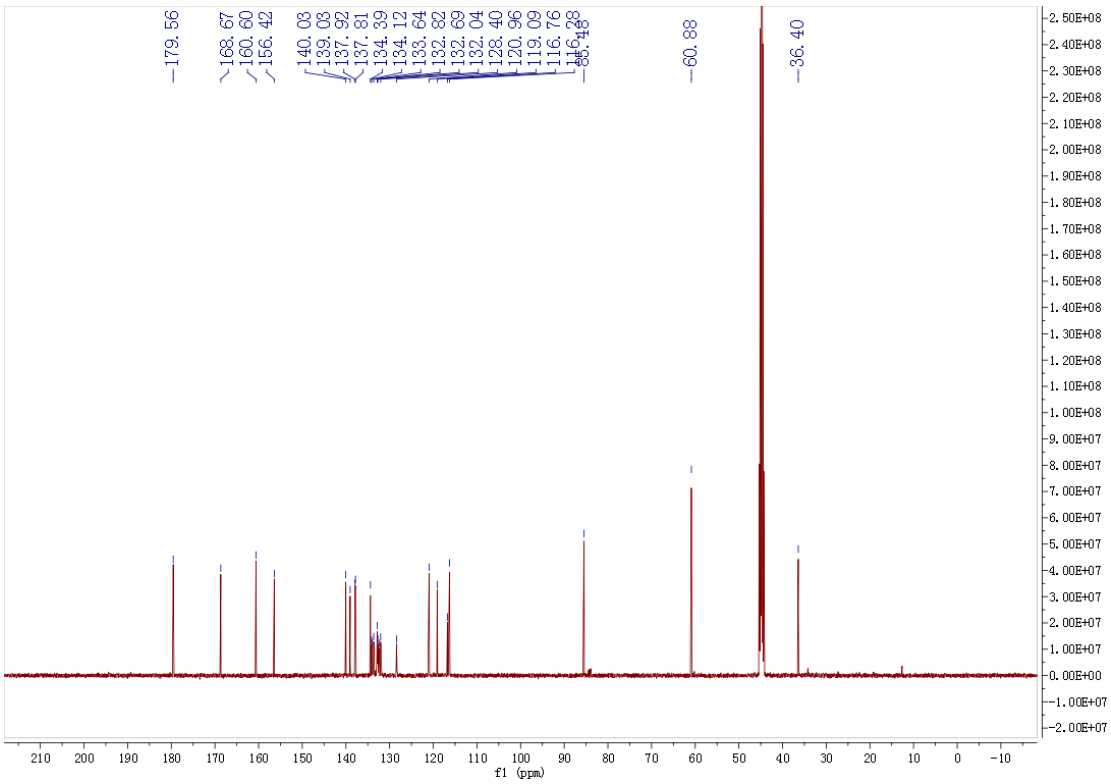
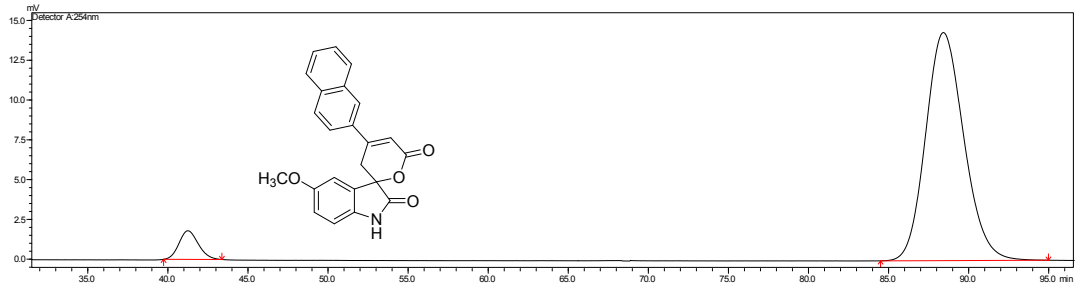
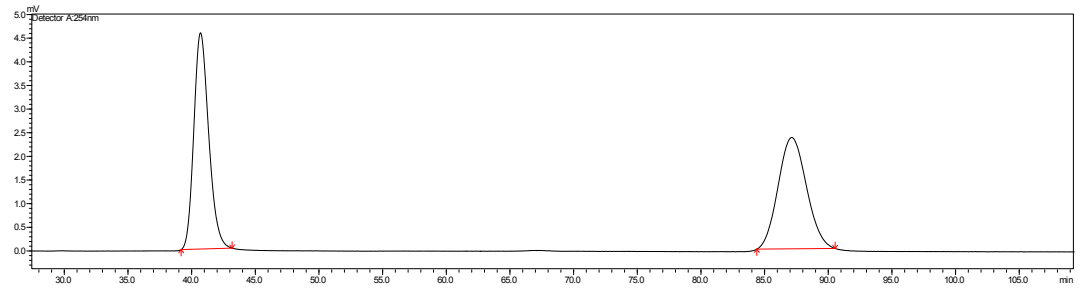
7.98
7.96
7.95
7.60
7.59
7.58
7.56
7.55
7.25
6.95
6.94
6.93
6.92
6.87
6.86
6.82
3.72
3.60
3.56
3.44
3.41
H3CO
O
O
O
N
H
1.03
1.00
4.07
2.06
0.98
1.02
1.02
1.00
3.00
1.01
1.00
f1 (ppm)

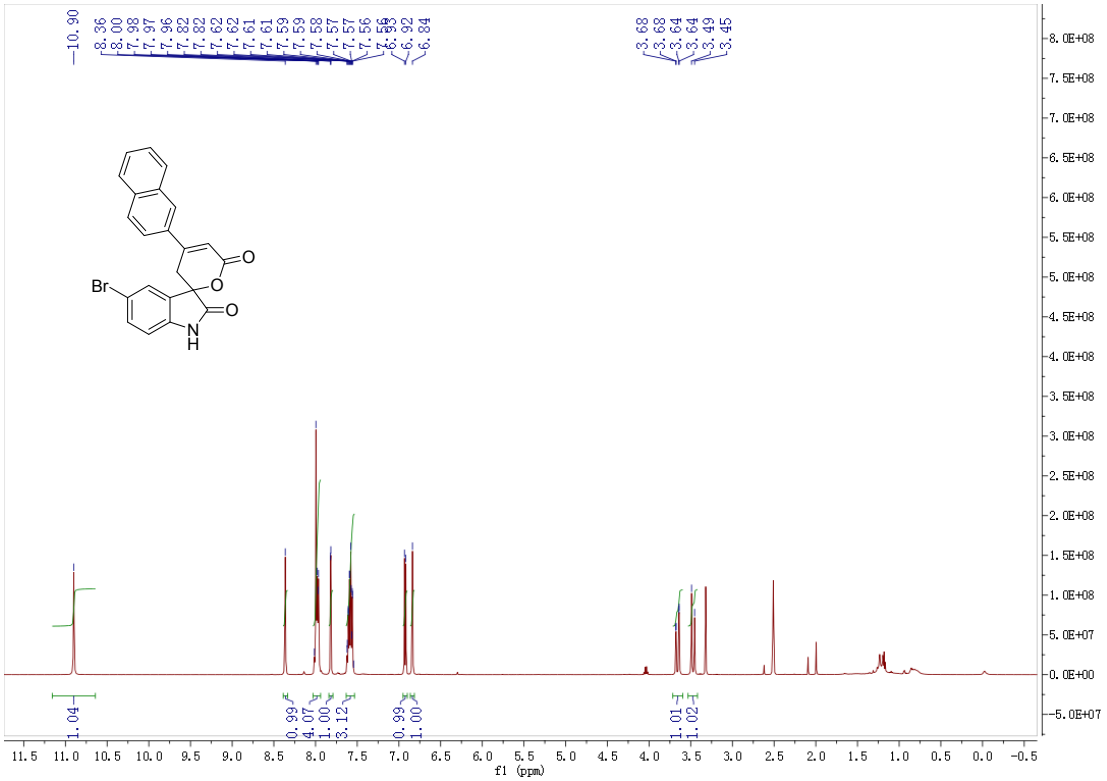

179.56
168.67
160.60
156.42
140.03
139.03
137.92
137.81
134.39
134.12
133.64
132.82
132.69
132.04
128.40
120.96
119.09
116.76
116.28
85.48
60.88
36.40
f1 (ppm)



