Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

[3+1+1] Type Cyclization of $ClCF_2COONa$ for the Assembly of Imidazoles and Tetrazoles via In-Situ Generated Isocyanides

Ya Wang,[a] Yao Zhou,[b] and Qiuling Song* [a]

[a] Institute of Next Generation Matter Transformation, College of Material Sciences & Engineering at Huaqiao University, 668 Jimei Blvd, Xiamen, Fujian, 361021, China.

[b] College of Chemistry and Chemical Engineering, Hubei Normal University, Huangshi 435002, Hubei, P. R China.

*Email: qsong@hqu.edu.cn

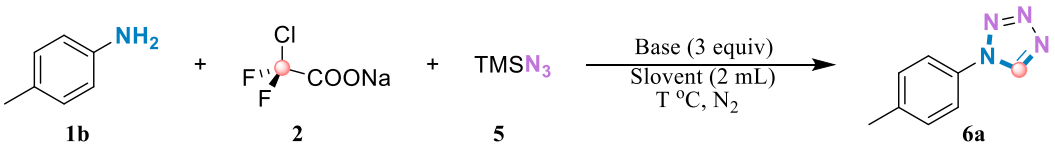
Table of Contents

1. General information

All chemicals were purchased from Adamas Reagent, Ltd, Energy chemical company, J&K Scientific Ltd, Alfa Aesa chemical company and so forth. CH_3CN was dried by CaH prior to use. Unless otherwise stated, all experiments were conducted in a seal tube under N_2 atmosphere. Reactions were monitored by TLC or GC-MS analysis. Flash column chromatography was performed over silica gel (200-300 mesh).

^{1}H-NMR and ^{13}C-NMR spectra were recorded in $CDCl_3$ on a Bruker Avance 500 spectrometer (500 MHz ^{1}H, 125 MHz ^{13}C) at room temperature. Chemical shifts were reported in ppm on the scale relative to $CDCl_3$ (δ = 7.26 for ^{1}H-NMR, δ = 77.00 for ^{13}C-NMR) or DMSO-d_6 (δ = 2.50 for ^{1}H-NMR, δ = 39.60 for ^{13}C-NMR) as an internal reference. High resolution mass spectra were recorded using Q-TOF time-of-flight mass spectrometer. Coupling constants (J) were reported in Hertz (Hz).

2. Screening of the Reaction Conditions

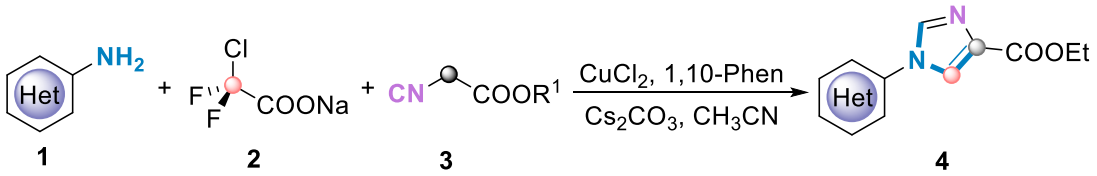


1b **2** **5** **6a**

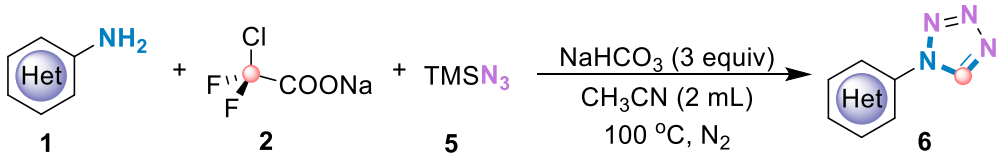
Entry[a]	[Cu]	Ligand	Base	Slovent	T °C	Yield[b]
1	$CuCl_2$	1,10-Phen	Cs_2CO_3	CH_3CN	100	31
2	$CuCl_2$	1,10-Phen	K_2CO_3	CH_3CN	100	25
3	$CuCl_2$	1,10-Phen	Na_2CO_3	CH_3CN	100	20
4	$CuCl_2$	1,10-Phen	K_3PO_4	CH_3CN	100	50
5	$CuCl_2$	1,10-Phen	$NaHCO_3$	CH_3CN	100	52
6	$CuBr_2$	1,10-Phen	$NaHCO_3$	CH_3CN	100	38
7	$Cu(OAc)_2$	1,10-Phen	$NaHCO_3$	CH_3CN	100	50
8	Cu_2O	1,10-Phen	$NaHCO_3$	CH_3CN	100	37
9	$CuCl_2$	1,10-Phen	$NaHCO_3$	1,4-dioxane	100	N.R.
10	$CuCl_2$	1,10-Phen	$NaHCO_3$	EA	100	trace
11	$CuCl_2$	1,10-Phen	$NaHCO_3$	THF	100	N.R.
12	$CuCl_2$	1,10-Phen	$NaHCO_3$	DCE	100	trace
13	$CuCl_2$	1,10-Phen	$NaHCO_3$	CH_3CN	80	48
14	$CuCl_2$	1,10-Phen	$NaHCO_3$	CH_3CN	90	52
16	$CuCl_2$	1,10-Phen	$NaHCO_3$	CH_3CN	110	50
17	$CuCl_2$	1,10-Phen	-	CH_3CN	100	N.R.
18	-	-	$NaHCO_3$	CH_3CN	100	52
19[c]	-	-	$NaHCO_3$	CH_3CN	100	78
20[d]	**-**	**-**	**$NaHCO_3$**	**CH_3CN**	**100**	**78**
21[e]	-	-	$NaHCO_3$	CH_3CN	100	64

[a]All reactions were carried out with **1** (0.2 mmol), **2** (0.4 mmol) **3** (0.6 mmol), base (0.8 mmol) Cu salt (15 mol%) and ligand (20 mol%) in slovent (2 mL) under N_2 atmosphere at 100 °C for 18 h. [b]Isolated yield [c]**2** (0.6 mmol). [d]**2** (0.6 mmol), base(0.6 mmol). [e]**2** (0.4 mmol), base (0.4 mmol).

3. General procedure for the synthesis of 4 and 6

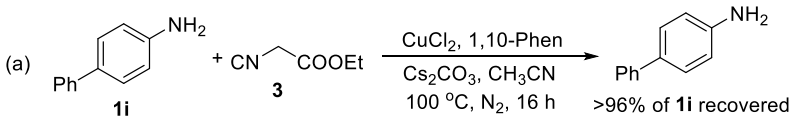


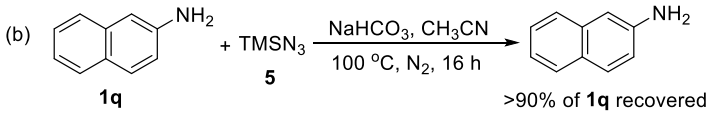
CH_3CN (2 mL) was added to a mixture of $CuCl_2$ (4.1 mg, 15 mol%), 1,10-Phen (20 mol%), anilines **1** (0.2 mmol, 1 equiv) , $ClCF_2COONa$ **2** (0.6 mmol, 3 equiv) and isocyanoacetates **3** (0.3 mmol, 1.5 equiv) in the presence of Cs_2CO_3 (0.6 mmol, 3 equiv) . Then the sealed tube was stirred at 100 ℃ under N_2 for 16 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 1:1, v/v) to give the desired product **4**.

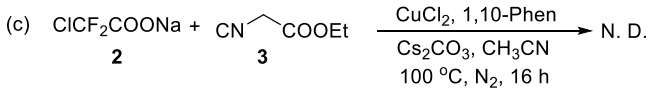


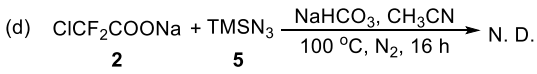
CH_3CN (2 mL) was added to a mixture of anilines **1** (0.2 mmol, 1 equiv), $ClCF_2COONa$ **2** (0.6 mmol, 3 equiv) and $TMSN_3$ **3** (0.6 mmol, 3 equiv) in the presence of $NaHCO_3$ (0.6 mmol, 3 equiv) . Then the sealed tube was stirred at 100 ℃ under N_2 for 16 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 3:1, v/v) to give the desired product **6**.

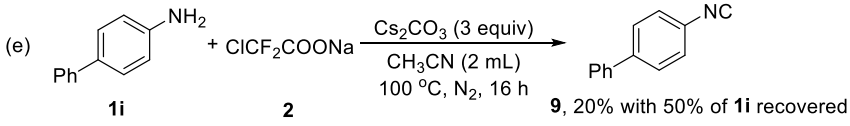
4. Control experiments

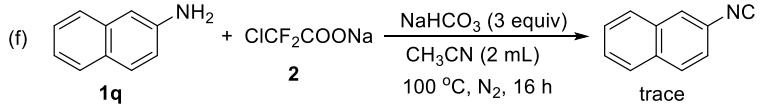


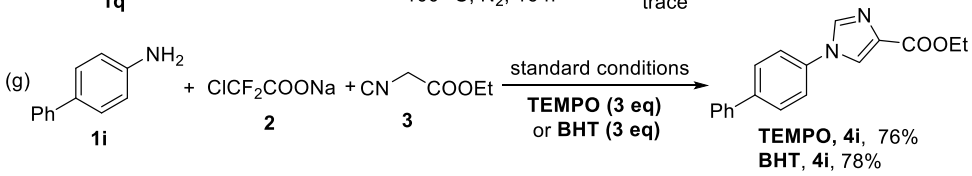


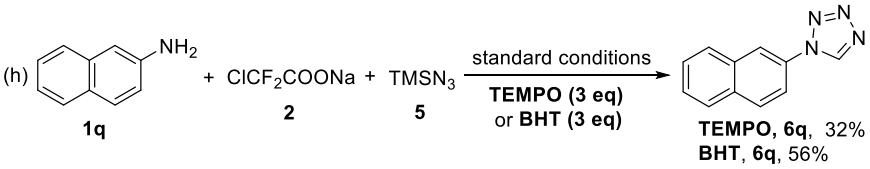


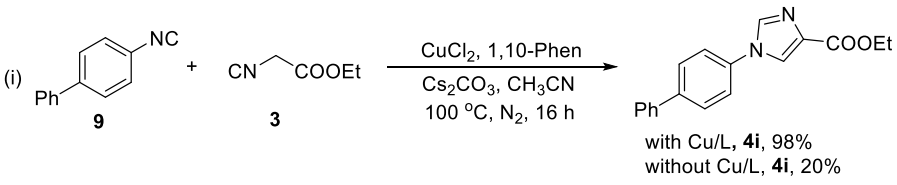


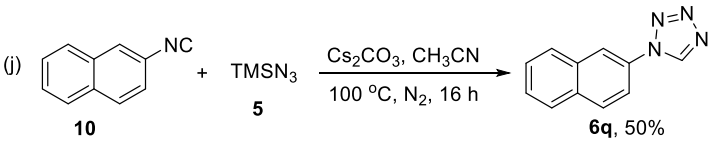


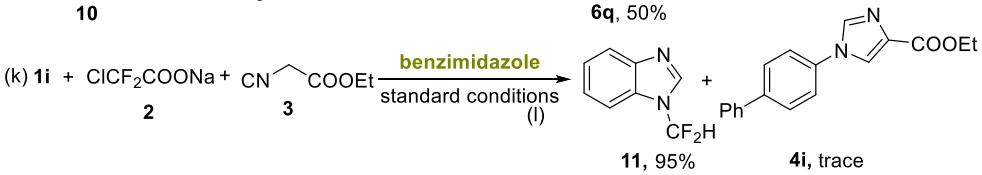


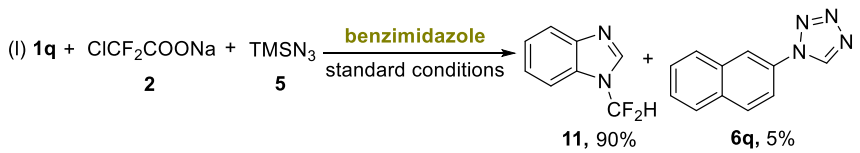






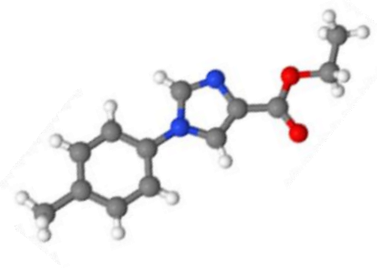






5. Crystal data of 4e, 4u and 6a

Crystallographic data for compound **4e** (CCDC-1917599) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email:deposit@ccdc.cam.ac.uk).



Bond precision: C-C = 0.0029 A Wavelength=0.71073

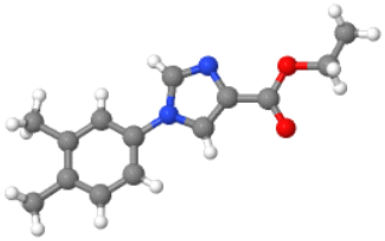
Cell: a=16.722(4) b=7.3514(16) c=20.934(4)
alpha=90 beta=102.85(2) gamma=90

Temperature: 293 K

	Calculated	Reported
Volume	2509.0(10)	2509.1(10)
Space group	I 2/a	I 1 2/a 1
Hall group	-I 2ya	-I 2ya
Moiety formula	C13 H14 N2 O2	C13 H14 N2 O2
Sum formula	C13 H14 N2 O2	C13 H14 N2 O2
Mr	230.26	230.26
Dx,g cm-3	1.219	1.219
Z	8	8
Mu (mm-1)	0.084	0.084
F000	976.0	976.0
F000'	976.43	
h,k,lmax	19,8,24	19,8,24
Nref	2208	2199
Tmin,Tmax		0.496,1.000
Tmin'		

Correction method= # Reported T Limits: Tmin=0.496 Tmax=1.000
AbsCorr = MULTI-SCAN
Data completeness= 0.996 Theta(max)= 24.999
R(reflections)= 0.0487(1614) wR2(reflections)= 0.1543(2199)
S = 1.004 Npar= 156

Crystallographic data for compound **4u** (CCDC-1917630) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email:deposit@ccdc.cam.ac.uk).



Bond precision: C-C = 0.0049 A Wavelength=0.71073

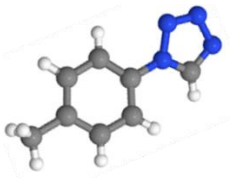
Cell: a=8.1279(14) b=8.6652(15) c=18.746(2)
alpha=90 beta=96.939(14) gamma=90

Temperature: 293 K

	Calculated	Reported
Volume	1310.6(4)	1310.6(4)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C14 H16 N2 O2	C14 H16 N2 O2
Sum formula	C14 H16 N2 O2	C14 H16 N2 O2
Mr	244.29	244.29
Dx,g cm-3	1.238	1.238
Z	4	4
Mu (mm-1)	0.084	0.084
F000	520.0	520.0
F000'	520.22	
h,k,lmax	9,10,22	9,10,22
Nref	2313	2276
Tmin,Tmax		0.649,1.000
Tmin'		

Correction method= # Reported T Limits: Tmin=0.649 Tmax=1.000
AbsCorr = MULTI-SCAN
Data completeness= 0.984 Theta(max)= 24.996
R(reflections)= 0.0743(1333) wR2(reflections)= 0.2180(2276)
S = 1.112 Npar= 166

Crystallographic data for compound **6a** (CCDC-1937993) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email:deposit@ccdc.cam.ac.uk).



Bond precision: C-C = 0.0021 A Wavelength=0.71073

Cell: a=9.7747(9) b=5.6834(5) c=14.3307(13)
alpha=90 beta=96.261(9) gamma=90

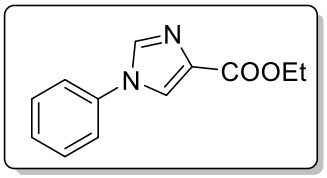
Temperature: 293 K

	Calculated	Reported
Volume	791.37(12)	791.37(12)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C8 H8 N4	C8 H8 N4
Sum formula	C8 H8 N4	C8 H8 N4
Mr	160.18	160.18
Dx,g cm-3	1.344	1.344
Z	4	4
Mu (mm-1)	0.089	0.089
F000	336.0	336.0
F000'	336.09	
h,k,lmax	13,7,19	12,7,19
Nref	2133	1834
Tmin,Tmax	0.989,0.991	0.733,1.000
Tmin'	0.989	

Correction method= # Reported T Limits: Tmin=0.733 Tmax=1.000
AbsCorr = MULTI-SCAN
Data completeness= 0.860 Theta(max)= 29.142
R(reflections)= 0.0483(1174) wR2(reflections)= 0.1511(1834)
S = 1.037 Npar= 111

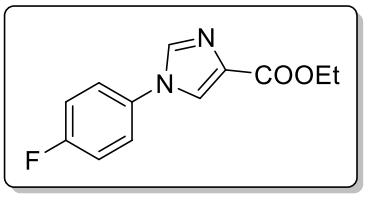
6. Characterization data for products

ethyl 1-phenyl-1*H*-imidazole-4-carboxylate (4a) (CAS Number: 197079-08-6)



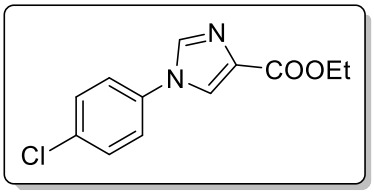
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 1:1, v/v) to give the product as a pale yellow solid (35.0 mg, 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 1.4 Hz, 1H), 7.84 (d, *J* = 1.3 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.41 (m, 3H), 4.38 (d, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.7, 136.5, 136.3, 135.1, 130.1, 128.4, 124.0, 121.7, 60.7, 14.4.

ethyl 1-(4-fluorophenyl)-1*H*-imidazole-4-carboxylate (4b)
(CAS Number: 114067-93-5)



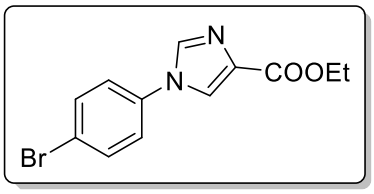
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 1:1, v/v) to give the product as a yellow solid (33.7 mg, 72%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 1.1 Hz, 1H), 7.77 (d, *J* = 1.2 Hz, 1H), 7.38 (dd, *J* = 8.9, 4.5 Hz, 2H), 7.18 (t, *J* = 8.5 Hz, 2H), 4.36 (m, 2H), 1.37 (td, *J* = 7.1, 0.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.6, 162.2 (d, *J* = 247.6 Hz), 136.5, 135.1, 132.7 (d, *J* = 3.1 Hz), 124.3, 123.8 (d, *J* = 8.6 Hz), 117.1 (d, *J* = 23.1 Hz), 60.8, 14.4.

ethyl 1-(4-chlorophenyl)-1*H*-imidazole-4-carboxylate (4c)
(CAS number: 1260654-52-1)



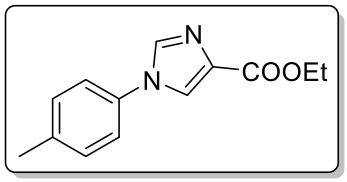
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 1:1, v/v) to give the product as a yellow solid (31.0 mg, 62%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 1.3 Hz, 1H), 7.82 (d, *J* = 1.2 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.35 (d, *J* = 8.8 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.6, 136.2, 135.3, 135.0, 134.3, 130.3, 123.9, 123.0, 60.9, 14.4.

ethyl 1-(4-bromophenyl)-1*H*-imidazole-4-carboxylate (4d)
(CAS Number: 1260758-76-6)



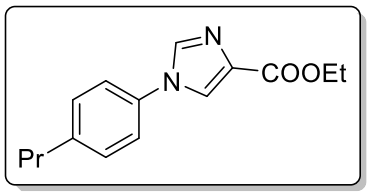
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 1:1, v/v) to give the product as a yellow solid (32.3 mg, 55%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 1.4 Hz, 1H), 7.83 (d, *J* = 1.3 Hz, 1H), 7.64 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 8.7 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.6, 136.1, 135.5, 135.4, 133.3, 123.8, 123.2, 122.1, 60.9, 14.4.

ethyl 1-(*p*-tolyl)-1*H*-imidazole-4-carboxylate (4e) (CAS Number: 943144-41-0)



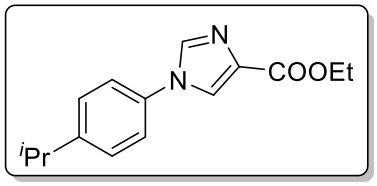
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 1:1, v/v) to give the product as a pale yellow solid (43.7 mg, 95%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 1.3 Hz, 1H), 7.79 (d, *J* = 1.2 Hz, 1H), 7.27 (s, 2H), 4.37 (q, 2H), 2.39 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.8, 138.5, 136.3, 134.9, 134.1, 130.6, 124.1, 121.6, 60.7, 21.0, 14.4.

ethyl 1-(4-propylphenyl)-1*H*-imidazole-4-carboxylate (4f)



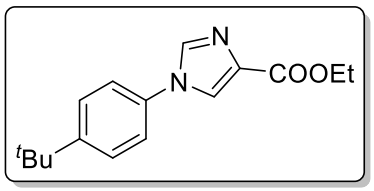
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 1:1, v/v) to give the product as a yellow solid (33.5 mg, 65%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 – 7.85 (m, 1H), 7.81 (d, *J* = 1.3 Hz, 1H), 7.29 (s, 3H), 4.38 (q, *J* = 7.1 Hz, 2H), 2.62 (d, *J* = 7.8 Hz, 1H), 1.64 (dt, *J* = 14.9, 7.5 Hz, 2H), 1.38 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.8, 143.3, 136.4, 134.9, 134.2, 130.0, 124.1, 121.6, 60.7, 37.4, 24.4, 14.4, 13.7. HRMS (ESI, m/z) calcd for $C_{15}H_{18}N_2O_2$ $[M+H]^+$: 259.1441; found: 259.1437.

ethyl 1-(4-isopropylphenyl)-1*H*-imidazole-4-carboxylate (4g)



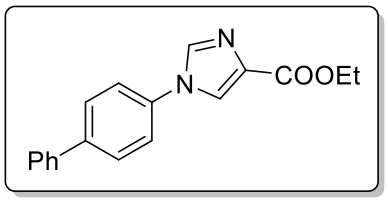
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 1:1, v/v) to give the product as a yellow solid (31.0 mg, 60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 – 7.89 (m, 1H), 7.81 (d, *J* = 1.2 Hz, 1H), 7.32 (t, *J* = 7.9 Hz, 4H), 4.38 (q, *J* = 7.1 Hz, 3H), 2.95 (dd, *J* = 13.8, 6.9 Hz, 1H), 1.39 (t, *J* = 7.1 Hz, 5H), 1.27 (s, 3H), 1.26 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.8, 149.5, 136.4, 134.9, 134.3, 128.0, 124.1, 121.7, 60.7, 33.8, 23.9, 14.4. HRMS (ESI, m/z) calcd for $C_{15}H_{18}N_2O_2$ $[M+H]^+$: 259.1441; found: 259.1439.

ethyl 1-(4-(tert-butyl)phenyl)-1*H*-imidazole-4-carboxylate (4h)



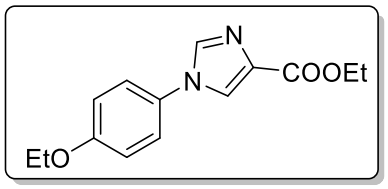
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 1:1, v/v) to give the product as a yellow solid (43.5 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 1.3 Hz, 1H), 7.81 (d, *J* = 1.3 Hz, 1H), 7.50 (d, *J* = 8.7 Hz, 2H), 7.32 (d, *J* = 8.7 Hz, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.34 (s, 7H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.8, 151.8, 136.4, 134.9, 134.0, 127.0, 124.1 121.4, 60.7, 34.8, 31.3, 14.4. HRMS (ESI, m/z) calcd for $C_{16}H_{20}N_2O_2$ $[M+H]^+$: 273.1598; found: 273.1599.

ethyl 1-([1,1'-biphenyl]-4-yl)-1*H*-imidazole-4-carboxylate (4i)



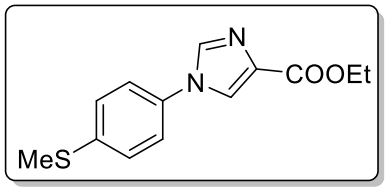
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 1:1, v/v) to give the product as a yellow solid (45.6 mg, 78%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 1.1 Hz, 1H), 7.89 (d, *J* = 1.1 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.59 (m, 2H), 7.47 (m, 4H), 7.39 (t, *J* = 7.3 Hz, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.8, 141.5, 139.4, 136.3, 135.5, 135.2, 129.0, 128.7, 128.0, 127.1, 123.9, 122.0, 60.8, 14.5. HRMS (ESI, m/z) calcd for $C_{18}H_{16}N_2O_2$ $[M+H]^+$: 293.1285; found: 293.1289.

ethyl 1-(4-ethoxyphenyl)-1*H*-imidazole-4-carboxylate (4j)
(CAS Number: 1923135-51-6)



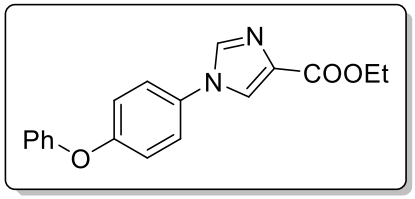
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 1:1, v/v) to give the product as a yellow solid (39.0 mg, 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 1.2 Hz, 1H), 7.75 (d, *J* = 1.0 Hz, 1H), 7.30 (d, *J* = 8.9 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 4.06 (q, *J* = 7.0 Hz, 2H), 1.41 (dt, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.8, 158.9, 136.6, 134.7, 129.5, 124.5, 123.3, 115.6, 63.9, 60.6, 14.7, 14.41.

ethyl 1-(4-(methylthio)phenyl)-1*H*-imidazole-4-carboxylate (4k)
(CAS: 1923054-90-3)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 1:1, v/v) to give the product as a yellow solid (36.7 mg, 70%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 1.3 Hz, 1H), 7.81 (d, *J* = 1.1 Hz, 1H), 7.34 (m, 4H), 4.40 (q, *J* = 7.1 Hz, 2H), 2.52 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.7, 139.7, 136.3, 135.1, 133.5, 127.5, 124.0, 122.2, 60.8, 15.7, 14.4.

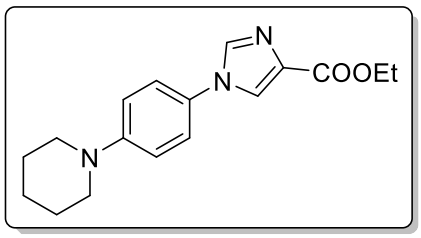
ethyl 1-(4-phenoxyphenyl)-1*H*-imidazole-4-carboxylate (4l)
(CAS Number: 124457-50-7)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 1:1, v/v) to give the product as a yellow solid (49.3 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 1.4 Hz, 1H), 7.79 (d, *J* = 1.3 Hz, 1H), 7.36 (m, 4H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.09 (m, 2H), 7.04 (m, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.8,

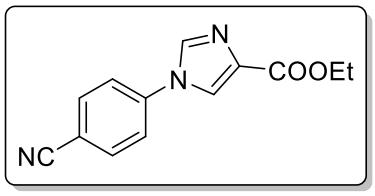
157.7, 156.2, 136.5, 135.0, 131.5, 130.1, 124.3, 124.3, 123.5, 119.6, 199.5, 60.8, 14.4.

ethyl 1-(4-(piperidin-1-yl)phenyl)-1*H*-imidazole-4-carboxylate (4m)



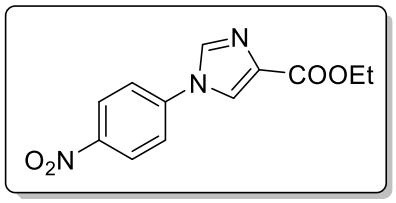
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 1:1, v/v) to give the product as a yellow solid (40.1 mg, 67%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 1.3 Hz, 1H), 7.75 (d, *J* = 1.3 Hz, 1H), 7.24 (d, *J* = 9.0 Hz, 2H), 6.97 (d, *J* = 9.0 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.21 (m, 4H), 1.71 (dt, *J* = 11.2, 5.7 Hz, 5H), 1.62 (m, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.9, 151.9, 136.5, 134.4, 127.5, 124.4, 122.8, 116.6, 60.6, 50.1, 25.5, 24.2, 14.4. HRMS (ESI, m/z) calcd for $C_{17}H_{21}N_3O_2$ $[M+H]^+$: 300.1707; found: 300.1706.

ethyl 1-(4-cyanophenyl)-1*H*-imidazole-4-carboxylate (4n)
(CAS Number: 910126-73-7)



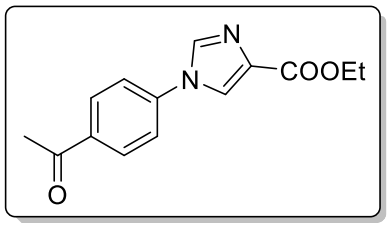
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 1:2, v/v) to give the product as a yellow solid (28.9 mg, 60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.97 (s, 1H), 7.85 (d, *J* = 8.5 Hz, 2H), 7.61 (d, *J* = 8.5 Hz, 2H), 4.40 (q, *J* = 7.1 Hz, 3H), 1.40 (t, *J* = 7.1 Hz, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.3, 139.6, 136.0 (d, *J* = 13.6 Hz), 134.3, 123.2, 121.8, 117.5, 112.2, 61.0, 14.4.

ethyl 1-(4-nitrophenyl)-1*H*-imidazole-4-carboxylate (4o)
(CAS Number: 197079-06-4)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 1:2, v/v) to give the product as a yellow solid (31.8 mg, 61%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.92 (s, 1H), 7.70 (d, *J* = 7.4 Hz, 2H), 7.65 (d, *J* = 7.6 Hz, 1H), 4.42 (q, *J* = 7.2 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.3, 147.0, 141.0, 136.2, 136.0, 125.9, 123.2, 121.7, 61.1, 14.4.

