

Electrochemical Oxidative One-Pot Fashion of Diazo Compounds with Triazoles and Nucleophiles

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Contents	Page
1. General Information	S2
2. General Procedure for the start materials and the Electrolysis	S4
3. Cyclic Voltammetry Studies	S8
4. Measure of charge consumption	S9
5. Control experiments	S10
6. Characterization data of products 4	S12
7. The electron paramagnetic resonance (EPR) experiment	S13
8. Anode potential monitoring	S15
9. Characterization Data for the Electrolysis Products	S16
10. NMR Spectra for New Compounds	S26
11. References	S72

1. Supplementary Methods

1.1 General Information

All reactions and manipulations were carried out under nitrogen atmosphere, in a 50 mL three-neck flask equipped with a stir bar and Platinum plate (1.0×1.0 cm²) electrodes. Pt plate electrodes and graphite plate electrodes are purchased from Beijing Jingke Instrument Science Instruments Co., Ltd. The instrument for electrolysis is dual display potentiostat (HSPY-36-03) (purchased from Beijing Hansheng Puyuan Technology Co., Ltd). The commercially available reagents were used without purification. Solvents and commercially available reagents were used without purification. Flash column chromatography was performed with silica gel (300–400 mesh). All ¹H NMR, ¹⁹F NMR and ¹³C NMR spectra were recorded using a Bruker 400 MHz spectrometer at 25 °C in solvents as indicated. Chemical shift values are reported in ppm with the solvent resonance refereed to the standard position (CDCl₃: ¹H NMR: δ = 7.26; ¹³C NMR: δ = 77.16). The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet and dd, doublet of doublets. The coupling constants J are reported in Hertz (Hz). LC-MS spectra were recorded on the HP-5989 instrument by ESI methods. High-resolution mass spectrometry (HRMS) was performed on IonSpec FT-ICR or Waters Micromass Q-TOF micro Synapt High-Definition Mass Spectrometer.

1.2 Experimental set-up

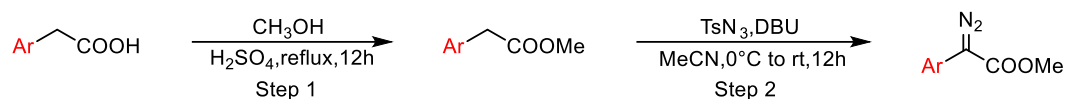
Platinum plate electrode (1.5 cm × 1.5 cm × 1 mm), rubber plug, undivided three-neck bottle were used in the experimental device.



Some photos of electrolysis device.

2. General Procedure for the start materials and the Electrolysis

2.1. General Procedures for Diazos ¹⁻⁴ (GP1)

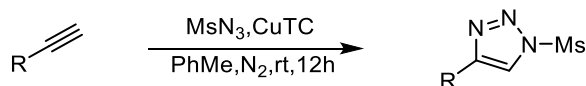


Step 1: To a stirred solution of aryl acetic acid (1.0 eq.) in MeOH was added sulfuric acid (0.5 mL) dropwise and heated to reflux. Stirring was then continued for 2 hours. The reaction mixture was then cooled and poured into saturated aqueous NaHCO₃ and extracted with EtOAc. The combined organic fractions were dried over Na₂SO₄, filtered, and concentrated under reduced pressure to crude product that was not further purified.

Step 2: To a mixture of methyl aryl acetate (1.0 eq.) and tosyl azide (1.5 eq.) in anhydrous CH₃CN (25.0 mL), 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) (1.5 eq.) was added slowly under 0°C. The reaction mixture was stirred at room temperature overnight. Upon complete consumption of the starting materials, the reaction mixture was quenched with saturated aqueous solution of NH₄Cl (5.0 mL), extracted with DCM (3 × 30 mL), washed with brine (3 × 10 mL), dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (ethyl acetate/petroleum ether) to give the diazos.

2.2 General procedure for preparation of *N*-sulfonyl-1,2,3-triazoles (GP2)

N-sulfonyl-1,2,3-triazoles were prepared from the corresponding alkynes and sulfonyl azides according to previously reported synthetic procedures.⁴⁻⁸ *Attention! Sulfonyl azides are potentially explosive materials and must be handled with caution!* Due to the potential danger of methane sulfonyl azide, we strongly recommend to avoid isolating this compound in large quantities.

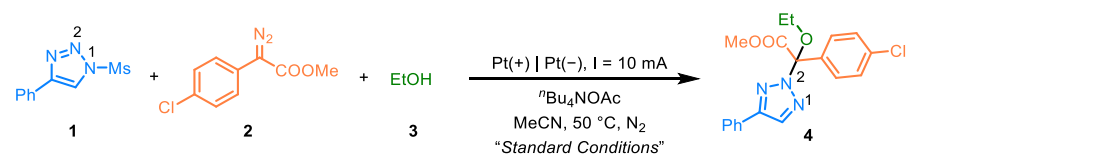


A scintillation vial was charged with copper (I) thiophene-2-carboxylate (CuTC, 0.1 eq.), toluene (20 mL), and the alkyne (1.0 eq.). The reaction mixture was cooled in an ice-water bath. Subsequently, the sulfonyl azide (1.0 eq.) was added slowly as the limiting reagent to avoid a runaway exotherm, and the reaction mixture allowed to warm to room temperature and stirred overnight. The reaction was diluted with saturated aq. NH₄Cl and extracted into DCM (2 × 20 mL). The combined organics were dried (Na₂SO₄) and filtered through celite. The eluent was

concentrated in vacuo. The obtained crude product was purified by SiO₂-column chromatography to give the desired product *N*-sulfonyl-1,2,3-triazoles.

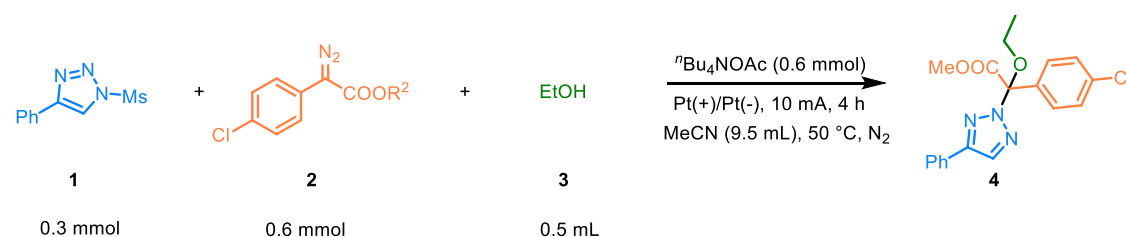
2.3 General Procedure for the Electrolysis (GP3)

Table 1. Optimization of the reaction conditions ^a



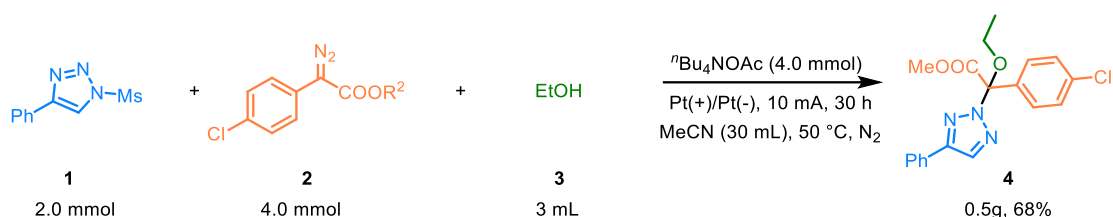
Entry	deviation from standard conditions	Yield ^b (%)
1	none	75 (4.16 F mol ⁻¹ , 48%) ^c
2	5 mA	47
3	15 mA	51
4	reaction at rt	58
5	reaction at 80 °C	69
6	C(+) Pt(-) instead of Pt(+) Pt(-)	41
7	ⁿ Bu ₄ NBF ₄ instead of ⁿ Bu ₄ NOAc	42
8	no electricity	0
9	In air	60
10	DCE as the solvent	36
11	1 (0.3 mmol), 2 (0.3 mmol), EtOH (0.5 mL)	41
12	1 (0.6 mmol), 2 (0.3 mmol), EtOH (0.5 mL)	29
13	1 (0.3 mmol), 2 (0.6 mmol), EtOH (0.2 mL)	55

^a Reaction conditions: undivided cell, Pt anode and Pt cathode, **1** (0.3 mmol), **2** (0.6 mmol), EtOH (0.5 mL), ⁿBu₄NOAc (0.6 mmol), MeCN (9.5 mL), N₂, 10 mA, 50 °C, 4 h. DCE: Dichloroethane. ^b Yield of isolated product. ^c Charge consumption and Faradaic efficiency.



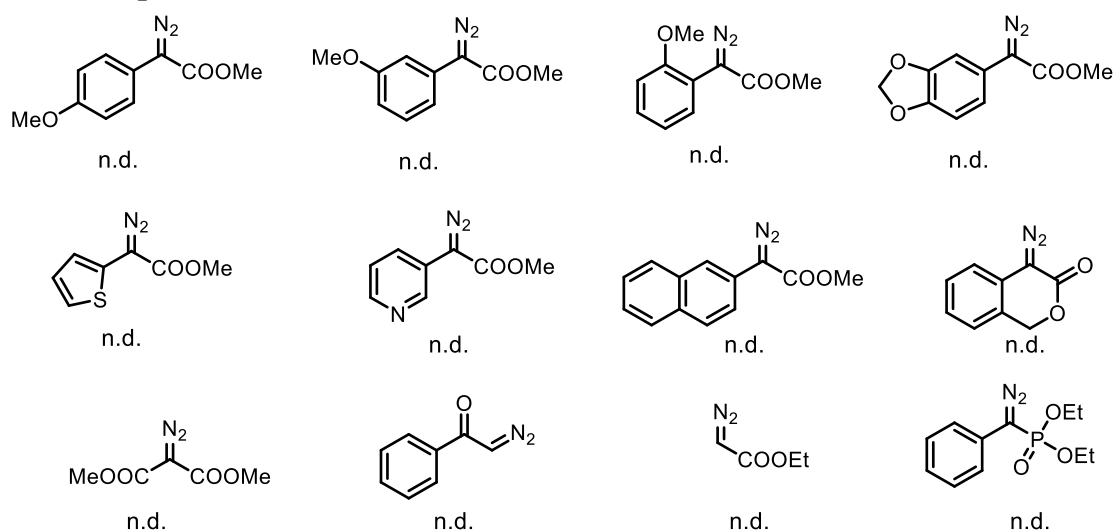
In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, ⁿBu₄NOAc (0.6 mmol) was added. The bottle was equipped with two platinum plates (1.5 cm × 1.5 cm × 1 mm) as the anode and the cathode. Under nitrogen atmosphere, 1-(methylsulfonyl)-4-phenyl-1*H*-1,2,3-triazole (**1**, 0.3 mmol), diazoacetate (**2**, 0.6 mmol), EtOH (**3**, 0.5 mL) and MeCN (9.5 mL) were injected respectively into the tube via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 8 mA for 5 h at 50 °C (oil bath). The reaction mixture was washed with water and extracted with EA (10 mL × 3). The organic layers were combined, dried over Na₂SO₄ and concentrated in vacuum. The pure product **4** was purified by silica gel flash column chromatography (PE/EA) in 75% yield.

2.4 Gram-scale experiments



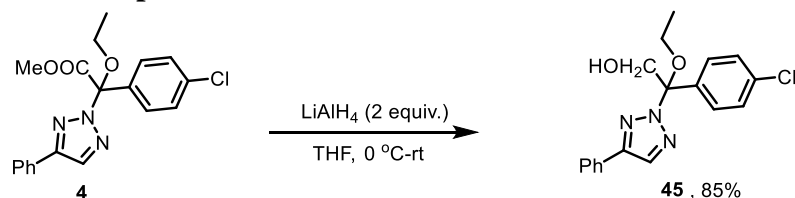
In an oven-dried undivided three-necked bottle (50 mL) equipped with a stir bar, $t\text{Bu}_4\text{NOAc}$ (4.0 mmol) was added. The bottle was equipped with two platinum plates (1.5 cm \times 1.5 cm \times 1 mm) as the anode and the cathode. Under nitrogen atmosphere, 1-(methylsulfonyl)-4-phenyl-1*H*-1,2,3-triazole (**1**, 2.0 mmol), diazoacetate (**2**, 4.0 mmol), EtOH (**3**, 3.0 mL) and MeCN (30.0 mL) were injected respectively into the tube via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 8 mA for 30 h at 50 °C (oil bath). The reaction mixture was washed with water and extracted with EA (10 mL \times 3). The organic layers were combined, dried over Na₂SO₄ and concentrated in vacuum. The pure product **4** was purified by silica gel flash column chromatography (PE/EA) in 68% yield.

2.5 Attempts for other ethers diazos



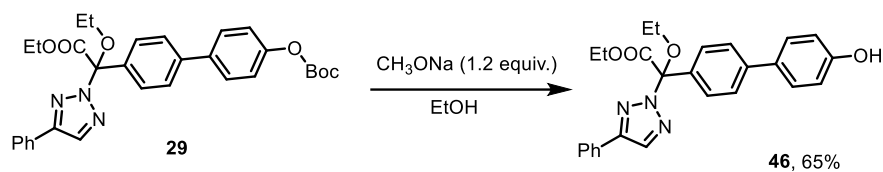
Scheme S1. Attempts for other diazos.

2.6 Derivatization of product



A stirring bar was added to the dry Schlenk tube for anhydrous and oxygen-free operation. Under nitrogen atmosphere, added **4** (0.3 mmol), dry THF (5 mL). LiAlH₄ (0.6 mmol) was added slowly to the THF solution at 0 °C and then the solution was stirred for two hours at room temperature. After that, a solution of NaOH (10% in water) was added carefully until a white solid

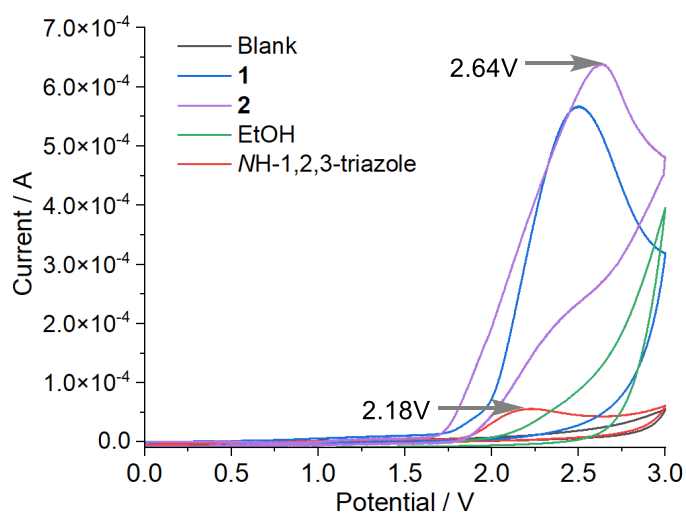
precipitated. After filtration over Na_2SO_4 and the pure product was purified by flash column chromatography (PE/EA) on silica gel resulted in **45** (Yield: 85%).



A stirring bar was added to the dry Schlenk tube, added **29** (0.3 mmol), CH_3ONa (0.6 mmol), EtOH (10 mL) and then the solution was stirred for until the product disappeared at rt. The aqueous mixture was extracted with ethyl acetate (10 mL \times 3). After filtration over Na_2SO_4 and the pure product was purified by flash column chromatography (PE/EA/HOAc) on silica gel resulted in **46** (Yield: 65%).

3. Cyclic Voltammetry Studies

Cyclic voltammograms were recorded with a Bio-logic VSP Potentiostat/Galvanostat equipped with electrochemical analysis software at room temperature in CH₃CN. Pt plate electrode (1.0×1.0 cm²) is purchased from Beijing Jingke Instrument Science Instruments Co., Ltd. and the graphite rod electrode (ϕ 6 mm) as well as Ag/AgCl reference electrode (with KCl solution) are purchased from Wuhan Gaoshi Ruilian Technology Co., Ltd. ⁿBu₄NOAc (0.2 mmol) was used as the supporting electrolyte, and a Pt plate electrode was used as the working electrode. The counter electrode was a graphite rod electrode. The distance between working electrode and counter electrode is 1 cm. All potentials are referenced by using the Ag/AgCl reference electrode. The scan rate is 100 mV • s⁻¹.



Cyclic Voltammetry Studies

4. Measure of charge consumption

Typical procedure: The reaction was set up according to general procedure GP2 except power source with a readable charge is used. The reaction was stop after 4 hours. The charge consumption was recorded.



1 (0.3 mmol), **2** (0.6 mmol), EtOH (0.5 mL) and ^tBu₄NOAc (0.6 mmol) in 9.5 mL anhydrous CH₃CN, platinum plate (1 cm x 1 cm x 0.3 cm), 50 °C, under argon, until the reaction is complete (about 2.5 hours), record the charge displayed by the instrument.



Charge consumption was calculated as $Q/M \cdot F$, Q was read from the experiment as item "Total Q", M was the molar of **1** used in the reaction ($3 \cdot 10^{-4}$ mol), and F was Faraday's constant: 96485. The charge consumption was $120558 \cdot 10^{-3} / (3 \cdot 10^{-4} \cdot 96485) = 4.16$ F/mol. Because the two equivalents of electrons were consumed to produce one equivalent aziridine, the Faradaic efficiency $FE = 2/4.16 = 48\%$.

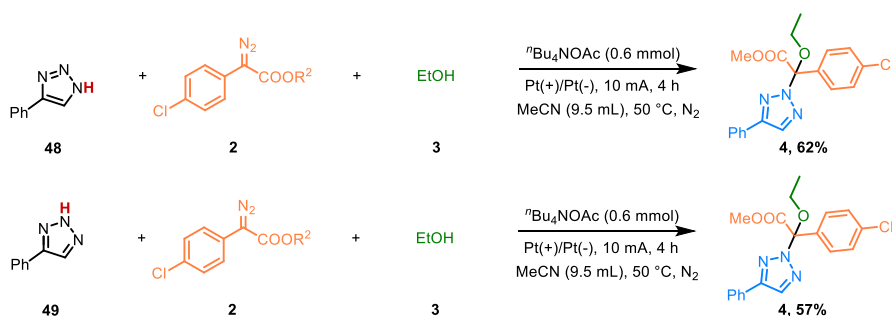
5. Control experiments

5.1 Addition reaction



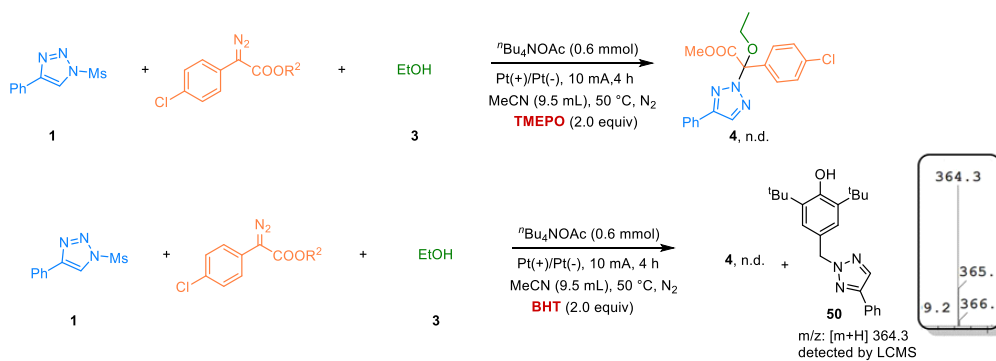
A 25-mL three-necked round-bottomed flask was charged with methyl 2-(4-chlorophenyl)-2-(4-phenyl-2*H*-1,2,3-triazol-2-yl) acetate **47** (0.5 mmol, 1.0 equiv) and ⁿBu₄NOAc (0.6 mmol, 2.0 equiv). The flask was equipped with two platinum plates (1 cm x 1 cm x 0.3 cm), and then flushed with argon. CH₃CN (9.5 mL) and EtOH (0.5 mL) were added. The constant current (10 mA) electrolysis was carried out at 50 °C (oil bath temperature) for 4 h. The reaction mixture was cooled to rt and concentrated under reduced pressure. We failed to obtain any target product.

5.2 Perform reactions by using NH-triazole



A 25-mL three-necked round-bottomed flask was charged with methyl 2-(4-chlorophenyl)-2-diazoacetate **2** (0.6 mmol, 2.0 equiv), *NH*-triazoles **48** or **49** (0.3 mmol, 1.0 equiv) and ⁿBu₄NOAc (0.6 mmol, 2.0 equiv). The flask was equipped with two platinum plates (1 cm x 1 cm x 0.3 cm), and then flushed with argon. CH₃CN (9.5 mL) and EtOH (0.5 mL) were added. The constant current (10 mA) electrolysis was carried out at 50 °C (oil bath temperature) for 4 h. The reaction mixture was cooled to rt and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give the product.

5.3 Radical trapping experiments



A 25-mL three-necked round-bottomed flask was charged with methyl 2-(4-chlorophenyl)-2-diazoacetate **2** (0.6 mmol, 2.0 equiv), triazoles **1** (0.3 mmol, 1.0 equiv) and t Bu₄NOAc (0.6 mmol, 2.0 equiv). The flask was equipped with a carbon plate (1 cm x 1 cm) anode and a platinum plate (1 cm x 1 cm x 0.3 cm) cathode, and then flushed with argon. CH₃CN (9.5 mL), EtOH (0.5 mL) and TEMPO (0.6 mmol, 2.0 equiv) or BHT (0.6 mmol, 2.0 equiv) were added. The constant current (10 mA) electrolysis was carried out at 50 °C (oil bath temperature) for 4 h. The reaction mixture was cooled to rt and concentrated under reduced pressure. The yield of desired product **4** was suppressed. And BHT-trapping adducts **50** was detected by LCMS.

6. Characterization data of products 4

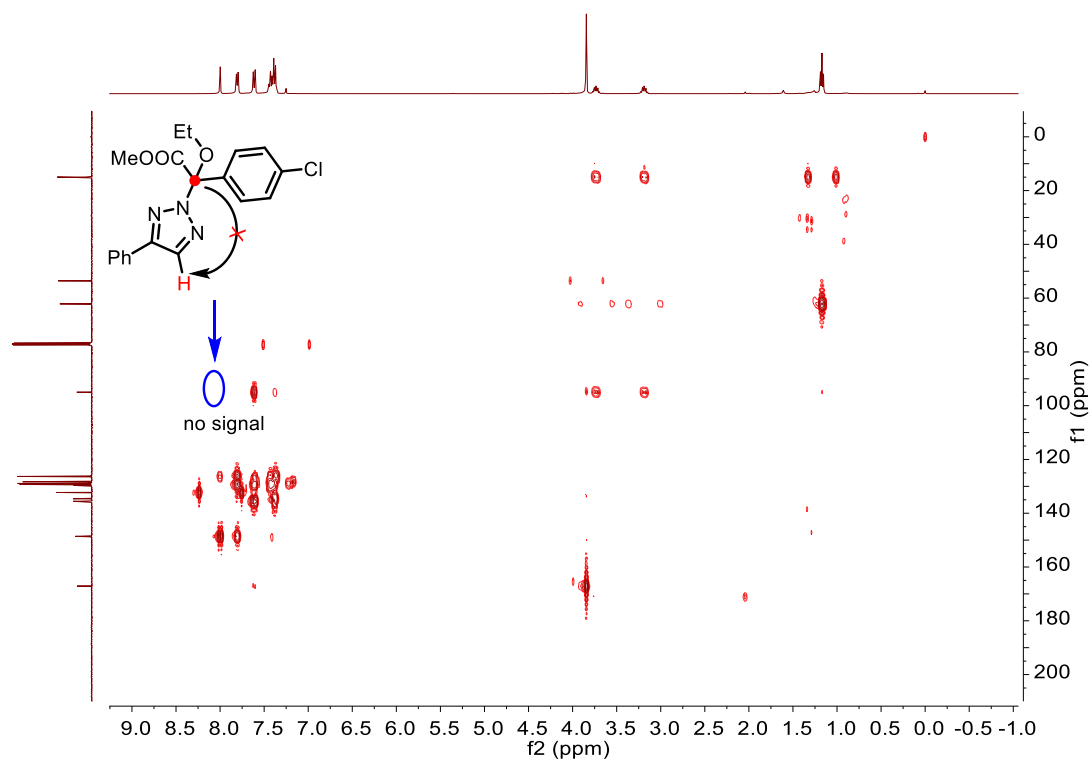


Figure S1. HMBC spectrum of product **4**

7. The electron paramagnetic resonance (EPR) experiment

In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, 1*H*-1,2,3-triazole **48** (0.3 mmol), and ⁿBu₄NOAc (0.6 mmol) were combined and added. The bottle was equipped with two platinum plates (1 cm x 1 cm x 0.3 cm) as the anode and the cathode and was then charged with nitrogen. Under the protection of N₂, DMPO (30 μL) and MeCN (9.5 mL) were injected respectively into the tubes via syringes. After 10 minutes, the solution sample was taken out into a small tube and analyzed by EPR, the typical signals of the spin adduct of a *N*-centered triazole radical trapped by DMPO with coupling constants of $A_{N1} = 13.23$ G, $A_{N2} = 4.58$ G and $A_H = 14.70$ G ($g = 2.0060$, the purple line). And EPR results shown that *N*-mesyl-1,2,3-triazole **1** can also form *N*-centered triazole radical under electrochemical conditions (the green line). EPR spectra was recorded at room temperature on EPR spectrometer operated at 9.816876 GHz. Typical spectrometer parameters are shown as follows, scan range: 200 G; center field set: 3500.00 G; time constant: 0.01 ms; scan time: 10.00 s; modulation amplitude: 1.0 G; modulation frequency: 100 kHz; receiver gain: 1.00×10⁴; microwave power: 20.00 mW.

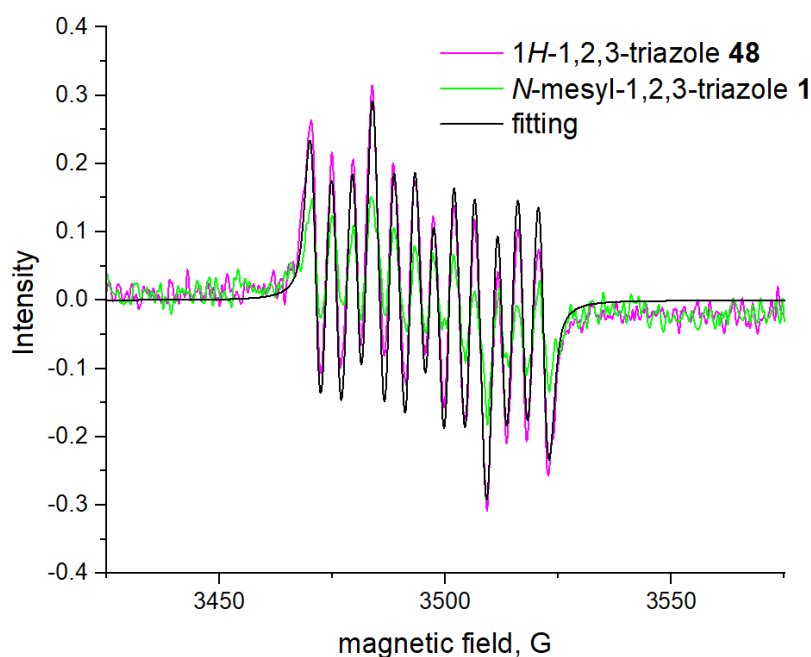


Figure S2. EPR spectrum

8. Anode potential monitoring

The anode potential during the synthesis of **4** was shown below.

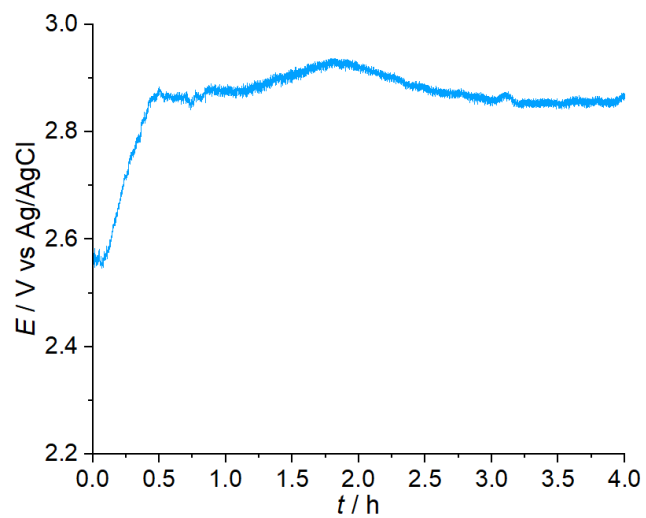
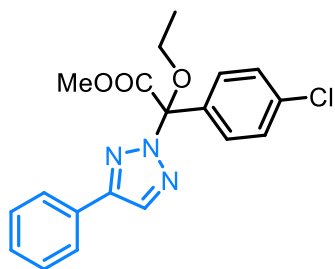


Figure S3. Anode potential monitoring

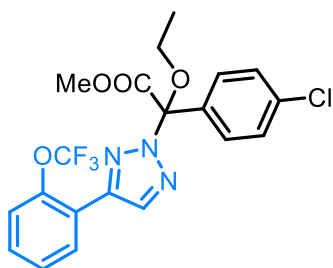
9. Characterization Data for the Electrolysis Products

methyl 2-(4-chlorophenyl)-2-ethoxy-2-(4-phenyl-2H-1,2,3-triazol-2-yl) acetate (4)



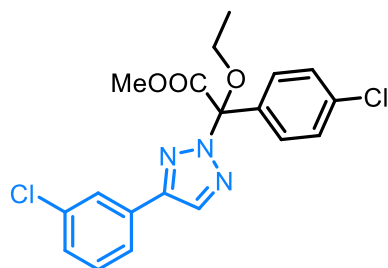
Compound **4** was obtained according to general procedure GP3 as a yellow oil (75% yield) after purification by column chromatography (SiO₂, hexane/EA=10:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.00 (s, 1H), 7.80 (d, *J* = 6.3 Hz, 2H), 7.68 – 7.56 (m, 2H), 7.40 (dd, *J* = 14.9, 7.5 Hz, 5H), 3.84 (s, 3H), 3.70 (d, *J* = 6.9 Hz, 1H), 3.20 (q, *J* = 8.3, 7.9 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.1, 148.6, 135.6, 134.6, 132.3, 129.7, 129.3, 129.1, 128.9, 128.3, 126.3, 95.0, 62.1, 53.6, 15.0. **ESI HRMS** *m/z* (M+Na)⁺ calcd 394.0929, obsd 394.0921.

methyl 2-(4-chlorophenyl)-2-ethoxy-2-(4-(2-(trifluoromethoxy) phenyl)-2H-1,2,3-triazol-2-yl) acetate (5)



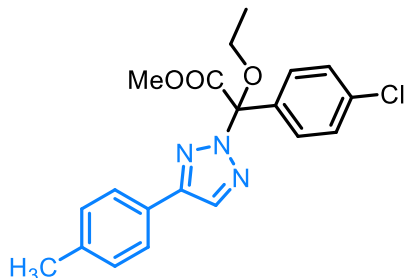
Compound **5** was obtained according to general procedure GP3 as a yellow oil (75% yield) after purification by column chromatography (SiO₂, hexane/EA=10:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.11 (s, 1H), 7.98 (d, *J* = 7.1 Hz, 1H), 7.67 – 7.56 (m, 2H), 7.40 (h, *J* = 8.1 Hz, 5H), 3.85 (s, 3H), 3.79 – 3.68 (m, 1H), 3.29 – 3.12 (m, 1H), 1.17 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.0, 146.4, 143.9, 135.6, 134.8, 134.4, 130.1, 129.9, 129.2, 128.3, 127.2, 123.1, 120.9, 95.1, 62.3, 53.6, 14.9. ¹⁹F NMR (376 MHz, CDCl₃) δ -56.94. **ESI HRMS** *m/z* (M+Na)⁺ calcd 478.0752, obsd 478.0748.

methyl 2-(4-chlorophenyl)-2-(4-(3-chlorophenyl)-2H-1,2,3-triazol-2-yl)-2-ethoxyacetate (6)



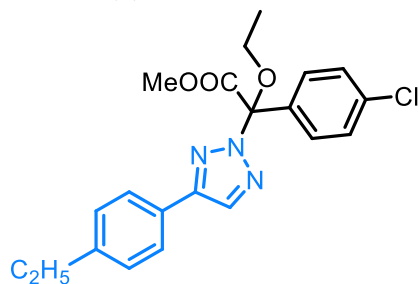
Compound **6** was obtained according to general procedure GP3 as a yellow oil (67% yield) after purification by column chromatography (SiO₂, hexane/EA=10:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.80 (s, 1H), 7.72 – 7.64 (m, 1H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.45 – 7.31 (m, 4H), 3.86 (s, 3H), 3.72 (p, *J* = 7.6, 7.2 Hz, 1H), 3.19 (p, *J* = 7.5 Hz, 1H), 1.22 – 1.07 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.0, 147.4, 135.7, 135.0, 134.4, 132.3, 131.4, 130.2, 129.2, 129.1, 128.3, 126.4, 124.4, 95.1, 62.3, 53.7, 15.0. **ESI HRMS** *m/z* (M+Na)⁺ calcd 428.0539, obsd 428.0532.

methyl 2-(4-chlorophenyl)-2-ethoxy-2-(4-(p-tolyl)-2H-1,2,3-triazol-2-yl) acetate (7)



Compound **7** was obtained according to general procedure GP3 as a yellow oil (71% yield) after purification by column chromatography (SiO₂, hexane/EA=10:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.88 (s, 1H), 7.61 (d, *J* = 7.8 Hz, 2H), 7.53 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 3.76 (s, 3H), 3.64 (dq, *J* = 8.8, 7.0 Hz, 1H), 3.10 (dq, *J* = 9.0, 7.0 Hz, 1H), 2.31 (s, 3H), 1.09 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.2, 148.7, 139.1, 135.5, 134.7, 132.1, 129.6, 129.3, 128.3, 126.8, 126.2, 94.9, 62.1, 53.6, 21.4, 15.0. **ESI HRMS** *m/z* (M+Na)⁺ calcd 408.1085, obsd 408.1081.

methyl 2-(4-chlorophenyl)-2-ethoxy-2-(4-(4-ethylphenyl)-2H-1,2,3-triazol-2-yl) acetate (8)



Compound **8** was obtained according to general procedure GP3 as a yellow oil (69% yield) after purification by column chromatography (SiO₂, hexane/EA=10:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.97 (s, 1H), 7.72 (d, *J* = 7.9 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 7.29 – 7.21 (m, 2H), 3.84 (s, 3H), 3.72 (dq, *J* = 9.0, 7.1 Hz, 1H), 3.25 – 3.10 (m, 1H), 2.68 (q, *J* = 7.6 Hz, 2H), 1.25 (t, *J* = 7.6 Hz, 3H), 1.16 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.2, 148.7, 145.5, 135.5, 134.7, 132.1, 129.3, 128.4, 128.3, 127.1, 126.3, 94.9, 62.1, 53.6, 28.8, 15.6, 15.0. ESI HRMS *m/z* (M+Na)⁺ calcd 422.1242, obsd 422.1233.

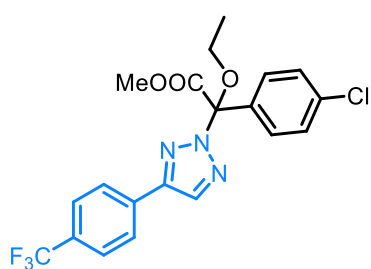
methyl 4-(2-(1-(4-chlorophenyl)-1-ethoxy-2-methoxy-2-oxoethyl)-2H-1,2,3-triazol-4-yl) benzoate (9)

Compound **9** was obtained according to general procedure GP3 as a yellow oil (78% yield) after purification by column chromatography (SiO₂, hexane/EA=10:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.16 – 8.02 (m, 3H), 7.88 (d, *J* = 7.9 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 3.94 (s, 3H), 3.86 (s, 3H), 3.73 (q, *J* = 7.7 Hz, 1H), 3.21 (p, *J* = 7.5 Hz, 1H), 1.19 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.0, 166.6, 147.6, 135.7, 134.4, 133.9, 132.7, 130.4, 130.2, 129.2, 128.3, 126.2, 95.2, 62.3, 53.6, 52.3, 15.0. ESI HRMS *m/z* (M+Na)⁺ calcd 452.0984, obsd 452.0976.

ethyl 4-(2-(1-(4-chlorophenyl)-1-ethoxy-2-methoxy-2-oxoethyl)-2H-1,2,3-triazol-4-yl) benzoate (10)

Compound **10** was obtained according to general procedure GP3 as a yellow oil (61% yield) after purification by column chromatography (SiO₂, hexane/EA=10:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 8.1 Hz, 2H), 8.06 (s, 1H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 4.40 (q, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 3.80 – 3.64 (m, 1H), 3.21 (p, *J* = 7.4 Hz, 1H), 1.42 (t, *J* = 7.2 Hz, 3H), 1.19 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.0, 166.2, 147.6, 135.7, 134.4, 133.8, 132.7, 130.8, 130.2, 129.2, 128.3, 126.1, 62.28, 61.2, 53.6, 14.9, 14.3. ESI HRMS *m/z* (M+Na)⁺ calcd 443.1248, obsd 443.1241.

methyl 2-(4-chlorophenyl)-2-ethoxy-2-(4-(4-(trifluoromethyl) phenyl)-2H-1,2,3-triazol-2-yl) acetate (11)

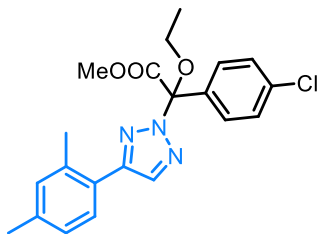


Compound **11** was obtained according to general procedure GP3 as a yellow oil (58% yield) after purification by column chromatography (SiO₂, hexane/EA=10:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.05 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 3.86 (s, 3H), 3.73 (dt, *J* = 14.3, 7.2 Hz, 1H), 3.34 – 3.15 (m, 1H), 1.19 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.9,

147.2, 135.7, 134.3, 133.1, 132.5, 130.9 (d, $J = 32.7$ Hz), 129.2, 128.4, 126.5, 125.9 (q, $J = 3.9$ Hz), 124.0 (d, $J = 272.1$ Hz), 95.2, 62.3, 53.7, 14.9. ^{19}F NMR (376 MHz, CDCl_3) δ -62.7. **ESI HRMS** m/z ($\text{M}+\text{Na}$) $^+$ calcd 462.0803, obsd 462.0811.

methyl 2-(4-chlorophenyl)-2-(4-(2,4-dimethylphenyl)-2H-1,2,3-triazol-2-yl)-2-ethoxyacetate (12)

Compound **12** was obtained according to general procedure GP3 as a yellow oil (65% yield) after purification by column chromatography (SiO_2 , hexane/EA=10:1).



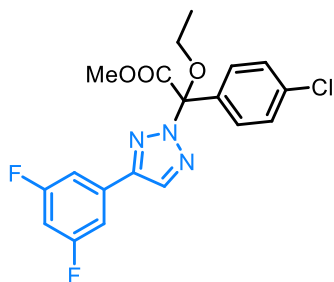
^1H NMR (400 MHz, Chloroform- d) δ 7.87 (s, 1H), 7.70 – 7.55 (m, 2H), 7.51 – 7.30 (m, 3H), 7.08 (d, $J = 13.3$ Hz, 2H), 3.83 (s, 3H), 3.74 (s, 1H), 3.20 (s, 1H), 2.39 (d, $J = 32.0$ Hz, 6H), 1.16 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 167.2, 148.5, 138.8, 136.2, 135.5, 134.7, 134.4, 132.0, 129.3, 129.0, 128.3, 126.8, 126.1, 94.9, 62.1,

53.5, 21.2, 21.2, 15.0. **ESI HRMS** m/z ($\text{M}+\text{Na}$) $^+$ calcd 422.1242, obsd 422.1238.

methyl 2-(4-chlorophenyl)-2-(4-(3,5-difluorophenyl)-2H-1,2,3-triazol-2-yl)-2-ethoxyacetate (13)

Compound **13** was obtained according to general procedure GP3 as a yellow oil (62% yield) after purification by column chromatography (SiO_2 , hexane/EA=10:1).



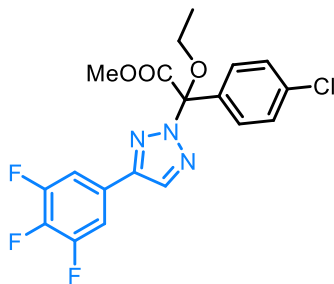
^1H NMR (400 MHz, Chloroform- d) δ 7.98 (s, 1H), 7.59 (d, $J = 8.2$ Hz, 2H), 7.39 (d, $J = 8.3$ Hz, 2H), 7.32 (d, $J = 7.0$ Hz, 2H), 6.82 (t, $J = 9.0$ Hz, 1H), 3.86 (s, 3H), 3.73 (p, $J = 7.3$ Hz, 1H), 3.20 (p, $J = 7.4$ Hz, 1H), 1.19 (t, $J = 7.0$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 166.9, 163.39 (dd, $J = 248.9, 13.0$ Hz), 146.6 (t, $J = 3.1$ Hz), 135.7, 134.2, 132.7 (t, $J = 10.4$ Hz), 132.4, 129.2, 128.4,

109.8 – 108.3 (m), 104.3 (t, $J = 25.3$ Hz), 95.3, 62.3, 53.7, 14.9. ^{19}F NMR (376 MHz, CDCl_3) δ -108.8. **ESI HRMS** m/z ($\text{M}+\text{Na}$) $^+$ calcd 430.0740, obsd 430.0748.

methyl 2-(4-chlorophenyl)-2-ethoxy-2-(4-(3,4,5-trifluorophenyl)-2H-1,2,3-triazol-2-yl) acetate (14)

Compound **14** was obtained according to general procedure GP3 as a yellow oil (57% yield) after purification by column chromatography (SiO_2 , hexane/EA=10:1).



