

# Ligandless Microwave-Assisted Pd(OAc)<sub>2</sub>-Catalyzed Direct Arylation of Thiazolo[3,2-*b*]-1,2,4-triazoles

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## Supporting Information

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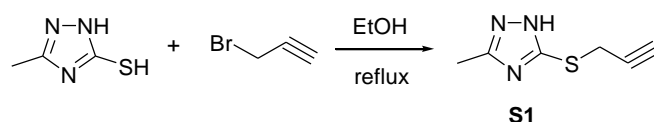
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## A. General method

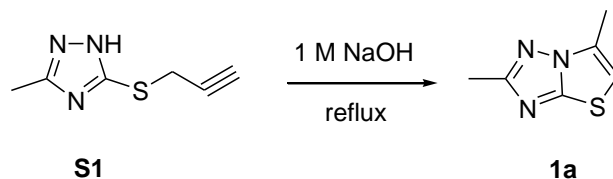
Unless otherwise noted, all reactions were carried out with a focused microwave unit (Biotage Initiator). Each reaction was run in a 5-mL glass pressure vial. The classical heating was performed in glassware heated in an oil bath. NMR spectra were recorded using a Bruker Avance 400 MHz NMR spectrometer (100 M Hz for carbon) and respectively referenced to 7.26 and 77.0 ppm for chloroform-d solvent with TMS as internal standard. ESI-MS spectra were measured on Finnigan Mat TSQ 7000 instruments. Elemental analyses were performed on a Heraeus elemental analyzer. Melting points were measured with a Tektronix X4 apparatus and are uncorrected. TLC was performed using commercially prepared 200-300 mesh silica gel plates (GF<sub>254</sub>), and visualization was effected at 254 nm.

## B. General Procedure

**Synthesis of 1a:** Compound **1a** was prepared according to the following procedure:



To a stirred solution of 5-methyl-2H-1,2,4-triazole-3-thiol (10 mmol) in C<sub>2</sub>H<sub>5</sub>OH (80 mL) at room temperature was added propynyl bromide (10 mmol) and heated under reflux for 3 h. After cooled to room temperature, the solvent was removed by vacuum. The reaction mixture was poured onto crushed ice and compound **S1** was separated by filtration.

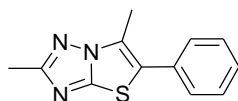


3-Methyl-5-(prop-2-ynylthio)-1H-1,2,4-triazole (5 mmol) was dissolved in 1 M NaOH (15 mL) and the mixture refluxed for 2 h. The mixture cooled to room

temperature and neutralized by addition of HCl. The solid was filtered off and crystallized from CHCl<sub>3</sub> to give a pure sample of **1a**.

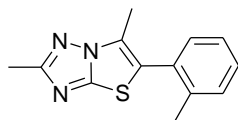
**Typical procedure for the synthesis of 3aa:** A 5-mL glass pressure vial was charged with 2,6-dimethylthiazolo[3,2-*b*]-1,2,4-triazole **1a** (0.5 mmol), bromobenzene **2a** (1.0 mmol), Pd(OAc)<sub>2</sub> (5 mol%), Cs<sub>2</sub>CO<sub>3</sub> (2.5 eq) and DMF (2 mL). The vial was sealed with a PTFE/silicone septum and heated to 140 °C for 0.5 h under microwave irradiation (400 W). The reaction mixture was allowed to cool to room and diluted with ethyl acetate (25 mL). The resulting solution was washed with brine (3×10 mL), dried over anhydrous MgSO<sub>4</sub>. The solvent was removed and the crude product was separated by column chromatography (eluted with petroleum ether : ethyl acetate=8 : 1) to afford target arylation product **3aa**.

## C. Analytical data for 3aa-3ef.



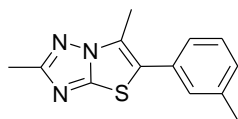
### 2,6-dimethyl-5-phenylthiazolo[3,2-*b*]-1,2,4-triazole(3aa)

White solid, m.p. 72-73 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.46-7.39 (m, 5H), 2.59 (s, 3H), 2.56 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.3, 155.3, 131.3, 129.1, 129.0, 128.8, 124.9, 124.0, 14.9, 11.7. ESI-MS m/z (%) 230 (100) [M+H]<sup>+</sup>. Anal. calcd. C, 62.86; H, 4.84; N, 18.33; Found: C, 62.82; H, 4.81; N, 18.27.



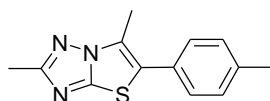
### 2,6-dimethyl-5-*o*-tolylthiazolo[3,2-*b*]-1,2,4-triazole(3ab)

Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.37-7.15 (m, 4H), 2.48 (s, 3H), 2.24 (s, 3H), 2.19 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.1, 155.2, 138.3, 131.6, 130.6, 129.7, 129.5, 126.1, 125.8, 122.4, 20.0, 14.9, 11.2. ESI-MS m/z (%) 244 [M+H]<sup>+</sup>. Anal. calcd. C, 64.17; H, 5.39; N, 17.27; Found: C, 64.12; H, 5.36; N, 17.21.



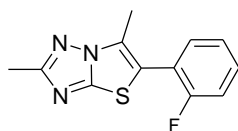
**2,6-dimethyl-5-*m*-tolylthiazolo[3,2-*b*]-1,2,4-triazole(3ac)**

Colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 (s, 1H), 7.37-7.35 (m, 1H), 7.23 (m, 2H), 2.60 (s, 3H), 2.57 (s, 3H), 2.43 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.2, 154.5, 138.9, 131.2, 129.6, 129.5, 129.1, 129.0, 128.9, 128.8, 126.1, 124.8, 124.2, 21.4, 14.9, 11.7. ESI-MS  $m/z$  (%) 244  $[\text{M}+\text{H}]^+$ . Anal. calcd. C, 64.17; H, 5.39; N, 17.27; Found: C, 64.10; H, 5.34; N, 17.20.



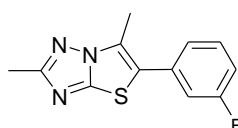
**2,6-dimethyl-5-*p*-tolylthiazolo[3,2-*b*]-1,2,4-triazole(3ad)**

White solid, m.p. 178-180 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 (d,  $J = 8.0$  Hz, 2H), 7.27 (d,  $J = 8.4$  Hz, 2H), 2.57 (s, 3H), 2.56 (s, 3H), 2.41 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.2, 154.4, 138.9, 129.8, 128.9, 128.3, 124.5, 124.1, 21.3, 14.9, 11.6. ESI-MS  $m/z$  (%) 244 (100)  $[\text{M}+\text{H}]^+$ . Anal. calcd. C, 64.17; H, 5.39; N, 17.27; Found: C, 64.11; H, 5.35; N, 17.22.



**5-(2-fluorophenyl)-2,6-dimethylthiazolo[3,2-*b*]-1,2,4-triazole(3ae)**

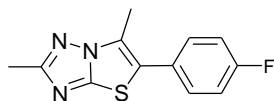
White solid, m.p. 106-107 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47-7.41 (m, 2H), 7.29-7.19 (m, 2H), 2.57(s, 3H), 2.48(s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.4, 161.0, 158.5, 155.3, 132.0, 131.9, 131.2, 131.1, 127.2, 124.7, 124.6, 118.8, 118.6, 116.7, 116.5, 116.3, 14.9, 11.8. ESI-MS  $m/z$  (%) 248 (100)  $[\text{M}+\text{H}]^+$ . Anal. calcd. C, 58.28; H, 4.08; N, 16.99; Found: C, 58.22; H, 4.03; N, 16.91.



**5-(3-fluorophenyl)-2,6-dimethylthiazolo[3,2-*b*]-1,2,4-triazole(3af)**

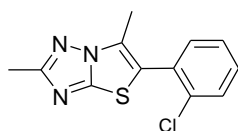
White solid, m.p. 84-85 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 (dd,  $J = 8.0$  Hz,  $J =$

7.6 Hz, 1H), 7.24-7.09 (m, 3H), 2.61 (s, 3H), 2.56(s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.5, 164.0, 161.6, 154.5, 133.3, 133.2, 130.8, 130.7, 129.1, 128.9, 125.6, 124.7, 124.6, 122.5, 115.9, 115.8, 115.7, 115.6, 14.9, 11.7. ESI-MS  $m/z$  (%) 248 (100)  $[\text{M}+\text{H}]^+$ . Anal. calcd. C, 58.28; H, 4.08; N, 16.99; Found: C, 58.22; H, 4.02; N, 16.93.



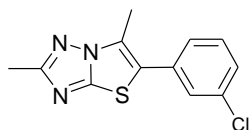
**5-(4-fluorophenyl)-2,6-dimethylthiazolo[3,2-*b*]-1,2,4-triazole(3ag)**

White solid, m.p. 131-132 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46-7.43 (m, 2H), 7.19-7.16 (m, 2H), 2.57 (s, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.1, 161.7, 154.4, 131.0, 130.9, 127.2, 125.1, 122.9, 116.4, 116.2, 14.9, 11.6. ESI-MS  $m/z$  (%) 248 (100)  $[\text{M}+\text{H}]^+$ . Anal. calcd. C, 58.28; H, 4.08; N, 16.99; Found: C, 58.21; H, 4.04; N, 16.92.



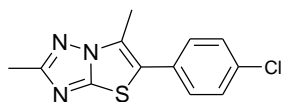
**5-(2-chlorophenyl)-2,6-dimethylthiazolo[3,2-*b*]-1,2,4-triazole(3ah)**

Colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (m, 1H), 7.40-7.30 (m, 3H), 2.53 (s, 3H), 2.35 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.3, 155.3, 135.0, 133.0, 130.9, 130.2, 129.3, 127.2, 127.1, 119.9, 14.9, 11.6. ESI-MS  $m/z$  (%) 264 (100)  $[\text{M}+\text{H}]^+$ . Anal. calcd. C, 54.65; H, 3.82; N, 15.93; Found: C, 54.58; H, 3.76; N, 15.86.



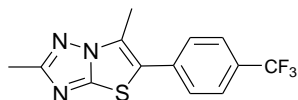
**5-(3-chlorophenyl)-2,6-dimethylthiazolo[3,2-*b*]-1,2,4-triazole(3ai)**

White solid, m.p. 92-93 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (s, 1H), 7.42-7.34 (m, 3H), 2.61 (s, 3H), 2.57 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.6, 154.5, 135.1, 133.0, 130.4, 128.9, 128.8, 127.2, 125.7, 122.4, 14.9, 11.8. ESI-MS  $m/z$  (%) 264 (100)  $[\text{M}+\text{H}]^+$ . Anal. calcd. C, 54.65; H, 3.82; N, 15.93; Found: C, 54.60; H, 3.75; N, 15.88.



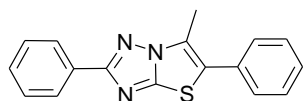
**5-(4-chlorophenyl)-2,6-dimethylthiazolo[3,2-*b*]-1,2,4-triazole(3aj)**

White solid, m.p. 158-160 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 2.58 (s, 3H), 2.56 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.5, 154.7, 134.9, 130.2, 129.7, 129.4, 125.3, 122.7, 14.9, 11.7. ESI-MS *m/z* (%) 264 (100) [M+H]<sup>+</sup>. Anal. calcd. C, 54.65; H, 3.82; N, 15.93; Found: C, 54.56; H, 3.75; N, 15.85.



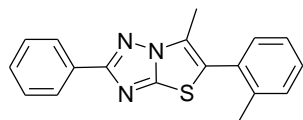
**5-(4-(trifluoromethyl)phenyl)-2,6-dimethylthiazolo[3,2-*b*]-1,2,4-triazole(3ak)**

White solid, m.p. 219-221 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 2.62 (s, 3H), 2.55 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.1, 154.6, 135.0, 130.9, 130.6, 129.2, 126.1, 126.0, 125.2, 122.3, 14.9, 11.8. ESI-MS *m/z* (%) 298 (100) [M+H]<sup>+</sup>. Anal. calcd. C, 52.52; H, 3.39; N, 14.13; Found: C, 52.46; H, 3.34; N, 14.07.



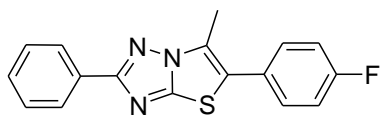
**6-methyl-2,5-diphenylthiazolo[3,2-*b*]-1,2,4-triazole(3ba)**

White solid, m.p. 135-137 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.21 (d, 2H), 7.48-7.41 (m, 8H), 2.65 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 166.0, 155.0, 131.3, 129.6, 129.1, 128.9, 128.8, 128.7, 126.7, 125.2, 124.7, 11.8. ESI-MS *m/z* (%) 292 (100) [M+H]<sup>+</sup>. Anal. calcd. C, 70.08; H, 4.50; N, 14.42; Found: C, 70.02; H, 4.46; N, 14.36.



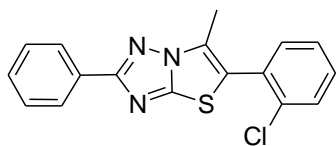
**6-methyl-2-phenyl-5-*o*-tolylthiazolo[3,2-*b*]-1,2,4-triazole(3bb)**

Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.21 (d, 2H) 7.47-7.40 (m, 3H), 7.35-7.27 (m, 4H), 2.39 (s, 3H), 2.29 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.9, 155.8, 138.4, 131.7, 131.4, 130.7, 129.8, 129.6, 129.5, 128.7, 126.7, 126.2, 123.2, 20.1, 11.3. ESI-MS *m/z* (%) 306 (100) [M+H]<sup>+</sup>. Anal. calcd. C, 70.79; H, 4.95; N, 13.76; Found: C, 70.70; H, 4.91; N, 13.71.



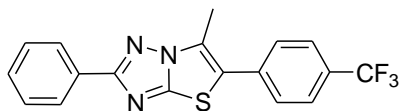
**5-(4-Fluorophenyl)-6-methyl-2-phenylthiazolo[3,2-*b*]-1,2,4-triazole(3bg)**

White solid, m.p. 173-175 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.20 (d, 2H), 7.49-7.43 (m, 5H), 7.20-7.16 (m, 2H), 2.64 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.1, 154.9, 131.2, 131.0, 130.9, 129.6, 128.7, 127.3, 126.7, 125.4, 123.5, 116.5, 116.2, 11.7. ESI-MS  $m/z$  (%) 310 (100)  $[\text{M}+\text{H}]^+$ . Anal. calcd. C, 66.00; H, 3.91; N, 13.58; Found: C, 65.93; H, 3.85; N, 13.51.



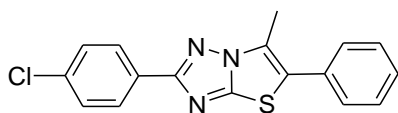
**5-(2-chlorophenyl)-6-methyl-2-phenylthiazolo[3,2-*b*]-1,2,4-triazole(3bh)**

Colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.21 (d, 2H) 7.50-7.29 (m, 7H), 2.43 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.1, 155.9, 135.0, 133.0, 131.3, 130.9, 130.3, 129.6, 129.3, 128.7, 127.6, 127.2, 126.7, 120.7, 11.8. ESI-MS  $m/z$  (%) 326 (100)  $[\text{M}+\text{H}]^+$ . Anal. calcd. C, 62.67; H, 3.71; N, 12.90; Found: C, 62.60; H, 3.66; N, 12.82.



**5-(4-(trifluoromethyl)phenyl)-6-methyl-2-phenylthiazolo[3,2-*b*]-1,2,4-triazole(3bk)**

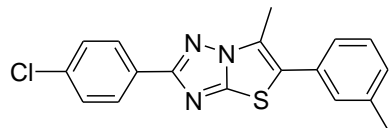
White solid, m.p. 247-249 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.20-8.17 (m, 2H), 7.73-7.71 (m, 2H), 7.59-7.58 (m, 2H), 7.47-7.41 (m, 3H), 2.66 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.4, 155.1, 135.0, 131.1, 130.9, 130.5, 129.7, 129.2, 128.7, 126.7, 126.4, 126.1, 126.0, 125.2, 122.9, 122.5, 11.9. ESI-MS  $m/z$  (%) 360 (100)  $[\text{M}+\text{H}]^+$ . Anal. calcd. C, 60.16; H, 3.37; N, 11.69; Found: C, 62.08; H, 3.31; N, 11.59.



**2-(4-chlorophenyl)-6-methyl-5-phenylthiazolo[3,2-*b*]-1,2,4-triazole(3ca)**

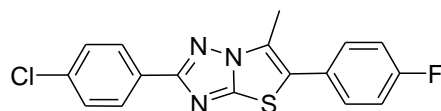
White solid, m.p. 188-190 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 (d, 2H), 7.50-7.49 (m, 4H), 7.45-7.43 (m, 3H), 2.67 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.9, 155.1,

135.4, 131.2, 130.3, 129.8, 129.2, 129.0, 128.9, 127.9, 125.2, 123.8, 11.7. ESI-MS  $m/z$  (%) 326 (100)  $[M+H]^+$ . Anal. calcd. C, 62.67; H, 3.71; N, 12.90; Found: C, 62.60; H, 3.66; N, 12.82.



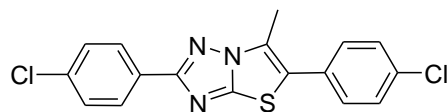
**2-(4-chlorophenyl)-6-methyl-5-*m*-tolylthiazolo[3,2-*b*]-1,2,4-triazole(3cc)**

White solid, m.p. 112-113 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13 (d, 2H), 7.44-7.34 (m, 3H), 7.29-7.22 (m, 3H), 2.65 (s, 3H), 2.43 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.0, 155.1, 139.1, 135.5, 131.1, 129.9, 129.7, 129.6, 129.0, 128.9, 127.9, 126.1, 125.2, 125.0, 21.4, 11.8. ESI-MS  $m/z$  (%) 340 (100)  $[M+H]^+$ . Anal. calcd. C, 63.62; H, 4.15; N, 12.36; Found: C, 63.55; H, 4.10; N, 12.28.



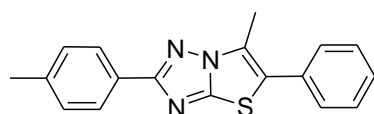
**2-(4-chlorophenyl)-5-(4-fluorophenyl)-6-methylthiazolo[3,2-*b*]-1,2,4-triazole(3cg)**

White solid, m.p. 153-155 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13 (d, 2H), 7.49-7.42 (m, 4H), 7.20-7.16 (m, 2H), 2.63 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.2, 155.0, 135.6, 131.0, 130.9, 129.8, 128.9, 127.9, 127.2, 125.4, 123.8, 116.4, 116.2, 11.6. ESI-MS  $m/z$  (%) 344 (100)  $[M+H]^+$ . Anal. calcd. C, 59.39; H, 3.22; N, 12.22; Found: C, 59.30; H, 3.17; N, 12.15.



**5-(4-chlorophenyl)-2-(4-chlorophenyl)-6-methylthiazolo[3,2-*b*]-1,2,4-triazole(3cj)**

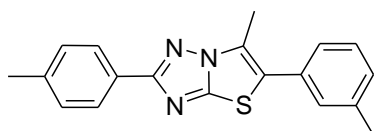
White solid, m.p. > 280 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.12 (d, 2H), 7.47-7.40 (m, 6H), 2.63 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.2, 155.0, 135.6, 135.1, 130.2, 129.7, 129.6, 129.4, 128.9, 127.9, 125.6, 123.6, 11.7. ESI-MS  $m/z$  (%) 360 (100)  $[M+H]^+$ . Anal. calcd. C, 56.68; H, 3.08; N, 11.66; Found: C, 56.60; H, 3.02; N, 11.57.



**6-methyl-5-phenyl-2-*p*-tolylthiazolo[3,2-*b*]-1,2,4-triazole(3da)**

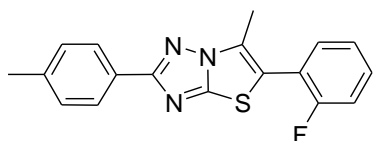


White solid, m.p. 169-170 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 (d, 2H), 7.49-7.40 (m, 5H), 7.28-7.26 (m, 2H), 2.65 (s, 3H), 2.40 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.2, 154.9, 139.6, 131.4, 129.4, 129.1, 128.9, 128.8, 128.5, 126.6, 125.2, 124.5, 21.5, 11.8. ESI-MS  $m/z$  (%) 306 (100)  $[\text{M}+\text{H}]^+$ . Anal. calcd. C, 70.79; H, 4.95; N, 13.76; Found: C, 70.72; H, 4.91; N, 13.68.



