Supplementary information for

NHC-Catalyzed [4+2] Cycloaddition Reactions for the Synthesis of 3'-Spirocyclic oxindoles via C–F Bond Cleavage Protocol

Jun Yan, Kuangxi Shi, Chengtao Zhao, Liyuan Ding, Shengsheng Jiang, Limin Yang* and Guofu Zhong*

College of Materials, Chemistry & Chemical Engineering, Hangzhou Normal University, Hangzhou 310036, China

E-mail: myang@hznu.edu.cn; zgf@hznu.edu.cn

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.

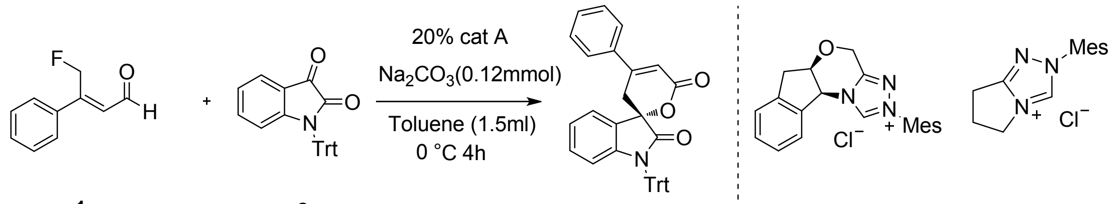
Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on Bruker AMX 500 spectrophotometer ($CDCl_3$ as solvent). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 7.26, 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 SiMe4 (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, CHIRALCEL IB, CHIRALCEL IA and CHIRALPAK OD-H. Optical rotations were measured in $CHCl_3$ on a Schmidt + Haensdchpolarimeter (Polartronic MH8) with a 10 cm cell (c given in 0.5 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 cat. D.

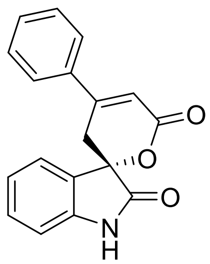
General procedure for NHC-Catalyzed [4+2] Cycloaddition Reactions:



1 **2** **3c** **cat. A** **cat. D**

To an oven dried 10 mL vial was added was added 2.0 mL solvent,aldehyde (0.20 mmol, 32.8 mg, 1.0 equiv), isatin (77.8 mg, 0.20 mmol, 1.0 equiv), cat.A (14.7 mg, 0.04 mmol, 20 mol %), Na_2CO_3 (25.2 mg, 0.24 mmol, 1.2 equiv). The resulting solution was stirred under at 0 °C until the reactants were 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 using EtOAc/PE = 1:8 as eluent to afford the desired product 3c. *The racemic products used to determine the e.e. values were synthesized using cat. D.*

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



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

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (d, J = 119.5 Hz, 1H), 7.66 – 7.51 (m, 2H), 7.51 – 7.35 (m, 4H), 7.30 (td, J = 7.8, 1.1 Hz, 1H), 7.02 (dd, J = 11.1, 4.1 Hz, 1H), 6.94 (d, J = 7.8 Hz, 1H), 6.59 (t, J = 1.3 Hz, 1H), 3.25 (dd, J = 115.0, 17.5 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.5, 162.3, 150.9, 139.2, 134.8, 130.1, 130.0, 128.1, 127.1, 125.1, 123.3, 122.5, 113.7, 110.0, 79.1, 31.6.

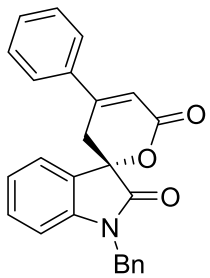
HRMS (ESI$^+$) calcd for $C_{18}H_{14}NO_3$, *m/z* 292.0968, found 292.0964.

HPLC: Chiralcel OD-H (n-hexane/i-PrOH, 92/8, flow rate 1.0 mL/min, λ = 220 nm), t_R (major) = 83.790 min, t_R (minor) = 96.502 min; 87% ee.

$[\alpha]_D^{25}$ = -29.04 (c = 0.5, $CHCl_3$).

Melting point: 187 °C – 188 °C

(S)-1-benzyl-4'-phenylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione 3b



The title compound was prepared according to the typical procedure, as described above, in 72% yield as white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.51 (m, 2H), 7.50 – 7.39 (m, 4H), 7.36 – 7.24 (m, 6H), 7.02 (td, J = 7.6, 0.8 Hz, 1H), 6.77 (d, J = 7.9 Hz, 1H), 6.62 (s, 1H), 4.98 – 4.84 (m, 2H), 3.30 (dd, J = 145.0, 20.0 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 171.7, 162.2, 151.0, 141.3, 134.9, 133.8, 130.0, 129.9, 128.1, 128.0, 127.0, 126.8, 126.3, 125.1, 123.1, 122.5, 113.8, 109.0, 78.8, 43.1, 31.7.

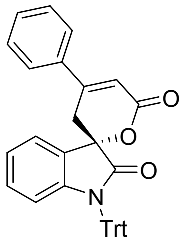
HRMS (ESI$^+$) calcd for $C_{25}H_{20}NO_3$,*m/z* 382.1438, found 382.1439.

HPLC: Chiralcel IA (n-hexane/i-PrOH, 75/25, flow rate 1.0 mL/min, λ = 220 nm), t_R (major) = 24.047 min, t_R (minor) = 26.494 min; 92% ee.

$[\alpha]_D^{25}$ = -20.26 (c = 0.5, $CHCl_3$).

Melting point: 179 °C – 180 °C

(S)-4'-phenyl-1-tritylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione 3c



The title compound was prepared according to the typical procedure, as described above, in 90% yield as white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 – 7.49 (m, 2H), 7.47 – 7.39 (m, 10H), 7.27 (d, *J* = 1.3 Hz, 1H), 7.26 – 7.18 (m, 8H), 6.97 (td, *J* = 7.9, 1.5 Hz, 1H), 6.92 (td, *J* = 7.6, 0.8 Hz, 1H), 6.51 (s, 1H), 6.34 (d, *J* = 8.0 Hz, 1H), 3.21 (dd, *J*= 145.0,15.0 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 172.5, 162.3, 150.4, 141.8, 140.4, 135.0, 129.3, 128.4, 128.0, 127.0, 126.8, 126.0, 125.0, 122.3, 121.8, 115.3, 114.0, 78.6, 73.5, 31.7.

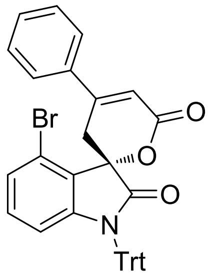
HRMS (ESI^+) calcd for $C_{37}H_{28}NO_3$, *m/z* 534.2064, found 534.2064.

HPLC: Chiralcel AD-H (n-hexane/i-PrOH, 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 8.980 min, t_R (minor) = 21.374 min; > 99% ee.

$[\alpha]_D^{25}$ = -42.26 (*c* = 0.5, $CHCl_3$).

Melting point: 229 °C – 230 °C

(S)-5-bromo-4'-phenyl-1-tritylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione 3d



The title compound was prepared according to the typical procedure, as described above, in 82% yield as yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H), 7.47 – 7.42 (m, 3H), 7.38 – 7.34 (m, 6H), 7.24 – 7.17 (m, 9H), 7.13 (t, *J* = 7.0 Hz, 1H), 6.84 (t, *J* = 8.2 Hz, 1H), 6.43 (d, *J* = 2.5 Hz, 1H), 6.32 (d, *J* = 8.2 Hz, 1H), 3.46 (dd, *J* = 495.0, 17.5 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.3, 162.2, 148.2, 143.8, 140.2, 135.2, 129.6, 129.4, 128.0, 127.9, 126.9, 126.24, 126.22, 125.0, 124.4, 118.4, 114.2, 113.8, 79.2, 73.6, 29.4.

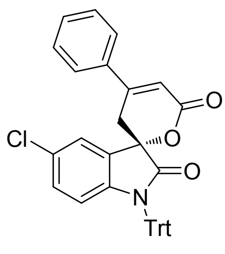
HRMS (ESI^+) calcd for $C_{37}H_{27}BrNO_3$, *m/z* 612.1023, found 612.1020.

HPLC: Chiralcel OD-H (n-hexane/i-PrOH, 98/2, flow rate 1.0 mL/min, λ = 220 nm), t_R (major) = 53.813 min, t_R (minor) = 64.090 min; 90% ee.

$[\alpha]_D^{25}$ = -50.04 (*c* = 0.5, $CHCl_3$).

Melting point: 250 °C – 251°C

(S)-5-chloro-4'-phenyl-1-tritylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione 3e



The title compound was prepared according to the typical procedure, as described above, in 91% yield as light yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (dd, J = 7.6, 1.9 Hz, 2H), 7.47 – 7.36 (m, 10H), 7.23 (tdd, J = 6.9, 4.6, 2.0 Hz, 9H), 6.93 (dd, J = 8.8, 2.3 Hz, 1H), 6.50 (s, 1H), 6.26 (d, J = 8.8 Hz, 1H), 3.20 (dd, J = 135.0, 17.5 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.2, 163.0, 151.3, 141.4, 141.2, 135.9, 131.1, 129.7, 129.5, 129.2, 129.1, 128.5, 128.0, 127.3, 126.1, 123.9, 117.5, 114.9, 79.4, 74.7, 32.7.

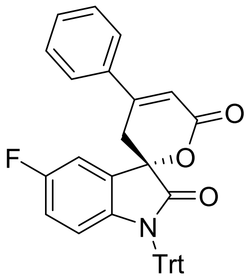
HRMS (ESI$^+$) calcd for $C_{37}H_{27}ClNO_3$, m/z 568.1674, found 568.1691.

HPLC: Chiralcel AD-H (n-hexane/i-PrOH, 80/20, flow rate 1.0 mL/min, λ = 220 nm), t_R (major) = 6.838 min, t_R (minor) = 12.086 min; > 99% ee.

$[\alpha]_D^{25}$ = -8.42 (c = 0.5, $CHCl_3$).

Melting point: 181 °C – 182 °C

(S)-5-fluoro-4'-phenyl-1-tritylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione 3f



The title compound was prepared according to the typical procedure, as described above, in 82% yield as white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.48 – 7.37 (m, 9H), 7.29 – 7.20 (m, 9H), 7.14 (dd, J = 7.4, 2.7 Hz, 1H), 6.67 (td, J = 8.9, 2.7 Hz, 1H), 6.50 (s, 1H), 6.27 (dd, J = 9.0, 4.2 Hz, 1H), 3.20 (dd, J = 155.0, 17.5 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 172.4, 162.0, 157.6(d, J = 244.3 Hz),150.4, 140.3, 137.8 (d, J= 2.5 Hz), 134.9, 130.1, 128.5 (d, J = 7.7 Hz), 128.2, 128.1, 127.0, 126.3, 125.1, 116.5(d, J = 7.5 Hz), 115.1(d, J = 22.9 Hz), 114.0,110.3 (d, J = 24.8 Hz), 78.6, 73.7, 31.7.

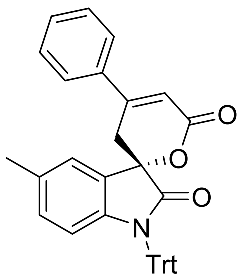
HRMS (ESI$^+$) calcd for $C_{37}H_{27}FNO_3$, *m/z* 552.1969, found 552.1963.

HPLC: Chiralcel AD-H (n-hexane/i-PrOH, 80/20, flow rate 1.0 mL/min, λ = 220 nm), t_R (major) = 6.492 min, t_R (minor) = 11.757 min; 95% ee.

$[\alpha]_D^{25}$ = -42.08 (c = 0.5, $CHCl_3$).

Melting point: 247°C – 248 °C

(S)-5-methyl-4'-phenyl-1-tritylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione 3g



The title compound was prepared according to the typical procedure, as described above, in 88% yield as white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 – 7.50 (m, 2H), 7.46 – 7.40 (m, 9H), 7.25 – 7.17 (m, 10H), 6.76 (dd, J = 8.3, 1.0 Hz, 1H), 6.50 (s, 1H), 6.20 (d, J = 8.4 Hz, 1H), 3.20 (dd, J= 125.0, 17.5 Hz, 2H), 2.18 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 172.4, 162.3, 150.2, 140.3, 139.1, 134.9, 131.3, 129.6, 128.7, 127.9, 127.9, 126.9, 126.6, 125.9, 124.9, 122.9, 115.0, 113.8, 78.6, 73.1, 31.6, 19.5.

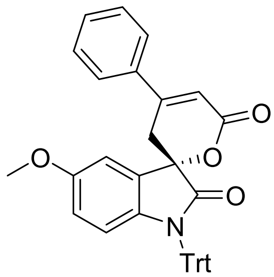
HRMS (ESI$^+$) calcd for $C_{38}H_{30}NO_3$, *m/z* 548.2220, found 548.2228.

HPLC: Chiralcel AD-H (n-hexane/i-PrOH, 70/30, flow rate 1.0 mL/min, λ = 220 nm), t_R(major) = 5.329 min, t_R (minor) = 14.519 min; 75% ee.

$[\alpha]_D^{25}$ = -21.58 (c = 0.5, $CHCl_3$).

Melting point: 217 °C – 218 °C

(S)-5-methoxy-4'-phenyl-1-tritylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione 3h



The title compound was prepared according to the typical procedure, as described above, in 76% yield as white solid.

in ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H), 7.46 – 7.38 (m, 9H), 7.23 (ddd, J = 14.4, 5.7, 3.6 Hz, 9H), 6.99 (d, J = 2.7 Hz, 1H), 6.53 – 6.42 (m, 2H), 6.22 (d, J = 9.0 Hz, 1H), 3.65 (s, 3H), 3.12 (dd, J= 135.0, 20.0 Hz, 2H).

^{13}C NMR (125 MHz, CDCl3) δ 172.4, 162.4, 154.5, 150.4, 140.5, 135.1, 134.8, 129.8, 128.2, 128.1, 128.1, 126.8, 126.1, 125.0, 116.1, 113.0, 114.1, 109.1, 78.9, 73.4, 54.6, 31.9.

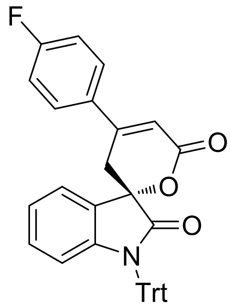
HRMS (ESI$^+$) calcd for $C_{38}H_{30}NO_4$, m/z 564.2169, found 564.2181

HPLC: Chiralcel IA (n-hexane/i-PrOH, 70/30, flow rate 1.0 mL/min, λ = 220 nm), t_R (major) = 7.578 min, t_R (minor) =13.179 min; 71% ee.

$[\alpha]_D^{25}$ = -6.56 (c = 0.5, $CHCl_3$).

Melting point: 232 °C – 233 °C

(S)-4'-(4-fluorophenyl)-1-tritylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione 3i



The title compound was prepared according to the typical procedure, as described above, in 78% yield as white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.48 (m, 2H), 7.45 – 7.39 (m, 7H), 7.26 – 7.19 (m, 9H), 7.13(t, *J* = 8.6 Hz, 2H), 6.97(td, *J* = 7.9, 1.5 Hz, 1H), 6.92 (td, *J* = 7.6, 0.8 Hz, 1H), 6.45 (s, 1H), 6.33 (d, *J* = 7.9 Hz, 1H), 3.16 (dd, *J* = 120.0, 17.5 Hz, 2H).

^{13}C NMR (125 MHz, CDCl3) δ 172.4, 163.2 (d, *J* = 257.3 Hz), 162.2, 149.2, 141.8, 140.4, 131.1 (d, *J* = 3.4 Hz), 128.5, 128.0, 127.1 (d, *J* = 8.6 Hz), 126.9, 126.8, 126.1, 122.1(d, *J* = 63.2 Hz), 115.4, 115.2 (d, *J* = 21.9 Hz), 113.8(d, *J* = 1.26 Hz), 78.5, 73.4, 31.7.

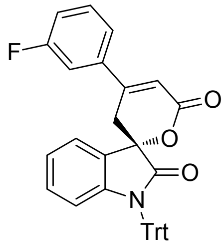
HRMS (ESI$^+$) calcd for $C_{37}H_{27}FNO_3$, *m/z* 552.1969, found 552.1967.

HPLC: ChiralcelIA (n-hexane/i-PrOH, 70/30, flow rate 1.0 mL/min, λ = 220 nm), t_R (major) = 6.555 min, t_R (minor) = 11.251 min; > 99% ee.

$[\alpha]_D^{25}$ = -28.82 (*c* = 0.5, $CHCl_3$).

Melting point: 256 °C – 257 °C

(S)-4'-(3-fluorophenyl)-1-tritylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione 3j



The title compound was prepared according to the typical procedure, as described above, in 81% yield, is white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (ddd, J = 13.6, 5.6, 3.7 Hz, 8H), 7.30 – 7.12 (m, 12H), 6.97 (dtd, J = 14.9, 8.0, 1.1 Hz, 2H), 6.50 (s, 1H), 6.34 (d, J = 8.0 Hz, 1H), 3.17 (dd, J = 100.0, 15.0 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 172.5, 162.1, 162.0(d, J = 244.3 Hz), 148.9 (d, J = 2.4 Hz), 141.9, 140.4, 137.3 (d, J = 7.4 Hz), 129.7 (d, J = 8.3 Hz), 128.6, 128.0, 126.8, 126.1, 122.4, 121.9, 120.8 (d, J = 2.9 Hz), 116.7 (d, J = 21.2 Hz), 115.4, 115.1, 112.2, 112.0, 78.6, 73.5, 31.8.

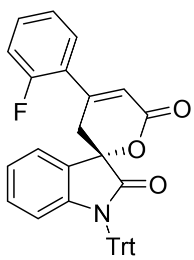
HRMS (ESI$^+$) calcd for $C_{37}H_{27}FNO_3$, *m/z* 552.1969, found 552.1963.

HPLC: Chiralcel IA (n-hexane/i-PrOH, 70/30, flow rate 1.0 mL/min, λ = 220 nm), t_R (major) = 7.129 min, t_R (minor) = 13.284 min; 97% ee.

$[\alpha]_D^{25}$ = -31.46 (c = 0.5, $CHCl_3$).

Melting point: 215 °C-216 °C

(S)-4'-(2-fluorophenyl)-1-tritylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione 3k



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

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (ddd, *J* = 13.9, 5.5, 3.4 Hz, 8H), 7.31 – 7.15 (m, 12H), 6.96 (tdd, *J* = 15.0, 10.9, 4.5 Hz, 2H), 6.49 (s, 1H), 6.34 (d, *J* = 8.2 Hz, 1H), 3.16 (dd, *J* = 100.0, 15.0 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 172.5, 162.1, 162.0 (d, *J* = 246.2 Hz), 148.9, 141.9, 140.4, 137.3 (d, *J* = 6.3 Hz), 129.7 (d, *J* = 8.8 Hz), 128.6, 128.1, 126.9, 126.8, 126.1, 122.4, 122.0, 120.8 (d, *J* = 2.5 Hz), 116.7 (d, *J* = 21.2 Hz), 115.5, 115.1, 112.1 (d, *J* = 22.5 Hz), 78.6, 73.5, 31.8.

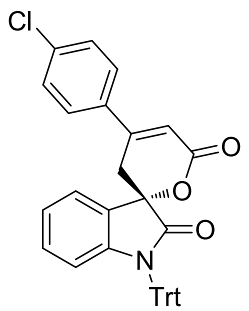
HRMS (ESI^+) calcd for $C_{37}H_{27}FNO_3$, *m/z* 552.1969, found 552.1966.

HPLC: Chiralcel IA (n-hexane/i-PrOH, 70/30, flow rate 1.0 mL/min, λ = 220 nm), t_R (major) = 6.927 min, t_R (minor) = 10.918 min; > 99% ee.

$[\alpha]_D^{25}$ = -35.18 (*c* = 0.5, $CHCl_3$).

Melting point: 188 ˚C – 189 ˚C

(S)-4'-(4-chlorophenyl)-1-tritylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione 3l



The title compound was prepared according to the typical procedure, as described above, in 86% yield as white solid.

[1]H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.37 (m, 11H), 7.26 – 7.18 (m, 9H), 6.98 (td, *J* = 7.9, 1.4 Hz, 1H), 6.92 (t, *J* = 7.3 Hz, 1H), 6.48 (s, 1H), 6.33 (d, *J* = 8.1 Hz, 1H), 3.16 (dd, *J* = 105.0, 17.5 Hz, 2H).

[13]C NMR (125 MHz, $CDCl_3$) δ 172.5, 162.2, 149.0, 141.9, 140.4, 136.0, 133.4, 128.6, 128.3, 128.0, 126.9, 126.8, 126.3, 126.1, 122.4, 121.9, 115.4, 114.3, 78.6, 73.5, 31.7.

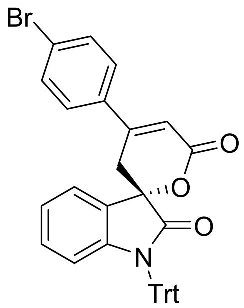
HRMS (ESI^+) calcd for $C_{37}H_{27}ClNO_3$,*m/z* 568.1674, found 568.1681.

HPLC: ChiralcelAD (n-hexane/i-PrOH, 70/30, flow rate 1.0 mL/min, λ = 220 nm), t_R (major) = 5.878 min, t_R (minor) = 12.023 min; 78% ee.

$[\alpha]_D^{25}$ = -57.72 (*c* = 0.5, $CHCl_3$).

Melting point: 217 °C-218 °C

(S)-4'-(4-bromophenyl)-1-tritylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione 3m



The title compound was prepared according to the typical procedure, as described above, in 73% yield as yellow solid.

[1]H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.6 Hz, 2H), 7.47 – 7.31 (m, 9H), 7.27 – 7.19 (m, 9H), 6.98 (td, *J* = 7.9, 1.4 Hz, 1H), 6.93 (t, *J* = 7.3 Hz, 1H), 6.49 (s, 1H), 6.33 (d, *J* = 8.1 Hz, 1H), 3.15 (dd, *J* = 100.0, 17.5 Hz, 2H).

[13]C NMR (125 MHz, $CDCl_3$) δ 172.5, 162.2, 149.1, 141.9, 140.4, 133.9, 131.3, 128.6,

128.0, 126.8, 126.5, 126.1, 124.3, 122.4, 121.9, 115.4, 114.4, 78.6, 73.5, 31.6.

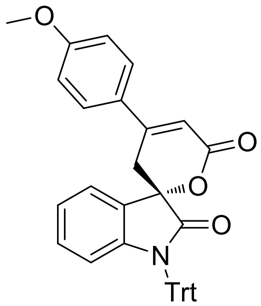
HRMS (ESI$^+$) calcd for $C_{37}H_{27}BrNO_3$, *m/z* 612.1023, found 612.1027.

