A Photocatalytic Electron-rich Acceptor-involved EDA Complexes for Markovnikov Addition of Alkynes with *N*-Sulfonyl-azoles

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1. General Information

All reactions and manipulations were carried out under a nitrogen atmosphere, in a 10 mL sealed vial equipped with a stir bar, **^{1}H NMR**, **^{19}F NMR** and **^{13}C NMR** spectra were recorded using a Brucker 400 MHz spectrometer in $CDCl_3$. Tetramethylsilane (TMS) served as an internal standard (δ = 0) for **^{1}H NMR**, and $CDCl_3$ was used as internal standard (δ = 77.0) for **^{13}C NMR**. Chemical shifts are reported in parts per million as follows: chemical shift, multiplicity (s =singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, br = broad). High-resolution mass spectrometry (**HRMS**) was performed on IonSpec FT-ICR or Waters Micromass Q-TOF micro Synapt High-Definition Mass Spectrometer. LC-MS spectra were recorded on the HP-5989 instrument by ESI methods. The light employed in this work was bought from Shanghai 3S Technology Co., Ltd.: SSSTECH-LAL1CV1.0, 12 W blue LEDs (λ = 465 nm). All reactions involving heating are carried out in an oil bath.

2. Determination of the minor isomer as (*Z*)-4a

2.1 Comparison ^{1}H NMR of (E)-4a, (Z)-4a, AM-4a-1 and AM-4a-2

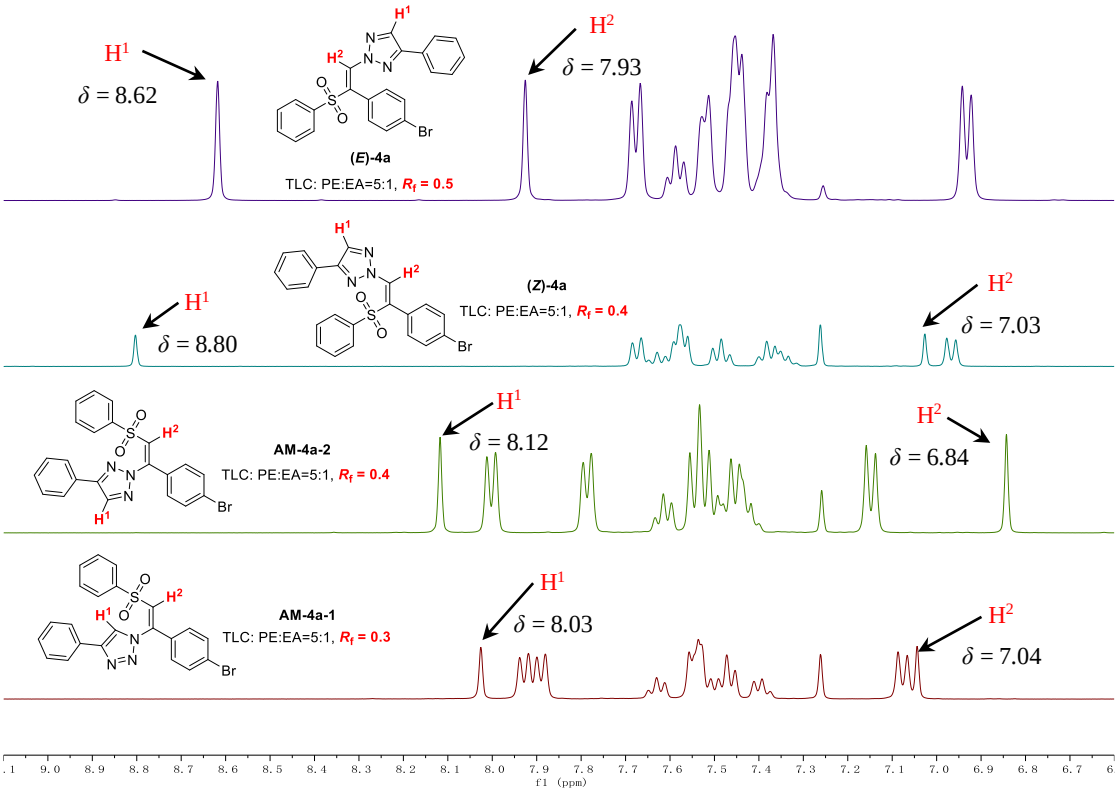
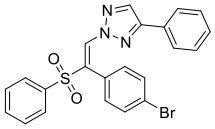


Figure S1

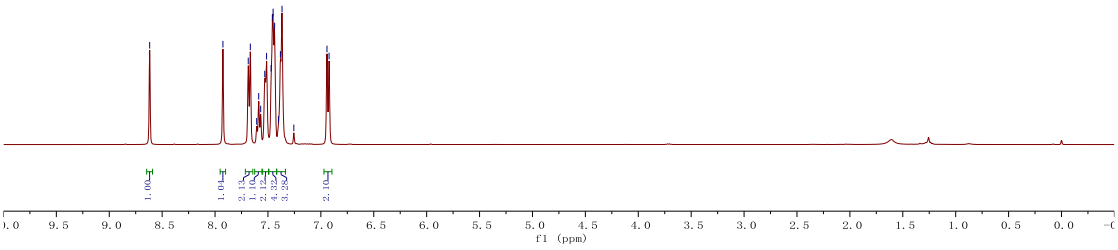
AM-4a-1 and **AM-4a-2** were synthesized according to literature.[1] Due to the single crystal confirmation in the literature, **AM-4a-1** and **AM-4a-2** are confirmed as the anti-Markovnikov addition and (*Z*)-configuration selectivity products. Based on our previous work,[2] compound **AM-4a-1** with higher polarity (R_f = 0.3) can be identified as N^1-regioselectivity product, while compound **AM-4a-2** with lower polarity (R_f = 0.4) is N^2-regioselectivity product. According to the difference in the chemical shift of H^1 (Figure S1) between **AM-4a-1**, **AM-4a-2** with **(*E*)-4a**, it can be ruled out that the minor by-product is an anti-Markovnikov addition product. The chemical shift of H^2 (Figure S1) between **(*E*)-4a** and the minor by-product is significantly different, indicating that the minor by-product is an (*Z*)-configuration selectivity product. In summary, we can infer that the minor by-product is (*Z*)-configuration selectivity product **(*Z*)-4a**.

2.2 The ^{1}H NMR data of (*E*)-4a

^{1}H NMR (400 MHz) Spectrum of (*E*)-4a in $CDCl_3$

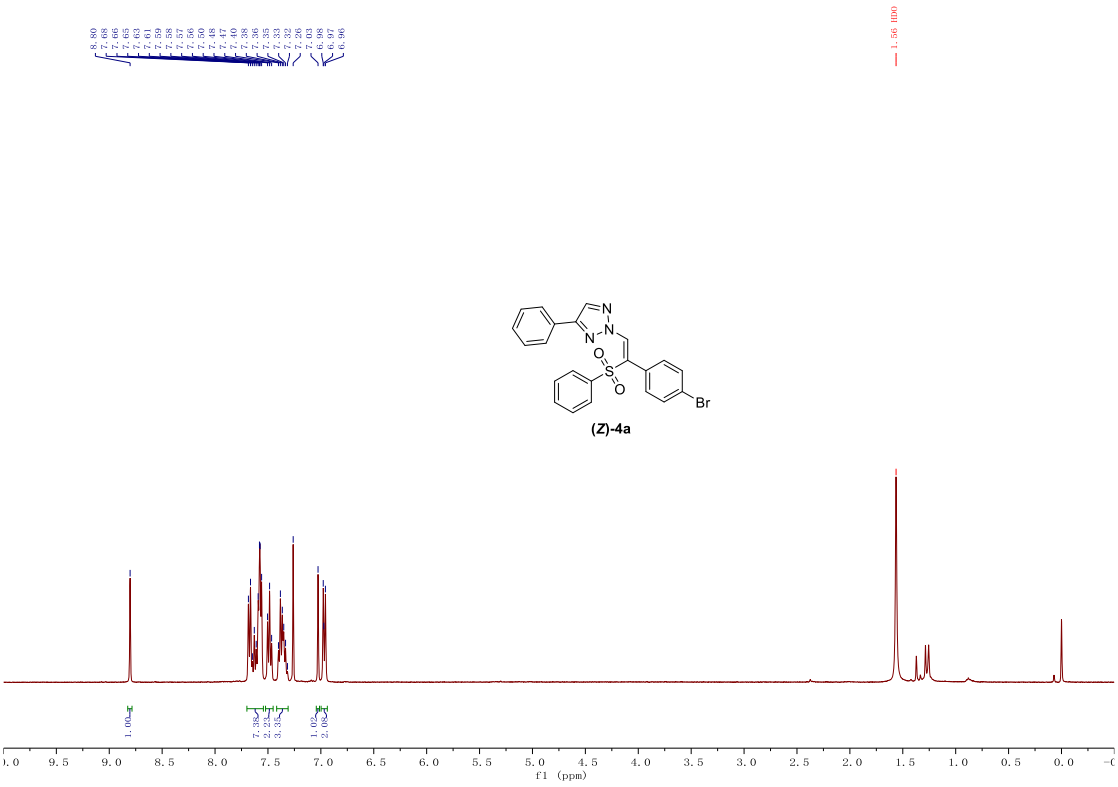


(*E*)-4a

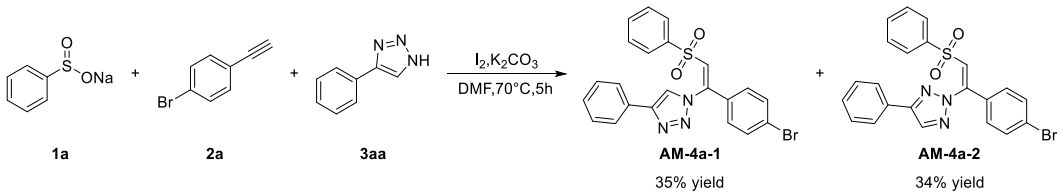


2.3 The ^{1}H NMR data of (*Z*)-4a

^{1}H NMR (400 MHz) Spectrum of (*Z*)-4a in $CDCl_3$

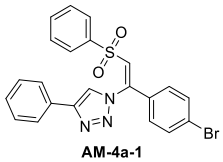


2.4 General Procedure for Products AM-4a-1 and AM-4a-2



According to the literature,[1] in an oven dried round bottomed flask equipped with a magnetic stirring bar, added 1-bromo-4-ethynylbenzene **2a** (0.50 mmol, 90 mg, 1.0 eq.), sodium benzenesulfinate **1a** (0.60 mmol, 98 mg, 1.2 eq.), 4-phenyl-1*H*-1,2,3-triazole (0.50 mmol, 72.5 mg, 1.0 eq.), iodine (0.50 mmol, 127 mg, 1.0 eq.) and K_2CO_3 (0.75 mmol, 104 mg, 1.5 eq.) in dry DMF (2.0 mL) under N_2 environment. The reaction mixture was stirred at 70°C in oil bath for 5h. After the reaction was completed, the mixture was quenched by the addition of satd aq $Na_2S_2O_3$ (5 mL). Further stirring was followed by extraction with ethyl acetate (2 × 15 mL). The organic

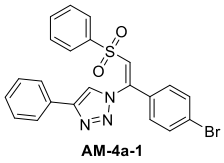
layer was dried with anhydrous $MgSO_4$, concentrated in vacuo. The crude product was purified by column chromatography with PE:EA (5:1) to afford **AM-4a-1** (R_f = 0.3) and **AM-4a-2** (R_f = 0.4).



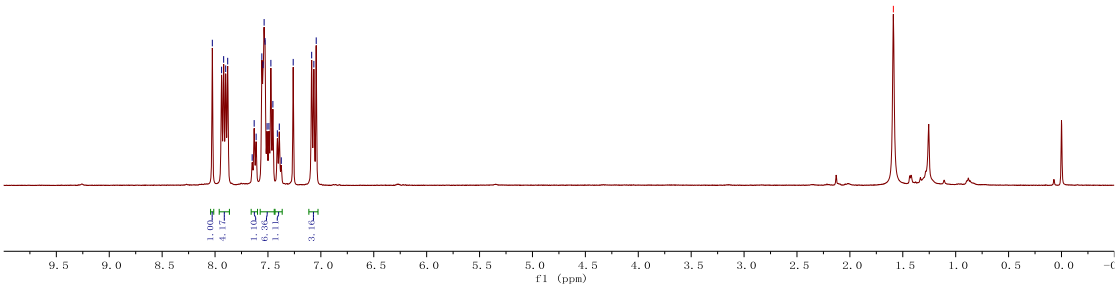
AM-4a-1

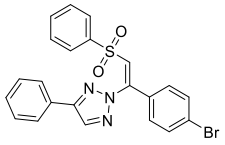
35% yield (81 mg) as a white solid. **(*Z*)-1-(1-(4-bromophenyl)-2-(phenylsulfonyl)vinyl)-4-phenyl-1*H*-1,2,3-triazole (AM-4a-1)**. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.03 (s, 1H), 7.91 (dd, *J* = 15.4, 7.7 Hz, 4H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.57 – 7.44 (m, 6H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.11 – 7.03 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) *δ* 148.1, 143.2, 139.8, 134.3, 132.7, 132.1, 129.5, 129.4, 129.0, 128.8, 128.3, 127.4, 126.3, 126.1, 122.9.

^{1}H NMR (400 MHz) Spectrum of AM-4a-1 in $CDCl_3$



AM-4a-1

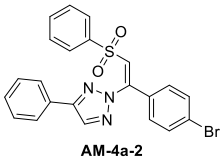




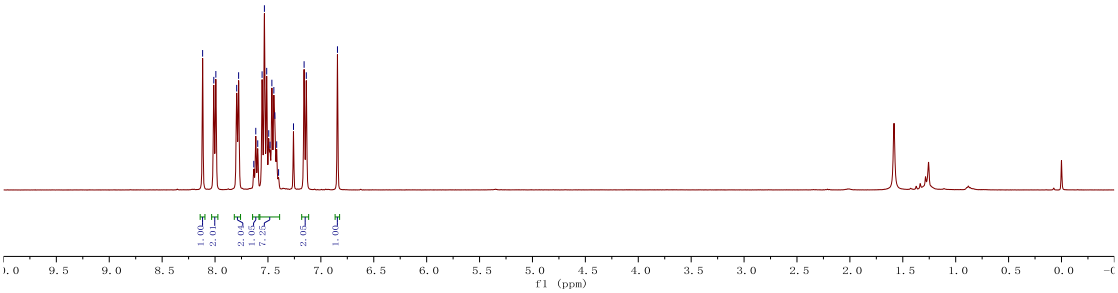
AM-4a-2

34% yield (79 mg) as a white solid. **(*Z*)-2-(1-(4-bromophenyl)-2-(phenylsulfonyl)vinyl)-4-phenyl-2*H*-1,2,3-triazole (AM-4a-2)**. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.12 (s, 1H), 8.00 (d, *J* = 7.8 Hz, 2H), 7.79 (d, *J* = 7.3 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.58 – 7.39 (m, 7H), 7.15 (d, *J* = 8.3 Hz, 2H), 6.84 (s, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 150.1, 146.0, 141.0, 134.2, 133.7, 132.3, 132.2, 130.0, 129.5, 129.1, 129.0, 128.9, 128.1, 126.8, 126.5, 123.6.

^{1}H NMR (400 MHz) Spectrum of AM-4a-2 in $CDCl_3$



AM-4a-2



3. Ternary EDA Complex Interaction Studies.

3.1 UV/Vis Studies

UV/vis absorption spectra were measured in a 1 cm quartz cuvette using a UV-2600 spectrophotometer from Shimadzu. Absorption spectra of individual reaction components and mixtures thereof were shown in Figure S2a. When **3a** (0.1 mmol) was mixed with **1a** (0.25 mmol) and **2a** (0.12 mmol) in DMF (4 mL), an obvious bathochromic shift was observed, which was visibly yellow in color. This indicates the formation of an electron donor-acceptor (EDA) complex (Fig. S2b, cyan band).

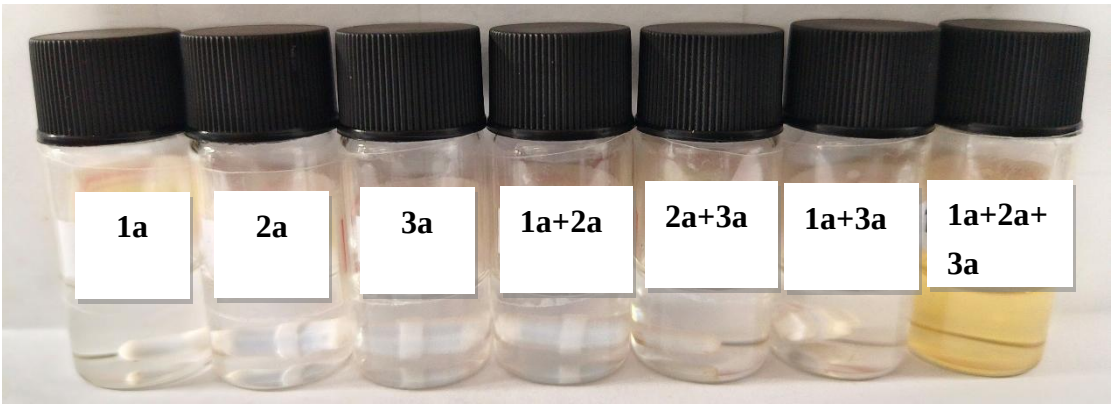


Figure S2a

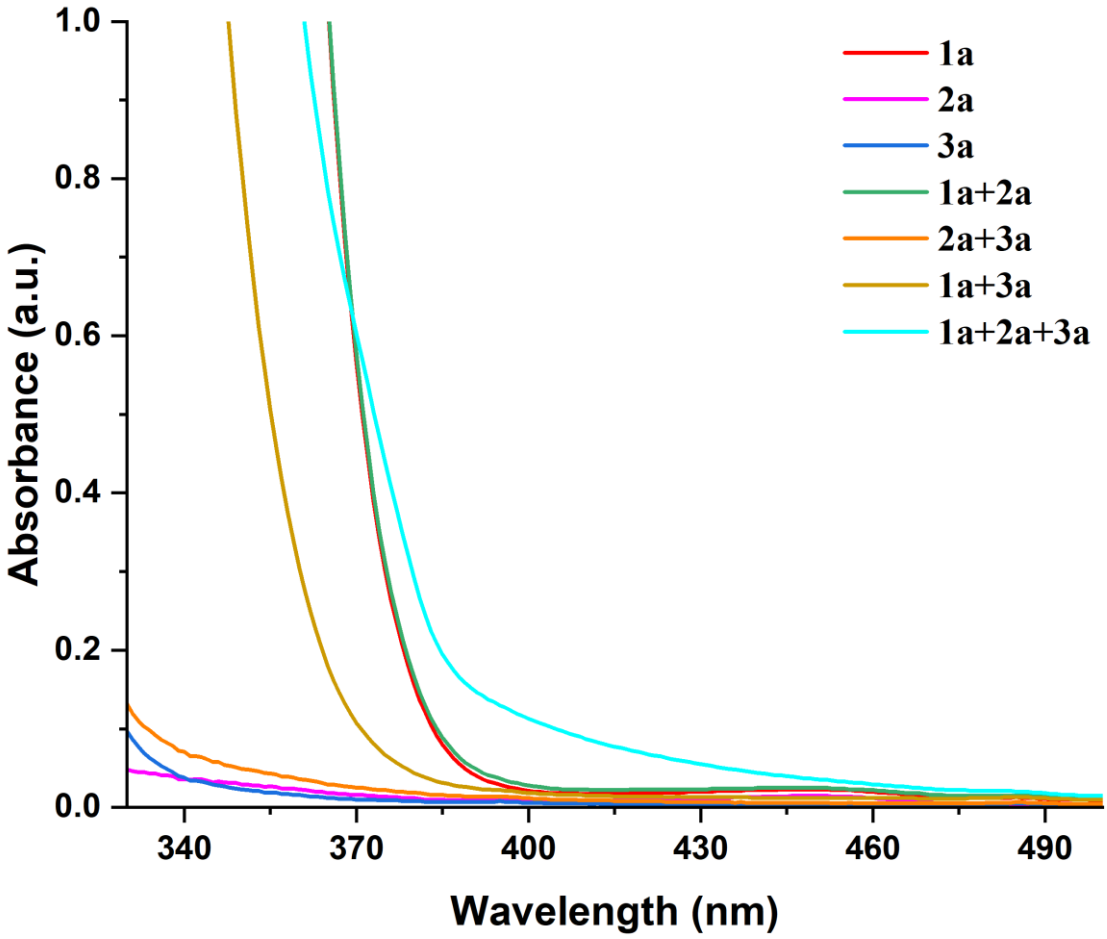


Figure S2b

Figure S2. UV−vis spectrum of **1a** (0.25 mmol), **2a** (0.12 mmol) and **3a** (0.1 mmol) in DMF (4 mL) solution and their mixture, taken after 5 min of stirring at r.t.

3.2 ^{1}H NMR Spectra Analysis

1a (0.125 mmol, 20.5 mg), **2b** (0.06 mmol, 6 mg), and **3a** (0.05 mmol, 15 mg) in DMSO-d_6 (0.5 mL) solution and their mixture were added into NMR tubes after 5 min of stirring at rt.^{1}H NMR analysis of the mixed solution of **1a**, **2b**, and **3a** in DMSO-d_6 shows that the signal of the proton of the triazole ring in **3a** has an obvious up-fielded shift when adding **1a** or **2b** respectively (Figure S3a). When **1a** and **2b** are simultaneously added to **3a** solution, the maximum up-fielded shift was observed. Except for the signal of the pro-ton of the triazole ring in **3a** (H^1), no significant change

of any other protons was observed (Figure S3b). These results further confirm that a weak interaction occurs among **1a**, **2b** and **3a**.

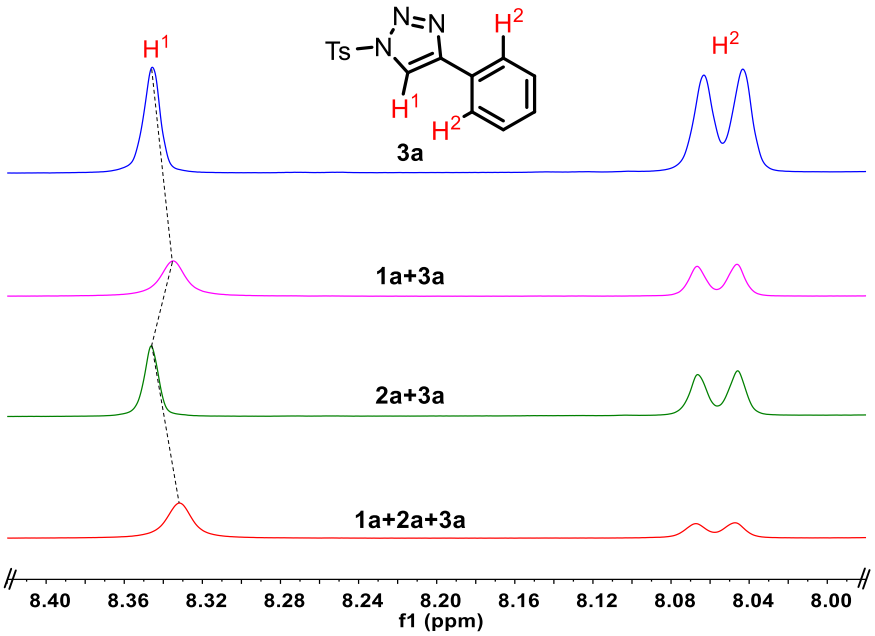


Figure S3a

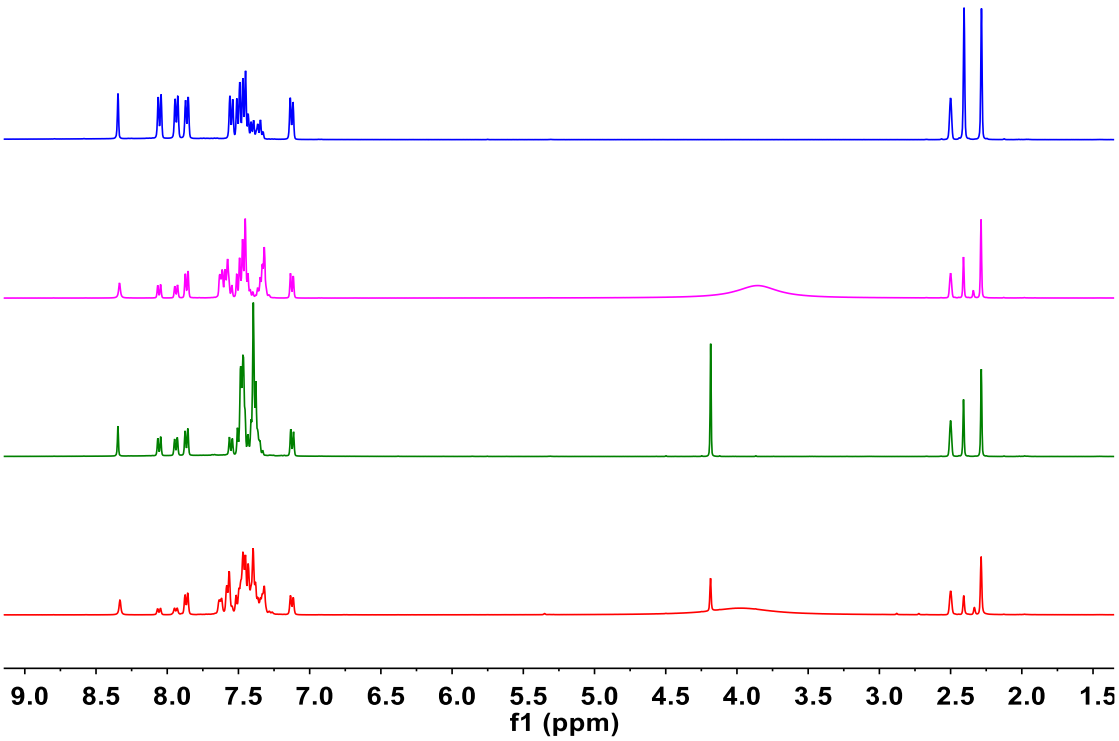


Figure S3b

3.3 Job's Plot Analysis

Job's plot analysis was performed to determine the stoichiometry of the EDA complex between **2a**-**3a** and **1a** in DMF (0.3 M total concentration) at 450 nm and 430 nm. The absorbance was plotted against the molar fraction of **1a**. Maximum absorbance was detected at 33.3% molar fraction of **1a** which is a 1:1:1 mixture of **1a**:**2a**:**3a**, indicating that this is the stoichiometry of the EDA complex. At both 430 nm and 450 nm, the 1:1:1 mixture of **1a**, **2a** and **3a** exhibited the most pronounced absorption profile, thus supporting the presence of a charge transfer interaction between the three species (Table S1 and Figure S4).

Table S1. Absorbance of 0.3 M DMF solutions of different molar ratios of **1a** and **2a**-**3a**

Entry	**2a**:**3a** (mmol)	**1a** (mmol)	Mole fraction of **1a** (%)	Absorbance (450 nm)	Absorbance (430 nm)
1	0.45:0.45	0	0	0.007	0.034
2	0.40:0.40	0.10	11.1	0.053	0.141
3	0.35:0.35	0.20	22.2	0.238	0.517
4	0.30:0.30	0.30	33.3	0.287	0.626
5	0.25:0.25	0.40	44.4	0.200	0.456
6	0.20:0.20	0.50	55.6	0.022	0.081
7	0.15:0.15	0.60	66.7	0.013	0.080
8	0:0	0.90	100	0.002	0.018

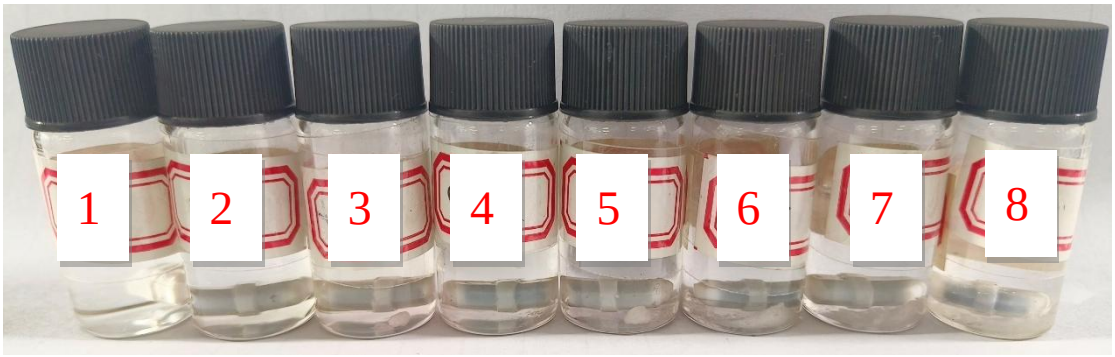


Figure S4a. The solutions of different molar ratios of **1a** and **2a**-**3a** before the formation of ternary EDA complexes

Figure S4b. The solutions of different molar ratios of **1a** and **2a-3a** after 10 min of stirring at rt.

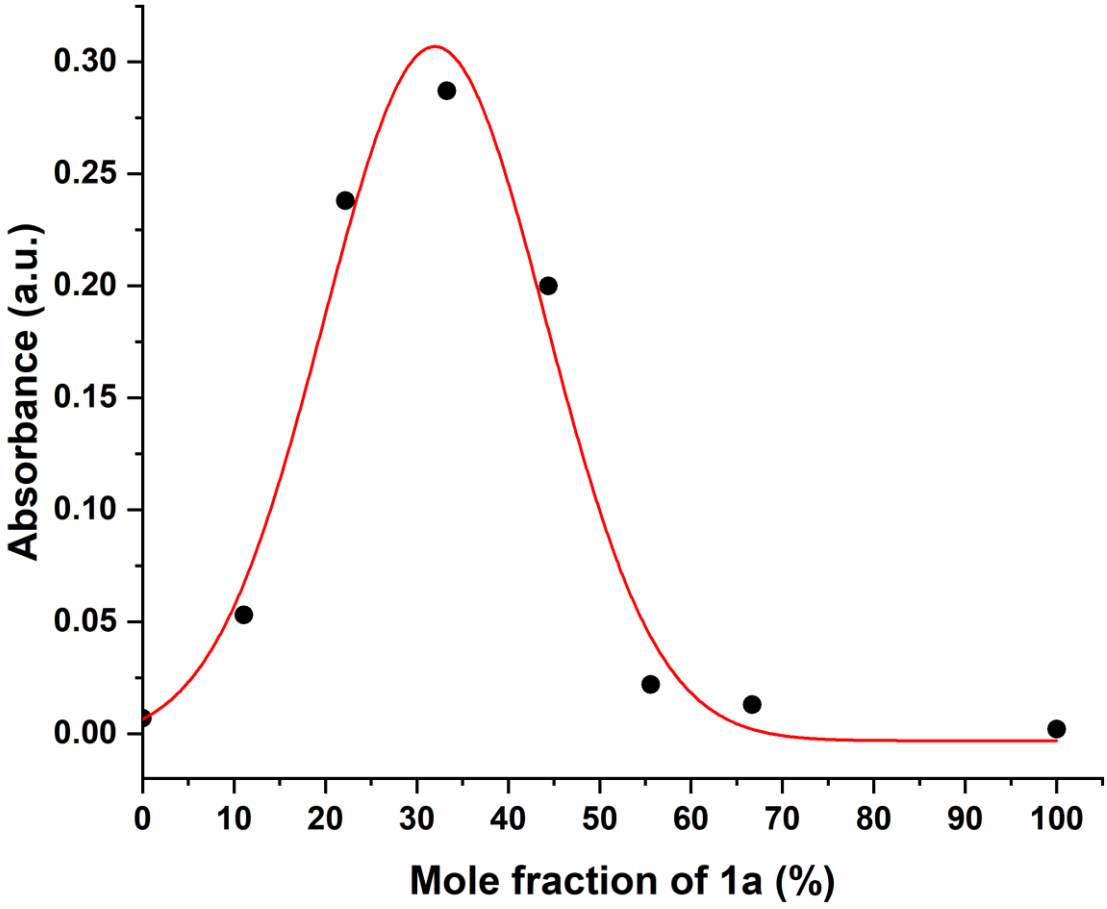


Figure S4c. Job's plot of the EDA complex (0.3 M total concentration in DMF) between **1a** and **2a-3a** recorded at 450 nm.

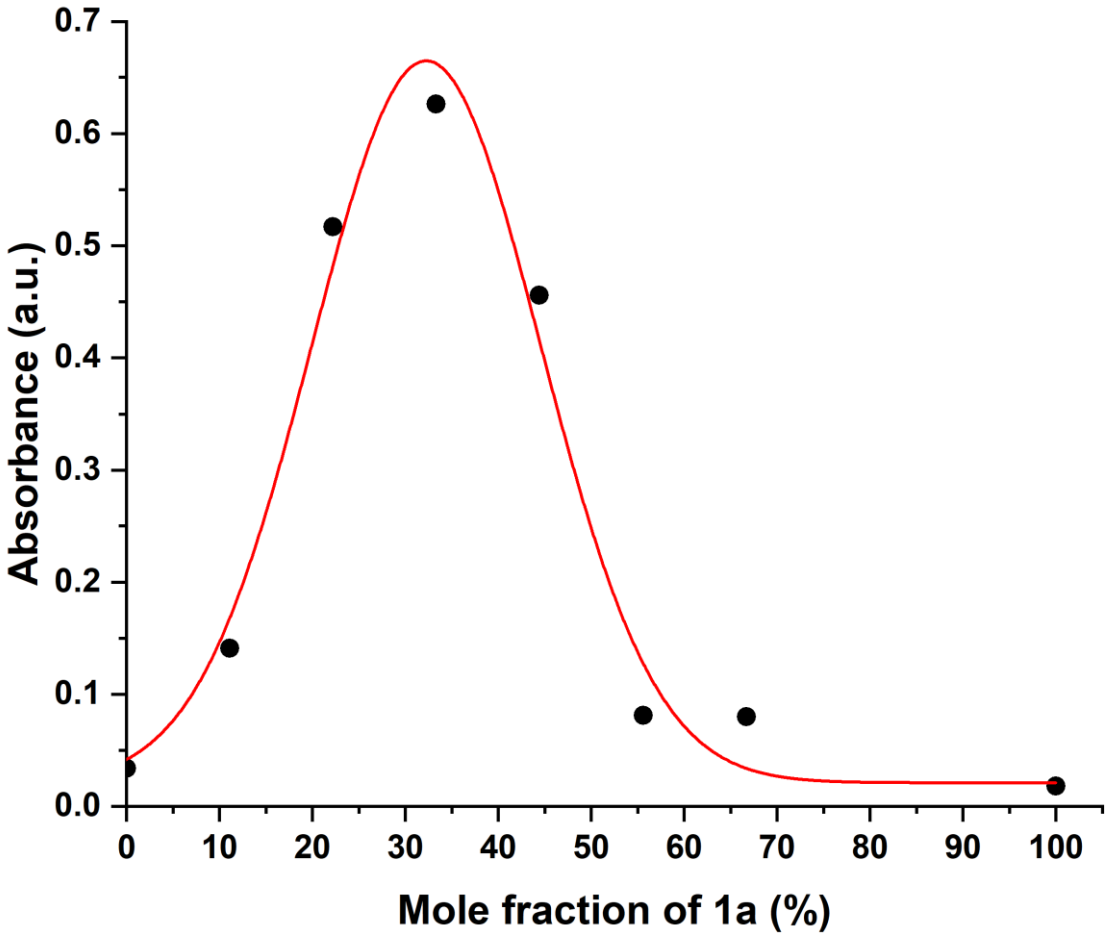


Figure S4d. Job's plot of the EDA complex (0.3 M total concentration in DMF) between **1a** and **2a**-**3a** recorded at 430 nm.

4. General Procedures for Preparation of Substrates

4.1 Sodium Sulfinates Used in This Study

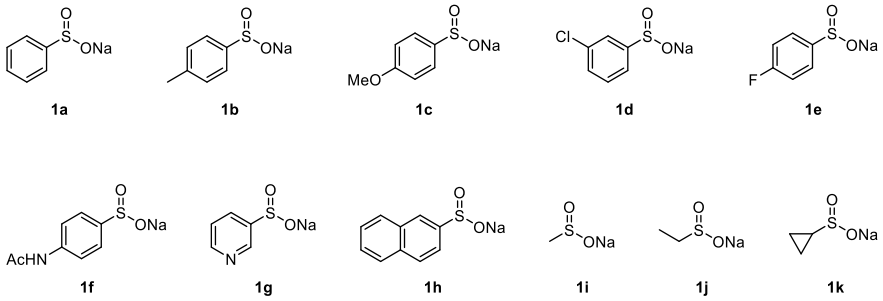
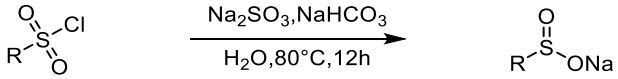


Figure S5

Sodium sulfinates **1a**, **1b**, **1i** and **1j** are commercially available. The synthetic methods and the NMR data of sodium sulfinates **1c**[3], **1d**[3], **1e**[3], **1f**[4], **1g**[4], **1h**[3] and **1k**[3] have been reported in the literatures.



The sulfonyl chlorides (5 mmol, 1.0 equiv) was dissolved in water (15 mL). Sodium sulfite (10 mmol, 2.0 equiv) and sodium hydrogencarbonate (15 mmol, 3.0 equiv) were added, and the reaction mixture was reacted at 80 ℃ for 12 h. The solvent was evaporated and ethanol (20 mL) was added to the residue. The suspension was heated to 80 ℃ for 10 min, refluxed and filtered. The solvent was evaporated under vacuum to give sodium sulfinates **1c**, **1d**, **1e**, **1f**, **1g**, **1h** and **1k**.

4.2 Alkynes Used in This Study

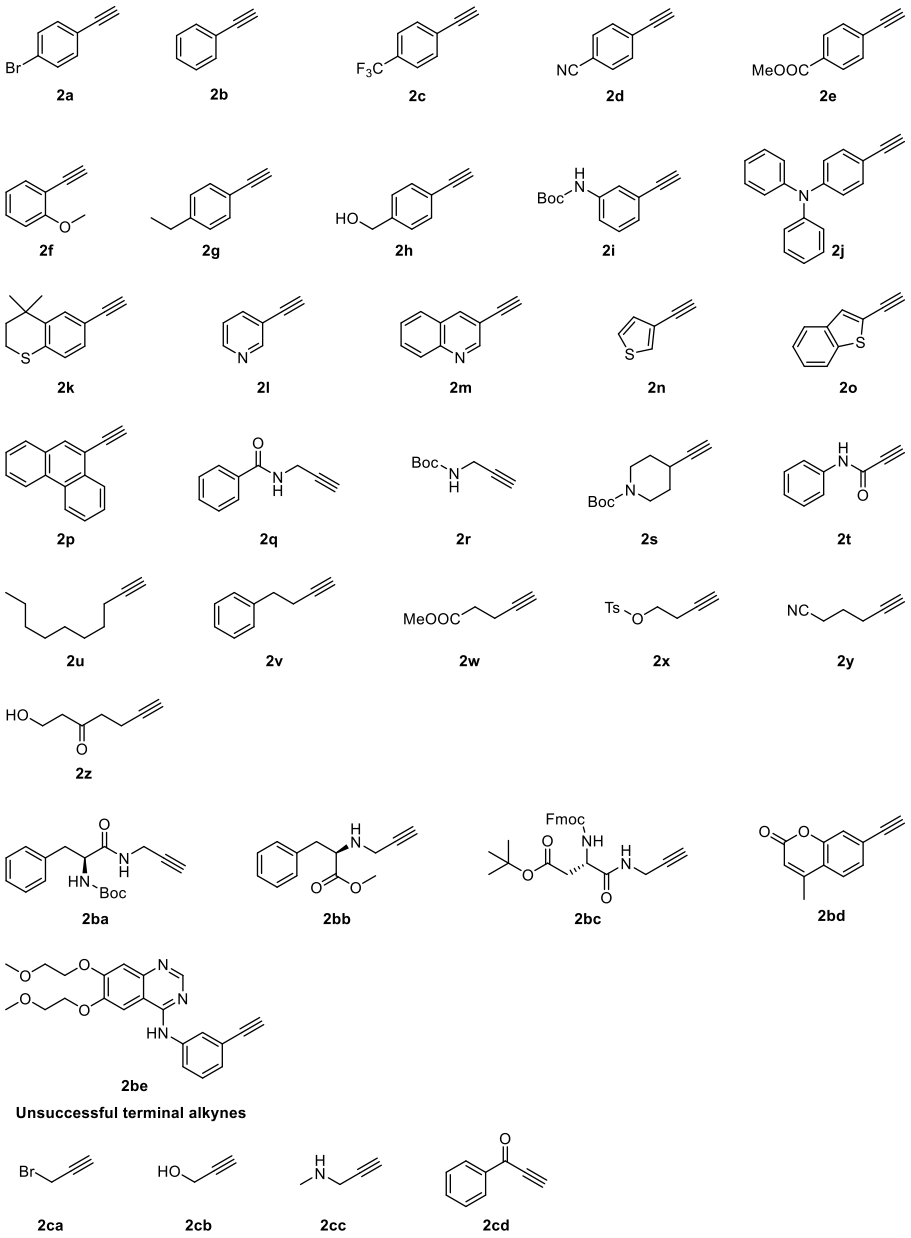


Figure S6

Alkynes **2a-h**, **2j-n**, **2p**, **2r**, **2s**, **2u-z** and **2be** are commercially available. Alkynes **2i**[5], **2o**[6], **2q**[7], **2t**[8], **2ba**[9], **2bb**[10], **2bc**[11] and **2bd**[12] are synthesized according to the literatures.

4.3 *N*-Ts-azoles Used in This Study

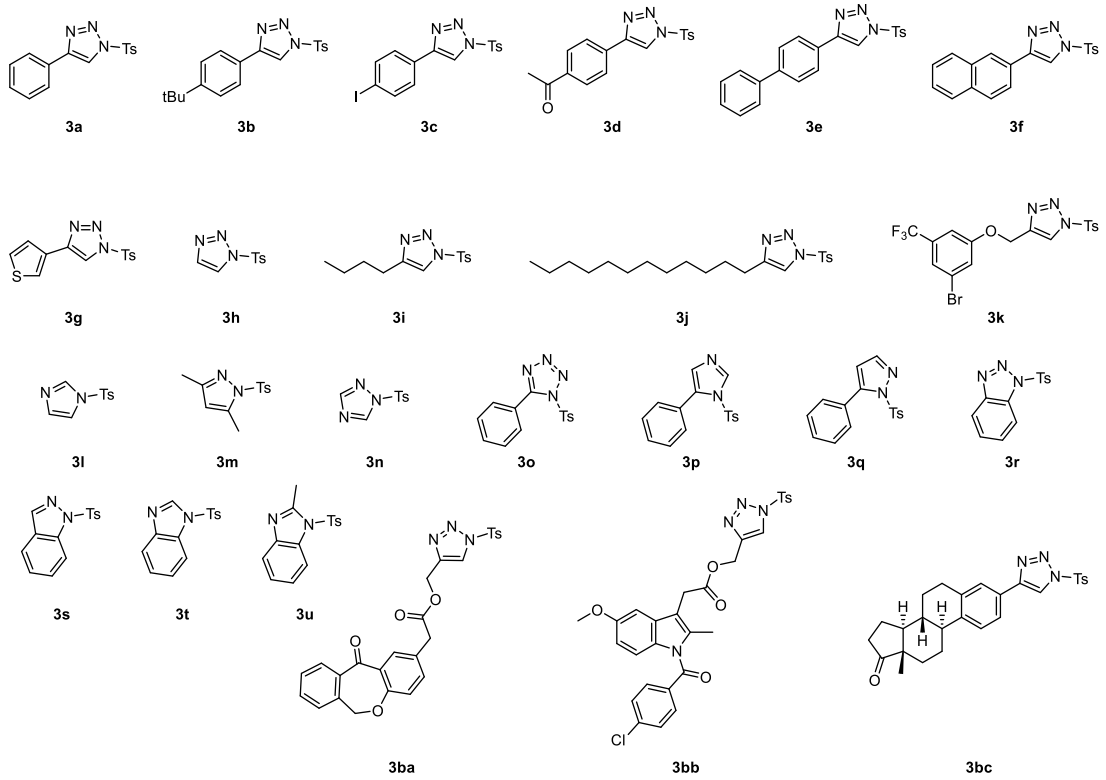
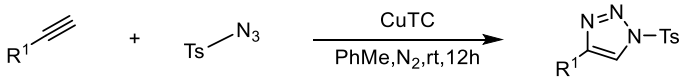


Figure S7

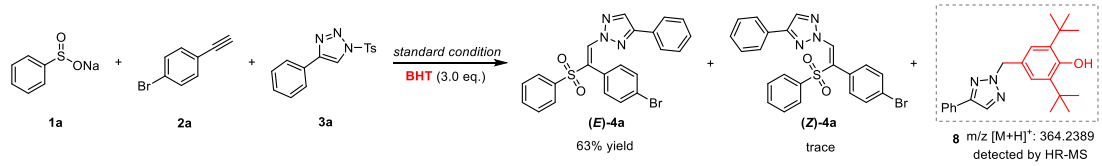
The synthetic methods and the NMR data of *N*-Ts-1,2,3-triazoles **3a**[13], **3b**[13], **3c**[14], **3d**[15], **3e**[2], **3f**[13], **3g**[13], **3h**[16], **3i**[15] and **3bc**[2] have been reported in the literatures.



A scintillation vial was charged with copper (I) thiophene-2-carboxylate (CuTC, 0.1 eq.), toluene (20 mL), and the alkyne (1.0 eq.). The reaction mixture was cooled in an ice-water bath. Subsequently, the sulfonyl azide (1.0 eq.) was added slowly as the limiting reagent to avoid a run-away exotherm, and the reaction mixture allowed to warm to room temperature and stirred overnight. The reaction was diluted with saturated aq. NH_4Cl and extracted into DCM (2 ×20 mL). The combined organics were dried (Na_2SO_4) and filtered through celite. The eluent was concentrated in vacuo. The obtained crude product was purified by SiO_2-column chromatography to give the de-

sired product 1-sulfonyl-1,2,3-triazoles **3a-g**, **3i-k** and **3ba-3bc**.

5. Control Experiments

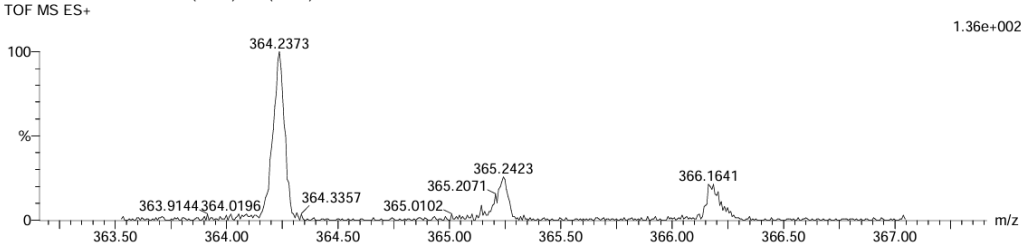


Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 1000.0 PPM / DBE: min = -50.0, max = 200.0
Element prediction: Off

Monoisotopic Mass, Even Electron Ions
2 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 23-23 H: 29-30 N: 3-3 O: 1-1 Er: 0-1

LJH-BHT-HRMS-INJECT 11 (0.075) Cm (10:16)
TOF MS ES+



Minimum:				-50.0	
Maximum:		500.0	1000.0	200.0	
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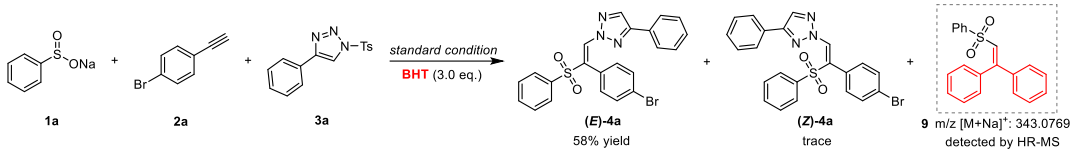

Elemental Composition Report

Single Mass Analysis

Tolerance = 1000.0 PPM / DBE: min = -50.0, max = 200.0
Element prediction: Off

Monoisotopic Mass, Even Electron Ions
2 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 20-20 H: 16-16 O: 2-2 S: 1-1 Er: 0-1 Na: 1-1

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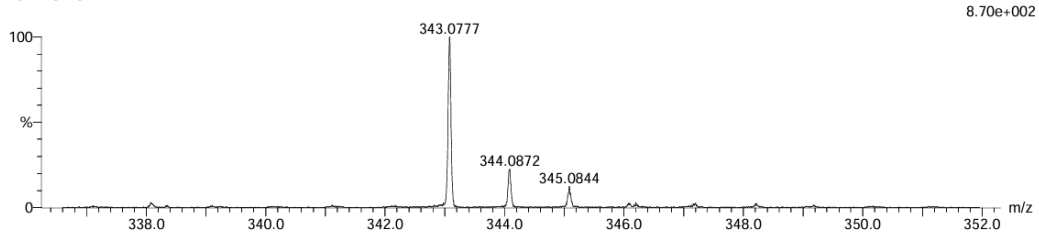
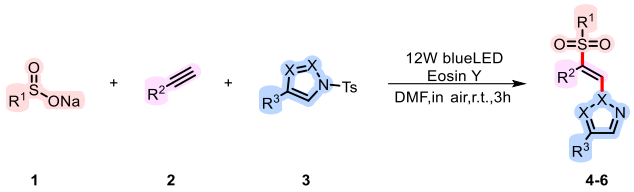
TOF MS ES+



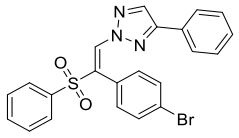
Minimum:				-50.0	
Maximum:		500.0	1000.0	200.0	
Mass	Calc. Mass	mDa	PPM	DBE	Formula
343.0777	343.0769	0.8	2.3	12.5	C20 H16 O2 S Na

6. General Procedures for Synthesis of α-Sulfonyl-β-Triazole Olefins (General Procedure 1)



In a 10 mL test tube equipped with a stir bar, sodium sulfinates **1** (0.5 mmol, 2.5 eq.), terminal alkynes **2** (0.24 mmol, 1.2 eq.), *N*-tosyl-1,2,3-triazoles **3** (0.2 mmol, 1.0 eq.) and Eosin Y (5 mol%) was added. Then DMF (2 ml) was added into the test tube. The reaction was stirred under 12W blue LED irradiation at room temperature for 3h. After the completion of the reaction, the mixture was diluted with 20ml water, and then extracted it with ethyl acetate (3×10 ml). The organic phase was washed with brine, dried with anhydrous Na_2SO_4, concentrated in vacuo, and purified by column chromatography using petroleum ether/ethyl acetate mixture as eluent to afford products **(*E*)-4a-4z**, **(*E*)-5a-5ad** and **(*E*)-6a-6h** in high yield and purity.

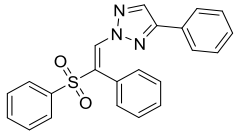
7. ^{1}H NMR, ^{19}F NMR and ^{13}C NMR data of compounds



(*E*)-4a

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), 1-bromo-4-ethynylbenzene **2a** (0.24 mmol, 43 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (5:1) as eluent to afford product **(*E*)-4a** in 88% yield (82 mg) as a white solid.

(*E*)-2-(2-(4-bromophenyl)-2-(phenylsulfonyl)vinyl)-4-phenyl-2*H*-1,2,3-triazole ((*E*)-4a). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.62 (s, 1H), 7.93 (s, 1H), 7.68 (d, J = 7.8 Hz, 2H), 7.59 (t, J = 7.5 Hz, 1H), 7.52 (d, J = 6.8 Hz, 2H), 7.49 – 7.42 (m, 4H), 7.37 (d, J = 6.1 Hz, 3H), 6.93 (d, J = 8.0 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 150.5, 138.3, 135.0, 133.7, 133.4, 132.5, 131.4, 130.7, 129.8, 129.1, 129.0, 128.7, 128.6, 128.4, 126.3, 123.7. **HRMS-ESI** (*m/z*): calcd for $C_{22}H_{16}BrN_3NaO_2S$ $[M+Na]^+$: 488.0039, found 488.0040.

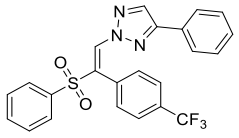


(*E*)-4b

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), ethynylbenzene **2b** (0.24 mmol, 25 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (5:1) as eluent to afford product **(*E*)-4b** in 81% yield (62 mg) as a white solid.

(*E*)-4-phenyl-2-(2-phenyl-2-(phenylsulfonyl)vinyl)-2*H*-1,2,3-triazole ((*E*)-4b). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.61 (s, 1H), 7.90 (s, 1H), 7.66 (d, J = 7.8 Hz, 2H), 7.57 (t, J = 7.5 Hz, 1H), 7.48 (d, J = 8.2 Hz, 2H), 7.46 – 7.39 (m, 3H), 7.36 (t, J = 7.0

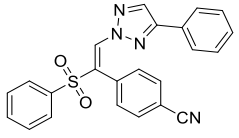
Hz, 3H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.04 (d, *J* = 7.6 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 149.3, 138.3, 134.5, 133.6, 132.8, 132.5, 132.2, 130.7, 129.4, 129.08, 128.9, 128.8, 128.1, 127.6, 127.6, 123.8. **HRMS-ESI** (*m/z*): calcd for $C_{22}H_{17}N_3NaO_2S$ $[M+Na]^+$: 410.0934, found 410.0948.



(*E*)-4c

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), 1-ethynyl-4-(trifluoromethyl)benzene **2c** (0.24 mmol, 41 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (5:1) as eluent to afford product **(*E*)-4c** in 85% yield (77 mg) as a white solid.

(*E*)-4-phenyl-2-(2-(phenylsulfonyl)-2-(4-(trifluoromethyl)phenyl)vinyl)-2*H*-1,2,3-triazole ((*E*)-4c). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.64 (s, 1H), 7.94 (s, 1H), 7.69 (d, *J* = 7.8 Hz, 2H), 7.60 (dd, *J* = 13.6, 7.6 Hz, 3H), 7.50 – 7.39 (m, 4H), 7.38 – 7.31 (m, 3H), 7.18 (d, *J* = 7.9 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 150.6, 138.2, 135.0, 133.9, 133.8 (d, *J* = 1.1 Hz), 133.6, 131.3, 131.1 (q, *J* = 33.3 Hz), 130.4, 129.8, 129.1, 129.0, 128.7, 128.3, 126.2, 125.1 (q, *J* = 4.0 Hz), 124.0 (q, *J* = 273.7 Hz). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -62.75. **HRMS-ESI** (*m/z*): calcd for $C_{23}H_{16}F_3N_3NaO_2S$ $[M+Na]^+$: 478.0808, found 478.0821.

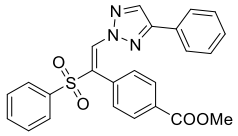


(*E*)-4d

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), 4-ethynylbenzonitrile **2d** (0.24 mmol, 30 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum

ether/ethyl acetate mixture (3:1) as eluent to afford product **(*E*)-4d** in 80% yield (66 mg) as a white solid.

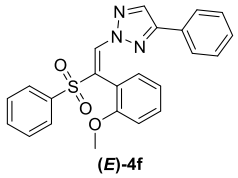
(*E*)-4-(2-(4-phenyl-2*H*-1,2,3-triazol-2-yl)-1-(phenylsulfonyl)vinyl)benzonitrile ((*E*)-4d). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.65 (s, 1H), 7.94 (s, 1H), 7.63 (dd, *J* = 20.2, 7.8 Hz, 5H), 7.47 (dd, *J* = 8.7, 6.5 Hz, 4H), 7.42 – 7.35 (m, 3H), 7.19 (d, *J* = 8.0 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 150.9, 138.1, 135.3, 134.9, 134.0, 133.6, 131.79, 131.76, 130.0, 129.8, 129.18, 129.16, 128.6, 128.2, 126.2, 118.5, 112.9. **HRMS-ESI** (*m/z*): calcd for $C_{24}H_{19}N_3NaO_4S$ $[M+Na]^+$: 435.0886, found 435.0887.



(*E*)-4e

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), methyl 4-ethynylbenzoate **2e** (0.24 mmol, 38 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (3:1) as eluent to afford product **(*E*)-4e** in 83% yield (74 mg) as a white solid.

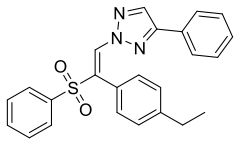
Methyl (*E*)-4-(2-(4-phenyl-2*H*-1,2,3-triazol-2-yl)-1-(phenylsulfonyl)vinyl)benzoate ((*E*)-4e). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.65 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.91 (s, 1H), 7.65 (d, *J* = 7.8 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.38 – 7.32 (m, 3H), 7.16 (d, *J* = 8.0 Hz, 2H), 3.94 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.7, 150.7, 138.2, 135.1, 134.5, 133.8, 133.3, 131.0, 130.9, 130.6, 129.7, 129.2, 129.1, 129.0, 128.7, 128.4, 126.2, 52.3. **HRMS-ESI** (*m/z*): calcd for $C_{24}H_{19}N_3NaO_4S$ $[M+Na]^+$: 468.0988, found 468.0995.



(*E*)-4f

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), 1-ethynyl-2-methoxybenzene **2f** (0.24 mmol, 32 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (3:1) as eluent to afford product **(*E*)-4f** in 83% yield (69 mg) as a white solid.

(*E*)-2-(2-(2-methoxyphenyl)-2-(phenylsulfonyl)vinyl)-4-phenyl-2*H*-1,2,3-triazole ((*E*)-4f). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.58 (s, 1H), 7.83 (s, 1H), 7.59 (d, J = 7.8 Hz, 2H), 7.47 – 7.40 (m, 3H), 7.33 – 7.24 (m, 7H), 6.92 (t, J = 7.5 Hz, 1H), 6.60 (d, J = 8.2 Hz, 1H), 3.08 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.7, 150.2, 139.2, 134.7, 134.1, 133.2, 131.7, 130.9, 129.5, 129.0, 128.9, 128.8, 128.4, 127.5, 126.1, 120.3, 118.5, 110.1, 55.0. **HRMS-ESI** (*m/z*): calcd for $C_{23}H_{19}N_3NaO_3S$ $[M+Na]^+$: 440.1039, found 440.1048.

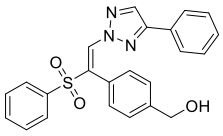


(*E*)-4g

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), 1-ethyl-4-ethynylbenzene **2g** (0.24 mmol, 31 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (5:1) as eluent to afford product **(*E*)-4g** in 80% yield (66 mg) as a white solid.

(*E*)-2-(2-(4-ethylphenyl)-2-(phenylsulfonyl)vinyl)-4-phenyl-2*H*-1,2,3-triazole ((*E*)-4g). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.61 (s, 1H), 7.92 (s, 1H), 7.68 (d, J = 7.8 Hz, 2H), 7.57 (t, J = 7.7 Hz, 1H), 7.53 – 7.40 (m, 4H), 7.33 (s, 3H), 7.14 (d, J = 7.7 Hz, 2H), 6.96 (d, J = 7.8 Hz, 2H), 2.68 (q, J = 7.6 Hz, 2H), 1.28 (t, J = 7.7 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 150.1, 145.4, 138.6, 134.6, 133.5, 133.0, 132.2,

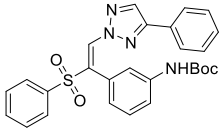
130.7, 129.5, 128.9, 128.8, 128.75, 128.69, 127.7, 126.7, 126.2, 28.9, 15.7. **HRMS-ESI** (*m/z*): calcd for $C_{24}H_{21}N_3NaO_2S$ $[M+Na]^+$: 438.1247, found 438.1263.



(*E*)-4h

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), (4-ethynylphenyl)methanol **2h** (0.24 mmol, 32 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (1:1) as eluent to afford product **(*E*)-4h** in 62% yield (51 mg) as a white solid.

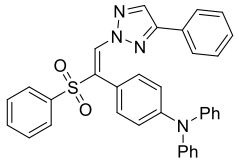
(*E*)-(4-(2-(4-phenyl-2*H*-1,2,3-triazol-2-yl)-1-(phenylsulfonyl)vinyl)phenyl)methanol ((*E*)-4h). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.64 (s, 1H), 7.89 (s, 1H), 7.67 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.39 – 7.33 (m, 3H), 7.31 (d, *J* = 7.7 Hz, 2H), 7.06 (d, *J* = 7.7 Hz, 2H), 4.74 (s, 2H), 1.87 (s, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 150.3, 141.9, 138.4, 134.9, 133.6, 133.3, 131.7, 131.0, 129.6, 129.0, 128.9, 128.71, 128.69, 128.6, 126.5, 126.2, 65.0. **HRMS-ESI** (*m/z*): calcd for $C_{23}H_{19}N_3NaO_3S$ $[M+Na]^+$: 440.1039, found 440.1058.



(*E*)-4i

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), *tert*-butyl (3-ethynylphenyl)carbamate **2i** (0.24 mmol, 52 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (3:1) as eluent to afford product **(*E*)-4i** in 72% yield (72 mg) as a white solid.

