

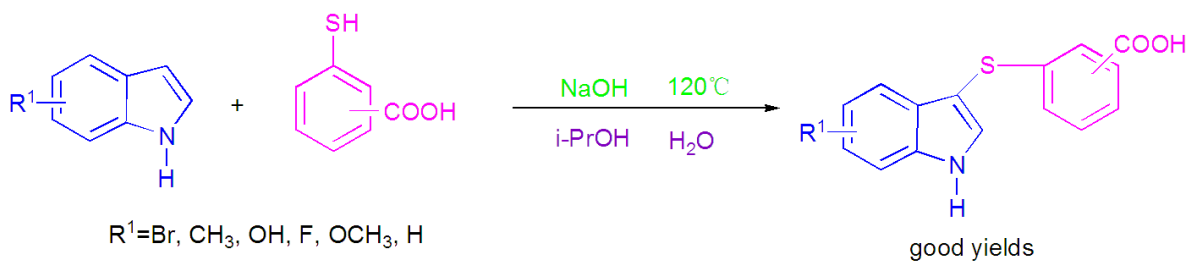
Supporting Information

Catalyst-free system for 3-sulfenylation of free (*N-H*) indoles with mercaptobenzoic acid under alkaline conditions

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General Information

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker advance DRX-500 MHz spectrometer in deuterated chloroform with tetramethylsilane (TMS) as an internal reference. All chemical shifts were reported relative to TMS at 0.0 ppm. Melting points were determined on a Yuhua digital melting-point apparatus and are uncorrected. Thin layer chromatography was done using commercial silica gel plates and chromatographic separations were performed using flash silica gel (200-300 mesh) columns. High resolution mass spectra were obtained using a micrOTOF-Q II. All reagents and chemicals (AR grade) were commercially obtained and used without further purification. Petroleum ether (PE) refers to the fraction boiling in the 60-90°C range.

General Procedure for the Sulfenylation of Indoles with mercaptobenzoic acid

A mixture of an indole **1** (5mmol), a mercaptobenzoic acid **2** (10 mmol) and sodium hydroxide (5 mmol) in 100 mL isopropanol/ H_2O (v:v ratio = 6:4) was stirred at 120°C for 48h or until complete consumption of the starting materials, as monitored by TLC. After the reaction was finished, the mixture was slowly cooled to room temperature, white solid was collected by filtration. In order to get pure product, the filtrate was poured into EtOAc (170 mL) and washed with sat. $\text{Na}_2\text{S}_2\text{O}_3$ soln (5×50 mL), followed by extraction of the aqueous layer with EtOAc (5×30 mL). The combined organic layer was dried (anhyd. Na_2SO_4) and concentrated under reduced pressure. The residue and the white solid were purified by flash chromatography (PE:EtOAc, 5:2) to afford the analytically pure sulfenylindole product **3**.

5-Methoxyl-3-[(2-Carboxyphenyl)thio]-1*H*-indole (**3a**)

Yield, 86 %; White solid; mp 202.3-203.7 °C. ^1H NMR (500 MHz, DMSO) δ 11.58 (d, J = 1.6 Hz, 1H), 7.92 (dd, J = 7.7, 1.3 Hz, 1H), 7.65 (d, J = 2.7 Hz, 1H), 7.41 (d, J = 8.8 Hz, 1H), 7.28-7.21 (m, 1H), 7.11 (t, J = 7.5 Hz, 1H), 6.83 (dd, J = 8.8, 2.4 Hz, 1H), 6.75 (d, J = 2.3 Hz, 1H), 6.69 (d, J = 8.1 Hz, 1H), 3.66 (s, 3H); ^{13}C NMR (126 MHz, DMSO) δ 167.5, 154.4, 143.8, 133.1, 132.2, 131.8, 131.0, 129.6, 126.7,

125.5, 123.8, 113.3, 112.4, 99.7, 99.5, 55.3. MS (ESI-Qq-TOF) m/z (amu) calcd for $C_{16}H_{14}NO_3S$ $[M + H]^+$: 300.0694; Found: 300.0689.

5-Bromo-3-[(2-Carboxyphenyl)thio]-1*H*-indole (3b)

Yield, 68 %; Yellow solid; mp 231.9-232.7°C. 1H NMR (500 MHz, DMSO): δ 13.18 (s, 1H), 11.94 (d, J = 1.5 Hz, 1H), 7.93 (dd, J = 7.8, 1.4 Hz, 1H), 7.81 (d, J = 2.6 Hz, 1H), 7.50 (d, J = 8.6 Hz, 1H), 7.40 (d, J = 1.8 Hz, 1H), 7.31 (dd, J = 8.6, 1.9 Hz, 1H), 7.28 -7.23 (m, 1H), 7.16-7.11 (m, 1H), 6.68-6.62 (m, 1H). ^{13}C NMR (126 MHz, DMSO): δ 167.41, 143.09, 135.71, 134.36, 132.26, 131.05, 130.66, 126.77, 125.46, 124.83, 123.98, 120.31, 114.59, 112.94, 99.83. MS (ESI-Qq-TOF) m/z (amu) calcd for $C_{15}H_{11}BrNO_2S$ $[M + H]^+$: 347.9693; Found: 347.9688.

5-Methyl-3-[(2-Carboxyphenyl)thio]-1*H*-indole (3c)

Yield, 65 %; White solid; mp 247.3-248.6°C. 1H NMR (500 MHz, DMSO): δ 11.60 (s, 1H), 7.92 (d, J = 7.7 Hz, 1H), 7.66 (d, J = 2.6 Hz, 1H), 7.40 (d, J = 8.3 Hz, 1H), 7.27-7.19 (m, 1H), 7.14-7.07 (m, 2H), 7.01 (d, J = 8.4 Hz, 1H), 6.67 (d, J = 8.2 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (126 MHz, DMSO): δ 167.51, 143.99, 135.31, 132.73, 132.17, 131.05, 129.03, 128.98, 126.62, 125.58, 123.89, 123.76, 117.80, 112.19, 99.27, 21.15. MS (ESI-Qq-TOF) m/z (amu) calcd for $C_{16}H_{14}NO_2S$ $[M + H]^+$: 284.0745; Found: 284.0740.

5-Hydroxyl-3-[(2-Carboxyphenyl)thio]-1*H*-indole (3d)

Yield, 42 %; White solid; mp 237.6-238.6°C. 1H NMR (500 MHz, DMSO): δ 11.42 (d, J = 2.1 Hz, 1H), 8.82 (s, 1H), 7.90 (dd, J = 7.8, 1.5 Hz, 1H), 7.58 (d, J = 2.7 Hz, 1H), 7.30 (d, J = 8.6 Hz, 1H), 7.28-7.19 (m, 1H), 7.11 (td, J = 7.7, 1.1 Hz, 1H), 6.75-6.65 (m, 2H), 6.61 (d, J = 2.3 Hz, 1H). ^{13}C NMR (126 MHz, DMSO): δ 167.51, 151.75, 143.80, 132.76, 132.12, 131.22, 131.02, 129.71, 126.68, 125.65, 123.73,

112.98, 112.54, 102.11, 98.70. MS (ESI-Qq-TOF) m/z (amu) calcd for $C_{15}H_{12}NO_3S$ $[M + H]^+$: 286.0538;
Found: 286.0532.

5-Fluoro-3-[(2-Carboxyphenyl)thio]-1*H*-indole (3e)

Yield, 68 %; Light yellow solid; mp 239.5-240.3 °C. 1H NMR (500 MHz, DMSO) δ 11.84 (d, J = 1.6 Hz, 1H), 7.93 (dd, J = 7.8, 1.4 Hz, 1H), 7.81 (d, J = 2.7 Hz, 1H), 7.53 (dd, J = 8.8, 4.4 Hz, 1H), 7.31-7.18 (m, 1H), 7.18- 7.09 (m, 1H), 7.04 (td, J = 9.2, 2.5 Hz, 1H), 6.99 (dd, J = 9.4, 2.5 Hz, 1H), 6.71-6.59 (m, 1H); ^{13}C NMR (126 MHz, DMSO) δ 167.5, 158.7, 156.8, 143.3, 134.8, 133.6, 132.2, 131.1, 129.5, 126.8, 125.5, 124.0, 113.8, 110.7, 110.5, 103.1, 102.9, 100.3. MS (ESI-Qq-TOF) m/z (amu) calcd for $C_{15}H_{10}FNO_2S$ $[M + H]^+$: 288.0494; Found: 288.0489.

6-Fluoro-3-[(2-Carboxyphenyl)thio]-1*H*-indole (3f)

Yield, 51 %; White solid; mp 215.7-216.7 °C. 1H NMR (500 MHz, DMSO) δ 11.76 (s, 1H), 7.92 (dd, J = 7.7, 1.3 Hz, 1H), 7.73 (d, J = 2.5 Hz, 1H), 7.33-7.25 (m, 2H), 7.25 -7.19 (m, 1H), 7.12 (t, J = 7.2 Hz, 1H), 6.91 (td, J = 9.6, 2.3 Hz, 1H), 6.67 (d, J = 8.0 Hz, 1H). ^{13}C NMR (126 MHz, DMSO) δ 167.5, 160.3, 158.4, 143.4, 136.9, 133.4, 132.2, 131.0, 126.8, 125.6, 125.4, 123.9, 119.5, 108.9, 108.7, 100.5, 98.7, 98.4. MS (ESI-Qq-TOF) m/z (amu) calcd for $C_{15}H_{10}FNO_2S$ $[M + H]^+$: 288.0494; Found: 288.0489.

3-[(2-Carboxyphenyl)thio]-1*H*-indole (3g)

Yield, 75 %; A light brown solid; mp 254-255 °C; 1H NMR (500 Hz, DMSO) δ 13.10 (s, 1H), 11.72 (s, 1H), 7.92 (dd, J = 7.7, 1.4 Hz, 1H), 7.73 (d, J = 2.6 Hz, 1H), 7.51 (d, J = 8.2 Hz, 1H), 7.31 (d, J = 7.9 Hz, 1H), 7.23-7.17 (m, 2H), 7.13-7.09 (m, 1H), 7.05 (t, J = 7.4 Hz, 1H), 6.68 (d, J = 7.6 Hz, 1H); ^{13}C NMR

(126 MHz, DMSO) δ 167.4, 143.7, 136.9, 132.6, 132.0, 130.9, 128.7, 126.7, 125.6, 123.7, 122.1, 120.1, 118.3, 112.4, 100.0. MS (ESI-Qq-TOF) m/z (amu) calcd for $C_{15}H_{12}NO_2S$ $[M + H]^+$: 270.0588. Found: 270.0583.

4-Methyl-3-[(2-Carboxyphenyl)thio]-1*H*-indole (3h)

Yield:41%; White solid; mp: 204.5–206.6. 1H NMR(500MHz,DMSO- d_6): δ 11.72(s,1H), 7.98(d,J=7Hz,1H), 7.69(d,J=2.5Hz,1H), 7.39(d,J=8.5Hz,1H), 7.33(t,J=7.8Hz,1H), 7.18(t,J=7.3Hz,1H), 7.11(t,J=7.5Hz,1H),6.81(dd,J=16.5,7.5Hz,2H), 2.47(s,3H). ^{13}C NMR (125 MHz, DMSO- d_6): δ 167.32, 145.96, 137.43, 133.16, 132.21, 130.87, 130.07, 126.59, 126.14, 125.91, 123.63, 122.20, 121.53, 110.30, 100.02, 17.91.

7-Bromo-3-[(2-Carboxyphenyl)thio]-1*H*-indole (3i)

Yield:48%; Light pink solid; mp: 240.5–241.5. 1HNMR (500MHz,DMSO- d_6): δ 12.00(s,1H), 7.94(dd, J=8.0,1.5Hz,1H), 7.81(d,J=3.0Hz, 1H),7.44(d,J=7.0hz,1H), 7.33(d,J=7.5Hz,1H), 7.26-7.23(m,1H), 7.15-7.12(m,1H), 7.03(t,J=7.5Hz,1H), 6.66(d,J=8.0Hz,1H). ^{13}C NMR (125 MHz, DMSO- d_6): δ 167.41, 142.99, 135.19, 133.93, 132.22, 130.99, 130.43, 126.69,125.60, 124.88, 123.94, 121.68, 117.89, 104.97, 101.78.

7-Fluoro-3-[(2-Carboxyphenyl)thio]-1*H*-indole (3j)

Yield:65%; White solid; mp: 222.7°C-224.1°C. 1HNMR (500MHz,DMSO- d_6): δ 13.13(s,1H), 12.25(s,1H), 7.93(d,J=8.0Hz,1H), 7.81(d,J=2.5Hz,1H), 7.24(t,J=7.5,1H), 7.14-7.11(m,2H), 7.05-7.02(m,2H), 6.66(d, J=8.5Hz,1H).

5-Bromo-3-[(4-Carboxyphenyl)thio]-1*H*-indole (3k)

Yield, 49 %; White solid; mp 273.0-274.2°C. ¹H NMR (500 MHz, DMSO): δ 12.01 (s, 1H), 7.89 (d, J = 2.6 Hz, 1H), 7.77 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.6 Hz, 1H), 7.46 (d, J = 1.4 Hz, 1H), 7.33 (dd, J = 8.6, 1.8 Hz, 1H), 7.06 (d, J = 8.4 Hz, 2H). ¹³C NMR (126 MHz, DMSO): δ 166.98, 145.23, 135.62, 134.56, 130.43, 129.95, 127.30, 125.04, 124.64, 120.23, 114.74, 113.15, 97.64.

5-Methyl-3-[(4-Carboxyphenyl)thio]-1*H*-indole (3l)

Yield, 32 %; White solid; mp: 253.4-254.2°C. ¹H NMR (500 MHz, DMSO): δ 11.66 (s, 1H), 7.74 (t, J = 6.2 Hz, 3H), 7.40 (d, J = 8.3 Hz, 1H), 7.15 (s, 1H), 7.04 (dd, J = 14.9, 8.4 Hz, 3H), 2.32 (s, 3H). ¹³C NMR (126 MHz, DMSO): δ 167.05, 146.12, 135.18, 132.89, 129.85, 129.19, 128.77, 127.00, 124.45, 124.02, 117.65, 112.29, 97.03, 21.17. MS (ESI-Qq-TOF) m/z (amu) calcd for C₁₆H₁₄NO₂S [M + H]⁺: 284.0745; Found: 284.0740.

5-Fluoro-3-[(4-Carboxyphenyl)thio]-1*H*-indole (3m)

Yield, 53 %; White solid; mp: 255.2-256.0°C. ¹H NMR (500 MHz, DMSO): δ 11.91 (s, 1H), 7.89 (d, J = 2.7 Hz, 1H), 7.77 (d, J = 8.4 Hz, 2H), 7.53 (dd, J = 9.6, 4.4 Hz, 1H), 7.15-6.97 (m, 4H). ¹³C NMR (126 MHz, DMSO): δ 167.05, 146.12, 135.18, 132.89, 129.85, 129.19, 128.77, 127.00, 124.45, 124.02, 117.65, 112.29, 97.03, 21.17. MS (ESI-Qq-TOF) m/z (amu) calcd for C₁₅H₁₁FNO₂S [M + H]⁺: 288.0494; Found: 288.0489.

6-Fluoro-3-[(4-Carboxyphenyl)thio]-1*H*-indole (3n)

Yield, 45 %; White solid; mp: 224.8-226.1 °C. ¹H NMR (500 MHz, DMSO): δ 11.76 (s, 1H), 7.92 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.73 (d, *J* = 2.5 Hz, 1H), 7.38-7.25 (m, 2H), 7.26-7.18 (m, 1H), 7.12 (t, *J* = 7.2 Hz, 1H), 6.91 (td, *J* = 9.6, 2.3 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H). ¹³C NMR (126 MHz, DMSO): δ 167.46, 160.31, 158.44, 143.35, 136.86, 133.38, 132.19, 131.01, 126.78, 125.60, 125.36, 123.92, 119.49, 108.89, 108.70, 100.48, 98.65, 98.44. MS (ESI-Qq-TOF) *m/z* (amu) calcd for C₁₅H₁₁FNO₂S [M + H]⁺: 288.0494; Found: 288.0489.

5-Methoxyl-3-[(4-Carboxyphenyl)thio]-1*H*-indole (3o)

Yield, 68 %; White solid; mp: 216.3-217.1 °C. ¹H NMR (500 MHz, DMSO): δ 11.67 (s, 1H), 7.75 (dd, *J* = 10.5, 5.6 Hz, 3H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.85 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.81 (d, *J* = 2.2 Hz, 1H), 3.67 (s, 3H). ¹³C NMR (126 MHz, DMSO): δ 167.08, 154.52, 146.00, 133.31, 131.75, 129.87, 129.32, 127.02, 124.48, 113.44, 112.55, 99.62, 97.23, 55.35. MS (ESI-Qq-TOF) *m/z* (amu) calcd for C₁₆H₁₄NO₃S [M + H]⁺: 300.0694; Found: 300.0689.