HPLC: Chiralcel IA (n-hexane/i-PrOH, 80/20, flow rate 1.0 mL/min, λ = 220 nm), t_R (major) = 12.004 min, t_R (minor) = 25.981min; 89% ee.

$[\alpha]_D^{25}$ = -41.30 (*c* = 0.5, $CHCl_3$).

Melting point: 201 °C – 202 °C

(S)-4'-(4-methoxyphenyl)-1-tritylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione 3n



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

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 1H), 7.34 (dd, *J* = 8.3, 1.2 Hz, 6H), 7.21 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.19 – 7.09 (m, 10H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.89 – 6.83 (m, 3H), 6.28 (s, 1H), 6.25 – 6.22 (m, 1H), 3.73 (s, 3H), 3.21 (dd, *J* = 135.0, 15.0 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 172.5, 162.7, 160.9, 150.0, 141.8, 140.5, 128.4, 128.1, 127.2, 127.1, 126.8, 126.7, 126.1, 122.4, 121.8, 115.4, 113.4, 111.6, 78.6, 73.4, 54.5, 31.4.

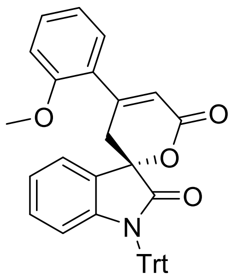
HRMS (ESI$^+$) calcd for $C_{38}H_{30}NO_4$, *m/z* 564.2169, found 564.2163.

HPLC: Chiralcel AD-H (n-hexane/i-PrOH, 70/30, flow rate 1.0 mL/min, λ = 220 nm), t_R (major) = 8.586 min, t_R (minor) = 16.954 min; >99% ee.

$[\alpha]_D^{25}$ = -35.84 (c = 0.5, $CHCl_3$).

Melting point: 222 °C-223 °C

(S)-4'-(2-methoxyphenyl)-1-tritylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione 3o



The title compound was prepared according to the typical procedure, as described above, in 77% yield as white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (dd, J = 7.2, 1.6 Hz, 1H), 7.37 – 7.29 (m, 7H), 7.20 – 7.09 (m, 10H), 6.96 – 6.82 (m, 4H), 6.28 (s, 1H), 6.25 – 6.21 (m, 1H), 3.73 (s, 3H), 3.21 (dd, J = 135.0, 15.0 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.0, 162.6, 156.1, 151.0, 141.7, 140.5, 130.3, 128.2, 128.1, 128.0, 127.2, 126.8, 126.0, 125.7, 122.6, 121.6, 120.0, 116.9, 115.2, 110.2, 79.2, 73.3, 54.4, 33.8.

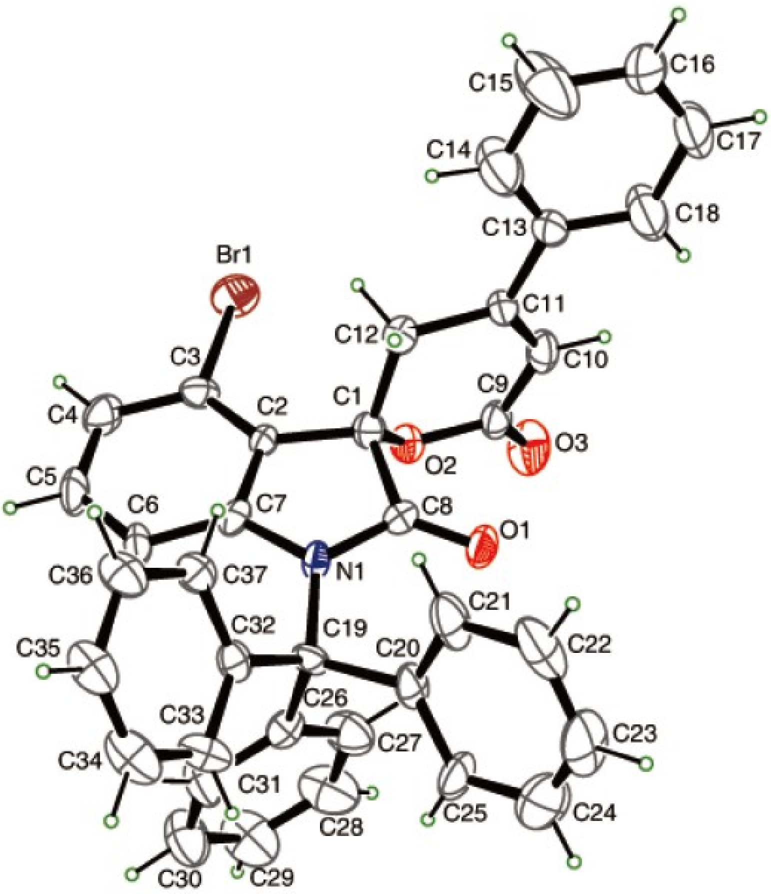
HRMS (ESI$^+$) calcd for $C_{38}H_{30}NO_4$, m/z 564.2169, found 564.2163.

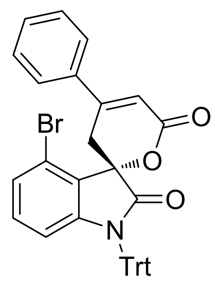
HPLC: Chiralcel IA (n-hexane/i-PrOH, 70/30, flow rate 1.0 mL/min, λ = 220 nm), t_R (major) = 6.990 min, t_R (minor) = 9.727 min; 94% ee.

$[\alpha]_D^{25}$ = -25.78(c = 0.5, $CHCl_3$).

Melting point: 180 °C-181 °C

X-ray crystal structure of 3d





3d

Figure S1 X-ray crystal structure of 3d. Thermal ellipsoids were shown at 50% probality.

Computational methods and structural geometries

Density functional theory calculations were employed with Gaussian 09 package.[1] B3LYP theory was applied,[2, 3] and 6-31G(d,p) Pople basis set was used for the rest of atoms.[4, 5, 6] All structures were optimized as energy minima or transition state using the theory. Atoms are color coded (Gray = C; blue = N; red = O; green = F; white = H).

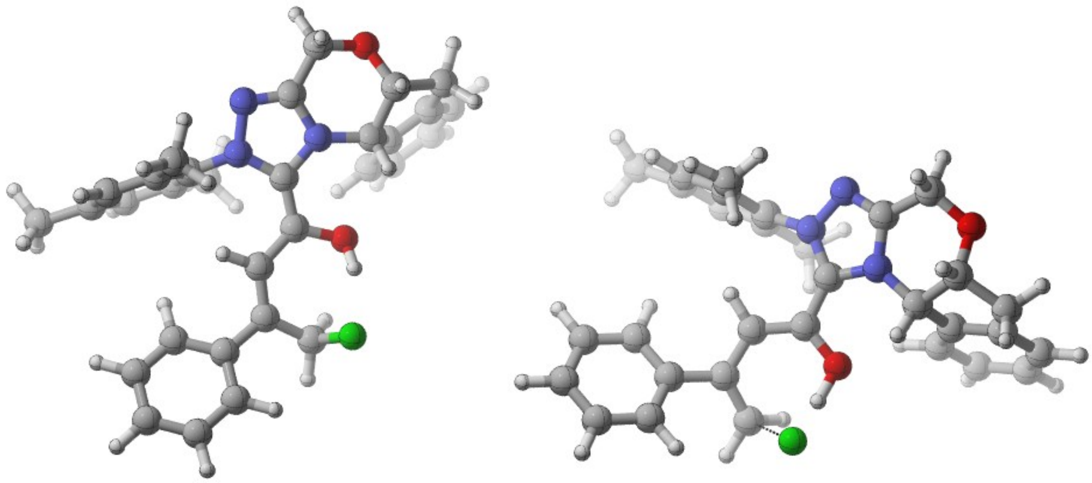


Figure S2 (Left) Structure of optimized Breslow intermediate II, 0 kcal/mol. (Right) Transition state (TS) structure of C-F bond cleavage. 10.8 kcal/mol. Bond distance of C···F in this transition state is 1.95 Å.

Cartesian coordinates of optimized structures and transition state

Breslow intermediate II

Zero-point correction= 0.548308 (Hartree/Particle)
Sum of electronic and zero-point Energies= -1613.350911
Sum of electronic and thermal Energies= -1613.318398
Sum of electronic and thermal Enthalpies= -1613.317454
Sum of electronic and thermal Free Energies= -1613.417000

C	-2.06756300	2.18203200	-0.06706600
C	-1.41698800	3.50324500	0.18680000
H	-0.63627500	3.44274300	0.94732200
H	-2.14271800	4.26634900	0.47031600
F	-0.75273500	4.00431500	-0.99373200
C	-3.54240000	2.15275100	-0.18000300
C	-6.36564000	2.11703400	-0.42206100
C	-4.30217000	1.05700300	0.27695600
C	-4.24305300	3.23187600	-0.75666000
C	-5.63124600	3.21477000	-0.87421800
C	-5.68920000	1.03805100	0.15136900
H	-3.79942800	0.22348700	0.75865100

H	-3.68640400	4.07785800	-1.15009100
H	-6.13986000	4.05884000	-1.33237200
H	-6.24684700	0.18079900	0.51941300
H	-7.44783200	2.10370900	-0.51216500
C	0.70337600	-0.36362800	-0.48830100
N	0.17558600	-1.64920500	-0.40425600
N	1.12262300	-2.62089900	-0.73836000
C	2.20445500	-1.95295700	-0.96924300
N	2.04946900	-0.59286000	-0.81109800
C	3.17786200	0.34321700	-0.91328200
H	2.83681300	1.20775200	-1.48658800
C	3.49445300	-2.51668600	-1.48326300
H	3.41405400	-2.66702200	-2.57350900
H	3.69318200	-3.48579100	-1.02124100
C	-1.08150100	-2.10163600	0.10527200
C	-3.52065200	-3.06603500	1.08489600
C	-2.01073300	-2.65614100	-0.79315500
C	-1.33748900	-2.03710800	1.48638400
C	-2.56913400	-2.51225200	1.94760700
C	-3.22044400	-3.13046000	-0.27991700
H	-2.78176500	-2.46142400	3.01282400
H	-3.94910200	-3.55464400	-0.96648400
C	-1.33481800	1.03145400	-0.24001800
H	-1.90586400	0.12855700	-0.42377900
C	0.07546000	0.86606000	-0.34335800
O	0.93233300	1.96968200	-0.33802700
H	0.50839800	2.68561500	-0.84667200
O	4.57777400	-1.66107600	-1.17776900
C	4.37509300	-0.32743300	-1.64623400
H	4.23760300	-0.33305000	-2.73763300
C	5.59349600	0.48101600	-1.17801200
H	5.74736500	1.34778400	-1.83434300
H	6.49740800	-0.13336900	-1.21941500
C	3.81316300	0.80821800	0.39122800
C	5.19952400	0.90768600	0.21977300
C	6.01046600	1.35339600	1.25970100
H	7.08718400	1.42591600	1.13137800
C	5.41888500	1.69208100	2.47995600
H	6.03956800	2.03260600	3.30374300
C	4.03519800	1.59149800	2.64856200
H	3.58796000	1.85849900	3.60159400
C	3.21871600	1.15484100	1.60102900
H	2.14395400	1.09931900	1.72699600
C	-4.82513900	-3.61088300	1.61635700

H	-5.63278500	-3.49577000	0.88735700
H	-5.12433000	-3.10514600	2.53881100
H	-4.74252600	-4.68123100	1.84291100
C	-1.71173900	-2.72984700	-2.26975400
H	-2.56997800	-3.12206800	-2.82050700
H	-0.84892000	-3.37485400	-2.46398100
H	-1.46901900	-1.74162300	-2.67533000
C	-0.32309100	-1.46976700	2.44627600
H	-0.62578700	-1.64993700	3.48056200
H	-0.20962300	-0.38854100	2.30814800
H	0.66270600	-1.92069400	2.29428500

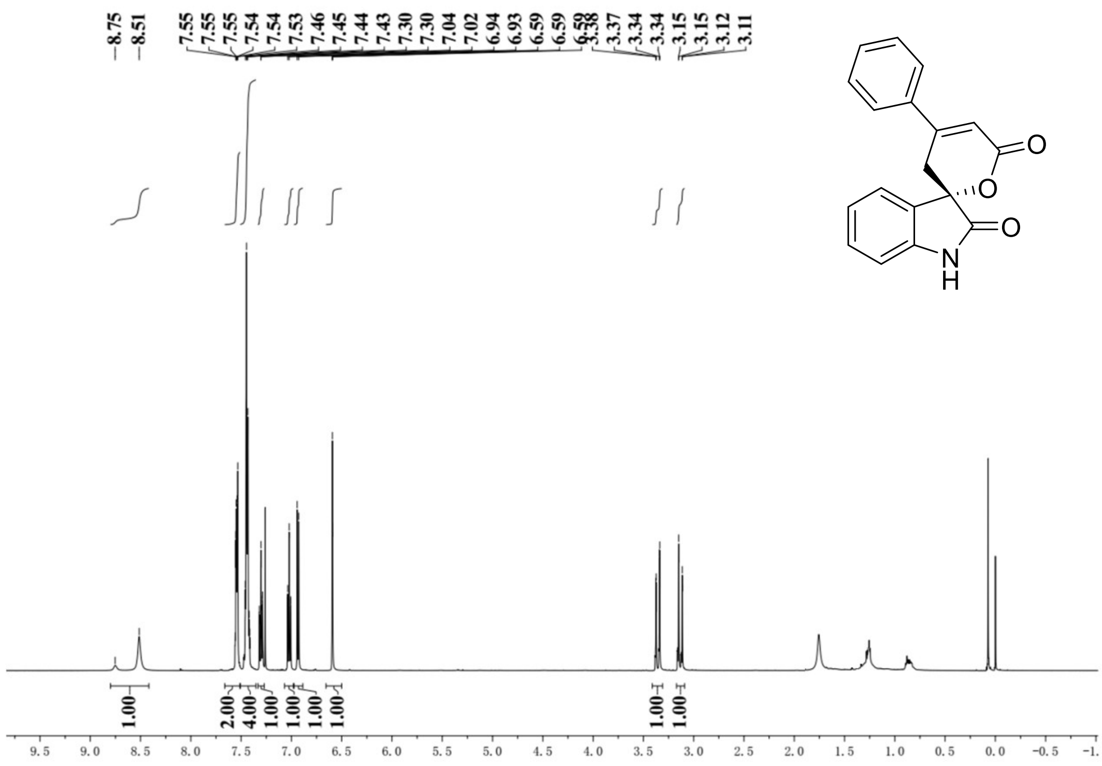
TS for C-F bond cleavage

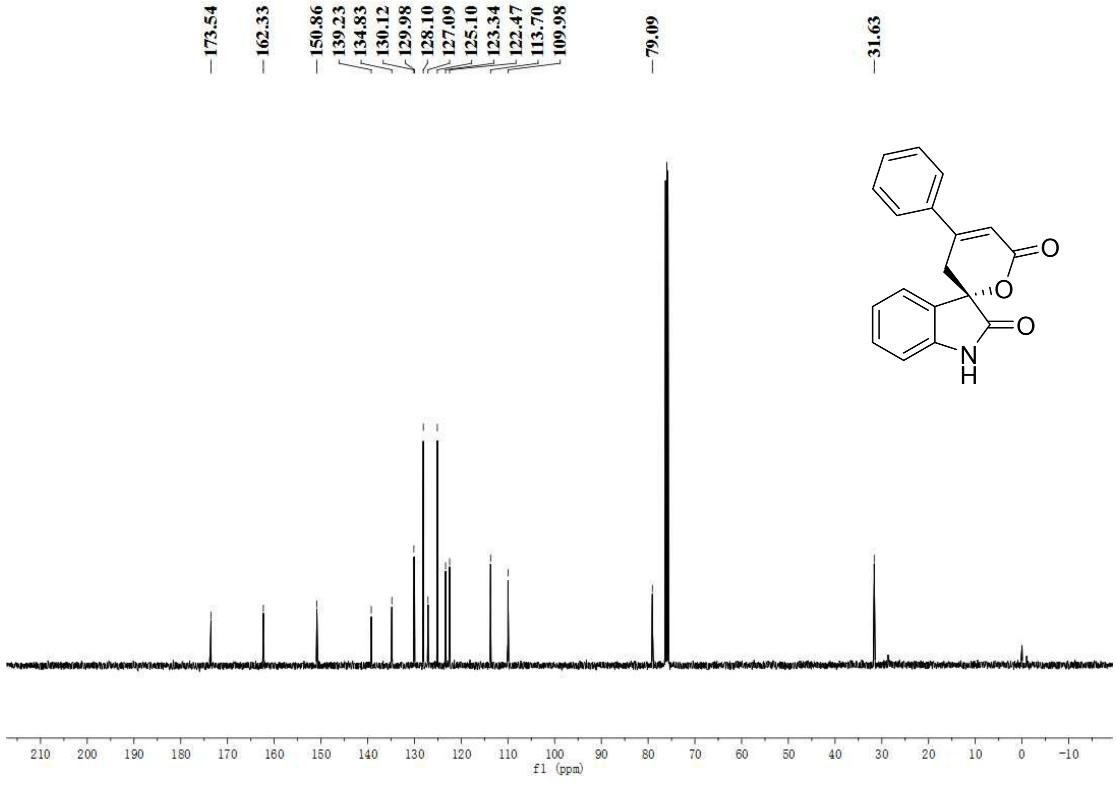
Zero-point correction= 0.543161 (Hartree/Particle)
Sum of electronic and zero-point Energies= -1613.334038
Sum of electronic and thermal Energies= -1613.301974
Sum of electronic and thermal Enthalpies= -1613.301030
Sum of electronic and thermal Free Energies= -1613.399863

C	-2.09671500	2.13414500	0.47137700
C	-1.47670500	3.17450000	1.15174200
H	-0.64407700	2.97414000	1.80985200
H	-2.03842600	4.07450000	1.37257700
F	-0.15474800	3.93689300	-0.05666000
C	-3.46965900	2.31969300	-0.06703800
C	-6.07559300	2.72673000	-1.08001300
C	-4.42922500	1.29277500	-0.03138400
C	-3.84330800	3.55155100	-0.63451200
C	-5.13105800	3.75414900	-1.12746200
C	-5.71454500	1.49389900	-0.53318200
H	-4.17282900	0.33415300	0.41238300
H	-3.09689000	4.33663300	-0.71407100
H	-5.39256300	4.71376000	-1.56552600
H	-6.44095200	0.68657600	-0.48705200
H	-7.07800800	2.88301500	-1.46794800
C	0.60695000	-0.40904400	-0.30564600
N	0.07661000	-1.67277900	-0.35882200
N	0.96874400	-2.58410500	-0.90477700
C	2.03878100	-1.88716800	-1.13743600
N	1.90254700	-0.57041700	-0.76779800
C	2.99986300	0.41064600	-0.91222100
H	2.55294900	1.33021500	-1.29345300

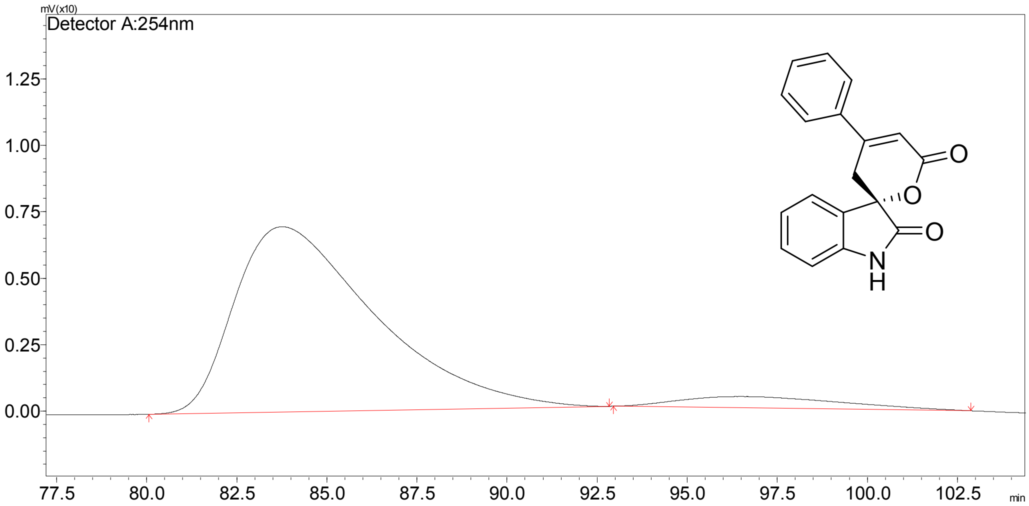
C	3.26434000	-2.36667800	-1.85653700
H	3.03547800	-2.43492900	-2.93369000
H	3.54152500	-3.36387400	-1.50744500
C	-1.17645700	-2.17804600	0.12954600
C	-3.58145500	-3.24880800	1.05728600
C	-2.15626400	-2.55376200	-0.80367300
C	-1.35427800	-2.34570900	1.51313900
C	-2.57050700	-2.87621100	1.94993600
C	-3.35119600	-3.08698300	-0.31278000
H	-2.72620200	-3.01153600	3.01735400
H	-4.12105300	-3.38147600	-1.02142800
C	-1.37758000	0.94689600	0.15640000
H	-1.95349600	0.09984300	-0.19586900
C	0.00748300	0.83274400	0.07273100
O	0.88975200	1.83662300	0.24830900
H	0.44550700	2.83218700	0.04611800
O	4.35861200	-1.50870800	-1.62416800
C	4.06965100	-0.13470100	-1.90019300
H	3.76446800	-0.01939600	-2.95023600
C	5.33945900	0.64108800	-1.52720900
H	5.37439700	1.59389500	-2.07144200
H	6.23037000	0.06756500	-1.79809100
C	3.82783000	0.70867900	0.33119700
C	5.17003200	0.85945300	-0.03915400
C	6.13372600	1.18090200	0.91228500
H	7.17646400	1.29485600	0.62852000
C	5.74009500	1.34283700	2.24345700
H	6.48187900	1.58488000	2.99902500
C	4.39875100	1.19847700	2.60828700
H	4.10458100	1.33681700	3.64447900
C	3.42765100	0.88942300	1.65145900
H	2.38145200	0.82353400	1.92356400
C	-4.89472300	-3.79524200	1.56375600
H	-5.58762000	-2.98305200	1.81535900
H	-4.75579300	-4.39405000	2.46877600
H	-5.38429900	-4.42138500	0.81271500
C	-1.93095000	-2.38615000	-2.28595500
H	-2.82929800	-2.65471100	-2.84611500
H	-1.10566500	-3.01599900	-2.63322000
H	-1.67431700	-1.35080200	-2.53573500
C	-0.28018400	-1.96118700	2.49857300
H	-0.52679900	-2.32327400	3.49919800
H	-0.16746600	-0.87226500	2.55166400
H	0.69194400	-2.37746500	2.21566700

