

Supporting Information

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A: General Information and Starting Materials

General Information. Proton nuclear magnetic resonance (^1H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker ACF300 spectrometer (500 MHz and 125 MHz). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent (CDCl_3 : δ 7.26). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent (CDCl_3 : δ 77.16). Data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz). All high resolution mass spectra were obtained on a Finnigan/MAT 95XL-T mass spectrometer. For thin layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. Flash chromatography separations were performed on Merck 60 (0.040-0.063 mm) mesh silica gel.

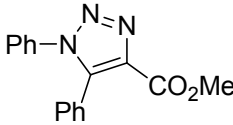
Starting Materials. All solvents and inorganic reagents were from commercial sources and used without purification unless otherwise noted. The azides were prepared following the literature procedures.¹

B: General Procedure for Cycloadditions of α,β -Unsaturated Esters with Azides.

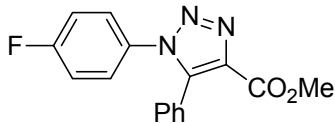
To a solution of CH_3CN (0.3 mL) were added α,β -unsaturated esters **1** (0.10 mmol), azides **2** (0.15 mmol), catalyst **V** (0.02 mmol) and Cs_2CO_3 (0.02 mmol). The reaction mixture was stirred at 80°C for 72 h in air and then the solvent was removed under vacuum to give a residue, which was purified by silica gel chromatography to yield the desired product.

C: Characterization Data for Triazoles

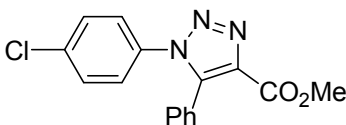
Methyl 1,5-diphenyl-1*H*-1,2,3-triazole-4-carboxylate (3aa)

 White solid, 61% yield. ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 7.42-7.36 (m, 6H), 7.30-7.28 (m, 4H), 3.91 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 161.4, 141.0, 136.6, 135.8, 130.2, 130.0, 129.5, 129.3, 128.4, 125.5, 125.2, 52.2. HRMS (EI): exact mass calculated for M (C₁₆H₁₃N₃O₂) requires m/z 279.1008, found m/z 279.1001.

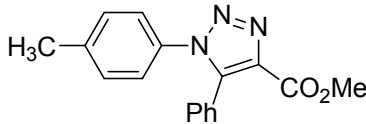
Methyl 1-(4-fluorophenyl)-5-phenyl-1*H*-1,2,3-triazole-4-carboxylate (3ab)

 White solid, 57% yield. ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 7.44-7.38 (m, 3H), 7.29-7.27 (m, 3H), 7.26-7.25 (m, 1H), 7.09-7.05 (m, 2H), 3.90 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 162.8 (d, *J* = 1000.0 Hz), 161.3, 141.1, 136.6, 131.8 (d, *J* = 15.0 Hz), 130.2, 130.1, 128.5, 127.1 (d, *J* = 35.0 Hz), 125.3, 116.4 (d, *J* = 95.0 Hz), 52.2. HRMS (EI): exact mass calculated for M (C₁₆H₁₂FN₃O₂) requires m/z 297.0914, found m/z 297.0905.

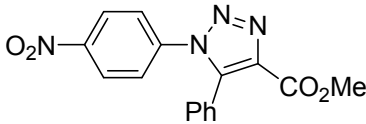
Methyl 1-(4-chlorophenyl)-5-phenyl-1*H*-1,2,3-triazole-4-carboxylate (3ac)

 White solid, 52% yield. ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 7.47-7.44 (m, 1H), 7.42-7.39 (m, 2H), 7.36-7.35 (m, 2H), 7.29-7.28 (m, 2H), 7.23-7.21 (m, 2H), 3.91 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 161.2, 140.9, 136.8, 135.6, 134.2, 130.2, 130.1, 129.6, 128.6, 126.3, 125.3, 52.2. HRMS (EI): exact mass calculated for M (C₁₆H₁₂ClN₃O₂) requires m/z 313.0618, found m/z 313.0613.

Methyl 5-phenyl-1-(*p*-tolyl)-1*H*-1,2,3-triazole-4-carboxylate (3ad)

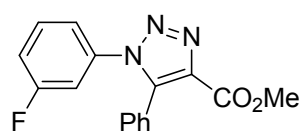
 White solid, 51% yield. ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 7.44-7.36 (m, 3H), 7.30-7.28 (m, 2H), 7.17-7.13 (m, 4H), 3.90 (s, 3H), 2.36 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 161.5, 140.9, 139.7, 136.5, 133.3, 130.2, 129.9, 129.8, 128.4, 125.7, 125.0, 52.1, 21.2. HRMS (EI): exact mass calculated for M (C₁₇H₁₅N₃O₂) requires m/z 293.1164, found m/z 293.1160.

Methyl 1-(4-nitrophenyl)-5-phenyl-1*H*-1,2,3-triazole-4-carboxylate (3ae)

 Yellow oil, 65% yield. ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 8.26-8.24 (m, 2H), 7.50-7.48 (m, 3H), 7.45-7.42 (m, 2H), 7.31-7.30 (m, 2H), 3.91 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 160.9, 147.7, 141.1,

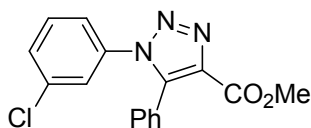
140.5, 137.3, 130.7, 130.1, 128.9, 125.5, 124.9, 124.8, 52.3. HRMS (EI): exact mass calculated for M (C₁₆H₁₂N₄O₄) requires m/z 324.0859, found m/z 324.0854.

Methyl 1-(3-fluorophenyl)-5-phenyl-1*H*-1,2,3-triazole-4-carboxylate (3af)



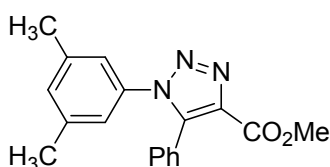
White solid, 53% yield. ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 7.47-7.45 (m, 1H), 7.42-7.39 (m, 2H), 7.37-7.29 (m, 3H), 7.14-7.11 (m, 1H), 7.07-7.04 (m, 2H), 3.91 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 162.4 (d, *J* = 995.0 Hz), 161.2, 141.0, 136.9 (d, *J* = 35.0 Hz), 136.8, 130.7 (d, *J* = 35.0 Hz), 130.3, 130.1, 128.6, 125.2, 120.8 (d, *J* = 15.0 Hz), 116.7 (d, *J* = 90.0 Hz), 112.9 (d, *J* = 90.0 Hz), 52.2. HRMS (EI): exact mass calculated for M (C₁₆H₁₂FN₃O₂) requires m/z 297.0914, found m/z 297.0911.

Methyl 1-(3-chlorophenyl)-5-phenyl-1*H*-1,2,3-triazole-4-carboxylate (3ag)



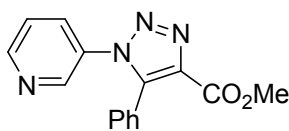
White solid, 55% yield. ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 7.47-7.44 (m, 1H), 7.42-7.38 (m, 4H), 7.30-7.27 (m, 3H), 7.09-7.07 (m, 1H), 3.90 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 161.2, 141.0, 136.8, 136.7, 135.1, 130.3, 130.2, 130.1, 129.7, 128.6, 125.4, 125.2, 123.2, 52.2. HRMS (EI): exact mass calculated for M (C₁₆H₁₂ClN₃O₂) requires m/z 313.0618, found m/z 313.0611.

Methyl 1-(3,5-dimethylphenyl)-5-phenyl-1*H*-1,2,3-triazole-4-carboxylate (3ah)



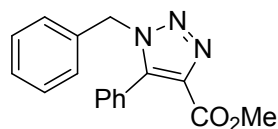
White solid, 49% yield. ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 7.44-7.36 (m, 3H), 7.30-7.29 (m, 2H), 7.02 (s, 1H), 6.86 (s, 2H), 3.91 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 161.5, 140.9, 139.2, 136.4, 135.6, 131.1, 130.2, 129.9, 128.3, 125.7, 122.9, 52.1, 21.1. HRMS (EI): exact mass calculated for M (C₁₈H₁₇N₃O₂) requires m/z 307.1321, found m/z 307.1316.

Methyl 5-phenyl-1-(pyridin-3-yl)-1*H*-1,2,3-triazole-4-carboxylate (3ai)



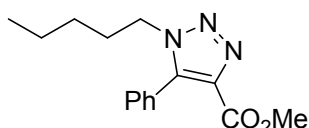
White solid, 63% yield. ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 8.65-8.64 (m, 1H), 8.54 (s, 1H), 7.67-7.65 (m, 1H), 7.47-7.44 (m, 1H), 7.42-7.35 (m, 3H), 7.30-7.28 (m, 2H), 3.90 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 161.1, 150.5, 145.8, 141.3, 136.9, 132.6, 132.3, 130.5, 130.1, 128.8, 124.9, 123.8, 52.3. HRMS (EI): exact mass calculated for M (C₁₅H₁₂N₄O₂) requires m/z 280.0960, found m/z 280.0958.

Methyl 1-benzyl-5-phenyl-1*H*-1,2,3-triazole-4-carboxylate (3aj)



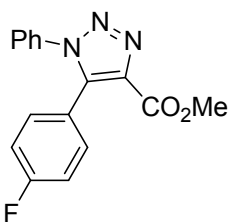
Yellow oil, 52% yield. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 7.51-7.48 (m, 1H), 7.45-7.42 (m, 2H), 7.24-7.23 (m, 3H), 7.20-7.19 (m, 2H), 7.00-6.98 (m, 2H), 5.43 (s, 2H), 3.83 (s, 3H). ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 161.3, 141.4, 136.8, 134.5, 130.2, 129.7, 128.8, 128.6, 128.4, 127.5, 125.7, 52.2, 52.0. HRMS (EI): exact mass calculated for M ($\text{C}_{17}\text{H}_{15}\text{N}_3\text{O}_2$) requires m/z 293.1164, found m/z 293.1156.

Methyl 1-pentyl-5-phenyl-1H-1,2,3-triazole-4-carboxylate (3ak)



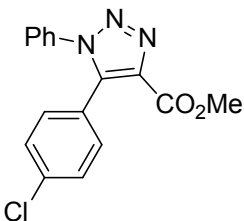
Yellow oil, 53% yield. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 7.53-7.51 (m, 3H), 7.36-7.35 (m, 2H), 4.22 (t, $J = 10.0$ Hz, 2H), 3.84 (s, 3H), 1.80-1.74 (m, 2H), 1.25-1.15 (m, 4H), 0.81 (t, $J = 10.0$ Hz, 3H). ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 161.5, 141.1, 136.5, 130.1, 129.6, 128.7, 126.1, 51.9, 48.5, 29.6, 28.4, 21.9, 13.7. HRMS (EI): exact mass calculated for M ($\text{C}_{15}\text{H}_{19}\text{N}_3\text{O}_2$) requires m/z 273.1477, found m/z 273.1472.

Methyl 5-(4-fluorophenyl)-1-phenyl-1H-1,2,3-triazole-4-carboxylate (3ba)



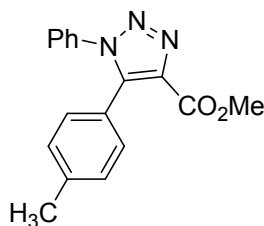
White solid, 50% yield. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 7.45-7.39 (m, 3H), 7.31-7.27 (m, 4H), 7.09-7.05 (m, 2H), 3.91 (s, 3H). ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 163.5 (d, $J = 1000.0$ Hz), 161.4, 140.1, 136.6, 135.6, 132.4 (d, $J = 35.0$ Hz), 129.7, 129.5, 125.3, 121.4 (d, $J = 15.0$ Hz), 115.8 (d, $J = 85.0$ Hz), 52.2. HRMS (EI): exact mass calculated for M ($\text{C}_{16}\text{H}_{12}\text{FN}_3\text{O}_2$) requires m/z 297.0914, found m/z 297.0910.

Methyl 5-(4-chlorophenyl)-1-phenyl-1H-1,2,3-triazole-4-carboxylate (3ca)



White solid, 52% yield. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 7.44-7.40 (m, 3H), 7.36-7.34 (m, 2H), 7.27-7.26 (m, 2H), 7.25-7.23 (m, 2H), 3.91 (s, 3H). ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 161.3, 139.9, 136.7, 136.4, 135.5, 131.6, 129.8, 129.5, 128.8, 125.2, 123.9, 52.2. HRMS (EI): exact mass calculated for M ($\text{C}_{16}\text{H}_{12}\text{ClN}_3\text{O}_2$) requires m/z 313.0618, found m/z 313.0607.

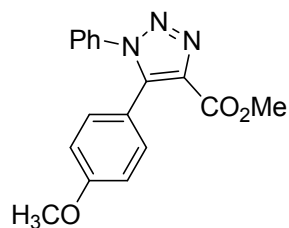
Methyl 1-phenyl-5-(p-tolyl)-1H-1,2,3-triazole-4-carboxylate (3da)



White solid, 53% yield. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 7.43-7.37 (m, 3H), 7.29-7.27 (m, 2H), 7.18 (s, 4H), 3.91 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 161.5, 141.2, 140.2, 136.5, 135.9, 130.1, 129.5, 129.3, 129.2, 125.2, 122.4, 52.1, 21.5. HRMS (EI): exact mass calculated for M

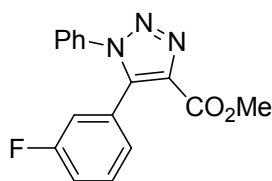
(C₁₇H₁₅N₃O₂) requires m/z 293.1164, found m/z 293.1159.

Methyl 5-(4-methoxyphenyl)-1-phenyl-1*H*-1,2,3-triazole-4-carboxylate (3ea)



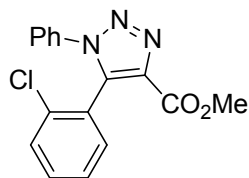
Yellow oil, 51% yield. ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 7.43-7.38 (m, 3H), 7.29-7.27 (m, 2H), 7.23 (d, *J* = 10.0 Hz, 2H), 6.88 (d, *J* = 10.0 Hz, 2H), 3.92 (s, 3H), 3.82 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 161.6, 160.8, 140.9, 136.3, 135.9, 131.7, 129.4, 129.3, 125.3, 117.2, 113.9, 55.3, 52.1. HRMS (EI): exact mass calculated for M (C₁₇H₁₅N₃O₃) requires m/z 309.1113, found m/z 309.1107.

Methyl 5-(3-fluorophenyl)-1-phenyl-1*H*-1,2,3-triazole-4-carboxylate (3fa)



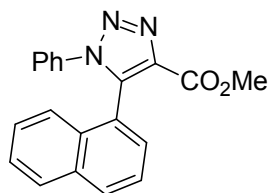
White solid, 51% yield. ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 7.44-7.39 (m, 3H), 7.37-7.33 (m, 1H), 7.28-7.27 (m, 2H), 7.15-7.11 (m, 1H), 7.07-7.03 (m, 2H), 3.92 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 163.2, 161.2, 139.6 (d, *J* = 10.0 Hz), 136.8, 135.5, 130.1 (d, *J* = 30.0 Hz), 129.8, 129.5, 127.5 (d, *J* = 30.0 Hz), 126.1 (d, *J* = 10.0 Hz), 125.2, 117.5 (d, *J* = 95.0 Hz), 117.2 (d, *J* = 80.0 Hz), 52.3. HRMS (EI): exact mass calculated for M (C₁₆H₁₂FN₃O₂) requires m/z 297.0914, found m/z 297.0911.

Methyl 5-(2-chlorophenyl)-1-phenyl-1*H*-1,2,3-triazole-4-carboxylate (3ga)



White solid, 46% yield. ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 7.45-7.44 (m, 1H), 7.42-7.35 (m, 4H), 7.33-7.30 (m, 3H), 7.25-7.24 (m, 1H), 3.88 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 161.0, 138.5, 137.9, 135.7, 134.2, 131.7, 131.5, 129.9, 129.7, 129.3, 126.9, 125.9, 124.5, 52.2. HRMS (EI): exact mass calculated for M (C₁₆H₁₂ClN₃O₂) requires m/z 313.0618, found m/z 313.0609.

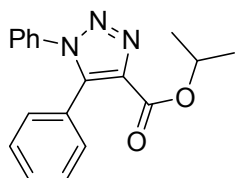
Methyl 5-(naphthalen-1-yl)-1-phenyl-1*H*-1,2,3-triazole-4-carboxylate (3ha)



Yellow solid, 52% yield. ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 7.98-7.91 (m, 2H), 7.54-7.38 (m, 5H), 7.31-7.24 (m, 5H), 3.79 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 161.0, 139.6, 138.5, 135.8, 133.3, 131.6, 130.6, 129.4, 129.2, 128.9, 128.7, 127.3, 126.5, 124.9, 124.4, 124.3, 123.7, 52.1. HRMS (EI): exact mass calculated for M (C₂₀H₁₅N₃O₂) requires m/z 329.1164, found m/z 329.1158.

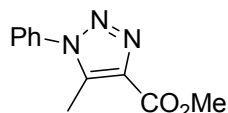
Isopropyl 1,5-diphenyl-1*H*-1,2,3-triazole-4-carboxylate (3ia)

White solid, 54% yield. ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 7.43-7.35 (m, 6H),



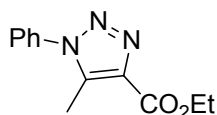
7.29-7.27 (m, 4H), 5.26-5.21 (m, 1H), 1.29 (d, $J = 5.0$ Hz, 6H). ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 160.5, 140.7, 137.4, 135.9, 130.3, 129.8, 129.4, 129.3, 128.3, 125.9, 125.2, 68.9, 21.7. HRMS (EI): exact mass calculated for M ($\text{C}_{18}\text{H}_{17}\text{N}_3\text{O}_2$) requires m/z 307.1312, found m/z 307.1314.

Methyl 5-methyl-1-phenyl-1H-1,2,3-triazole-4-carboxylate (3ja)



Yellow oil, 56% yield. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 7.60-7.54 (m, 3H), 7.46-7.44 (m, 2H), 3.99 (s, 3H), 2.60 (s, 3H). ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 162.2, 138.9, 136.5, 135.4, 130.1, 129.7, 125.3, 52.0, 9.9. HRMS (EI): exact mass calculated for M ($\text{C}_{11}\text{H}_{11}\text{N}_3\text{O}_2$) requires m/z 217.0851, found m/z 217.0846.

Ethyl 5-methyl-1-phenyl-1H-1,2,3-triazole-4-carboxylate (3ka)



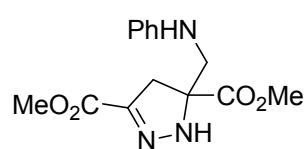
Yellow oil, 65% yield. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 7.58-7.55 (m, 3H), 7.46-7.44 (m, 2H), 4.47 (q, $J = 10.0$ Hz, 2H), 2.59 (s, 3H), 1.45 (t, $J = 10.0$ Hz, 3H). ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 161.8, 138.8, 136.7, 135.5, 130.1, 129.7, 125.4, 61.1, 14.4, 9.9. HRMS (EI): exact mass calculated for M ($\text{C}_{12}\text{H}_{13}\text{N}_3\text{O}_2$) requires m/z 231.1008, found m/z 231.1002.

D: General Procedure for Cycloadditions of Acrylic esters with Azides

To a solution of CHCl_3 (0.3 mL) were added acrylic esters **4** (0.10 mmol), azides **2** (0.20 mmol), catalyst **I** (0.005 mmol) and KH_2PO_4 (0.005 mmol). The reaction mixture was stirred at 50°C for 48 h in air and then the solvent was removed under vacuum to give a residue, which was purified by silica gel chromatography to yield the desired product.

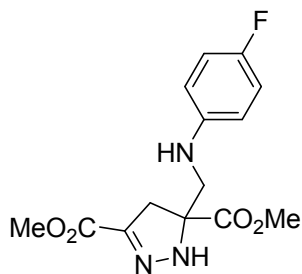
E: Characterization Data for Dihydropyrazoles

Dimethyl 5-((phenylamino)methyl)-4,5-dihydro-1H-pyrazole-3,5-dicarboxylate (**5aa**)



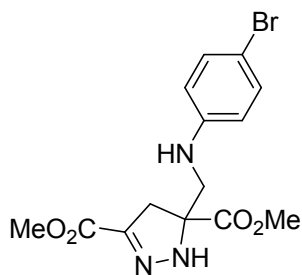
Yellow solid, 88% yield. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 7.19-7.17 (m, 2H), 6.89 (s, 1H), 6.77-6.74 (m, 1H), 6.65-6.64 (m, 2H), 3.84 (s, 3H), 3.77 (s, 3H), 3.53 (s, 2H), 3.41 (d, $J = 15.0$ Hz, 1H), 3.14 (d, $J = 15.0$ Hz, 1H). ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 173.3, 162.3, 147.4, 143.2, 129.5, 118.7, 113.5, 73.6, 53.4, 52.5, 49.0, 38.5. HRMS (ESI): exact mass calculated for M^+ ($\text{C}_{14}\text{H}_{18}\text{N}_3\text{O}_4$) requires m/z 292.1297, found m/z 292.1292.

Dimethyl 5-(((4-fluorophenyl)amino)methyl)-4,5-dihydro-1H-pyrazole-3,5-dicarboxylate (**5ab**)



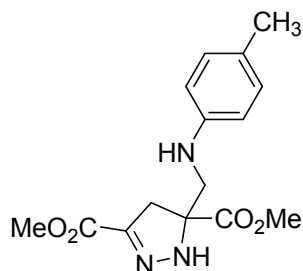
Yellow oil, 92% yield. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 6.90-6.88 (m, 2H), 6.86 (s, 1H), 6.59-6.57 (m, 2H), 3.84 (s, 3H), 3.77 (s, 3H), 3.51-3.45 (m, 2H), 3.41 (d, $J = 15.0$ Hz, 1H), 3.13 (d, $J = 15.0$ Hz, 1H). ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 173.1, 162.1, 156.3 (d, $J = 940.0$ Hz), 143.6 (d, $J = 10.0$ Hz), 143.2, 115.8 (d, $J = 85.0$ Hz), 114.4 (d, $J = 30.0$ Hz), 73.3, 53.3, 52.4, 49.7, 38.5. HRMS (ESI): exact mass calculated for M^+ ($\text{C}_{14}\text{H}_{17}\text{FN}_3\text{O}_4$) requires m/z 310.1198, found m/z 310.1191.

Dimethyl 5-(((4-bromophenyl)amino)methyl)-4,5-dihydro-1H-pyrazole-3,5-dicarboxylate (**5ac**)



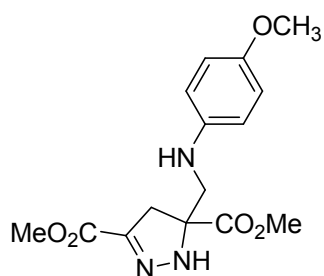
Yellow oil, 86% yield. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 7.24 (d, $J = 10.0$ Hz, 2H), 6.87 (s, 1H), 6.52 (d, $J = 10.0$ Hz, 2H), 3.84 (s, 3H), 3.77 (s, 3H), 3.49 (s, 2H), 3.41 (d, $J = 20.0$ Hz, 1H), 3.10 (d, $J = 20.0$ Hz, 1H). ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 173.0, 162.1, 146.3, 143.3, 132.1, 114.9, 110.2, 73.3, 53.4, 52.4, 48.8, 38.4. HRMS (ESI): exact mass calculated for M^+ ($\text{C}_{14}\text{H}_{17}\text{BrN}_3\text{O}_4$) requires m/z 370.0402, found m/z 370.0406.

Dimethyl 5-((*p*-tolylamino)methyl)-4,5-dihydro-1*H*-pyrazole-3,5-dicarboxylate (5ad)



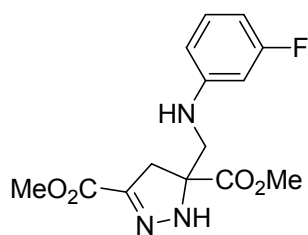
Yellow oil, 95% yield. ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 6.99 (d, *J* = 5.0 Hz, 2H), 6.88 (s, 1H), 6.57 (d, *J* = 5.0 Hz, 2H), 3.84 (s, 3H), 3.77 (s, 3H), 3.50 (s, 2H), 3.40 (d, *J* = 20.0 Hz, 1H), 3.13 (d, *J* = 20.0 Hz, 1H), 2.23 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 173.2, 162.2, 144.9, 143.1, 129.8, 127.9, 113.5, 73.5, 53.2, 52.4, 49.3, 38.4, 20.4. HRMS (ESI): exact mass calculated for M⁺ (C₁₅H₂₀N₃O₄) requires *m/z* 306.1454, found *m/z* 306.1449.

Dimethyl 5-(((4-methoxyphenyl)amino)methyl)-4,5-dihydro-1*H*-pyrazole-3,5-dicarboxylate (5ae)



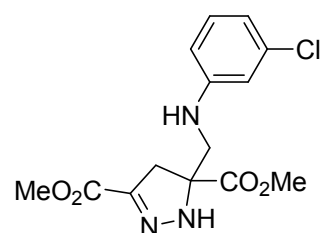
Yellow oil, 94% yield. ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 6.89 (s, 1H), 6.77 (d, *J* = 10.0 Hz, 2H), 6.61 (d, *J* = 10.0 Hz, 2H), 3.84 (s, 3H), 3.77 (s, 3H), 3.74 (s, 3H), 3.50-3.43 (m, 2H), 3.40 (d, *J* = 20.0 Hz, 1H), 3.14 (d, *J* = 20.0 Hz, 1H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 173.2, 162.2, 152.8, 143.1, 141.3, 114.9, 114.8, 73.5, 55.8, 53.3, 52.4, 50.1, 38.5. HRMS (ESI): exact mass calculated for M⁺ (C₁₅H₂₀N₃O₅) requires *m/z* 322.1397, found *m/z* 322.1401.

Dimethyl 5-(((3-fluorophenyl)amino)methyl)-4,5-dihydro-1*H*-pyrazole-3,5-dicarboxylate (5af)



Yellow oil, 68% yield. ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 7.11-7.07 (m, 1H), 6.89 (s, 1H), 6.44-6.39 (m, 2H), 6.35-6.33 (m, 1H), 3.84 (s, 3H), 3.77 (s, 3H), 3.51 (s, 2H), 3.41 (d, *J* = 20.0 Hz, 1H), 3.11 (d, *J* = 20.0 Hz, 1H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 172.9, 163.9 (d, *J* = 970.0 Hz), 162.1, 149.1 (d, *J* = 40.0 Hz), 143.2, 130.5 (d, *J* = 40.0 Hz), 109.1 (d, *J* = 5.0 Hz), 104.9 (d, *J* = 90.0 Hz), 100.1 (d, *J* = 90.0 Hz), 73.3, 53.3, 52.4, 48.7, 38.4. HRMS (ESI): exact mass calculated for M⁺ (C₁₄H₁₇FN₃O₄) requires *m/z* 310.1198, found *m/z* 310.1192.

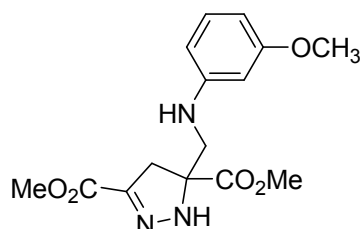
Dimethyl 5-(((3-chlorophenyl)amino)methyl)-4,5-dihydro-1*H*-pyrazole-3,5-dicarboxylate (5ag)



Yellow oil, 96% yield. ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 7.09-7.06 (m, 1H), 6.88 (s, 1H), 6.72-6.70 (m, 1H), 6.62 (s, 1H), 6.52-6.50 (m, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 3.51 (s, 2H), 3.42 (d, *J* = 20.0 Hz, 1H), 3.10 (d, *J* = 20.0 Hz, 1H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 172.9,

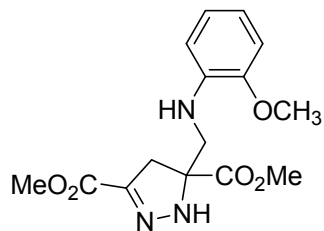
162.1, 148.4, 143.3, 135.1, 130.3, 118.4, 113.0, 111.7, 73.2, 53.3, 52.4, 48.6, 38.5. HRMS (ESI): exact mass calculated for M^+ ($C_{14}H_{17}ClN_3O_4$) requires m/z 326.0908, found m/z 326.0903.

Dimethyl 5-(((3-methoxyphenyl)amino)methyl)-4,5-dihydro-1H-pyrazole-3,5-dicarboxylate (5ah)



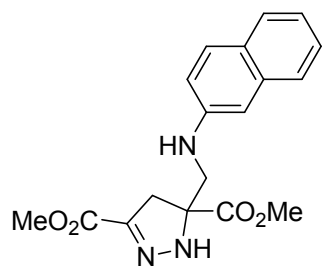
Yellow oil, 84% yield. 1H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.09-7.06 (m, 1H), 6.87 (s, 1H), 6.32-6.31 (m, 1H), 6.26-6.24 (m, 1H), 6.20 (s, 1H), 3.84 (s, 3H), 3.77 (s, 3H), 3.76 (s, 3H), 3.52 (s, 2H), 3.41 (d, $J = 15.0$ Hz, 1H), 3.13 (d, $J = 15.0$ Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 173.1, 162.2, 160.8, 148.7, 143.2, 130.1, 106.2, 103.7, 99.5, 73.4, 55.1, 53.3, 52.3, 48.8, 38.4. HRMS (ESI): exact mass calculated for M^+ ($C_{15}H_{20}N_3O_5$) requires m/z 322.1397, found m/z 322.1402.

Dimethyl 5-(((2-methoxyphenyl)amino)methyl)-4,5-dihydro-1H-pyrazole-3,5-dicarboxylate (5ai)



Yellow oil, 55% yield. 1H NMR ($CDCl_3$, 500 MHz): δ (ppm) 6.91 (s, 1H), 6.86-6.83 (m, 1H), 6.78-6.76 (m, 1H), 6.72-6.69 (m, 1H), 6.66-6.65 (m, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 3.75 (s, 3H), 3.59-3.53 (m, 2H), 3.41 (d, $J = 20.0$ Hz, 1H), 3.11 (d, $J = 20.0$ Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 173.2, 162.3, 146.9, 142.8, 137.2, 121.1, 117.7, 110.4, 109.7, 73.8, 55.4, 53.2, 52.3, 49.0, 38.4. HRMS (ESI): exact mass calculated for M^+ ($C_{15}H_{20}N_3O_5$) requires m/z 322.1397, found m/z 322.1400.

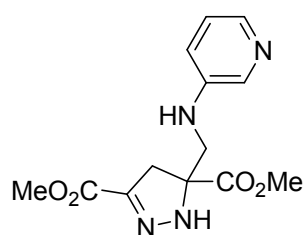
Dimethyl 5-((naphthalen-2-ylamino)methyl)-4,5-dihydro-1H-pyrazole-3,5-dicarboxylate (5aj)



Yellow oil, 45% yield. 1H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.80-7.77 (m, 2H), 7.48-7.45 (m, 2H), 7.35-7.29 (m, 2H), 6.98 (s, 1H), 6.67-6.65 (m, 1H), 3.85 (s, 3H), 3.81 (s, 3H), 3.72 (d, $J = 10.0$ Hz, 1H), 3.61 (d, $J = 10.0$ Hz, 1H), 3.52 (d, $J = 15.0$ Hz, 1H), 3.29 (d, $J = 15.0$ Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 173.2, 162.1, 143.5, 142.5, 134.3, 128.7, 126.3, 126.0, 125.2, 123.8, 119.9, 118.8, 105.3, 73.2, 53.4, 52.4, 48.5, 38.7. HRMS (ESI): exact mass calculated for M^+ ($C_{18}H_{20}N_3O_4$) requires m/z 342.1454, found m/z 342.1458.

Dimethyl 5-((pyridin-3-ylamino)methyl)-4,5-dihydro-1H-pyrazole-3,5-dicarboxylate (5ak)

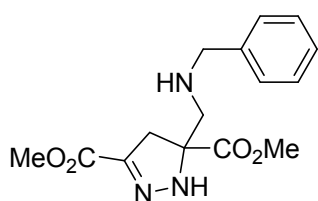
Yellow oil, 93% yield. 1H NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.06 (s, 1H), 7.99-7.98



found m/z 293.1255.

