Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

for

Co-Catalyzed Highly Selective C(sp^3)−H Nitration

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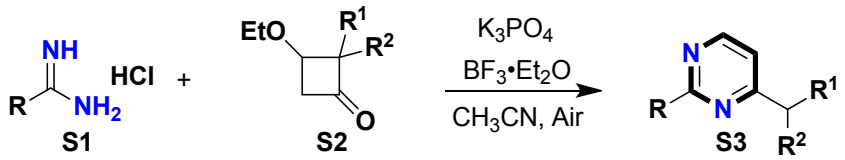
1、General information

All chemicals were purchased from Adamas Reagent, energy chemical company, J&K Scientific Ltd, Bide Pharmatech Ltd and Tansoole. The reagents and solvents were purchased from commercial suppliers and used without further purification. 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) as an internal reference. High resolution mass spectra were recorded using a Thermo Fisher Scientific LTQ FT Ultra or Waters Micromass GCT Premier instrument. Coupling constants (*J*) were reported in Hertz (Hz).

2、 General procedure for starting materials

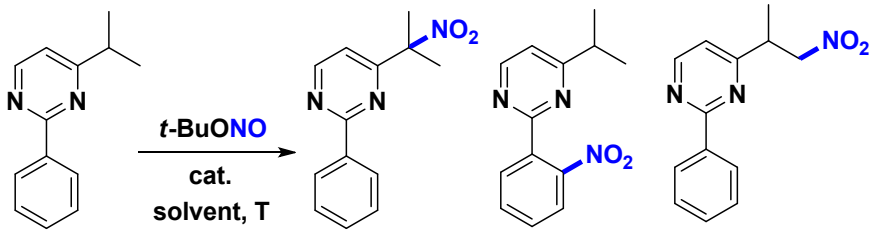


In a dried sealed tube were placed amidine **S1** (2 mmol, 1 equiv) and K_3PO_4 (636.8 mg, 3 mmol, 1.5 equiv) in CH_3CN (10 mL). The resulting mixture was stirred at room temperature for 1 h. Then, cyclobutanones **S2** (3 mmol, 1.5 equiv) and BF_3•Et_2O (426 mg, 3 mmol, 1.5 equiv) in CH_3CN (5 mL) were added to the resulting solution. The tube was stirred at 80 °C for 18 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 50:1, v/v) to give the desired pyrimidine product **S3**.[1]

[1] Zhou, Y.; Tang, Z.; Song, Q. *Adv. Synth. Catal.* **2017**, *359*, 952.

3. Screening of Conditions

Table S1 Optimization of the reaction with 1a and *t*-BuONO

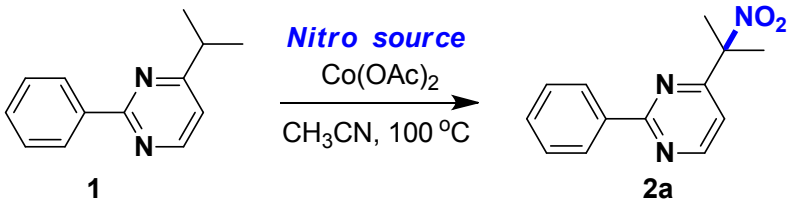


1a **2a** **3a** **3aa (N.D.)**

entry[a]	catalyst	T (°C)	solvent	product	yield (%)[b]
1	$Pd(OAc)_2$	100	PhCl	**3a**	67[c]
2[d]	$[IrCp^*Cl_2]_2$	100	PhCl	**N.D.**	-
3[e]	$[RhCp^*Cl_2]_2$	100	PhCl	**N.D.**	-
4	$Cp^*Co(CO)I_2$	100	PhCl	**2a**	47
5	$Cu(OAc)_2$	100	PhCl	**2a**	30
6	$Co(OAc)_2$	100	PhCl	**2a**	62[c]
7	CoI_2	100	PhCl	**2a**	38
8	$CoBr_2$	100	PhCl	**2a**	56
9	$Co(acac)_2$	100	PhCl	**2a**	35
10	$Co(OAc)_2$	80	PhCl	**2a**	50
11	$Co(OAc)_2$	100	TFE	**N.D.**	-
12	$Co(OAc)_2$	100	HFIP	**N.D.**	-
13	$Co(OAc)_2$	100	PhMe	**2a**	30
14	$Co(OAc)_2$	100	DCE	**2a**	71
15	$Co(OAc)_2$	100	Dioxane	**2a**	46
16	$Co(OAc)_2$	100	MeCN	**2a**	80[c]
17[f]	$Co(OAc)_2$	100	MeCN	**2a**	77[c]
18[g]	$Co(OAc)_2$	100	MeCN	**2a**	50%
19[h]	$Co(OAc)_2$	100	MeCN	**2a**	78[c]
20[i]	$Co(OAc)_2$	100	MeCN	**2a**	14
21	-	100	MeCN	**2a**	25[c]

[a] Reaction conditions: **1a** (0.15 mmol), *t*-BuONO (0.45 mmol), catalyst (10 mol%), under O_2, 24 h. [b] GC yelids. [c] Isolated yields. [d] 10 mol% $AgNTf_2$ was added, under air. [e] 10 mol% $AgSF_6$ was added, under air. [f] 20 mol% $Co(OAc)_2$. [g] 5 mol% $Co(OAc)_2$. [h] under air. [i] under N_2

Table S2 Screening of other nitrating agents

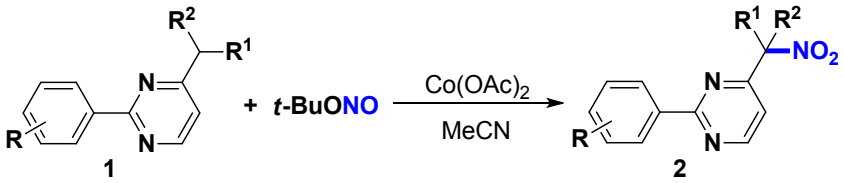


1 2a

Entry[a]	Nitro source	Oxidant	Yield of **2a**[b]
1	$Ce(NH4)_2(NO_3)_6$	O_2	49%
2	$AgNO_3$	O_2	N.D.
3	$NaNO_3$	O_2	N.D.
4	$Cu(NO_3)_2$	O_2	31%
5	$Fe(NO_3)_3 \bullet 6H_2O$	O_2	40%
6	*i*-BuONO	O_2	76%
7	$NaNO_2$	O_2	trace
8	$AgNO_2$	O_2	trace
9[c]	$AgNO_2$	$K_2S_2O_8$	17%

Reaction conditions: **1** (0.2 mmol), Nitro source (0.6 mmol), 100 °C, under O_2, 24h. [b] GC yield. [c] $K_2S_2O_8$ (0.6 mmol)

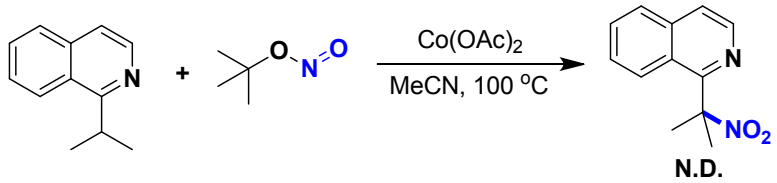
4. General process for the synthesis of 2

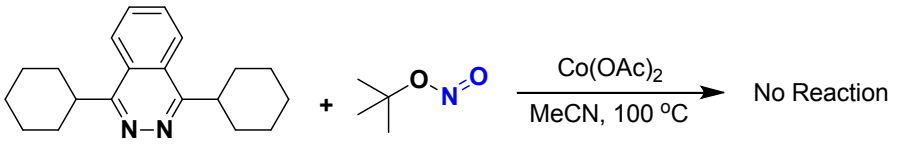


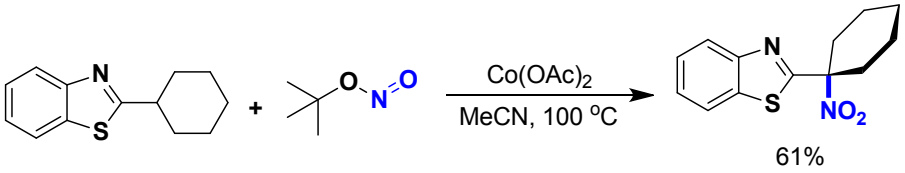
1 2

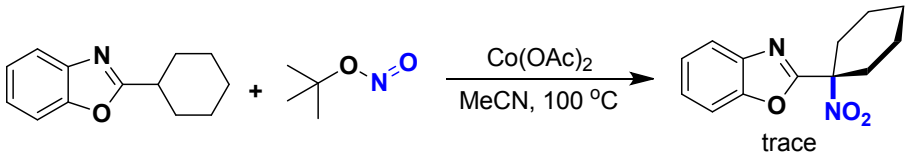
To a mixture of $Co(OAc)_2$ (5.3 mg, 10 mol%) and **1** (0.3 mmol, 1 equiv) in CH_3CN (1 mL) was added *t*-BuONO (92 mg, 0.9 mmol, 3 equiv). The resulting mixture was stirred under O_2 at 100 °C for 24 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 25:1, v/v) to give the desired product **2**.

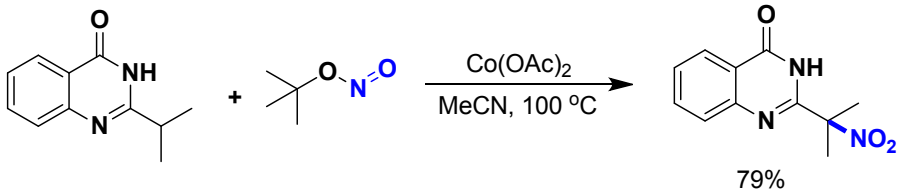
5、The reaction of other heterocycles





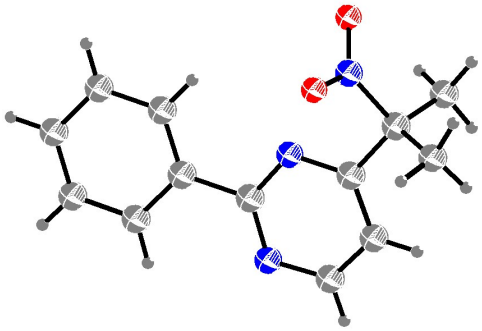






6、Crystal data of 2a

Crystallographic data for compound **2a** (CCDC-1526577) 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).



Displacement ellipsoids are drawn at 30% probability level

Bond precision: C-C = 0.0062 A Wavelength=0.71073

Cell: a=7.3577(9) b=9.9881(11) c=16.612(2)
alpha=89.395(10) beta=88.058(10) gamma=89.171(10)

Temperature: 295 K

	Calculated	Reported
Volume	1219.9(2)	1219.9(3)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C13 H13 N3 O2	C13 H13 N3 O2
Sum formula	C13 H13 N3 O2	C13 H13 N3 O2
Mr	243.26	243.26
Dx,g cm-3	1.324	1.325
Z	4	4
Mu (mm-1)	0.092	0.092
F000	512.0	512.0
F000'	512.22	
h,k,lmax	10,13,22	9,13,21
Nref	6545	4325
Tmin,Tmax	0.957,0.973	0.743,1.000
Tmin'	0.955	

Correction method= # Reported T Limits: Tmin=0.743 Tmax=1.000 AbsCorr = MULTI-SCAN

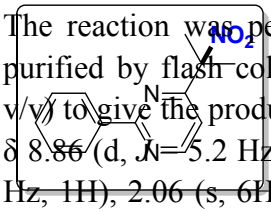
Data completeness= 0.661 Theta(max)= 29.106

R(reflections)= 0.0862(2451) wR2(reflections)= 0.2856(4325)

S = 1.056 Npar= 329

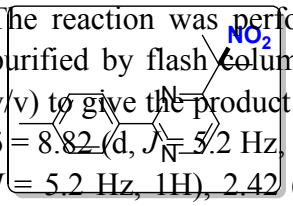
7、Characterization data for products

4-(2-nitropropan-2-yl)-2-phenylpyrimidine (2a)



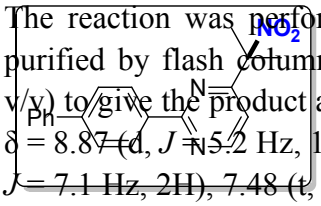
The reaction was performed by following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 25:1, v/v) to give the product as a white solid (58.3 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.86 (d, J = 5.2 Hz, 1H), 8.49 – 8.42 (m, 2H), 7.54 – 7.47 (m, 3H), 7.21 (d, J = 5.2 Hz, 1H), 2.06 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 166.8, 164.4, 158.6, 136.8, 131.2, 128.6, 128.3, 114.3, 91.1, 26.0.
HRMS (EI, m/z) calcd for $C_{13}H_{13}N_3O_2$ [M]$^+$: 243.1008; found: 243.1011.

4-(2-nitropropan-2-yl)-2-(p-tolyl)pyrimidine (2b)



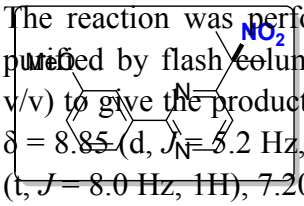
The reaction was performed by following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 20:1, v/v) to give the product as a white solid (53.2 mg, 69%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.82 (d, J = 5.2 Hz, 1H), 8.34 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 5.2 Hz, 1H), 2.42 (s, 3H), 2.05 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.7, 164.5, 158.5, 141.5, 134.2, 129.3, 128.3, 113.9, 91.1, 26.0, 21.5.
HRMS (EI, m/z) calcd for $C_{14}H_{15}N_3O_2$ [M]$^+$: 257.1164; found: 257.1162.

2-([1,1'-biphenyl]-4-yl)-4-(2-nitropropan-2-yl)pyrimidine (2c)



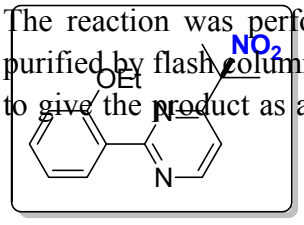
The reaction was performed by following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 20:1, v/v) to give the product as a white solid (79.6 mg, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.87 (d, J = 5.2 Hz, 1H), 8.54 (d, J = 8.5 Hz, 2H), 7.74 (d, J = 8.5 Hz, 2H), 7.68 (d, J = 7.1 Hz, 2H), 7.48 (t, J = 7.6 Hz, 2H), 7.40 (t, J = 7.4 Hz, 1H), 7.21 (d, J = 5.2 Hz, 1H), 2.08 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 166.7, 164.1, 158.6, 143.8, 140.3, 135.7, 128.8, 128.8, 127.8, 127.3, 127.1, 114.2, 91.1, 26.0.
HRMS (ESI, m/z) calcd for $C_{19}H_{18}N_3O_2$ [M+H]$^+$: 320.1399; found: 320.1394.

2-(3-methoxyphenyl)-4-(2-nitropropan-2-yl)pyrimidine (2d)



The reaction was performed by following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 10:1, v/v) to give the product as a yellow oil (54.8 mg, 67%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.85 (d, J = 5.2 Hz, 1H), 8.08 – 8.04 (m, 1H), 8.01 (dd, J = 2.6, 1.5 Hz, 1H), 7.40 (t, J = 8.0 Hz, 1H), 7.20 (d, J = 5.2 Hz, 1H), 7.05 (ddd, J = 8.2, 2.7, 0.9 Hz, 1H), 3.90 (s, 3H), 2.06 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 166.7, 164.2, 159.9, 158.5, 138.2, 129.6, 120.9, 117.4, 114.4, 113.1, 91.1, 55.4, 26.0.
HRMS (EI, m/z) calcd for $C_{14}H_{15}N_3O_3$ [M]$^+$: 273.1113; found: 273.1109.

