Supporting Information

Copper-catalyzed Tandem Cyclization Reaction of Ethynylbenzoxazinones and Thiols: Facile Construction of 2-Thiomethylene Indoles

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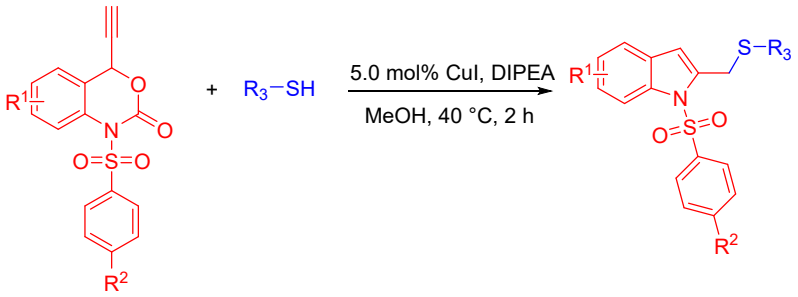
1. General Information:

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All solvents were purified and dried according to standard methods prior to use. Organic solutions were concentrated under reduced pressure on a rotary evaporator or an oil pump. Reactions were monitored through thin layer chromatography (TLC) on silica gel-precoated glass plates. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm. Flash column chromatography was performed using Qingdao Haiyang flash silica gel (300 - 400 mesh). Melting points were measured using a WRS-1B digital melting point instrument. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a 400 or 500 MHz NMR instrument (referenced internally to Me_4Si). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet; d = doublet; q = quartet; m = multiplet; br = broad), coupling constant (Hz), and integral. Data for ^{13}C NMR spectra are reported in terms of chemical shift. Accurate mass measurements were performed using an Agilent instrument with the ESI-MS technique. X-ray crystallographic data were collected using a Gemini E Rigaku. The substrates **1** was prepared according to the relevant literature.[1]

2.1. Procedure for Synthesis of 3 (3aa - 3ag, 3ba - 3ha):

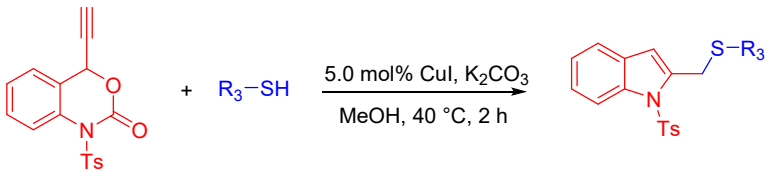
To a solution of Ethynylbenzoxazinones **1** (0.20 mmol), Thiophenol (0.40 mmol) **2,** CuI (5.0 mol%) and DIPEA (0.40 mmol) in CH_3OH (2.0 mL). The resulting solution was stirred at 40 °C for 2 h. The crude reaction mixture was directly purified by column chromatography (PE/EA = 4:1) on silica gel to give the corresponding product.



1 **2** **3aa-3ag, 3ba-3ha**

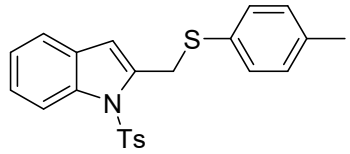
2.2. Procedure for Synthesis of 3 (3ia - 3la):

To a solution of Ethynylbenzoxazinones **1a** (0.20 mmol), Thiol (0.40 mmol) **2**, CuI (5.0 mol%) and K_2CO_3 (0.40 mmol) in CH_3OH (2.0 mL). The resulting solution was stirred at 40 °C for 2 h. The crude reaction mixture was directly purified by column chromatography (PE/EA = 4:1) on silica gel to give the corresponding product.



1a **2** **3ia - 3la**

3. Characterization data



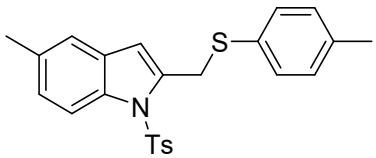
2-((*p*-tolylthio)methyl)-1-tosyl-1*H*-indole (**3aa**). The crude product was purified by flash chromatography (PE/EA=5:1) to obtain **3aa** (white solid, 76.5 mg, 94% yield).

m.p.: 138.7 - 139.4 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 1 H), 7.73 (d, *J* = 8.4 Hz, 2 H), 7.35 (d, *J* = 7.6 Hz, 1 H), 7.25 (t, *J* = 7.6 Hz, 1 H), 7.18 - 7.16 (m, 5 H), 7.02 (d, *J* = 7.6 Hz, 2 H), 6.45 (s, 1 H), 4.45 (s, 2 H), 2.32 (s, 3 H), 2.29 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 137.5, 137.4, 137.1, 136.1, 132.0, 131.3, 129.9, 129.8, 129.2, 126.8, 124.6, 123.7, 120.8, 116.5, 111.6, 33.7, 22.2, 21.2.

HRMS（ESI）: m/z $[M+Na]^+$ calcd for $C_{23}H_{21}NO_2S_2Na^+$, 430.0906, found: 430.0900.

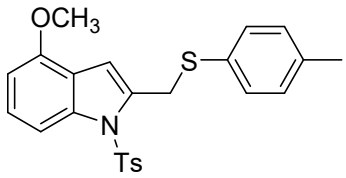


5-methyl-2-((*p*-tolylthio)methyl)-1-tosyl-1*H*-indole (**3ab**). The crude product was purified by flash chromatography (PE/EA=5:1) to obtain **3ab** (yellow oil, 67.4 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.8 Hz, 1 H), 7.72 (d, *J* = 8.0 Hz, 2 H), 7.19 - 7.16 (m, 5 H), 7.08 (d, *J* = 8.4 Hz, 1 H), 7.03 (d, *J* = 8.0 Hz, 2 H), 6.38 (s, 1 H), 4.43 (s, 2 H), 2.37 (s, 3 H), 2.34 (s, 3 H), 2.30 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 137.4, 136.9, 136.1, 135.6, 133.1, 132.0, 131.2, 129.7, 129.6, 129.4, 126.6, 125.8, 120.5, 114.4, 111.3, 33.5, 21.5, 21.1, 21.0.

HRMS（ESI）: m/z $[M+ Na]^+$ calcd for $C_{24}H_{23}NO_2S_2Na^+$, 444.1062, found: 444.1068.

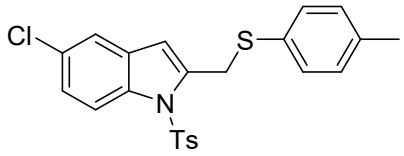


4-methoxy-2-((*p*-tolylthio)methyl)-1-tosyl-1*H*-indole (**3ac**). The crude product was purified by flash chromatography (PE/EA=5:1) to obtain **3ac** (white oil, 51.6 mg, 59% yield).

^{1}H NMR (501 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 2 H), 7.22 (d, *J* = 8.0 Hz, 2 H), 7.18 (t, *J* = 4.0 Hz, 2 H), 7.00 (t, *J* = 8.0 Hz, 3 H), 6.92 (d, *J* = 7.5 Hz, 1 H), 6.59 (d, *J* = 8.0 Hz, 1 H), 6.33 (s, 1 H), 4.53 (s, 2 H), 3.50 (s, 3 H), 2.34 (s, 3 H) 2.24, (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.3, 143.6, 138.8, 138.3, 136.4, 134.8, 134.8, 129.6, 129.5, 129.0, 128.8, 127.9, 121.9, 121.9, 121.6, 110.2, 55.1, 39.3, 21.6, 21.4.

HRMS（ESI）: m/z [M+ Na]$^+$ calcd for $C_{24}H_{23}NO_3S_2Na^+$, 460.1012, found: 460.1015.

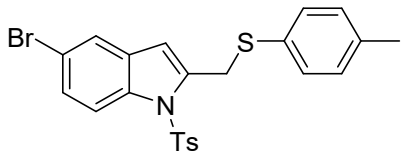


5-chloro-2-((*p*-tolylthio)methyl)-1-tosyl-1*H*-indole (**3ad**). The crude product was purified by flash chromatography (PE/EA=5:1) to obtain **3ad** (white oil, 73.2 mg, 83% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.8 Hz, 1 H), 7.71 (d, *J* = 8.4 Hz, 2 H), 7.33 (s, 1 H), 7.23 - 7.20 (m, 3 H), 7.15 (d, *J* = 8.0 Hz, 2 H), 7.04 (d, *J* = 7.6 Hz, 2 H), 6.36 (s, 1 H), 4,42 (s, 2 H), 2.36 (s, 3 H), 2.30 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 139.0, 137.2, 135.8, 135.7, 131.6, 131.4, 130.3, 129.9, 129.7, 129.3, 126.6, 124.6, 120.2, 115.7, 110.6, 33.5, 21.5, 21.0.

HRMS（ESI）: m/z [M+ Na]$^+$ calcd for $C_{23}H_{20}ClNO_2S_2Na^+$, 464.0516, found: 464.0517.



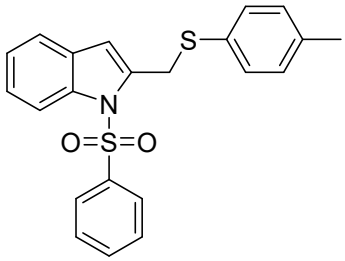
5-bromo-2-((*p*-tolylthio)methyl)-1-tosyl-1*H*-indole (**3ae**). The crude product was

purified by flash chromatography (PE/EA=5:1) to obtain **3ae** (yellow oil, 75.7 mg, 78% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.8 Hz, 1 H), 7.71 (d, *J* = 8.4 Hz, 2 H), 7.47 (s, 1 H), 7.34 (dd, *J* = 1.6, 8.8 Hz, 1 H), 7.20 (d, *J* = 8.0 Hz, 2 H), 7.15 (d, *J* = 8.4 Hz, 2 H), 7.03 (d, *J* = 7.6 Hz, 2 H), 6.34 (s, 1 H), 4.42 (s, 2 H), 2.35 (s, 3 H), 2.30 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 138.9, 137.2, 136.0, 135.8, 131.6, 131.4, 130.8, 129.9, 129.7, 127.2, 126.6, 123.2, 117.0, 116.1, 110.4, 33.5, 21.5, 21.0.

HRMS（ESI）: m/z [M+ Na]$^+$ calcd for $C_{23}H_{20}BrNO_2S_2Na^+$, 508.0011, found: 508.0016.

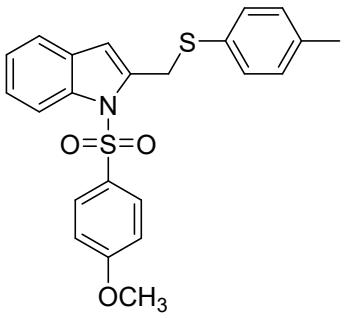


1-(phenylsulfonyl)-2-((*p*-tolylthio)methyl)-1*H*-indole (**3af**). The crude product was purified by flash chromatography (PE/EA=5:1) to obtain **3af** (white oil, 69.8 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 1 H), 7,85 (d, *J* = 7.2 Hz, 2 H), 7.52 (t, *J* = 7.6 Hz, 1 H), 7.42 - 7.36 (m, 3 H), 7.31 - 7.27 (m, 1 H), 7.21 - 7.15 (m, 3 H), 7.03 (d, *J* = 8.0 Hz, 2 H), 6.46 (s, 1 H), 4.45 (s, 2 H), 2.29 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 137.5, 137.1, 133.8, 131.9, 131.3, 129.8, 129.5, 129.3, 129.2, 126.7, 124.6, 123.7, 120.8, 114.7, 111.7, 33.6, 21.1.

HRMS（ESI）: m/z [M+ Na]$^+$ calcd for $C_{23}H_{20}BrNO_2S_2Na^+$, 508.0011, found: 508.0016.

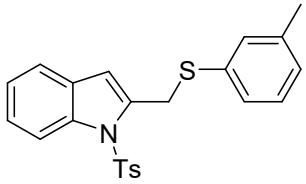


1-((4-methoxyphenyl)sulfonyl)-2-((*p*-tolylthio)methyl)-1*H*-indole (**3ag**). The crude product was purified by flash chromatography (PE/EA=5:1) to obtain **3ag** (white oil, 66.0 mg, 78% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 1 H), 7.82 (d, *J* = 8.8 Hz, 2 H), 7.37 (d, *J* = 7.6 Hz, 1 H), 7.29 - 7.26 (m, 1 H), 7.20 - 7.17 (m, 3 H), 7.04 (d, *J* = 8.0 Hz, 2 H), 6.85 (d, *J* = 9.2 Hz, 2 H), 6.44 (s, 1 H), 4.46 (s, 2 H), 3.79 (s, 3 H), 2.30 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7, 137.4, 137.3, 137.1, 132.0, 131.3, 130.6, 129.8, 129.2, 129.0, 124.5, 123.5, 120.7, 114.7, 114.4, 111.4, 55.7, 33.7, 21.1.

HRMS（ESI）: m/z [M+ Na]$^+$ calcd for $C_{23}H_{21}NO_3S_2Na^+$,446.0861, found: 446.0859.



2-((*m*-tolylthio)methyl)-1-tosyl-1*H*-indole (**3ba**). The crude product was purified by flash chromatography (PE/EA=5:1) to obtain **3ba** (white solid, 69.2 mg, 85% yield).

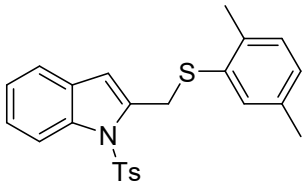
m.p.: 136.0 - 138.8 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.0 Hz, 1 H), 7.73 (d, *J* = 8.0 Hz, 2 H), 7.37 (d, *J* = 7.6 Hz, 1 H), 7.25 (d, *J* = 9.2 Hz, 1 H), 7.20 - 7.16 (m, 3 H), 7.12 - 7.08 (m, 2 H), 7.04 (d, *J* = 8.0 Hz, 1 H), 6.99 (d, *J* = 7.6 Hz, 1 H), 6.51 (s, 1 H), 4.49 (s, 2 H), 2.33 (s, 3 H), 2.24 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 138.7, 137.4, 137.3, 136.1, 135.4, 130.9, 129.8, 129.1, 128.7, 127.6, 127.2, 126.6, 124.5, 123.6, 120.6, 114.7, 111.5, 32.8, 21.5, 21.2.

HRMS（ESI）: m/z [M+ Na]$^+$ calcd for $C_{23}H_{21}NO_2S_2Na^+$, 430.0906, found:

430.0901.



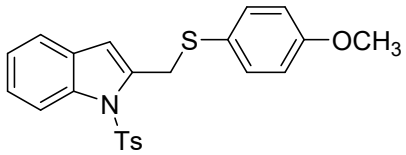
2-(((2,5-dimethylphenyl)thio)methyl)-1-tosyl-1*H*-indole (**3ca**). The crude product was purified by flash chromatography (PE/EA=5:1) to obtain **3ca** (white solid, 58.9 mg, 70% yield).

m.p.: 122.6 - 124.6 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 1 H), 7.74 (d, *J* = 7.6 Hz, 2 H), 7.35 (d, *J* = 7.6 Hz, 1 H), 7.27 (t, *J* = 8.0 Hz, 1 H), 7.18 - 7.16 (m, 2 H), 7.03 (d, *J* = 7.6 Hz, 1 H), 6.95 (s, 1 H), 6.90 (d, *J* = 7.6 Hz, 1 H), 6.44 (s, 1 H), 4.46 (s, 2 H), 2.31 (s, 3 H), 2.26 (s, 3 H), 2.16 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 137.4, 137.2, 136.1, 135.6, 134.5, 130.6, 130.1, 129.9, 129.3, 127.6, 126.7, 126.5, 124.6, 123.7, 120.7, 114.8, 111.6, 32.2, 21.6, 21.0, 20.0.

HRMS（ESI）: m/z [M+ Na]$^+$ calcd for $C_{24}H_{23}NO_2S_2Na^+$, 444.1062, found: 444.1064.



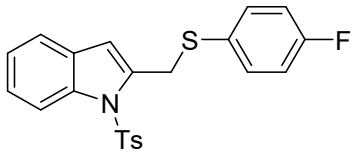
2-(((4-methoxyphenyl)thio)methyl)-1-tosyl-1*H*-indole (**3da**). The crude product was purified by flash chromatography (PE/EA=5:1) to obtain **3da** (yelow solid, 76.2 mg, 90% yield).

m.p.: 142.4 - 144.6 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 1 H), 7.66 (d, *J* = 8.4 Hz, 2 H), 7.25 (d, *J* = 7.2 Hz, 1 H), 7.16-7.13 (m, 3 H), 7.09 - 7.06 (m, 3 H), 6.67 (d, *J* = 8.4 Hz, 2 H), 6.21 (s, 1 H), 4.30 (s, 2 H), 3.65 (s, 3 H), 2.21 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 145.0, 137.6, 137.3, 136.0, 134.7, 129.9, 129.2, 126.8, 125.8, 124.6, 123.7, 120.7, 114.8, 114.6, 111.6, 55.4, 35.1, 21.7.

HRMS（ESI）: m/z [M+ Na]$^+$ calcd for $C_{23}H_{21}NO_3S_2Na^+$, 446.0855, found: 446.0852.



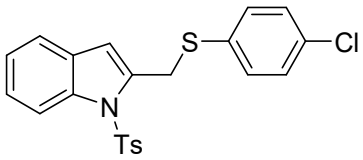
2-(((4-fluorophenyl)thio)methyl)-1-tosyl-1*H*-indole (**3ea**). The crude product was purified by flash chromatography (PE/EA=5:1) to obtain **3ea** (white oil, 51.8 mg, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 1 H), 7.74 (d, *J* = 8.0 Hz, 2 H), 7.37 (d, *J* = 7.6 Hz, 1 H), 7.30 - 7.27 (m, 1 H), 7.26 - 7.24 (m, 2 H), 7.21 - 7.17 (m, 3 H), 6.92 (t, *J* = 8.4 Hz, 2 H), 6.36 (s, 1 H), 4.31 (s, 2 H), 2.34 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (d, *J* = 246.0 Hz), 145.0, 137.2 (d, *J* = 32.0 Hz), 136.0, 134.0 (d, *J* = 8.0 Hz), 130.4 (d, *J* = 3.0 Hz), 129.8, 129.0, 126.7, 124.7, 123.7, 120.7, 116.2, 115.9, 114.8, 111.6, 34.4, 21.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.2.

HRMS（ESI）: m/z [M+ Na]$^+$ calcd for $C_{22}H_{18}FNO_2S_2Na^+$, 434.0655, found: 434.0653.

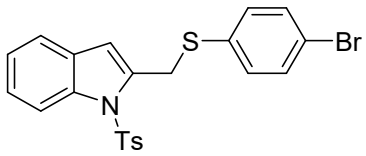


2-(((4-chlorophenyl)thio)methyl)-1-tosyl-1*H*-indole (**3fa**). The crude product was purified by flash chromatography (PE/EA=5:1) to obtain **3fa** (white oil, 55.5 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 1 H), 7.71 (d, *J* = 8.0 Hz, 2 H), 7.37 (d, *J* = 7.6 Hz, 1 H), 7.28 (t, *J* = 7.6 Hz, 1 H), 7.19-7.17 (m, 7 H), 6.45 (s, 1 H), 4.46 (s, 2 H), 2.33 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 137.5, 136.8, 135.9, 134.2, 133.0, 132.1, 130.0, 129.2, 129.0, 126.7, 124.8, 123.8, 120.8, 114.8, 111.7, 33.4, 21.7.

HRMS（ESI）: m/z [M+ Na]$^+$ calcd for $C_{22}H_{18}ClNO_2S_2Na^+$, 450.0360, found: 450.0353.