5-Methoxyl-3-[(3-Carboxyphenyl)thio]-1*H*-indole (3q)

Yield, 34 %; White solid. ¹H NMR (500 MHz, DMSO) δ 11.62 (s, 1H), 7.74 (s, 1H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.56 (s, 1H), 7.41 (dd, *J* = 9.3, 1.9 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.28 (d, *J* = 7.4 Hz, 1H), 6.88-6.79 (m, 2H), 3.68 (s, 3H). ¹³C NMR (126 MHz, DMSO) δ 166.90 (s, 1H), 154.45 (s, 1H), 140.30 (s, 1H), 133.23 (s, 2H), 131.73 (s, 1H), 131.51 (s, 1H), 129.42 (d, *J* = 7.0 Hz, 3H), 129.13 (s, 2H), 125.74 (d, *J* = 13.9 Hz, 4H), 113.36 (s, 2H), 112.45 (s, 2H), 99.71 (s, 2H), 98.05 (s, 1H), 55.34 (s, 2H). MS (ESI-Qq-TOF) *m/z* (amu) calcd for C₁₆H₁₄NO₃S [M + H]⁺: 300.0694; Found: 300.0689.

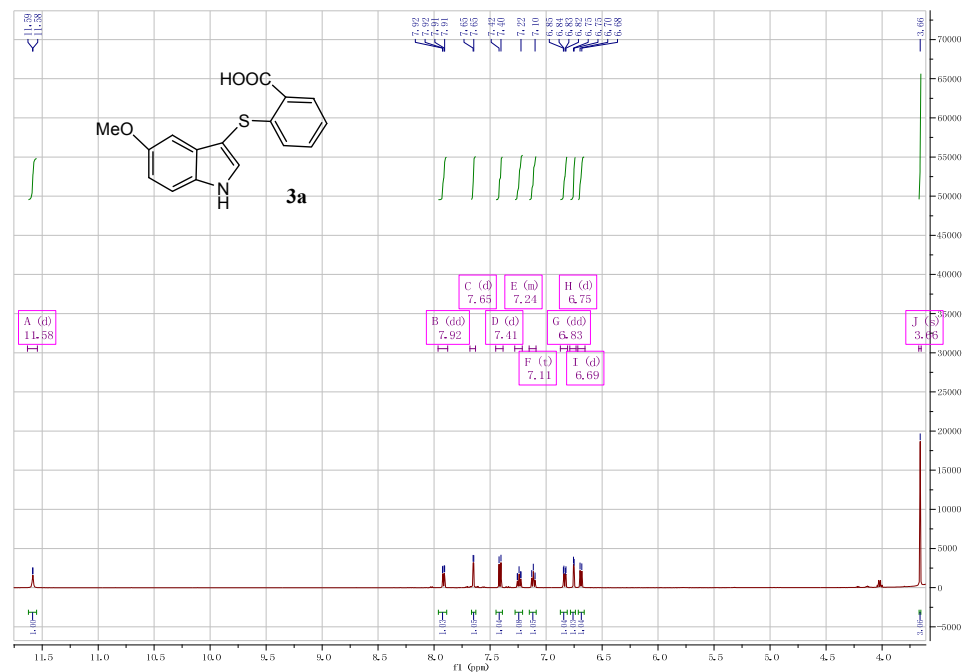


Figure S1. ¹H NMR spectrum for 5-Methoxy-3-[(2-Carboxyphenyl)thio]-1*H*-indole (3a)

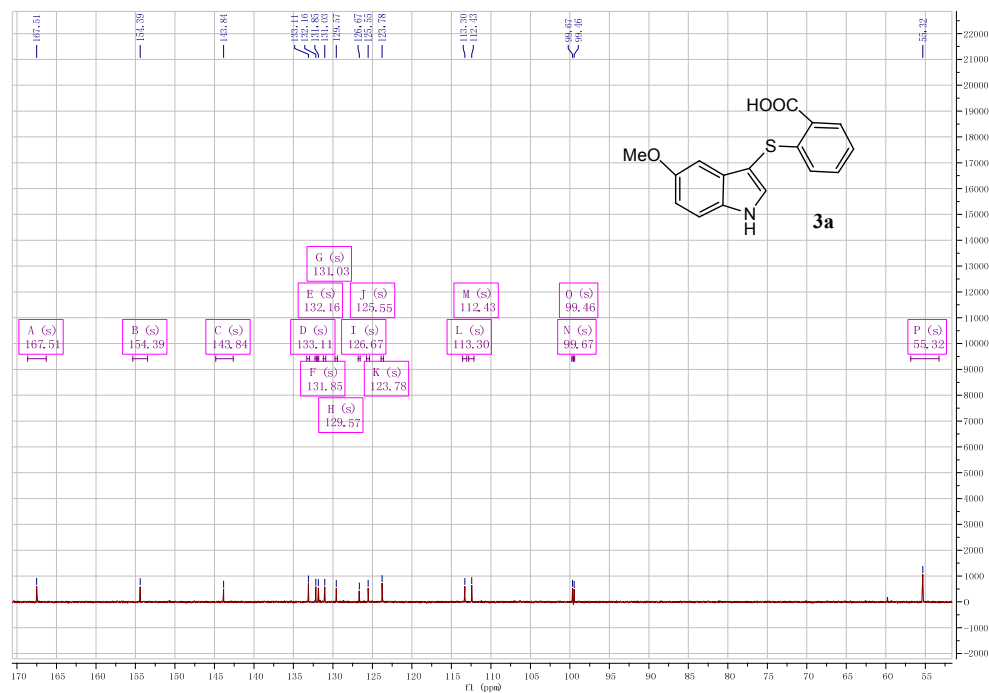


Figure S2. ¹³C NMR spectrum for 5-Methoxy-3-[(2-Carboxyphenyl)thio]-1*H*-indole (3a)

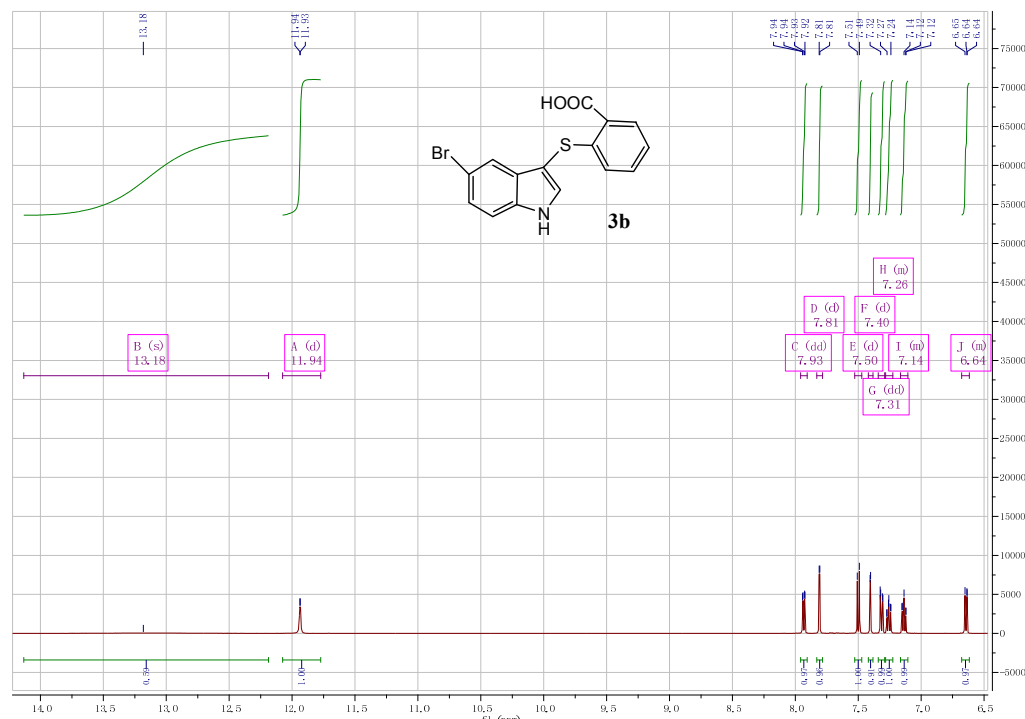


Figure S3. ¹H NMR spectrum for 5-Bromo-3-[(2-Carboxyphenyl)thio]-1*H*-indole (**3b**).

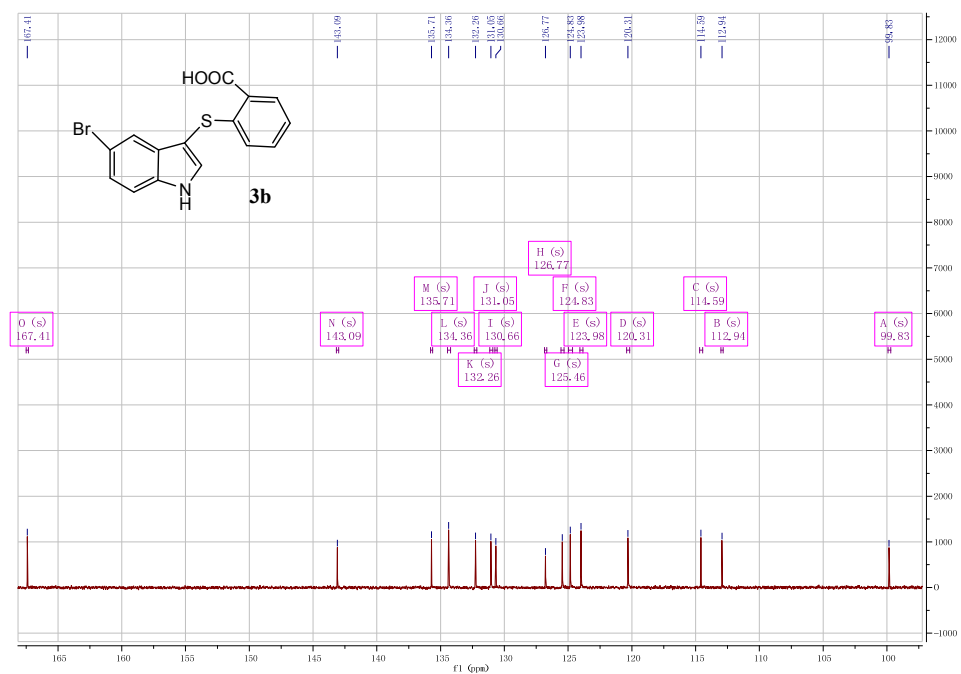


Figure S4. ¹³C NMR spectrum for 5-Bromo-3-[(2-Carboxyphenyl)thio]-1*H*-indole (**3b**).

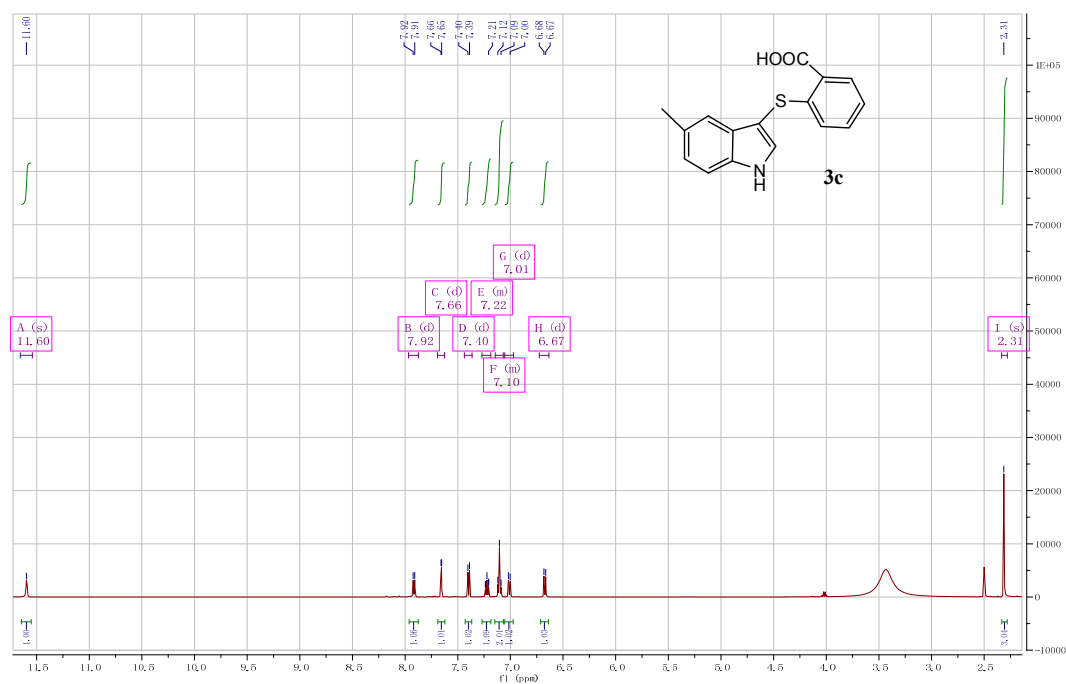


Figure S5. ¹H NMR spectrum for 5- Methyl-3-[(2-Carboxyphenyl)thio]-1H-indole (3c).

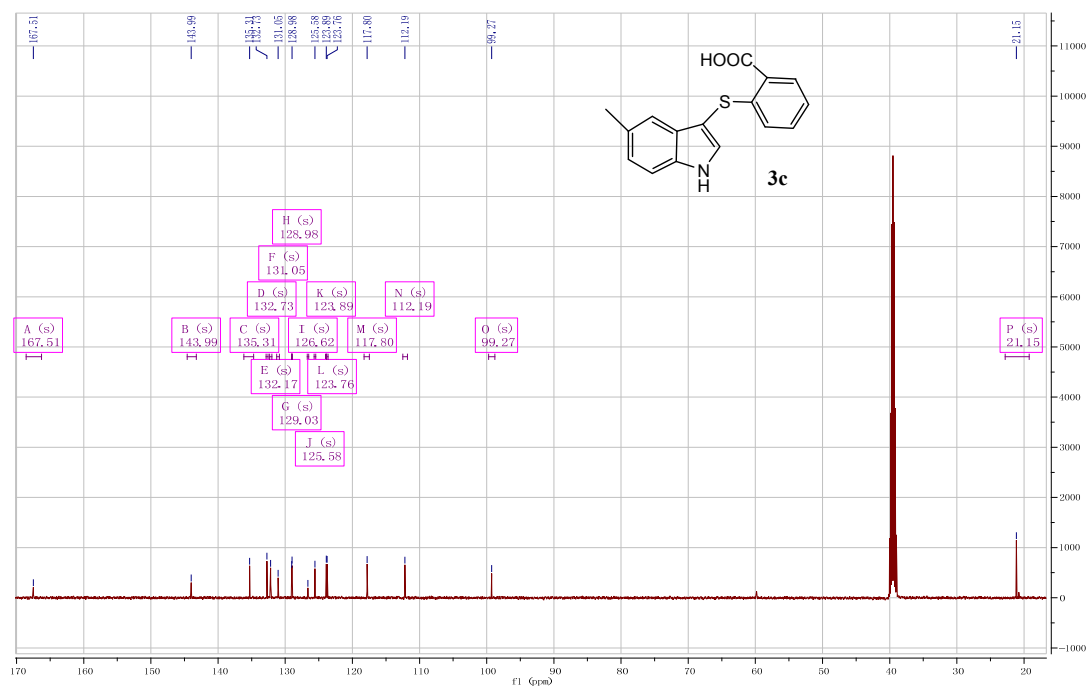


Figure S6. ¹³C NMR spectrum for 5- Methyl-3-[(2-Carboxyphenyl)thio]-1H-indole (3c).

