Supporting Information for

$NiSO_4$-Catalyzed C-H Activation/C-S Cross-Coupling of 1,2,3-Triazole *N*-Oxides with Thiols

Jiayi Zhu, Yu Chen, Feng Lin, Baoshuang Wang,
Zhengwang Chen,* and Liangxian Liu*
Key Laboratory of Organo-Pharmaceutical Chemistry of Jiangxi Province, Gannan Normal University, Ganzhou 341000, PR China
E-mail: lxliu@xmu.edu.cn; chenzwang@126.com

CONTENTS

1. General Methods

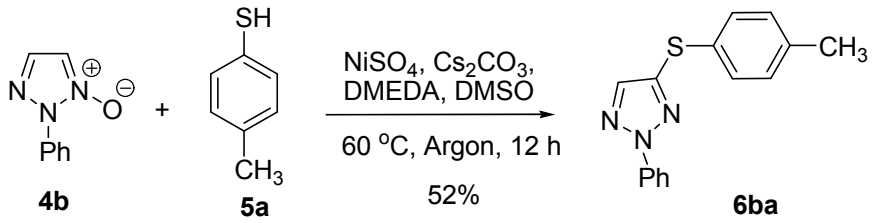
All reagents were obtained from commercial sources and used without further purification. Infrared spectra were measured with a Nicolet Avatar 360 FT-IR spectrometer using film KBr pellet techniques. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker spectrometers at 400 and 100 MHz, respectively. Chemical shifts were reported in ppm relative to TMS for ^{1}H and ^{13}C NMR spectra. $CDCl_3$ was used as the NMR solvent. Mass spectra were recorded with GC-MS spectrometer at an ionization voltage of 70 eV equipped with a DB-WAX capillary column (internal diameter: 0.25 mm, length: 30 m). Elemental analysis was carried out on a Perkin-Elmer 240B instrument. HRFABMS spectra were recorded on a FTMS apparatus. Silica gel (300-400 mesh) was used for flash column chromatography, eluting (unless otherwise stated) with an ethyl acetate/petroleum ether (PE) (60-90 °C) mixture.

2. General Procedure for the Preparation of 6.

4 **5** **6**

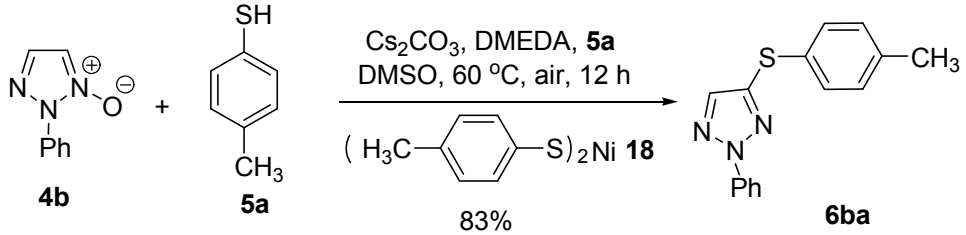
To a solution of 2-aryl-1,2,3-triazole *N*-oxide (0.2 mmol), $NiSO_4$ (0.02 mmol), DMEDA (0.08 mmol) and Cs_2CO_3 (0.4 mmol) in DMSO (1 mL) was added thiol (0.24 mmol) under an air atmosphere and the mixture was stirred at 60 ^{o}C for 12-24 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/PE = 1:15) to yield the corresponding product **6**.

3. Preliminary Mechanism Study.



4b **5a** **6ba**

To a solution of 2-phenyl-1,2,3-triazole *N*-oxide **4b** (32 mg, 0.2 mmol), $NiSO_4$ (31 mg, 0.02 mmol), DMEDA (7 mg, 0.08 mmol) and Cs_2CO_3 (130 mg, 0.4 mmol) in DMSO (0.6 mL) was added 4-methylbenzenethiol **5a** (30 mg, 0.24 mmol) under an argon atmosphere and the mixture was stirred at 60 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/PE = 1:15) to yield the corresponding product **6ba** (28 mg, 52%).

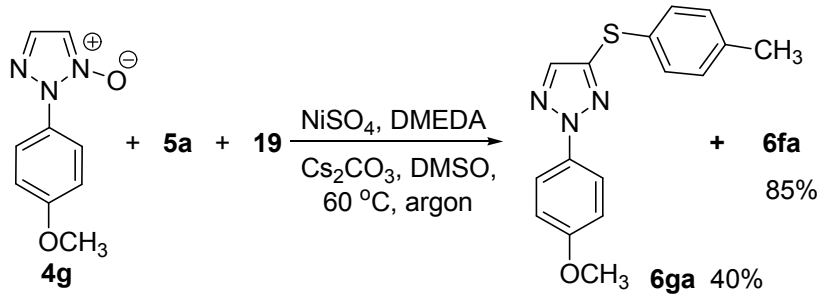


4b **5a** **6ba**

To a solution of 2-phenyl-1,2,3-triazole *N*-oxide **4b** (32 mg, 0.2 mmol), bis(*p*-tolylthio)nickel **18** (6 mg, 0.02 mmol), DMEDA (7 mg, 0.08 mmol) and Cs_2CO_3 (130 mg, 0.4 mmol) in DMSO (0.6

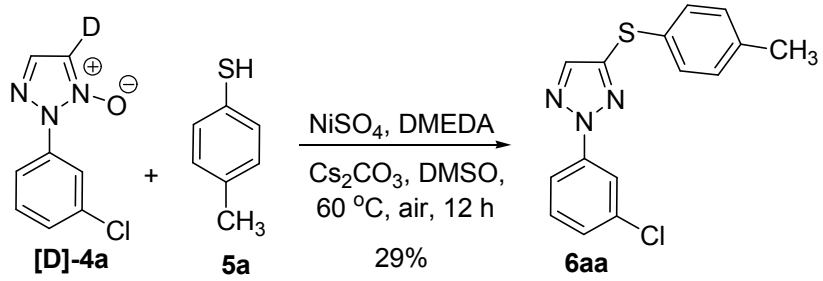
mL) was added 4-methylbenzenethiol **5a** (30 mg, 0.24 mmol) under an air atmosphere and the mixture was stirred at 60 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/PE = 1:15) to yield the corresponding product **6ba** (44 mg, 83%).

4. Competition Experiments.



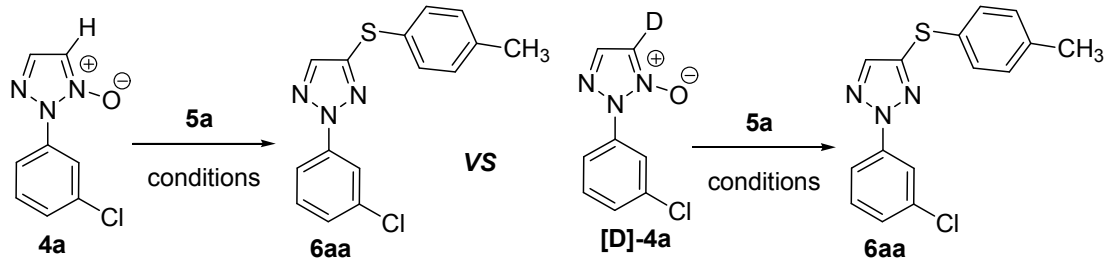
To a solution of 2-(4-methoxyphenyl)-5-(*p*-tolylthio)-2*H*-1,2,3- triazole *N*-oxide **4g** (31 mg, 0.1 mmol), $NiSO_4$ (2 mg, 0.013 mmol), 2-(2,5-dimethyllphenyl)-2*H*-1,2,3-triazole *N*-oxide **19** (31 mg, 0.1 mmol), DMEDA (4 mg, 0.045 mmol) and Cs_2CO_3 (65 mg, 0.2 mmol) in DMSO (0.6 mL) was added 4-methylbenzenethiol **5a** (15 mg, 0.12 mmol) under an argon atmosphere and the mixture was stirred at 60 °C for 12 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/PE = 1:15) to yield the corresponding product **6ga** (12 mg, 40%) and **6fa** (25 mg, 85%).

5. Kinetic Isotope Effect (KIE) Study.



To a solution of 2-(3-Chlorophenyl)-1,2,3-triazole *N*-oxide (0.2 mmol) in CD_3OD (1 mL) was added Cs_2CO_3 (65 mg, 0.2 mmol) under an air atmosphere and the mixture was stirred at rt for 2 h. The reaction mitxure was concentrated under reduced pressure. After the residue was dissolved in DMSO (0.6 mL), 4-methylbenzenethiol (30 mg, 0.24 mmol), $NiSO_4$ (31 mg, 0.02 mmol), DMEDA (7 mg, 0.08 mmol) and Cs_2CO_3 (130 mg, 0.4 mmol) were added. The mixture was stirred at 60 °C for 12 h. The reaction mitxure was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/PE = 1:15) to yield the corresponding product **6aa** (17.5 mg, 29%).

6. Rate Comparison Experiment of 4a and [D]-4a.



To a solution of 2-(3-Chlorophenyl)-1,2,3-triazole *N*-oxide **4a** (0.2 mmol) in CD_3OD (1 mL) was added Cs_2CO_3 (65 mg, 0.2 mmol) under an air atmosphere and the mixture was stirred at rt for 2 h. The reaction mixture was concentrated under reduced pressure. After the residue was dissolved in DMSO (0.6 mL), 4-methylbenzenethiol **5a** (30 mg, 0.24 mmol), $NiSO_4$ (31 mg, 0.02 mmol), DMEDA (7 mg, 0.08 mmol) and Cs_2CO_3 (130 mg, 0.4 mmol) were added. The mixture was stirred at 60 °C. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/PE = 1:15) to yield the corresponding product **6aa** (44 mg, 73%). The GC yield of desired product was determined by integration using an internal standard (benzenethiol).

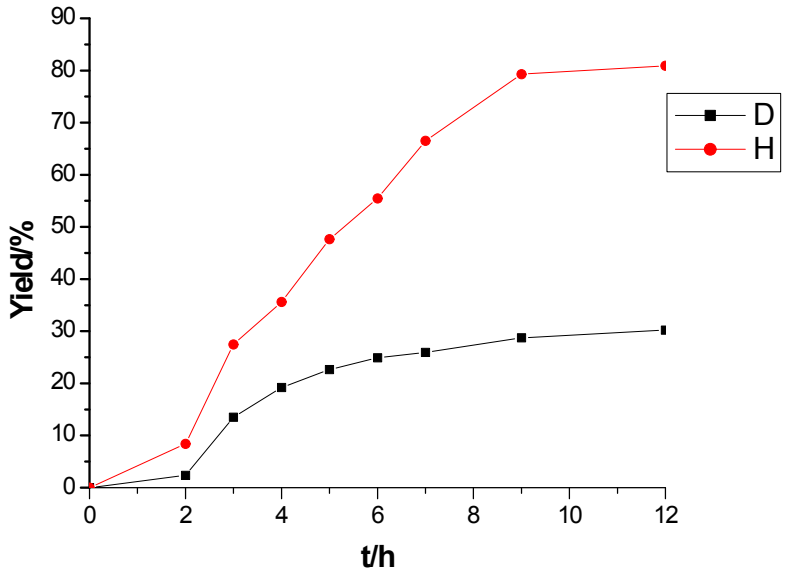
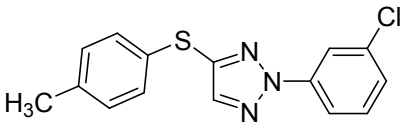


Figure **S1**. Reaction yields over time between **4a** and [D]-**4a**.

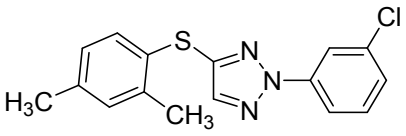
7. Spectroscopic Data of the Products 6, 10, 14, 16 and 19.

2-(3-Chlorophenyl)-4-(*p*-tolylthio)-2*H*-1,2,3-triazole (6aa)



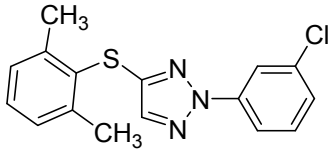
Colorless liquid (49 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H, CH_3), 7.16 (d, J = 7.9 Hz, 2H, Ar-H), 7.33 (dt, J = 2.0, 8.0 Hz, 1H, Ar-H), 7.38 (d, J = 8.0 Hz, 2H, Ar-H), 7.41 (t, J = 8.0 Hz, 1H, Ar-H), 7.62 (s, 1H, Ar-H), 7.96 (dt, J = 2.0, 8.0 Hz, 1H, Ar-H), 8.10 (t, J = 2.0 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 116.7, 119.0, 127.6, 129.0, 130.2, 130.4, 131.6, 135.2, 137.9, 138.3, 140.3, 144.7. IR (KBr) ν_{max}: 1593, 1478, 1440, 1135, 781 cm^{-1}. HRESIMS calcd for $[C_{15}H_{12}ClN_3S + H]^+$ 302.05187 (100%), 304.04892 (32%), found 302.05115 (100%), 304.04788 (32%).

2-(3-Chlorophenyl)-4-(2,4-dimethylphenylthio)-2*H*-1,2,3-triazole (6ab)



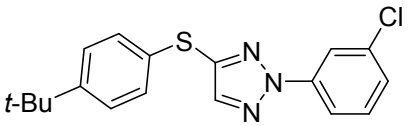
Colorless liquid (45 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.34 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 7.00 (d, J = 7.9 Hz, 1H, Ar-H), 7.11 (s, 1H, Ar-H), 7.31 (d, J = 7.9 Hz, 1H, Ar-H), 7.34 (d, J = 7.9 Hz, 1H, Ar-H), 7.40 (t, J = 8.0 Hz, 1H, Ar-H), 7.47 (s, 1H, Ar-H), 7.93 (dd, J = 8.0, 2.0 Hz, 1H, Ar-H), 8.08 (t, J = 2.0 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.6, 21.0, 116.6, 118.9, 127.5, 127.6, 127.7, 130.3, 131.7, 133.4, 135.2, 137.2, 139.0, 140.1, 140.4, 145.0. IR (KBr) ν_{max}: 1594, 1481, 1442, 1133 cm^{-1}. HRESIMS calcd for $[C_{16}H_{14}ClN_3S + H]^+$ 316.06752 (100%), 318.06457 (32%), found 316.06678 (100%), 318.06340 (32%).

2-(3-Chlorophenyl)-4-(2,6-dimethylphenylthio)-2*H*-1,2,3-triazole (6ac)



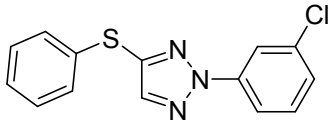
Colorless liquid (44 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.54 (s, 6H, 2XCH_3), 7.17-7.23 (m, 3H, Ar-H), 7.24-7.32 (m, 2H, Ar-H), 7.38 (t, J = 8.1 Hz, 1H, Ar-H), 7.89 (d, J = 8.1 Hz, 1H, Ar-H), 8.03 (t, J = 2.0 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.0, 116.5, 118.7, 127.2, 128.7, 128.9, 129.7, 130.3, 135.1, 135.2, 140.4, 143.5, 146.1. IR (KBr) ν_{max}: 1590, 1477, 1123, 776 cm^{-1}. HRESIMS calcd for $[C_{16}H_{14}ClN_3S + H]^+$ 316.06752 (100%), 318.06457 (32%), found 316.06672 (100%), 318.06336 (32%).

4-(4-*tert*-Butylphenylthio)-2-(3-chlorophenyl)-2*H*-1,2,3-triazole (6ad)



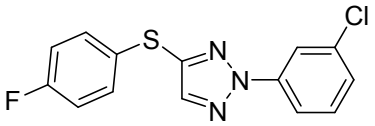
Colorless liquid (54 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (m, 9H, 3XCH_3), 7.33 (dt, J = 1.8, 8.0 Hz, 1H, Ar-H), 7.36-7.45 (m, 5H, Ar-H), 7.66 (s, 1H, Ar-H), 7.97 (dt, J = 1.8, 9.0 Hz, 1H, Ar-H), 8.11 (t, J = 2.0 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.2, 34.6, 116.7, 119.0, 126.5, 127.6, 129.2, 130.4, 131.1, 135.2, 138.2, 140.4, 144.3, 151.4. IR (KBr) ν_{max}: 1593, 1483, 1133, 1010, 782 cm^{-1}. HRESIMS calcd for $[C_{18}H_{18}ClN_3S + H]^+$ 344.09882 (100%), 346.09587 (32%), found 344.09789 (100%), 346.09452 (32%).

2-(3-Chlorophenyl)-4-(phenylthio)-2*H*-1,2,3-triazole (6ae)



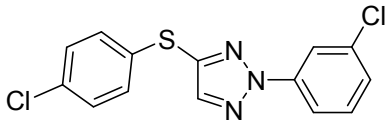
Colorless liquid (41 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.38 (m, 4H, Ar-H), 7.42 (t, J = 8.0 Hz, 1H, Ar-H), 7.46 (d, J = 7.6 Hz, 2H, Ar-H), 7.70 (s, 1H, Ar-H), 7.98 (d, J = 8.0 Hz, 1H, Ar-H), 8.12 (s, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 116.8, 119.1, 127.7, 127.8, 129.4, 130.4, 130.7, 133.1, 135.2, 138.5, 140.4, 143.6. IR (KBr) ν_{max}: 1592, 1481, 1440, 1135, 782 cm^{-1}. HRESIMS calcd for $[C_{14}H_{10}ClN_3S + H]^+$ 288.03622 (100%), 290.03327 (32%), found 288.03462 (100%), 290.03137 (32%).

2-(3-Chlorophenyl)-4-(4-fluorophenyl)thio)-2*H*-1,2,3-triazol (6af)



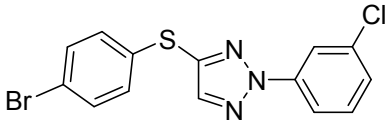
Colorless liquid (47 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06 (t, J = 8.5 Hz, 2H, Ar-H), 7.33 (d, J = 8.0 Hz, 1H, Ar-H), 7.41 (t, J = 8.0 Hz, 1H, Ar-H), 7.48 (d, J = 8.4 Hz, 1H, Ar-H), 7.50 (d, J = 8.4 Hz, 1H, Ar-H), 7.64 (s, 1H, Ar-H), 7.95 (d, J = 8.0 Hz, 1H, Ar-H), 8.09 (s, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 116.5, 116.7 (d, J = 5.9 Hz), 119.1, 127.7, 127.8, 130.4, 133.7 (d, J = 8.3 Hz), 135.2, 137.9, 140.3, 144.1, 162.7 (d, J = 248.8 Hz). IR (KBr) ν_{max}: 1592, 1487, 1228, 1137, 781 cm^{-1}. HRESIMS calcd for $[C_{14}H_9ClFN_3S + H]^+$ 306.02680 (100%), 308.02385 (32%), found 306.02512 (100%), 308.02163 (32%).

2-(3-Chlorophenyl)-4-(4-chlorophenylthio)-2*H*-1,2,3-triazole (6ag)



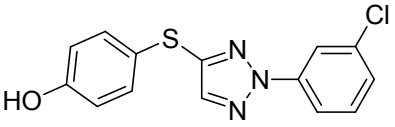
Colorless liquid (41 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.39 (m, 5H, Ar-H), 7.42 (t, J = 8.1 Hz, 1H, Ar-H), 7.72 (s, 1H, Ar-H), 7.97 (dt, J = 2.0, 8.1 Hz, 1H, Ar-H), 8.11 (t, J = 2.0 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 116.8, 119.1, 127.9, 129.5, 130.4, 131.7, 132.0, 133.9, 135.3, 138.5, 140.2, 142.8. IR (KBr) ν_{max}: 1480, 1133, 1008, 818, 754 cm^{-1}. HRESIMS calcd for $[C_{14}H_9Cl_2N_3S + H]^+$ 321.99725 (100%), 323.99430 (64%), found 321.99661 (100%), 323.99329 (32%).

4-(4-Bromophenylthio)-2-(3-chlorophenyl)-2*H*-1,2,3-triazole (6ah)



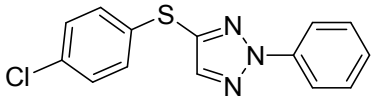
Colorless liquid (46 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, J = 8.5 Hz, 2H, Ar-H), 7.35 (dd, J = 8.1, 1.0 Hz, 1H, Ar-H), 7.43 (t, J = 8.1 Hz, 1H, Ar-H), 7.46 (d, J = 8.5 Hz, 2H, Ar-H), 7.73 (s, 1H, Ar-H), 7.97 (d, J = 8.1 Hz, 1H, Ar-H), 8.12 (t, J = 1.9 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$) : δ 116.8, 119.1, 121.9, 127.9, 130.4, 132.0, 132.4, 132.5, 135.3, 138.6, 140.3, 142.6. IR (KBr) ν_{max}: 1591, 1478, 1080, 1004, 814, 789 cm^{-1}. HRESIMS calcd for $[C_{14}H_9BrClN_3S + H]^+$ 365.94673 (100%), 367.94469 (97%), found 365.94598 (100%), 367.94342 (97%).

4-(2-(3-Chlorophenyl)-2*H*-1,2,3-triazol-4-ylthio)phenol (6ai)



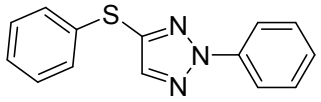
Colorless liquid (36 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.29 (s, 1H, OH), 6.86 (d, J = 8.6 Hz, 2H, Ar-H), 7.31 (d, J = 8.2 Hz, 1H, Ar-H), 7.40 (t, J = 8.2 Hz, 1H, Ar-H), 7.46 (d, J = 8.6 Hz, 2H, Ar-H), 7.53 (s, 1H, Ar-H), 7.93 (d, J = 8.2 Hz, 1H, Ar-H), 8.07 (t, J = 2.0 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 116.6, 116.7, 119.0, 122.6, 127.6, 130.3, 134.7, 135.2, 137.1, 140.4, 145.9, 156.3. IR (KBr) ν_{max}: 3420, 1592, 1487, 1436 cm^{-1}. HRESIMS calcd for $[C_{14}H_{10}ClN_3OS - H]^-$ 302.01549 (100%), 304.01254 (32%), found 302.01468 (100%), 304.01157 (32%).

4-(4-Chlorophenylthio)-2-phenyl-2*H*-1,2,3-triazole (6bg)



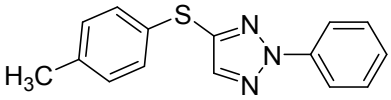
Colorless liquid (35 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (dt, J = 2.1, 8.7 Hz, 1H, Ar-H), 7.30 (s, 1H, Ar-H), 7.34-7.40 (m, 3H, Ar-H), 7.50 (t, J = 8.3 Hz, 2H, Ar-H), 7.75 (s, 1H, Ar-H), 8.08 (dd, J = 8.7, 2.1 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 118.8, 128.0, 129.2, 129.3, 129.4, 131.4, 131.7, 133.6, 138.5, 141.7. IR (KBr) ν_{max}: 1582, 1475, 1130, 785 cm^{-1}. HRESIMS calcd for $[C_{14}H_{10}ClN_3S + H]^+$ 288.03622 (100%), 290.03327 (32%), found 288.03523 (100%), 290.03206 (32%).

2-Phenyl-4-(phenylthio)-2*H*-1,2,3-triazole (6be)



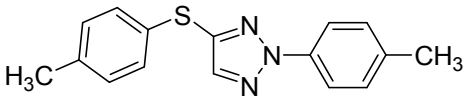
Colorless liquid (32 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.36 (m, 3H, Ar-H), 7.38 (t, J = 7.6 Hz, 1H, Ar-H), 7.43 (d, J = 7.9 Hz, 2H, Ar-H), 7.50 (t, J = 7.6 Hz, 2H, Ar-H), 7.73 (s, 1H, Ar-H), 8.09 (d, J = 8.2 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 118.8, 127.5, 127.8, 129.2, 129.3, 130.3, 133.7, 138.4, 139.6, 142.4. IR (KBr) ν_{max}: 1495, 1445, 1376, 1134, 750 cm^{-1}. HRESIMS calcd for $[C_{14}H_{11}N_3S + H]^+$ 254.07519 (100%), found 254.07480 (100%).

2-Phenyl-4-(*p*-tolylthio)-2*H*-1,2,3-triazole (6ba)



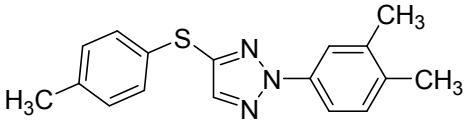
Colorless liquid (34 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.35 (s, 3H, CH_3), 7.15 (d, J = 8.0 Hz, 2H, Ar-H), 7.35-7.40 (m, 3H, Ar-H), 7.49 (dt, J = 1.7, 8.4 Hz, 2H, Ar-H), 7.65 (s, 1H, Ar-H), 8.08 (dt, J = 1.2, 8.4 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 118.8, 127.7, 129.3, 129.6, 130.1, 131.2, 137.9, 137.9, 139.6, 143.5. IR (KBr) ν_{max}: 1495, 1133, 1020, 806 cm^{-1}. HRESIMS calcd for $[C_{15}H_{13}N_3S + H]^+$ 268.09084 (100%), found 268.08997 (100%).

2-*p*-Tolyl-4-(*p*-tolylthio)-2*H*-1,2,3-triazole (6ca)



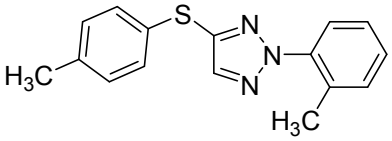
Colorless liquid (34 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.35 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 7.14 (d, J = 8.0 Hz, 2H, Ar-H), 7.28 (d, J = 7.9 Hz, 2H, Ar-H), 7.36 (d, J = 8.0 Hz, 2H, Ar-H), 7.64 (s, 1H, Ar-H), 7.94 (d, J = 7.9 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.9, 21.0, 118.7, 129.8, 129.9, 130.1, 131.0, 137.5, 137.6, 137.7, 137.8, 143.0. IR (KBr) ν_{max}: 1511, 1112, 810 cm^{-1}. HRESIMS calcd for $[C_{16}H_{15}N_3S + H]^+$ 282.10649 (100%), found 282.10553 (100%).

2-(3,4-Dimethylphenyl)-4-(*p*-tolylthio)-2*H*-1,2,3-triazole (6da)



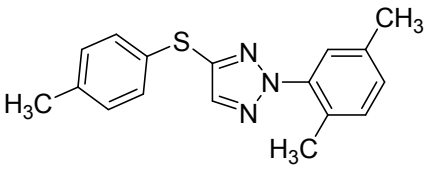
Colorless liquid (40 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.31 (s, 3H, CH_3), 2.35 (s, 6H, 2XCH_3), 7.14 (d, J = 8.0 Hz, 2H, Ar-H), 7.22 (d, J = 8.2 Hz, 1H, Ar-H), 7.35 (d, J = 8.0 Hz, 2H, Ar-H), 7.64 (s, 1H, Ar-H), 7.78 (d, J = 8.2 Hz, 1H, Ar-H), 7.86 (s, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.3, 19.8, 21.0, 116.2, 119.9, 129.7, 130.0, 130.1, 130.3, 130.7, 130.9, 136.4, 137.7, 137.8, 142.8. IR (KBr) ν_{max}: 1496, 1457, 1126, 812 cm^{-1}. HRESIMS calcd for $[C_{17}H_{17}N_3S + H]^+$ 296.12214 (100%), found 296.12097 (100%).

2-*o*-Tolyl-4-(*p*-tolylthio)-2*H*-1,2,3-triazole (6ea)



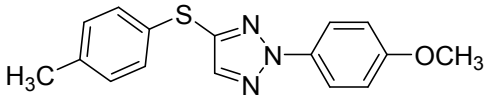
Colorless liquid (36 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.35 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 7.15 (d, J = 8.0 Hz, 2H, Ar-H), 7.29-7.36 (m, 3H, Ar-H), 7.38 (d, J = 8.0 Hz, 2H, Ar-H), 7.58 (d, J = 7.2 Hz, 1H, Ar-H), 7.69 (s, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.9, 21.0, 125.1, 126.5, 128.9, 129.9, 130.0, 131.1, 131.7, 132.6, 137.4, 137.8, 139.5, 142.7. IR (KBr) ν_{max}: 1494, 1454, 1125 cm^{-1}. HRESIMS calcd for $[C_{16}H_{15}N_3S + H]^+$ 282.10649 (100%), found 282.10556 (100%).

2-(2,5-Dimethylphenyl)-4-(*p*-tolylthio)-2*H*-1,2,3-triazole (6fa)



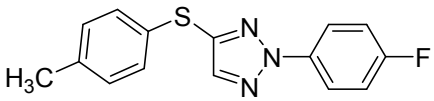
Colorless liquid (35 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.31 (s, 3H, CH_3), 2.35 (s, 6H, 2XCH_3), 7.14 (d, J = 7.9 Hz, 2H, Ar-H), 7.23 (d, J = 8.2 Hz, 1H, Ar-H), 7.35 (d, J = 7.9 Hz, 2H, Ar-H), 7.64 (s, 1H, Ar-H), 7.78 (d, J = 8.2 Hz, 1H, Ar-H), 7.86 (s, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.3, 19.8, 21.0, 116.2, 119.9, 130.0 (2C), 130.3, 130.8, 130.9, 136.4, 137.7, 137.8, 137.9, 142.8. IR (KBr) ν_{max}: 1494, 1458, 1124, 1007, 814 cm^{-1}. HRESIMS calcd for $[C_{17}H_{17}N_3S + H]^+$ 296.12214 (100%), found 296.12100 (100%).

2-(4-Methoxyphenyl)-4-(*p*-tolylthio)-2*H*-1,2,3-triazole (6ga)



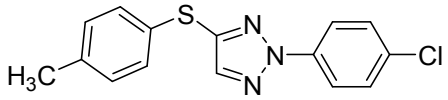
Colorless liquid (33 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.34 (s, 3H, CH_3), 3.87 (s, 3H, OCH_3), 6.99 (d, J = 9.0 Hz, 2H, Ar-H), 7.14 (d, J = 7.9 Hz, 2H, Ar-H), 7.35 (d, J = 7.9 Hz, 2H, Ar-H), 7.64 (s, 1H, Ar-H), 7.98 (d, J = 9.0 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.0, 55.6, 114.4, 120.3, 130.0, 130.9, 133.5, 137.6, 137.7, 142.6, 159.2. IR (KBr) ν_{max}: 1510, 1250, 1167, 1134 cm^{-1}. HRESIMS calcd for $[C_{16}H_{15}N_3OS + H]^+$ 298.10141 (100%), found 298.10039 (100%).

2-(4-Fluorophenyl)-4-(*p*-tolylthio)-2*H*-1,2,3-triazole (6ha)



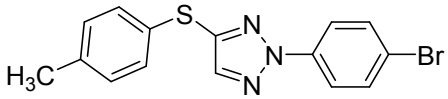
Colorless liquid (45 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.35 (s, 3H, CH_3), 7.14 (d, J = 2.7 Hz, 1H, Ar-H), 7.16 (d, J = 2.7 Hz, 2H, Ar-H), 7.18 (d, J = 8.2 Hz, 1H, Ar-H), 7.37 (d, J = 8.2 Hz, 2H, Ar-H), 7.63 (s, 1H, Ar-H), 8.03 (dd, J = 9.1, 2.2 Hz, 1H, Ar-H), 8.06 (dd, J = 9.1, 2.2 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 116.1 (d, J = 23.2 Hz), 120.5 (d, J = 8.4 Hz), 129.4, 130.1, 131.3, 135.9 (d, J = 2.9 Hz), 137.8, 138.1, 143.8, 161.9 (d, J = 247.5 Hz). IR (KBr) ν_{max}: 1509, 1451, 1133, 626 cm^{-1}. HRESIMS calcd for $[C_{15}H_{12}FN_3S + H]^+$ 286.08142 (100%), found 286.08043 (100%).

2-(4-Chlorophenyl)-4-(*p*-tolylthio)-2*H*-1,2,3-triazole (6ia)



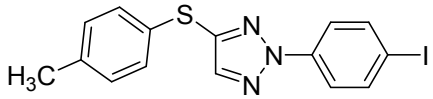
Colorless liquid (46 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H, CH_3), 7.16 (d, J = 8.1 Hz, 2H, Ar-H), 7.38 (d, J = 8.1 Hz, 2H, Ar-H), 7.45 (dt, J = 2.0, 6.9 Hz, 2H, Ar-H), 7.62 (s, 1H, Ar-H), 8.01(dt, J = 2.1, 6.9 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 119.9, 129.2, 129.4, 130.2, 131.5, 133.3, 137.8, 138.1, 138.2, 144.3. IR (KBr) ν_{max}: 1490, 1092, 829 cm^{-1}. HRESIMS calcd for $[C_{15}H_{12}ClN_3S + H]^+$ 302.05187 (100%), 304.04892 (32%), found 302.05139 (100%), 304.04811 (32%).

2-(4-Bromophenyl)-4-(*p*-tolylthio)-2*H*-1,2,3-triazole (6ja)



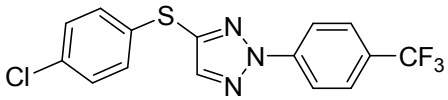
Colorless liquid (51 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H, CH_3), 7.16 (d, J = 8.0 Hz, 2H, Ar-H), 7.38 (d, J = 8.0 Hz, 2H, Ar-H), 7.60 (t, J = 8.8 Hz, 2H, Ar-H), 7.62 (s, 1H, Ar-H), 7.94 (d, J = 8.8 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 120.2, 121.2, 129.1, 130.2, 131.6, 132.4, 137.8, 138.2, 138.6, 144.4. IR (KBr) ν_{max}: 1487, 1006, 959, 826 cm^{-1}. HRESIMS calcd for $[C_{15}H_{12}BrN_3S + H]^+$ 346.00136 (100%), 347.99931 (97%), found 346.00006 (100%), 347.99757 (32%).

2-(4-Iodoophenyl)-4-(*p*-tolylthio)-2*H*-1,2,3-triazole (6ka)



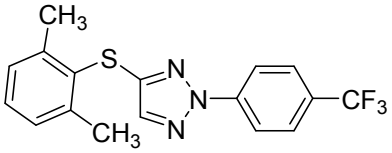
Colorless liquid (46 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H, CH_3), 7.16 (d, J = 8.0 Hz, 2H, Ar-H), 7.38 (t, J = 4.1 Hz, 2H, Ar-H), 7.61 (s, 1H, Ar-H), 7.78-7.85 (m, 4H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 92.3, 120.4, 129.1, 130.2, 131.6, 137.8, 138.2, 138.3, 139.3, 144.4. IR (KBr) ν_{max}: 1486, 1051 953, 830 cm^{-1}. MS (EI) calcd for $[C_{15}H_{12}IN_3S]^+$ 393 (100%), found 393 (100%). Anal calcd for $C_{15}H_{12}IN_3S$: C, 45.81; H, 3.08; N, 10.69; S, 8.15. Found C, 46.13; H, 3.27; N, 10.45, S, 7.82.

4-(4-Chlorophenylthio)-2-(4-(trifluoromethyl)phenyl)-2*H*-1,2,3-triazole (6lg)



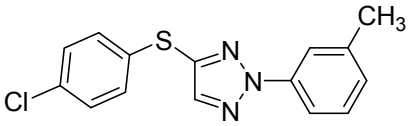
Colorless liquid (48 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (dt, J = 2.0, 8.6 Hz, 2H, Ar-H), 7.40 (dt, J = 2.0, 8.6 Hz, 2H, Ar-H), 7.73 (s, 1H, Ar-H), 7.76 (d, J = 8.6 Hz, 2H, Ar-H), 8.20 (d, J = 8.6 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 118.8, 123.8 (q, J = 272.2 Hz), 126.7 (q, J = 3.8 Hz), 129.6, 129.9, 131.4, 132.2, 134.2, 138.6, 141.7, 143.7. IR (KBr) ν_{max}: 1386, 1331, 1172, 1124, 815 cm^{-1}. HRESIMS calcd for $[C_{15}H_9ClF_3N_3S + H]^+$ 356.02361 (100%), 358.02066 (32%), found 356.02271 (100%), 358.01926 (32%).

4-(2,6-Dimethylphenylthio)-2-(4-(trifluoromethyl)phenyl)-2*H*-1,2,3-triazole (6lc)



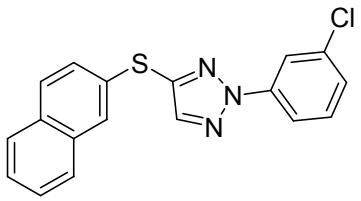
White solid (50 mg, 72%), mp 41-42 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.55 (s, 6H, 2XCH_3), 7.21 (d, J = 7.8 Hz, 2H, Ar-H), 7.23 (s, 1H, Ar-H), 7.26 (d, J = 7.8 Hz, 1H, Ar-H), 7.72 (d, J = 8.6 Hz, 2H, Ar-H), 8.12 (d, J = 8.6 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 118.4, 123.8 (q, J = 272.0 Hz), 123.9 (q, J = 3.8 Hz), 128.0, 128.6, 128.7, 129.2, 129.8, 135.4, 143.5, 146.7. IR (KBr) ν_{max}: 1615, 1385, 1324, 1125 cm^{-1}. HRESIMS calcd for $[C_{17}H_{14}F_3N_3S + H]^+$ 350.09388 (100%), found 350.09305 (100%).

4-(4-Chlorophenylthio)-2-*m*-tolyl-2*H*-1,2,3-triazole (6mg)



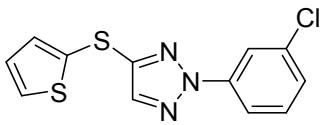
Colorless liquid (39 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.45 (s, 3H, CH_3), 7.20 (d, J = 7.4 Hz, 1H, Ar-H), 7.26-7.31 (m, 3H, Ar-H), 7.34 (d, J = 2.1 Hz, 1H, Ar-H), 7.38 (t, J = 8.0 Hz, 1H, Ar-H), 7.74 (s, 1H, Ar-H), 7.87 (d, J = 8.0 Hz, 1H, Ar-H), 7.92 (s, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.4, 116.0, 119.4, 128.8, 129.2, 129.4, 131.3, 132.5, 133.5, 135.3, 138.5, 139.5, 141.5. IR (KBr) ν_{max}: 1447, 1227, 1009 cm^{-1}. HRESIMS calcd for $[C_{15}H_{12}ClN_3S + H]^+$ 302.05187 (100%), 304.04892 (32%), found 302.05112 (100%), 304.04780 (32%).

2-(3-Chlorophenyl)-4-(naphthalen-2-ylthio)-2*H*-1,2,3-triazole (6aj)



Colorless liquid (43 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, J = 8.3 Hz, 1H, Ar-H), 7.42 (t, J = 8.1 Hz, 1H, Ar-H), 7.47-7.53 (m, 3H, Ar-H), 7.72 (s, 1H, Ar-H), 7.75-7.86 (m, 3H, Ar-H), 7.94 (d, J = 1.0 Hz, 1H, Ar-H), 7.99 (dd, J = 8.1, 1.0 Hz, 1H, Ar-H), 8.14 (t, J = 2.0 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 116.8, 119.1, 126.6, 126.9, 127.5, 127.7, 127.8, 128.0, 129.2, 129.8, 130.2, 130.4, 132.5, 133.7, 135.2, 138.5, 140.4, 143.6. IR (KBr) ν_{max}: 1590, 1482, 1439, 1135, 782 cm^{-1}. HRESIMS calcd for $[C_{18}H_{12}ClN_3S + H]^+$ 338.05187 (100%), 340.04892 (32%), found 338.04941 (100%), 340.04630 (32%).

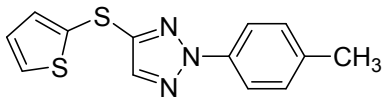
2-(3-Chlorophenyl)-4-(thiophen-2-ylthio)-2*H*-1,2,3-triazole (6ak)



Colorless liquid (40 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (dd, J = 5.4, 3.6 Hz, 1H, Ar-H), 7.32 (dq, J = 8.0, 1.0 Hz, 1H, Ar-H), 7.38 (dd, J = 3.6, 1.2 Hz, 1H, Ar-H), 7.40 (t, J = 8.0 Hz, 1H, Ar-H), 7.48 (dd, J = 5.4, 1.2 Hz, 1H, Ar-H), 7.58 (s, 1H, Ar-H), 7.57 (s, 1H, Ar-H), 7.93 (dq, J = 1.0, 8.0 Hz, 1H, Ar-H), 8.07 (t, J = 2.0 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 116.7, 119.0, 127.6, 127.9, 128.9, 130.3, 131.4, 135.2, 135.6, 136.5, 140.4, 145.8. IR (KBr) ν_{max}: 1595,

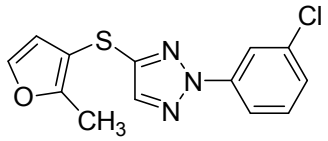
1483, 1445, 1129 cm^{-1}. MS (ESI): 294 ($M+H^+$, 100), 296 ($M+H^+$, 30). Anal calcd for $C_{12}H_8ClN_3S_2$: C, 49.06; H, 2.74; N, 14.30, S, 21.83. Found C, 49.43; H, 2.95; N, 14.17, S, 21.52.

4-(Thiophen-2-ylthio)-2-*p*-tolyl-2*H*-1,2,3-triazole (6ck)



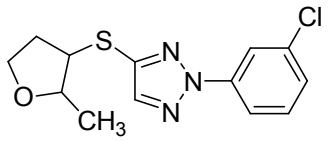
Colorless liquid (35 mg, 64%). ^1H NMR (400 MHz, $CDCl_3$): δ 2.40 (s, 3H, CH_3), 7.04 (dd, J = 5.4, 3.6 Hz, 1H, Ar-H), 7.26 (d, J = 8.4 Hz, 2H, Ar-H), 7.36 (dd, J = 3.6, 1.2 Hz, 1H, Ar-H), 7.45 (dd, J = 5.4, 1.2 Hz, 1H, Ar-H), 7.58 (s, 1H, Ar-H), 7.91 (d, J = 8.4 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.0, 118.7, 127.8, 129.8, 131.0, 135.1, 136.2, 136.7, 137.5, 137.7, 144.4. IR (KBr) ν_{max}: 1512, 1127, 474 cm^{-1}. HRESIMS calcd for $[C_{13}H_{11}N_3S_2 + H]^+$ 274.04726 (100%), found 274.04564 (100%).

2-(3-Chlorophenyl)-4-(2-methylfuran-3-ylthio)-2*H*-1,2,3-triazole (6al)



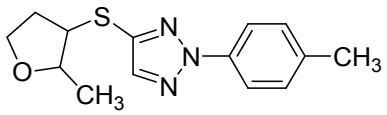
Colorless liquid (45 mg, 77%). ^1H NMR (400 MHz, $CDCl_3$): δ 2.43 (s, 3H, CH_3), 6.47 (d, J = 2.0 Hz, 1H, Ar-H), 7.31 (dq, J = 1.0, 8.1 Hz, 1H, Ar-H), 7.37 (d, J = 2.0 Hz, 2H, Ar-H), 7.46 (s, 1H, Ar-H), 7.91 (dq, J = 1.0, 8.1 Hz, 1H, Ar-H), 8.05 (t, J = 2.0 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.9, 106.5, 114.9, 116.6, 118.8, 127.4, 130.3, 135.1, 135.7, 140.4, 141.2, 146.0, 156.3. IR (KBr) ν_{max}: 1593, 1483, 1131, 782 cm^{-1}. MS (ESI): 292 ($M+H^+$, 100), 294 ($M+H^+$, 30). Anal calcd for $C_{13}H_{10}ClN_3OS$: C, 53.52; H, 3.45; N, 14.40, S, 10.99. Found C, 53.89; H, 3.53; N, 14.06, S, 10.74.

