

# Supporting Information

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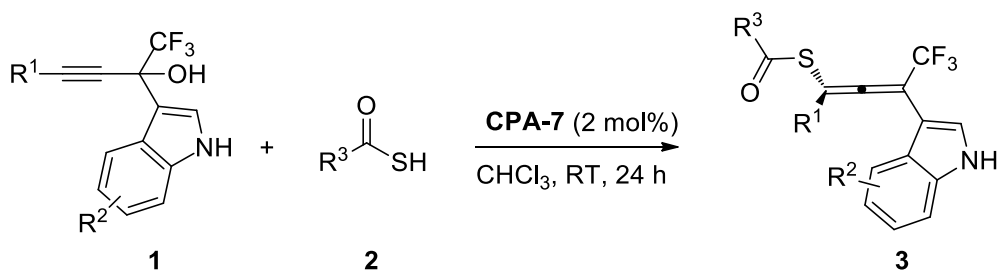
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## A: General Information and Starting Materials

**General Information.** Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra, carbon nuclear magnetic resonance ( $^{13}\text{C}$  NMR) spectra and fluorine nuclear magnetic resonance ( $^{19}\text{F}$  NMR) spectra were recorded on a Bruker ACF300 spectrometer (500 MHz, 126 MHz and 471 MHz). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ( $\text{CDCl}_3$ :  $\delta$  7.26;  $\text{DMSO-}d_6$ :  $\delta$  2.50). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ( $\text{CDCl}_3$ :  $\delta$  77.0;  $\text{DMSO-}d_6$ :  $\delta$  39.50). Data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz). All high resolution mass spectra were obtained on a Finnigan/MAT 95XL-T mass spectrometer. For thin layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. Flash chromatography separations were performed on Merck 60 (0.040-0.063 mm) mesh silica gel.

**Starting Materials.** All solvents, inorganic reagents were from commercial sources and used without purification unless otherwise noted.  $\alpha$ -indolyl propargylic alcohols were prepared following the literature procedures.<sup>1-2</sup>

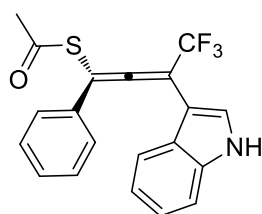
## B: General Procedure



To a solution of  $\text{CHCl}_3$  (0.3 mL) were added  $\alpha$ -indolyl propargylic alcohols **1** (0.05 mmol), thiolacetic acid **2** (0.06 mmol) and CPA-7 (0.001 mmol). The reaction mixture was stirred at room temperature for 24 h and then the solvent was removed under vacuum. The residue was purified by silica gel chromatography to yield the desired product **3**.

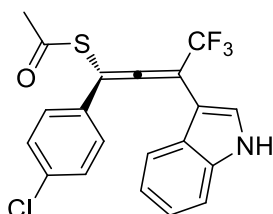
## C: Characterization Data

### (*S,S*)-(4,4,4-trifluoro-3-(1*H*-indol-3-yl)-1-phenylbuta-1,2-dien-1-yl) ethanethioate (3aa)



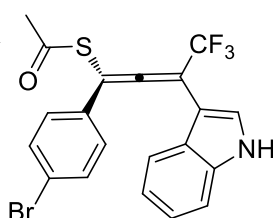
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 50:1. Brown oil, 17.7 mg, 95% yield.  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz):  $\delta$  (ppm) 11.74 (s, 1H), 7.61-7.59 (m, 2H), 7.52-7.50 (m, 2H), 7.44-7.38 (m, 3H), 7.35-7.31 (m, 1H), 7.15-7.11 (m, 1H), 6.98-6.95 (m, 1H), 2.44 (s, 3H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 126 MHz):  $\delta$  (ppm) 207.6, 192.0, 136.9, 133.0, 129.6, 127.1, 126.2, 126.1, 125.2, 122.0 (q,  $J = 270.0$  Hz), 122.2, 112.8, 105.5, 100.5, 99.5 (q,  $J = 43.8$  Hz), 30.8.  $^{19}\text{F}$  NMR (DMSO- $d_6$ , 471 MHz):  $\delta$  (ppm) -60.16. HRMS (ESI): exact mass calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{20}\text{H}_{15}\text{F}_3\text{NOS}$ ) requires  $m/z$  374.0821, found  $m/z$  374.08020. The enantiomeric excess was determined to be 92% by HPLC. [OD column, 254 nm, *n*-hexane:IPA = 90:10, 1.0 mL/min]: 8.2 min (minor), 10.3 min (major).  $[\alpha]_D^{22} = +28.4$  ( $c = 1.00$ ,  $\text{CH}_2\text{Cl}_2$ ).

### (*S,S*)-(1-(4-chlorophenyl)-4,4,4-trifluoro-3-(1*H*-indol-3-yl)buta-1,2-dien-1-yl) ethanethioate (3ba)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 50:1. Brown oil, 17.3 mg, 85% yield.  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz):  $\delta$  (ppm) 11.83 (s, 1H), 7.67 (s, 1H), 7.64-7.62 (d,  $J = 10.0$  Hz, 1H), 7.59-7.57 (m, 2H), 7.54-7.52 (m, 2H), 7.51-7.49 (m, 1H), 7.22-7.18 (m, 1H), 7.06-7.02 (m, 1H), 2.51 (s, 3H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 126 MHz):  $\delta$  207.8, 191.9, 136.9, 134.3, 132.1, 129.7, 128.8, 126.4, 126.3, 124.8, 122.1 (q,  $J = 263.8$  Hz), 122.0, 112.8, 104.7, 100.4, 100.2, 99.9 (q,  $J = 43.8$  Hz), 30.8.  $^{19}\text{F}$  NMR (DMSO- $d_6$ , 471 MHz):  $\delta$  (ppm) -60.12. HRMS (ESI): exact mass calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{20}\text{H}_{14}\text{ClF}_3\text{NOS}$ ) requires  $m/z$  408.0431, found  $m/z$  408.0431. The enantiomeric excess was determined to be 90% by HPLC. [IA column, 254 nm, *n*-hexane:EtOH = 95:5, 1.0 mL/min]: 9.2 min (minor), 8.4 min (major).  $[\alpha]_D^{22} = +32.2$  ( $c = 1.00$ ,  $\text{CH}_2\text{Cl}_2$ ).

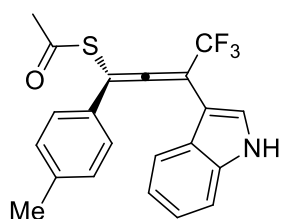
### (*S,S*)-(1-(4-bromophenyl)-4,4,4-trifluoro-3-(1*H*-indol-3-yl)buta-1,2-dien-1-yl) ethanethioate (3ca)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 50:1. Brown oil, 18.7 mg, 83% yield.  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz):  $\delta$  (ppm) 11.83 (s, 1H), 7.68-7.62 (m, 4H), 7.52-7.49 (m, 3H), 7.22-7.18 (m, 1H), 7.06-7.02 (m, 1H), 2.51 (s, 3H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 126 MHz): 207.8, 191.9, 136.9, 132.6, 132.5, 129.1, 126.4, 126.3, 124.8, 123.0, 122.1 (q,  $J = 263.8$  Hz), 121.0, 112.8, 104.9, 100.16, 99.9 (q,  $J = 43.8$  Hz), 30.8.  $^{19}\text{F}$

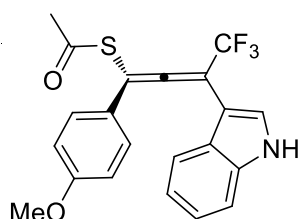
NMR (DMSO-*d*<sub>6</sub>, 471 MHz):  $\delta$  (ppm) -60.12. HRMS (ESI): exact mass calculated for  $[M+H]^+$  (C<sub>20</sub>H<sub>14</sub>BrF<sub>3</sub>NOS) requires  $m/z$  451.9926, found  $m/z$  451.9922. The enantiomeric excess was determined to be 92% by HPLC. [IA column, 254 nm, *n*-hexane:EtOH = 95:5, 1.0 mL/min]: 9.5 min (minor), 8.6 min (major).  $[\alpha]_D^{22} = +32.5$  ( $c = 1.00$ , CH<sub>2</sub>Cl<sub>2</sub>).

**(*S,S*)-(4,4,4-trifluoro-3-(1*H*-indol-3-yl)-1-(*p*-tolyl)buta-1,2-dien-1-yl)ethanethioate (3da)**



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 50:1. Brown oil, 17.6 mg, 91% yield. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz):  $\delta$  (ppm) 11.78 (s, 1H), 7.68-7.65 (m, 2H), 7.50-7.45 (m, 3H), 7.27-7.25 (d,  $J = 10.0$  Hz, 2H), 7.21-7.17 (m, 1H), 7.04-7.01 (m, 1H), 2.49 (s, 3H), 2.31 (s, 3H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 126 MHz):  $\delta$  (ppm) 207.2, 192.0, 139.4, 136.9, 130.2, 130.1, 127.0, 126.0, 126.0, 124.9, 122.2, 122.0 (q,  $J = 271.3$  Hz), 119.3, 112.7, 105.4, 100.7, 99.4 (q,  $J = 43.8$  Hz), 30.8, 21.2. <sup>19</sup>F NMR (DMSO-*d*<sub>6</sub>, 471 MHz):  $\delta$  (ppm) -60.20. HRMS (ESI): exact mass calculated for  $[M+H]^+$  (C<sub>21</sub>H<sub>17</sub>F<sub>3</sub>NOS) requires  $m/z$  388.0977, found  $m/z$  388.0975. The enantiomeric excess was determined to be 91% by HPLC. [OD column, 254 nm, *n*-hexane:IPA = 95:5, 1.0 mL/min]: 7.3 min (minor), 8.1 min (major).  $[\alpha]_D^{22} = +119.1$  ( $c = 1.00$ , CH<sub>2</sub>Cl<sub>2</sub>).

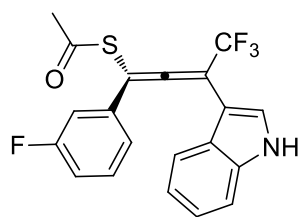
**(*S,S*)-(4,4,4-trifluoro-3-(1*H*-indol-3-yl)-1-(4-methoxyphenyl)buta-1,2-dien-1-yl)ethanethioate (3ea)**



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 20:1. Brown oil, 19.8 mg, 98% yield. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz):  $\delta$  (ppm) 11.77 (s, 1H), 7.68-7.64 (m, 2H), 7.50-7.48 (d,  $J = 10.0$  Hz, 3H), 7.21-7.17 (m, 1H), 7.05-7.01 (m, 3H), 3.78 (s, 3H), 2.49 (s, 3H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 126 MHz):  $\delta$  (ppm) 206.8, 192.0, 160.5, 136.9, 128.6, 126.0, 125.9, 125.2, 122.2, 122.1 (q,  $J = 270.0$  Hz), 115.1, 112.7, 105.1, 100.9, 99.2 (q,  $J = 43.8$  Hz), 55.8, 30.8. <sup>19</sup>F NMR (DMSO-*d*<sub>6</sub>, 471 MHz):  $\delta$  (ppm) -60.23. HRMS (ESI): exact mass calculated for  $[M+H]^+$  (C<sub>21</sub>H<sub>17</sub>F<sub>3</sub>NO<sub>2</sub>S) requires  $m/z$  404.0927, found  $m/z$  404.0925. The enantiomeric excess was determined to be 90% by HPLC. [OD column, 254 nm, *n*-hexane:IPA = 90:10, 1.0 mL/min]: 10.6 min (minor), 11.6 min (major).  $[\alpha]_D^{22} = +139.9$  ( $c = 1.00$ , CH<sub>2</sub>Cl<sub>2</sub>).

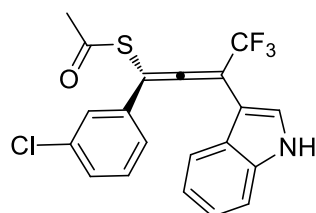
**(*S,S*)-(4,4,4-trifluoro-1-(3-fluorophenyl)-3-(1*H*-indol-3-yl)buta-1,2-dien-1-yl)ethanethioate (3fa)**

Eluent for flash column chromatography: petroleum ether/ethyl acetate = 50:1. Brown oil, 18.5 mg, 95% yield. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz):  $\delta$  (ppm) 11.85 (s, 1H), 7.69 (s, 1H), 7.65-7.63 (d,  $J = 10.0$  Hz, 1H), 7.55-7.50 (m, 2H), 7.43-7.41 (m, 1H),



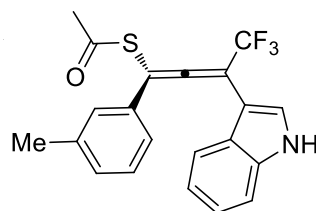
7.36-7.32 (m, 1H), 7.29-7.23 (m, 1H), 7.23-7.19 (m, 1H), 7.07-7.03 (m, 1H) 2.52 (s, 3H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 126 MHz):  $\delta$  (ppm) 208.1, 191.9, 163.0 (d,  $J = 307.4$  Hz), 136.9, 135.9 (d,  $J = 8.8$  Hz), 131.7 (d,  $J = 8.8$  Hz), 126.5, 126.4, 124.8, 123.4, 123.3, 122.1 (q,  $J = 263.8$  Hz), 122.0, 116.5 (d,  $J = 26.3$  Hz), 113.7 (d,  $J = 28.8$  Hz), 112.8, 104.7, 104.6, 100.1, 100.0 (q,  $J = 43.8$  Hz), 30.8.  $^{19}\text{F}$  NMR (DMSO- $d_6$ , 471 MHz):  $\delta$  (ppm) -60.11, -112.15. HRMS (ESI): exact mass calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{20}\text{H}_{14}\text{F}_4\text{NOS}$ ) requires  $m/z$  392.0727, found  $m/z$  392.0725. The enantiomeric excess was determined to be 88% by HPLC. [OD column, 254 nm,  $n$ -hexane:IPA = 90:10, 1.0 mL/min]: 7.7 min (minor), 8.7 min (major).  $[\alpha]_D^{22} = +61.5$  ( $c = 1.00$ ,  $\text{CH}_2\text{Cl}_2$ ).

**(S)-S-(1-(3-chlorophenyl)-4,4,4-trifluoro-3-(1H-indol-3-yl)buta-1,2-dien-1-yl)ethanethioate (3ga)**



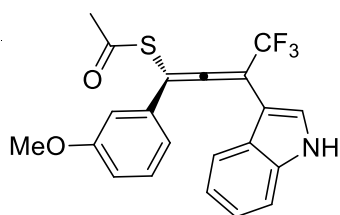
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 50:1. Brown oil, 17.3 mg, 85% yield.  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz):  $\delta$  (ppm) 11.86 (s, 1H), 7.69 (s, 1H), 7.65-7.63 (d,  $J = 10.0$  Hz, 1H), 7.54-7.49 (m, 5H), 7.23-7.19 (m, 1H), 7.08-7.04 (m, 1H), 2.53 (s, 3H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 126 MHz):  $\delta$  (ppm) 208.1, 191.9, 172.5, 136.9, 135.6, 134.4, 131.6, 129.5, 126.5, 126.4, 125.9, 124.8, 122.1 (q,  $J = 263.8$  Hz), 122.0, 112.9, 104.5, 100.1 (q,  $J = 43.8$  Hz), 100.0, 30.8.  $^{19}\text{F}$  NMR (DMSO- $d_6$ , 471 MHz):  $\delta$  (ppm) -60.08. HRMS (ESI): exact mass calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{20}\text{H}_{14}\text{ClF}_3\text{NOS}$ ) requires  $m/z$  408.0431, found  $m/z$  408.0429. The enantiomeric excess was determined to be 86% by HPLC. [OD column, 254 nm,  $n$ -hexane:IPA = 90:10, 1.0 mL/min]: 7.8 min (minor), 8.4 min (major).  $[\alpha]_D^{22} = +145.5$  ( $c = 1.00$ ,  $\text{CH}_2\text{Cl}_2$ ).

**(S)-S-(4,4,4-trifluoro-3-(1H-indol-3-yl)-1-(*m*-tolyl)buta-1,2-dien-1-yl)ethanethioate (3ha)**



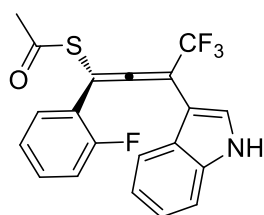
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 50:1. Brown oil, 18.8 mg, 97% yield.  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz):  $\delta$  (ppm) 11.80 (s, 1H), 7.68-7.66 (m, 2H), 7.51-7.49 (d,  $J = 10.0$  Hz, 1H), 7.38-7.32 (m, 3H), 7.22-7.17 (m, 2H), 7.06-7.02 (m, 1H), 2.50 (s, 3H), 2.32 (s, 3H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 126 MHz):  $\delta$  (ppm) 207.6, 192.0, 139.0, 137.0, 133.1, 130.4, 129.6, 127.5, 126.2, 124.5, 124.4, 122.7, 122.0 (q,  $J = 263.8$  Hz), 112.8, 105.5, 100.6, 99.4 (q,  $J = 28.8$  Hz), 30.9, 21.5.  $^{19}\text{F}$  NMR (DMSO- $d_6$ , 471 MHz):  $\delta$  (ppm) -60.05. HRMS (ESI): exact mass calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{21}\text{H}_{17}\text{F}_3\text{NOS}$ ) requires  $m/z$  388.0977, found  $m/z$  388.0975. The enantiomeric excess was determined to be 91% by HPLC. [OD column, 254 nm,  $n$ -hexane:IPA = 95:5, 1.0 mL/min]: 11.3 min (minor), 12.9 min (major).  $[\alpha]_D^{22} = +109.7$  ( $c = 1.00$ ,  $\text{CH}_2\text{Cl}_2$ ).

**(S)-S-(4,4,4-trifluoro-3-(1H-indol-3-yl)-1-(3-methoxyphenyl)buta-1,2-dien-1-yl)ethanethioate (3ia)**



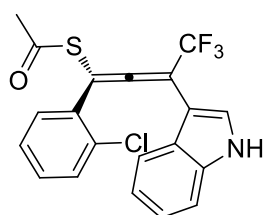
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 20:1. Brown oil, 18.1 mg, 90% yield.  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz):  $\delta$  (ppm) 11.80 (s, 1H), 7.67-7.65 (m, 2H), 7.51-7.49 (d,  $J = 10.0$  Hz, 1H), 7.41-7.37 (m, 1H), 7.21-7.14 (m, 2H), 7.06-6.99 (m, 3H), 3.75 (s, 3H), 2.50 (s, 3H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 126 MHz):  $\delta$  (ppm) 207.7, 191.9, 160.2, 136.9, 134.6, 130.8, 126.2, 126.1, 124.9, 122.1, 122.0 (q,  $J = 268.8$  Hz), 119.5, 114.6, 113.0, 112.8, 105.2, 100.4, 99.5 (q,  $J = 43.8$  Hz), 55.7, 30.8.  $^{19}\text{F}$  NMR (DMSO- $d_6$ , 471 MHz):  $\delta$  (ppm) -60.05. HRMS (ESI): exact mass calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{21}\text{H}_{17}\text{F}_3\text{NO}_2\text{S}$ ) requires  $m/z$  404.0927, found  $m/z$  404.0927. The enantiomeric excess was determined to be 89% by HPLC. [OD column, 254 nm, *n*-hexane:IPA = 90:10, 1.0 mL/min]: 9.3 min (minor), 10.5 min (major).  $[\alpha]_{\text{D}}^{22} = +174.8$  ( $c = 1.00$ ,  $\text{CH}_2\text{Cl}_2$ ).

**(S)-S-(4,4,4-trifluoro-1-(2-fluorophenyl)-3-(1H-indol-3-yl)buta-1,2-dien-1-yl)ethanethioate (3ja)**



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 50:1. Brown oil, 15.8 mg, 81% yield.  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz):  $\delta$  (ppm) 11.77 (s, 1H), 7.69-7.61 (m, 3H), 7.49-7.44 (m, 2H), 7.34-7.26 (m, 2H), 7.21-7.17 (m, 1H), 7.06-7.03 (m, 1H), 2.49 (s, 3H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 126 MHz):  $\delta$  (ppm) 210.0, 192.0, 160.0 (d,  $J = 315.0$  Hz), 136.9, 131.7 (d,  $J = 11.3$  Hz), 130.0, 126.1, 126.0, 125.5, 125.4, 124.9, 122.2, 121.9 (q,  $J = 278.8$  Hz), 121.3 (d,  $J = 12.5$  Hz), 116.8 (d,  $J = 26.3$  Hz), 112.7, 100.4, 99.0, 97.5 (q,  $J = 43.8$  Hz), 30.7.  $^{19}\text{F}$  NMR (DMSO- $d_6$ , 471 MHz):  $\delta$  (ppm) -60.33, -111.97. HRMS (ESI): exact mass calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{20}\text{H}_{14}\text{F}_4\text{NOS}$ ) requires  $m/z$  392.0727, found  $m/z$  392.0724. The enantiomeric excess was determined to be 90% by HPLC. [OD column, 254 nm, *n*-hexane:IPA = 90:10, 1.0 mL/min]: 8.8 min (minor), 10.7 min (major).  $[\alpha]_{\text{D}}^{22} = +36.4$  ( $c = 1.00$ ,  $\text{CH}_2\text{Cl}_2$ ).

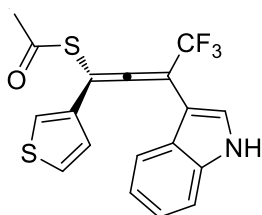
**(S)-S-(1-(2-chlorophenyl)-4,4,4-trifluoro-3-(1H-indol-3-yl)buta-1,2-dien-1-yl)ethanethioate (3ka)**



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 50:1. Brown oil, 17.3 mg, 85% yield.  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz):  $\delta$  (ppm) 11.79 (s, 1H), 7.81-7.79 (d,  $J = 10.0$  Hz, 1H), 7.68-7.65 (m, 1H), 7.61 (s, 1H), 7.55-7.53 (m, 1H), 7.50-7.48 (m, 1H), 7.45-7.41 (m, 2H), 7.23-7.19 (m, 1H), 7.12-7.08 (m, 1H), 2.45 (s, 3H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 126 MHz):  $\delta$  (ppm) 208.3, 191.8, 136.9, 132.7, 132.3, 131.1, 131.0, 130.8, 128.2, 126.3, 126.2, 125.0, 122.2, 121.9 (q,  $J = 265.0$  Hz), 112.8, 102.3, 100.3, 98.2 (q,  $J = 43.8$

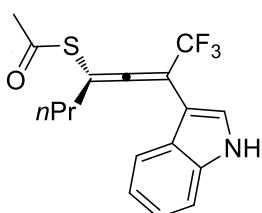
Hz), 30.7.  $^{19}\text{F}$  NMR (DMSO- $d_6$ , 471 MHz):  $\delta$  (ppm) -59.91. HRMS (ESI): exact mass calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{20}\text{H}_{14}\text{ClF}_3\text{NOS}$ ) requires  $m/z$  408.0431, found  $m/z$  408.0430. The enantiomeric excess was determined to be 90% by HPLC. [OD column, 254 nm, *n*-hexane:IPA = 90:10, 1.0 mL/min]: 8.5 min (minor), 9.4 min (major).  $[\alpha]_{\text{D}}^{22} = -4.0$  ( $c = 1.00$ ,  $\text{CH}_2\text{Cl}_2$ ).

**(*S*)-*S*-(4,4,4-trifluoro-3-(1*H*-indol-3-yl)-1-(thiophen-3-yl)buta-1,2-dien-1-yl) ethanethioate (3la)**



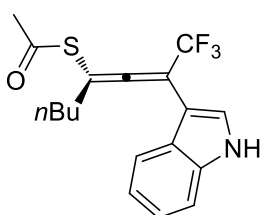
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 50:1. Brown oil, 18.3 mg, 97% yield.  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz):  $\delta$  (ppm) 11.77 (s, 1H), 7.75-7.74 (m, 1H), 7.68-7.64 (m, 3H), 7.50-7.48 (d,  $J = 10.0$  Hz, 1H), 7.21-7.17 (m, 1H), 7.12-7.11 (m, 1H), 7.06-7.02 (m, 1H), 2.50 (s, 3H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 126 MHz):  $\delta$  (ppm) 207.3, 191.8, 136.8, 134.7, 128.8, 126.3, 126.1, 126.0, 125.7, 124.8, 122.0, 121.9 (q,  $J = 272.5$  Hz), 112.7, 100.8, 100.7, 99.1 (q,  $J = 43.8$  Hz), 30.8.  $^{19}\text{F}$  NMR (DMSO- $d_6$ , 471 MHz):  $\delta$  (ppm) -60.15. HRMS (ESI): exact mass calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{18}\text{H}_{12}\text{F}_3\text{NOS}_2$ ) requires  $m/z$  380.0385, found  $m/z$  380.0383. The enantiomeric excess was determined to be 89% by HPLC. [OD column, 254 nm, *n*-hexane:IPA = 95:5, 1.0 mL/min]: 15.6 min (minor), 20.9 min (major).  $[\alpha]_{\text{D}}^{22} = +41.8$  ( $c = 1.00$ ,  $\text{CH}_2\text{Cl}_2$ ).

**(*S*)-*S*-(1,1,1-trifluoro-2-(1*H*-indol-3-yl)hepta-2,3-dien-4-yl) ethanethioate (3ma)**



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 50:1. Yellow oil, 10.1 mg, 60% yield.  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz):  $\delta$  (ppm) 11.68 (s, 1H), 7.74-7.72 (d,  $J = 10.0$  Hz, 1H), 7.54 (s, 1H), 7.49-7.47 (d,  $J = 8.0$  Hz, 1H), 7.22-7.18 (m, 1H), 7.12-7.08 (m, 1H), 2.55-2.47 (m, 2H), 2.43 (s, 3H), 1.56-1.51 (m, 2H), 0.91 (t,  $J = 10.0$  Hz, 3H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 126 MHz):  $\delta$  (ppm) 204.3, 192.8, 136.9, 125.6, 125.5, 125.1, 121.8 (q,  $J = 280.0$  Hz), 122.4, 112.6, 104.8, 101.2, 97.7 (q,  $J = 43.8$  Hz), 36.9, 30.8, 20.9, 13.6.  $^{19}\text{F}$  NMR (DMSO- $d_6$ , 471 MHz):  $\delta$  (ppm) -60.59. HRMS (ESI): exact mass calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{17}\text{H}_{17}\text{F}_3\text{NOS}$ ) requires  $m/z$  340.0977, found  $m/z$  340.0978. The enantiomeric excess was determined to be 77% by HPLC. [OD column, 254 nm, *n*-hexane:IPA = 95:5, 1.0 mL/min]: 9.4 min (minor), 10.3 min (major).  $[\alpha]_{\text{D}}^{22} = -333.0$  ( $c = 1.00$ ,  $\text{CH}_2\text{Cl}_2$ ).

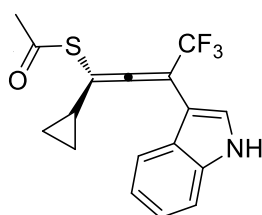
**(*S*)-*S*-(1,1,1-trifluoro-2-(1*H*-indol-3-yl)octa-2,3-dien-4-yl) ethanethioate (3na)**



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 50:1. Yellow oil, 12.4 mg, 70% yield.  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz):  $\delta$  (ppm) 11.67 (s, 1H), 7.73-7.71 (m, 1H), 7.53 (s, 1H), 7.49-7.47 (d,  $J = 10.0$  Hz, 1H), 7.22-7.18 (m, 1H), 7.11-7.07 (m, 1H), 2.57-2.54 (m, 1H), 2.49-2.45 (m, 1H),

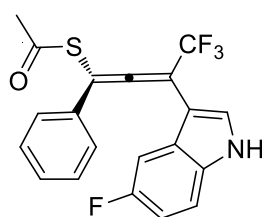
2.42 (s, 3H), 1.51-1.46 (m, 2H), 1.36-1.30 (m, 2H), 0.85-0.81 (t,  $J = 10.0$  Hz, 3H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 126 MHz):  $\delta$  (ppm) 204.2, 192.8, 136.9, 125.6, 125.5, 125.1, 122.4, 121.8 (q,  $J = 282.5$  Hz), 112.6, 104.9, 101.2, 97.8 (q,  $J = 43.8$  Hz), 34.6, 30.8, 29.6, 21.7, 14.0.  $^{19}\text{F}$  NMR (DMSO- $d_6$ , 471 MHz):  $\delta$  (ppm) -60.64. HRMS (ESI): exact mass calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{18}\text{H}_{19}\text{F}_3\text{NOS}$ ) requires  $m/z$  354.1134, found  $m/z$  354.1134. The enantiomeric excess was determined to be 87% by HPLC. [OD column, 254 nm,  $n$ -hexane:IPA = 98:2, 0.5 mL/min]: 27.4 min (minor), 30.2 min (major).  $[\alpha]_{\text{D}}^{22} = -286.6$  ( $c = 1.00$ ,  $\text{CH}_2\text{Cl}_2$ ).

**(S)-S-(1-cyclopropyl-4,4,4-trifluoro-3-(1H-indol-3-yl)buta-1,2-dien-1-yl)ethanethioate (30a)**



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 50:1. Brown oil, 13.4 mg, 80% yield.  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz):  $\delta$  (ppm) 11.69 (s, 1H), 7.73-7.71 (d,  $J = 10.0$  Hz, 1H), 7.54 (s, 1H), 7.50-7.48 (m, 1H), 7.23-7.19 (m, 1H), 7.13-7.10 (m, 1H), 2.44 (s, 3H), 1.81-1.77 (m, 1H), 0.92-0.90 (m, 2H), 0.63-0.51 (m, 2H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 126 MHz):  $\delta$  (ppm) 204.0, 192.4, 136.8, 125.6, 125.5, 124.9, 122.2, 121.8 (q,  $J = 282.5$  Hz), 112.6, 107.7, 101.3, 98.5 (q,  $J = 43.8$  Hz), 30.7, 15.2, 8.2, 7.4.  $^{19}\text{F}$  NMR (DMSO- $d_6$ , 471 MHz):  $\delta$  (ppm) -60.63. HRMS (ESI): exact mass calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{17}\text{H}_{15}\text{F}_3\text{NOS}$ ) requires  $m/z$  338.0821, found  $m/z$  338.0819. The enantiomeric excess was determined to be 80% by HPLC. [OD column, 254 nm,  $n$ -hexane:IPA = 95:5, 1.0 mL/min]: 12.2 min (minor), 14.2 min (major).  $[\alpha]_{\text{D}}^{22} = -336.7$  ( $c = 1.00$ ,  $\text{CH}_2\text{Cl}_2$ ).

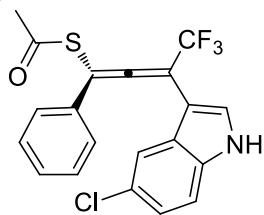
**(S)-S-(4,4,4-trifluoro-3-(5-fluoro-1H-indol-3-yl)-1-phenylbuta-1,2-dien-1-yl)ethanethioate (3pa)**



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 50:1. Brown oil, 17.6 mg, 90% yield.  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz):  $\delta$  (ppm) 11.92 (s, 1H), 7.74 (s, 1H), 7.59-7.57 (m, 2H), 7.53-7.46 (m, 3H), 7.43-7.36 (m, 2H), 7.08-7.03 (m, 1H), 2.51 (s, 3H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 126 MHz):  $\delta$  (ppm) 207.3, 192.0, 158.1 (d,  $J = 195.3$  Hz), 133.6, 132.9, 129.8, 129.7, 128.1, 127.1, 125.5 (d,  $J = 8.8$  Hz), 123.5 (q,  $J = 230.6$  Hz), 114.0 (d,  $J = 7.5$  Hz), 111.4 (d,  $J = 21.3$  Hz), 105.9, 104.3 (d,  $J = 20.2$  Hz), 100.7, 99.3 (q,  $J = 43.8$  Hz), 30.9.  $^{19}\text{F}$  NMR (DMSO- $d_6$ , 471 MHz):  $\delta$  (ppm) -60.22, -122.08. HRMS (ESI): exact mass calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{20}\text{H}_{14}\text{F}_4\text{NOS}$ ) requires  $m/z$  392.0727, found  $m/z$  392.0724. The enantiomeric excess was determined to be 90% by HPLC. [AS column, 254 nm,  $n$ -hexane:IPA = 95:5, 0.8 mL/min]: 18.9 min (minor), 21.1 min (major).  $[\alpha]_{\text{D}}^{22} = +95.8$  ( $c = 1.00$ ,  $\text{CH}_2\text{Cl}_2$ ).

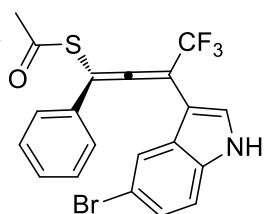
**(S)-S-(3-(5-chloro-1H-indol-3-yl)-4,4,4-trifluoro-1-phenylbuta-1,2-dien-1-yl)ethanethioate (3qa)**





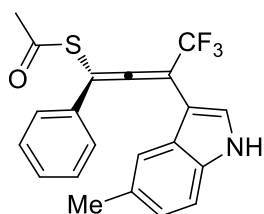
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 50:1. Yellow solid, 15.7 mg, 77% yield.  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz):  $\delta$  (ppm) 11.98 (s, 1H), 7.74 (s, 1H), 7.62 (s, 1H), 7.58-7.55 (m, 2H), 7.52-7.46 (m, 3H), 7.44-7.40 (m, 1H), 7.22-7.19 (m, 1H), 2.52 (s, 3H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 126 MHz):  $\delta$  (ppm) 207.4, 191.8, 135.4, 132.8, 129.9, 129.8, 127.8, 127.1, 126.3, 124.3, 122.5, 120.9 (q,  $J$  = 308.8 Hz), 114.4, 105.9, 100.4, 99.0 (q,  $J$  = 30.0 Hz), 30.9.  $^{19}\text{F}$  NMR (DMSO- $d_6$ , 471 MHz):  $\delta$  (ppm) -60.31. HRMS (ESI): exact mass calculated for  $[\text{M}-\text{H}]^-$  ( $\text{C}_{20}\text{H}_{12}\text{ClF}_3\text{NOS}$ ) requires  $m/z$  406.0275, found  $m/z$  406.0286. The enantiomeric excess was determined to be 86% by HPLC. [AS column, 254 nm, *n*-hexane:IPA = 95:5, 1.0 mL/min]: 14.9 min (minor), 18.5 min (major).  $[\alpha]_{\text{D}}^{22} = +219.1$  ( $c$  = 1.00,  $\text{CH}_2\text{Cl}_2$ ).

**(S)-S-(3-(5-bromo-1H-indol-3-yl)-4,4,4-trifluoro-1-phenylbuta-1,2-dien-1-yl) ethanethioate (3ra)**



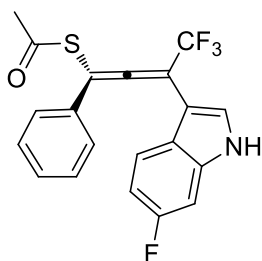
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 50:1. Yellow solid, 18.0 mg, 80% yield. mp 100.7-102.5 °C.  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz):  $\delta$  (ppm) 11.99 (s, 1H), 7.76-7.72 (m, 2H), 7.57-7.55 (d,  $J$  = 10.0 Hz, 2H), 7.50-7.46 (m, 3H), 7.43-7.39 (m, 1H), 7.33-7.30 (m, 1H), 2.52 (s, 3H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 126 MHz):  $\delta$  (ppm) 207.4, 191.7, 135.7, 129.8, 128.4 (q,  $J$  = 330.1 Hz), 127.6, 127.0, 124.3, 122.5, 121.6, 114.8, 113.6, 105.9, 100.4, 99.0 (q,  $J$  = 28.8 Hz), 30.9.  $^{19}\text{F}$  NMR (DMSO- $d_6$ , 471 MHz):  $\delta$  (ppm) -60.35. HRMS (ESI): exact mass calculated for  $[\text{M}-\text{H}]^-$  ( $\text{C}_{20}\text{H}_{12}\text{BrF}_3\text{NOS}$ ) requires  $m/z$  449.9770, found  $m/z$  449.9782. The enantiomeric excess was determined to be 90% by HPLC. [AS column, 254 nm, *n*-hexane:IPA = 95:5, 1.0 mL/min]: 15.4 min (minor), 20.3 min (major).  $[\alpha]_{\text{D}}^{22} = +255.2$  ( $c$  = 1.00,  $\text{CH}_2\text{Cl}_2$ ).

**(S)-S-(4,4,4-trifluoro-3-(5-methyl-1H-indol-3-yl)-1-phenylbuta-1,2-dien-1-yl) ethanethioate (3sa)**



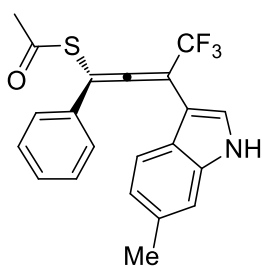
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 50:1. Yellow solid, 16.6 mg, 86% yield. mp 129.1-131.0 °C.  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz):  $\delta$  (ppm) 11.66 (s, 1H), 7.59-7.55 (m, 3H), 7.49-7.45 (m, 3H), 7.42-7.36 (m, 2H), 7.03-7.00 (m, 1H), 2.51 (s, 3H), 2.27 (s, 3H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 126 MHz):  $\delta$  (ppm) 207.7, 192.1, 135.2, 133.3, 129.6, 129.5, 127.1, 126.1, 126.0, 124.9, 122.3 (q,  $J$  = 285.0 Hz) 122.2, 112.4, 105.5, 99.9, 99.5 (q,  $J$  = 42.5 Hz), 30.8, 21.6.  $^{19}\text{F}$  NMR (DMSO- $d_6$ , 471 MHz):  $\delta$  (ppm) -60.14. HRMS (ESI): exact mass calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{21}\text{H}_{17}\text{F}_3\text{NOS}$ ) requires  $m/z$  388.0977, found  $m/z$  388.0976. The enantiomeric excess was determined to be 88% by HPLC. [AS column, 254 nm, *n*-hexane:IPA = 97:3, 0.5 mL/min]: 30.1 min (minor), 31.9 min (major).  $[\alpha]_{\text{D}}^{22} = +182.8$  ( $c$  = 1.00,  $\text{CH}_2\text{Cl}_2$ ).

**(S)-S-(4,4,4-trifluoro-3-(6-fluoro-1H-indol-3-yl)-1-phenylbuta-1,2-dien-1-yl)ethanethioate (3ta)**



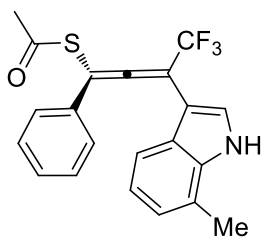
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 50:1. Yellow oil, 15.6 mg, 80% yield.  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz):  $\delta$  (ppm) 11.85 (s, 1H), 7.67-7.62 (m, 2H), 7.58-7.56 (m, 2H), 7.49-7.38 (m, 3H), 7.30-7.27 (m, 1H), 6.94-6.89 (m, 1H), 2.51 (s, 3H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 126 MHz):  $\delta$  (ppm) 207.4, 192.0, 159.9 (d,  $J = 197.8$  Hz), 137.1 (d,  $J = 10.0$  Hz), 132.8, 129.8, 129.7, 127.2, 126.9, 123.5 (q,  $J = 228.8$  Hz), 122.0, 120.4 (d,  $J = 7.0$  Hz), 109.5 (d,  $J = 20.0$  Hz), 105.7, 100.8, 98.9 (q,  $J = 28.8$  Hz), 30.9.  $^{19}\text{F}$  NMR (DMSO- $d_6$ , 471 MHz):  $\delta$  (ppm) -60.16, -119.83. HRMS (ESI): exact mass calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{20}\text{H}_{14}\text{F}_4\text{NOS}$ ) requires  $m/z$  392.0727, found  $m/z$  392.0727. The enantiomeric excess was determined to be 89% by HPLC. [IA column, 254 nm, *n*-hexane:IPA = 97:3, 0.5 mL/min]: 26.8 min (minor), 27.9 min (major).  $[\alpha]_D^{22} = +117.4$  ( $c = 1.00$ ,  $\text{CH}_2\text{Cl}_2$ ).

**(S)-S-(4,4,4-trifluoro-3-(6-methyl-1H-indol-3-yl)-1-phenylbuta-1,2-dien-1-yl)ethanethioate (3ua)**



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 50:1. Yellow oil, 16.6 mg, 86% yield.  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz):  $\delta$  (ppm) 11.64 (s, 1H), 7.57-7.53 (m, 4H), 7.48-7.44 (m, 2H), 7.42-7.38 (m, 1H), 7.27 (s, 1H), 6.87-6.85 (m, 1H), 2.50 (s, 3H), 2.37 (s, 3H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 126 MHz):  $\delta$  (ppm) 207.6, 192.0, 137.4, 133.1, 132.4, 129.6, 129.6, 127.6, 127.1, 125.5, 125.4, 122.2, 121.9 (q,  $J = 232.5$  Hz), 112.4, 105.4, 100.3, 99.6 (q,  $J = 43.8$  Hz), 30.8, 21.7.  $^{19}\text{F}$  NMR (DMSO- $d_6$ , 471 MHz):  $\delta$  (ppm) -60.02. HRMS (ESI): exact mass calculated for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{21}\text{H}_{17}\text{F}_3\text{NOS}$ ) requires  $m/z$  388.0977, found  $m/z$  388.0977. The enantiomeric excess was determined to be 90% by HPLC. [AS column, 254 nm, *n*-hexane:IPA = 95:5, 1.0 mL/min]: 12.8 min (minor), 13.6 min (major).  $[\alpha]_D^{22} = +93.2$  ( $c = 1.00$ ,  $\text{CH}_2\text{Cl}_2$ ).

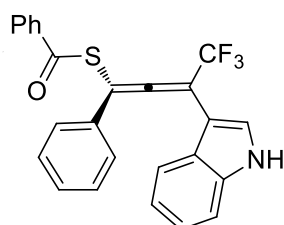
**(S)-S-(4,4,4-trifluoro-3-(7-methyl-1H-indol-3-yl)-1-phenylbuta-1,2-dien-1-yl)ethanethioate (3va)**



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 50:1. Yellow oil, 16.1 mg, 83% yield.  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz):  $\delta$  (ppm) 11.80 (s, 1H), 7.61-7.56 (m, 3H), 7.50-7.44 (m, 3H), 7.41-7.37 (m, 1H), 7.00-6.92 (m, 2H), 2.50 (s, 6H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 126 MHz):  $\delta$  (ppm) 207.7, 192.0, 136.4, 133.1, 129.7, 127.6, 127.1, 125.0, 124.5, 122.7, 122.4 (q,  $J = 260.0$  Hz), 122.1, 105.5, 101.0, 99.6 (q,  $J = 28.8$  Hz) 30.9, 17.2.  $^{19}\text{F}$  NMR (DMSO- $d_6$ , 471 MHz):  $\delta$  (ppm) -60.03. HRMS (ESI): exact mass calculated for

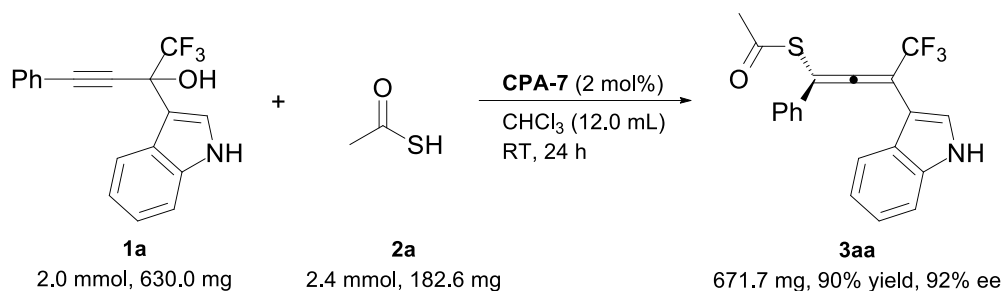
$[M+H]^+$  ( $C_{21}H_{17}F_3NOS$ ) requires  $m/z$  388.0977, found  $m/z$  388.0976. The enantiomeric excess was determined to be 91% by HPLC. [IA column, 254 nm, *n*-hexane:IPA = 95:5, 1.0 mL/min]: 15.6 min (minor), 12.9 min (major).  $[\alpha]_D^{22} = +57.1$  ( $c = 1.00$ ,  $CH_2Cl_2$ ).

**(S)-S-(4,4,4-trifluoro-3-(1*H*-indol-3-yl)-1-phenylbuta-1,2-dien-1-yl) benzothioate (3ab)**



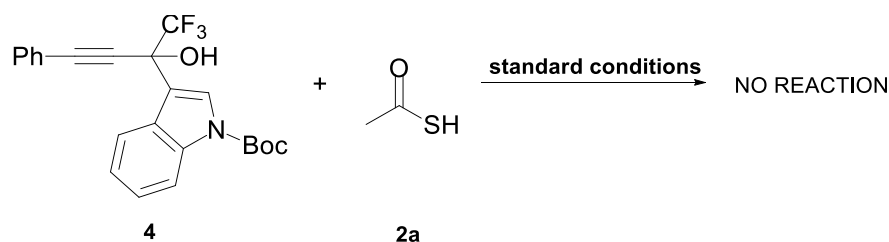
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 50:1. Yellow oil, 16.3 mg, 75% yield.  $^1H$  NMR ( $DMSO-d_6$ , 500 MHz):  $\delta$  (ppm) 11.84 (s, 1H), 8.02-8.00 (m, 2H), 7.78-7.73 (m, 2H), 7.69 (s, 1H), 7.65-7.58 (m, 4H), 7.52-7.46 (m, 3H), 7.43-7.41 (m, 1H), 7.23-7.19 (m, 1H), 7.08-7.04 (m, 1H).  $^{13}C$  NMR ( $DMSO-d_6$ , 126 MHz):  $\delta$  (ppm) 208.0, 187.8, 137.0, 135.8, 135.2, 133.2, 129.9, 129.7, 127.9, 127.1, 126.4, 126.3, 124.9, 122.2, 122.1 (q,  $J = 267.5$  Hz), 112.8, 105.0, 100.4, 99.7 (q,  $J = 43.8$  Hz).  $^{19}F$  NMR ( $DMSO-d_6$ , 471 MHz):  $\delta$  (ppm) -60.10. HRMS (ESI): exact mass calculated for  $[M-H]^-$  ( $C_{25}H_{15}F_3NOS$ ) requires  $m/z$  434.8021, found  $m/z$  434.0832. The enantiomeric excess was determined to be 70% by HPLC. [IA column, 254 nm, *n*-hexane:IPA = 90:10, 1.0 mL/min]: 10.2 min (minor), 12.1 min (major).  $[\alpha]_D^{22} = -152.5$  ( $c = 1.00$ ,  $CH_2Cl_2$ ).