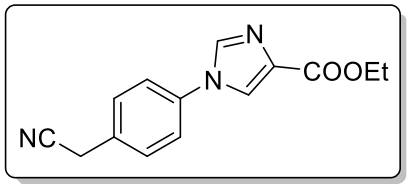
ethyl 1-(4-acetylphenyl)-1*H*-imidazole-4-carboxylate (4p)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 1:2, v/v) to give the product as a yellow solid (26.8 mg, 52%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.6 Hz, 2H), 8.01 (d, *J* = 1.4 Hz, 1H), 7.94 (d, *J* = 1.4 Hz, 1H), 7.53 (d, *J* = 8.6 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 2.64 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.4, 162.5, 139.8, 136.6, 136.0,

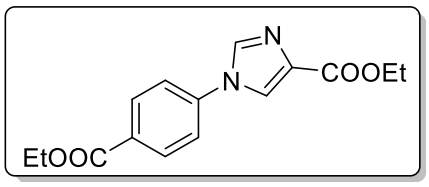
135.7, 130.5, 123.4, 121.2, 61.0, 26.7, 14.4. HRMS (ESI, m/z) calcd for $C_{14}H_{14}N_2O_3$ $[M+H]^+$: 259.1077; found: 259.1079.

ethyl 1-(4-(cyanomethyl)phenyl)-1*H*-imidazole-4-carboxylate (4q)



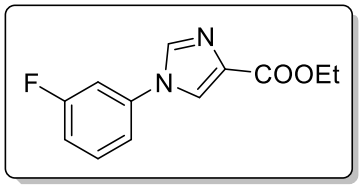
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 1:2, v/v) to give the product as a yellow solid (24.5 mg, 48%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 1.3 Hz, 1H), 7.86 (d, *J* = 1.2 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.44 (m, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.6, 136.3, 136.2, 135.4, 130.4, 129.8, 123.8, 122.3, 117.2, 60.9, 23.3, 14.4. HRMS (ESI, m/z) calcd for $C_{14}H_{13}N_3O_2$ $[M+H]^+$: 256.1081; found: 256.1085.

ethyl 1-(4-(ethoxycarbonyl)phenyl)-1*H*-imidazole-4-carboxylate (4r)



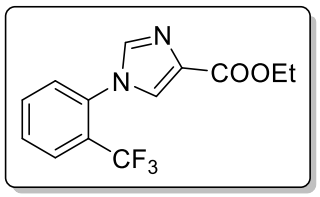
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 1:2, v/v) to give the product as a yellow solid (31.7 mg, 55%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.7 Hz, 1H), 8.00 (d, *J* = 1.4 Hz, 1H), 7.93 (d, *J* = 1.4 Hz, 1H), 7.49 (d, *J* = 8.7 Hz, 1H), 4.39 (qd, *J* = 7.1, 3.4 Hz, 1H), 1.40 (td, *J* = 7.1, 5.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.3, 162.5, 139.7, 136.0, 135.6, 131.7, 130.3, 123.5, 121.0, 61.5, 60.9, 14.4, 14.3. HRMS (ESI, m/z) calcd for $C_{15}H_{16}N_2O_4$ $[M+H]^+$: 289.1183; found: 289.1181.

ethyl 1-(3-fluorophenyl)-1*H*-imidazole-4-carboxylate (4s)
(CAS Number: 1260654-52-1)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 1:1, v/v) to give the product as a yellow solid (23.4 mg, 50%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 1.2 Hz, 1H), 7.86 (d, *J* = 1.1 Hz, 1H), 7.49 (td, *J* = 8.1, 6.1 Hz, 1H), 7.22 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.14 (m, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ163.2 (d, *J* = 248.3 Hz), 162.5, 137.7 (d, *J* = 9.6 Hz), 136.1, 135.4, 131.6 (d, *J* = 9.1 Hz), 123.7, 117.2 (d, *J* = 3.2 Hz), 115.4 (d, *J* = 20.8 Hz), 109.4 (d, *J* = 25.0 Hz), 60.9, 14.4.

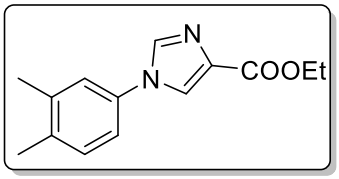
ethyl 1-(2-(trifluoromethyl)phenyl)-1*H*-imidazole-4-carboxylate (4t)
(CAS Number: 2111149-39-2)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 1:1, v/v) to give the product as a yellow solid (29.5 mg, 52%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.92 (s, 1H), 7.70 (d, *J* = 7.4 Hz, 2H), 7.65 (d, *J* = 7.6 Hz, 1H), 4.42 (q, *J* = 7.2 Hz, 2H), 1.42 (t, *J*

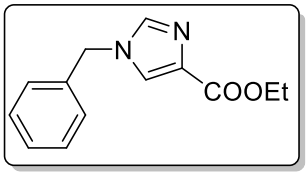
= 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5, 136.9, 136.2, 135.7, 132.8 (q, *J* = 33.2 Hz), 131.0, 125.2 (q, *J* = 7.4, 3.7 Hz), 124.9, 124.3, 123.7, 122.1, 118.6 (q, *J* = 3.8 Hz), 60.9, 14.4.

ethyl 1-(3,4-dimethylphenyl)-1*H*-imidazole-4-carboxylate (4u)
(CAS Number: 1983822-50-9)



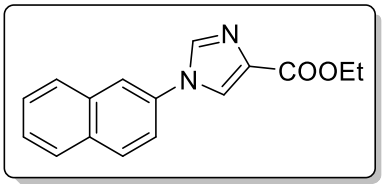
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 1:1, v/v) to give the product as a yellow solid (39.5 mg, 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 1.3 Hz, 1H), 7.79 (d, *J* = 1.1 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.15 (s, 1H), 7.10 (dd, *J* = 8.0, 2.0 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 2.29 (d, *J* = 9.4 Hz, 6H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.8, 138.7, 137.2, 136.3, 134.7, 134.3, 130.9, 124.1, 122.8, 118.9, 60.7, 19.9, 19.4, 14.4.

ethyl 1-benzyl-1*H*-imidazole-4-carboxylate (4v) (CAS Number: 76075-03-1)



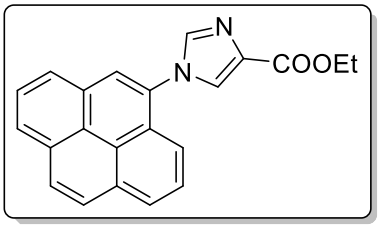
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 1:1, v/v) to give the product as a yellow liquid (18.9 mg, 41%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 1.1 Hz, 1H), 7.55 (s, 1H), 7.36 (d, *J* = 6.8 Hz, 2H), 7.17 (d, *J* = 7.5 Hz, 2H), 5.12 (s, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.8, 138.1, 135.0, 134.4, 129.2, 128.7, 127.5, 125.3, 60.6, 51.4, 14.4.

ethyl 1-(naphthalen-2-yl)-1*H*-imidazole-4-carboxylate (4w)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 1:1, v/v) to give the product as a yellow liquid (35.6 mg, 67%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 1.1 Hz, 1H), 7.97 (d, *J* = 8.6 Hz, 2H), 7.88 (t, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 1.9 Hz, 1H), 7.57 (m, 2H), 7.51 (dd, *J* = 8.7, 2.2 Hz, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.8, 136.5, 135.2, 133.8, 133.4, 132.6, 130.5, 128.0, 127.9, 127.7, 127.0, 124.2, 119.9, 119.7, 60.8, 14.5. HRMS (ESI, m/z) calcd for $C_{16}H_{14}N_2O_2$ $[M+H]^+$: 267.1128; found: 267.1129.

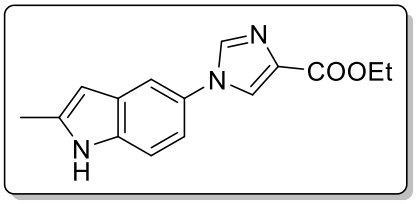
ethyl 1-(pyren-4-yl)-1*H*-imidazole-4-carboxylate (4x)
(CAS Number: 2107665-94-9)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 2:1, v/v) to give the product as a yellow liquid (44.2 mg, 65%).1H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, J = 7.6 Hz, 1H), 8.23 – 8.19 (m, 2H), 8.15 (d, J = 8.9 Hz, 1H), 8.12 – 8.02 (m, 4H), 7.92 – 7.86 (m, 2H), 7.72 (d, J = 9.2 Hz, 1H), 4.47 (q, J = 7.1 Hz, 2H), 1.45 (t, J = 7.1 Hz, 3H). 13C NMR (126 MHz, $CDCl_3$) δ 163.0, 139.5,

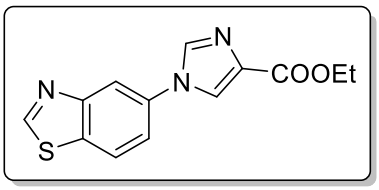
134.7, 131.9, 131.1, 130.6, 129.9, 129.6, 128.9, 127.7, 126.9, 126.9, 126.6, 126.5, 126.1, 124.8, 124.1, 123.6, 120.4, 60.9, 14.5. HRMS (ESI, m/z) calcd for $C_{22}H_{16}N_2O_2$ $[M+H]^+$: 341.1285; found: 341.1288.

ethyl 1-(2-methyl-1*H*-indol-5-yl)-1*H*-imidazole-4-carboxylate (4y)
(CAS Number: 2107665-94-9)



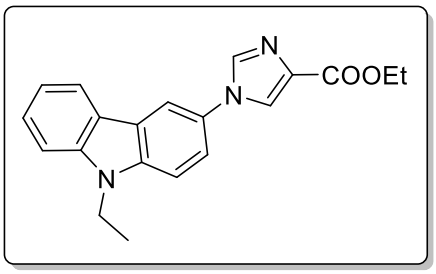
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 1:3, v/v) to give the product as a yellow solid (32.8 mg, 61%). ^{1}H NMR (500 MHz, DMSO) δ 11.21 (s, 1H), 8.30 (d, *J* = 1.4 Hz, 1H), 8.23 (d, *J* = 1.4 Hz, 1H), 7.68 (d, *J* = 2.1 Hz, 1H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.27 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.21 (m, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.41 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, DMSO) δ 162.8, 138.5, 137.8, 135.7, 133.7, 129.4, 128.9, 125.4, 114.5, 112.2, 111.8 100.2, 60.1, 14.8, 13.9.

ethyl 1-(benzo[*d*]thiazol-6-yl)-1*H*-imidazole-4-carboxylate (4z)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 1:2, v/v) to give the product as a yellow solid (21.8 mg, 40%).^{1}H NMR (500 MHz, $CDCl_3$) δ 9.14 (s, 1H), 8.19 (d, *J* = 2.1 Hz, 1H), 8.10 (d, *J* = 8.6 Hz, 1H), 8.04 (d, *J* = 1.4 Hz, 1H), 7.94 (d, *J* = 1.3 Hz, 1H), 7.52 (dd, *J* = 8.5, 2.1 Hz, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.7, 156.9, 154.0, 136.6, 135.4, 135.1, 133.7, 124.3 123.5, 119.6, 116.7, 60.9, 14.4. HRMS (ESI, m/z) calcd for $C_{13}H_{11}N_3O_2S$ $[M+H]^+$: 274.0645; found: 274.0639.

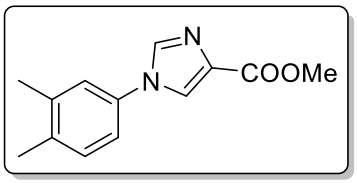
ethyl 1-(9-ethyl-9*H*-carbazol-3-yl)-1*H*-imidazole-4-carboxylate (4aa)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 1:1, v/v) to give the product as a yellow liquid (53.9 mg, 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.8 Hz, 1H), 8.07 (d, *J* = 1.9 Hz, 1H), 8.01 (d, *J* = 1.0 Hz, 1H), 7.89 (d, *J* = 1.0 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.46 (m, 3H), 7.28 (t, *J* = 7.5 Hz, 1H), 4.41 (dq, *J* = 10.8, 7.2 Hz, 4H), 1.44 (dt, *J* = 14.2, 7.2 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.0, 140.8, 139.3, 137.2, 134.6, 128.5, 126.9, 125.2, 123.5, 122.2, 120.8, 120.1, 119.6, 114.4, 109.4, 109.0, 60.7, 37.9, 14.5, 13.8. HRMS (ESI, m/z) calcd for $C_{20}H_{19}N_3O_2$ $[M+H]^+$: 334.1550; found: 334.1552.

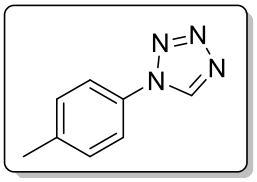
methyl 1-(3,4-dimethylphenyl)-1*H*-imidazole-4-carboxylate (4ab)

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 1:1, v/v) to give the product as a yellow solid (32.2 mg, 70%). ^{1}H NMR (500 MHz,



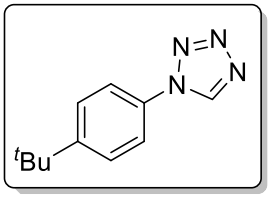
$CDCl_3$) δ 7.90 (d, *J* = 1.3 Hz, 1H), 7.79 (d, *J* = 1.3 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 1.8 Hz, 1H), 7.10 (dd, *J* = 8.0, 2.2 Hz, 1H), 3.89 (d, *J* = 7.5 Hz, 3H), 2.30 (s, 2H), 2.28 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2, 138.8, 137.2, 136.4, 134.4, 134.2, 131.0, 124.2, 122.8, 118.9, 51.8, 19.9, 19.4. HRMS (ESI, m/z) calcd for $C_{13}H_{14}N_2O_2$ $[M+H]^+$: 231.1128; found: 231.1126.

1-(*p*-tolyl)-1*H*-tetrazole (6a) (CAS Number: 25109-04-0)



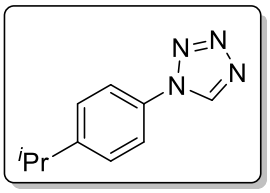
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 3:1, v/v) to give the product as a yellow solid (27.0 mg, 78%), ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.96 (s, 1H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.5, 140.5, 130.7, 121.1, 21.2.

1-(4-(tert-butyl)phenyl)-1*H*-tetrazole (6b) (CAS Number: 1631073-38-5)



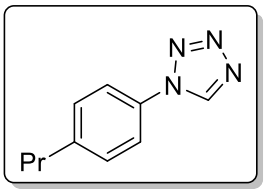
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 4:1, v/v) to give the product as a yellow solid (26.3 mg, 65%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.00 (d, *J* = 1.2 Hz, 1H), 7.60 (ddd, *J* = 19.5, 7.7, 4.4 Hz, 4H), 1.36 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.6, 140.6, 131.3, 127.1, 120.9, 35.0, 31.2.

1-(4-isopropylphenyl)-1*H*-tetrazole (6c) (CAS Number: 932034-62-3)



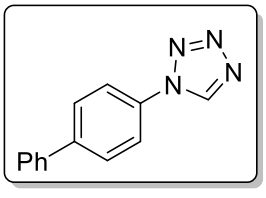
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 4:1, v/v) to give the product as a yellow liquid (26.7 mg, 71%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.99 (d, *J* = 1.8 Hz, 1H), 7.61 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 3.00 (dt, *J* = 13.8, 6.9 Hz, 1H), 1.29 (s, 3H), 1.28 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.3, 140.6, 131.6, 128.2, 121.3, 33.9, 23.8.

1-(4-propylphenyl)-1*H*-tetrazole (6d)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 4:1, v/v) to give the product as a yellow solid (24.4 mg, 65%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.98 (s, 1H), 7.59 (m, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 2.67 (m, 2H), 1.68 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.2, 140.5, 131.6, 130.1, 121.2, 37.6, 24.4, 13.7. HRMS (ESI, m/z) calcd for $C_{10}H_{12}N_4$ $[M+H]^+$: 189.1135; found: 189.1139.

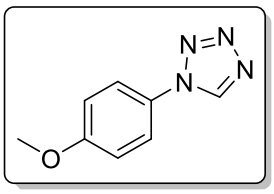
1-([1,1'-biphenyl]-4-yl)-1*H*-tetrazole (6e) (CAS Number: 63472-38-8)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 4:1, v/v) to give the

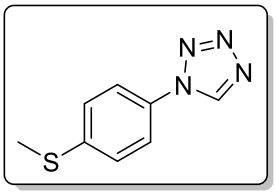
product as a white solid (29.3 mg, 66%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.06 (s, 1H), 7.79 (s, 4H), 7.62 (dq, *J* = 2.6, 1.7 Hz, 2H), 7.49 (m, 2H), 7.42 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.2, 140.5, 139.1, 132.8, 129.1 128.8, 1284, 127.2, 121.5.

1-(4-methoxyphenyl)-1*H*-tetrazole (6f) (CAS Number: 21788-28-3)



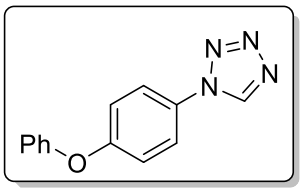
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 2:1, v/v) to give the product as a white solid (28.5 mg, 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.93 (s, 1H), 7.59 (d, *J* = 9.0 Hz, 2H), 7.05 (d, *J* = 9.0 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.7, 140.7, 123.0, 115.2, 55.8.

1-(4-(methylthio)phenyl)-1*H*-tetrazole (6g) (CAS Number: 64022-99-7)



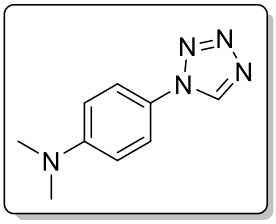
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 2:1, v/v) to give the product as a white solid (26.9 mg, 70%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.00 (s, 1H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 8.7 Hz, 2H), 2.53 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.0, 140.4, 130.5, 127.1, 121.6, 15.4.

1-(4-phenoxyphenyl)-1*H*-tetrazole (6h) (CAS Number: 330996-10-6)



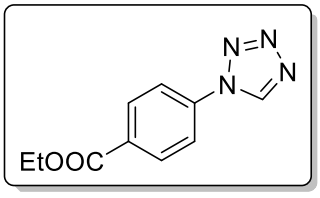
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 2:1, v/v) to give the product as a yellow solid (36.2 mg, 76%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.96 (s, 1H), 7.63 (d, *J* = 9.0 Hz, 2H), 7.40 (dd, *J* = 8.5, 7.5 Hz, 2H), 7.21 (m, 1H), 7.15 (d, *J* = 9.0 Hz, 2H), 7.07 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.1, 155.8, 140.6, 130.2, 128.5, 124.6, 123.1, 119.8, 119.3.

***N,N*-dimethyl-4-(1*H*-tetrazol-1-yl)aniline (6i) (CAS Number: 102236-05-5)**



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 2:1, v/v) to give the product as a white solid (24.6 mg, 65%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.84 (s, 1H), 7.48 (d, *J* = 9.1 Hz, 2H), 6.77 (d, *J* = 9.1 Hz, 2H), 3.04 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.2, 140.5, 122.6, 112.3, 40.4.

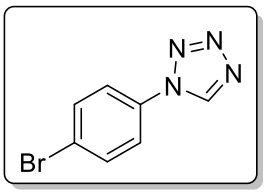
ethyl 4-(1*H*-tetrazol-1-yl)benzoate (6j) (CAS Number: 1514839-59-8)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 2:1, v/v) to give the product as a yellow solid (15.7 mg, 36%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.09 (s, 1H), 8.27 (d, *J* =

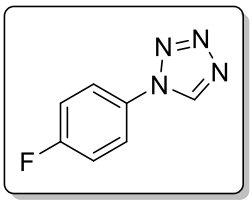
8.4 Hz, 2H), 7.83 (d, *J* = 8.4 Hz, 2H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0, 140.4, 136.8, 132.0, 131.7, 120.7, 61.8, 14.3.

1-(4-bromophenyl)-1*H*-tetrazole (6k) (CAS Number: 57058-01-2)



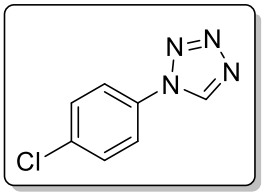
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 4:1, v/v) to give the product as a yellow solid (21.1 mg, 47%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.01 (s, 1H), 7.73 (m, 2H), 7.62 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.4, 133.5, 124.0, 122.6.

1-(4-fluorophenyl)-1*H*-tetrazole (6l) (CAS Number: 14210-81-2)



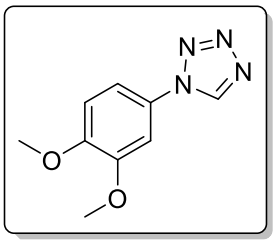
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 4:1, v/v) to give the product as a yellow solid (23.9 mg, 73%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.01 (s, 1H), 7.71 (dd, *J* = 7.9, 3.8 Hz, 2H), 7.29 (t, *J* = 8.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.1 (d, *J* = 249.9 Hz), 140.7, 123.0, 123.5 (d, *J* = 8.8 Hz), 117.3 (d, *J* = 23.4 Hz).

1-(4-chlorophenyl)-1*H*-tetrazole (6m) (CAS Number: 25108-32-1)



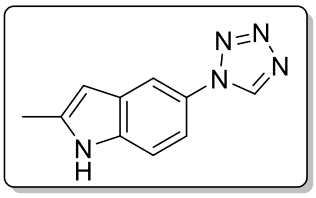
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 4:1, v/v) to give the product as a yellow solid (22.4 mg, 62%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.00 (s, 1H), 7.68 (d, *J* = 8.9 Hz, 2H), 7.57 (d, *J* = 8.9 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.1, 140.8, 140.0, 127.1, 125.7, 123.4, 122.2, 120.9, 119.9, 119.1, 113.9, 109.4, 109.2, 37.9, 13.8.

1-(3,4-dimethoxyphenyl)-1*H*-tetrazole (6n) (CAS Number: 899368-12-8)



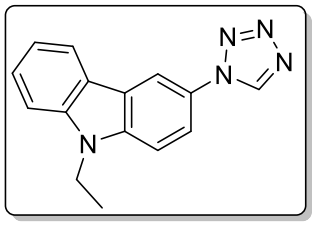
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 1:1, v/v) to give the product as a yellow solid (25.1 mg, 61%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.24 (d, *J* = 2.5 Hz, 1H), 7.17 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.98 (d, *J* = 8.6 Hz, 1H), 3.95 (d, *J* = 5.4 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.3, 150.1, 140.7, 127.0, 113.4, 111.3, 105.4, 56.4, 56.3.

2-methyl-5-(1*H*-tetrazol-1-yl)-1*H*-indole (6o)



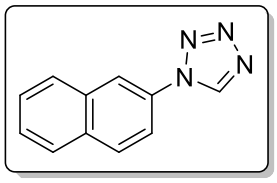
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 4:1, v/v) to give the product as a yellow solid (23.9 mg, 60%). ^{1}H NMR (500 MHz, DMSO) δ 11.36 (s, 1H), 9.97 (s, 1H), 7.88 (d, J = 1.9 Hz, 1H), 7.51 – 7.39 (m, 2H), 6.29 (s, 1H), 2.42 (s, 3H). ^{13}C NMR (125 MHz, DMSO) δ 142.7, 139.1, 136.6, 129.1, 126.5, 114.2, 112.5, 111.9, 100.5, 13.9. HRMS (ESI, m/z) calcd for $C_{10}H_9N_5$ $[M+H]^+$: 200.0931; found: 200.0925.

1-(naphthalen-2-yl)-1*H*-tetrazole (6p) (CAS Number: 369636-71-5)



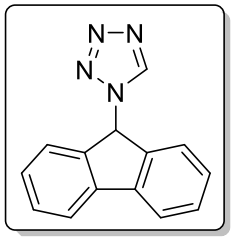
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 3:1, v/v) to give the product as a yellow solid (31.6 mg, 60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.14 (s, 1H), 8.17 (s, 1H), 8.05 (d, *J* = 8.8 Hz, 1H), 7.94 (s, 2H), 7.80 (d, *J* = 8.8 Hz, 1H), 7.62 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.7, 133.3, 133.1, 131.1, 130.6, 128.4, 128.1, 128.0, 127.8, 119.7, 118.8.

1-(naphthalen-2-yl)-1*H*-tetrazole (6q)



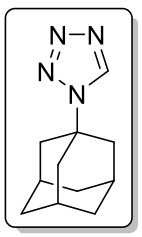
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 1:1, v/v) to give the product as a yellow solid (22.0 mg, 56%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.13 (s, 1H), 8.18 (d, *J* = 2.1 Hz, 1H), 8.1 (d, *J* = 8.8 Hz, 1H), 8.0 – 7.9 (m, 2H), 7.8 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.7 – 7.6 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.7, 133.4, 133.1, 130.7, 128.4, 128.1, 128.0, 127.8, 119.7, 118.8. HRMS (ESI, m/z) calcd for $C_{11}H_8N_4$ $[M+H]^+$: 197.0822; found: 197.0826.

1-(9*H*-fluoren-9-yl)-1*H*-tetrazole (6r)



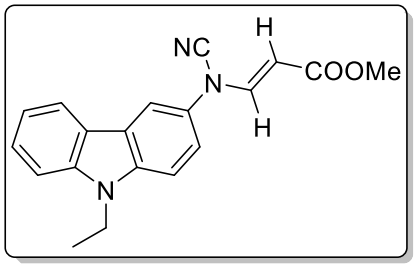
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 1:1, v/v) to give the product as a white solid (30.4 mg, 65%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.8 (d, *J* = 7.6 Hz, 2H), 7.5 (t, *J* = 7.6 Hz, 2H), 7.5 (dd, *J* = 7.5, 0.5 Hz, 2H), 7.4 (td, *J* = 7.5, 0.9 Hz, 2H), 6.8(s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.7, 140.6, 139.4, 130.5, 128.7, 125.4, 120.9, 62.7. HRMS (ESI, m/z) calcd for $C_{14}H_{10}N_4$ $[M+H]^+$: 235.0978; found: 235.0981.

1-((3s,5s,7s)-adamantan-1-yl)-1*H*-tetrazole (6s) (CAS Number: 50987-38-7)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 1:1, v/v) to give the product as a white solid (25.3 mg, 62%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.6 (s, 1H), 2.3 (d, *J* = 2.6 Hz, 6H), 1.9 – 1.8 (m, 7H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.3, 59.8, 42.8, 35.6, 35.5, 29.3.

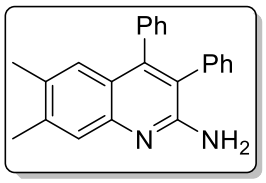
methyl (*E*)-3-(*N*-(9-ethyl-9*H*-carbazol-3-yl)cyanamido)acrylate (7)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 1:1, v/v) to give the product as a white solid (26.8 mg, 42%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.1 (d, J = 7.8 Hz, 1H), 8.0 (d, J = 2.2 Hz, 1H), 7.6 (d, J = 13.6 Hz, 1H), 7.5 (td, J = 7.7,

7.2, 1.1 Hz, 1H), 7.5 (d, J = 8.4 Hz, 2H), 7.4 (dd, J = 8.7, 2.3 Hz, 1H), 7.3 (m, 1H), 5.8 (d, J = 13.6 Hz, 1H), 4.4 (q, J = 7.2 Hz, 2H), 3.8 (s, 3H), 1.4 (t, J = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8, 143.7, 140.8, 139.0, 129.4, 127.0, 123.8, 122.1, 120.8, 119.8, 119.7, 114.5, 110.1, 109.6, 109.0, 103.2, 51.8, 37.9, 13.8. HRMS (ESI, m/z) calcd for $C_{19}H_{17}N_3O_2$ $[M+H]^+$: 319.1312; found: 319.1314.

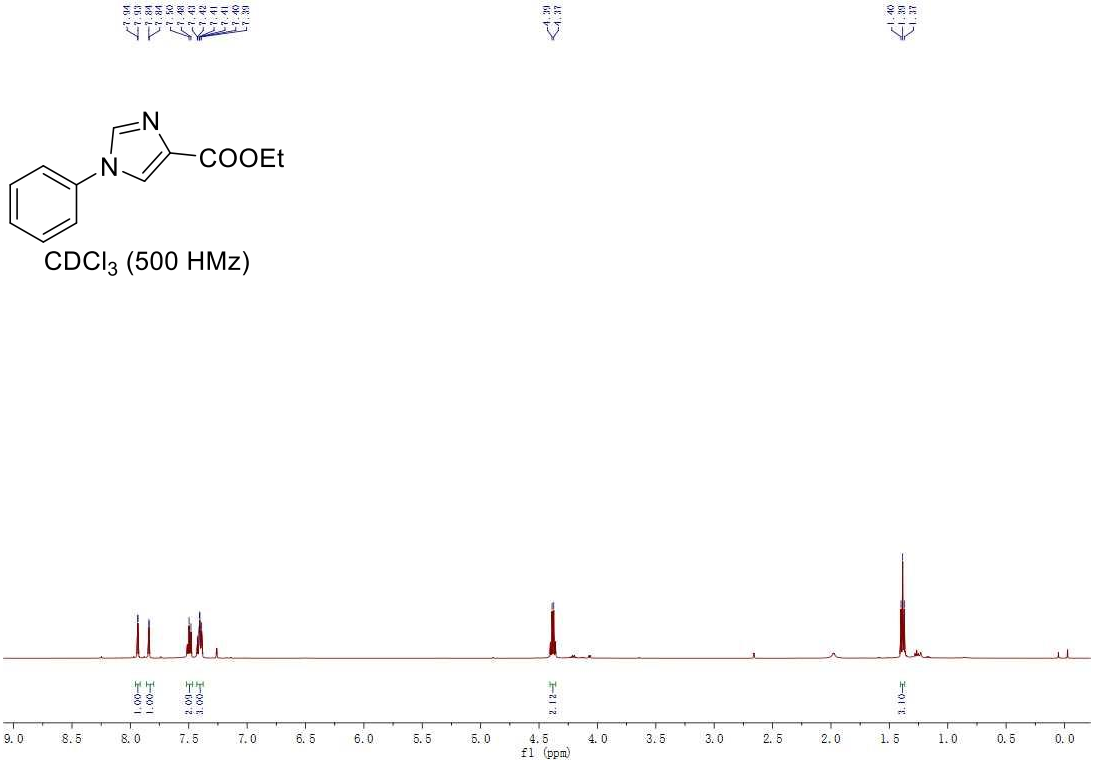
6,7-dimethyl-3,4-diphenylquinolin-2-amine (8) (CAS Number: 1638213-25-8)

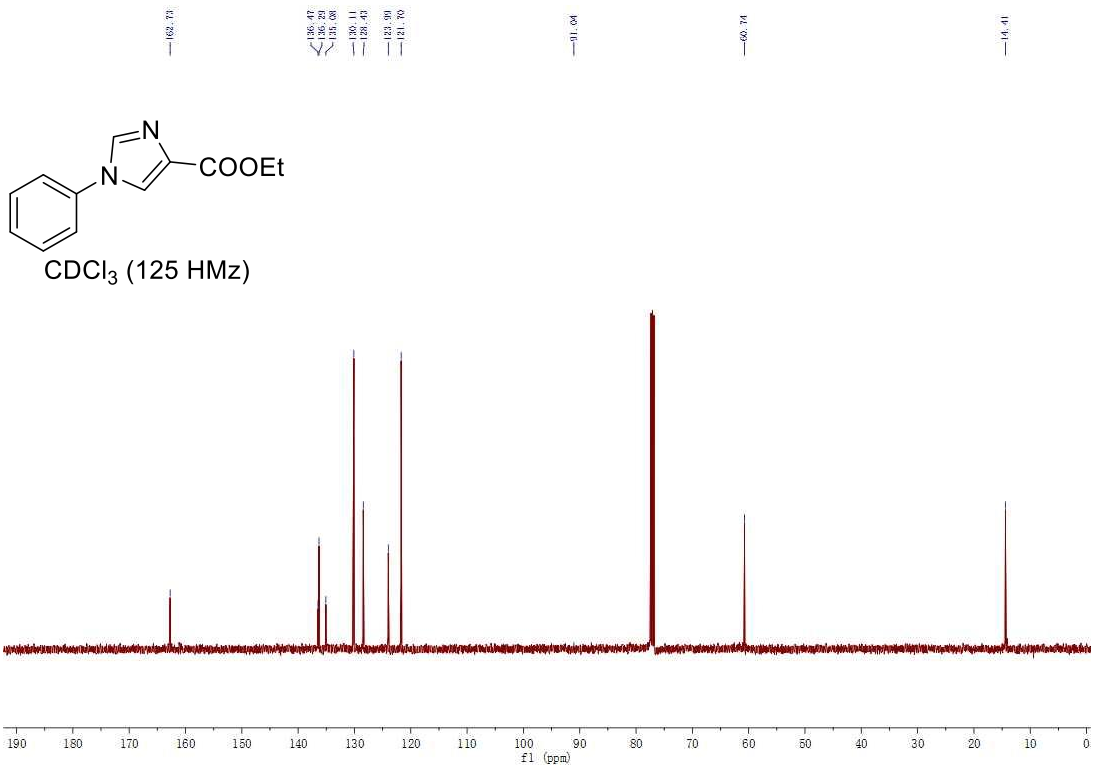


The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 3:1, v/v) to give the product as a white solid (32.4 mg, 50%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.5 (s, 1H), 7.3 – 7.2 (m, 6H), 7.2 – 7.1 (m, 5H), 4.7 (s, 2H), 2.4 (s, 3H), 2.2 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 155.0, 147.2, 145.9, 139.5, 137.1, 136.4, 132.0, 130.5, 130.0, 128.6, 127.4, 127.1, 126.1, 125.7, 122.5, 122.1, 20.3, 19.8.

