

**Electronic Supplementary Information (ESI) for**  
**Rational design and synthesis of L-carvone-derived 4-methyl-1,2,4-triazole-**  
**thioether/nanochitosan complexes as potent nanopesticides for sustainable**  
**and efficient herbicidal application**

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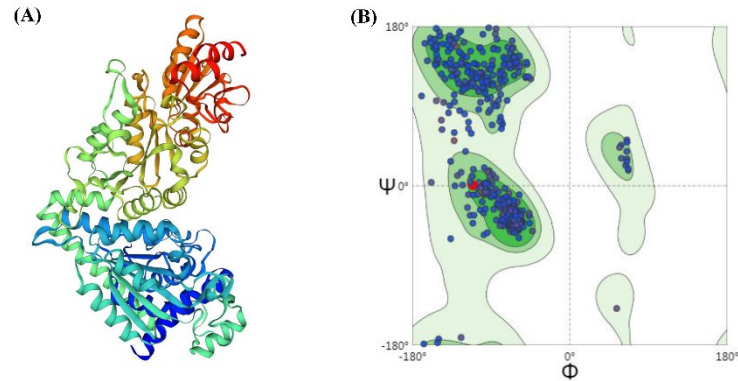
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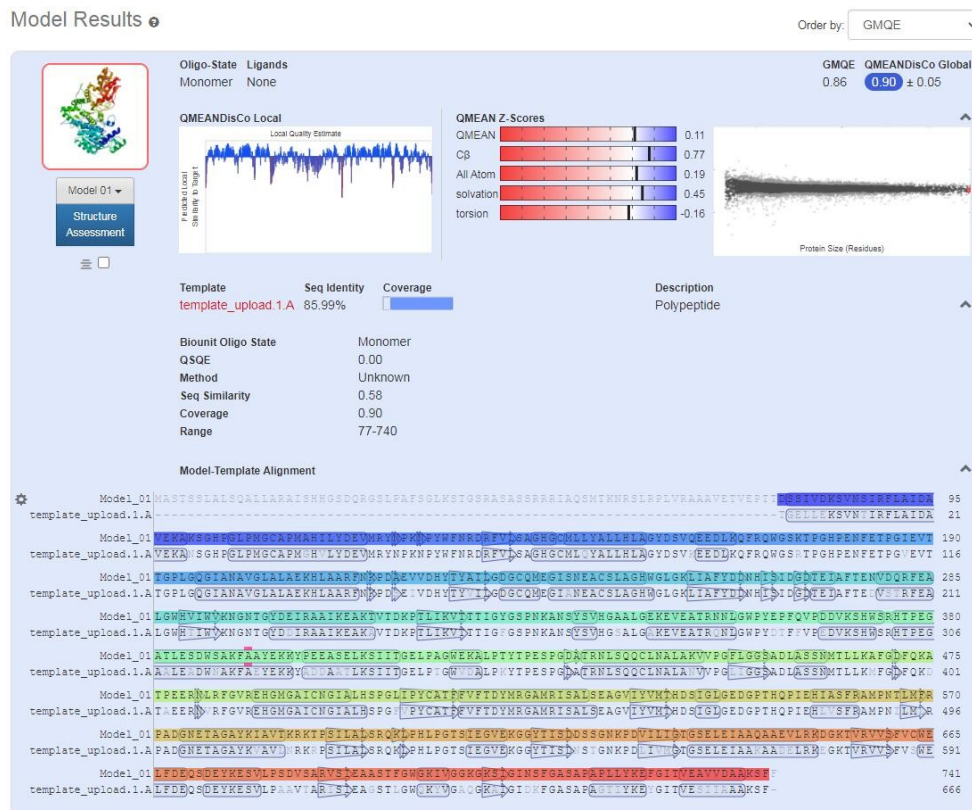
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# 1. Quality assessment of the 3D-structure of *Arabidopsis thaliana* transketolase (At TK) established by homology modeling



**Figure S1.** 3D structure (A) and Ramachandran plot (B) of the 3D-structure of *Arabidopsis thaliana* transketolase (*At TK*) established by homology modeling.



**Figure S2.** the results of the quality assessment of the 3D structure of *At TK* established by homology modeling.

## 2. Preparation of intermediates 2, 4a ~ 4u and 6

### Preparation of *L*-carvone chloride (2)

A mixture of *L*-carvone (5.04 g, 33.6 mmol) and dichloromethane (DCM, 60 mL) was added into an aqueous solution (60 mL) of NaH<sub>2</sub>PO<sub>4</sub> (8.08 g, 67.4 mmol). The above mixture was cooled in an ice bath, and then an aqueous solution of NaClO (reactive chlorine  $\geq$  7.5%, 60 mL) was dropwise added into the mixture. The resulting mixture was continuously stirred at room temperature for 4 h. Upon the completion of the reaction, the organic layer was separated, and the aqueous phase was extracted with DCM (30 mL  $\times$  3). The combined organic layer was concentrated in vacuum, and the residue was further purified by silica gel column chromatography (PE:EA = 50:1, v/v), to give a yellow oily liquid in the yield of 87.3%.

### Preparation of 5-substituted 4-methyl-1,2,4-triazole-3-thiols (4a ~ 4u)

Taking the preparation of intermediate **4a** as a representative, a mixture of methyl isothiocyanate (0.75 g, 10.2 mmol) and benzoyl hydrazine (**3a**, 1.37 g, 10.1 mmol) in ethanol (30 mL) was refluxed for 5 h. Upon completion of the reaction, the reaction mixtures were cooled down to room temperature, filtered and the residue was re-solved in an aqueous solution of NaOH (10%, 50 mL). The mixture was stirred and refluxed for 6 h. Then, the mixtures were cooled down to room temperature, and acidized with aqueous hydrochloric acid solution. Subsequently, a mass of white solid was precipitated and filtered off, which was further purified by recrystallization in ethanol. The other intermediates **4b** ~ **4u** were prepared by the analogous procedure from the corresponding aryl hydrazides (**3b** ~ **3u**), respectively.

### Preparation of *L*-carvone-derived epoxide (6)

To a solution of *L*-carvone (7.57 g, 50.4 mmol) in DCM (120 mL) under an ice bath, 3-chloroperoxybenzoic acid (*m*-CPBA, 9.98 g, 57.8 mmol) was added for several batches. The mixture was continually stirred at room temperature until the completion of the reaction indicated by TLC. Then, a saturated aqueous solution of NaHCO<sub>3</sub> (50 mL) was poured into the

mixture, and the organic layer was separated out. The organic layer was concentrated, and the crude product was further purified by silica gel column chromatography (PE:EA = 30:1, v/v), to give a colorless oily liquid in the yield of 88.4%.

### 3. Instrumental methods and information of all the characterization in this work

The UV-vis and IR spectra of compounds **5a** ~ **5u** were recorded by Shimadzu UV-1800 (in ethanol solution) and Nicolet iS50 FT-IR (in KBr tablet) spectrometers, respectively. Besides, the NMR and HRMS spectra of intermediate **2** and compounds **5a** ~ **5u** were determined on Bruker Avance III HD 600 MHz (chloroform-d as the solvent and TMS as the internal standard substance) and Thermo Scientific Q Exactive (APCI as ion source) instruments, respectively. The melting point of compound **5m** was measured by MP420 automatic melting point apparatus.

For qualitative determination of the grafting degrees of *L*-carvone-derived nanochitosan carriers **7a** ~ **7d**, their UV-vis spectra analyses along with that of chitosan were conducted by dissolving the tested carriers in 5% aqueous solution of HCl. The instrument information for the UV-vis spectra of carriers **7a** ~ **7d** and chitosan, FT-IR spectra of **7b** and chitosan, and <sup>1</sup>H/<sup>13</sup>C NMR spectra of intermediate **6** were as the description in the characterization of compounds **5a** ~ **5u**.

In addition, XRD and TG analyses of **7b** and Cs were performed on Rigaku Ultima IV X-ray diffractometer equipped with copper target and NETZSCH TG 209F3 thermal analyzer at a nitrogen flow rate of 20 mL/min, respectively. The size distribution of **7b** was characterized by Malvern Zetasizer Nano As instrument based on DLS technology. **7b** was stained with phosphomolybdic acid (1%), and then its TEM image was obtained on Thermo Scientific Talos F200i S transmission electron microscope. The micro-morphologies of **7b** ~ **7d** were observed on Zeiss Sigma 300 scanning electron microscope.

The HPLC analysis was carried out on a Waters 1525 instrument equipped with SunFire C18 column (5 μm, 4.6 mm×150 mm) and 2998 PDA detector, and the detected wavelength

was 238 nm. Moreover, the micro-morphology of complex **7b/5a** was also viewed by using Zeiss Sigma 300 scanning electron microscope, and compared with that of carrier **7b**.

#### 4. Spectra of compounds **2**, **5a** ~ **5u**, and **6**

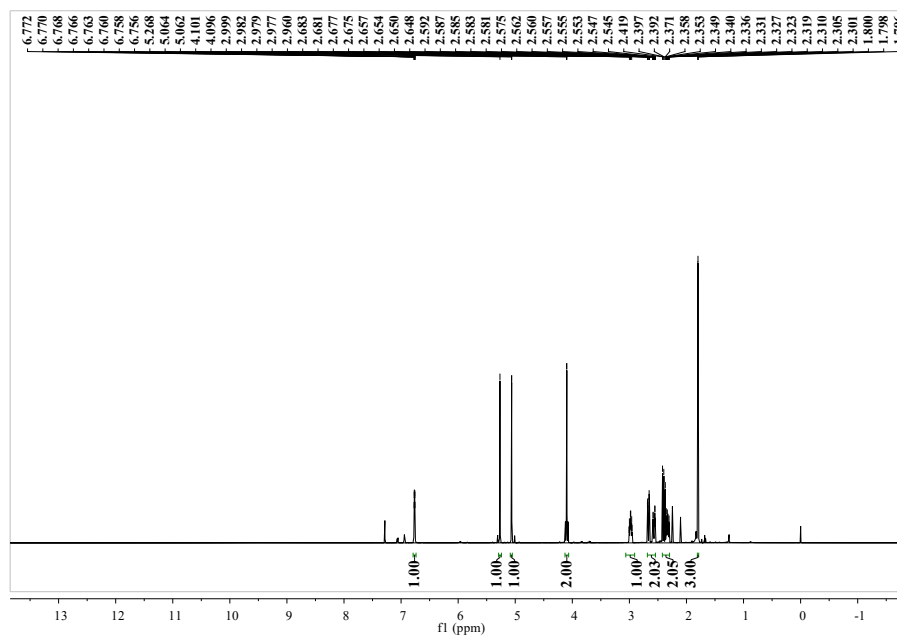


Figure S3  $^1\text{H}$  NMR spectrum of compound **2**.

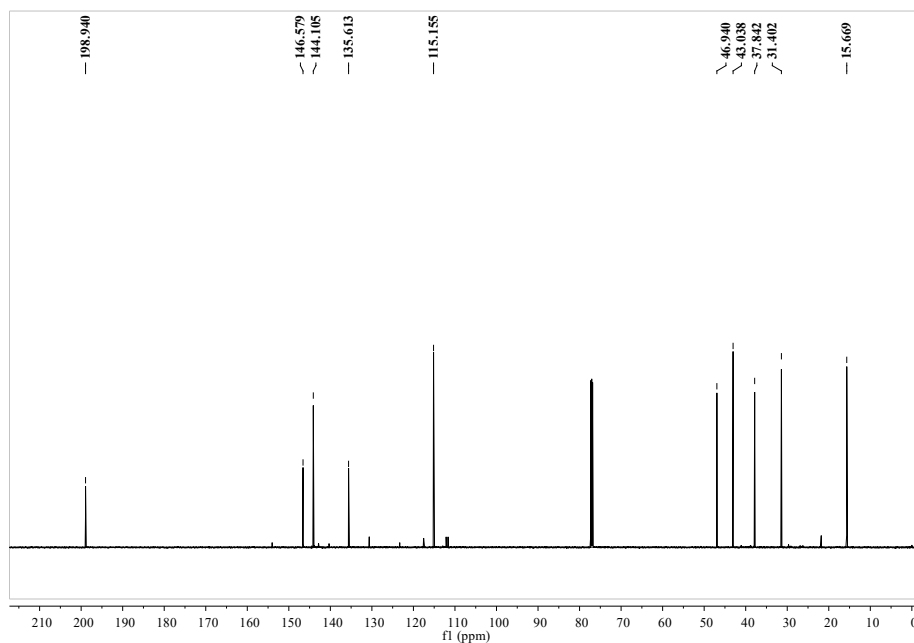


Figure S4  $^{13}\text{C}$  NMR spectrum of compound **2**.

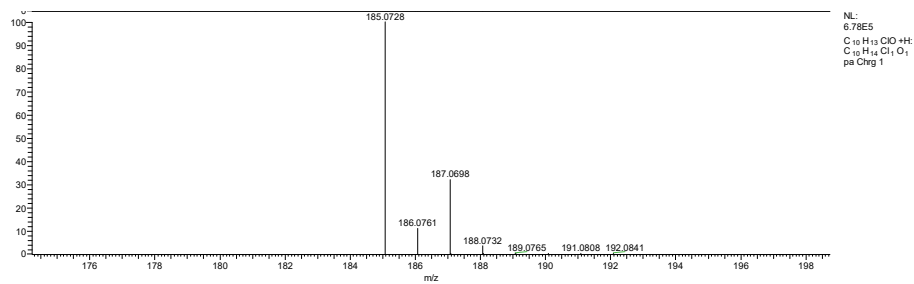


Figure S5 HRMS spectrum of compound 2.

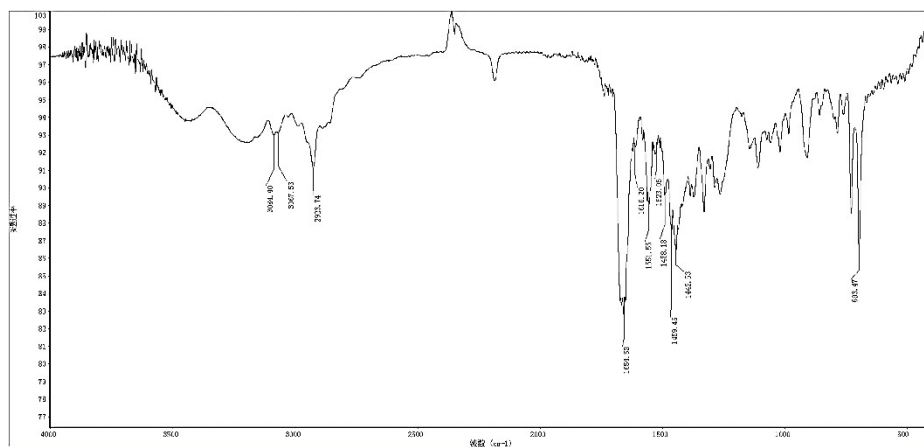


Figure S6 IR spectrum of compound 5a.

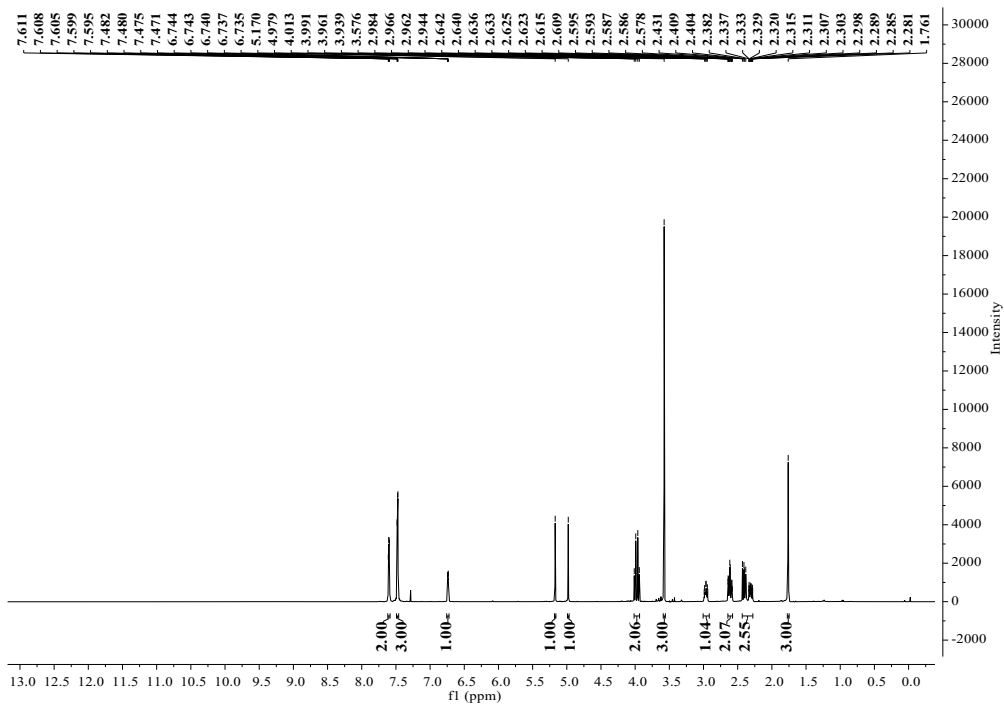


Figure S7 <sup>1</sup>H NMR spectrum of compound 5a.

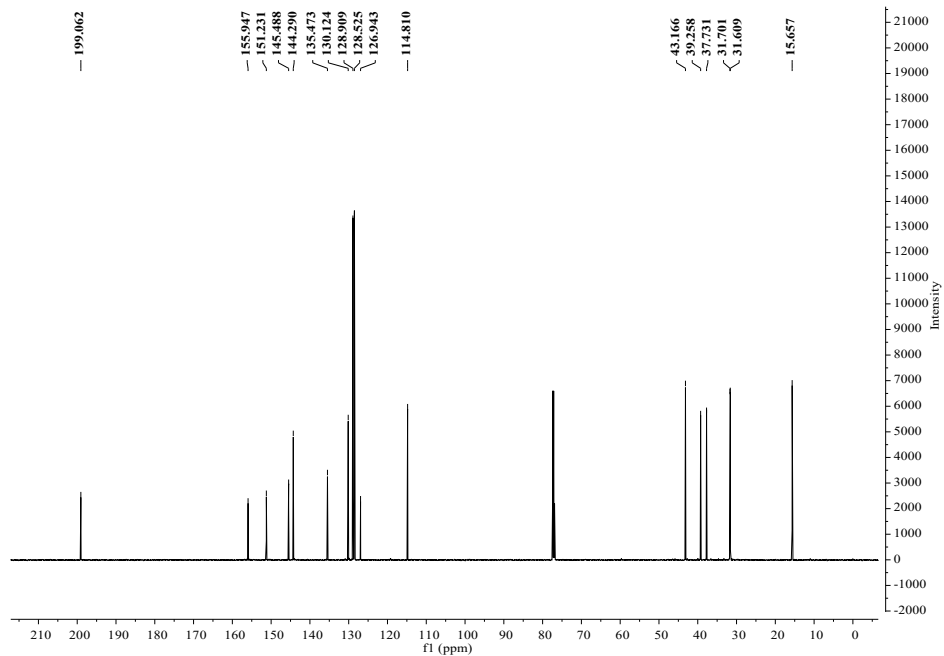


Figure S8  $^{13}\text{C}$  NMR spectrum of compound **5a**.

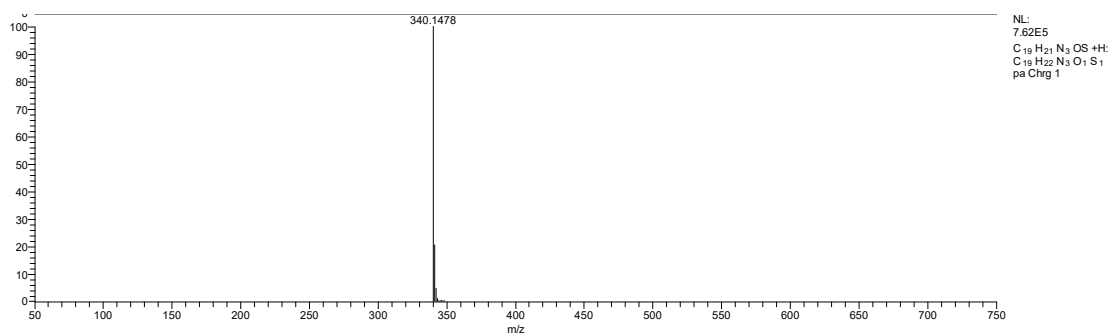


Figure S9 HRMS spectrum of compound **5a**.

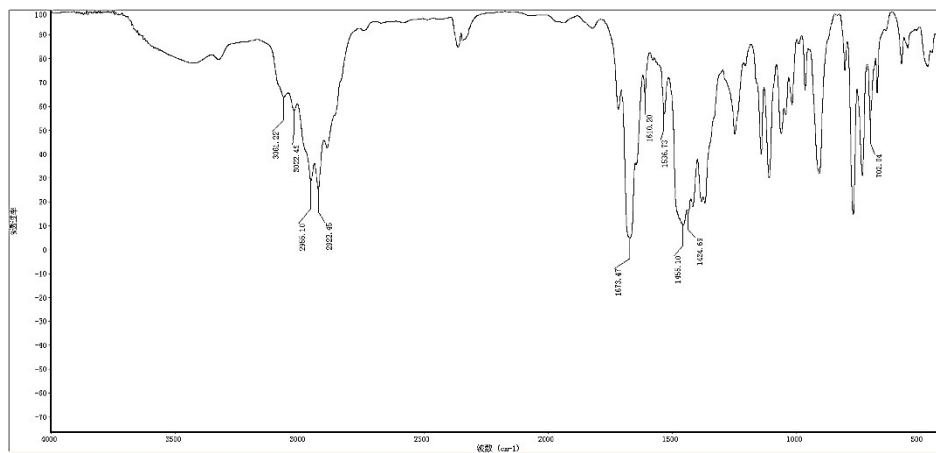


Figure S10 IR spectrum of compound **5b**.