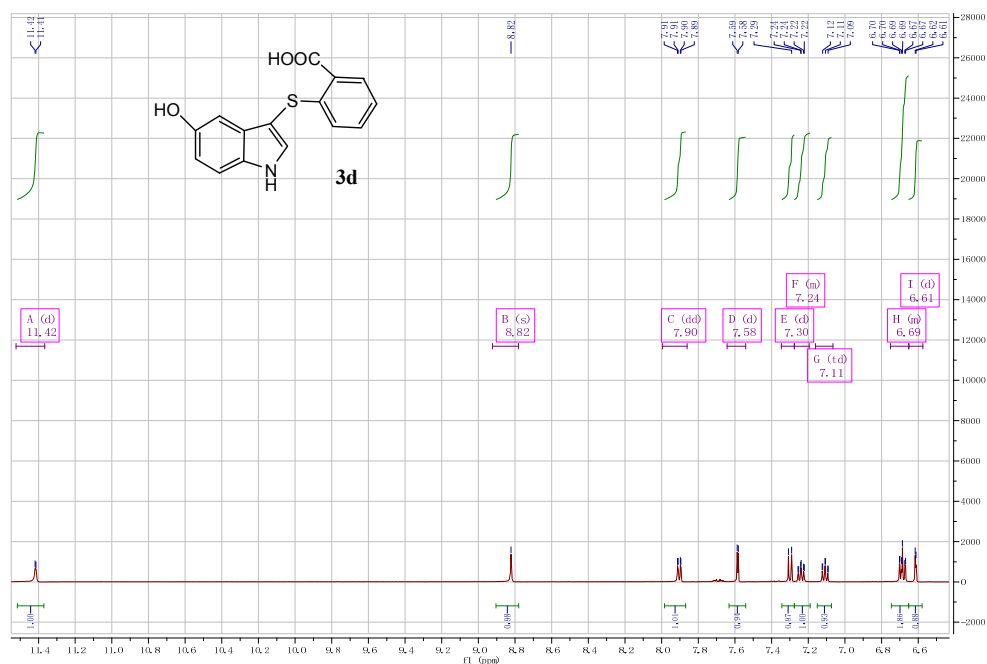


Figure S7. ¹H NMR spectrum for 5-Hydroxyl-3-[(2-Carboxyphenyl)thio]-1*H*-indole (**3d**)

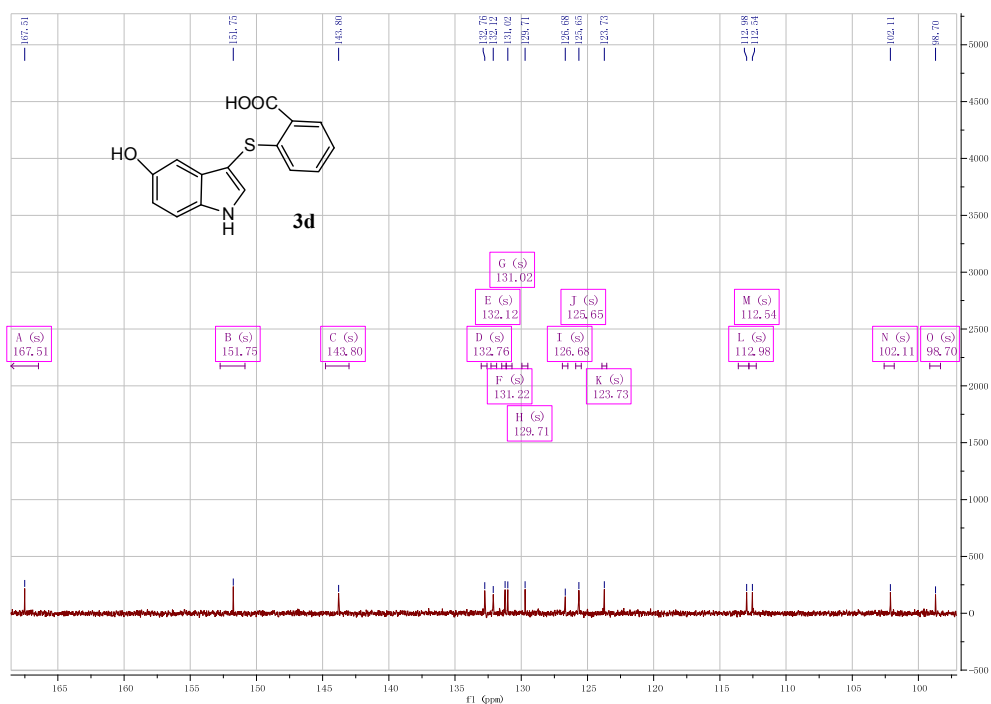


Figure S8. ¹³C NMR spectrum for 5-Hydroxyl-3-[(2-Carboxyphenyl)thio]-1*H*-indole (**3d**)

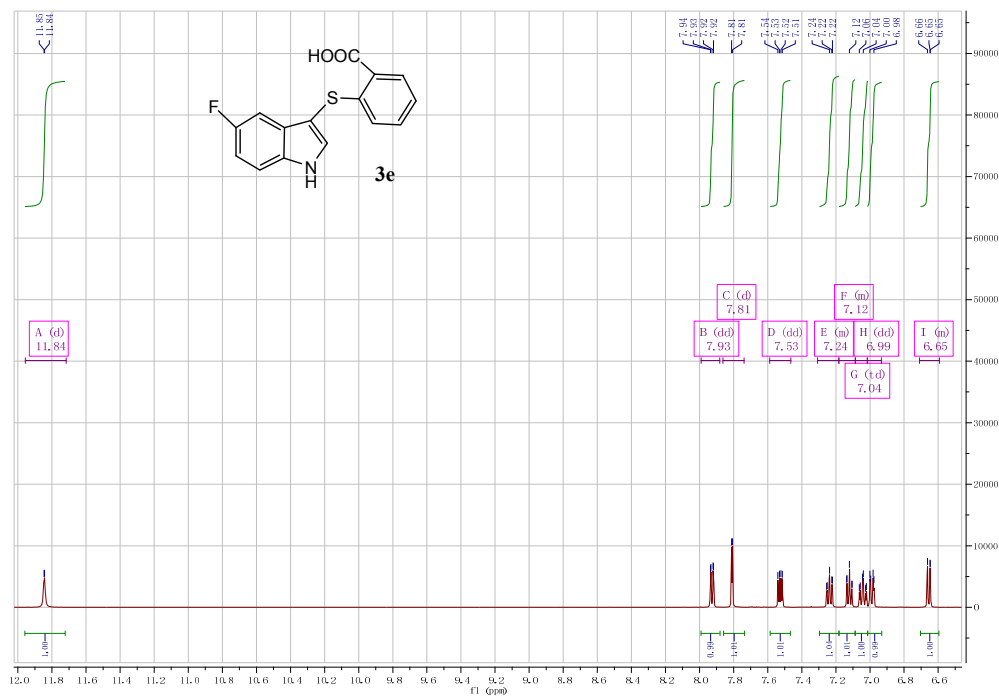


Figure S9. ¹H NMR spectrum for 5-Fluoro-3-[(2-Carboxyphenyl)thio]-1*H*-indole (**3e**)

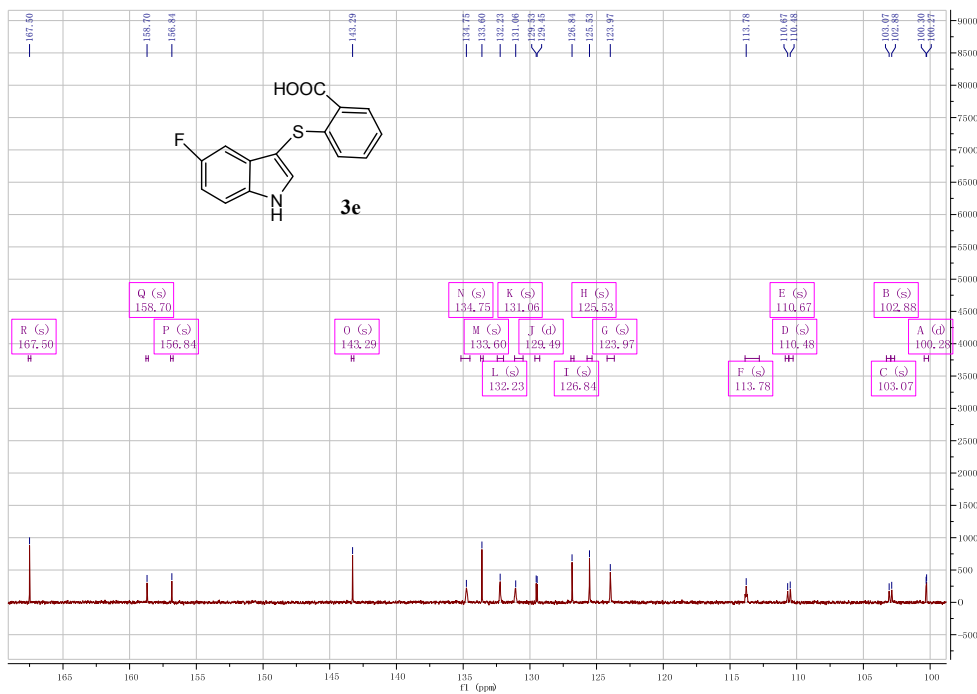


Figure S10. ¹³C NMR spectrum for 5-Fluoro-3-[(2-Carboxyphenyl)thio]-1*H*-indole (**3e**)

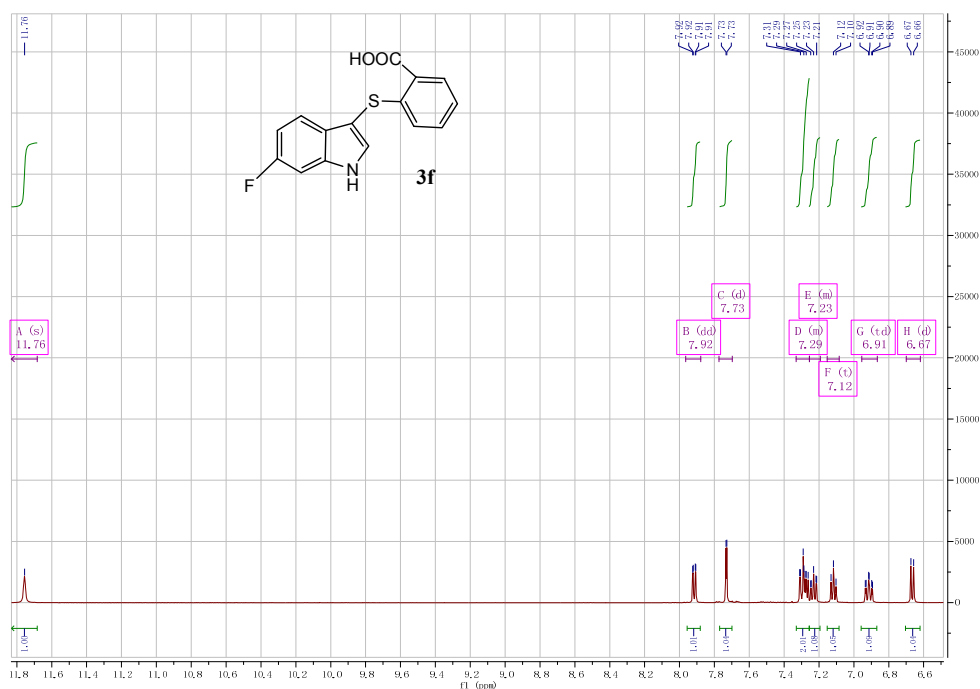


Figure S11. ¹H NMR spectrum for 6-Fluoro-3-[(2-Carboxyphenyl)thio]-1H-indole (**3f**)

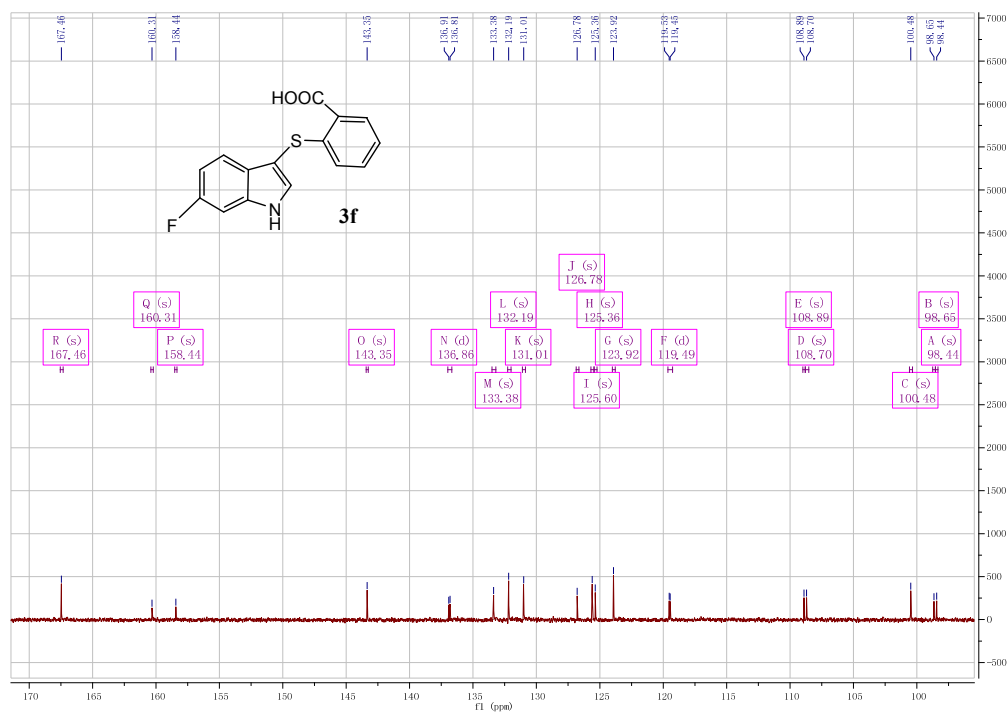


Figure S12. ¹³C NMR spectrum for 6-Fluoro-3-[(2-Carboxyphenyl)thio]-1H-indole (**3f**)

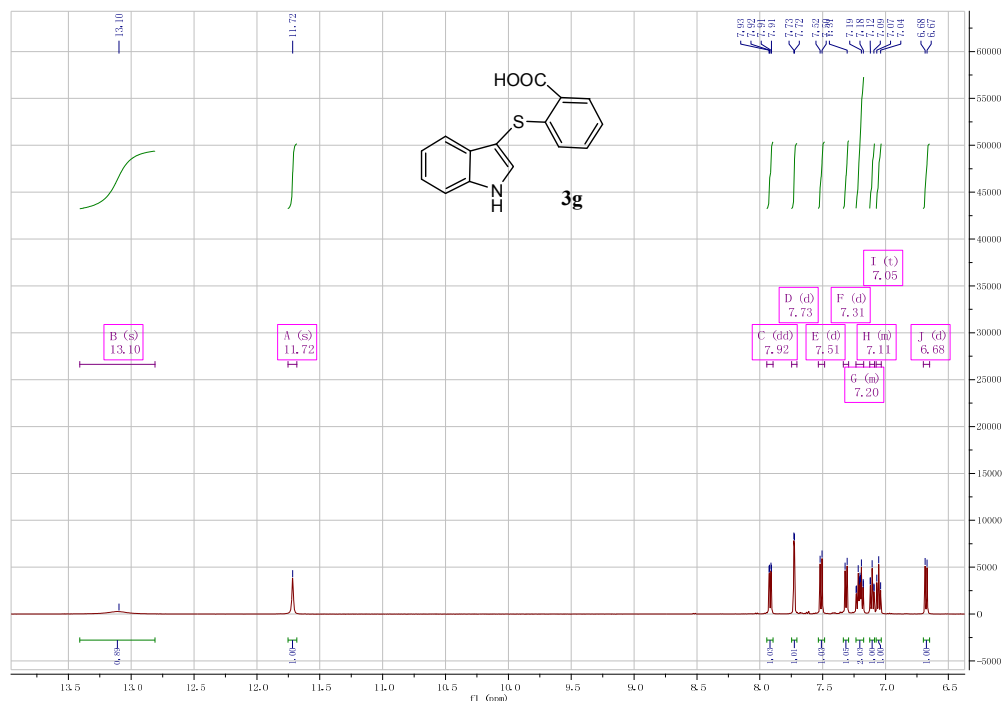


Figure S13. ¹H spectrum for 3-[(2-Carboxyphenyl)thio]-1*H*-indole (**3g**).

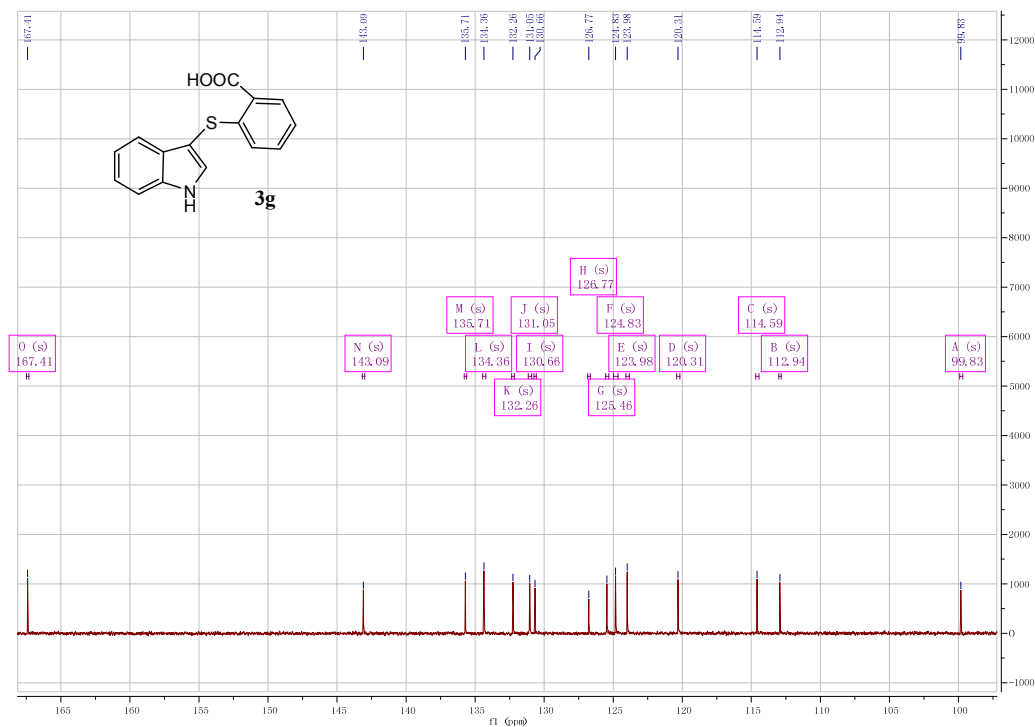


Figure S14. ¹³C NMR spectrum for 3-[(2-Carboxyphenyl)thio]-1*H*-indole (**3g**).