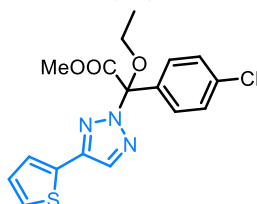
^1H NMR (400 MHz, Chloroform- d) δ 7.94 (s, 1H), 7.66 – 7.53 (m, 2H), 7.46 – 7.36 (m, 4H), 3.86 (t, $J = 1.5$ Hz, 3H), 3.72 (p, $J = 7.5$ Hz, 1H), 3.20 (p, $J = 7.5$ Hz, 1H), 1.19 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 166.8, 152.9 (dd, $J = 10.3, 4.0$ Hz), 150.4 (dd, $J = 10.0, 4.1$ Hz), 146.0, 135.8, 134.2, 132.1, 129.1, 128.4, 125.7 (d, $J = 4.0$ Hz), 113.2 – 108.5 (m), 95.3, 62.4,

53.7, 14.9. ^{19}F NMR (376 MHz, CDCl_3) δ -133.16, -133.21, -159.21, -159.26, -159.32. **ESI HRMS** m/z ($\text{M}+\text{Na}$) $^+$ calcd 448.0646, obsd 448.0637.

methyl 2-(4-chlorophenyl)-2-ethoxy-2-(4-(thiophen-2-yl)-2H-1,2,3-triazol-2-yl) acetate (15)

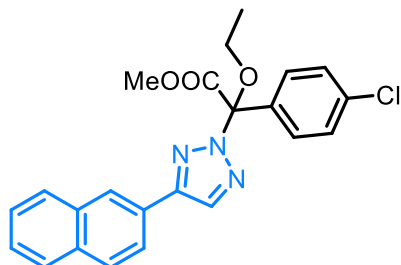
Compound **15** was obtained according to general procedure GP3 as a yellow oil (70% yield) after purification by column chromatography (SiO_2 , hexane/EA=10:1).



^1H NMR (400 MHz, Chloroform- d) δ 7.89 (s, 1H), 7.75 – 7.66 (m, 1H), 7.65 – 7.56 (m, 2H), 7.47 (d, $J = 5.1$ Hz, 1H), 7.38 (t, $J = 6.8$ Hz, 3H), 3.84 (s, 3H), 3.71 (p, $J = 7.4$ Hz, 1H), 3.16 (p, $J = 7.4$ Hz, 1H),

1.17 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.1, 144.8, 135.6, 134.6, 132.4, 131.0, 129.3, 128.3, 126.6, 126.1, 122.8, 94.9, 62.1, 53.6, 15.0. **ESI HRMS** m/z ($\text{M}+\text{Na}$) $^+$ calcd 400.0493, obsd 400.0498.

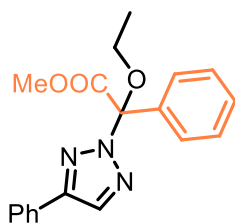
methyl 2-(4-chlorophenyl)-2-ethoxy-2-(4-(naphthalen-2-yl)-2H-1,2,3-triazol-2-yl) acetate (16)



Compound **16** was obtained according to general procedure GP3 as a yellow oil (55% yield) after purification by column chromatography (SiO_2 , hexane/EA=10:1). ^1H NMR (400 MHz, Chloroform- d) δ 8.27 (s, 1H), 8.12 (d, $J = 1.9$ Hz, 1H), 7.89 (ddt, $J = 16.8, 9.0, 5.3$ Hz, 4H), 7.68 – 7.61 (m, 2H), 7.56 – 7.48 (m, 2H), 7.44 – 7.37 (m, 2H), 3.87 (s, 3H), 3.80 – 3.70 (m, 1H), 3.32 – 3.17 (m, 1H), 1.19 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR

(101 MHz, CDCl_3) δ 167.1, 148.7, 135.6, 134.6, 133.6, 133.4, 132.5, 129.3, 128.7, 128.3, 128.3, 127.8, 127.0, 126.6, 126.6, 125.4, 124.0, 95.1, 62.2, 53.6, 15.0. **ESI HRMS** m/z ($\text{M}+\text{Na}$) $^+$ calcd 444.1085, obsd 444.1076.

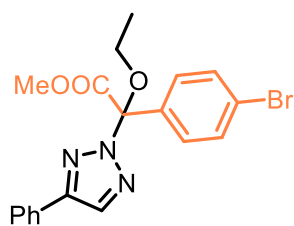
methyl 2-ethoxy-2-phenyl-2-(4-phenyl-2H-1,2,3-triazol-2-yl) acetate (18)



Compound **18** was obtained according to general procedure GP3 as a yellow oil (64% yield) after purification by column chromatography (SiO_2 , hexane/EA=10:1). ^1H NMR (400 MHz, Chloroform- d) δ 8.00 (s, 1H), 7.82 (d, $J = 7.5$ Hz, 2H), 7.70 – 7.63 (m, 2H), 7.41 (h, $J = 7.2$ Hz, 6H), 3.84 (s, 3H), 3.70 (p, $J = 7.6$ Hz, 1H), 3.32 – 3.16 (m, 1H), 1.18 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.4, 148.4, 135.9, 132.1, 129.8, 129.4,

128.9, 128.9, 128.1, 127.8, 126.3, 95.5, 62.0, 53.5, 15.0. **ESI HRMS** m/z ($\text{M}+\text{Na}$) $^+$ calcd 360.1319, obsd 360.1326.

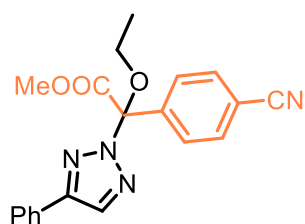
methyl 2-(4-bromophenyl)-2-ethoxy-2-(4-phenyl-2H-1,2,3-triazol-2-yl) acetate (19)



Compound **19** was obtained according to general procedure GP3 as a yellow oil (62% yield) after purification by column chromatography (SiO_2 , hexane/EA=10:1). ^1H NMR (400 MHz, Chloroform- d) δ 8.00 (s, 1H), 7.81 (d, $J = 7.5$ Hz, 2H), 7.54 (s, 4H), 7.42 (dt, $J = 14.7, 7.2$ Hz, 3H), 3.85 (s, 3H), 3.72 (p, $J = 7.5, 7.1$ Hz, 1H), 3.18 (p, $J = 7.3$ Hz, 1H), 1.17 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.0, 148.6,

135.1, 132.3, 131.2, 129.6, 129.6, 129.1, 128.9, 126.3, 123.9, 95.0, 62.1, 53.6, 15.0. **ESI HRMS** m/z ($\text{M}+\text{Na}$) $^+$ calcd 438.0424, obsd 438.0432.

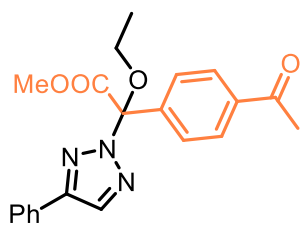
methyl 2-(4-cyanophenyl)-2-ethoxy-2-(4-phenyl-2H-1,2,3-triazol-2-yl) acetate (20)



Compound **20** was obtained according to general procedure GP3 as a yellow oil (52% yield) after purification by column chromatography (SiO_2 , hexane/EA=10:1). ^1H NMR (400 MHz, Chloroform- d) δ 7.94 (s, 1H), 7.78 – 7.70 (m, 4H), 7.62 (dd, $J = 8.5, 2.4$ Hz, 2H), 7.41 – 7.26 (m, 3H), 3.78 (s, 3H), 3.79 – 3.69 (m, 1H), 3.16 – 2.94 (m, 1H), 1.11 (td, $J = 7.0, 2.2$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.5, 148.9, 141.2,

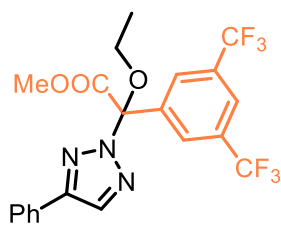
132.5, 131.8, 129.4, 129.2, 129.0, 128.7, 126.3, 118.4, 113.3, 94.6, 62.4, 53.8, 15.0. **ESI HRMS** m/z ($\text{M}+\text{Na}$) $^+$ calcd 385.1271, obsd 385.1279.

methyl 2-(4-acetylphenyl)-2-ethoxy-2-(4-phenyl-2H-1,2,3-triazol-2-yl) acetate (21)



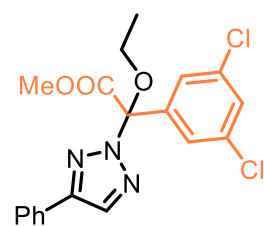
Compound **21** was obtained according to general procedure GP3 as a yellow oil (59% yield) after purification by column chromatography (SiO₂, hexane/EA=10:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.10 – 7.95 (m, 3H), 7.84 – 7.74 (m, 4H), 7.42 (dt, *J* = 14.3, 6.8 Hz, 3H), 3.85 (s, 3H), 3.76 (td, *J* = 7.1, 2.1 Hz, 1H), 3.20 (dq, *J* = 8.8, 7.0 Hz, 1H), 2.63 (s, 3H), 1.19 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 197.70, 166.9, 148.7, 140.8, 137.7, 132.4, 129.6, 129.1, 128.9, 128.2, 128.0, 126.3, 95.1, 62.2, 53.7, 26.8, 15.0. ESI HRMS *m/z* (M+Na)⁺ calcd 402.1424, obsd 402.1421.

methyl 2-(3,5-bis(trifluoromethyl)phenyl)-2-ethoxy-2-(4-phenyl-2H-1,2,3-triazol-2-yl) acetate (22)



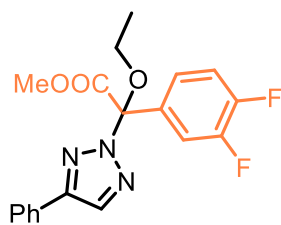
Compound **22** was obtained according to general procedure GP3 as a yellow oil (74% yield) after purification by column chromatography (SiO₂, hexane/EA=10:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.14 (s, 2H), 8.03 (s, 1H), 7.94 (s, 1H), 7.79 (d, *J* = 7.4 Hz, 2H), 7.47 – 7.37 (m, 3H), 3.89 (s, 3H), 3.87 – 3.71 (m, 1H), 3.21 – 3.06 (m, 1H), 1.21 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.3, 149.1, 139.0, 132.8, 131.5 (q, *J* = 33.6 Hz), 129.3, 129.0, 128.3 (d, *J* = 4.1 Hz), 126.3, 124.5, 123.4 (p, *J* = 3.7 Hz), 121.8, 94.1, 62.6, 53.9, 14.9. ¹⁹F NMR (376 MHz, CDCl₃) δ -62.8. ESI HRMS *m/z* (M+Na)⁺ calcd 496.1066, obsd 496.1058.

methyl 2-(3,5-dichlorophenyl)-2-ethoxy-2-(4-phenyl-2H-1,2,3-triazol-2-yl) acetate (23)



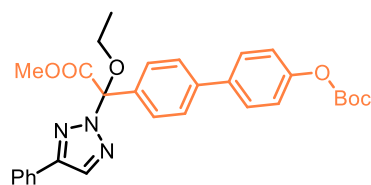
Compound **23** was obtained according to general procedure GP3 as a yellow oil (78% yield) after purification by column chromatography (SiO₂, hexane/EA=10:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.01 (s, 1H), 7.86 – 7.77 (m, 2H), 7.56 (d, *J* = 2.1 Hz, 2H), 7.50 – 7.33 (m, 4H), 3.88 (s, 3H), 3.80 (dq, *J* = 9.0, 7.1 Hz, 1H), 3.12 (dq, *J* = 9.0, 7.1 Hz, 1H), 1.18 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.5, 148.9, 139.5, 134.7, 132.6, 129.6, 129.5, 129.2, 129.0, 126.5, 126.4, 94.1, 62.4, 53.8, 14.9. ESI HRMS *m/z* (M+Na)⁺ calcd 428.0539, obsd 428.0534.

methyl 2-(3,4-difluorophenyl)-2-ethoxy-2-(4-phenyl-2H-1,2,3-triazol-2-yl) acetate (24)



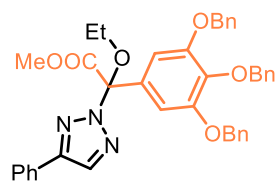
Compound **24** was obtained according to general procedure GP3 as a yellow oil (68% yield) after purification by column chromatography (SiO₂, hexane/EA=10:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.00 (s, 1H), 7.80 (d, *J* = 7.4 Hz, 2H), 7.54 (dd, *J* = 11.2, 8.1 Hz, 1H), 7.42 (dt, *J* = 14.7, 7.8 Hz, 4H), 7.19 (q, *J* = 8.9 Hz, 1H), 3.87 (s, 3H), 3.82 – 3.73 (m, 1H), 3.15 (p, *J* = 7.2 Hz, 1H), 1.18 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.9, 154.2 – 147.8 (m), 148.7, 133.5 – 132.9 (m), 132.4, 129.5, 129.1, 128.9, 126.3, 124.2 (dd, *J* = 6.6, 3.6 Hz), 117.2 (dd, *J* = 75.4, 18.7 Hz), 94.3, 62.3, 53.6, 14.9. ¹⁹F NMR (376 MHz, CDCl₃) δ -136.44, -136.48, -136.56, -136.56, -137.04, -137.09, -137.12, -137.15. ESI HRMS *m/z* (M+Na)⁺ calcd 396.1130, obsd 396.1139.

methyl 2-(4'-((*tert*-butoxycarbonyl) oxy)-[1,1'-biphenyl]-4-yl)-2-ethoxy-2-(4-phenyl-2*H*-1,2,3-triazol-2-yl) acetate (25)



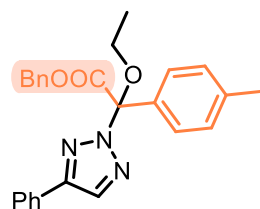
Compound **25** was obtained according to general procedure GP3 as a yellow oil (79% yield) after purification by column chromatography (SiO₂, hexane/EA=10:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.02 (s, 1H), 7.83 (d, *J* = 7.5 Hz, 2H), 7.76 – 7.69 (m, 2H), 7.60 (ddt, *J* = 6.6, 4.5, 1.9 Hz, 4H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 7.1 Hz, 1H), 7.26 (d, *J* = 2.0 Hz, 2H), 3.87 (s, 3H), 3.72 (p, *J* = 7.4 Hz, 1H), 3.26 (p, *J* = 7.5 Hz, 1H), 1.58 (s, 9H), 1.19 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.4, 151.9, 150.8, 148.5, 141.4, 138.2, 134.9, 132.2, 129.8, 129.0, 128.9, 128.3, 128.2, 126.8, 126.3, 121.6, 95.4, 83.7, 62.1, 53.6, 27.7, 15.0. **ESI HRMS** *m/z* (M+Na)⁺ calcd 552.2105, obsd 552.2113.

benzyl 2-ethoxy-2-(4-phenyl-2*H*-1,2,3-triazol-2-yl)-2-(3,4,5-tris(benzyloxy)phenyl) acetate (26)



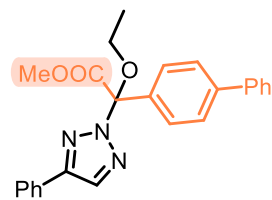
Compound **26** was obtained according to general procedure GP3 as a yellow oil (12% yield) after purification by column chromatography (SiO₂, hexane/EA=10:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.82 (d, *J* = 7.5 Hz, 2H), 7.41 (dd, *J* = 16.9, 7.1 Hz, 10H), 7.32 (q, *J* = 5.9, 4.6 Hz, 8H), 6.98 (s, 2H), 5.08 (s, 6H), 3.79 (s, 3H), 3.61 (dd, *J* = 15.9, 7.6 Hz, 1H), 3.17 (dd, *J* = 15.7, 8.0 Hz, 1H), 1.12 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.3, 152.3, 137.9, 137.0, 132.2, 131.0, 129.0, 128.9, 128.5, 128.4, 128.2, 127.8, 127.8, 127.6, 126.3, 107.9, 75.2, 71.2, 62.1, 53.5, 15.0. **ESI HRMS** *m/z* (M+Na)⁺ calcd 678.2575, obsd 678.2571.

benzyl 2-ethoxy-2-(4-phenyl-2*H*-1,2,3-triazol-2-yl)-2-(*p*-tolyl) acetate (27)



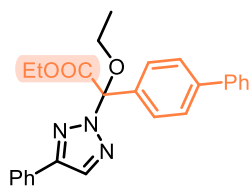
Compound **27** was obtained according to general procedure GP3 as a yellow oil (56% yield) after purification by column chromatography (SiO₂, hexane/EA=10:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.98 (s, 1H), 7.77 (d, *J* = 7.4 Hz, 2H), 7.55 (d, *J* = 7.9 Hz, 2H), 7.40 (dt, *J* = 13.8, 7.1 Hz, 3H), 7.29 – 7.16 (m, 7H), 5.34 (d, *J* = 12.5 Hz, 1H), 5.21 (d, *J* = 12.5 Hz, 1H), 3.69 (p, *J* = 7.5 Hz, 1H), 3.22 (p, *J* = 7.4 Hz, 1H), 2.38 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.8, 148.2, 139.3, 135.2, 132.8, 132.1, 129.8, 128.9, 128.8, 128.8, 128.4, 128.1, 127.9, 127.8, 126.3, 95.6, 67.9, 61.9, 21.3. **ESI HRMS** *m/z* (M+Na)⁺ calcd 450.1788, obsd 450.1785.

methyl 2-([1,1'-biphenyl]-4-yl)-2-ethoxy-2-(4-phenyl-2*H*-1,2,3-triazol-2-yl) acetate (28)



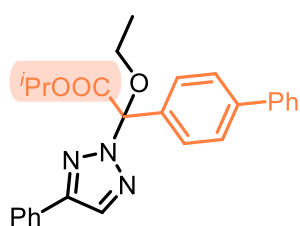
Compound **28** was obtained according to general procedure GP3 as a yellow oil (73% yield) after purification by column chromatography (SiO₂, hexane/EA=10:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.02 (s, 1H), 7.83 (d, *J* = 7.5 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.66 – 7.58 (m, 4H), 7.47 – 7.41 (m, 4H), 7.40 – 7.34 (m, 2H), 3.87 (s, 3H), 3.78 – 3.66 (m, 1H), 3.38 – 3.22 (m, 1H), 1.20 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.4, 148.5, 142.2, 140.5, 134.8, 132.2, 129.8, 129.0, 128.9, 128.8, 128.3, 127.6, 127.3, 126.8, 126.3, 95.5, 62.1, 53.5, 15.0. **ESI HRMS** *m/z* (M+Na)⁺ calcd 436.1632, obsd 436.1639.

ethyl 2-([1,1'-biphenyl]-4-yl)-2-ethoxy-2-(4-phenyl-2H-1,2,3-triazol-2-yl) acetate (29)



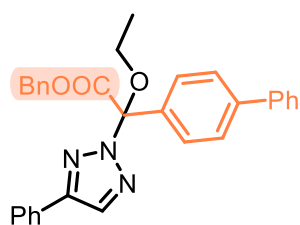
Compound **29** was obtained according to general procedure GP3 as a yellow oil (63% yield) after purification by column chromatography (SiO₂, hexane/EA=10:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.94 (s, 1H), 7.76 (d, *J* = 7.5 Hz, 2H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.55 (dd, *J* = 8.1, 3.7 Hz, 4H), 7.37 (q, *J* = 6.9 Hz, 4H), 7.29 (q, *J* = 7.2, 6.5 Hz, 2H), 4.47 – 4.16 (m, 2H), 3.77 – 3.58 (m, 1H), 3.19 (p, *J* = 7.4 Hz, 1H), 1.20 (t, *J* = 7.2 Hz, 3H), 1.12 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.8, 148.3, 142.1, 140.5, 135.0, 132.1, 129.9, 128.9, 128.9, 128.8, 128.3, 127.6, 127.2, 126.7, 126.3, 95.4, 62.7, 62.0, 15.0, 13.9. **ESI HRMS** *m/z* (M+Na)⁺ calcd 450.1788, obsd 450.1796.

isopropyl 2-([1,1'-biphenyl]-4-yl)-2-ethoxy-2-(4-phenyl-2H-1,2,3-triazol-2-yl) acetate (30)



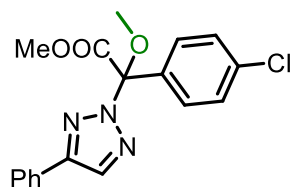
Compound **30** was obtained according to general procedure GP3 as a yellow oil (67% yield) after purification by column chromatography (SiO₂, hexane/EA=10:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.01 (s, 1H), 7.83 (d, *J* = 7.6 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 4H), 7.50 – 7.40 (m, 4H), 7.37 (q, *J* = 6.7 Hz, 2H), 5.18 (p, *J* = 6.3 Hz, 1H), 3.76 (dt, *J* = 14.2, 7.1 Hz, 1H), 3.38 – 3.12 (m, 1H), 1.31 (d, *J* = 6.3 Hz, 3H), 1.18 (d, *J* = 6.6 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 166.1, 148.2, 142.0, 140.5, 135.1, 132.1, 130.0, 128.9, 128.9, 128.8, 128.2, 127.6, 127., 126.62, 126.2, 95., 70.70, 62.0, 21.5, 21.4, 15.0. **ESI HRMS** *m/z* (M+Na)⁺ calcd 464.1945, obsd 464.1942.

benzyl 2-([1,1'-biphenyl]-4-yl)-2-ethoxy-2-(4-phenyl-2H-1,2,3-triazol-2-yl) acetate (31)



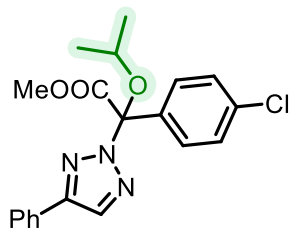
Compound **31** was obtained according to general procedure GP3 as a yellow oil (52% yield) after purification by column chromatography (SiO₂, hexane/EA=10:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.01 (s, 1H), 7.79 (d, *J* = 7.5 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.61 (d, *J* = 7.5 Hz, 4H), 7.41 (ddd, *J* = 24.4, 12.1, 5.2 Hz, 6H), 7.24 (q, *J* = 5.2 Hz, 5H), 5.41 – 5.19 (m, 2H), 4.02 – 3.69 (m, 1H), 3.31 – 3.18 (m, 1H), 1.18 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.6, 148.4, 142.2, 140.5, 135.1, 134.8, 132.2, 129.8, 129.0, 128.9, 128.8, 128.4, 128.3, 128.2, 127.9, 127.6, 127.3, 126.8, 126.3, 95.6, 68.1, 62.1, 15.0. **ESI HRMS** *m/z* (M+Na)⁺ calcd 512.1945, obsd 512.1941.

methyl 2-(4-chlorophenyl)-2-methoxy-2-(4-phenyl-2H-1,2,3-triazol-2-yl) acetate (33)



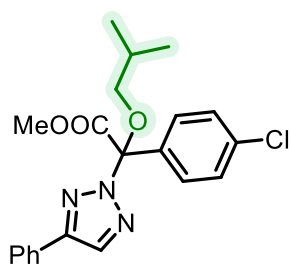
Compound **33** was obtained according to general procedure GP3 as a yellow oil (72% yield) after purification by column chromatography (SiO₂, hexane/EA=10:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.02 (s, 1H), 7.81 (d, *J* = 7.4 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.41 (dd, *J* = 14.2, 7.7 Hz, 5H), 3.86 (s, 3H), 3.27 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.8, 148.7, 135.7, 134.5, 132.4, 129.6, 129.4, 129.1, 128.9, 128.4, 126.3, 95.2, 53.7, 53.7. **ESI HRMS** *m/z* (M+Na)⁺ calcd 380.0772, obsd 380.0779.

methyl 2-(4-chlorophenyl)-2-isopropoxy-2-(4-phenyl-2H-1,2,3-triazol-2-yl) acetate (34)



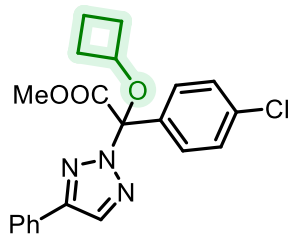
Compound **34** was obtained according to general procedure GP3 as a yellow oil (55% yield) after purification by column chromatography (SiO₂, hexane/EA=10:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.92 (s, 1H), 7.73 (d, *J* = 7.5 Hz, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.33 (dt, *J* = 23.5, 7.9 Hz, 5H), 4.25 (q, *J* = 6.1 Hz, 1H), 3.76 (s, 3H), 1.24 (d, *J* = 6.3 Hz, 3H), 0.43 (d, *J* = 6.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.7, 148.6, 135.4, 135.3, 132.2, 129.7, 129.4, 129.0, 128.9, 128.1, 126.3, 95.0, 70.3, 53.4, 23.3, 22.5. **ESI HRMS** *m/z* (M+Na)⁺ calcd 408.1085, obsd 408.1089.

methyl 2-(4-chlorophenyl)-2-isobutoxy-2-(4-phenyl-2H-1,2,3-triazol-2-yl) acetate (35)



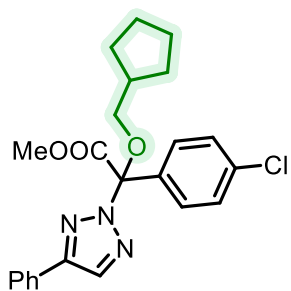
Compound **35** was obtained according to general procedure GP3 as a yellow oil (61% yield) after purification by column chromatography (SiO₂, hexane/EA=10:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.80 (d, *J* = 7.5 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.49 – 7.33 (m, 5H), 3.84 (s, 3H), 3.58 (dd, *J* = 8.9, 6.7 Hz, 1H), 2.84 (dd, *J* = 9.0, 6.5 Hz, 1H), 1.80 (dt, *J* = 13.4, 6.8 Hz, 1H), 0.89 (d, *J* = 6.8 Hz, 3H), 0.84 (d, *J* = 6.8 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.1, 148.5, 135.5, 135.0, 132.2, 129.7, 129.2, 129.0, 128.9, 128.2, 126.3, 94.7, 72.5, 53.4, 28.5, 26.9, 19.3. **ESI HRMS** *m/z* (M+Na)⁺ calcd 422.1242, obsd 422.1236.

methyl 2-(4-chlorophenyl)-2-cyclobutoxy-2-(4-phenyl-2H-1,2,3-triazol-2-yl) acetate (36)



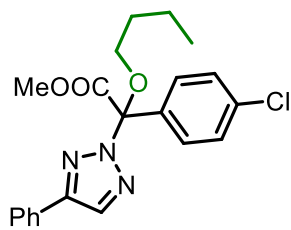
Compound **36** was obtained according to general procedure GP3 as a yellow oil (52% yield) after purification by column chromatography (SiO₂, hexane/EA=10:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.97 (s, 1H), 7.79 (d, *J* = 7.5 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.40 (dd, *J* = 16.8, 7.9 Hz, 5H), 4.36 (p, *J* = 7.6 Hz, 1H), 3.83 (s, 3H), 2.01 (dq, *J* = 18.0, 9.3, 8.6 Hz, 2H), 1.77 (q, *J* = 10.0 Hz, 1H), 1.52 (d, *J* = 11.3 Hz, 1H), 1.31 (d, *J* = 19.6 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 167.1, 148.8, 135.6, 134.4, 132.3, 129.7, 129.5, 129.0, 128.9, 128.3, 126.3, 94.5, 70.1, 53.6, 31.0, 12.3. **ESI HRMS** *m/z* (M+Na)⁺ calcd 420.1085, obsd 420.1078.

methyl 2-(4-chlorophenyl)-2-(cyclopentylmethoxy)-2-(4-phenyl-2H-1,2,3-triazol-2-yl) acetate (37)



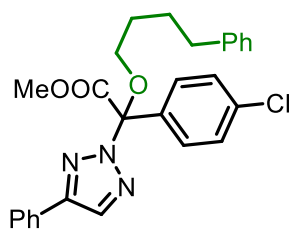
Compound **37** was obtained according to general procedure GP3 as a yellow oil (48% yield) after purification by column chromatography (SiO₂, hexane/EA=10:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.86 – 7.77 (m, 2H), 7.67 – 7.58 (m, 2H), 7.47 – 7.35 (m, 5H), 3.84 (s, 3H), 3.68 (dd, *J* = 8.9, 7.2 Hz, 1H), 2.91 (dd, *J* = 8.9, 6.8 Hz, 1H), 2.11 (p, *J* = 7.5 Hz, 1H), 1.78 – 1.64 (m, 2H), 1.55 – 1.44 (m, 4H), 1.35 – 1.22 (m, 1H), 1.15 (dt, *J* = 13.1, 7.1 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 167.2, 148.5, 135.5, 135.0, 132.2, 129.7, 129.2, 129.0, 128.9, 128.2, 126.3, 94.7, 70.2, 53.5, 39.3, 29.3, 29.3, 25.3, 25.3. **ESI HRMS** *m/z* (M+Na)⁺ calcd 425.1506, obsd 425.1511.

methyl 2-butoxy-2-(4-chlorophenyl)-2-(4-phenyl-2H-1,2,3-triazol-2-yl) acetate (38)



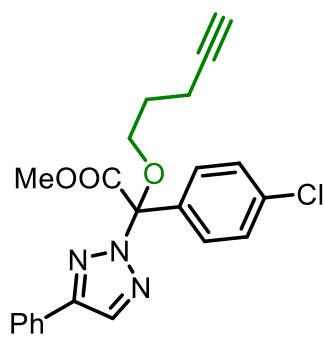
Compound **38** was obtained according to general procedure GP3 as a yellow oil (55% yield) after purification by column chromatography (SiO₂, hexane/EA=10:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.80 (d, *J* = 7.5 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 7.4 Hz, 2H), 7.38 (dd, *J* = 8.6, 2.3 Hz, 3H), 3.84 (s, 3H), 3.78 – 3.69 (m, 1H), 3.17 – 2.98 (m, 1H), 1.52 (p, *J* = 7.1 Hz, 2H), 1.35 (p, *J* = 7.4 Hz, 2H), 0.85 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.1, 148.5, 135.5, 134.8, 132.3, 129.7, 129.2, 129.0, 128.9, 128.3, 126.3, 94.9, 66.0, 53.5, 31.5, 19.1, 13.8. **ESI HRMS** *m/z* (M+Na)⁺ calcd 422.1242, obsd 422.1238.

methyl 2-(4-chlorophenyl)-2-(4-phenyl-2H-1,2,3-triazol-2-yl)-2-(4-phenylbutoxy) acetate (39)



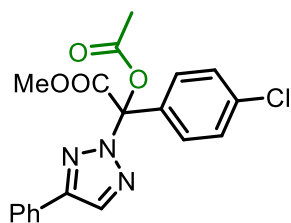
Compound **39** was obtained according to general procedure GP3 as a yellow oil (44% yield) after purification by column chromatography (SiO₂, hexane/EA=10:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 1.7 Hz, 1H), 7.78 (d, *J* = 7.4 Hz, 2H), 7.64 – 7.54 (m, 2H), 7.48 – 7.33 (m, 5H), 7.28 – 7.19 (m, 2H), 7.17 – 7.08 (m, 3H), 3.84 (s, 3H), 3.77 (q, *J* = 7.3 Hz, 1H), 3.09 (q, *J* = 7.2 Hz, 1H), 2.56 (t, *J* = 7.5 Hz, 2H), 1.64 (q, *J* = 7.2 Hz, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 167.1, 148.6, 142.2, 135.5, 134.8, 132.3, 129.6, 129.2, 129.1, 128.9, 128.4, 128.3, 128.3, 126.3, 125.7, 94.9, 66.1, 53.5, 35.5, 29.0, 27.6. **ESI HRMS** *m/z* (M+Na)⁺ calcd 498.1555, obsd 498.1550.

methyl 2-(4-chlorophenyl)-2-(pent-4-yn-1-yloxy)-2-(4-phenyl-2H-1,2,3-triazol-2-yl) acetate (40)



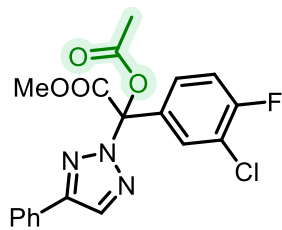
Compound **40** was obtained according to general procedure GP3 as a yellow oil (41% yield) after purification by column chromatography (SiO₂, hexane/EA=10:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.00 (s, 1H), 7.80 (d, *J* = 7.5 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.40 (dd, *J* = 17.7, 8.1 Hz, 5H), 3.89 (d, *J* = 7.0 Hz, 1H), 3.85 (s, 3H), 3.37 – 3.10 (m, 1H), 2.29 (t, *J* = 7.5 Hz, 2H), 1.84 (s, 1H), 1.76 (q, *J* = 6.8 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 167.0, 148.7, 135.6, 134.6, 132.4, 129.6, 129.2, 129.1, 128.9, 128.3, 126.3, 94.8, 83.7, 68.5, 64.7, 53.6, 28.6, 15.2. **ESI HRMS** *m/z* (M+Na)⁺ calcd 432.1085, obsd 432.1081.

methyl 2-acetoxy-2-(4-chlorophenyl)-2-(4-phenyl-2H-1,2,3-triazol-2-yl) acetate (41)



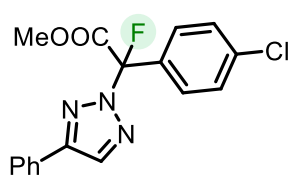
Compound **41** was obtained according to general procedure GP3 as a yellow oil (45% yield) after purification by column chromatography (SiO₂, hexane/EA=10:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.96 (s, 1H), 7.80 – 7.69 (m, 2H), 7.60 – 7.46 (m, 2H), 7.39 (p, *J* = 7.7, 7.2 Hz, 5H), 3.88 (s, 3H), 2.33 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 168.2, 165.34, 148.54, 136.11, 133.48, 132.36, 129.59, 128.99, 128.94, 128.84, 128.6, 128.3, 126.3, 54.0, 21.2. **ESI HRMS** *m/z* (M+Na)⁺ calcd 408.0722, obsd 408.0721.

methyl 2-acetoxy-2-(3-chloro-4-fluorophenyl)-2-(4-phenyl-2H-1,2,3-triazol-2-yl) acetate (42)



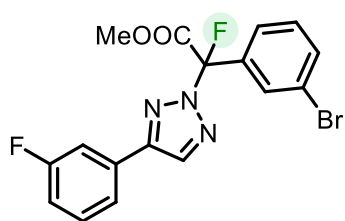
Compound **42** was obtained according to general procedure GP3 as a yellow oil (57% yield) after purification by column chromatography (SiO₂, hexane/EA=10:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.97 (s, 1H), 7.77 – 7.74 (m, 3H), 7.72 (dd, *J* = 6.6, 2.2 Hz, 1H), 7.48 (ddd, *J* = 8.8, 4.3, 2.3 Hz, 1H), 7.40 (dt, *J* = 13.2, 7.1 Hz, 2H), 7.19 (t, *J* = 8.7 Hz, 1H), 3.90 (s, 3H), 2.34 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 168.0, 165.1, 158.9 (d, *J* = 252.9 Hz), 148.7, 132.0 (d, *J* = 4.0 Hz), 132.0, 129.6, 129.5, 129.1, 128.9, 127.2 (d, *J* = 7.8 Hz), 126.3, 121.3 (d, *J* = 18.3 Hz), 116.5 (d, *J* = 21.8 Hz), 91.0, 54.1, 21.1. ¹⁹F NMR (376 MHz, CDCl₃) δ -112.96. **ESI HRMS** *m/z* (M+Na)⁺ calcd 426.0627, obsd 426.0622.

methyl 2-(4-chlorophenyl)-2-fluoro-2-(4-phenyl-2H-1,2,3-triazol-2-yl) acetate (43)



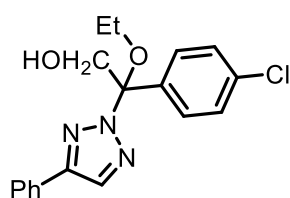
Compound **43** was obtained according to general procedure GP3 as a yellow oil (65% yield) after purification by column chromatography (SiO₂, hexane/EA=10:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.04 (s, 1H), 7.79 (d, *J* = 7.2 Hz, 2H), 7.65 (dd, *J* = 8.6, 1.7 Hz, 2H), 7.52 – 7.38 (m, 5H), 3.96 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 164.8 (d, *J* = 33.7 Hz), 150.3, 136.8, 136.8, 134.1, 131.0 (d, *J* = 26.9 Hz), 129.50, 128.97, 128.70, 128.6, 128.5, 126.5, 100.7 (d, *J* = 226.8 Hz), 54.2. ¹⁹F NMR (376 MHz, CDCl₃) δ -120.00. **ESI HRMS** *m/z* (M+Na)⁺ calcd 368.0573, obsd 368.0568.

methyl 2-(3-bromophenyl)-2-fluoro-2-(4-(3-fluorophenyl)-2H-1,2,3-triazol-2-yl) acetate (44)



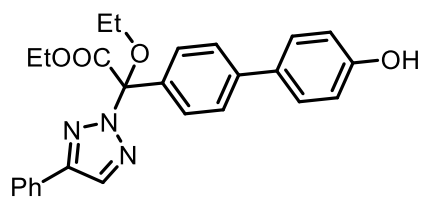
Compound **44** was obtained according to general procedure GP3 as a yellow oil (53% yield) after purification by column chromatography (SiO₂, hexane/EA=10:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.03 (s, 1H), 7.86 (s, 1H), 7.64 (dd, *J* = 14.7, 8.0 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.39 (dt, *J* = 19.8, 7.2 Hz, 2H), 7.10 (td, *J* = 8.4, 2.5 Hz, 1H), 3.98 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 164.5 (d, *J* = 31.5 Hz), 161.9, 149.3, 134.5, 134.2, 133.7, 132.5, 131.0, 130.6 (d, *J* = 8.3 Hz), 130.0 (d, *J* = 8.5 Hz), 129.9, 125.8 (d, *J* = 7.5 Hz), 122.2 (d, *J* = 2.8 Hz), 122.2, 116.4 (d, *J* = 21.1 Hz), 113.5 (d, *J* = 23.1 Hz), 54.3. ¹⁹F NMR (376 MHz, CDCl₃) δ -112.08, -120.09. **ESI HRMS** *m/z* (M+Na)⁺ calcd 429.9973, obsd 429.9966.

