Supporting Information for

Photochemical synthesis of 1,2,4-triazoles via addition reaction of triplet intermediates to diazoalkanes and azomethine ylide intermediates

Bao-Gui Cai,[†1] Ye-Peng Bao,[†1] Chao Pei,[2] Qian Li, Lei Li,[1] Rene M. Koenigs*[2] and Jun Xuan*[1,3]

[1] Anhui Province Key Laboratory of Chemistry for Inorganic/Organic Hybrid Functionalized Materials, College of Chemistry & Chemical Engineering, Anhui University, Hefei, Anhui 230601, People's Republic of China

[2] Institute of Organic Chemistry, RWTH Aachen University, Landoltweg 1, 52074 Aachen (Germany)

[3] Key Laboratory of Structure and Functional Regulation of Hybrid Materials (Anhui University), Ministry of Education, Hefei, 230601, People's Republic of China

[†] These authors contributed equally.

Table of contents

1. General

All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in pre-heated glassware under an argon atmosphere using standard Schlenk techniques. THF was freshly distilled from Na under argon. All other solvents and reagents were purified according to standard procedures or were used as received from chemical suppliers. The starting materials were synthesized according to literature procedures. The light employed in this work was bought from GeAo Chemical: model H106062, 24 W blue LEDs. All reactions involving heating are carried out in an oil bath.

Chromatography: Analytical thin layer chromatography was performed using Qingdao Puke Parting Materials Co. silica gel plates (Silica gel 60 F254). Visualisation was by ultraviolet fluorescence (λ = 254 nm) and/or staining with phosphomolybdic acid or potassium permanganate ($KMnO_4$). Flash column chromatography was performed using 200-300 mesh silica gel.

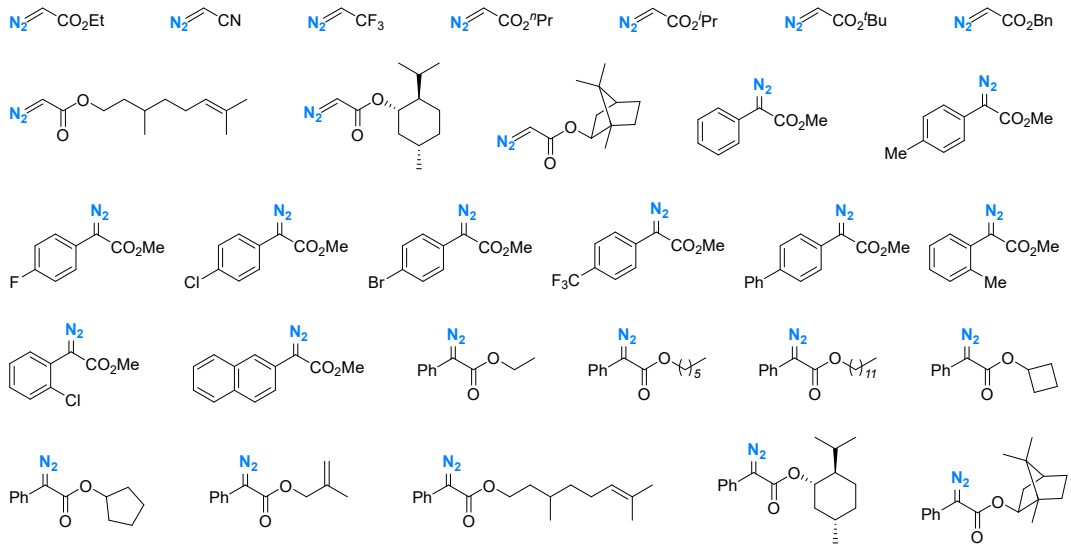
^{1}H NMR and **^{13}C NMR** spectra were recorded on a JEOL JNM ECZ000R at 300 K. Spectra were calibrated relative to solvent's residual proton and carbon chemical shift: $CHCl_3$ (δ = 7.26 for ^{1}H NMR and δ = 77.0 for ^{13}C NMR). Data are reported as follows: chemical shift δ/ppm, integration (^{1}H only), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet or combinations thereof; ^{13}C signals are singlets unless otherwise stated), coupling constants *J* in Hz, assignment.

High Resolution Mass Spectrometry (HRMS): All were recorded on LTQ Orbitrap XL using a positive electrospray ionization (ESI^+). Measured values are reported to 4 decimal places of the calculated value. The calculated values are based on the most abundant isotope.

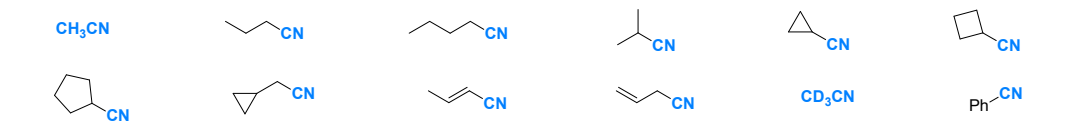
X-ray diffraction measurements were performed on a CCD area detector using graphite monochromated MoKα radiation (λ = 0.71069 Å) at 298(2) K.

2. Scope of starting materials

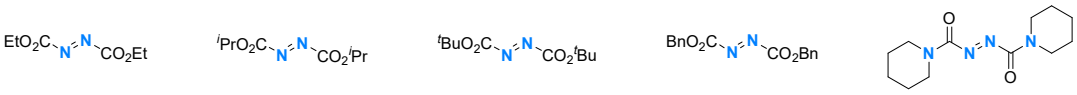
Scop of diazo compound



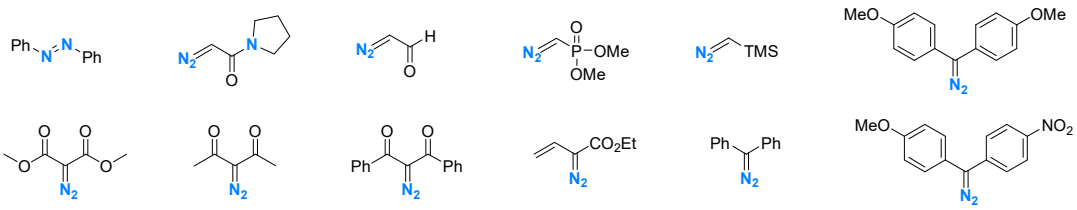
Scop of nitrile compound



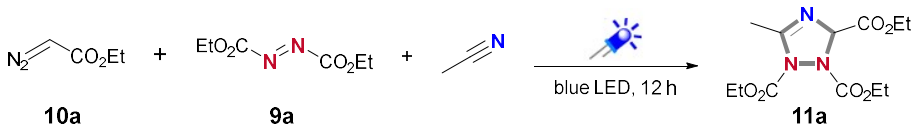
Scop of azo compound



Unsuccessful examples



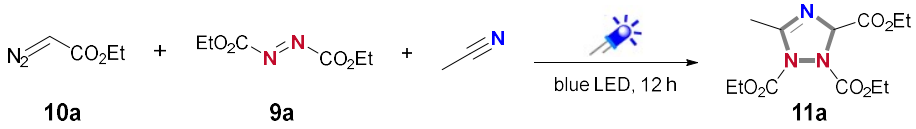
3. The condition optimization [a]



10a **9a** **11a**

Entry	Ratio of **10a**:**9a**	Yield of **11a** (%)[b]
1	0.4 mmol : 0.1 mmol	86%
2	0.3 mmol : 0.1 mmol	74%
3	0.2 mmol : 0.1 mmol	69%
4	0.1 mmol : 0.1 mmol	36%
5	0.1 mmol : 0.2 mmol	21%
6	0.1 mmol : 0.3 mmol	19%
7[c]	0.4 mmol : 0.1 mmol	Not detected

[a] Reaction conditions: **10a** and **9a** dissolved in degassed CH_3CN (1 mL) under 24 W Blue LEDs for 12 h. [b] Yield of the isolated product. [c] under dark.

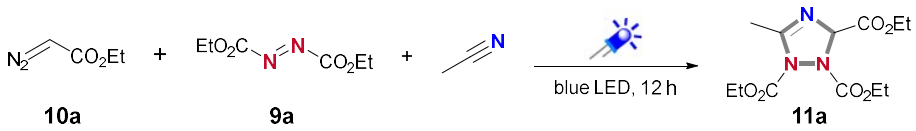


10a **9a** **11a**

Entry	Solvent	Yield of **11a** (%)[b]
1	DCM : MeCN = 1:1	41
2	DCM : MeCN = 2:1	36
3	DCM + 0.5 mmol MeCN	Trace
4	DCM + 1 mmol MeCN	Trace

[a] Reaction conditions: 0.4 mmol **10a** and 0.1 mmol **9a** dissolved in degassed solvent (1 mL) under 24 W Blue LEDs for 12 h. [b] Yield of the isolated product.

4. General procedure and spectral data of products

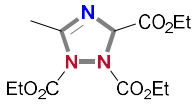


10a 9a 11a

General procedure (*GP1*): To a 10 mL Schlenk flask equipped with a magnetic stir bar was added ethyl diazoacetate (0.40 mmol), diethylazodiformiat (0.10 mmol), dry MeCN (1.0 mL). The resulting mixture was stirred at a distance of ~3 cm from a 24 W blue LED at room temperature for 12 h. The solvent was removed by vacuum and the crude product was purified by flash chromatography on silica gel silica: 200~300; eluant: petroleum ether/ethyl acetate (5:1~1:1) to provide pure product **11a** as a colorless oil in 86% yield (25.9 mg).

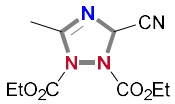
1.0 mmol procedure: To a 25 mL Schlenk flask equipped with a magnetic stir bar was added ethyl diazoacetate (4.0 mmol), diethylazodiformiat (1.0 mmol), dry MeCN (10 mL). The resulting mixture was stirred at a distance of ~3 cm from a 24 W blue LED at room temperature for 24 h. The solvent was removed by vacuum and the crude product was purified by flash chromatography on silica gel silica: 200~300; eluant: petroleum ether/ethyl acetate (5:1~1:1) to provide pure product **11a** as a colorless oil in 84% yield.

1,2-Diethyl 3-propyl 5-methyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (11a)



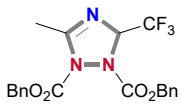
According to *GP1* with diazo compound (45.6 mg, 0.40 mmol, 4.0 equiv.) and diethylazodiformiat (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL MeCN for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 86% yield (25.9 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 5.98 (s, 1H), 4.38 – 4.19 (m, 6H), 2.49 (s, 3H), 1.36 – 1.28 (m, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.7, 158.6, 156.9, 151.6, 82.4, 63.7, 63.5, 62.1, 17.1, 14.3, 14.2, 13.9. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{12}H_{20}N_3O_6$: 302.1347; Found: 302.1345.

Diethyl 3-cyano-5-methyl-1*H*-1,2,4-triazole-1,2(3*H*)-dicarboxylate (11b)



According to *GP1* with diazo compound (26.8 mg, 0.40 mmol, 4.0 equiv.) and diethylazodiformiat (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL MeCN for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 85% yield (21.6 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 6.30 (d, J = 1.3 Hz, 1H), 4.42 – 4.24 (m, 4H), 2.51 (d, J = 1.2 Hz, 3H), 1.38 – 1.32 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 160.5, 155.9, 150.5, 114.1, 72.2, 64.5, 64.1, 16.9, 14.2, 14.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{10}H_{15}N_4O_4$: 255.1088; Found: 255.1091.

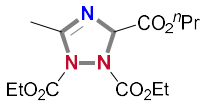
Dibenzyl 5-methyl-3-(trifluoromethyl)-1*H*-1,2,4-triazole-1,2(3*H*)-dicarboxylate (11c)



According to *GP1* with diazo compound (44.0 mg, 0.40 mmol, 4.0 equiv.) and diethylazodiformiat (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL MeCN for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 24% yield (10.2 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.37 – 7.26 (m, 10H), 5.95 – 5.87 (m, 1H), 5.27 – 5.18 (m, 4H), 2.49 (d, J = 1.2 Hz, 3H). **^{13}C NMR** (150 MHz,

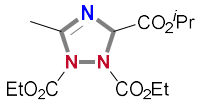
$CDCl_3$, 300 K): δ (ppm) = 161.0, 156.4, 151.1, 134.6, 134.6, 128.7, 128.7, 128.7, 128.6, 128.1, 127.9, 81.2 (q, *J* = 100.6 Hz), 69.5, 69.2, 17.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{20}H_{19}F_3N_3O_4$: 422.1322; Found: 422.1315.

1,2-Diethyl 3-propyl 5-methyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (11d)



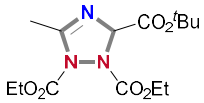
According to *GP1* with diazo compound (51.2 mg, 0.40 mmol, 4.0 equiv.) and diethylazodiformiat (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL MeCN for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 84% yield (26.5 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 5.99 (d, *J* = 1.6 Hz, 1H), 4.39 – 4.21 (m, 4H), 4.17 – 4.09 (m, 2H), 2.49 (s, 3H), 1.72 – 1.65 (m, 2H), 1.37 – 1.29 (m, 6H), 0.94 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.7, 158.6, 156.8, 151.6, 82.4, 67.5, 63.6, 63.5, 21.7, 17.1, 14.3, 14.2, 10.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{13}H_{22}N_3O_6$: 316.1503; Found: 316.1501.

1,2-Diethyl 3-isopropyl 5-methyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (11e)



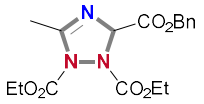
According to *GP1* with diazo compound (51.2 mg, 0.40 mmol, 4.0 equiv.) and diethylazodiformiat (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL MeCN for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 76% yield (24.0 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 5.94 (s, 1H), 5.08 – 4.98 (m, 1H), 4.39 – 4.19 (m, 4H), 2.49 (s, 3H), 1.36 – 1.30 (m, 6H), 1.29 – 1.24 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.2, 158.6, 156.8, 151.7, 82.6, 70.0, 63.6, 63.5, 21.6, 21.5, 17.1, 14.3, 14.2. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{13}H_{22}N_3O_6$: 316.1503; Found: 316.1501.

3-Tert-butyl 1,2-diethyl 5-methyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (11f)



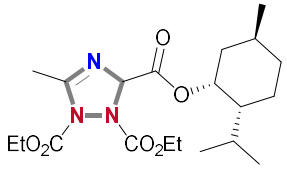
According to *GP1* with diazo compound (56.8 mg, 0.40 mmol, 4.0 equiv.) and diethylazodiformiat (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL MeCN for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 58% yield (19.1 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 5.86 (s, 1H), 4.39 – 4.19 (m, 4H), 2.48 (d, *J* = 1.3 Hz, 3H), 1.46 (s, 9H), 1.37 – 1.29 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 165.6, 158.4, 156.9, 151.8, 83.2, 83.0, 63.5, 63.4, 27.8, 17.1, 14.3, 14.2. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{14}H_{24}N_3O_6$: 330.1660; Found: 330.1664.

3-Benzyl 1,2-diethyl 5-methyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (11g)



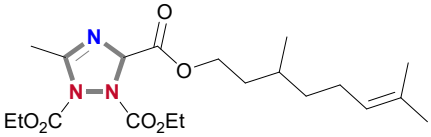
According to *GP1* with diazo compound (70.4 mg, 0.40 mmol, 4.0 equiv.) and diethylazodiformiat (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL MeCN for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 63% yield (22.9 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.37 – 7.32 (m, 5H), 6.04 (s, 1H), 5.23 – 5.15 (m, 2H), 4.35 – 4.14 (m, 4H), 2.48 (s, 3H), 1.33 – 1.24 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.5, 158.8, 156.8, 151.5, 134.9, 128.6, 128.5, 128.2, 82.4, 67.6, 63.7, 63.5, 17.1, 14.3, 14.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{17}H_{22}N_3O_6$: 364.1503; Found: 364.1503.

1,2-Diethyl 3-((1R,2R,5S)-2-isopropyl-5-methylcyclohexyl) (R)-5-methyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (11h)



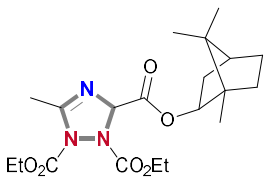
According to *GP1* with diazo compound (89.7 mg, 0.40 mmol, 4.0 equiv.) and diethyl azodicarboxylate (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL acetonitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 75% yield (32.5 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 5.88 (s, 1H), 4.68 – 4.58 (m, 1H), 4.31 – 4.13 (m, 4H), 2.41 (s, 3H), 1.98 – 1.90 (m, 1H), 1.84 – 1.72 (m, 1H), 1.63 – 1.58 (m, 2H), 1.45 – 1.18 (m, 9H), 1.03 – 0.88 (m, 2H), 0.84 – 0.80 (m, 6H), 0.70 – 0.65 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.1, 158.8, 156.7, 151.7, 82.6, 76.2, 63.6, 63.5, 47.0, 40.4, 34.1, 31.3, 26.2, 23.5, 21.9, 20.6, 17.1, 16.4, 14.3. **HRMS** (ESI) m/z: $[M+Na]^+$ Calculated for $C_{20}H_{33}N_3NaO_6$: 434.2262; Found: 434.2264.

3-(3,7-Dimethyloct-6-en-1-yl) 1,2-diethyl (3R)-5-methyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (11i)



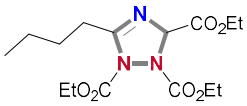
According to *GP1* with diazo compound (89.7 mg, 0.40 mmol, 4.0 equiv.) and diethyl azodicarboxylate (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL acetonitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 67% yield (29.1 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 5.91 (d, *J* = 1.3 Hz, 1H), 5.05 – 4.96 (m, 1H), 4.31 – 4.07 (m, 6H), 2.42 (d, *J* = 1.3 Hz, 3H), 1.97 – 1.80 (m, 2H), 1.61 (s, 4H), 1.53 (s, 3H), 1.49 – 1.37 (m, 2H), 1.29 – 1.23 (m, 6H), 1.19 – 1.05 (m, 2H), 0.83 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.7, 158.6, 156.8, 151.6, 131.4, 124.4, 82.4, 64.7, 63.7, 63.5, 36.9, 36.9, 35.1, 29.5, 29.4, 25.7, 25.3, 19.3, 19.3, 17.6, 17.1, 14.3, 14.2. **HRMS** (ESI) m/z: $[M+Na]^+$ Calculated for $C_{20}H_{33}N_3NaO_6$: 434.2262; Found: 434.2275.

1,2-Diethyl 3-((1R,2S,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl) (R)-5-methyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (11j)



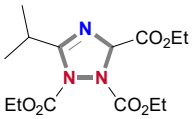
According to *GP1* with diazo compound (88.9 mg, 0.40 mmol, 4.0 equiv.) and diethyl azodicarboxylate (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL acetonitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 81% yield (d.r. = 1:1, 34.9 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 5.91 (d, *J* = 1.4 Hz, 1H), 4.92 – 4.82 (m, 1H), 4.30 – 4.13 (m, 4H), 2.43 (d, *J* = 1.3 Hz, 3H), 2.32 – 2.22 (m, 1H), 1.84 – 1.74 (m, 1H), 1.72 – 1.60 (m, 2H), 1.28 – 1.23 (m, 6H), 1.21 – 1.08 (m, 3H), 0.81 (d, *J* = 8.6 Hz, 6H), 0.75 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.7, 158.6, 158.5, 156.8, 151.5, 82.7, 82.6, 81.8, 81.6, 63.6, 63.5, 49.1, 48.9, 48.0, 47.9, 44.8, 44.8, 36.5, 36.2, 27.9, 27.9, 26.9, 19.6, 18.8, 17.1, 17.1, 14.3, 14.2, 13.3. **HRMS** (ESI) m/z: $[M+Na]^+$ Calculated for $C_{20}H_{31}N_3NaO_6$: 432.2105; Found: 432.2112.

Triethyl 5-propyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (11k)



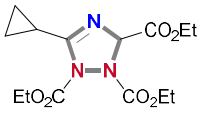
According to *GP1* with diazo compound (45.6 mg, 0.40 mmol, 4.0 equiv.) and diethylazodiformiat (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL valeronitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 61% yield (20.9 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 5.99 (s, 1H), 4.37 – 4.18 (m, 6H), 2.86 (t, *J* = 7.1 Hz, 2H), 1.75 – 1.65 (m, 2H), 1.42 – 1.27 (m, 11H), 0.93 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.7, 162.3, 156.9, 151.7, 82.3, 63.6, 63.4, 62.0, 30.0, 28.2, 22.2, 14.3, 14.2, 13.9, 13.7. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{15}H_{26}N_3O_6$: 344.1816; Found: 344.1833.

Triethyl 5-isopropyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (11l)



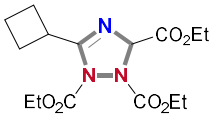
According to *GP1* with diazo compound (45.6 mg, 0.40 mmol, 4.0 equiv.) and diethylazodiformiat (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL isobutyronitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 55% yield (18.1 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 5.98 (s, 1H), 4.36 – 4.18 (m, 6H), 3.50 – 3.41 (m, 1H), 1.35 – 1.26 (m, 15H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 167.0, 166.7, 157.0, 151.7, 82.3, 63.5, 63.4, 62.0, 29.3, 20.8, 19.2, 14.3, 14.2, 13.9. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{14}H_{24}N_3O_6$: 330.1660; Found: 330.1673.

Triethyl 5-cyclopropyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (11m)



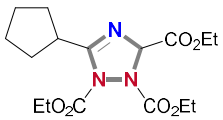
According to *GP1* with diazo compound (45.6 mg, 0.40 mmol, 4.0 equiv.) and diethylazodiformiat (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL cyclopropanecarbonitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 71% yield (23.3 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 5.94 (s, 1H), 4.40 – 4.18 (m, 6H), 2.42 – 2.34 (m, 1H), 1.37 – 1.24 (m, 11H), 1.18 – 0.97 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.7, 164.6, 156.7, 152.1, 81.9, 63.5, 63.4, 61.9, 14.3, 14.2, 13.9, 11.6, 10.2, 9.7. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{14}H_{22}N_3O_6$: 328.1503; Found: 328.1521.

Triethyl 5-cyclobutyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (11n)



According to *GP1* with diazo compound (45.6 mg, 0.40 mmol, 4.0 equiv.) and diethylazodiformiat (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL cyclobutanecarbonitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 52% yield (17.8 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 6.03 (d, *J* = 1.1 Hz, 1H), 4.36 – 4.18 (m, 6H), 3.86 – 3.76 (m, 1H), 2.44 – 2.27 (m, 4H), 2.07 – 1.85 (m, 2H), 1.35 – 1.27 (m, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.7, 164.7, 156.9, 151.4, 82.5, 63.6, 63.4, 62.0, 34.5, 26.8, 26.6, 18.1, 14.3, 14.2, 13.9. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{15}H_{24}N_3O_6$: 342.1660; Found: 342.1671.

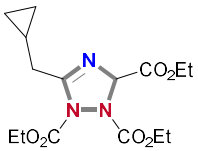
Triethyl 5-cyclopentyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (11o)



According to *GP1* with diazo compound (45.6 mg, 0.40 mmol, 4.0 equiv.) and diethylazodiformiat (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL cyclopentanecarbonitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 47% yield (16.7 mg). **^{1}H NMR** (400 MHz,

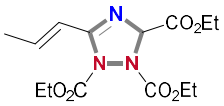
$CDCl_3$, 300 K): δ (ppm) = 5.98 (d, *J* = 0.9 Hz, 1H), 4.37 – 4.17 (m, 6H), 3.59 – 3.48 (m, 1H), 2.17 – 1.88 (m, 3H), 1.77 – 1.60 (m, 5H), 1.35 – 1.26 (m, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.7, 165.9, 157.0, 151.6, 82.3, 63.5, 63.3, 62.0, 39.5, 31.7, 30.3, 25.5, 25.5, 14.3, 14.3, 13.9. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{16}H_{26}N_3O_6$: 356.1816; Found: 356.1828.

Triethyl 5-(cyclopropylmethyl)-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (11p)



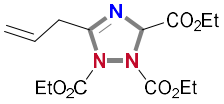
According to *GP1* with diazo compound (45.6 mg, 0.40 mmol, 4.0 equiv.) and diethylazodiformiat (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL 2-cyclopropylacetonitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 47% yield (16.1 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 6.02 (d, *J* = 1.1 Hz, 1H), 4.38 – 4.19 (m, 6H), 2.93 – 2.83 (m, 1H), 2.75 – 2.65 (m, 1H), 1.35 – 1.27 (m, 9H), 1.22 – 1.11 (m, 1H), 0.62 – 0.51 (m, 2H), 0.29 – 0.17 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.7, 161.8, 156.9, 151.7, 82.4, 63.6, 63.5, 62.0, 35.1, 14.3, 14.2, 13.9, 7.8, 4.5, 4.4. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{15}H_{24}N_3O_6$: 342.1660; Found: 342.1671.

(*E*)-Triethyl 5-(prop-1-en-1-yl)-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (11q)



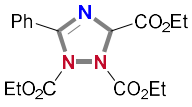
According to *GP1* with diazo compound (45.6 mg, 0.40 mmol, 4.0 equiv.) and diethylazodiformiat (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL (2*E*)-2-butenenitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 64% yield (20.9 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.03 – 6.92 (m, 1H), 6.60 – 6.52 (m, 1H), 6.05 (s, 1H), 4.38 – 4.17 (m, 6H), 1.97 – 1.91 (m, 3H), 1.35 – 1.26 (m, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.7, 157.5, 156.8, 152.5, 142.0, 119.1, 82.1, 63.6, 63.5, 62.0, 18.7, 14.3, 14.2, 13.9. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{14}H_{22}N_3O_6$: 328.1503; Found: 328.1517.

Triethyl 5-allyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (11r)



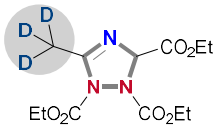
According to *GP1* with diazo compound (45.6 mg, 0.40 mmol, 4.0 equiv.) and diethylazodiformiat (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL but-3-enenitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 59% yield (19.3 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 6.07 – 5.92 (m, 2H), 5.29 – 5.16 (m, 2H), 4.39 – 4.18 (m, 6H), 3.71 – 3.57 (m, 2H), 1.36 – 1.27 (m, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.6, 160.4, 156.8, 151.5, 130.6, 118.6, 82.4, 63.7, 63.6, 62.1, 34.6, 14.3, 14.2, 13.9. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{14}H_{22}N_3O_6$: 328.1503; Found: 328.1515.

Triethyl 5-phenyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (11s)



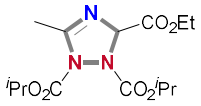
According to *GP1* with diazo compound (45.6 mg, 0.40 mmol, 4.0 equiv.) and diethylazodiformiat (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL benzonitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 51% yield (18.6 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.90 – 7.84 (m, 2H), 7.56 – 7.50 (m, 1H), 7.46 – 7.40 (m, 2H), 6.23 (s, 1H), 4.39 – 4.17 (m, 6H), 1.38 – 1.28 (m, 6H), 1.16 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.5, 161.2, 156.8, 153.2, 132.2, 129.9, 128.8, 128.1, 82.5, 63.7, 62.3, 14.5, 14.0. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{17}H_{22}N_3O_6$: 364.1503; Found: 364.1521.

Triethyl 5-D3-methyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (11t)



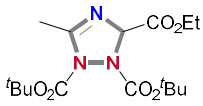
According to *GP1* with diazo compound (45.6 mg, 0.40 mmol, 4.0 equiv.) and diethylazodiformiat (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL acetonitrile-D3 for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 61% yield (18.6 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 5.98 (s, 1H), 4.38 – 4.19 (m, 6H), 1.36 – 1.28 (m, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.7, 158.6, 156.9, 151.6, 82.4, 63.7, 63.5, 62.1, 14.3, 14.2, 13.9. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{12}H_{17}D_3N_3O_6$: 305.1535; Found: 305.1554.

3-Ethyl 1,2-diisopropyl 5-methyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (11u)



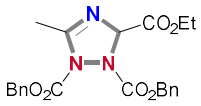
According to *GP1* with diazo compound (45.6 mg, 0.40 mmol, 4.0 equiv.) and diisopropyl azodicarboxylate (20.2 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL acetonitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 64% yield (21.1 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 5.96 (d, *J* = 1.3 Hz, 1H), 5.12 – 4.96 (m, 2H), 4.26 – 4.17 (m, 2H), 2.48 (d, *J* = 1.3 Hz, 3H), 1.35 – 1.27 (m, 15H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.7, 158.8, 156.5, 151.2, 82.2, 71.8, 71.7, 62.0, 21.9, 21.8, 21.7, 17.2, 13.9. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{14}H_{24}N_3O_6$: 330.1660; Found: 330.1676.

1,2-Di-tert-butyl 3-ethyl 5-methyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (11v)



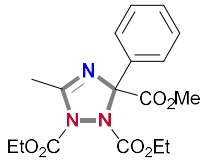
According to *GP1* with diazo compound (45.6 mg, 0.40 mmol, 4.0 equiv.) and di-*tert*-butyl azodicarboxylate (23.0 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL acetonitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 78% yield (27.9 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 5.89 (s, 1H), 4.25 – 4.17 (m, 2H), 2.46 (d, *J* = 1.3 Hz, 3H), 1.53 (s, 9H), 1.50 (s, 9H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 167.0, 158.9, 155.4, 150.1, 83.7, 83.4, 82.0, 61.8, 28.0, 28.0, 27.9, 17.4, 14.0. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{16}H_{28}N_3O_6$: 358.1973; Found: 358.1984.

1,2-Dibenzyl 3-ethyl 5-methyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (11w)



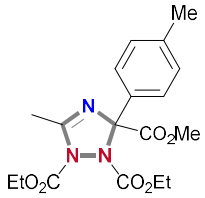
According to *GP1* with diazo compound (45.6 mg, 0.40 mmol, 4.0 equiv.) and dibenzyl azodicarboxylate (29.8 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL acetonitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 61% yield (25.9 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.33 (d, *J* = 4.3 Hz, 10H), 6.02 (d, *J* = 1.3 Hz, 1H), 5.28 – 5.16 (m, 4H), 4.23 – 4.11 (m, 2H), 2.47 (d, *J* = 1.3 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.4, 158.6, 156.7, 151.6, 134.9, 128.6, 128.6, 128.6, 128.5, 128.1, 128.0, 82.5, 69.0, 68.9, 62.1, 17.2, 13.9. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{22}H_{24}N_3O_6$: 426.1660; Found: 426.1678.

1,2-Diethyl 3-methyl 5-methyl-3-phenyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (13a)



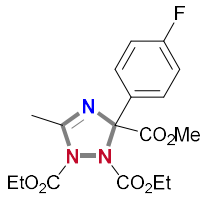
According to *GP1* with diazo compound (70.4 mg, 0.40 mmol, 4.0 equiv.) and diethyl azodicarboxylate (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL acetonitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 87% yield (31.6 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.63 (d, *J* = 8.2 Hz, 2H), 7.38 (q, *J* = 8.7, 7.6 Hz, 3H), 4.31 – 4.19 (m, 4H), 3.75 (s, 3H), 2.45 (s, 3H), 1.34 – 1.24 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 168.3, 156.1, 155.2, 151.2, 137.5, 128.6, 128.0, 127.2, 94.1, 63.7, 63.2, 53.4, 17.0, 14.3, 14.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{17}H_{22}N_3O_6$: 364.1503; Found: 364.1506.

1,2-Diethyl 3-methyl 5-methyl-3-(p-tolyl)-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (13b)



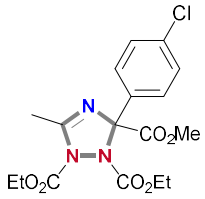
According to *GP1* with diazo compound (76.0 mg, 0.40 mmol, 4.0 equiv.) and diethyl azodicarboxylate (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL acetonitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 60% yield (22.6 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.50 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 4.31 – 4.16 (m, 4H), 3.74 (s, 3H), 2.42 (s, 3H), 2.35 (s, 3H), 1.34 – 1.23 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 168.3, 156.0, 155.2, 151.2, 138.5, 134.6, 128.7, 127.1, 94.1, 63.7, 63.1, 53.4, 21.1, 17.0, 14.2, 14.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{18}H_{24}N_3O_6$: 378.1660; Found: 378.1659.

1,2-Diethyl 3-methyl 3-(4-fluorophenyl)-5-methyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (13c)



According to *GP1* with diazo compound (77.6 mg, 0.40 mmol, 4.0 equiv.) and diethyl azodicarboxylate (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL acetonitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 89% yield (33.9 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.64 – 7.56 (m, 2H), 7.06 (t, *J* = 8.7 Hz, 2H), 4.33 – 4.18 (m, 4H), 3.75 (s, 3H), 2.45 (s, 3H), 1.35 – 1.24 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 168.1, 164.1, 161.6, 156.3, 155.1, 151.1, 133.5, 133.4, 129.2, 129.1, 115.0, 114.8, 93.6, 63.8, 63.3, 53.5, 17.0, 14.3, 14.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{17}H_{21}FN_3O_6$: 382.1409; Found: 382.1409.

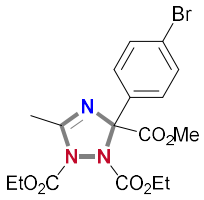
1,2-Diethyl 3-methyl 3-(4-chlorophenyl)-5-methyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (13d)



According to *GP1* with diazo compound (84.0 mg, 0.40 mmol, 4.0 equiv.) and diethyl azodicarboxylate (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL acetonitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 91% yield (36.1 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.56 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 4.34 – 4.17 (m, 4H), 3.75 (s, 3H), 2.44 (s, 3H), 1.35 – 1.25 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 168.0, 156.4, 155.1, 151.1, 136.2, 134.6, 128.7, 128.2, 93.6, 63.9, 63.3,

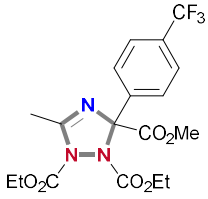
53.5, 17.0, 14.3, 14.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{17}H_{21}ClN_3O_6$: 398.1113; Found: 398.1111.

1,2-Diethyl 3-methyl 3-(4-bromophenyl)-5-methyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (13e)



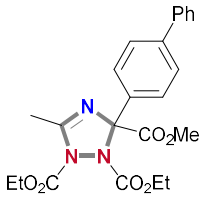
According to *GP1* with diazo compound (101.6 mg, 0.40 mmol, 4.0 equiv.) and diethyl azodicarboxylate (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL acetonitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 95% yield (41.9 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.50 (s, 4H), 4.32 – 4.17 (m, 4H), 3.75 (s, 3H), 2.44 (s, 3H), 1.34 – 1.24 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 167.9, 156.5, 155.1, 151.0, 136.7, 131.3, 131.1, 129.0, 128.8, 122.9, 93.6, 63.9, 63.3, 53.5, 17.0, 14.2, 14.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{17}H_{21}BrN_3O_6$: 442.0608; Found: 442.0607.

1,2-Diethyl 3-methyl 5-methyl-3-(4-(trifluoromethyl)phenyl)-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (13f)



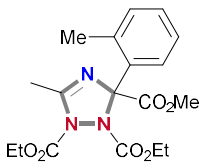
According to *GP1* with diazo compound (97.6 mg, 0.40 mmol, 4.0 equiv.) and diethyl azodicarboxylate (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL acetonitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 94% yield (40.5 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.76 (d, J = 8.2 Hz, 2H), 7.64 (d, J = 8.3 Hz, 2H), 4.36 – 4.21 (m, 4H), 3.76 (s, 3H), 2.45 (s, 3H), 1.35 – 1.26 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 167.8, 156.7, 155.1, 151.0, 141.5, 130.9 (d, J = 32.2 Hz), 127.7, 125.0 (d, J = 3.8 Hz), 93.7, 64.0, 63.4, 53.6, 17.0, 14.2, 14.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{18}H_{21}F_3N_3O_6$: 432.1377; Found: 432.1377.

1,2-Diethyl 3-methyl 3-([1,1'-biphenyl]-4-yl)-5-methyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (13g)



According to *GP1* with diazo compound (100.8 mg, 0.40 mmol, 4.0 equiv.) and diethyl azodicarboxylate (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL acetonitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 63% yield (27.7 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.70 (d, J = 8.5 Hz, 2H), 7.64 – 7.56 (m, 4H), 7.44 (t, J = 7.5 Hz, 2H), 7.35 (t, J = 7.4 Hz, 1H), 4.35 – 4.19 (m, 4H), 3.78 (s, 3H), 2.46 (s, 3H), 1.36 – 1.26 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 168.3, 156.2, 155.2, 151.2, 141.6, 140.7, 136.5, 128.7, 127.6, 127.4, 127.2, 126.8, 94.1, 63.8, 63.2, 53.5, 17.1, 14.3, 14.2. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{23}H_{26}N_3O_6$: 440.1816; Found: 440.1795.

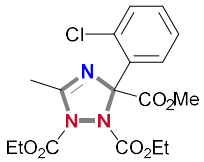
1,2-Diethyl 3-methyl 5-methyl-3-(o-tolyl)-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (13h)



According to *GP1* with diazo compound (76.0 mg, 0.40 mmol, 4.0 equiv.) and diethyl azodicarboxylate (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL acetonitrile for 12 h. Purification by silica gel chromatography afforded the

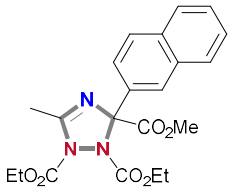
desired product and as a colorless oil in 67% yield (25.3 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.64 (d, *J* = 8.3 Hz, 1H), 7.29 – 7.17 (m, 3H), 4.37 – 4.16 (m, 4H), 3.77 (s, 3H), 2.48 (s, 3H), 2.42 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 167.8, 155.5, 155.0, 151.2, 137.6, 135.0, 131.8, 128.7, 126.4, 125.5, 95.3, 63.6, 63.2, 53.3, 21.5, 17.0, 14.2, 14.2. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{18}H_{24}N_3O_6$: 378.1660; Found: 378.1658.

1,2-Diethyl 3-methyl 3-(2-chlorophenyl)-5-methyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (13i)



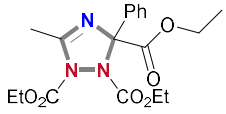
According to *GP1* with diazo compound (84.0 mg, 0.40 mmol, 4.0 equiv.) and diethyl azodicarboxylate (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL acetonitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 92% yield (36.5 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.76 – 7.70 (m, 1H), 7.46 – 7.41 (m, 1H), 7.34 – 7.25 (m, 2H), 4.41 – 4.16 (m, 4H), 3.80 (s, 3H), 2.47 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.28 – 1.20 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.8, 156.5, 154.9, 150.9, 134.5, 133.7, 131.2, 130.1, 128.0, 126.7, 94.2, 63.8, 63.4, 53.4, 17.0, 14.2, 14.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{17}H_{21}ClN_3O_6$: 398.1133; Found: 398.1115.

1,2-Diethyl 3-methyl 5-methyl-3-(naphthalen-2-yl)-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (13j)



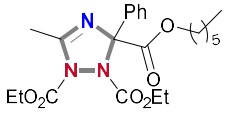
According to *GP1* with diazo compound (90.4 mg, 0.40 mmol, 4.0 equiv.) and diethyl azodicarboxylate (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL acetonitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 71% yield (29.3 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.07 (s, 1H), 7.85 (t, *J* = 8.4 Hz, 3H), 7.76 – 7.73 (m, 1H), 7.52 – 7.45 (m, 2H), 4.36 – 4.20 (m, 4H), 3.77 (s, 3H), 2.47 (s, 3H), 1.35 – 1.26 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 168.3, 156.4, 155.3, 151.2, 135.0, 133.4, 132.8, 128.6, 127.6, 127.6, 126.5, 126.1, 126.0, 125.3, 94.2, 63.8, 63.3, 53.5, 17.1, 14.3, 14.2. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{21}H_{24}N_3O_6$: 414.1660; Found: 414.1660.

Triethyl 5-methyl-3-phenyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (13k)



According to *GP1* with diazo compound (76.0 mg, 0.40 mmol, 4.0 equiv.) and diethyl azodicarboxylate (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL acetonitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 81% yield (30.6 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.63 (d, *J* = 8.4 Hz, 2H), 7.42 – 7.31 (m, 3H), 4.34 – 4.14 (m, 6H), 2.44 (s, 3H), 1.34 – 1.22 (m, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 167.6, 156.0, 155.2, 151.2, 137.5, 128.5, 127.9, 127.3, 94.2, 63.7, 63.0, 62.8, 17.0, 14.2, 14.1, 13.9. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{18}H_{24}N_3O_6$: 378.1660; Found: 378.1660.

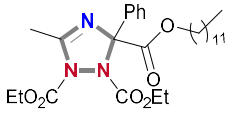
1,2-Diethyl 3-hexyl 5-methyl-3-phenyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (13l)



According to *GP1* with diazo compound (98.5 mg, 0.40 mmol, 4.0 equiv.) and diethyl azodicarboxylate (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL

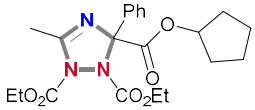
acetonitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 78% yield (33.8 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.66 – 7.59 (m, 2H), 7.41 – 7.31 (m, 3H), 4.31 – 4.06 (m, 6H), 2.44 (s, 3H), 1.64 – 1.56 (m, 2H), 1.34 – 1.23 (m, 12H), 0.87 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 167.7, 155.9, 155.2, 151.3, 137.6, 128.5, 127.9, 127.2, 94.2, 66.9, 63.7, 63.0, 31.2, 28.2, 25.3, 22.4, 17.0, 14.2, 14.1, 13.9. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{22}H_{32}N_3O_6$: 434.2286; Found: 434.2287.

3-Dodecyl 1,2-diethyl 5-methyl-3-phenyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (13m)



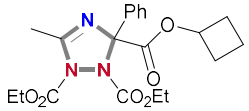
According to *GP1* with diazo compound (132.1 mg, 0.40 mmol, 4.0 equiv.) and diethyl azodicarboxylate (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL acetonitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 77% yield (39.8 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.63 (d, *J* = 6.9 Hz, 2H), 7.40 – 7.32 (m, 3H), 4.29 – 4.06 (m, 6H), 2.44 (s, 3H), 1.66 – 1.57 (m, 2H), 1.31 – 1.23 (m, 24H), 0.88 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 167.7, 155.9, 155.2, 151.3, 137.6, 128.5, 127.9, 127.2, 94.3, 66.9, 63.7, 63.0, 31.9, 29.6, 29.6, 29.5, 29.4, 29.3, 29.1, 28.2, 25.6, 22.7, 17.0, 14.4, 14.2, 14.1, 14.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{28}H_{44}N_3O_6$: 518.3225; Found: 518.3209.