3a

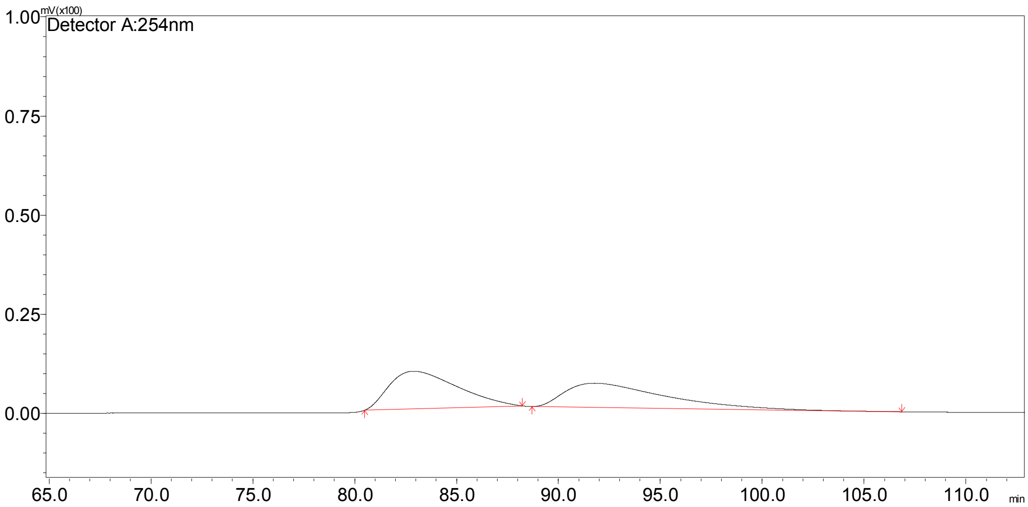

8.75
8.51
7.55
7.55
7.55
7.54
7.54
7.53
7.46
7.45
7.44
7.43
7.30
7.30
7.04
7.02
6.94
6.93
6.59
6.59
6.59
3.38
3.37
3.34
3.34
3.15
3.15
3.12
3.11
1.00
2.00
4.00
1.00
1.00
1.00
1.00
1.00
1.00
O
O
O
NH


173.54
162.33
150.86
139.23
134.83
130.12
129.98
128.10
127.09
125.10
123.34
122.47
113.70
109.98
79.09
31.63
O
O
O
NH
f1 (ppm)

3a

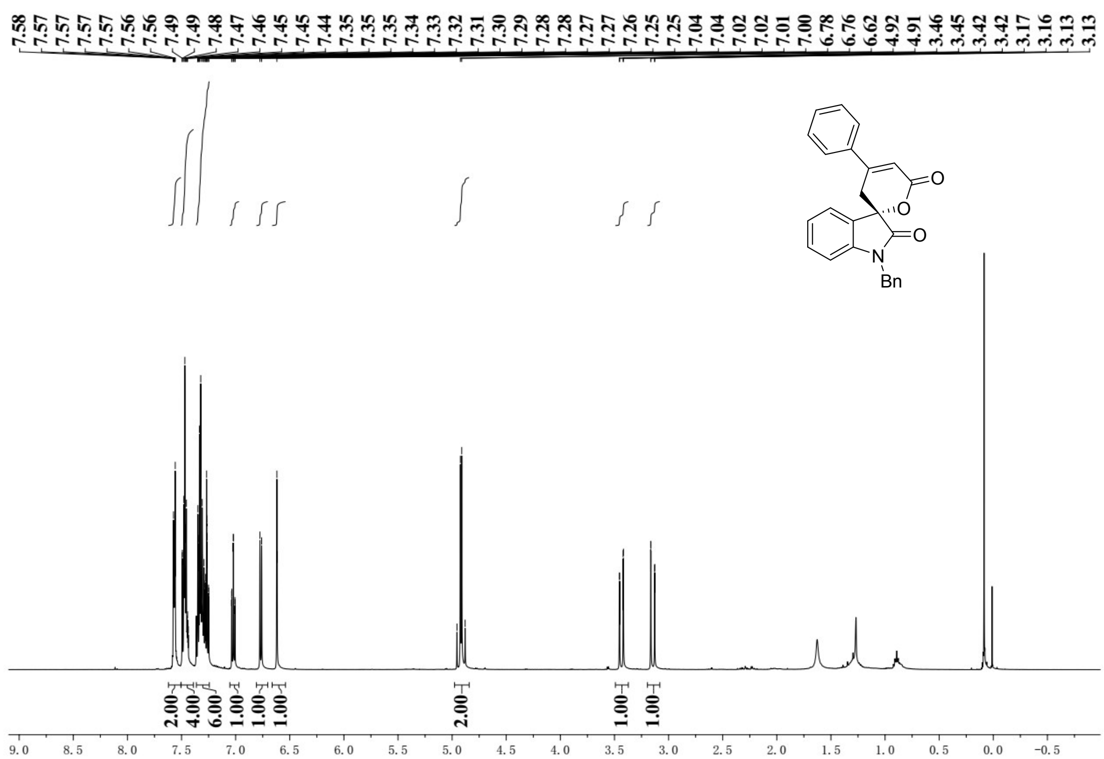


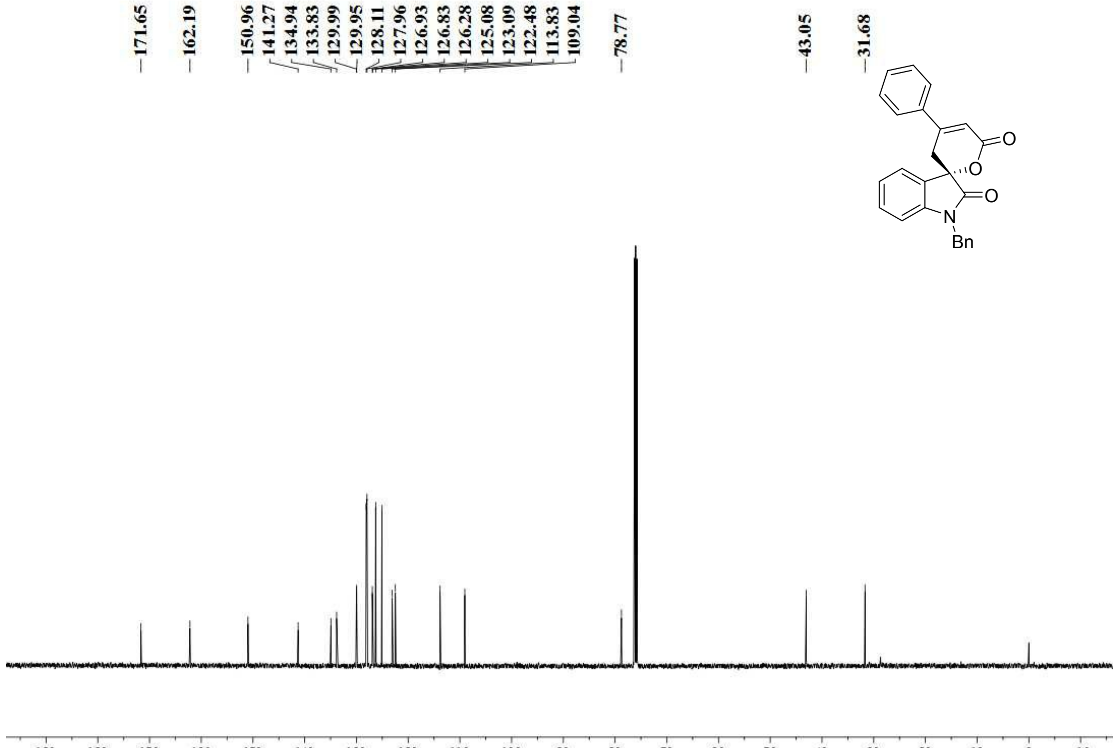
Peak	Ret .Time	Area	Height	Area %	Height %
1	83.790	1898974	6969	93.436	94.230
2	96.502	133407	427	6.564	5.770
Total		2032382	7395	100.000	100.000



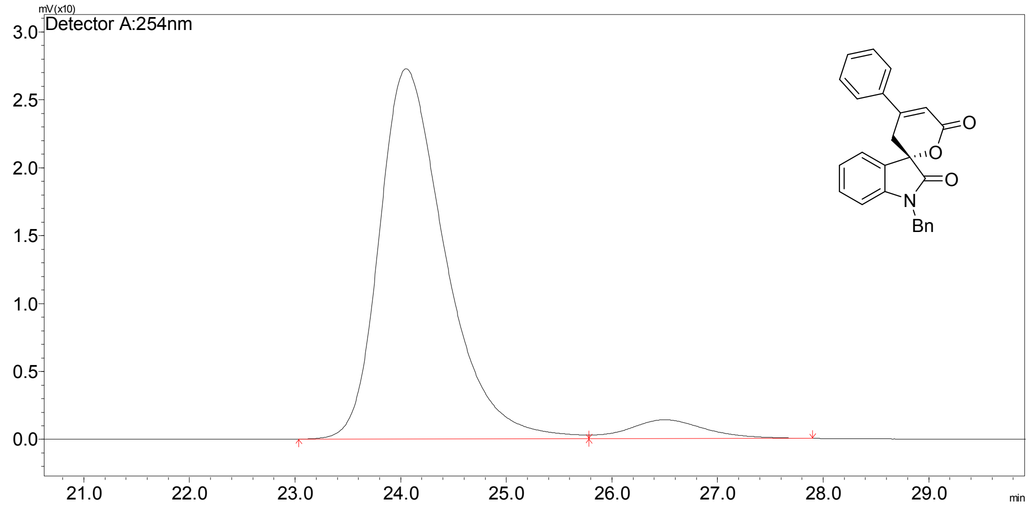
Peak	Ret .Time	Area	Height	Area %	Height %
1	82.890	2211594	9506	51.284	60.819
2	91.764	2100848	6124	48.716	39.181
Total		4312442	15630	100.000	100.000

3b

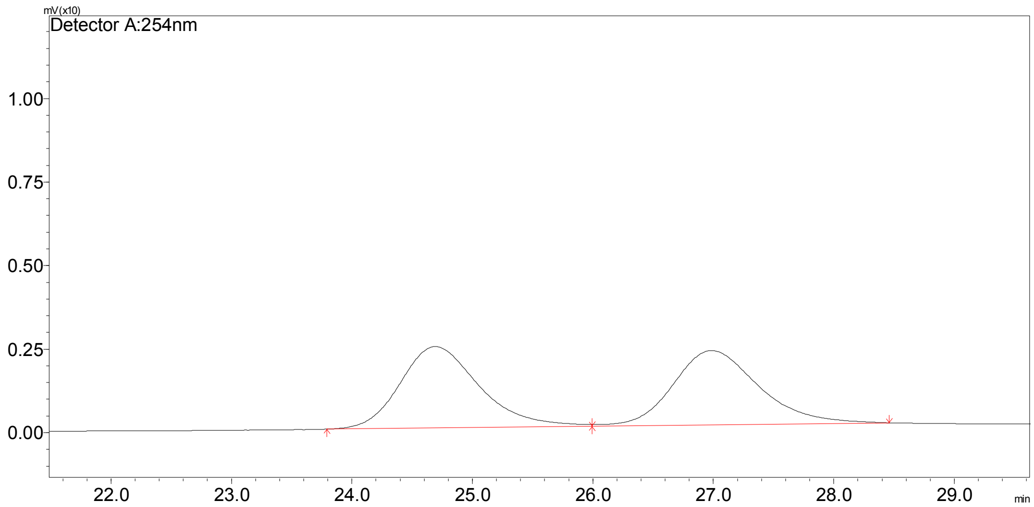

7.58
7.57
7.57
7.57
7.57
7.56
7.56
7.49
7.49
7.48
7.47
7.46
7.45
7.45
7.44
7.35
7.35
7.35
7.34
7.33
7.32
7.31
7.30
7.29
7.28
7.28
7.27
7.27
7.26
7.25
7.25
7.04
7.04
7.02
7.02
7.01
7.00
6.78
6.76
6.62
4.92
4.91
3.46
3.45
3.42
3.42
3.17
3.16
3.13
3.13
O
O
O
N
Bn
2.00
4.00
6.00
1.00
1.00
1.00
2.00
1.00
1.00


171.65
162.19
150.96
141.27
134.94
133.83
129.99
129.95
128.11
127.96
126.93
126.83
126.28
125.08
123.09
122.48
113.83
109.04
78.77
43.05
31.68
O
O
O
N
Bn
f1 (ppm)

3b

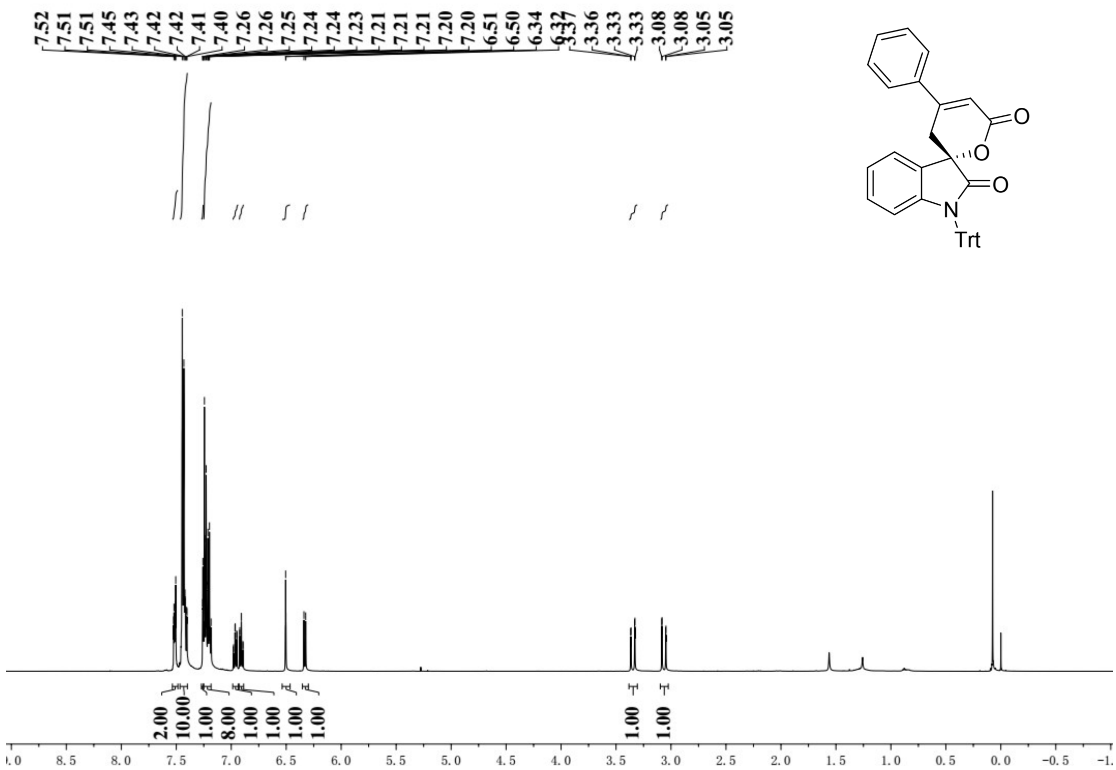


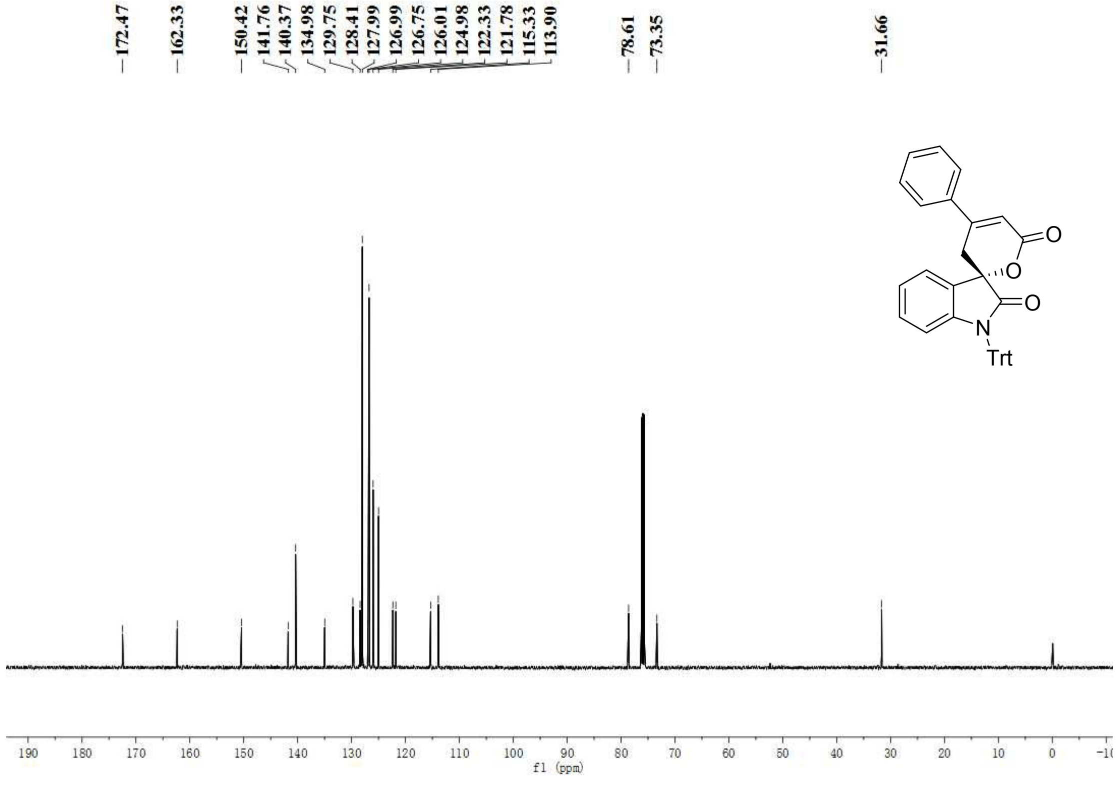
Peak	Ret .Time	Area	Height	Area%	Height%
1	24.047	1157858	27141	96.281	96.066
2	26.494	44721	1111	3.719	3.934
Total		1202578	28252	100.000	100.000



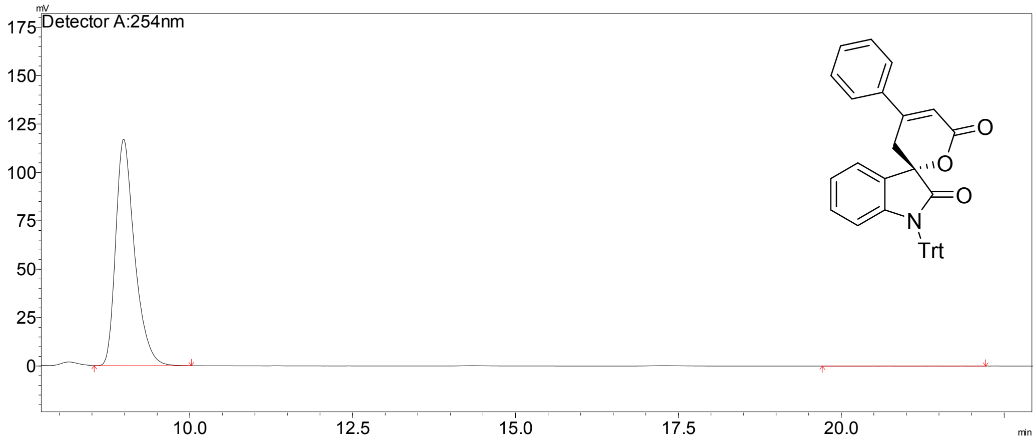
Peak	Ret .Time	Area	Height	Area%	Height%
1	24.686	111362	2435	50.333	52.287
2	26.982	109890	2222	49.667	47.713
Total		221252	4658	100.000	100.000