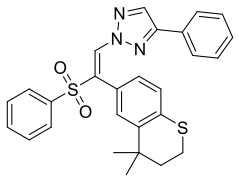
***Tert*-butyl (*E*)-(3-(2-(4-phenyl-2*H*-1,2,3-triazol-2-yl)-1-(phenylsulfonyl)vinyl)phenyl)carbamate ((*E*)-4i)**. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.60 (s, 1H), 7.91 (s, 1H), 7.67 (d, *J* = 7.9 Hz, 3H), 7.60 – 7.51 (m, 3H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.39 – 7.32 (m, 3H), 7.19 (t, *J* = 7.9 Hz, 1H), 7.01 (t, *J* = 2.0 Hz, 1H), 6.59 (d, *J* = 7.7 Hz, 1H), 6.52 (s, 1H), 1.48 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 152.5, 150.4, 138.4, 138.3, 134.9, 133.6, 133.1, 131.5, 130.0, 129.6, 129.0, 128.9, 128.7, 128.6, 126.3, 125.4, 120.5, 119.0, 80.6, 28.3. **HRMS-ESI** (*m/z*): calcd for $C_{27}H_{26}N_4NaO_4S$ $[M+Na]^+$: 525.1567, found 525.1589.



(*E*)-4j

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), 4-ethynyl-*N*,*N*-diphenylaniline **2j** (0.24 mmol, 64 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (5:1) as eluent to afford product **(*E*)-4j** in 68% yield (75 mg) as a yellow solid.

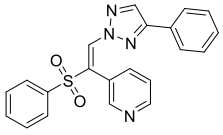
(*E*)-*N*,*N*-diphenyl-4-(2-(4-phenyl-2*H*-1,2,3-triazol-2-yl)-1-(phenylsulfonyl)vinyl)aniline ((*E*)-4j). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.57 (s, 1H), 7.97 (s, 1H), 7.71 (d, *J* = 7.8 Hz, 2H), 7.61 – 7.53 (m, 3H), 7.47 – 7.36 (m, 5H), 7.23 (d, *J* = 7.6 Hz, 4H), 7.10 (d, *J* = 7.9 Hz, 4H), 7.03 (t, *J* = 7.4 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.3 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 150.3, 148.5, 147.3, 138.7, 134.5, 133.5, 132.9, 132.1, 131.7, 129.6, 129.4, 129.0, 128.84, 128.79, 126.3, 124.8, 123.4, 122.5, 122.3. **HRMS-ESI** (*m/z*): calcd for $C_{34}H_{26}N_4NaO_2S$ $[M+Na]^+$: 577.1669, found 577.1682.



(*E*)-4k

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), 6-ethynyl-4,4-dimethylthiochromane **2k** (0.24 mmol, 48 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (5:1) as eluent to afford product **(*E*)-4k** in 71% yield (69 mg) as a white solid.

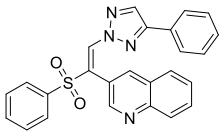
(*E*)-2-(2-(4,4-dimethylthiochroman-6-yl)-2-(phenylsulfonyl)vinyl)-4-phenyl-2*H*-1,2,3-triazole ((*E*)-4k). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.59 (s, 1H), 7.93 (s, 1H), 7.68 (d, *J* = 7.8 Hz, 2H), 7.54 (t, *J* = 7.1 Hz, 3H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.36 (d, *J* = 6.5 Hz, 3H), 7.07 (d, *J* = 8.1 Hz, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 6.81 (s, 1H), 3.03 (t, *J* = 5.9 Hz, 2H), 1.90 (t, *J* = 6.0 Hz, 2H), 1.05 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 150.2, 141.6, 138.6, 134.6, 133.4, 133.3, 132.3, 132.1, 129.6, 129.3, 129.0, 128.9, 128.8, 128.6, 128.0, 126.4, 126.2, 124.8, 37.5, 32.9, 30.0, 23.2. **HRMS-ESI** (*m/z*): calcd for $C_{27}H_{25}N_3NaO_2S_2$ $[M+Na]^+$: 510.1280, found 510.1296.



(*E*)-4l

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), 3-ethynylpyridine **2l** (0.24 mmol, 25 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (3:1) as eluent to afford product **(*E*)-4l** in 73% yield (56 mg) as a white solid.

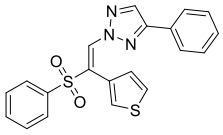
(*E*)-3-(2-(4-phenyl-2*H*-1,2,3-triazol-2-yl)-1-(phenylsulfonyl)vinyl)pyridine ((*E*)-4l). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.70 (s, 1H), 8.64 (d, *J* = 4.9 Hz, 1H), 8.13 (s, 1H), 7.94 (s, 1H), 7.67 (d, *J* = 7.8 Hz, 2H), 7.65 – 7.55 (m, 2H), 7.47 (m, 4H), 7.34 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 151.1, 150.8, 149.8, 138.4, 138.1, 135.3, 134.1, 134.0, 129.8, 129.2, 129.1, 128.6, 128.3, 128.2, 126.3, 126.2, 123.0. **HRMS-ESI** (*m/z*): calcd for $C_{21}H_{16}N_4NaO_2S$ $[M+Na]^+$: 411.0886, found 411.0911.



(*E*)-4m

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), 3-ethynylquinoline **2m** (0.24 mmol, 37 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (3:1) as eluent to afford product **(*E*)-4m** in 81% yield (71 mg) as a white solid.

(*E*)-3-(2-(4-phenyl-2*H*-1,2,3-triazol-2-yl)-1-(phenylsulfonyl)vinyl)quinoline ((*E*)-4m). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.79 (s, 1H), 8.33 (s, 1H), 8.20 (s, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 7.88 (s, 1H), 7.85 – 7.75 (m, 2H), 7.67 (d, *J* = 7.8 Hz, 2H), 7.63 – 7.52 (m, 2H), 7.41 (t, *J* = 7.9 Hz, 4H), 7.27 (d, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 151.6, 150.8, 147.6, 138.3, 138.1, 135.3, 134.3, 134.0, 130.5, 129.8, 129.3, 129.2, 129.0, 128.5, 128.4, 128.3, 128.2, 127.2, 127.1, 126.3, 123.2. **HRMS-ESI** (*m/z*): calcd for $C_{25}H_{18}N_4NaO_2S$ $[M+Na]^+$: 461.1043, found 461.1066.

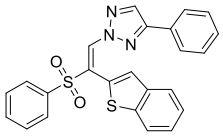


(*E*)-4n

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), 3-ethynylthiophene **2n** (0.24 mmol, 26 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (5:1) as eluent to afford product **(*E*)-4n** in 78% yield (61 mg) as a white solid.

(*E*)-4-phenyl-2-(2-(phenylsulfonyl)-2-(thiophen-3-yl)vinyl)-2*H*-1,2,3-triazole ((*E*)-4n). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.62 (s, 1H), 7.98 (s, 1H), 7.70 (d, *J* = 7.9 Hz, 2H), 7.63 – 7.54 (m, 3H), 7.47 – 7.36 (m, 5H), 7.26 (d, J = 3.2 Hz, 2H), 6.80 (dd, *J* = 4.1, 2.2 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 150.5, 138.7, 134.9,

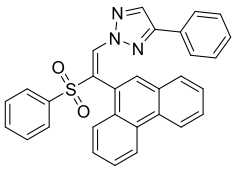
133.5, 133.2, 129.68, 129.66, 129.1, 128.9, 128.6, 128.5, 128.2, 127.7, 127.5, 126.3, 124.8. **HRMS-ESI** (*m/z*): calcd for $C_{25}H_{18}N_4NaO_2S$ $[M+Na]^+$: 416.0498, found 416.0508.



(*E*)-4o

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), 2-ethynylbenzo[*b*]thiophene **2o** (0.24 mmol, 38 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (4:1) as eluent to afford product **(*E*)-4o** in 55% yield (49 mg) as a yellow solid.

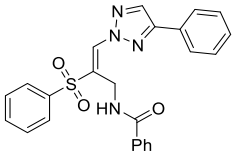
(*E*)-2-(2-(benzo[*b*]thiophen-2-yl)-2-(phenylsulfonyl)vinyl)-4-phenyl-2*H*-1,2,3-triazole ((*E*)-4o). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.75 (s, 1H), 7.96 (s, 1H), 7.78 (d, *J* = 7.9 Hz, 4H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.51 (d, *J* = 7.0 Hz, 2H), 7.44 (t, *J* = 7.7 Hz, 3H), 7.39 – 7.35 (m, 2H), 7.31 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 150.9, 141.7, 139.2, 138.3, 135.5, 135.1, 133.8, 129.8, 129.5, 129.0, 128.7, 128.4, 128.3, 126.3, 125.3, 125.0, 124.30, 124.28, 122.1. **HRMS-ESI** (*m/z*): calcd for $C_{24}H_{17}N_3NaO_2S_2$ $[M+Na]^+$: 466.0654, found 466.0673.



(*E*)-4p

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), 9-ethynylphenanthrene **2p** (0.24 mmol, 48 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (5:1) as eluent to afford product **(*E*)-4p** in 79% yield (77 mg) as a white solid.

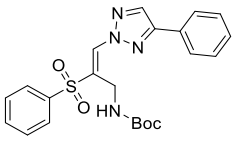
(*E*)-2-(2-(phenanthren-9-yl)-2-(phenylsulfonyl)vinyl)-4-phenyl-2*H*-1,2,3-triazole ((*E*)-4p). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.94 (s, 1H), 8.69 (dd, *J* = 16.4, 8.3 Hz, 2H), 7.78 – 7.64 (m, 5H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.46 (m, 4H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.15 (m, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 150.5, 138.2, 135.1, 134.8, 133.6, 130.9, 130.8, 130.7, 130.3, 130.1, 129.5, 129.4, 129.3, 129.0, 128.84, 128.81, 128.4, 127.6, 126.7, 126.6, 126.5, 126.2, 126.1, 125.3, 122.6, 122.6. **HRMS-ESI** (*m/z*): calcd for $C_{30}H_{21}N_3NaO_2S$ $[M+Na]^+$: 510.1247, found 510.1249.



(*E*)-4q

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), *N*-(prop-2-yn-1-yl)benzamide **2q** (0.24 mmol, 38 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (3:1) as eluent to afford product **(*E*)-4q** in 76% yield (67 mg) as a white solid.

(*E*)-*N*-(3-(4-phenyl-2*H*-1,2,3-triazol-2-yl)-2-(phenylsulfonyl)allyl)benzamide ((*E*)-4q). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.58 (s, 1H), 8.19 (s, 1H), 8.00 (d, *J* = 7.6 Hz, 2H), 7.83 (d, *J* = 7.0 Hz, 2H), 7.57 (dd, *J* = 15.5, 7.3 Hz, 3H), 7.47 (m, 6H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.01 (t, *J* = 6.0 Hz, 1H), 4.94 (d, *J* = 5.6 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.6, 151.6, 138.9, 135.9, 135.8, 134.1, 133.9, 131.5, 130.2, 129.4, 129.3, 128.5, 128.4, 128.1, 127.6, 126.9, 126.5, 35.1. **HRMS-ESI** (*m/z*): calcd for $C_{24}H_{20}N_4NaO_3S$ $[M+Na]^+$: 467.1148, found 467.1152.

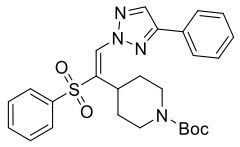


(*E*)-4r

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), *tert*-butyl prop-2-yn-1-ylcarbamate **2r** (0.24 mmol, 37 mg, 1.2 eq.), 4-phenyl-1-

tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (3:1) as eluent to afford product **(*E*)-4r** in 78% yield (68 mg) as a white solid.

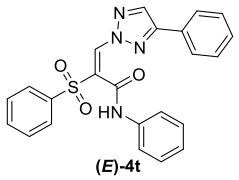
***tert*-Butyl (*E*)-(3-(4-phenyl-2*H*-1,2,3-triazol-2-yl)-2-(phenylsulfonyl)allyl)carbamate ((*E*)-4r)**. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.52 (s, 1H), 8.17 (s, 1H), 8.01 (d, *J* = 7.6 Hz, 2H), 7.85 (d, *J* = 7.2 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 8.0 Hz, 3H), 5.35 (s, 1H), 4.60 (d, *J* = 6.2 Hz, 2H), 1.35 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 154.9, 151.5, 139.2, 135.7, 135.6, 133.7, 130.1, 129.3, 129.2, 128.5, 128.3, 126.6, 79.5, 35.9, 28.3. **HRMS-ESI** (*m/z*): calcd for $C_{22}H_{24}N_4NaO_4S$ $[M+Na]^+$: 463.1410, found 463.1421.



(*E*)-4s

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), *tert*-butyl 4-ethynylpiperidine-1-carboxylate **2s** (0.24 mmol, 50 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (3:1) as eluent to afford product **(*E*)-4s** in 55% yield (54 mg) as a white solid.

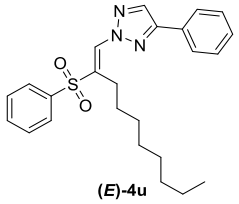
***tert*-Butyl (*E*)-4-(2-(4-phenyl-2*H*-1,2,3-triazol-2-yl)-1-(phenylsulfonyl)vinyl)piperidine-1-carboxylate((*E*)-4s). ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.55 (s, 1H), 8.13 (s, 1H), 8.00 – 7.91 (m, 2H), 7.85 – 7.78 (m, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 2H), 7.42 – 7.50 (m, 3H), 4.14 (s, 2H), 3.75 – 3.56 (m, 1H), 2.64 (s, 2H), 2.21 – 2.03 (m, 2H), 1.62 (s, 1H), 1.46 (s, 9H), 1.34 (s, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 154.7, 150.9, 140.7, 134.9, 134.6, 134.0, 133.6, 129.9, 129.32, 129.28, 128.6, 128.0, 126.4, 79.5, 44.0, 36.7, 29.7, 28.5. **HRMS-ESI** (*m/z*): calcd for $C_{26}H_{30}N_4NaO_4S$ $[M+Na]^+$: 517.1880, found 517.1889.



(*E*)-4t

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), *N*-phenylpropiolamide **2t** (0.24 mmol, 35 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (3:1) as eluent to afford product **(*E*)-4t** in 58% yield (50 mg) as a white solid.

(*E*)-*N*-phenyl-3-(4-phenyl-2*H*-1,2,3-triazol-2-yl)-2-(phenylsulfonyl)acrylamide ((E)-4t). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.40 (s, 1H), 8.09 (d, *J* = 8.0 Hz, 2H), 7.99 (d, *J* = 7.8 Hz, 2H), 7.65 (t, *J* = 8.1 Hz, 3H), 7.56 (q, *J* = 8.1, 7.7 Hz, 4H), 7.41 – 7.31 (m, 5H), 7.19 (t, *J* = 7.5 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.0, 152.0, 138.7, 137.4, 136.4, 134.4, 134.2, 130.1, 129.4, 129.1, 129.0, 128.5, 128.0, 127.1, 126.6, 125.2, 120.3.

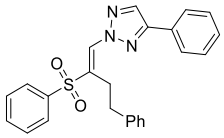


(*E*)-4u

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), dec-1-yne **2u** (0.24 mmol, 33 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (5:1) as eluent to afford product **(*E*)-4u** in 58% yield (49 mg) as a white solid.

(*E*)-4-phenyl-2-(2-(phenylsulfonyl)dec-1-en-1-yl)-2*H*-1,2,3-triazole ((*E*)-4u). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.42 (s, 1H), 8.10 (s, 1H), 7.97 (d, *J* = 7.6 Hz, 2H), 7.82 (d, *J* = 7.3 Hz, 2H), 7.64 (t, *J* = 7.3 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.46 (m, 3H), 2.88 – 2.76 (m, 2H), 1.50 – 1.42 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 2H), 1.24 (d, *J*

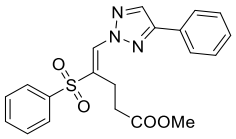
= 13.3 Hz, 8H), 0.86 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 150.6, 139.5, 134.5, 133.6, 133.2, 132.5, 129.7, 129.3, 129.1, 128.9, 128.4, 126.3, 31.8, 29.9, 29.2, 29.1, 28.3, 27.1, 22.7, 14.1. **HRMS-ESI** (*m/z*): calcd for $C_{24}H_{29}N_3NaO_2S$ $[M+Na]^+$: 446.1873, found 446.1885.



(***E***)-**4v**

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), but-3-yn-1-ylbenzene **2v** (0.24 mmol, 31 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (5:1) as eluent to afford product **(*E*)-4v** in 70% yield (58 mg) as a white solid.

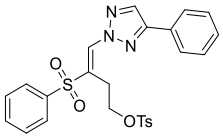
(*E*)-4-phenyl-2-(4-phenyl-2-(phenylsulfonyl)but-1-en-1-yl)-2*H*-1,2,3-triazole ((*E*)-4v). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.55 (s, 1H), 8.19 (s, 1H), 8.05 (d, *J* = 7.7 Hz, 2H), 7.87 (d, *J* = 7.2 Hz, 2H), 7.73 – 7.58 (m, 3H), 7.50 (q, *J* = 7.3 Hz, 3H), 7.33 – 7.22 (m, 5H), 3.27 – 3.10 (m, 2H), 2.96 – 2.73 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 150.9, 141.2, 139.3, 134.9, 133.8, 133.6, 131.2, 129.8, 129.5, 129.2, 128.7, 128.49, 128.46, 128.43, 126.5, 126.3, 34.4, 29.3. **HRMS-ESI** (*m/z*): calcd for $C_{24}H_{21}N_3NaO_2S$ $[M+Na]^+$: 438.1247, found 438.1253.



(***E***)-**4w**

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), methyl pent-4-ynoate **2w** (0.24 mmol, 27 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (3:1) as eluent to afford product **(*E*)-4w** in 52% yield (41 mg) as a white solid.

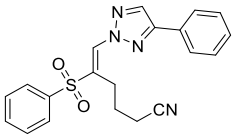
Methyl (*E*)-5-(4-phenyl-2*H*-1,2,3-triazol-2-yl)-4-(phenylsulfonyl)pent-4-enoate ((*E*)-4w). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.47 (s, 1H), 8.12 (s, 1H), 7.97 (d, *J* = 7.7 Hz, 2H), 7.81 (d, *J* = 7.3 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 2H), 7.47 – 7.39 (m, 3H), 3.68 (s, 3H), 3.18 – 3.03 (m, 2H), 2.71 – 2.62 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 172.8, 151.0, 138.9, 135.0, 134.1, 133.8, 129.87, 129.85, 129.5, 129.2, 128.5, 128.4, 126.4, 51.8, 32.4, 22.5. **HRMS-ESI** (*m/z*): calcd for $C_{20}H_{19}N_3NaO_4S$ $[M+Na]^+$: 420.0988, found 420.0995.



(*E*)-4x

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), but-3-yn-1-yl 4-methylbenzenesulfonate **2x** (0.24 mmol, 54 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (3:1) as eluent to afford product **(*E*)-4x** in 43% yield (44 mg) as a white solid.

(*E*)-4-(4-phenyl-2*H*-1,2,3-triazol-2-yl)-3-(phenylsulfonyl)but-3-en-1-yl 4-methylbenzenesulfonate ((*E*))-4x). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.46 (s, 1H), 8.09 (s, 1H), 7.91 (d, *J* = 7.7 Hz, 2H), 7.87 – 7.80 (m, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.65 (t, *J* = 7.3 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 2H), 7.48 (q, *J* = 8.1, 7.1 Hz, 3H), 7.27 (d, *J* = 7.9 Hz, 2H), 4.22 (t, *J* = 7.8 Hz, 2H), 3.25 (t, *J* = 7.9 Hz, 2H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 151.36, 144.8, 138.4, 135.4, 135.3, 134.0, 132.8, 130.1, 129.8, 129.5, 129.3, 128.4, 128.3, 128.0, 126.6, 125.5, 67.2, 26.9, 21.7. **HRMS-ESI** (*m/z*): calcd for $C_{25}H_{23}N_3NaO_5S_2$ $[M+Na]^+$: 532.0971, found 532.0977.

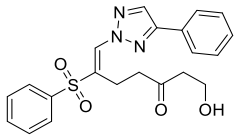


(*E*)-4y

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), hex-5-ynenitrile **2y** (0.24 mmol, 22 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-

triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (4:1) as eluent to afford product **(*E*)-4y** in 68% yield (51 mg) as a white solid.

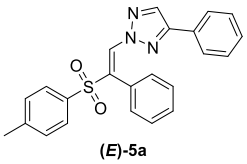
(*E*)-6-(4-phenyl-2*H*-1,2,3-triazol-2-yl)-5-(phenylsulfonyl)hex-5-enenitrile ((*E*)-4y). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.49 (s, 1H), 8.15 (s, 1H), 7.97 (d, *J* = 7.7 Hz, 2H), 7.83 (d, *J* = 7.3 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 2H), 7.49 – 7.41 (m, 3H), 2.94 (t, *J* = 8.0 Hz, 2H), 2.44 (t, *J* = 7.0 Hz, 2H), 2.01 – 1.93 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 151.1, 138.9, 135.2, 134.2, 133.9, 130.0, 129.7, 129.6, 129.3, 128.4, 128.3, 126.5, 119.1, 26.1, 24.1, 17.3. **HRMS-ESI** (*m/z*): calcd for $C_{20}H_{18}N_4NaO_2S$ $[M+Na]^+$: 401.1043, found 401.1050.



(*E*)-4z

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), 1-hydroxyhept-6-yn-3-one **2z** (0.24 mmol, 24 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (1:1) as eluent to afford product **(*E*)-4z** in 73% yield (60 mg) as a white solid.

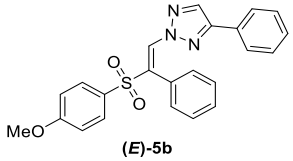
(*E*)-1-hydroxy-7-(4-phenyl-2*H*-1,2,3-triazol-2-yl)-6-(phenylsulfonyl)hept-6-en-3-one ((*E*)-4z). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.45 (s, 1H), 8.11 (s, 1H), 7.95 (d, *J* = 7.7 Hz, 2H), 7.77 (d, *J* = 7.4 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 2H), 7.44 (p, *J* = 6.7, 6.1 Hz, 3H), 3.84 – 3.88 (m, 2H), 3.08 – 3.01 (m, 2H), 2.91 – 2.84 (m, 2H), 2.66 (t, *J* = 5.6 Hz, 2H), 2.46 (s, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 209.9, 150.9, 138.7, 135.0, 133.8, 130.4, 130.0, 129.5, 129.2, 128.5, 128.4, 126.3, 57.9, 44.4, 41.6, 21.0. **HRMS-ESI** (*m/z*): calcd for $C_{21}H_{21}N_3NaO_4S$ $[M+Na]^+$: 434.1145, found 434.1150.



(*E*)-5a

Following **General Procedure 1**, sodium 4-methylbenzenesulfinate **1b** (0.5 mmol, 89 mg, 2.5 eq.), ethynylbenzene **2b** (0.24 mmol, 25 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (5:1) as eluent to afford product **(*E*)-5a** in 80% yield (64 mg) as a white solid.

(*E*)-4-phenyl-2-(2-phenyl-2-tosylvinyl)-2*H*-1,2,3-triazole ((*E*)-5a). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.61 (s, 1H), 7.91 (s, 1H), 7.52 (dd, *J* = 12.9, 6.6 Hz, 4H), 7.29 – 7.42 (m, 6H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 7.6 Hz, 2H), 2.40 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 150.2, 144.6, 135.5, 134.7, 132.8, 132.3, 130.8, 129.62, 129.56, 129.5, 129.0, 128.8, 128.7, 128.1, 126.2, 21.7. **HRMS-ESI** (*m/z*): calcd for $C_{23}H_{19}N_3NaO_2S$ $[M+Na]^+$: 424.1090, found 424.1096.

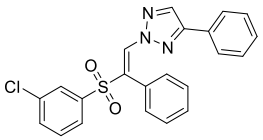


(*E*)-5b

Following **General Procedure 1**, sodium 4-methoxybenzenesulfinate **1c** (0.5 mmol, 97 mg, 2.5 eq.), ethynylbenzene **2b** (0.24 mmol, 25 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (4:1) as eluent to afford product **(*E*)-5b** in 69% yield (57 mg) as a white solid.

(*E*)-2-(2-((4-methoxyphenyl)sulfonyl)-2-phenylvinyl)-4-phenyl-2*H*-1,2,3-triazole ((*E*)-5b). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.59 (s, 1H), 7.90 (s, 1H), 7.60 – 7.54 (m, 2H), 7.50 (dd, *J* = 6.7, 2.9 Hz, 2H), 7.40 (dd, *J* = 8.4, 6.3 Hz, 1H), 7.32 (d, *J* = 7.7 Hz, 4H), 7.07 (d, *J* = 7.5 Hz, 2H), 6.89 – 6.85 (m, 2H), 3.83 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 163.7, 150.2, 134.6, 132.6, 132.4, 131.0, 130.8, 129.9, 129.7,

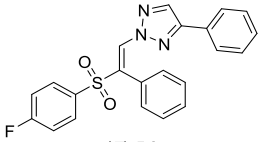
129.5, 129.0, 128.7, 128.1, 126.2, 114.1, 55.7. **HRMS-ESI** (*m/z*): calcd for $C_{23}H_{19}N_3NaO_3S$ $[M+Na]^+$: 440.1039, found 440.1056.



(***E***)-5c

Following **General Procedure 1**, sodium 3-chlorobenzenesulfinate **1d** (0.5 mmol, 99 mg, 2.5 eq.), ethynylbenzene **2b** (0.24 mmol, 25 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (5:1) as eluent to afford product **(*E*)-5c** in 76% yield (64 mg) as a white solid.

(*E*)-2-(2-((3-chlorophenyl)sulfonyl)-2-phenylvinyl)-4-phenyl-2*H*-1,2,3-triazole ((*E*)-5c). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.62 (s, 1H), 7.92 (s, 1H), 7.65 (s, 1H), 7.50 (d, J = 6.8 Hz, 4H), 7.42 (t, J = 7.5 Hz, 1H), 7.37 – 7.30 (m, 6H), 7.09 (d, J = 7.5 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 150.5, 140.2, 135.2, 135.0, 133.7, 133.5, 131.2, 130.9, 130.1, 129.7, 129.3, 129.2, 129.0, 128.6, 128.5, 128.2, 126.9, 126.2. **HRMS-ESI** (*m/z*): calcd for $C_{22}H_{16}ClN_3NaO_2S$ $[M+Na]^+$: 444.0544, found 444.0552.

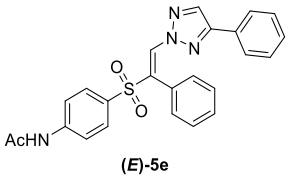


(***E***)-5d

Following **General Procedure 1**, sodium 4-fluorobenzenesulfinate **1e** (0.5 mmol, 91 mg, 2.5 eq.), ethynylbenzene **2b** (0.24 mmol, 25 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (5:1) as eluent to afford product **(*E*)-5d** in 74% yield (60 mg) as a white solid.

(*E*)-2-(2-((4-fluorophenyl)sulfonyl)-2-phenylvinyl)-4-phenyl-2*H*-1,2,3-triazole ((*E*)-5d). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.62 (s, 1H), 7.92 (s, 1H), 7.65 (dd, J

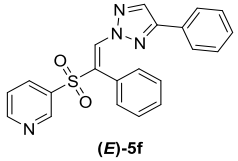
= 8.5, 5.1 Hz, 2H), 7.54 – 7.48 (m, 2H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 6.4 Hz, 5H), 7.09 (dd, *J* = 10.7, 7.8 Hz, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.7 (d, *J* = 257.4 Hz), 150.4, 134.9, 134.5 (d, *J* = 3.0 Hz), 133.0, 131.8, 131.6 (d, *J* = 9.7 Hz), 130.8, 129.6, 129.4, 129.2, 129.0, 128.6, 128.2, 126.2, 116.2 (d, *J* = 22.7 Hz). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -103.45 (tt, *J* = 8.9, 5.3 Hz). **HRMS-ESI** (*m/z*): calcd for $C_{22}H_{16}FN_3NaO_2S$ $[M+Na]^+$: 428.0839, found 428.0848.



(*E*)-5e

Following **General Procedure 1**, sodium 4-acetamidobenzenesulfinate **1f** (0.5 mmol, 110 mg, 2.5 eq.), ethynylbenzene **2b** (0.24 mmol, 25 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (3:1) as eluent to afford product **(*E*)-5e** in 73% yield (64 mg) as a white solid.

(*E*)-N-(4-((1-phenyl-2-(4-phenyl-2*H*-1,2,3-triazol-2-yl)vinyl)sulfonyl)phenyl)acetamide ((*E*)-5e). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.59 (s, 1H), 8.04 (s, 1H), 7.91 (s, 1H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.49 (dd, *J* = 6.7, 2.8 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.36 – 7.27 (m, 5H), 7.06 (d, *J* = 7.5 Hz, 2H), 2.18 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 169.1, 150.4, 143.1, 134.82, 132.81, 132.5, 132.0, 130.8, 130.0, 129.6, 129.4, 129.2, 129.0, 128.6, 128.2, 126.2, 118.9, 24.8. **HRMS-ESI** (*m/z*): calcd for $C_{24}H_{20}N_4NaO_3S$ $[M+Na]^+$: 467.1148, found 467.1165.

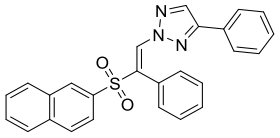


(*E*)-5f

Following **General Procedure 1**, sodium pyridine-3-sulfinate **1g** (0.5 mmol, 82 mg, 2.5 eq.), ethynylbenzene **2b** (0.24 mmol, 25 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The

crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (3:1) as eluent to afford product **(*E*)-5f** in 79% yield (61 mg) as a white solid.

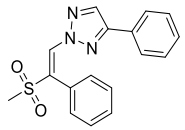
(*E*)-3-((1-phenyl-2-(4-phenyl-2*H*-1,2,3-triazol-2-yl)vinyl)sulfonyl)pyridine ((*E*)-5f). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.83 (s, 1H), 8.78 (d, *J* = 5.6 Hz, 1H), 8.66 (s, 1H), 7.94 (s, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.34 (dd, *J* = 9.5, 5.9 Hz, 6H), 7.10 (d, *J* = 7.6 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 153.9, 150.6, 149.5, 136.3, 135.2, 135.1, 133.7, 131.2, 130.9, 129.7, 129.5, 129.0, 128.9, 128.4, 128.4, 126.2, 123.4. **HRMS-ESI** (*m/z*): calcd for $C_{21}H_{16}N_4NaO_2S$ $[M+Na]^+$: 411.0886, found 411.0911.



(*E*)-5g

Following **General Procedure 1**, sodium naphthalene-2-sulfinate **1h** (0.5 mmol, 107 mg, 2.5 eq.), ethynylbenzene **2b** (0.24 mmol, 25 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (5:1) as eluent to afford product **(*E*)-5g** in 71% yield (62 mg) as a white solid.

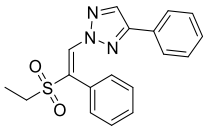
(*E*)-2-(2-(naphthalen-2-ylsulfonyl)-2-phenylvinyl)-4-phenyl-2*H*-1,2,3-triazole ((*E*)-5g). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.70 (s, 1H), 8.20 (s, 1H), 7.95 – 7.82 (m, 4H), 7.64 (t, *J* = 7.9 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.50 (dd, *J* = 6.7, 2.9 Hz, 2H), 7.41 – 7.32 (m, 4H), 7.26 (t, *J* = 7.7 Hz, 2H), 7.05 (d, *J* = 7.6 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 150.3, 135.3, 135.2, 134.8, 133.2, 132.0, 132.0, 130.8, 130.7, 129.6, 129.5, 129.5, 129.3, 129.1, 129.1, 129.0, 128.6, 128.1, 127.9, 127.5, 126.2, 123.3. **HRMS-ESI** (*m/z*): calcd for $C_{26}H_{19}N_3NaO_2S$ $[M+Na]^+$: 460.1090, found 460.1113.



(*E*)-5h

Following **General Procedure 1**, sodium methanesulfinate **1i** (0.5 mmol, 51 mg, 2.5 eq.), ethynylbenzene **2b** (0.24 mmol, 25 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (4:1) as eluent to afford product **(*E*)-5h** in 53% yield (34 mg) as a white solid.

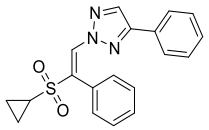
(*E*)-2-(2-(methylsulfonyl)-2-phenylvinyl)-4-phenyl-2*H*-1,2,3-triazole ((*E*)-5h). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.47 (s, 1H), 7.95 (s, 1H), 7.57 – 7.48 (m, 7H), 7.41 – 7.35 (m, 3H), 2.91 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 150.5, 134.9, 133.4, 130.8, 130.6, 129.69, 129.67, 129.6, 129.0, 128.7, 128.6, 126.2, 40.6. **HRMS-ESI** (*m/z*): calcd for $C_{17}H_{15}N_3NaO_2S$ $[M+Na]^+$: 348.0777, found 348.0804.



(*E*)-5i

Following **General Procedure 1**, sodium ethanesulfinate **1j** (0.5 mmol, 58 mg, 2.5 eq.), ethynylbenzene **2b** (0.24 mmol, 25 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (4:1) as eluent to afford product **(*E*)-5i** in 75% yield (51 mg) as a white solid.

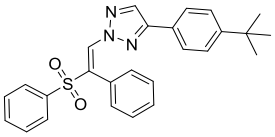
(*E*)-2-(2-(ethylsulfonyl)-2-phenylvinyl)-4-phenyl-2*H*-1,2,3-triazole ((*E*)-5i). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.43 (s, 1H), 7.95 (s, 1H), 7.54 (dd, J = 6.7, 2.9 Hz, 2H), 7.49 (s, 5H), 7.37 (dd, J = 5.1, 2.0 Hz, 3H), 2.98 – 2.93 (m, 2H), 1.36 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 150.4, 134.8, 134.2, 130.5, 129.7, 129.6, 129.5, 129.0, 128.66, 128.65, 128.5, 126.2 46.1, 7.1. **HRMS-ESI** (*m/z*): calcd for $C_{18}H_{17}N_3NaO_2S$ $[M+Na]^+$: 362.0934, found 362.0954.



(*E*)-5j

Following **General Procedure 1**, sodium cyclopropanesulfinate **1k** (0.5 mmol, 64 mg, 2.5 eq.), ethynylbenzene **2b** (0.24 mmol, 25 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (4:1) as eluent to afford product **(*E*)-5j** in 66% yield (66 mg) as a white solid.

(*E*)-2-(2-(cyclopropylsulfonyl)-2-phenylvinyl)-4-phenyl-2*H*-1,2,3-triazole ((*E*)-5j). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.38 (s, 1H), 7.93 (s, 1H), 7.54 – 7.45 (m, 7H), 7.36 (d, J = 5.4 Hz, 3H), 2.37 – 2.30 (m, 1H), 1.20 – 1.11 (m, 2H), 0.97 (dd, J = 7.9, 5.5 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 150.2, 134.7, 132.8, 130.9, 130.8, 130.1, 129.6, 129.3, 129.0, 128.7, 128.4, 126.2, 29.8, 5.8. **HRMS-ESI** (*m/z*): calcd for $C_{19}H_{17}N_3NaO_2S$ $[M+Na]^+$: 374.0934, found 374.0949.

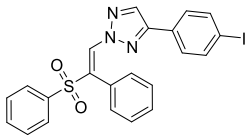


(*E*)-5k

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), ethynylbenzene **2b** (0.24 mmol, 25 mg, 1.2 eq.), 4-(4-(*tert*-butyl)phenyl)-1-tosyl-1*H*-1,2,3-triazole **3b** (0.2 mmol, 71 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (5:1) as eluent to afford product **(*E*)-5k** in 79% yield (70 mg) as a white solid.

(*E*)-4-(4-(*tert*-butyl)phenyl)-2-(2-phenyl-2-(phenylsulfonyl)vinyl)-2*H*-1,2,3-triazole ((*E*)-5k). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.63 (s, 1H), 7.89 (s, 1H), 7.66 (d, J = 7.8 Hz, 2H), 7.55 (t, J = 7.5 Hz, 1H), 7.44 – 7.35 (m, 7H), 7.30 (t, J = 7.6 Hz, 2H), 7.06 (d, J = 7.6 Hz, 2H), 1.30 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 152.9, 150.3, 138.5, 134.8, 133.5, 133.1, 131.7, 130.9, 129.6, 129.0, 128.9, 128.7,

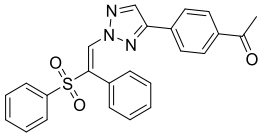
128.1, 126.0, 126.0, 125.8, 34.8, 31.2. **HRMS-ESI** (*m/z*): calcd for $C_{26}H_{25}N_3NaO_2S$ $[M+Na]^+$: 466.1560, found 466.1573.



(*E*)-5l

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), ethynylbenzene **2b** (0.24 mmol, 25 mg, 1.2 eq.), 4-(4-iodophenyl)-1-tosyl-1*H*-1,2,3-triazole **3c** (0.2 mmol, 85 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (5:1) as eluent to afford product **(*E*)-5l** in 73% yield (75 mg) as a white solid.

(*E*)-4-(4-iodophenyl)-2-(2-phenyl-2-(phenylsulfonyl)vinyl)-2*H*-1,2,3-triazole ((*E*)-5l). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.61 (s, 1H), 7.90 (s, 1H), 7.67 (t, J = 8.8 Hz, 4H), 7.57 (t, J = 7.6 Hz, 1H), 7.44 – 7.37 (dt, J = 12.3, 7.5 Hz, 3H), 7.29 (t, J = 7.6 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 7.04 (d, J = 7.6 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 149.4, 138.3, 138.2, 134.6, 133.6, 132.9, 132.5, 130.7, 129.4, 129.1, 128.9, 128.8, 128.1, 127.8, 95.6. **HRMS-ESI** (*m/z*): calcd for $C_{22}H_{16}IN_3NaO_2S$ $[M+Na]^+$: 535.9900, found 535.9923.

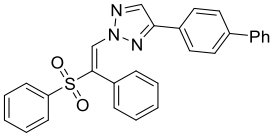


(*E*)-5m

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), ethynylbenzene **2b** (0.24 mmol, 25 mg, 1.2 eq.), 1-(4-(1-tosyl-1*H*-1,2,3-triazol-4-yl)phenyl)ethan-1-one **3d** (0.2 mmol, 68 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (4:1) as eluent to afford product **(*E*)-5m** in 73% yield (62 mg) as a white solid.

(*E*)-1-(4-(2-(2-phenyl-2-(phenylsulfonyl)vinyl)-2*H*-1,2,3-triazol-4-yl)phenyl)ethan-1-one ((*E*)-5m)). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.64 (s, 1H),

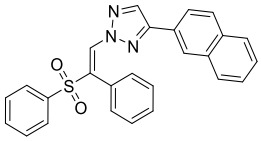
7.99 (s, 1H), 7.94 (d, *J* = 8.1 Hz, 2H), 7.67 (d, *J* = 7.6 Hz, 2H), 7.58 (dd, *J* = 7.8, 4.6 Hz, 3H), 7.47 – 7.39 (m, 3H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.06 (d, *J* = 7.3 Hz, 2H), 2.60 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 197.3, 149.1, 138.2, 137.5, 135.0, 133.7, 133.0, 132.9, 132.8, 130.7, 129.4, 129.2, 129.0, 128.9, 128.8, 128.1, 126.3, 26.7. **HRMS-ESI** (*m/z*): calcd for $C_{24}H_{19}N_3NaO_3S$ $[M+Na]^+$: 452.1039, found 452.1047.



(***E***)-5n

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), ethynylbenzene **2b** (0.24 mmol, 25 mg, 1.2 eq.), 4-([1,1'-biphenyl]-4-yl)-1-tosyl-1*H*-1,2,3-triazole **3e** (0.2 mmol, 75 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (5:1) as eluent to afford product **(*E*)-5n** in 76% yield (69 mg) as a white solid.

(*E*)-4-([1,1'-biphenyl]-4-yl)-2-(2-phenyl-2-(phenylsulfonyl)vinyl)-2*H*-1,2,3-triazole ((*E*)-5n). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.65 (s, 1H), 7.94 (s, 1H), 7.67 (d, *J* = 7.9 Hz, 2H), 7.57 (d, *J* = 3.8 Hz, 7H), 7.45 – 7.39 (m, 5H), 7.30 – 7.37 (m, 3H), 7.07 (d, *J* = 7.6 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 150.0, 142.4, 140.2, 138.4, 134.8, 133.6, 133.0, 132.0, 130.8, 129.5, 129.1, 128.91, 128.88, 128.8, 128.1, 127.8, 127.7, 127.5, 127.0, 126.6. **HRMS-ESI** (*m/z*): calcd for $C_{28}H_{21}N_3NaO_2S$ $[M+Na]^+$: 486.1247, found 486.1250.

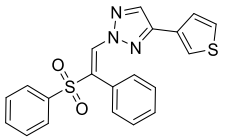


(***E***)-5o

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), ethynylbenzene **2b** (0.24 mmol, 25 mg, 1.2 eq.), 4-(naphthalen-2-yl)-1-tosyl-1*H*-1,2,3-triazole **3f** (0.2 mmol, 70 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum

ether/ethyl acetate mixture (5:1) as eluent to afford product **(*E*)-5o** in 61% yield (53 mg) as a white solid.

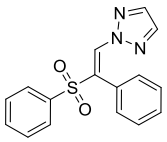
(*E*)-4-(naphthalen-2-yl)-2-(2-phenyl-2-(phenylsulfonyl)vinyl)-2*H*-1,2,3-triazole ((*E*)-5o). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.66 (s, 1H), 8.05 (s, 1H), 7.99 (s, 1H), 7.81 (d, *J* = 7.9 Hz, 3H), 7.68 (d, *J* = 7.8 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.49 (dd, *J* = 6.2, 3.3 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 3H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.09 (d, *J* = 7.6 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 150.3, 138.4, 135.0, 133.7, 133.6, 133.2, 133.0, 132.1, 130.9, 129.6, 129.1, 128.89, 128.87, 128.77, 128.3, 128.1, 127.8, 126.9, 126.7, 125.7, 123.5. **HRMS-ESI** (*m/z*): calcd for $C_{26}H_{19}N_3NaO_2S$ $[M+Na]^+$: 460.1090, found 460.1097.



(*E*)-5p

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), ethynylbenzene **2b** (0.24 mmol, 25 mg, 1.2 eq.), 4-(thiophen-3-yl)-1-tosyl-1*H*-1,2,3-triazole **3g** (0.2 mmol, 61 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (5:1) as eluent to afford product **(*E*)-5p** in 55% yield (43 mg) as a white solid.

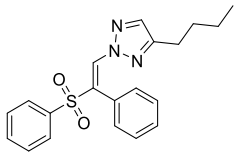
(*E*)-2-(2-phenyl-2-(phenylsulfonyl)vinyl)-4-(thiophen-3-yl)-2*H*-1,2,3-triazole ((*E*)-5p). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.61 (s, 1H), 7.81 (s, 1H), 7.66 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.48 – 7.37 (m, 4H), 7.30 (q, *J* = 7.7, 6.3 Hz, 3H), 7.14 (d, *J* = 5.1 Hz, 1H), 7.04 (d, *J* = 7.7 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.4, 138.4, 134.9, 133.6, 133.0, 131.8, 130.8, 130.1, 129.5, 129.0, 128.8, 128.7, 128.0, 126.9, 125.7, 123.5. **HRMS-ESI** (*m/z*): calcd for $C_{20}H_{15}N_3NaO_2S_2$ $[M+Na]^+$: 416.0498, found 416.0508.



(*E*)-5q

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), ethynylbenzene **2b** (0.24 mmol, 25 mg, 1.2 eq.), 1-tosyl-1*H*-1,2,3-triazole **3h** (0.2 mmol, 44 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (5:1) as eluent to afford product **(*E*)-5q** in 65% yield (40 mg) as a white solid.

(*E*)-2-(2-phenyl-2-(phenylsulfonyl)vinyl)-2H-1,2,3-triazole ((*E*)-5q). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.65 (s, 1H), 7.65 (s, 2H), 7.62 (d, *J* = 7.8 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.9 Hz, 2H), 7.36 (d, *J* = 7.3 Hz, 1H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.02 (d, *J* = 7.6 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 138.2, 137.5, 133.6, 132.9, 132.6, 130.8, 129.2, 128.8, 128.8, 128.1. **HRMS-ESI** (*m/z*): calcd for $C_{16}H_{13}N_3NaO_2S$ $[M+Na]^+$: 334.0621, found 334.0635.

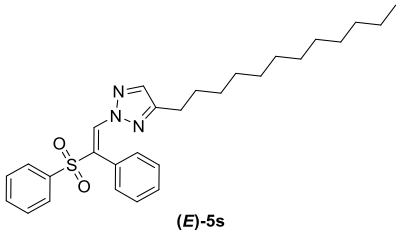


(*E*)-5r

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), ethynylbenzene **2b** (0.24 mmol, 25 mg, 1.2 eq.), 4-butyl-1-tosyl-1*H*-1,2,3-triazole **3i** (0.2 mmol, 56 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (5:1) as eluent to afford product **(*E*)-5r** in 76% yield (56 mg) as a white solid.

(*E*)-4-butyl-2-(2-phenyl-2-(phenylsulfonyl)vinyl)-2*H*-1,2,3-triazole ((E)-5r). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.55 (s, 1H), 7.62 (d, *J* = 7.8 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.43 – 7.37 (m, 3H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.01 (d, *J* = 7.6 Hz, 2H), 2.54 (t, *J* = 7.5 Hz, 2H), 1.51 – 1.44 (m, 2H), 1.30 – 1.18 (m,

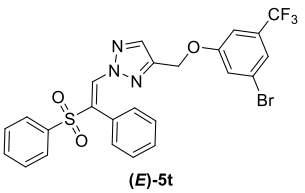
2H), 0.84 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 152.1, 138.6, 137.1, 133.4, 133.0, 130.90, 130.87, 129.5, 128.9, 128.8, 128.6, 128.0, 30.3, 24.9, 22.0, 13.7. **HRMS-ESI** (*m/z*): calcd for $C_{20}H_{21}N_3NaO_2S$ $[M+Na]^+$: 390.1247, found 390.1274.



(*E*)-5s

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), ethynylbenzene **2b** (0.24 mmol, 25 mg, 1.2 eq.), 4-dodecyl-1-tosyl-1H-1,2,3-triazole **3j** (0.2 mmol, 78 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (5:1) as eluent to afford product **(*E*)-5s** in 82% yield (78 mg) as a white solid.

(*E*)-4-dodecyl-2-(2-phenyl-2-(phenylsulfonyl)vinyl)-2*H*-1,2,3-triazole ((*E*)-5s). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.55 (s, 1H), 7.62 (d, *J* = 7.8 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 3H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.01 (d, *J* = 7.6 Hz, 2H), 2.53 (t, *J* = 7.6 Hz, 2H), 1.48 (t, *J* = 7.2 Hz, 2H), 1.23 (d, *J* = 13.3 Hz, 18H), 0.88 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 152.2, 138.6, 137.1, 133.4, 133.1, 130.9, 130.8, 129.5, 128.9, 128.8, 128.7, 128.0, 31.9, 29.67, 29.65, 29.63, 29.48, 29.37, 29.25, 28.98, 28.22, 25.28, 22.71, 14.15. **HRMS-ESI** (*m/z*): calcd for $C_{28}H_{37}N_3NaO_2S$ $[M+Na]^+$: 502.2499, found 502.2515.

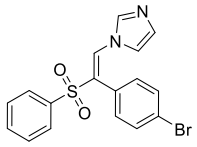


(*E*)-5t

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), ethynylbenzene **2b** (0.24 mmol, 25 mg, 1.2 eq.), 4-((3-bromo-5-(trifluoromethyl)phenoxy)methyl)-1-tosyl-1*H*-1,2,3-triazole **3k** (0.2 mmol, 95 mg, 1.0

eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (4:1) as eluent to afford product **(*E*)-5t** in 85% yield (95 mg) as a white solid.

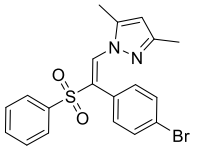
(*E*)-4-((3-bromo-5-(trifluoromethyl)phenoxy)methyl)-2-(2-phenyl-2-(phenylsulfonyl)vinyl)-2*H*-1,2,3-triazole ((*E*)-5t). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.59 (s, 1H), 7.70 (s, 1H), 7.59 (dd, *J* = 23.1, 7.7 Hz, 3H), 7.46 – 7.32 (m, 4H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.18 (s, 1H), 7.07 – 6.97 (m, 3H), 5.04 (s, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.6, 146.4 (d, *J* = 1.3 Hz), 138.0, 136.80 (d, *J* = 2.3 Hz), 133.7, 133.24 (d, *J* = 2.1 Hz), 133.21 (dd, *J* = 1.0, 33.2 Hz), 132.6, 130.6, 129.2, 128.9, 128.8, 128.7, 128.1, 123.3, 122.9 (q, *J* = 274.2 Hz), 121.5 (q, *J* = 2.2 Hz), 121.2, 110.9 (q, *J* = 3.7 Hz), 61.8. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -62.91. **HRMS-ESI** (*m/z*): calcd for $C_{24}H_{17}BrF_3N_3NaO_3S$ $[M+Na]^+$: 586.0018, found 586.0033.



(*E*)-5u

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), 1-bromo-4-ethynylbenzene **2a** (0.24 mmol, 43 mg, 1.2 eq.), 1-tosyl-1*H*-imidazole **3l** (0.2 mmol, 44 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (3:1) as eluent to afford product **(*E*)-5u** in 61% yield (47 mg) as a white solid.

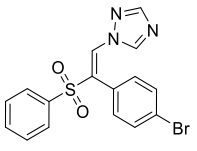
(*E*)-1-(2-(4-bromophenyl)-2-(phenylsulfonyl)vinyl)-1*H*-imidazole ((*E*)-5u). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.24 (s, 1H), 7.62 (m, 3H), 7.57 – 7.42 (m, 5H), 6.92 (t, *J* = 10.4 Hz, 3H), 6.48 (s, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 137.9, 133.9, 132.7, 132.3, 131.5, 131.0, 129.1, 128.6, 127.7, 125.0.



(*E*)-5v

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), 1-bromo-4-ethynylbenzene **2a** (0.24 mmol, 43 mg, 1.2 eq.), 3,5-dimethyl-1-tosyl-1*H*-pyrazole **3m** (0.2 mmol, 44 mg, 1.0 eq.) and $Ir(ppy)_3$ (1 mg, 1 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (4:1) as eluent to afford product **(*E*)-5v** in 64% yield (53 mg) as a white solid.

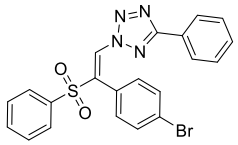
(*E*)-1-(2-(4-bromophenyl)-2-(phenylsulfonyl)vinyl)-3,5-dimethyl-1*H*-pyrazole ((*E*)-5v). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.15 (s, 1H), 7.62 (d, *J* = 7.8 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 6.90 (d, *J* = 8.1 Hz, 2H), 5.87 (s, 1H), 2.40 (s, 3H), 1.92 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 153.0, 142.8, 139.0, 133.2, 133.0, 130.8, 130.0, 129.5, 128.8, 128.4, 126.0, 122.9, 108.8, 13.8, 11.2.



(*E*)-5w

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), 1-bromo-4-ethynylbenzene **2a** (0.24 mmol, 43 mg, 1.2 eq.), 1-tosyl-1*H*-1,2,4-triazole **3n** (0.2 mmol, 45 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (3:1) as eluent to afford product **(*E*)-5w** in 70% yield (54 mg) as a white solid.

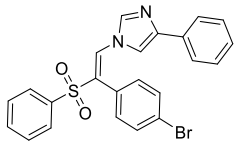
(*E*)-1-(2-(4-bromophenyl)-2-(phenylsulfonyl)vinyl)-1*H*-1,2,4-triazole ((*E*)-5w). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.45 (s, 1H), 7.95 (s, 1H), 7.69 – 7.59 (m, 4H), 7.56 – 7.43 (m, 4H), 6.92 (d, *J* = 8.0 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 152.9, 143.8, 137.5, 134.1, 132.8, 131.9, 131.8, 131.4, 129.2, 128.7, 127.6, 125.2.



(*E*)-5x

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), 1-bromo-4-ethynylbenzene **2a** (0.24 mmol, 43 mg, 1.2 eq.), 5-phenyl-1-tosyl-1*H*-tetrazole **3o** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (5:1) as eluent to afford product **(*E*)-5x** in 68% yield (63 mg) as a white solid.

(*E*)-2-(2-(4-bromophenyl)-2-(phenylsulfonyl)vinyl)-5-phenyl-2*H*-tetrazole ((*E*)-5x). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.83 (s, 1H), 7.86 (d, *J* = 6.1 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 2H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.46 (m, 7H), 6.93 (d, *J* = 8.1 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.3, 137.2, 136.3, 134.3, 131.9, 131.7, 131.2, 129.4, 129.2, 129.1, 129.0, 127.5, 127.1, 125.8, 124.5.

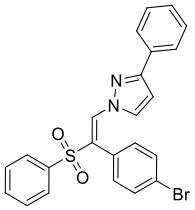


(*E*)-5y

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), 1-bromo-4-ethynylbenzene **2a** (0.24 mmol, 43 mg, 1.2 eq.), 5-phenyl-1-tosyl-1*H*-imidazole **3p** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (3:1) as eluent to afford product **(*E*)-5y** in 77% yield (71 mg) as a white solid.

(*E*)-1-(2-(4-bromophenyl)-2-(phenylsulfonyl)vinyl)-4-phenyl-1*H*-imidazole ((*E*)-5y). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.23 (s, 1H), 7.67 – 7.51 (m, 8H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 6.5 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.71 (s, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.0, 139.2, 138.0, 133.9,

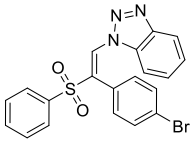
132.8, 132.4, 132.2, 130.9, 129.1, 128.9, 128.7, 128.6, 128.0, 127.8, 125.2, 125.1, 112.8.



(*E*)-5z

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), 1-bromo-4-ethynylbenzene **2a** (0.24 mmol, 43 mg, 1.2 eq.), 5-phenyl-1-tosyl-1*H*-pyrazole **3q** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (5:1) as eluent to afford product **(*E*)-5z** in 63% yield (58 mg) as a white solid.

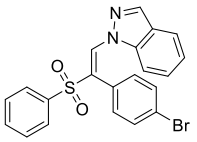
(*E*)-1-(2-(4-bromophenyl)-2-(phenylsulfonyl)vinyl)-3-phenyl-1*H*-pyrazole ((*E*)-5z). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.50 (s, 1H), 7.67 (t, *J* = 6.2 Hz, 4H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.39 (m, 5H), 6.96 (t, *J* = 6.1 Hz, 3H), 6.55 (d, *J* = 2.9 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 154.6, 138.7, 135.4, 133.6, 132.7, 132.4, 131.4, 131.3, 129.1, 129.0, 128.8, 128.6, 128.5, 126.3, 126.0, 124.4, 107.3.



(*E*)-5aa

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), 1-bromo-4-ethynylbenzene **2a** (0.24 mmol, 43 mg, 1.2 eq.), 1-tosyl-1*H*-benzo[*d*][1,2,3]triazole **3r** (0.2 mmol, 55 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (5:1) as eluent to afford product **(*E*)-5aa** in 45% yield (39 mg) as a white solid.

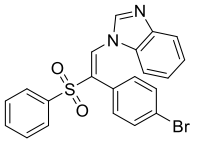
(*E*)-1-(2-(4-bromophenyl)-2-(phenylsulfonyl)vinyl)-1*H*-benzo[*d*][1,2,3]triazole ((*E*)-5aa). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.74 (s, 1H), 8.04 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 2H), 7.58 (m, 2H), 7.44 (m, 6H), 7.00 (d, *J* = 8.0 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 145.5, 137.9, 133.9, 132.4, 132.33, 132.30, 131.8, 129.4, 129.1, 128.7, 128.3, 128.2, 125.6, 124.3, 120.7, 109.8.



(*E*)-5ab

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), 1-bromo-4-ethynylbenzene **2a** (0.24 mmol, 43 mg, 1.2 eq.), 1-tosyl-1*H*-indazole **3s** (0.2 mmol, 55 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (5:1) as eluent to afford product **(*E*)-5ab** in 57% yield (50 mg) as a white solid.

(*E*)-1-(2-(4-bromophenyl)-2-(phenylsulfonyl)vinyl)-1*H*-indazole ((*E*)-5ab). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.66 (s, 1H), 7.92 (s, 1H), 7.77 – 7.64 (m, 4H), 7.56 (t, *J* = 8.2 Hz, 2H), 7.42 (dd, *J* = 15.4, 7.9 Hz, 4H), 7.32 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 7.8 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 140.8, 139.8, 139.0, 133.3, 133.0, 131.2, 129.7, 128.9, 128.5, 128.4, 128.0, 125.2, 124.9, 123.7, 123.2, 121.6, 109.7.

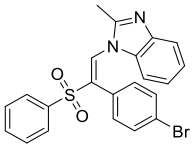


(*E*)-5ac

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), 1-bromo-4-ethynylbenzene **2a** (0.24 mmol, 43 mg, 1.2 eq.), 1-tosyl-1*H*-benzo[*d*]imidazole **3t** (0.2 mmol, 54 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using pe-

troleum ether/ethyl acetate mixture (3:1) as eluent to afford product **(*E*)-5ac** in 84% yield (73 mg) as a white solid.

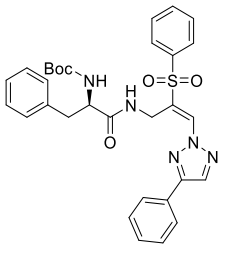
(*E*)-1-(2-(4-bromophenyl)-2-(phenylsulfonyl)vinyl)-1*H*-benzo[*d*]imidazole ((*E*)-5ac). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.46 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 3H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.50 – 7.43 (m, 3H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.27 (d, *J* = 5.8 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.1, 142.7, 139.8, 138.1, 133.8, 133.1, 132.2, 129.1, 128.7, 128.6, 128.2, 125.2, 125.1, 124.6, 121.1, 115.2, 109.8.



(*E*)-5ad

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), 1-bromo-4-ethynylbenzene **2a** (0.24 mmol, 43 mg, 1.2 eq.), 2-methyl-1-tosyl-1*H*-benzo[*d*]imidazole **3u** (0.2 mmol, 57 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (2:1) as eluent to afford product **(*E*)-5ad** in 76% yield (69 mg) as a white solid.

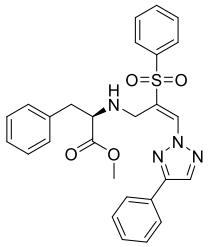
(*E*)-1-(2-(4-bromophenyl)-2-(phenylsulfonyl)vinyl)-2-methyl-1*H*-benzo[*d*]imidazole ((*E*)-5ad). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.34 (s, 1H), 7.72 (d, *J* = 7.8 Hz, 2H), 7.58 (dd, *J* = 18.9, 7.9 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.19 (t, *J* = 7.7 Hz, 1H), 7.10 – 6.99 (m, 3H), 6.83 (d, *J* = 8.2 Hz, 1H), 2.44 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 151.2, 142.9, 138.4, 136.9, 133.9, 133.2, 132.3, 131.4, 130.8, 129.3, 128.2, 127.9, 124.6, 123.6, 123.3, 119.5, 110.9, 15.0.



(*E*)-6a

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), *tert*-butyl (*R*)-(1-oxo-3-phenyl-1-(prop-2-yn-1-ylamino)propan-2-yl)carbamate **2ba** (0.24 mmol, 72 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (1:1) as eluent to afford product **(*E*)-6a** in 55% yield (64 mg) as a white solid.

***tert*-Butyl (*R*,*E*)-(1-oxo-3-phenyl-1-((3-(4-phenyl-2*H*-1,2,3-triazol-2-yl)-2-(phenylsulfonyl)allyl)amino)propan-2-yl)carbamate ((*E*)-6a**. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.43 (s, 1H), 8.08 (s, 1H), 8.01 (d, *J* = 7.7 Hz, 2H), 7.79 (d, *J* = 7.2 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 2H), 7.51 – 7.44 (m, 3H), 7.05 (t, *J* = 7.2 Hz, 2H), 6.95 (d, *J* = 7.5 Hz, 2H), 6.41 (s, 1H), 5.28 – 4.91 (m, 1H), 4.73 (dd, *J* = 15.2, 6.9 Hz, 1H), 4.43 (d, *J* = 15.5 Hz, 1H), 4.15 (s, 1H), 2.96 (d, *J* = 13.1 Hz, 1H), 2.68 (t, *J* = 11.4 Hz, 1H), 1.37 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 169.9, 155.2, 151.5, 138.9, 136.8, 135.8, 135.6, 133.9, 130.2, 129.4, 129.3, 129.1, 128.7, 128.4, 128.1, 127.4, 126.6, 126.5, 79.9, 56.0, 39.2, 34.1, 28.3. **HRMS-ESI** (*m/z*): calcd for $C_{31}H_{33}N_5NaO_5S$ $[M+Na]^+$: 610.2095, found 610.2101.