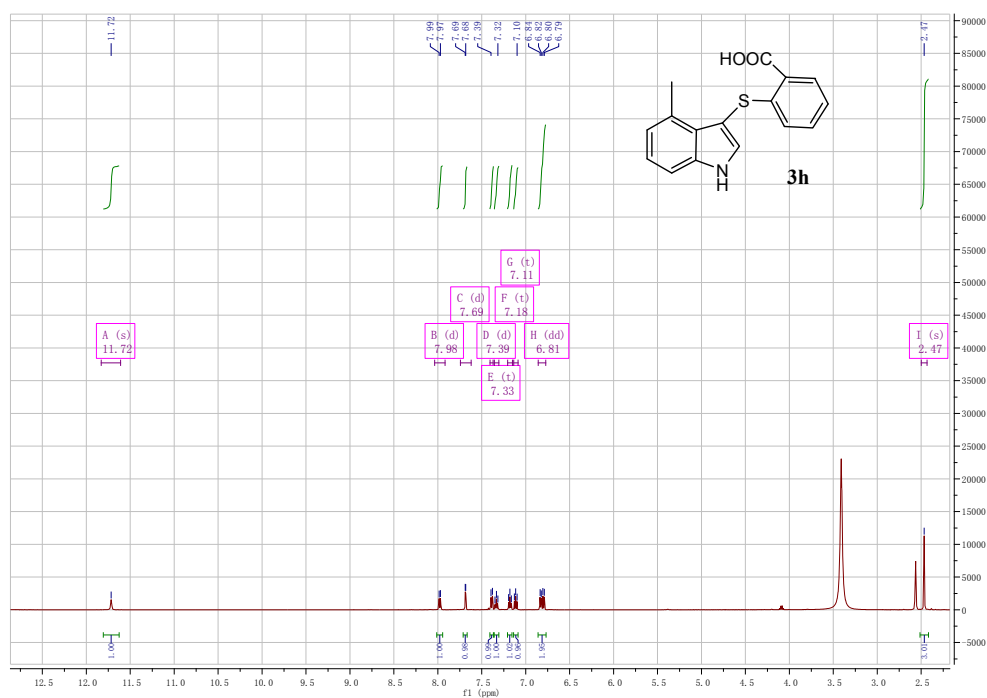


Figure S15. ¹H NMR spectrum for 4-Methyl-3-[(2-Carboxyphenyl)thio]-1*H*-indole (**3h**)

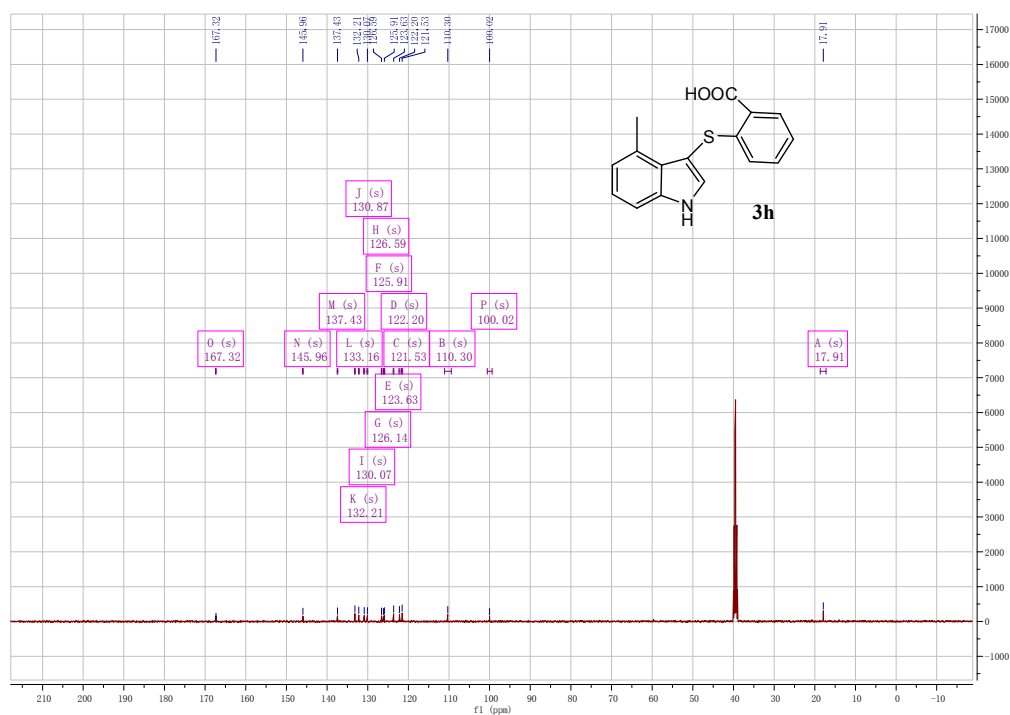


Figure S16. ¹³C NMR spectrum for 4-Methyl-3-[(2-Carboxyphenyl)thio]-1*H*-indole (**3h**)

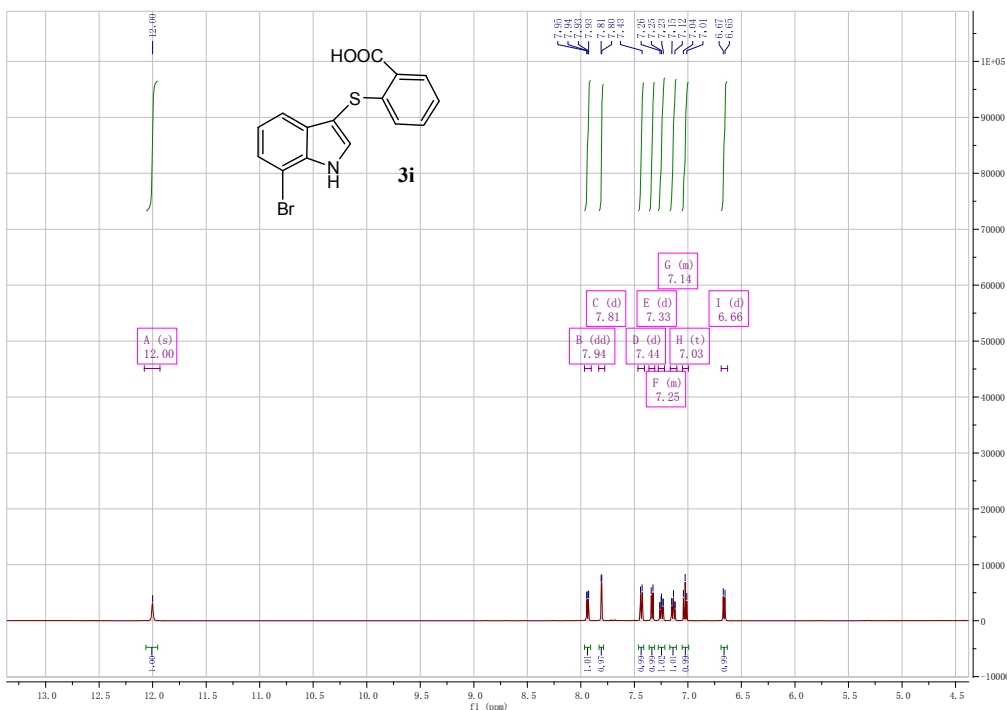


Figure S17. ¹H NMR spectrum for 7-Bromo-3-[(2-Carboxyphenyl)thio]-1*H*-indole (**3i**)

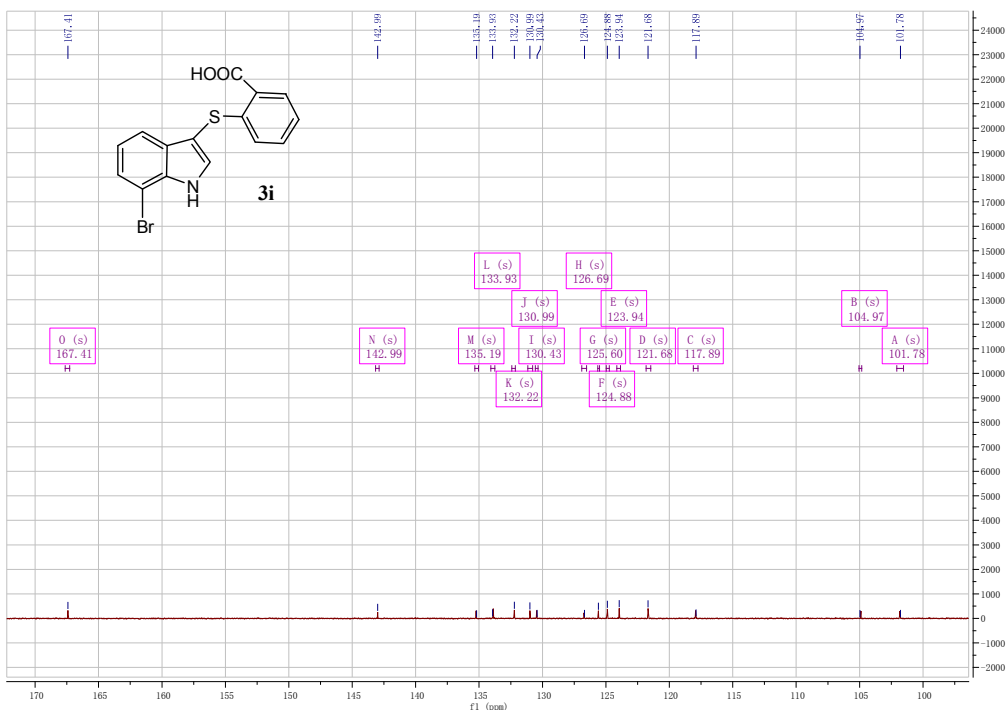


Figure S18. ¹³C NMR spectrum for 7-Bromo-3-[(2-Carboxyphenyl)thio]-1*H*-indole (**3i**)

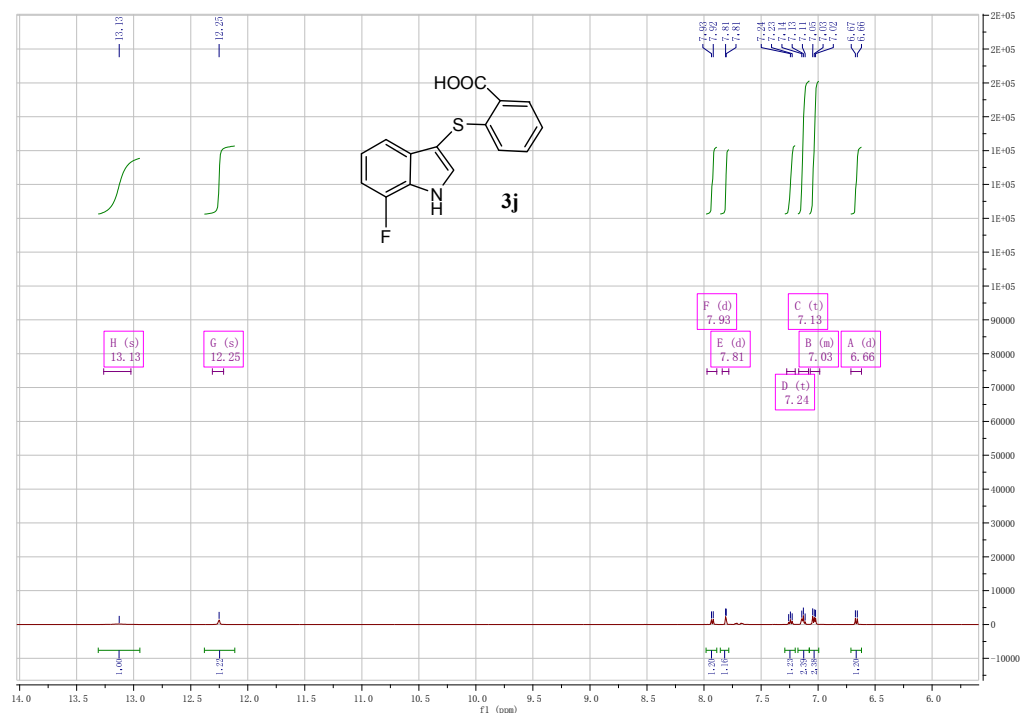


Figure S19. ¹H NMR spectrum for 7-Fluoro-3-[(2-Carboxyphenyl)thio]-1*H*-indole (**3j**)

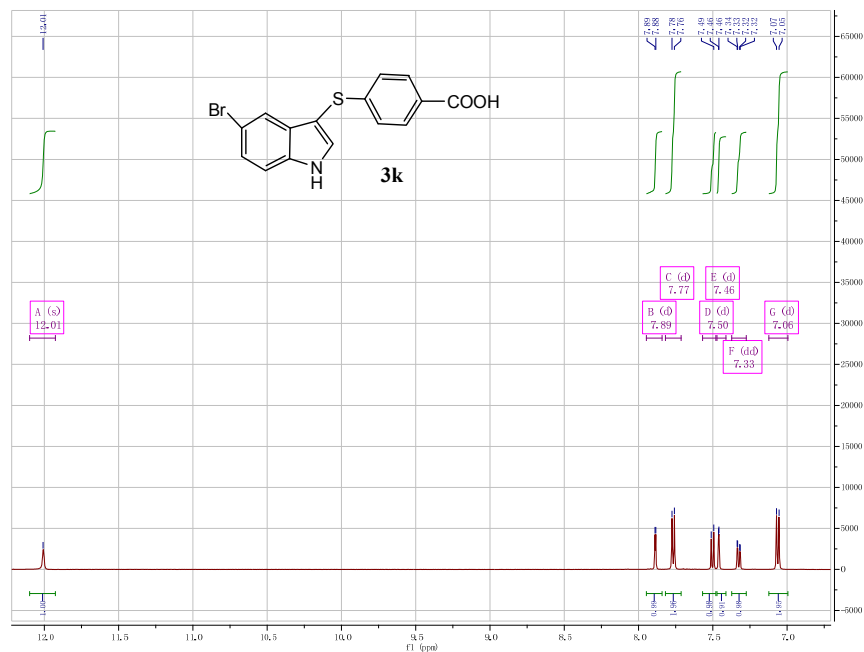


Figure S20. ¹H NMR spectrum for 5-Bromo-3-[(4-Carboxyphenyl)thio]-1*H*-indole (**3k**)

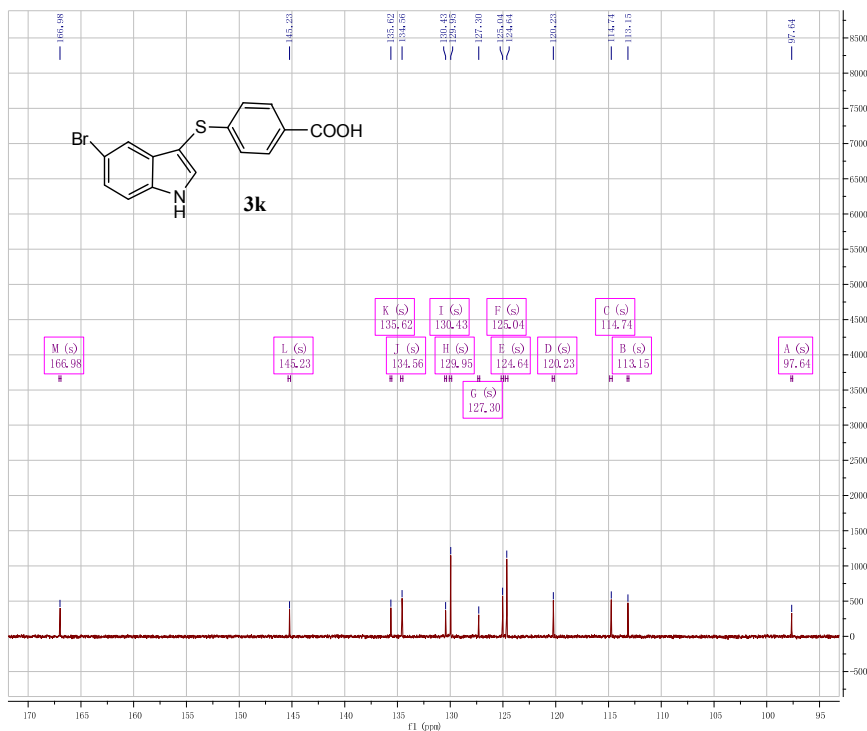


Figure S21. ¹³C NMR spectrum for 5-Bromo-3-[(4-Carboxyphenyl)thio]-1*H*-indole (**3k**)

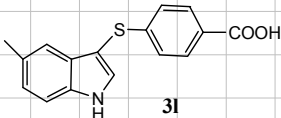


Figure S22. ¹H NMR spectrum for 5-Methyl-3-[(4-Carboxyphenyl)thio]-1*H*-indole (**31**)

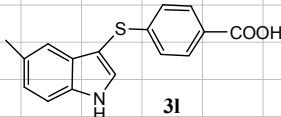


Figure S23. ^{13}C NMR spectrum for 5-Methyl-3-[(4-Carboxyphenyl)thio]-1*H*-indole (**31**)