## D: Gram Scale Reaction



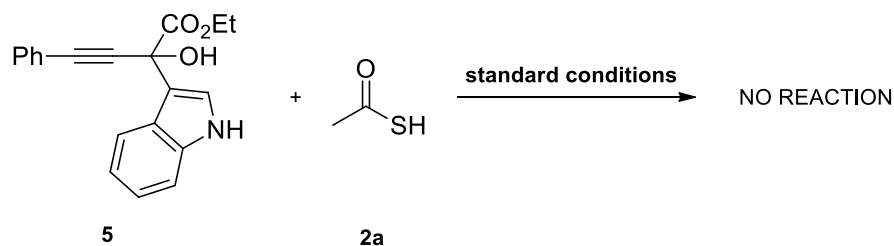
To a solution of  $\text{CHCl}_3$  (12.0 mL) were added  $\alpha$ -indolyl- $\alpha$ -trifluoromethyl propargylic alcohol **1a** (630.0 mg, 2.0 mmol), thiolacetic acid **2a** (182.6 mg, 2.4 mmol) and **CPA-7** (28.7 mg, 0.04 mmol). The reaction mixture was stirred at room temperature  $^\circ\text{C}$  for 24 h. The solvent was evaporated to give the crude product, which was purified by silica gel chromatography (PE/EA = 50:1) to provide the desired product **3aa** as a brown oil (671.7 mg, 90% yield, 92% ee).

## E: Control Experiments



When *t*-butyloxy carbonyl protected substrate **4** was used, no desired products were observed under the optimized conditions.

## F: Limitation of The Reaction

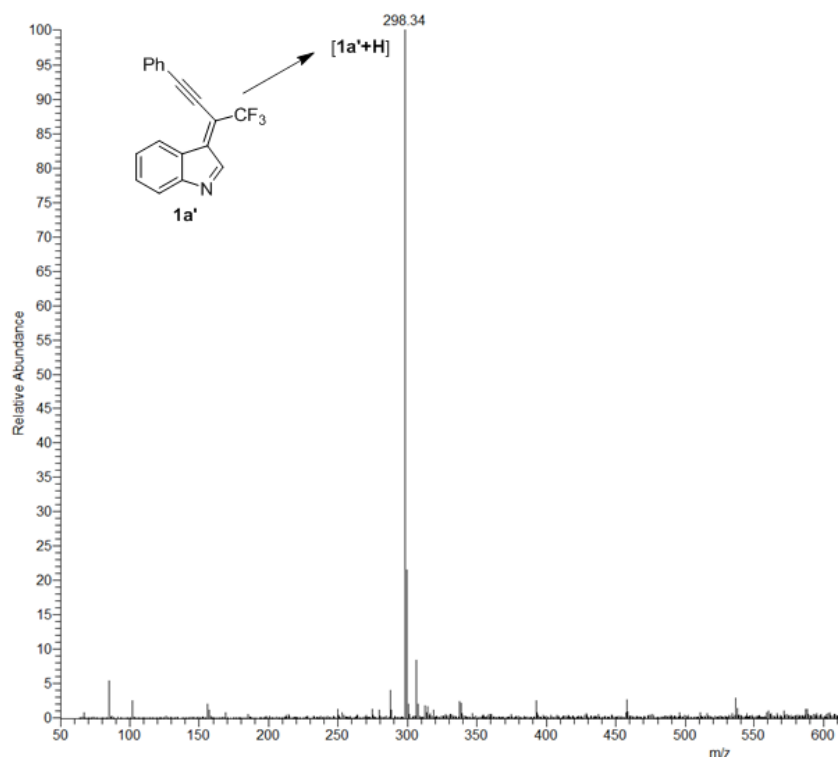


When  $\text{CF}_3$  group was replaced with ester group, substrate **5** didn't get the desired products under the optimized conditions.

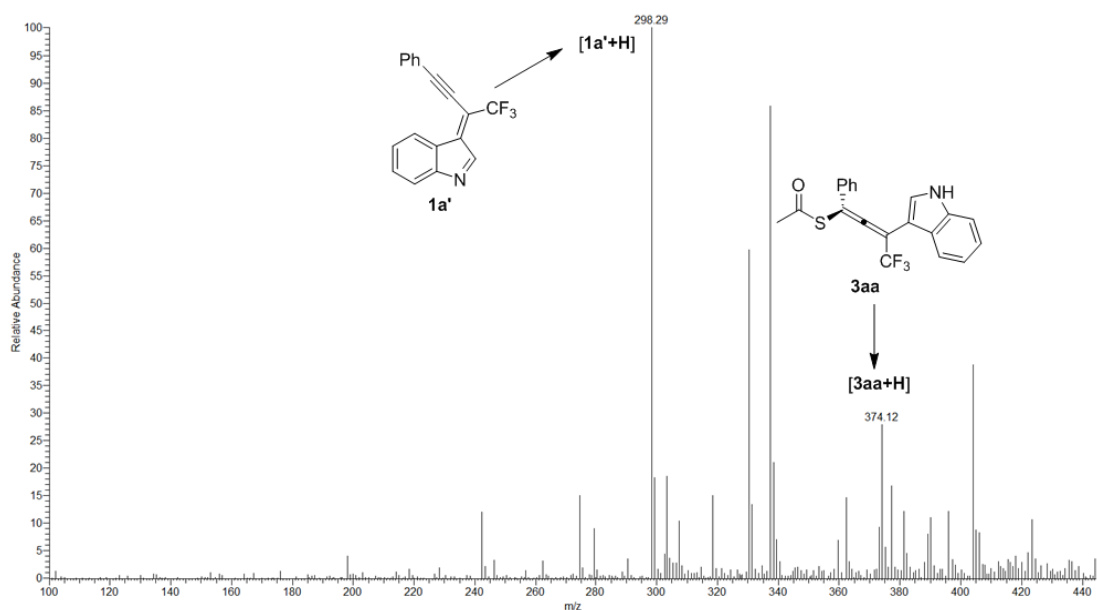
## G: ESI-MS Studies

a) ESI(+)-MS spectra for the reaction of catalyst **CPA-7** and  $\alpha$ -indolyl propargylic alcohol **1a** for 1 h; b) ESI(+)-MS spectra for the 1,6-conjugate addition of  $\alpha$ -indolyl propargylic alcohol **1a** and thiolacetic acid **2a** catalyzed by catalyst **CPA-7** for 24 h. Other unidentified ions are likely to correspond to either impurities or side-reaction products.

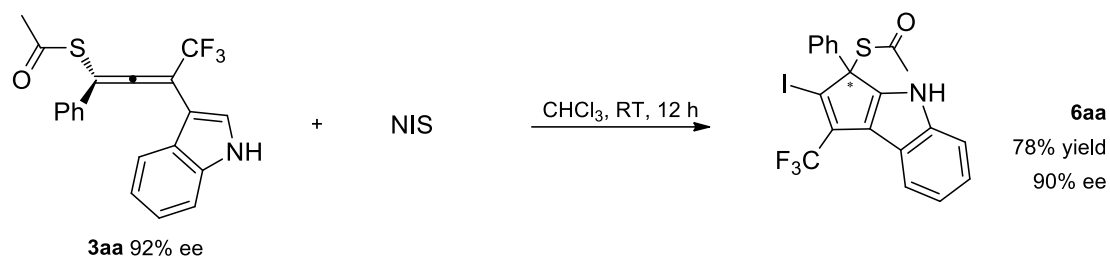
a)



b)

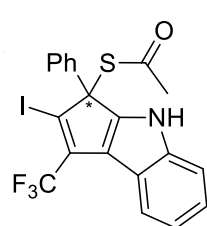


## H: Synthetic Transformations



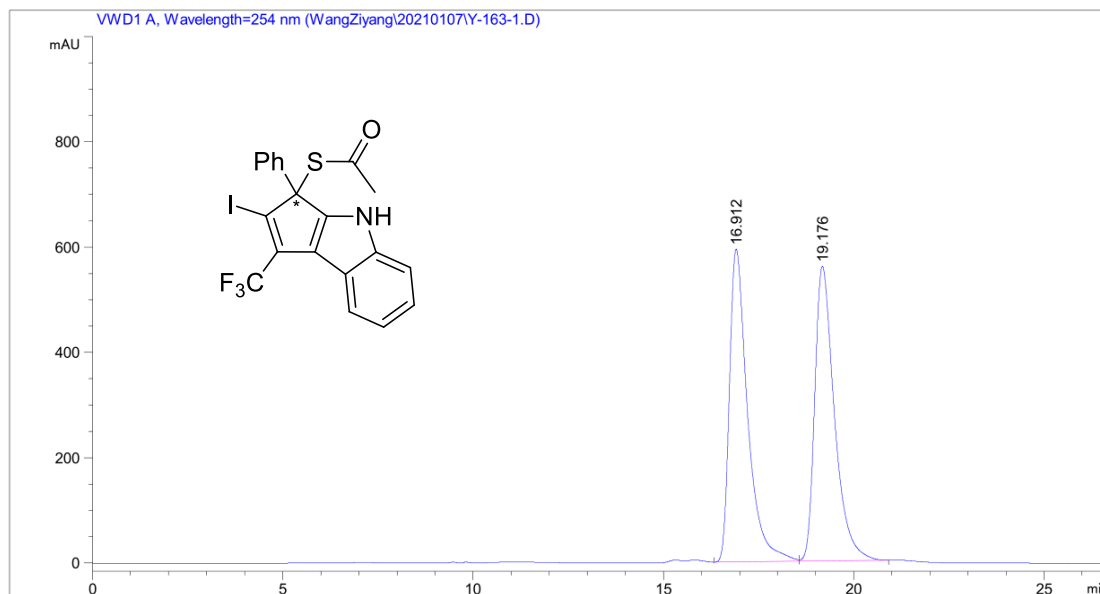
To a solution of **3aa** (37.3 mmol, 0.1 mmol) in  $\text{CHCl}_3$  (1.0 mL) was added dropwise the solution of NIS (24.7 mmol, 0.11 mmol) in  $\text{CHCl}_3$  (0.5 mL). The mixture was further stirred at room temperature for 12 h. The crude product was purified directly by flash column chromatography on silica gel to give the desired compound **6aa** as a brown oil (39.1 mg, 78% yield, 90% ee).

### **S**-(2-iodo-3-phenyl-1-(trifluoromethyl)-3,4-dihydrocyclopenta[*b*]indol-3-yl) ethanethioate (**6aa**)

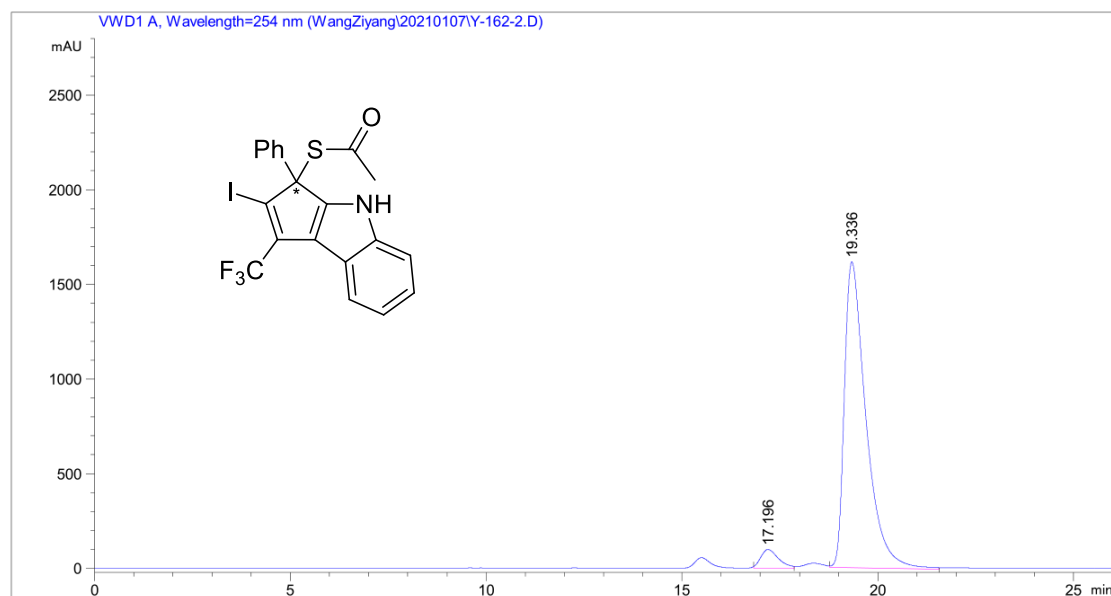


Eluent for flash column chromatography: petroleum ether/ethyl acetate = 70:1. Brown oil, 39.1 mg, 78% yield.  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ , 500 MHz):  $\delta$  (ppm) 11.45 (s, 1H), 7.56-7.54 (d,  $J = 10.0$  Hz, 2H), 7.35-7.34 (m, 3H), 7.21-7.16 (m, 2H), 7.13-7.11 (m, 2H), 2.44 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{DMSO}-d_6$ , 126 MHz):  $\delta$  (ppm) 194.3, 150.9, 140.4, 134.7, 134.5, 134.2, 129.3, 128.9, 127.1, 121.6, 120.0 (q,  $J = 322.5$  Hz), 119.1, 119.0, 117.8, 114.1, 100.8 (d,  $J = 6.3$  Hz), 65.0, 30.9.  $^{19}\text{F}$  NMR ( $\text{DMSO}-d_6$ , 471 MHz):  $\delta$  (ppm) -59.68. HRMS (ESI): exact mass calculated for  $[\text{M}-\text{H}]^-$  ( $\text{C}_{20}\text{H}_{12}\text{F}_3\text{INOS}$ ) requires  $m/z$  497.9631, found  $m/z$  497.9630. The enantiomeric excess was determined to be 90% by HPLC. [OD column, 254 nm, *n*-hexane:IPA = 90:10, 0.8 mL/min]: 17.2 min (minor), 19.3 min (major).  $[\alpha]_D^{22} = +1440$  ( $c = 1.00$ ,  $\text{CH}_2\text{Cl}_2$ ).

**S-(2-iodo-3-phenyl-1-(trifluoromethyl)-3,4-dihydrocyclopenta[b]indol-3-yl) ethanethioate (6aa)**

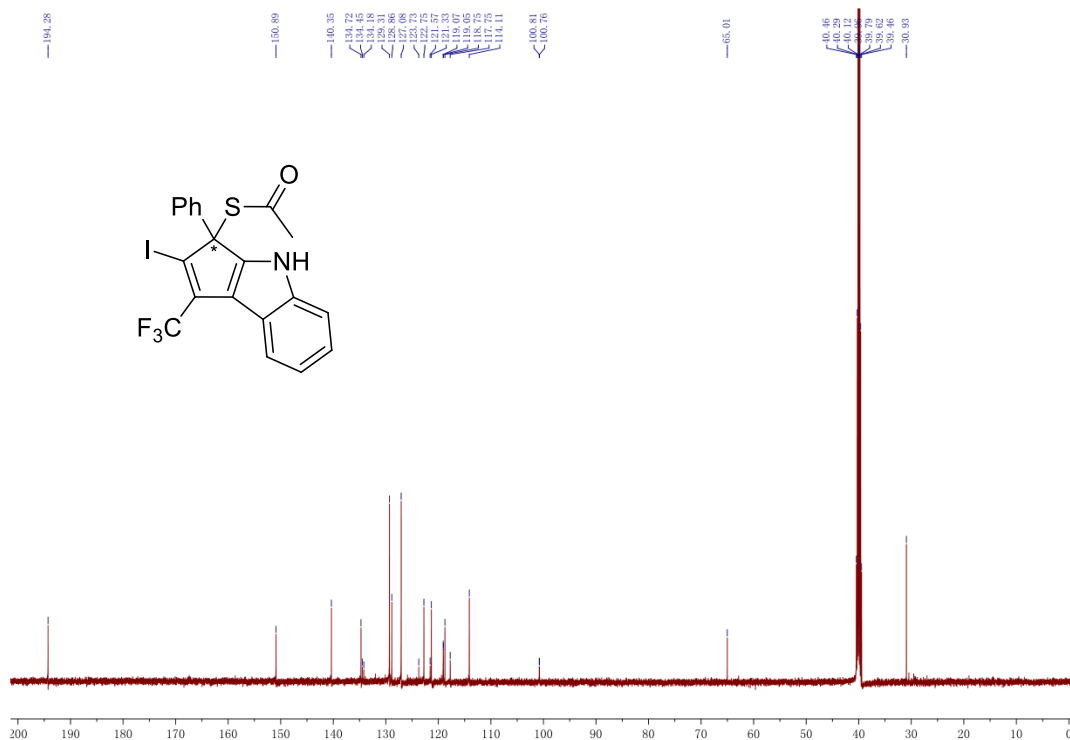
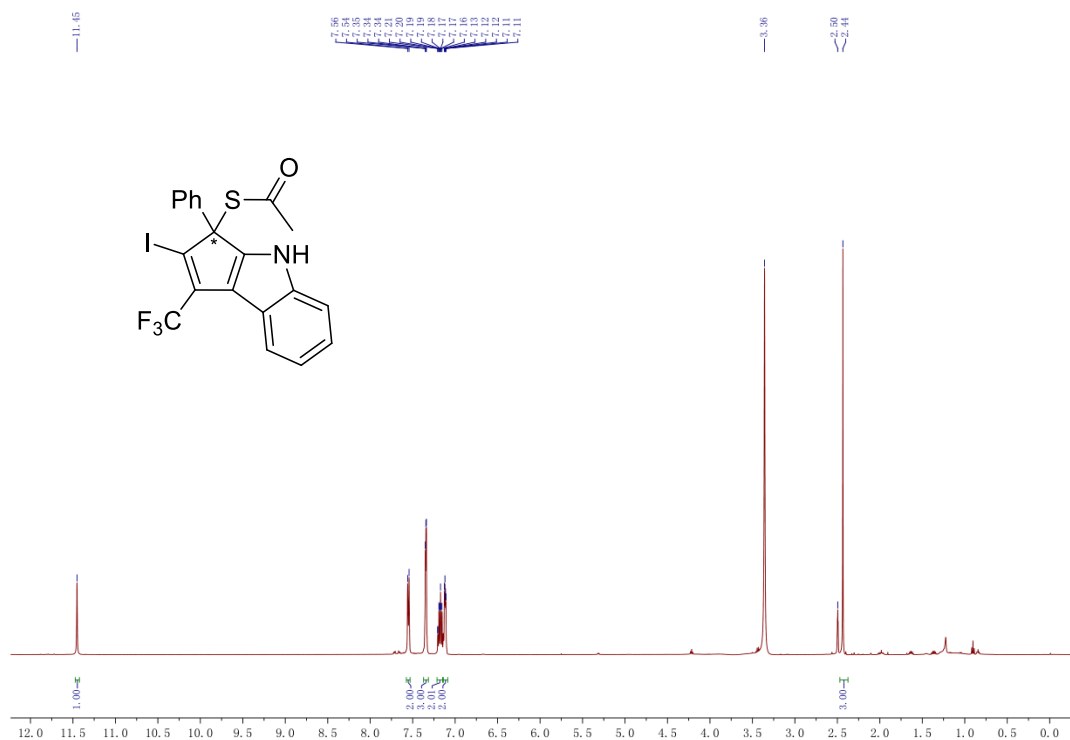


#	Time	Area	Height	Width	Symmetry	Area %
1	16.912	19769.1	594.1	0.4962	0.539	49.589
2	19.176	20096.7	559.6	0.541	0.591	50.411

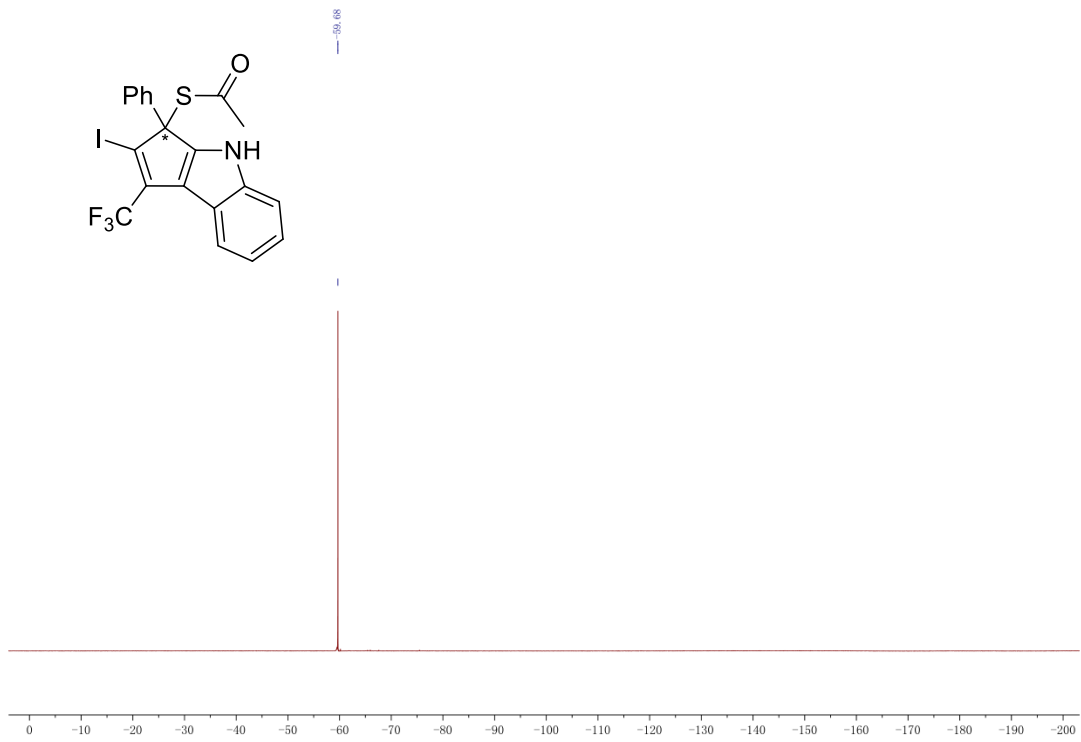


#	Time	Area	Height	Width	Symmetry	Area %
1	17.196	3158.1	99.6	0.5287	0.677	4.844
2	19.336	62045.4	1615.5	0.6401	0.504	95.156

**S-(2-iodo-3-phenyl-1-(trifluoromethyl)-3,4-dihydrocyclopenta[b]indol-3-yl) ethanethioate (6aa)**

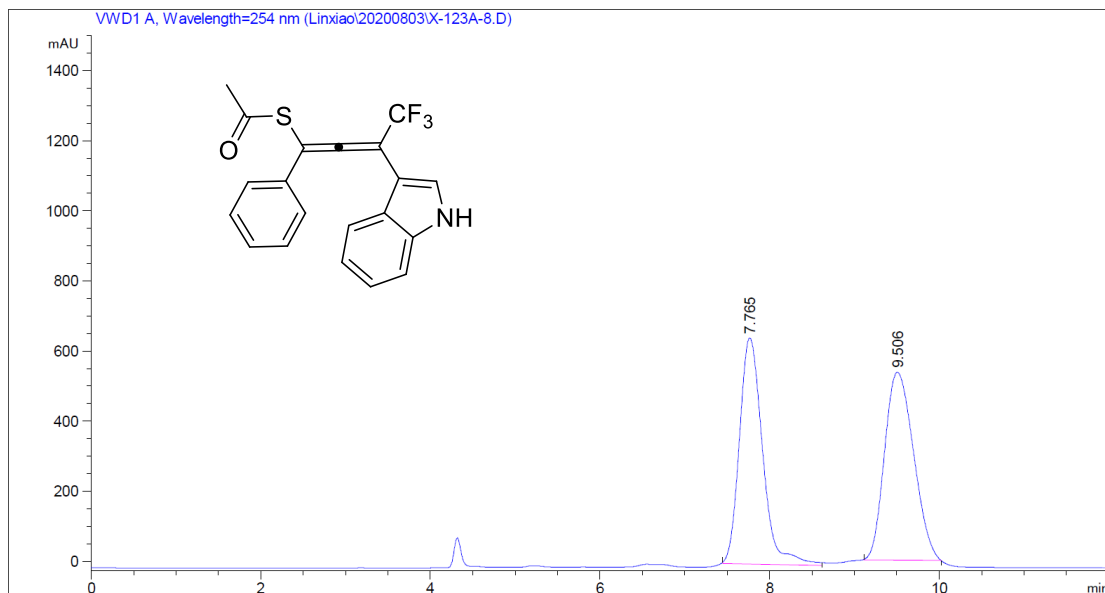




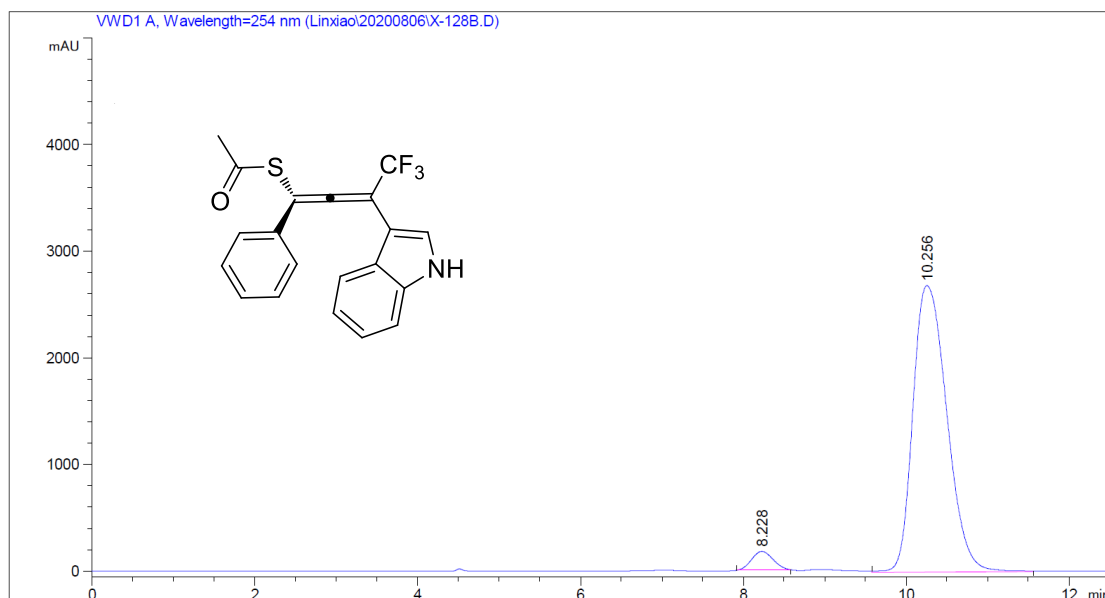


## I: HPLC Analysis

### (S)-S-(4,4,4-trifluoro-3-(1H-indol-3-yl)-1-phenylbuta-1,2-dien-1-yl) ethanethioate (3aa)

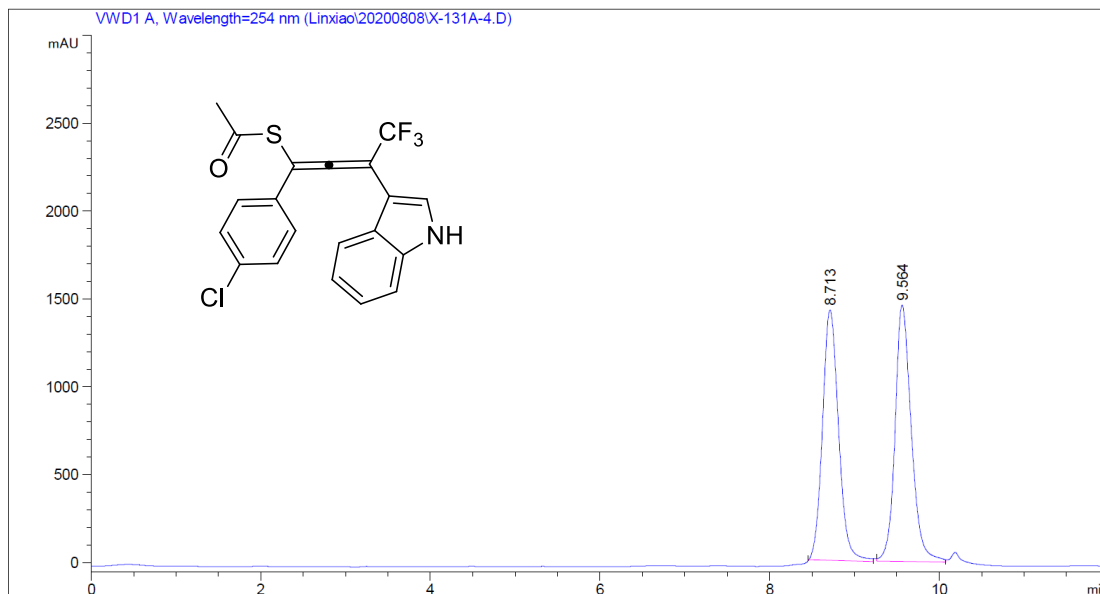


#	Time	Area	Height	Width	Symmetry	Area %
1	7.765	12246.4	644.7	0.3166	0.766	49.021
2	9.506	12735.3	535.8	0.3962	0.771	50.979

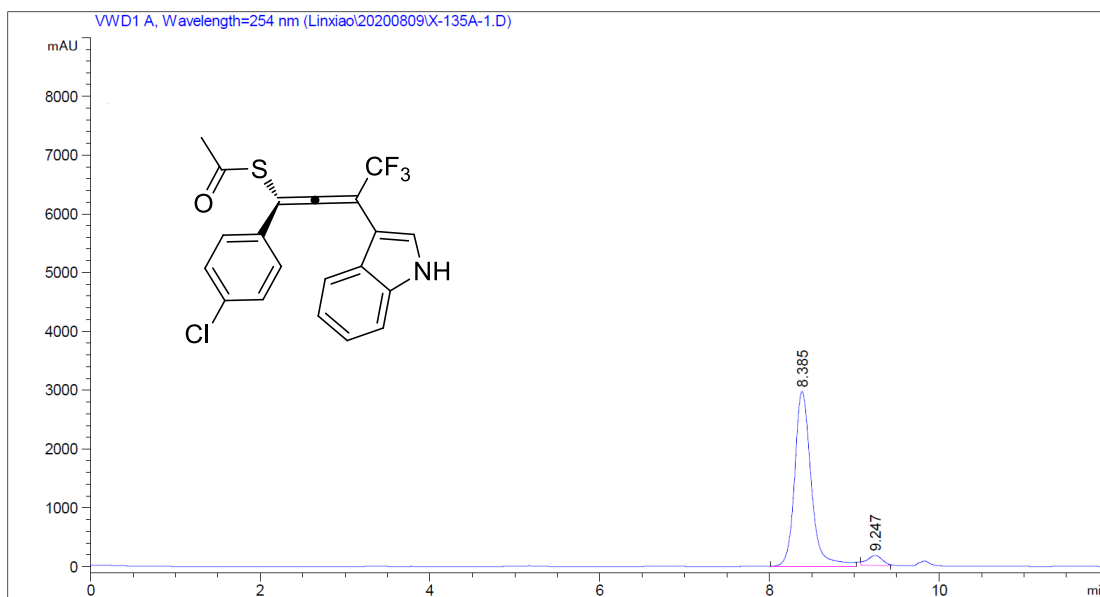


#	Time	Area	Height	Width	Symmetry	Area %
1	8.228	3102.8	172.6	0.2995	0.874	3.834
2	10.256	77828.4	2685.7	0.483	0.684	96.166

**(S)-S-(1-(4-chlorophenyl)-4,4,4-trifluoro-3-(1H-indol-3-yl)buta-1,2-dien-1-yl) ethanethioate (3ba)**

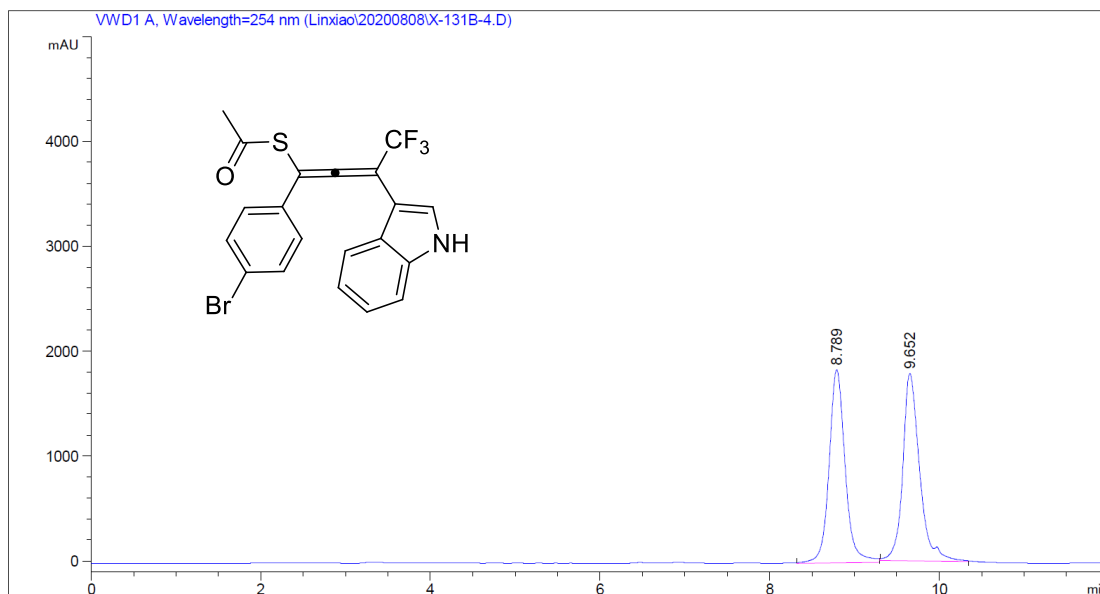


#	Time	Area	Height	Width	Symmetry	Area %
1	8.713	19069.8	1437.9	0.221	0.869	50.024
2	9.564	19051.6	1450.2	0.219	0.735	49.976

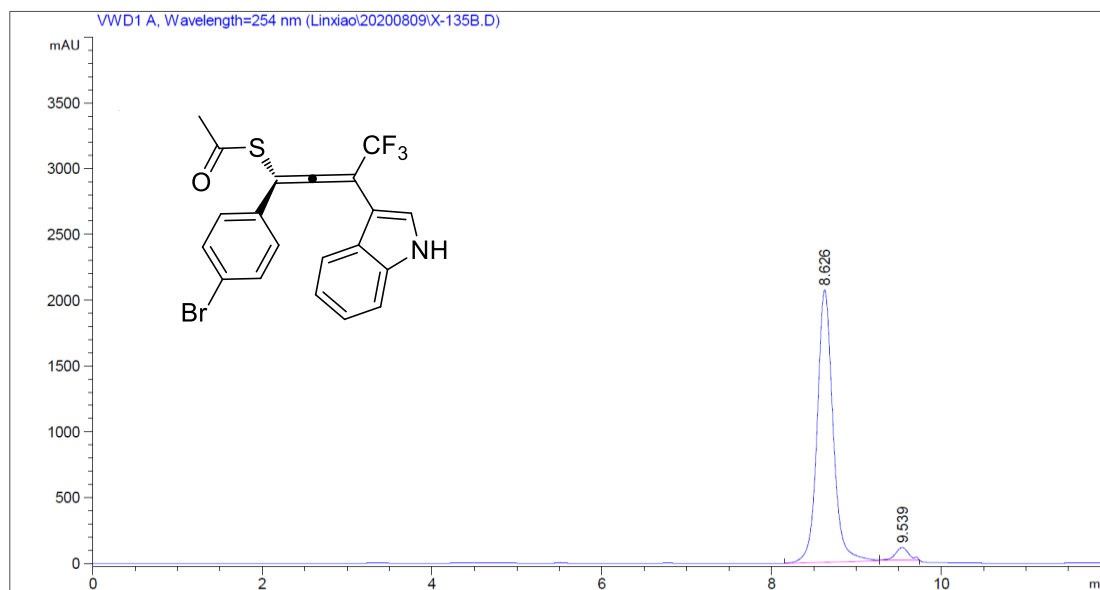


#	Time	Area	Height	Width	Symmetry	Area %
1	8.385	40262.2	2971.6	0.2258	0.768	94.870
2	9.247	2176.9	173.5	0.2091	1.068	5.130

**(S)-S-(1-(4-bromophenyl)-4,4,4-trifluoro-3-(1H-indol-3-yl)buta-1,2-dien-1-yl) ethanethioate (3ca)**

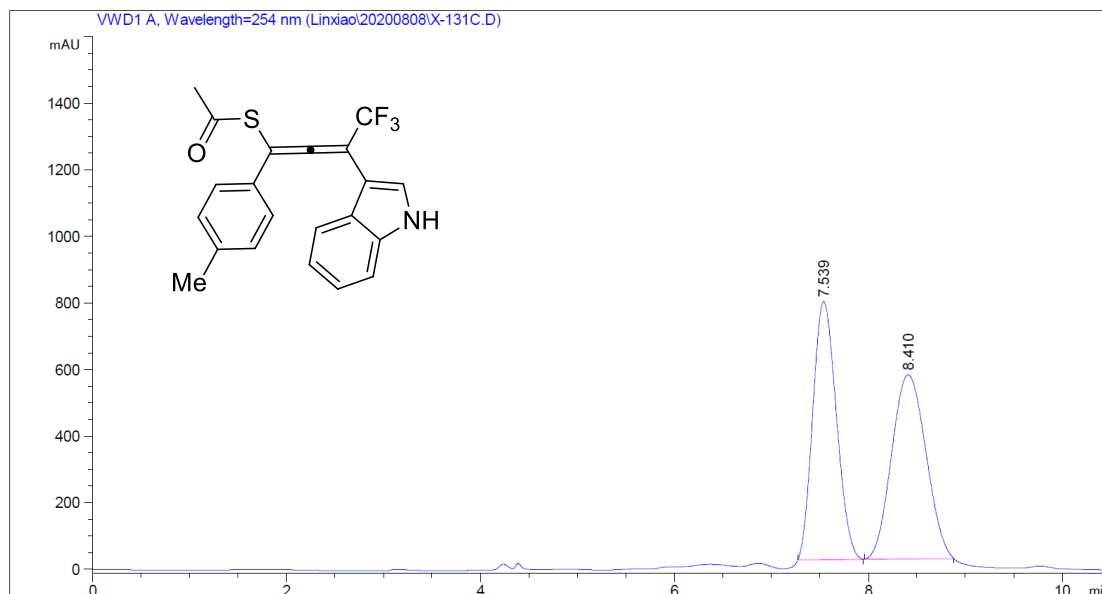


#	Time	Area	Height	Width	Symmetry	Area %
1	8.789	24326.1	1842.3	0.2201	0.864	49.673
2	9.652	24646.2	1785.9	0.23	0.704	50.327

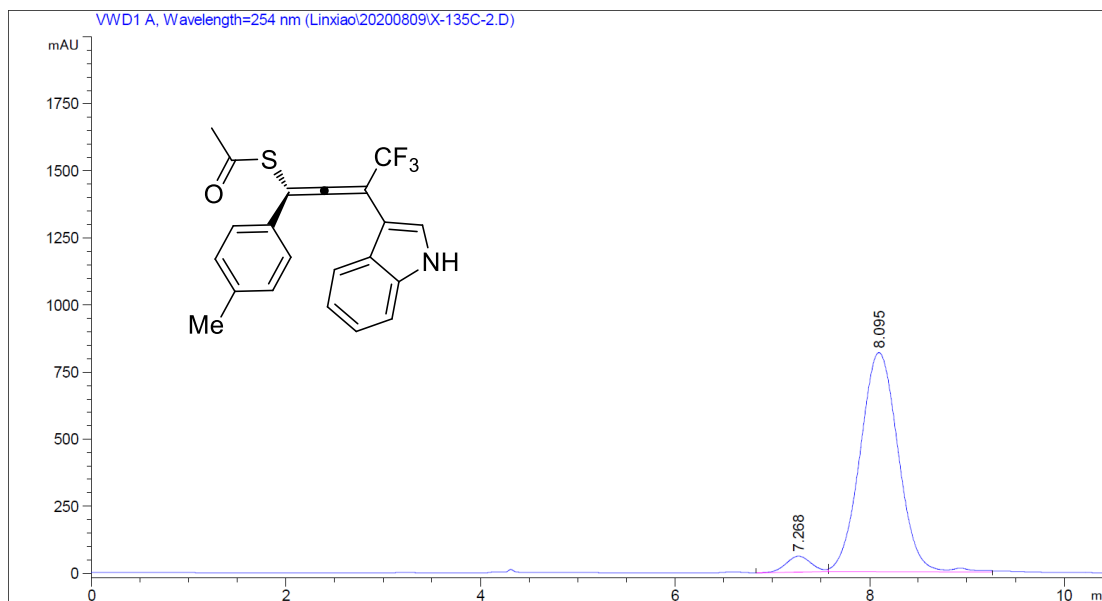


#	Time	Area	Height	Width	Symmetry	Area %
1	8.626	26845.9	2070.7	0.2161	0.863	96.056
2	9.539	1102.2	97.7	0.188	0.976	3.944

**(S)-S-(4,4,4-trifluoro-3-(1H-indol-3-yl)-1-(p-tolyl)buta-1,2-dien-1-yl)ethanethioate (3da)**

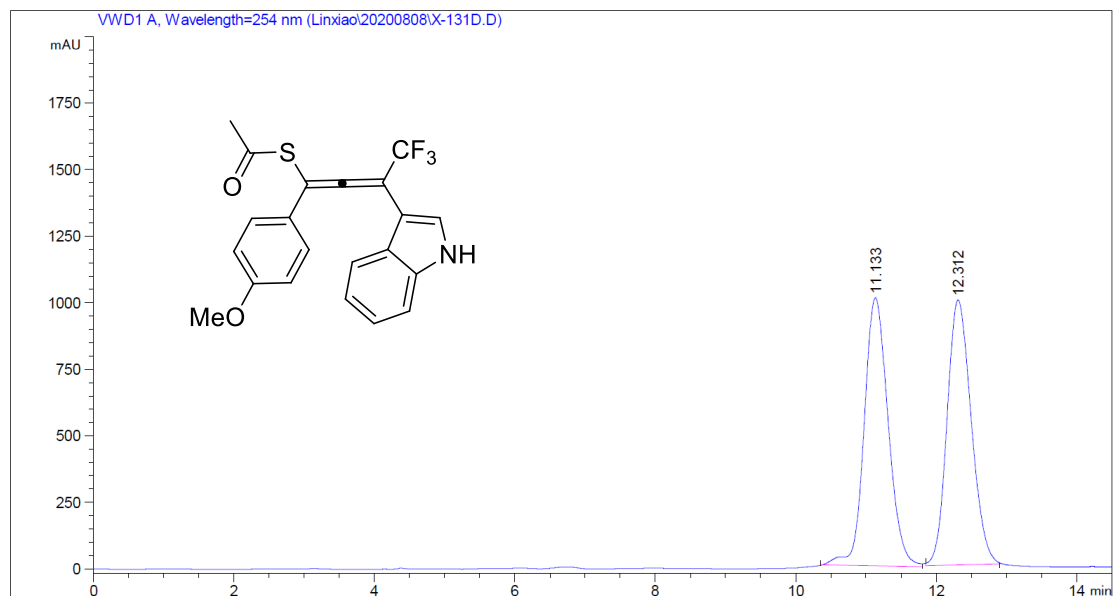


#	Time	Area	Height	Width	Symmetry	Area %
1	7.539	13061.1	774.5	0.281	0.827	49.038
2	8.410	13573.7	553.1	0.409	0.903	50.962