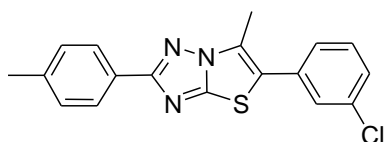
**6-methyl-5-*m*-tolyl-2-*p*-tolylthiazolo[3,2-*b*]-1,2,4-triazole(3dc)**

White solid, m.p. 100-101 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (d, 2H), 7.36-7.21 (m, 6H), 2.66 (s, 3H), 2.42 (s, 3H), 2.40 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.1, 154.9, 139.6, 139.0, 131.2, 129.6, 129.4, 129.0, 128.5, 126.6, 126.1, 125.1, 124.7, 21.5, 11.9. ESI-MS  $m/z$  (%) 320 (91)  $[\text{M}+\text{H}]^+$ . Anal. calcd. C, 71.44; H, 5.36; N, 13.15; Found: C, 71.36; H, 5.32; N, 13.04.



**5-(2-fluorophenyl)-6-methyl-2-*p*-tolylthiazolo[3,2-*b*]-1,2,4-triazole(3de)**

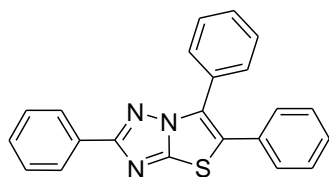
White solid, m.p. 125-126 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.11 (d, 2H), 7.46-7.42 (m, 2H), 7.30-7.19 (m, 4H), 2.55 (s, 3H), 2.42 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.3, 161.0, 158.6, 155.7, 139.7, 131.9, 131.2, 131.1, 129.4, 128.4, 127.5, 126.7, 124.7, 124.6, 118.8, 118.7, 117.2, 116.6, 116.3, 21.5, 11.9. ESI-MS  $m/z$  (%) 324 (100)  $[\text{M}+\text{H}]^+$ . Anal. calcd. C, 66.85; H, 4.36; N, 12.99; Found: C, 66.79; H, 4.32; N, 13.06.



**5-(3-chlorophenyl)-6-methyl-2-*p*-tolylthiazolo[3,2-*b*]-1,2,4-triazole(3di)**

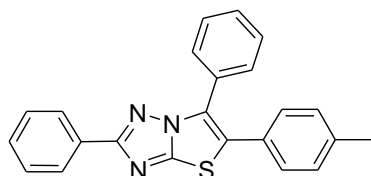
White solid, m.p. 130-131 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (d, 2H), 7.46 (s, 1H), 7.39-7.35 (m, 3H), 7.27-7.25 (m, 2H), 2.64 (s, 3H), 2.39 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.4, 154.9, 139.8, 135.1, 133.1, 130.4, 129.4, 128.8, 128.3, 127.1, 126.6, 125.9, 122.8, 21.5, 11.9. ESI-MS  $m/z$  (%) 340 (96)  $[\text{M}+\text{H}]^+$ . Anal. calcd. C,

63.62; H, 4.15; N, 12.36; Found: C, 63.54; H, 4.09; N, 12.28.



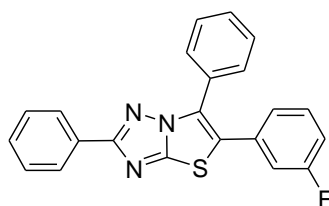
**2,5,6-triphenylthiazolo[3,2-*b*]-1,2,4-triazole(3ea)**

White solid, m.p. 255-257 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.19 (d, 2H), 7.69-7.67 (m, 2H), 7.47-7.40 (m, 6H), 7.38-7.33 (m, 5H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 166.0, 155.3, 131.4, 131.2, 129.9, 129.6, 129.4, 129.1, 129.0, 128.7, 128.6, 128.3, 127.8, 126.8, 126.3. ESI-MS m/z (%) 354 (96) [M+H]<sup>+</sup>. Anal. calcd. C, 74.76; H, 4.28; N, 11.89; Found: C, 74.70; H, 4.24; N, 11.80.



**2,6-diphenyl-5-*p*-tolylthiazolo[3,2-*b*]-1,2,4-triazole(3ed)**

White solid, m.p. 233-235 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.19 (d, 2H), 7.70-7.68 (m, 2H), 7.46-7.40 (m, 6H), 7.26-7.24 (m, 2H), 7.16-7.14 (m, 2H), 2.36 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.9, 155.3, 139.2, 131.4, 129.9, 129.8, 129.6, 129.2, 128.7, 128.6, 127.9, 126.8, 125.1, 124.6, 21.3. ESI-MS m/z (%) 368 (100) [M+H]<sup>+</sup>. Anal. calcd. C, 75.18; H, 4.66; N, 11.44; Found: C, 75.11; H, 4.61; N, 11.38.

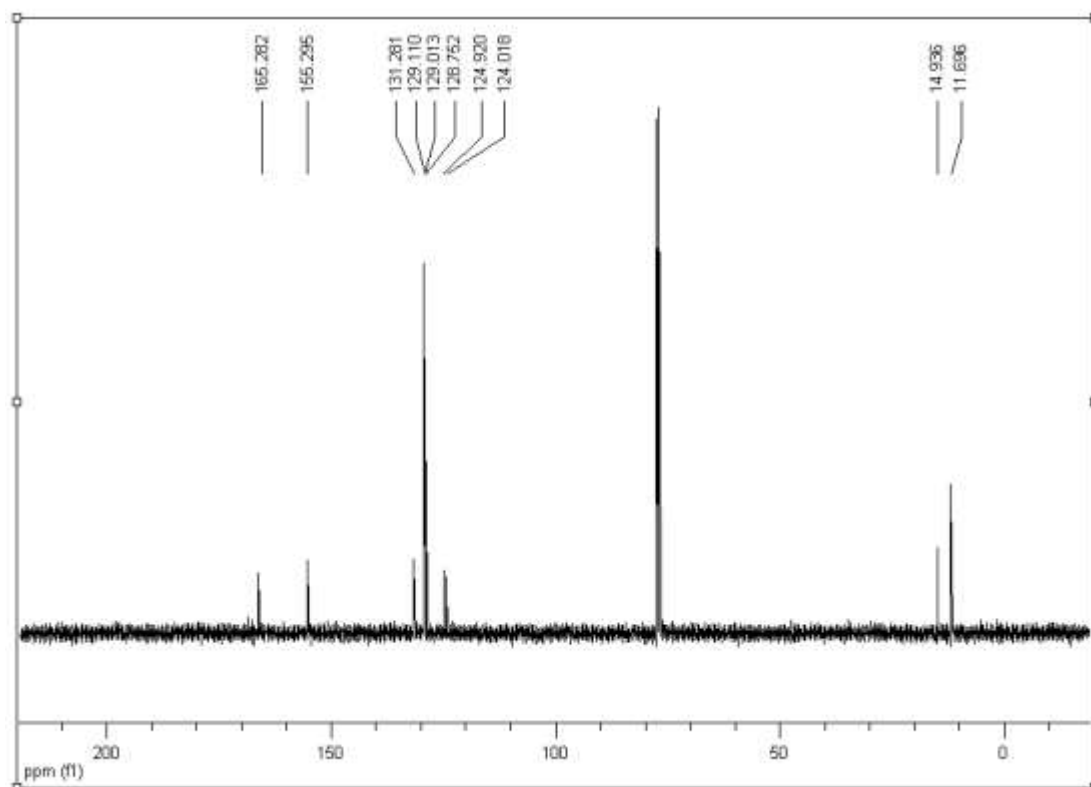
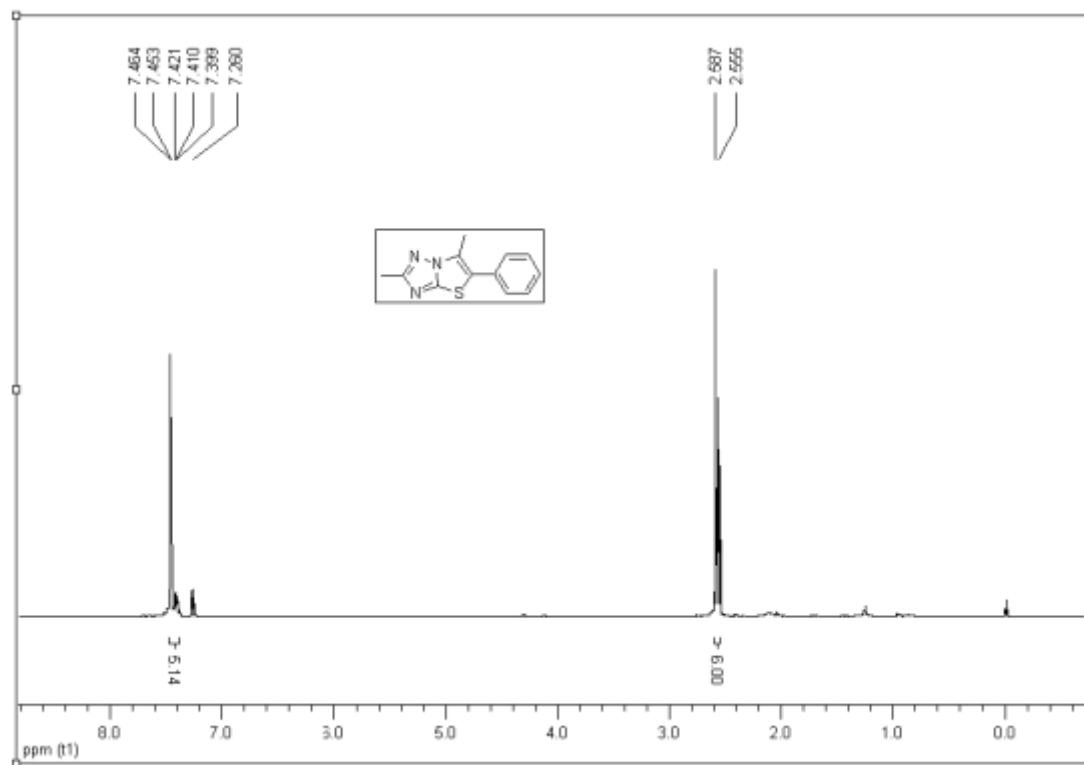


**5-(3-fluorophenyl)-2,6-diphenylthiazolo[3,2-*b*]-1,2,4-triazole(3ef)**

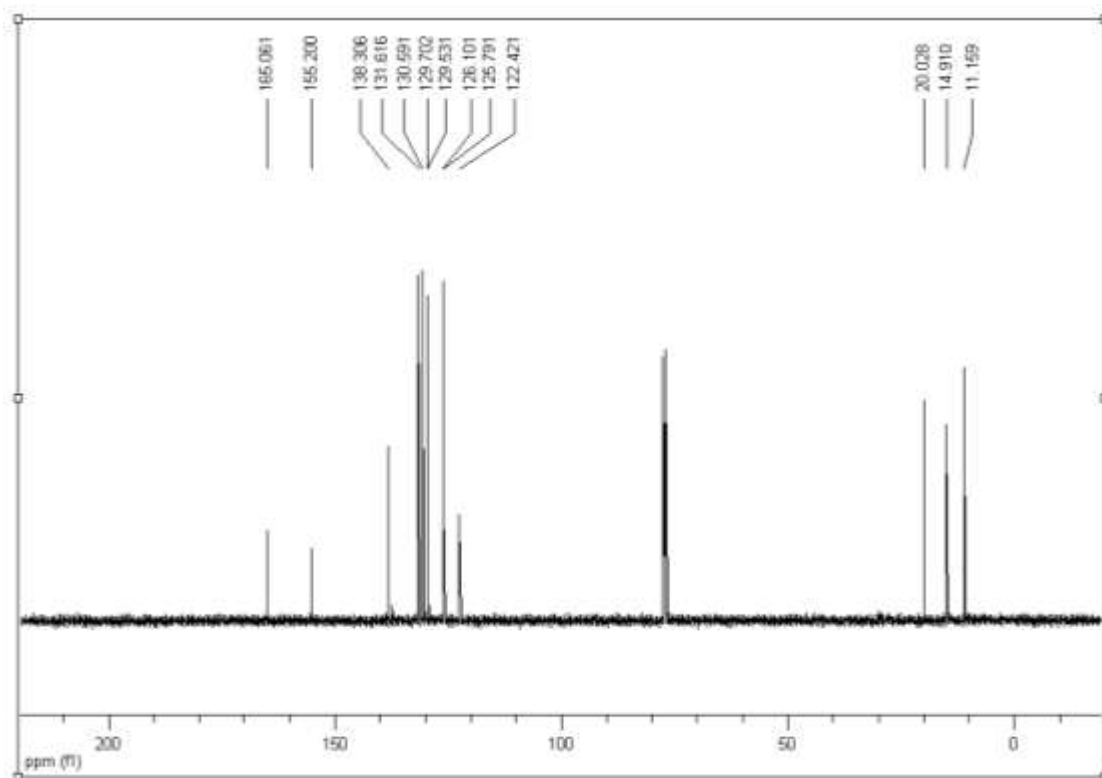
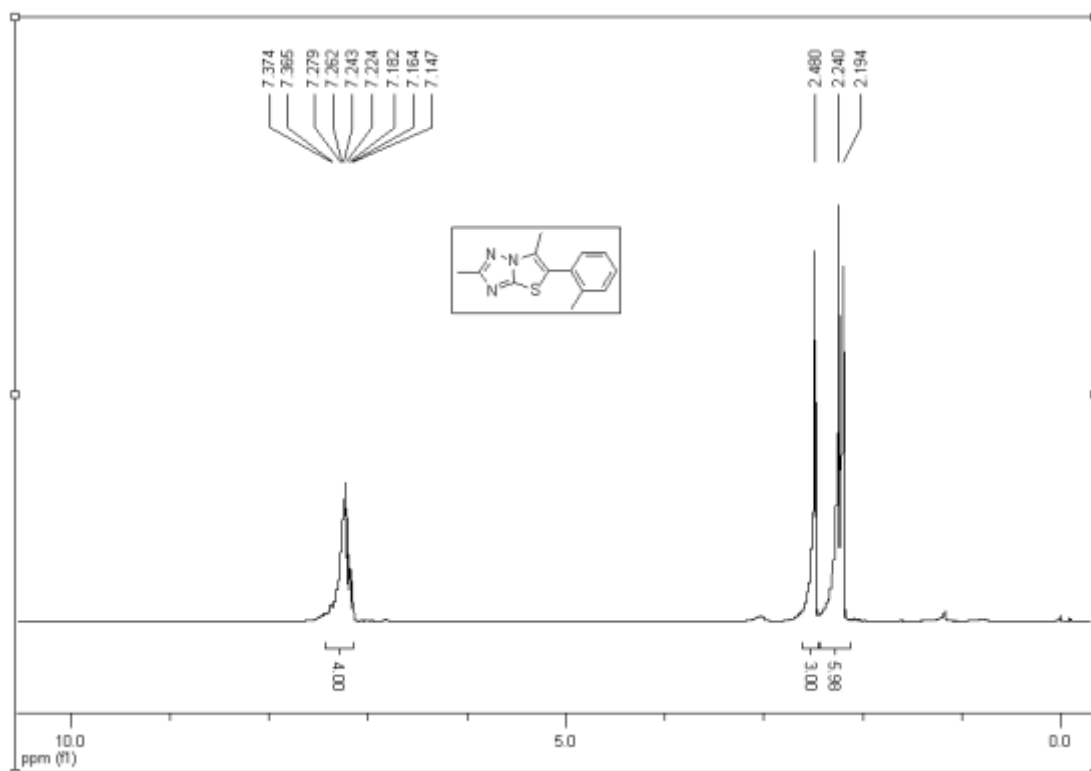
White solid, m.p. 228-230 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.20-8.18 (m, 2H), 7.69-7.67 (m, 2H), 7.47-7.43 (m, 6H), 7.34-7.29 (m, 1H), 7.16-7.14 (m, 1H), 7.08-7.03 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 166.3, 164.0, 161.6, 155.2, 133.4, 131.0, 130.8, 130.7, 130.0, 129.9, 129.7, 129.0, 128.9, 128.6, 127.4, 126.8, 125.1, 125.0, 124.7, 116.4, 116.1, 115.9. ESI-MS m/z (%) 372 (100) [M+H]<sup>+</sup>. Anal. calcd. C, 71.14; H, 3.80; N, 11.31; Found: C, 71.06; H, 3.75; N, 11.24.

## D. NMR spectra

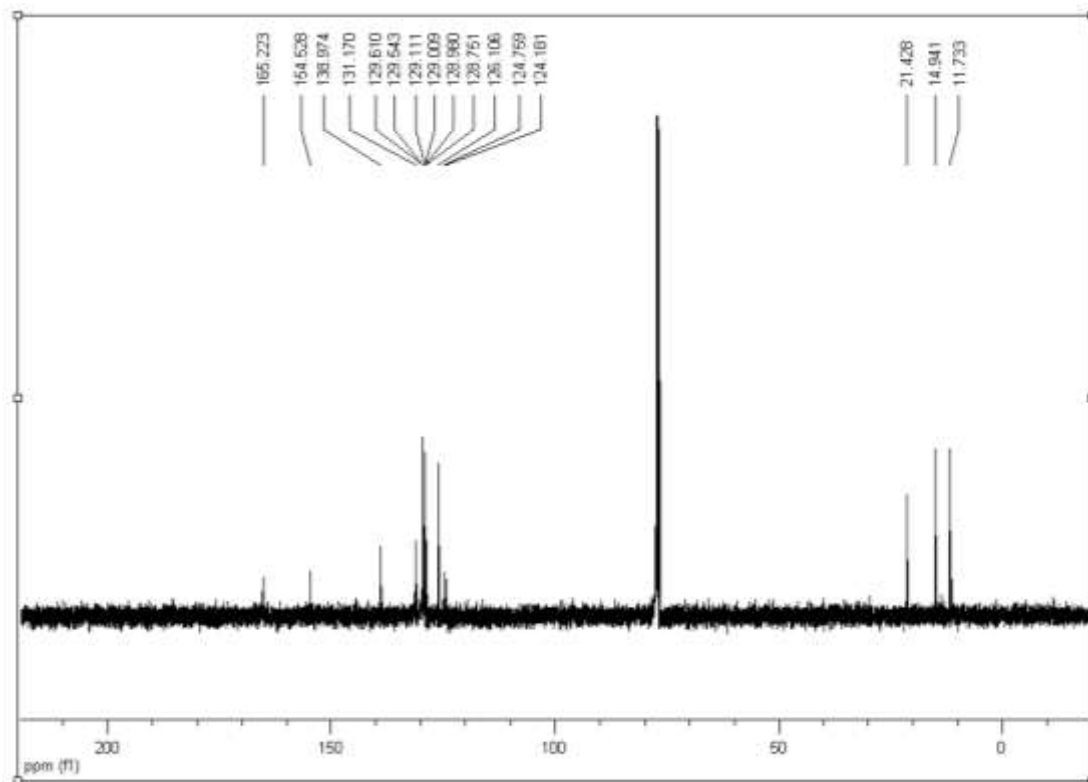
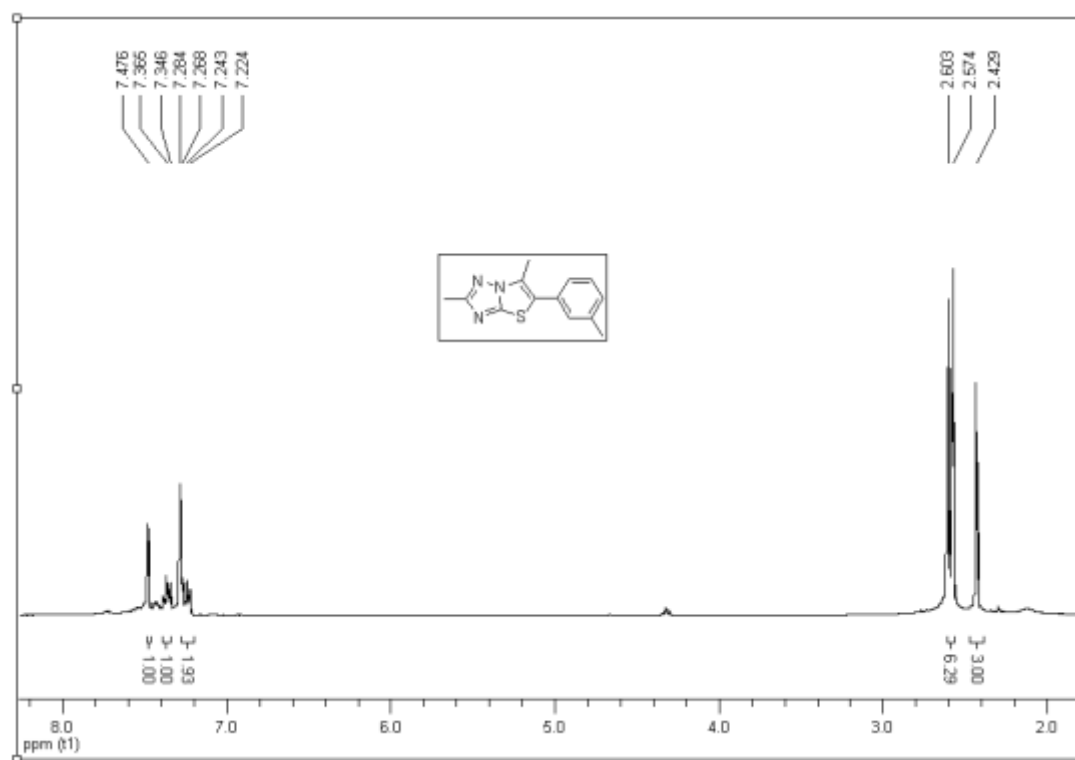
2,6-dimethyl-5-phenylthiazolo[3,2-*b*]-1,2,4-triazole(3aa)