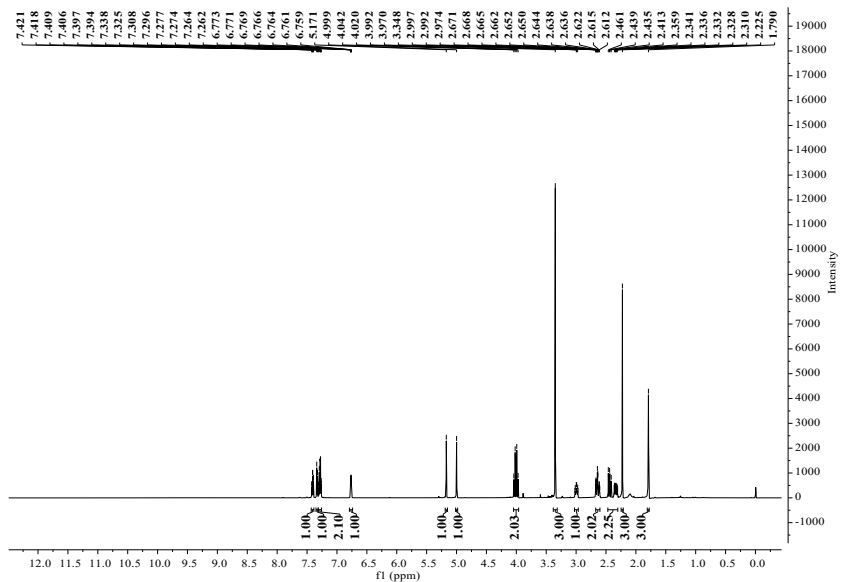


Figure S11  $^1\text{H}$  NMR spectrum of compound **5b**.

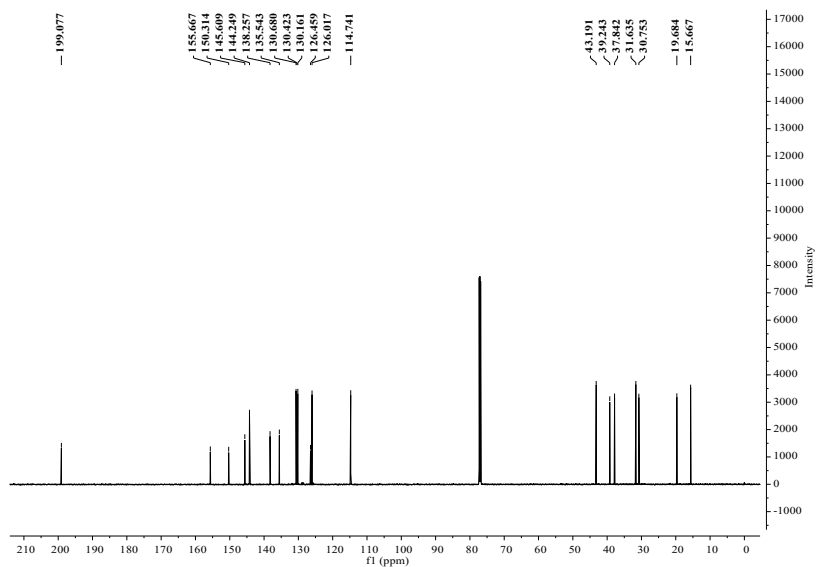


Figure S12  $^{13}\text{C}$  NMR spectrum of compound **5b**.

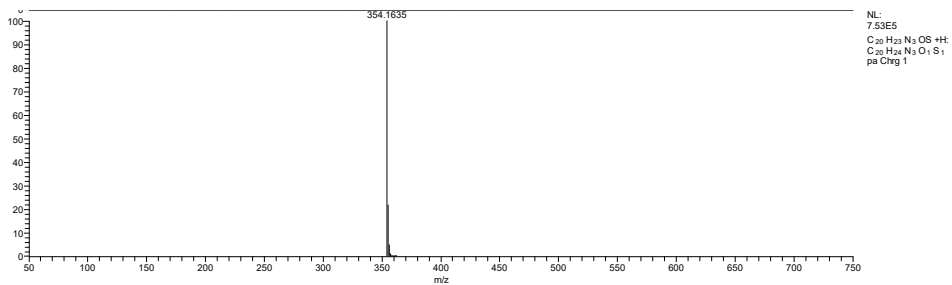


Figure S13 HRMS spectrum of compound **5b**.



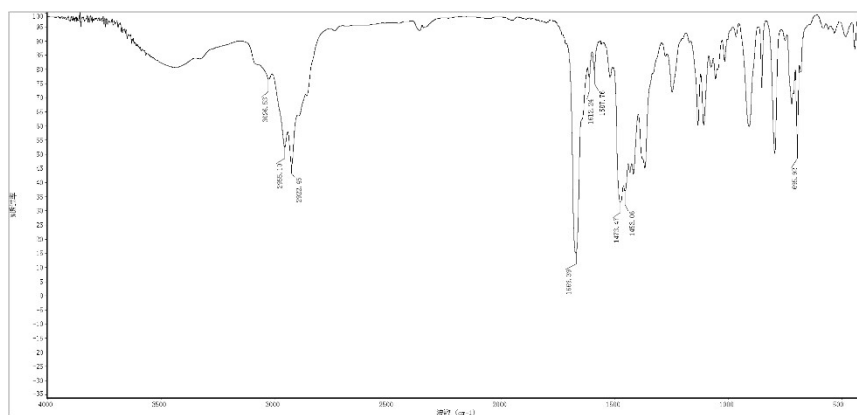


Figure S14 IR spectrum of compound **5c**.

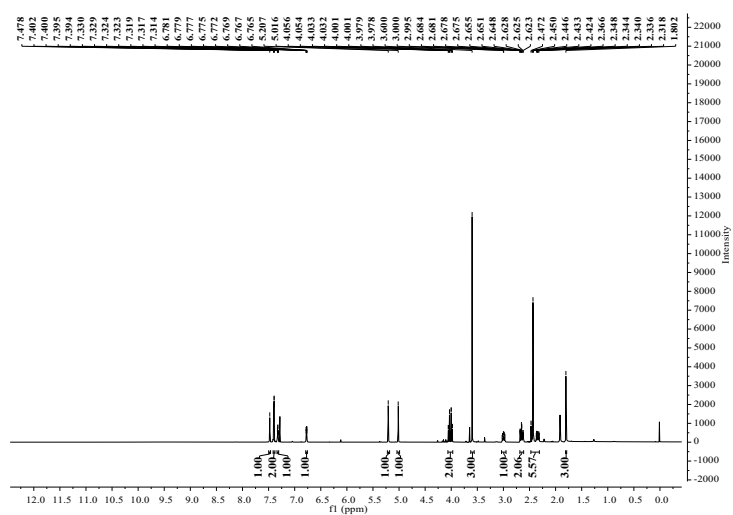


Figure S15  $^1\text{H}$  NMR spectrum of compound **5c**.

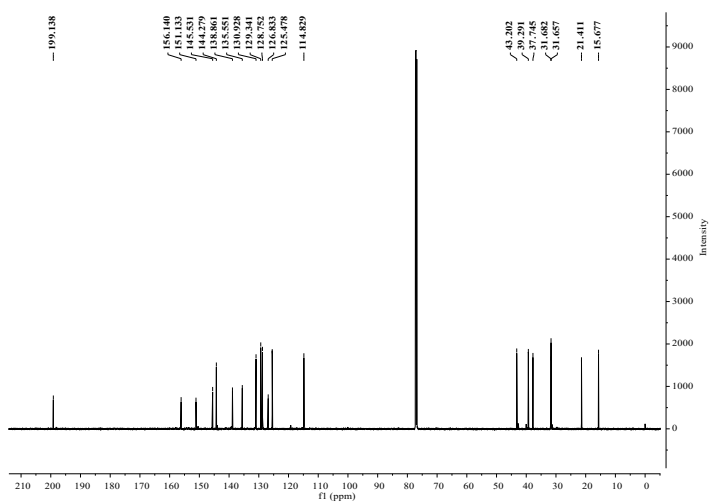


Figure S16  $^{13}\text{C}$  NMR spectrum of compound **5c**.

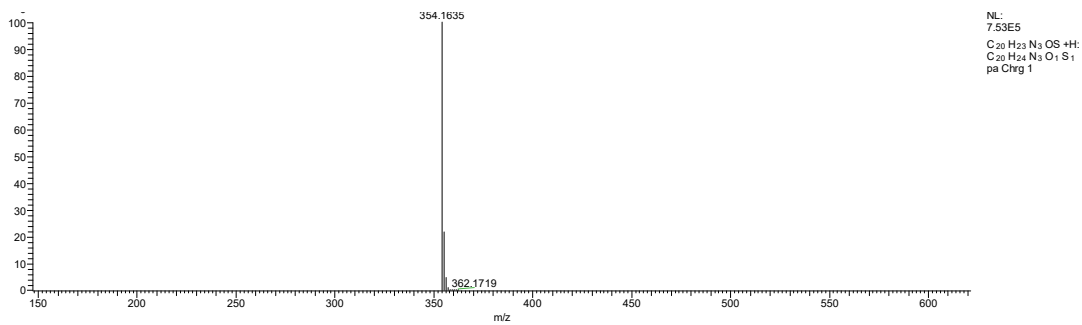


Figure S17 HRMS spectrum of compound 5c.

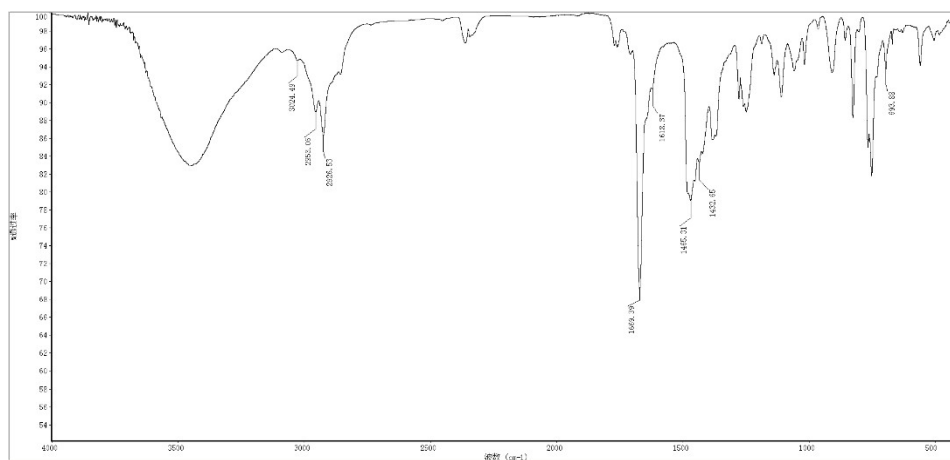


Figure S18 IR spectrum of compound 5d.

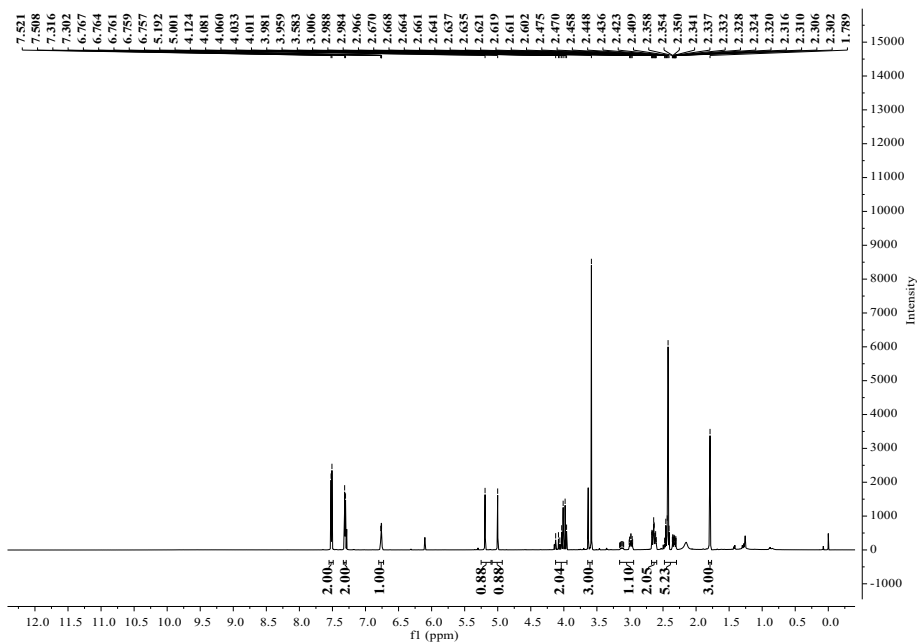


Figure S19 <sup>1</sup>H NMR spectrum of compound 5d.

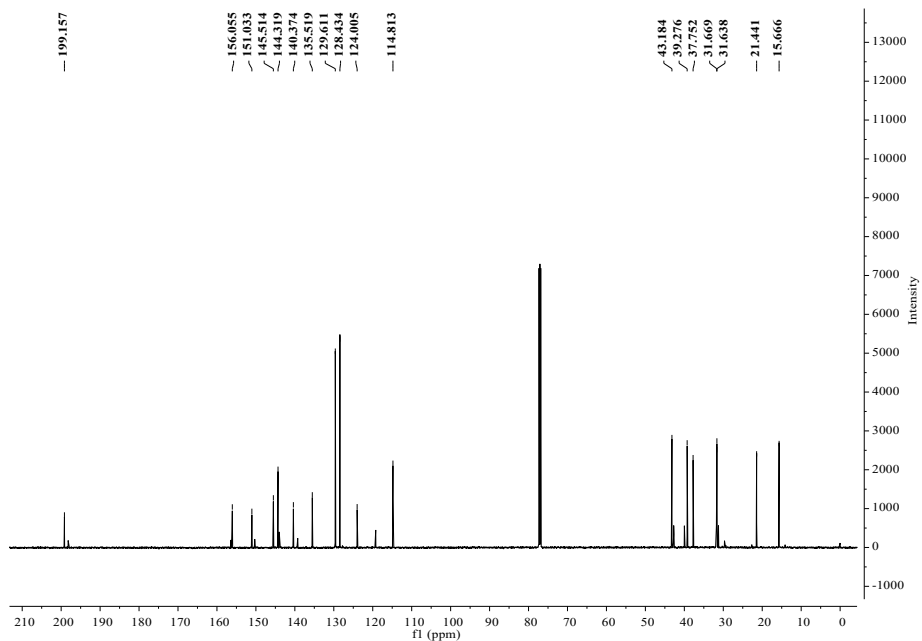


Figure S20  $^{13}\text{C}$  NMR spectrum of compound **5d**.

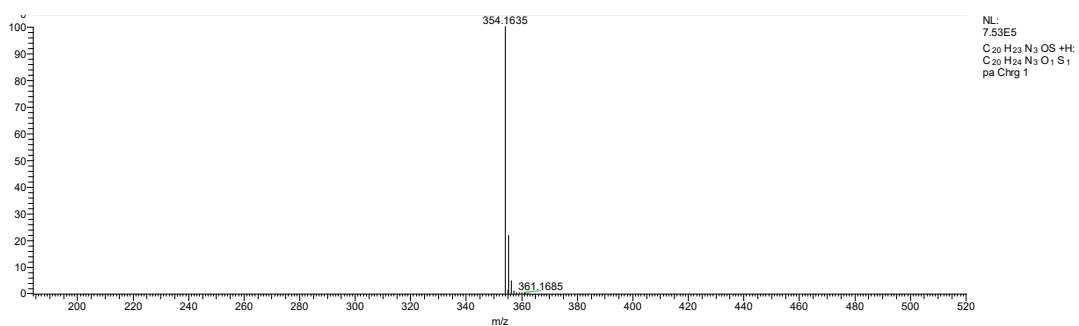


Figure S21 HRMS spectrum of compound **5d**.

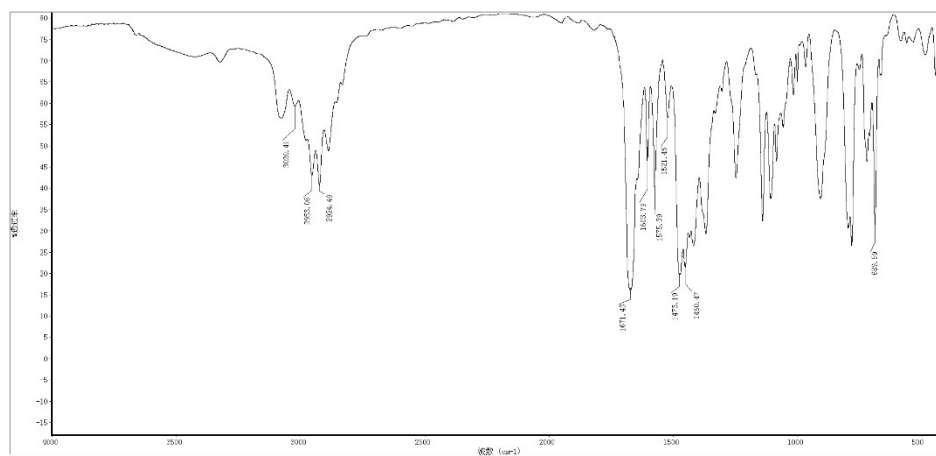


Figure S22 IR spectrum of compound **5e**.

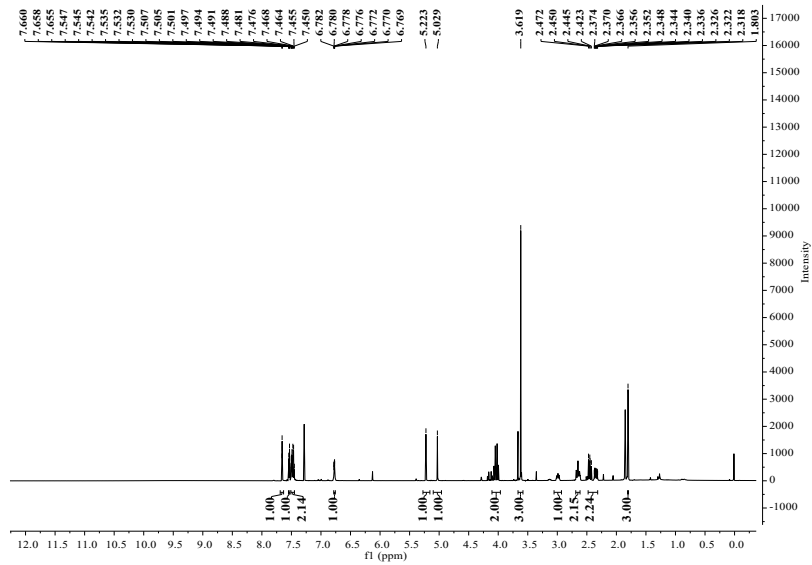


Figure S23  $^1\text{H}$  NMR spectrum of compound **5e**.

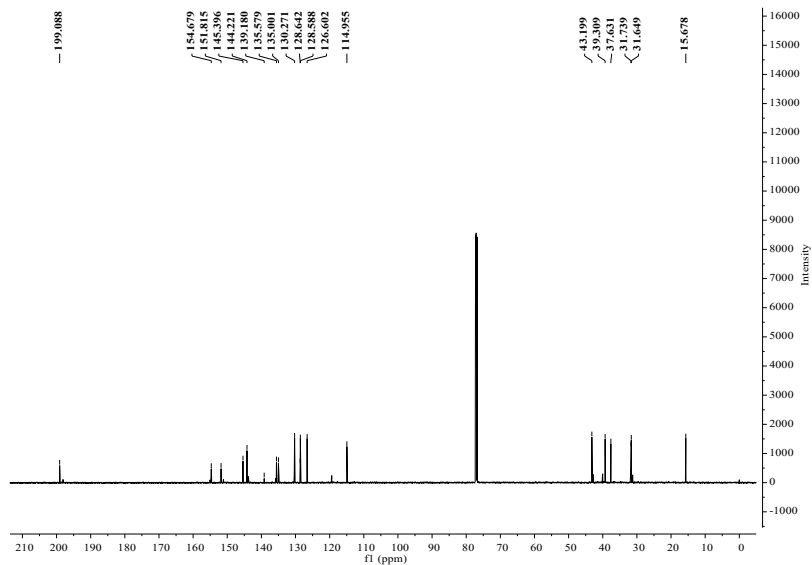


Figure S24  $^{13}\text{C}$  NMR spectrum of compound **5e**.

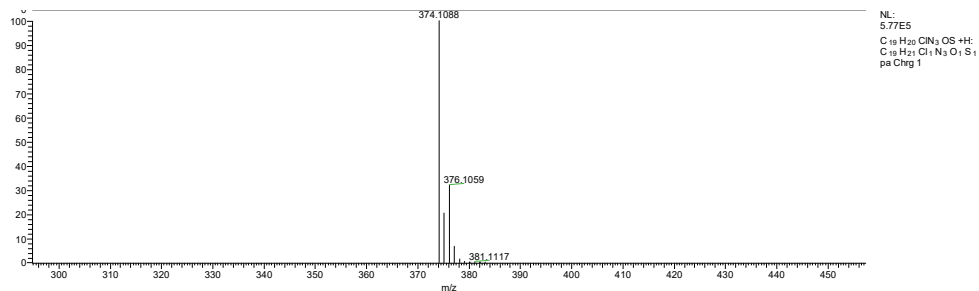


Figure S25 HRMS spectrum of compound **5e**.

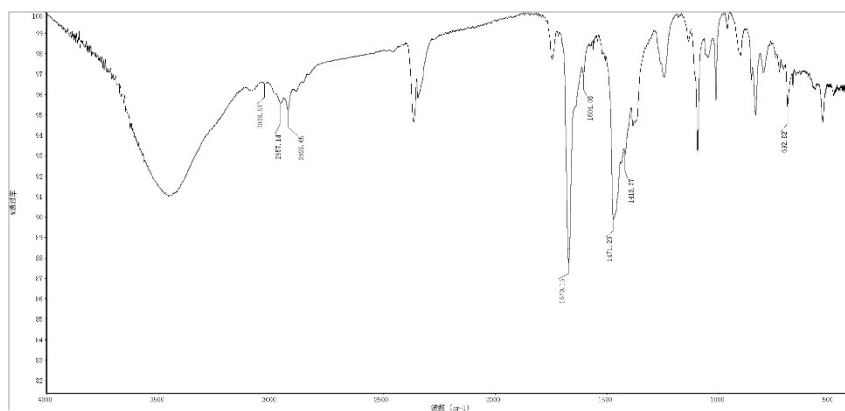


Figure S26 IR spectrum of compound 5f.