3c

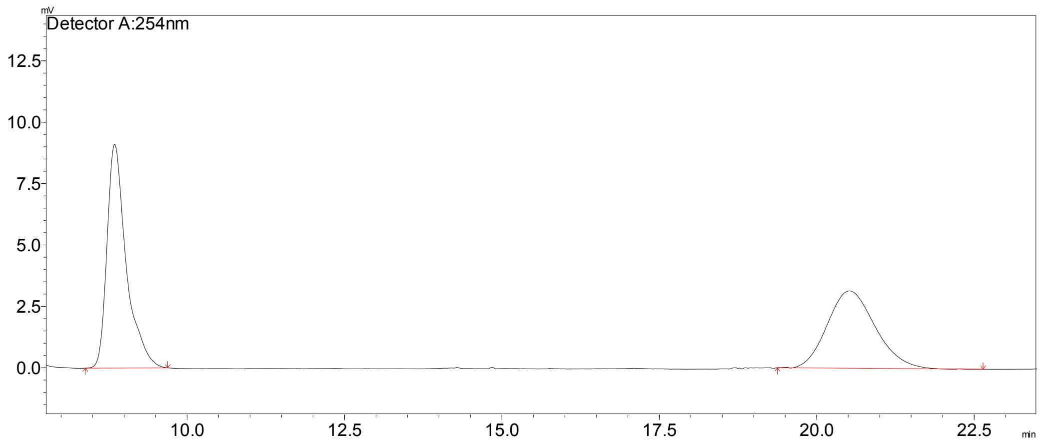




3c

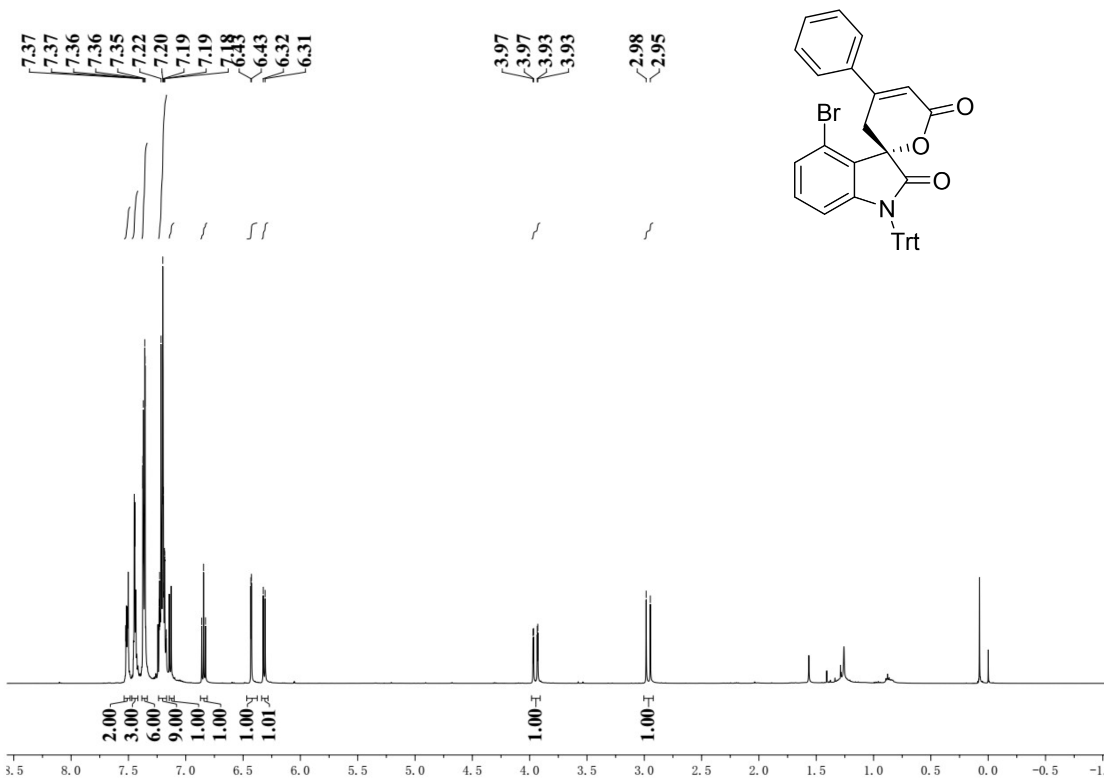


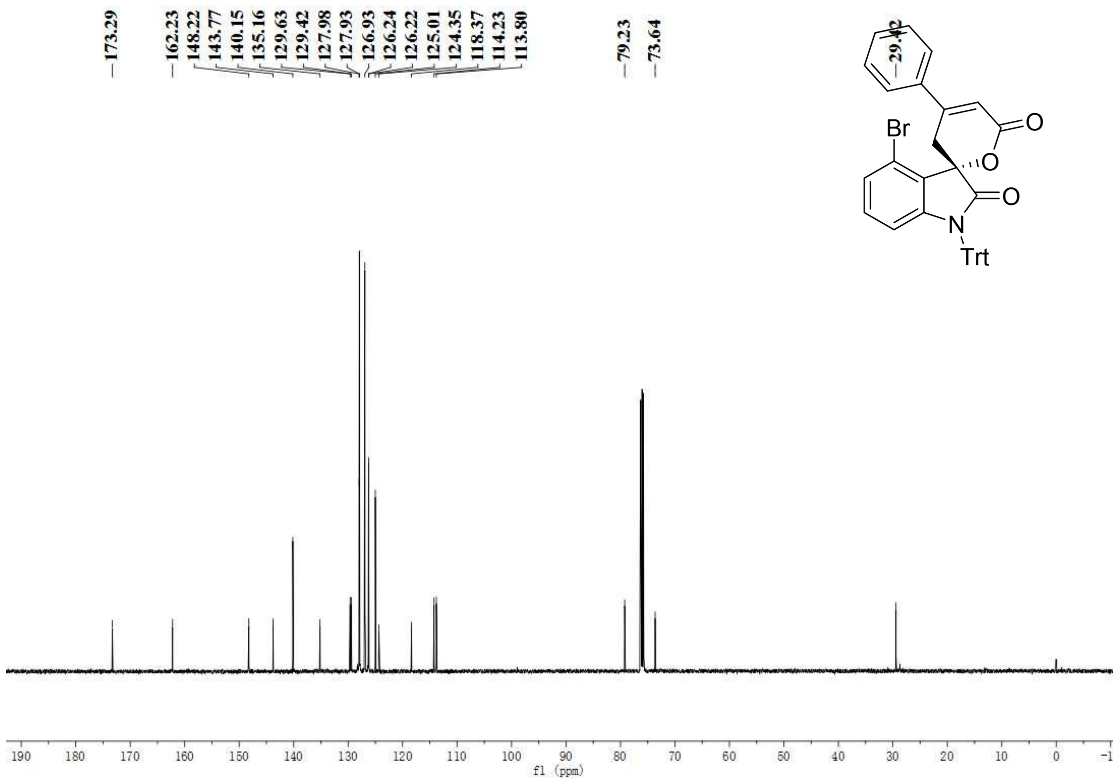
Peak	Ret .Time	Area	Height	Area%	Height%
1	8.980	2361916	117082	99.936	99.958
2	21.374	1514	49	0.064	0.042
Total		2363430	117131	100.000	100.000



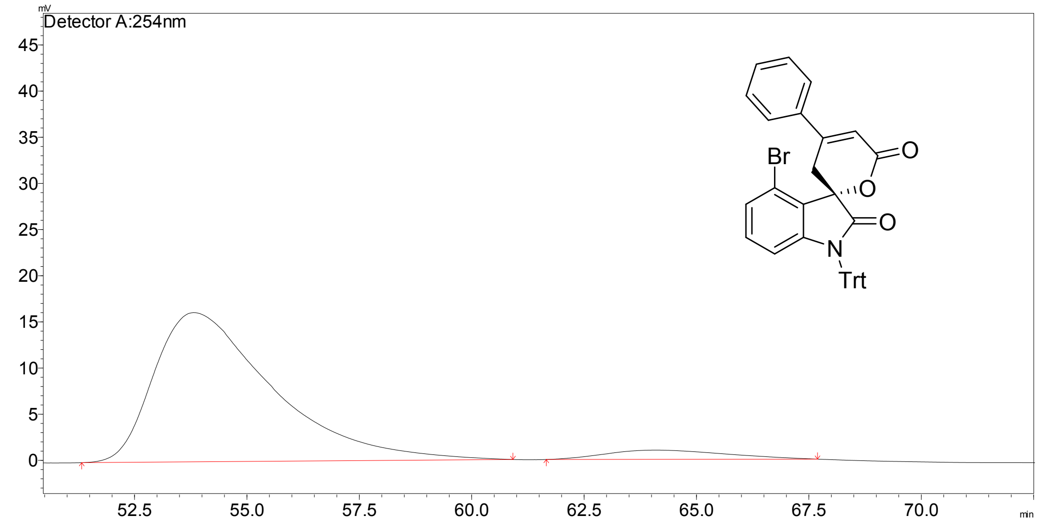
Peak	Ret .Time	Area	Height	Area%	Height%
1	8.845	194074	9114	53.873	74.333
2	20.517	166167	3147	46.127	25.667
Total		360241	12261	100.000	100.000

3d

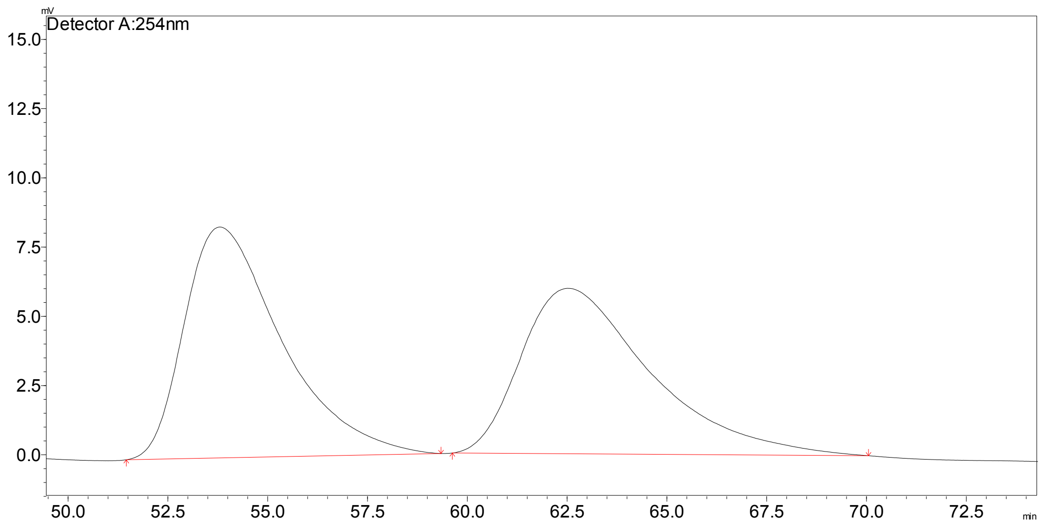

7.37
7.37
7.36
7.36
7.35
7.22
7.20
7.19
7.19
7.18
6.43
6.43
6.32
6.31
3.97
3.97
3.93
3.93
2.98
2.95
2.00
3.00
6.00
9.00
1.00
1.00
1.00
1.01
1.00
1.00
Br
O
O
O
N
Trt


173.29
162.23
148.22
143.77
140.15
135.16
129.63
129.42
127.98
127.93
126.93
126.24
126.22
125.01
124.35
118.37
114.23
113.80
79.23
73.64
29.42
Br
O
O
O
N
Trt
f1 (ppm)

3d

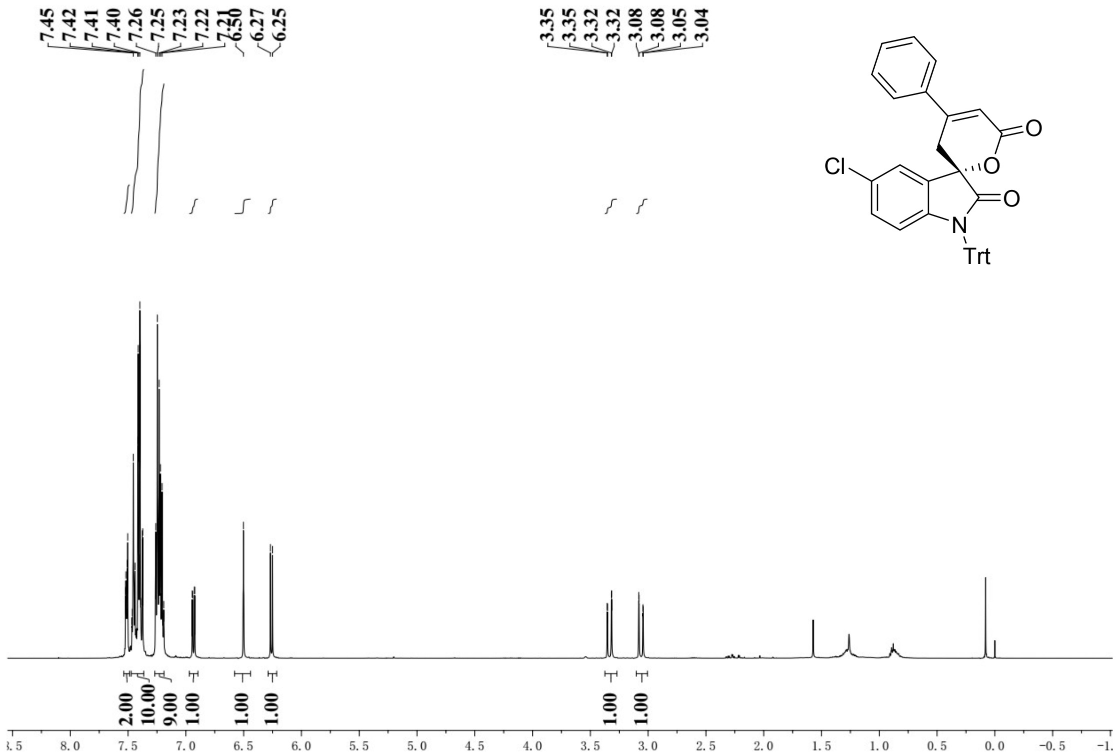


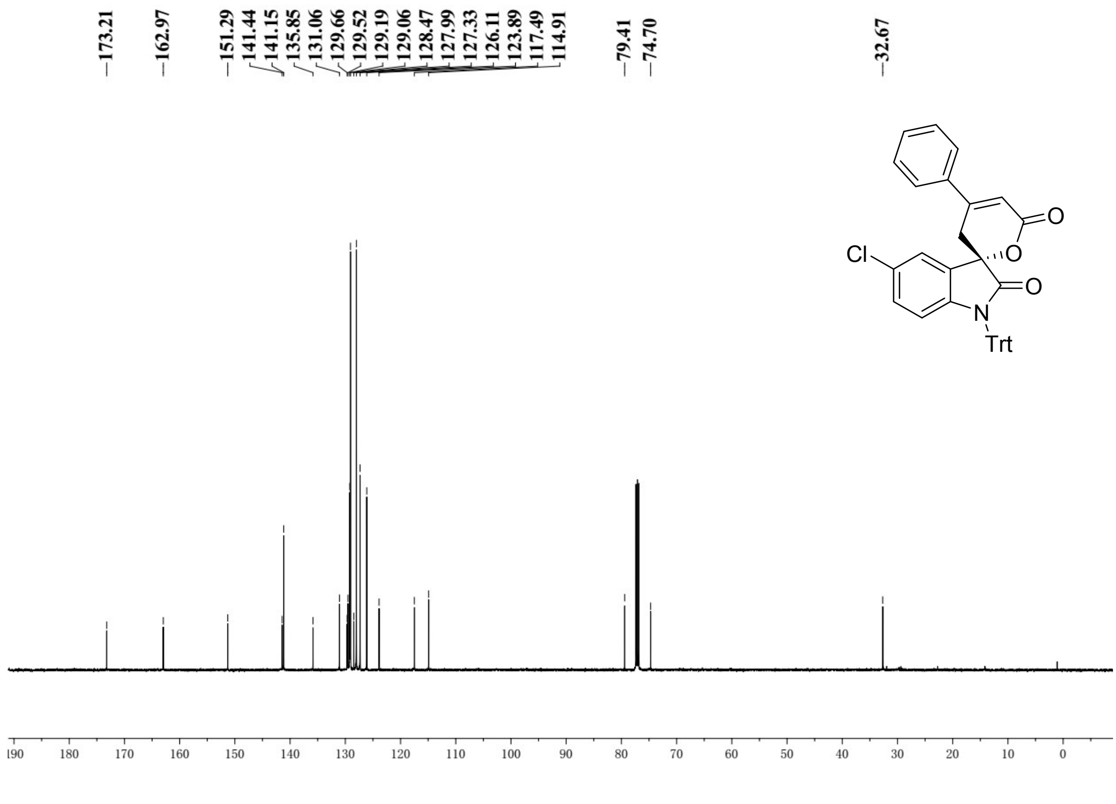
Peak	Ret .Time	Area	Height	Area%	Height%
1	53.813	2966699	16166	94.169	94.169
2	64.090	185638	1001	5.889	5.831
Total		3152337	17167	100.000	100.000



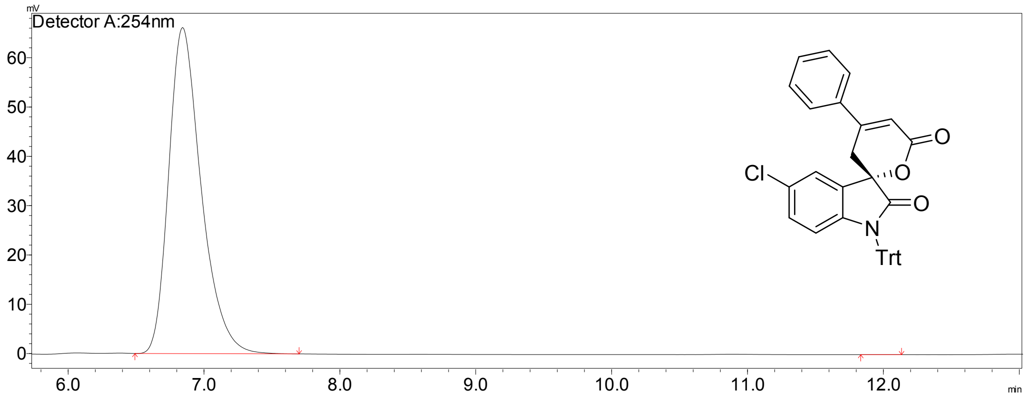
Peak	Ret .Time	Area	Height	Area%	Height%
1	53.798	1413661	8338	51.234	58.256
2	62.502	1345546	5974	48.766	41.744
Total		2759207	14312	100.000	100.000

3e

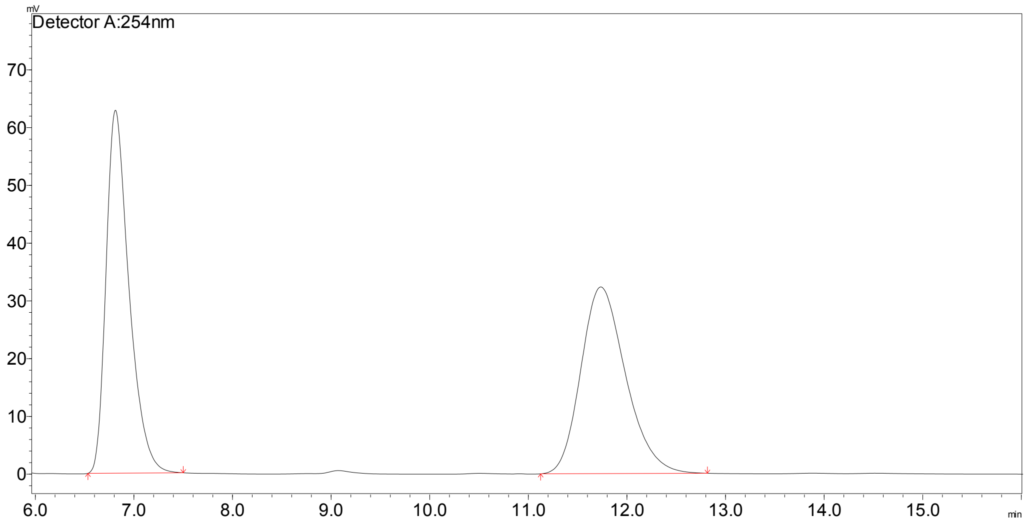

7.45
7.42
7.41
7.40
7.26
7.25
7.23
7.22
7.21
6.50
6.27
6.25
3.35
3.35
3.32
3.32
3.08
3.08
3.05
3.04
Cl
O
O
O
N
Trt
2.00
10.00
9.00
1.00
1.00
1.00
1.00
1.00


173.21
162.97
151.29
141.44
141.15
135.85
131.06
129.66
129.52
129.19
129.06
128.47
127.99
127.33
126.11
123.89
117.49
114.91
79.41
74.70
32.67
Cl
O
O
O
N
Trt

3e

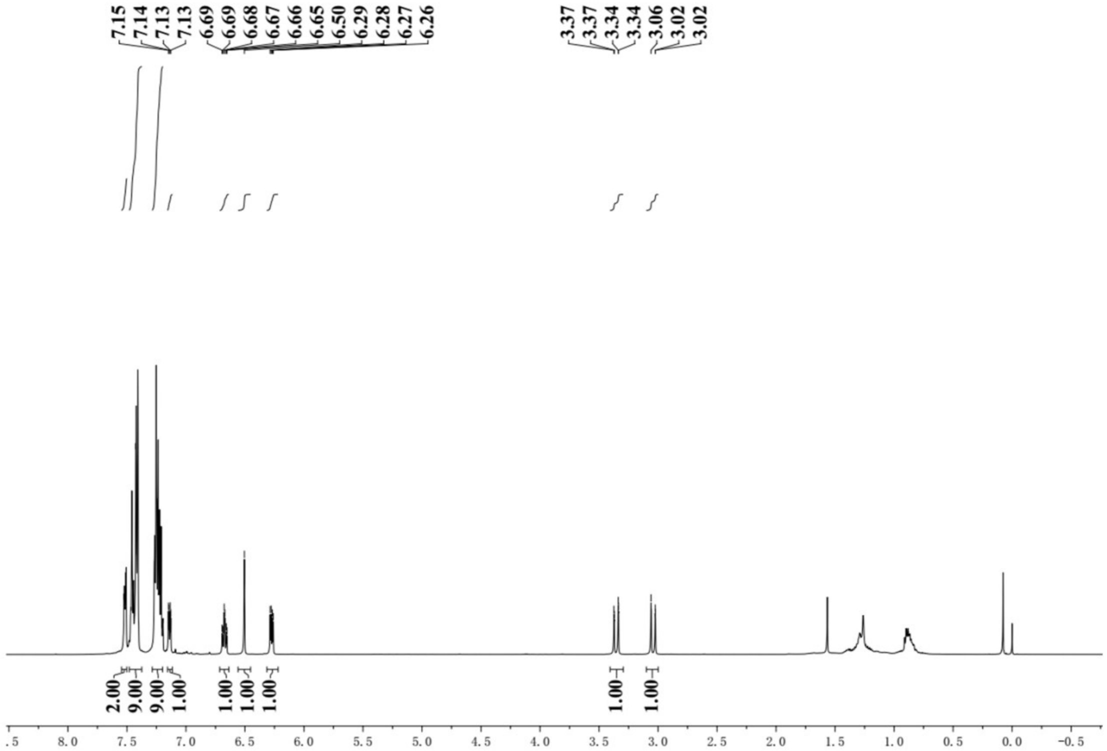


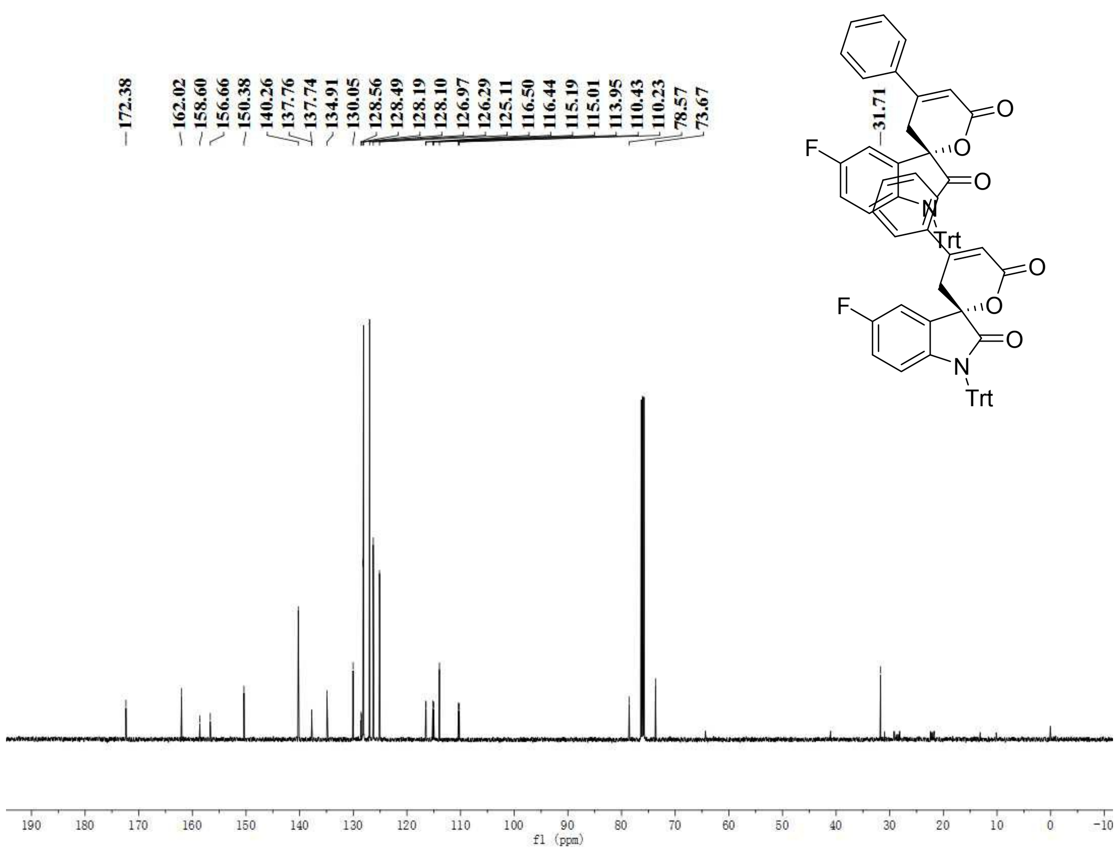
Peak	Ret .Time	Area	Height	Area%	Height%
1	6.838	1098531	66148	99.999	99.997
2	12.086	15	2	0.001	0.003
Total		1098545	66150	100.000	100.000