2-(3-Chlorophenyl)-4-(2-methyl-tetrahydrofuran-3-ylthio)-2*H*-1,2,3-triazole (6am)



Colorless liquid (43 mg, 73%). ^1H NMR (400 MHz, $CDCl_3$): δ 1.36 (d, J = 6.4 Hz, 3H, CH_3), 2.08-2.17 (m, 1H, CH), 2.46-2.55 (m, 1H, CH), 3.82 (dt, J = 1.8, 8.3 Hz, 1H, CH), 4.03-4.10 (m, 2H, CH_2), 4.29 (dq, J = 8.0, 6.4 Hz, 1H, CH), 7.32 (dt, J = 1.0, 8.0 Hz, 1H, Ar-H), 7.41 (t, J = 8.0 Hz, 1H, Ar-H), 7.70 (s, 1H, Ar-H), 7.94 (dt, J = 1.0, 8.0 Hz, 1H, Ar-H), 8.07 (t, J = 2.0 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.9, 33.8, 50.0, 65.9, 77.1, 116.5, 118.8, 127.4, 130.4, 135.2, 136.6, 140.4, 144.4. IR (KBr) ν_{max}: 1593, 1483, 1108, 781 cm^{-1}. MS (ESI): 296 ($M+H^+$, 100), 298 ($M+H^+$, 30). Anal calcd for $C_{13}H_{14}ClN_3OS$: C, 52.79; H, 4.77; N, 14.21, S, 10.84. Found C, 53.08; H, 4.92; N, 13.97, S, 10.71.

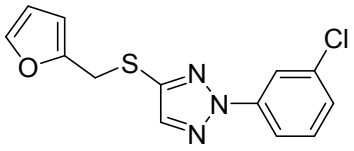
4-(2-Methyl-tetrahydrofuran-3-ylthio)-2-*p*-tolyl -2*H*-1,2,3-triazole (6cm)



Colorless liquid (35 mg , 63%). ^1H NMR (400 MHz, $CDCl_3$): δ 1.36 (d, J = 6.3 Hz, 3H, CH_3), 2.09-2.17 (m, 1H, CH), 2.41 (s, 3H, CH_3), 2.43-2.52 (m, 1H, CH), 3.81 (dt, J = 8.2, 6.3 Hz, 1H, CH), 4.00-4.09 (m, 2H, CH_2), 4.27 (dq, J = 5.9, 6.3 Hz, 1H, CH), 7.28 (d, J = 8.5 Hz, 2H, Ar-H),

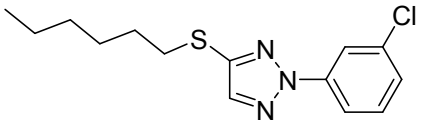
7.69 (s, 1H, Ar-H), 7.92 (d, J = 8.5 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.9, 21.0, 33.8, 50.2, 65.9, 77.1, 118.5, 129.8, 136.3, 137.4, 137.5, 142.9. IR (KBr) ν_{max}: 1513, 1381, 1109, 964 cm^{-1}. HRESIMS calcd for $[C_{14}H_{17}N_3OS + H]^+$ 276.11706 (100%), found 276.11542 (100%).

2-(3-Chlorophenyl)-4-(furan-2-ylmethylthio)-2*H*-1,2,3-triazole (6an)



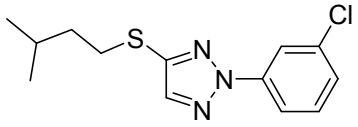
Colorless liquid (42 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.25 (s, 2H, SCH_2), 6.20 (t, J = 2.6 Hz, 1H, Ar-H), 6.31 (t, J = 2.6 Hz, 1H, Ar-H), 7.33 (d, J = 8.1 Hz, 1H, Ar-H), 7.38 (s, 1H, Ar-H), 7.42 (t, J = 8.1 Hz, 1H, Ar-H), 7.61 (s, 1H, Ar-H), 7.95 (d, J = 8.1 Hz, 1H, Ar-H), 8.09 (t, J = 1.8 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.9, 107.7, 108.5, 110.6, 116.6, 118.9, 127.5, 130.4, 135.2, 137.4, 142.5, 143.5, 150.3. IR (KBr) ν_{max}: 1593, 1483, 1141, 781 cm^{-1}. HRESIMS calcd for $[C_{13}H_{10}ClN_3OS + H]^+$ 292.03114 (100%), 294.02819 (32%), found 292.03030 (100%), 294.02701 (32%).

2-(3-Chlorophenyl)-4-(hexylthio)-2*H*-1,2,3-triazole (6ao)



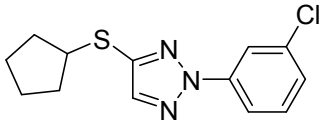
Colorless liquid (40 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (t, J = 6.9 Hz, 3H, CH_3), 1.28-1.38 (m, 4H, CH_2), 1.46 (dt, J = 7.1, 14.7 Hz, 2H, CH_2), 1.73 (dt, J = 7.4, 14.7 Hz, 2H, CH_2), 3.07 (t, J = 7.4 Hz, 2H, SCH_2), 7.31 (dt, J = 0.8, 8.1 Hz, 1H, Ar-H), 7.41 (t, J = 8.1 Hz, 1H, Ar-H), 7.68 (s, 1H, Ar-H), 7.94 (dt, J = 0.8, 8.1 Hz, 1H, Ar-H), 8.08 (t, J = 2.0 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 22.5, 28.3, 29.5, 31.3, 33.7, 116.5, 118.8, 127.3, 130.3, 135.1, 136.3, 140.4, 145.2. IR (KBr) ν_{max}: 1594, 1483, 1442, 1134 cm^{-1}. HRESIMS calcd for $[C_{14}H_{18}ClN_3S + H]^+$ 296.09882 (100%), 298.09587 (32%), found 296.09810 (100%), 298.09484 (32%).

2-(3-Chlorophenyl)-4-(isopentylthio)-2*H*-1,2,3-triazole (6ap)



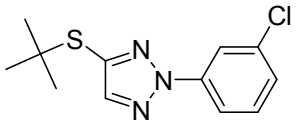
Colorless liquid (41 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95 (d, J = 6.5 Hz, 6H, 2XCH_3), 1.63 (dt, J = 7.1, 15.0 Hz, 2H, CH_2), 1.71-1.82 (m, 1H, CH), 3.08 (t, J = 7.7 Hz, 2H, SCH_2), 7.31 (d, J = 8.1 Hz, 1H, Ar-H), 7.41 (t, J = 8.1 Hz, 1H, Ar-H), 7.68 (s, 1H, Ar-H), 7.94 (d, J = 8.1 Hz, 1H, Ar-H), 8.08 (s, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.2, 27.3, 31.8, 38.5, 116.5, 118.8, 127.2, 130.3, 135.1, 136.3, 140.4, 145.1. IR (KBr) ν_{max}: 1594, 1482, 1133 cm^{-1}. HRESIMS calcd for $[C_{13}H_{16}ClN_3S + H]^+$ 282.08317 (100%), 284.08022 (32%), found 282.08237 (100%), 284.07913 (32%).

2-(3-Chlorophenyl)-4-(cyclopentylthio)-2*H*-1,2,3-triazole (6aq)



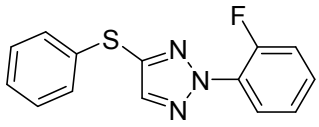
Colorless liquid (44 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.62-1.73 (m, 4H, CH_2), 1.78-1.86 (m, 2H, CH_2), 2.08-2.18 (m, 2H, CH_2), 3.71 (dd, J = 13.1, 6.5 Hz, 1H, CH), 7.31 (d, J = 8.1 Hz, 1H, Ar-H), 7.41 (t, J = 8.1 Hz, 1H, Ar-H), 7.71 (s, 1H, Ar-H), 7.96 (d, J = 7.4 Hz, 1H, Ar-H), 8.09 (t, J = 1.8 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.8, 33.8, 46.6, 116.6, 118.9, 127.3, 130.3, 135.1, 137.3, 140.4, 144.9. IR (KBr) ν_{max}: 1593, 1483, 1441, 1136, 781 cm^{-1}. HRESIMS calcd for $[C_{13}H_{14}ClN_3S + H]^+$ 280.06752 (100%), 282.06457 (32%), found 280.06677 (100%), 282.06357 (32%).

4-(*tert*-Butylthio)-2-(3-chlorophenyl)-2*H*-1,2,3-triazole (6ar)



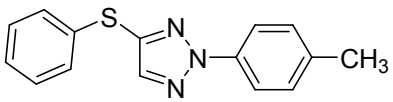
Colorless liquid (46 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.41 (s, 9H, 3XCH_3), 7.34 (d, J = 8.1 Hz, 1H, Ar-H), 7.43 (t, J = 8.1 Hz, 1H, Ar-H), 7.81 (s, 1H, Ar-H), 8.01 (d, J = 8.1 Hz, 1H, Ar-H), 8.15 (t, J = 1.9 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.1, 47.2, 116.9, 119.2, 127.7, 130.4, 135.2, 140.4, 141.3, 141.8. IR (KBr) ν_{max}: 1594, 1482, 1133, 782 cm^{-1}. HRESIMS calcd for $[C_{12}H_{14}ClN_3S + H]^+$ 268.06752 (100%), 270.06457 (32%), found 268.06676 (100%), 270.06362 (32%).

2-(2-Fluorophenyl)-4-(phenylthio)-2*H*-1,2,3-triazole (6ie)



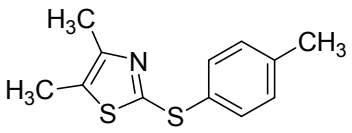
Colorless liquid (45 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.37 (m, 5H, Ar-H), 7.39-7.43 (m, 1H, Ar-H), 7.46 (d, J = 7.6 Hz, 2H, Ar-H), 7.76 (s, 1H, Ar-H), 7.83 (t, J = 7.6 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 117.5 (d, J = 20.0 Hz), 124.5 (d, J = 4.1 Hz), 125.1, 127.7, 129.3, 129.9 (d, J = 7.7 Hz), 130.7, 132.2, 133.3, 138.5 (d, J = 0.8 Hz), 143.3, 154.5 (d, J = 256.0 Hz). IR (KBr) ν_{max}: 1609, 1508, 1449, 1128, 753 cm^{-1}. HRESIMS calcd for $[C_{14}H_{10}FN_3S + H]^+$ 272.06577 (100%), found 272.06536 (100%).

4-(Phenylthio)-2-*p*-tolyl-2*H*-1,2,3-triazole (6ce)



Colorless liquid (36 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.42 (s, 3H, CH_3), 7.28-7.35 (m, 5H, Ar-H), 7.42 (d, J = 7.9 Hz, 2H, Ar-H), 7.72 (s, 1H, Ar-H), 7.96 (d, J = 8.2 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.0, 118.8, 127.3, 129.2, 129.8, 130.1, 134.0, 137.5, 137.8, 138.3, 141.9. IR (KBr) ν_{max}: 1513, 1448, 1382, 1131, 963 cm^{-1}. HRESIMS calcd for $[C_{15}H_{13}N_3S + H]^+$ 268.09084 (100%), found 268.08968 (100%).

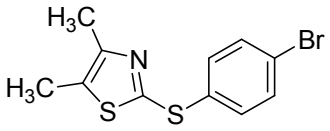
4,5-Dimethyl-2-(*p*-tolylthio)thiazole (10a)



Colorless liquid (37 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.26 (s, 3H, CH_3), 2.28 (s, 3H,

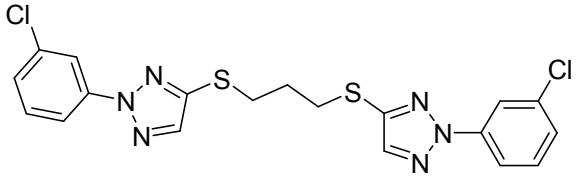
CH_3), 2.37 (s, 3H, CH_3), 7.21 (d, J = 8.0 Hz, 2H, Ar-H), 7.49 (d, J = 8.0 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.1, 13.1, 21.3, 123.7, 125.9, 130.5, 130.6, 133.9, 140.3, 141.5. IR (KBr) ν_{max}: 1297, 1232, 1106, 1073 cm^{-1}. HRESIMS calcd for $[C_{12}H_{13}NS_2 + H]^+$ 236.05677 (100%), found 236.05560 (100%).

2-(4-Bromophenylthio)-4,5-dimethylthiazole (10b)



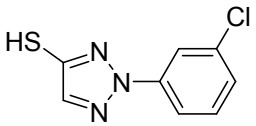
Colorless liquid (38 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.30 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 7.40 (d, J = 8.4 Hz, 2H, Ar-H), 7.50 (d, J = 8.4 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 13.2, 123.8, 125.5, 129.8, 132.9, 133.8, 134.0, 142.1. IR (KBr) ν_{max}: 1471, 1359, 1299, 1007 cm^{-1}. HRESIMS calcd for $[C_{11}H_{10}BrNS_2 + H]^+$ 299.95163 (100%), 301.94958 (100%), found 299.95045(100%), 301.94826 (100%).

1,3-Bis(2-(3-chlorophenyl)-2*H*-1,2,3-triazole-4-ylthio)propane (14)



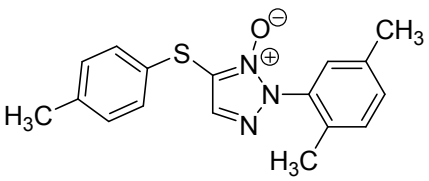
Colorless liquid (44 mg, 48%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.19 (dt, J = 6.9, 13.9 Hz, 2H, CH_2), 3.24 (t, J = 6.9 Hz, 4H, SCH_2), 7.30 (d, J = 8.1.0 Hz, 2H, Ar-H), 7.38 (t, J = 8.1 Hz, 2H, Ar-H), 7.69 (s, 2H, Ar-H), 7.89 (d, J = 8.1 Hz, 2H, Ar-H), 8.04 (s, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.3, 32.2, 116.5, 118.8, 127.4, 130.3, 135.2, 136.4, 140.3, 144.3. IR (KBr) ν_{max}: 1593, 1482, 1137, 1004, 1137, 1004, 963, 781 cm^{-1}. HRESIMS calcd for $[C_{19}H_{16}Cl_2N_6S_2 + H]^+$ 463.03332 (100%), 465.03037 (64%), found 463.03177 (100%), 465.02859 (64%).

2-(3-Chlorophenyl)-2*H*-1,2,3-triazole-4-thiol (16)



Colorless amorphous solid (21 mg, 49%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.27 (d, J = 8.1 Hz, 1H, Ar-H), 7.47 (t, J = 8.1 Hz, 1H, Ar-H), 7.86 (d, J = 8.1 Hz, 1H, Ar-H), 7.99 (s, 1H, Ar-H), 8.15 (s, 1H, Ar-H), 12.07 (s, 1H, S-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 116.5, 117.5, 125.0, 131.3, 133.9, 137.5, 139.5, 152.6. IR (KBr) ν_{max}: 3387, 1595, 1480, 1146, 785 cm^{-1}. HRESIMS calcd for $[C_8H_6ClN_3S - H]^-$ 209.98927 (100%), 211.98632 (32%), found 209.98860 (100%), 211.98547 (32%).

2-(2,5-Dimethylphenyl)-5-(*p*-tolylthio)-2*H*-1,2,3-triazole *N*-oxide (19)

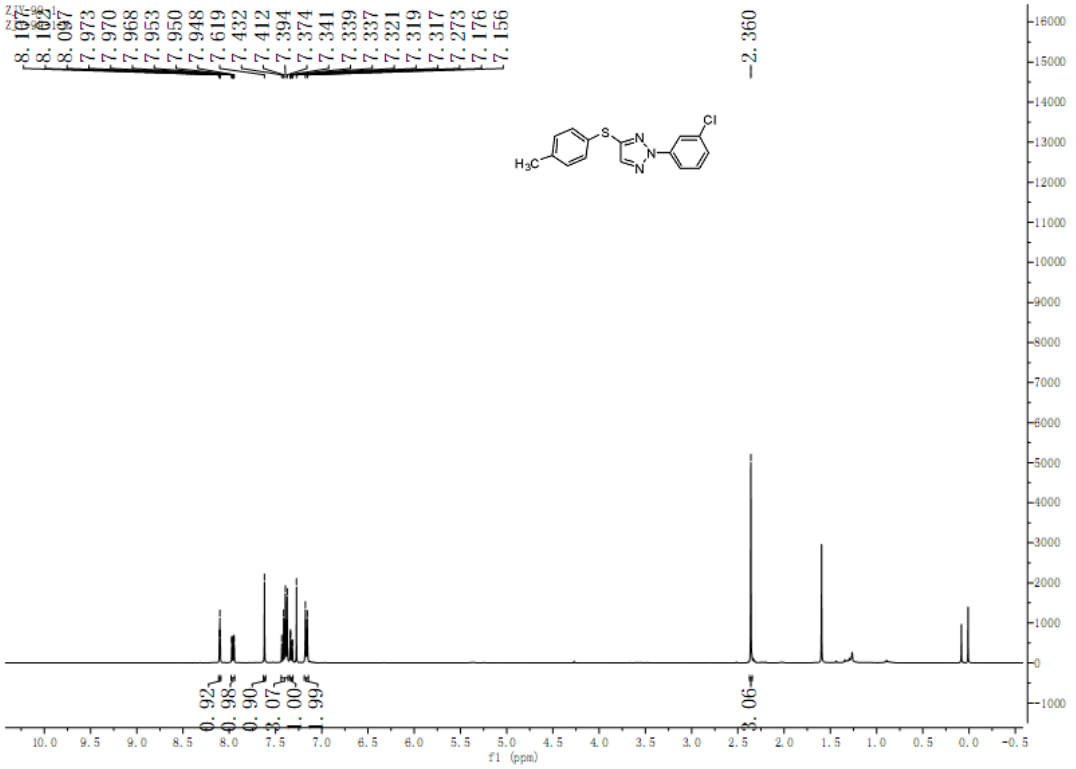


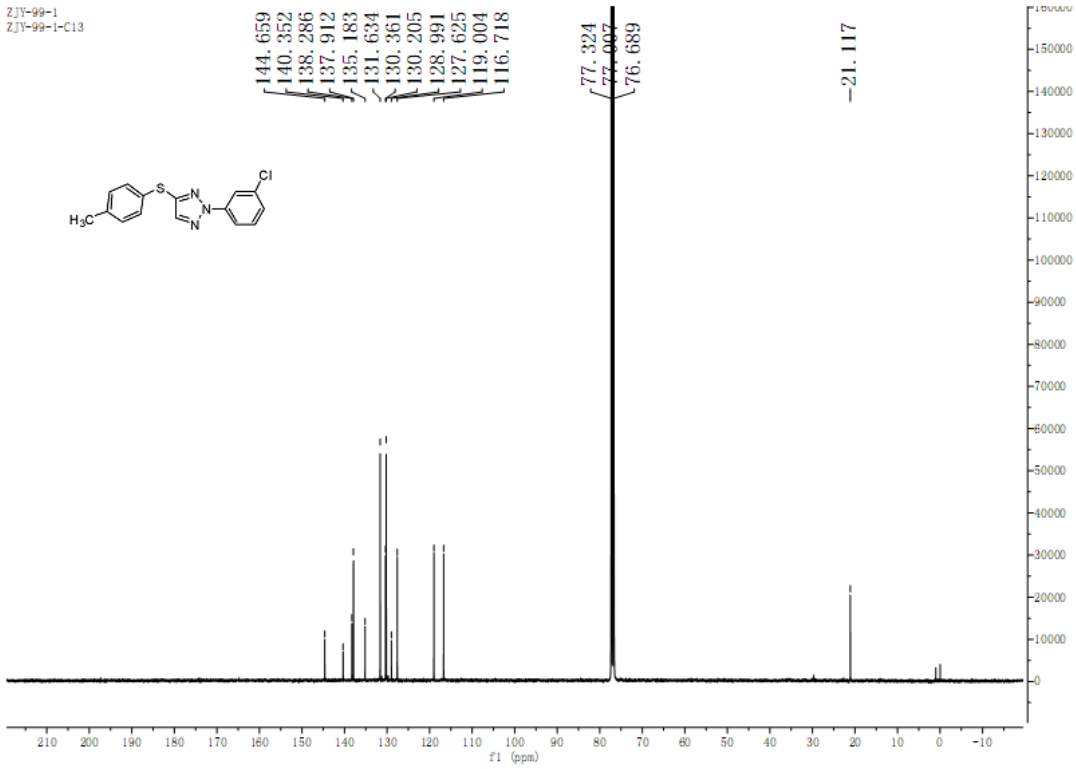
Colorless liquid (25 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.32 (s, 3H, CH_3), 2.35 (s, 3H,

CH_3), 2.38 (s, 3H, CH_3), 7.14 (d, J = 7.9 Hz, 2H, Ar-H), 7.16 (d, J = 7.9 Hz, 1H, Ar-H), 7.21 (d, J = 7.9 Hz, 1H, Ar-H), 7.37 (d, J = 7.9 Hz, 2H, Ar-H), 7.41 (s, 1H, Ar-H), 7.69 (s, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.4, 20.7, 21.0, 125.5, 129.4, 129.7, 130.0, 130.1, 131.0, 131.5, 136.5, 137.4, 137.7, 139.2, 142.5. IR (KBr) ν_{max}: 1502, 1452, 1128, 1010, 809 cm^{-1}. HRESIMS calcd for $[C_{17}H_{17}N_3OS + H]^+$ 312.11706 (100%), found 312.11560 (100%).

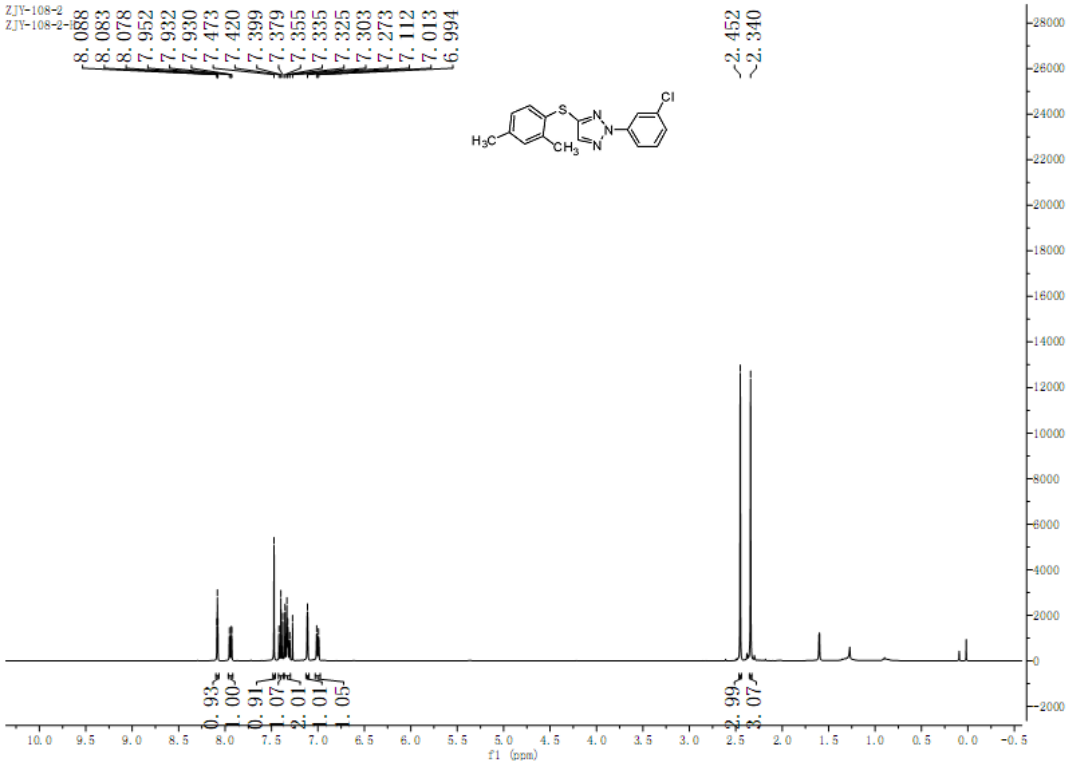
8. Copies of ^{1}H, ^{13}C Spectra

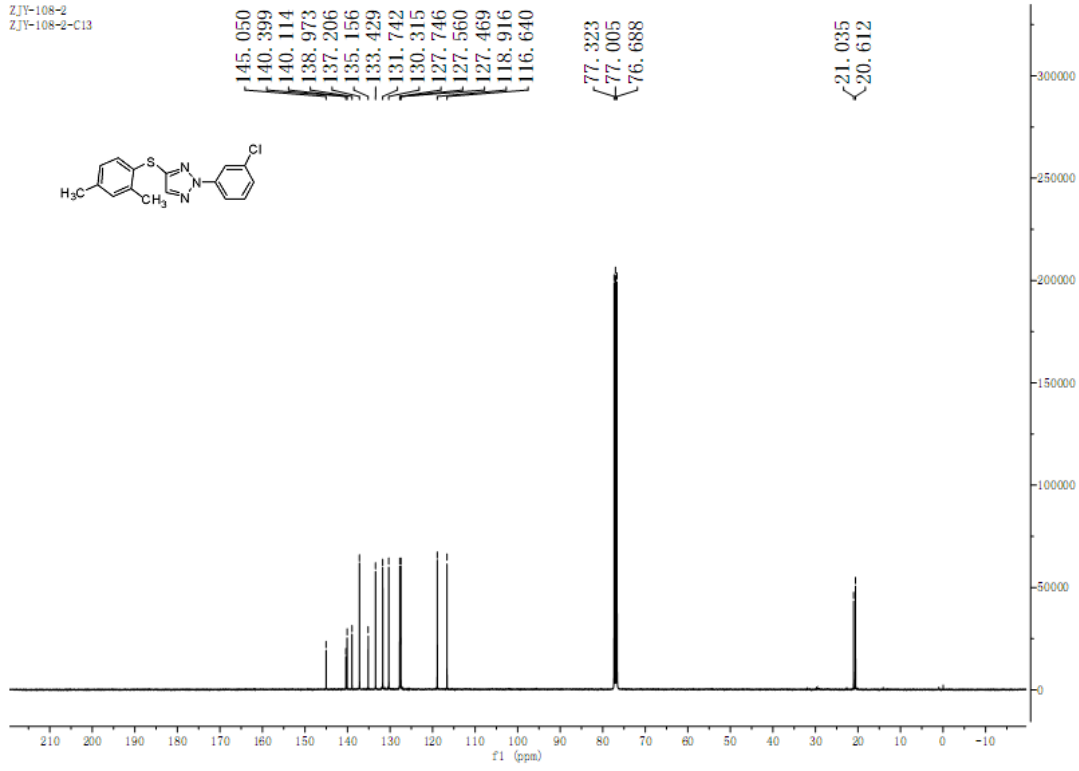
^{1}H and ^{13}C NMR Spectra for **6aa**



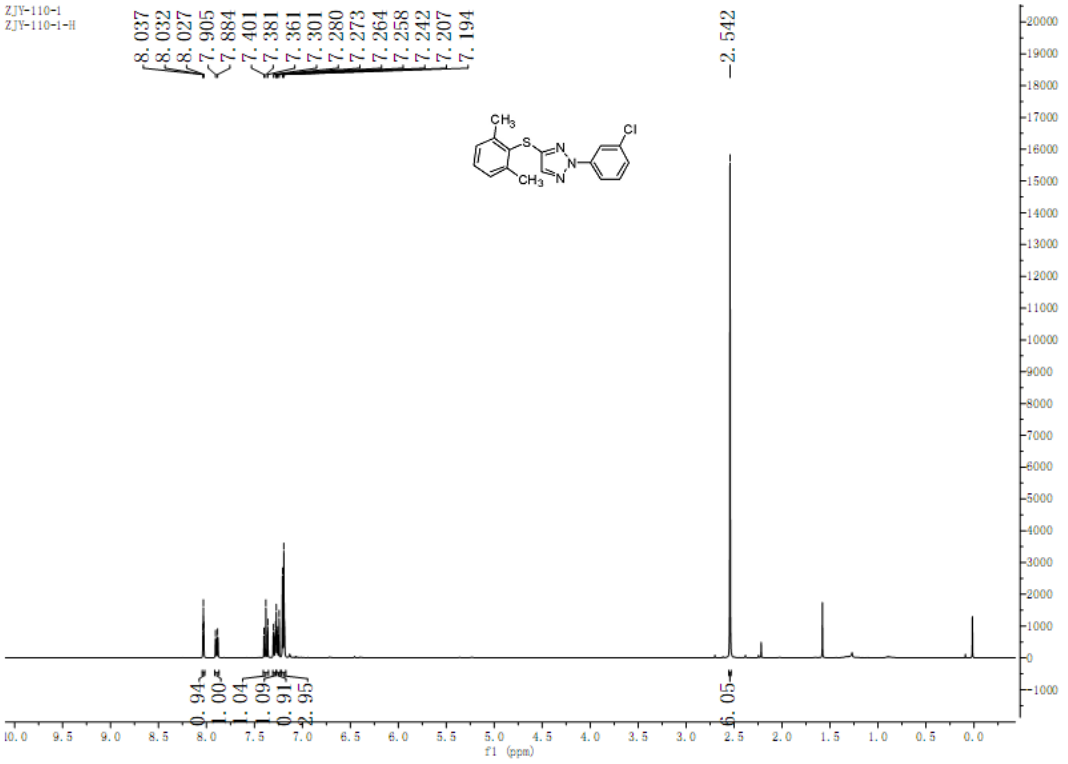


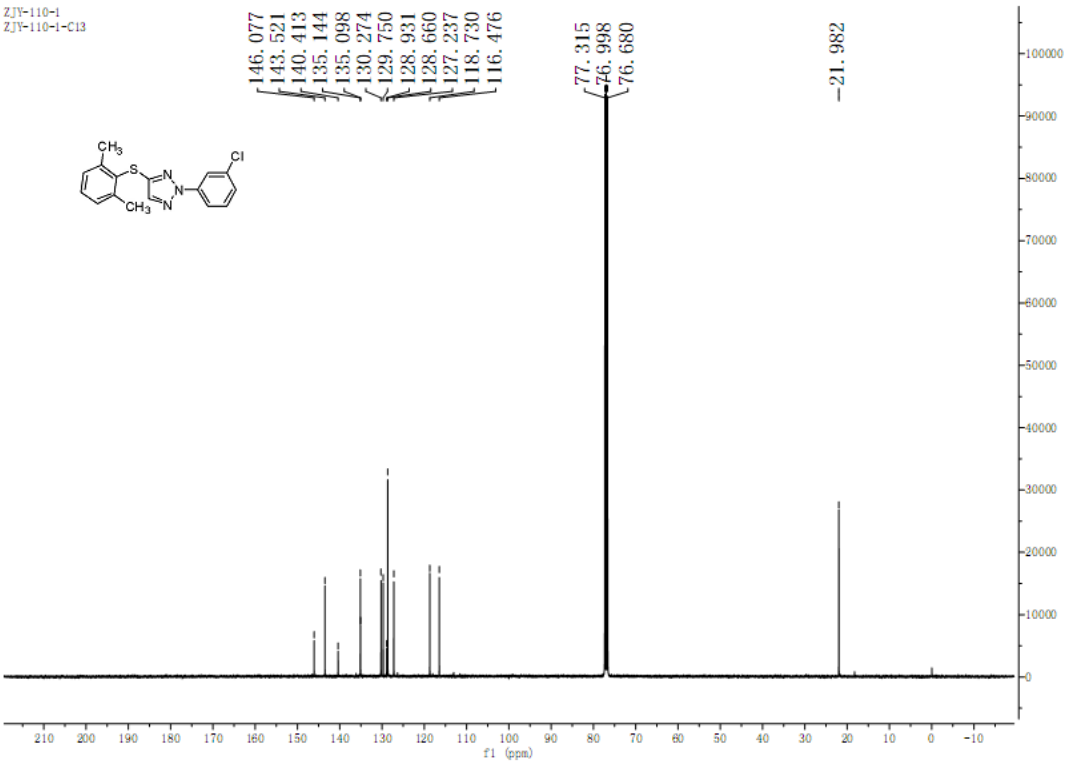
^{1}H and ^{13}C NMR Spectra for **6ab**



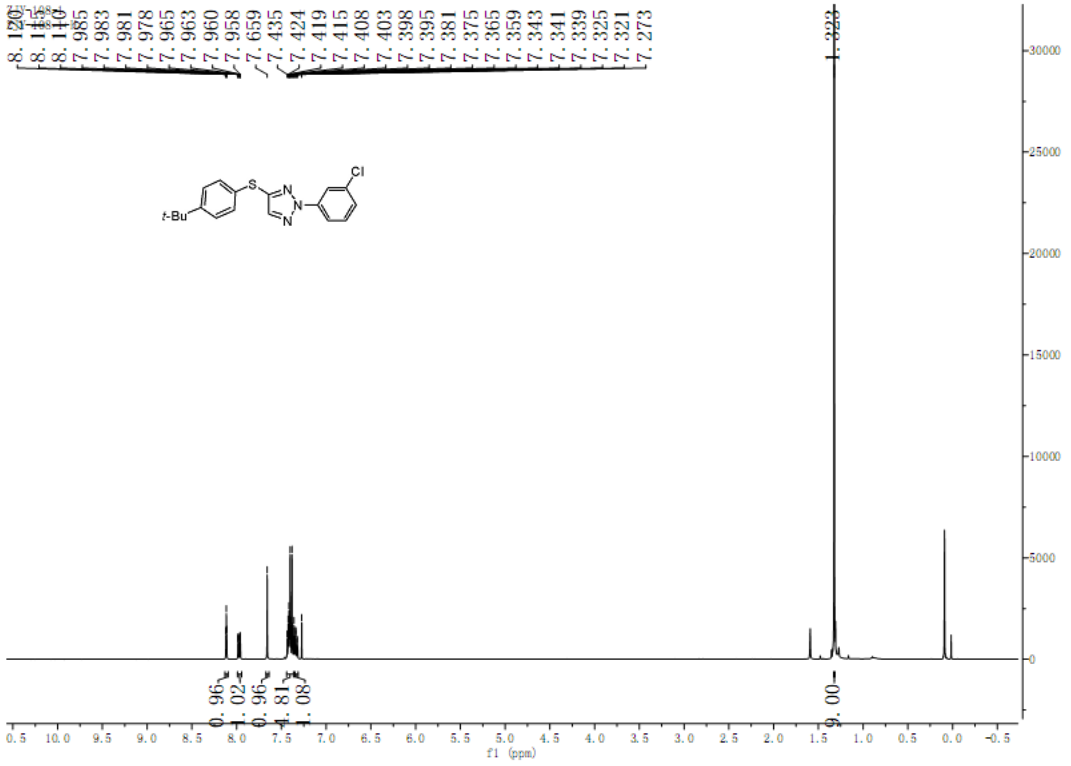


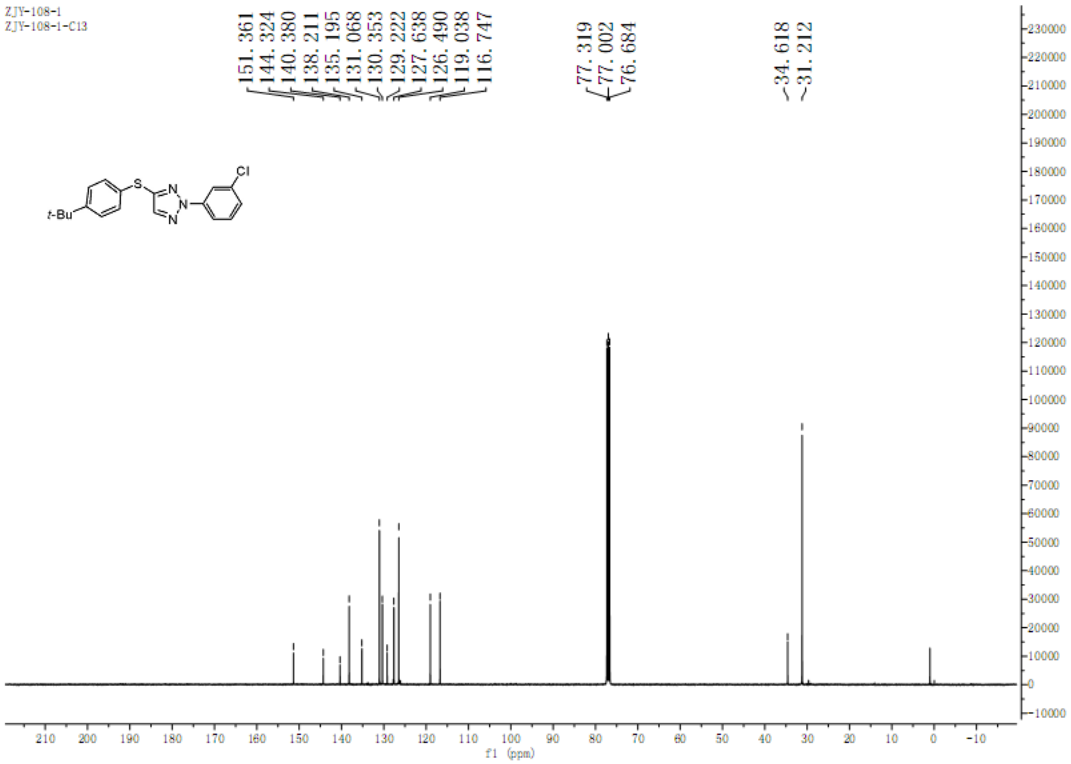
^{1}H and ^{13}C NMR Spectra for **6ac**



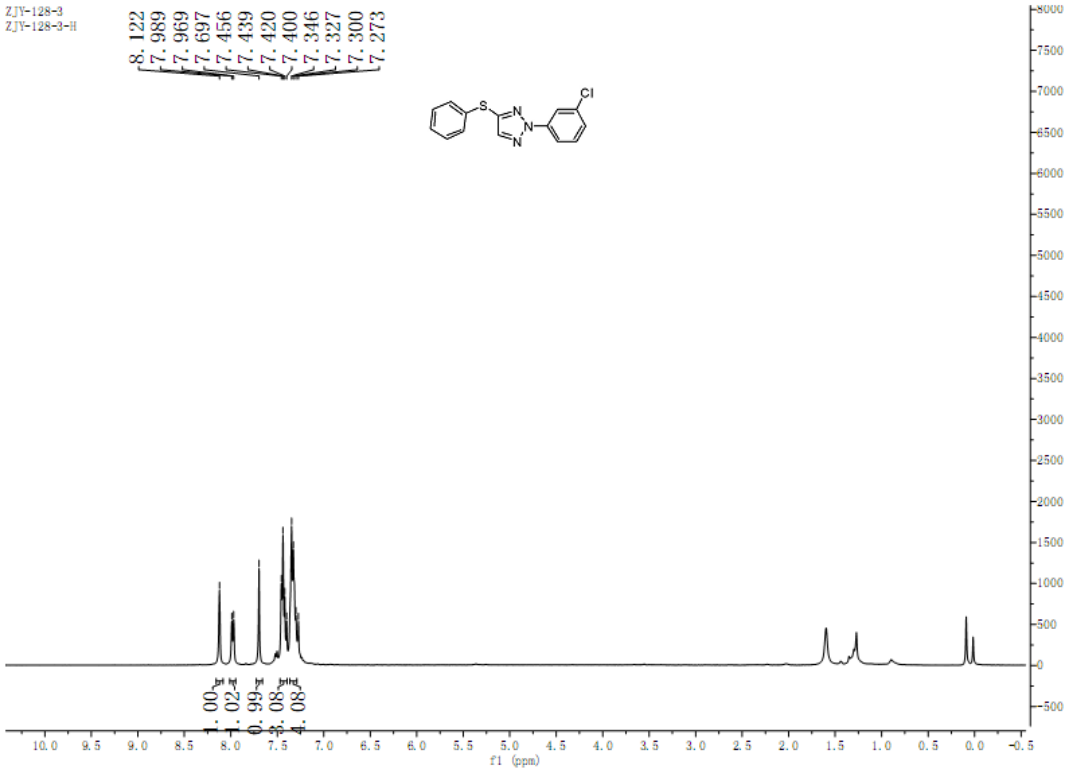


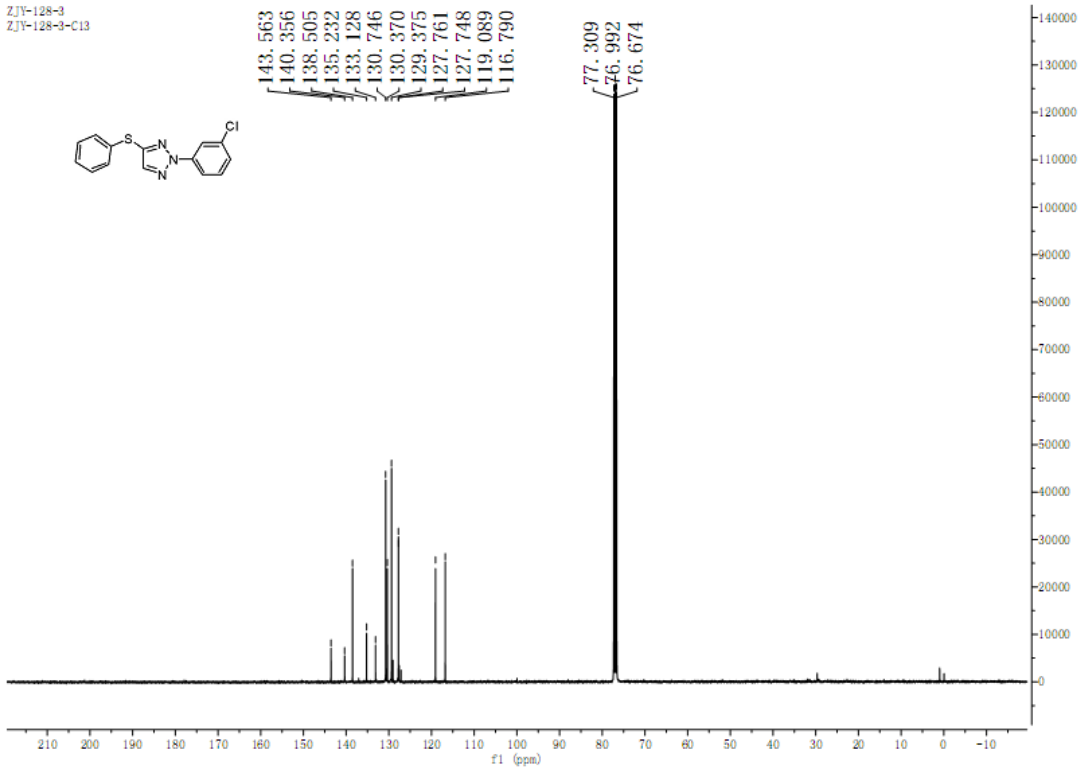
^{1}H and ^{13}C NMR Spectra for **6ad**