3-Cyclopentyl 1,2-diethyl 5-methyl-3-phenyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (13n)



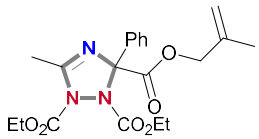
According to *GP1* with diazo compound (92.0 mg, 0.40 mmol, 4.0 equiv.) and diethyl azodicarboxylate (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL acetonitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a white solid in 81% yield (33.8 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.66 – 7.59 (m, 2H), 7.40 – 7.30 (m, 3H), 5.21 – 5.15 (m, 1H), 4.33 – 4.15 (m, 4H), 2.43 (s, 3H), 1.83 – 1.54 (m, 8H), 1.34 – 1.24 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 167.2, 155.8, 155.2, 151.3, 137.6, 128.4, 127.8, 127.3, 94.2, 79.9, 63.7, 62.9, 32.6, 32.1, 23.5, 23.5, 16.9, 14.2, 14.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{21}H_{28}N_3O_6$: 418.1973; Found: 418.1970.

3-Cyclobutyl 1,2-diethyl 5-methyl-3-phenyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (13o)



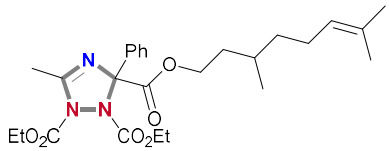
According to *GP1* with diazo compound (86.4 mg, 0.40 mmol, 4.0 equiv.) and diethyl azodicarboxylate (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL acetonitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 84% yield (33.9 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.63 (d, *J* = 8.8 Hz, 2H), 7.42 – 7.31 (m, 3H), 5.07 – 4.96 (m, 1H), 4.33 – 4.12 (m, 4H), 2.45 (s, 3H), 2.38 – 2.25 (m, 2H), 2.13 – 2.00 (m, 2H), 1.83 – 1.71 (m, 1H), 1.63 – 1.54 (m, 1H), 1.35 – 1.24 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.8, 156.0, 155.2, 151.3, 137.5, 128.5, 127.9, 127.3, 94.0, 70.9, 63.7, 63.0, 30.1, 29.8, 17.0, 14.2, 14.1, 13.3. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{20}H_{26}N_3O_6$: 404.1816; Found: 404.1816.

1,2-Diethyl 3-(2-methylallyl) 5-methyl-3-phenyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (13p)



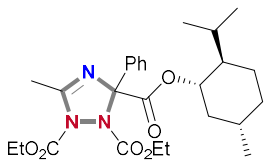
According to *GP1* with diazo compound (86.4 mg, 0.40 mmol, 4.0 equiv.) and diethyl azodicarboxylate (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL acetonitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 73% yield (29.4 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.65 (d, *J* = 8.4 Hz, 2H), 7.42 – 7.32 (m, 3H), 4.89 (d, *J* = 3.6 Hz, 2H), 4.59 (d, *J* = 13.2 Hz, 1H), 4.49 (d, *J* = 13.2 Hz, 1H), 4.32 – 4.15 (m, 4H), 2.45 (s, 3H), 1.68 (s, 3H), 1.35 – 1.22 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 167.4, 156.1, 155.2, 151.3, 138.8, 137.5, 128.6, 127.9, 127.2, 113.4, 94.3, 69.6, 63.7, 63.1, 19.3, 17.0, 14.2, 14.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{20}H_{26}N_3O_6$: 404.1816; Found: 404.1816.

3-(3,7-Dimethyloct-6-en-1-yl) 1,2-diethyl 5-methyl-3-phenyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (13q)



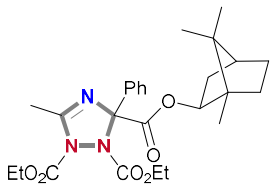
According to *GP1* with diazo compound (120.0 mg, 0.40 mmol, 4.0 equiv.) and diethyl azodicarboxylate (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL acetonitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 65% yield (31.7 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.63 (d, *J* = 6.7 Hz, 2H), 7.42 – 7.31 (m, 3H), 5.06 (t, *J* = 7.2 Hz, 1H), 4.33 – 4.09 (m, 6H), 2.44 (s, 3H), 2.01 – 1.83 (m, 2H), 1.68 (s, 3H), 1.59 (s, 4H), 1.49 – 1.36 (m, 2H), 1.34 – 1.22 (m, 7H), 1.18 – 1.08 (m, 1H), 0.88 – 0.82 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 167.8, 156.0, 155.2, 151.3, 137.6, 131.3, 128.5, 127.9, 127.2, 124.5, 94.2, 65.4, 65.4, 63.7, 63.0, 36.9, 36.9, 35.1, 35.0, 29.5, 29.5, 25.7, 25.4, 19.3, 17.6, 17.0, 14.3, 14.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{26}H_{38}N_3O_6$: 488.2755; Found: 488.2754.

1,2-Diethyl 3-((1S,2R,5S)-2-isopropyl-5-methylcyclohexyl) 5-methyl-3-phenyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (13r)



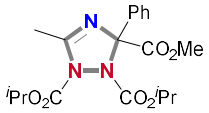
According to *GP1* with diazo compound (120.0 mg, 0.40 mmol, 4.0 equiv.) and diethyl azodicarboxylate (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL acetonitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 71% yield (34.6 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.67 – 7.59 (m, 2H), 7.42 – 7.30 (m, 3H), 4.70 – 4.60 (m, 1H), 4.35 – 4.10 (m, 4H), 2.42 (s, 3H), 2.09 – 2.01 (m, 1H), 1.82 – 1.73 (m, 1H), 1.70 – 1.60 (m, 2H), 1.51 – 1.39 (m, 1H), 1.33 – 1.26 (m, 7H), 1.09 – 0.97 (m, 1H), 0.95 – 0.86 (m, 5H), 0.82 (d, *J* = 7.0 Hz, 3H), 0.73 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.8, 155.8, 155.1, 151.5, 137.5, 128.4, 127.8, 127.4, 94.4, 63.7, 62.9, 47.0, 40.2, 34.1, 31.3, 25.9, 23.4, 22.0, 20.6, 16.8, 16.3, 14.3, 14.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{26}H_{38}N_3O_6$: 488.2755; Found: 488.2753.

1,2-Diethyl 3-((1R,2S,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl) 5-methyl-3-phenyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (13s)



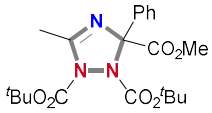
According to *GP1* with diazo compound (119.3 mg, 0.40 mmol, 4.0 equiv.) and diethyl azodicarboxylate (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL acetonitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 74% yield (d.r. = 2:1, 35.9 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.65 (d, *J* = 6.7 Hz, 2H), 7.41 – 7.30 (m, 3H), 4.93 – 4.85 (m, 0.66H), 4.81 – 4.75 (m, 0.33H), 4.36 – 4.15 (m, 4H), 2.45 (d, *J* = 3.1 Hz, 3H), 2.40 – 2.25 (m, 1H), 1.74 – 1.61 (m, 2H), 1.57 – 1.47 (m, 1H), 1.34 – 1.25 (m, 6H), 1.20 – 0.99 (m, 3H), 0.88 – 0.82 (m, 6H), 0.79 (d, *J* = 18.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 167.8, 155.9, 155.2, 151.5, 137.7, 128.4, 127.8, 127.3, 94.3, 83.1, 82.6, 63.7, 63.0, 49.1, 48.8, 47.8, 47.7, 44.8, 44.7, 36.5, 36.0, 27.8, 27.7, 26.7, 19.6, 18.8, 16.9, 14.2, 14.2, 13.4, 13.3. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{26}H_{36}N_3O_6$: 486.2599; Found: 486.2598.

1,2-Diisopropyl 3-methyl 5-methyl-3-phenyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (13t)



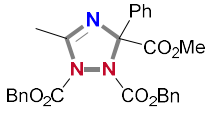
According to *GP1* with diazo compound (70.4 mg, 0.40 mmol, 4.0 equiv.) and diisopropyl azodicarboxylate (20.2 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL acetonitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 82% yield (32.1 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.66 – 7.58 (m, 2H), 7.41 – 7.32 (m, 3H), 5.06 – 4.95 (m, 2H), 3.75 (s, 3H), 2.43 (s, 3H), 1.34 – 1.24 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 168.3, 156.3, 154.6, 150.8, 137.6, 128.5, 127.9, 127.2, 93.9, 72.2, 71.4, 53.3, 22.0, 21.7, 21.7, 17.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{19}H_{26}N_3O_6$: 392.1816; Found: 392.1816.

1,2-Di-tert-butyl 3-methyl 5-methyl-3-phenyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (13u)



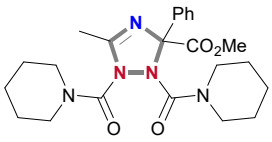
According to *GP1* with diazo compound (70.4 mg, 0.40 mmol, 4.0 equiv.) and di-tert-butyl azodicarboxylate (23.0 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL acetonitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 87% yield (36.5 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.66 – 7.59 (m, 2H), 7.42 – 7.30 (m, 3H), 3.75 (s, 3H), 2.40 (s, 3H), 1.50 (d, *J* = 9.9 Hz, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 168.6, 156.5, 153.7, 149.8, 137.9, 128.4, 127.8, 127.2, 93.6, 84.2, 83.1, 53.2, 28.0, 27.9, 17.2. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{21}H_{30}N_3O_6$: 420.2129; Found: 420.2117.

1,2-Dibenzyl 3-methyl 5-methyl-3-phenyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (13v)



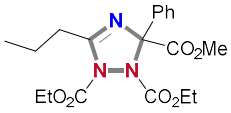
According to *GP1* with diazo compound (70.4 mg, 0.40 mmol, 4.0 equiv.) and dibenzyl azodicarboxylate (29.8 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL acetonitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 91% yield (44.3 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.63 – 7.56 (m, 2H), 7.37 – 7.26 (m, 13H), 5.25 – 5.09 (m, 4H), 3.46 (s, 3H), 2.42 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 168.0, 156.1, 155.2, 151.2, 137.2, 135.0, 134.5, 128.7, 128.6, 128.5, 128.5, 128.4, 128.1, 128.0, 127.2, 94.2, 69.2, 68.6, 53.3, 17.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{27}H_{26}N_3O_6$: 488.1816; Found: 488.1812.

Methyl 5-methyl-3-phenyl-1,2-di(piperidine-1-carbonyl)-2,3-dihydro-1*H*-1,2,4-triazole-3-carboxylate (13w)



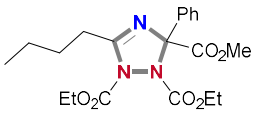
According to *GP1* with diazo compound (70.4 mg, 0.40 mmol, 4.0 equiv.) and 1,1'-(azodicarbonyl)-dipiperidine (25.2 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL acetonitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 40% yield (17.7 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.44 – 7.31 (m, 5H), 3.82 (s, 3H), 3.61 – 3.47 (m, 4H), 2.99 (s, 3H), 2.52 (s, 3H), 1.66 – 1.51 (m, 7H), 1.40 – 1.21 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 170.3, 161.4, 158.4, 153.5, 133.8, 129.6, 128.0, 127.8, 95.8, 53.0, 46.8, 45.8, 26.0, 25.6, 24.5, 24.1, 16.3. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{23}H_{32}N_5O_4$: 442.2449; Found: 442.2446.

1,2-Diethyl 3-methyl 3-phenyl-5-propyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (13x)



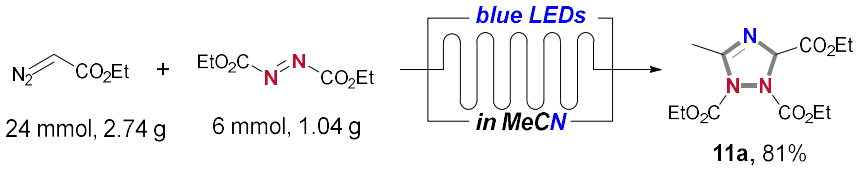
According to *GP1* with diazo compound (70.4 mg, 0.40 mmol, 4.0 equiv.) and diethyl azodicarboxylate (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL butyronitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 55% yield (21.5 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.63 (d, J = 8.2 Hz, 2H), 7.41 – 7.32 (m, 3H), 4.33 – 4.16 (m, 4H), 3.75 (s, 3H), 2.90 – 2.80 (m, 1H), 2.73 – 2.63 (m, 1H), 1.86 – 1.75 (m, 2H), 1.33 – 1.24 (m, 6H), 1.01 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 168.3, 159.5, 155.3, 151.3, 137.6, 128.6, 127.9, 127.2, 94.0, 63.6, 63.1, 53.3, 31.9, 19.8, 14.3, 14.1, 13.3. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{19}H_{26}N_3O_6$: 392.1816; Found: 392.1817.

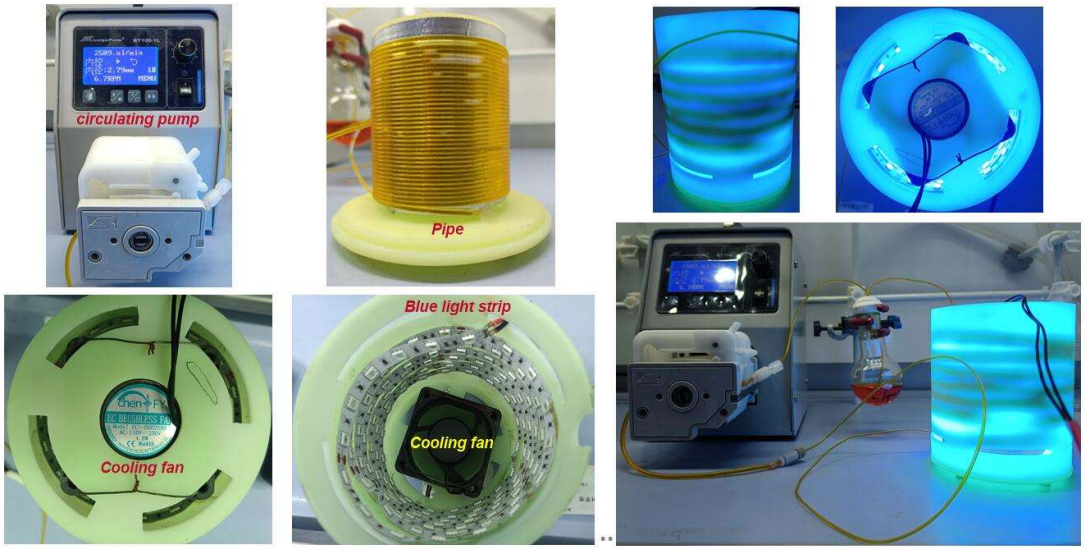
1,2-Diethyl 3-methyl 5-butyl-3-phenyl-1*H*-1,2,4-triazole-1,2,3(3*H*)-tricarboxylate (13y)



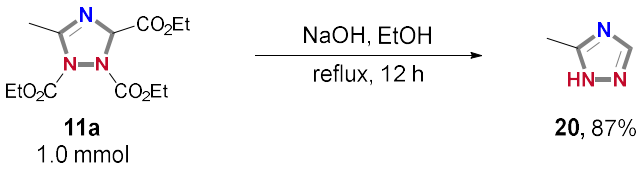
According to *GP1* with diazo compound (70.4 mg, 0.40 mmol, 4.0 equiv.) and diethyl azodicarboxylate (17.4 mg, 0.10 mmol, 1.0 equiv.) in 1.0 mL pentanenitrile for 12 h. Purification by silica gel chromatography afforded the desired product and as a colorless oil in 43% yield (17.4 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.62 (d, J = 6.4 Hz, 2H), 7.41 – 7.33 (m, 3H), 4.32 – 4.17 (m, 4H), 3.75 (s, 3H), 2.91 – 2.80 (m, 1H), 2.77 – 2.67 (m, 1H), 1.80 – 1.70 (m, 2H), 1.46 – 1.37 (m, 2H), 1.33 – 1.24 (m, 6H), 0.94 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 168.4, 159.7, 155.3, 151.3, 137.6, 128.6, 127.9, 127.2, 94.0, 63.6, 63.1, 53.4, 29.9, 28.3, 22.1, 14.3, 14.1, 13.7. **HRMS** (ESI) m/z: $[M+H]^+$ Calculated for $C_{20}H_{28}N_3O_6$: 406.1973; Found: 406.1974.

5. Follow-up chemistry

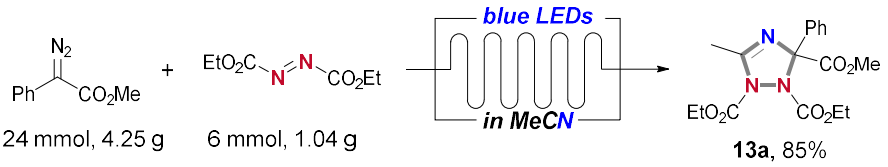




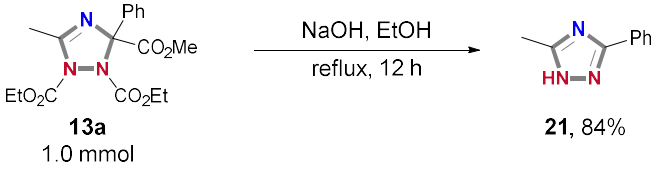
Ethyl diazoacetate (2.74 g, 24.0 mmol, 4.0 equiv.) and diethyl azodicarboxylate (1.04 g, 6.0 mmol, 1.0 equiv.) in dry CH_3CN (25 mL) was pushed *via* circulating pump to pass through the flow photoreactor (PFA tubing, O.D. 2.0 mm, I.D. 1.0 mm, 6.5 meters) under irradiation with blue light strip (20 W) equipped with a fan cooling. The flow rate is 2.509 mL/min and the flow protocol were recirculated. After 12 h, the solvent was removed by vacuum and the crude product were purified by flash chromatography on silica gel silica: 200~300; eluant: petroleum ether/ethyl acetate = 5:1 to provide pure product **11a** as a colorless oil in 81% yield (1.46 g).



To a solution of **11a** (301 mg, 1.0 mmol) in EtOH was added NaOH (400 mg, 10 mmol), The reaction mixture was stirred for 12 h at 85 °C. The reaction mixture was warmed up to room temperature gradually and the reaction mixture was quenched with HCl extracted with EtOAc. The residue was purified by column chromatography (petroleum ether/EtOAc = 3/1) to afford **20** as white solid in 87% yield (72.2 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 9.24 (s, 1H), 8.02 (s, 1H), 2.51 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 155.1, 148.5, 12.3.

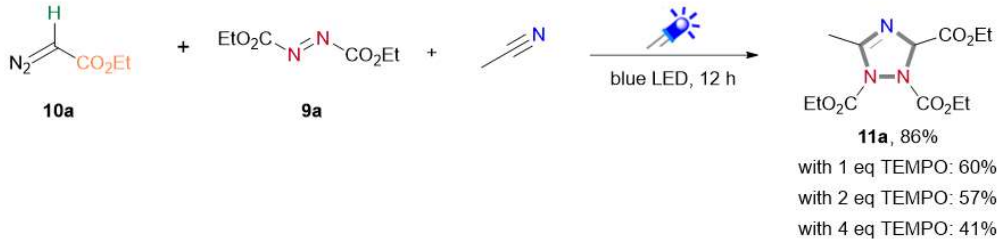


Methyl 2-diazo-2-phenylacetate (4.25 g, 24.0 mmol, 4.0 equiv.) and diethyl azodicarboxylate (1.04 g, 6.0 mmol, 1.0 equiv.) in dry CH_3CN (25 mL) was pushed via circulating pump to pass through the flow photoreactor (PFA tubing, O.D. 2.0 mm, I.D. 1.0 mm, 6.5 meters) under irradiation with blue light strip (20 W) equipped with a fan cooling. The flow rate is 2.509 mL/min and the flow protocol were recirculated. After 12 h, the solvent was removed by vacuum and the crude product were purified by flash chromatography on silica gel silica: 200~300; eluant: petroleum ether/ethyl acetate = 5:1 to provide pure product **13a** as a colorless oil in 85% yield (1.85 g).



To a solution of **13a** (363 mg, 1.0 mmol) in EtOH was added NaOH (400 mg, 10 mmol), The reaction mixture was stirred for 12 h at 85 °C. The reaction mixture was warmed up to room temperature gradually and the reaction mixture was quenched with HCl extracted with EtOAc. The residue was purified by column chromatography (petroleum ether/EtOAc = 3/1) to afford **21** as white solid in 84% yield (133.6 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 14.0 – 10.0 (s, 1H), 8.02 – 7.96 (m, 2H), 7.41 – 7.36 (m, 3H), 2.45 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 160.6, 156.0, 129.7, 128.8, 126.4, 12.5.

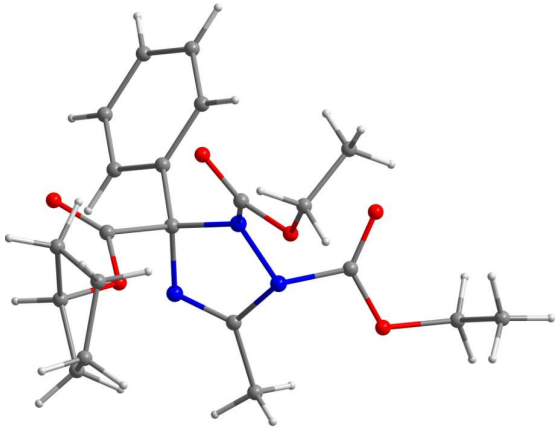
6. TEMPO trapping experiment



To a 10 mL Schlenk flask equipped with a magnetic stir bar was added ethyl diazoacetate (0.40 mmol), diethylazodiformiat (0.10 mmol), dry MeCN (1.0 mL) and TEMPO (1~4 equivalents). The resulting mixture was stirred at a distance of ~3 cm from a 24 W blue LED at room temperature for 12 h. The solvent was removed by vacuum and the crude product was purified by flash chromatography on silica gel silica: 200~300; eluant: petroleum ether/ethyl acetate (5:1~1:1) to provide pure product **11a** as a colorless oil.

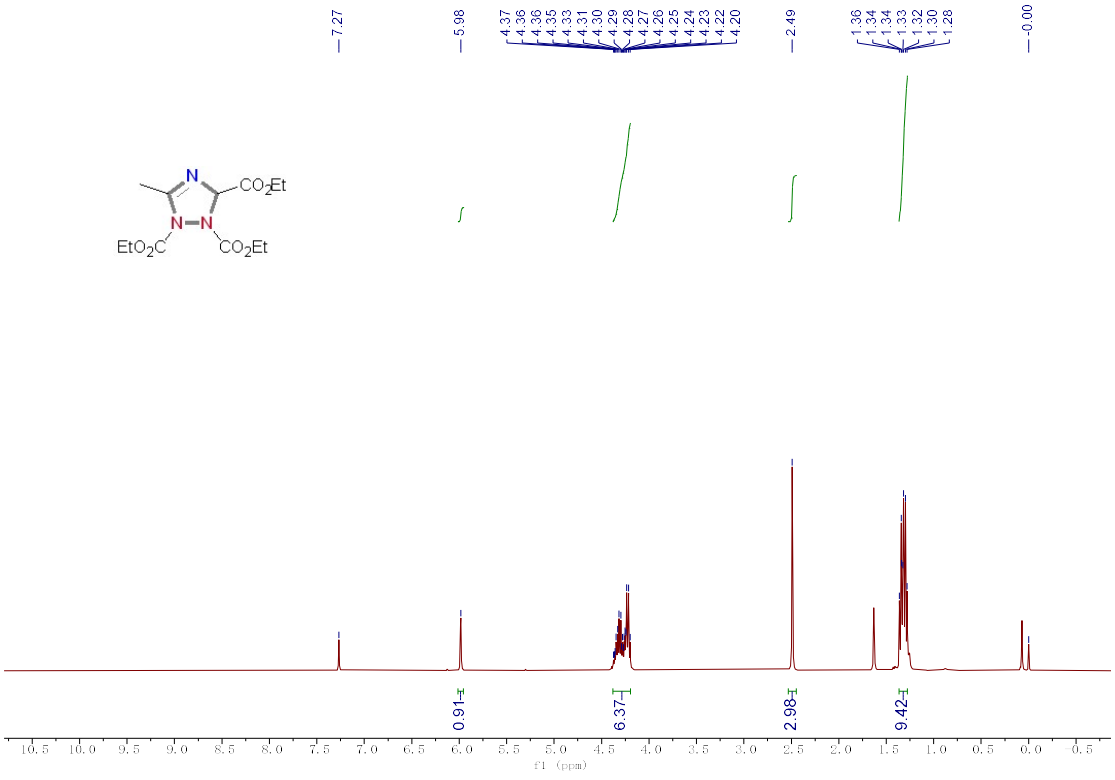
7. Crystal data of 13n

Method for single crystals cultivation: The single crystal for compound **13n** (CCDC-2166508) were prepared from a mixture solvent of DCM and PE (v/v = 1:1). a pure solid sample (10–20 mg) was dissolved in DCM (2 mL) in a vial at room temperature, and PE (2-3 mL) was added into the above solution slowly while keeping the sample completely dissolved. The vial was properly sealed with parafilm and kept at room temperature to allow the slow evaporation of the solvents until a single crystal was obtained.

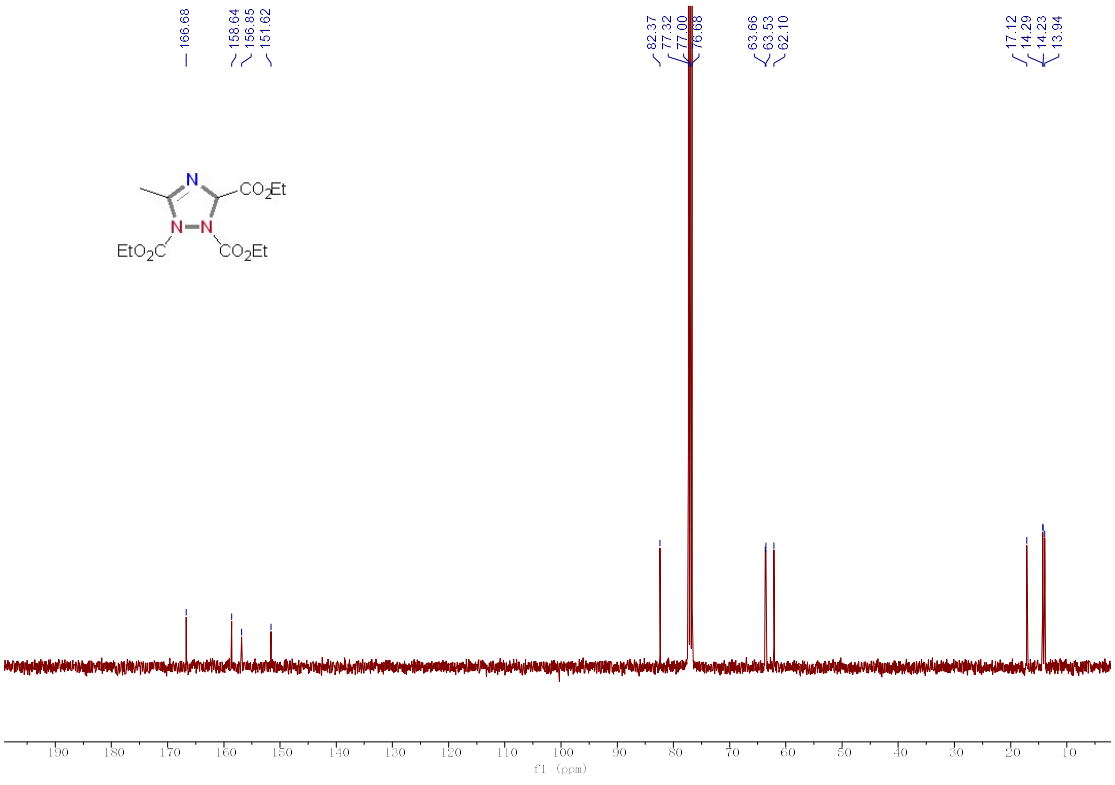


8. Copies of ^{1}H NMR and ^{13}C NMR spectra

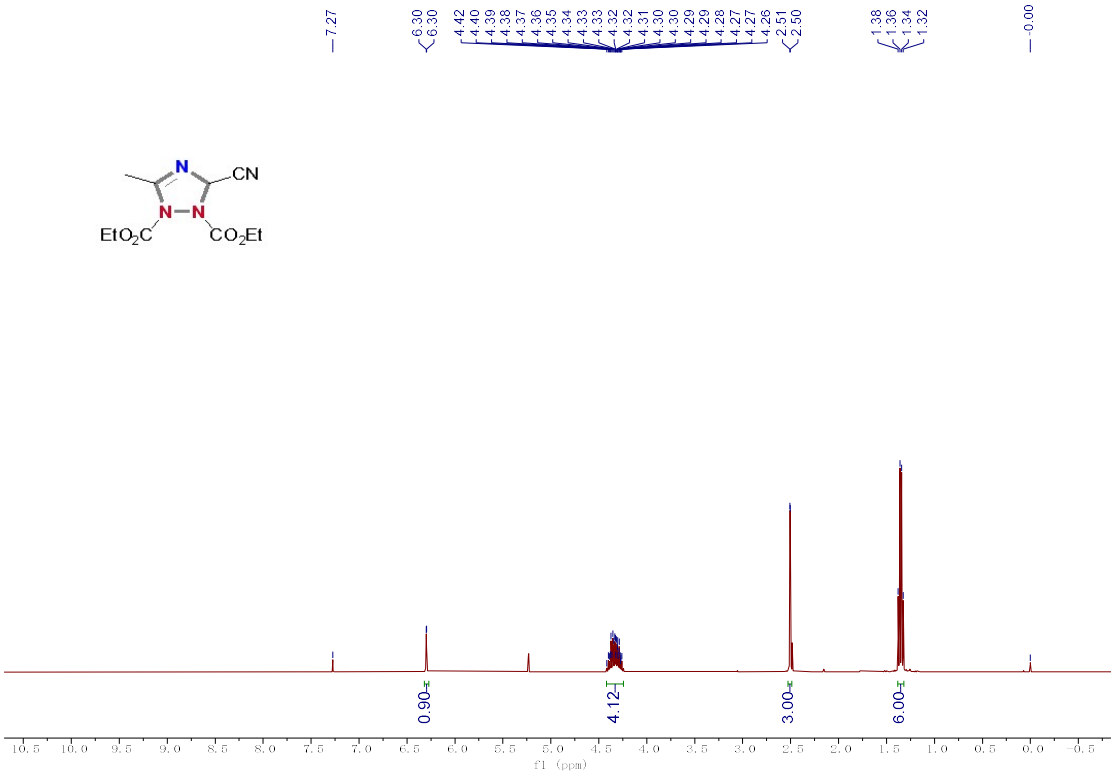
^{1}H NMR (400 MHz) Spectrum of 11a in $CDCl_3$



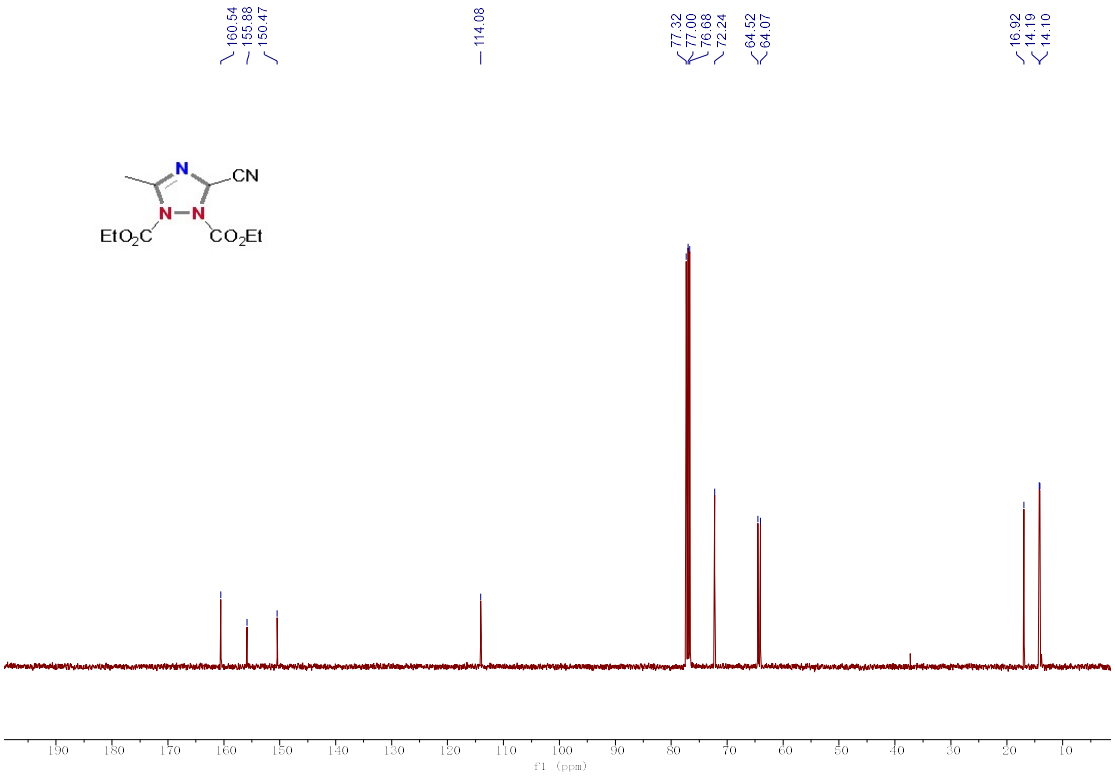
^{13}CNMR (100 MHz) Spectrum of 11a in $CDCl_3$



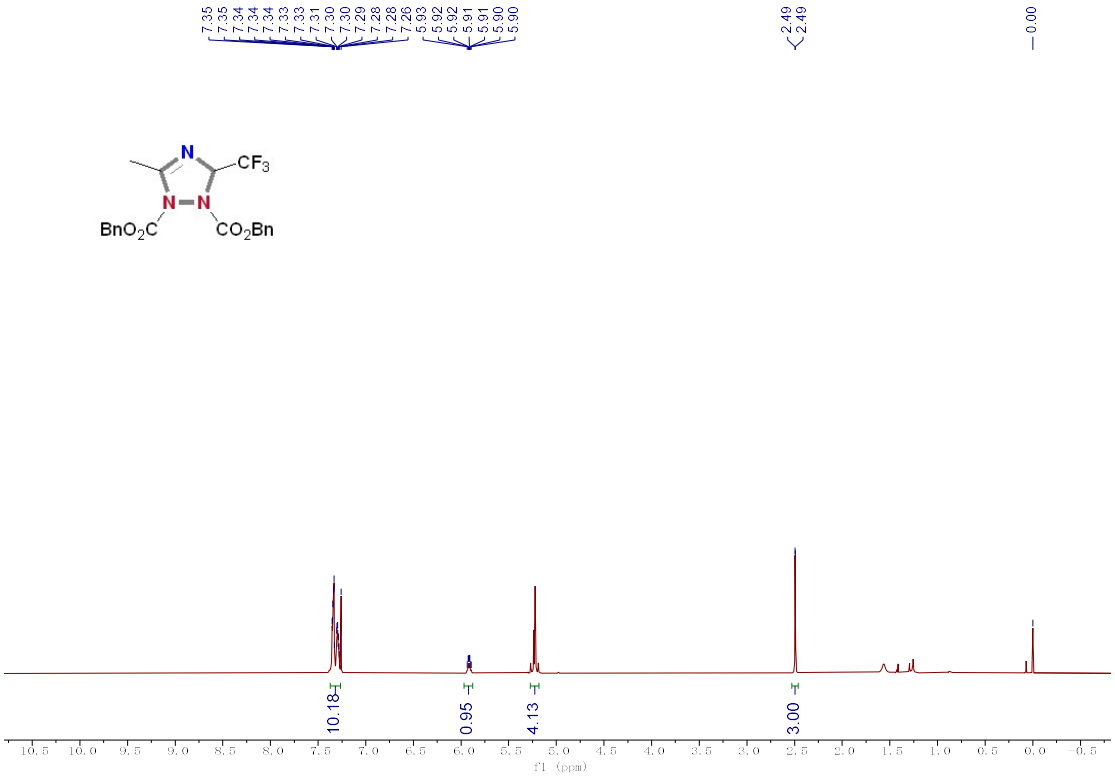
^{1}H NMR (400 MHz) Spectrum of 11b in $CDCl_3$



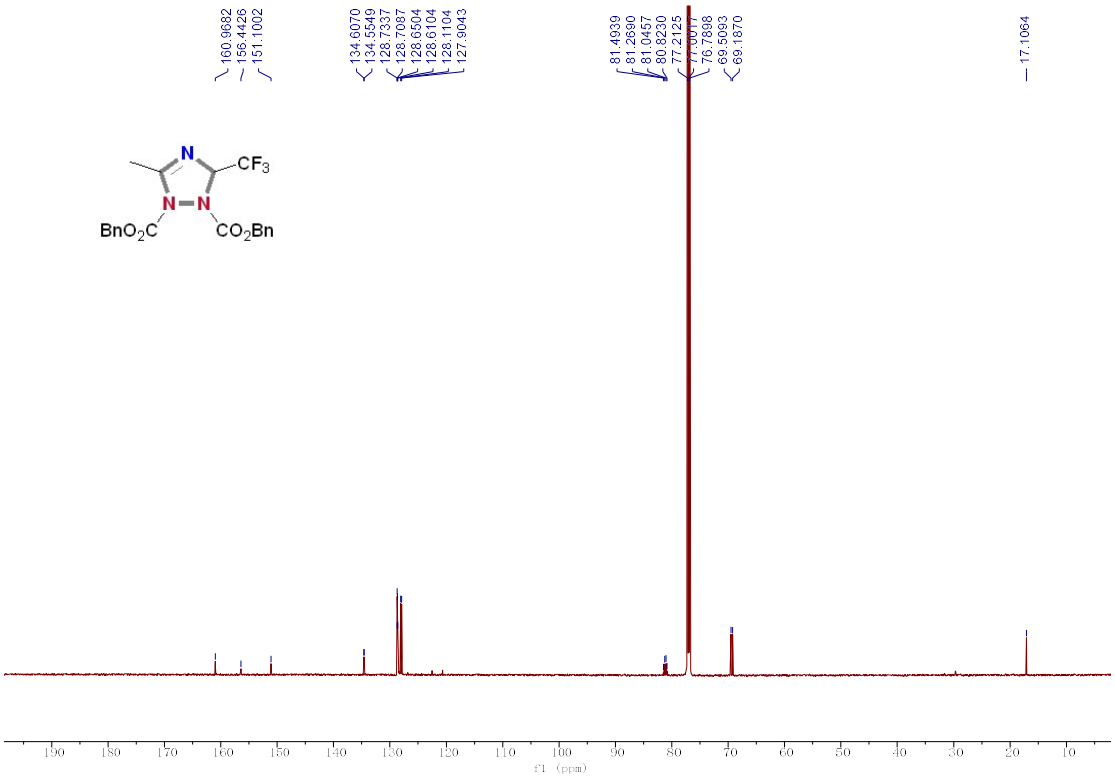
^{13}CNMR (100 MHz) Spectrum of 11b in $CDCl_3$



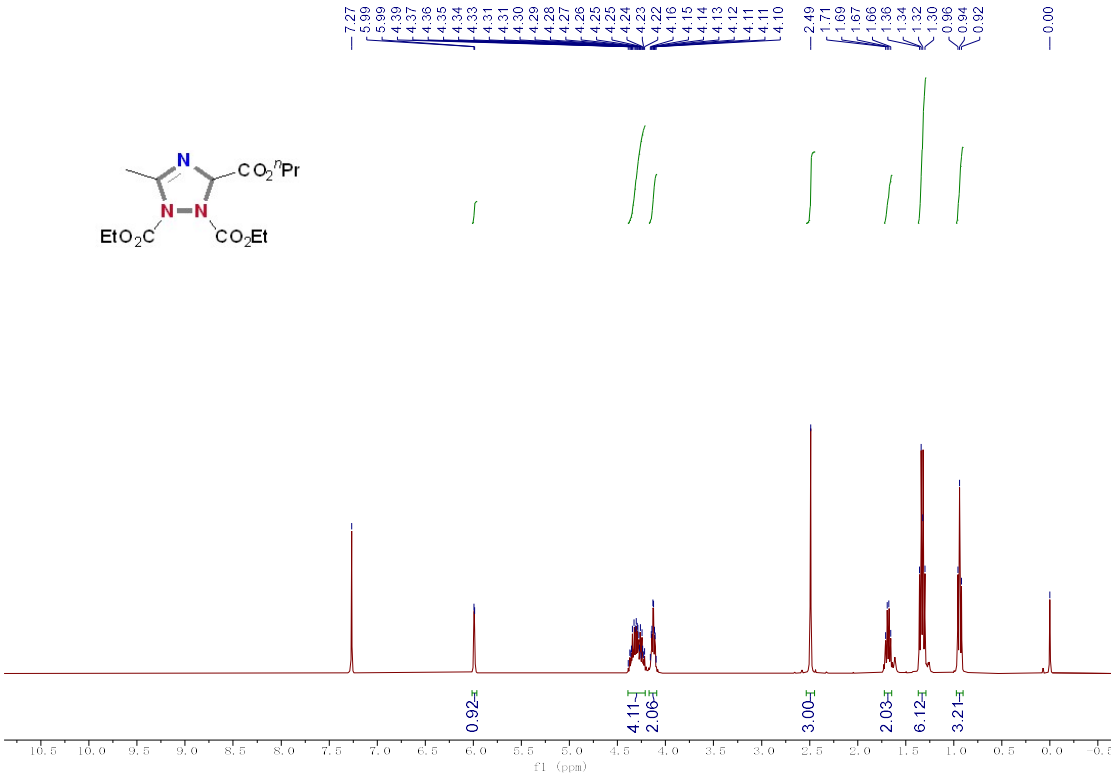
^{1}H NMR (400 MHz) Spectrum of 11c in $CDCl_3$