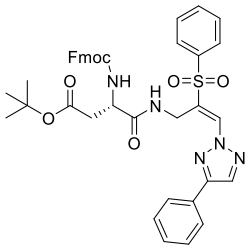


(*E*)-6b

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), methyl prop-2-yn-1-yl-*D*-phenylalaninate **2bb** (0.24 mmol, 52 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (2:1) as eluent to afford product **(*E*)-6b** in 63% yield (63 mg) as a white solid.

methyl (*E*)-(3-(4-phenyl-2H-1,2,3-triazol-2-yl)-2-(phenylsulfonyl)allyl)-*D*-phenylalaninate ((*E*)-6b). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.39 (s, 1H), 7.97 (s,

1H), 7.91 (d, *J* = 7.7 Hz, 2H), 7.75 (d, *J* = 6.8 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 7.45 (d, *J* = 6.5 Hz, 3H), 7.04 – 6.90 (m, 5H), 4.03 (d, *J* = 14.9 Hz, 1H), 3.88 (d, *J* = 14.9 Hz, 1H), 3.75 – 3.62 (m, 4H), 2.98 (dd, *J* = 13.5, 5.2 Hz, 1H), 2.69 (dd, *J* = 13.6, 8.8 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 174.2, 151.2, 139.5, 137.0, 135.2, 135.0, 133.6, 130.0, 129.7, 129.4, 129.1, 128.8, 128.3, 126.5, 126.5, 60.7, 51.8, 42.4, 39.3. **HRMS-ESI** (*m/z*): calcd for $C_{27}H_{26}N_4NaO_4S$ $[M+Na]^+$: 525.1567, found 525.1578.

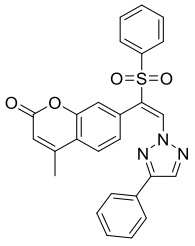


(***E***)-6c

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), *tert*-butyl (*S*)-3-((((9*H*-fluoren-9-yl)methoxy)carbonyl)amino)-4-oxo-4-(prop-2-yn-1-ylamino)butanoate **2bc** (0.24 mmol, 90 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (1:1) as eluent to afford product **(*E*)-6c** in 35% yield (51 mg) as a white solid.

***tert*-Butyl (*S*,*E*)-3-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-4-oxo-4-((3-(4-phenyl-2*H*-1,2,3-triazol-2-yl)-2-(phenylsulfonyl)allyl)amino)butanoate ((*E*)-6c)**. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.52 (s, 1H), 8.08 (s, 1H), 7.98 (d, *J* = 7.8 Hz, 2H), 7.76 (dd, *J* = 13.8, 7.4 Hz, 4H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.9 Hz, 4H), 7.45 - 7.37 (m, 6H), 7.31 (d, *J* = 6.8 Hz, 2H), 5.79 (d, *J* = 8.4 Hz, 1H), 4.76 (dd, *J* = 15.2, 6.5 Hz, 1H), 4.63 (dd, *J* = 15.1, 5.3 Hz, 1H), 4.31 (dd, *J* = 10.5, 7.0 Hz, 2H), 4.22 (t, *J* = 8.8 Hz, 1H), 4.11 (t, *J* = 7.1 Hz, 1H), 2.74 (dd, *J* = 17.3, 4.5 Hz, 1H), 2.43 (dd, *J* = 16.7, 6.6 Hz, 1H), 1.38 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 171.1, 169.6, 155.8, 143.7, 141.3, 135.9, 135.7, 133.8, 130.1, 129.4, 129.2, 128.6, 127.8,

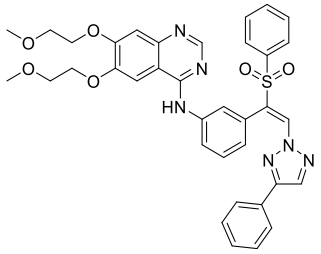
127.4, 127.1, 126.5, 125.0, 120.0, 81.8, 67.2, 51.0, 47.0, 37.4, 34.6, 28.0. **HRMS-ESI** (*m/z*): calcd for $C_{40}H_{39}N_5NaO_7S$ $[M+Na]^+$: 756.2462, found 756.2482.



(*E*)-6d

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), 7-ethynyl-4-methyl-2*H*-chromen-2-one **2bd** (0.24 mmol, 44 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (5:1) as eluent to afford product **(*E*)-6d** in 81% yield (76 mg) as a white solid.

(*E*)-4-methyl-7-(2-(4-phenyl-2*H*-1,2,3-triazol-2-yl)-1-(phenylsulfonyl)vinyl)-2*H*-chromen-2-one ((*E*)-6d). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.68 (s, 1H), 7.90 (s, 1H), 7.70 (d, *J* = 7.8 Hz, 2H), 7.61 (q, *J* = 7.7 Hz, 2H), 7.53 (dd, *J* = 6.8, 2.9 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.40 – 7.32 (m, 3H), 7.17 (d, *J* = 8.1 Hz, 1H), 6.91 (s, 1H), 6.34 (s, 1H), 2.47 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 160.4, 152.9, 152.0, 150.8, 138.2, 135.4, 134.0, 133.8, 133.5, 129.9, 129.8, 129.2, 129.1, 128.6, 128.3, 127.0, 126.3, 124.3, 120.3, 119.4, 116.0, 18.7.

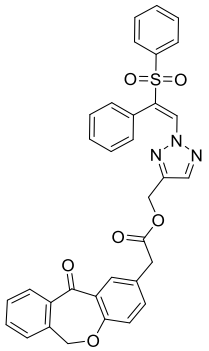


(*E*)-6e

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), Erlotinib **2be** (0.24 mmol, 94 mg, 1.2 eq.), 4-phenyl-1-tosyl-1*H*-1,2,3-triazole **3a** (0.2 mmol, 60 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reac-

tion mixture was purified by column chromatography using DCM/MeOH mixture (20:1) as eluent to afford product **(*E*)-6e** in 64% yield (86 mg) as a white solid.

(*E*)-6,7-bis(2-methoxyethoxy)-*N*-(3-(2-(4-phenyl-2*H*-1,2,3-triazol-2-yl)-1-(phenylsulfonyl)vinyl)phenyl)quinazolin-4-amine ((E)-6e). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.59 (s, 1H), 8.53 (s, 1H), 8.15 (d, *J* = 8.3 Hz, 1H), 7.89 (s, 1H), 7.79 (s, 1H), 7.71 (d, *J* = 7.8 Hz, 2H), 7.57 – 7.52 (m, 3H), 7.48 (s, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.35 – 7.30 (m, 3H), 7.30 – 7.26 (m, 2H), 7.18 (s, 1H), 6.59 (d, *J* = 7.6 Hz, 1H), 4.28 – 4.21 (m, 4H), 3.79 (dd, *J* = 9.8, 4.8 Hz, 4H), 3.41 (d, *J* = 5.6 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 156.2, 154.5, 153.1, 149.0, 138.3, 135.0, 133.6, 133.3, 131.3, 130.0, 129.7, 129.0, 129.0, 128.7, 128.6, 126.3, 123.3, 122.2, 109.1, 108.2, 102.3, 70.8, 70.4, 69.2, 68.4, 59.3. **HRMS-ESI** (*m/z*): calcd for $C_{36}H_{34}N_6NaO_6S$ $[M+Na]^+$: 701.2153, found 701.2206.

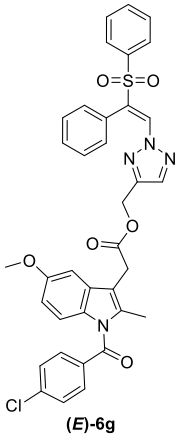


***E*)-6f**

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), ethynylbenzene **2b** (0.24 mmol, 25 mg, 1.2 eq.), (1-tosyl-1*H*-1,2,3-triazol-4-yl)methyl 2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl)acetate **3ba** (0.2 mmol, 100 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (3:1) as eluent to afford product **(*E*)-6f** in 58% yield (68 mg) as a white solid.

(*E*)-(2-(2-phenyl-2-(phenylsulfonyl)vinyl)-2*H*-1,2,3-triazol-4-yl)methyl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate ((*E*)-6f). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.57 (s, 1H), 8.07 (s, 1H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.67 – 7.53 (m, 5H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.42 – 7.33 (m, 5H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.01 (dd, *J* =

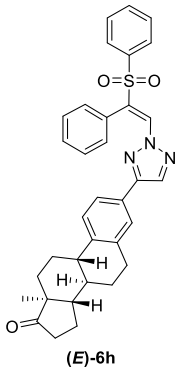
8.2, 4.7 Hz, 3H), 5.18 (s, 2H), 5.08 (s, 2H), 3.62 (s, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 190.8, 170.9, 160.6, 146.4, 138.2, 137.2, 136.2, 135.5, 133.6, 133.0, 132.9, 132.7, 132.5, 130.7, 129.5, 129.3, 129.2, 129.0, 128.9, 128.8, 128.1, 127.9, 127.1, 125.2, 121.2, 73.6, 57.5, 39.8. **HRMS-ESI** (*m/z*): calcd for $C_{33}H_{25}N_3NaO_6S$ $[M+Na]^+$: 614.1356, found 614.1359.



(*E*)-6g

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), ethynylbenzene **2b** (0.24 mmol, 25 mg, 1.2 eq.), (1-tosyl-1*H*-1,2,3-triazol-4-yl)methyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate **3bb** (0.2 mmol, 118 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (1:1) as eluent to afford product **(*E*)-6g** in 74% yield (100 mg) as a white solid.

(*E*)-(2-(2-phenyl-2-(phenylsulfonyl)vinyl)-2*H*-1,2,3-triazol-4-yl)methyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate ((*E*)-6g). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.58 (s, 1H), 7.70 – 7.52 (m, 6H), 7.50 – 7.35 (m, 5H), 7.32 – 7.26 (m, 2H), 7.01 (d, *J* = 7.5 Hz, 2H), 6.87 (d, *J* = 11.4 Hz, 2H), 6.68 (d, *J* = 9.0 Hz, 1H), 5.10 (s, 2H), 3.80 (s, 3H), 3.68 (s, 2H), 2.36 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.3, 156.0, 146.4, 139.4, 137.2, 136.1, 133.8, 133.7, 133.1, 132.6, 131.2, 130.8, 130.7, 129.22, 129.18, 129.0, 128.9, 128.8, 128.1, 115.0, 111.9, 111.6, 101.3, 57.5, 55.7, 30.1, 13.4. **HRMS-ESI** (*m/z*): calcd for $C_{36}H_{29}ClN_4NaO_6S$ $[M+Na]^+$: 703.1389, found 703.1413.



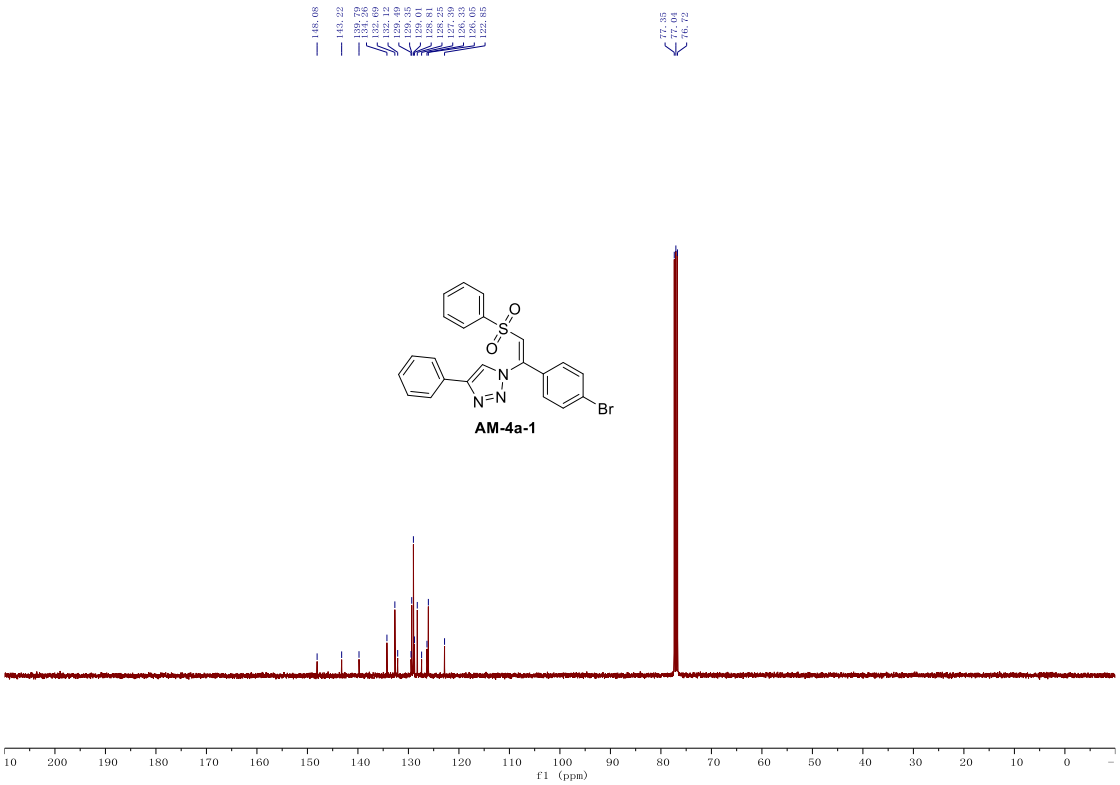
(*E*)-6h

Following **General Procedure 1**, sodium benzenesulfinate **1a** (0.5 mmol, 82 mg, 2.5 eq.), ethynylbenzene **2b** (0.24 mmol, 25 mg, 1.2 eq.), (8*R*,9*S*,13*S*,14*S*)-13-methyl-3-(1-tosyl-1*H*-1,2,3-triazol-4-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one **3bc** (0.2 mmol, 95 mg, 1.0 eq.) and Eosin Y (6 mg, 5 mol%) were used. The crude reaction mixture was purified by column chromatography using petroleum ether/ethyl acetate mixture (2:1) as eluent to afford product **(*E*)-6h** in 71% yield (80 mg) as a white solid.

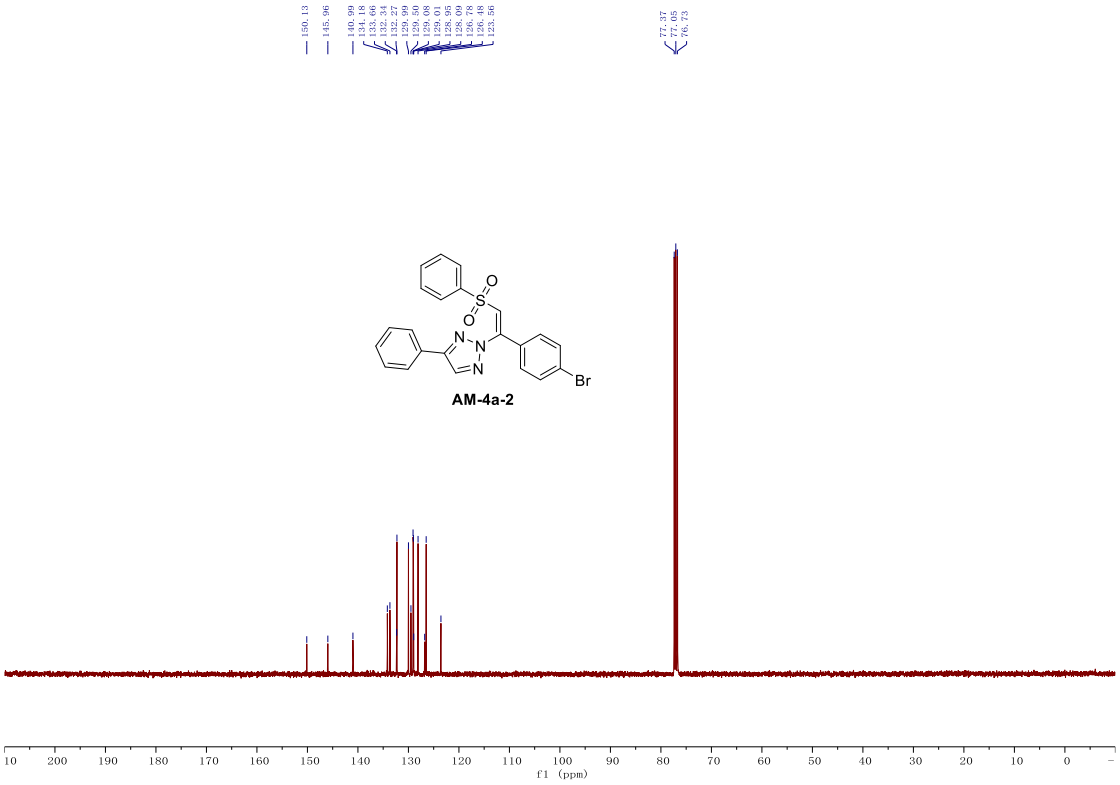
(8*R*,9*S*,13*S*,14*S*)-13-methyl-3-(2-((*E*)-2-phenyl-2-(phenylsulfonyl)vinyl)-2*H*-1,2,3-triazol-4-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one ((*E*)-6h). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.60 (s, 1H), 7.86 (s, 1H), 7.64 (d, *J* = 7.7 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.45 – 7.35 (m, 3H), 7.31 – 7.22 (m, 5H), 7.03 (d, *J* = 7.6 Hz, 2H), 2.87 (dd, *J* = 9.2, 4.2 Hz, 2H), 2.49 (dd, *J* = 18.8, 8.6 Hz, 1H), 2.43 – 2.36 (m, 1H), 2.30 – 2.24 (m, 1H), 2.19 – 1.92 (m, 4H), 1.66 – 1.52 (m, 3H), 1.48 – 1.32 (m, 2H), 0.88 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 220.6, 150.2, 141.6, 137.3, 134.8, 133.5, 133.0, 131.8, 130.9, 129.0, 128.9, 128.7, 128.06, 126.80, 126.01, 123.59, 50.49, 47.93, 44.46, 37.99, 35.84, 31.55, 29.26, 26.32, 25.6, 21.6, 13.8. **HRMS-ESI** (*m/z*): calcd for $C_{34}H_{33}N_3NaO_3S$ $[M+Na]^+$: 586.2135, found 586.2159.

8. NMR Spectra of Compounds

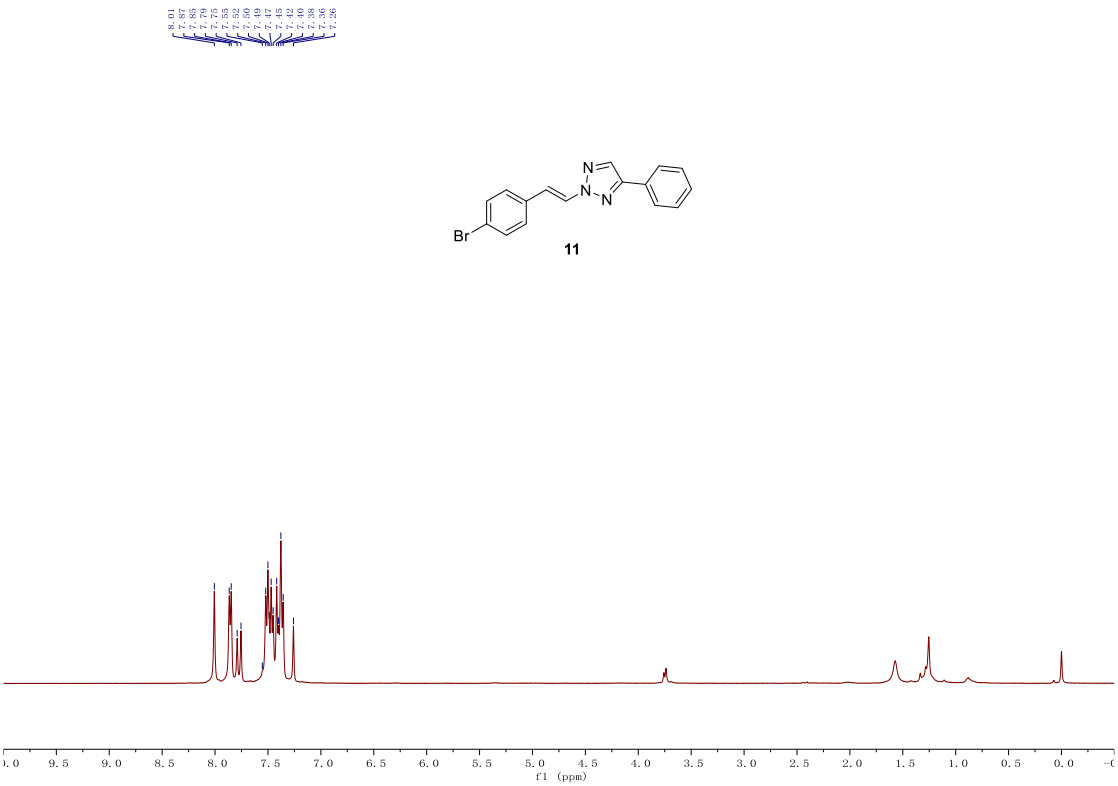
^{13}C NMR (101 MHz) Spectrum of AM-4a-1 in $CDCl_3$



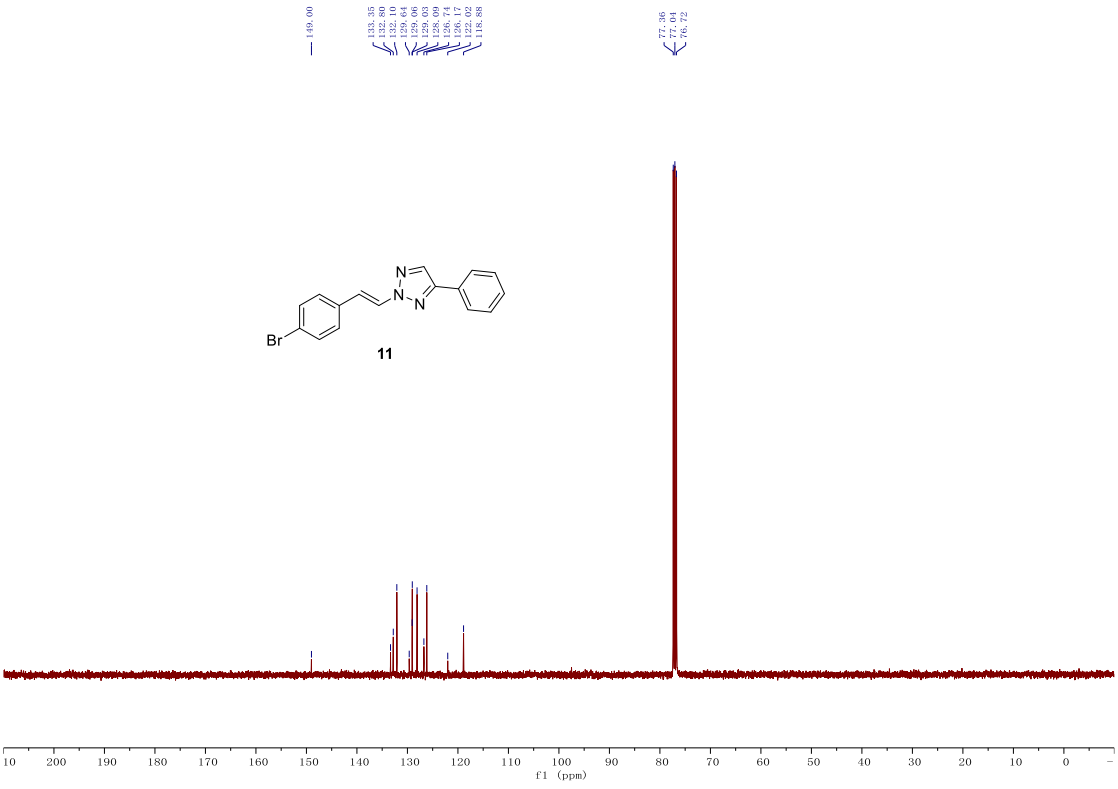
^{13}C NMR (101 MHz) Spectrum of AM-4a-2 in $CDCl_3$



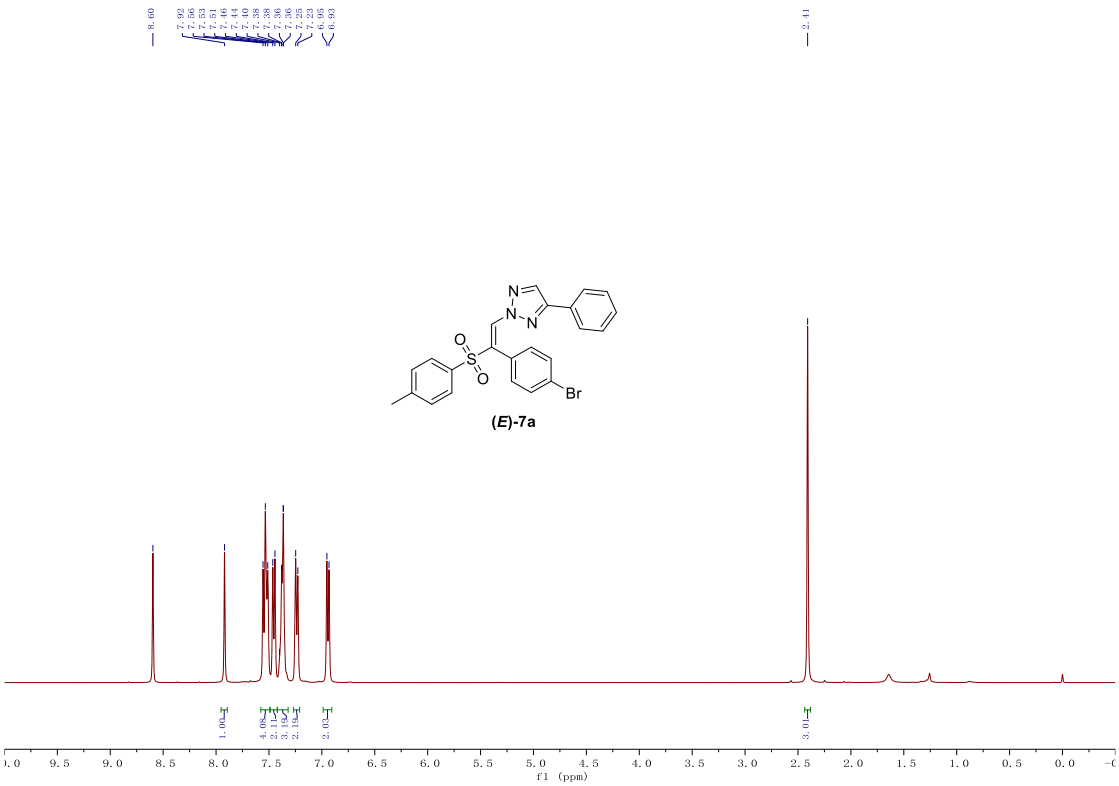
^{1}H NMR (400 MHz) Spectrum of 11 in $CDCl_3$



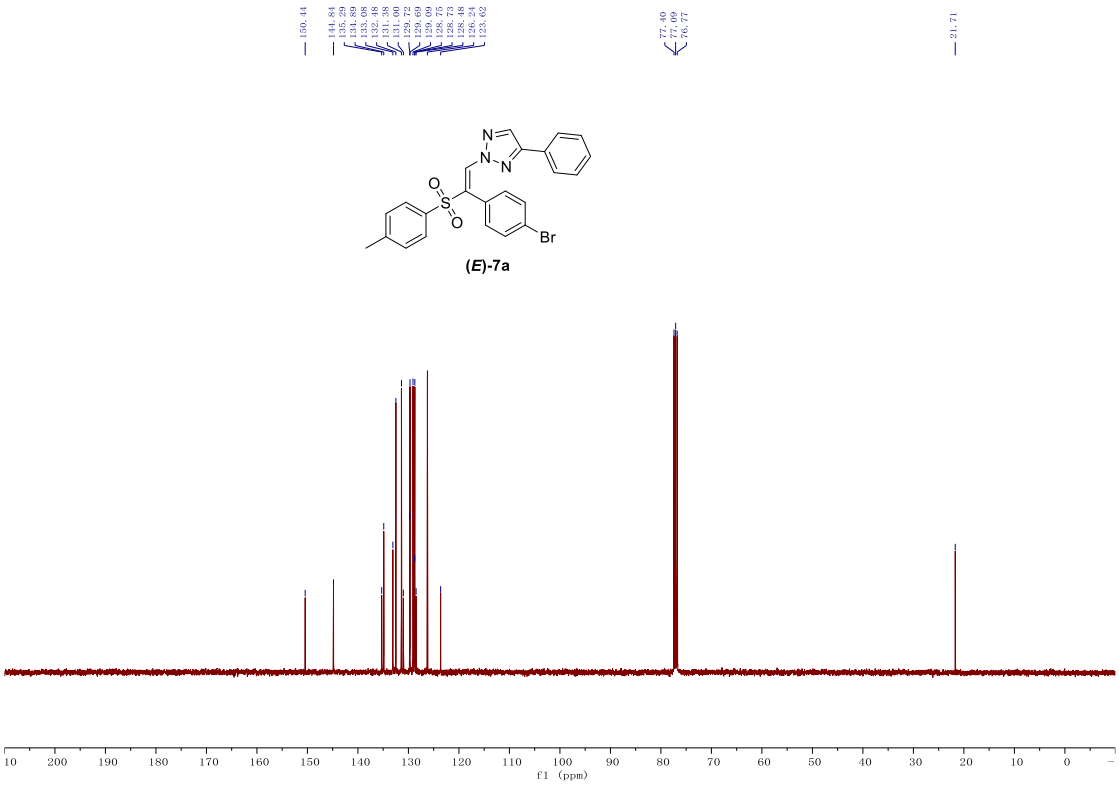
^{13}C NMR (101 MHz) Spectrum of 11 in $CDCl_3$



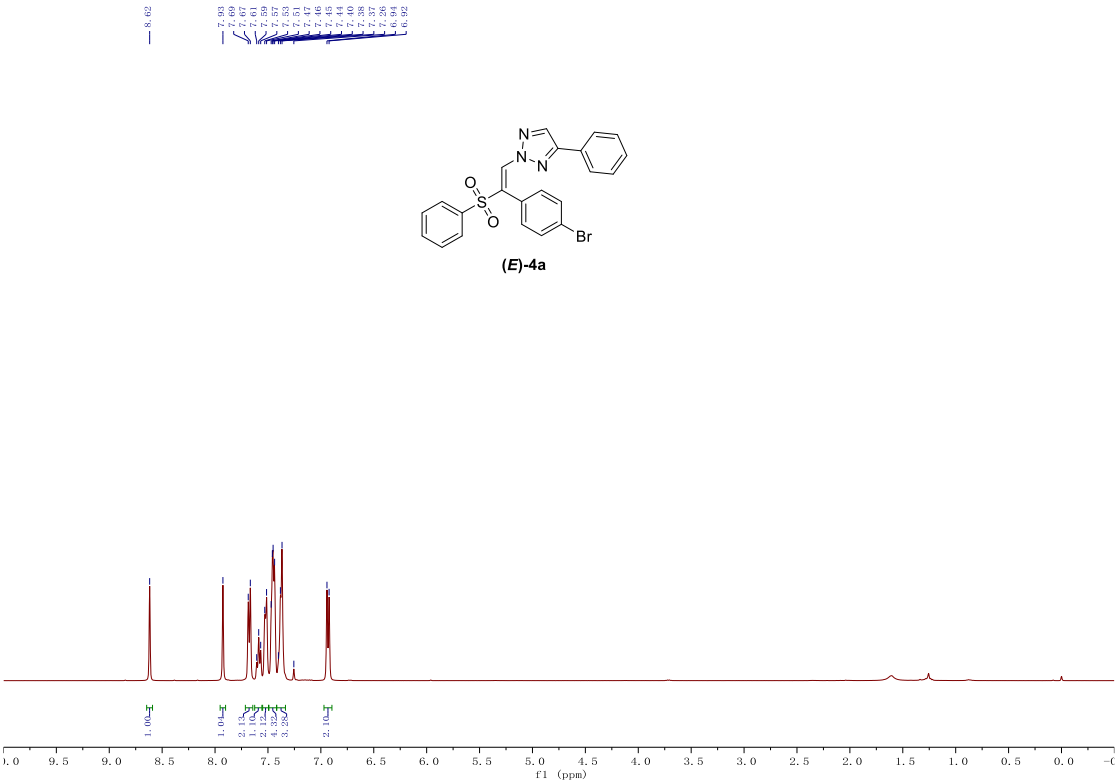
^{1}H NMR (400 MHz) Spectrum of (*E*)-7a in $CDCl_3$



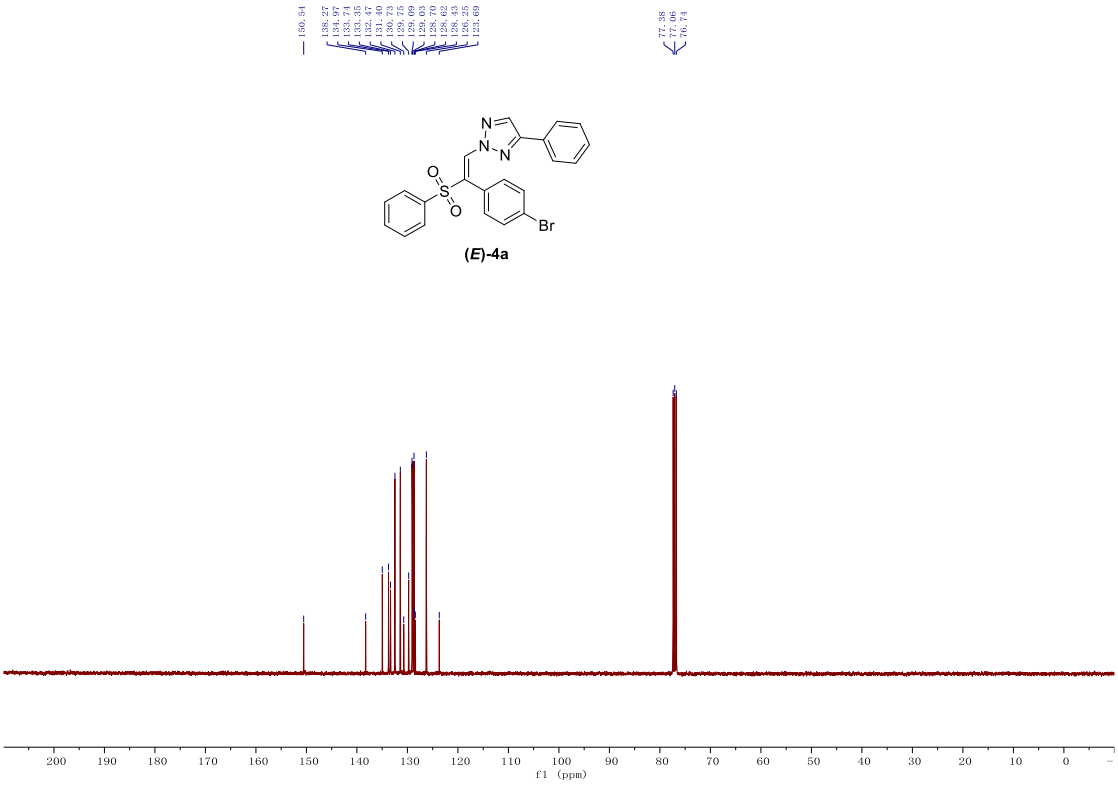
^{13}C NMR (101 MHz) Spectrum of (*E*)-7a in $CDCl_3$



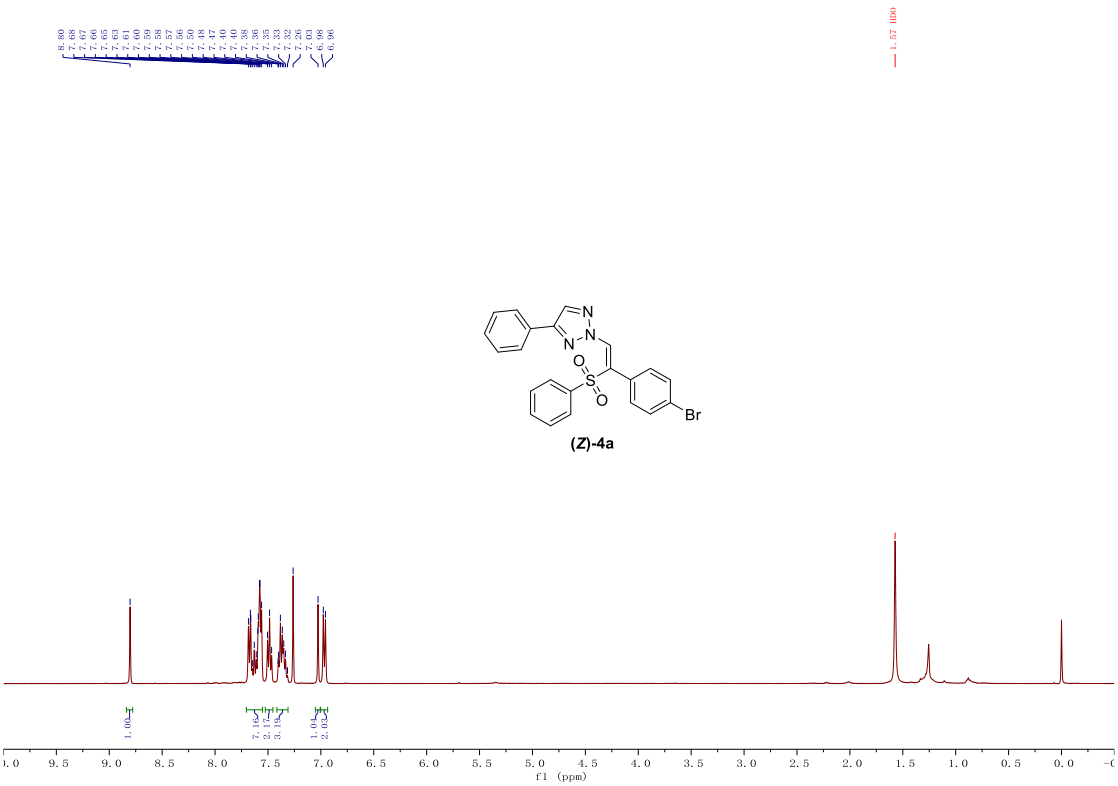
^{1}H NMR (400 MHz) Spectrum of (*E*)-4a in $CDCl_3$



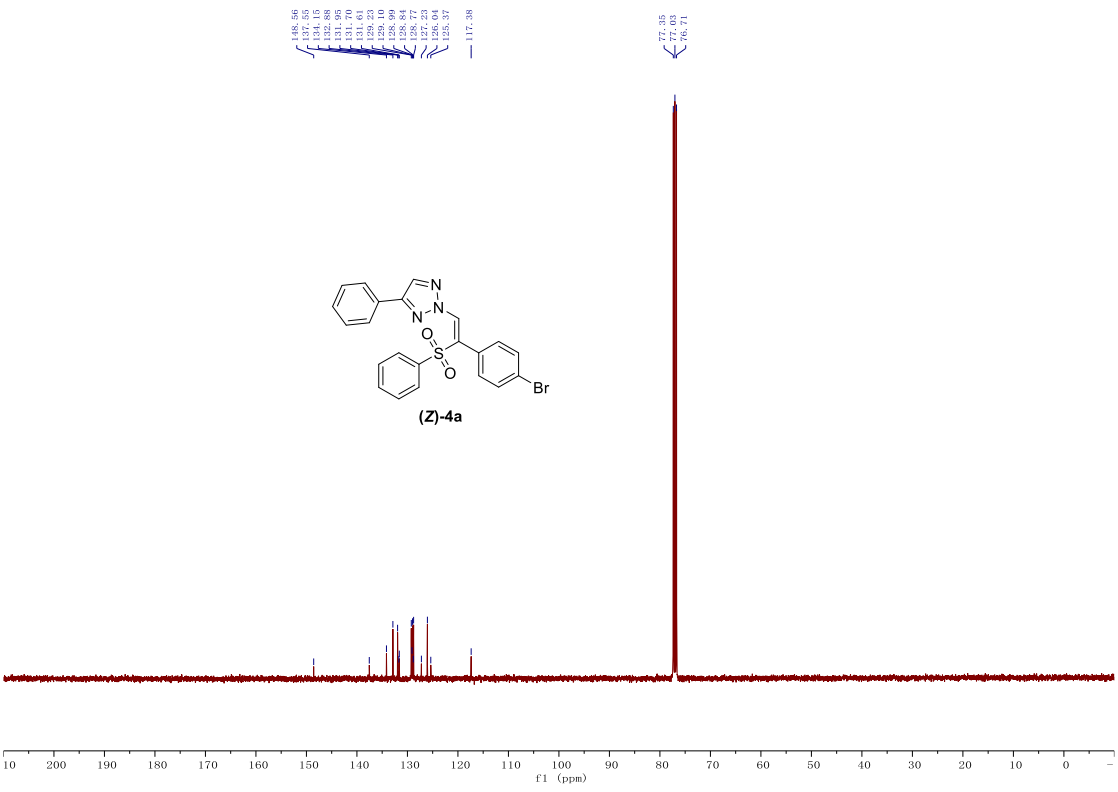
^{13}C NMR (101 MHz) Spectrum of (*E*)-4a in $CDCl_3$



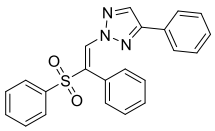
^{1}H NMR (400 MHz) Spectrum of (*Z*)-4a in $CDCl_3$



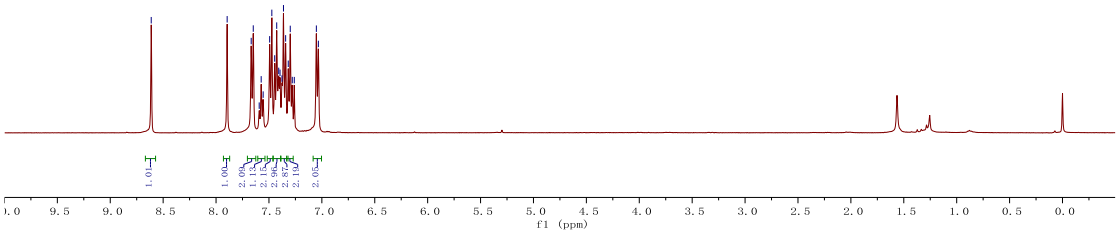
^{13}C NMR (101 MHz) Spectrum of (*Z*)-4a in $CDCl_3$



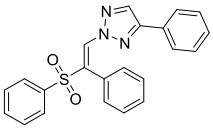
^{1}H NMR (400 MHz) Spectrum of (*E*)-4b in $CDCl_3$



(*E*)-4b

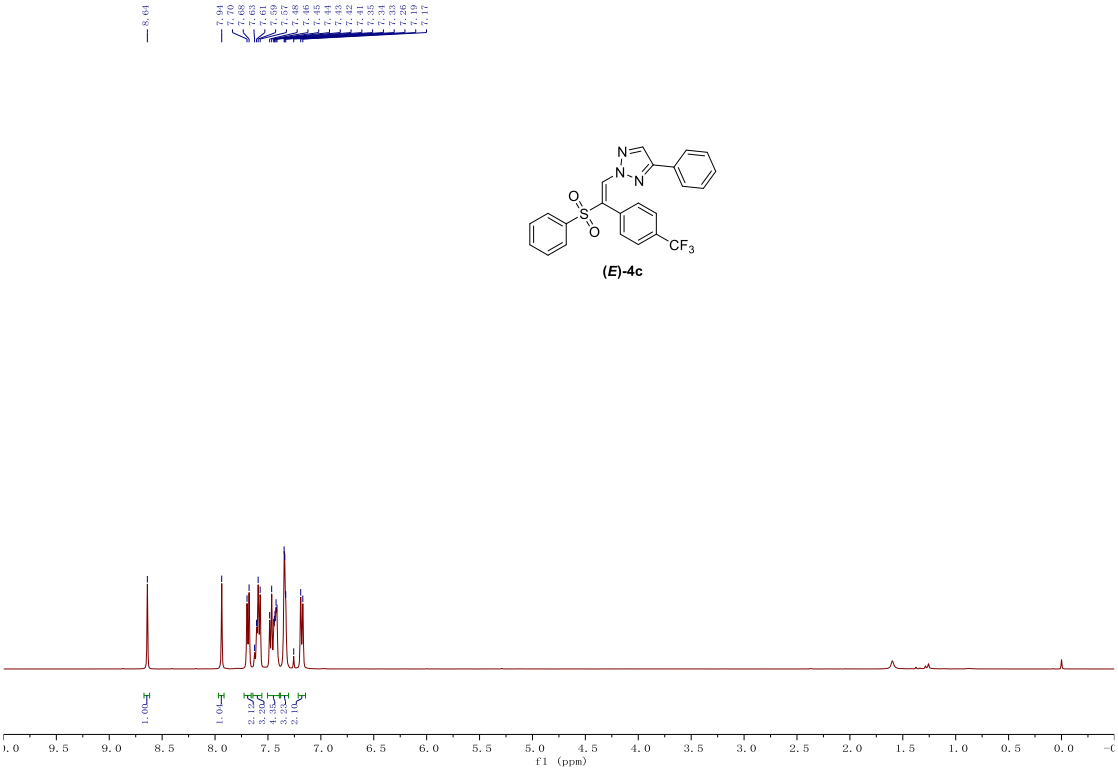


^{13}C NMR (101 MHz) Spectrum of (*E*)-4b in $CDCl_3$

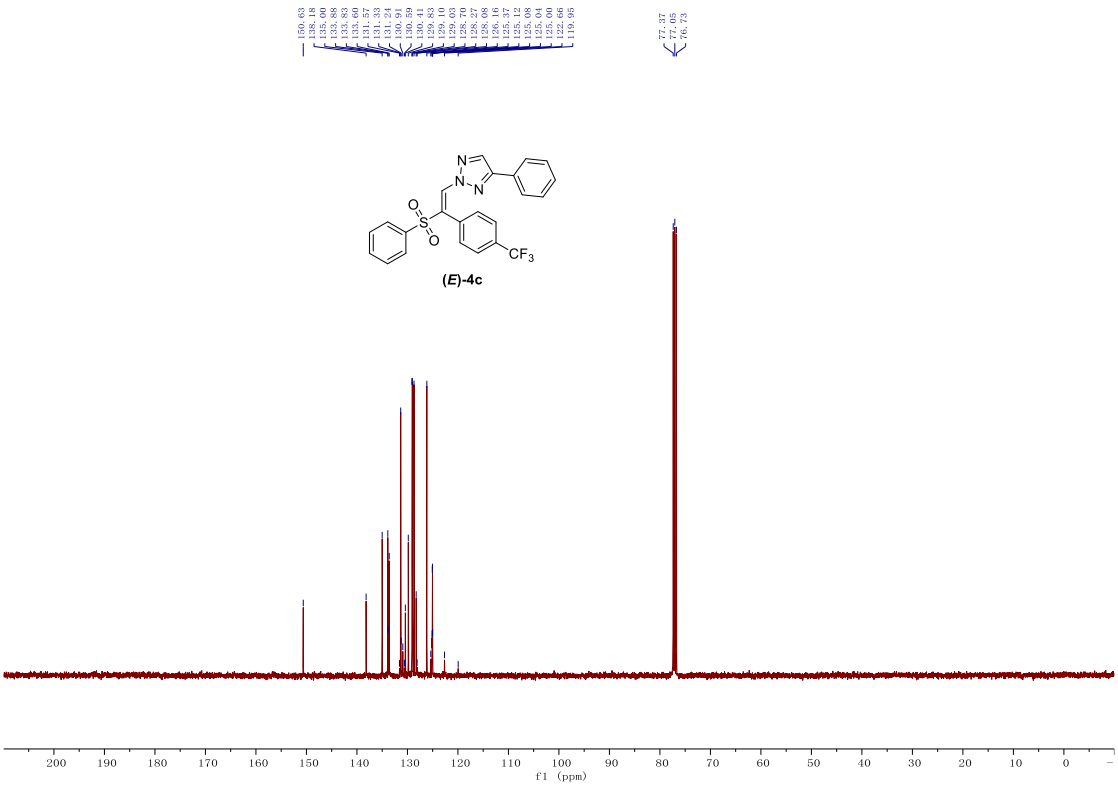


(*E*)-4b

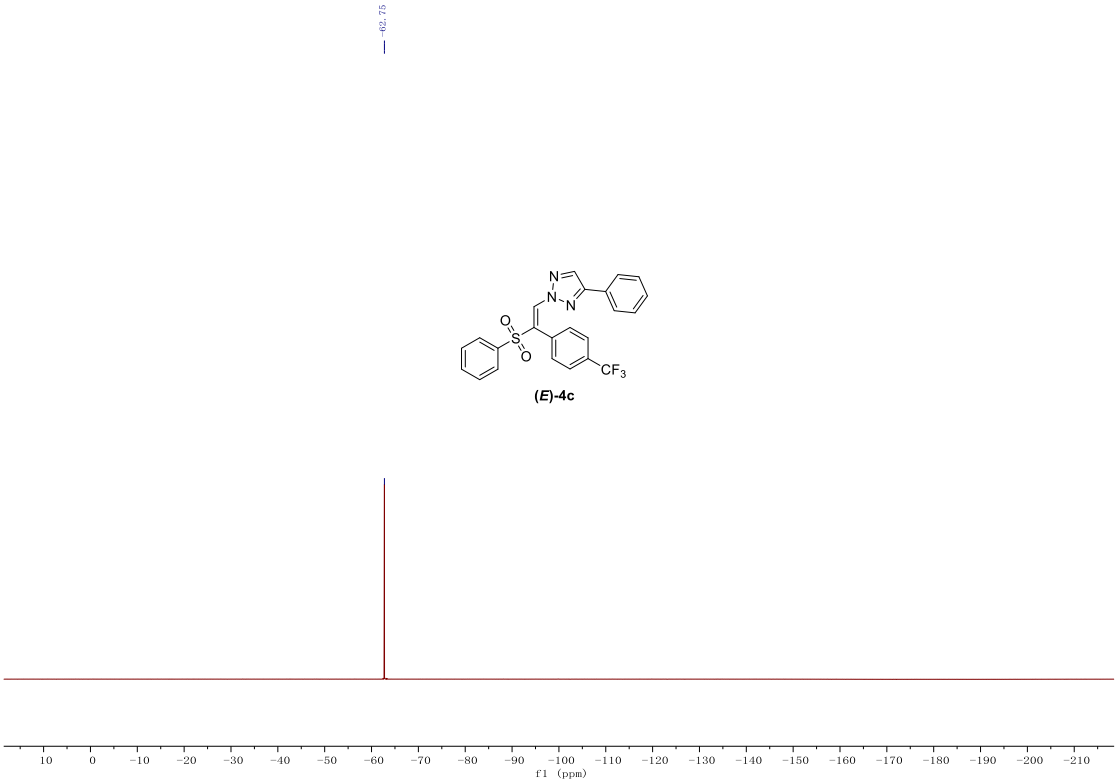
^{1}H NMR (400 MHz) Spectrum of (*E*)-4c in $CDCl_3$



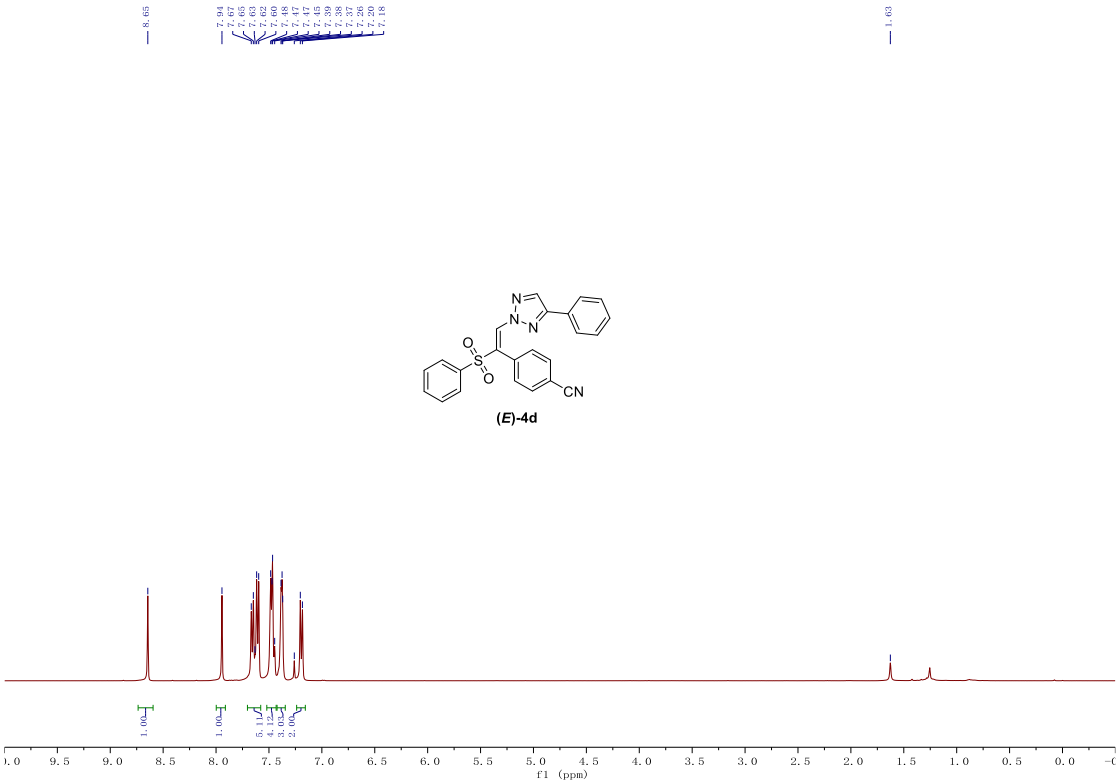
^{13}C NMR (101 MHz) Spectrum of (*E*)-4c in $CDCl_3$



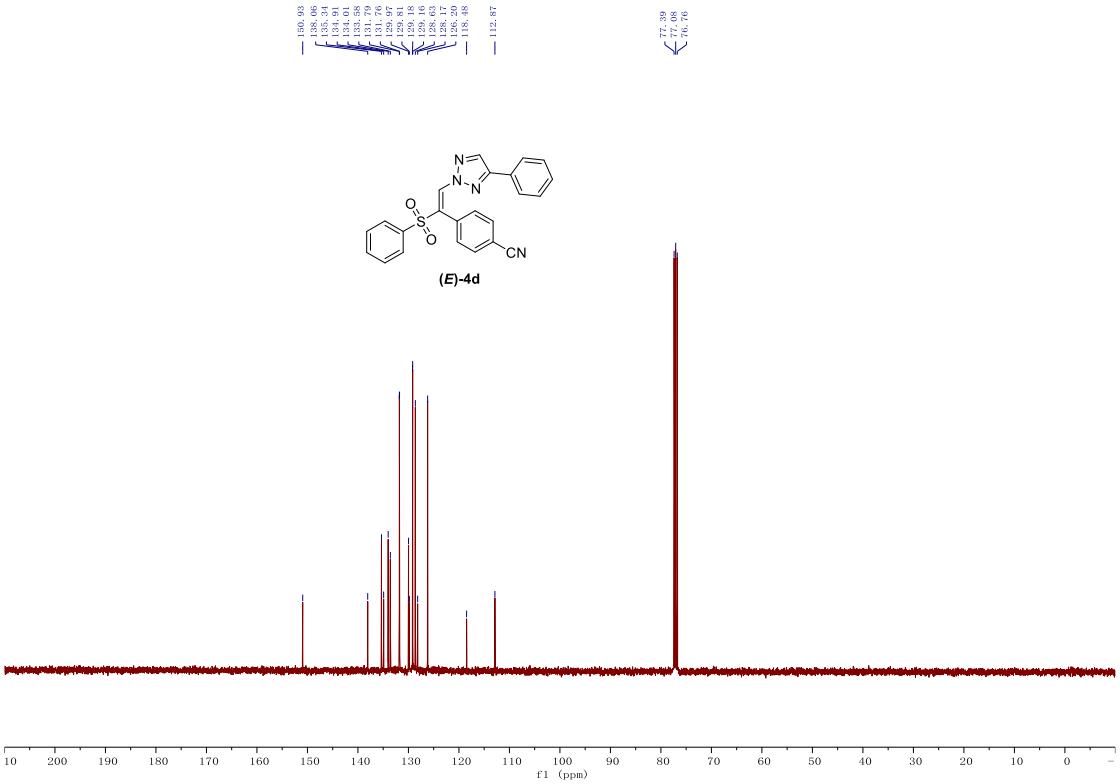
^{19}F NMR (376 MHz) Spectrum of (*E*)-4c in $CDCl_3$



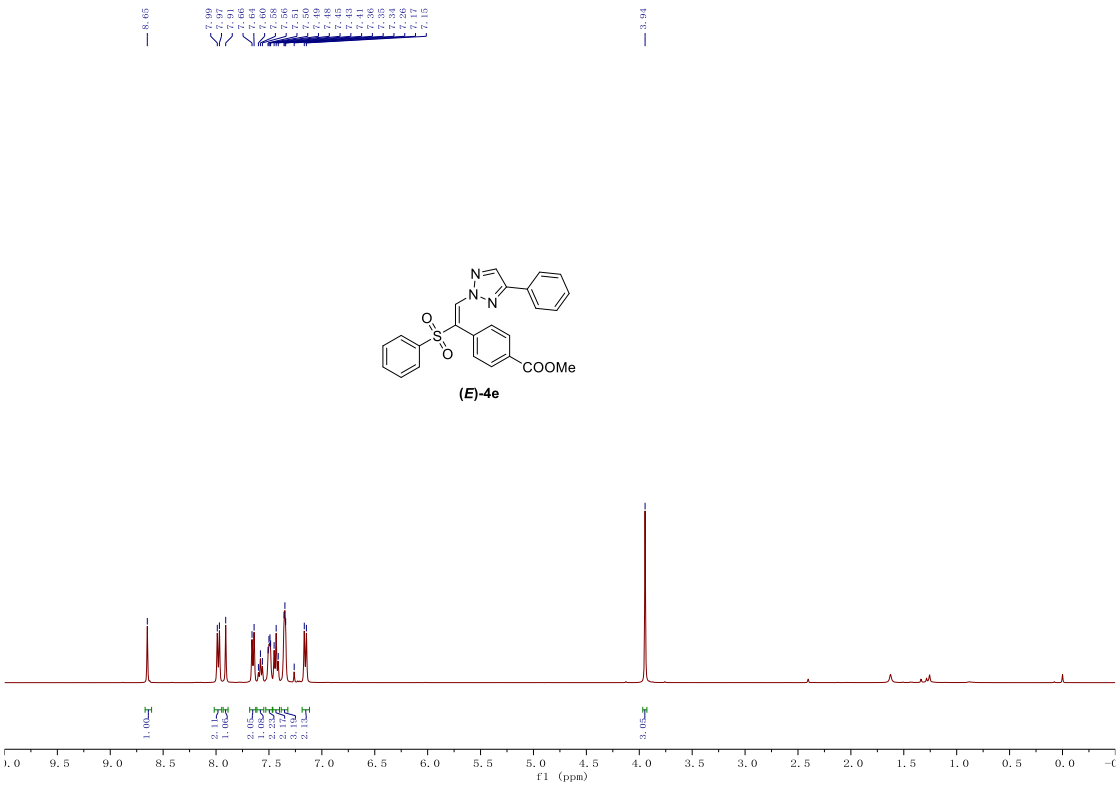
^{1}H NMR (400 MHz) Spectrum of (*E*)-4d in $CDCl_3$



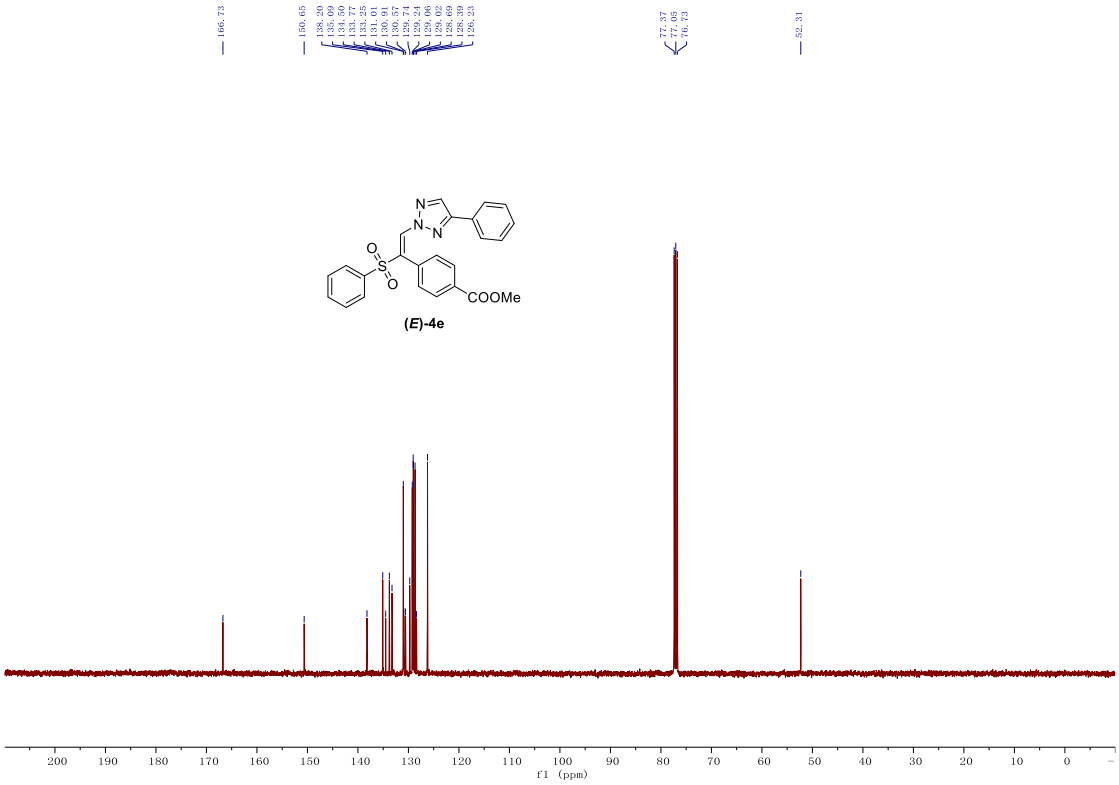
^{13}C NMR (101 MHz) Spectrum of (*E*)-4d in $CDCl_3$