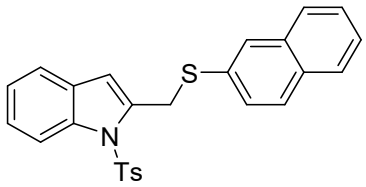


2-(((4-bromophenyl)thio)methyl)-1-tosyl-1*H*-indole (**3ga**). The crude product was purified by flash chromatography (PE/EA=5:1) to obtain **3ga** (yellow oil, 62.2 mg, 66% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 1 H), 7.71 (d, *J* = 8.0 Hz, 2 H), 7.38 (d, *J* = 8.0 Hz, 1 H), 7.34 - 7.28 (m, 3 H), 7.22 - 7.19 (m, 3 H), 7.10 (d, *J* = 8.0 Hz, 2 H), 6.47 (s, 1 H), 4.47 (s, 2 H), 2.35 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 137.4, 136.7, 136.0, 134.8, 132.1, 132.0, 129.9, 129.0, 126.6, 124.7, 123.7, 120.9, 120.8, 114.7, 111.6, 33.1, 21.6.

HRMS（ESI）: m/z [M+ Na]$^+$ calcd for $C_{22}H_{18}BrNO_2S_2Na^+$, 493.9855, found: 493.9853.

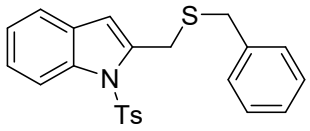


2-((naphthalen-2-ylthio)methyl)-1-tosyl-1*H*-indole (**3ha**). The crude product was purified by flash chromatography (PE/EA=5:1) to obtain **3ha** (yellow oil, 62.0 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 1 H), 7.75 - 7.68 (m, 4 H), 7.64 (s, 1 H), 7.58 (d, *J* = 5.2 Hz, 1 H), 7.43 - 7.28 (m, 5 H), 7.25 - 7.23 (m, 1 H), 7.18 - 7.16 (m, 2 H), 6.52 (s, 1 H), 4.60 (s, 2 H), 2.32 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 137.4, 137.1, 136.0, 133.6, 133.1, 132.1, 129.9, 129.1, 128.6, 128.5, 128.0, 127.7, 127.3, 126.6, 126.5, 126.0, 124.6, 123.6, 120.7, 114.7, 111.6, 32.8, 21.6.

HRMS（ESI）: m/z [M+ Na]$^+$ calcd for $C_{26}H_{21}NO_2S_2Na^+$, 466.0906, found: 466.0910.



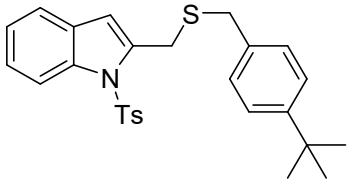
2-((benzylthio)methyl)-1-tosyl-1*H*-indole (**3ia**). The crude product was purified by flash chromatography (PE/EA=5:1) to obtain **3ia** (white solid, 75.7 mg, 93% yield).

m.p.: 136.6 - 138.0 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 1 H), 7.68 (d, *J* = 8.8 Hz, 2 H), 7.44 (d, *J* = 8.4 Hz, 1 H), 7.31 - 7.27 (m, 5 H), 7.24 - 7.19 (m, 2 H), 7.15 (d, *J* = 8.0 Hz, 2 H), 6.57 (s, 1 H), 4.02 (s, 2 H), 3.72 (s, 2 H), 2.32 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 137.8, 137.7, 137.4, 136.1, 129.8, 129.1, 128.6, 127.2, 126.7, 126.6, 124.5, 123.7, 120.6, 114.8, 111.1, 36.3, 29.0, 21.6.

HRMS（ESI）: m/z [M+ Na]$^+$ calcd for $C_{23}H_{21}NO_2S_2Na^+$, 430.0911, found: 430.0912.



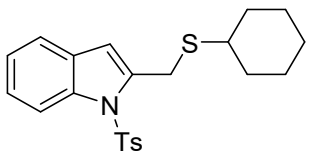
2-(((4-(tert-butyl)benzyl)thio)methyl)-1-tosyl-1*H*-indole (**3ja**). The crude product was purified by flash chromatography (PE/EA=5:1) to obtain **3ja** (white solid, 70.4 mg, 76% yield).

m.p.: 145.0 - 146.2 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 1 H), 7.70 (d, *J* = 8.4 Hz, 2 H), 7.44 (d, *J* = 7.6 Hz, 1 H), 7.33 (d, *J* = 8.4 Hz, 2 H), 7.25 - 7.21 (m, 4 H), 7.16 (d, *J* = 8.0 Hz, 2 H), 6.56 (s, 1 H), 4.04 (s, 2 H),3.70 (s, 2 H), 2.32 (s, 3 H), 1.31 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 144.8, 137.8, 137.4, 136.1, 134.8, 129.8, 128.7, 126.8, 126.5, 125.5, 124.5, 123.6, 120.6, 114.8, 111.0, 35.9, 34.6, 31.4, 29.1, 21.6.

HRMS（ESI）: m/z [M+ Na]$^+$ calcd for $C_{27}H_{29}NO_2S_2Na^+$, 486.1537, found: 486.1534.



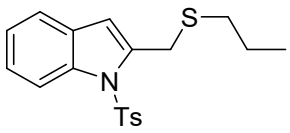
2-((cyclohexylthio)methyl)-1-tosyl-1*H*-indole (**3ka**). The crude product was purified by flash chromatography (PE/EA=5:1) to obtain **3ka** (white oil, 62.1 mg, 67% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.6 Hz, 1 H), 7.74 (d, *J* =8.4 Hz, 2 H),

7.45 (d, *J* = 7.6 Hz, 1 H), 7.29 – 7.23 (m, 2 H), 7.21-7.18 (m, 2 H), 6.68 (s, 1 H), 4.14 (s, 2 H), 2.66 (t, *J* = 10.4 Hz, 1 H), 2.34 (s, 3 H), 1.92 (d, *J* = 12.8 Hz, 2 H), 1.76 – 1.72 (m, 2 H), 1.32 (t, *J* = 10.4 Hz, 2 H), 1.25 (t, *J* = 10.0 Hz, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 138.7, 137.4, 136.1, 129.8, 129.3, 126.7, 124.4, 123.6, 120.6, 114.8, 110.9, 43.6, 33.4, 27.9, 26.1, 25.9, 21.6.

HRMS（ESI）: m/z [M+ Na]$^+$ calcd for $C_{22}H_{25}NO_2S_2Na^+$, 422.1224, found: 422.1227.

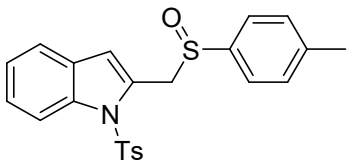


2-((propylthio)methyl)-1-tosyl-1*H*-indole (**3la**). The crude product was purified by flash chromatography (PE/EA=5:1) to obtain **3la**(white oil, 51.7 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.0 Hz, 1 H), 7.74 (d, *J* =7.6 Hz, 2 H), 7.44 (d, *J* = 7.2 Hz, 1 H), 7.29 - 7.26 (m, 1 H), 7.23 - 7.17 (m, 3 H), 6.63 (s, 1 H), 4.13 (s, 2 H), 2.58 - 2.49 (m, 2 H), 2.33 (s, 3 H), 1.62 - 1.56 (m, 2 H), 0.96 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 138.2, 137.4, 136.1, 129.8, 129.2, 126.7, 124.4, 123.6, 120.6, 114.8, 111.0, 34.2, 29.7, 22.6, 21.6, 13.6.

HRMS（ESI）: m/z [M+ Na]$^+$ calcd for $C_{19}H_{21}NO_2S_2Na^+$, 382.0911, found: 382.0903.



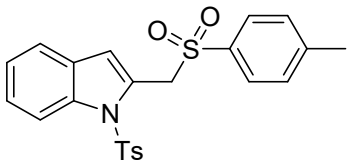
2-benzyl-3-(*p*-tolylsulfinyl)-1-tosyl-1*H*-indole (**4**). The crude product was purified by flash chromatography (PE/EA=10:1) to obtain **4** (white oil, 79.8 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 1 H), 7.64 (d, *J* =8.0 Hz, 2 H), 7.58 (d, *J* = 7.6 Hz, 2 H), 7.45 (d, *J* = 7.2 Hz, 1 H), 7.33 - 7.31 (m, 3 H), 7.25 - 7.16 (m, 3 H), 6.65 (s, 1 H), 4.64 (d, *J* = 13.2 Hz, 1 H), 4.29 (d, *J* = 13.2 Hz, 1 H), 2.42 (s, 3 H), 2.31 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 141.8, 140.6, 137.5, 135.5, 130.2, 130.0, 129.9,

129.3, 126.5, 125.3, 124.2, 124.0, 121.2, 115.2, 114.9, 59.7, 21.6, 21.5.

HRMS（ESI）: m/z [M+ Na]$^+$ calcd for $C_{23}H_{21}NO_3S_2Na^+$, 446.0861, found: 446.0865.



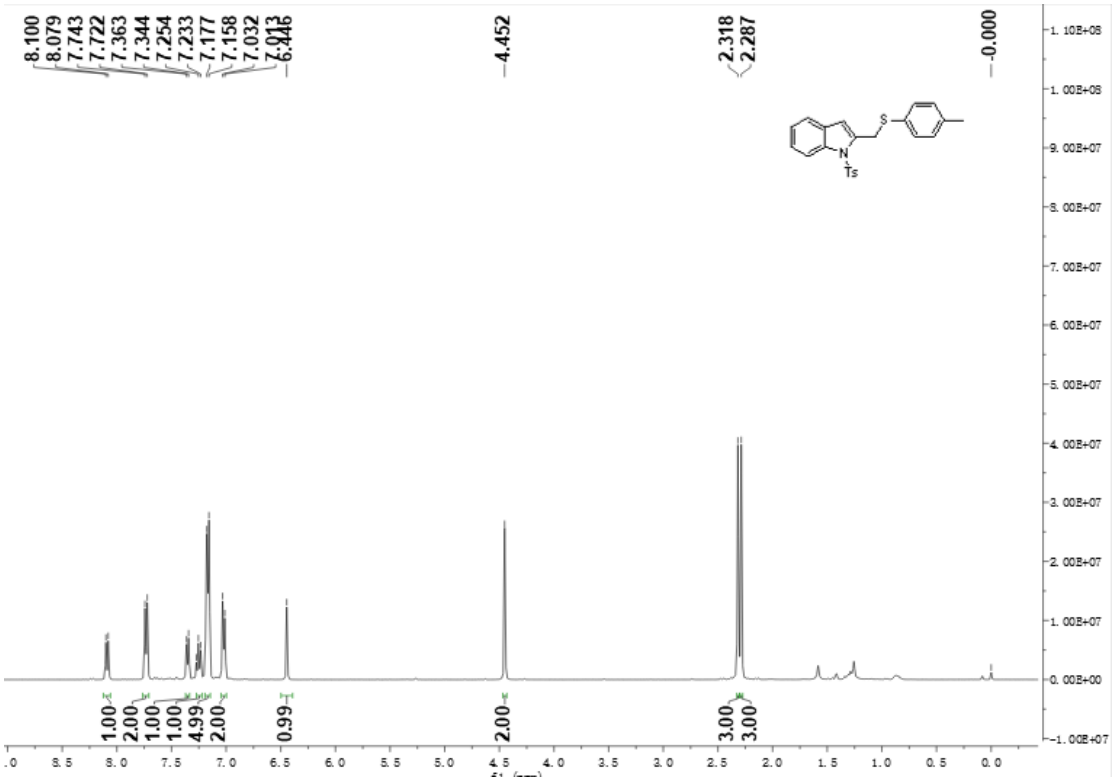
2-benzyl-1,3-ditosyl-1*H*-indole (**5**). The crude product was purified by flash chromatography (PE/EA=5:1) to obtain **5** (white oil, 96.8 mg, 94% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 1 H), 7.67 (d, *J* =8.4 Hz, 2 H), 7.56 (d, *J* = 8.4 Hz, 2 H), 7.48 (d, *J* = 7.2 Hz, 1 H), 7.28 - 7.26 (m, 4 H), 7.14 (d, *J* = 8.0 Hz, 2 H), 6.90 (s, 1 H), 5.04 (s, 2 H), 2.43 (s, 3 H), 2.30 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 145.1, 137.3, 135.5, 135.2, 129.9, 129.7, 129.2, 128.8, 127.6, 126.5, 125.5, 124.1, 121.3, 116.1, 115.2, 55.2, 21.8, 21.6.

HRMS（ESI）: m/z [M+ Na]$^+$ calcd for $C_{23}H_{21}NO_4S_2Na^+$, 462.0810, found: 462.0807.