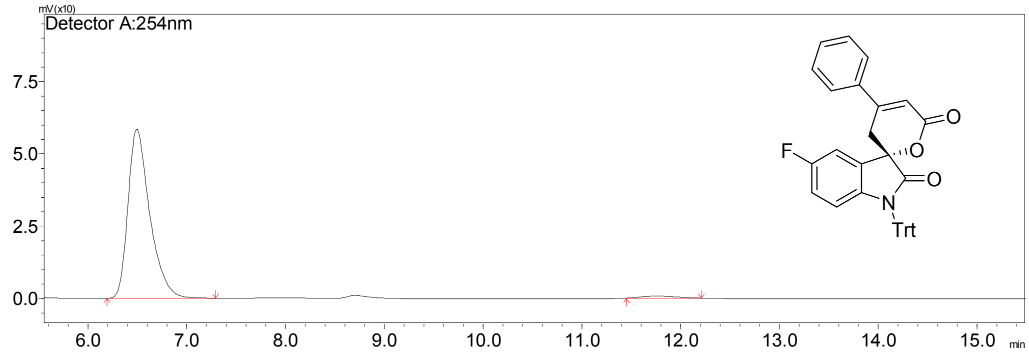
Peak	Ret .Time	Area	Height	Area%	Height%
1	6.808	1018088	62828	49.903	66.023
2	11.731	1022060	32332	50.097	33.977
Total		1101008	95161	100.000	100.000

3f

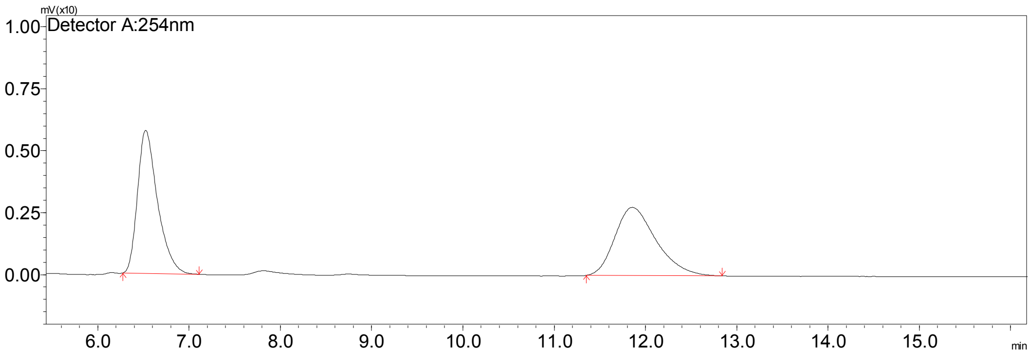

7.15
7.14
7.13
7.13
6.69
6.69
6.68
6.67
6.66
6.65
6.50
6.29
6.28
6.27
6.26
3.37
3.37
3.34
3.34
3.06
3.02
3.02
2.00
9.00
9.00
1.00
1.00
1.00
1.00
1.00
1.00


172.38
162.02
158.60
156.66
150.38
140.26
137.76
137.74
134.91
130.05
128.56
128.49
128.19
128.10
126.97
126.29
125.11
116.50
116.44
115.19
115.01
113.95
110.43
110.23
78.57
73.67
31.71
F
O
O
N
Trt
F
O
O
N
Trt
O
O
f1 (ppm)

3f

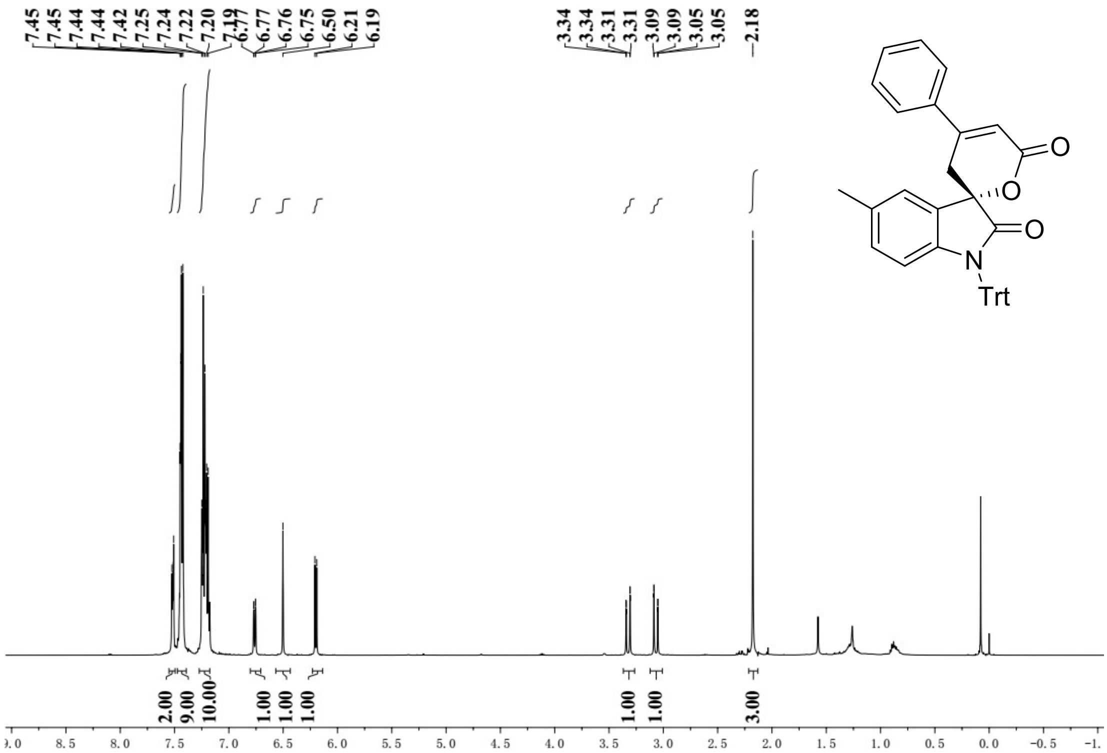


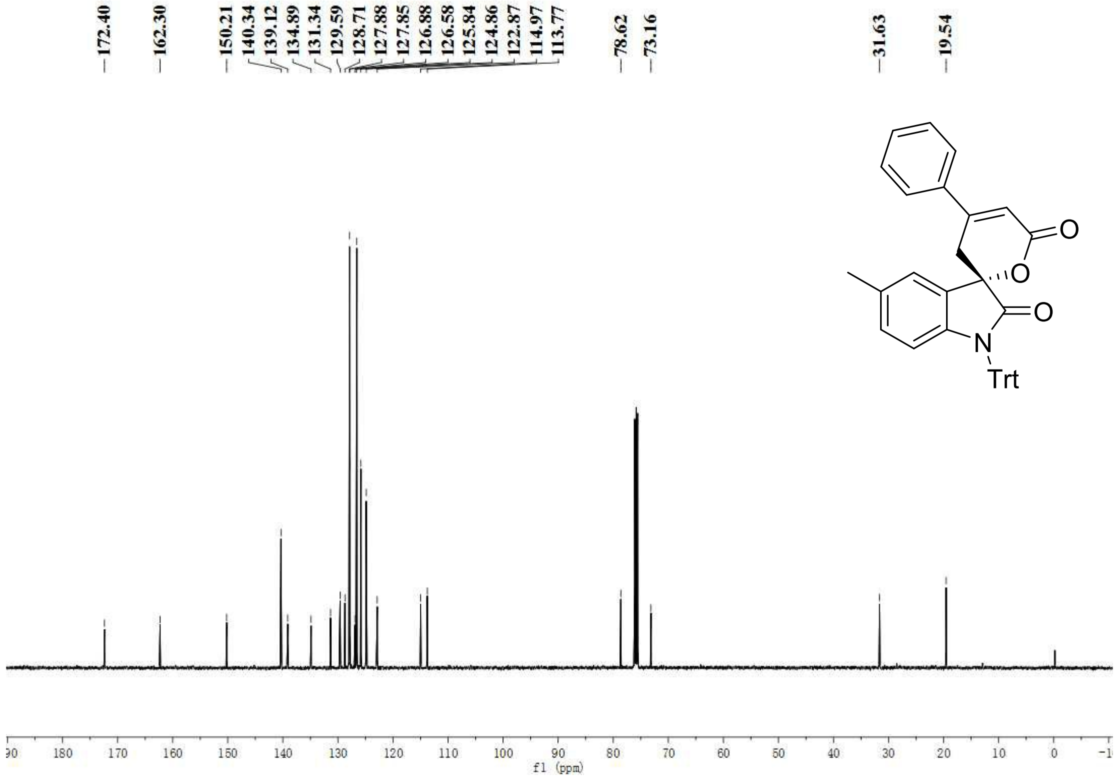
Peak	Ret .Time	Area	Height	Area %	Height %
1	6.492	896514	58495	97.477	98.607
2	11.757	23492	827	2.553	1.393
Total		920006	59322	100.000	100.000



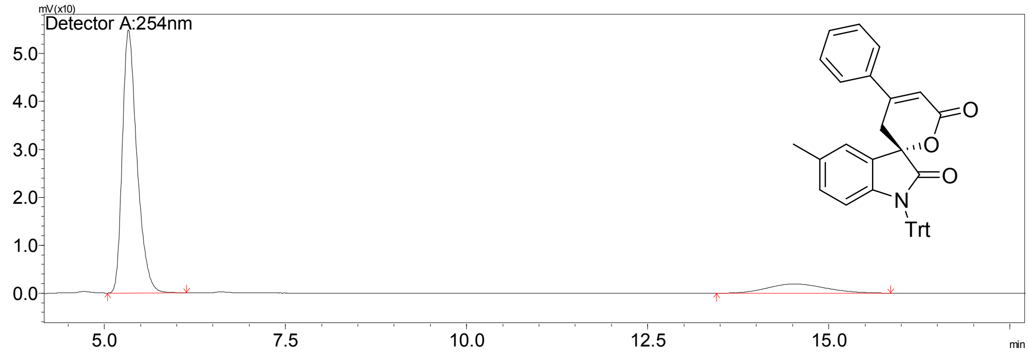
Peak	Ret .Time	Area	Height	Area %	Height %
1	6.521	88823	5792	50.288	67.676
2	11.853	87805	2766	49.712	32.324
Total		176628	8558	100.000	100.000

3g

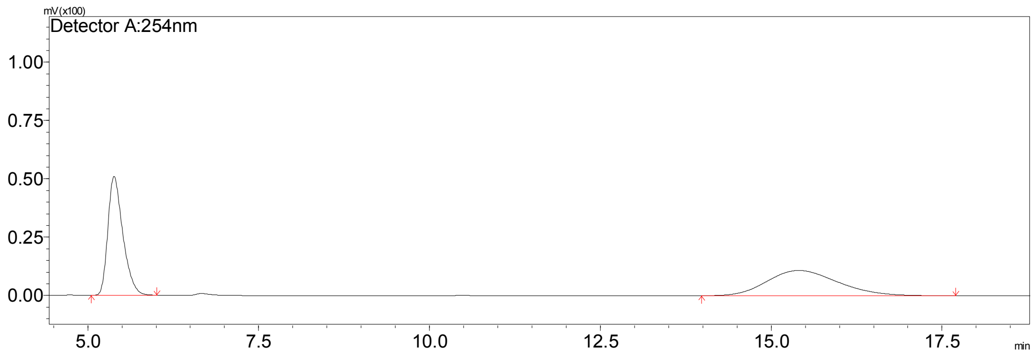




3g

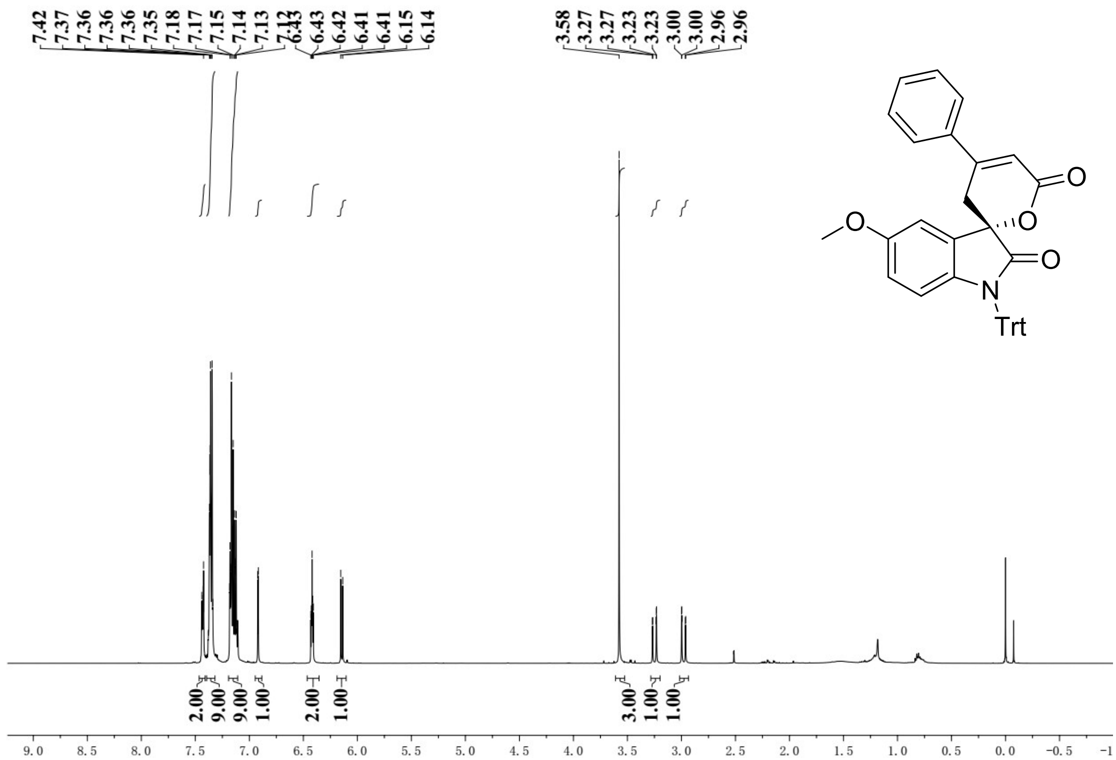


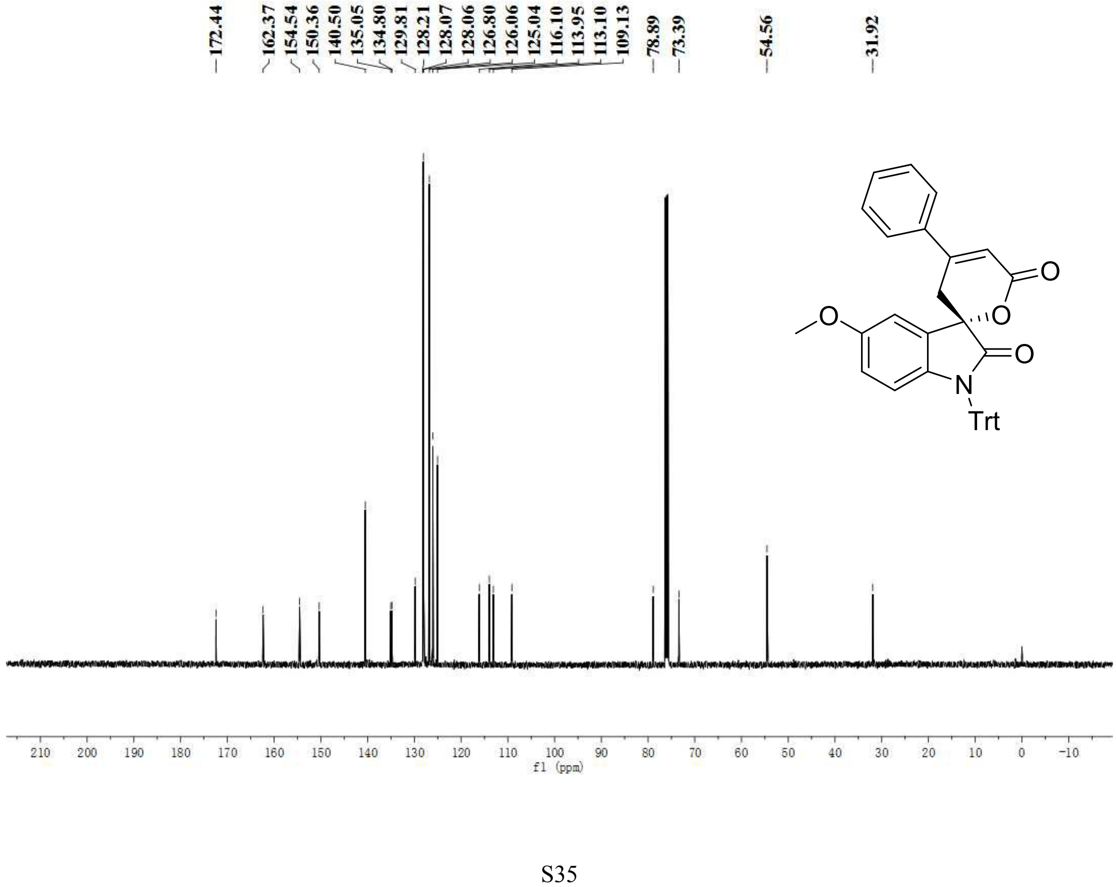
Peak	Ret .Time	Area	Height	Area%	Height%
1	5.329	771659	54907	87.777	96.612
2	14.519	107455	1926	12.223	3.388
Total		879114	56833	100.000	100.000



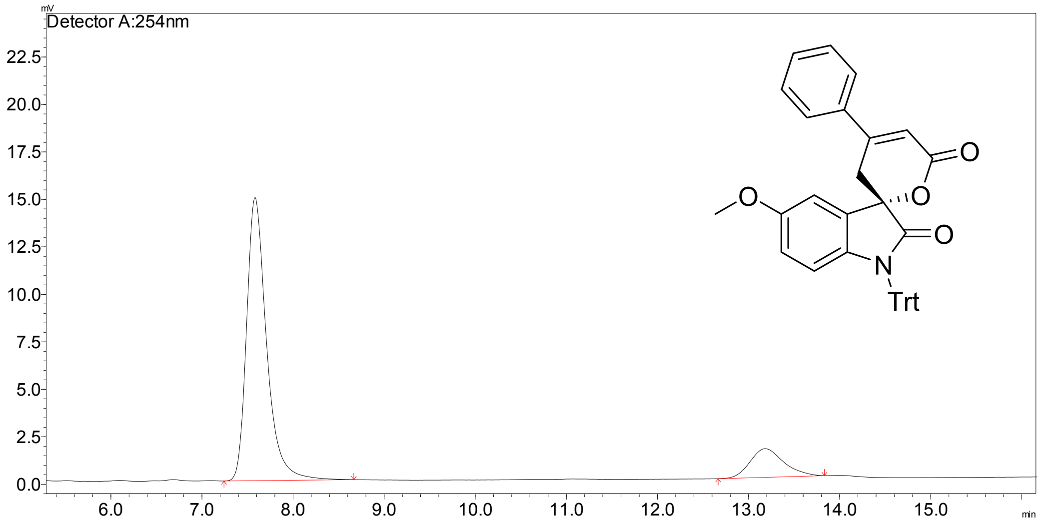
Peak	Ret .Time	Area	Height	Area%	Height%
1	5.380	778239	50958	49.867	82.485
2	15.398	782398	10821	50.133	17.515
Total		1560638	61779	100.000	100.000

3h

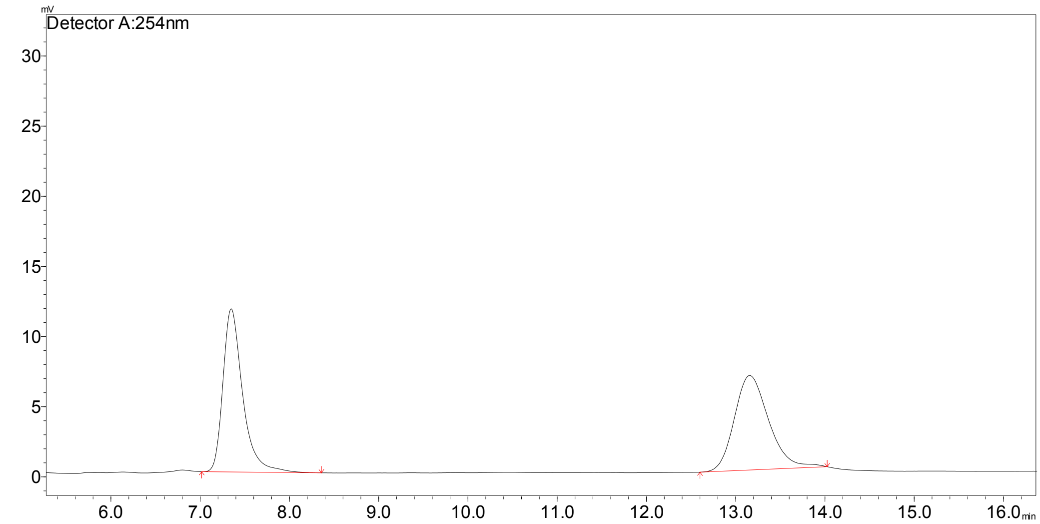

7.42
7.37
7.36
7.36
7.36
7.35
7.18
7.17
7.15
7.14
7.13
7.12
6.43
6.43
6.42
6.41
6.41
6.15
6.14
3.58
3.27
3.27
3.23
3.23
3.00
3.00
2.96
2.96
2.00
9.00
9.00
1.00
2.00
1.00
3.00
1.00
1.00
O
O
O
O
N
Trt