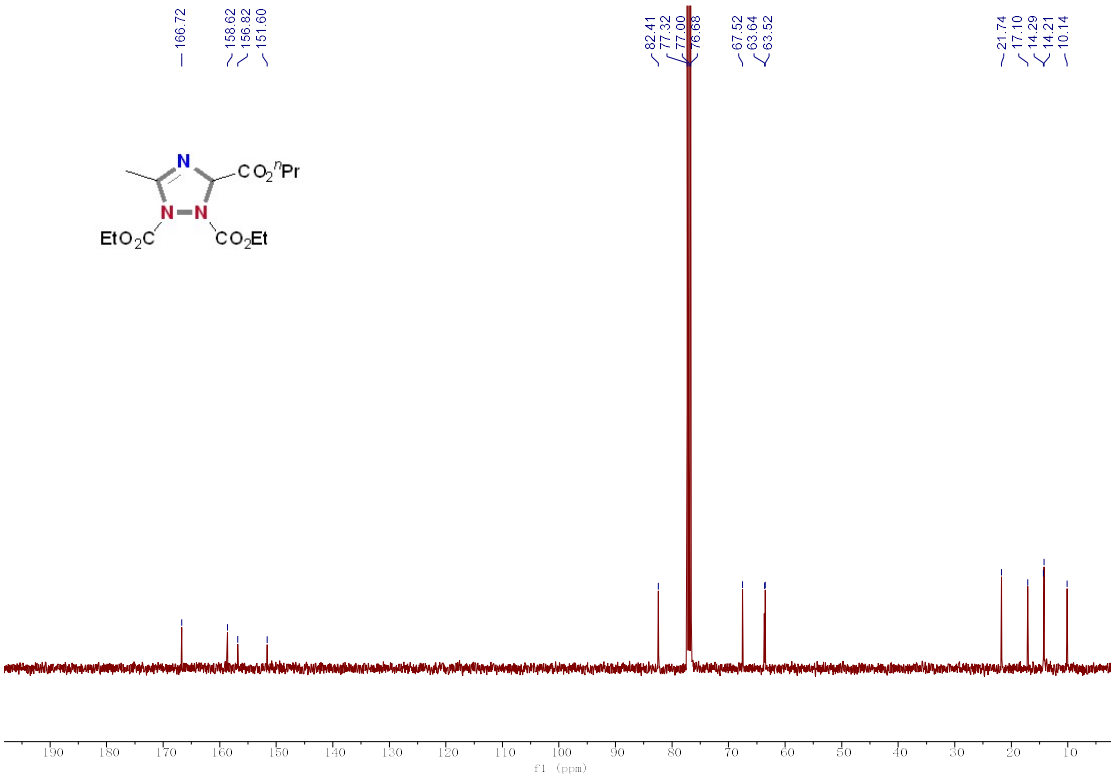
^{13}CNMR (100 MHz) Spectrum of 11c in $CDCl_3$



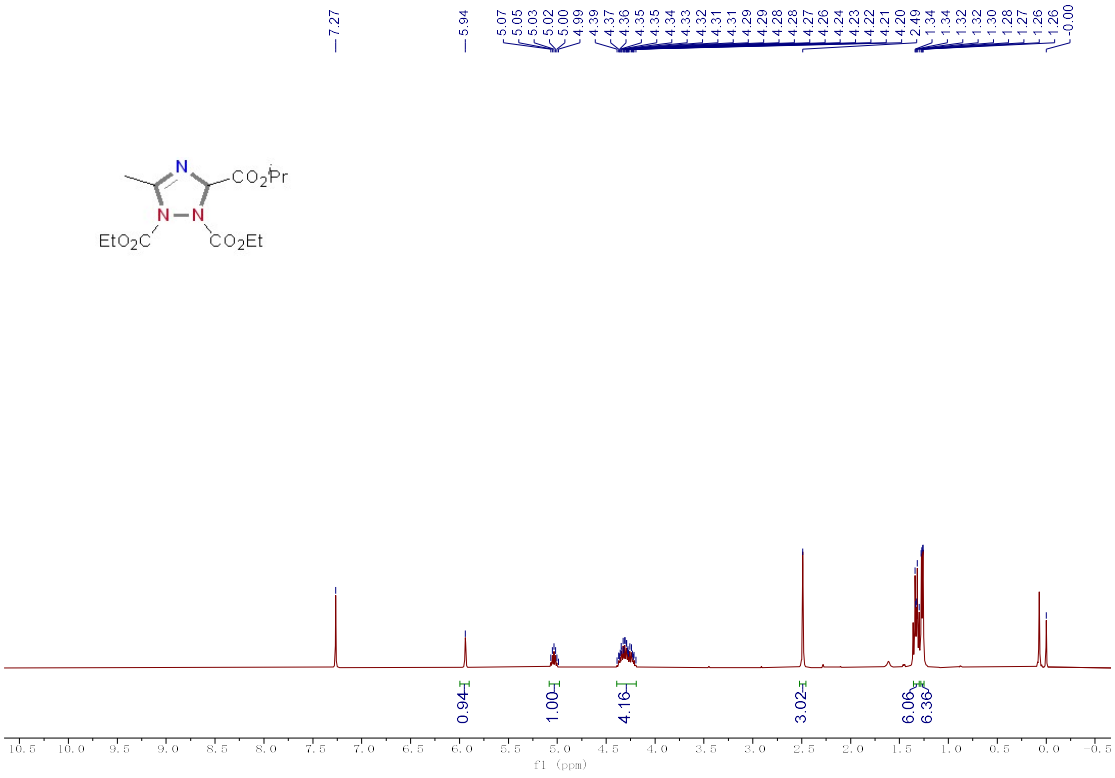
^{1}H NMR (400 MHz) Spectrum of 11d in $CDCl_3$



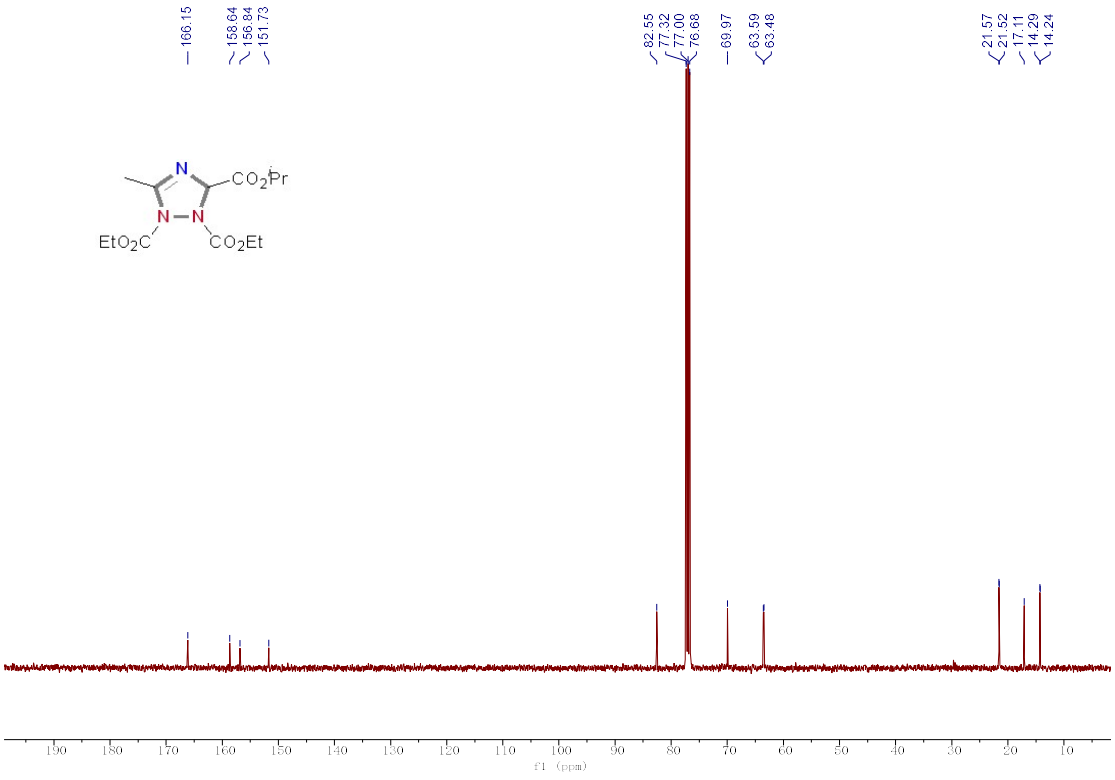
^{13}CNMR (100 MHz) Spectrum of 11d in $CDCl_3$



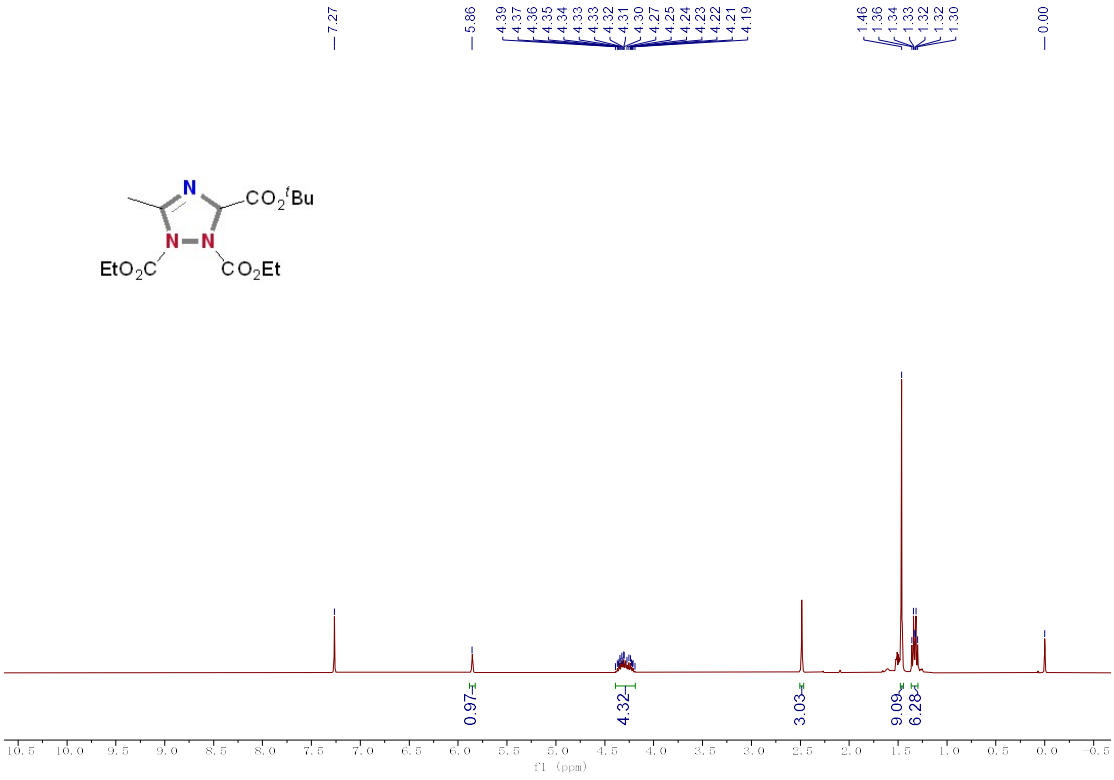
^{1}H NMR (400 MHz) Spectrum of 11e in $CDCl_3$



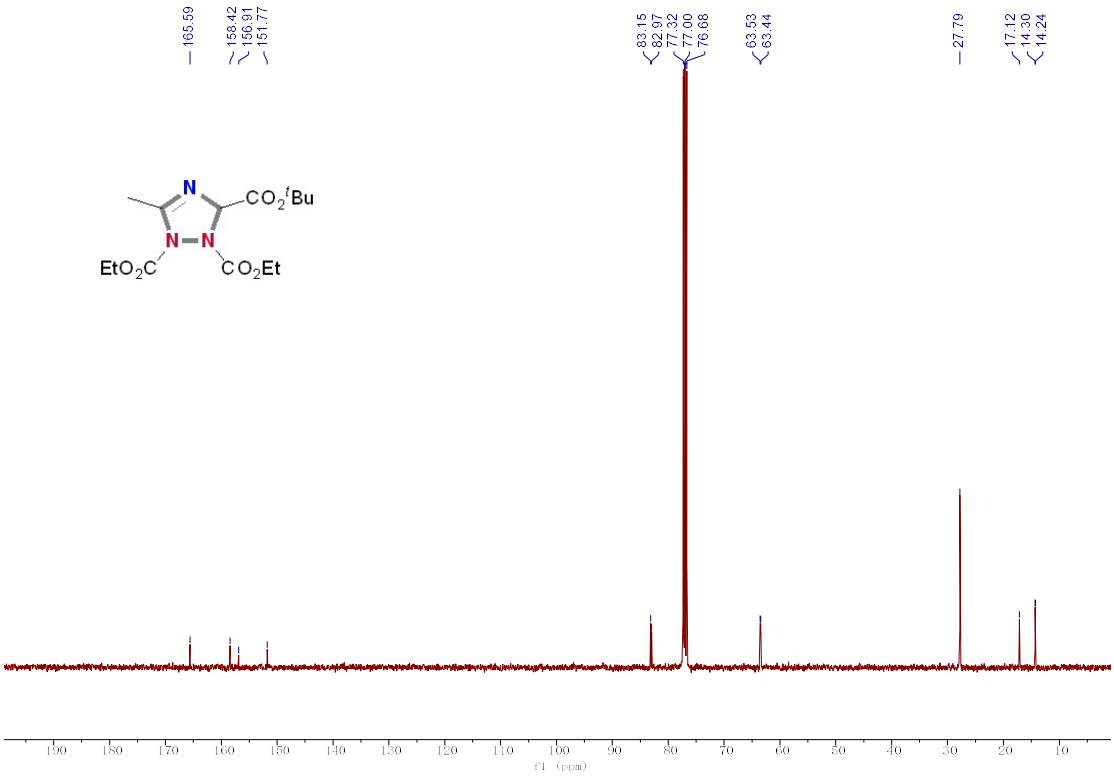
^{13}CNMR (100 MHz) Spectrum of 11e in $CDCl_3$



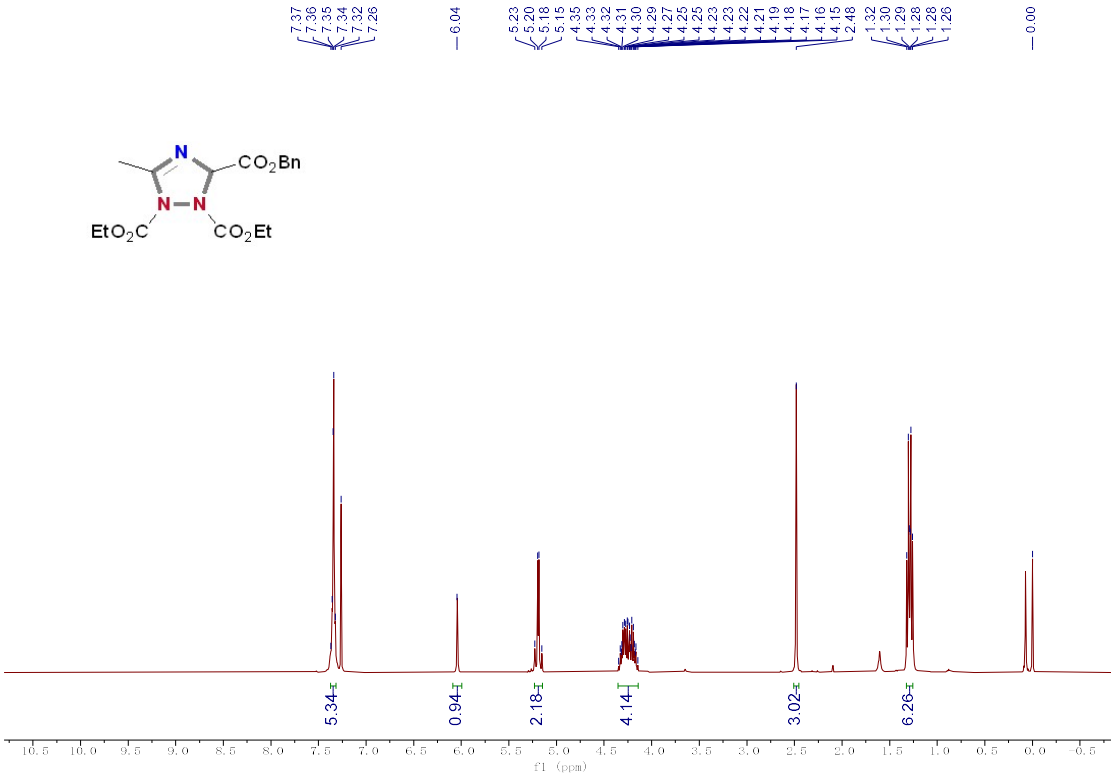
^{1}H NMR (400 MHz) Spectrum of 11f in $CDCl_3$



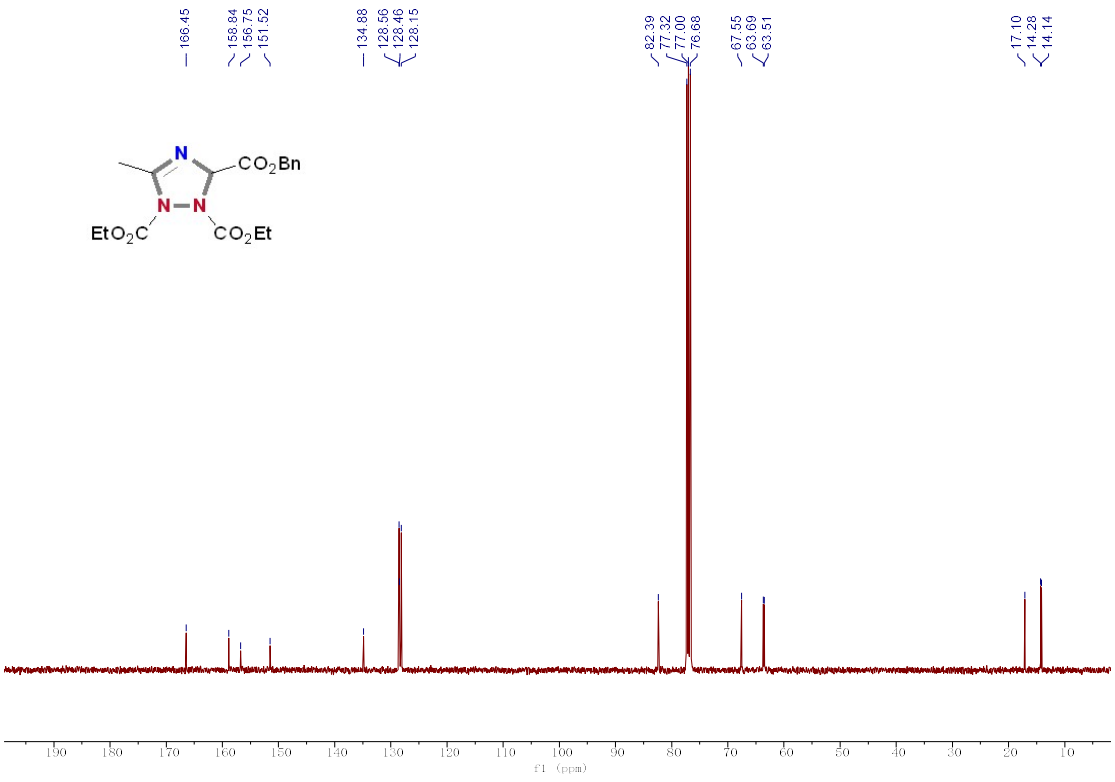
^{13}CNMR (100 MHz) Spectrum of 11f in $CDCl_3$



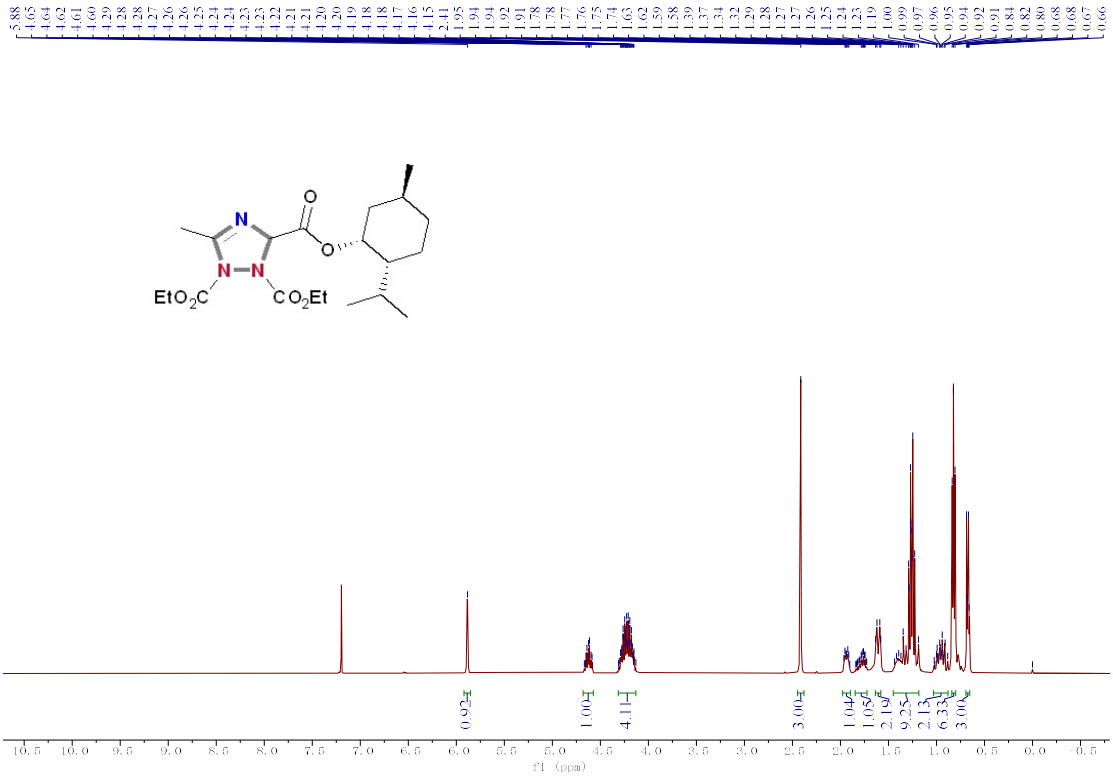
^{1}H NMR (400 MHz) Spectrum of 11g in $CDCl_3$



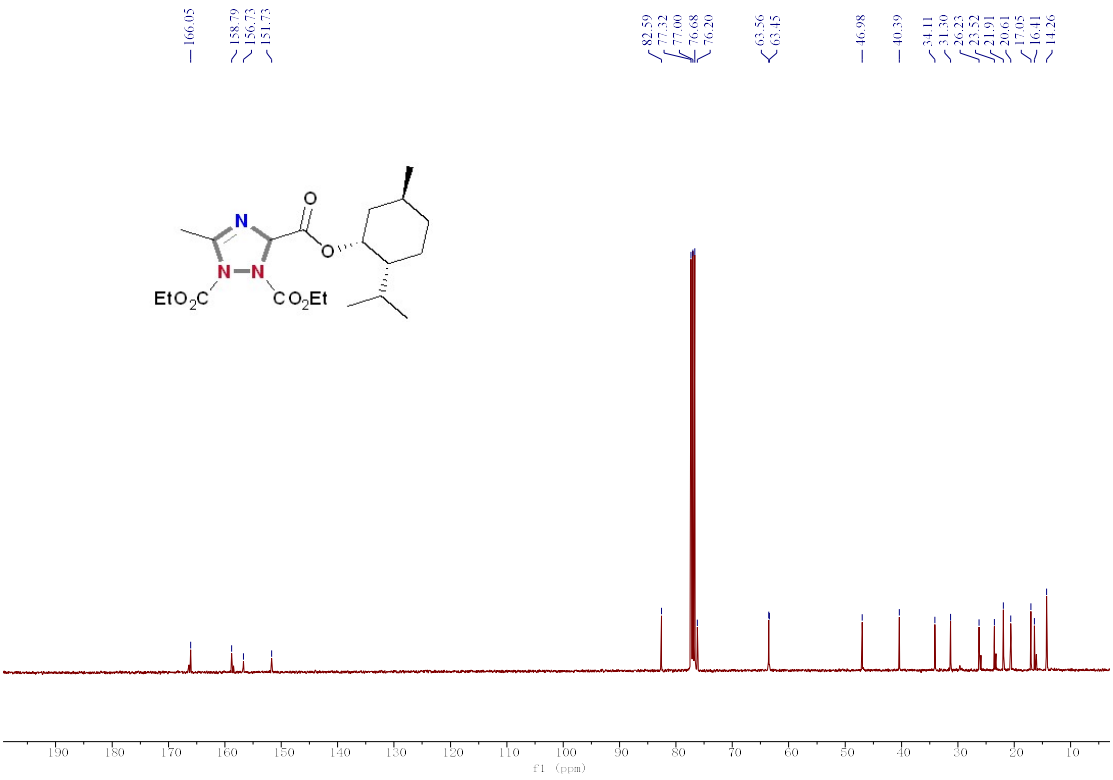
^{13}CNMR (100 MHz) Spectrum of 11g in $CDCl_3$



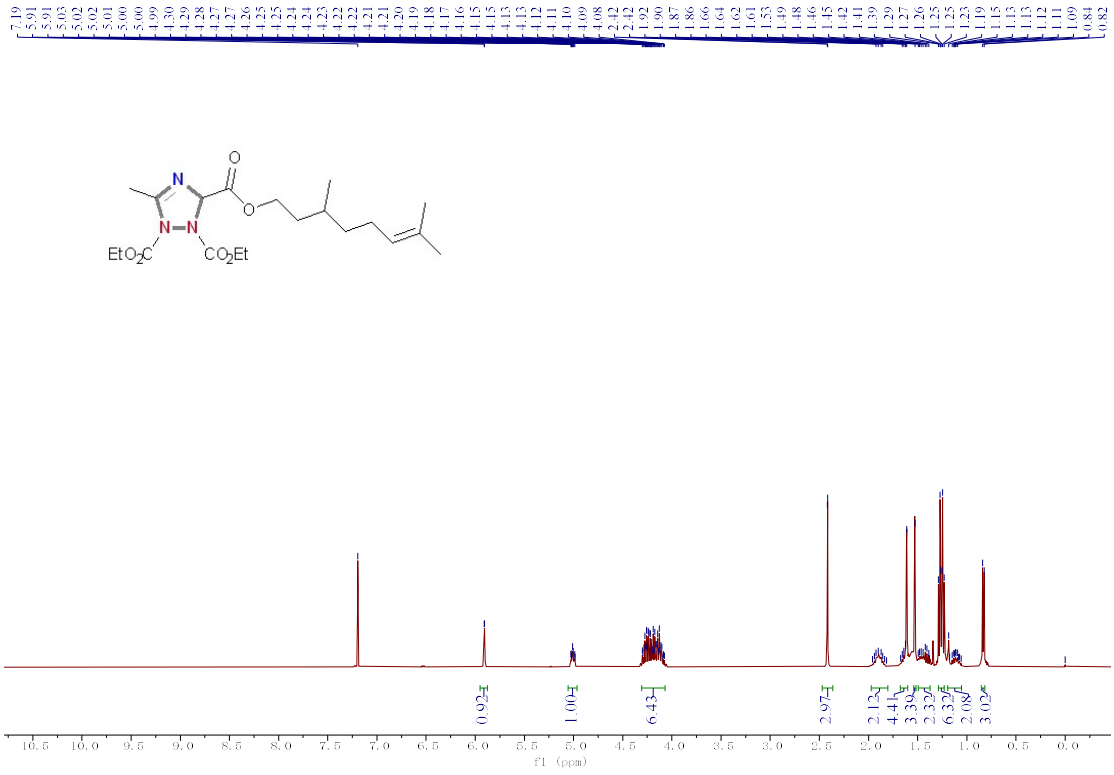
^{1}H NMR (400 MHz) Spectrum of 11h in $CDCl_3$



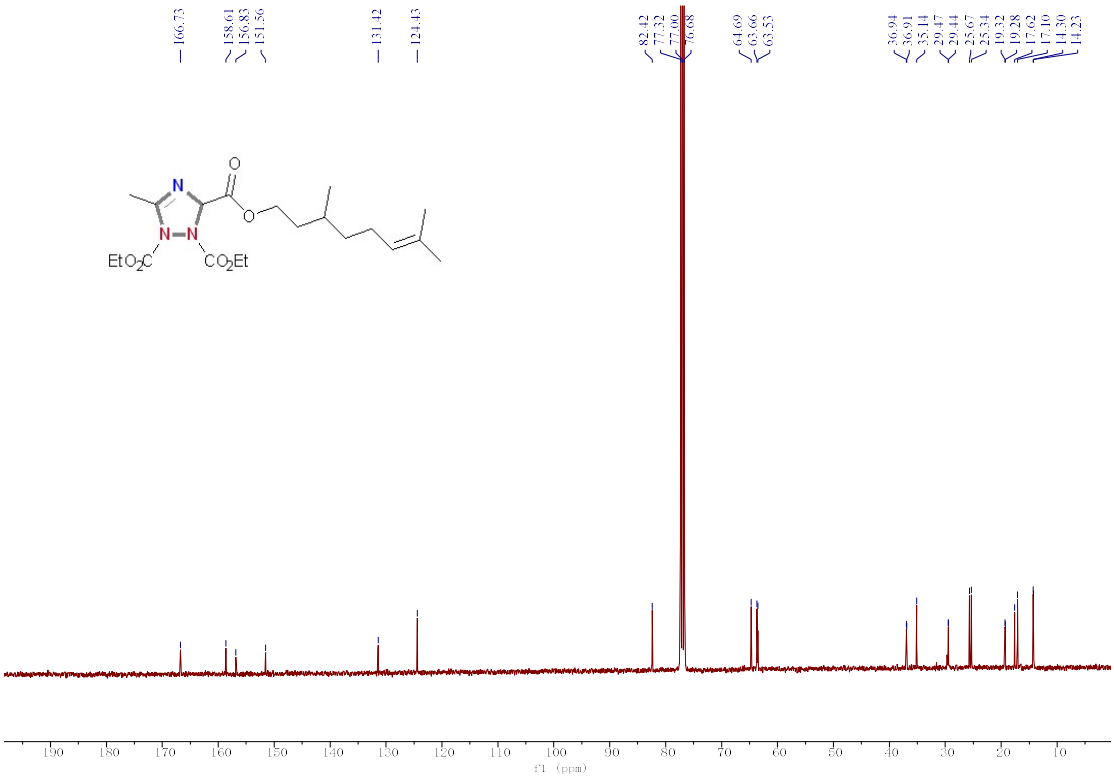
^{13}CNMR (100 MHz) Spectrum of 11h in $CDCl_3$



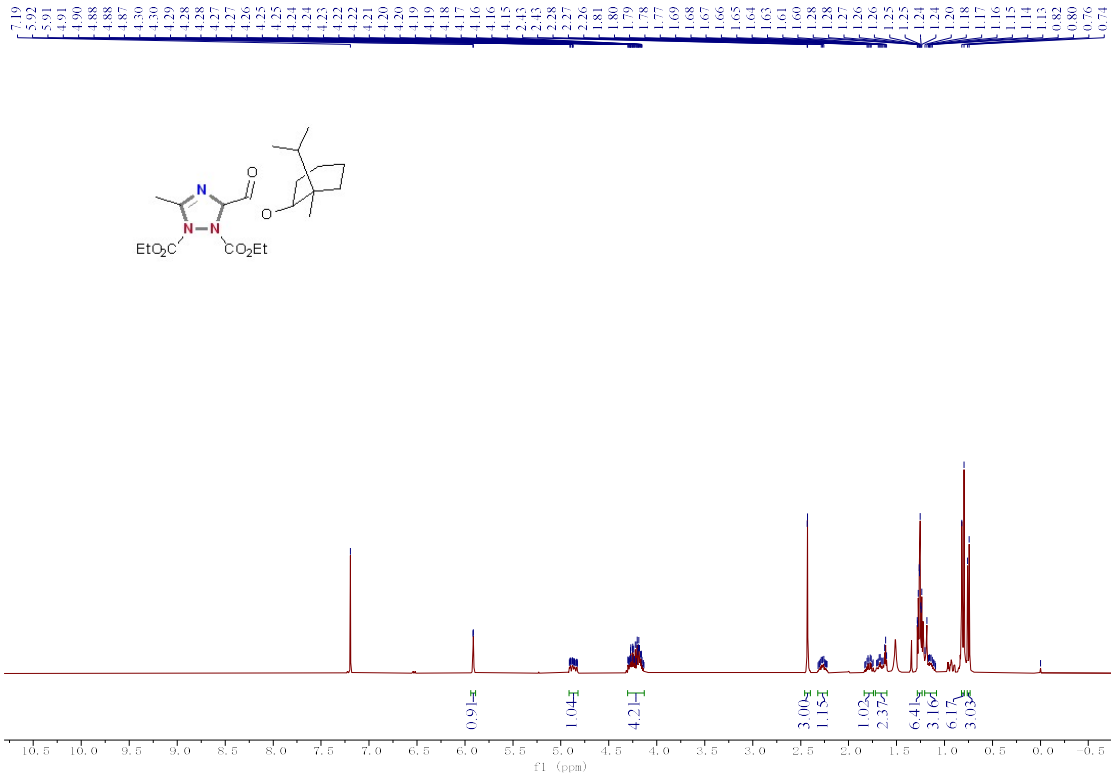
^{1}H NMR (400 MHz) Spectrum of 11i in $CDCl_3$



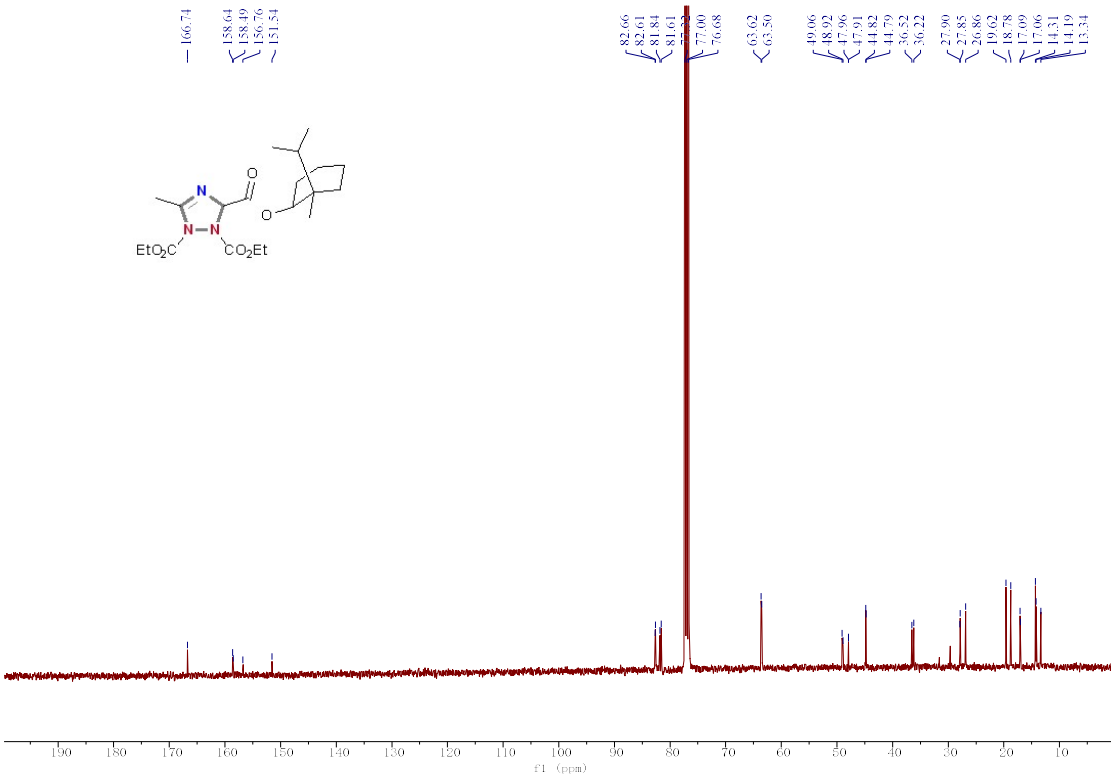
^{13}CNMR (100 MHz) Spectrum of 11i in $CDCl_3$



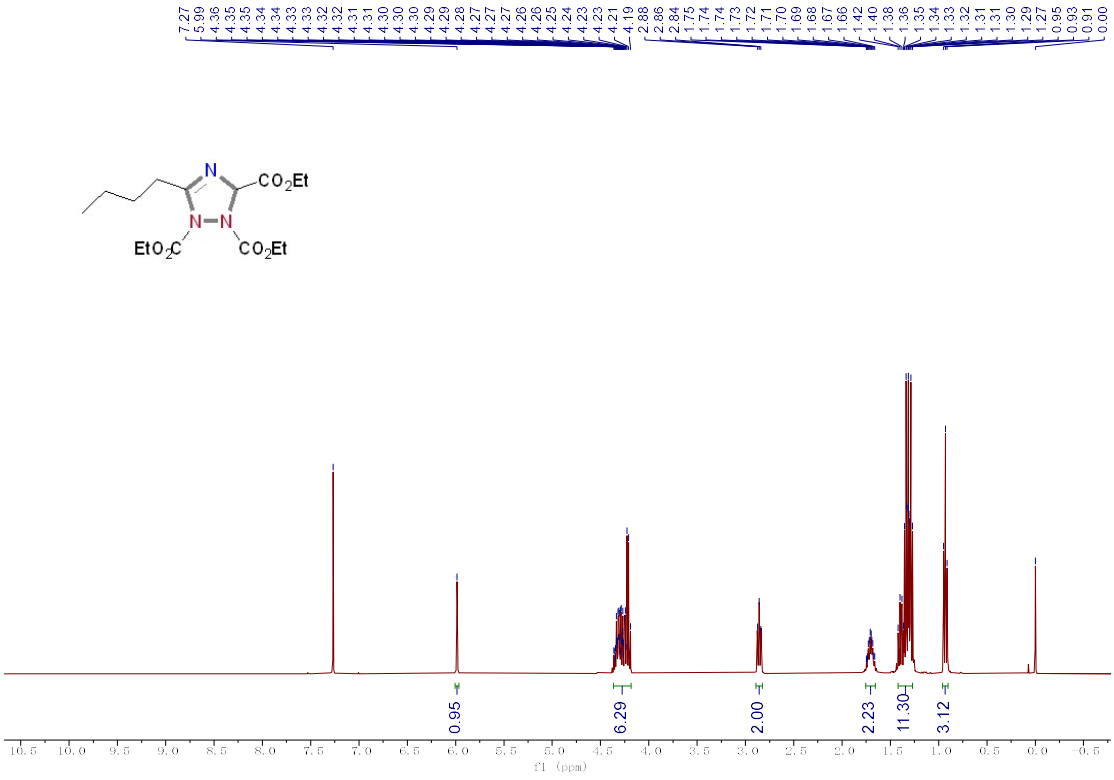
^{1}H NMR (400 MHz) Spectrum of 11j in $CDCl_3$



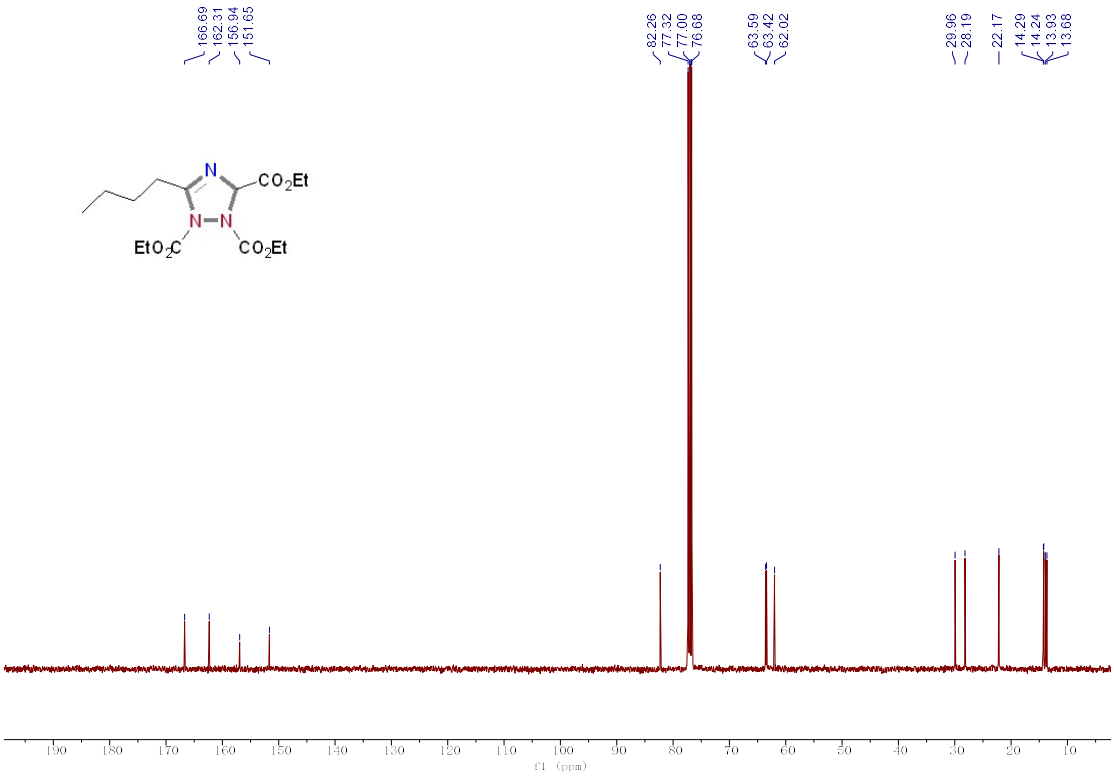
^{13}CNMR (100 MHz) Spectrum of 11j in $CDCl_3$