[1] Wang, Q.; Li, T.-R.; Lu, L.-Q.; Li, M.-M.; Zhang, K.; Xiao, W.-J. Catalytic Asymmetric [4+1] Annulation of Sulfur Ylides with Copper−Allenylidene Intermediates. *J. Am. Chem. Soc.* **2016**, *138*, 8360-8363.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7.233
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7.158
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6.446
4.452
2.318
2.287
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Ts
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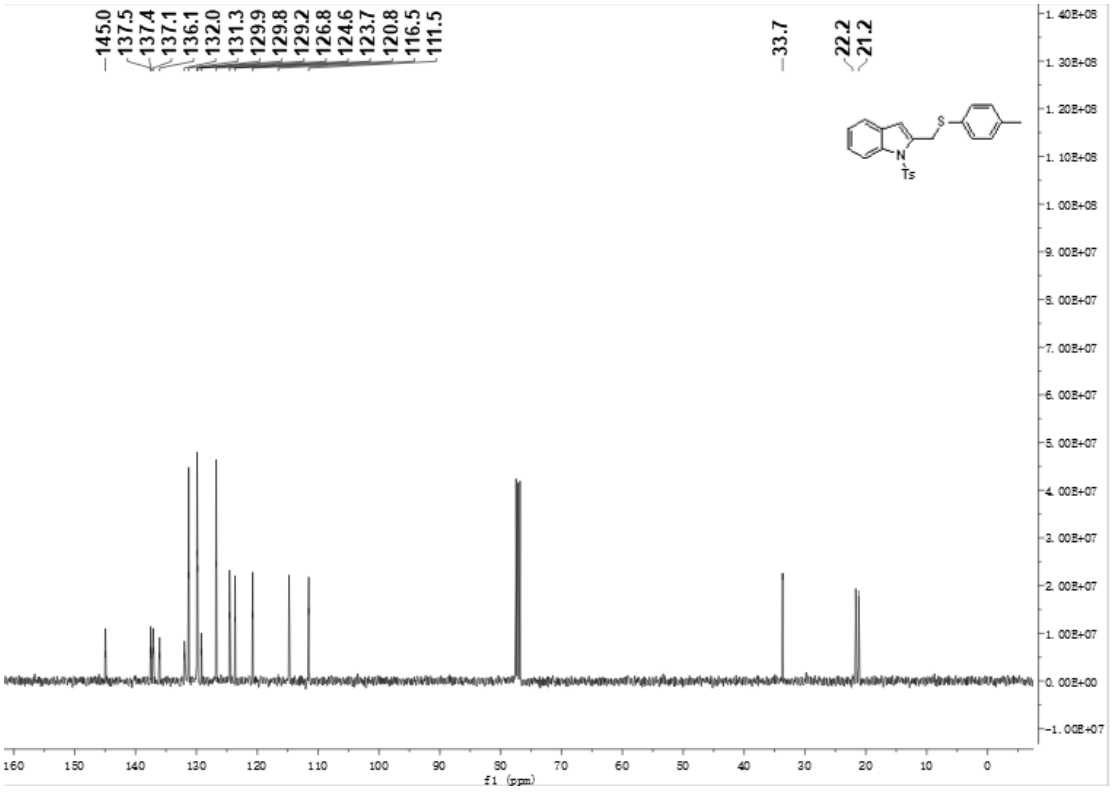
2.00
1.00
1.00
4.99
2.00
0.99
2.00
3.00
3.00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136.1
132.0
131.3
129.9
129.8
129.2
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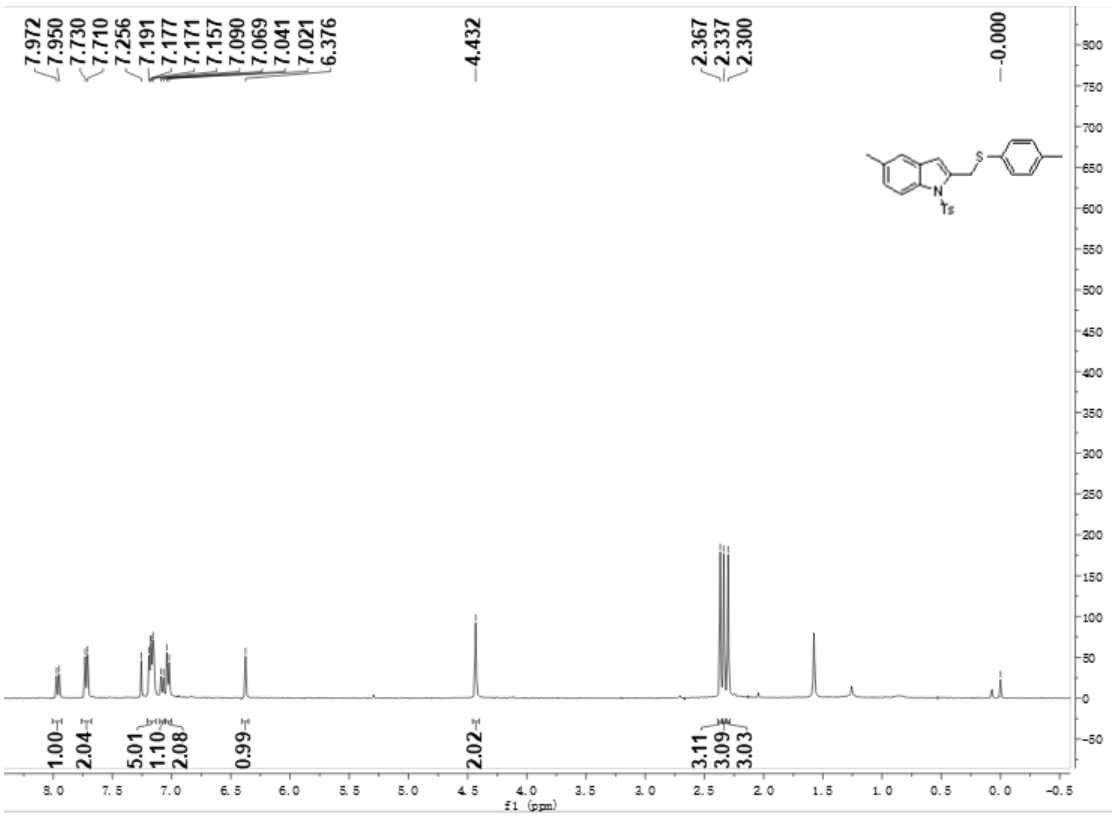
124.6
123.7
120.8
116.5
111.5
33.7
22.2
21.2
Ts
f1 (ppm)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7.256
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7.171
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7.090
7.069
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7.021
6.376
4.432
2.367
2.337
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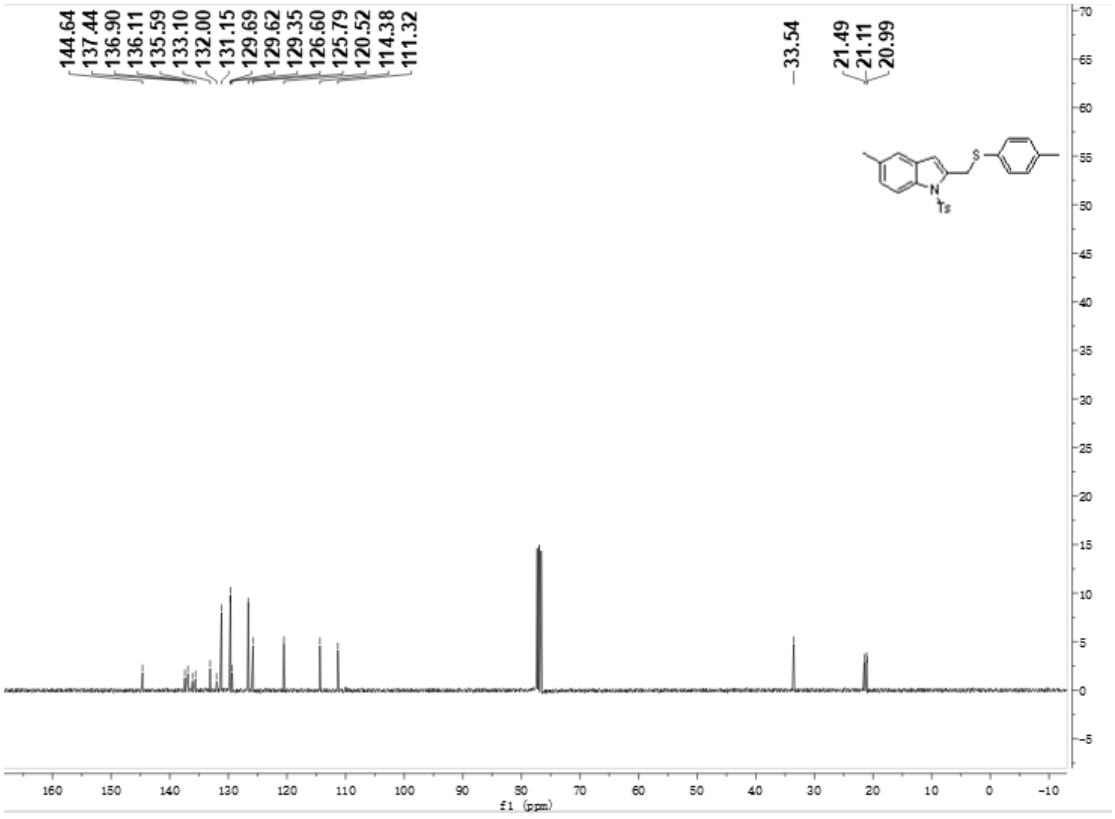
5.01
1.10
2.08
0.99
2.02
3.11
3.09
3.03
f1 (ppm)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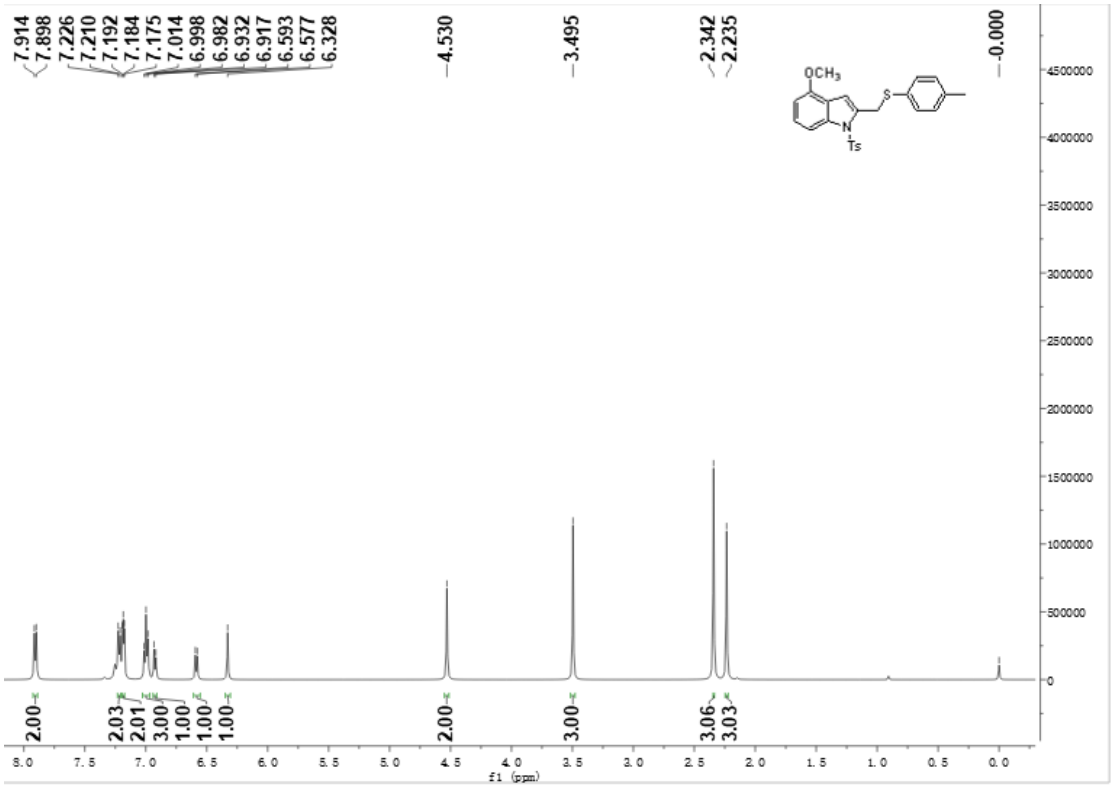
33.54
21.49
21.11
20.99
f1 (ppm)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6.917
6.593
6.577
6.328
4.530
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2.342
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OCH3
S
N
Ts
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2.00
3.00
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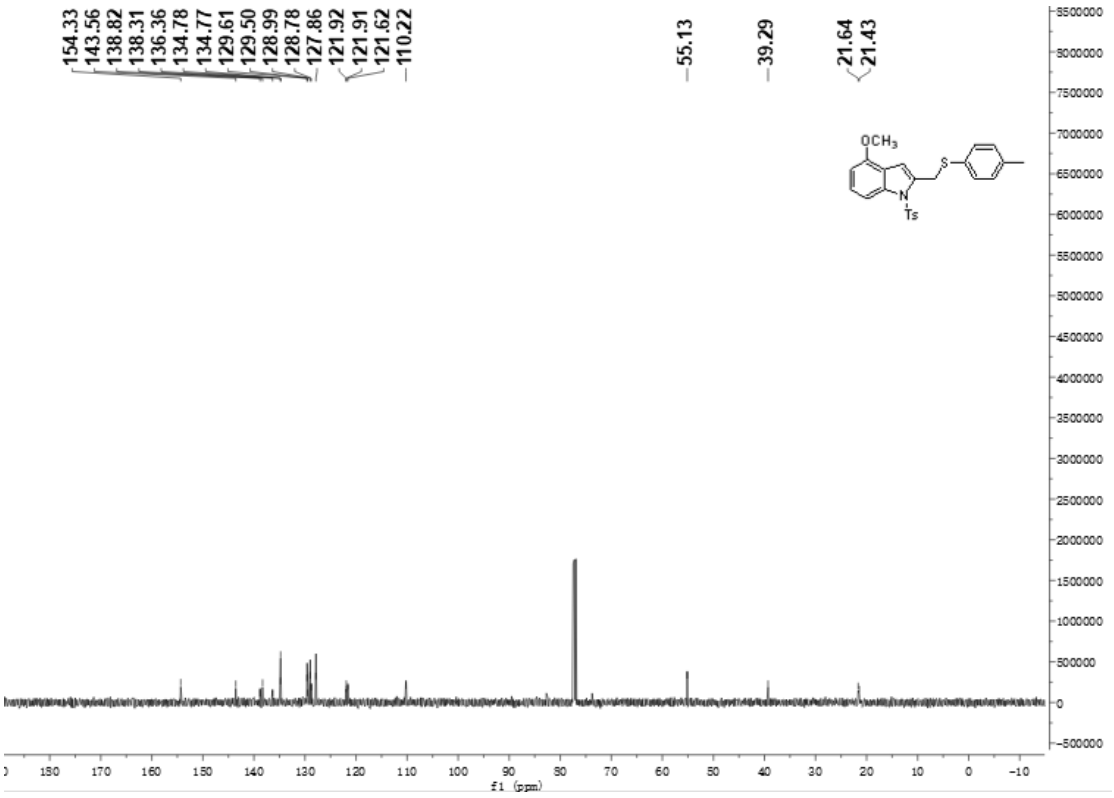
3.03
f1 (ppm)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129.61
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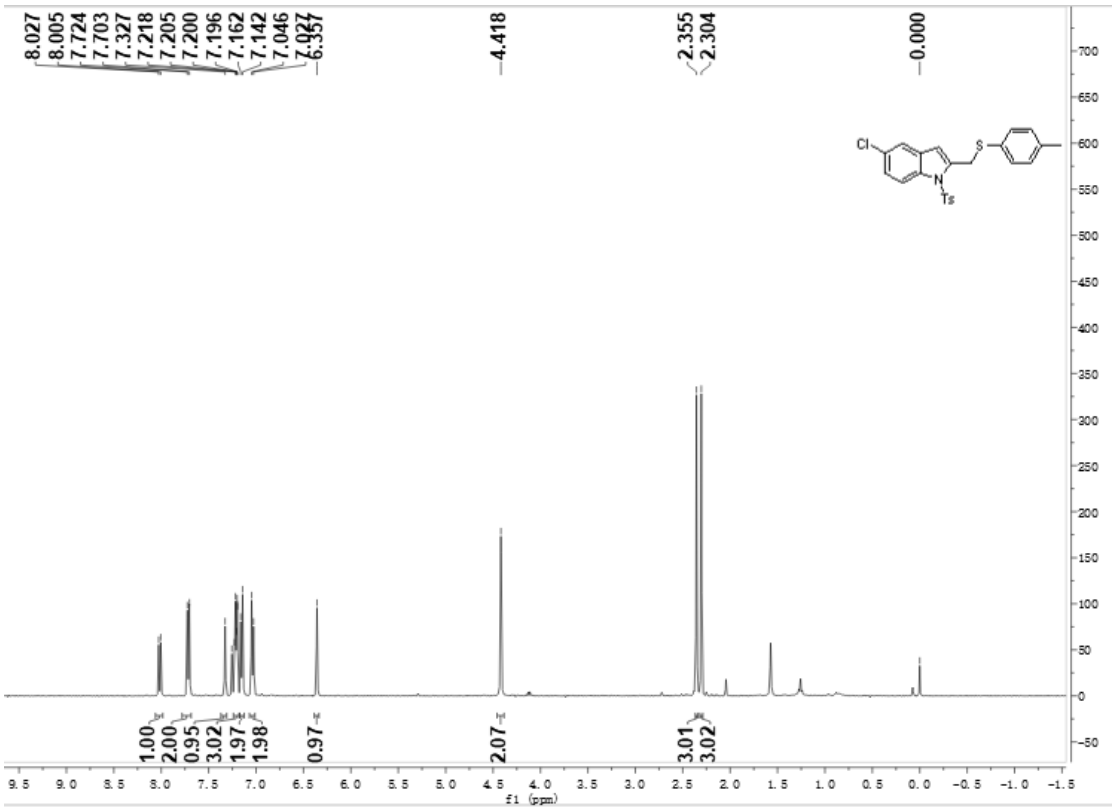
128.99
128.78
127.86
121.92
121.91
121.62
110.22
55.13
39.29
21.64
21.43
OCH3
S
N
Ts
f1 (ppm)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4.418
2.355
2.304
0.000
Cl
S
N
Ts
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1.97