2-(4-chlorophenyl)-2-ethoxy-2-(4-phenyl-2H-1,2,3-triazol-2-yl) ethan-1-ol (45)



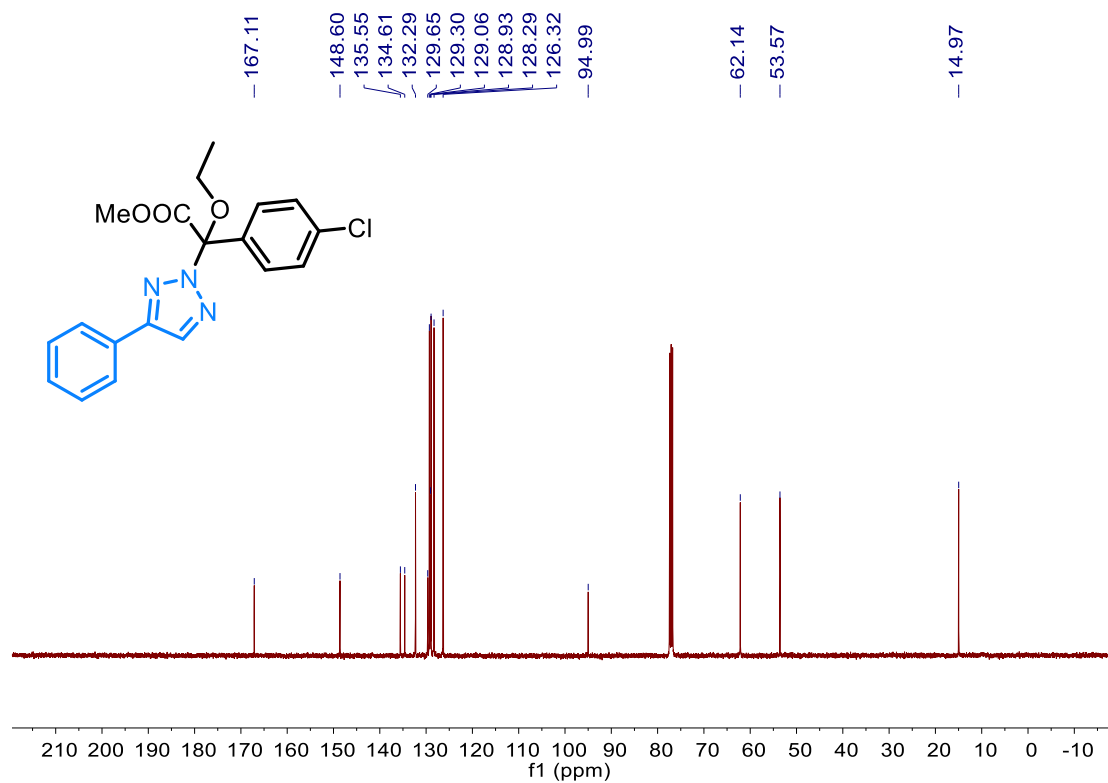
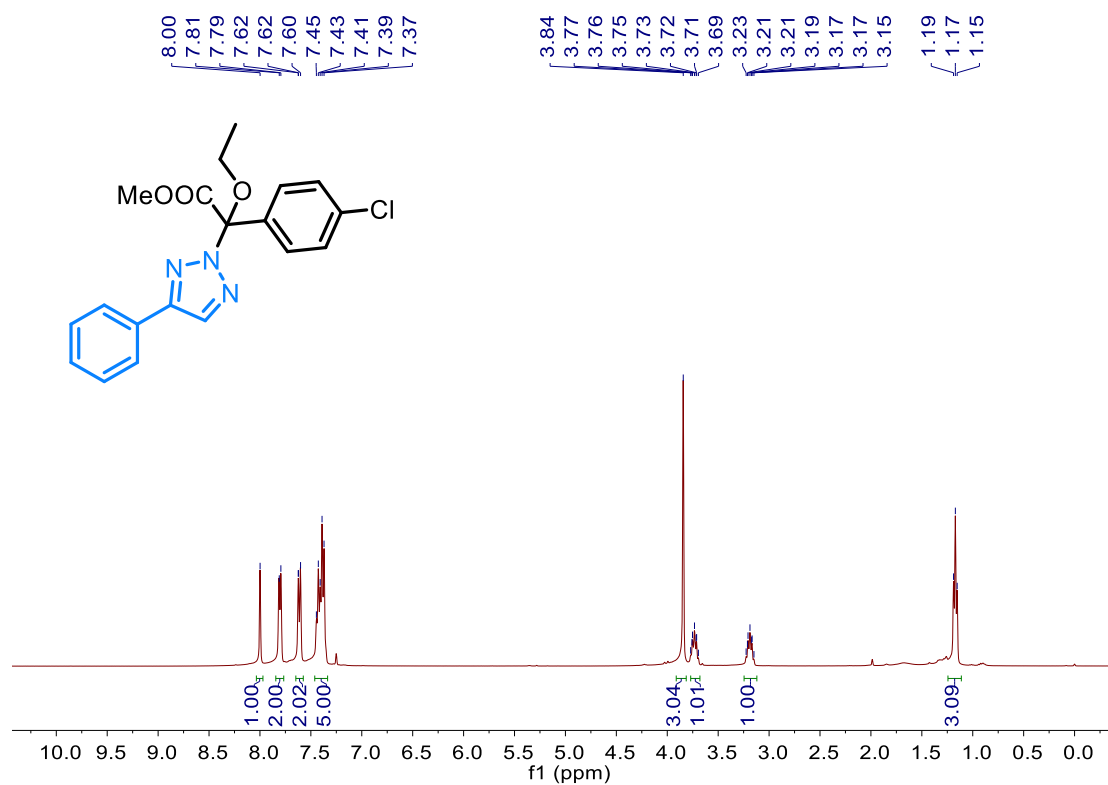
Yellow oil. ¹H NMR δ 8.01 (s, 1H), 7.90 – 7.78 (m, 3H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.42 – 7.31 (m, 3H), 7.22 – 7.16 (m, 2H), 4.46 (d, *J* = 12.5 Hz, 1H), 4.32 (d, *J* = 12.4 Hz, 1H), 3.64 (p, *J* = 7.5 Hz, 1H), 3.53 (dq, *J* = 15.7, 7.9, 7.2 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 148.0, 136.9, 134.9, 131.6, 129.6, 129.0, 128.7, 128.5, 128.4, 126.2, 96.5, 68.7, 61.1, 15.3. **ESI HRMS** *m/z* (M+Na)⁺ calcd 366.0980, obsd 366.0971.

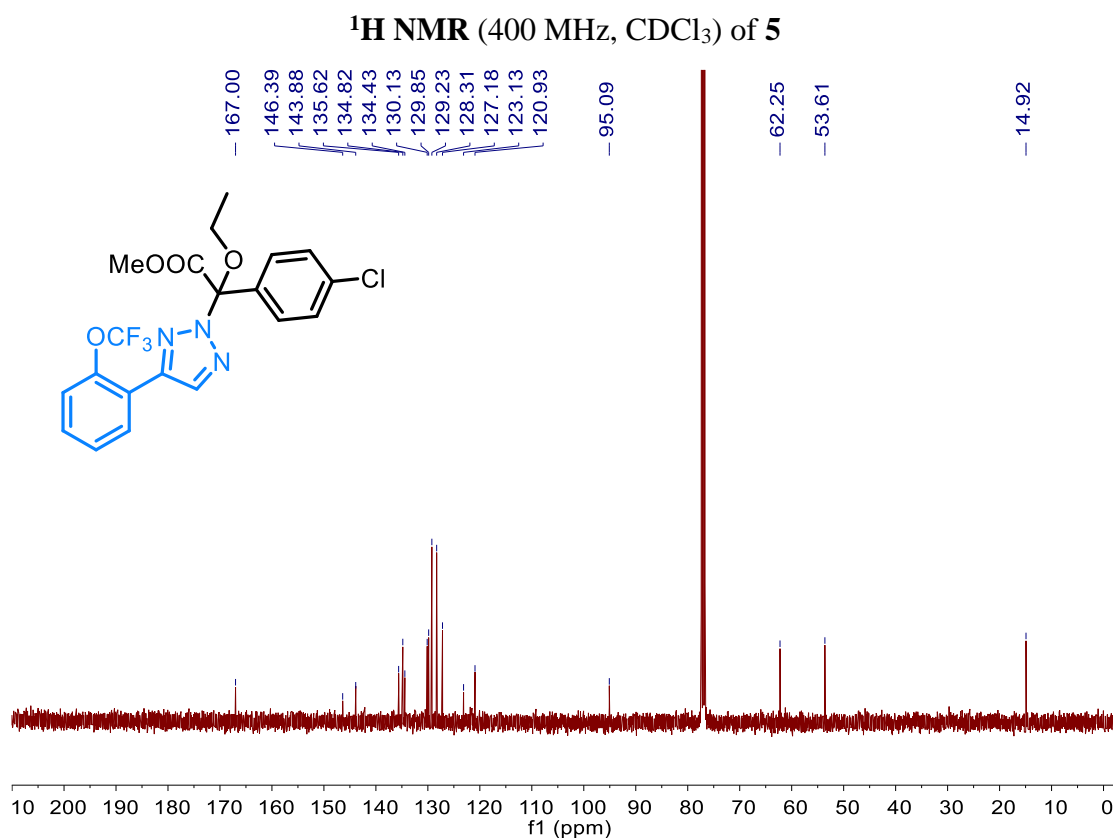
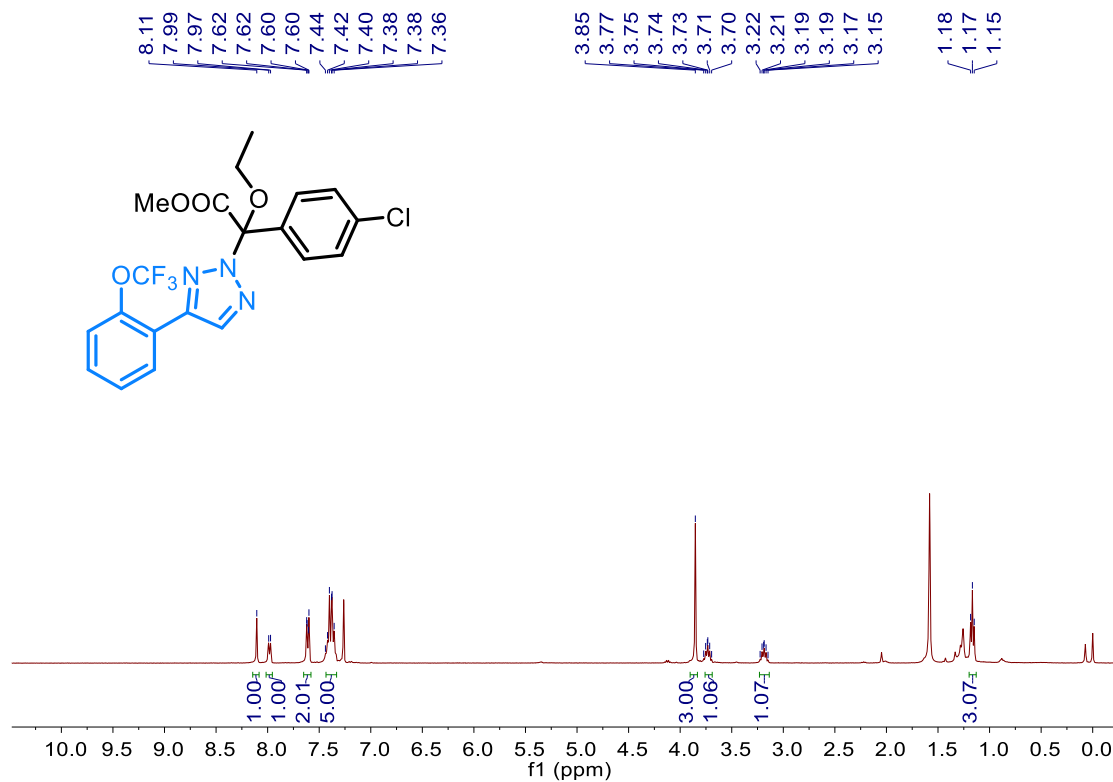
methyl 2-ethoxy-2-(4'-hydroxy-[1,1'-biphenyl]-4-yl)-2-(4-phenyl-2H-1,2,3-triazol-2-yl) acetate (46)

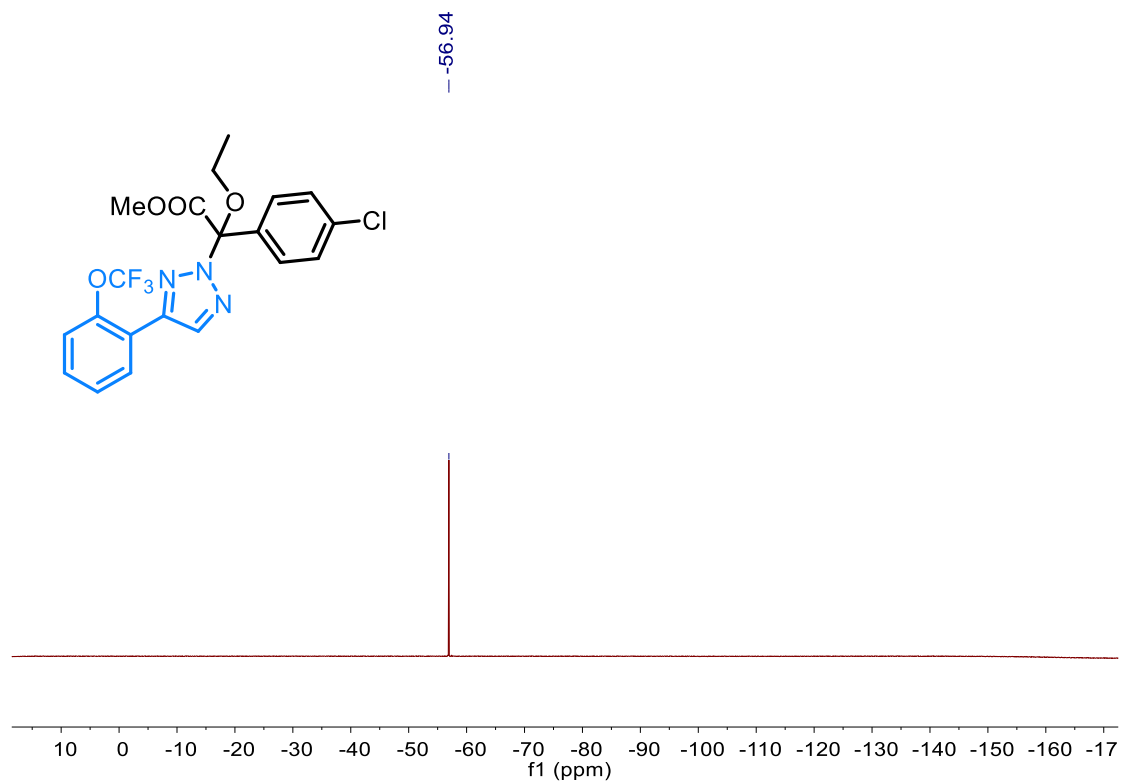


Yellow oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.02 (s, 1H), 7.83 (d, $J = 7.5$ Hz, 2H), 7.71 (d, $J = 8.1$ Hz, 2H), 7.56 (d, $J = 8.2$ Hz, 2H), 7.49 (d, $J = 8.1$ Hz, 2H), 7.43 (t, $J = 7.4$ Hz, 2H), 7.38 (d, $J = 7.1$ Hz, 1H), 6.89 (d, $J = 8.1$ Hz, 2H), 5.25 (s, 1H), 4.34 (ddq, $J = 23.5, 10.3, 6.3, 5.0$ Hz, 2H), 3.73 (p, $J = 7.6$ Hz, 1H), 3.38 – 3.16 (m, 1H), 1.38 – 1.23 (m, 3H), 1.19 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 166.9, 155.5, 148.3, 141.7, 134.2, 133.1, 132.1, 129.9, 128.9, 128.5, 128.2, 126.3, 126.2, 115.7, 95.5, 62.8, 62.0, 29.7, 15.0, 13.9. **ESI HRMS** m/z ($\text{M}+\text{Na}$) $^+$ calcd 443.1845, obsd 429.443.1839.

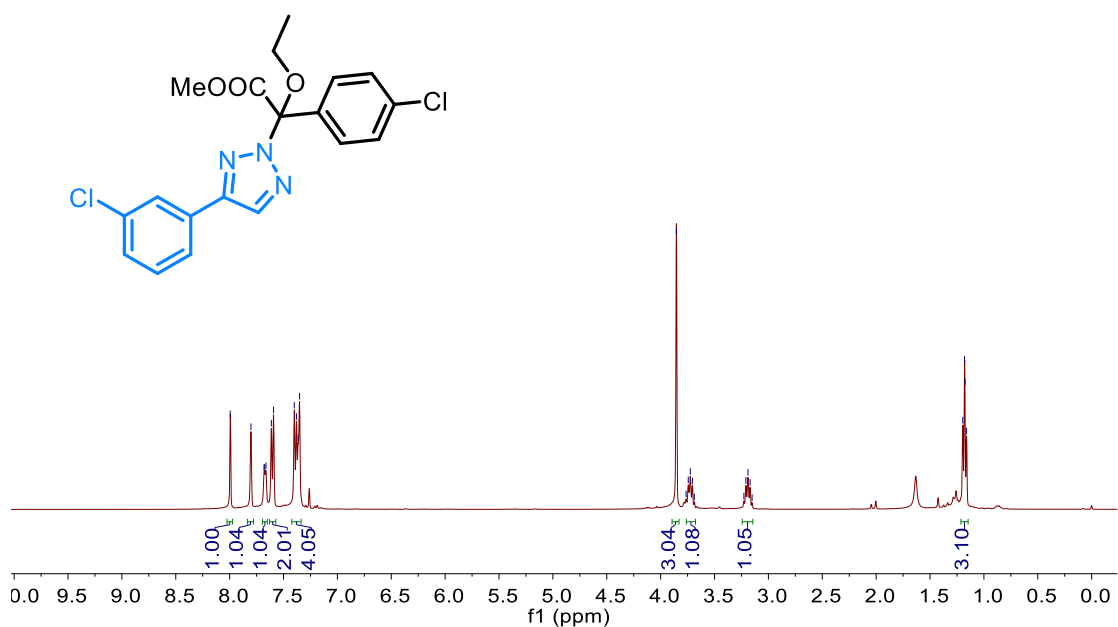
10. NMR Spectra for New Compounds



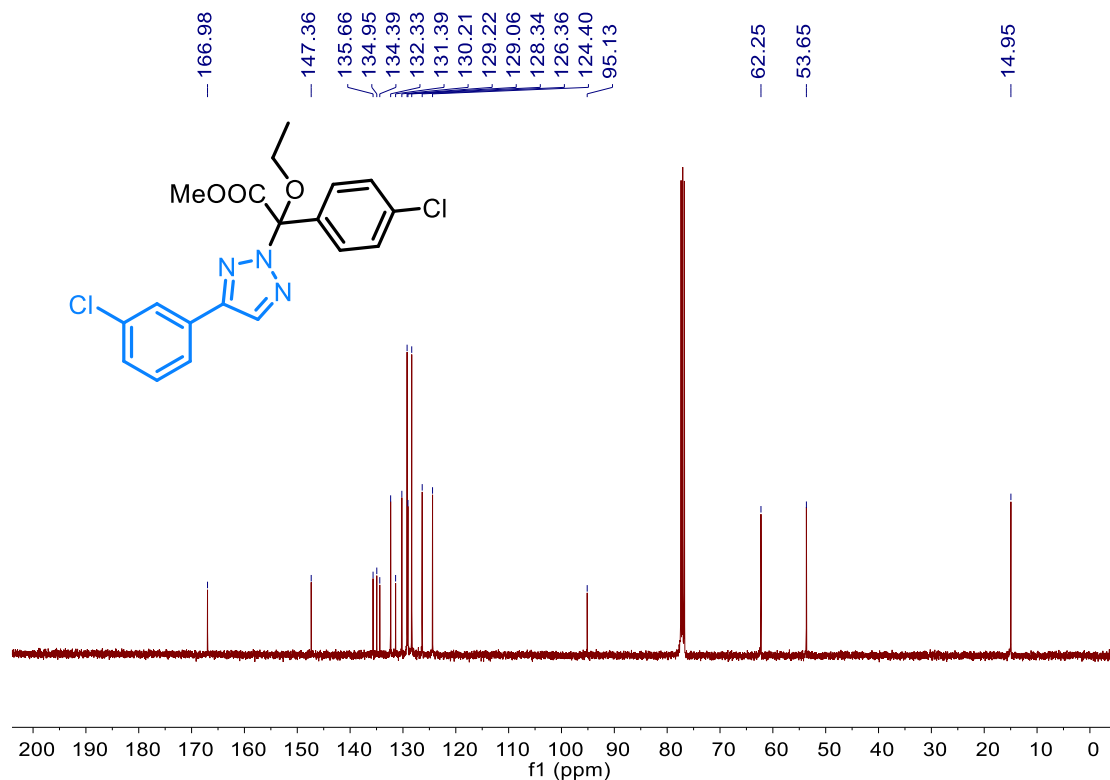




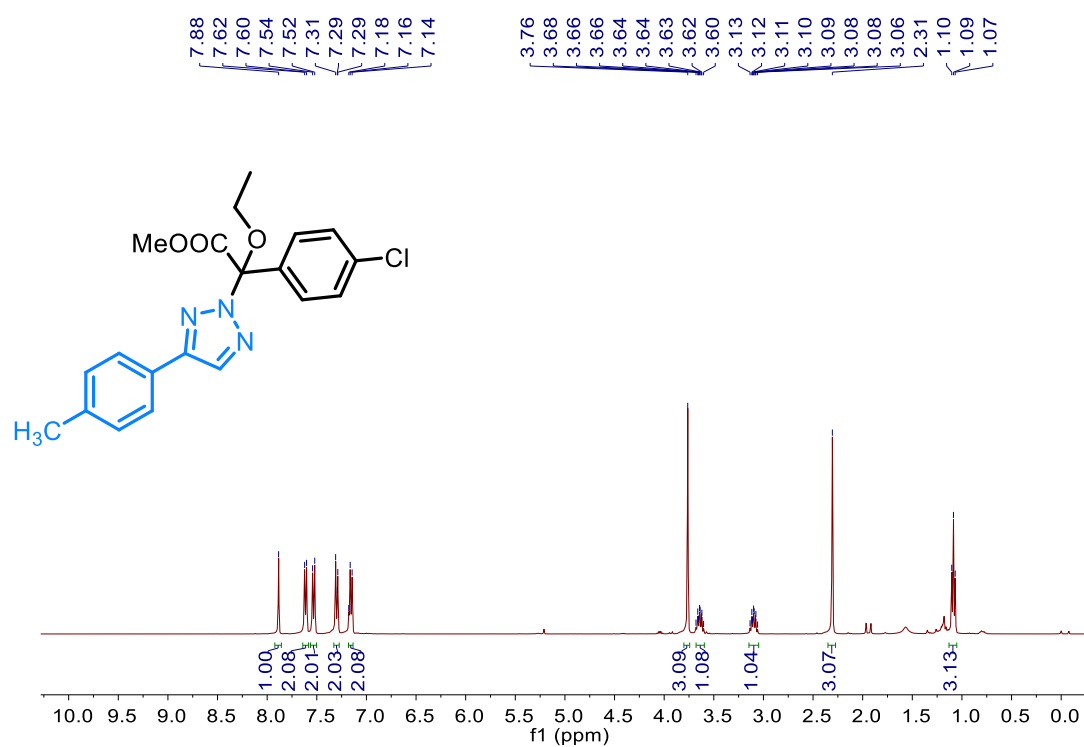
¹⁹F NMR (376 MHz, CDCl₃) of 5



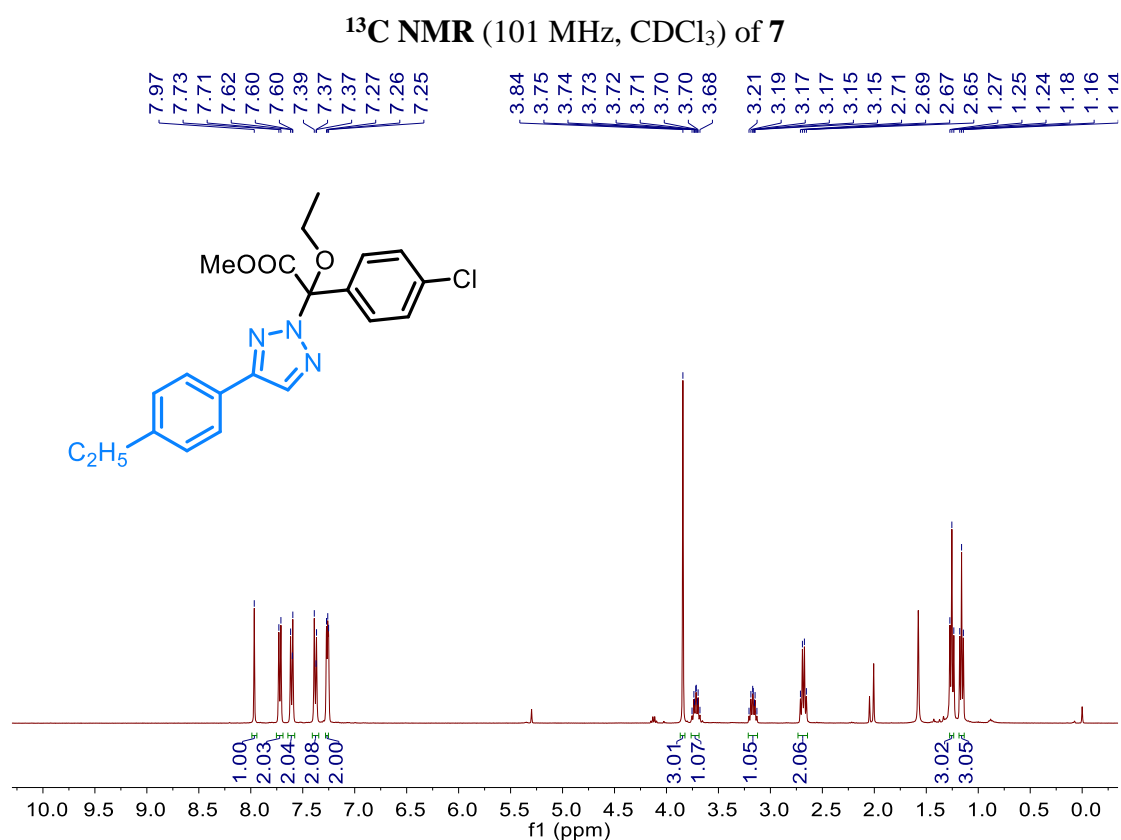
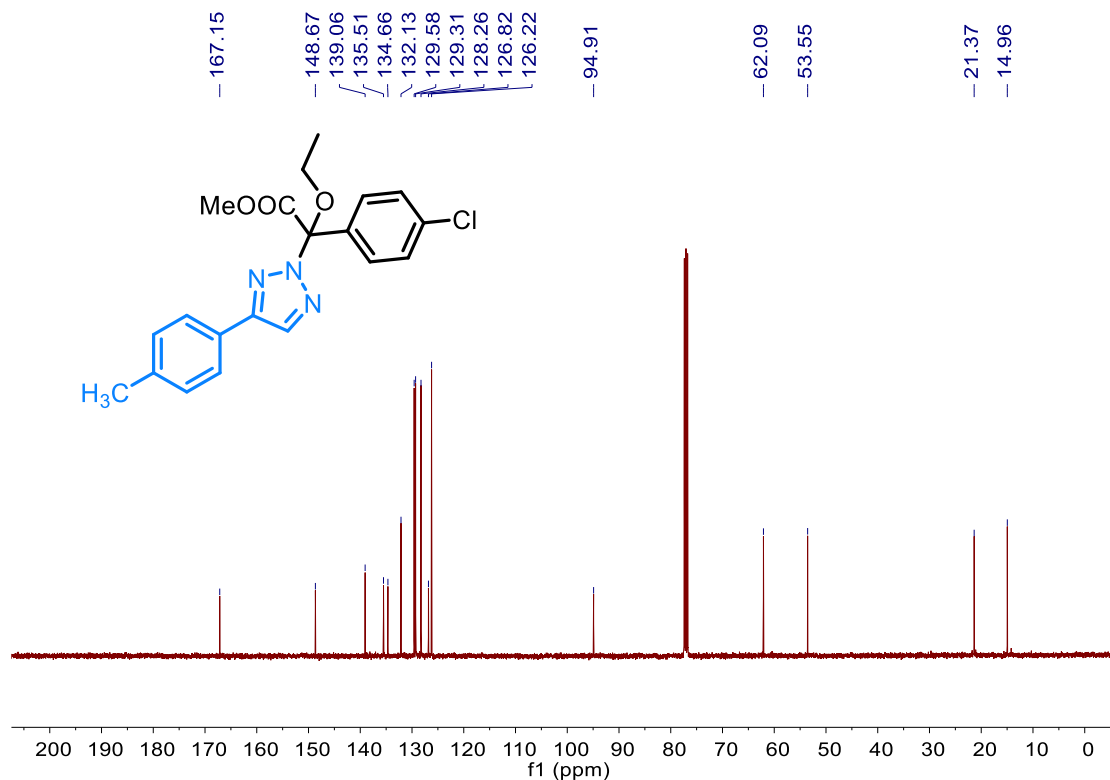
¹H NMR (400 MHz, CDCl₃) of 6

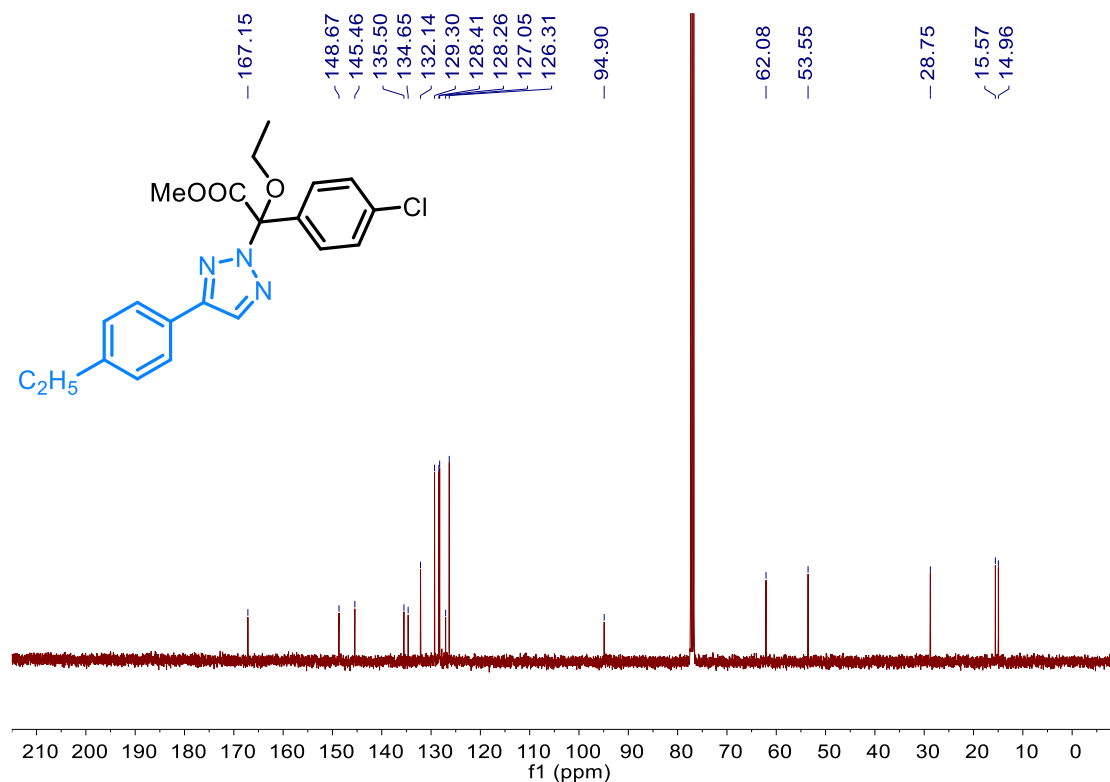


¹³C NMR (101 MHz, CDCl₃) of 6

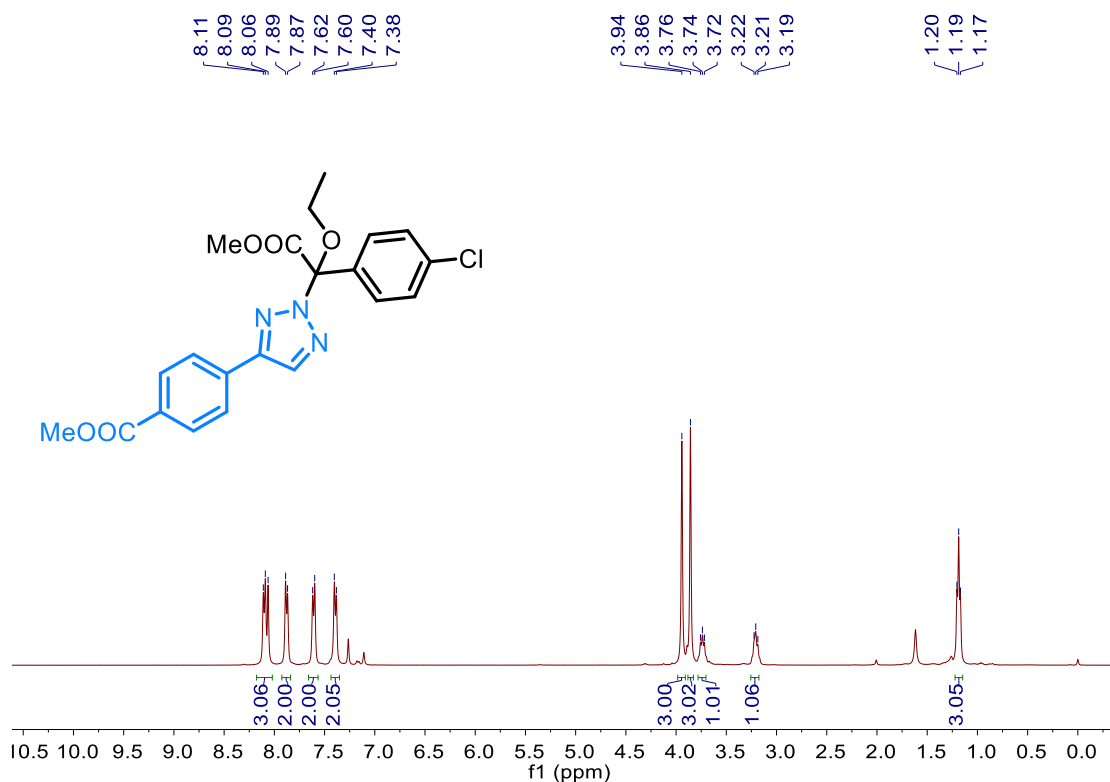


¹H NMR (400 MHz, CDCl₃) of 7

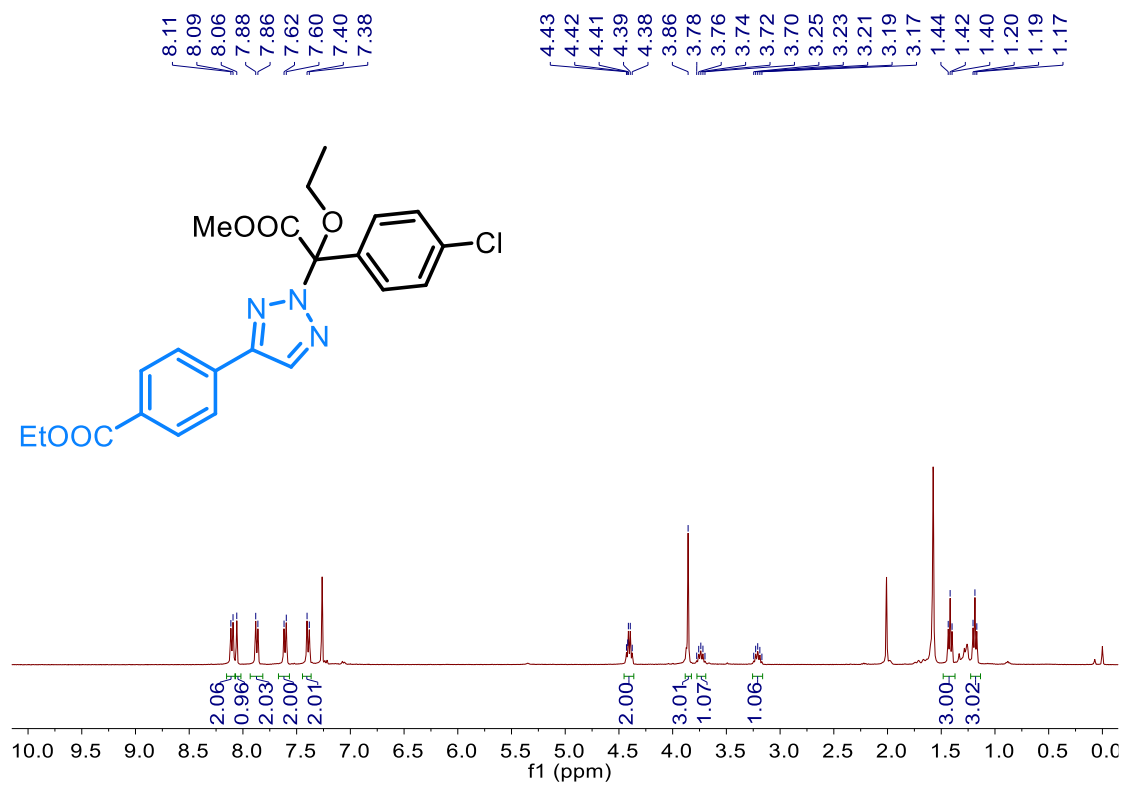
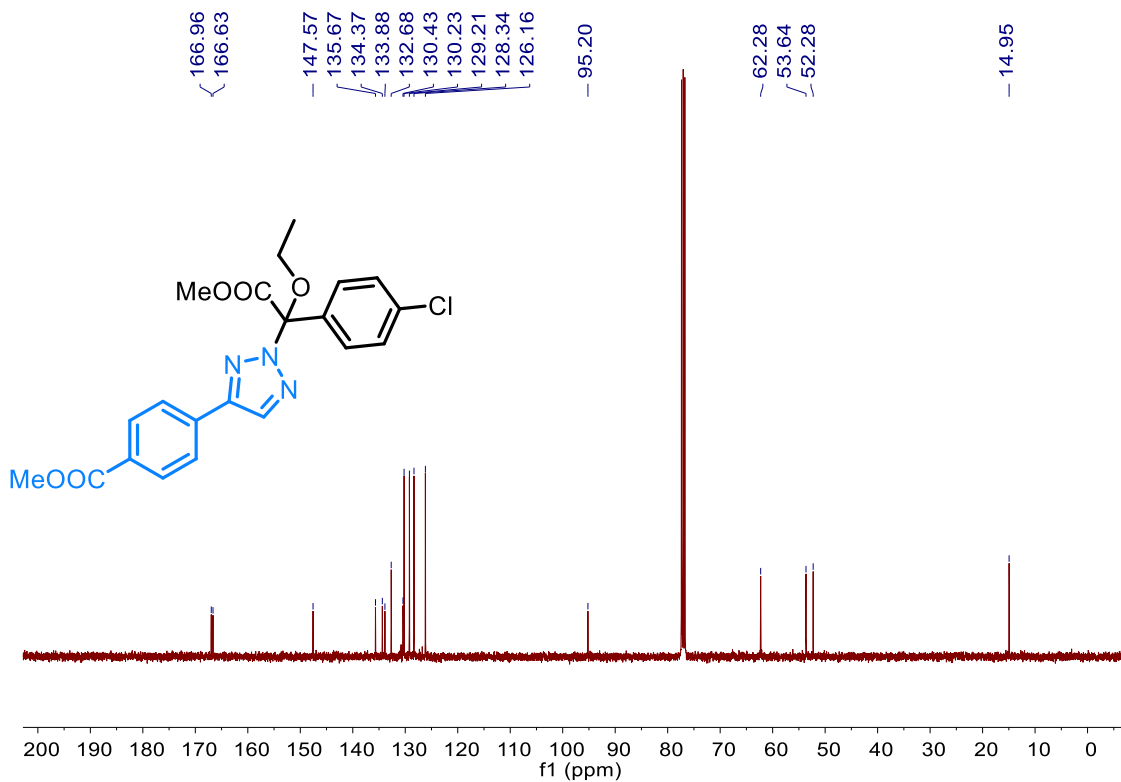


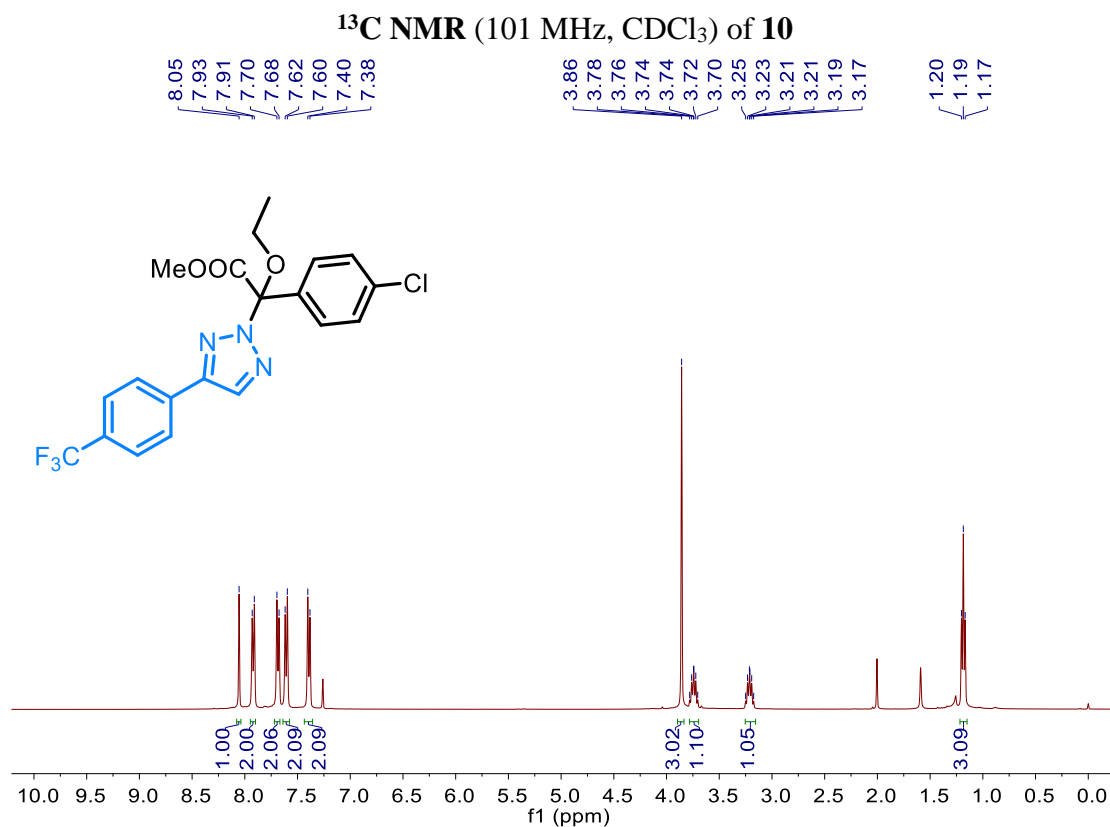
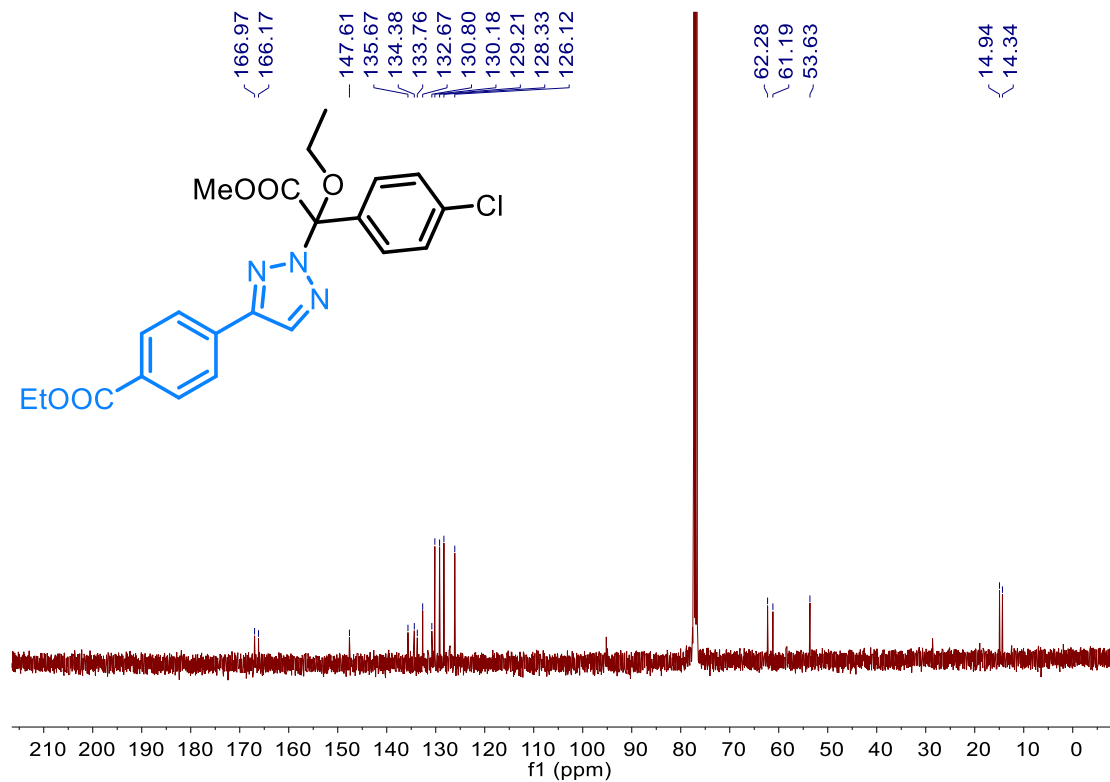