Peak	Ret .Time	Area	Height	Area%	Height%
1	41.246	151142	1799	5.975	11.155
2	88.421	2378445	14327	94.025	88.845
Total		2529587	16126	100.000	100.000



Peak	Ret .Time	Area	Height	Area%	Height%
1	40.695	371432	4573	50.436	65.995
2	87.117	365007	2356	49.564	34.005
Total		736439	6930	100.000	100.000


10.90
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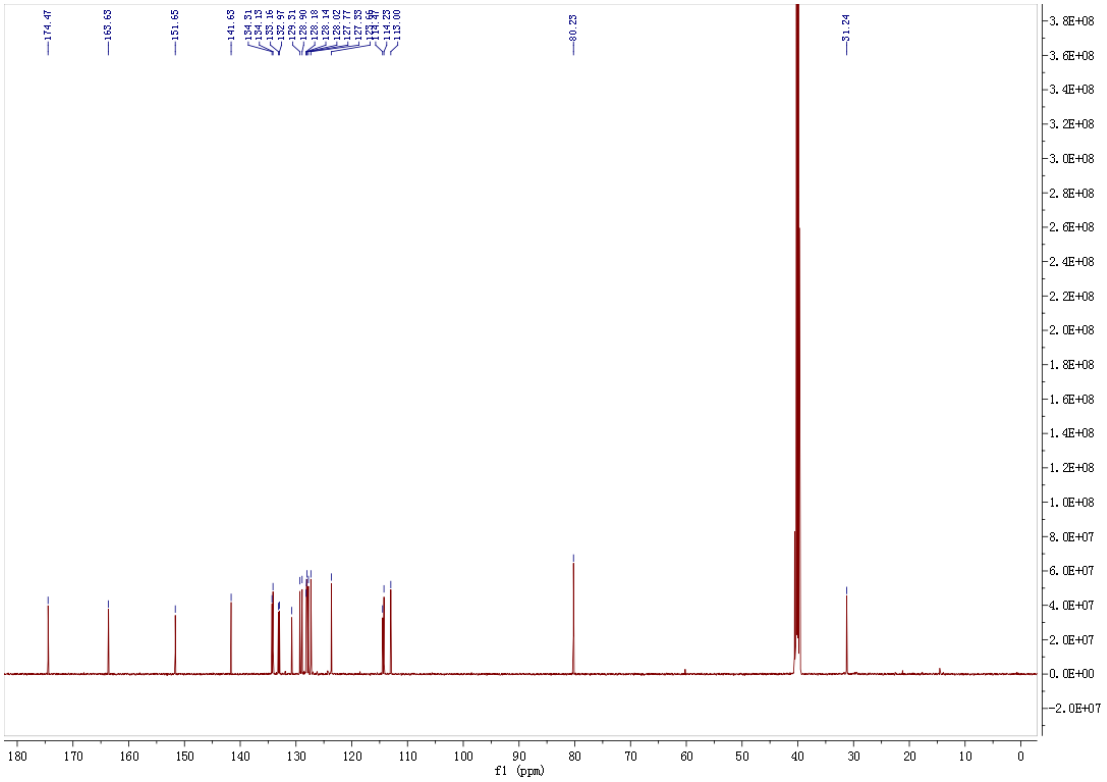
8.00
7.98
7.97
7.96
7.82
7.82
7.62
7.62
7.61
7.61
7.59
7.59
7.58
7.57
7.57
7.56
7.56
6.93
6.92
6.84
3.68
3.68
3.64
3.64
3.49
3.45
Br
O
O
O
N
H
1.04
0.99
4.07
1.00
3.12
0.99
1.00
1.01
1.02
f1 (ppm)


174.47
163.63
151.65
141.63
134.31
134.13
133.46
132.97
129.31
128.90
128.18
128.14
128.02
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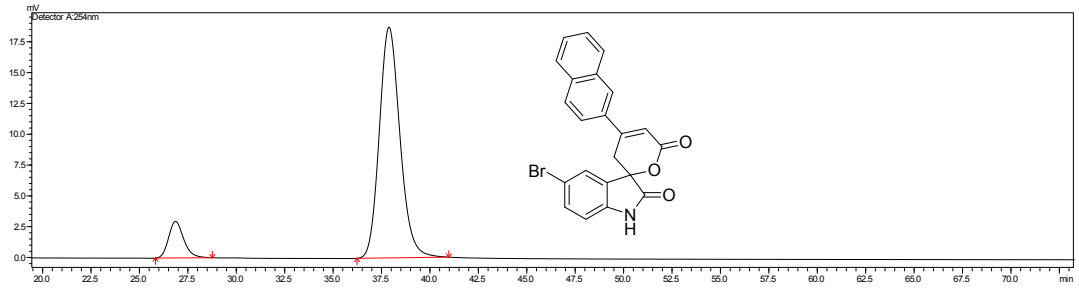
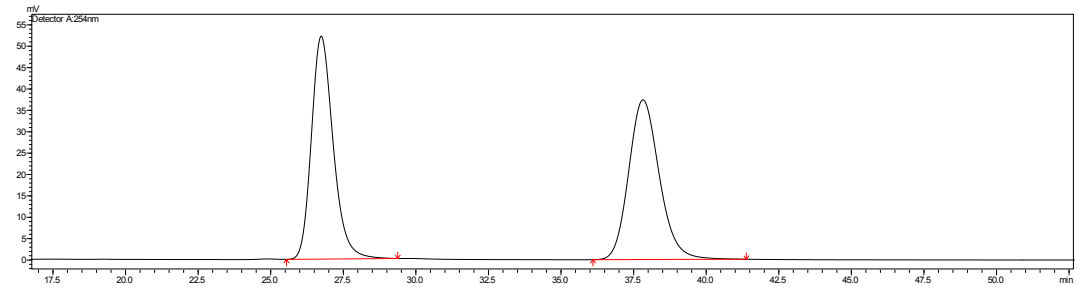
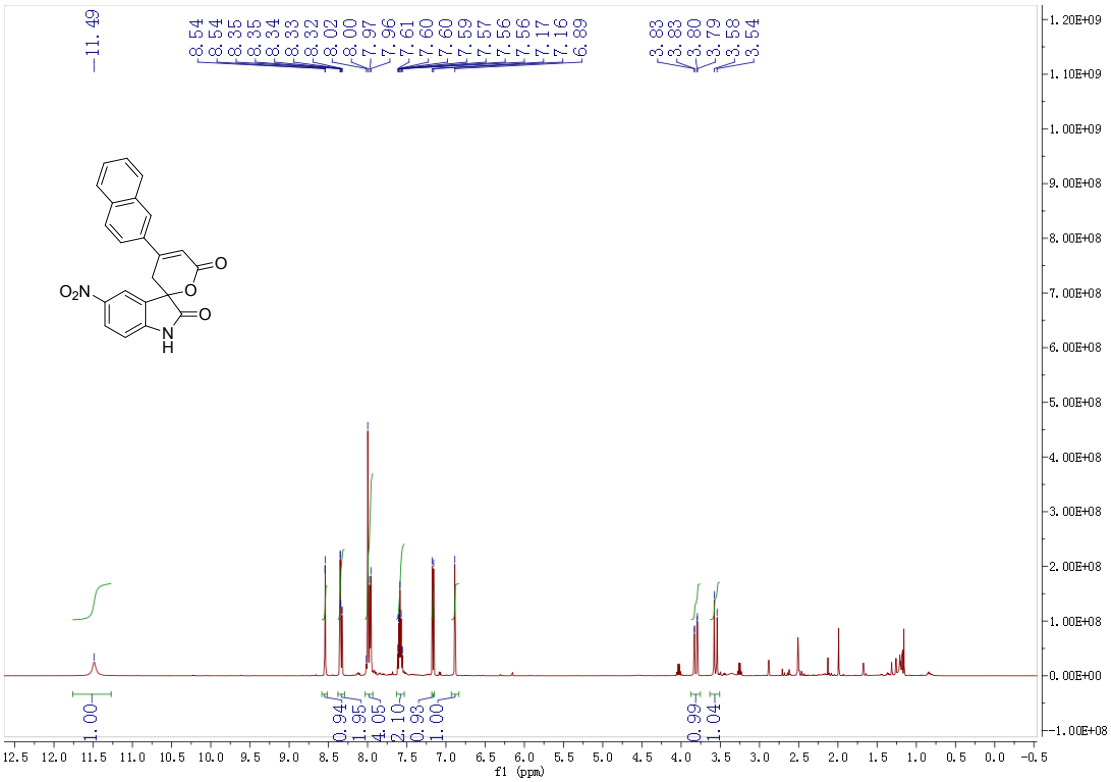
114.23
113.00
80.23
31.24
f1 (ppm)