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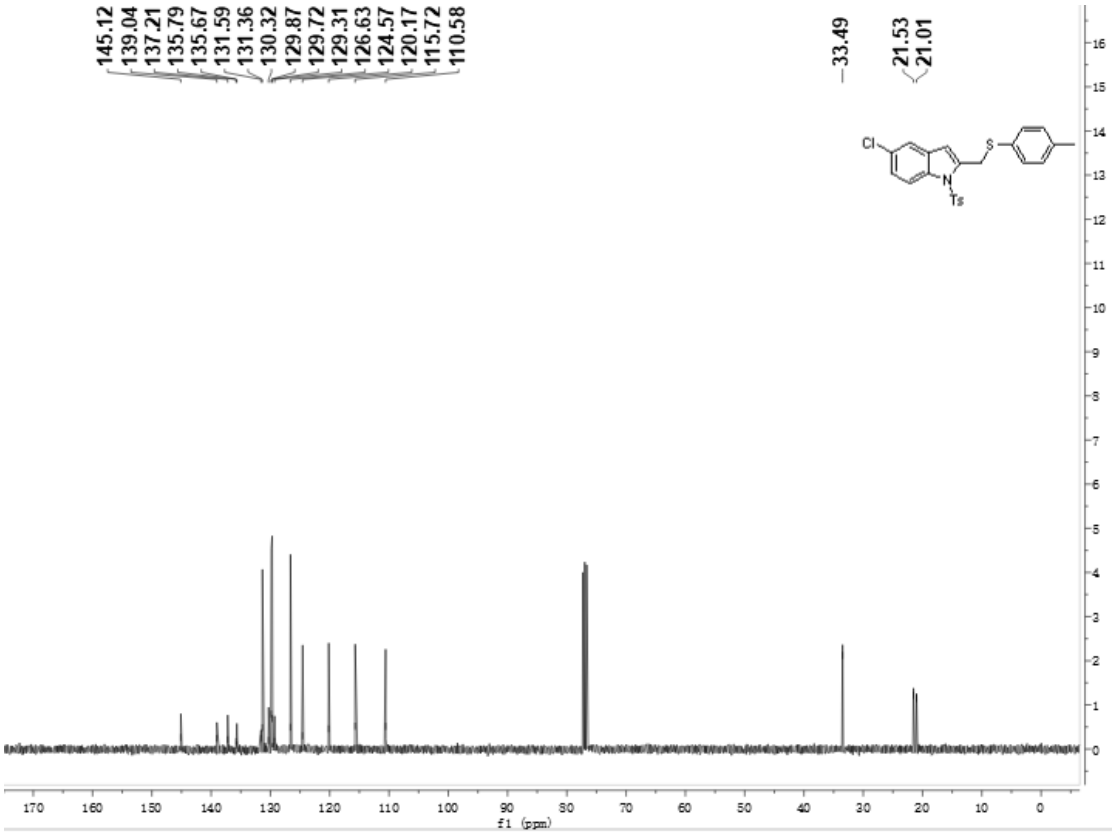
2.07
3.01
3.02
f1 (ppm)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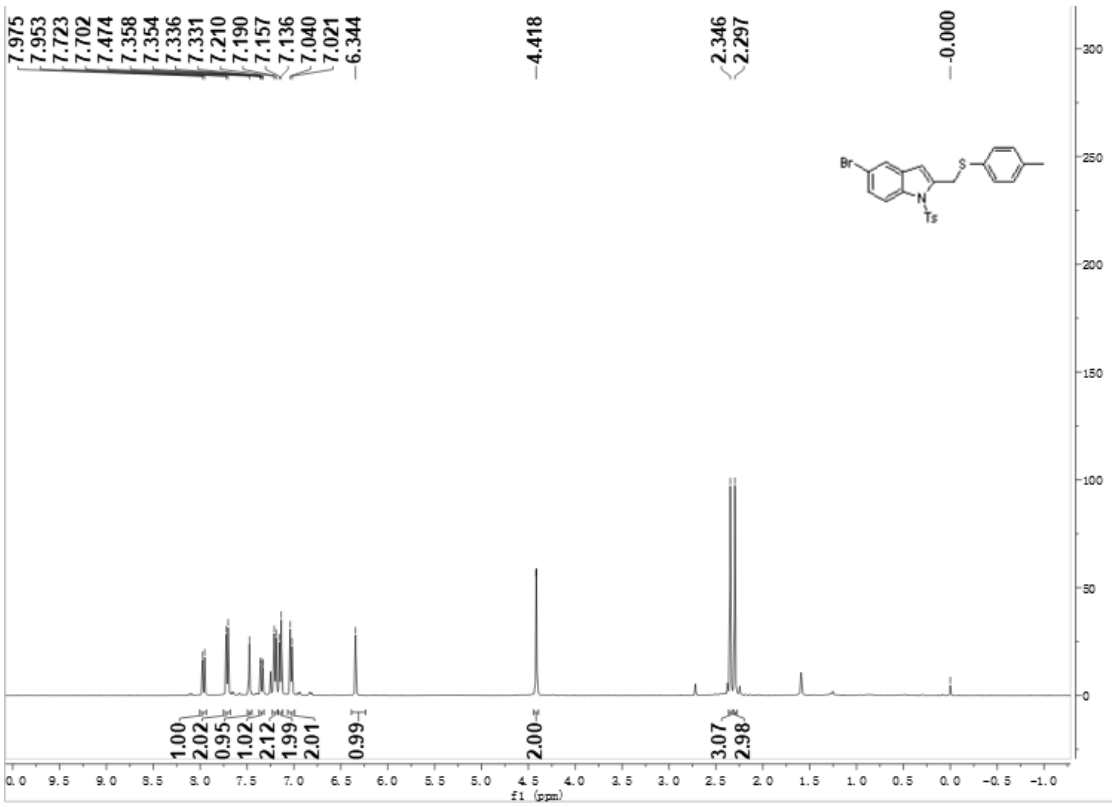
115.72
110.58
33.49
21.53
21.01
Cl
S
N
Ts
f1 (ppm)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S
N
Ts
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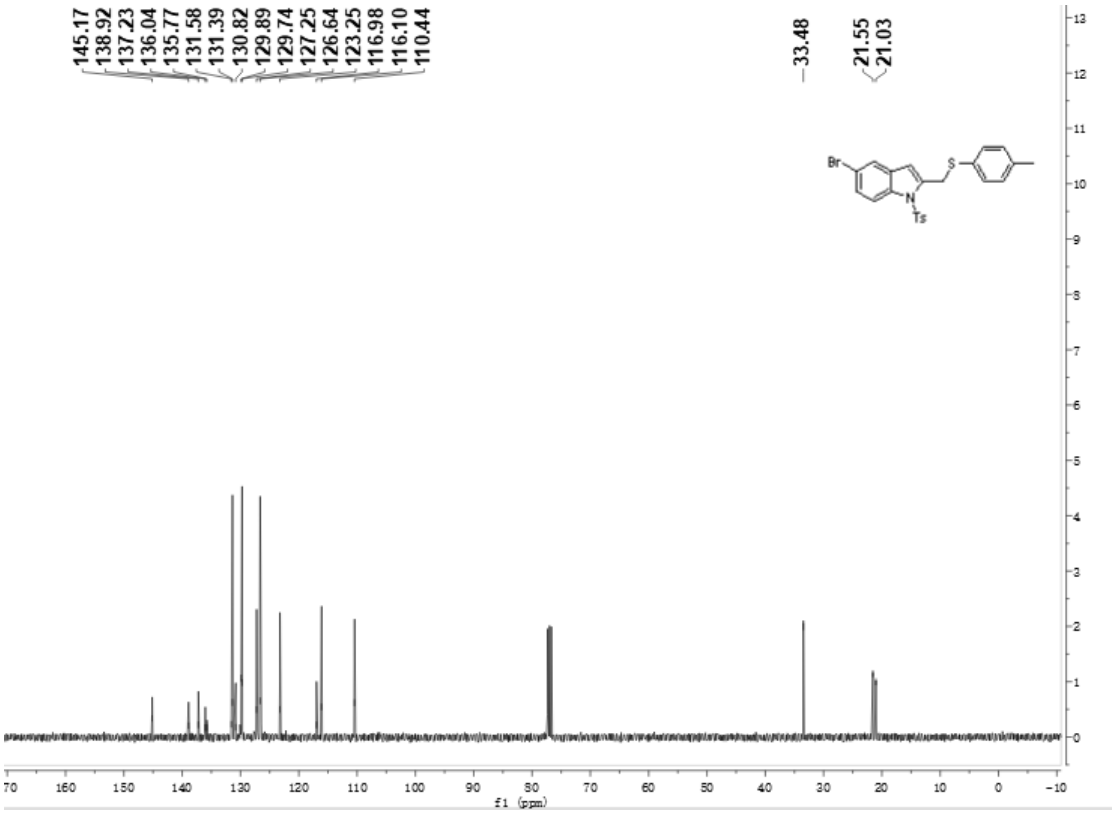
0.99
2.00
3.07
2.98
f1 (ppm)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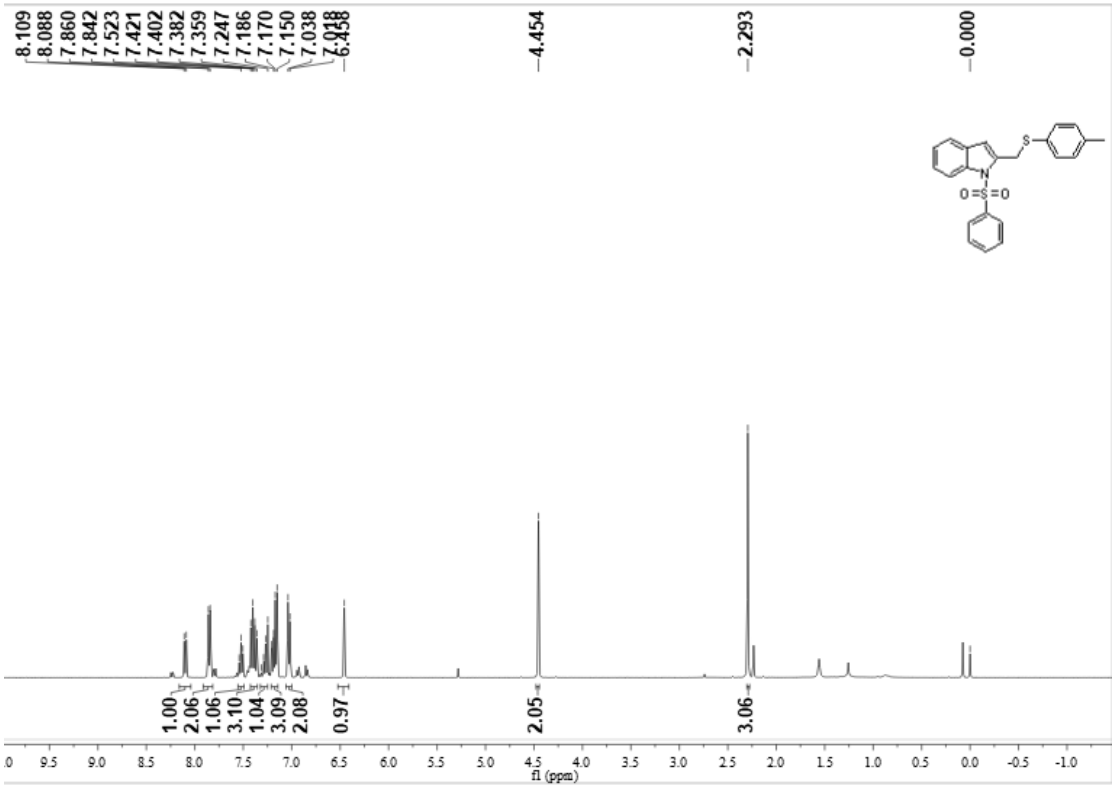
21.03
Br
S
N
Ts
f1 (ppm)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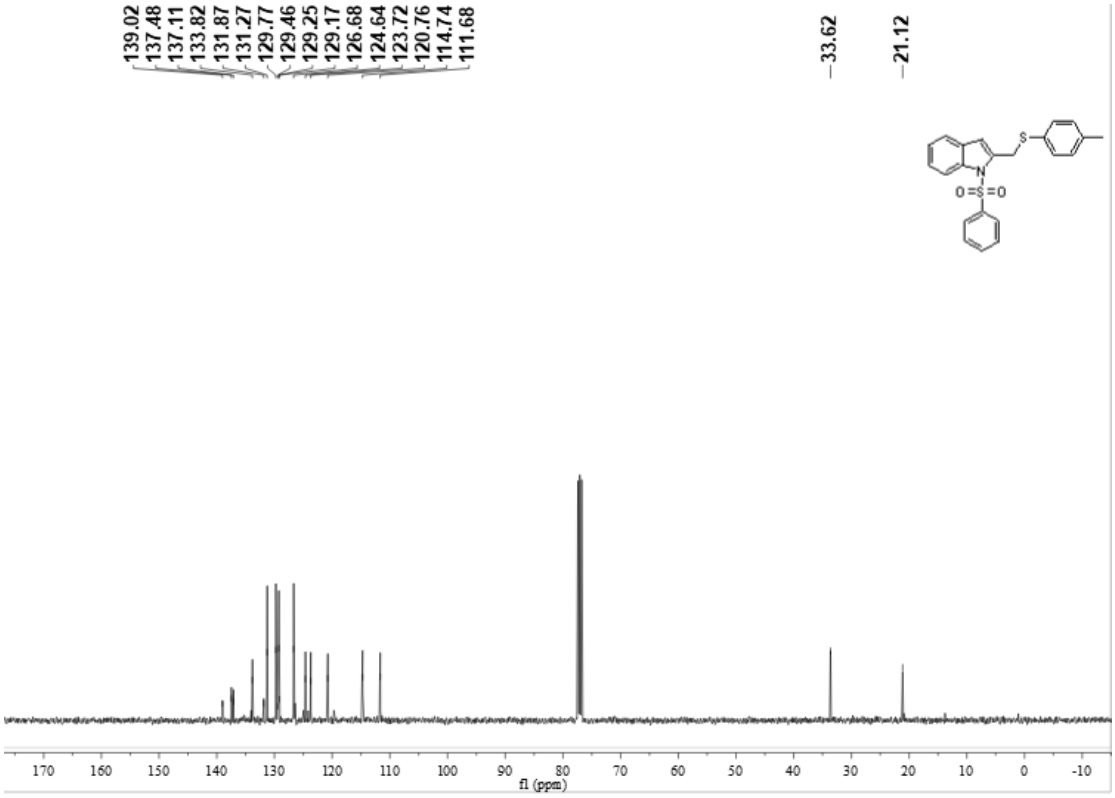
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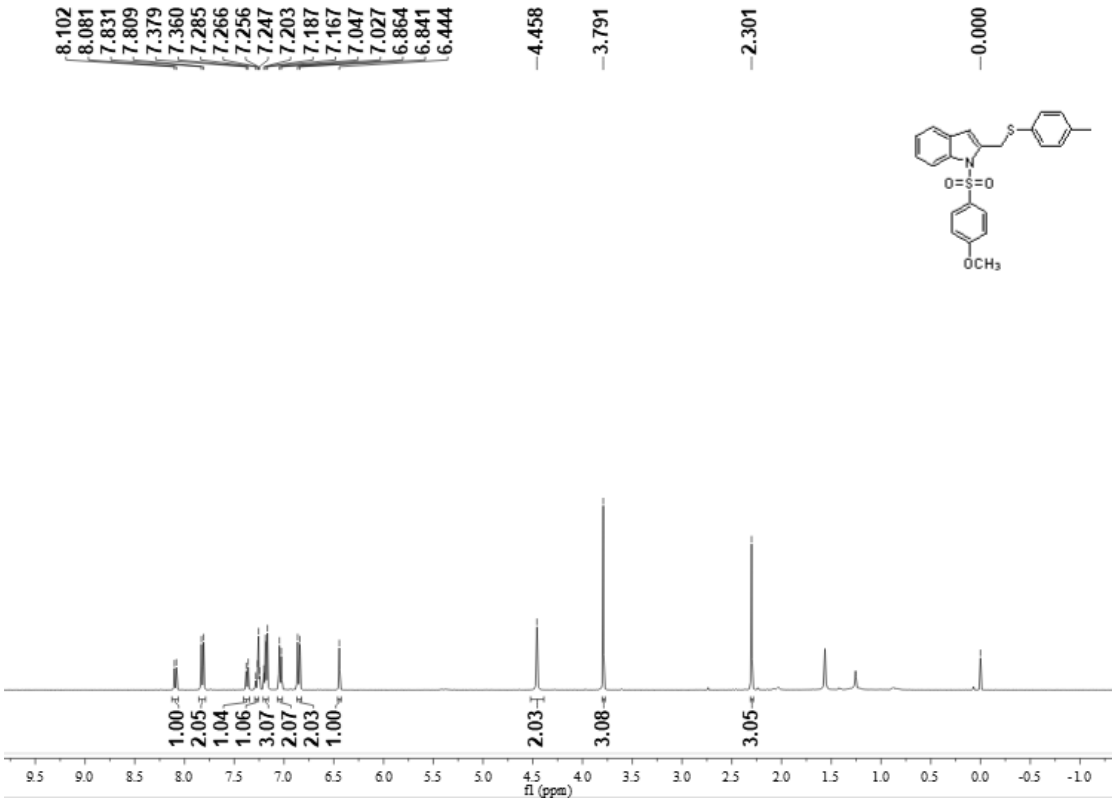
f1 (ppm)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7.047
7.027
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6.841
6.444
4.458
3.791
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1.00
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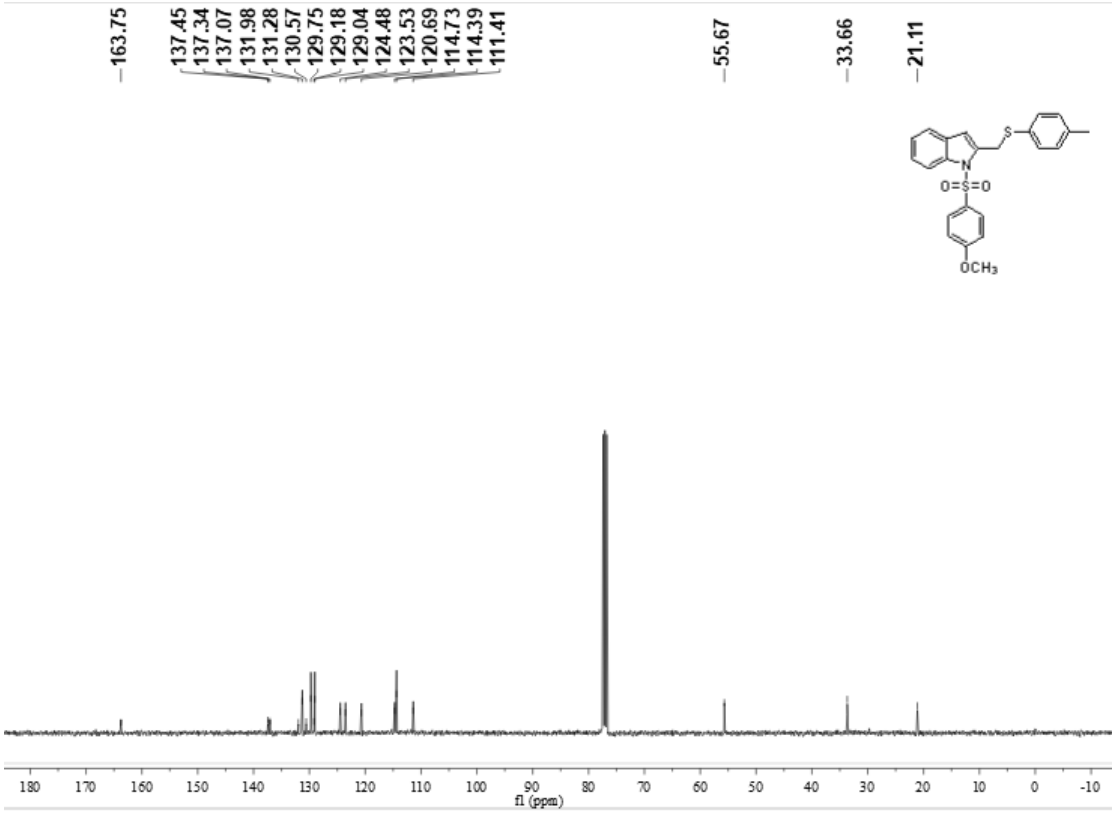
fl (ppm)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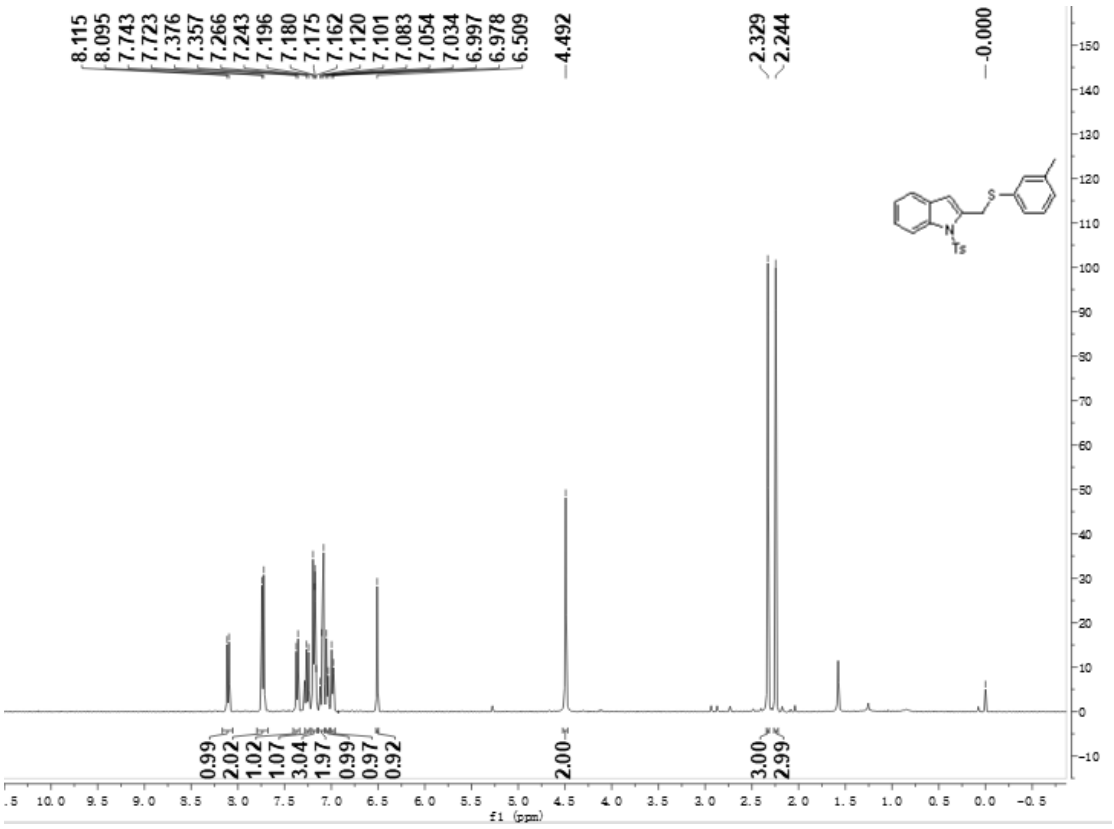
21.11
fl (ppm)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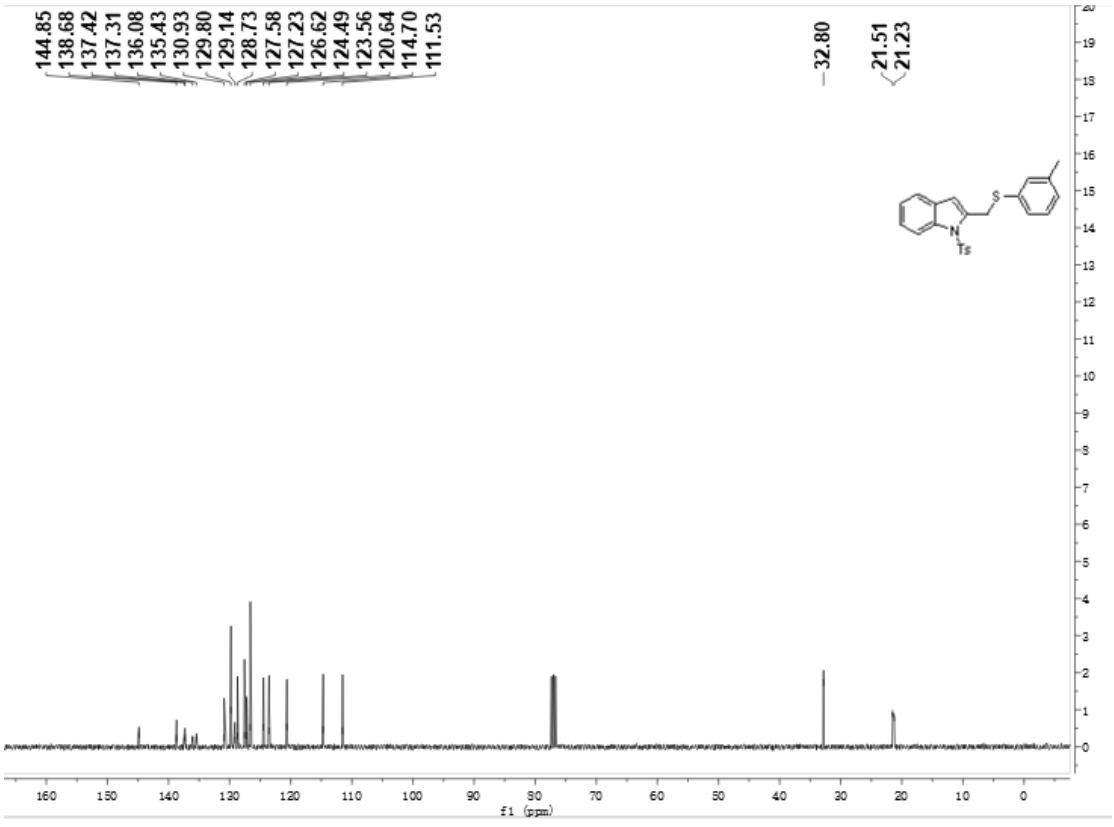
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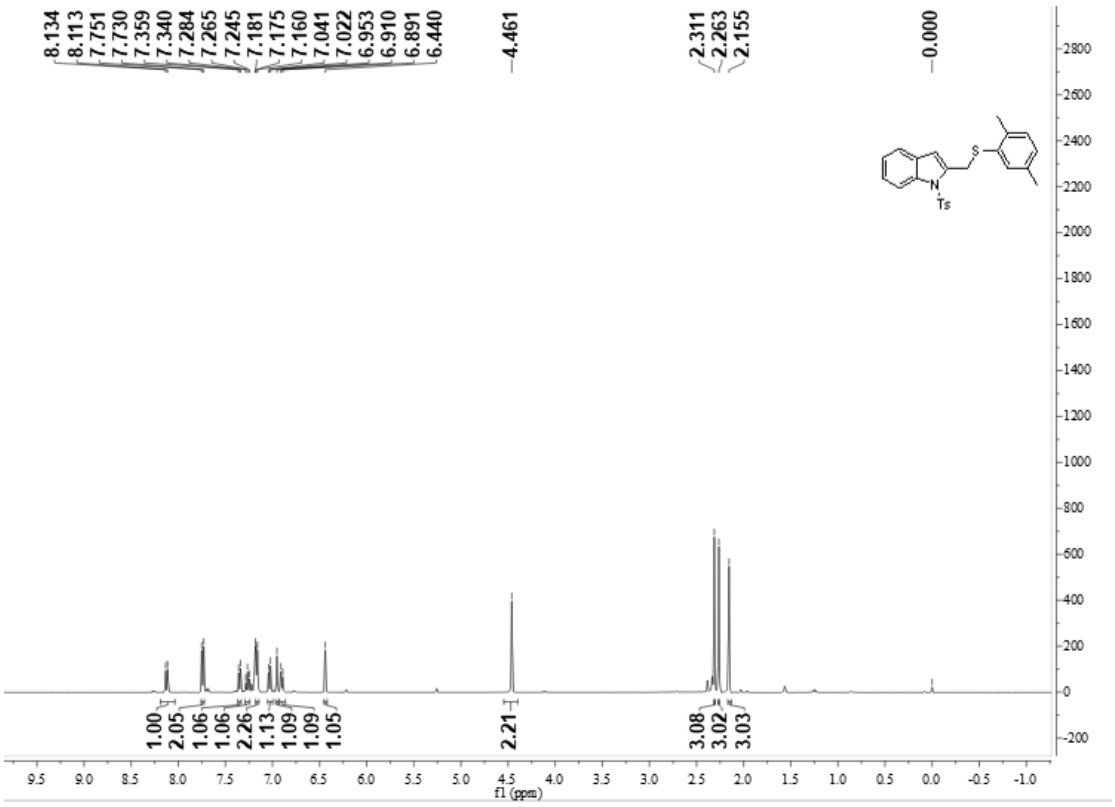
f1 (ppm)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6.910
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6.440
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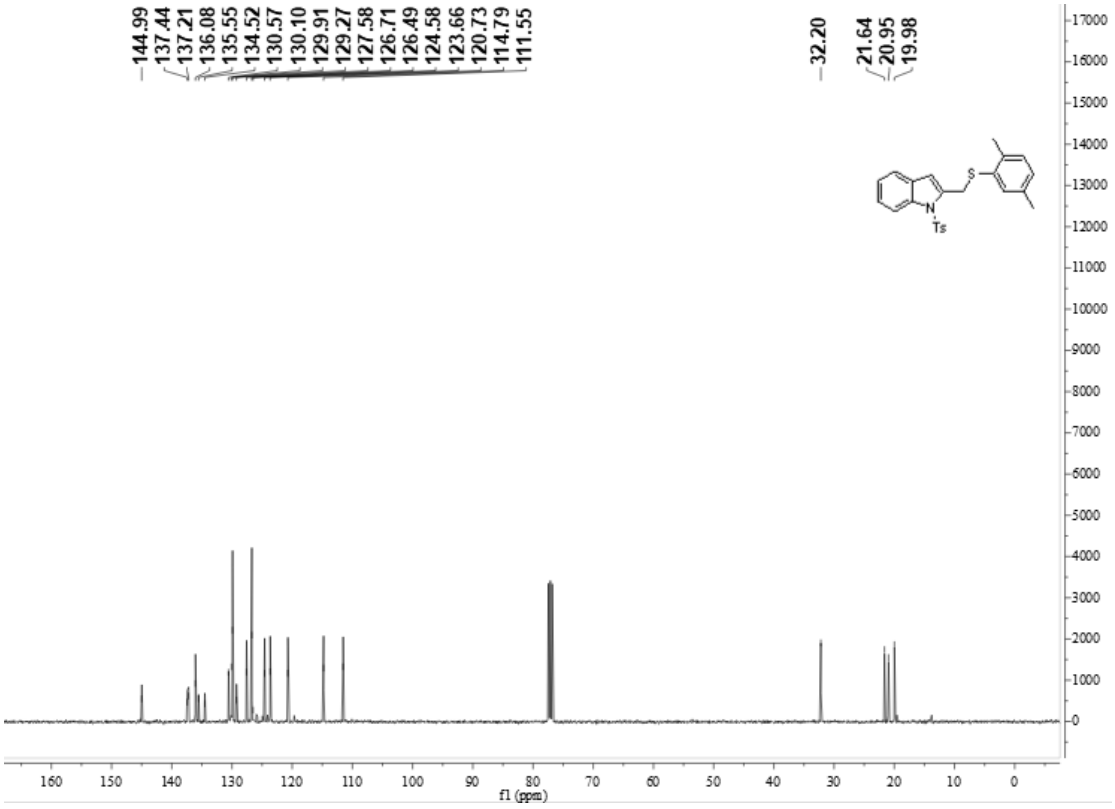
3.03
f1 (ppm)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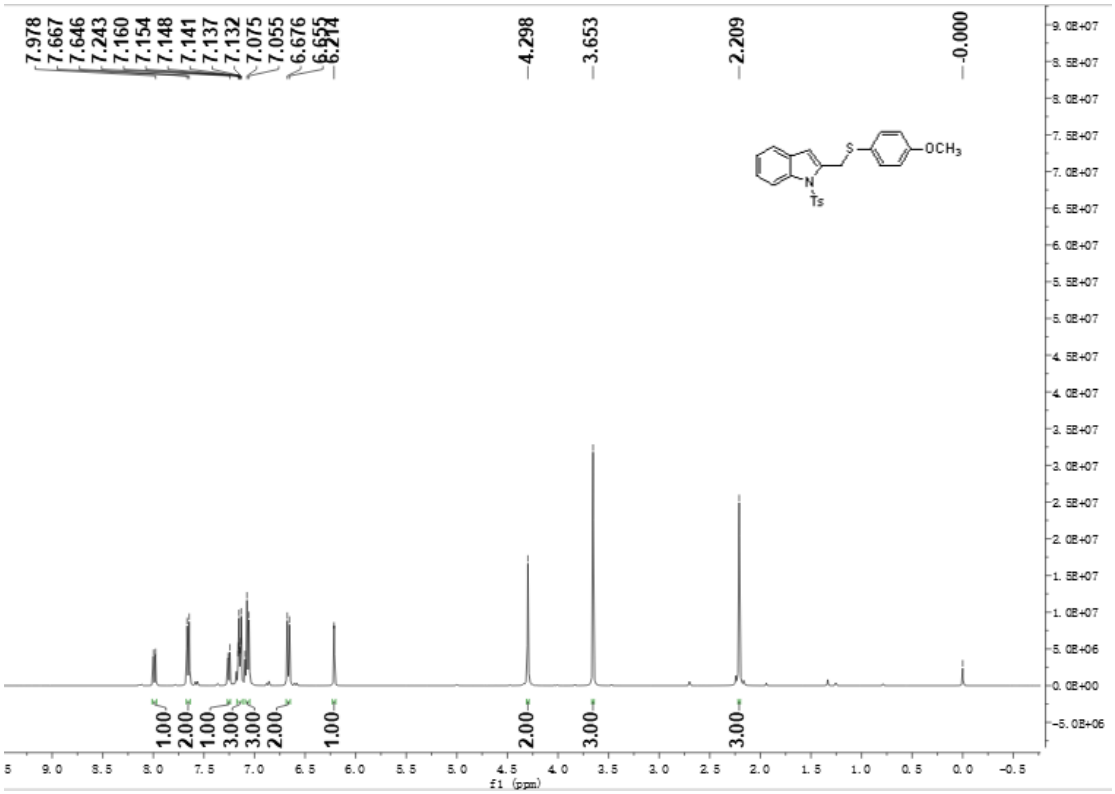
123.66
120.73
114.79
111.55
32.20
21.64
20.95
19.98
Ts
f1 (ppm)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7.667
7.646
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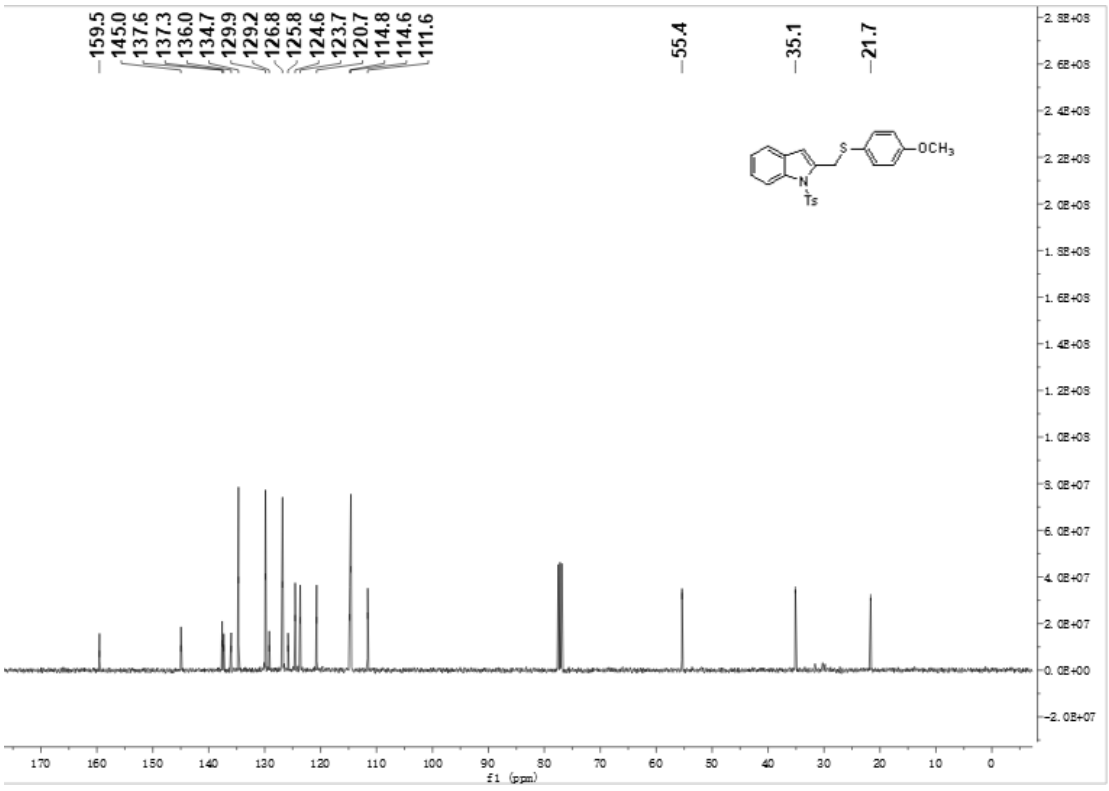
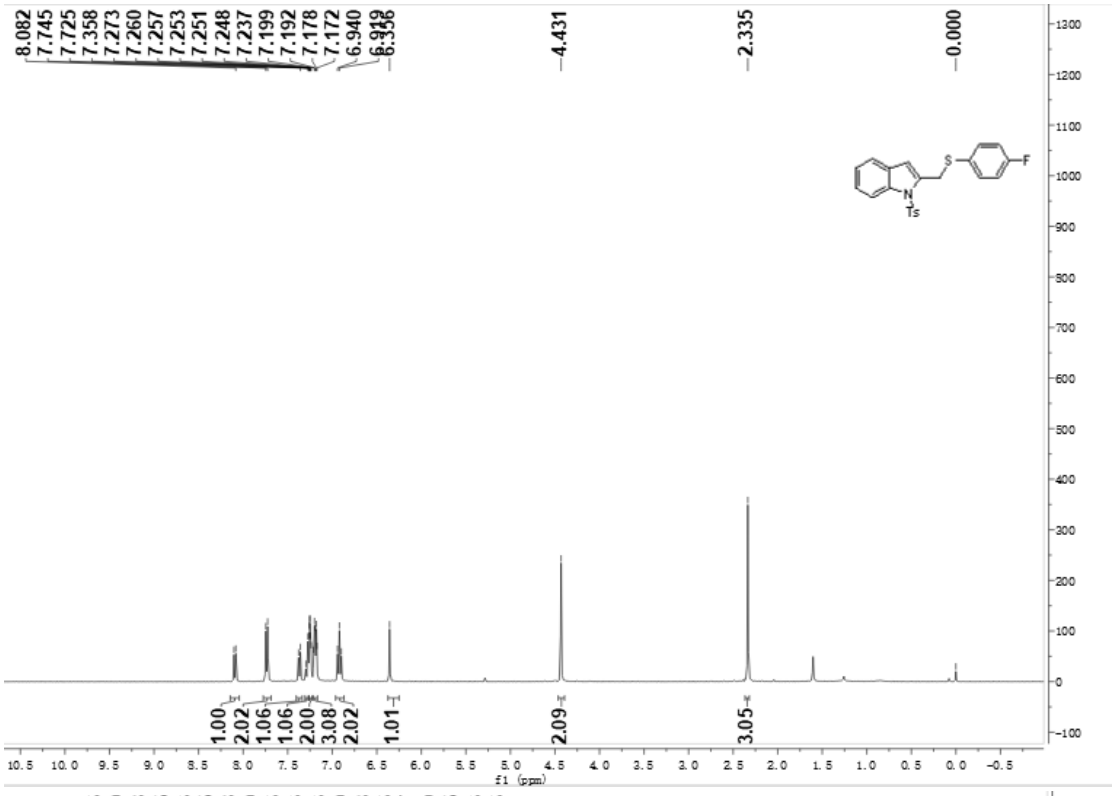
7.160
7.154
7.148
7.141
7.137
7.132
7.075
7.055
6.676
6.655
6.214
4.298
3.653
2.209
-0.000
OCH3
S
N
Ts
1.00
2.00
1.00
3.00
3.00
2.00
1.00
2.00
3.00
3.00
f1 (ppm)