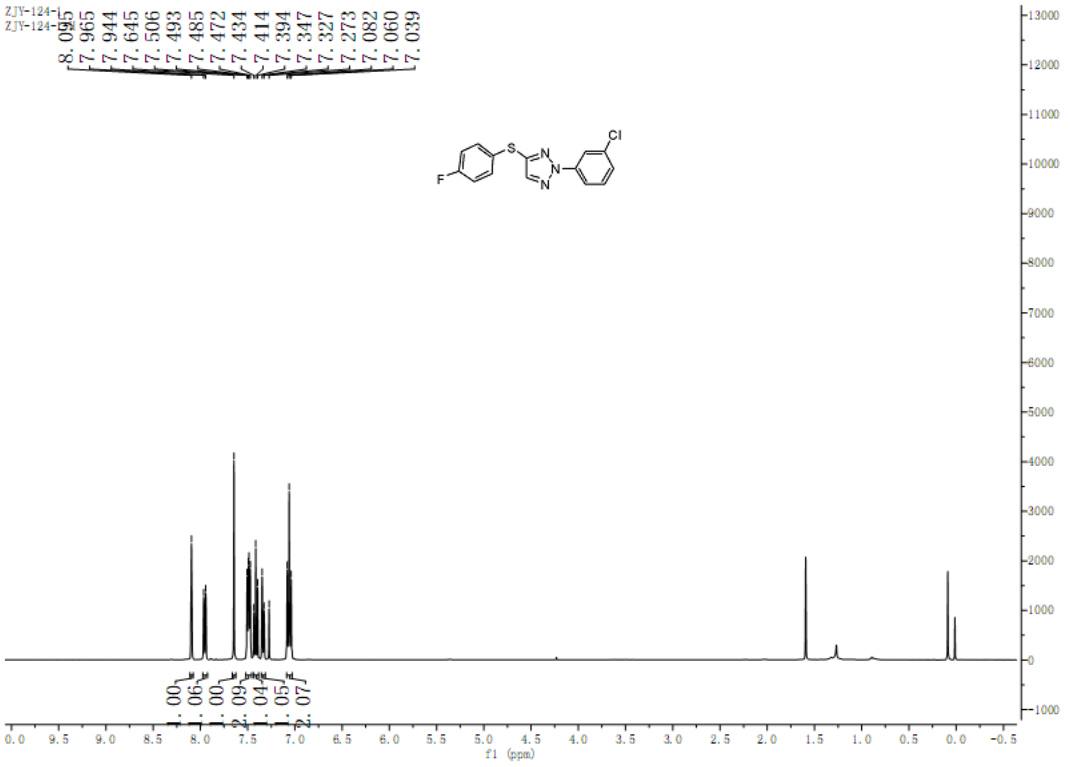


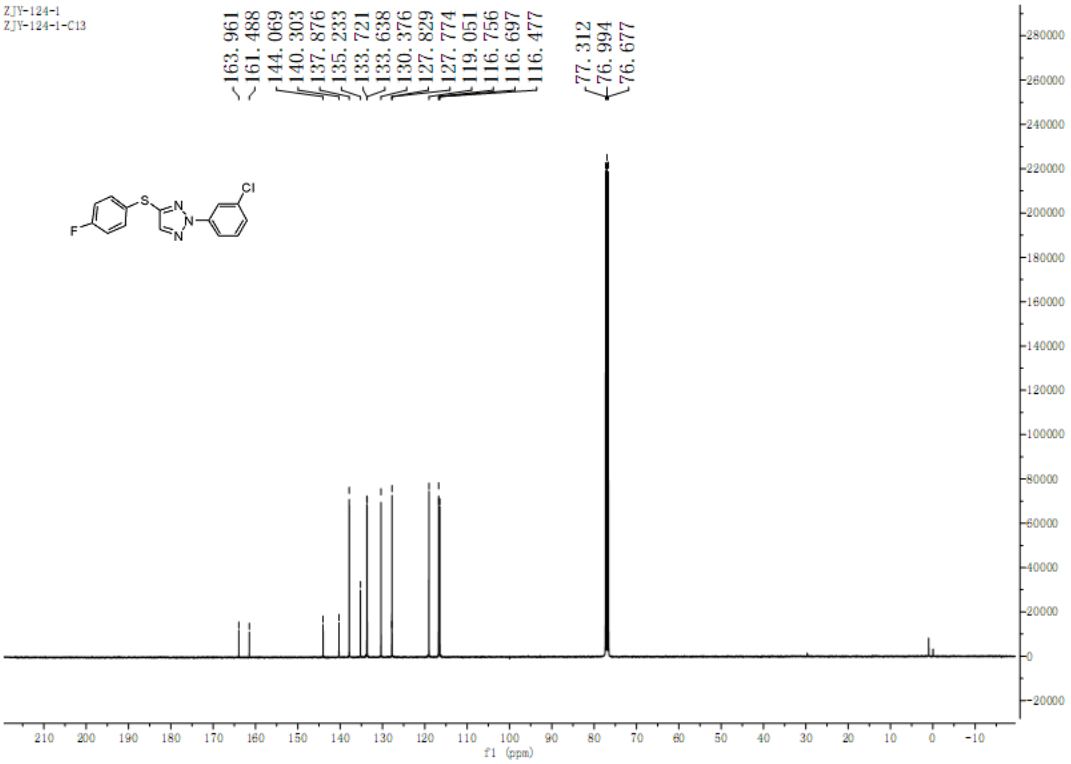
^{1}H and ^{13}C NMR Spectra for **6ae**



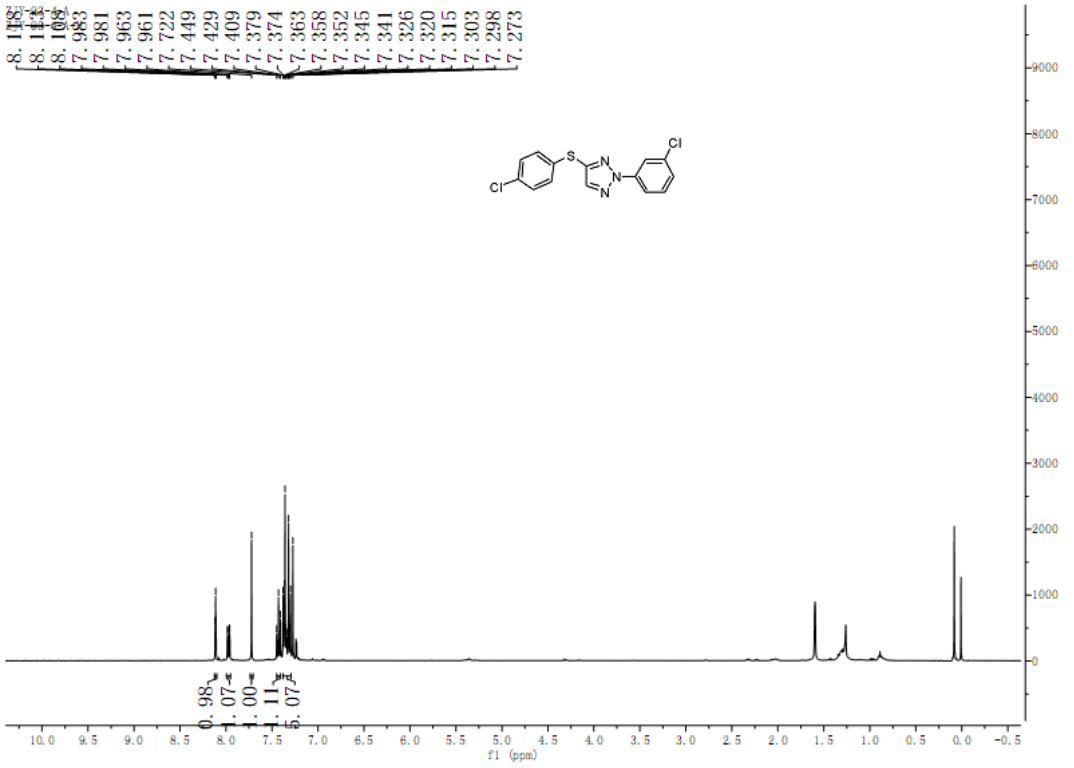


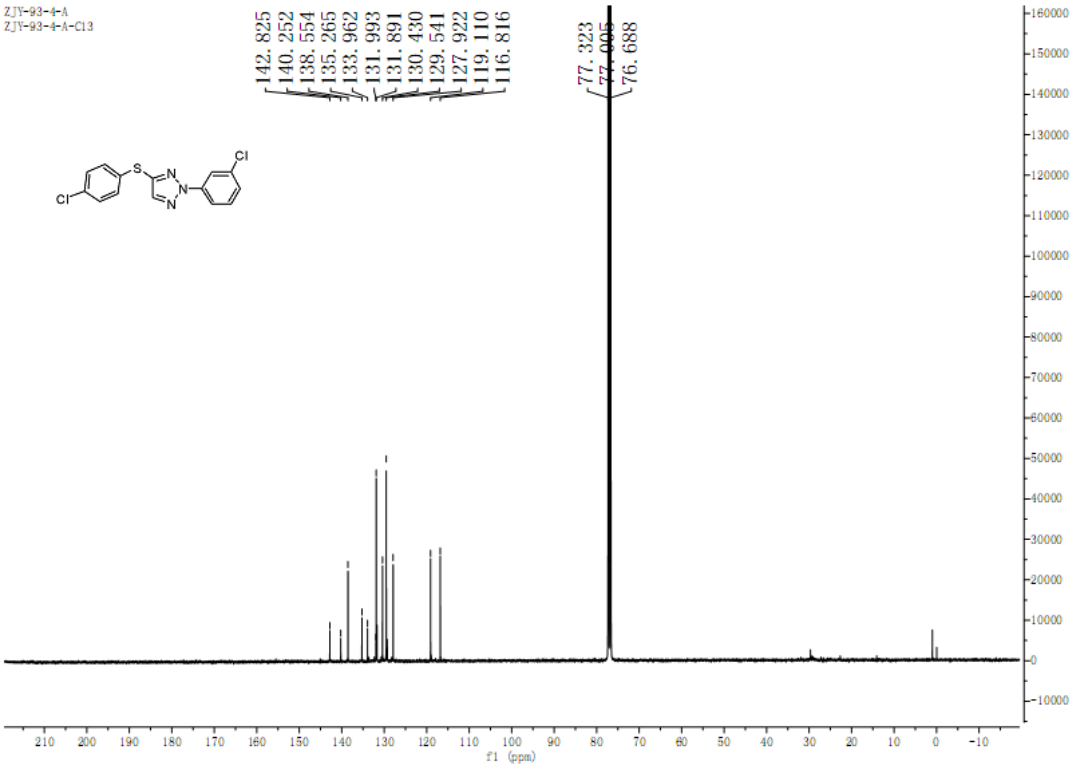
^{1}H and ^{13}C NMR Spectra for **6af**



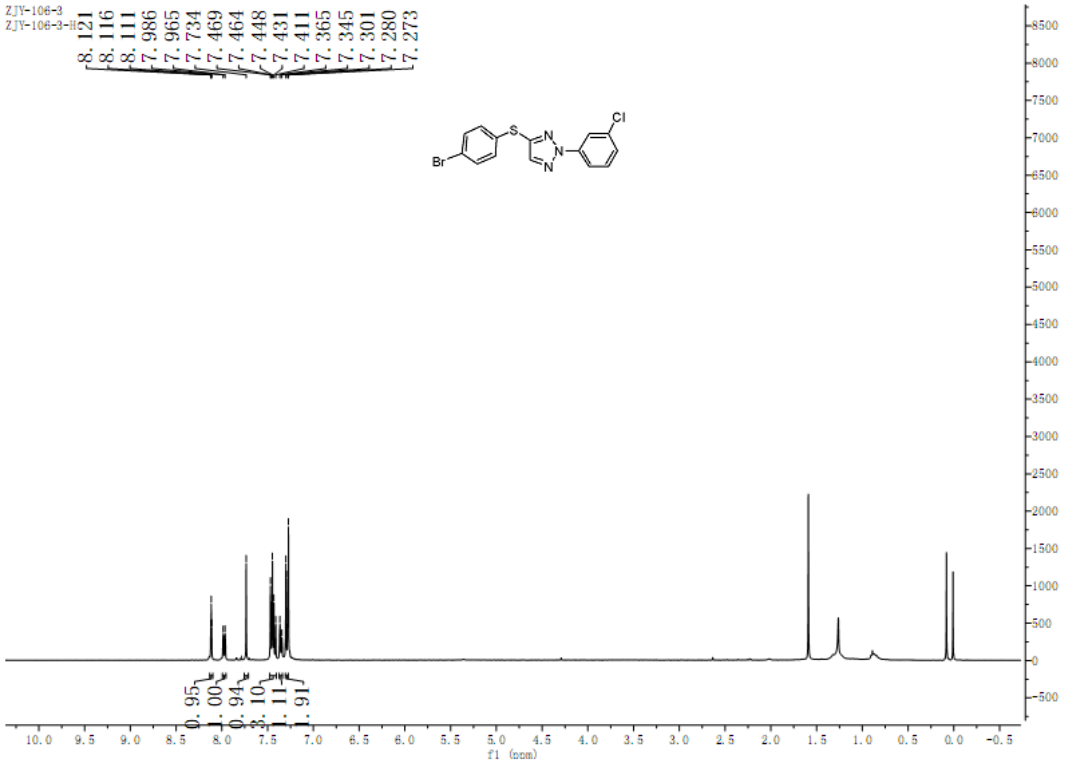


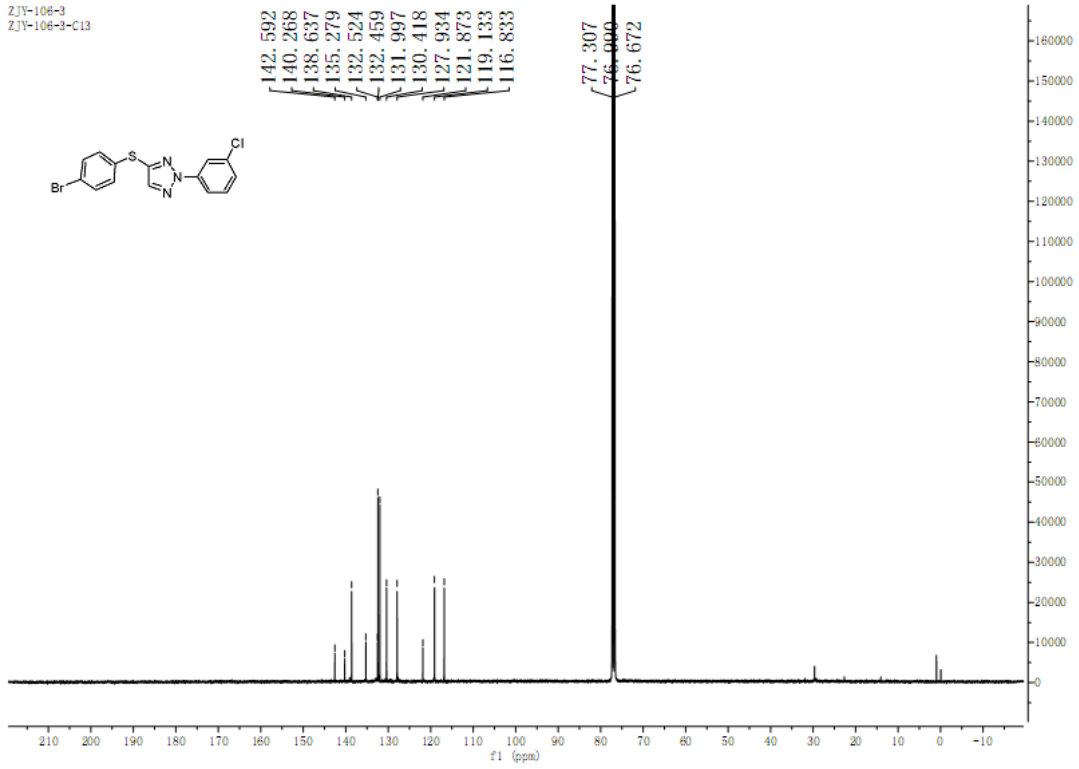
^{1}H and ^{13}C NMR Spectra for **6ag**



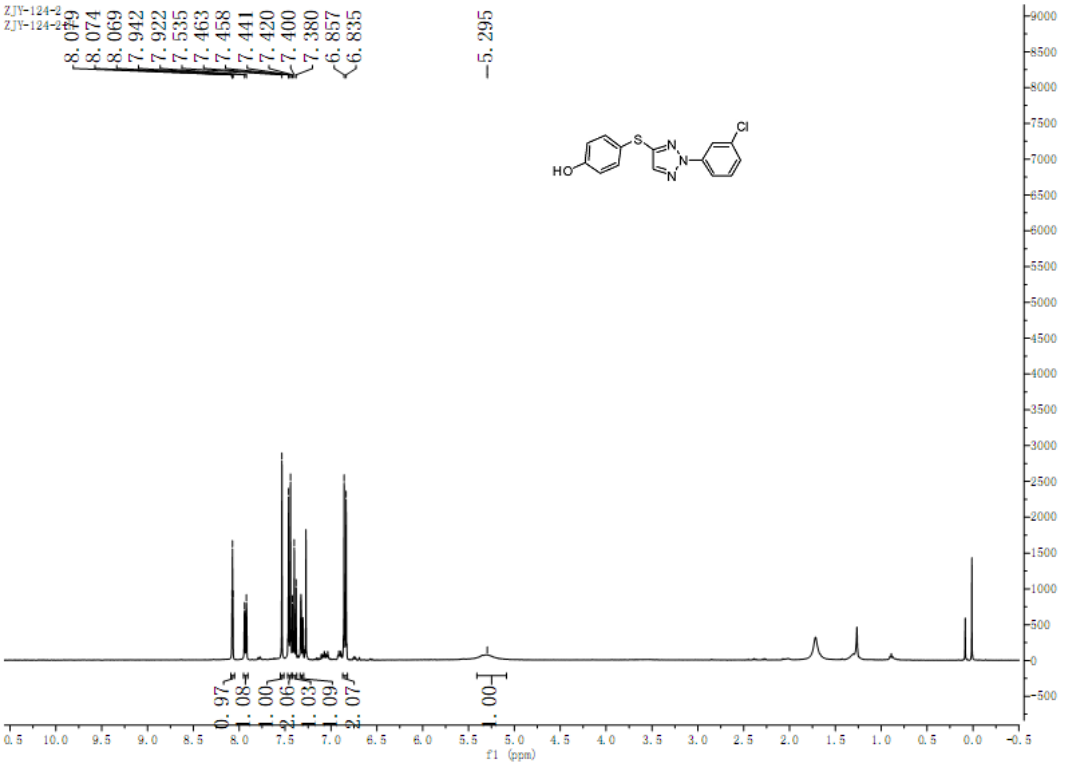


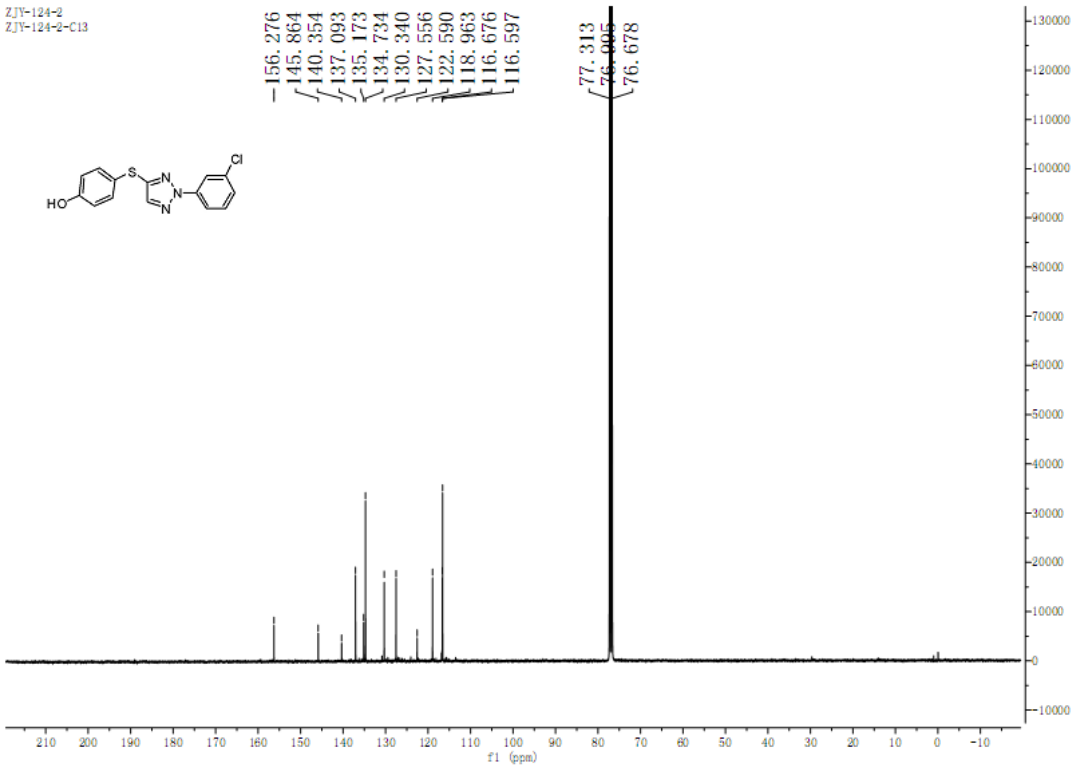
^{1}H and ^{13}C NMR Spectra for **6ah**



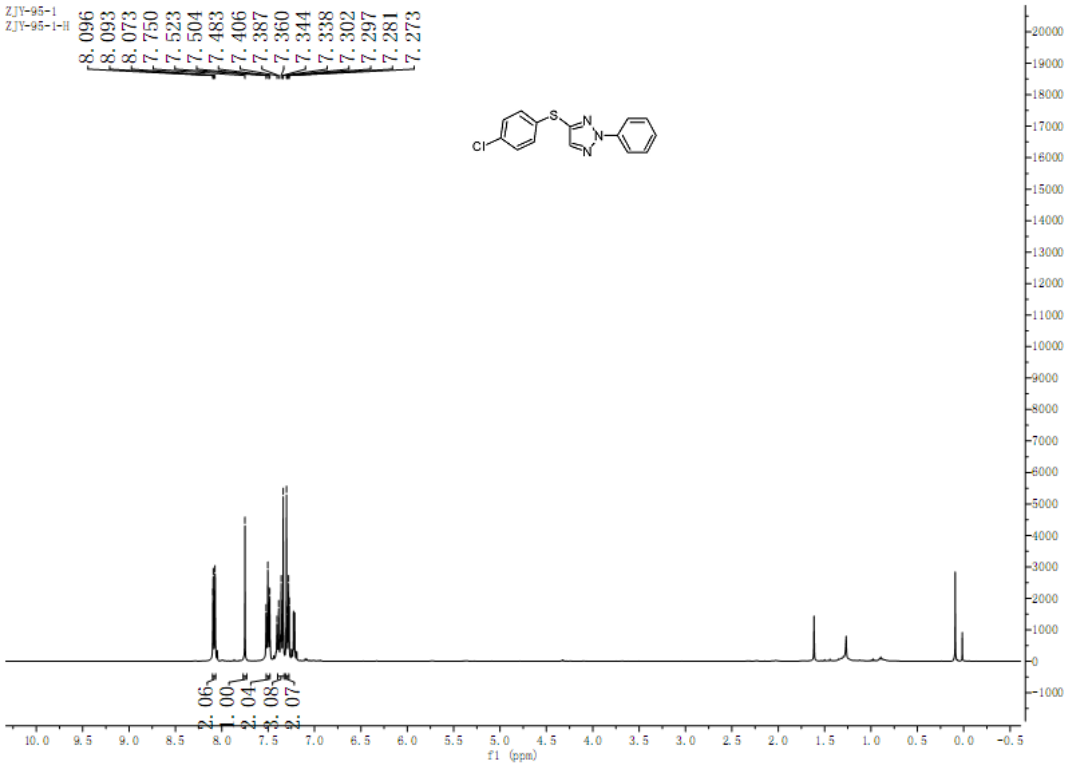


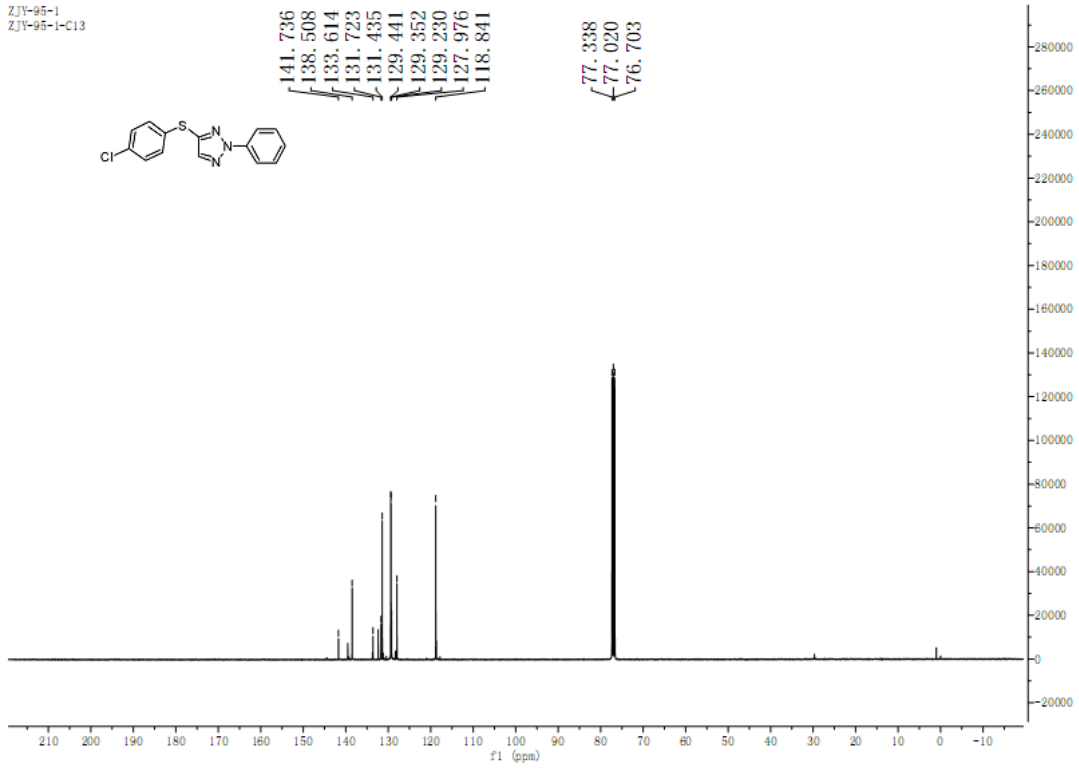
^{1}H and ^{13}C NMR Spectra for **6ai**



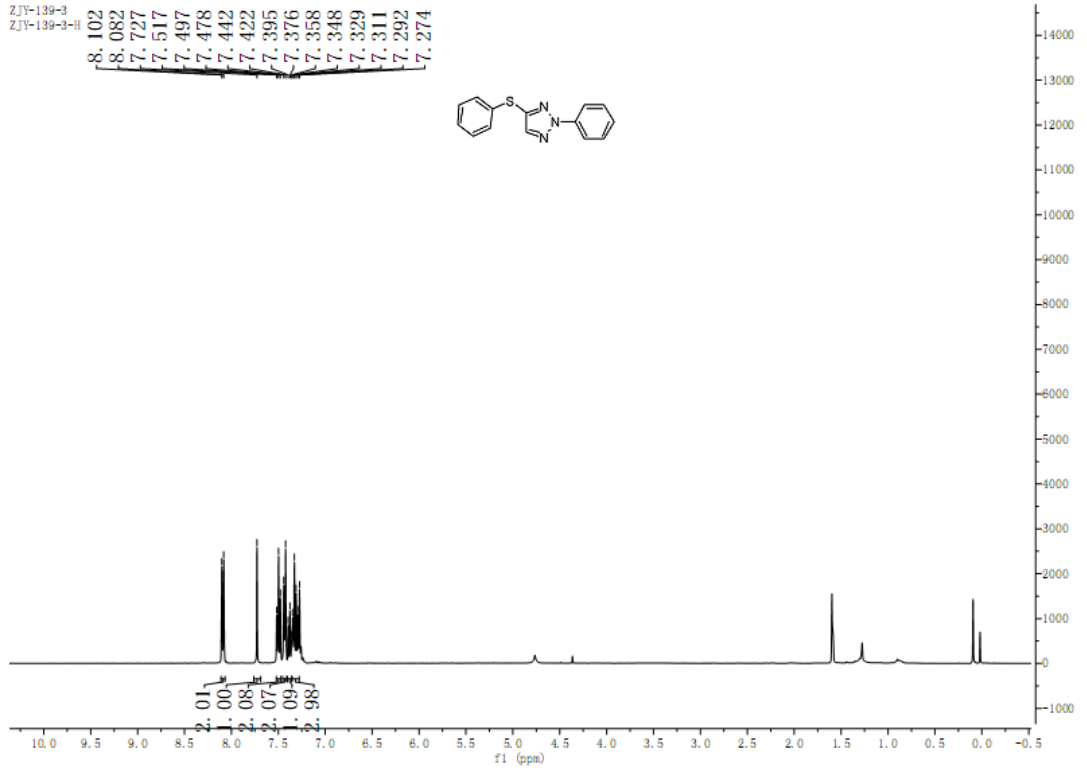


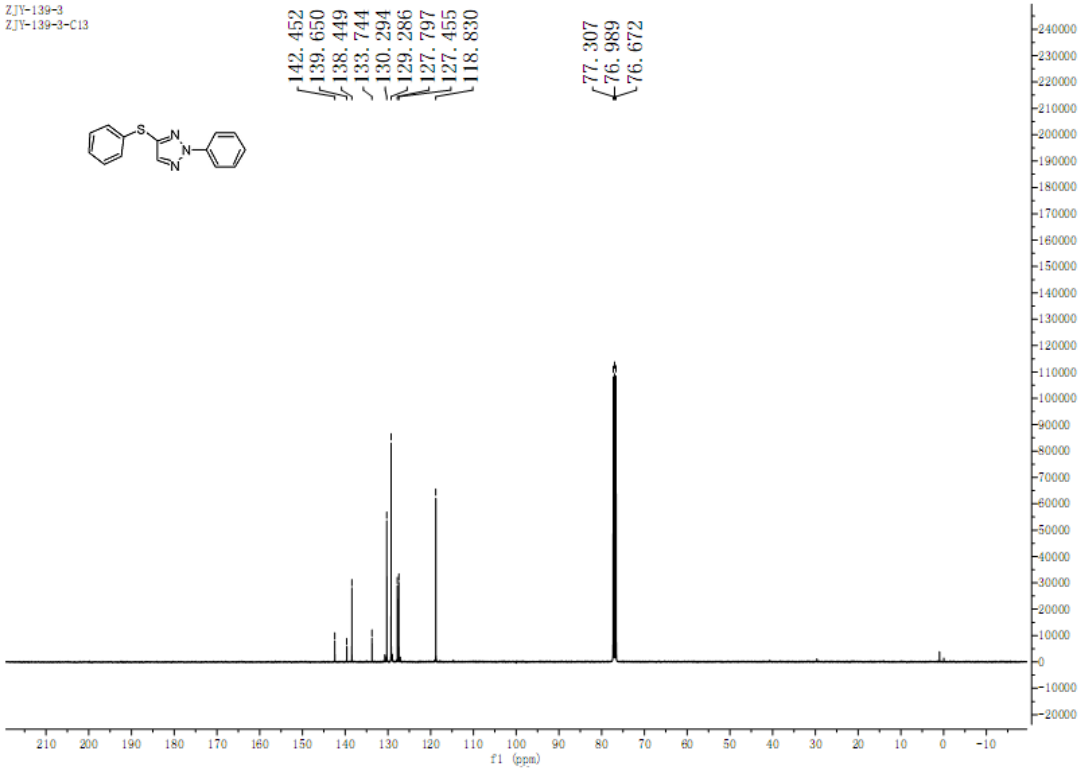
^{1}H and ^{13}C NMR Spectra for **6bg**



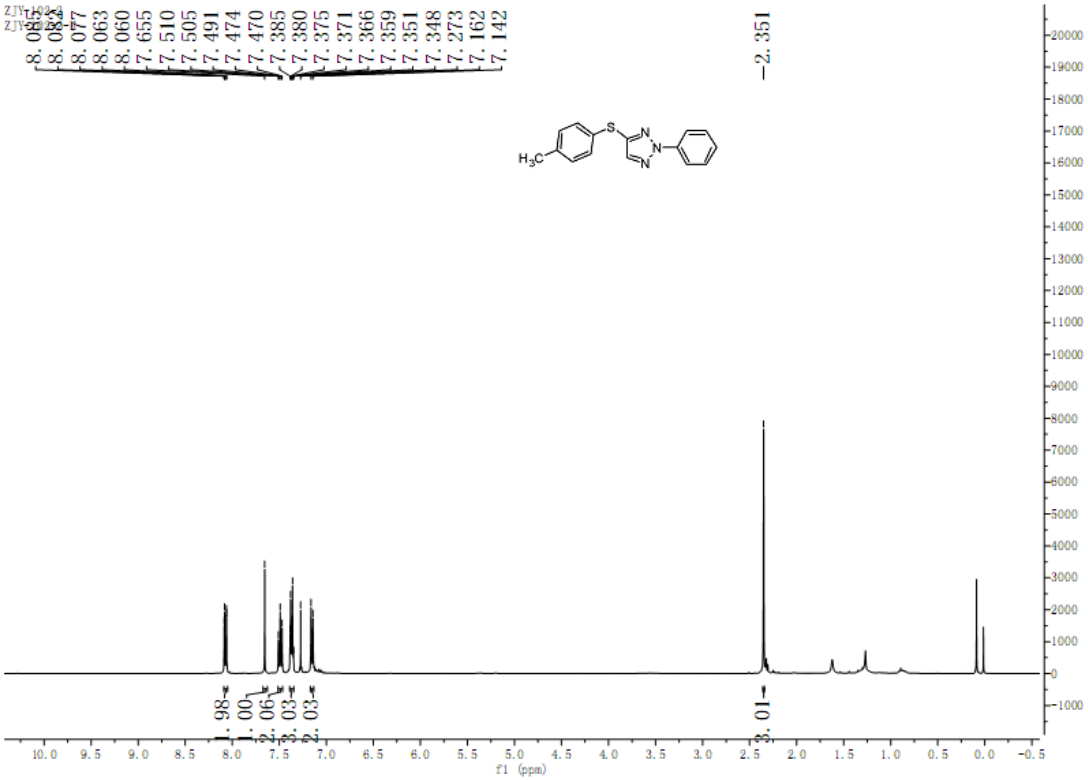


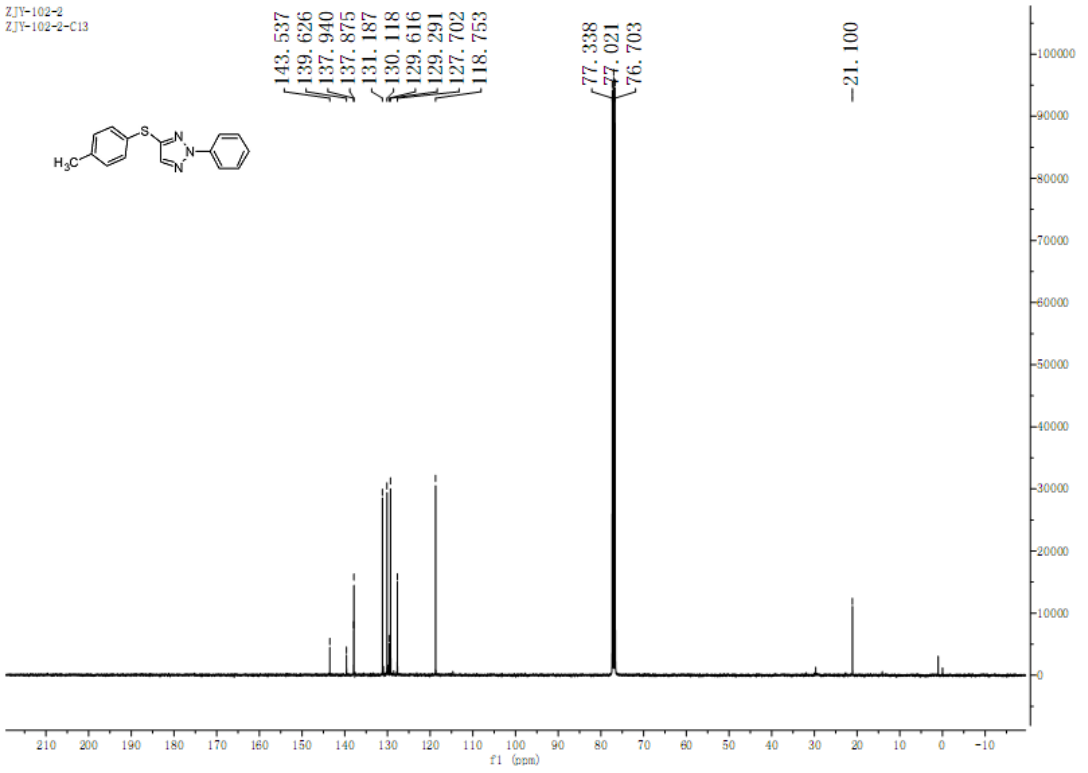
^{1}H and ^{13}C NMR Spectra for **6be**



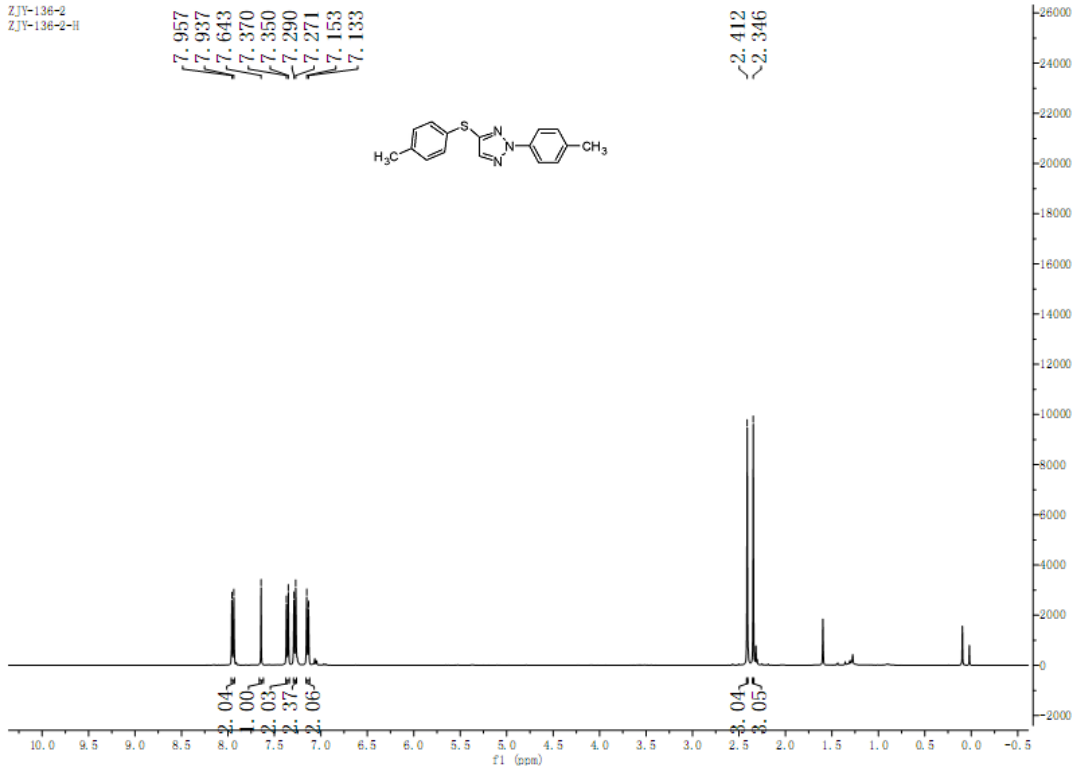


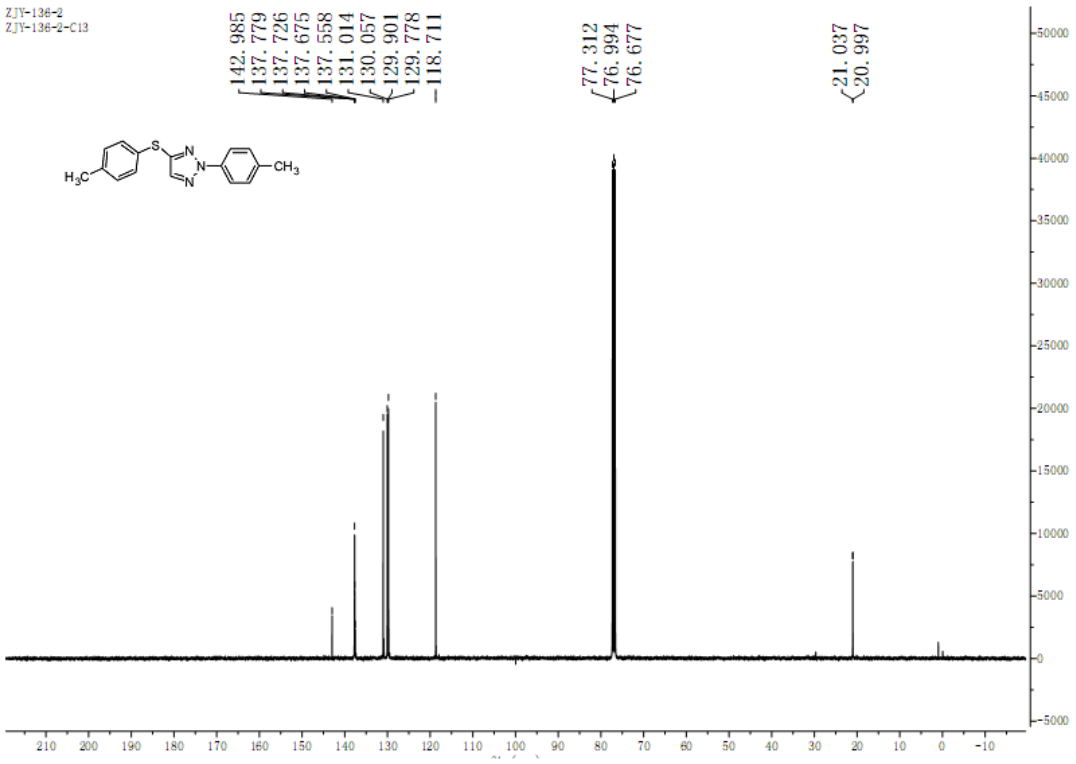
^{1}H and ^{13}C NMR Spectra for **6ba**



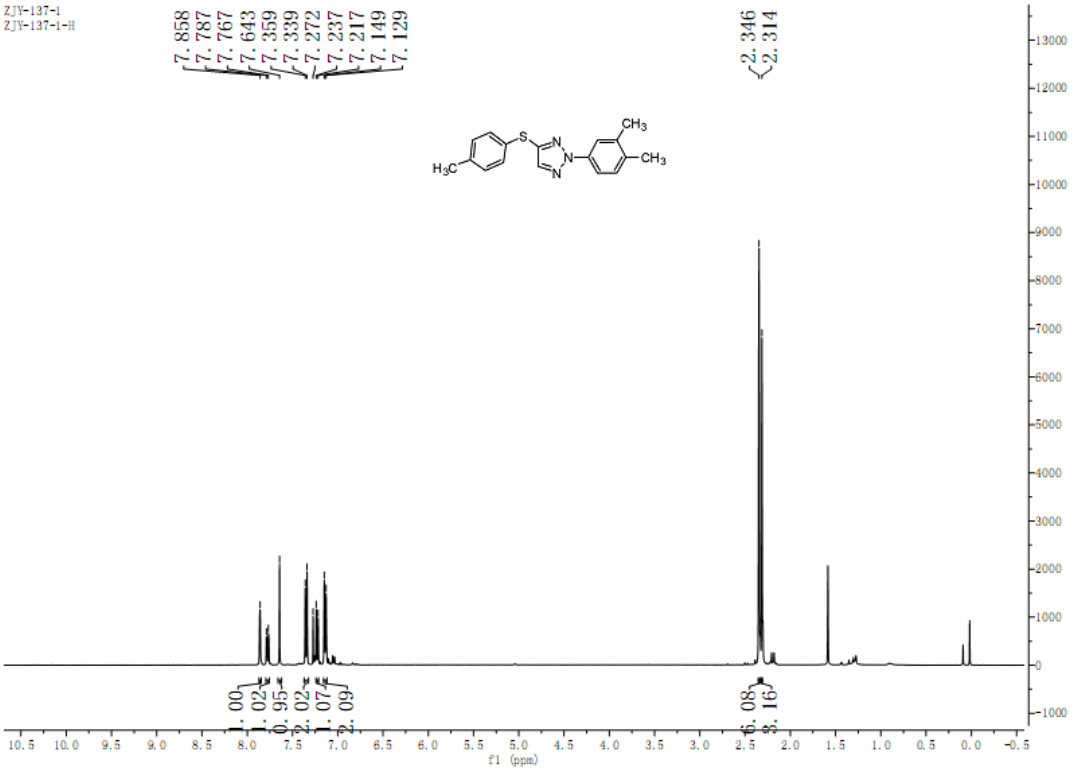


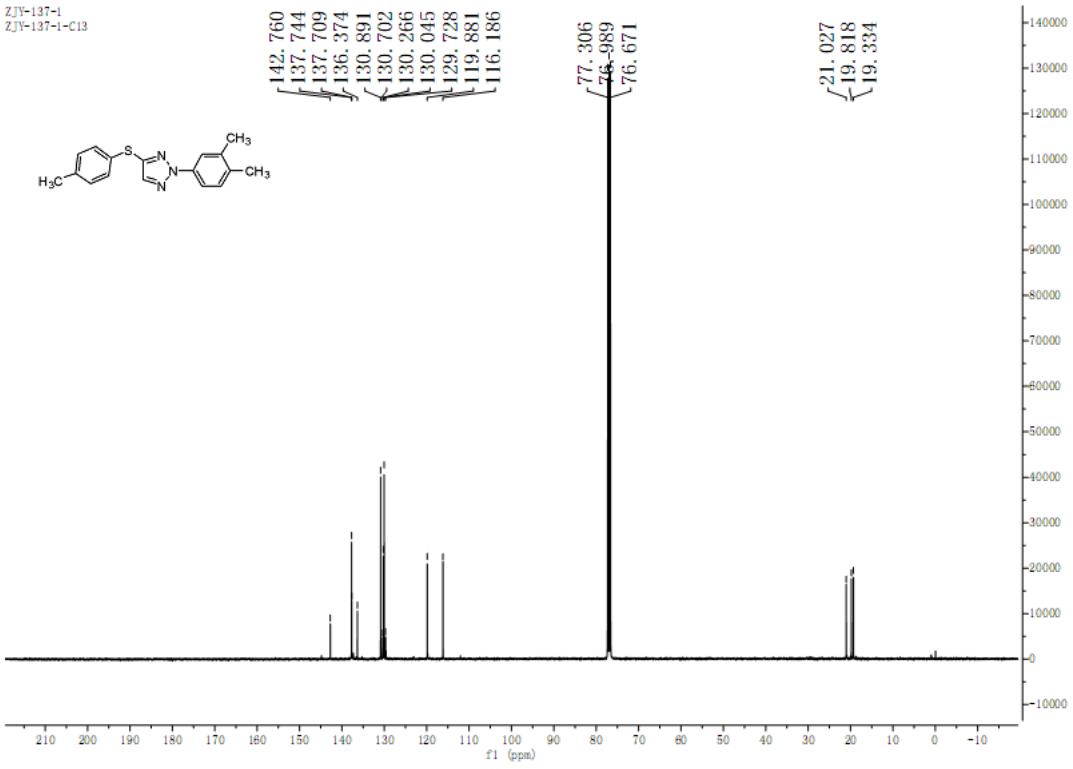
^{1}H and ^{13}C NMR Spectra for **6ca**