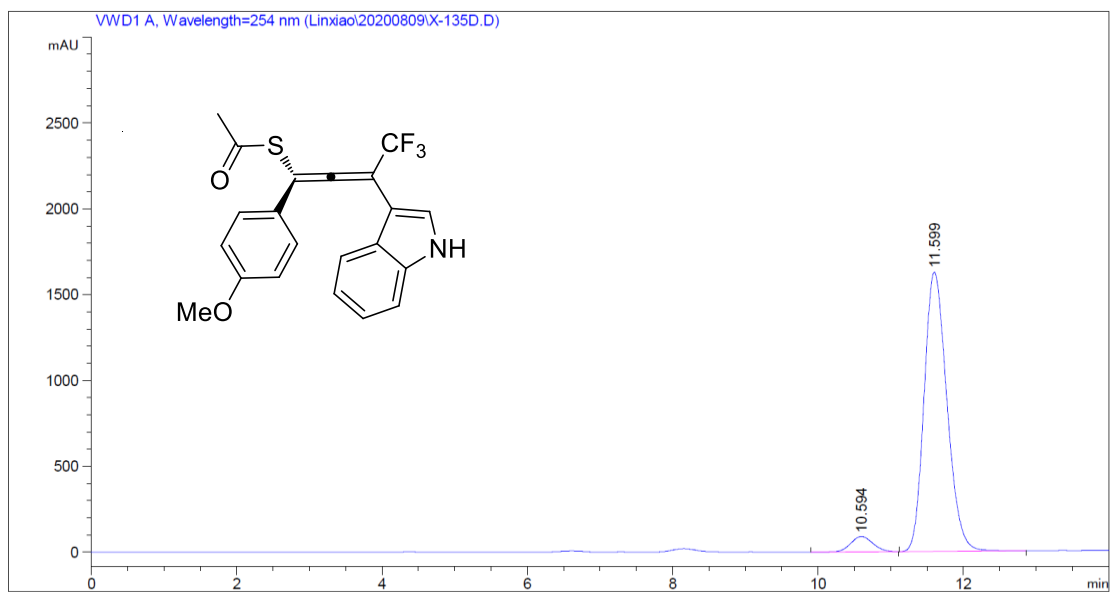


#	Time	Area	Height	Width	Symmetry	Area %
1	7.268	1059.9	59.1	0.299	0.979	4.554
2	8.095	22217.4	816.4	0.4535	0.931	95.446

**(S)-S-(4,4,4-trifluoro-3-(1H-indol-3-yl)-1-(4-methoxyphenyl)buta-1,2-dien-1-yl) ethanethioate (3ea)**

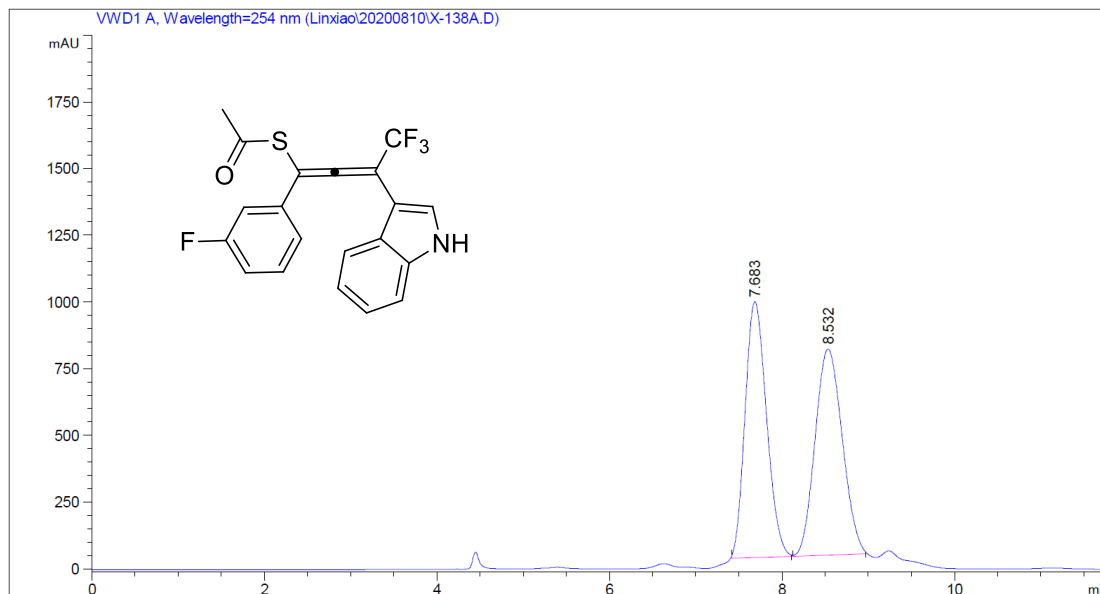


#	Time	Area	Height	Width	Symmetry	Area %
1	11.133	23961.5	1007.4	0.3964	0.849	50.253
2	12.312	23719.8	995.6	0.3971	0.812	49.747

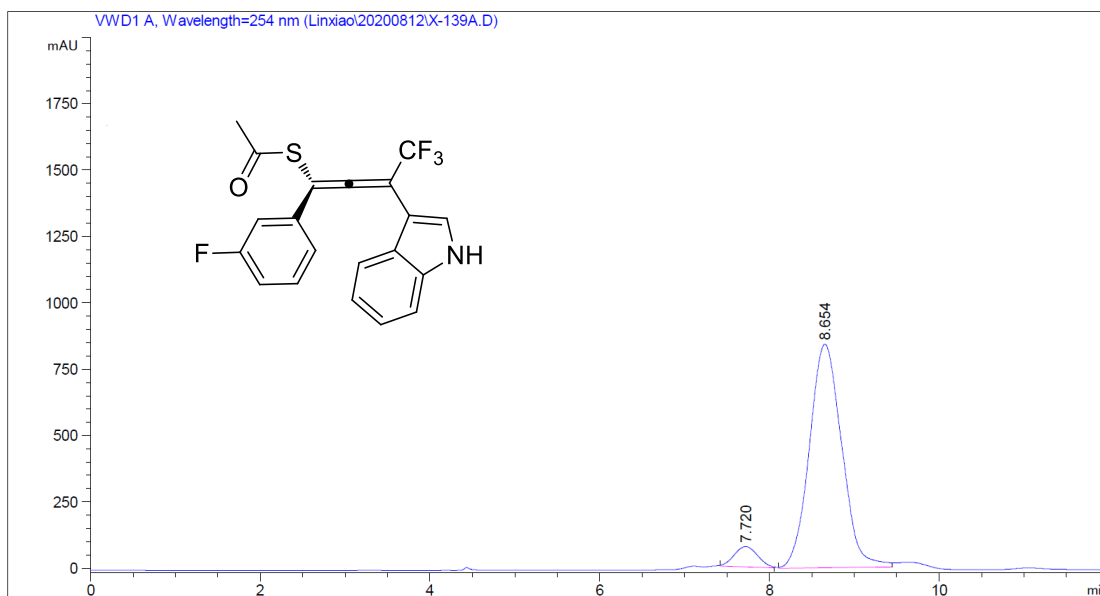


#	Time	Area	Height	Width	Symmetry	Area %
1	10.594	1884.3	89.2	0.3304	0.897	5.047
2	11.599	35452.5	1626	0.3394	0.77	94.953

**(S)-S-(4,4,4-trifluoro-1-(3-fluorophenyl)-3-(1H-indol-3-yl)buta-1,2-dien-1-yl) ethanethioate (3fa)**

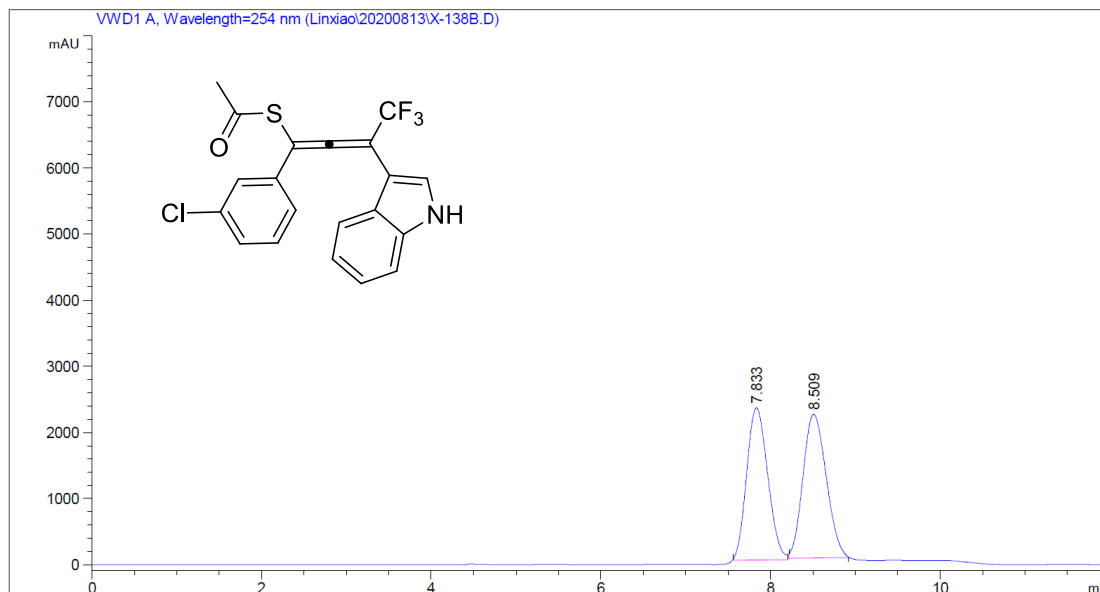


#	Time	Area	Height	Width	Symmetry	Area %
1	7.683	16536.9	957.7	0.2878	0.805	49.519
2	8.532	16858.5	771.8	0.364	0.883	50.481

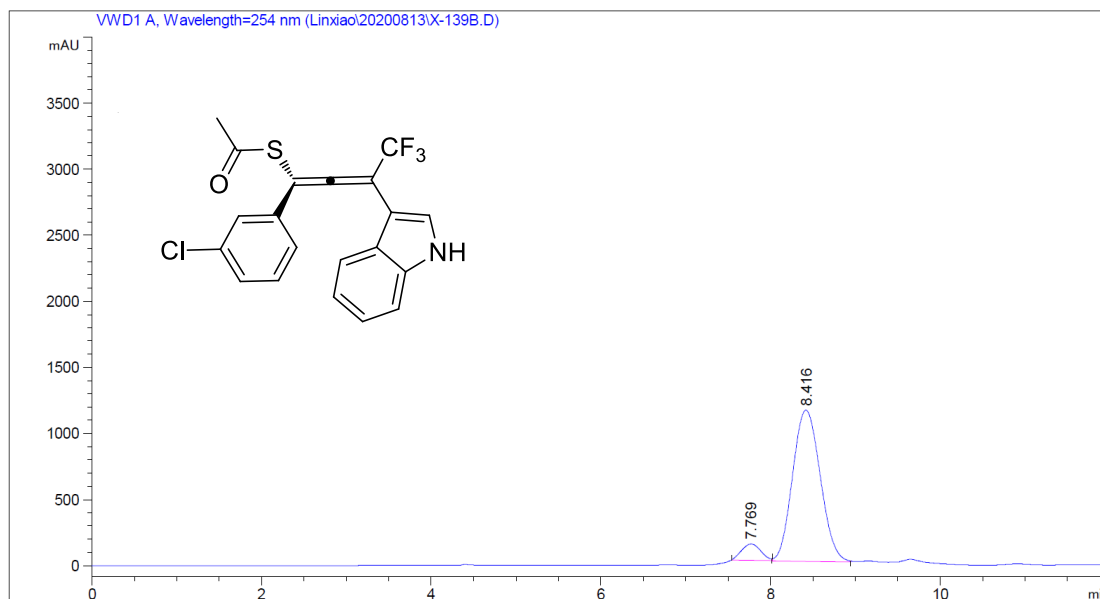


#	Time	Area	Height	Width	Symmetry	Area %
1	7.72	1480.5	77	0.3204	0.919	6.228
2	8.654	22290.8	841.5	0.4415	0.884	93.772

**(S)-S-(1-(3-chlorophenyl)-4,4,4-trifluoro-3-(1H-indol-3-yl)buta-1,2-dien-1-yl) ethanethioate (3ga)**



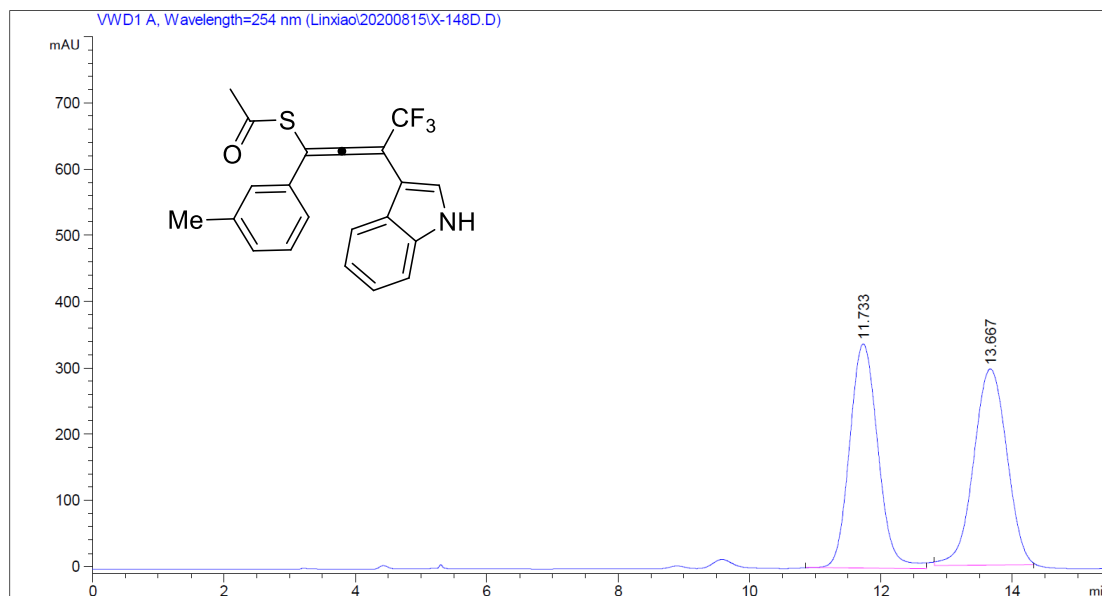
#	Time	Area	Height	Width	Symmetry	Area %
1	7.833	39649.7	2300.3	0.2873	0.829	49.029
2	8.509	41220	2169.9	0.3166	0.827	50.971



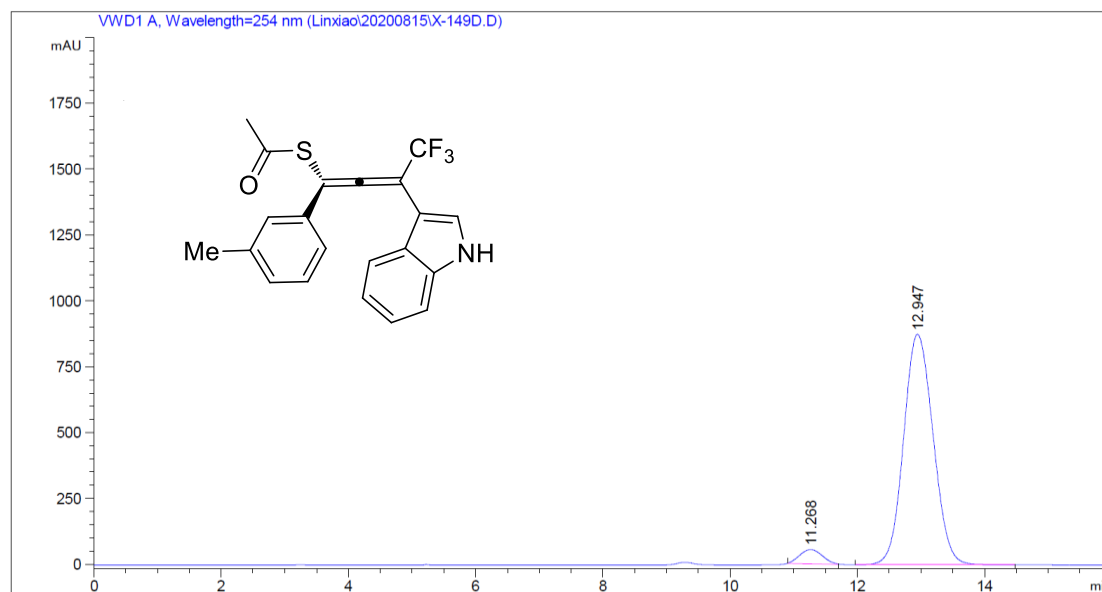
#	Time	Area	Height	Width	Symmetry	Area %
1	7.769	1957.4	124	0.263	0.949	7.021
2	8.416	25921.7	1144.2	0.3776	0.893	92.979



**(S)-S-(4,4,4-trifluoro-3-(1H-indol-3-yl)-1-(*m*-tolyl)buta-1,2-dien-1-yl)ethanethioate (3ha)**

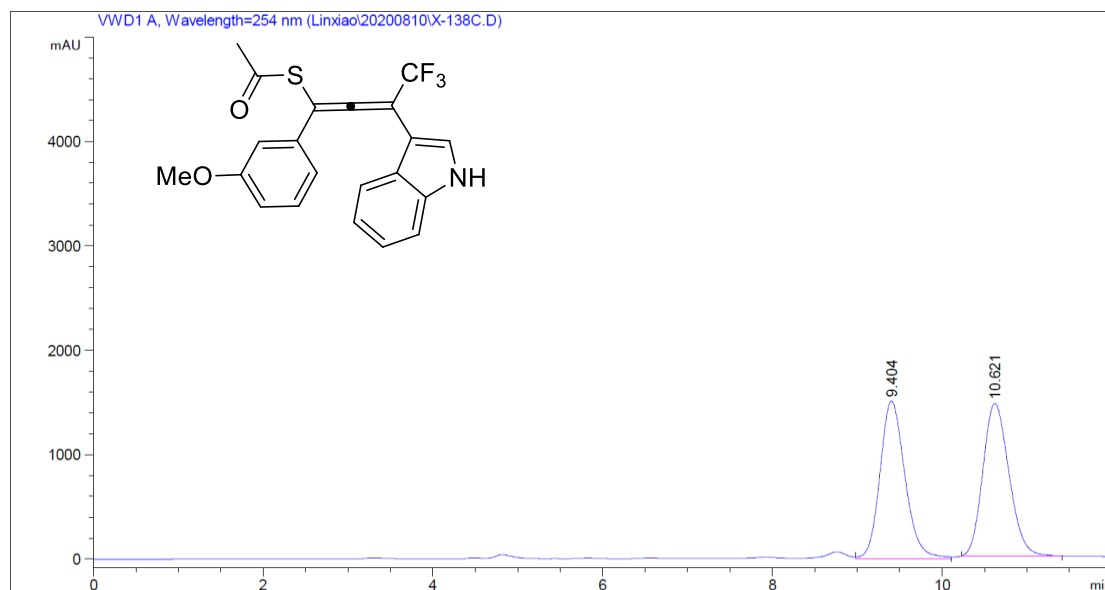


#	Time	Area	Height	Width	Symmetry	Area %
1	11.733	10143.1	338.3	0.4997	0.879	49.447
2	13.667	10370	296	0.584	0.994	50.553

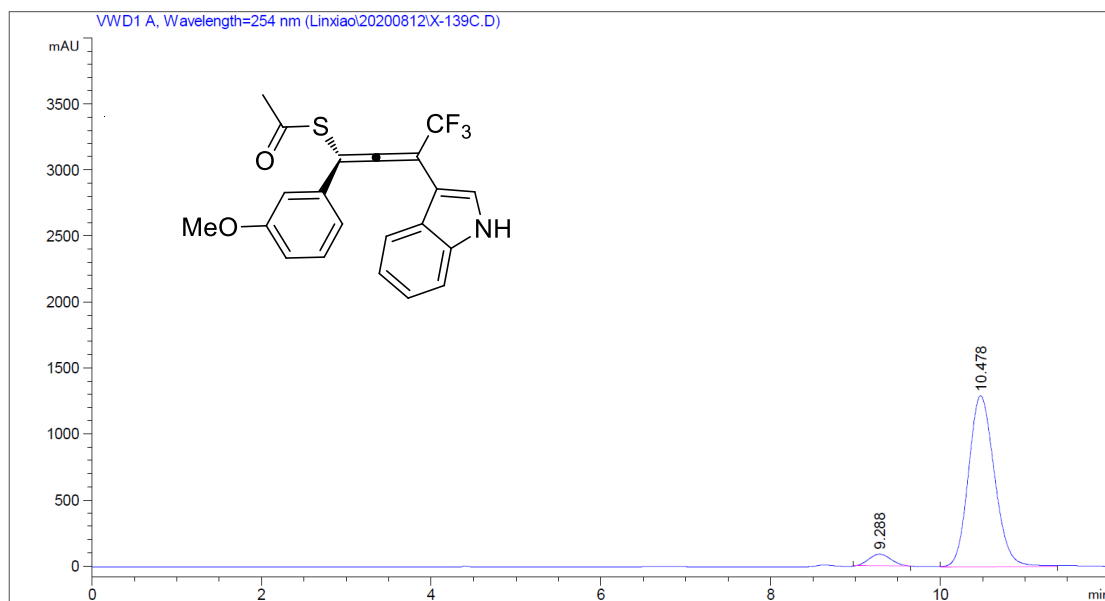


#	Time	Area	Height	Width	Symmetry	Area %
1	11.268	1303.4	53.5	0.406	0.914	4.416
2	12.947	28207.9	874.8	0.5092	0.86	95.584

**(S)-S-(4,4,4-trifluoro-3-(1H-indol-3-yl)-1-(3-methoxyphenyl)buta-1,2-dien-1-yl) ethanethioate (3ia)**

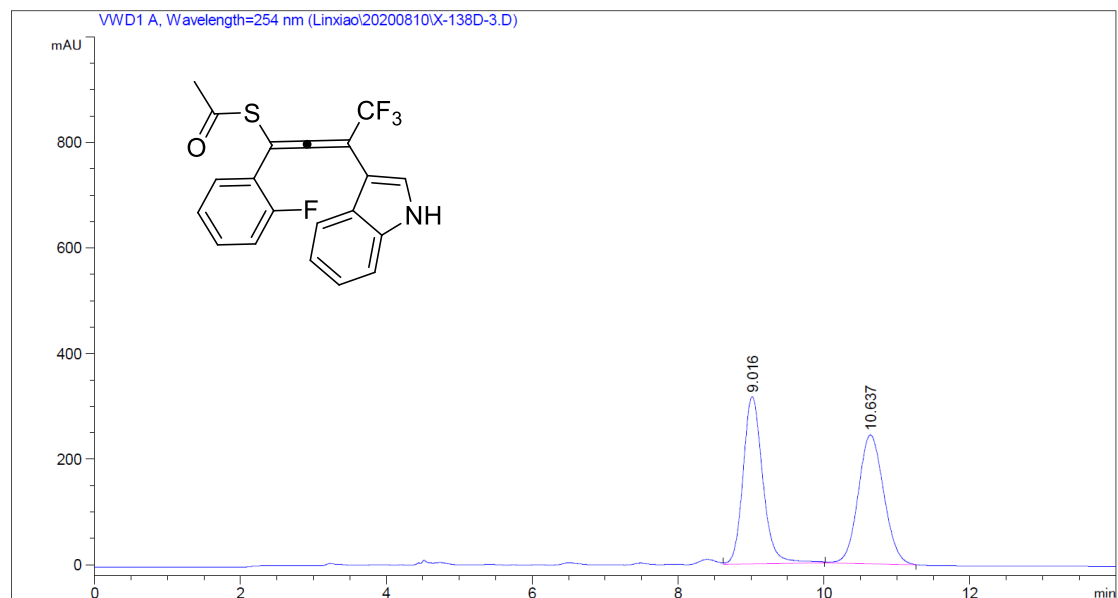


#	Time	Area	Height	Width	Symmetry	Area %
1	9.404	30634.9	1506.1	0.339	0.819	49.315
2	10.621	31486	1463.9	0.3585	0.812	50.685

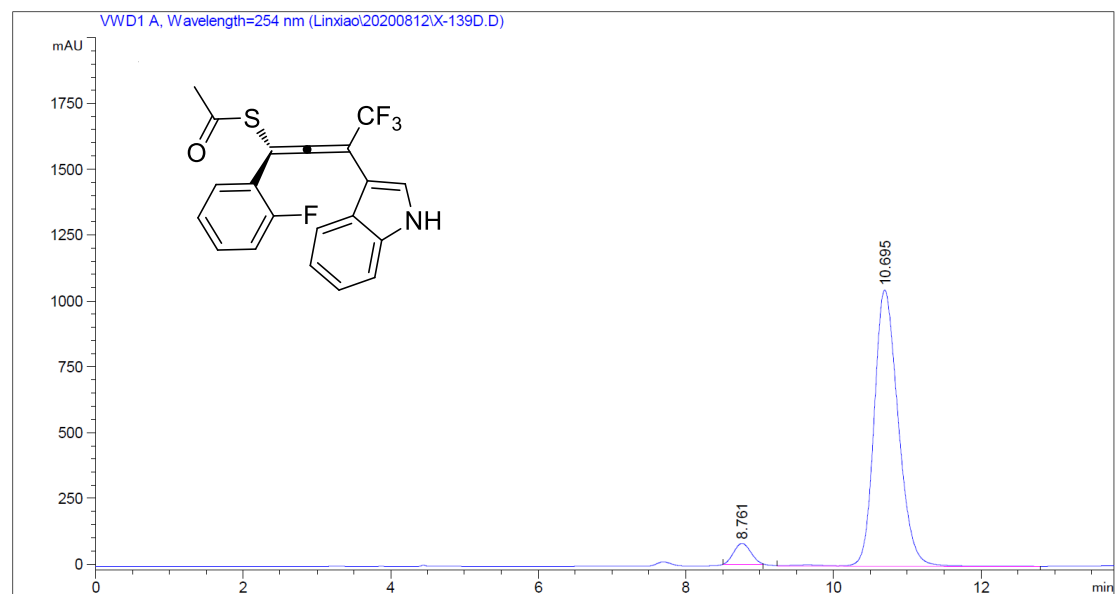


#	Time	Area	Height	Width	Symmetry	Area %
1	9.288	1586.5	88.7	0.298	0.901	5.414
2	10.478	27719.1	1296.3	0.3564	0.832	94.586

**(S)-S-(4,4,4-trifluoro-1-(2-fluorophenyl)-3-(1H-indol-3-yl)buta-1,2-dien-1-yl) ethanethioate (3ja)**

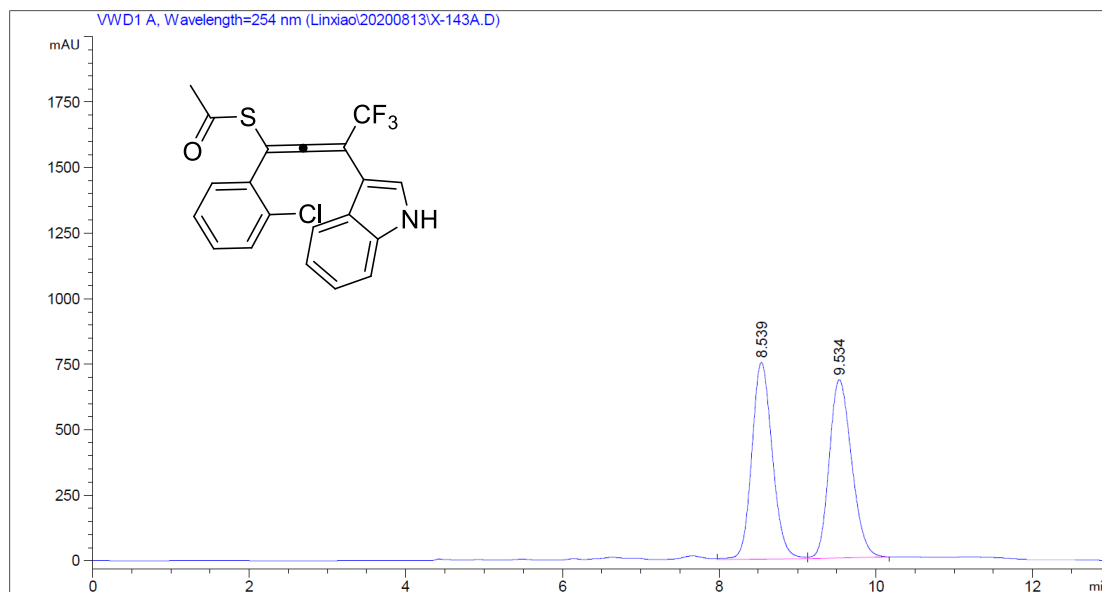


#	Time	Area	Height	Width	Symmetry	Area %
1	9.016	5959.8	316.8	0.3135	0.806	50.044
2	10.637	5949.3	244.1	0.4062	0.887	49.956

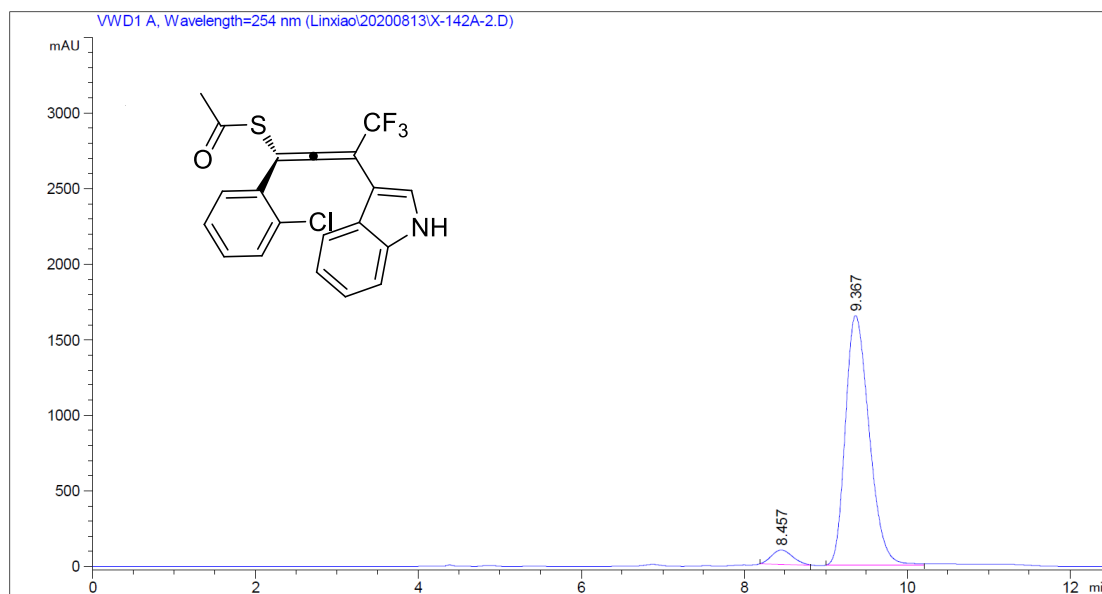


#	Time	Area	Height	Width	Symmetry	Area %
1	8.761	1260.8	78.9	0.2664	0.92	5.030
2	10.695	23807.3	1049.1	0.3782	0.759	94.970

**(S)-S-(1-(2-chlorophenyl)-4,4,4-trifluoro-3-(1H-indol-3-yl)buta-1,2-dien-1-yl) ethanethioate (3ka)**

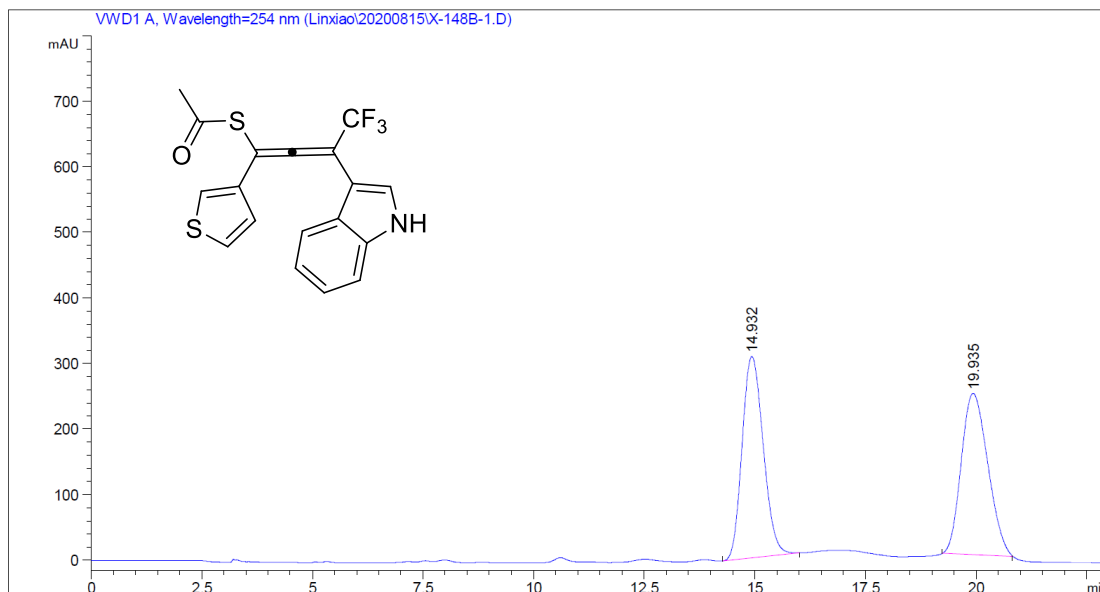


#	Time	Area	Height	Width	Symmetry	Area %
1	8.539	13649.7	750.5	0.3031	0.845	50.207
2	9.534	13537.3	680.5	0.3316	0.788	49.793

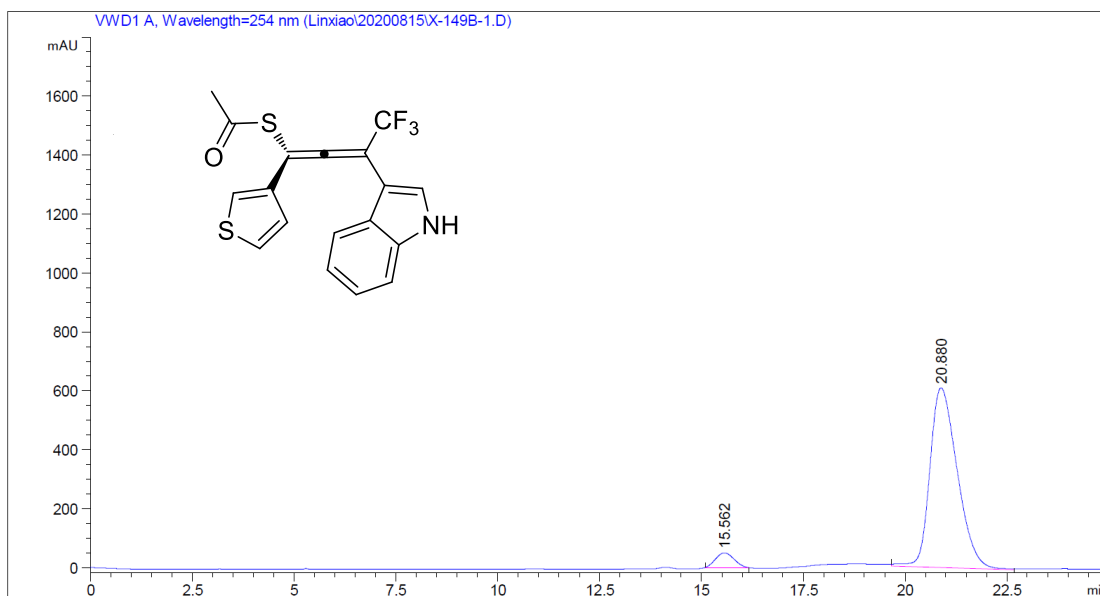


#	Time	Area	Height	Width	Symmetry	Area %
1	8.457	1680.1	94.6	0.2958	0.82	4.758
2	9.367	33632.9	1653.2	0.3391	0.716	95.242

**(S)-S-(4,4,4-trifluoro-3-(1H-indol-3-yl)-1-(thiophen-3-yl)buta-1,2-dien-1-yl) ethanethioate (3la)**

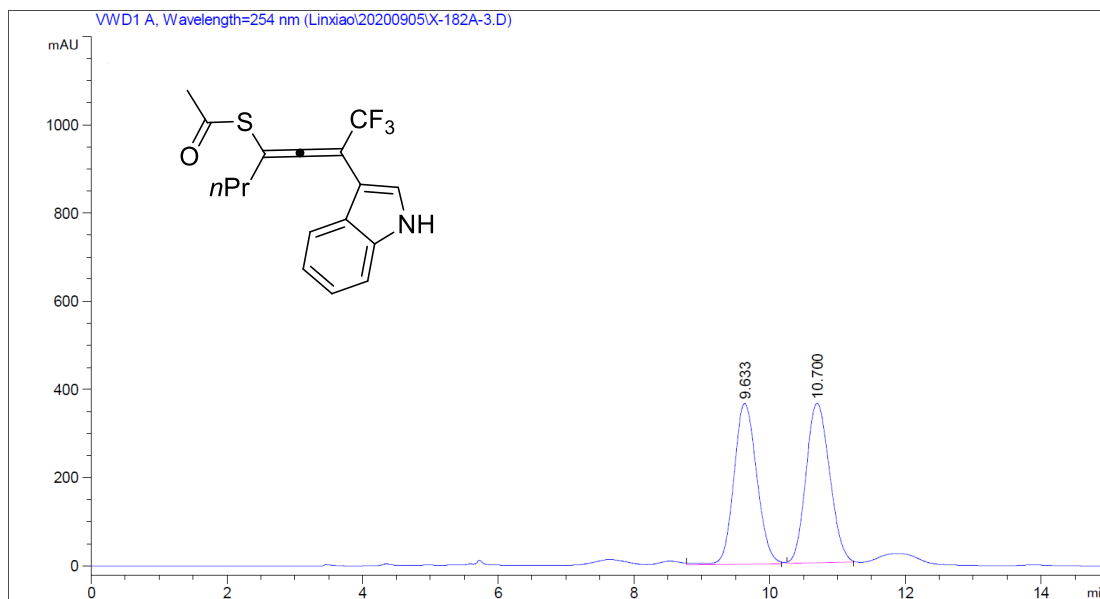


#	Time	Area	Height	Width	Symmetry	Area %
1	14.932	10209.7	307.3	0.5226	0.807	49.862
2	19.935	10266	246.1	0.6954	0.776	50.138

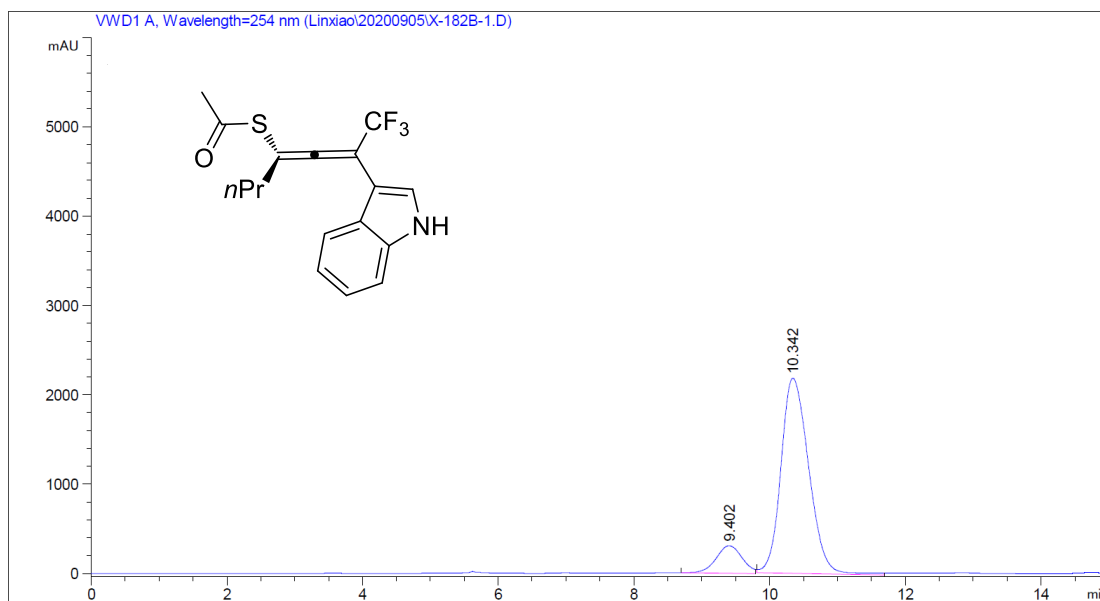


#	Time	Area	Height	Width	Symmetry	Area %
1	15.562	1657.4	51.3	0.5382	0.897	5.470
2	20.88	28640.2	610.3	0.7822	0.673	94.530

**(S)-S-(1,1,1-trifluoro-2-(1H-indol-3-yl)hepta-2,3-dien-4-yl) ethanethioate (3ma)**

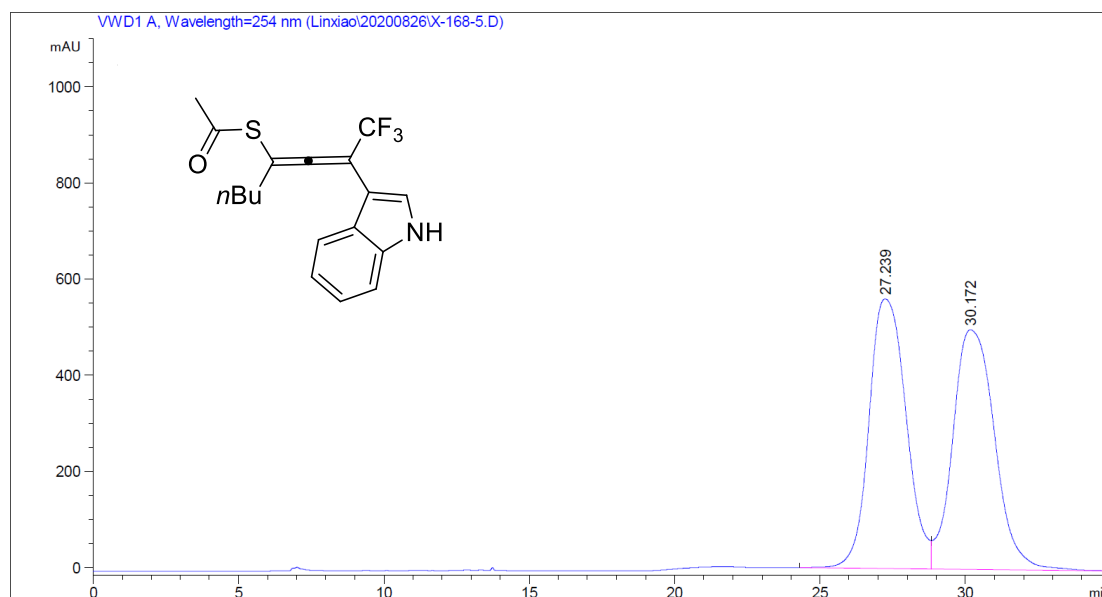


#	Time	Area	Height	Width	Symmetry	Area %
1	9.633	8530.6	364.3	0.3903	0.864	49.401
2	10.7	8737.5	361.3	0.403	0.85	50.599

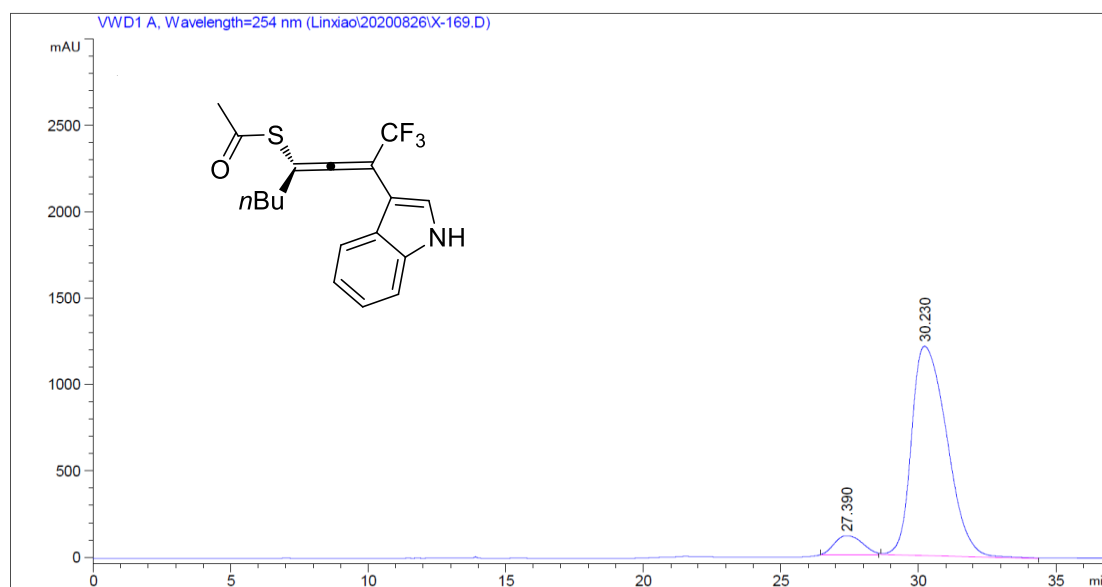


#	Time	Area	Height	Width	Symmetry	Area %
1	9.402	8264	308.6	0.4463	0.996	11.705
2	10.342	62340.8	2188.3	0.4748	0.728	88.295

**(S)-S-(1,1,1-trifluoro-2-(1H-indol-3-yl)octa-2,3-dien-4-yl) ethanethioate (3na)**

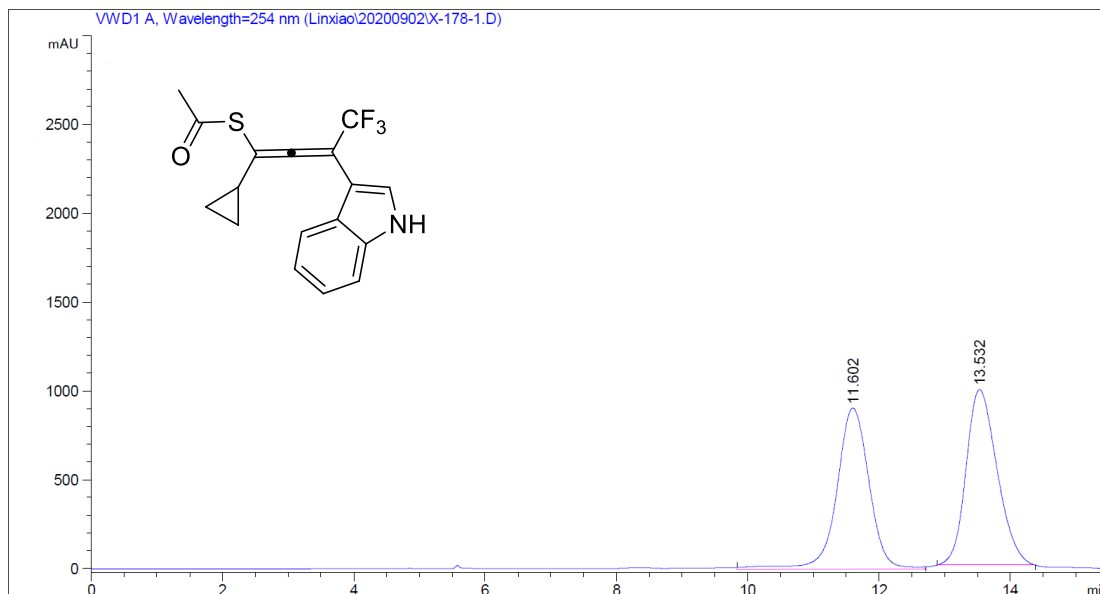


#	Time	Area	Height	Width	Symmetry	Area %
1	27.239	49715.9	560.3	1.3872	0.767	49.909
2	30.172	49896.5	497.9	1.5841	0.722	50.091