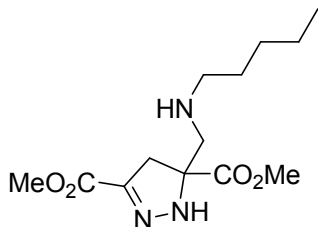
(m, 1H), 7.11-7.08 (m, 2H), 6.96-6.95 (m, 1H), 3.83 (s, 3H), 3.76 (s, 3H), 3.58-3.51 (m, 2H), 3.42 (d, $J = 20.0$ Hz, 1H), 3.10 (d, $J = 20.0$ Hz, 1H). ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 172.9, 162.1, 143.5, 142.9, 139.4, 136.1, 123.8, 119.5, 73.2, 53.4, 52.4, 48.5, 38.6. HRMS (ESI): exact mass calculated for M^+ ($\text{C}_{13}\text{H}_{17}\text{N}_4\text{O}_4$) requires m/z 293.1250,

Dimethyl 5-((benzylamino)methyl)-4,5-dihydro-1H-pyrazole-3,5-dicarboxylate (5al)



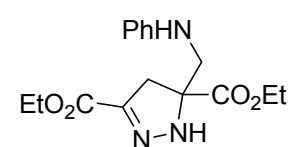
White solid, 97% yield. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 7.32-7.29 (m, 2H), 7.25-7.23 (m, 3H), 6.92 (s, 1H), 3.81 (s, 3H), 3.78 (s, 2H), 3.74 (s, 3H), 3.30 (d, $J = 20.0$ Hz, 1H), 3.08 (d, $J = 20.0$ Hz, 1H), 3.02 (d, $J = 10.0$ Hz, 1H), 2.82 (d, $J = 10.0$ Hz, 1H). ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 173.4, 162.4, 142.7, 139.8, 128.4, 127.9, 127.2, 73.4, 53.8, 53.7, 52.9, 52.2, 38.6. HRMS (ESI): exact mass calculated for M^+ ($\text{C}_{15}\text{H}_{20}\text{N}_3\text{O}_4$) requires m/z 306.1454, found m/z 306.1450.

Dimethyl 5-((pentylamino)methyl)-4,5-dihydro-1H-pyrazole-3,5-dicarboxylate (5am)



Yellow oil, 92% yield. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 6.92 (s, 1H), 3.82 (s, 3H), 3.76 (s, 3H), 3.30 (d, $J = 15.0$ Hz, 1H), 3.07-3.02 (m, 2H), 2.80 (d, $J = 15.0$ Hz, 1H), 2.62-2.52 (m, 2H), 1.44-1.38 (m, 2H), 1.31-1.25 (m, 4H), 0.87 (t, $J = 10.0$ Hz, 3H). ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 173.5, 162.4, 142.6, 73.5, 54.5, 52.9, 52.2, 50.1, 38.7, 29.7, 29.3, 22.5, 14.0. HRMS (ESI): exact mass calculated for M^+ ($\text{C}_{13}\text{H}_{24}\text{N}_3\text{O}_4$) requires m/z 286.1767, found m/z 286.1762.

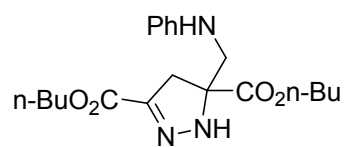
Diethyl 5-((phenylamino)methyl)-4,5-dihydro-1H-pyrazole-3,5-dicarboxylate (5ba)



Yellow oil, 86% yield. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) 7.19-7.16 (m, 2H), 6.88 (s, 1H), 6.77-6.74 (m, 1H), 6.66-6.64 (m, 2H), 4.30 (q, $J = 10.0$ Hz, 2H), 4.21 (q, $J = 10.0$ Hz, 2H), 3.52 (m, 2H), 3.42 (d, $J = 20.0$ Hz, 1H), 3.13 (d, $J = 20.0$ Hz, 1H), 1.35 (t, $J = 10.0$ Hz, 3H), 1.28 (t, $J = 10.0$ Hz, 3H). ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) 172.7, 161.8, 147.3, 143.5, 129.3, 118.6, 113.4, 73.3, 62.6, 61.5, 48.9, 38.4, 14.2, 14.1. HRMS (ESI): exact mass calculated for M^+ ($\text{C}_{16}\text{H}_{22}\text{N}_3\text{O}_4$) requires m/z 320.1610, found m/z 320.1613.

Dibutyl 5-((phenylamino)methyl)-4,5-dihydro-1H-pyrazole-3,5-dicarboxylate

(5ca)

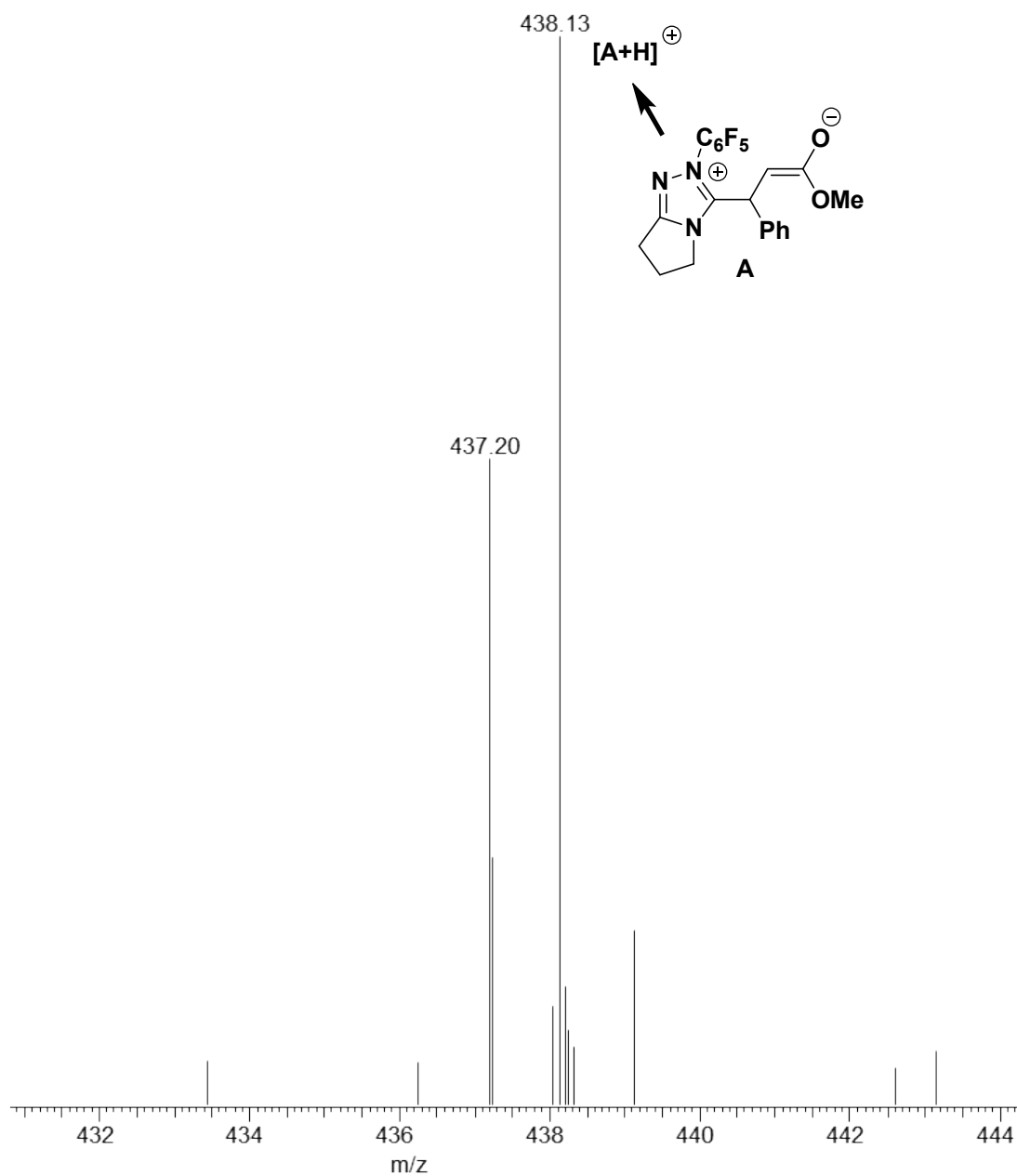


Yellow solid, 90% yield. ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 7.19-7.16 (m, 2H), 6.88 (s, 1H), 6.76-6.73 (m, 1H), 6.65-6.63 (m, 2H), 4.24 (t, *J* = 10.0 Hz, 2H), 4.16 (t, *J* = 10.0 Hz, 2H), 3.52 (m, 2H), 3.41 (d, *J* = 20.0 Hz, 1H), 3.13 (d, *J* = 20.0 Hz, 1H), 1.71-1.61 (m, 4H), 1.43-1.33 (m, 4H), 0.96-0.91 (m, 6H). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) 172.8, 161.9, 147.3, 143.5, 129.3, 118.5, 113.4, 73.4, 66.4, 65.3, 48.9, 38.5, 30.6, 30.4, 19.1, 19.0, 13.7, 13.6. HRMS (ESI): exact mass calculated for M⁺ (C₂₀H₃₀N₃O₄) requires *m/z* 376.2236, found *m/z* 376.2231.

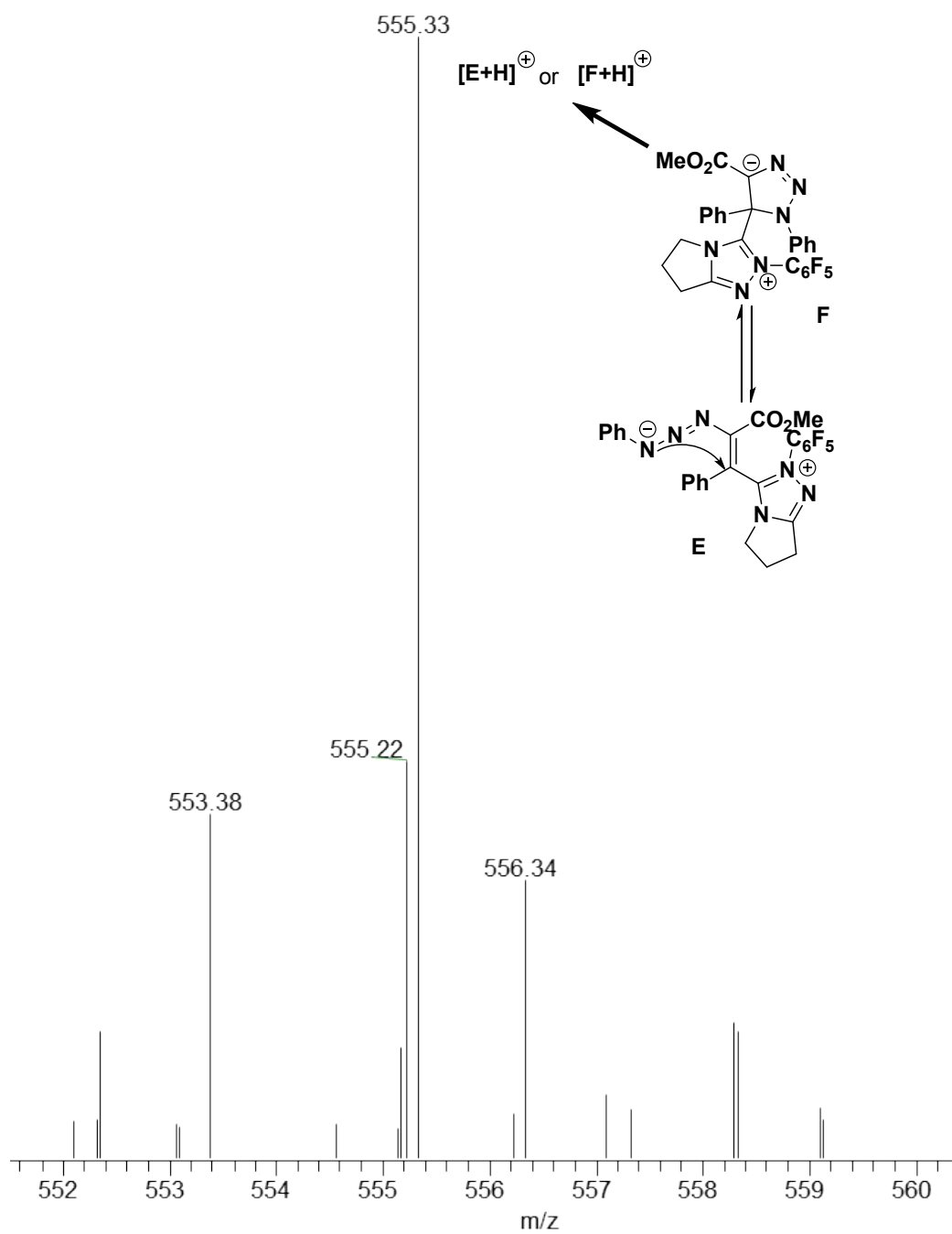
F: ESI-MS Studies

Figure 1. (a) ESI(+)-MS spectra for the reaction of NHC catalyst **V** and cinnamate **1a** in CH₃CN for 2 h; (b) ESI(+)-MS spectra for the cycloaddition reaction of **1a** and **2a** catalyzed by NHC catalyst in CH₃CN for 2 h. Other unidentified ions are likely to correspond to either impurities or side-reaction products.

a)



b)



c)

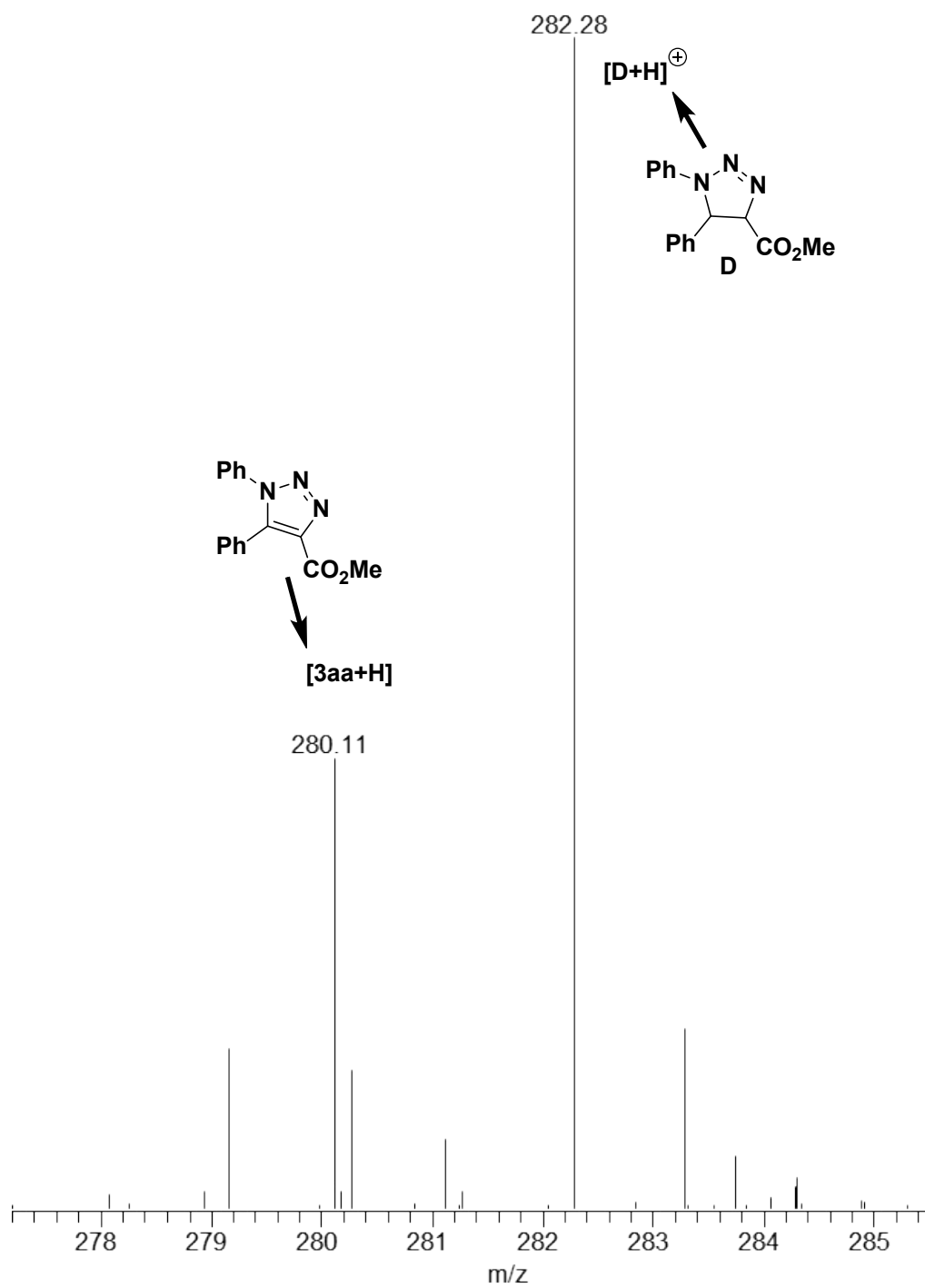
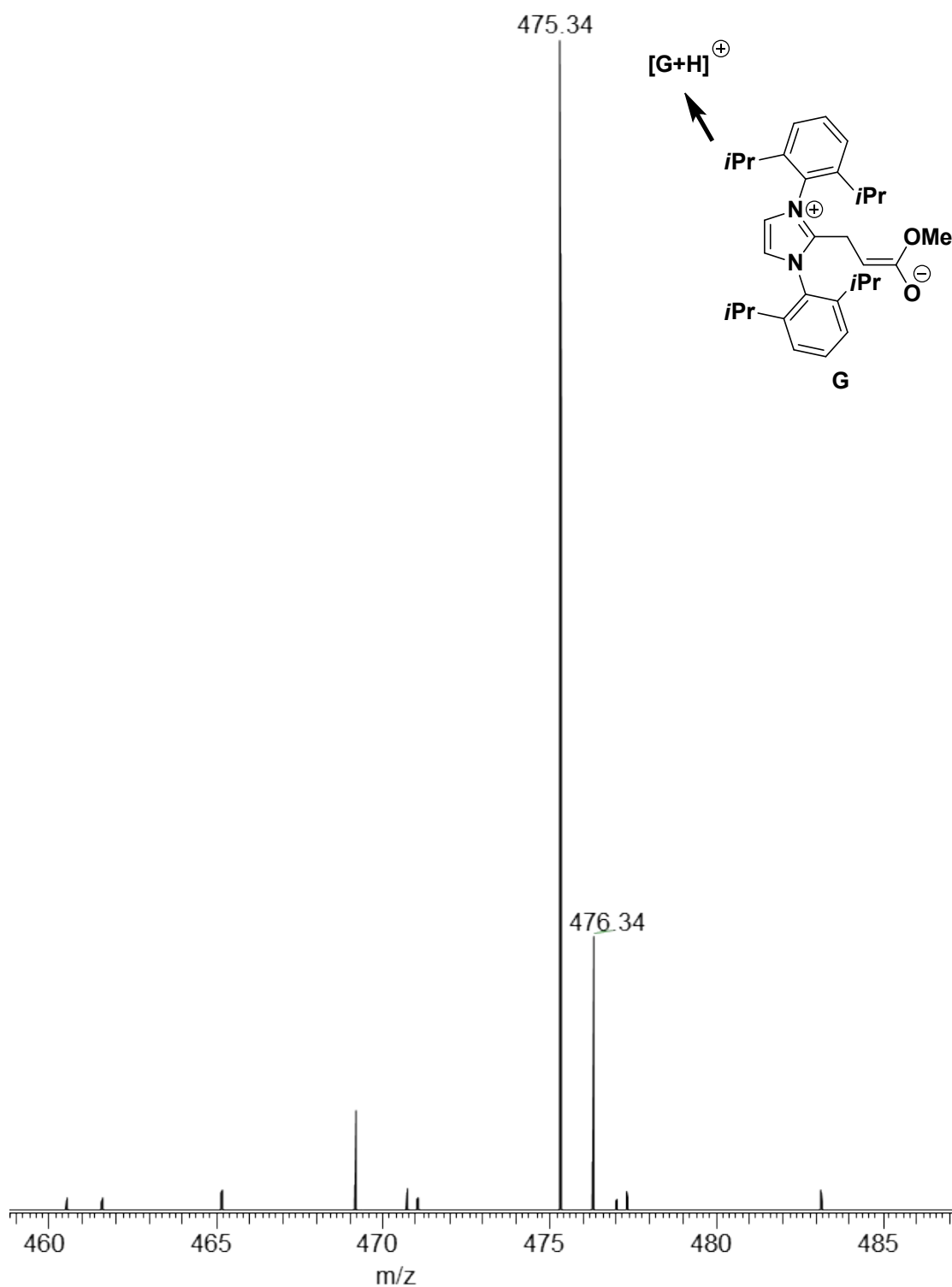
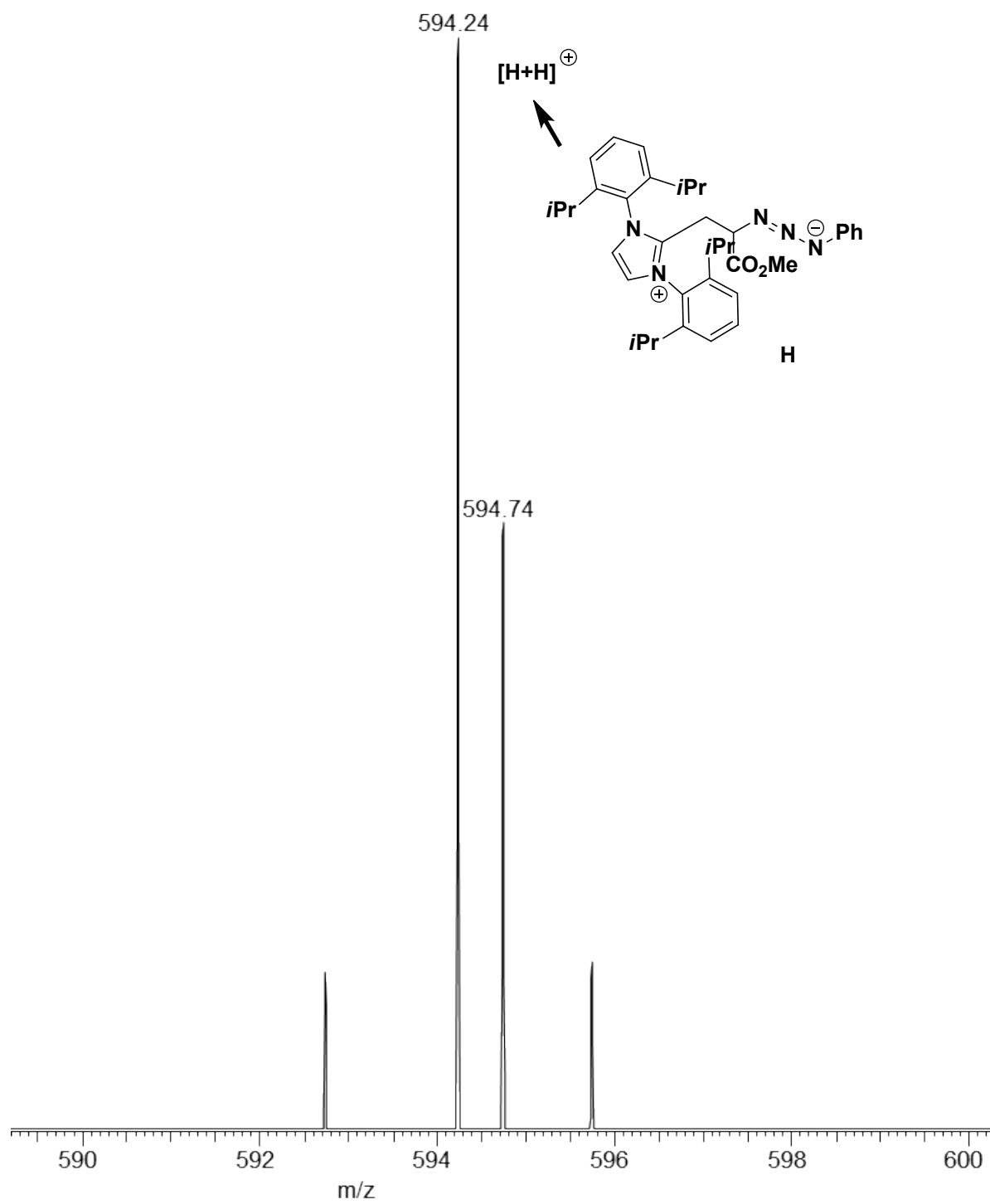


Figure 2. (d) ESI(+)-MS spectra for the reaction of NHC catalyst **I** and methyl acrylate **4a** in CHCl₃ for 2 h; (e) ESI(+)-MS spectra for the cycloaddition reaction of **4a** and **2a** catalyzed by NHC catalyst in CHCl₃ for 2 h. Other unidentified ions are likely to correspond to either impurities or side-reaction products.

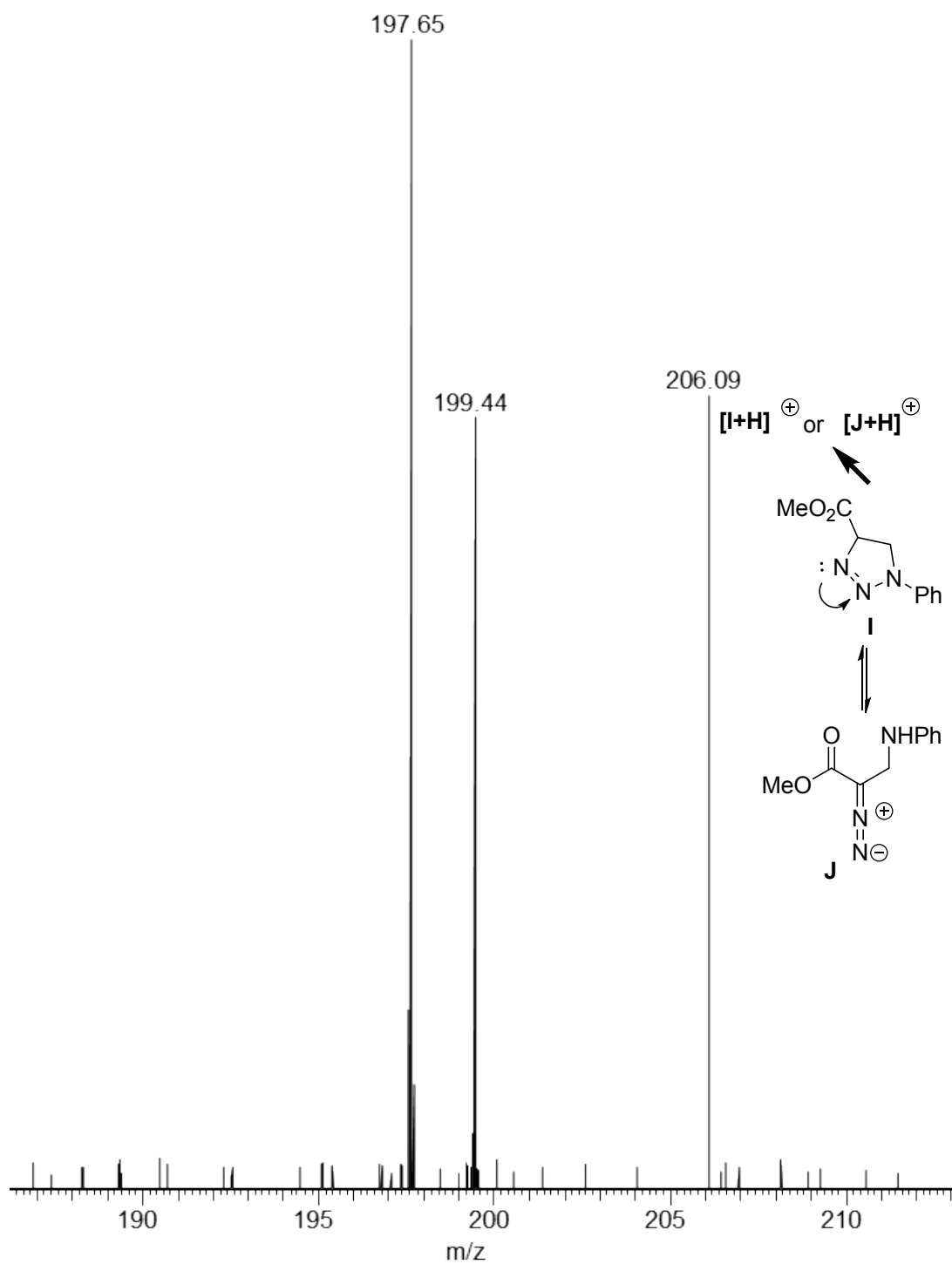
d)



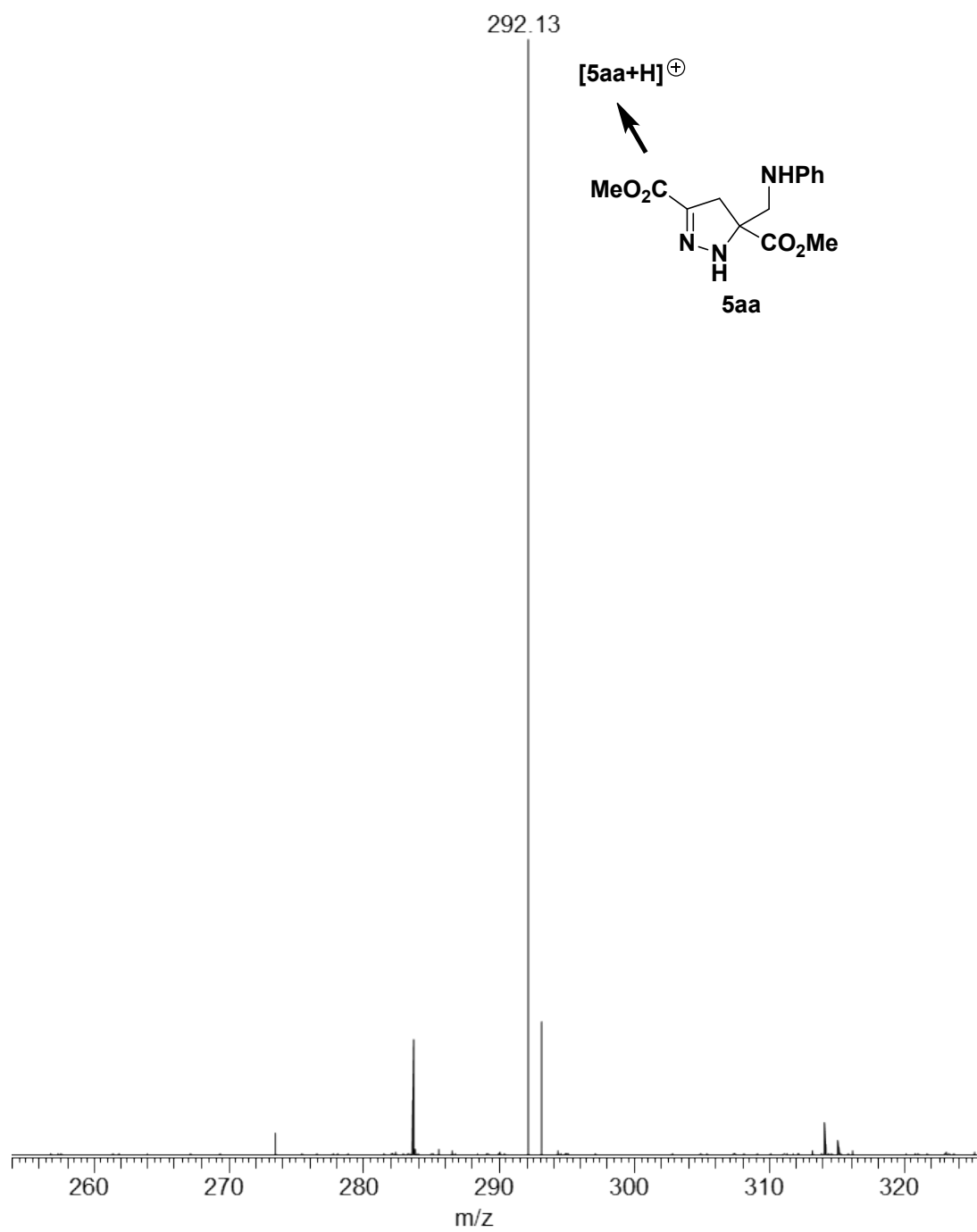
e)



f)