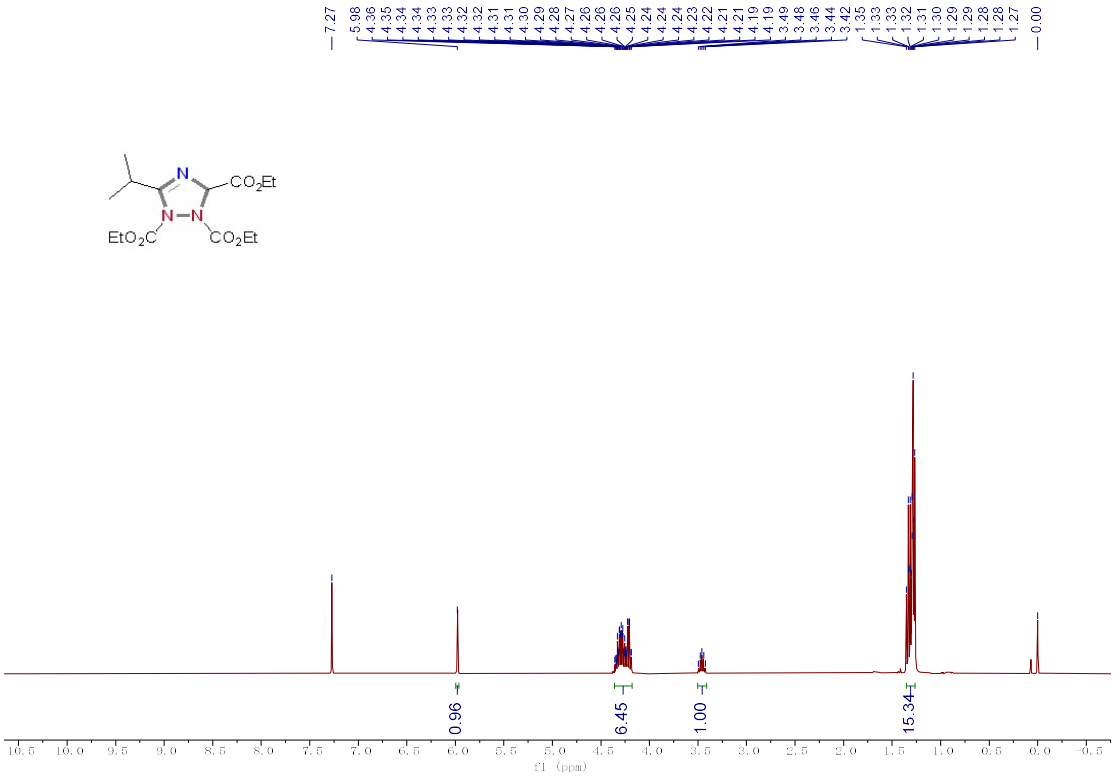
^{1}H NMR (400 MHz) Spectrum of 11k in $CDCl_3$



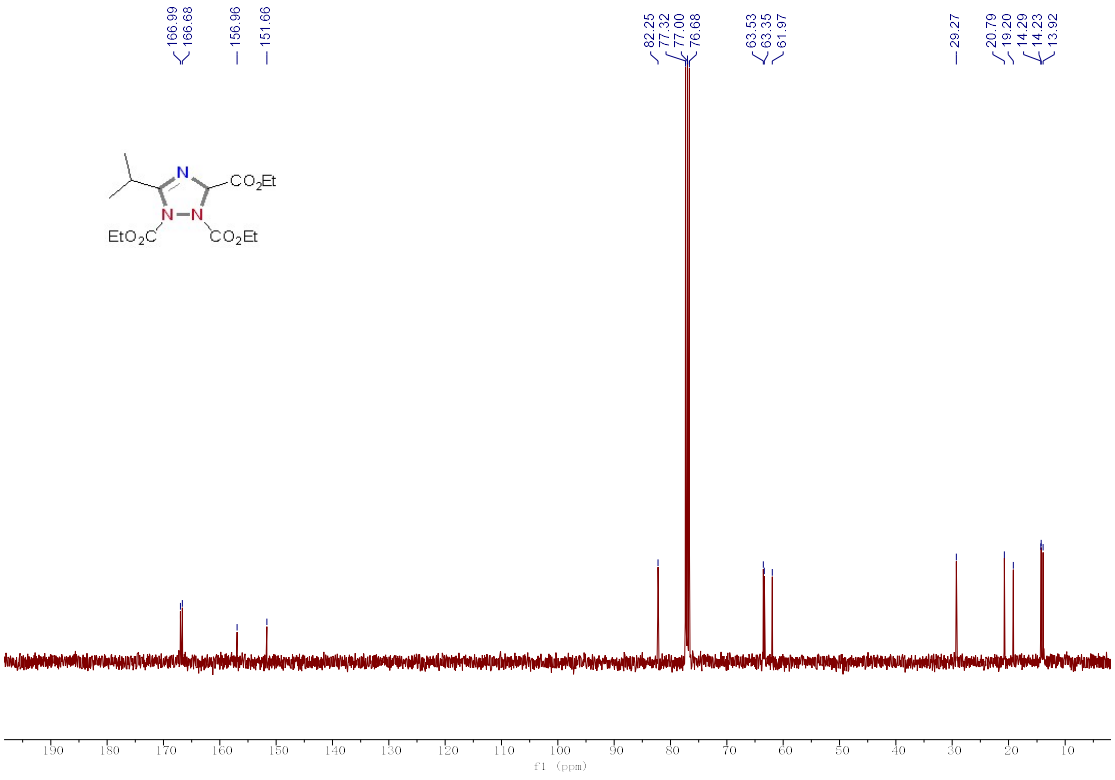
^{13}CNMR (100 MHz) Spectrum of 11k in $CDCl_3$



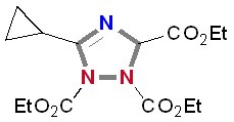
^{1}H NMR (400 MHz) Spectrum of 11l in $CDCl_3$

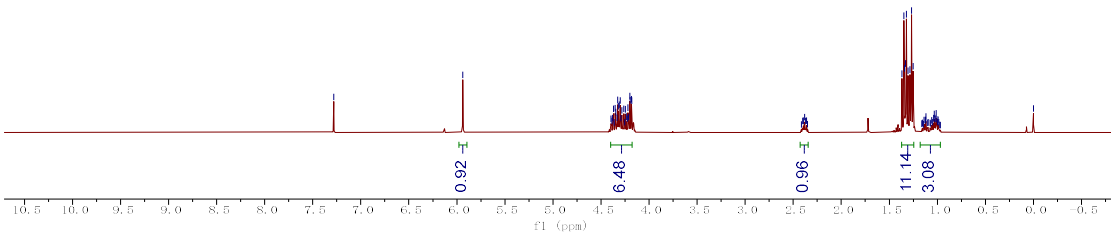


^{13}CNMR (100 MHz) Spectrum of 11l in $CDCl_3$

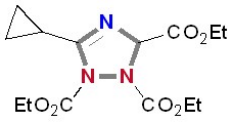


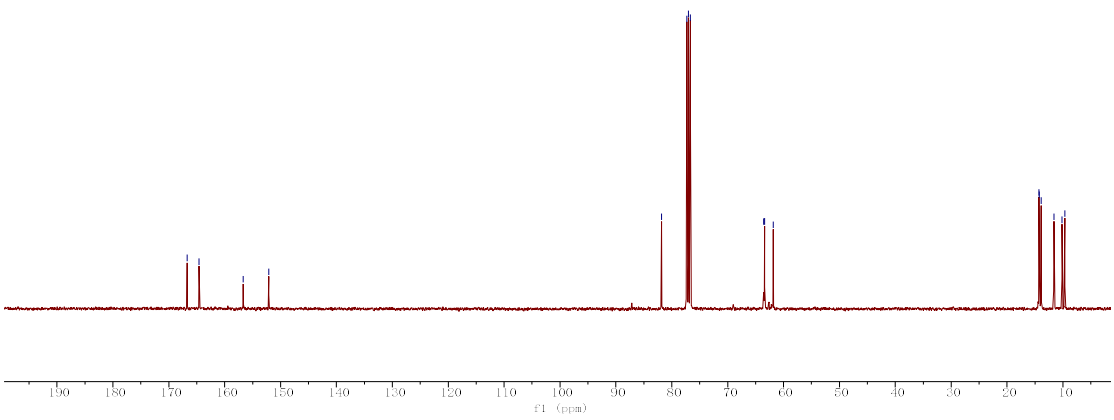
^{1}H NMR (400 MHz) Spectrum of 11m in $CDCl_3$



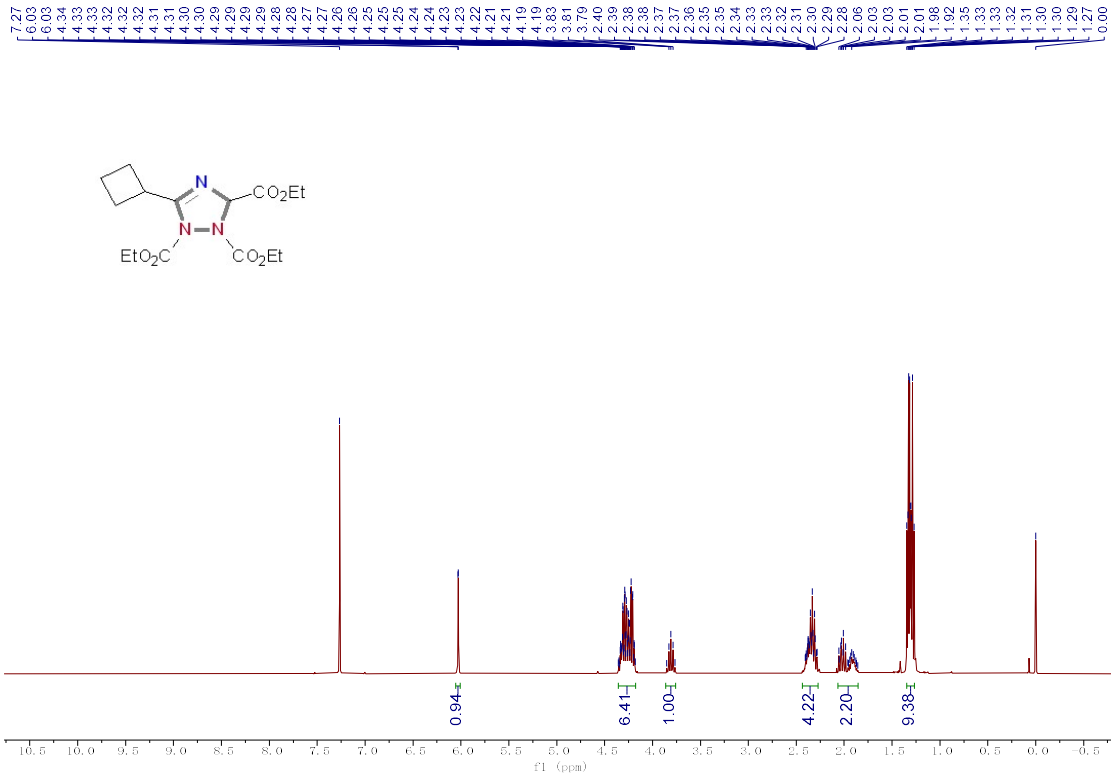


^{13}CNMR (100 MHz) Spectrum of 11m in $CDCl_3$

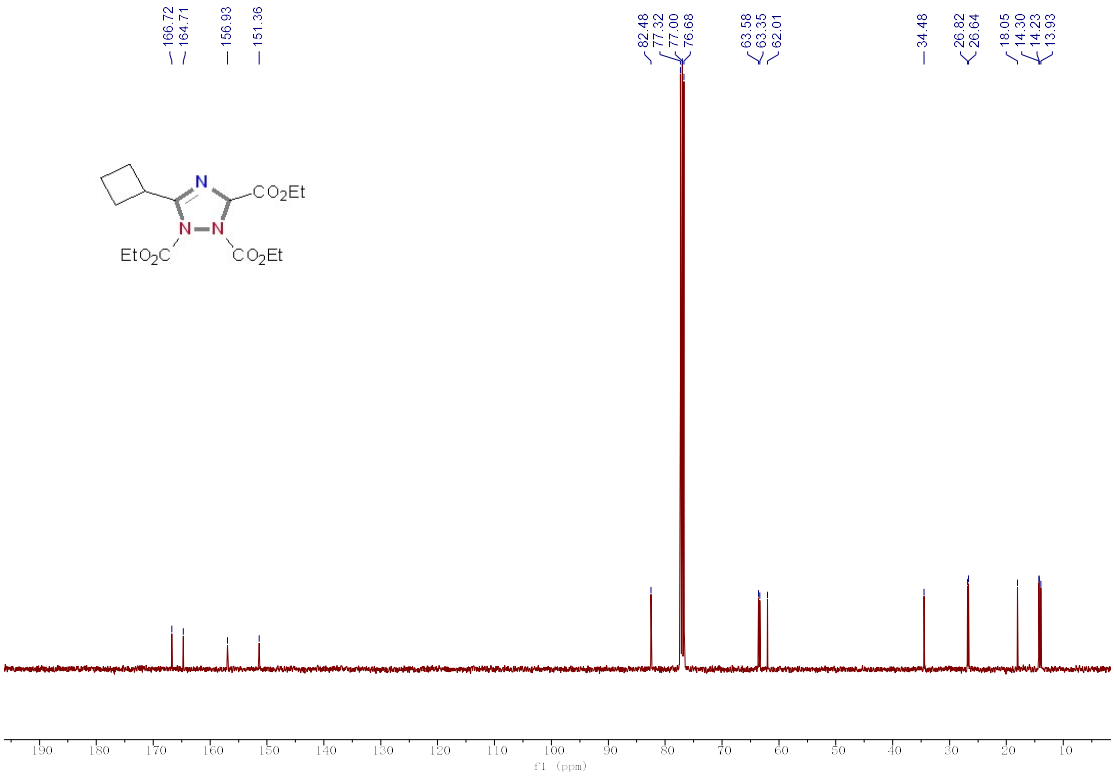




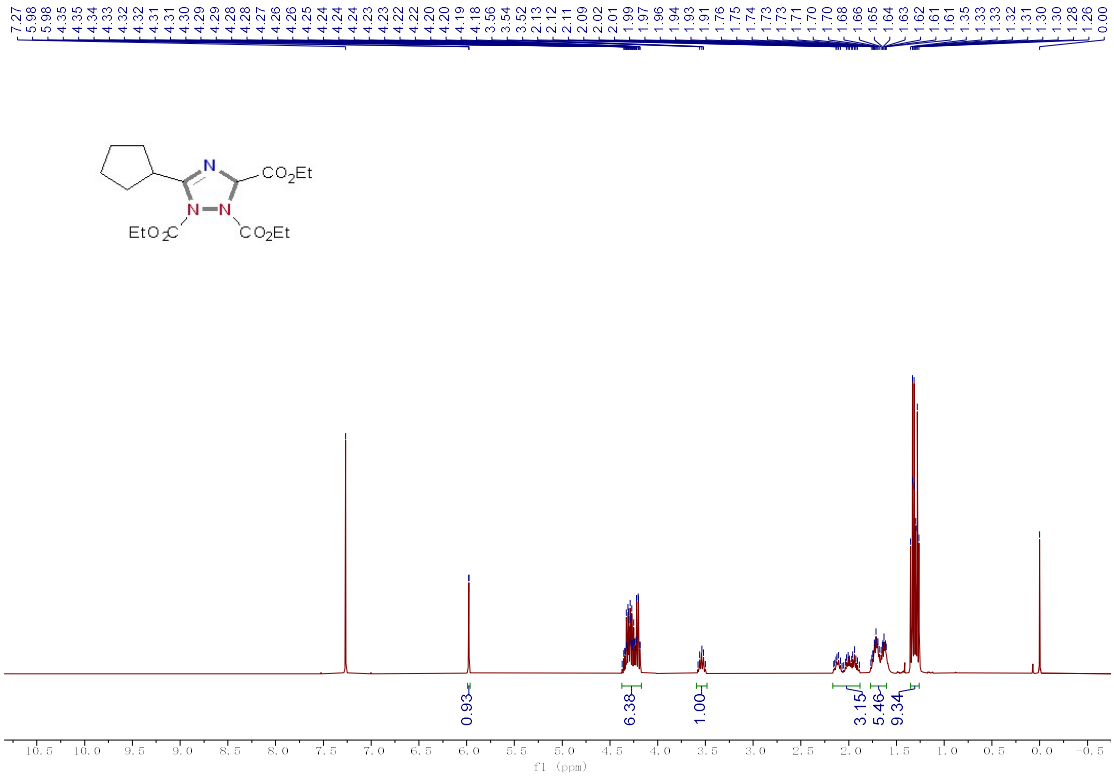
^{1}H NMR (400 MHz) Spectrum of 11n in $CDCl_3$



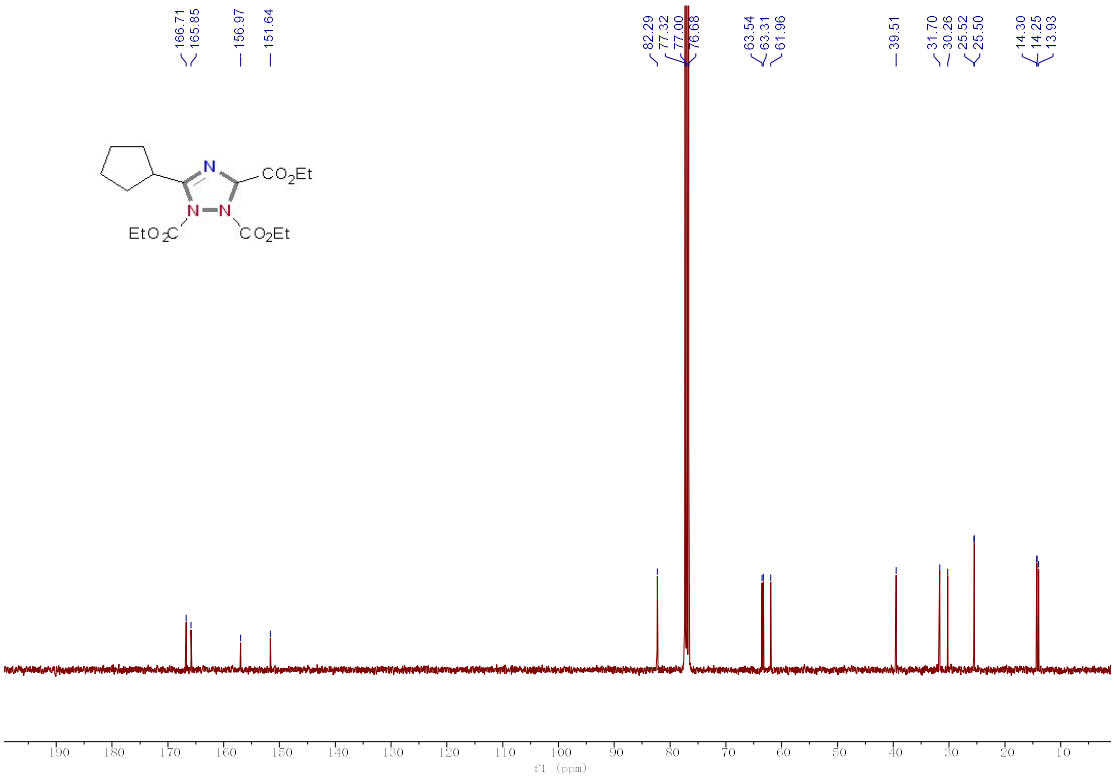
^{13}CNMR (100 MHz) Spectrum of 11n in $CDCl_3$



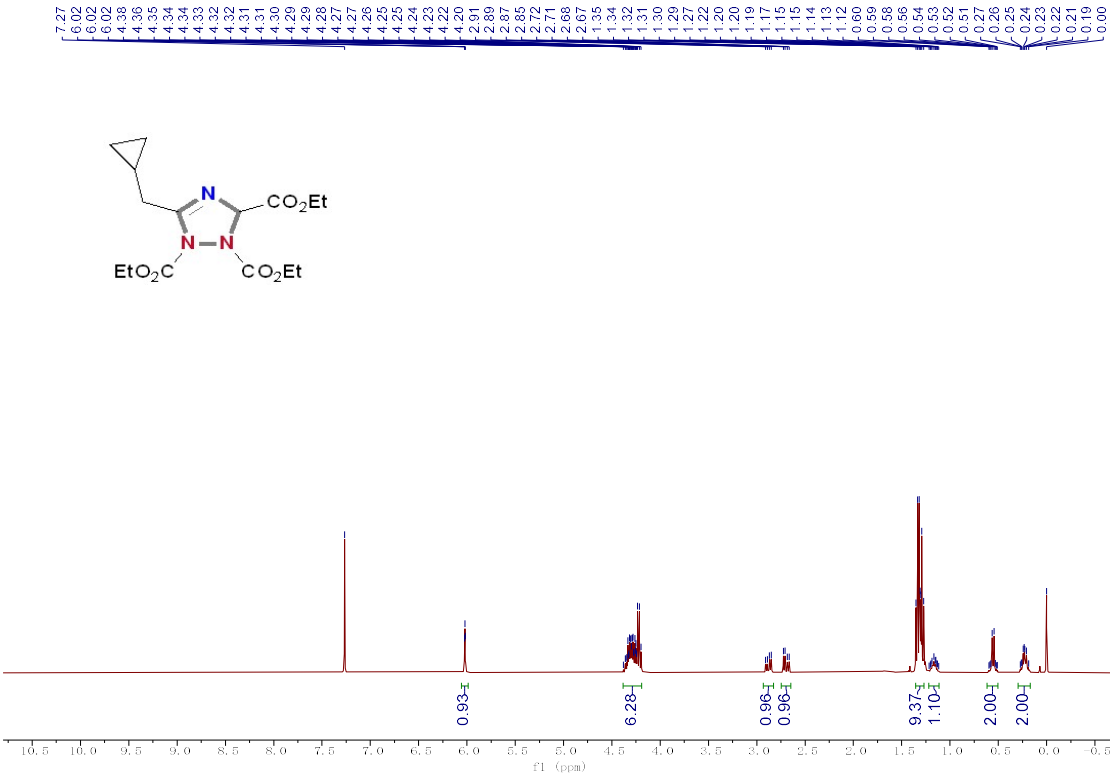
^{1}H NMR (400 MHz) Spectrum of 11o in $CDCl_3$



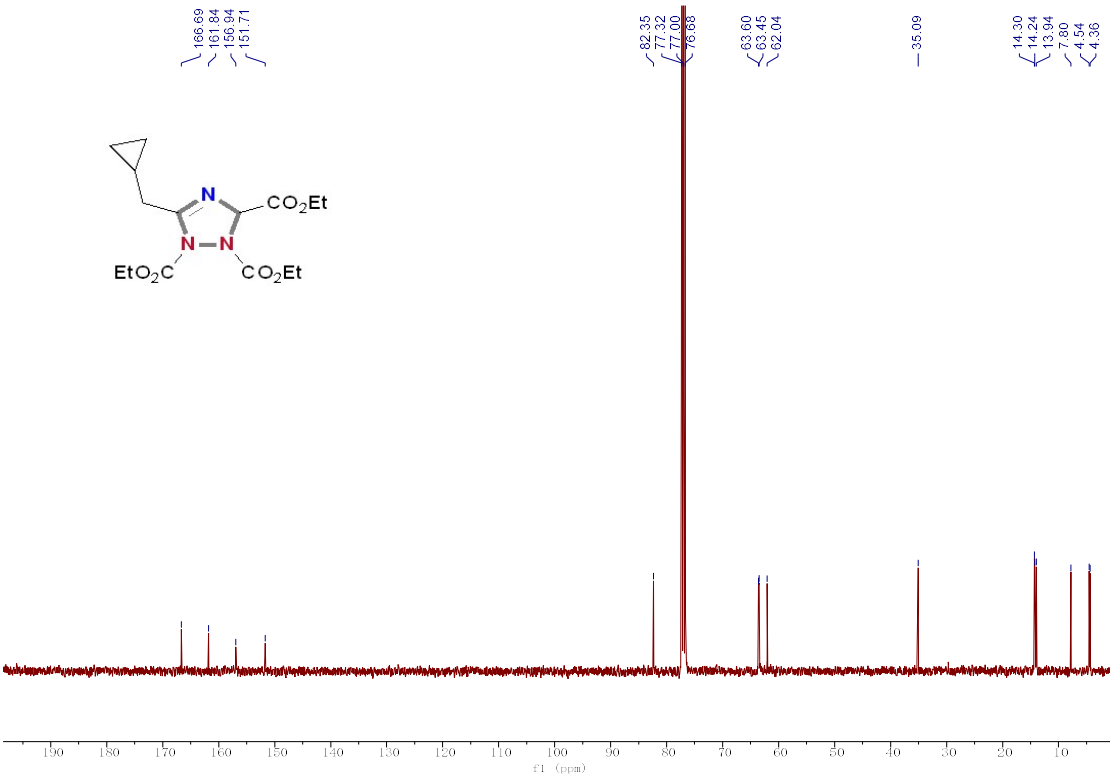
^{13}CNMR (100 MHz) Spectrum of 11o in $CDCl_3$



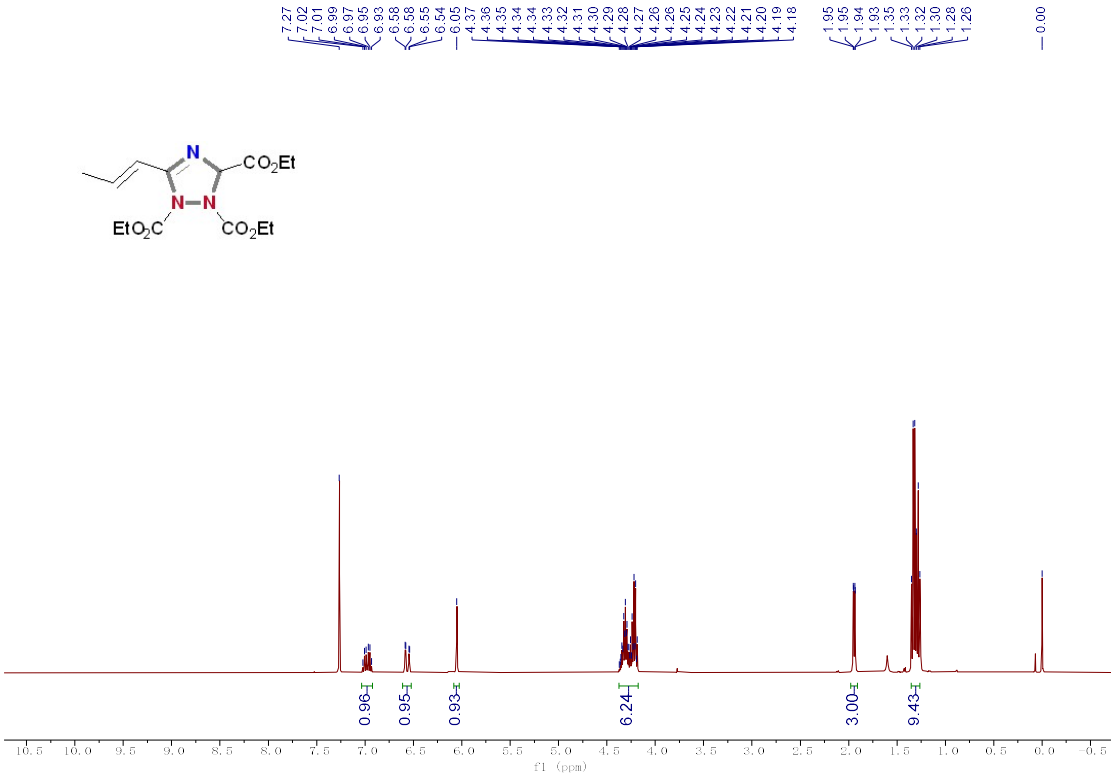
^{1}H NMR (400 MHz) Spectrum of 11p in $CDCl_3$



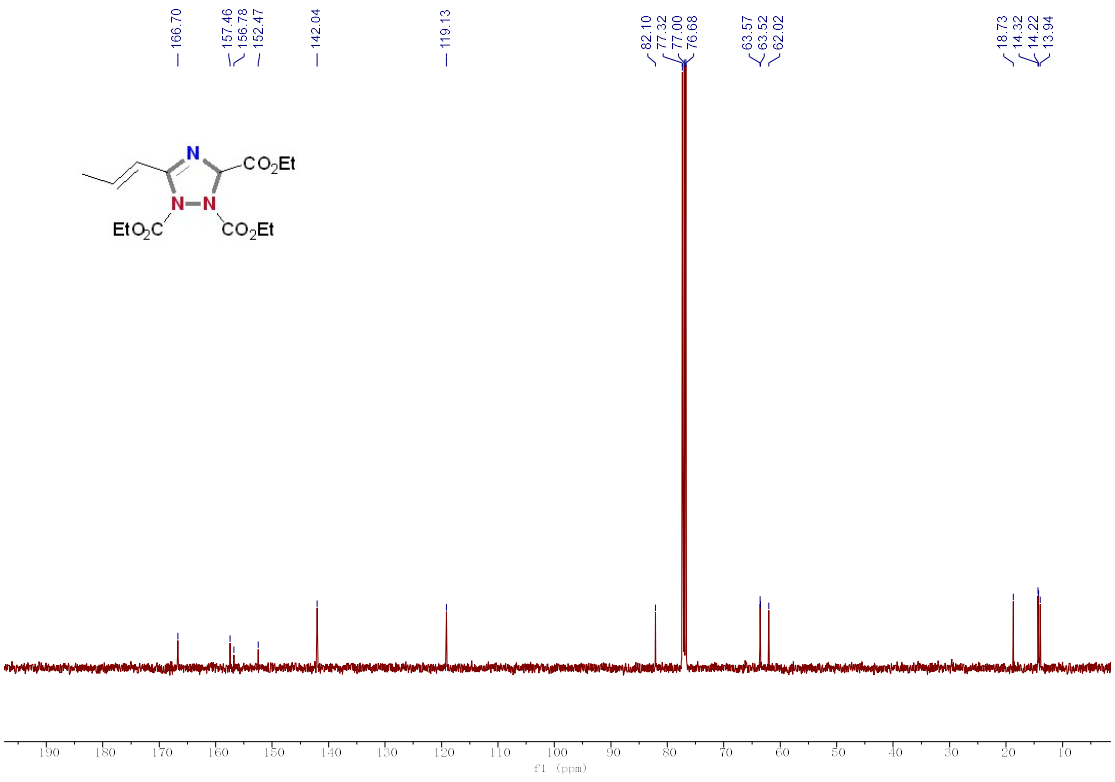
^{13}CNMR (100 MHz) Spectrum of 11p in $CDCl_3$



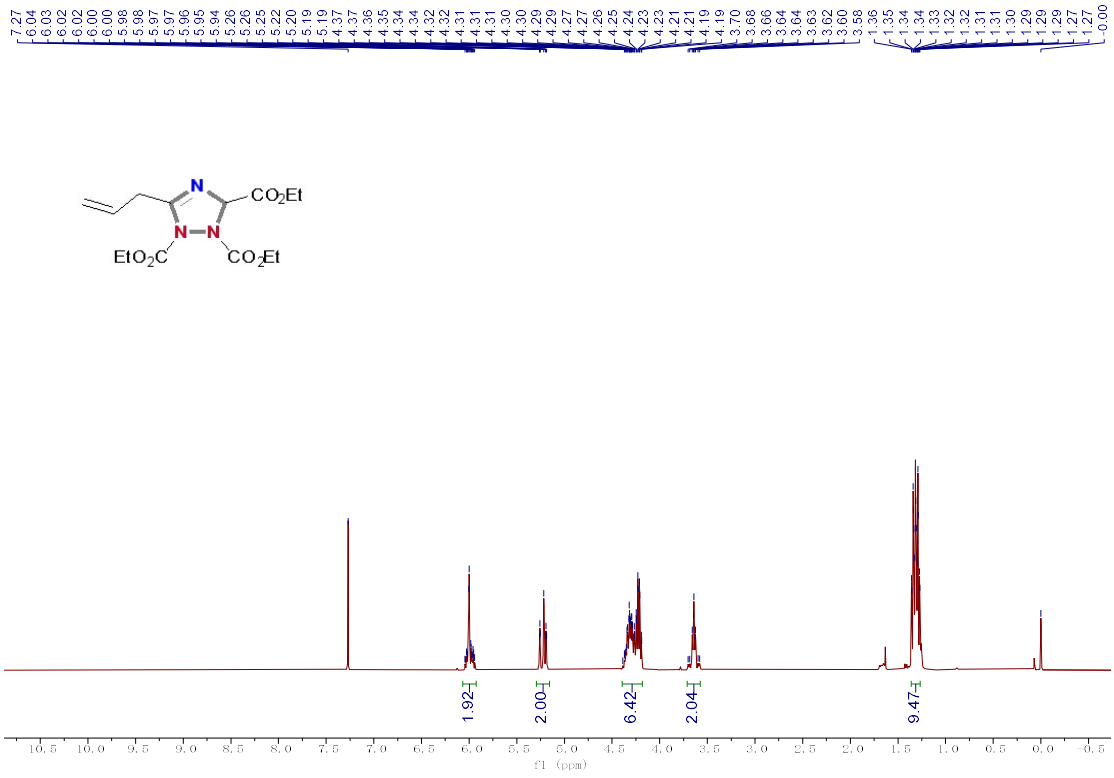
^{1}H NMR (400 MHz) Spectrum of 11q in $CDCl_3$



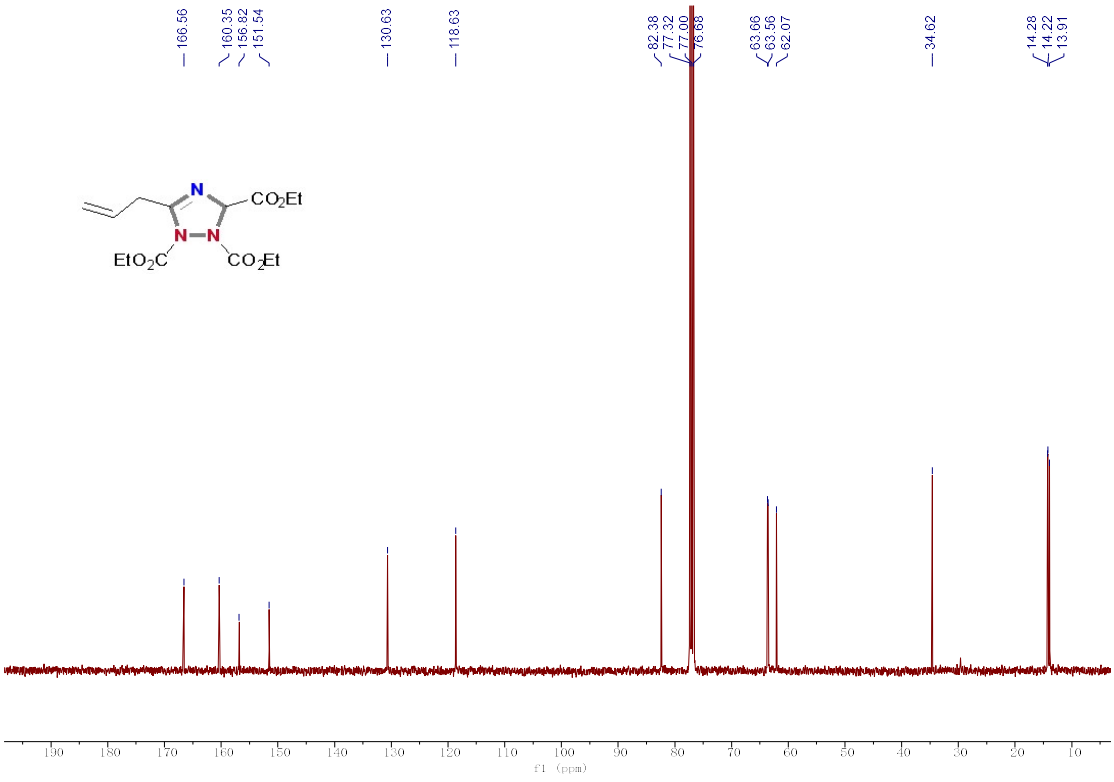
^{13}CNMR (100 MHz) Spectrum of 11q in $CDCl_3$



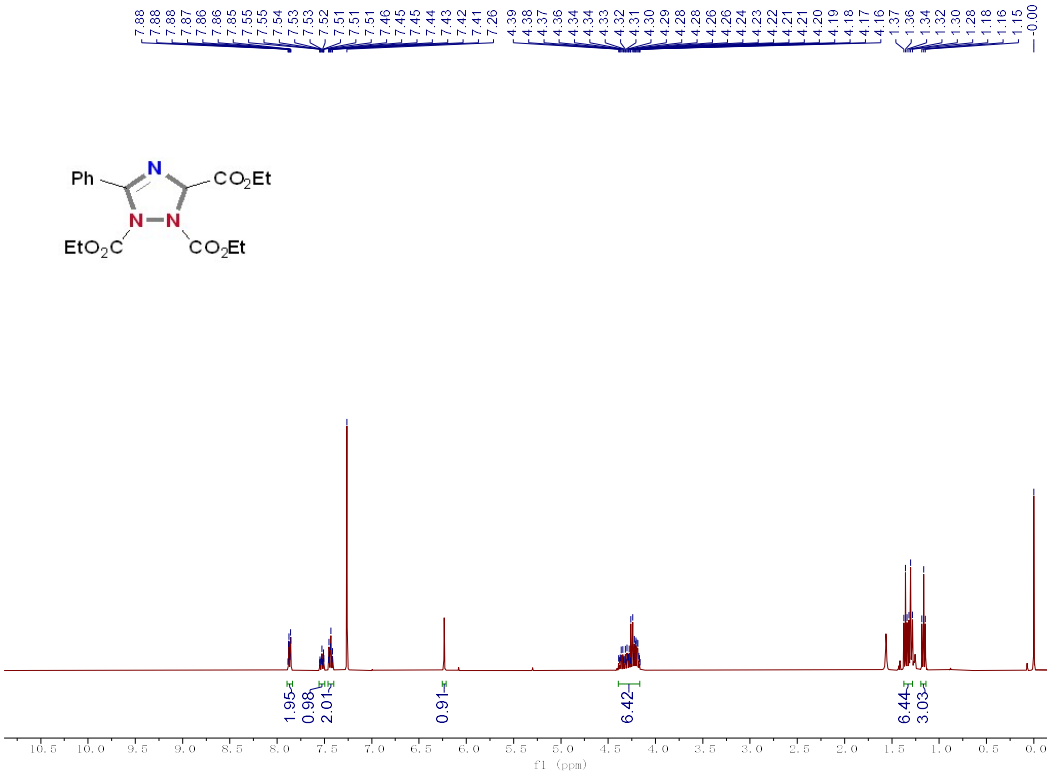
^{1}H NMR (400 MHz) Spectrum of 11r in $CDCl_3$



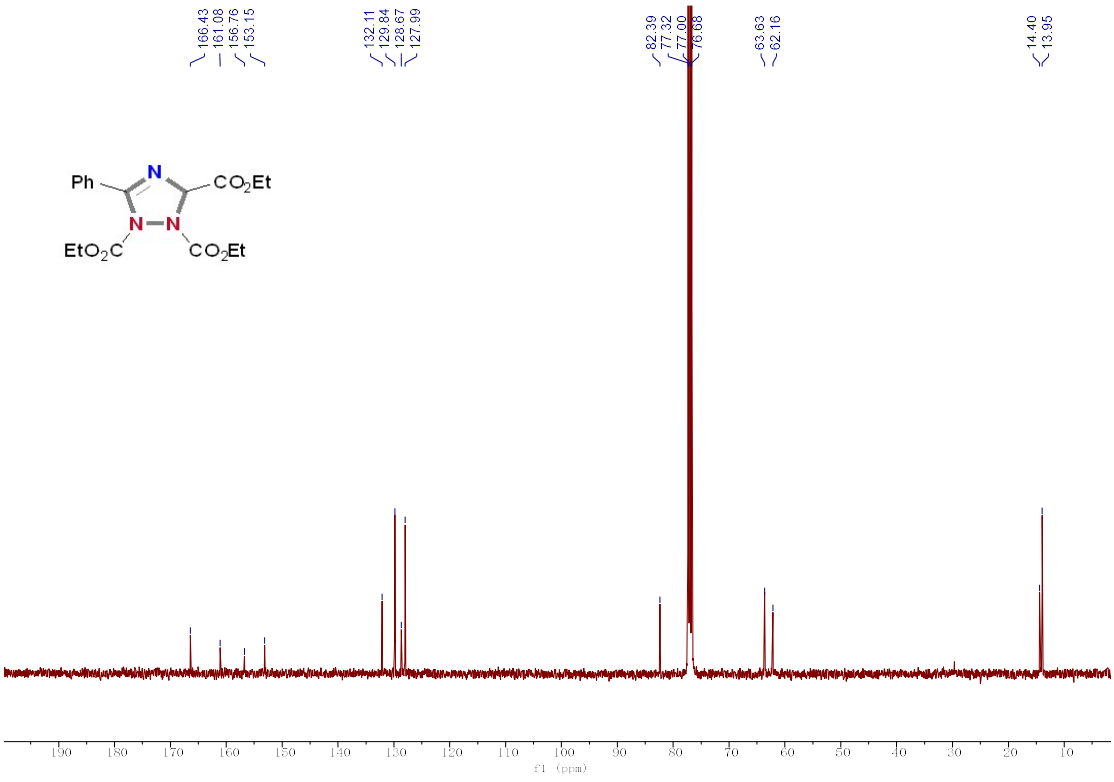
^{13}CNMR (100 MHz) Spectrum of 11r in $CDCl_3$