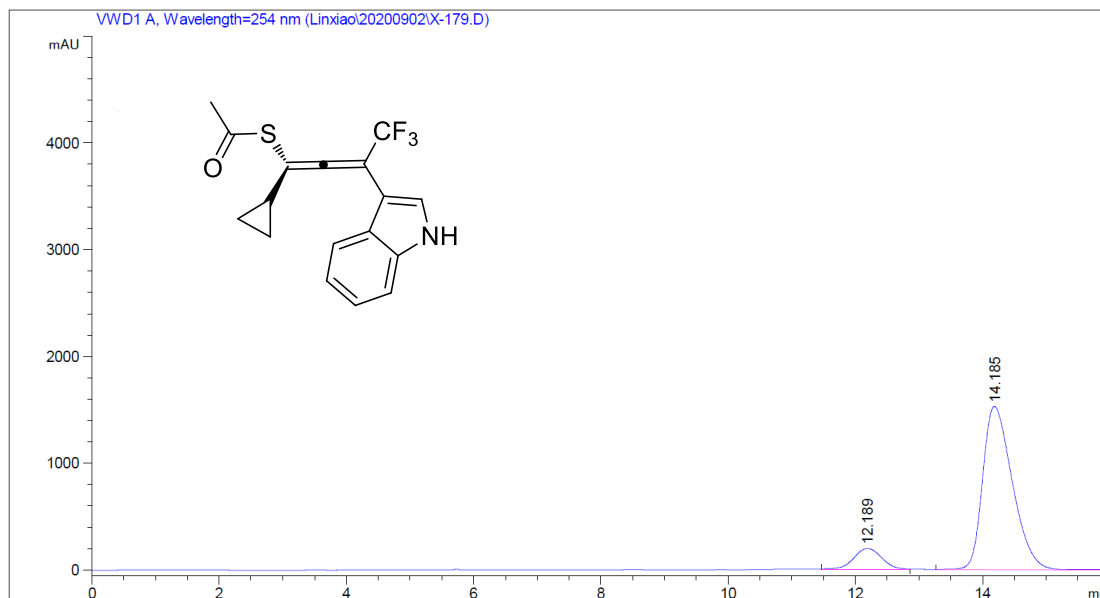


#	Time	Area	Height	Width	Symmetry	Area %
1	27.39	7537.1	108	1.1632	0.747	6.512
2	30.23	108204.8	1211.2	1.4889	0.575	93.488

**(S)-S-(1-cyclopropyl-4,4,4-trifluoro-3-(1H-indol-3-yl)buta-1,2-dien-1-yl) ethanethioate (30a)**



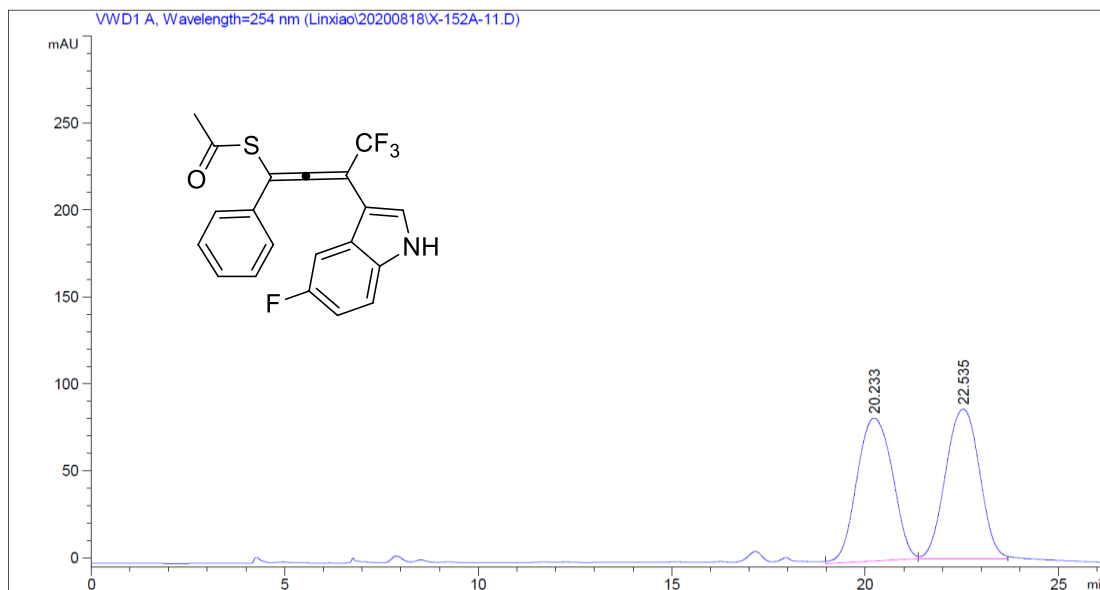
#	Time	Area	Height	Width	Symmetry	Area %
1	11.602	31495.6	907.9	0.5782	1.004	49.432
2	13.532	32219.5	985.3	0.545	0.748	50.568



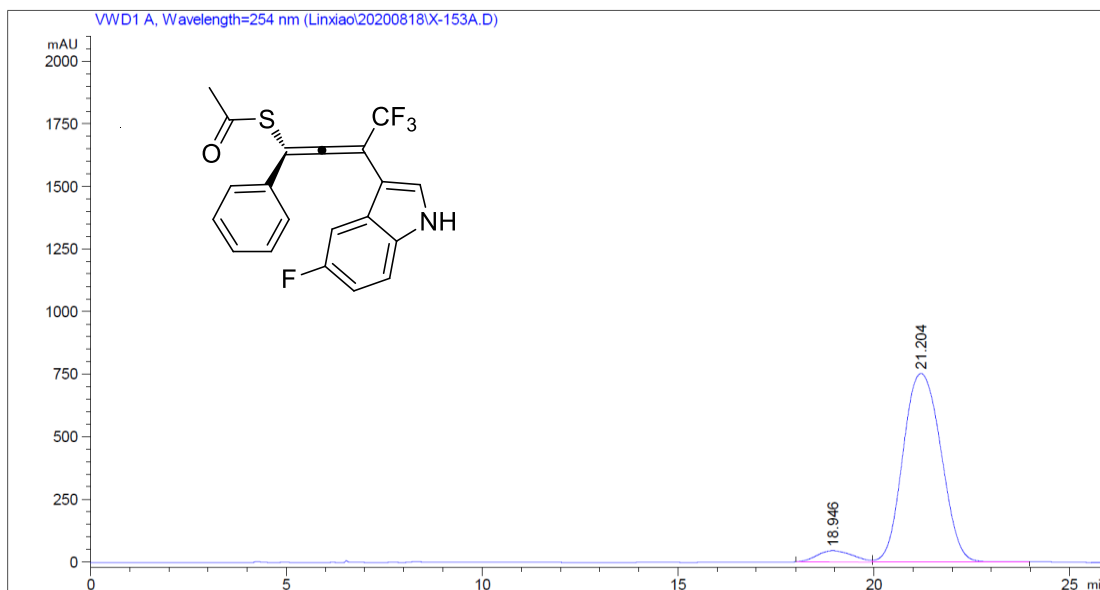
#	Time	Area	Height	Width	Symmetry	Area %
1	12.189	5642.3	191.3	0.4915	0.949	10.156
2	14.185	49916.6	1530.4	0.5255	0	89.844



**(S)-S-(4,4,4-trifluoro-3-(5-fluoro-1H-indol-3-yl)-1-phenylbuta-1,2-dien-1-yl) ethanethioate (3pa)**

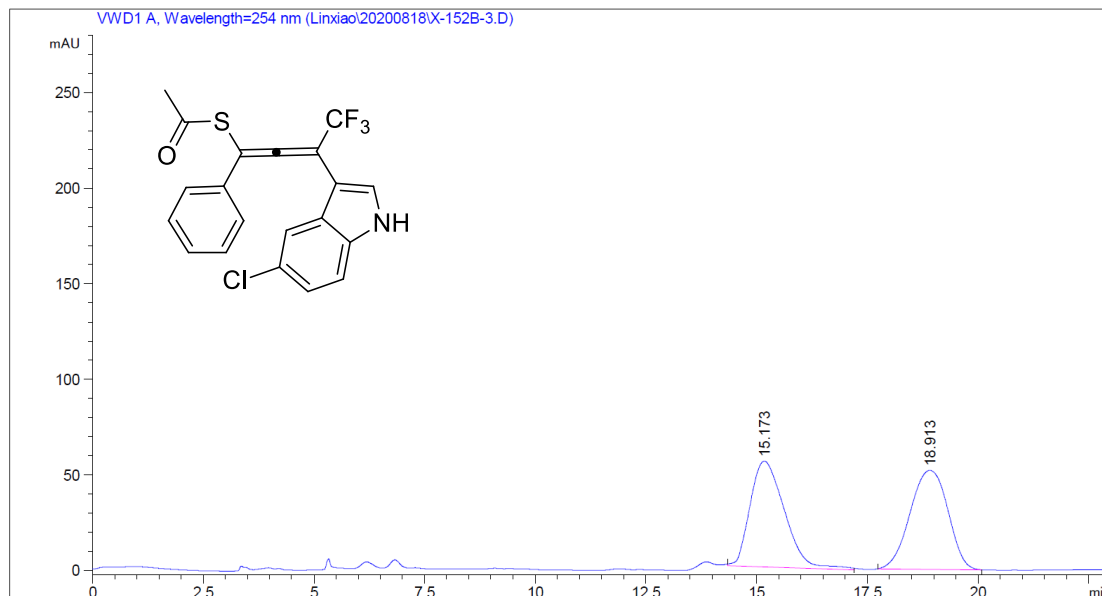


#	Time	Area	Height	Width	Symmetry	Area %
1	20.233	5271.3	82.2	1.0683	0.924	50.114
2	22.535	5247.4	86	1.0169	1.04	49.886

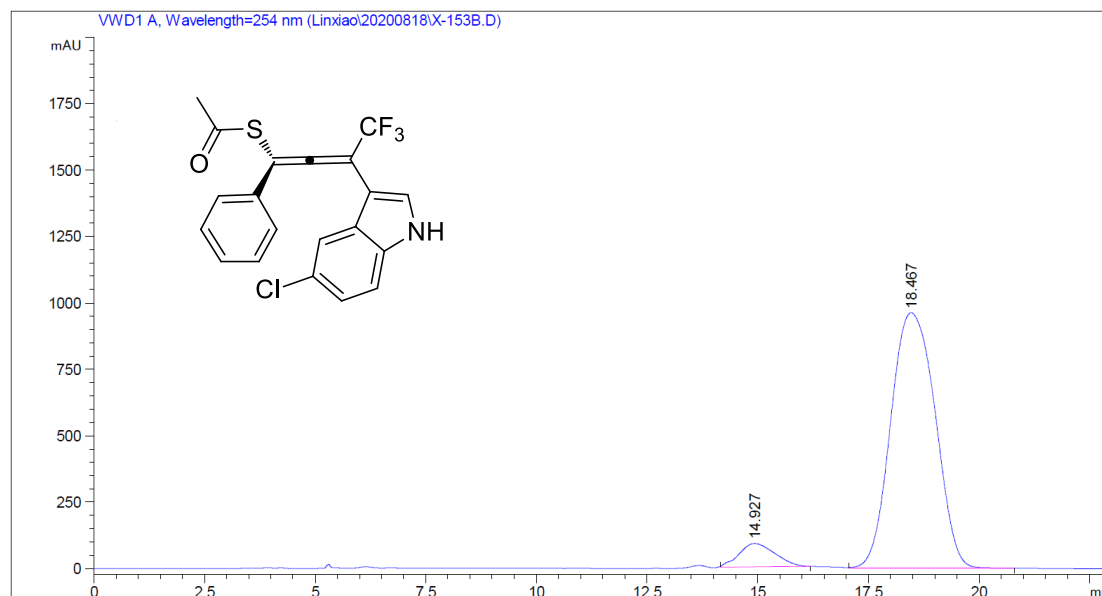


#	Time	Area	Height	Width	Symmetry	Area %
1	18.946	2733.4	43.8	1.04	0.75	5.106
2	21.204	50803.6	753.5	1.0389	0	94.894

**(S)-S-(3-(5-chloro-1H-indol-3-yl)-4,4,4-trifluoro-1-phenylbuta-1,2-dien-1-yl) ethanethioate (3qa)**

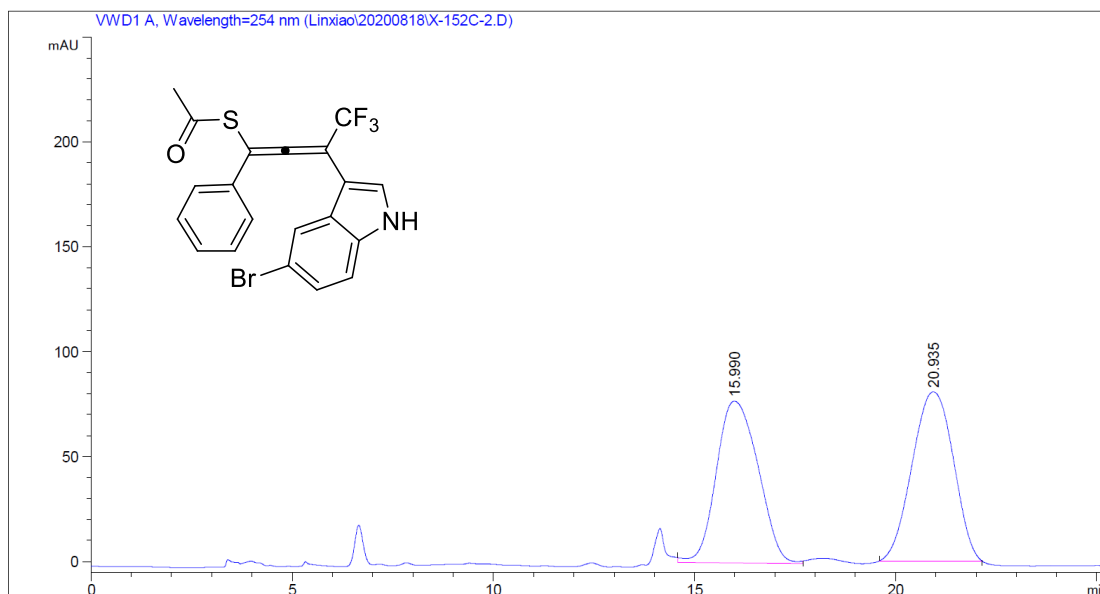


#	Time	Area	Height	Width	Symmetry	Area %
1	15.173	3006.2	55.5	0.8815	0	49.458
2	18.913	3072.1	51.8	0.9886	1.066	50.542

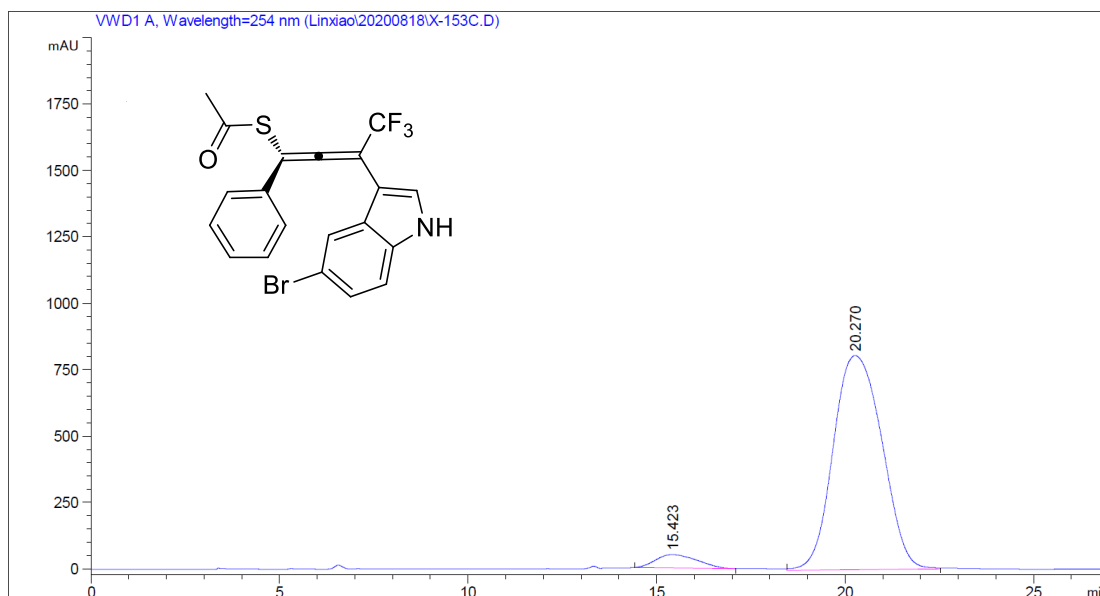


#	Time	Area	Height	Width	Symmetry	Area %
1	14.927	5029.6	89.1	0.9412	0.755	6.986
2	18.467	66967.9	961.3	1.0643	0	93.014

**(S)-S-(3-(5-bromo-1H-indol-3-yl)-4,4,4-trifluoro-1-phenylbuta-1,2-dien-1-yl) ethanethioate (3ra)**

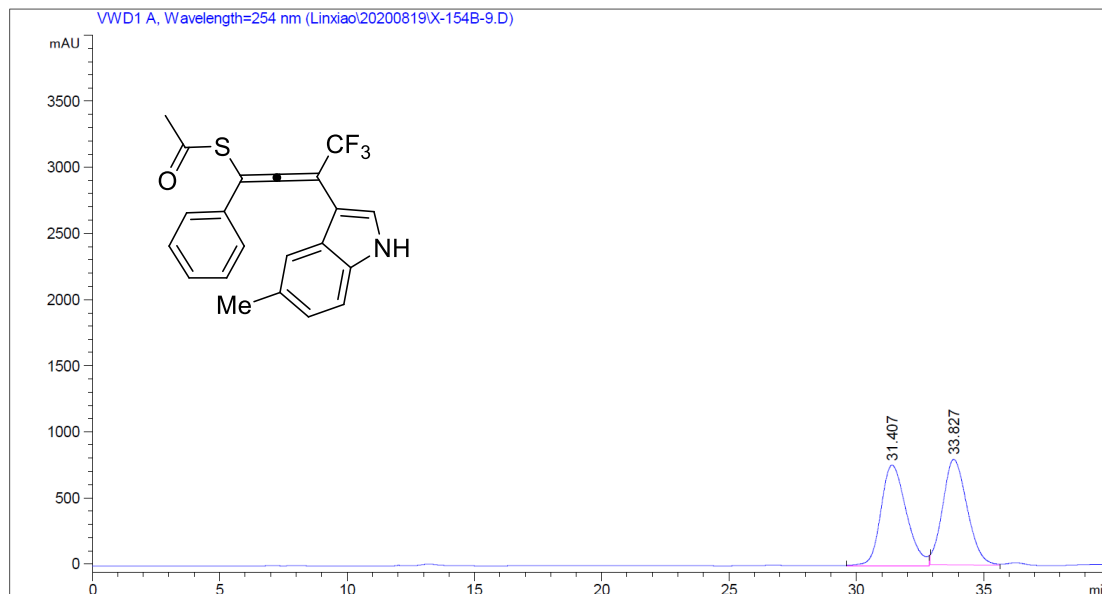


#	Time	Area	Height	Width	Symmetry	Area %
1	15.99	5572.2	77.1	1.2051	0.758	49.242
2	20.935	5743.7	80.6	1.1882	1.034	50.758

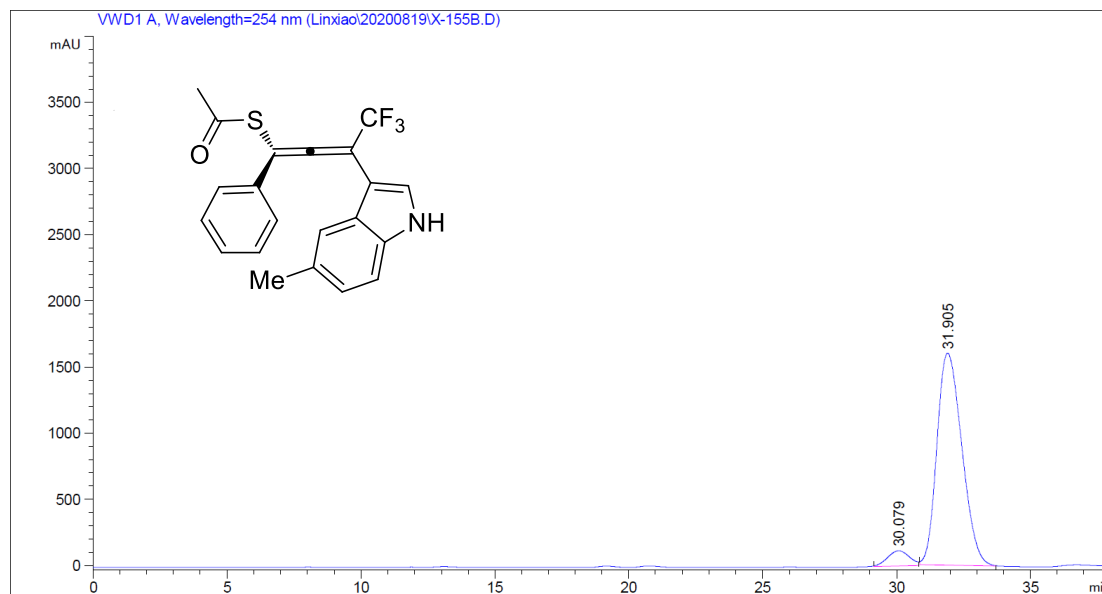


#	Time	Area	Height	Width	Symmetry	Area %
1	15.423	3797.4	49.9	1.1331	0.657	4.984
2	20.27	72396.5	805.9	1.4876	0	95.016

**(S)-S-(4,4,4-trifluoro-3-(5-methyl-1H-indol-3-yl)-1-phenylbuta-1,2-dien-1-yl) ethanethioate (3sa)**

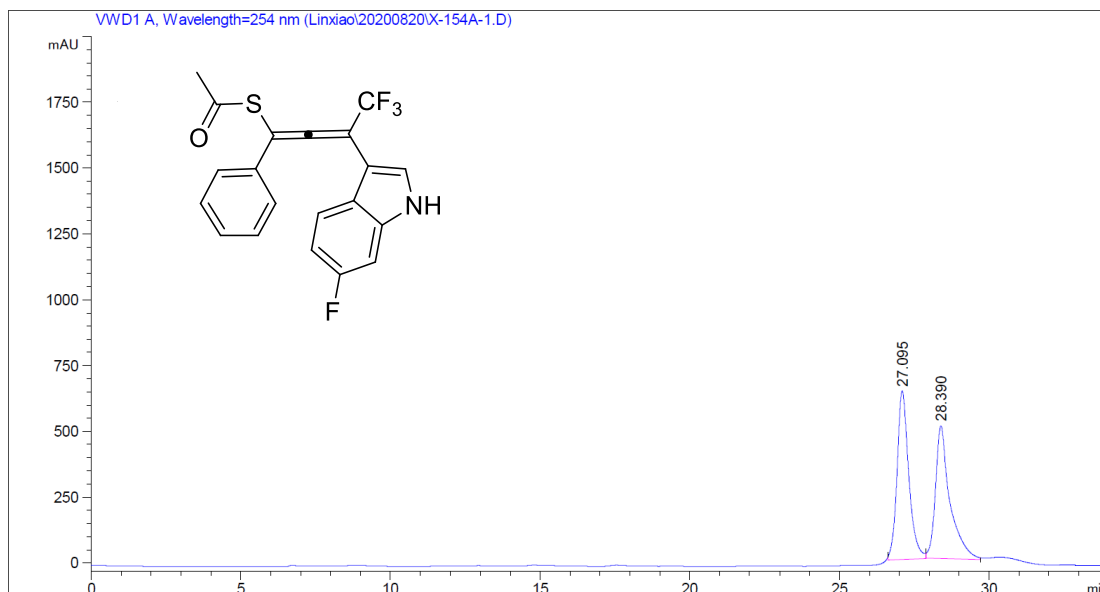


#	Time	Area	Height	Width	Symmetry	Area %
1	31.407	52993.9	760.5	1.1614	0.761	49.844
2	33.827	53325	798.3	1.1133	0.792	50.156

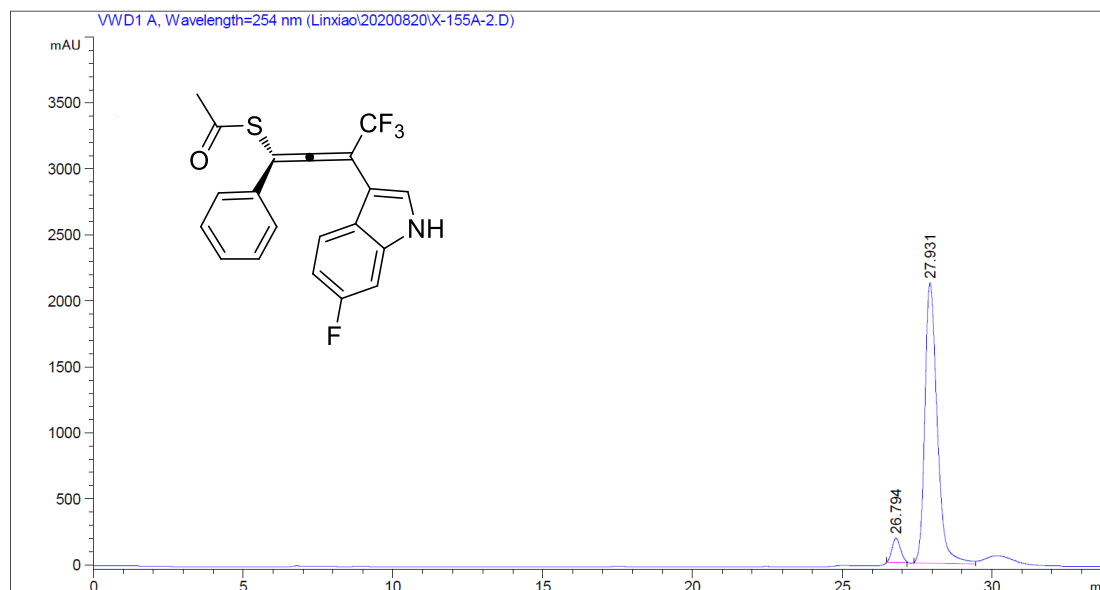


#	Time	Area	Height	Width	Symmetry	Area %
1	30.079	6353.8	113.2	0.9351	1.023	5.765
2	31.905	103854	1602.6	1.0801	0.728	94.235

**(S)-S-(4,4,4-trifluoro-3-(6-fluoro-1H-indol-3-yl)-1-phenylbuta-1,2-dien-1-yl) ethanethioate (3ta)**

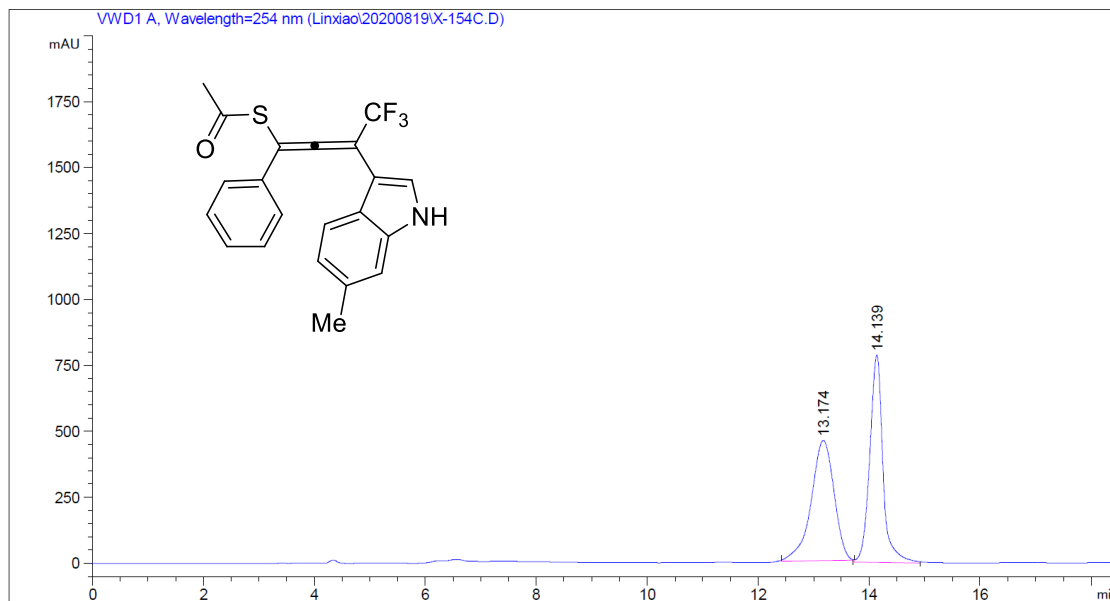


#	Time	Area	Height	Width	Symmetry	Area %
1	27.095	17405.1	641	0.4526	0.747	50.730
2	28.39	16904	504.8	0.5581	0.586	49.270

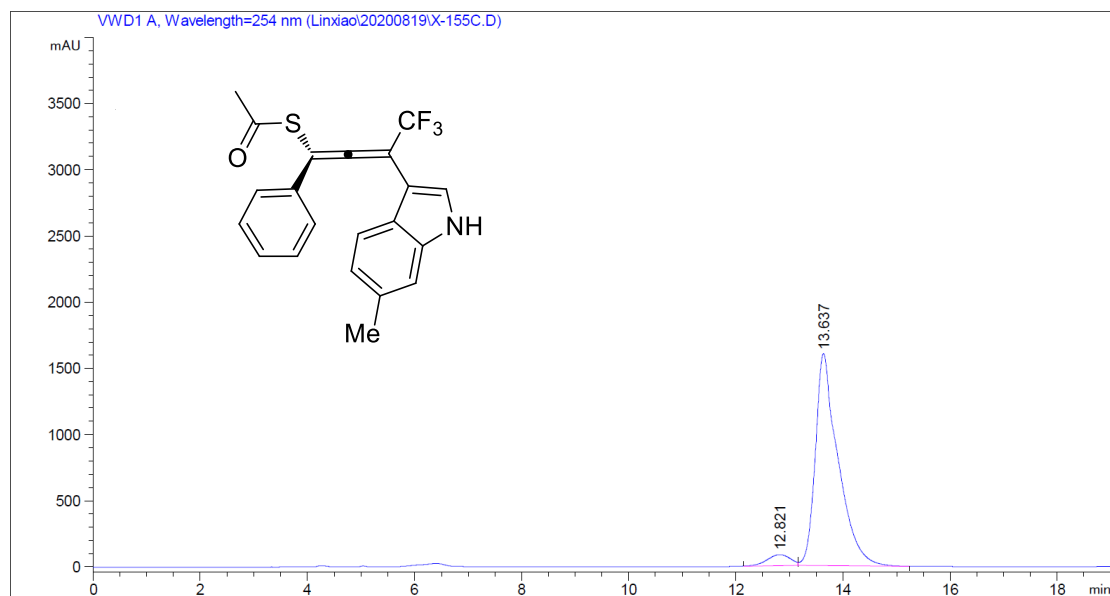


#	Time	Area	Height	Width	Symmetry	Area %
1	26.794	3569	184	0.3234	0.869	5.514
2	27.931	61153	2125.5	0.4214	0	94.486

**(S)-S-(4,4,4-trifluoro-3-(6-methyl-1H-indol-3-yl)-1-phenylbuta-1,2-dien-1-yl) ethanethioate (3ua)**

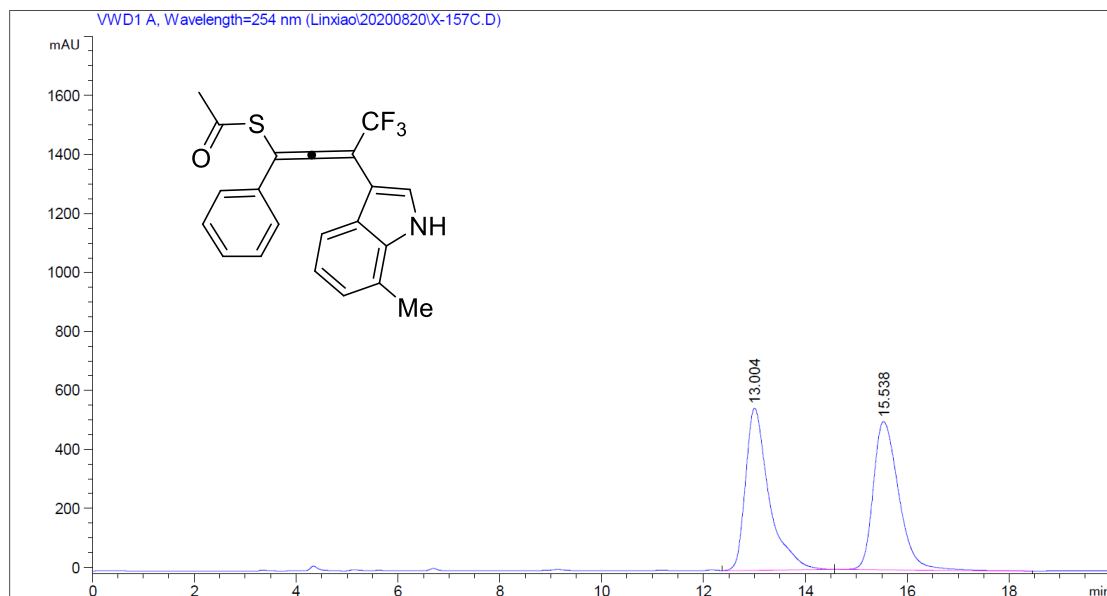


#	Time	Area	Height	Width	Symmetry	Area %
1	13.174	13076.9	456	0.4779	1.113	50.206
2	14.139	12969.4	785.8	0.2751	1.077	49.794

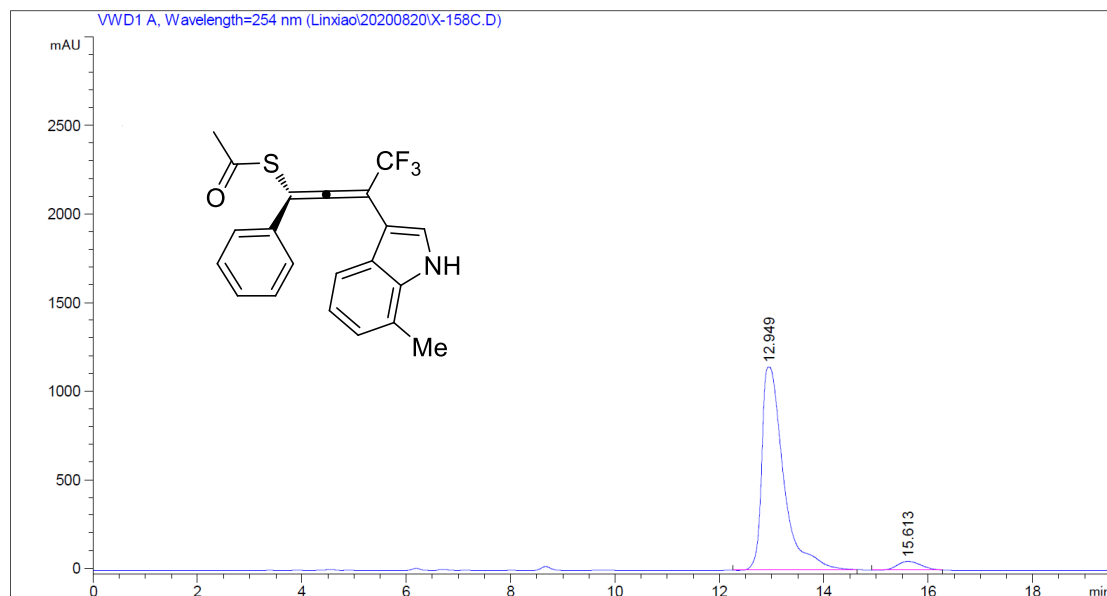


#	Time	Area	Height	Width	Symmetry	Area %
1	12.821	2538.2	84.1	0.5028	1.2	5.081
2	13.637	47412.3	1602.8	0.493	0.541	94.919

**(S)-S-(4,4,4-trifluoro-3-(7-methyl-1H-indol-3-yl)-1-phenylbuta-1,2-dien-1-yl) ethanethioate (3va)**

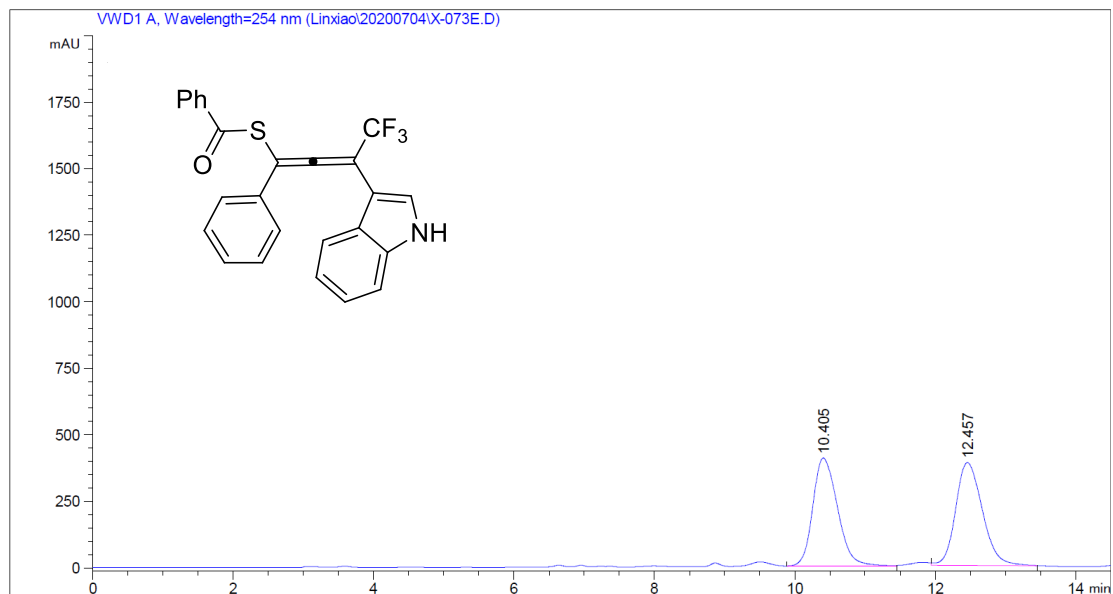


#	Time	Area	Height	Width	Symmetry	Area %
1	13.004	17670.2	549.5	0.4722	0.575	50.341
2	15.538	17430.8	502.3	0.5398	0.641	49.659

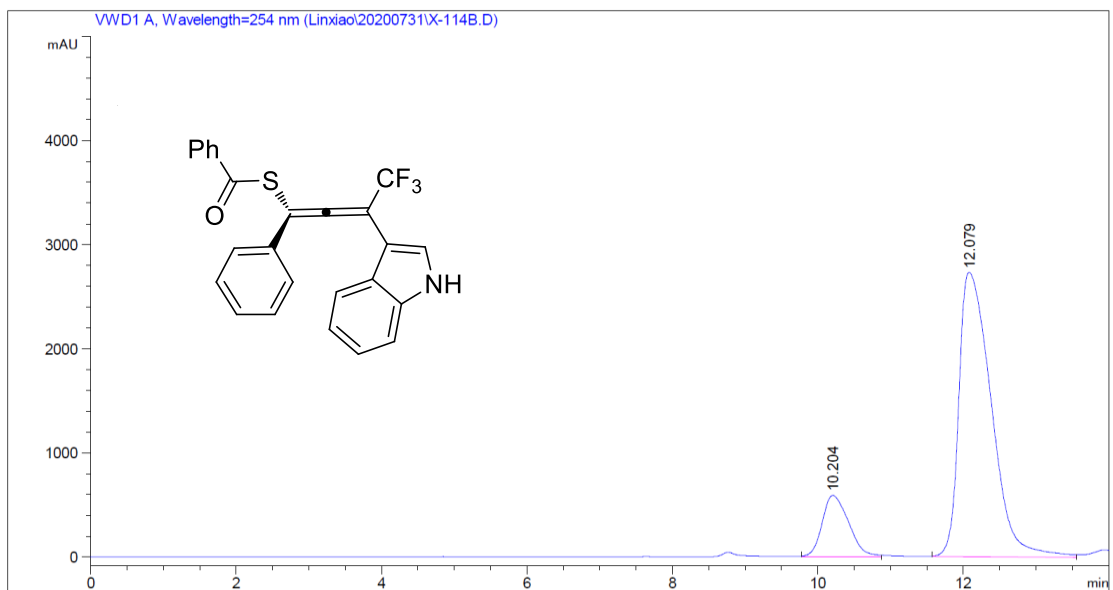


#	Time	Area	Height	Width	Symmetry	Area %
1	12.949	33117	1147.3	0.4811	0.465	95.623
2	15.613	1515.9	48.6	0.5197	0.784	4.377

**(S)-S-(4,4,4-trifluoro-3-(1H-indol-3-yl)-1-phenylbuta-1,2-dien-1-yl) benzothioate (3ab)**



#	Time	Area	Height	Width	Symmetry	Area %
1	10.405	9933.8	406	0.4078	0.714	49.230
2	12.457	10244.5	386.8	0.4414	0.763	50.770

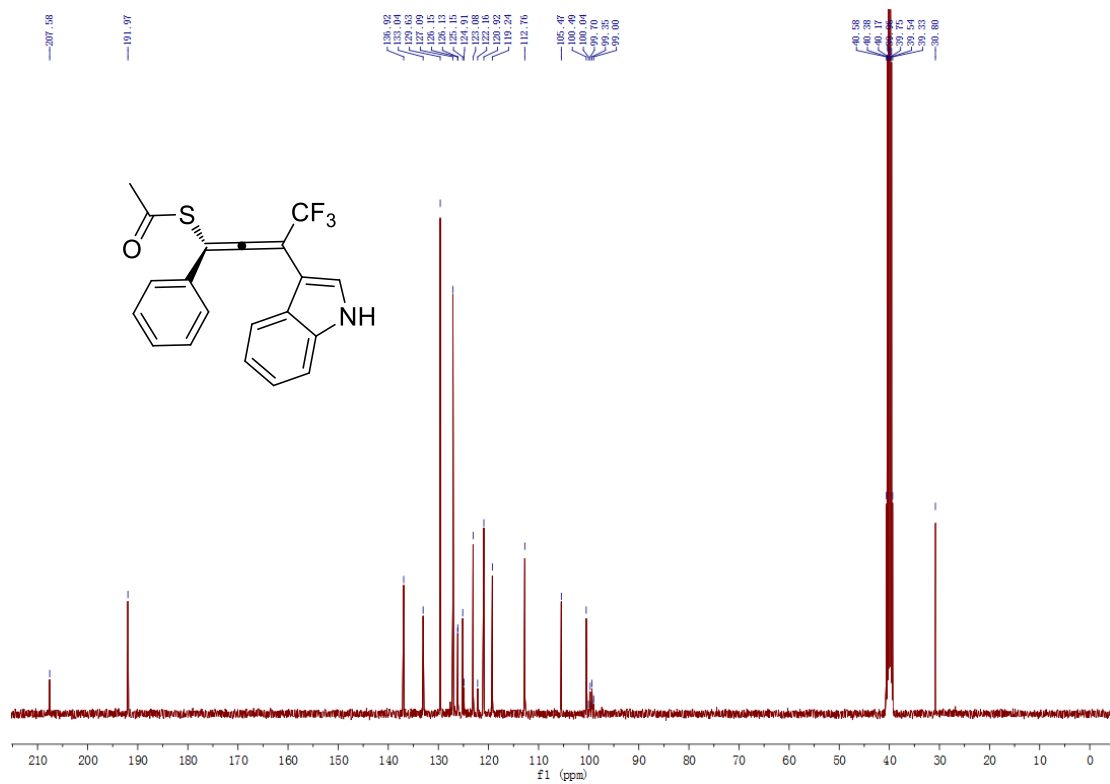
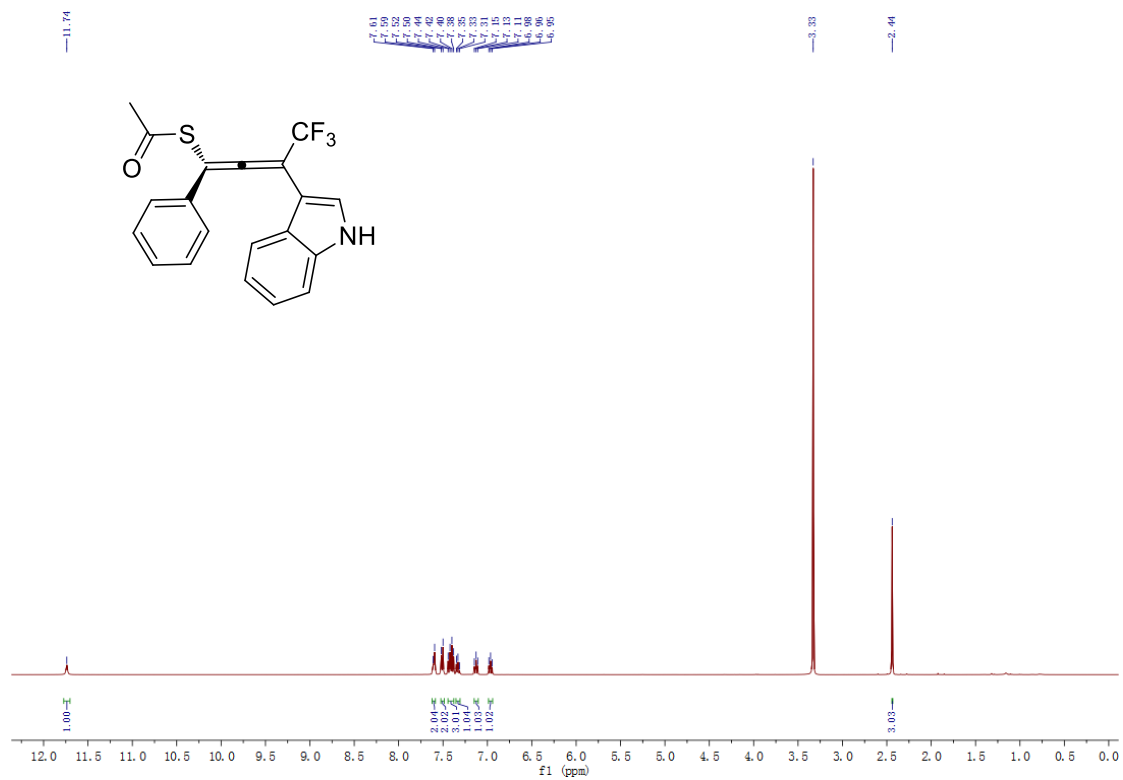


#	Time	Area	Height	Width	Symmetry	Area %
1	10.204	15071.9	589.2	0.4145	0.641	14.973
2	12.079	85589.8	2730.1	0.4955	0.444	85.027