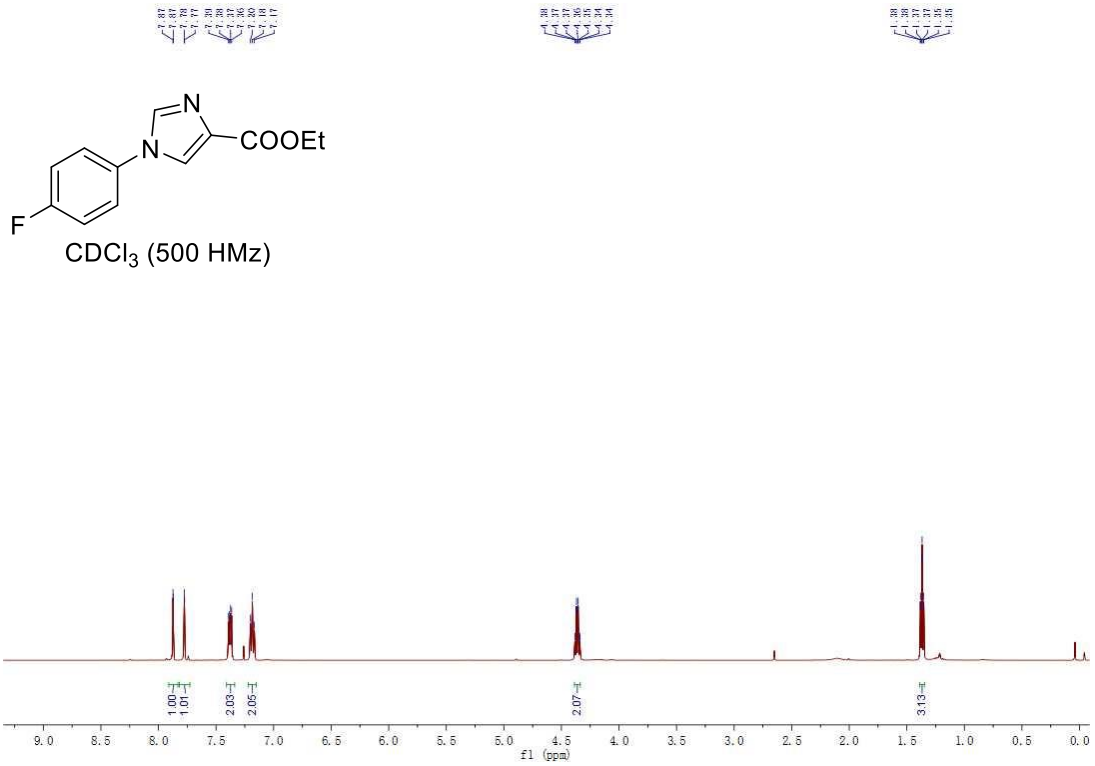
7. NMR spectroscopic data

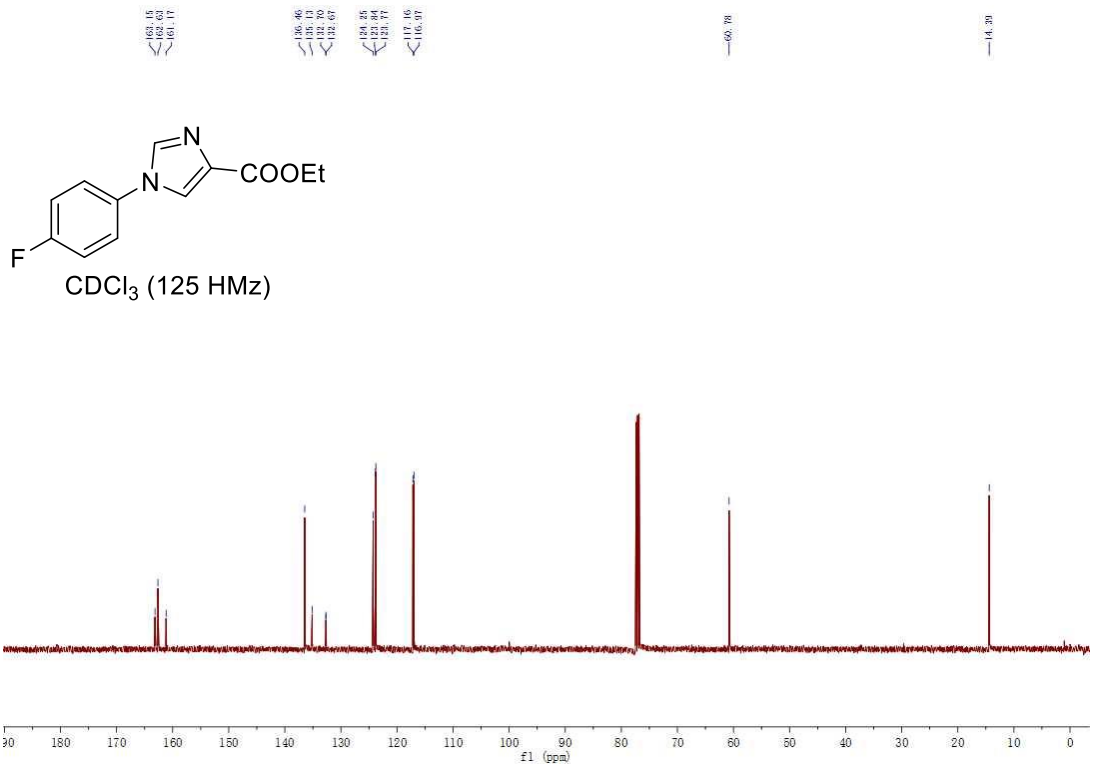
ethyl 1-phenyl-1*H*-imidazole-4-carboxylate (4a)



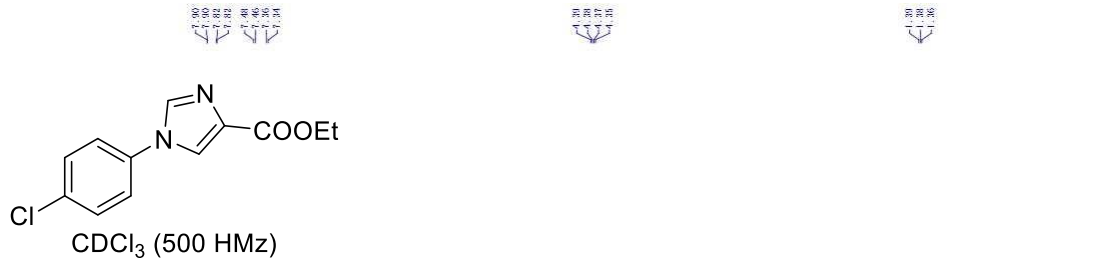


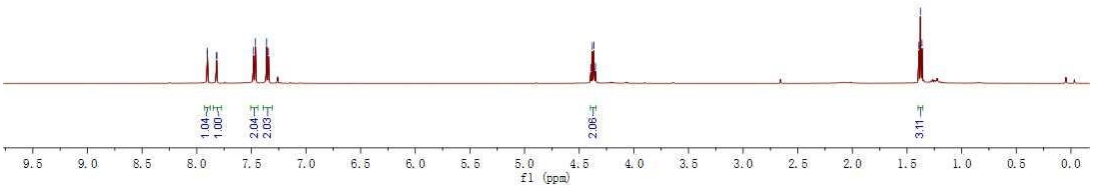
ethyl 1-(4-fluorophenyl)-1*H*-imidazole-4-carboxylate (4b)



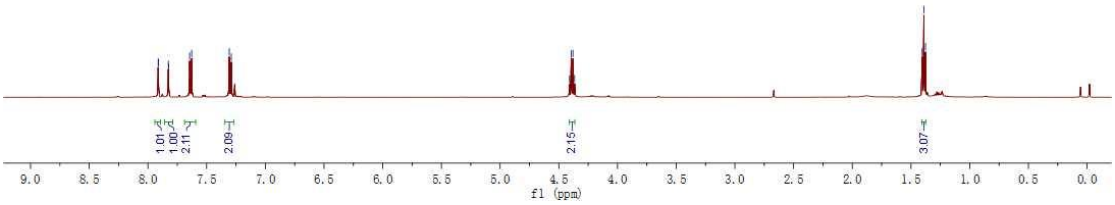


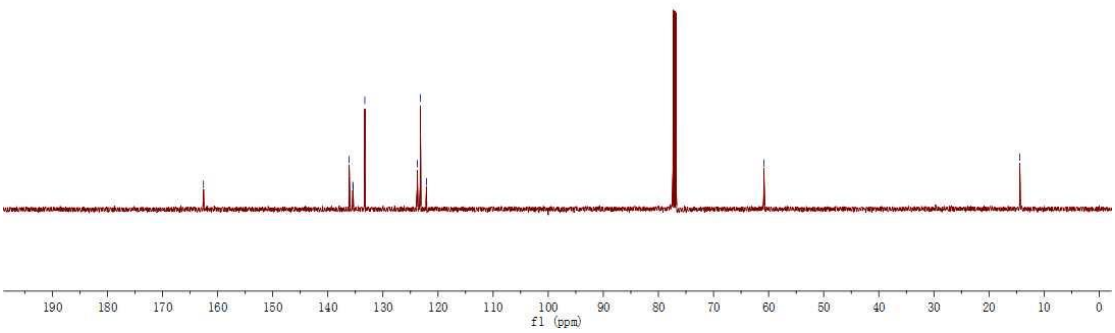
ethyl 1-(4-chlorophenyl)-1*H*-imidazole-4-carboxylate (4c)



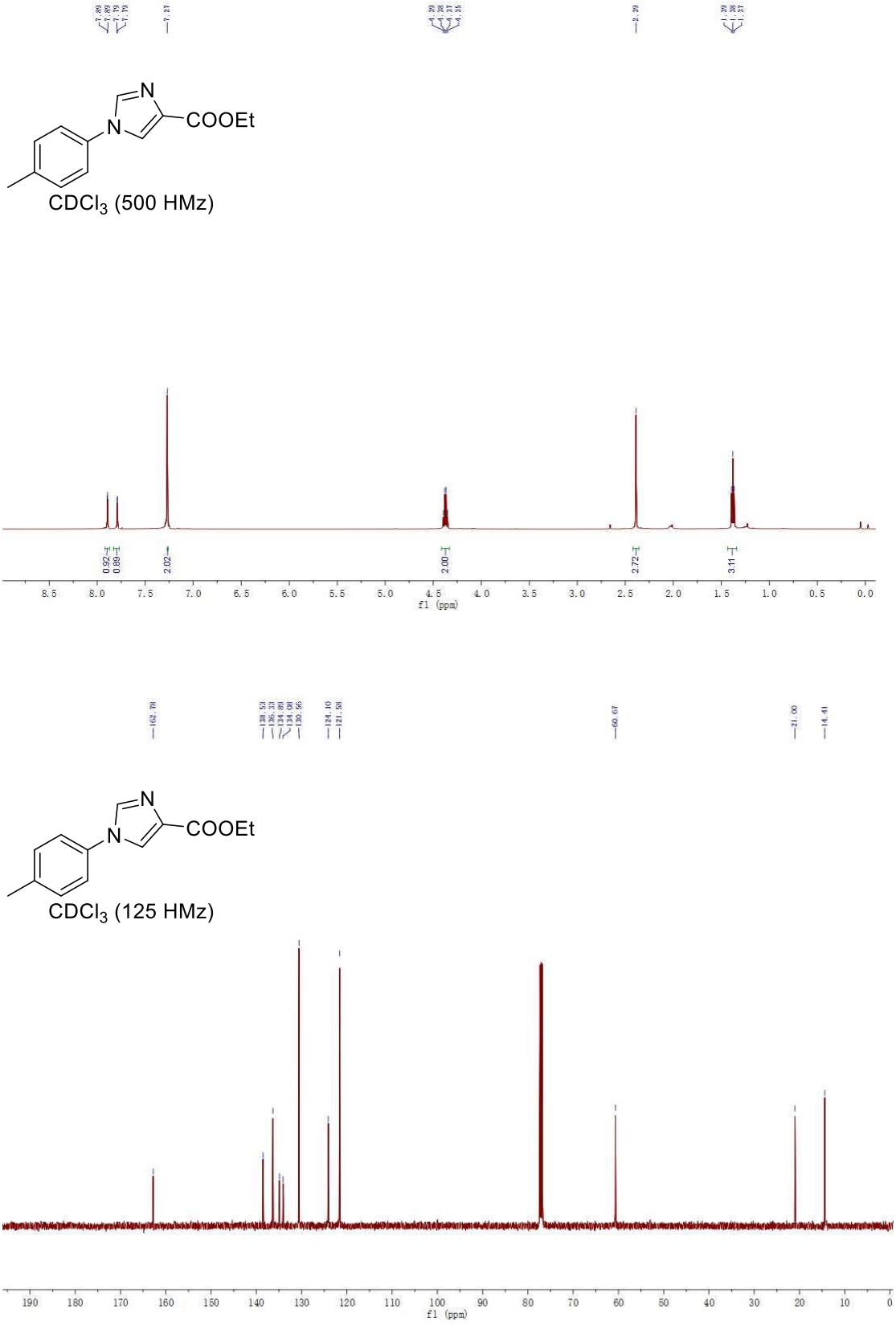


ethyl 1-(4-bromophenyl)-1*H*-imidazole-4-carboxylate (4d)

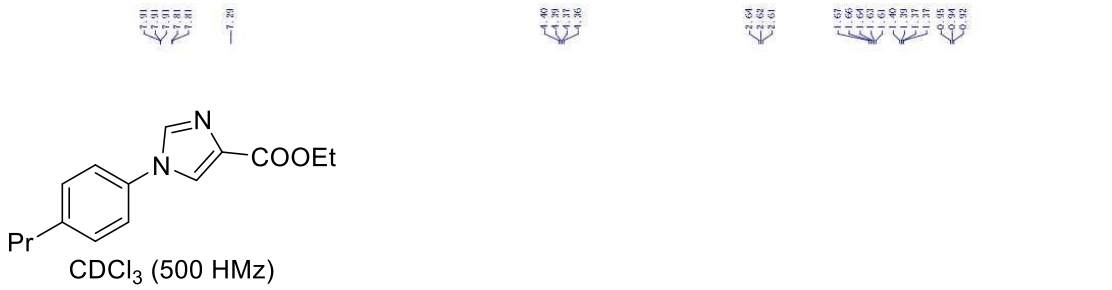




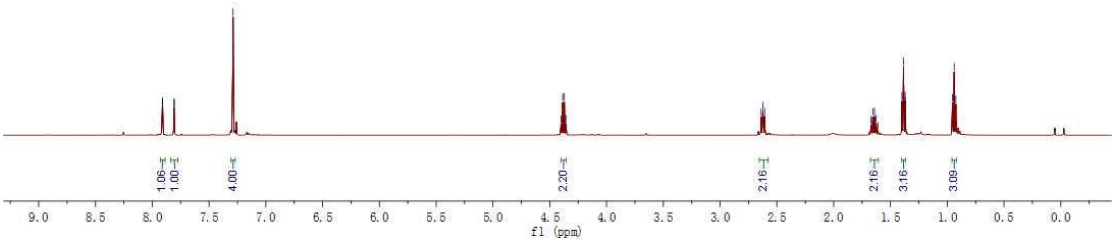
ethyl 1-(*p*-tolyl)-1*H*-imidazole-4-carboxylate (4e)

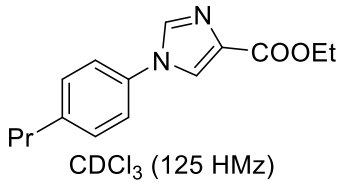


ethyl 1-(4-propylphenyl)-1*H*-imidazole-4-carboxylate (4f)

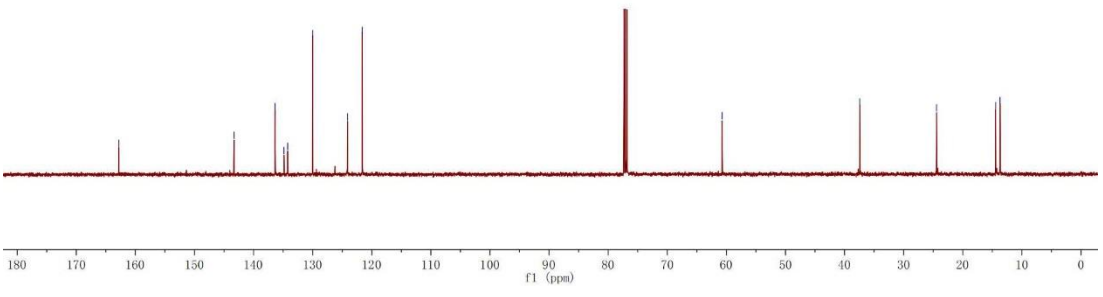


$CDCl_3$ (500 HMz)

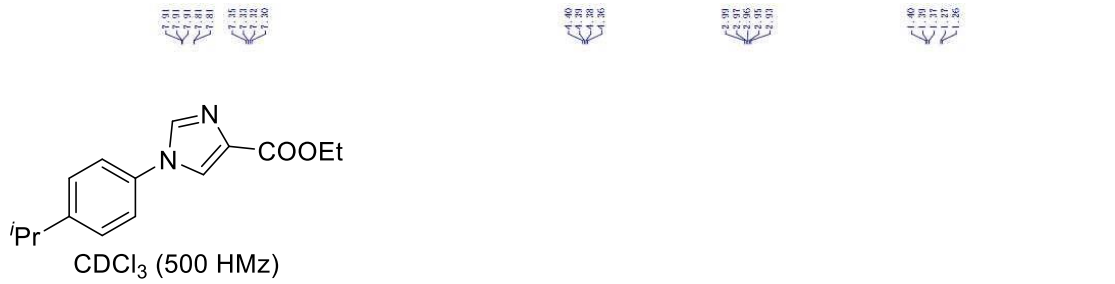


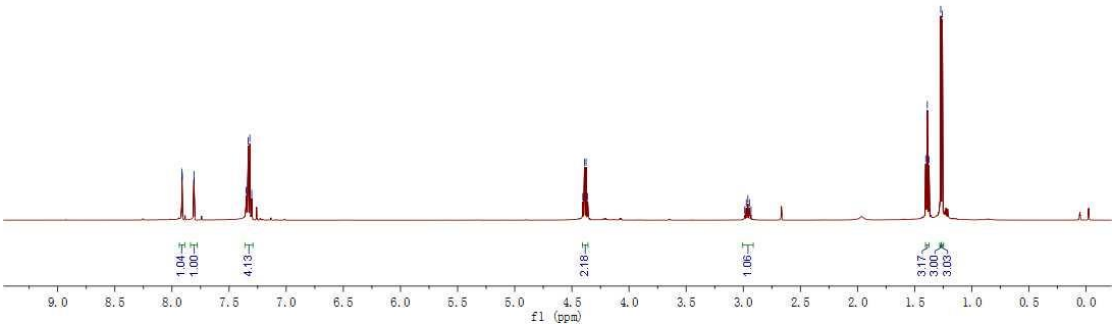


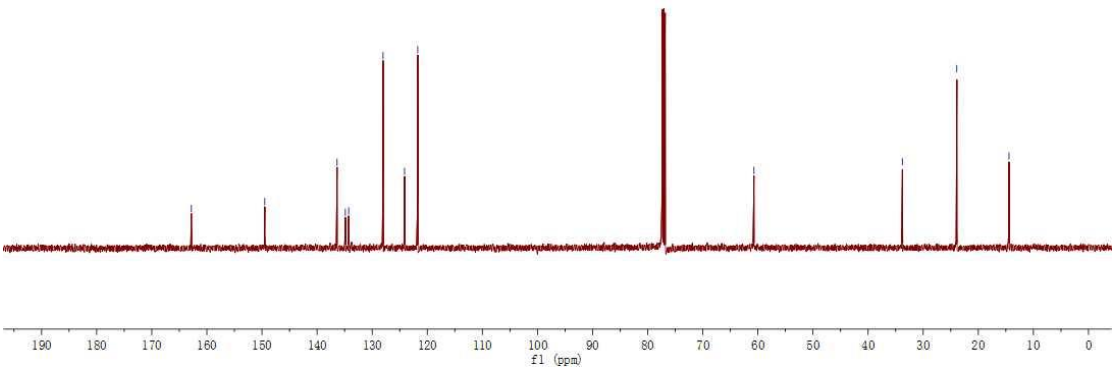
$CDCl_3$ (125 HMz)



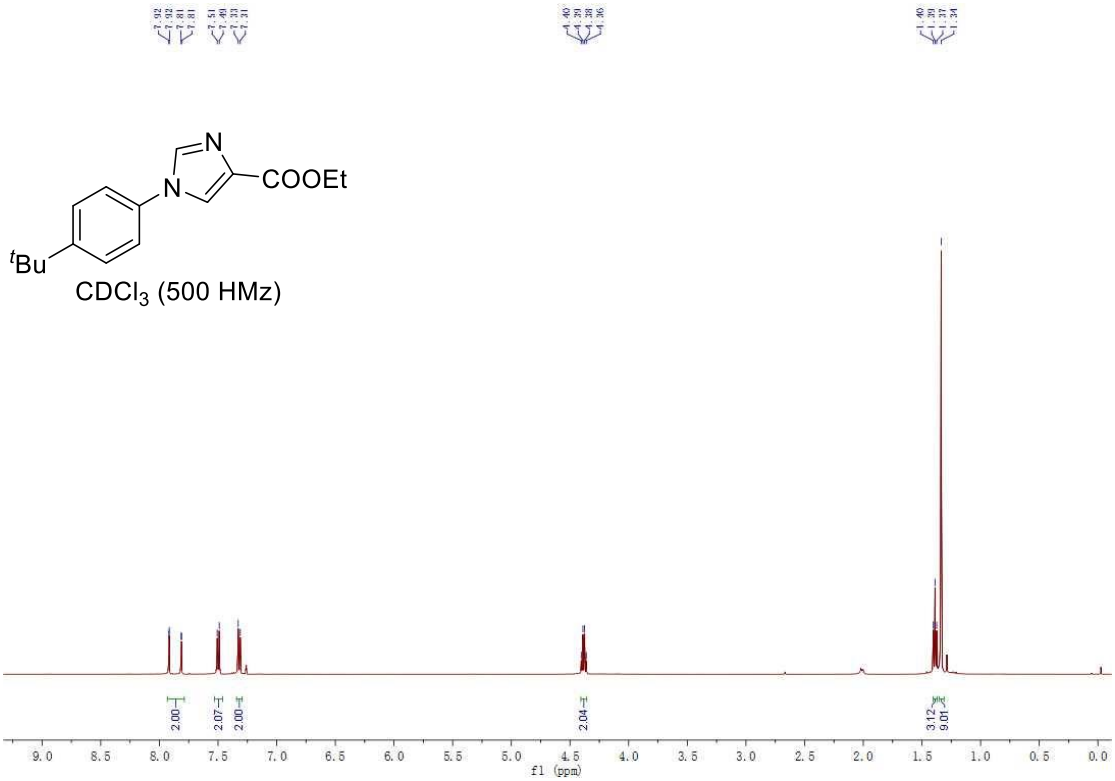
ethyl 1-(4-isopropylphenyl)-1*H*-imidazole-4-carboxylate (4g)

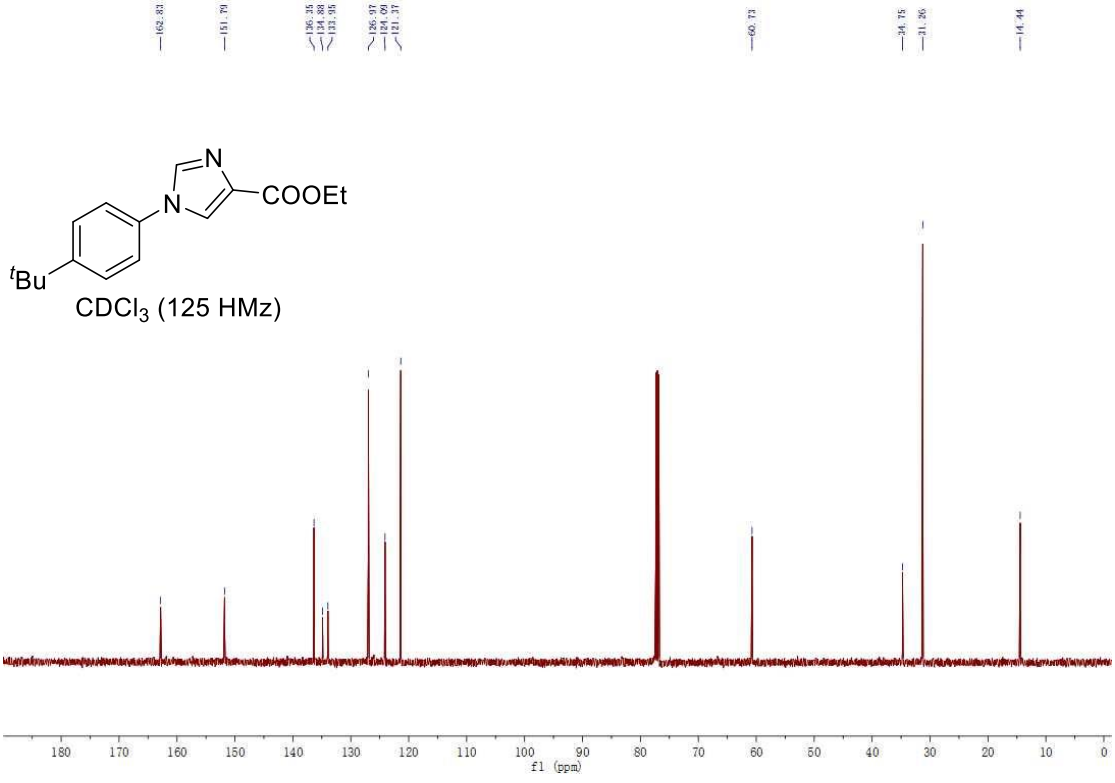




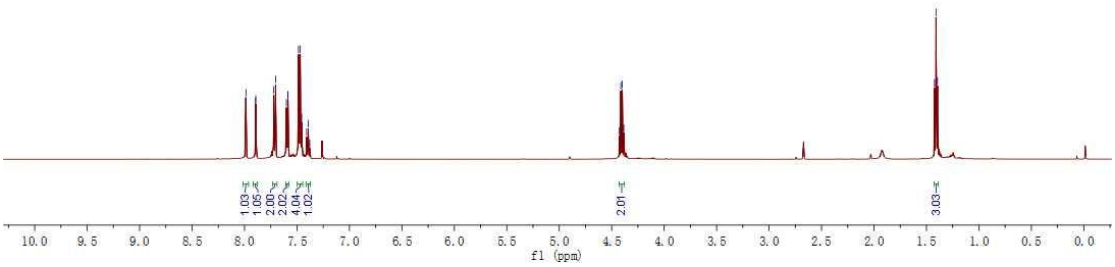


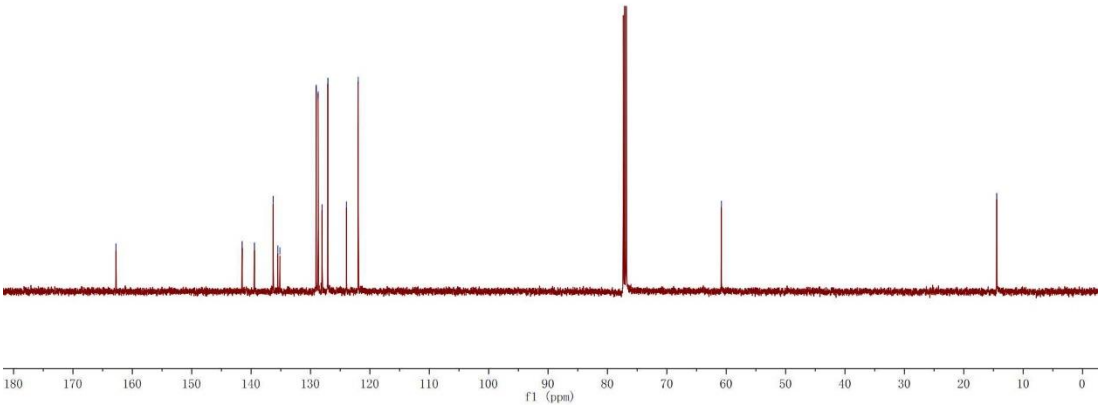
ethyl 1-(4-(*tert*-butyl)phenyl)-1*H*-imidazole-4-carboxylate (4h)