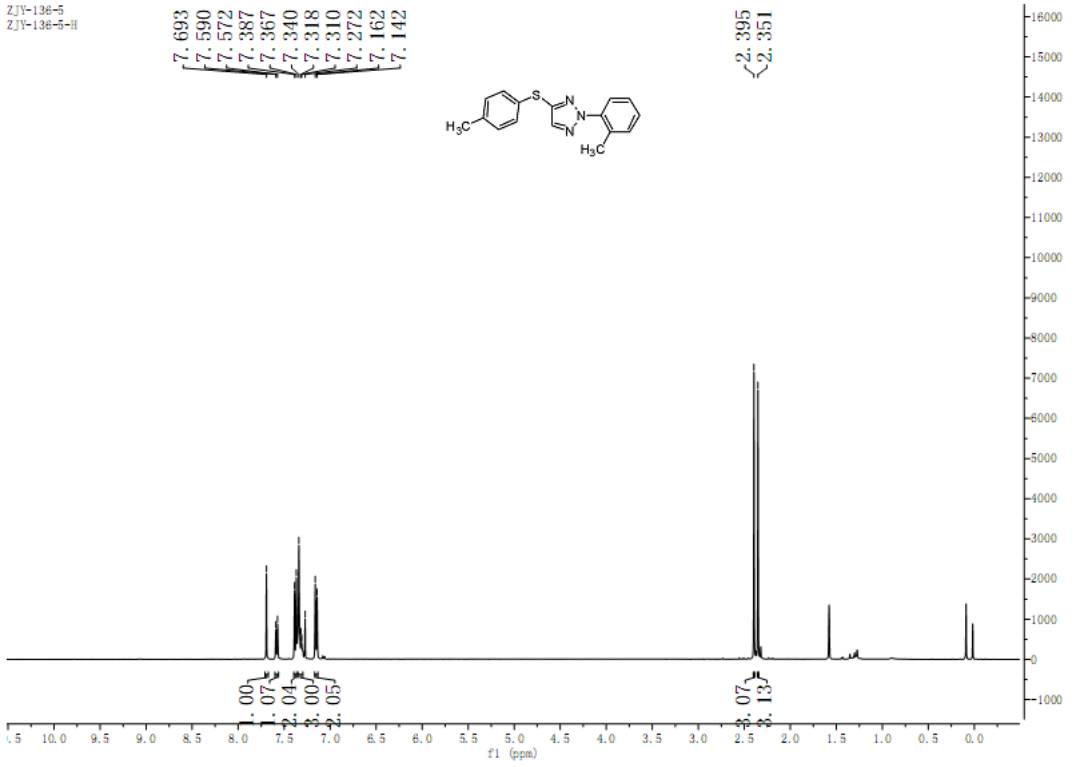


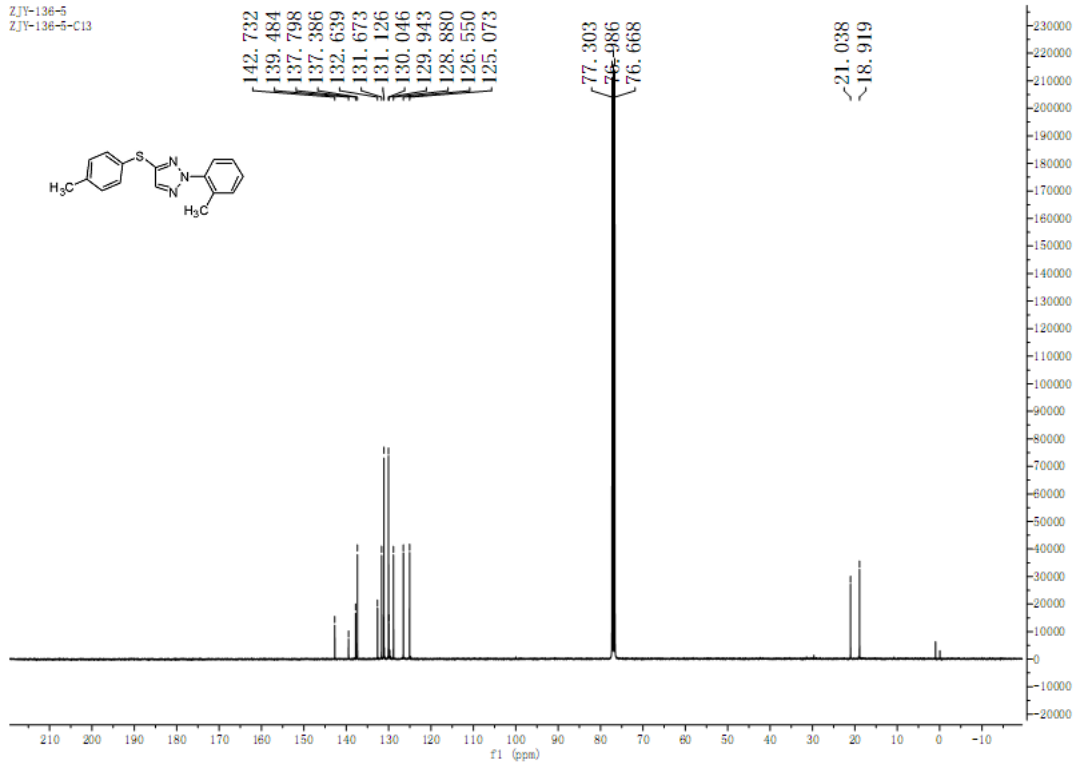
^{1}H and ^{13}C NMR Spectra for **6da**



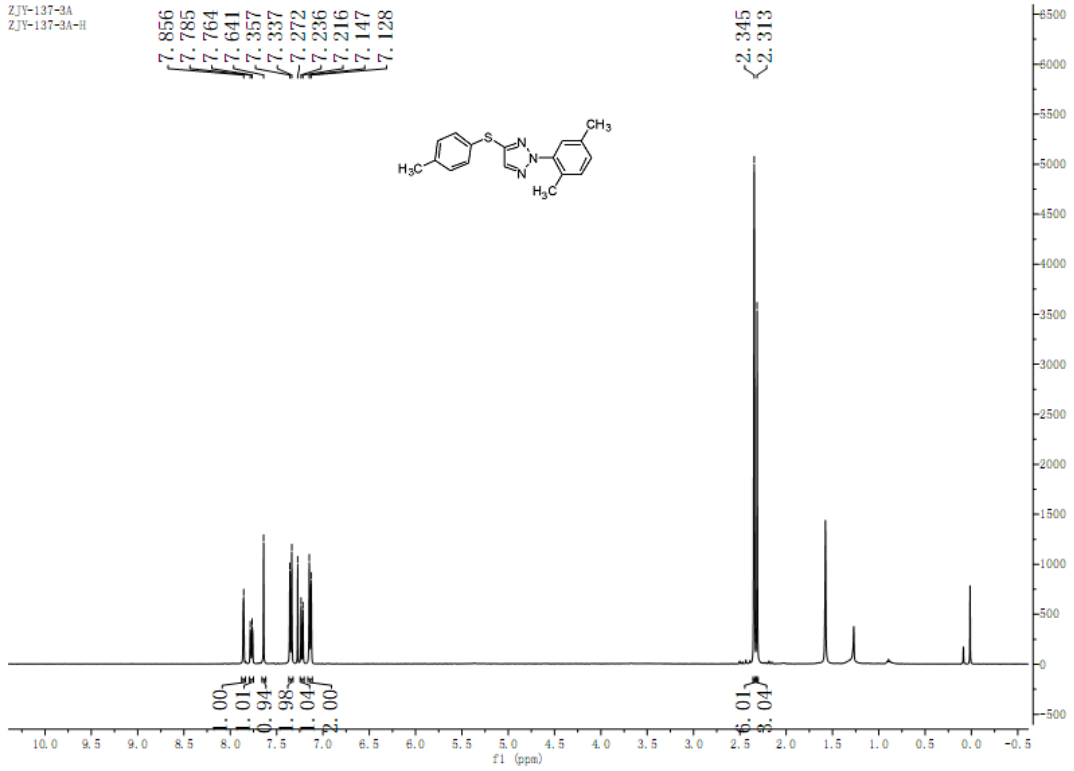


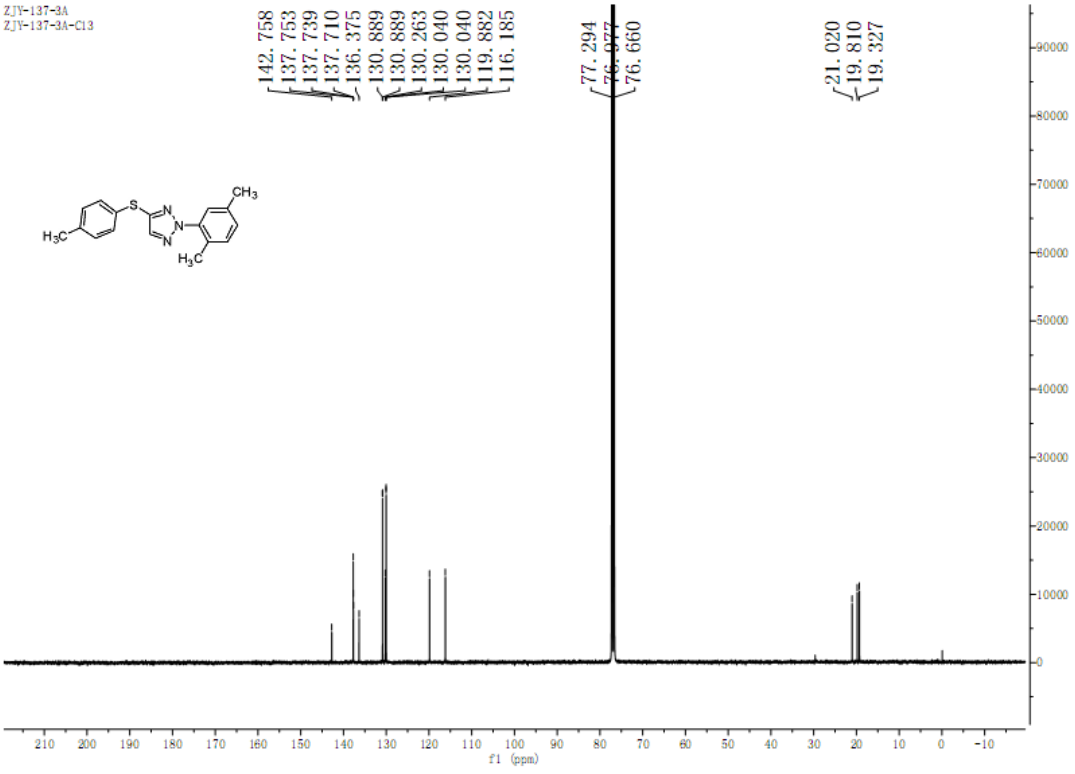
^{1}H and ^{13}C NMR Spectra for **6ea**



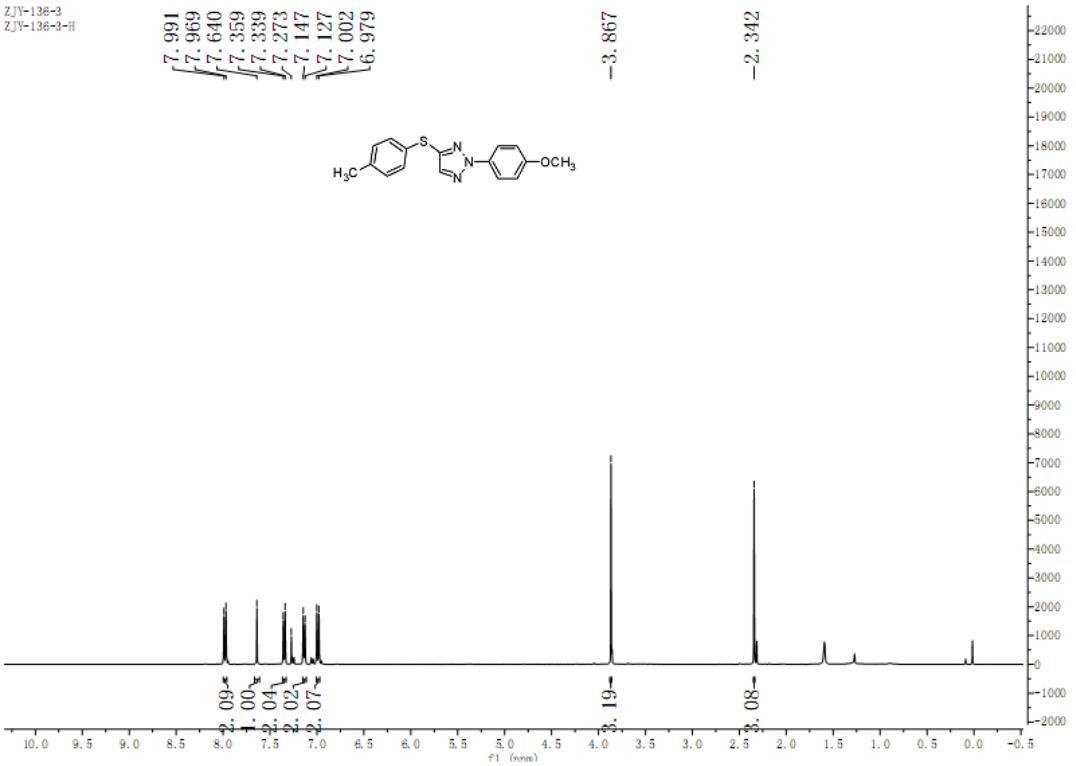


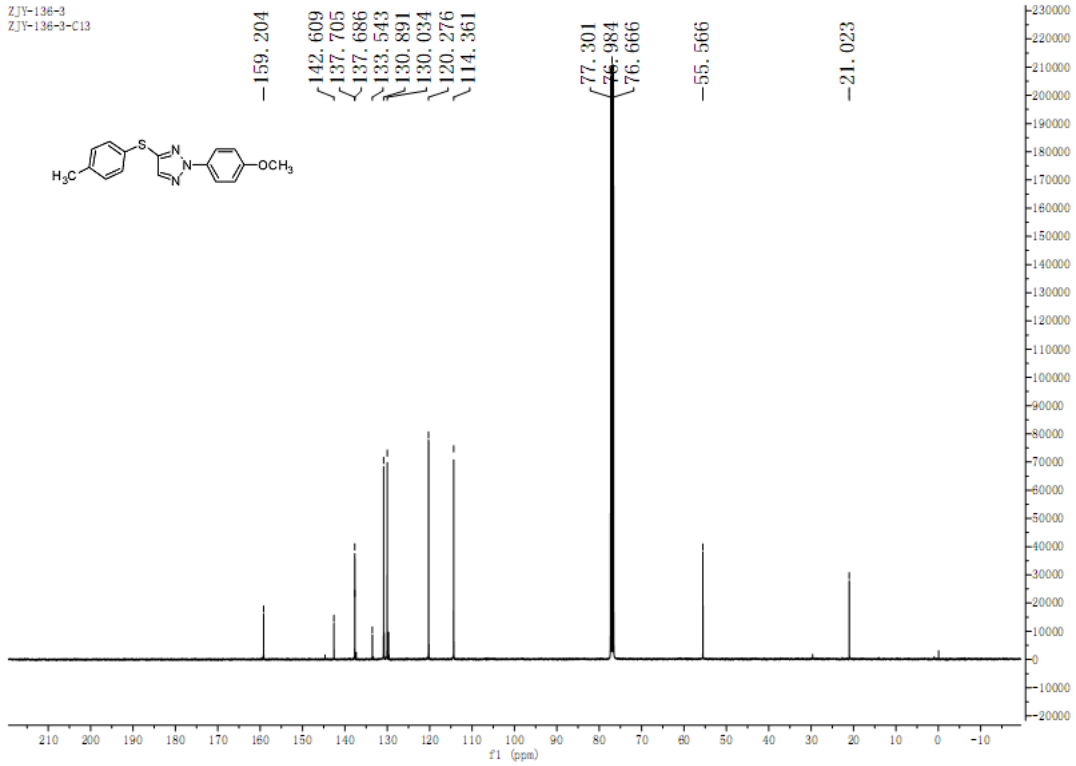
^{1}H and ^{13}C NMR Spectra for **6fa**



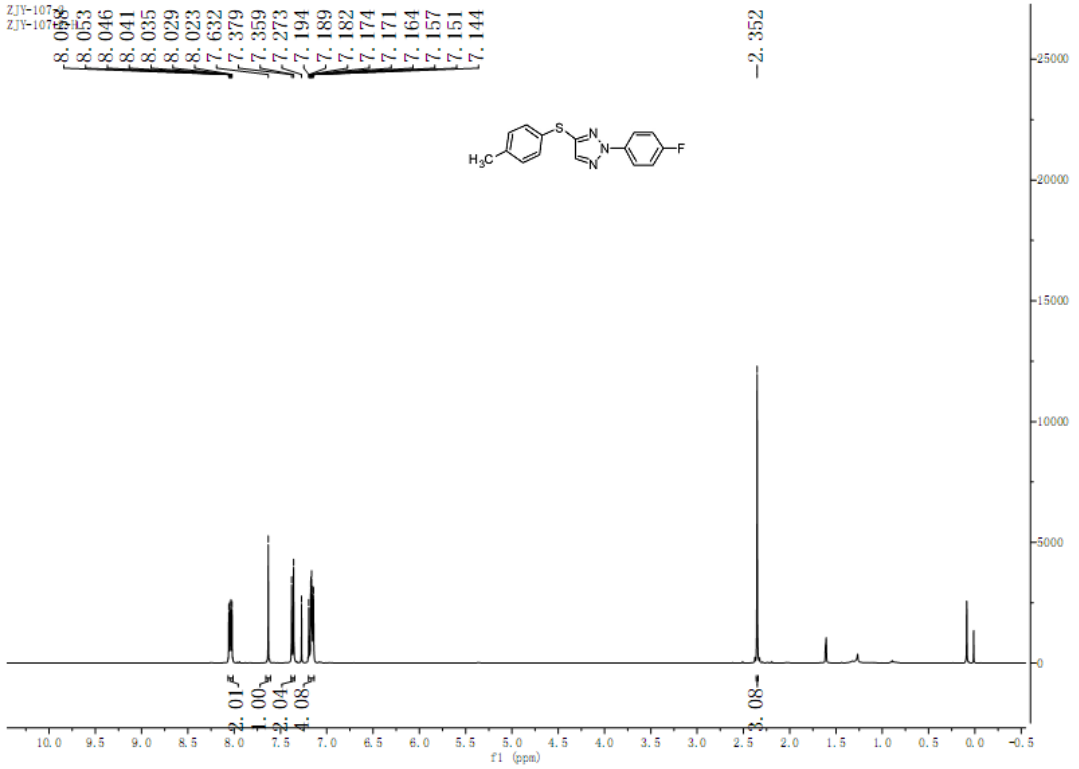


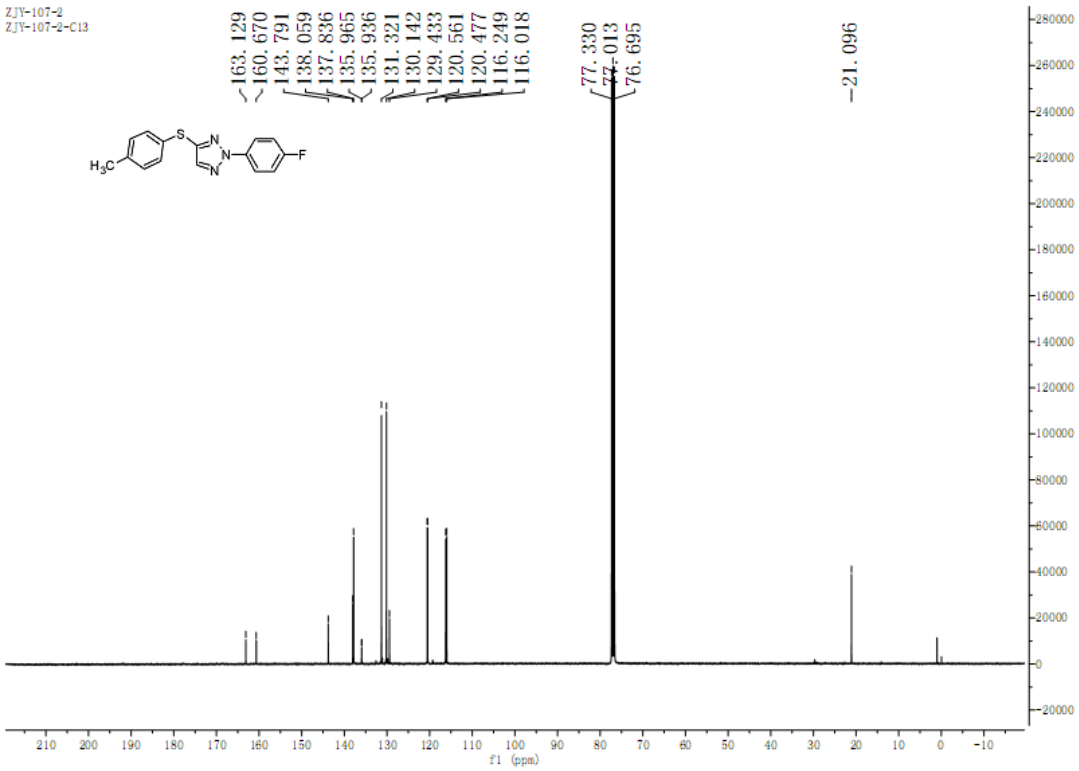
^{1}H and ^{13}C NMR Spectra for **6ga**



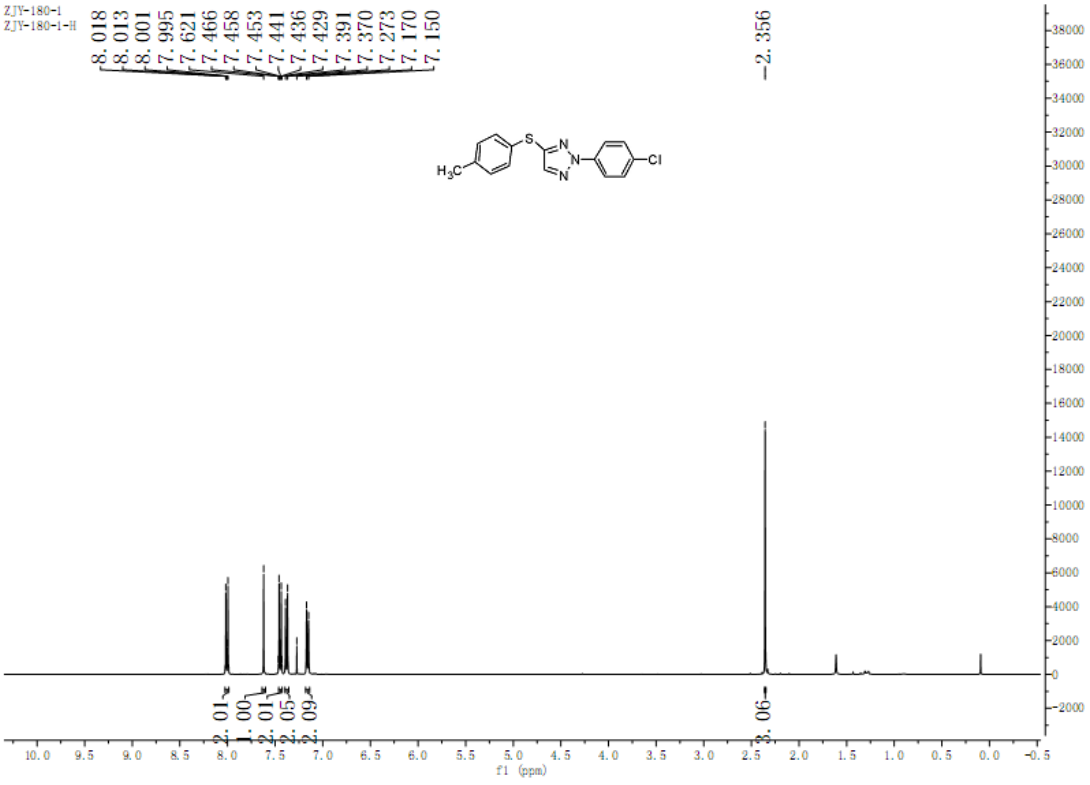


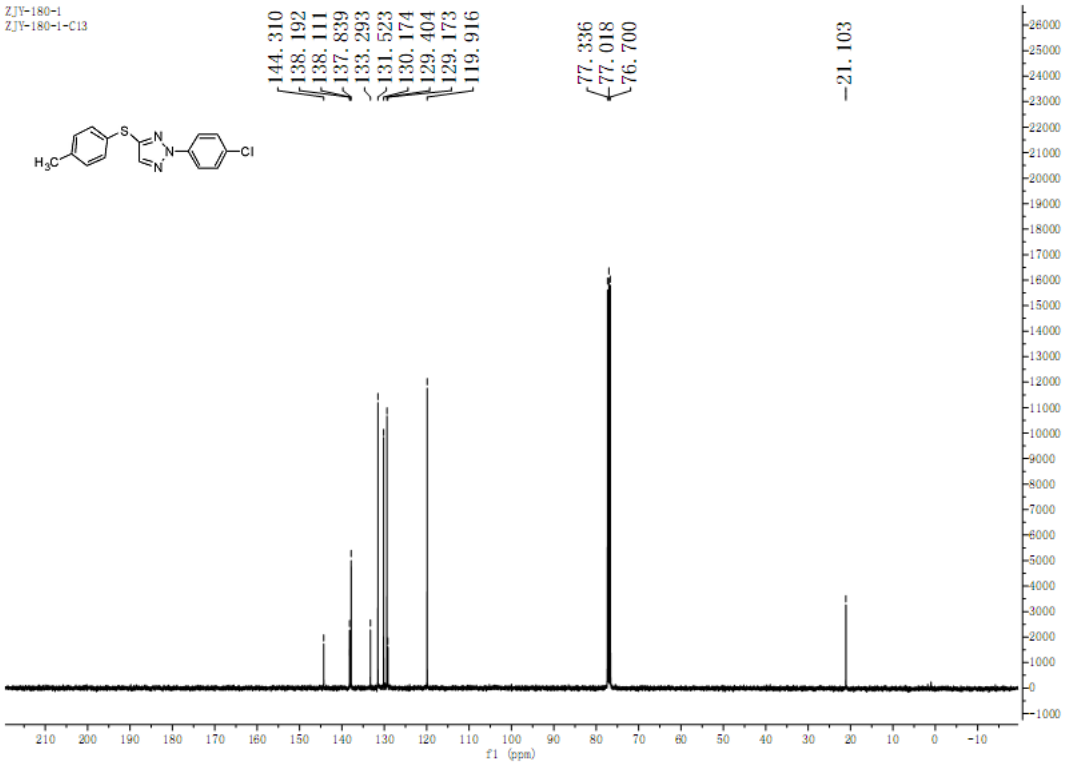
^{1}H and ^{13}C NMR Spectra for **6ha**



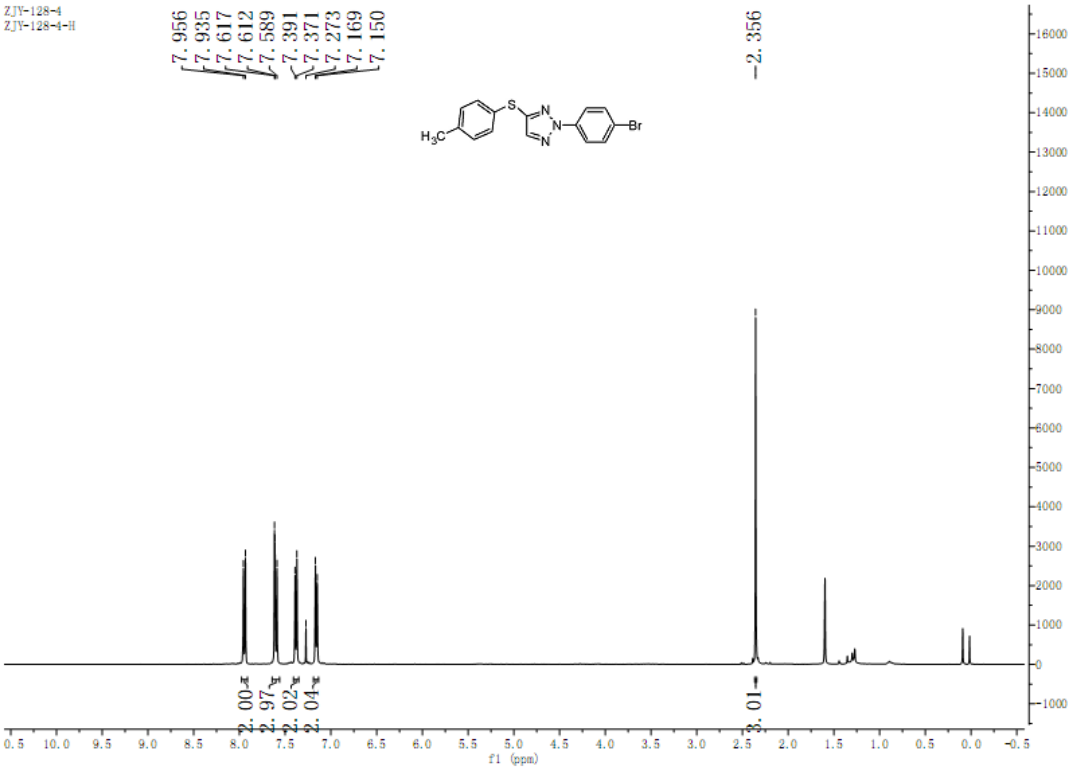


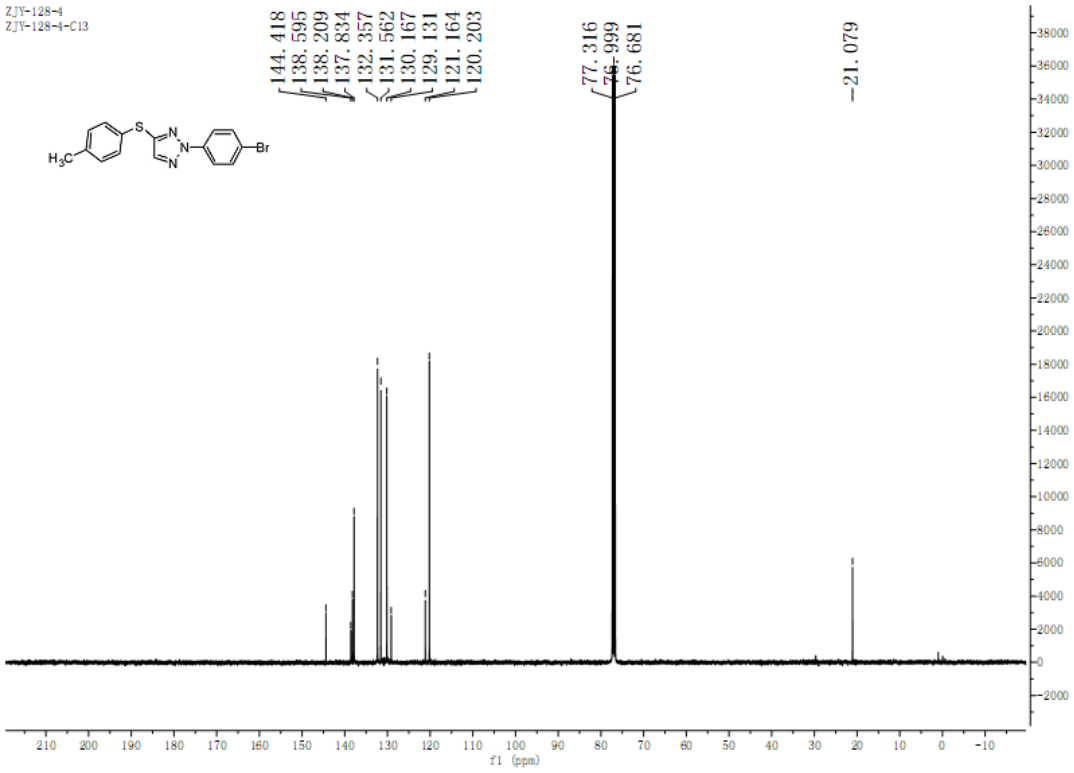
^{1}H and ^{13}C NMR Spectra for **6ia**



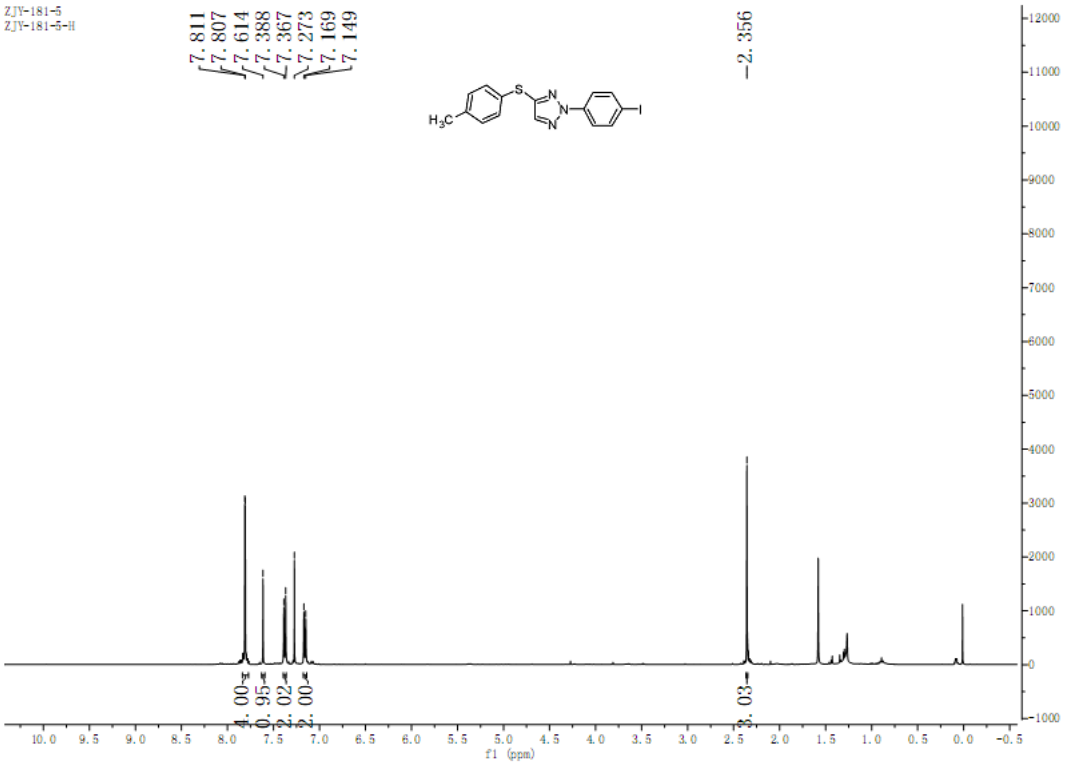


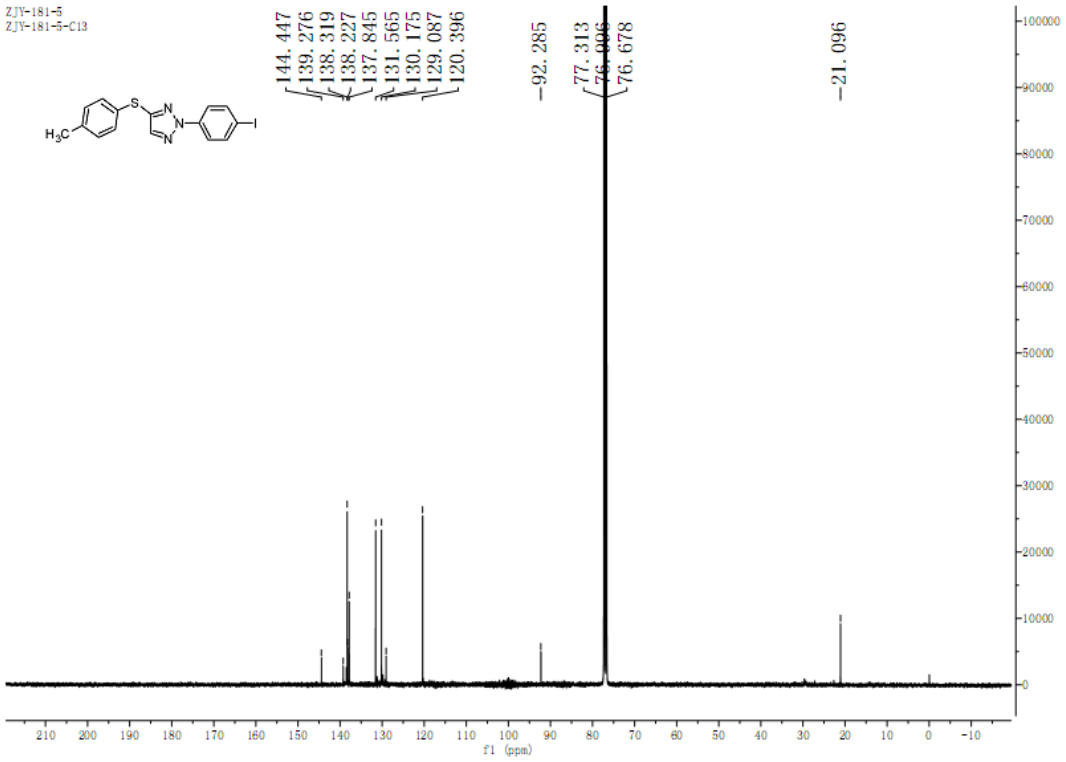
^{1}H and ^{13}C NMR Spectra for **6ja**



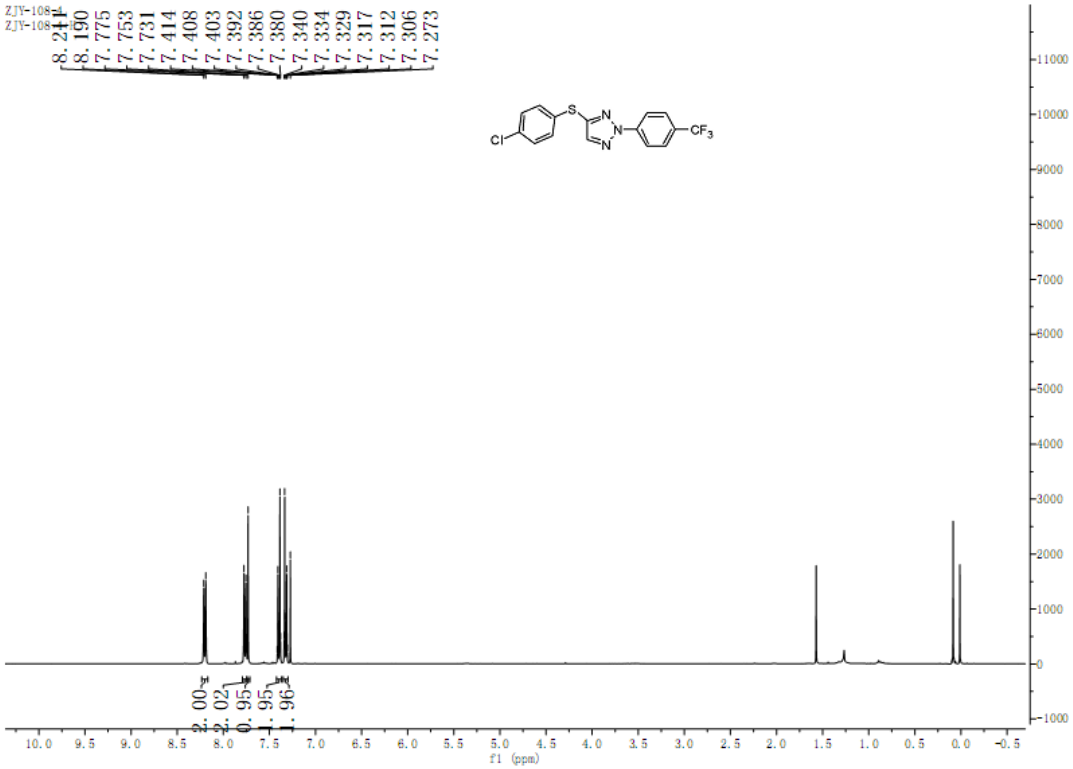


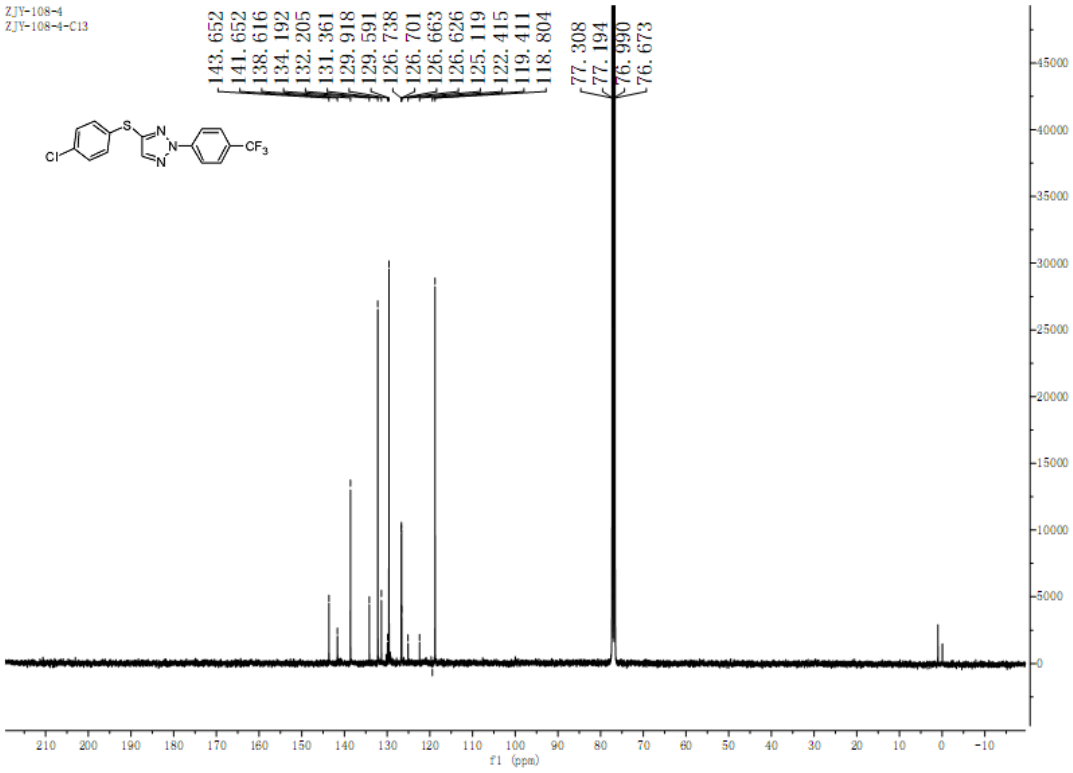
^{1}H and ^{13}C NMR Spectra for **6ka**