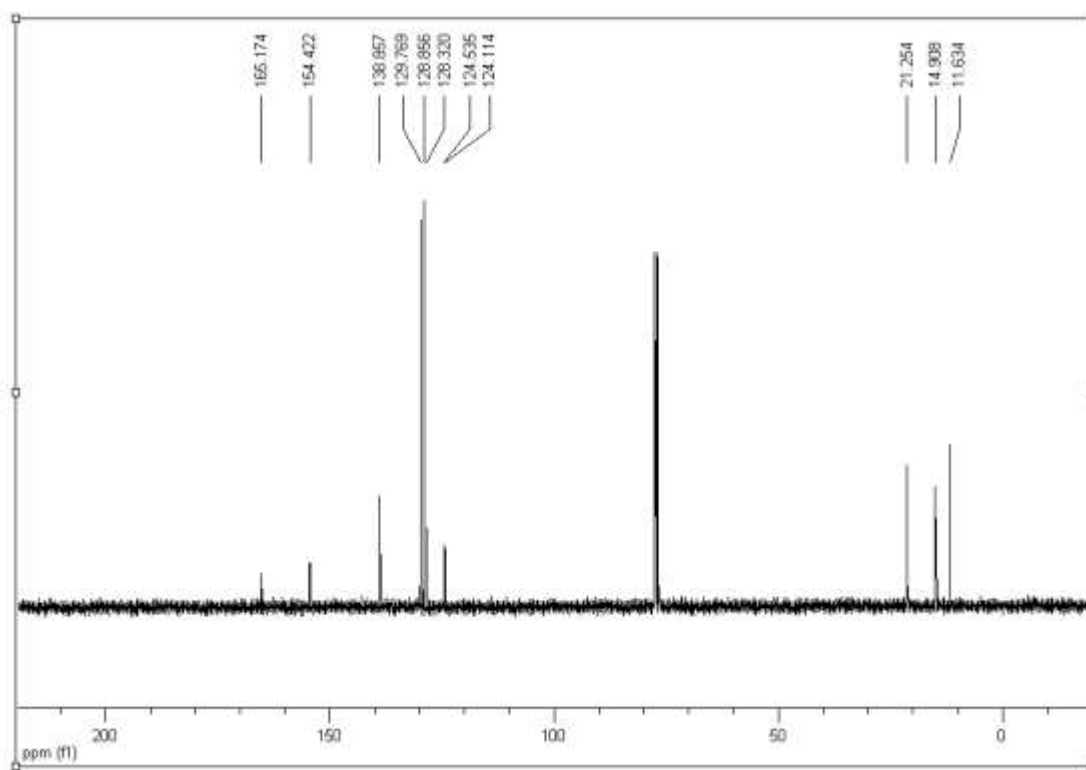
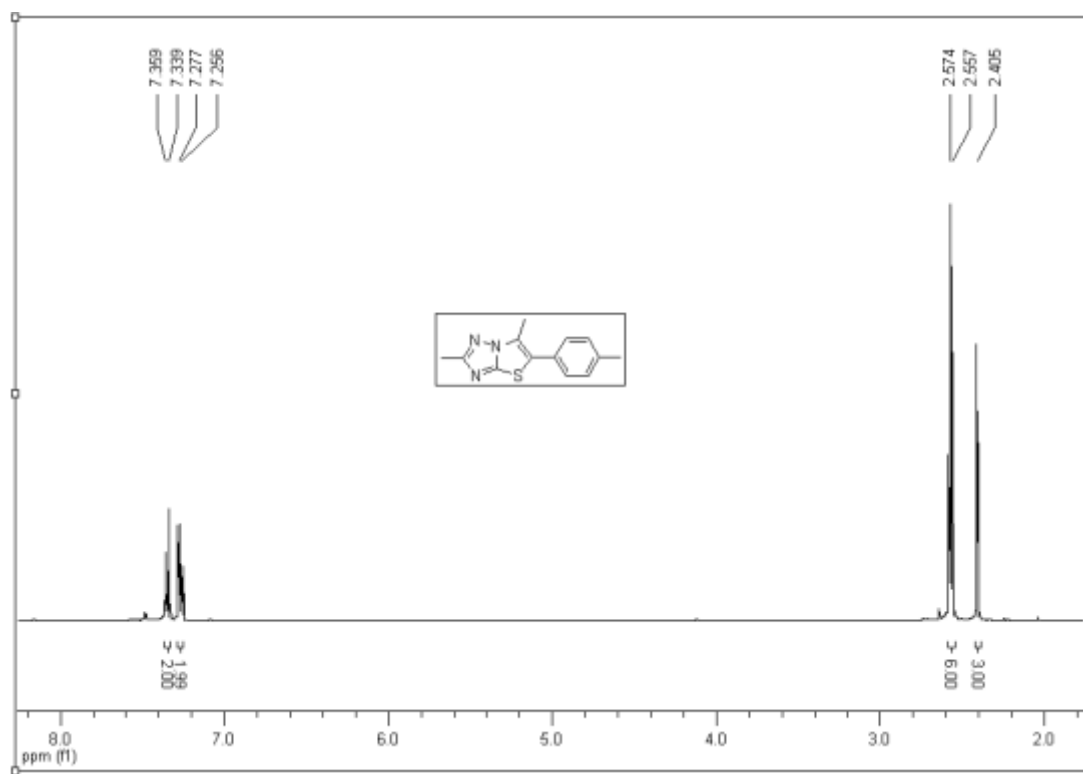
2,6-dimethyl-5-*o*-tolylthiazolo[3,2-*b*]-1,2,4-triazole(3ab)



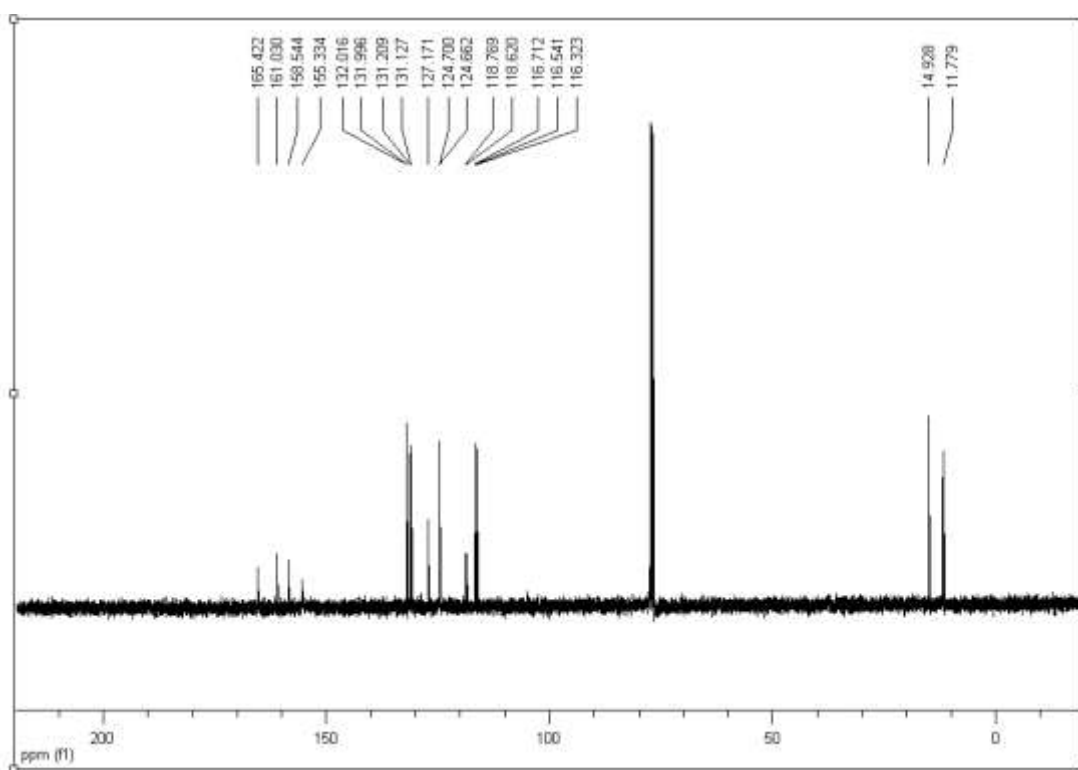
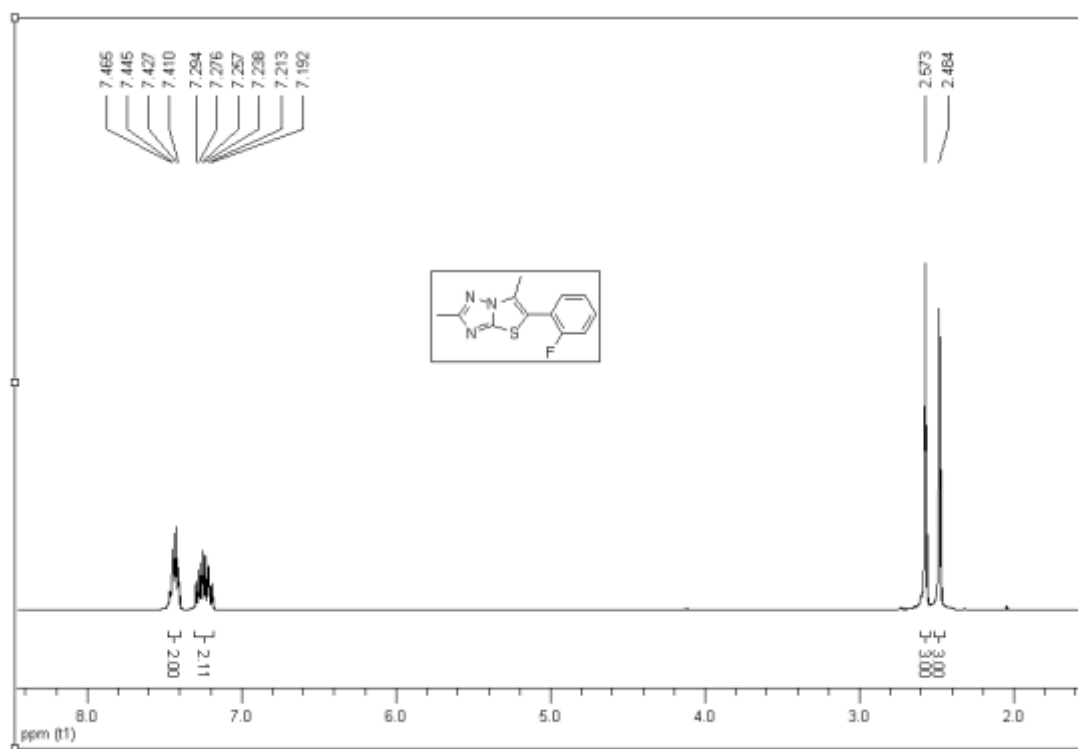
**2,6-dimethyl-5-*m*-tolylthiazolo[3,2-*b*]-1,2,4-triazole(3ac)**



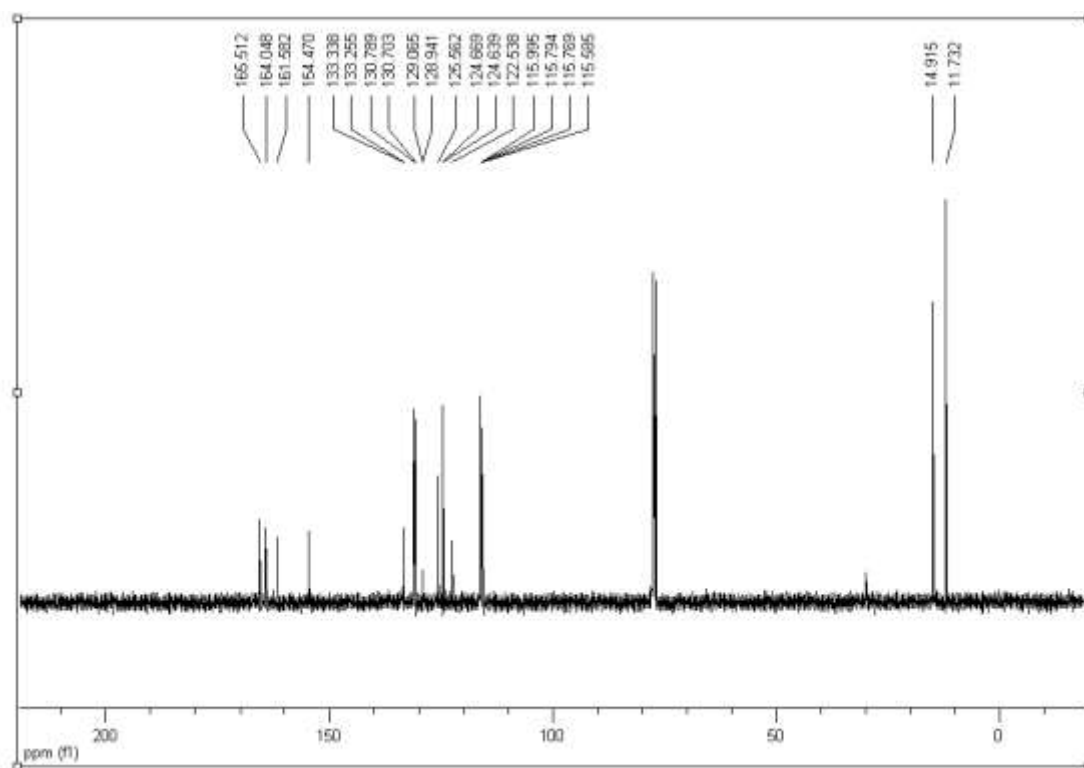
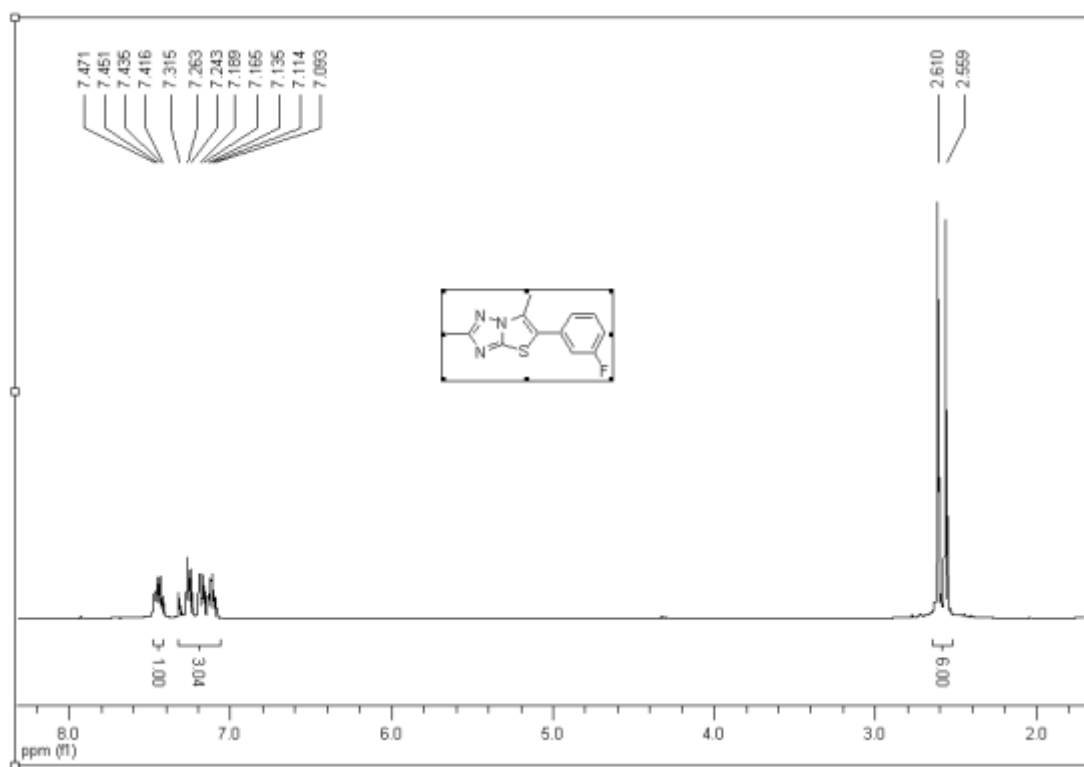
### 2,6-dimethyl-5-p-tolylthiazolo[3,2-b]-1,2,4-triazole(3ad)