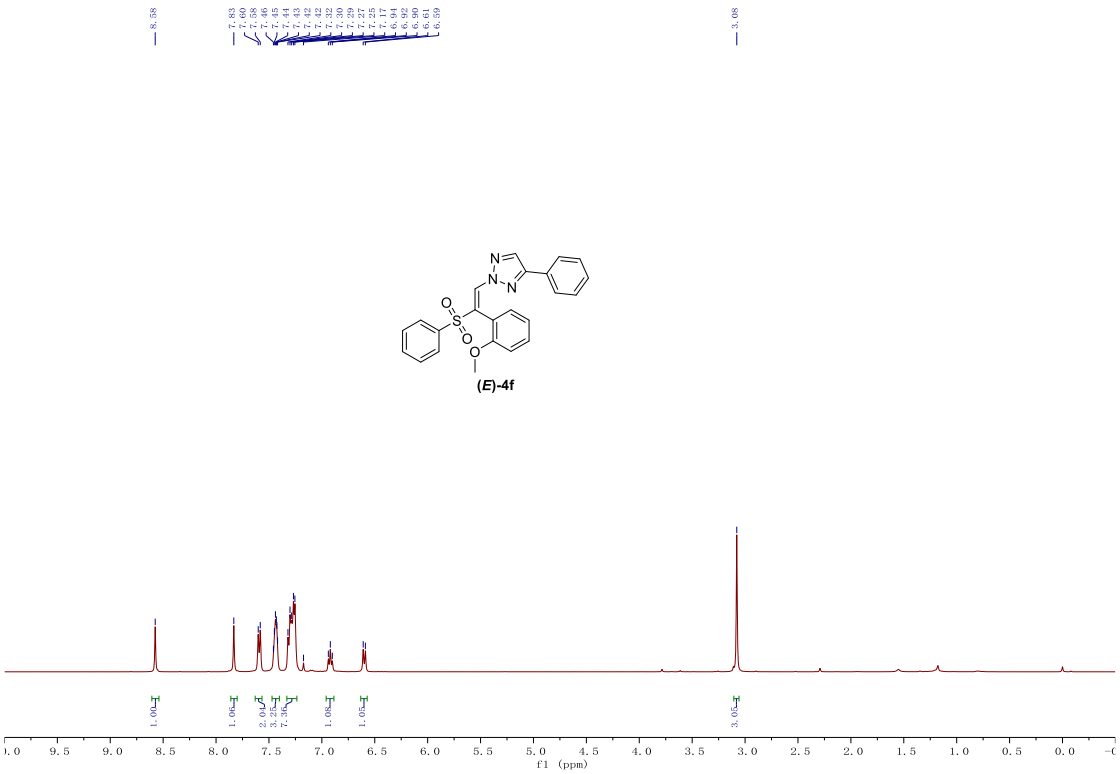
^{1}H NMR (400 MHz) Spectrum of (*E*)-4e in $CDCl_3$



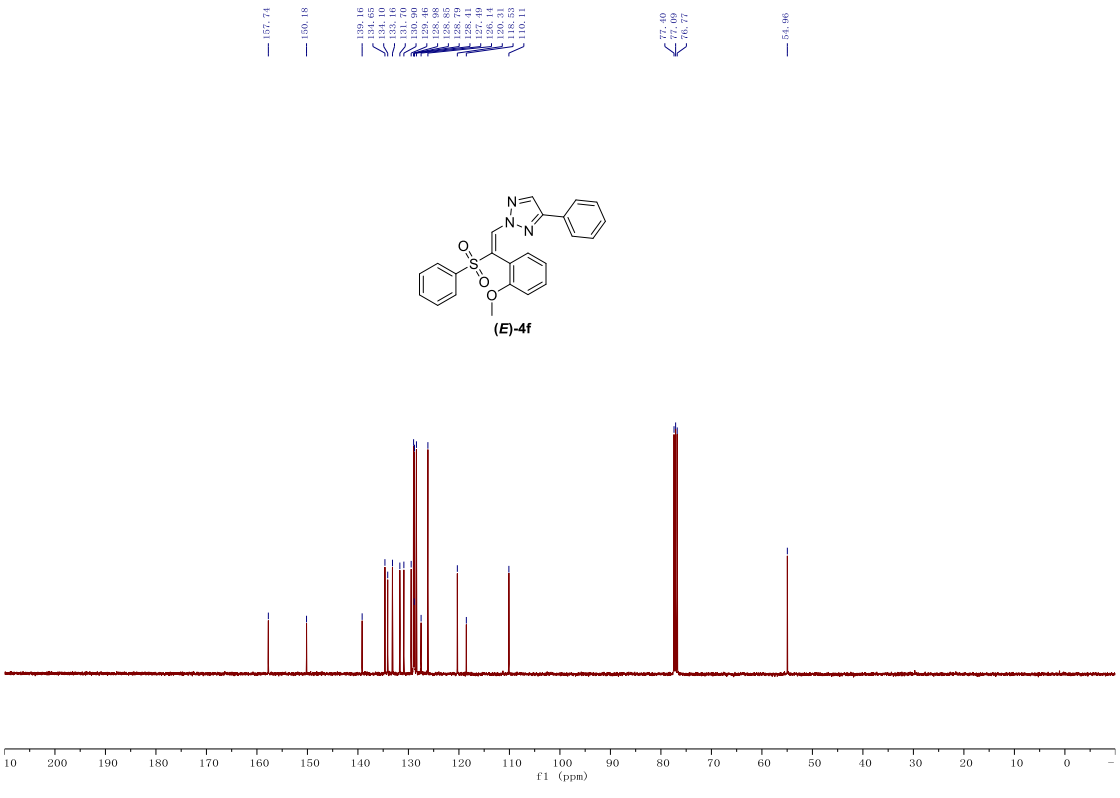
^{13}C NMR (101 MHz) Spectrum of (*E*)-4e in $CDCl_3$



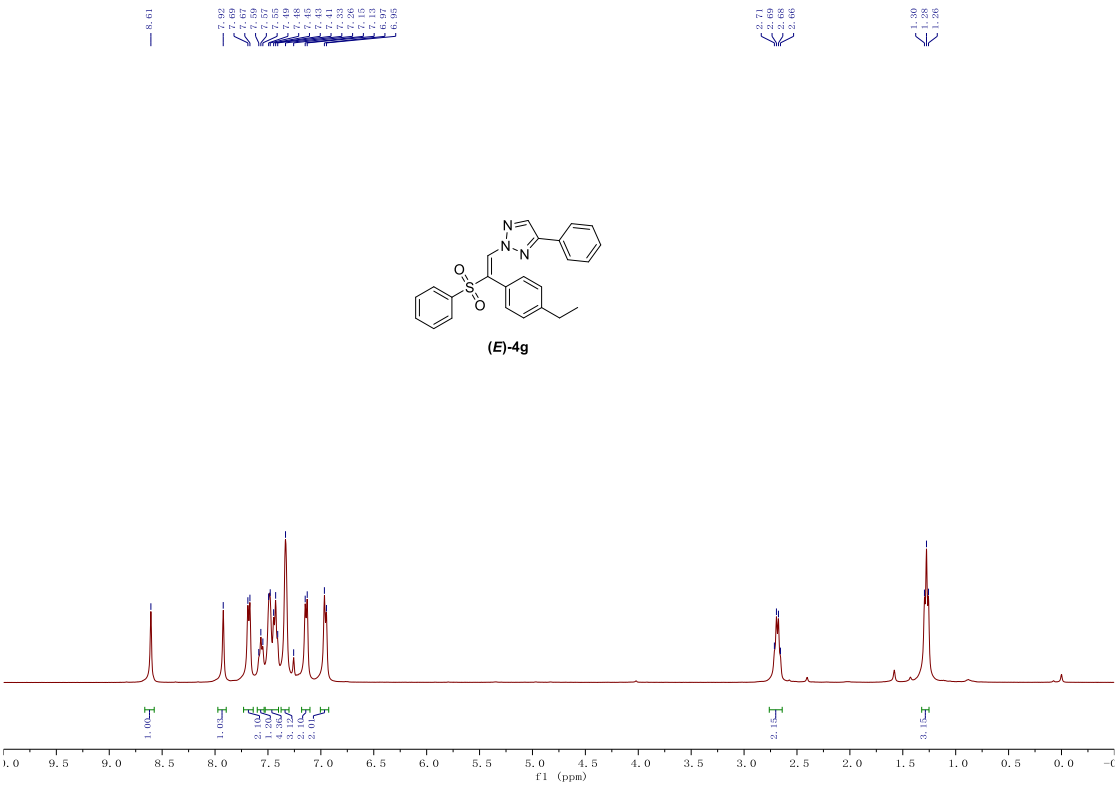
^{1}H NMR (400 MHz) Spectrum of (*E*)-4f in $CDCl_3$



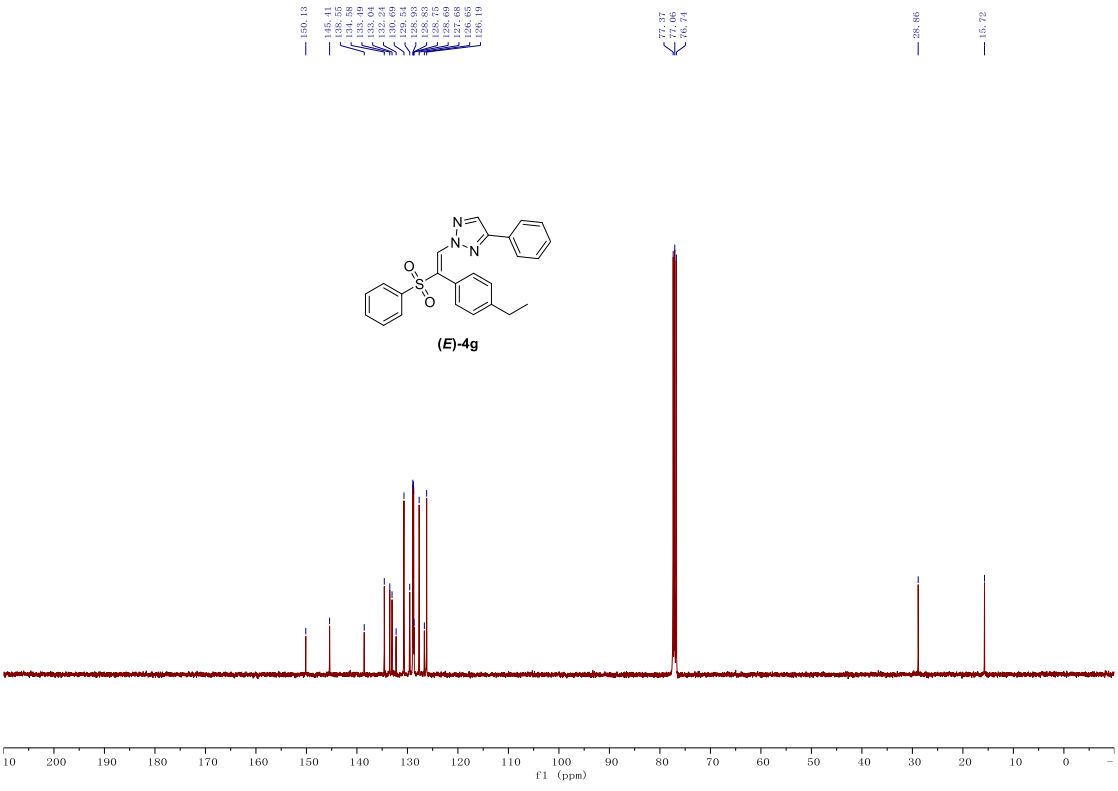
^{13}C NMR (101 MHz) Spectrum of (*E*)-4f in $CDCl_3$



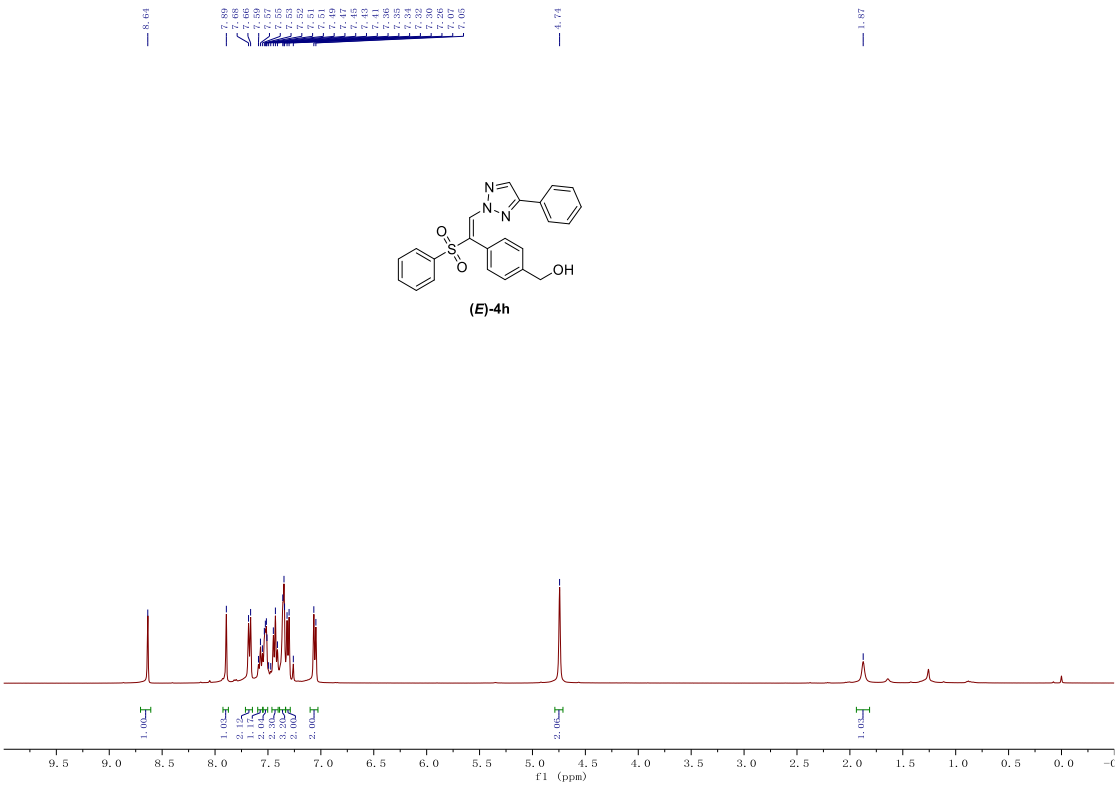
^{1}H NMR (400 MHz) Spectrum of (*E*)-4g in $CDCl_3$



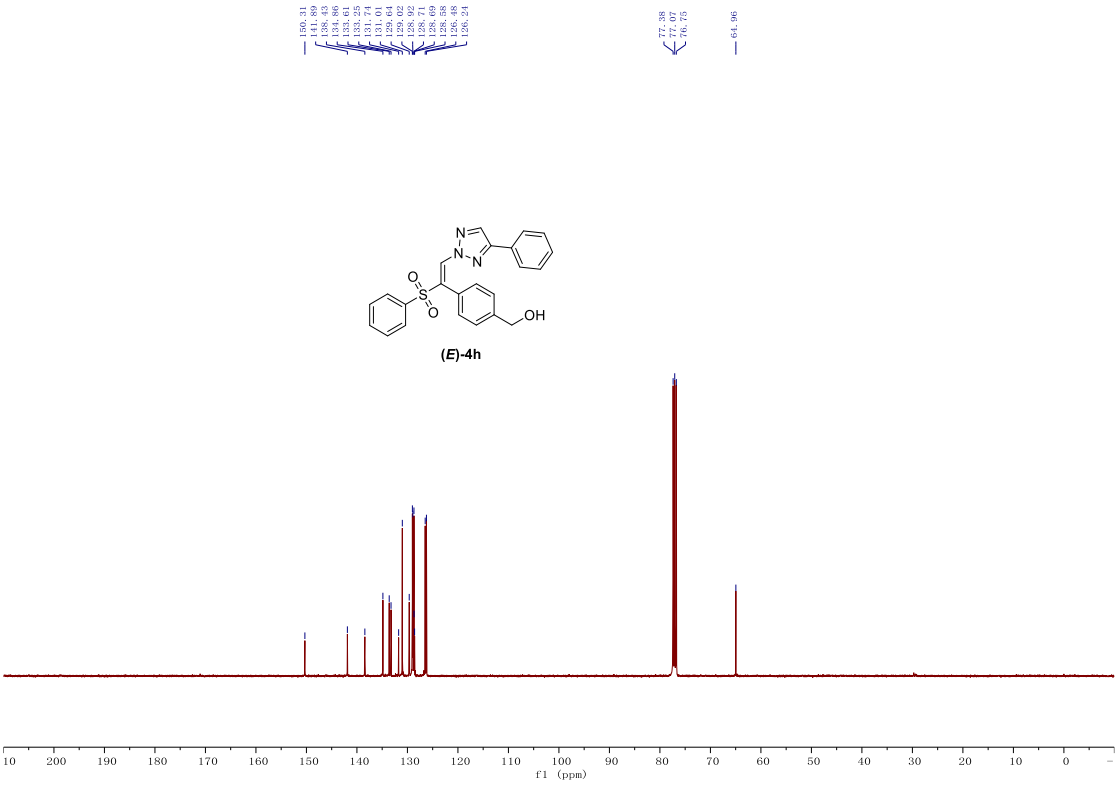
^{13}C NMR (101 MHz) Spectrum of (*E*)-4g in $CDCl_3$



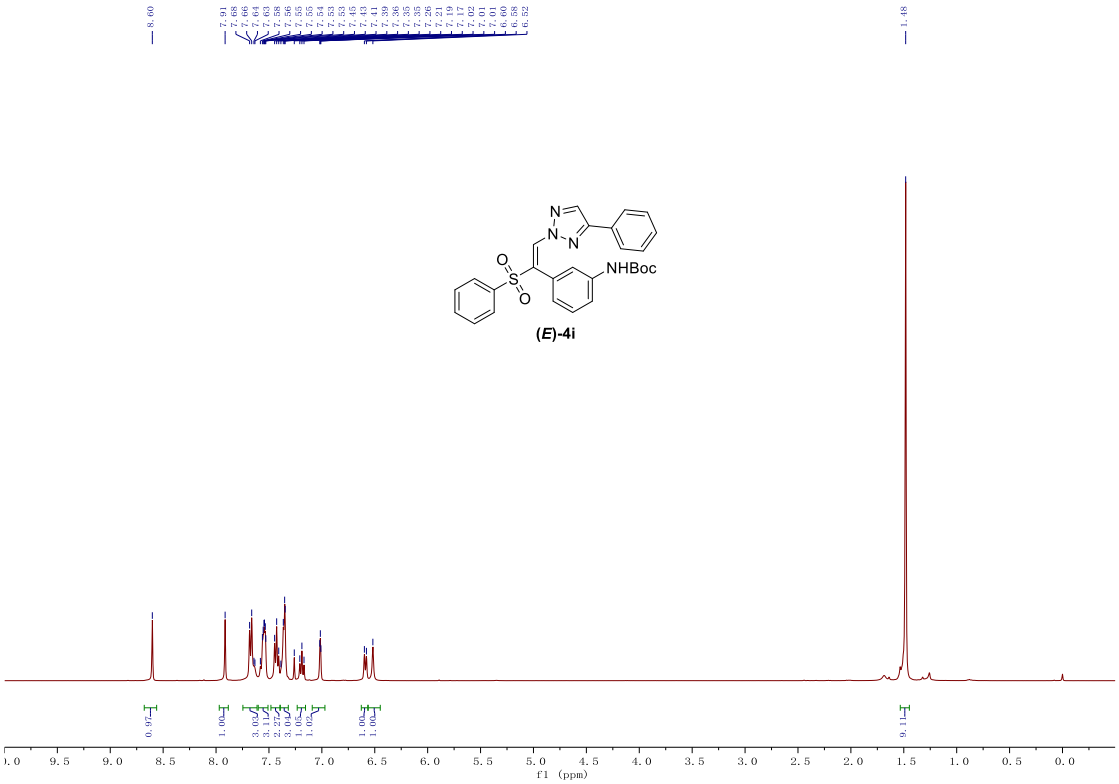
^{1}H NMR (400 MHz) Spectrum of (*E*)-4h in $CDCl_3$



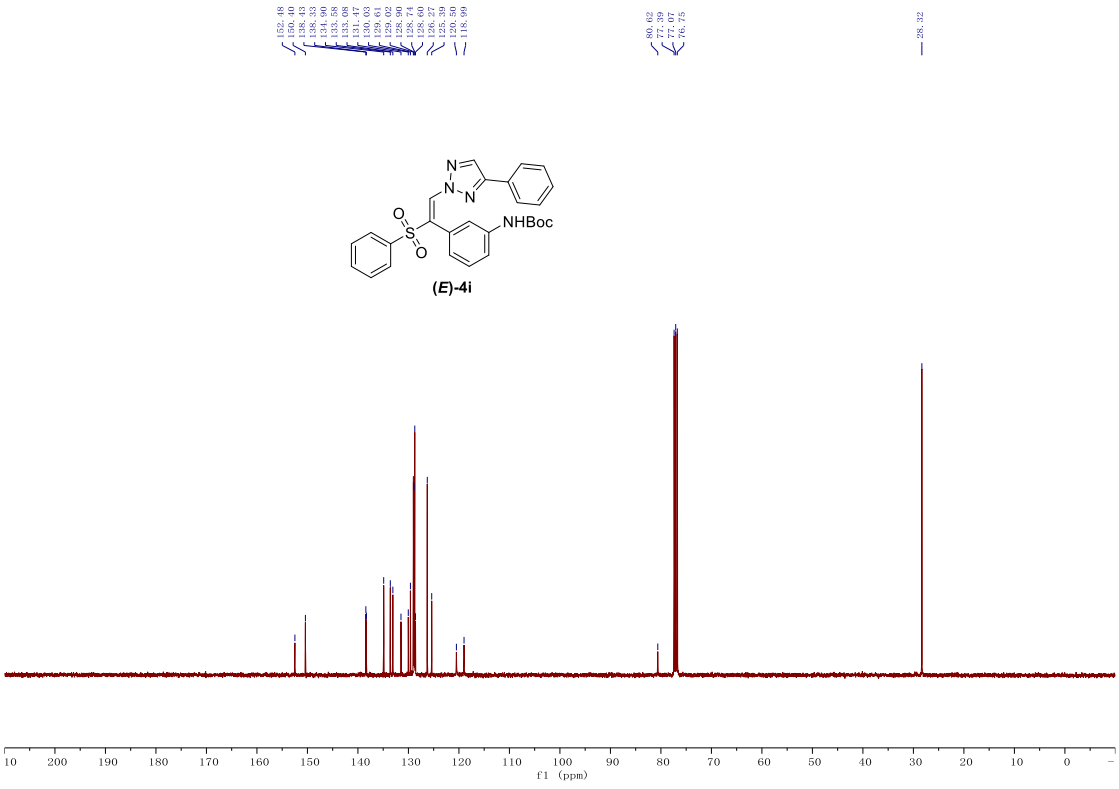
^{13}C NMR (101 MHz) Spectrum of (*E*)-4h in $CDCl_3$



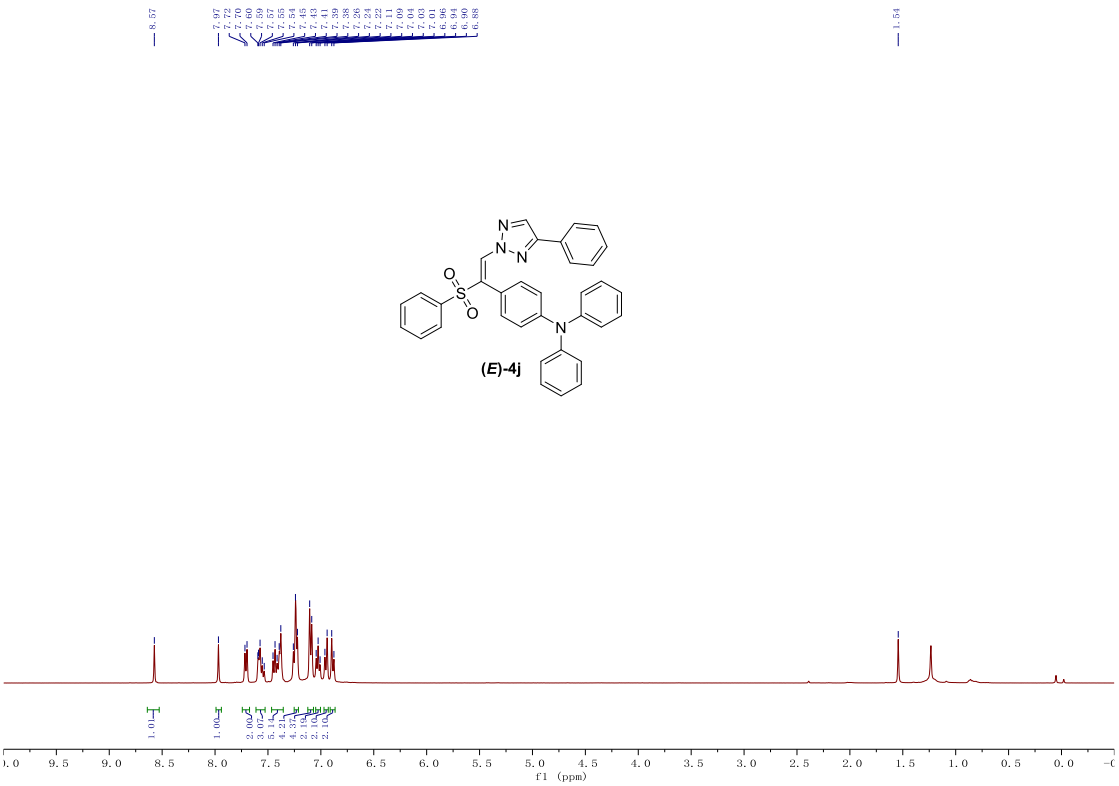
^{1}H NMR (400 MHz) Spectrum of (*E*)-4i in $CDCl_3$



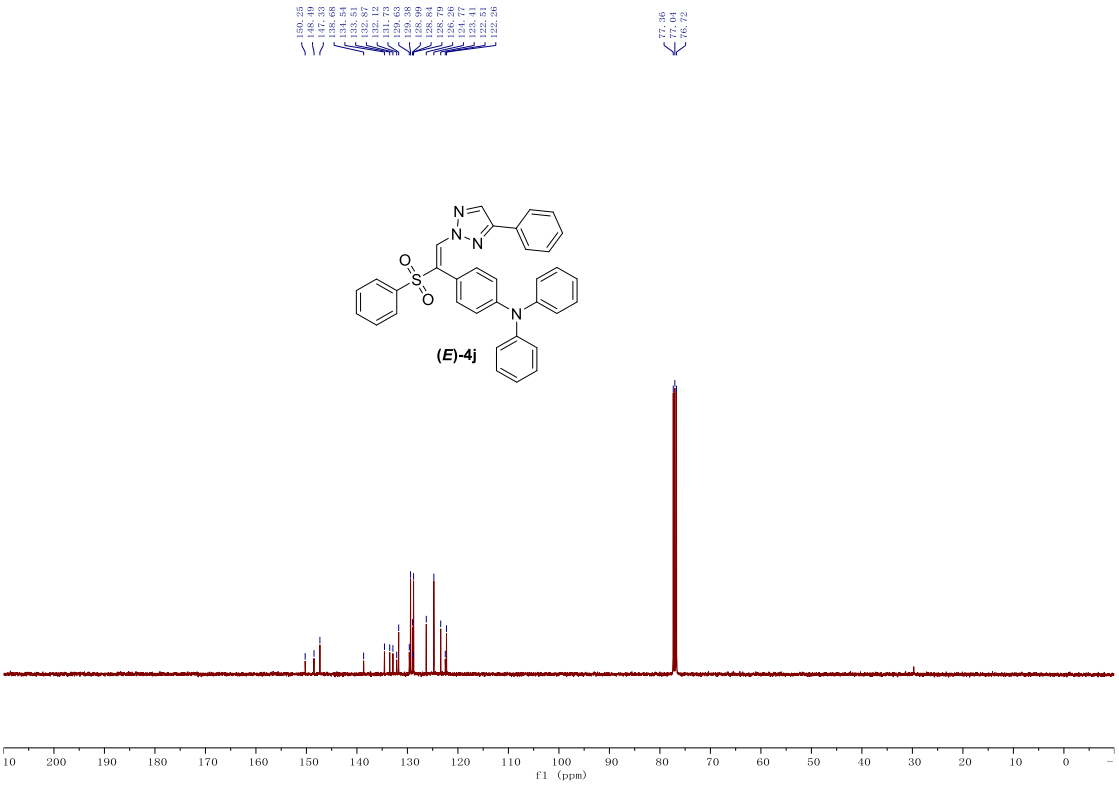
^{13}C NMR (101 MHz) Spectrum of (*E*)-4i in $CDCl_3$



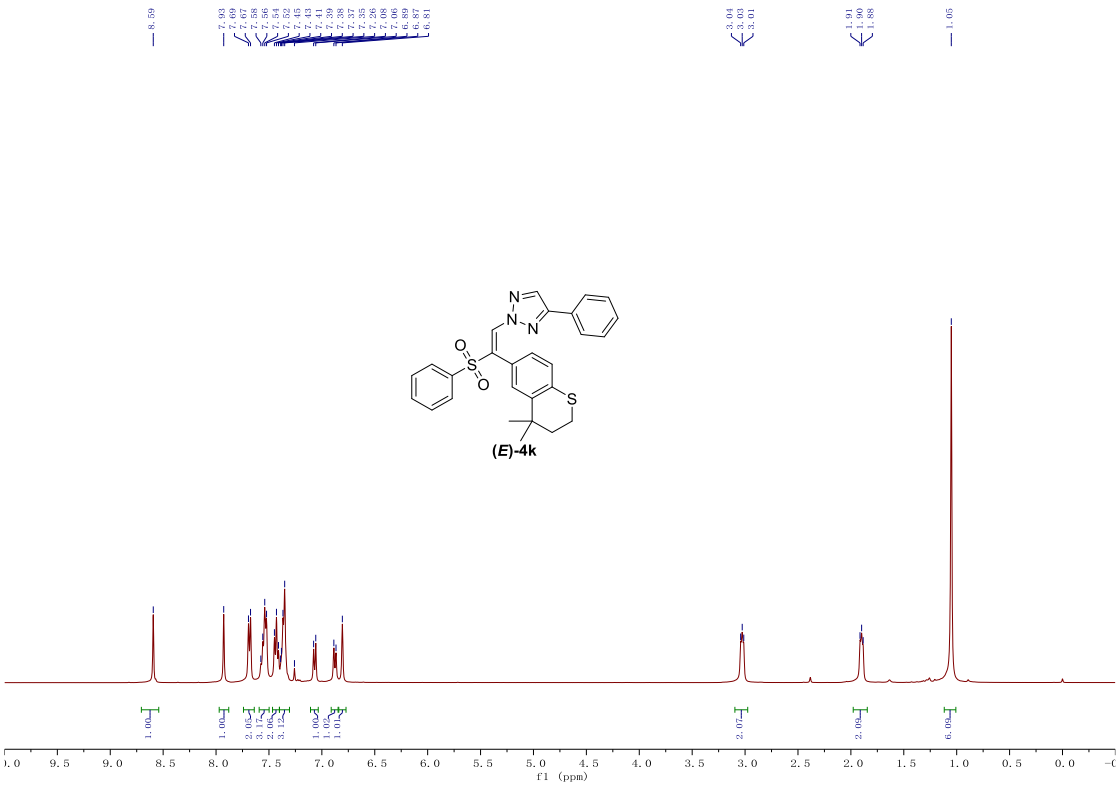
^{1}H NMR (400 MHz) Spectrum of (*E*)-4j in $CDCl_3$



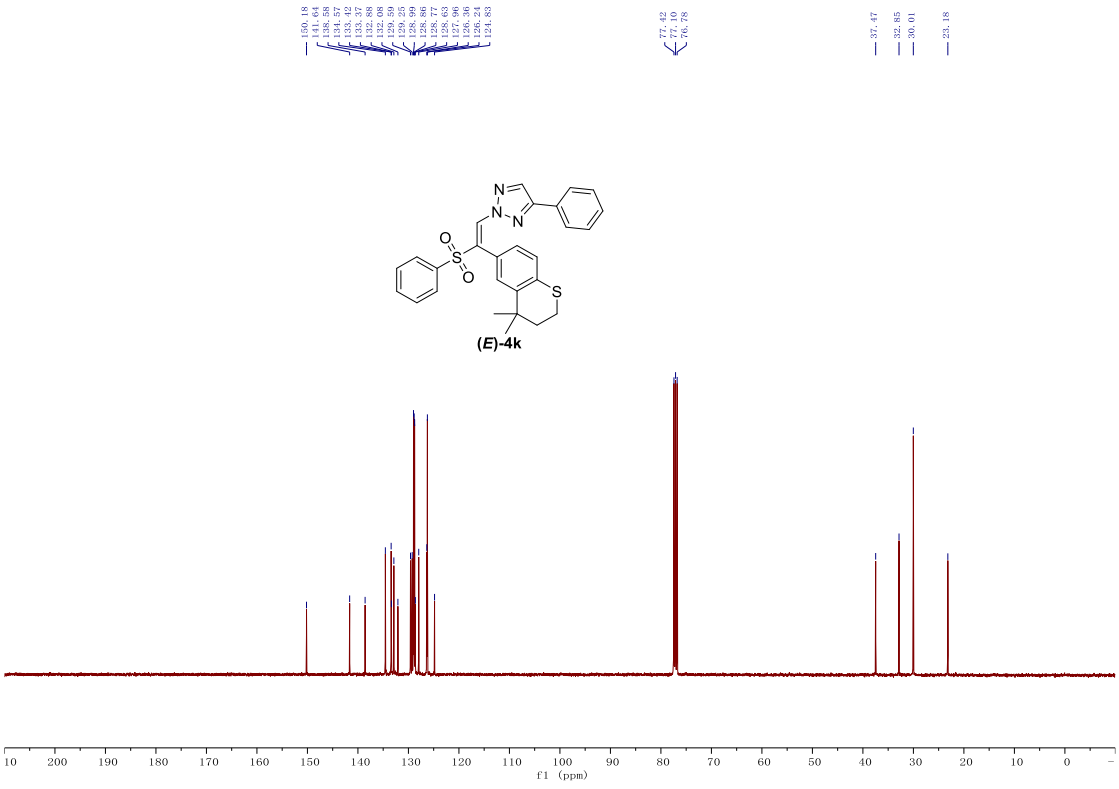
^{13}C NMR (101 MHz) Spectrum of (*E*)-4j in $CDCl_3$



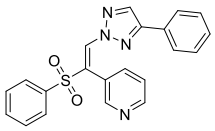
^{1}H NMR (400 MHz) Spectrum of (*E*)-4k in $CDCl_3$



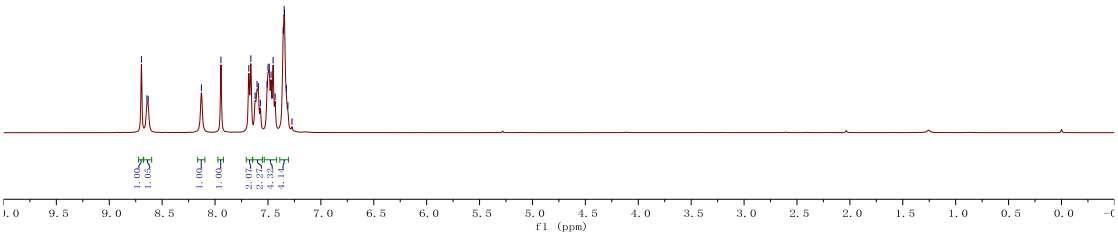
^{13}C NMR (101 MHz) Spectrum of (*E*)-4k in $CDCl_3$



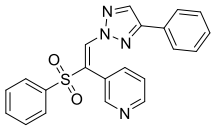
^{1}H NMR (400 MHz) Spectrum of (*E*)-4l in $CDCl_3$



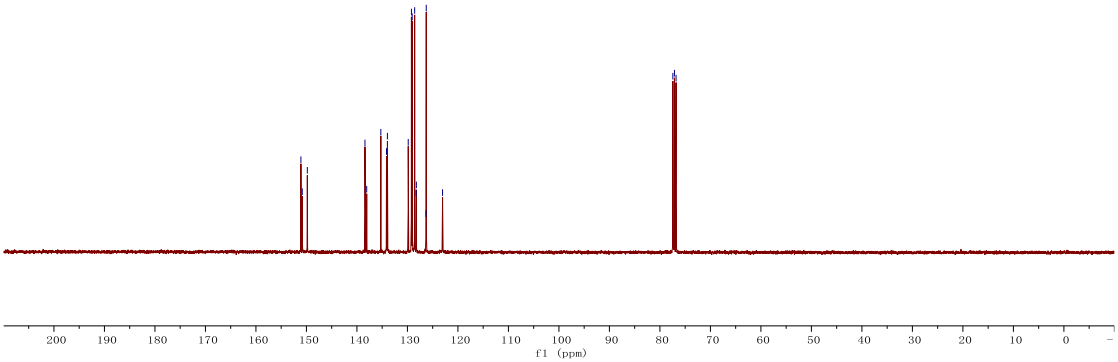
(*E*)-4l



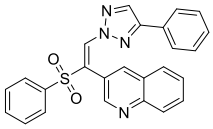
^{13}C NMR (101 MHz) Spectrum of (*E*)-4l in $CDCl_3$



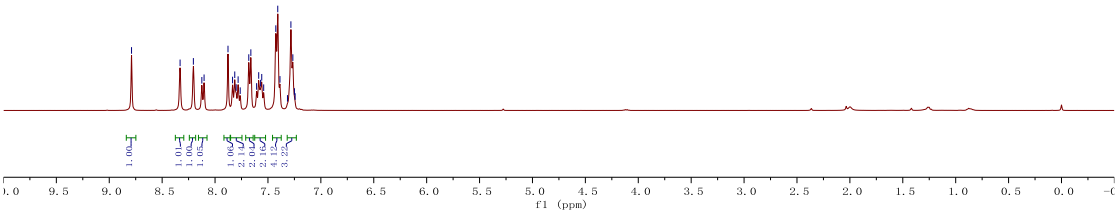
(*E*)-4l



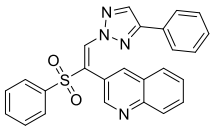
^{1}H NMR (400 MHz) Spectrum of (*E*)-4m in $CDCl_3$



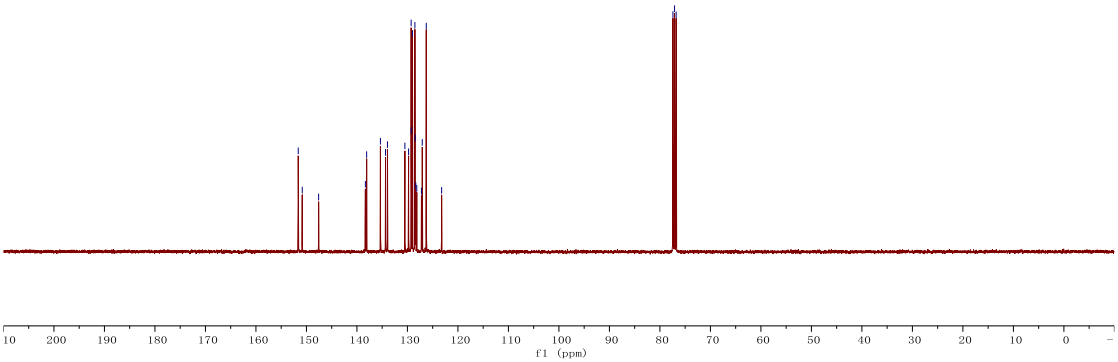
(*E*)-4m



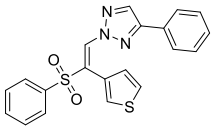
^{13}C NMR (101 MHz) Spectrum of (*E*)-4m in $CDCl_3$



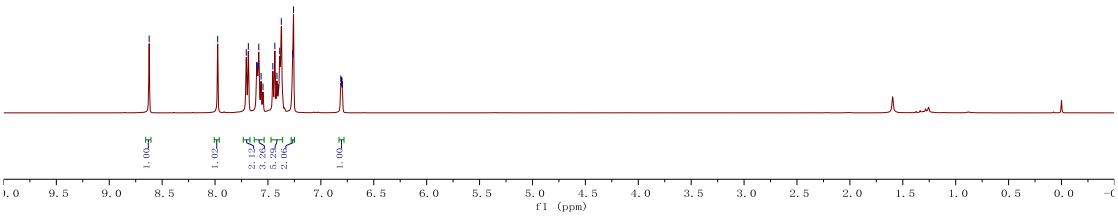
(*E*)-4m



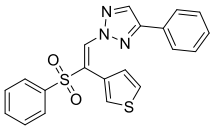
^{1}H NMR (400 MHz) Spectrum of (*E*)-4n in $CDCl_3$



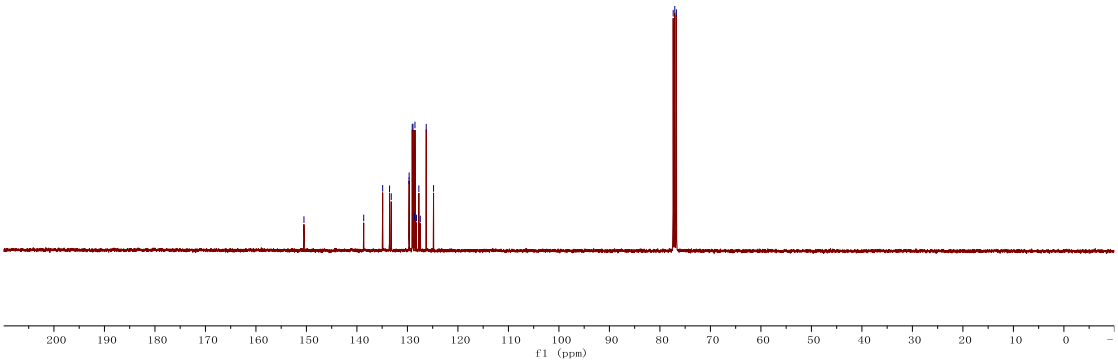
(*E*)-4n



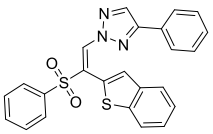
^{13}C NMR (101 MHz) Spectrum of (*E*)-4n in $CDCl_3$



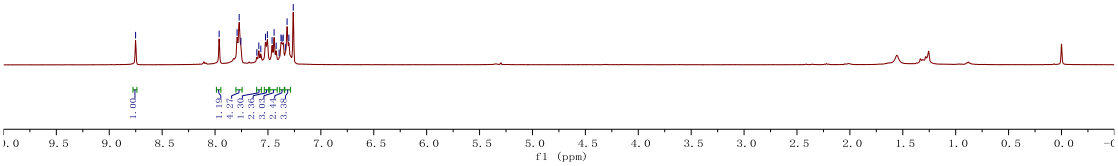
(*E*)-4n



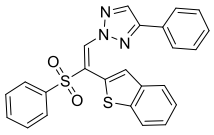
^{1}H NMR (400 MHz) Spectrum of (*E*)-4o in $CDCl_3$



(*E*)-4o

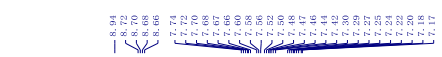


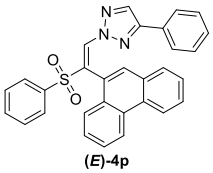
^{13}C NMR (101 MHz) Spectrum of (*E*)-4o in $CDCl_3$

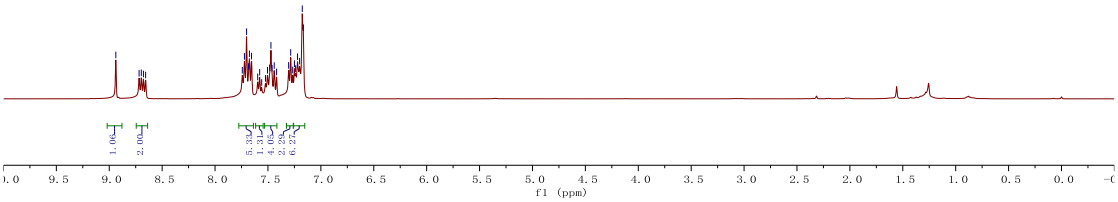


(*E*)-4o

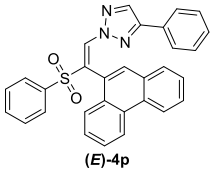
^{1}H NMR (400 MHz) Spectrum of (*E*)-4p in $CDCl_3$

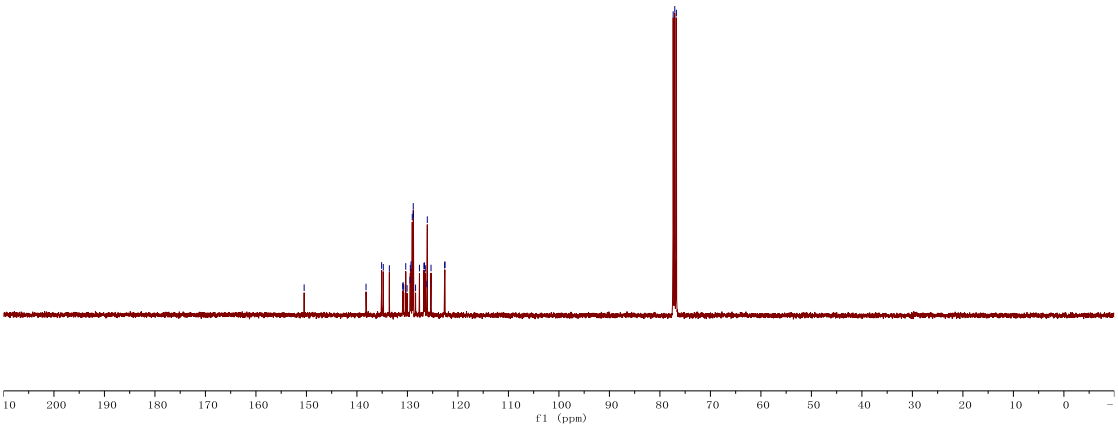




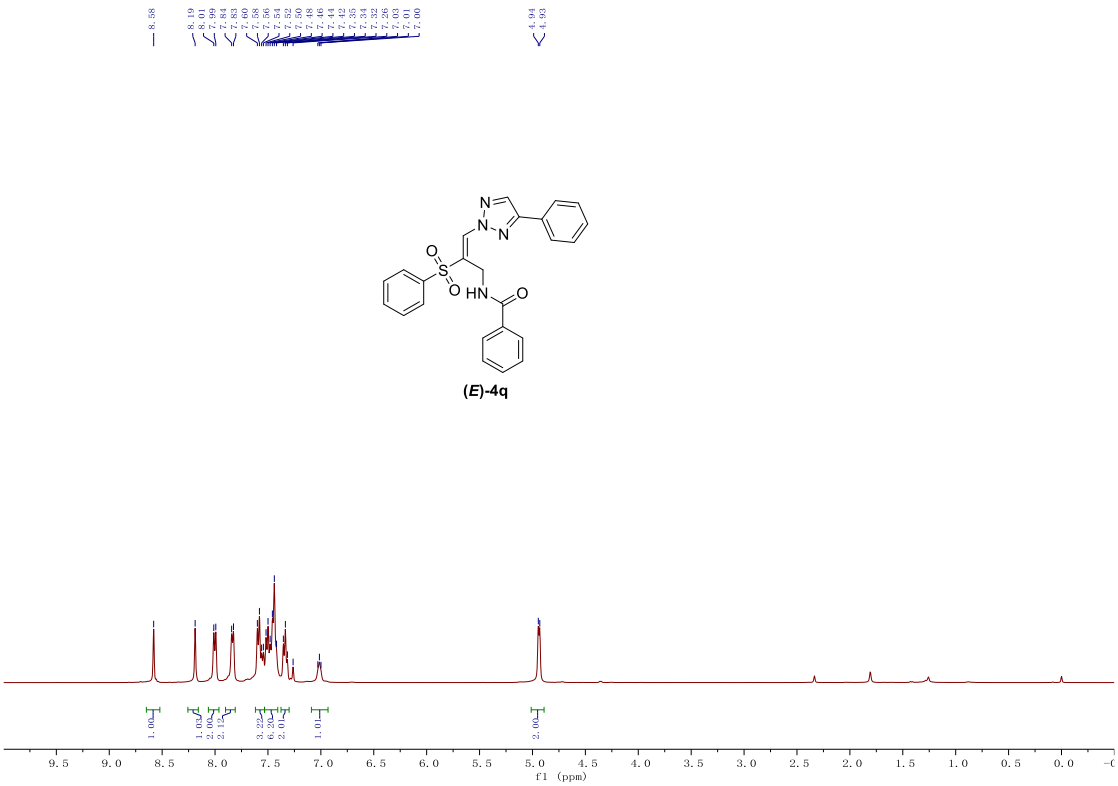


^{13}C NMR (101 MHz) Spectrum of (*E*)-4p in $CDCl_3$

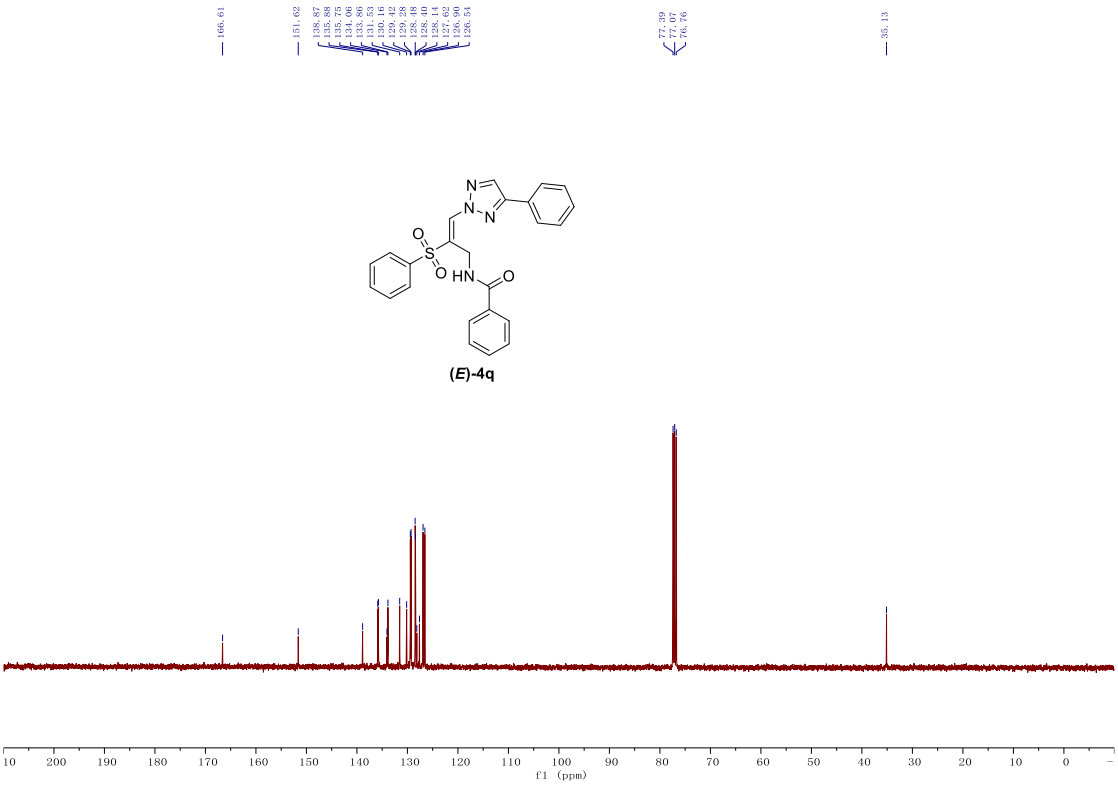




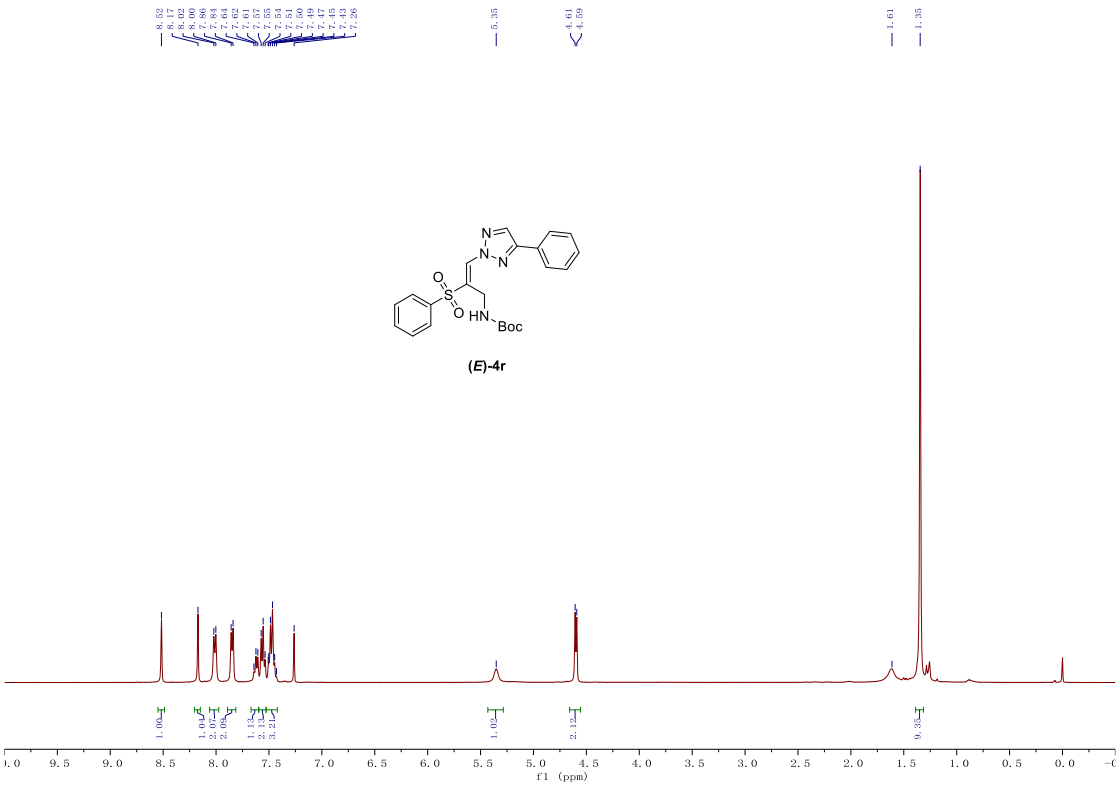
^{1}H NMR (400 MHz) Spectrum of (*E*)-4q in $CDCl_3$



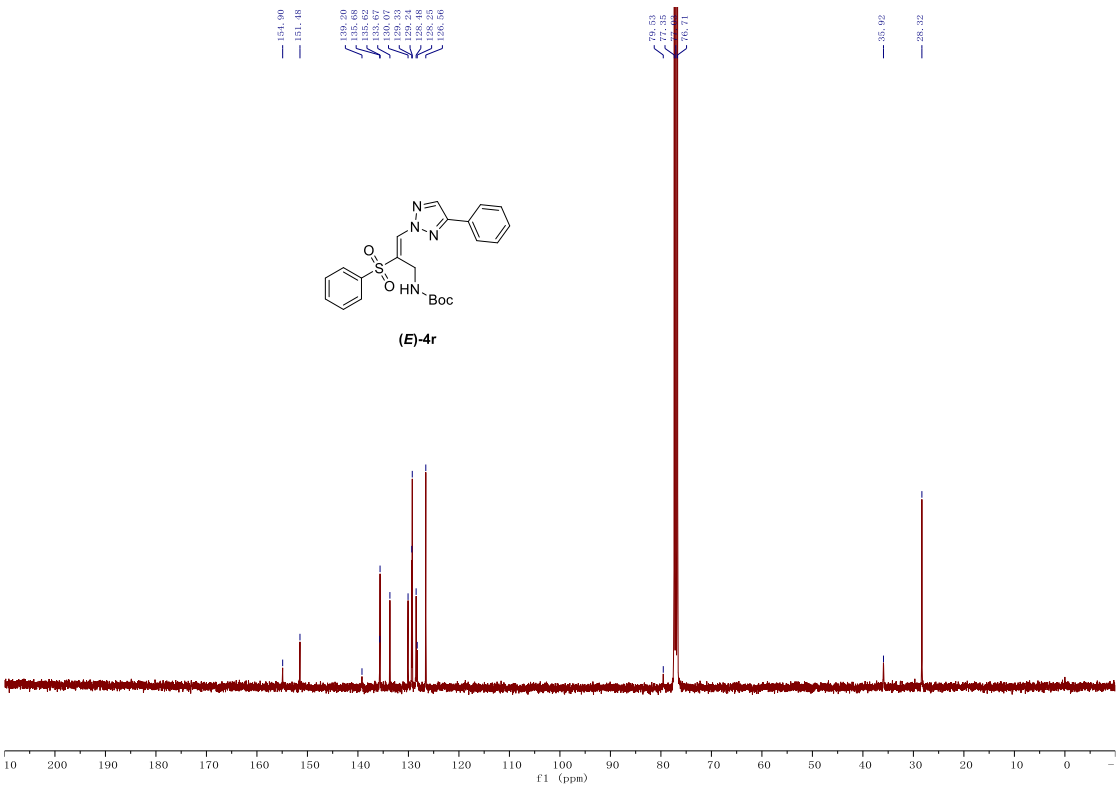
^{13}C NMR (101 MHz) Spectrum of (*E*)-4q in $CDCl_3$



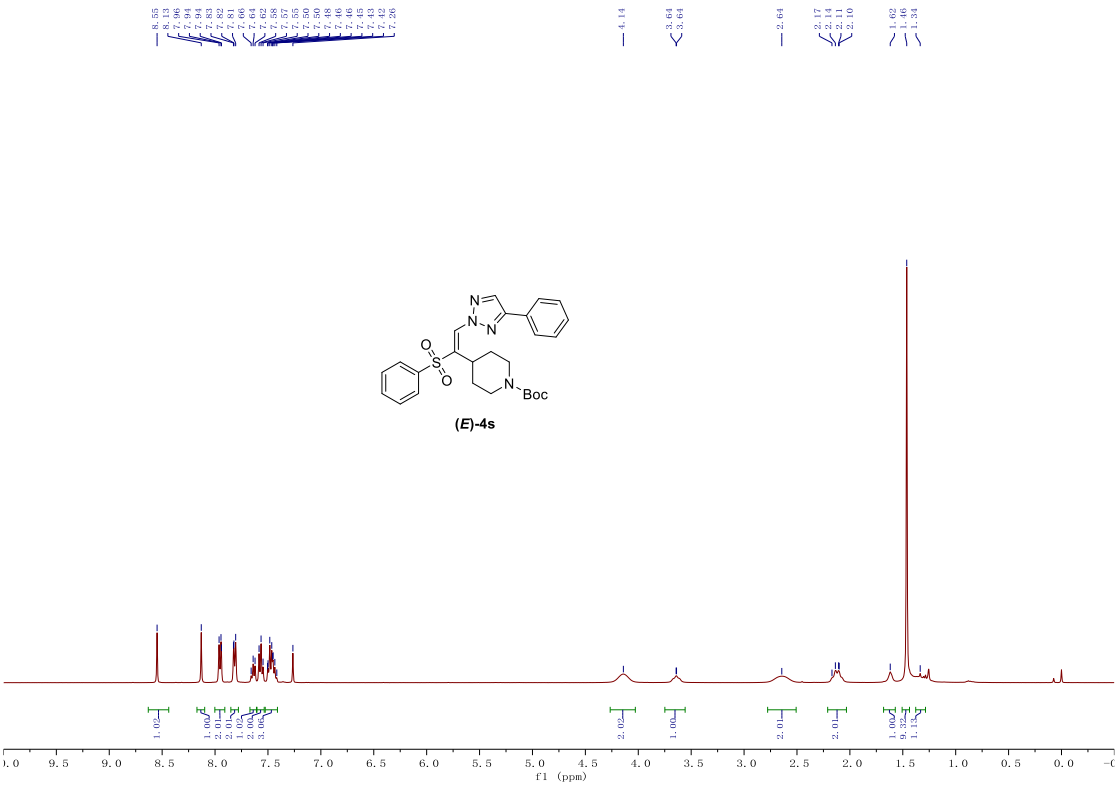
^{1}H NMR (400 MHz) Spectrum of (*E*)-4r in $CDCl_3$