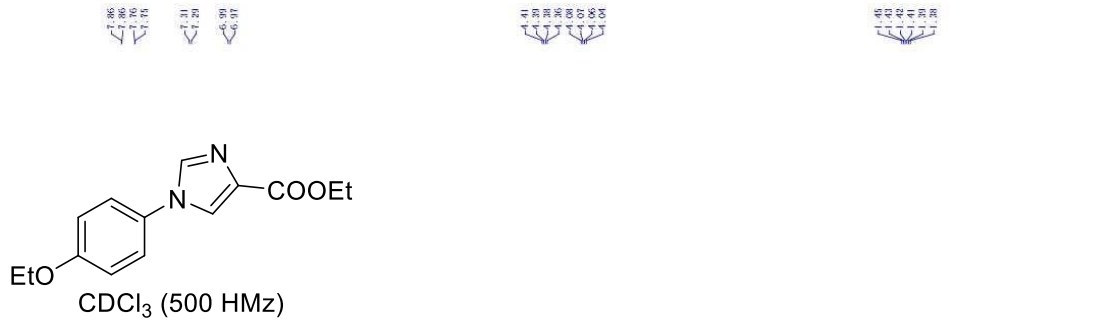


ethyl 1-([1,1'-biphenyl]-4-yl)-1*H*-imidazole-4-carboxylate (4i)

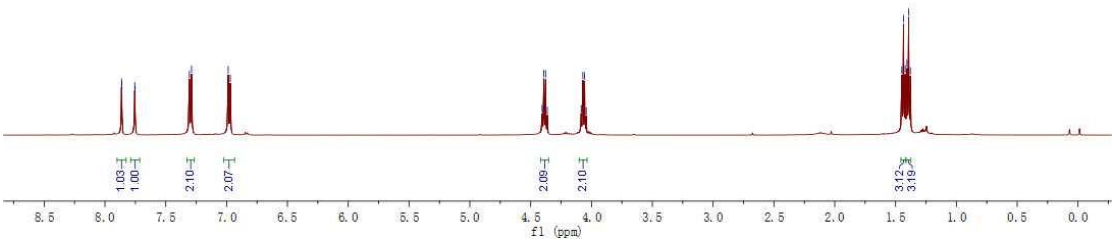


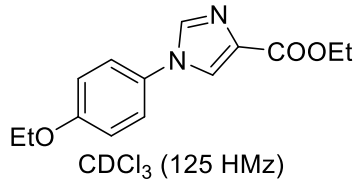


ethyl 1-(4-ethoxyphenyl)-1*H*-imidazole-4-carboxylate (4j)

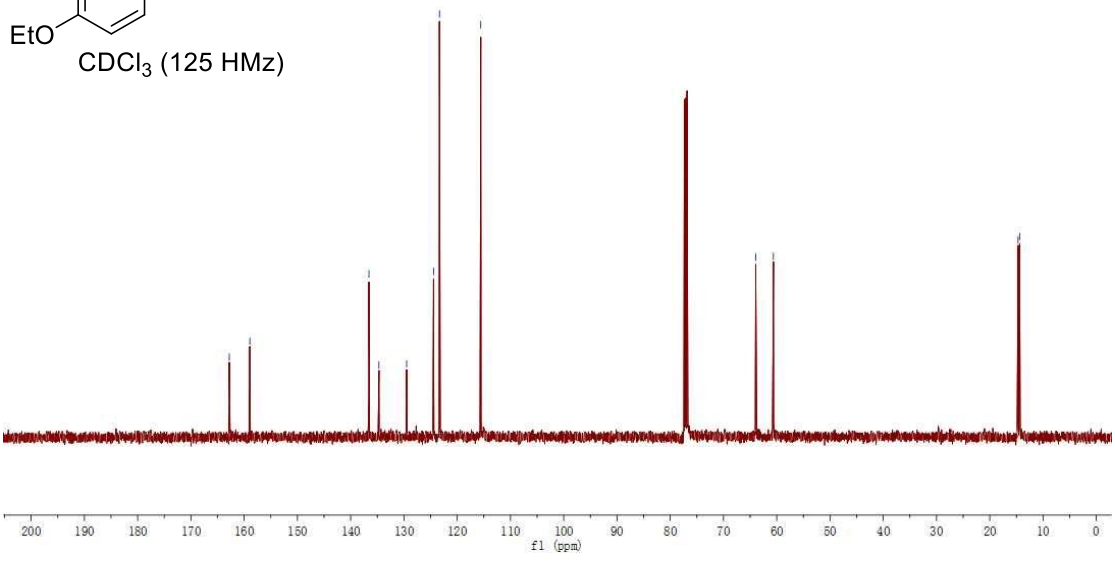


$CDCl_3$ (500 HMz)

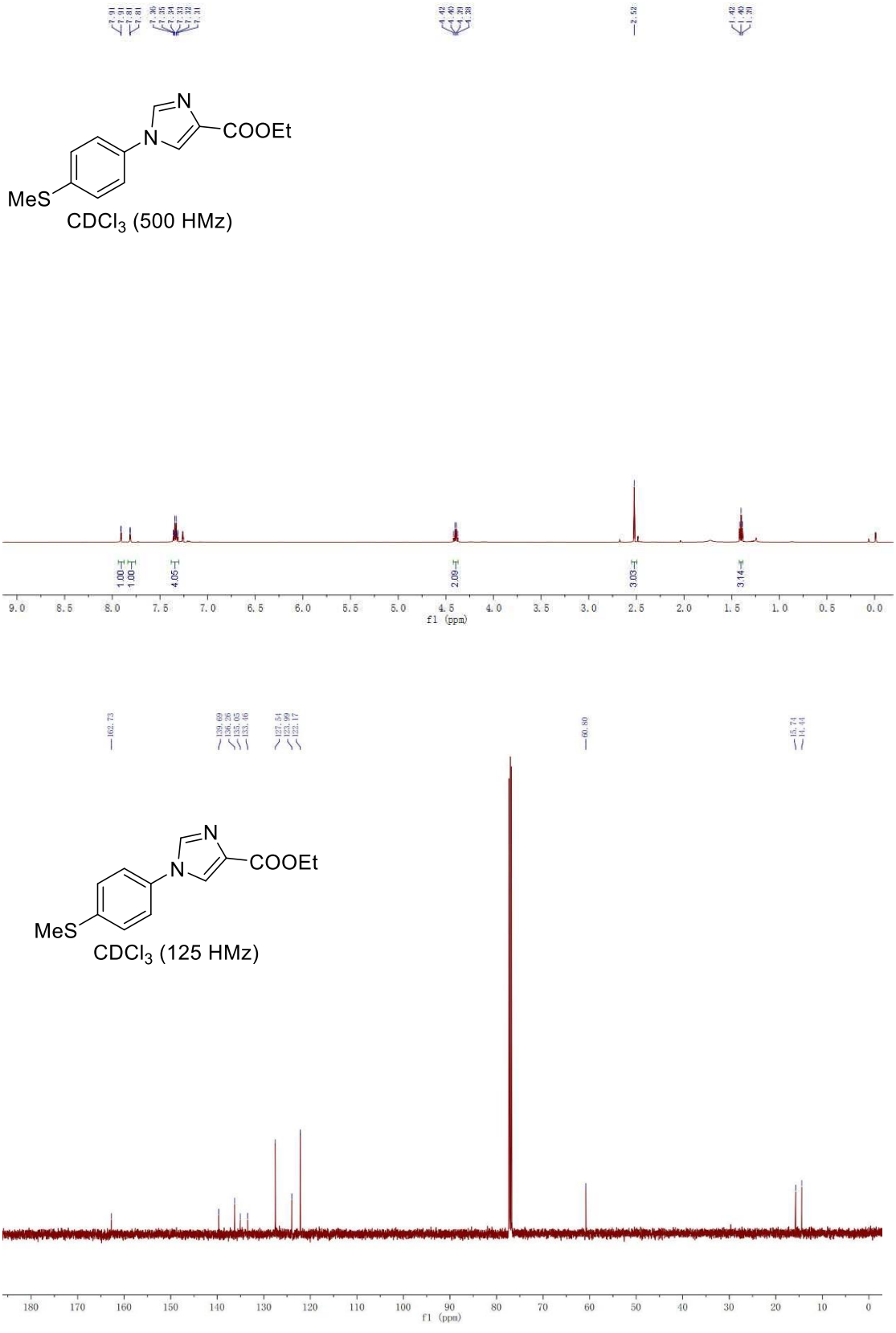




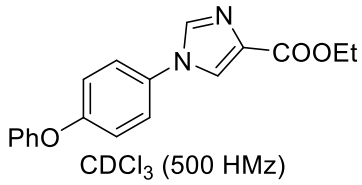
$CDCl_3$ (125 HMz)



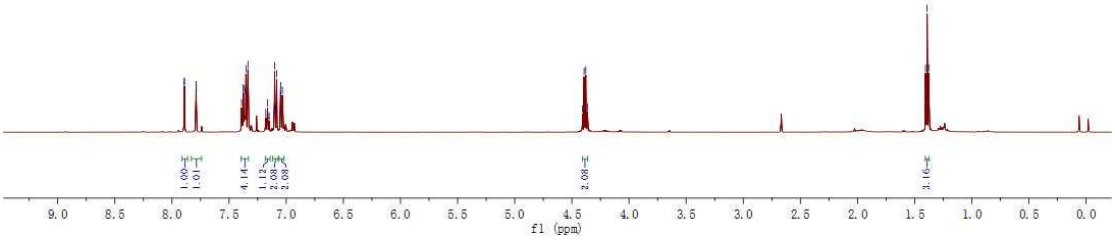
ethyl 1-(4-(methylthio)phenyl)-1*H*-imidazole-4-carboxylate (4k)

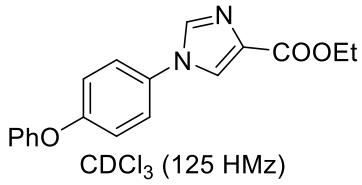


ethyl 1-(4-phenoxyphenyl)-1*H*-imidazole-4-carboxylate (4l)

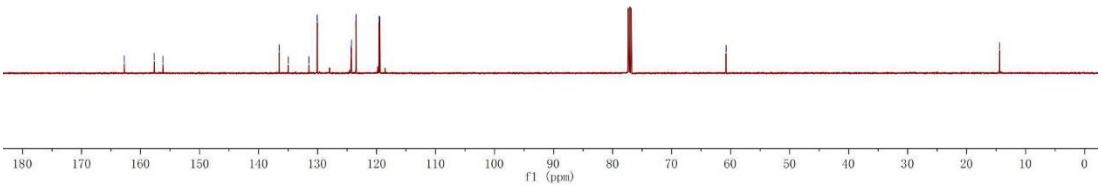


$CDCl_3$ (500 HMz)

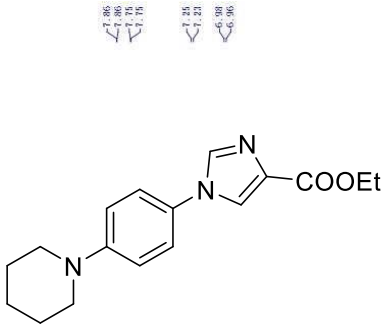




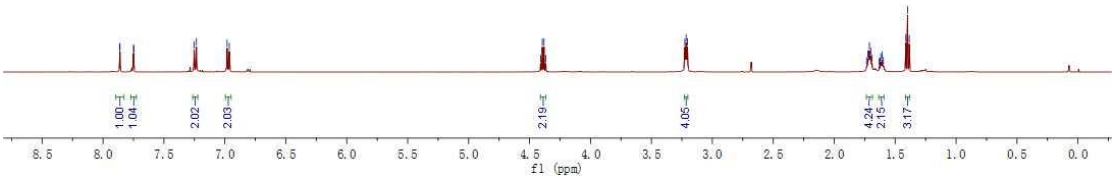
$CDCl_3$ (125 HMz)

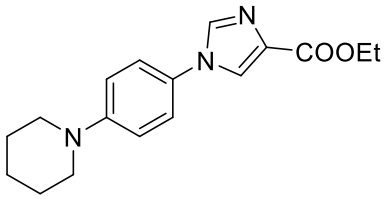


ethyl 1-(4-(piperidin-1-yl)phenyl)-1*H*-imidazole-4-carboxylate (4m)

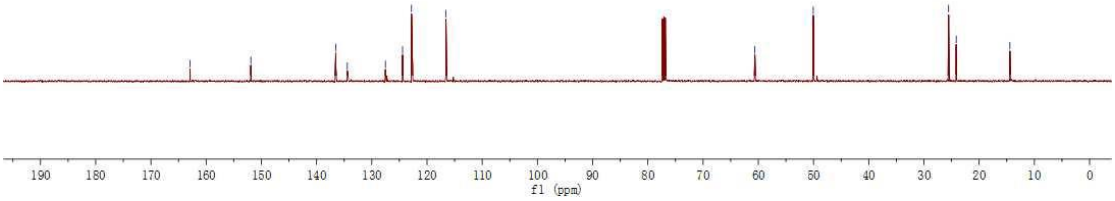


$CDCl_3$ (500 HMz)

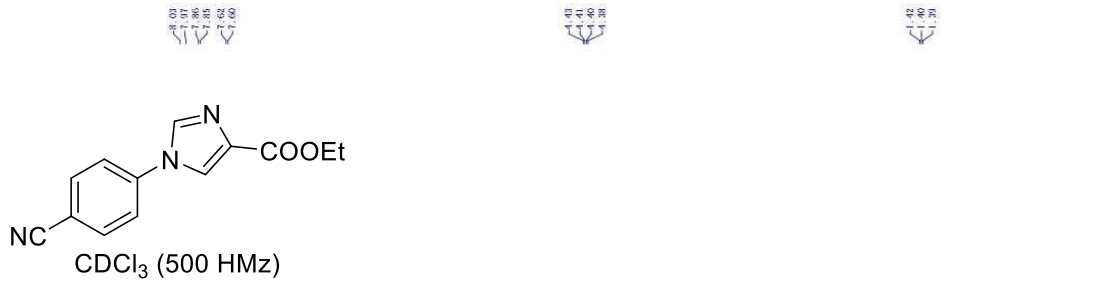


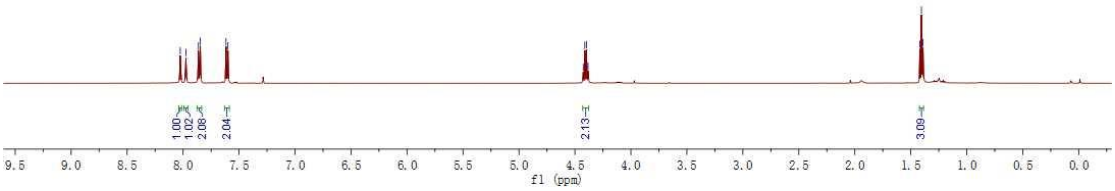


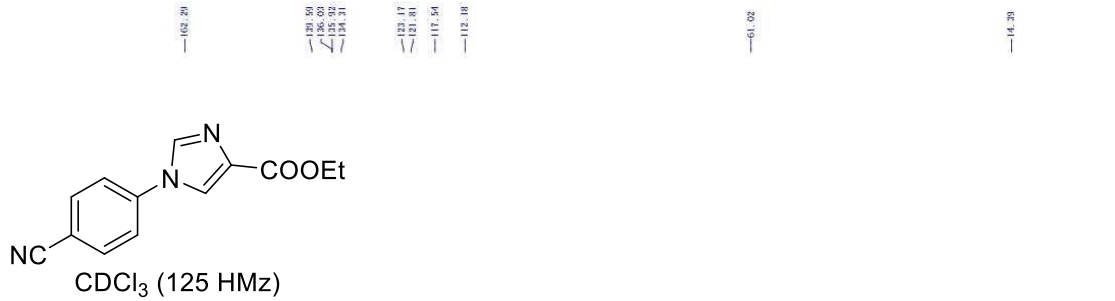
$CDCl_3$ (125 HMz)

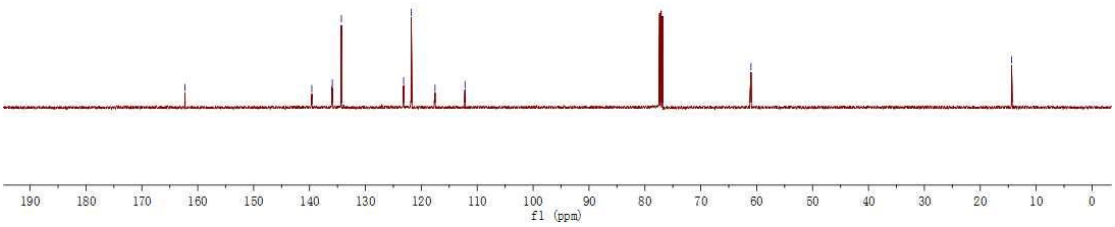


ethyl 1-(4-cyanophenyl)-1*H*-imidazole-4-carboxylate (4n)



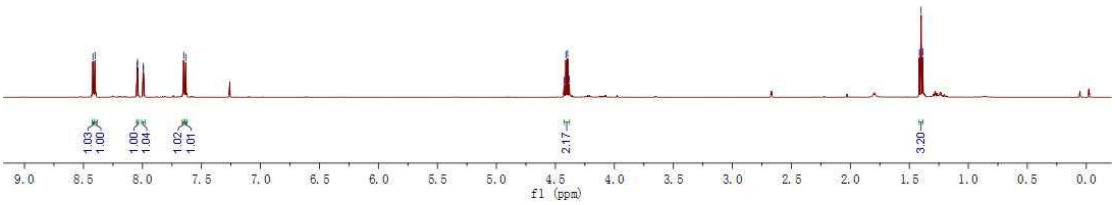


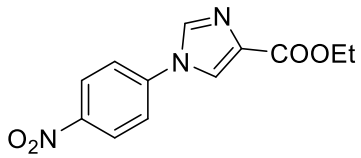




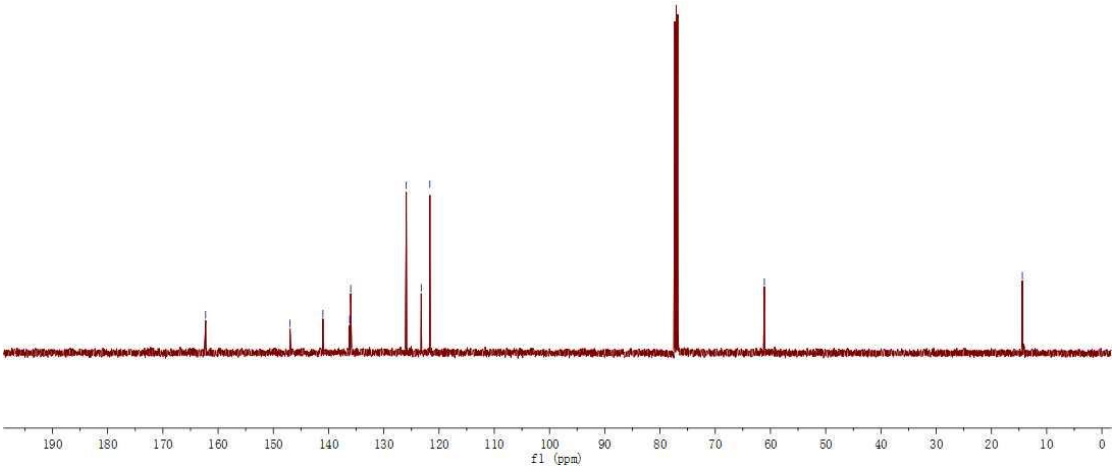
ethyl 1-(4-nitrophenyl)-1*H*-imidazole-4-carboxylate (4o)

$CDCl_3$ (500 HMz)

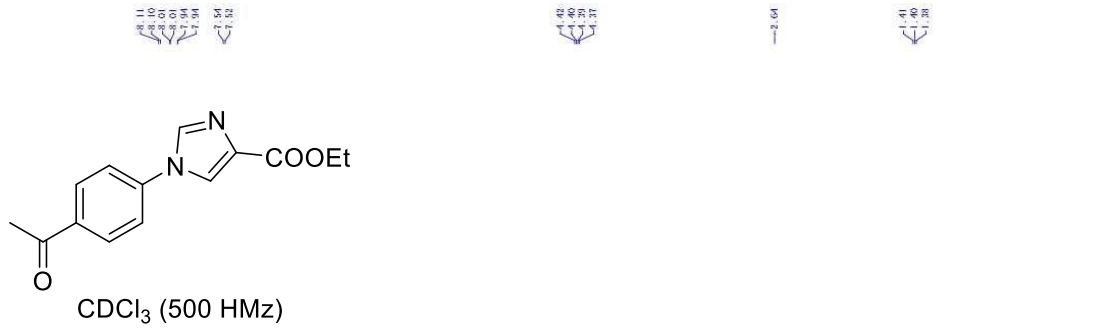




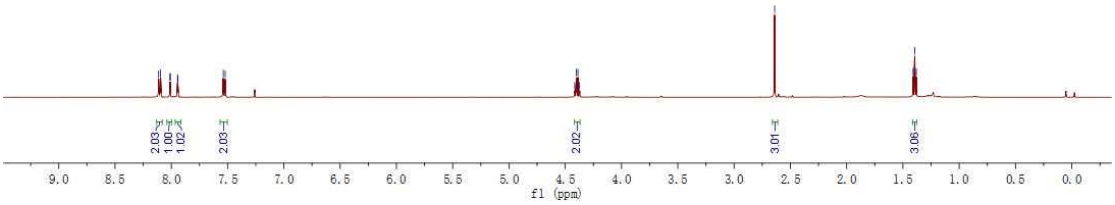
$CDCl_3$ (125 HMz)



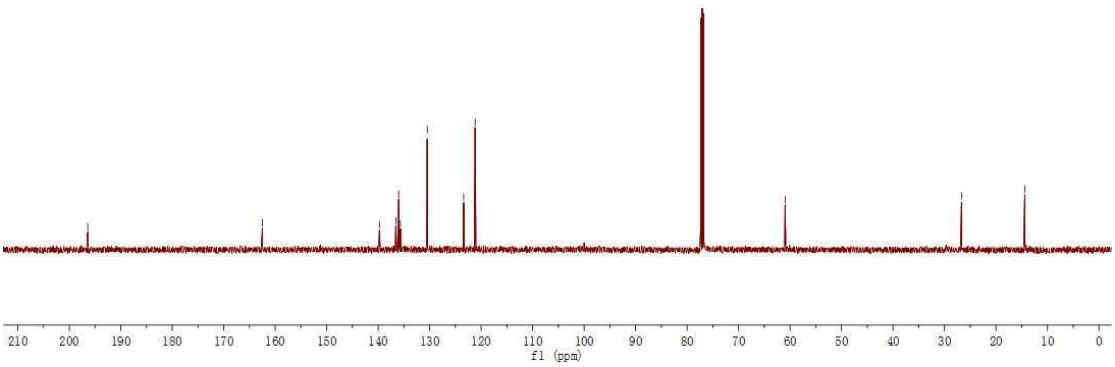
ethyl 1-(4-acetylphenyl)-1*H*-imidazole-4-carboxylate (4p)



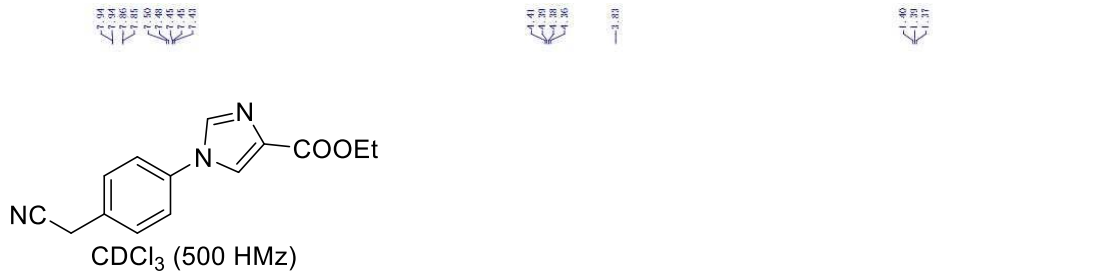
$CDCl_3$ (500 HMz)

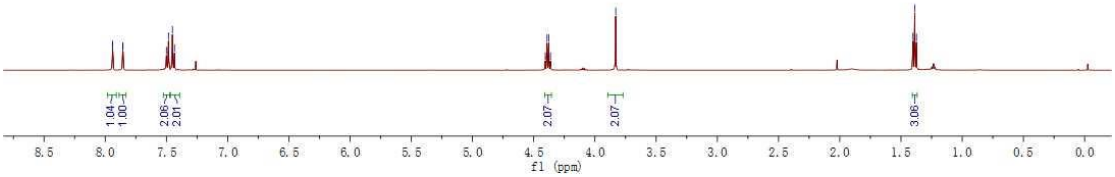


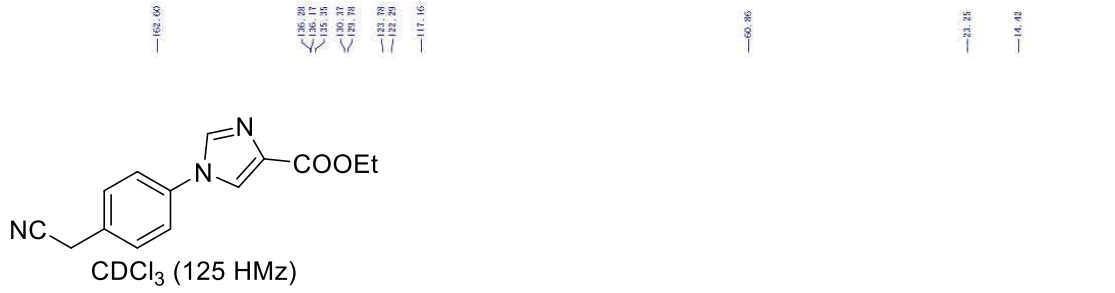
$CDCl_3$ (125 HMz)

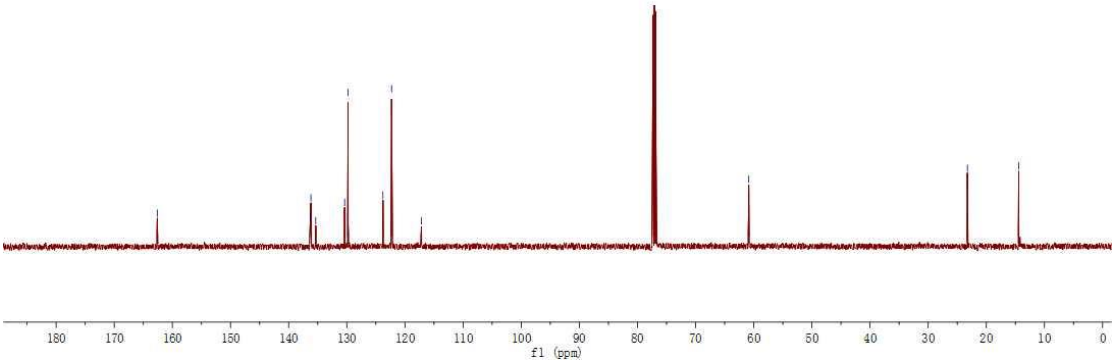


ethyl 1-(4-(cyanomethyl)phenyl)-1*H*-imidazole-4-carboxylate (4q)

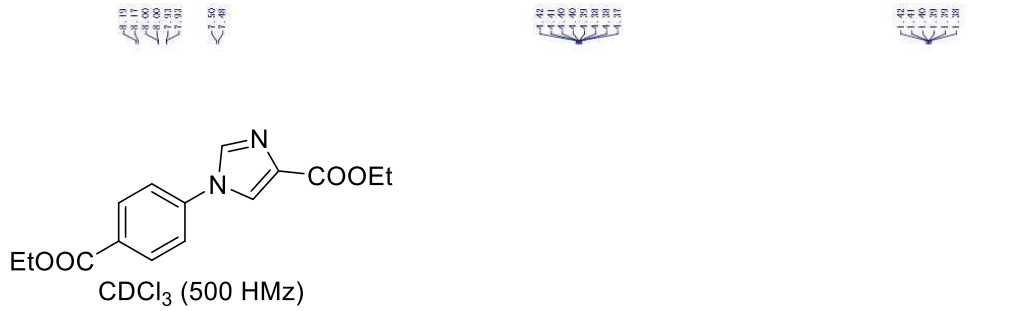


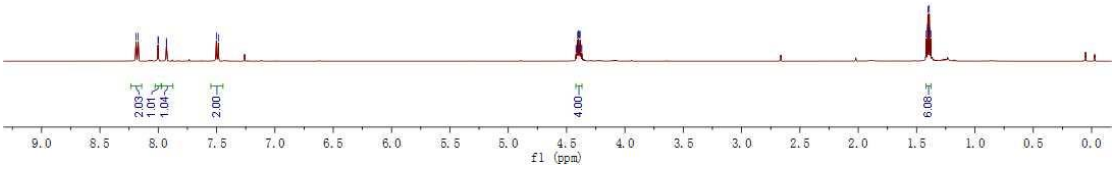


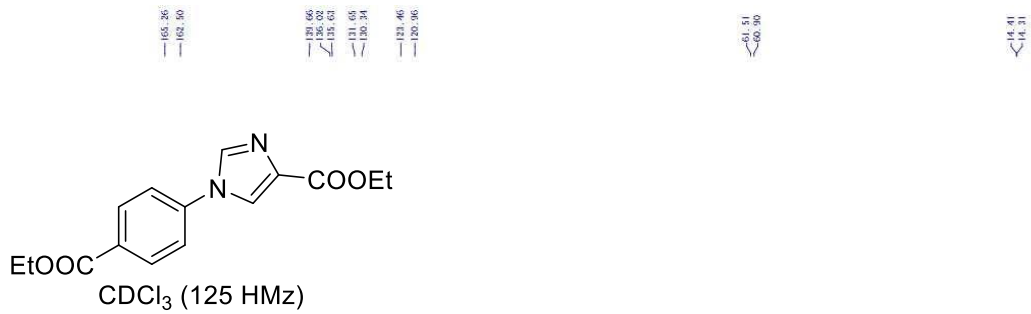


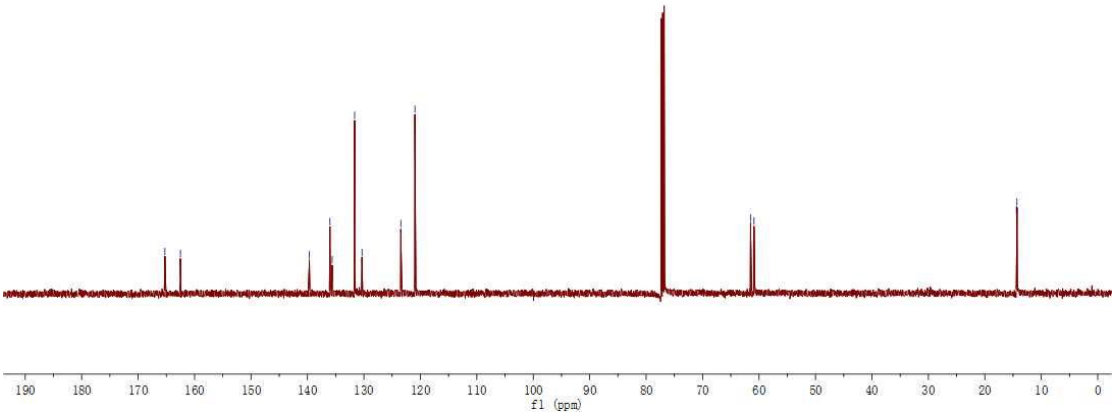


ethyl 1-(4-(ethoxycarbonyl)phenyl)-1*H*-imidazole-4-carboxylate (4r)