### 5-(2-fluorophenyl)-2,6-dimethylthiazolo[3,2-*b*]-1,2,4-triazole(3ae)

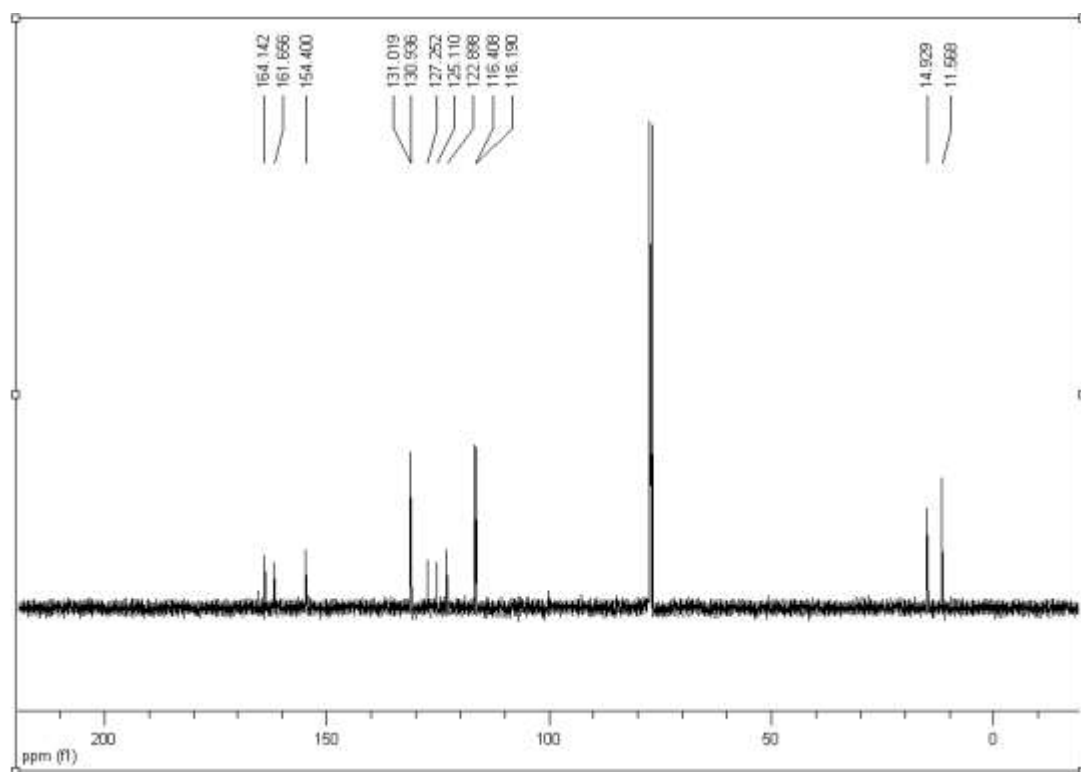
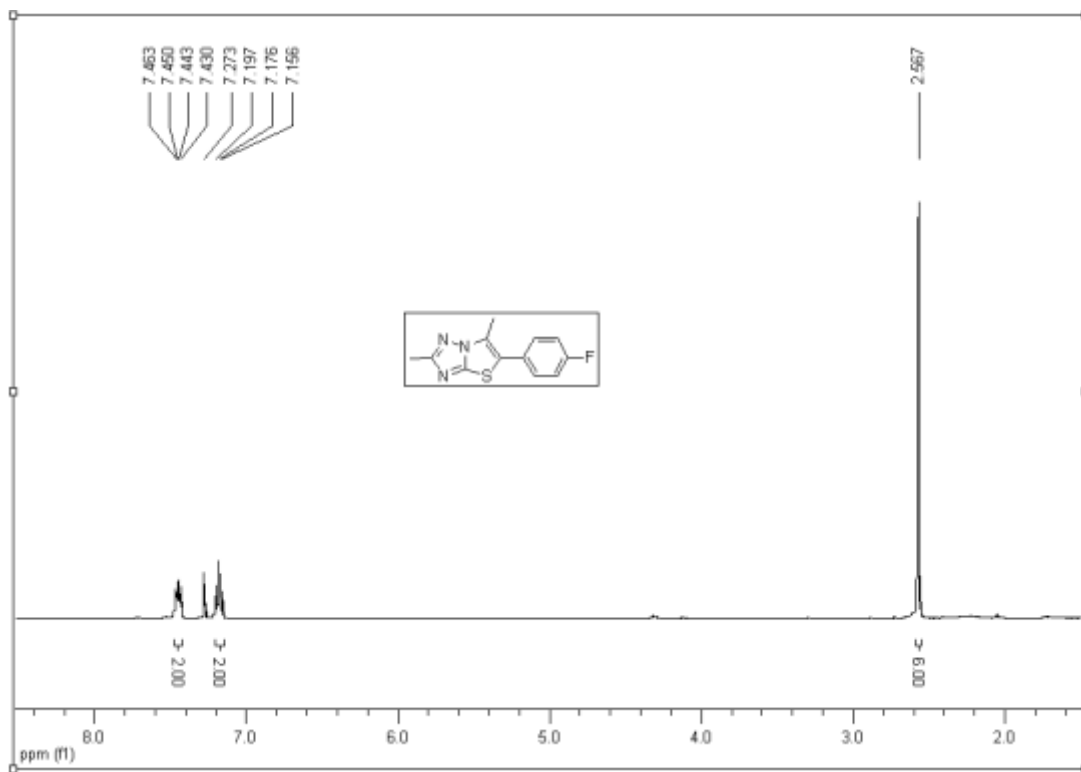


**5-(3-fluorophenyl)-2,6-dimethylthiazolo[3,2-*b*]-1,2,4-triazole(3af)**

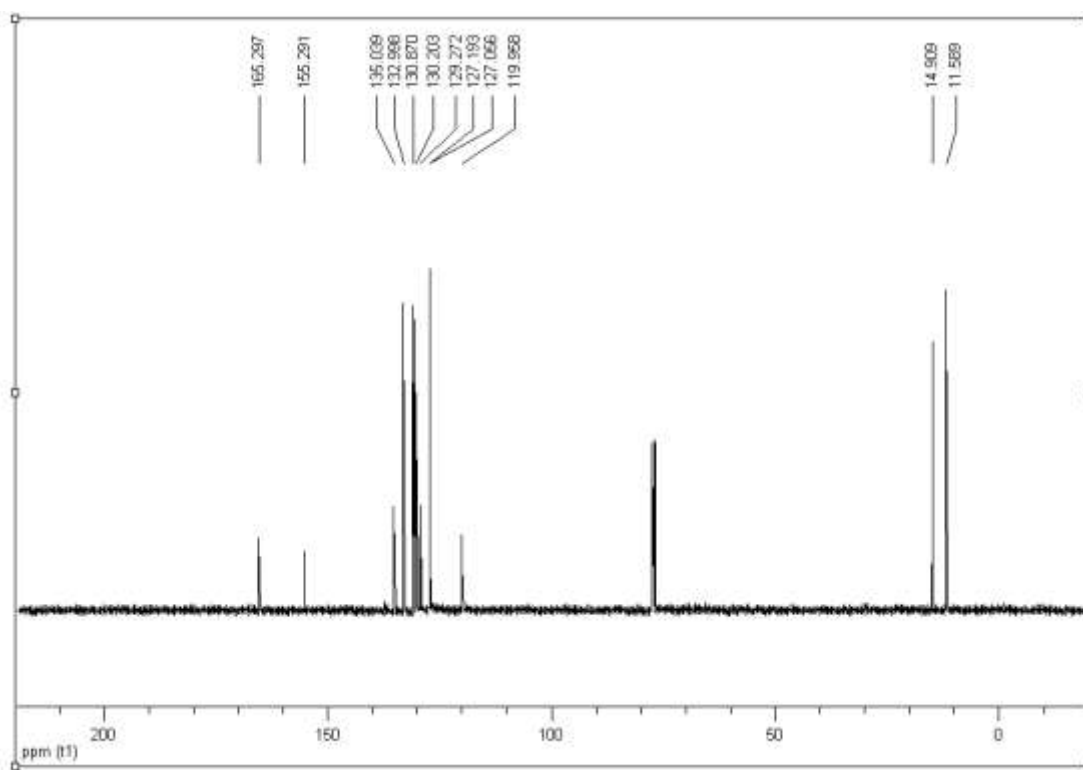
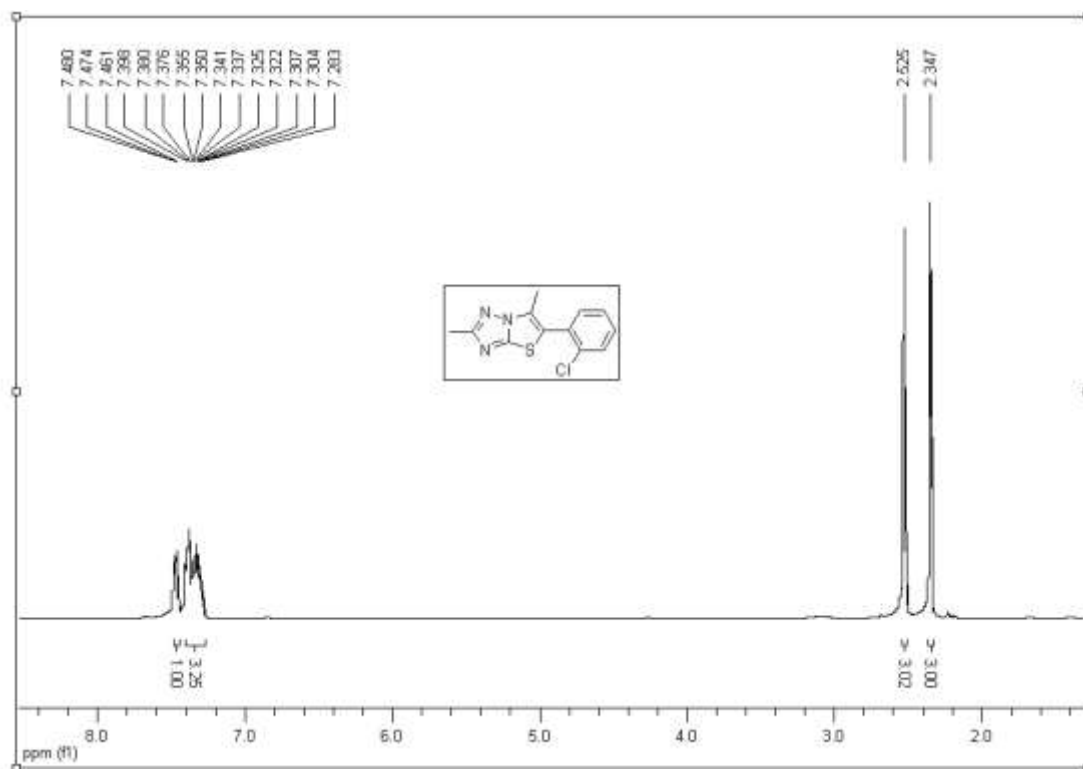




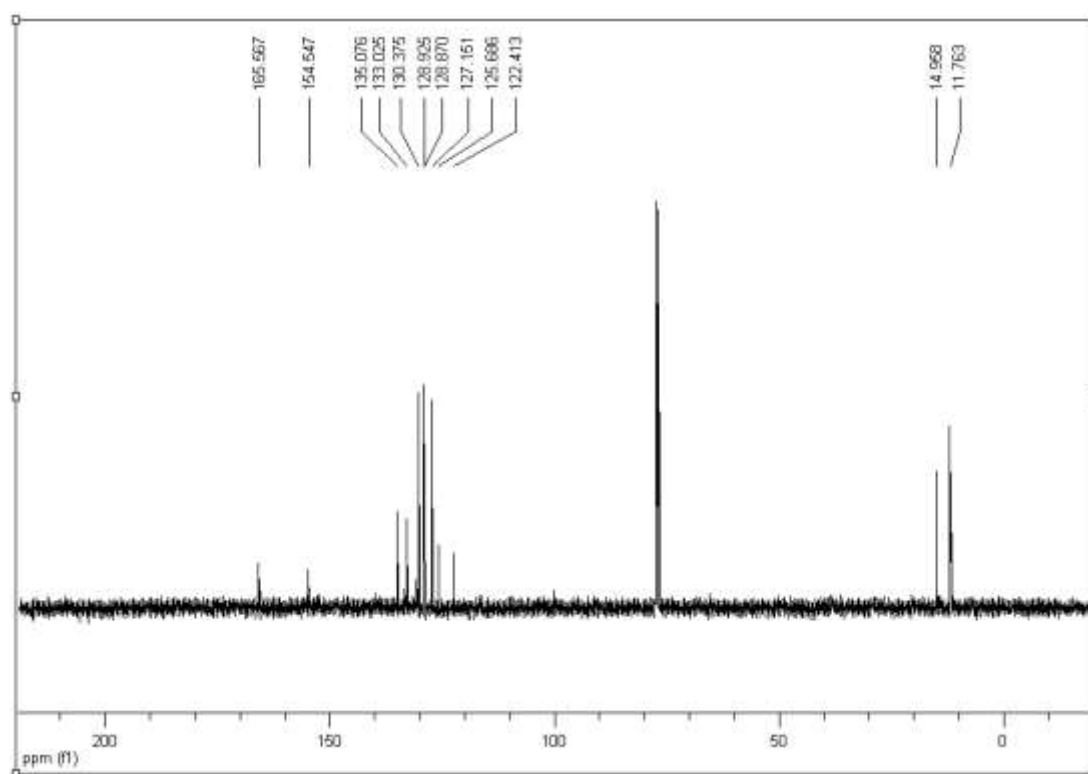
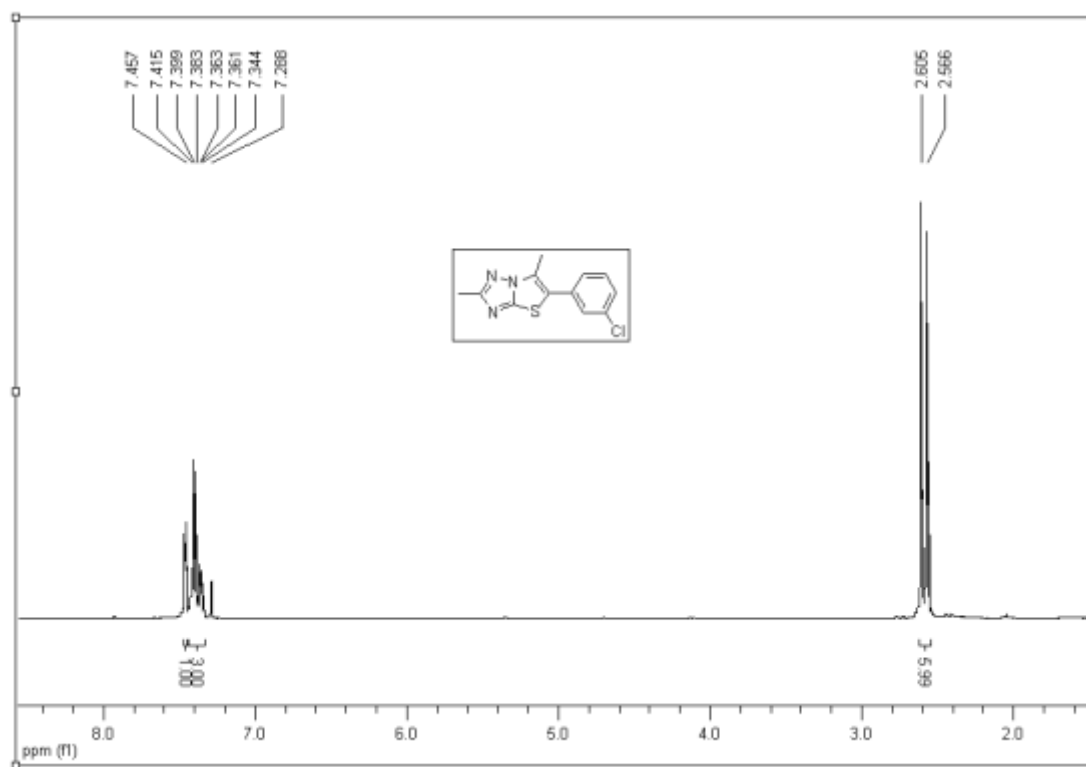
**5-(4-fluorophenyl)-2,6-dimethylthiazolo[3,2-*b*]-1,2,4-triazole(3ag)**



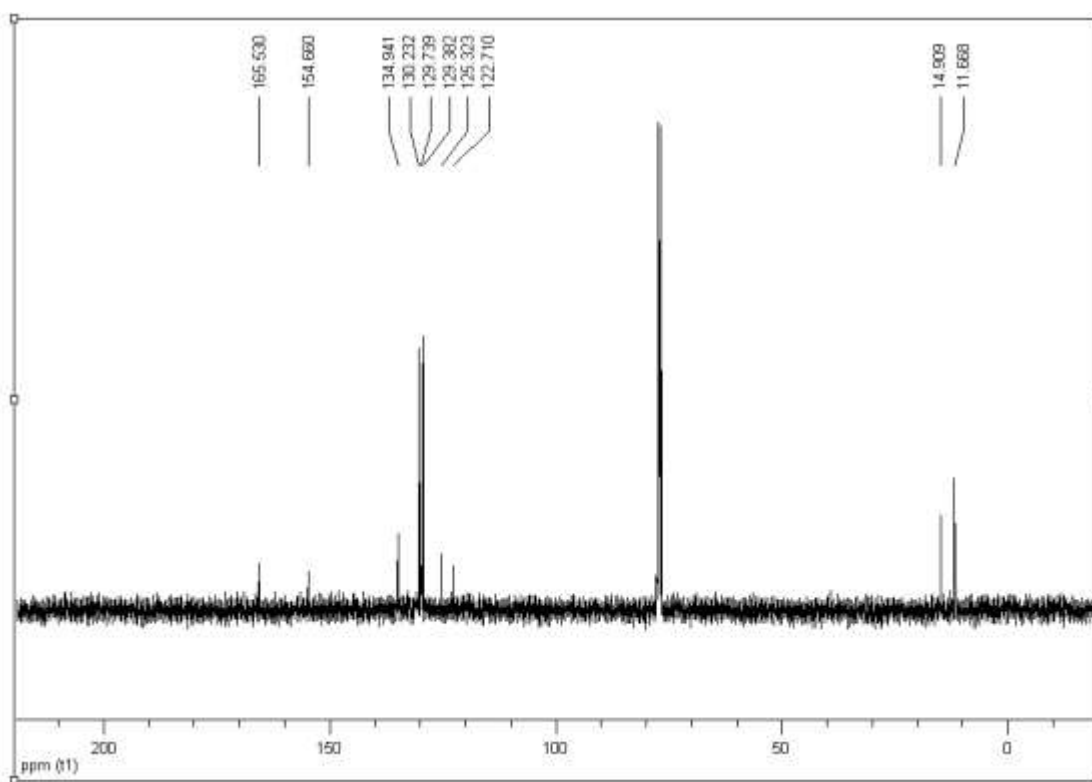
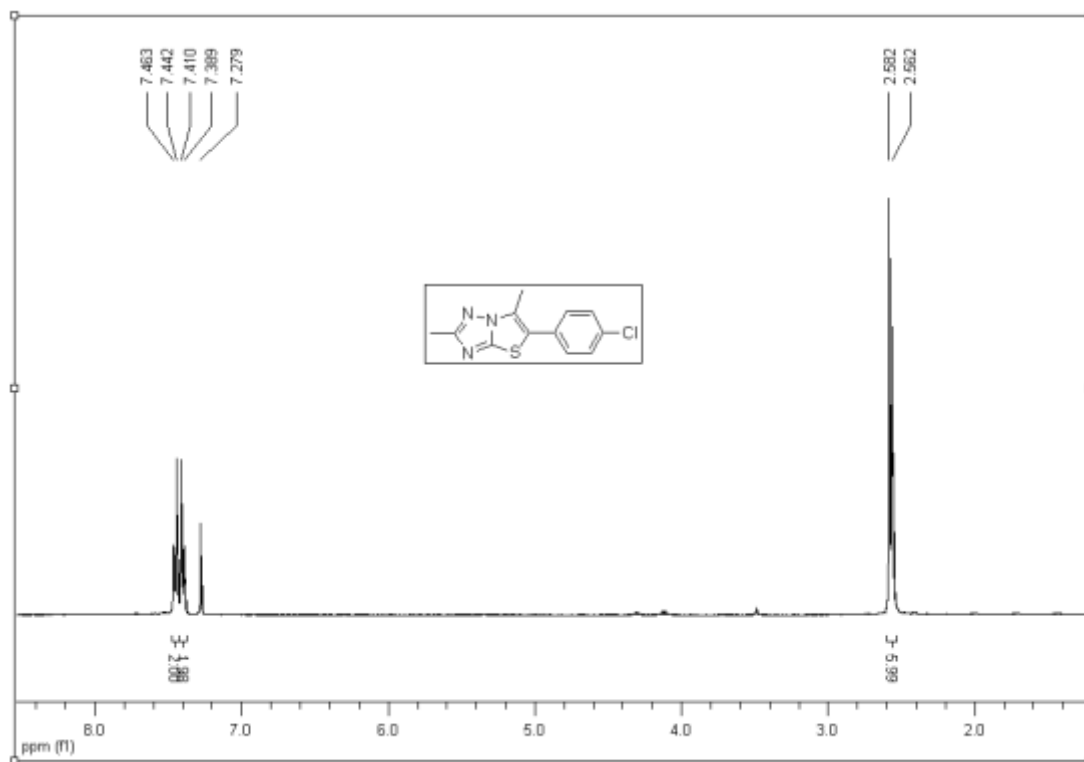
**5-(2-chlorophenyl)-2,6-dimethylthiazolo[3,2-*b*]-1,2,4-triazole(3ah)**