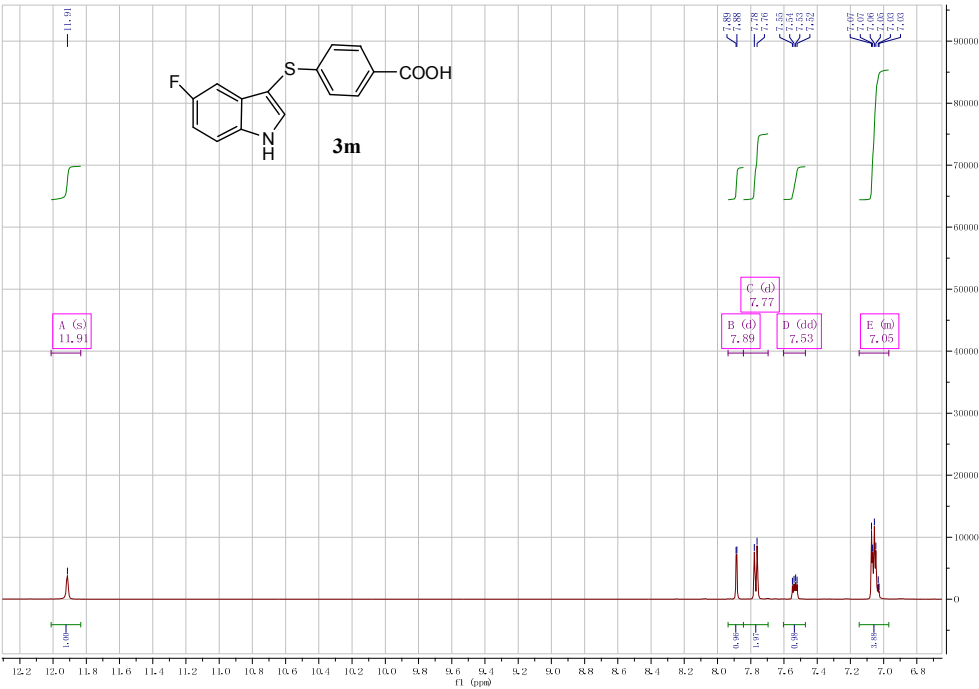


Figure S24. ¹H NMR spectrum for 5-Fluoro-3-[(4-Carboxyphenyl)thio]-1H-indole (**3m**)

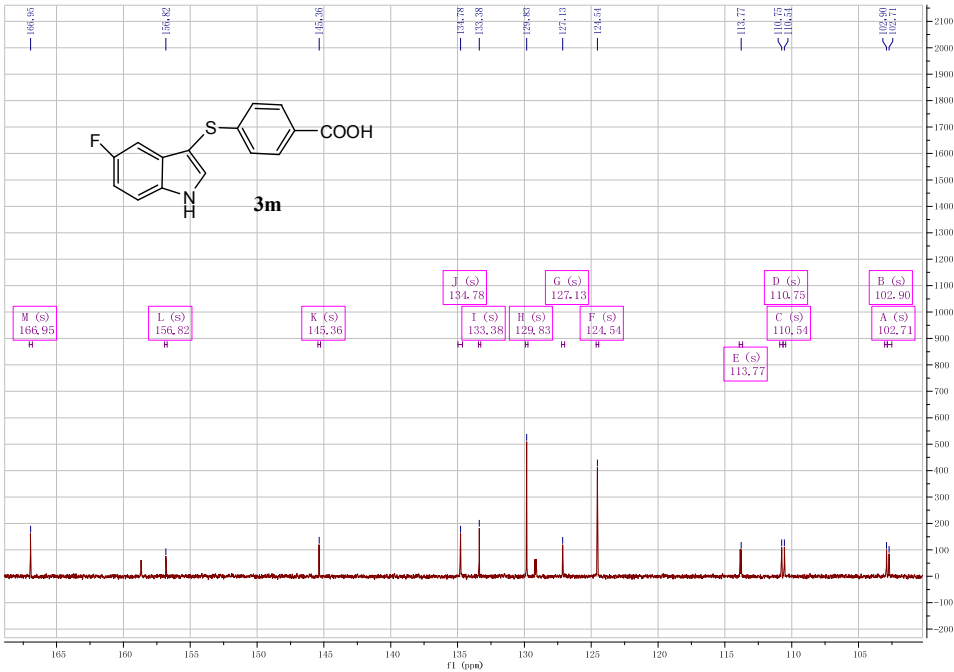


Figure S25. ¹³C NMR spectrum for 5-Fluoro-3-[(4-Carboxyphenyl)thio]-1H-indole (**3m**)

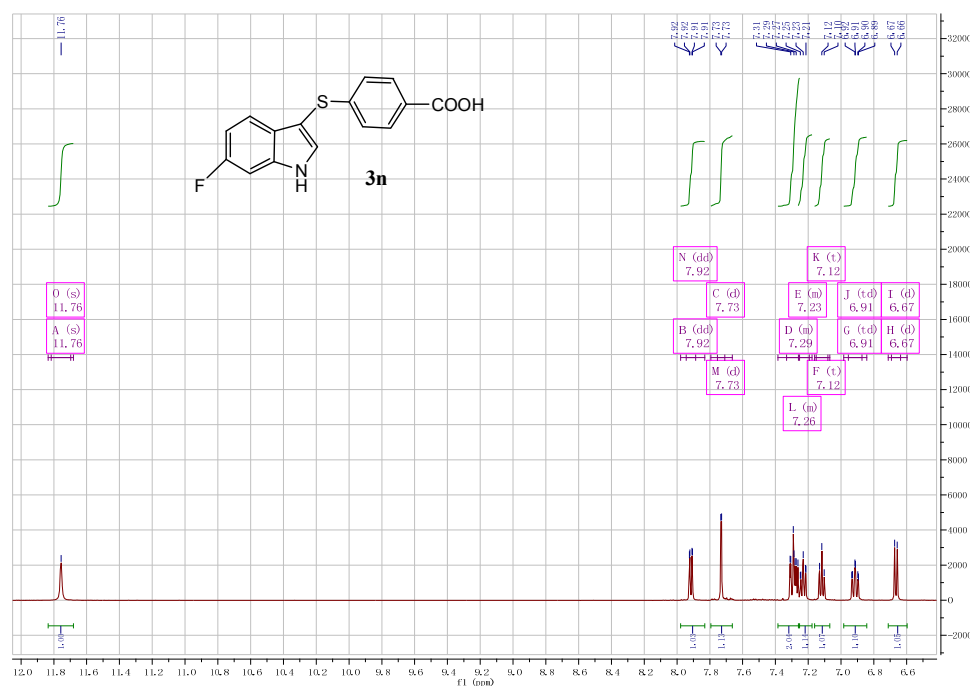


Figure S26. ¹H NMR spectrum for 6-Fluoro-3-[(4-Carboxyphenyl)thio]-1H-indole (3n)

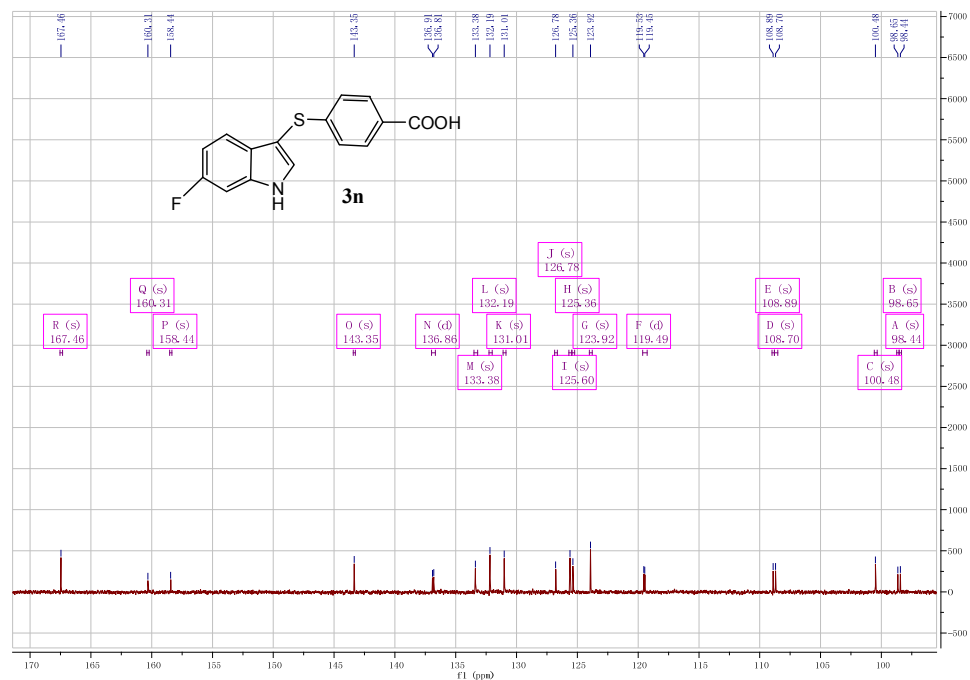


Figure S27. ¹³C NMR spectrum for 6-Fluoro-3-[(4-Carboxyphenyl)thio]-1H-indole (3n)

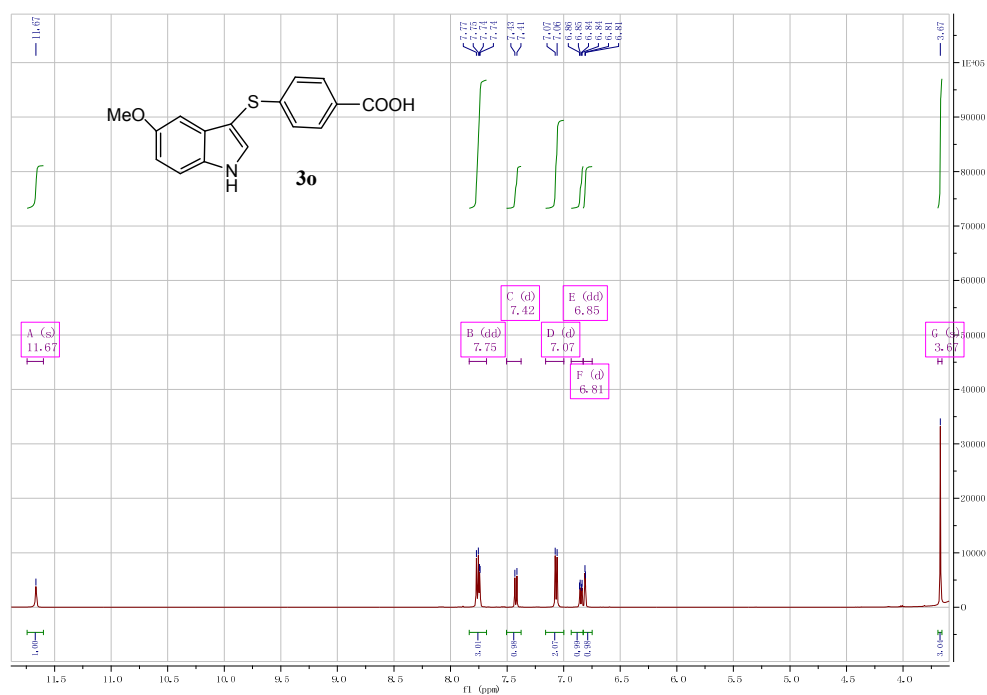


Figure S28. ¹H NMR spectrum for 5-Methoxyl-3-[(4-Carboxyphenyl)thio]-1*H*-indole (**30**)

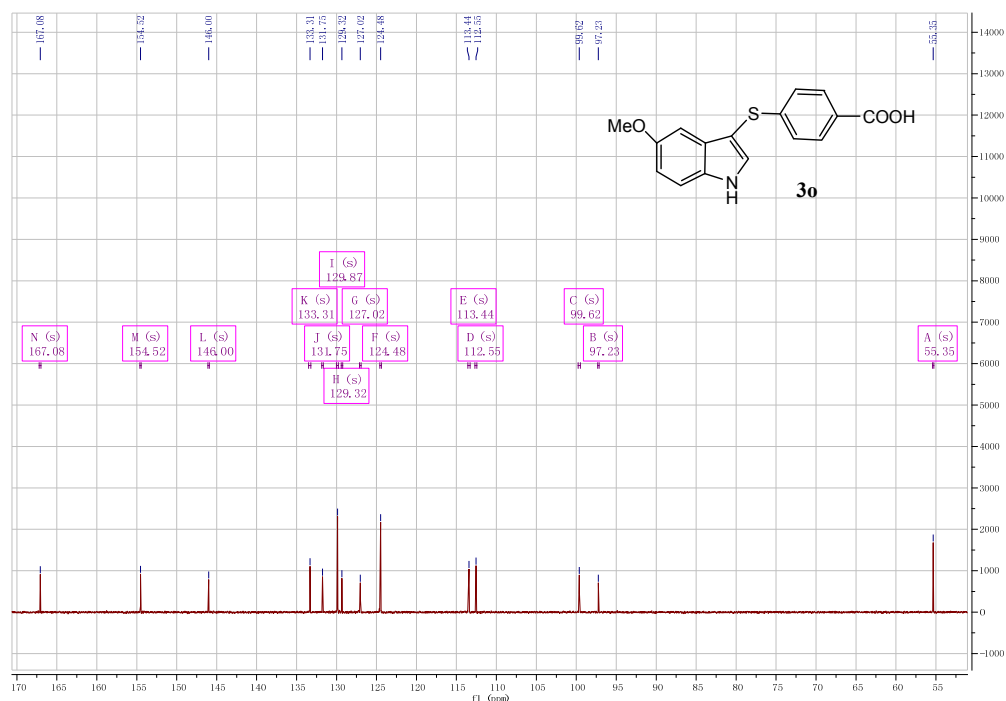


Figure S29. ^{13}C NMR spectrum for 5-Methoxy-1-3-[(4-Carboxyphenyl)thio]-1*H*-indole (**30**)

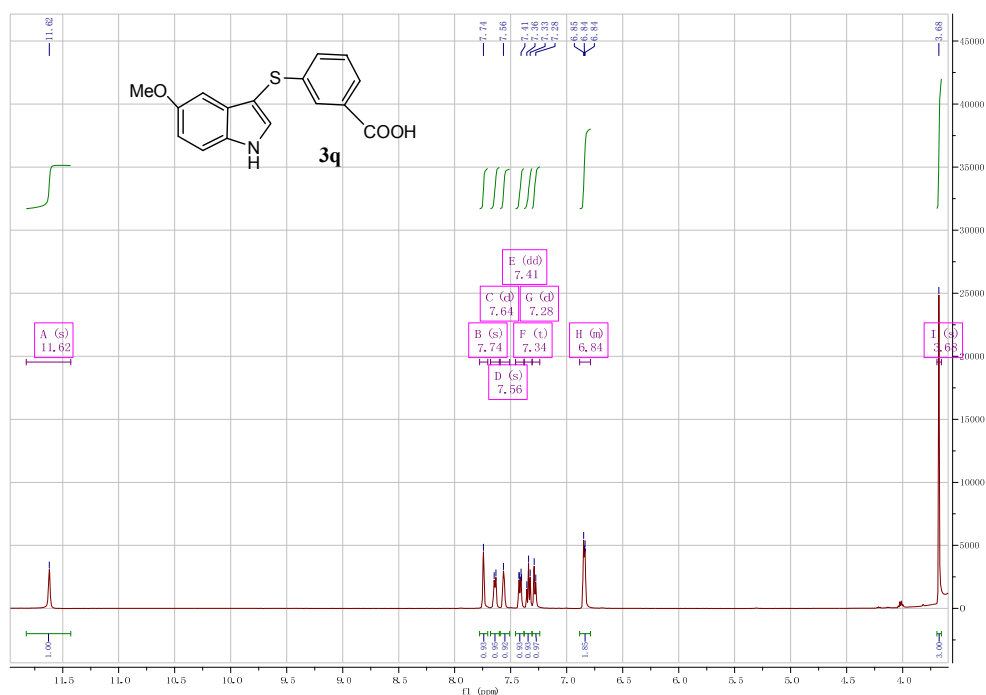


Figure S30. ¹H NMR spectrum for 5-Methoxy-3-[(3-Carboxyphenyl)thio]-1H-indole (**3q**)

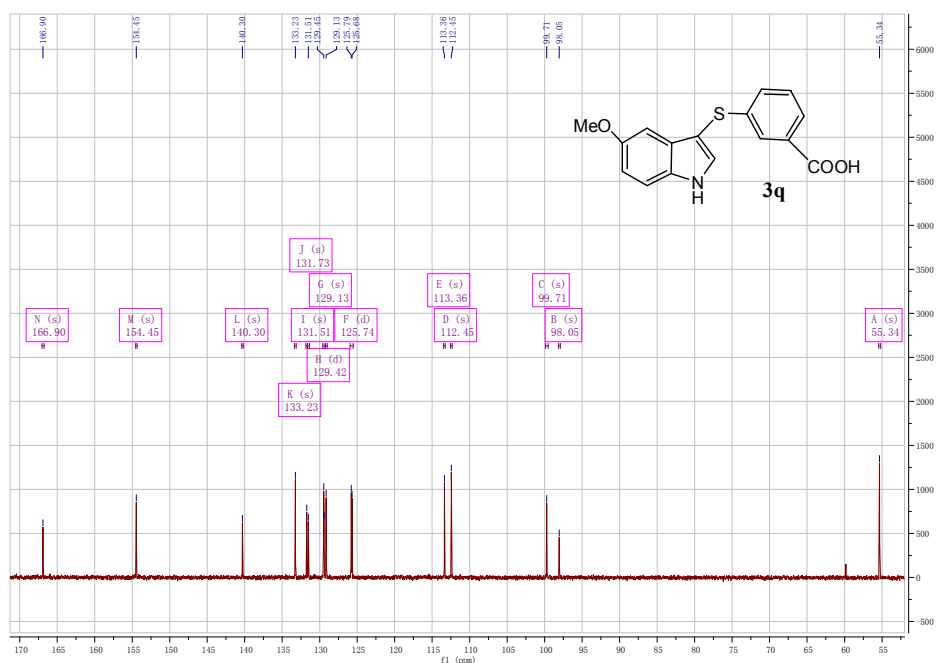


Figure S31. ¹³C NMR spectrum for 5-Methoxy-3-[(3-Carboxyphenyl)thio]-1H-indole (**3q**)