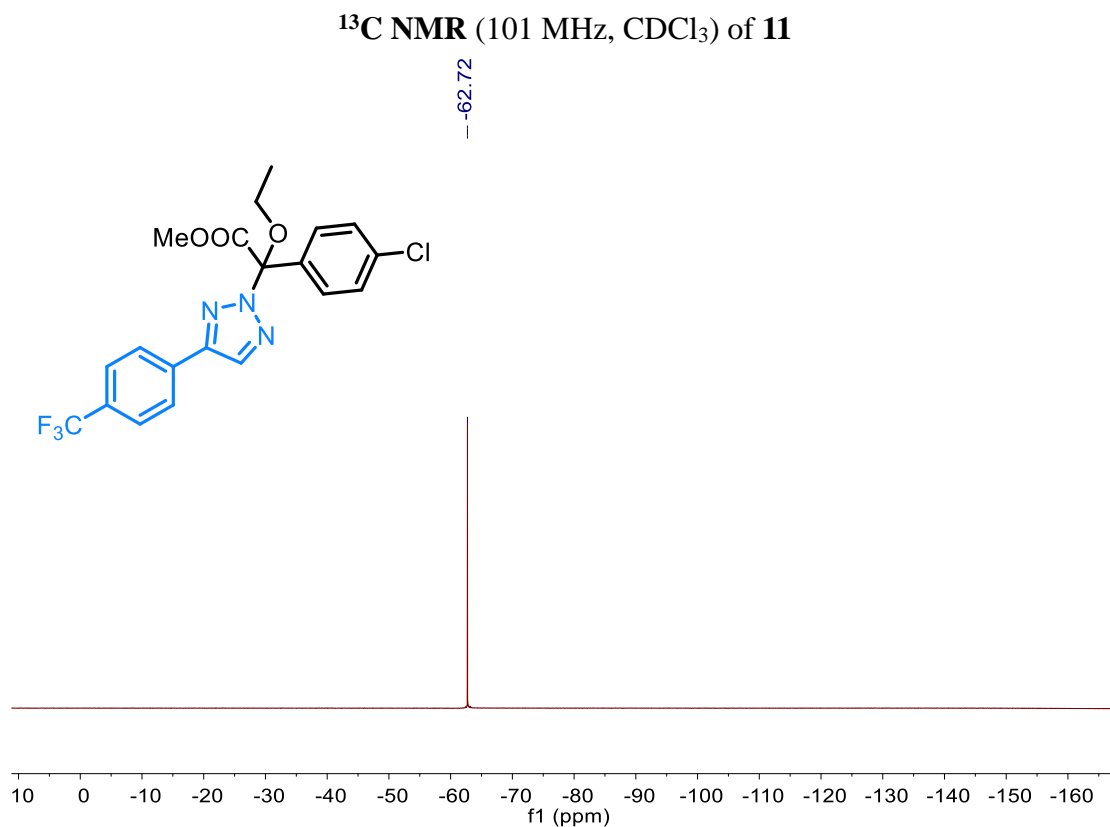
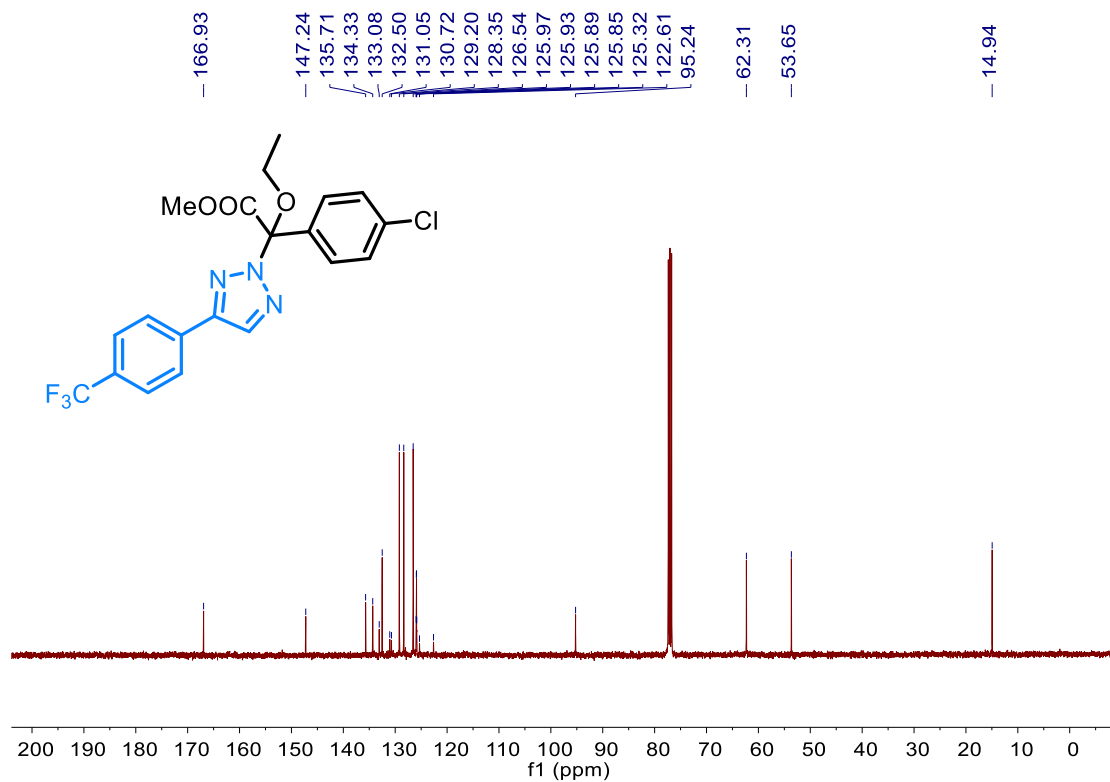
^{13}C NMR (101 MHz, CDCl_3) of **8**

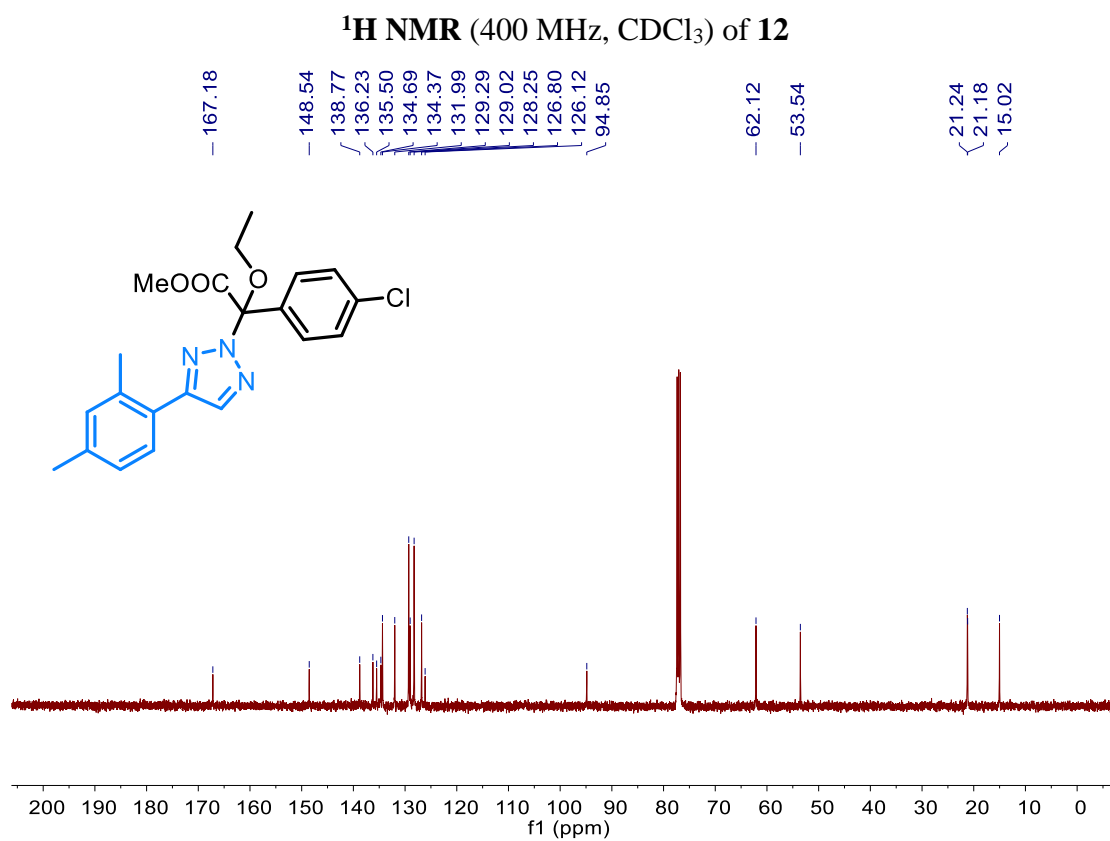
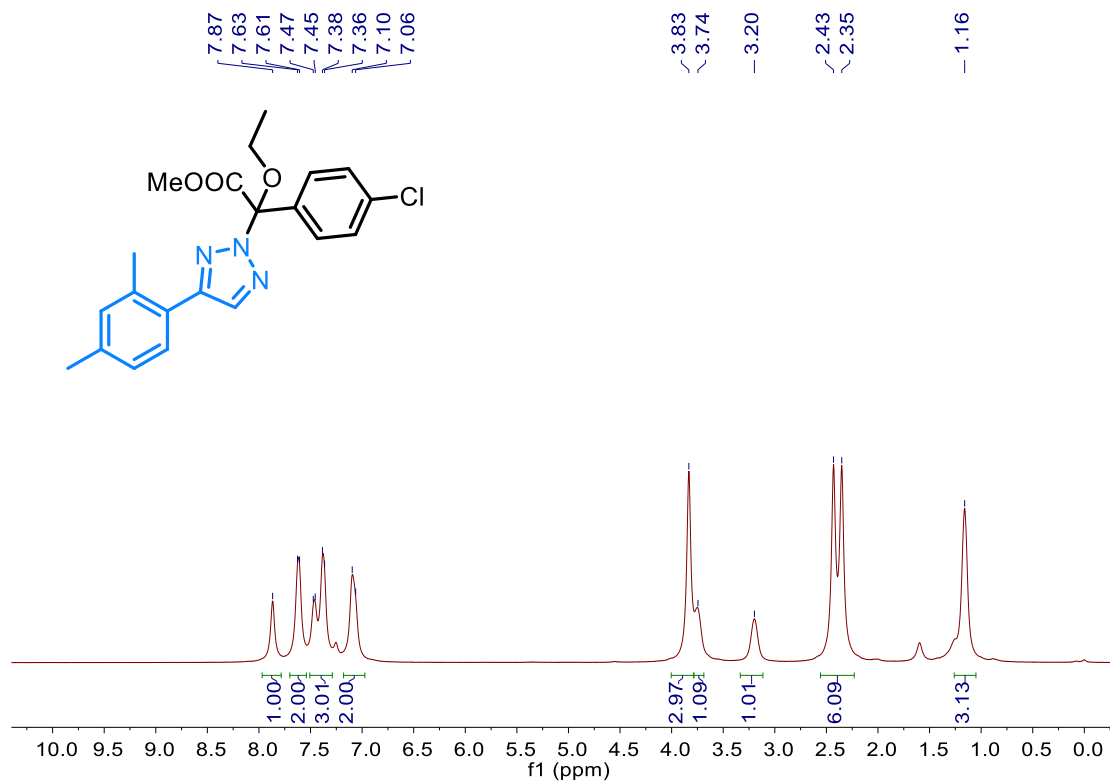


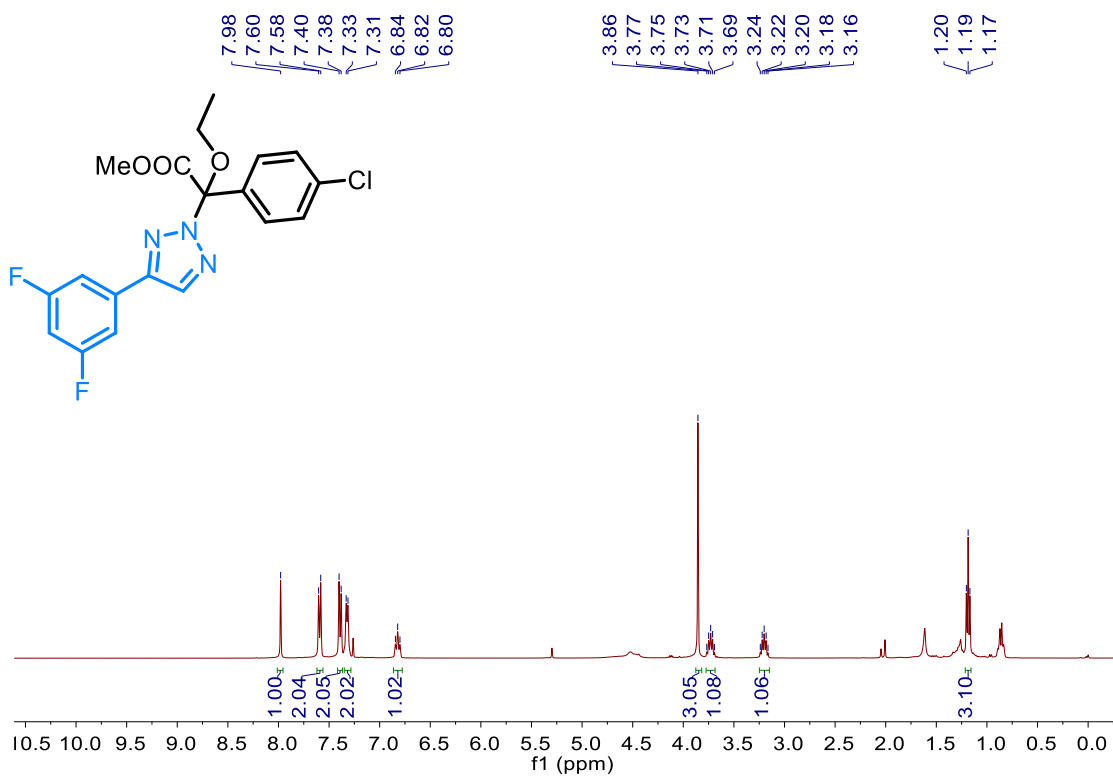
^1H NMR (400 MHz, CDCl_3) of **9**



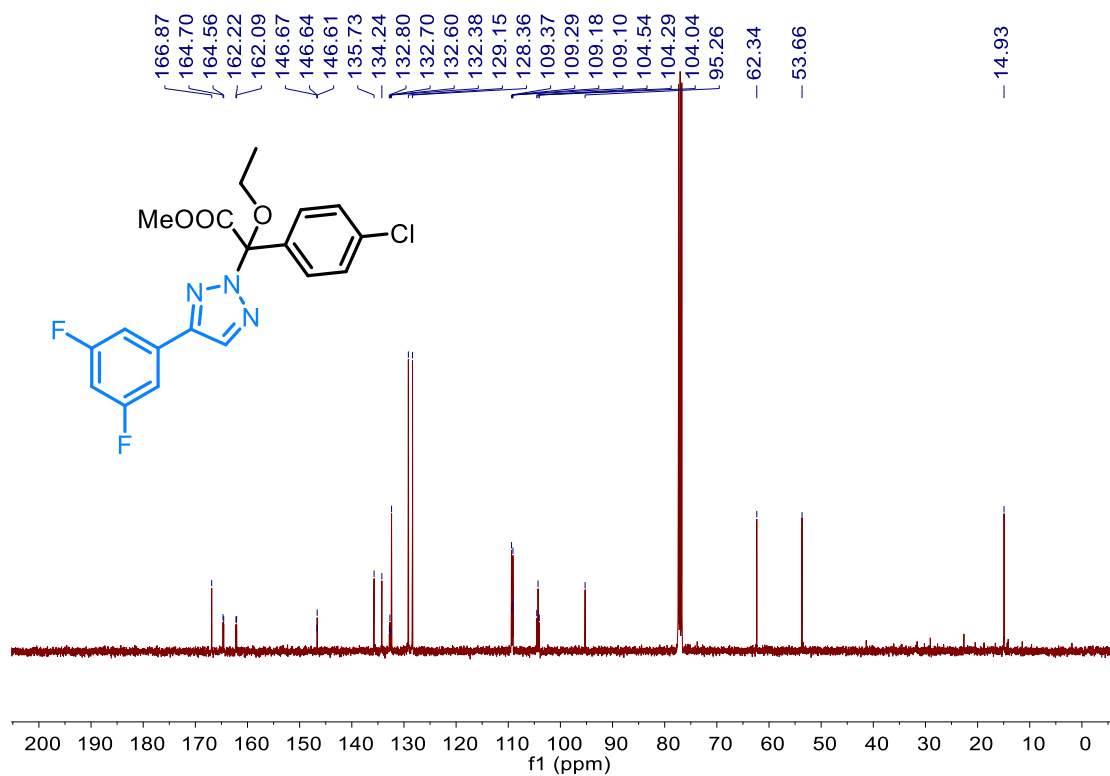




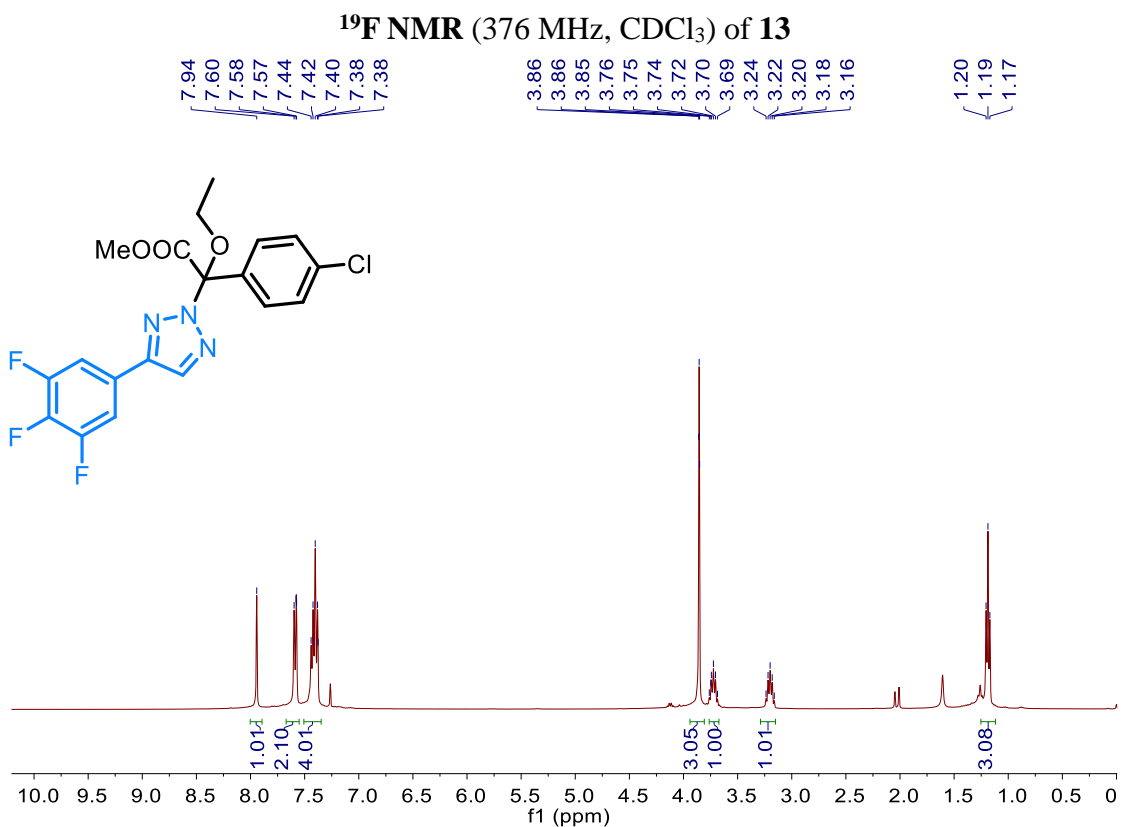
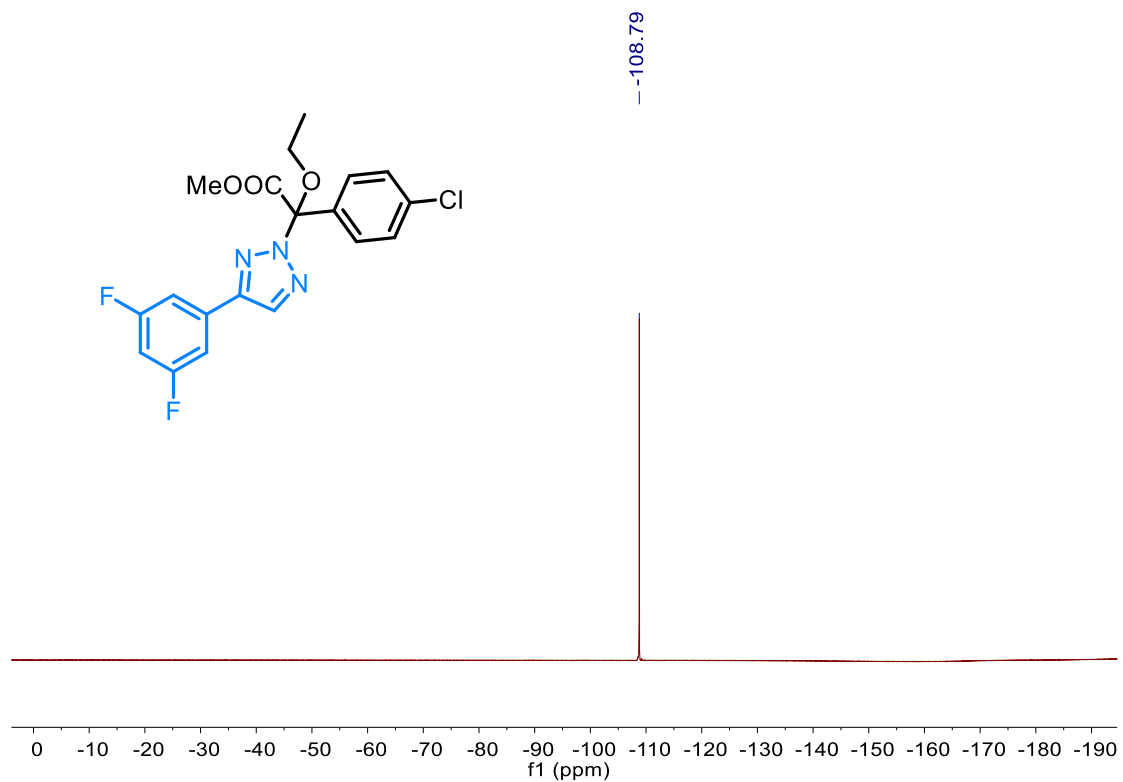


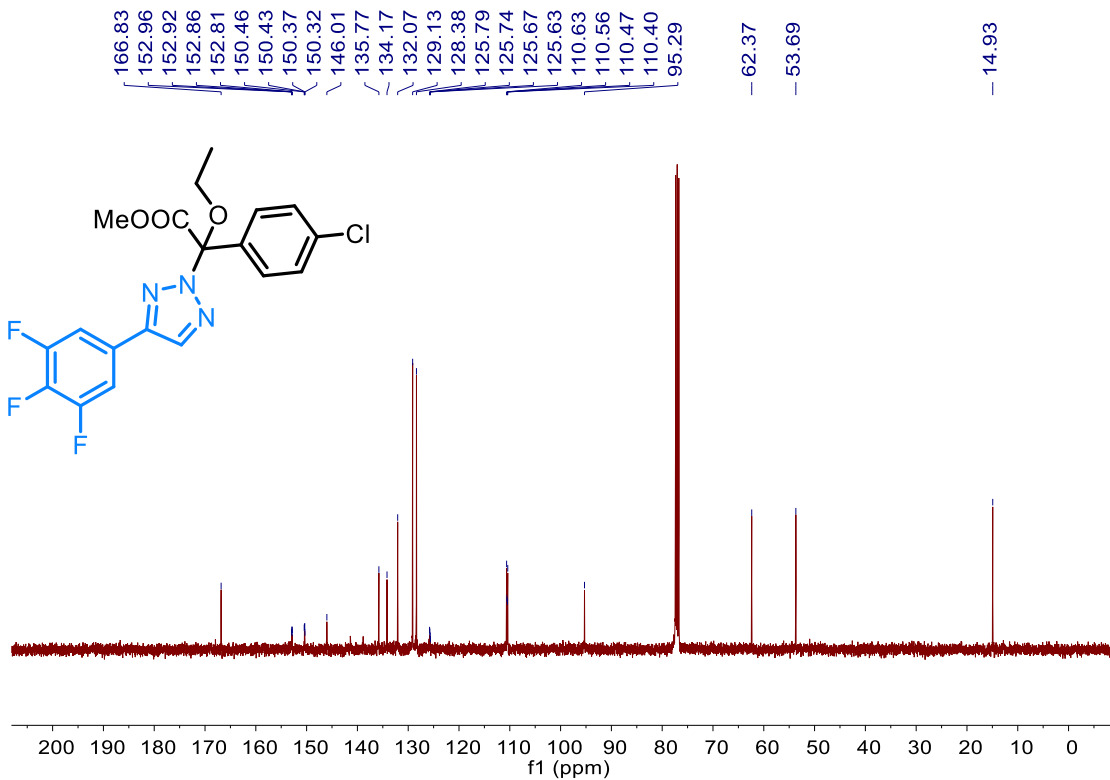


¹H NMR (400 MHz, CDCl₃) of 13

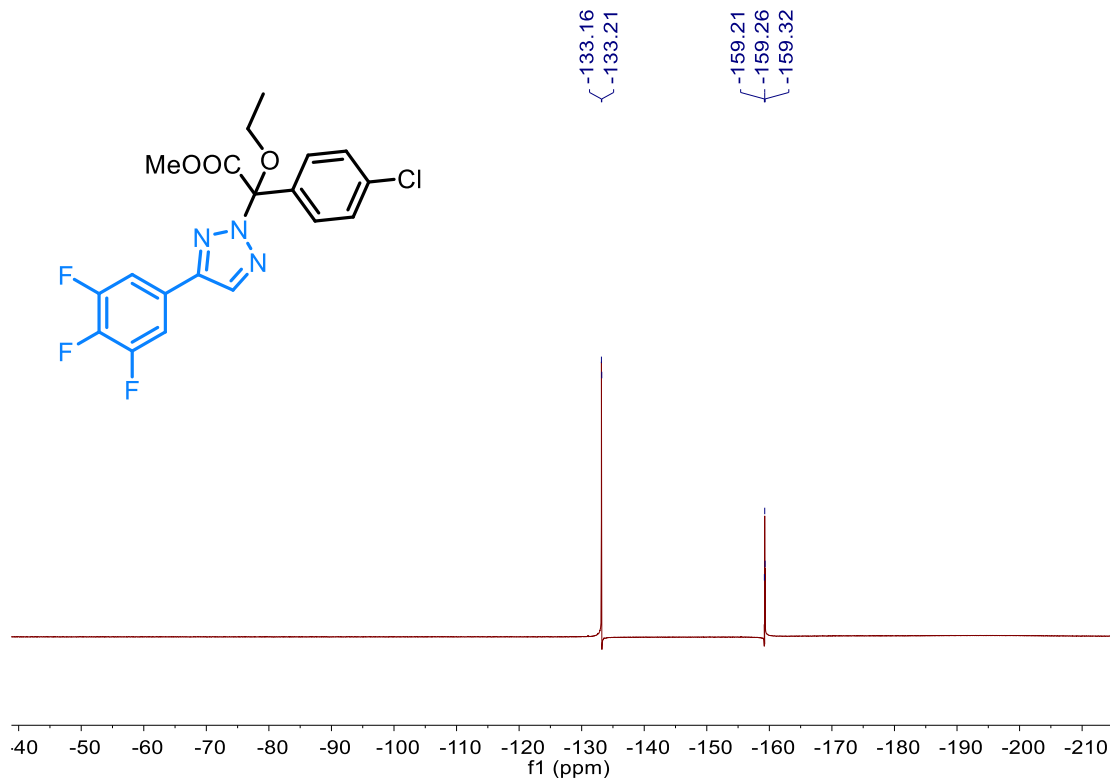


¹³C NMR (101 MHz, CDCl₃) of 13

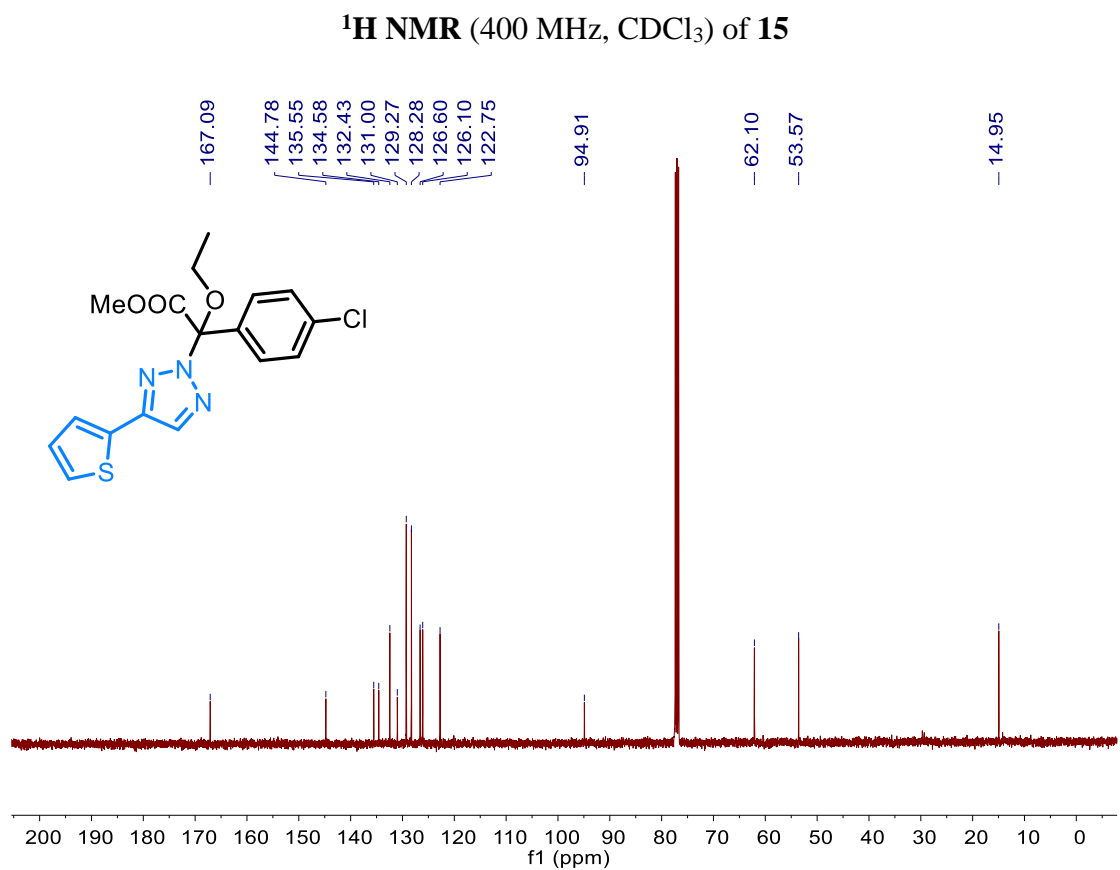
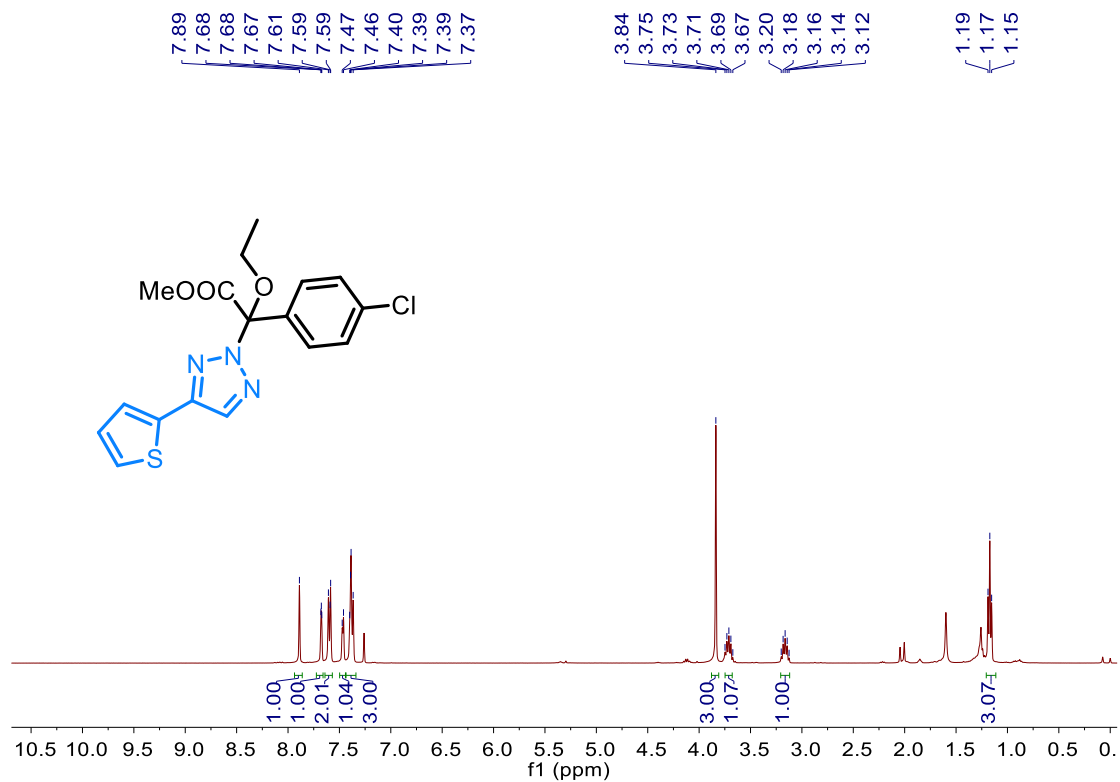


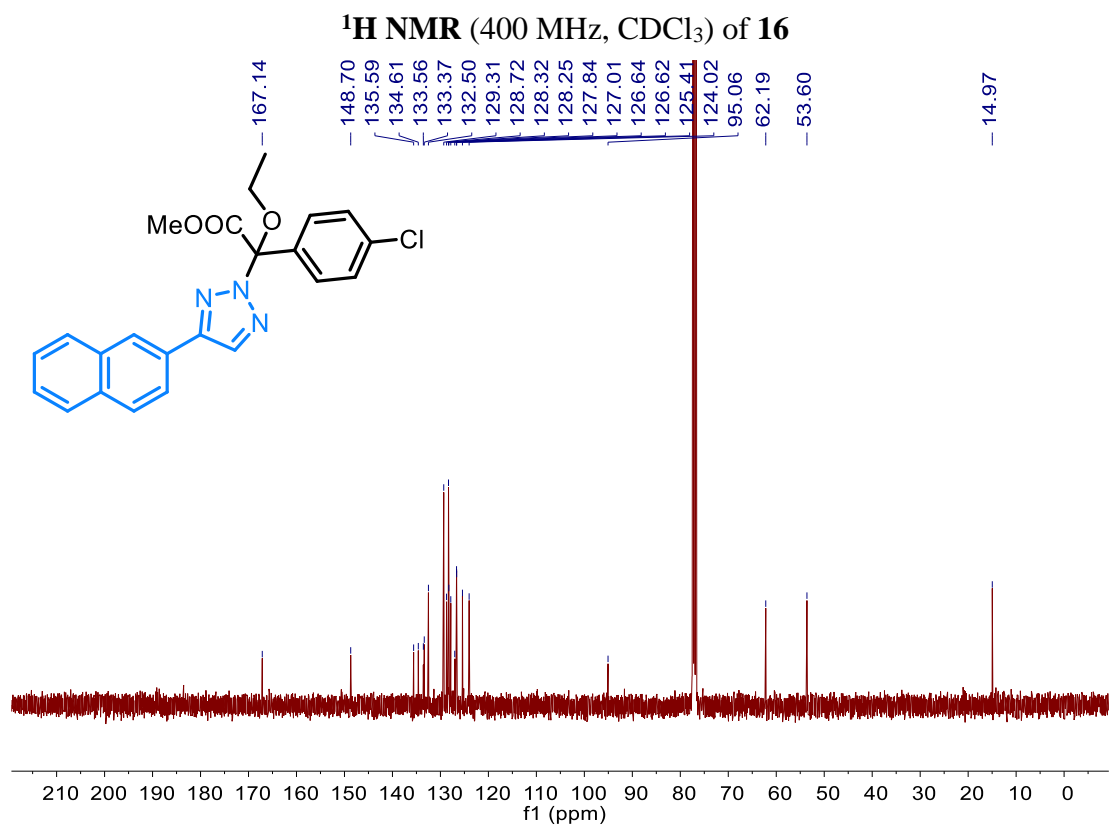
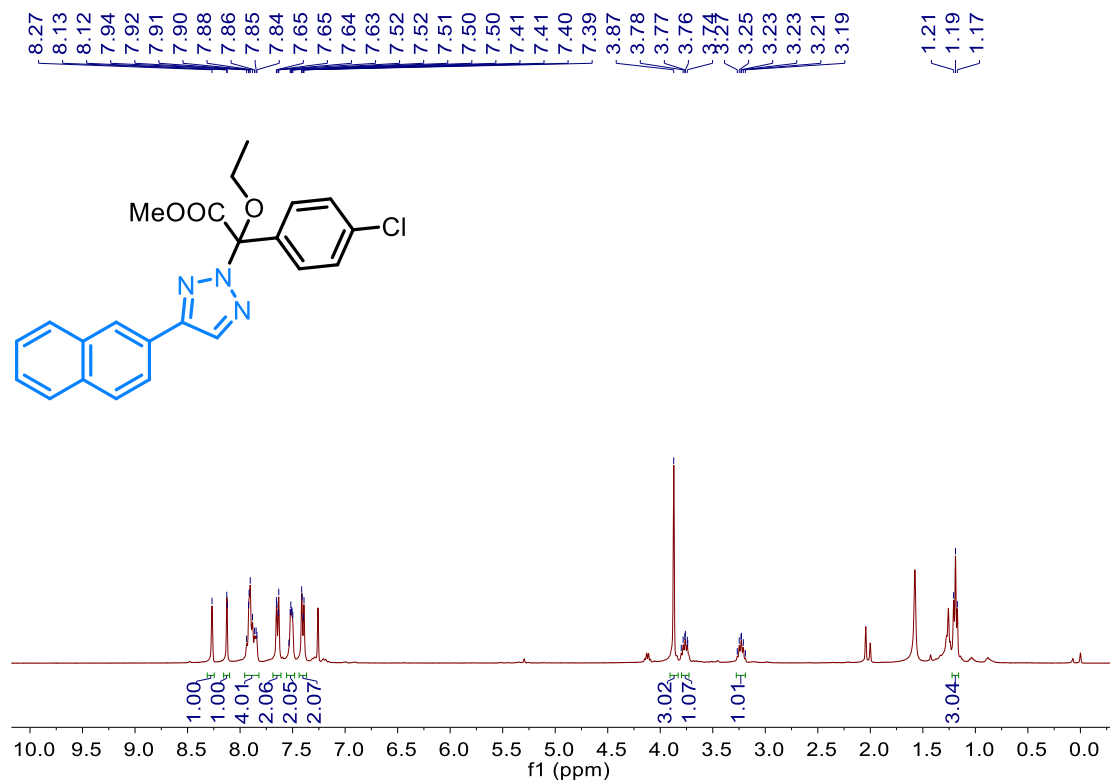