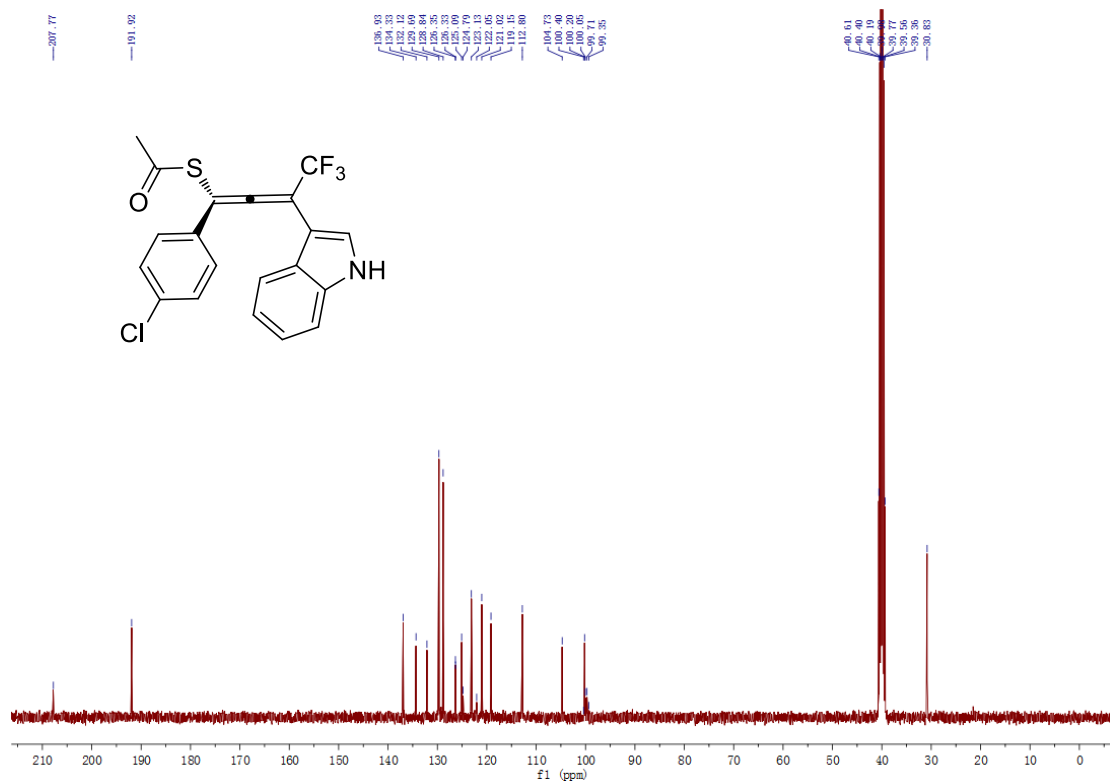
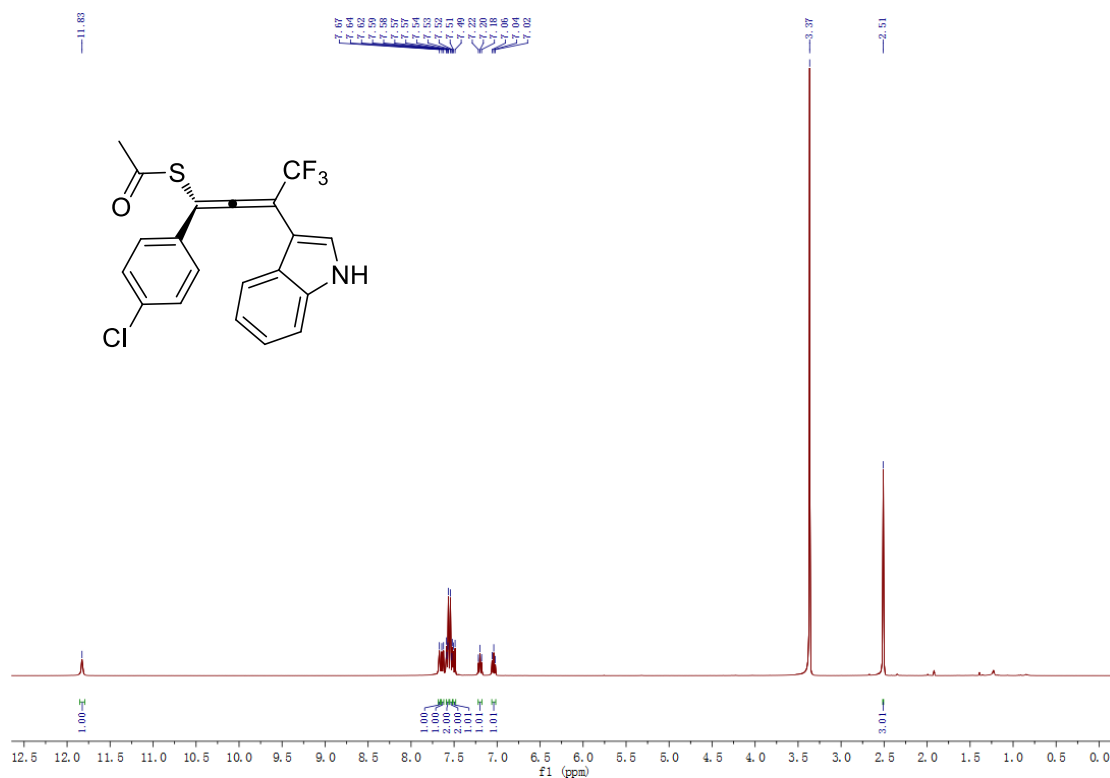


## J: NMR Analysis

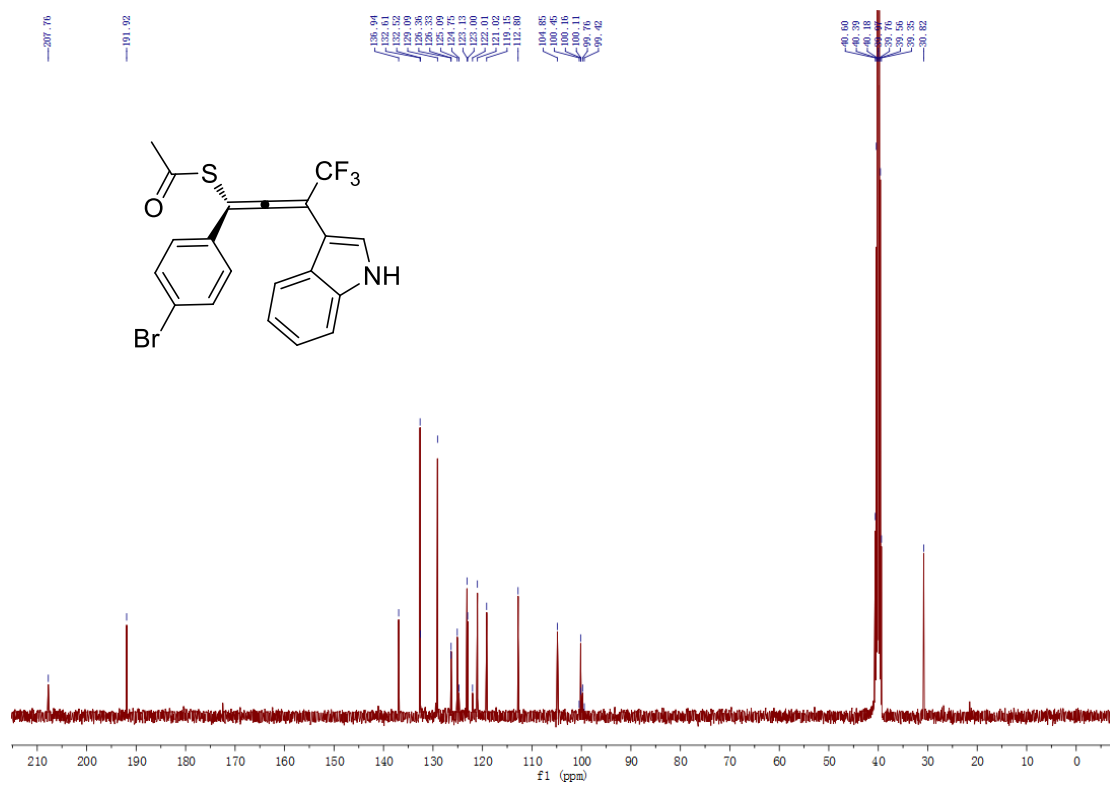
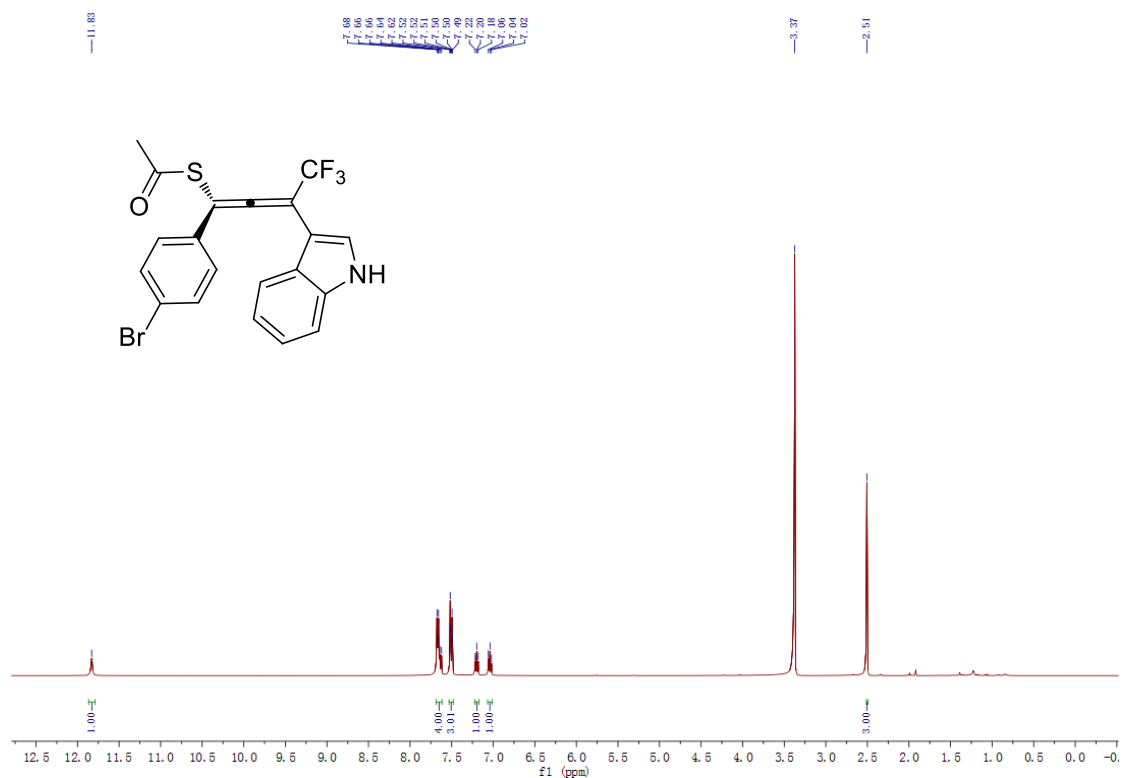
### (*S,S*)-(4,4,4-trifluoro-3-(1*H*-indol-3-yl)-1-phenylbuta-1,2-dien-1-yl) ethanethioate (3aa)



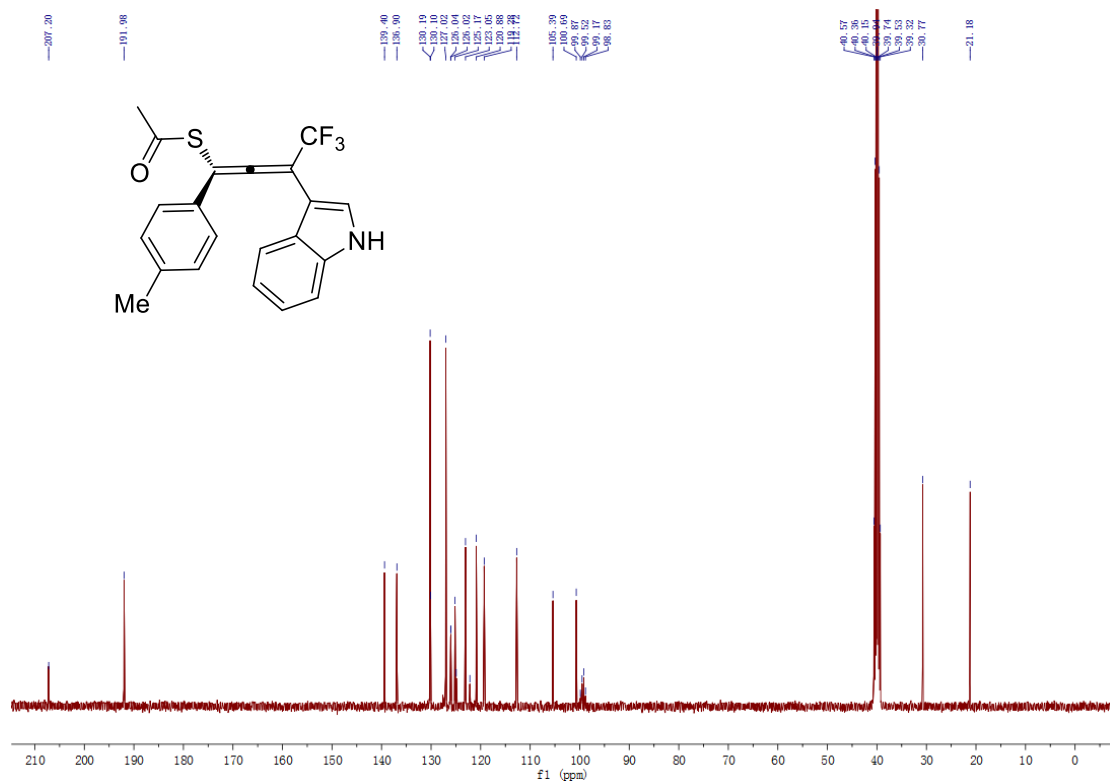
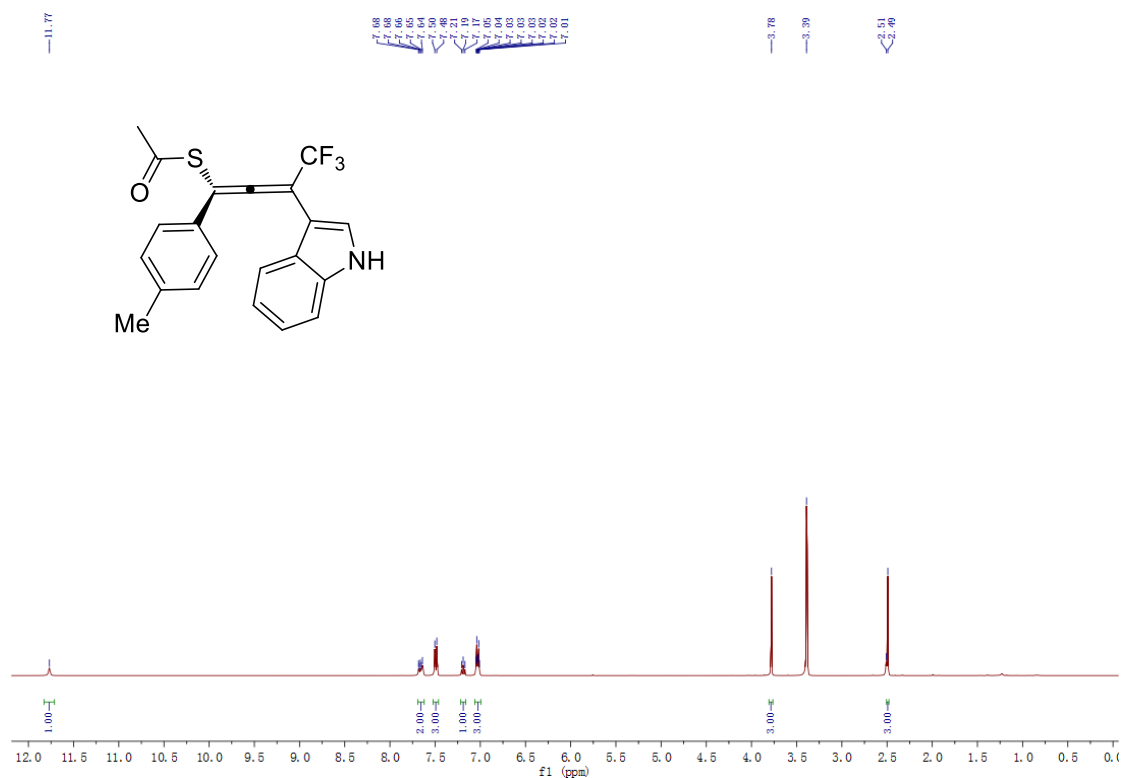
**(S)-S-(1-(4-chlorophenyl)-4,4,4-trifluoro-3-(1H-indol-3-yl)buta-1,2-dien-1-yl) ethanethioate (3ba)**



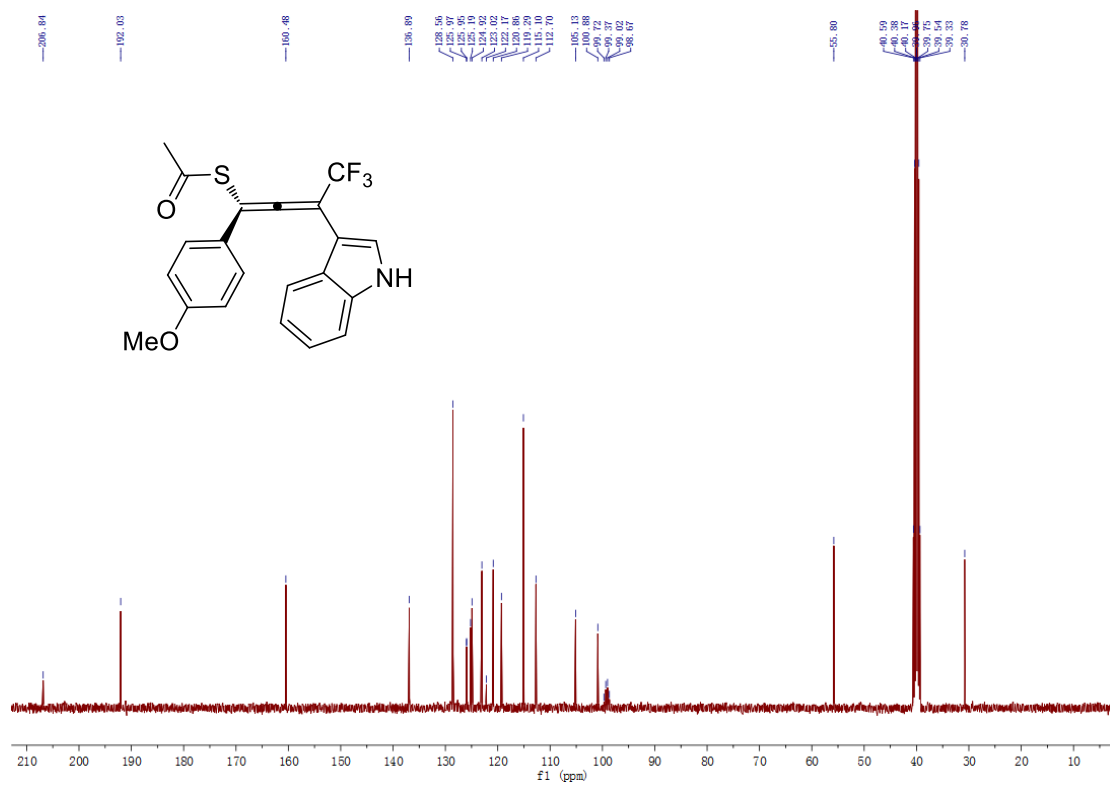
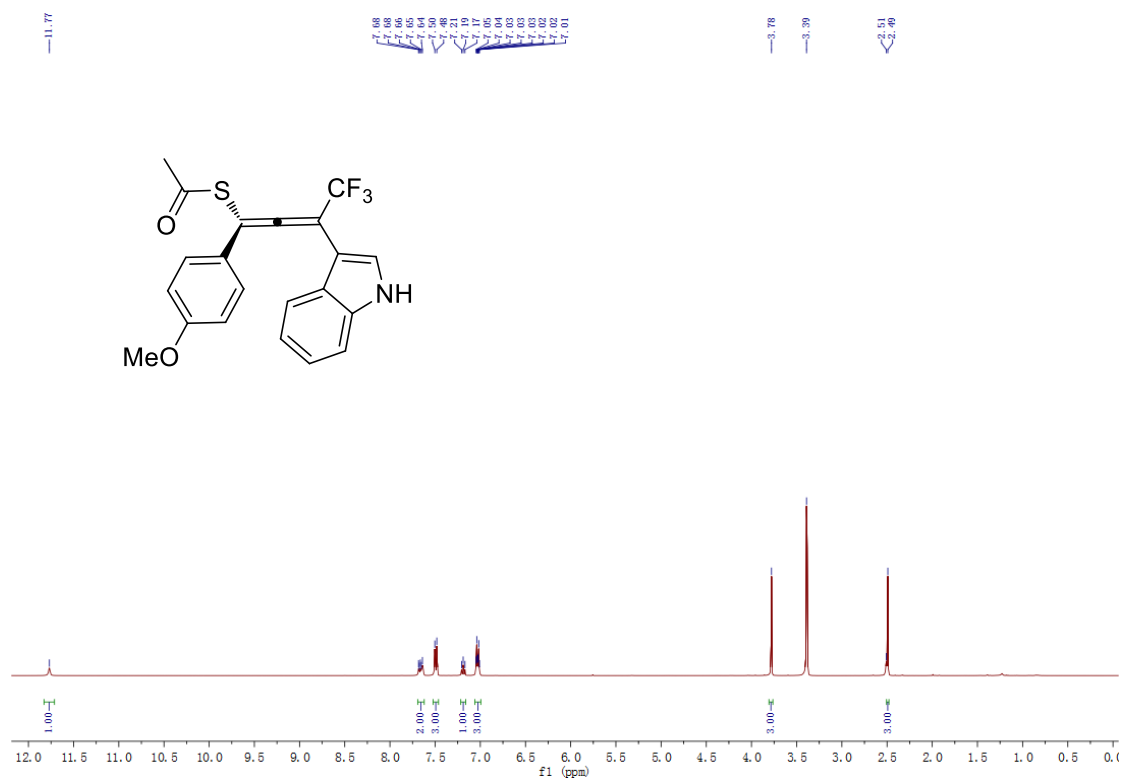
**(S)-S-(1-(4-bromophenyl)-4,4,4-trifluoro-3-(1H-indol-3-yl)buta-1,2-dien-1-yl) ethanethioate (3ca)**



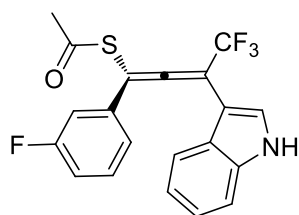
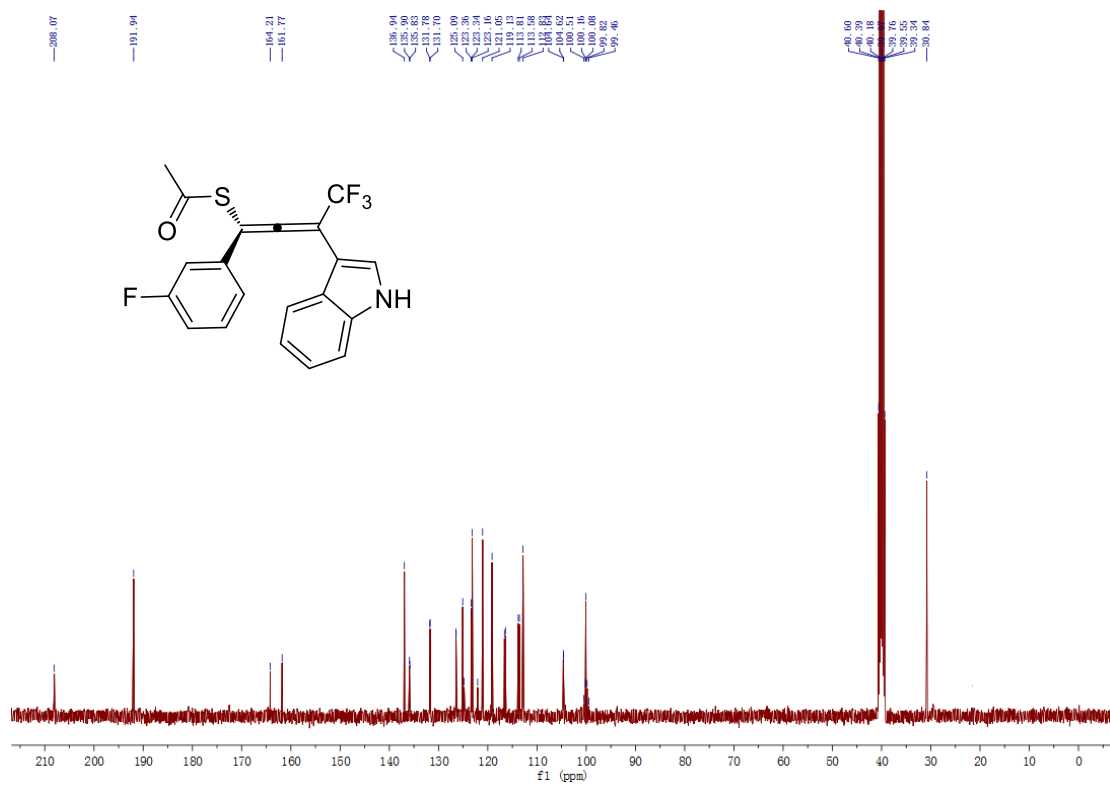
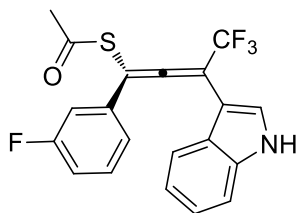
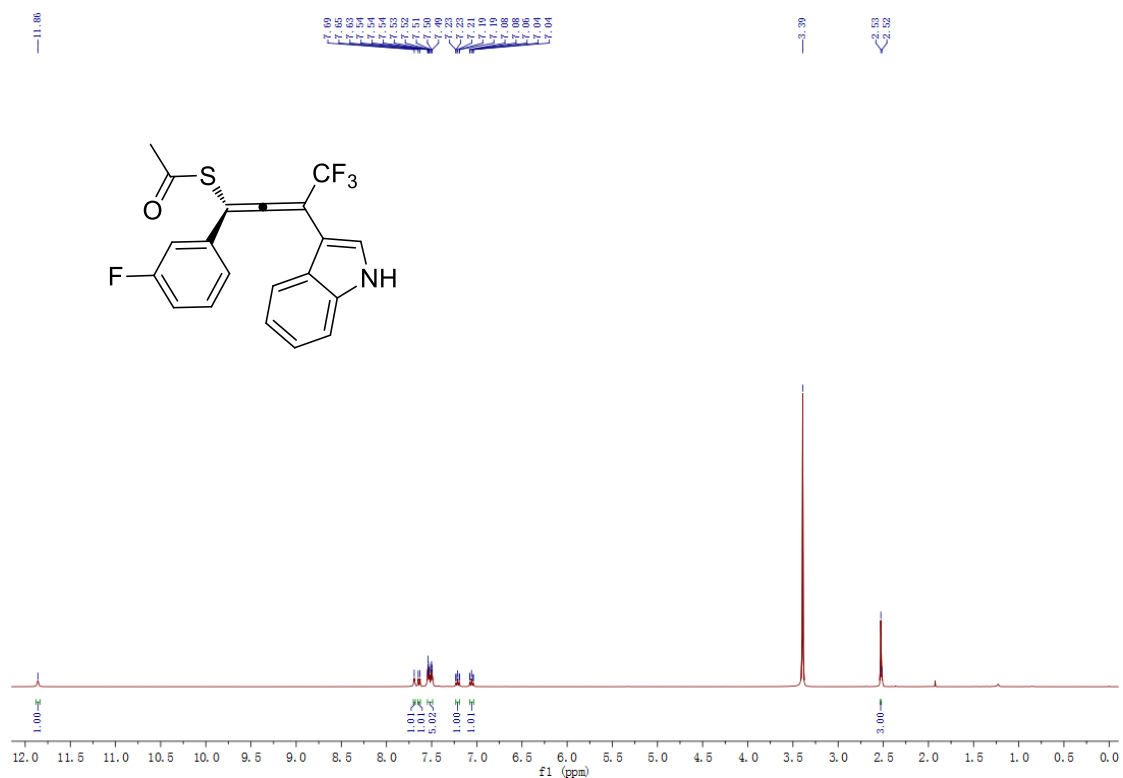
**(S)-S-(4,4,4-trifluoro-3-(1H-indol-3-yl)-1-(p-tolyl)buta-1,2-dien-1-yl)ethanethioate (3da)**



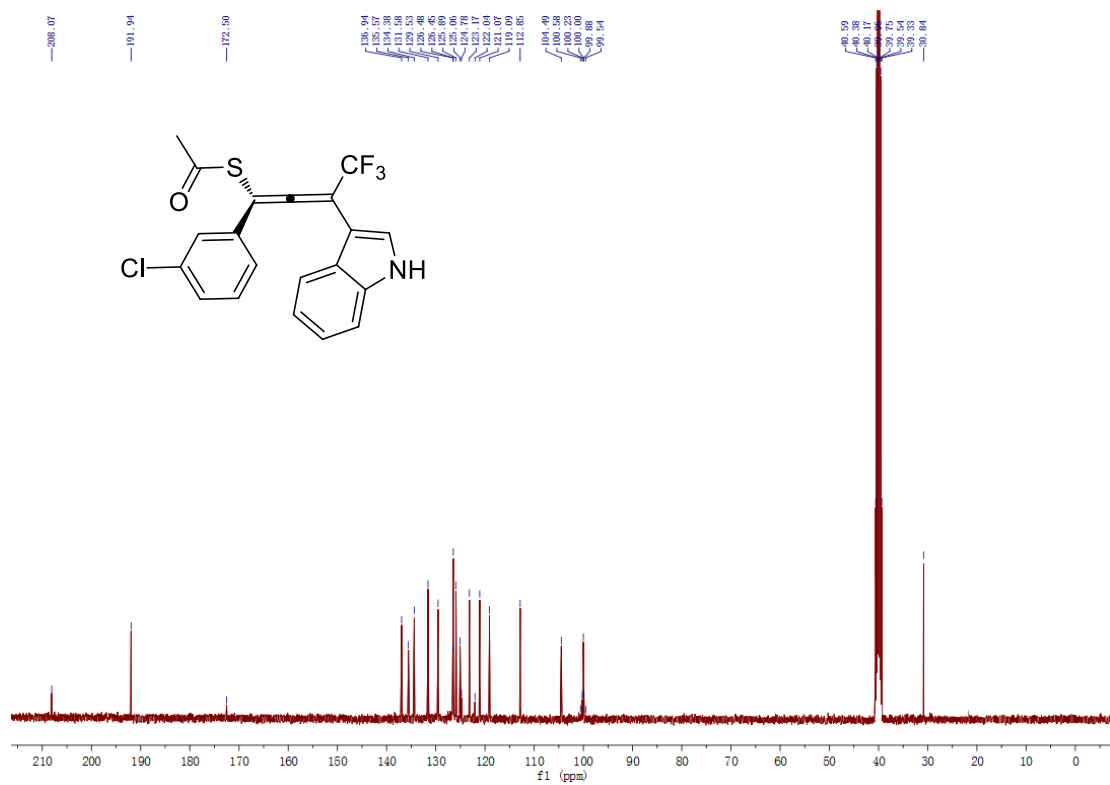
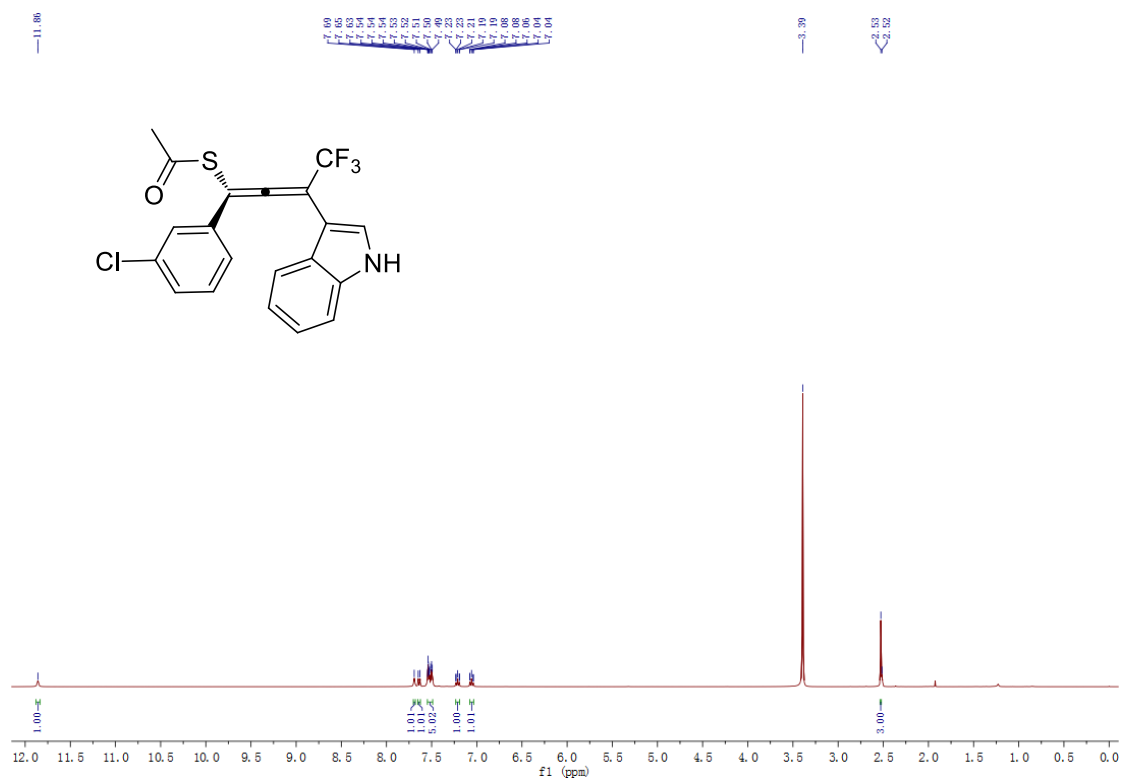
**(S)-S-(4,4,4-trifluoro-3-(1H-indol-3-yl)-1-(4-methoxyphenyl)buta-1,2-dien-1-yl) ethanethioate (3ea)**



**(S)-S-(4,4,4-trifluoro-1-(3-fluorophenyl)-3-(1H-indol-3-yl)buta-1,2-dien-1-yl)ethanethioate (3fa)**



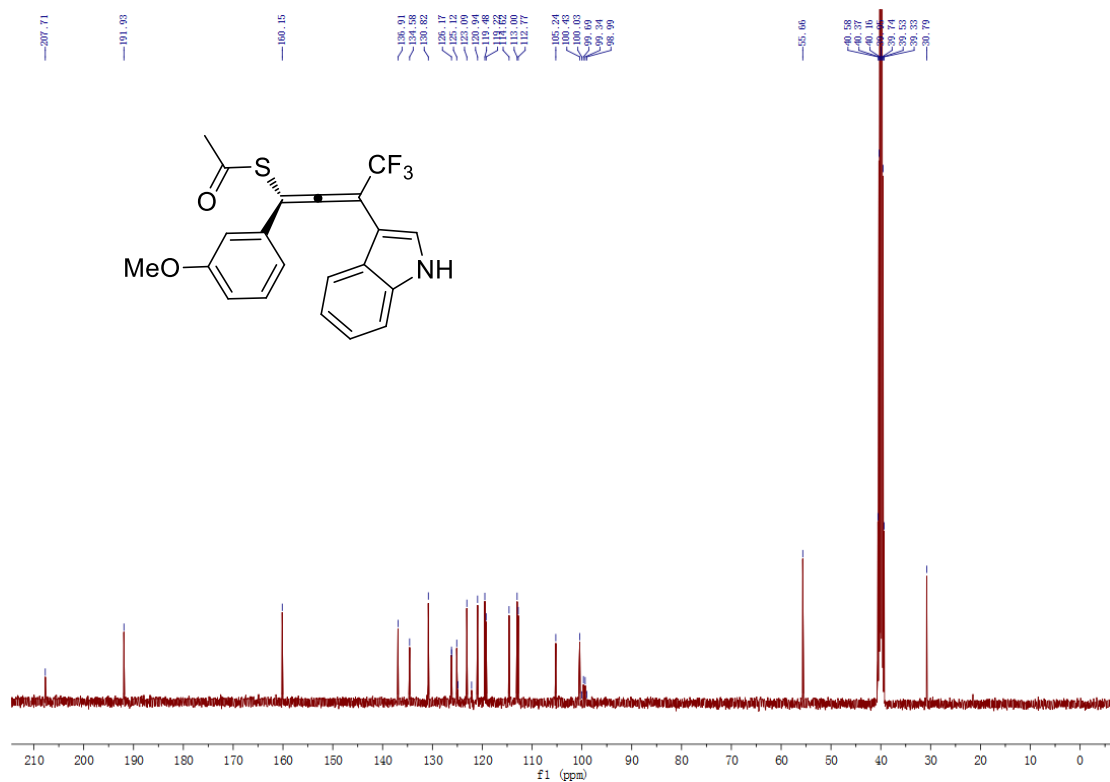
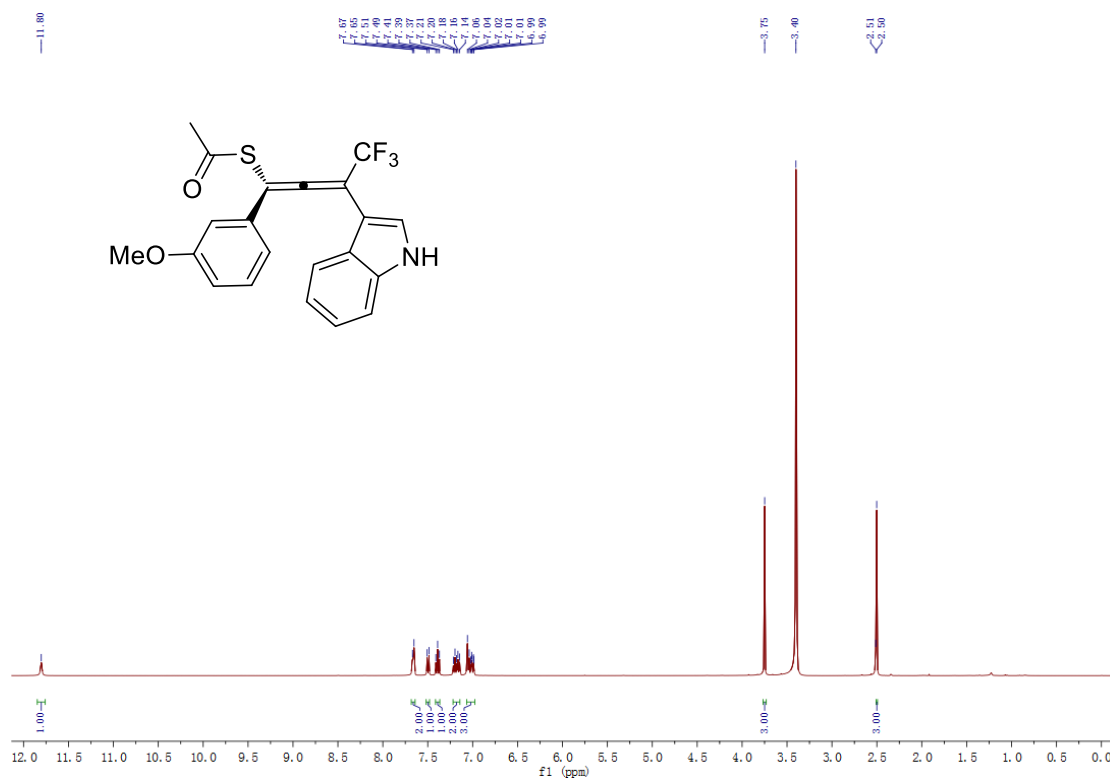
**(S)-S-(1-(3-chlorophenyl)-4,4,4-trifluoro-3-(1H-indol-3-yl)buta-1,2-dien-1-yl)ethanethioate (3ga)**



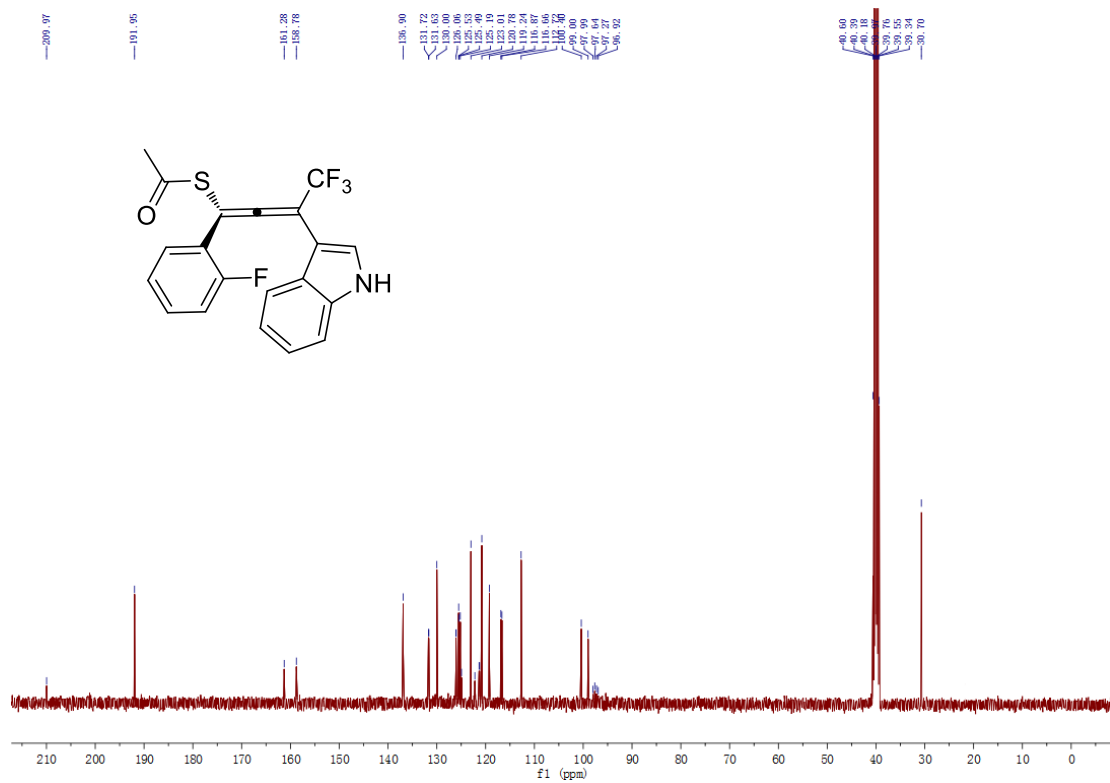
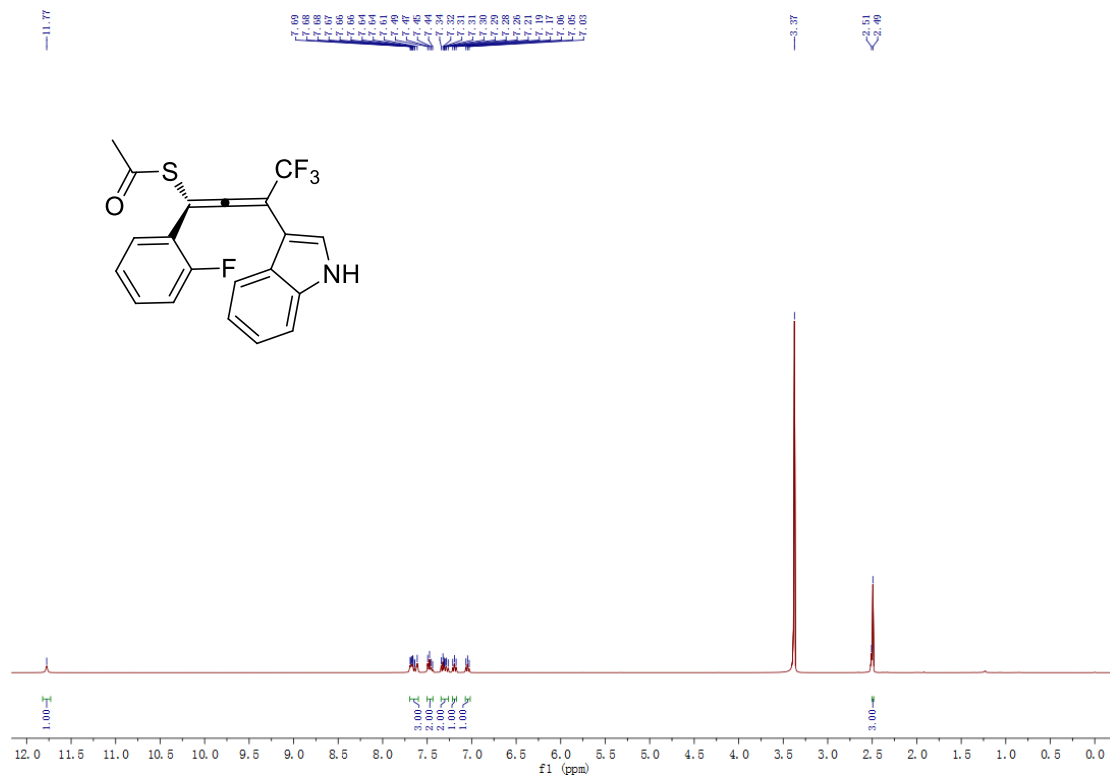