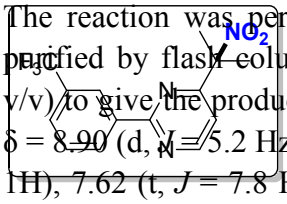
2-(2-ethoxyphenyl)-4-(2-nitropropan-2-yl)pyrimidine (2e)



The reaction was performed by following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 5:1, v/v) to give the product as a yellow oil (50.8 mg, 59%) .^{1}H NMR (500 MHz, $CDCl_3$) δ =

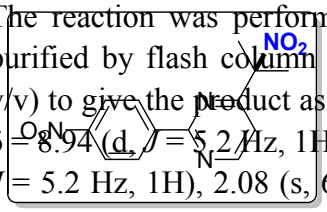
8.88 (d, J = 5.3 Hz, 1H), 7.75 (d, J = 1.8 Hz, 1H), 7.44 – 7.37 (m, 1H), 7.20 (d, J = 5.3 Hz, 1H), 7.07 – 6.99 (m, 2H), 4.10 (q, J = 7.0 Hz, 2H), 2.04 (s, 6H), 1.37 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 166.4, 165.6, 158.0, 157.4, 131.9, 131.3, 127.8, 120.5, 113.6, 113.3, 91.1, 64.4, 26.0, 14.8.
HRMS (ESI, m/z) calcd for $C_{15}H_{18}FN_3O_3$ $[M+H]^+$: 288.1343; found: 288.1345.

4-(2-nitropropan-2-yl)-2-(3-(trifluoromethyl)phenyl)pyrimidine (2f)



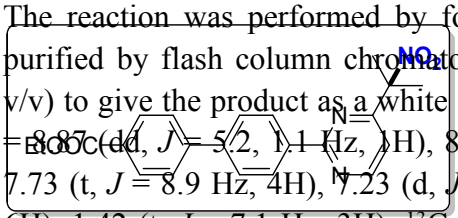
The reaction was performed by following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 20:1, v/v) to give the product as a yellow oil (77.4 mg, 83%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.90 (d, J = 5.2 Hz, 1H), 8.73 (s, 1H), 8.64 (d, J = 7.9 Hz, 1H), 7.75 (d, J = 7.7 Hz, 1H), 7.62 (t, J = 7.8 Hz, 1H), 7.28 (d, J = 5.2 Hz, 1H), 2.08 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 167.0, 163.0, 158.8, 137.6, 131.5, 129.1, 127.7 (q, J = 7.4, 3.8 Hz), 125.2 (q, J = 7.8, 3.8 Hz), 115.0, 91.0, 26.0.
HRMS (EI, m/z) calcd for $C_{14}H_{12}F_3N_3O_2$ $[M]^+$: 311.0882; found: 311.0884.

2-(4-nitrophenyl)-4-(2-nitropropan-2-yl)pyrimidine (2g)



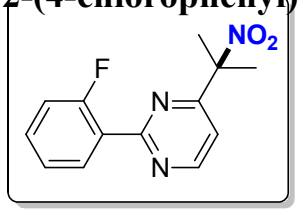
The reaction was performed by following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 10:1, v/v) to give the product as a white solid (59.6 mg, 69%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.94 (d, J = 5.2 Hz, 1H), 8.62 (d, J = 9.0 Hz, 2H), 8.32 (d, J = 9.0 Hz, 2H), 7.34 (d, J = 5.2 Hz, 1H), 2.08 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 167.2, 162.3, 158.9, 149.5, 142.4, 129.3, 123.7, 115.56, 90.9, 26.0.
HRMS (ESI, m/z) calcd for $C_{13}H_{13}N_4O_4$ $[M+H]^+$: 289.0937; found: 289.0932.

ethyl4'-(4-(2-nitropropan-2-yl)pyrimidin-2-yl)-[1,1'-biphenyl]-4-carboxylate (2h)



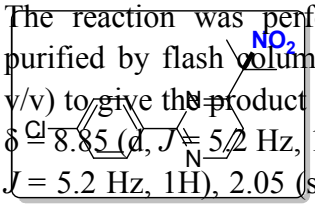
The reaction was performed by following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 10:1, v/v) to give the product as a white solid (95 mg, 81%. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.87 (dd, J = 5.2, 1.1 Hz, 1H), 8.54 (d, J = 8.2 Hz, 2H), 8.14 (d, J = 8.1 Hz, 2H), 7.73 (t, J = 8.9 Hz, 4H), 7.23 (d, J = 5.2 Hz, 1H), 4.41 (q, J = 7.1 Hz, 2H), 2.08 (s, 6H), 1.42 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 166.8 166.4, 163.9, 158.6, 144.6, 142.6, 136.5, 130.1, 129.6, 128.9, 127.4, 127.0, 114.4, 91.1, 61.0, 26.0, 14.3.
HRMS (ESI, m/z) calcd for $C_{22}H_{22}N_3O_4$ $[M+H]^+$: 392.1610; found: 392.1605.

2-(4-chlorophenyl)-4-(2-nitropropan-2-yl)pyrimidine (2i)



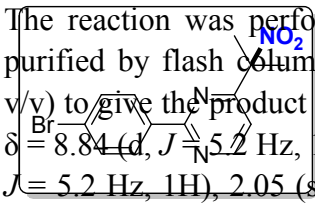
The reaction was performed by following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 25:1, v/v) to give the product as a yellow oil (47.7 mg, 61%).^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.95 (d, *J* = 5.2 Hz, 1H), 8.12 (td, *J* = 7.8, 1.8 Hz, 1H), 7.52 – 7.46 (m, 1H), 7.29 (d, *J* = 14.3 Hz, 2H), 7.22 (dd, *J* = 11.2, 8.3 Hz, 1H), 2.08 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 166.9, 163.1 (d, *J* = 5.0 Hz), 161.4 (d, *J* = 255.0 Hz), 158.5, 132.3 (d, *J* = 8.7 Hz), 132.0, 124.1 (d, *J* = 3.8 Hz), 117.0, 116.9, 114.4, 91.1, 26.0.
HRMS (EI, m/z) calcd for $C_{13}H_{12}FN_3O_2$ $[M]^+$: 261.0914; found: 261.0909.

2-(4-chlorophenyl)-4-(2-nitropropan-2-yl)pyrimidine (2j)



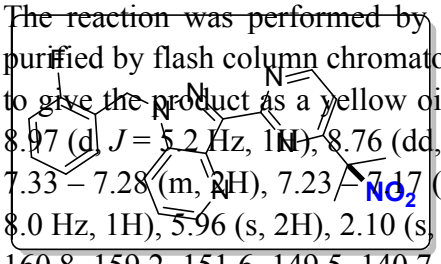
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 25:1, v/v) to give the product as a white solid (59.8 mg, 72%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.85 (d, *J* = 5.2 Hz, 1H), 8.39 (d, *J* = 8.7 Hz, 2H), 7.45 (d, *J* = 8.7 Hz, 2H), 7.22 (d, *J* = 5.2 Hz, 1H), 2.05 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 166.8, 163.5, 158.7, 137.5, 135.3, 129.7, 128.8, 114.5, 91.0, 26.0.
HRMS (EI, m/z) calcd for $C_{13}H_{12}ClN_3O_2$ $[M]^+$: 277.0618; found: 277.0619.

2-(4-bromophenyl)-4-(2-nitropropan-2-yl)pyrimidine (2k)



The reaction was performed by following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 20:1, v/v) to give the product as a white solid (74.1 mg, 77%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.84 (d, *J* = 5.2 Hz, 1H), 8.32 (d, *J* = 8.7 Hz, 2H), 7.61 (d, *J* = 8.7 Hz, 2H), 7.23 (d, *J* = 5.2 Hz, 1H), 2.05 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 166.9, 163.6, 158.7, 135.8, 131.8, 129.9, 126.0, 114.6, 91.0, 26.0.
HRMS (EI, m/z) calcd for $C_{13}H_{12}BrN_3O_2$ $[M]^+$: 321.0113; found: 321.0118.

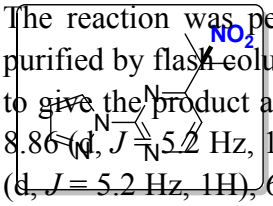
1-(2-fluorobenzyl)-3-(4-(2-nitropropan-2-yl)pyrimidin-2-yl)-1H-pyrazolo[4,3-b]pyridine (2l)



The reaction was performed by 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 oil (77.6 mg, 66%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.97 (d, *J* = 5.2 Hz, 1H), 8.76 (dd, *J* = 8.1, 1.6 Hz, 1H), 8.61 (dd, *J* = 4.5, 1.6 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.23 – 7.17 (m, 1H), 7.04 (dd, *J* = 16.9, 8.5 Hz, 2H), 6.96 (t, *J* = 8.0 Hz, 1H), 5.96 (s, 2H), 2.10 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 167.2, 161.2, 160.8, 159.2, 151.6, 149.5, 140.7, 132.6, 129.3 (d, *J* = 8.0 Hz), 129.2 (d, *J* = 3.6 Hz),

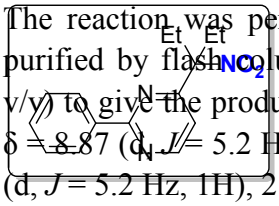
124.1 (d, J = 3.6 Hz), 123.8 (d, J = 14.5 Hz), 118.8, 115.4, 115.3 (d, J = 6.6 Hz), 114.6, 90.8, 44.9 (d, J = 5.0 Hz), 26.0.
HRMS (ESI, m/z) calcd for $C_{20}H_{18}FN_6O_2[M+H]^+$: 393.1475; found: 393.1470.

4-(2-nitropropan-2-yl)-2-(1H-pyrazol-1-yl)pyrimidine (2m)



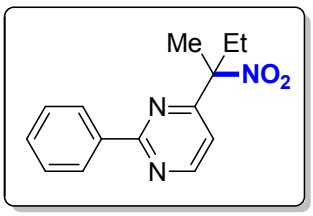
The reaction was performed by following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 2:1, v/v) to give the product as a yellow oil (54.5 mg, 78%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.86 (d, J = 5.2 Hz, 1H), 8.57 (dd, J = 2.7, 0.6 Hz, 1H), 7.86 (d, J = 0.9 Hz, 1H), 7.24 (d, J = 5.2 Hz, 1H), 6.52 (dd, J = 2.7, 1.6 Hz, 1H), 2.07 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 168.6, 160.6, 155.6, 144.1, 129.4, 114.0, 109.0, 90.7, 25.9.
HRMS (EI, m/z) calcd for $C_{10}H_{11}N_5O_2$ $[M]^+$: 233.0913; found: 233.0910.

4-(3-nitropentan-3-yl)-2-phenylpyrimidine (2o)



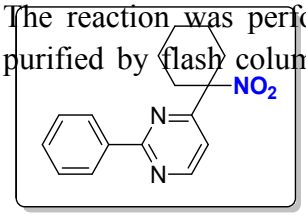
The reaction was performed by following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 25:1, v/v) to give the product as a yellow oil (58.4 mg, 71%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.87 (d, J = 5.2 Hz, 1H), 8.50 – 8.45 (m, 2H), 7.52 (dd, J = 5.4, 1.9 Hz, 3H), 7.19 (d, J = 5.2 Hz, 1H), 2.57 (dq, J = 14.3, 7.1 Hz, 4H), 0.90 (t, J = 7.5 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 165.8, 164.3, 158.1, 136.9, 131.1, 128.6, 128.3, 115.9, 98.6, 27.6, 8.1.
HRMS (ESI, m/z) calcd for $C_{15}H_{18}N_3O_2[M+H]^+$: 272.1399; found: 272.1394.

4-(2-nitrobutan-2-yl)-2-phenylpyrimidine (2p)



The reaction was performed by following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 25:1, v/v) to give the product as a yellow oil (59.6 mg, 77%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.85 (d, J = 5.2 Hz, 1H), 8.48 – 8.42 (m, 2H), 7.52 – 7.47 (m, 3H), 7.18 (d, J = 5.2 Hz, 1H), 2.59 (dq, J = 14.7, 7.4 Hz, 1H), 2.51 – 2.40 (m, 1H), 2.00 (s, 3H), 0.99 (t, J = 7.4 Hz, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ = 166.6, 164.3, 158.4, 136.8, 131.2, 128.6, 128.3, 114.8, 95.0, 31.4, 22.5, 8.5.
HRMS (ESI, m/z) calcd for $C_{15}H_{18}N_3O_2[M+H]^+$: 258.1237; found: 272.1238.

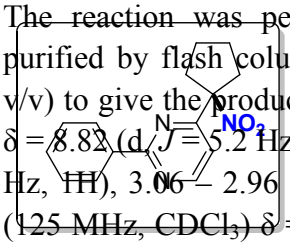
4-(1-nitrocyclohexyl)-2-phenylpyrimidine (2q)



The reaction was performed by following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 25:1,

v/v) to give the product as a yellow oil (62.8 mg, 74%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.83 (d, *J* = 5.2 Hz, 1H), 8.46 (dd, *J* = 6.6, 3.2 Hz, 2H), 7.49 (dd, *J* = 5.2, 1.9 Hz, 3H), 7.21 (d, *J* = 5.2 Hz, 1H), 2.78 (d, *J* = 14.1 Hz, 2H), 2.37 (t, *J* = 14.3 Hz, 2H), 1.81 – 1.66 (m, 4H), 1.61 – 1.55 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 166.2, 164.4, 158.6, 136.9, 131.2, 128.6, 128.3, 114.5, 94.9, 33.9, 24.4, 22.4.
HRMS (ESI, m/z) calcd for $C_{16}H_{18}N_3O_2$ $[M+H]^+$: 284.1399; found: 284.1394.

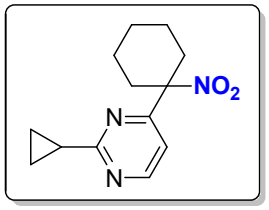
4-(1-nitrocyclopentyl)-2-phenylpyrimidine (2r)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 25:1, v/v) to give the product as a yellow oil (64.4 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.82 (d, *J* = 5.2 Hz, 1H), 8.52 – 8.42 (m, 2H), 7.55 – 7.45 (m, 3H), 7.17 (d, *J* = 5.2 Hz, 1H), 3.06 – 2.96 (m, 2H), 2.61 – 2.50 (m, 2H), 1.99 – 1.89 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 165.9, 164.3, 158.4, 136.9, 131.1, 128.6, 128.3, 115.0, 103.0, 37.7, 24.1.

HRMS (EI, m/z) calcd for $C_{15}H_{15}N_3O_2$ $[M]^+$: 269.1164; found: 269.1168.

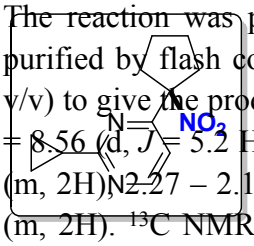
2-cyclopropyl-4-(1-nitrocyclohexyl)pyrimidine (2u)



The reaction was performed by following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether: EtOAc = 25:1, v/v) to give the product as a yellow oil (50.4 mg, 69%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.57 (d, *J* = 5.3 Hz, 1H), 7.03 (d, *J* = 5.3 Hz, 1H), 2.66 (d, *J* = 14.1 Hz, 2H), 2.28 – 2.18 (m, 3H), 1.70 – 1.64 (m, 3H), 1.57 – 1.48 (m, 2H), 1.43 – 1.34 (m, 1H), 1.13 – 1.09 (m, 2H), 1.09 – 1.05 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 172.3, 165.7, 157.9, 113.2, 94.7, 33.7, 24.3, 22.3, 18.2, 11.3.

HRMS (ESI, m/z) calcd for $[C_{13}H_{18}N_3O_2]$: 248.1394; found: 248.1390.