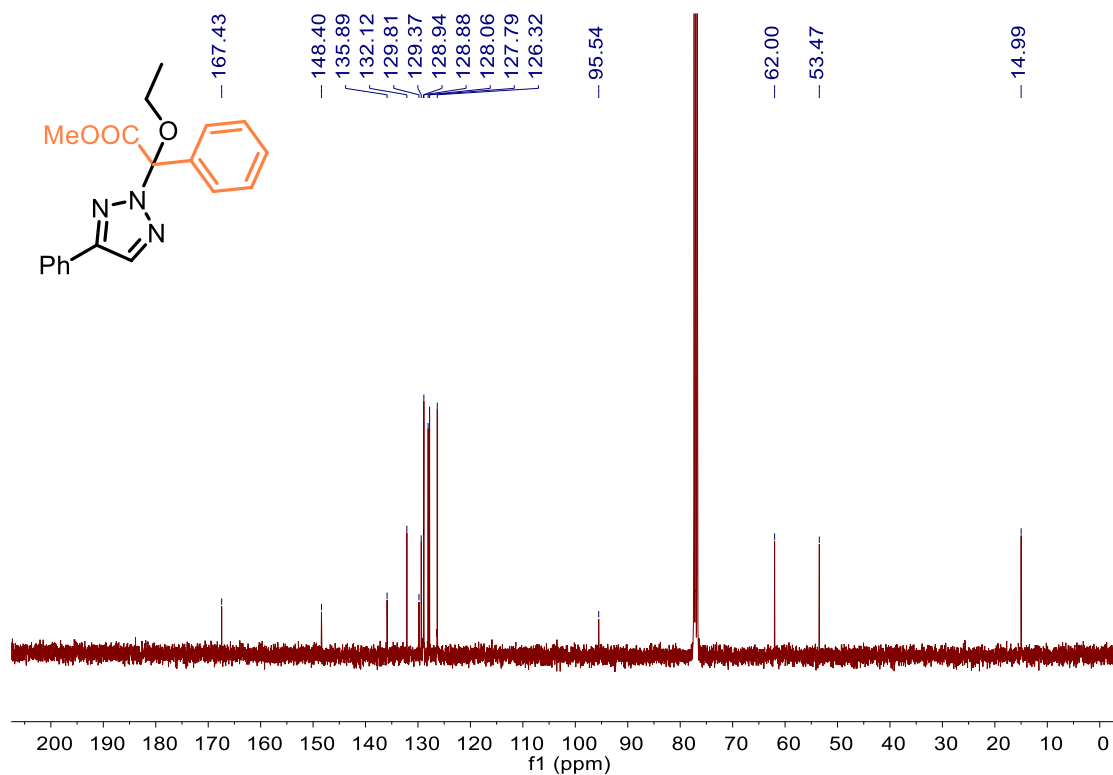
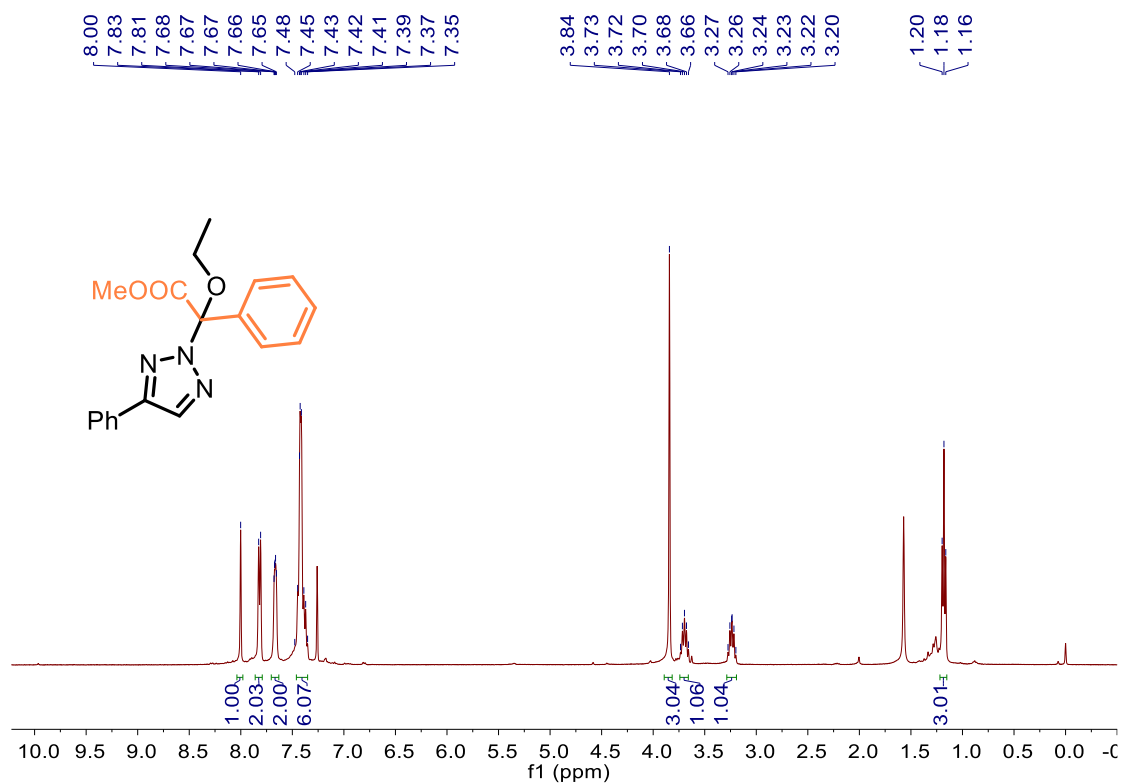
¹³C NMR (101 MHz, CDCl₃) of 14

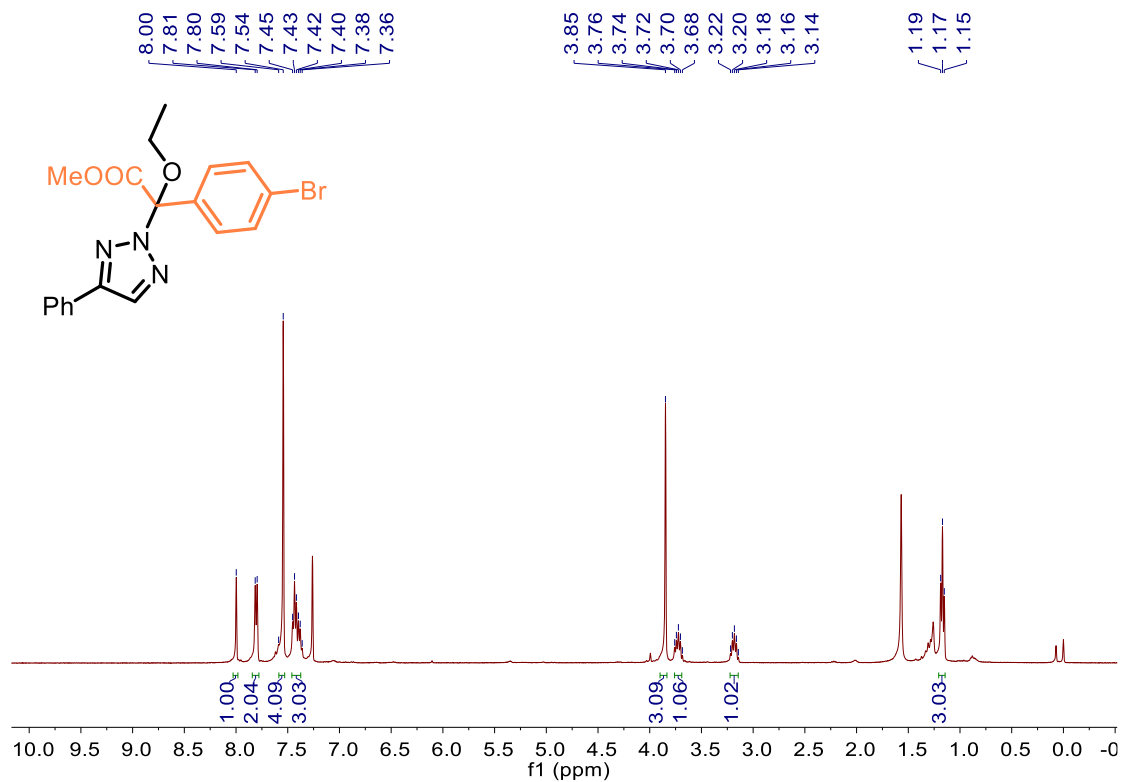


¹⁹F NMR (376 MHz, CDCl₃) of 14

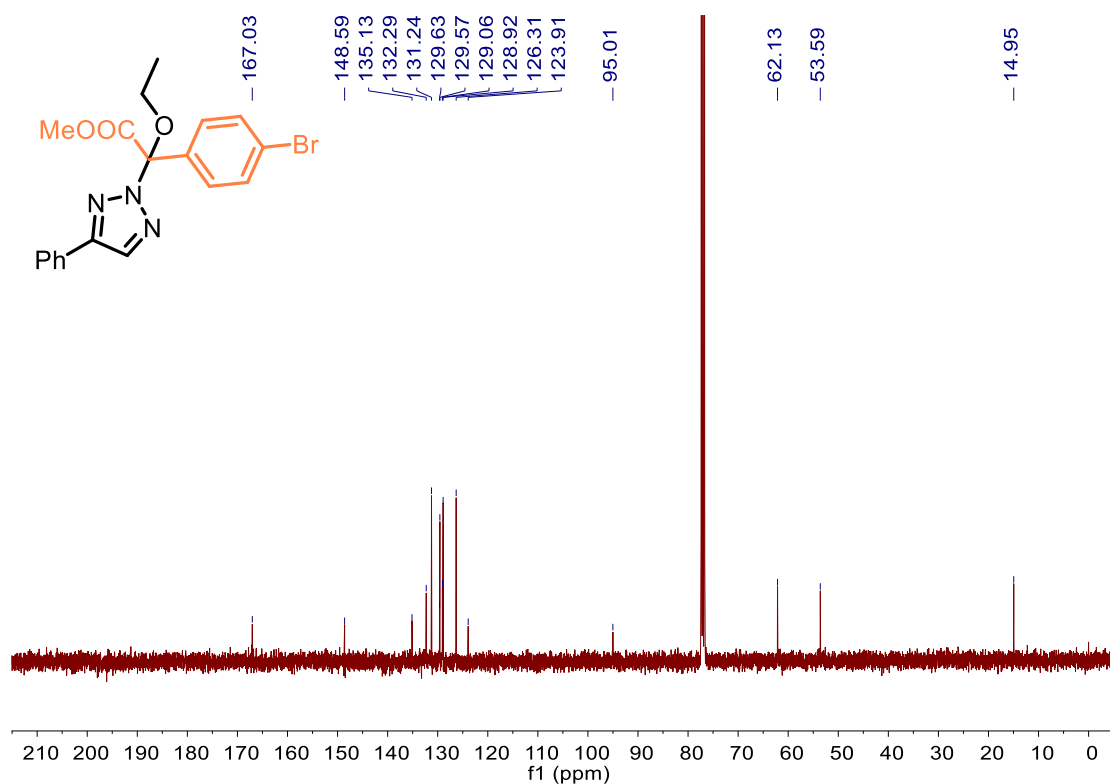




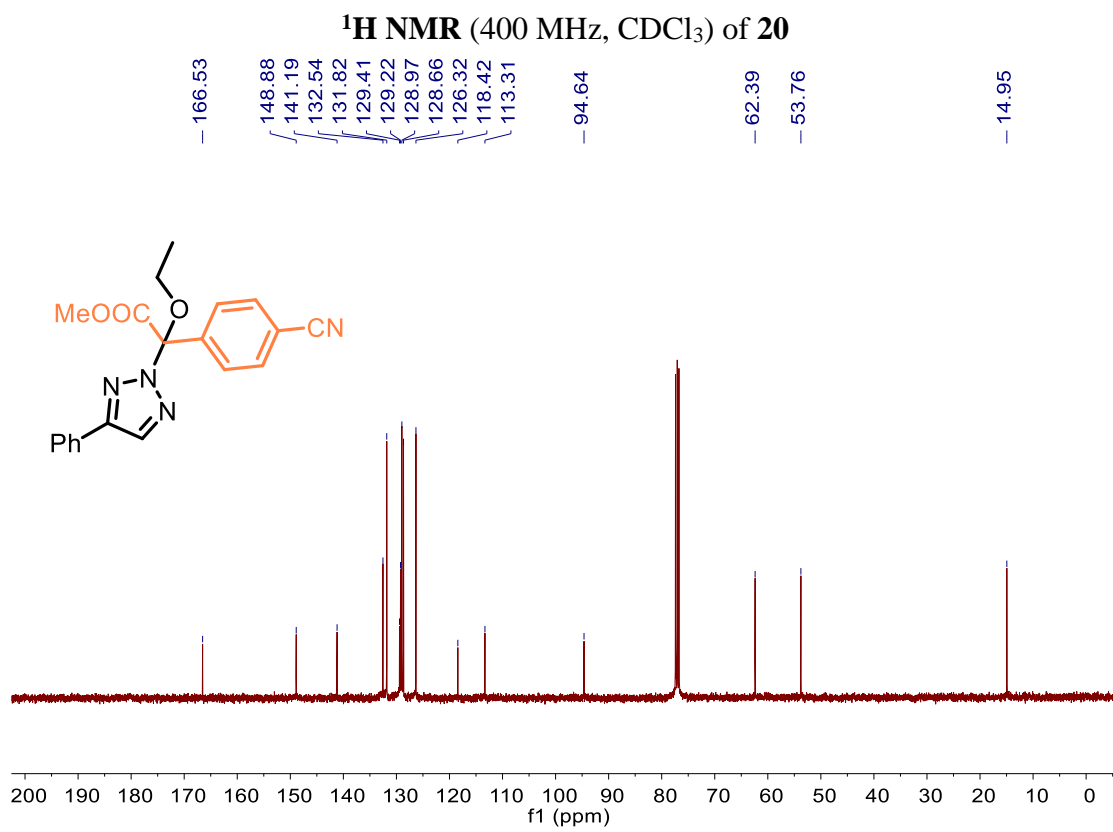
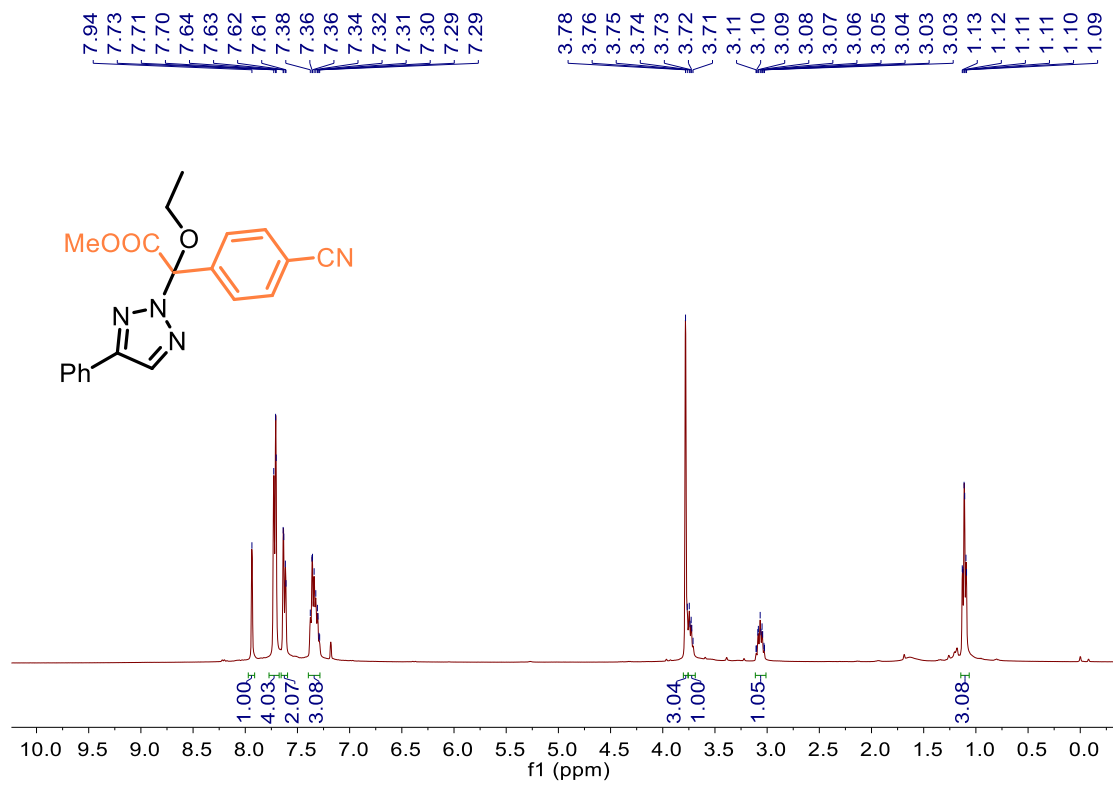


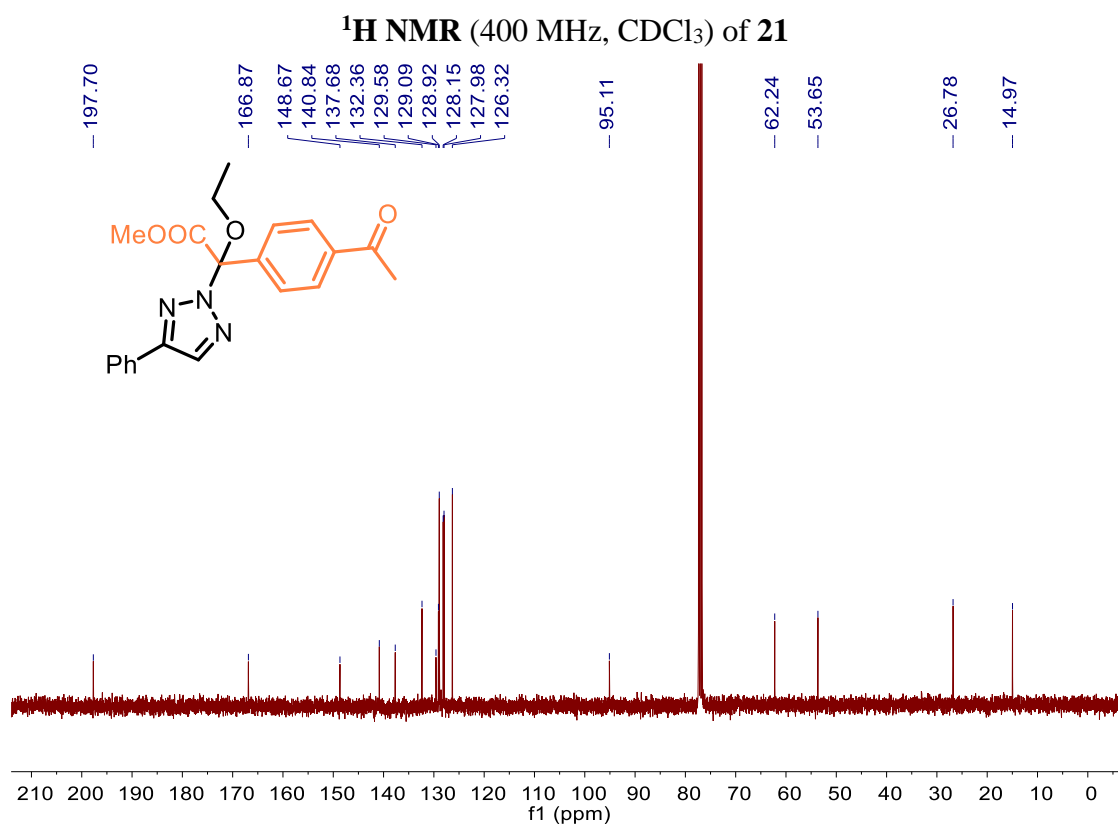
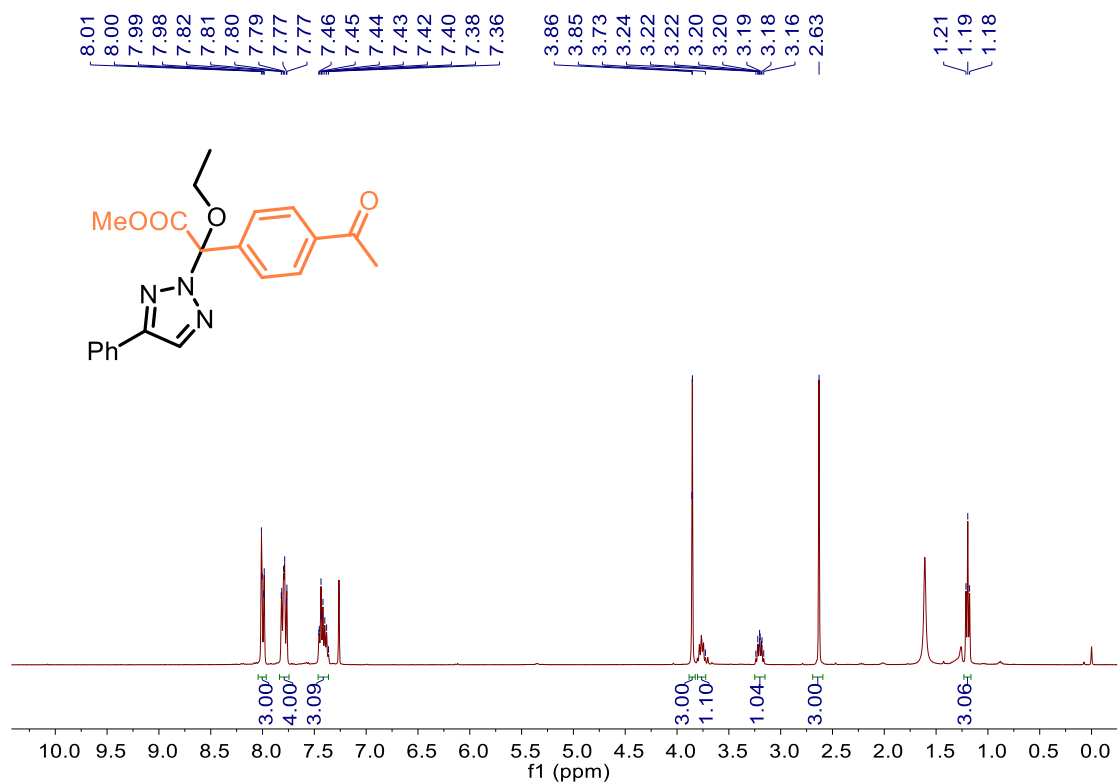


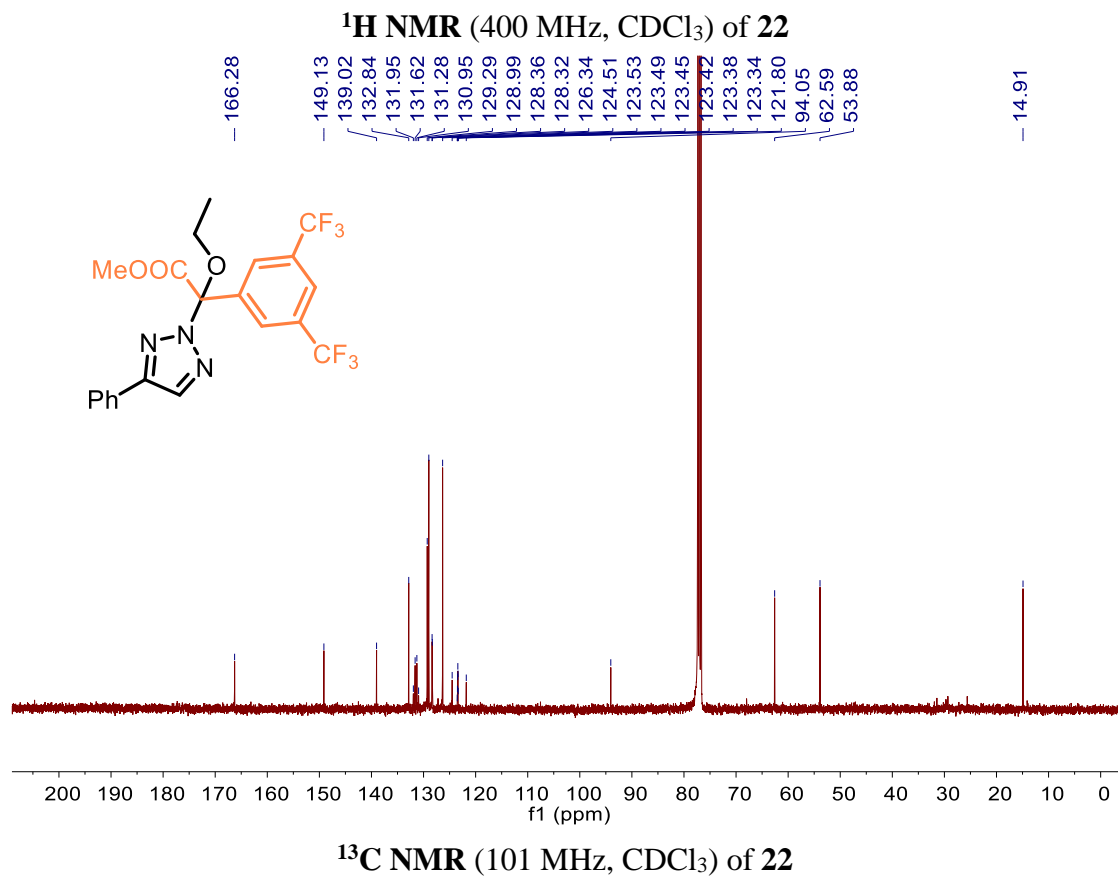
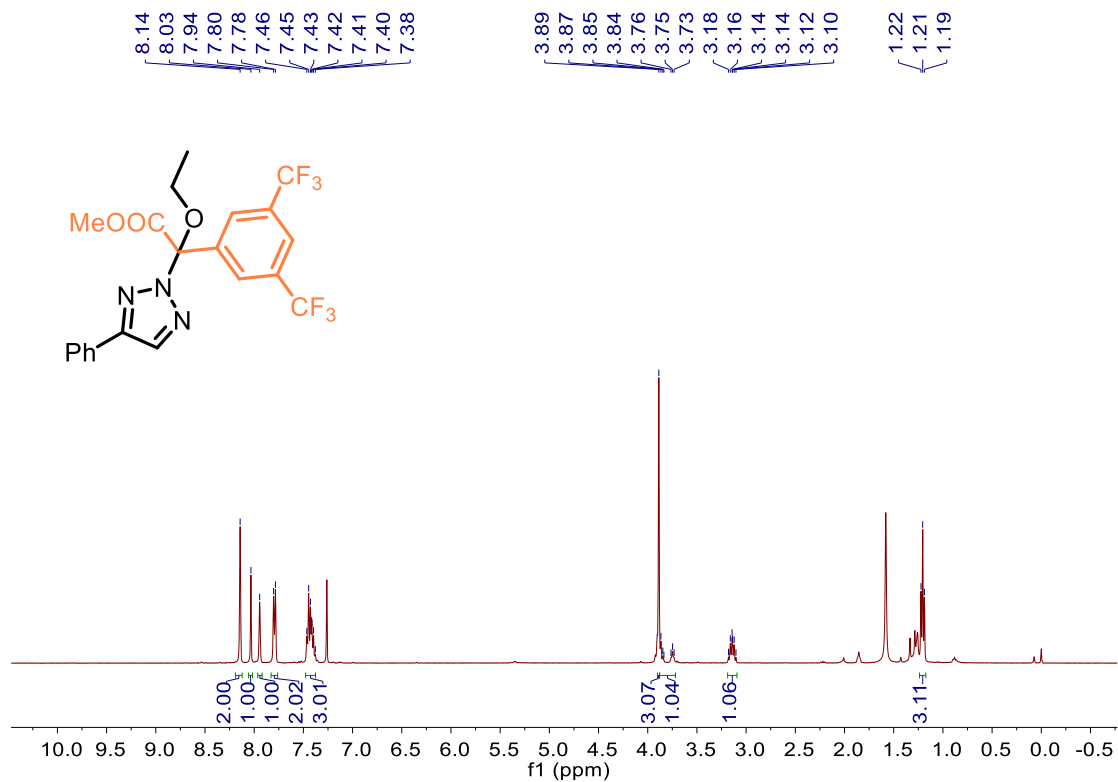
¹H NMR (400 MHz, CDCl₃) of 19

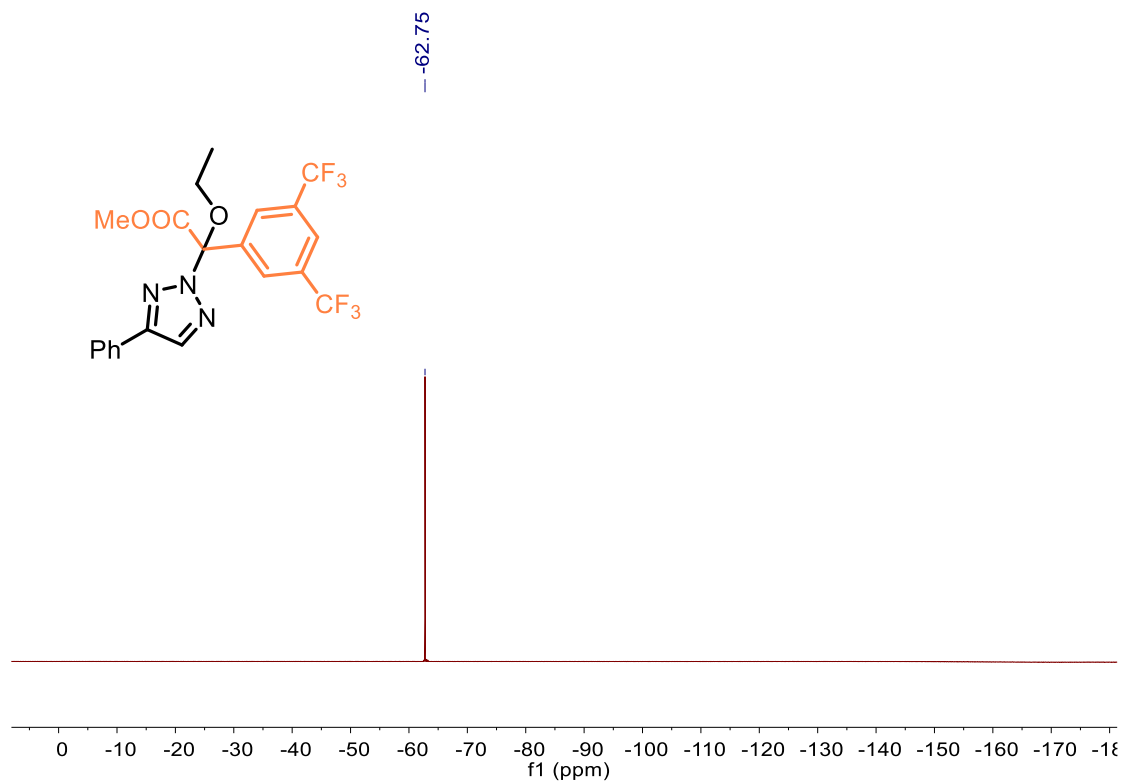


¹³C NMR (101 MHz, CDCl₃) of 19

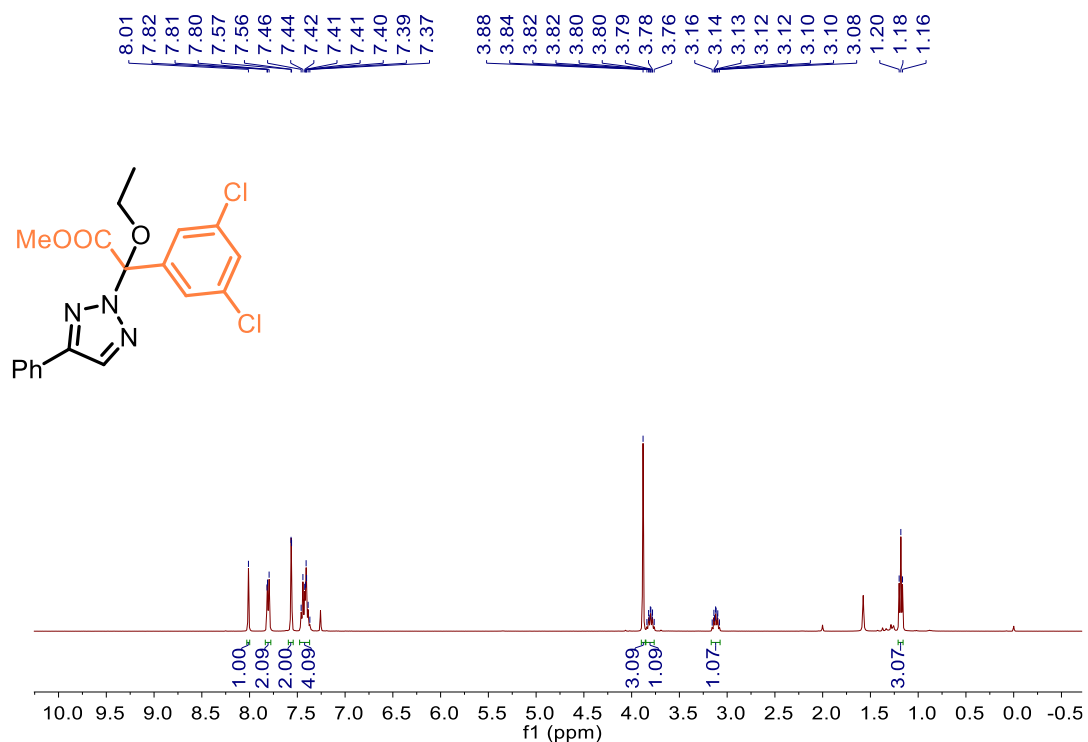




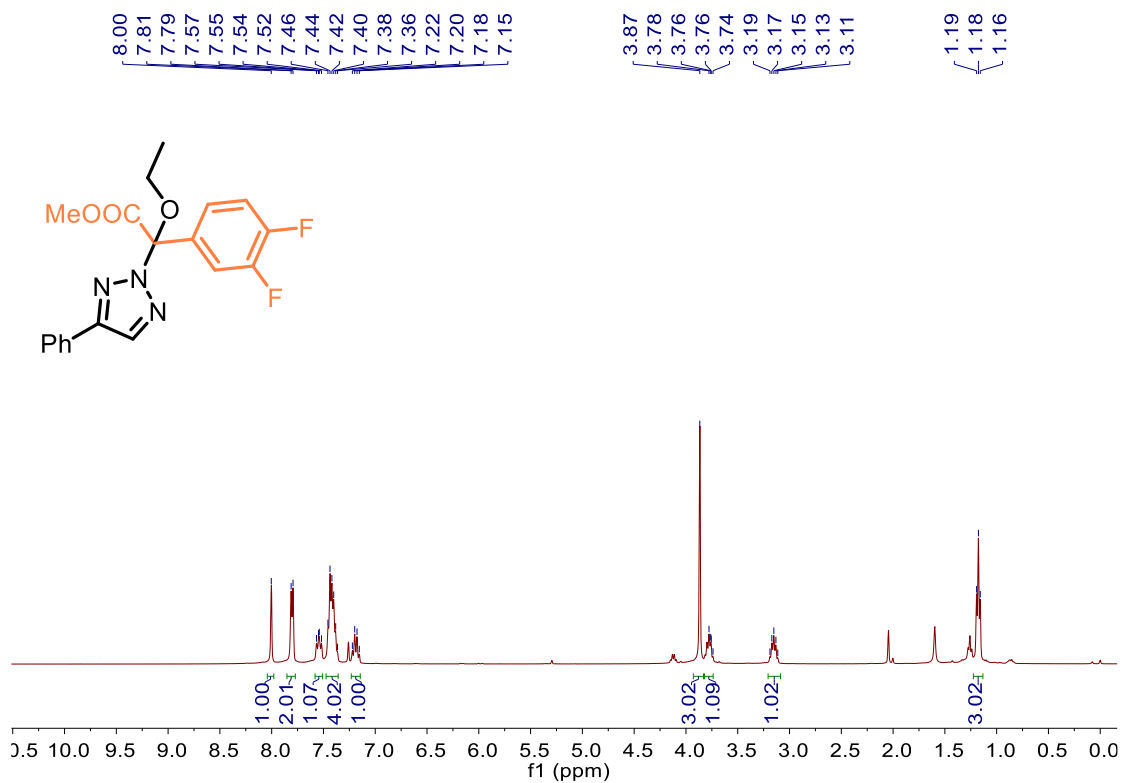
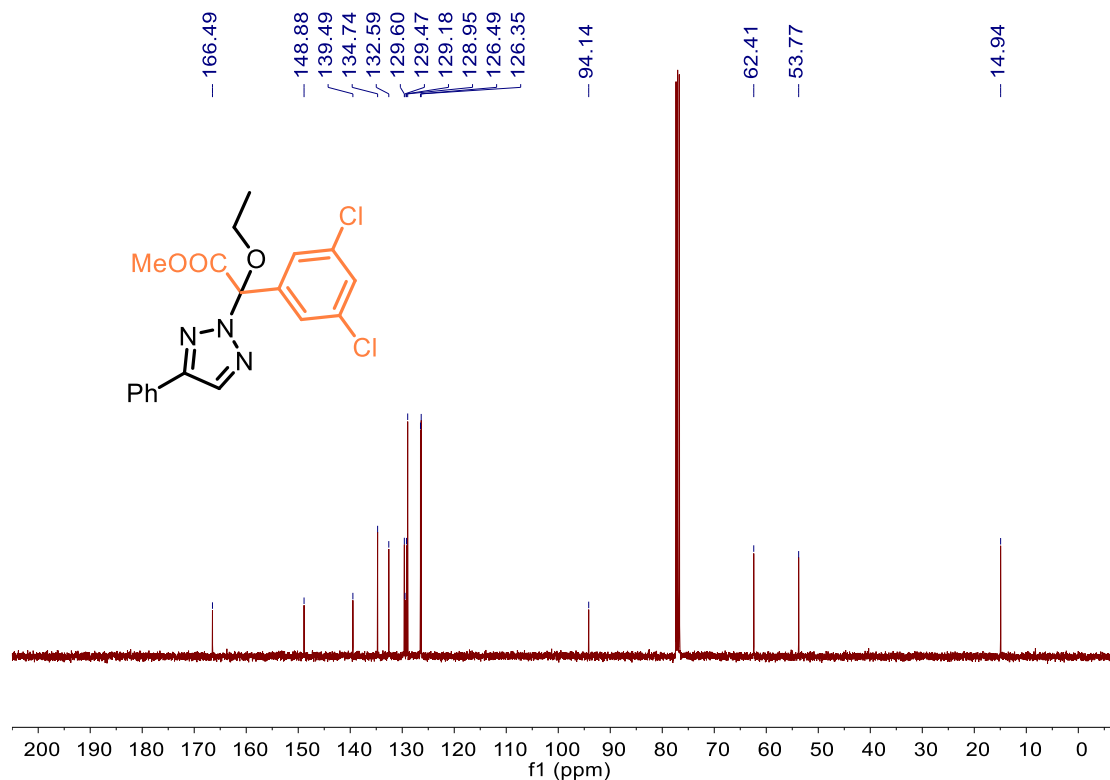