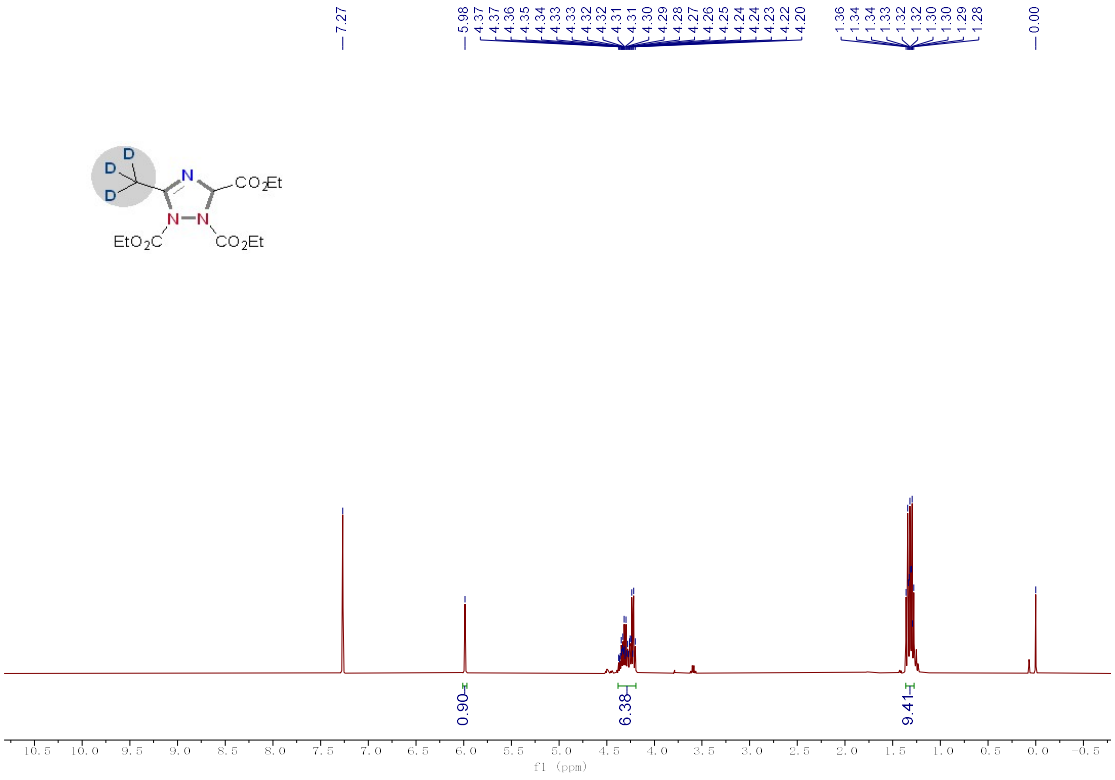
^{1}H NMR (400 MHz) Spectrum of 11s in $CDCl_3$



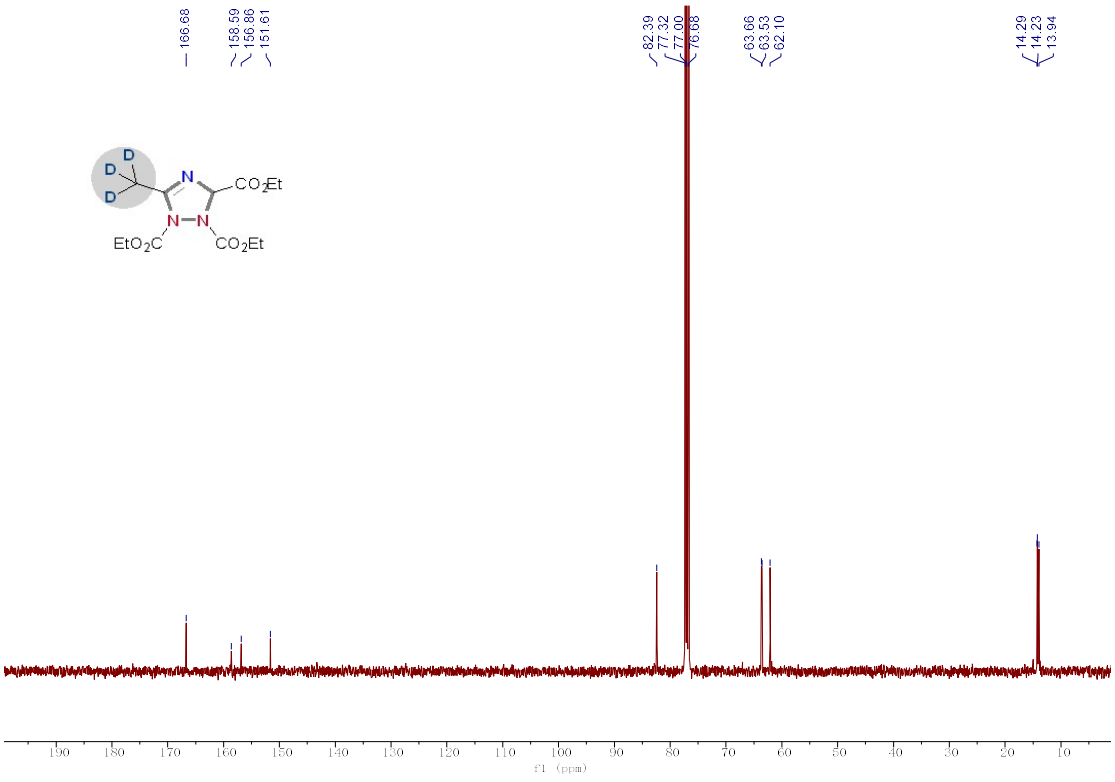
^{13}CNMR (100 MHz) Spectrum of 11s in $CDCl_3$



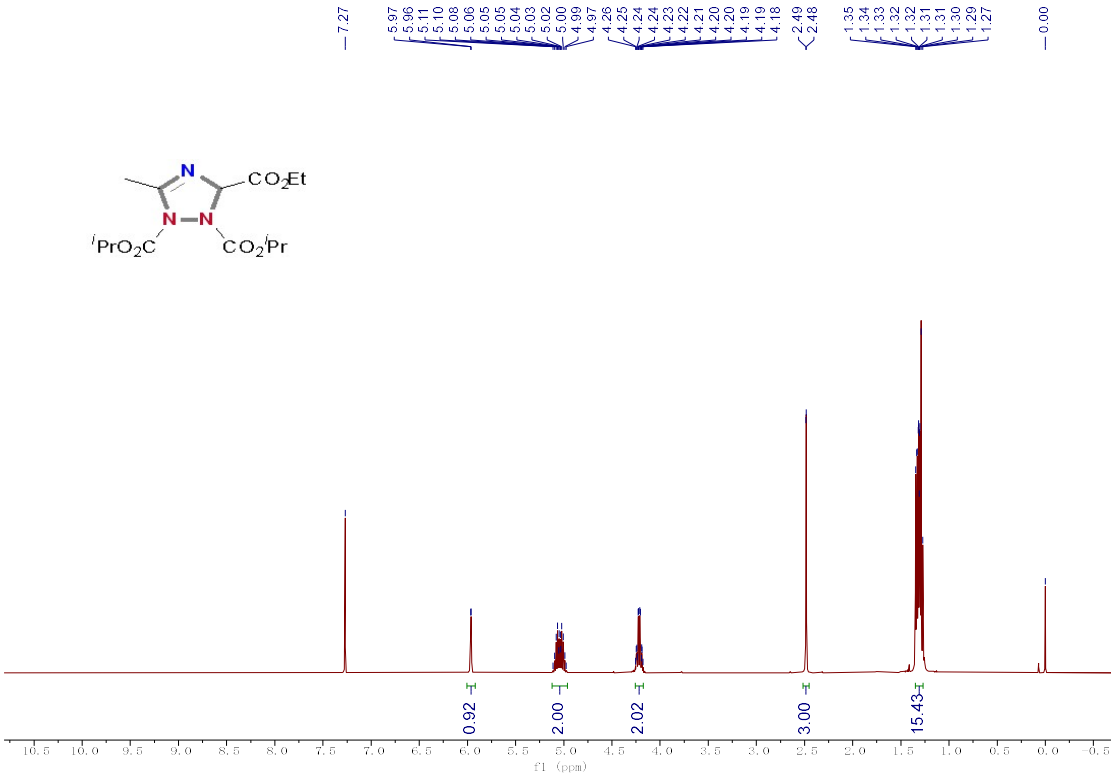
^{1}H NMR (400 MHz) Spectrum of 11t in $CDCl_3$



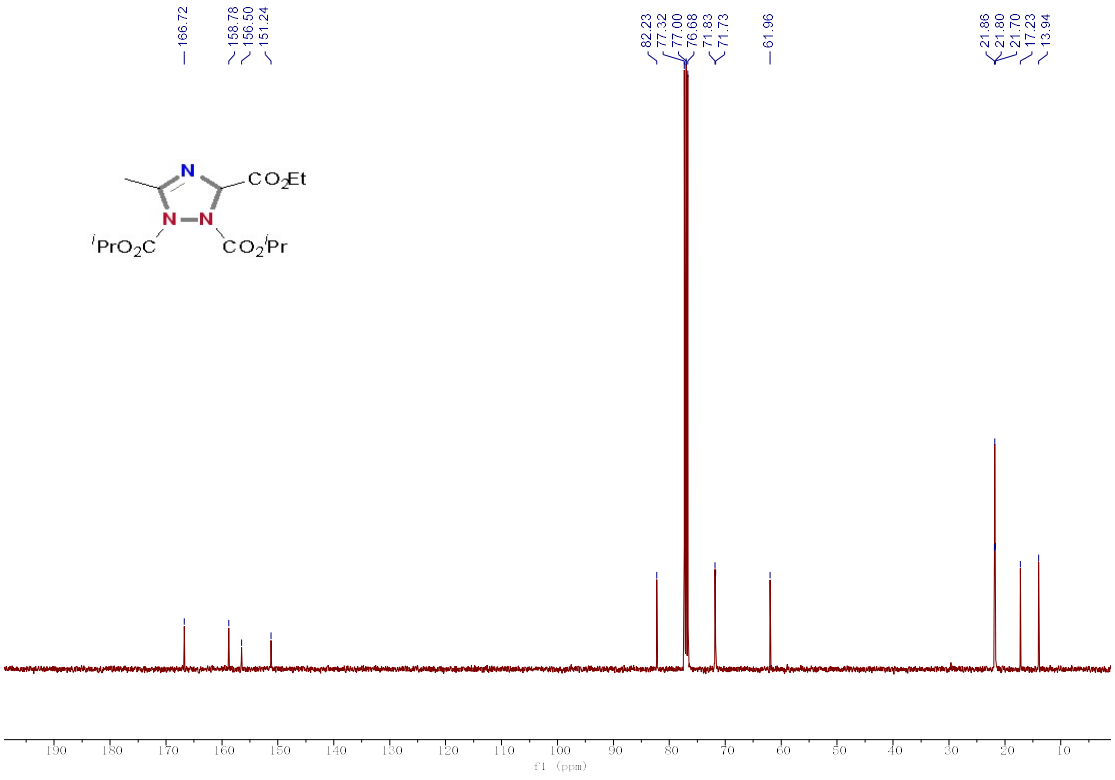
^{13}CNMR (100 MHz) Spectrum of 11t in $CDCl_3$



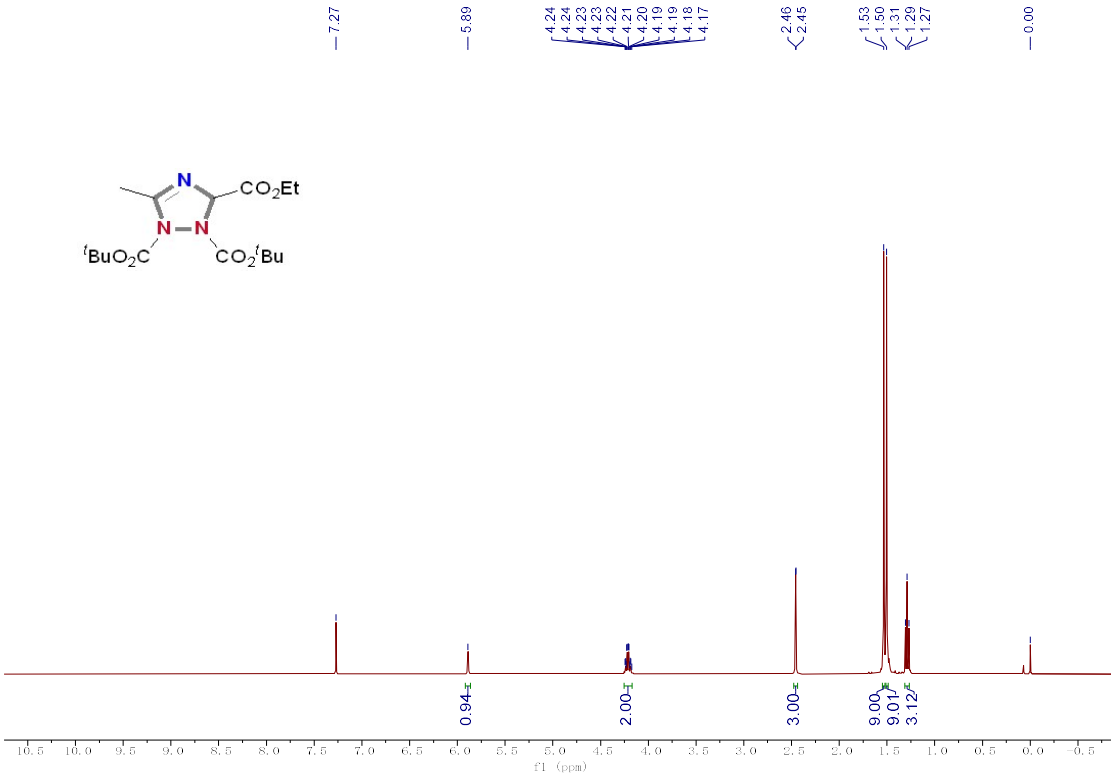
^{1}H NMR (400 MHz) Spectrum of 11u in $CDCl_3$



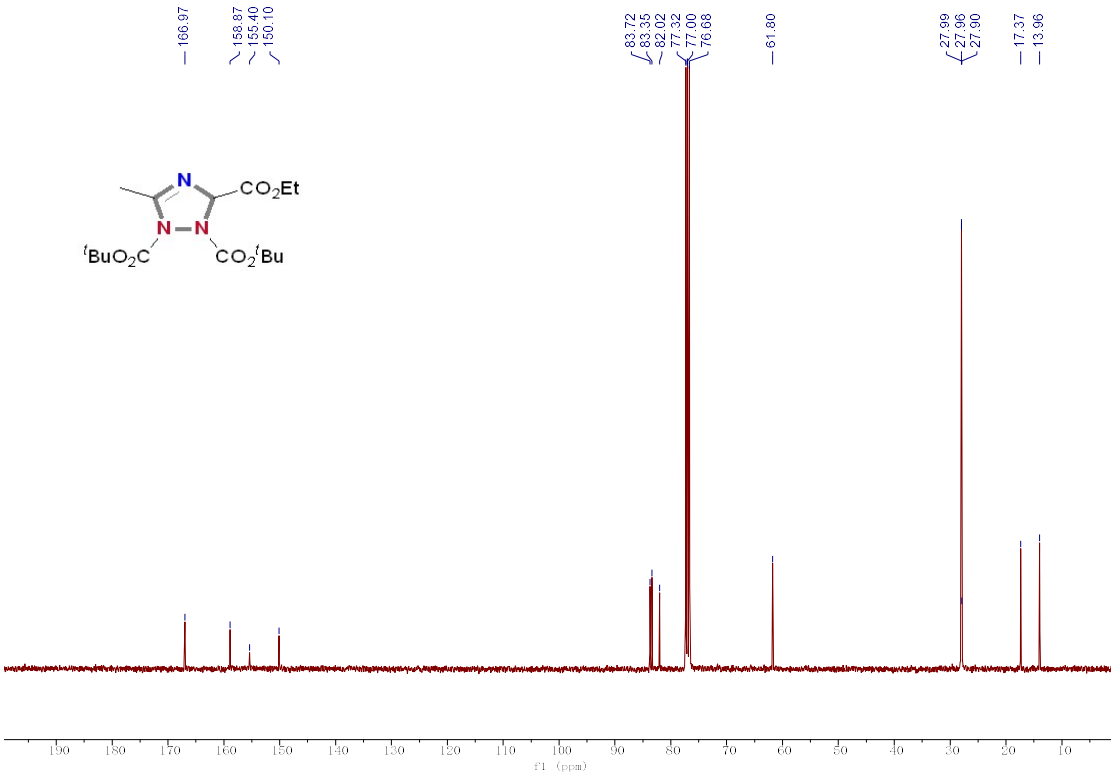
^{13}CNMR (100 MHz) Spectrum of 11u in $CDCl_3$



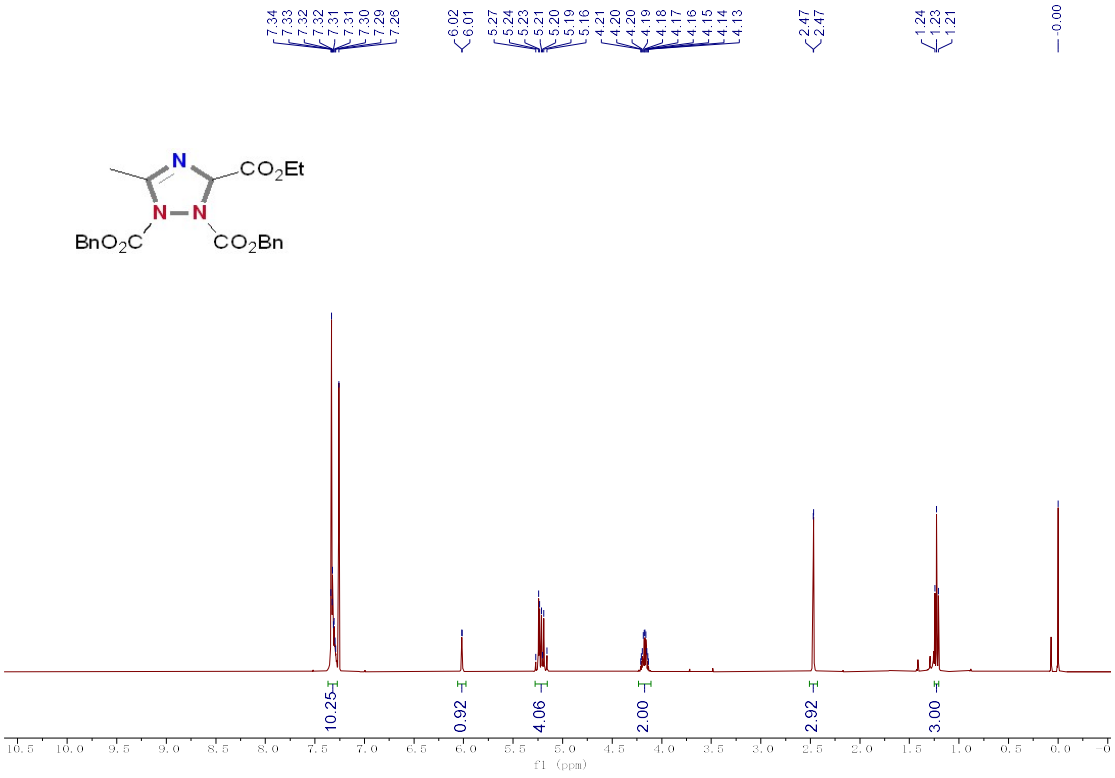
^{1}H NMR (400 MHz) Spectrum of 11v in $CDCl_3$



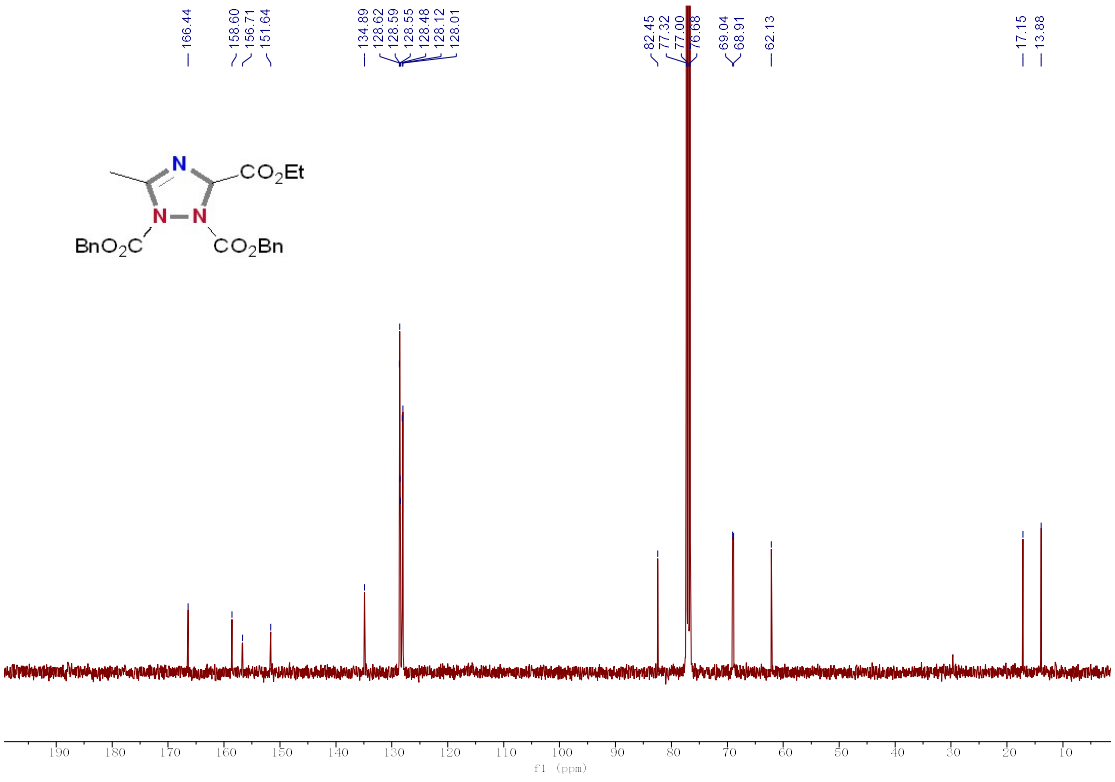
^{13}CNMR (100 MHz) Spectrum of 11v in $CDCl_3$



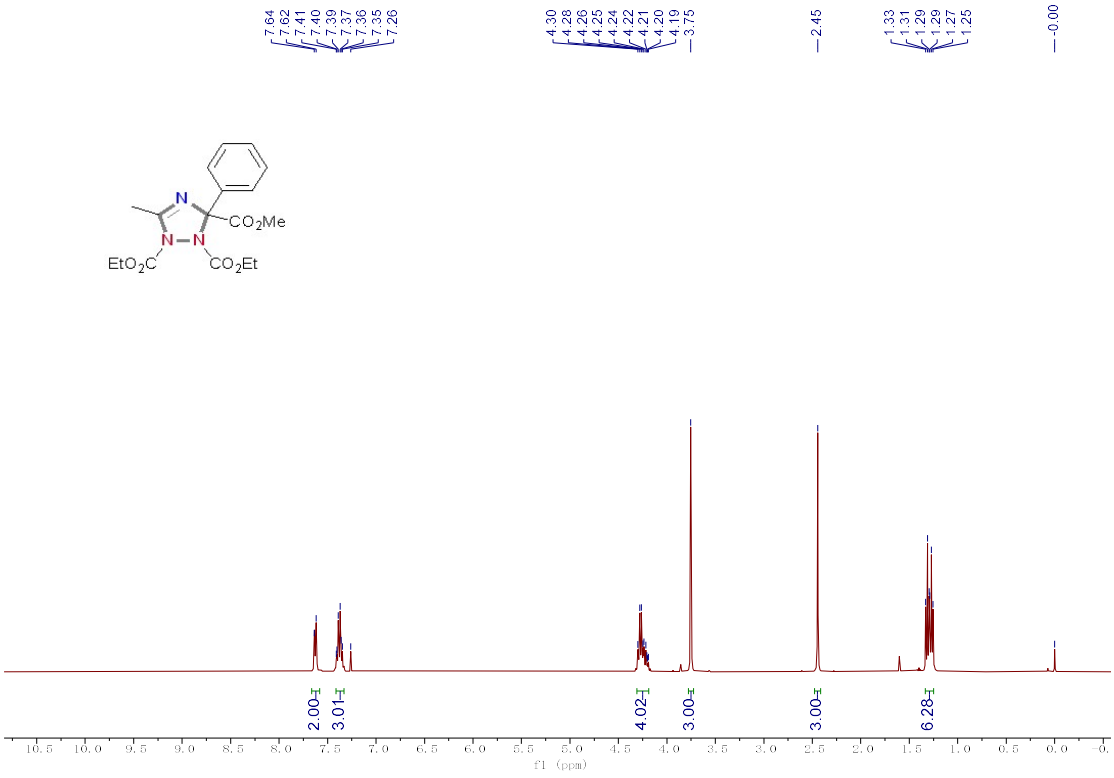
^{1}H NMR (400 MHz) Spectrum of 11w in $CDCl_3$



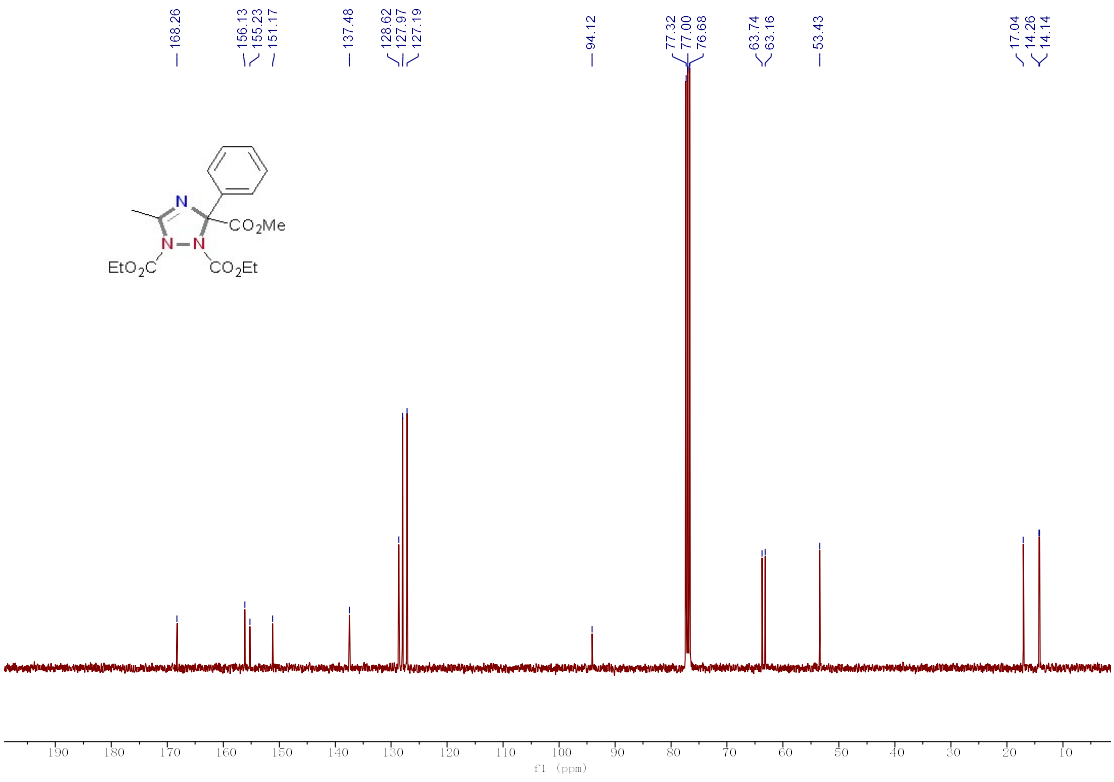
^{13}CNMR (100 MHz) Spectrum of 11w in $CDCl_3$



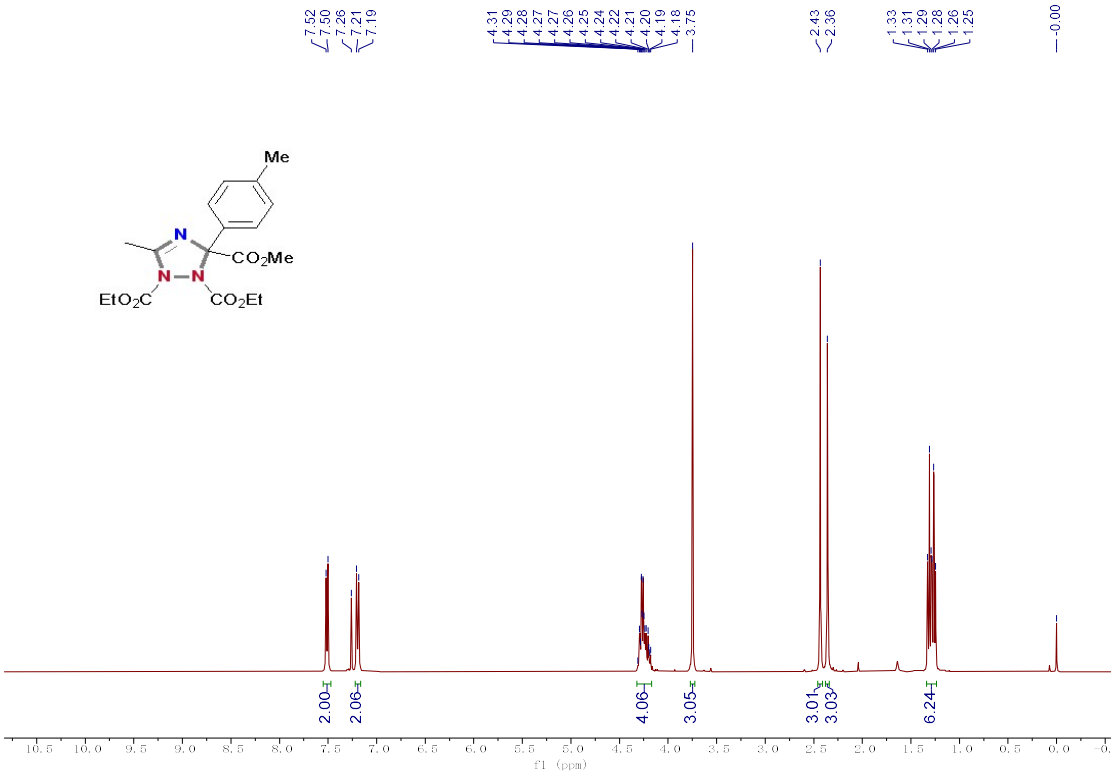
^{1}H NMR (400 MHz) Spectrum of 13a in $CDCl_3$



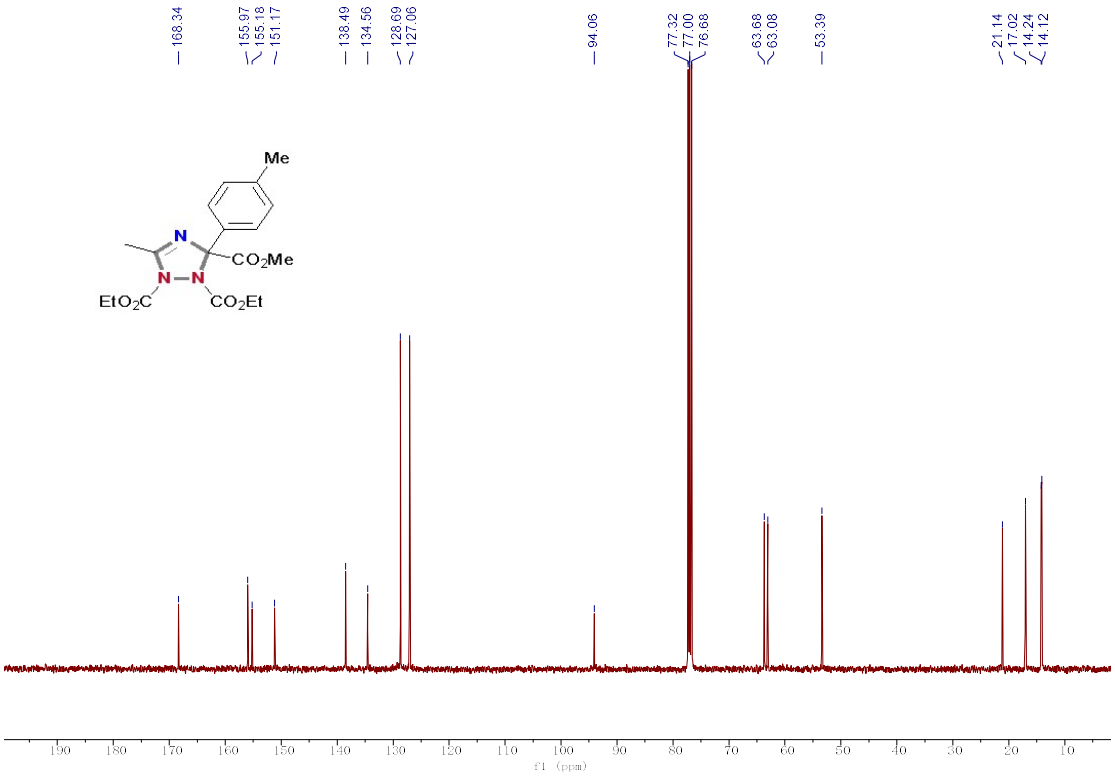
^{13}CNMR (100 MHz) Spectrum of 13a in $CDCl_3$



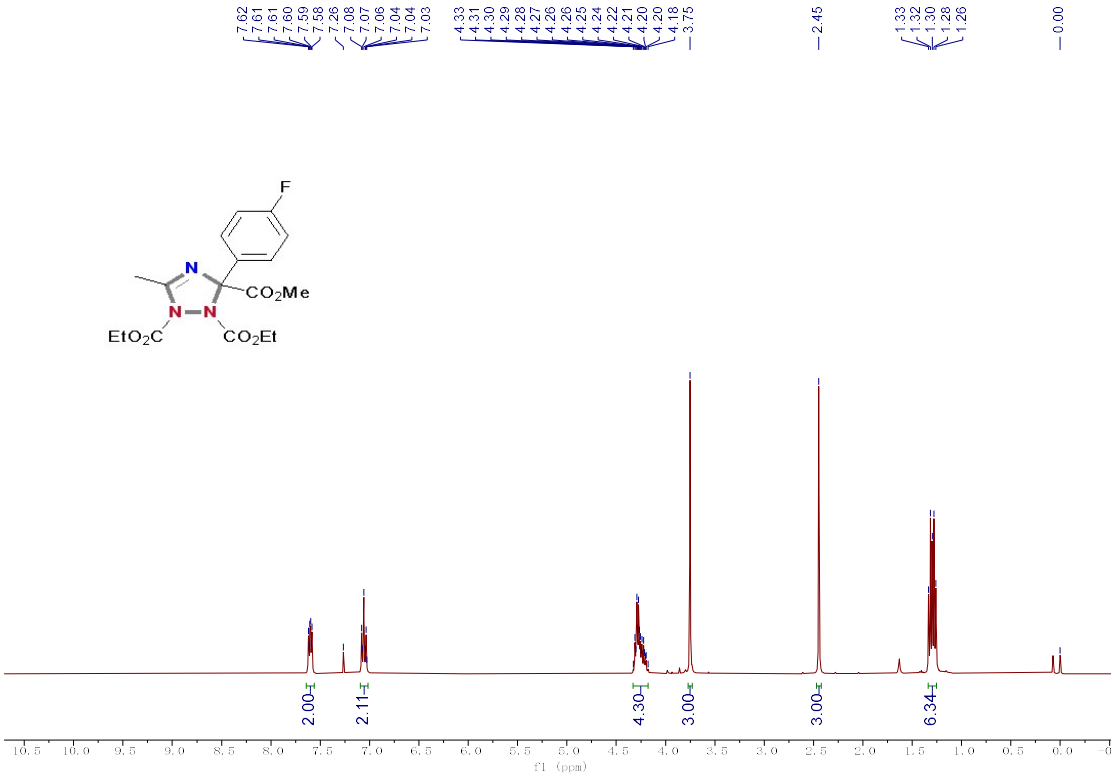
^{1}H NMR (400 MHz) Spectrum of 13b in $CDCl_3$



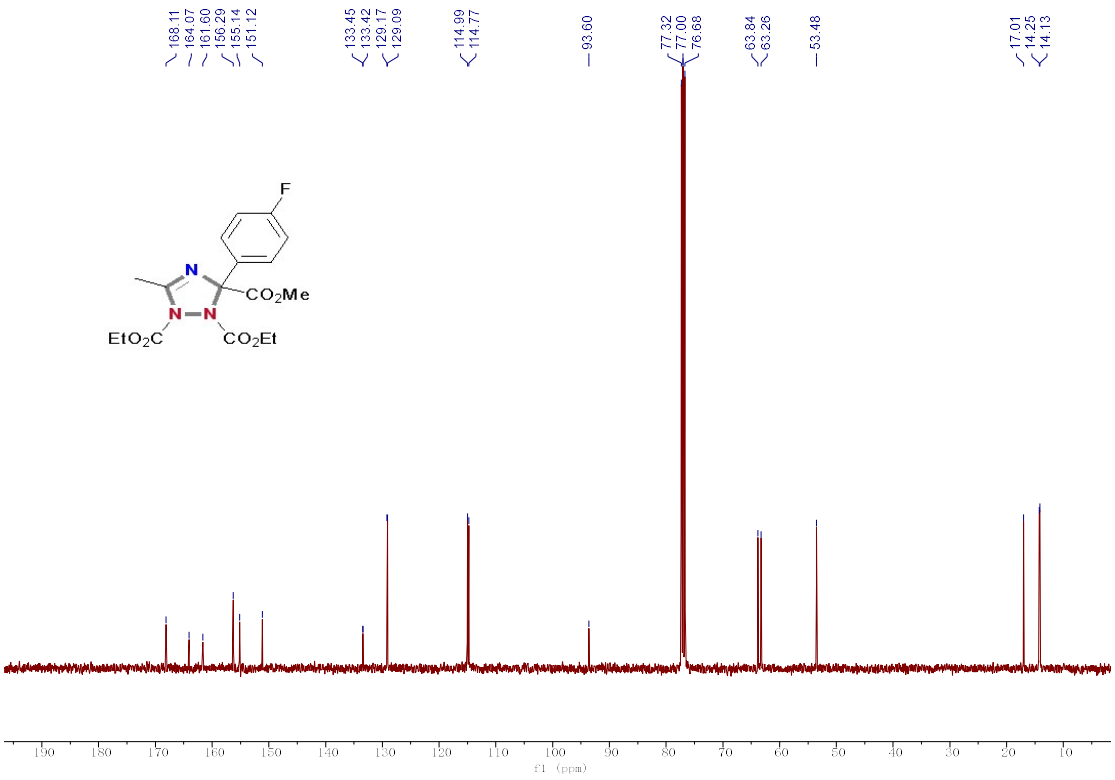
^{13}CNMR (100 MHz) Spectrum of 13b in $CDCl_3$



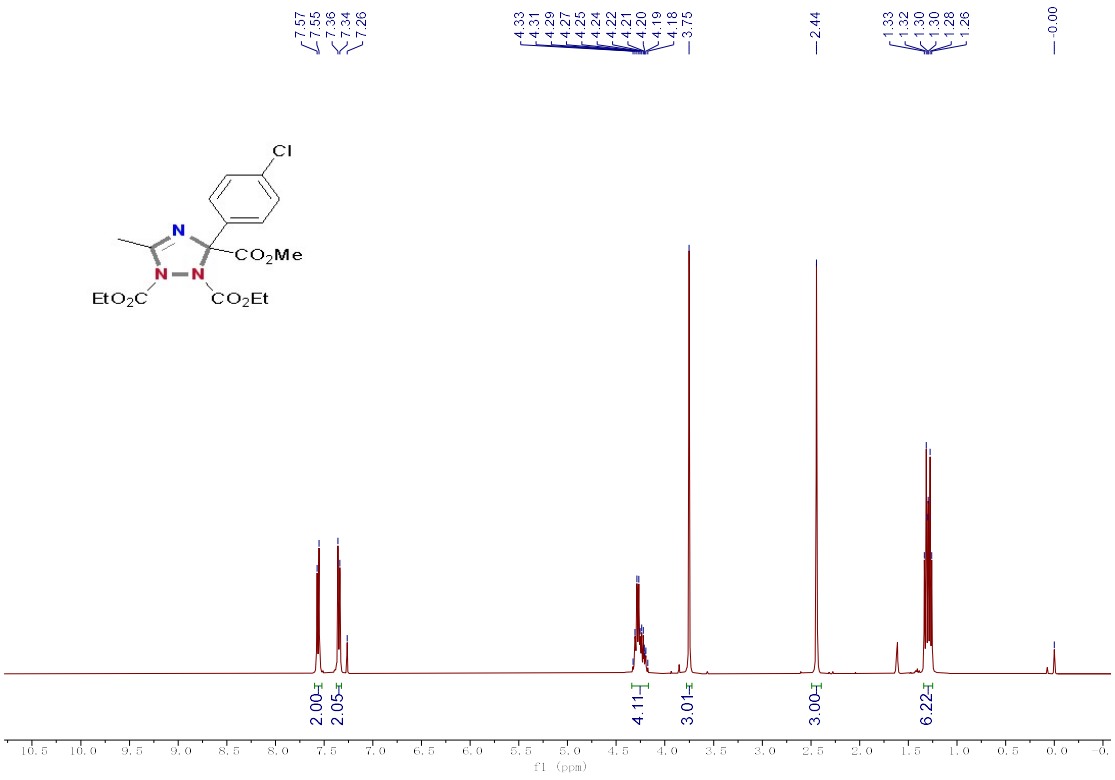
^{1}H NMR (400 MHz) Spectrum of 13c in $CDCl_3$



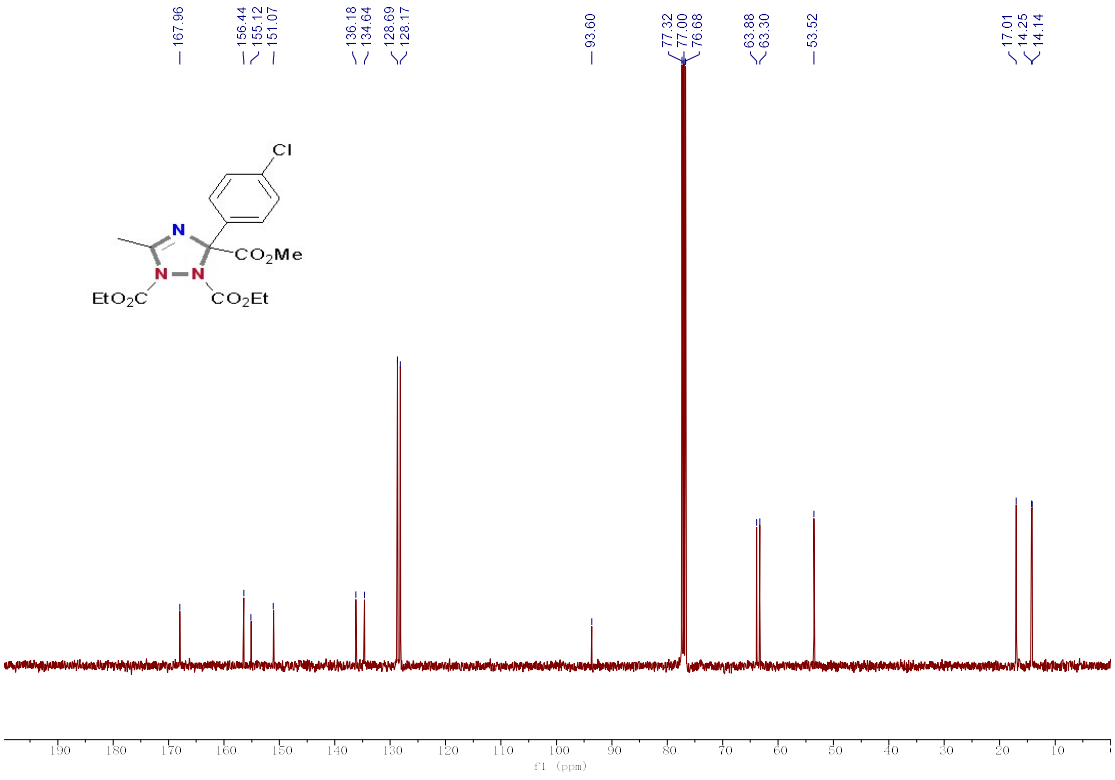
^{13}CNMR (100 MHz) Spectrum of 13c in $CDCl_3$