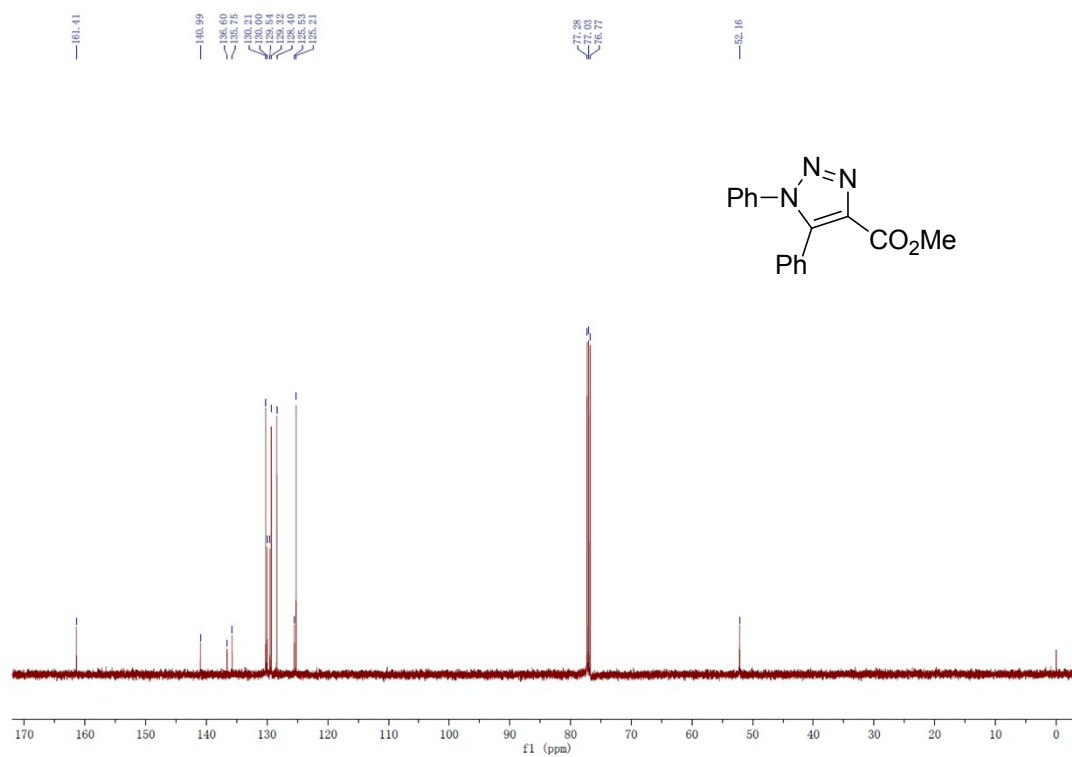
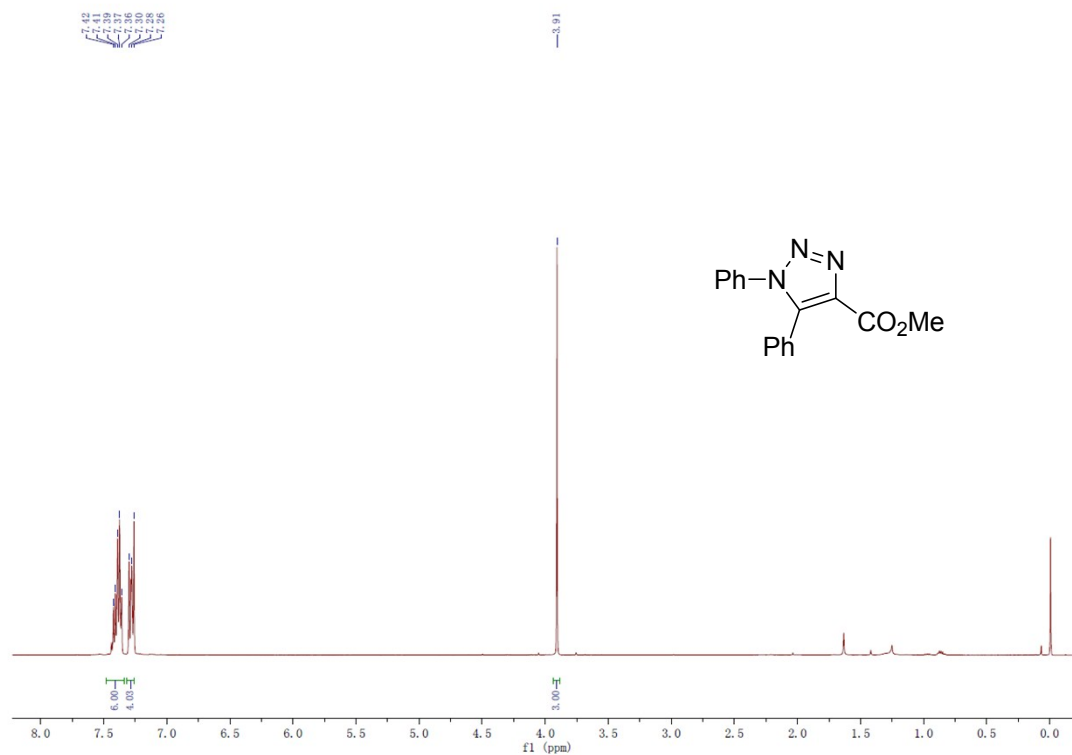


g)

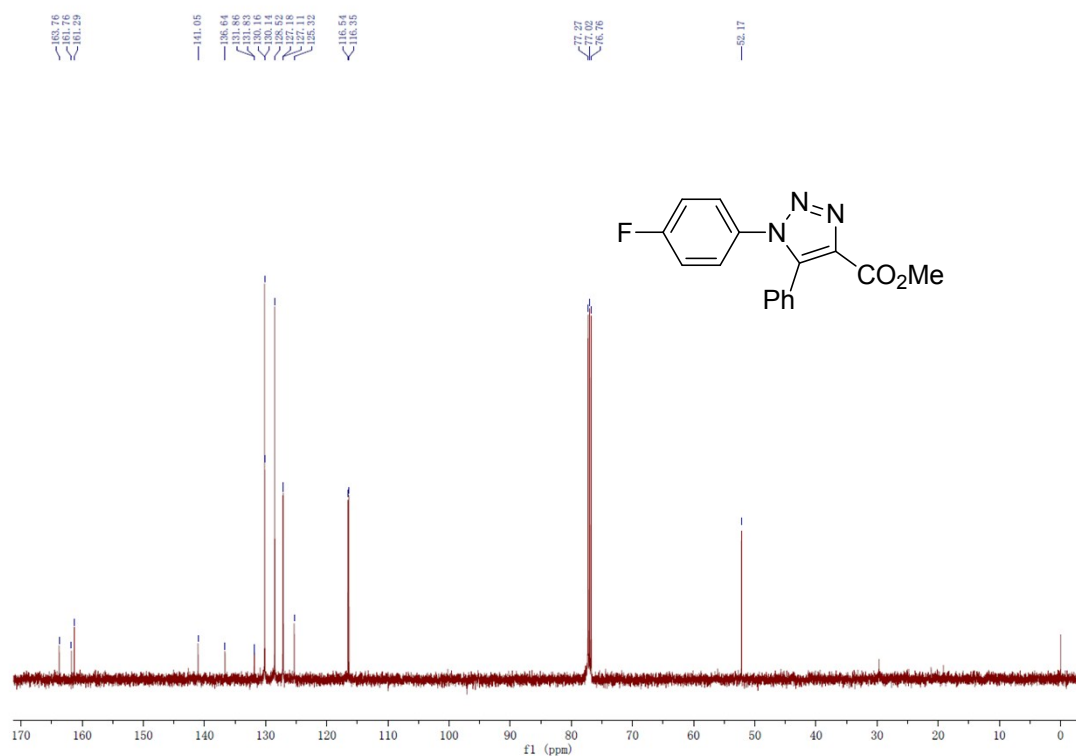
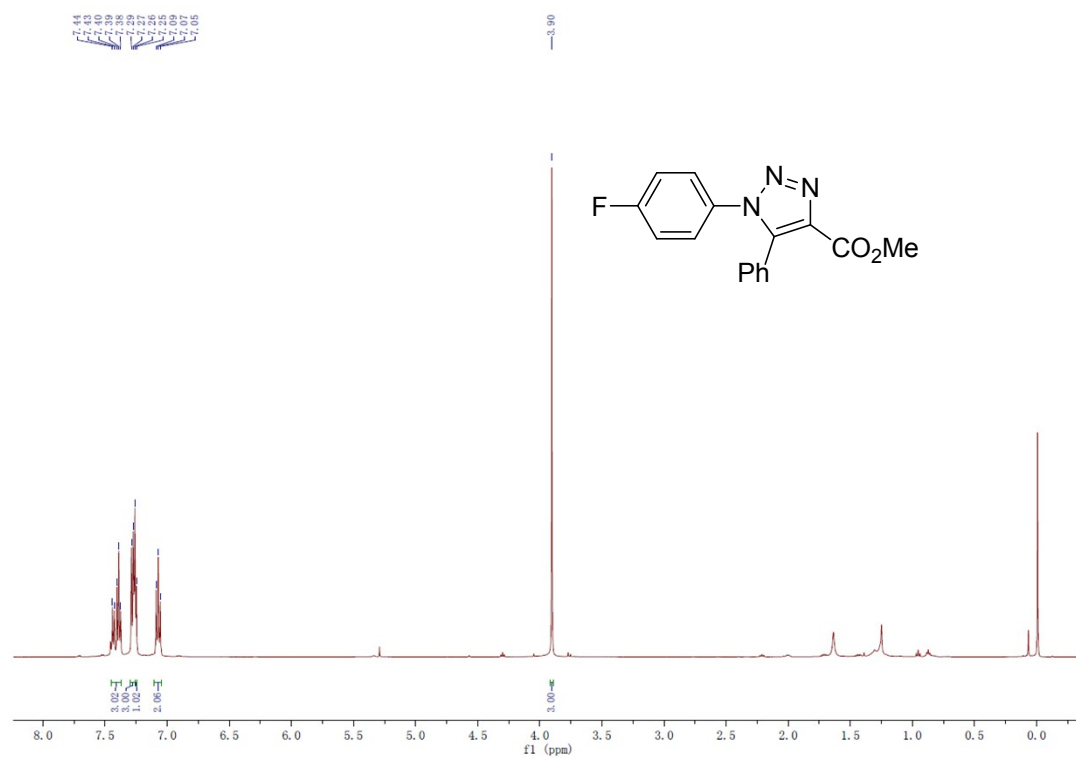


G: NMR Analysis

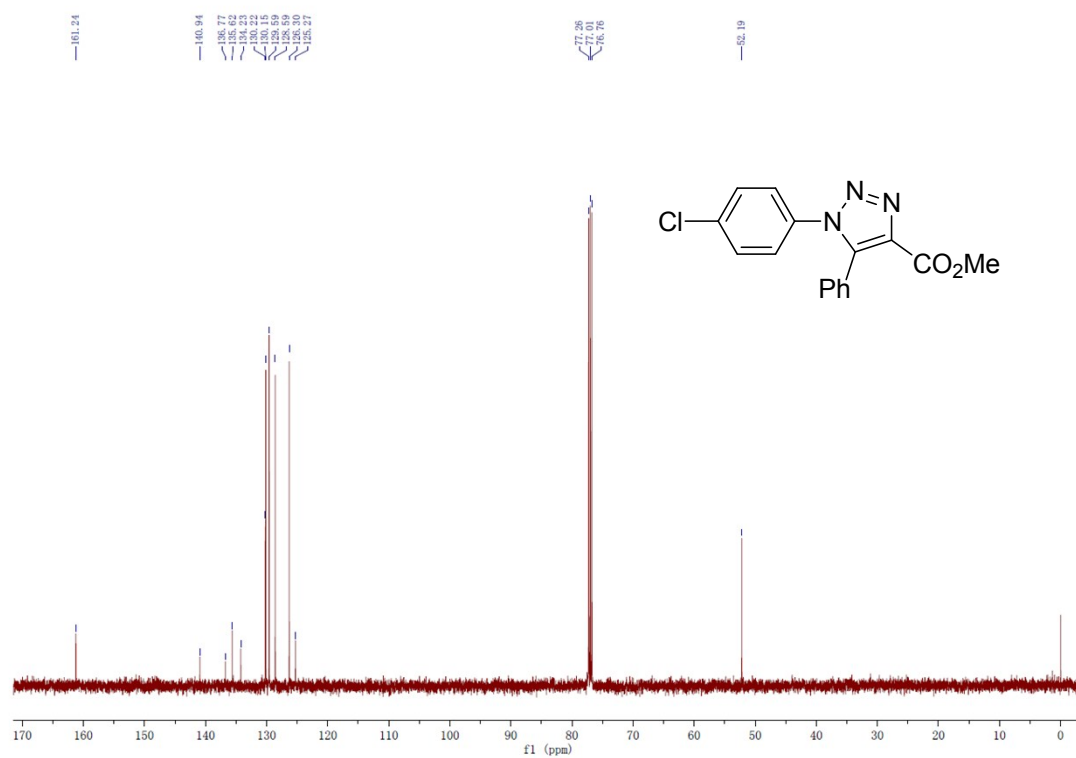
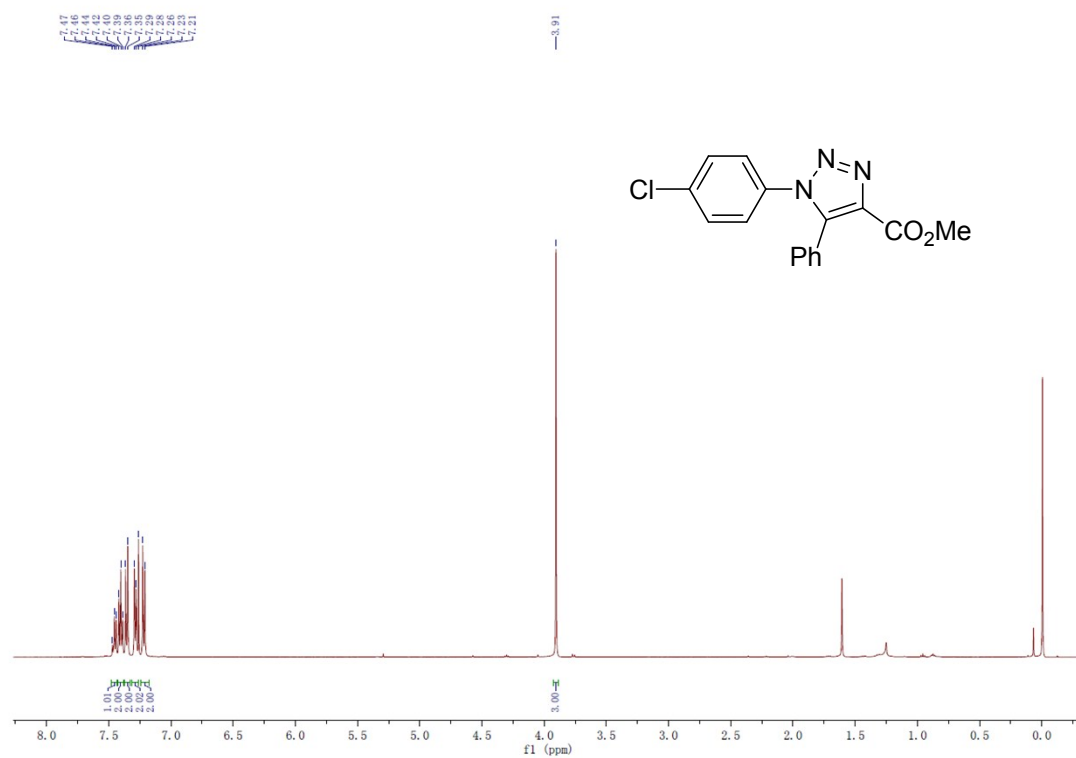
Methyl 1,5-diphenyl-1H-1,2,3-triazole-4-carboxylate (3aa)



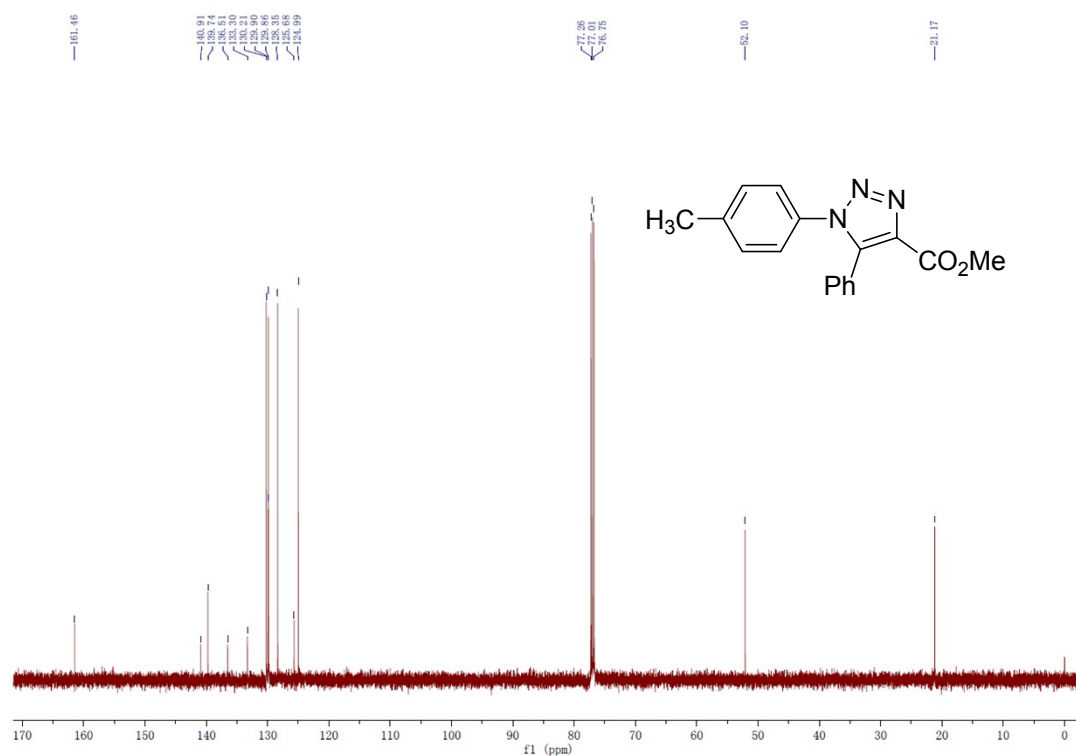
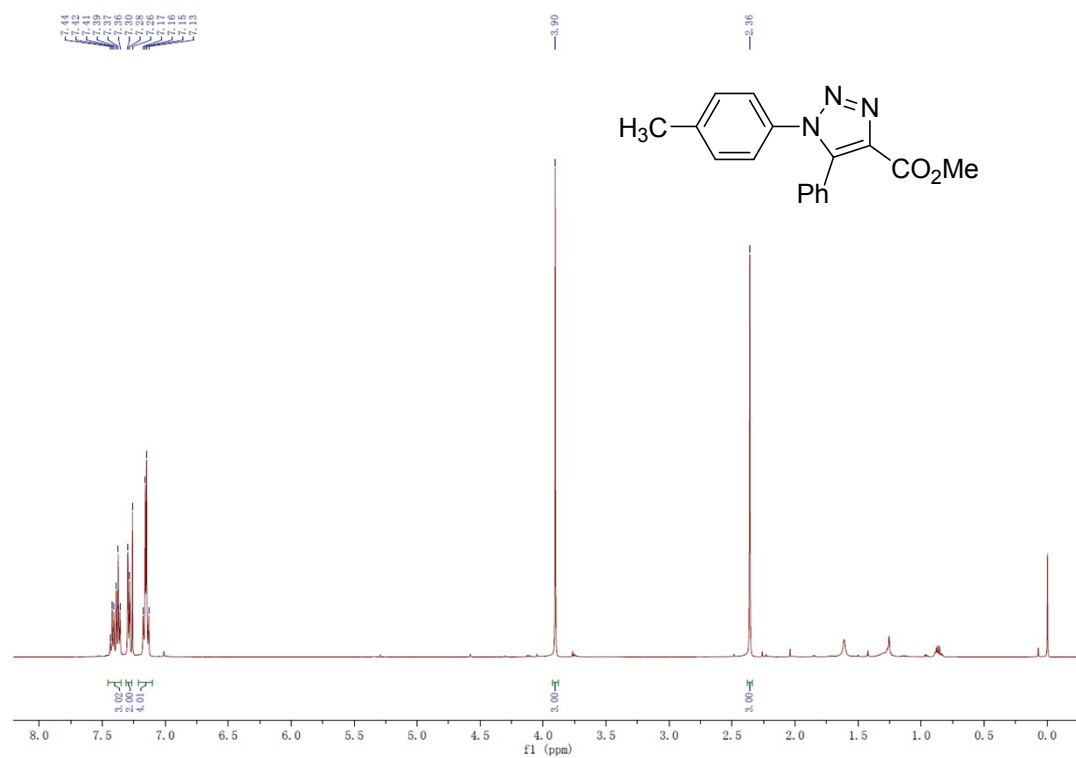
Methyl 1-(4-fluorophenyl)-5-phenyl-1*H*-1,2,3-triazole-4-carboxylate (3ab)



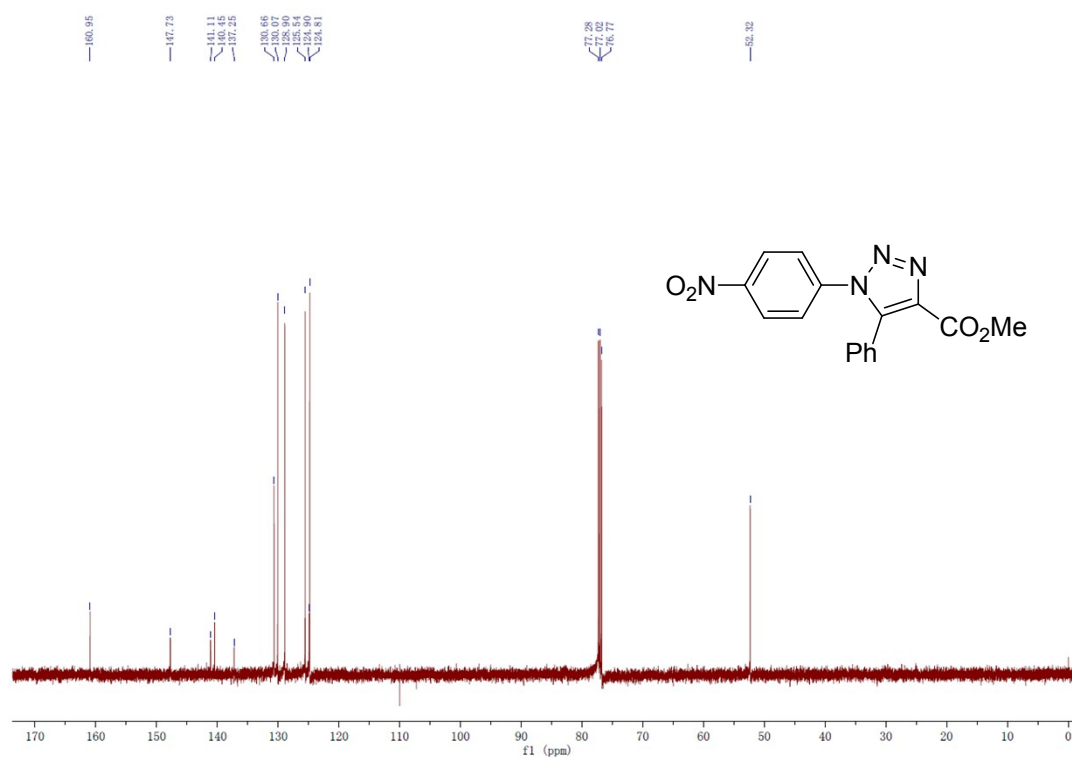
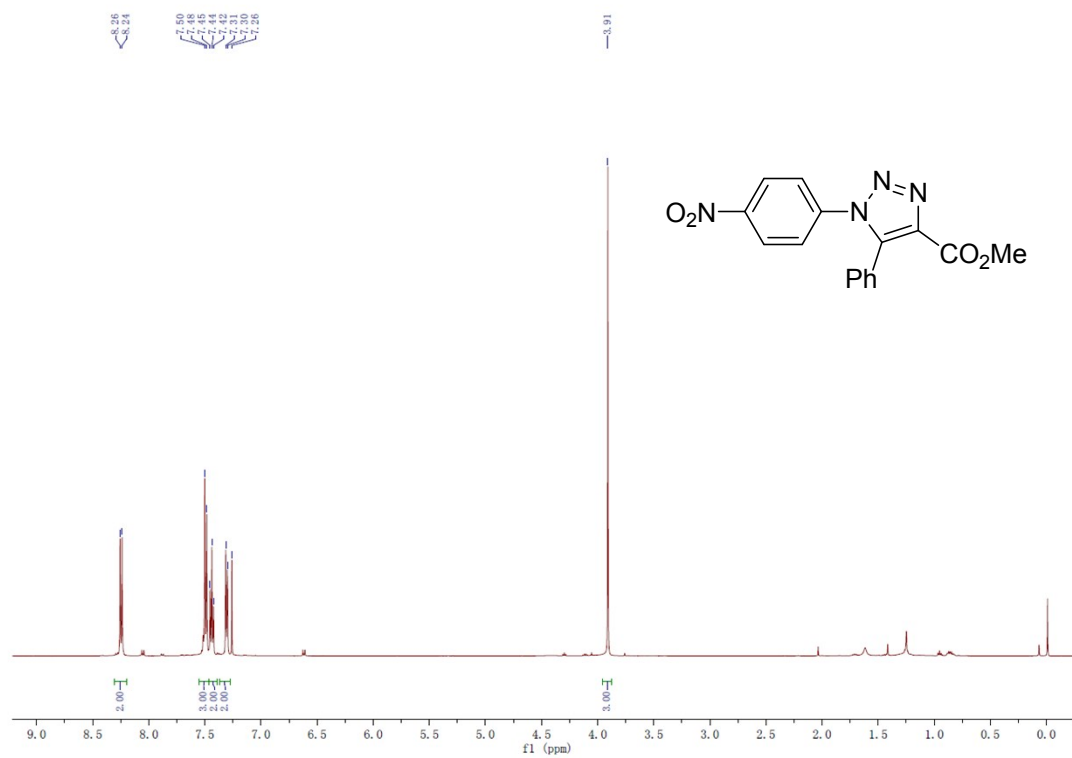
Methyl 1-(4-chlorophenyl)-5-phenyl-1*H*-1,2,3-triazole-4-carboxylate (3ac)



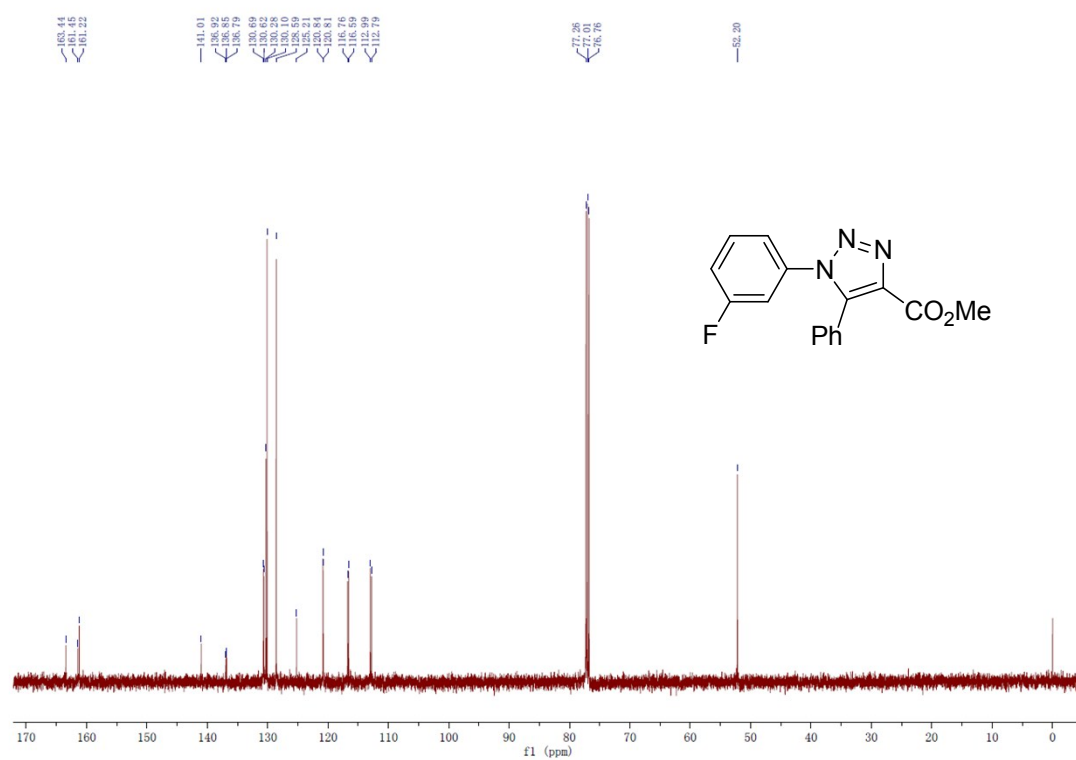
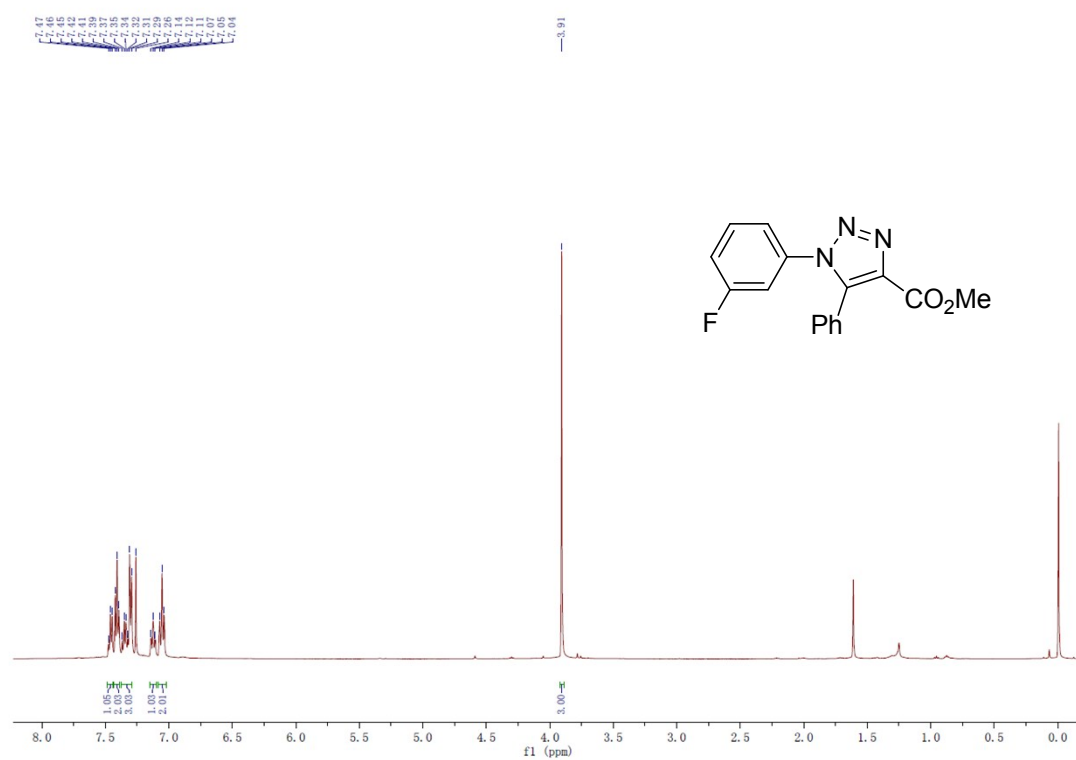
Methyl 5-phenyl-1-(*p*-tolyl)-1*H*-1,2,3-triazole-4-carboxylate (3ad)