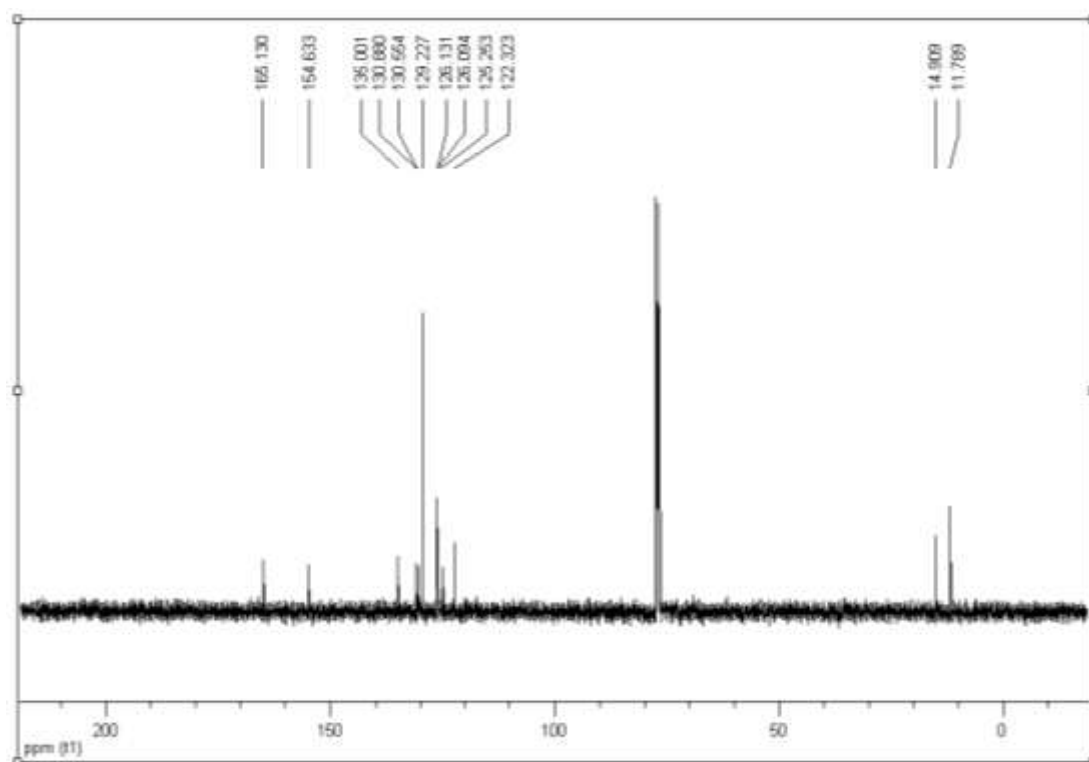
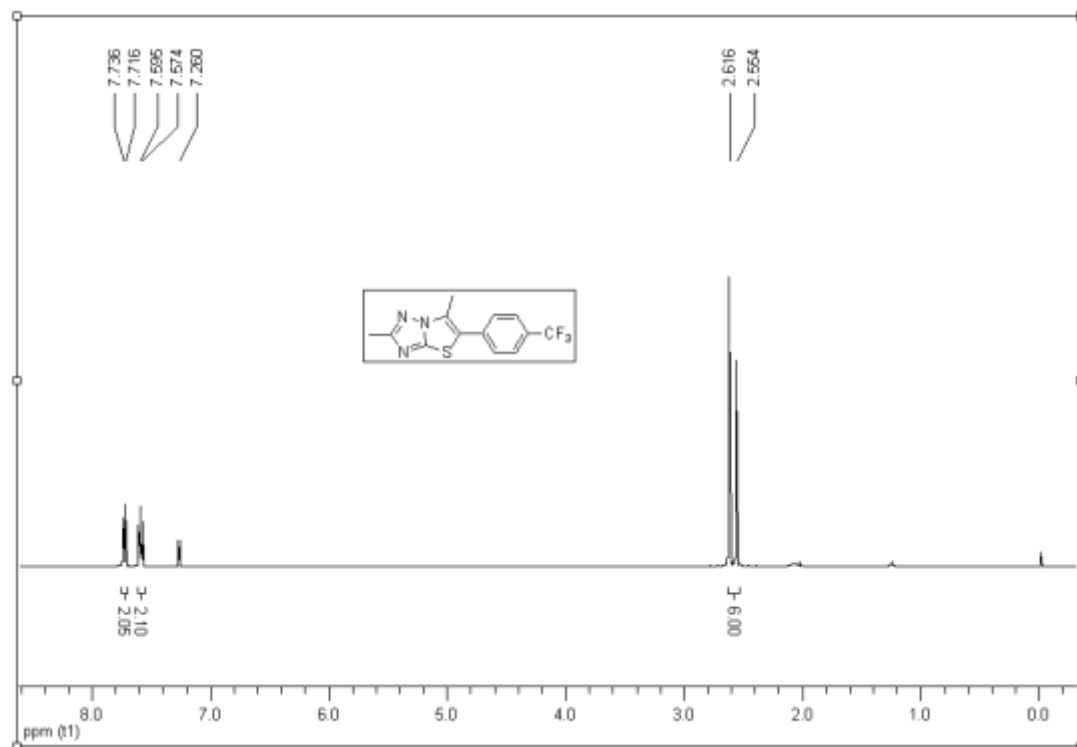
**5-(3-chlorophenyl)-2,6-dimethylthiazolo[3,2-*b*]-1,2,4-triazole(3ai)**



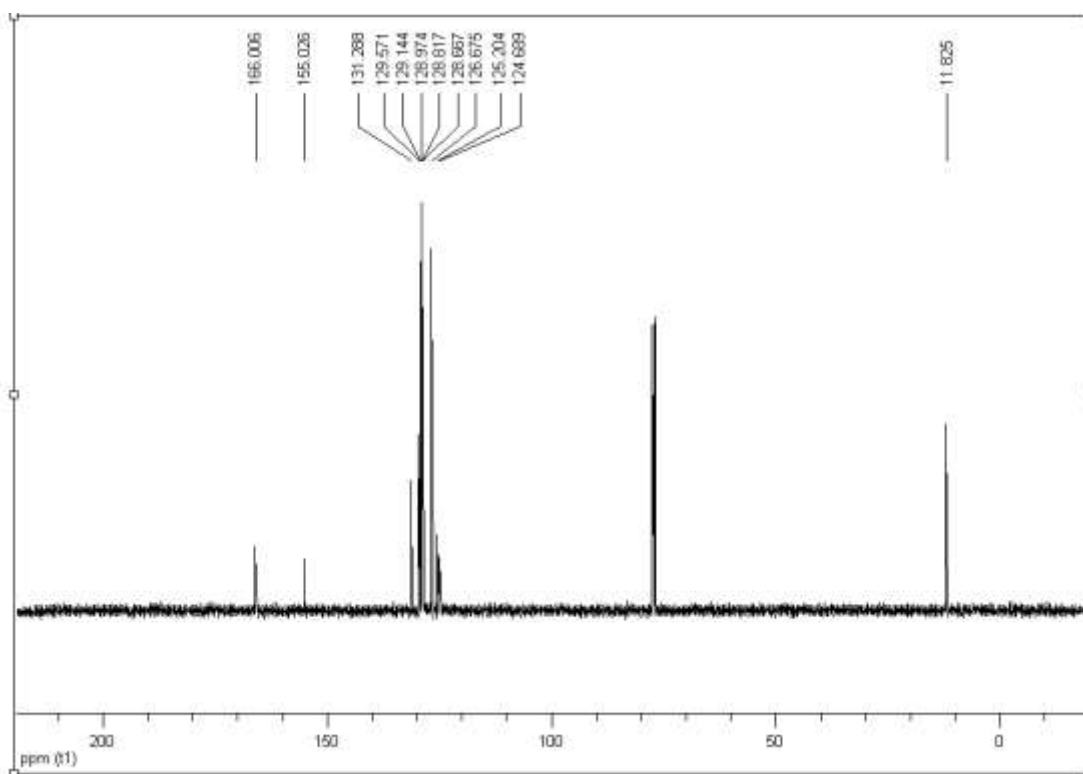
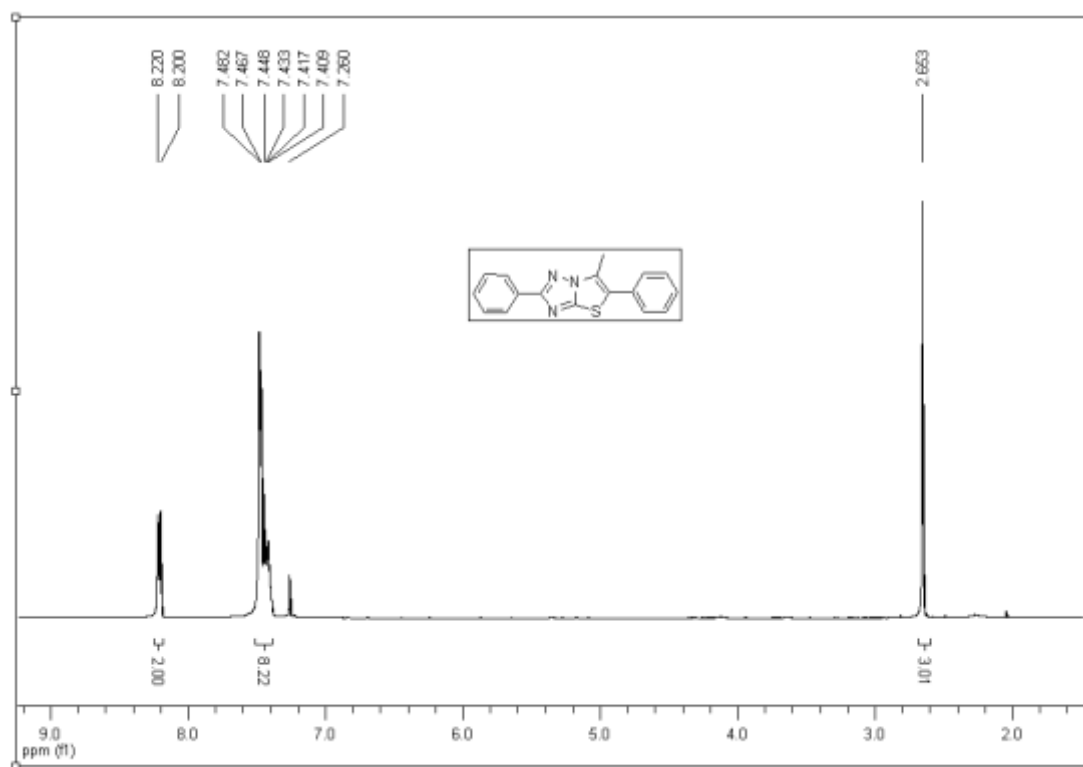
**5-(4-chlorophenyl)-2,6-dimethylthiazolo[3,2-*b*]-1,2,4-triazole(3aj)**



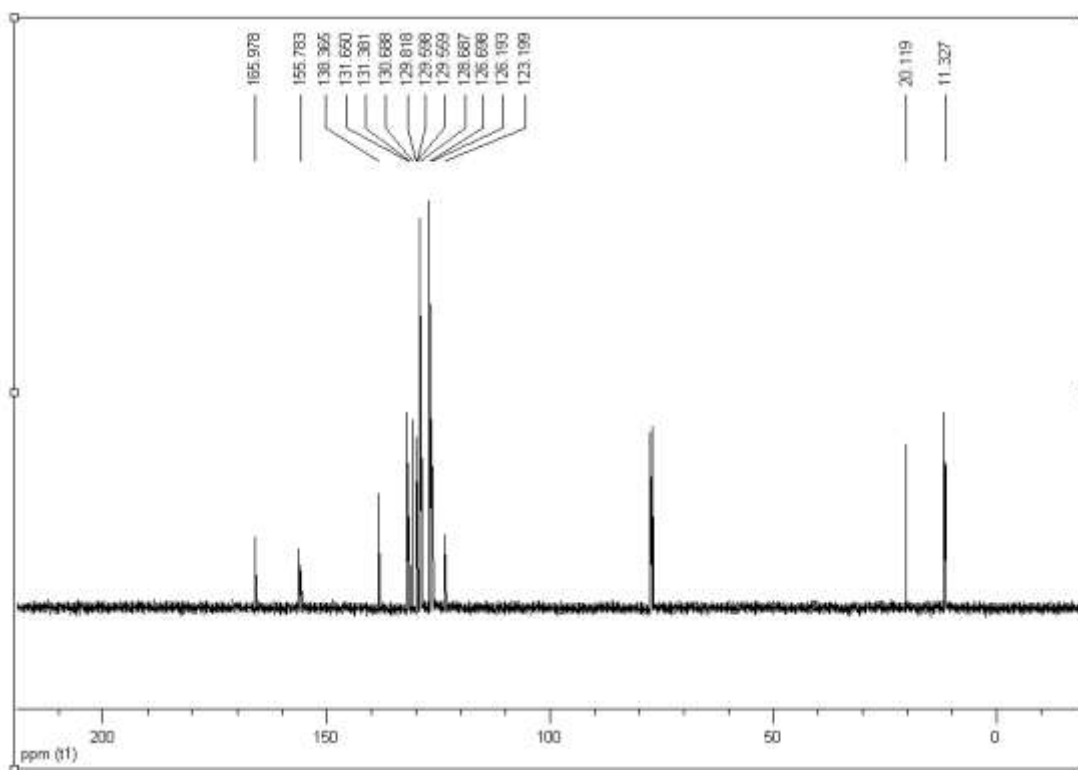
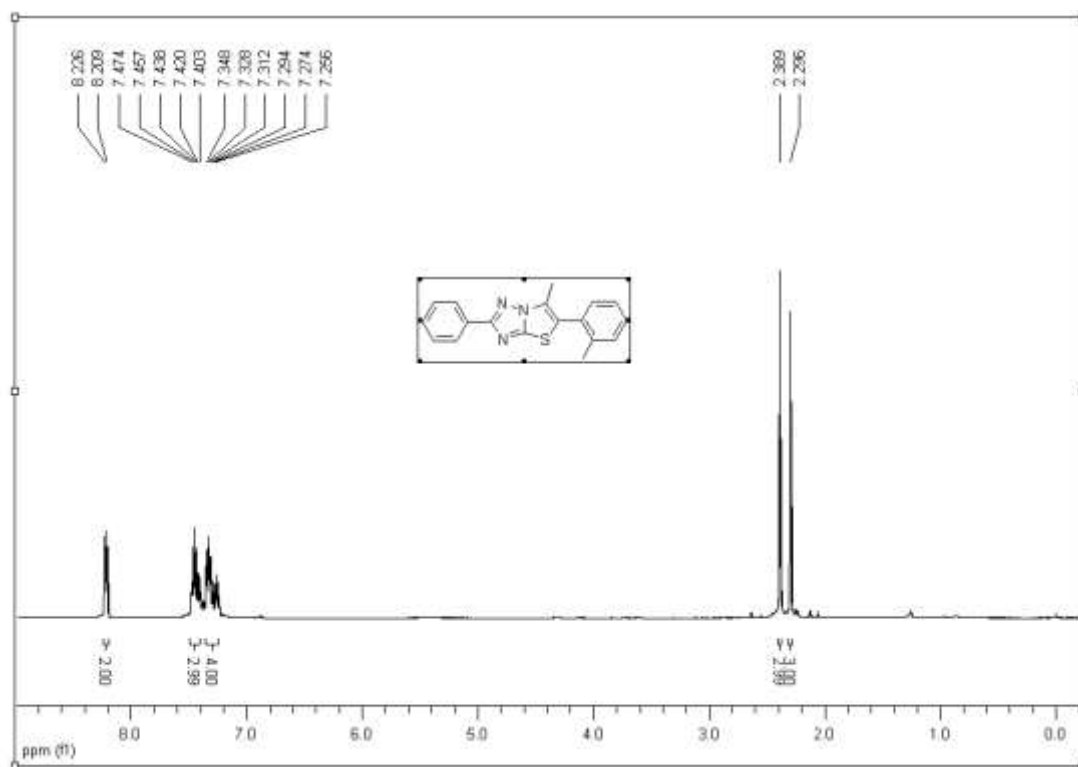
**5-(4-(trifluoromethyl)phenyl)-2,6-dimethylthiazolo[3,2-*b*]-1,2,4-triazole(3ak)**



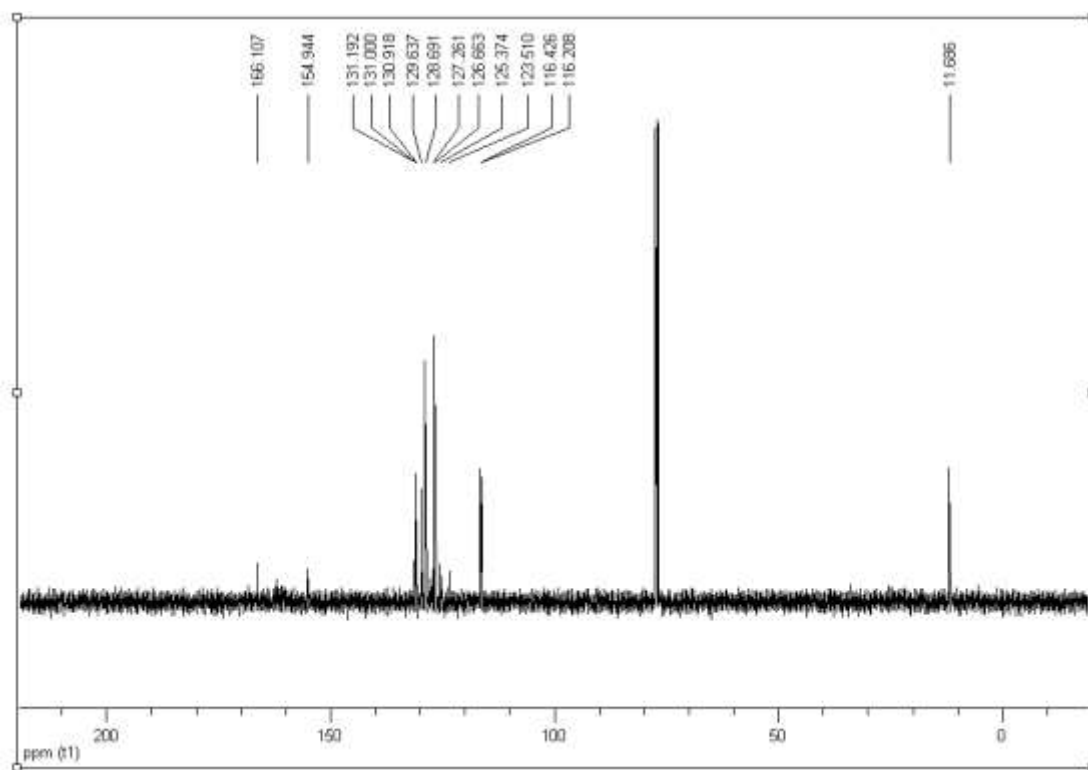
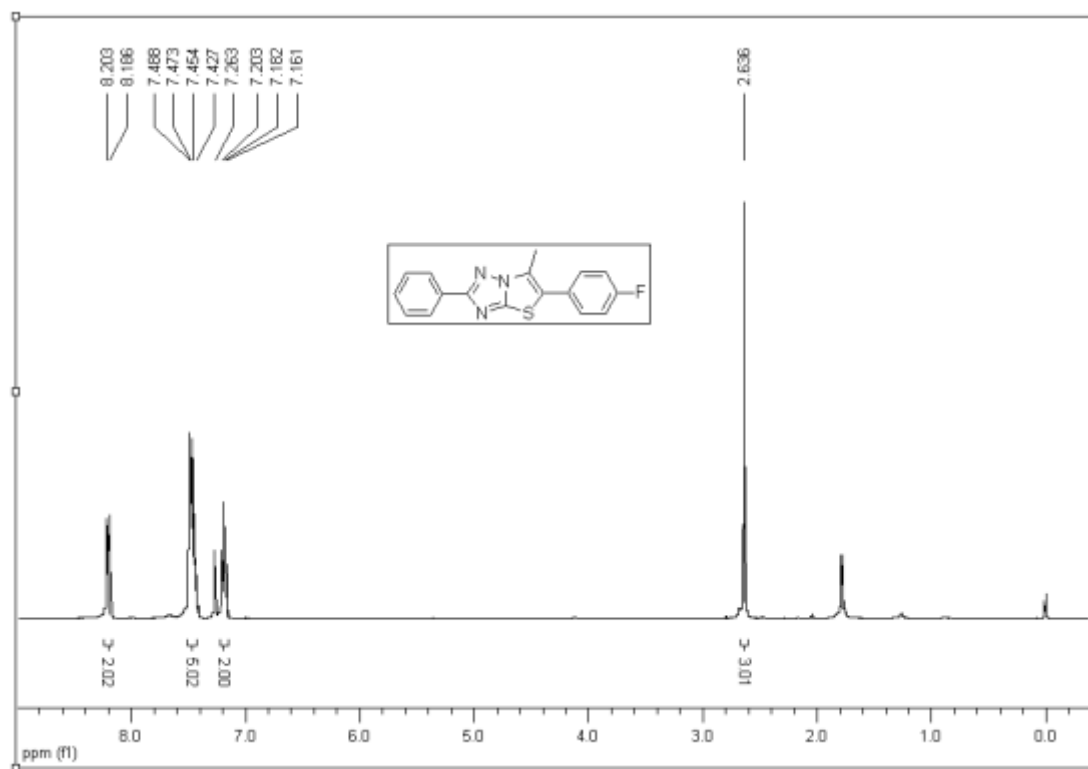
### 6-methyl-2,5-diphenylthiazolo[3,2-b]-1,2,4-triazole(3ba)