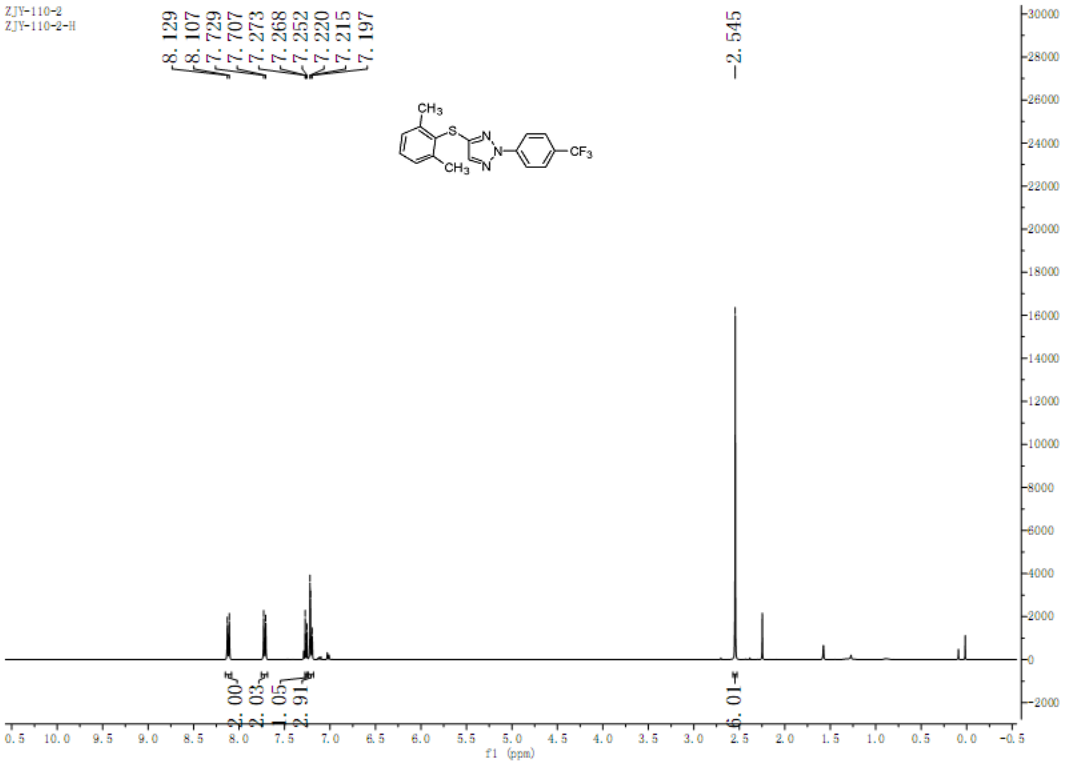


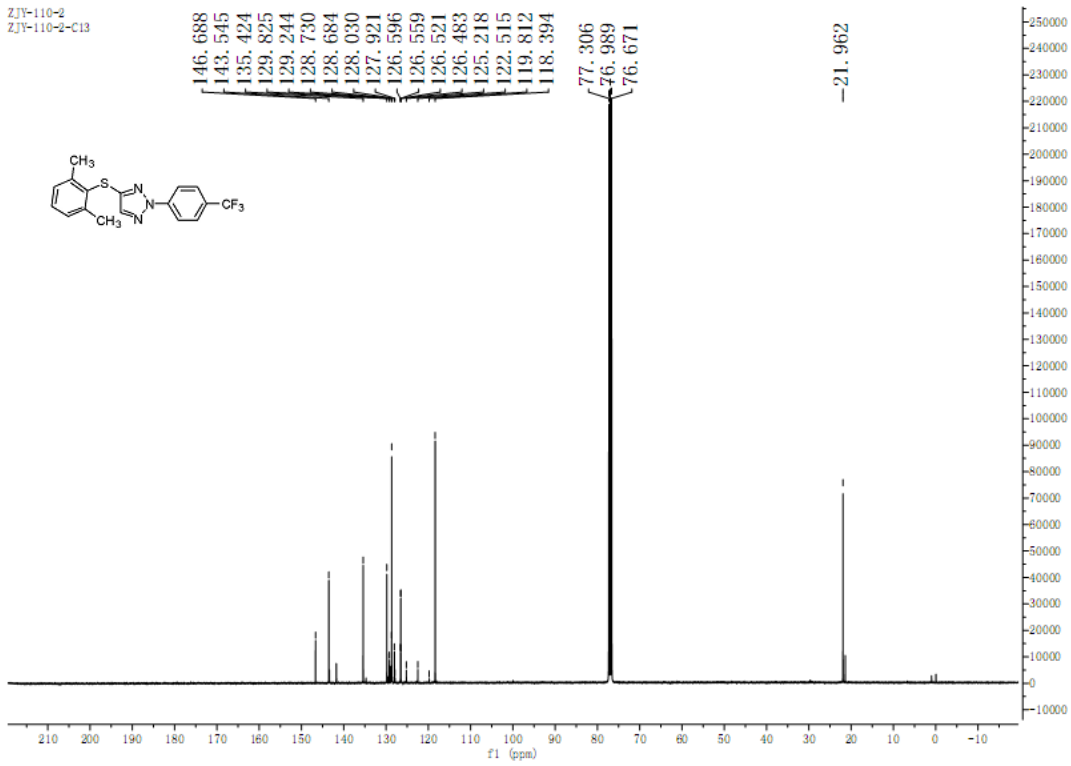
^{1}H and ^{13}C NMR Spectra for **6lg**



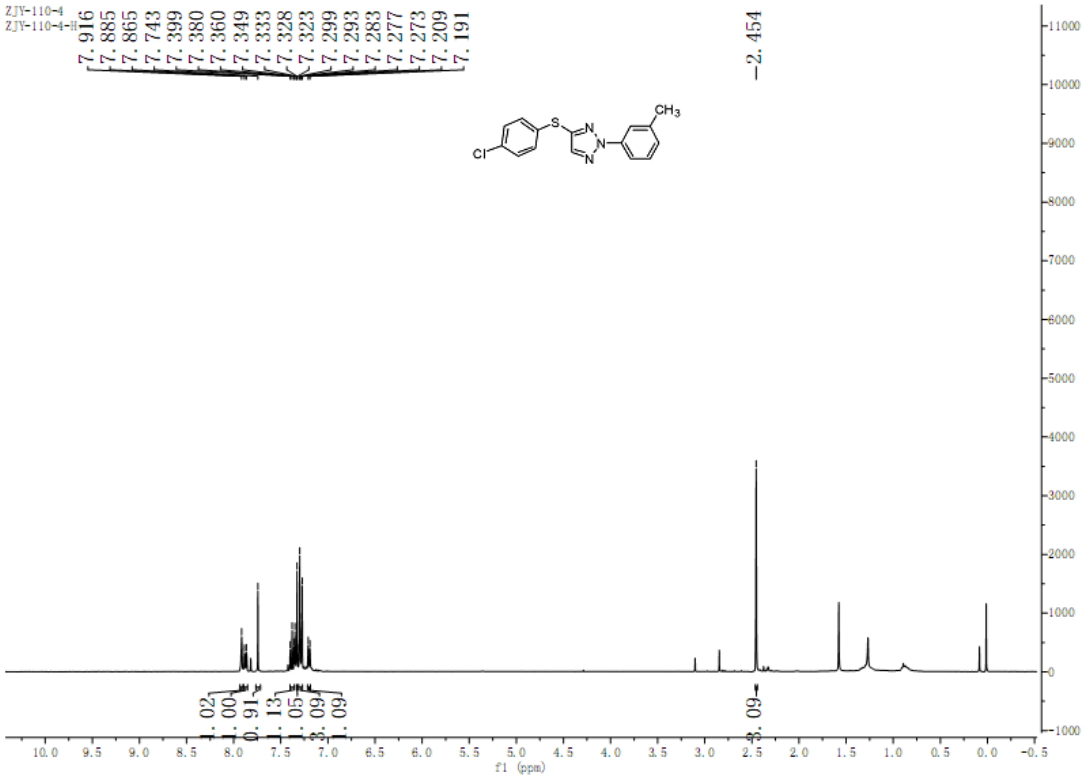


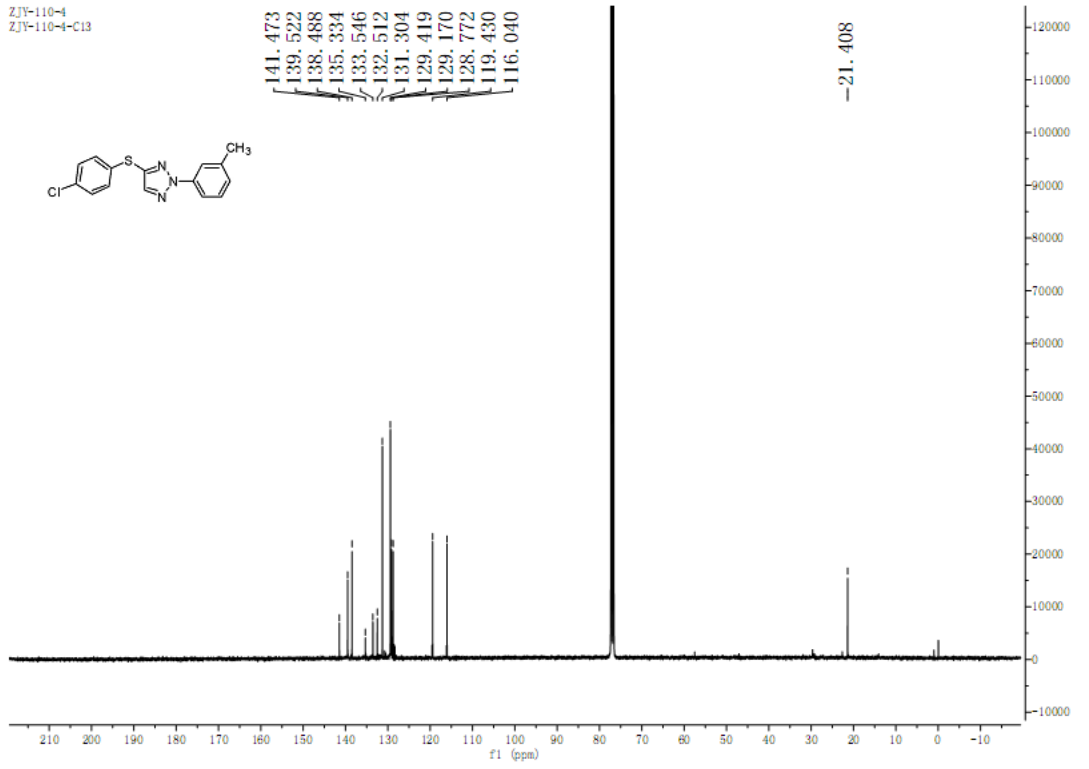
^{1}H and ^{13}C NMR Spectra for **6lc**



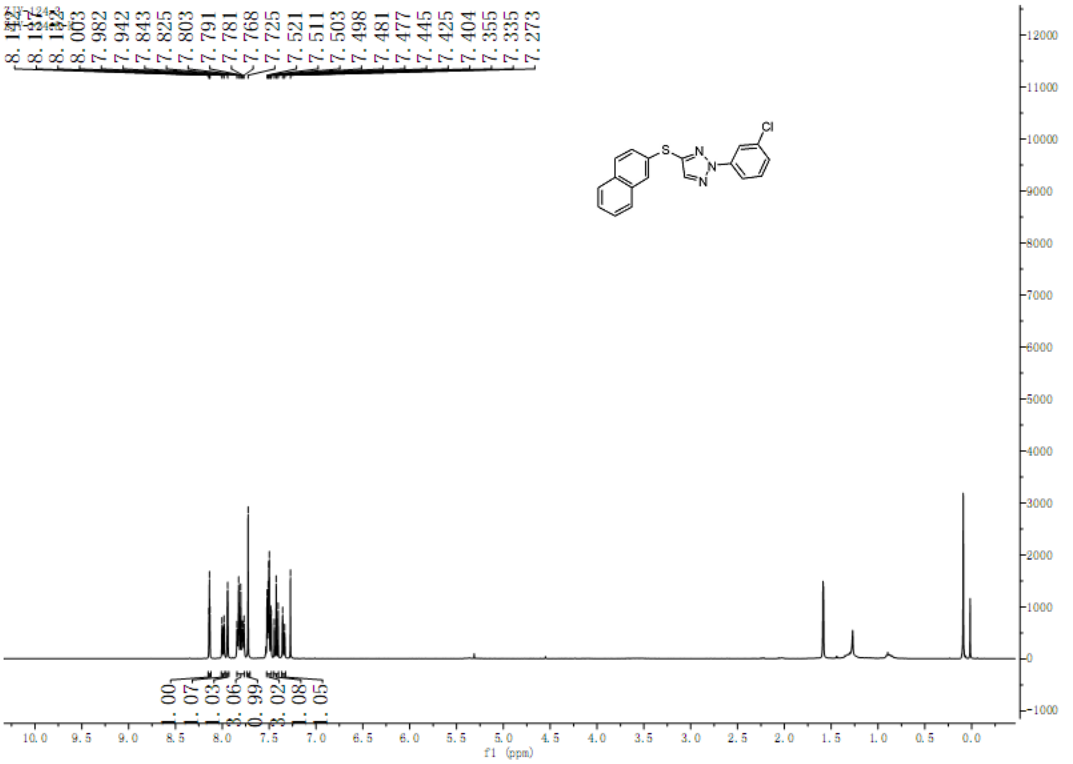


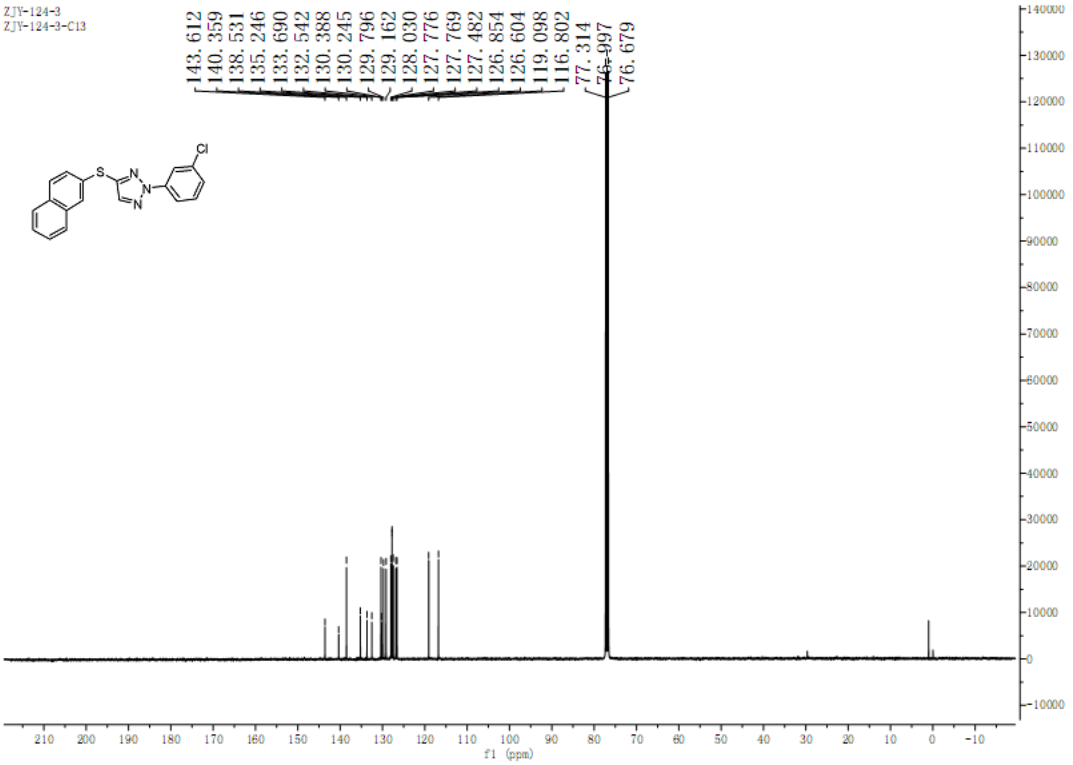
^{1}H and ^{13}C NMR Spectra for **6mg**



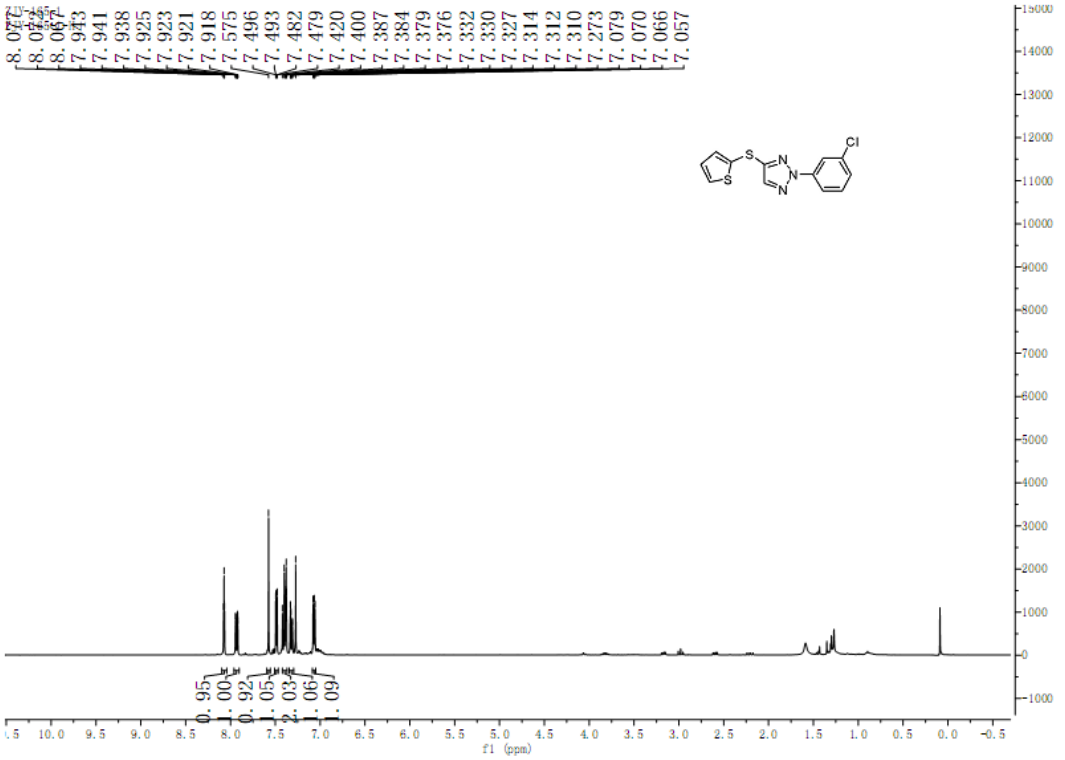


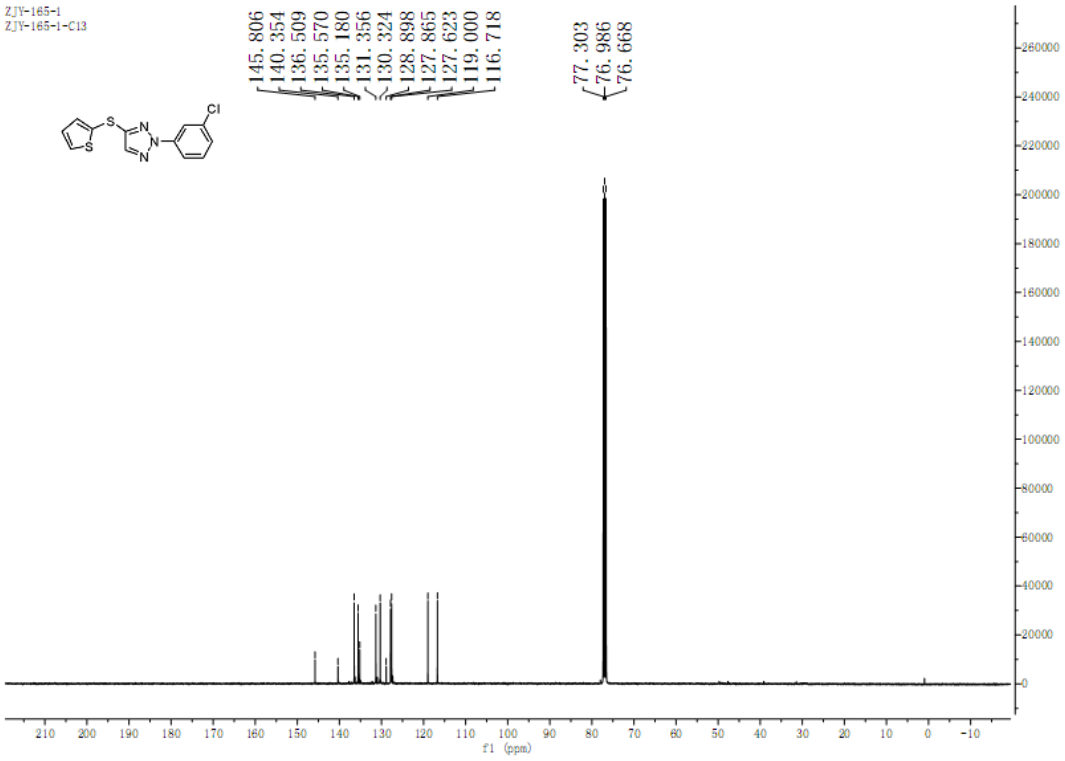
^{1}H and ^{13}C NMR Spectra for **6aj**



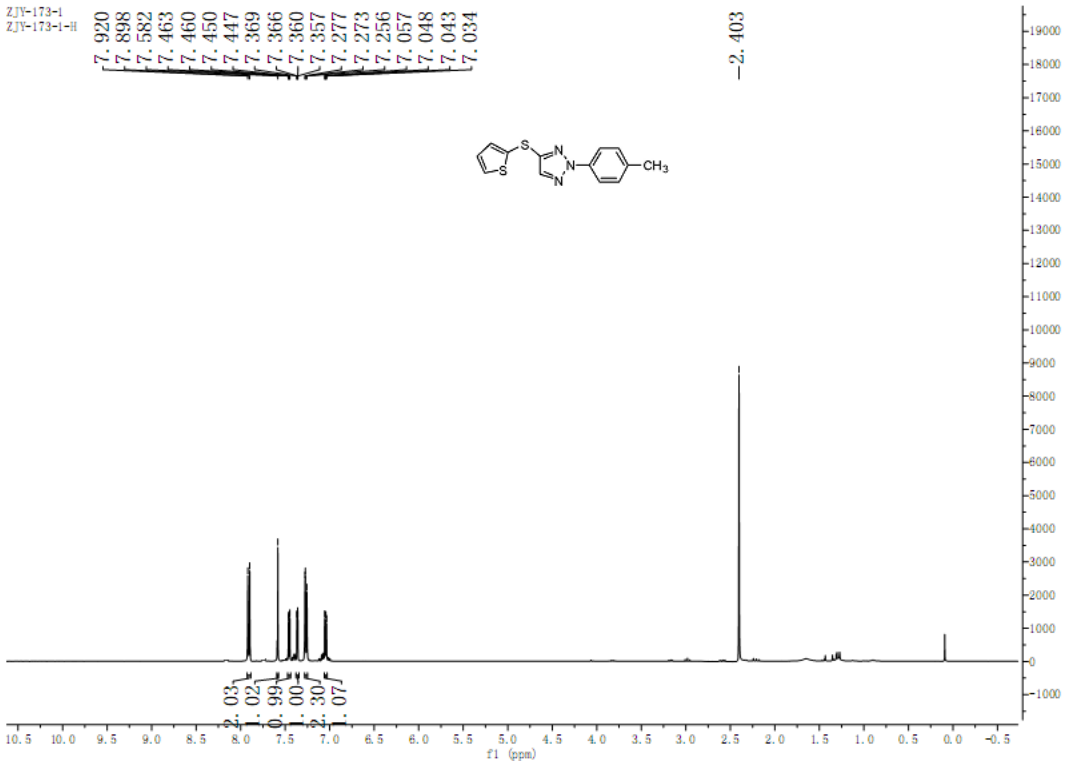


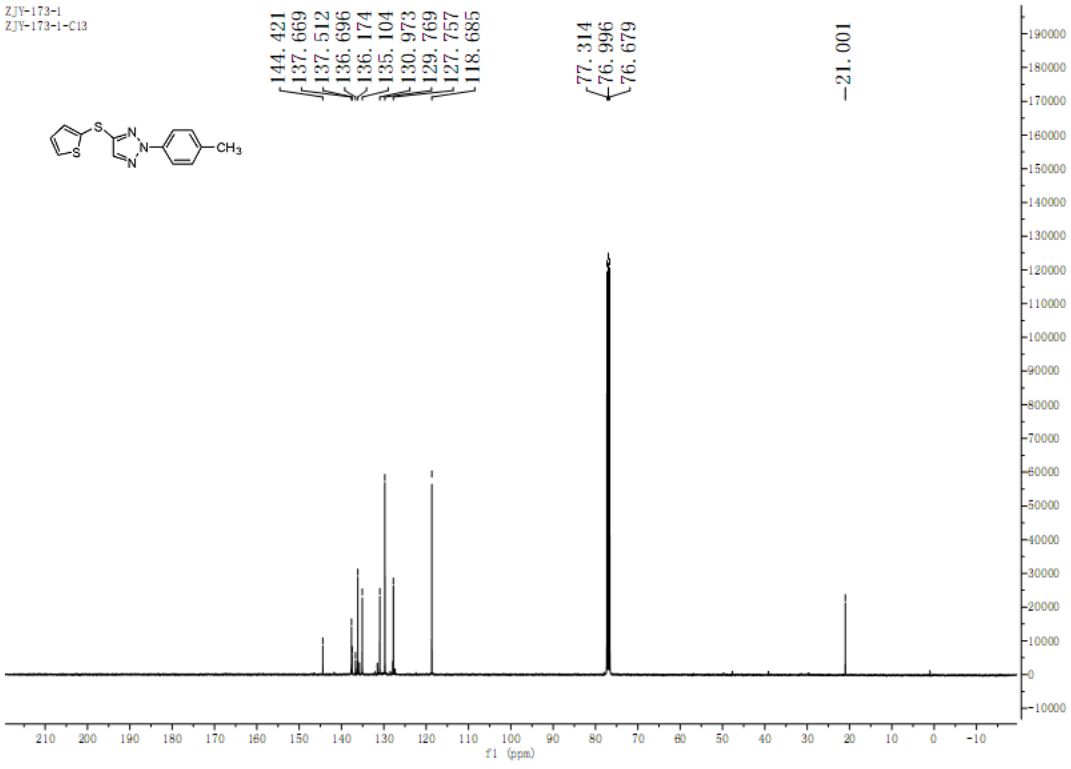
^{1}H and ^{13}C NMR Spectra for **6ak**



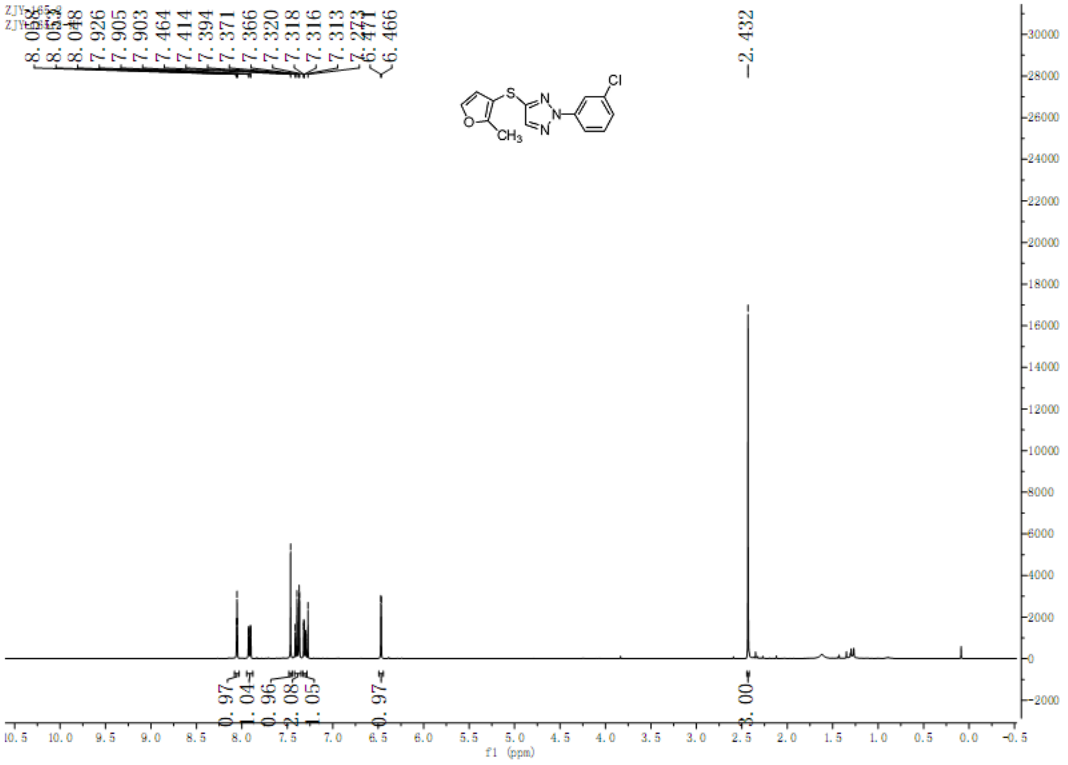


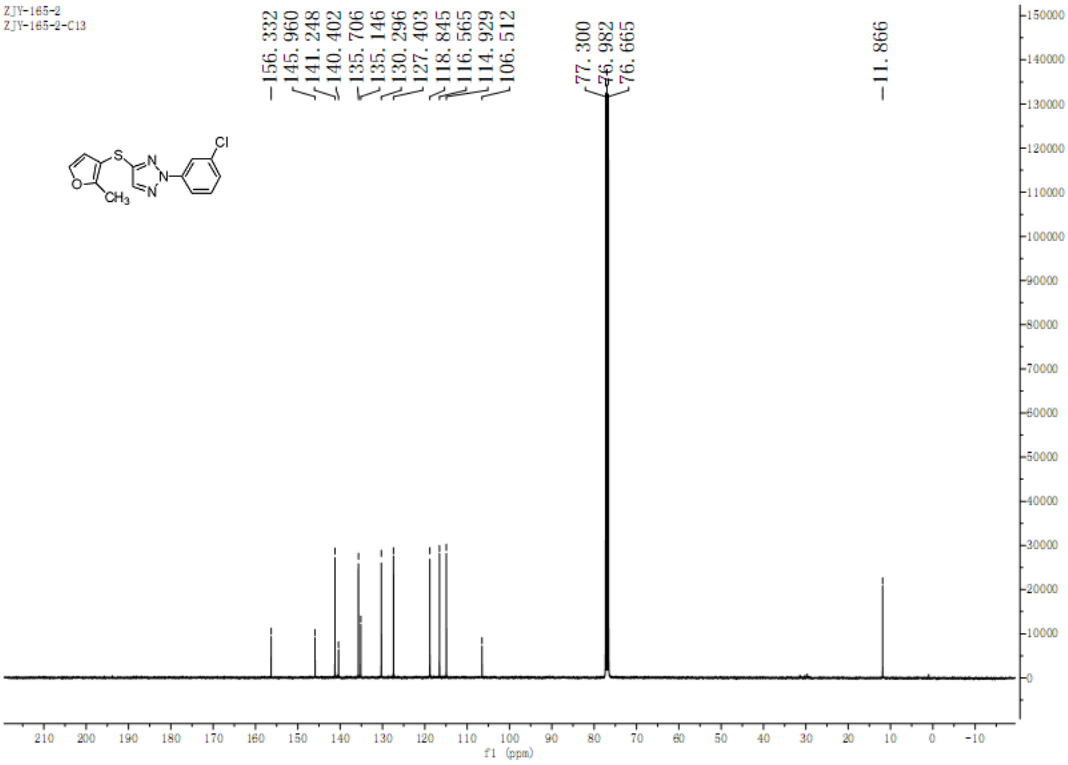
^{1}H and ^{13}C NMR Spectra for **6ck**



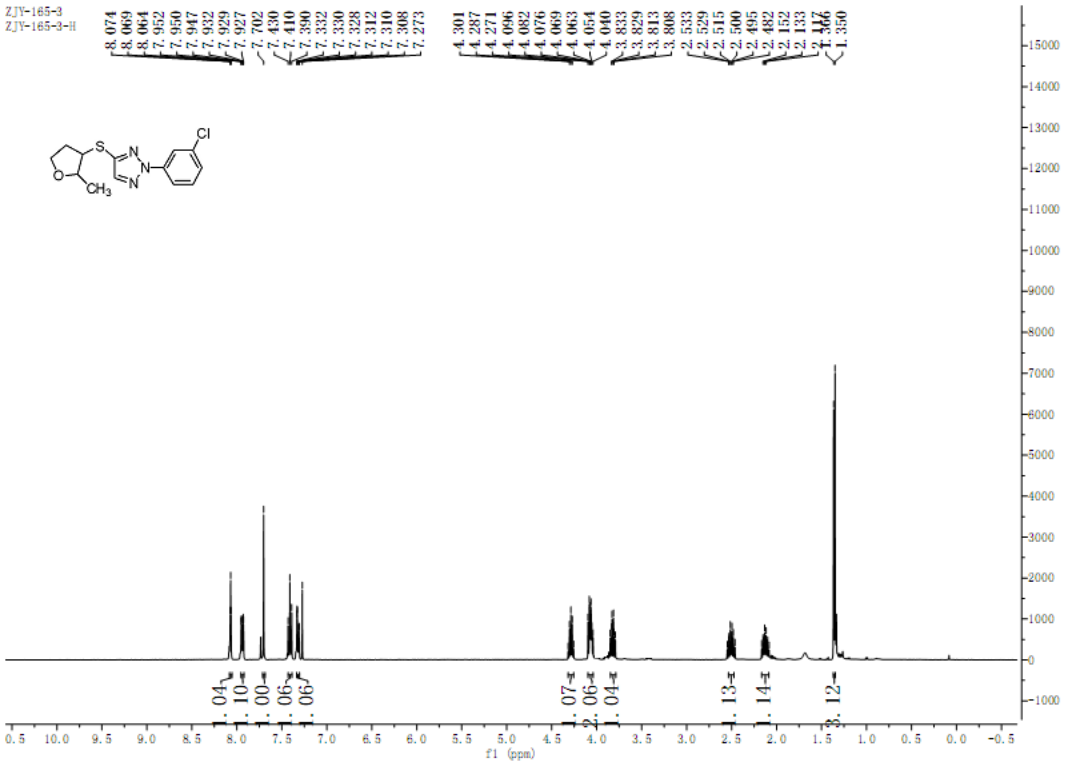


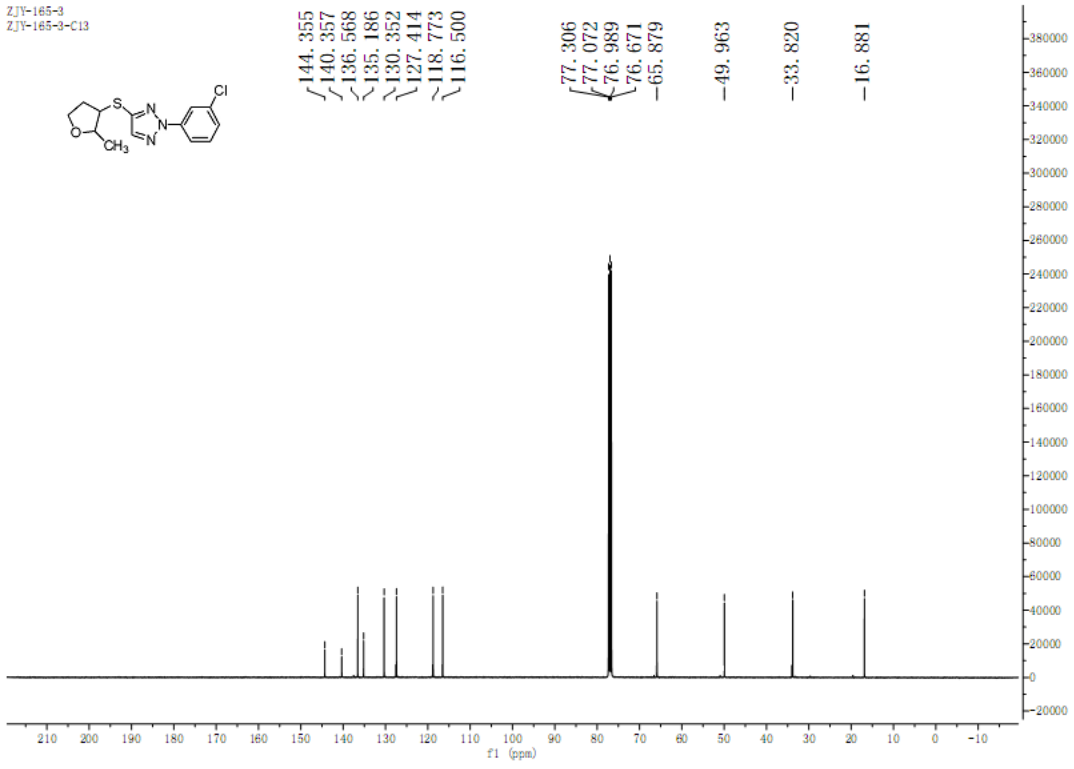
^{1}H and ^{13}C NMR Spectra for **6al**



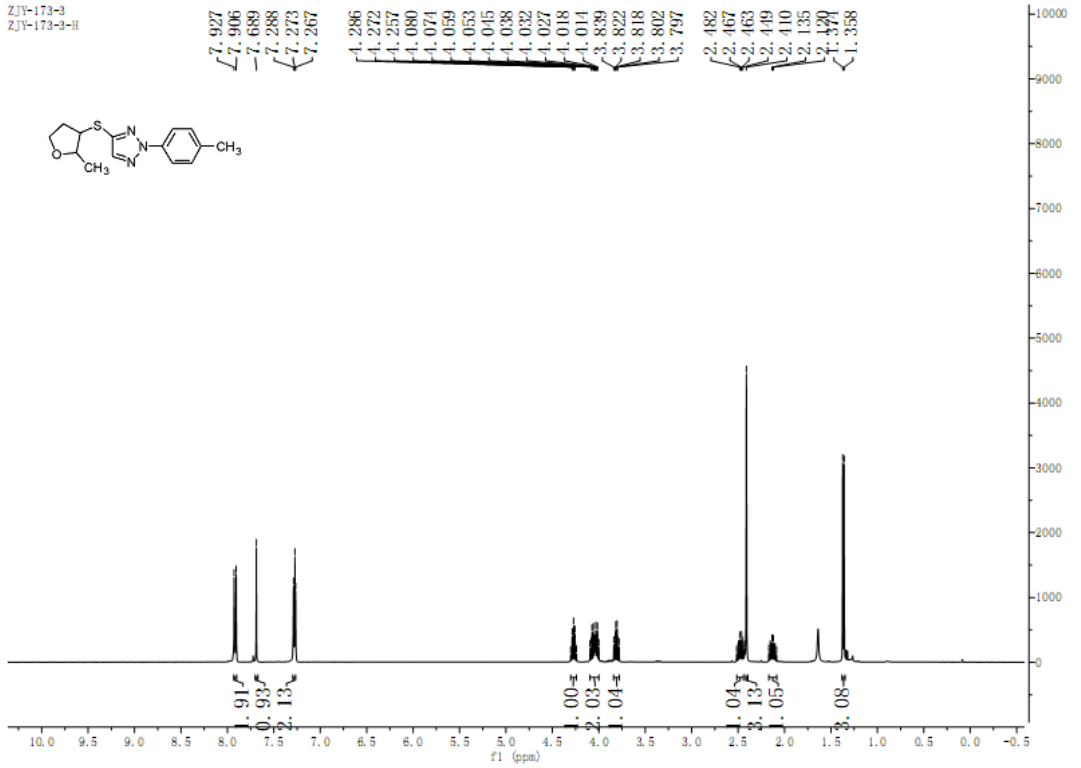


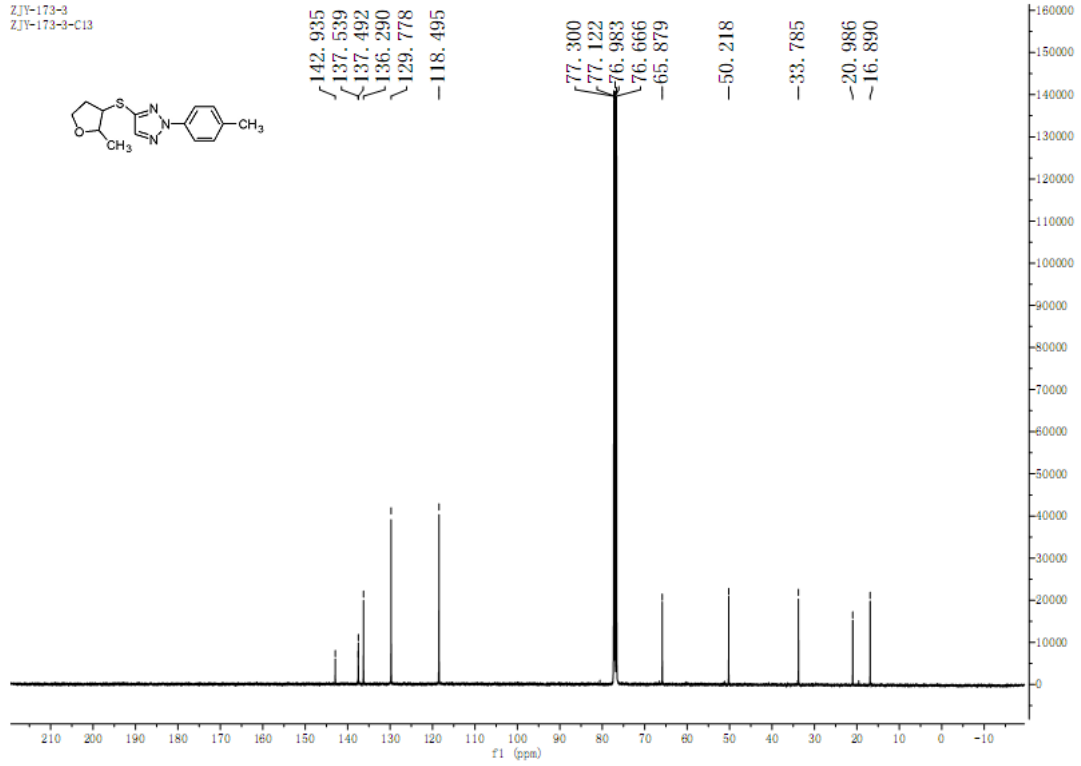
^{1}H and ^{13}C NMR Spectra for **6am**