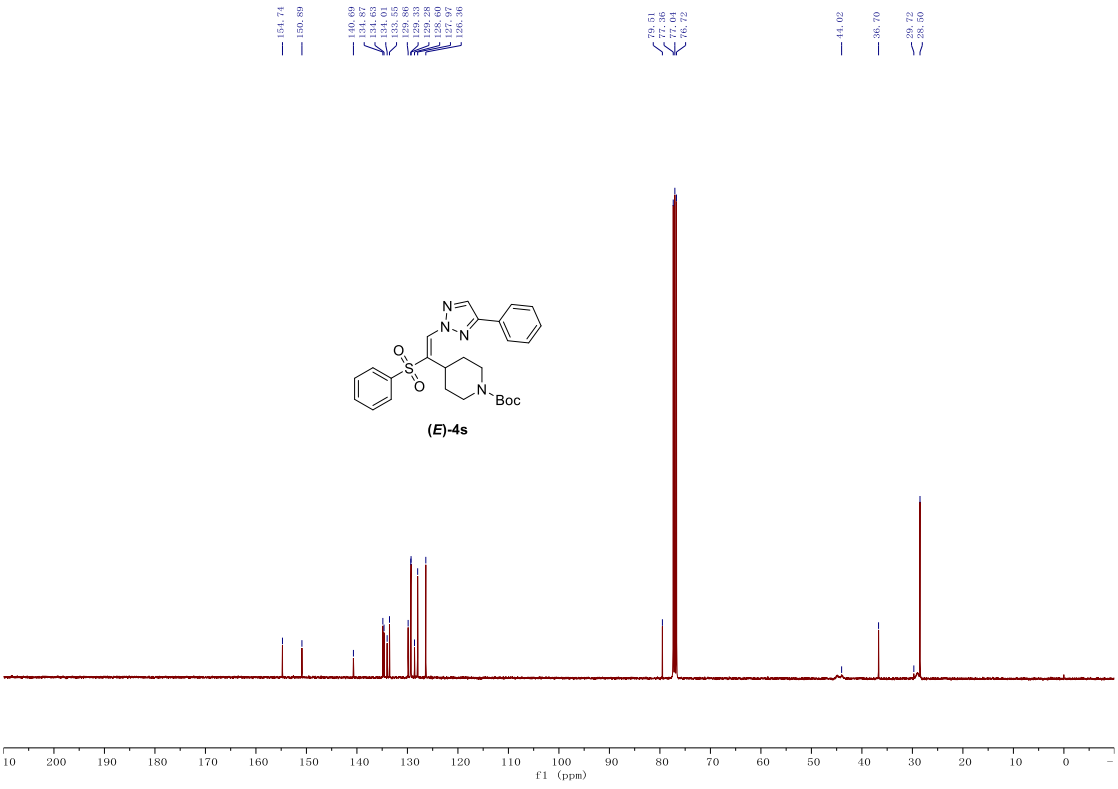
^{13}C NMR (101 MHz) Spectrum of (*E*)-4r in $CDCl_3$



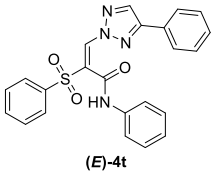
^{1}H NMR (400 MHz) Spectrum of (*E*)-4s in $CDCl_3$



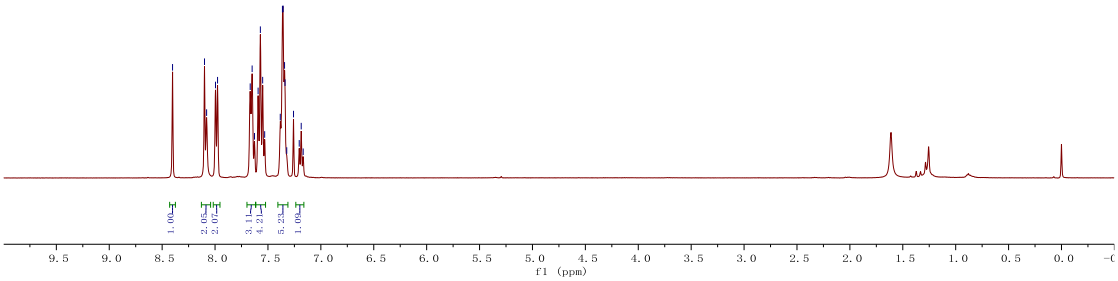
^{13}C NMR (101 MHz) Spectrum of (*E*)-4s in $CDCl_3$



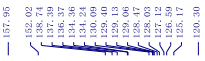
^{1}H NMR (400 MHz) Spectrum of (*E*)-4t in $CDCl_3$

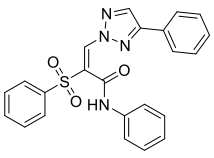


(*E*)-4t

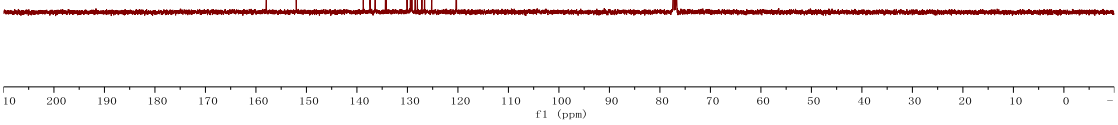


^{13}C NMR (101 MHz) Spectrum of (*E*)-4t in $CDCl_3$

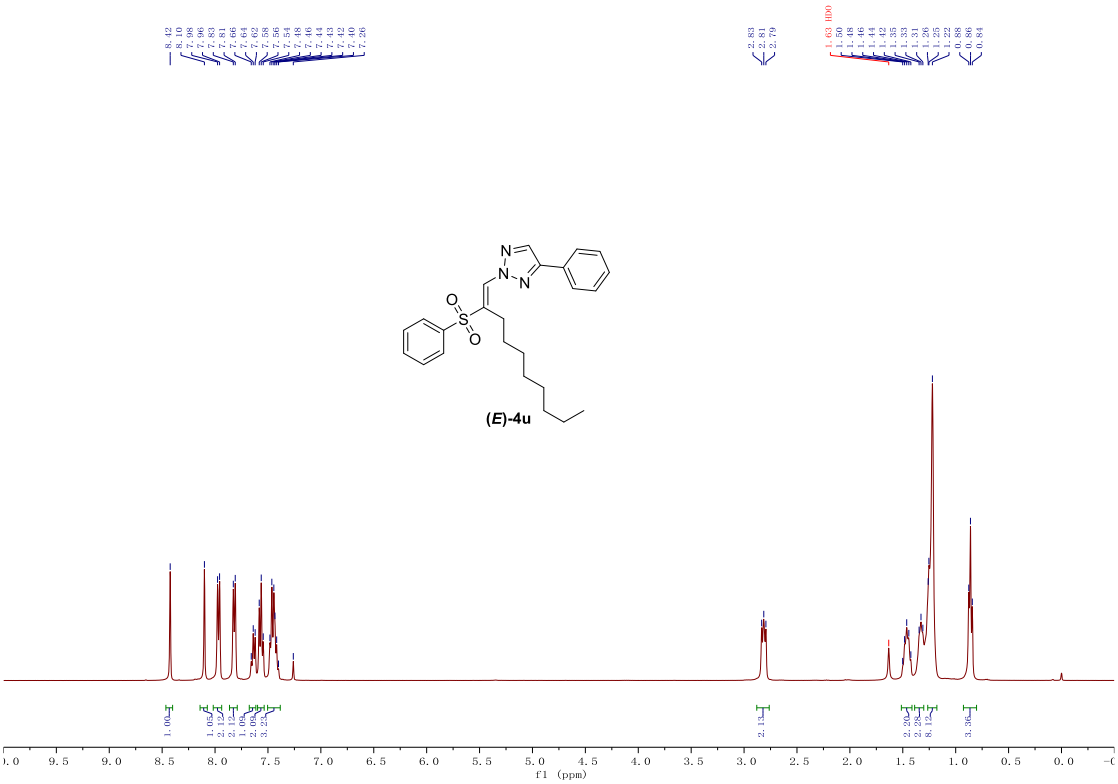




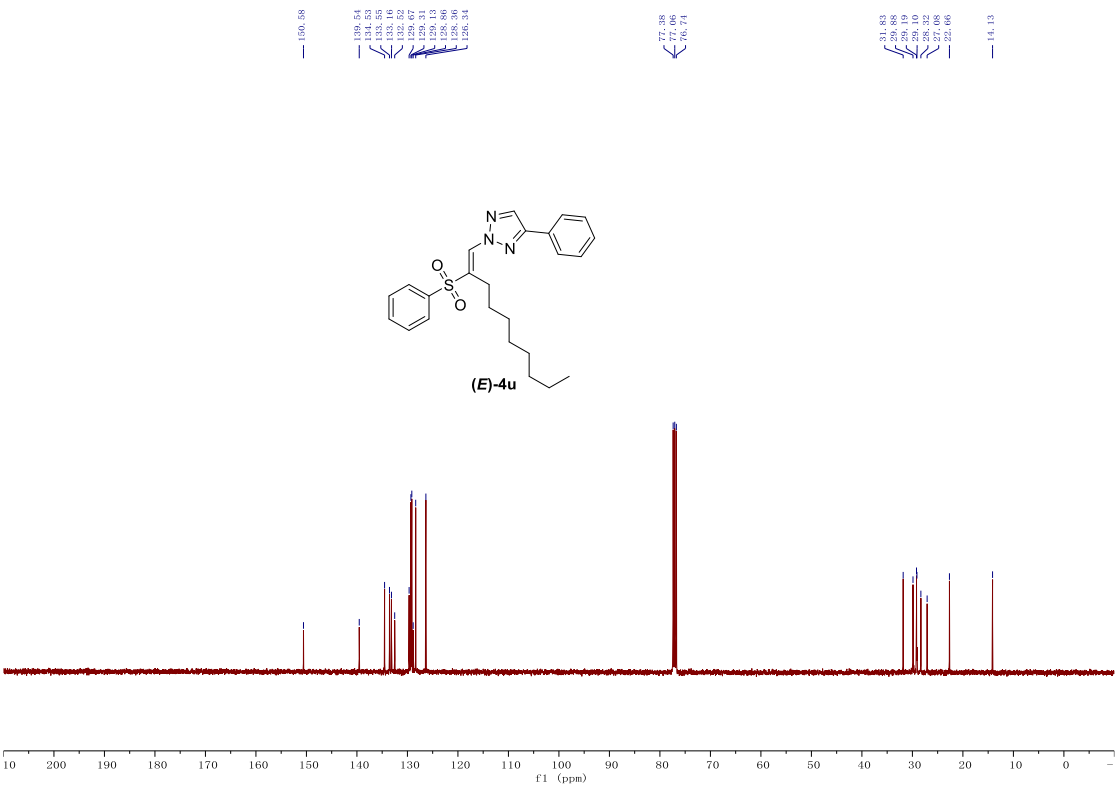
(*E*)-4t



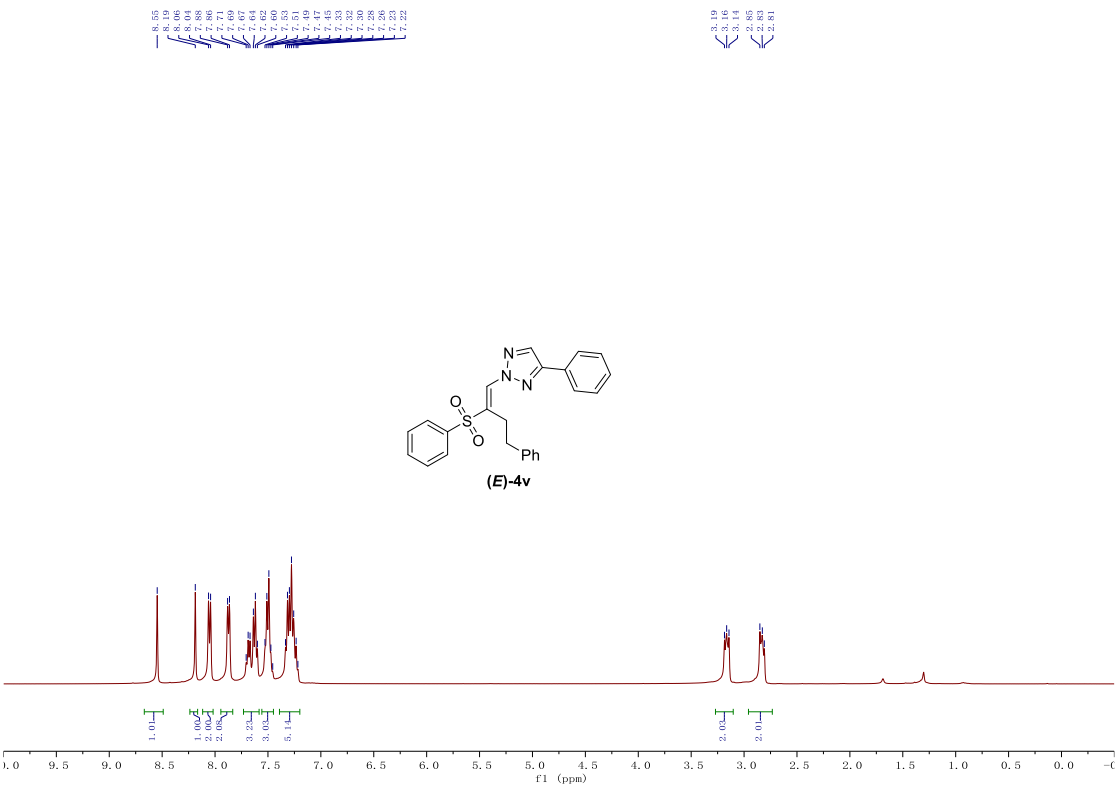
^{1}H NMR (400 MHz) Spectrum of (*E*)-4u in $CDCl_3$



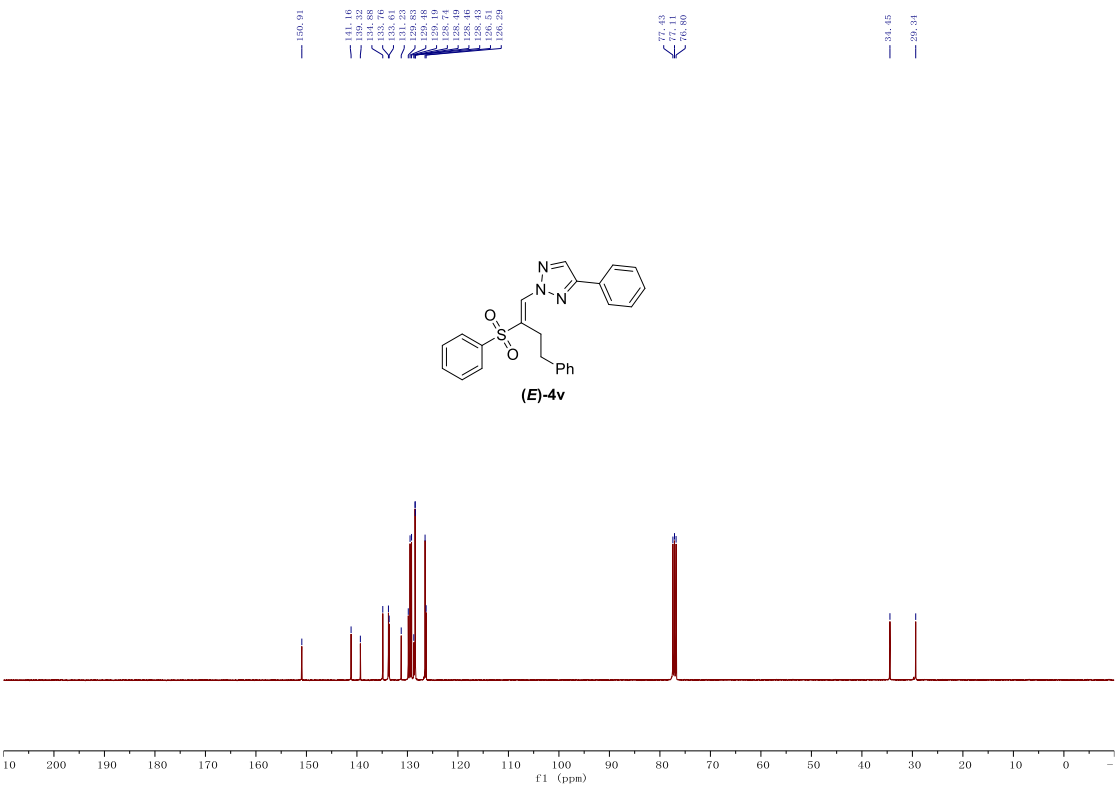
^{13}C NMR (101 MHz) Spectrum of (*E*)-4u in $CDCl_3$



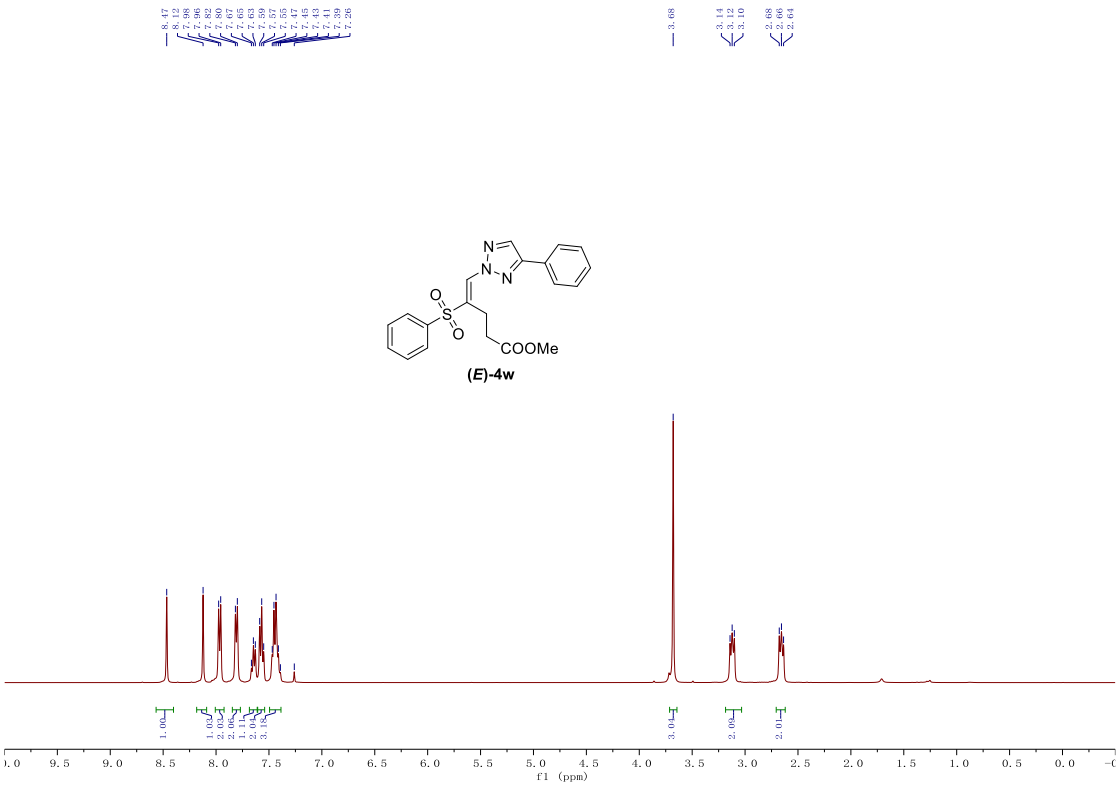
^{1}H NMR (400 MHz) Spectrum of (*E*)-4v in $CDCl_3$



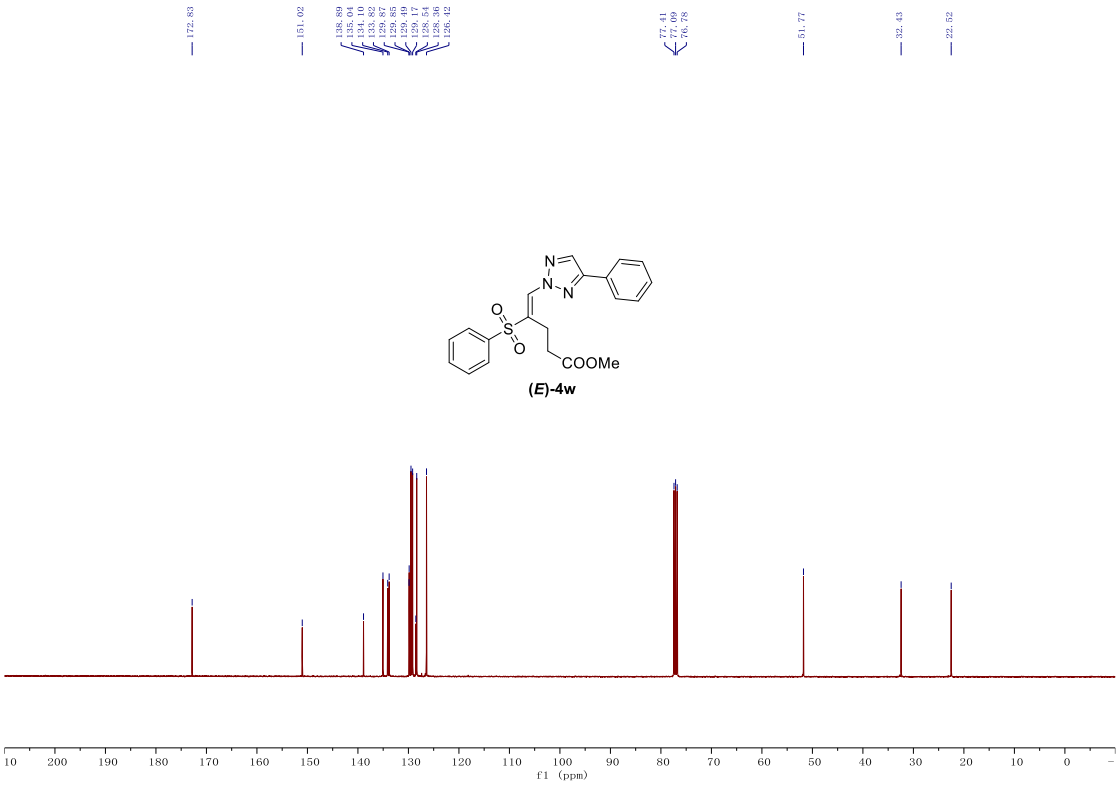
^{13}C NMR (101 MHz) Spectrum of (*E*)-4v in $CDCl_3$



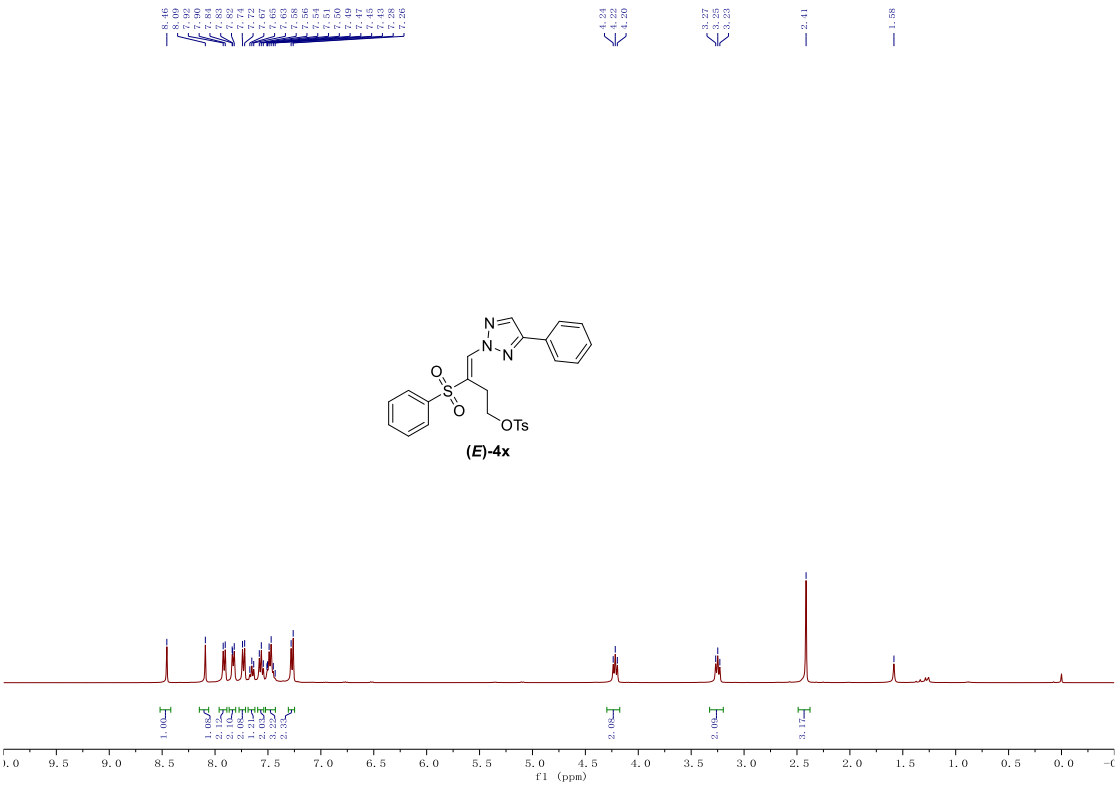
^{1}H NMR (400 MHz) Spectrum of (*E*)-4w in $CDCl_3$



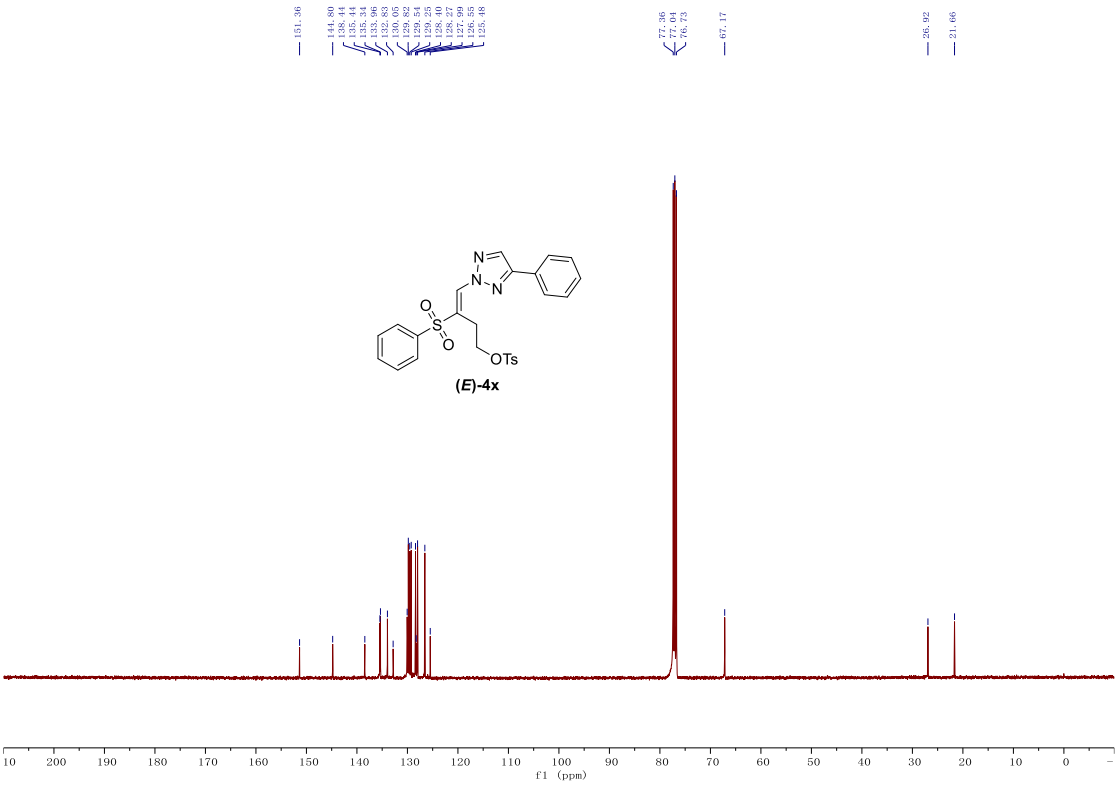
^{13}C NMR (101 MHz) Spectrum of (*E*)-4w in $CDCl_3$



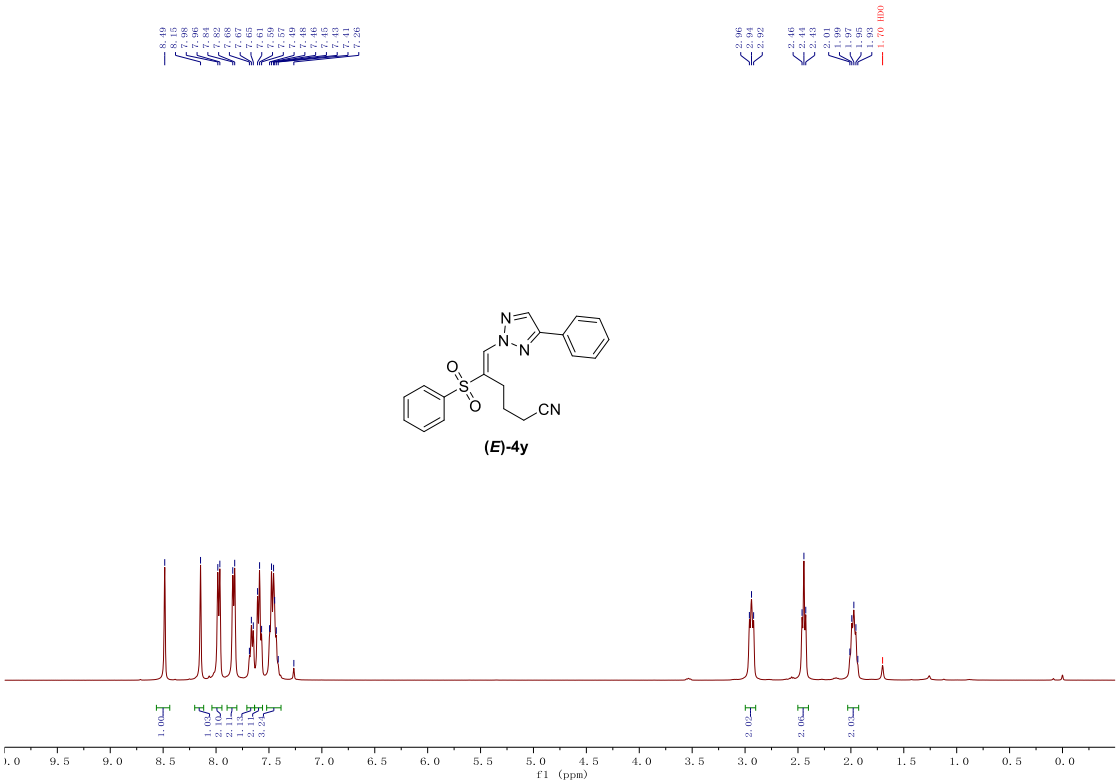
^{1}H NMR (400 MHz) Spectrum of (*E*)-4x in $CDCl_3$



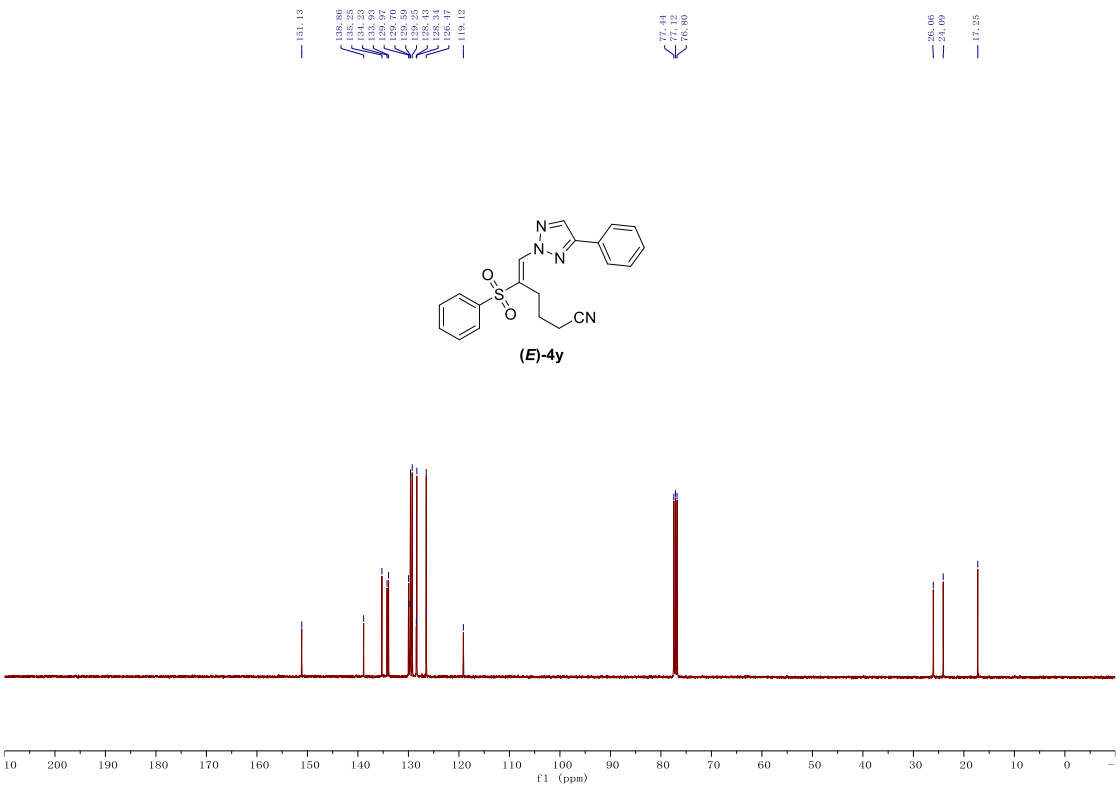
^{13}C NMR (101 MHz) Spectrum of (*E*)-4x in $CDCl_3$



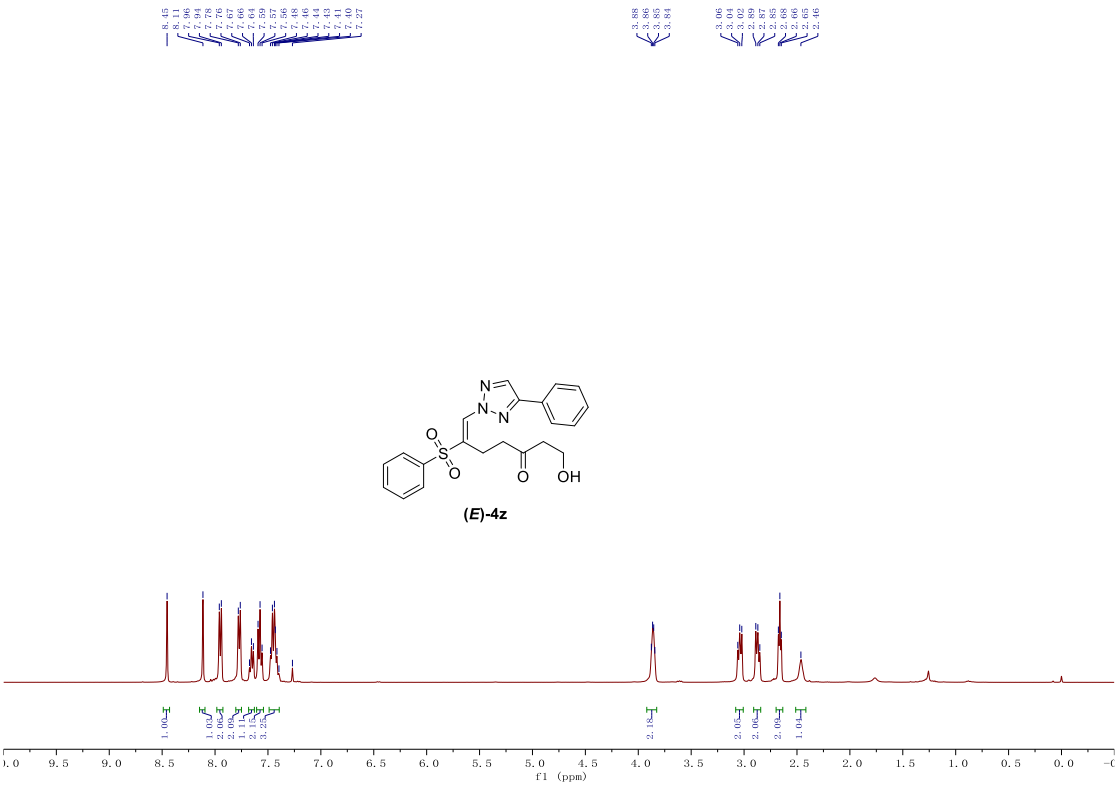
^{1}H NMR (400 MHz) Spectrum of (*E*)-4y in $CDCl_3$



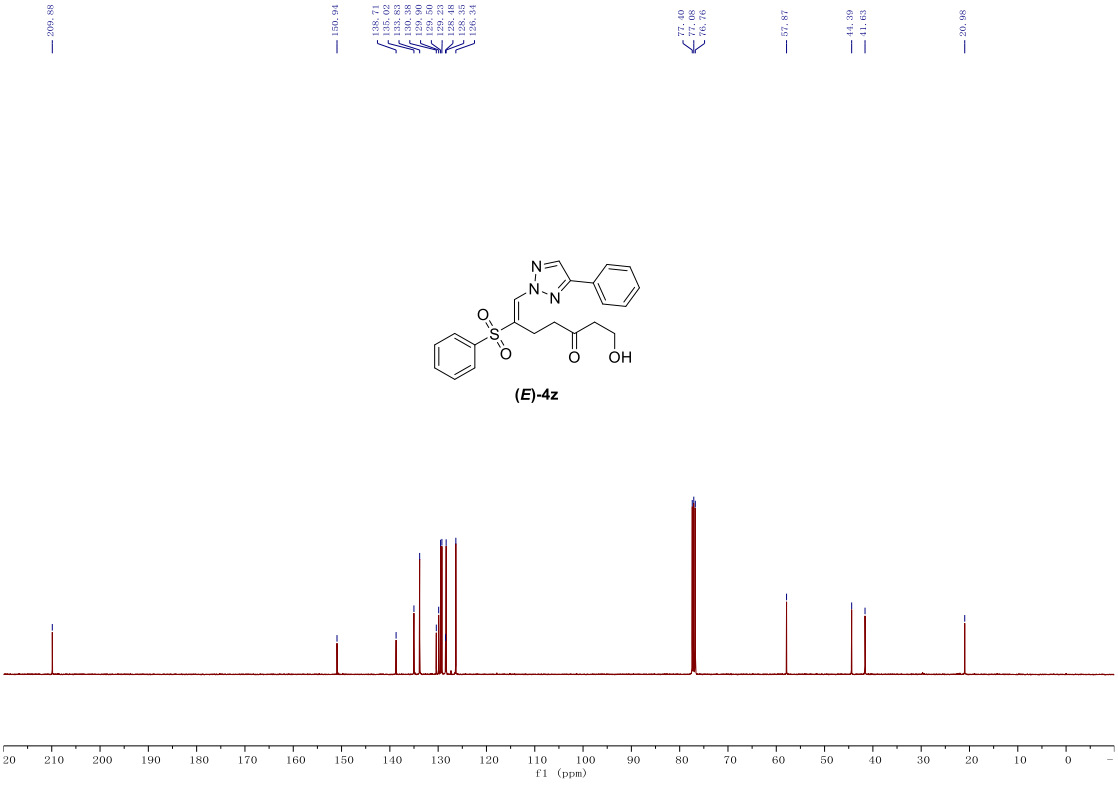
^{13}C NMR (101 MHz) Spectrum of (*E*)-4y in $CDCl_3$



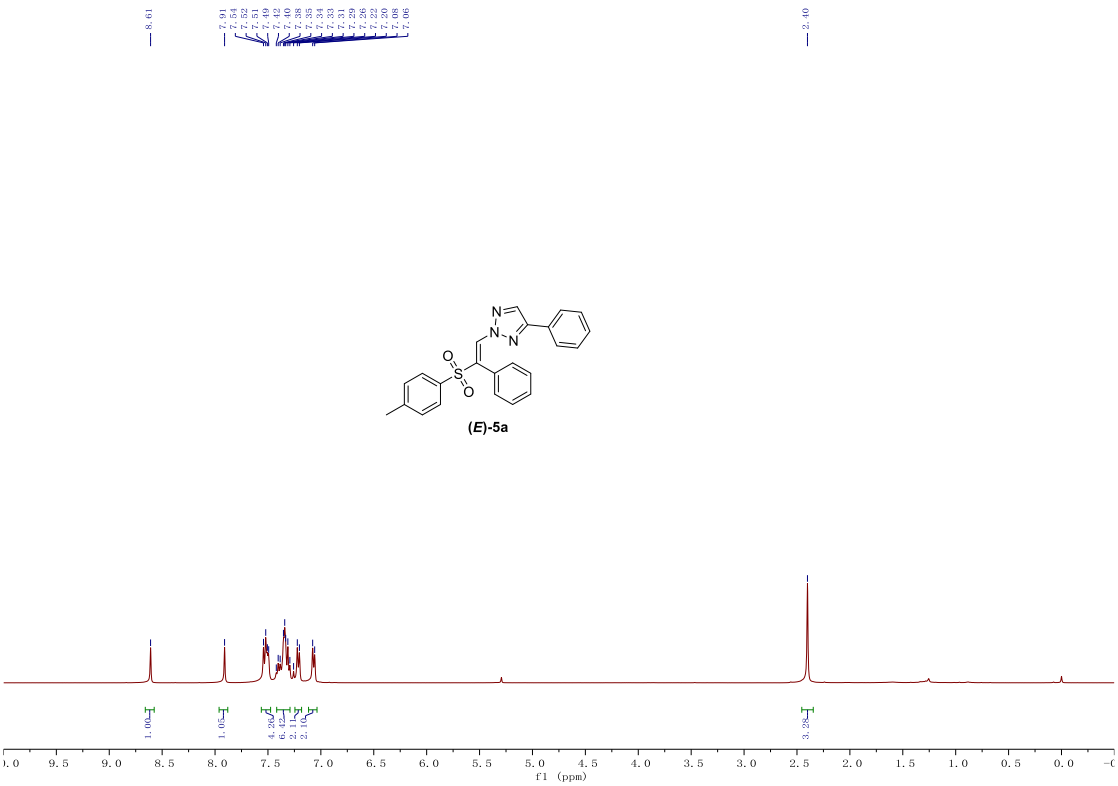
^{1}H NMR (400 MHz) Spectrum of (*E*)-4z in $CDCl_3$



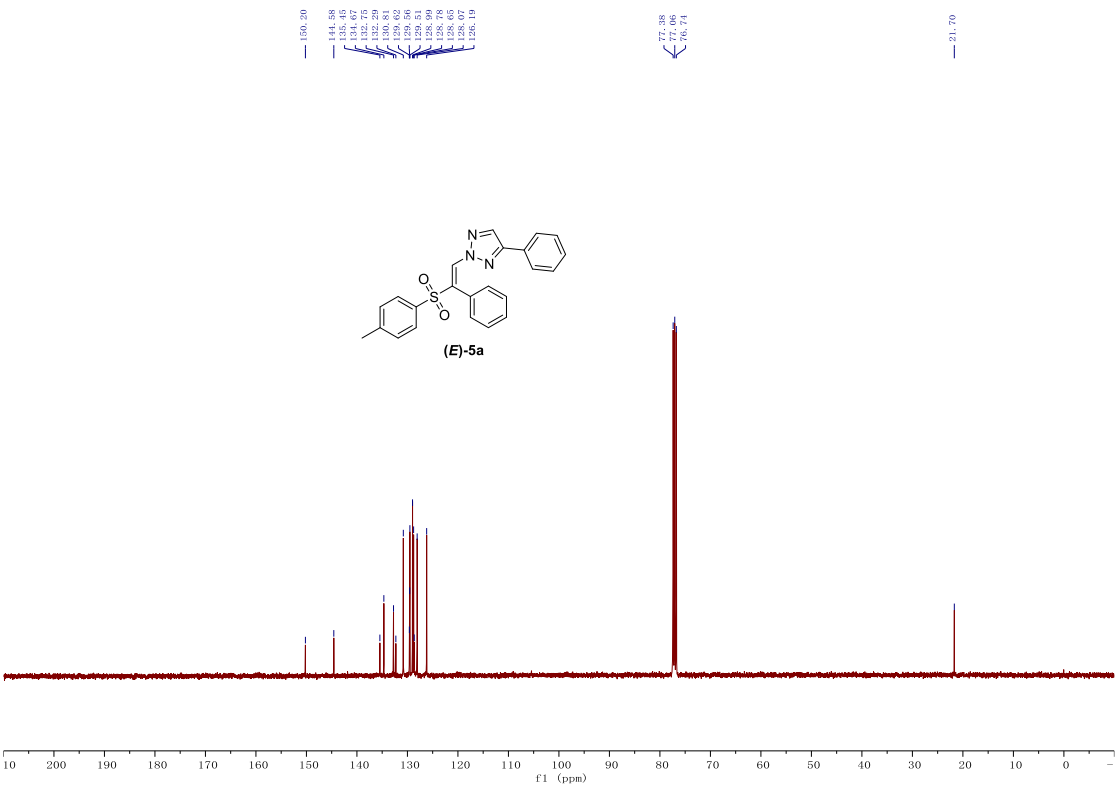
^{13}C NMR (101 MHz) Spectrum of (*E*)-4z in $CDCl_3$



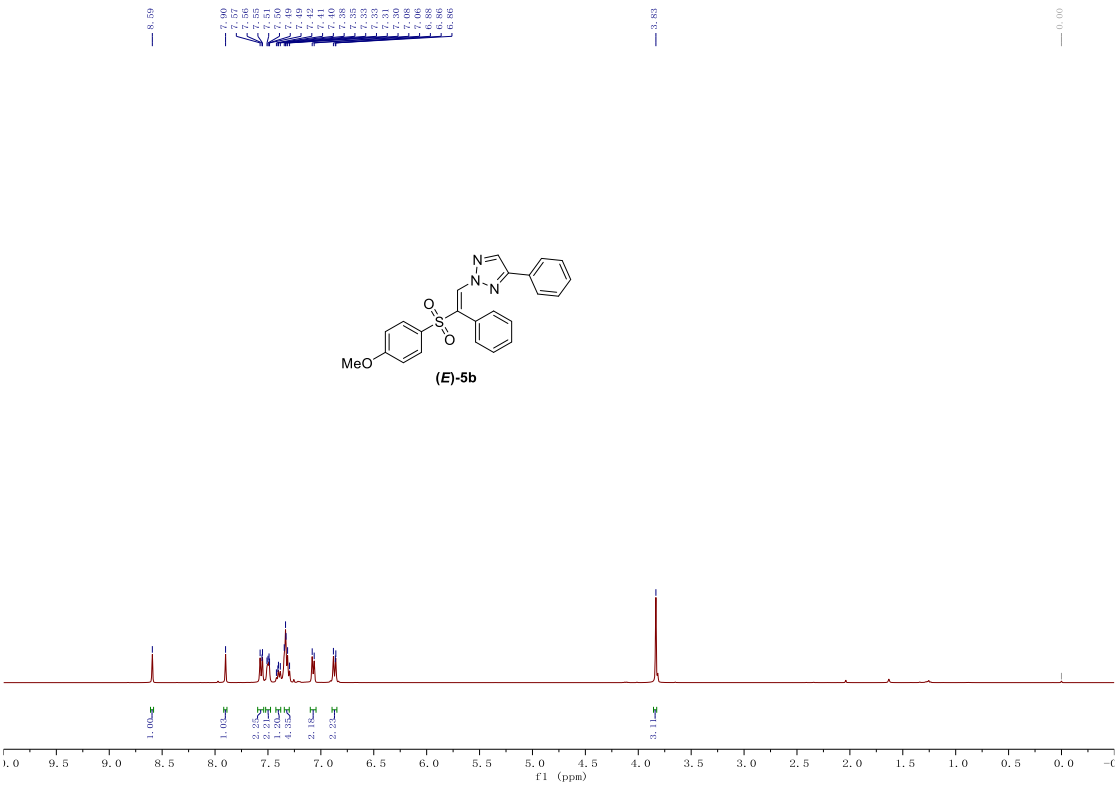
^{1}H NMR (400 MHz) Spectrum of (*E*)-5a in $CDCl_3$



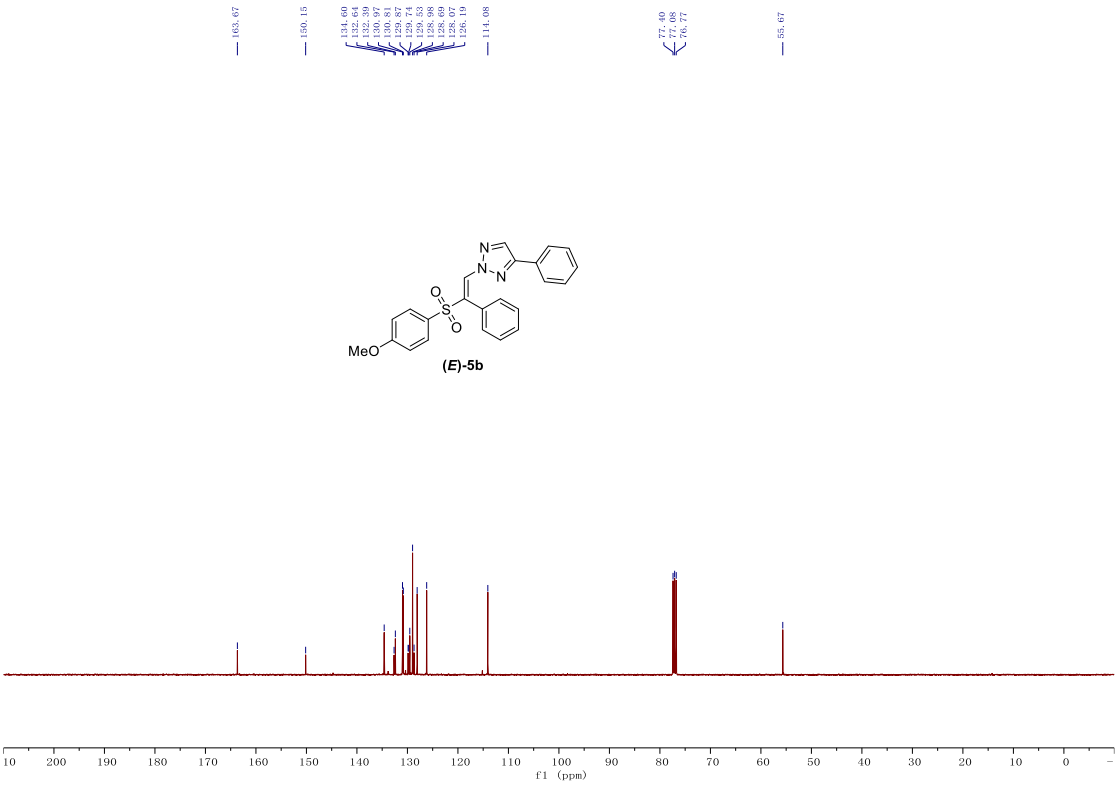
^{13}C NMR (101 MHz) Spectrum of (*E*)-5a in $CDCl_3$



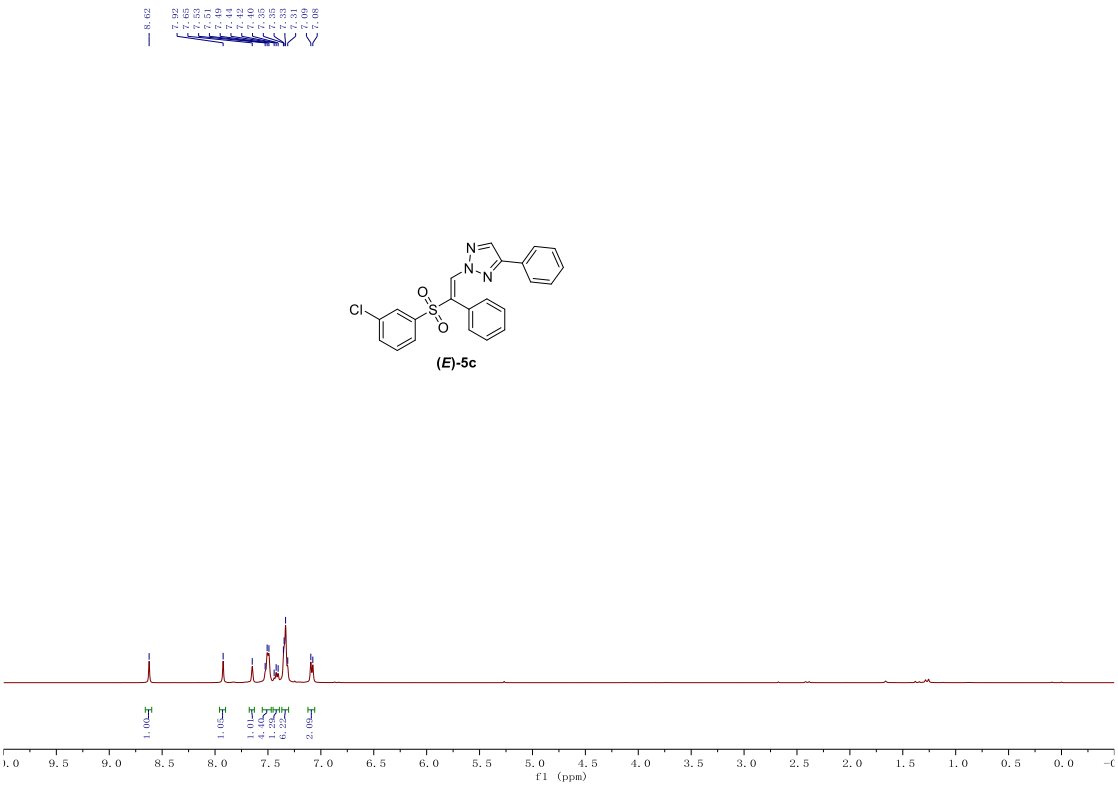
^{1}H NMR (400 MHz) Spectrum of (*E*)-5b in $CDCl_3$



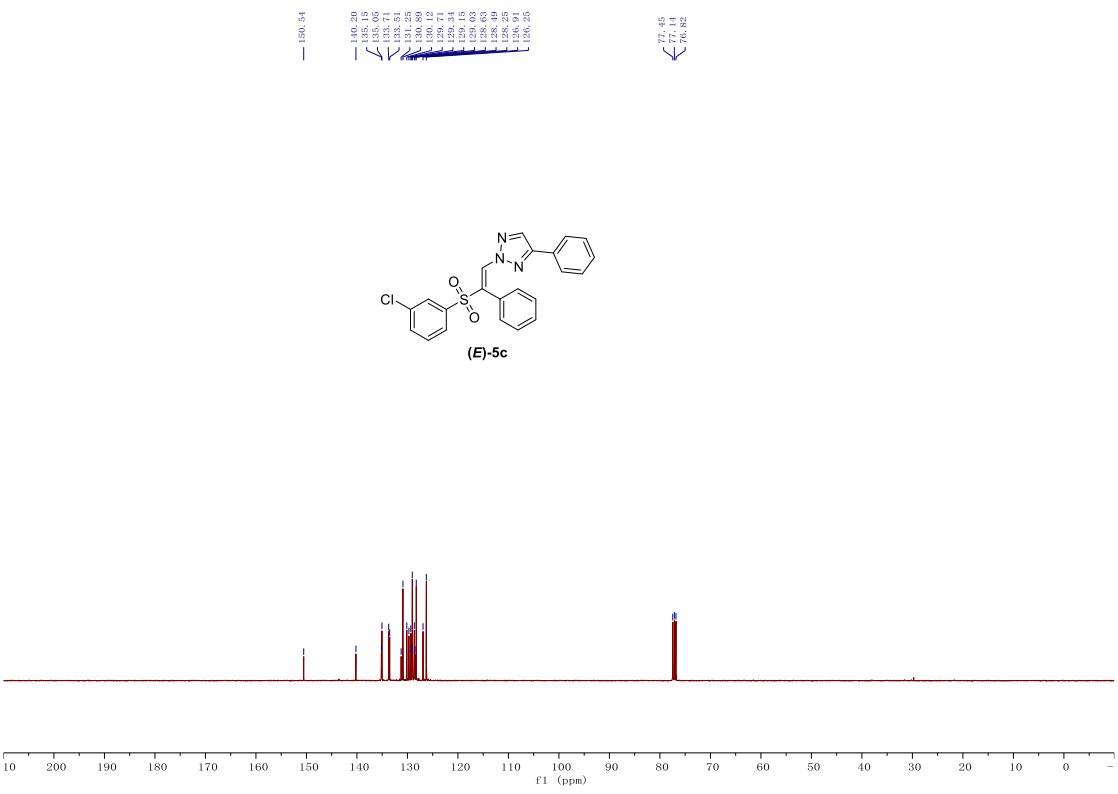
^{13}C NMR (101 MHz) Spectrum of (*E*)-5b in $CDCl_3$



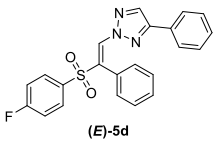
^{1}H NMR (400 MHz) Spectrum of (*E*)-5c in $CDCl_3$



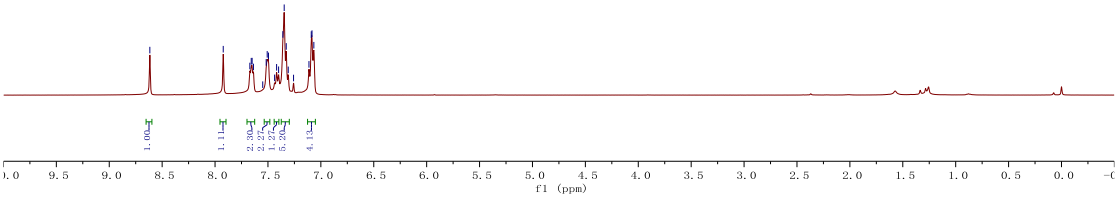
^{13}C NMR (101 MHz) Spectrum of (*E*)-5c in $CDCl_3$



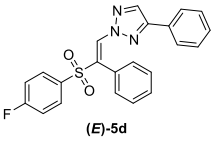
^{1}H NMR (400 MHz) Spectrum of (*E*)-5d in $CDCl_3$



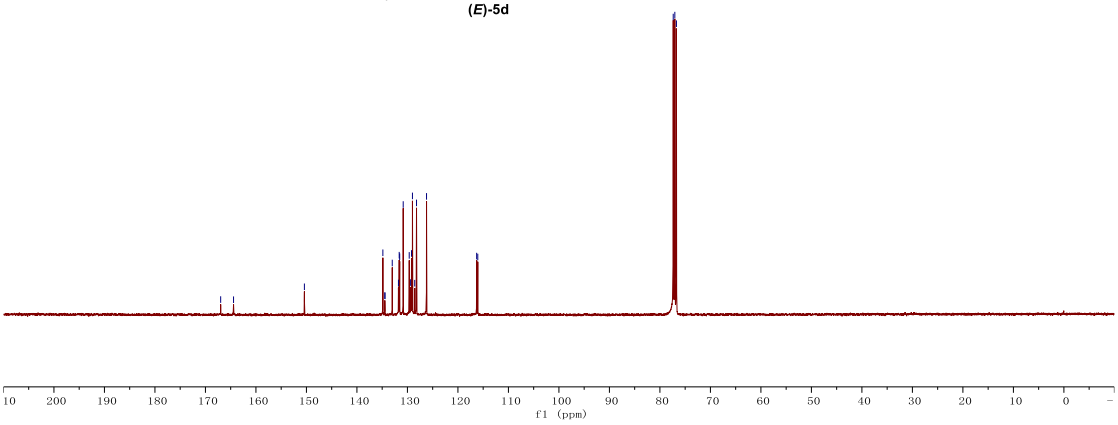
(*E*)-5d



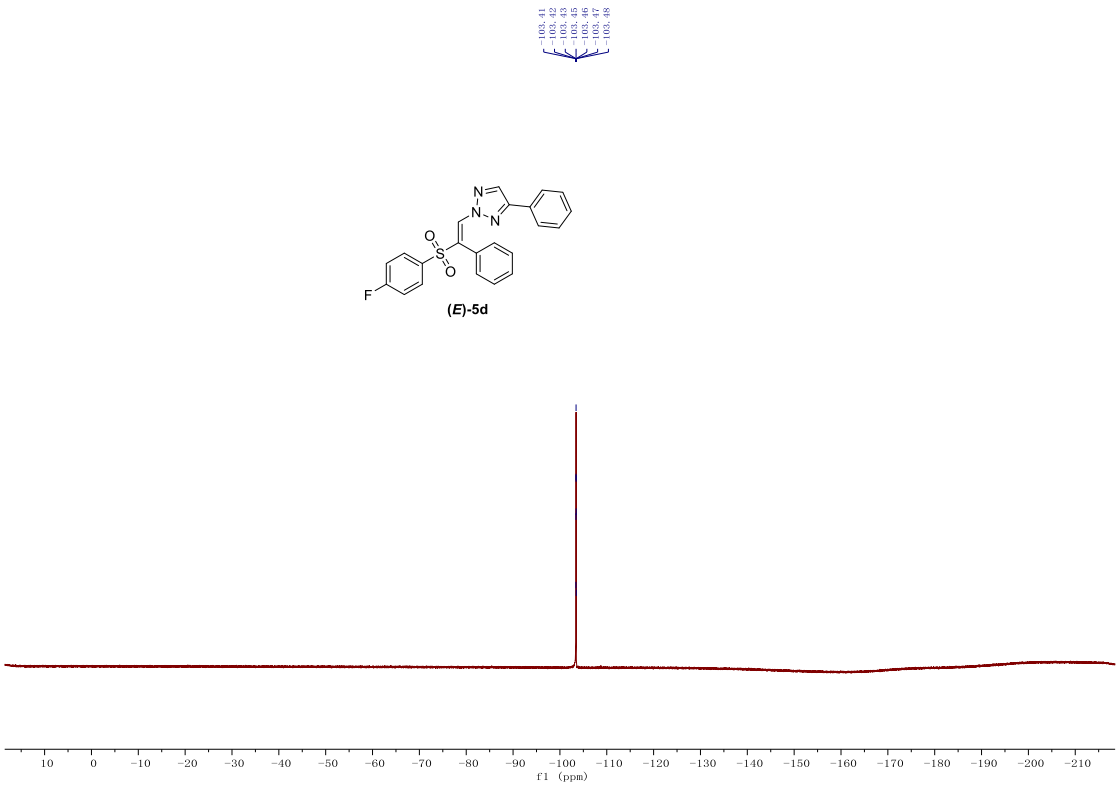
^{13}C NMR (101 MHz) Spectrum of (*E*)-5d in $CDCl_3$