159.5
145.0
137.6
137.3
136.0
134.7
129.9
129.2
126.8
125.8
124.6
123.7
120.7
114.8
114.6
111.6
55.4
35.1
21.7
OCH3
S
N
Ts
f1 (ppm)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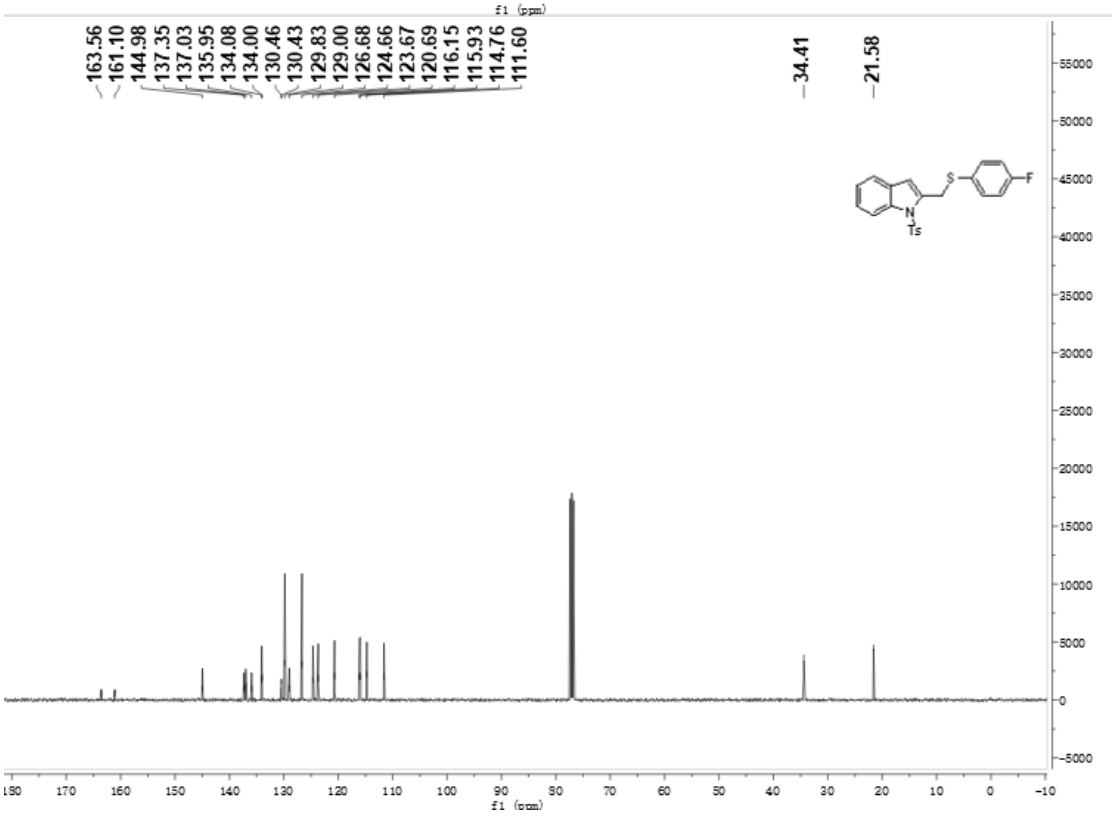
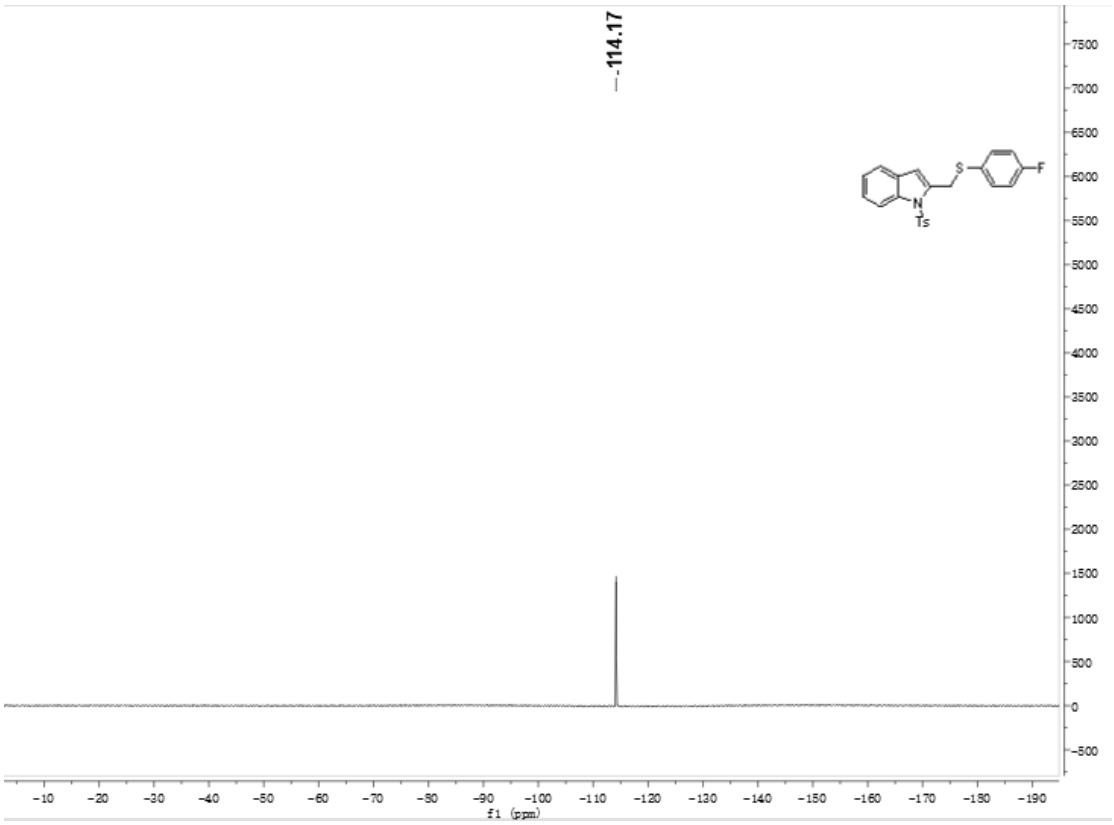
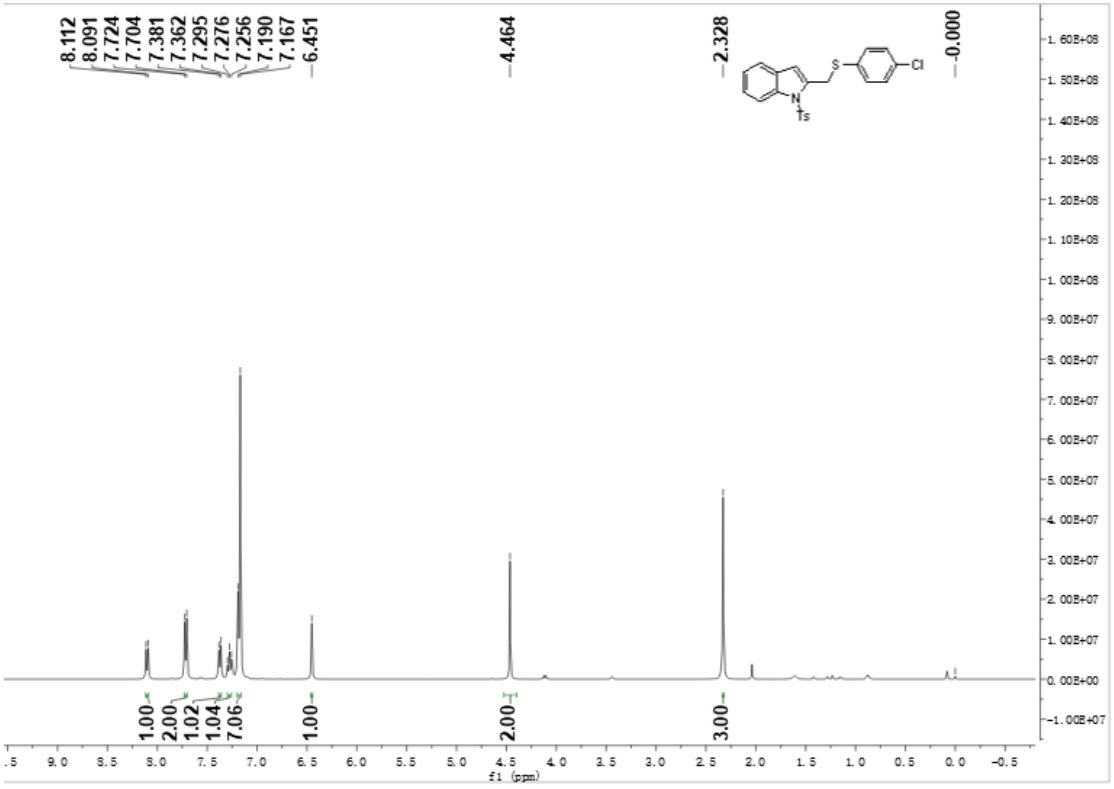
7.745
7.725
7.358
7.273
7.260
7.257
7.253
7.251
7.248
7.237
7.199
7.192
7.178
7.172
6.940
4.431
2.335
0.000
1.00
2.02
1.06
1.06
2.00
3.08
2.02
1.01
2.09
3.05
f1 (ppm)
Ts
S
F