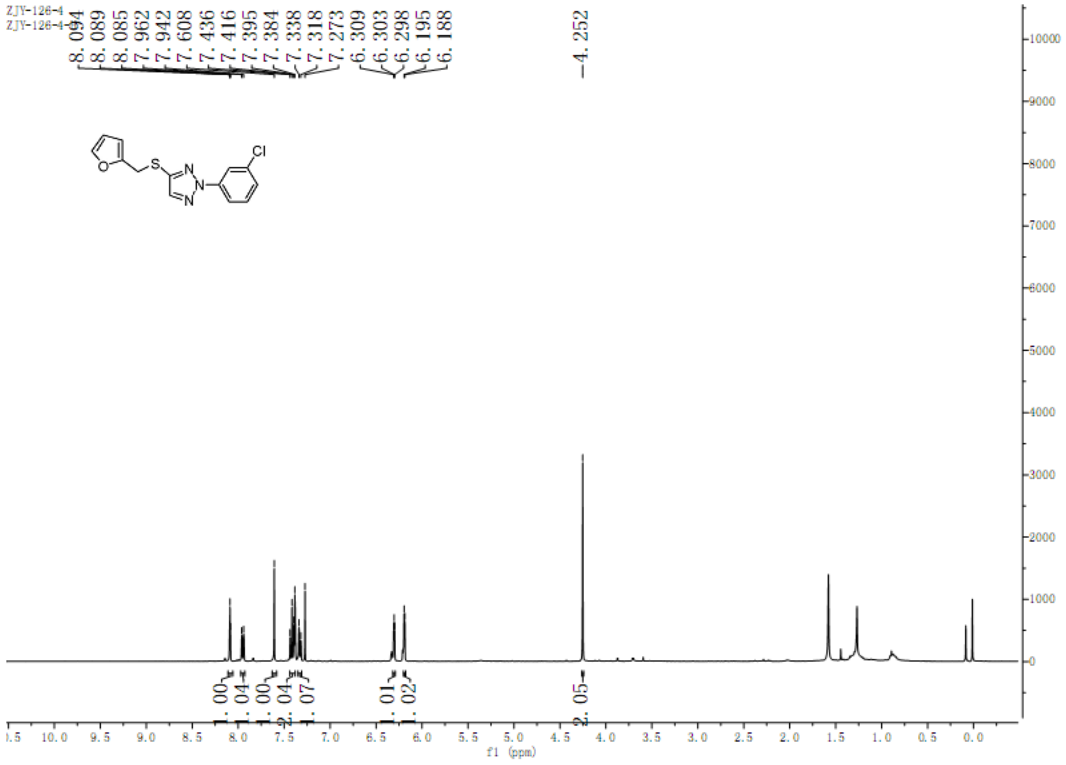


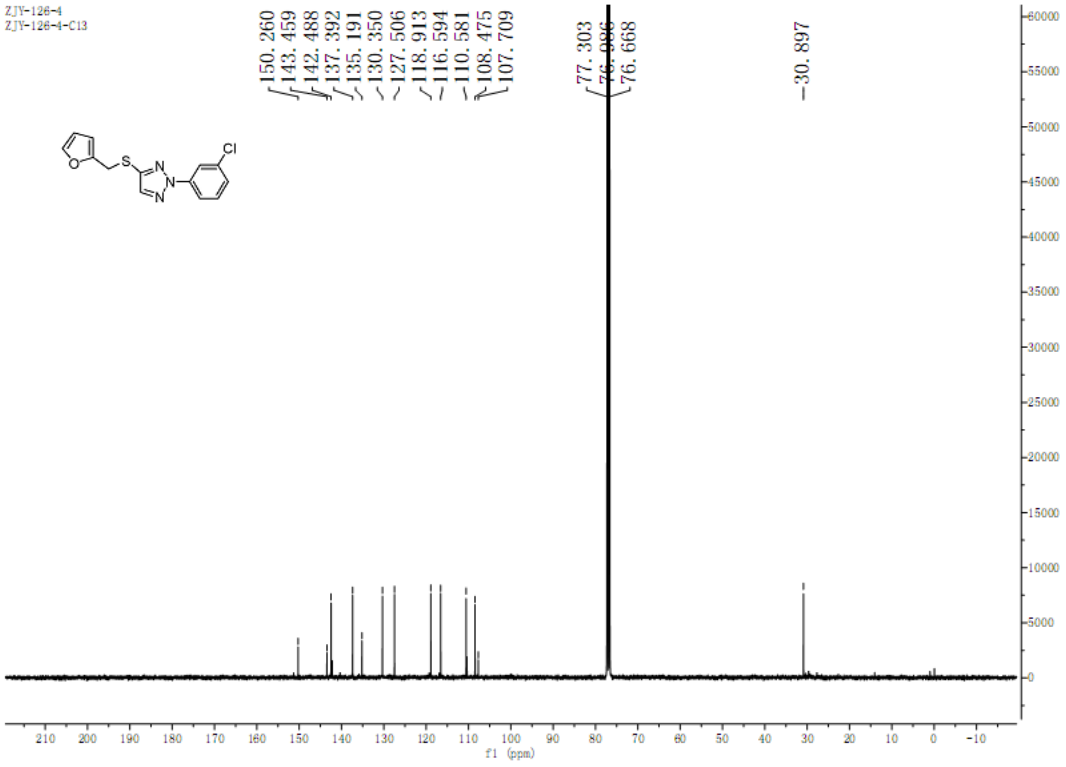
^{1}H and ^{13}C NMR Spectra for **6cm**



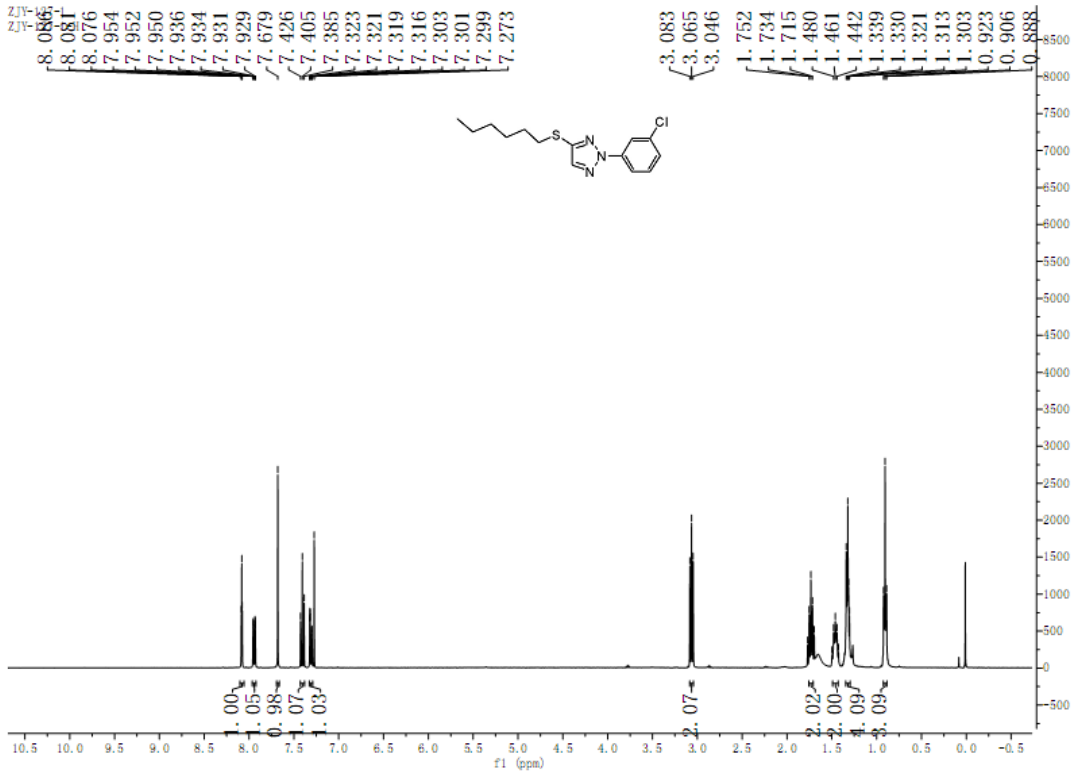


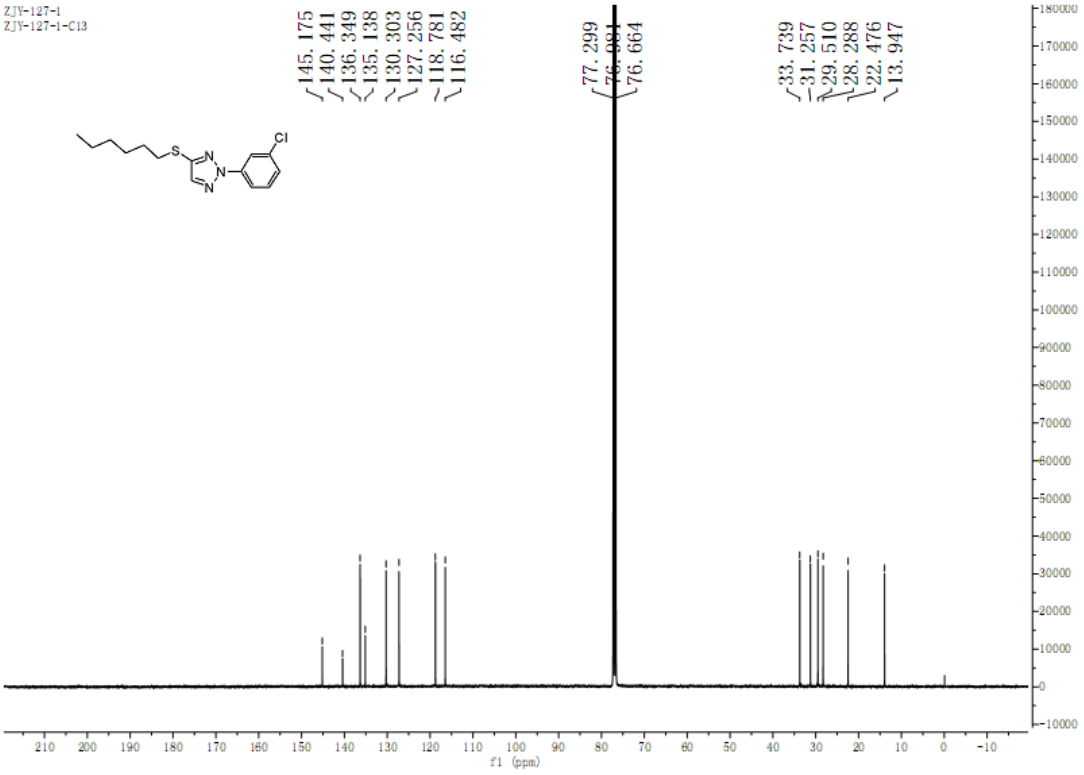
^{1}H and ^{13}C NMR Spectra for **6an**



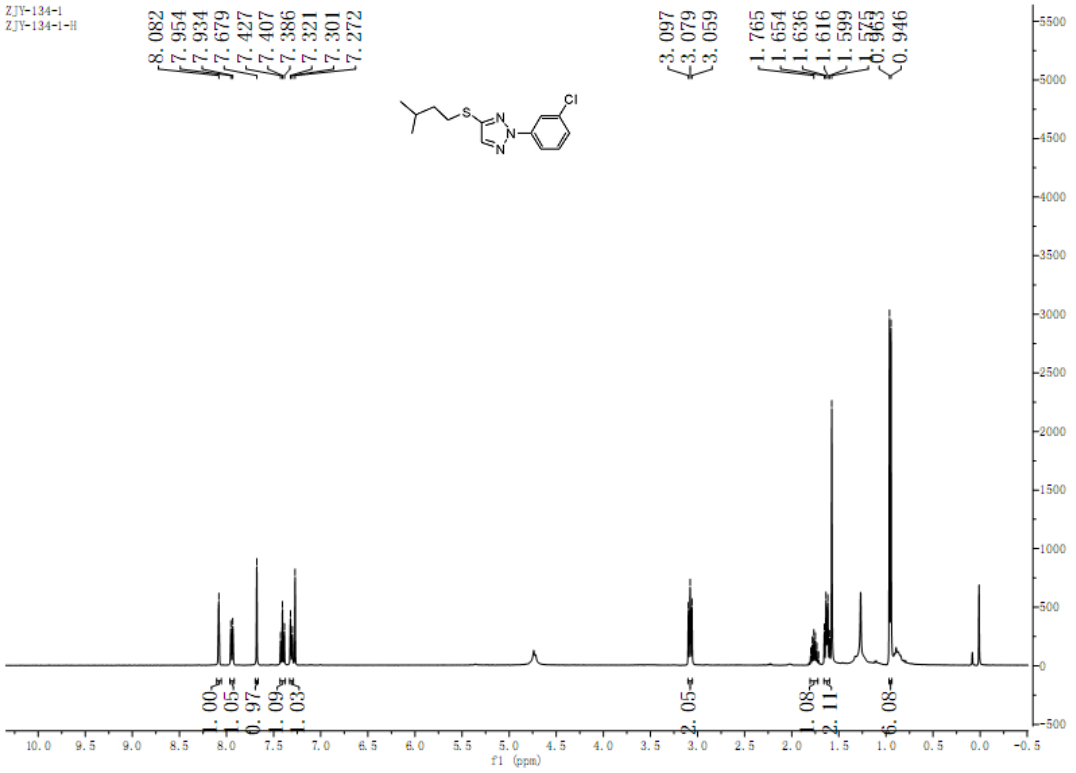


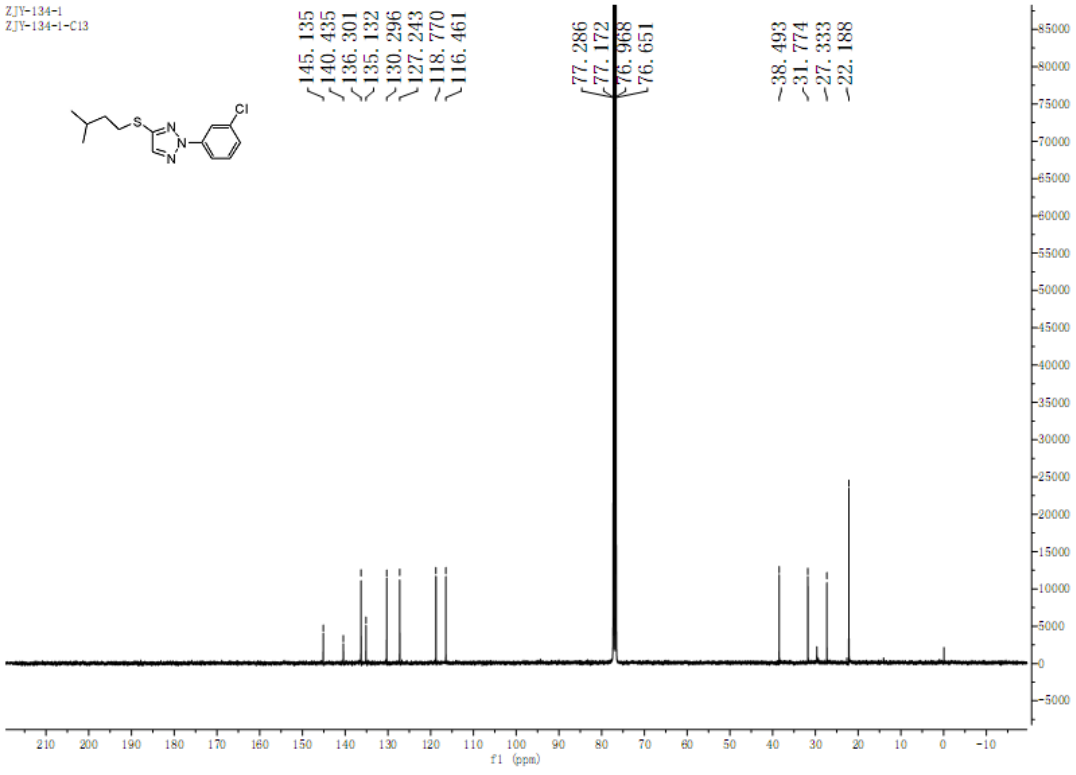
^{1}H and ^{13}C NMR Spectra for **6ao**



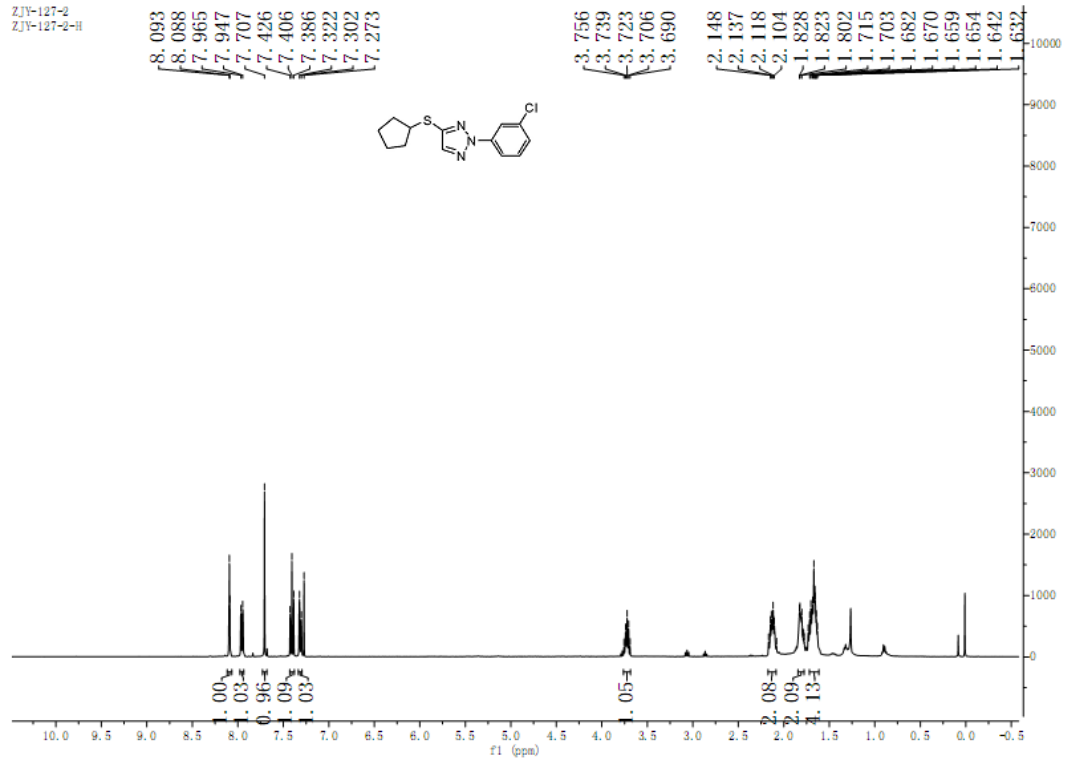


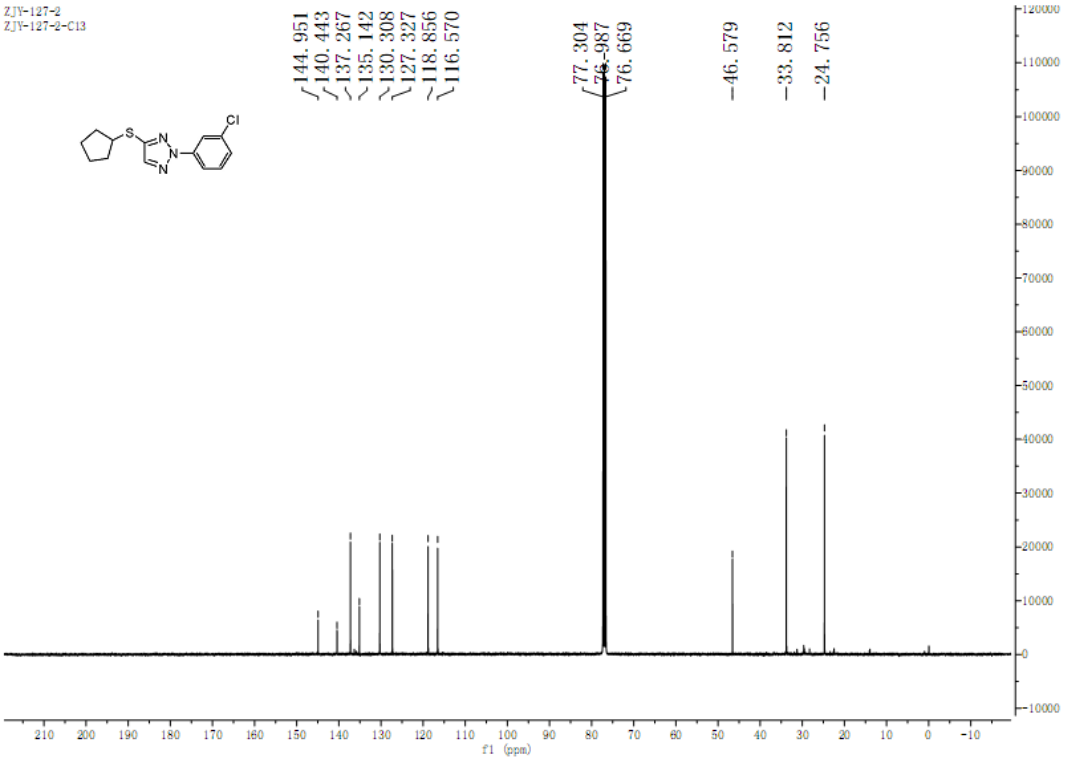
^{1}H and ^{13}C NMR Spectra for **6ap**



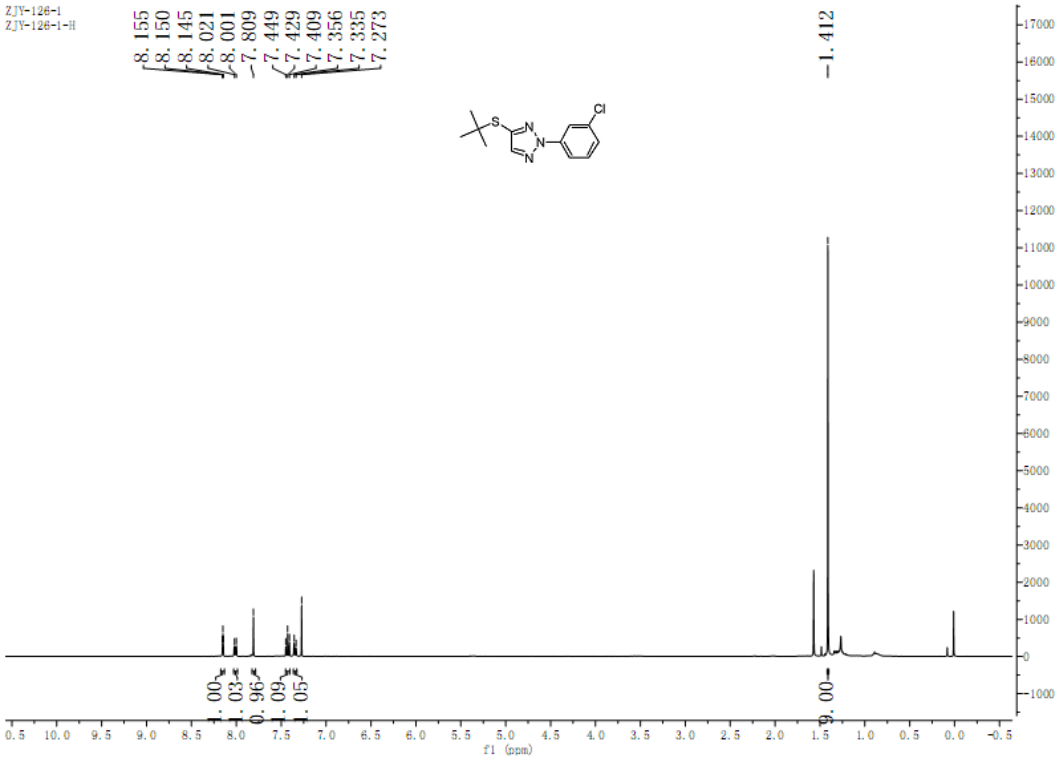


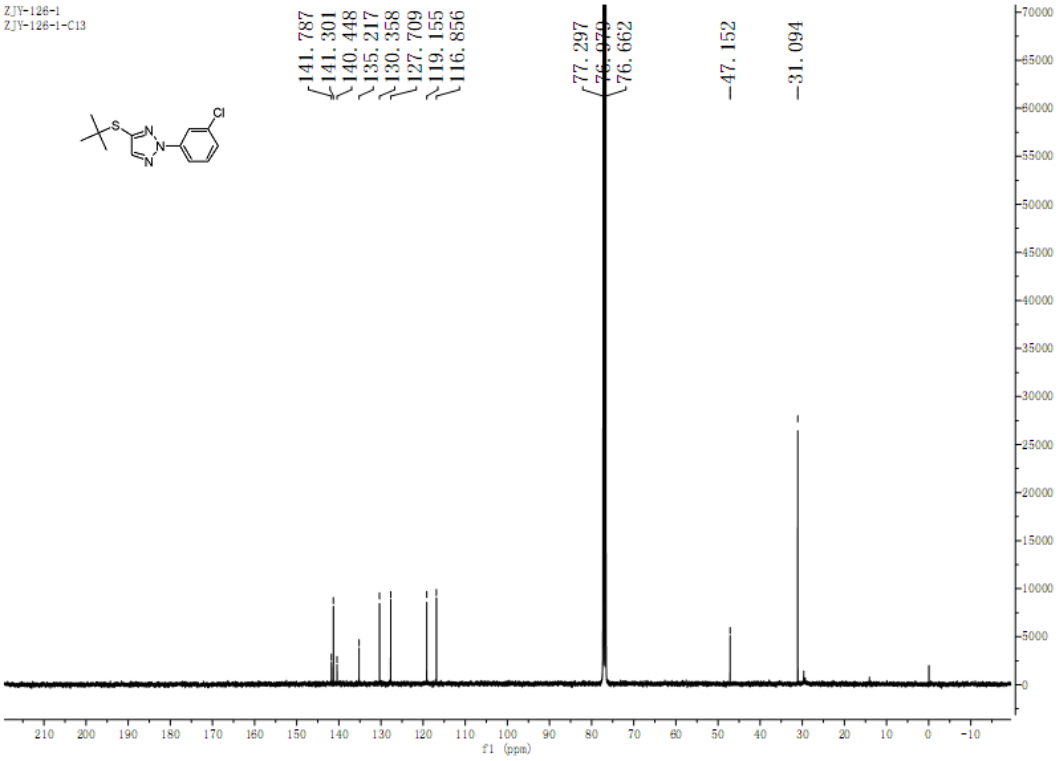
^{1}H and ^{13}C NMR Spectra for **6aq**



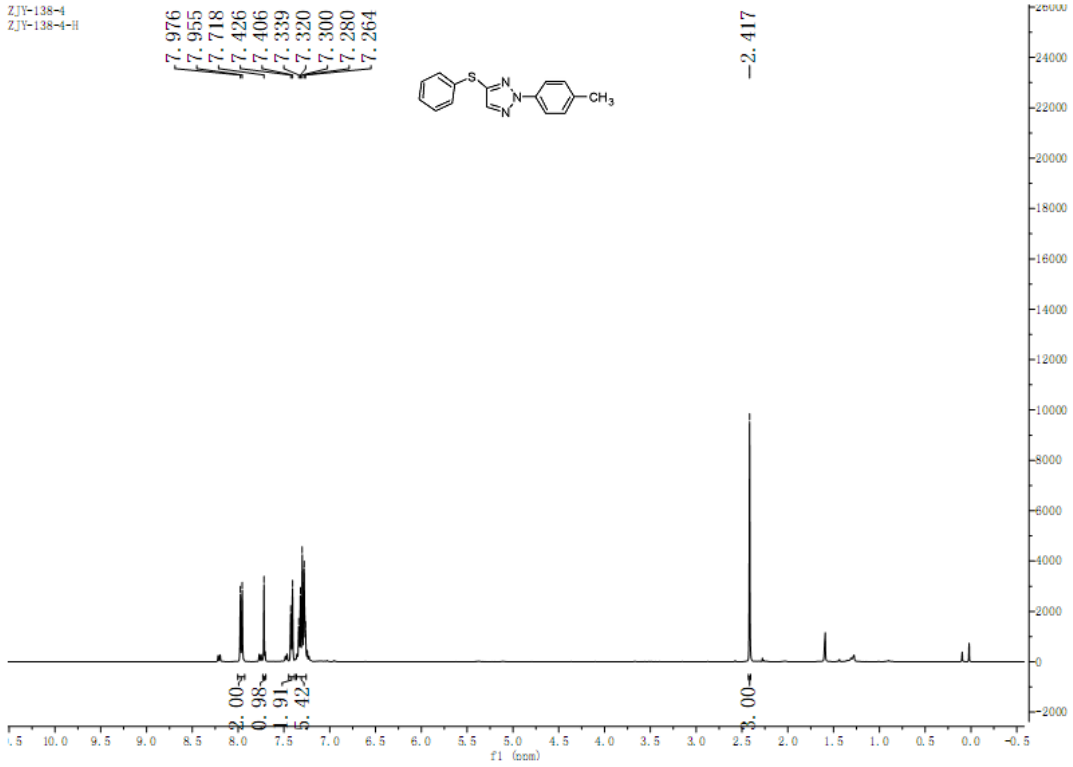


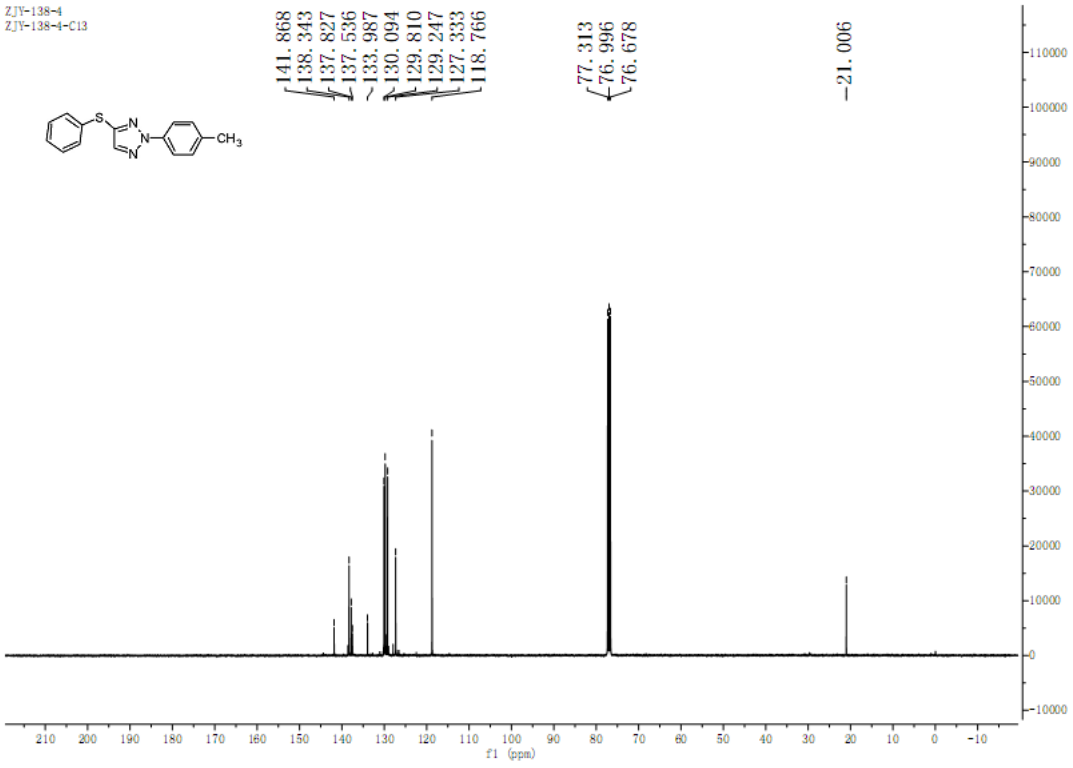
^{1}H and ^{13}C NMR Spectra for **6ar**



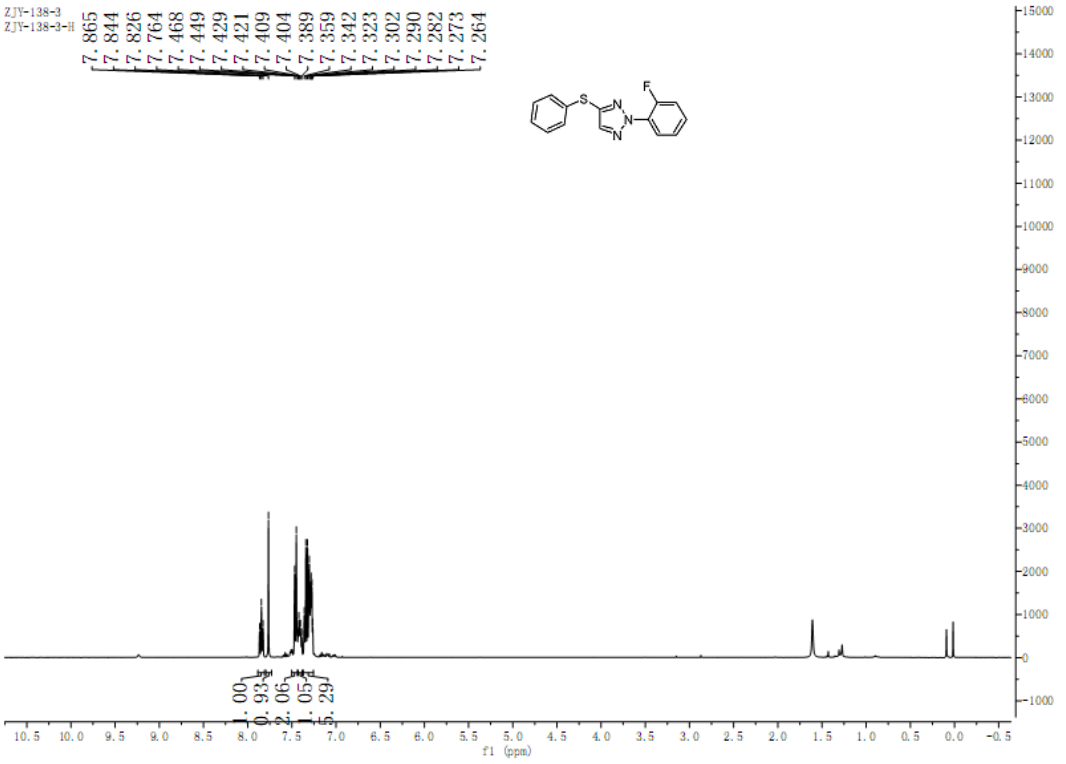


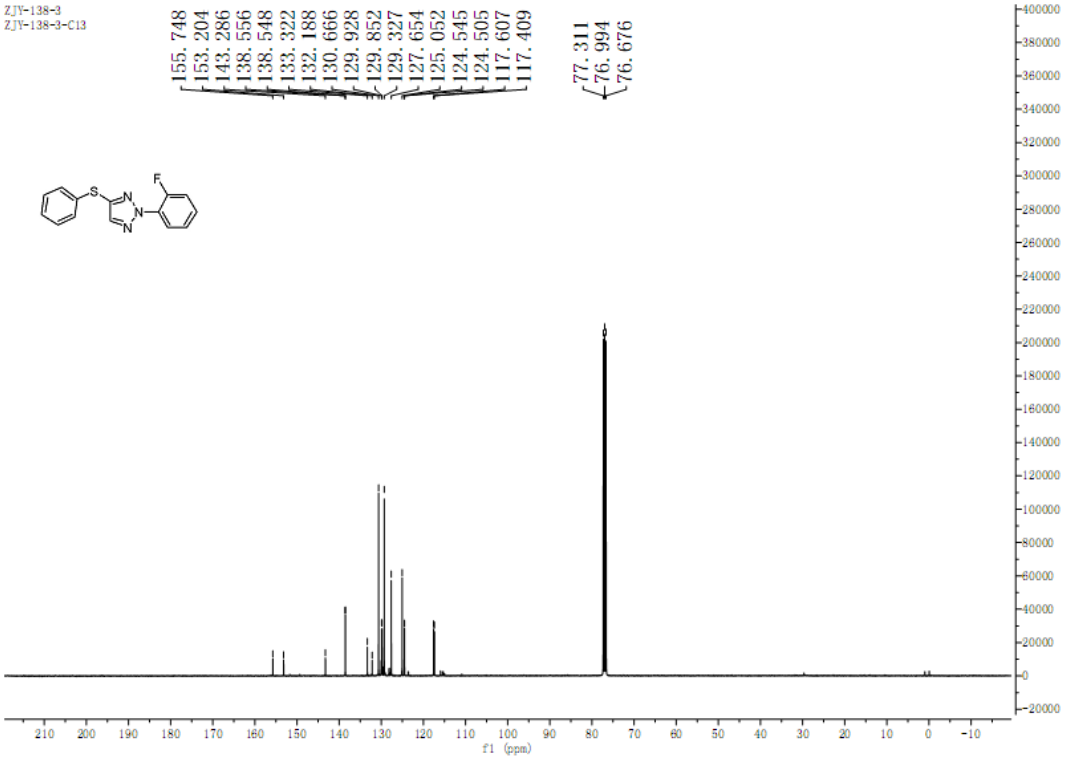
^{1}H and ^{13}C NMR Spectra for **6ce**



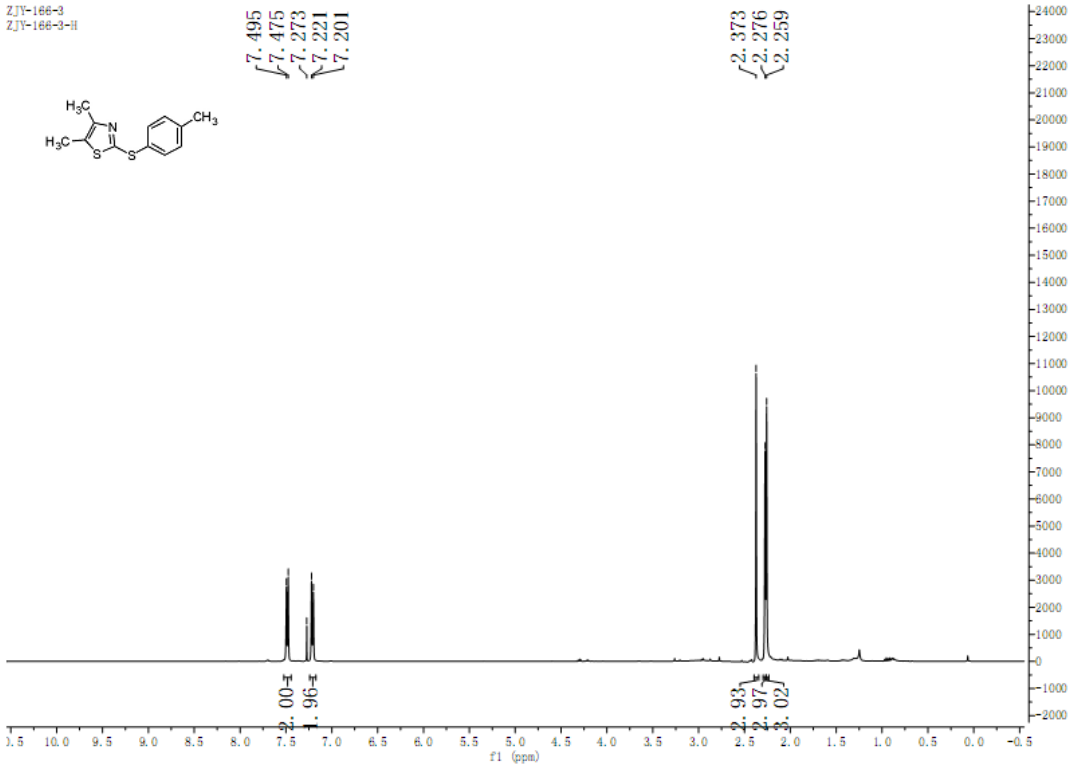


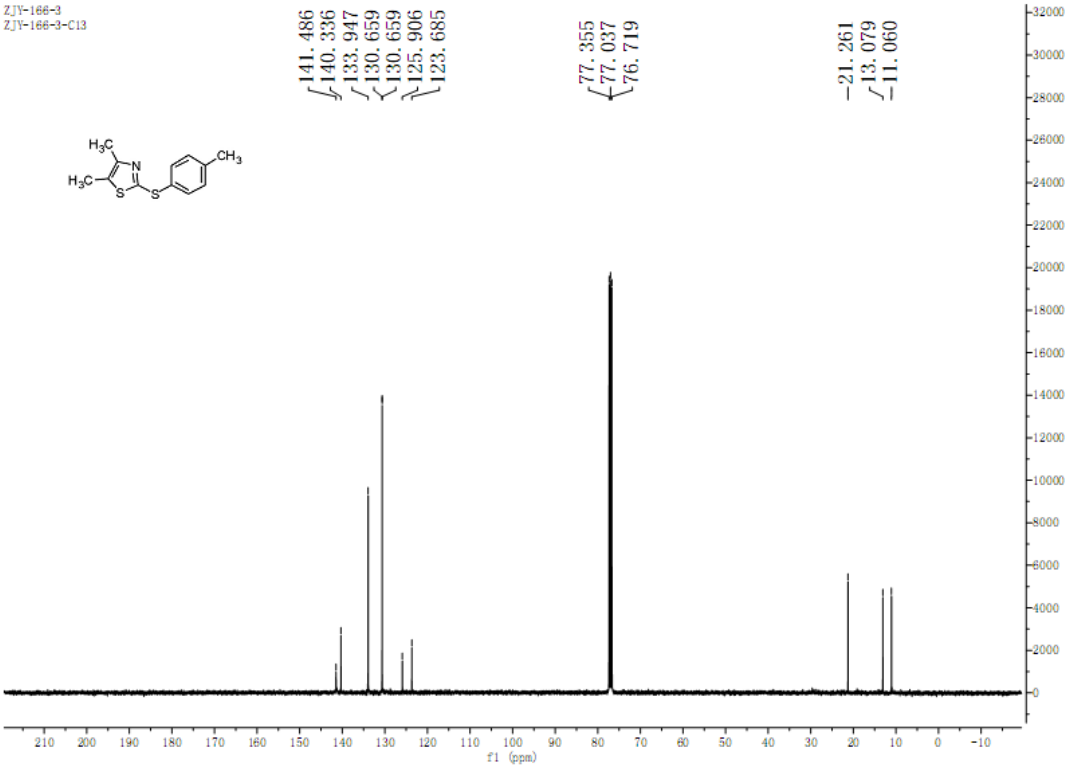
^{1}H and ^{13}C NMR Spectra for **6ie**