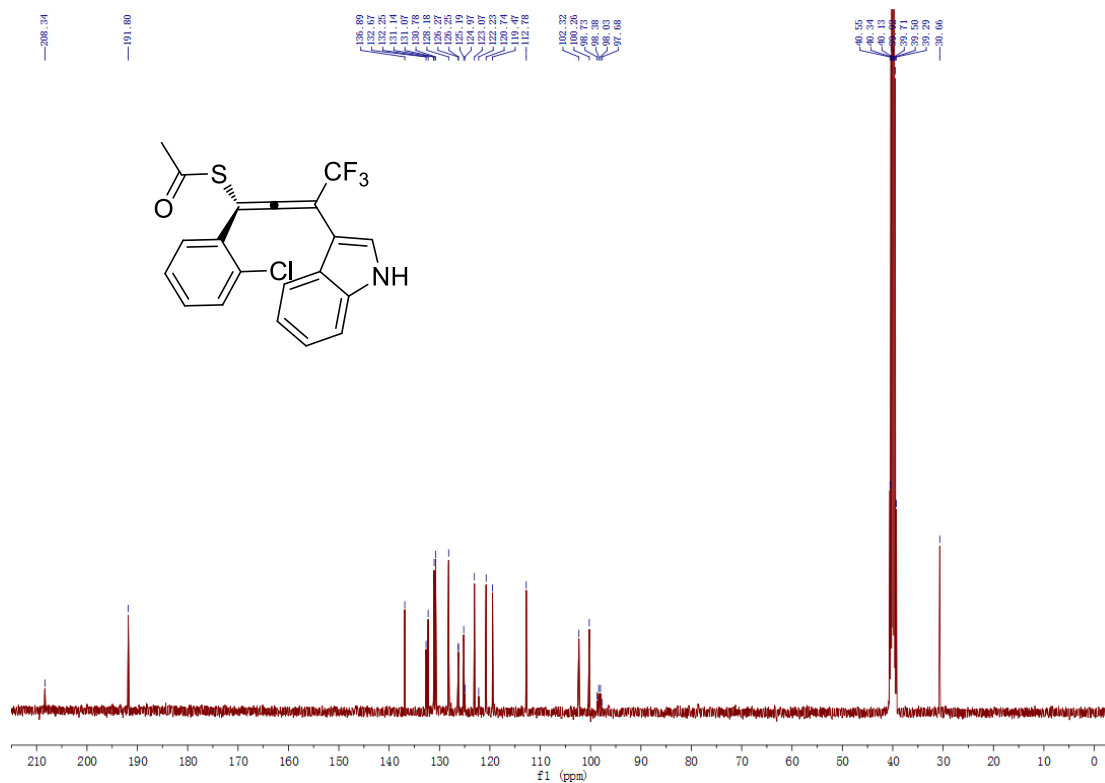
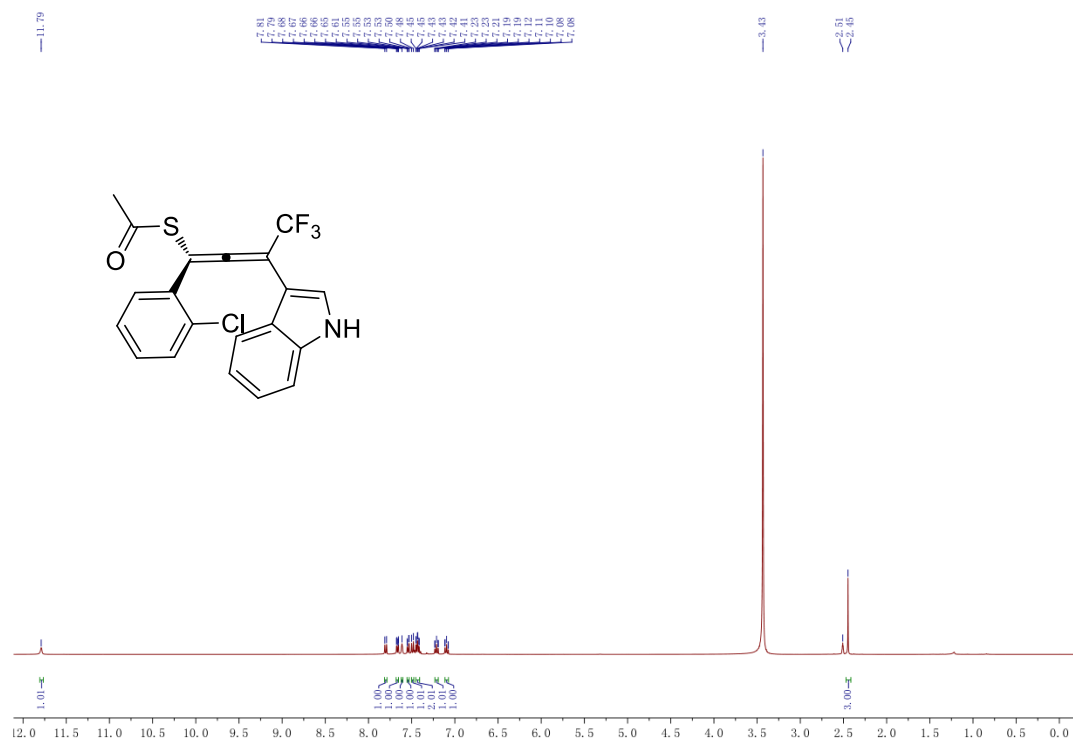
**(S)-S-(4,4,4-trifluoro-3-(1H-indol-3-yl)-1-(3-methoxyphenyl)buta-1,2-dien-1-yl) ethanethioate (3ia)**



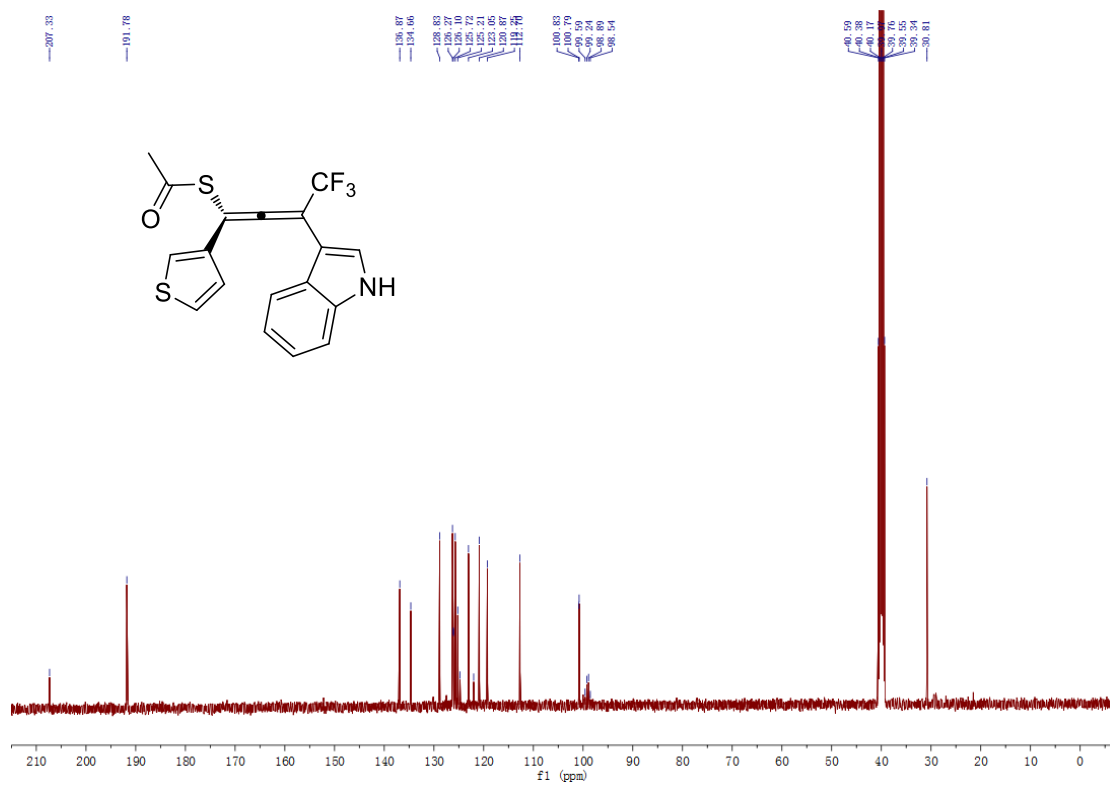
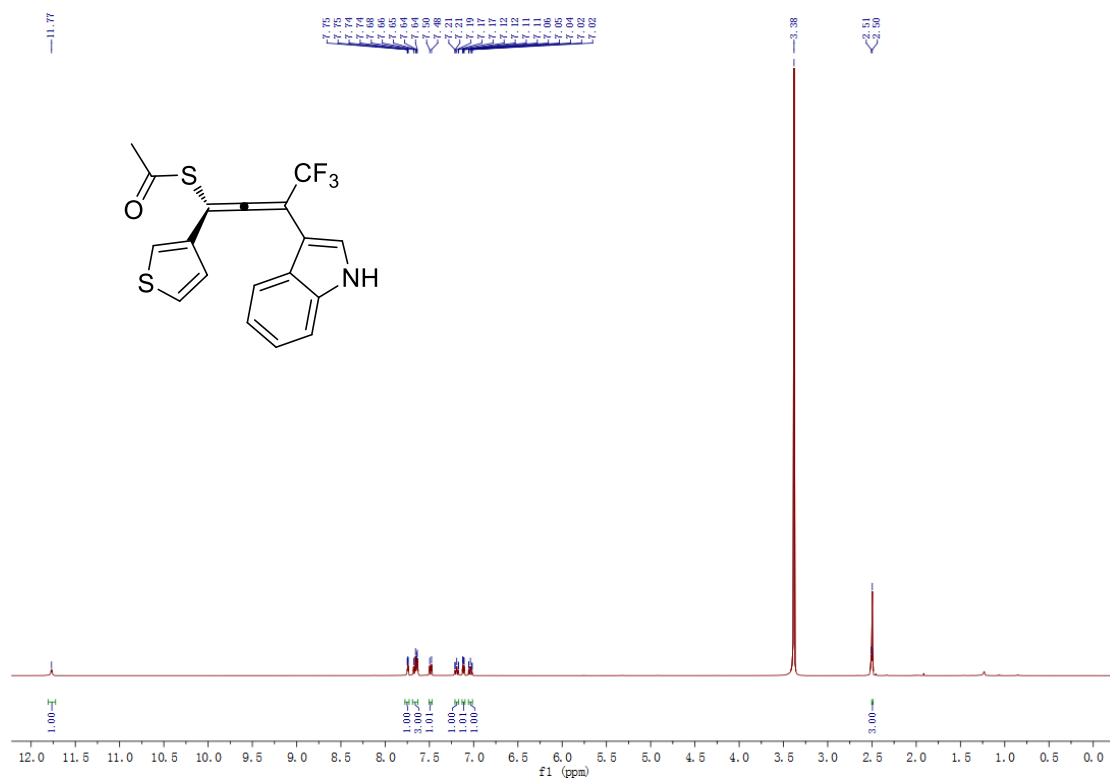
**(S)-S-(4,4,4-trifluoro-1-(2-fluorophenyl)-3-(1H-indol-3-yl)buta-1,2-dien-1-yl)ethanethioate (3ja)**



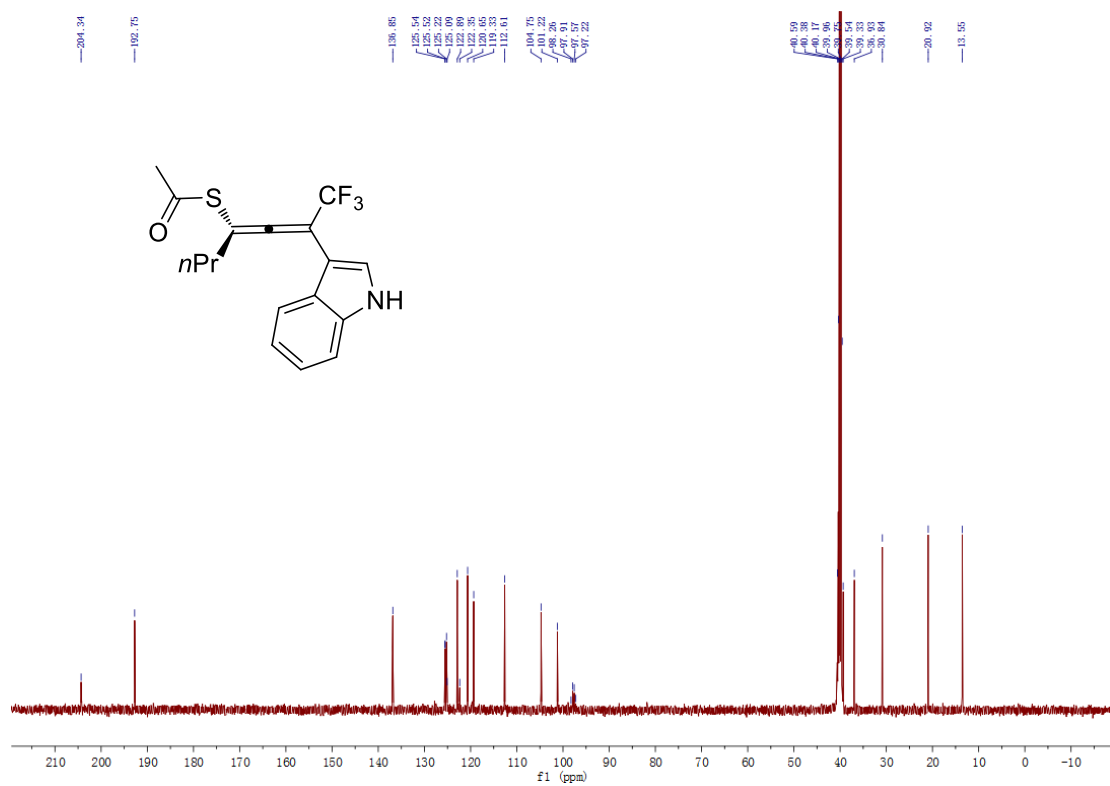
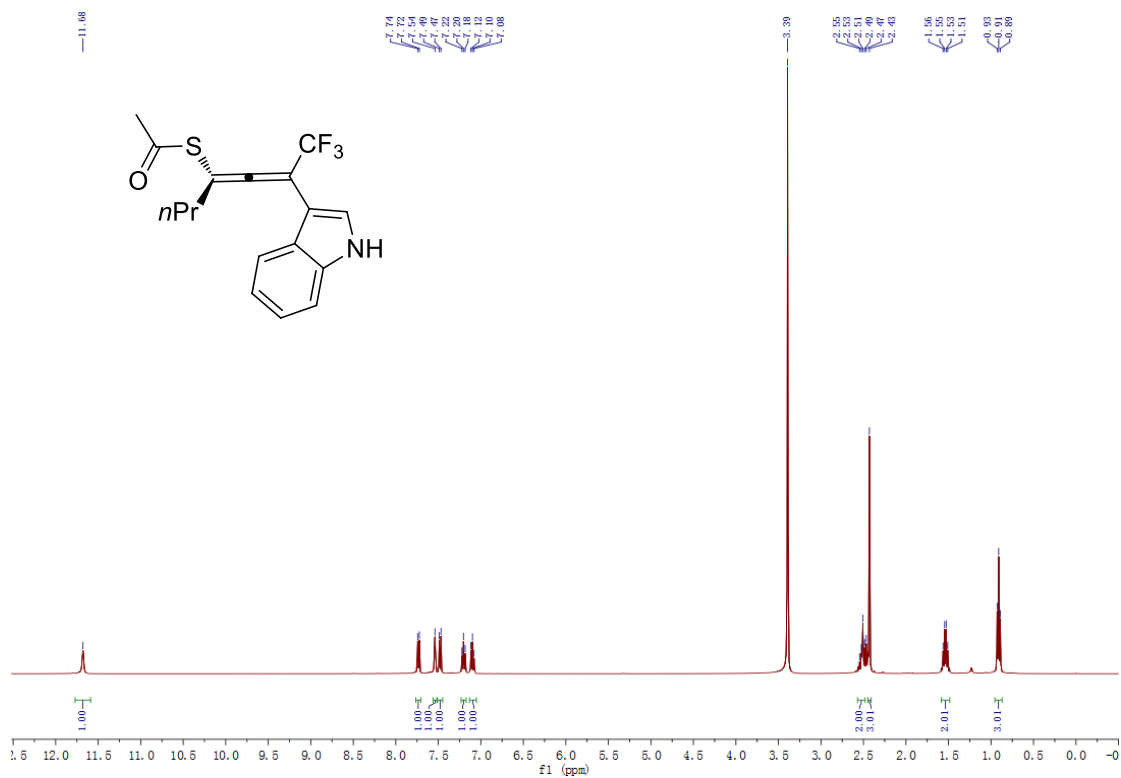
**(S)-S-(1-(2-chlorophenyl)-4,4,4-trifluoro-3-(1H-indol-3-yl)buta-1,2-dien-1-yl) ethanethioate (3ka)**



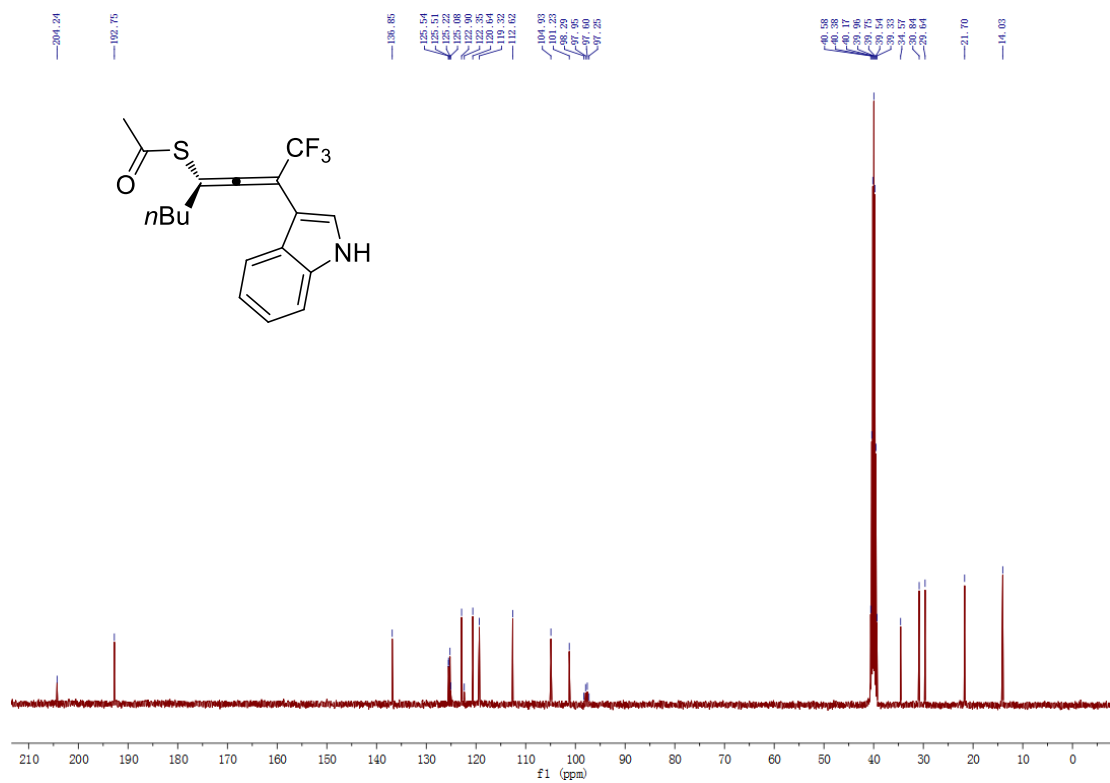
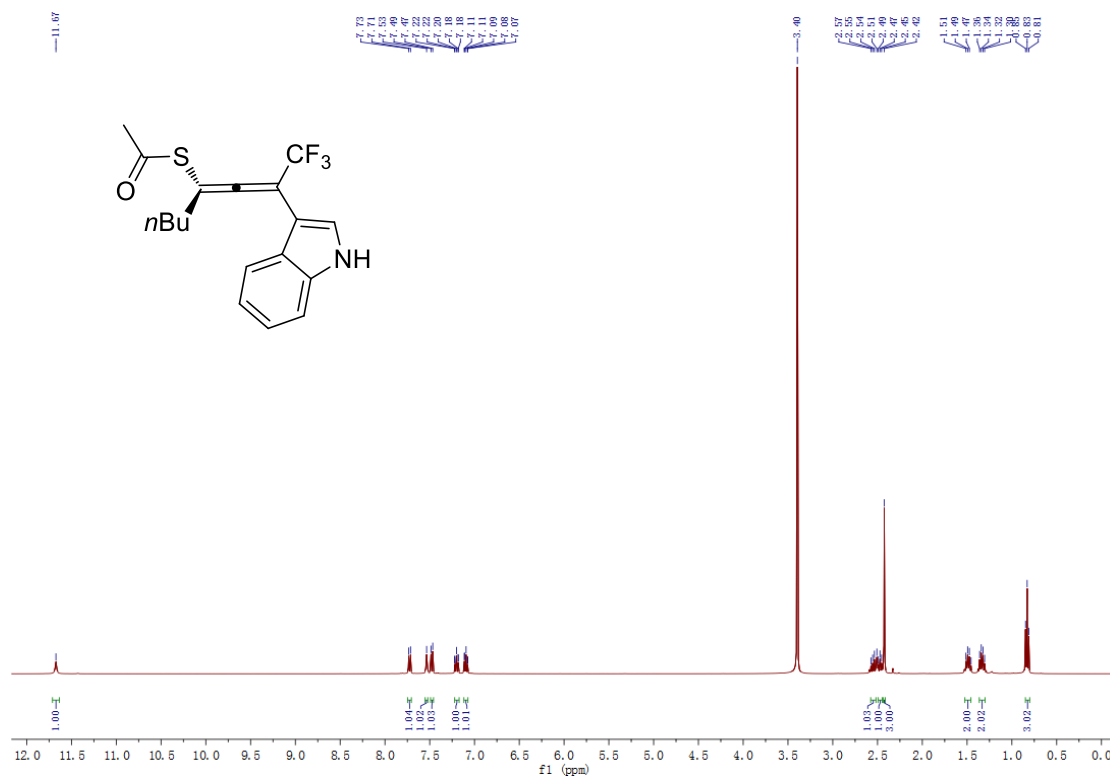
**(S)-S-(4,4,4-trifluoro-3-(1H-indol-3-yl)-1-(thiophen-3-yl)buta-1,2-dien-1-yl) ethanethioate (3la)**



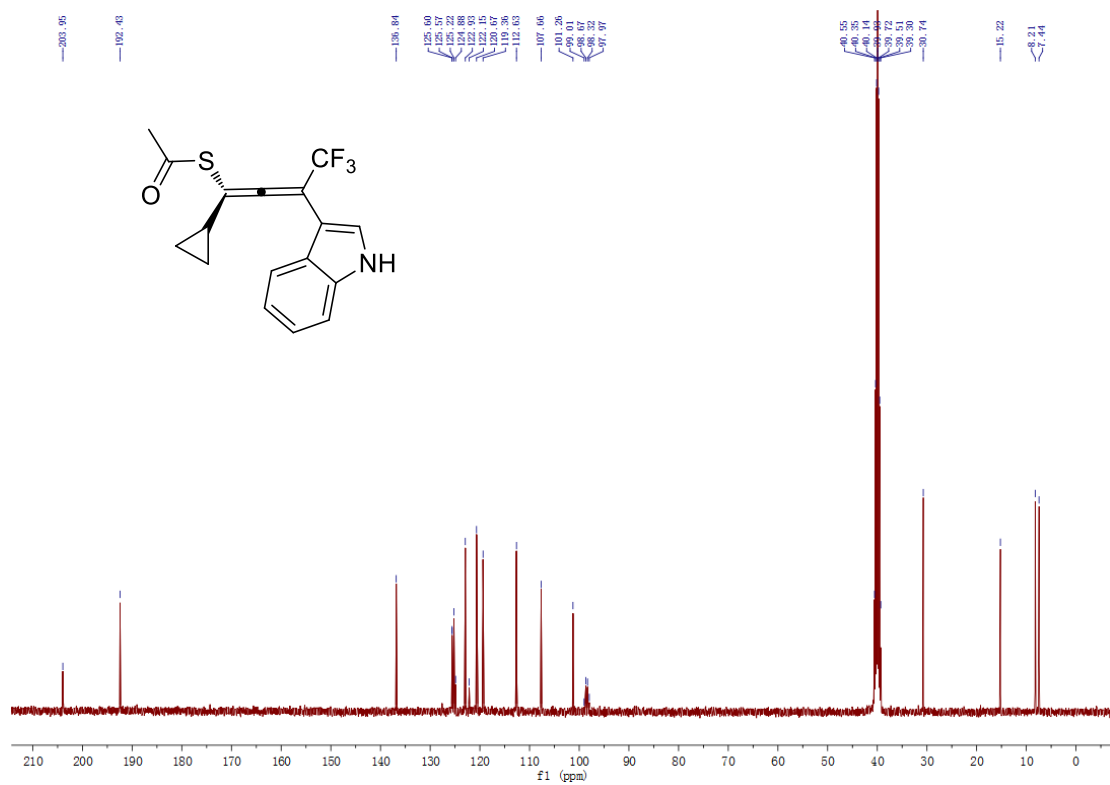
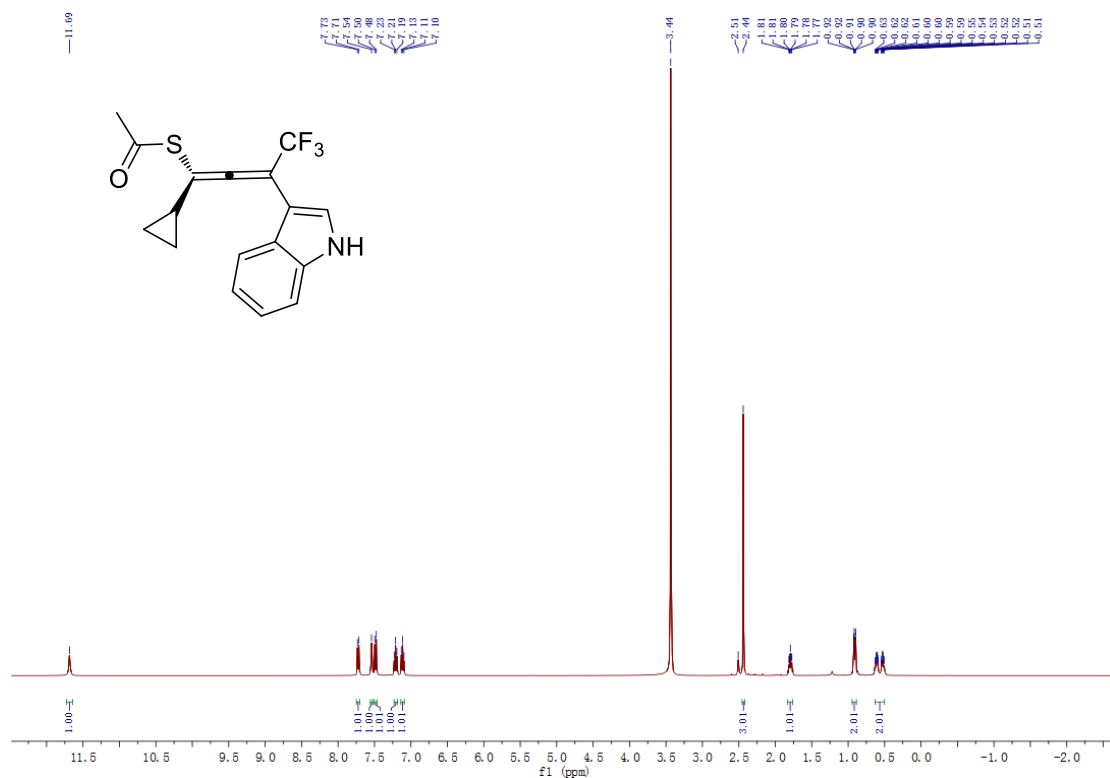
**(S)-S-(1,1,1-trifluoro-2-(1H-indol-3-yl)hepta-2,3-dien-4-yl) ethanethioate (3ma)**



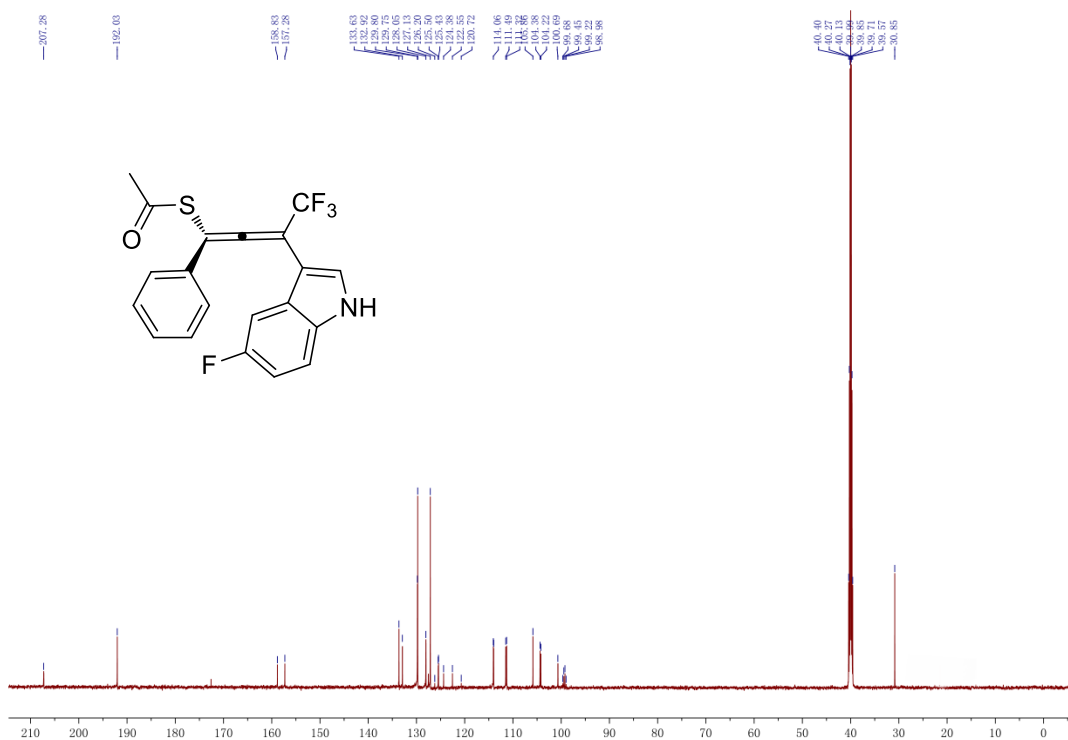
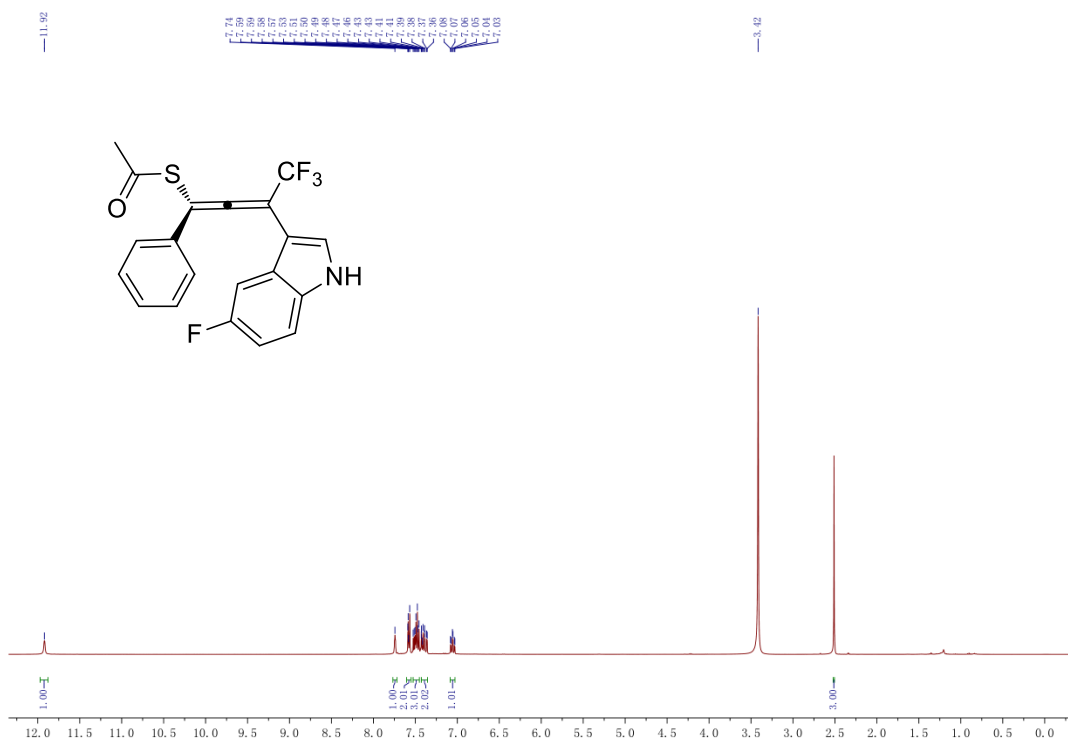
(S)-S-(1,1,1-trifluoro-2-(1H-indol-3-yl)octa-2,3-dien-4-yl) ethanethioate (3na)



**(S)-S-(1-cyclopropyl-4,4,4-trifluoro-3-(1H-indol-3-yl)buta-1,2-dien-1-yl) ethanethioate (30a)**

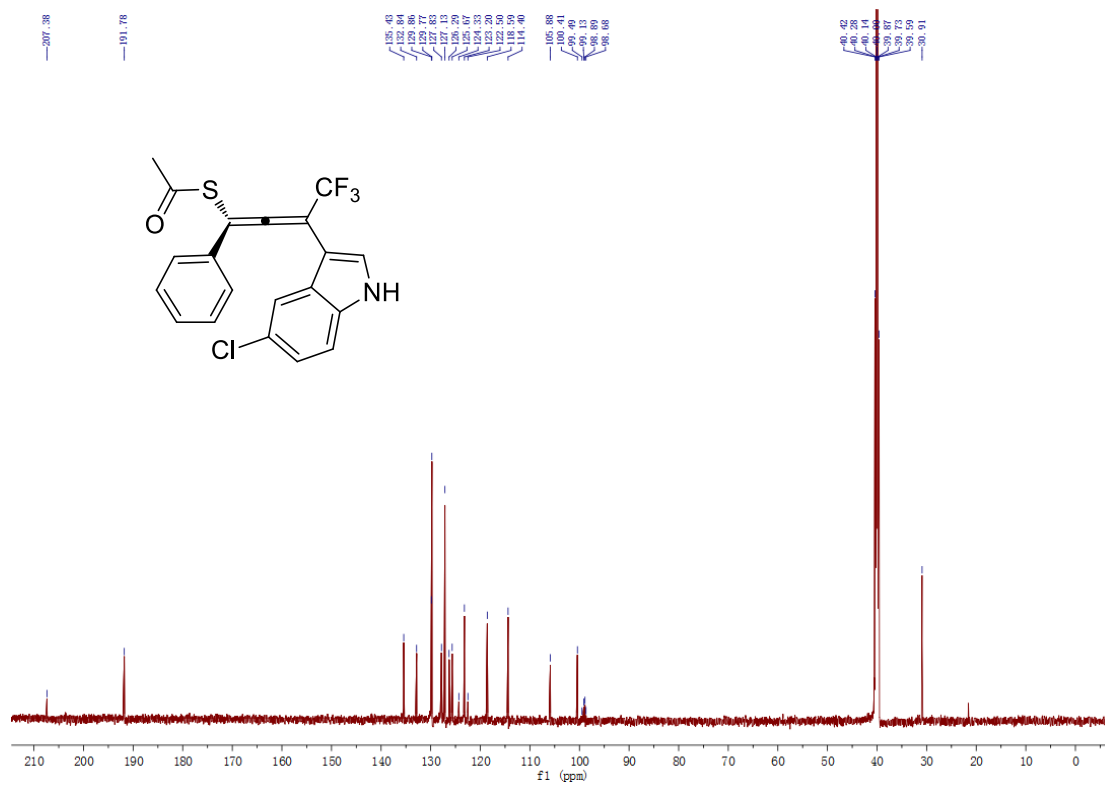
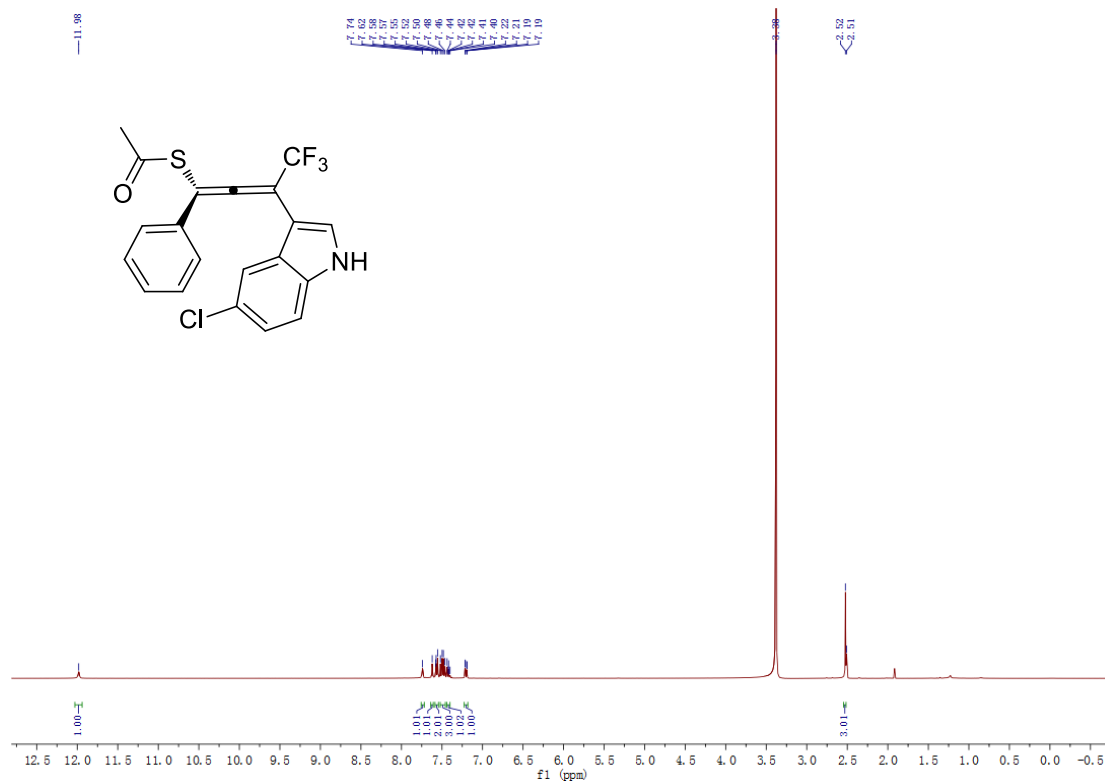


**(S)-S-(4,4,4-trifluoro-3-(5-fluoro-1H-indol-3-yl)-1-phenylbuta-1,2-dien-1-yl) ethanethioate (3pa)**

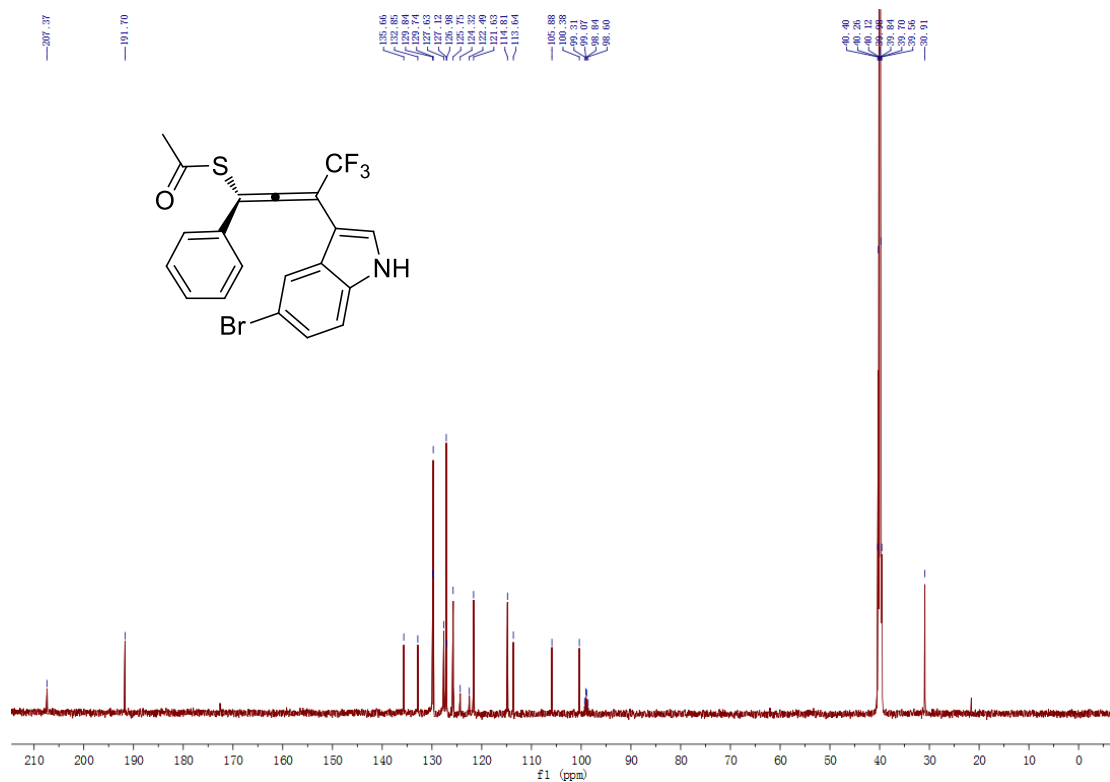
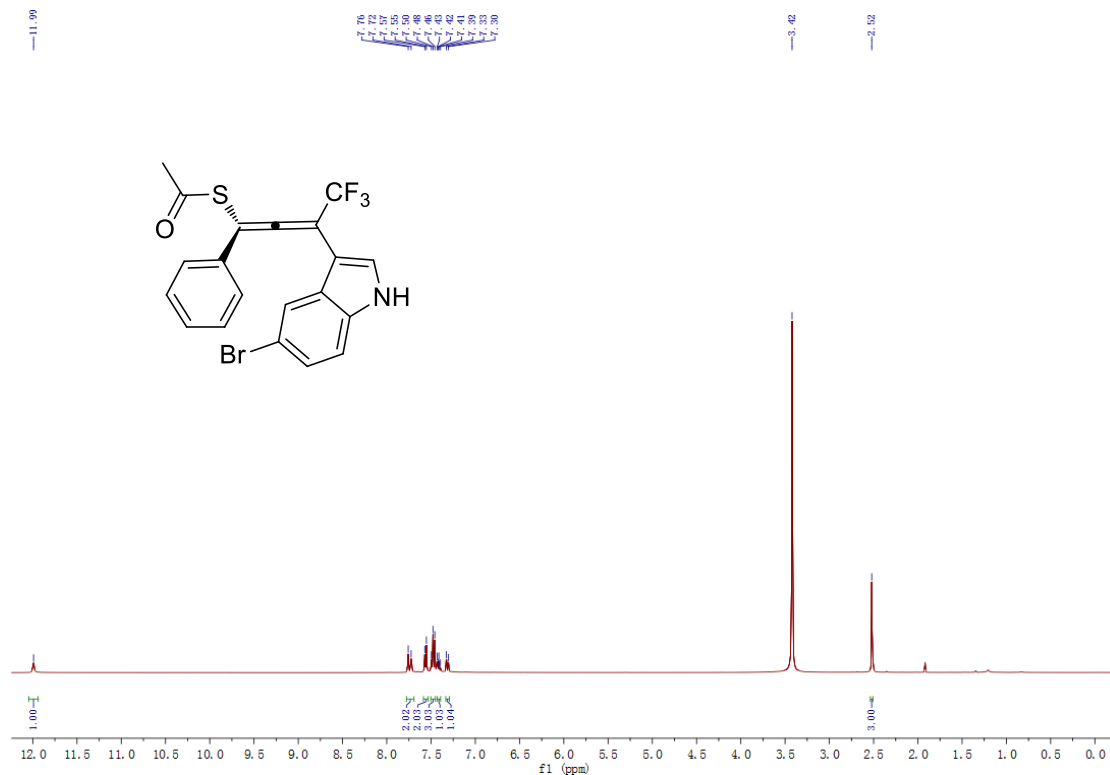