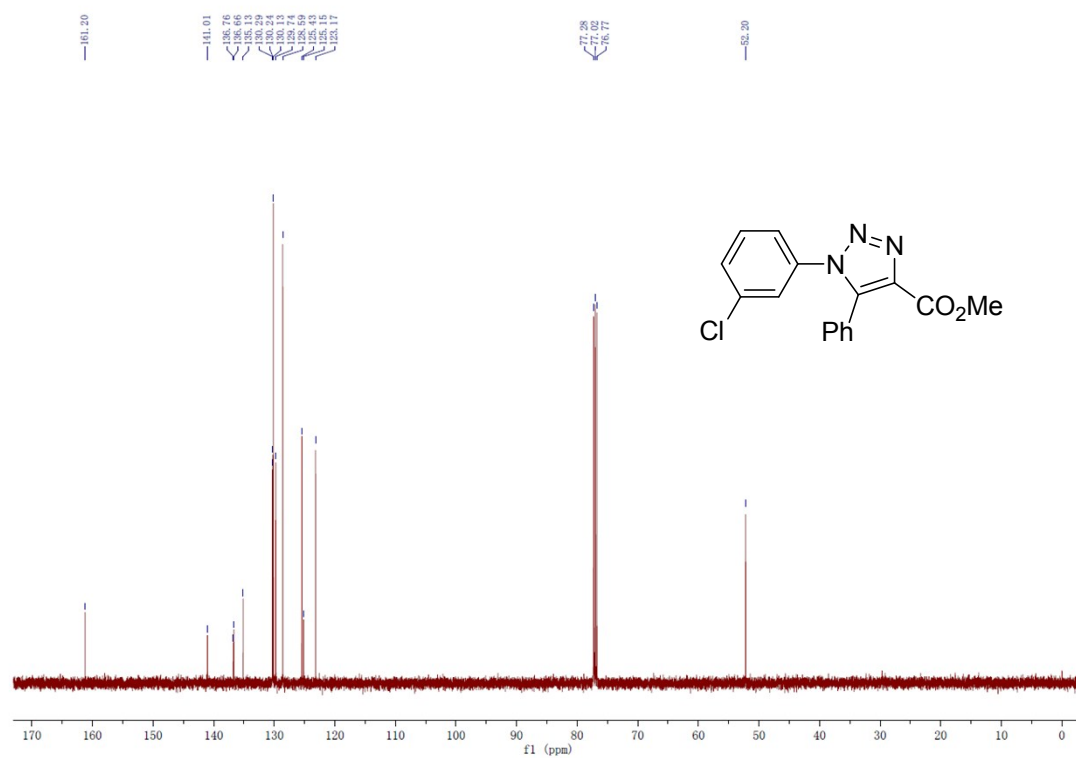
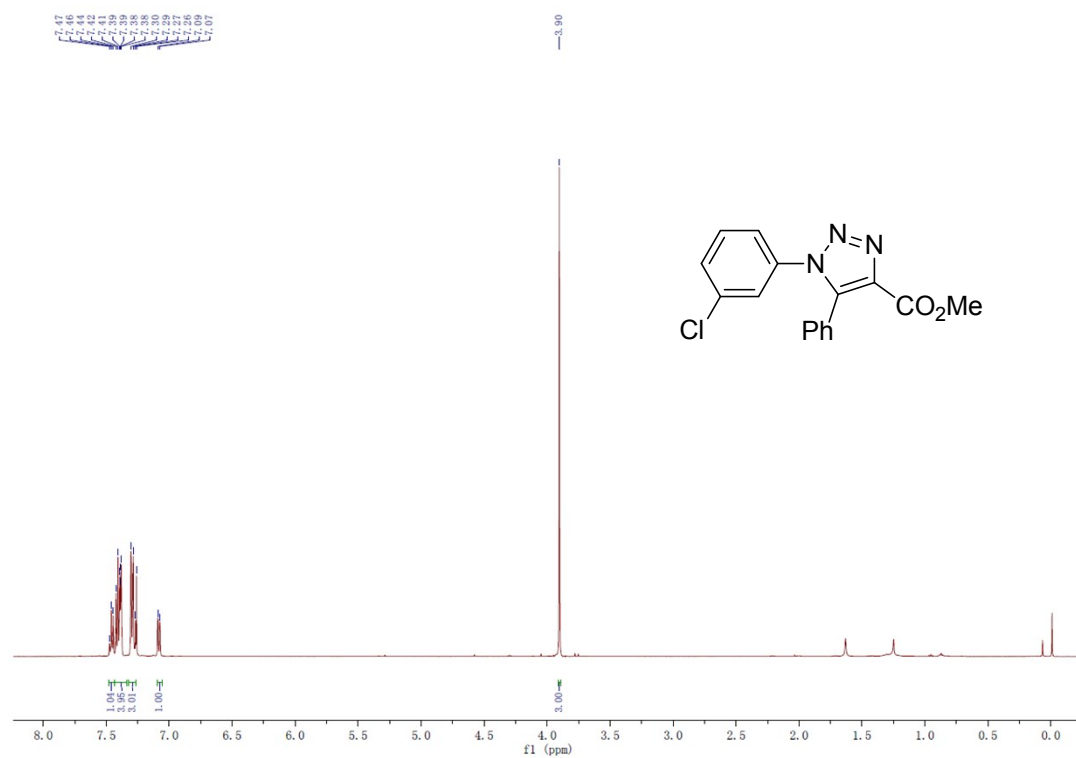
Methyl 1-(4-nitrophenyl)-5-phenyl-1*H*-1,2,3-triazole-4-carboxylate (3ae)



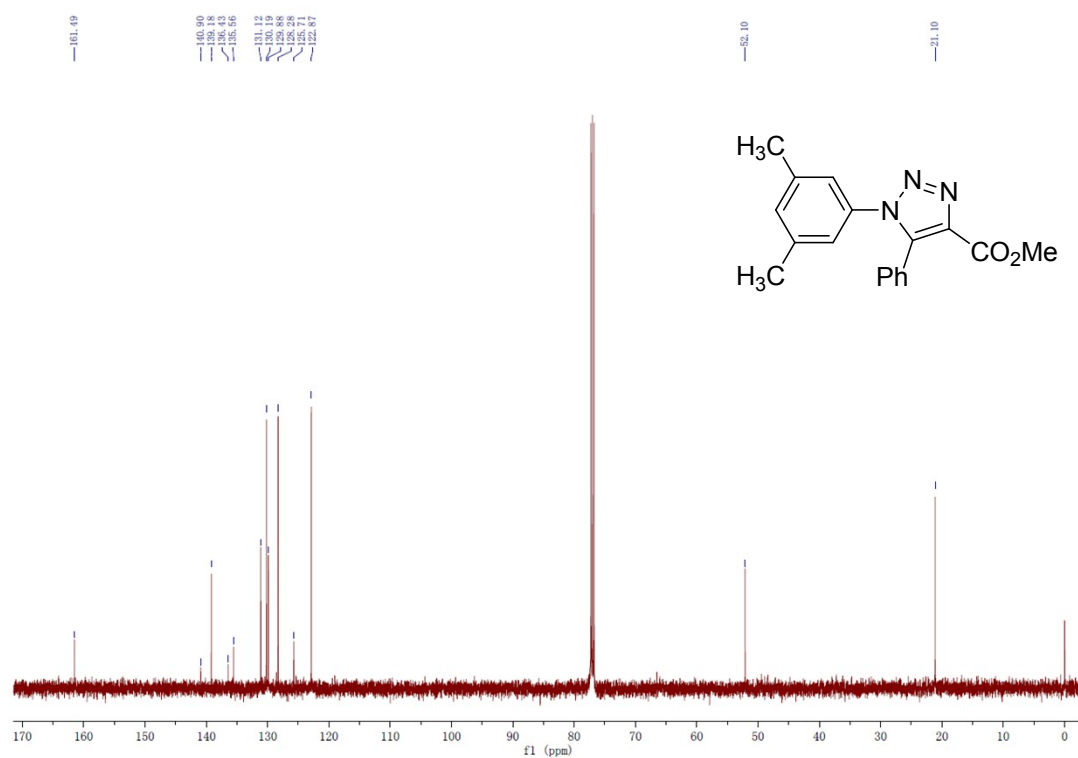
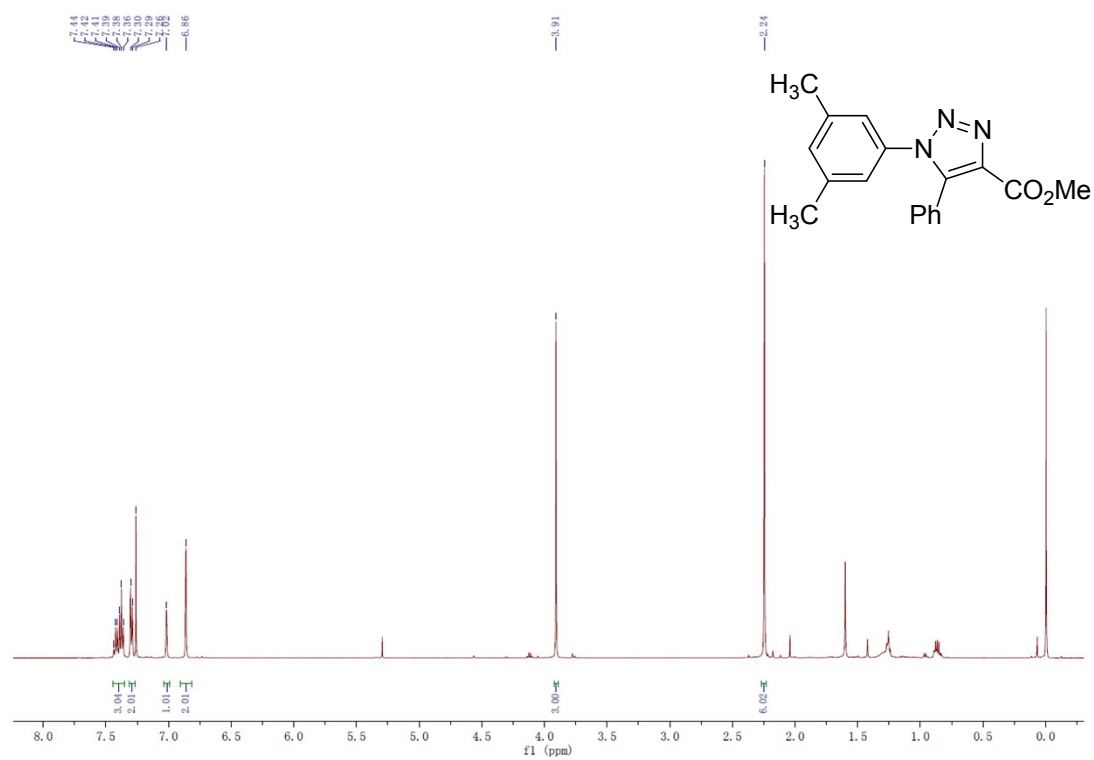
Methyl 1-(3-fluorophenyl)-5-phenyl-1*H*-1,2,3-triazole-4-carboxylate (3af)



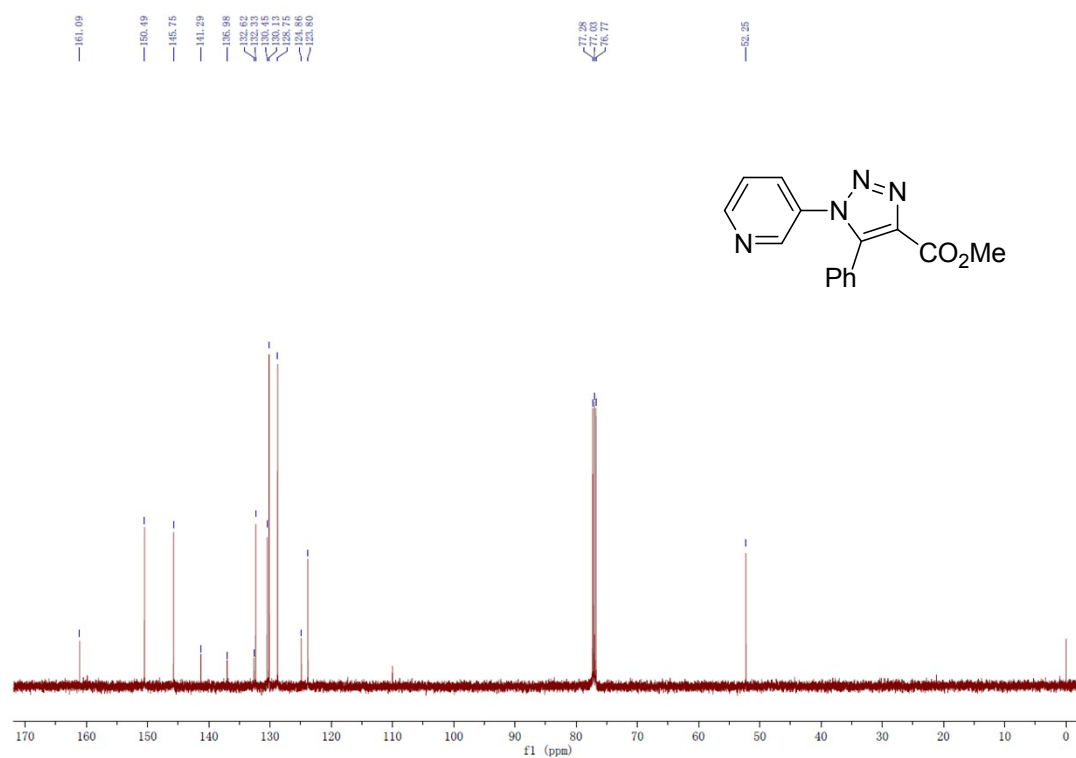
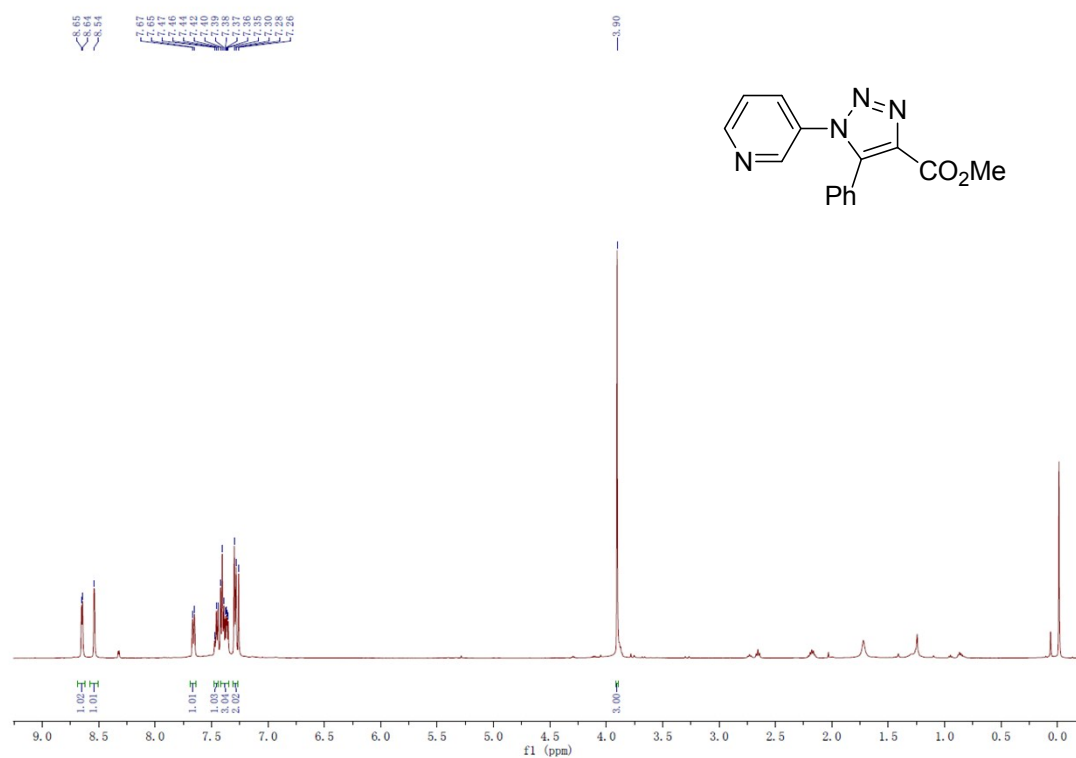
Methyl 1-(3-chlorophenyl)-5-phenyl-1*H*-1,2,3-triazole-4-carboxylate (3ag)



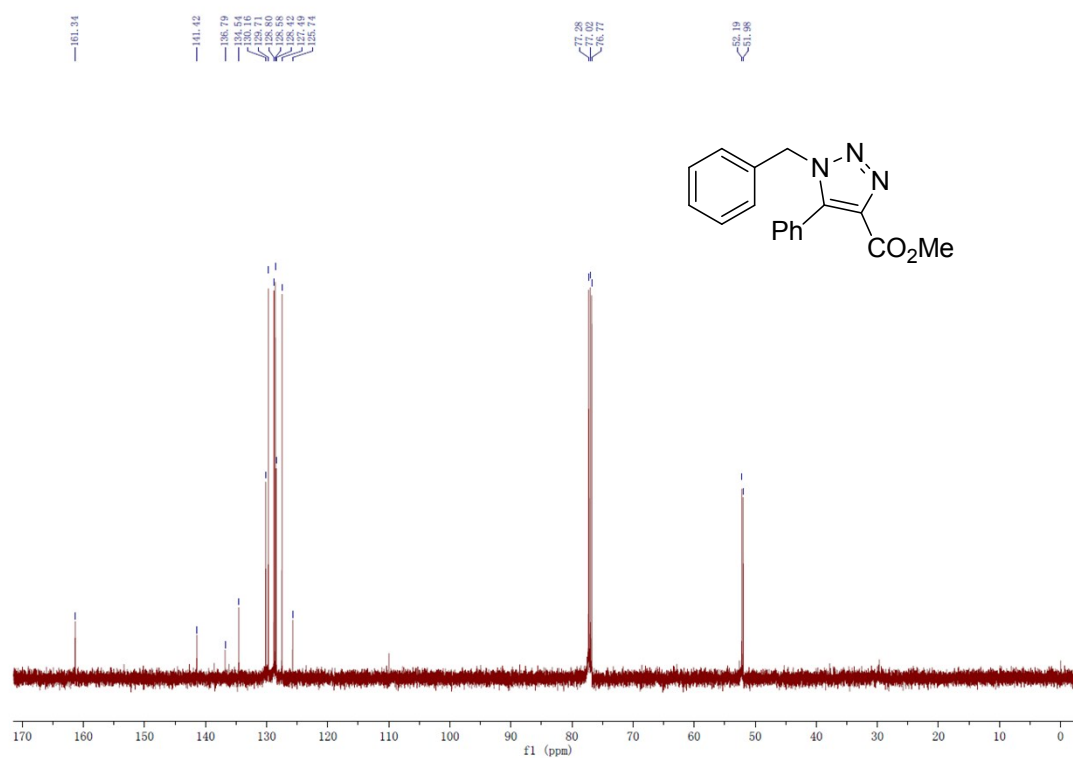
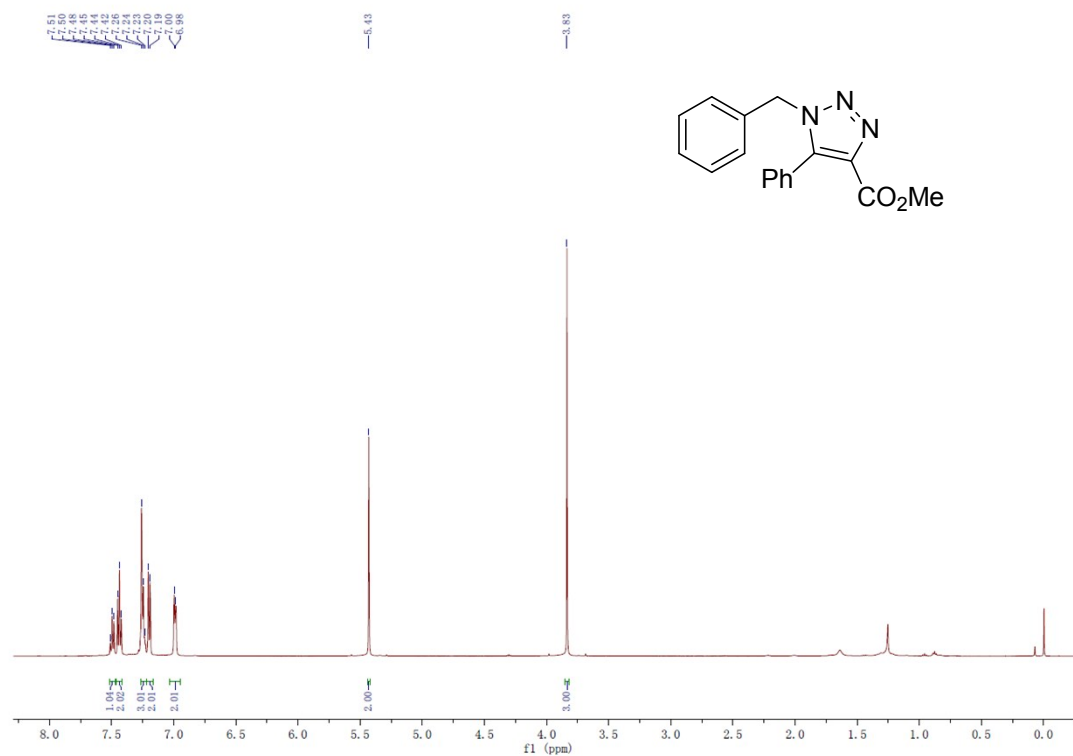
Methyl 1-(3,5-dimethylphenyl)-5-phenyl-1*H*-1,2,3-triazole-4-carboxylate (3ah)



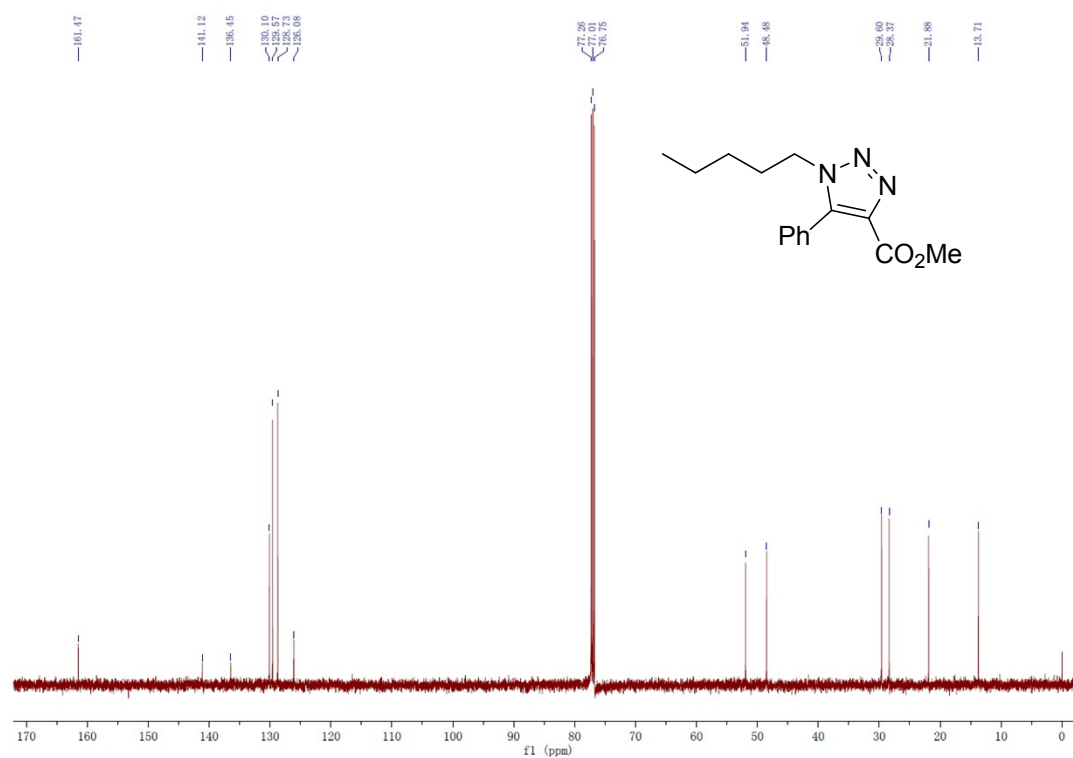
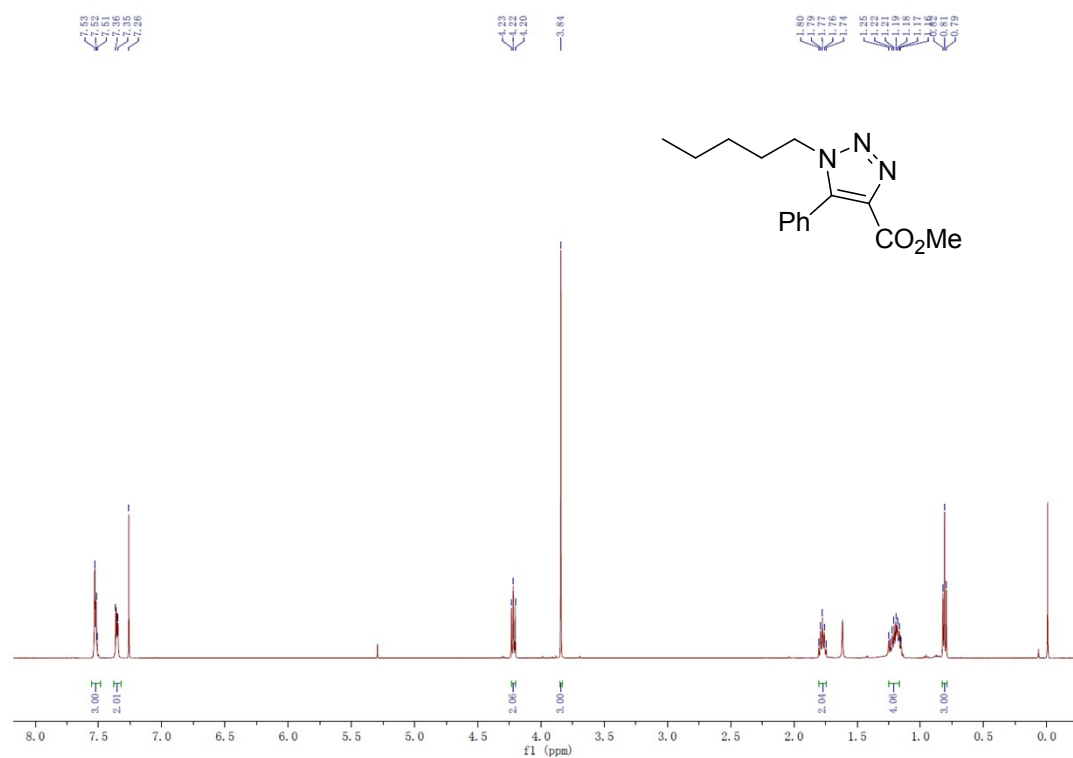
Methyl 5-phenyl-1-(pyridin-3-yl)-1*H*-1,2,3-triazole-4-carboxylate (3ai)



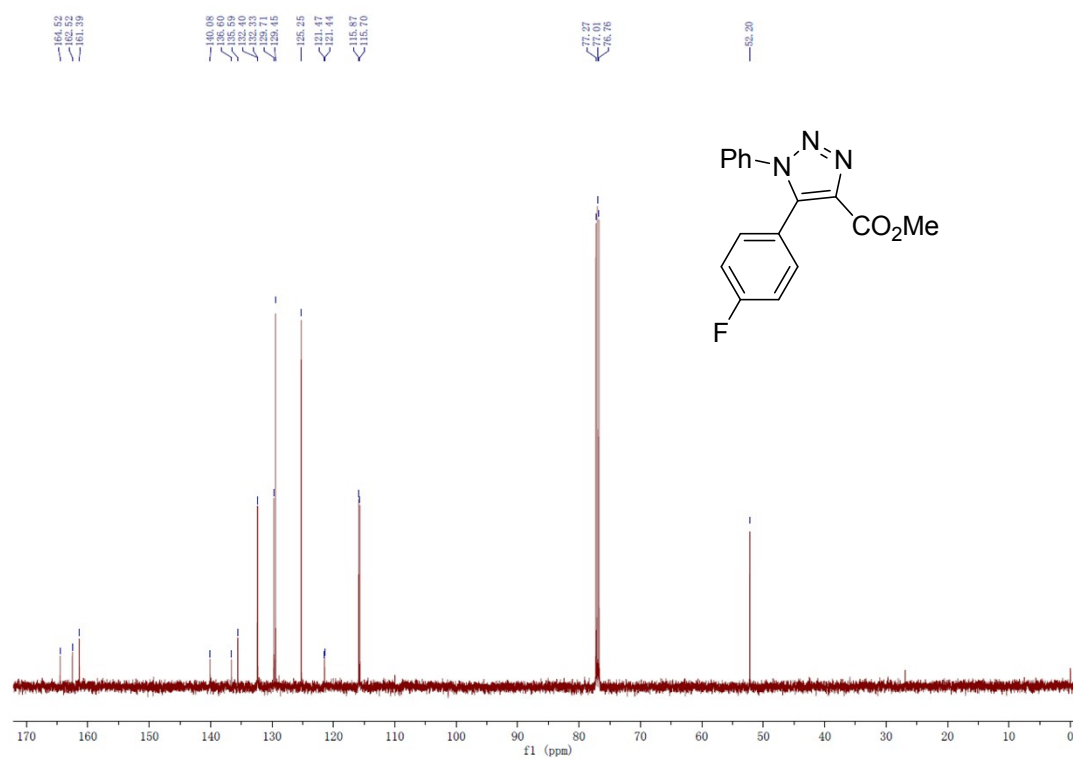
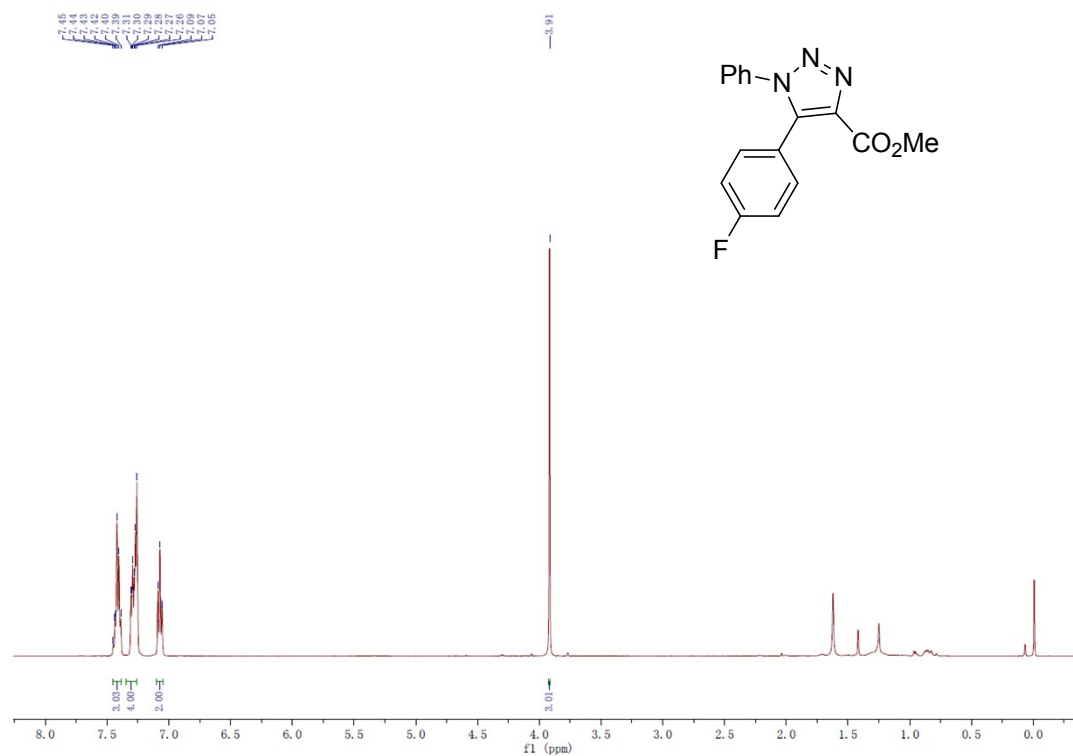
Methyl 1-benzyl-5-phenyl-1*H*-1,2,3-triazole-4-carboxylate (3aj)



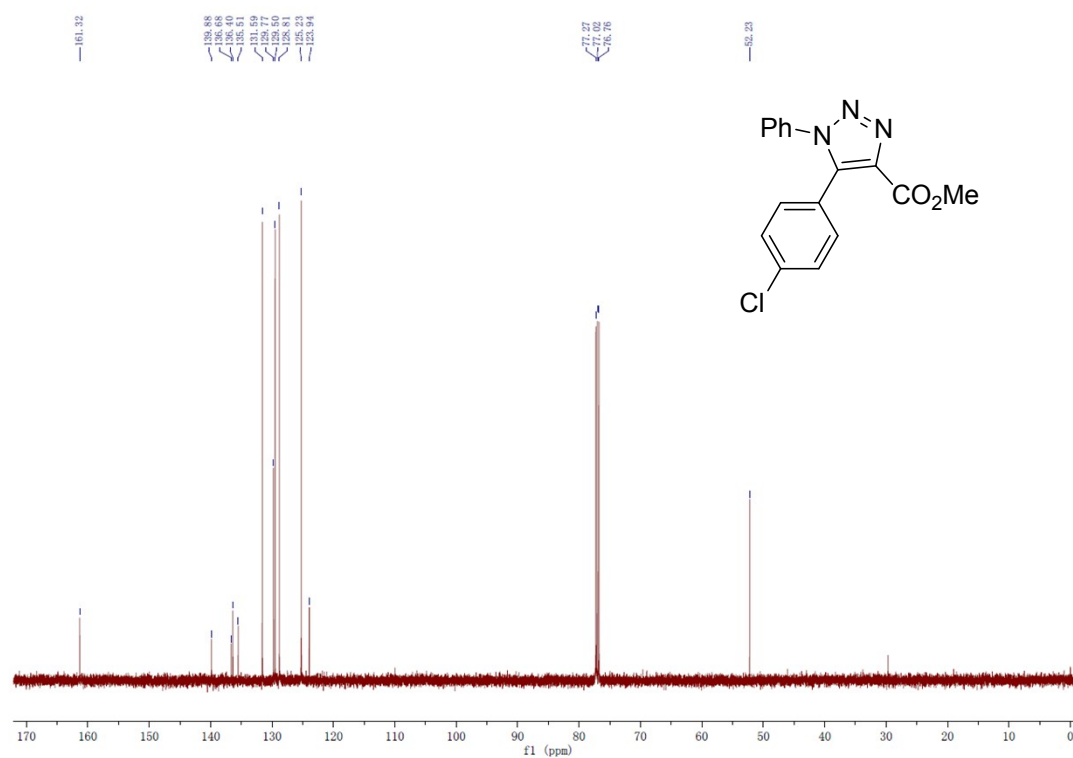
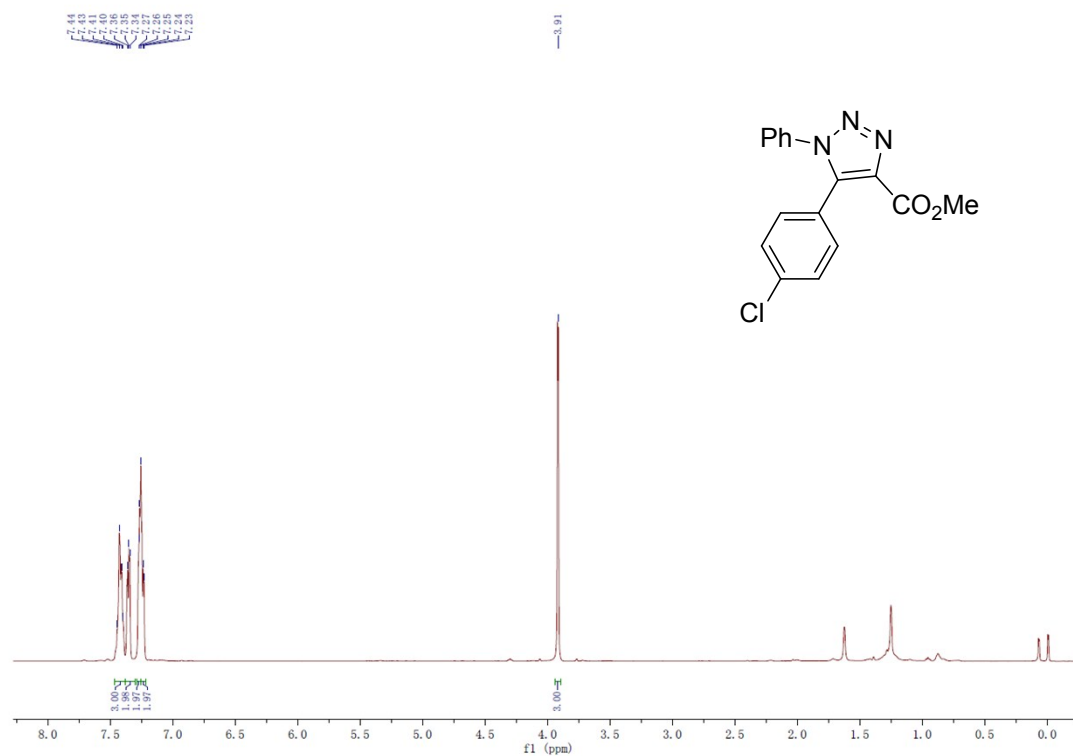
Methyl 1-pentyl-5-phenyl-1*H*-1,2,3-triazole-4-carboxylate (3ak)