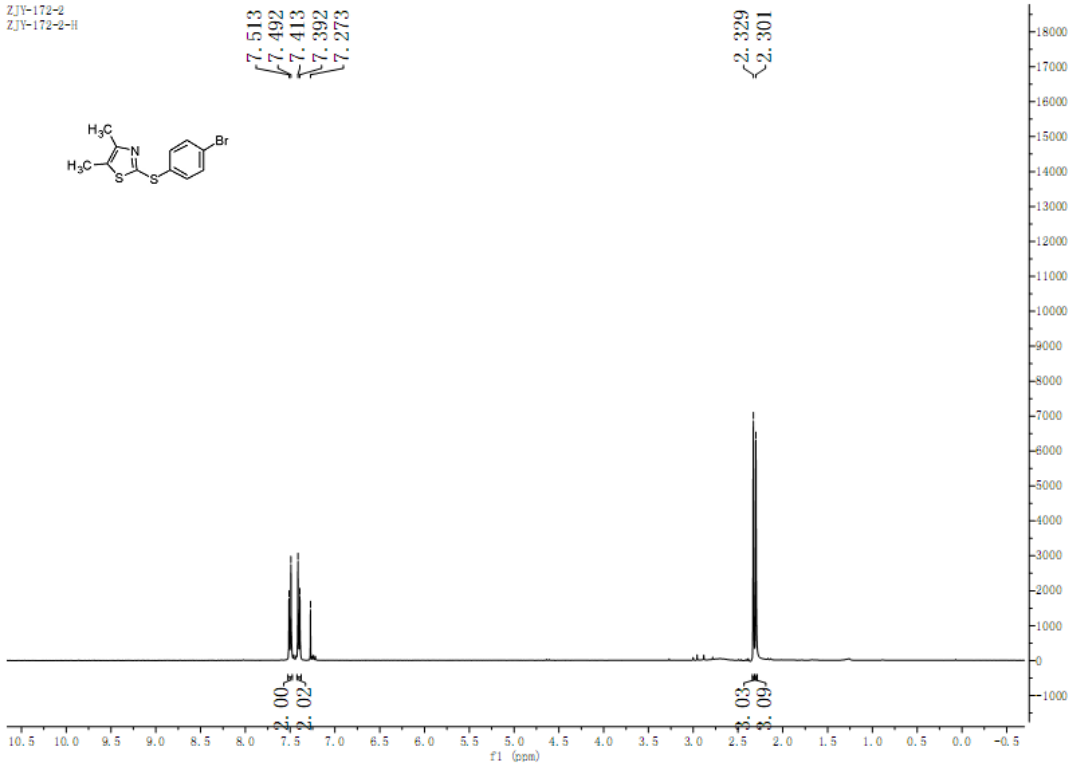


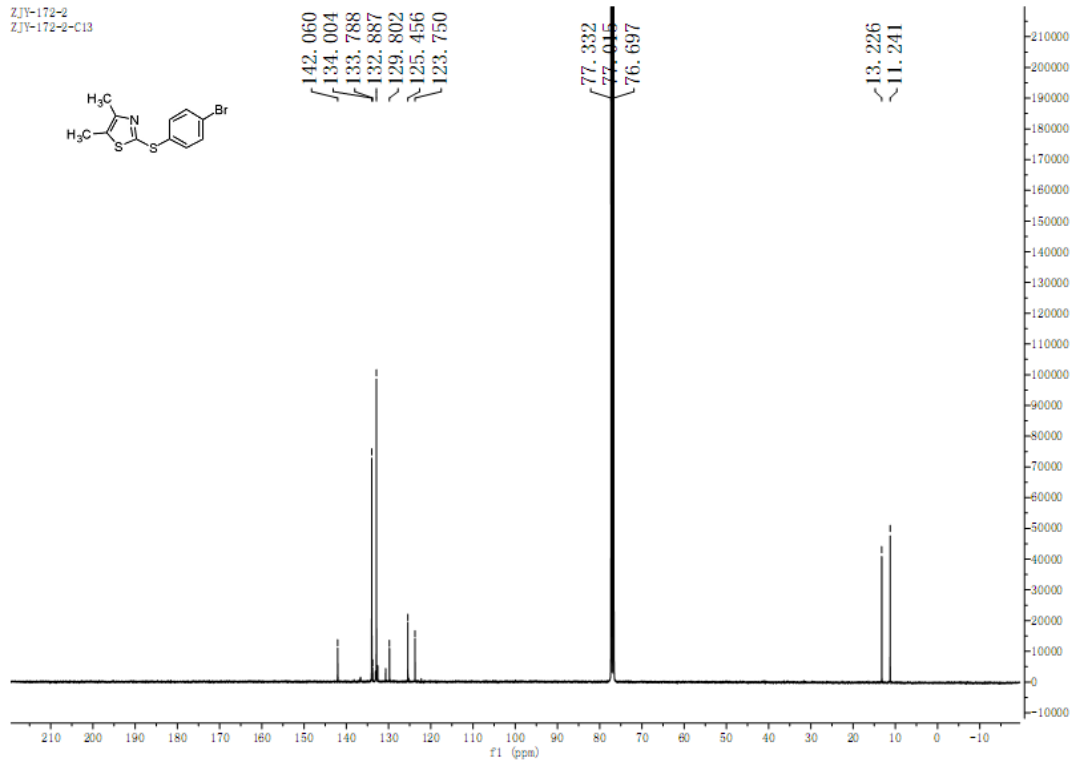
^{1}H and ^{13}C NMR Spectra for **10a**



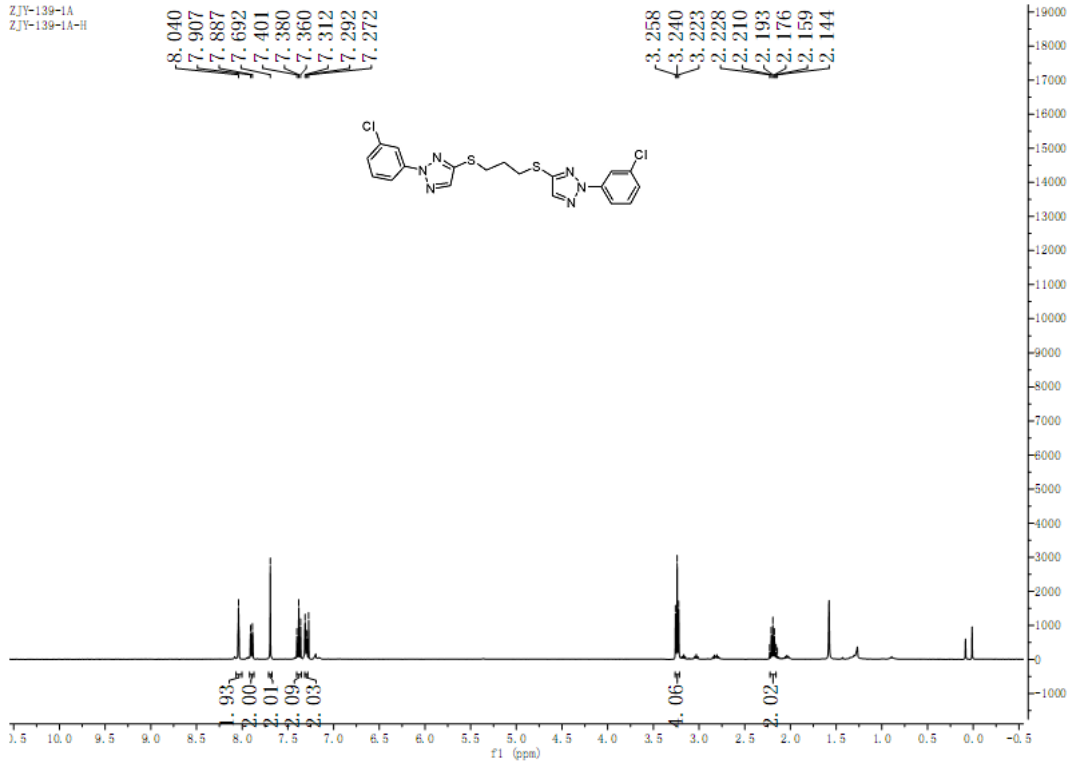


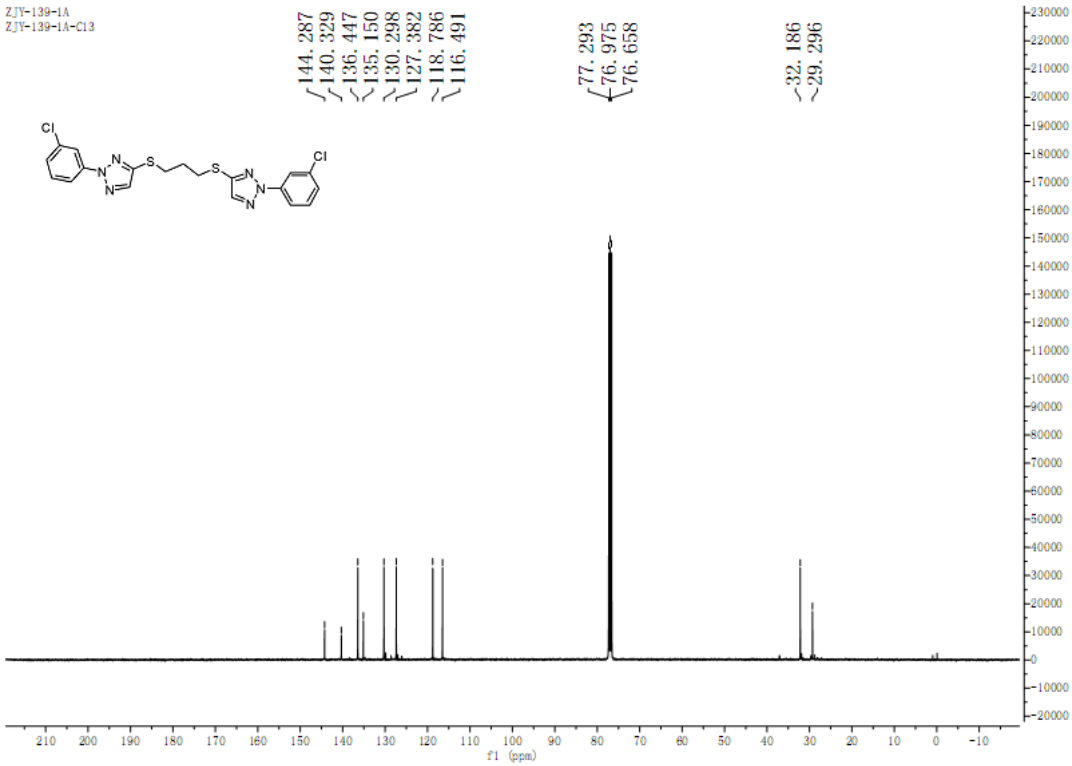
^{1}H and ^{13}C NMR Spectra for **10b**