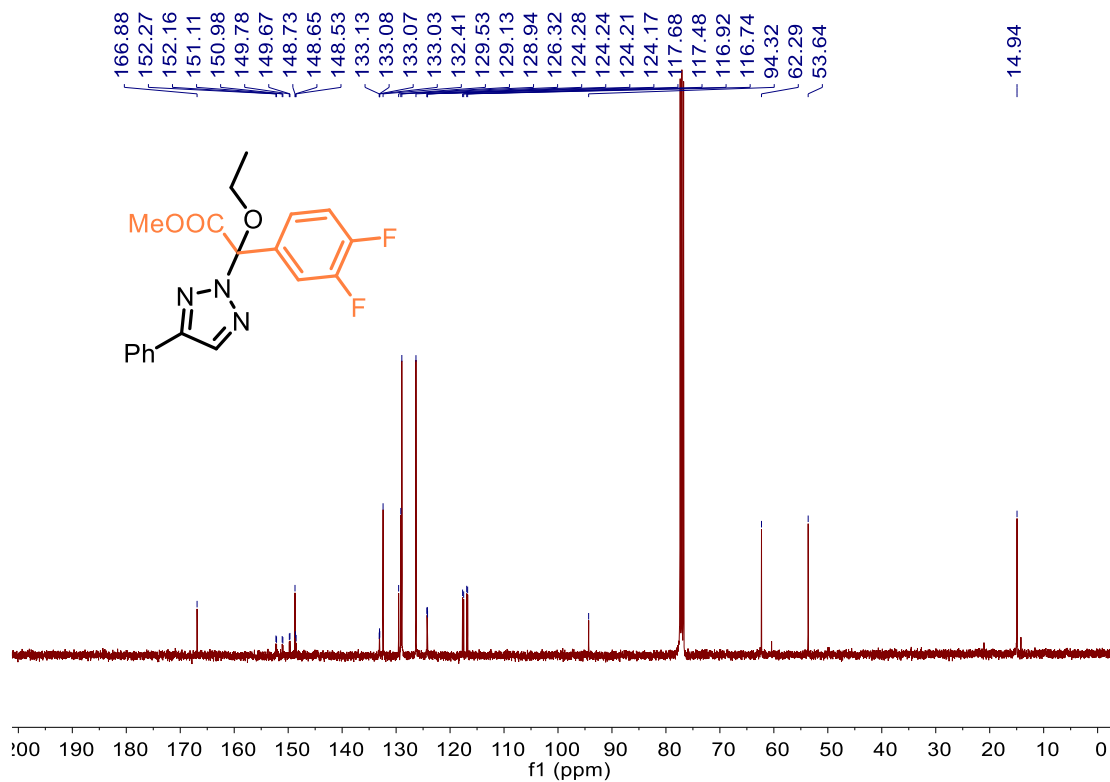


¹⁹F NMR (376 MHz, CDCl₃) of 22

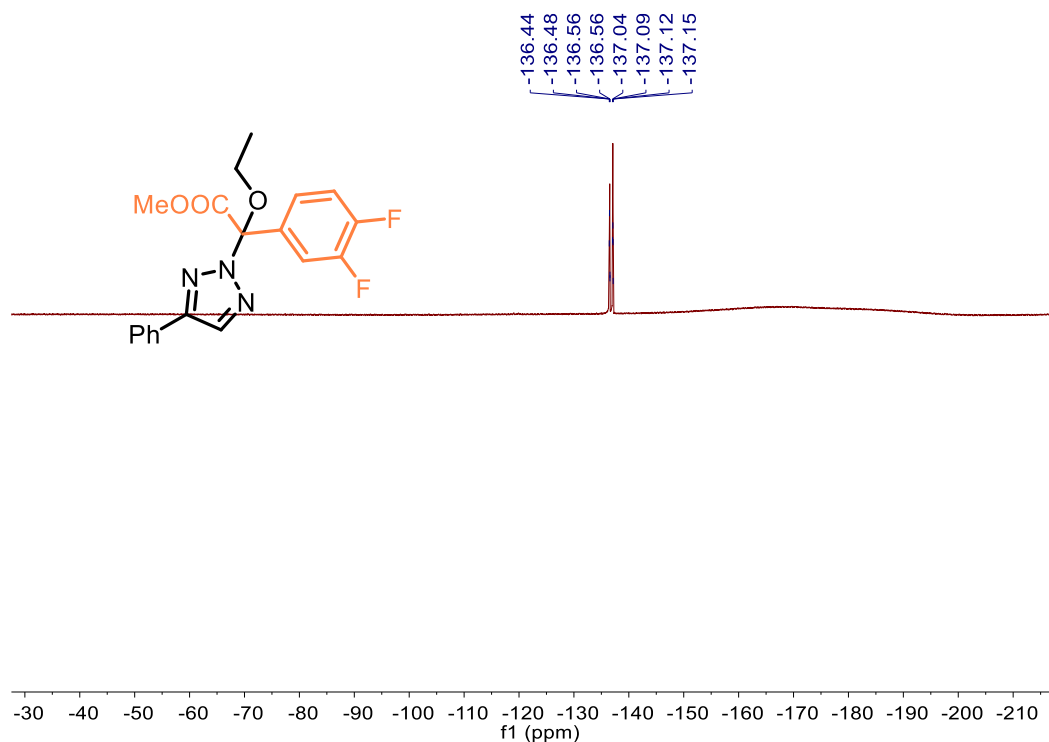


¹H NMR (400 MHz, CDCl₃) of 23

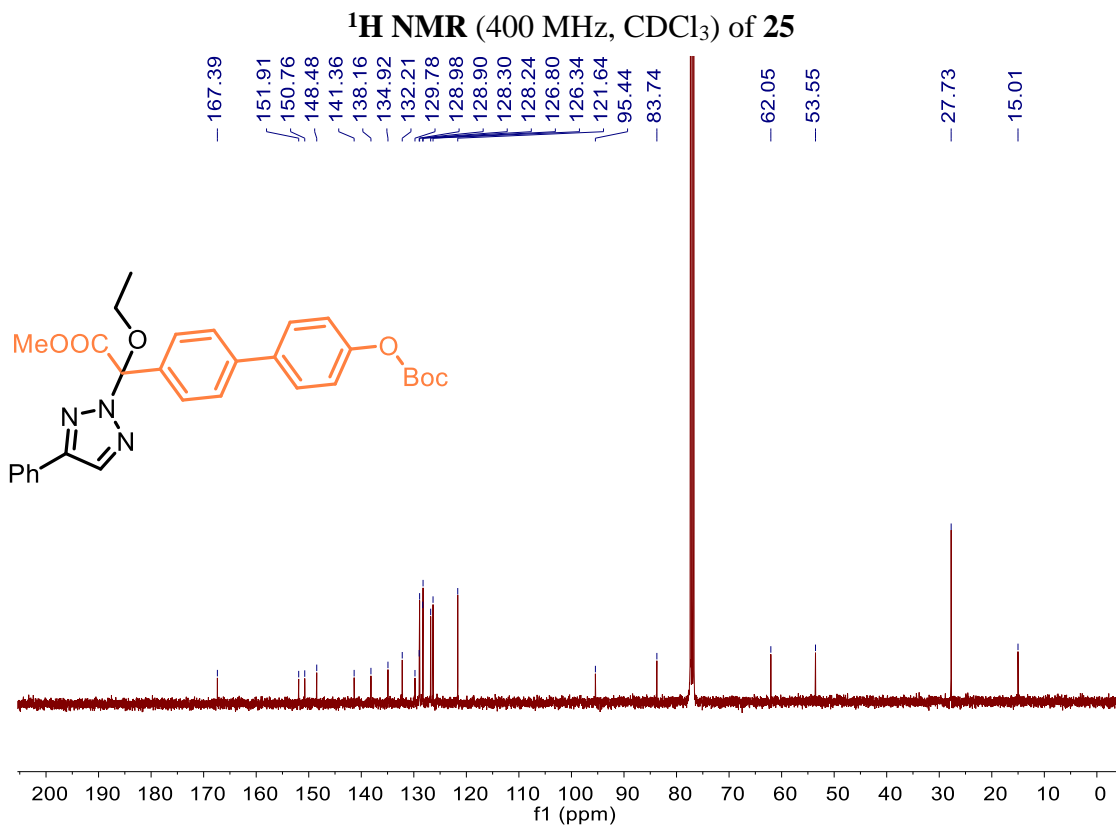
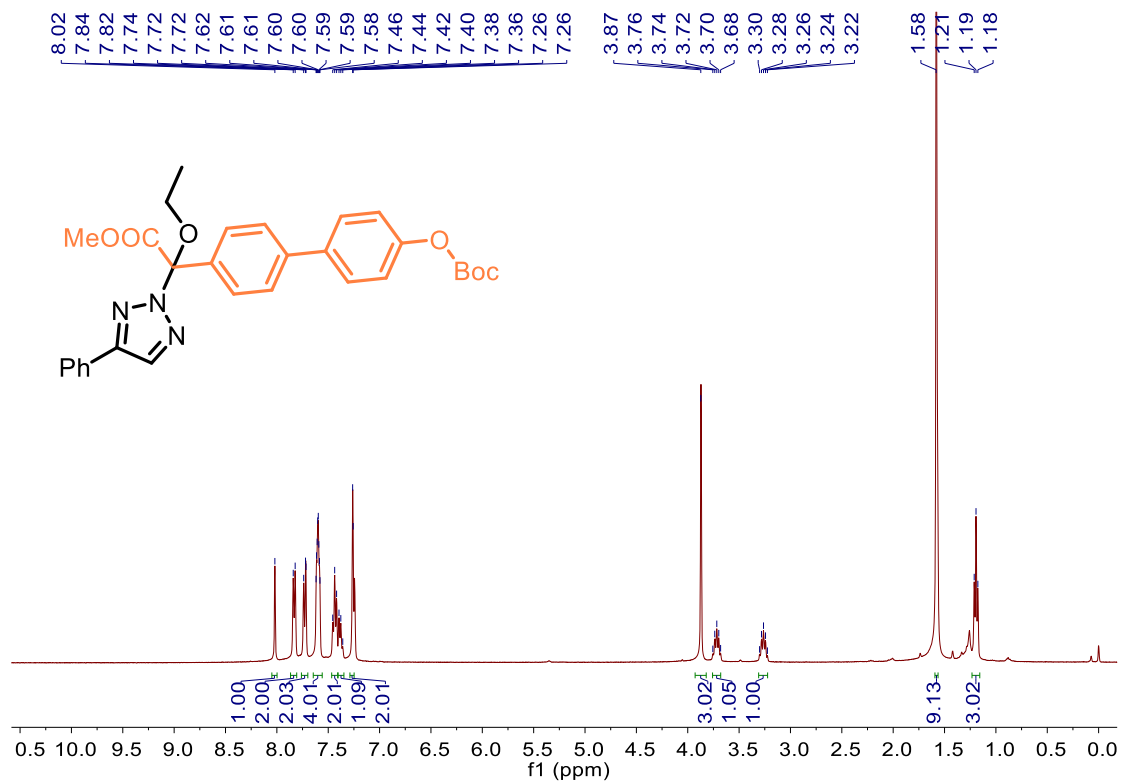


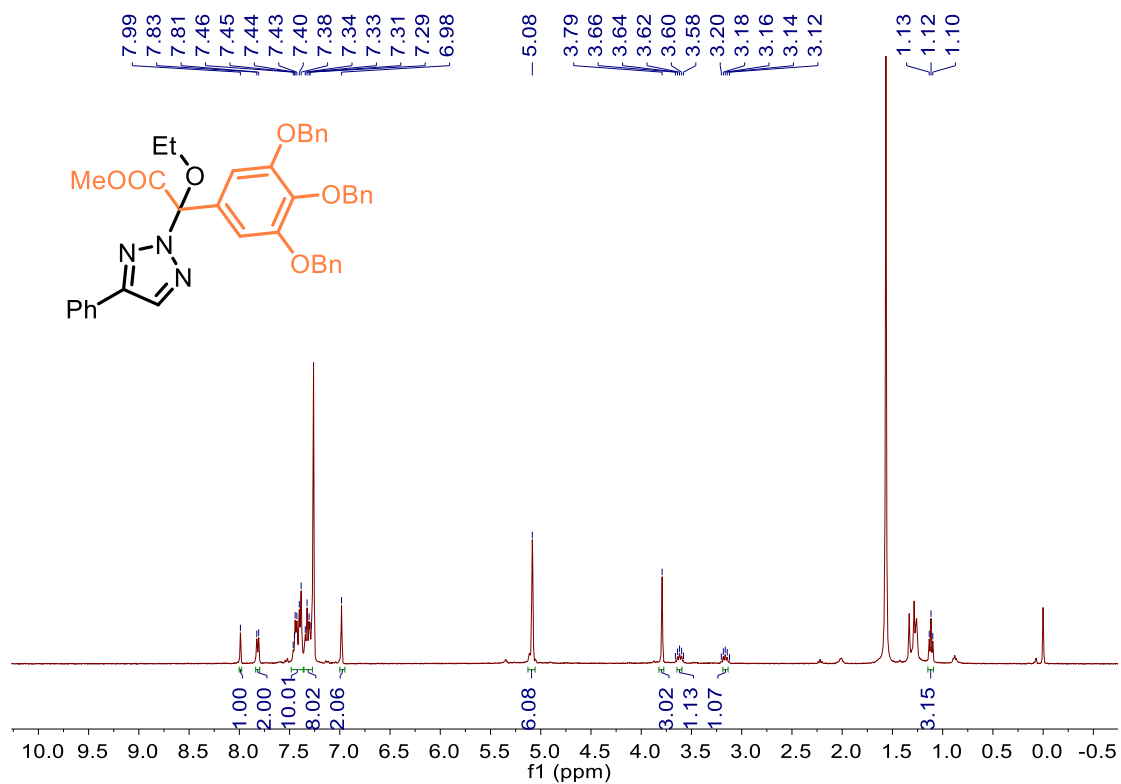


¹³C NMR (101 MHz, CDCl₃) of 24

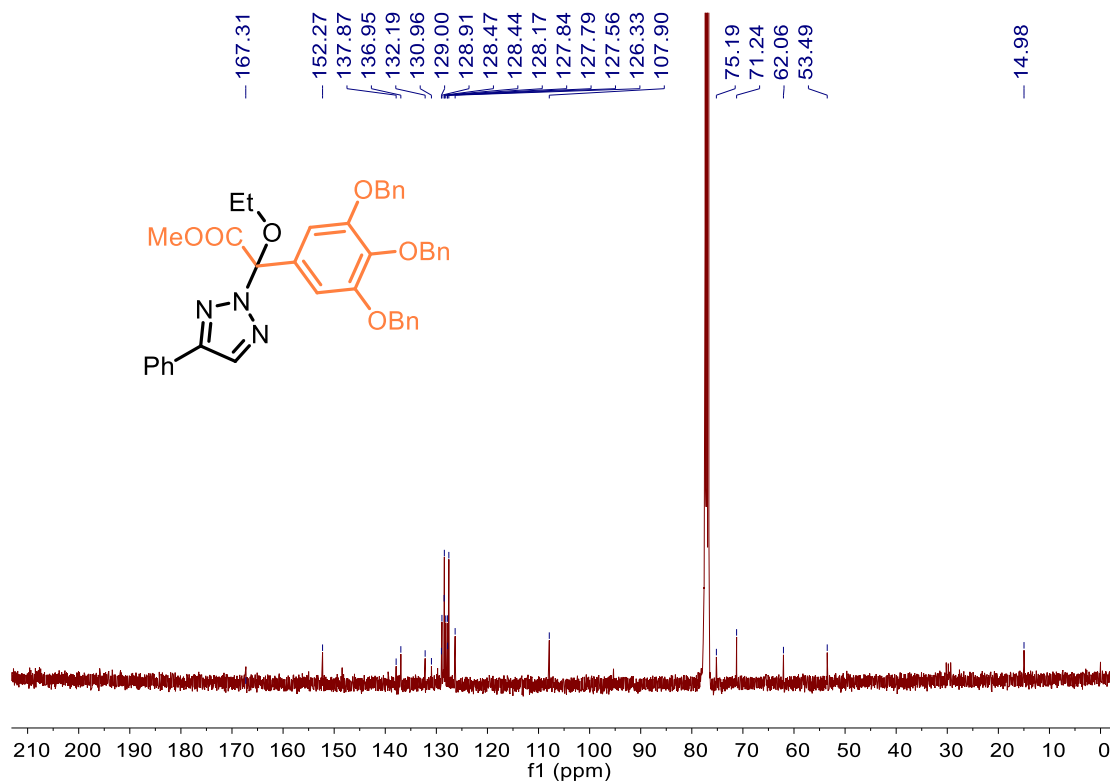


¹⁹F NMR (376 MHz, CDCl₃) of 24

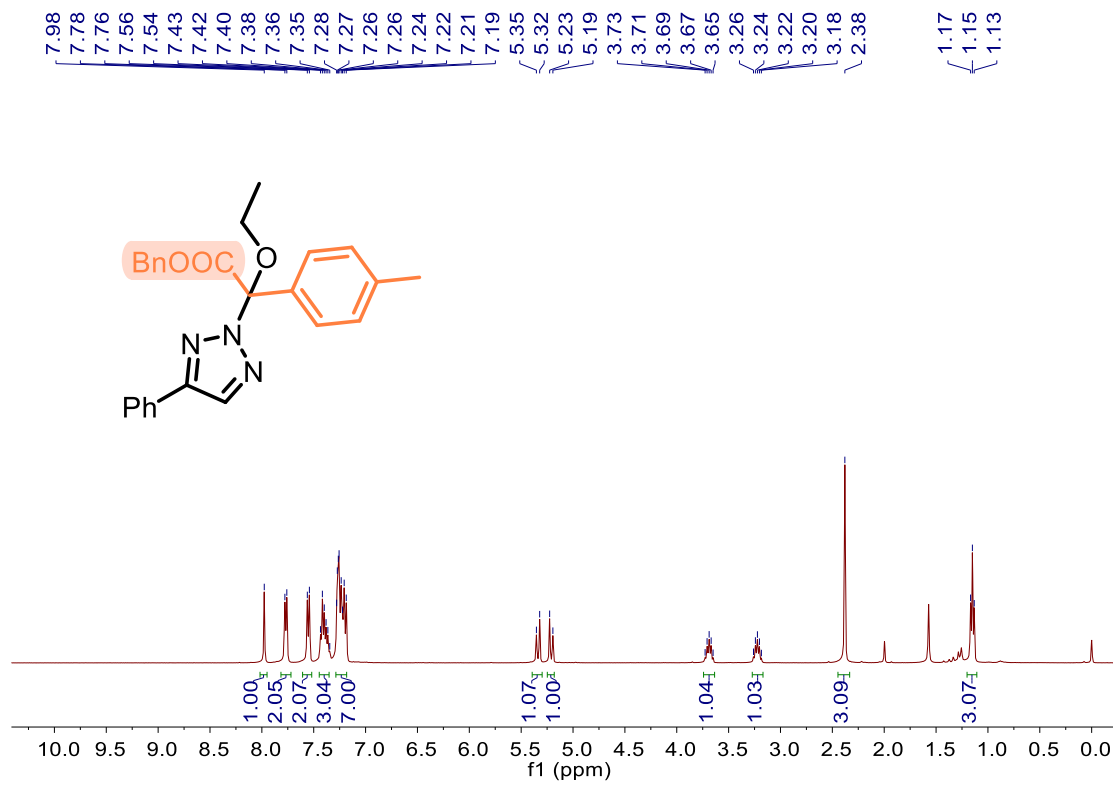




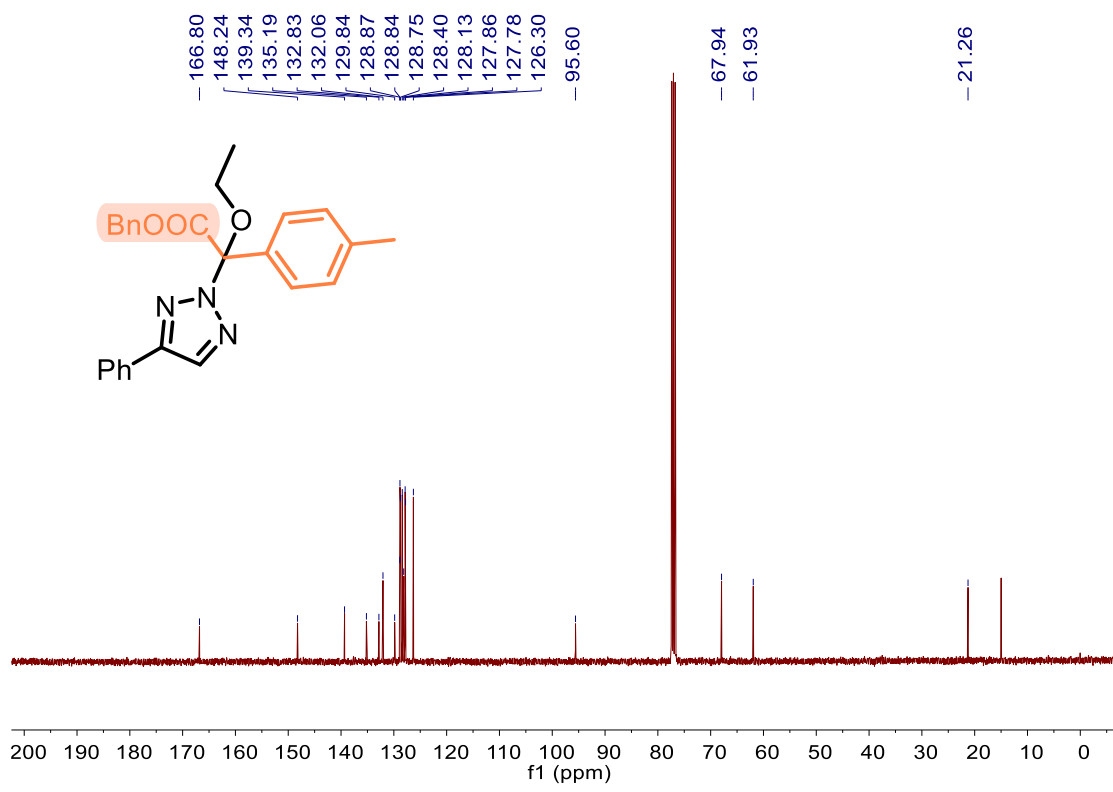
¹H NMR (400 MHz, CDCl₃) of **26**



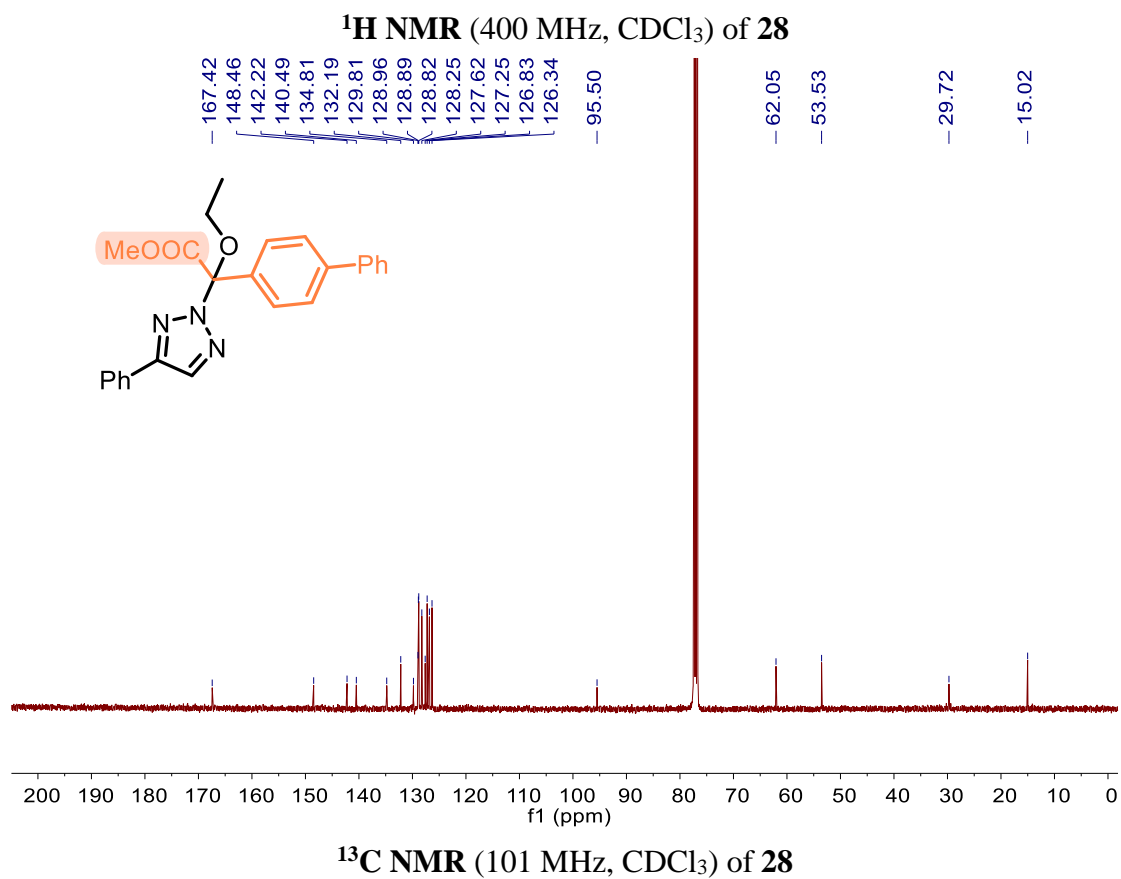
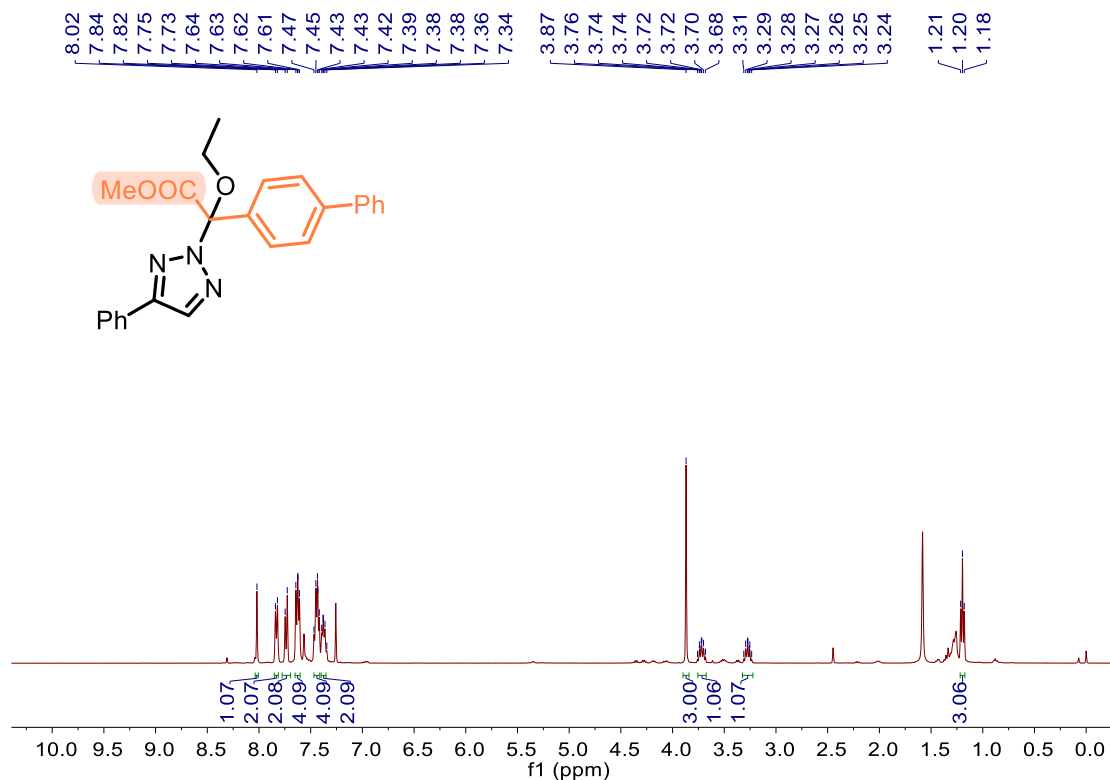
¹³C NMR (101 MHz, CDCl₃) of **26**

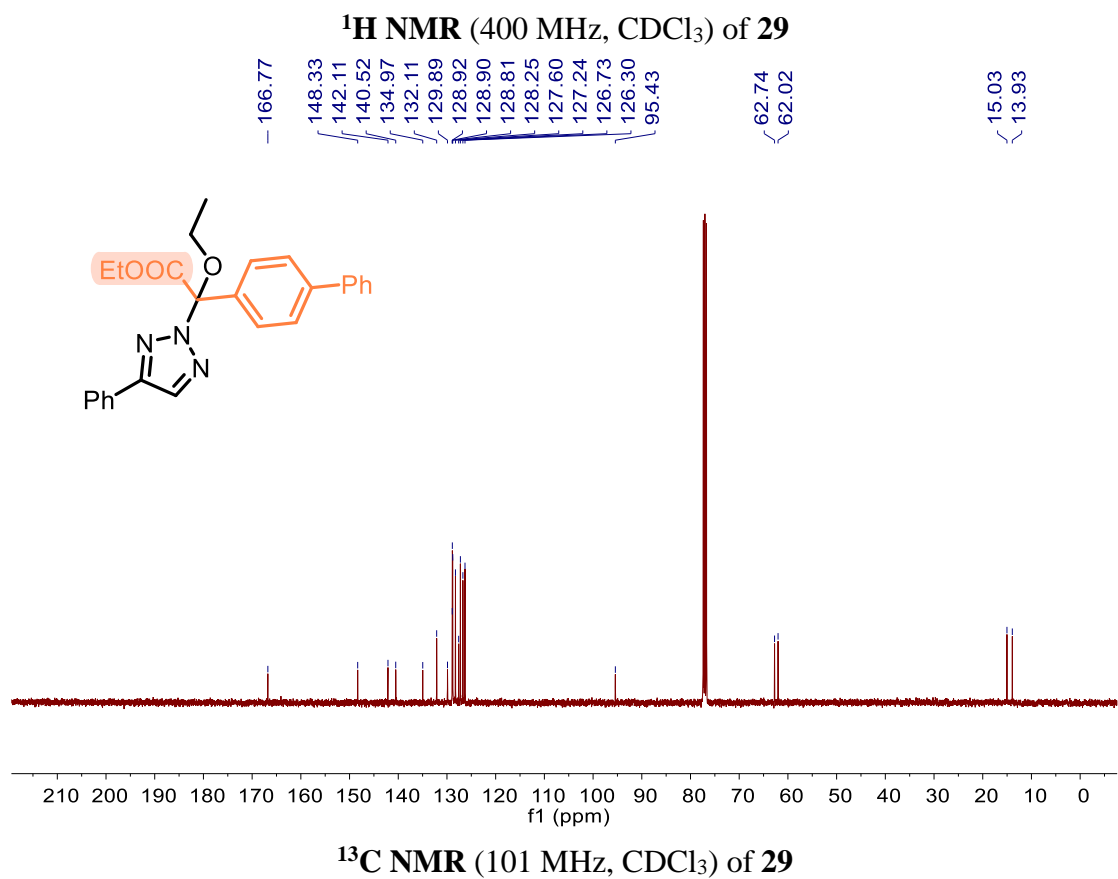
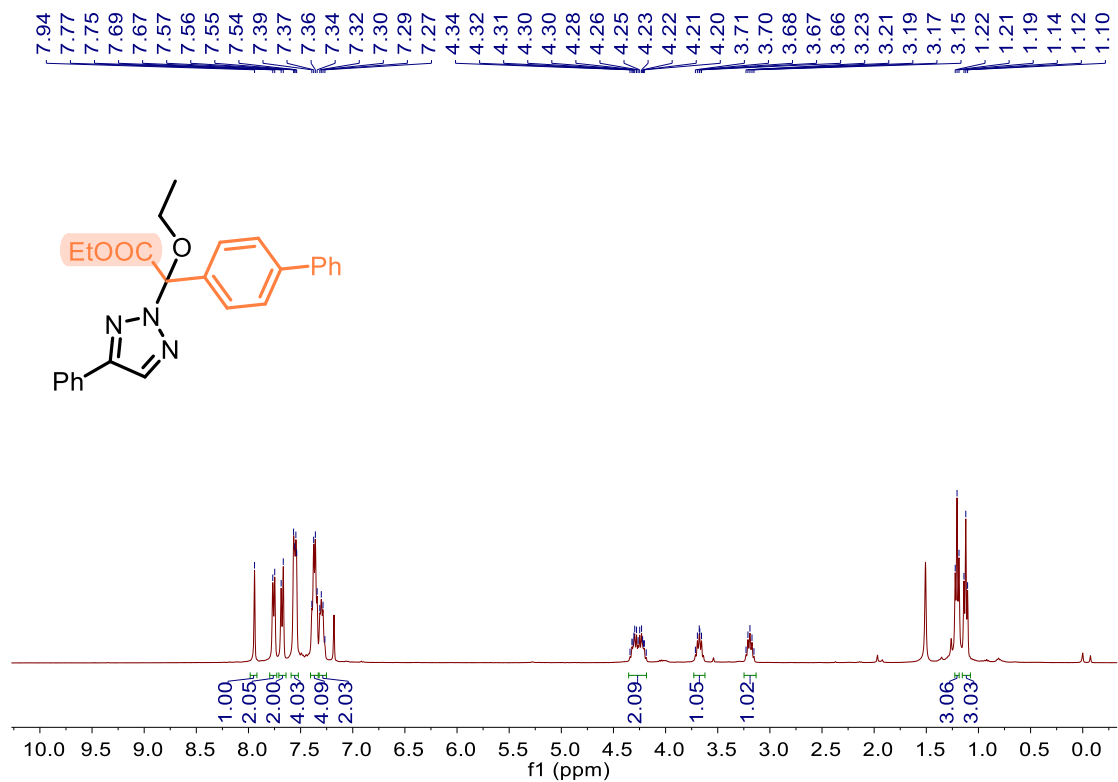


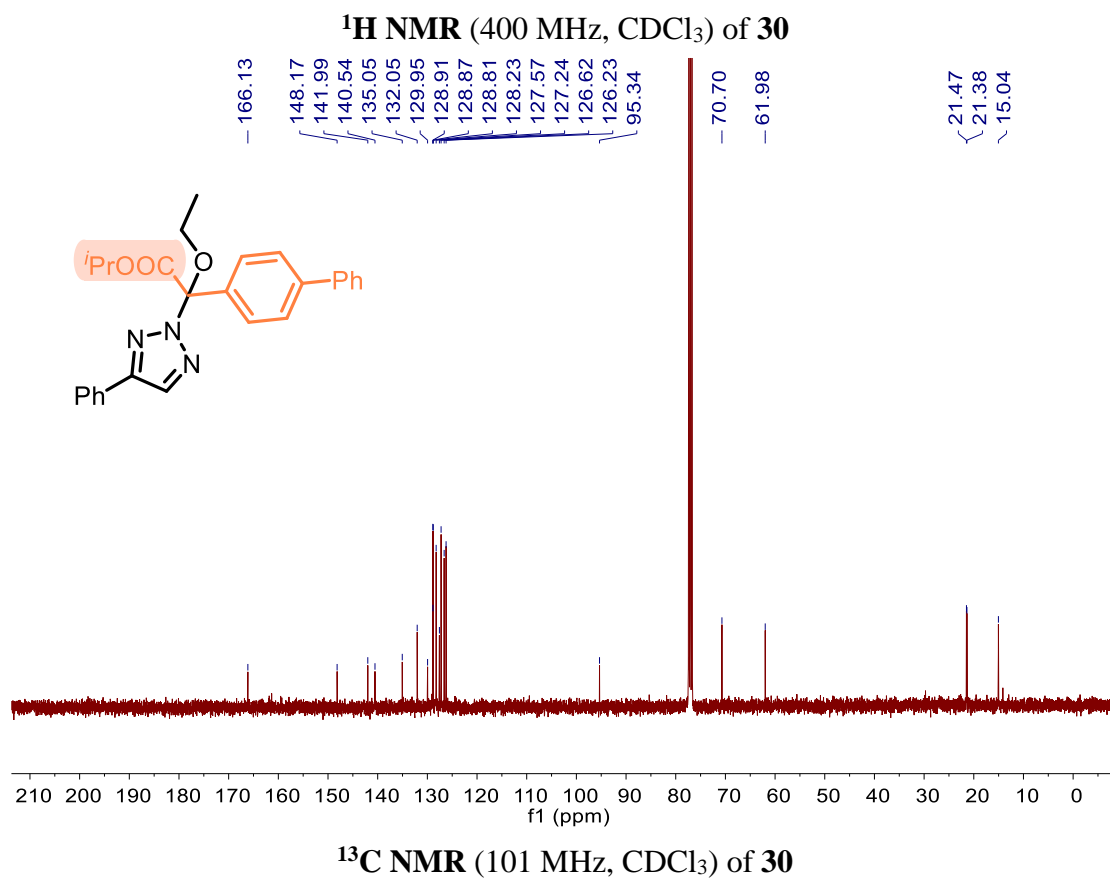
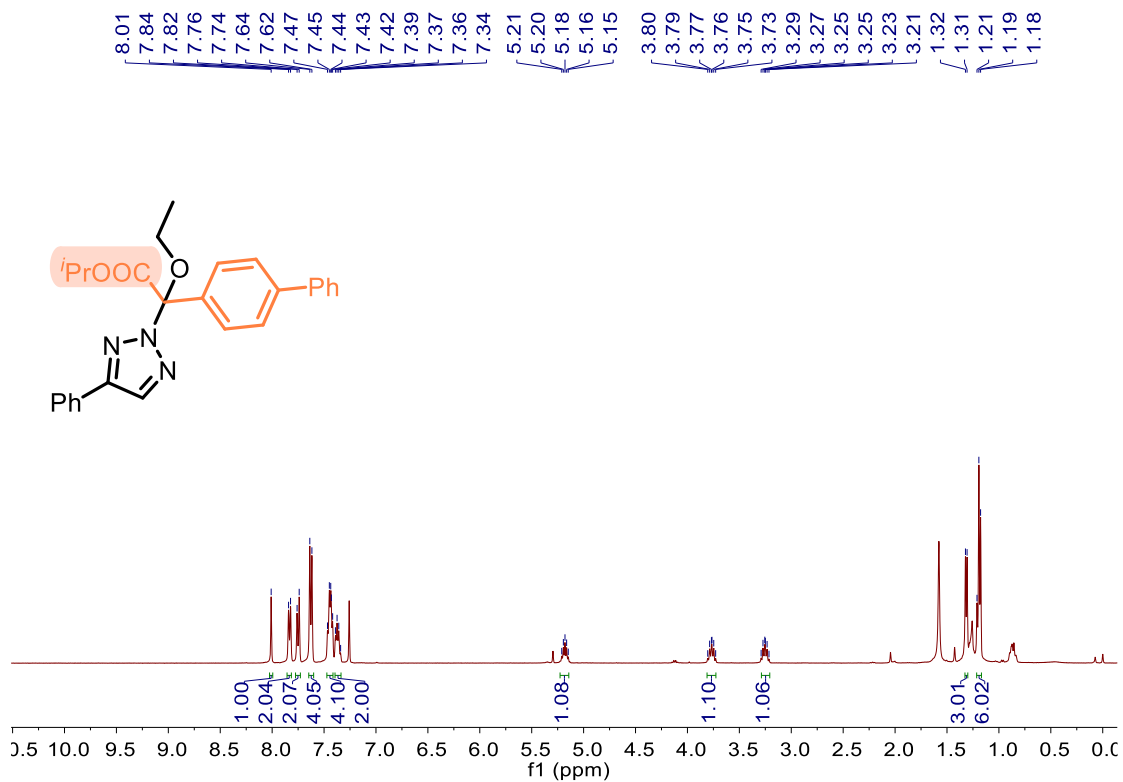
¹H NMR (400 MHz, CDCl₃) of **27**