163.56
161.10
144.98
137.35
137.03
135.95
134.08
134.00
130.46
130.43
129.83
129.00
126.68
124.66
123.67
120.69
116.15
115.93
114.76
111.60
34.41
21.58
f1 (ppm)
Ts
S
F


-114.17
S
F
N
Ts
f1 (ppm)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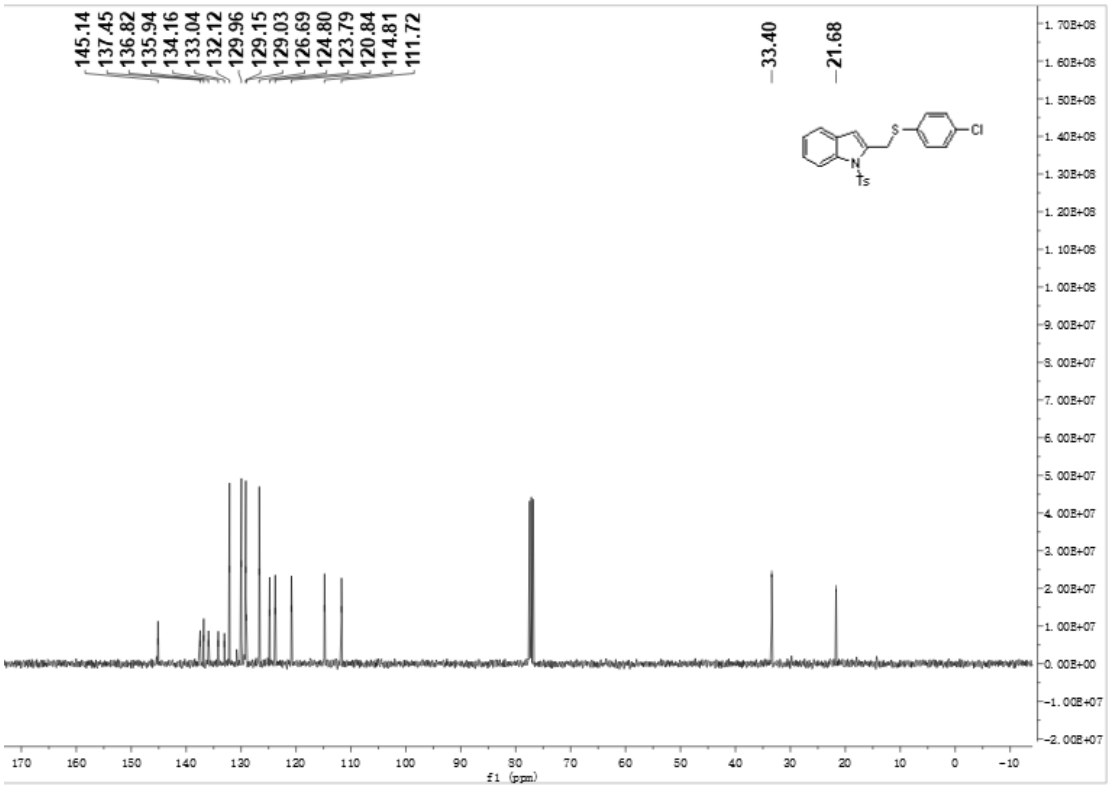
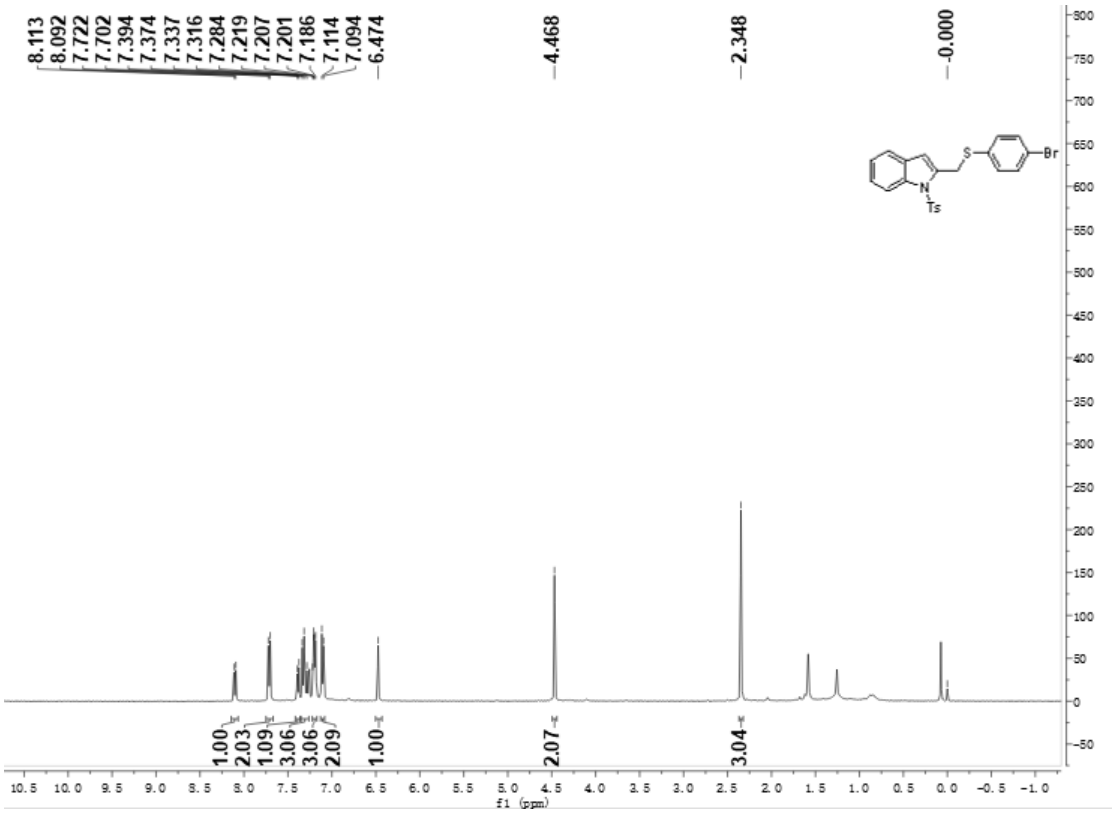
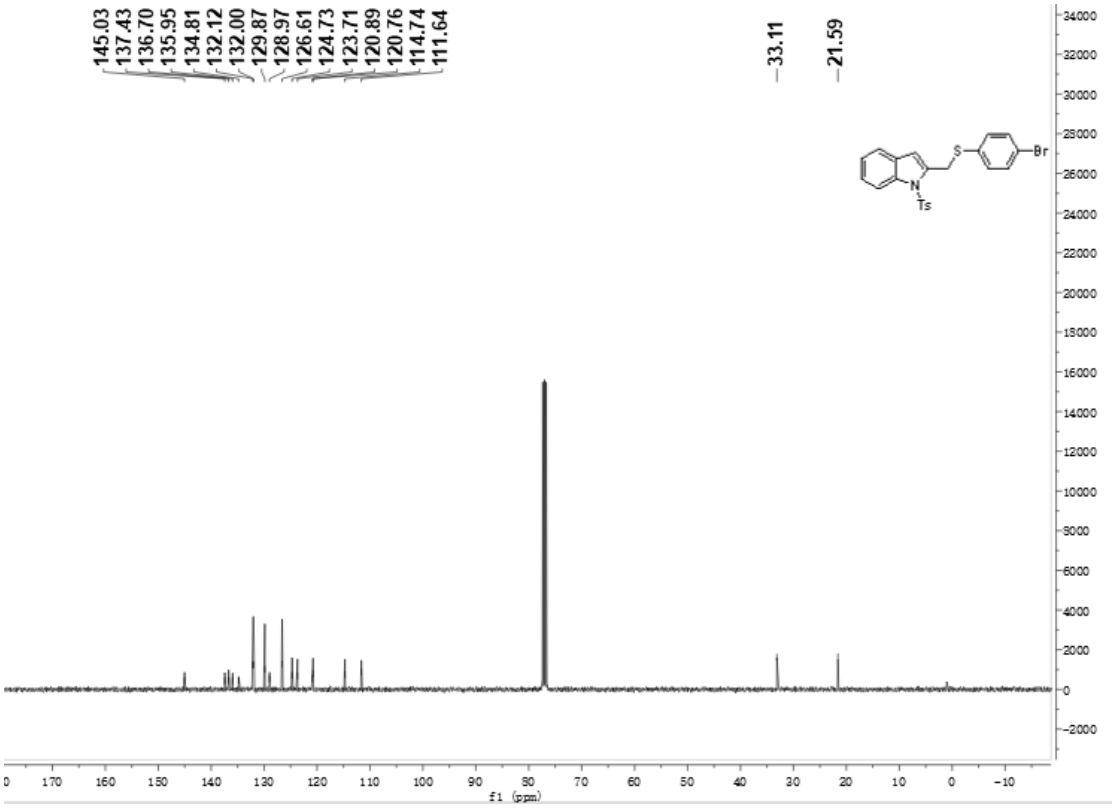
8.091
7.724
7.704
7.381
7.362
7.295
7.276
7.256
7.190
7.167
6.451
4.464
2.328
-0.000
S
Cl
N
Ts
1.00
2.00
1.02
1.04
7.06
1.00
2.00
3.00
f1 (ppm)


145.14
137.45
136.82
135.94
134.16
133.04
132.12
129.96
129.15
129.03
126.69
124.80
123.79
120.84
114.81
111.72
33.40
21.68
Cl
S
N
Ts
f1 (ppm)


8.113
8.092
7.722
7.702
7.394
7.374
7.337
7.316
7.284
7.219
7.207
7.201
7.186
7.114
7.094
6.474
4.468
2.348
0.000
Br
S
N
Ts
1.00
2.03
1.09
3.06
3.06
2.09
1.00
2.07
3.04
f1 (ppm)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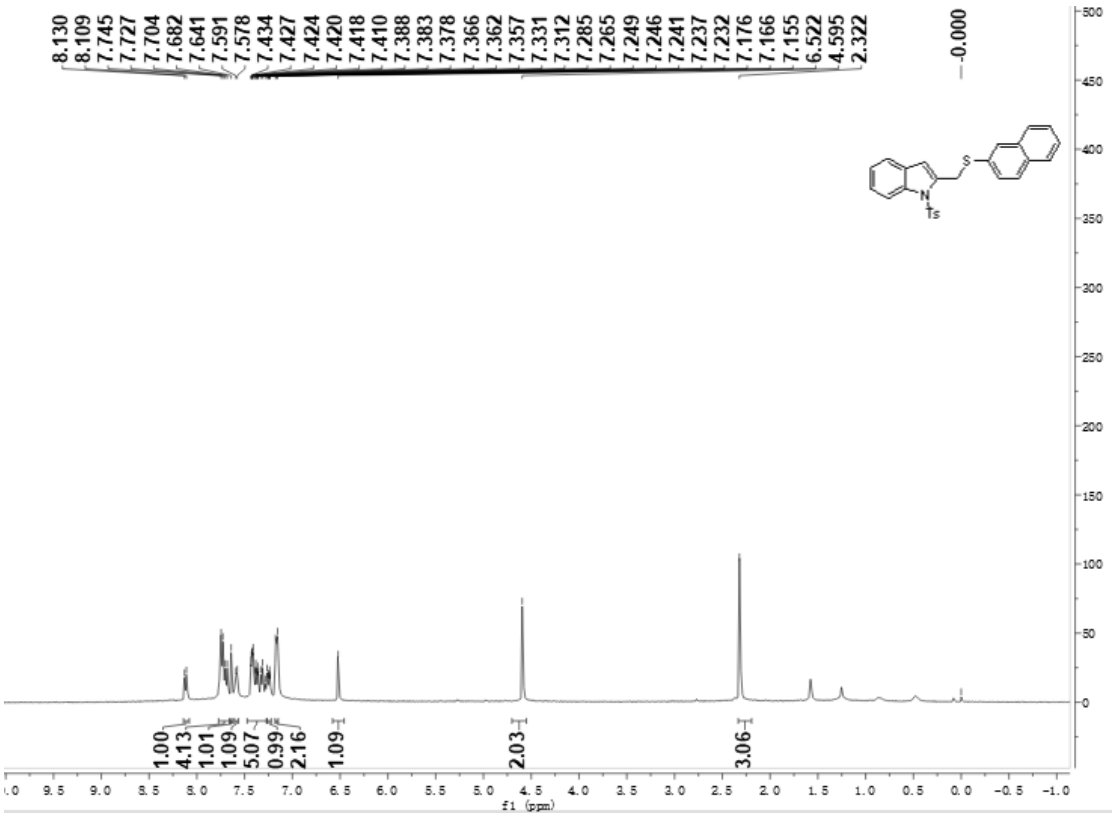
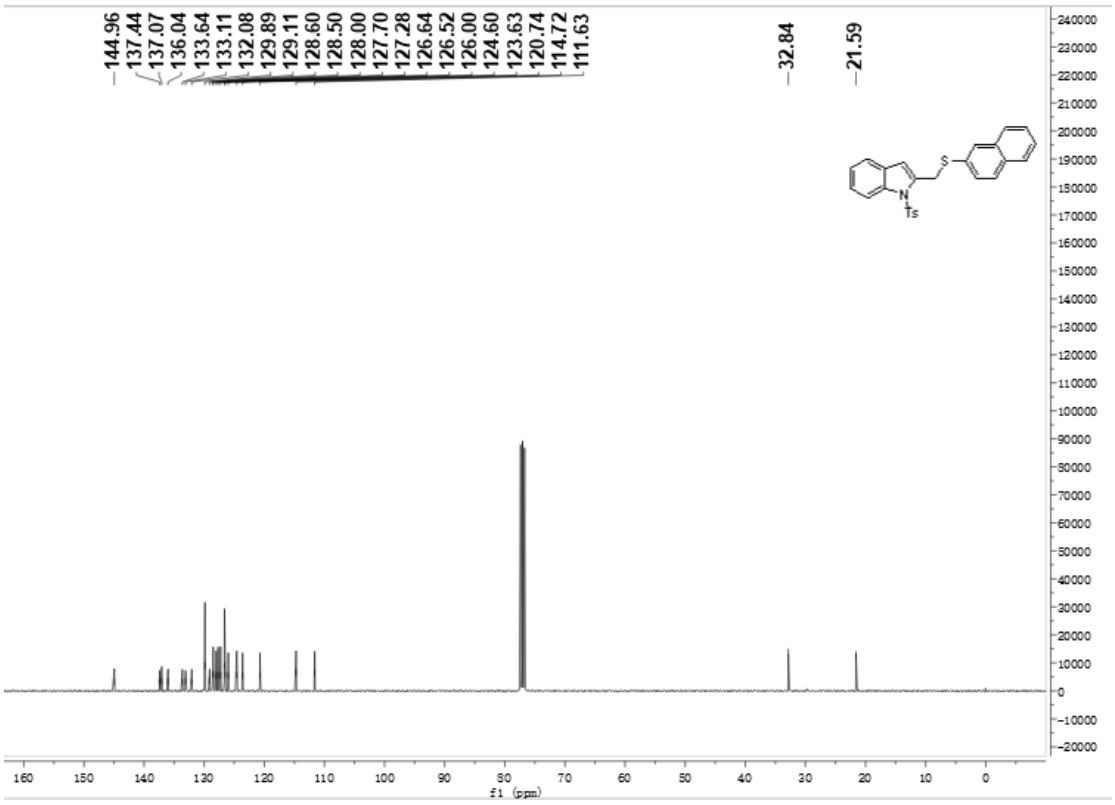
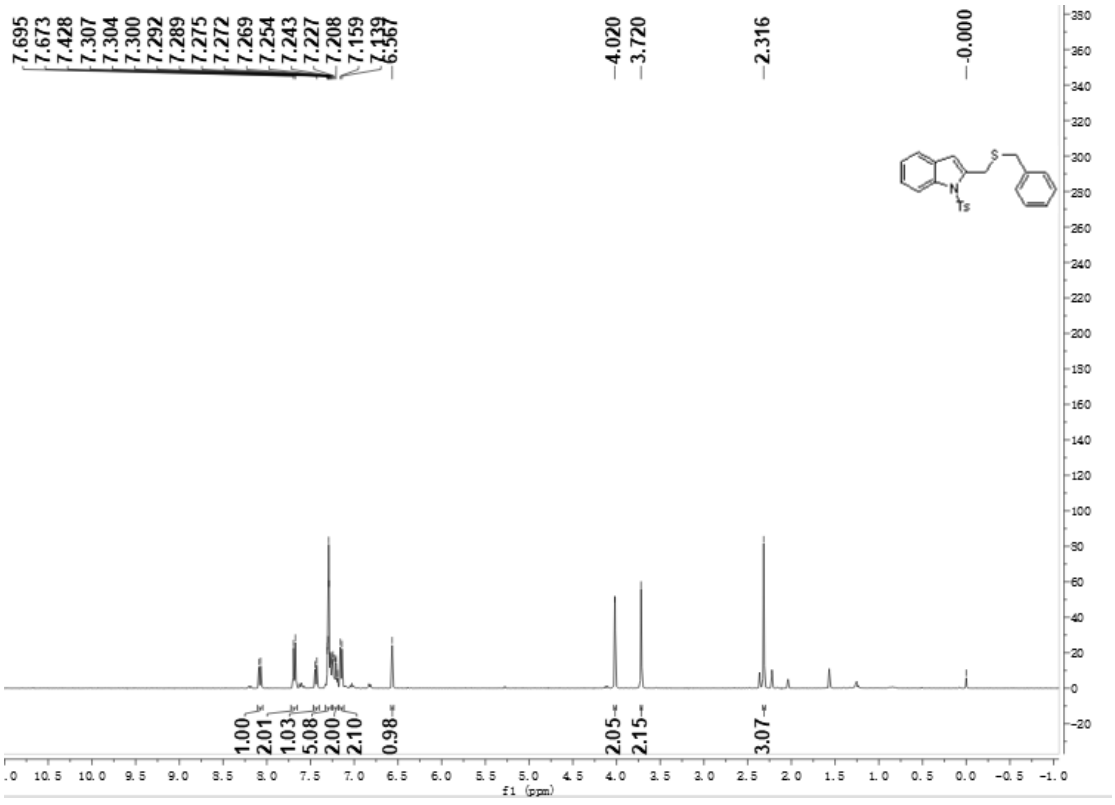
137.43
136.70
135.95
134.81
132.12
132.00
129.87
128.97
126.61
124.73
123.71
120.89
120.76
114.74
111.64
33.11
21.59
S
Br
N
Ts
f1 (ppm)