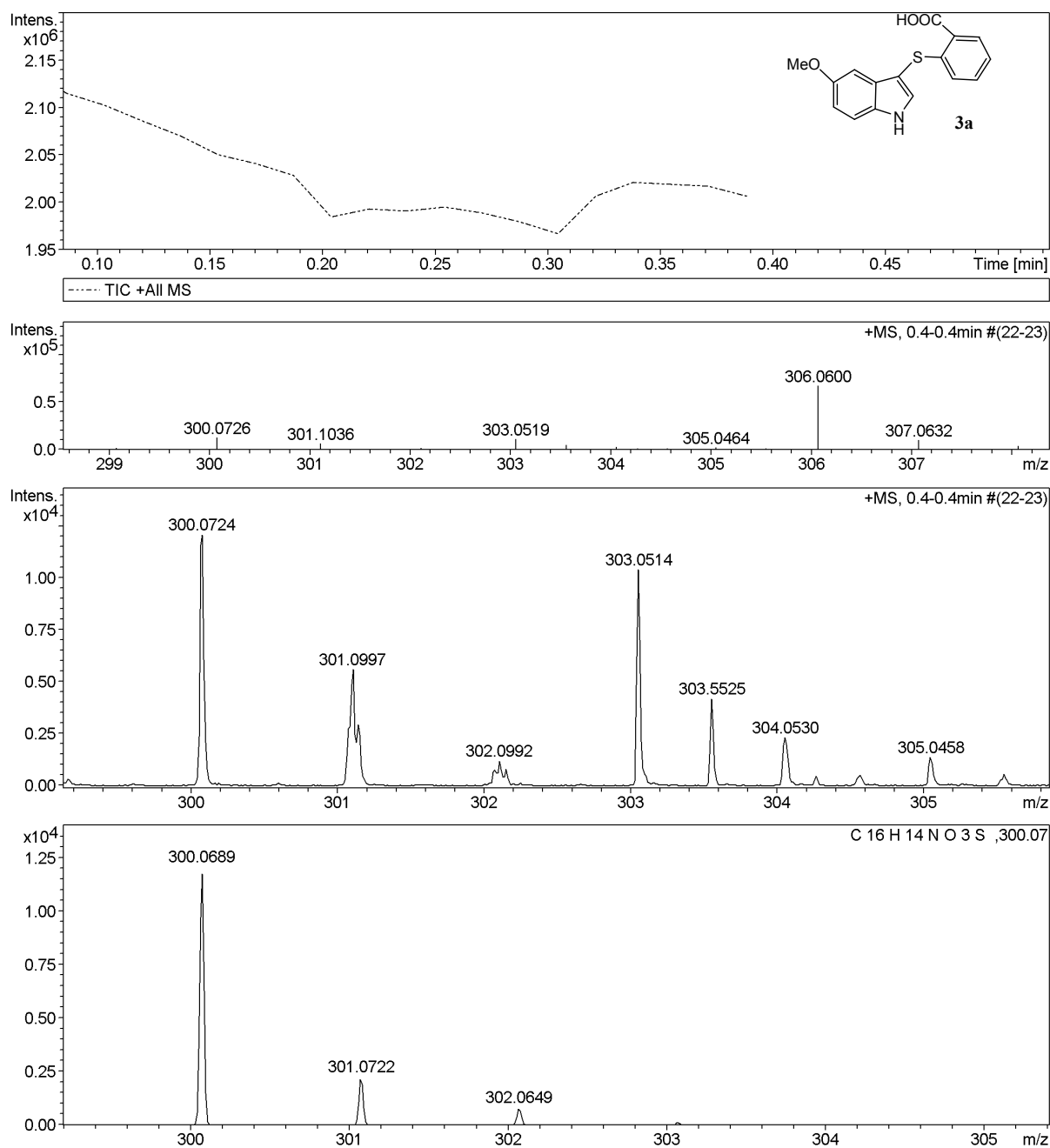


Figure S32. ESI-Qq-TOF mass spectrum for 5-Methoxy-3-[(2-Carboxyphenyl)thio]-1H-indole (**3a**).

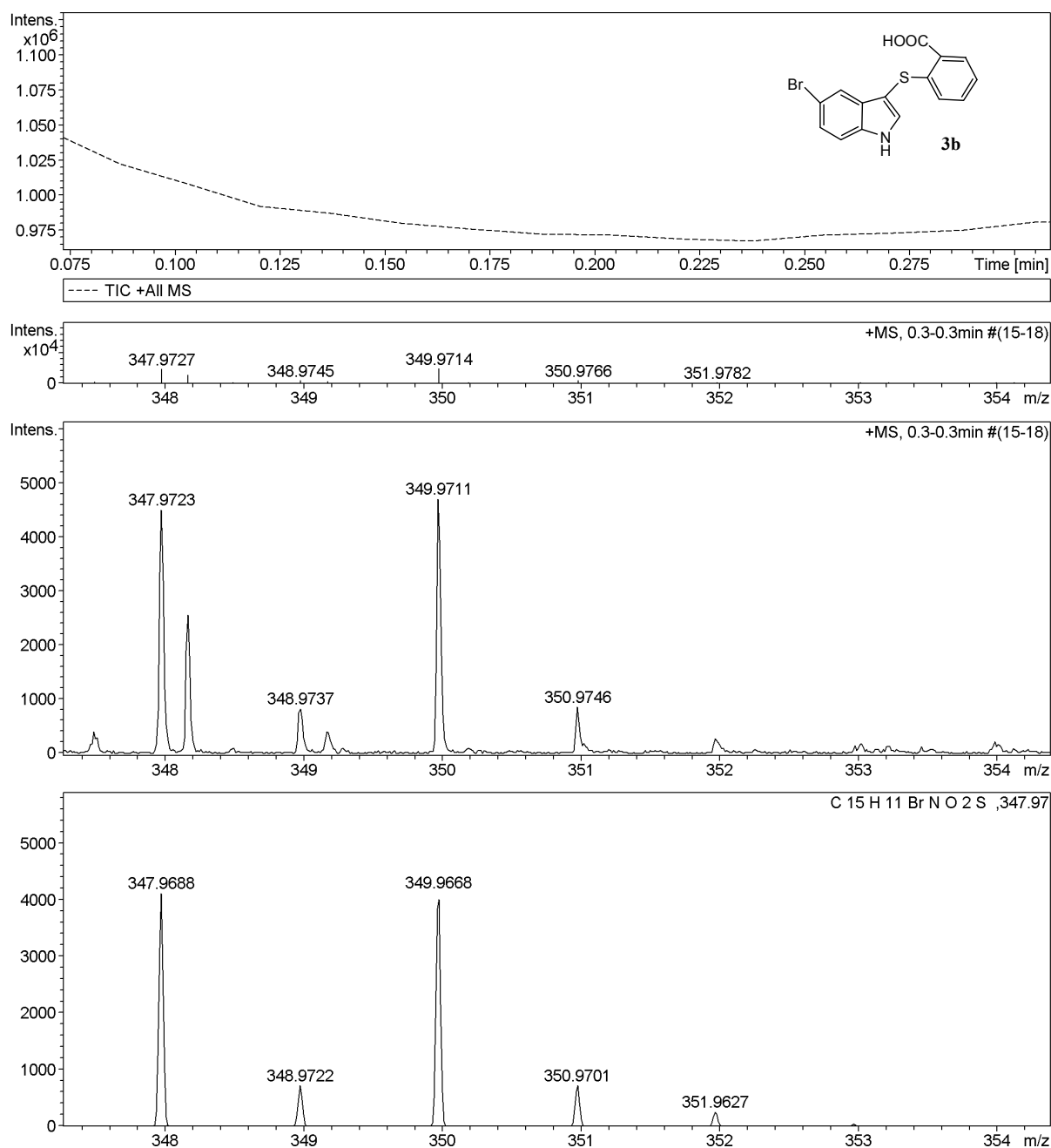


Figure S33. ESI-Qq-TOF mass spectrum for 5-Bromo-3-[(2-Carboxyphenyl)thio]-1H-indole (**3b**).

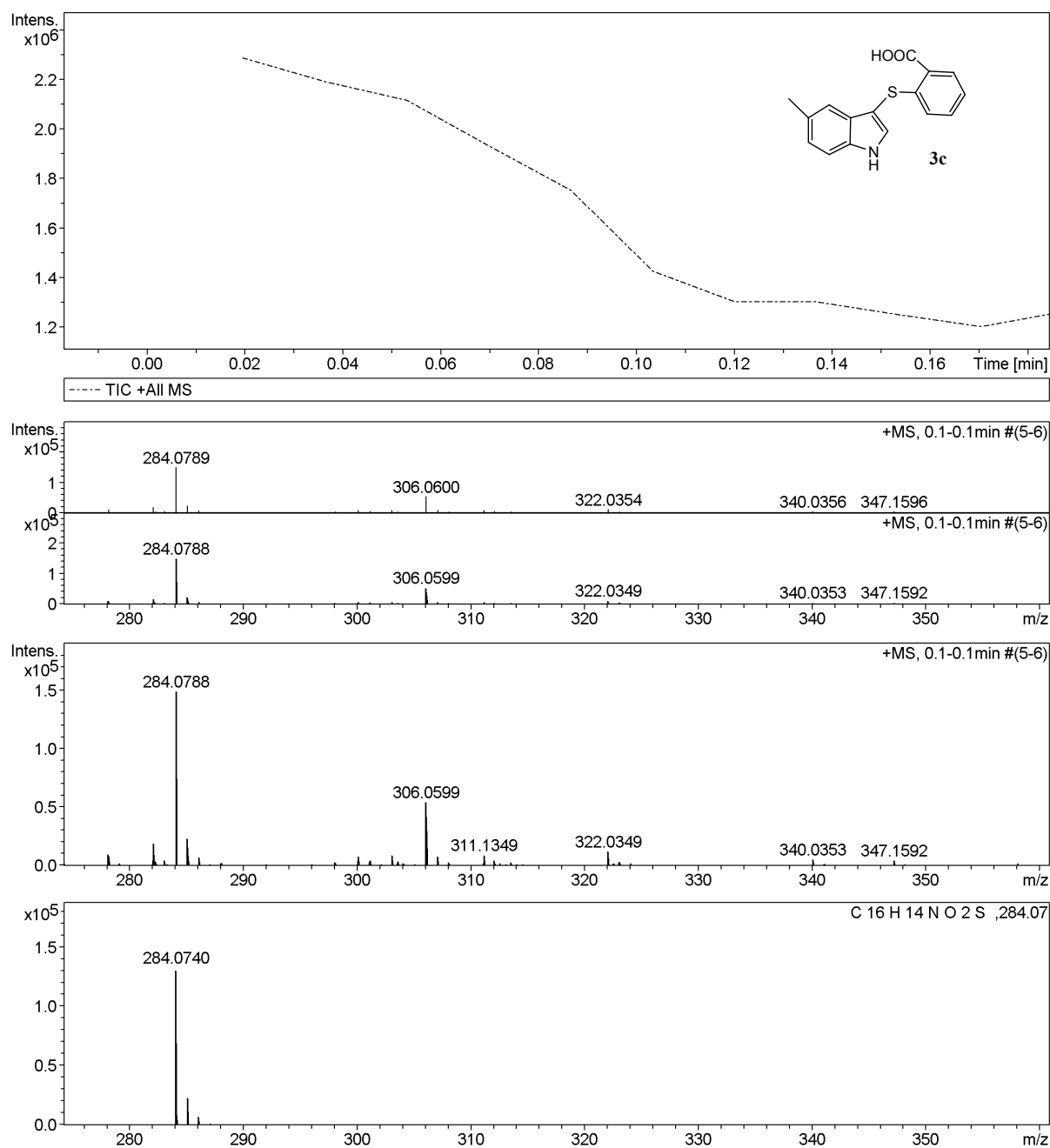


Figure S34. ESI-Qq-TOF mass spectrum for 5-Methyl-3-[(2-Carboxyphenyl)thio]-1H-indole (**3c**).

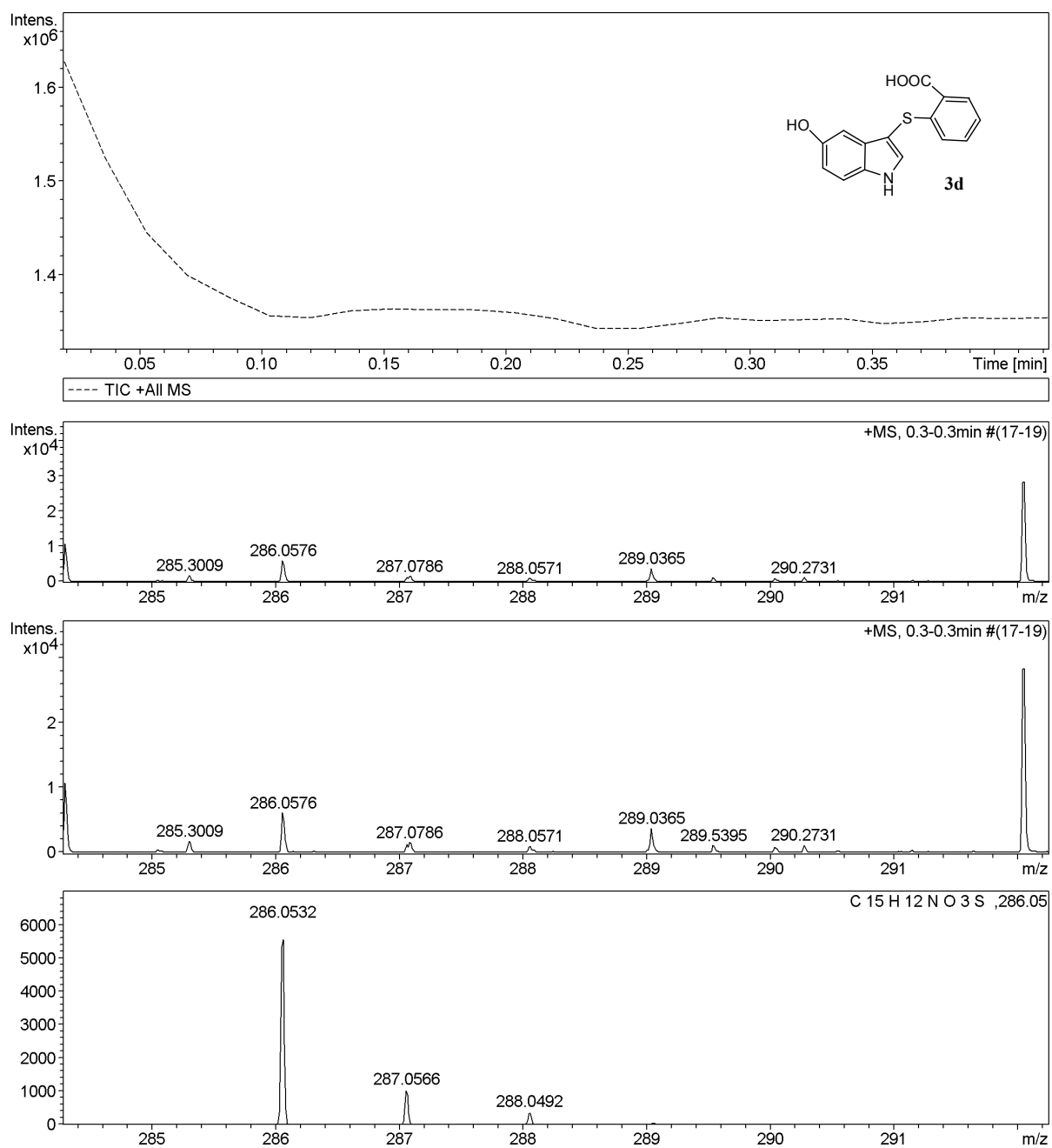


Figure S35. ESI-Qq-TOF mass spectrum for 5-Hydroxyl-3-[(2-Carboxyphenyl)thio]-1*H*-indole (**3d**)