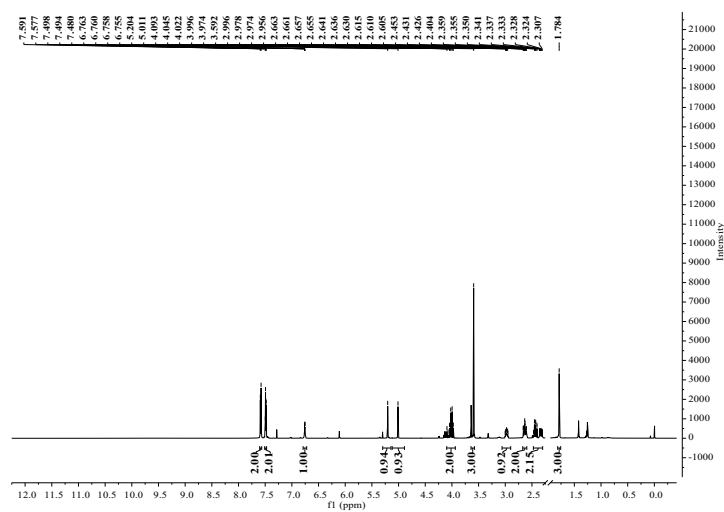


Figure S27 <sup>1</sup>H NMR spectrum of compound 5f.

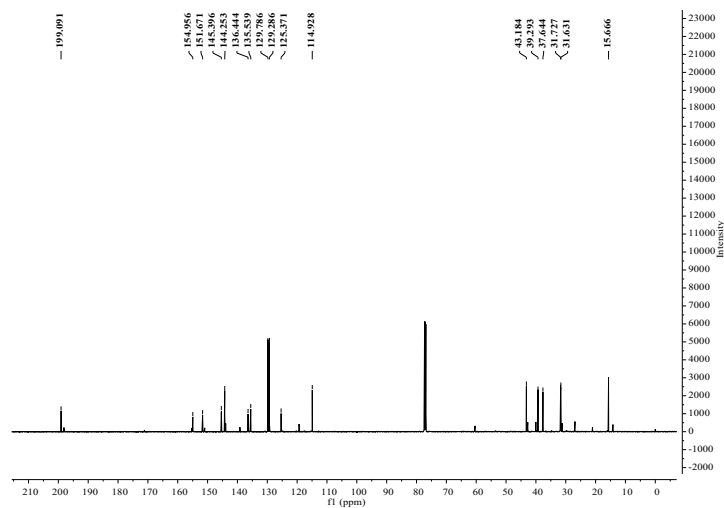


Figure S28 <sup>13</sup>C NMR spectrum of compound 5f.

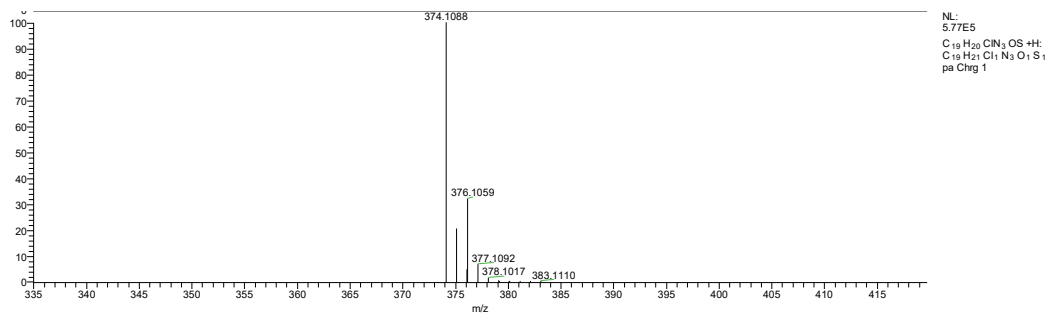


Figure S29 HRMS spectrum of compound **5f**.

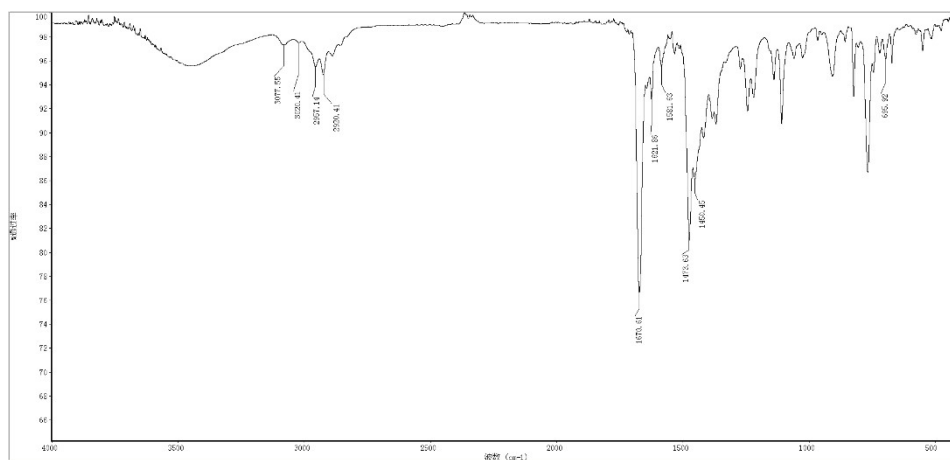


Figure S30 IR spectrum of compound **5g**.

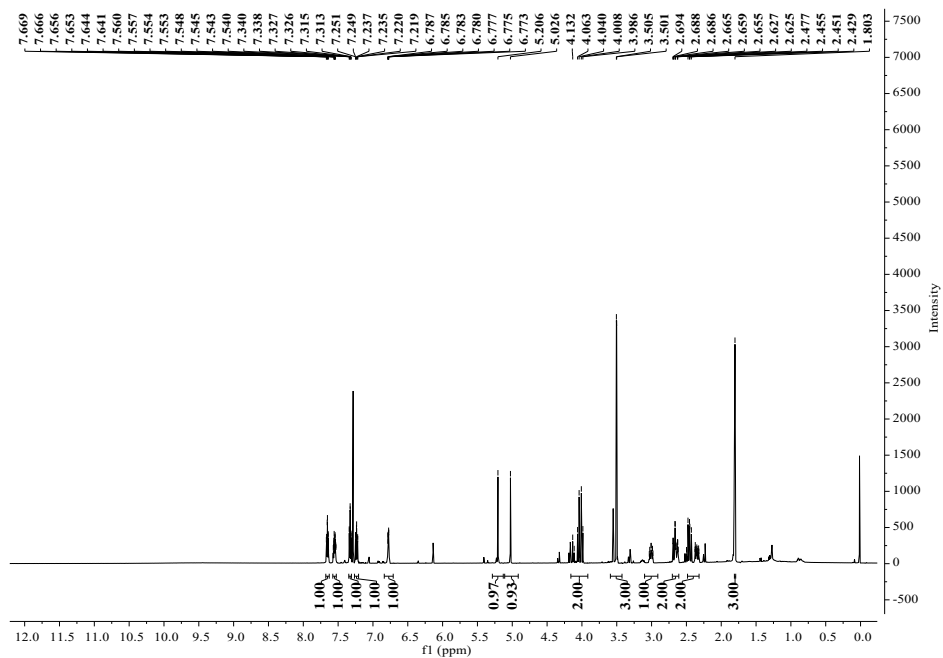


Figure S31 <sup>1</sup>H NMR spectrum of compound **5g**.

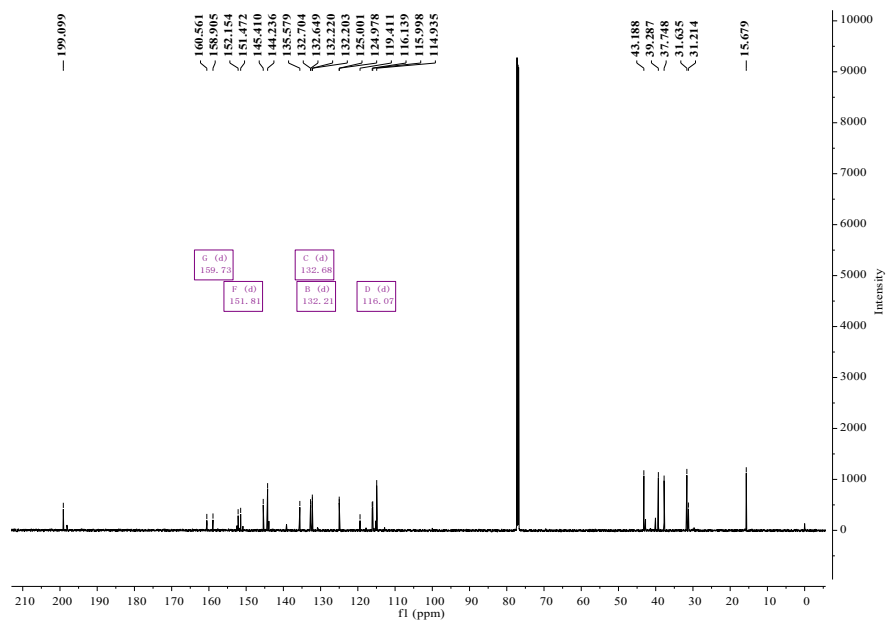


Figure S32  $^{13}\text{C}$  NMR spectrum of compound **5g**.

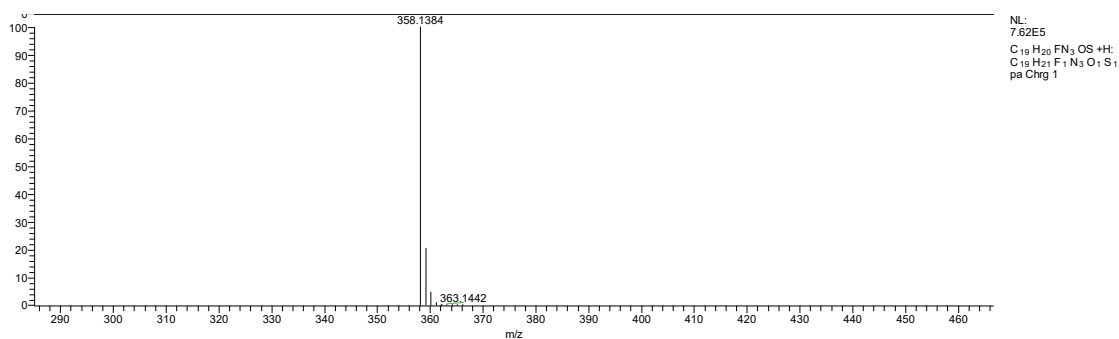


Figure S33 HRMS spectrum of compound **5g**.

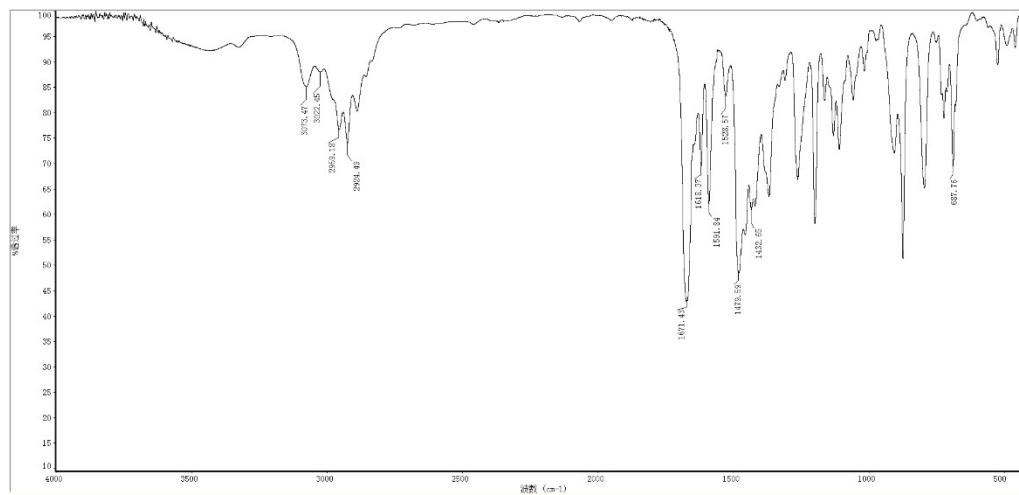


Figure S34 IR spectrum of compound **5h**.







Figure S40  $^{13}\text{C}$  NMR spectrum of compound **5i**.

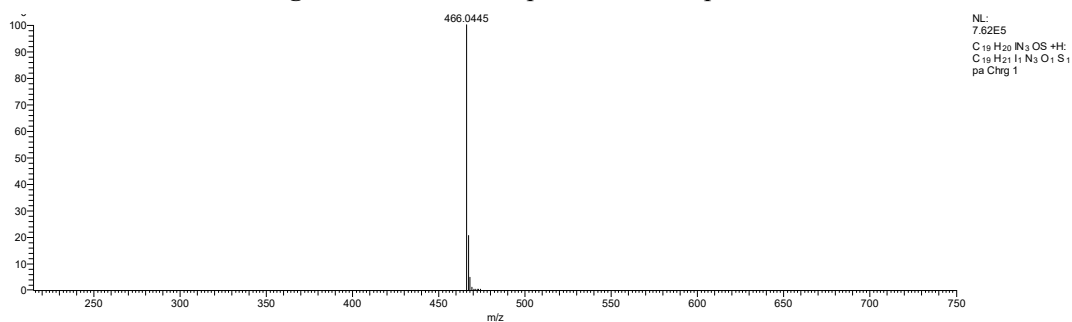


Figure S41 HRMS spectrum of compound **5i**.

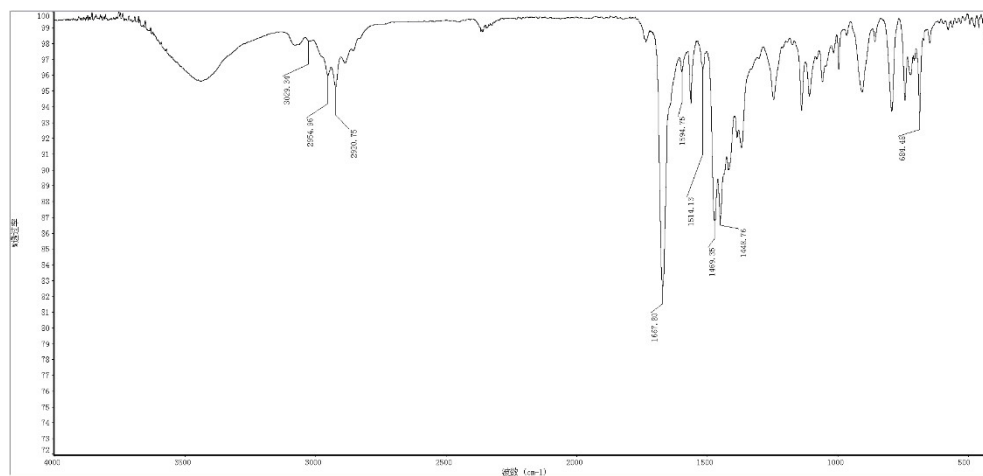


Figure S42 IR spectrum of compound **5j**.

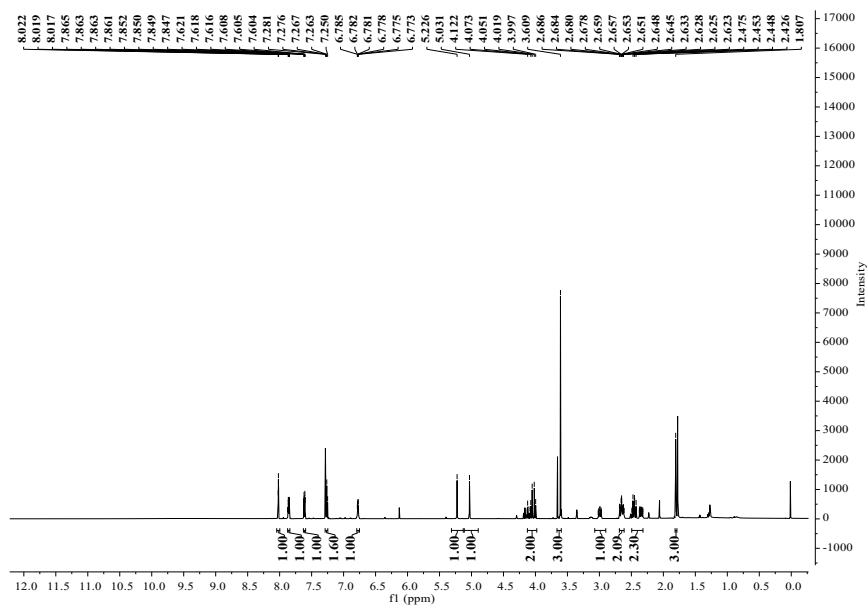


Figure S43 <sup>1</sup>H NMR spectrum of compound 5j.

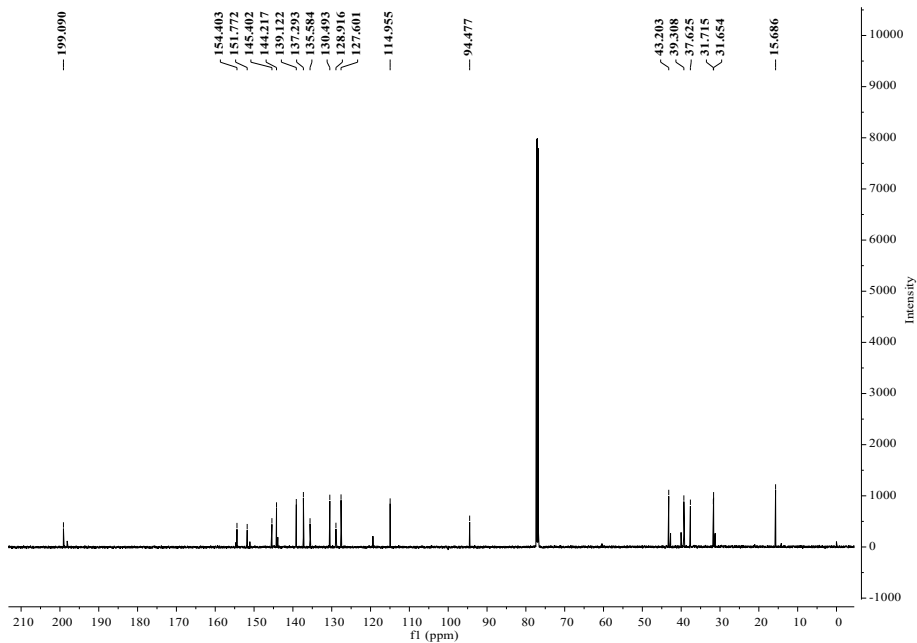


Figure S44 <sup>13</sup>C NMR spectrum of compound 5j.

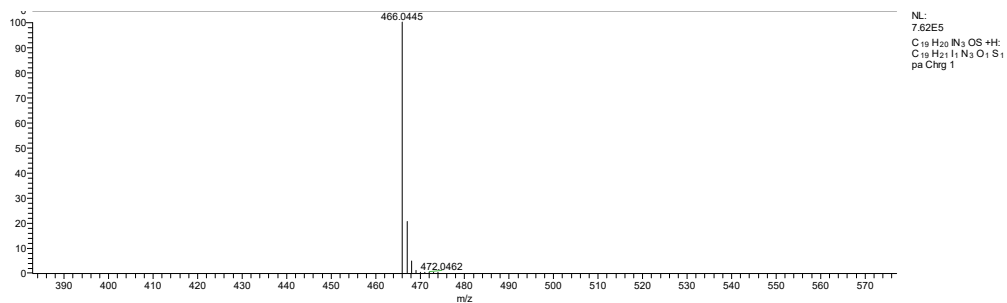


Figure S45 HRMS spectrum of compound 5j.

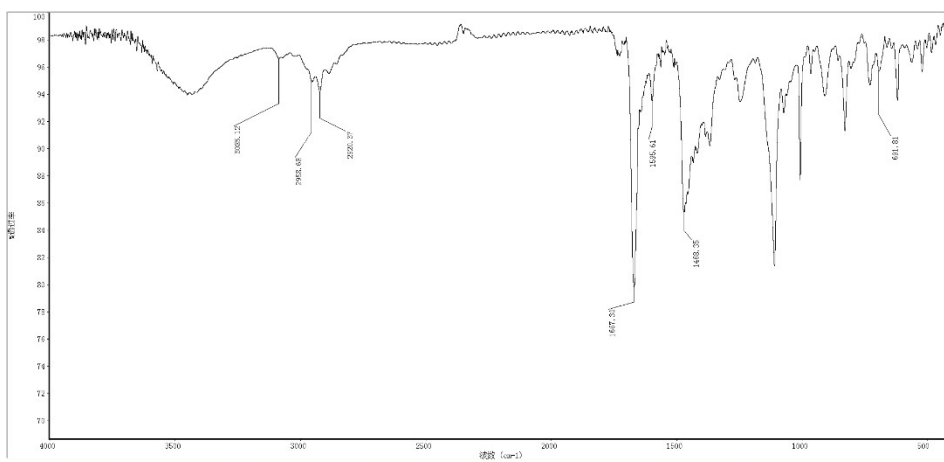


Figure S46 IR spectrum of compound 5k.

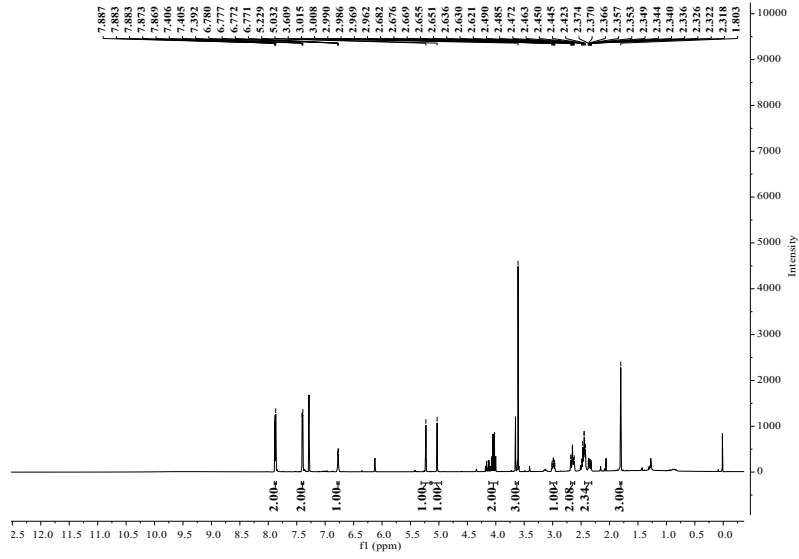


Figure S47 <sup>1</sup>H NMR spectrum of compound 5k.