**6-methyl-2-phenyl-5-*o*-tolylthiazolo[3,2-*b*]-1,2,4-triazole(3bb)**

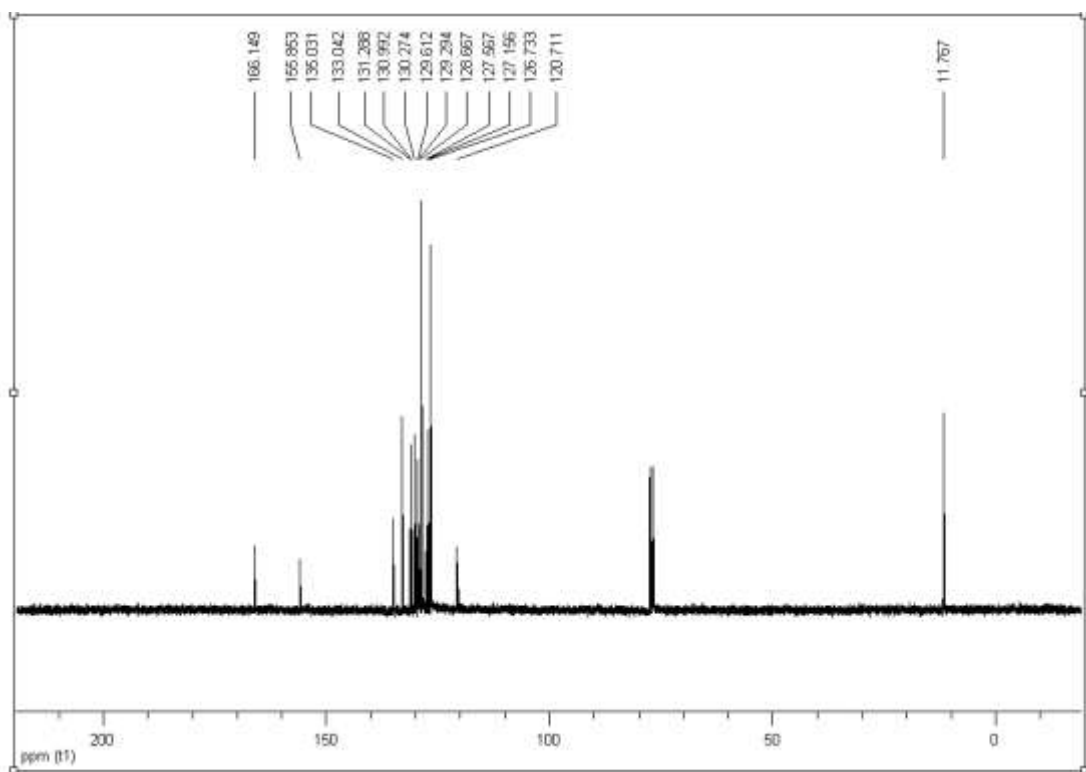
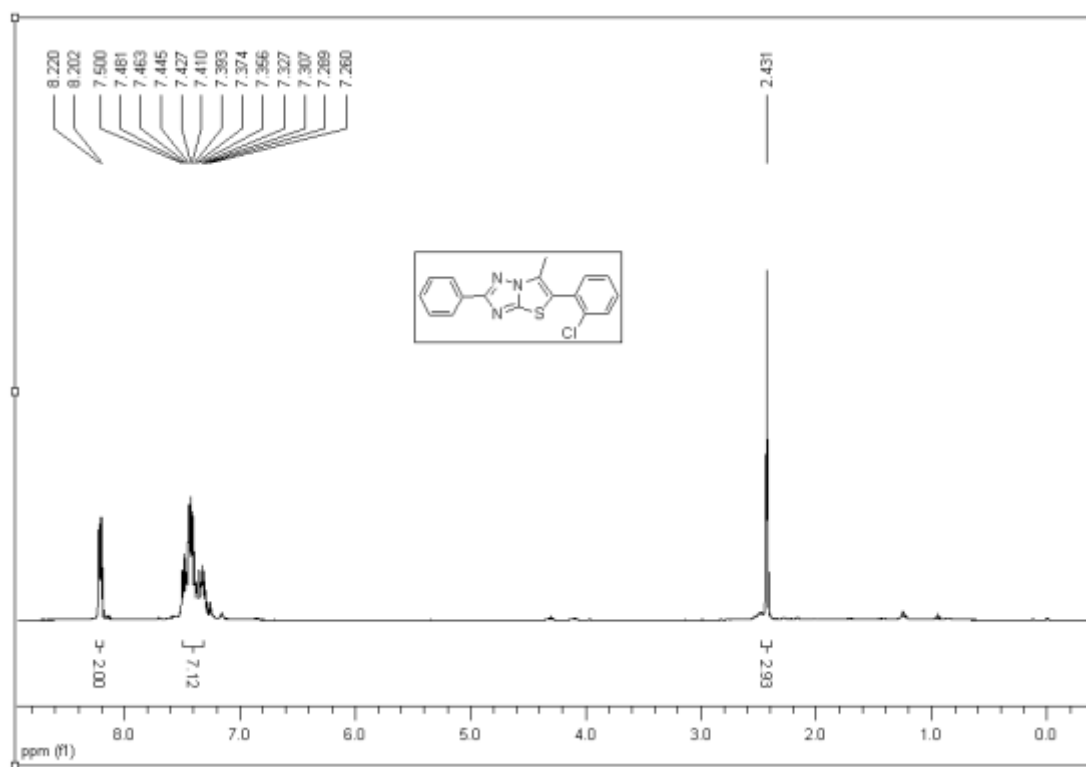


### 5-(4-fluorophenyl)-6-methyl-2-phenylthiazolo[3,2-*b*]-1,2,4-triazole(3bg)



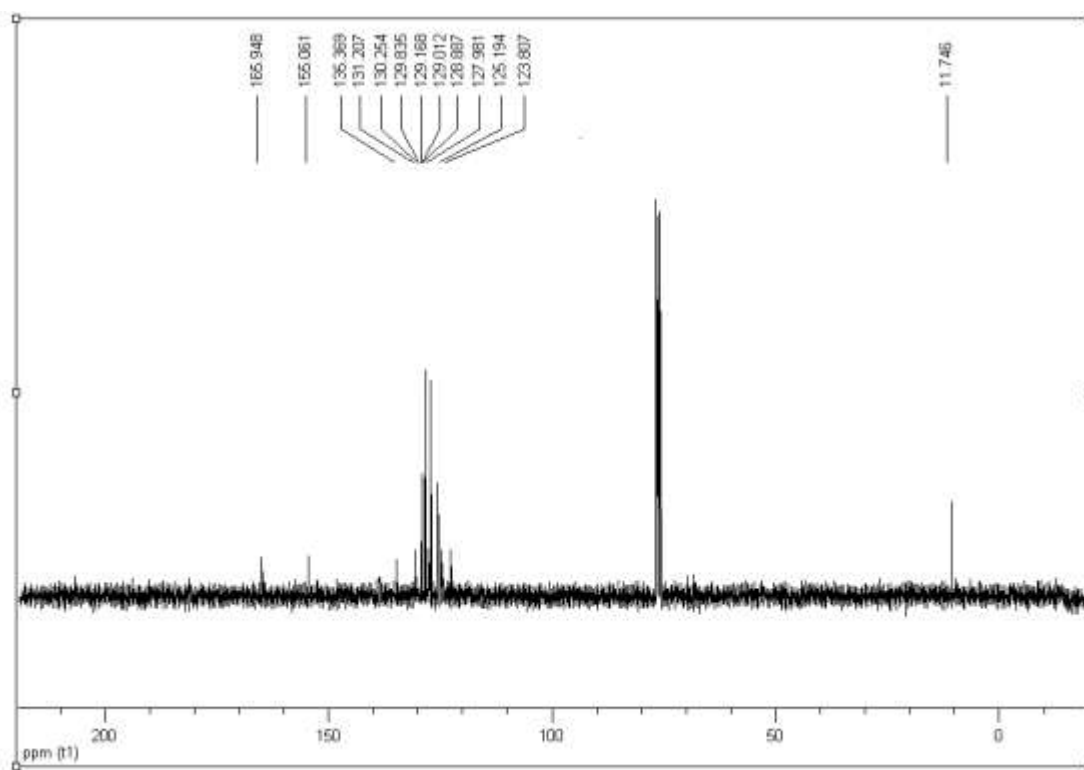
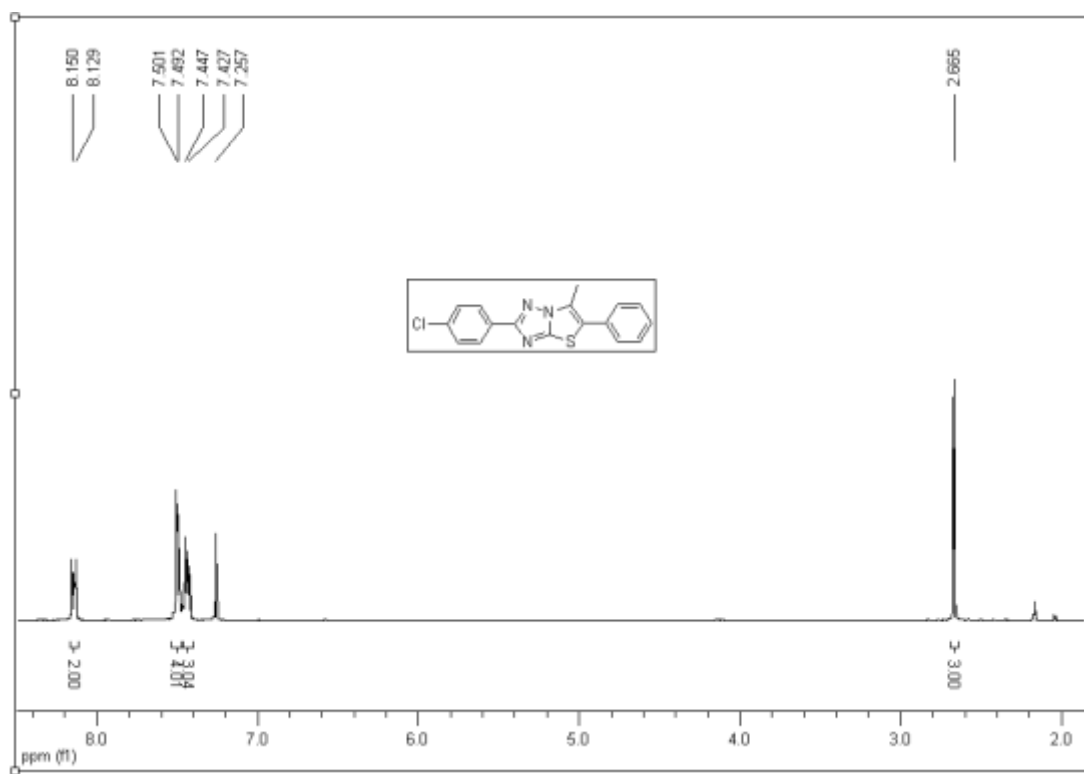


### 5-(2-chlorophenyl)-6-methyl-2-phenylthiazolo[3,2-*b*]-1,2,4-triazole(3bh)

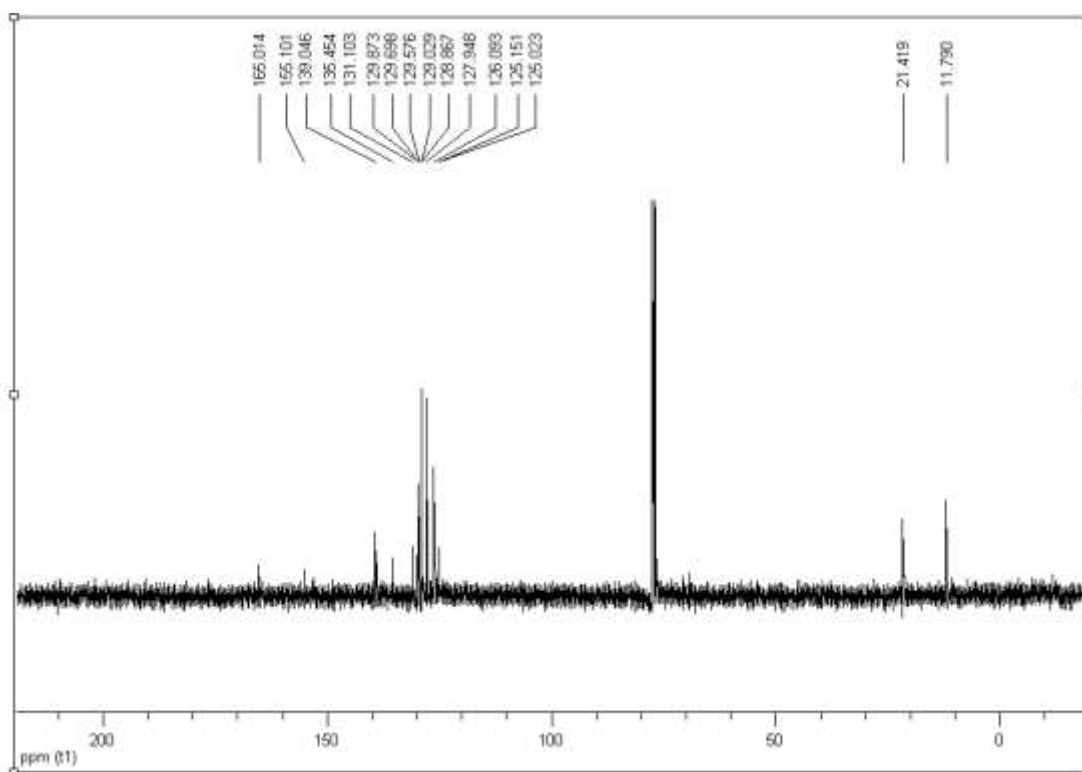
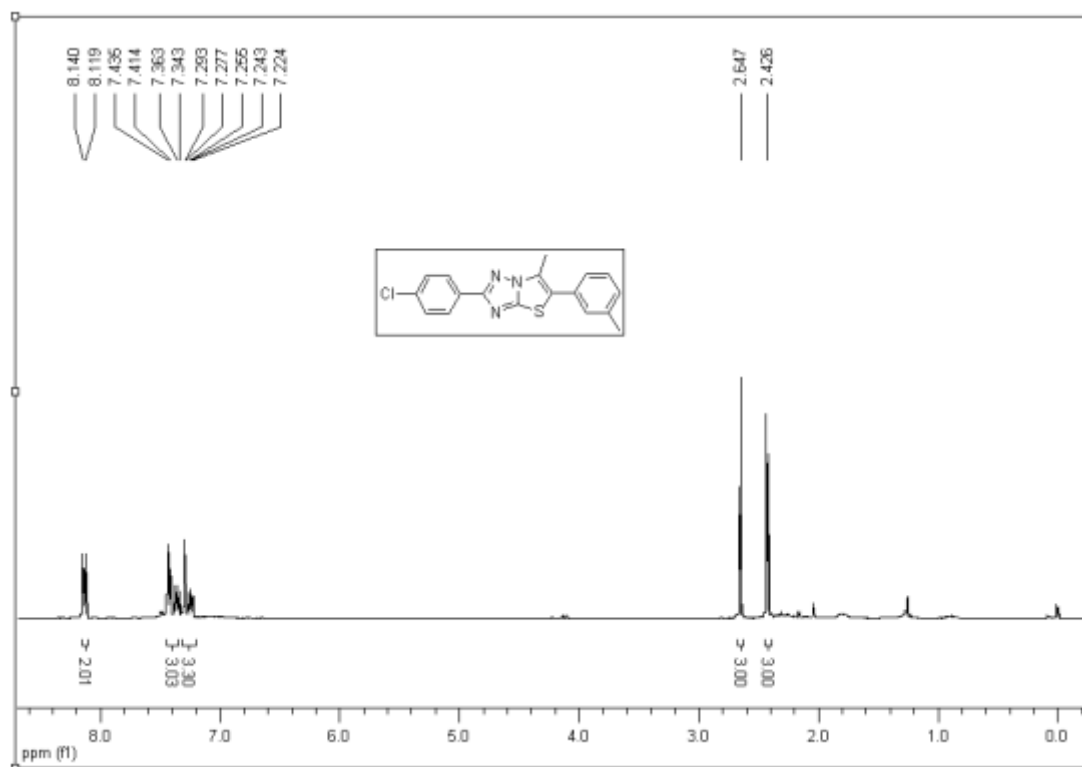




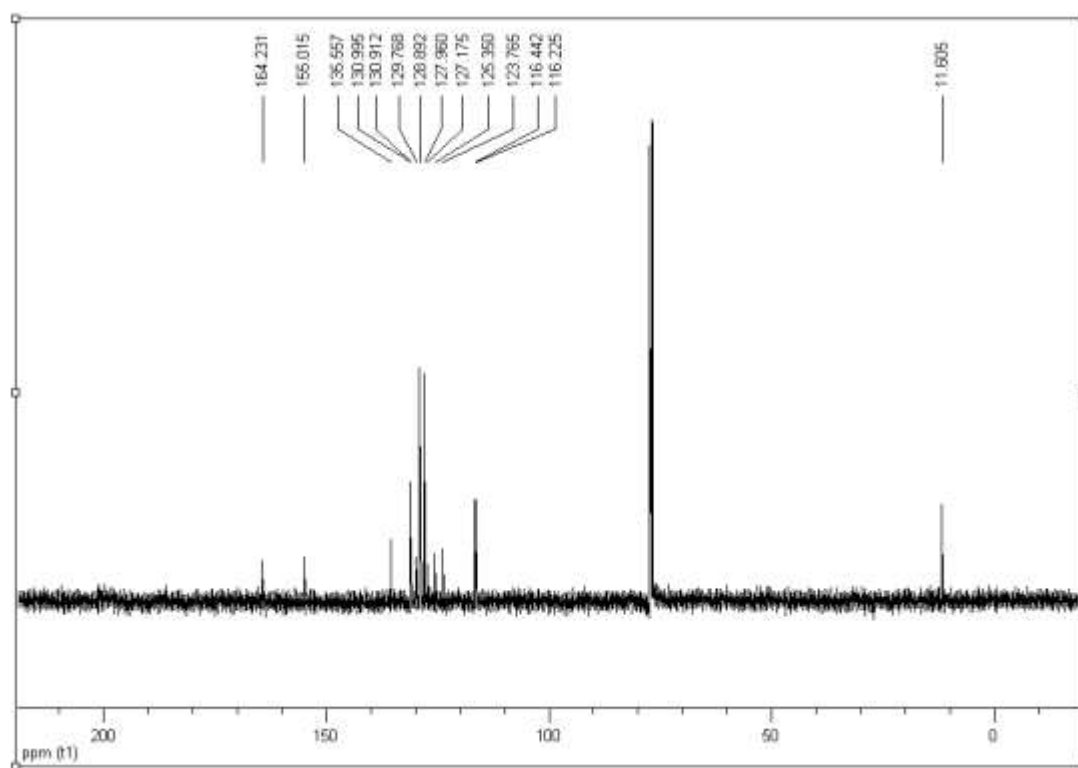
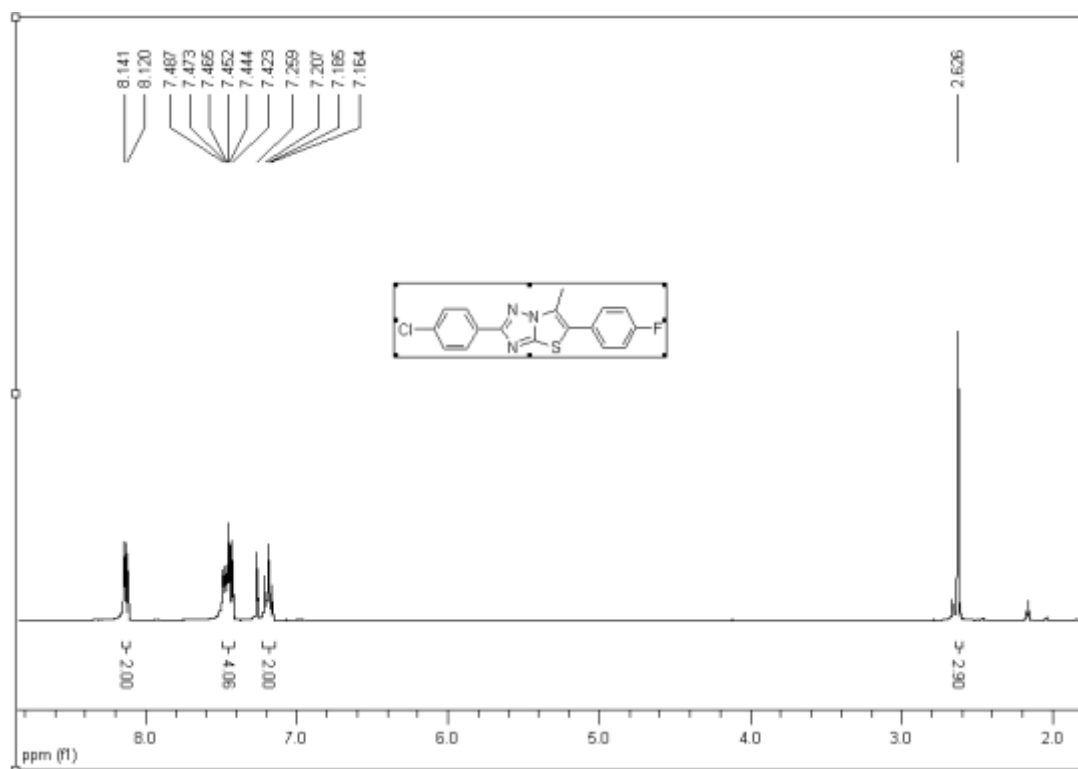
**2-(4-chlorophenyl)-6-methyl-5-phenylthiazolo[3,2-*b*]-1,2,4-triazole(3ca)**