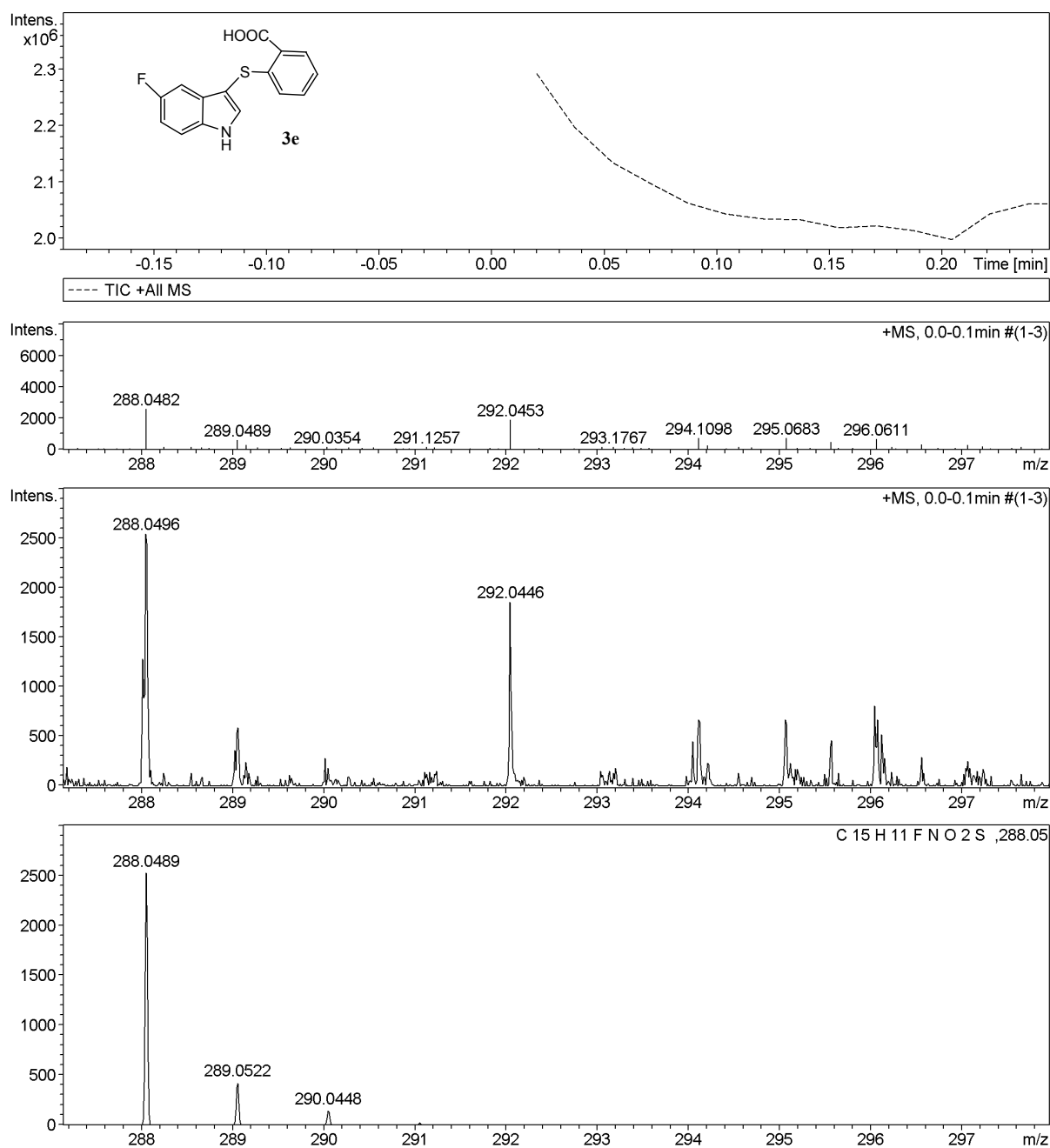


Figure S36. ESI-Qq-TOF mass spectrum for 5-Fluoro-3-[(2-Carboxyphenyl)thio]-1H-indole (**3e**)

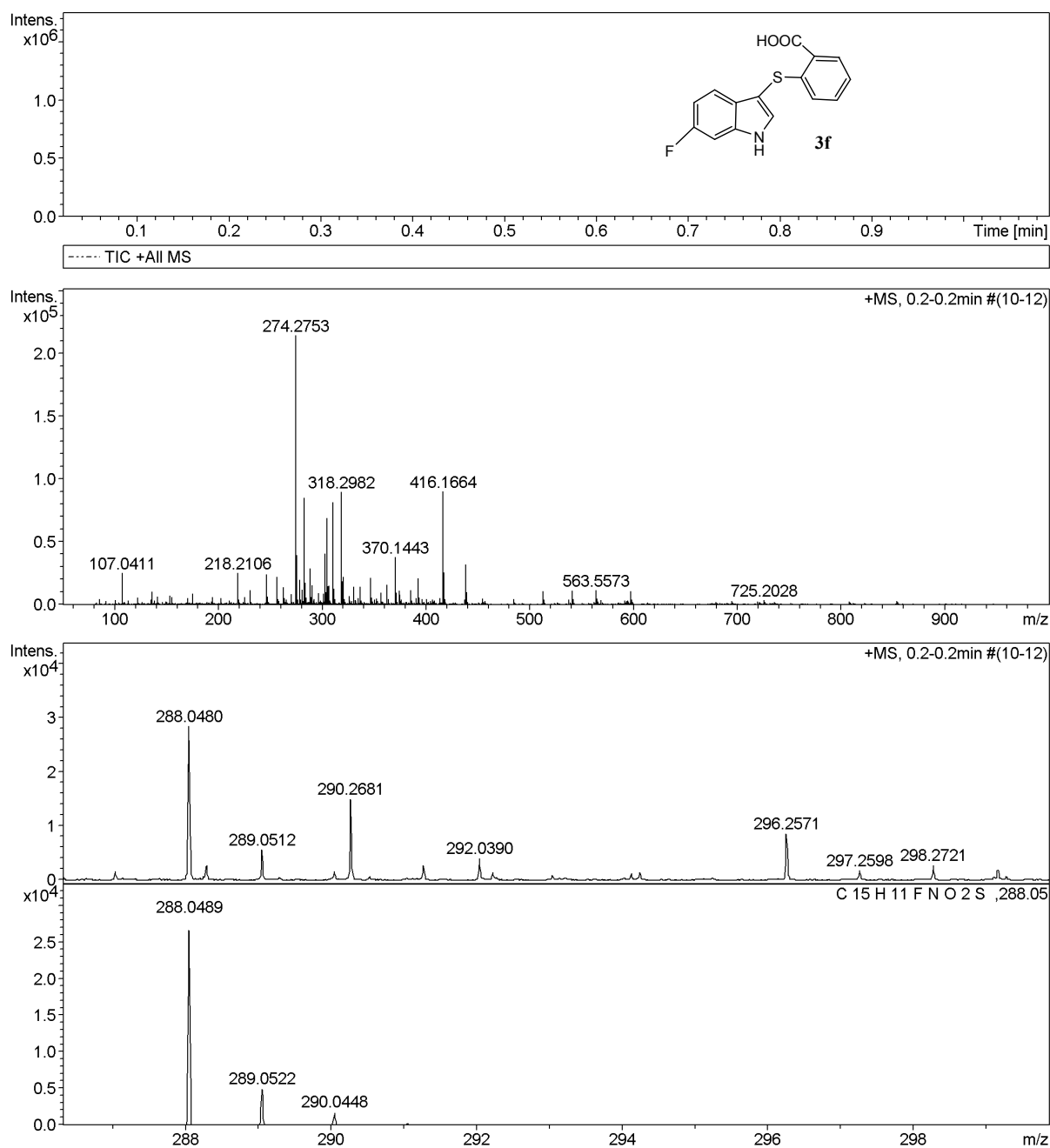


Figure S37. ESI-Qq-TOF mass spectrum for 6-Fluoro-3-[(2-Carboxyphenyl)thio]-1*H*-indole (**3f**)

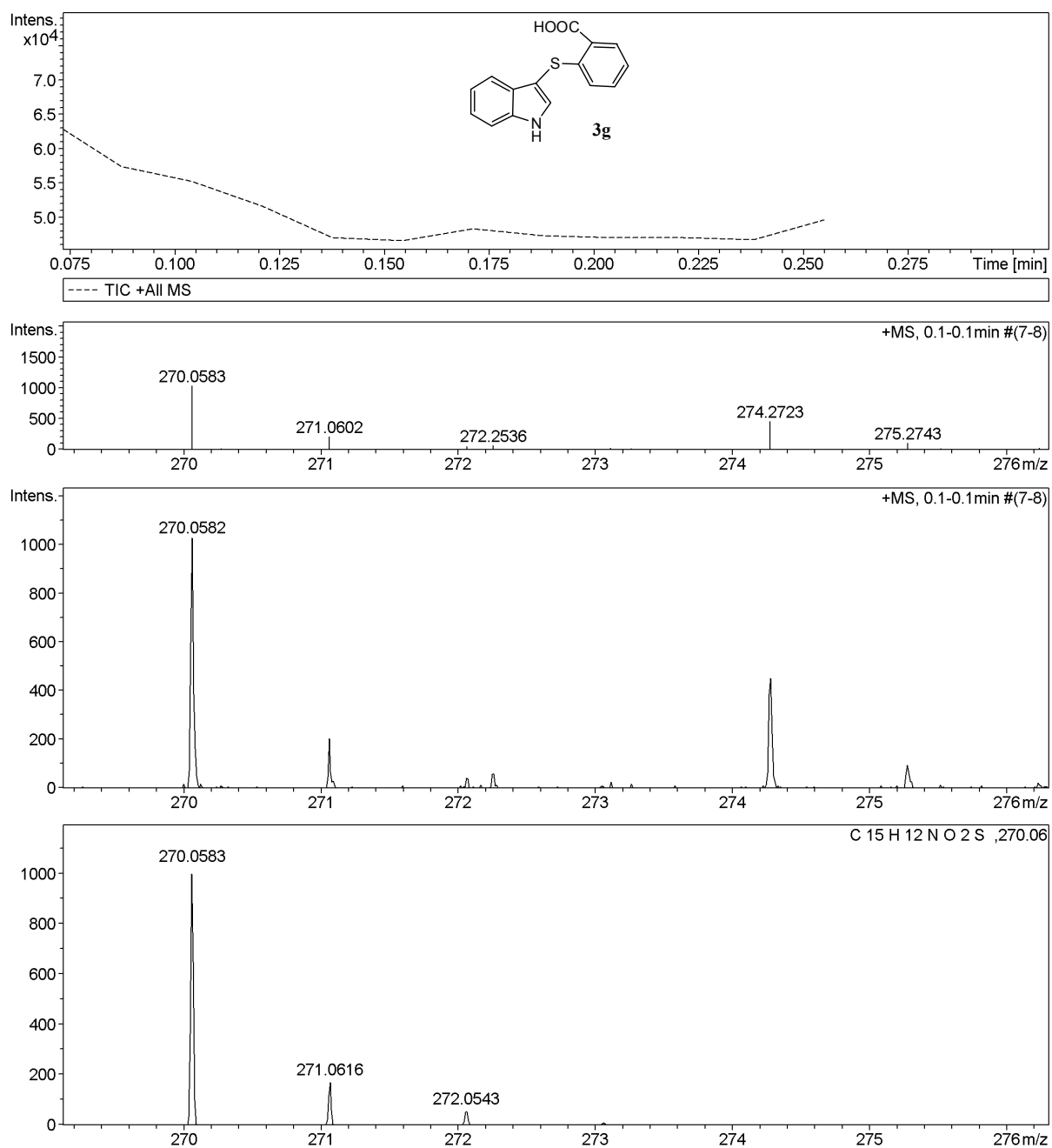


Figure S38. ESI-Qq-TOF mass spectrum for 3-[(2-Carboxyphenyl)thio]-1H-indole (**3g**)

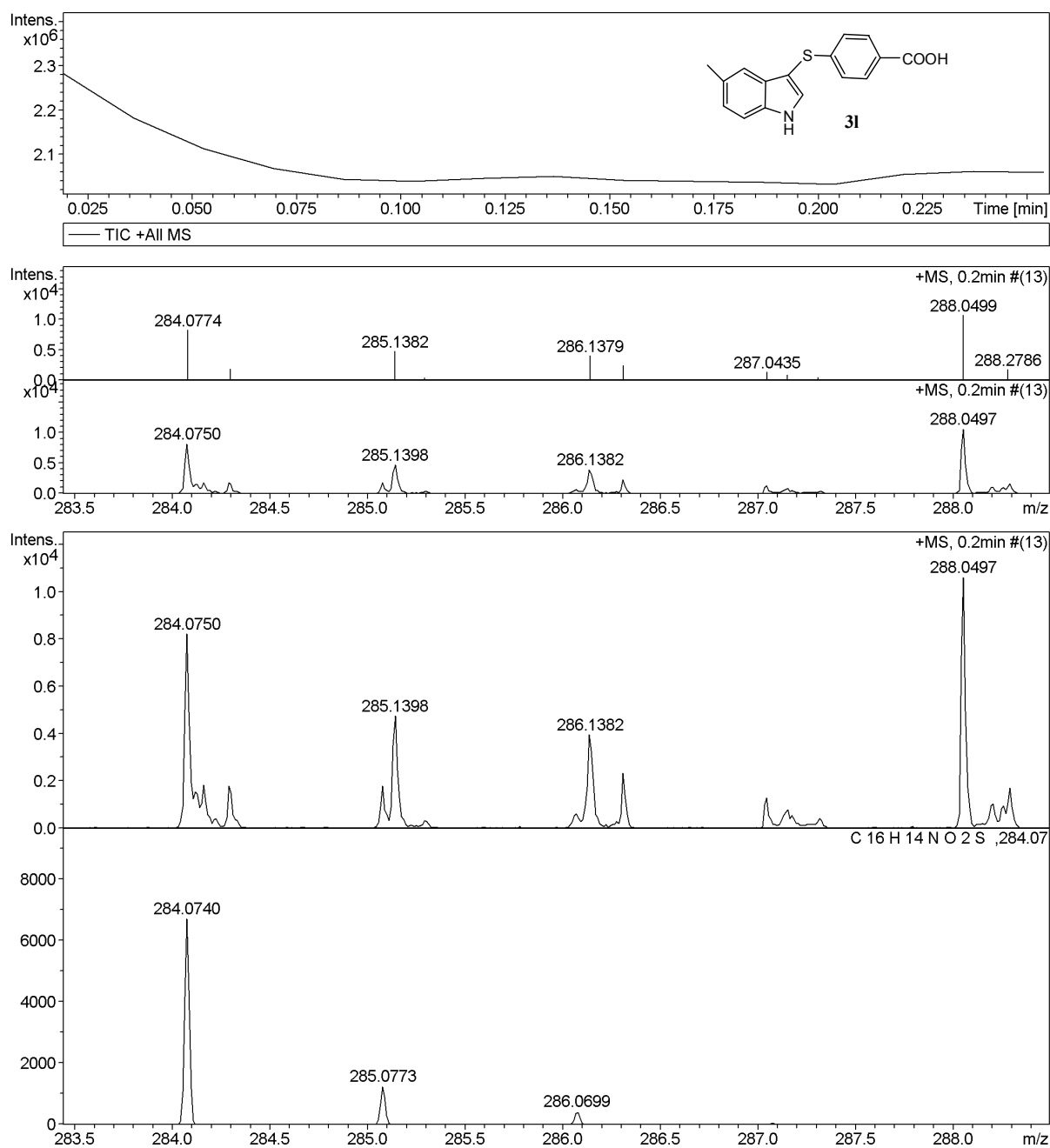


Figure S39. ESI-Qq-TOF mass spectrum for 5-Methyl-3-[(4-Carboxyphenyl)thio]-1H-indole (**31**)