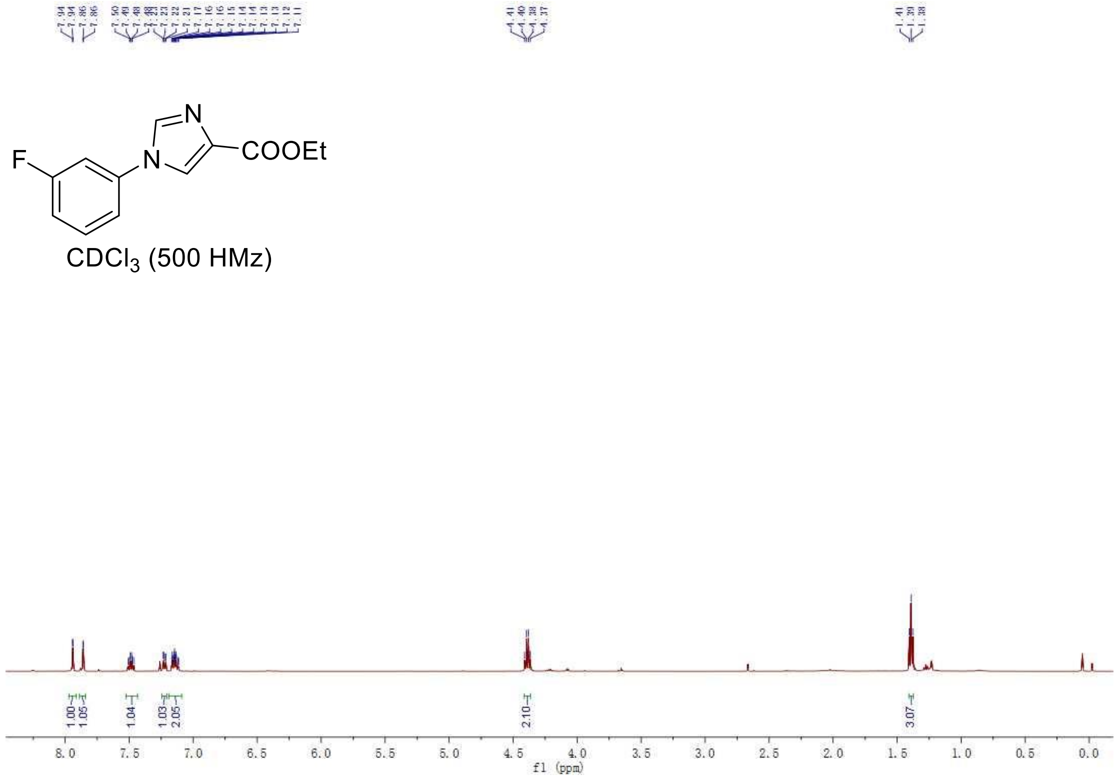


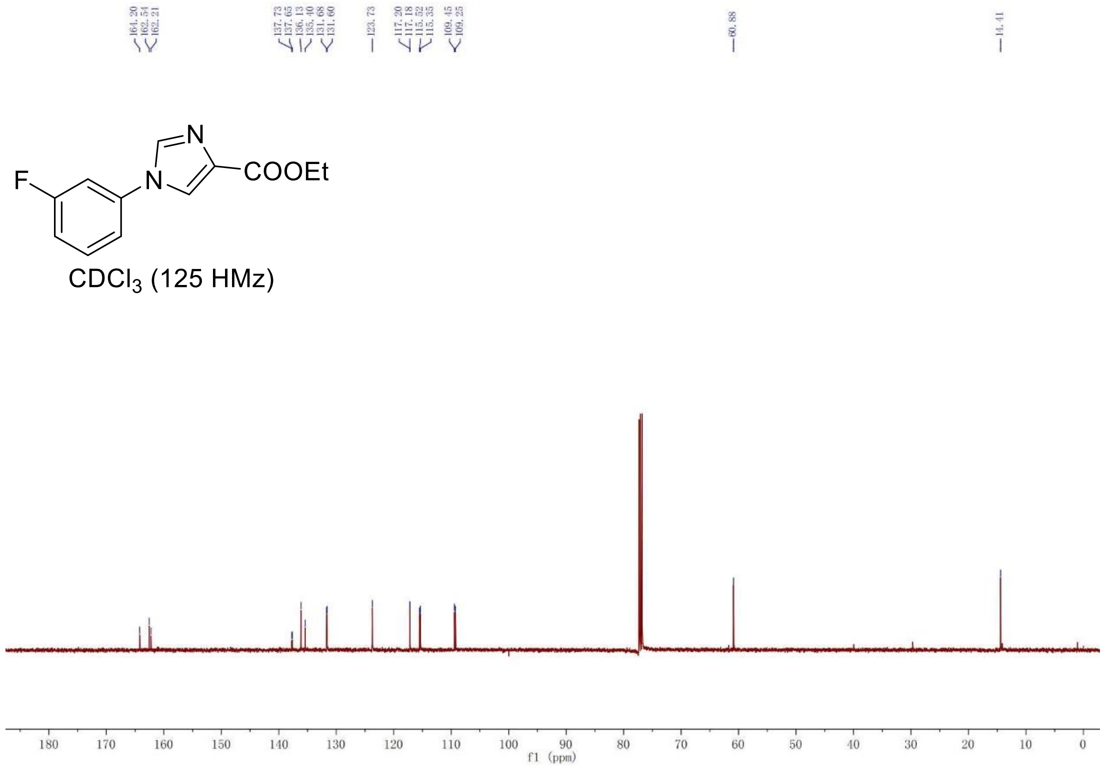




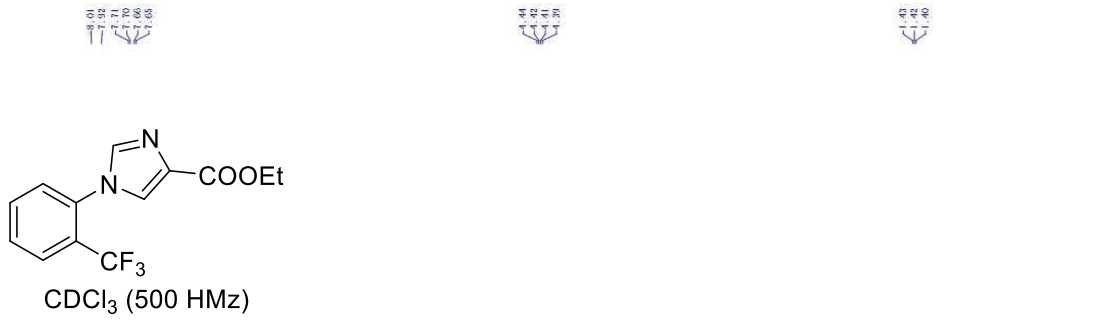


ethyl 1-(3-fluorophenyl)-1*H*-imidazole-4-carboxylate (4s)

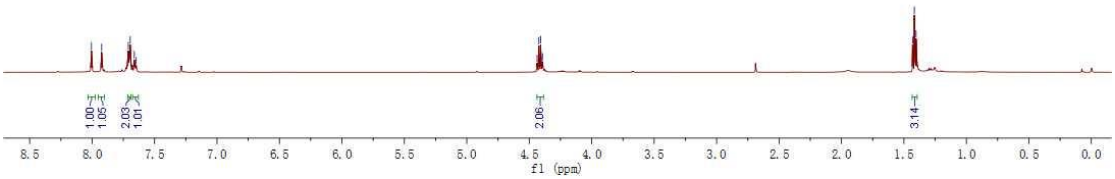


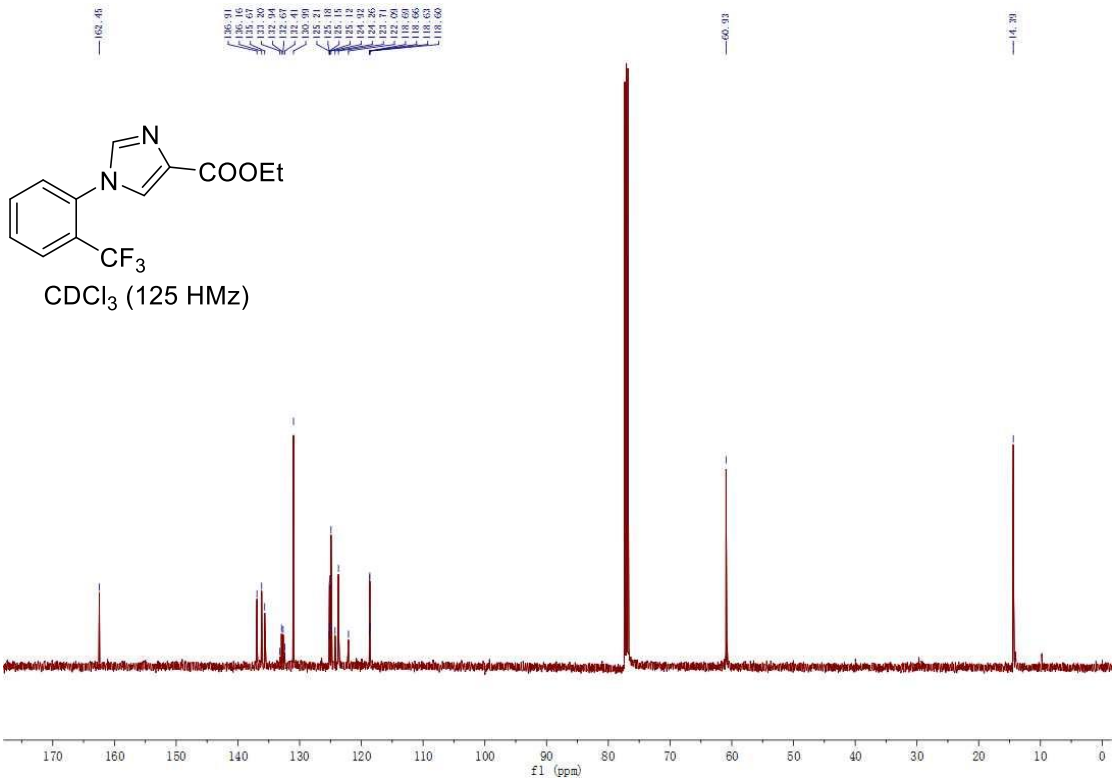


ethyl 1-(2-(trifluoromethyl)phenyl)-1*H*-imidazole-4-carboxylate (4t)



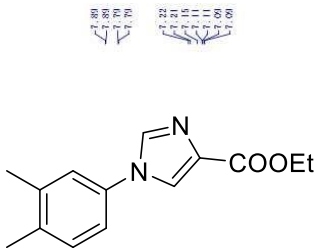
$CDCl_3$ (500 HMz)



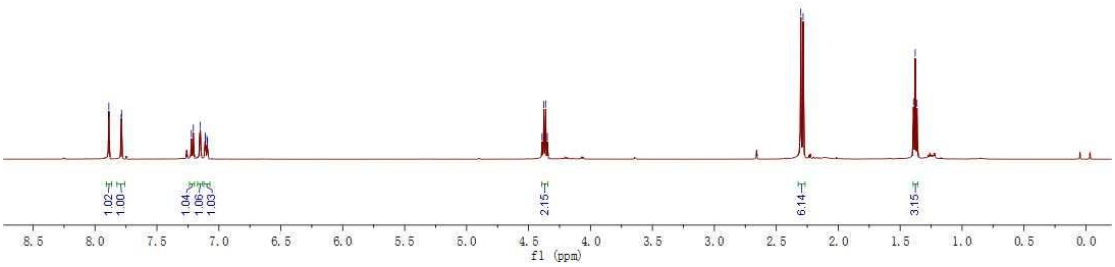


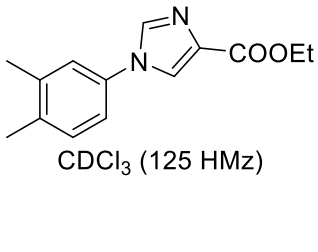
$CDCl_3$ (125 HMz)

ethyl 1-(3,4-dimethylphenyl)-1*H*-imidazole-4-carboxylate (4u)

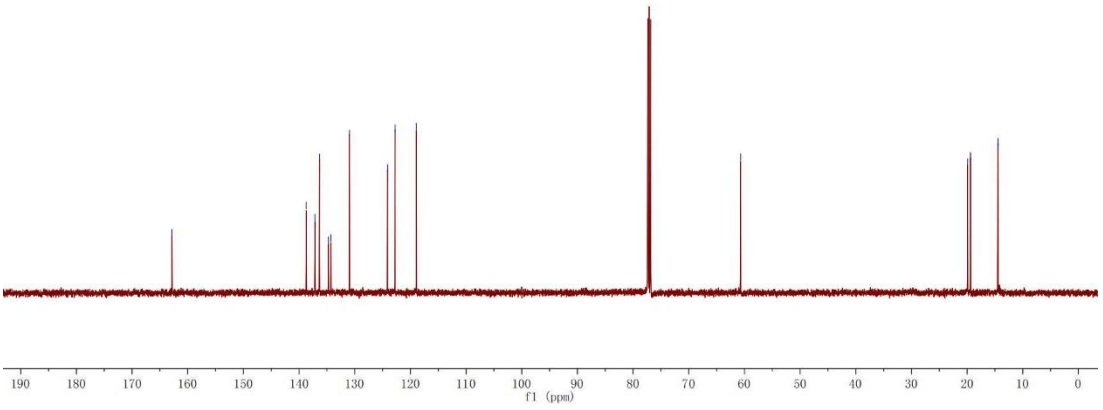


$CDCl_3$ (500 HMz)

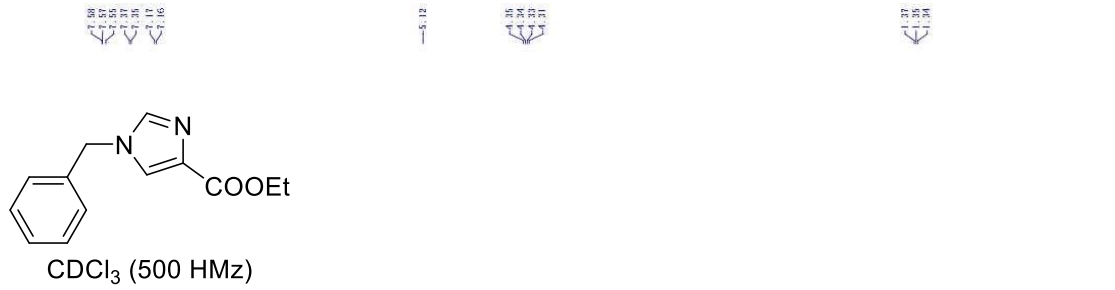




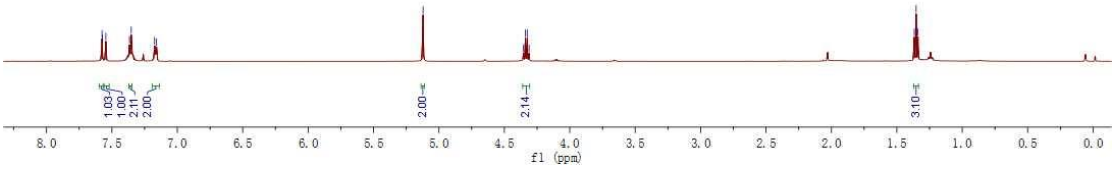
$CDCl_3$ (125 HMz)

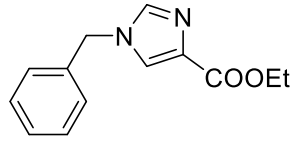


ethyl 1-benzyl-1*H*-imidazole-4-carboxylate (4v)

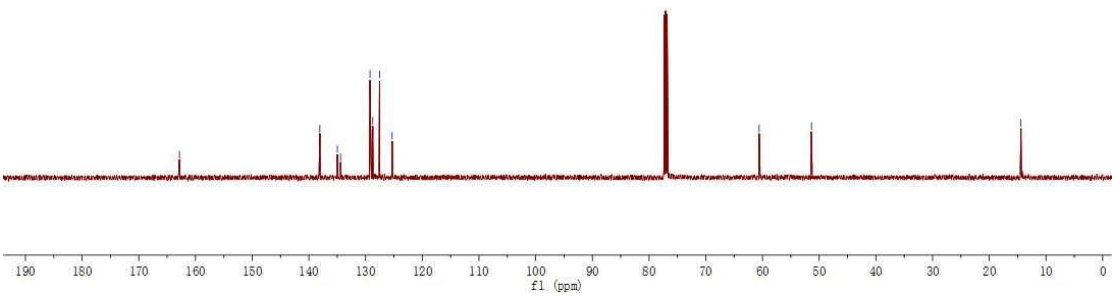


$CDCl_3$ (500 HMz)

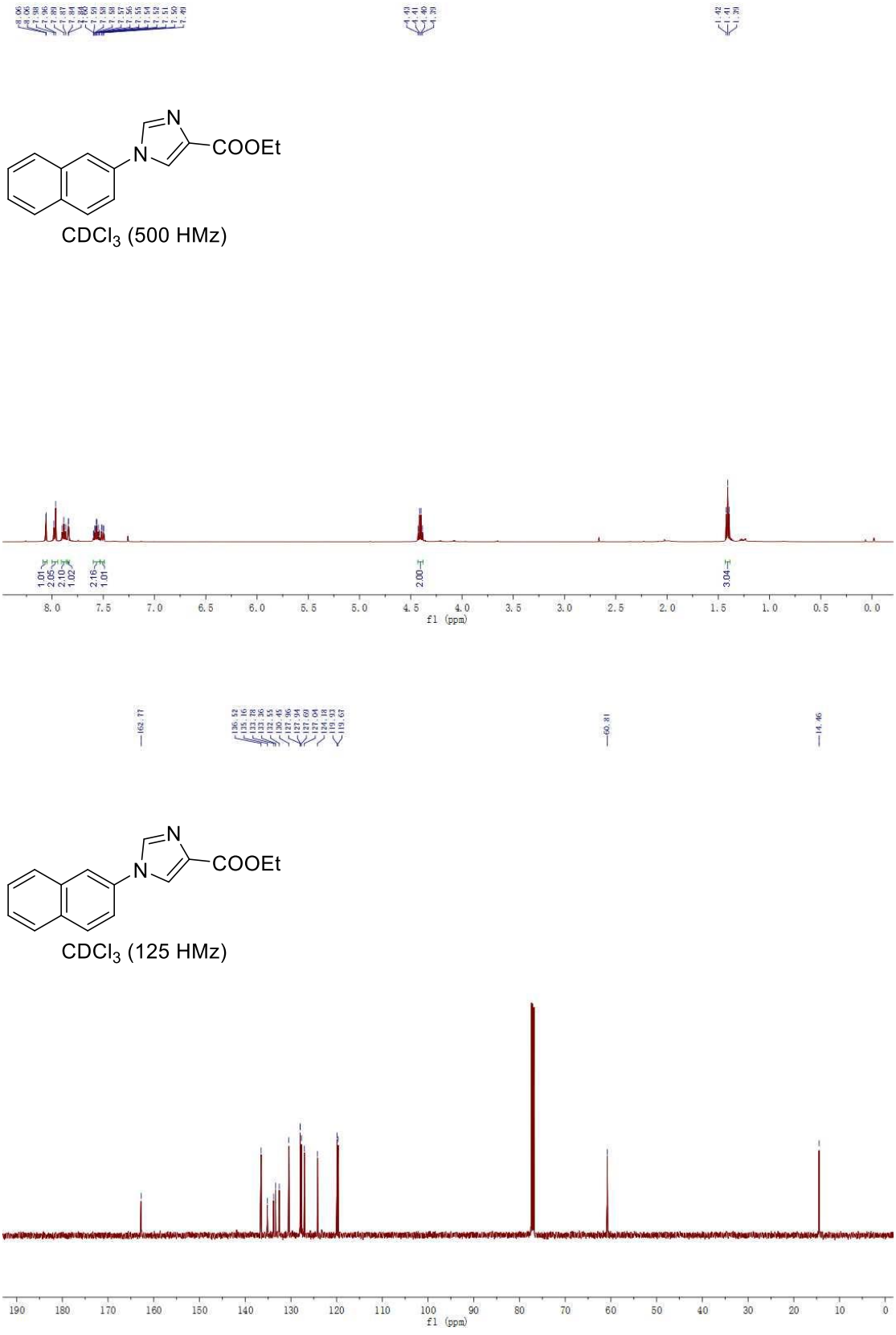




$CDCl_3$ (125 HMz)

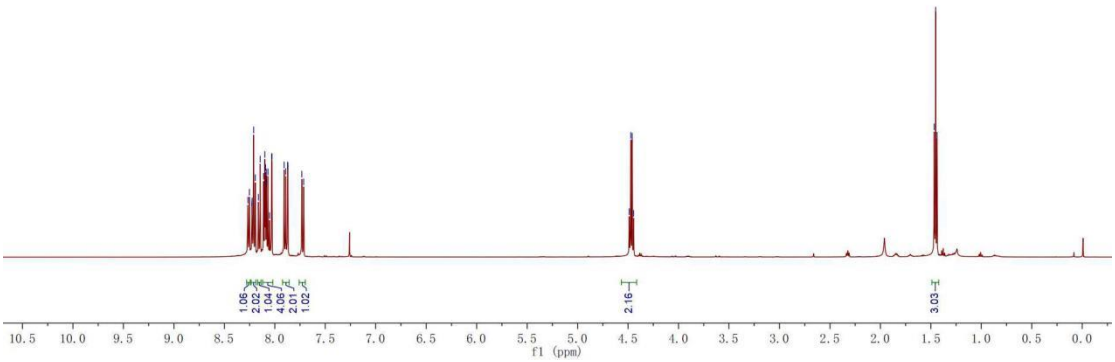


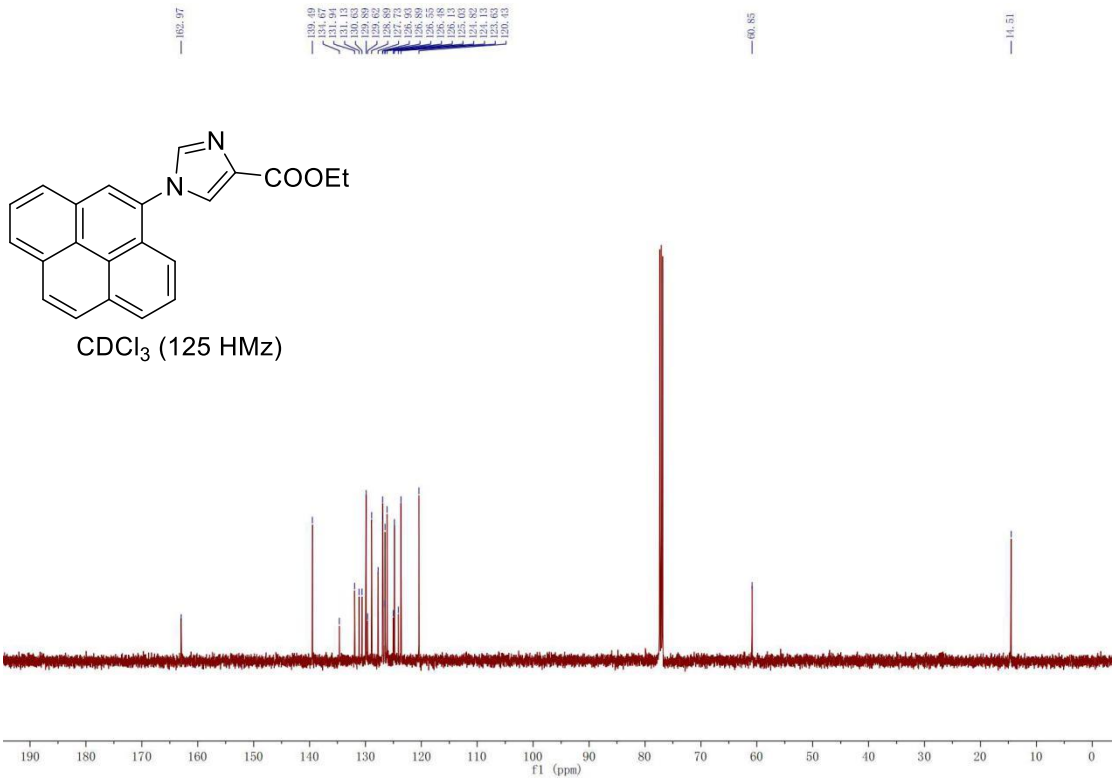
ethyl 1-(naphthalen-2-yl)-1*H*-imidazole-4-carboxylate (4w)



ethyl 1-(pyren-4-yl)-1*H*-imidazole-4-carboxylate (4x)

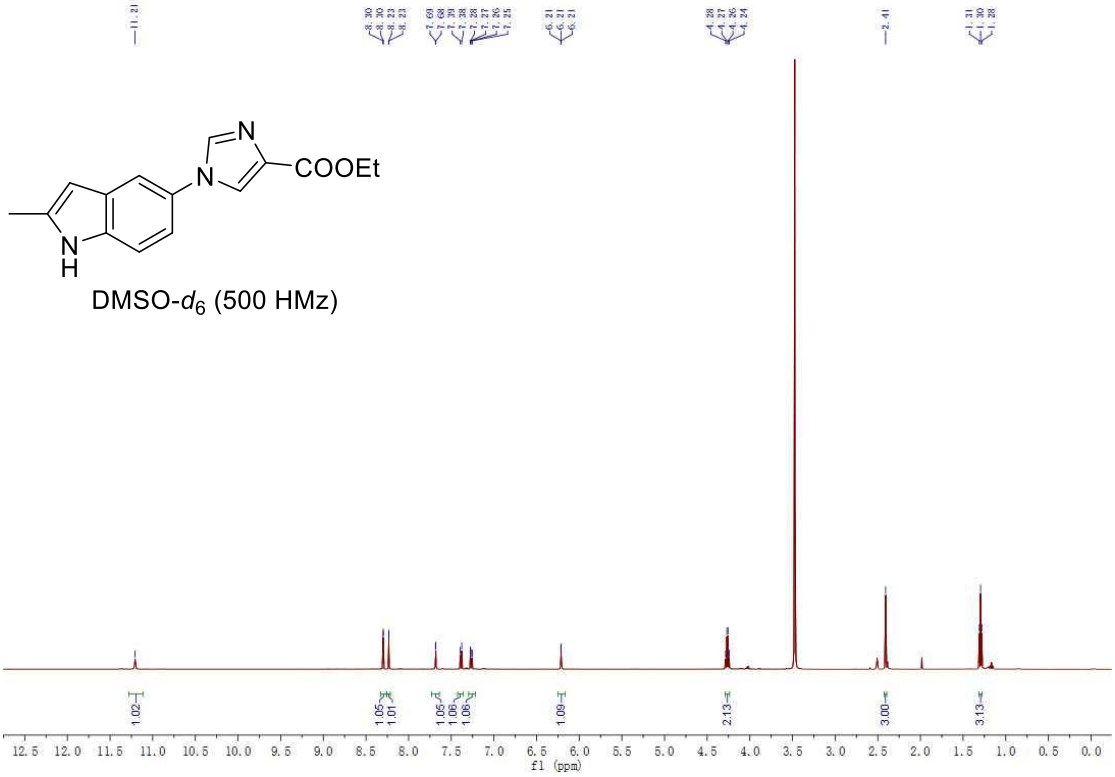
$CDCl_3$ (500 HMz)

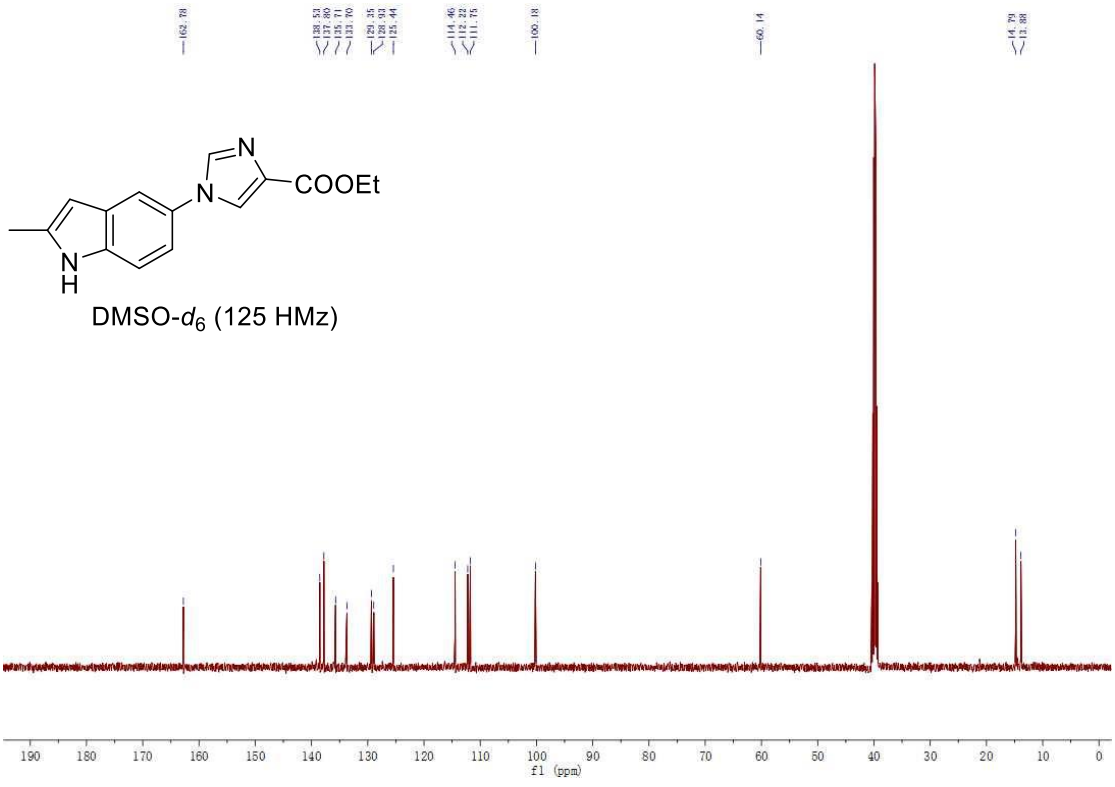




$CDCl_3$ (125 HMz)