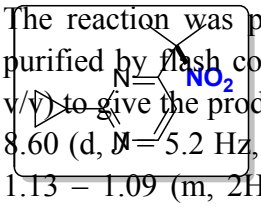
2-cyclopropyl-4-(1-nitrocyclopentyl)pyrimidine (2v)



The reaction was performed by following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether: EtOAc = 25:1, v/v) to give the product as a yellow oil (56.6 mg, 81%).^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.56 (d, *J* = 5.2 Hz, 1H), 7.00 (d, *J* = 5.2 Hz, 1H), 2.94 – 2.84 (m, 2H), 2.45 – 2.35 (m, 2H), 2.27 – 2.19 (m, 1H), 1.91 – 1.82 (m, 4H), 1.13 – 1.09 (m, 2H), 1.09 – 1.04 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 172.2, 165.4, 157.7, 113.8, 102.8, 37.4, 23.9, 18.2, 11.3.

HRMS (ESI, m/z) calcd for $C_{12}H_{16}N_3O_2[M+H]^+$: 234.1237; found: 234.1232.

2-cyclopropyl-4-(2-nitropropan-2-yl)pyrimidine (2w)



The reaction was performed by following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether: EtOAc = 25:1, v/v) to give the product as a yellow oil (46.6 mg, 75%).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (d, *J* = 5.2 Hz, 1H), 7.04 (d, *J* = 5.3 Hz, 1H), 2.27 – 2.21 (m, 1H), 1.94 (s, 6H), 1.13 – 1.09 (m, 2H), 1.09-1.05 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 172.3, 166.3, 157.9, 113.0, 90.9, 25.89, 18.19, 11.39.

HRMS (ESI, m/z) calcd for $C_{10}H_{14}N_3O_2[M+H]^+$: 208.1081; found: 208.1080.

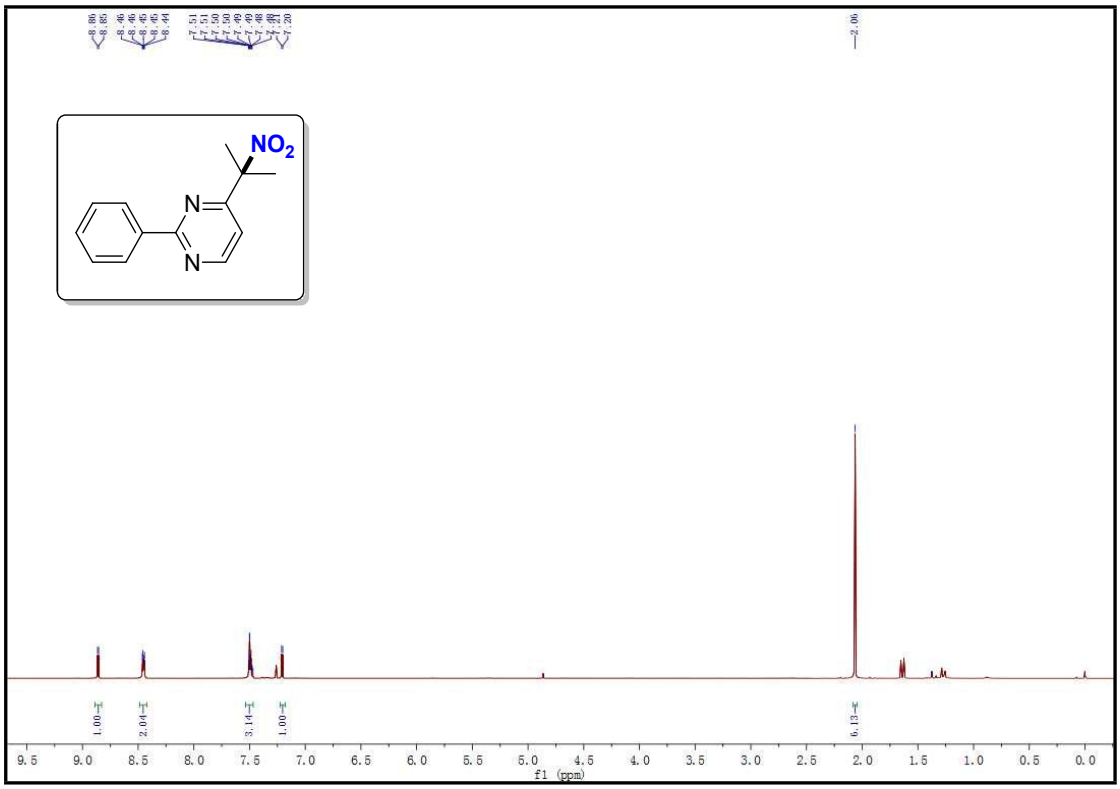
2-(2-cyclopropylpyrimidin-4-yl)propan-2-amine (5) (CAS: No. 1192801-28-7)[2]

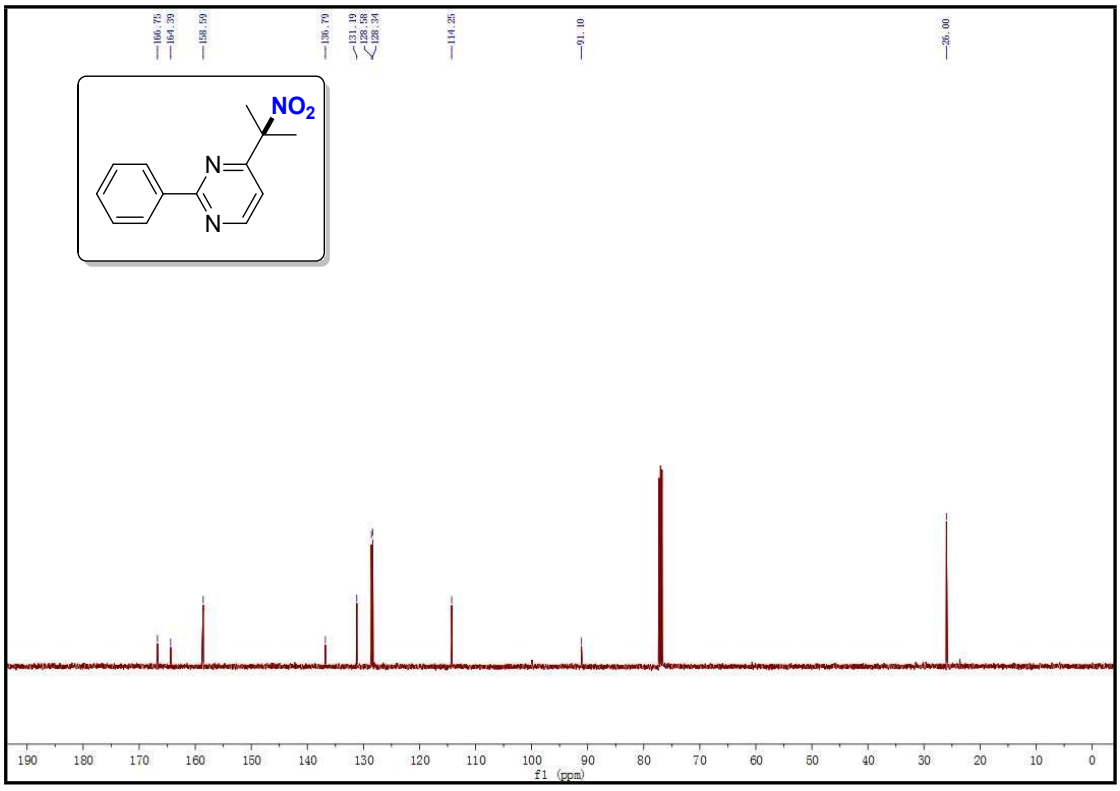
2w (0.3 mmol) and $NiCl_2$ (10 mol %) were dissolved in MeOH (2 mL), $NaBH_4$ (4.5 mmol) was slowly added (in portions) at 0 °C and the mixture was continued to react for another 3h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel using EtOAc as eluent to give the product **5** as a yellow oil (47.5 mg, 89%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.48 (d, *J* = 5.3 Hz, 1H), 7.13 (d, *J* = 5.3 Hz, 1H), 4.48 (br s, 2H), 2.24 – 2.19 (m, 1H), 1.51 (s, 6H), 1.15 – 1.12 (m, 2H), 1.03 – 0.99 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 173.6, 171.5, 157.2, 112.3, 54.7, 29.1, 18.1, 10.9.

[2] B. Schaus and J. Mehnert, 2009, WO2009/131815 A1.

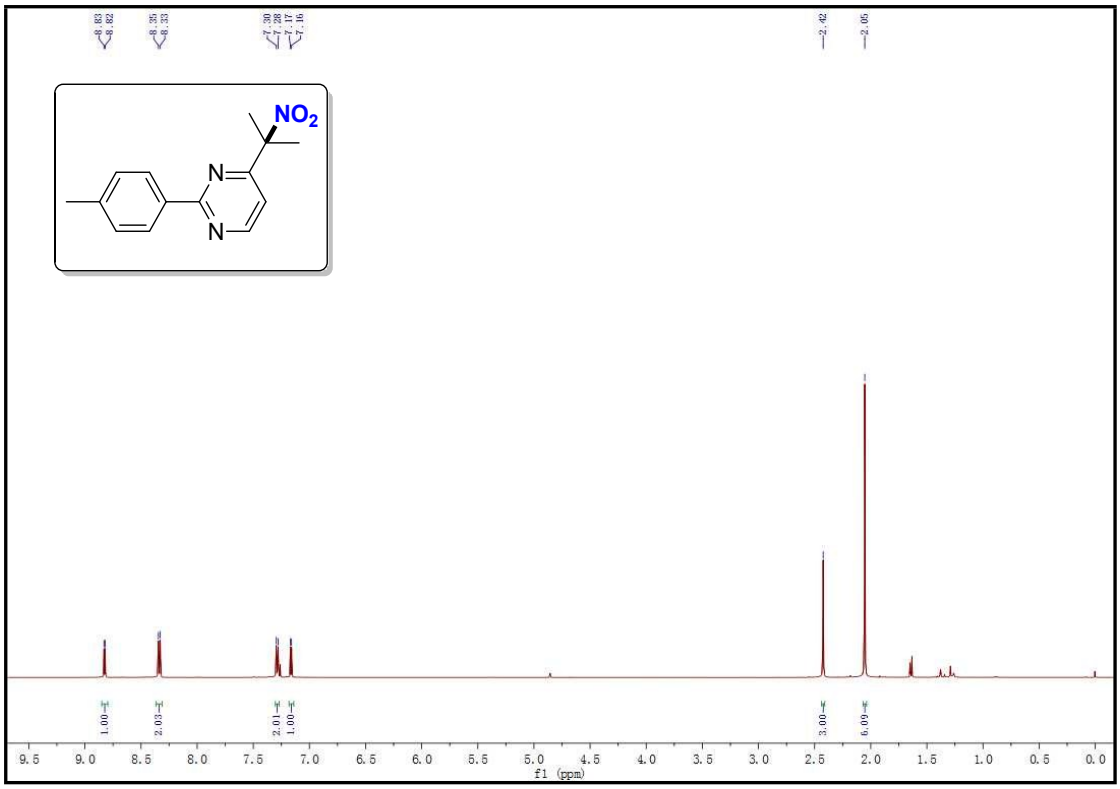
8、NMR spectroscopic data

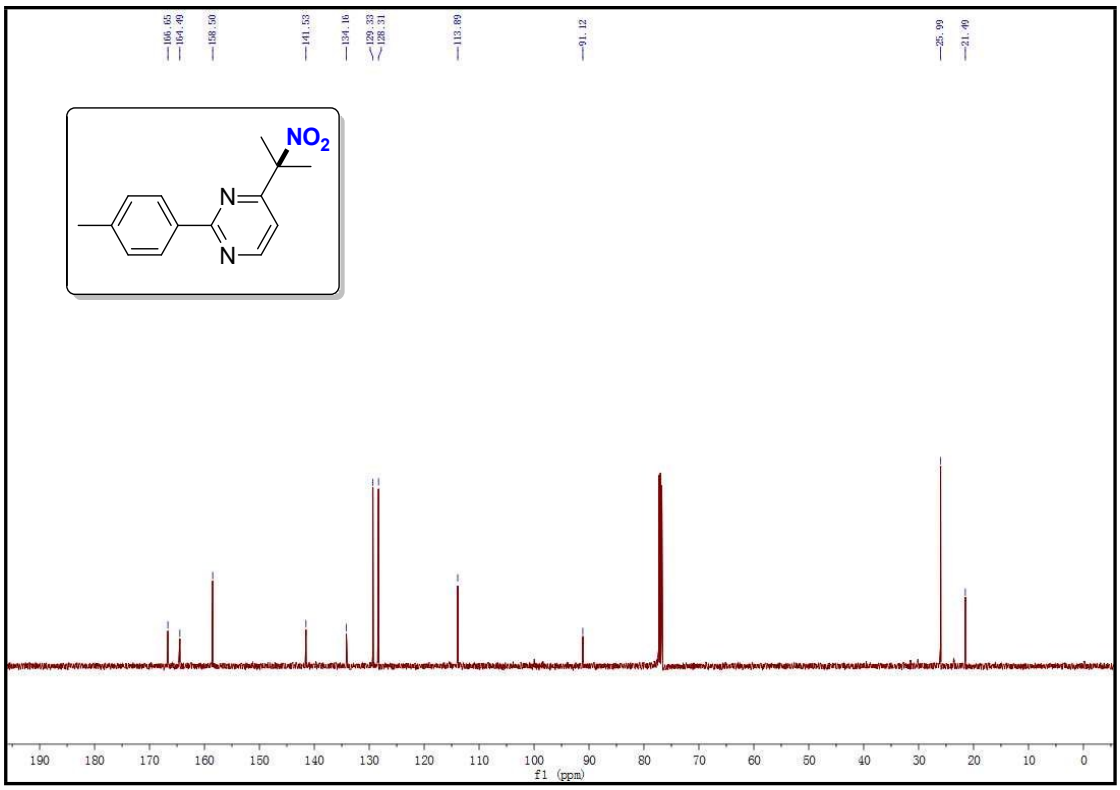
4-(2-nitropropan-2-yl)-2-phenylpyrimidine (2a)