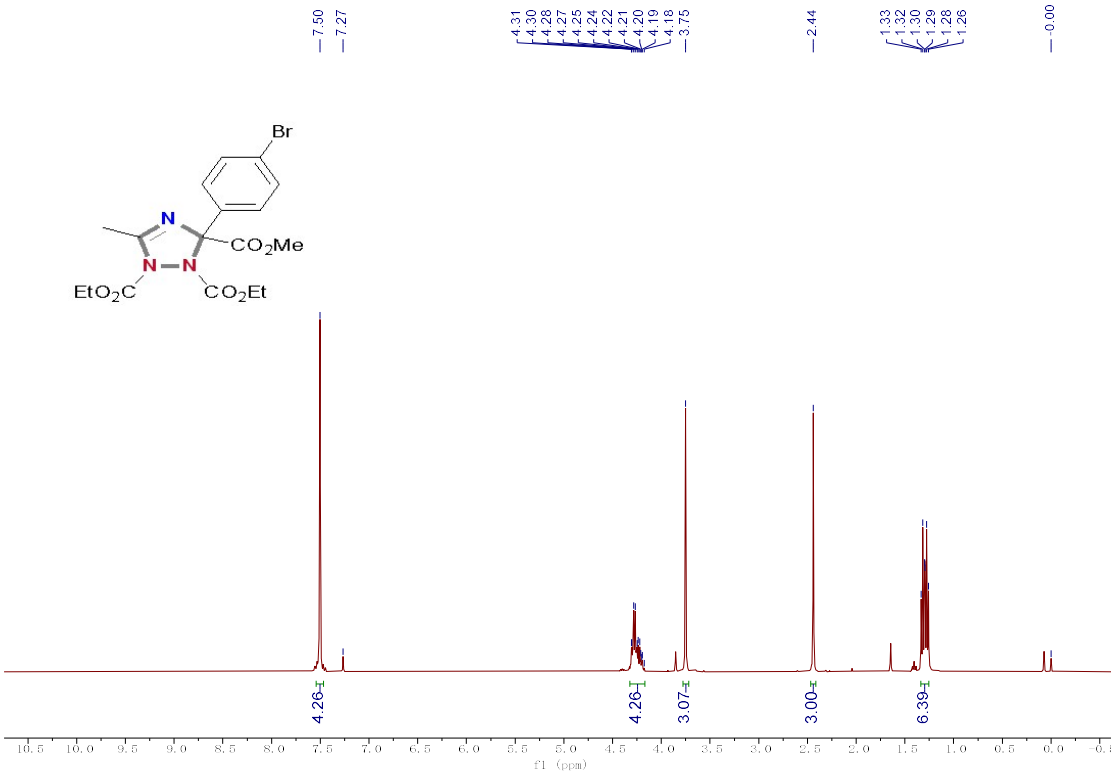
^{1}H NMR (400 MHz) Spectrum of 13d in $CDCl_3$



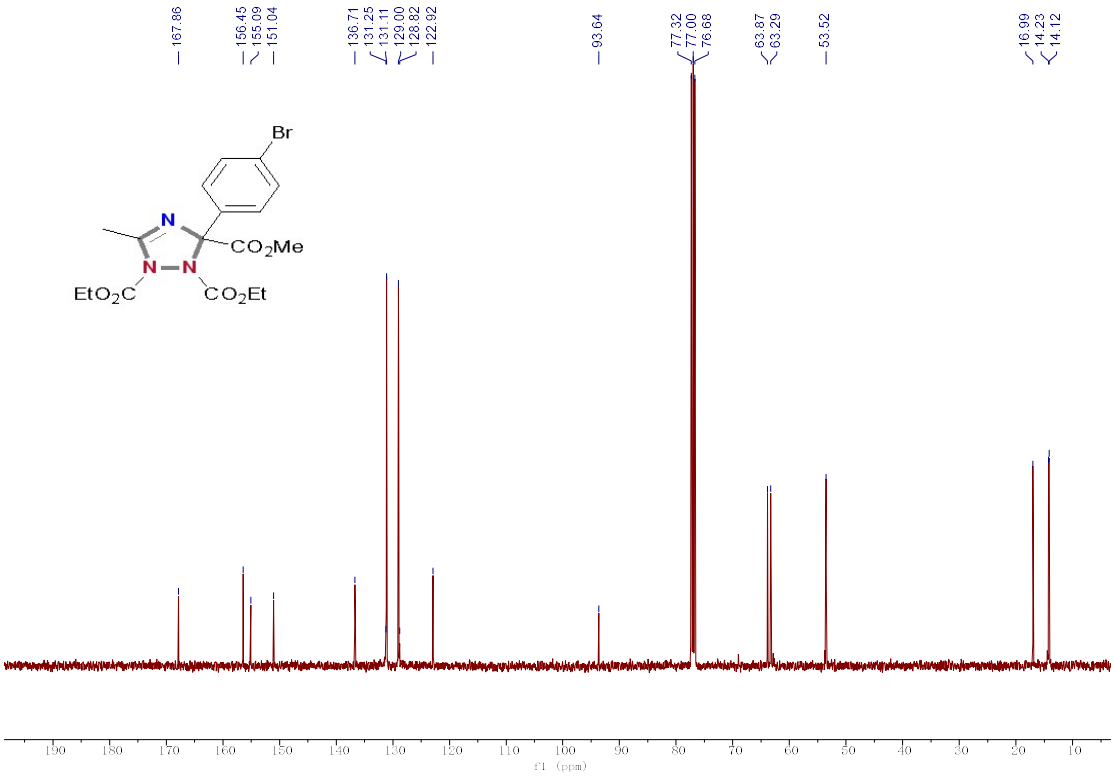
^{13}CNMR (100 MHz) Spectrum of 13d in $CDCl_3$



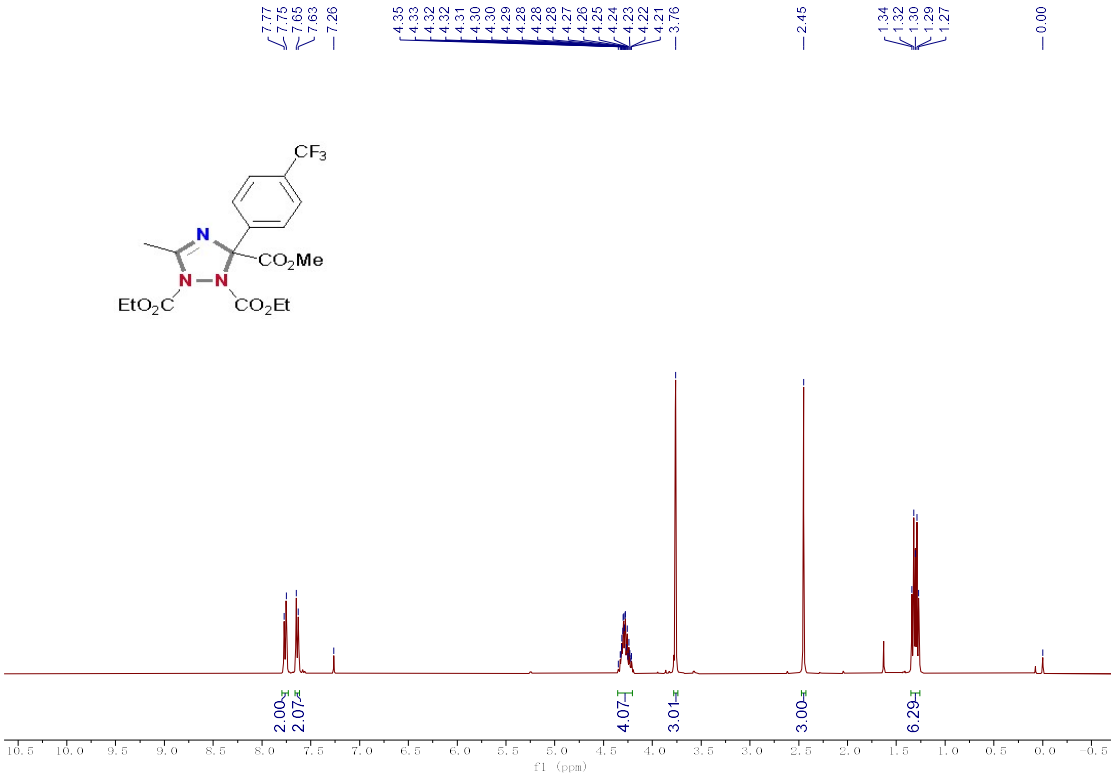
^{1}H NMR (400 MHz) Spectrum of 13e in $CDCl_3$



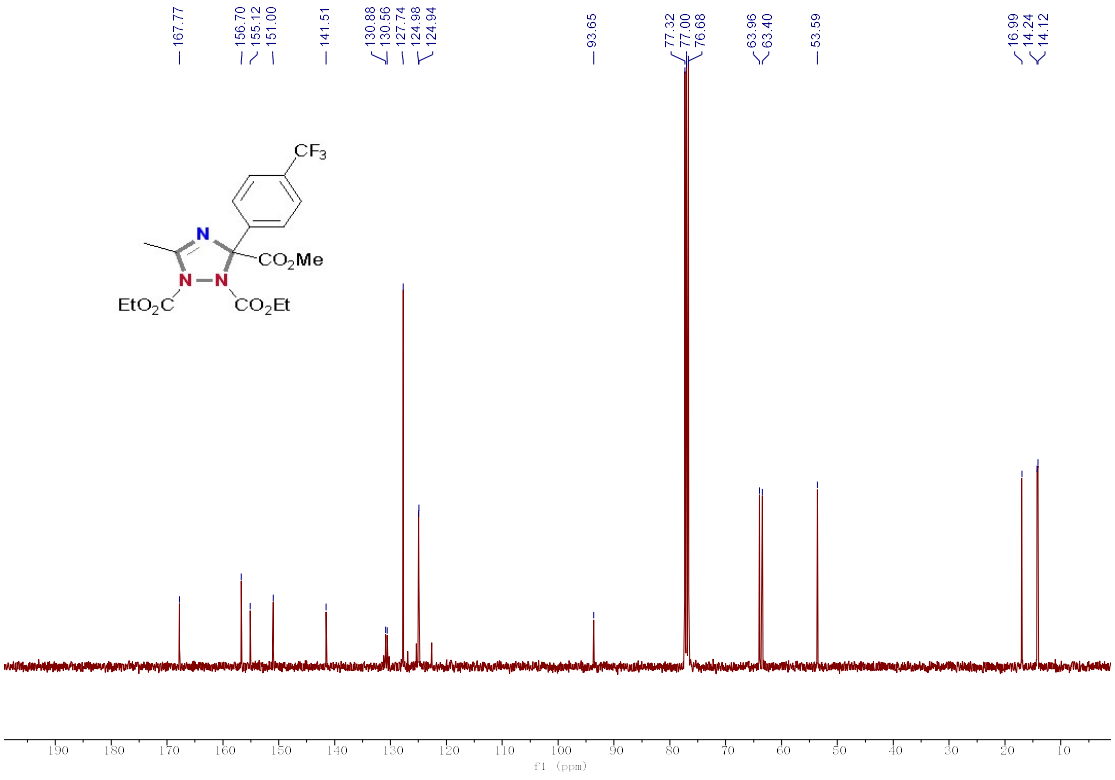
^{13}CNMR (100 MHz) Spectrum of 13e in $CDCl_3$



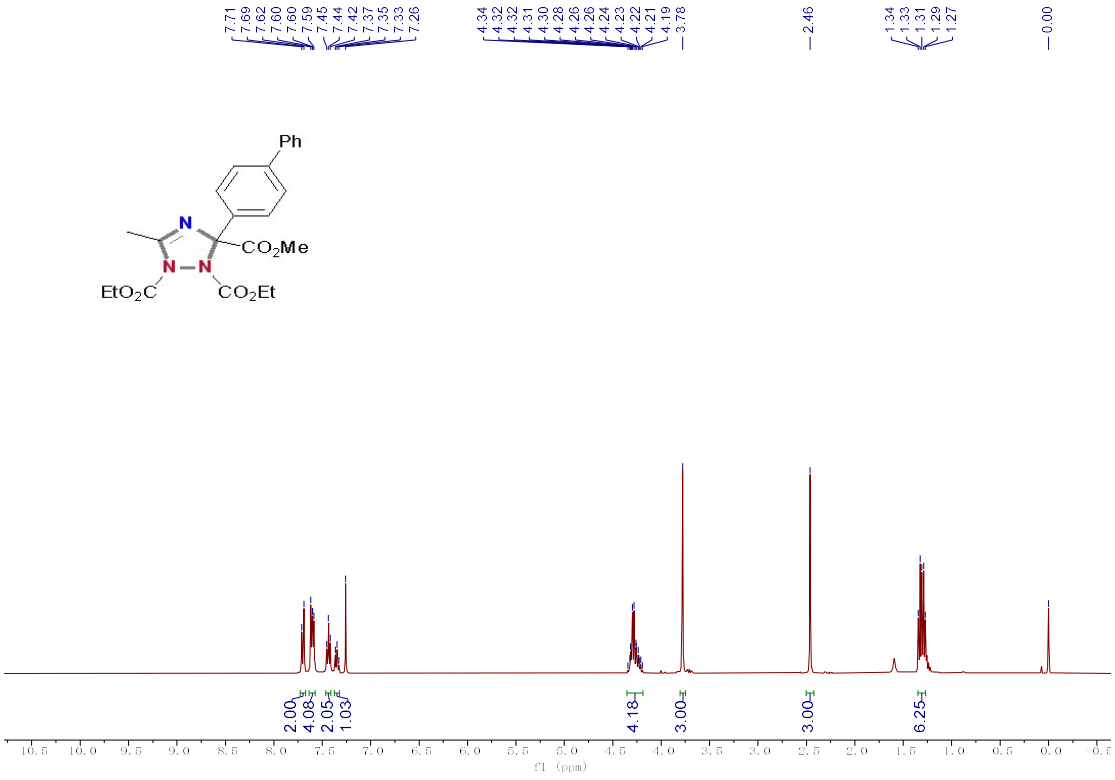
^{1}H NMR (400 MHz) Spectrum of 13f in $CDCl_3$



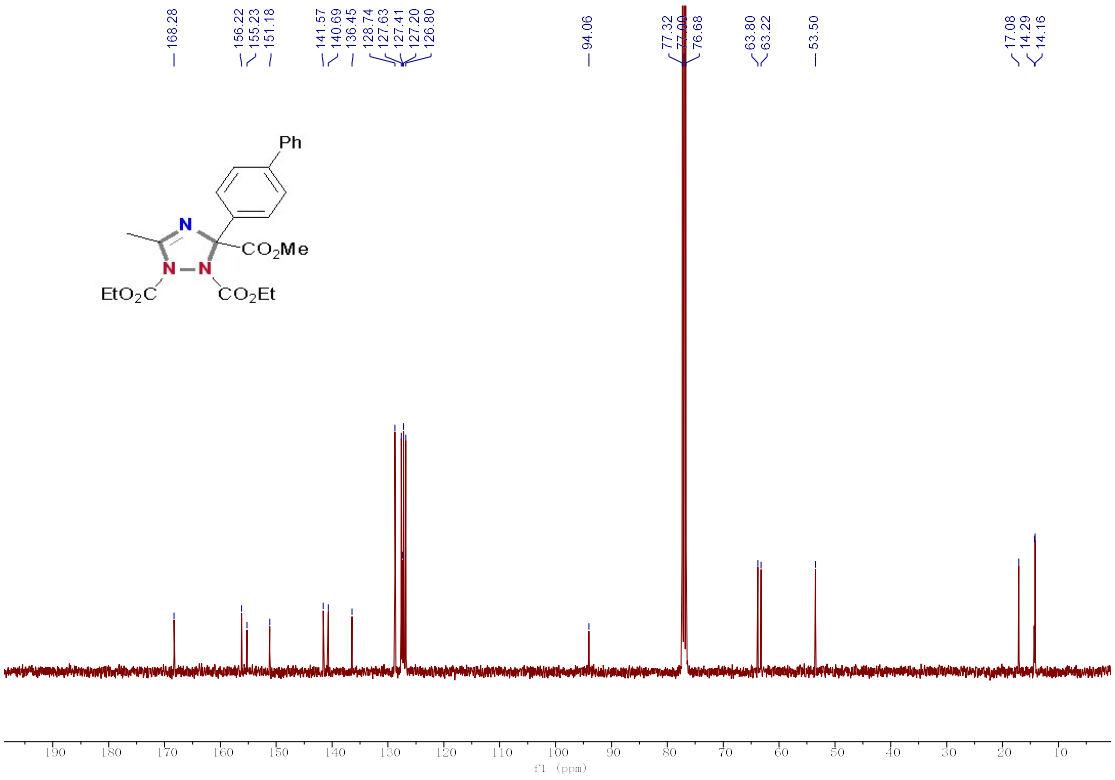
^{13}CNMR (100 MHz) Spectrum of 13f in $CDCl_3$



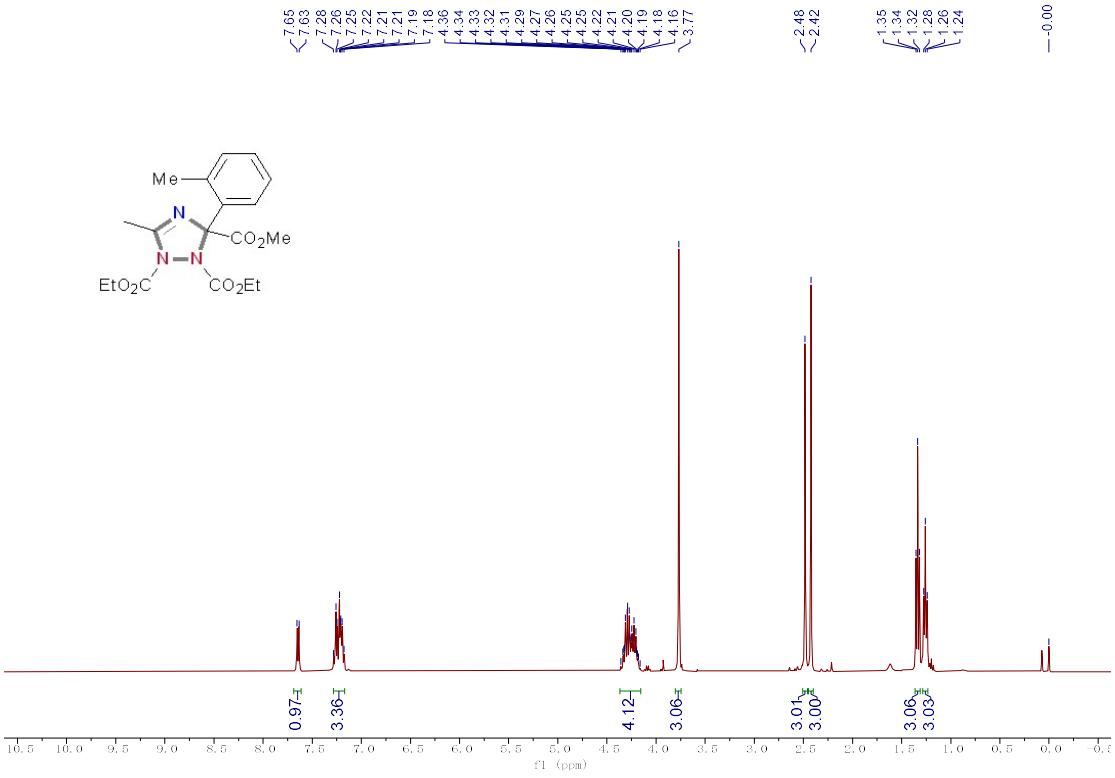
^{1}H NMR (400 MHz) Spectrum of 13g in $CDCl_3$



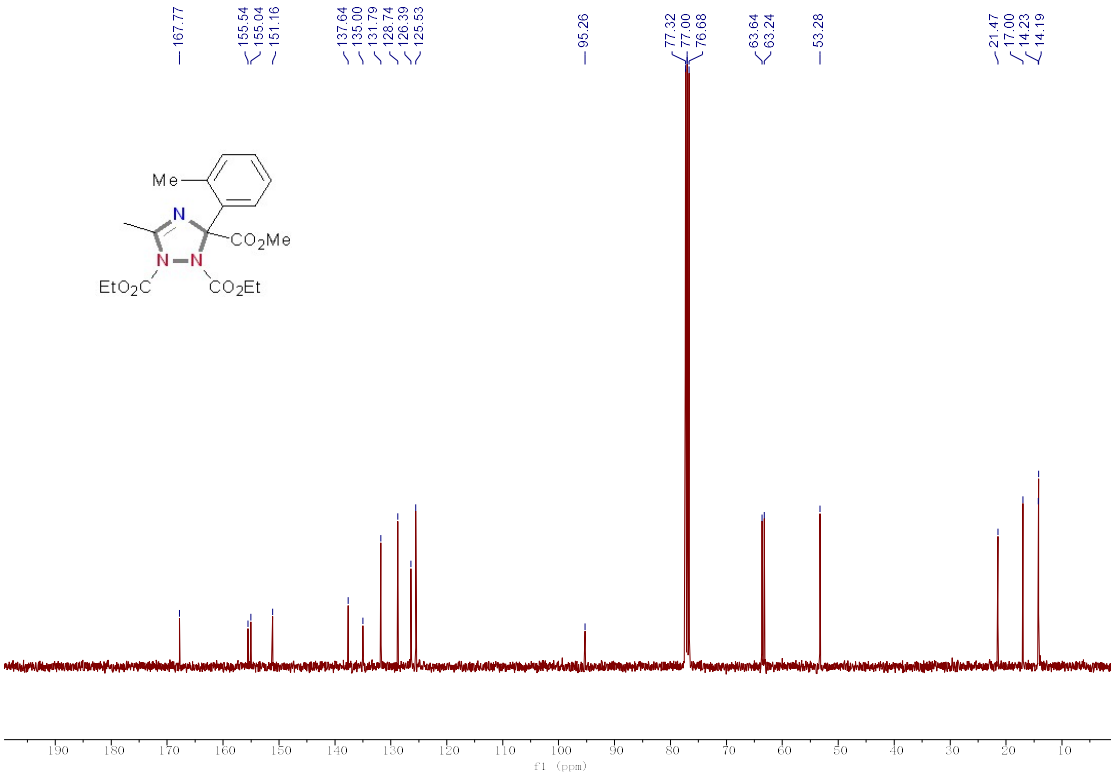
^{13}CNMR (100 MHz) Spectrum of 13g in $CDCl_3$



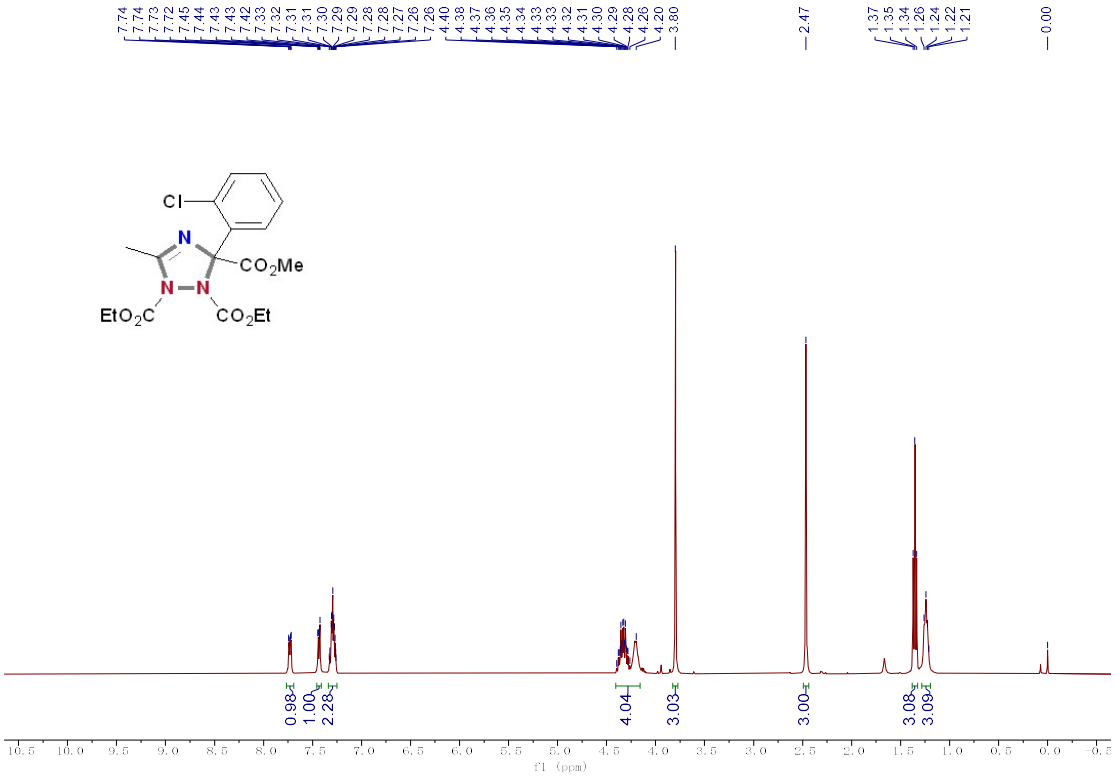
^{1}H NMR (400 MHz) Spectrum of 13h in $CDCl_3$



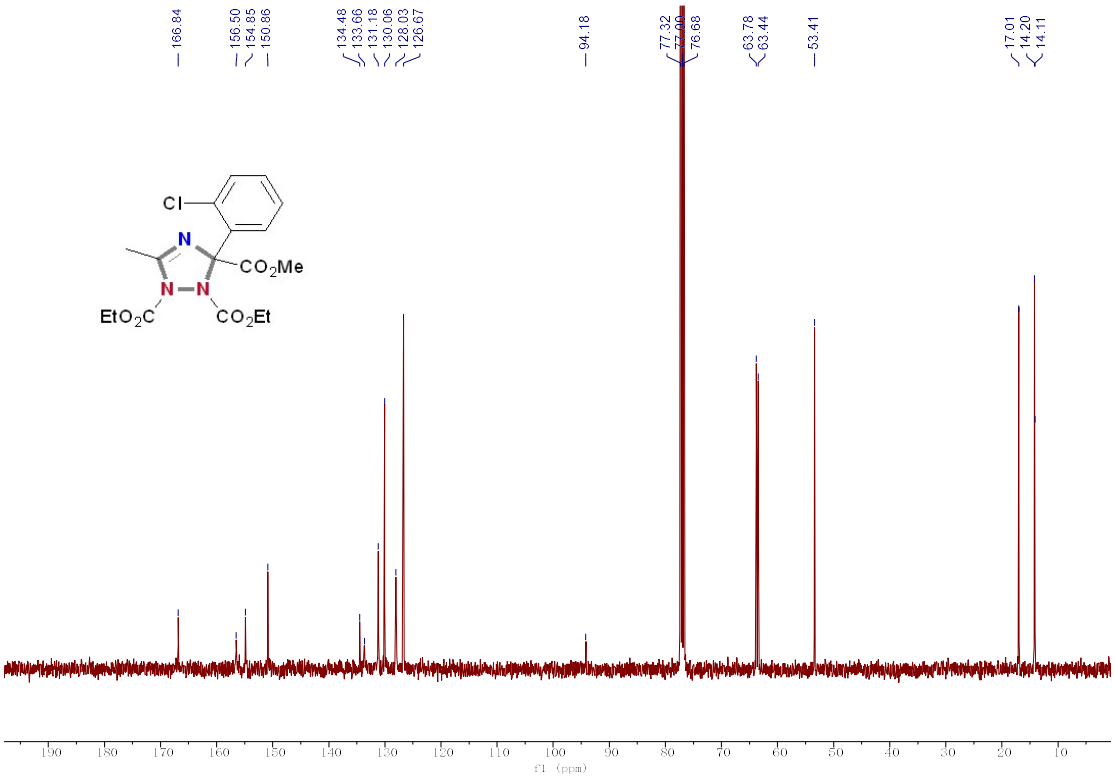
^{13}CNMR (100 MHz) Spectrum of 13h in $CDCl_3$



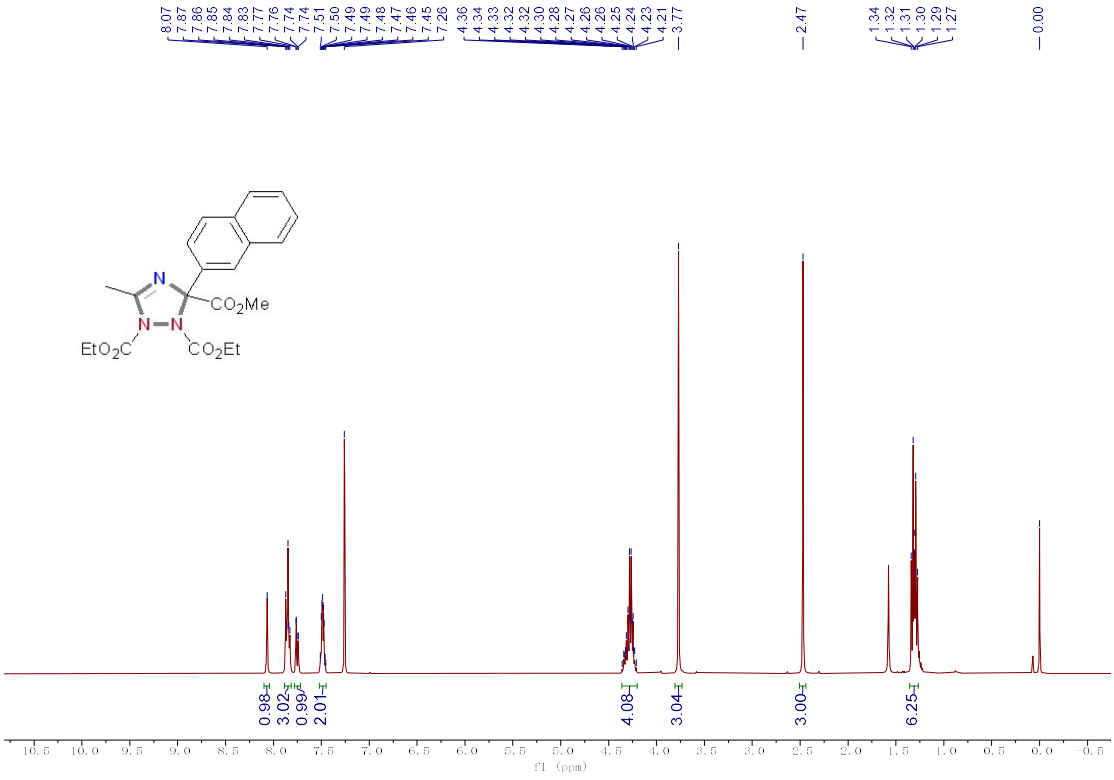
^{1}H NMR (400 MHz) Spectrum of 13i in $CDCl_3$



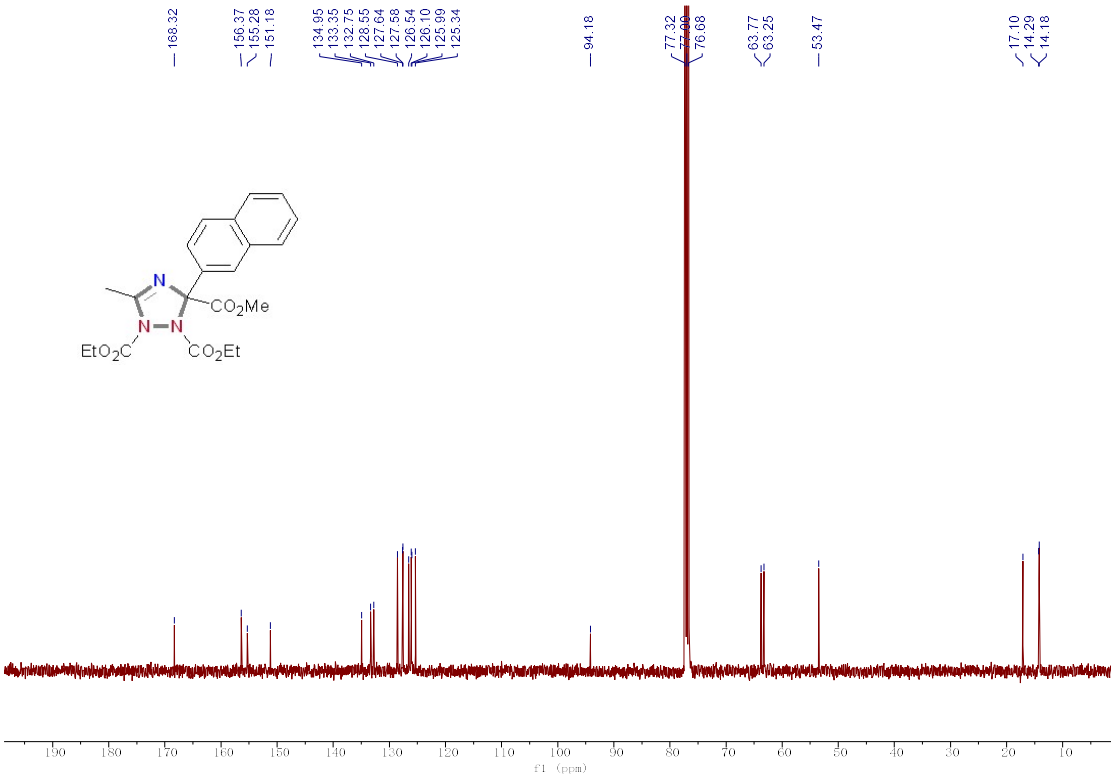
^{13}CNMR (100 MHz) Spectrum of 13i in $CDCl_3$



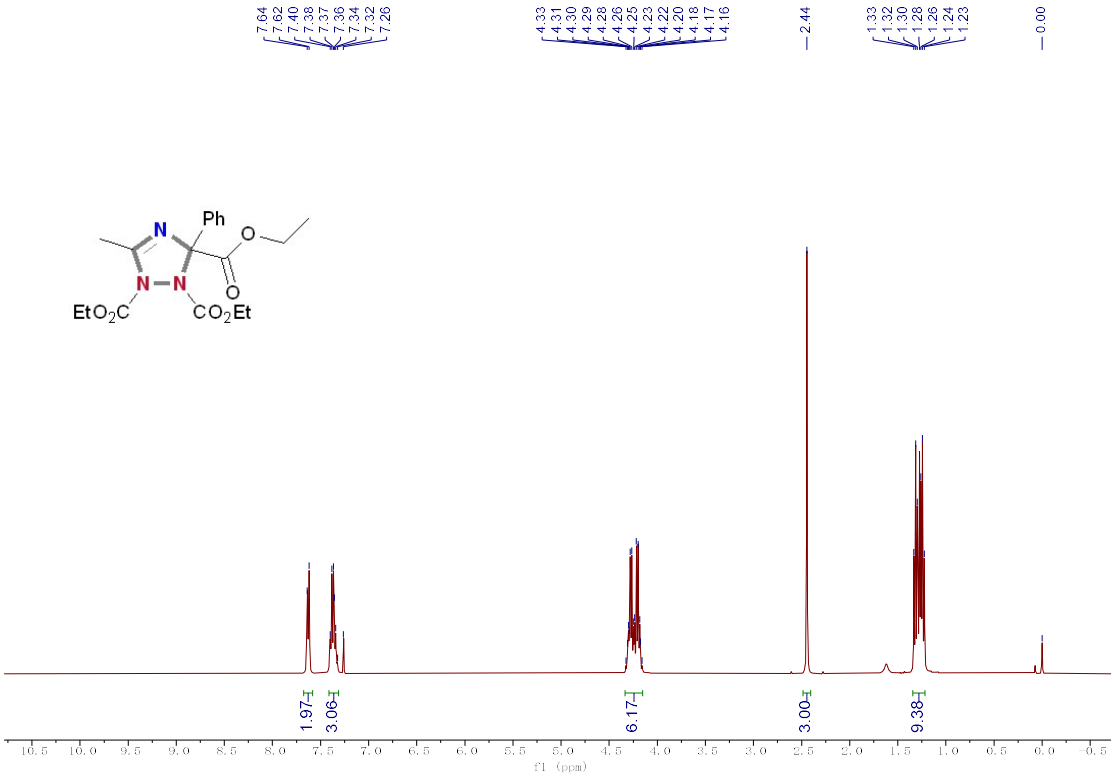
^{1}H NMR (400 MHz) Spectrum of 13j in $CDCl_3$



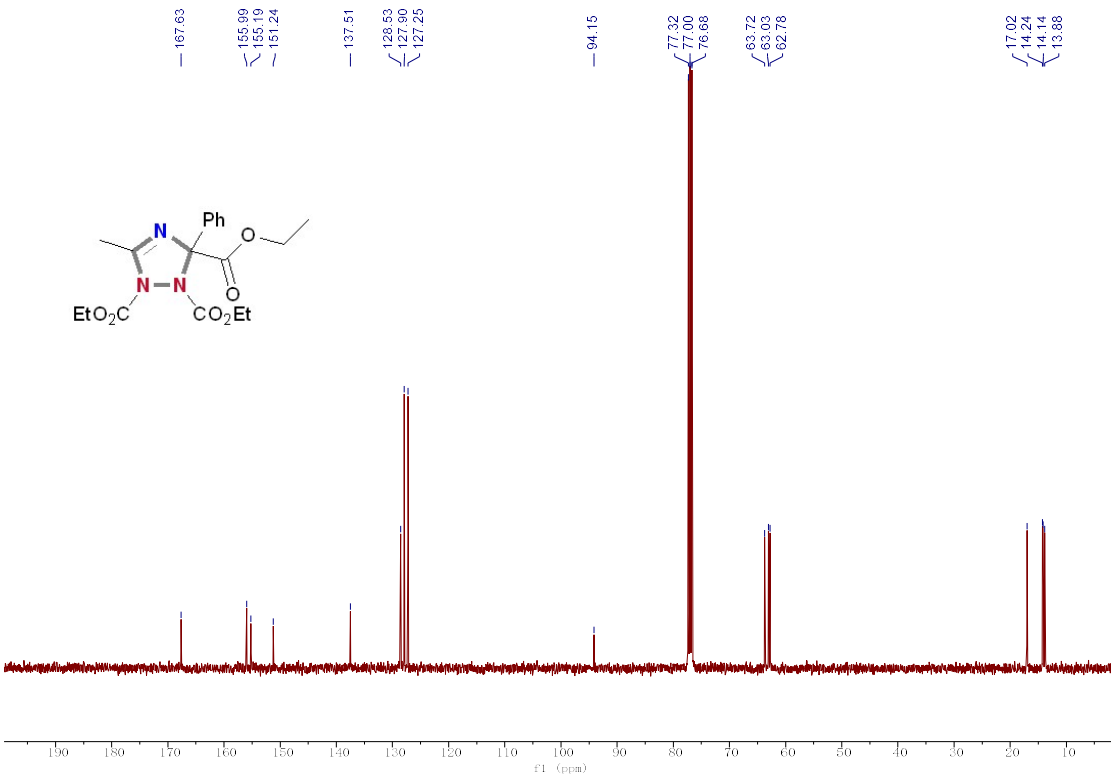
^{13}CNMR (100 MHz) Spectrum of 13j in $CDCl_3$



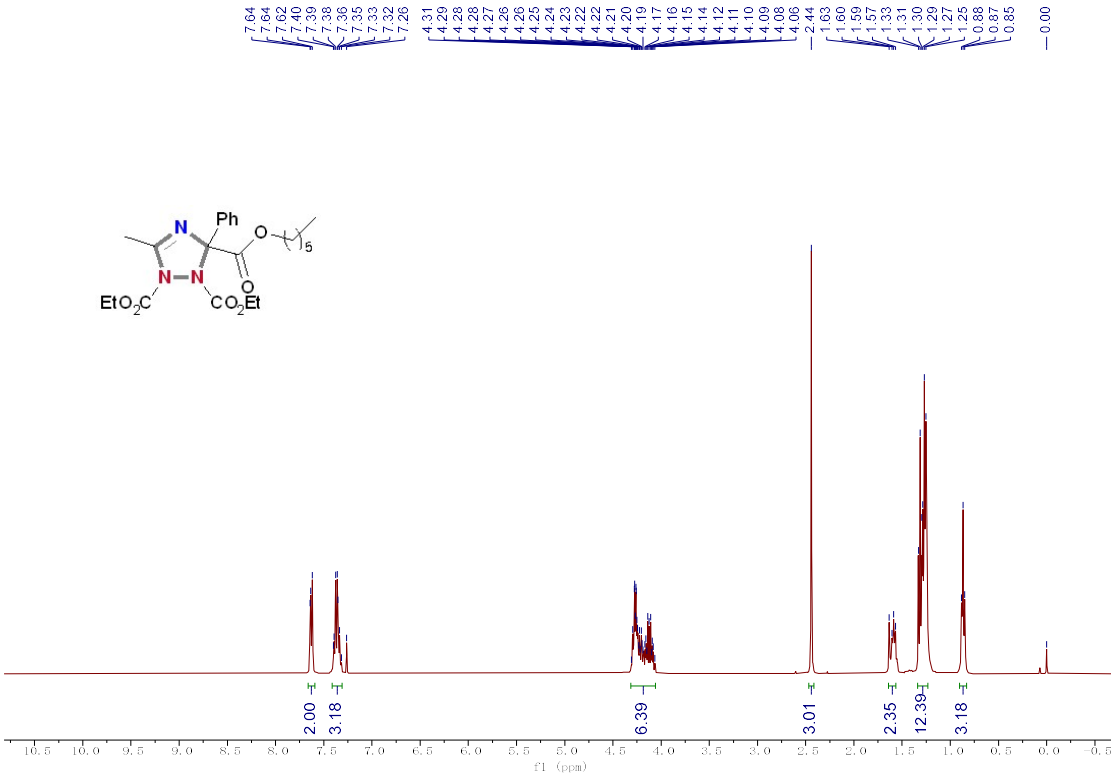
^{1}H NMR (400 MHz) Spectrum of 13k in $CDCl_3$