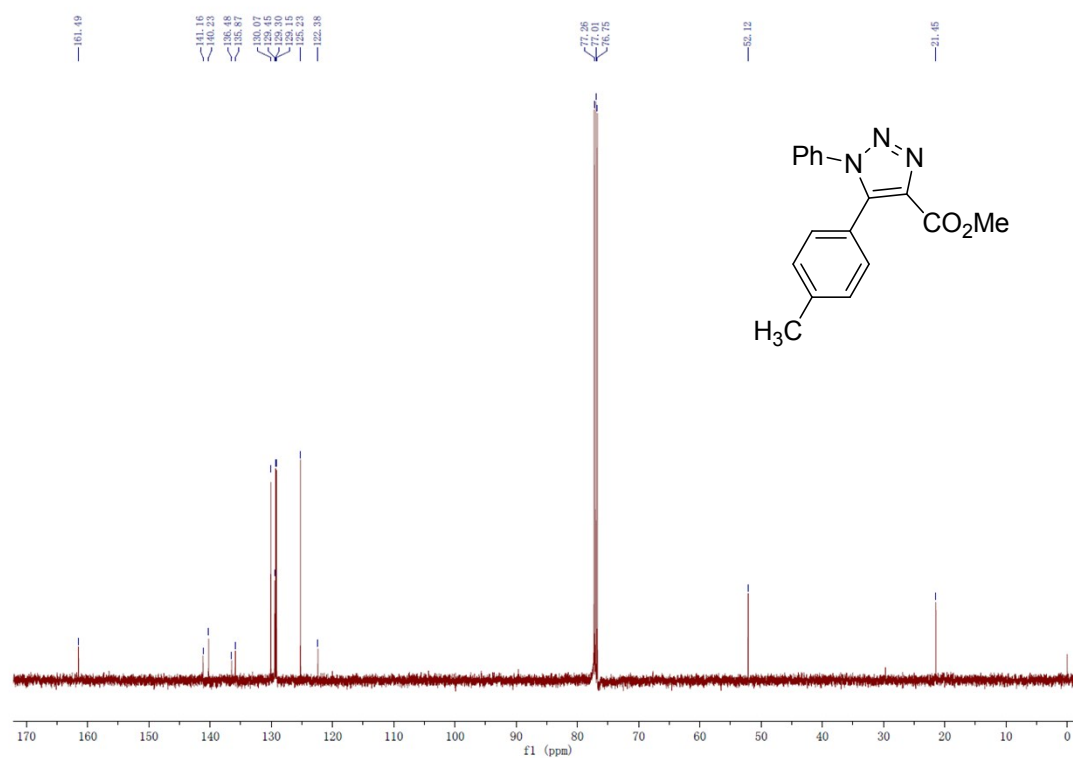
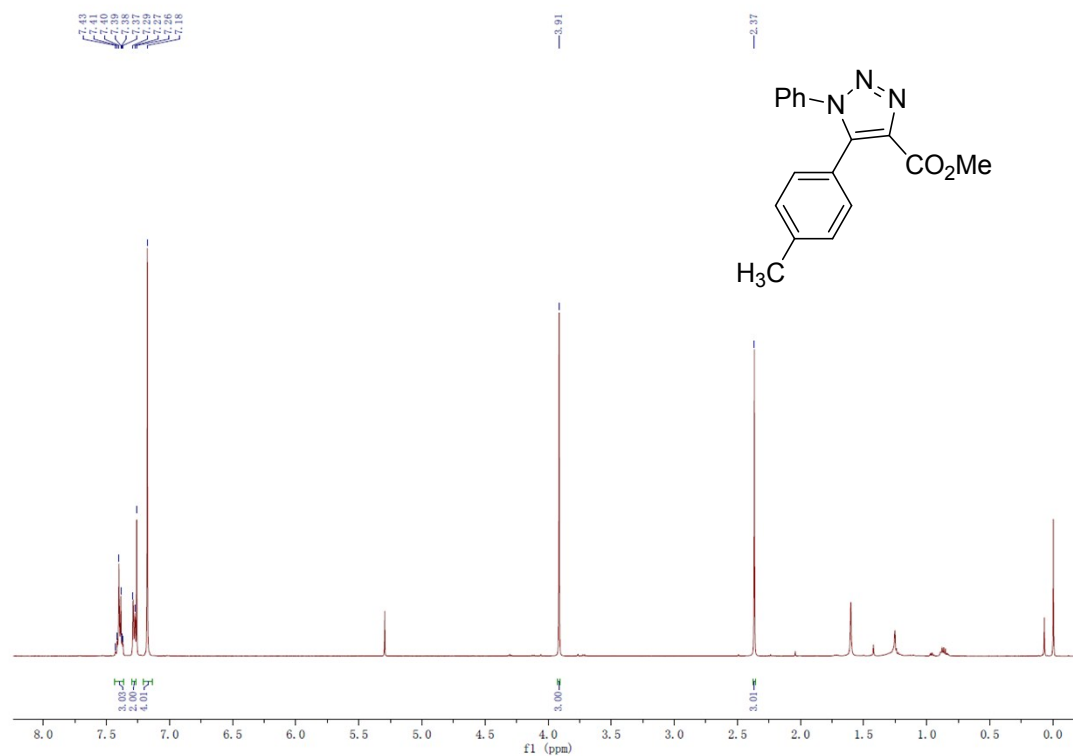
Methyl 5-(4-fluorophenyl)-1-phenyl-1H-1,2,3-triazole-4-carboxylate (3ba)



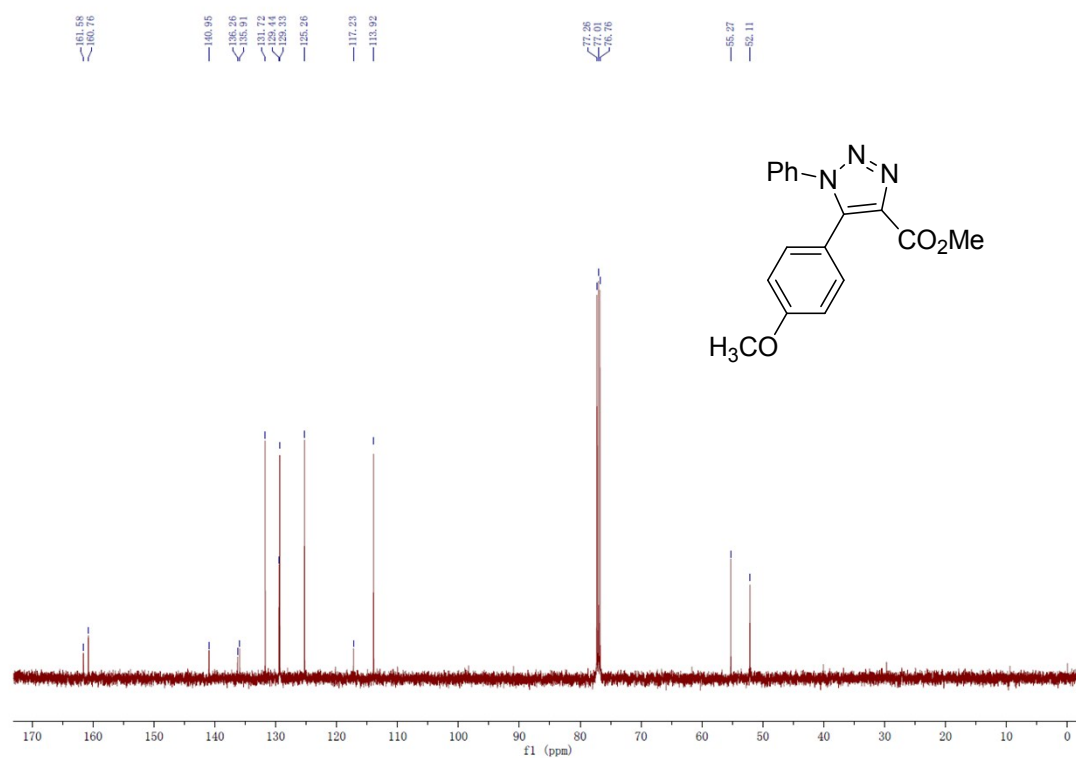
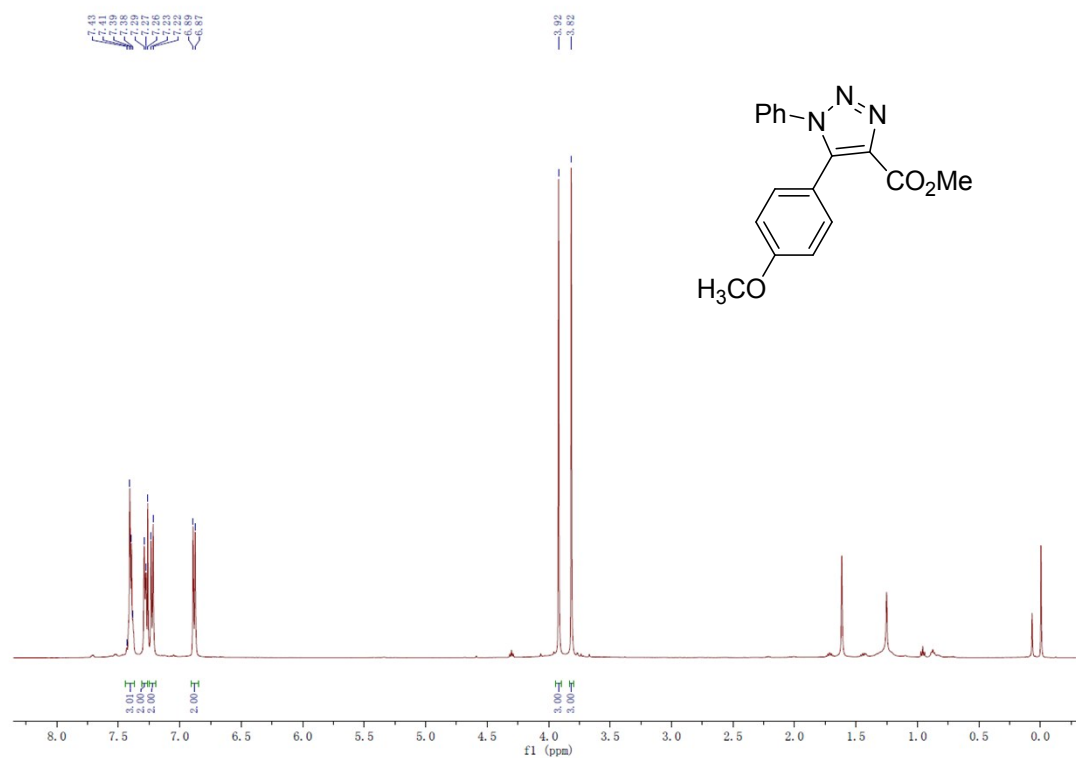
Methyl 5-(4-chlorophenyl)-1-phenyl-1*H*-1,2,3-triazole-4-carboxylate (3ca)



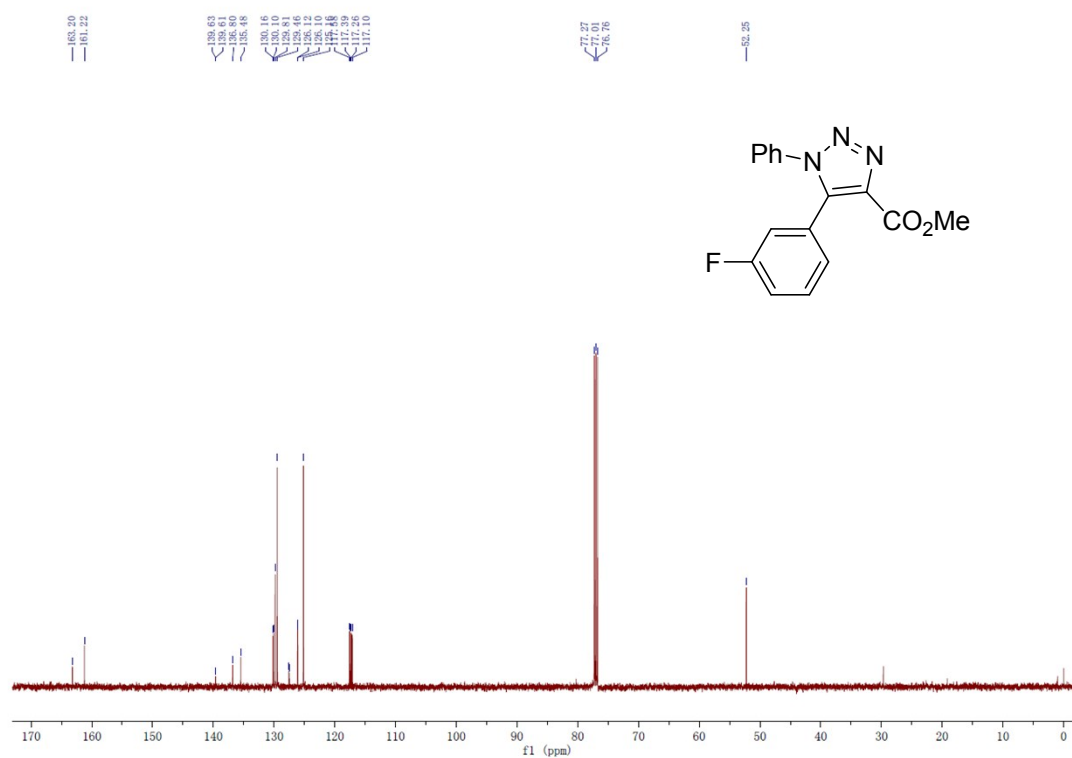
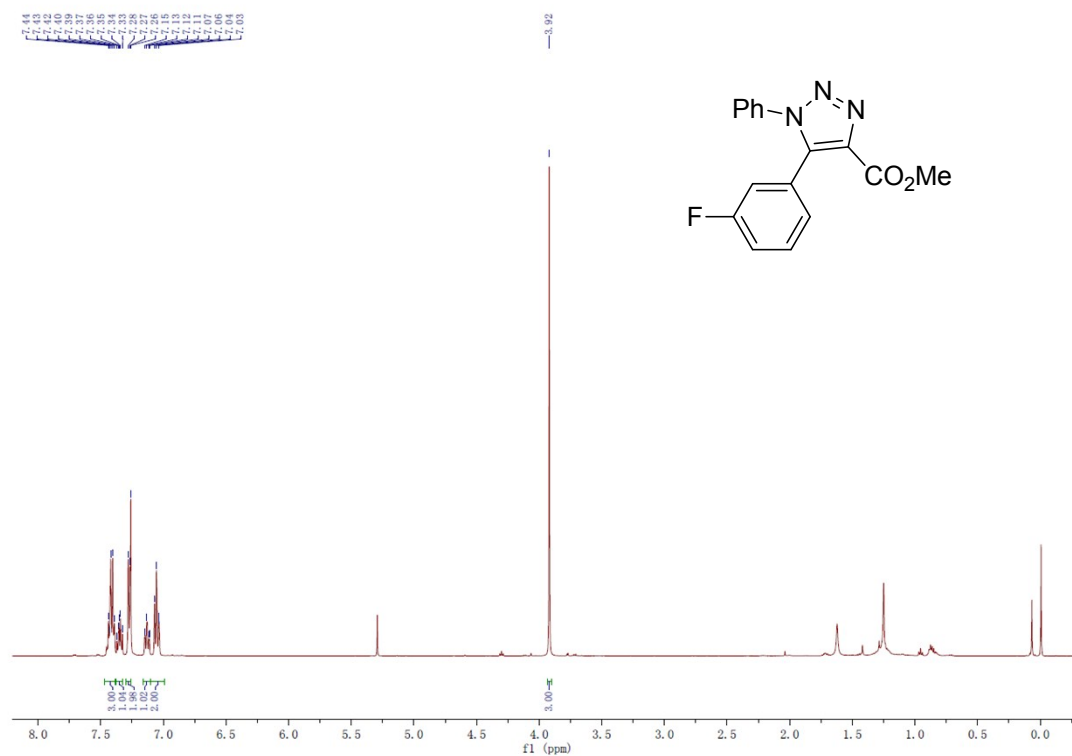
Methyl 1-phenyl-5-(*p*-tolyl)-1*H*-1,2,3-triazole-4-carboxylate (3da)



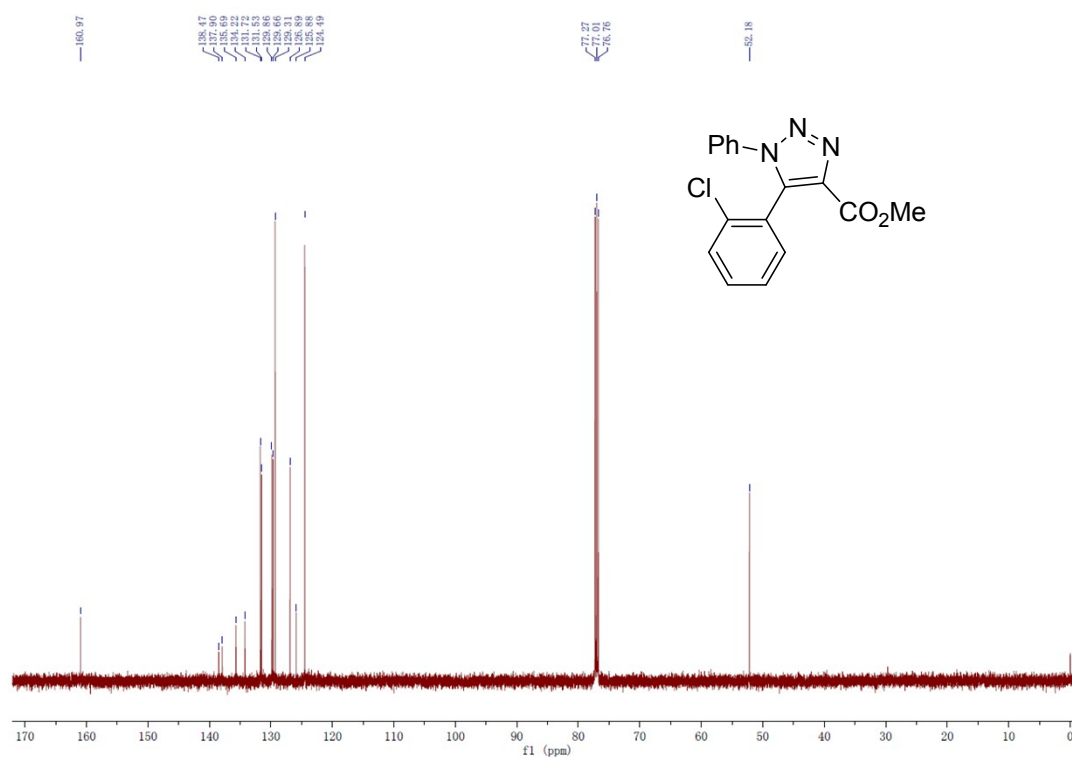
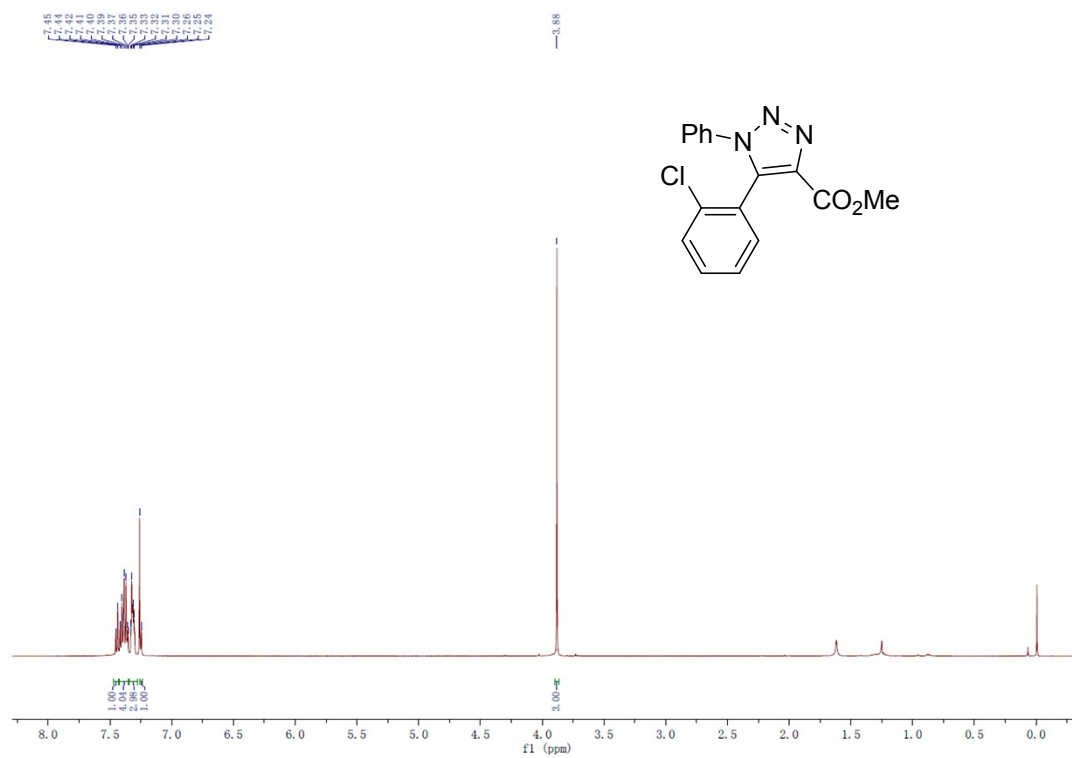
Methyl 5-(4-methoxyphenyl)-1-phenyl-1*H*-1,2,3-triazole-4-carboxylate (3ea)



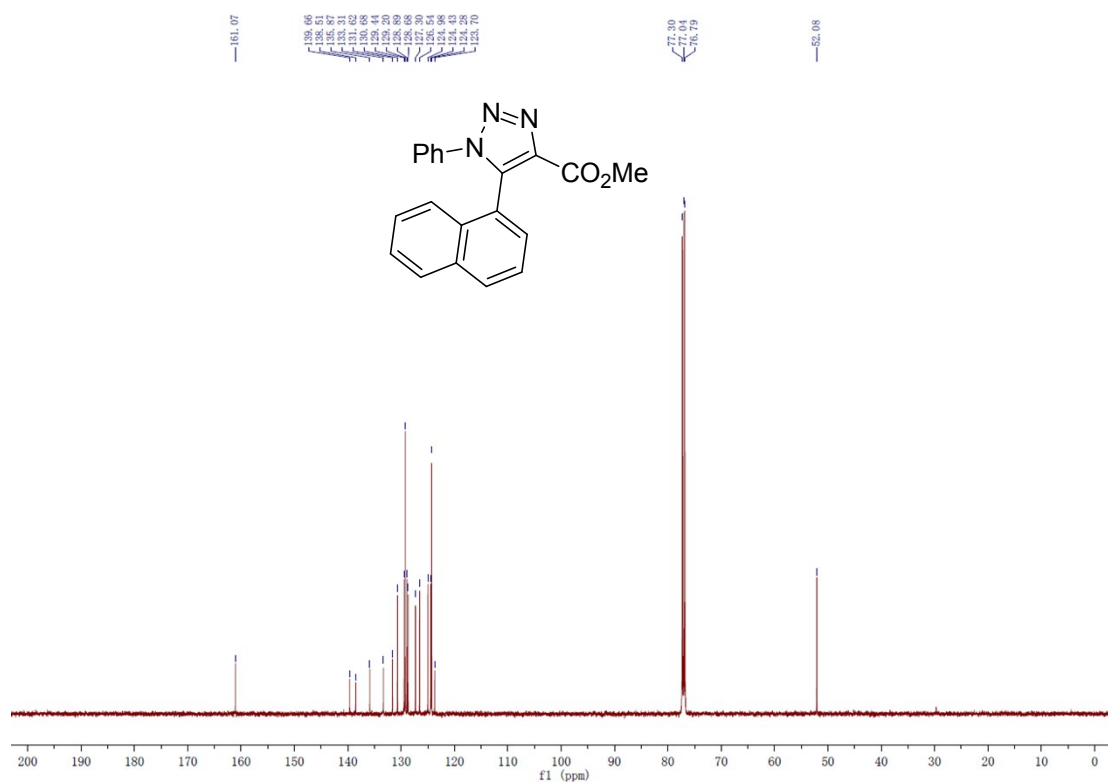
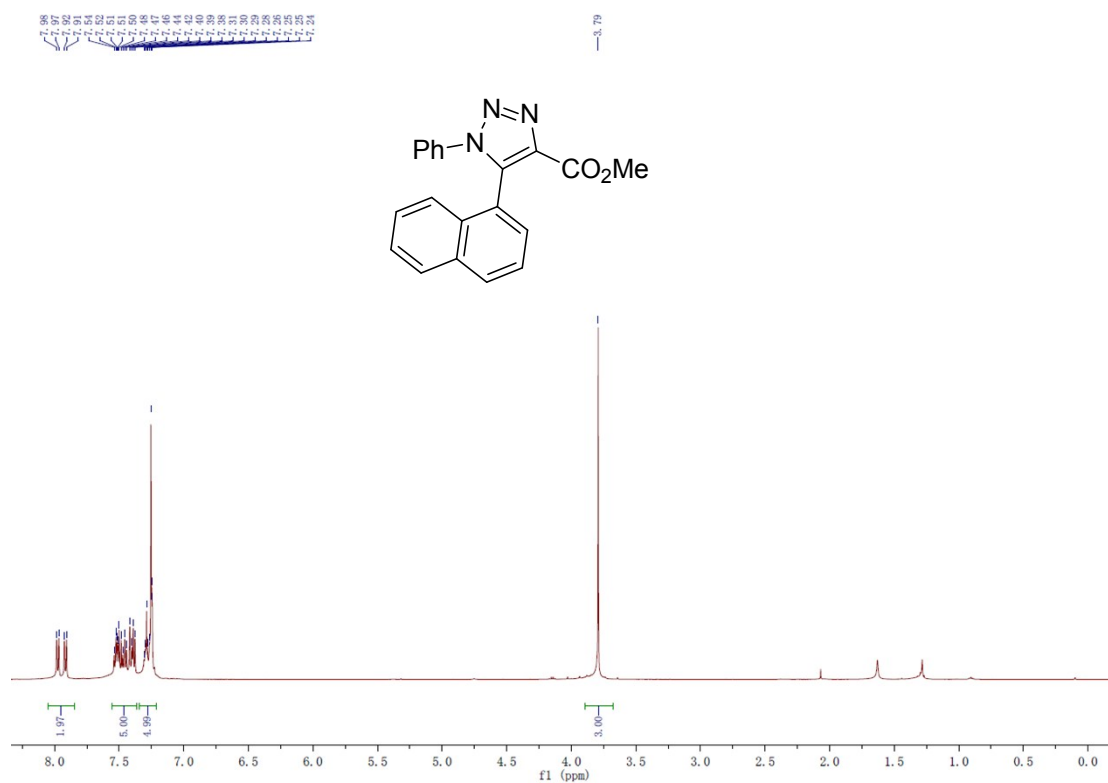
Methyl 5-(3-fluorophenyl)-1-phenyl-1H-1,2,3-triazole-4-carboxylate (3fa)



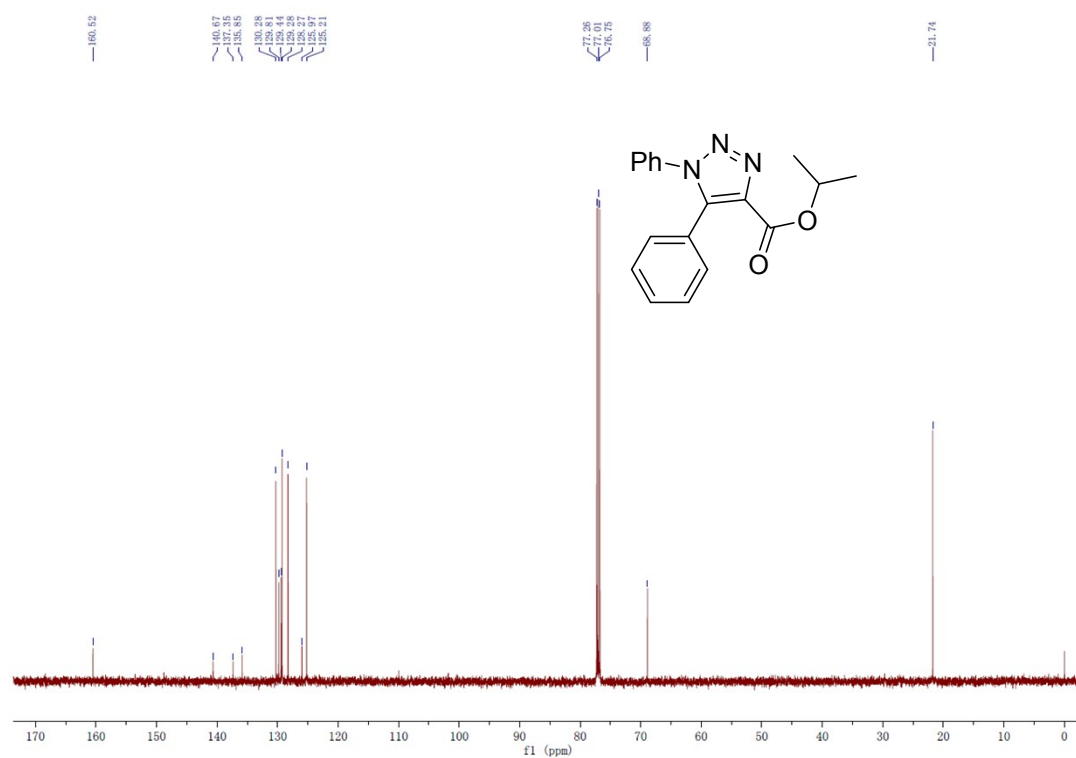
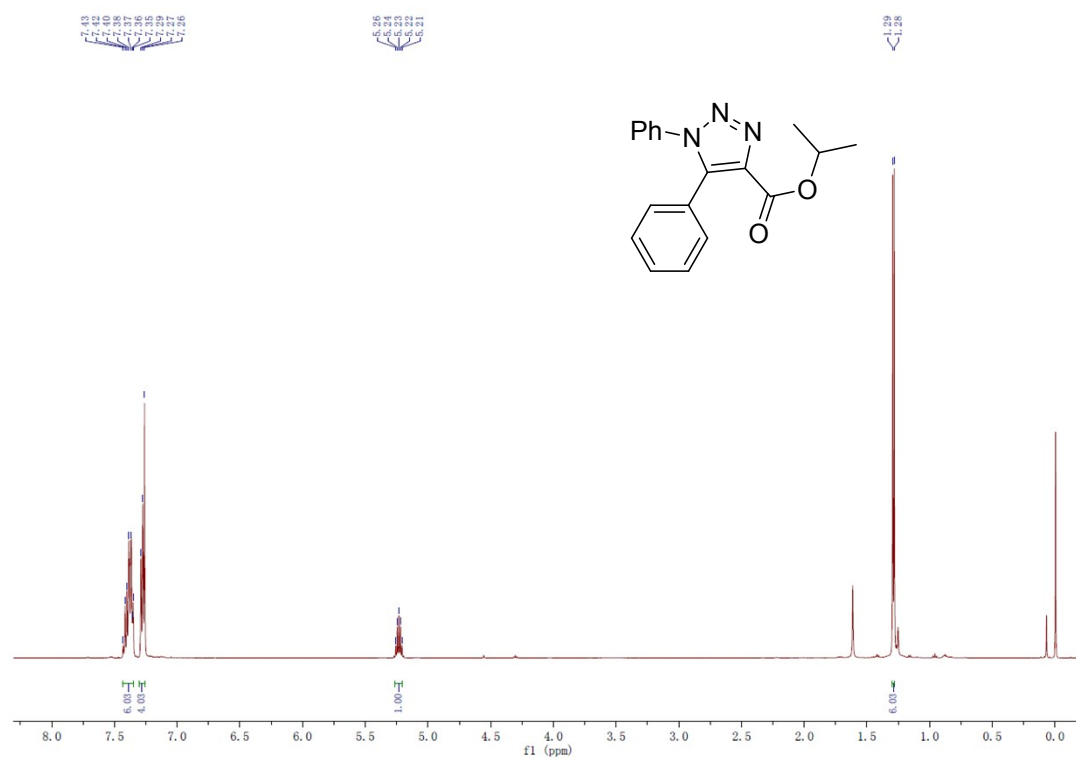
Methyl 5-(2-chlorophenyl)-1-phenyl-1*H*-1,2,3-triazole-4-carboxylate (3ga)