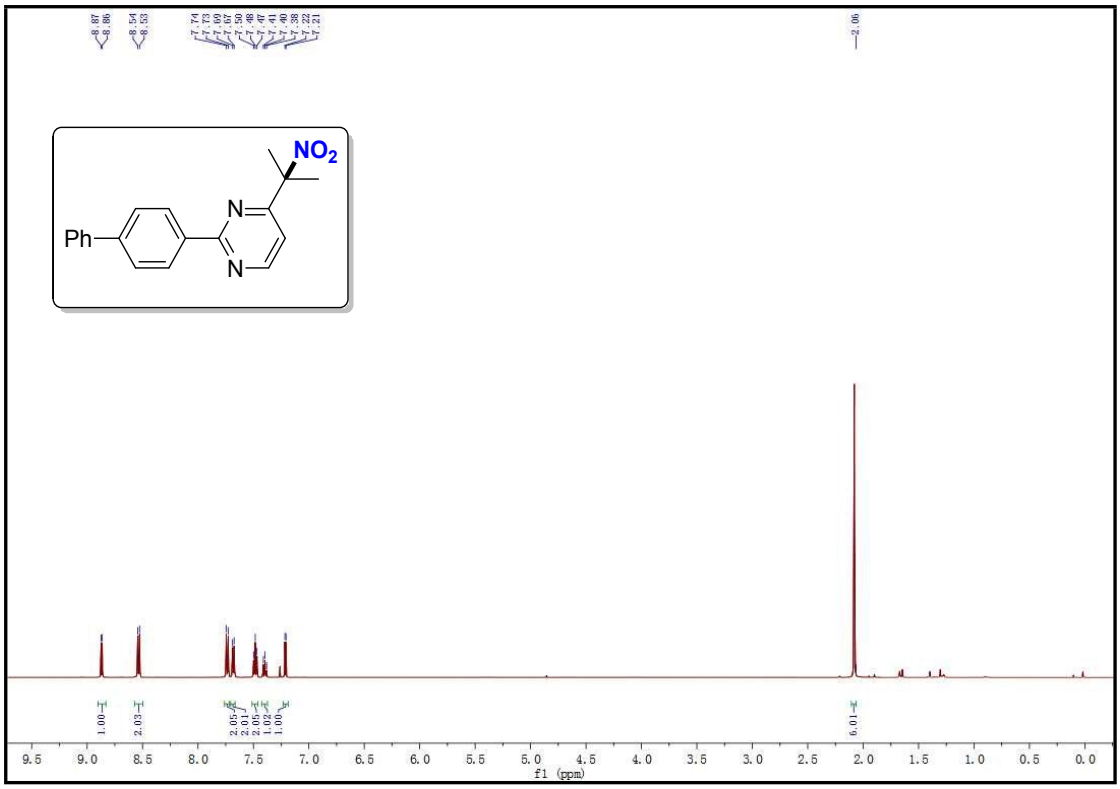


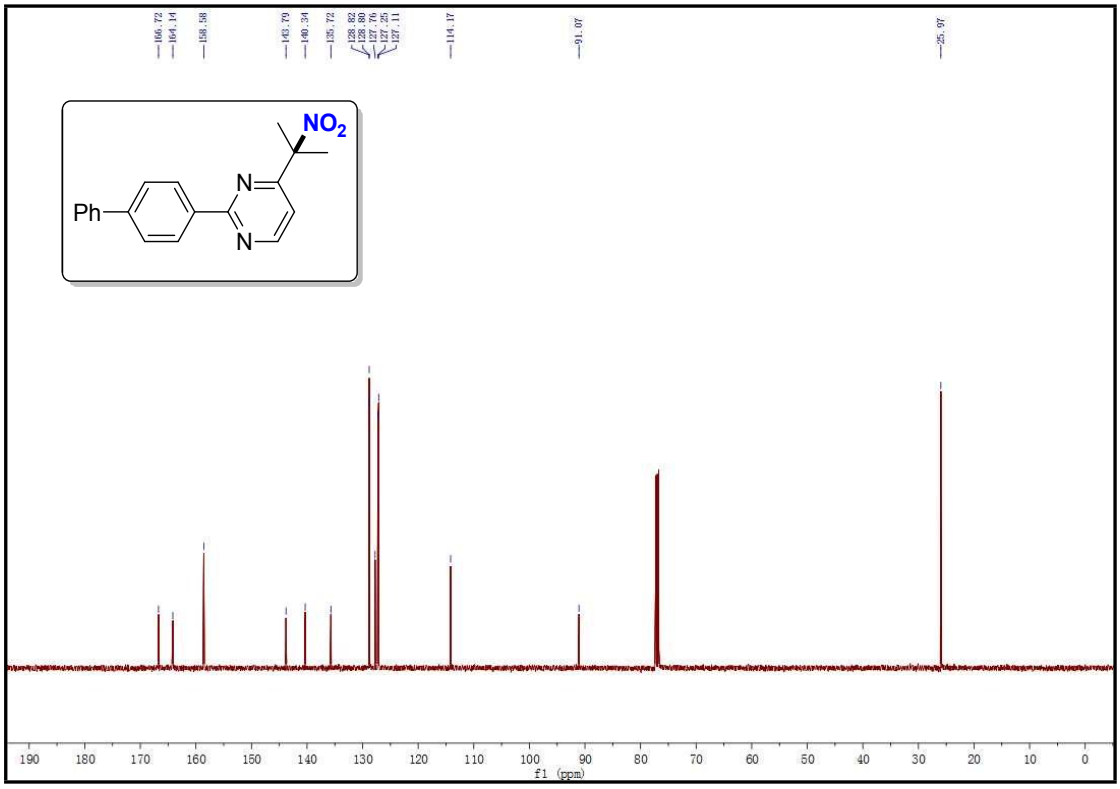
4-(2-nitropropan-2-yl)-2-(p-tolyl)pyrimidine (2b)



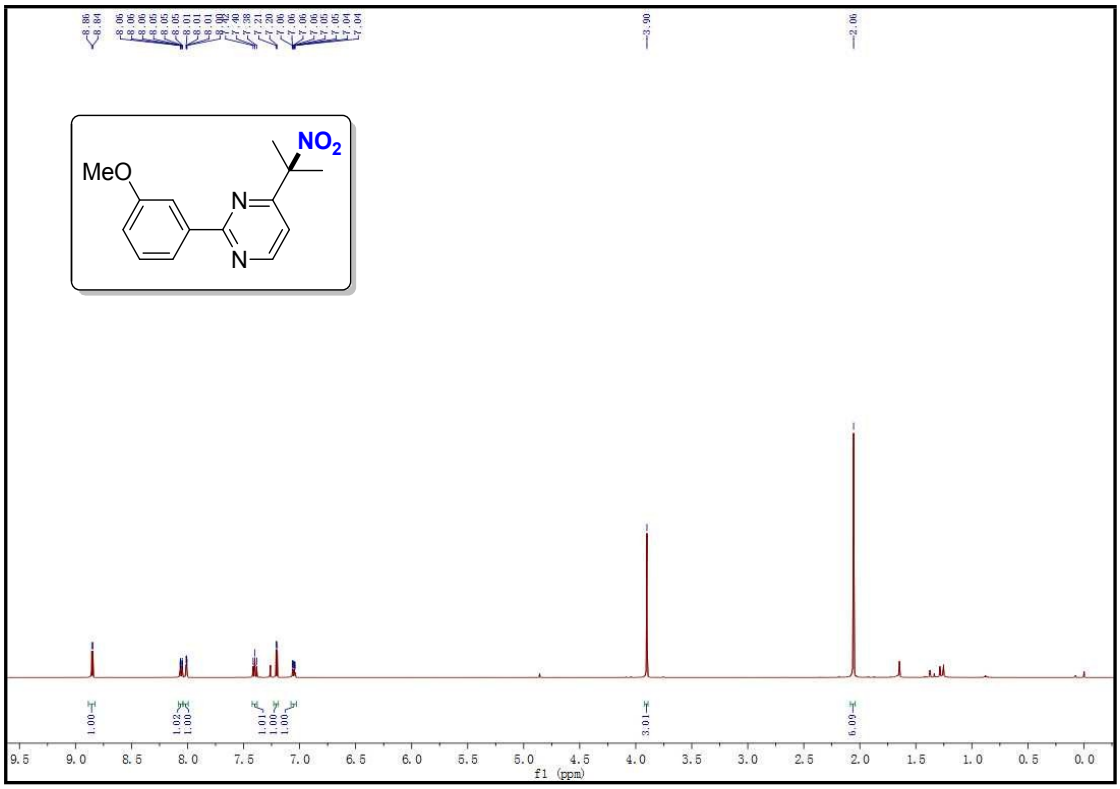


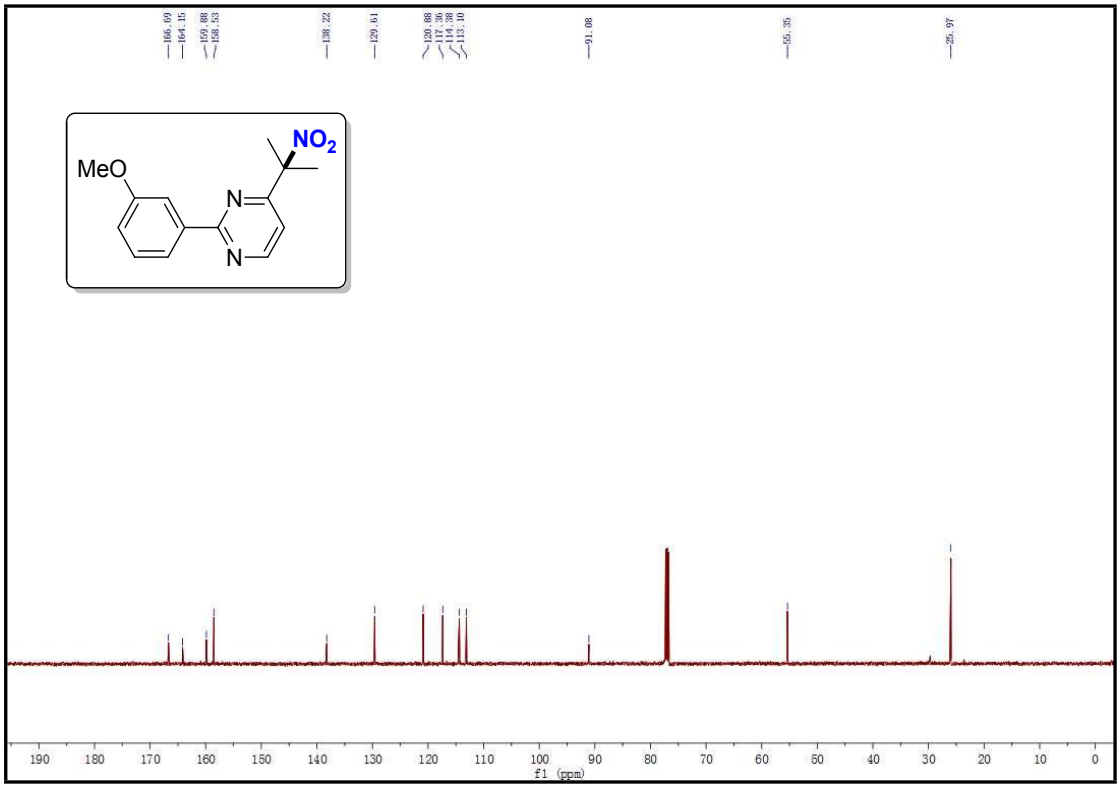
2-([1,1'-biphenyl]-4-yl)-4-(2-nitropropan-2-yl)pyrimidine (2c)



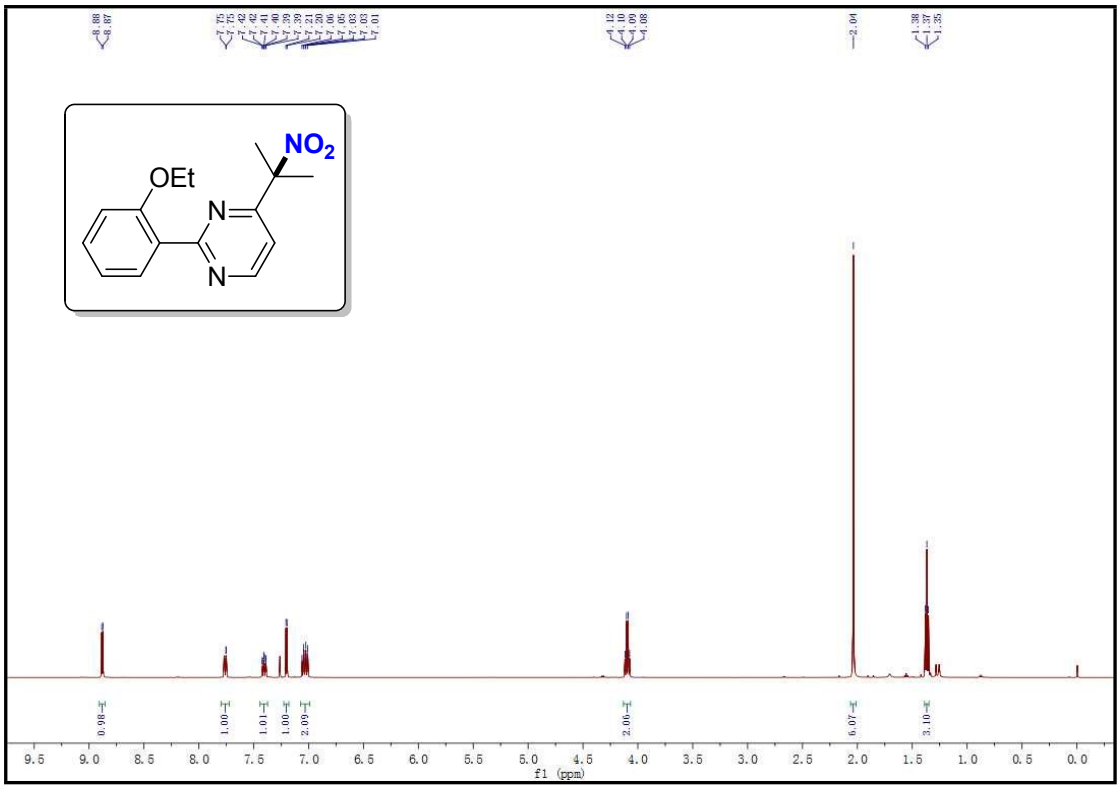


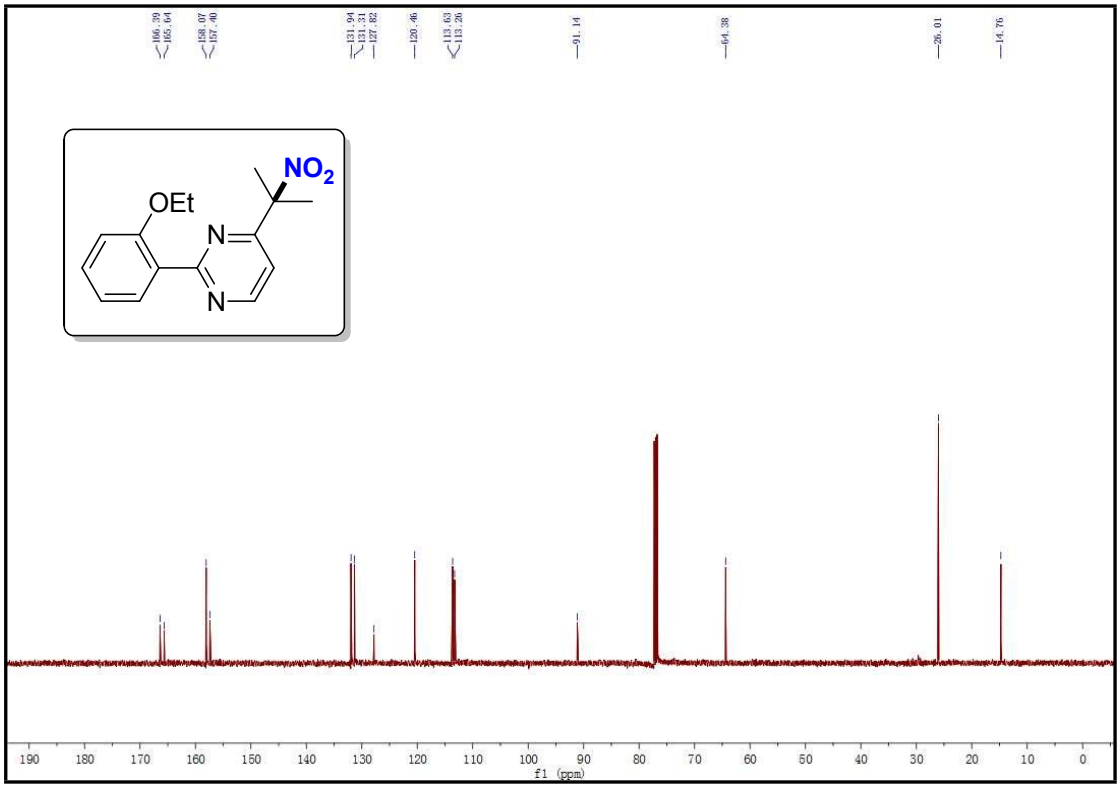
2-(3-methoxyphenyl)-4-(2-nitropropan-2-yl)pyrimidine (2d)