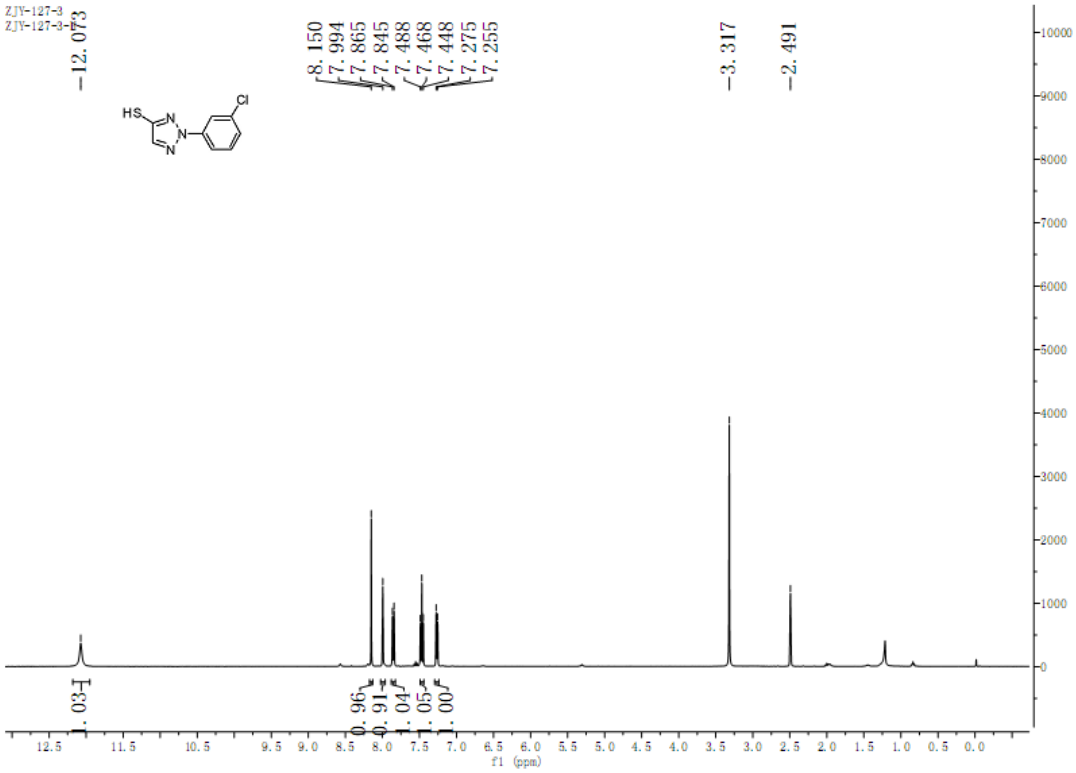


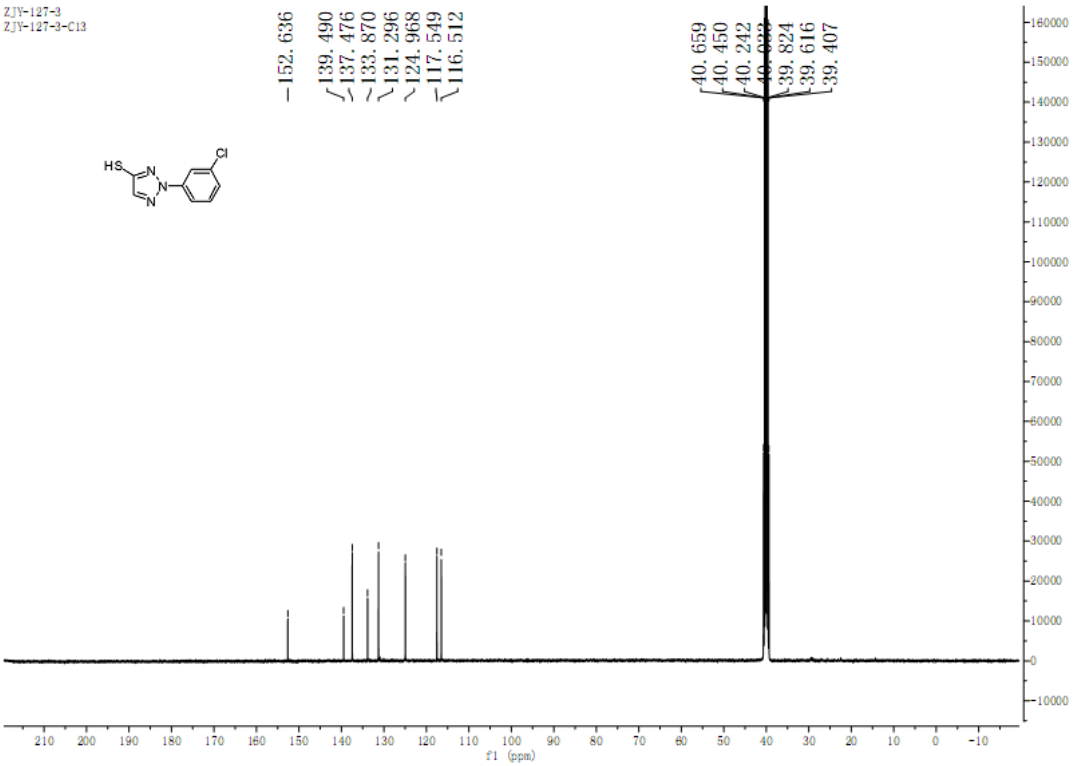
^{1}H and ^{13}C NMR Spectra for **14**



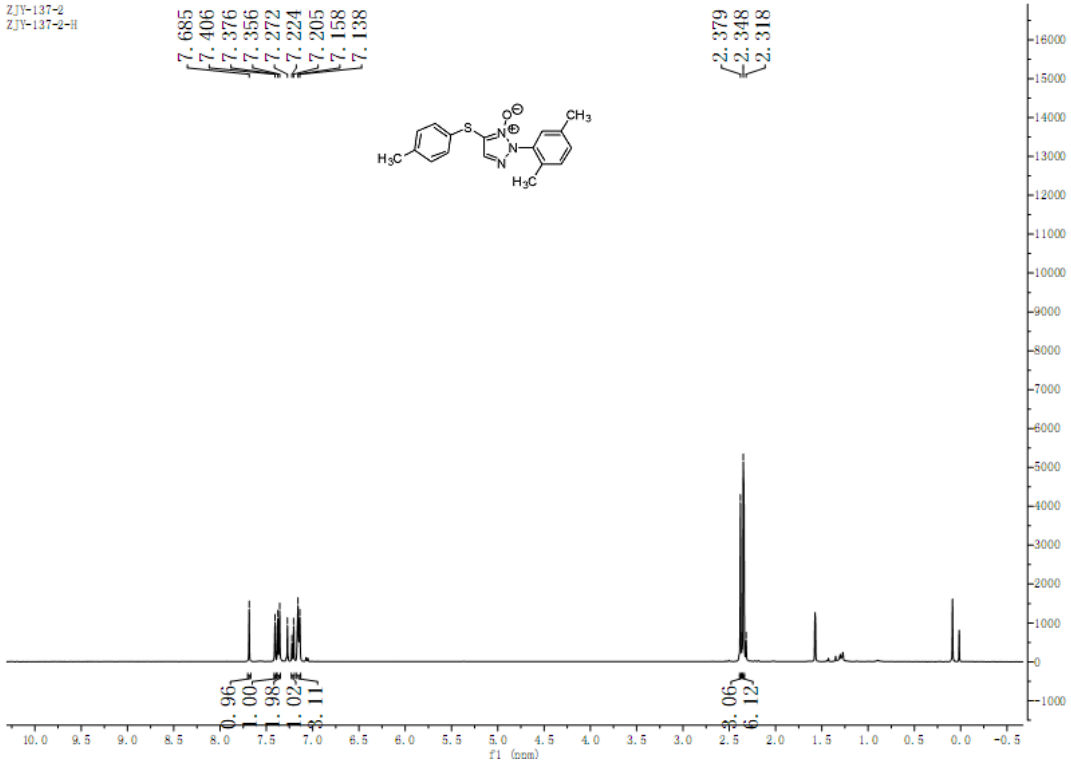


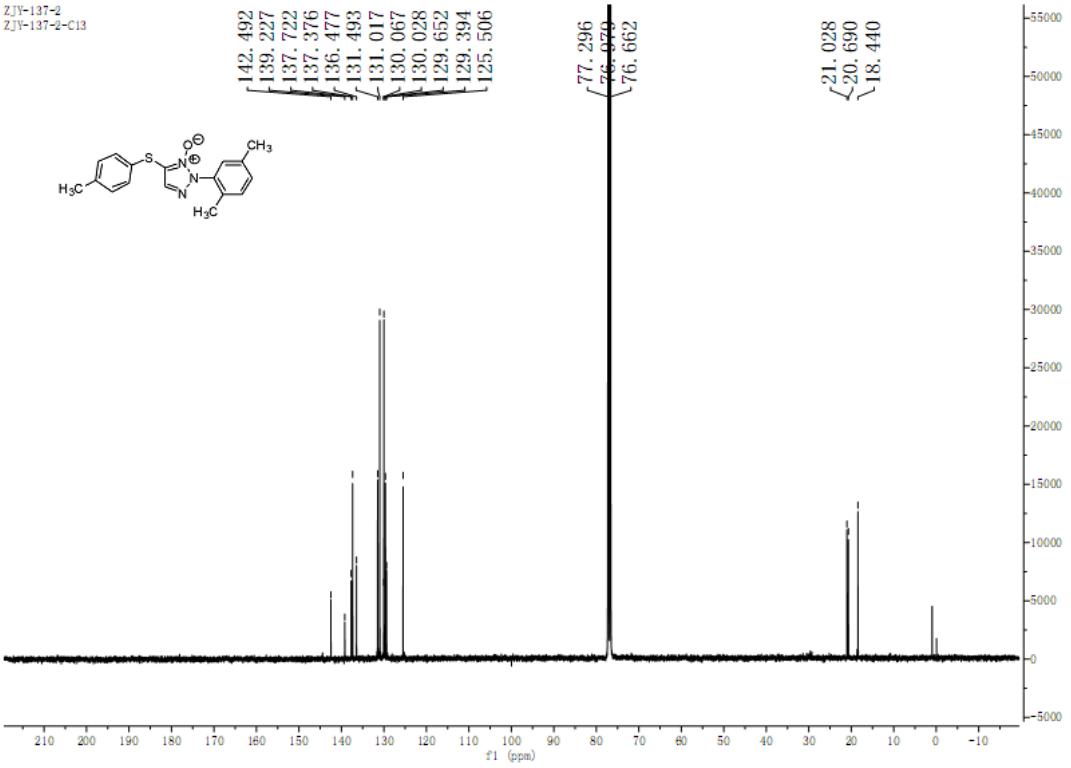
^{1}H and ^{13}C NMR Spectra for **16**





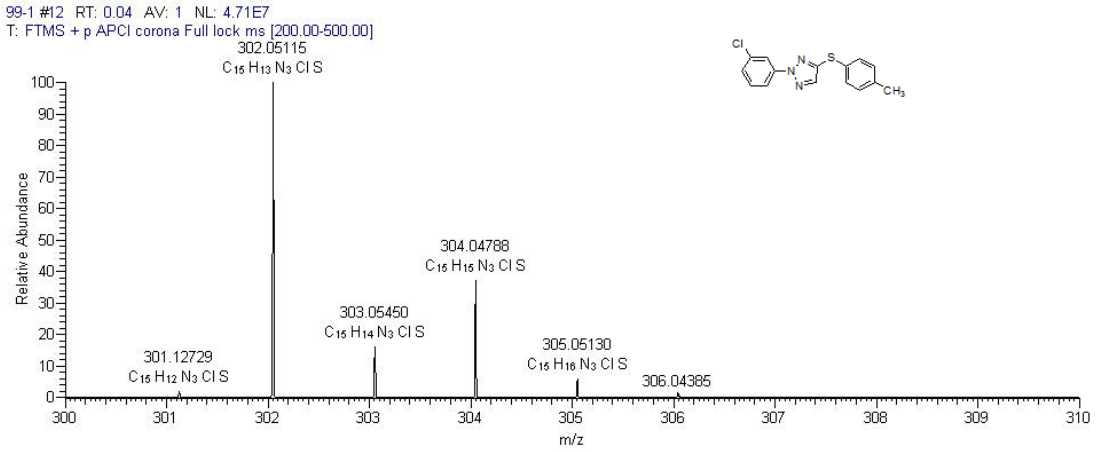
^{1}H and ^{13}C NMR Spectra for **19**



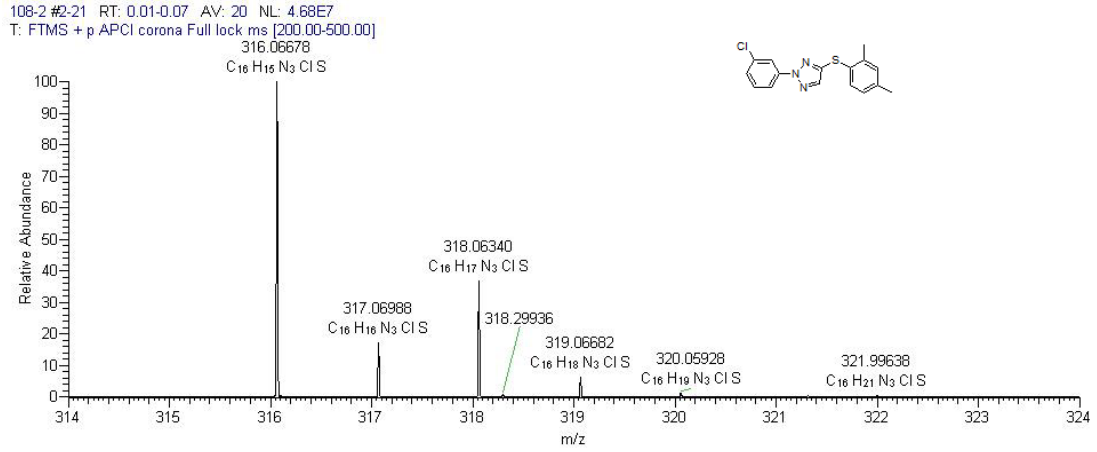


9. Copies of HRESIMS Spectra

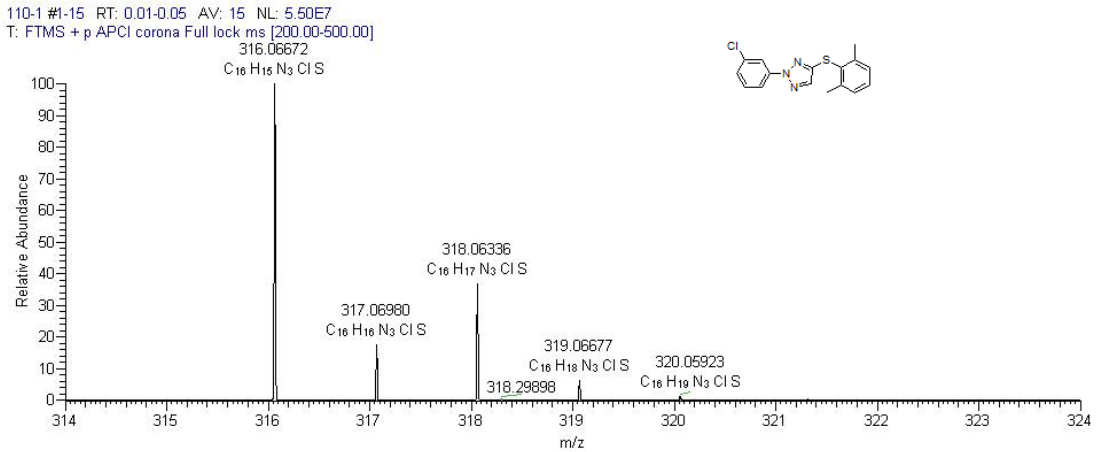
HRESIMS for **6aa**



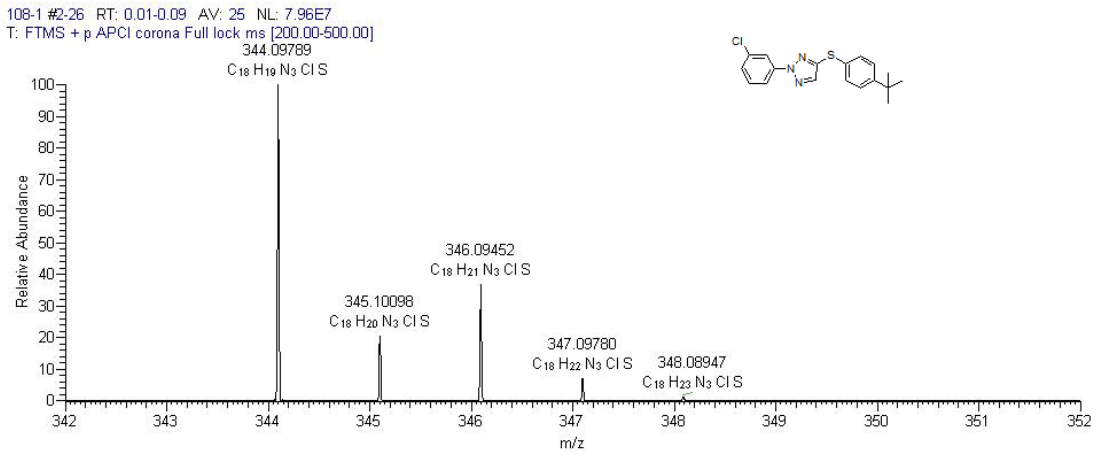
HRESIMS for **6ab**



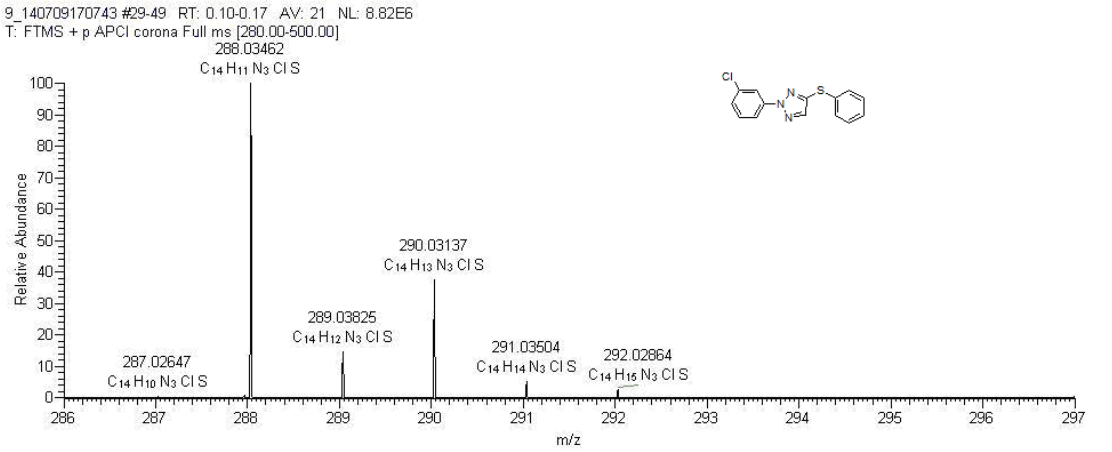
HRESIMS for **6ac**



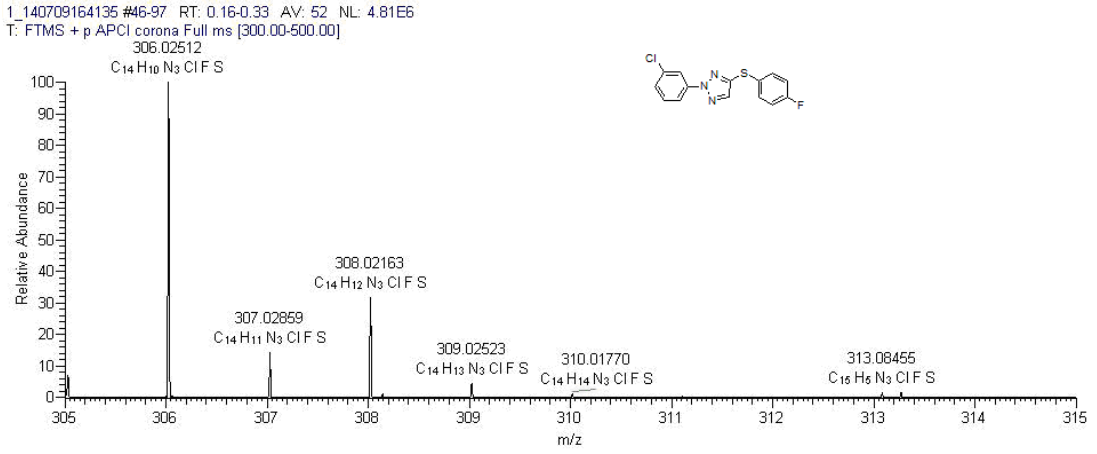
HRESIMS for **6ad**



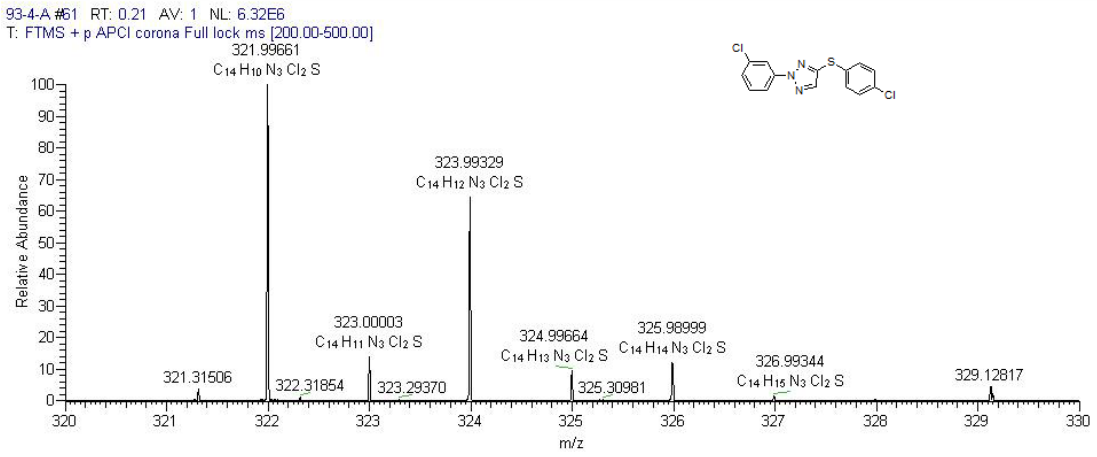
HRESIMS for **6ae**



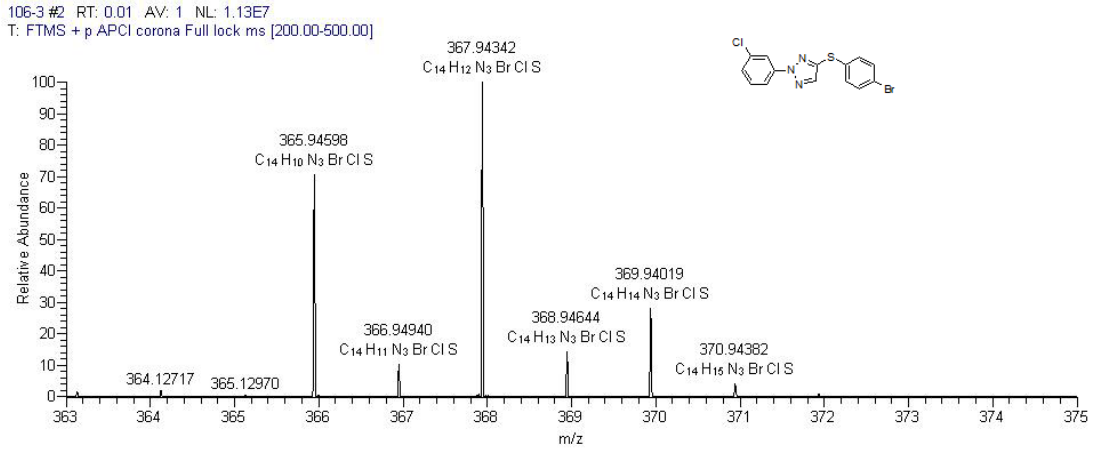
HRESIMS for **6af**



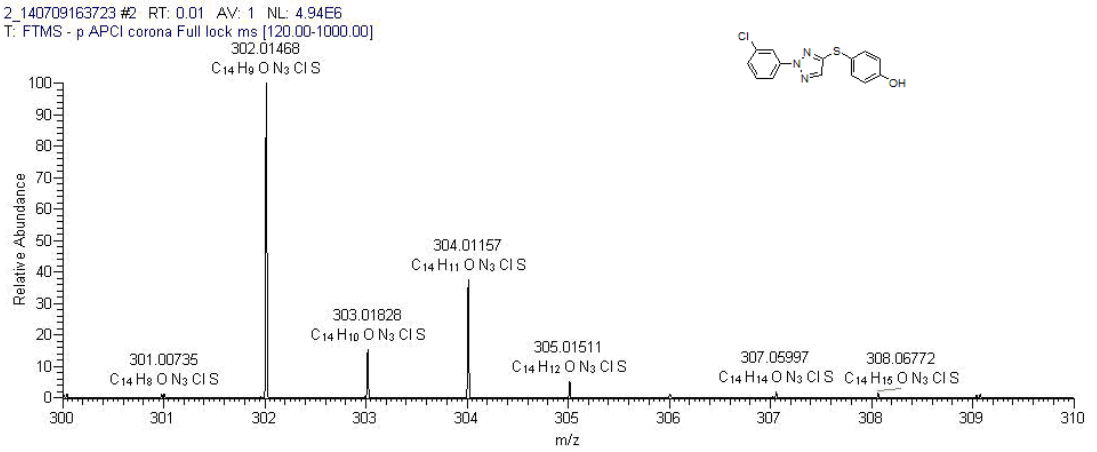
HRESIMS for **6ag**



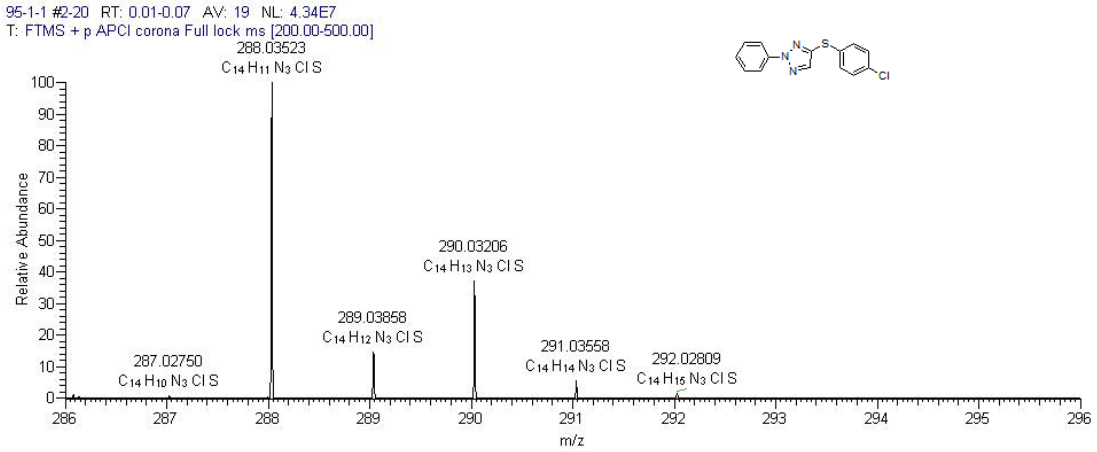
HRESIMS for **6ah**



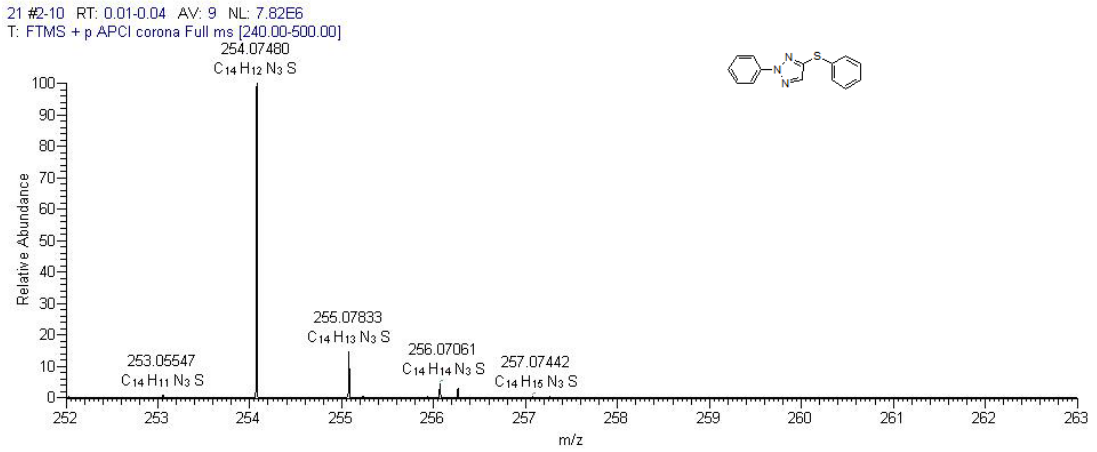
HRESIMS for **6ai**



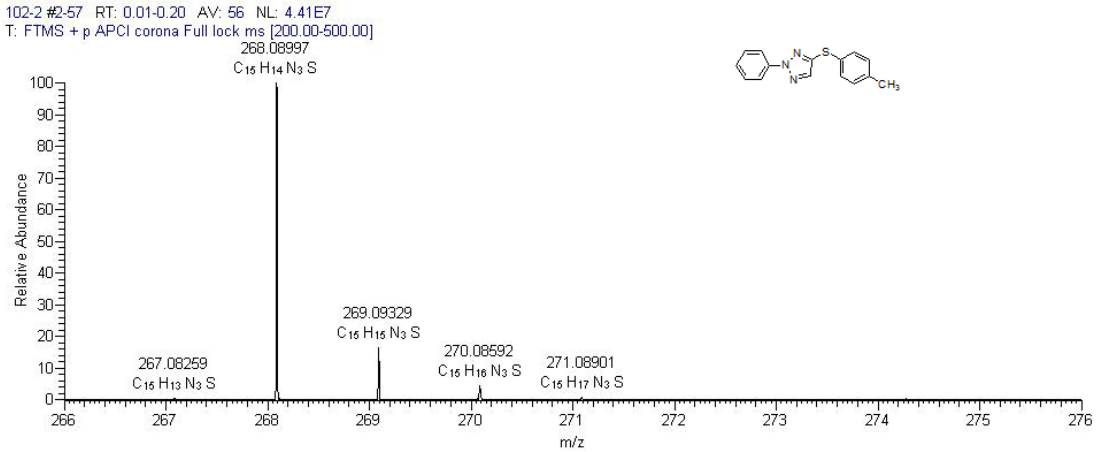
HRESIMS for **6bg**



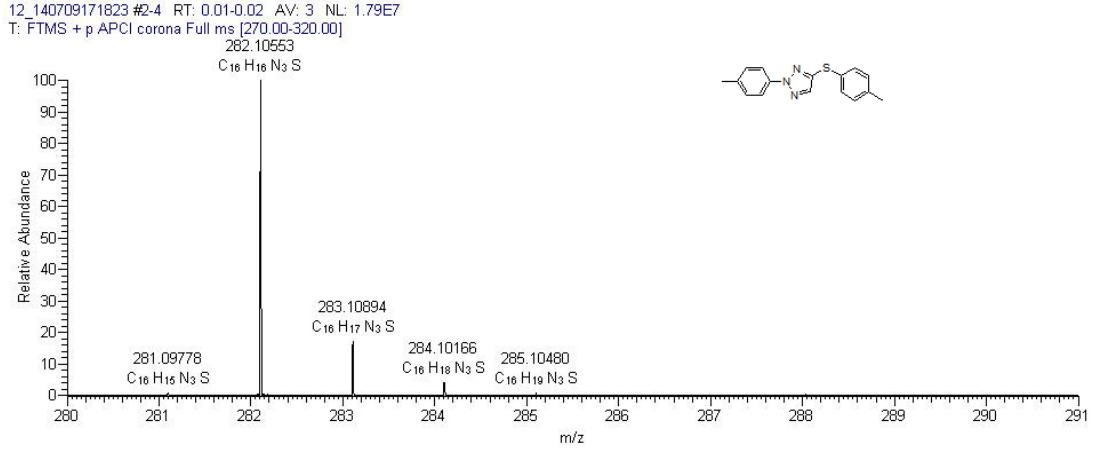
HRESIMS for **6be**



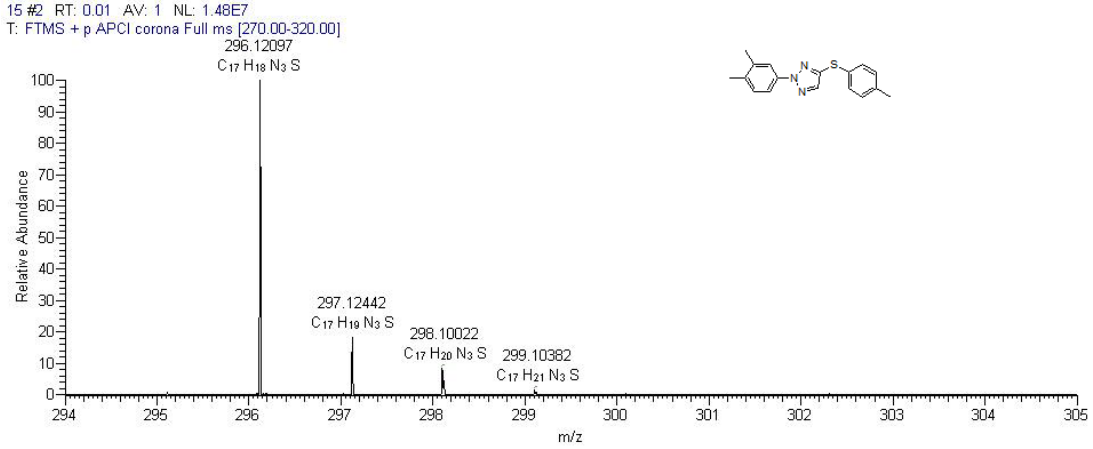
HRESIMS for **6ba**



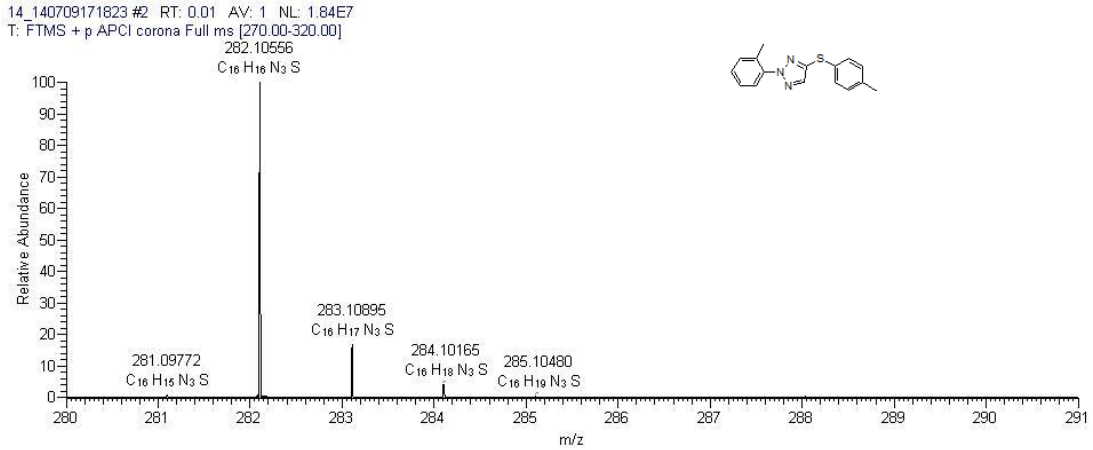
HRESIMS for **6ca**



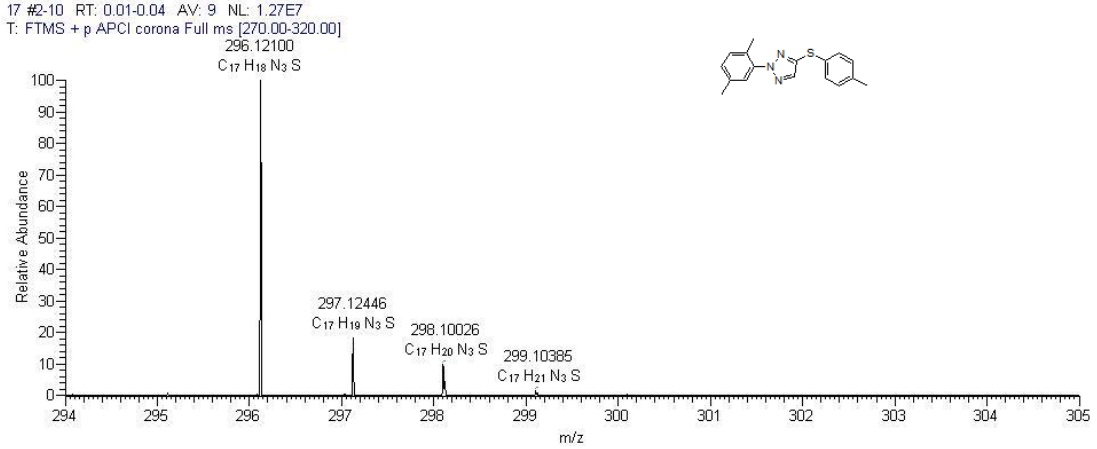
HRESIMS for **6da**



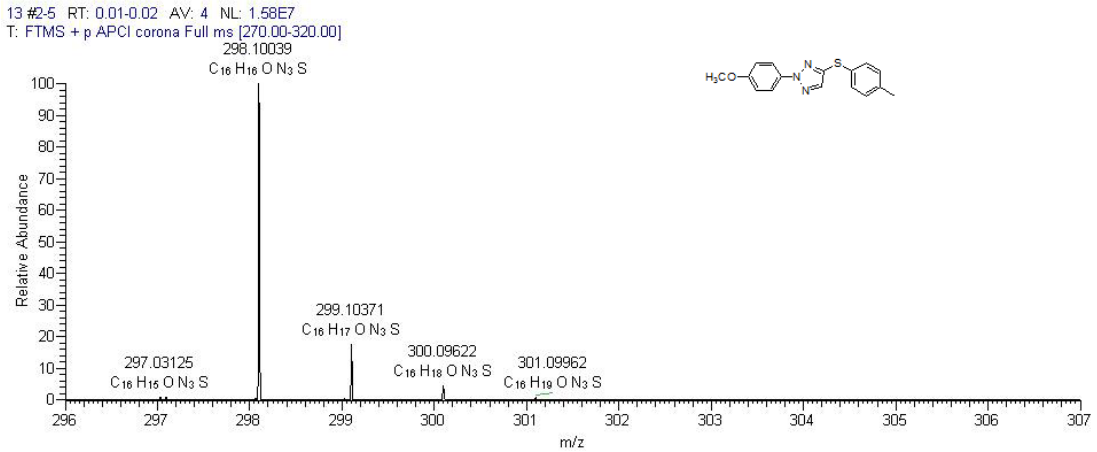
HRESIMS for **6ea**



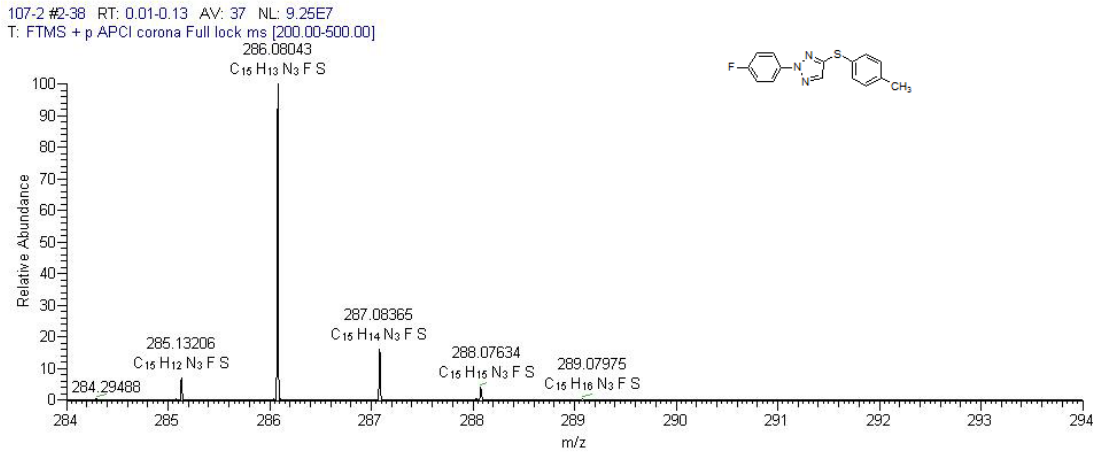
HRESIMS for **6fa**



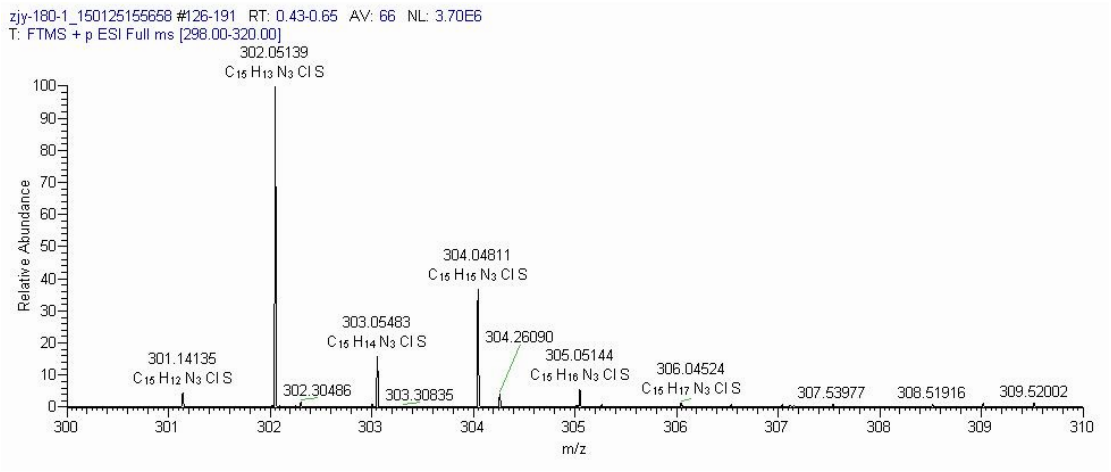
HRESIMS for **6ga**



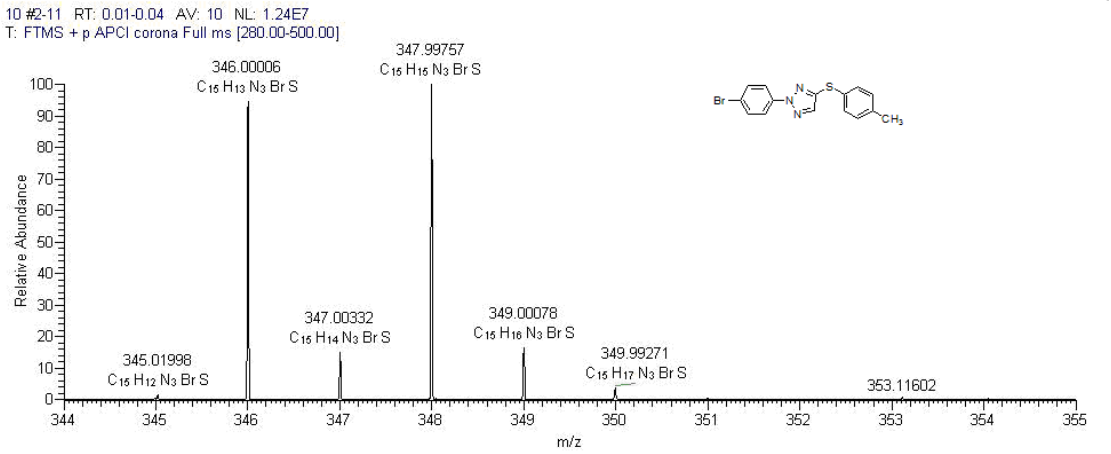
HRESIMS for **6ha**



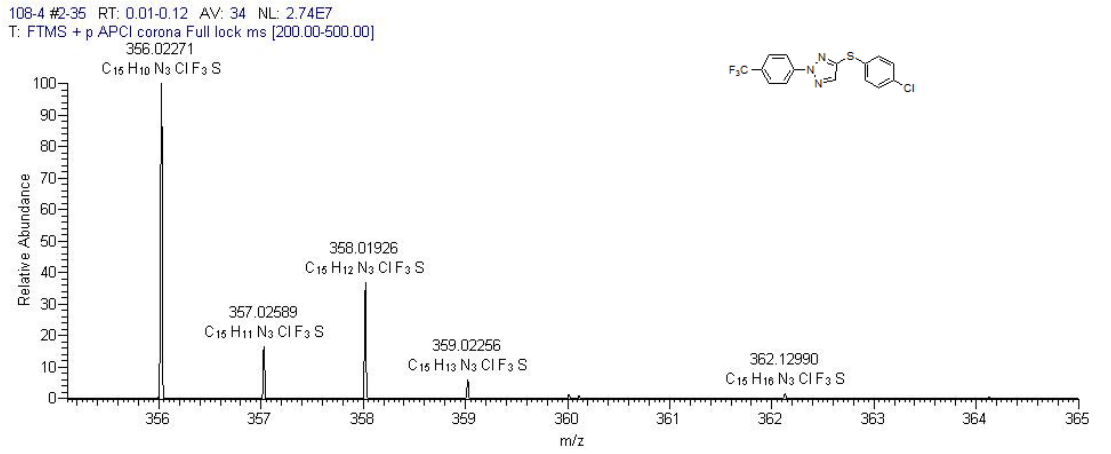
HRESIMS for **6ia**



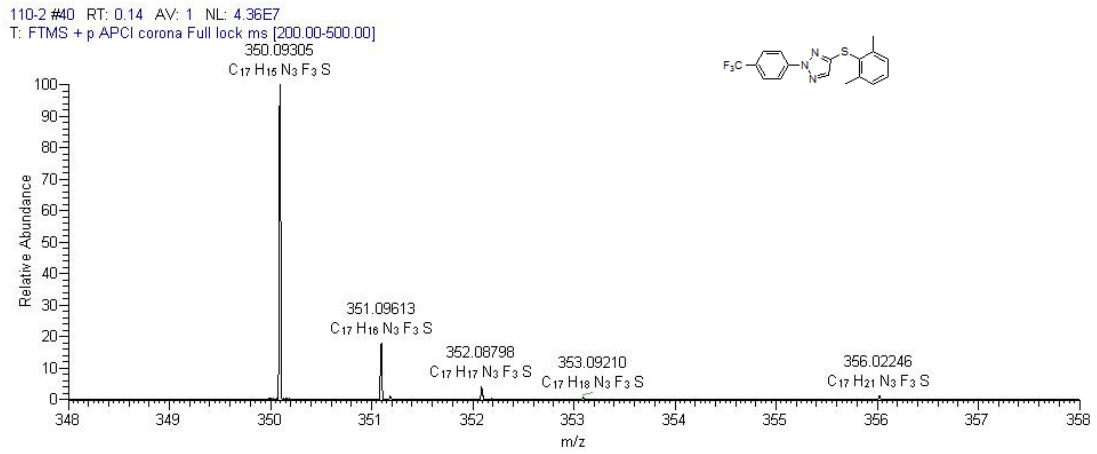
HRESIMS for **6ja**



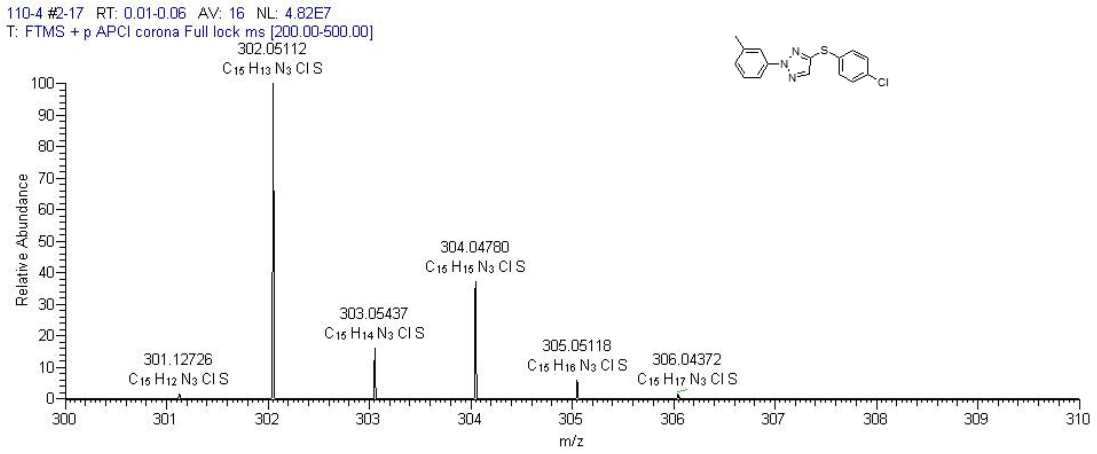
HRESIMS for **6lg**



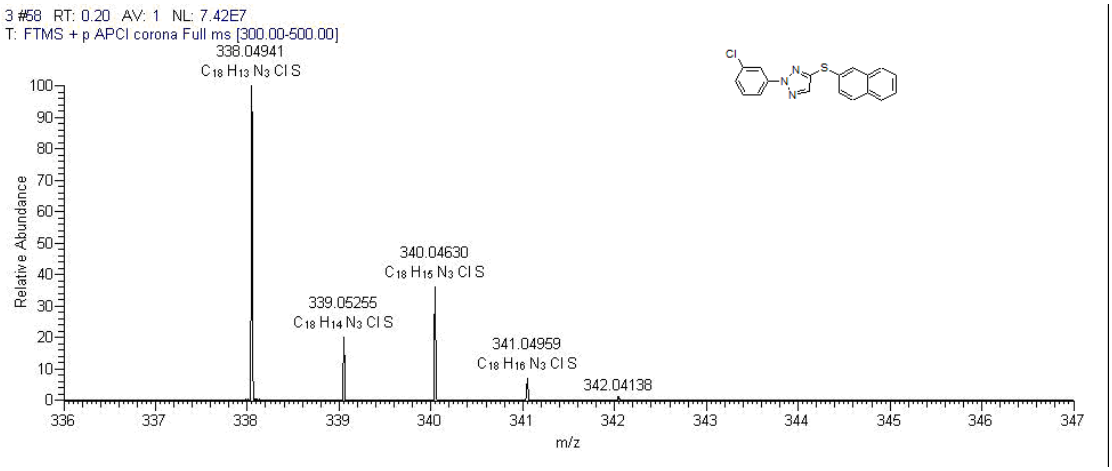
HRESIMS for **6lc**



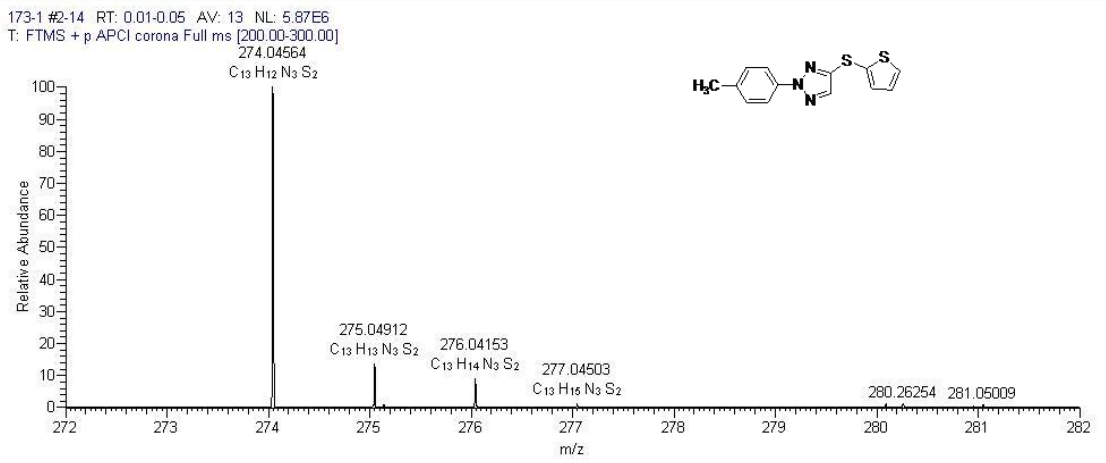
HRESIMS for **6mg**



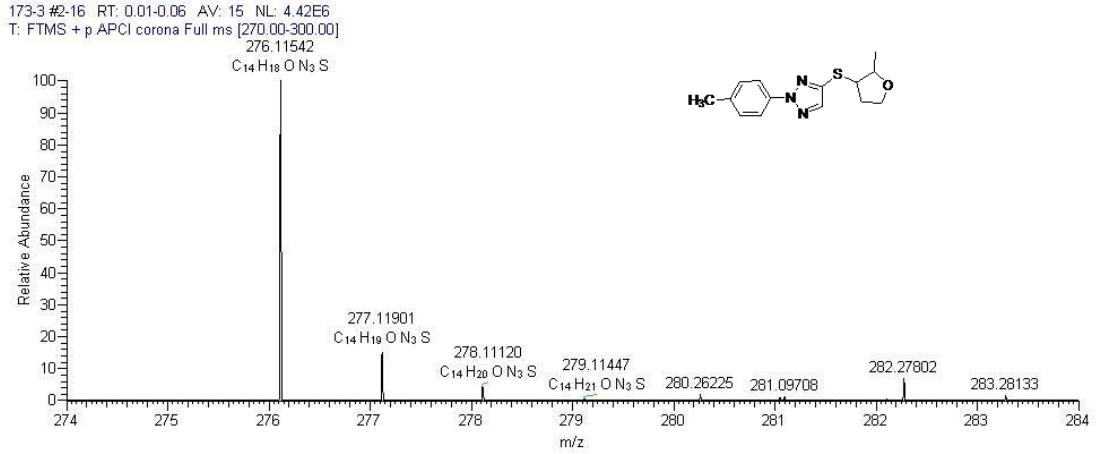
HRESIMS for **6aj**



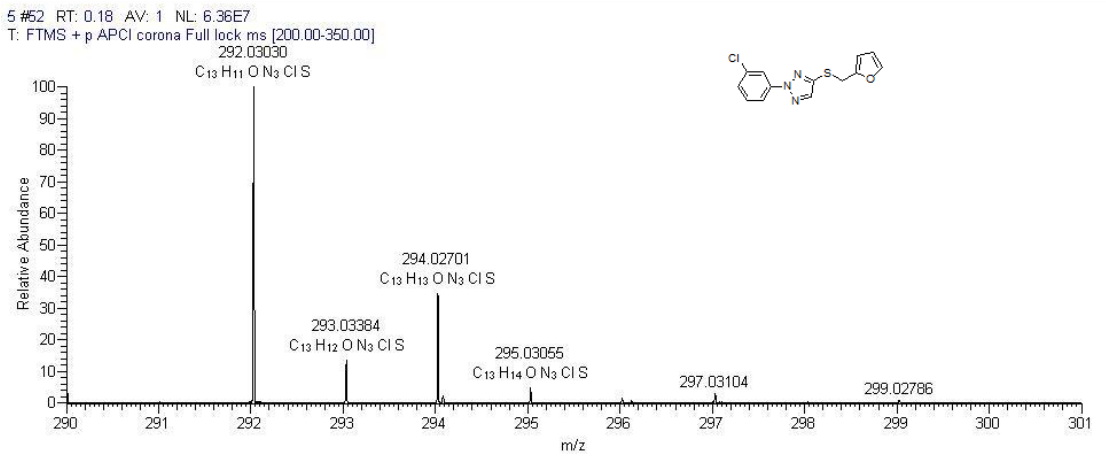
HRESIMS for **6ck**



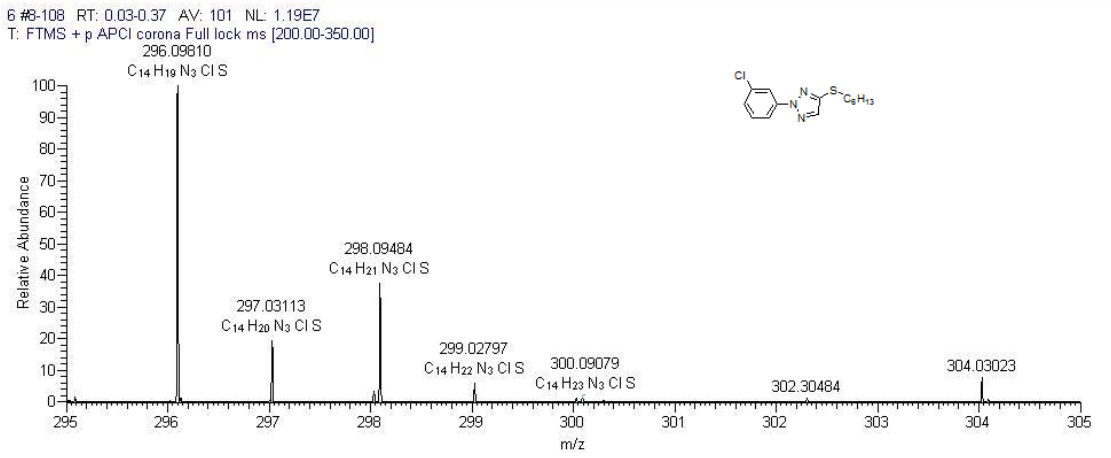
HRESIMS for **6cm**



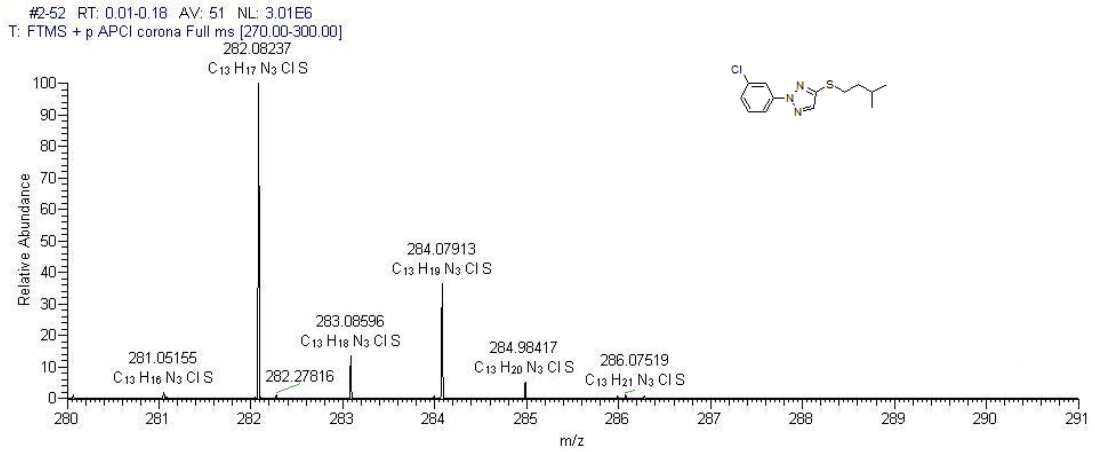
HRESIMS for **6an**



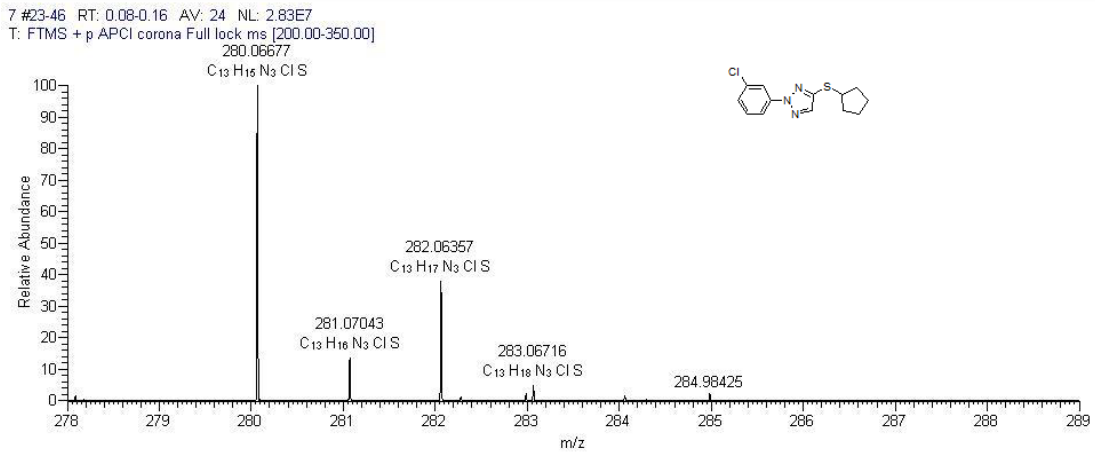
HRESIMS for **6ao**



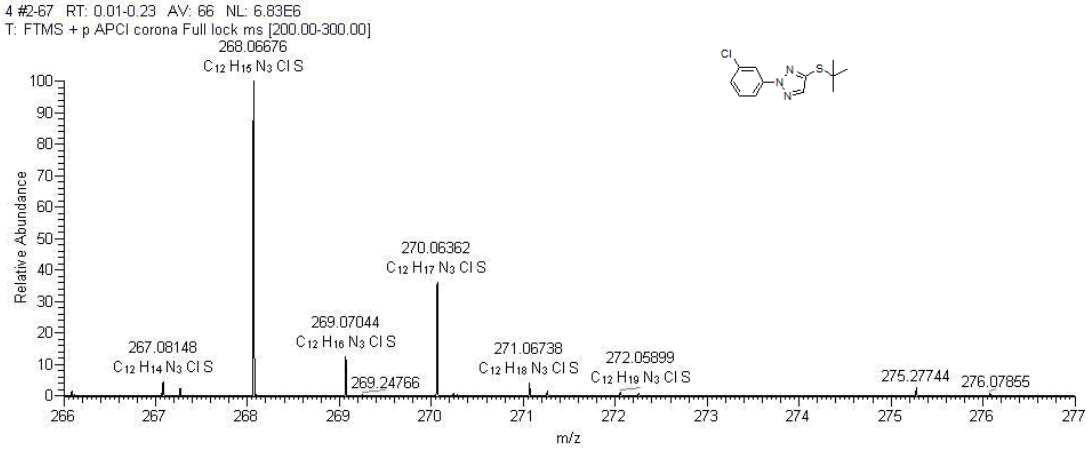
HRESIMS for **6ap**



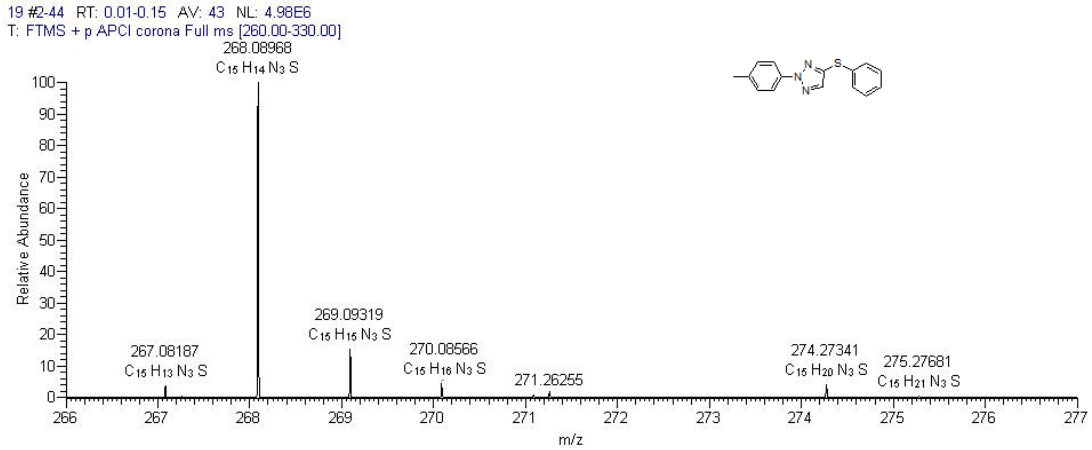
HRESIMS for **6aq**



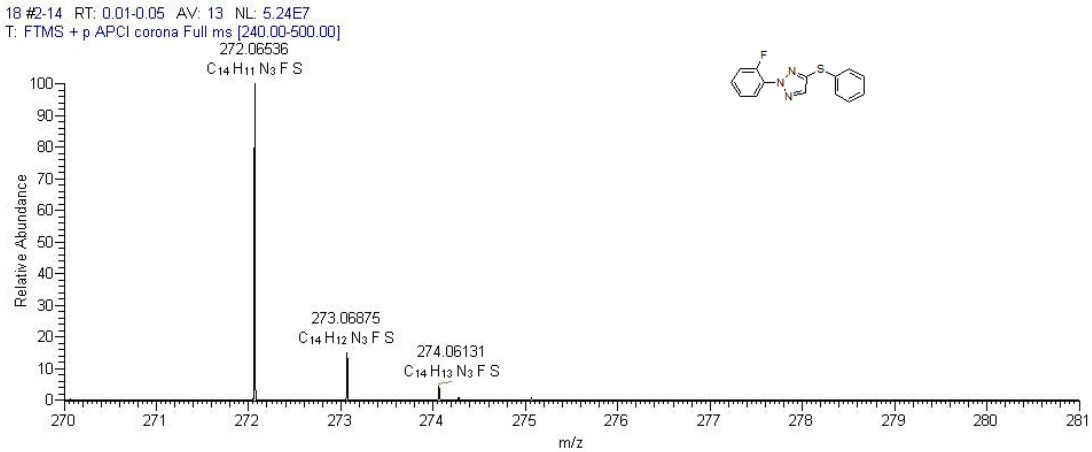
HRESIMS for **6ar**



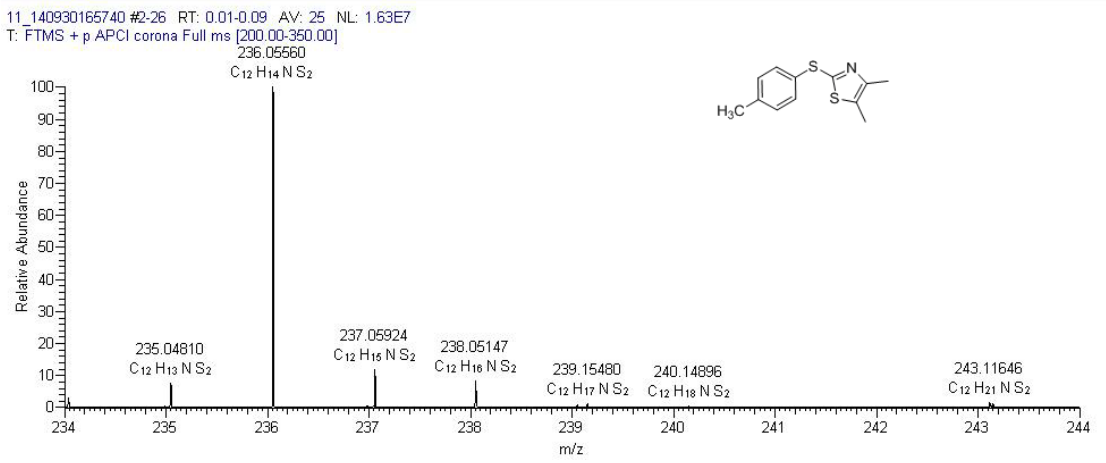
HRESIMS for **6ce**



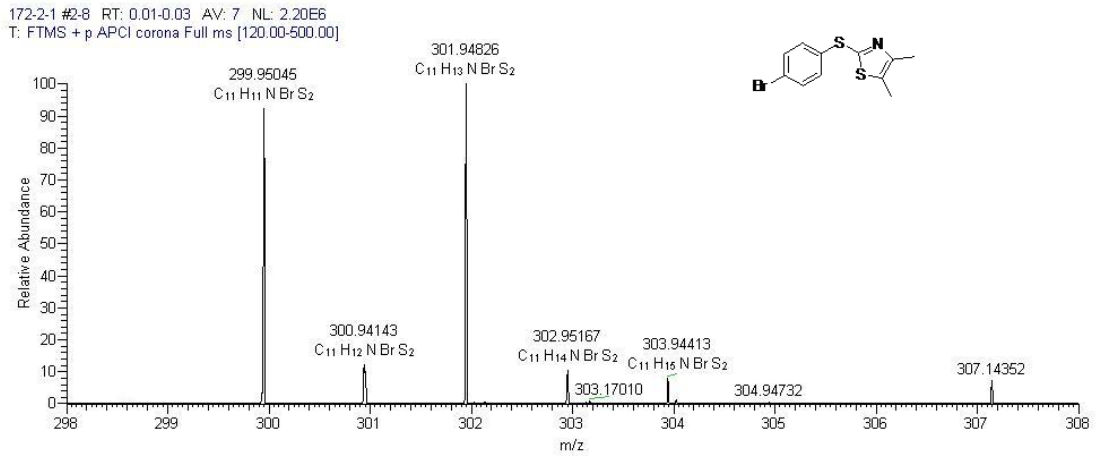
HRESIMS for **6ie**



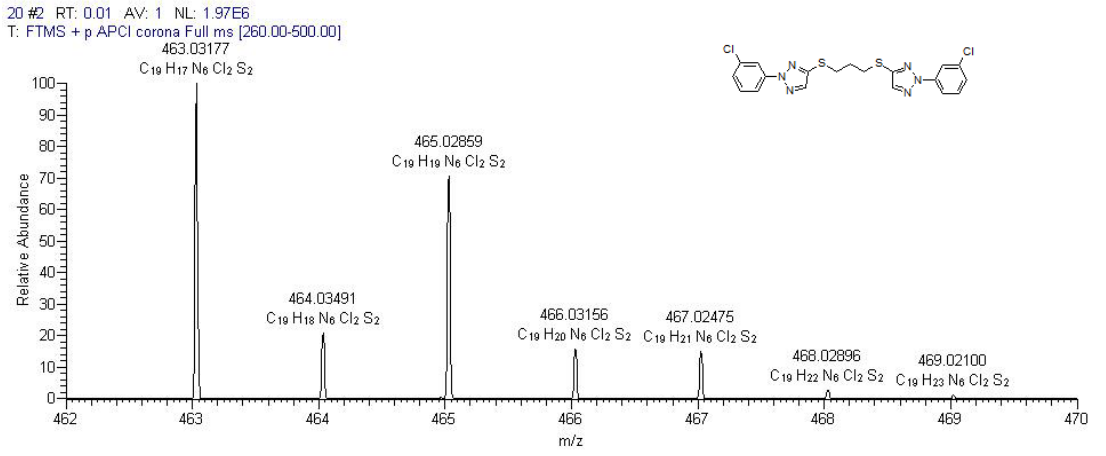
HRESIMS for **10a**



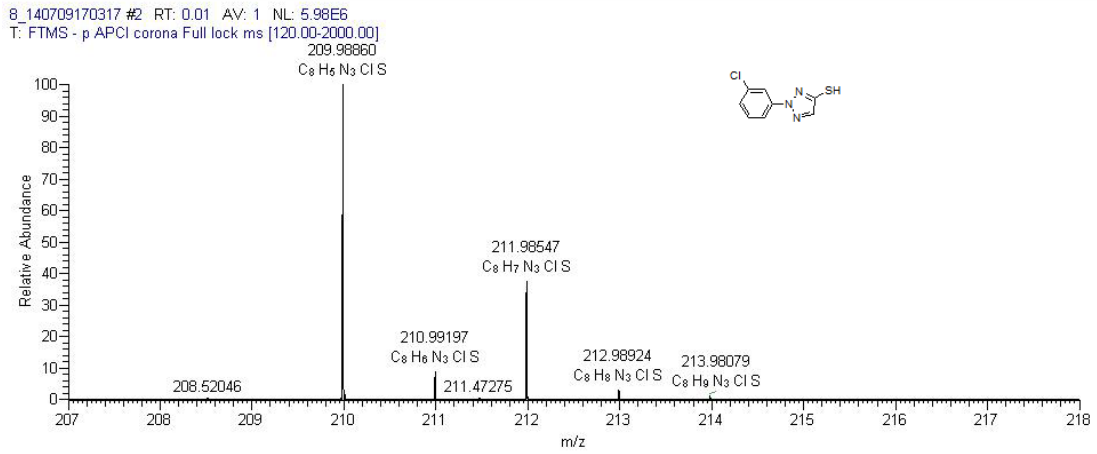
HRESIMS for **10b**



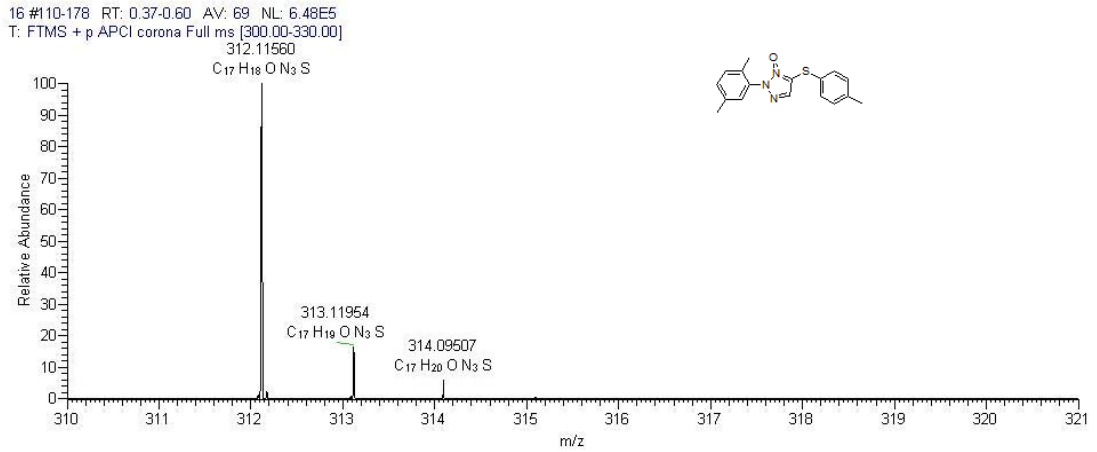
HRESIMS for **14**



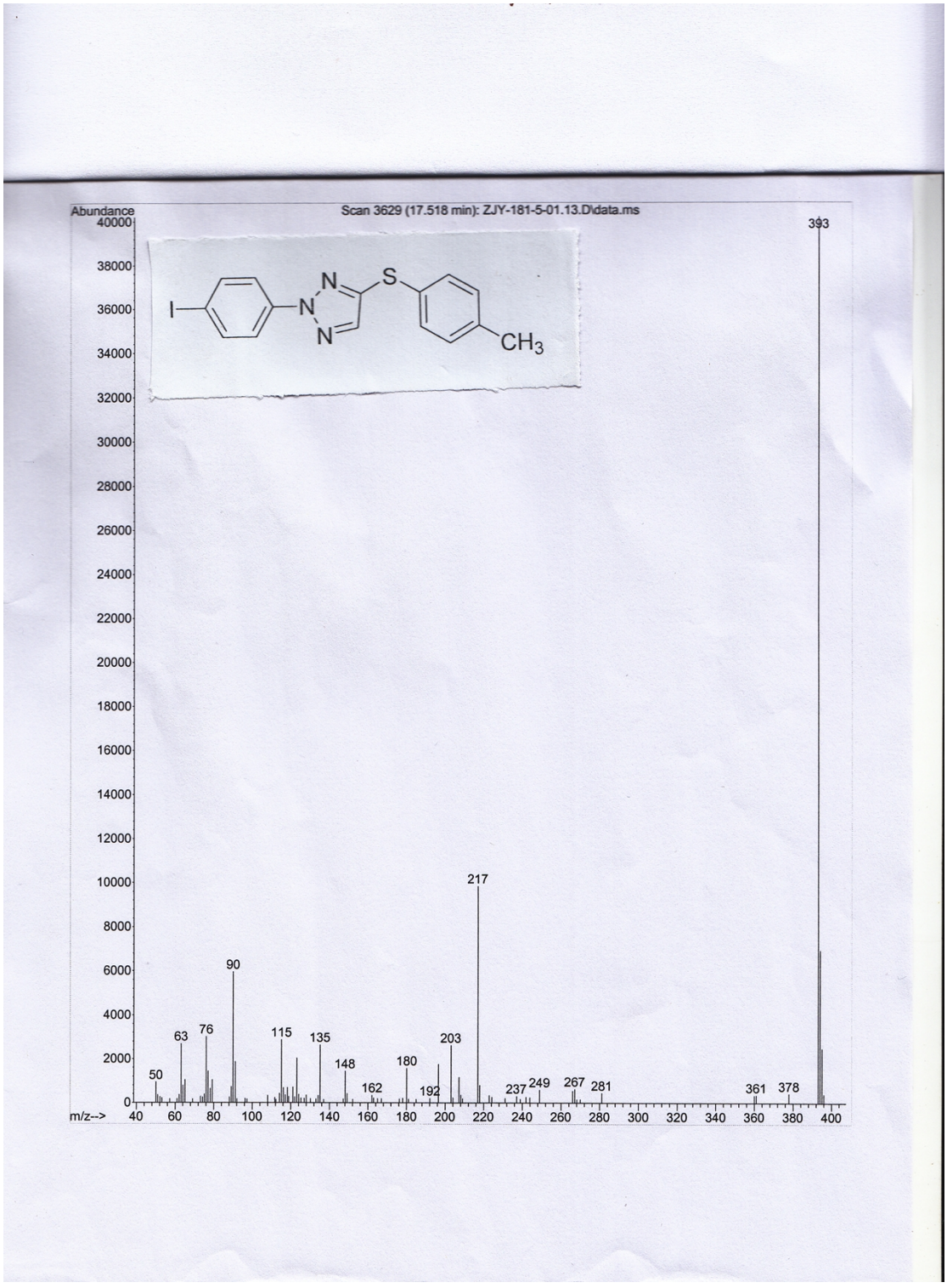
HRESIMS for **16**



HRESIMS for **19**



10. Copy of MS Spectra of Compound 6ka



11. X-ray Data of Compound 6lc

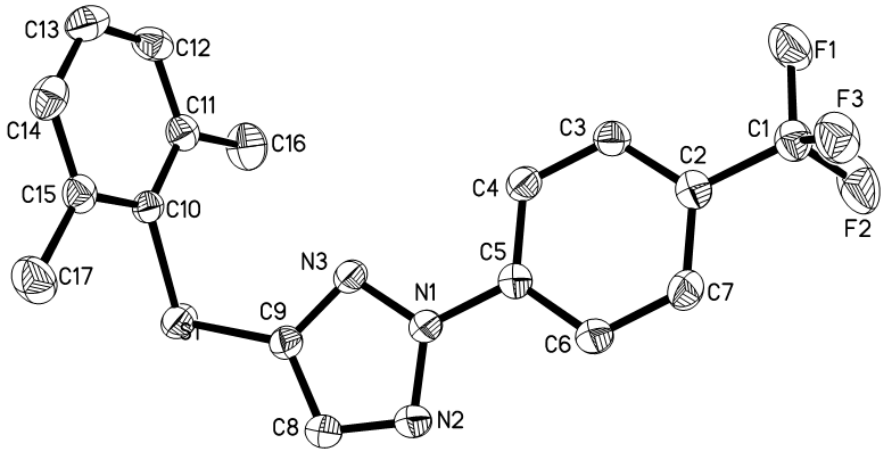


Figure **1**. ORTEP representation of the molecular structure of **6lc** with H atoms omitted for clarity.