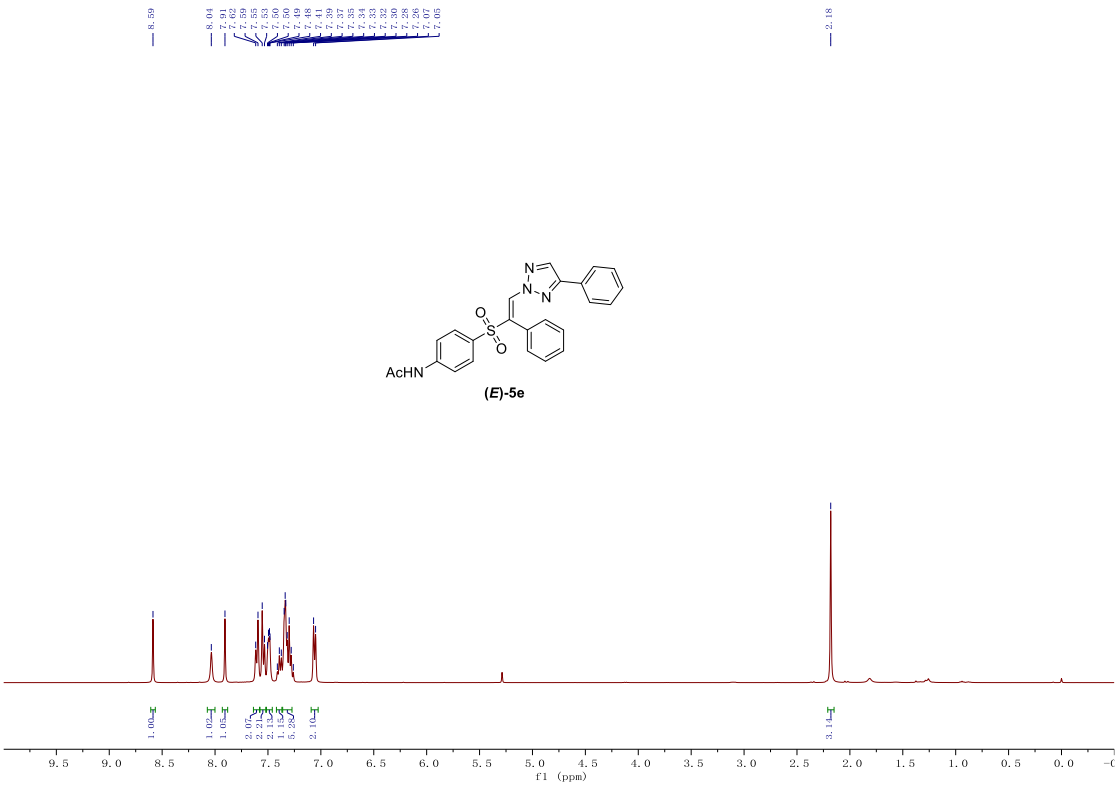
(*E*)-5d



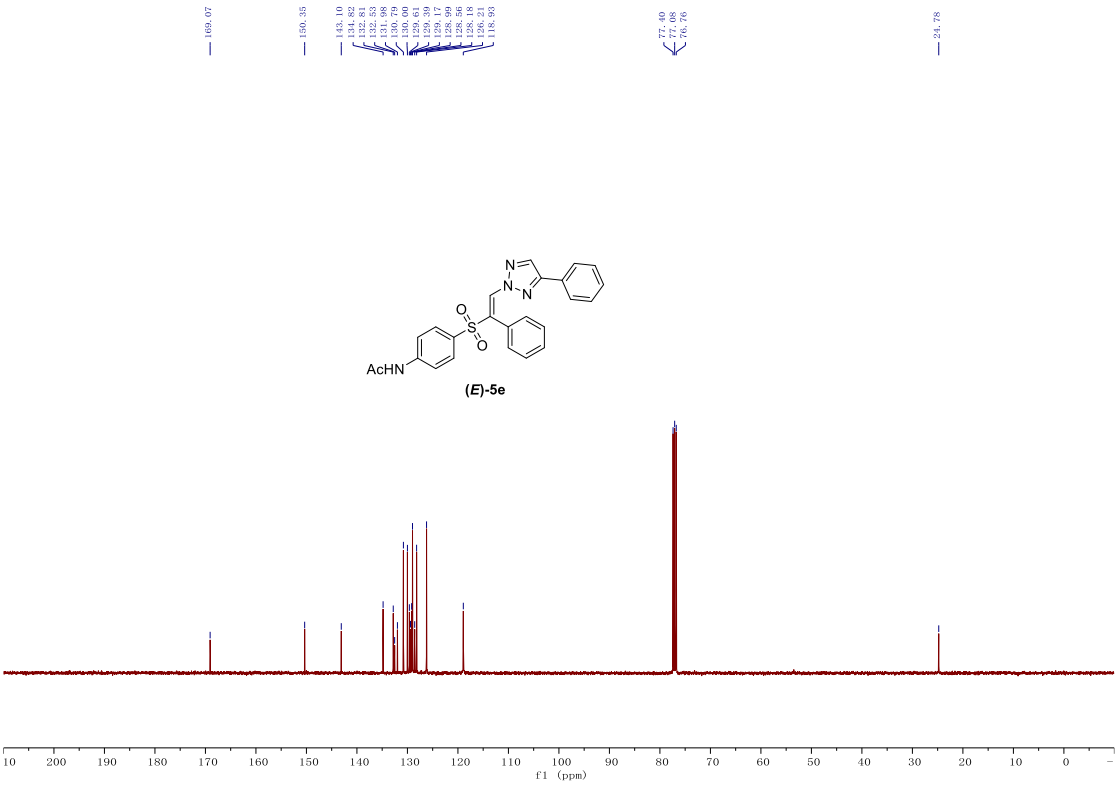
^{19}F NMR (376 MHz) Spectrum of (*E*)-5d in $CDCl_3$



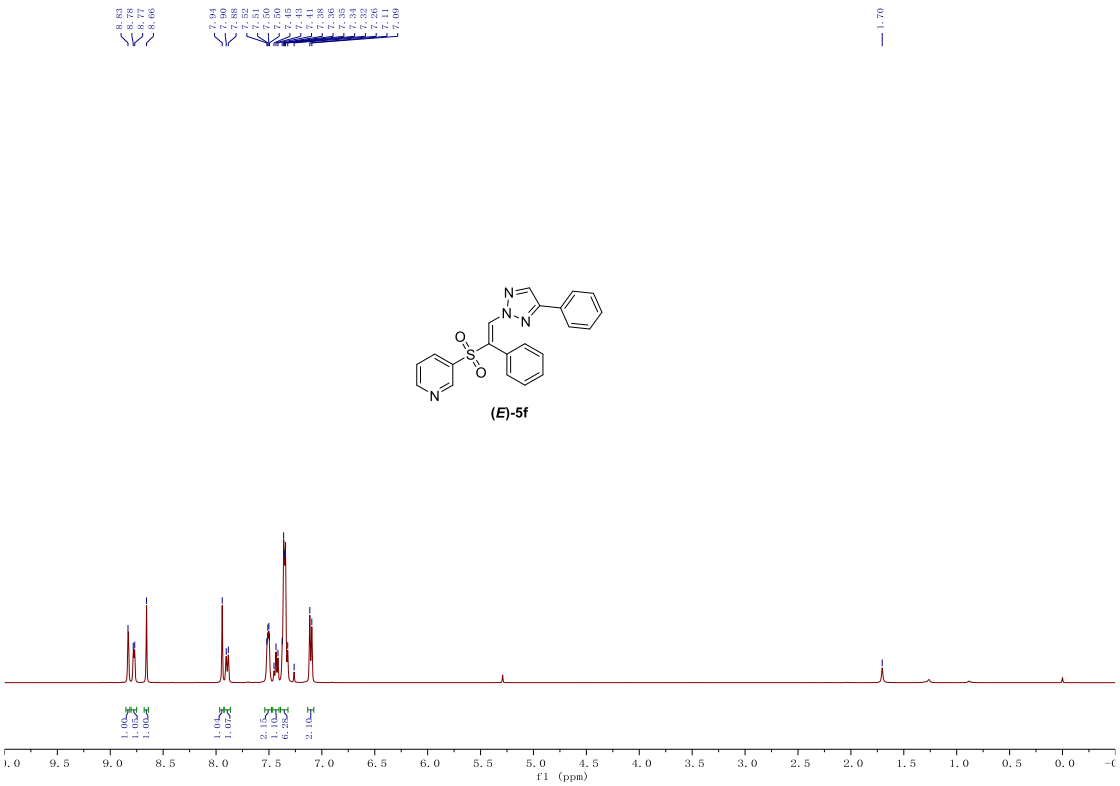
^{1}H NMR (400 MHz) Spectrum of (*E*)-5e in $CDCl_3$



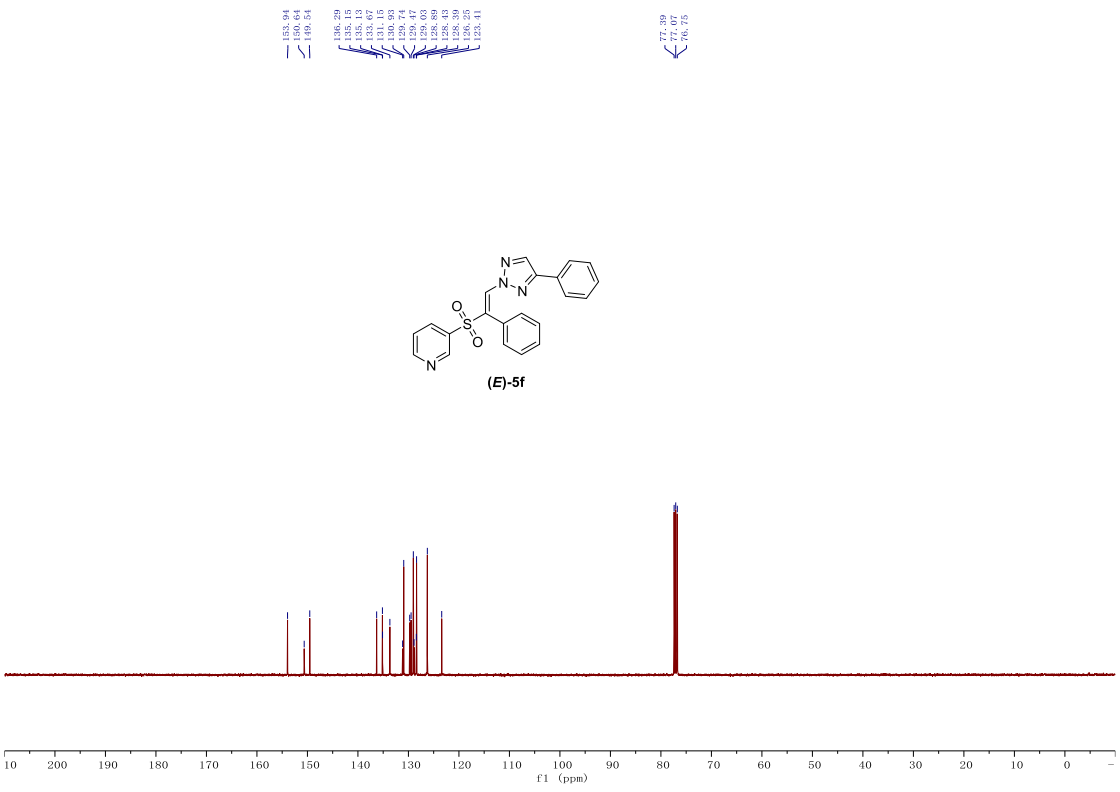
^{13}C NMR (101 MHz) Spectrum of (*E*)-5e in $CDCl_3$



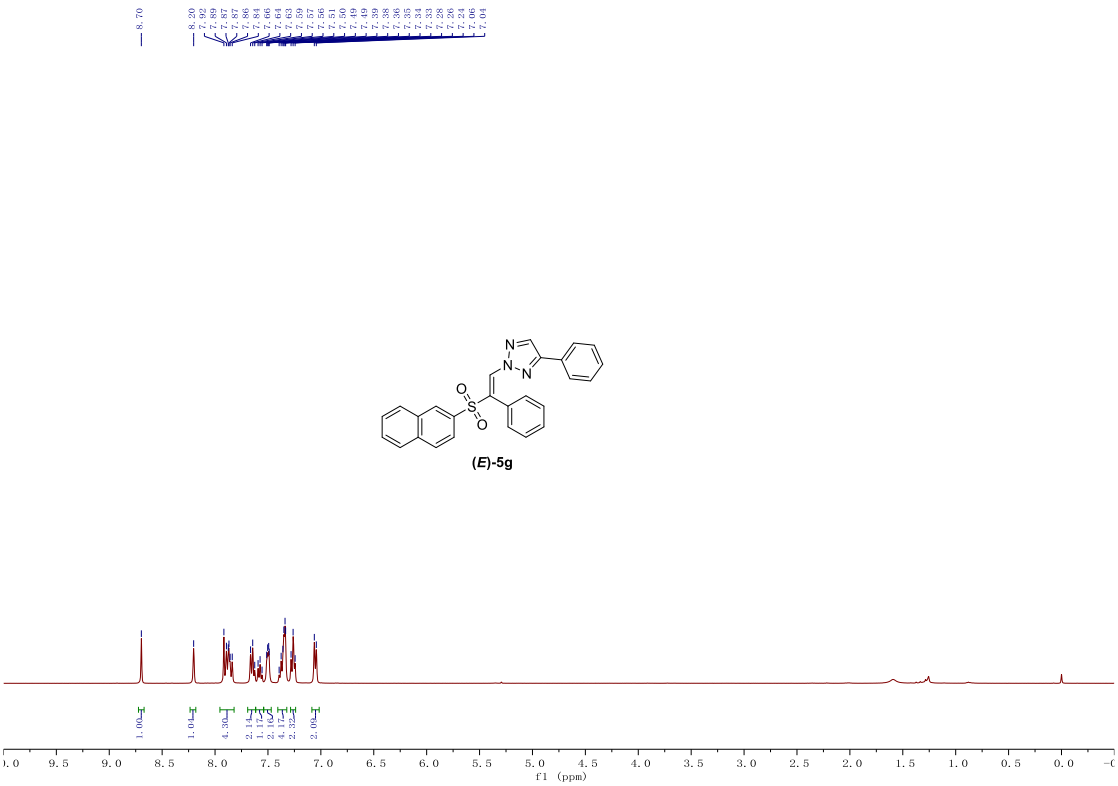
^{1}H NMR (400 MHz) Spectrum of (*E*)-5f in $CDCl_3$



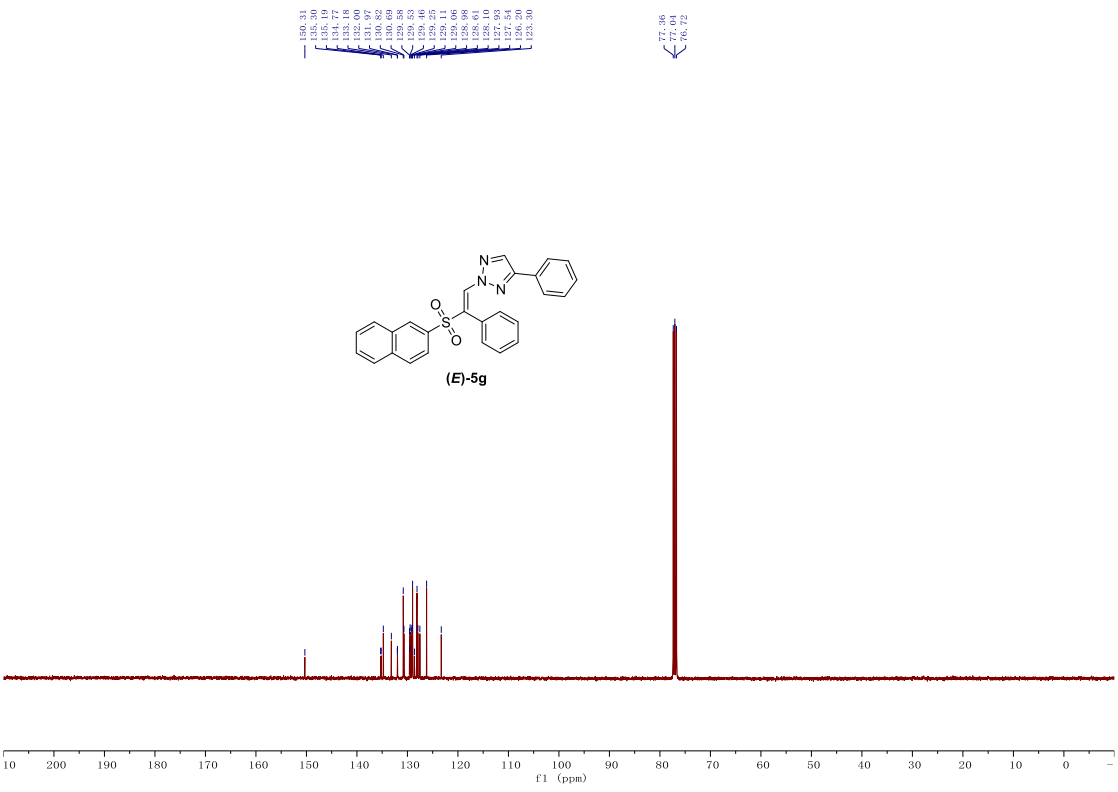
^{13}C NMR (101 MHz) Spectrum of (*E*)-5f in $CDCl_3$



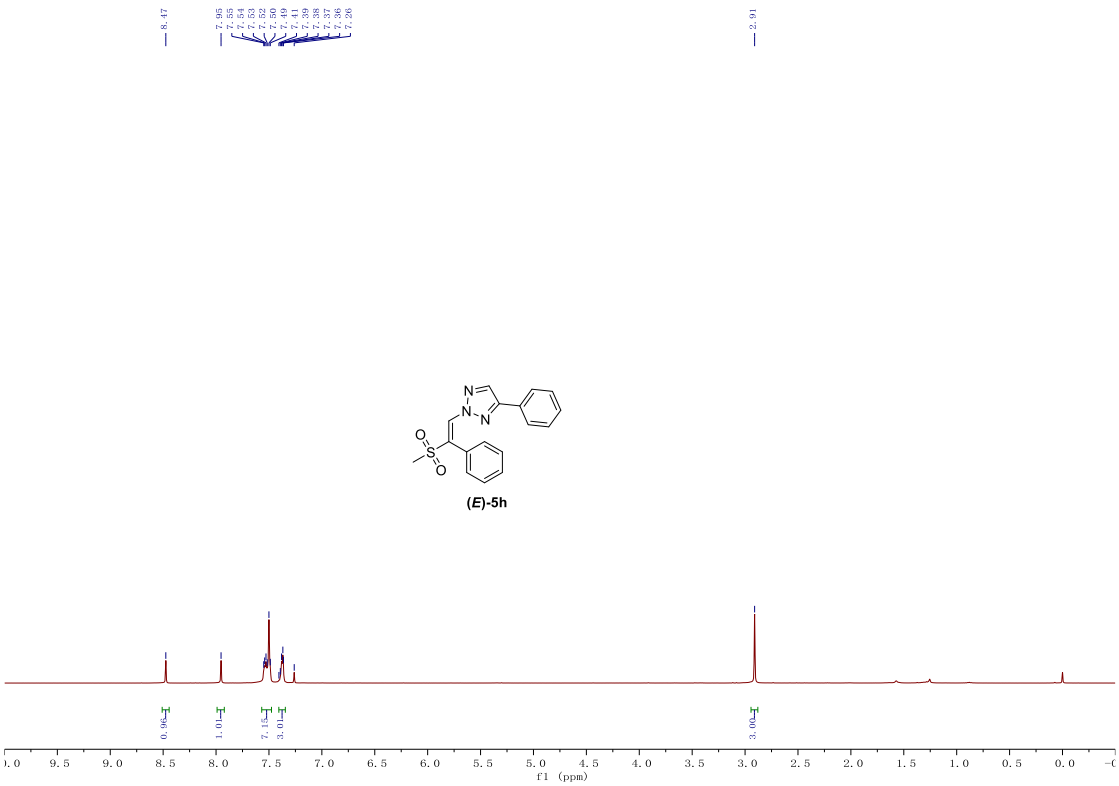
^{1}H NMR (400 MHz) Spectrum of (*E*)-5g in $CDCl_3$



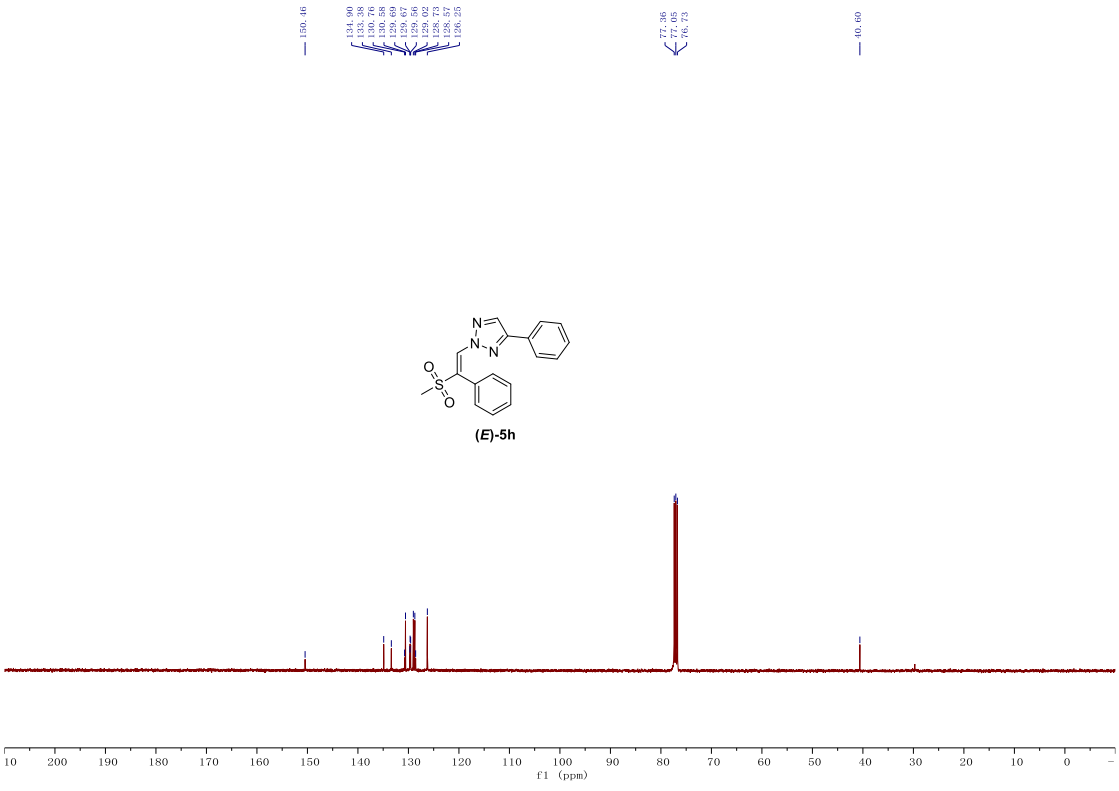
^{13}C NMR (101 MHz) Spectrum of (*E*)-5g in $CDCl_3$



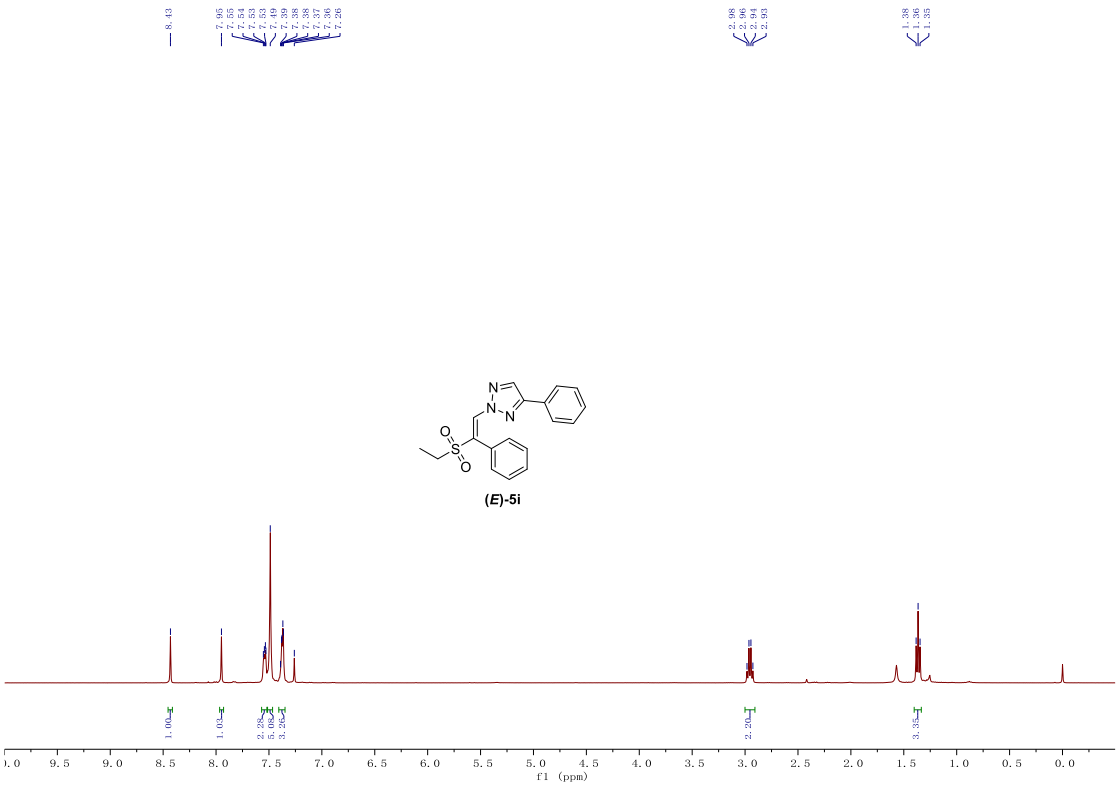
^{1}H NMR (400 MHz) Spectrum of (*E*)-5h in $CDCl_3$



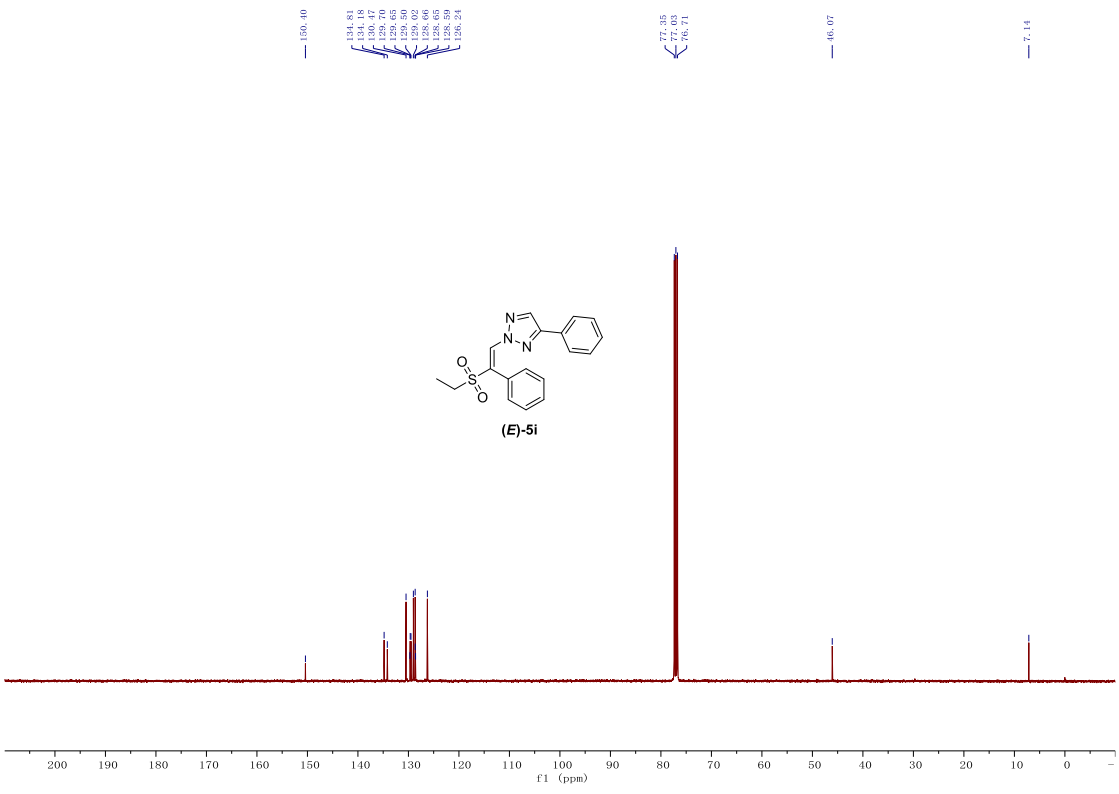
^{13}C NMR (101 MHz) Spectrum of (*E*)-5h in $CDCl_3$



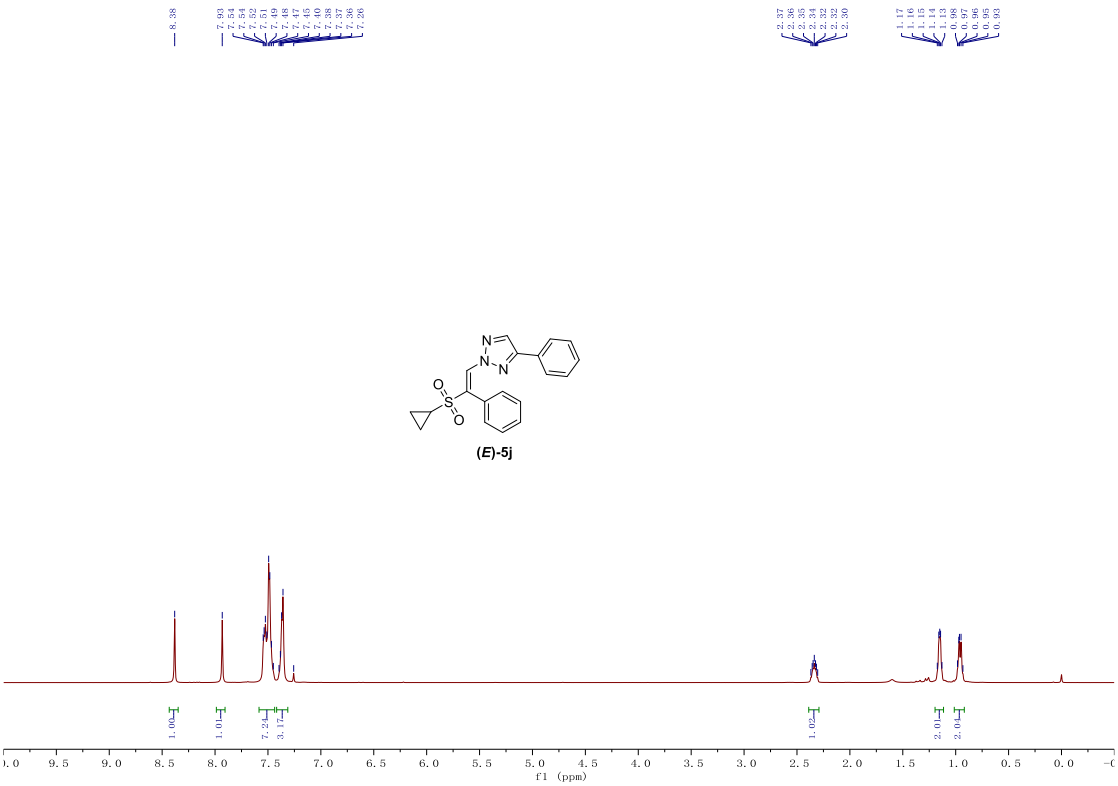
^{1}H NMR (400 MHz) Spectrum of (*E*)-5i in $CDCl_3$



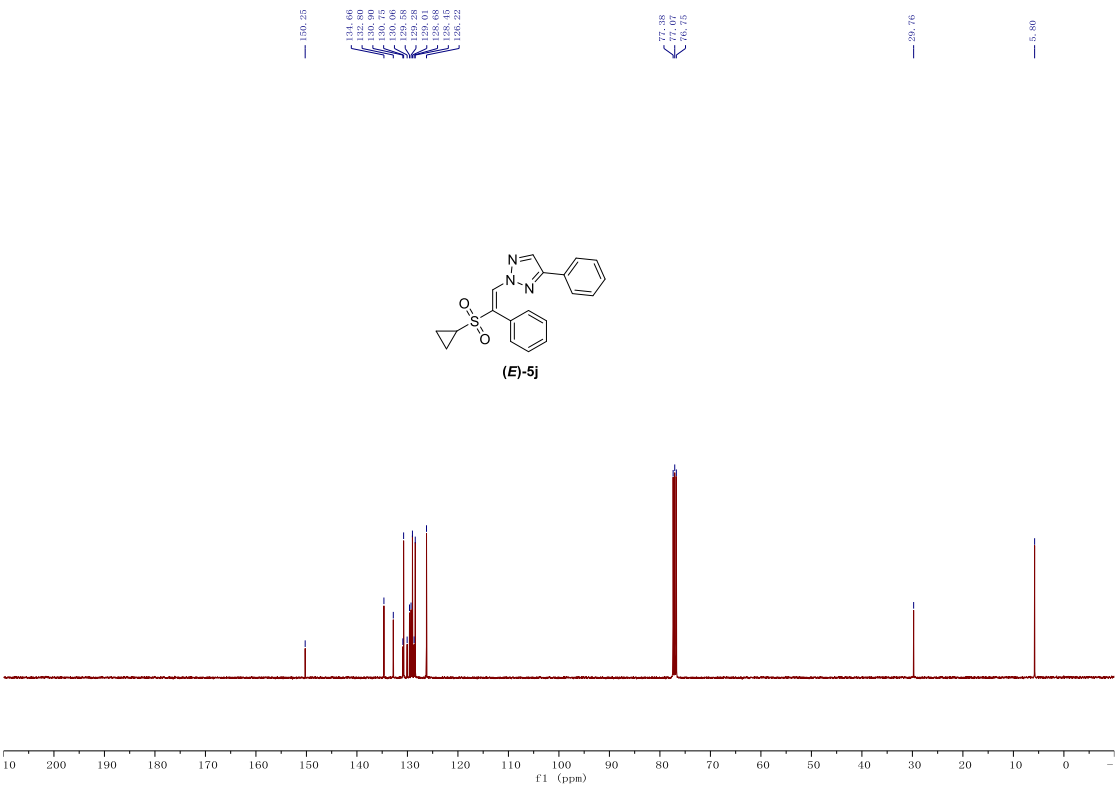
^{13}C NMR (101 MHz) Spectrum of (*E*)-5i in $CDCl_3$



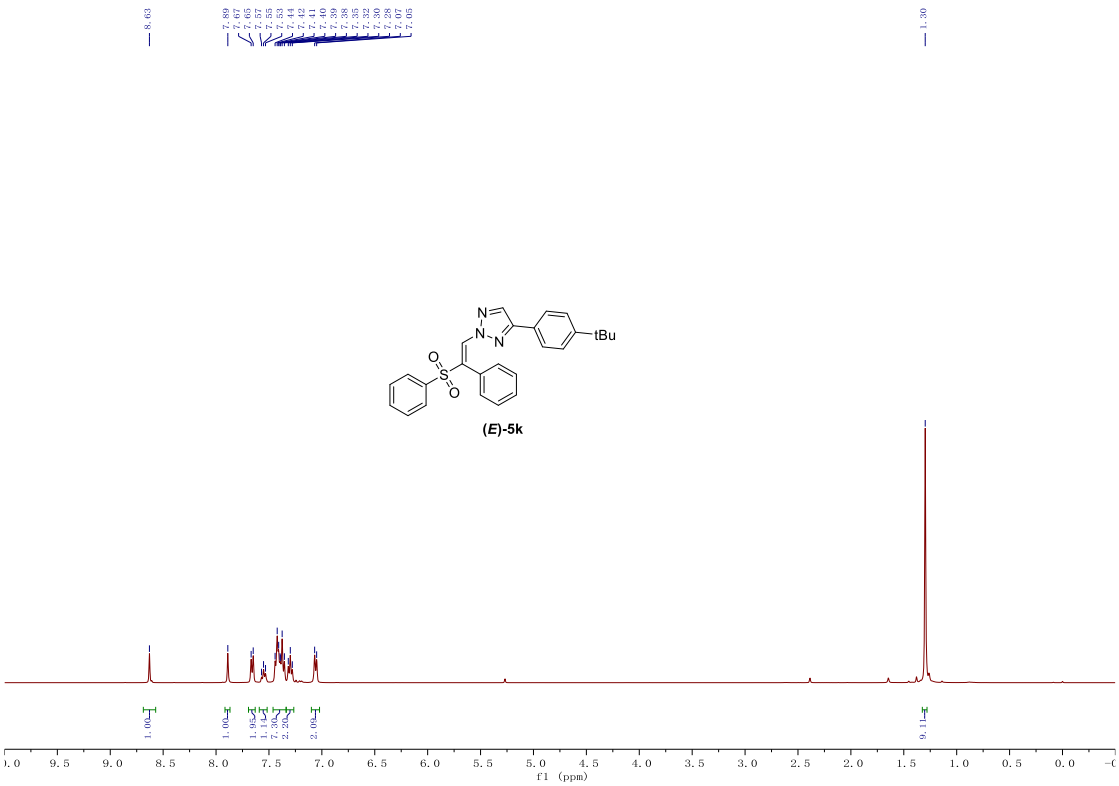
^{1}H NMR (400 MHz) Spectrum of (*E*)-5j in $CDCl_3$



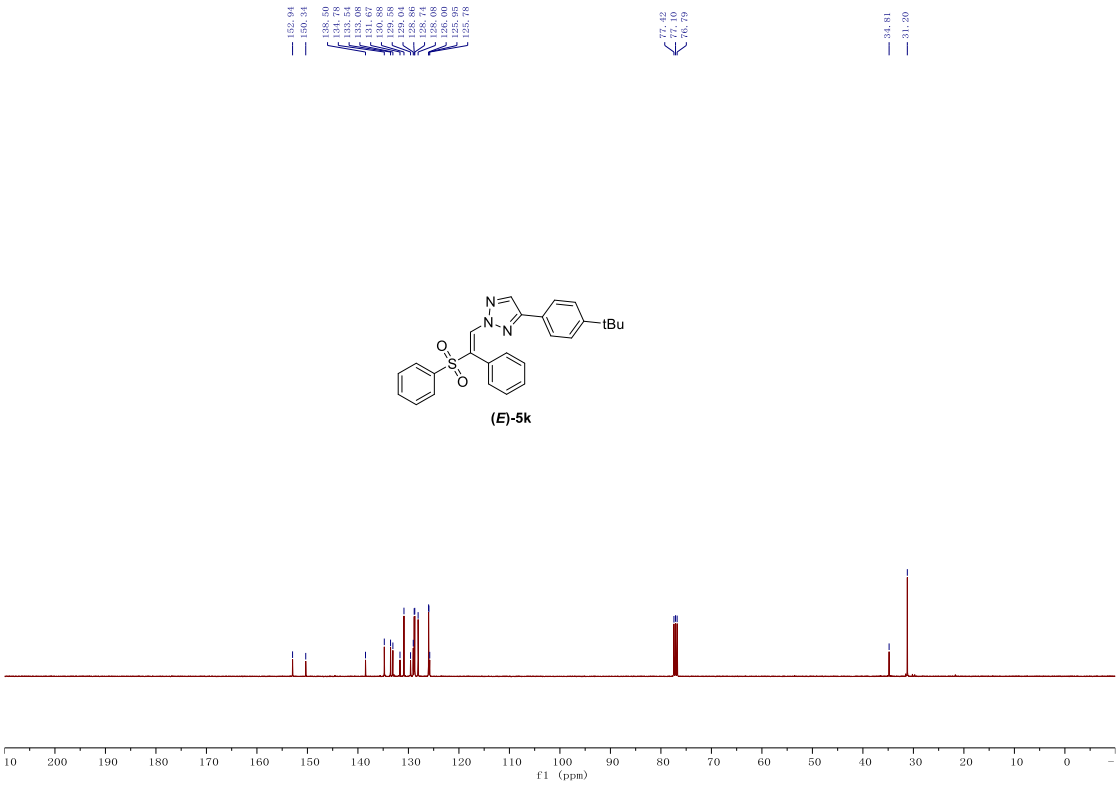
^{13}C NMR (101 MHz) Spectrum of (*E*)-5j in $CDCl_3$



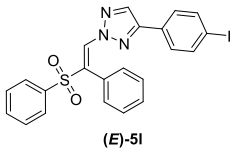
^{1}H NMR (400 MHz) Spectrum of (*E*)-5k in $CDCl_3$



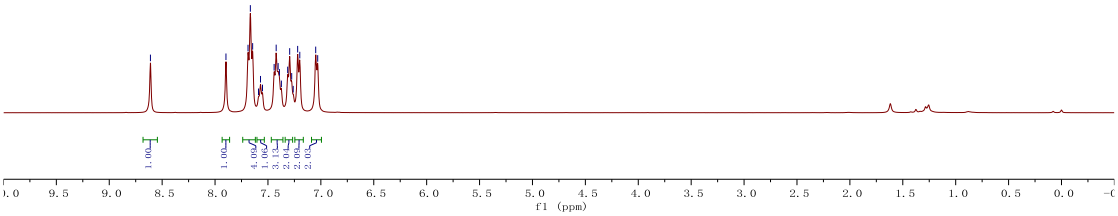
^{13}C NMR (101 MHz) Spectrum of (*E*)-5k in $CDCl_3$



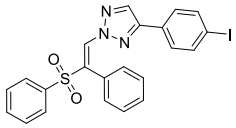
^{1}H NMR (400 MHz) Spectrum of (*E*)-5l in $CDCl_3$



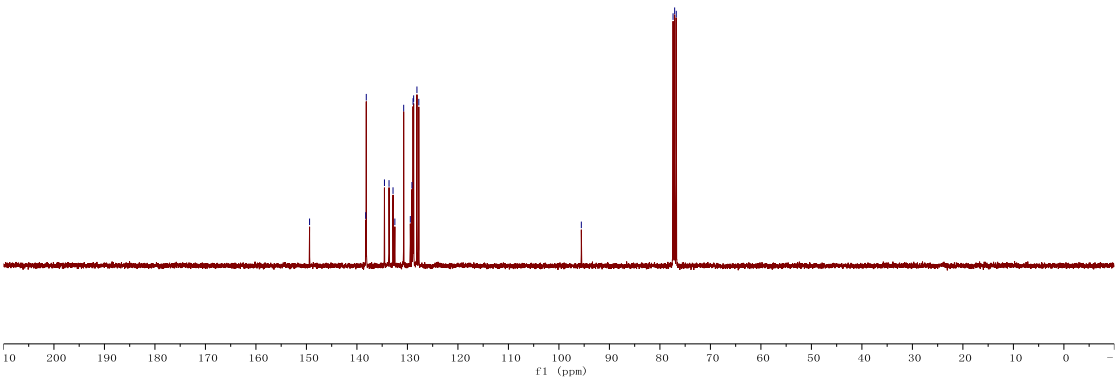
(*E*)-5l



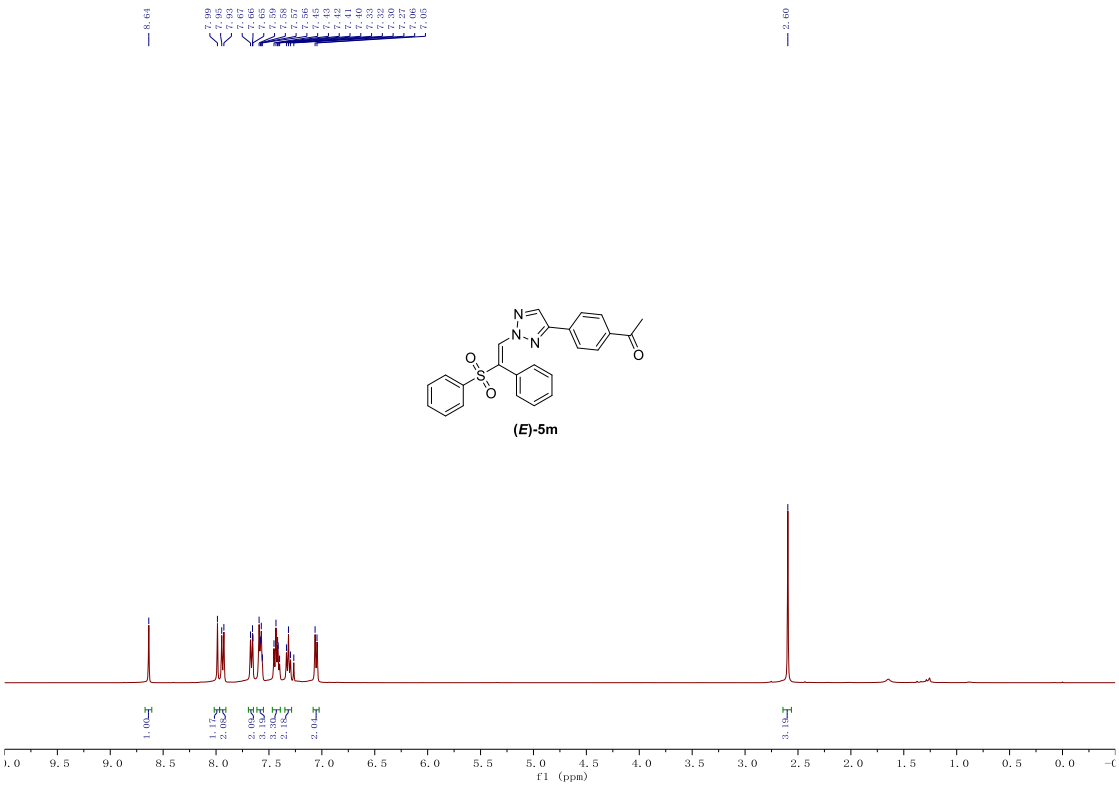
^{13}C NMR (101 MHz) Spectrum of (*E*)-5l in $CDCl_3$



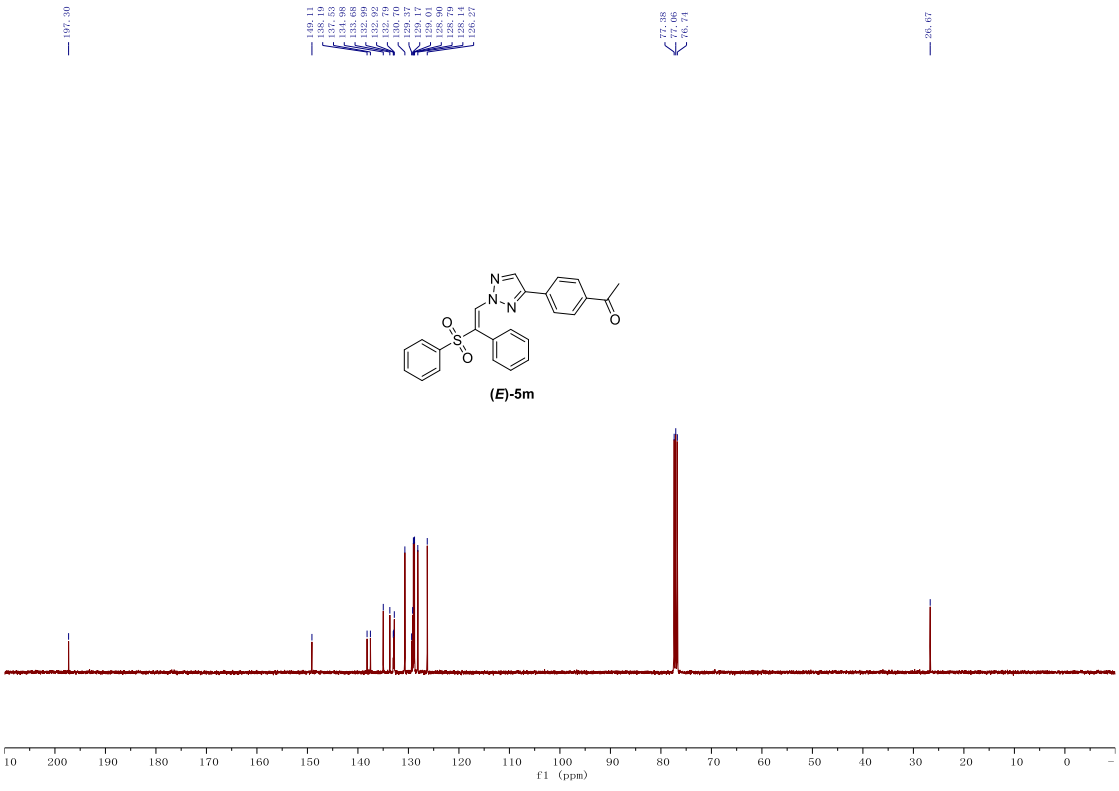
(*E*)-5l



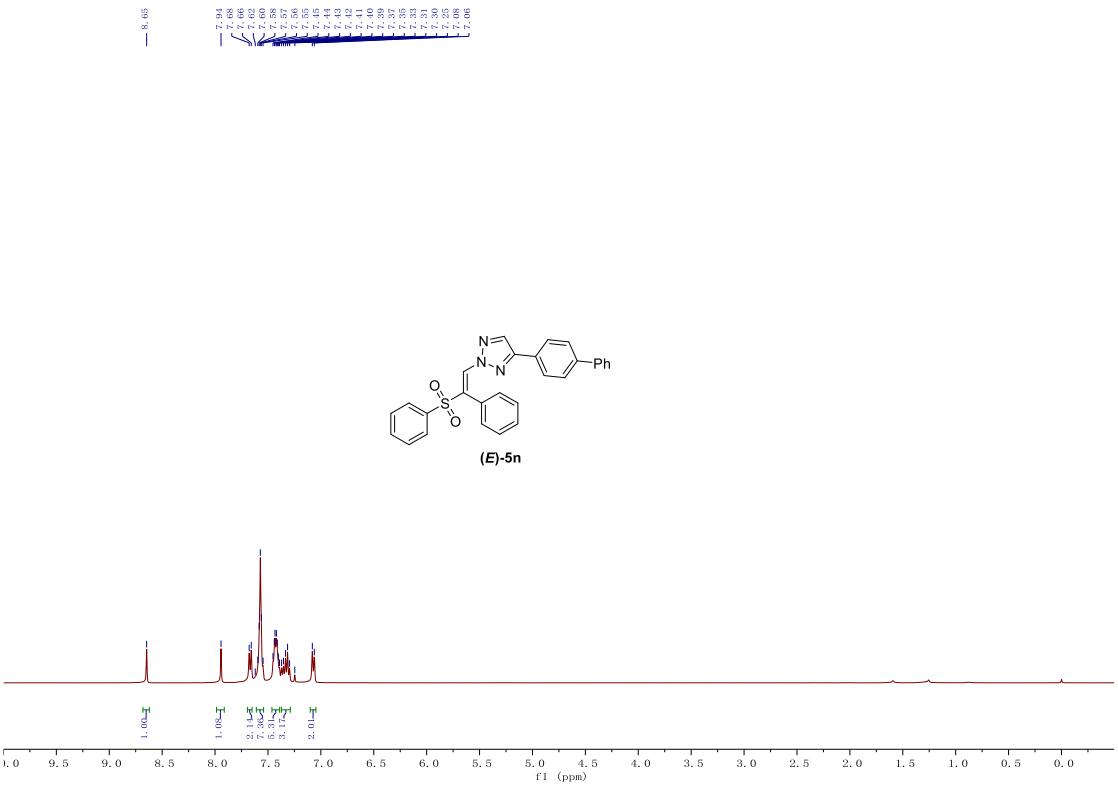
^{1}H NMR (400 MHz) Spectrum of (*E*)-5m in $CDCl_3$



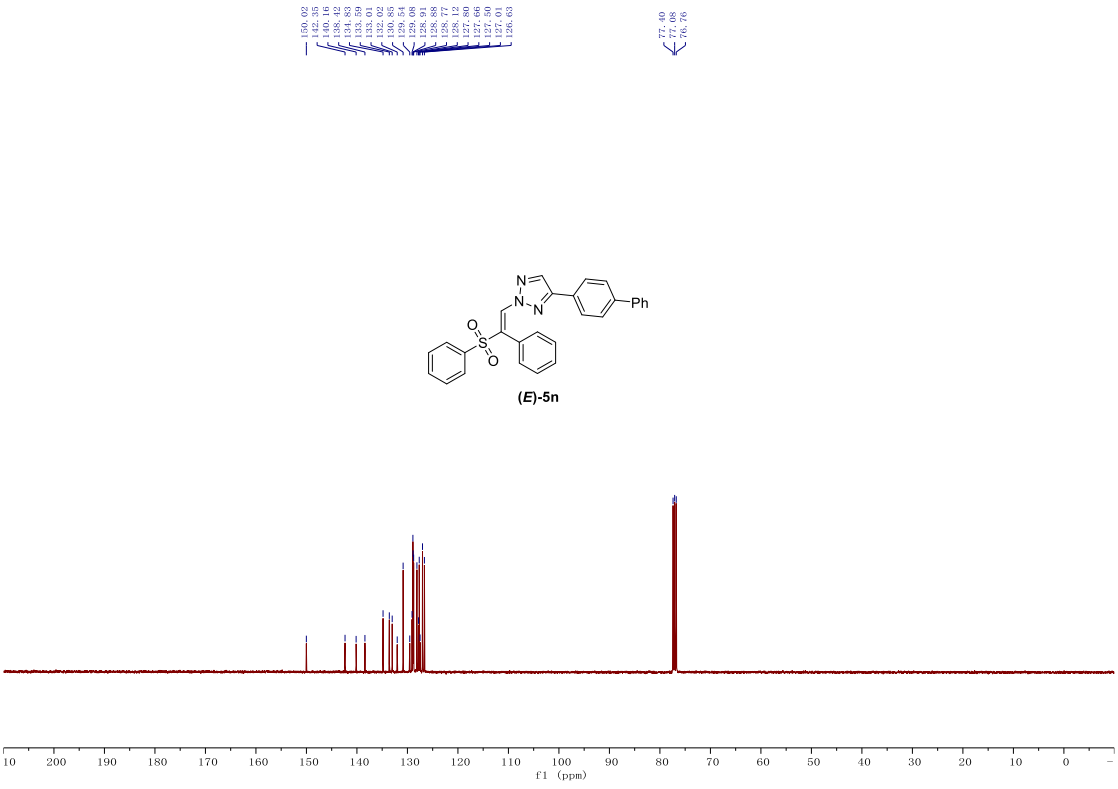
^{13}C NMR (101 MHz) Spectrum of (*E*)-5m in $CDCl_3$



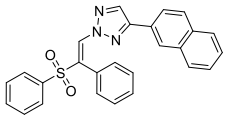
^{1}H NMR (400 MHz) Spectrum of (*E*)-5n in $CDCl_3$



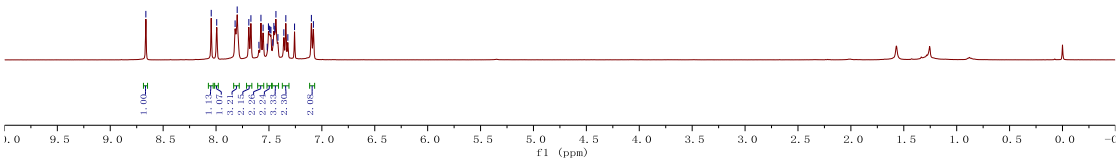
^{13}C NMR (101 MHz) Spectrum of (*E*)-5n in $CDCl_3$



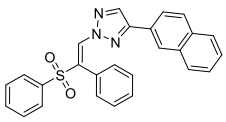
^{1}H NMR (400 MHz) Spectrum of (*E*)-5o in $CDCl_3$