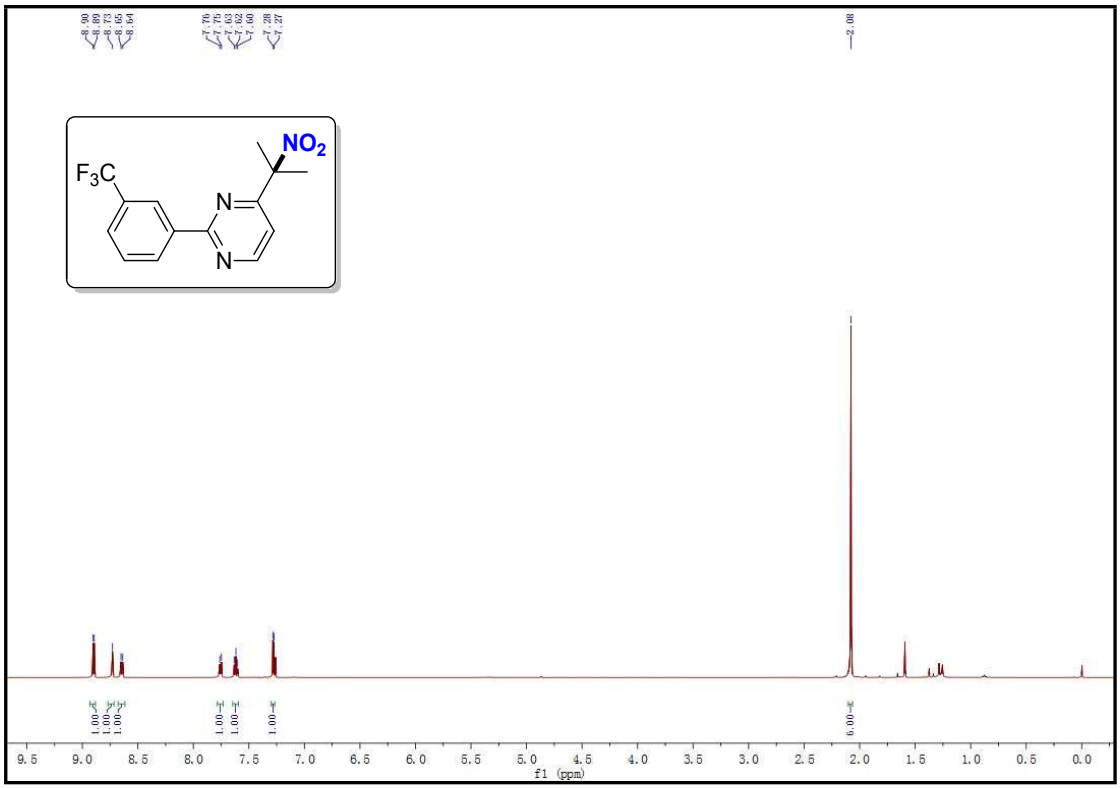


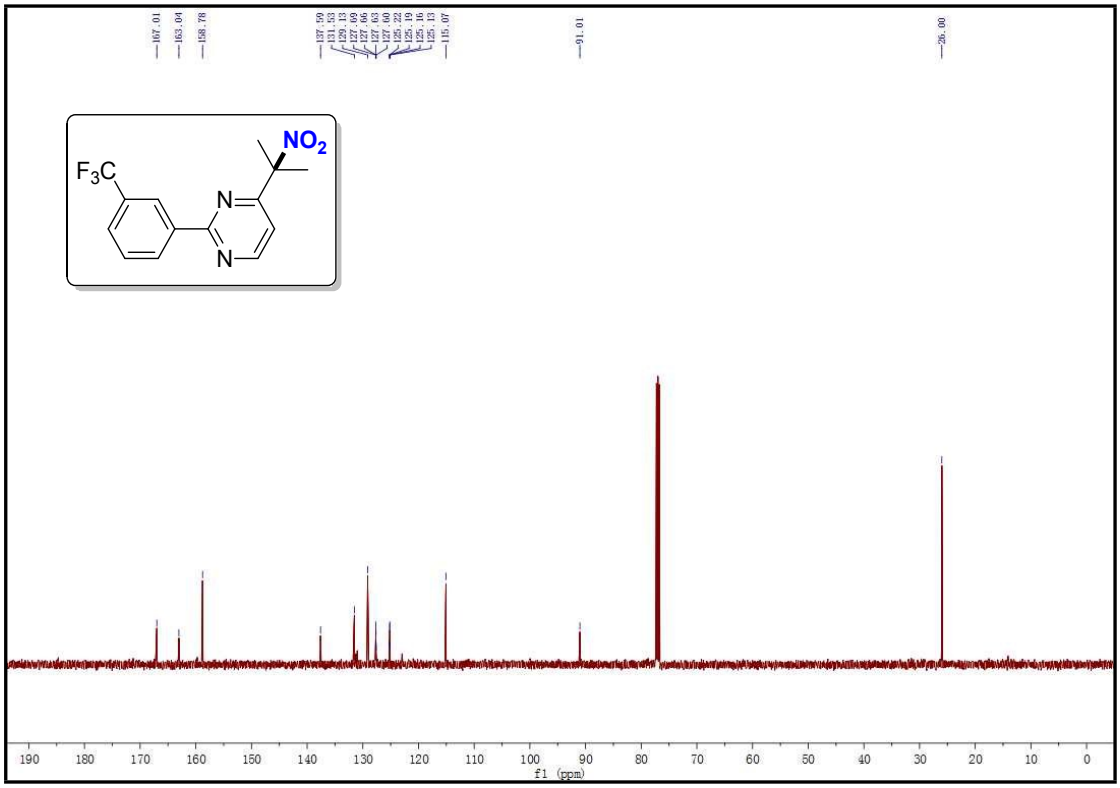
2-(2-ethoxyphenyl)-4-(2-nitropropan-2-yl)pyrimidine (2e)



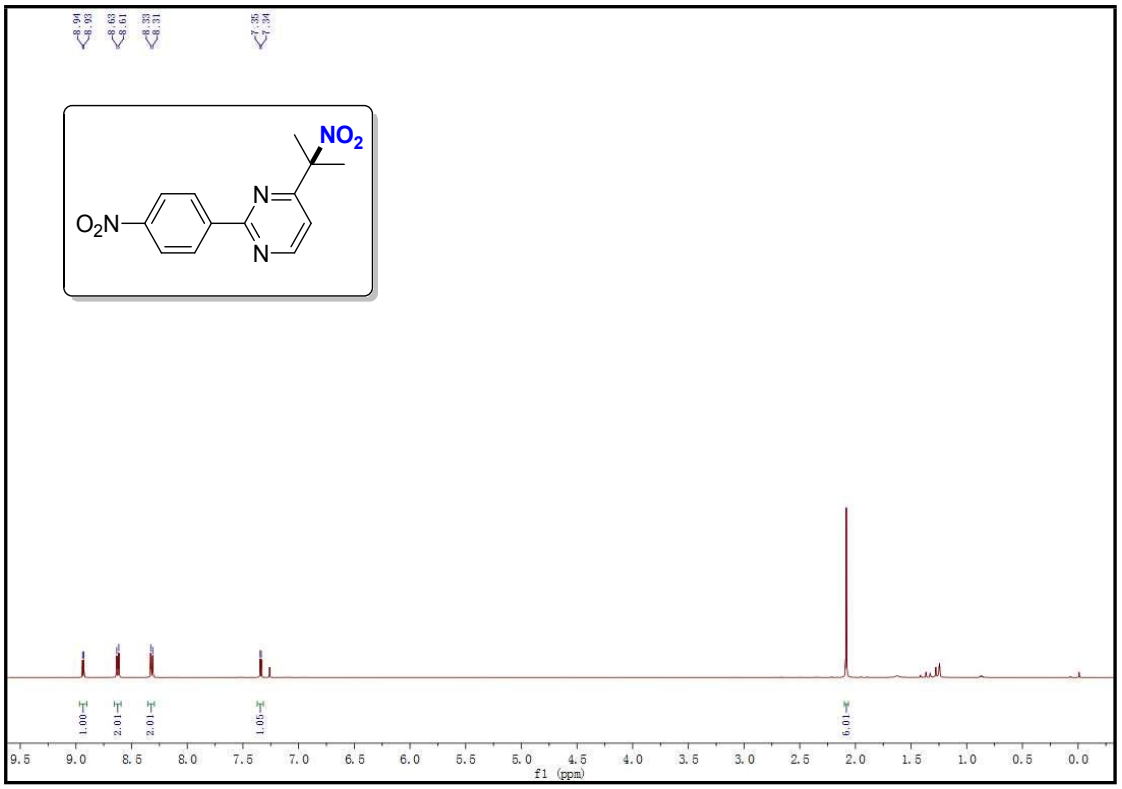


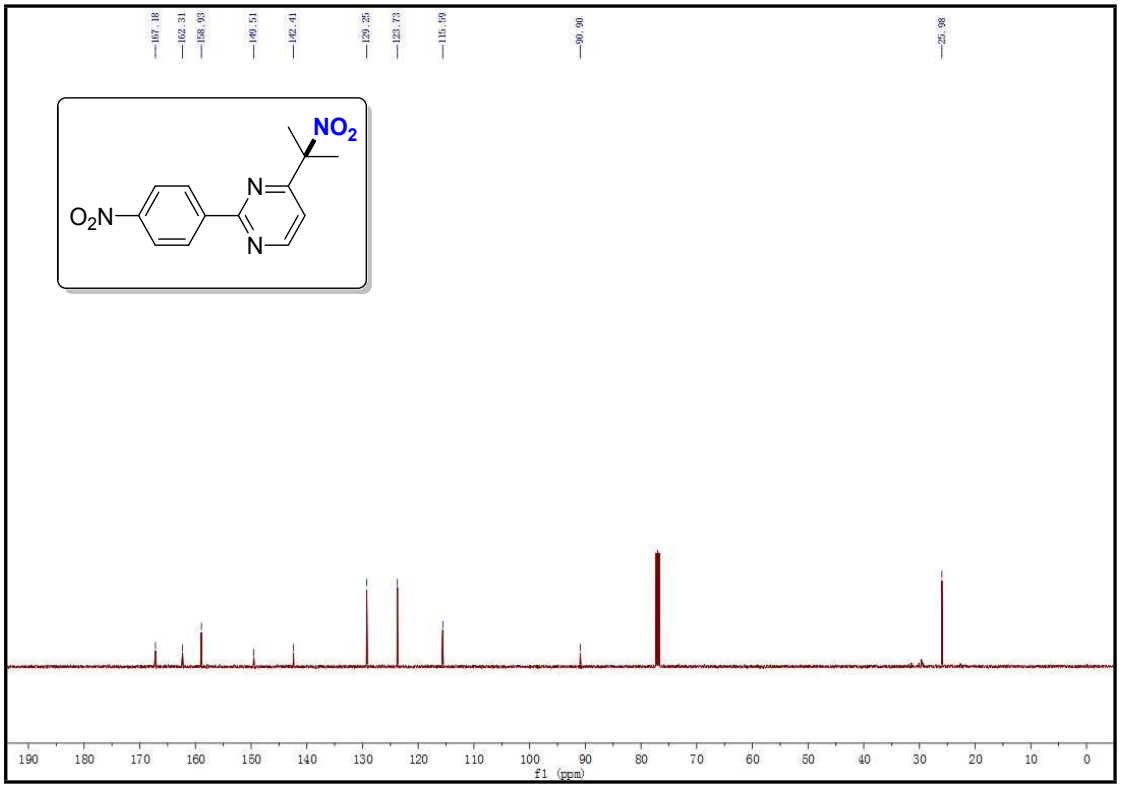
4-(2-nitropropan-2-yl)-2-(3-(trifluoromethyl)phenyl)pyrimidine (2f)



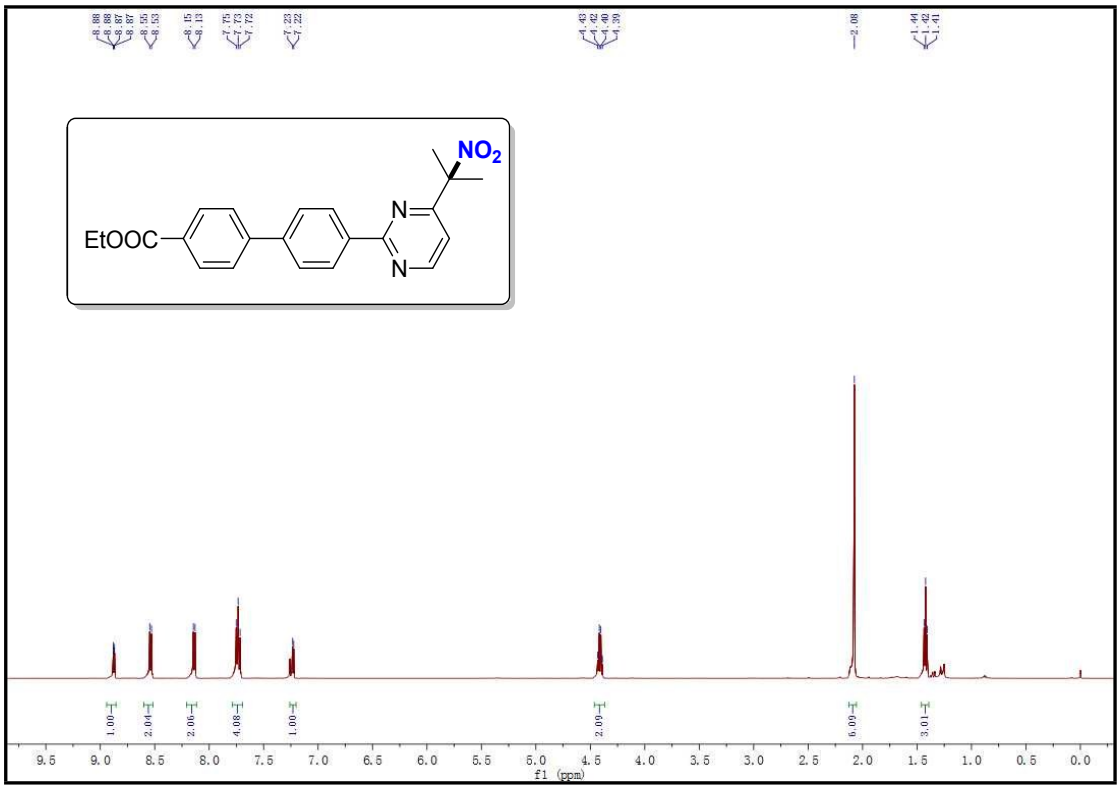


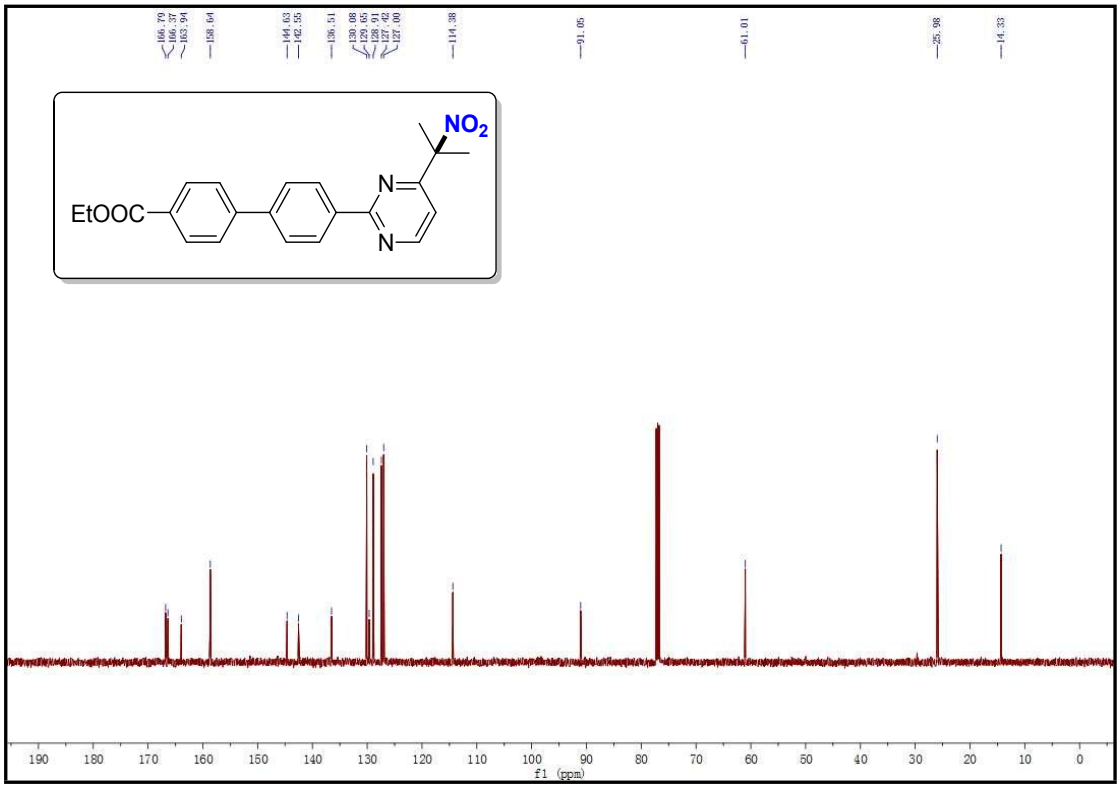
2-(4-nitrophenyl)-4-(2-nitropropan-2-yl)pyrimidine (2g)