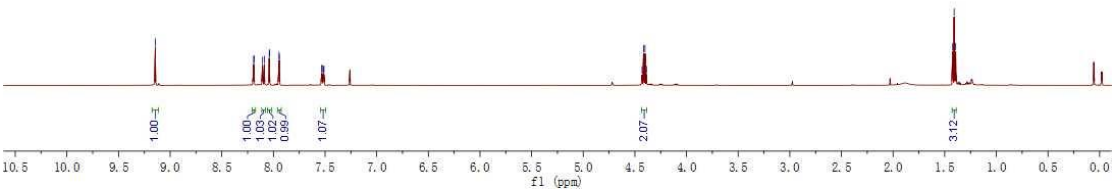
ethyl 1-(2-methyl-1*H*-indol-5-yl)-1*H*-imidazole-4-carboxylate (4y)

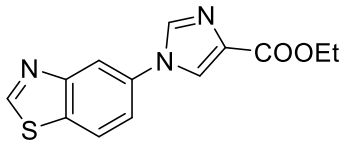




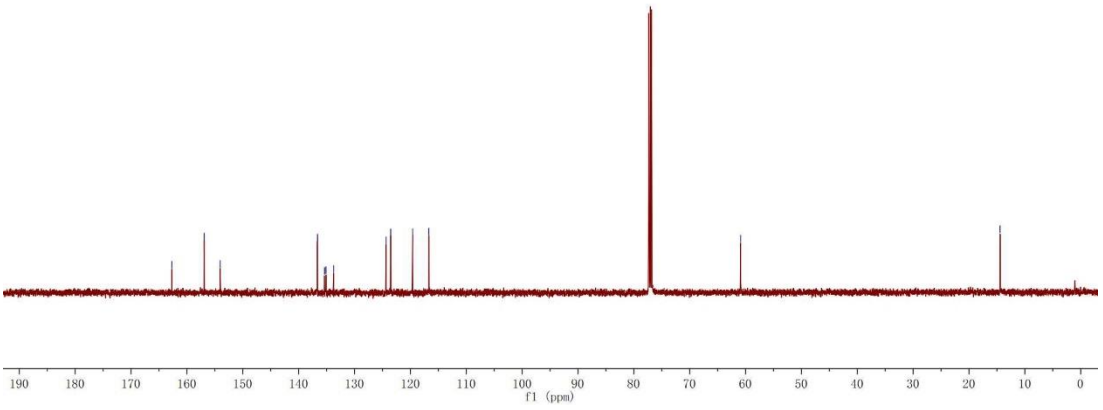
ethyl 1-(benzo[*d*]thiazol-5-yl)-1*H*-imidazole-4-carboxylate (4z)

$CDCl_3$ (500 HMz)

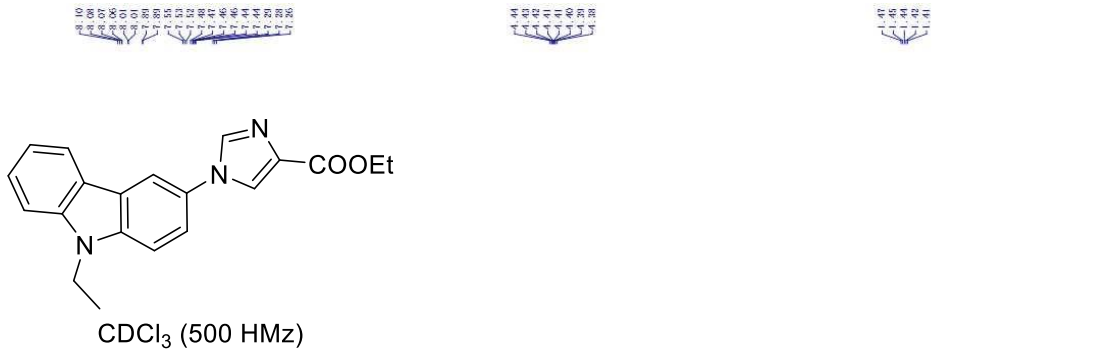




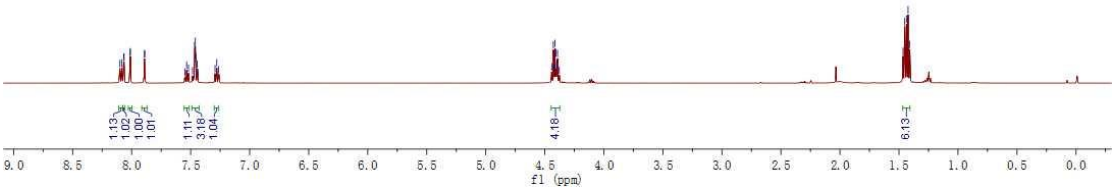
$CDCl_3$ (125 HMz)

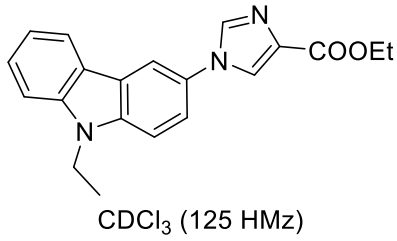


ethyl 1-(9-ethyl-9*H*-carbazol-3-yl)-1*H*-imidazole-4-carboxylate (4aa)

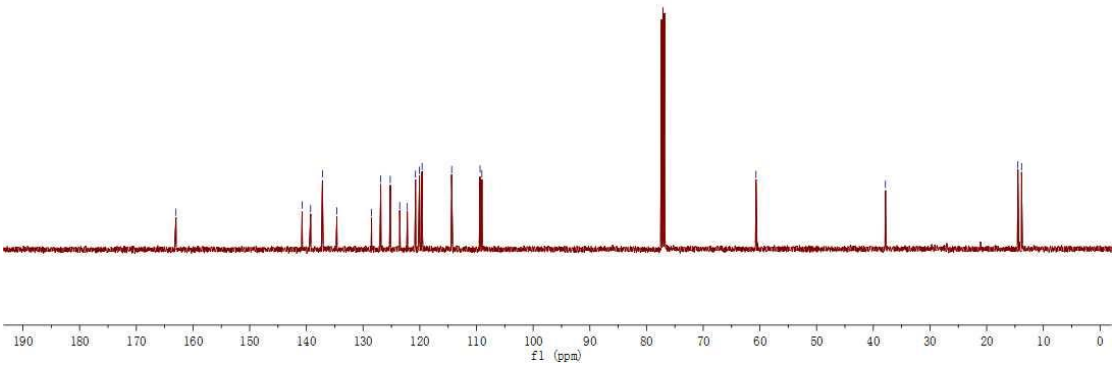


$CDCl_3$ (500 HMz)

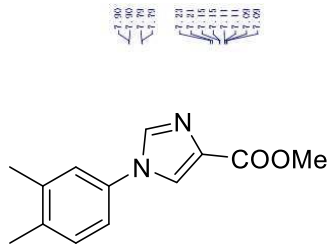




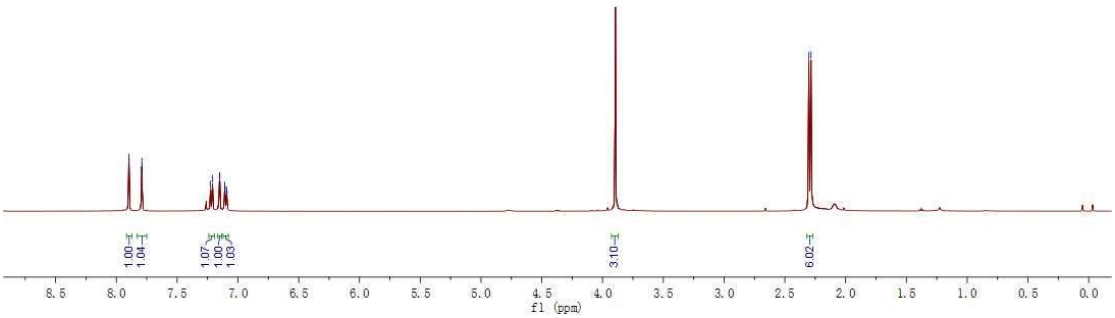
$CDCl_3$ (125 HMz)

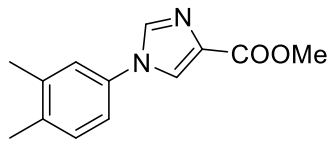


methyl 1-(3,4-dimethylphenyl)-1*H*-imidazole-4-carboxylate (4ab)

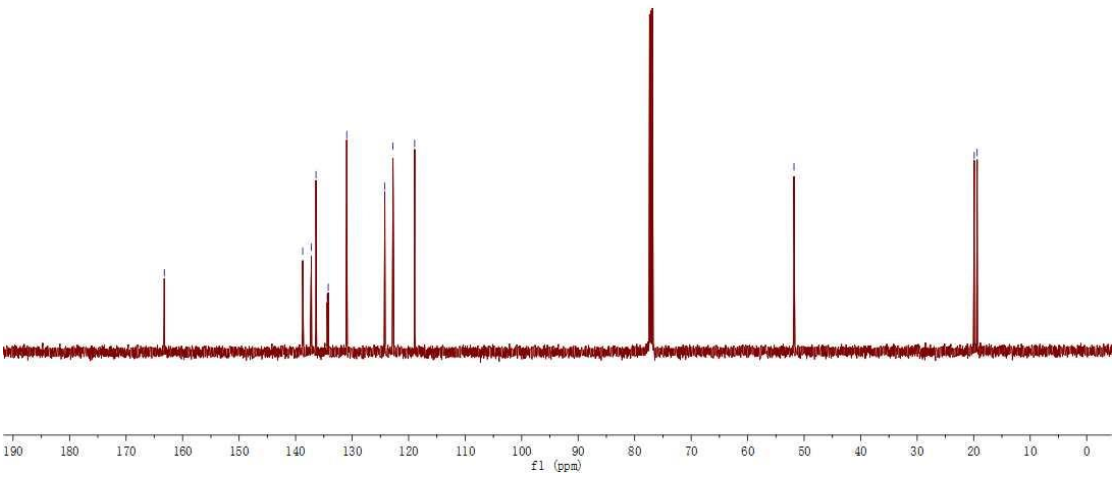


$CDCl_3$ (500 HMz)

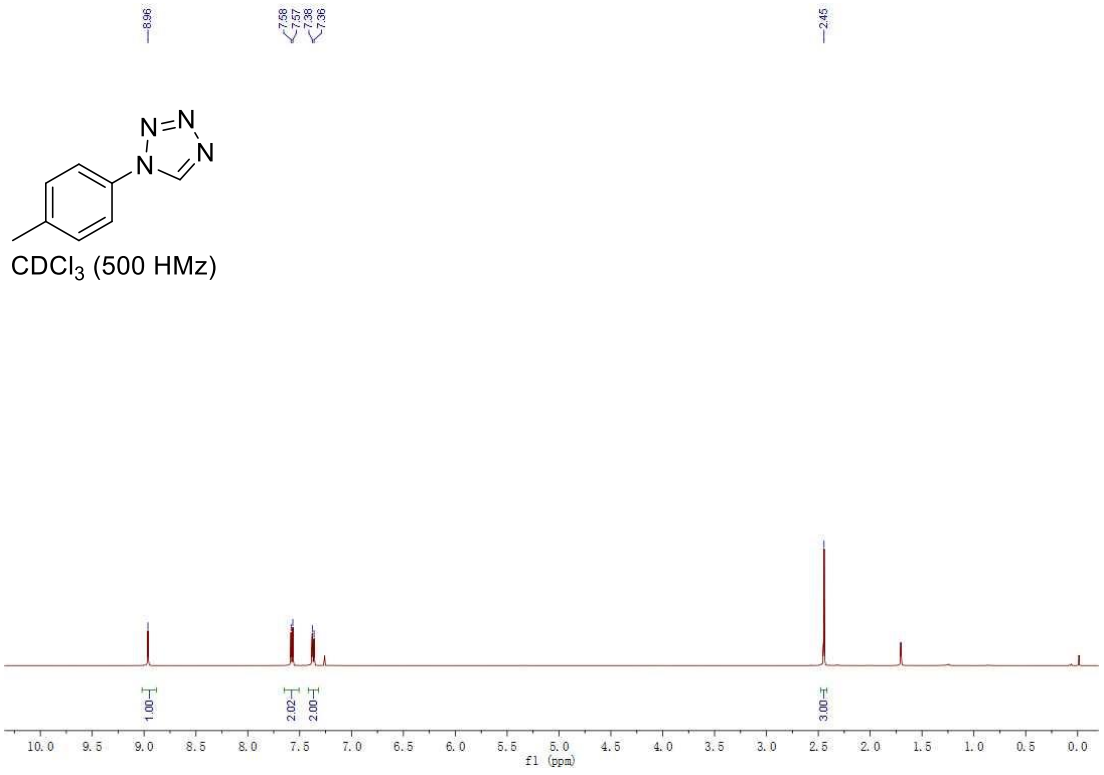




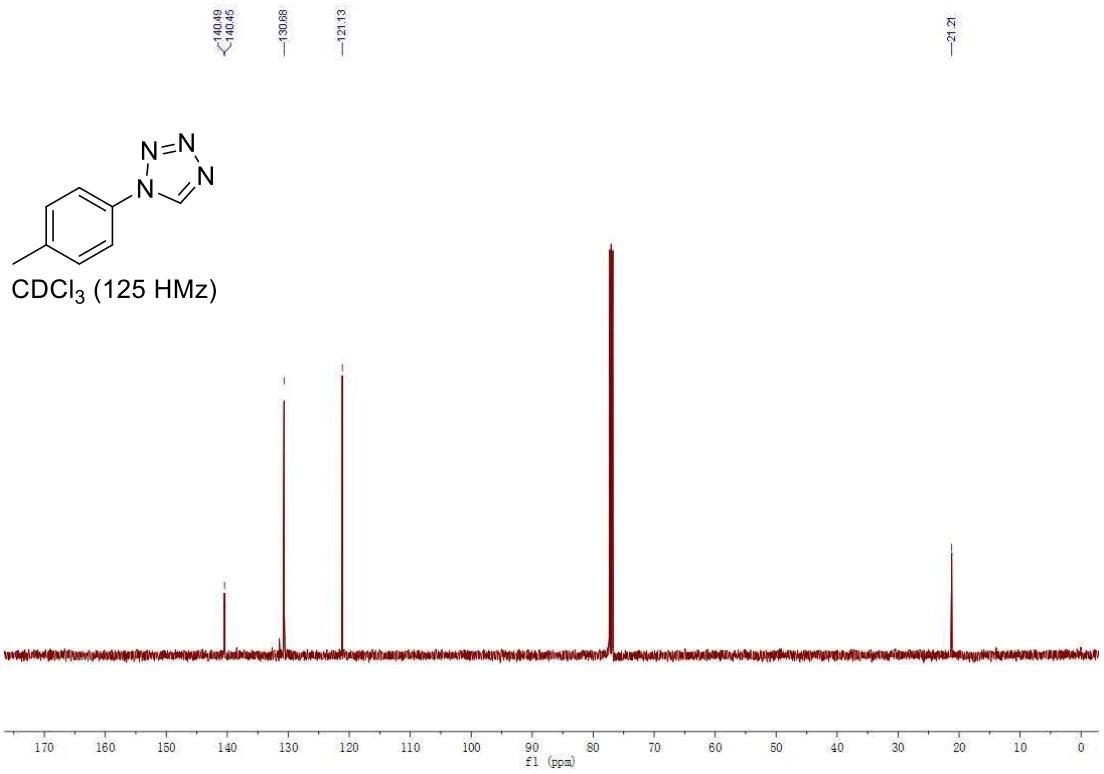
$CDCl_3$ (125 HMz)



1-(*p*-tolyl)-1*H*-tetrazole (6a)

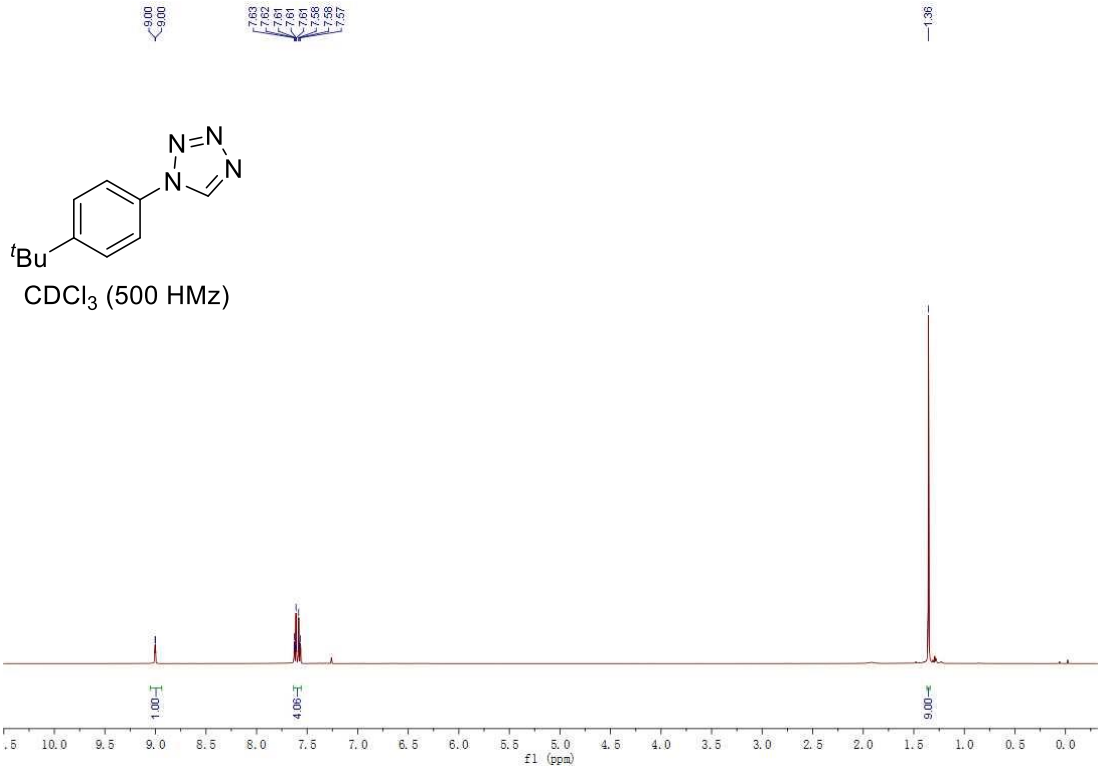


$CDCl_3$ (500 HMz)

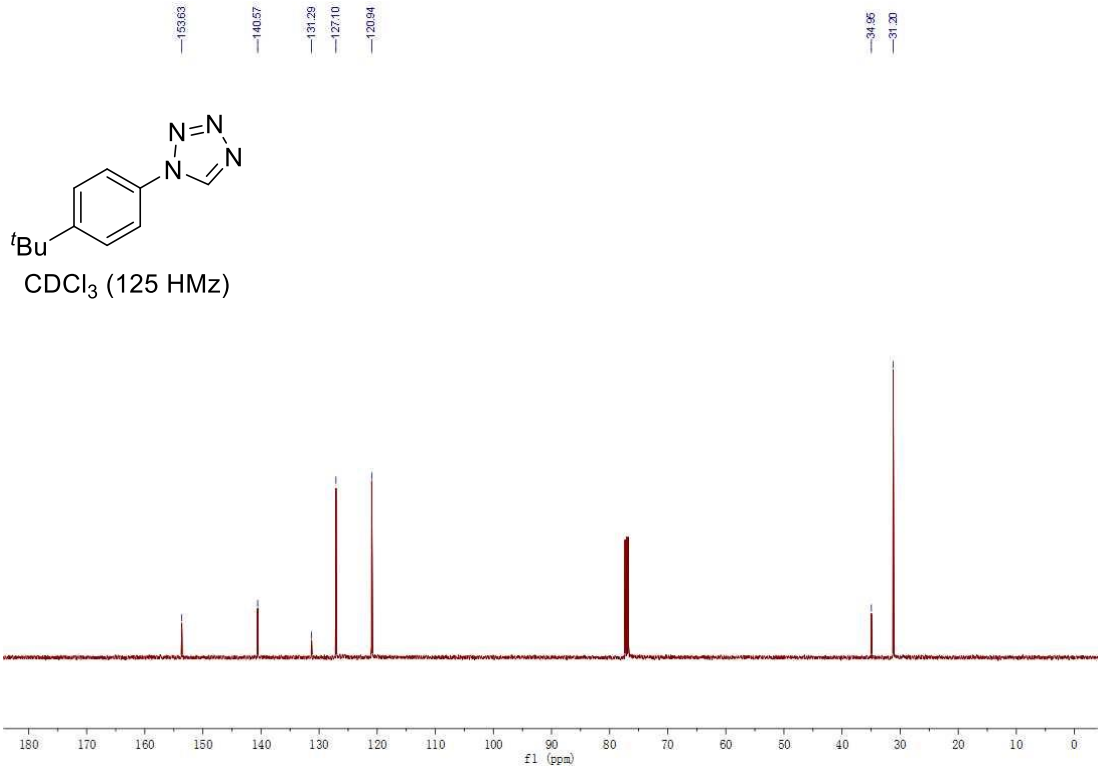


$CDCl_3$ (125 HMz)

1-(4-(*tert*-butyl)phenyl)-1*H*-tetrazole (6b)



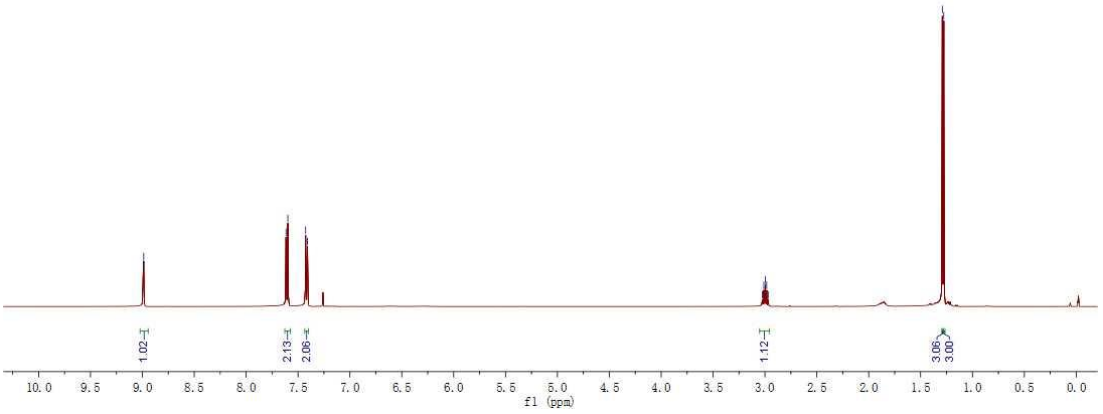
$CDCl_3$ (500 HMz)



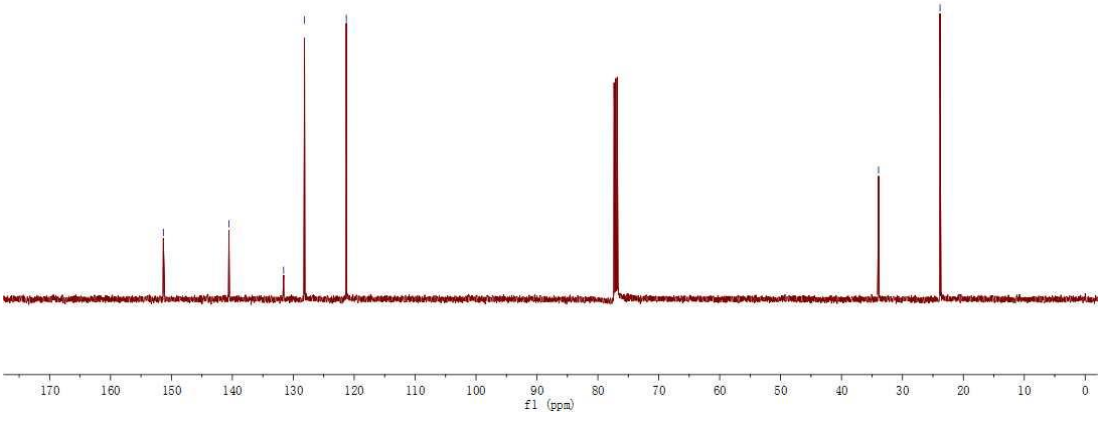
$CDCl_3$ (125 HMz)

1-(4-isopropylphenyl)-1*H*-tetrazole (6c)

$CDCl_3$ (500 HMz)

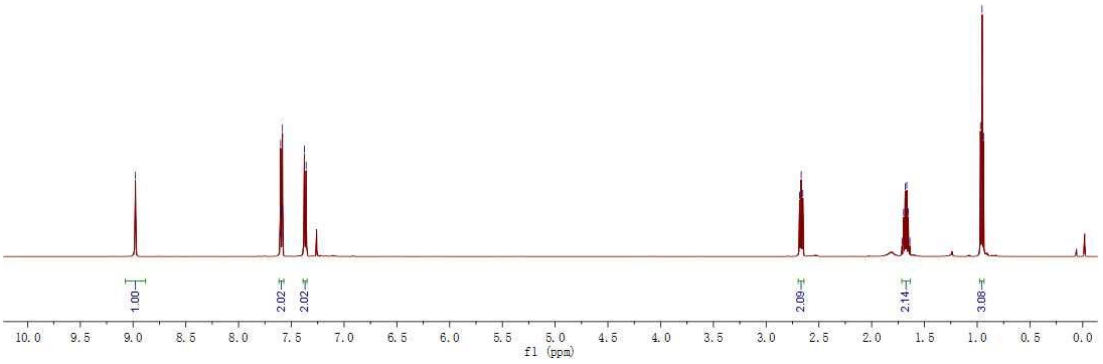


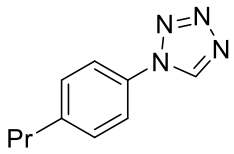
$CDCl_3$ (125 HMz)



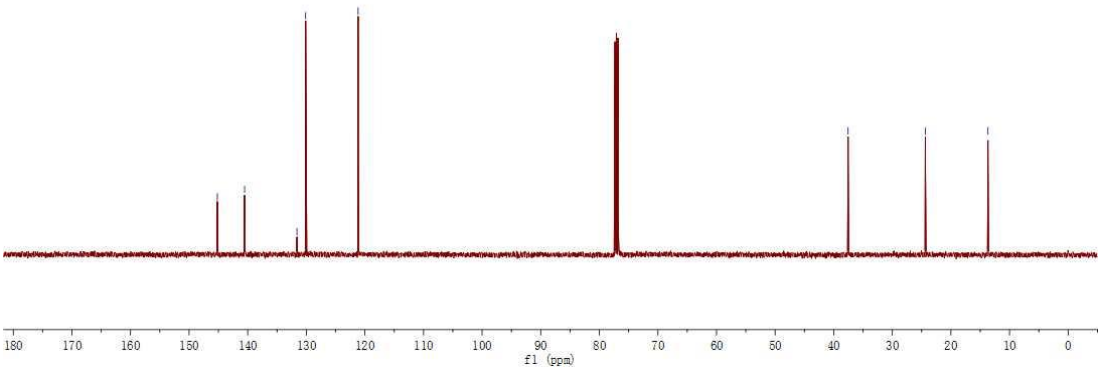
1-(4-propylphenyl)-1*H*-tetrazole (6d)

$CDCl_3$ (500 HMz)

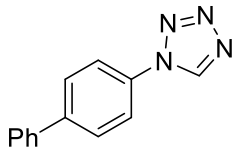




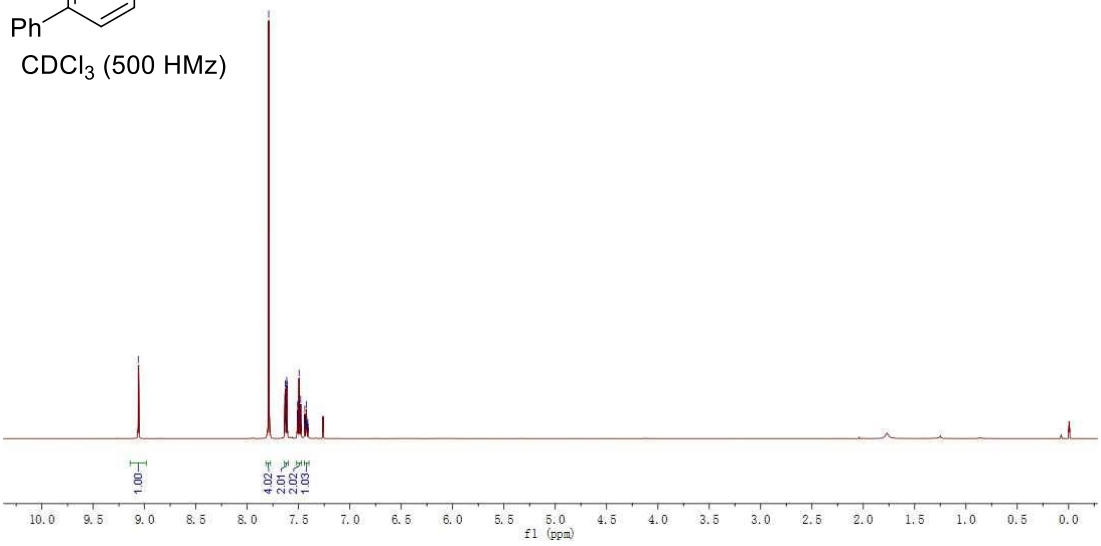
$CDCl_3$ (125 HMz)

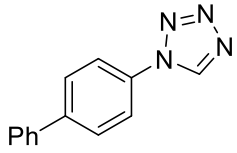


1-([1,1'-biphenyl]-4-yl)-1*H*-tetrazole (6e)