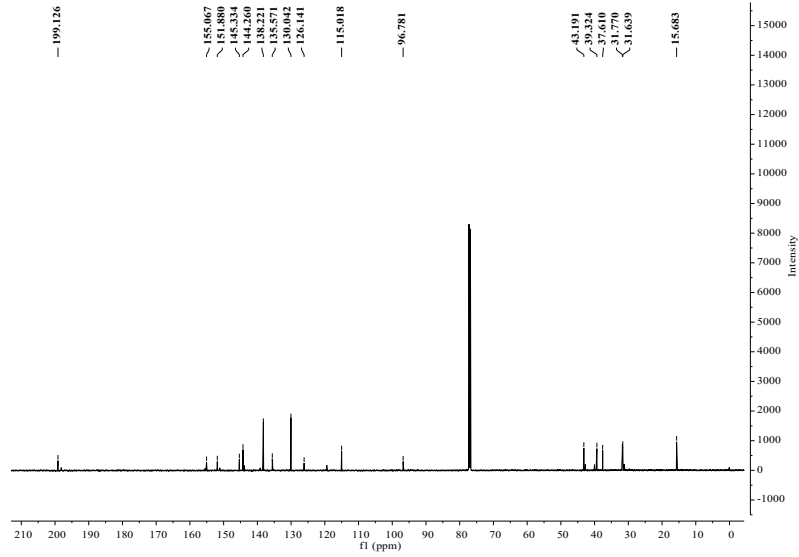


Figure S48 <sup>13</sup>C NMR spectrum of compound 5k.

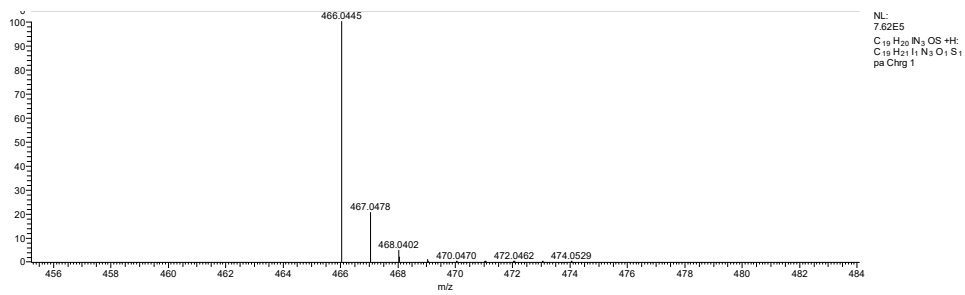


Figure S49 HRMS spectrum of compound 5k.

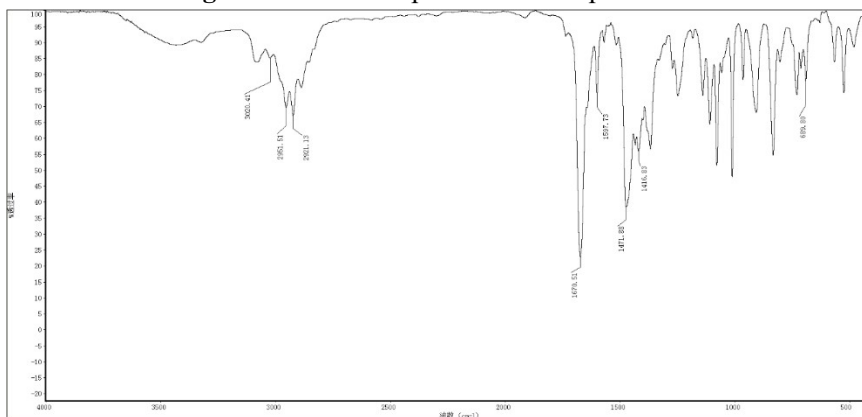


Figure S50 IR spectrum of compound 5l.

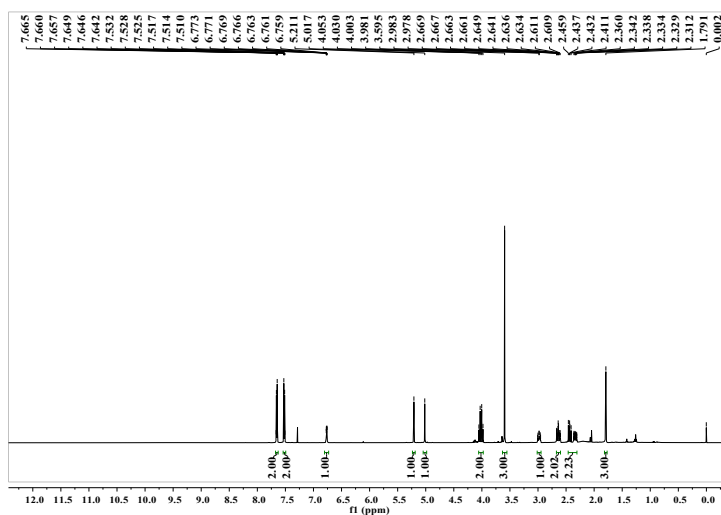


Figure S51 <sup>1</sup>H NMR spectrum of compound 5l.

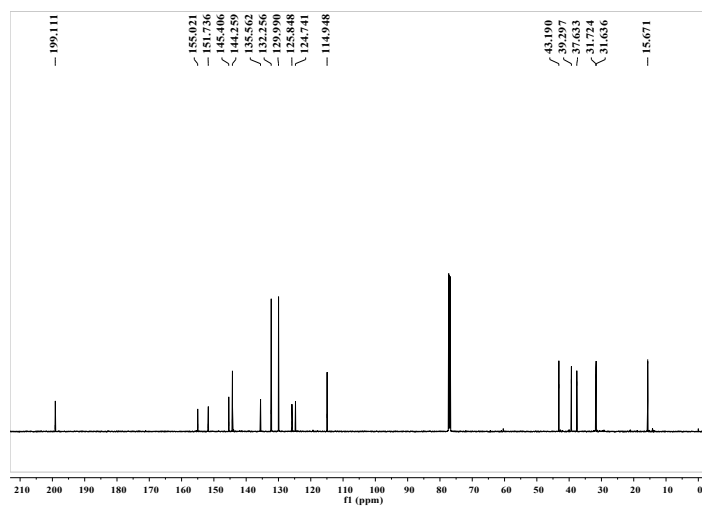


Figure S52  $^{13}\text{C}$  NMR spectrum of compound 5l.

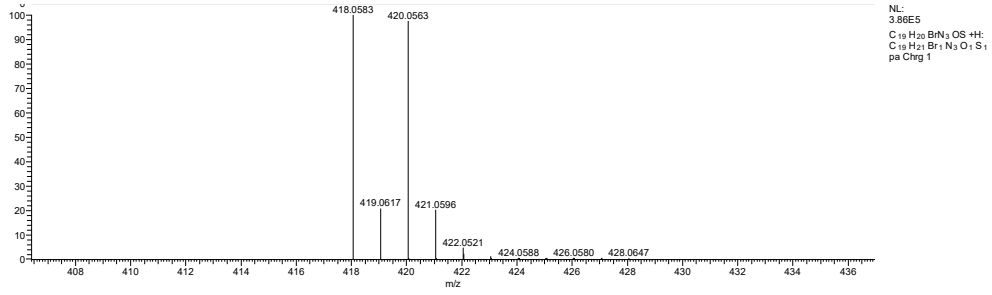


Figure S53 HRMS spectrum of compound 5l.

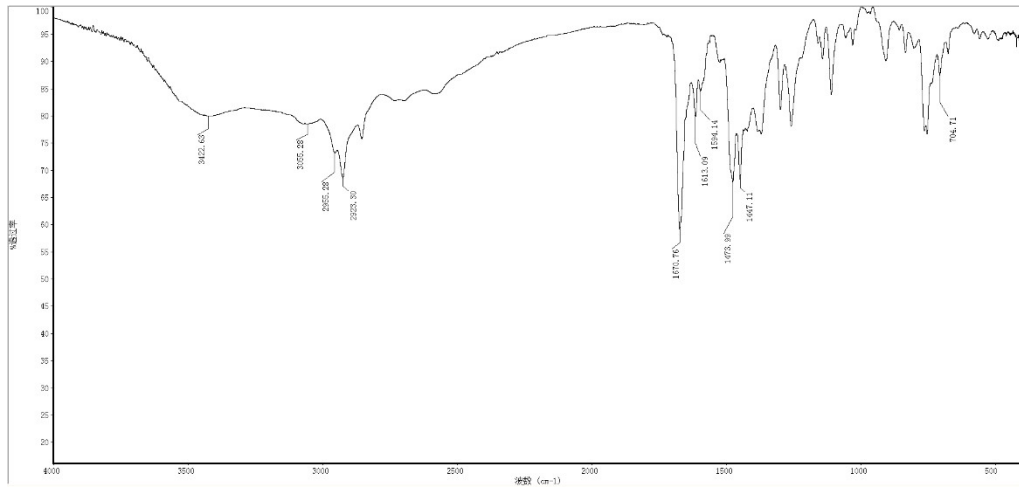


Figure S54 IR spectrum of compound 5m.

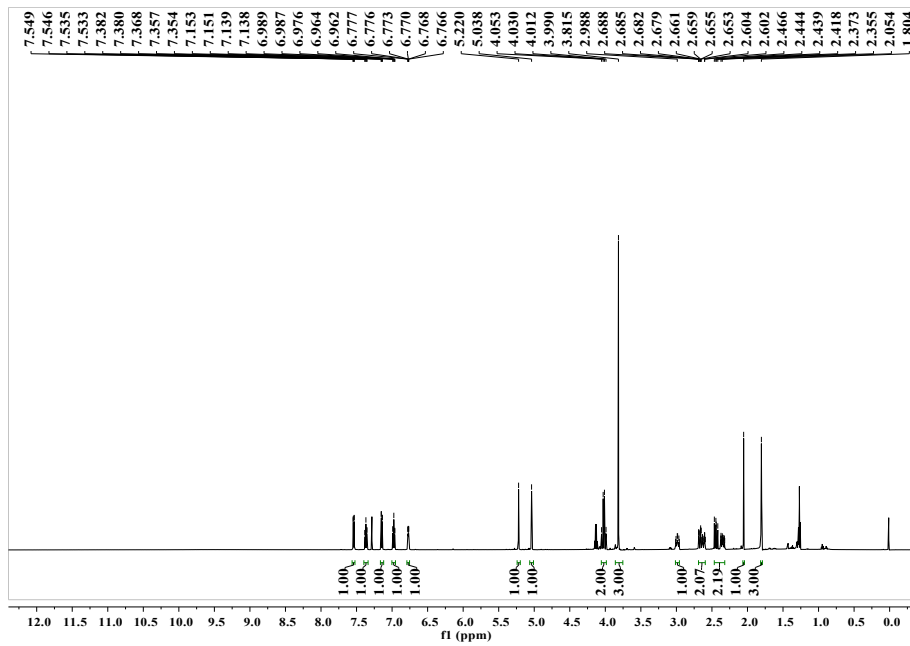


Figure S55  $^1\text{H}$  NMR spectrum of compound **5m**.

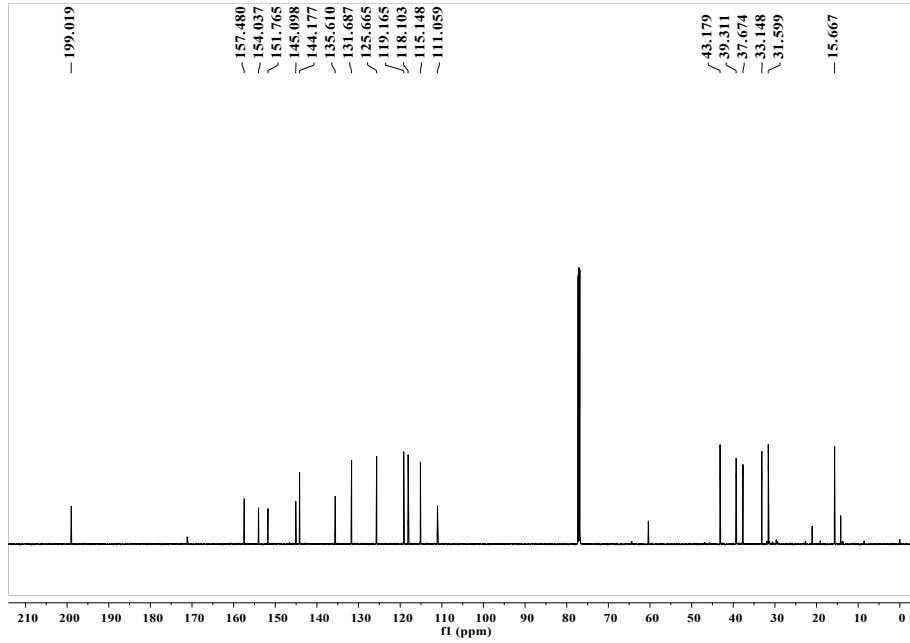


Figure S56  $^{13}\text{C}$  NMR spectrum of compound **5m**.

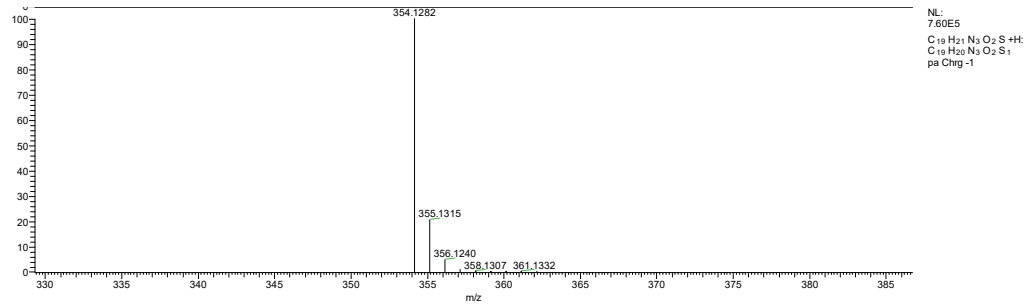


Figure S57 HRMS spectrum of compound **5m**.

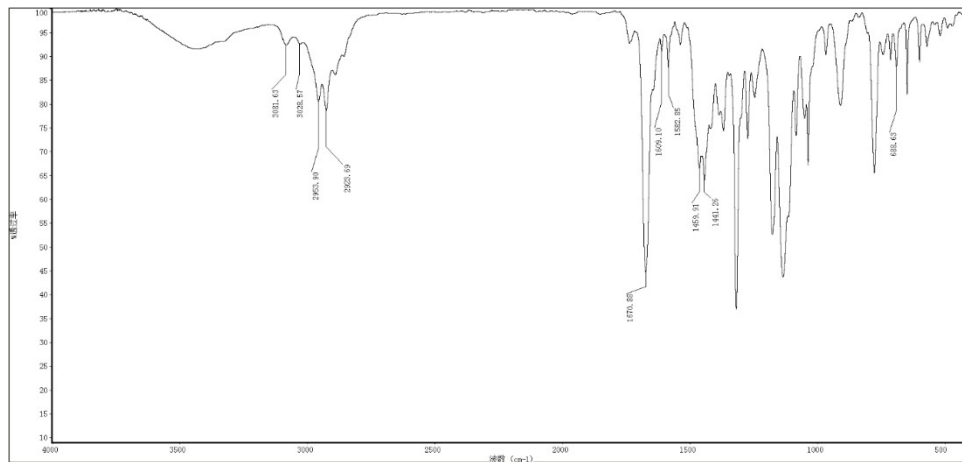


Figure S58 IR spectrum of compound 5n.

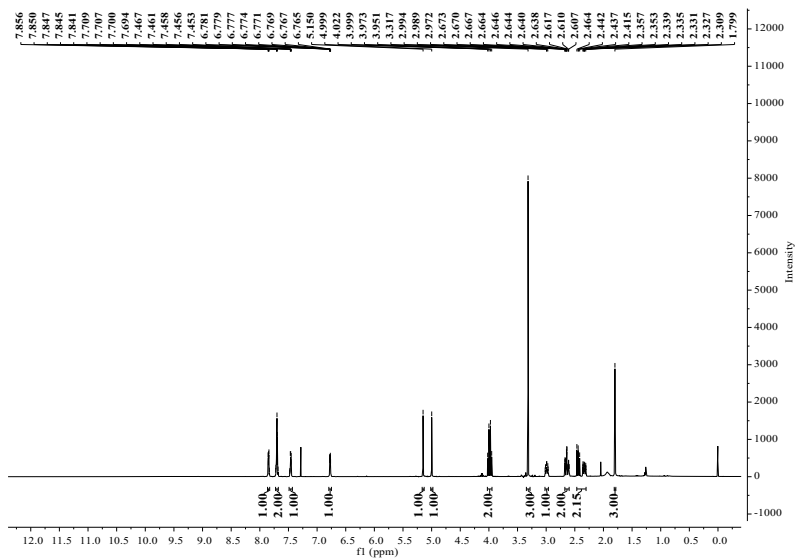


Figure S59 <sup>1</sup>H NMR spectrum of compound 5n.

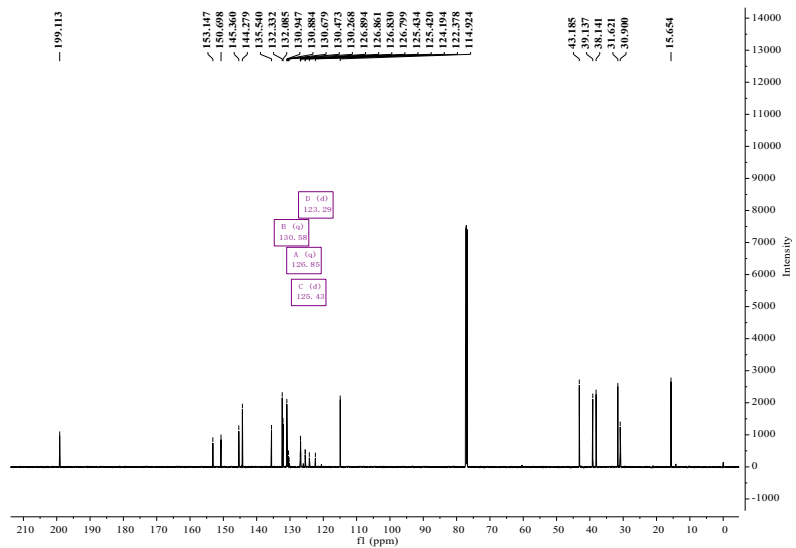


Figure S60 <sup>13</sup>C NMR spectrum of compound 5n.

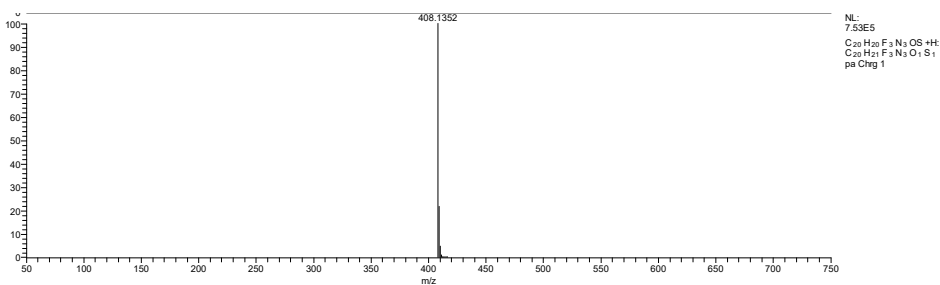


Figure S61 HRMS spectrum of compound 5n.



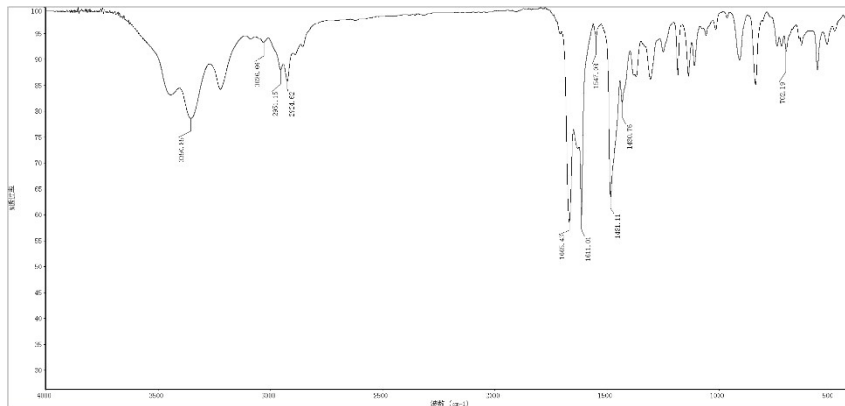


Figure S62 IR spectrum of compound 50.

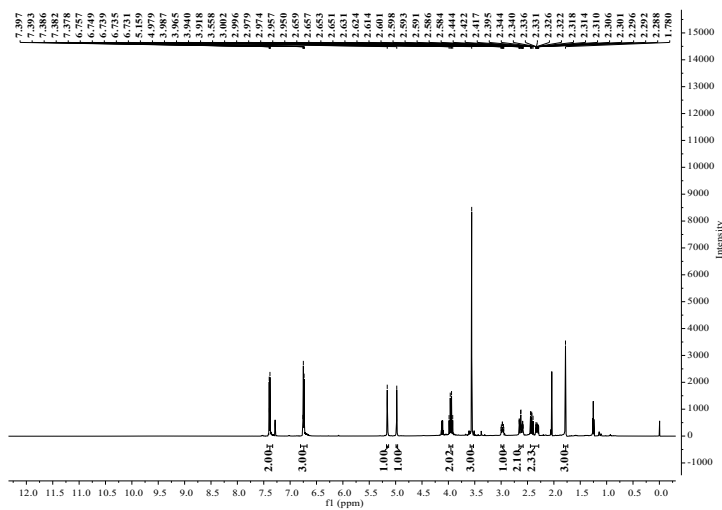


Figure S63 <sup>1</sup>H NMR spectrum of compound 50.