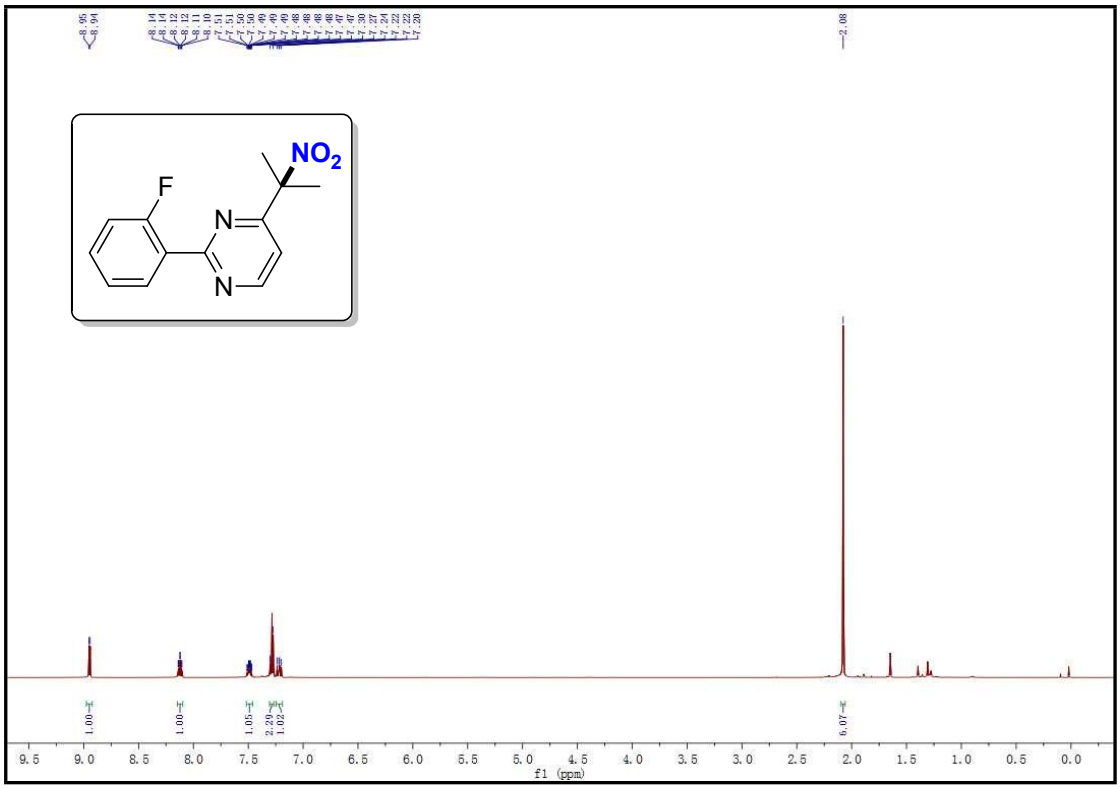


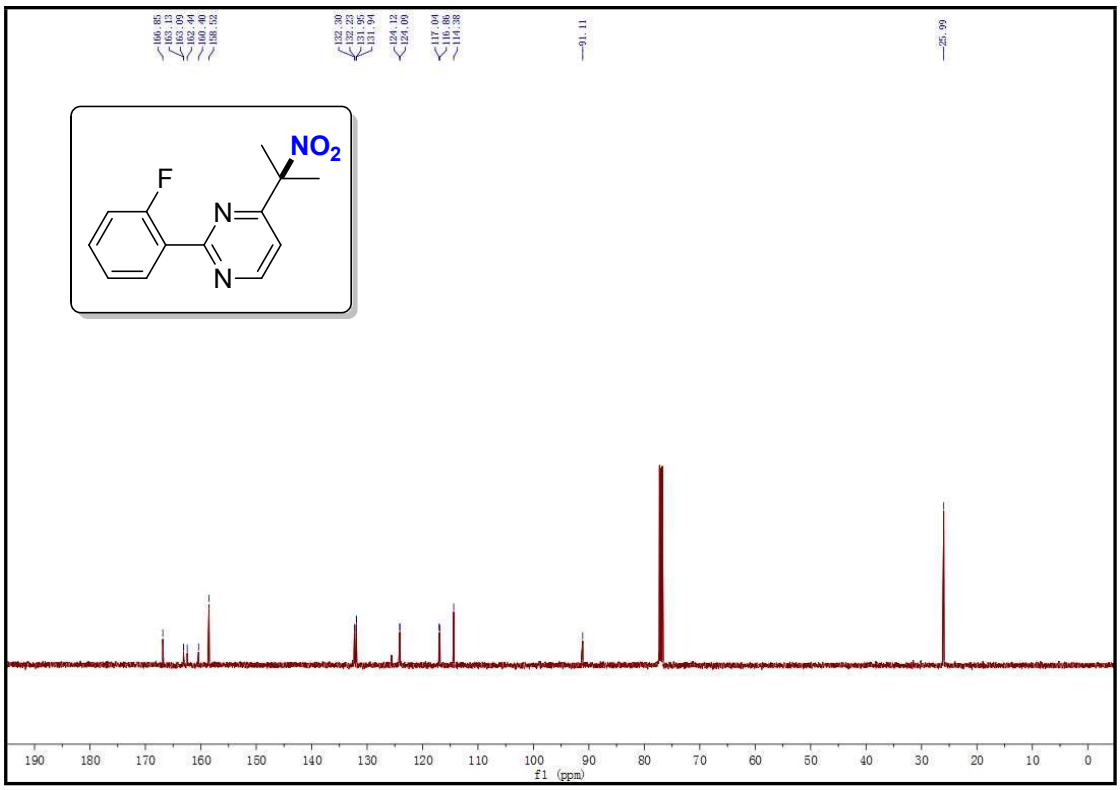
ethyl4'-(4-(2-nitropropan-2-yl)pyrimidin-2-yl)-[1,1'-biphenyl]-4-carboxylate (2h)



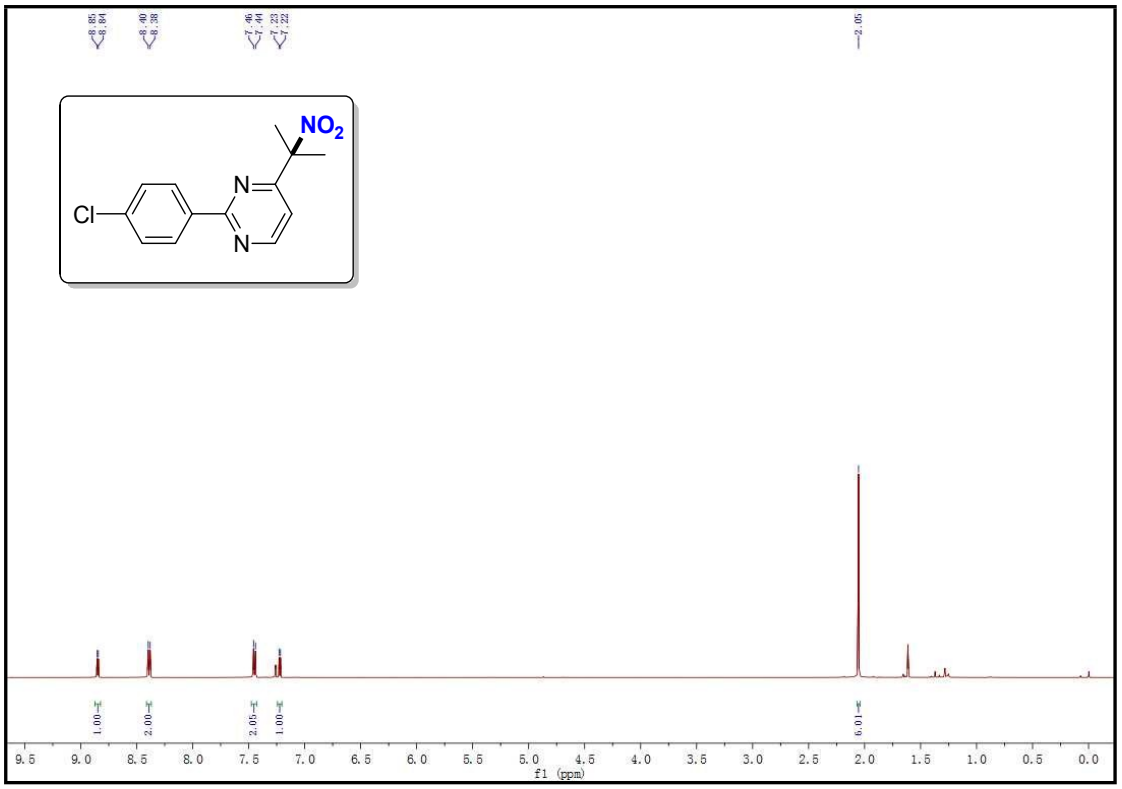


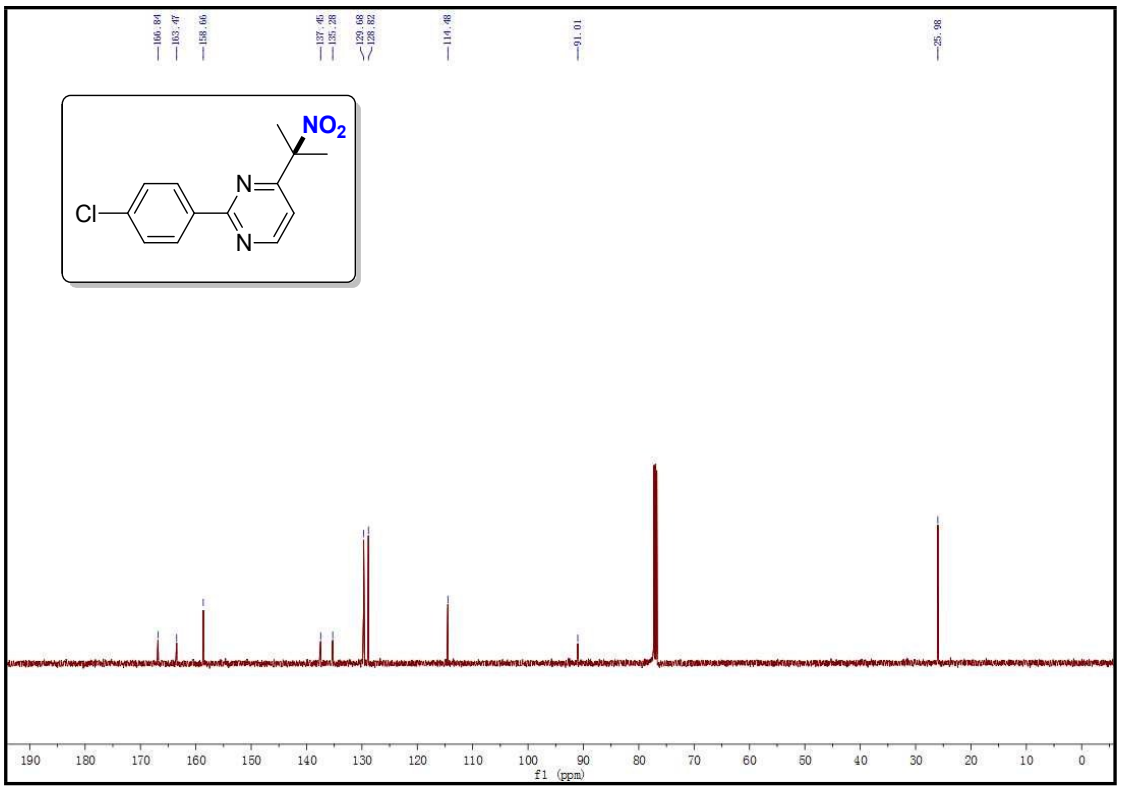
2-(4-chlorophenyl)-4-(2-nitropropan-2-yl)pyrimidine (2i)