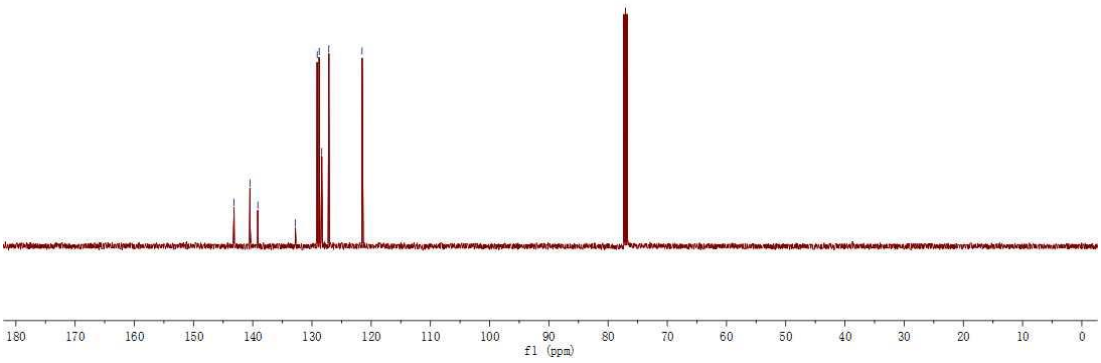


$CDCl_3$ (500 HMz)

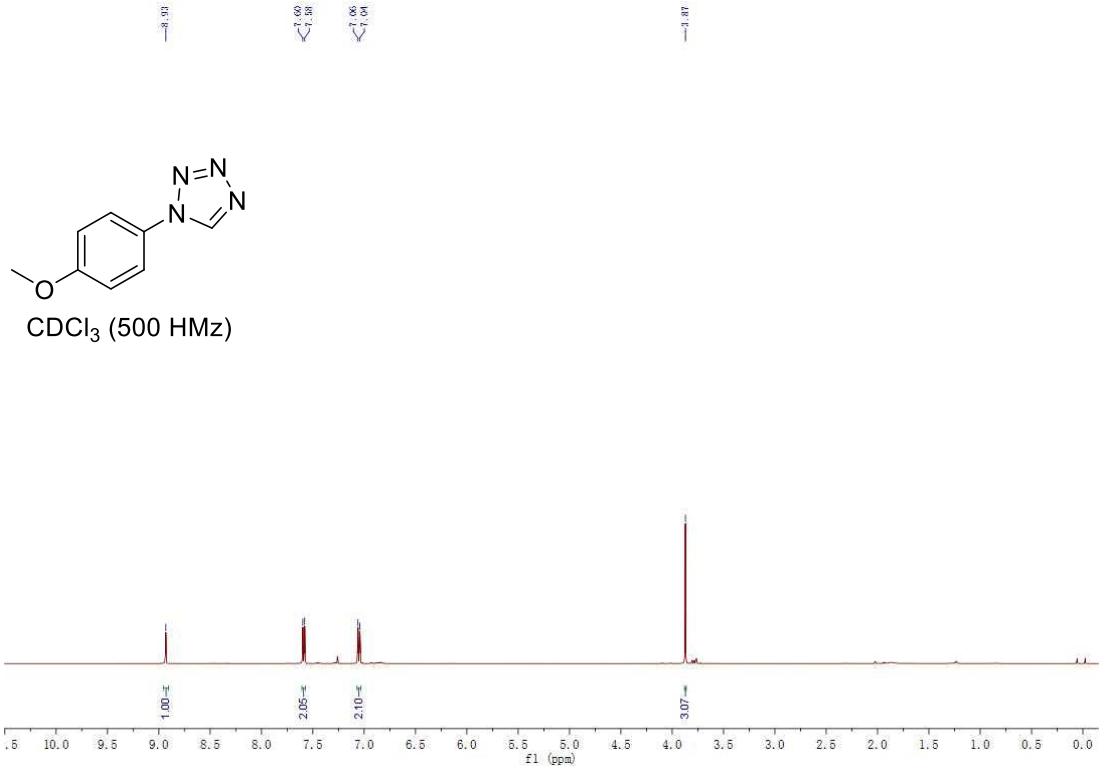




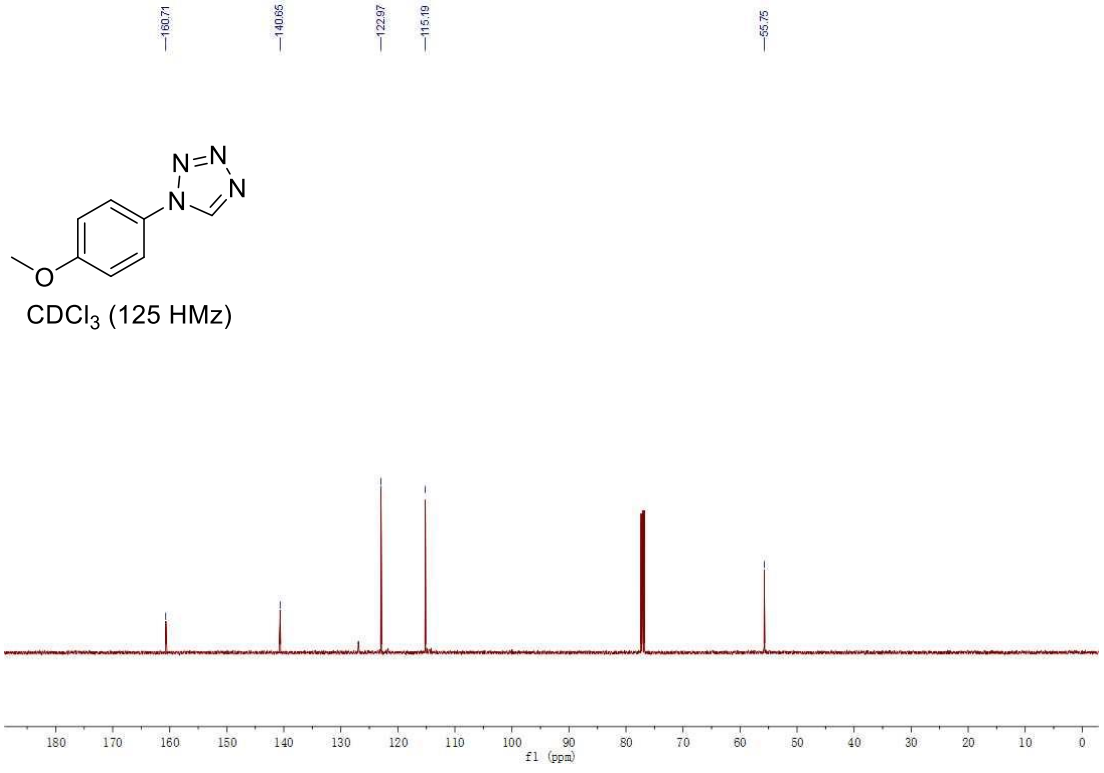
$CDCl_3$ (125 HMz)



1-(4-methoxyphenyl)-1*H*-tetrazole (6f)

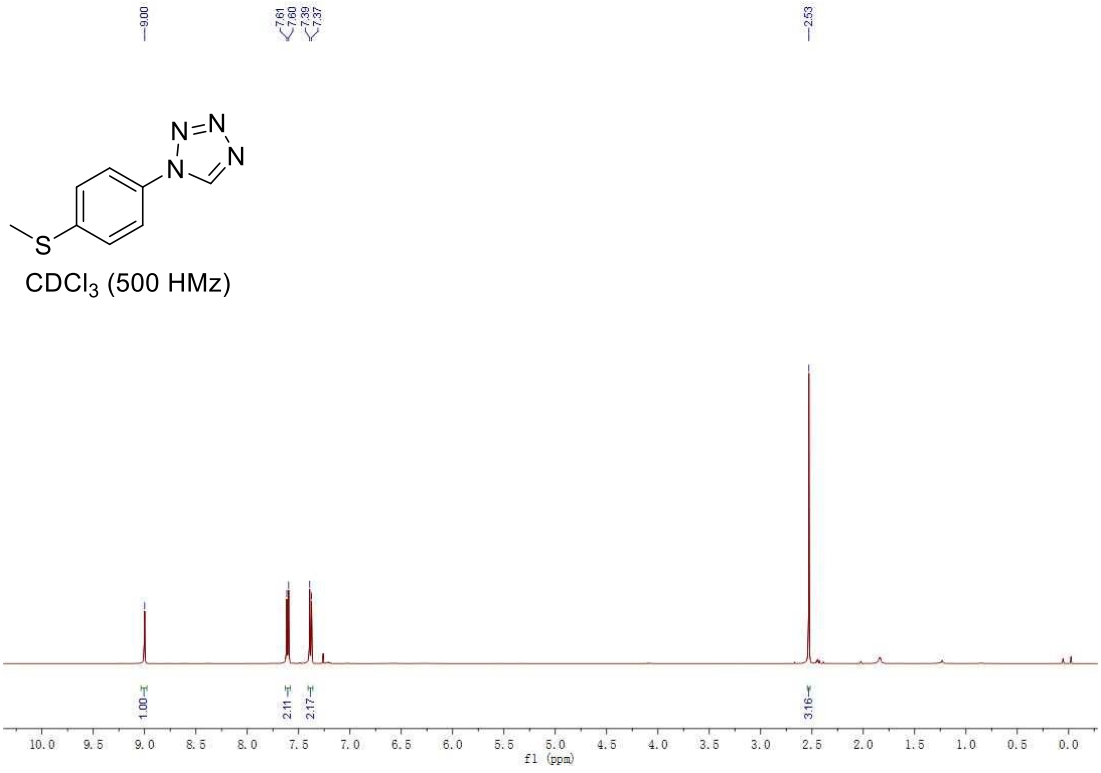


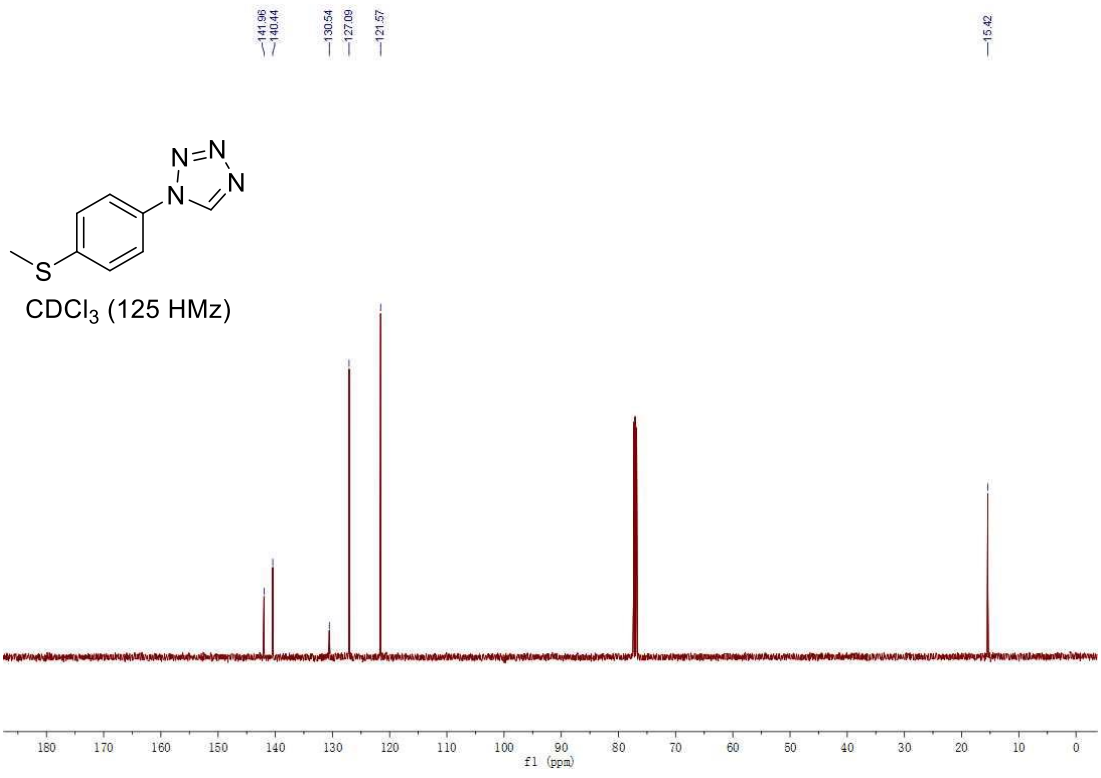
$CDCl_3$ (500 HMz)



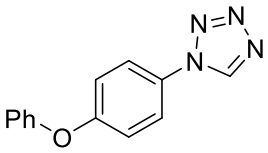
$CDCl_3$ (125 HMz)

1-(4-(methylthio)phenyl)-1*H*-tetrazole (6g)

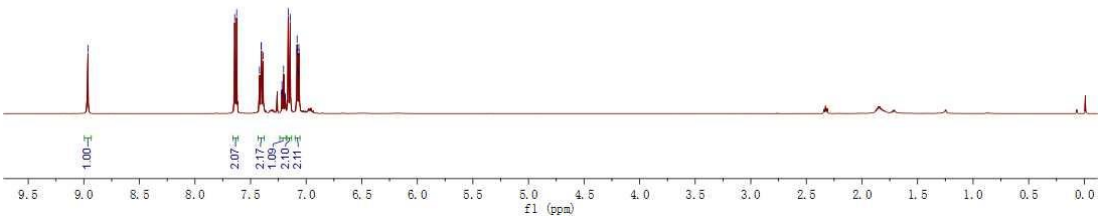


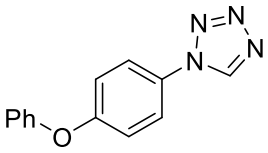


1-(4-phenoxyphenyl)-1*H*-tetrazole (6h)

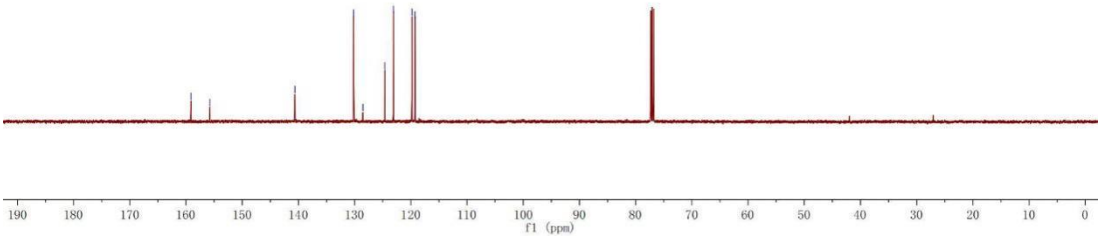


$CDCl_3$ (500 HMz)

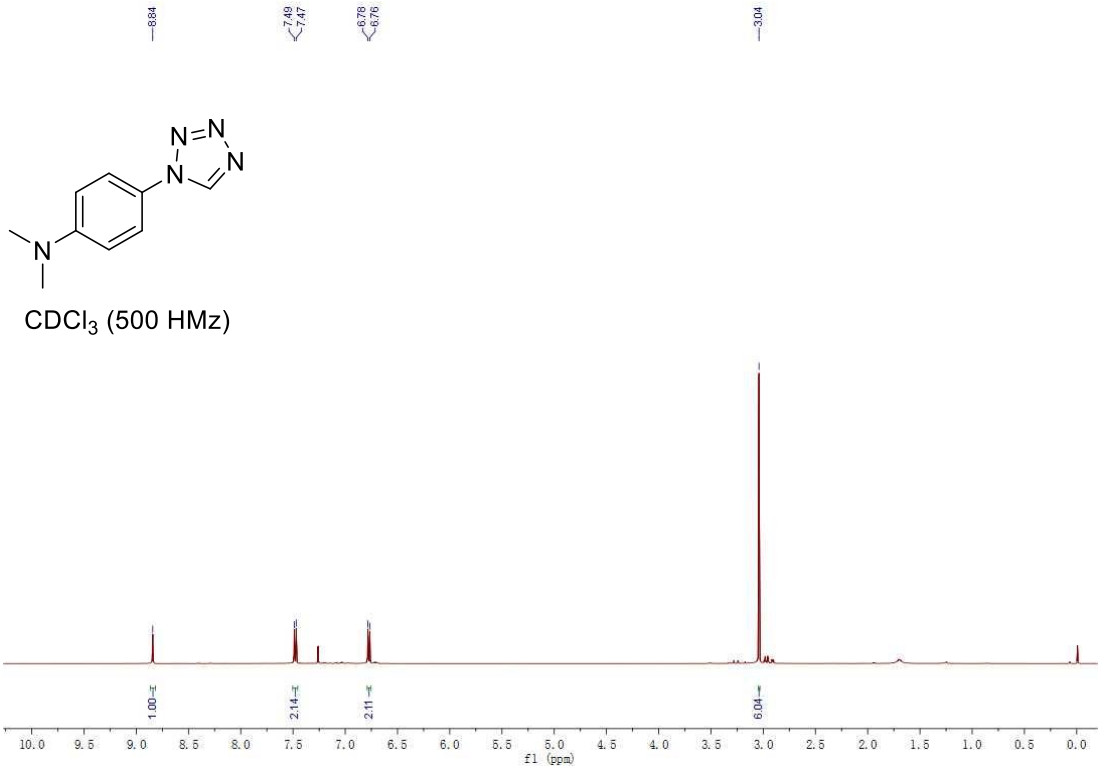


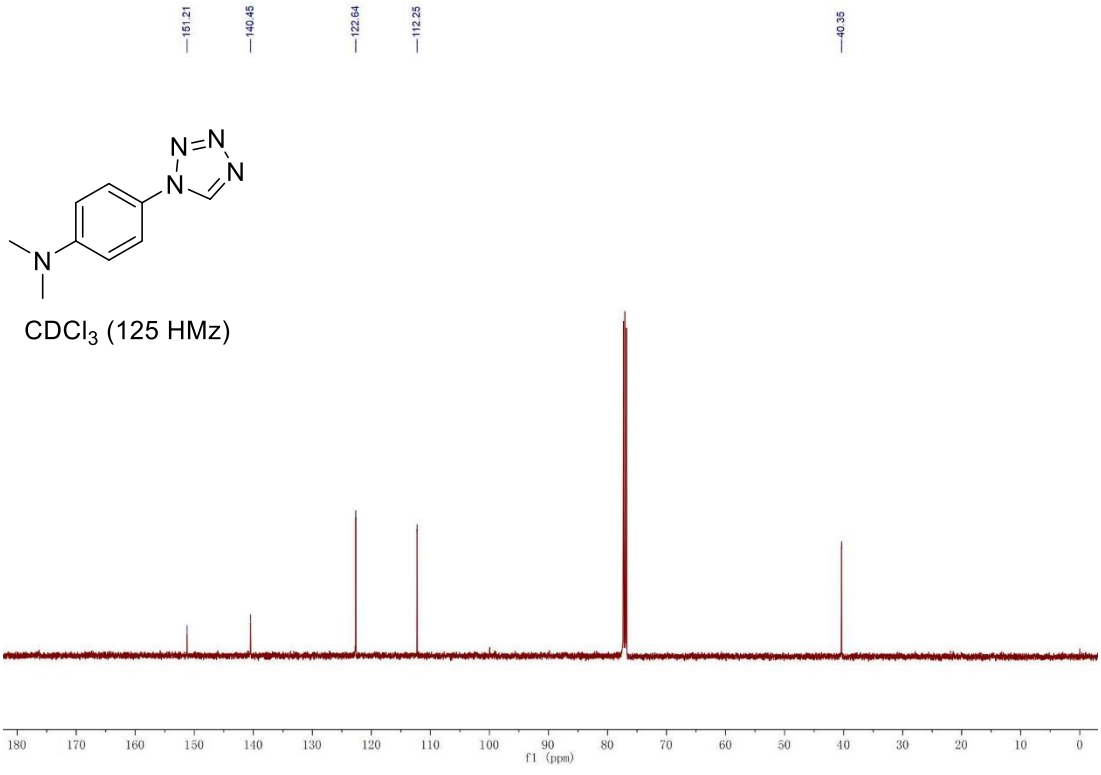


$CDCl_3$ (125 HMz)

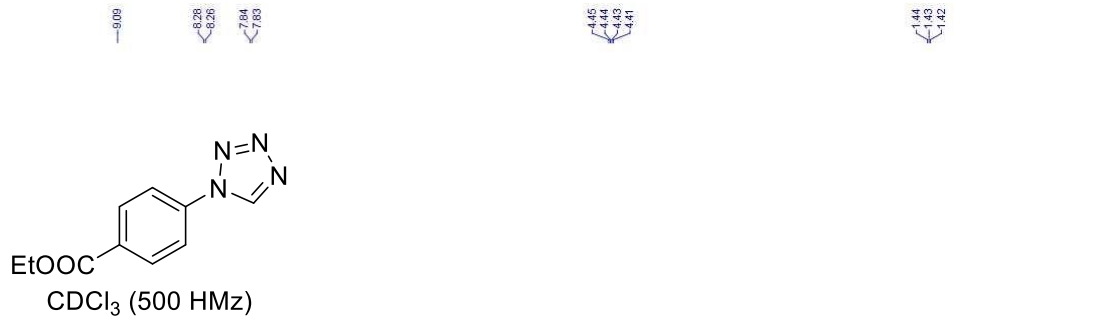


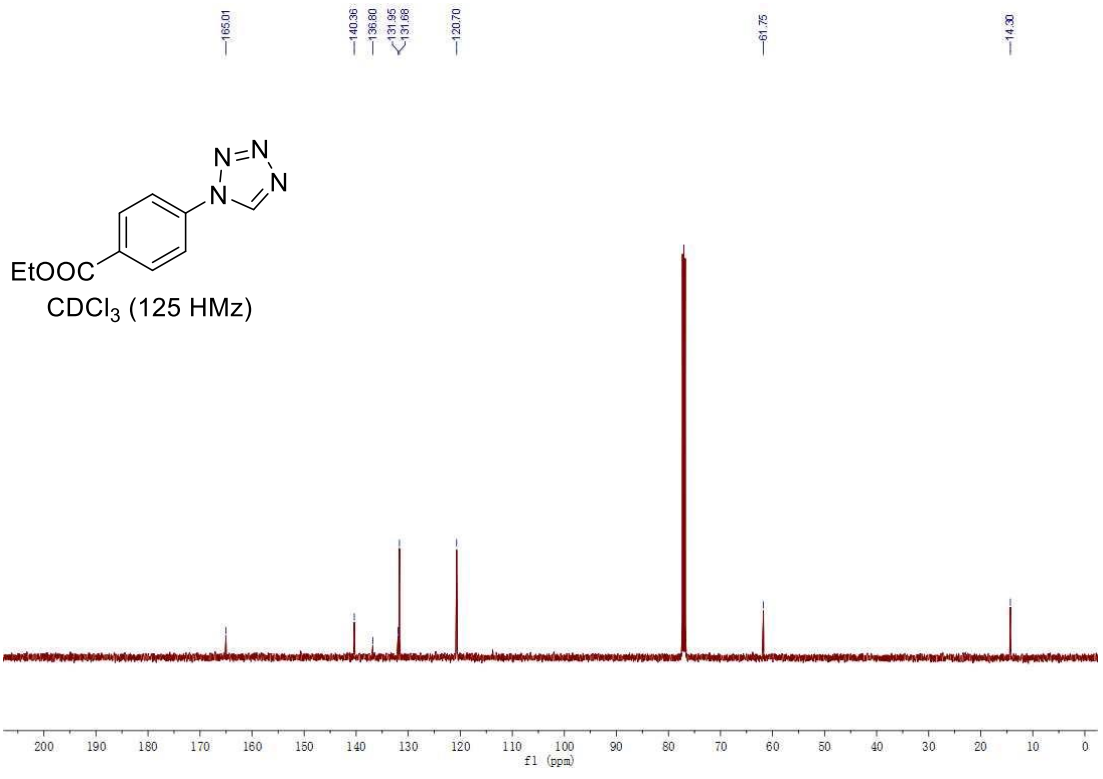
N,*N*-dimethyl-4-(1*H*-tetrazol-1-yl)aniline (6i)



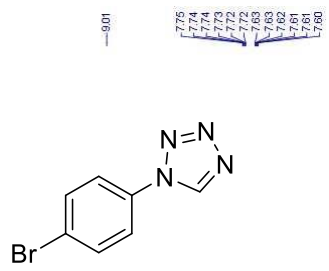


ethyl 4-(1*H*-tetrazol-1-yl)benzoate (6j)

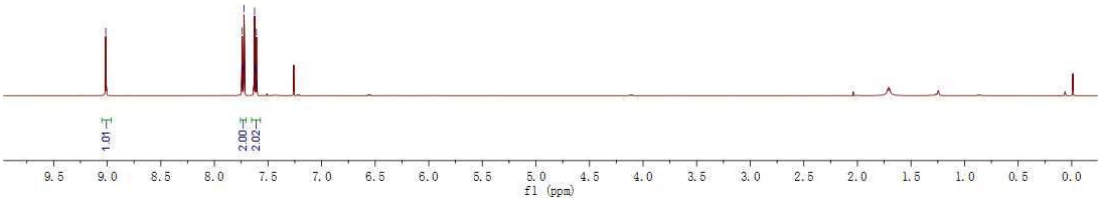


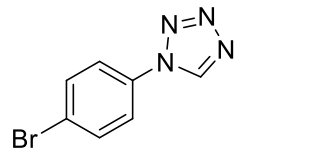


1-(4-bromophenyl)-1*H*-tetrazole (6k)

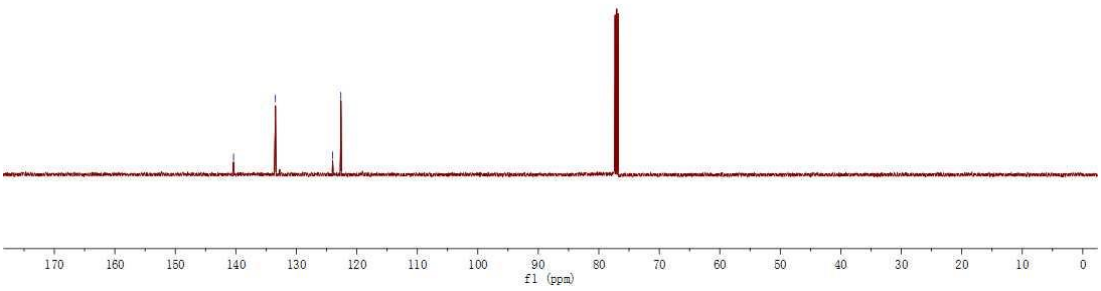


$CDCl_3$ (500 HMz)

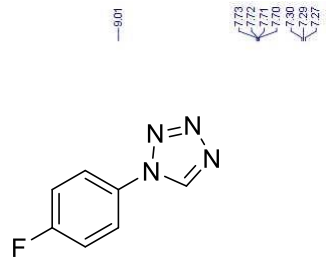




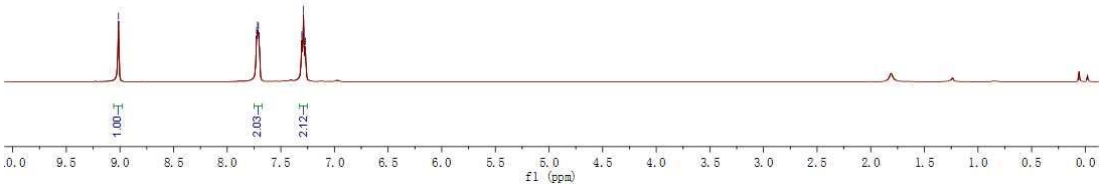
$CDCl_3$ (125 HMz)

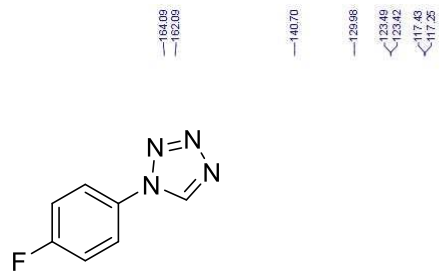


1-(4-fluorophenyl)-1*H*-tetrazole (6l)

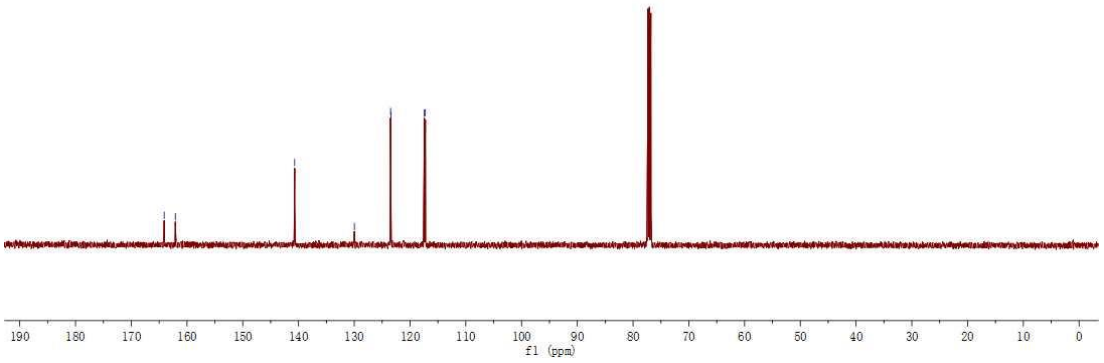


$CDCl_3$ (500 HMz)



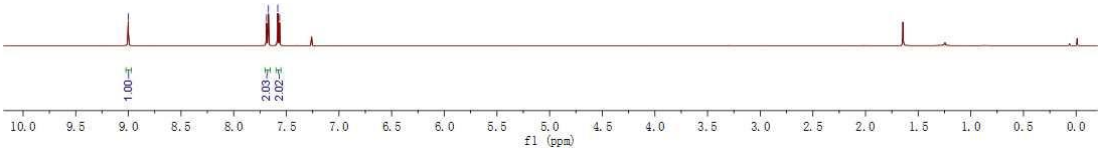


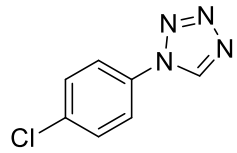
$CDCl_3$ (125 HMz)



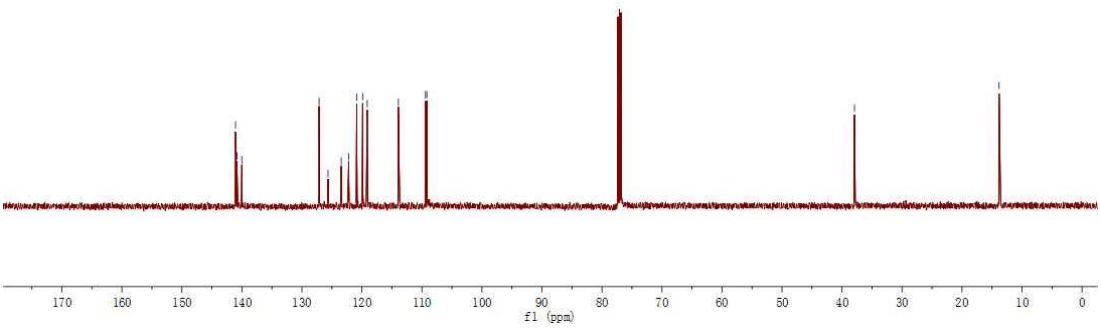
1-(4-chlorophenyl)-1*H*-tetrazole (6m)