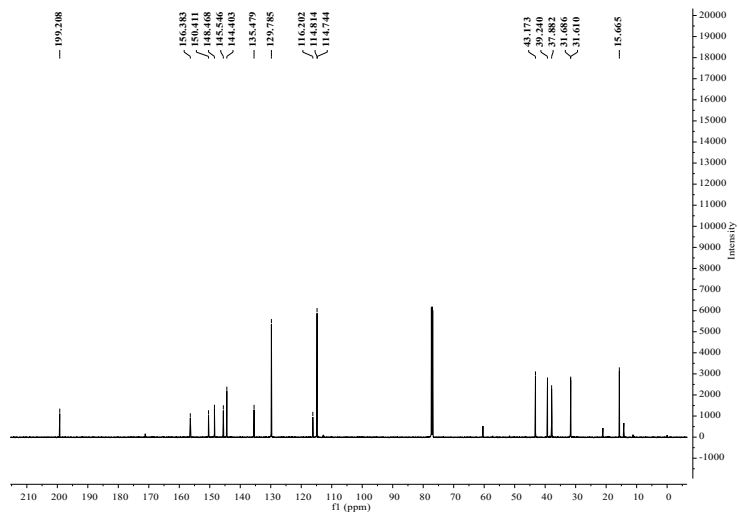
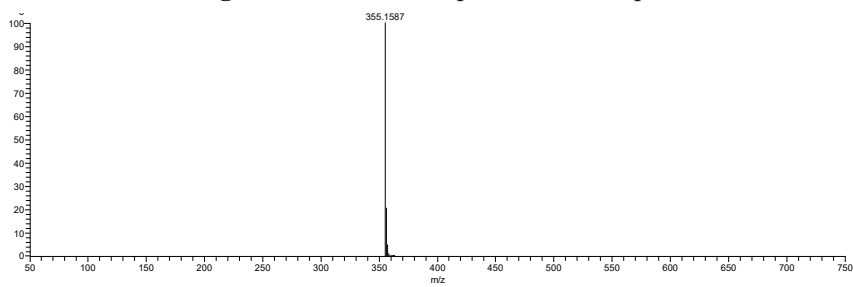


Figure S64  $^{13}\text{C}$  NMR spectrum of compound 5o.



NI:  
7.59E5  
C<sub>19</sub>H<sub>22</sub>N<sub>4</sub>O<sub>5</sub>·H<sub>2</sub>O  
C<sub>19</sub>H<sub>23</sub>N<sub>4</sub>O<sub>5</sub>·S<sub>1</sub>  
pd Chng 1

Figure S65 HRMS spectrum of compound 5o.

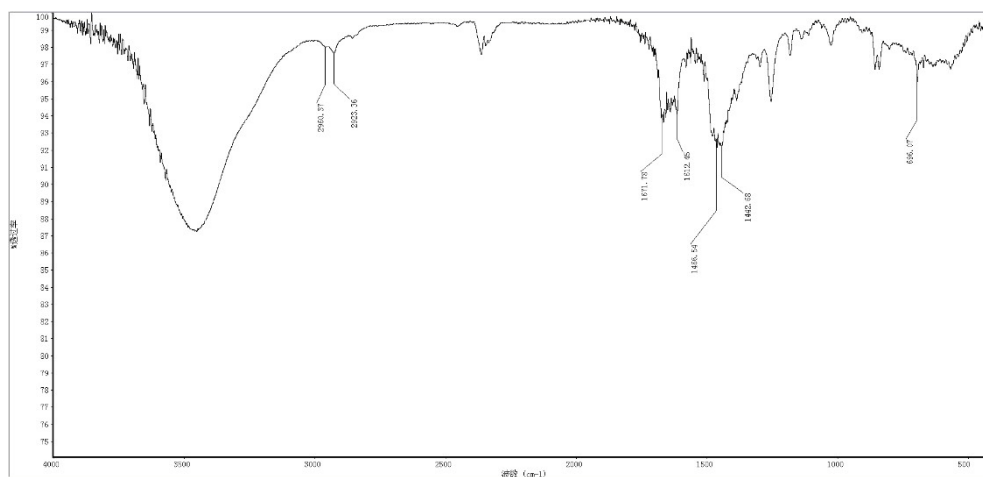


Figure S66 IR spectrum of compound 5p.

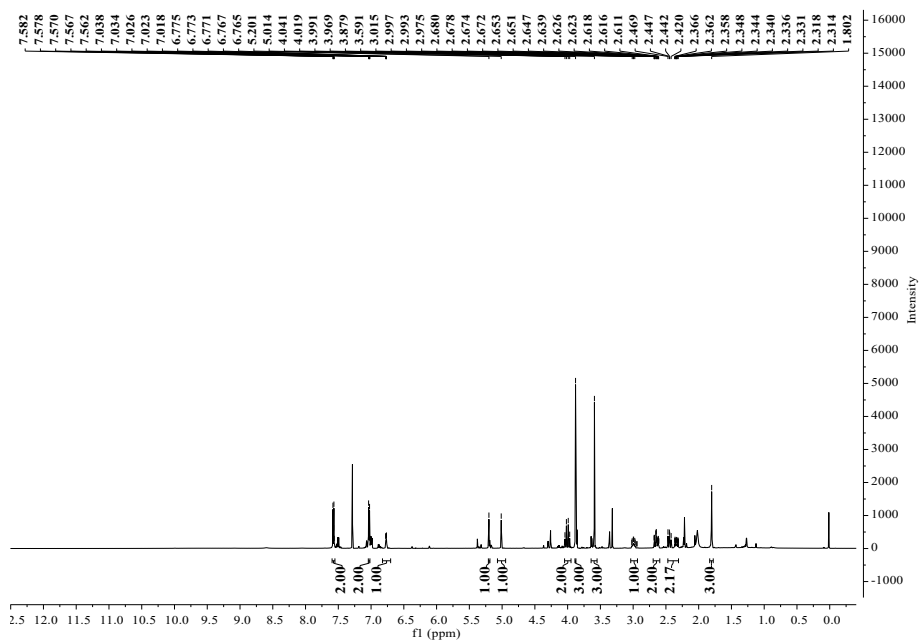


Figure S67 <sup>1</sup>H NMR spectrum of compound 5p.

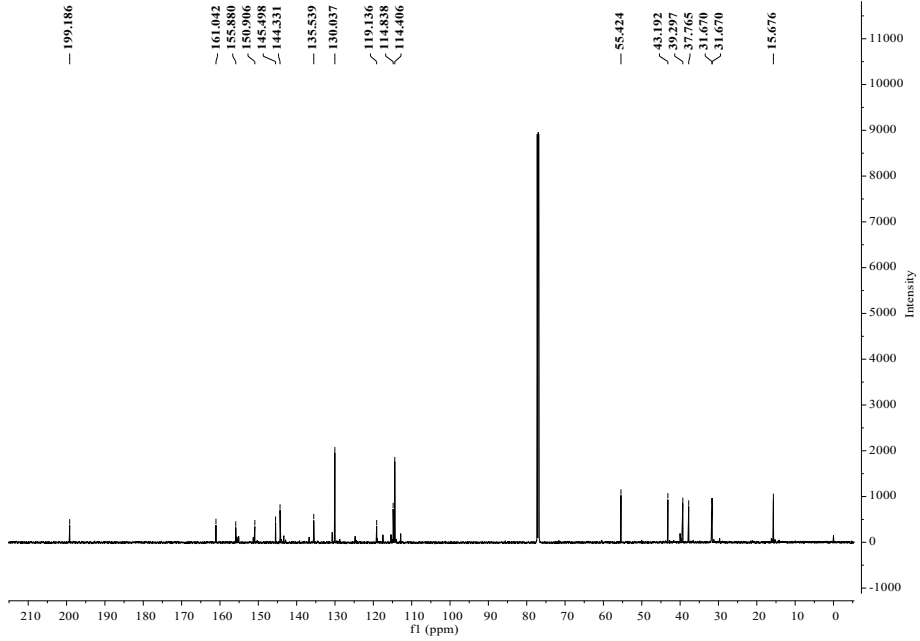


Figure S68 <sup>13</sup>C NMR spectrum of compound 5p.

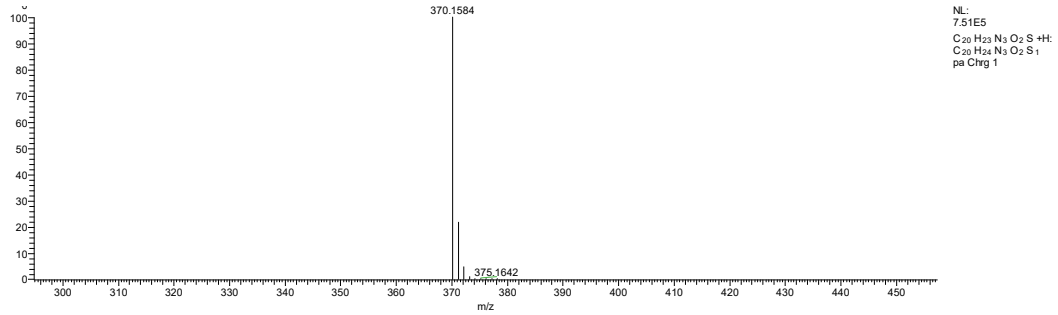
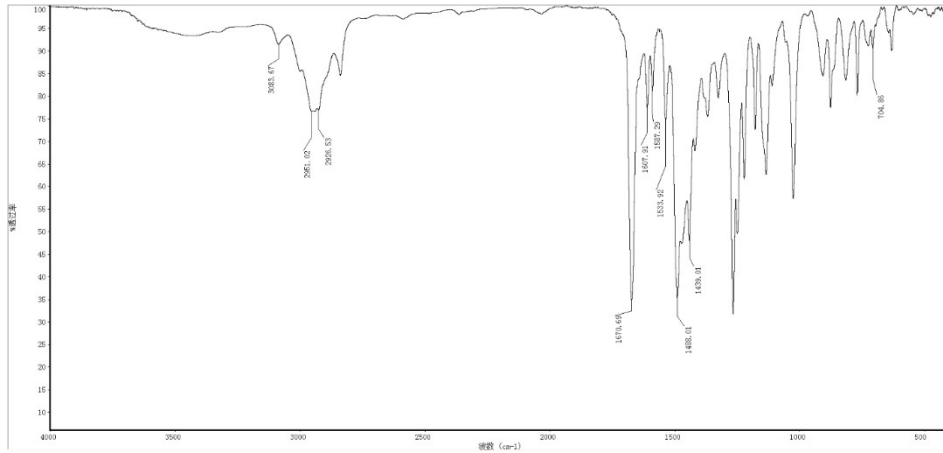
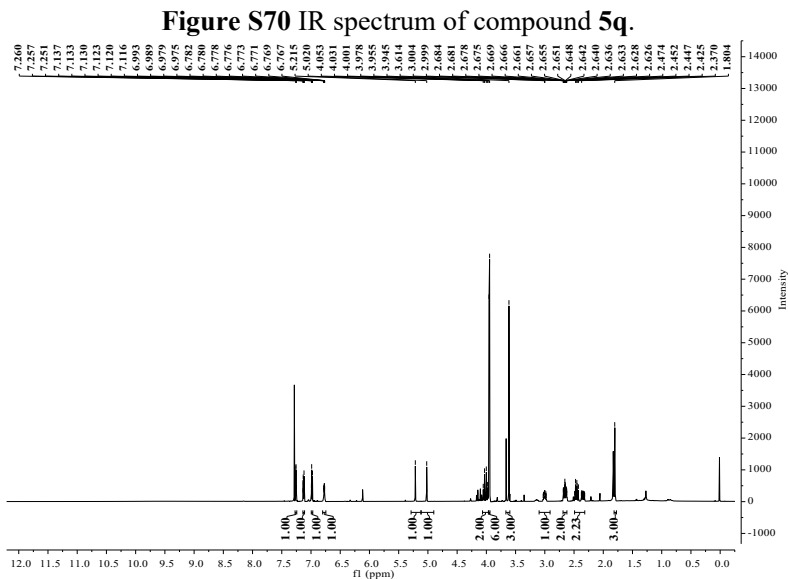
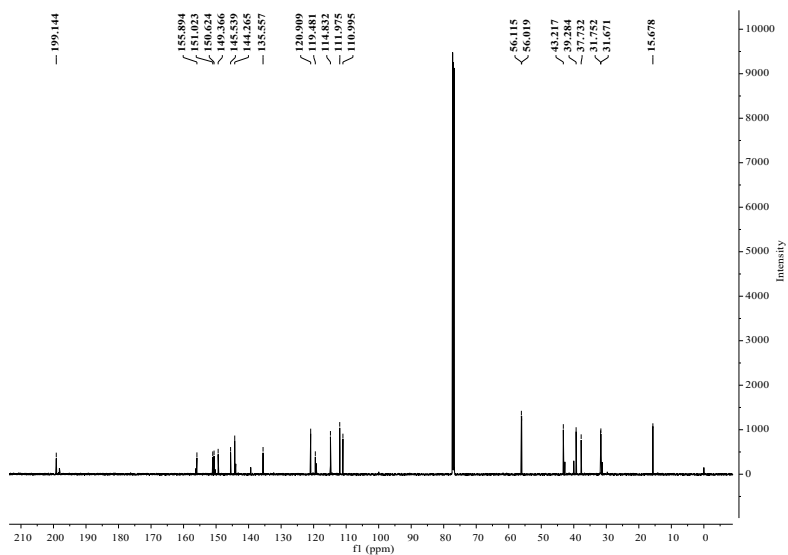


Figure S69 HRMS spectrum of compound 5p.

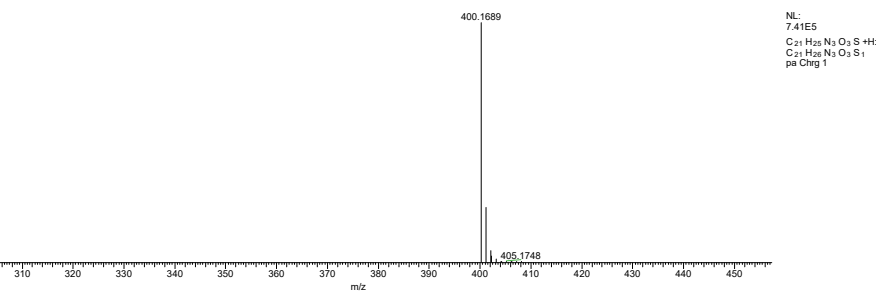




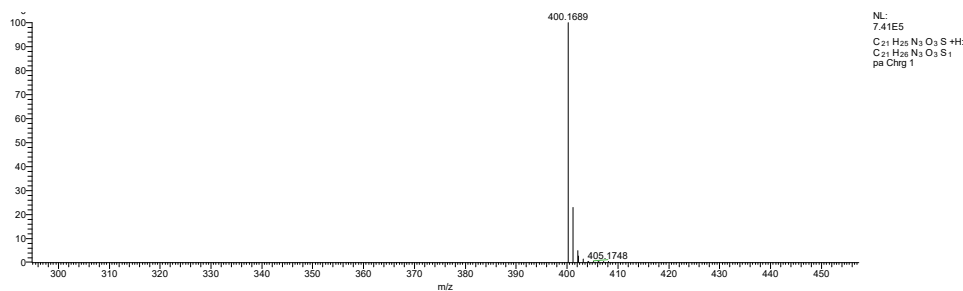
**Figure S71 <sup>1</sup>H NMR spectrum of compound 5q.**



**Figure S72 <sup>13</sup>C NMR spectrum of compound 5q.**



**Figure S73 HRMS spectrum of compound 5q.**



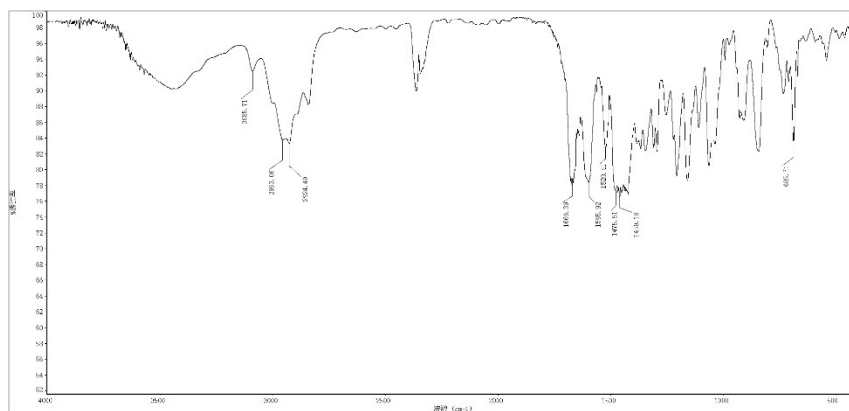


Figure S74 IR spectrum of compound **5r**.

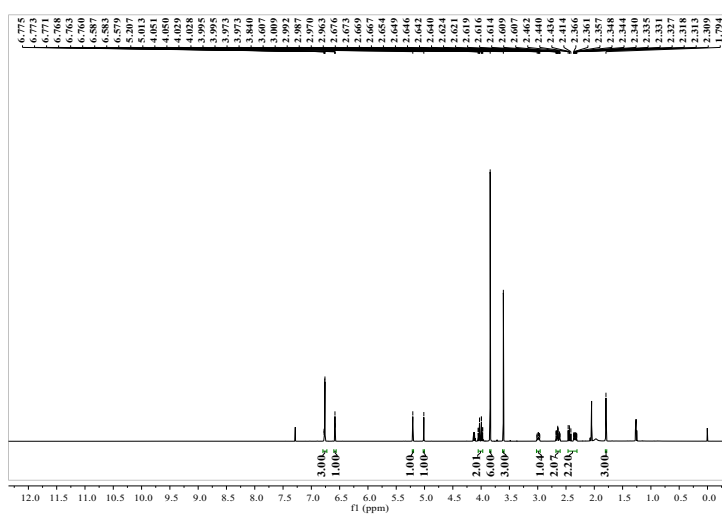


Figure S75 <sup>1</sup>H NMR spectrum of compound **5r**.

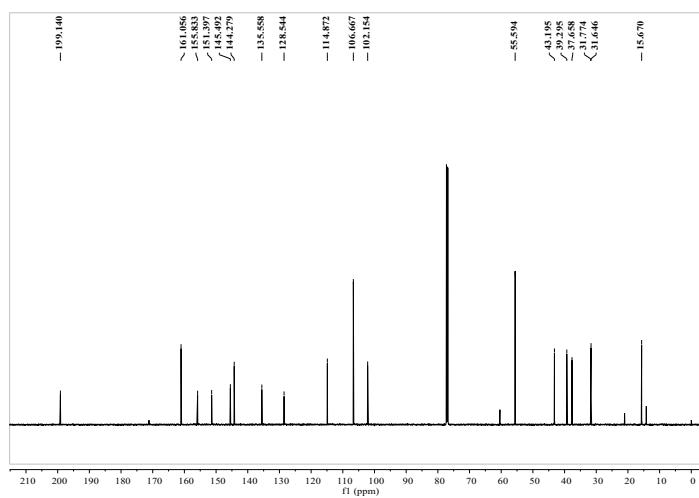


Figure S76 <sup>13</sup>C NMR spectrum of compound **5r**.

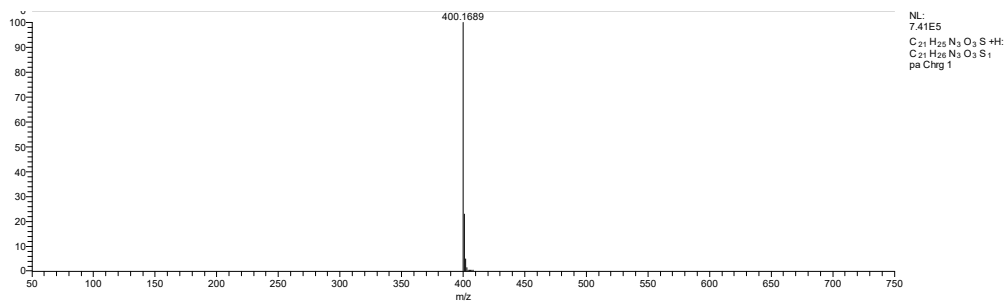


Figure S77 HRMS spectrum of compound 5r.

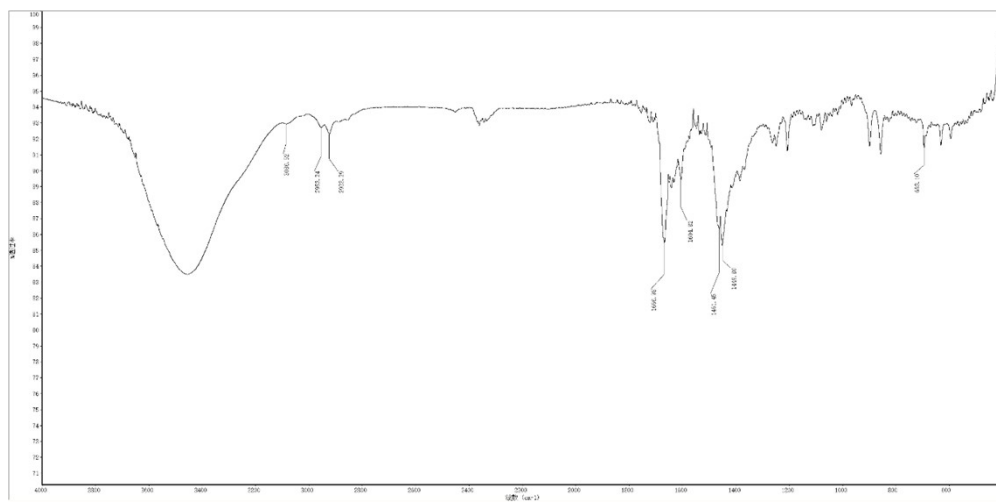


Figure S78 IR spectrum of compound 5s.

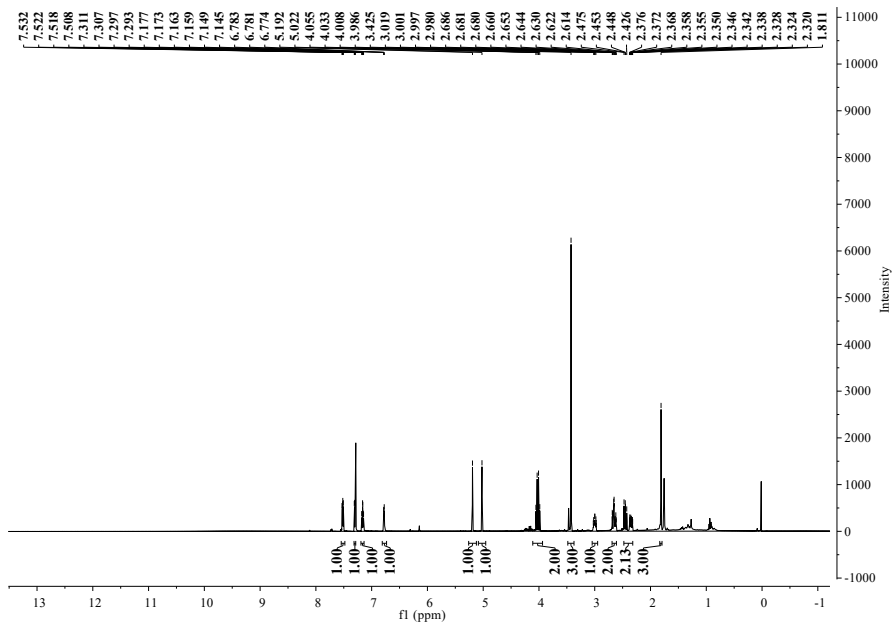


Figure S79 <sup>1</sup>H NMR spectrum of compound 5s.