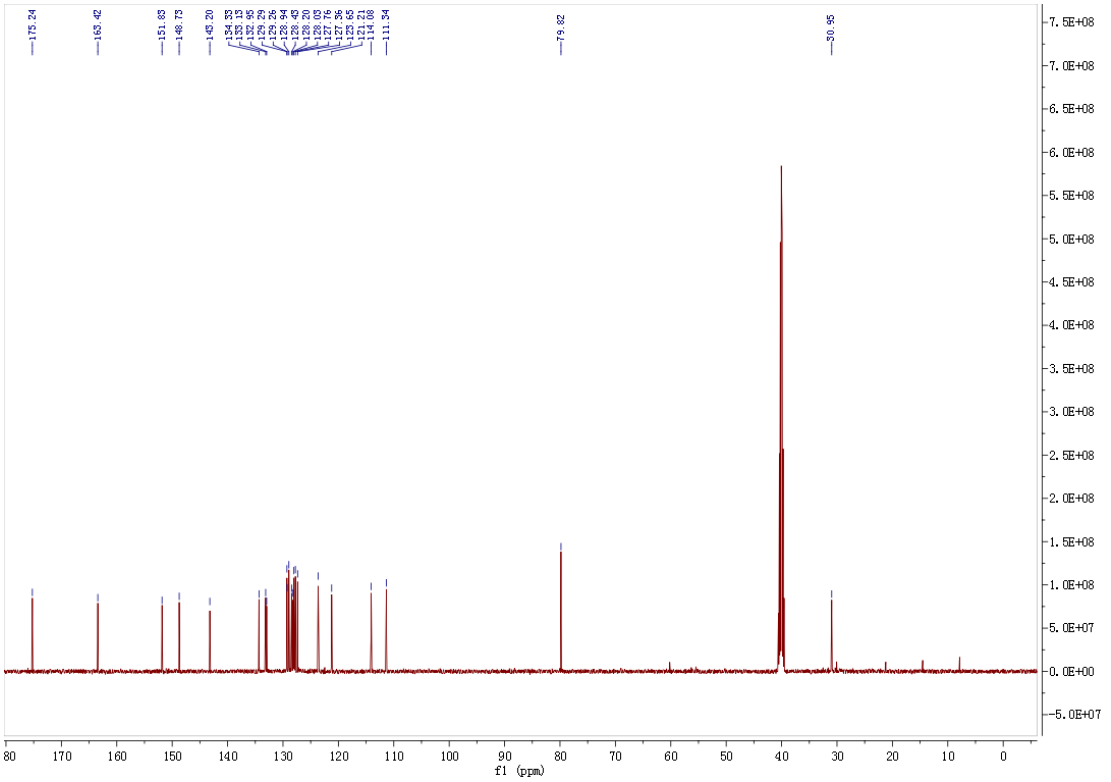


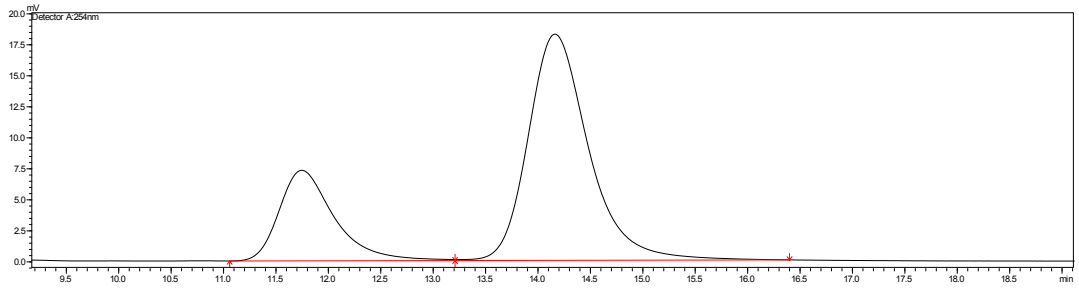
Peak	Ret .Time	Area	Height	Area%	Height%
1	26.854	161172	2970	10.403	13.691
2	37.880	1388067	18722	89.597	86.309
Total		1549239	21692	100.000	100.000



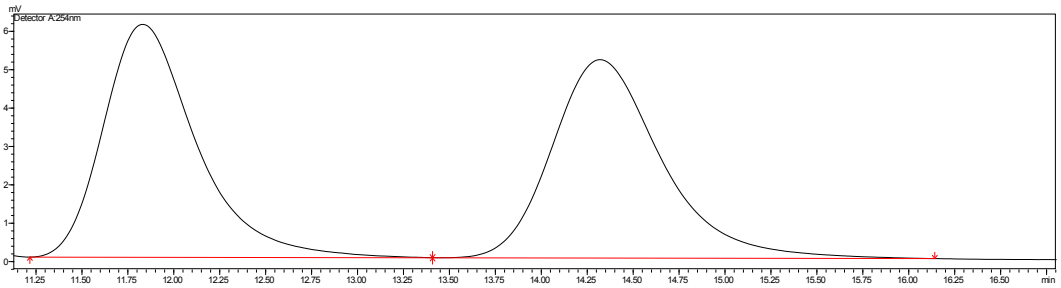
Peak	Ret .Time	Area	Height	Area%	Height%
1	26.735	2722911	52142	49.807	58.262
2	37.818	2744052	37353	50.193	41.738
Total		5466962	89485	100.000	100.000


11.49
8.54
8.54
8.35
8.35
8.34
8.33
8.32
8.02
8.00
7.97
7.96
7.61
7.60
7.60
7.59
7.57
7.56
7.56
7.17
7.16
6.89
3.83
3.83
3.80
3.79
3.58
3.54
O2N
O
O
O
N
H
1.00
0.94
1.95
4.05
2.10
0.93
1.00
0.99
1.04
f1 (ppm)

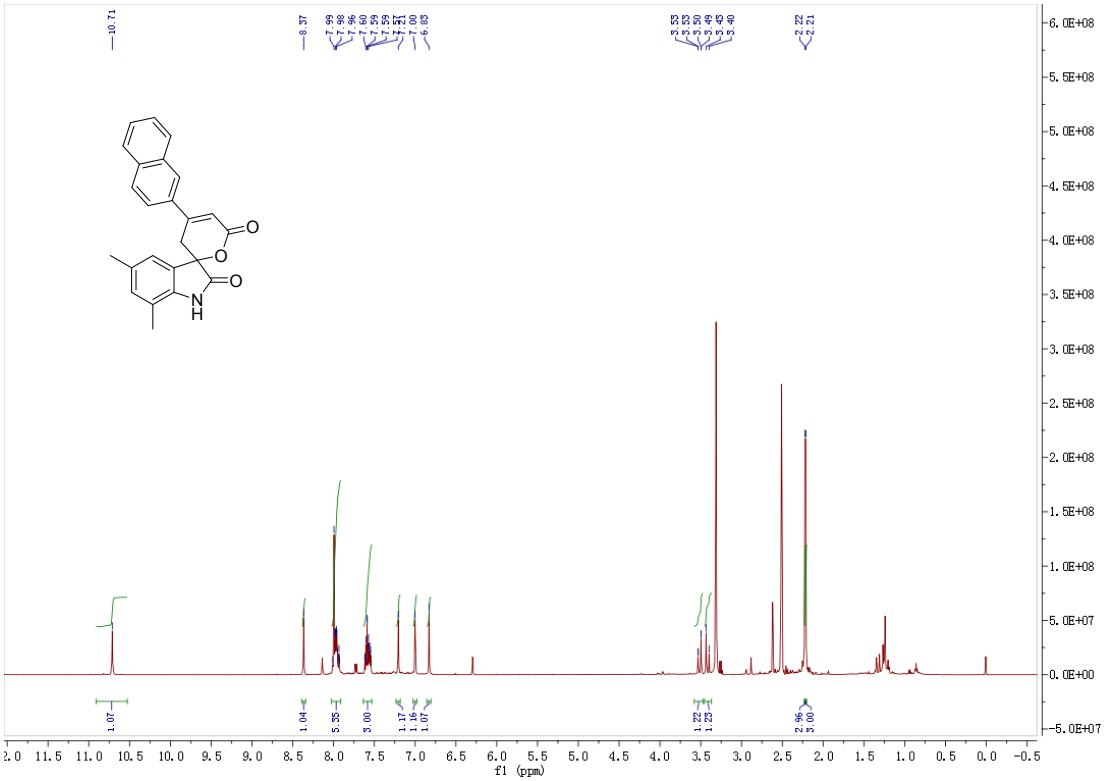

175.24
163.42
151.83
148.73
145.20
134.33
133.13
132.95
129.29
129.26
128.94
128.45
128.20
128.03
127.76
127.56
123.56
121.21
114.08
111.34
79.82
30.95
f1 (ppm)