$CDCl_3$ (500 HMz)

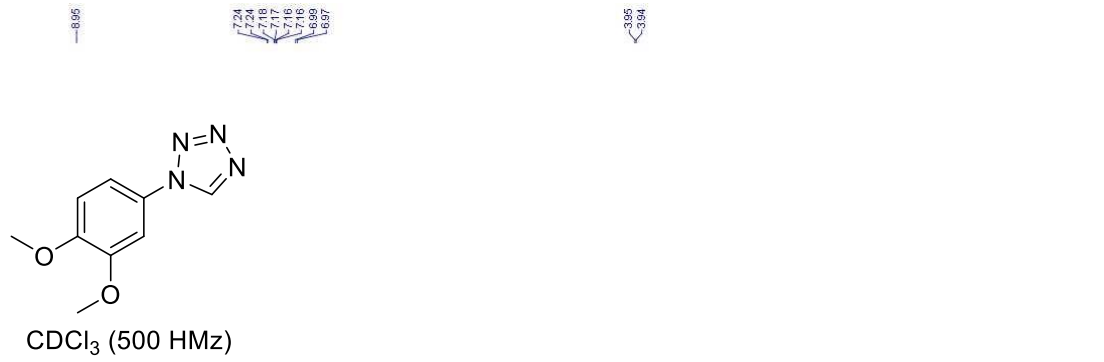




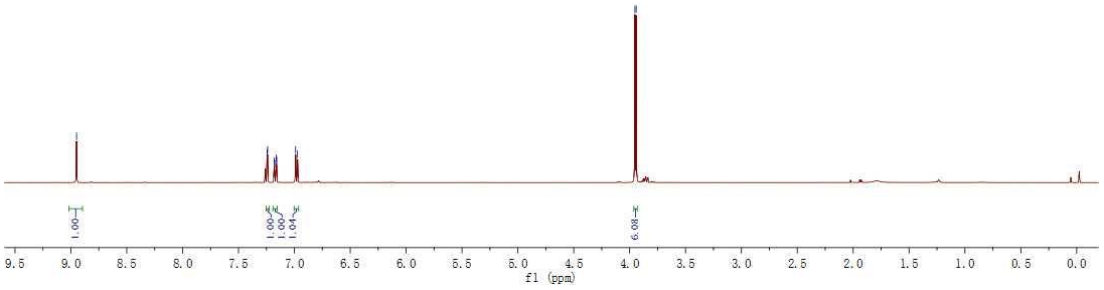
$CDCl_3$ (125 HMz)



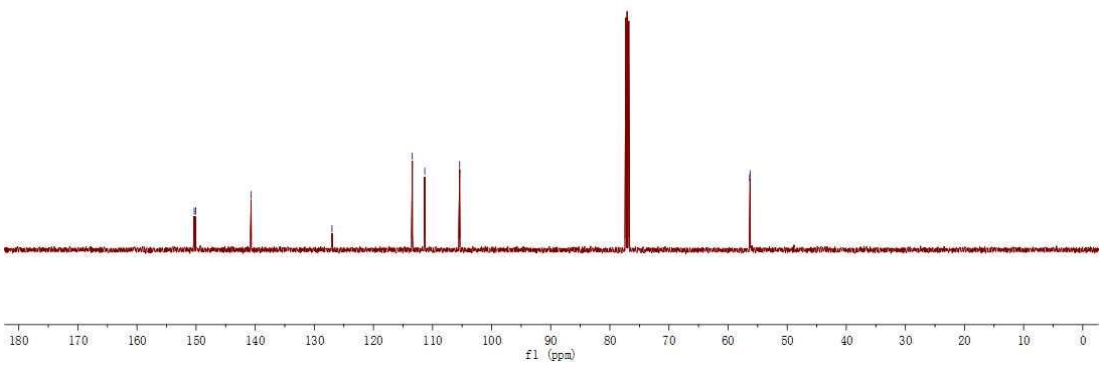
1-(3,4-dimethoxyphenyl)-1*H*-tetrazole (6n)



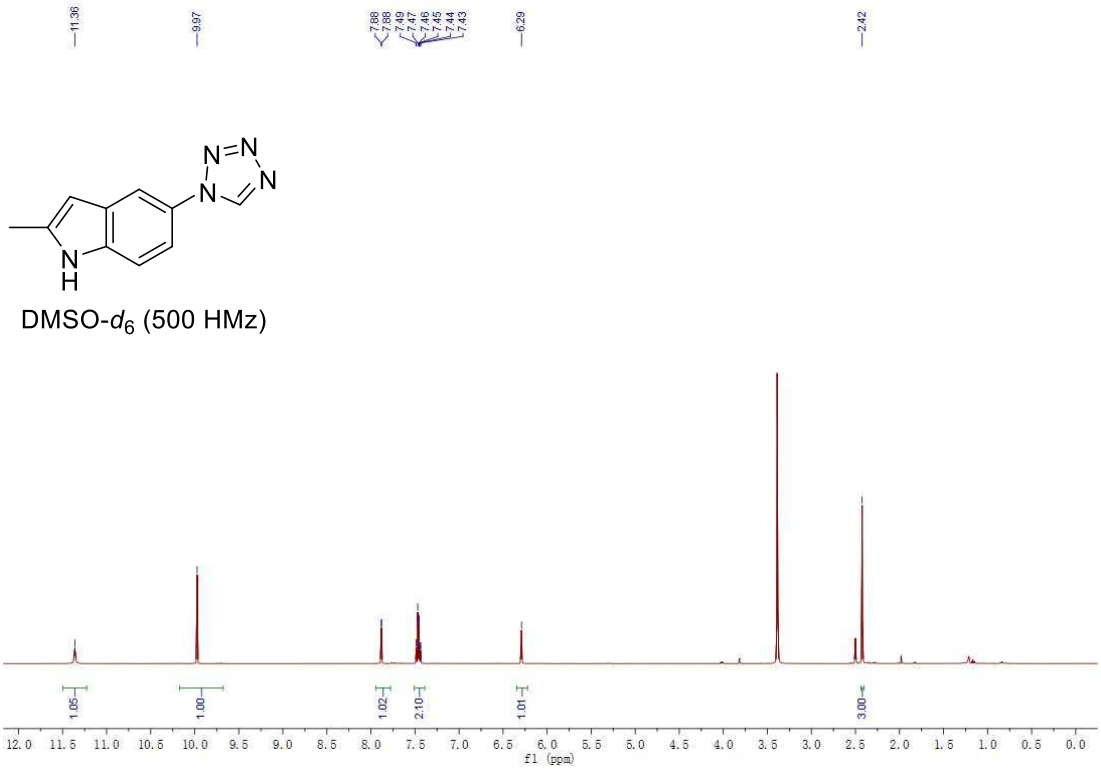
$CDCl_3$ (500 HMz)



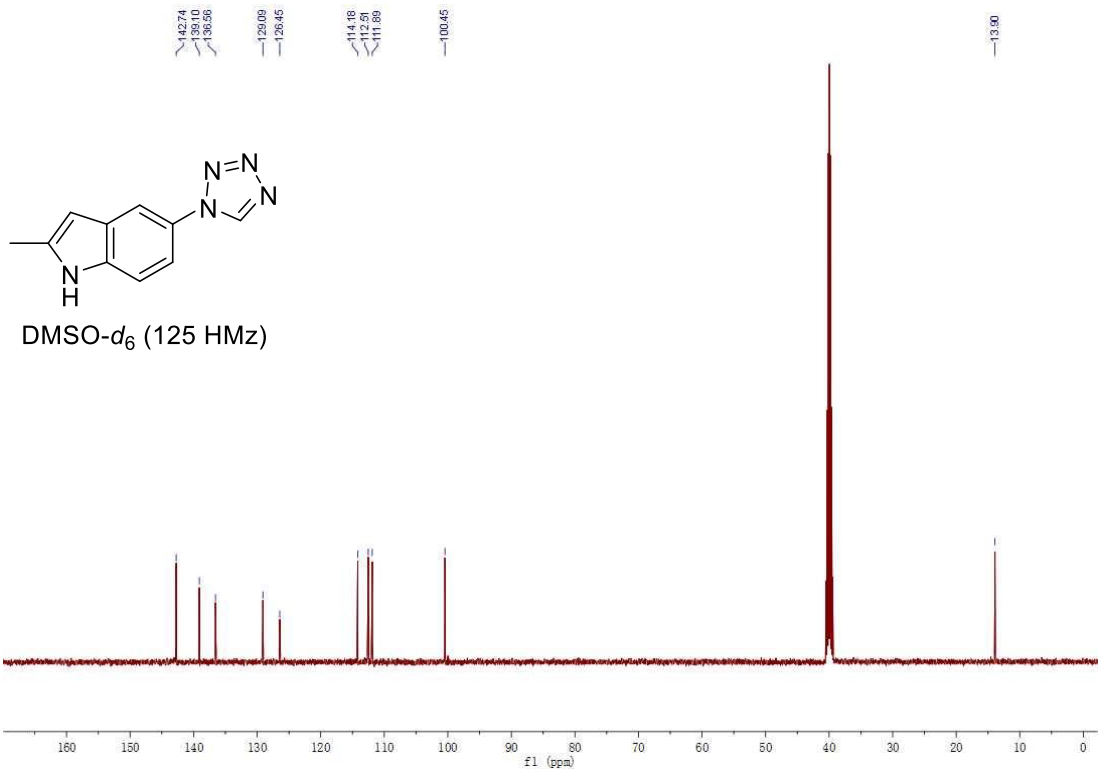
$CDCl_3$ (125 HMz)



2-methyl-5-(1*H*-tetrazol-1-yl)-1*H*-indole (6o)

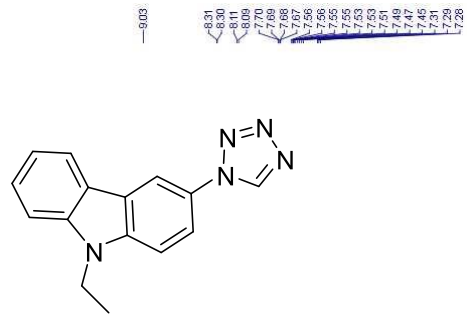


DMSO-d_6 (500 HMz)

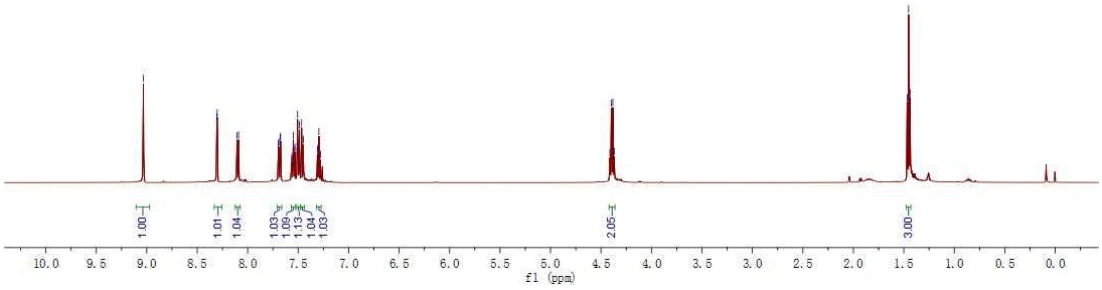


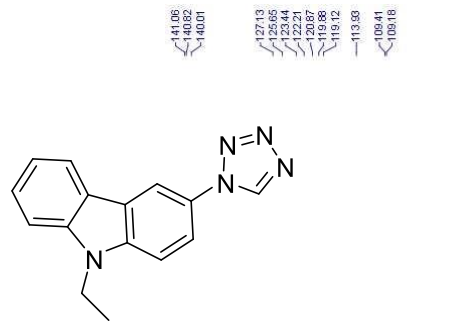
DMSO-d_6 (125 HMz)

9-ethyl-3-(1*H*-tetrazol-1-yl)-9*H*-carbazole (6p)

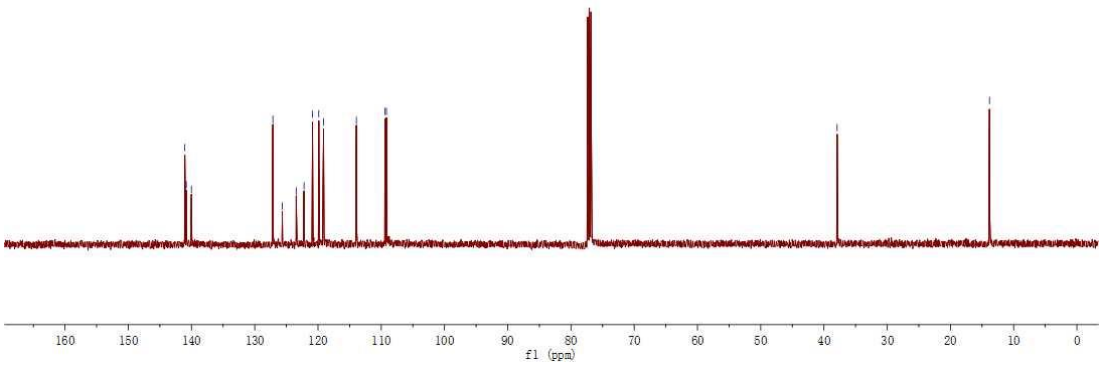


$CDCl_3$ (500 HMz)

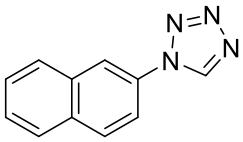




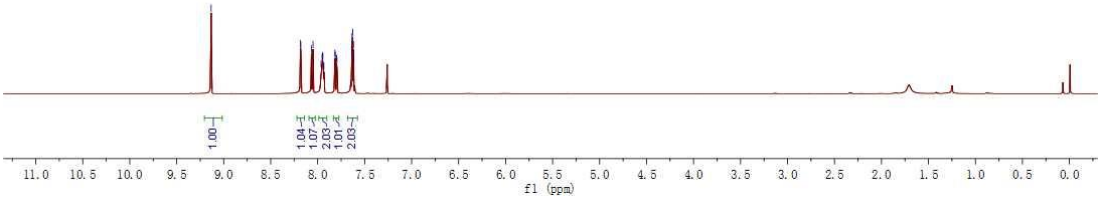
$CDCl_3$ (125 HMz)

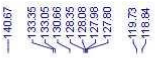


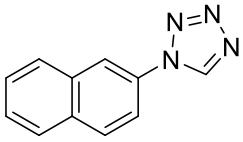
1-(naphthalen-2-yl)-1*H*-tetrazole (6q)



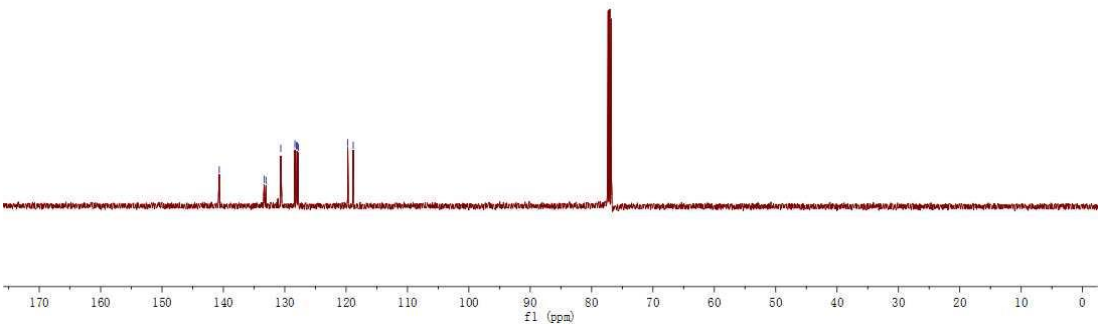
$CDCl_3$ (500 HMz)



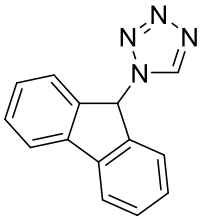




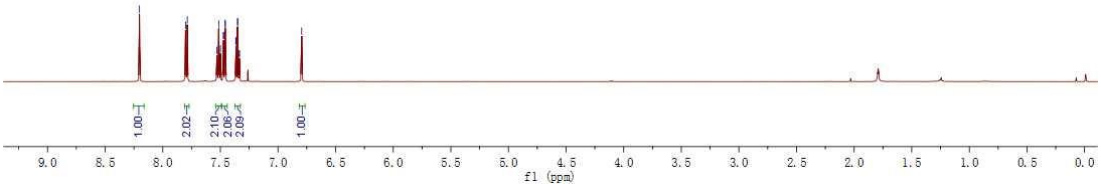
$CDCl_3$ (125 HMz)

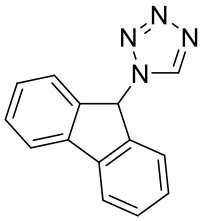


1-(9*H*-fluoren-9-yl)-1*H*-tetrazole (6r)

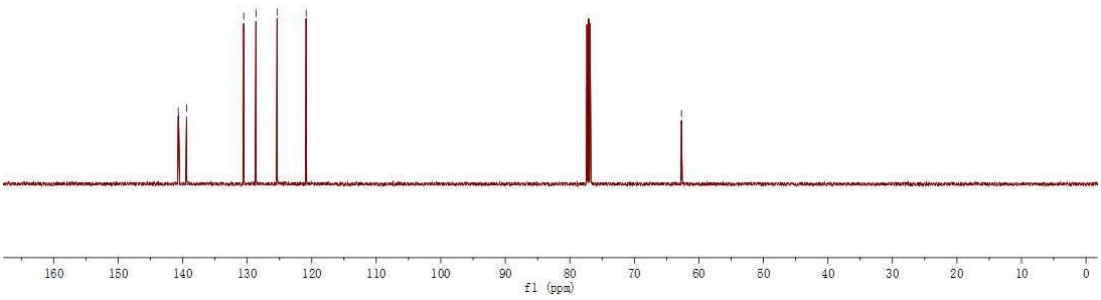


$CDCl_3$ (500 HMz)

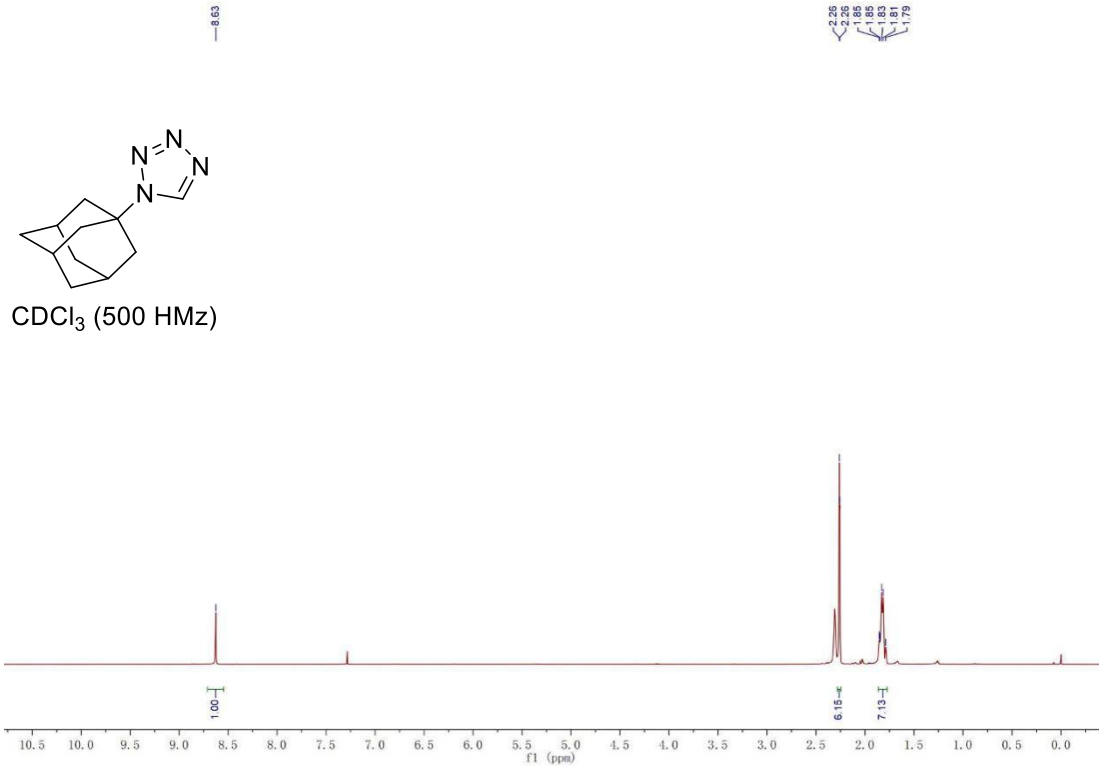




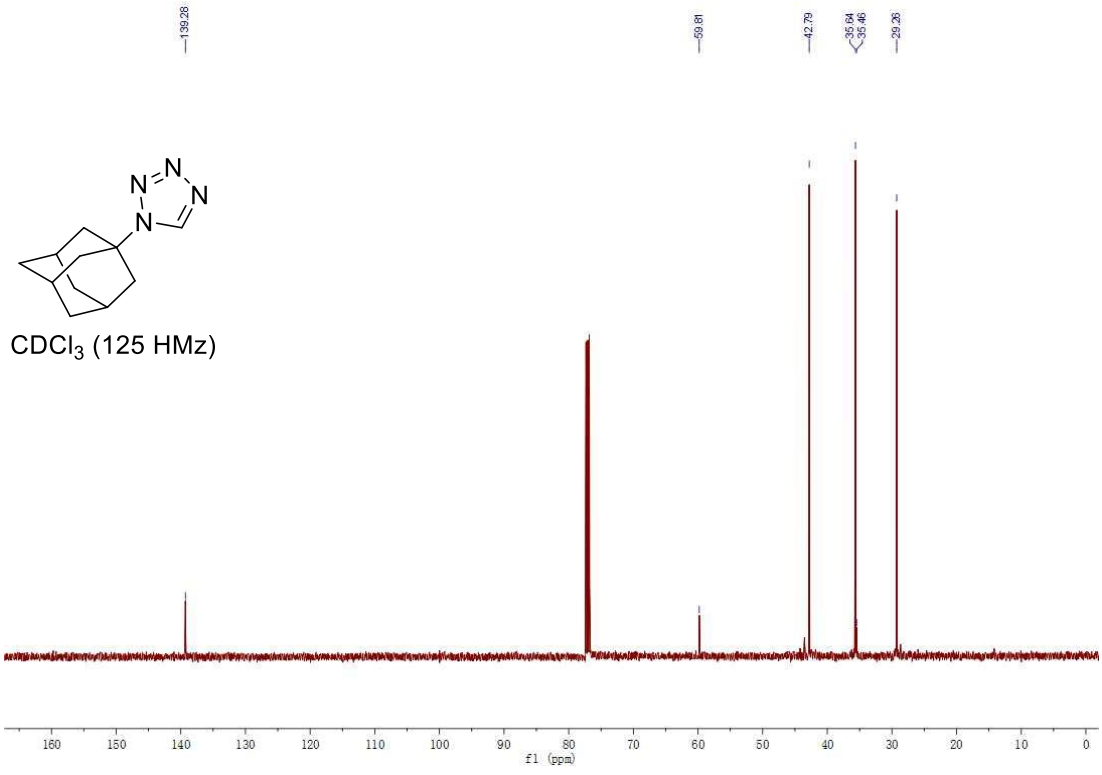
$CDCl_3$ (125 HMz)



1-((3s,5s,7s)-adamantan-1-yl)-1*H*-tetrazole (6s)

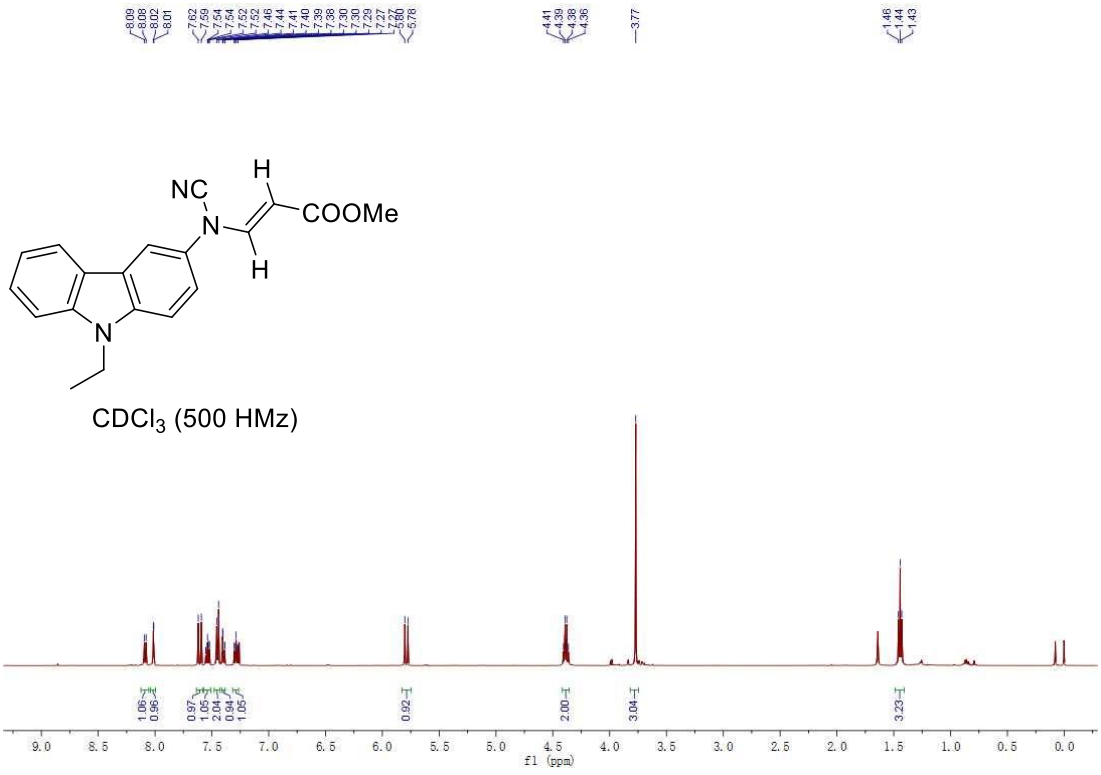


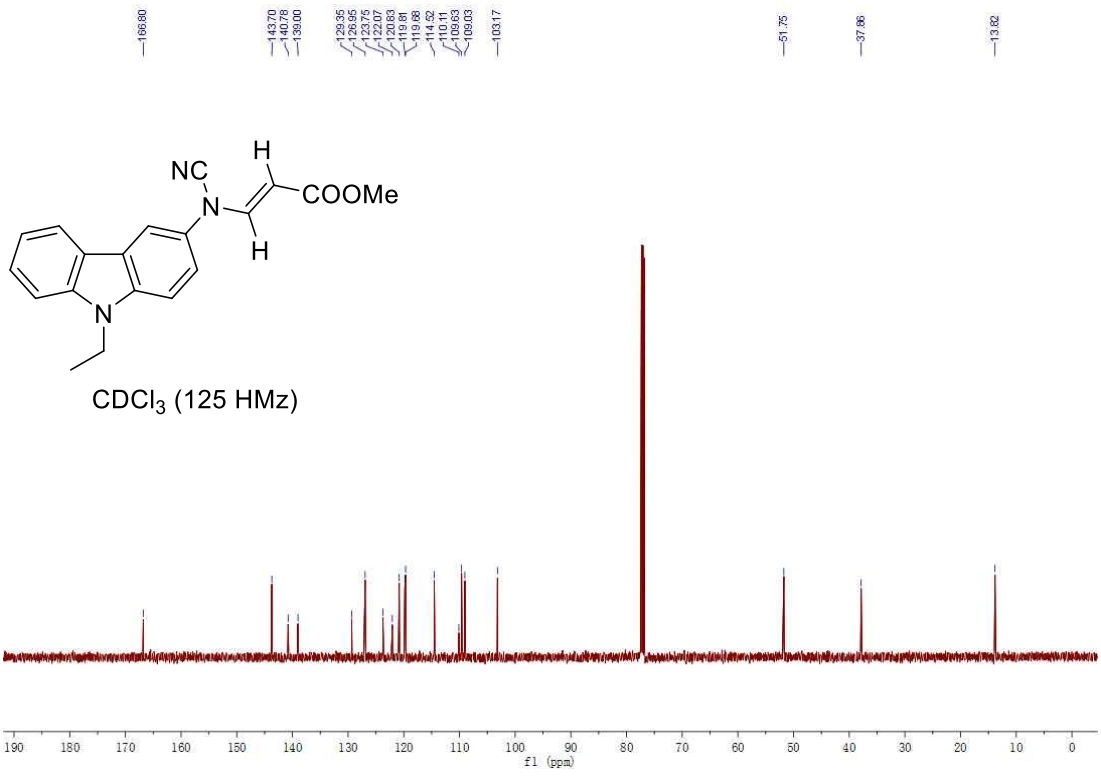
$CDCl_3$ (500 HMz)



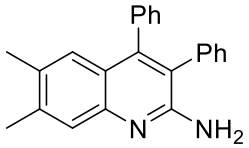
$CDCl_3$ (125 HMz)

methyl (*E*)-3-(*N*-(9-ethyl-9*H*-carbazol-3-yl)cyanamido)acrylate (7)

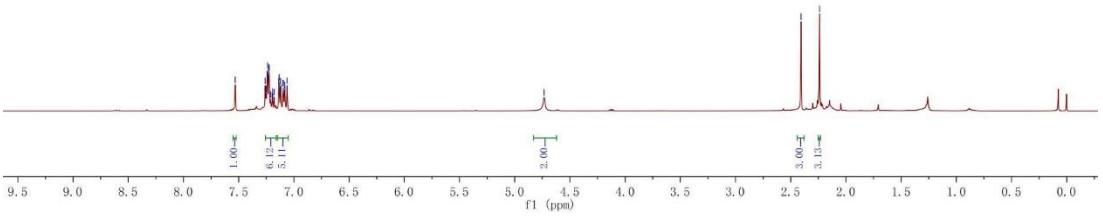


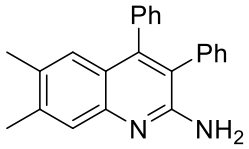


6,7-dimethyl-3,4-diphenylquinolin-2-amine (8)



$CDCl_3$ (500 HMz)





$CDCl_3$ (125 HMz)