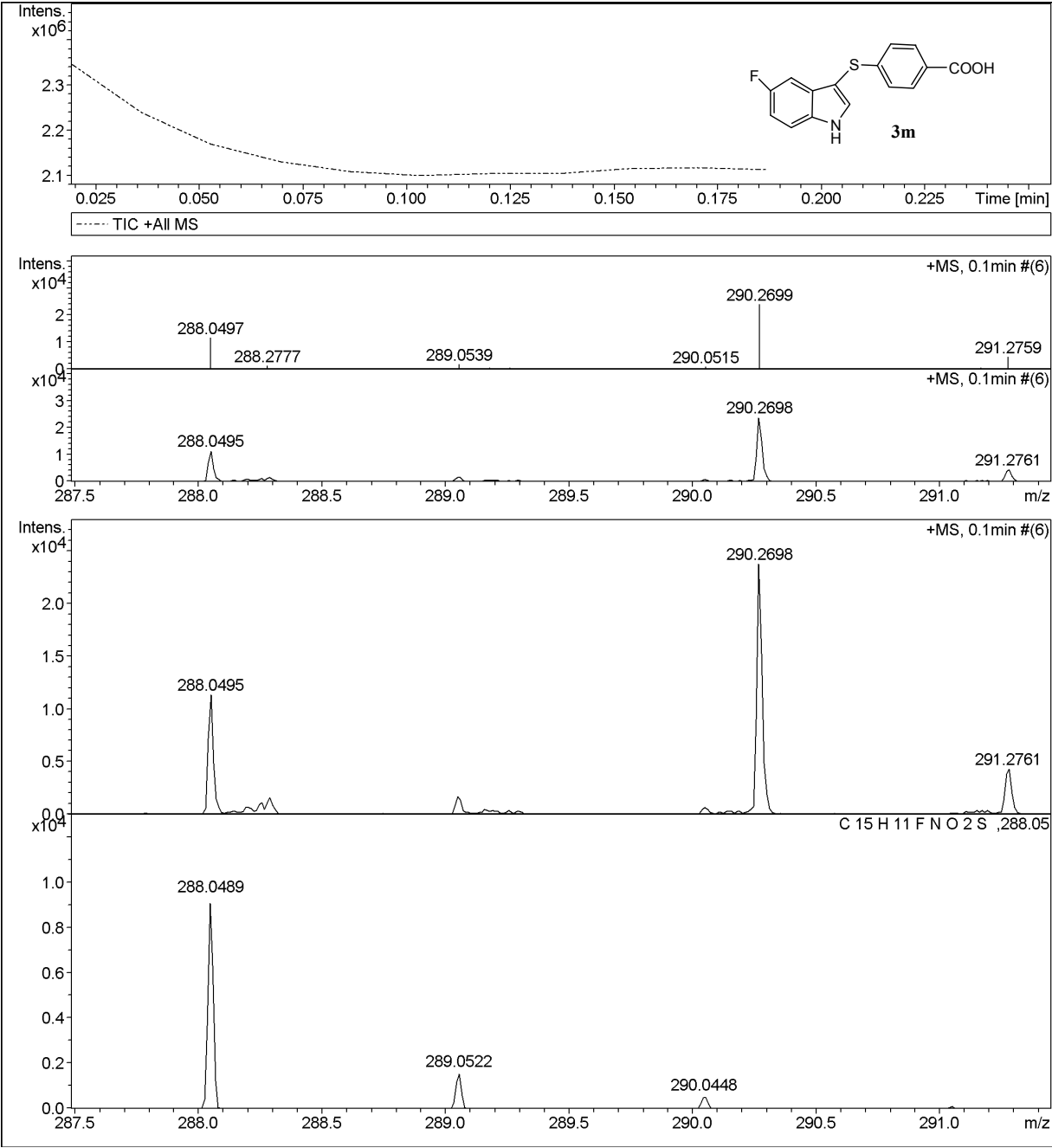


Figure S40. ESI-Qq-TOF mass spectrum for 5-Fluoro-3-[(4-Carboxyphenyl)thio]-1*H*-indole (**3m**)

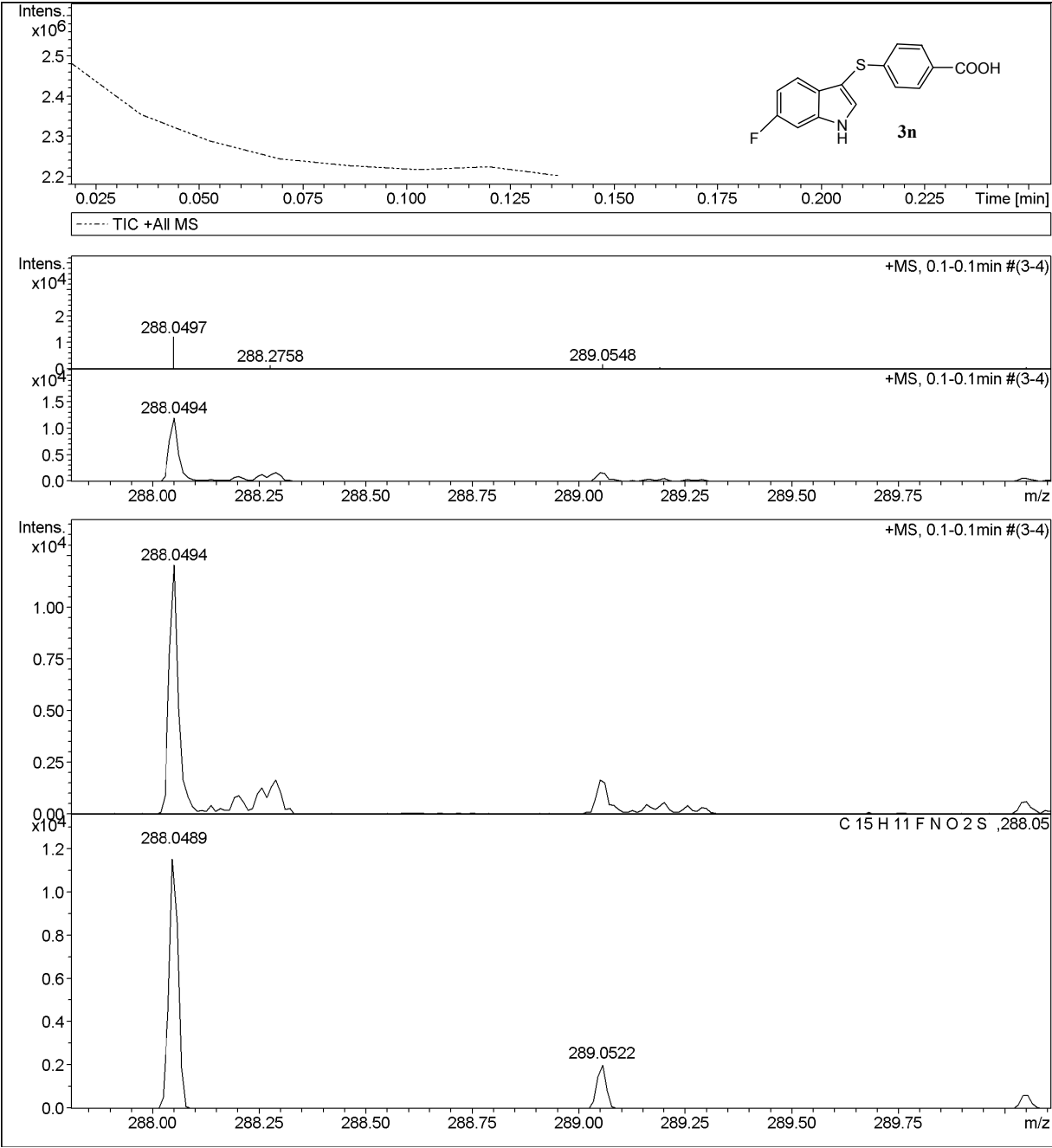


Figure S41. ESI-Qq-TOF mass spectrum for 6-Fluoro-3-[(4-Carboxyphenyl)thio]-1*H*-indole (**3n**)

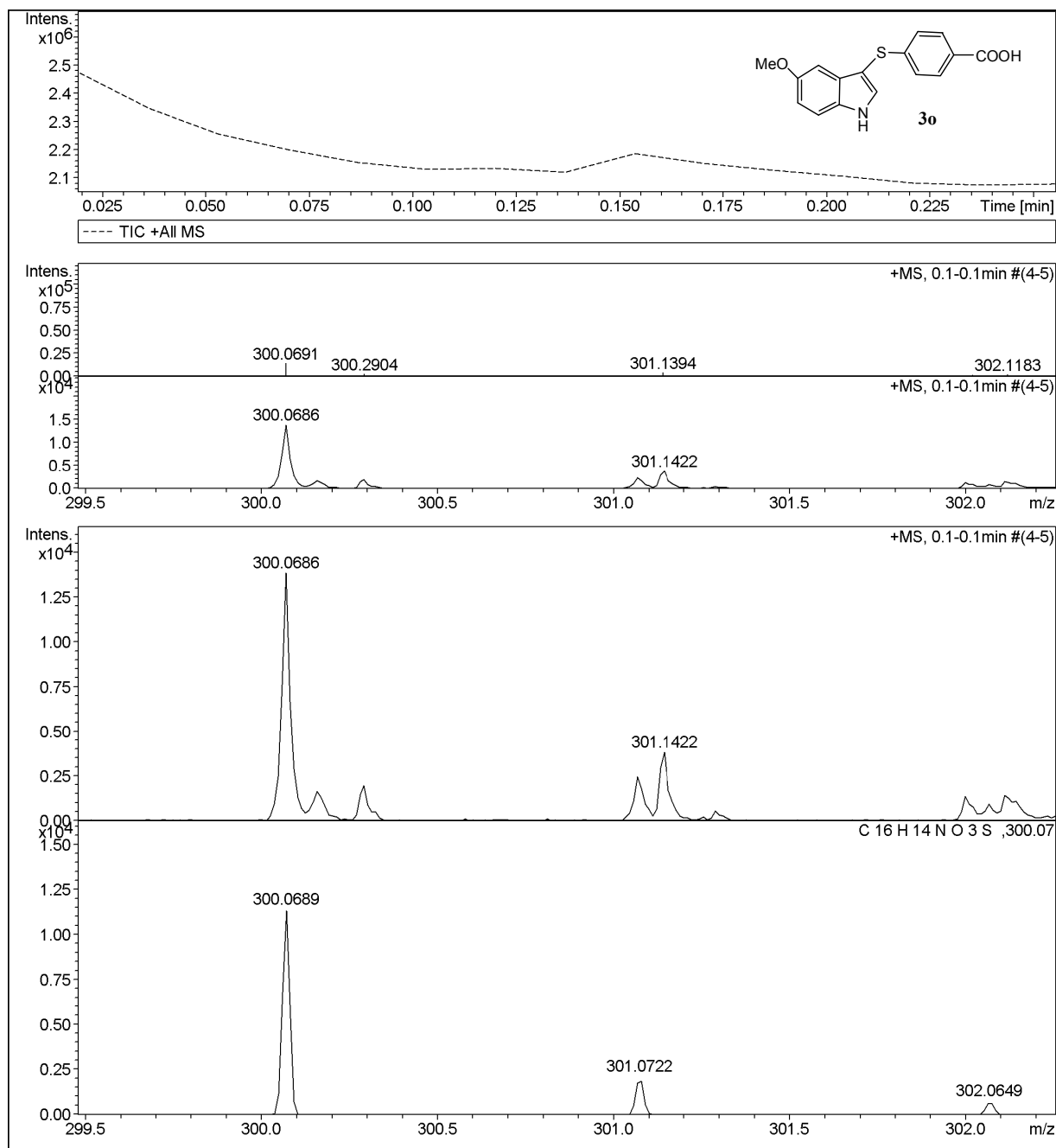


Figure S42. ESI-Qq-TOF mass spectrum for 5-Methoxy-3-[(4-Carboxyphenyl)thio]-1H-indole (**3o**)

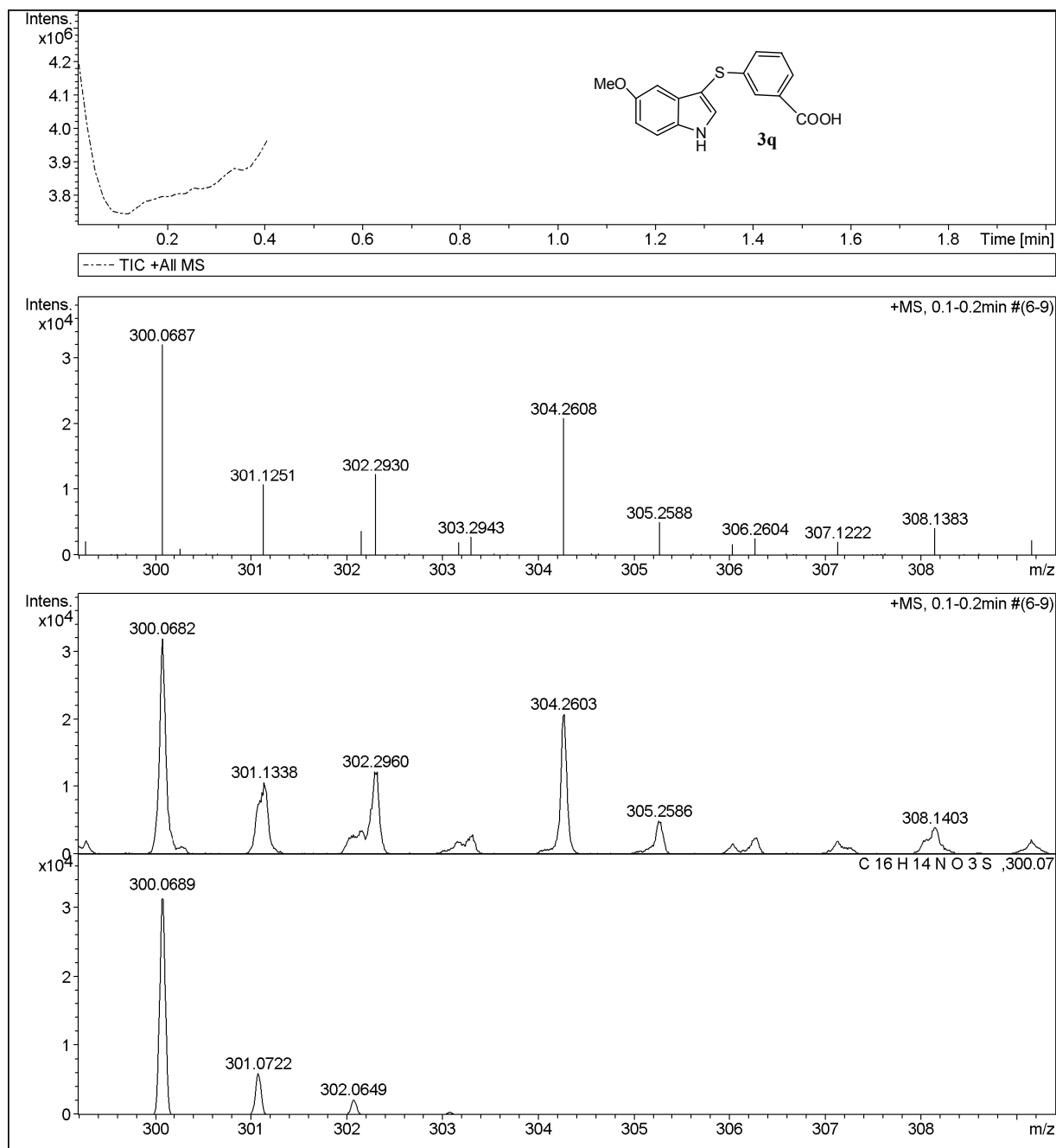


Figure S43. ESI-Qq-TOF mass spectrum for 5-Methoxy-3-[(3-Carboxyphenyl)thio]-1*H*-indole (**3q**)

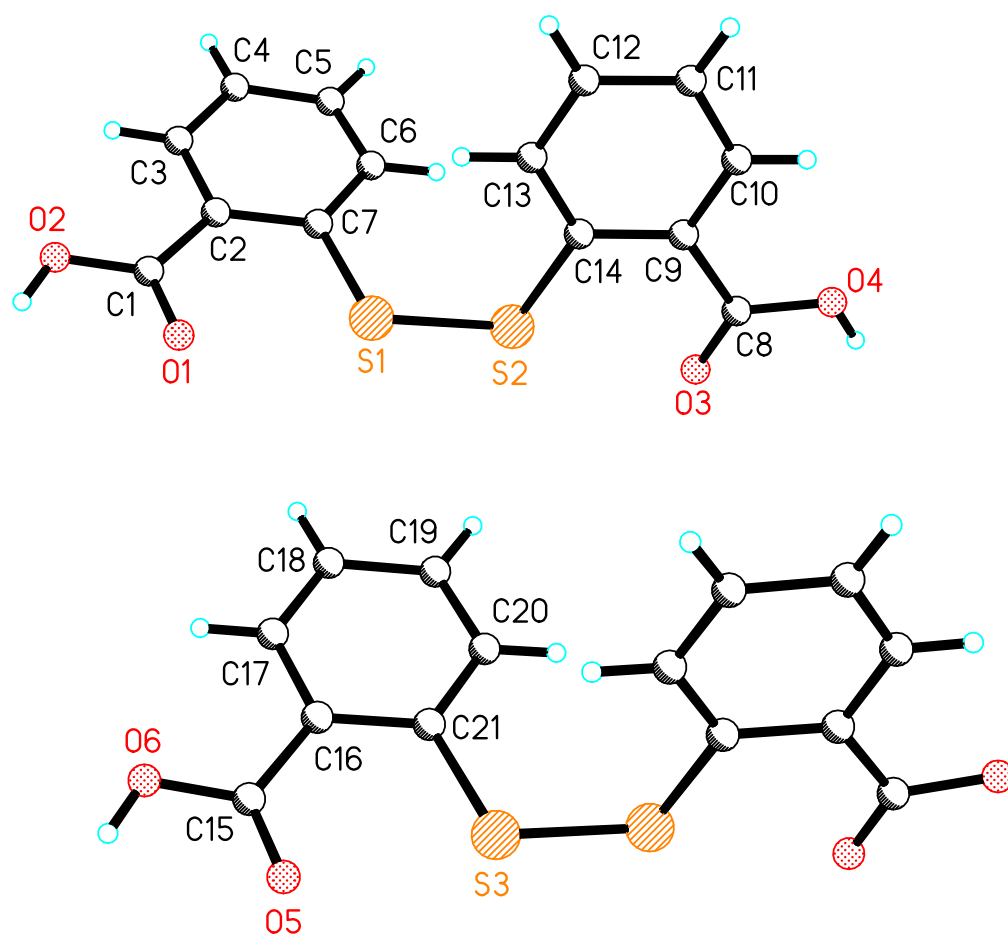


Figure S44. Crystal structure of 2,2'-dithiosalicylic acid separated from reaction system. C15 is disordered for the quality of single crystal.