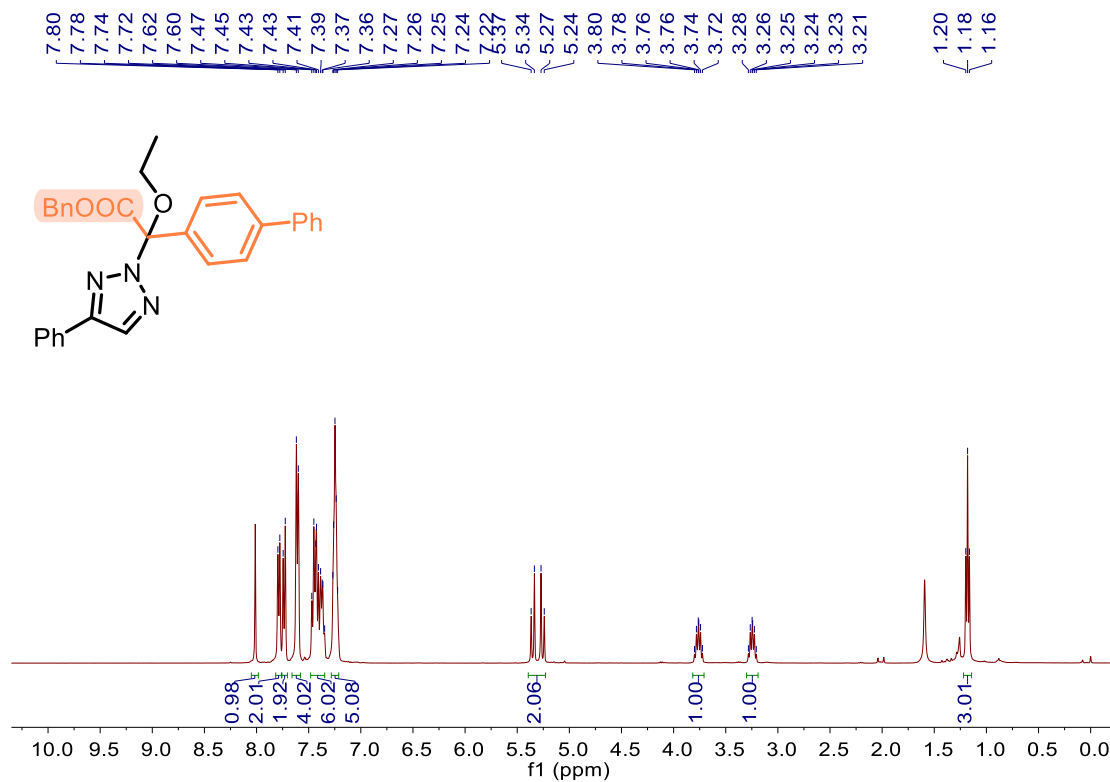


¹³C NMR (101 MHz, CDCl₃) of **27**

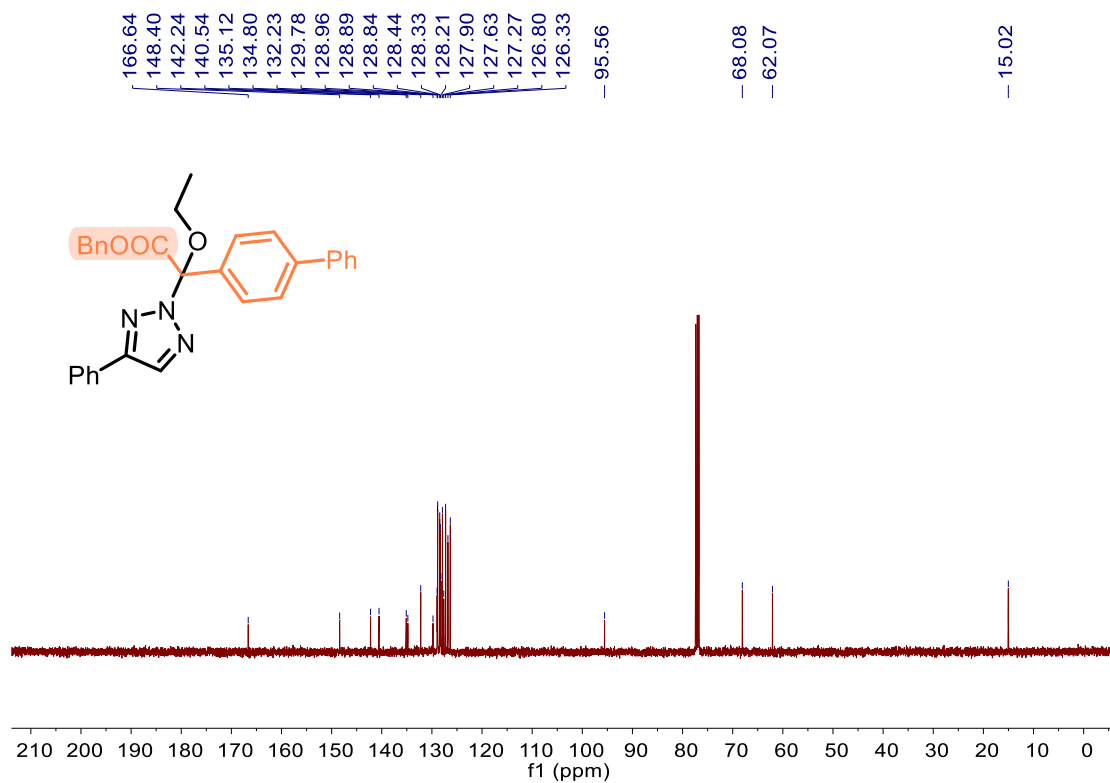




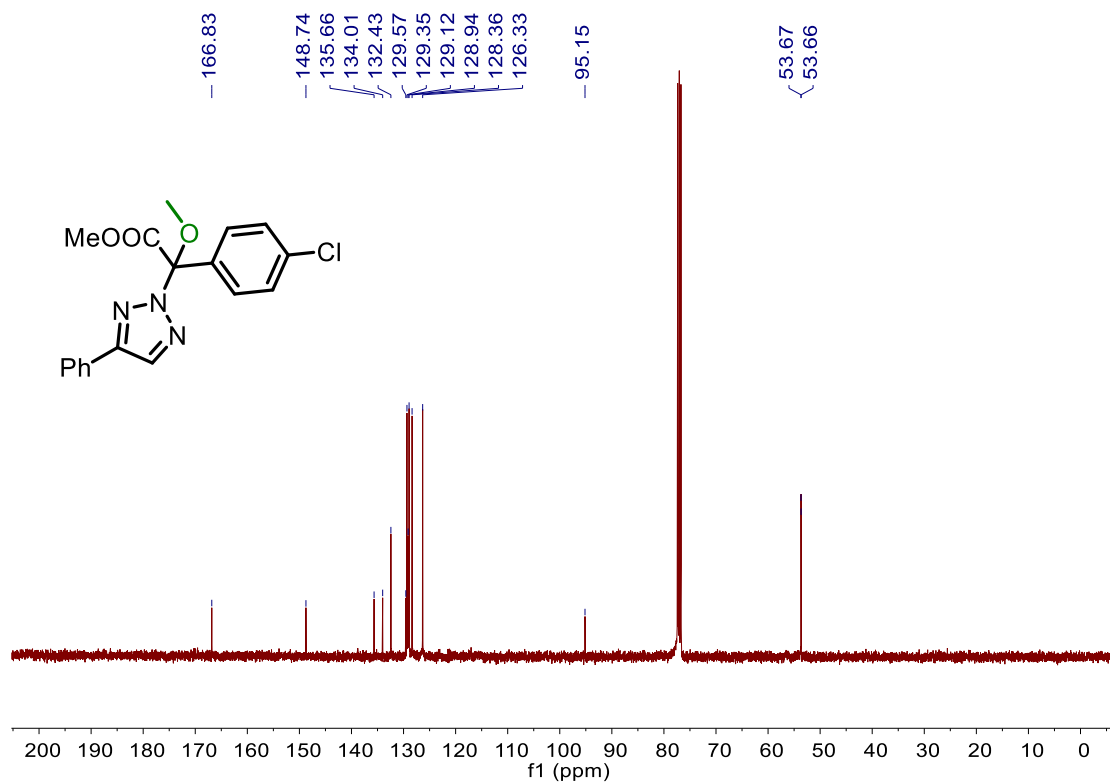
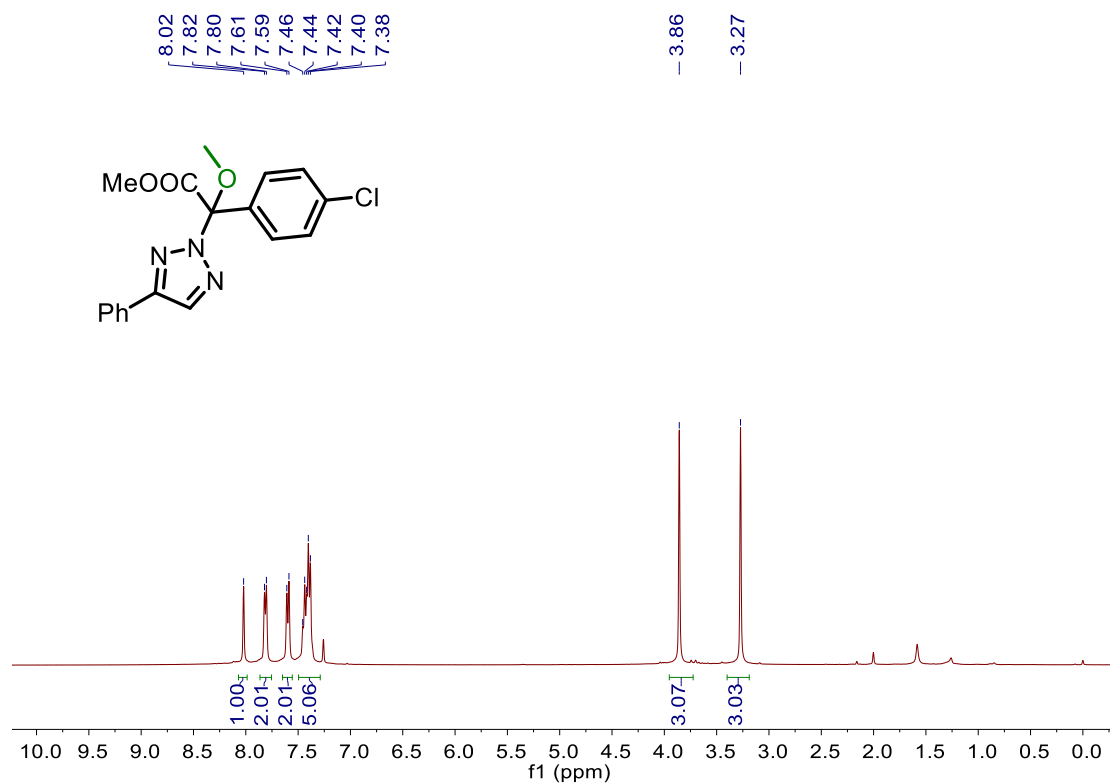


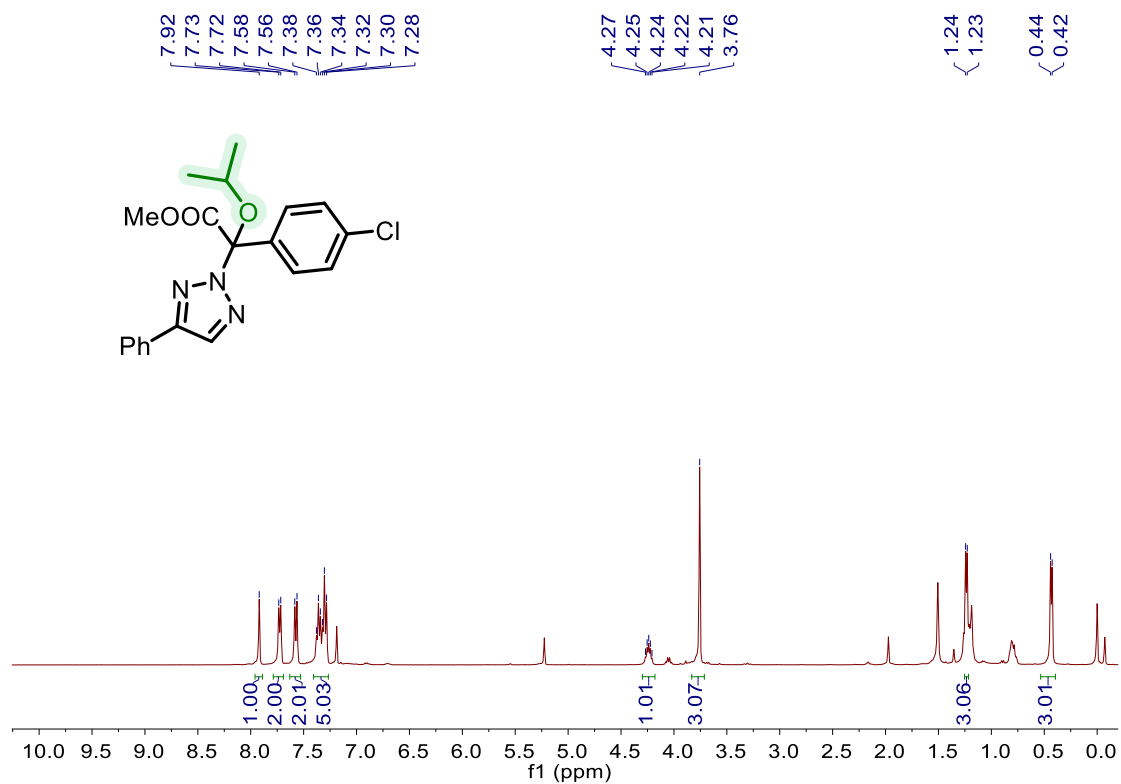


¹H NMR (400 MHz, CDCl₃) of 31

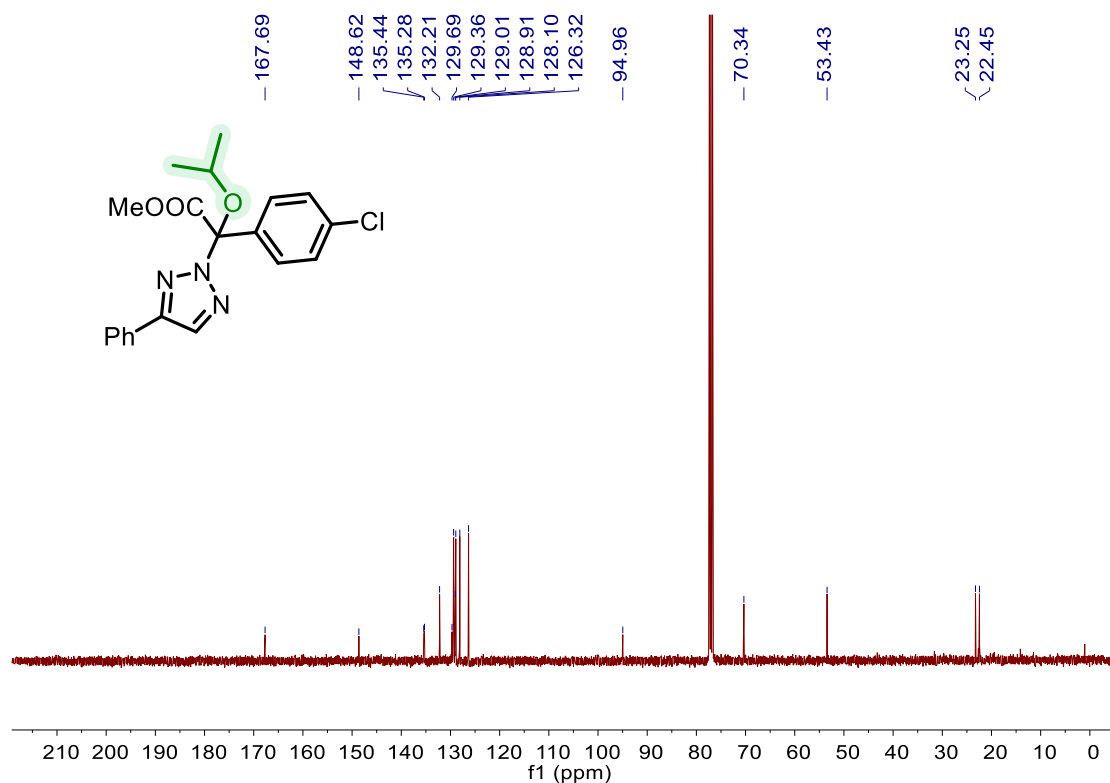


¹³C NMR (101 MHz, CDCl₃) of 31

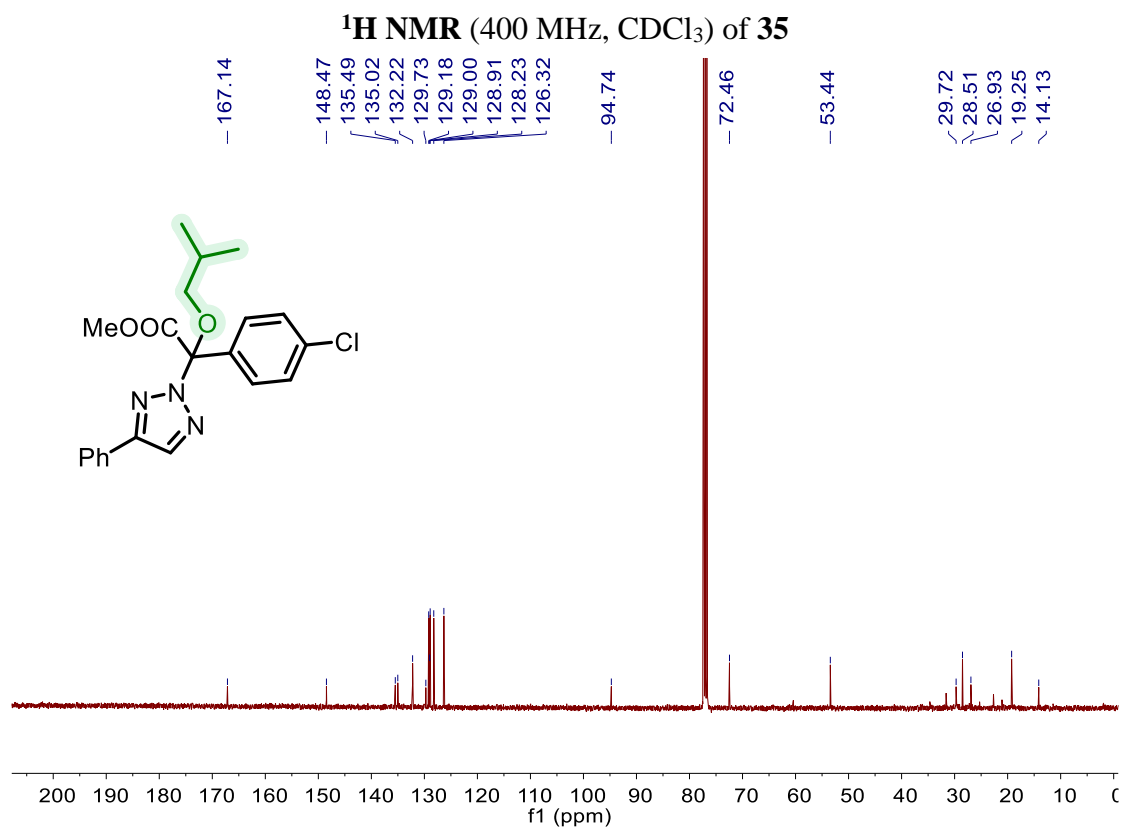
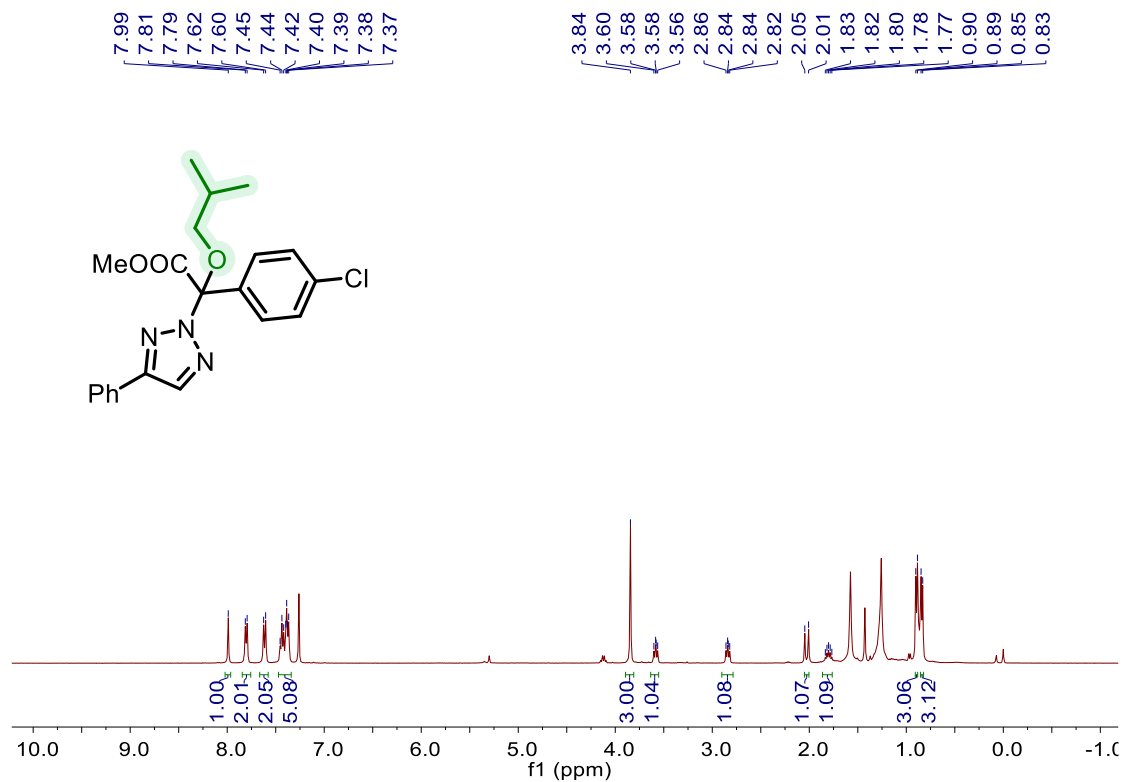


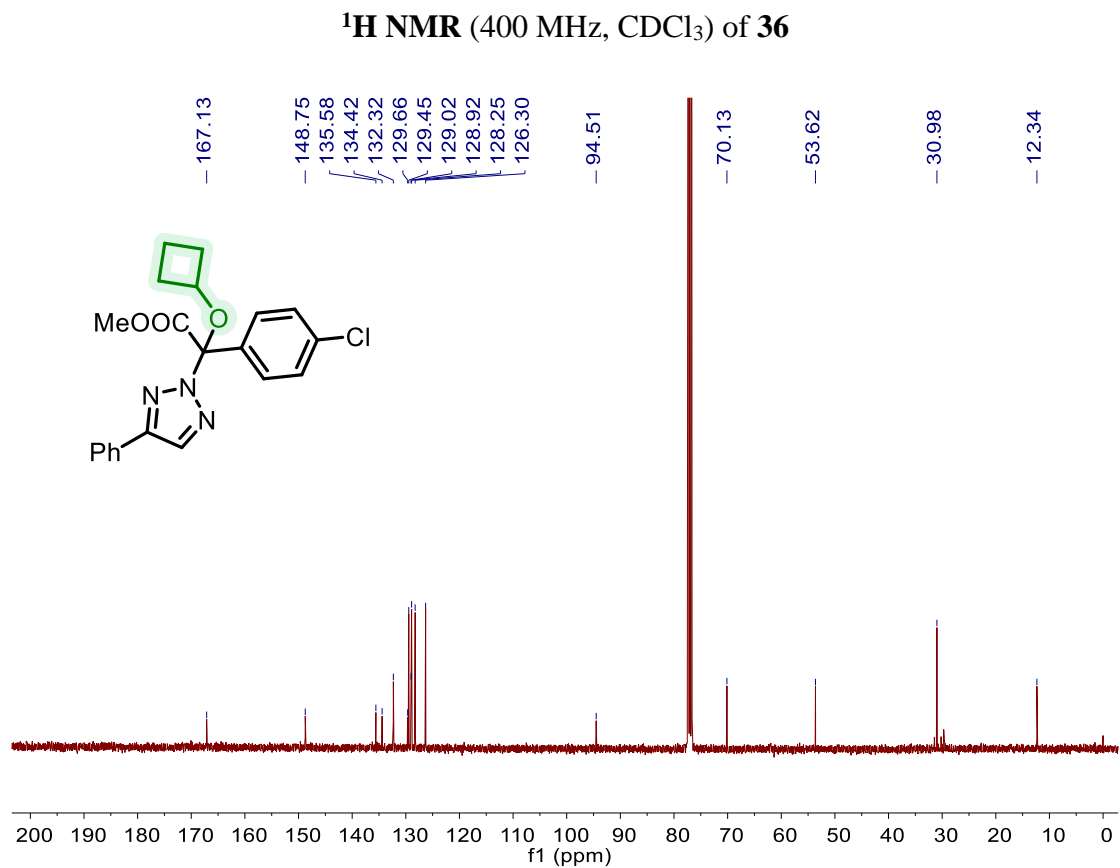
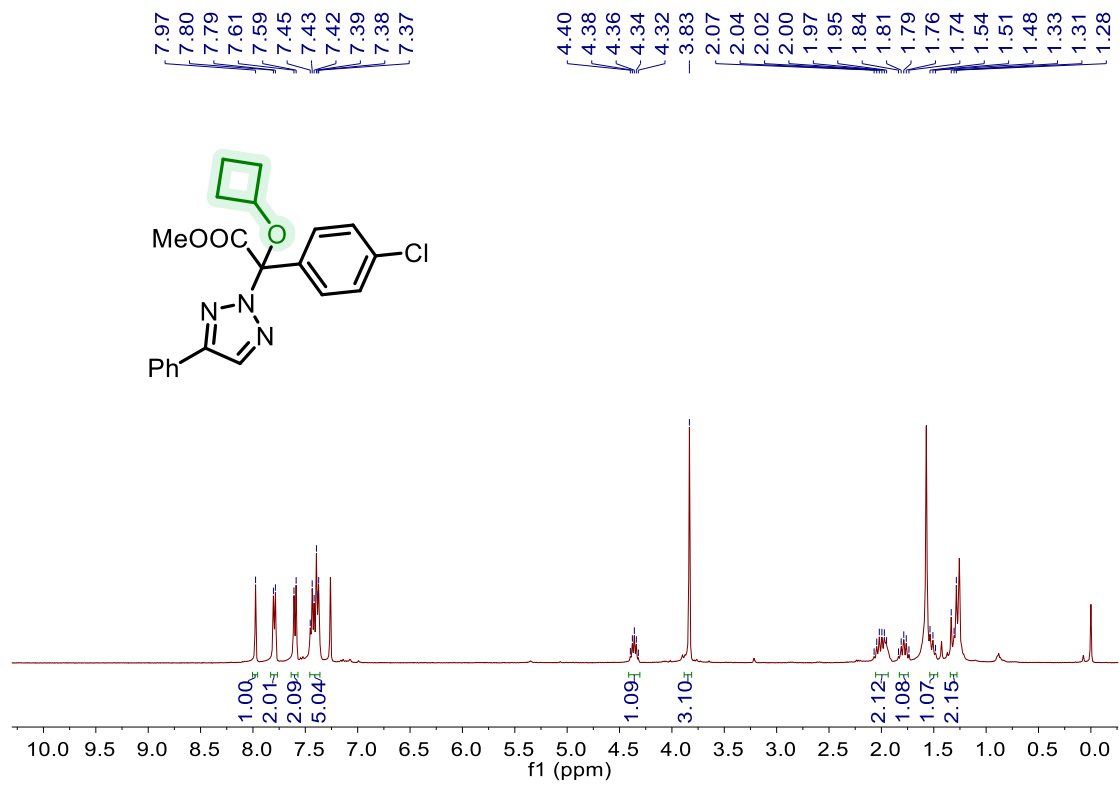


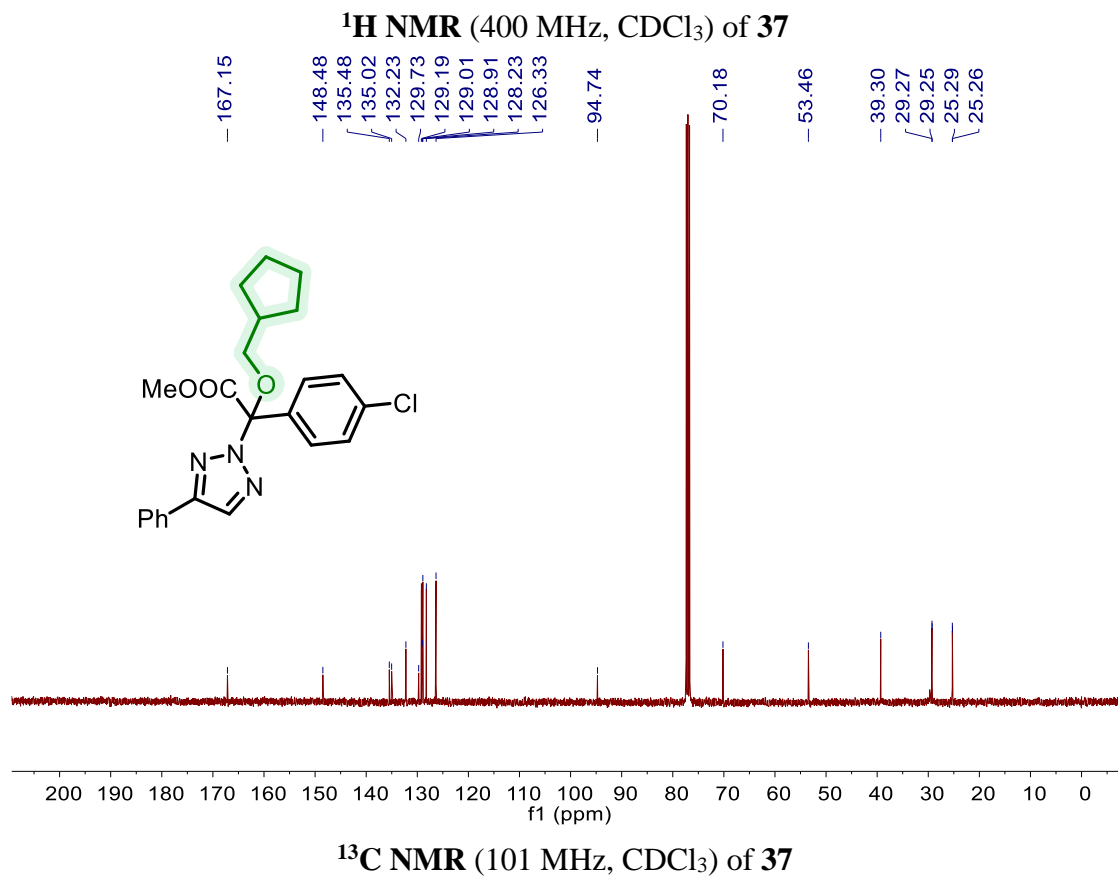
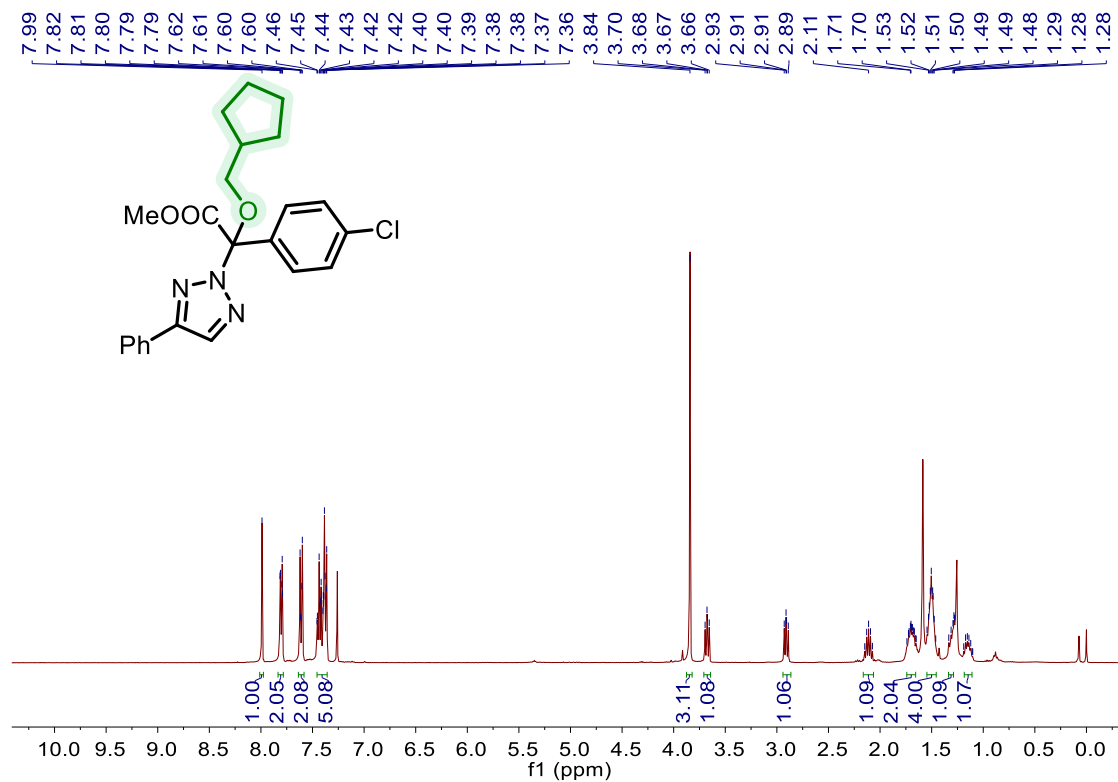
¹H NMR (400 MHz, CDCl₃) of **34**

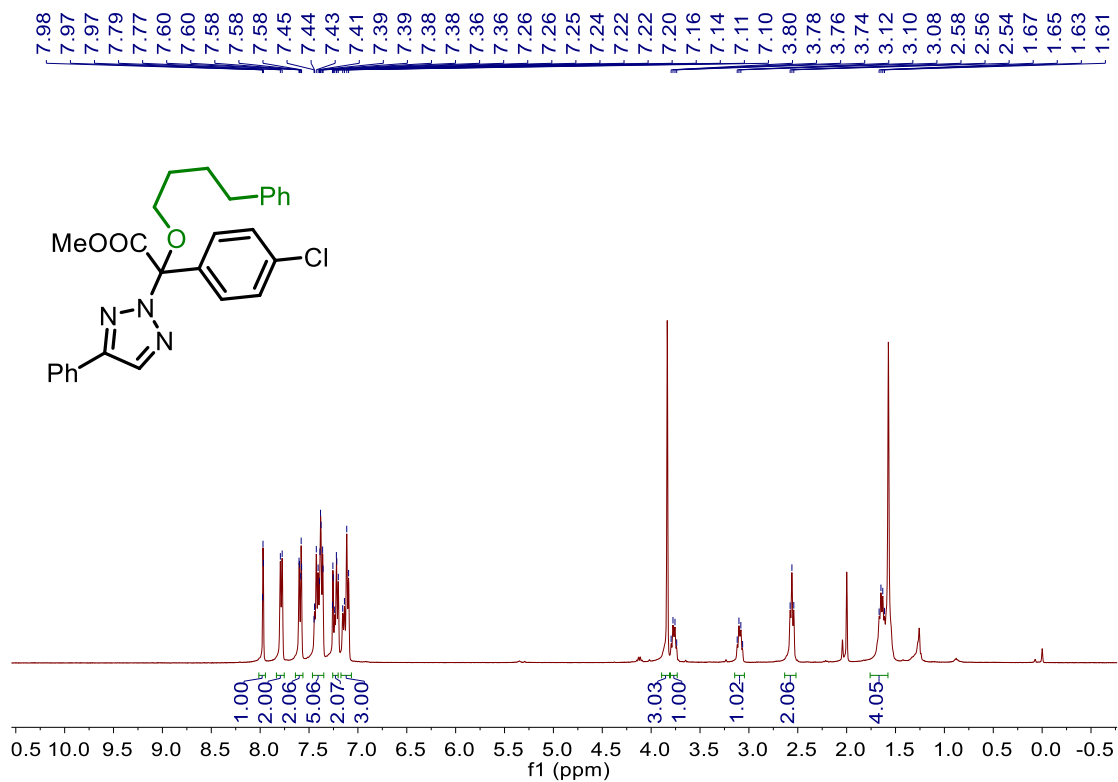


¹³C NMR (101 MHz, CDCl₃) of **34**

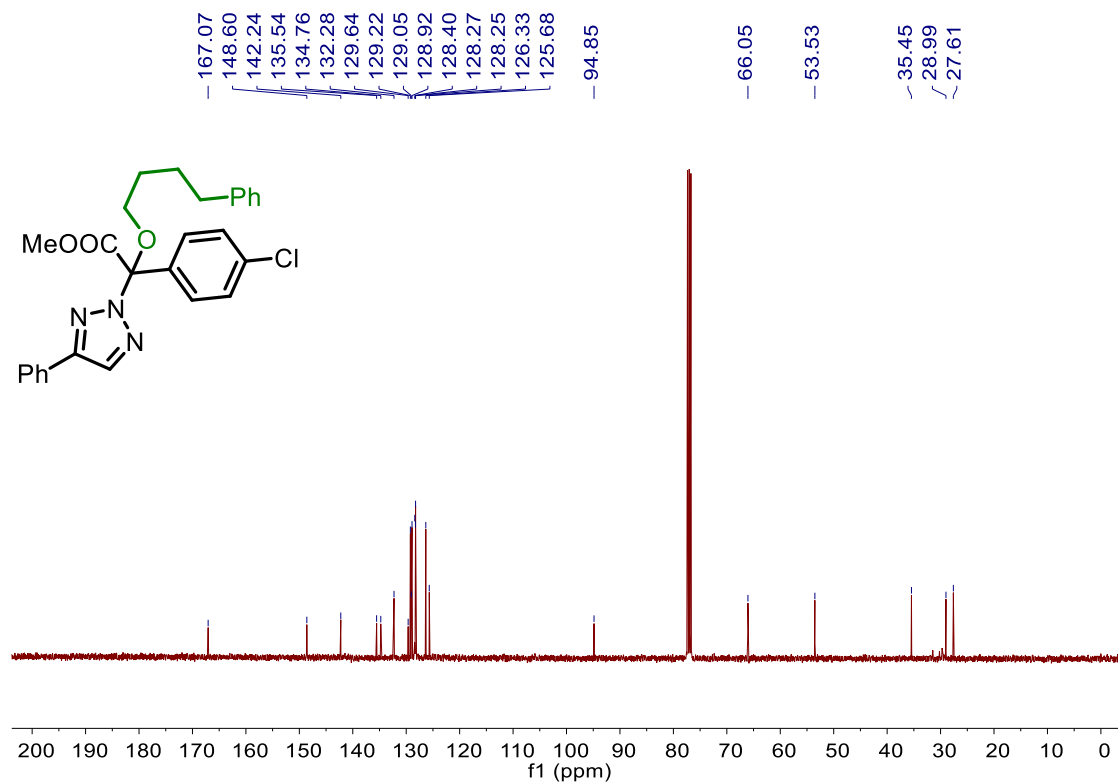




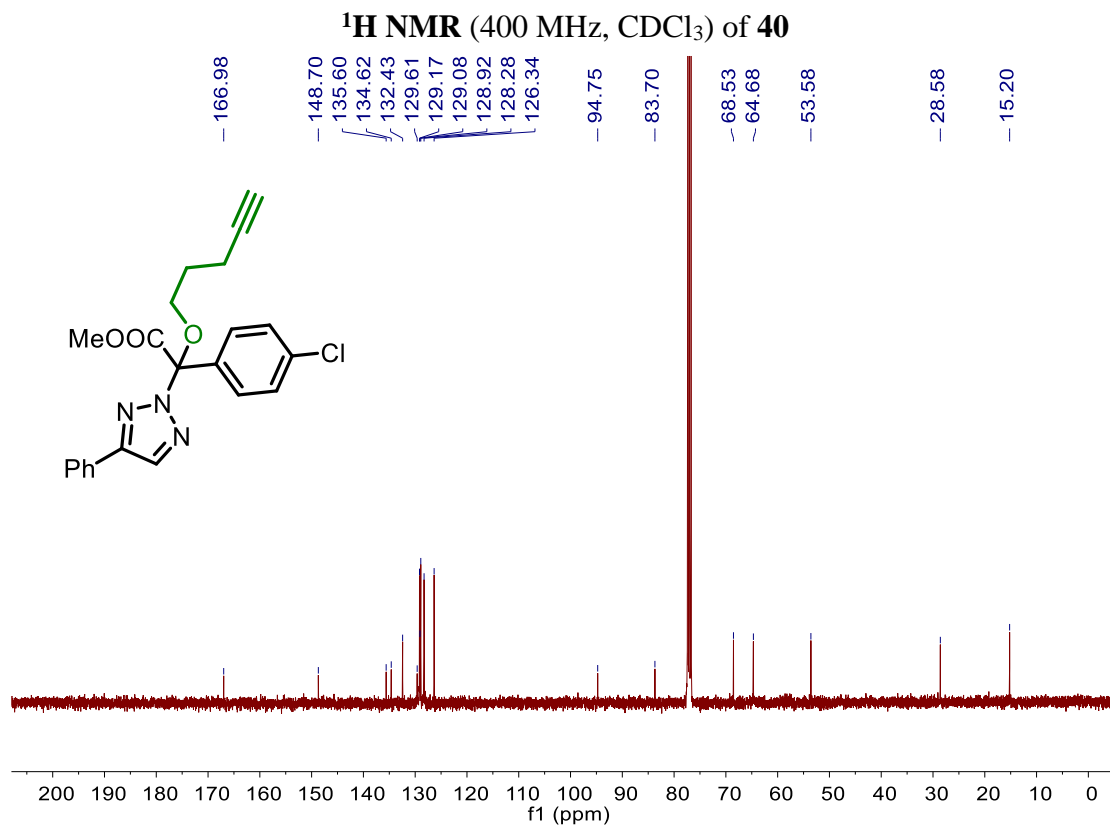
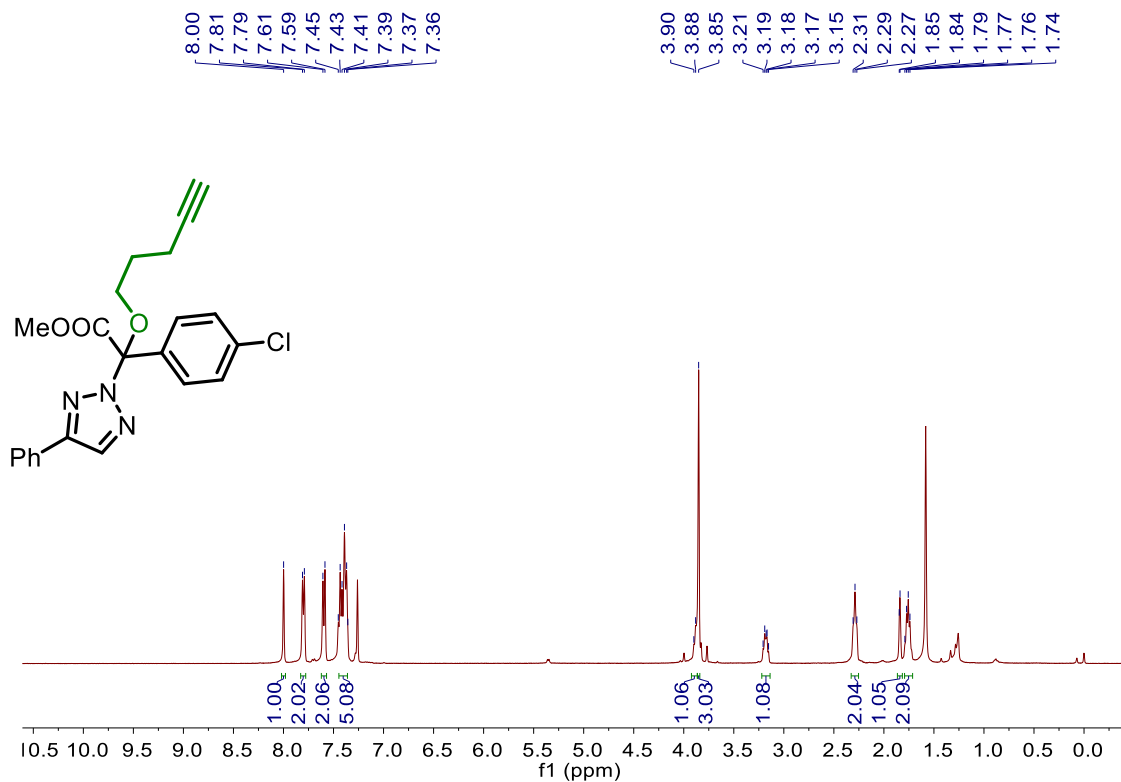