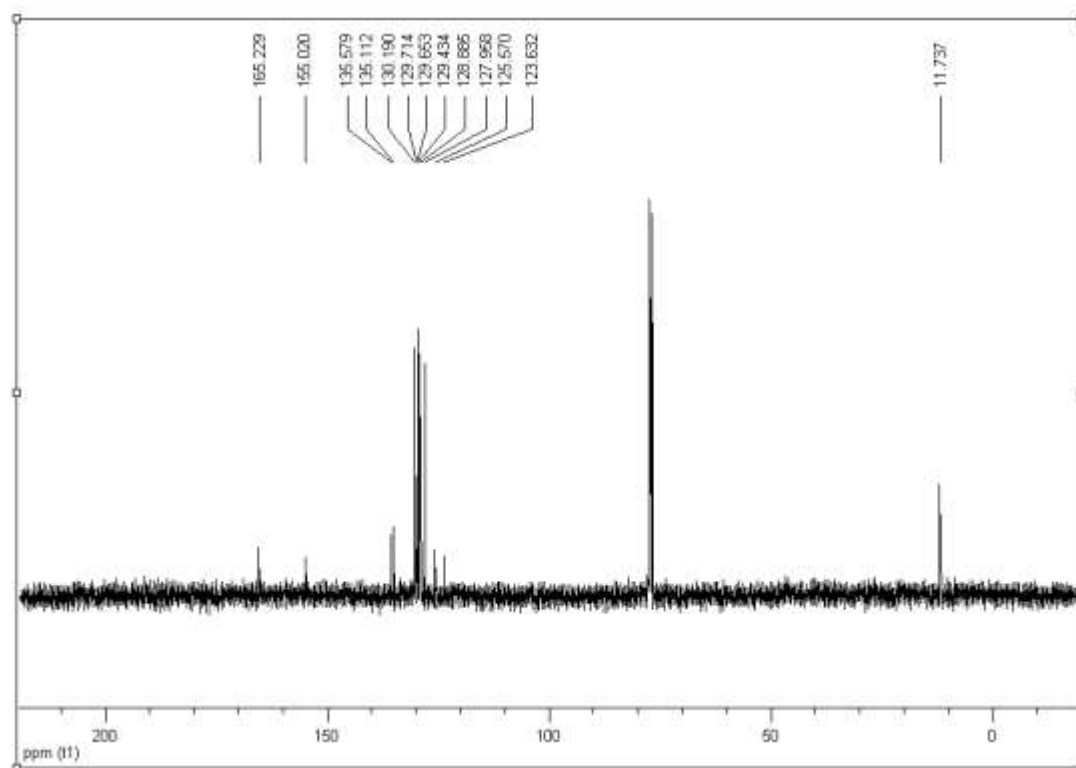
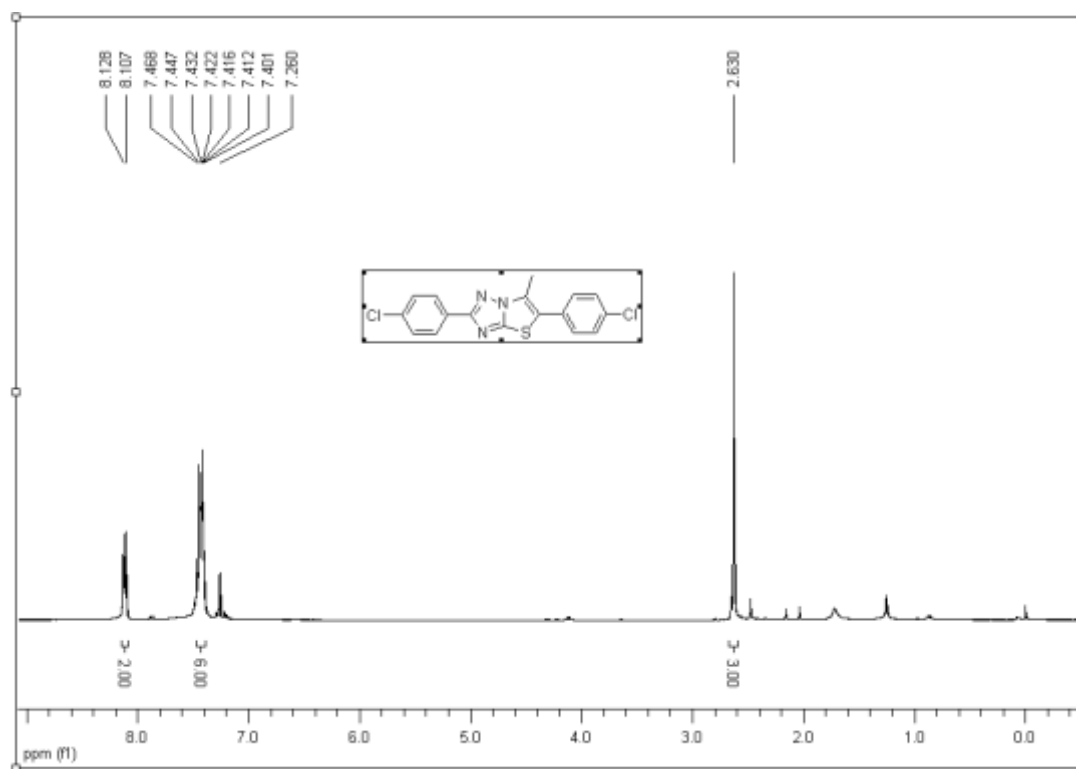
**2-(4-chlorophenyl)-6-methyl-5-*m*-tolylthiazolo[3,2-*b*]-1,2,4-triazole(3cc)**



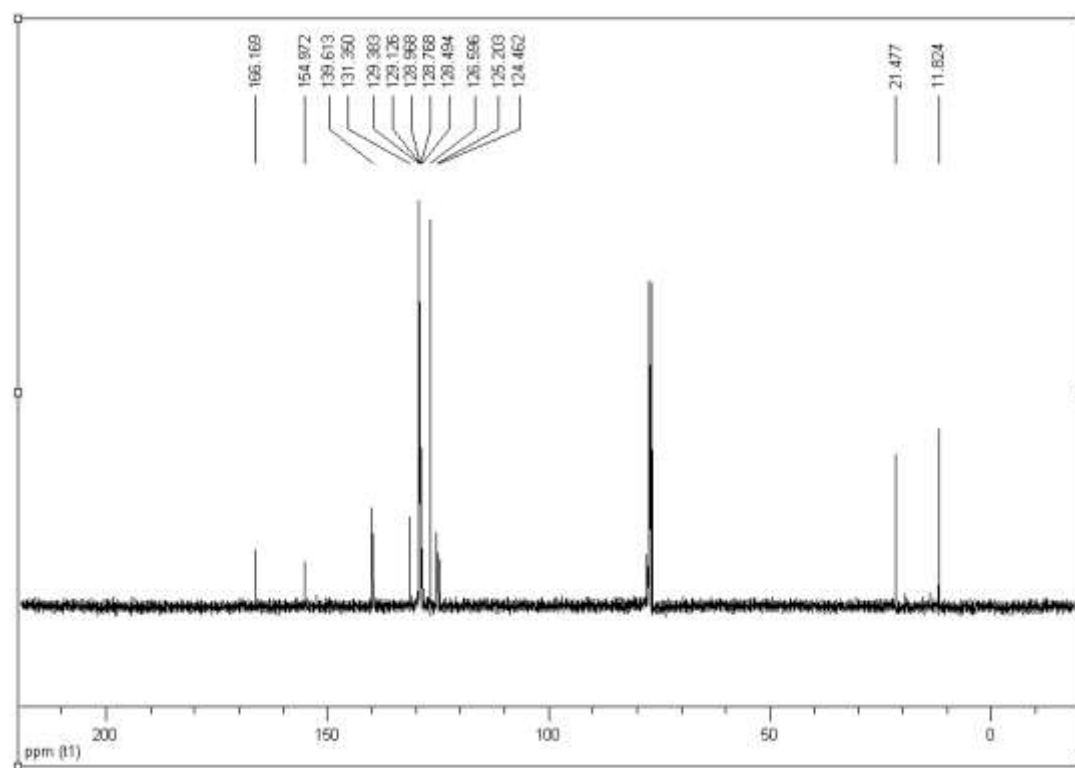
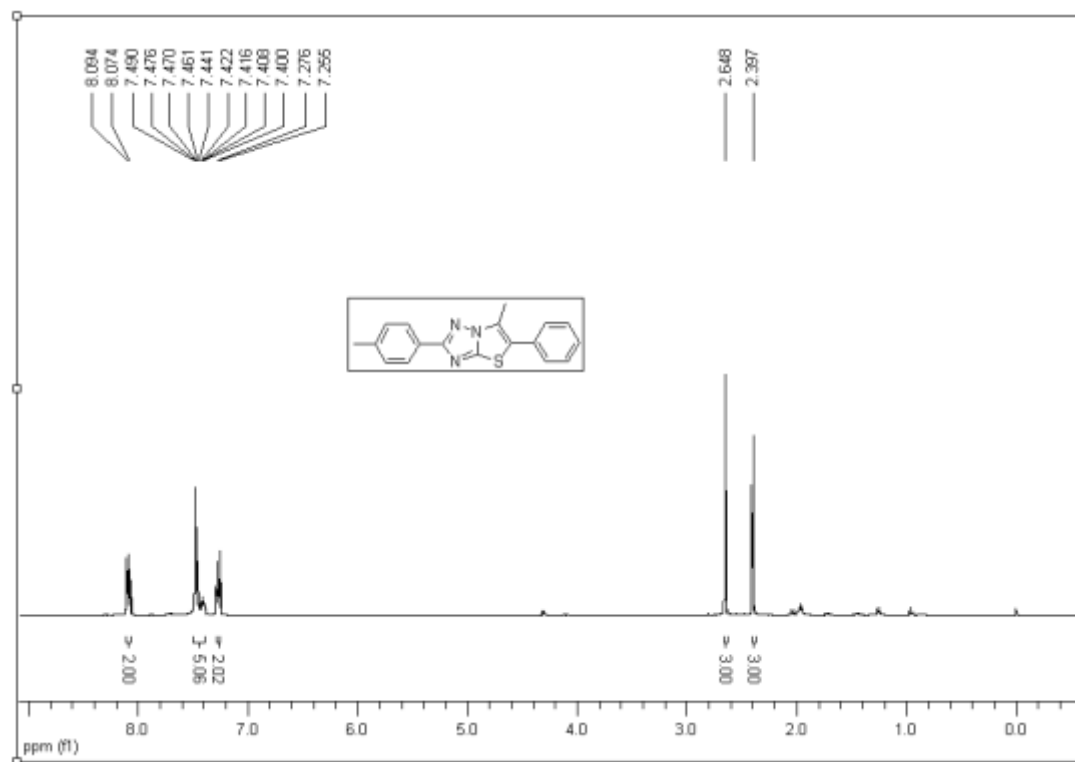
2-(4-chlorophenyl)-5-(4-fluorophenyl)-6-methylthiazolo[3,2-*b*]-1,2,4-triazole(3cg)



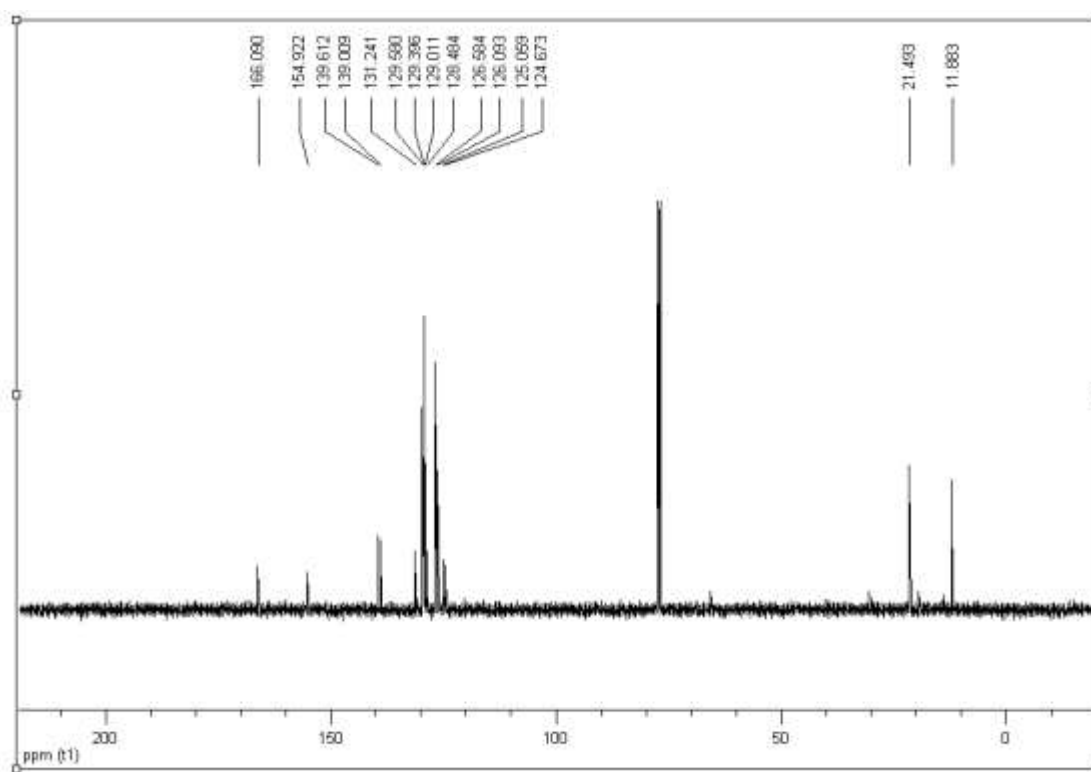
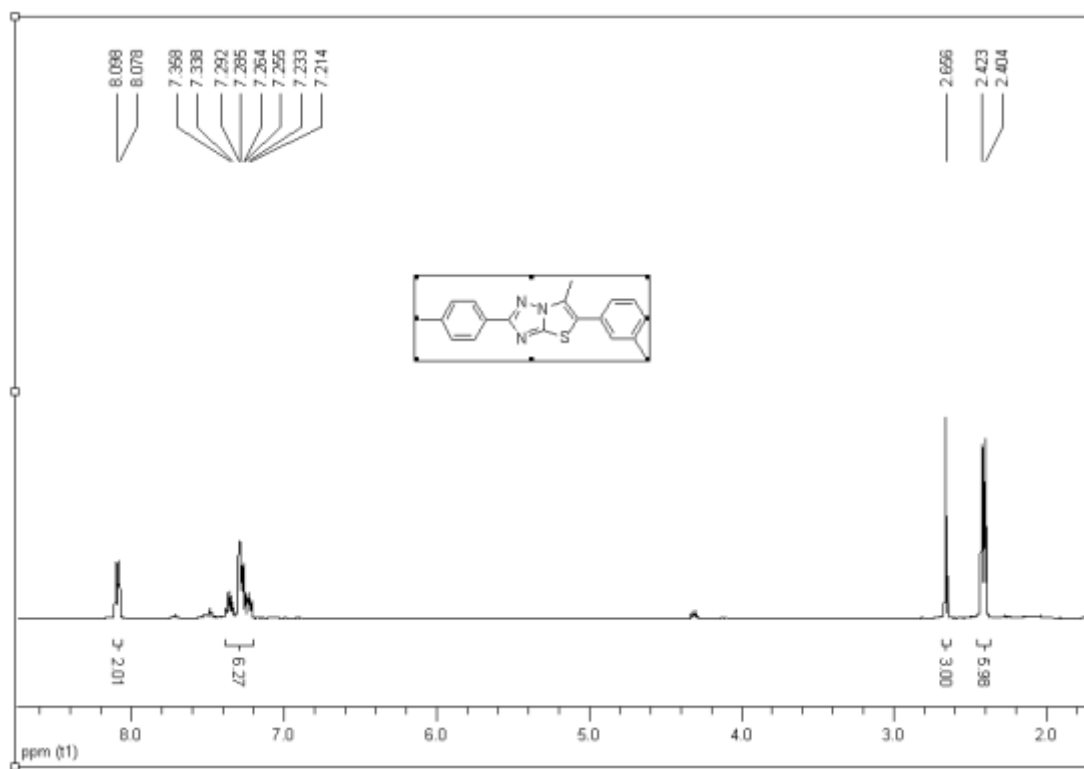
5-(4-chlorophenyl)-2-(4-chlorophenyl)-6-methylthiazolo[3,2-*b*]-1,2,4-triazole(3c<sub>j</sub>)