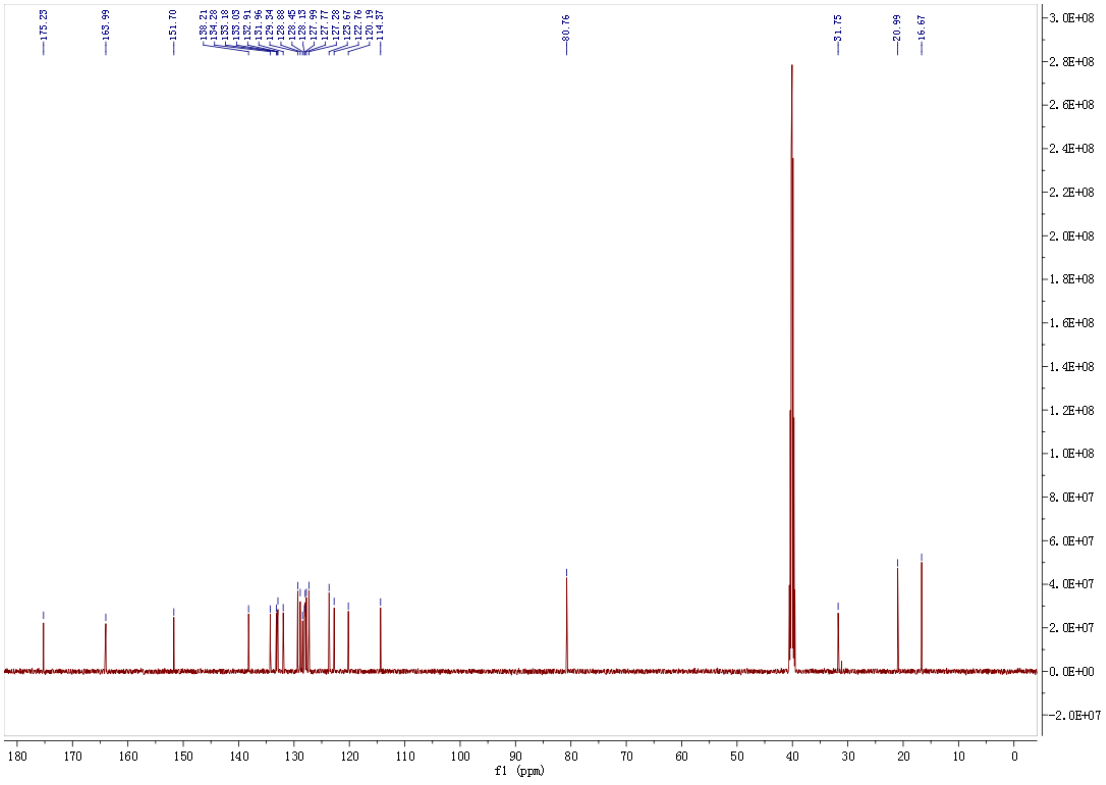


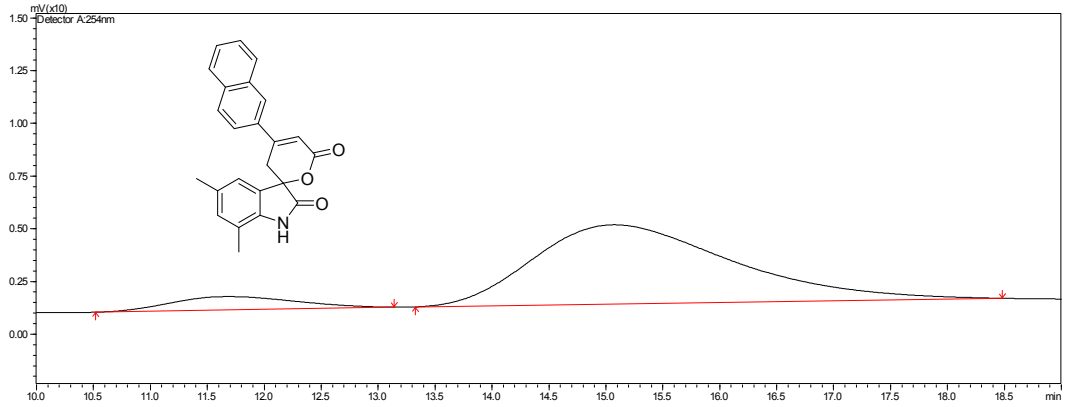
Peak	Ret .Time	Area	Height	Area%	Height%
1	11.742	266656	7302	26.710	28.588
2	14.158	731668	18242	73.290	71.412
Total		998324	25544	100.000	100.000



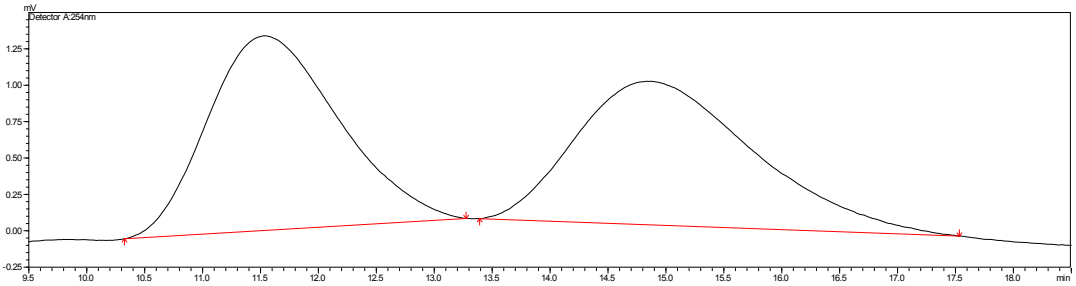
Peak	Ret .Time	Area	Height	Area%	Height%
1	11.826	213933	6069	49.940	53.999
2	14.316	214446	5170	50.060	46.001
Total		428379	11238	100.000	100.000


10.71
8.37
7.99
7.98
7.96
7.60
7.59
7.59
7.21
7.21
7.00
6.83
3.53
3.53
3.50
3.49
3.45
3.40
2.22
2.21
O
O
O
N
H
1.07
1.04
5.35
3.00
1.17
1.16
1.07
1.22
1.23
2.96
3.00
f1 (ppm)