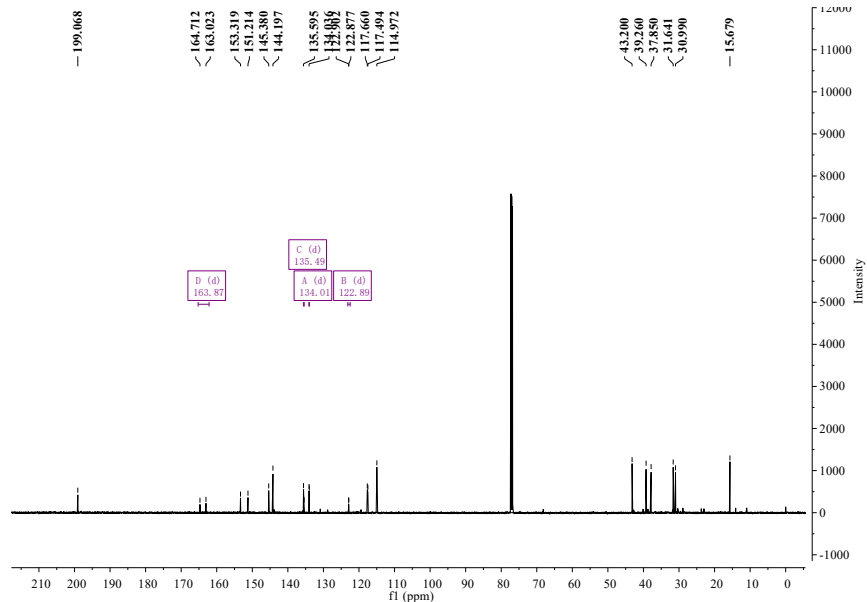


Figure S80  $^{13}\text{C}$  NMR spectrum of compound **5s**.

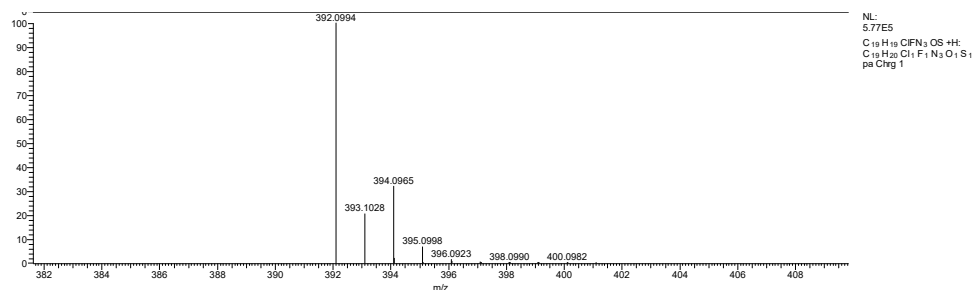


Figure S81 HRMS spectrum of compound **5s**.

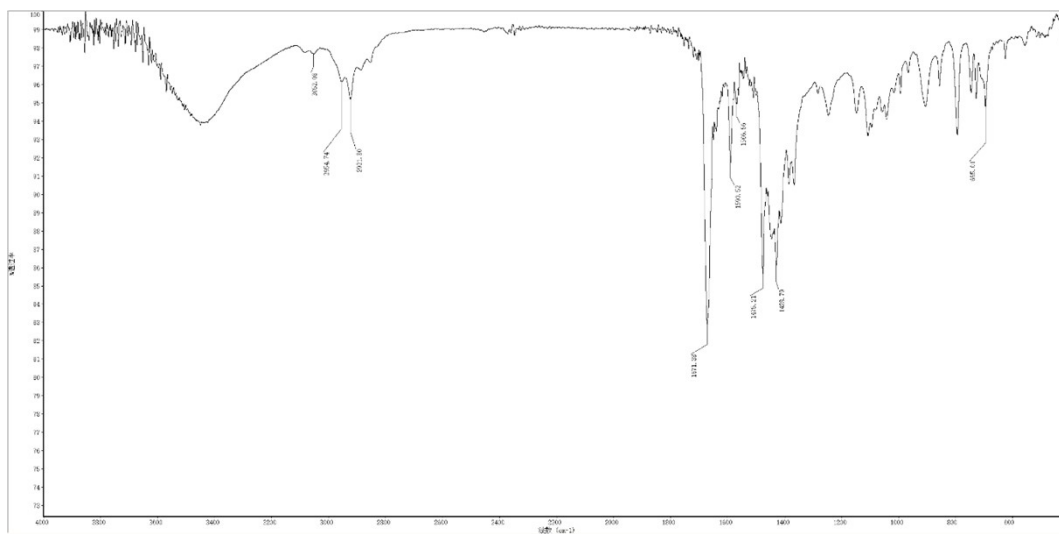


Figure S82 IR spectrum of compound **5t**.

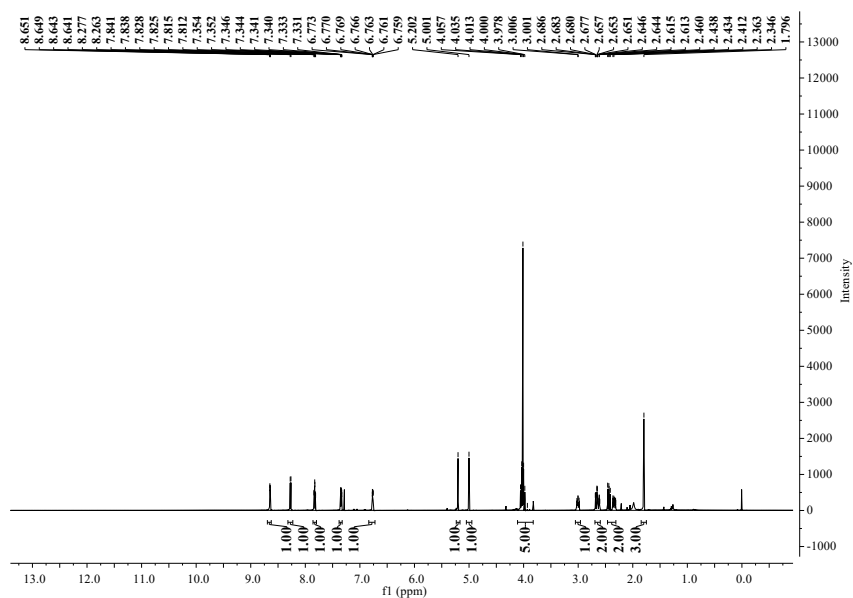


Figure S83  $^1\text{H}$  NMR spectrum of compound **5t**.

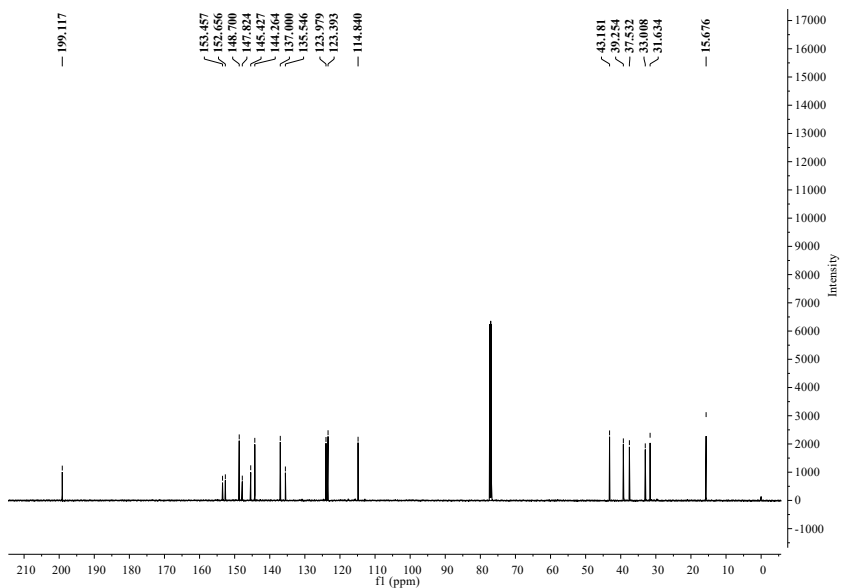


Figure S84  $^{13}\text{C}$  NMR spectrum of compound **5t**.

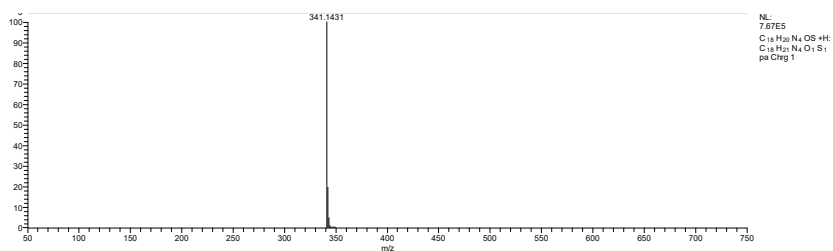


Figure S85 HRMS spectrum of compound **5t**.



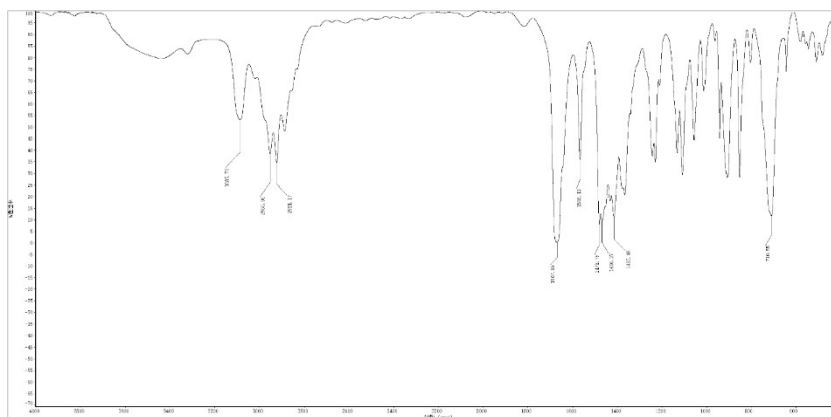


Figure S86 IR spectrum of compound **5u**.

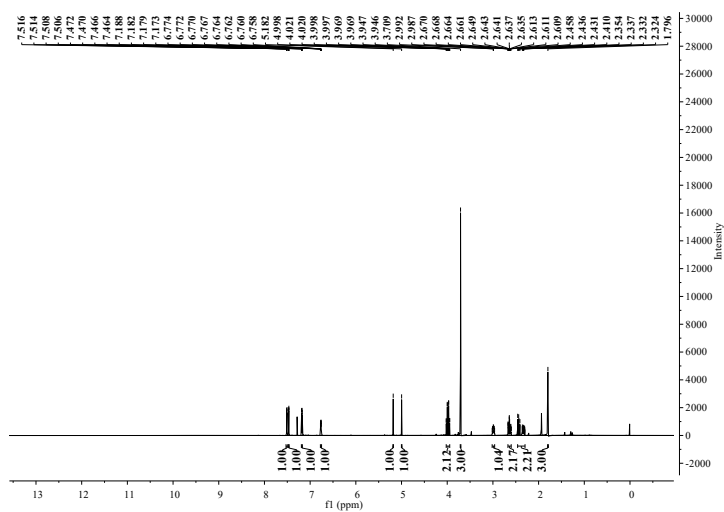


Figure S87  $^1\text{H}$  NMR spectrum of compound **5u**.

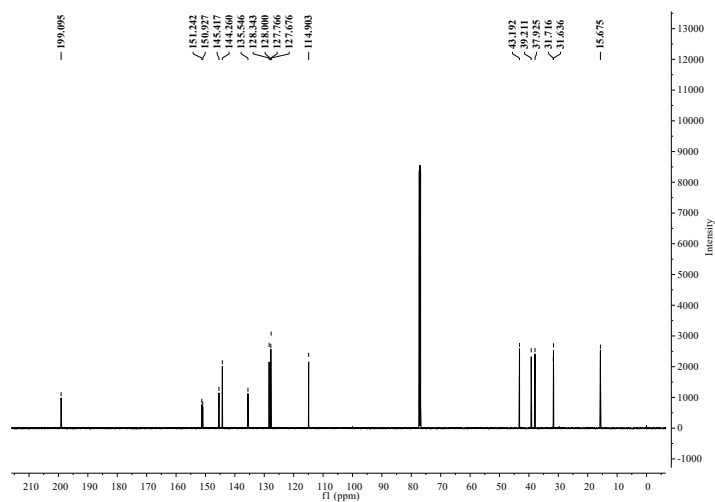


Figure S88  $^{13}\text{C}$  NMR spectrum of compound **5u**.

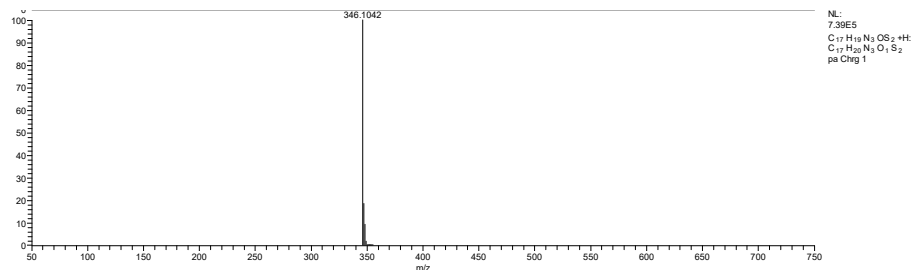


Figure S89 HRMS spectrum of compound 5u.

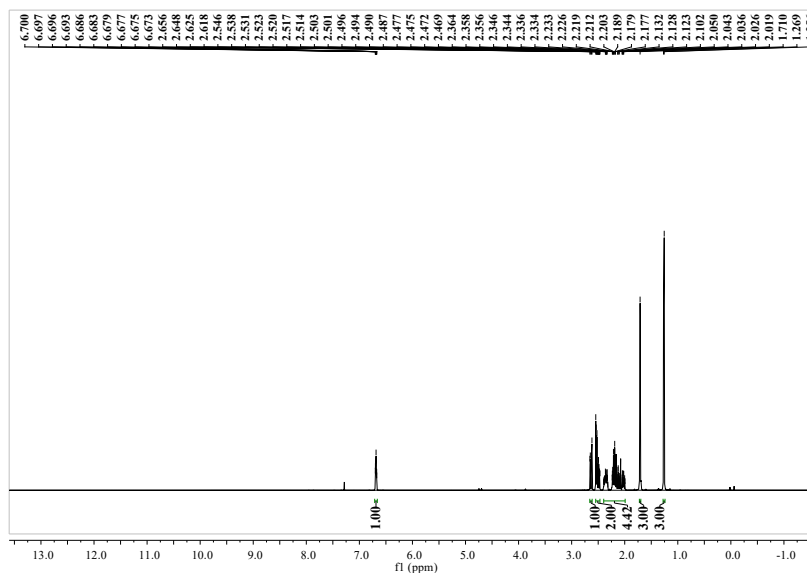


Figure S90 <sup>1</sup>H NMR spectrum of compound 6.

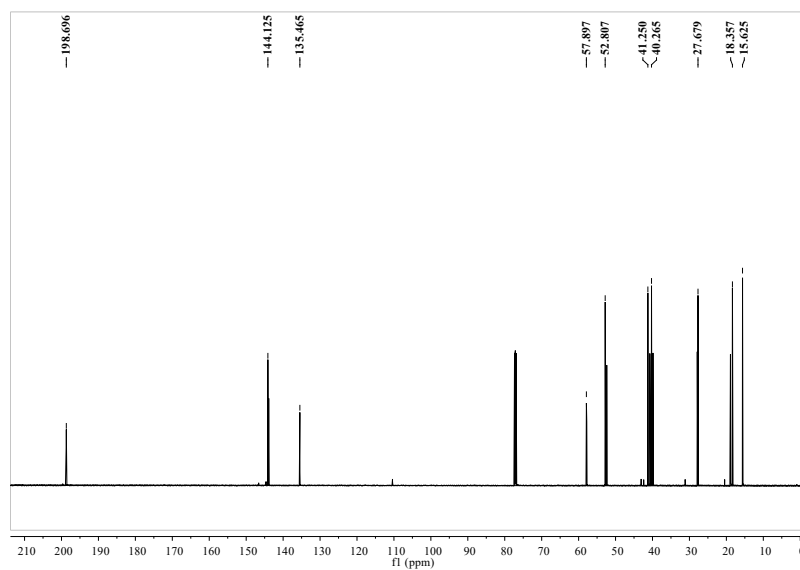
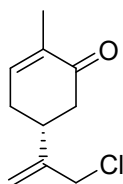
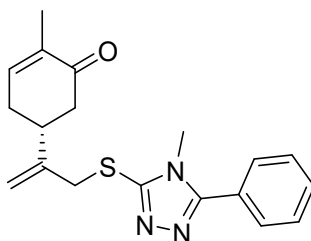


Figure S91 <sup>13</sup>C NMR spectrum of compound 6.

## 5. Characterization data of compounds **2**, **5a** ~ **5u** and **6**

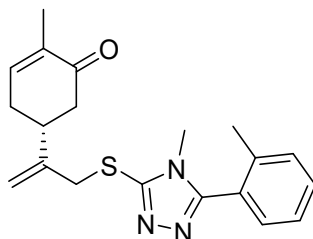


(*R*)-5-(3-Chloroprop-1-en-2-yl)-2-methylcyclohex-2-en-1-one (compound **2** / L-carvone chloride): yellow oily liquid; yield, 87.3%;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.76 (ddd,  $J = 5.7, 2.5, 1.3$  Hz, 1H, =C-H), 5.27 (s, 1H, =CH<sub>2</sub>), 5.06 (d,  $J = 1.1$  Hz, 1H, =CH<sub>2</sub>), 4.10 (d,  $J = 2.8$  Hz, 2H, Cl-CH<sub>2</sub>), 3.06 – 2.91 (m, 1H, CH), 2.68 – 2.54 (m, 2H, CH<sub>2</sub>), 2.42 – 2.30 (m, 2H, CH<sub>2</sub>), 1.81 – 1.79 (m, 3H, =C-CH<sub>3</sub>);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  198.9, 146.6, 144.1, 135.6, 115.2, 46.9, 43.0, 37.8, 31.4, 15.7; HRMS (APCI,  $m/z$ ): calcd. for  $\text{C}_{10}\text{H}_{14}\text{ClO}^+$  ( $[\text{M}+\text{H}]^+$ ) 185.0733, found 185.0728.



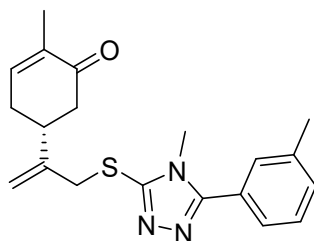
(*R*)-2-Methyl-5-(3-((4-methyl-5-phenyl-4*H*-1,2,4-triazol-3-yl)thio)prop-1-en-2-yl)cyclohex-2-en-1-one (compound **5a**): colorless oily liquid; yield, 83.6%; UV-vis (EtOH)  $\lambda_{\text{max}}$ : 239.00 nm; IR (KBr,  $\text{v}/\text{cm}^{-1}$ ): 3084.40, 3067.53 (=C-H, Ar-H), 2923.74 (C-H), 1654.58 (C=O), 1610.20 (C=C), 1551.55, 1523.05, 1488.18, 1459.46, 1442.53 (Ar), 693.47 (C-S-C);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.62 –

7.59 (m, 2H, Ar-H), 7.48 (dd,  $J = 4.9, 1.7$  Hz, 3H, Ar-H), 6.76 – 6.72 (m, 1H, =C-H), 5.17 (s, 1H, =CH<sub>2</sub>), 4.98 (s, 1H, =CH<sub>2</sub>), 4.02 – 3.94 (m, 2H, -S-CH<sub>2</sub>), 3.58 (s, 3H, N-CH<sub>3</sub>), 2.96 (td,  $J = 14.4, 3.9$  Hz, 1H, CH), 2.64 – 2.57 (m, 2H, CH<sub>2</sub>), 2.43 – 2.28 (m, 2H, CH<sub>2</sub>), 1.76 (s, 3H, =C-CH<sub>3</sub>); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 199.1, 156.0, 151.2, 145.5, 144.3, 135.5, 130.1, 128.9, 128.5, 126.9, 114.8, 43.2, 39.3, 37.7, 31.7, 31.6, 15.7; HRMS (APCI, m/z): calcd. for C<sub>19</sub>H<sub>22</sub>N<sub>3</sub>OS<sup>+</sup> ([M+H]<sup>+</sup>) 340.1484, found 340.1478.