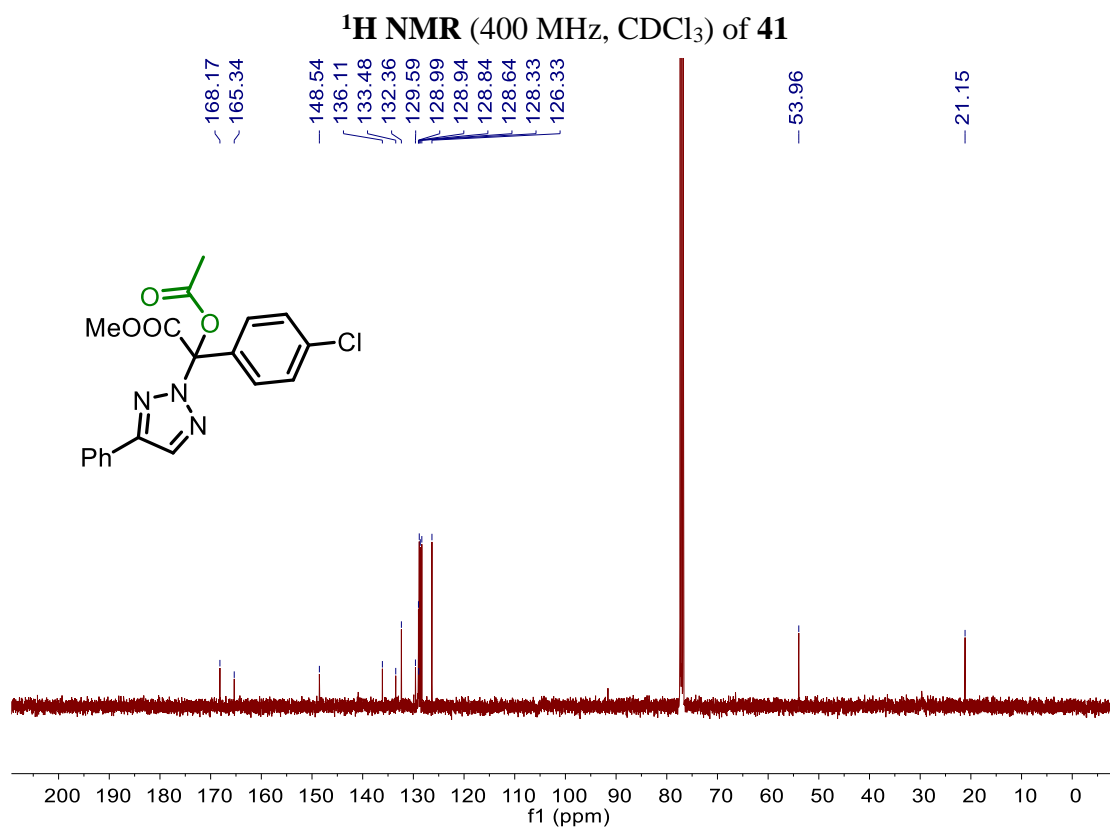
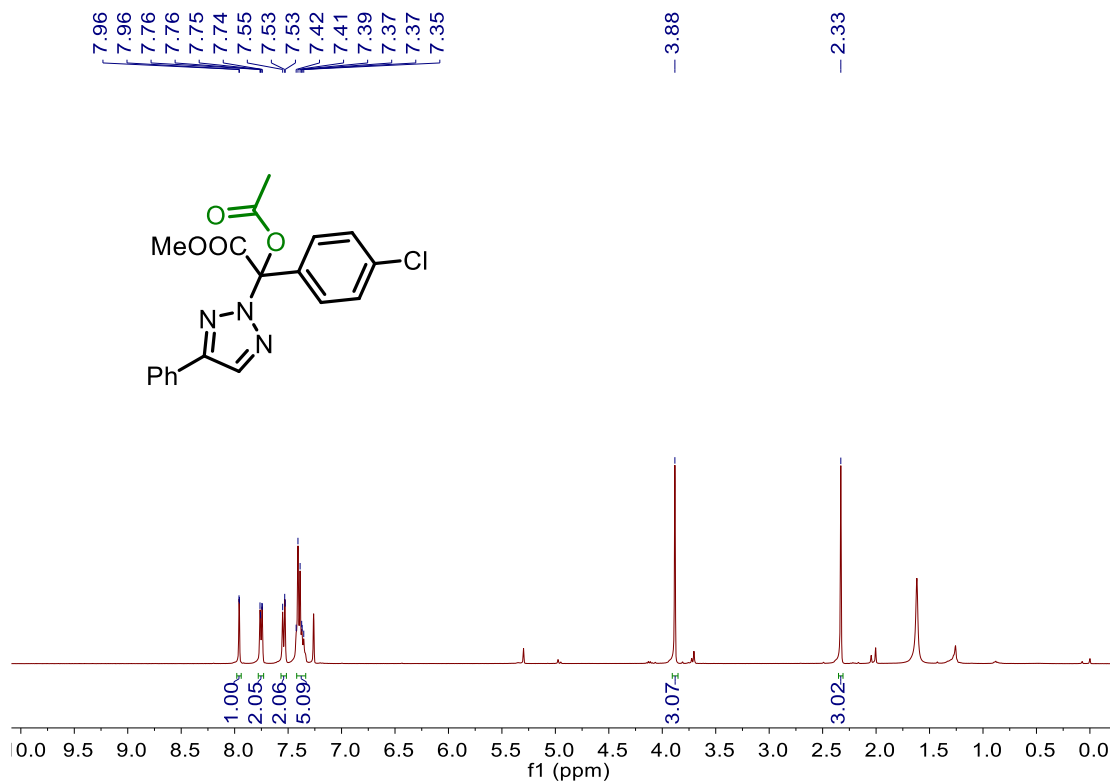


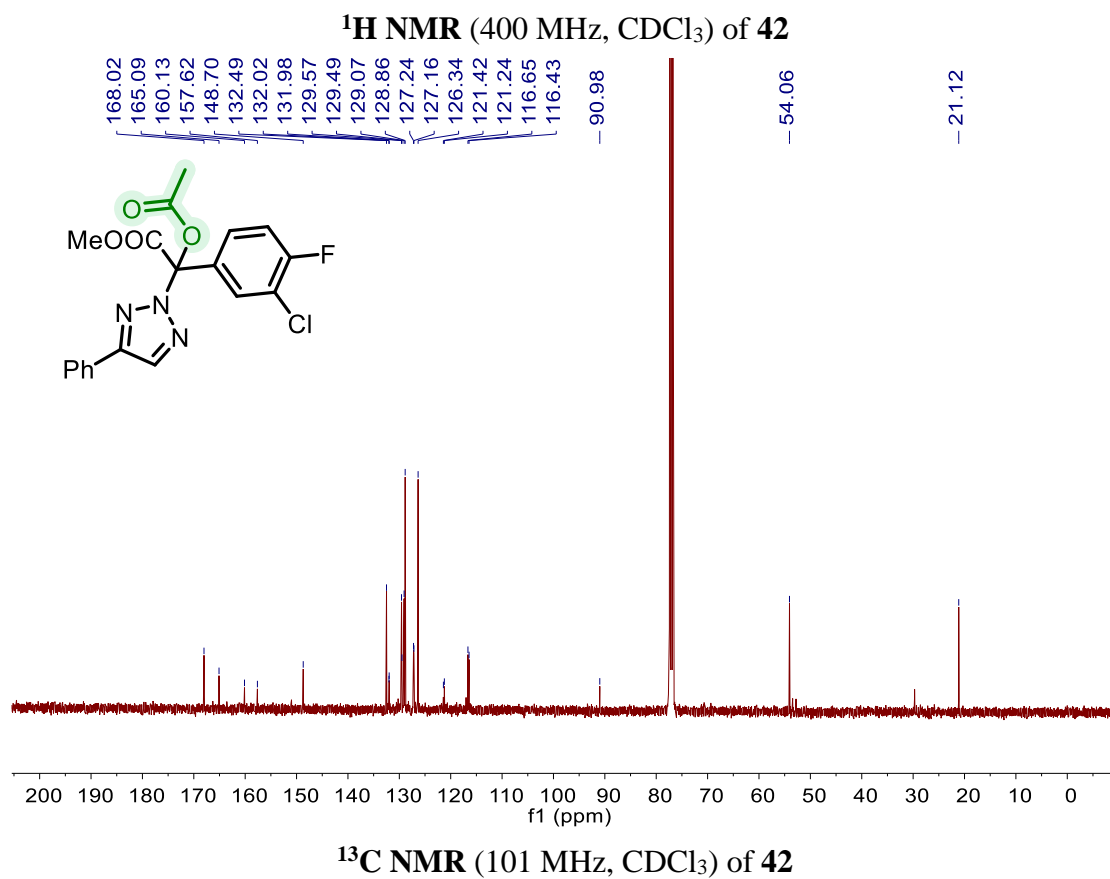
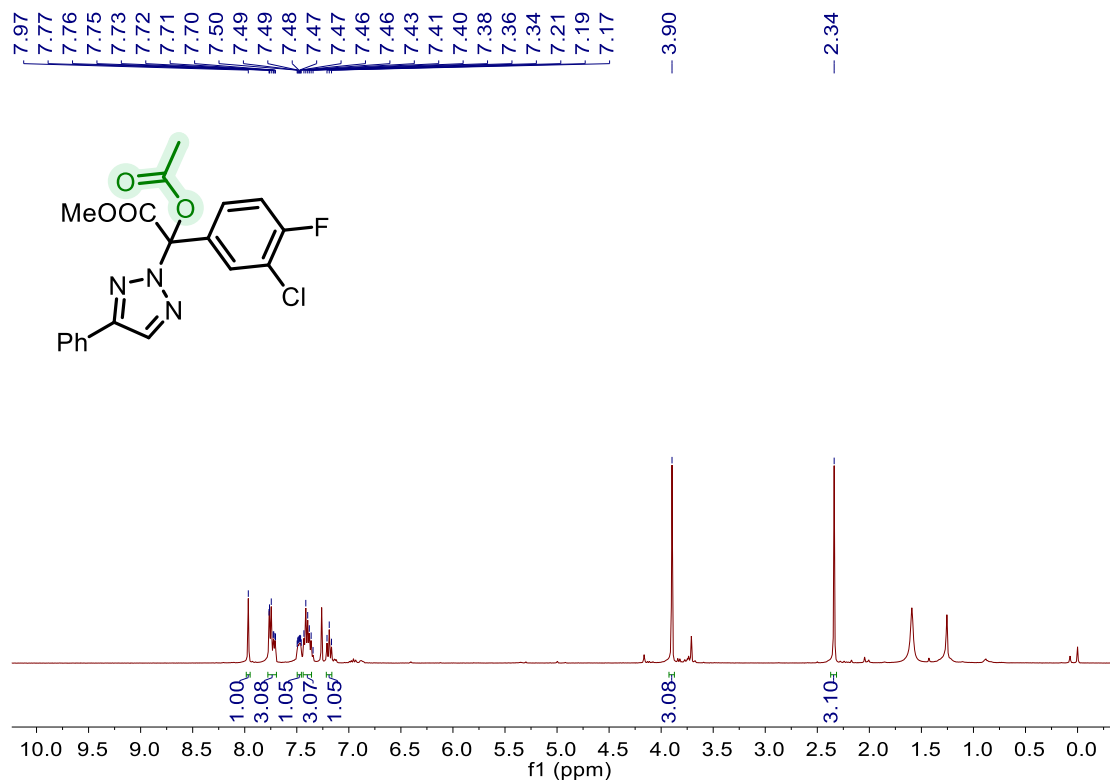
¹H NMR (400 MHz, CDCl₃) of 39

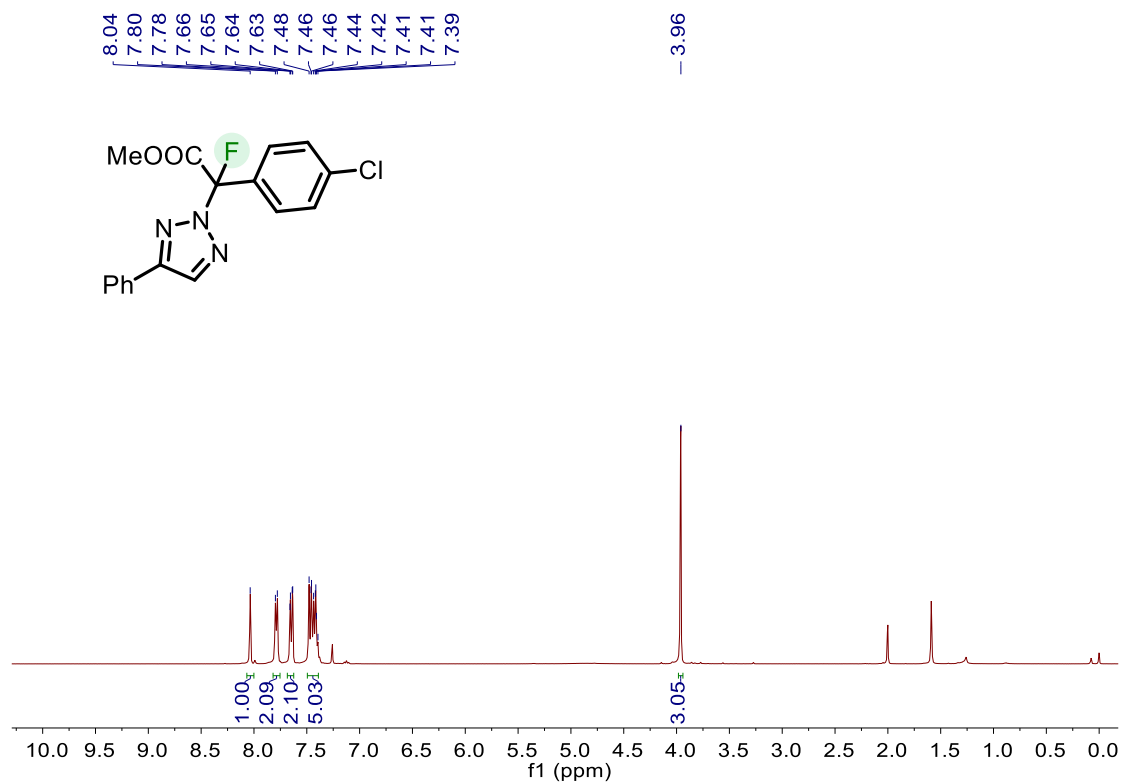
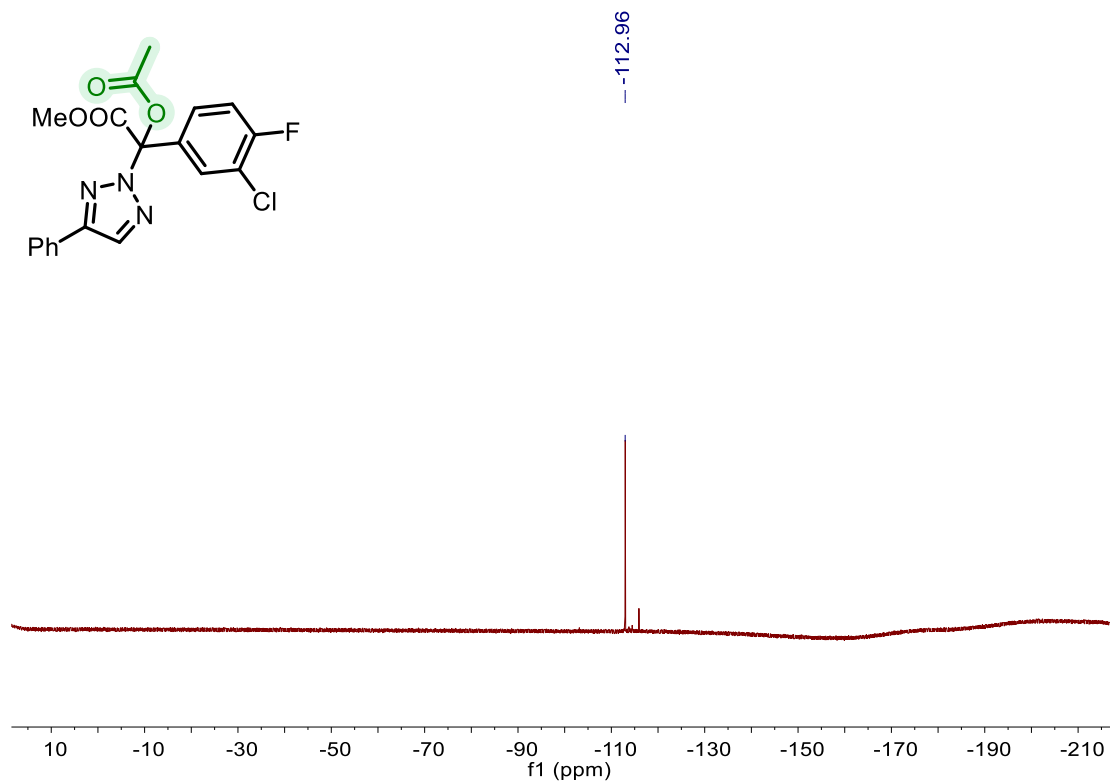


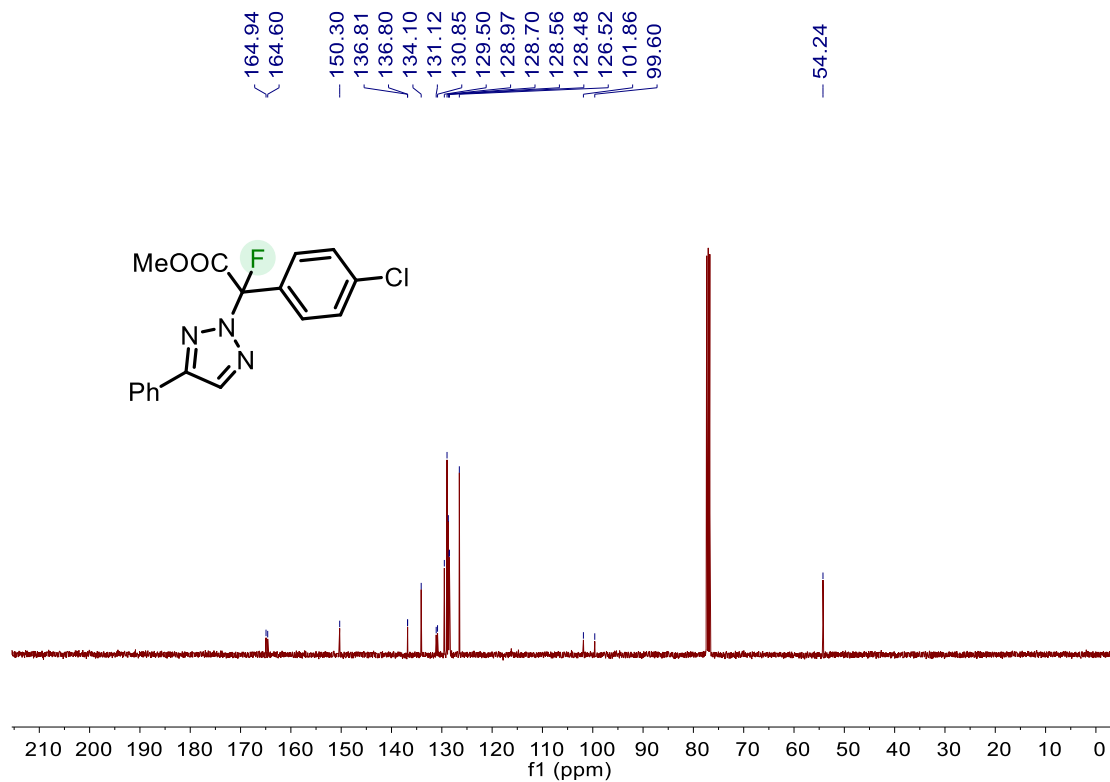
¹³C NMR (101 MHz, CDCl₃) of 39



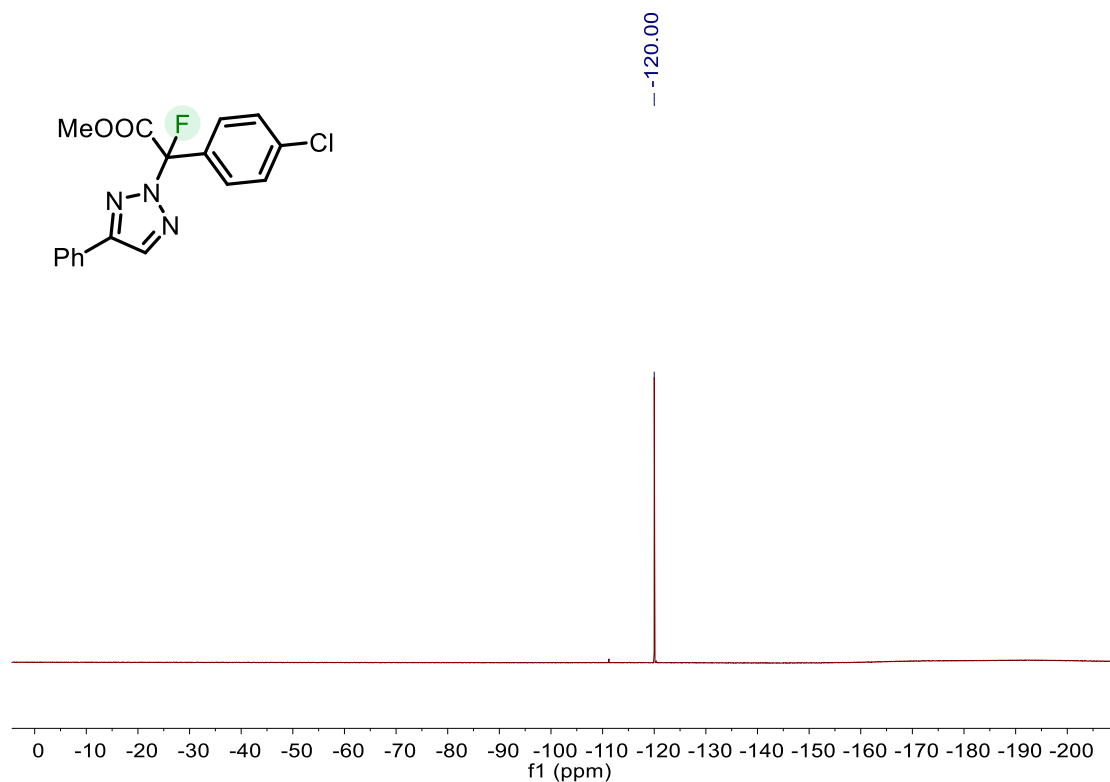




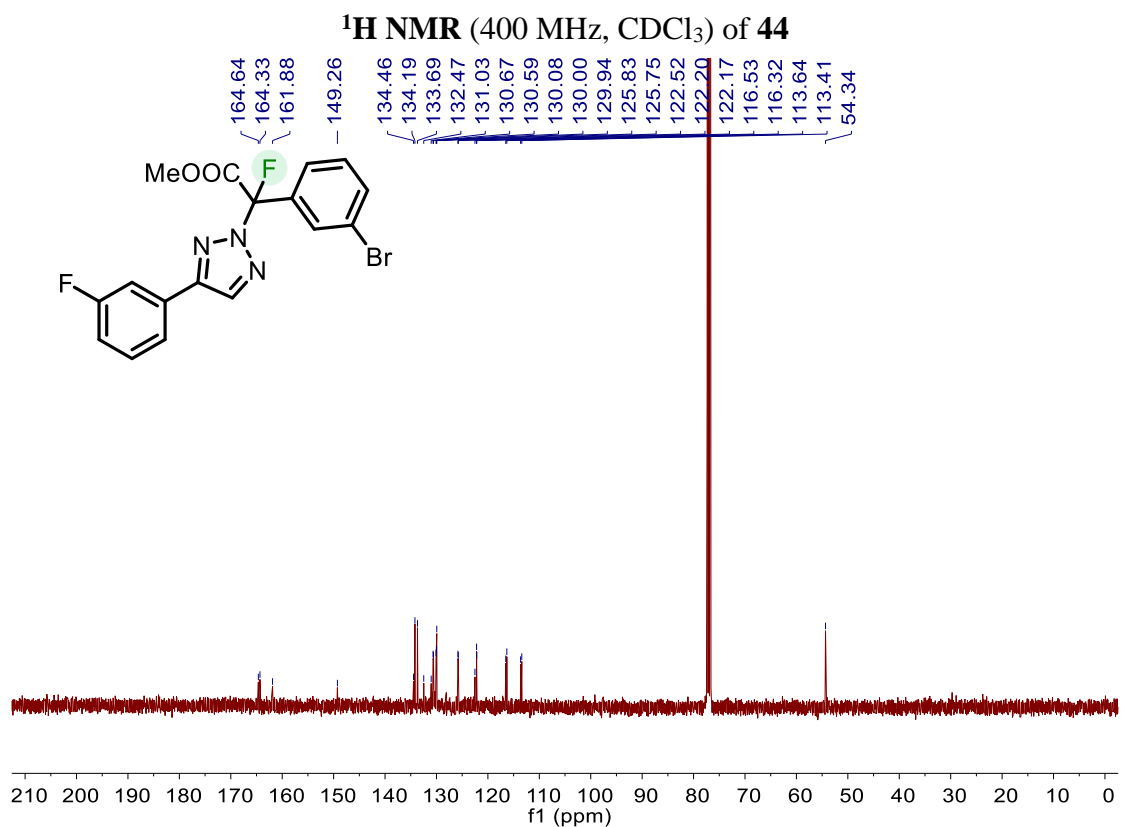
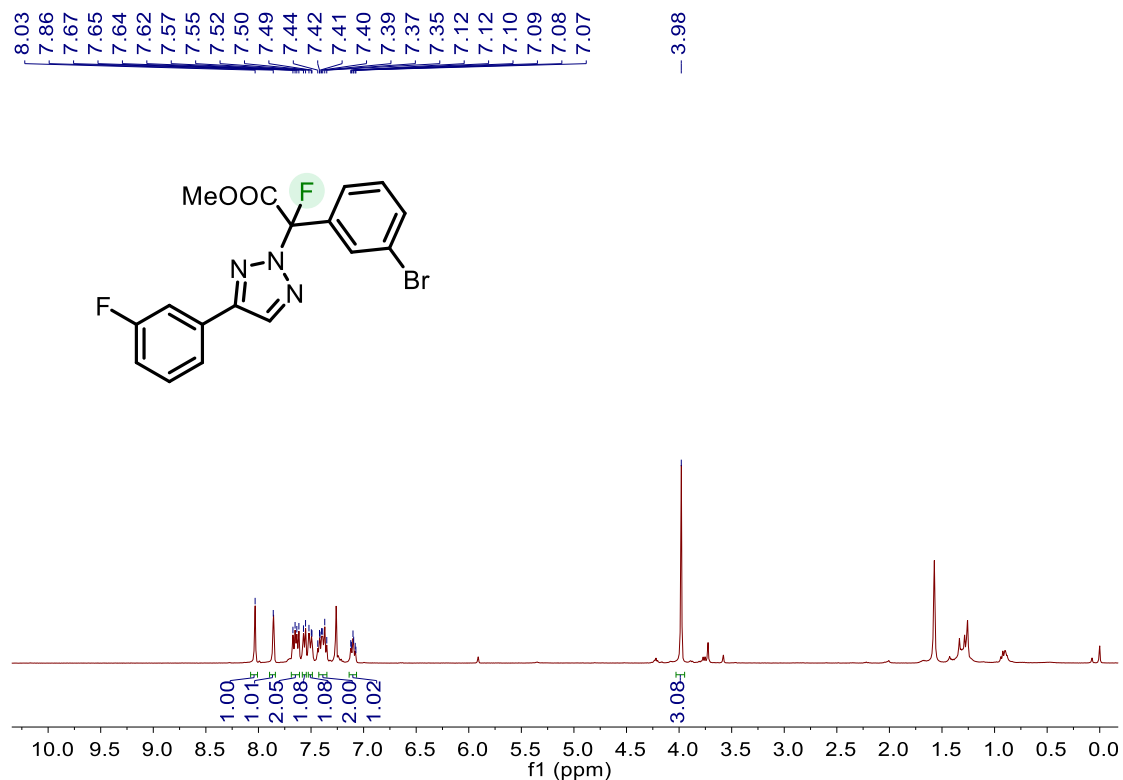


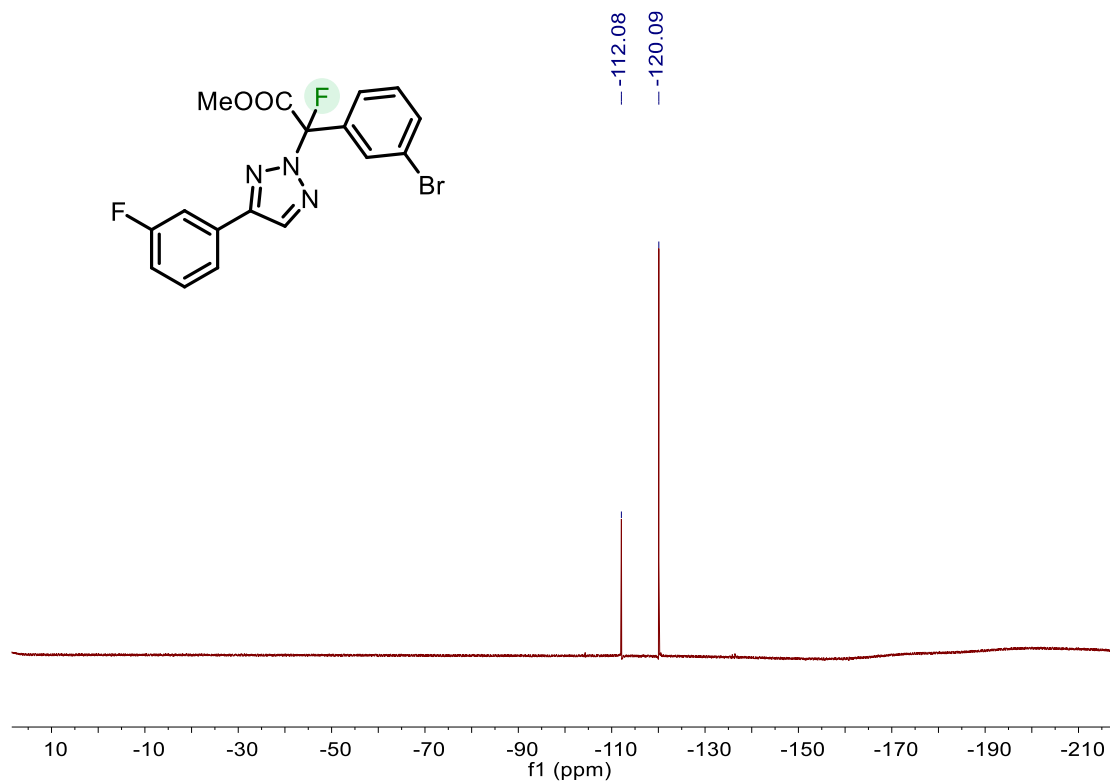


^{13}C NMR (101 MHz, CDCl_3) of **43**

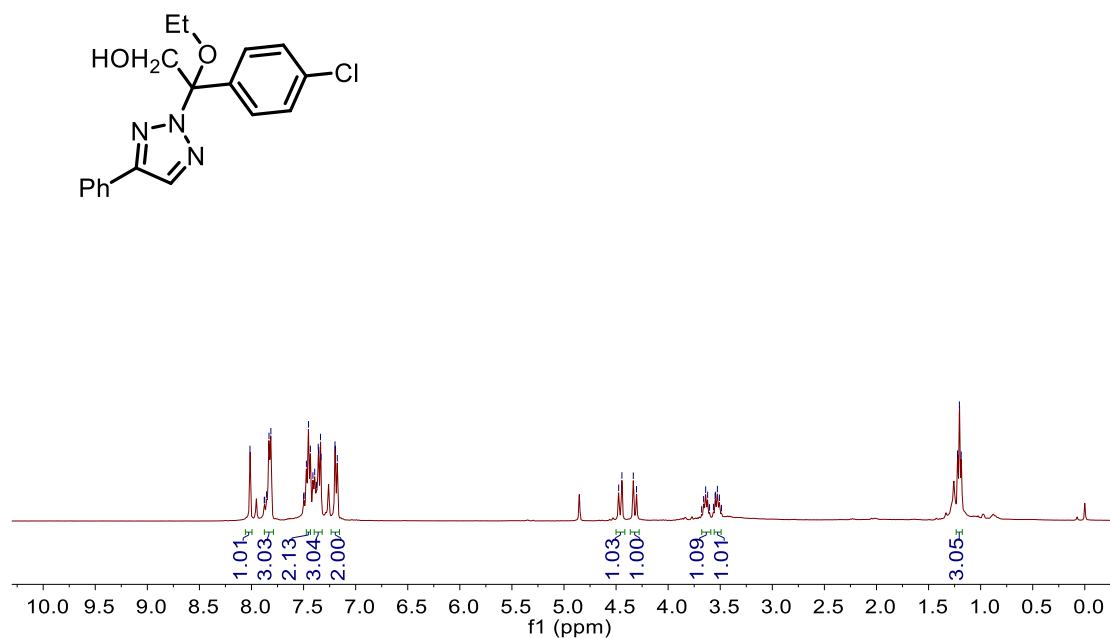


^{19}F NMR (376 MHz, CDCl_3) of **43**

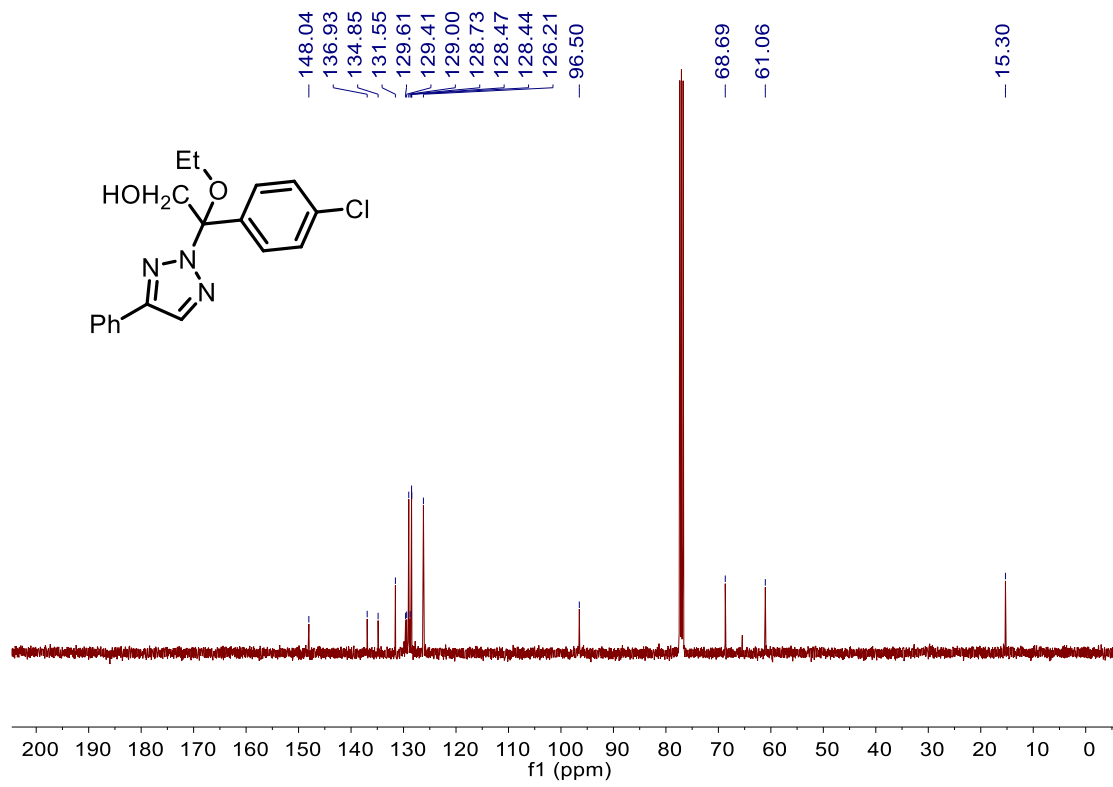




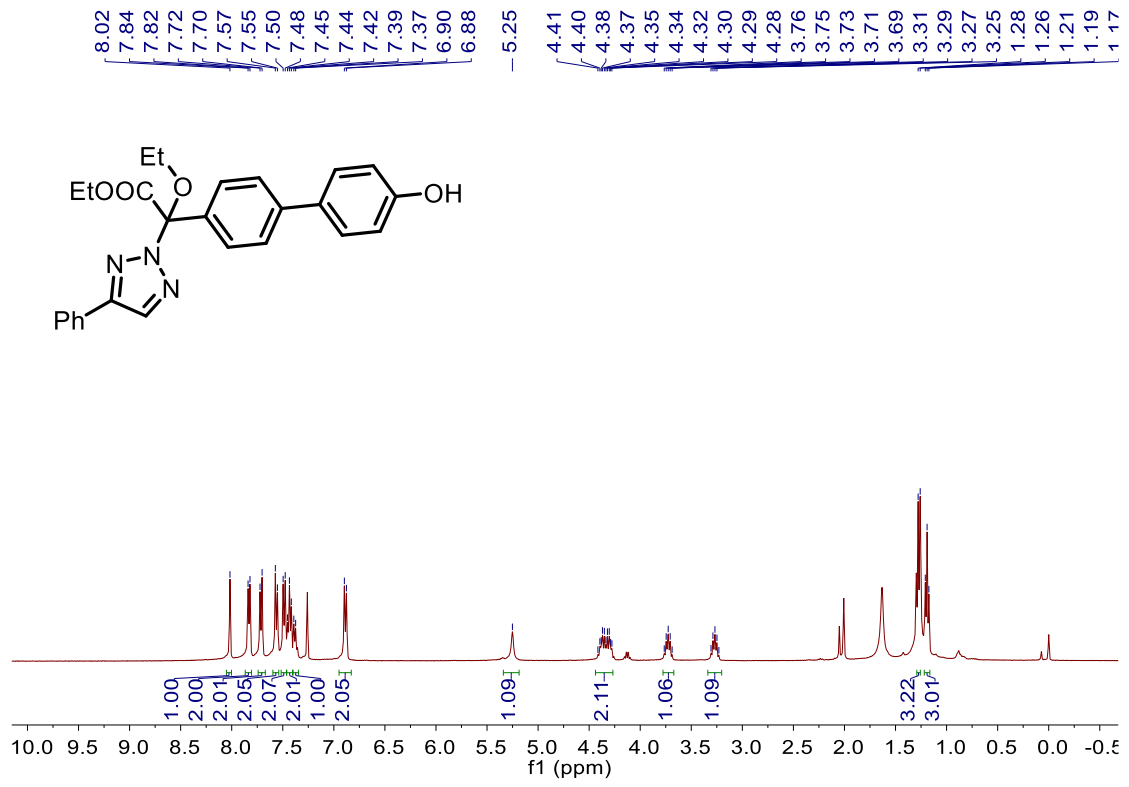
8.01, 7.88, 7.87, 7.86, 7.83, 7.81, 7.50, 7.47, 7.45, 7.43, 7.41, 7.39, 7.38, 7.36, 7.35, 7.34, 7.33, 7.20, 7.19, 7.18, 4.48, 4.44, 4.33, 4.30, 3.68, 3.66, 3.64, 3.62, 3.60, 3.57, 3.55, 3.54, 3.53, 3.51, 3.49, 1.22, 1.20, 1.19



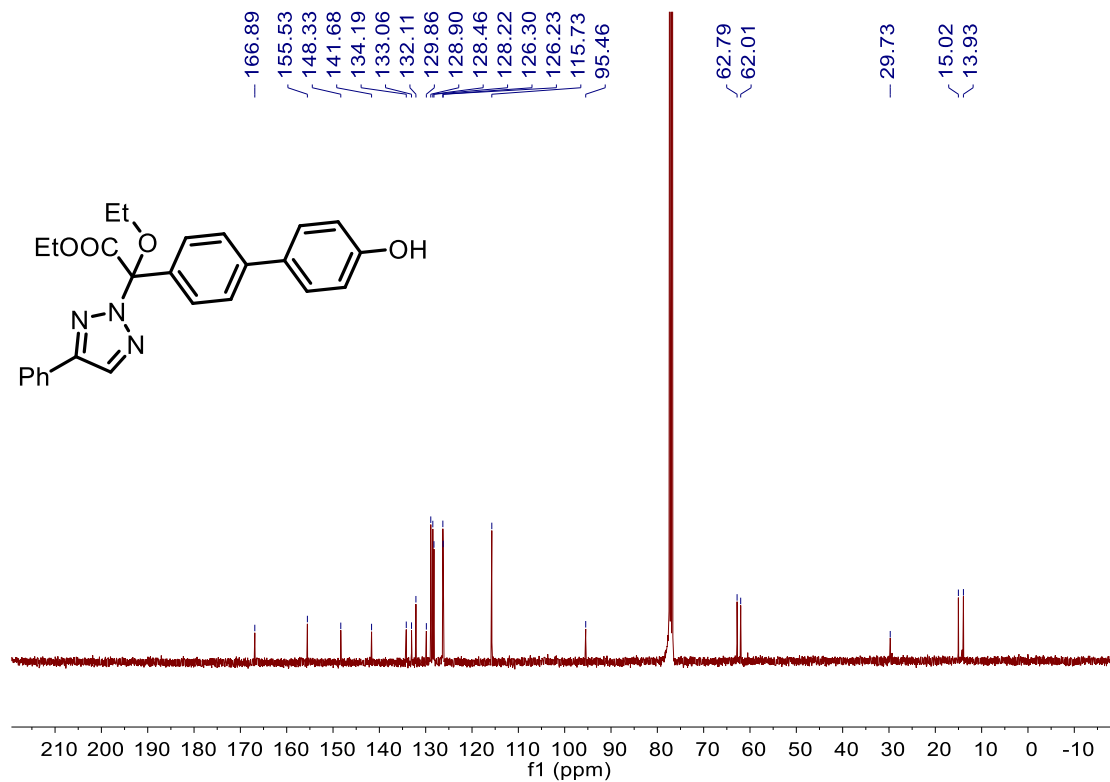
^1H NMR (400 MHz, CDCl_3) of 45



¹³C NMR (101 MHz, CDCl₃) of 45



¹H NMR (400 MHz, CDCl₃) of 46



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