8.130
8.109
7.745
7.727
7.704
7.682
7.641
7.591
7.578
7.434
7.427
7.424
7.420
7.418
7.410
7.388
7.383
7.378
7.366
7.362
7.357
7.331
7.312
7.285
7.265
7.249
7.246
7.241
7.237
7.232
7.176
7.166
7.155
6.522
4.595
2.322
0.000
S
N
Ts
1.00
4.13
1.01
1.09
5.07
0.99
2.16
1.09
2.03
3.06
f1 (ppm)


144.96
137.44
137.07
136.04
133.64
133.11
132.08
129.89
129.11
128.60
128.50
128.00
127.70
127.28
126.64
126.52
126.00
124.60
123.63
120.74
114.72
111.63
32.84
21.59
Ts
f1 (ppm)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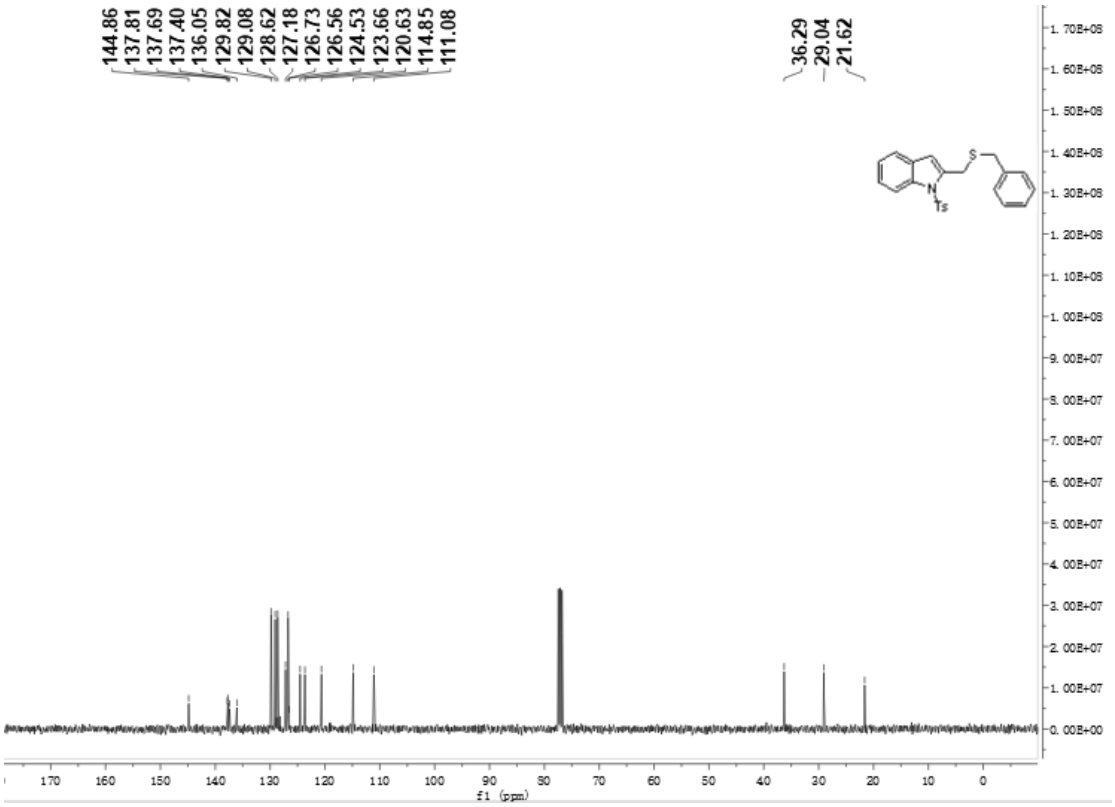
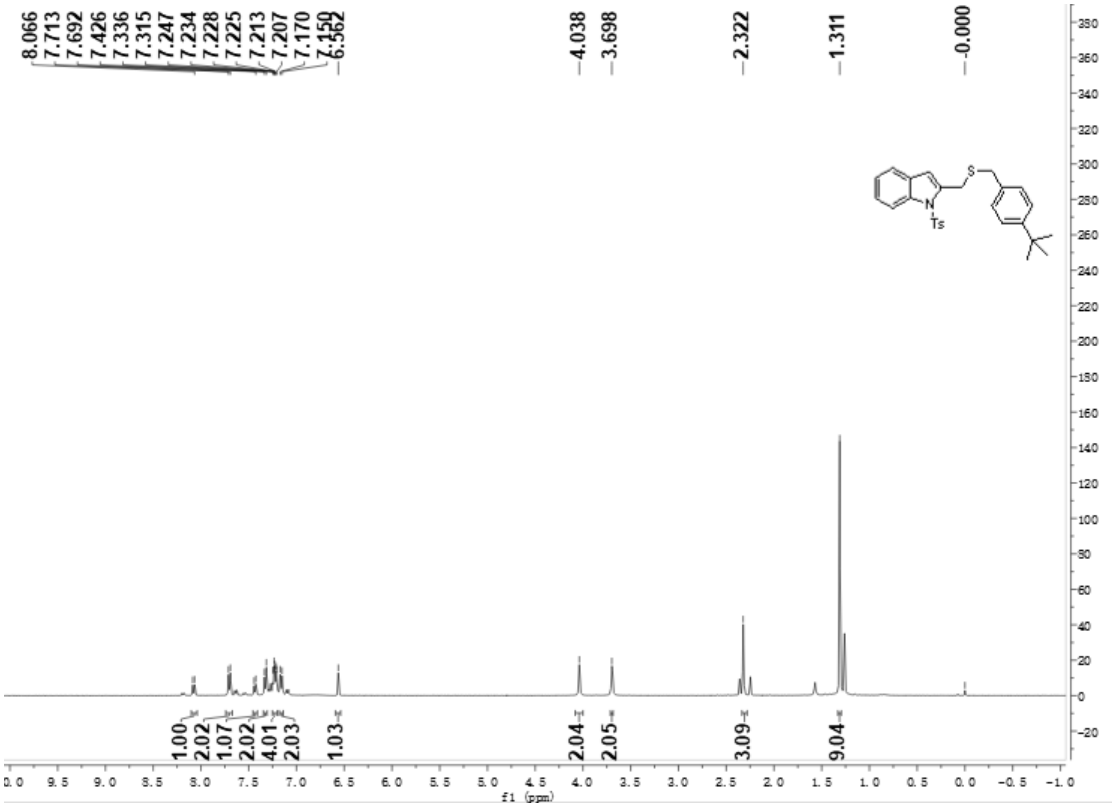
7.307
7.304
7.300
7.292
7.289
7.275
7.272
7.269
7.254
7.243
7.227
7.208
7.159
7.139
6.567
4.020
3.720
2.316
0.000
1.00
2.01
1.03
5.08
2.00
2.10
0.98
2.05
2.15
3.07
Ts
f1 (ppm)


144.86
137.81
137.69
137.40
136.05
129.82
129.08
128.62
127.18
126.73
126.56
124.53
123.66
120.63
114.85
111.08
36.29
29.04
21.62
Ts
f1 (ppm)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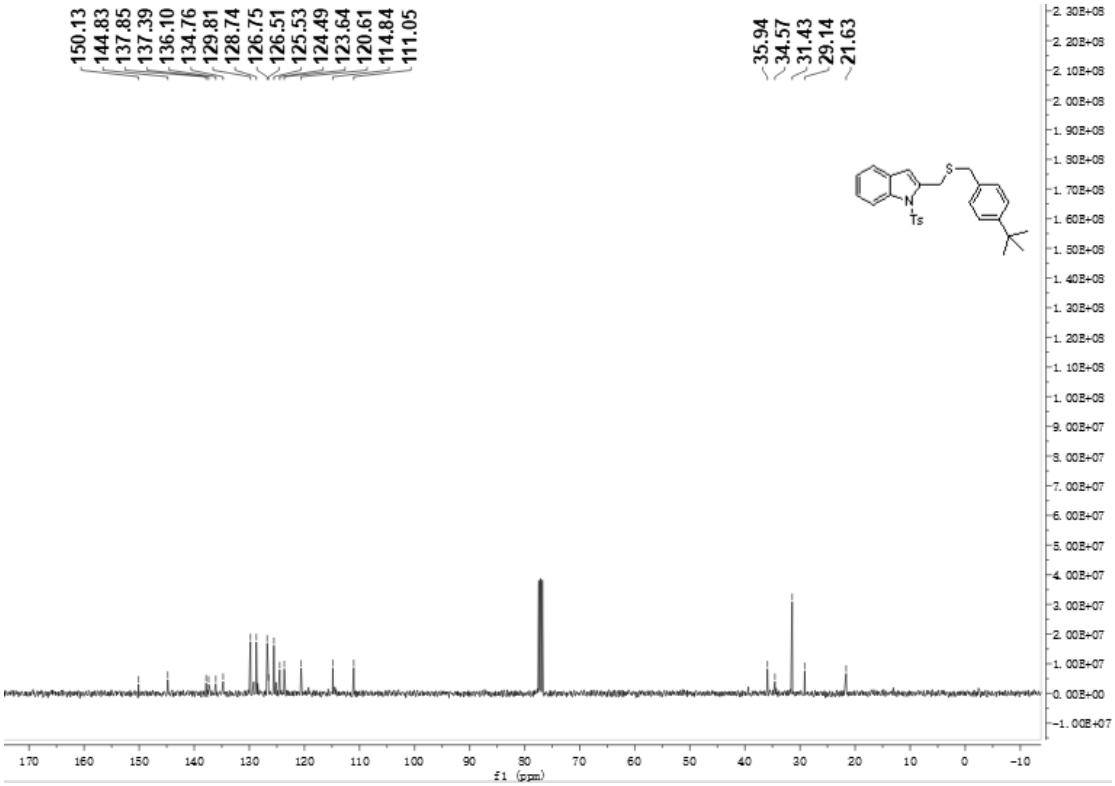
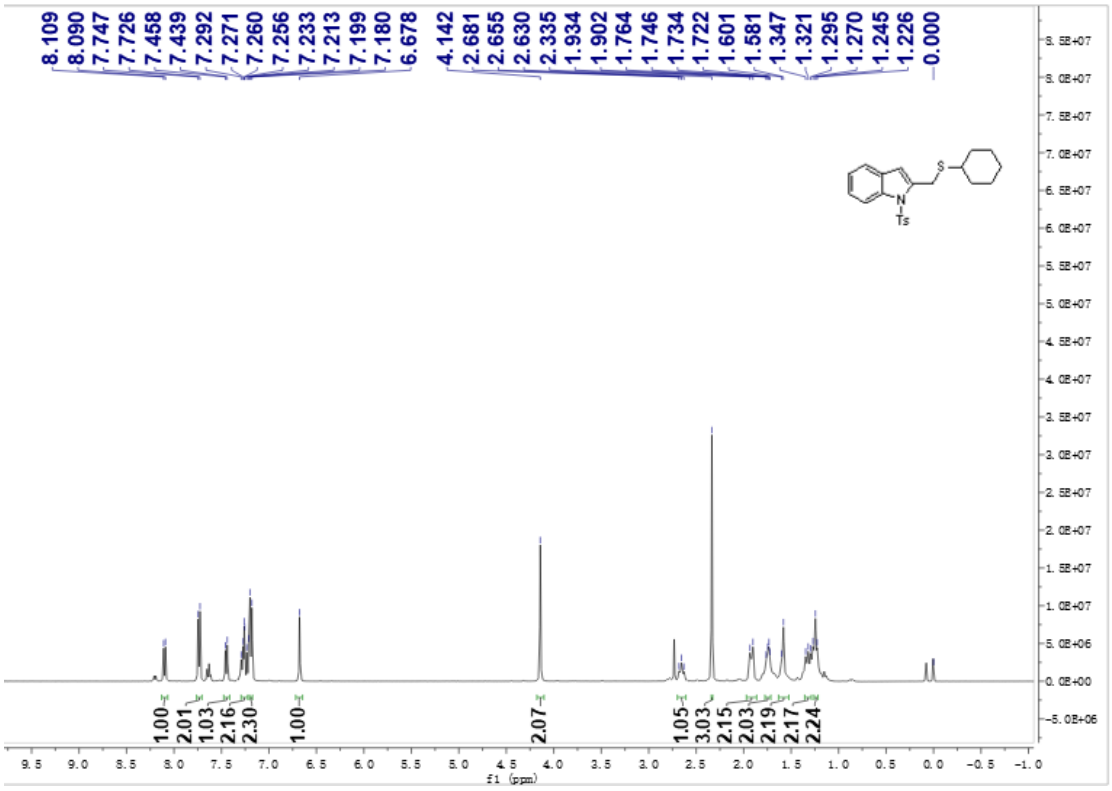
7.336
7.315
7.247
7.234
7.228
7.225
7.213
7.207
7.170
7.150
6.562
4.038
3.698
2.322
1.311
-0.000
Ts
1.00
2.02
1.07
2.02
4.01
2.03
1.03
2.04
2.05
3.09
9.04
f1 (ppm)


150.13
144.83
137.85
137.39
136.10
134.76
129.81
128.74
126.75
126.51
125.53
124.49
123.64
120.61
114.84
111.05
35.94
34.57
31.43
29.14
21.63
Ts
f1 (ppm)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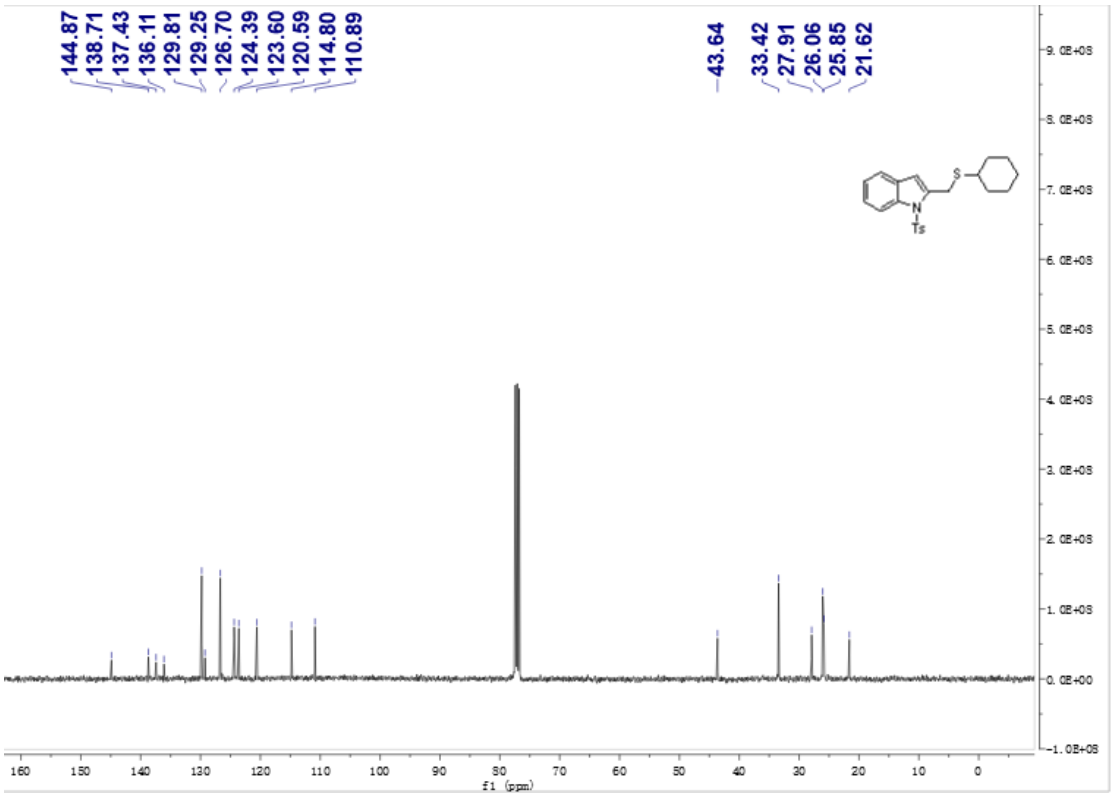
7.439
7.292
7.271
7.260
7.256
7.233
7.213
7.199
7.180
6.678
4.142
2.681
2.655
2.630
2.335
1.934
1.902
1.764
1.746
1.734
1.722
1.601
1.581
1.347
1.321
1.295
1.270
1.245
1.226
0.000
1.00
2.01
1.03
2.16
2.30
1.00
2.07
1.05
3.03
2.15
2.03
2.19
2.17
2.24
Ts
f1 (ppm)