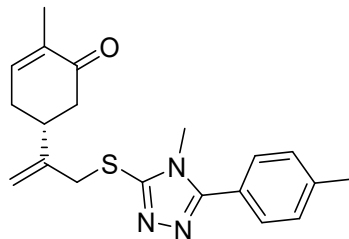


(*R*)-2-Methyl-5-(3-((4-methyl-5-(*o*-tolyl)-4*H*-1,2,4-triazol-3-yl)thio)prop-1-en-2-yl)cyclohex-2-en-1-one (compound **5b**): yellow oily liquid; yield, 81.9%; UV-vis (EtOH)  $\lambda_{\text{max}}$ : 233.50 nm; IR (KBr, v/cm<sup>-1</sup>): 3061.22, 3022.45 (=C-H, Ar-H), 2955.10, 2922.45 (C-H), 1673.47 (C=O), 1610.20 (C=C), 1536.73, 1455.10, 1434.69 (Ar), 702.04 (C-S-C); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.41 (td,  $J = 7.5, 1.7$  Hz, 1H, Ar-H), 7.33 (d,  $J = 7.7$  Hz, 1H, Ar-H), 7.31 – 7.26 (m, 2H, Ar-H), 6.77 (dq,  $J = 4.3, 1.3$  Hz, 1H, =C-H), 5.17 (s, 1H, =CH<sub>2</sub>), 5.00 (s, 1H, =CH<sub>2</sub>), 4.05 – 3.96 (m, 2H, -S-CH<sub>2</sub>), 3.35 (s, 3H, N-CH<sub>3</sub>), 2.99 (td,  $J = 14.2, 3.9$  Hz, 1H, CH), 2.67 – 2.60 (m, 2H, CH<sub>2</sub>), 2.47 – 2.30 (m, 2H, CH<sub>2</sub>), 2.22 (s, 3H, Ar-CH<sub>3</sub>), 1.79 (s, 3H, =C-CH<sub>3</sub>); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 199.1, 155.7, 150.3, 145.6,

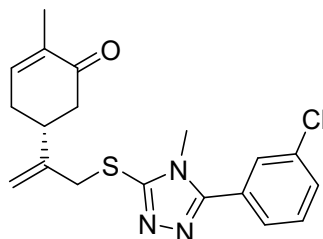
144.3, 138.3, 135.5, 130.7, 130.4, 130.2, 126.5, 126.0, 114.7, 43.2, 39.2, 37.8, 31.6, 30.8, 19.7, 15.7; HRMS (APCI, m/z): calcd. for C<sub>20</sub>H<sub>24</sub>N<sub>3</sub>OS<sup>+</sup> ([M+H]<sup>+</sup>) 354.1640, found 354.1635.



(*R*)-2-Methyl-5-(3-((4-methyl-5-(*m*-tolyl)-4*H*-1,2,4-triazol-3-yl)thio)prop-1-en-2-yl)cyclohex-2-en-1-one (compound **5c**): yellow oily liquid; yield, 78.8%; UV-vis (EtOH)  $\lambda_{\text{max}}$ : 239.00 nm; IR (KBr, v/cm<sup>-1</sup>): 3026.53 (=C-H, Ar-H), 2955.10, 2922.45 (C-H), 1669.39 (C=O), 1612.24 (C=C), 1587.76, 1473.47, 1453.06 (Ar), 695.92 (C-S-C); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.48 (s, 1H, Ar-H), 7.40 (dd, *J* = 4.1, 1.1 Hz, 2H, Ar-H), 7.32 (ddd, *J* = 5.0, 3.3, 1.3 Hz, 1H, Ar-H), 6.77 (ddd, *J* = 5.7, 2.5, 1.3 Hz, 1H, =C-H), 5.21 (s, 1H, =CH<sub>2</sub>), 5.02 (s, 1H, =CH<sub>2</sub>), 4.06 – 3.97 (m, 2H, -S-CH<sub>2</sub>), 3.60 (s, 3H, N-CH<sub>3</sub>), 3.00 (td, *J* = 14.0, 3.9 Hz, 1H, CH), 2.68 – 2.61 (m, 2H, CH<sub>2</sub>), 2.47 – 2.31 (m, 5H, CH<sub>2</sub> & Ar-CH<sub>3</sub>), 1.80 (s, 3H, =C-CH<sub>3</sub>); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>):  $\delta$  199.1, 156.1, 151.1, 145.5, 144.3, 138.9, 135.6, 130.9, 129.3, 128.8, 126.8, 125.5, 114.8, 43.2, 39.3, 37.8, 31.7, 31.7, 21.4, 15.7; HRMS (APCI, m/z): calcd. for C<sub>20</sub>H<sub>24</sub>N<sub>3</sub>OS<sup>+</sup> ([M+H]<sup>+</sup>) 354.1640, found 354.1635.

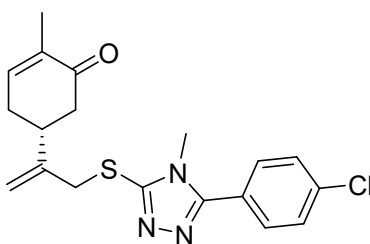


(*R*)-2-Methyl-5-(3-((4-methyl-5-(*p*-tolyl)-4*H*-1,2,4-triazol-3-yl)thio)prop-1-en-2-yl)cyclohex-2-en-1-one (compound **5d**): yellow oily liquid; yield, 83.3%; UV-vis (EtOH)  $\lambda_{\text{max}}$ : 241.50 nm; IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3024.49 (=C-H, Ar-H), 2953.06, 2926.53 (C-H), 1669.39 (C=O), 1618.37 (C=C), 1465.31, 1432.65 (Ar), 693.88 (C-S-C);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.51 (d,  $J = 8.1$  Hz, 2H, Ar-H), 7.31 (d,  $J = 8.1$  Hz, 2H, Ar-H), 6.80 – 6.73 (m, 1H, =C-H), 5.19 (s, 1H, =CH<sub>2</sub>), 5.00 (s, 1H, =CH<sub>2</sub>), 4.12 – 3.95 (m, 2H, -S-CH<sub>2</sub>), 3.58 (s, 3H, N-CH<sub>3</sub>), 3.05 (dtd,  $J = 81.3, 14.5, 3.8$  Hz, 1H, CH), 2.67 – 2.60 (m, 2H, CH<sub>2</sub>), 2.48 – 2.30 (m, 5H CH<sub>2</sub> & Ar-CH<sub>3</sub>), 1.79 (s, 3H, =C-CH<sub>3</sub>);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  199.2, 156.1, 151.0, 145.5, 144.3, 140.4, 135.5, 129.6, 128.4, 124.0, 114.8, 43.2, 39.3, 37.8, 31.7, 31.6, 21.4, 15.7; HRMS (APCI,  $m/z$ ): calcd. for  $\text{C}_{20}\text{H}_{24}\text{N}_3\text{OS}^+$  ( $[\text{M}+\text{H}]^+$ ) 354.1640, found 354.1635.



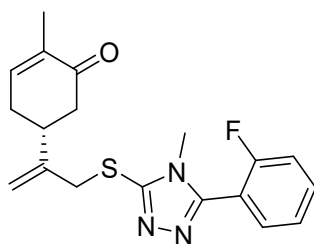
(*R*)-5-(3-((5-(3-Chlorophenyl)-4-methyl-4*H*-1,2,4-triazol-3-yl)thio)prop-1-en-2-yl)-2-methylcyclohex-2-en-1-one (compound **5e**): yellow oily liquid; yield,

75.9%; UV-vis (EtOH)  $\lambda_{\text{max}}$ : 240.50 nm; IR (KBr,  $\text{v}/\text{cm}^{-1}$ ): 3020.41 (=C-H, Ar-H), 2953.06, 2924.49 (C-H), 1671.43 (C=O), 1603.79 (C=C), 1575.39, 1521.45, 1473.19, 1450.47 (Ar), 689.59 (C-S-C);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.66 (t,  $J = 1.6$  Hz, 1H, Ar-H), 7.54 (dt,  $J = 7.4, 1.4$  Hz, 1H, Ar-H), 7.51 – 7.45 (m, 2H, Ar-H), 6.78 – 6.76 (m, 1H, =C-H), 5.22 (s, 1H, =CH<sub>2</sub>), 5.03 (s, 1H, =CH<sub>2</sub>), 4.11 – 3.96 (m, 2H, -S-CH<sub>2</sub>), 3.62 (s, 3H, N-CH<sub>3</sub>), 3.06 – 2.93 (m, 1H, CH), 2.69 – 2.62 (m, 2H, CH<sub>2</sub>), 2.48 – 2.32 (m, 2H, CH<sub>2</sub>), 1.80 (s, 3H, =C-CH<sub>3</sub>);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  199.1, 154.7, 151.8, 145.4, 144.2, 139.2, 135.6, 135.0, 130.3, 128.6, 128.6, 126.6, 115.0, 43.2, 39.3, 37.6, 31.7, 31.7, 15.7; HRMS (APCI,  $m/z$ ): calcd. for  $\text{C}_{19}\text{H}_{21}\text{ClN}_3\text{OS}^+$  ( $[\text{M}+\text{H}]^+$ ) 374.1094, found 374.1088.



(*R*)-5-(3-((5-(4-Chlorophenyl)-4-methyl-4*H*-1,2,4-triazol-3-yl)thio)prop-1-en-2-yl)-2-methylcyclohex-2-en-1-one (compound **5f**): yellow oily liquid; yield, 78.5%; UV-vis (EtOH)  $\lambda_{\text{max}}$ : 242.00 nm; IR (KBr,  $\text{v}/\text{cm}^{-1}$ ): 3028.57 (=C-H, Ar-H), 2957.14, 2922.65 (C-H), 1670.15 (C=O), 1604.08 (C=C), 1471.23, 1418.37 (Ar), 692.82 (C-S-C);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.58 (d,  $J = 8.5$  Hz, 2H, Ar-H), 7.51 – 7.47 (m, 2H, Ar-H), 6.76 (dd,  $J = 3.2, 1.6$  Hz, 1H, =C-H), 5.20 (s, 1H,

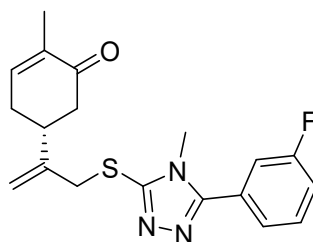
=CH<sub>2</sub>), 5.01 (s, 1H, =CH<sub>2</sub>), 4.10 – 3.94 (m, 2H, -S-CH<sub>2</sub>), 3.59 (s, 3H, N-CH<sub>3</sub>), 2.98 (td, *J* = 14.4, 3.9 Hz, 1H, CH), 2.67 – 2.60 (m, 2H, CH<sub>2</sub>), 2.47 – 2.30 (m, 2H, CH<sub>2</sub>), 1.78 (s, 3H, =C-CH<sub>3</sub>); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 199.1, 155.0, 151.7, 145.4, 144.3, 136.4, 135.5, 129.8, 129.3, 125.4, 114.9, 43.2, 39.3, 37.6, 31.7, 31.6, 15.7; HRMS (APCI, *m/z*): calcd. for C<sub>19</sub>H<sub>21</sub>ClN<sub>3</sub>OS<sup>+</sup> ([M+H]<sup>+</sup>) 374.1094, found 374.1088.



(*R*)-5-(3-((5-(2-Fluorophenyl)-4-methyl-4*H*-1,2,4-triazol-3-yl)thio)prop-1-en-2-yl)-2-methylcyclohex-2-en-1-one (compound **5g**): yellow oily liquid; yield, 71.3%; UV-vis (EtOH) λ<sub>max</sub>: 235.00 nm; IR (KBr, v/cm<sup>-1</sup>): 3077.55, 3020.41 (=C-H, Ar-H), 2957.14, 2920.41 (C-H), 1670.61 (C=O), 1621.86 (C=C), 1581.63, 1473.63, 1450.45 (Ar), 695.92 (C-S-C); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.65 (ddd, *J* = 7.4, 6.3, 1.8 Hz, 1H, Ar-H), 7.58 – 7.53 (m, 1H, Ar-H), 7.33 (td, *J* = 7.6, 1.0 Hz, 1H, Ar-H), 7.27 – 7.21 (m, 1H, Ar-H), 6.78 (dq, *J* = 4.2, 1.2 Hz, 1H, =C-H), 5.21 (s, 1H, =CH<sub>2</sub>), 5.03 (s, 1H, =CH<sub>2</sub>), 4.16 – 3.92 (m, 2H, -S-CH<sub>2</sub>), 3.50 (d, *J* = 2.3 Hz, 3H, N-CH<sub>3</sub>), 3.01 (td, *J* = 14.2, 3.9 Hz, 1H, CH), 2.70 – 2.61 (m, 2H, CH<sub>2</sub>), 2.48 – 2.32 (m, 2H, CH<sub>2</sub>), 1.80 (s, 3H, =C-CH<sub>3</sub>); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ

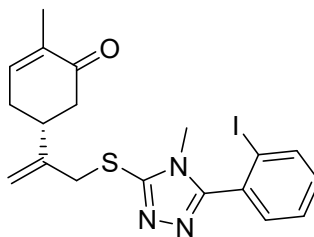


199.1, 159.7 (d,  $J = 249.9$  Hz), 151.8 (d,  $J = 102.8$  Hz), 145.4, 144.2, 135.6, 132.7 (d,  $J = 8.3$  Hz), 132.2 (d,  $J = 2.7$  Hz), 125.0, 125.0, 119.4, 116.1 (d,  $J = 21.3$  Hz), 114.9, 43.2, 39.3, 37.8, 31.6, 31.2, 15.7; HRMS (APCI,  $m/z$ ): calcd. for  $C_{19}H_{21}FN_3OS^+$  ( $[M+H]^+$ ) 358.1389, found 358.1384.

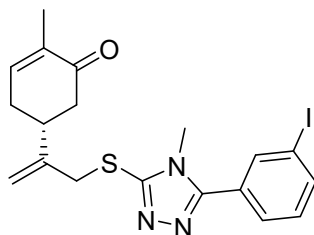


(*R*)-5-(3-((5-(3-Fluorophenyl)-4-methyl-4*H*-1,2,4-triazol-3-yl)thio)prop-1-en-2-yl)-2-methylcyclohex-2-en-1-one (compound **5h**): yellow oily liquid; yield, 69.8%; UV-vis (EtOH)  $\lambda_{\max}$ : 239.50 nm; IR (KBr,  $\nu/cm^{-1}$ ): 3073.47, 3022.45 (=C-H, Ar-H), 2959.18, 2924.49 (C-H), 1671.43 (C=O), 1618.37 (C=C), 1591.84, 1528.57, 1479.59, 1432.65 (Ar), 687.76 (C-S-C);  $^1H$  NMR (600 MHz,  $CDCl_3$ ):  $\delta$  7.50 (ddd,  $J = 8.1, 6.8, 4.3$  Hz, 1H, Ar-H), 7.44 (dt,  $J = 7.7, 1.1$  Hz, 1H, Ar-H), 7.40 – 7.37 (m, 1H, Ar-H), 7.24 – 7.20 (m, 1H, Ar-H), 6.79 – 6.76 (m, 1H, =C-H), 5.22 (s, 1H, =CH<sub>2</sub>), 5.03 (s, 1H, =CH<sub>2</sub>), 4.12 – 3.96 (m, 2H, -S-CH<sub>2</sub>), 3.62 (s, 3H, N-CH<sub>3</sub>), 2.99 (td,  $J = 14.2, 3.9$  Hz, 1H, CH), 2.68 – 2.61 (m, 2H, CH<sub>2</sub>), 2.49 – 2.32 (m, 2H, CH<sub>2</sub>), 1.80 (s, 3H, =C-CH<sub>3</sub>);  $^{13}C$  NMR (151 MHz,  $CDCl_3$ ):  $\delta$  199.1, 162.7 (d,  $J = 247.8$  Hz), 154.8 (d,  $J = 2.8$  Hz), 151.8, 145.4, 144.2, 135.6, 130.7 (d,  $J = 8.3$  Hz), 124.2 (d,  $J = 3.0$  Hz), 119.4, 117.2 (d,  $J = 21.0$  Hz), 115.7 (d,  $J = 23.3$  Hz), 115.0, 43.2, 39.3, 37.6, 31.7, 31.7, 15.7; HRMS (APCI,  $m/z$ ): calcd. for

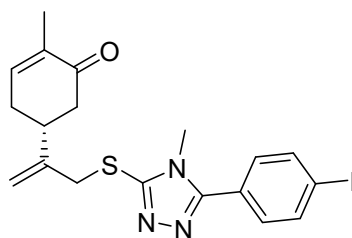
C<sub>19</sub>H<sub>21</sub>FN<sub>3</sub>OS<sup>+</sup> ([M+H]<sup>+</sup>) 358.1389, found 358.1384.



(*R*)-5-(3-((5-(2-Iodophenyl)-4-methyl-4*H*-1,2,4-triazol-3-yl)thio)prop-1-en-2-yl)-2-methylcyclohex-2-en-1-one (compound **5i**): colorless oily liquid; yield, 82.0%; UV-vis (EtOH)  $\lambda_{\text{max}}$ : 232.50 nm; IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3057.14 (=C-H, Ar-H), 2950.20, 2921.35 (C-H), 1667.90 (C=O), 1590.99, 1463.84, 1433.90 (Ar), 686.78 (C-S-C); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.97 (dd,  $J = 8.0, 0.9$  Hz, 1H, Ar-H), 7.50 (td,  $J = 7.5, 1.1$  Hz, 1H, Ar-H), 7.40 (dd,  $J = 7.6, 1.7$  Hz, 1H, Ar-H), 7.24 (td,  $J = 7.8, 1.7$  Hz, 1H, Ar-H), 6.78 (dq,  $J = 4.4, 1.3$  Hz, 1H, =C-H), 5.19 (s, 1H, =CH<sub>2</sub>), 5.01 (s, 1H, =CH<sub>2</sub>), 4.05 – 3.97 (m, 2H, -S-CH<sub>2</sub>), 3.39 (s, 3H, N-CH<sub>3</sub>), 3.00 (td,  $J = 14.2, 3.9$  Hz, 1H, CH), 2.66 (dddd,  $J = 18.2, 14.6, 4.0, 1.4$  Hz, 2H, CH<sub>2</sub>), 2.47 – 2.32 (m, 2H, CH<sub>2</sub>), 1.80 (s, 3H, =C-CH<sub>3</sub>); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>):  $\delta$  199.1, 157.2, 150.6, 145.4, 144.3, 139.4, 135.6, 133.0, 132.0, 132.0, 128.5, 115.0, 98.8, 43.2, 39.2, 38.1, 31.7, 31.2, 15.7; HRMS (APCI,  $m/z$ ): calcd. for C<sub>19</sub>H<sub>21</sub>IN<sub>3</sub>OS<sup>+</sup> ([M+H]<sup>+</sup>) 466.0450, found 466.0445.

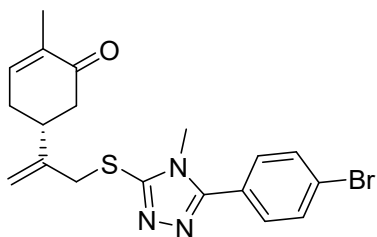


(*R*)-5-(3-((5-(3-Iodophenyl)-4-methyl-4*H*-1,2,4-triazol-3-yl)thio)prop-1-en-2-yl)-2-methylcyclohex-2-en-1-one (compound **5j**): yellow oily liquid; yield, 71.6%; UV-vis (EtOH)  $\lambda_{\text{max}}$ : 233.00 nm; IR (KBr,  $\text{v}/\text{cm}^{-1}$ ): 3029.34 (=C-H, Ar-H), 2954.96, 2920.75 (C-H), 1667.80 (C=O), 1594.75, 1514.13, 1469.35, 1448.76 (Ar), 684.48 (C-S-C);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.02 (t,  $J = 1.5$  Hz, 1H, Ar-H), 7.88 – 7.84 (m, 1H, Ar-H), 7.61 (dt,  $J = 7.7, 1.2$  Hz, 1H, Ar-H), 7.27 (td,  $J = 7.9, 2.7$  Hz, 2H, Ar-H), 6.79 – 6.75 (m, 1H, =C-H), 5.23 (s, 1H, =CH<sub>2</sub>), 5.03 (s, 1H, =CH<sub>2</sub>), 4.13 – 3.98 (m, 2H, -S-CH<sub>2</sub>), 3.61 (s, 3H, N-CH<sub>3</sub>), 2.99 (ddt,  $J = 14.2, 8.6, 3.9$  Hz, 1H, CH), 2.69 – 2.61 (m, 2H, CH<sub>2</sub>), 2.49 – 2.32 (m, 2H, CH<sub>2</sub>), 1.81 (s, 3H, =C-CH<sub>3</sub>);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  199.1, 154.4, 151.8, 145.4, 144.2, 139.1, 137.3, 135.6, 130.5, 128.9, 127.6, 115.0, 94.5, 43.2, 39.3, 37.6, 31.7, 31.7, 15.7; HRMS (APCI,  $m/z$ ): calcd. for  $\text{C}_{19}\text{H}_{21}\text{IN}_3\text{OS}^+$  ( $[\text{M}+\text{H}]^+$ ) 466.0450, found 466.0445.



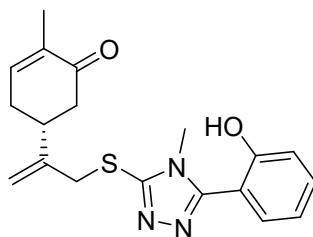
(*R*)-5-(3-((5-(4-Iodophenyl)-4-methyl-4*H*-1,2,4-triazol-3-yl)thio)prop-1-en-2-

yl)-2-methylcyclohex-2-en-1-one (compound **5k**): yellow oily liquid; yield, 66.1%; UV-vis (EtOH)  $\lambda_{\text{max}}$ : 251.00 nm; IR (KBr,  $\text{v}/\text{cm}^{-1}$ ): 3085.12 (=C-H, Ar-H), 2958.68, 2920.37 (C-H), 1667.30 (C=O), 1595.61, 1468.35 (Ar), 691.81 (C-S-C);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.90 – 7.86 (m, 2H, Ar-H), 7.42 – 7.38 (m, 2H, Ar-H), 6.79 – 6.76 (m, 1H, =C-H), 5.23 (s, 1H, =CH<sub>2</sub>), 5.03 (s, 1H, =CH<sub>2</sub>), 4.12 – 3.97 (m, 2H, -S-CH<sub>2</sub>), 3.61 (s, 3H, N-CH<sub>3</sub>), 2.99 (td,  $J = 14.6, 4.0$  Hz, 1H, CH), 2.65 (ddd,  $J = 17.8, 12.3, 4.5$  Hz, 2H, CH<sub>2</sub>), 2.44 – 2.31 (m, 2H, CH<sub>2</sub>), 1.80 (s, 3H, =C-CH<sub>3</sub>);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  199.1, 155.1, 151.9, 145.3, 144.3, 138.2, 135.6, 130.0, 126.1, 115.0, 96.8, 43.2, 39.3, 37.6, 31.8, 31.6, 15.7; HRMS (APCI,  $m/z$ ): calcd. for  $\text{C}_{19}\text{H}_{21}\text{N}_3\text{OS}^+$  ( $[\text{M}+\text{H}]^+$ ) 466.0450, found 466.0445.