### 6-methyl-5-phenyl-2-*p*-tolylthiazolo[3,2-*b*]-1,2,4-triazole(3da)

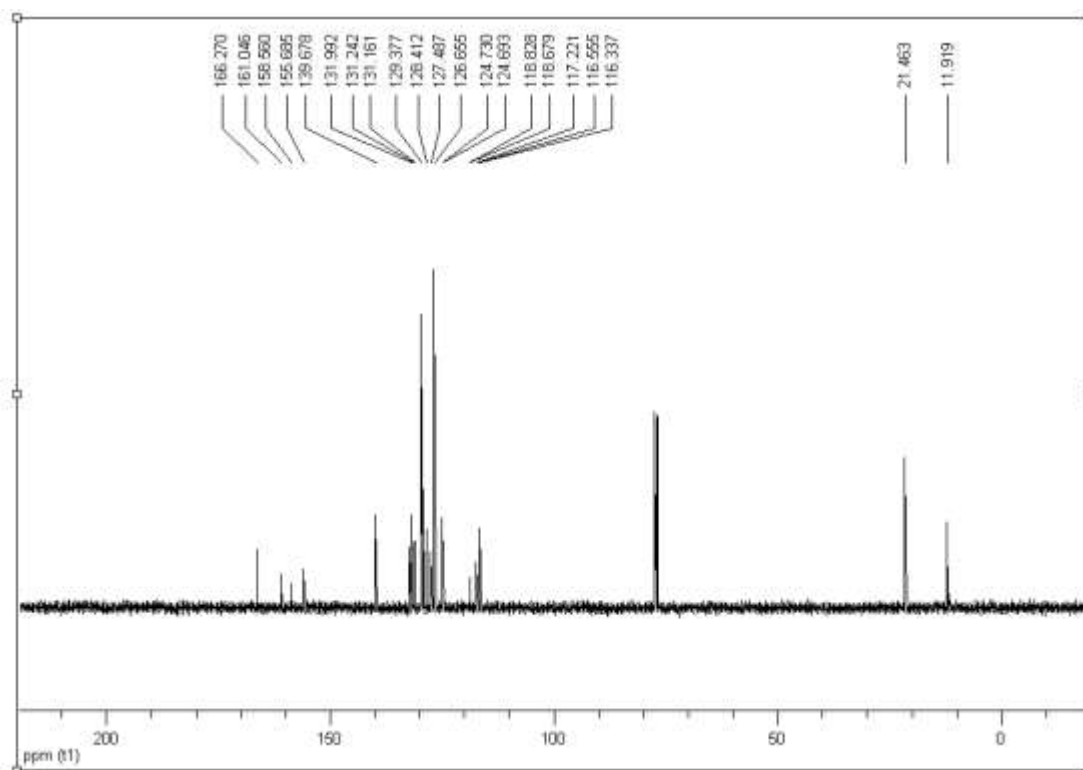
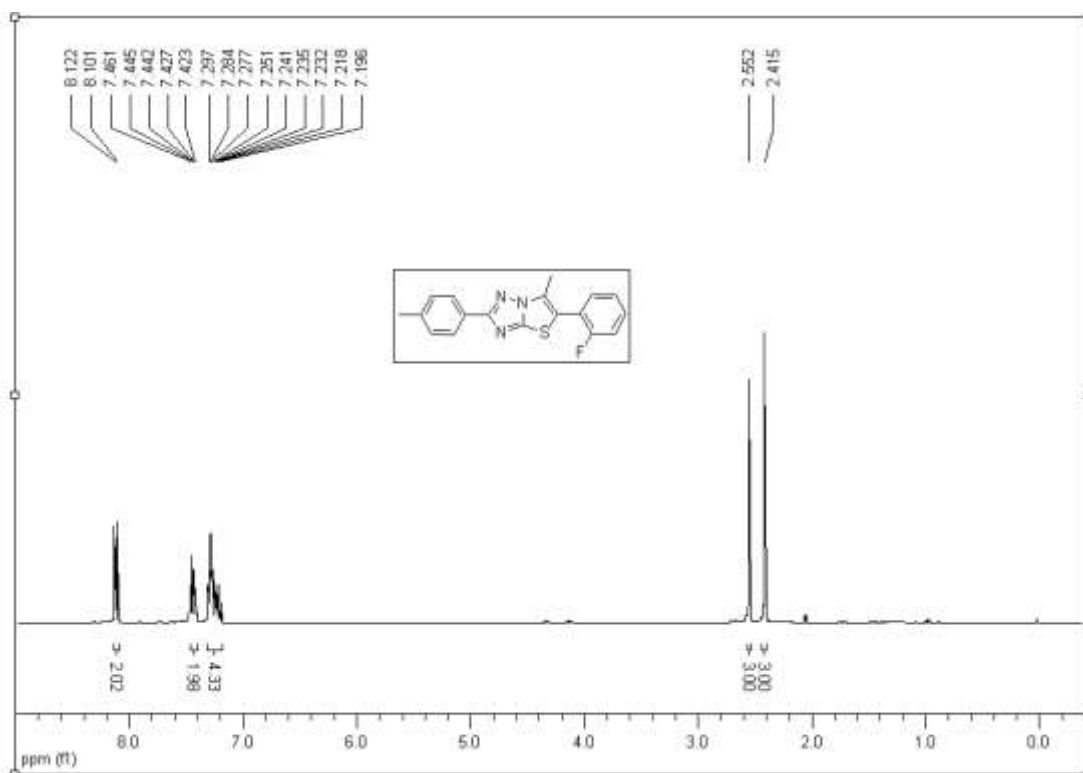


**6-methyl-5-*m*-tolyl-2-*p*-tolylthiazolo[3,2-*b*]-1,2,4-triazole(3dc)**

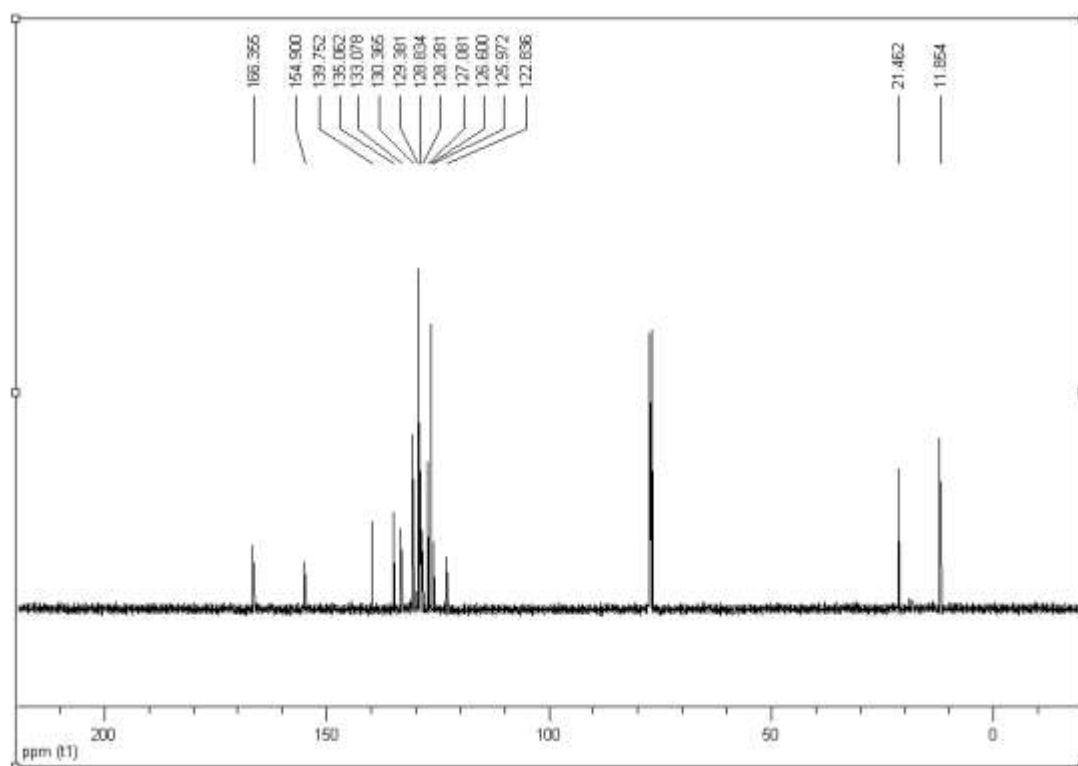
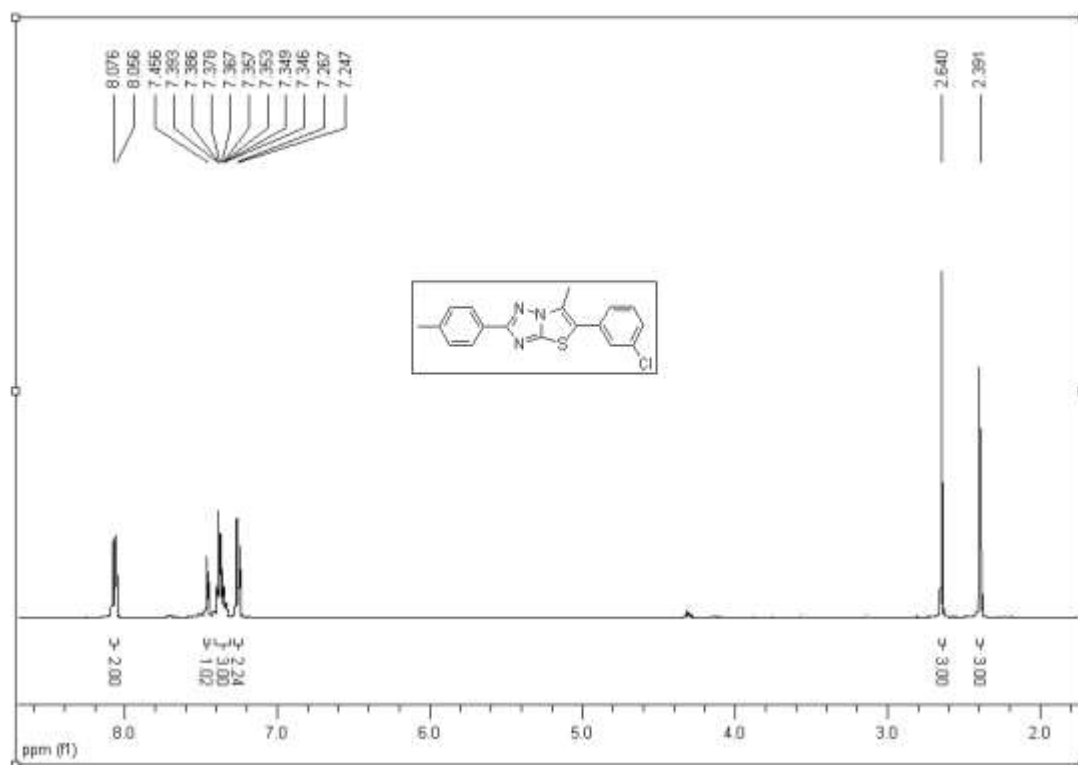




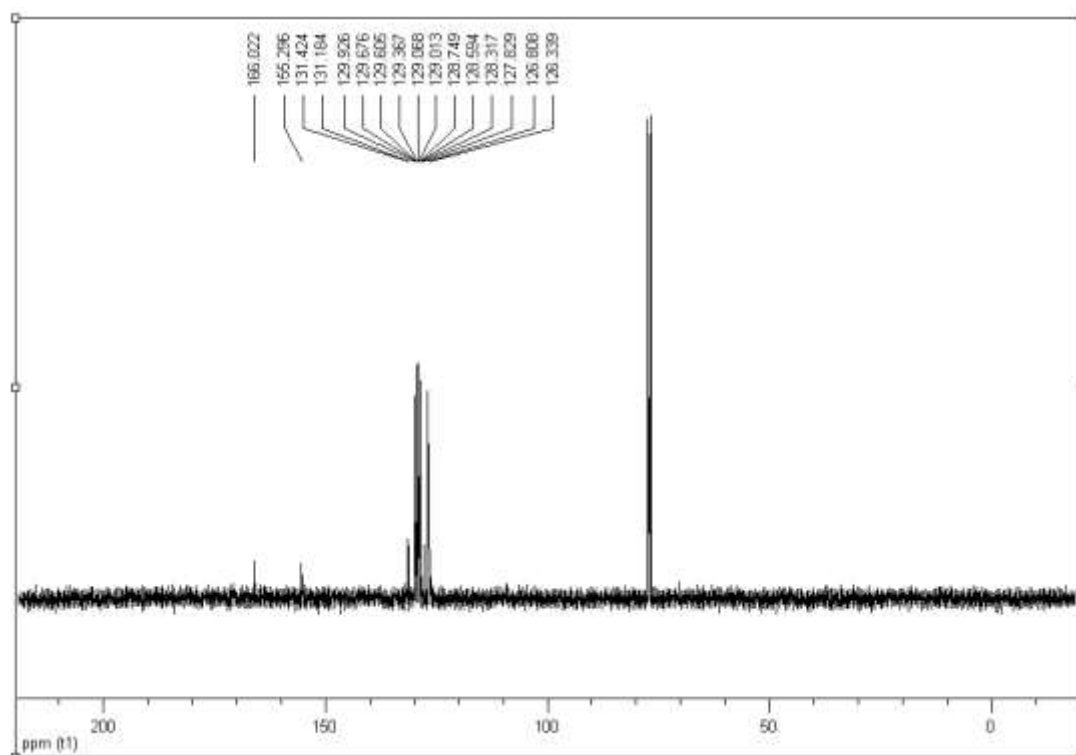
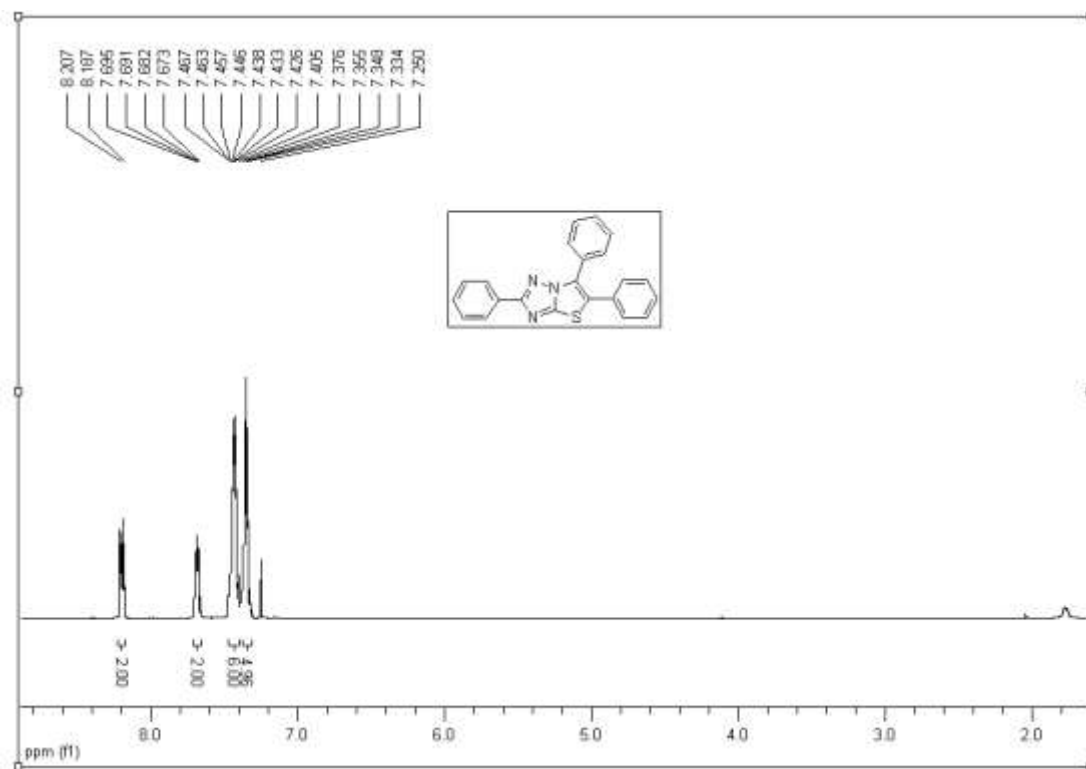
5-(2-fluorophenyl)-6-methyl-2-*p*-tolylthiazolo[3,2-*b*]-1,2,4-triazole(3de)



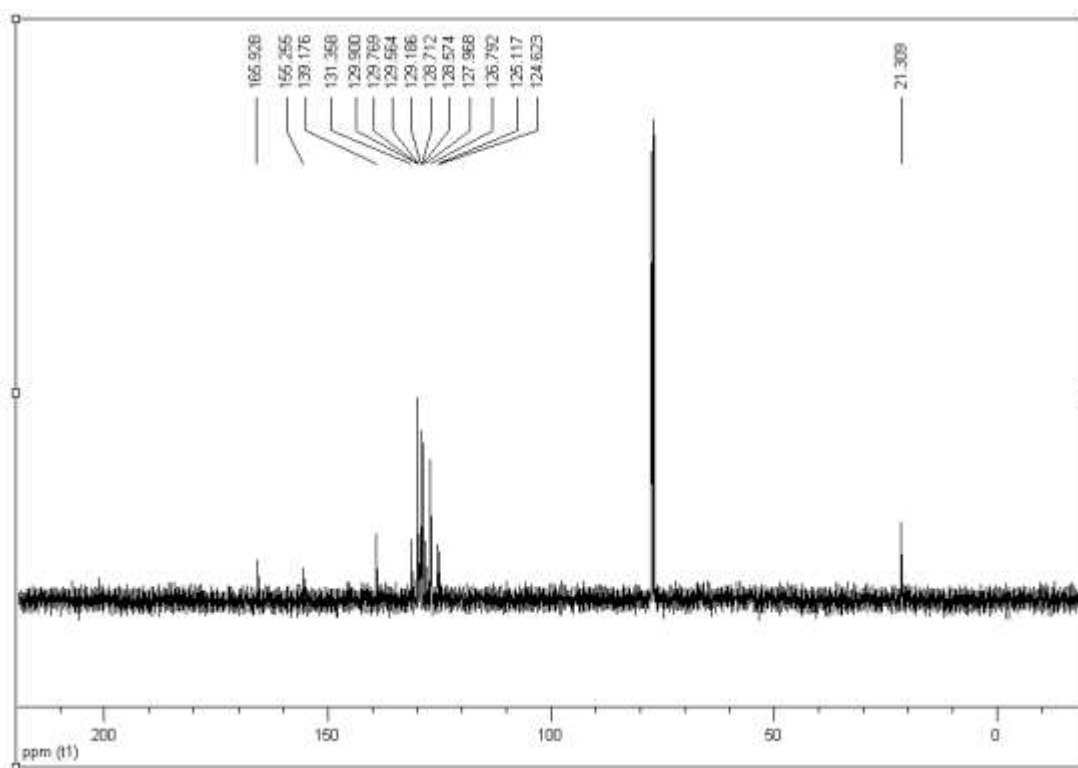
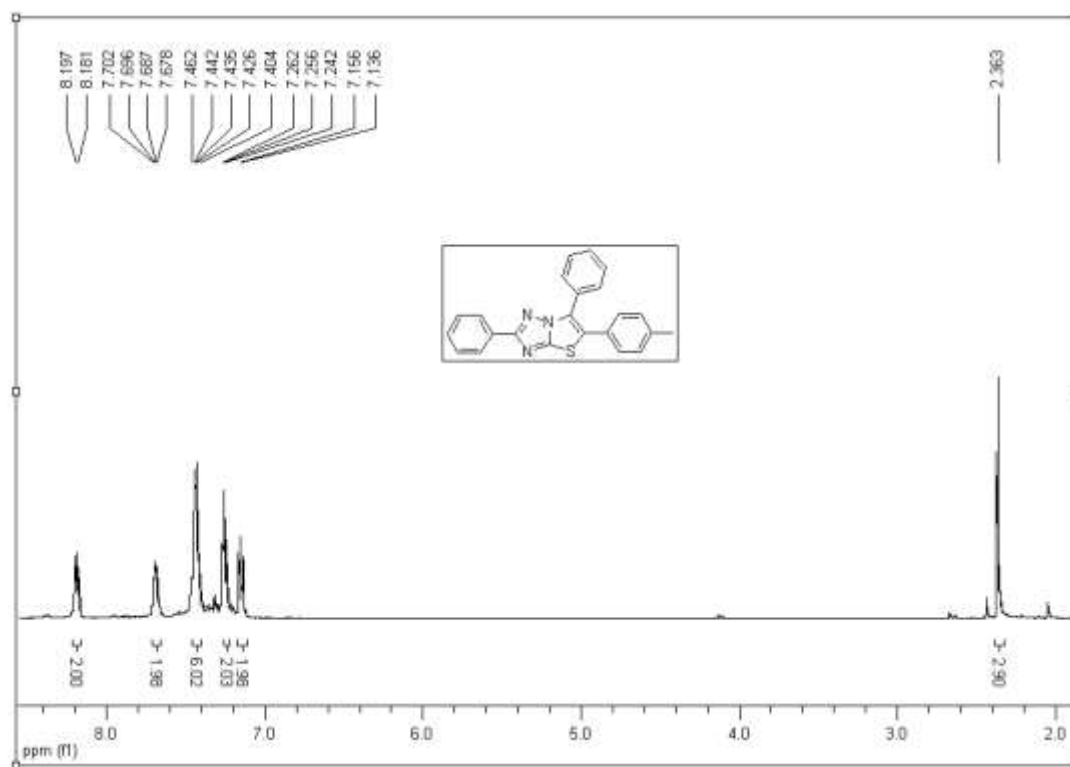
5-(3-chlorophenyl)-6-methyl-2-*p*-tolylthiazolo[3,2-*b*]-1,2,4-triazole(3di)



### 2,5,6-triphenylthiazolo[3,2-*b*]-1,2,4-triazole(3ea)



### 2,6-diphenyl-5-*p*-tolylthiazolo[3,2-*b*]-1,2,4-triazole(3ed)



### 5-(3-fluorophenyl)-2,6-diphenylthiazolo[3,2-b]-1,2,4-triazole(3ef)