172.44
162.37
154.54
150.36
140.50
135.05
134.80
129.81
128.21
128.07
128.06
126.80
126.06
125.04
116.10
113.95
113.10
109.13
78.89
73.39
54.56
31.92
O
O
O
O
N
Trt
f1 (ppm)

3h

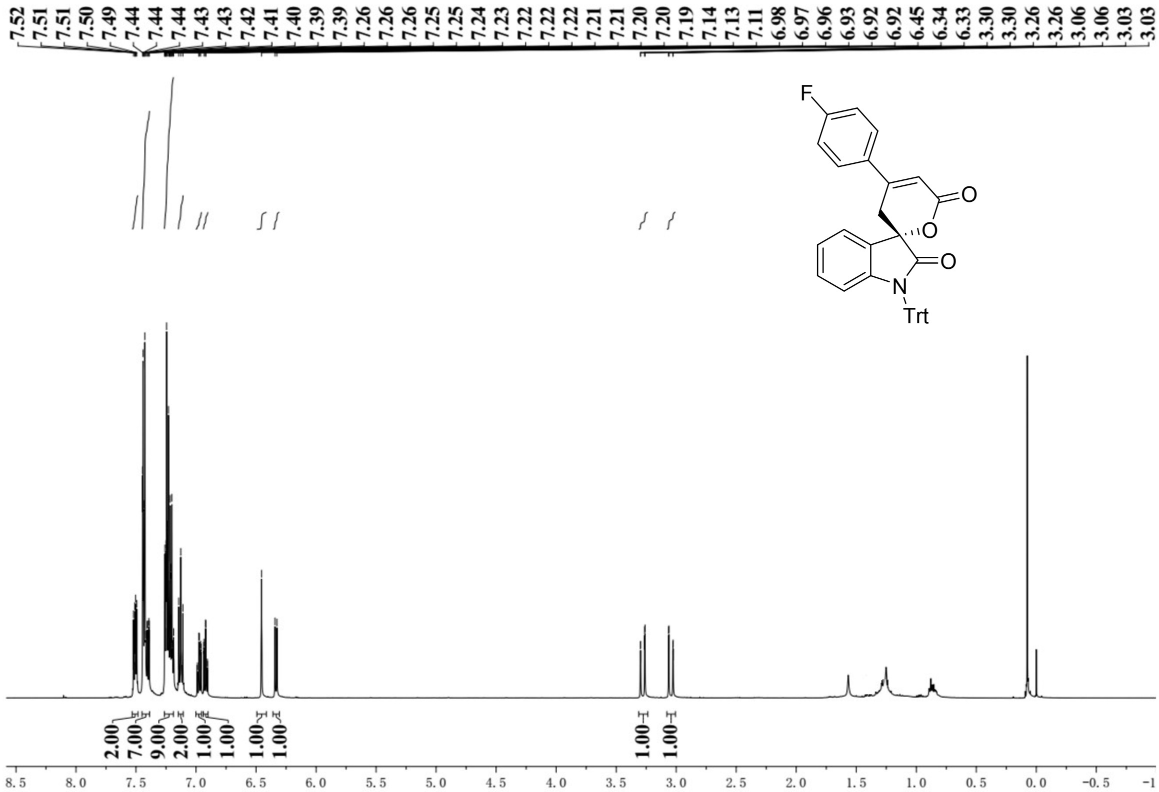


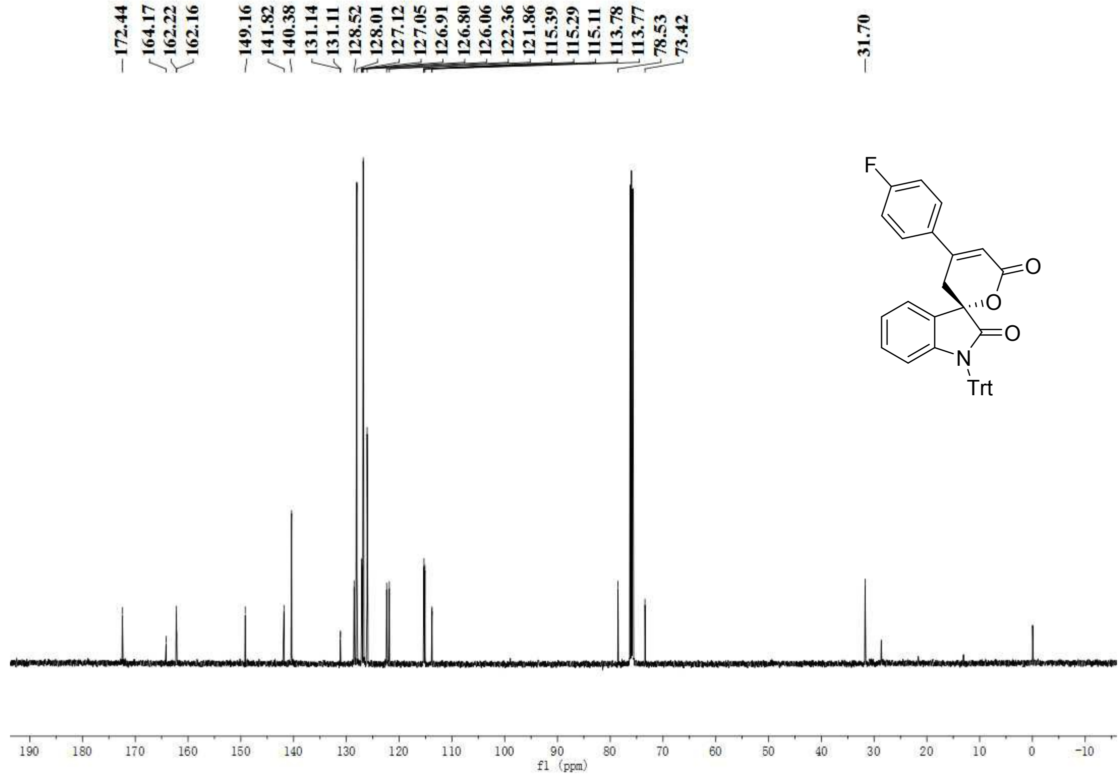
Peak	Ret .Time	Area	Height	Area%	Height%
1	7.578	227252	14824	85.372	99..787
2	13.179	38938	1514	14.628	9.213
Total		266190	16438	100.000	100.000



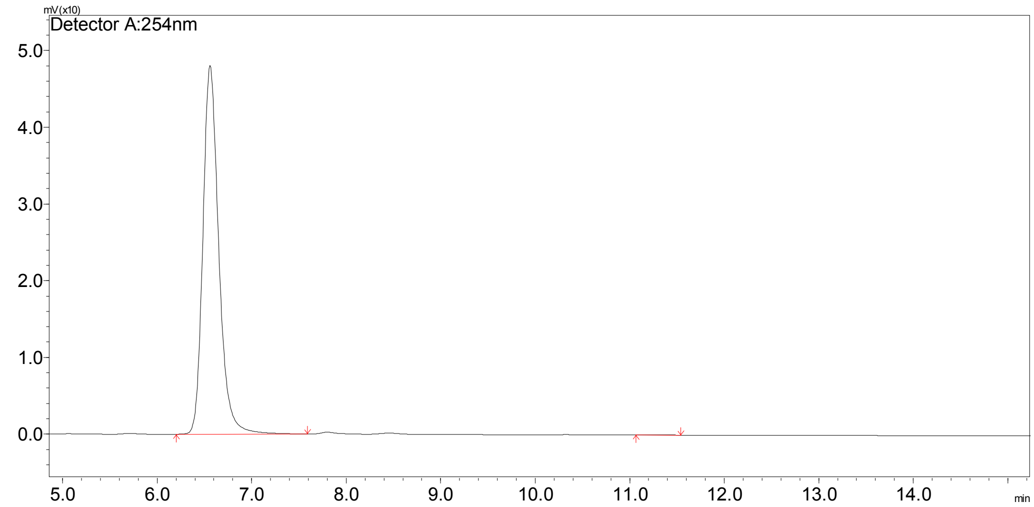
Peak	Ret .Time	Area	Height	Area%	Height%
1	7.343	178870	11630	49.814	63.307
2	13.152	180204	6741	50.186	36.693
Total		359074	18371	100.000	100.000

3i

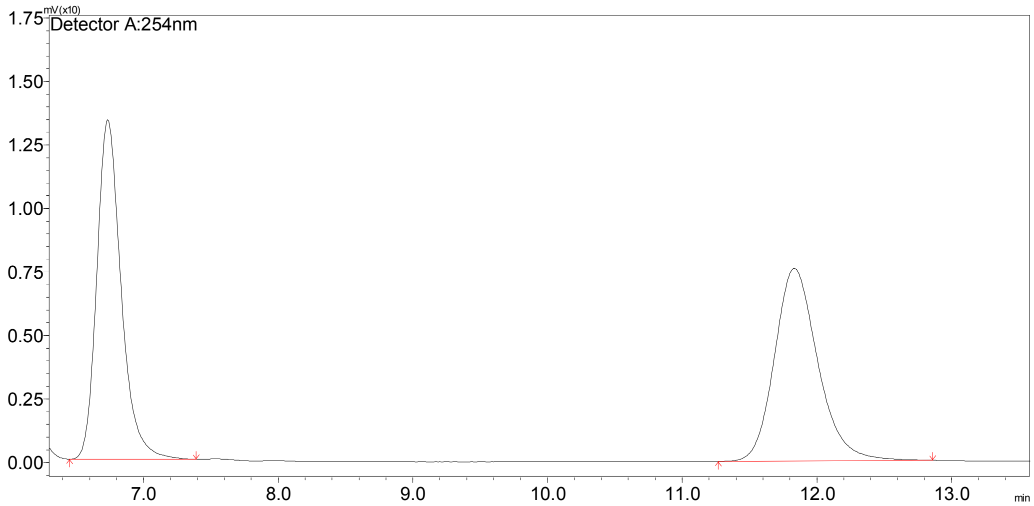

7.52 7.51 7.51 7.50 7.49 7.44 7.44 7.44 7.43 7.43 7.42 7.41 7.40 7.39 7.39 7.26 7.26 7.26 7.25 7.25 7.24 7.23 7.22 7.22 7.22 7.21 7.21 7.20 7.20 7.19 7.14 7.13 7.11 6.98 6.97 6.96 6.93 6.92 6.92 6.45 6.34 6.33 3.30 3.30 3.26 3.06 3.06 3.03 3.03
F
O
O
O
N
Trt
2.00
7.00
9.00
2.00
1.00
1.00
1.00
1.00
1.00
1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1


172.44 164.17 162.22 162.16 149.16 141.82 140.38 131.14 131.11 128.52 128.01 127.12 127.05 126.91 126.80 126.06 122.36 121.86 115.39 115.29 115.11 113.78 113.77 78.53 73.42 31.70
F
O
O
O
N
Trt
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3i

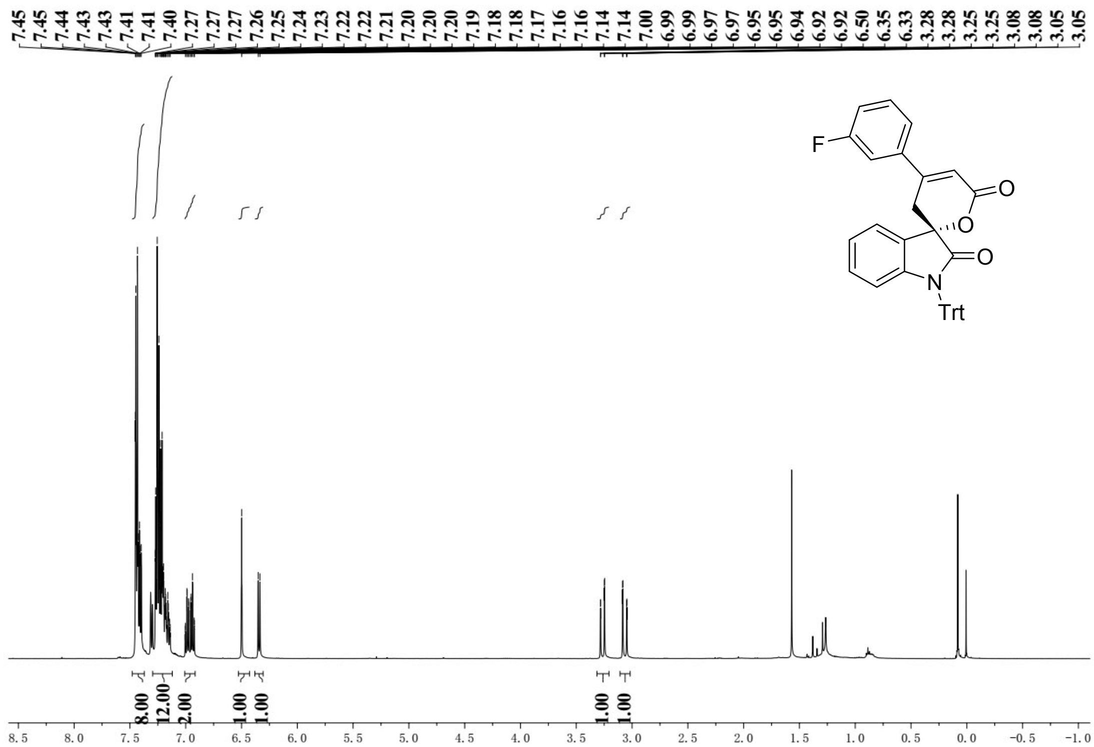


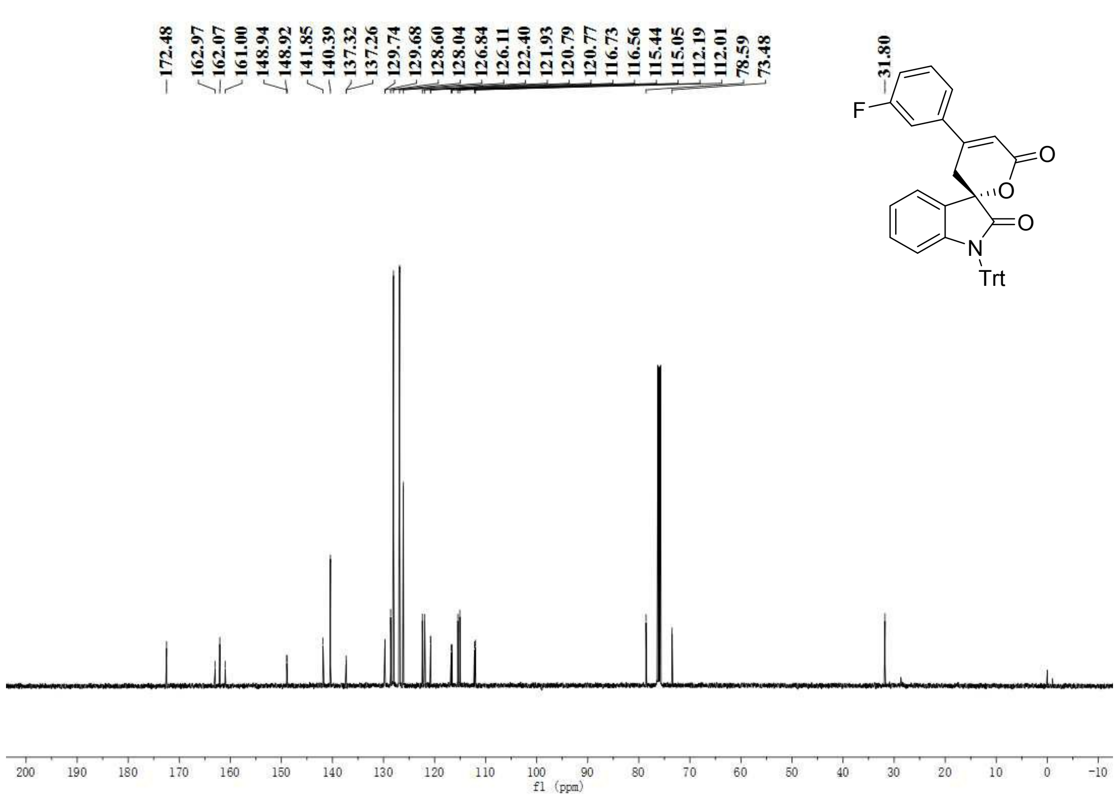
Peak	Ret .Time	Area	Height	Area %	Height %
1	6.555	561888	48027	99.935	99.947
2	11.251	364	25	0.065	0.053
Total		562252	48052	100.000	100.000



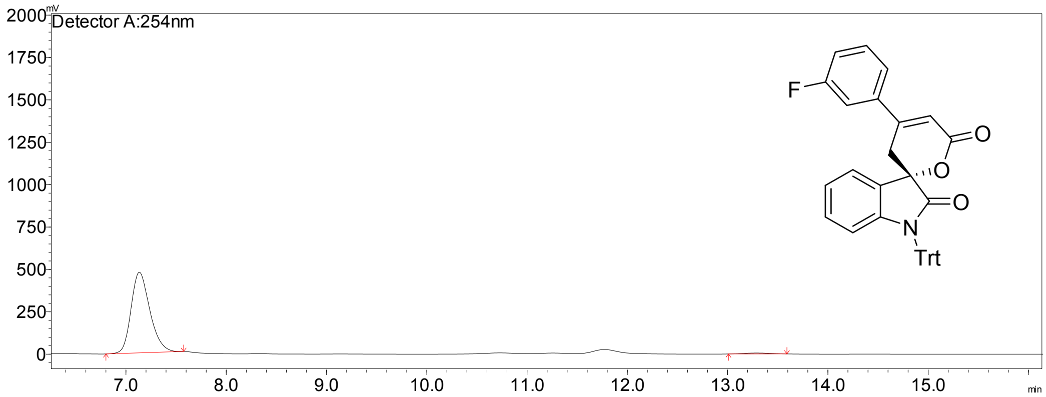
Peak	Ret .Time	Area	Height	Area %	Height %
1	6.730	167771	13363	49.746	63.773
2	11.828	169487	7591	50.254	36.227
Total		337528	20954	100.000	100.000

3j

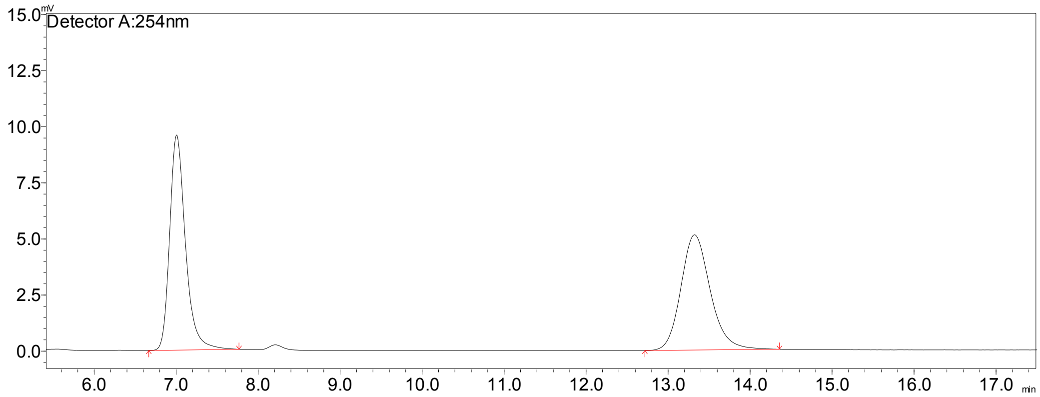




3j

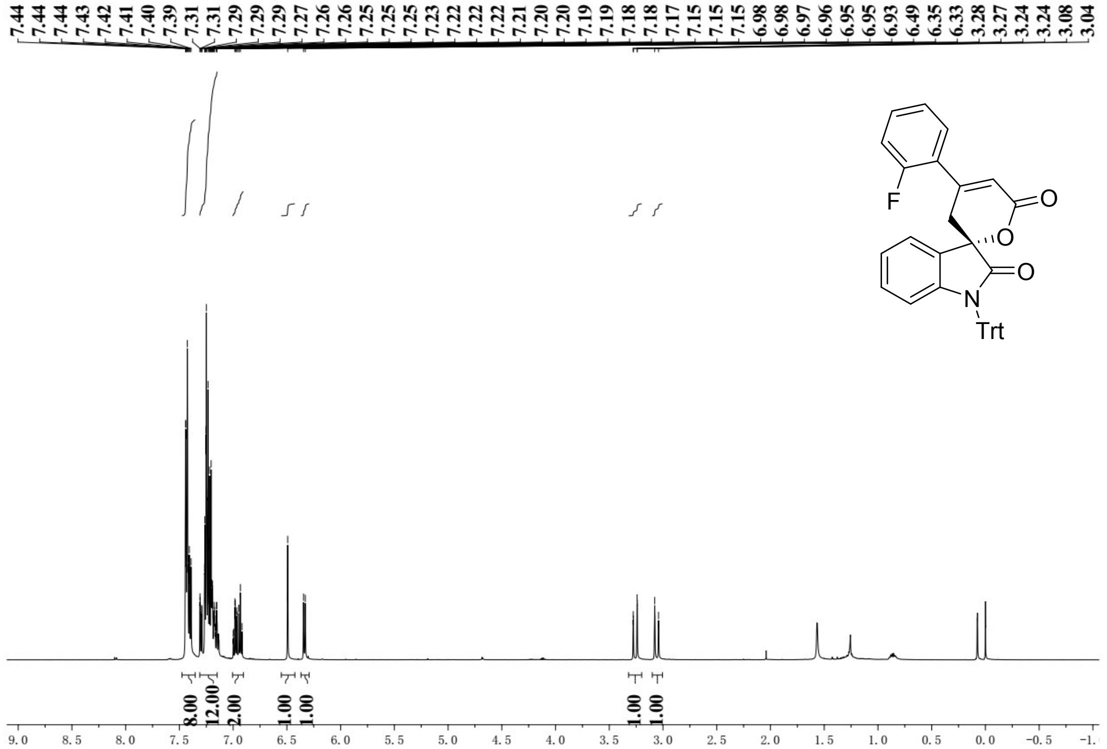


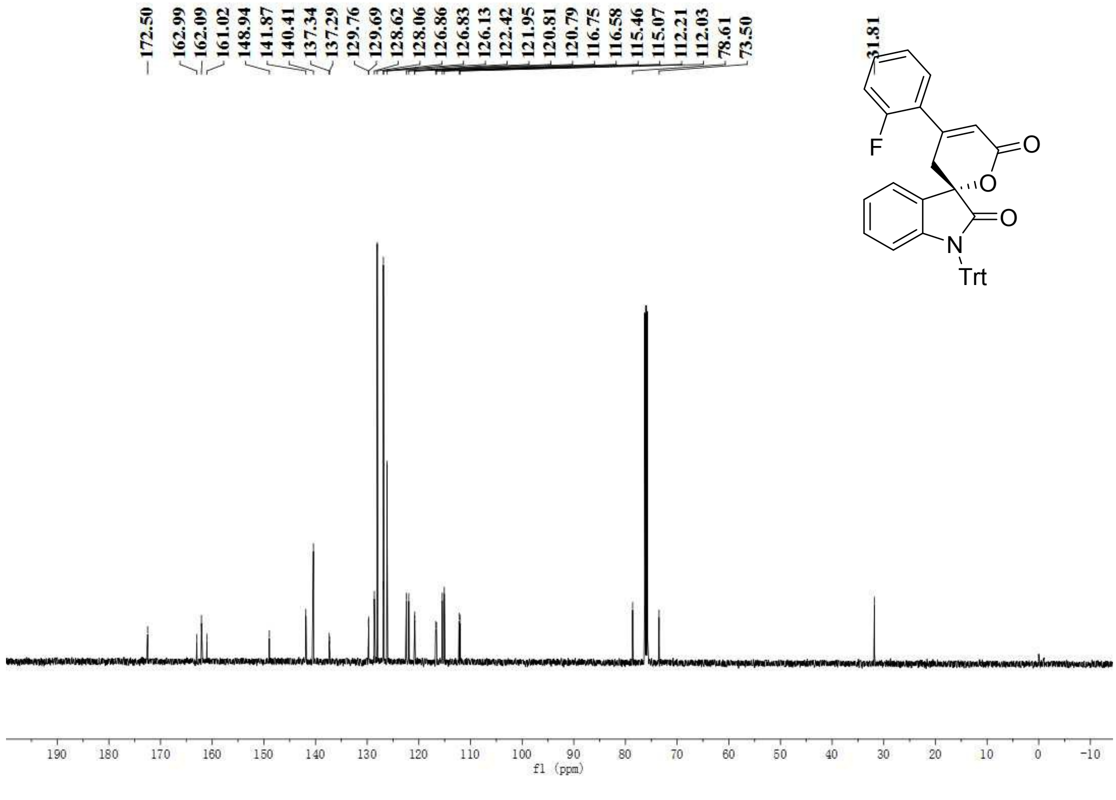
Peak	Ret .Time	Area	Height	Area%	Height%
1	7.129	6185451	475908	98.396	98.893
2	13.284	100862	5325	1.604	1.107
Total		6286313	481233	100.000	100.000