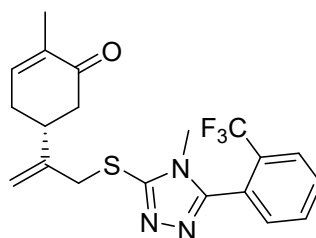
(*R*)-5-(3-((5-(4-Bromophenyl)-4-methyl-4*H*-1,2,4-triazol-3-yl)thio)prop-1-en-2-yl)-2-methylcyclohex-2-en-1-one (compound **5l**): yellow oily liquid; yield, 81.9%; UV-vis (EtOH)  $\lambda_{\text{max}}$ : 244.00 nm; IR (KBr,  $\text{v}/\text{cm}^{-1}$ ): 3020.41 (=C-H, Ar-H), 2951.51, 2921.13 (C-H), 1670.51 (C=O), 1597.73, 1471.88, 1416.83 (Ar), 689.80 (C-S-C);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.68 – 7.63 (m, 2H, Ar-H), 7.54 – 7.49 (m, 2H, Ar-H), 6.77 (dq,  $J = 4.5, 1.2$  Hz, 1H, =C-H), 5.21 (s, 1H, =CH<sub>2</sub>), 5.02 (s, 1H, =CH<sub>2</sub>), 4.06 – 3.98 (m, 2H, -S-CH<sub>2</sub>), 3.59 (s, 3H, N-CH<sub>3</sub>), 2.98 (td,  $J = 14.2,$

3.9 Hz, 1H, CH), 2.67 – 2.60 (m, 2H, CH<sub>2</sub>), 2.46 – 2.31 (m, 2H, CH<sub>2</sub>), 1.79 (s, 3H, =C-CH<sub>3</sub>); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 199.1, 155.0, 151.8, 145.4, 144.3, 135.6, 132.3, 130.0, 125.9, 124.7, 115.0, 43.2, 39.3, 37.6, 31.7, 31.6, 15.7; HRMS (APCI, m/z): calcd. for C<sub>19</sub>H<sub>21</sub>BrN<sub>3</sub>OS<sup>+</sup> ([M+H]<sup>+</sup>) 418.0589, 420.0568, found 418.0583, 420.0563.

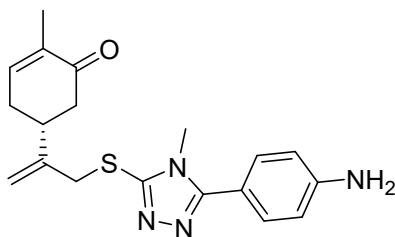


(*R*)-5-(3-((5-(2-Hydroxyphenyl)-4-methyl-4*H*-1,2,4-triazol-3-yl)thio)prop-1-en-2-yl)-2-methylcyclohex-2-en-1-one (compound **5m**): colorless solid; yield, 84.5%; m.p. 106.7 – 111.6 °C; UV-vis (EtOH) λ<sub>max</sub>: 285.00 nm; IR (KBr, v/cm<sup>-1</sup>): 3422.63 (O-H), 3055.28 (=C-H, Ar-H), 2955.28, 2923.30 (C-H), 1670.76 (C=O), 1613.09 (C=C), 1594.14, 1473.99, 1447.11 (Ar), 704.71 (C-S-C); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.54 (dd, *J* = 8.0, 1.6 Hz, 1H, Ar-H), 7.40 – 7.34 (m, 1H, Ar-H), 7.16 – 7.12 (m, 1H, Ar-H), 7.00 – 6.95 (m, 1H, Ar-H), 6.79 – 6.75 (m, 1H, =C-H), 5.22 (s, 1H, =CH<sub>2</sub>), 5.04 (s, 1H, =CH<sub>2</sub>), 4.06 – 3.99 (m, 2H, -S-CH<sub>2</sub>), 3.82 (s, 3H, N-CH<sub>3</sub>), 2.99 (td, *J* = 14.3, 3.9 Hz, 1H, CH), 2.69 – 2.59 (m, 2H, CH<sub>2</sub>), 2.47 – 2.32 (m, 2H, CH<sub>2</sub>), 2.05 (s, 1H, OH), 1.80 (s, 3H, =C-CH<sub>3</sub>); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 199.0, 157.5, 154.0, 151.8, 145.1, 144.2, 135.6, 131.7, 125.7, 119.2, 118.1, 115.2, 111.1, 43.2, 39.3, 37.7, 33.2, 31.6, 15.7; HRMS (APCI, m/z): calcd.

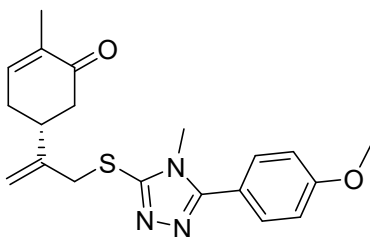
for  $C_{19}H_{20}N_3O_2S^+$  ( $[M-H]^+$ ) 354.1276, found 354.1282.



(*R*)-2-Methyl-5-(3-((4-methyl-5-(2-(trifluoromethyl)phenyl)-4*H*-1,2,4-triazol-3-yl)thio)prop-1-en-2-yl)cyclohex-2-en-1-one (compound **5n**): yellow oily liquid; yield, 67.7%; UV-vis (EtOH)  $\lambda_{\max}$ : 268.50 nm; IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3081.63, 3028.57 (=C-H, Ar-H), 2953.90, 2923.69 (C-H), 1670.88 (C=O), 1609.10 (C=C), 1582.85, 1459.91, 1441.26 (Ar), 688.63 (C-S-C);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.87 – 7.83 (m, 1H, Ar-H), 7.73 – 7.68 (m, 2H, Ar-H), 7.49 – 7.43 (m, 1H, Ar-H), 6.77 (ddd,  $J = 5.7, 2.5, 1.3$  Hz, 1H, =C-H), 5.15 (s, 1H, =CH<sub>2</sub>), 5.00 (s, 1H, =CH<sub>2</sub>), 4.03 – 3.95 (m, 2H, -S-CH<sub>2</sub>), 3.32 (s, 3H, N-CH<sub>3</sub>), 2.99 (td,  $J = 14.1, 3.9$  Hz, 1H, CH), 2.64 (tdd,  $J = 18.3, 4.0, 1.4$  Hz, 2H, CH<sub>2</sub>), 2.47 – 2.30 (m, 2H, CH<sub>2</sub>), 1.80 (s, 3H, =C-CH<sub>3</sub>);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  199.1, 153.2, 150.7, 145.4, 144.3, 135.5, 132.3, 132.1, 131.0, 130.6 (q,  $J = 31.0$  Hz), 126.9 (q,  $J = 4.8$  Hz), 125.4 (d,  $J = 2.0$  Hz), 123.3 (d,  $J = 274.1$  Hz) 114.9, 43.2, 39.1, 38.1, 31.6, 30.9, 15.7; HRMS (APCI,  $m/z$ ): calcd. for  $C_{20}H_{21}F_3N_3O_2S^+$  ( $[M+H]^+$ ) 408.1357, found 408.1352.

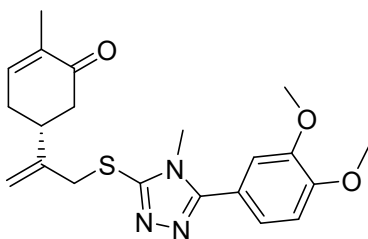


(*R*)-5-(3-((5-(4-Aminophenyl)-4-methyl-4*H*-1,2,4-triazol-3-yl)thio)prop-1-en-2-yl)-2-methylcyclohex-2-en-1-one (compound **5o**): yellow oily liquid; yield, 74.6%; UV-vis (EtOH)  $\lambda_{\text{max}}$ : 279.00 nm; IR (KBr,  $\text{v}/\text{cm}^{-1}$ ): 3350.85 (N-H), 3026.66 (=C-H, Ar-H), 2951.15, 2924.62 (C-H), 1665.43 (C=O), 1611.01 (C=C), 1547.08, 1481.11, 1430.76 (Ar), 702.19 (C-S-C);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.44 – 7.35 (m, 2H, Ar-H), 6.77 – 6.72 (m, 3H, =C-H & Ar-H), 5.16 (s, 1H, =CH<sub>2</sub>), 4.98 (s, 1H, =CH<sub>2</sub>), 4.03 – 3.88 (m, 2H, -S-CH<sub>2</sub>), 3.56 (s, 3H, N-CH<sub>3</sub>), 2.98 (td,  $J$  = 14.4, 3.9 Hz, 1H, CH), 2.75 – 2.53 (m, 2H, CH<sub>2</sub>), 2.48 – 2.25 (m, 2H, CH<sub>2</sub>), 1.78 (s, 1H, =C-CH<sub>3</sub>);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  199.2, 156.4, 150.4, 148.5, 145.6, 144.4, 135.5, 129.8, 116.2, 114.8, 114.7, 43.2, 39.2, 37.9, 31.7, 31.6, 15.7; HRMS (APCI,  $m/z$ ): calcd. for  $\text{C}_{19}\text{H}_{23}\text{N}_4\text{OS}^+$  ( $[\text{M}+\text{H}]^+$ ) 355.1593, found 355.1587.



(*R*)-5-(3-((5-(4-Methoxyphenyl)-4-methyl-4*H*-1,2,4-triazol-3-yl)thio)prop-1-en-2-yl)-2-methylcyclohex-2-en-1-one (compound **5p**): yellow oily liquid; yield,

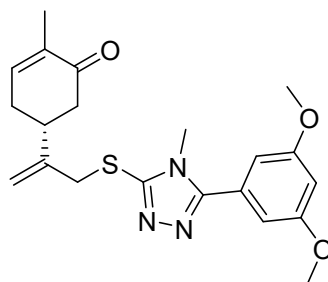
81.2%; UV-vis (EtOH)  $\lambda_{\text{max}}$ : 250.00 nm; IR (KBr,  $\text{v}/\text{cm}^{-1}$ ): 2960.37, 2923.36 (C-H), 1671.78 (C=O), 1612.45 (C=C), 1466.54, 1442.68 (Ar), 696.07 (C-S-C);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.59 – 7.55 (m, 2H, Ar-H), 7.04 – 7.02 (m, 2H, Ar-H), 6.83 – 6.70 (m, 1H, =C-H), 5.20 (s, 1H, =CH<sub>2</sub>), 5.01 (s, 1H, =CH<sub>2</sub>), 4.05 – 3.95 (m, 2H, -S-CH<sub>2</sub>), 3.88 (s, 3H, -OCH<sub>3</sub>), 3.59 (s, 3H, N-CH<sub>3</sub>), 3.00 (td,  $J = 14.3, 3.9$  Hz, 1H, CH), 2.69 – 2.59 (m, 2H, CH<sub>2</sub>), 2.47 – 2.31 (m, 2H, CH<sub>2</sub>), 1.80 (s, 3H, =C-CH<sub>3</sub>);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  199.2, 161.0, 155.9, 150.9, 145.5, 144.3, 135.5, 130.0, 119.1, 114.8, 114.4, 55.4, 43.2, 39.3, 37.8, 31.7, 31.7, 15.7; HRMS (APCI,  $m/z$ ): calcd. for  $\text{C}_{20}\text{H}_{24}\text{N}_3\text{O}_2\text{S}^+$  ( $[\text{M}+\text{H}]^+$ ) 370.1589, found 370.1584.



(*R*)-5-(3-((5-(3,4-Dimethoxyphenyl)-4-methyl-4*H*-1,2,4-triazol-3-yl)thio)prop-1-en-2-yl)-2-methylcyclohex-2-en-1-one (compound **5q**): yellow oily liquid; yield, 75.7%; IR (KBr,  $\text{v}/\text{cm}^{-1}$ ): 3083.67 (=C-H, Ar-H), 2951.02, 2926.53 (C-H), 1670.69 (C=O), 1607.91 (C=C), 1587.29, 1533.92, 1488.01, 1439.01 (Ar), 704.86 (C-S-C);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.27 – 7.24 (m, 1H, Ar-H), 7.13 (dt,  $J = 8.3, 2.0$  Hz, 1H, Ar-H), 6.98 (dd,  $J = 8.3, 2.4$  Hz, 1H, Ar-H), 6.77 (ddd,  $J = 5.4, 2.4, 1.3$  Hz, 1H, =C-H), 5.22 (s, 1H, =CH<sub>2</sub>), 5.02 (s, 1H, =CH<sub>2</sub>), 4.07 – 3.96 (m,

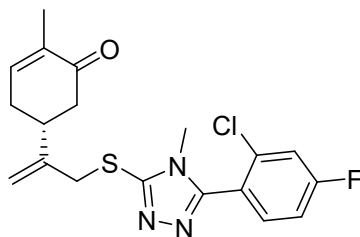


2H, -S-CH<sub>2</sub>), 3.95 (d, *J* = 6.3 Hz, 6H, -OCH<sub>3</sub>), 3.61 (s, 3H, N-CH<sub>3</sub>), 3.00 (ddt, *J* = 14.4, 8.8, 4.0 Hz, 1H, CH), 2.69 – 2.62 (m, 2H, CH<sub>2</sub>), 2.49 – 2.32 (m, 2H, CH<sub>2</sub>), 1.80 (s, 3H, =C-CH<sub>3</sub>); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 199.1, 155.9, 151.0, 150.6, 149.4, 145.5, 144.3, 135.6, 120.9, 119.5, 114.8, 112.0, 111.0, 56.1, 56.0, 43.2, 39.3, 37.7, 31.8, 31.7, 15.7; HRMS (APCI, *m/z*): calcd. for C<sub>21</sub>H<sub>26</sub>N<sub>3</sub>O<sub>3</sub>S<sup>+</sup> ([M+H]<sup>+</sup>) 400.1695, found 400.1689.

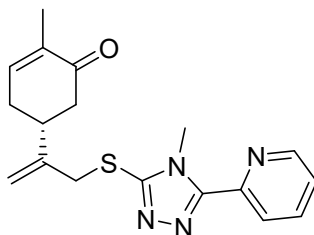


(*R*)-5-(3-((5-(3,5-Dimethoxyphenyl)-4-methyl-4*H*-1,2,4-triazol-3-yl)thio)prop-1-en-2-yl)-2-methylcyclohex-2-en-1-one (compound **5r**): yellow oily liquid; yield, 67.6%; UV-vis (EtOH) λ<sub>max</sub>: 211.00 nm; IR (KBr, v/cm<sup>-1</sup>): 3085.71 (=C-H, Ar-H), 2953.06, 2924.49 (C-H), 1669.39 (C=O), 1607.91 (C=C), 1595.92, 1520.41, 1475.51, 1459.18 (Ar), 685.71 (C-S-C); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 6.80 – 6.73 (m, 3H, =C-H & Ar-H), 6.58 (t, *J* = 2.3 Hz, 1H, Ar-H), 5.21 (s, 1H, =CH<sub>2</sub>), 5.01 (s, 1H, =CH<sub>2</sub>), 4.05 – 3.97 (m, 2H, -S-CH<sub>2</sub>), 3.84 (s, 6H, -OCH<sub>3</sub>), 3.61 (s, 3H, N-CH<sub>3</sub>), 2.99 (td, *J* = 14.1, 3.9 Hz, 1H, CH), 2.68 – 2.60 (m, 2H, CH<sub>2</sub>), 2.46 – 2.31 (m, 2H, CH<sub>2</sub>), 1.79 (s, 3H, =C-CH<sub>3</sub>); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 199.1, 161.1, 155.8, 151.4, 145.5, 144.3, 135.6, 128.5, 114.9, 106.7, 102.2, 55.6, 43.2,

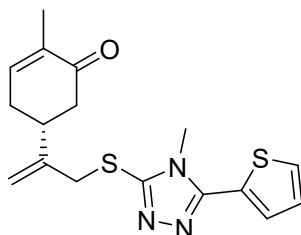
39.3, 37.7, 31.8, 31.7, 15.7; HRMS (APCI, m/z): calcd. for C<sub>21</sub>H<sub>26</sub>N<sub>3</sub>O<sub>3</sub>S<sup>+</sup> ([M+H]<sup>+</sup>) 400.1695, found 400.1689.



(*R*)-5-(3-((5-(2-Chloro-4-fluorophenyl)-4-methyl-4*H*-1,2,4-triazol-3-yl)thio)prop-1-en-2-yl)-2-methylcyclohex-2-en-1-one (compound **5s**): yellow oily liquid; yield, 77.8%; IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3086.52 (=C-H, Ar-H), 2953.24, 2923.29 (C-H), 1666.98 (C=O), 1604.82 (C=C), 1461.45, 1449.80 (Ar), 693.10 (C-S-C); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.52 (t,  $J = 4.3$  Hz, 1H, Ar-H), 7.30 (dd,  $J = 8.3, 2.4$  Hz, 1H, Ar-H), 7.19 – 7.14 (m, 1H, Ar-H), 6.78 – 6.77 (m, 1H, =C-H), 5.19 (s, 1H, =CH<sub>2</sub>), 5.02 (s, 1H, =CH<sub>2</sub>), 4.11 – 3.94 (m, 2H, -S-CH<sub>2</sub>), 3.42 (s, 3H, N-CH<sub>3</sub>), 3.01 (dd,  $J = 13.9, 3.3$  Hz, 1H, CH), 2.69 – 2.61 (m, 2H, CH<sub>2</sub>), 2.48 – 2.32 (m, 2H, CH<sub>2</sub>), 1.81 (s, 3H, =C-CH<sub>3</sub>); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>):  $\delta$  199.1, 163.9 (d,  $J = 255.0$  Hz), 153.3, 151.2, 145.4, 144.2, 135.6, 135.5 (d,  $J = 10.6$  Hz), 134.0 (d,  $J = 9.3$  Hz), 122.9 (d,  $J = 3.7$  Hz) 117.7, 117.5, 115.0, 43.2, 39.3, 37.9, 31.6, 31.0, 15.7; HRMS (APCI, m/z): calcd. for C<sub>19</sub>H<sub>20</sub>ClFN<sub>3</sub>OS<sup>+</sup> ([M+H]<sup>+</sup>) 392.1000, found 392.0994.

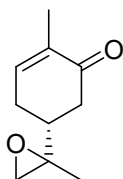


(*R*)-2-Methyl-5-(3-((4-methyl-5-(pyridin-2-yl)-4*H*-1,2,4-triazol-3-yl)thio)prop-1-en-2-yl)cyclohex-2-en-1-one (compound **5t**): yellow oily liquid; yield, 80.2%; IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3052.08 (=C-H, Ar-H), 2954.74, 2921.80 (C-H), 1671.38 (C=O), 1590.52, 1566.56, 1475.21, 1428.79 (Ar), 695.01 (C-S-C);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.65 (dd,  $J = 4.8, 0.8$  Hz, 1H, Ar-H), 8.27 (d,  $J = 8.0$  Hz, 1H, Ar-H), 7.83 (td,  $J = 7.8, 1.7$  Hz, 1H, Ar-H), 7.34 (ddd,  $J = 7.4, 4.9, 1.0$  Hz, 1H, Ar-H), 6.84 – 6.72 (m, 1H, =C-H), 5.20 (s, 1H, =CH<sub>2</sub>), 5.00 (s, 1H, =CH<sub>2</sub>), 4.11 – 3.82 (m, 5H, -S-CH<sub>2</sub> & N-CH<sub>3</sub>), 3.05 – 2.96 (m, 1H, CH), 2.69 – 2.59 (m, 2H, CH<sub>2</sub>), 2.46 – 2.31 (m, 2H, CH<sub>2</sub>), 1.80 (s, 3H, =C-CH<sub>3</sub>);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  199.1, 153.5, 152.7, 148.7, 147.8, 145.4, 144.3, 137.0, 135.6, 124.0, 123.4, 114.8, 43.2, 39.3, 37.5, 33.0, 31.6, 15.7; HRMS (APCI,  $m/z$ ): calcd. for  $\text{C}_{18}\text{H}_{21}\text{N}_4\text{OS}^+$  ( $[\text{M}+\text{H}]^+$ ) 341.1436, found 341.1431.



(*R*)-2-Methyl-5-(3-((4-methyl-5-(thiophen-2-yl)-4*H*-1,2,4-triazol-3-yl)thio)prop-1-en-2-yl)cyclohex-2-en-1-one (compound **5u**): yellow oily liquid; yield, 74.6%;

UV-vis (EtOH)  $\lambda_{\text{max}}$ : 240.50 nm; IR (KBr,  $\text{v}/\text{cm}^{-1}$ ): 3085.70 (=C-H, Ar-H), 2950.96, 2921.17 (C-H), 1667.89 (C=O), 1565.13, 1478.75, 1466.37, 1412.46 (Ar), 710.55 (C-S-C);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.53 – 7.49 (m, 1H, Ar-H), 7.48 – 7.46 (m, 1H, Ar-H), 7.18 (t,  $J = 2.5$  Hz, 1H, Ar-H), 6.78 – 6.75 (m, 1H, =C-H), 5.18 (s, 1H, =CH<sub>2</sub>), 5.00 (s, 1H, =CH<sub>2</sub>), 4.02 – 3.95 (m, 2H), 3.71 (s, 3H, N-CH<sub>3</sub>), 3.02 – 2.96 (m, 1H, CH), 2.67 – 2.60 (m, 2H, CH<sub>2</sub>), 2.46 – 2.30 (m, 2H, CH<sub>2</sub>), 1.80 (s, 3H, =C-CH<sub>3</sub>);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  199.1, 151.2, 150.9, 145.4, 144.3, 135.6, 128.3, 128.0, 127.8, 127.7, 114.9, 43.2, 39.2, 37.9, 31.7, 31.6, 15.7; HRMS (APCI,  $m/z$ ): calcd. for  $\text{C}_{17}\text{H}_{20}\text{N}_3\text{OS}_2^+$  ( $[\text{M}+\text{H}]^+$ ) 346.1048, found 346.1042.



(*R*)-2-Methyl-5-(2-methyloxiran-2-yl)cyclohex-2-en-1-one (compound **6**): colorless oily liquid; yield, 88.4%;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.71 – 6.66 (m, 1H, =C-H), 2.64 (dd,  $J = 18.3, 4.5$  Hz, 1H, CH), 2.55 – 2.47 (m, 2H, CH<sub>2</sub>), 2.40 – 1.99 (m, 4H, -OCH<sub>2</sub>- & CH<sub>2</sub>), 1.71 (s, 3H, =C-CH<sub>3</sub>), 1.26 (d,  $J = 8.0$  Hz, 3H, -CH<sub>3</sub>);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  198.7, 144.1, 135.5, 57.9, 52.8, 41.3, 40.3, 27.7, 18.4, 15.6.