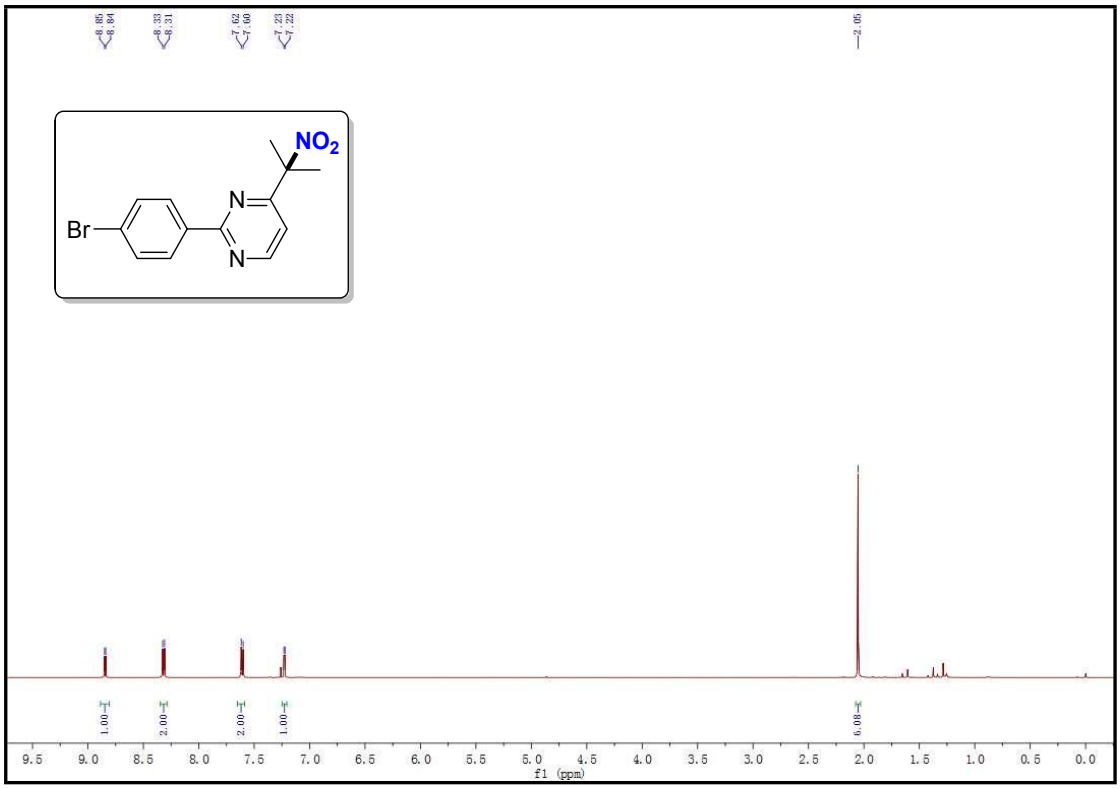


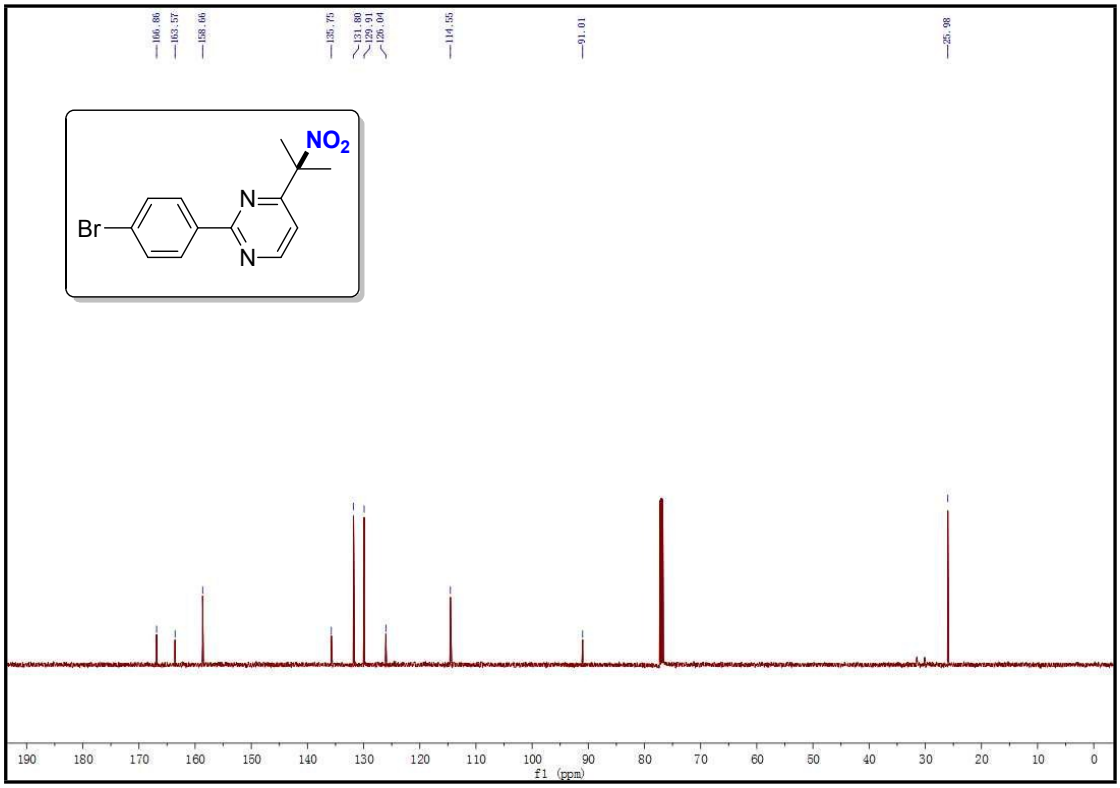
2-(4-chlorophenyl)-4-(2-nitropropan-2-yl)pyrimidine (2j)



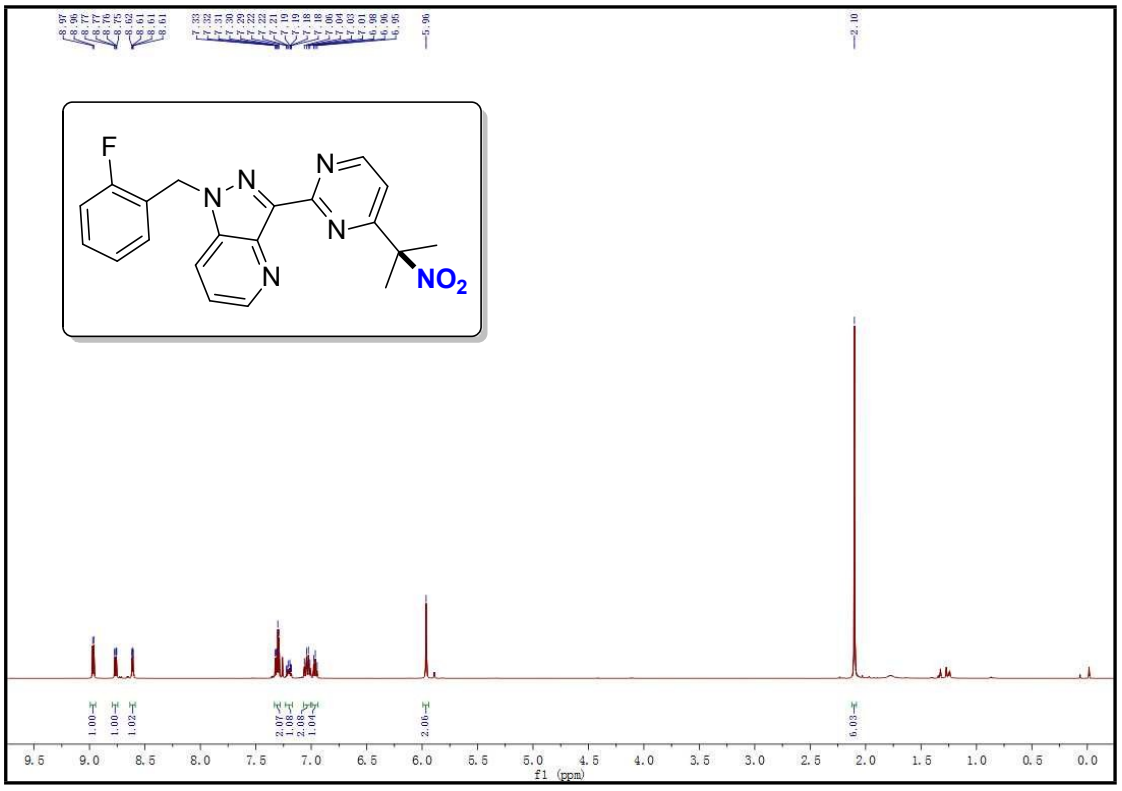


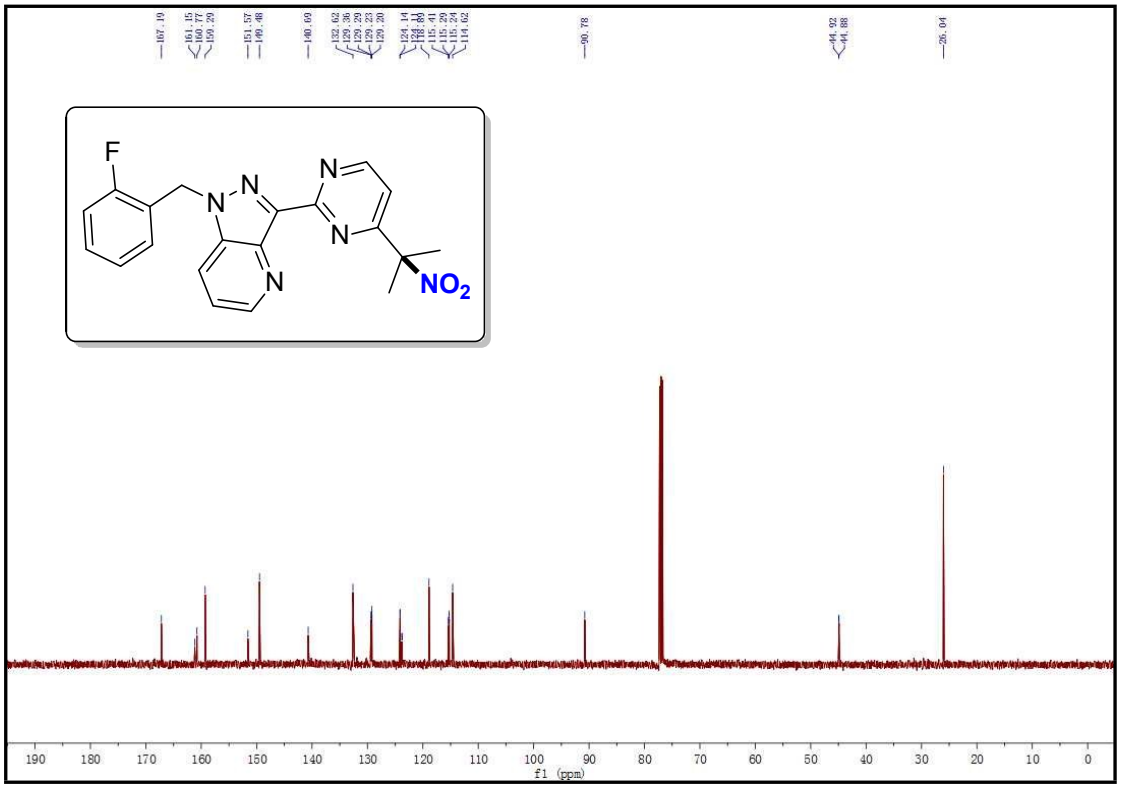
2-(4-bromophenyl)-4-(2-nitropropan-2-yl)pyrimidine (2k)



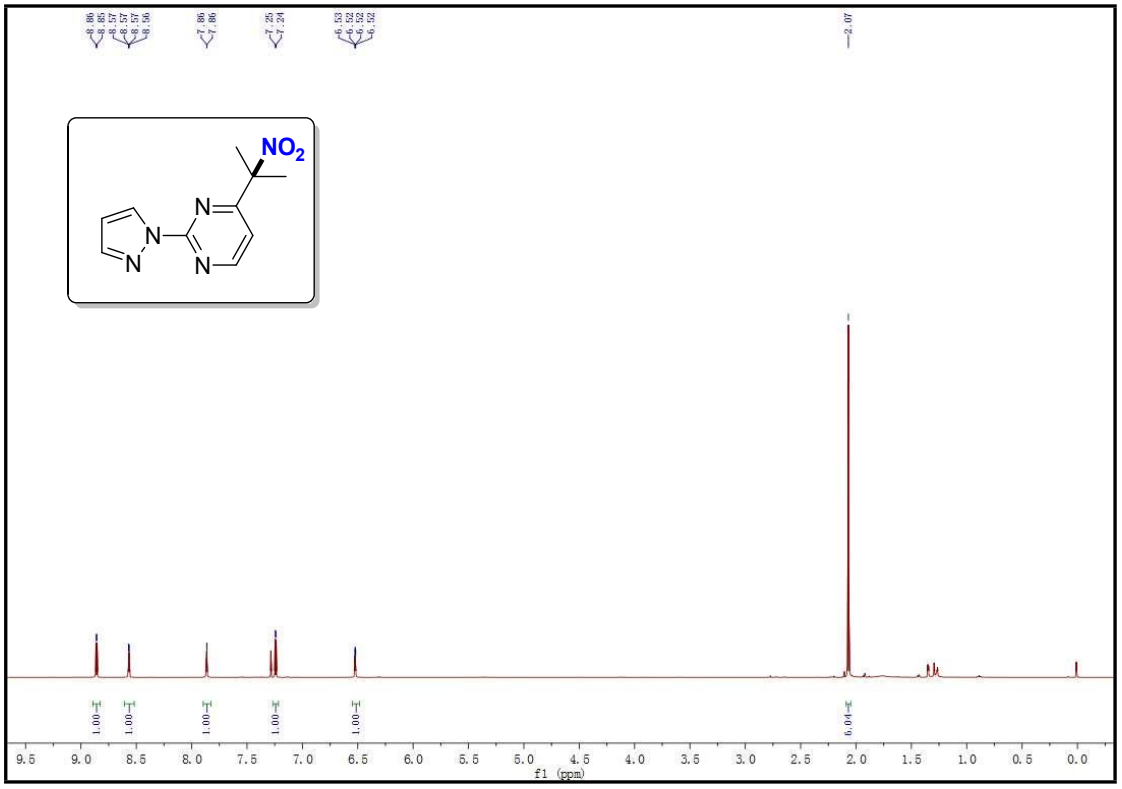


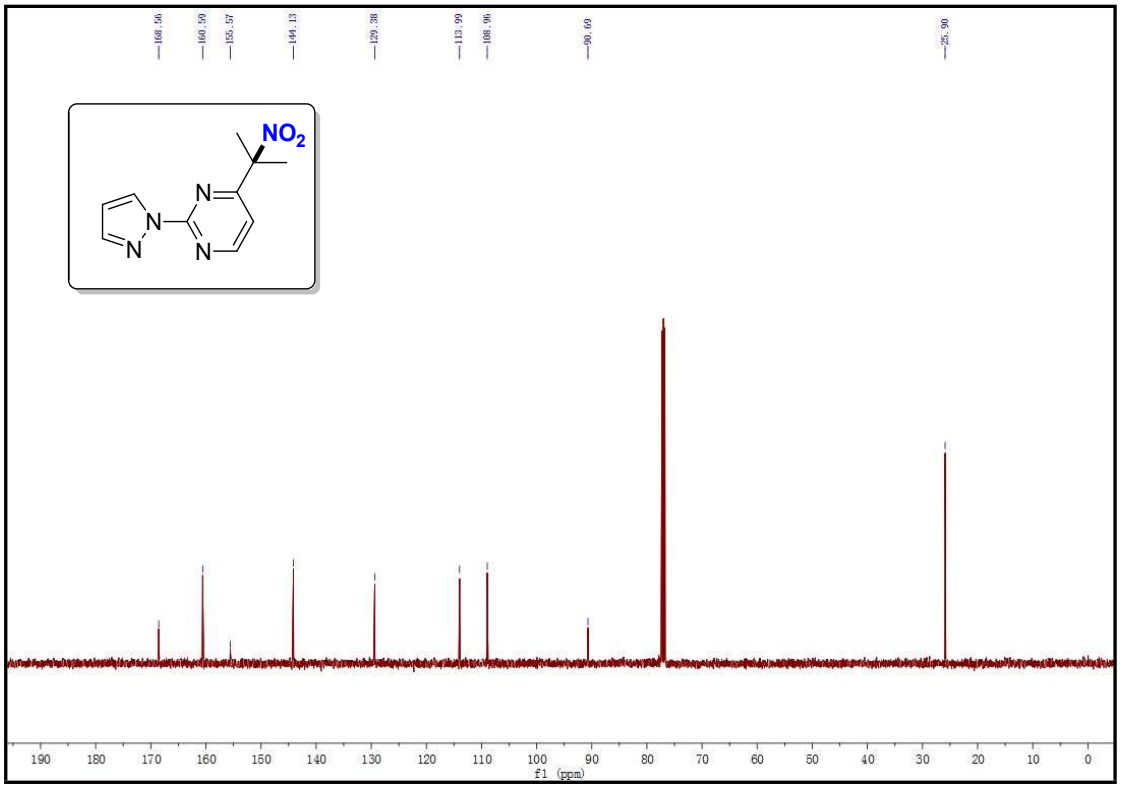
1-(2-fluorobenzyl)-3-(4-(2-nitropropan-2-yl)pyrimidin-2-yl)-1H-pyrazolo[4,3-b]pyridine (2l)