(*E*)-5o

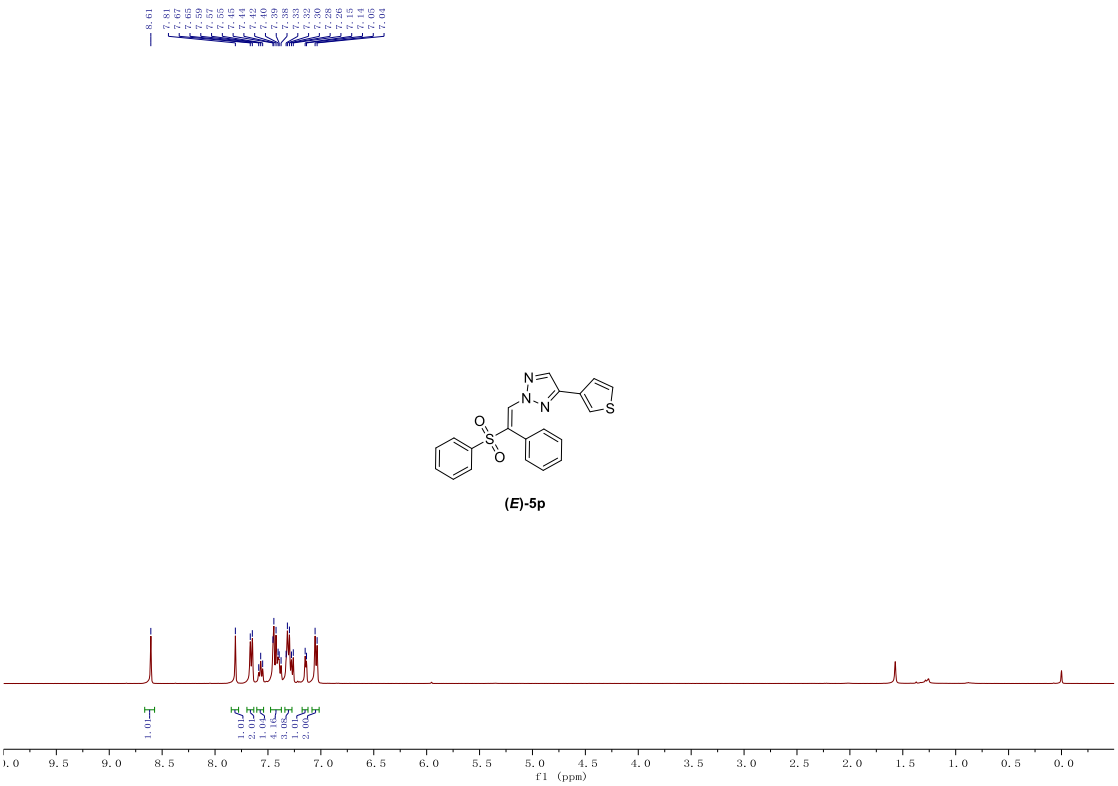


^{13}C NMR (101 MHz) Spectrum of (*E*)-5o in $CDCl_3$

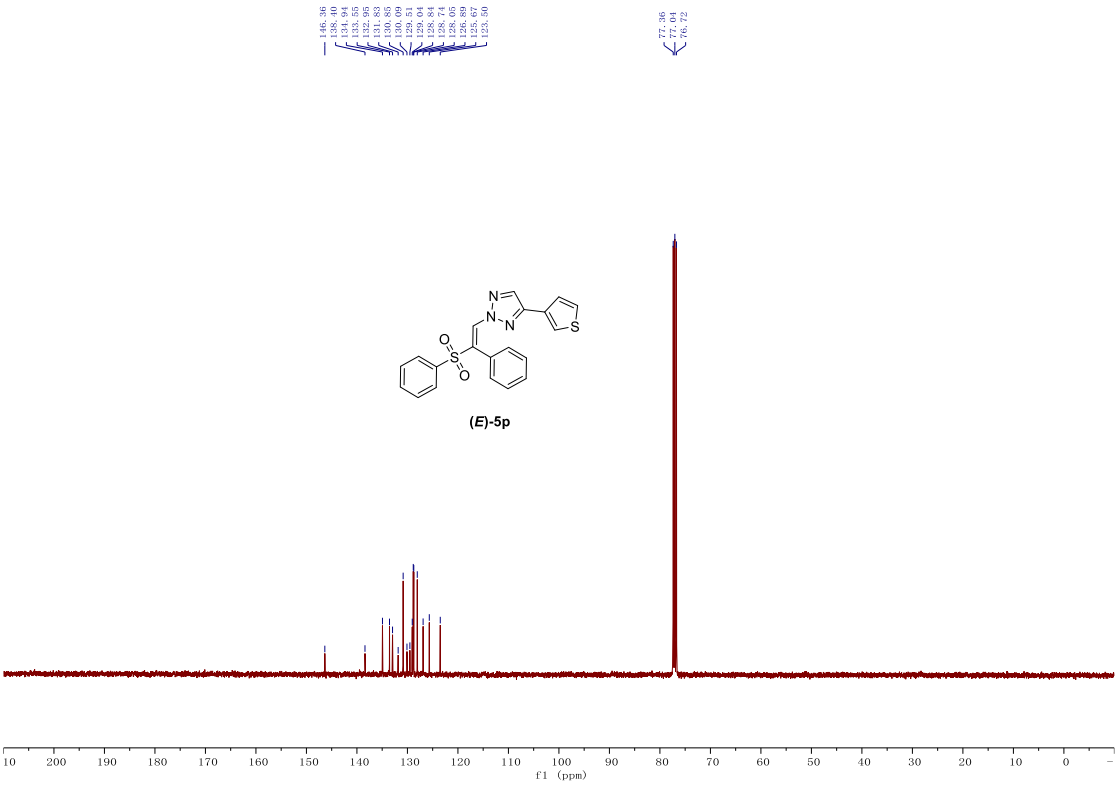


(*E*)-5o

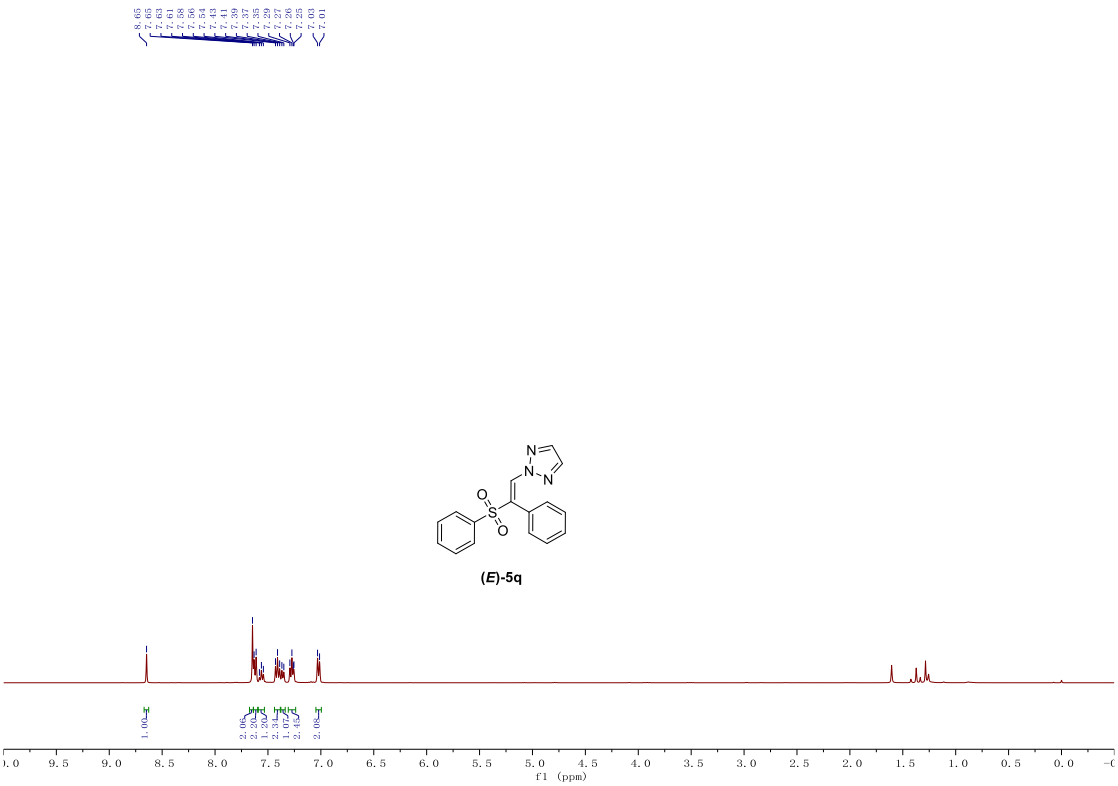
^{1}H NMR (400 MHz) Spectrum of (*E*)-5p in $CDCl_3$



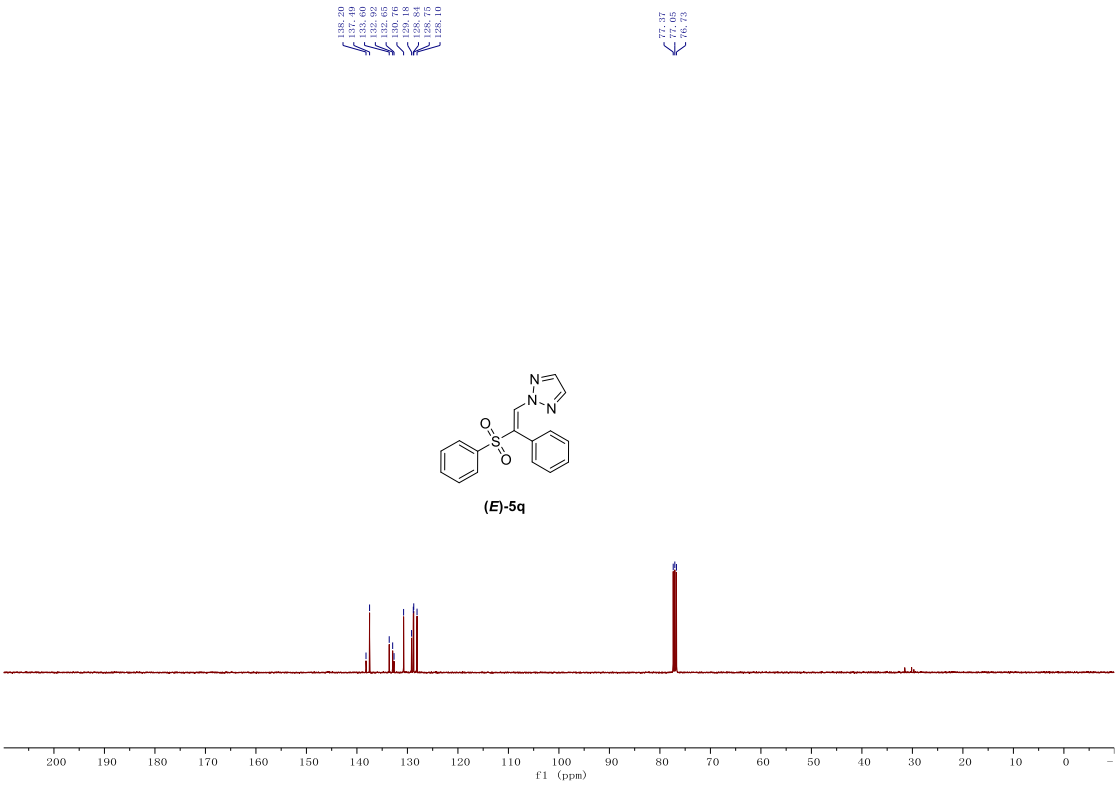
^{13}C NMR (101 MHz) Spectrum of (*E*)-5p in $CDCl_3$



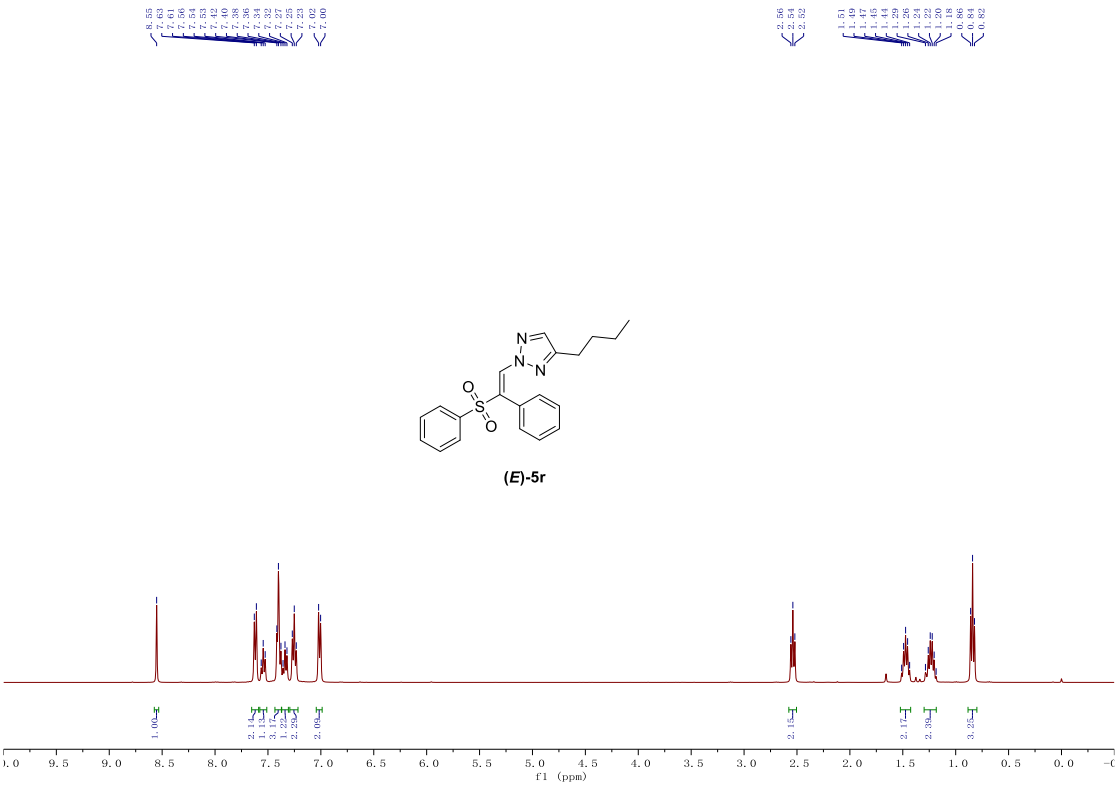
^{1}H NMR (400 MHz) Spectrum of (*E*)-5q in $CDCl_3$



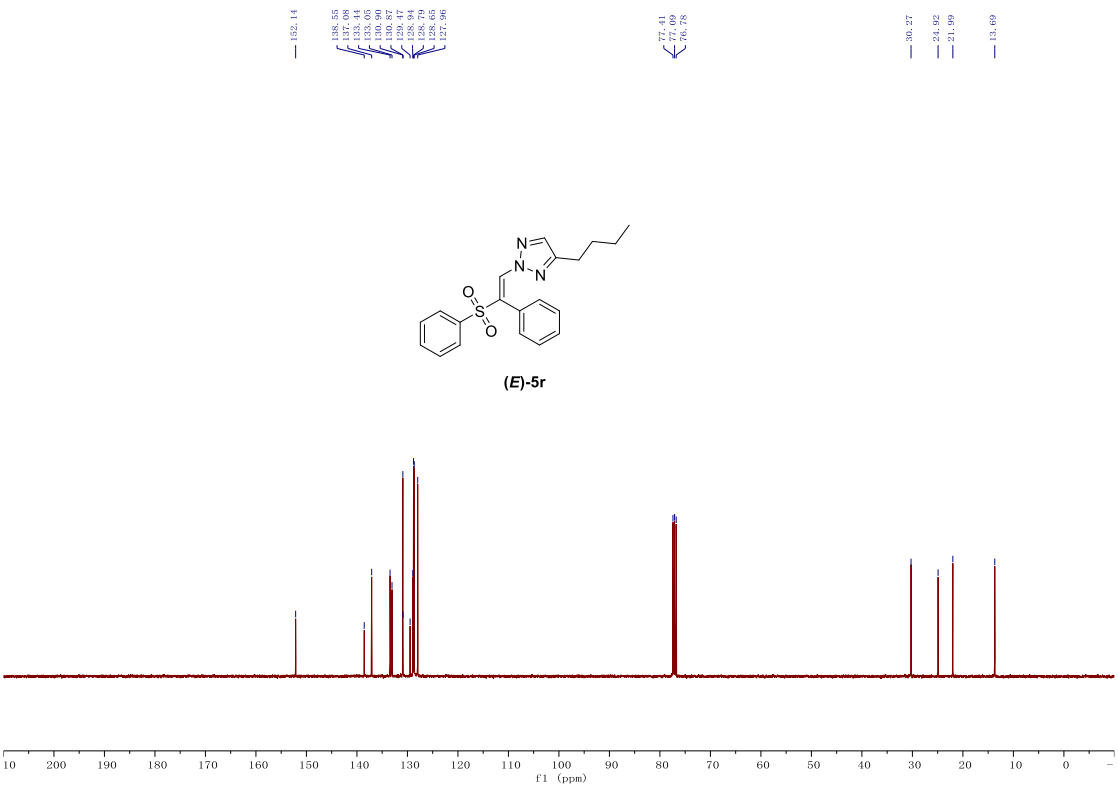
^{13}C NMR (101 MHz) Spectrum of (*E*)-5q in $CDCl_3$



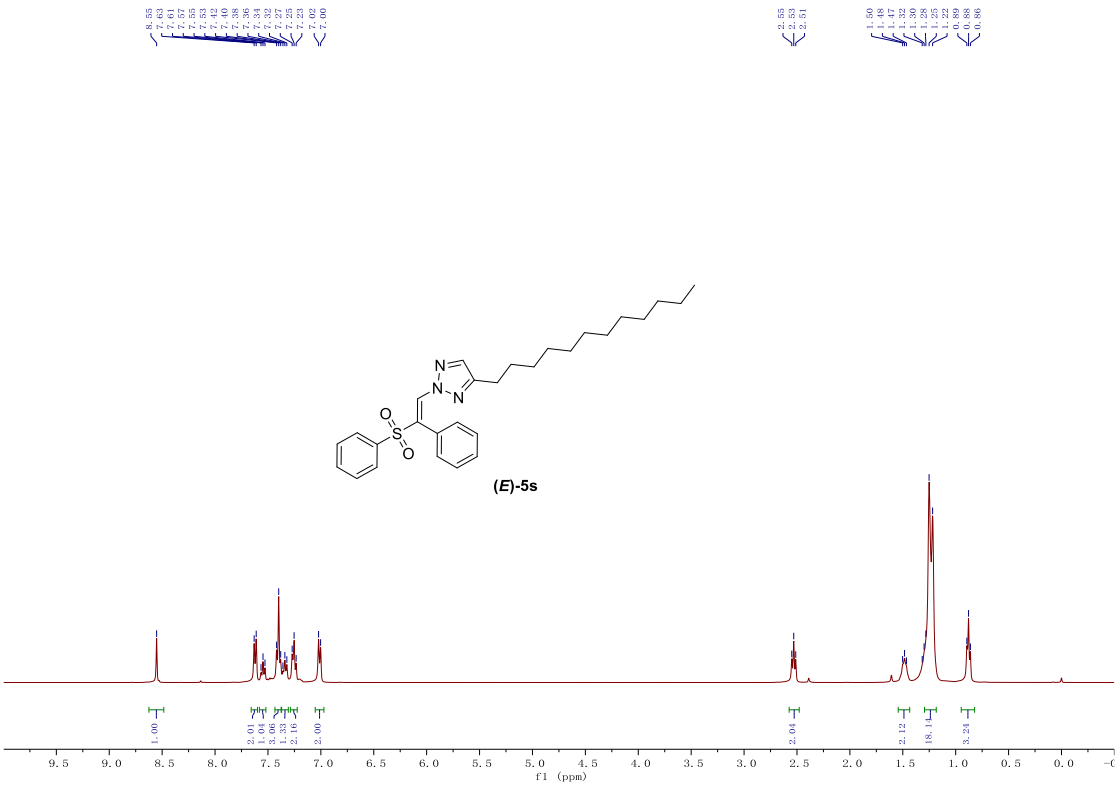
^{1}H NMR (400 MHz) Spectrum of (*E*)-5r in $CDCl_3$



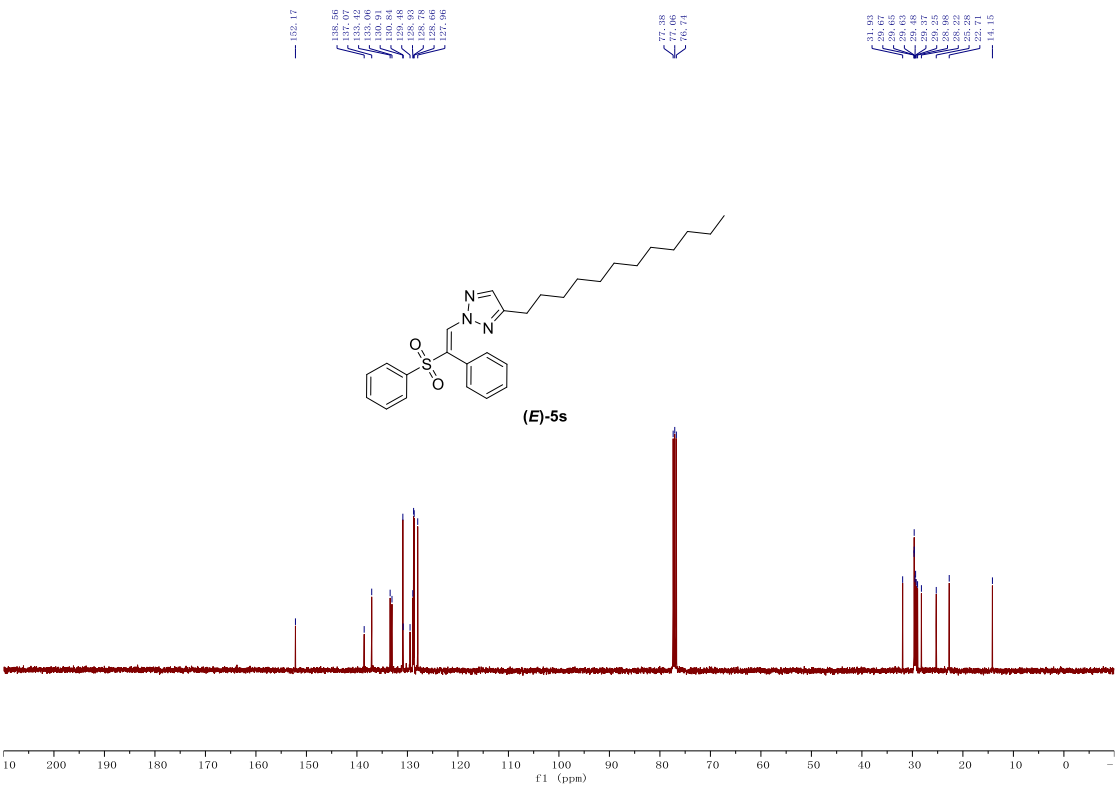
^{13}C NMR (101 MHz) Spectrum of (*E*)-5r in $CDCl_3$



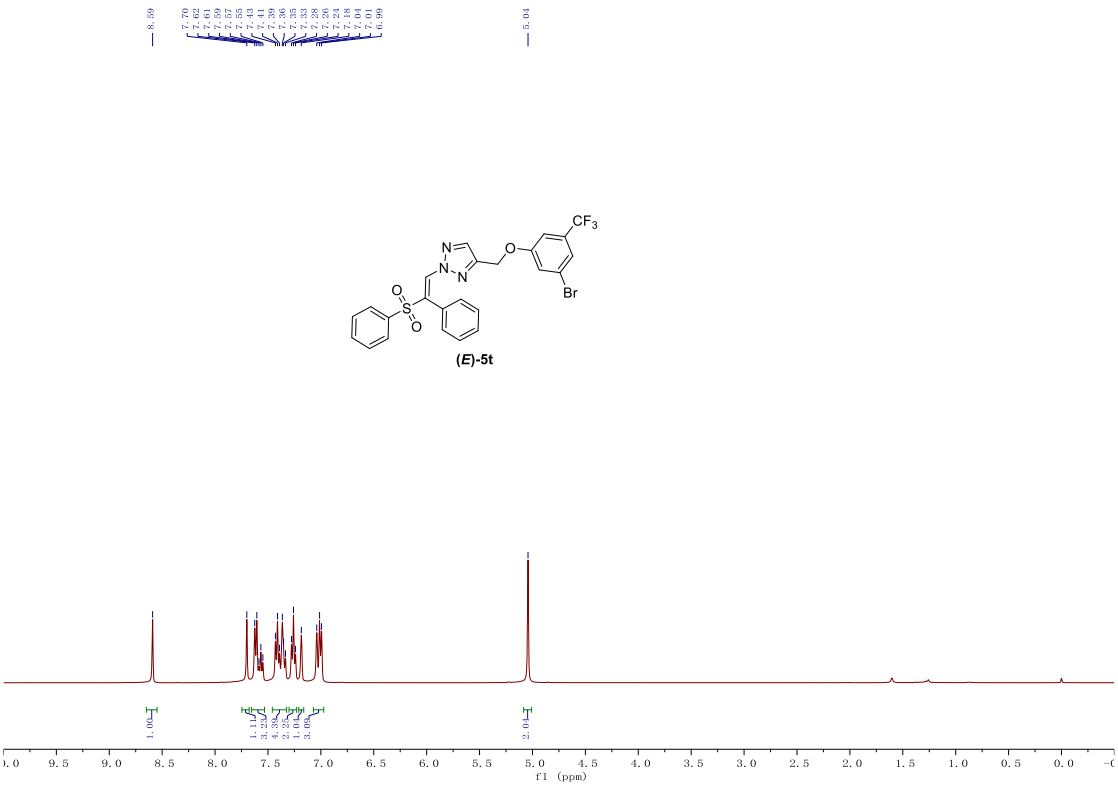
^{1}H NMR (400 MHz) Spectrum of (*E*)-5s in $CDCl_3$



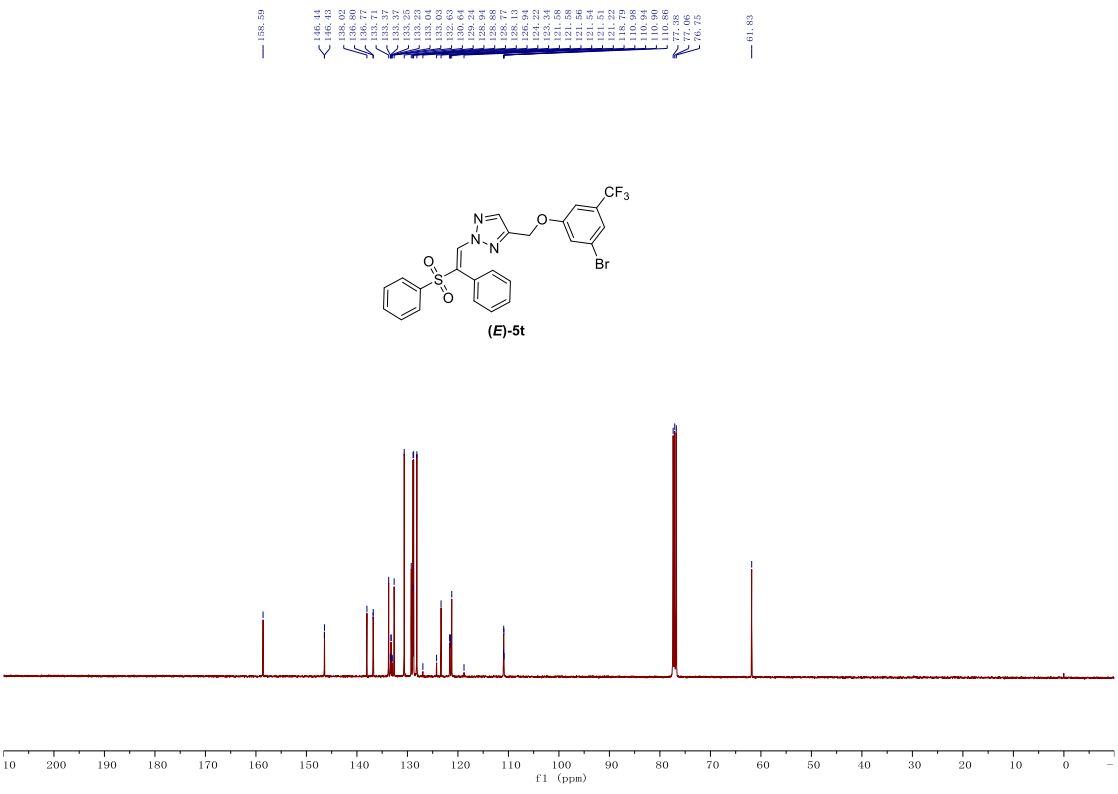
^{13}C NMR (101 MHz) Spectrum of (*E*)-5s in $CDCl_3$



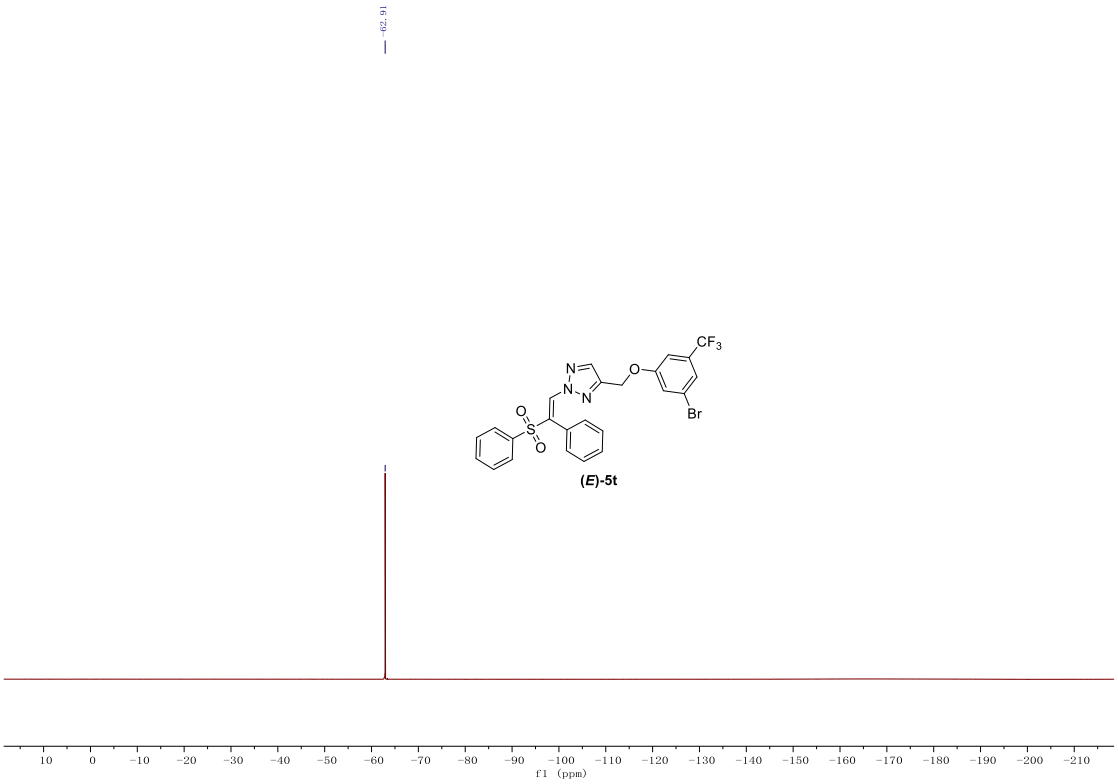
^{1}H NMR (400 MHz) Spectrum of (*E*)-5t in $CDCl_3$



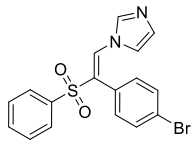
^{13}C NMR (101 MHz) Spectrum of (*E*)-5t in $CDCl_3$



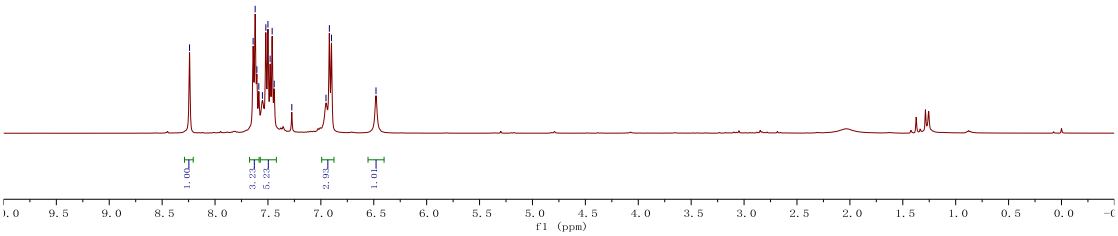
^{19}F NMR (376 MHz) Spectrum of (*E*)-5t in $CDCl_3$



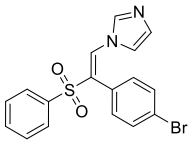
^{1}H NMR (400 MHz) Spectrum of (*E*)-5u in $CDCl_3$



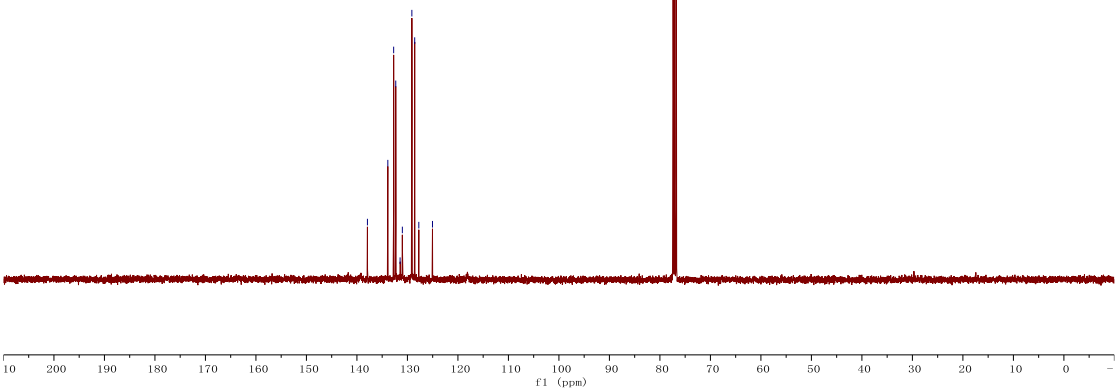
(*E*)-5u



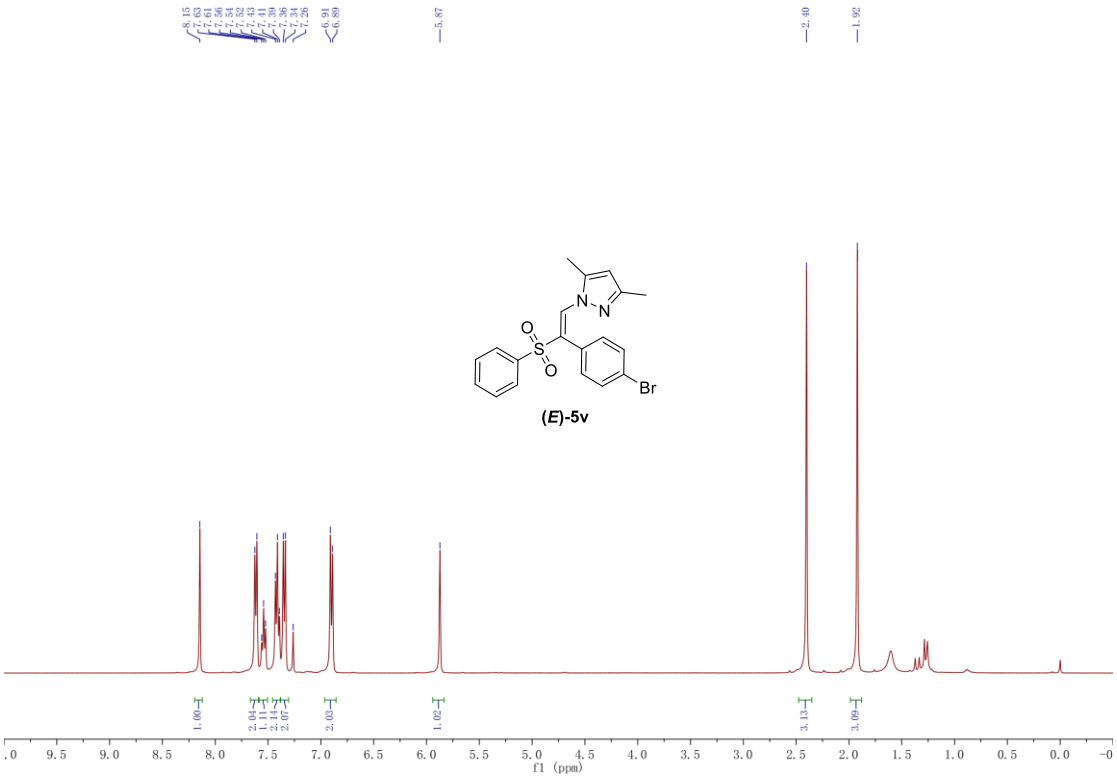
^{13}C NMR (101 MHz) Spectrum of (*E*)-5u in $CDCl_3$



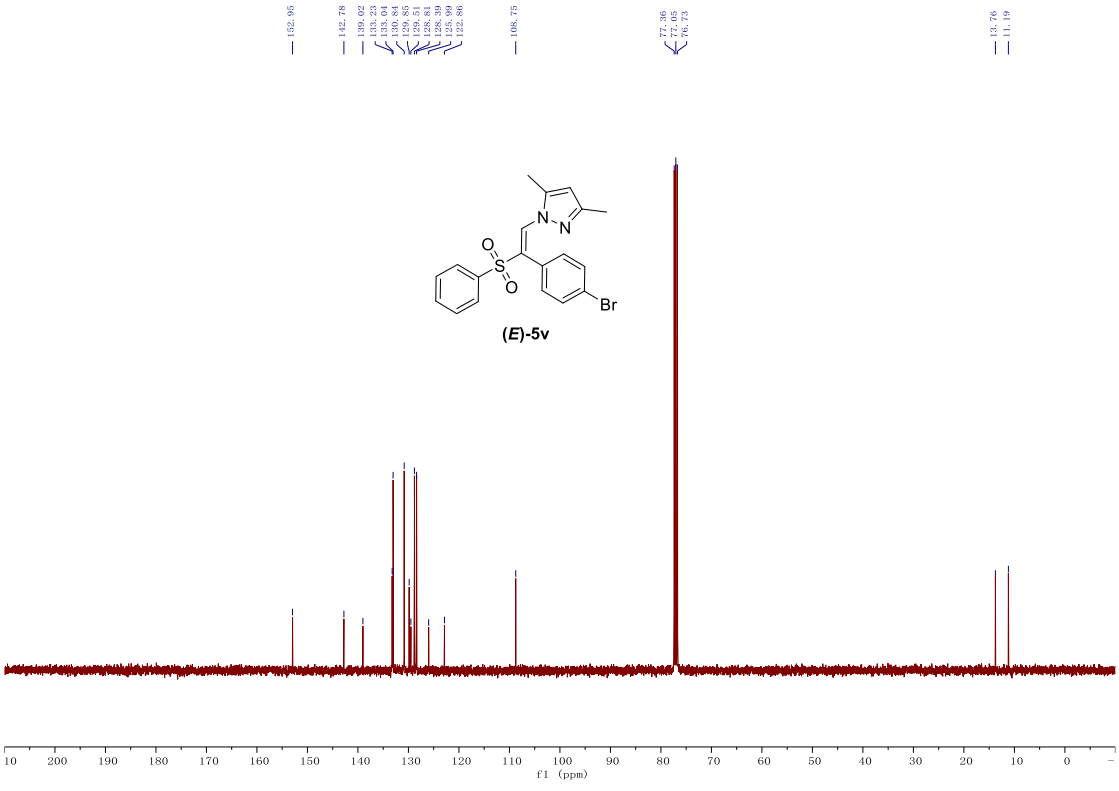
(*E*)-5u



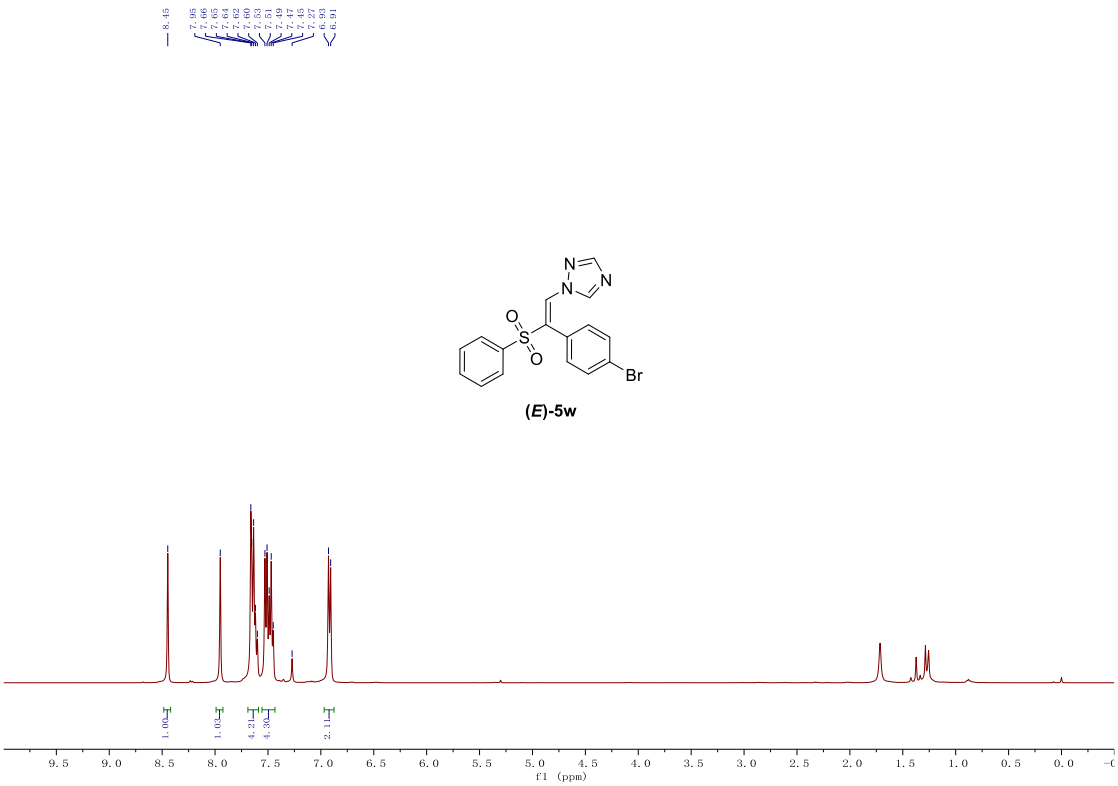
^{1}H NMR (400 MHz) Spectrum of (*E*)-5v in $CDCl_3$



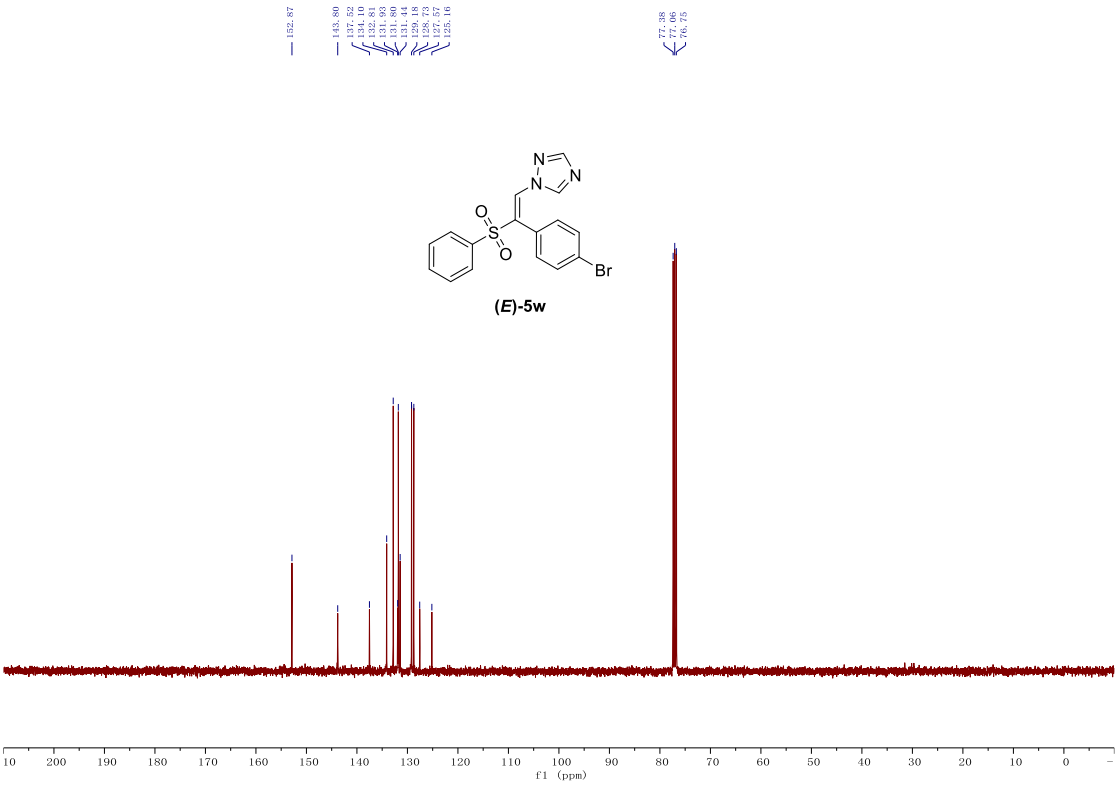
^{13}C NMR (101 MHz) Spectrum of (*E*)-5v in $CDCl_3$



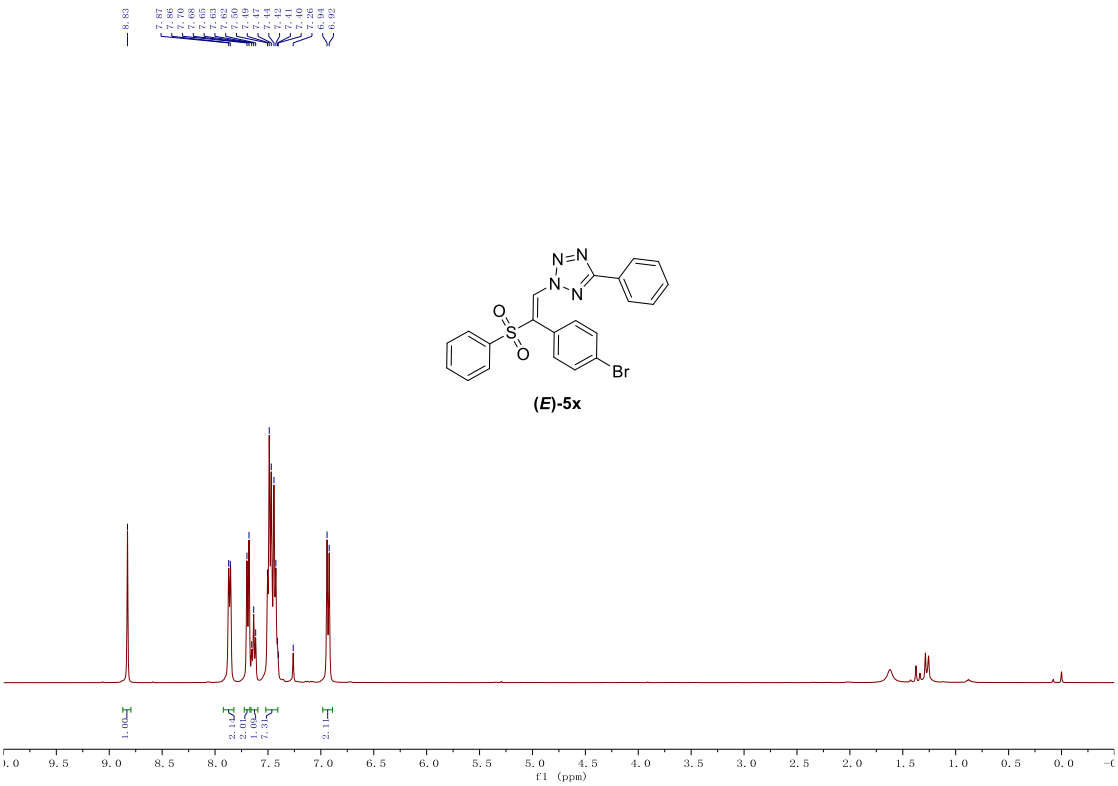
^{1}H NMR (400 MHz) Spectrum of (*E*)-5w in $CDCl_3$



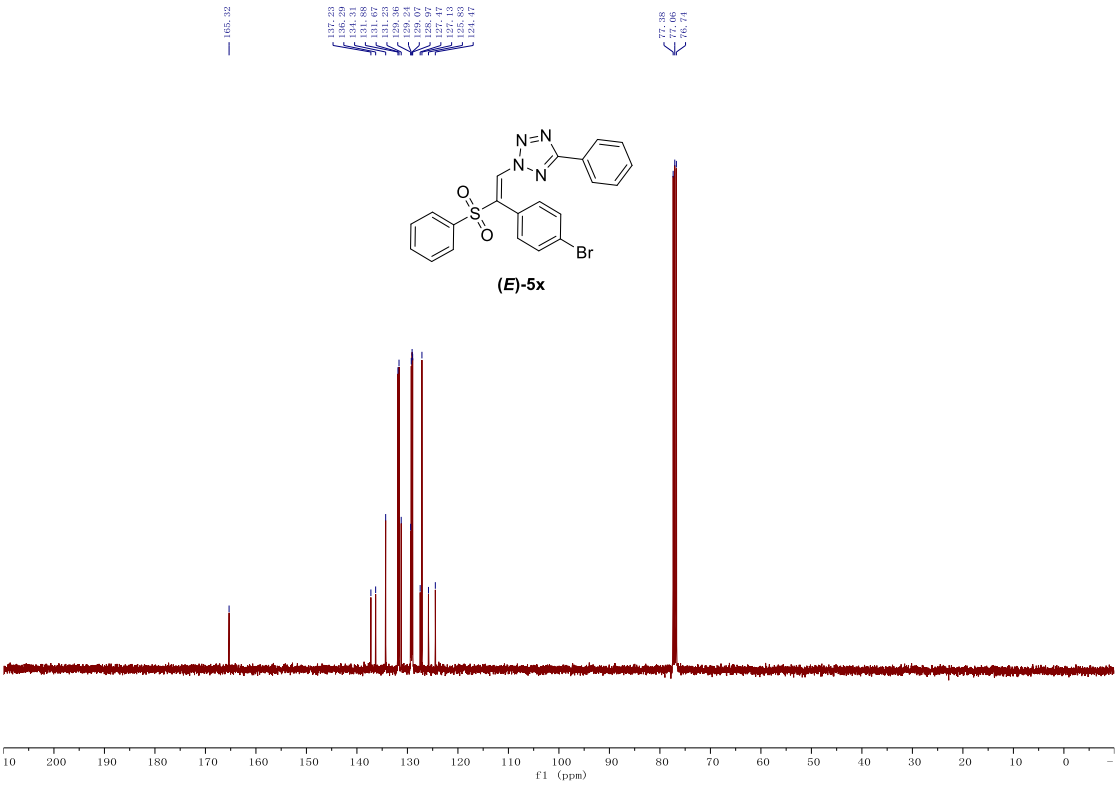
^{13}C NMR (101 MHz) Spectrum of (*E*)-5w in $CDCl_3$



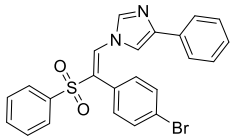
^{1}H NMR (400 MHz) Spectrum of (*E*)-5x in $CDCl_3$



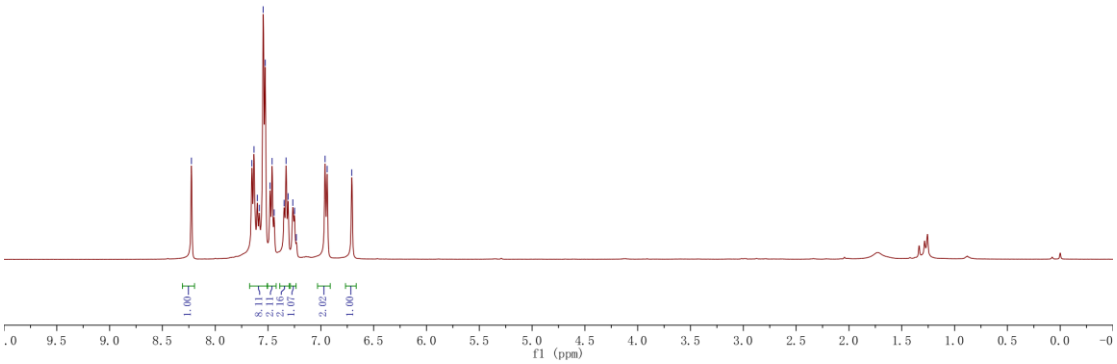
^{13}C NMR (101 MHz) Spectrum of (*E*)-5x in $CDCl_3$



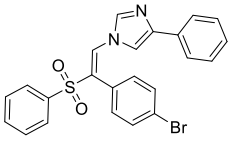
^{1}H NMR (400 MHz) Spectrum of (*E*)-5y in $CDCl_3$



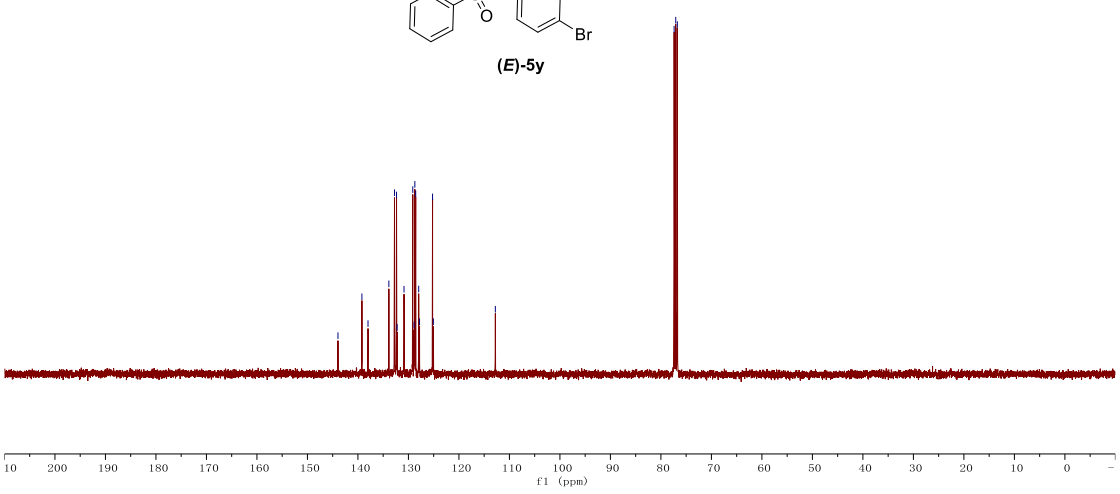
(*E*)-5y



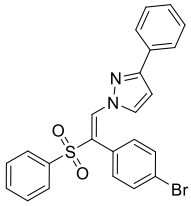
^{13}C NMR (101 MHz) Spectrum of (*E*)-5y in $CDCl_3$



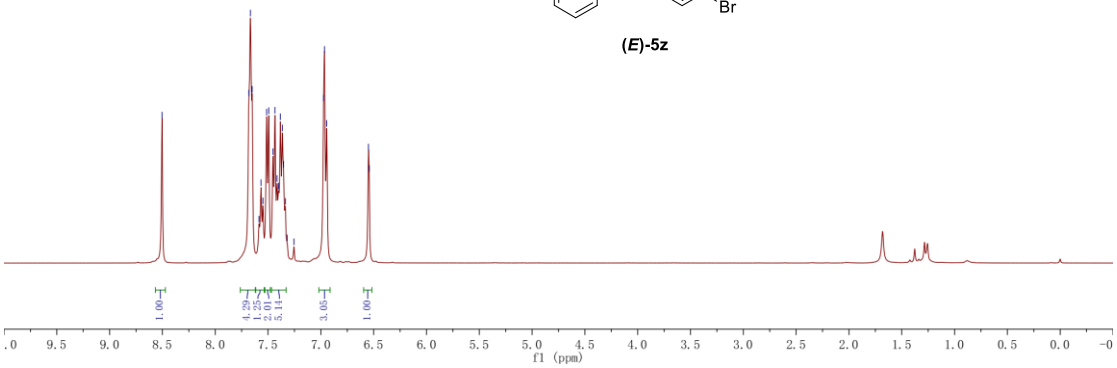
(*E*)-5y



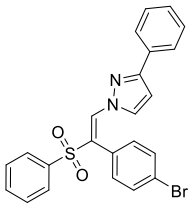
^{1}H NMR (400 MHz) Spectrum of (*E*)-5z in $CDCl_3$



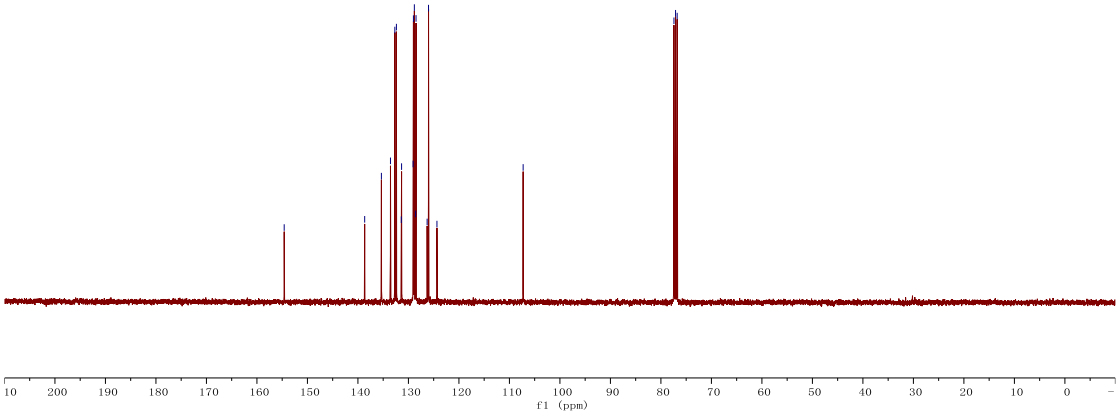
(*E*)-5z



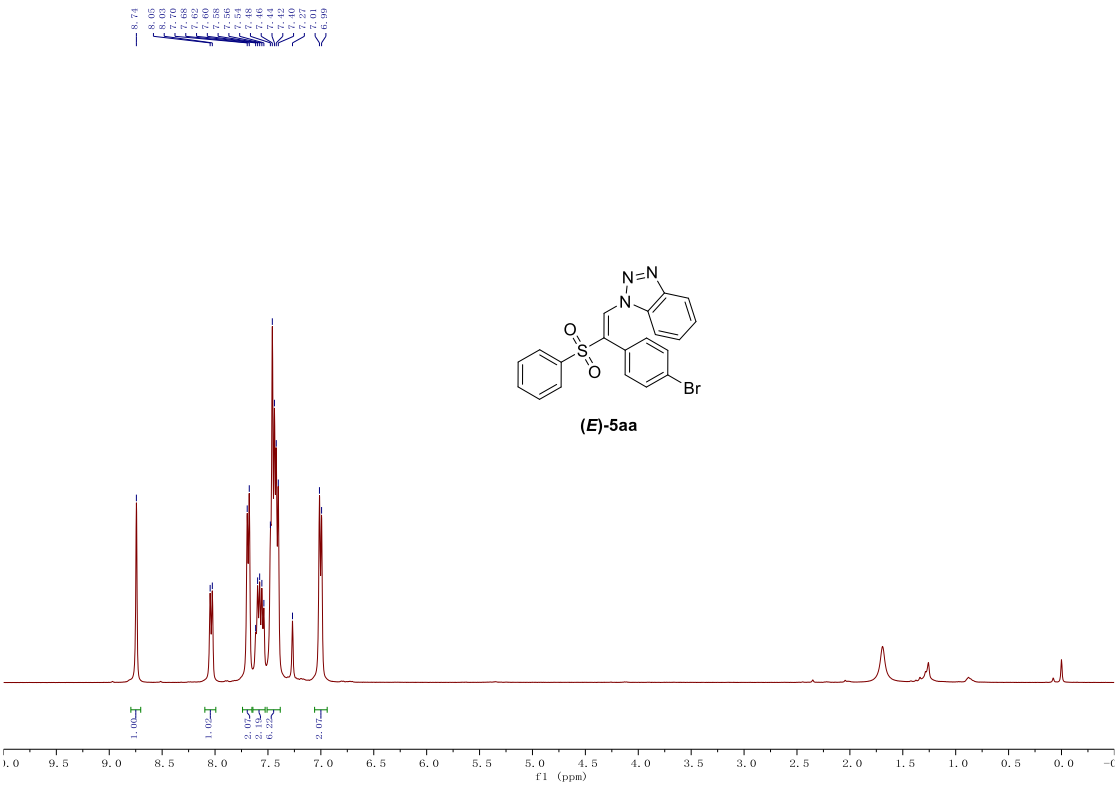
^{13}C NMR (101 MHz) Spectrum of (*E*)-5z in $CDCl_3$



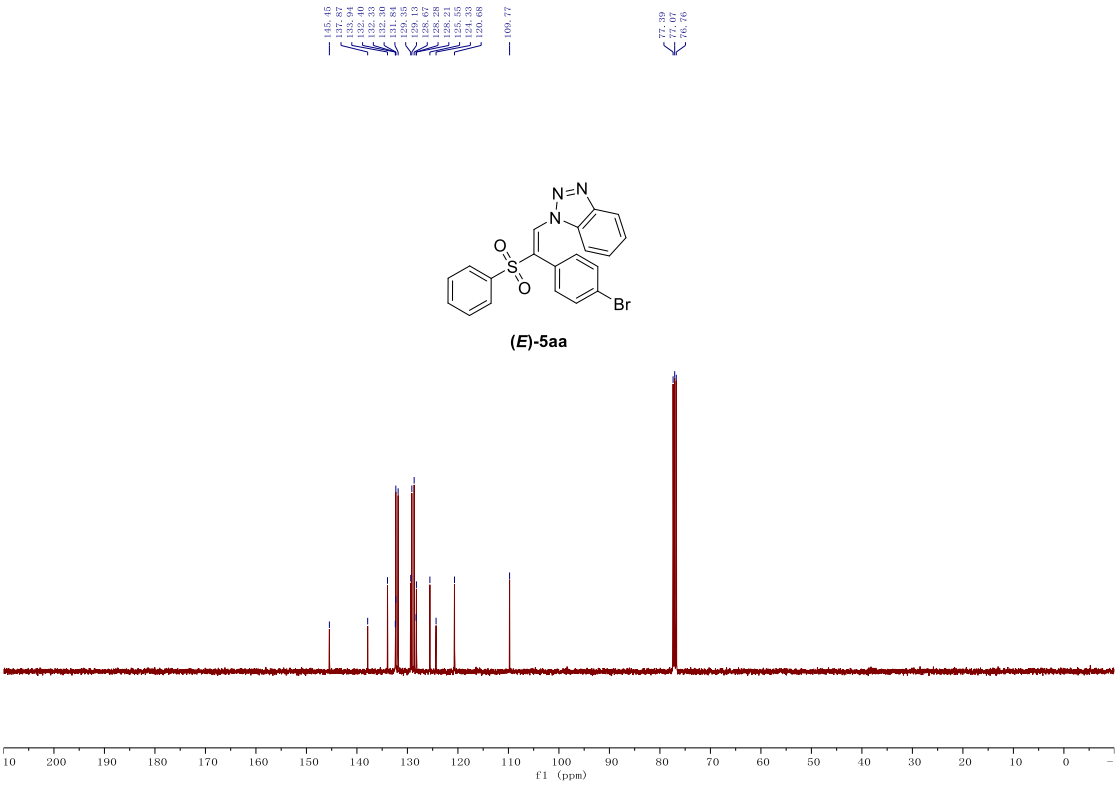
(*E*)-5z



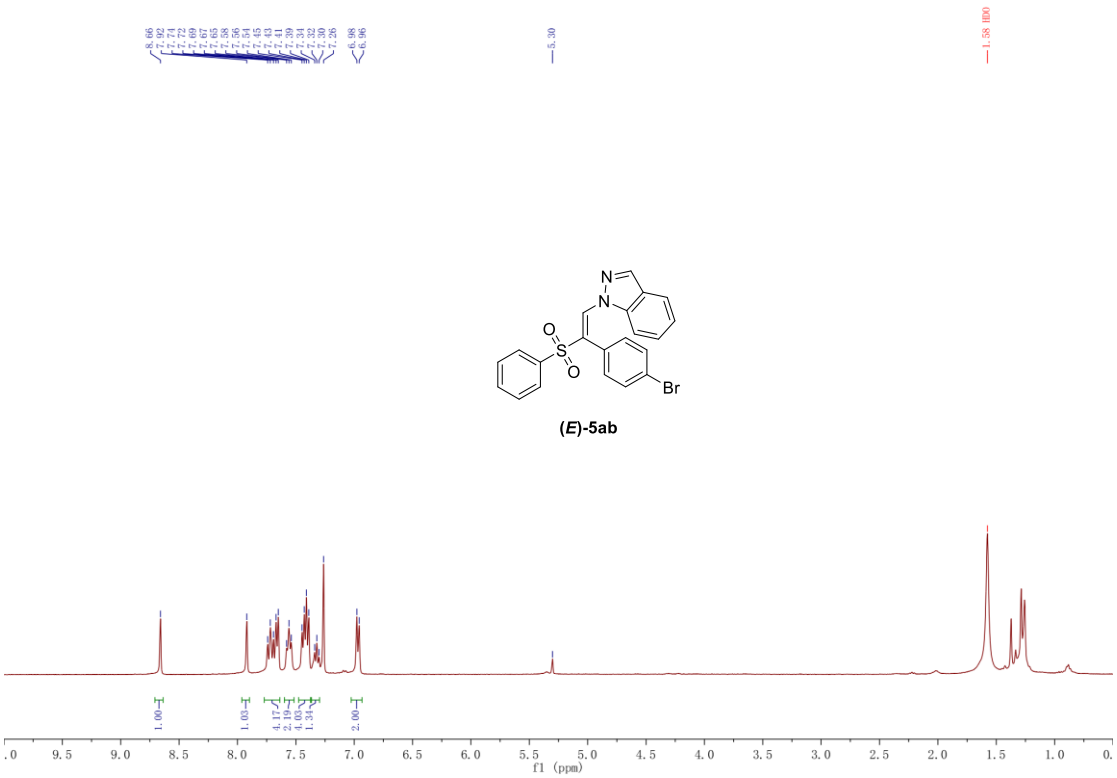
^{1}H NMR (400 MHz) Spectrum of (*E*)-5aa in $CDCl_3$