144.87
138.71
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129.81
129.25
126.70
124.39
123.60
120.59
114.80
110.89
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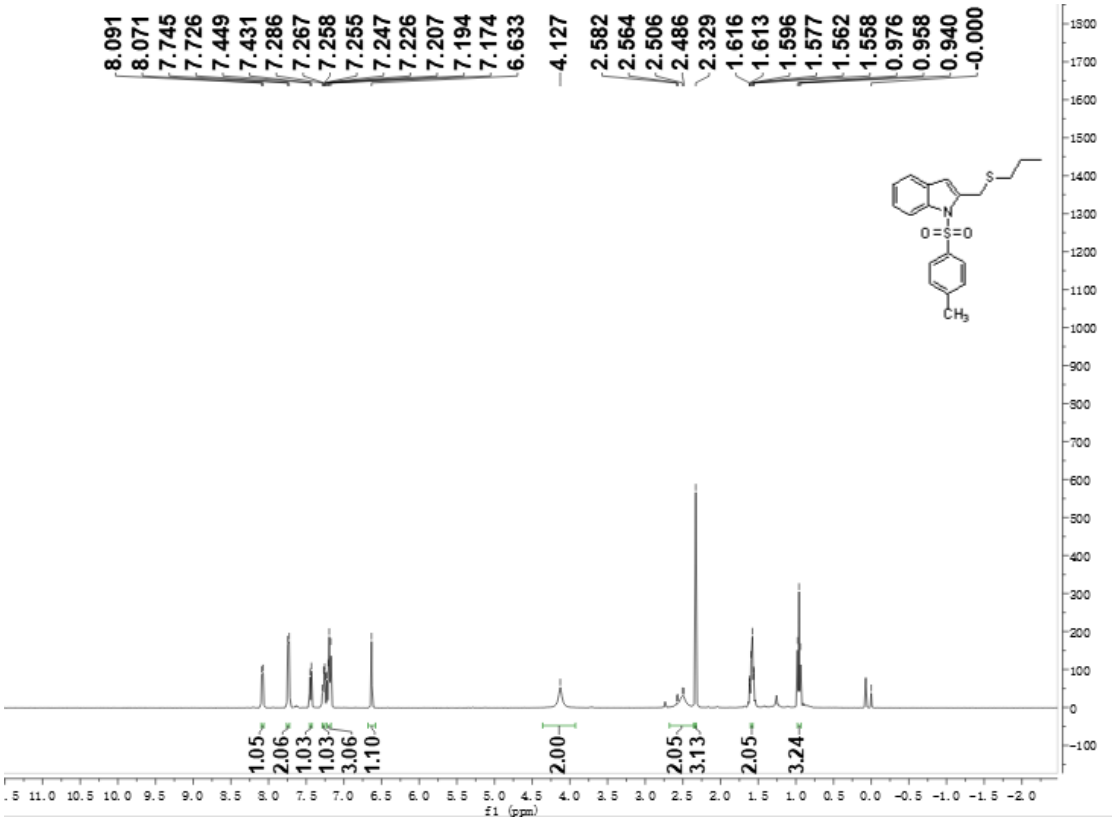
27.91
26.06
25.85
21.62
f1 (ppm)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8.071
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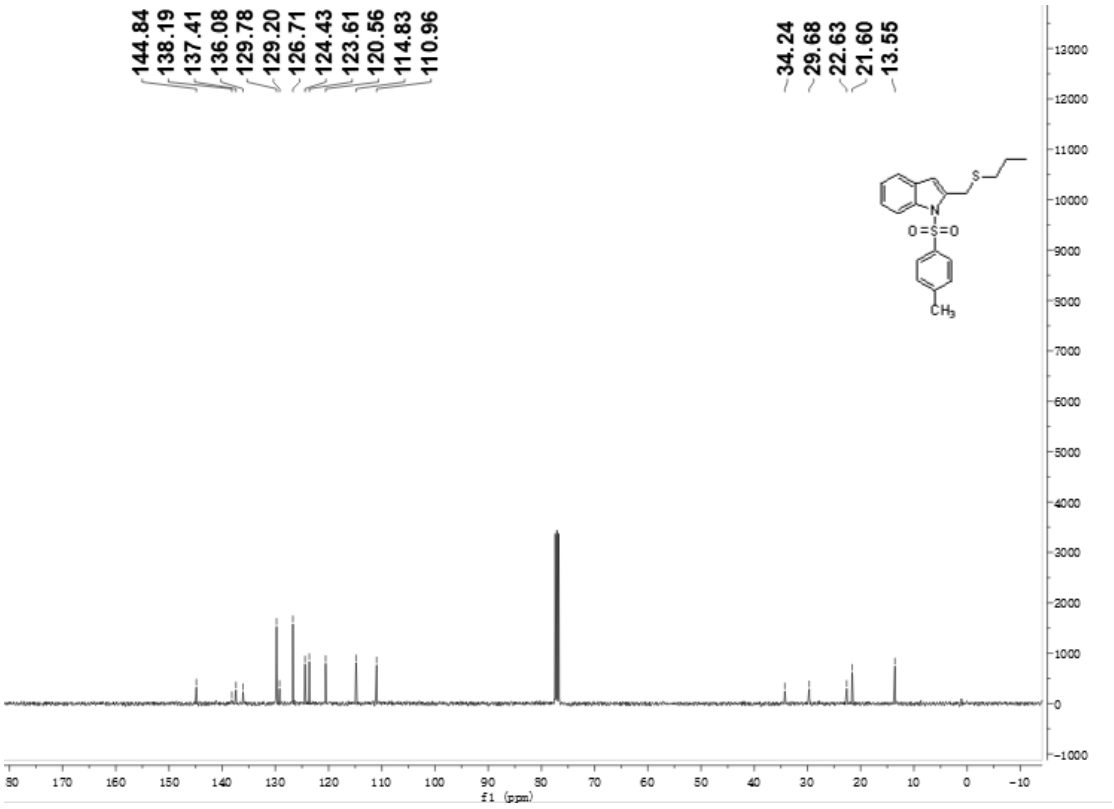
7.726
7.449
7.431
7.286
7.267
7.258
7.255
7.247
7.226
7.207
7.194
7.174
6.633
4.127
2.582
2.564
2.506
2.486
2.329
1.616
1.613
1.596
1.577
1.562
1.558
0.976
0.958
0.940
-0.000
1.05
2.06
1.03
1.03
3.06
1.10
2.00
2.05
3.13
2.05
3.24
f1 (ppm)


144.84
138.19
137.41
136.08
129.78
129.20
126.71
124.43
123.61
120.56
114.83
110.96
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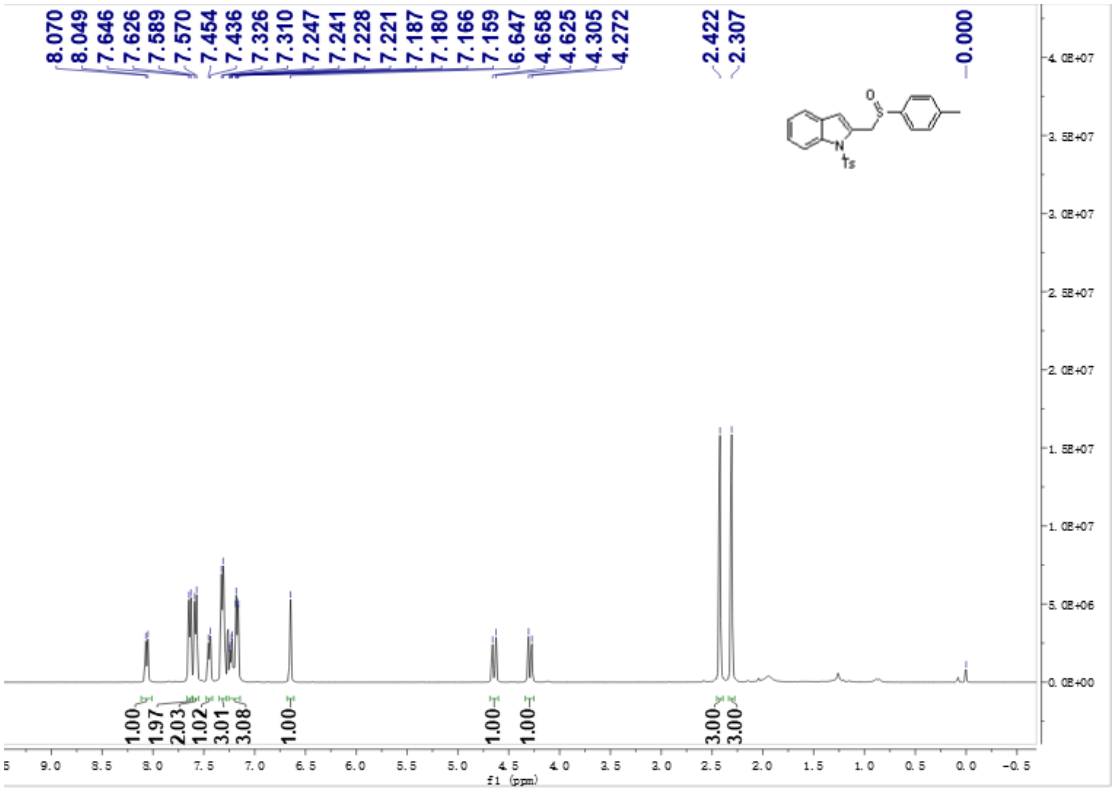
29.68
22.63
21.60
13.55
f1 (ppm)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8.049
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7.570
7.454
7.436
7.326
7.310
7.247
7.241
7.228
7.221
7.187
7.180
7.166
7.159
6.647
4.658
4.625
4.305
4.272
2.422
2.307
0.000
1.00
1.97
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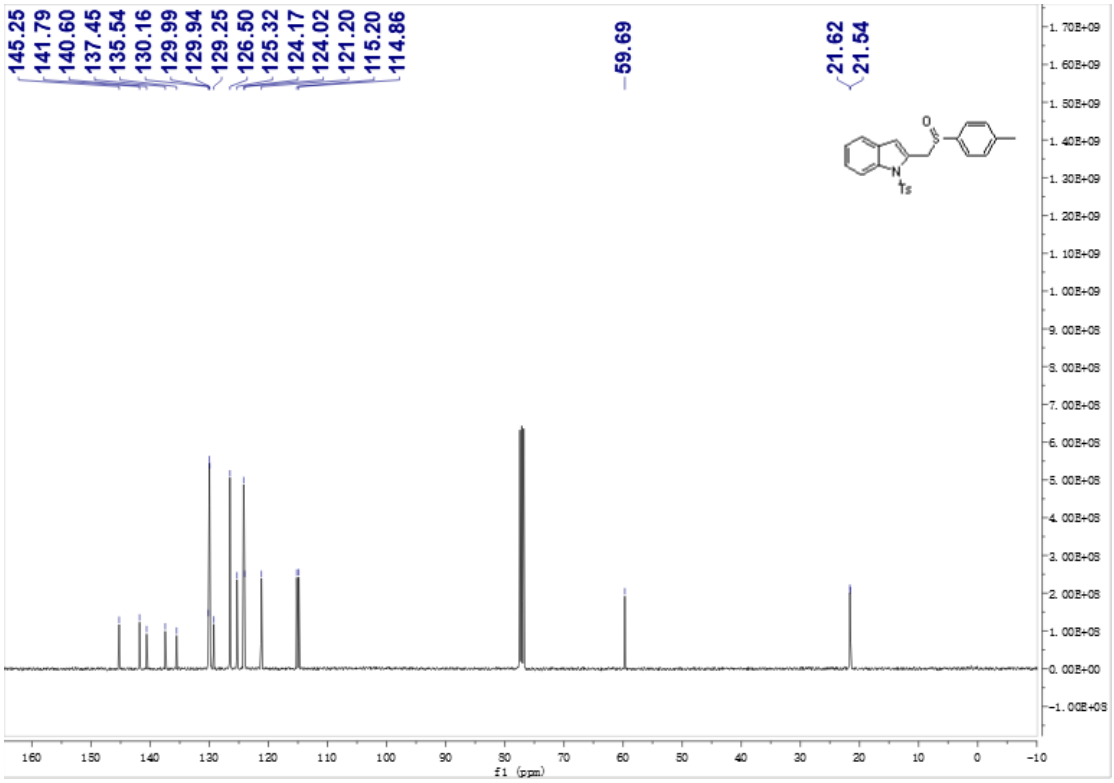
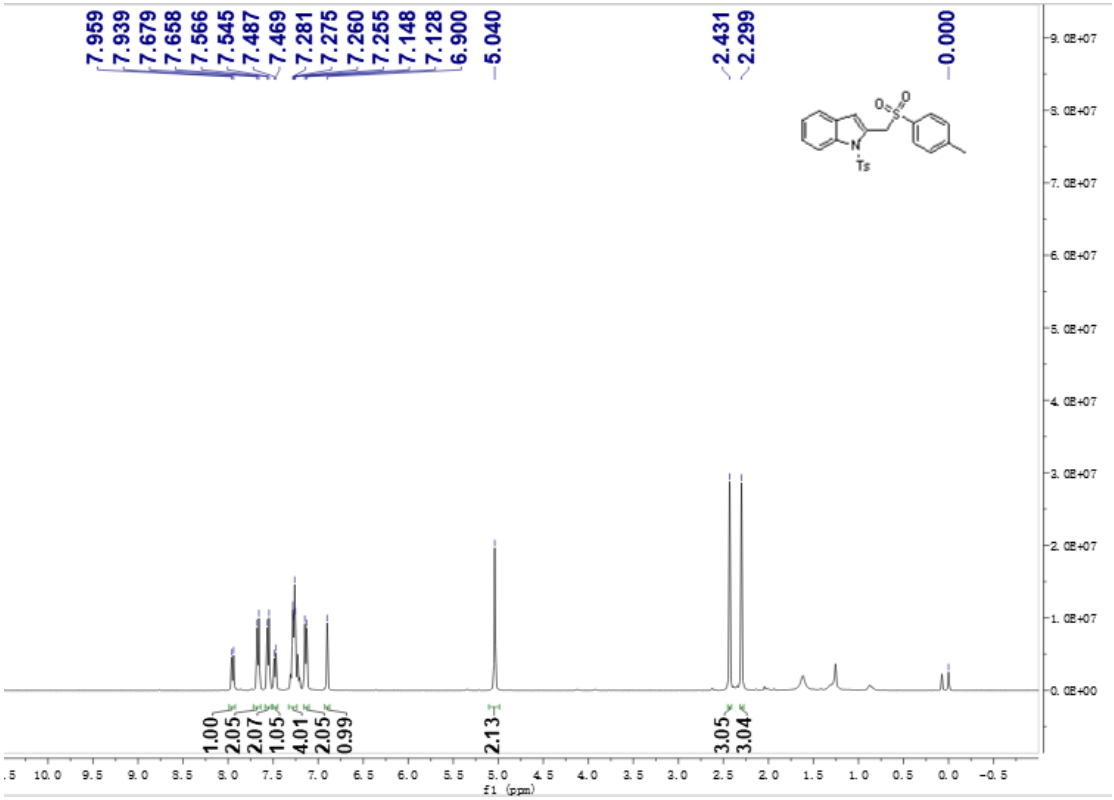
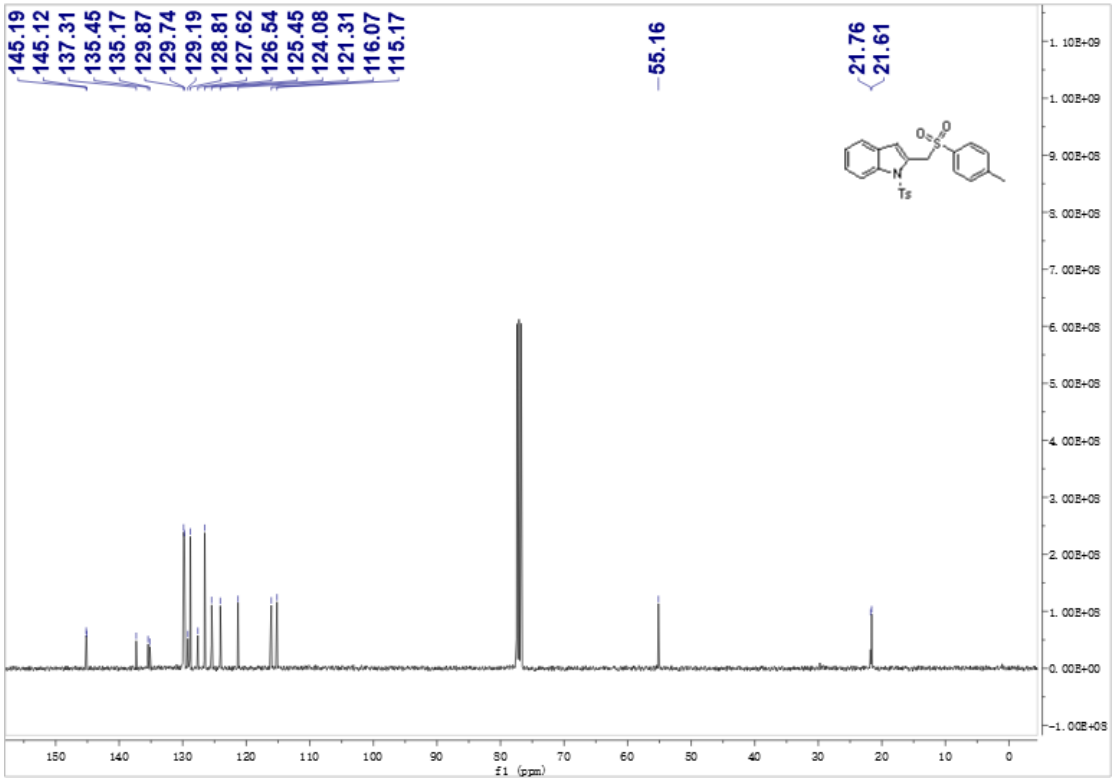
1.02
3.01
3.08
1.00
1.00
1.00
3.00
3.00
f1 (ppm)

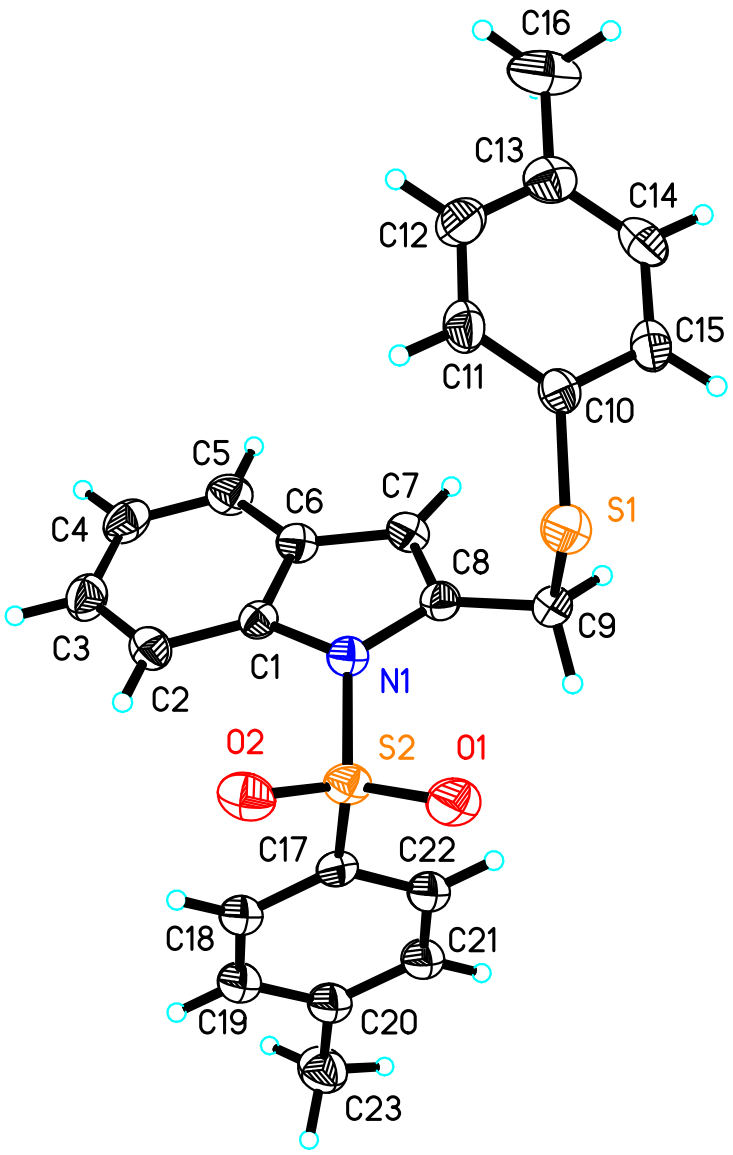

145.25
141.79
140.60
137.45
135.54
130.16
129.99
129.94
129.25
126.50
125.32
124.17
124.02
121.20
115.20
114.86
59.69
21.62
21.54
Ts
f1 (ppm)


7.959
7.939
7.679
7.658
7.566
7.545
7.487
7.469
7.281
7.275
7.260
7.255
7.148
7.128
6.900
5.040
2.431
2.299
0.000
1.00
2.05
2.07
1.05
4.01
2.05
0.99
2.13
3.05
3.04
Ts
f1 (ppm)


145.19
145.12
137.31
135.45
135.17
129.87
129.74
129.19
128.81
127.62
126.54
125.45
124.08
121.31
116.07
115.17
55.16
21.76
21.61
Ts
f1 (ppm)

4. X-ray Data of 3aa

The structure of product **3aa** was confirmed by X-ray diffraction analysis. CCDC 2301526.



Crystal data and structure refinement for **3aa**.

Identification code	mo_d8v21954_0m	
Empirical formula	$C_{23}H_{21}NO_2S_2$	
Formula weight	407.53	
Temperature	213(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 40.4573(14) Å	α = 90°.
	b = 6.1031(2) Å	β=107.8990(10)°.
	c = 17.4802(6) Å	γ = 90°.
Volume	4107.2(2) $Å^3$	
Z	8	
Density (calculated)	1.318 Mg/m^3	
Absorption coefficient	0.278 mm^{-1}	
F(000)	1712	
Crystal size	0.200 x 0.140 x 0.090 mm	
Theta range for data collection	3.362 to 25.499°.	
Index ranges	-48<=h<=48, -7<=k<=7, -21<=l<=21	
Reflections collected	27272	
Independent reflections	3798 [R(int) = 0.0721]	
Completeness to theta = 25.242°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5339	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3798 / 214 / 296	
Goodness-of-fit on F^2	1.142	
Final R indices [I>2sigma(I)]	R1 = 0.0966, wR2 = 0.2288	
R indices (all data)	R1 = 0.1023, wR2 = 0.2320	
Extinction coefficient	0.0090(12)	
Largest diff. peak and hole	0.489 and -0.446 $e.Å^{-3}$	