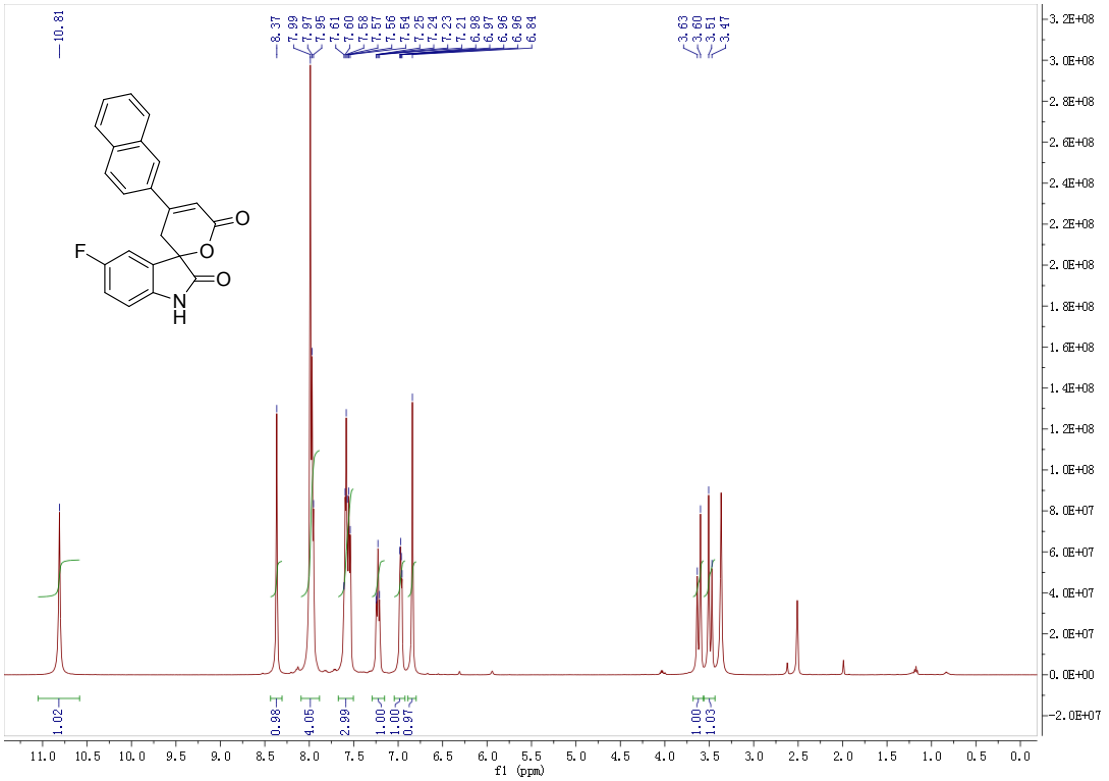

175.23
163.99
151.70
138.21
134.28
133.38
133.03
132.91
131.96
129.34
128.88
128.45
128.13
127.99
127.77
127.28
123.67
122.76
120.19
114.37
80.76
31.75
20.99
16.67
f1 (ppm)

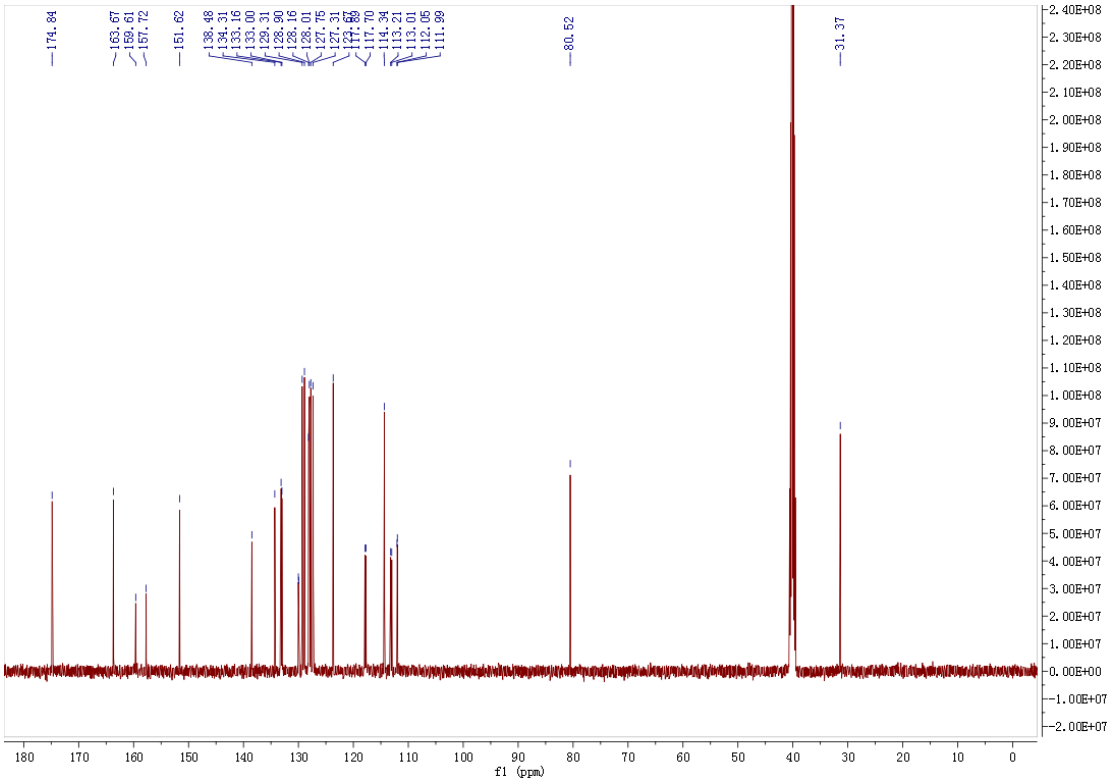


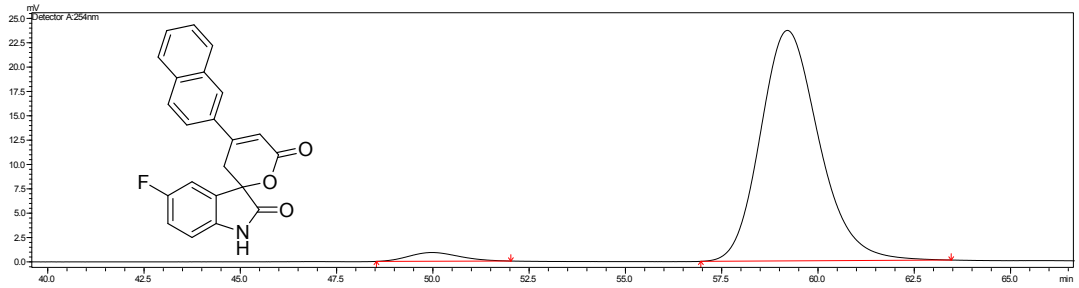
Peak	Ret .Time	Area	Height	Area%	Height%
1	11.694	47979	634	9.503	14.424
2	15.073	456919	3759	90.497	85.576
Total		504899	4393	100.000	100.000



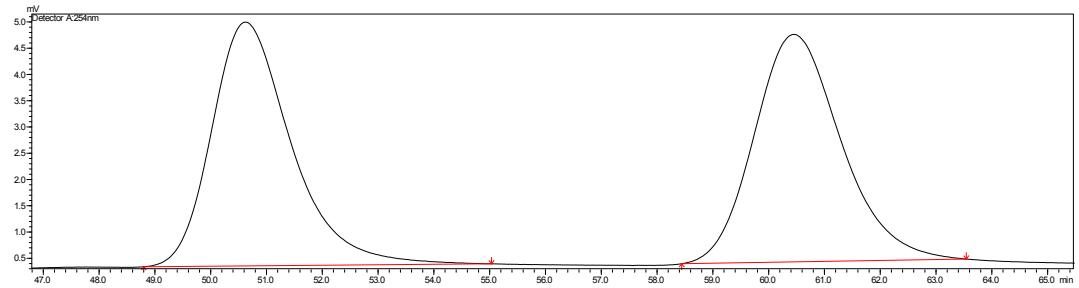
Peak	Ret .Time	Area	Height	Area%	Height%
1	11.536	105102	1338	49.891	57.590
2	14.831	105562	985	50.109	42.410
Total		210664	2324	100.000	100.000


10.81
8.37
7.99
7.97
7.95
7.61
7.60
7.58
7.57
7.56
7.54
7.25
7.24
7.23
7.21
6.98
6.97
6.96
6.96
6.84
3.63
3.60
3.51
3.47
F
O
O
O
N
H
1.02
0.98
4.05
2.99
1.00
1.00
0.97
1.00
1.03
f1 (ppm)