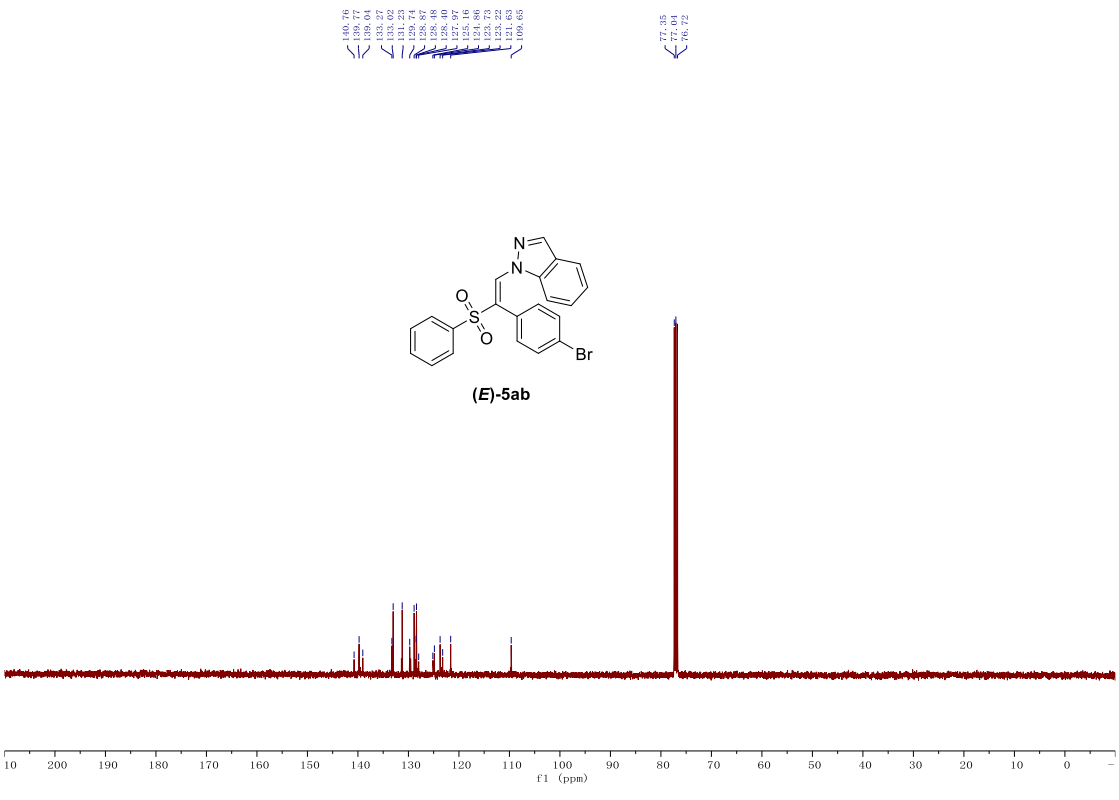
^{13}C NMR (101 MHz) Spectrum of (*E*)-5aa in $CDCl_3$



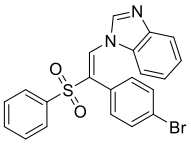
^{1}H NMR (400 MHz) Spectrum of (*E*)-5ab in $CDCl_3$



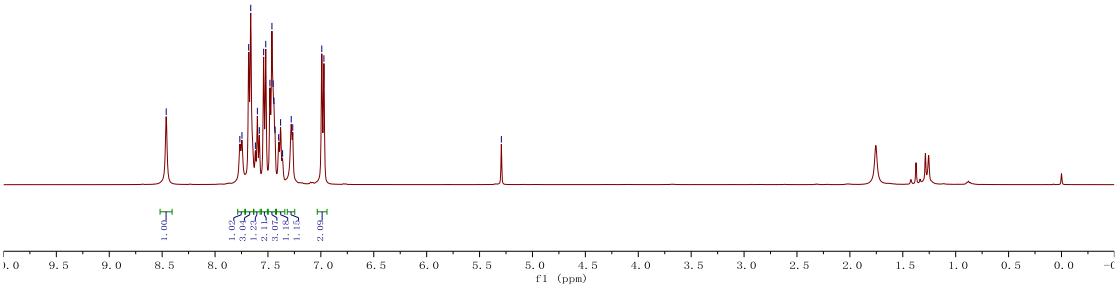
^{13}C NMR (101 MHz) Spectrum of (*E*)-5ab in $CDCl_3$



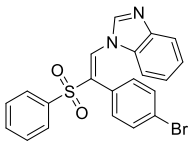
^{1}H NMR (400 MHz) Spectrum of (*E*)-5ac in $CDCl_3$



(*E*)-5ac

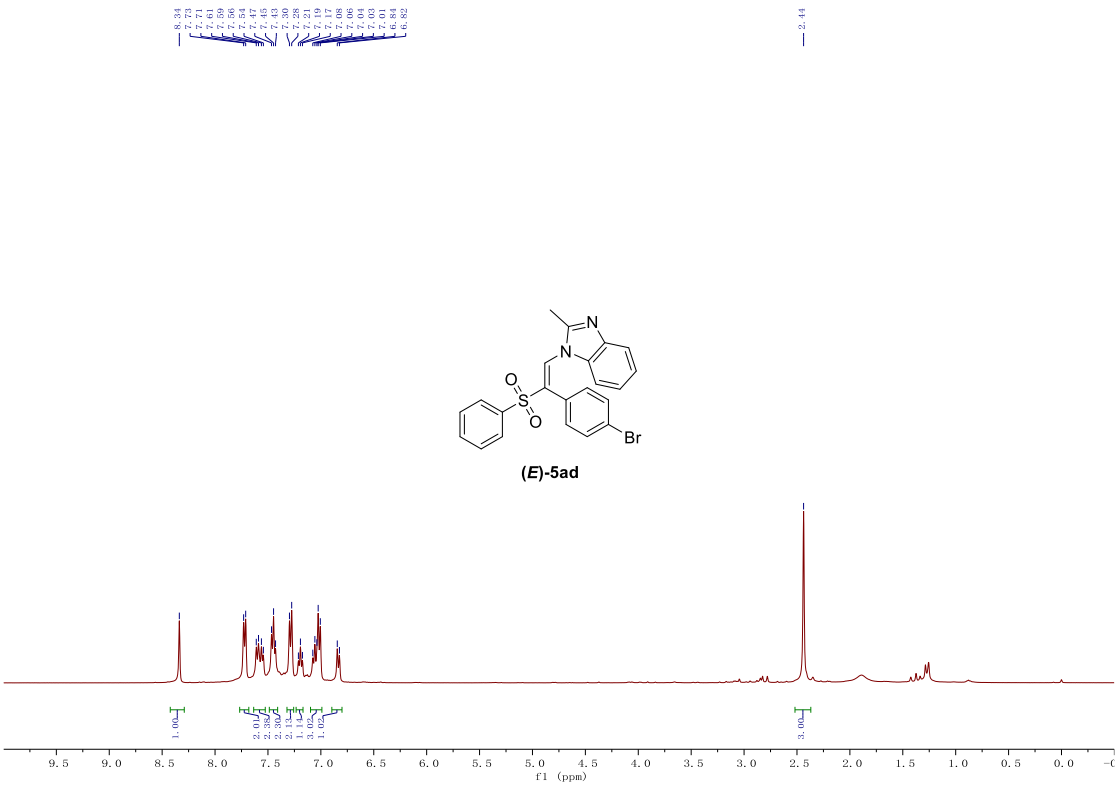


^{13}C NMR (101 MHz) Spectrum of (*E*)-5ac in $CDCl_3$

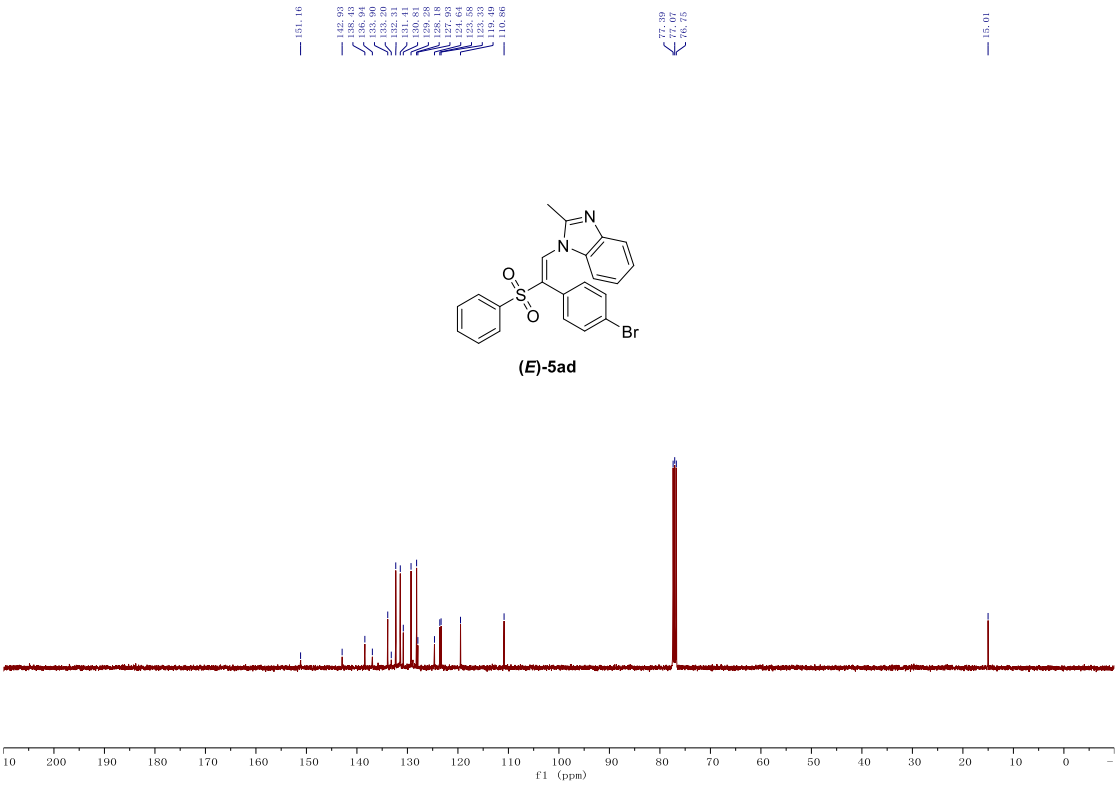


(*E*)-5ac

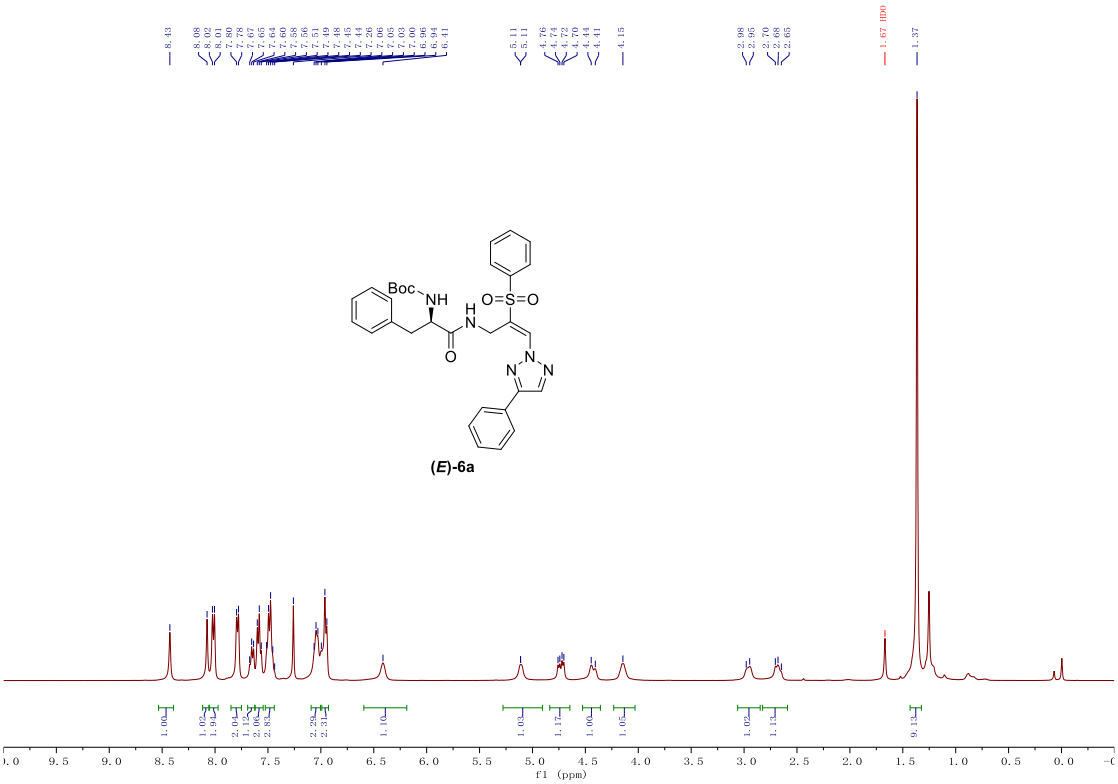
^{1}H NMR (400 MHz) Spectrum of (*E*)-5ad in $CDCl_3$



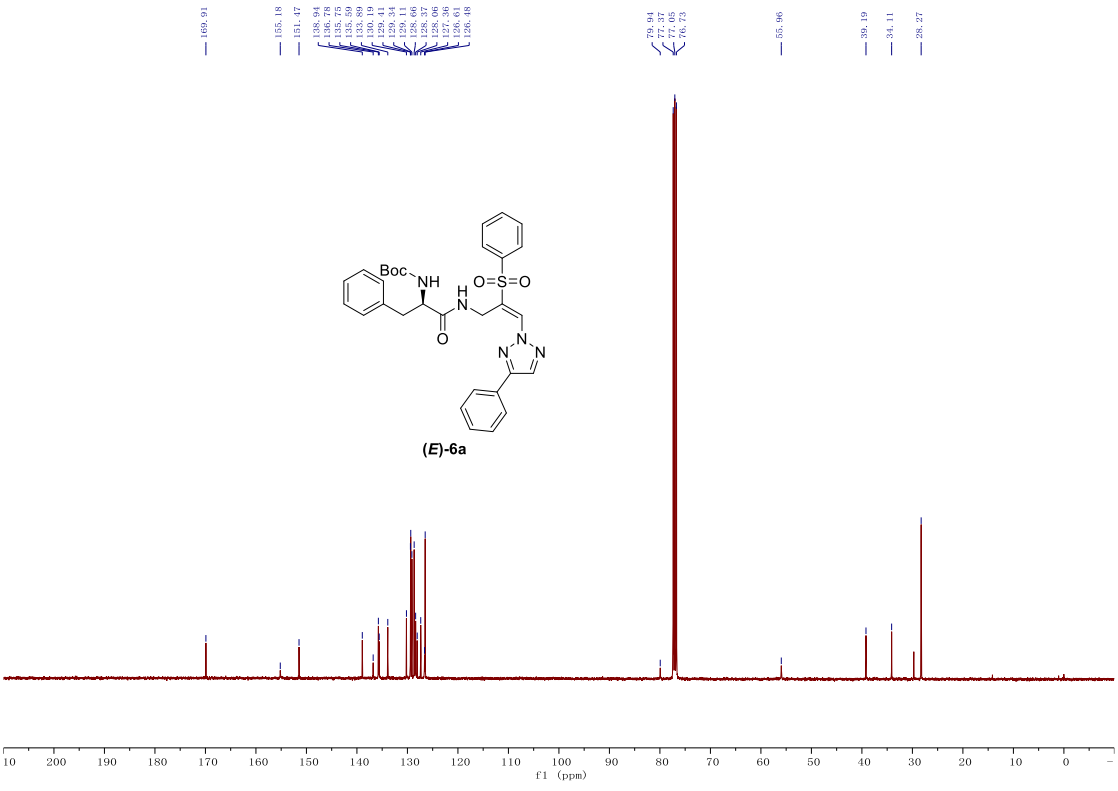
^{13}C NMR (101 MHz) Spectrum of (*E*)-5ad in $CDCl_3$



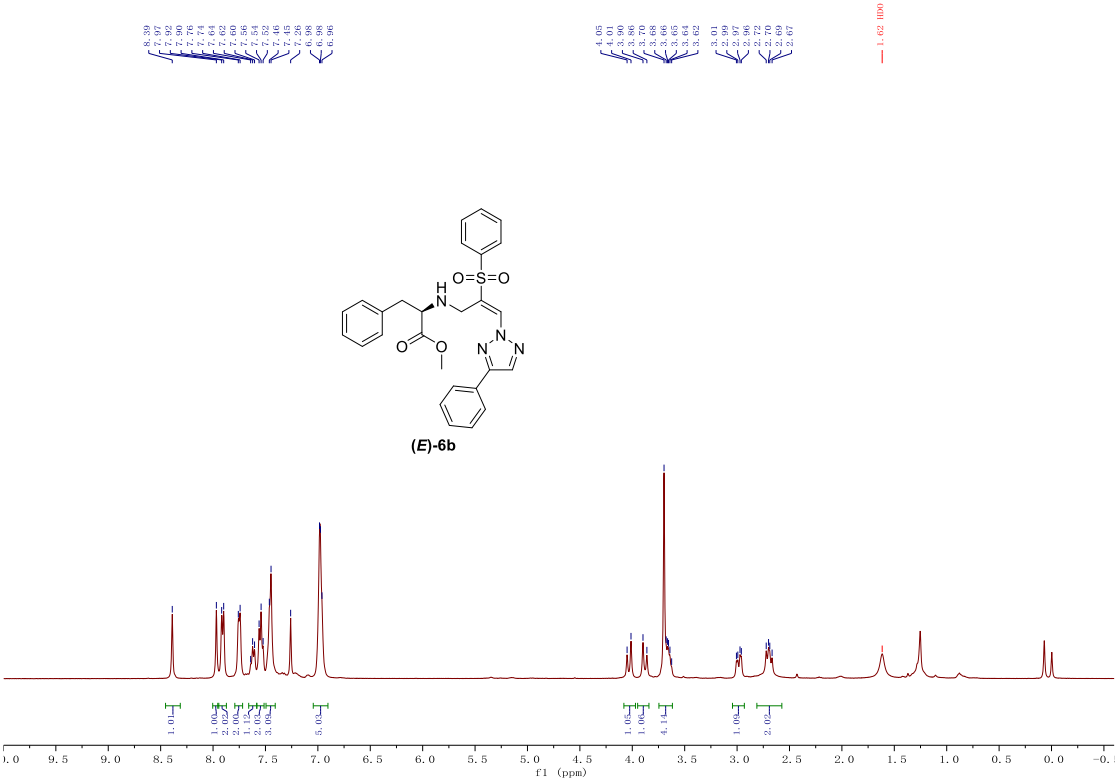
^{1}H NMR (400 MHz) Spectrum of (*E*)-6a in $CDCl_3$



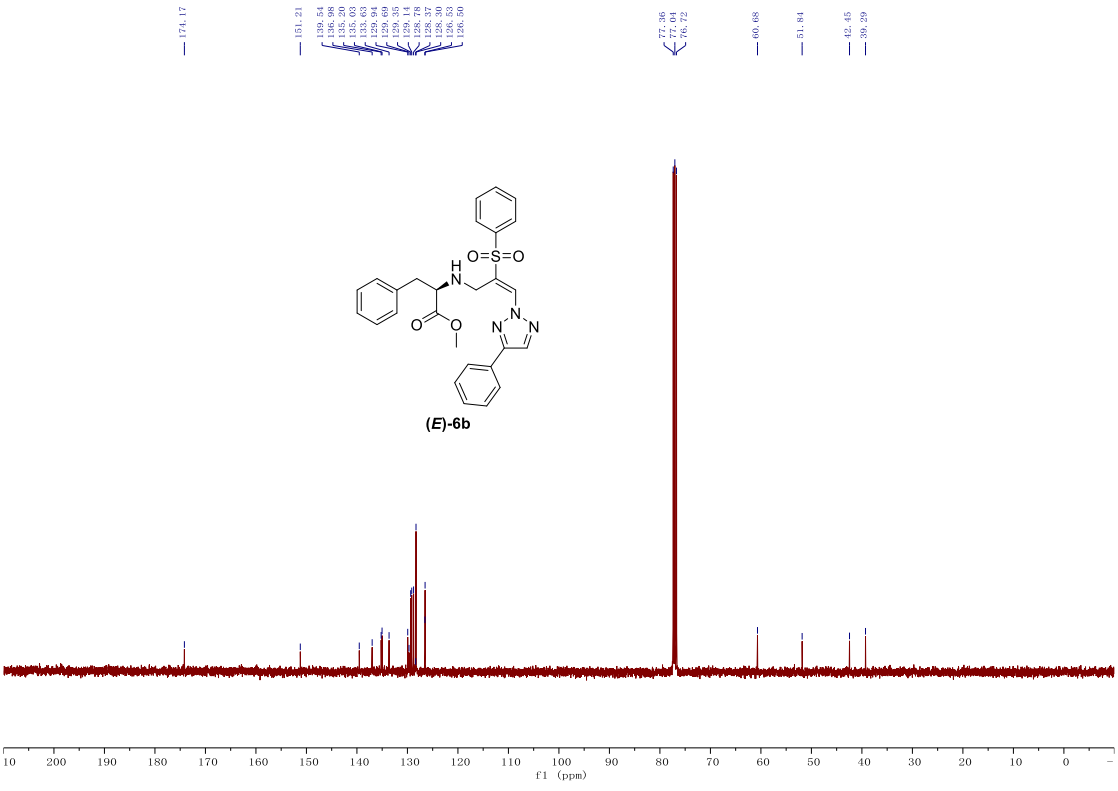
^{13}C NMR (101 MHz) Spectrum of (*E*)-6a in $CDCl_3$



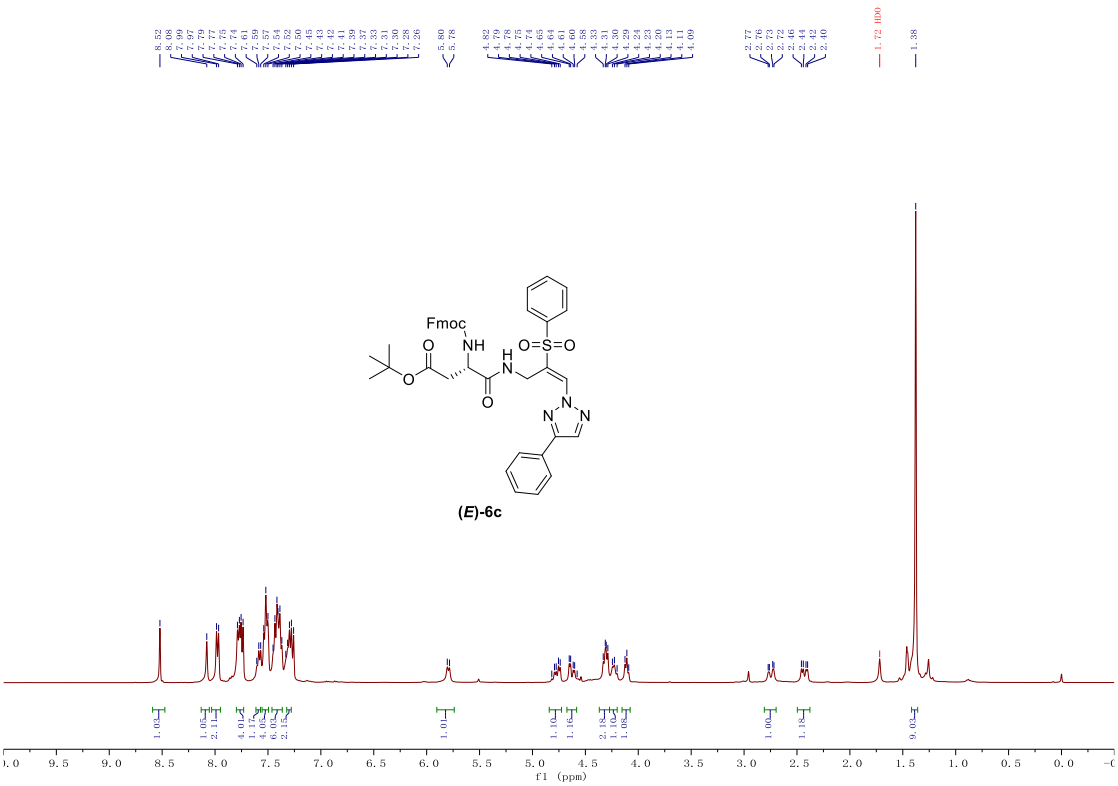
^{1}H NMR (400 MHz) Spectrum of (*E*)-6b in $CDCl_3$



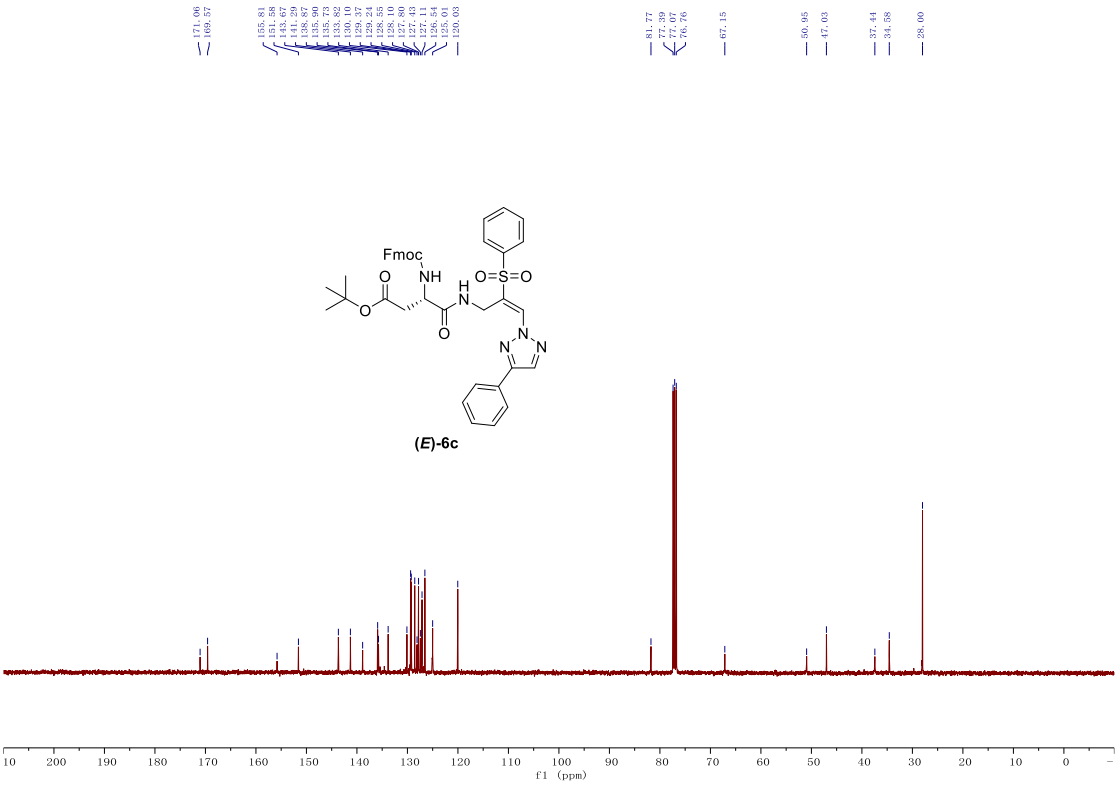
^{13}C NMR (101 MHz) Spectrum of (*E*)-6b in $CDCl_3$



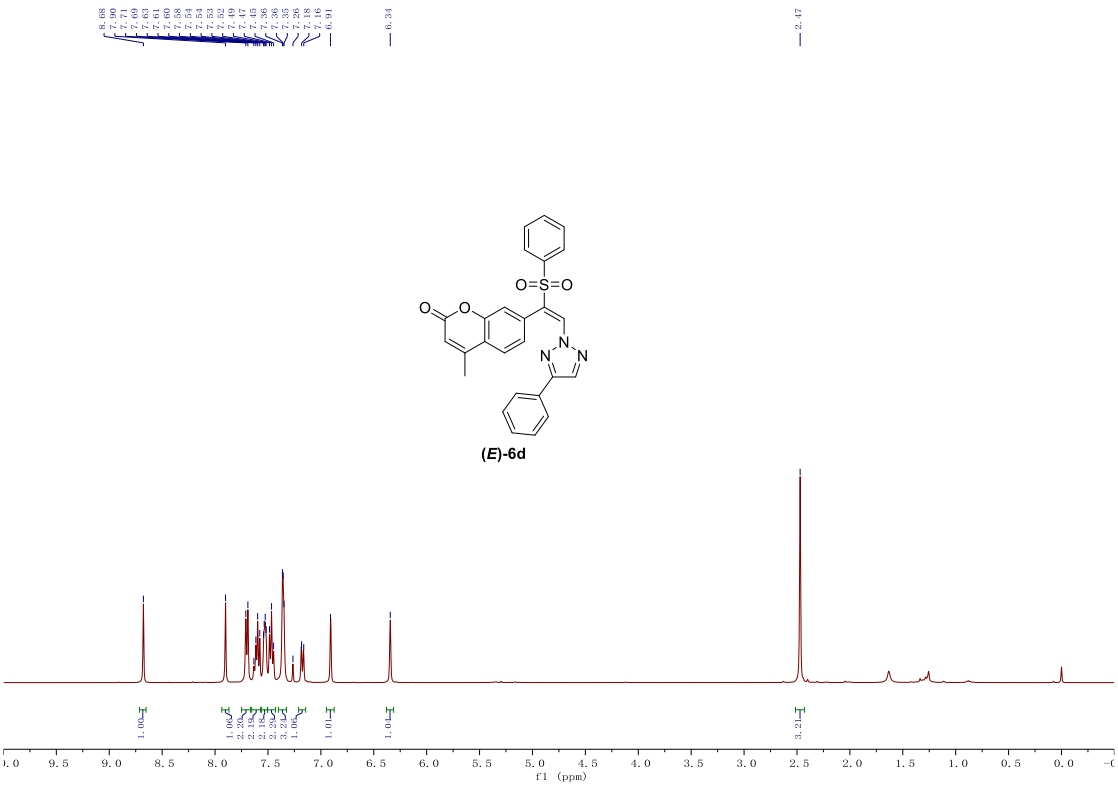
^{1}H NMR (400 MHz) Spectrum of (*E*)-6c in $CDCl_3$



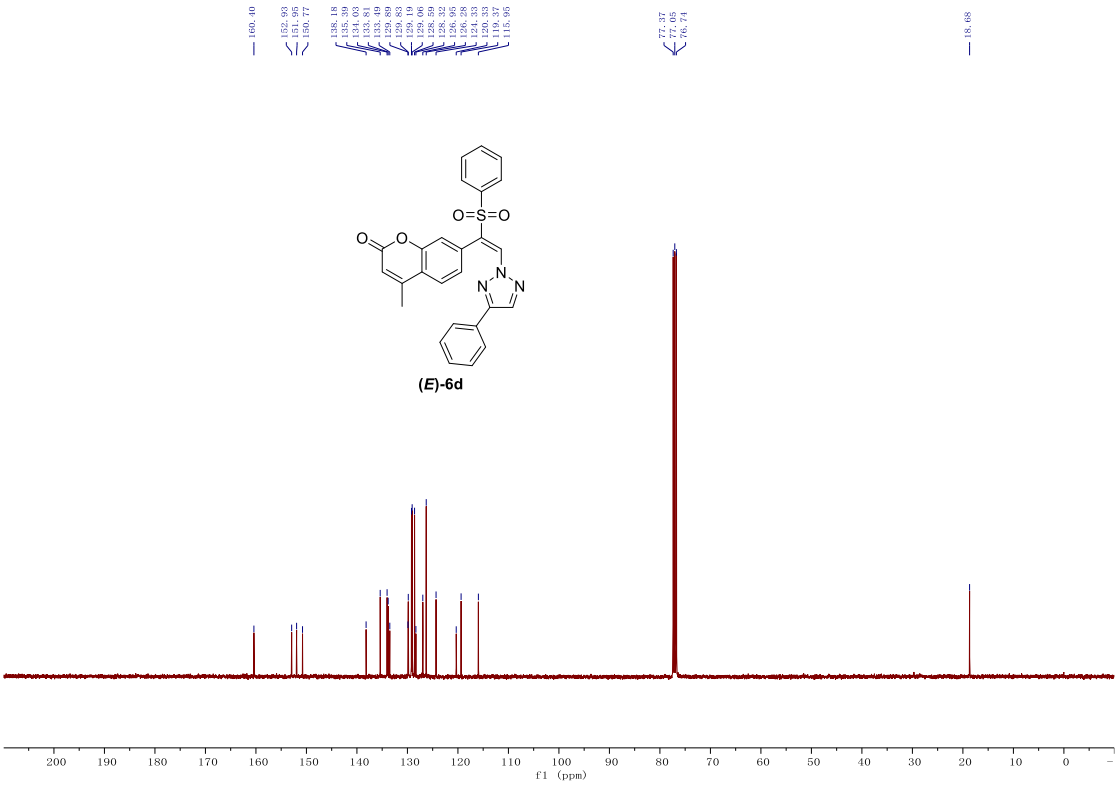
^{13}C NMR (101 MHz) Spectrum of (*E*)-6c in $CDCl_3$



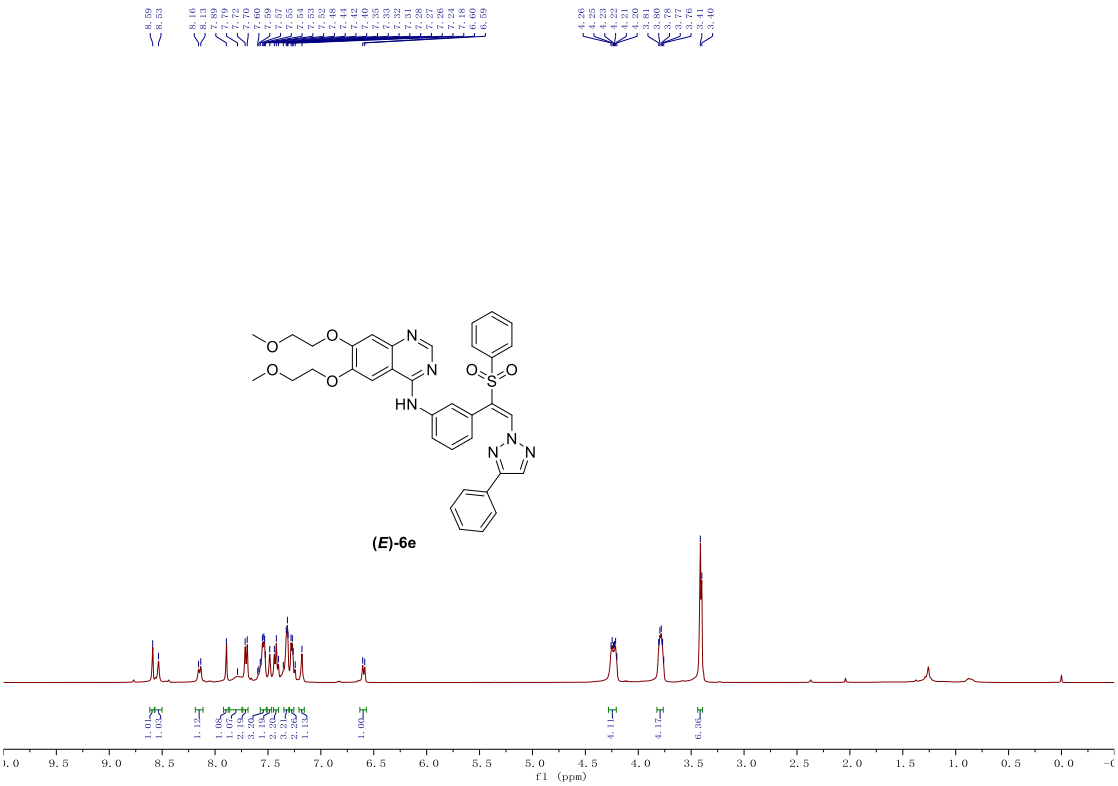
^{1}H NMR (400 MHz) Spectrum of (*E*)-6d in $CDCl_3$



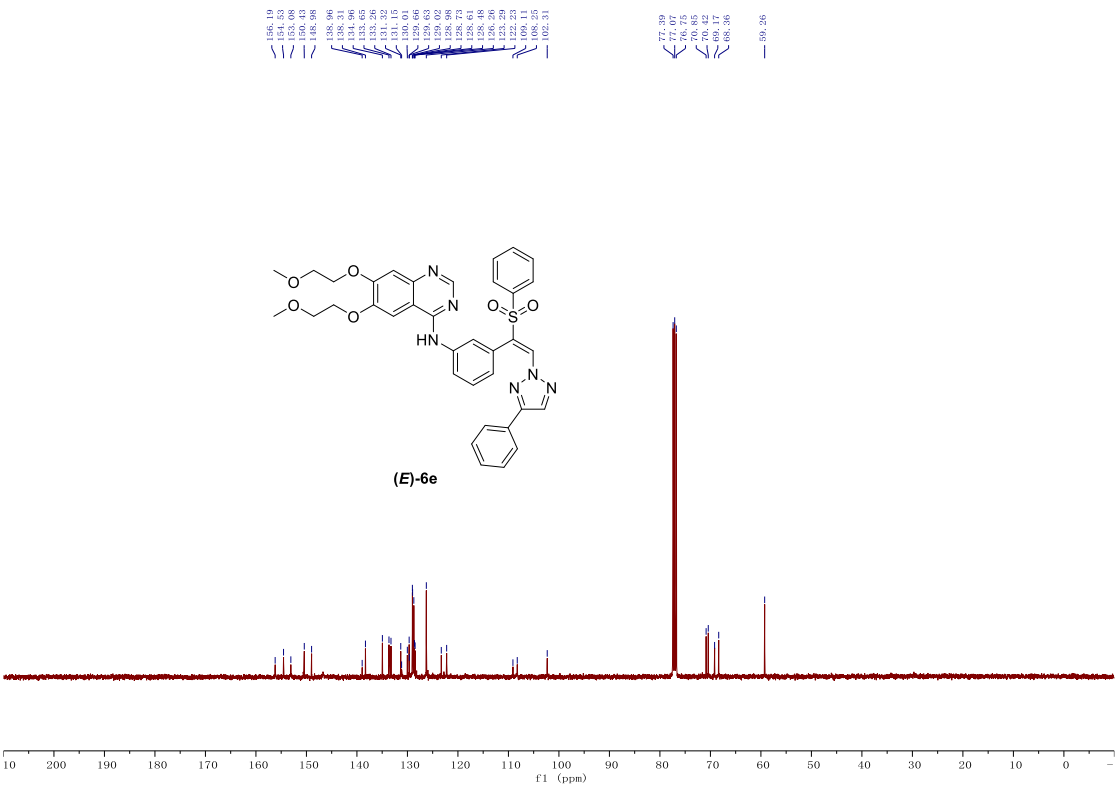
^{13}C NMR (101 MHz) Spectrum of (*E*)-6d in $CDCl_3$



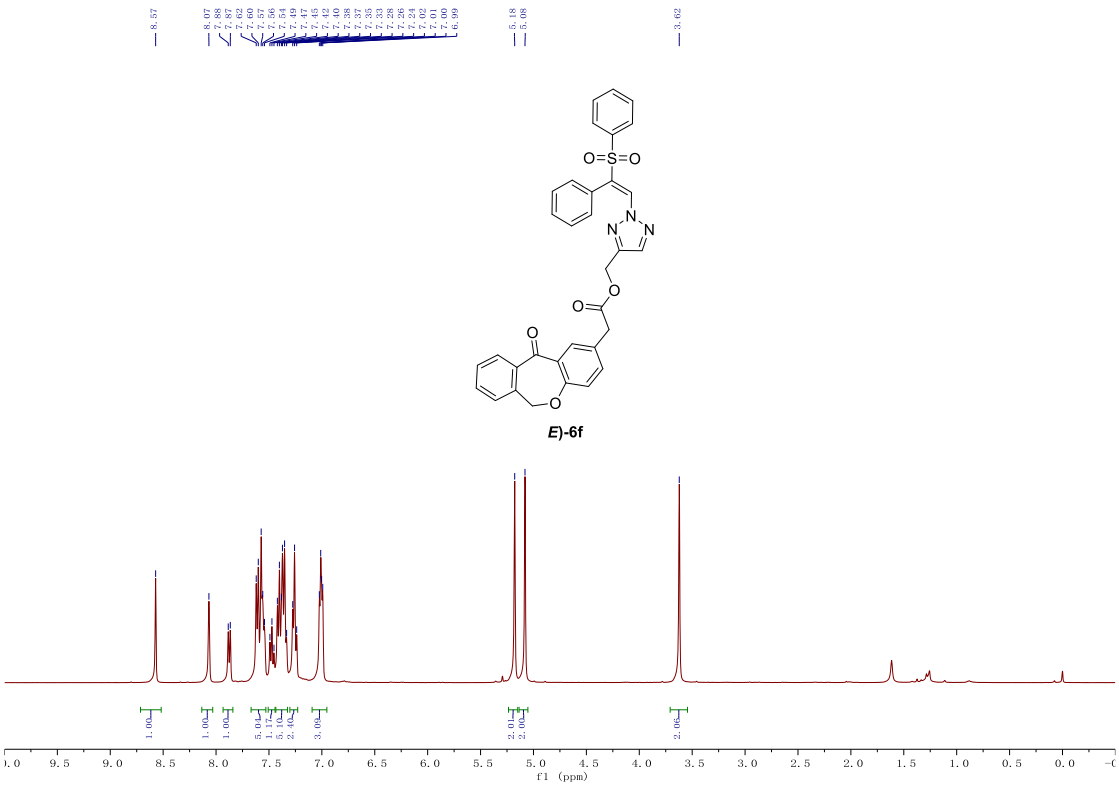
^{1}H NMR (400 MHz) Spectrum of (*E*)-6e in $CDCl_3$



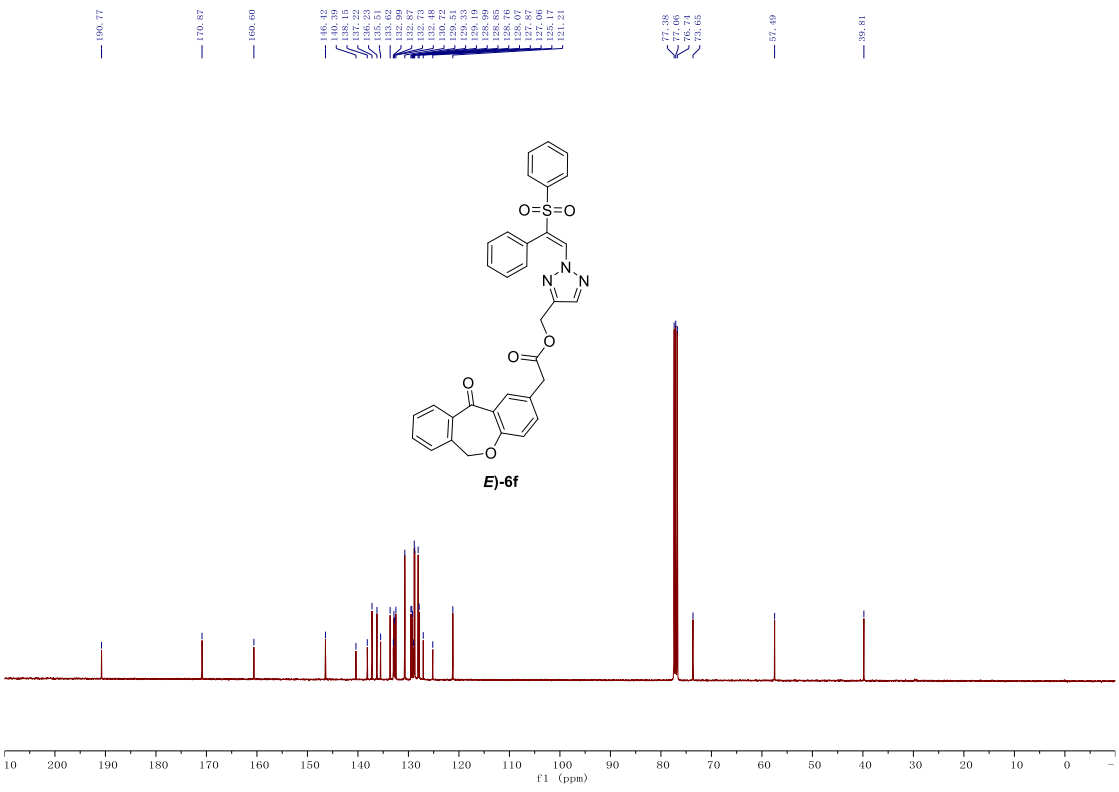
^{13}C NMR (101 MHz) Spectrum of (*E*)-6e in $CDCl_3$



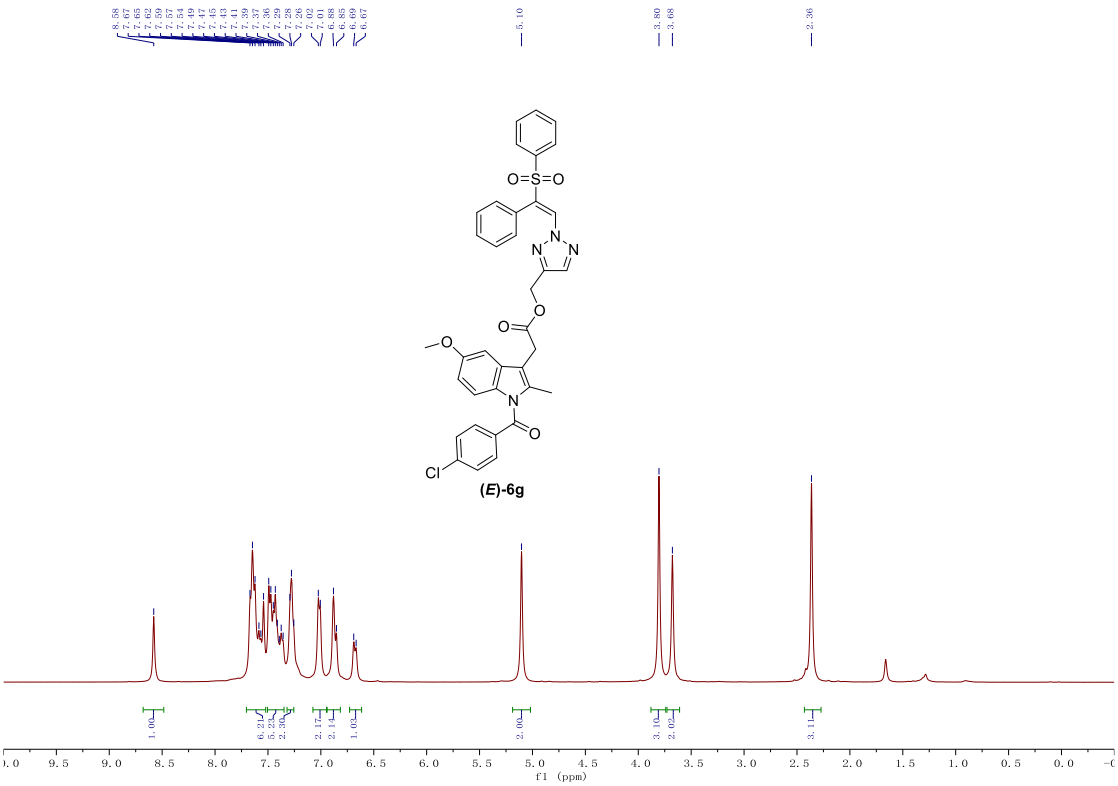
^{1}H NMR (400 MHz) Spectrum of (*E*)-6f in $CDCl_3$



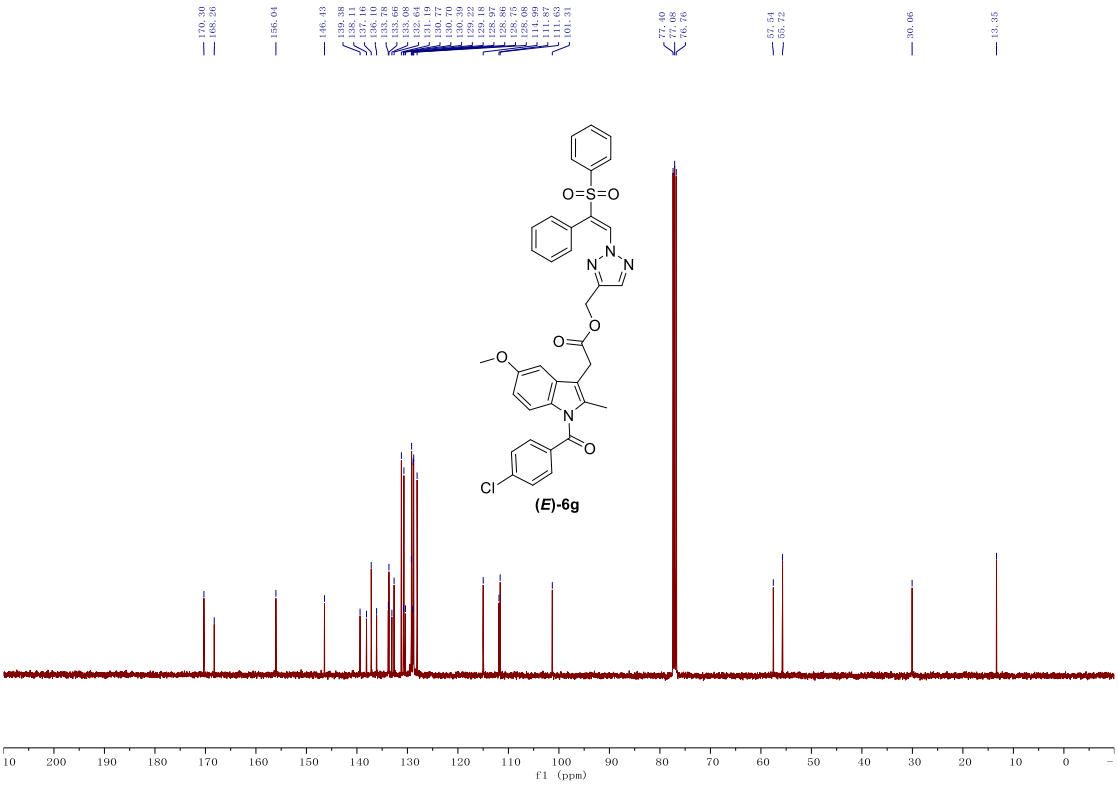
^{13}C NMR (101 MHz) Spectrum of (*E*)-6f in $CDCl_3$



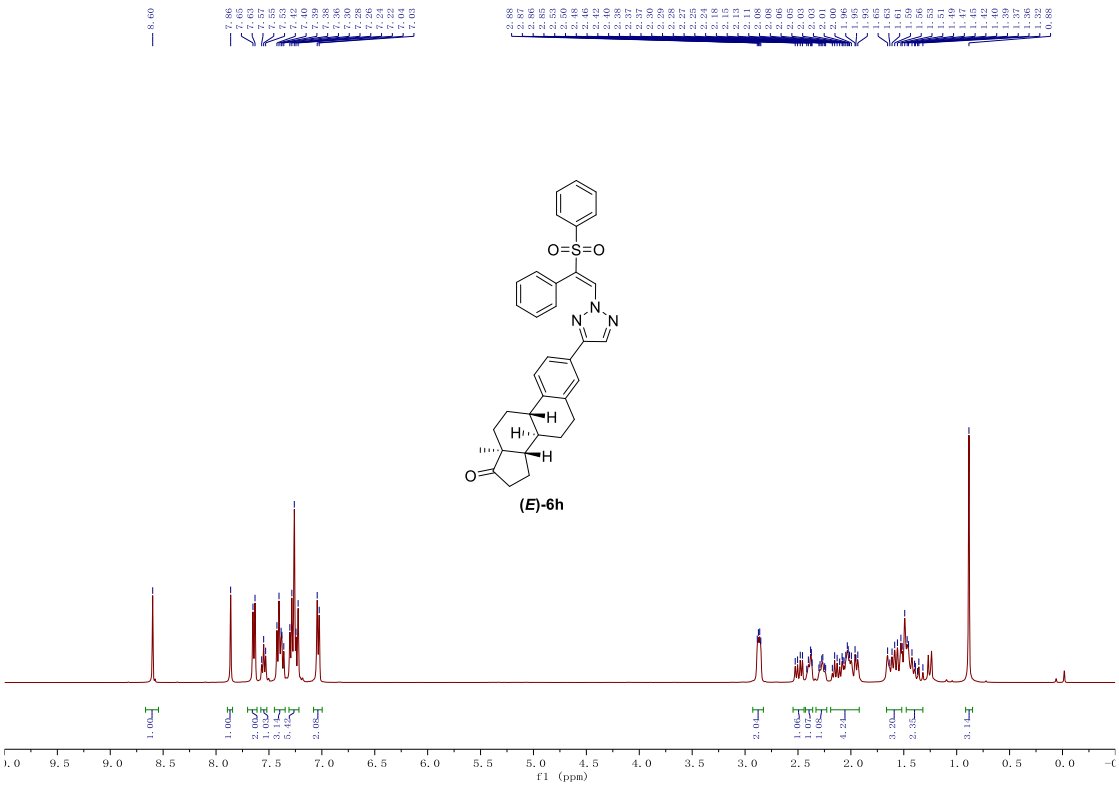
^{1}H NMR (400 MHz) Spectrum of (*E*)-6g in $CDCl_3$



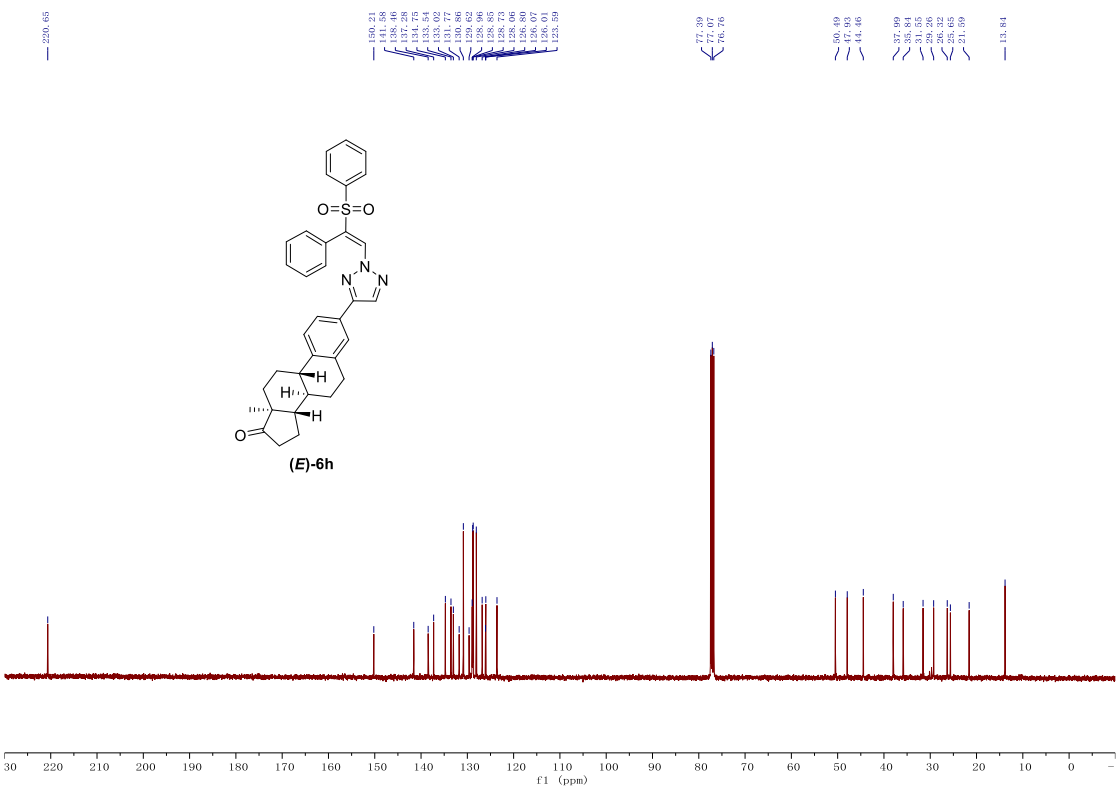
^{13}C NMR (101 MHz) Spectrum of (*E*)-6g in $CDCl_3$



^{1}H NMR (400 MHz) Spectrum of (*E*)-6h in $CDCl_3$

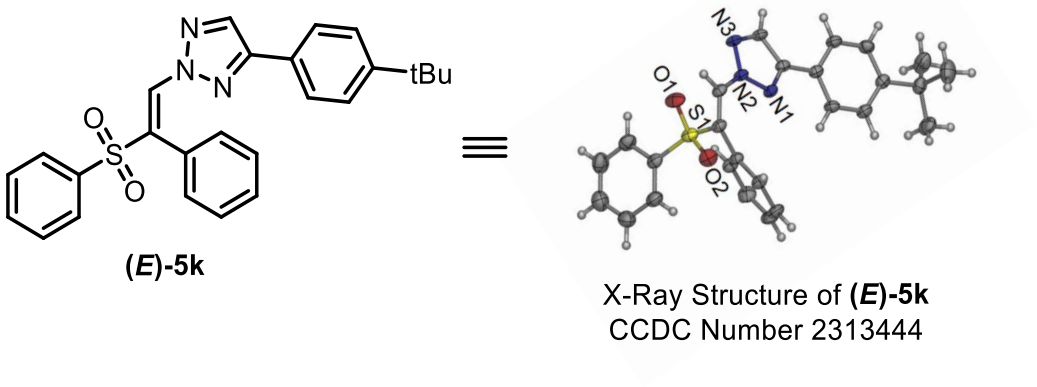


^{13}C NMR (101 MHz) Spectrum of (*E*)-6h in $CDCl_3$



9. Determination of the Absolute Configuration

The method for the crystal growth of **(*E*)-5k** is as follows: In a 10 mL vial, **(*E*)-5k** (30 mg) was dissolved in 2 mL DCM, then 5 mL hexane was added carefully, making a clear stratification of solution. The vial was placed at -20 ^{0}C about 10 days.



X-ray crystallography of (*E*)-5k

Crystal data and structure refinement

Identification code	exp_3736_auto
Empirical formula	$C_{26}H_{25}N_3O_2S$
Formula weight	443.55
Temperature/K	173.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.7738(3)
b/Å	16.7514(3)
c/Å	11.9627(3)

α/°	90
β/°	99.423(2)
γ/°	90
Volume/Å^3	2327.54(9)
Z	4
ρ_{calc}g/cm^3	1.266
μ/mm^{-1}	1.452
F(000)	936.0
Crystal size/mm^3	0.26 × 0.22 × 0.16
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.166 to 134.154
Index ranges	-14 ≤ h ≤ 13, -20 ≤ k ≤ 15, -14 ≤ l ≤ 14
Reflections collected	25756
Independent reflections	4160 [R_{int} = 0.0869, R_{sigma} = 0.0538]
Data/restraints/parameters	4160/0/293
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0481, wR_2 = 0.1187
Final R indexes [all data]	R_1 = 0.0545, wR_2 = 0.1232
Largest diff. peak/hole / e Å^{-3}	0.66/-0.41

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