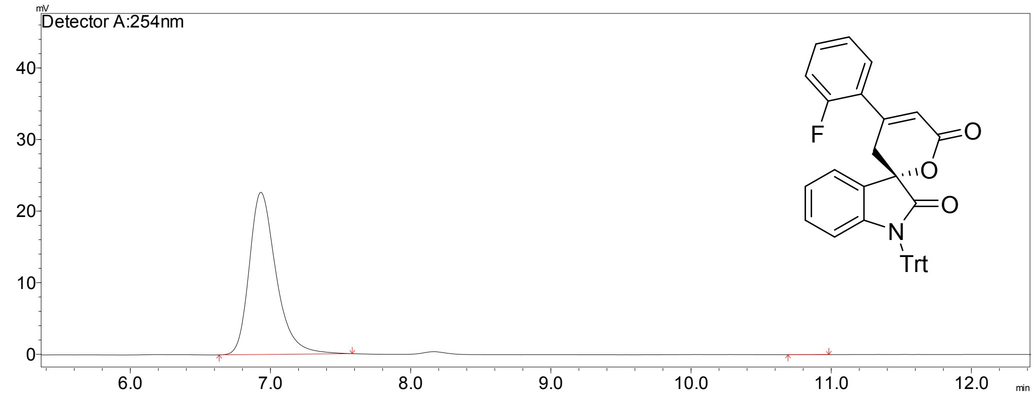
Peak	Ret .Time	Area	Height	Area%	Height%
1	7.001	128686	9595	50.143	65.128
2	13.318	127951	5138	49.857	34.872
Total		256637	14733	100.000	100.000

3k

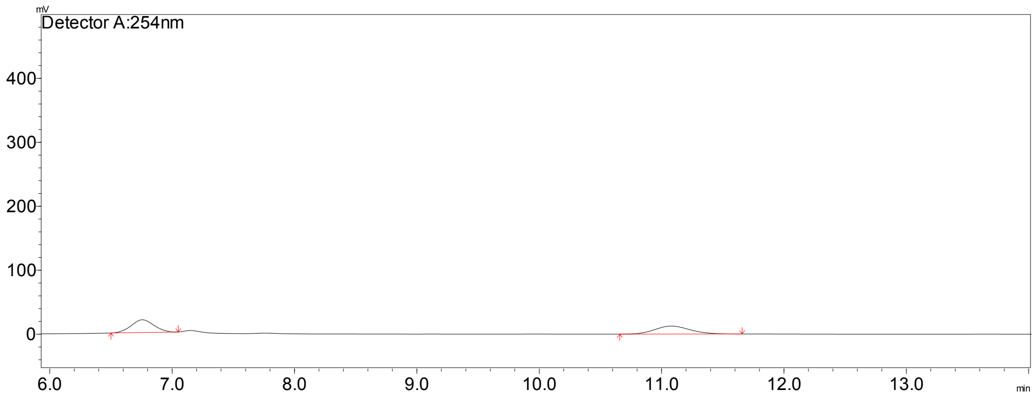

7.44
7.44
7.44
7.43
7.42
7.41
7.40
7.39
7.31
7.31
7.29
7.29
7.29
7.27
7.26
7.26
7.25
7.25
7.25
7.23
7.22
7.22
7.22
7.21
7.20
7.20
7.19
7.19
7.18
7.18
7.17
7.15
7.15
7.15
6.98
6.98
6.97
6.96
6.95
6.95
6.93
6.49
6.35
6.33
3.28
3.27
3.24
3.24
3.08
3.04
F
O
O
O
N
Trt
8.00
12.00
2.00
1.00
1.00
1.00
1.00


172.50
162.99
162.09
161.02
148.94
141.87
140.41
137.34
137.29
129.76
129.69
128.62
128.06
126.86
126.83
126.13
122.42
121.95
120.81
120.79
116.75
116.58
115.46
115.07
112.21
112.03
78.61
73.50
31.81
F
O
O
O
N
Trt
f1 (ppm)

3k

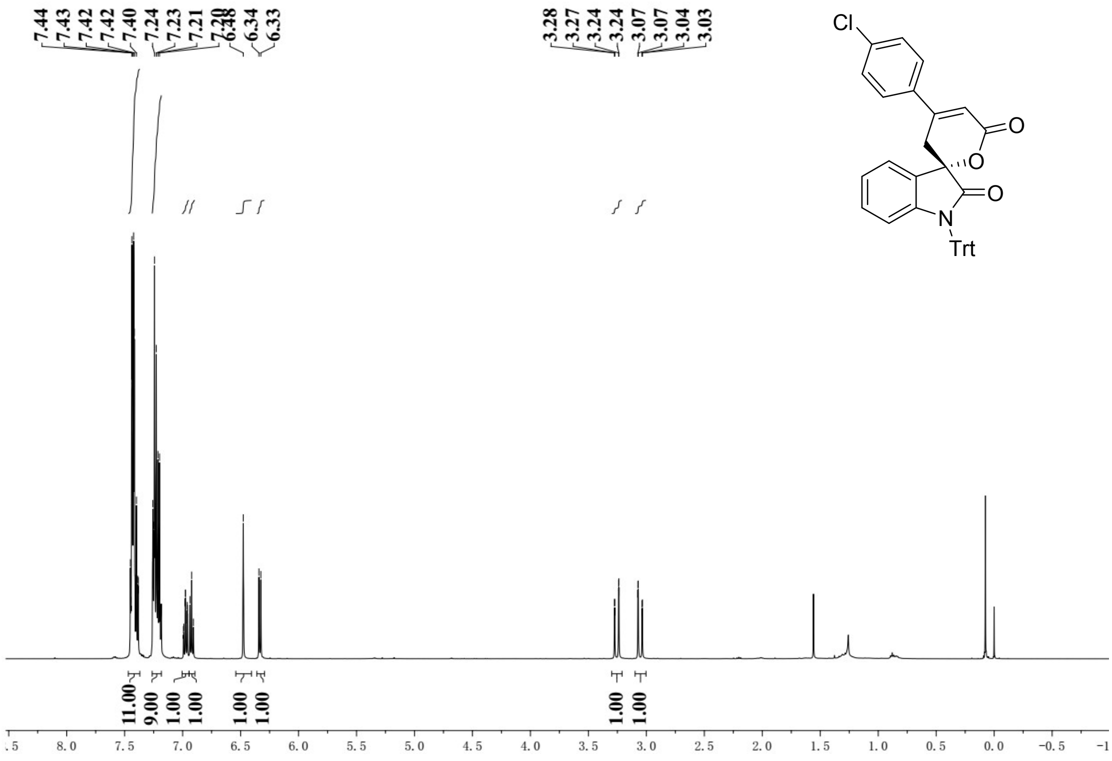


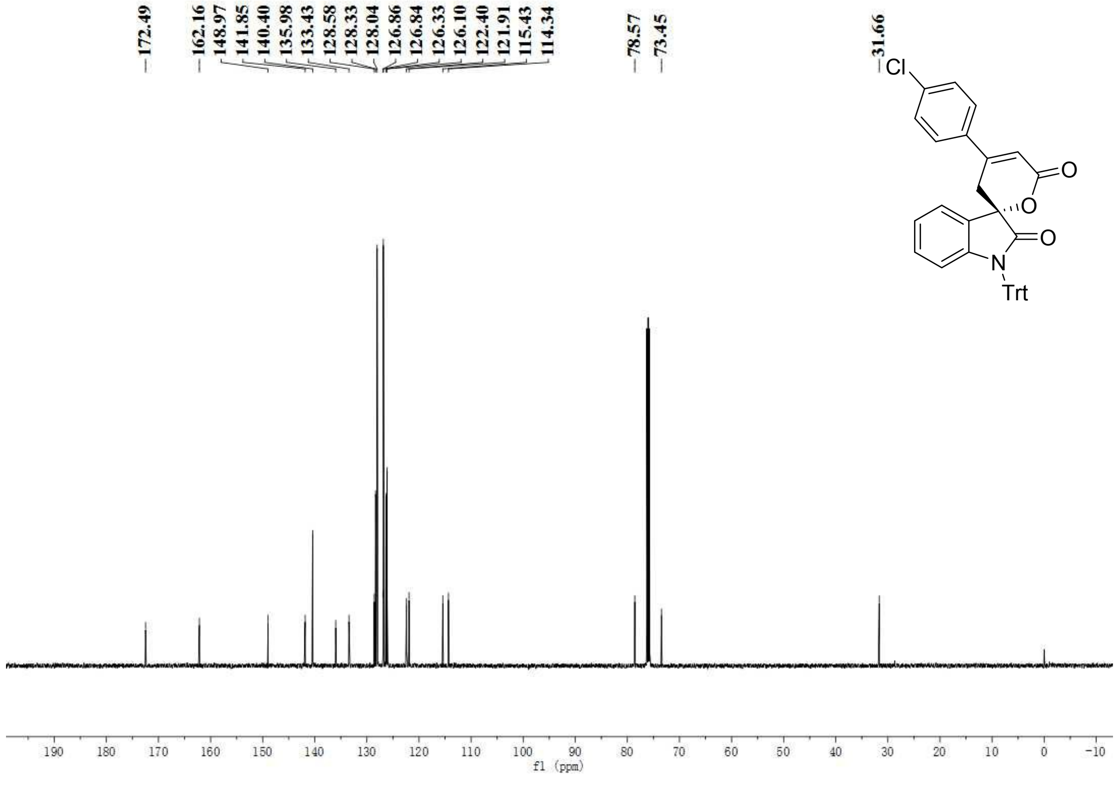
Peak	Ret .Time	Area	Height	Area%	Height%
1	6.927	301193	22671	99.998	99.993
2	10.918	5	2	0.002	0.007
Total		301198	22673	100.000	100.000



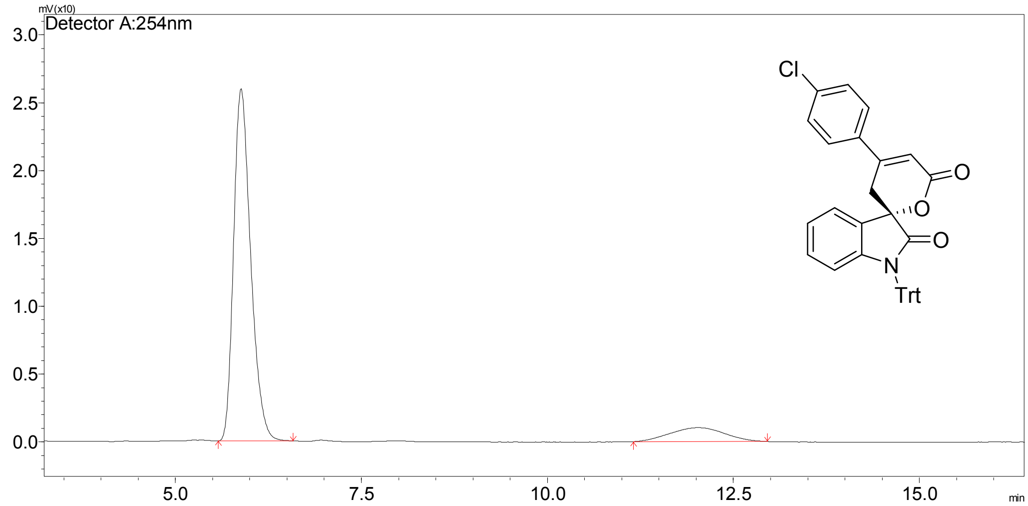
Peak	Ret .Time	Area	Height	Area%	Height%
1	6.752	257994	19975	50.562	61.507
2	11.075	252258	12501	49.438	38.493
Total		510252	22238	100.000	100.000

3l

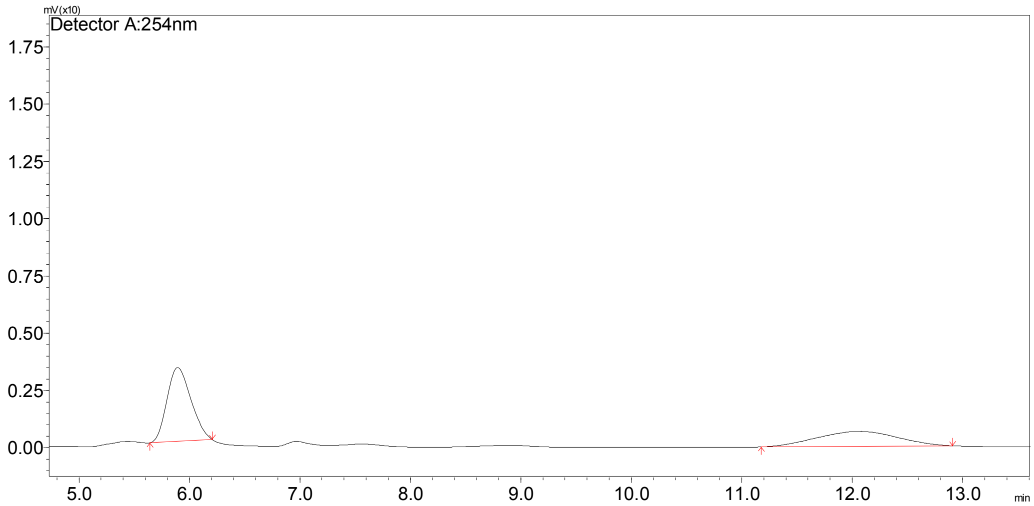

7.44
7.43
7.42
7.42
7.40
7.24
7.23
7.21
7.20
6.48
6.34
6.33
3.28
3.27
3.24
3.24
3.07
3.07
3.04
3.03
Cl
O
O
O
N
Trt
11.00
9.00
1.00
1.00
1.00
1.00
1.00
1.00


172.49
162.16
148.97
141.85
140.40
135.98
133.43
128.58
128.33
128.04
126.86
126.84
126.33
126.10
122.40
121.91
115.43
114.34
78.57
73.45
31.66
Cl
O
O
O
N
Trt
f1 (ppm)

3l

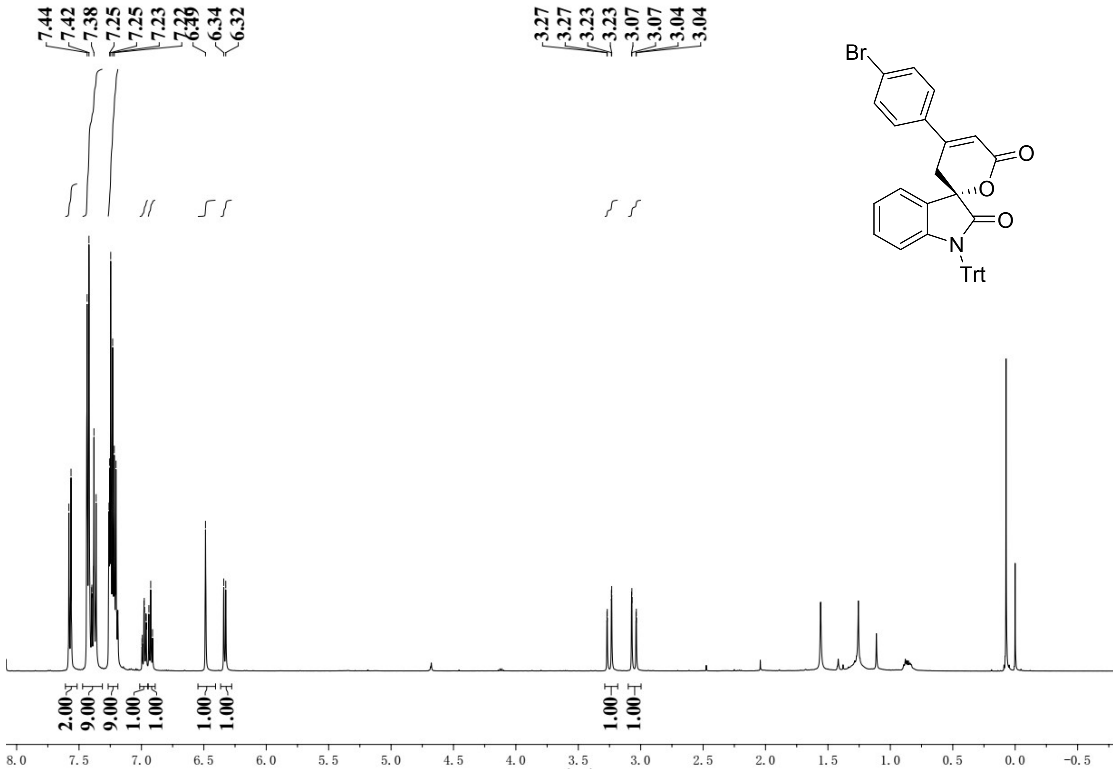


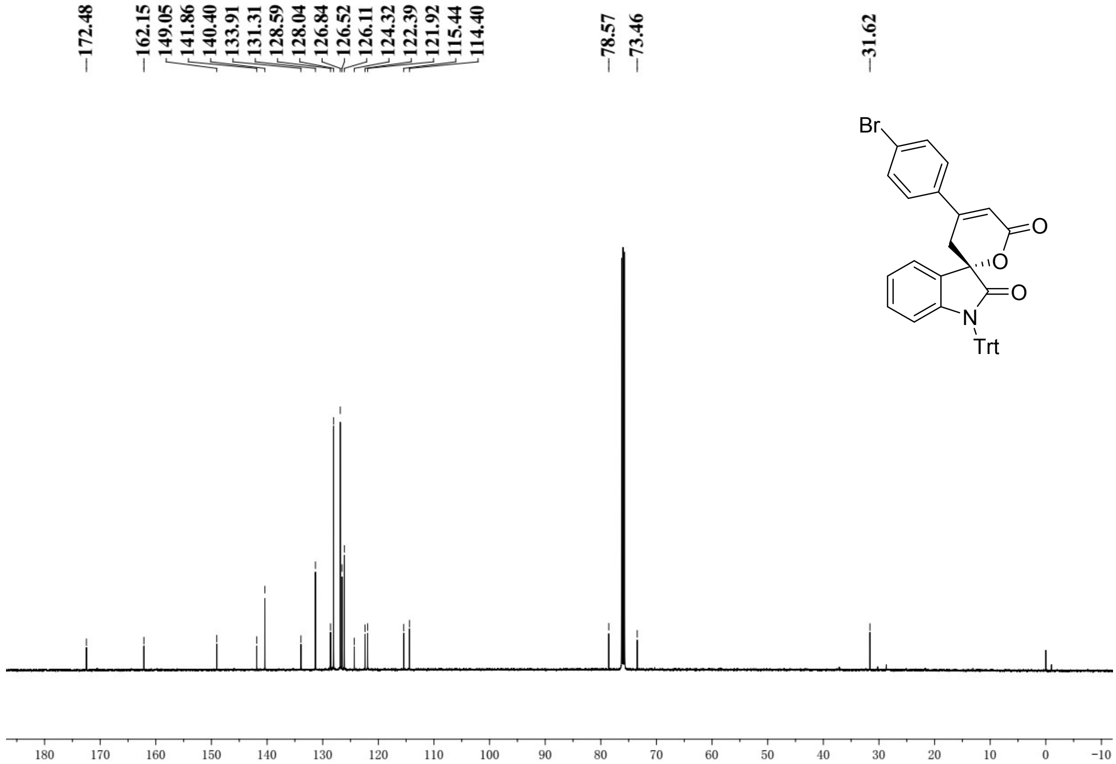
Peak	Ret .Time	Area	Height	Area %	Height %
1	5.878	413622	25963	88.760	96.18
2	12.023	52376	1029	11.240	3.812
Total		465999	26992	100.000	100.000



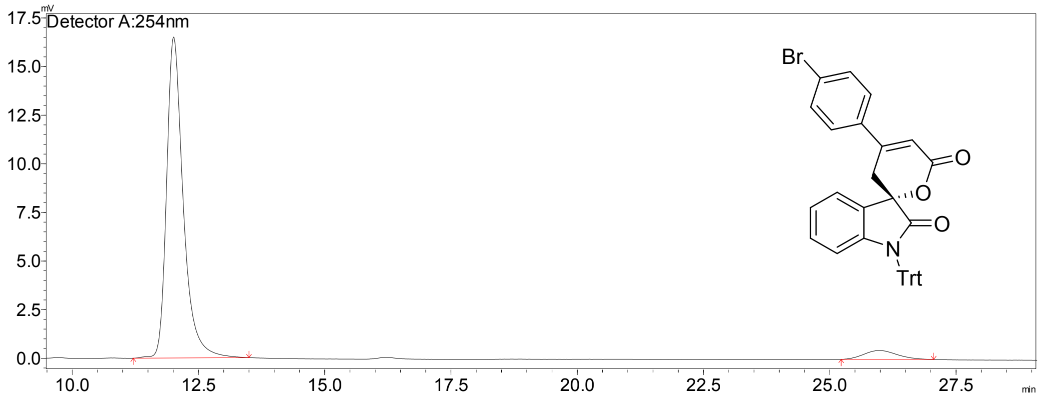
Peak	Ret .Time	Area	Height	Area %	Height %
1	5.888	48538	3224	59.589	83.206
2	12.077	32917	651	40.411	16.794
Total		81455	3875	100.000	100.000