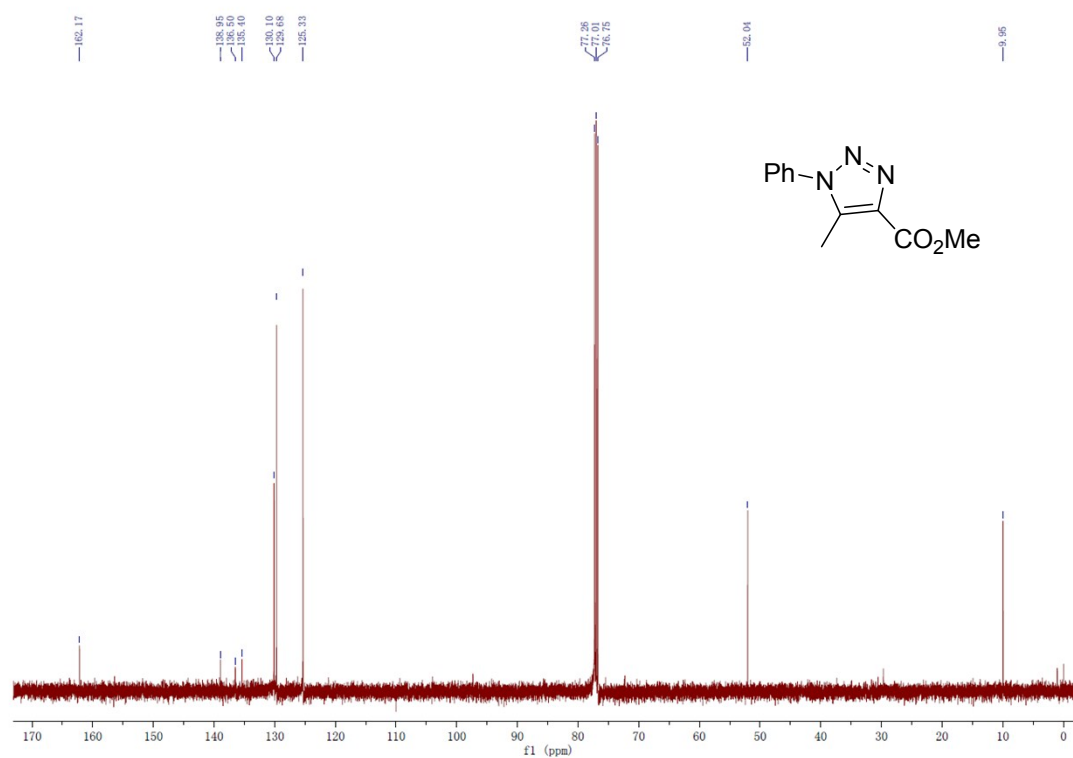
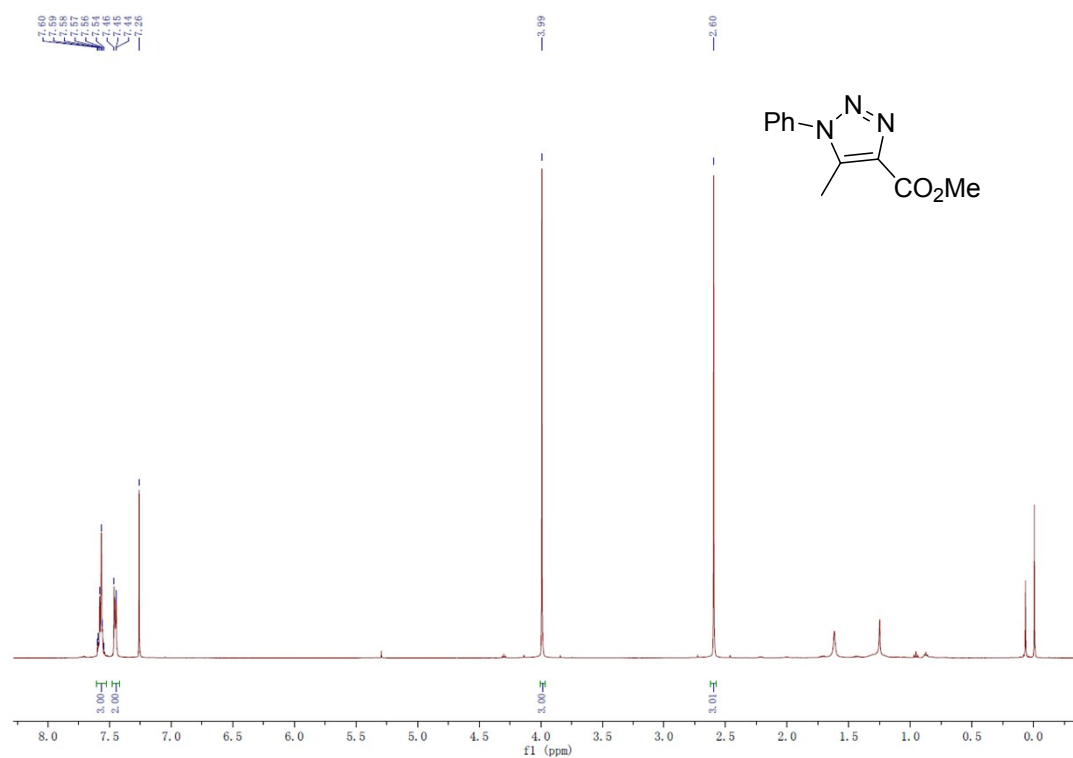
Methyl 5-(naphthalen-1-yl)-1-phenyl-1*H*-1,2,3-triazole-4-carboxylate (3ha)



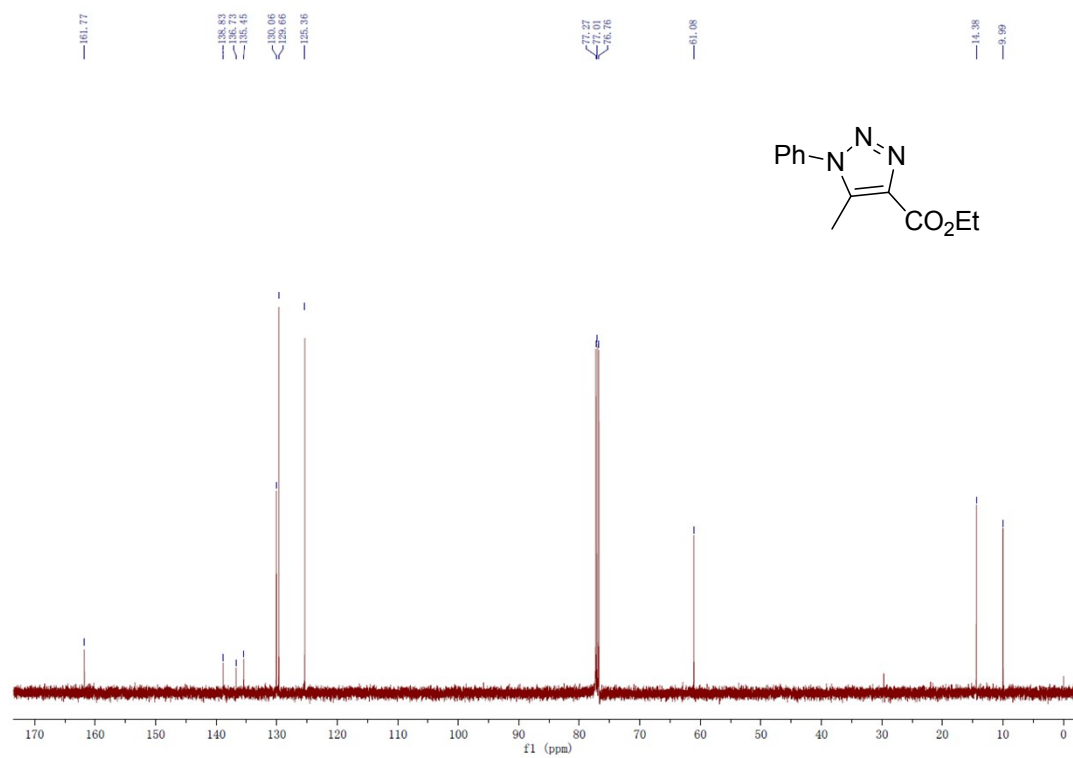
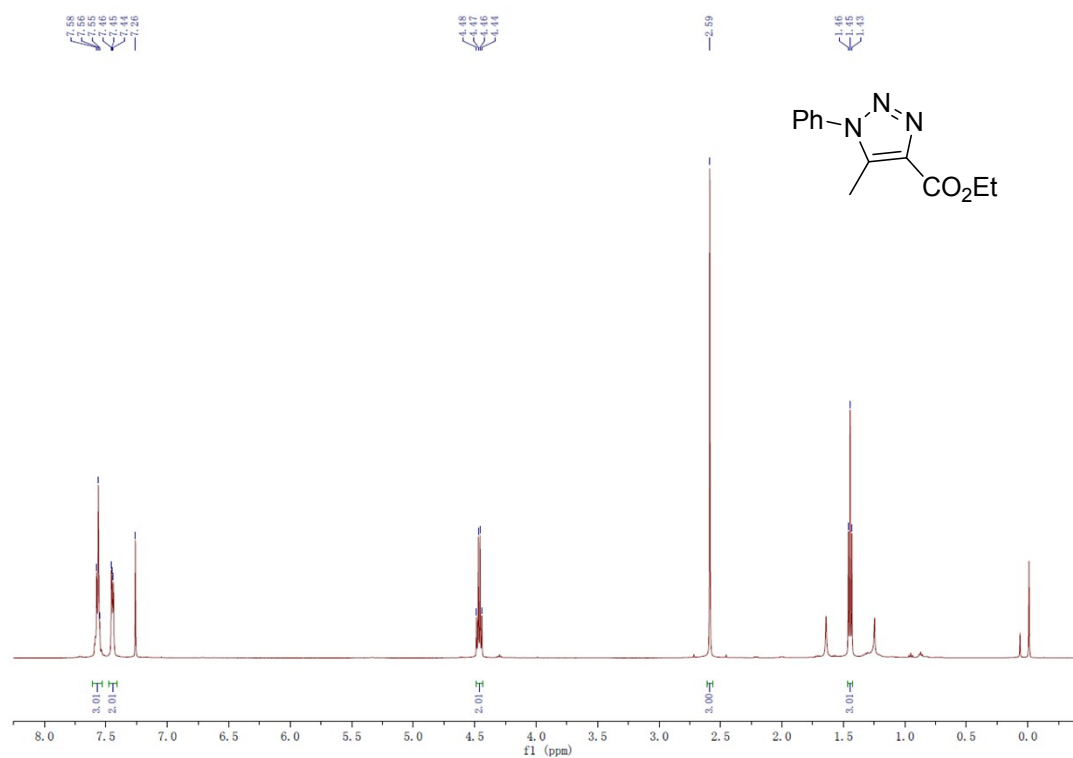
Isopropyl 1,5-diphenyl-1*H*-1,2,3-triazole-4-carboxylate (3ia)



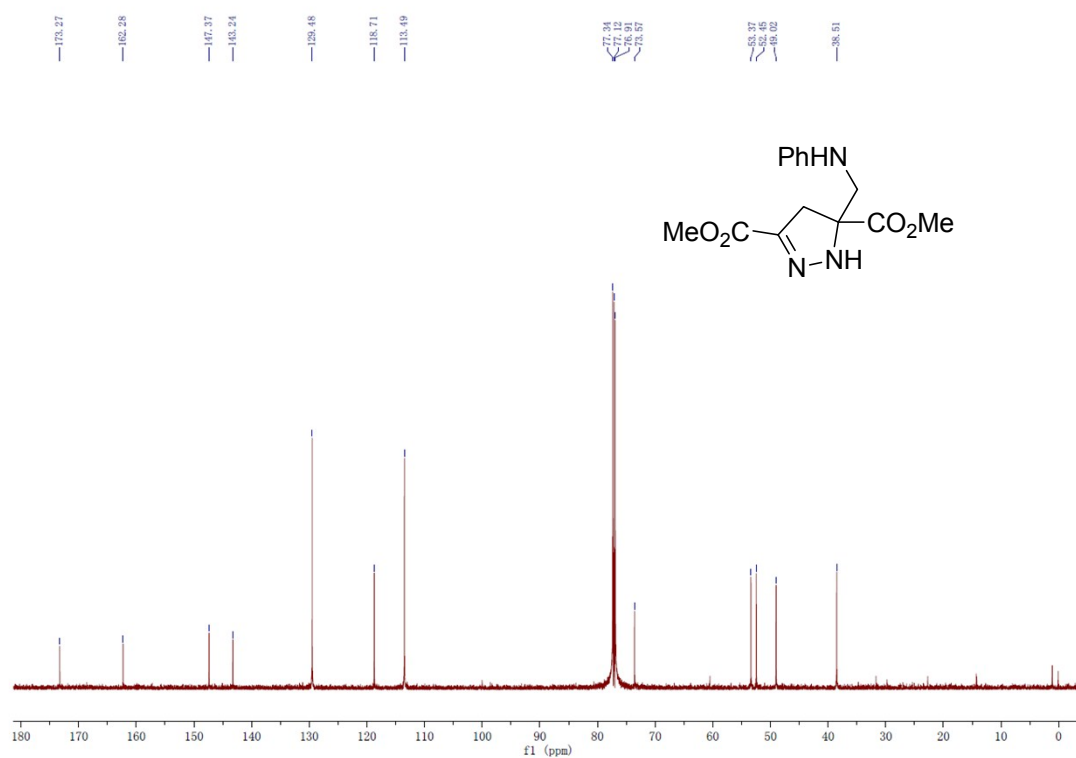
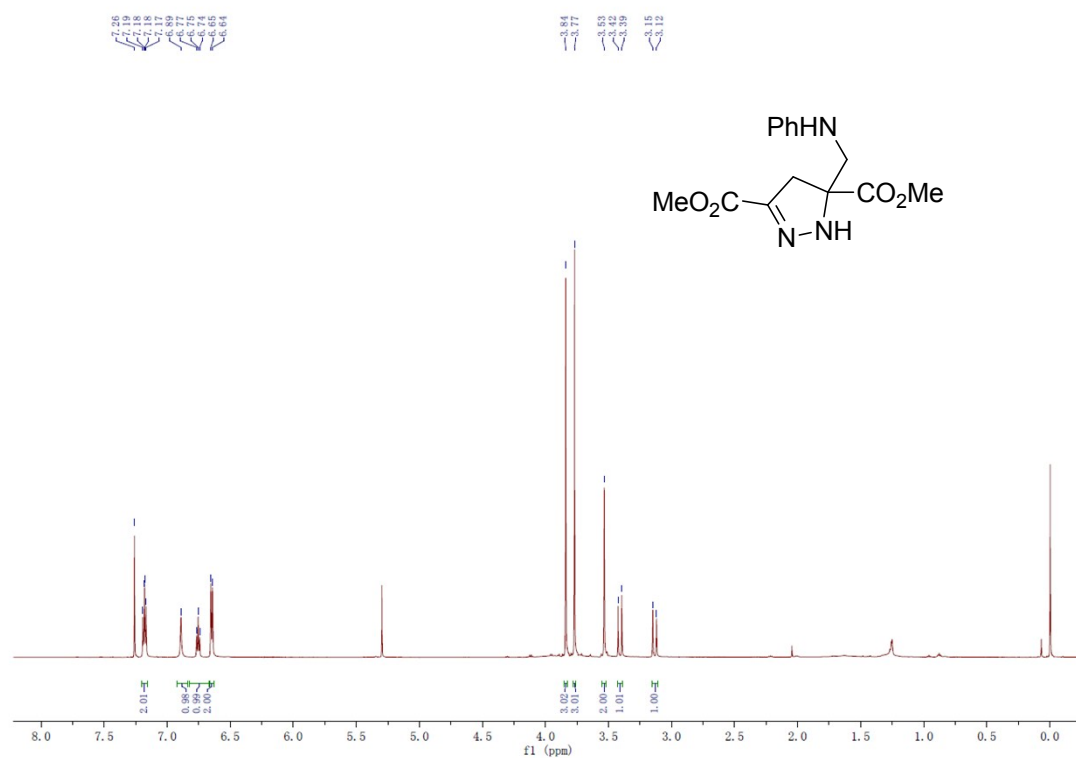
Methyl 5-methyl-1-phenyl-1*H*-1,2,3-triazole-4-carboxylate (3ja)



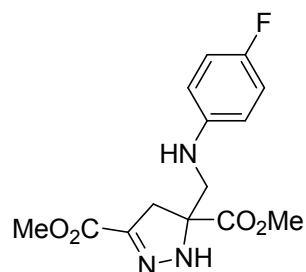
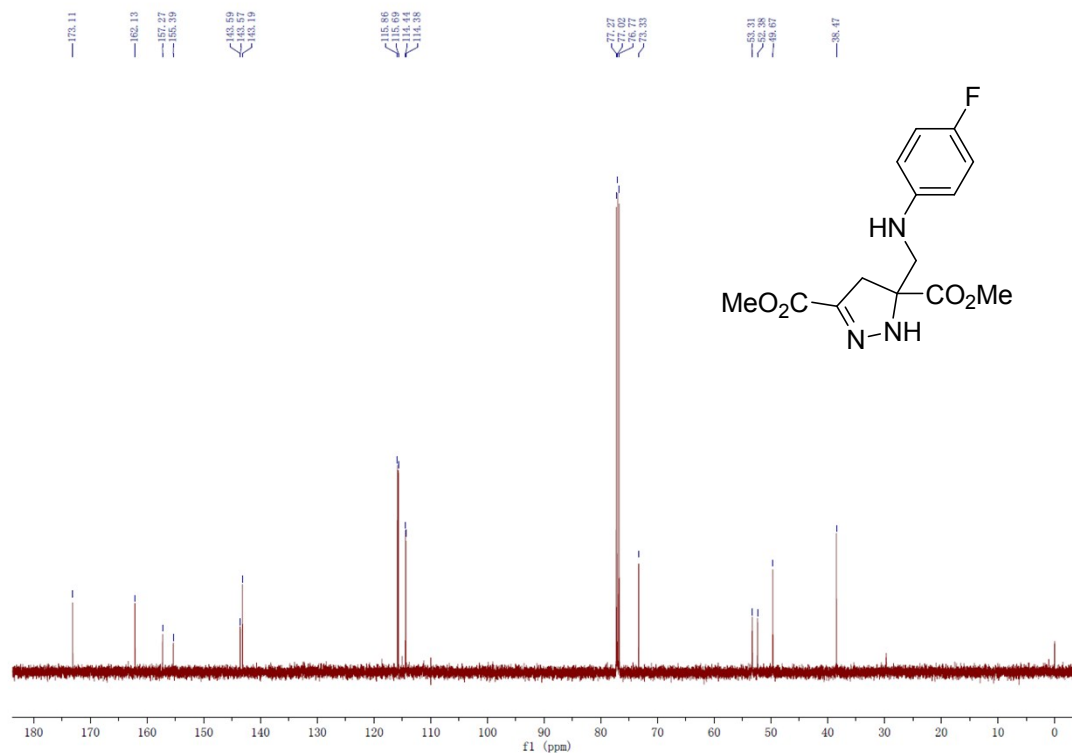
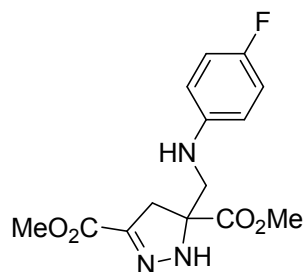
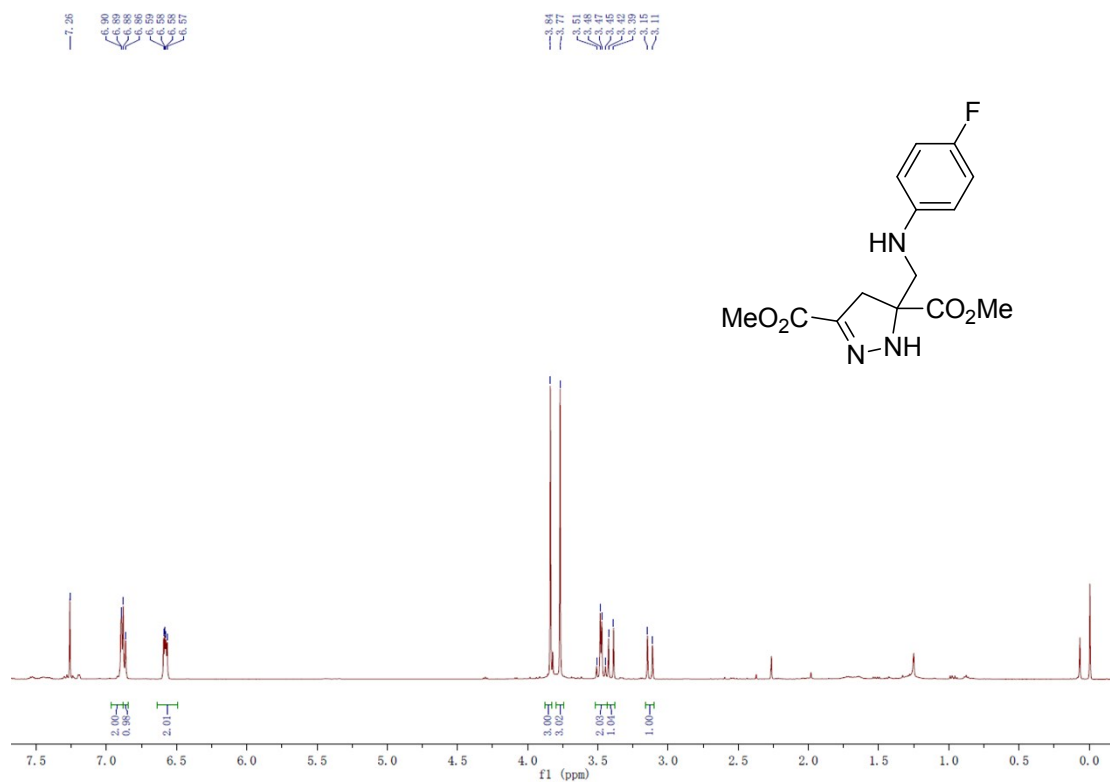
Ethyl 5-methyl-1-phenyl-1*H*-1,2,3-triazole-4-carboxylate (3ka)



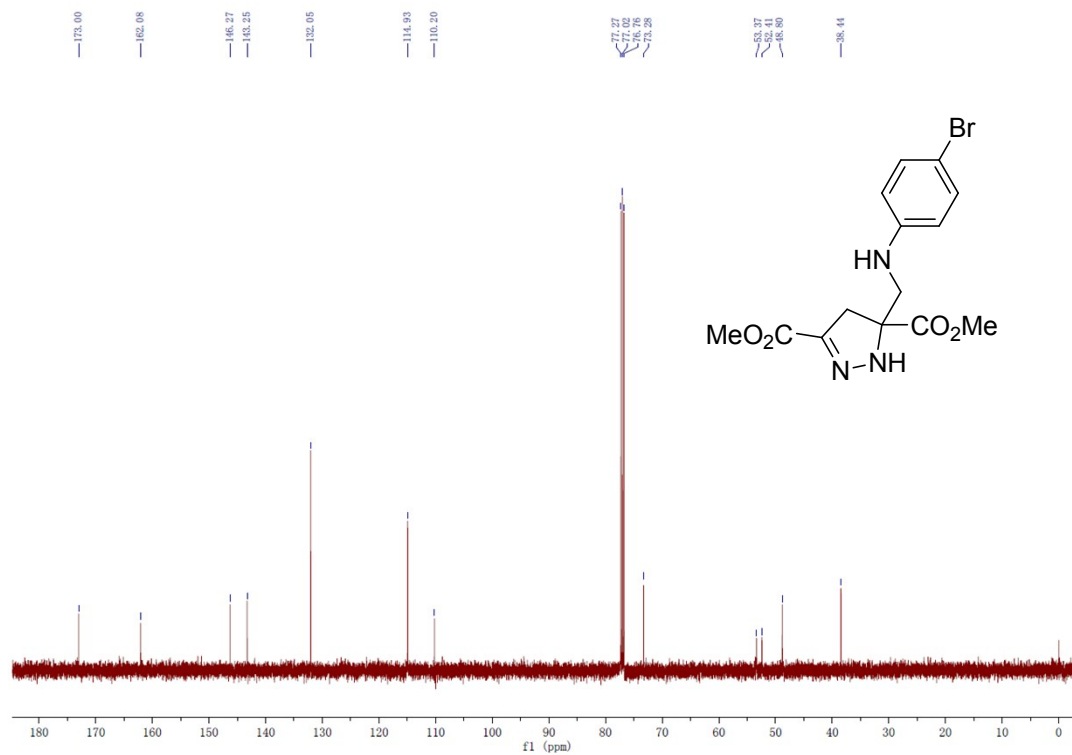
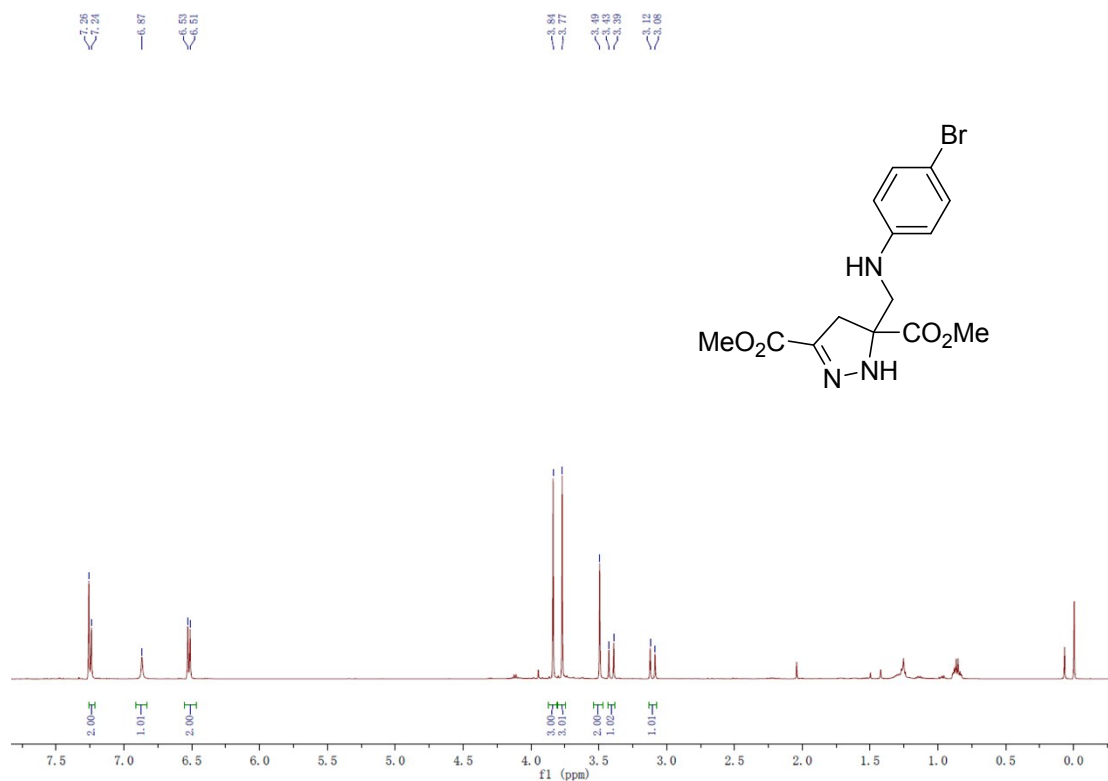
Dimethyl 5-((phenylamino)methyl)-4,5-dihydro-1H-pyrazole-3,5-dicarboxylate (5aa)



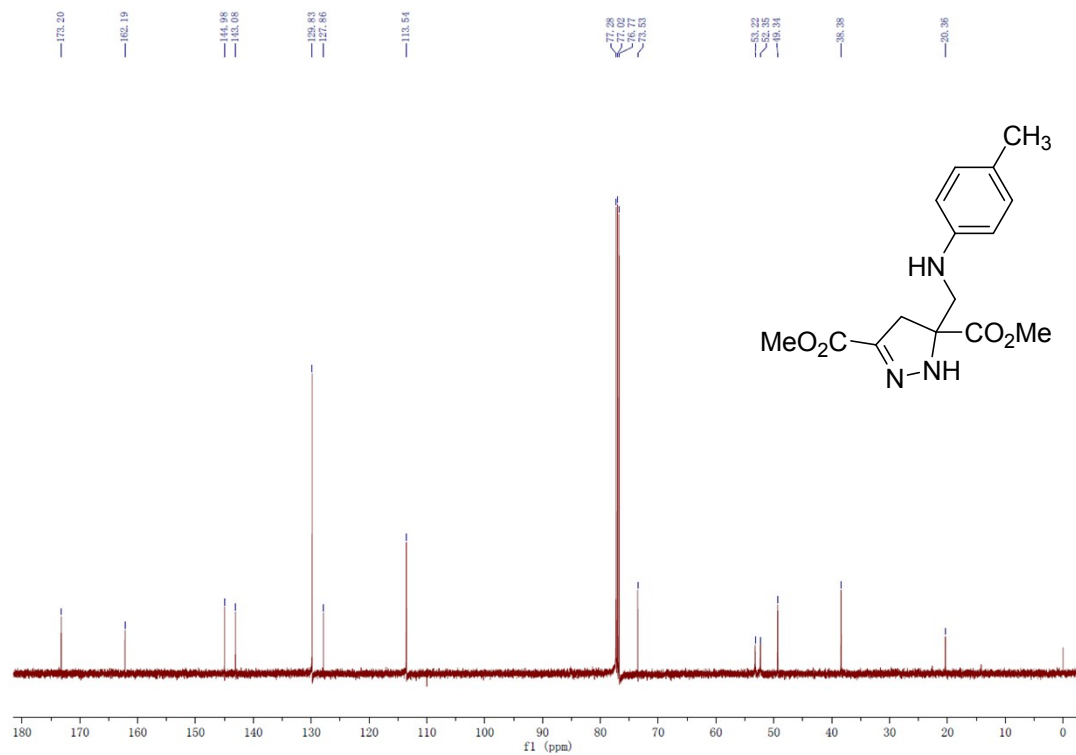
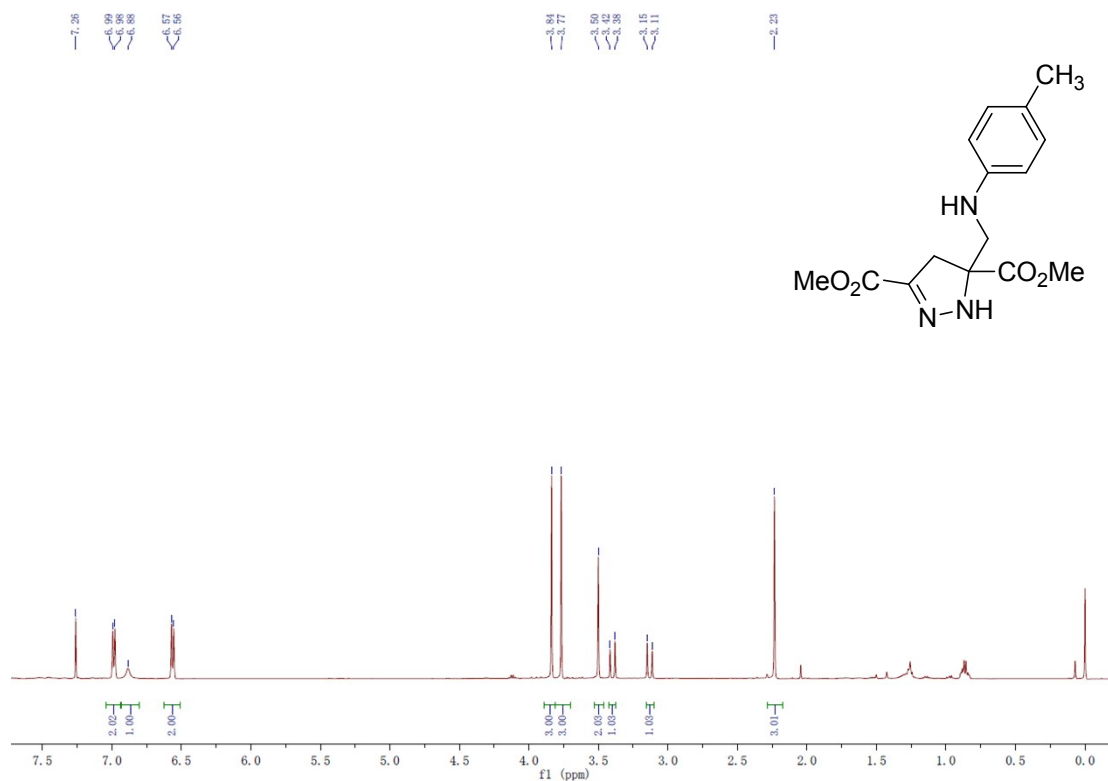
Dimethyl 5-(((4-fluorophenyl)amino)methyl)-4,5-dihydro-1H-pyrazole-3,5-dicarboxylate (5ab)