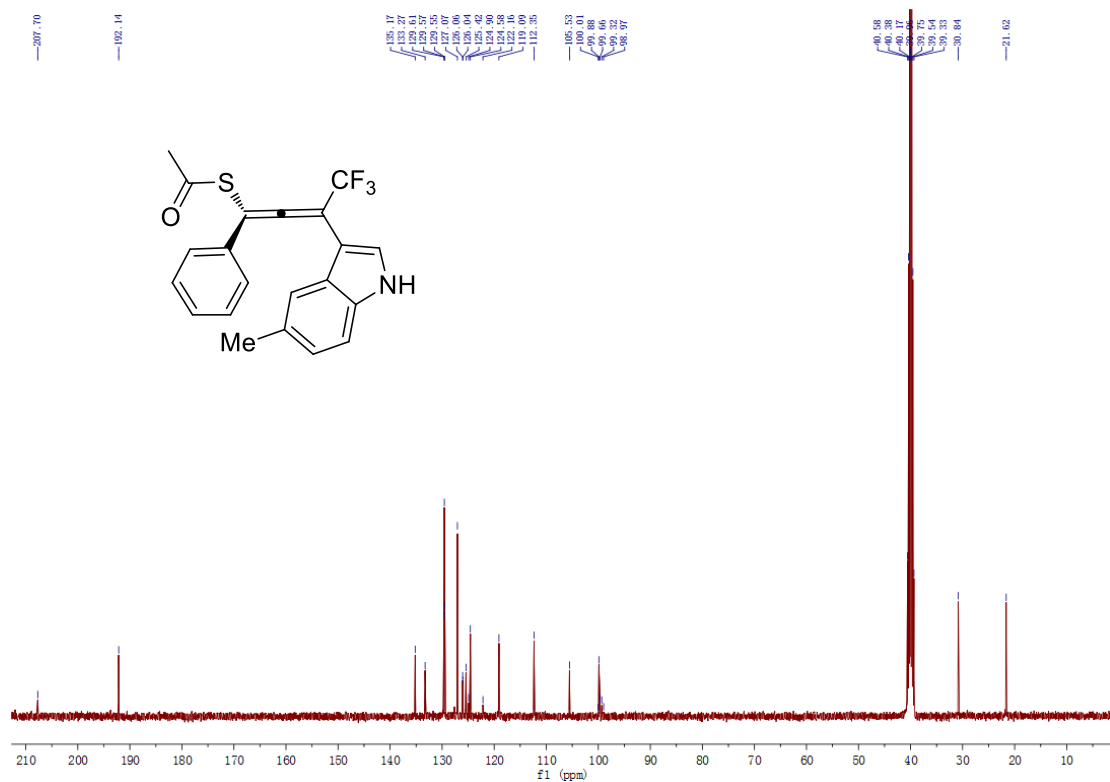
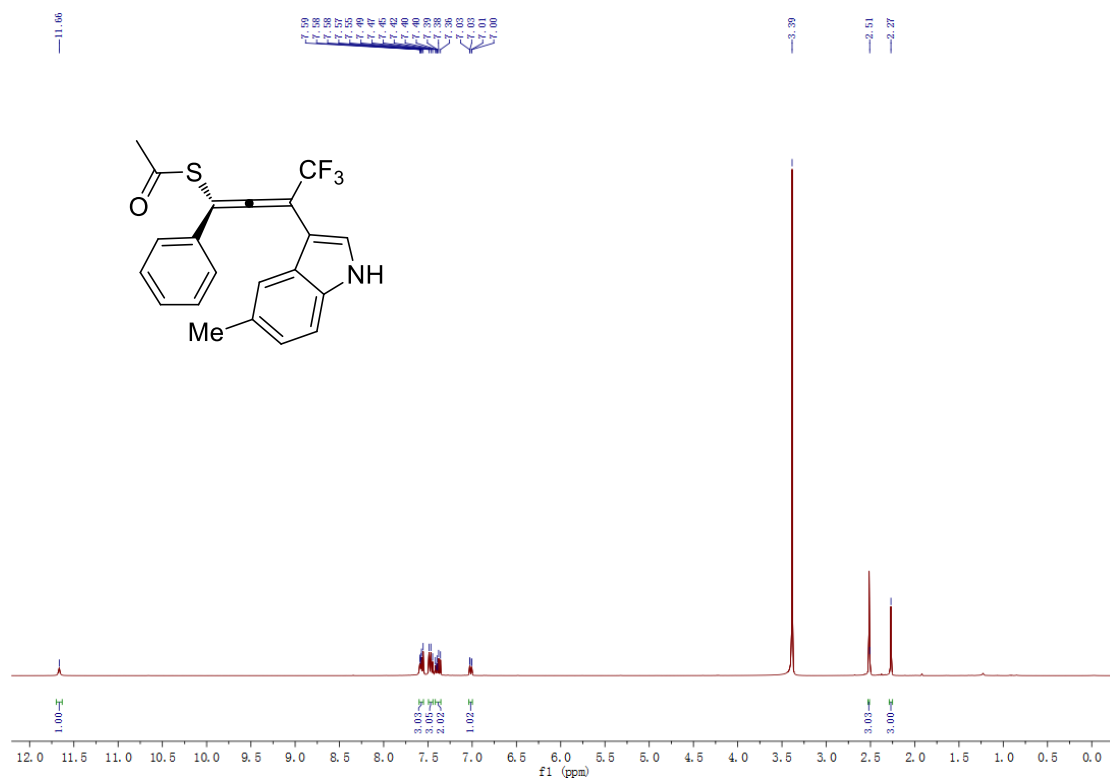
**(S)-S-(3-(5-chloro-1H-indol-3-yl)-4,4,4-trifluoro-1-phenylbuta-1,2-dien-1-yl) ethanethioate (3qa)**



**(S)-S-(3-(5-bromo-1H-indol-3-yl)-4,4,4-trifluoro-1-phenylbuta-1,2-dien-1-yl) ethanethioate (3ra)**

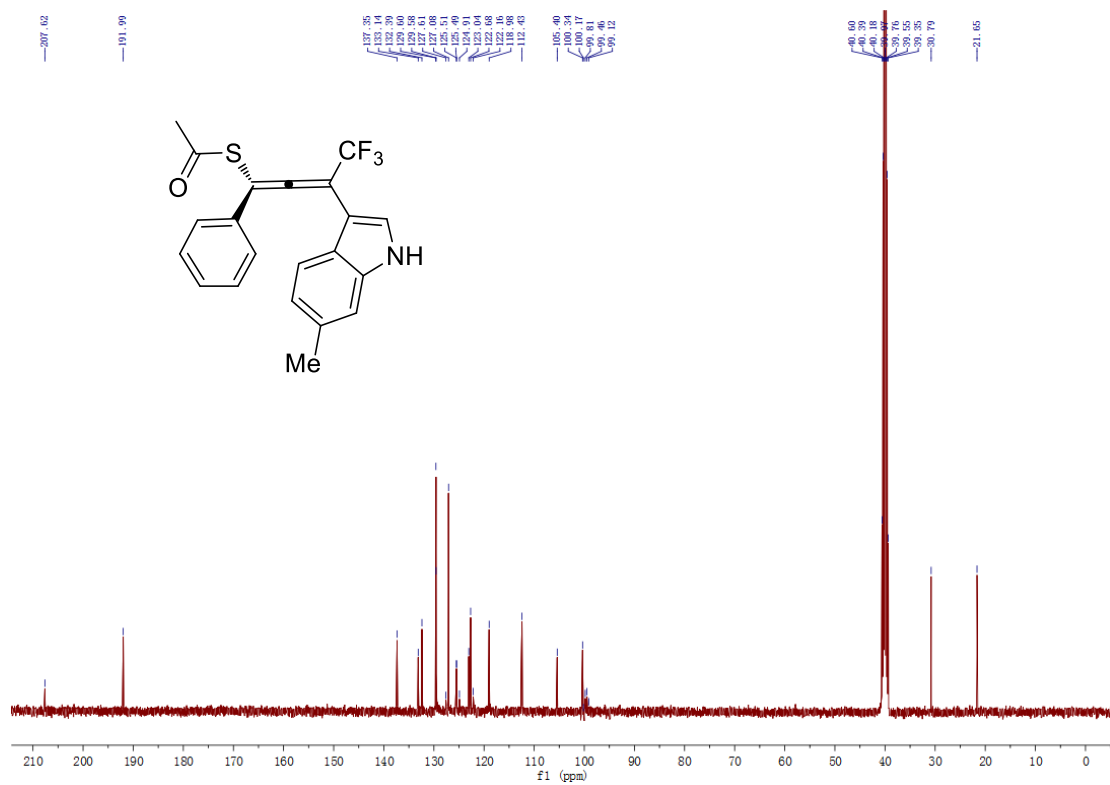
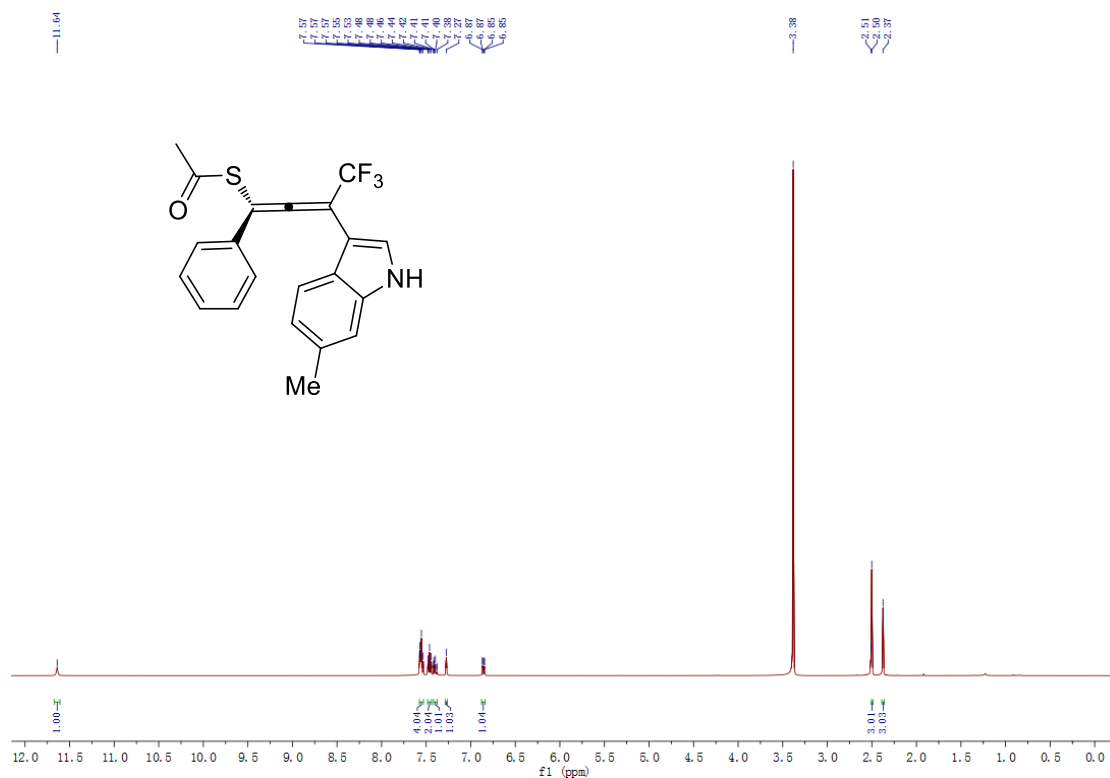


**(S)-S-(4,4,4-trifluoro-3-(5-methyl-1H-indol-3-yl)-1-phenylbuta-1,2-dien-1-yl) ethanethioate (3sa)**

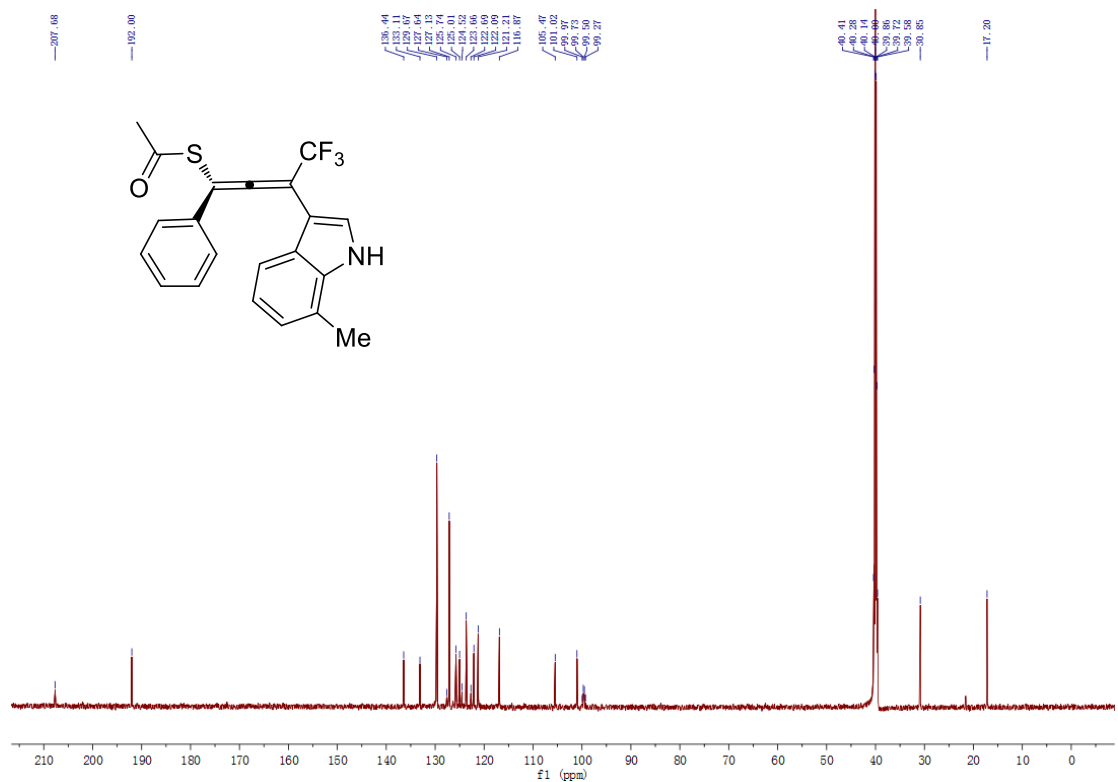
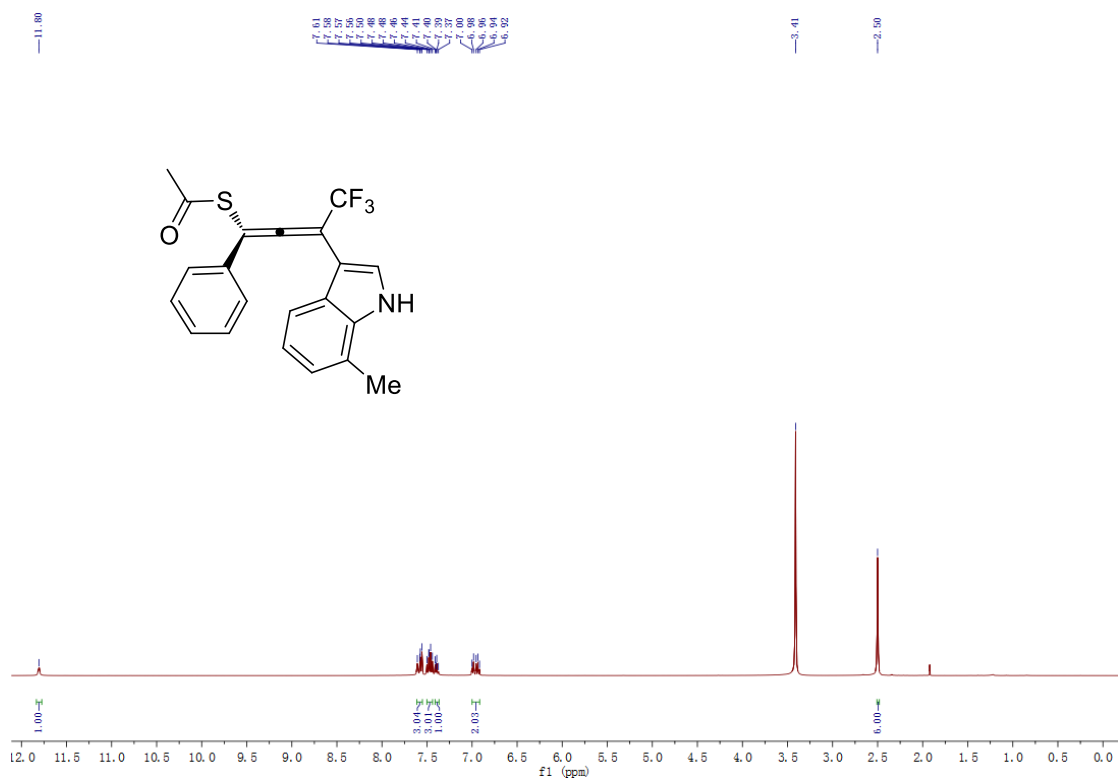




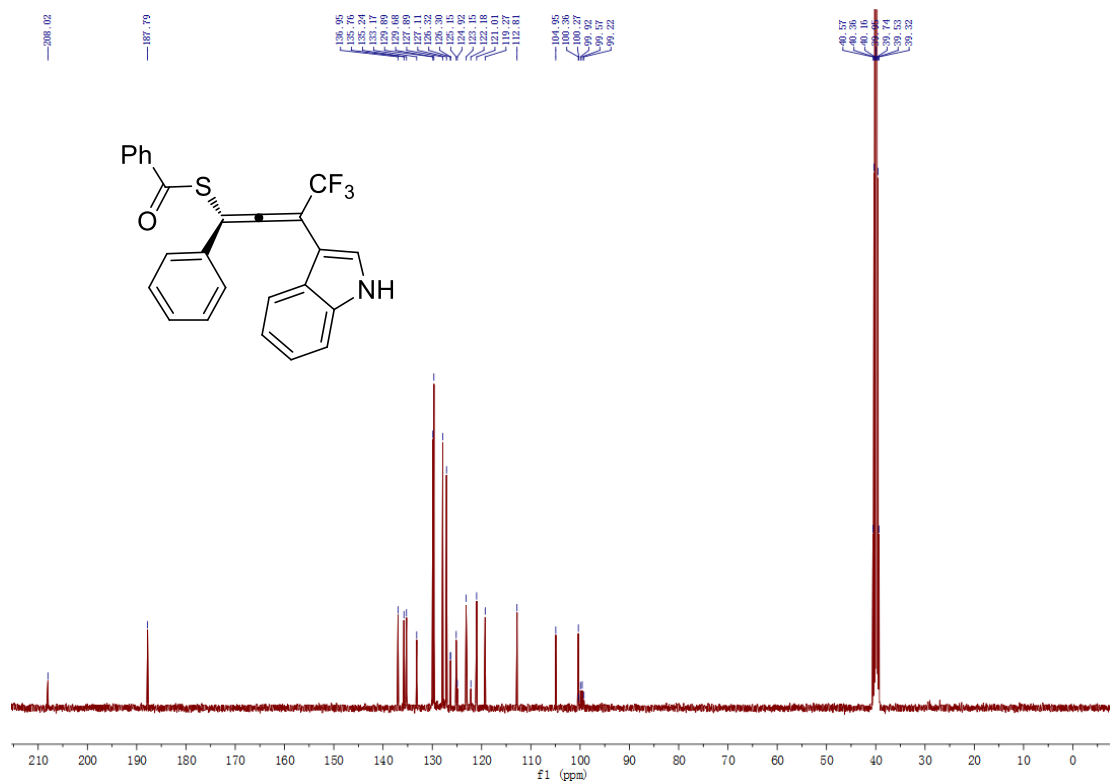
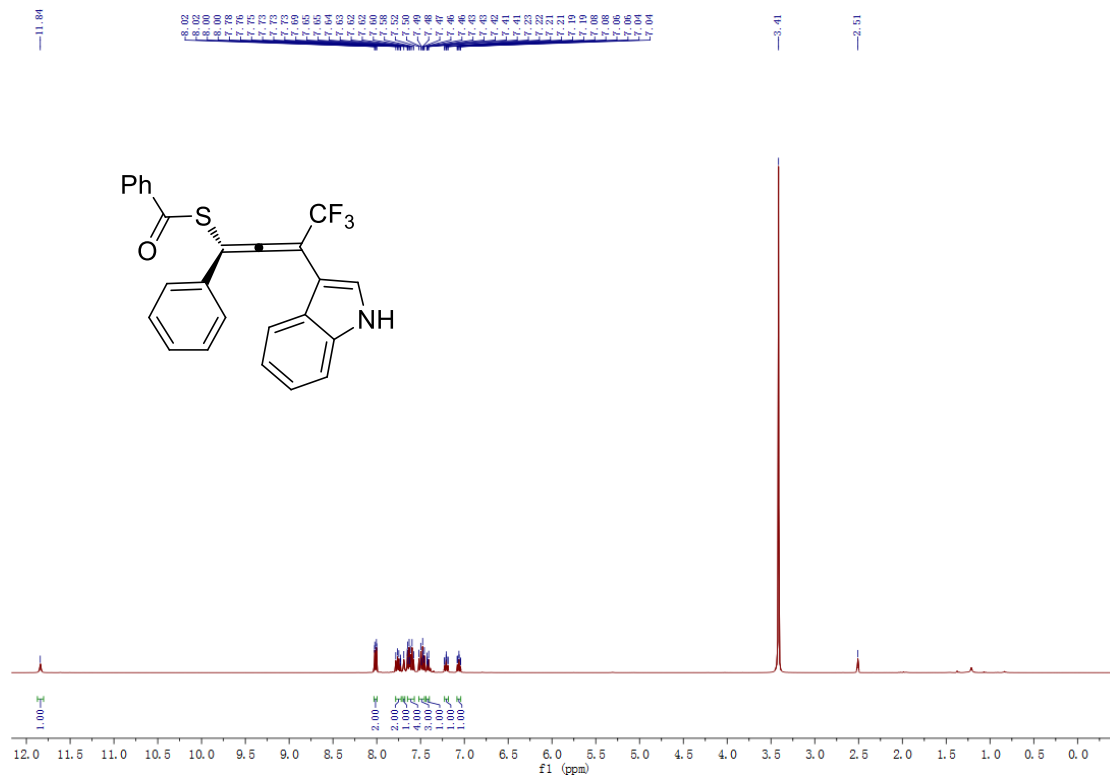
**(S)-S-(4,4,4-trifluoro-3-(6-methyl-1H-indol-3-yl)-1-phenylbuta-1,2-dien-1-yl) ethanethioate (3ua)**



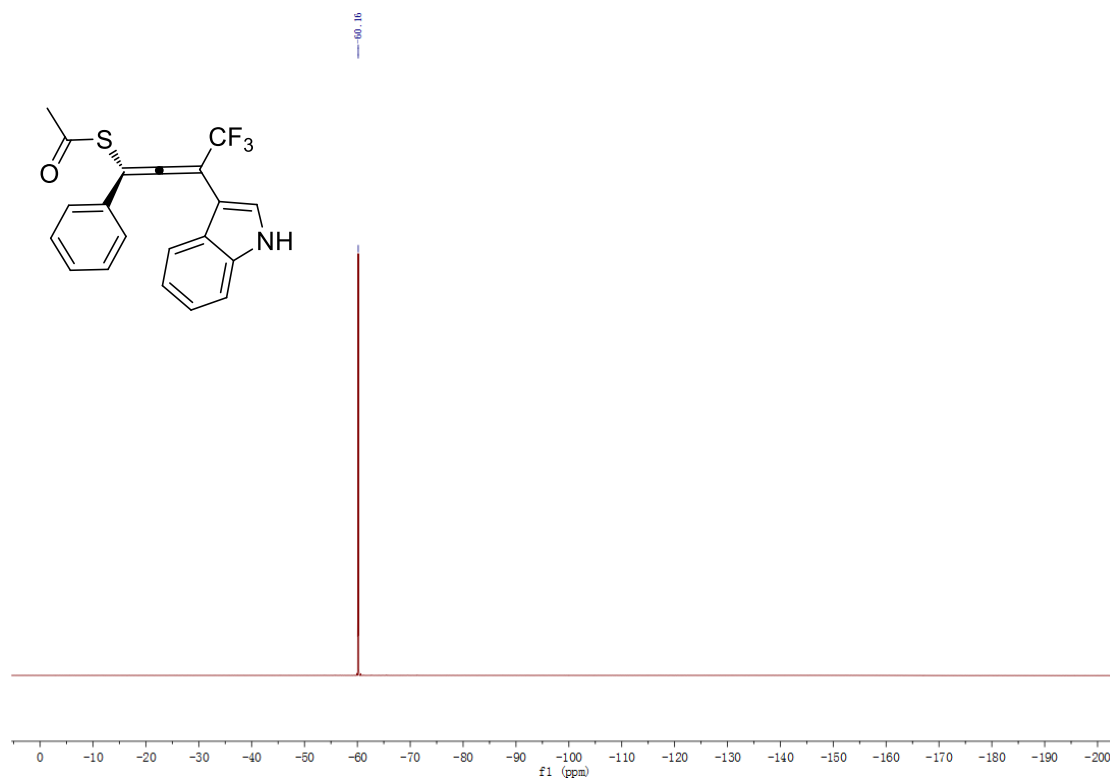
**(S)-S-(4,4,4-trifluoro-3-(7-methyl-1H-indol-3-yl)-1-phenylbuta-1,2-dien-1-yl) ethanethioate (3va)**



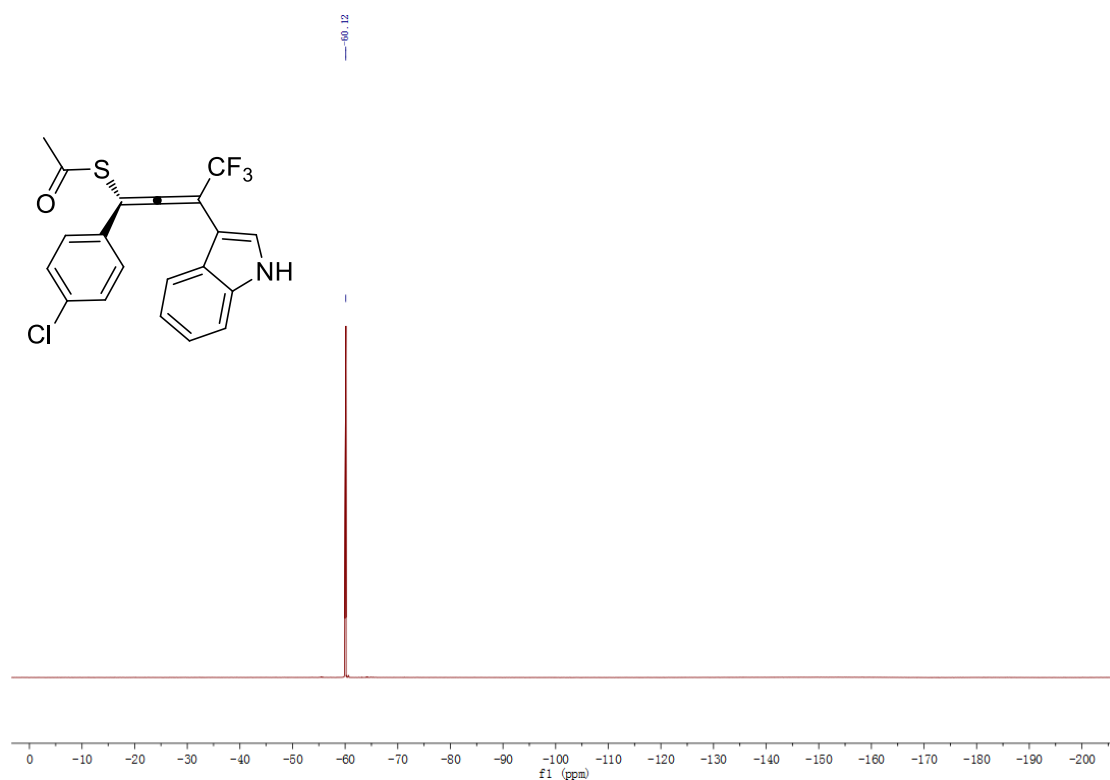
**(S)-S-(4,4,4-trifluoro-3-(1H-indol-3-yl)-1-phenylbuta-1,2-dien-1-yl) benzothioate (3ab)**



**(S)-S-(4,4,4-trifluoro-3-(1H-indol-3-yl)-1-phenylbuta-1,2-dien-1-yl) ethanethioate (3aa)**

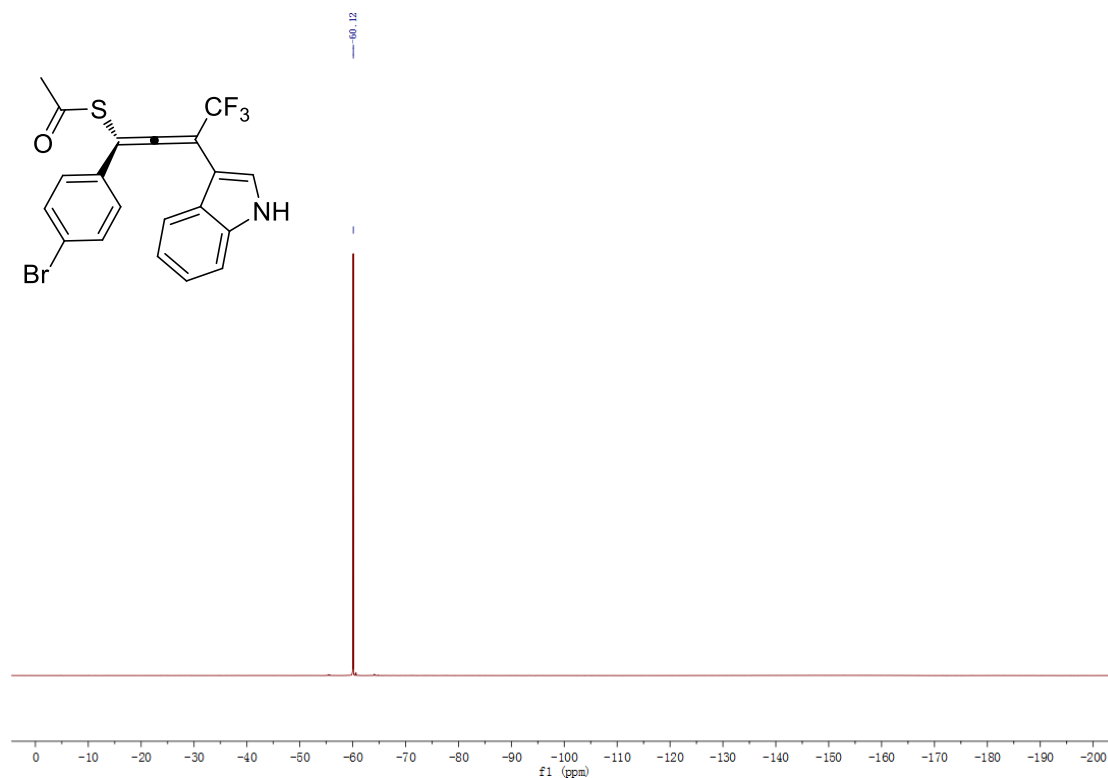


**(S)-S-(1-(4-chlorophenyl)-4,4,4-trifluoro-3-(1H-indol-3-yl)buta-1,2-dien-1-yl) ethanethioate (3ba)**

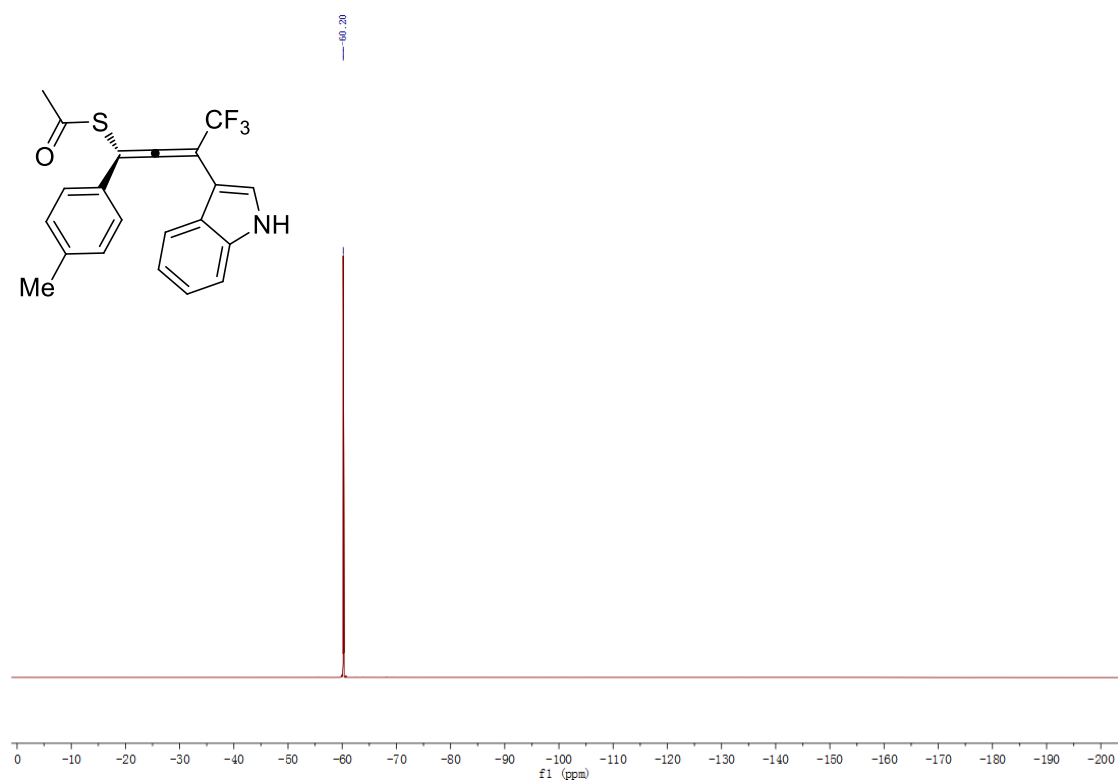




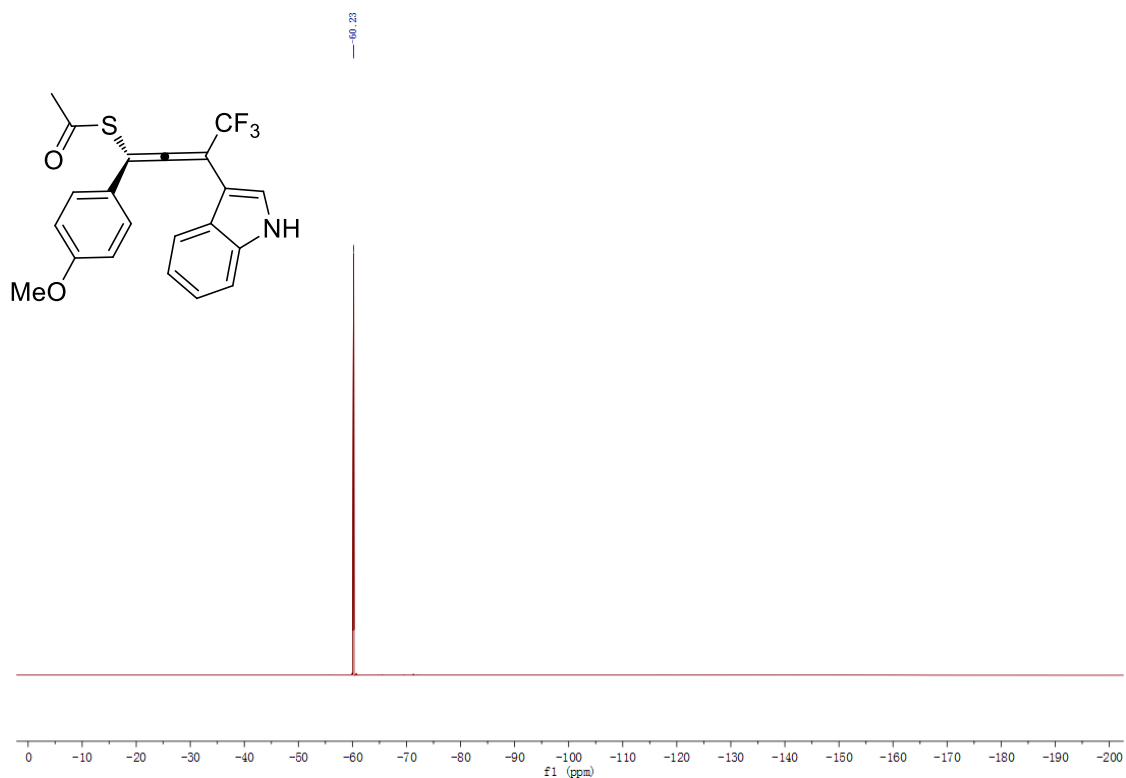
**(S)-S-(1-(4-bromophenyl)-4,4,4-trifluoro-3-(1H-indol-3-yl)buta-1,2-dien-1-yl) ethanethioate (3ca)**



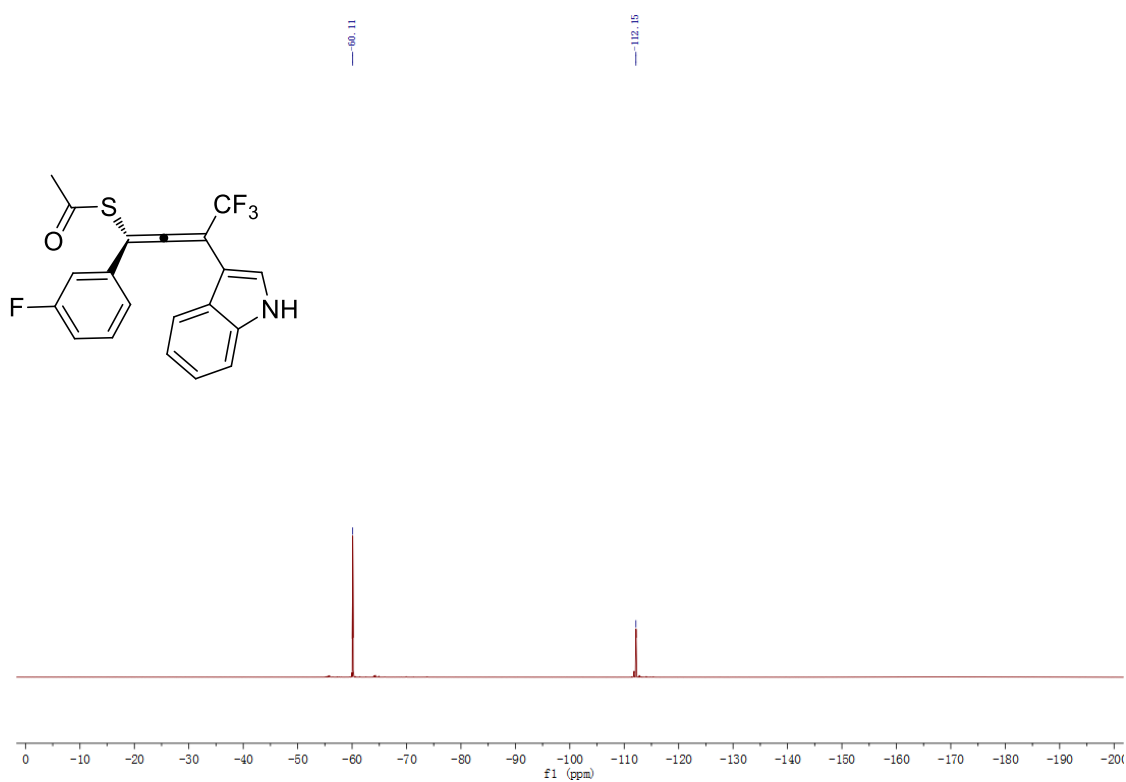
**(S)-S-(4,4,4-trifluoro-3-(1H-indol-3-yl)-1-(p-tolyl)buta-1,2-dien-1-yl) ethanethioate (3da)**



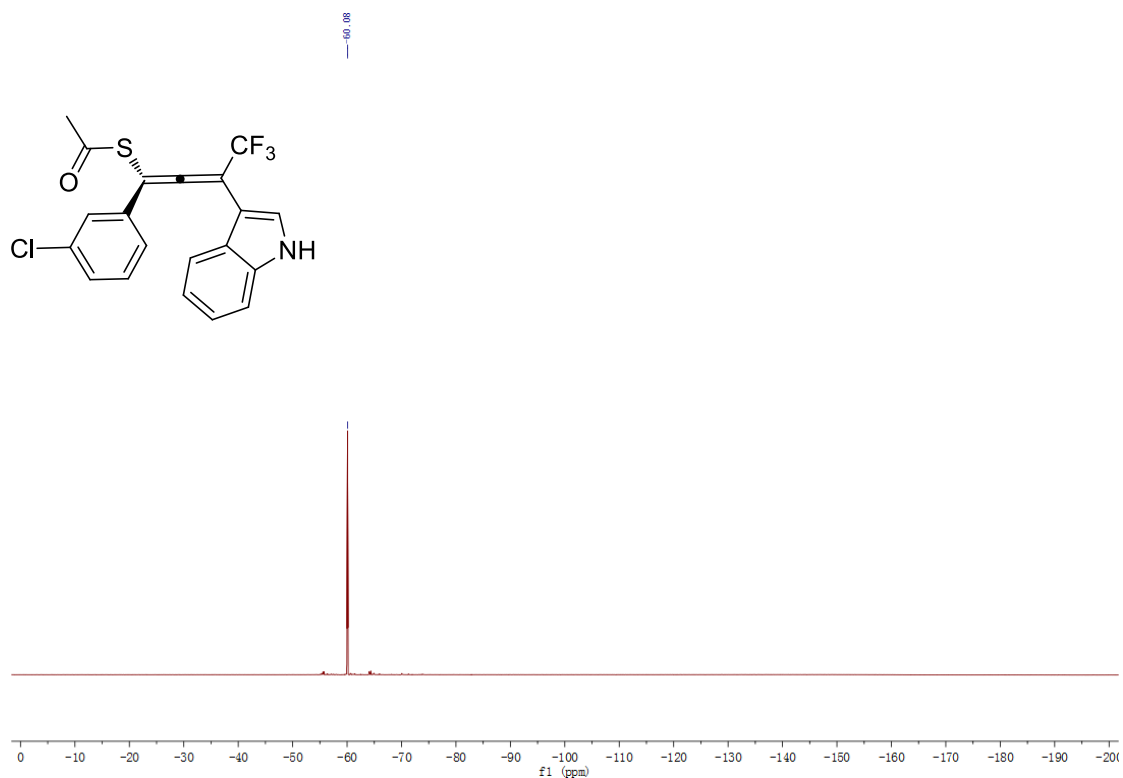
**(S)-S-(4,4,4-trifluoro-3-(1H-indol-3-yl)-1-(4-methoxyphenyl)buta-1,2-dien-1-yl) ethanethioate (3ea)**



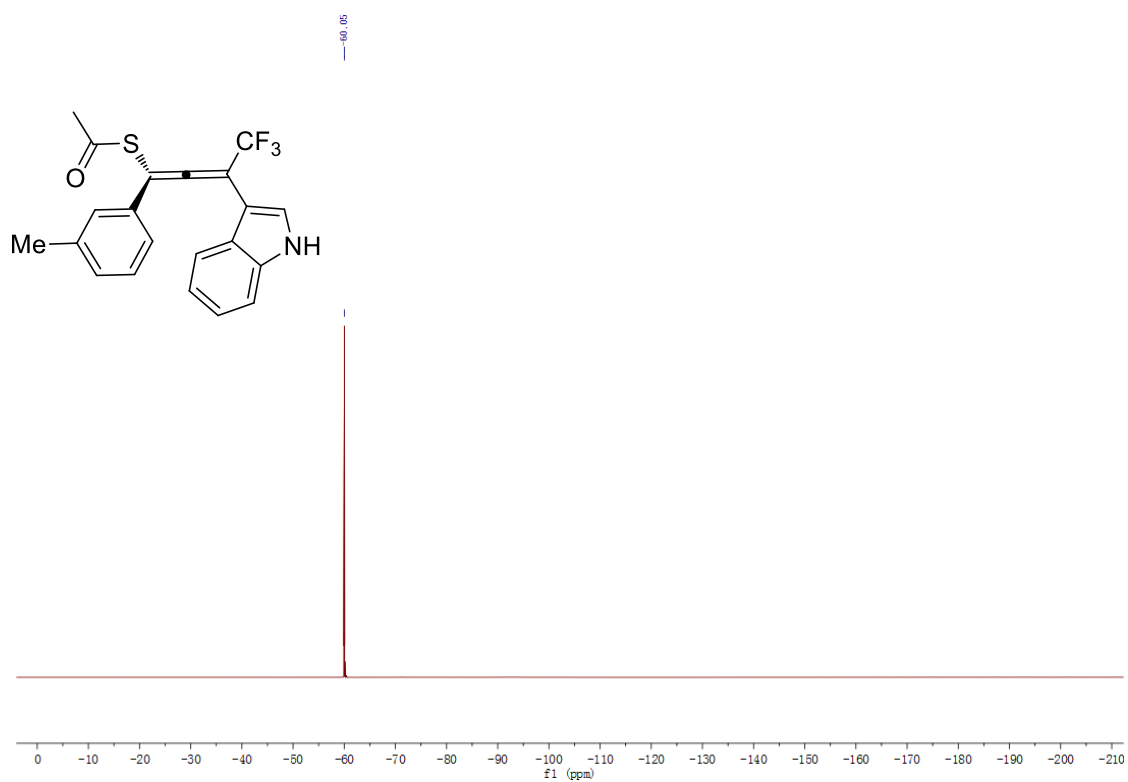
**(S)-S-(4,4,4-trifluoro-1-(3-fluorophenyl)-3-(1H-indol-3-yl)buta-1,2-dien-1-yl) ethanethioate (3fa)**



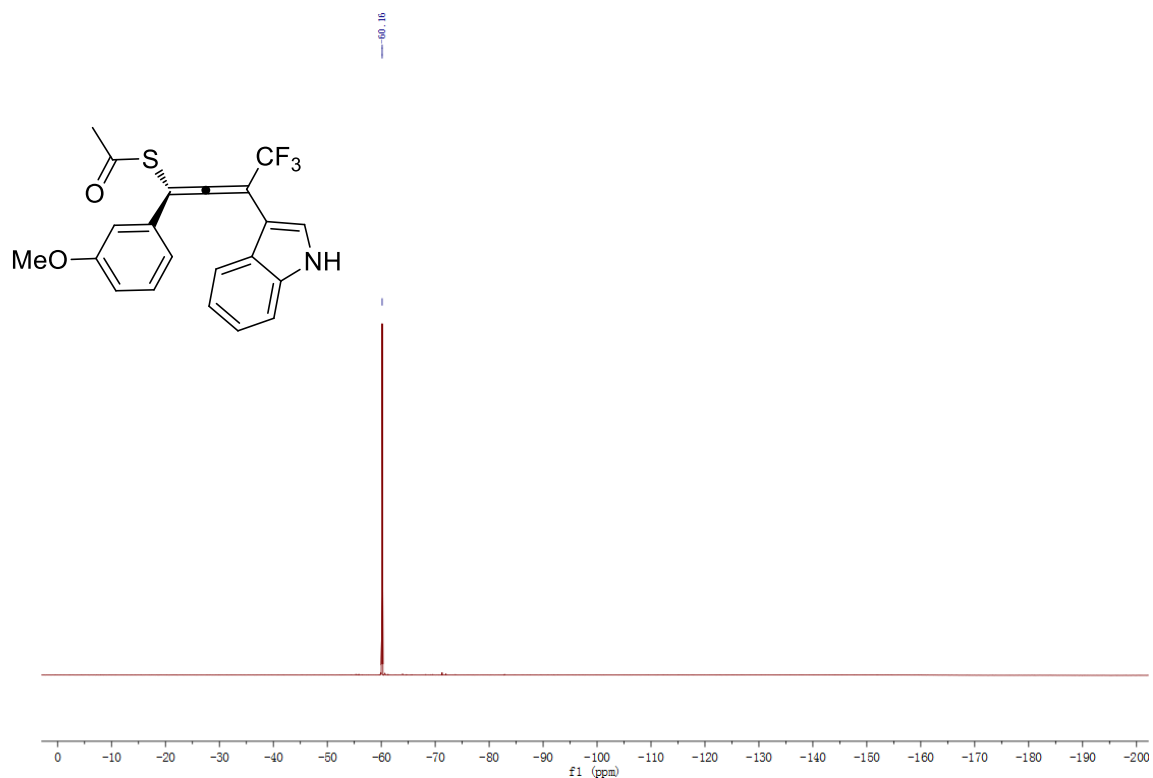
**(S)-S-(1-(3-chlorophenyl)-4,4,4-trifluoro-3-(1H-indol-3-yl)buta-1,2-dien-1-yl)ethanethioate (3ga)**