3m

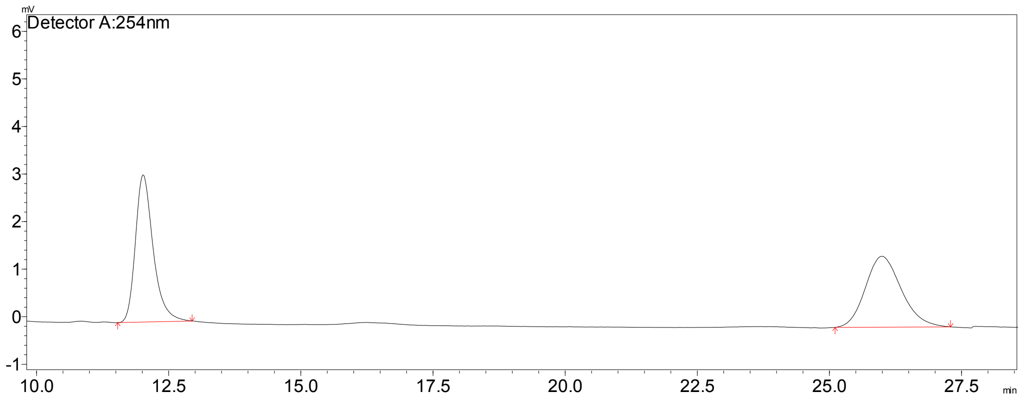

7.44
7.42
7.38
7.25
7.25
7.23
7.22
6.49
6.34
6.32
3.27
3.27
3.23
3.23
3.07
3.07
3.04
3.04
Br
O
O
O
N
Trt
2.00
9.00
9.00
1.00
1.00
1.00
1.00
1.00
1.00


172.48
162.15
149.05
141.86
140.40
133.91
131.31
128.59
128.04
126.84
126.52
126.11
124.32
122.39
121.92
115.44
114.40
78.57
73.46
31.62
Br
O
O
O
N
Trt

3m

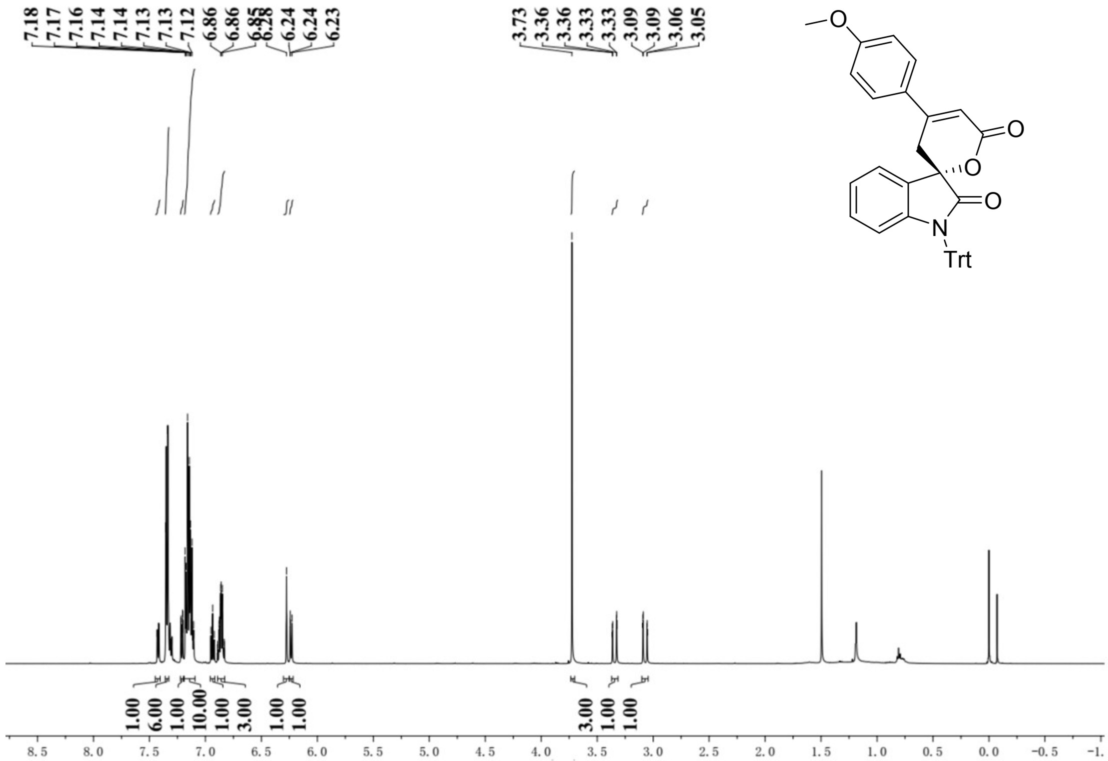


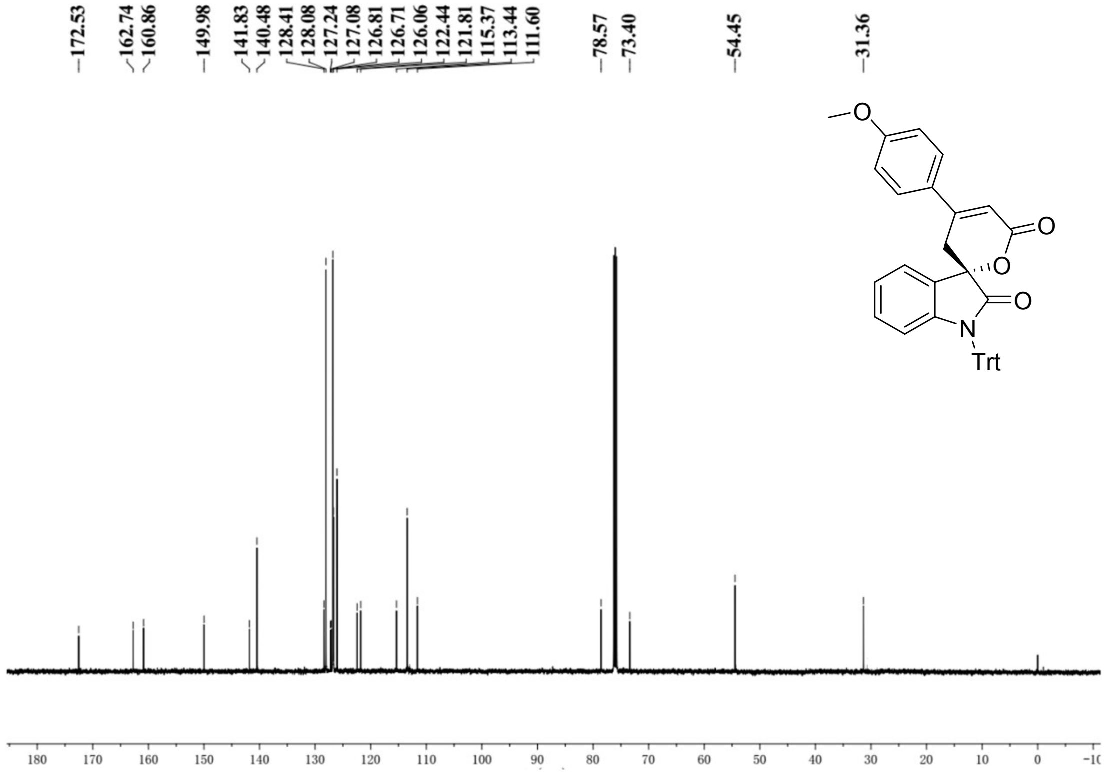
Peak	Ret .Time	Area	Height	Area%	Height%
1	12.004	379356	16508	94.687	97.277
2	25.981	21288	462	5.313	2.723
Total		400643	16970	100.000	100.000



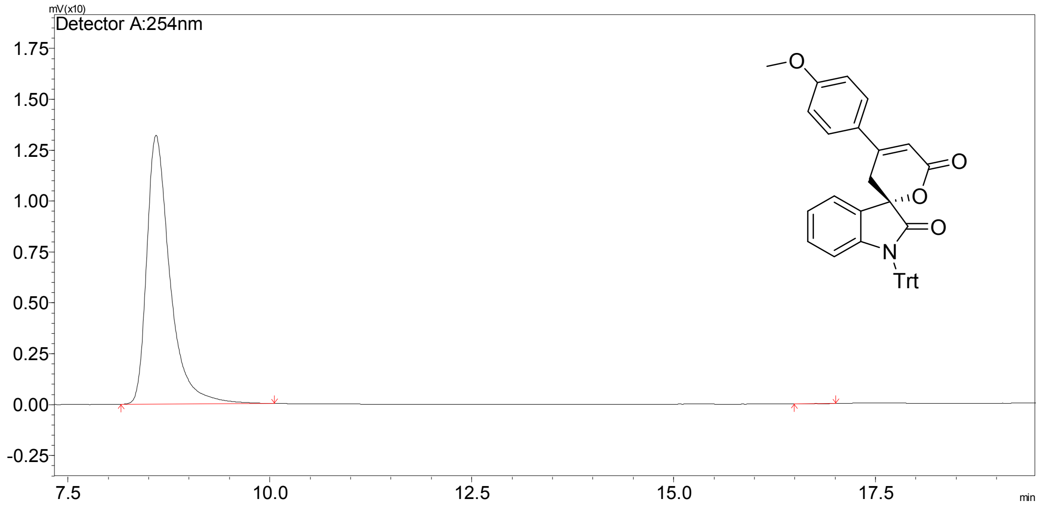
Peak	Ret .Time	Area	Height	Area%	Height%
1	12.012	72468	3094	50.659	67.488
2	25.986	70583	1491	49.341	32.512
Total		143051	4585	100.000	100.000

3n

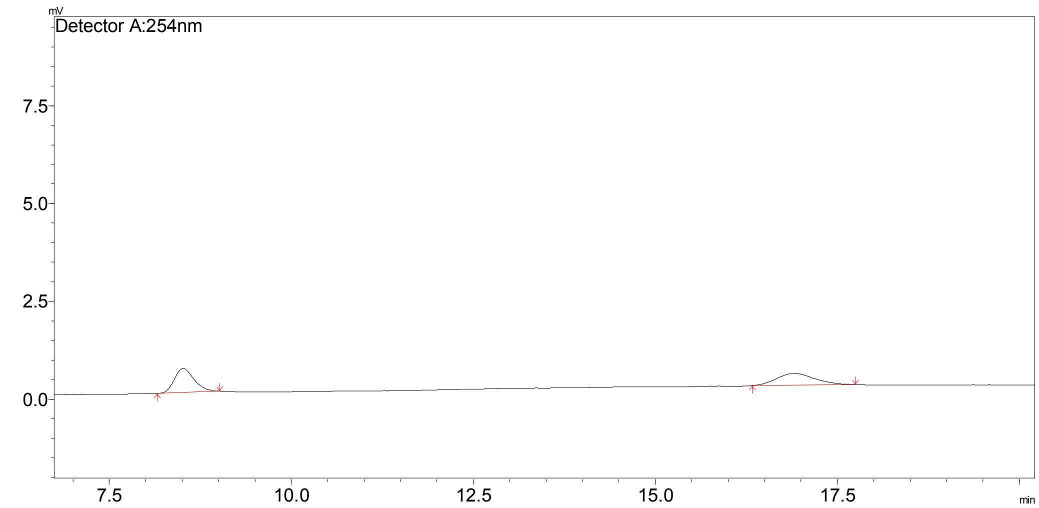

7.18
7.17
7.16
7.14
7.14
7.13
7.13
7.12
6.86
6.86
6.85
6.28
6.24
6.24
6.23
3.73
3.36
3.36
3.33
3.33
3.09
3.09
3.06
3.05
O
O
O
N
Trt
1.00
6.00
1.00
10.00
1.00
3.00
1.00
1.00
3.00
1.00
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


172.53
162.74
160.86
149.98
141.83
140.48
128.41
128.08
127.24
127.08
126.81
126.71
126.06
122.44
121.81
115.37
113.44
111.60
78.57
73.40
54.45
31.36
O
O
O
N
Trt
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

3n

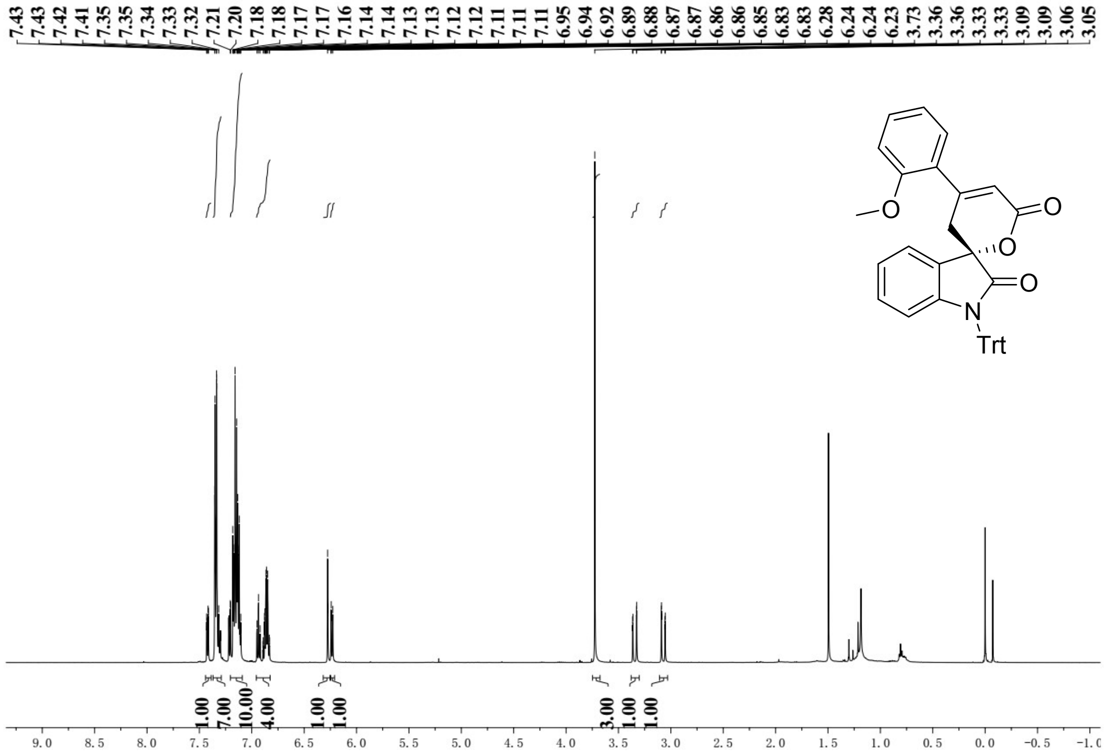


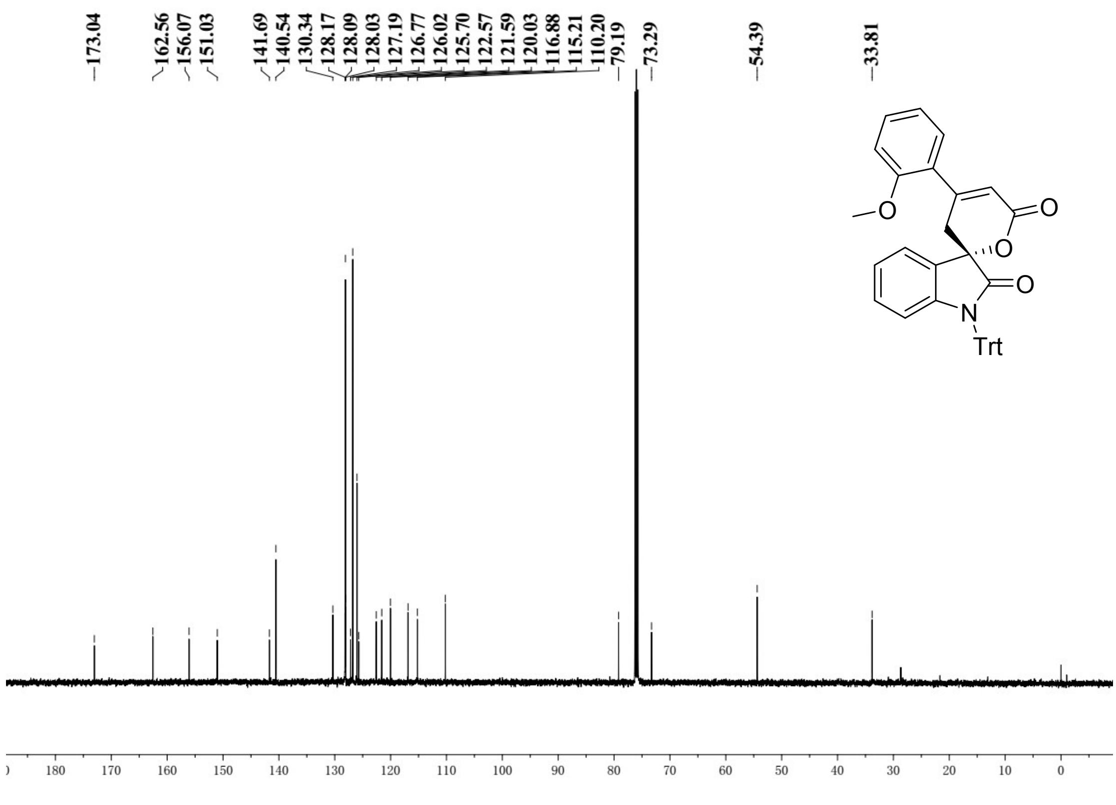
Peak	Ret .Time	Area	Height	Area %	Height %
1	8.586	263901	13199	99.976	99.982
2	16.954	64	2	0.024	0.018
Total		263965	13201	100.000	100.000



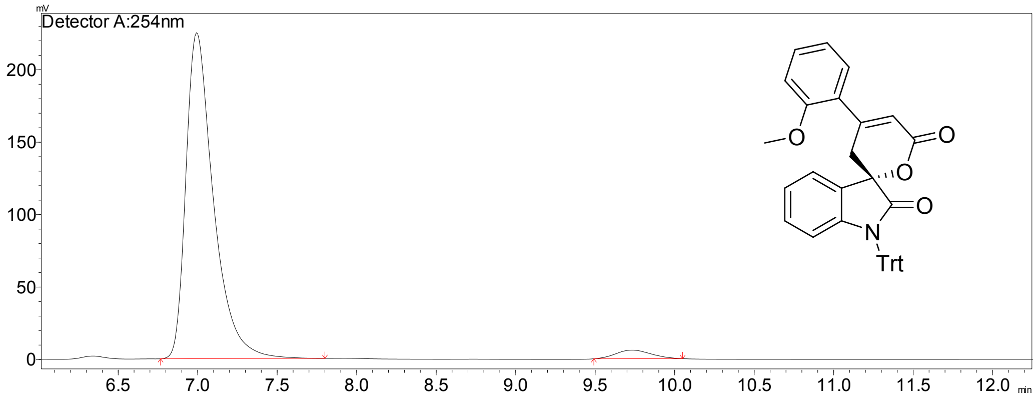
Peak	Ret .Time	Area	Height	Area %	Height %
1	8.510	11611	618	51.449	67.284
2	16.900	10957	301	48.551	32.716
Total		22568	919	100.000	100.000

3o

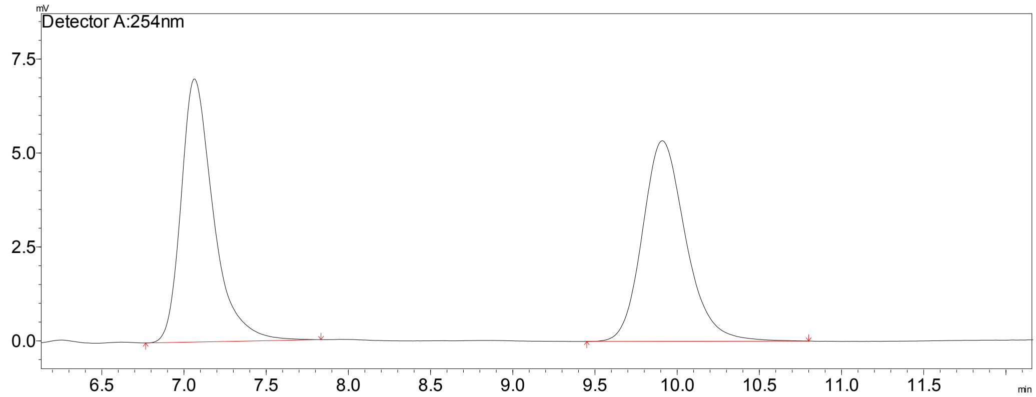

7.43
7.43
7.42
7.41
7.35
7.35
7.34
7.33
7.32
7.21
7.20
7.18
7.18
7.17
7.17
7.16
7.14
7.14
7.13
7.13
7.12
7.12
7.11
7.11
7.11
6.95
6.94
6.92
6.89
6.88
6.87
6.87
6.86
6.86
6.85
6.83
6.83
6.28
6.24
6.24
6.23
3.73
3.36
3.36
3.33
3.33
3.09
3.09
3.06
3.05
O
O
O
N
Trt
1.00
7.00
10.00
4.00
1.00
1.00
3.00
1.00
1.00


173.04
162.56
156.07
151.03
141.69
140.54
130.34
128.17
128.09
128.03
127.19
126.77
126.02
125.70
122.57
121.59
120.03
116.88
115.21
110.20
79.19
73.29
54.39
33.81
O
O
O
N
Trt

3o



Peak	Ret .Time	Area	Height	Area%	Height%
1	6.990	2711676	224988	96.733	97.427
2	9.727	91593	5943	3.267	2.573
Total		2803268	230931	100.000	100.000



Peak	Ret .Time	Area	Height	Area%	Height%
1	7.059	96042	7003	49.539	56.732
2	9.905	97828	5341	50.461	43.268
Total		193869	12344	100.000	100.000

Reference

1. Gaussian 09, Revision A.2, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

2. A. D. Becke, *J. Chem. Phys.,* 1993, **98**, 5648-5652.

3. C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B.*, 1988, **37**, 785-789.

4. R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys.,* 1971, **54**, 724-728.

5. W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.,* 1972, **56**, 2257-2261.

6. P. C. Hariharan, J. A. Pople, *Theor. Chem. Acc.,* 1973, **28**, 213-222.