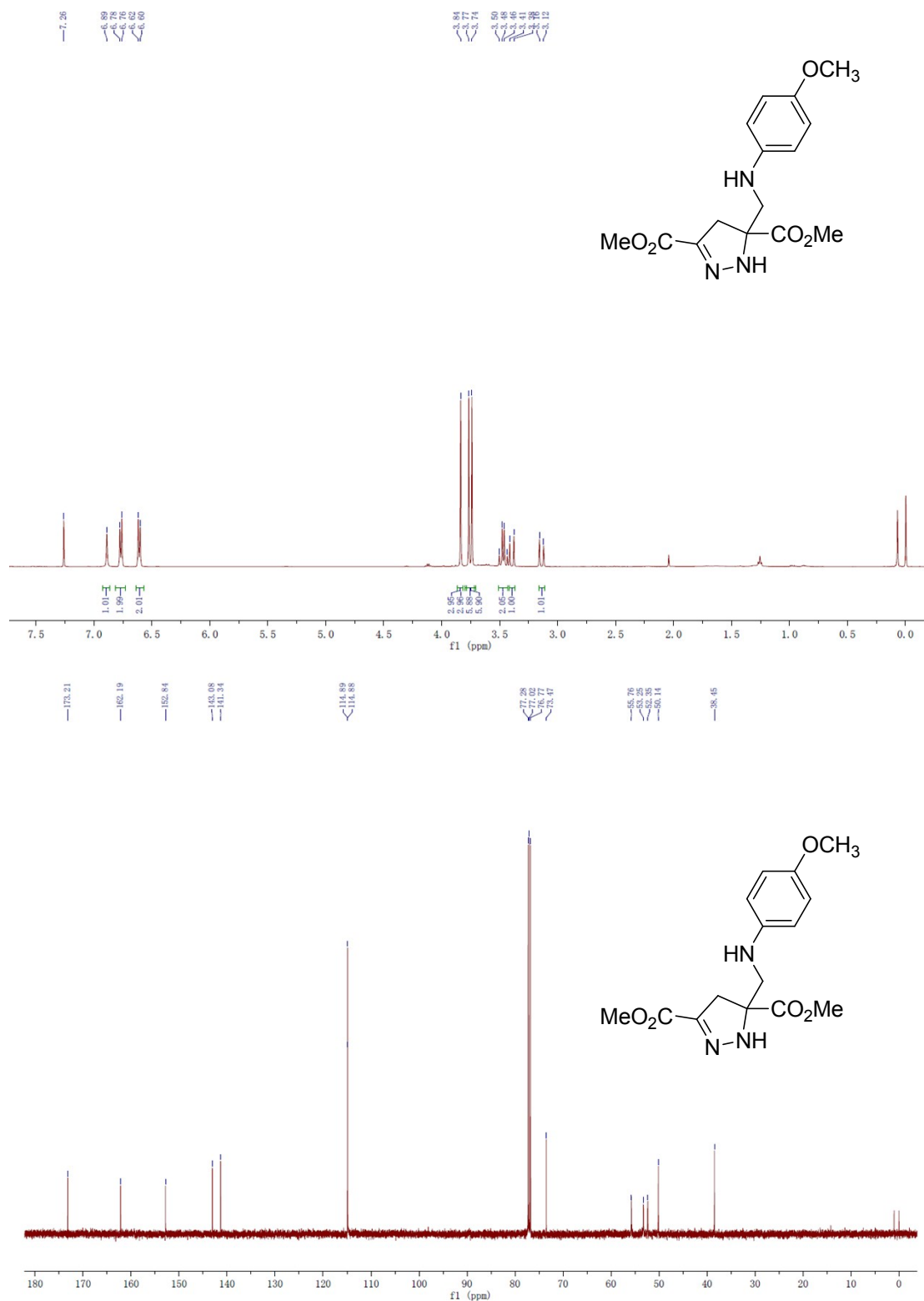
Dimethyl 5-(((4-bromophenyl)amino)methyl)-4,5-dihydro-1H-pyrazole-3,5-dicarboxylate (5ac)



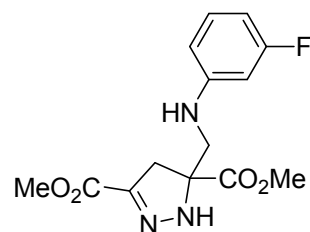
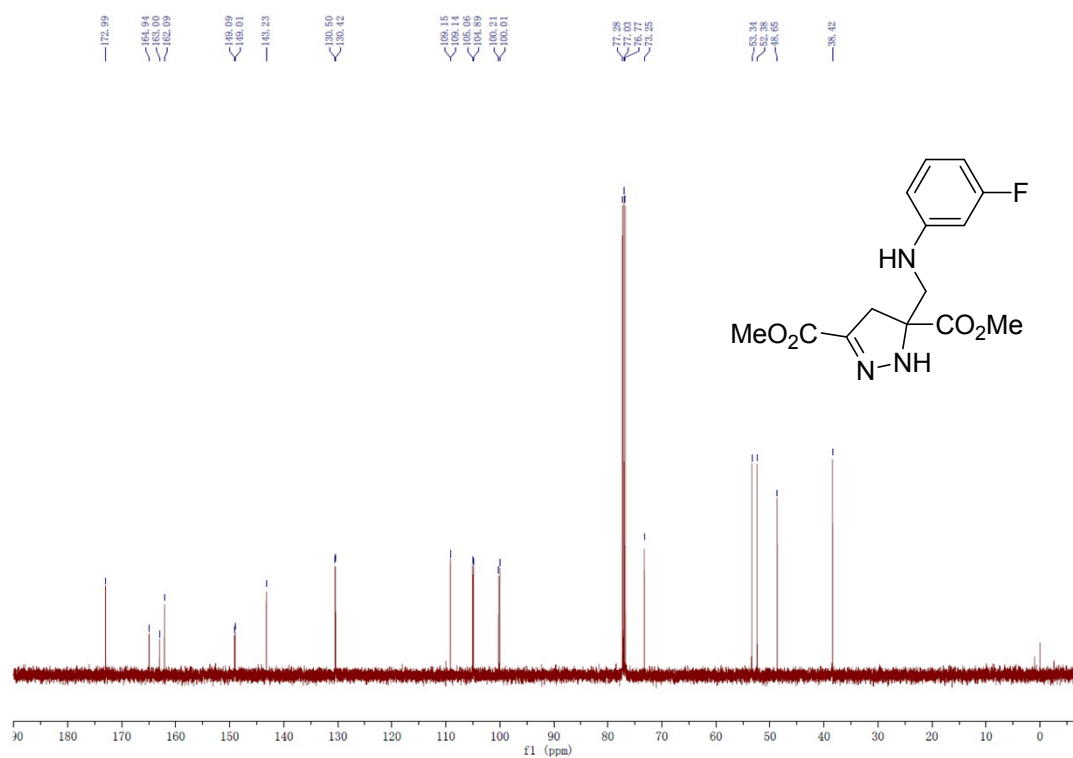
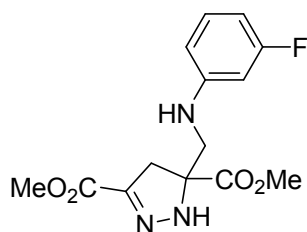
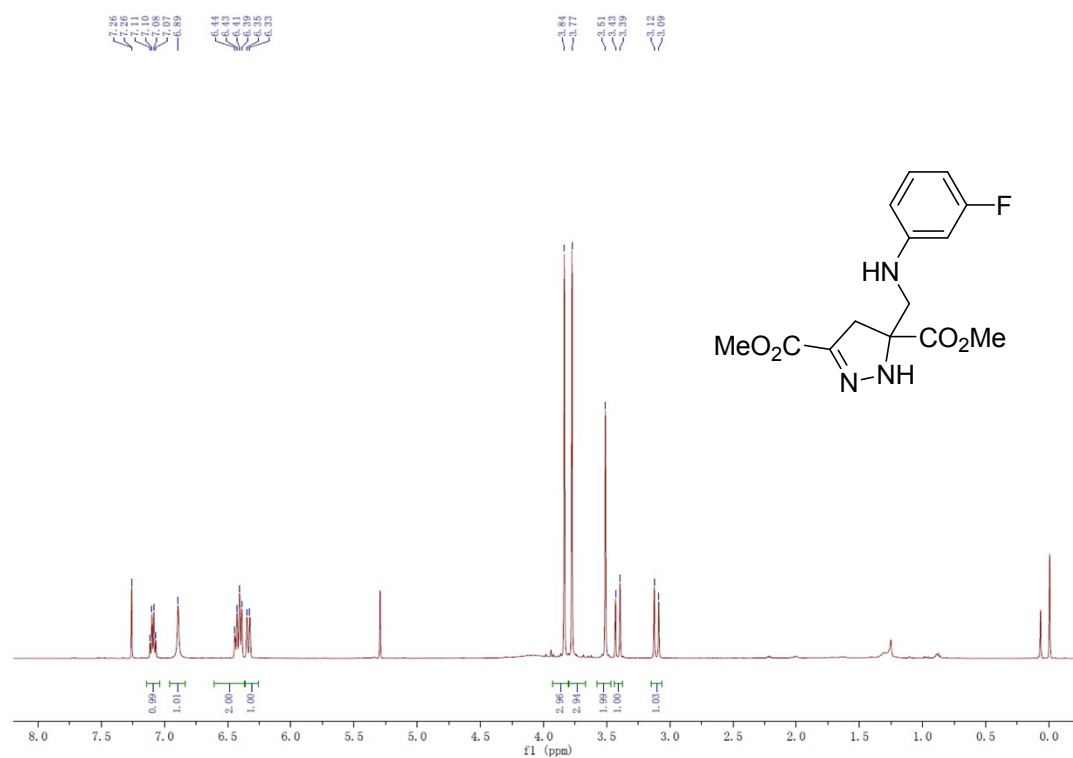
Dimethyl 5-((*p*-tolylamino)methyl)-4,5-dihydro-1*H*-pyrazole-3,5-dicarboxylate (5ad)



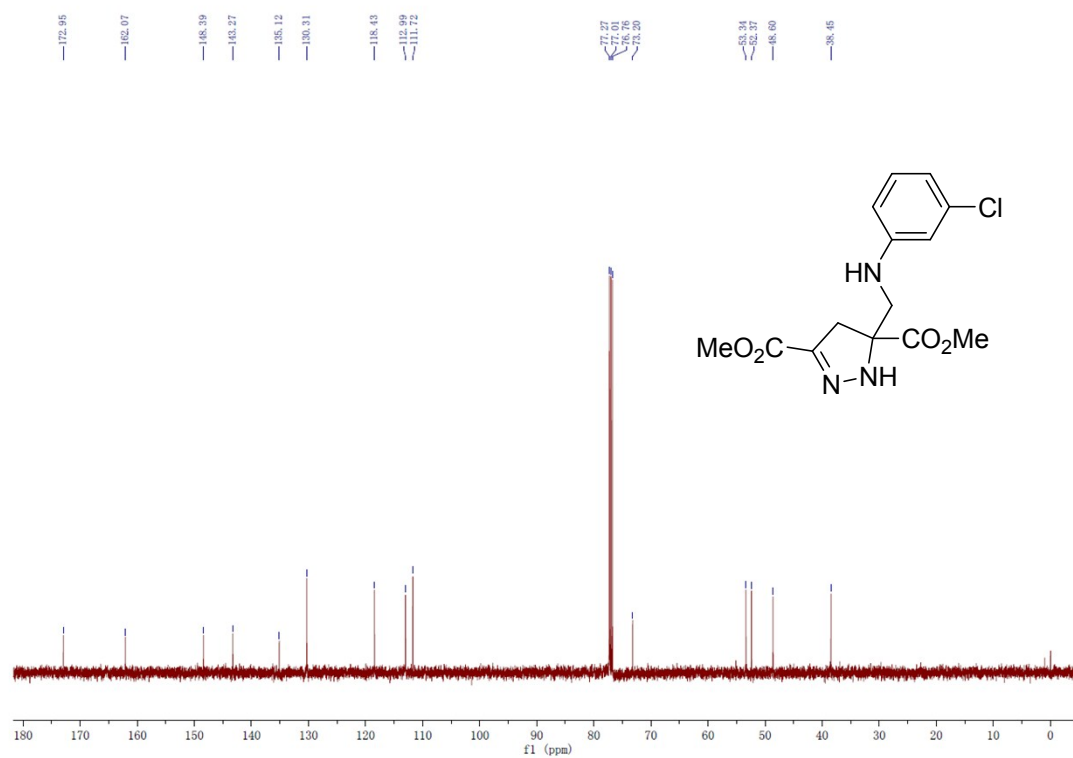
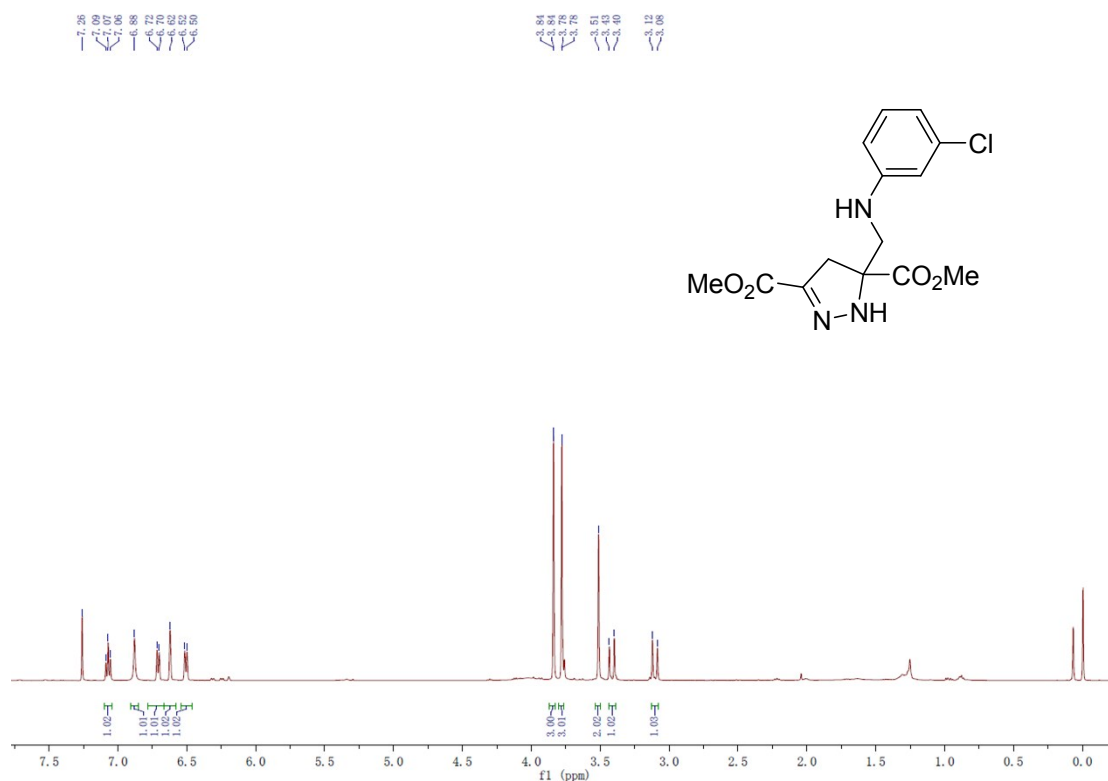
Dimethyl 5-(((4-methoxyphenyl)amino)methyl)-4,5-dihydro-1H-pyrazole-3,5-dicarboxylate (5ae)



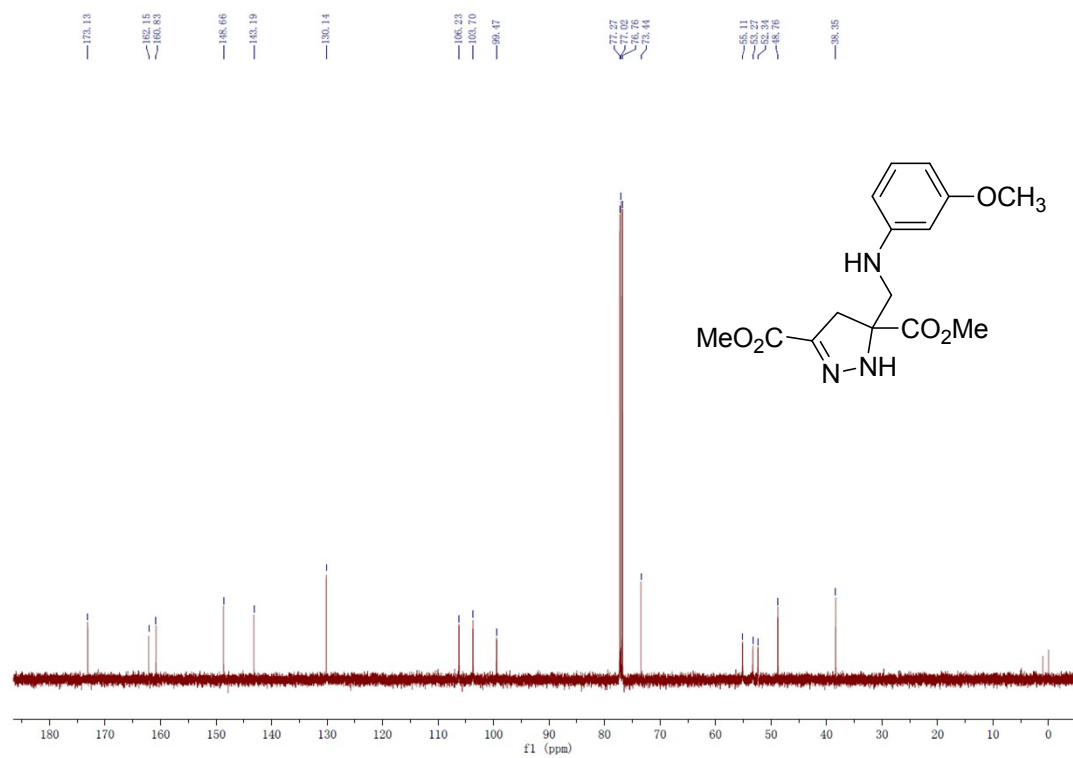
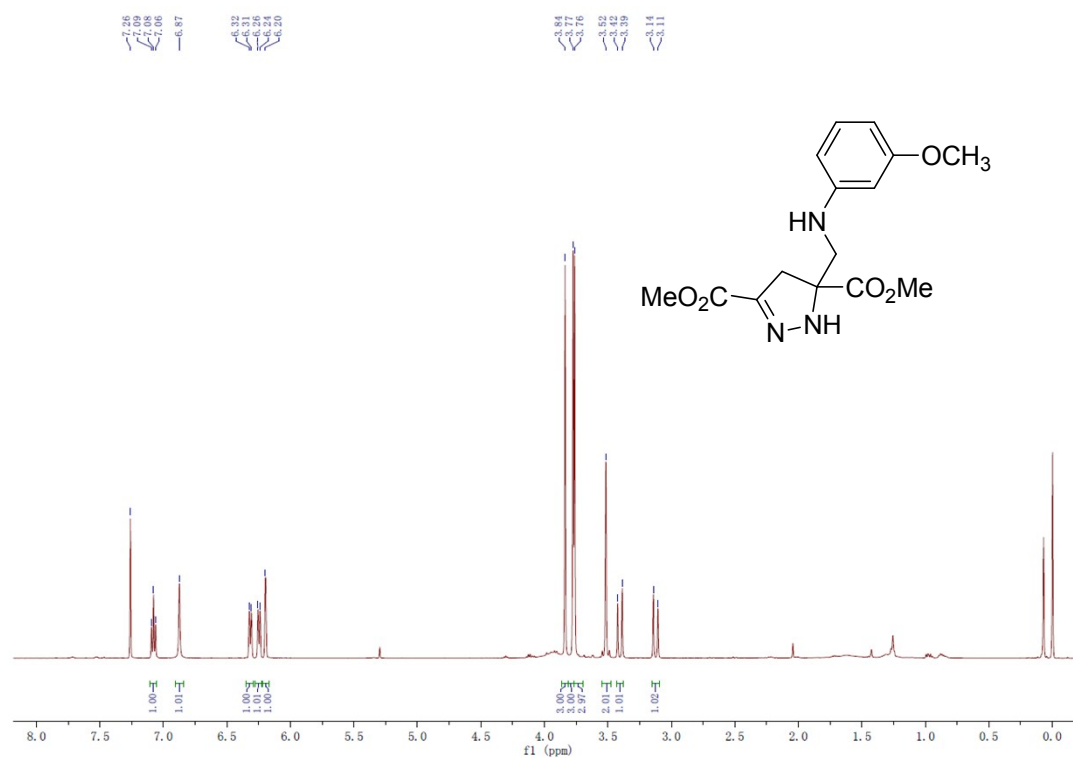
Dimethyl 5-(((3-fluorophenyl)amino)methyl)-4,5-dihydro-1H-pyrazole-3,5-dicarboxylate (5af)



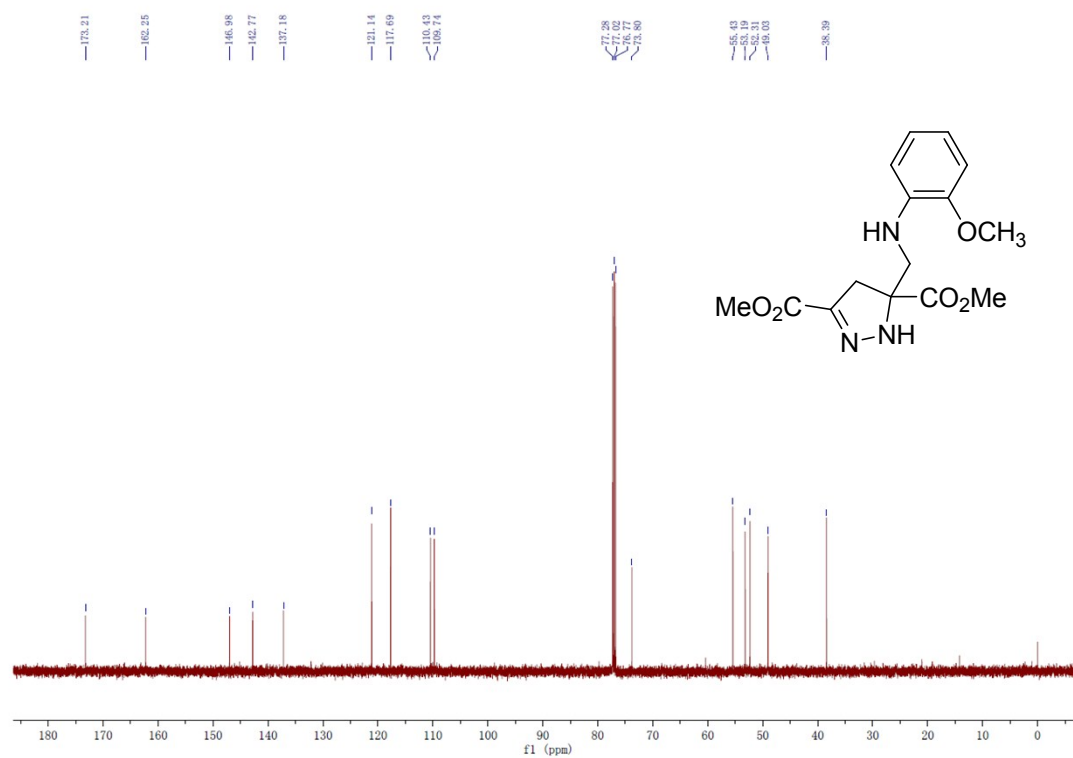
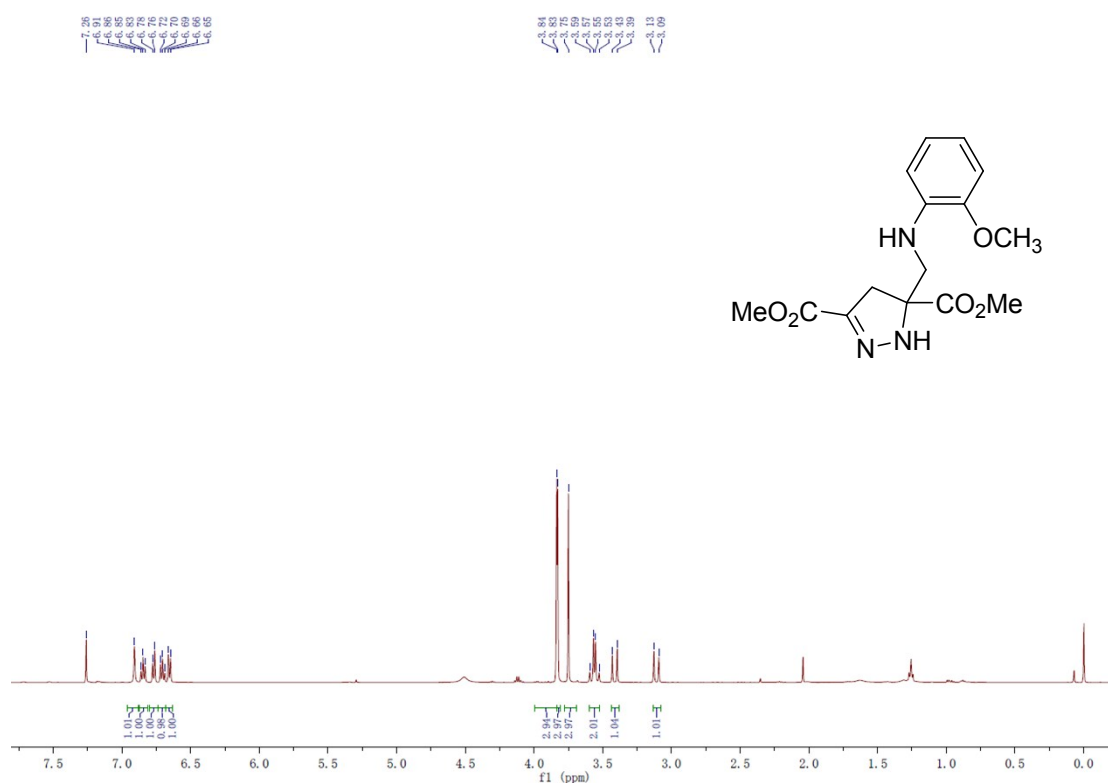
Dimethyl 5-(((3-chlorophenyl)amino)methyl)-4,5-dihydro-1H-pyrazole-3,5-dicarboxylate (5ag)



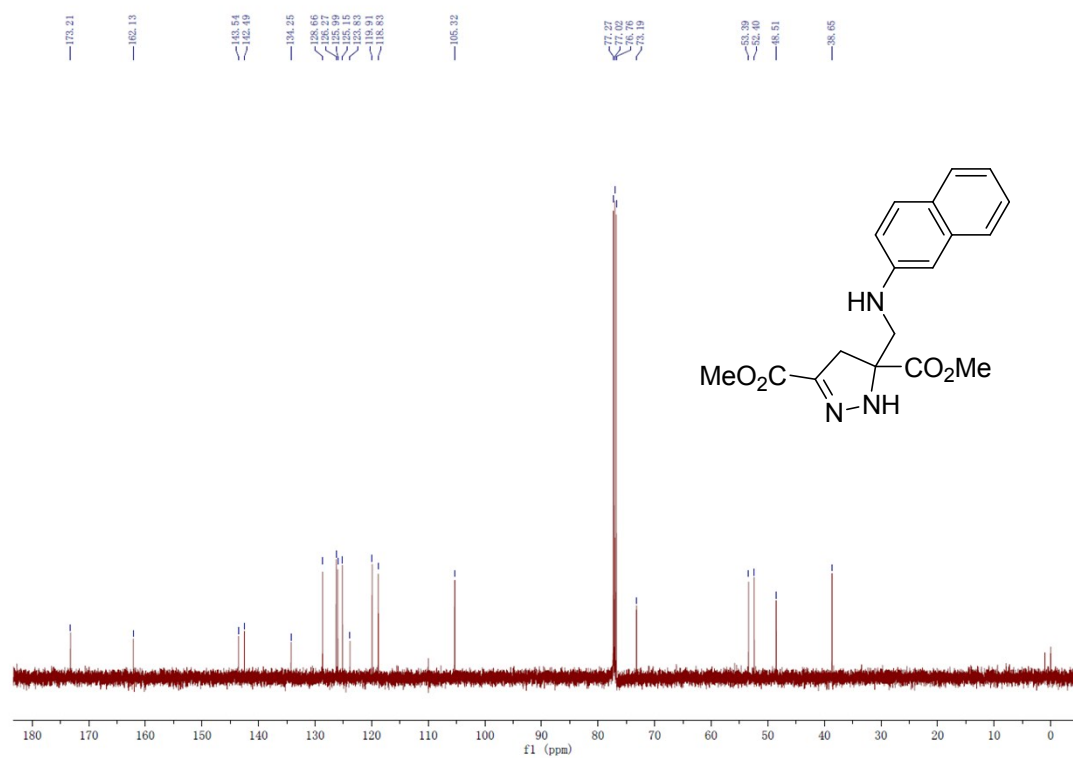
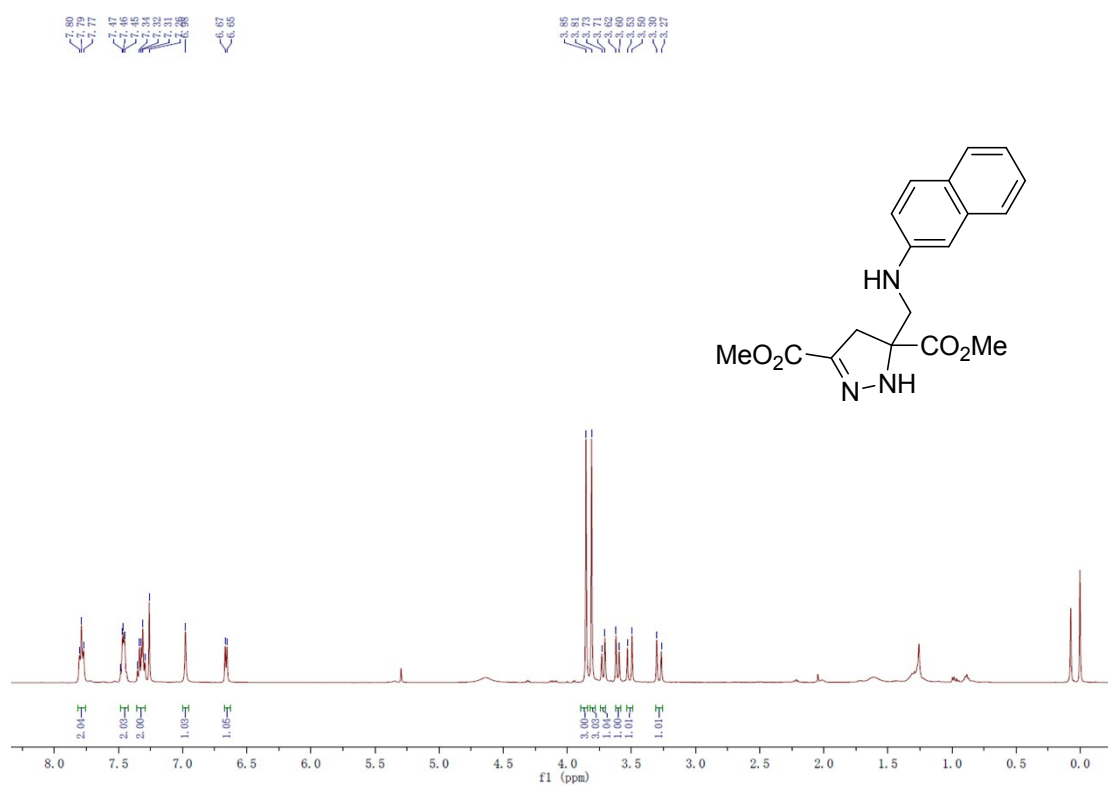
Dimethyl 5-(((3-methoxyphenyl)amino)methyl)-4,5-dihydro-1H-pyrazole-3,5-dicarboxylate (5ah)