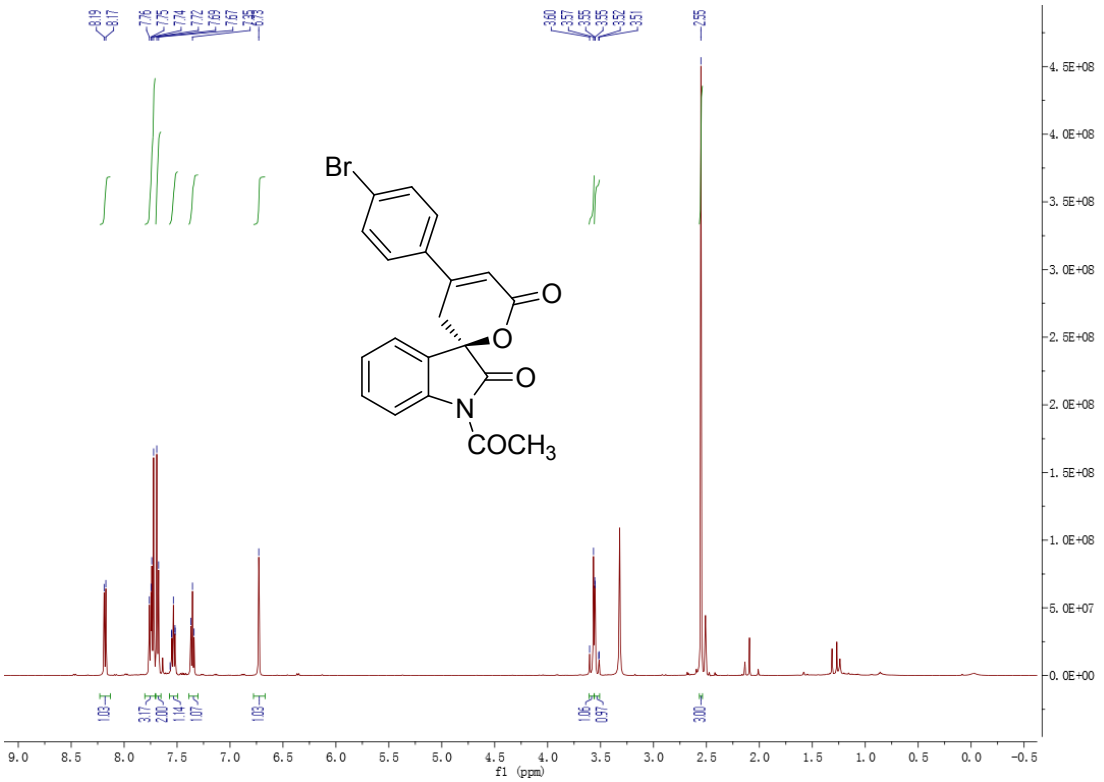

174.84
163.67
159.61
157.72
151.62
138.48
134.31
133.16
133.00
129.31
128.90
128.16
128.01
127.75
127.31
123.67
117.89
117.70
114.34
113.21
113.01
112.05
111.99
80.52
31.37
f1 (ppm)

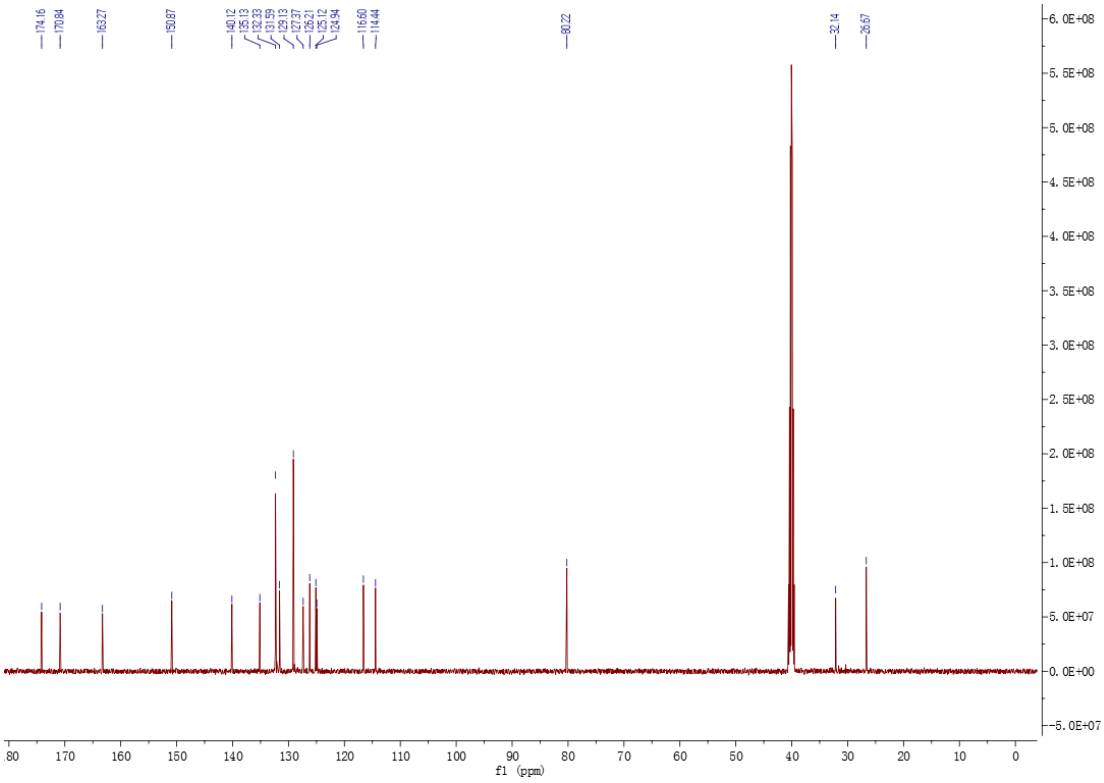


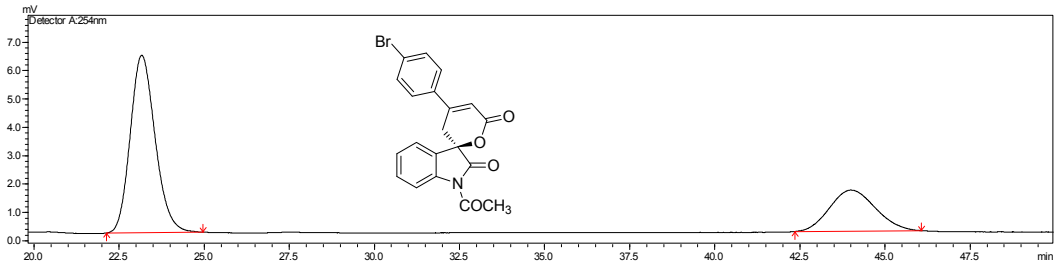
Peak	Ret .Time	Area	Height	Area%	Height%
1	49.971	81707	896	3.166	3.650
2	59.202	2498746	23666	96.834	96.350
Total		2580452	24562	100.000	100.000



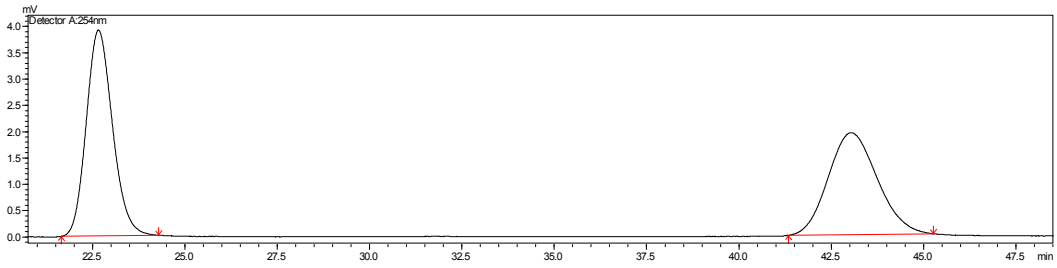
Peak	Ret .Time	Area	Height	Area%	Height%
1	50.623	460056	4642	49.534	51.734
2	60.449	468709	4331	50.466	48.266
Total		928765	8973	100.000	100.000


Br
O
O
O
N
COCH3
f1 (ppm)