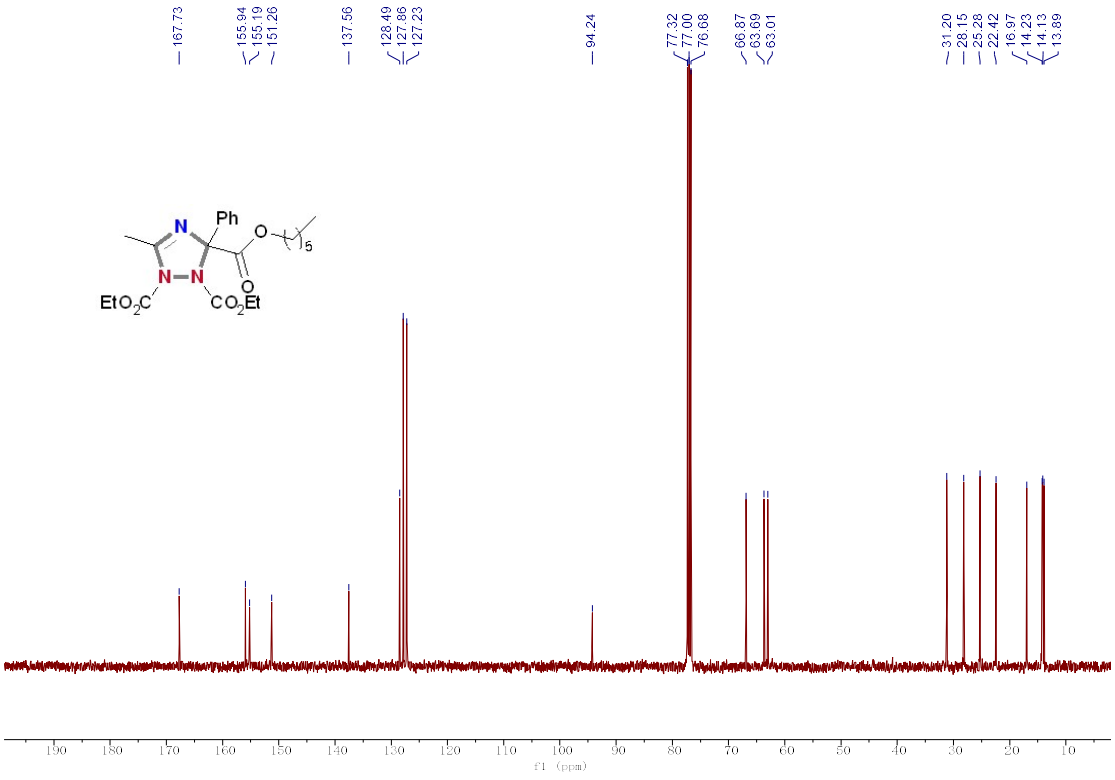
^{13}CNMR (100 MHz) Spectrum of 13k in $CDCl_3$



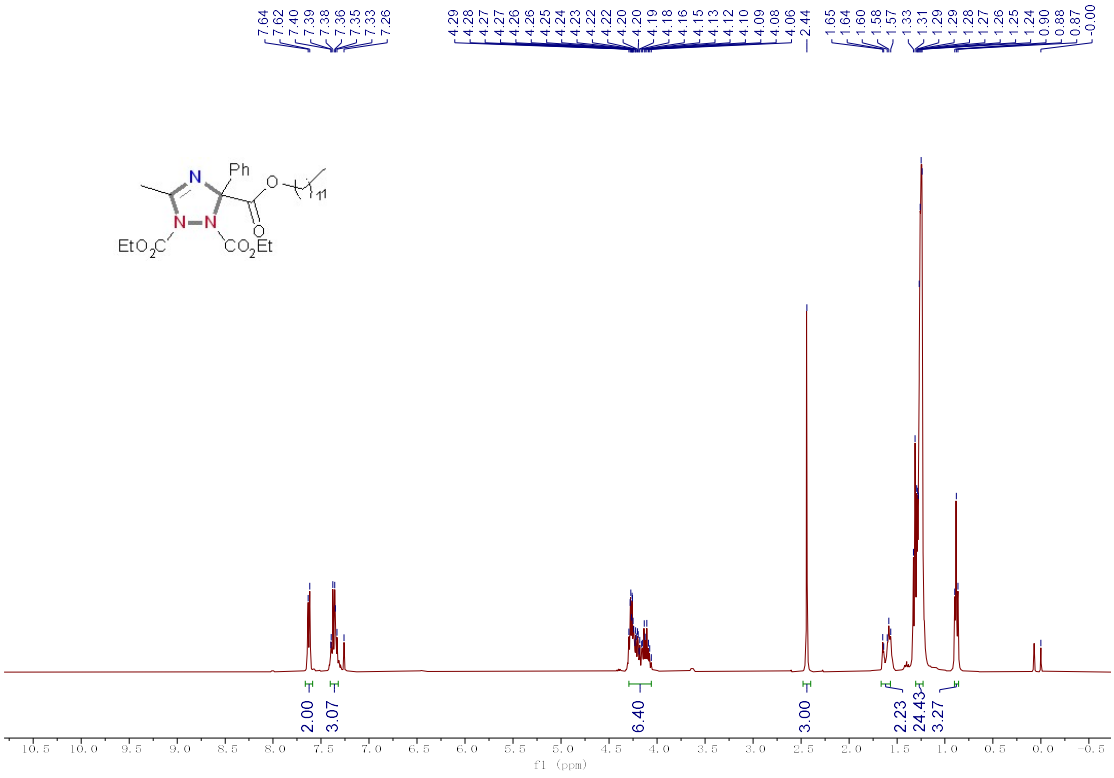
^{1}H NMR (400 MHz) Spectrum of 13l in $CDCl_3$



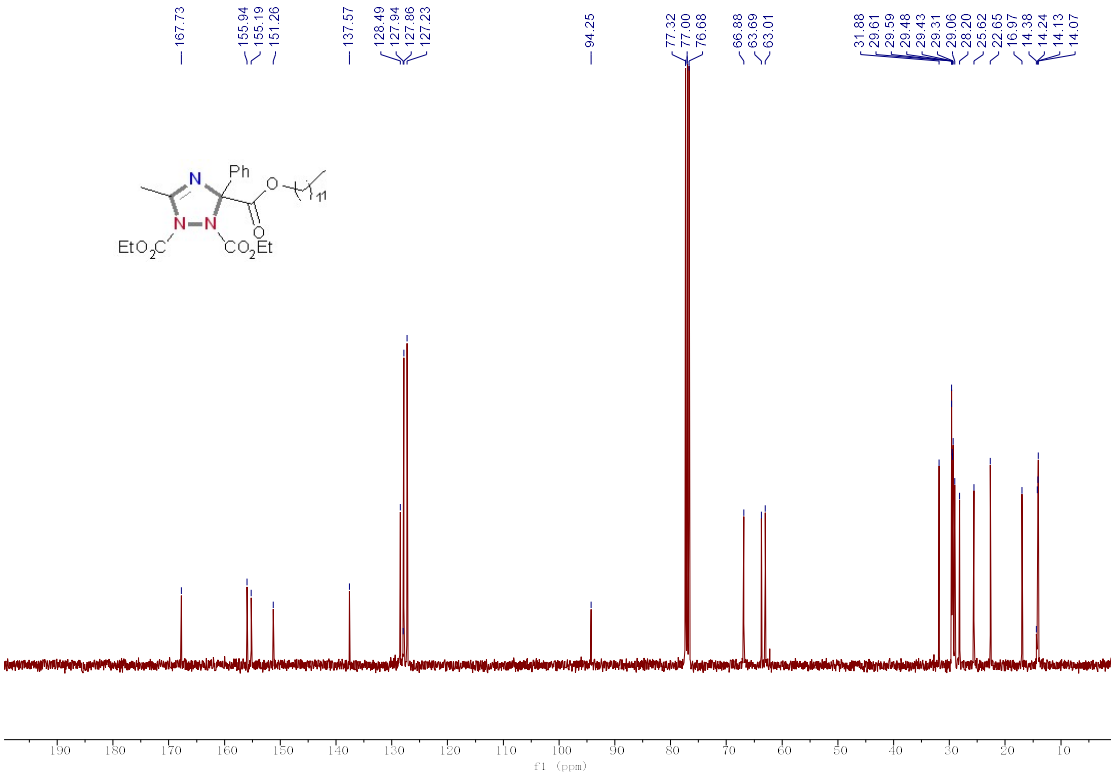
^{13}CNMR (100 MHz) Spectrum of 13l in $CDCl_3$



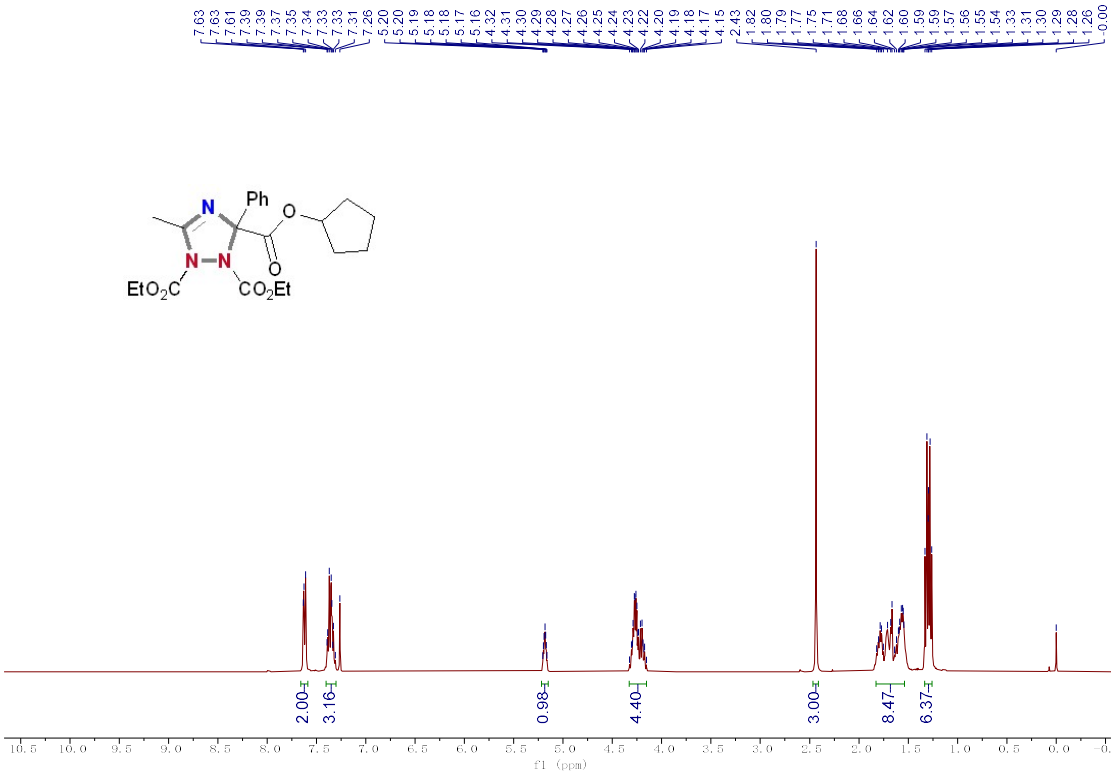
^{1}H NMR (400 MHz) Spectrum of 13m in $CDCl_3$



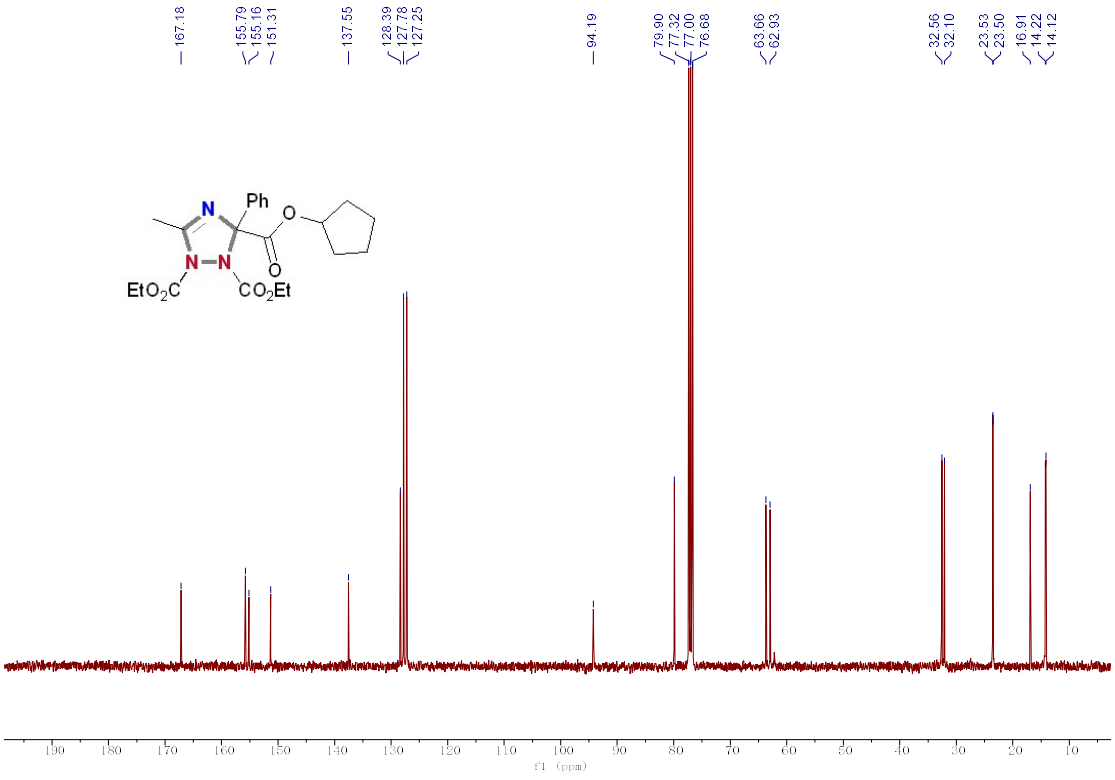
^{13}CNMR (100 MHz) Spectrum of 13m in $CDCl_3$



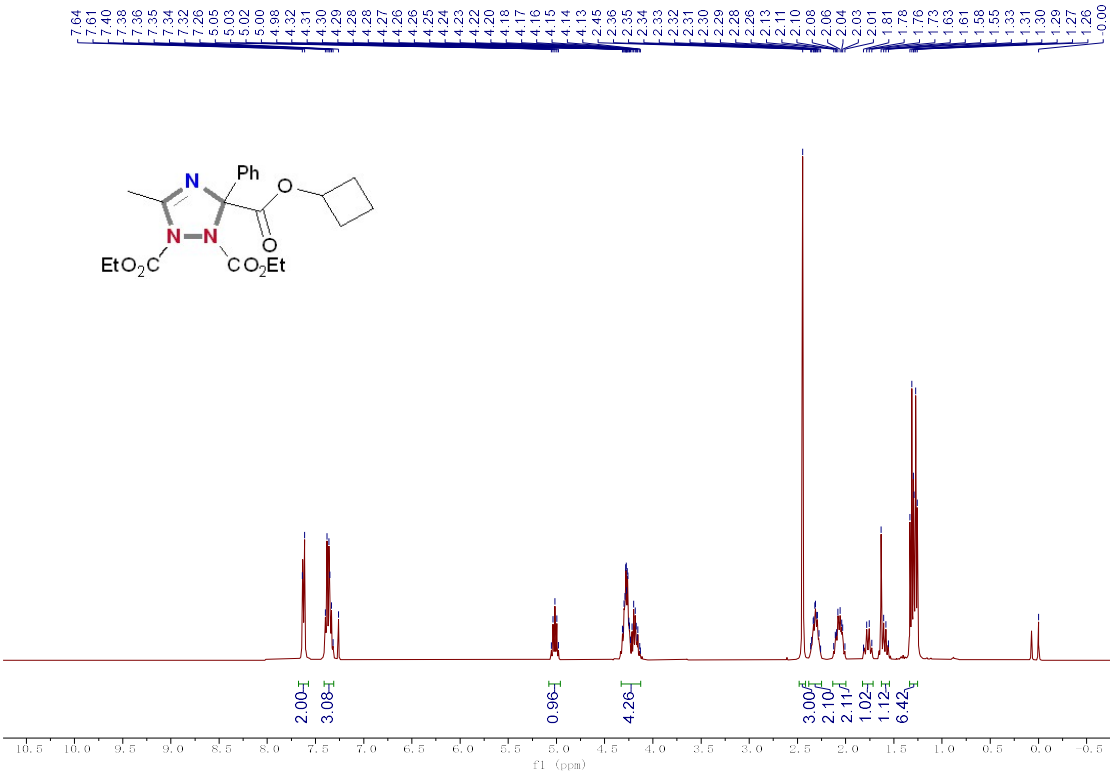
^{1}H NMR (400 MHz) Spectrum of 13n in $CDCl_3$



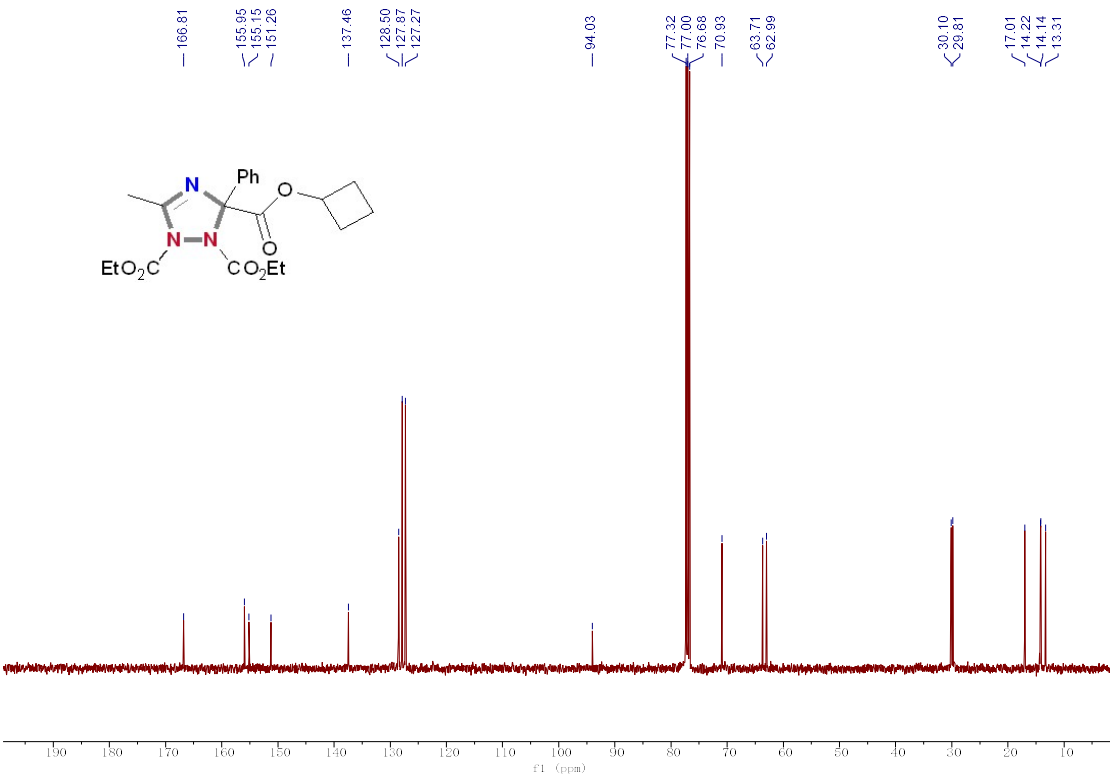
^{13}CNMR (100 MHz) Spectrum of 13n in $CDCl_3$



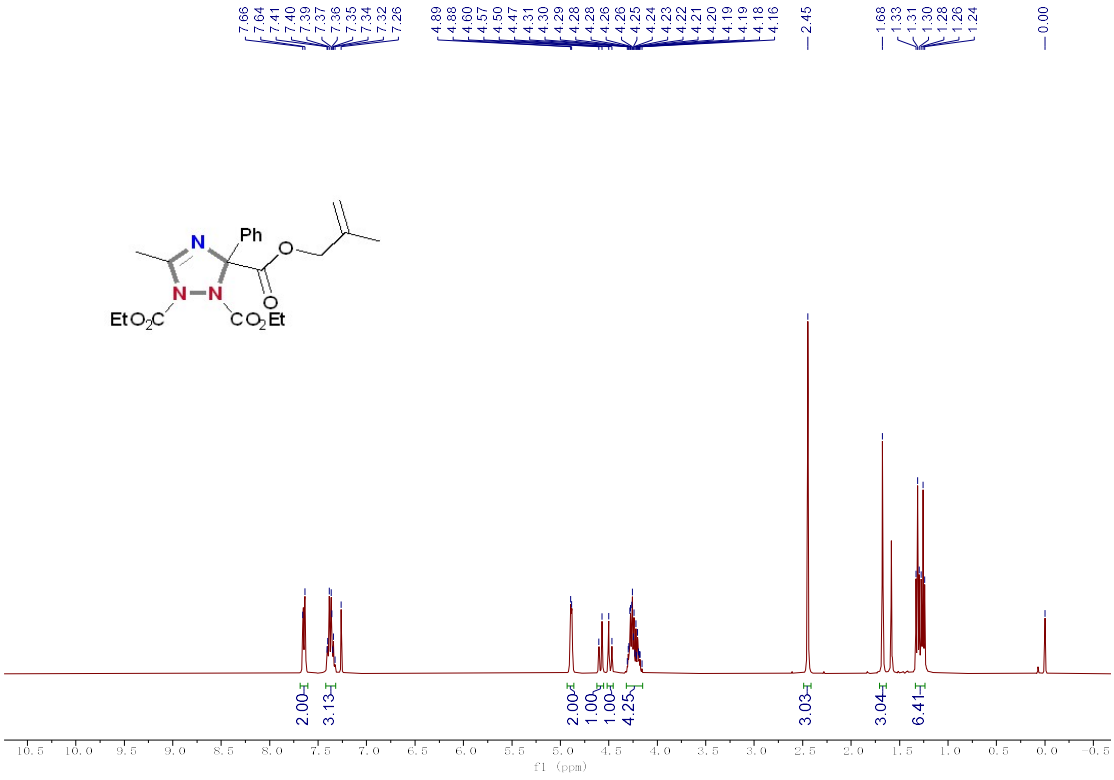
^{1}H NMR (400 MHz) Spectrum of 13o in $CDCl_3$



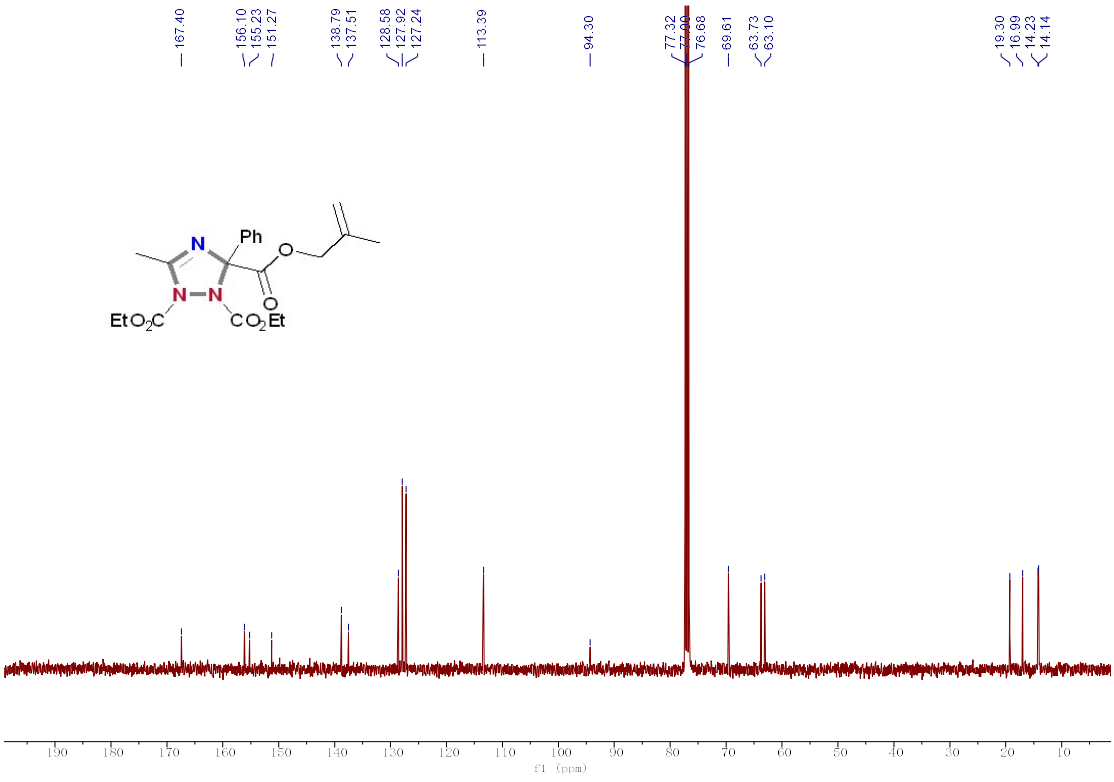
^{13}CNMR (100 MHz) Spectrum of 13o in $CDCl_3$



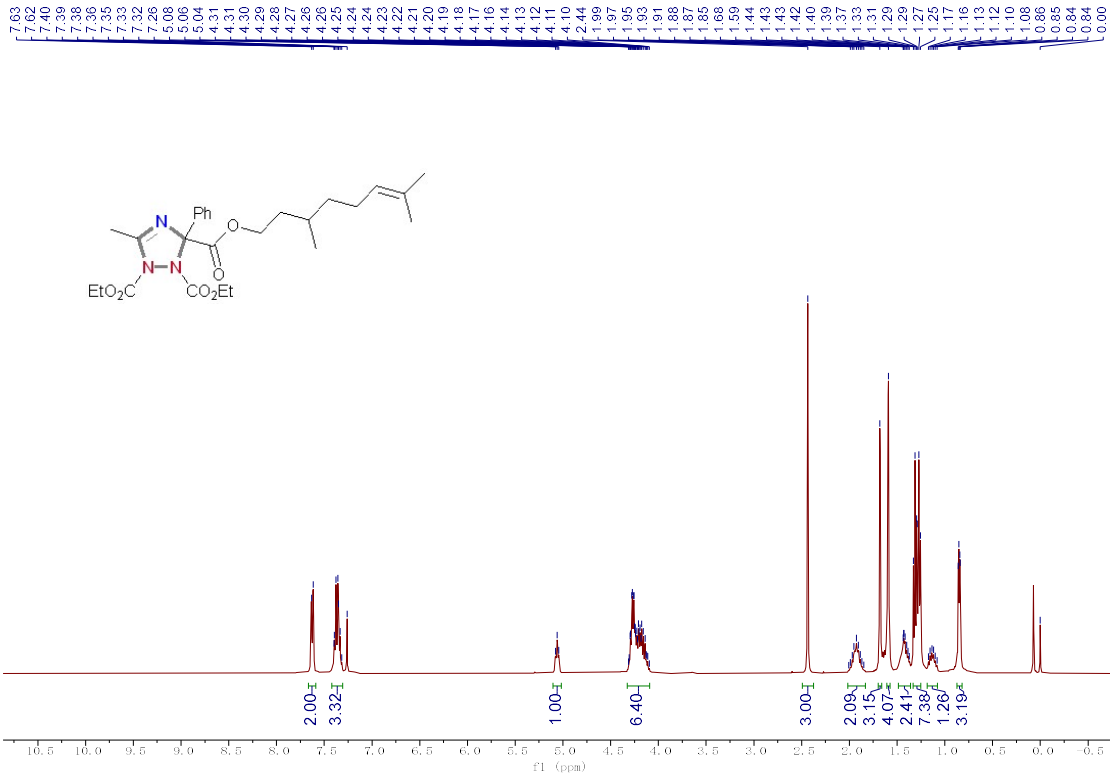
^{1}H NMR (400 MHz) Spectrum of 13p in $CDCl_3$



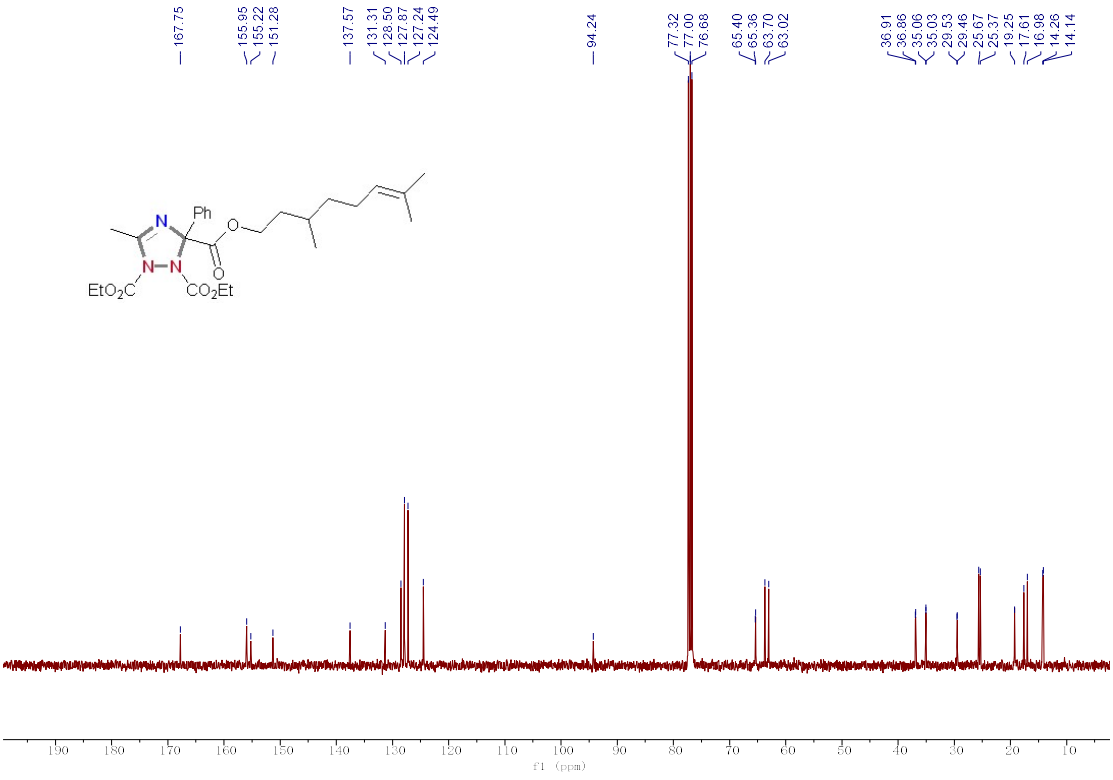
^{13}CNMR (100 MHz) Spectrum of 13p in $CDCl_3$



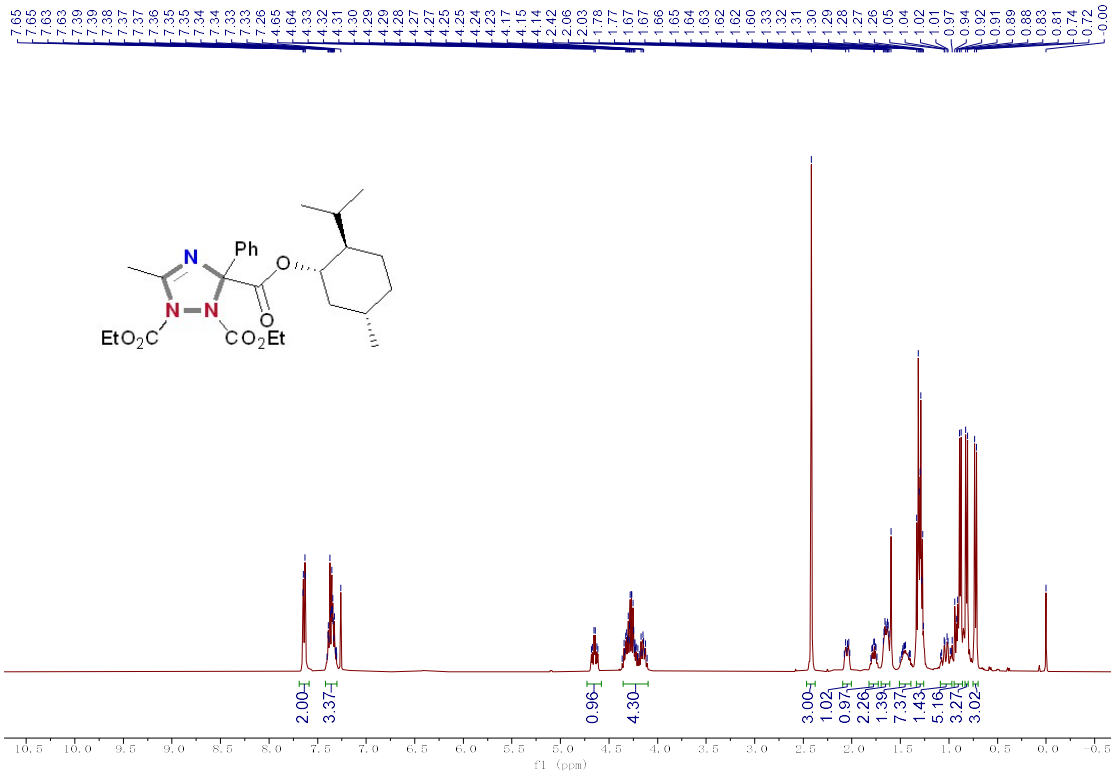
^{1}H NMR (400 MHz) Spectrum of 13q in $CDCl_3$



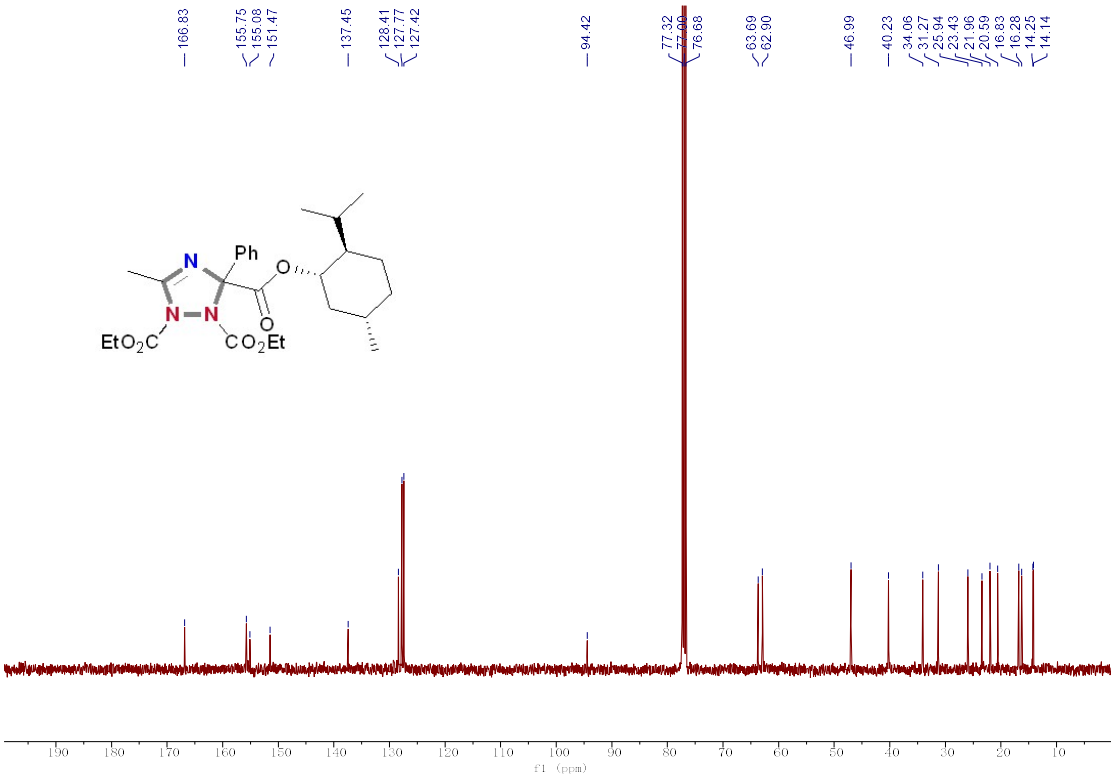
^{13}CNMR (100 MHz) Spectrum of 13q in $CDCl_3$



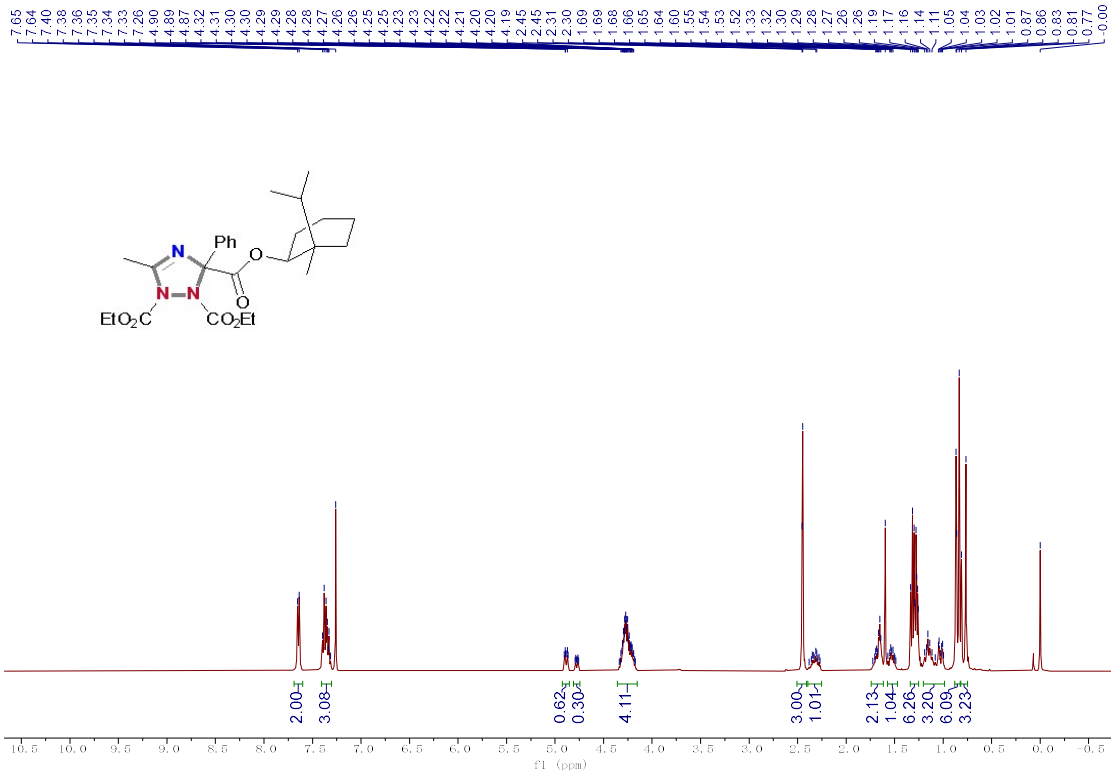
^{1}H NMR (400 MHz) Spectrum of 13r in $CDCl_3$



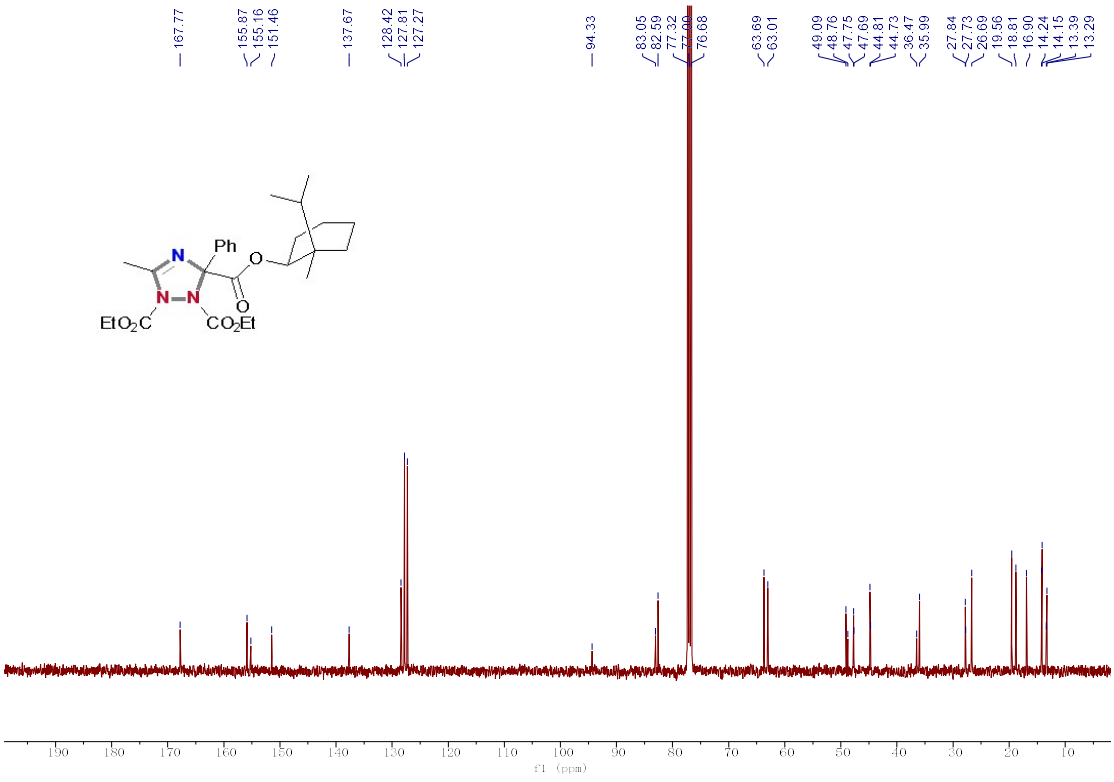
^{13}CNMR (100 MHz) Spectrum of 13r in $CDCl_3$