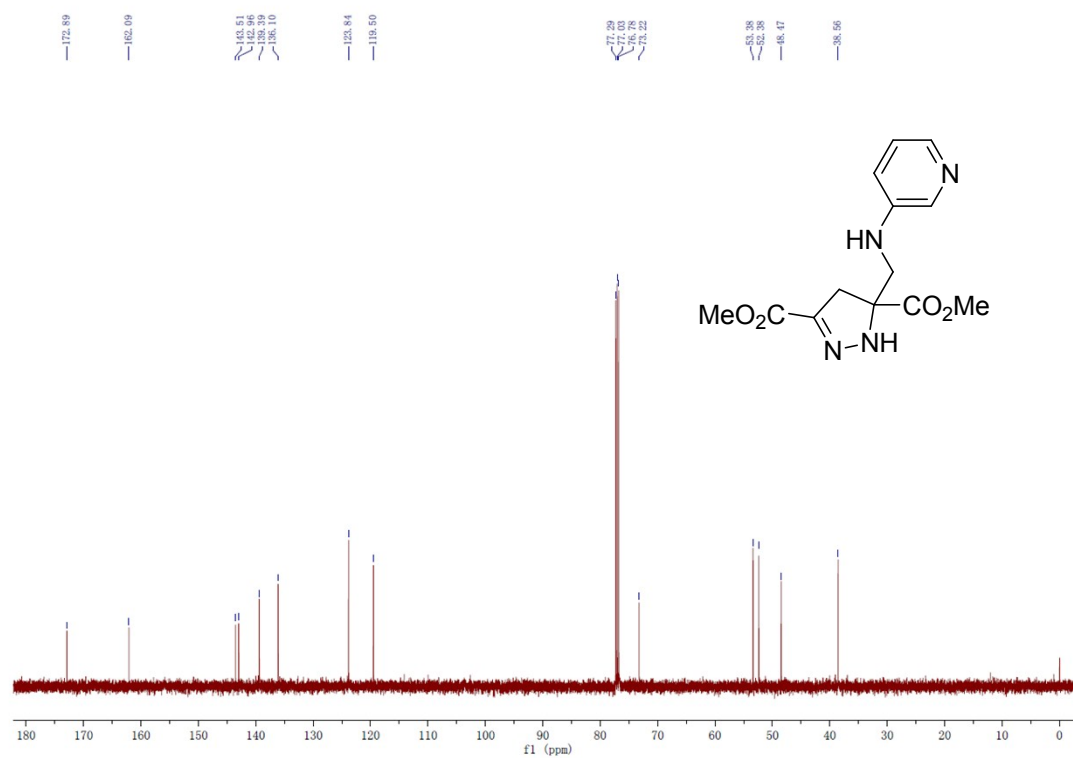
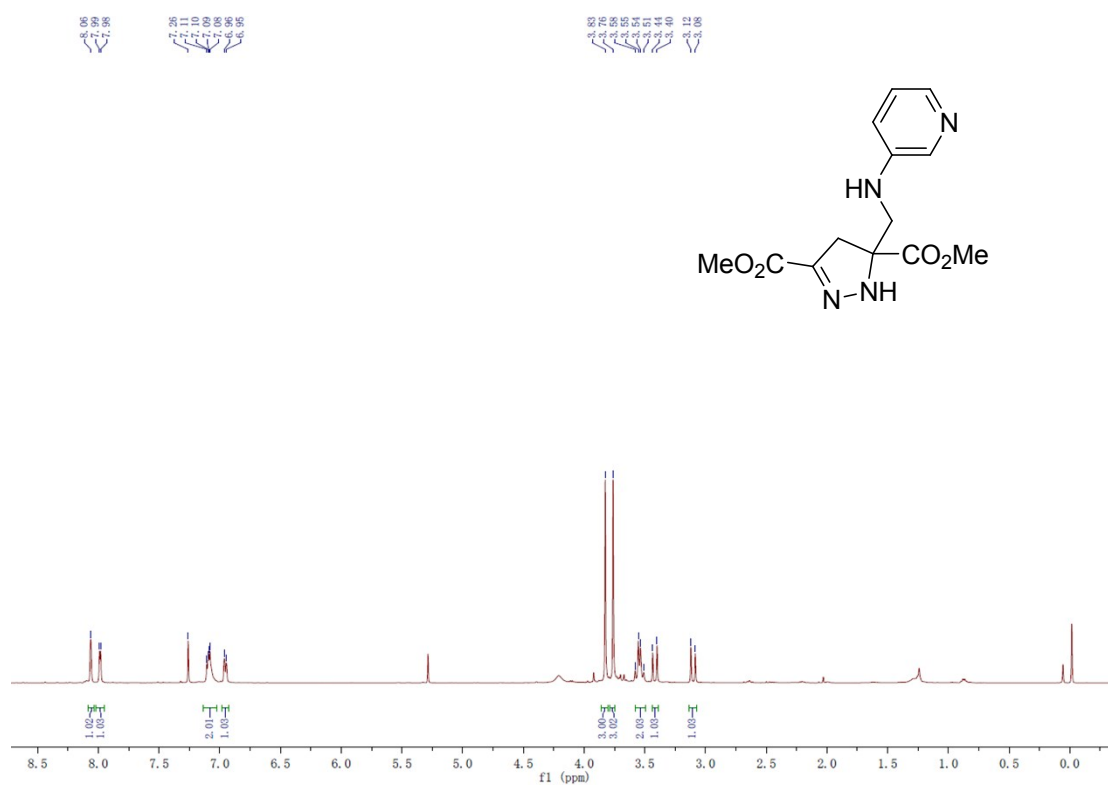
Dimethyl 5-(((2-methoxyphenyl)amino)methyl)-4,5-dihydro-1H-pyrazole-3,5-dicarboxylate (5ai)



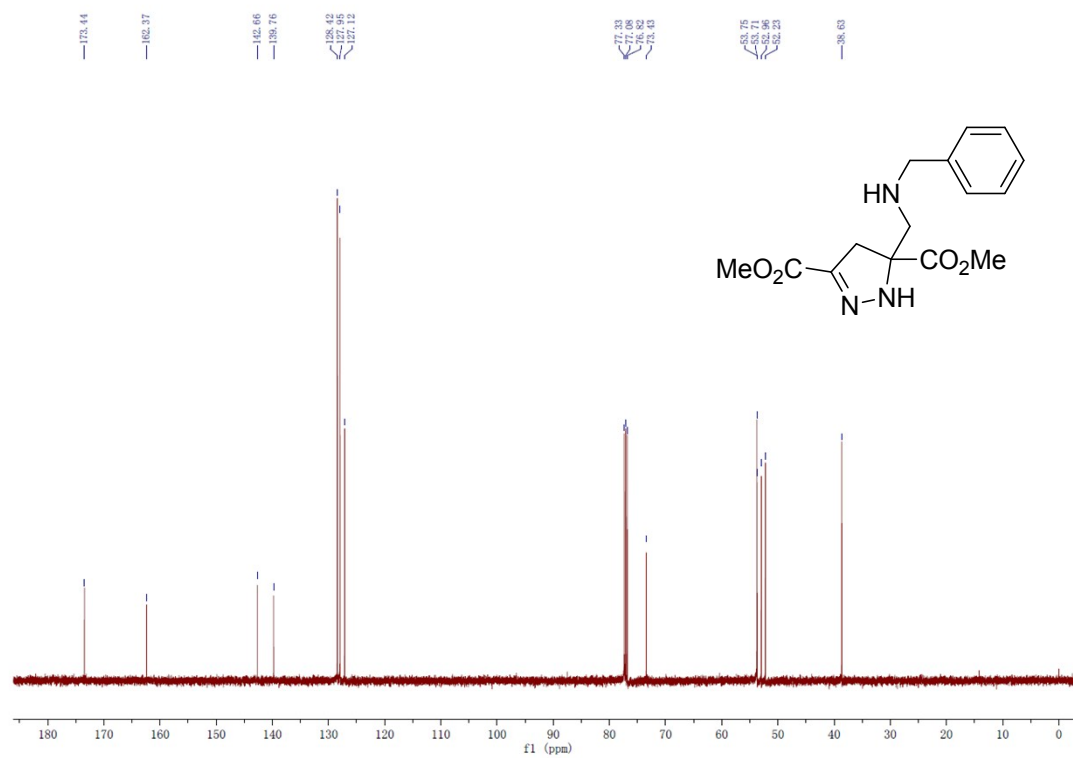
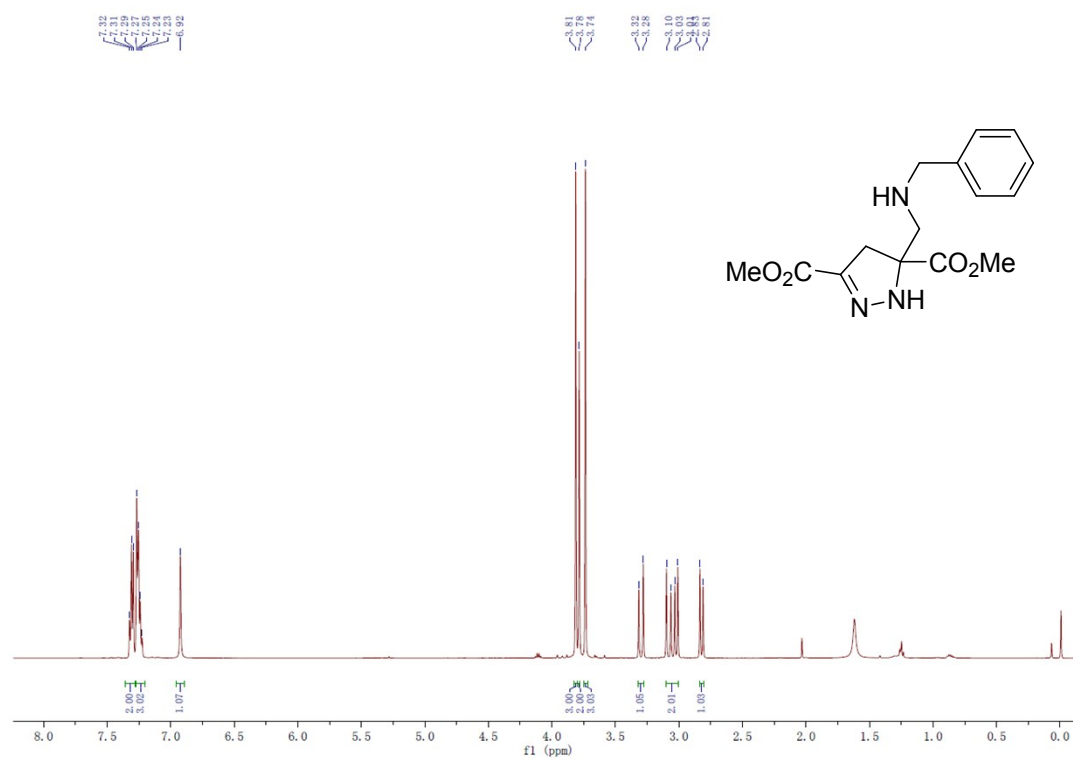
Dimethyl 5-((naphthalen-2-ylamino)methyl)-4,5-dihydro-1H-pyrazole-3,5-dicarboxylate (5aj)



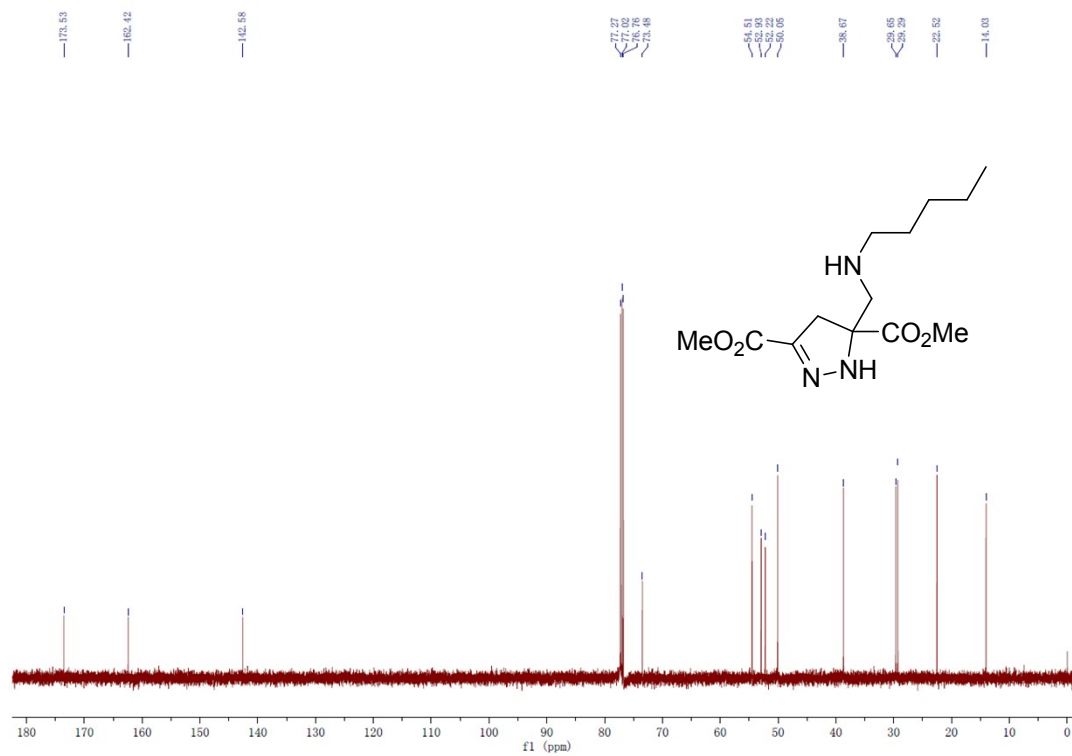
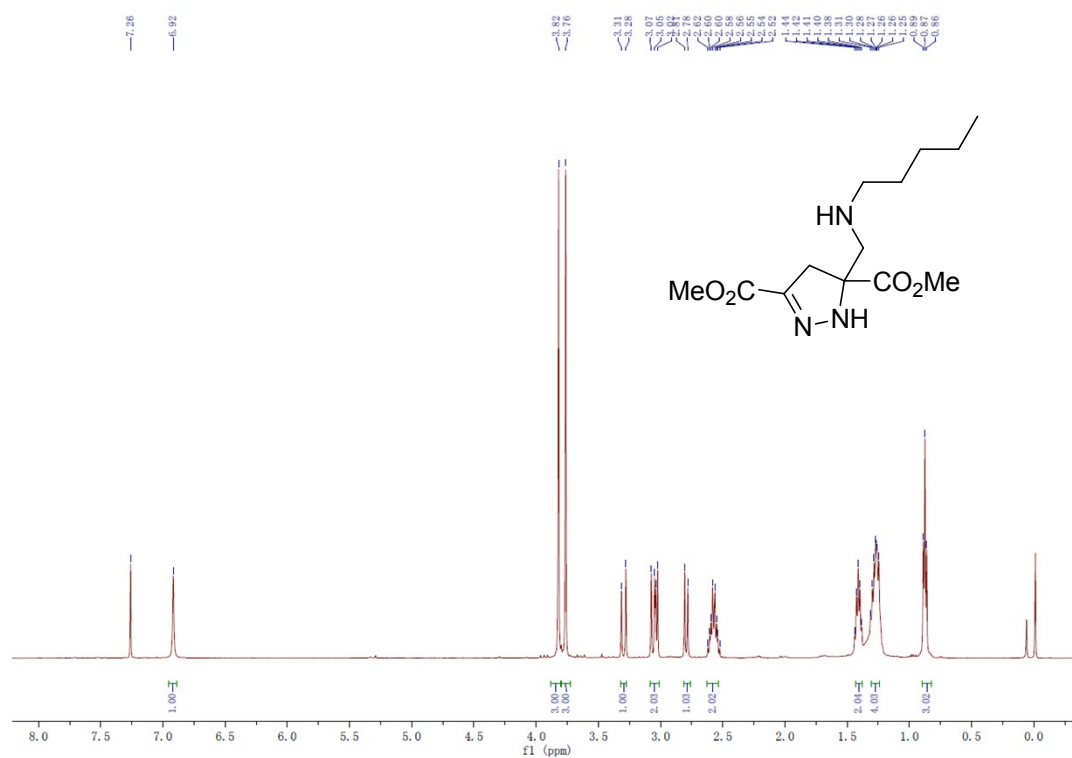
Dimethyl 5-((pyridin-3-ylamino)methyl)-4,5-dihydro-1H-pyrazole-3,5-dicarboxylate (5ak)



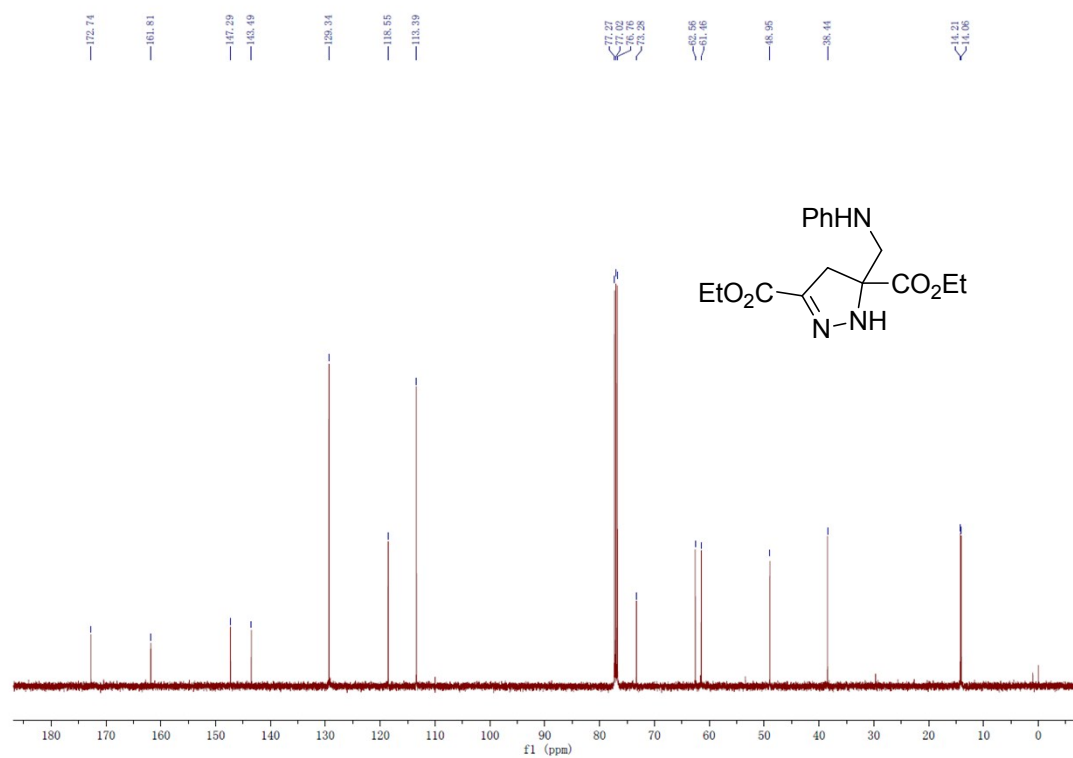
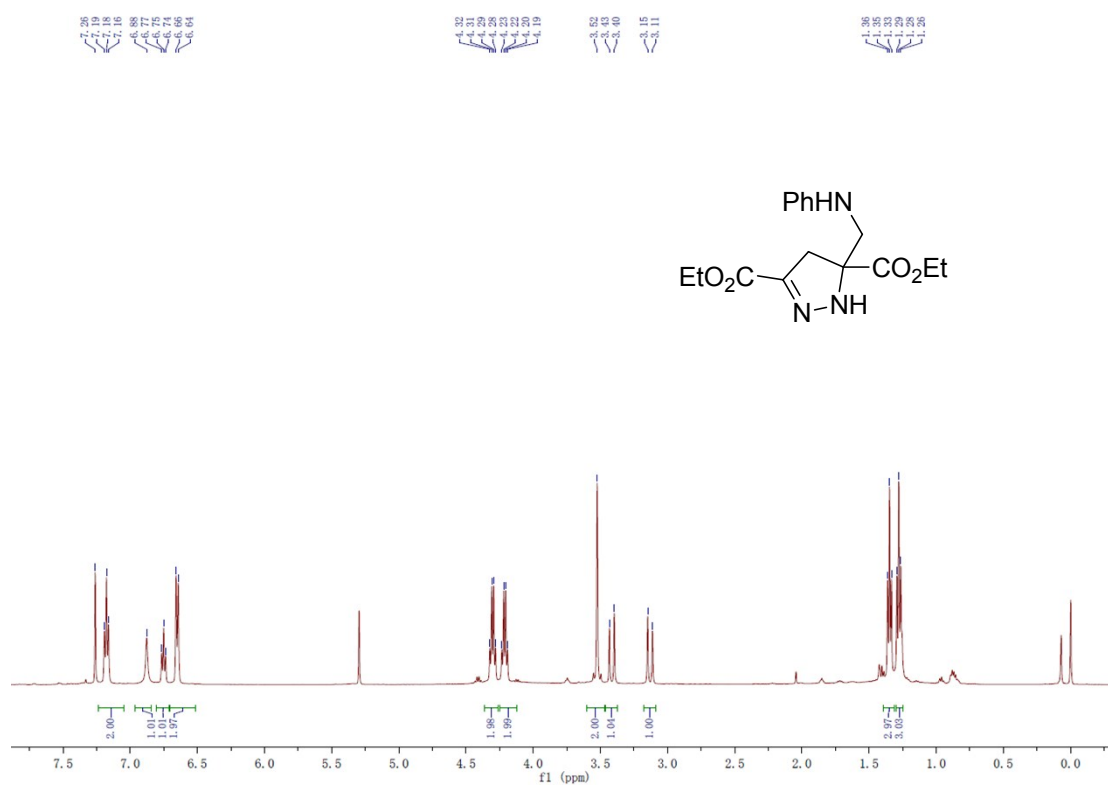
Dimethyl 5-((benzylamino)methyl)-4,5-dihydro-1H-pyrazole-3,5-dicarboxylate (5al)



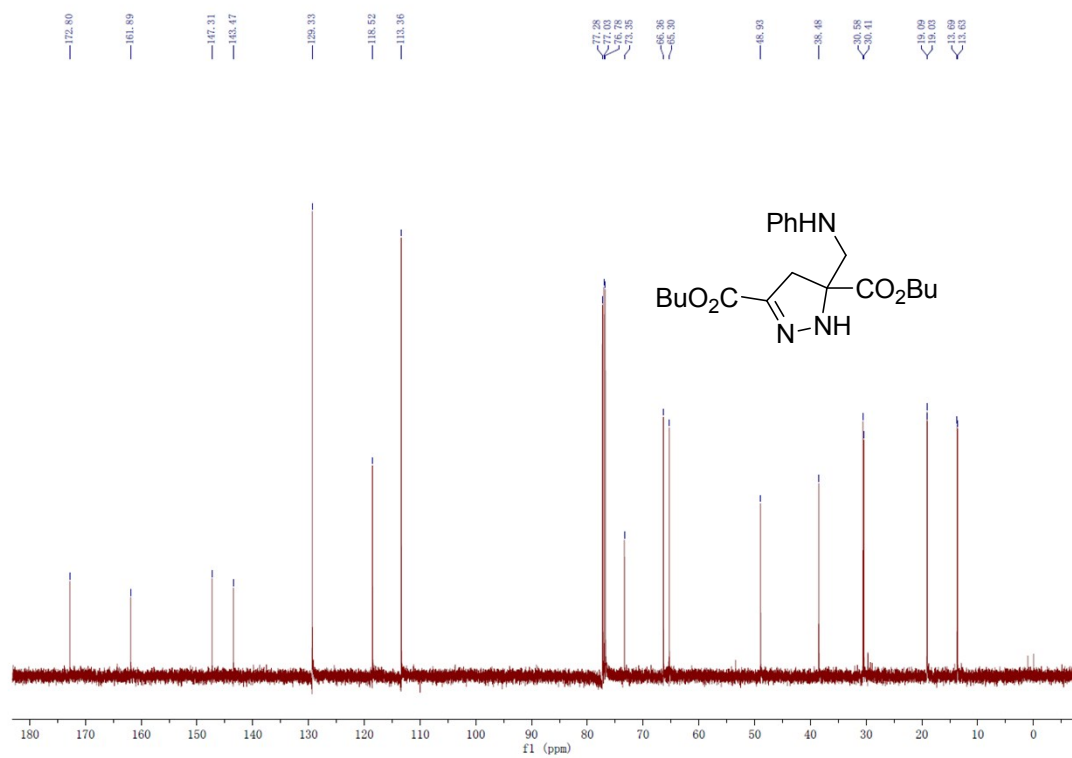
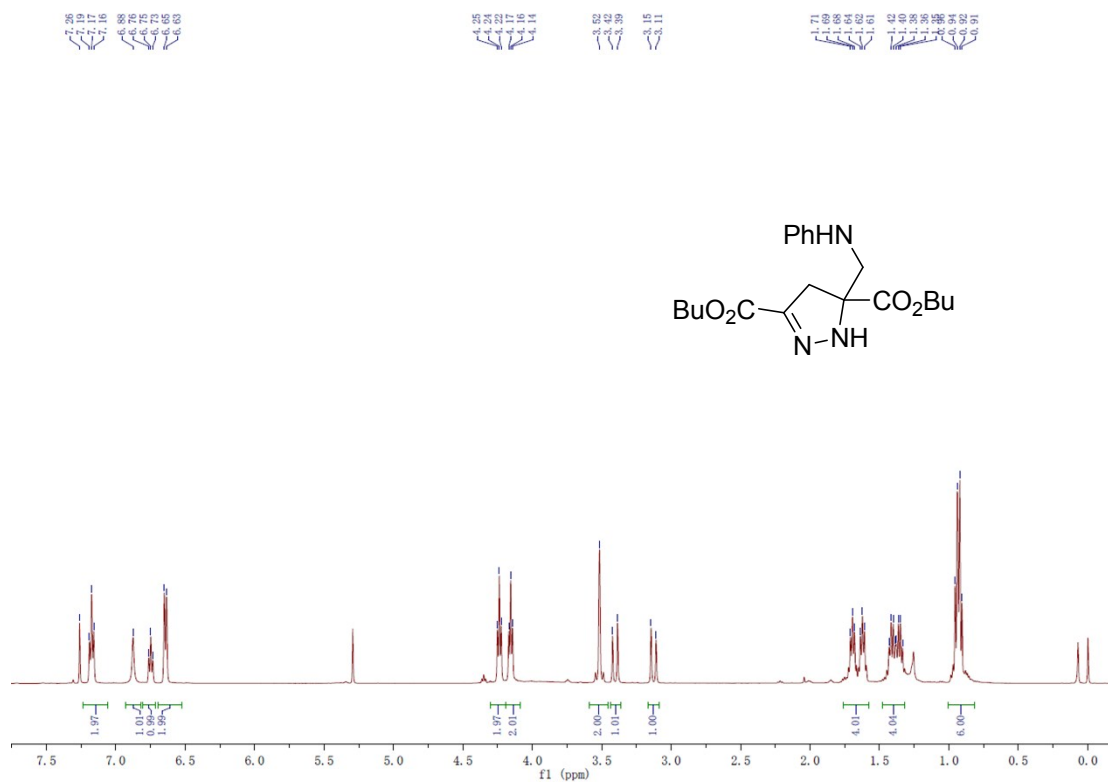
Dimethyl 5-((pentylamino)methyl)-4,5-dihydro-1H-pyrazole-3,5-dicarboxylate (5am)



Diethyl 5-((phenylamino)methyl)-4,5-dihydro-1H-pyrazole-3,5-dicarboxylate (5ba)



Dibutyl 5-((phenylamino)methyl)-4,5-dihydro-1H-pyrazole-3,5-dicarboxylate (5ca)



H: X-ray Analysis

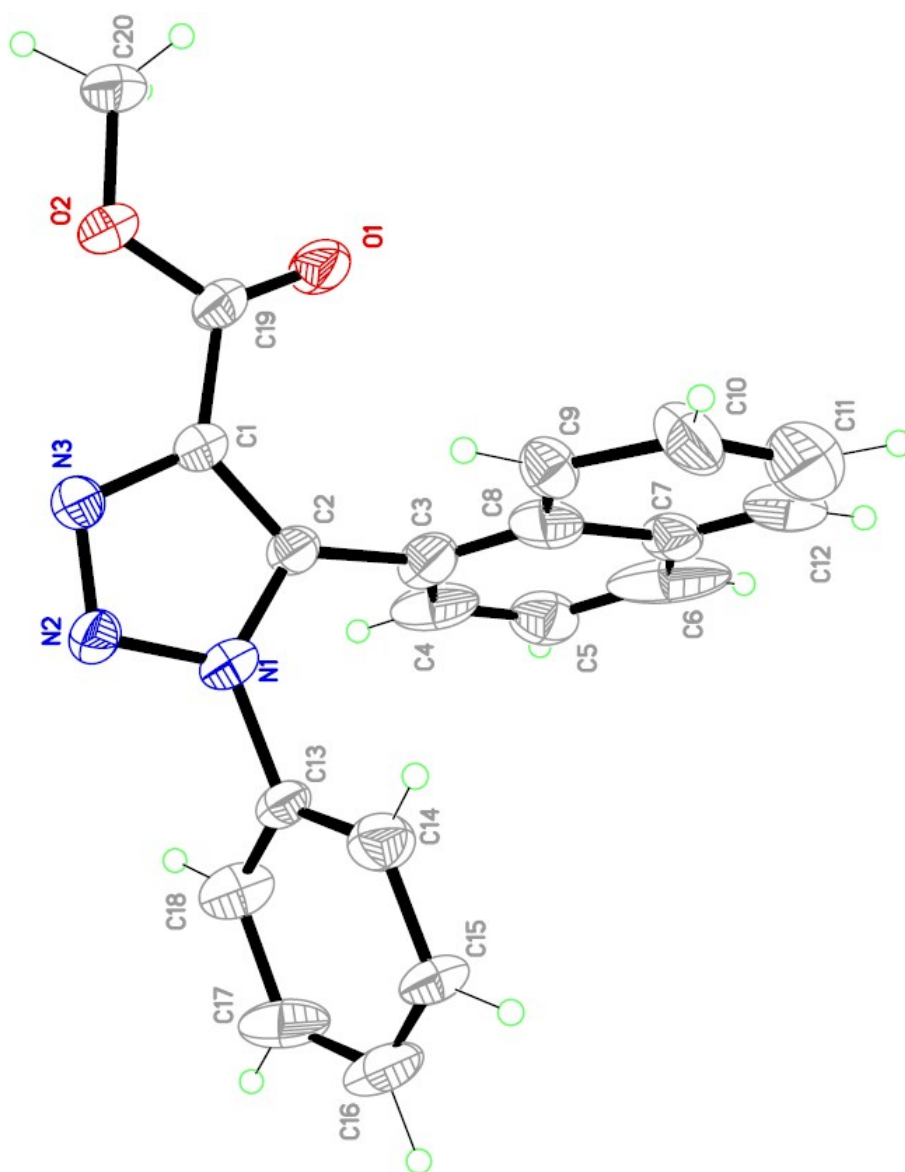


Table 1. Crystal data and structure refinement for **3ha**.

Identification code	3ha	
Empirical formula	C ₂₀ H ₁₅ N ₃ O ₂	
Formula weight	329.35	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P c a 21	
Unit cell dimensions	a = 18.9625(10) Å	$\alpha = 90^\circ$.
	b = 8.7607(5) Å	$\beta = 90^\circ$.
	c = 19.5836(10) Å	$\gamma = 90^\circ$.
Volume	3253.3(3) Å ³	
Z	8	
Density (calculated)	1.345 Mg/m ³	
Absorption coefficient	0.089 mm ⁻¹	
F(000)	1376	
Crystal size	0.501 x 0.297 x 0.150 mm ³	
Theta range for data collection	2.148 to 25.678°.	
Index ranges	-22 ≤ h ≤ 23, -10 ≤ k ≤ 10, -23 ≤ l ≤ 23	
Reflections collected	25449	
Independent reflections	6090 [R(int) = 0.0533]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.6516	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6090 / 1 / 453	
Goodness-of-fit on F ²	1.077	
Final R indices [I > 2σ(I)]	R1 = 0.1052, wR2 = 0.2594	
R indices (all data)	R1 = 0.1250, wR2 = 0.2808	
Absolute structure parameter	1.4(10)	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.267 and -0.464 e.Å ⁻³	

I: Reference

1. O. Berger, A. Kanthi, C. Tran van Ba, H. Vial, S. A. Ward, G. A. Biagini, P. G. Gray, P. M. O'Neil, *ChemMedChem* **2011**, 6, 2094-2108.