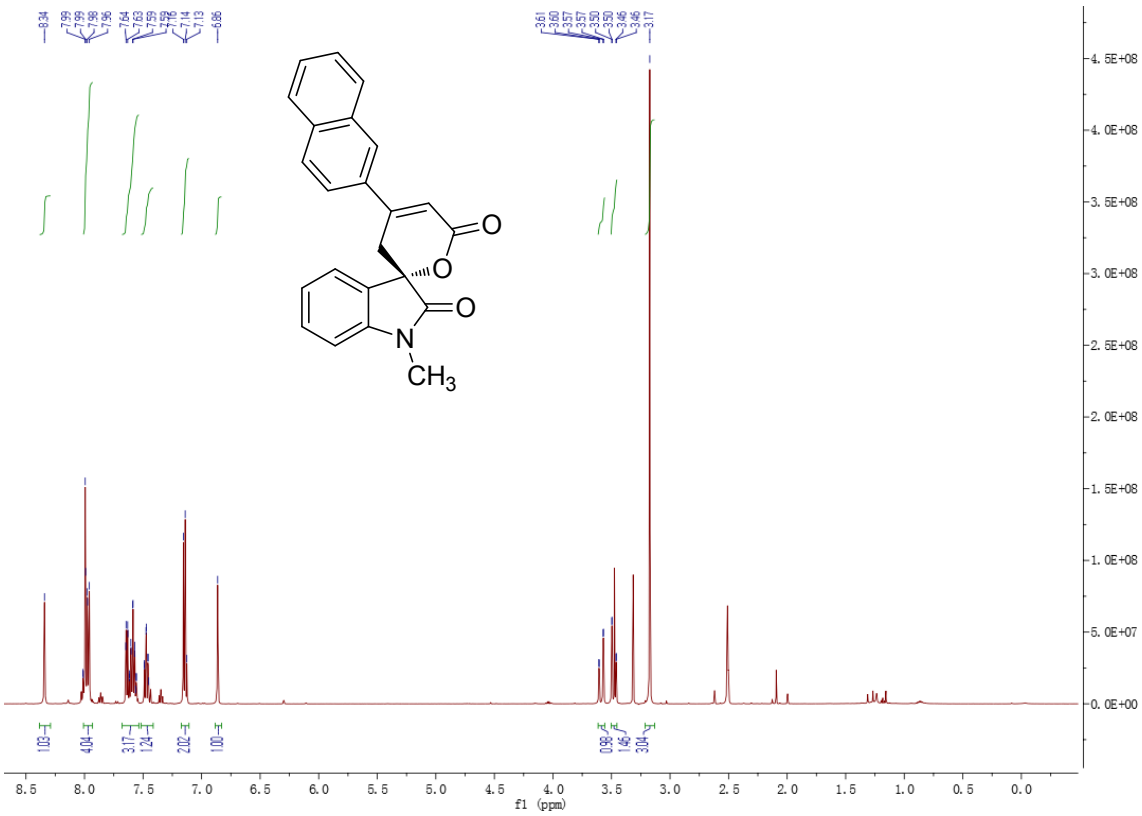

f1 (ppm)

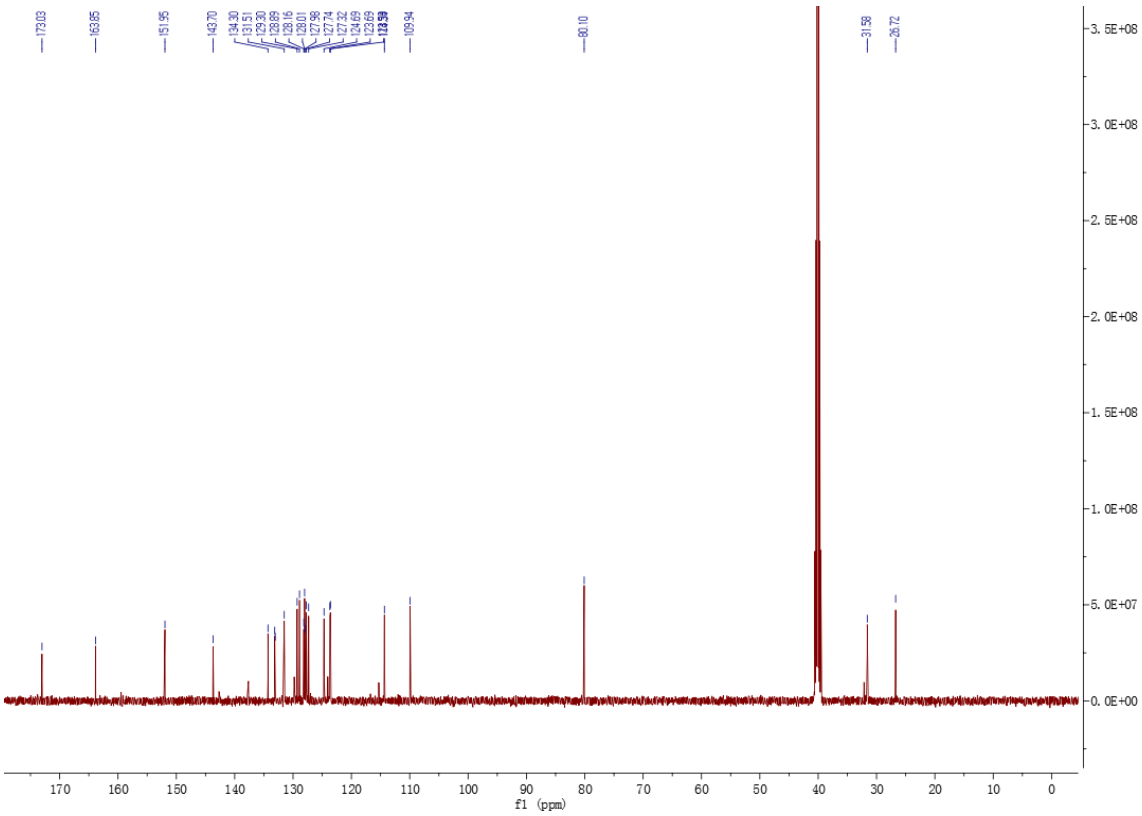


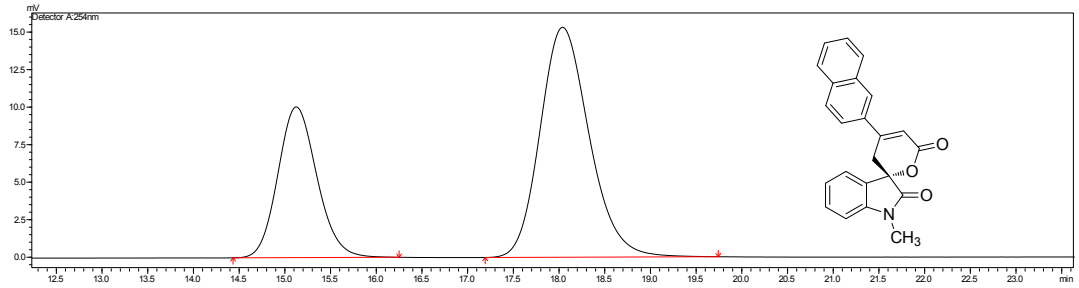
Peak	Ret .Time	Area	Height	Area%	Height%
1	23.163	318746	6258	70.107	81.209
2	43.983	135912	1448	29.893	18.791
Total		454659	7707	100.000	100.000



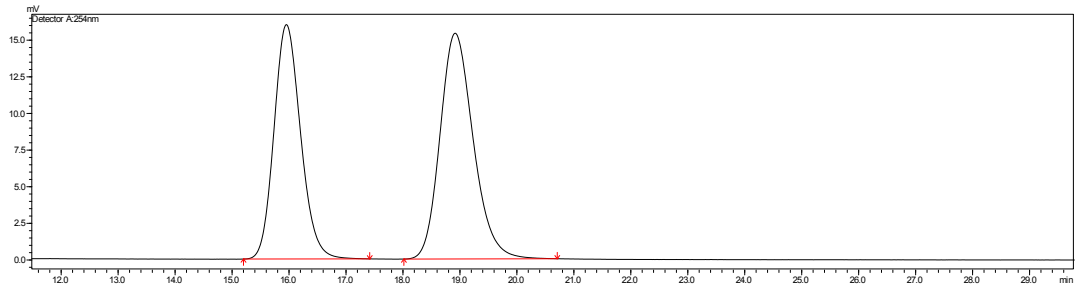
Peak	Ret .Time	Area	Height	Area%	Height%
1	22.659	193551	3911	51.941	66.861
2	43.032	179082	1939	48.059	33.139
Total		372634	5850	100.000	100.000


8.34
7.99
7.98
7.96
7.64
7.63
7.59
7.16
7.14
7.13
6.86
3.61
3.60
3.57
3.53
3.50
3.46
3.45
3.17
O
O
O
N
CH3
1.03
4.04
3.17
1.24
2.02
1.00
0.95
1.45
3.04
f1 (ppm)