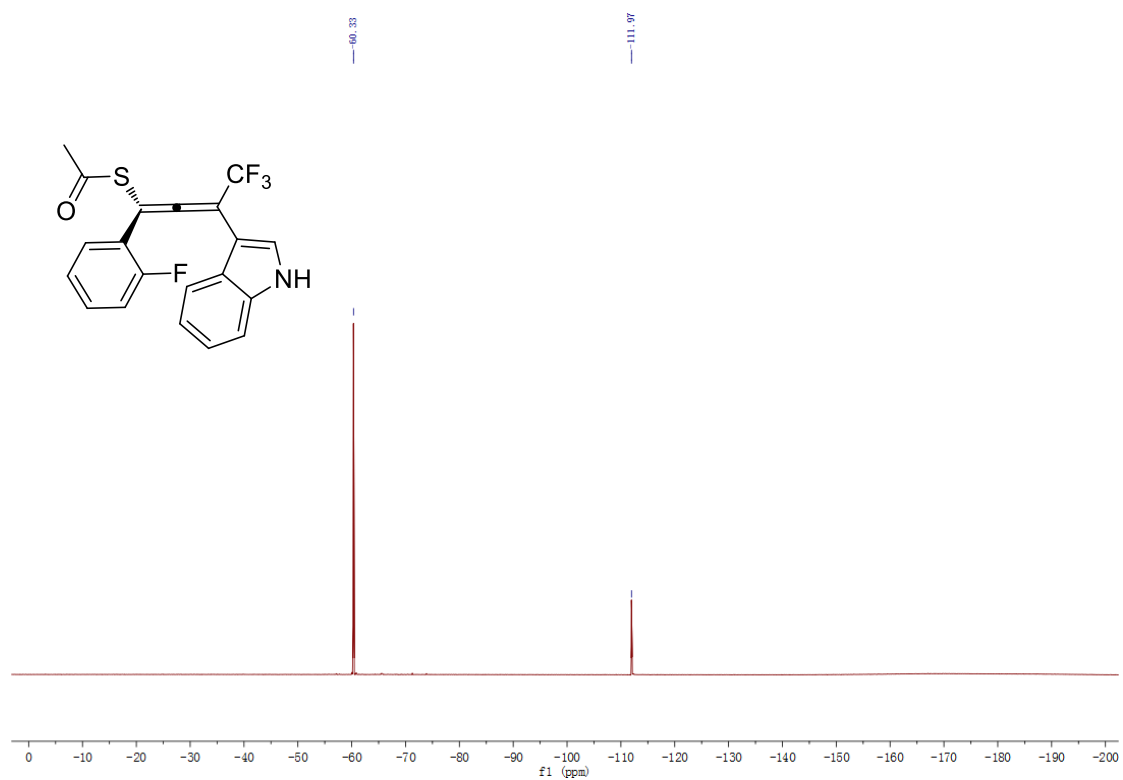
**(S)-S-(4,4,4-trifluoro-3-(1H-indol-3-yl)-1-(m-tolyl)buta-1,2-dien-1-yl)ethanethioate (3ha)**



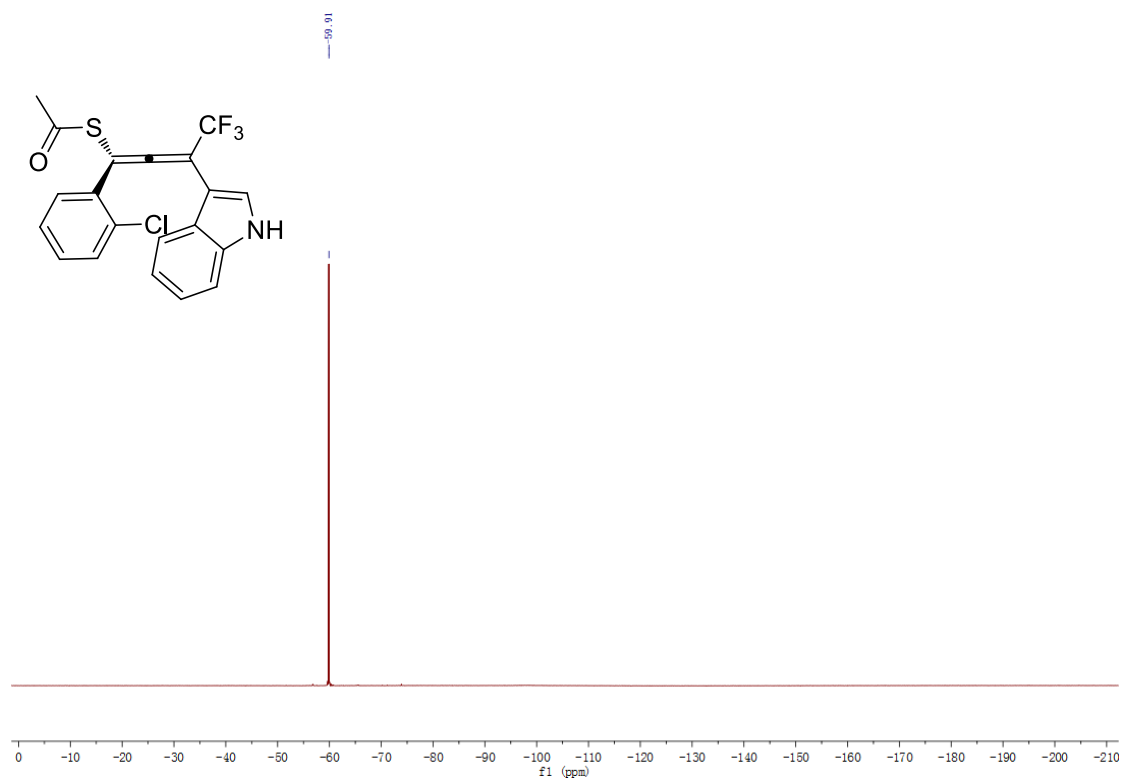
**(S)-S-(4,4,4-trifluoro-3-(1H-indol-3-yl)-1-(3-methoxyphenyl)buta-1,2-dien-1-yl) ethanethioate (3ia)**



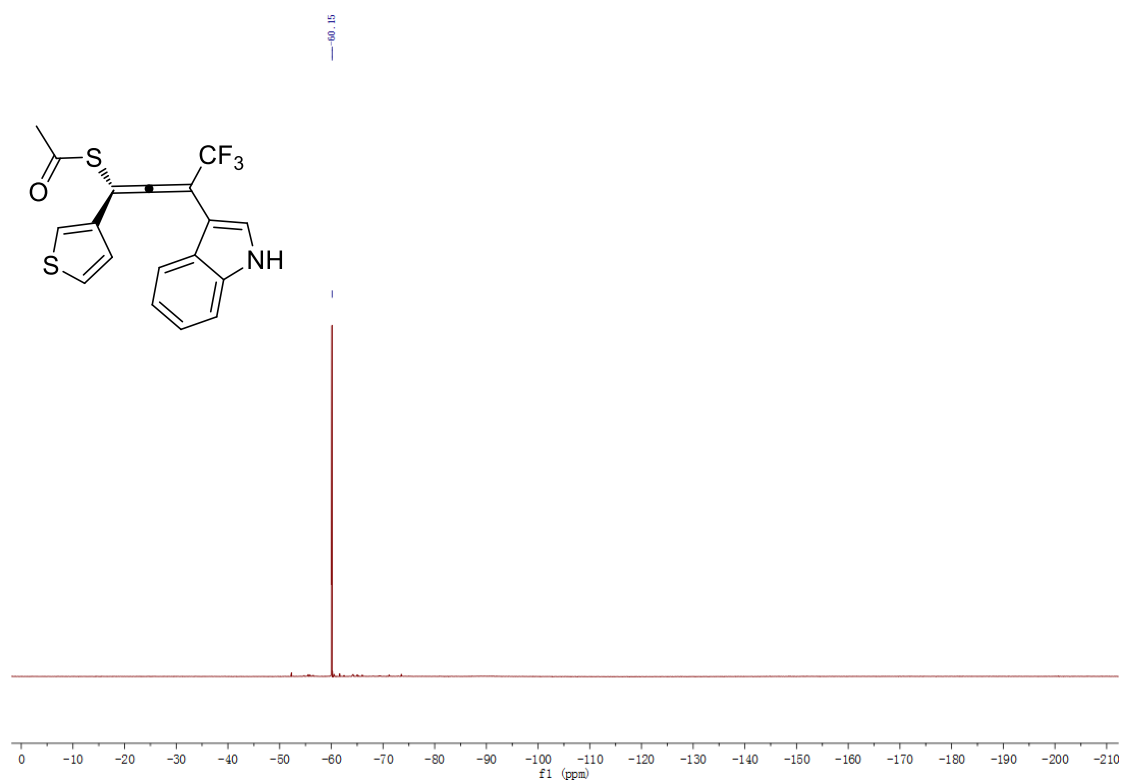
**(S)-S-(4,4,4-trifluoro-1-(2-fluorophenyl)-3-(1H-indol-3-yl)buta-1,2-dien-1-yl) ethanethioate (3ja)**



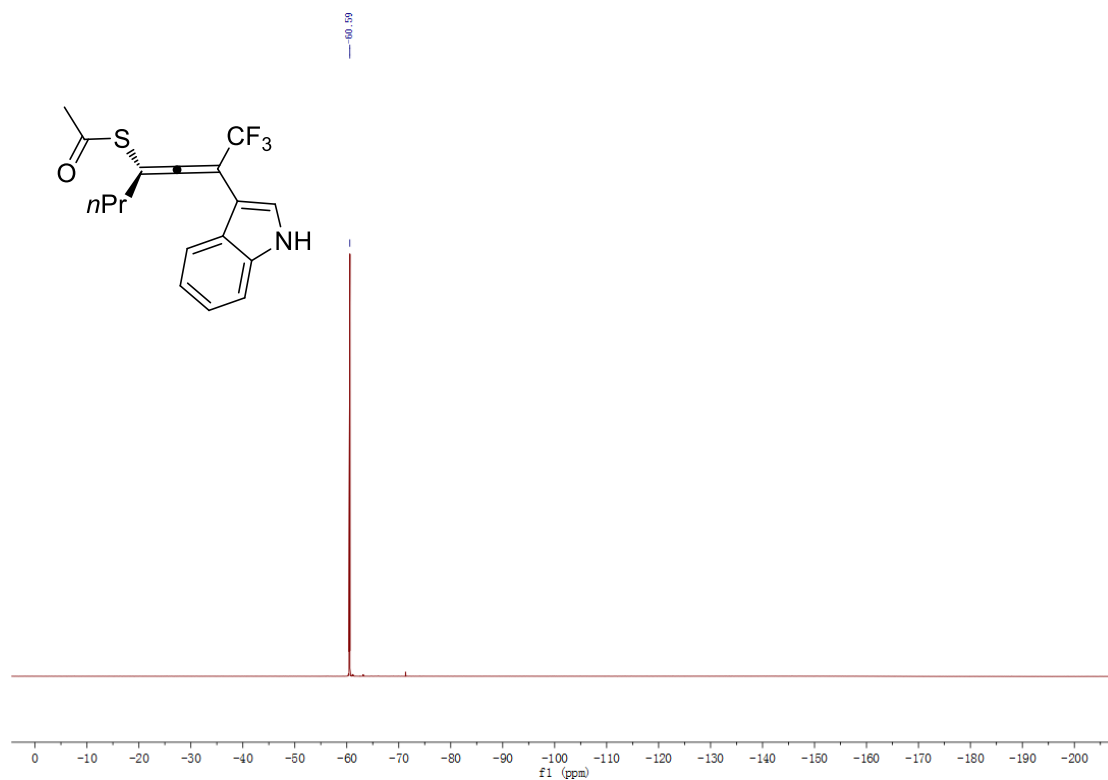
**(S)-S-(1-(2-chlorophenyl)-4,4,4-trifluoro-3-(1H-indol-3-yl)buta-1,2-dien-1-yl)ethanethioate (3ka)**



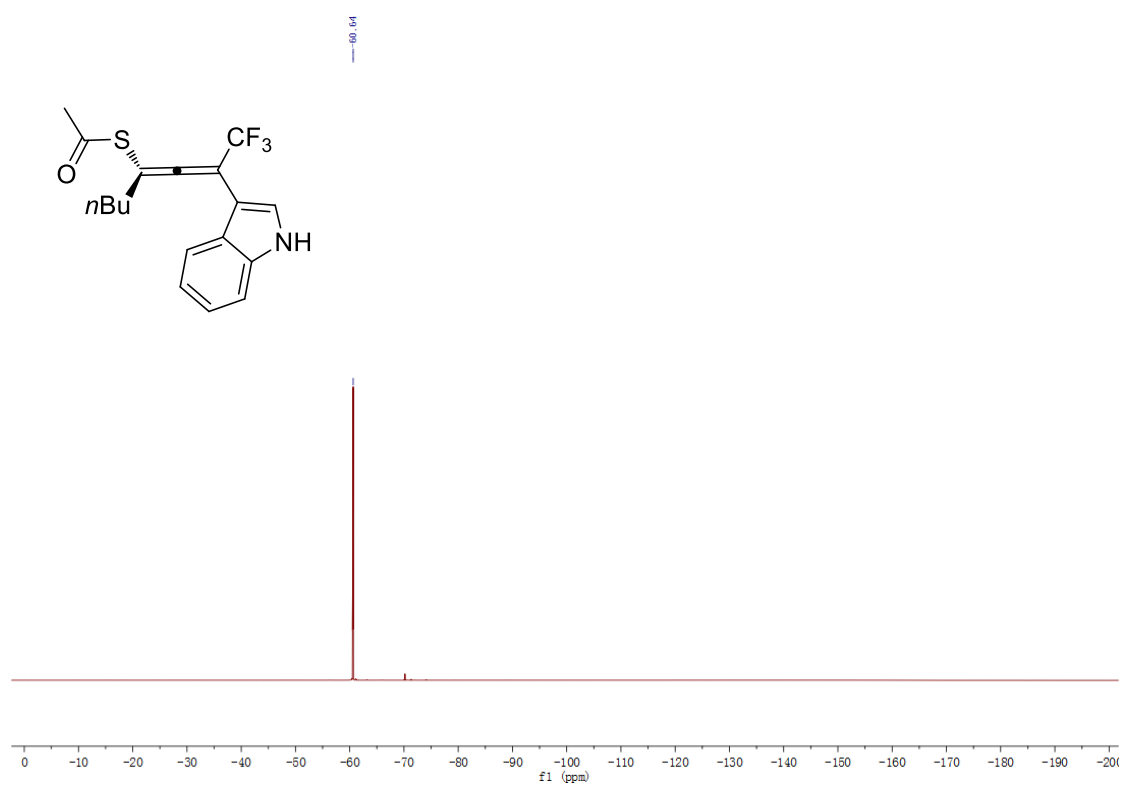
**(S)-S-(4,4,4-trifluoro-3-(1H-indol-3-yl)-1-(thiophen-3-yl)buta-1,2-dien-1-yl)ethanethioate (3la)**



**(S)-S-(1,1,1-trifluoro-2-(1H-indol-3-yl)hepta-2,3-dien-4-yl) ethanethioate (3ma)**

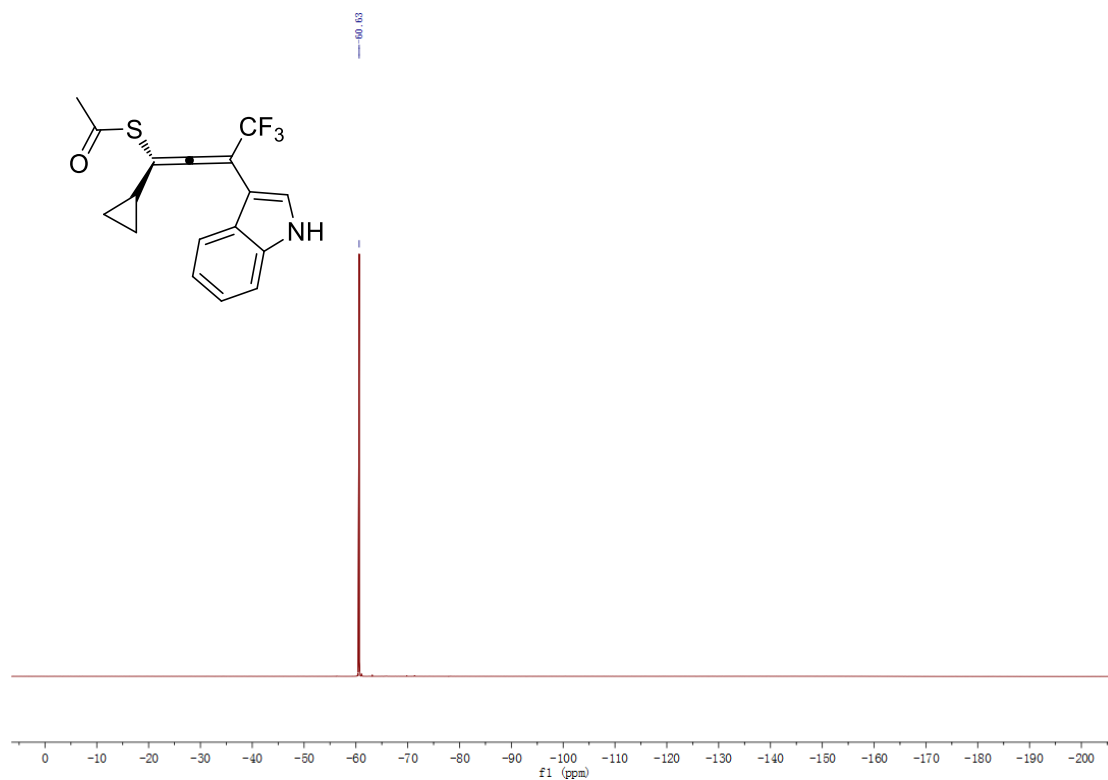


**(S)-S-(1,1,1-trifluoro-2-(1H-indol-3-yl)octa-2,3-dien-4-yl) ethanethioate (3na)**

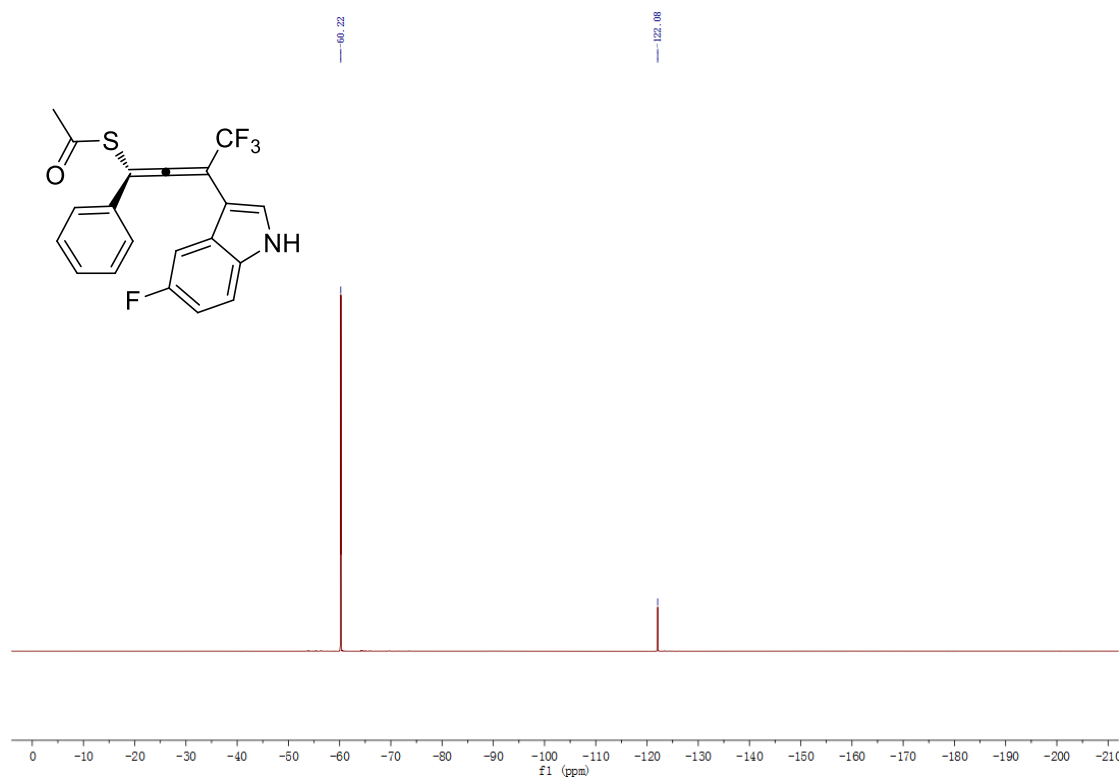


**(S)-S-(1-cyclopropyl-4,4,4-trifluoro-3-(1H-indol-3-yl)buta-1,2-dien-1-yl)**

**ethanethioate (30a)**

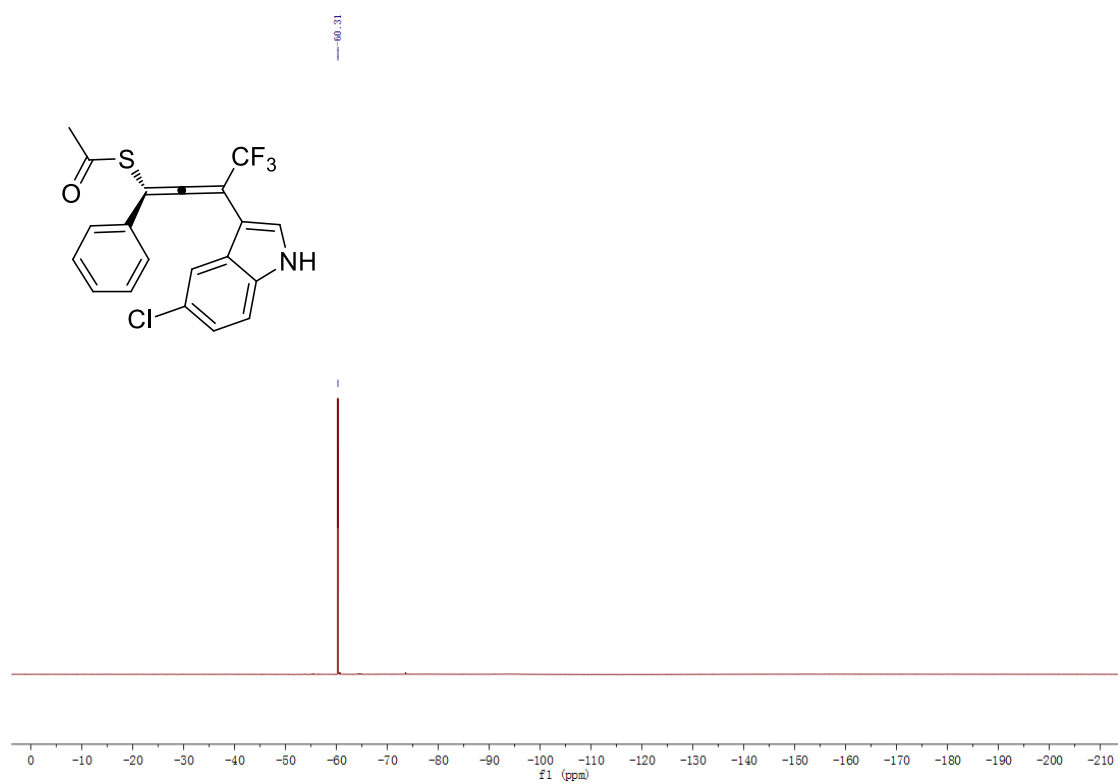


**(S)-S-(4,4,4-trifluoro-3-(5-fluoro-1H-indol-3-yl)-1-phenylbuta-1,2-dien-1-yl) ethanethioate (3pa)**

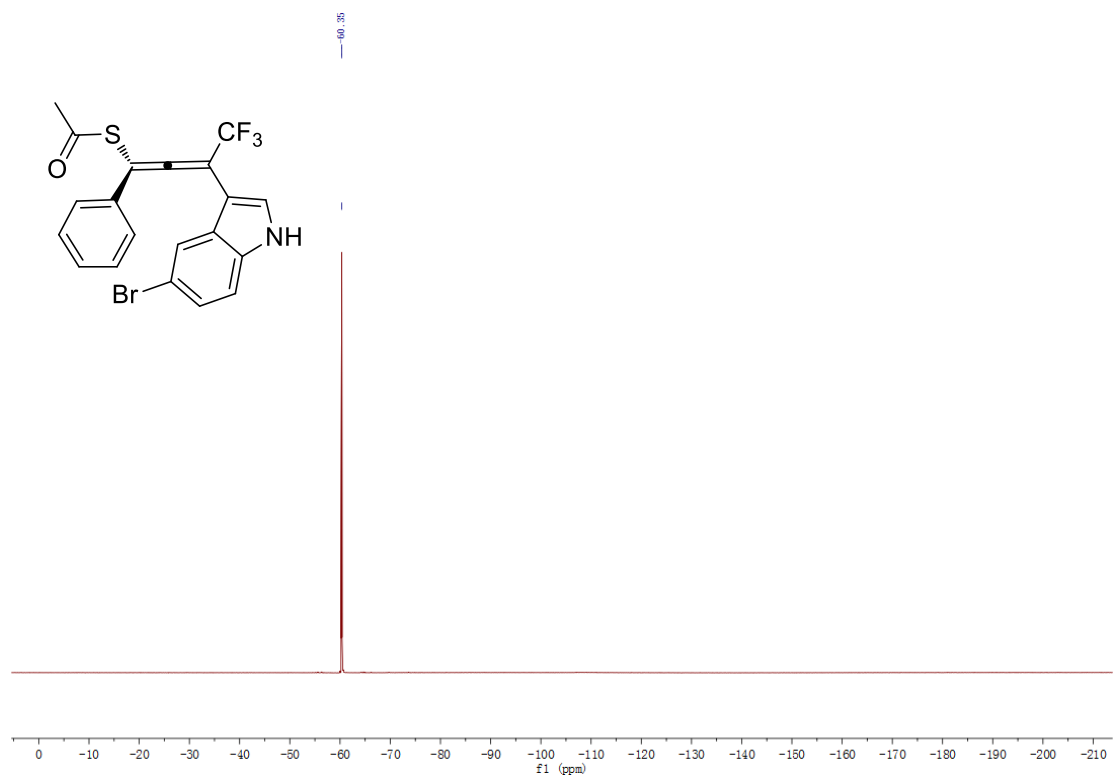


**(S)-S-(3-(5-chloro-1H-indol-3-yl)-4,4,4-trifluoro-1-phenylbuta-1,2-dien-1-yl)**

**ethanethioate (3qa)**



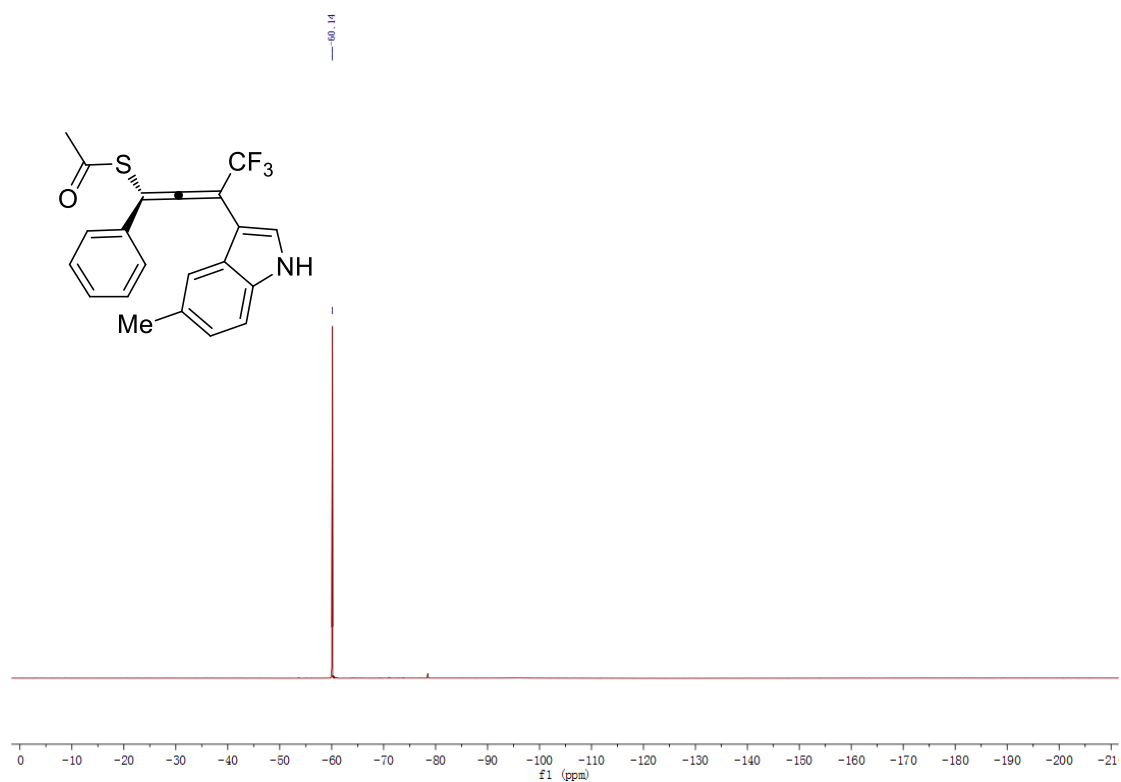
**(S)-S-(3-(5-bromo-1H-indol-3-yl)-4,4,4-trifluoro-1-phenylbuta-1,2-dien-1-yl)ethanethioate (3ra)**



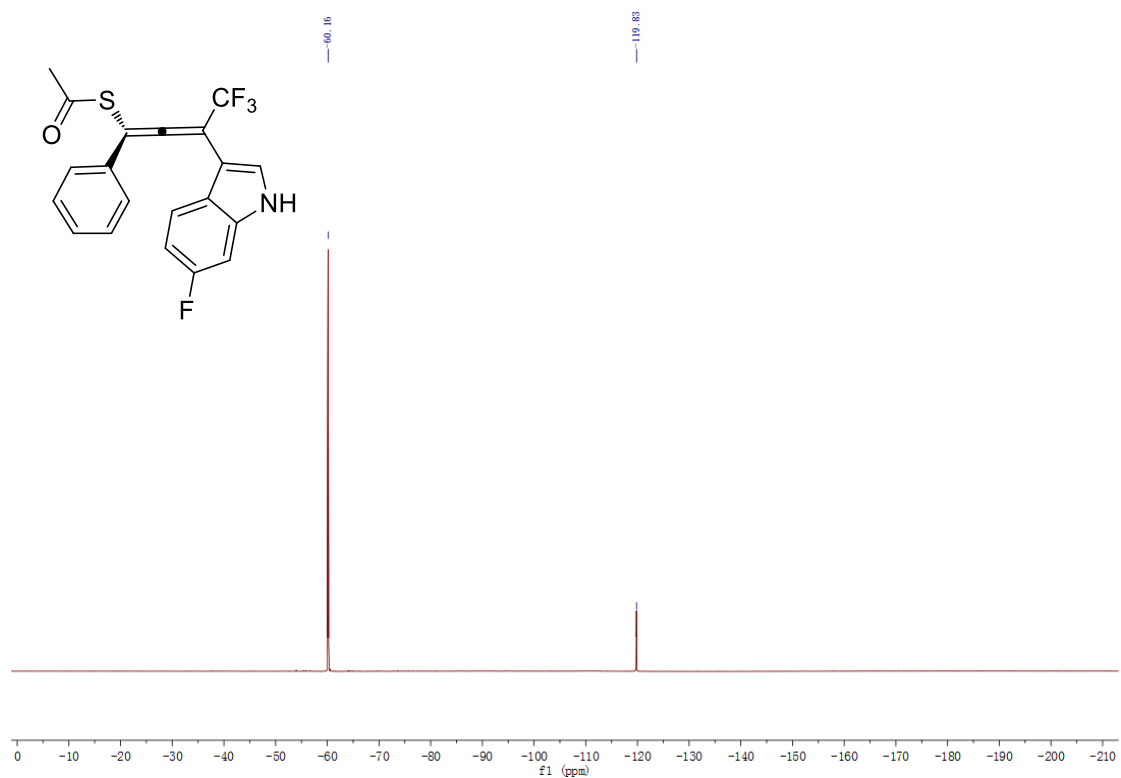
**(S)-S-(4,4,4-trifluoro-3-(5-methyl-1H-indol-3-yl)-1-phenylbuta-1,2-dien-1-yl)**



**ethanethioate (3sa)**

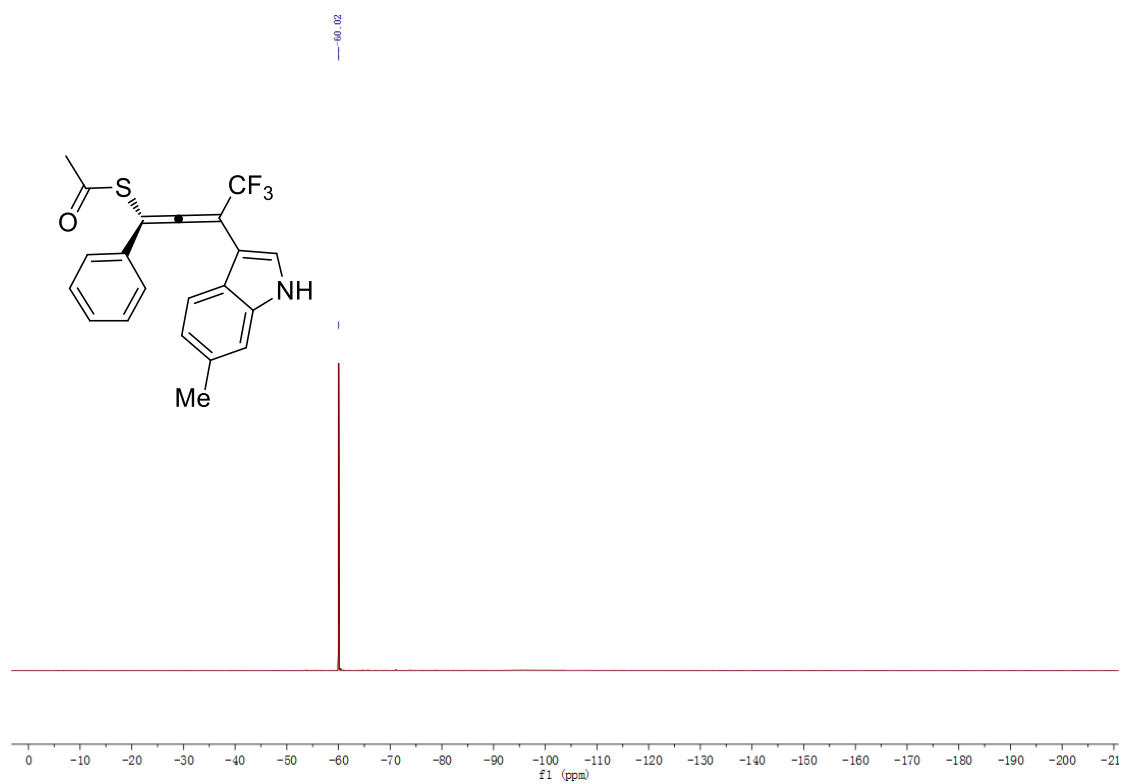


**(S)-S-(4,4,4-trifluoro-3-(6-fluoro-1H-indol-3-yl)-1-phenylbuta-1,2-dien-1-yl) ethanethioate (3ta)**

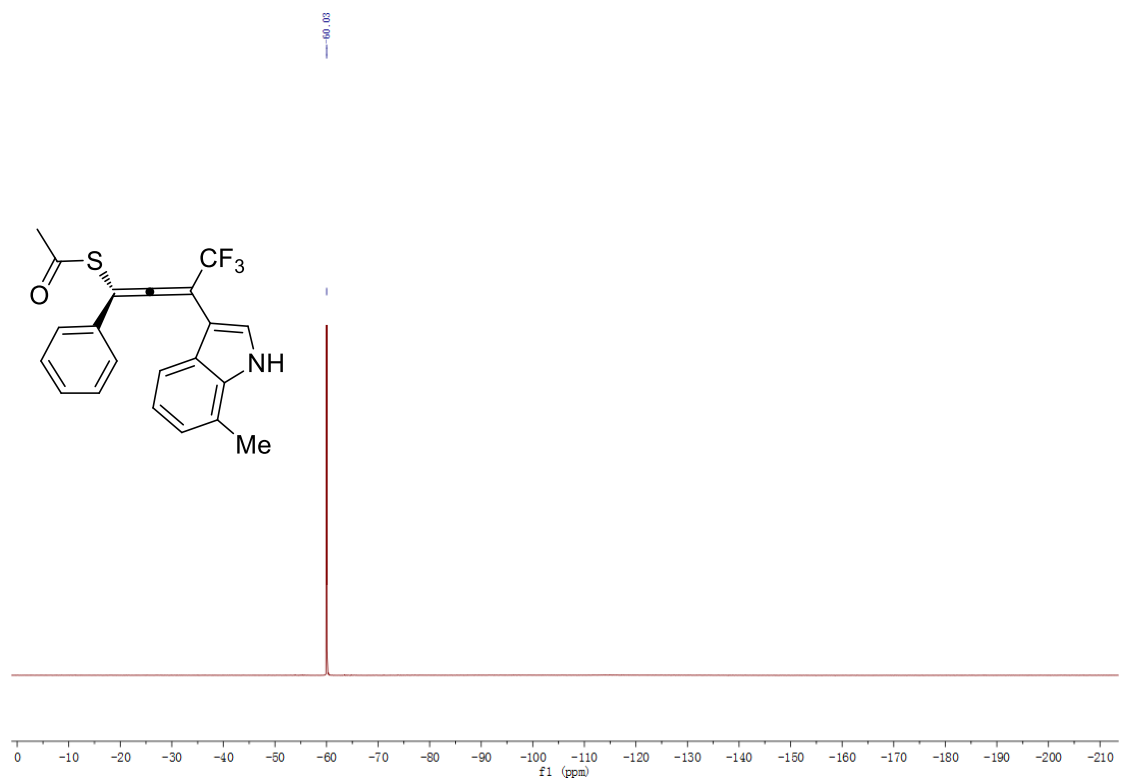


**(S)-S-(4,4,4-trifluoro-3-(6-methyl-1H-indol-3-yl)-1-phenylbuta-1,2-dien-1-yl)**

**ethanethioate (3ua)**

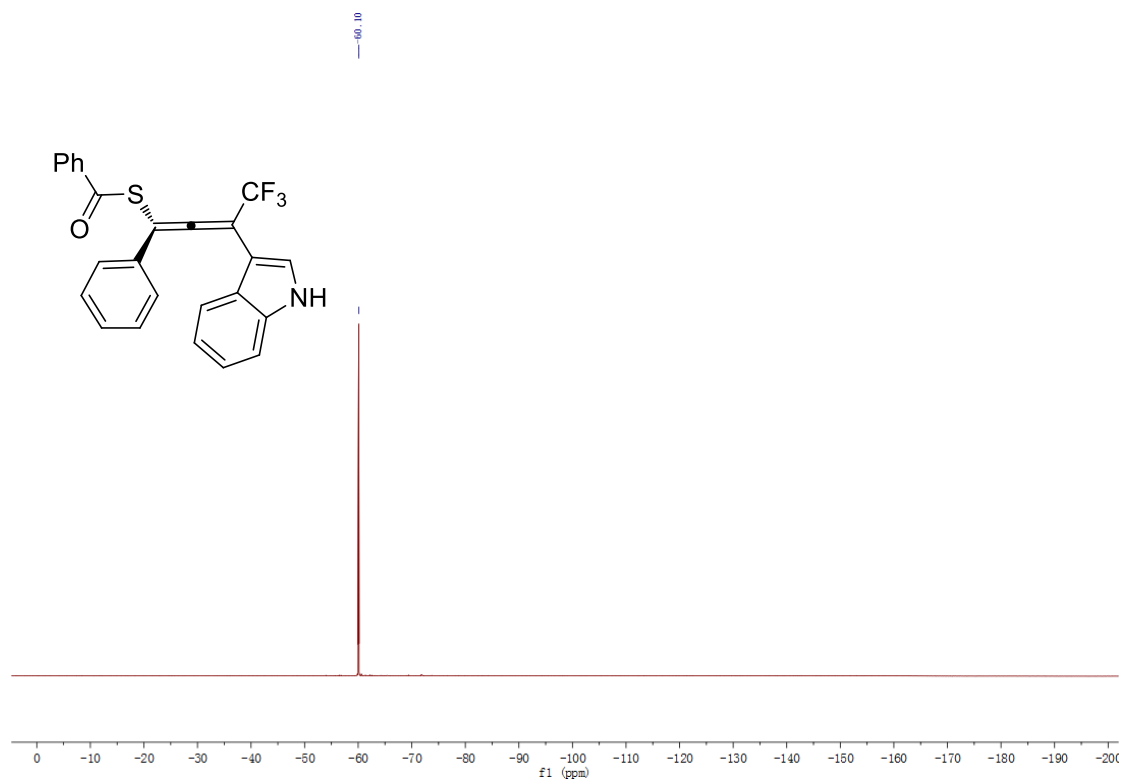


**(S)-S-(4,4,4-trifluoro-3-(7-methyl-1H-indol-3-yl)-1-phenylbuta-1,2-dien-1-yl) ethanethioate (3va)**

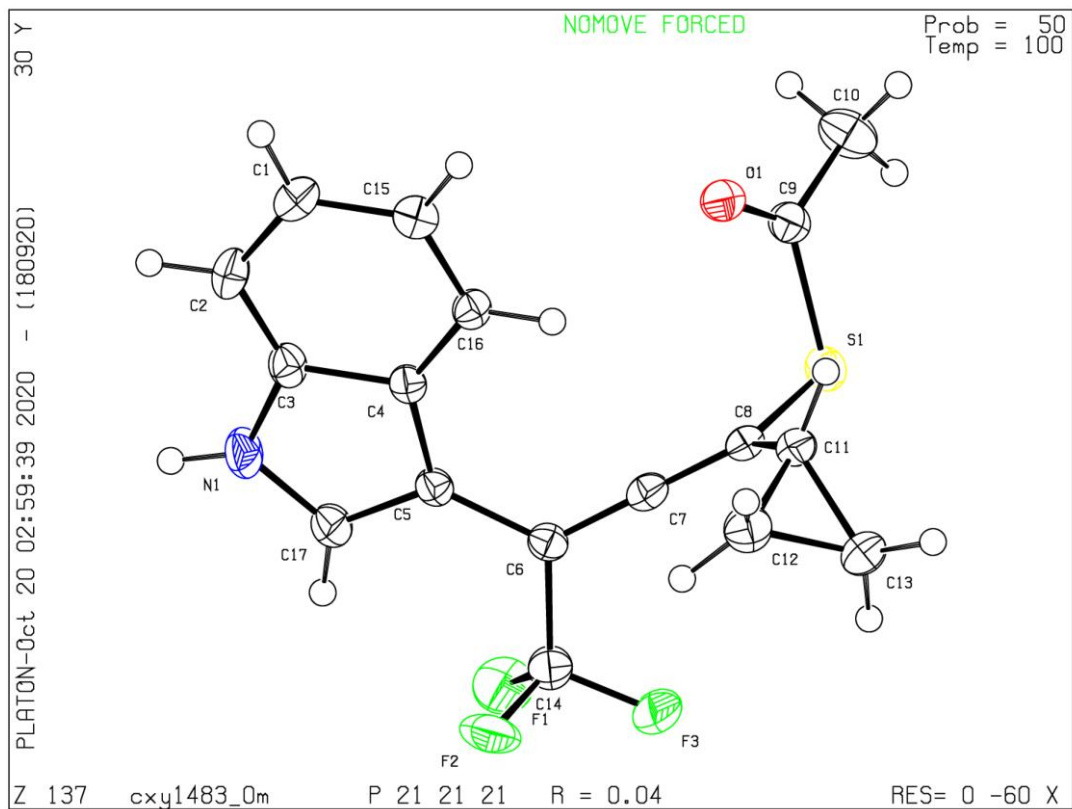


**(S)-S-(4,4,4-trifluoro-3-(1H-indol-3-yl)-1-phenylbuta-1,2-dien-1-yl) benzothioate**

(3ab)



# K: X-ray Analysis



**Table Crystal data and structure refinement for 3oa.**

Identification code	<b>3oa</b>
Empirical formula	C <sub>17</sub> H <sub>14</sub> F <sub>3</sub> NOS
Formula weight	337.35
Temperature/K	100
Crystal system	orthorhombic
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a/Å	8.9035(15)
b/Å	9.1118(17)
c/Å	20.094(4)
α/°	90
β/°	90
γ/°	90
Volume/Å <sup>3</sup>	1630.1(5)
Z	4
ρ <sub>calc</sub> /g/cm <sup>3</sup>	1.375
μ/mm <sup>-1</sup>	0.231
F(000)	696.0
Crystal size/mm <sup>3</sup>	0.31 × 0.24 × 0.14
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.908 to 55.626
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -25 ≤ l ≤ 26
Reflections collected	27976
Independent reflections	3831 [R <sub>int</sub> = 0.0760, R <sub>sigma</sub> = 0.0439]
Data/restraints/parameters	3831/0/209
Goodness-of-fit on F <sup>2</sup>	1.047
Final R indexes [I >= 2σ (I)]	R <sub>1</sub> = 0.0358, wR <sub>2</sub> = 0.0802
Final R indexes [all data]	R <sub>1</sub> = 0.0508, wR <sub>2</sub> = 0.0863
Largest diff. peak/hole / e Å <sup>-3</sup>	0.23/-0.21
Flack parameter	0.01(4)

## **L: Reference**

1. E. Martinelli, A. Vicini, M. Mancinelli, A. Mazzanti, P. Zani, L. Bernardi, M. Fochi, *Chem. Commun.* **2015**, *51*, 658-660.
2. X. Li, J. Sun, *Angew.Chem. Int. Ed.* **2020**, *59*, 17049-17054.