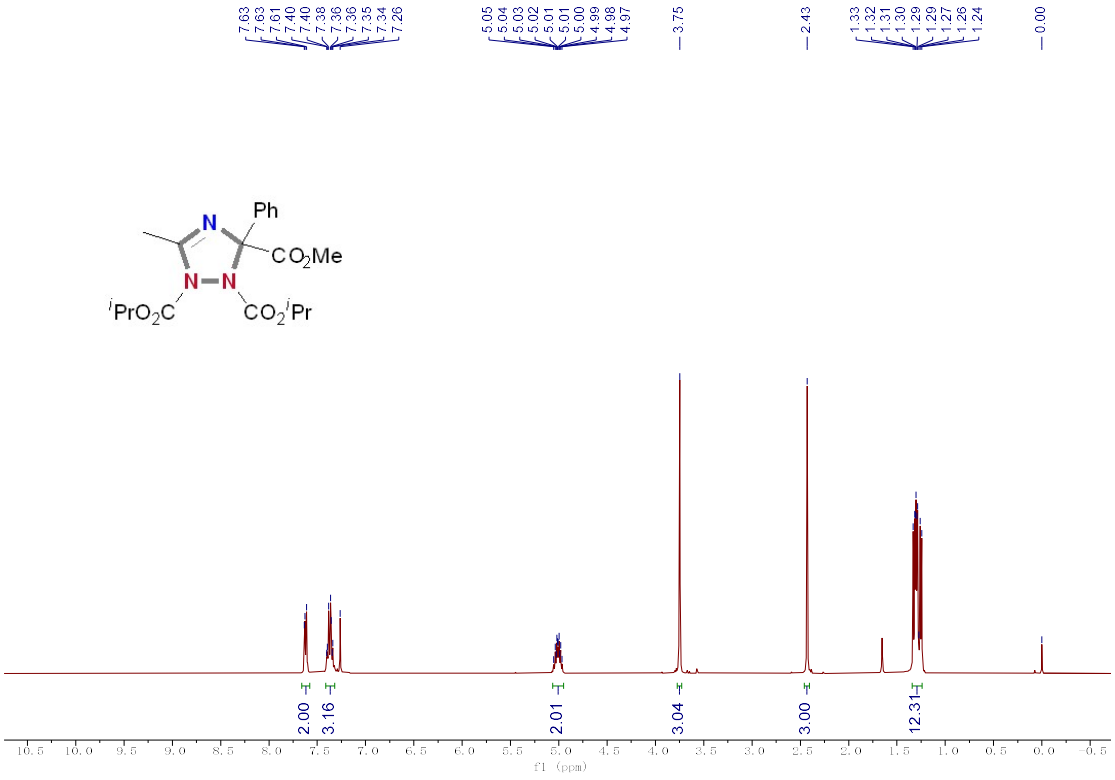
^{1}H NMR (400 MHz) Spectrum of 13s in $CDCl_3$



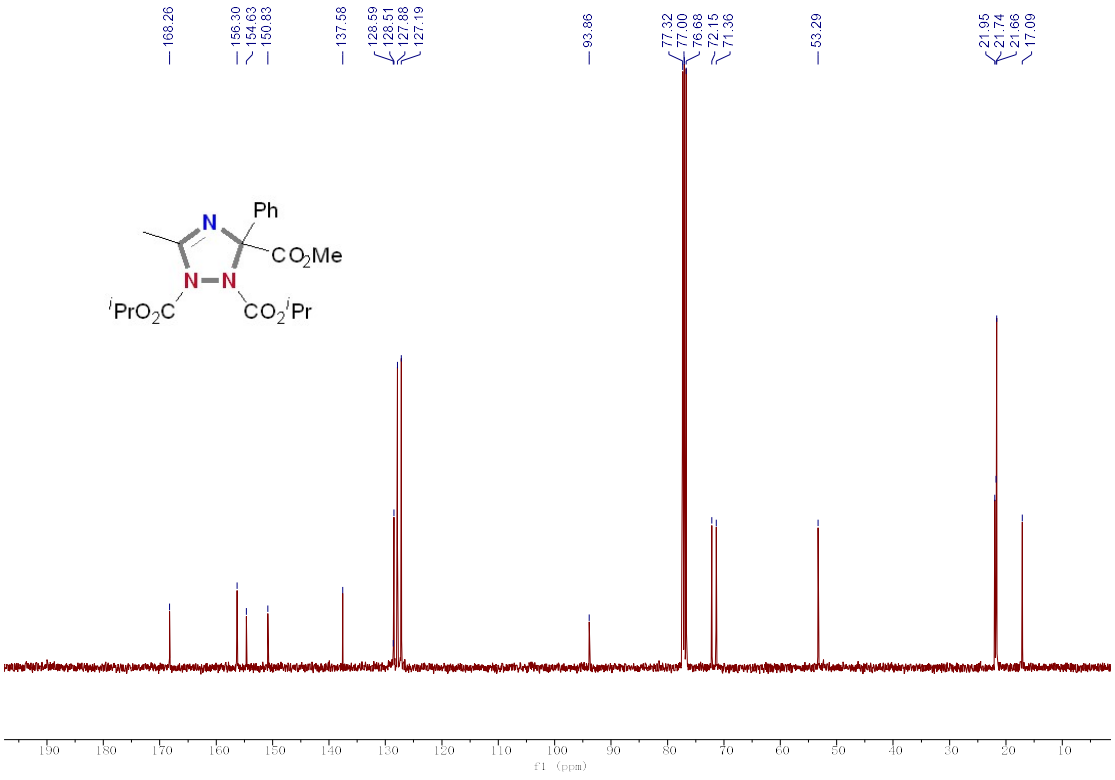
^{13}CNMR (100 MHz) Spectrum of 13s in $CDCl_3$



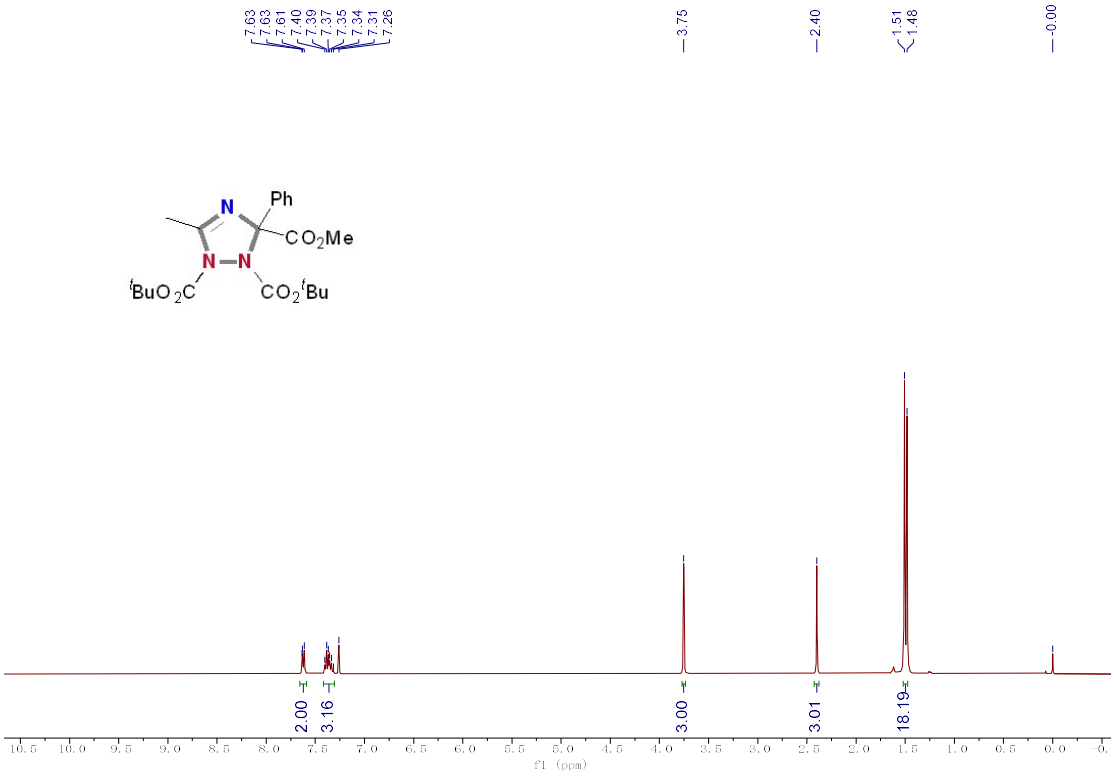
^{1}H NMR (400 MHz) Spectrum of 13t in $CDCl_3$



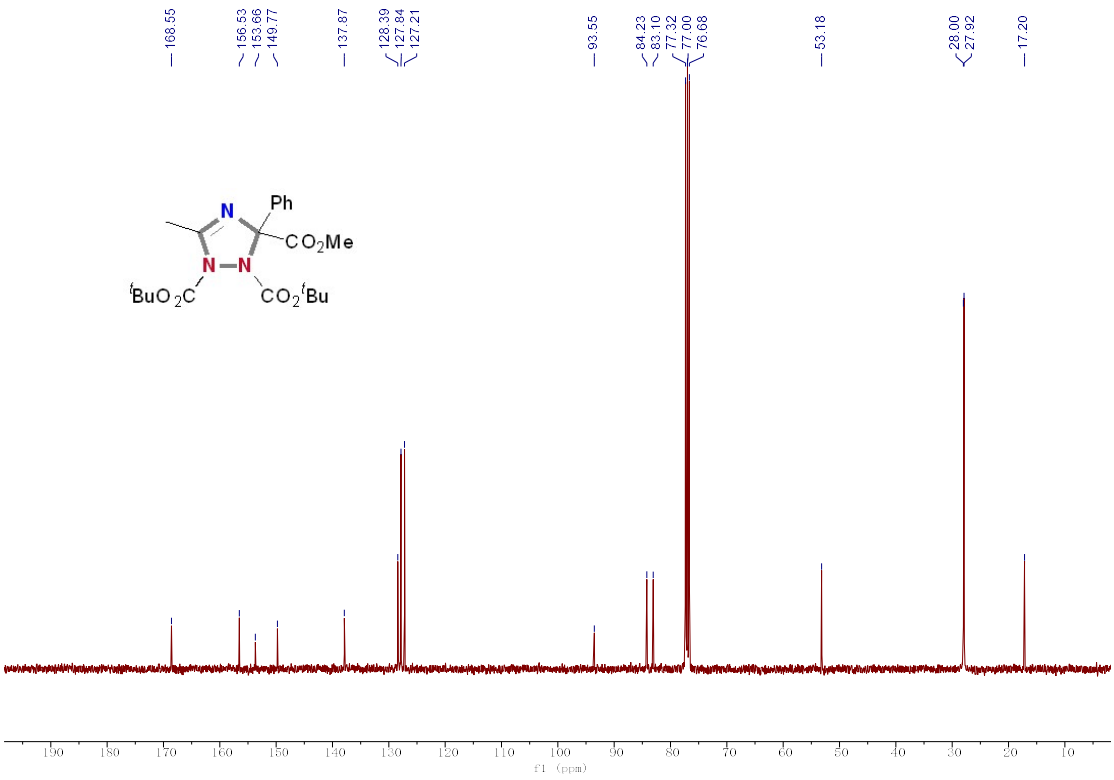
^{13}CNMR (100 MHz) Spectrum of 13t in $CDCl_3$



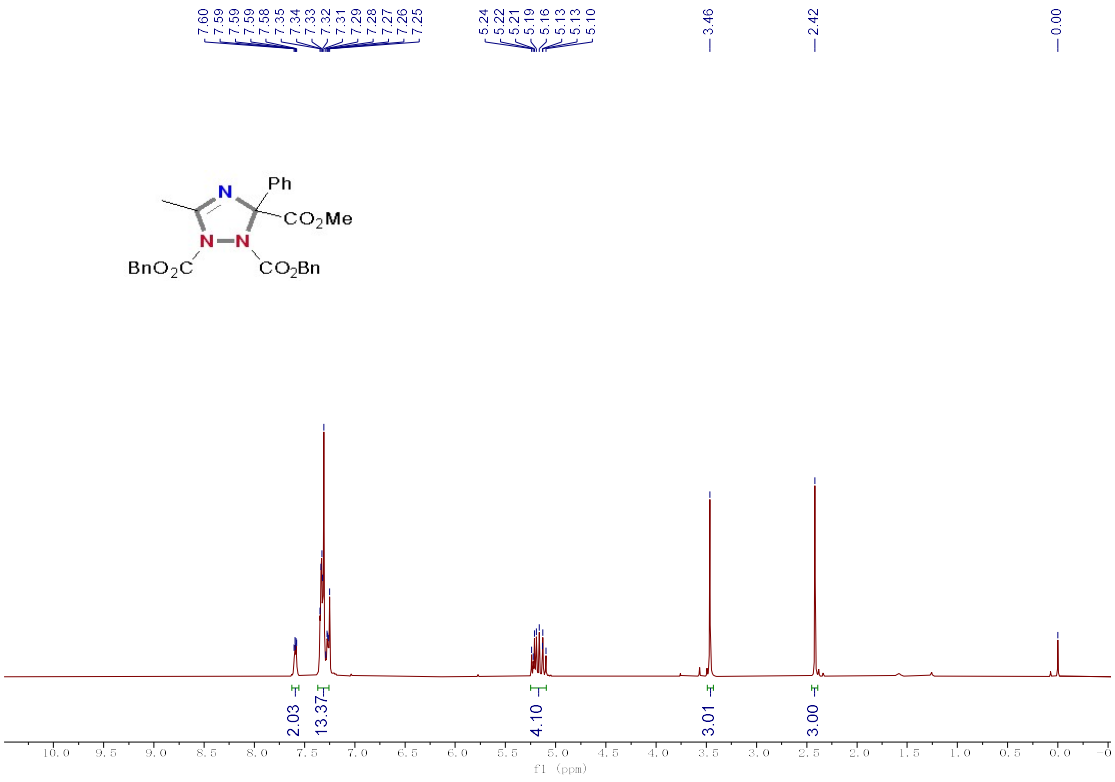
^{1}H NMR (400 MHz) Spectrum of 13u in $CDCl_3$



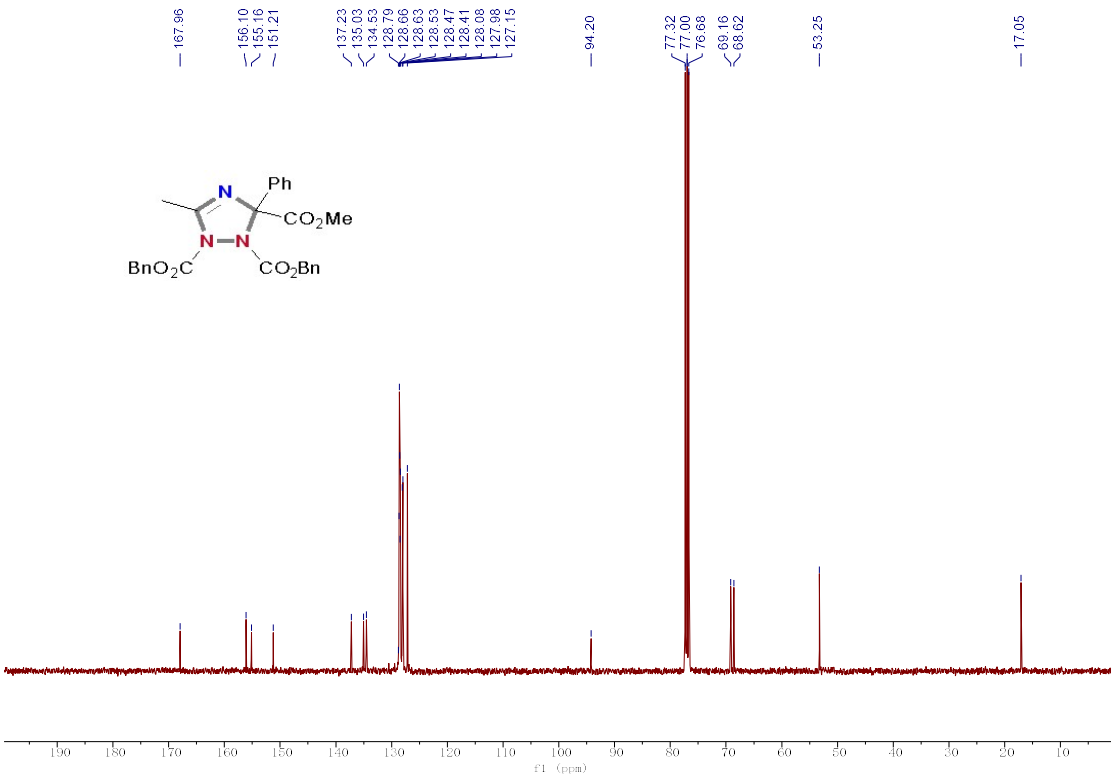
^{13}CNMR (100 MHz) Spectrum of 13u in $CDCl_3$



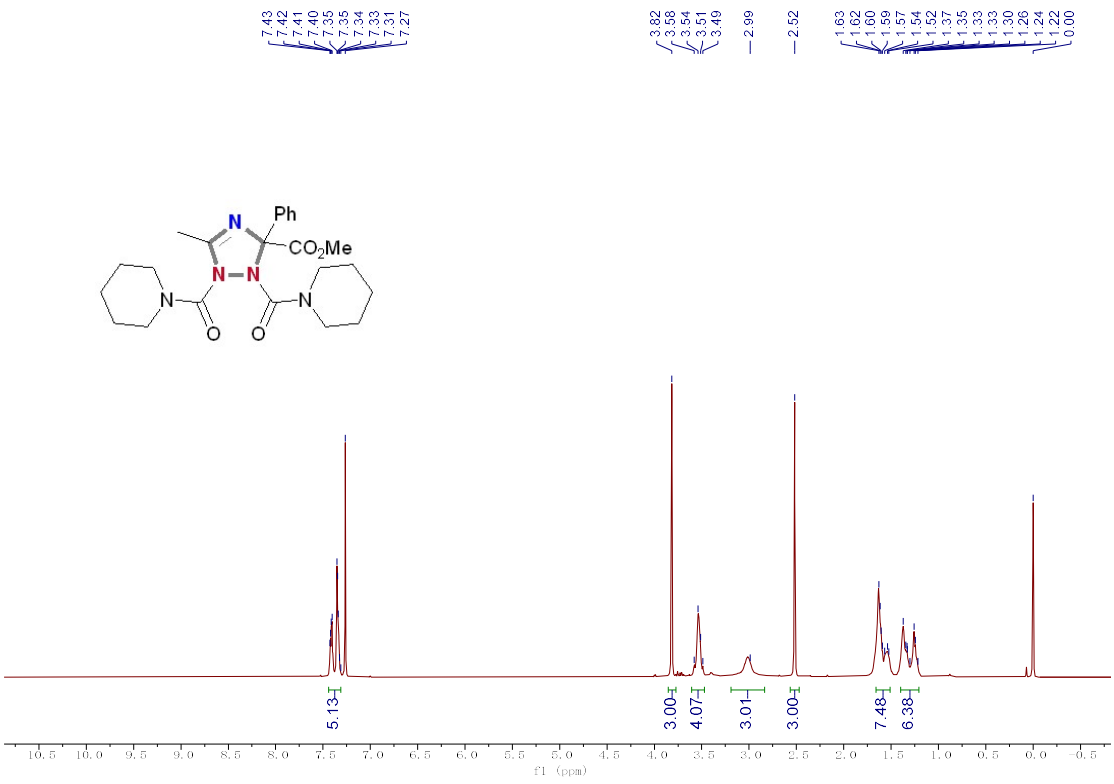
^{1}H NMR (400 MHz) Spectrum of 13v in $CDCl_3$



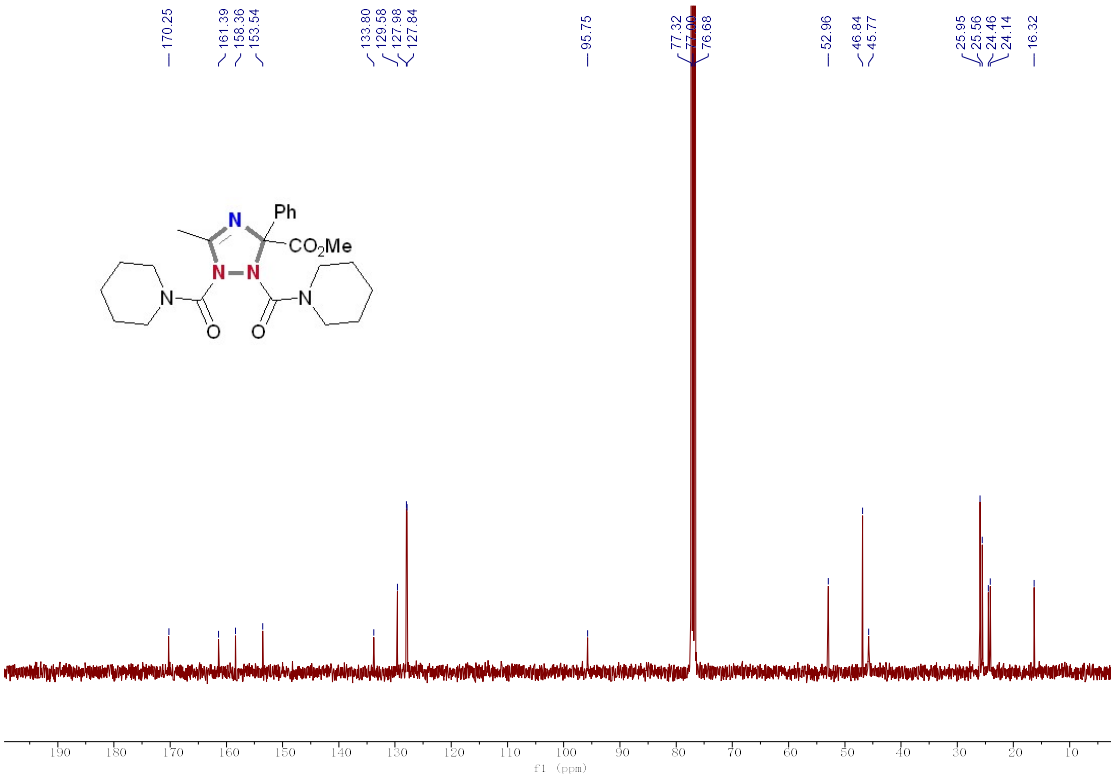
^{13}CNMR (100 MHz) Spectrum of 13v in $CDCl_3$



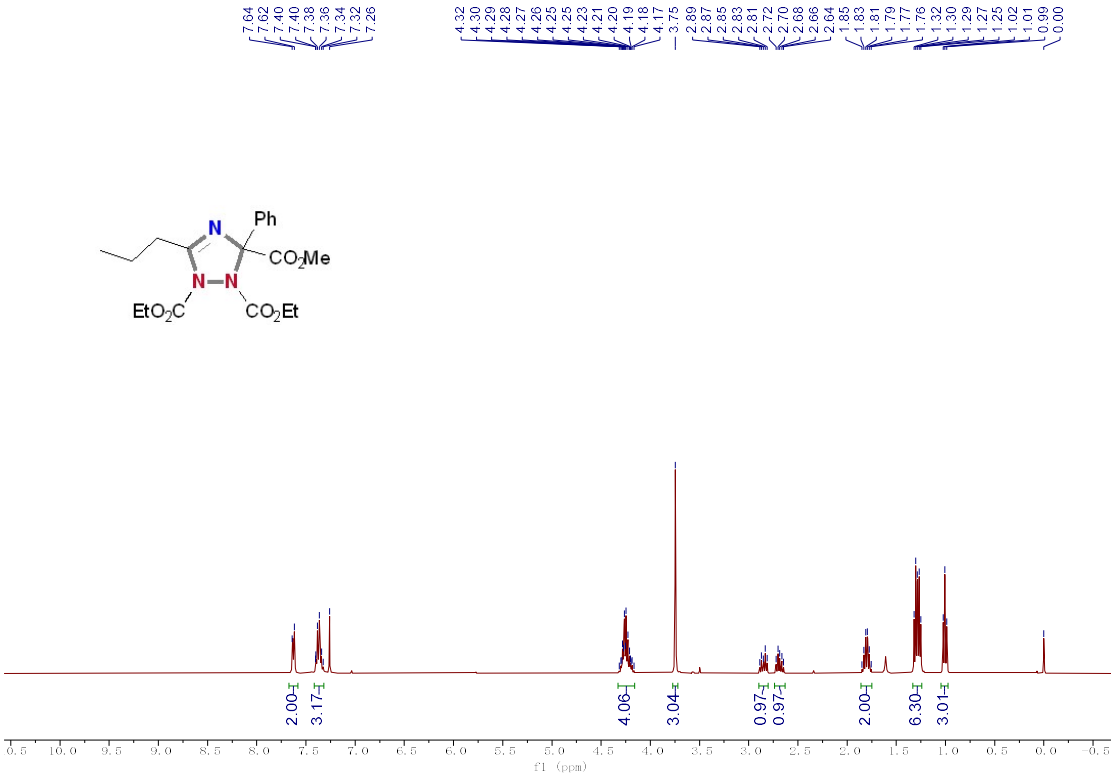
^{1}H NMR (400 MHz) Spectrum of 13w in $CDCl_3$



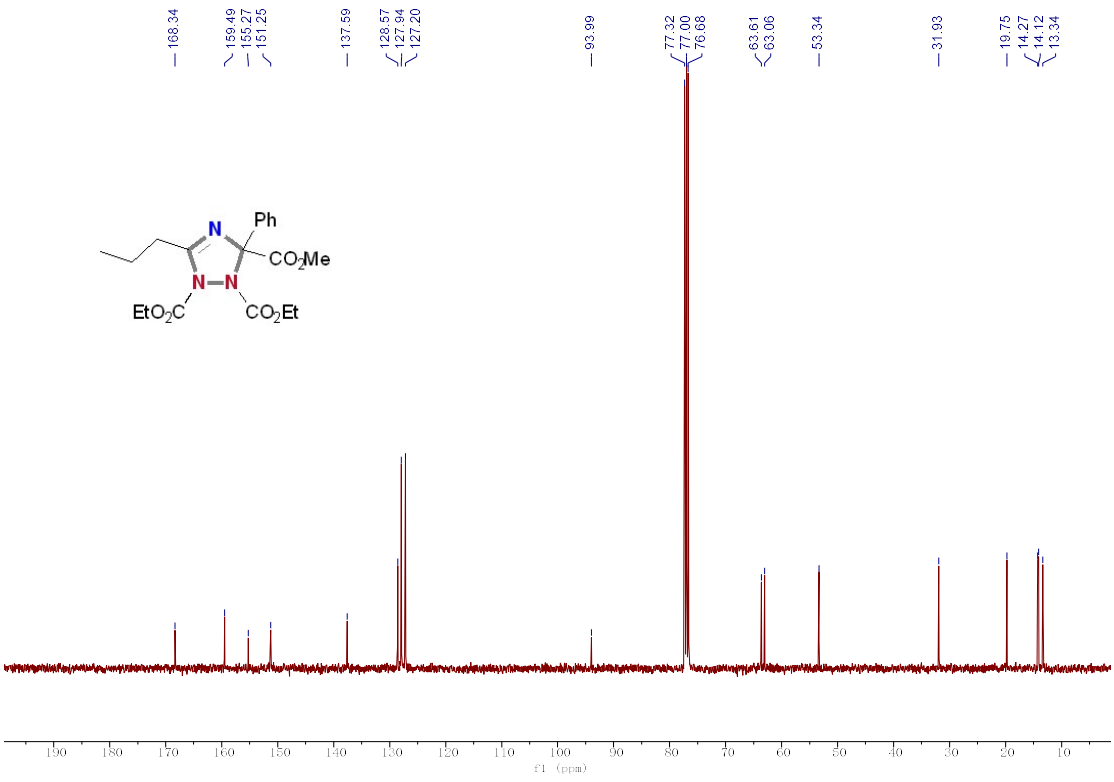
^{13}CNMR (100 MHz) Spectrum of 13w in $CDCl_3$



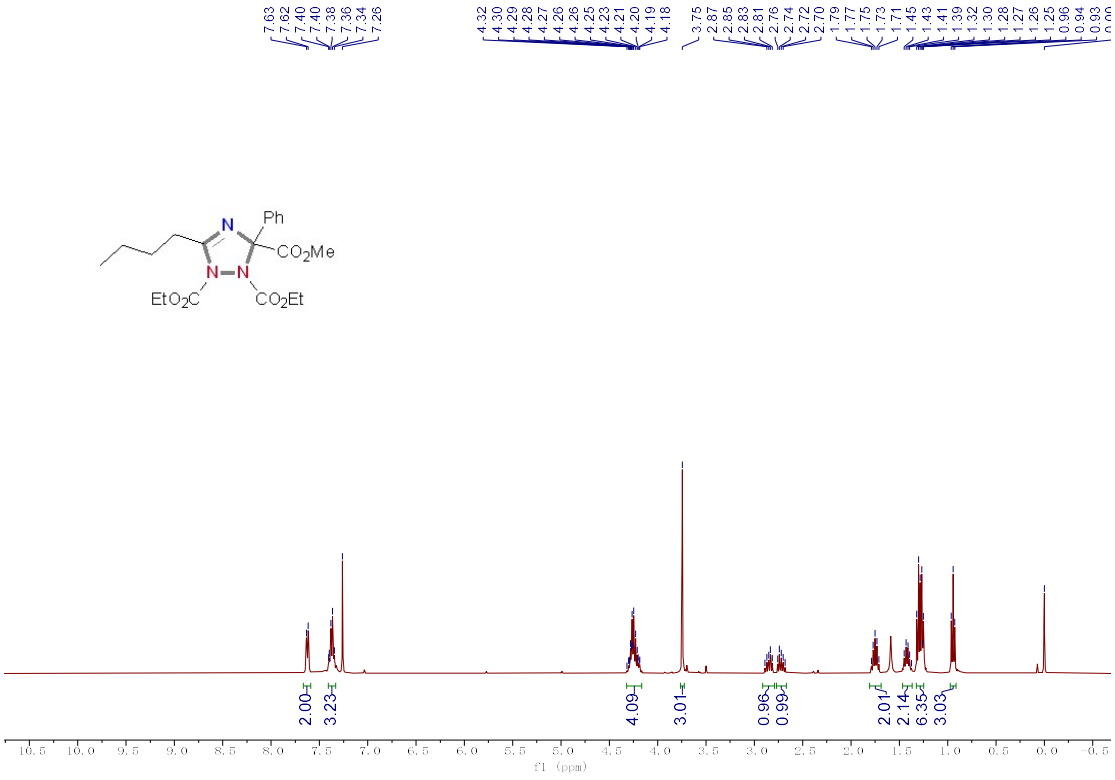
^{1}H NMR (400 MHz) Spectrum of 13x in $CDCl_3$



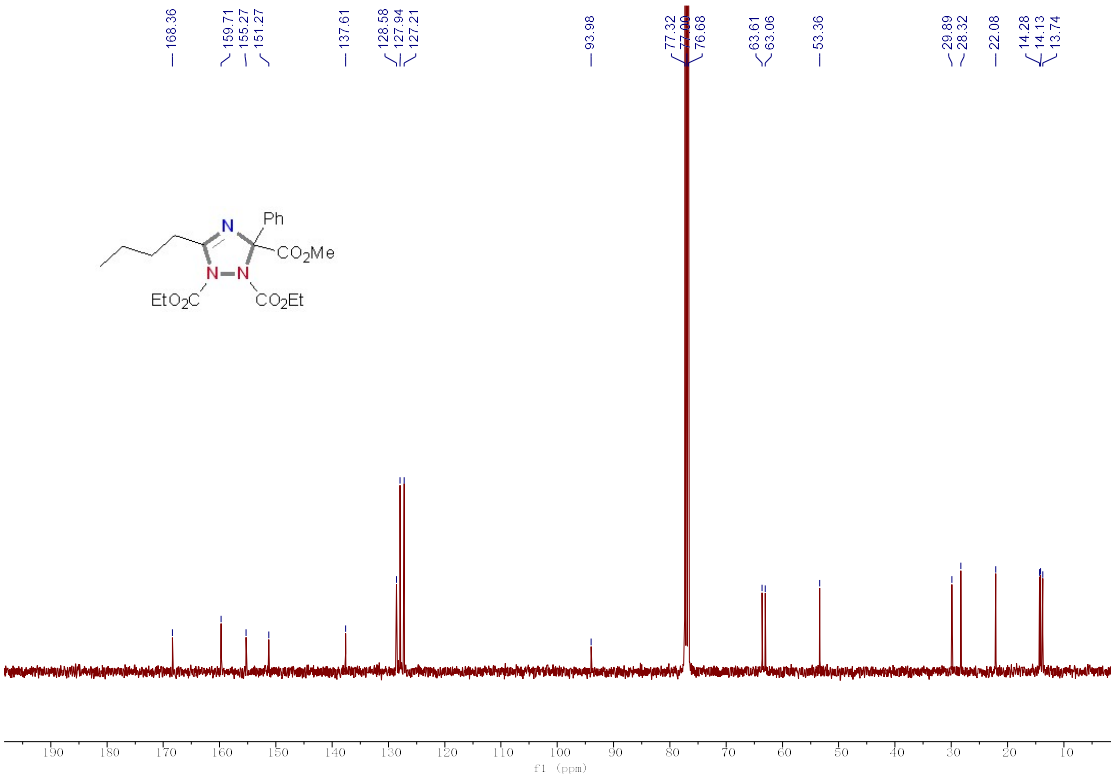
^{13}CNMR (100 MHz) Spectrum of 13x in $CDCl_3$



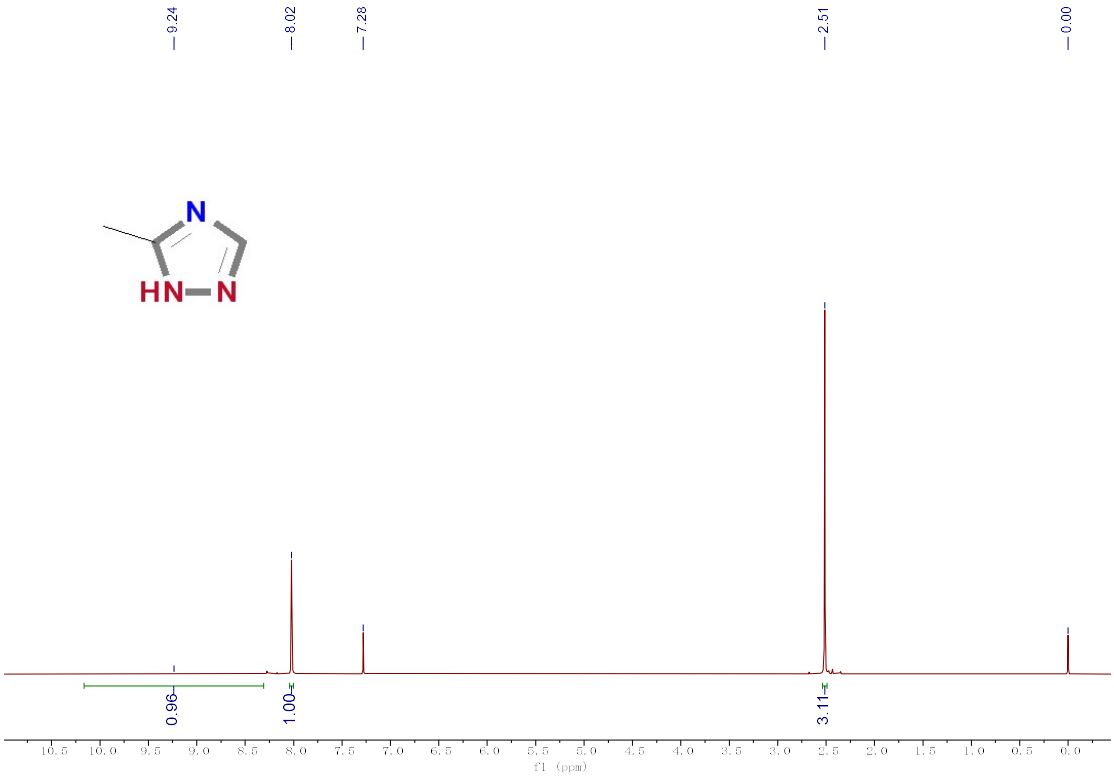
^{1}H NMR (400 MHz) Spectrum of 13y in $CDCl_3$



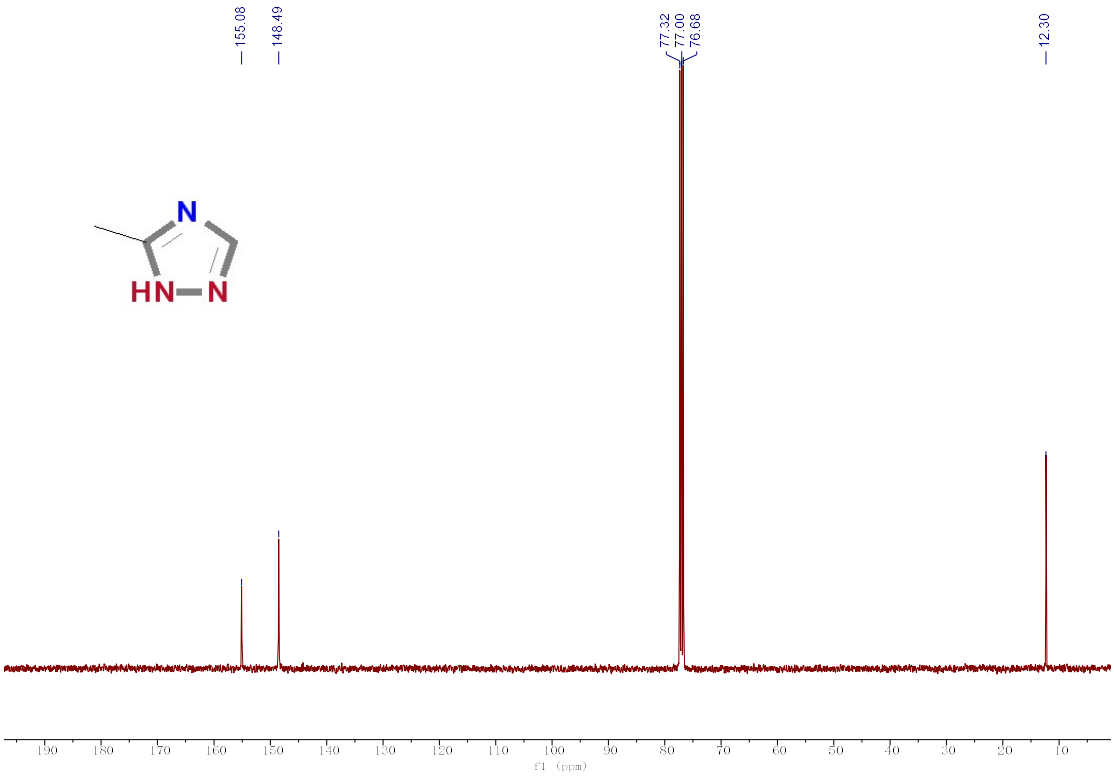
^{13}CNMR (100 MHz) Spectrum of 13y in $CDCl_3$



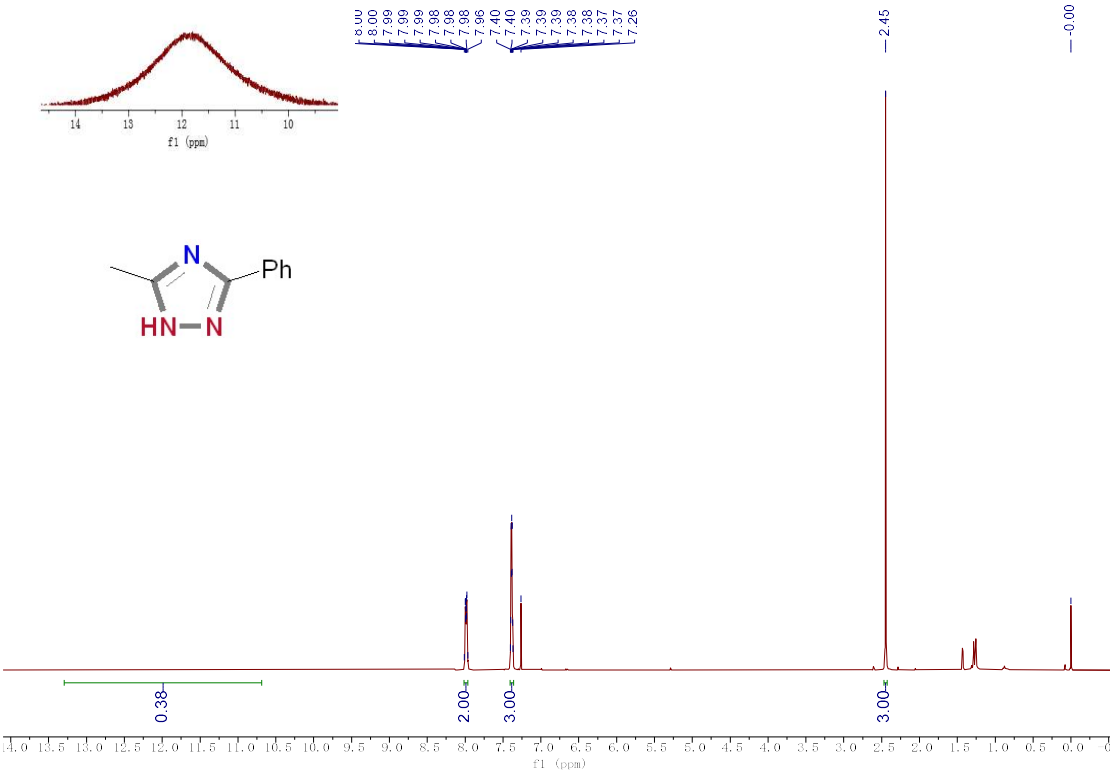
^{1}H NMR (400 MHz) Spectrum of 20 in $CDCl_3$



^{13}CNMR (100 MHz) Spectrum of 20 in $CDCl_3$



^{1}H NMR (400 MHz) Spectrum of 21 in $CDCl_3$



^{13}CNMR (100 MHz) Spectrum of 21 in $CDCl_3$