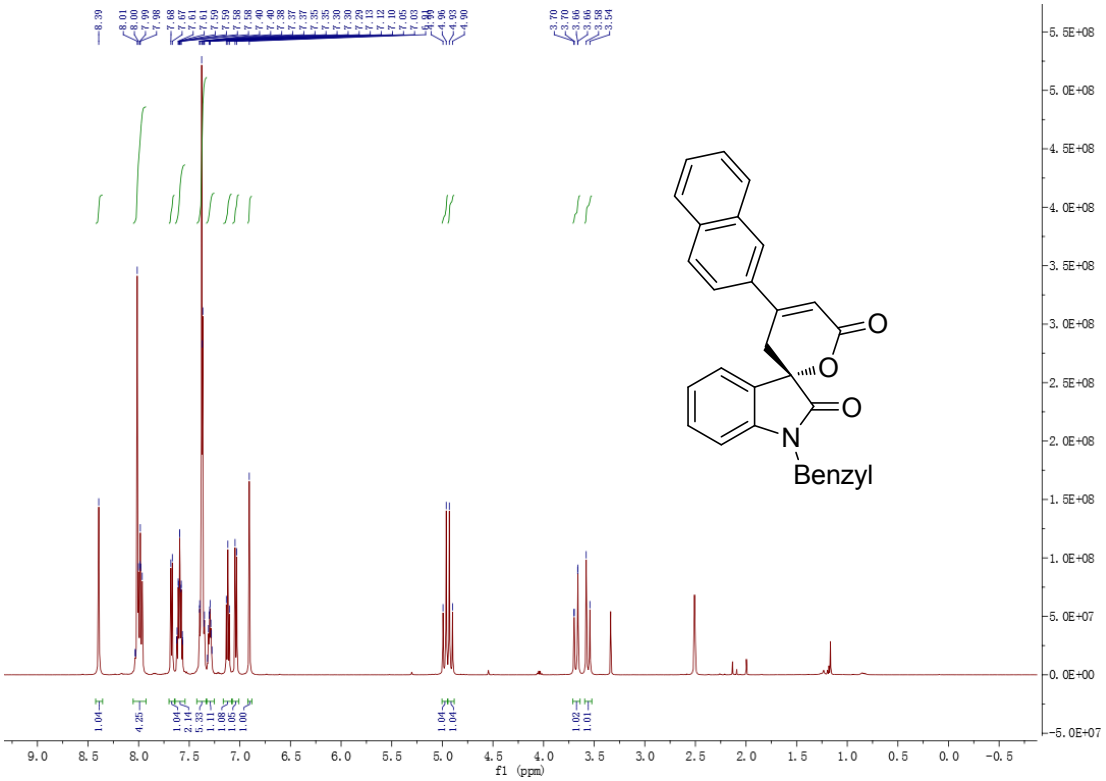

173.03
163.85
151.95
143.70
134.30
131.51
129.30
128.89
128.16
128.01
127.98
127.74
127.32
124.69
123.69
109.94
80.10
31.58
26.72
f1 (ppm)

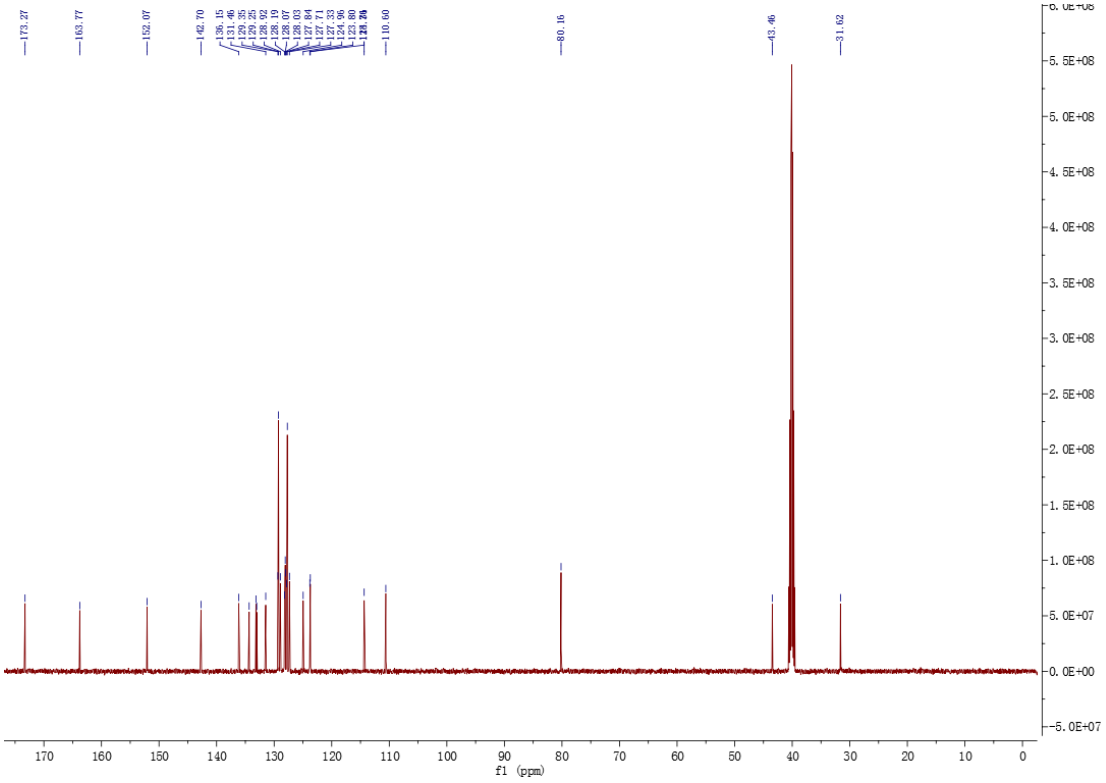


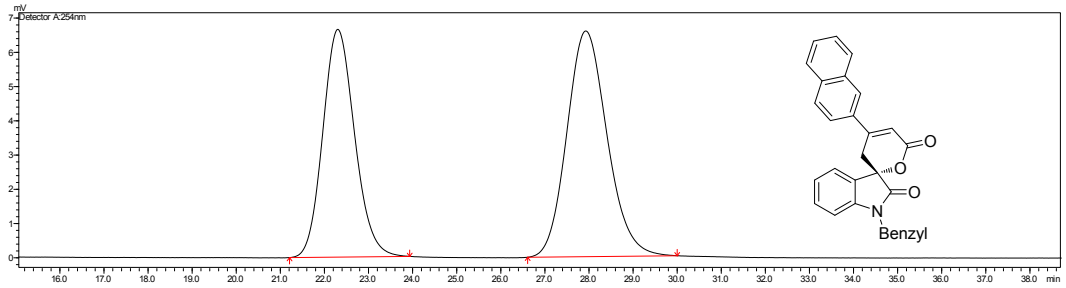
Peak	Ret .Time	Area	Height	Area%	Height%
1	15.120	298383	10040	34.260	39.595
2	18.034	572554	15317	65.740	60.405
Total		870937	25357	100.000	100.000



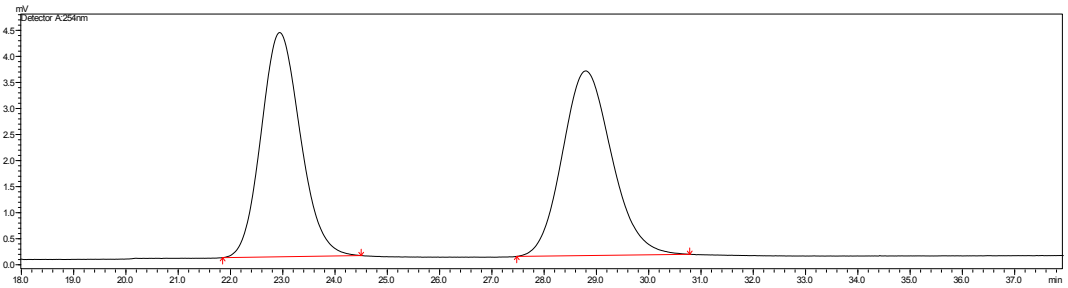
Peak	Ret .Time	Area	Height	Area%	Height%
1	15.949	519723	15994	45.446	50.936
2	18.912	623881	15406	54.554	49.064
Total		1143605	31400	100.000	100.000


O
O
O
N
Benzyl
f1 (ppm)


f1 (ppm)



Peak	Ret .Time	Area	Height	Area%	Height%
1	22.298	333029	6651	44.371	50.232
2	27.924	417520	6589	55.629	49.768
Total		750548	13240	100.000	100.000



Peak	Ret .Time	Area	Height	Area%	Height%
1	22.936	224695	4304	49.146	54.843
2	28.793	232500	3544	50.854	45.157
Total		457195	7849	100.000	100.000