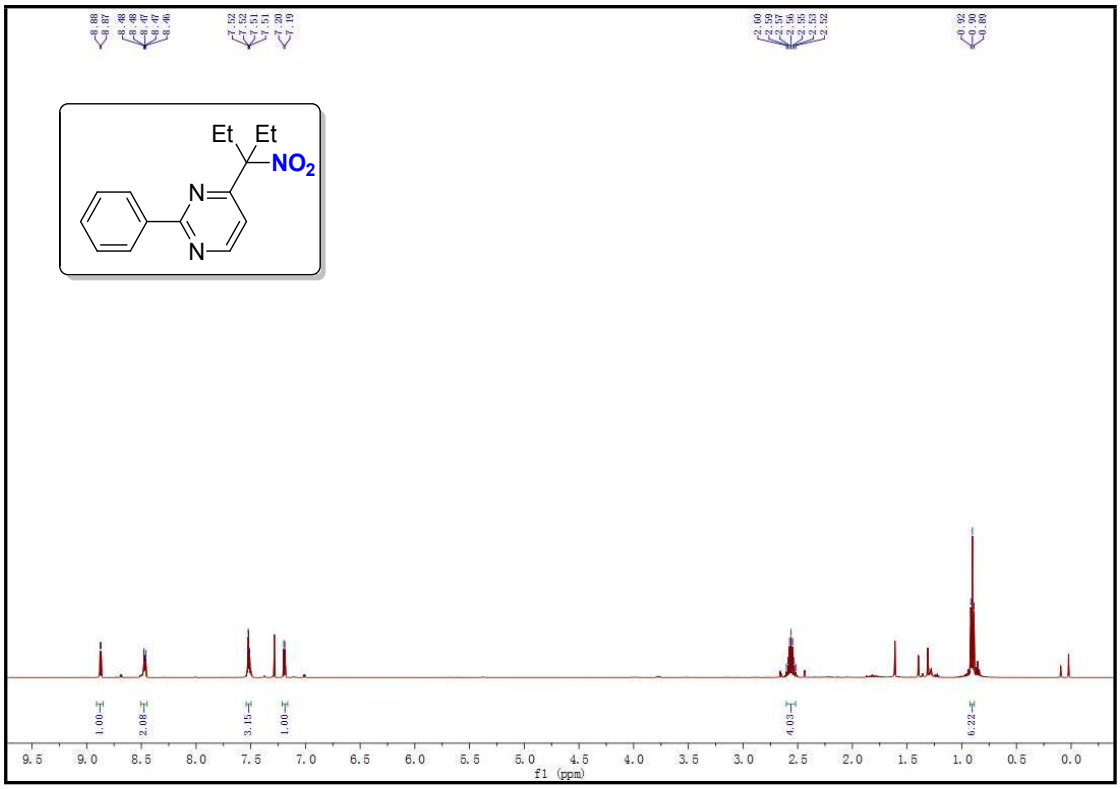


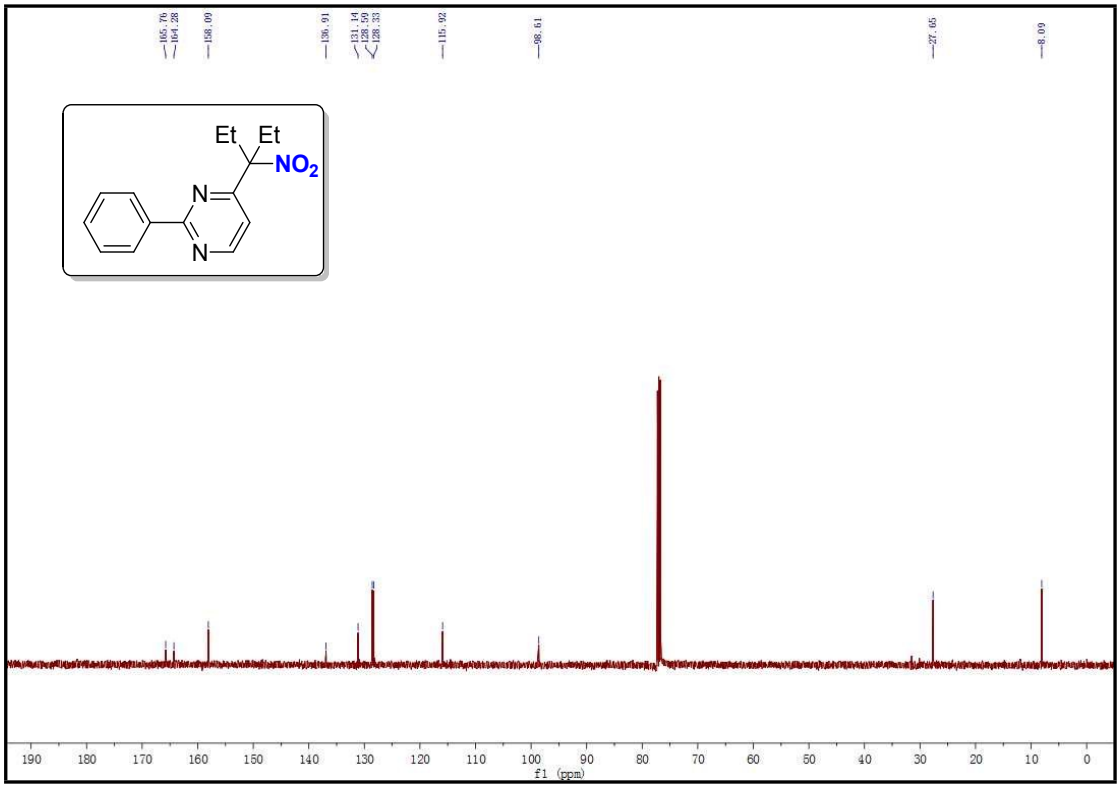
4-(2-nitropropan-2-yl)-2-(1H-pyrazol-1-yl)pyrimidine (2m)



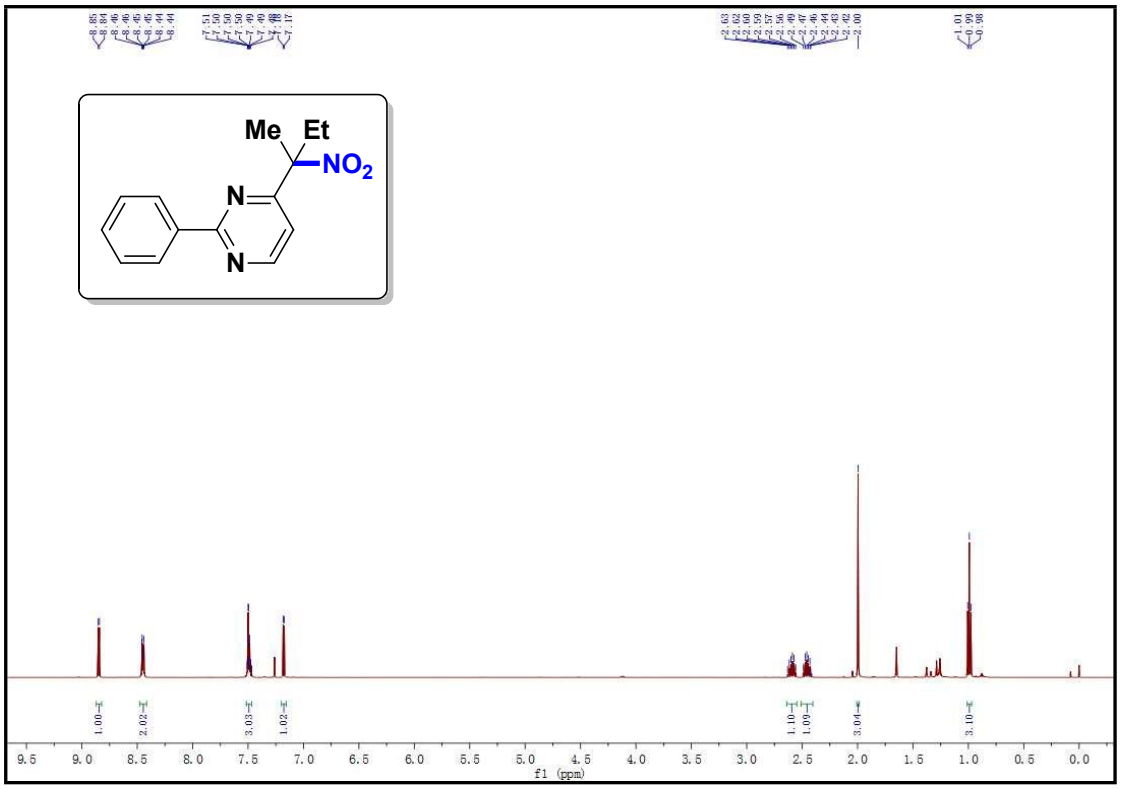


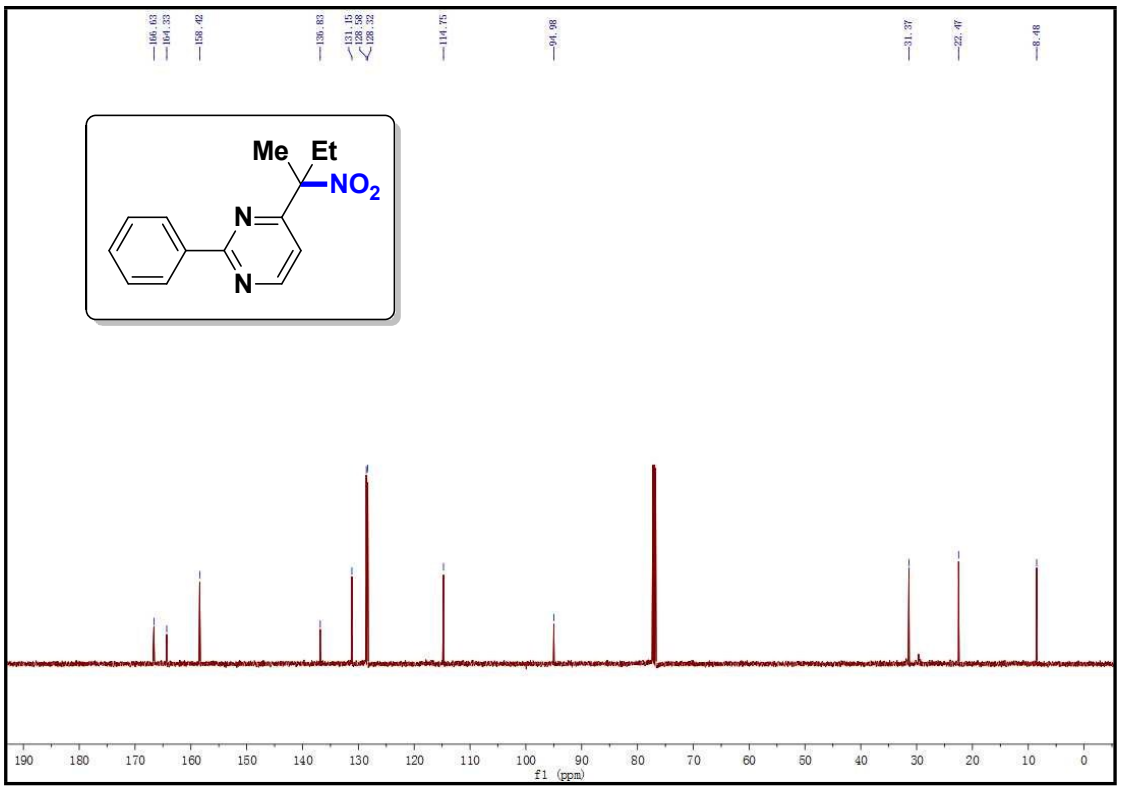
4-(3-nitropentan-3-yl)-2-phenylpyrimidine (2o)



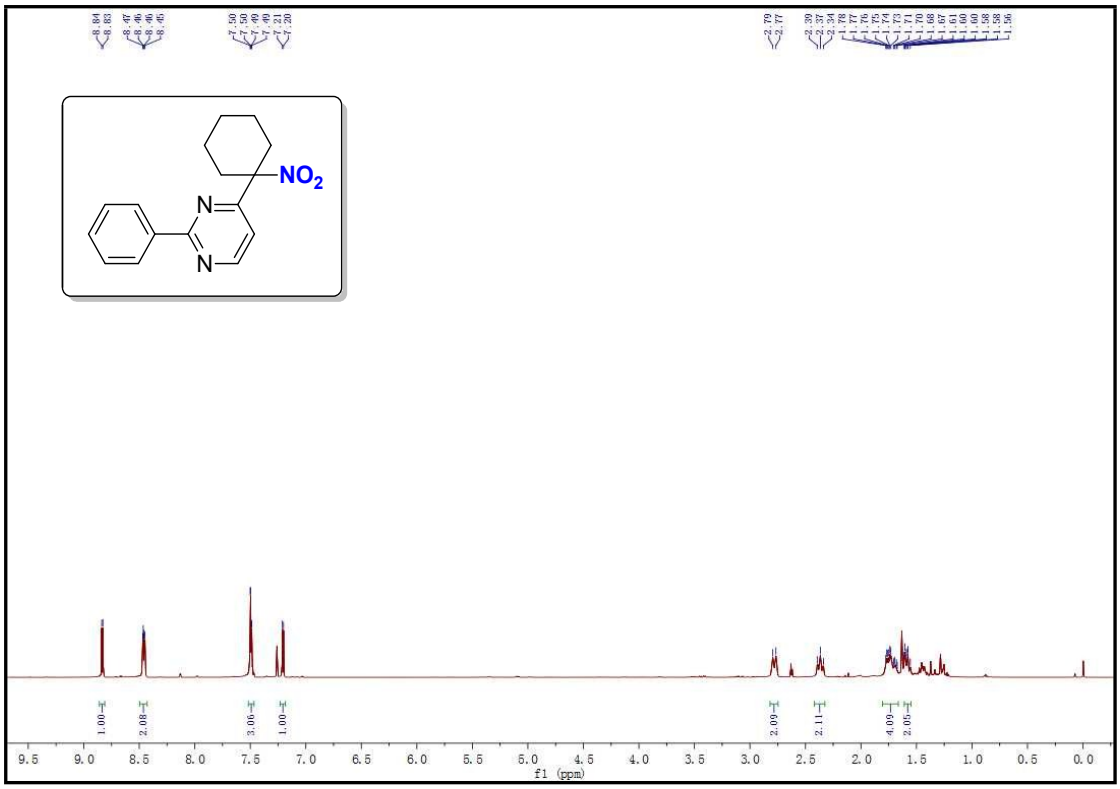


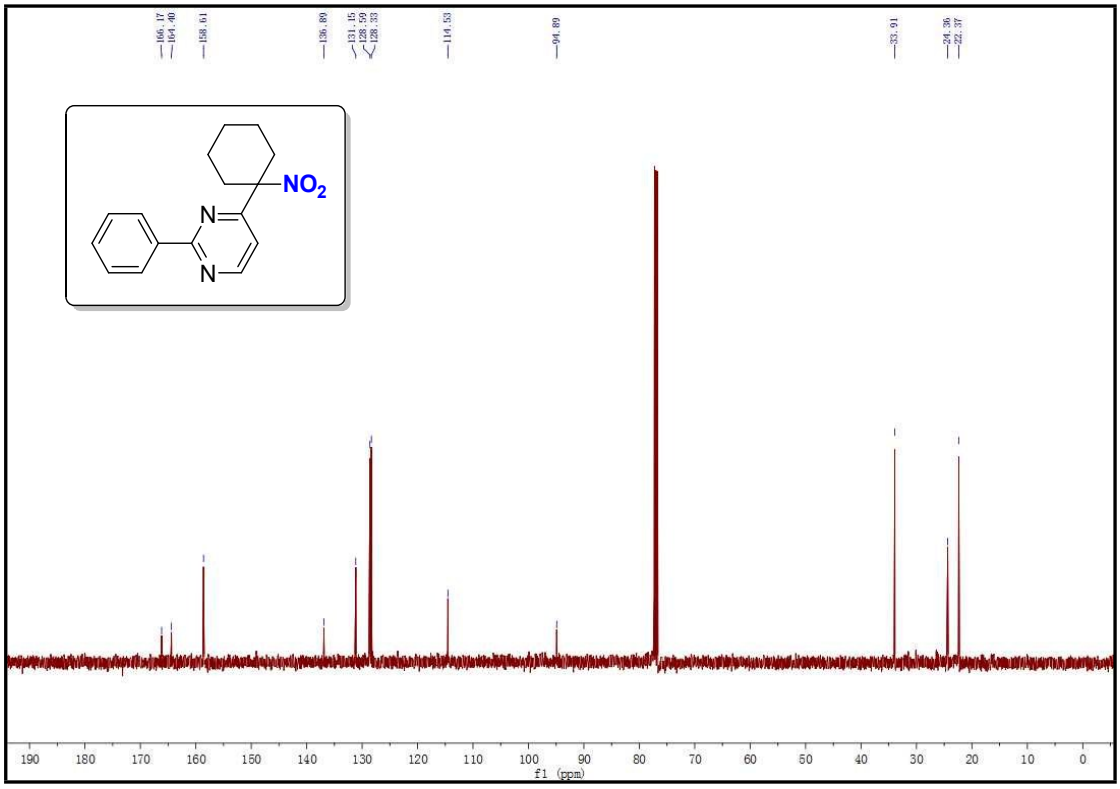
4-(2-nitrobutan-2-yl)-2-phenylpyrimidine (2p)



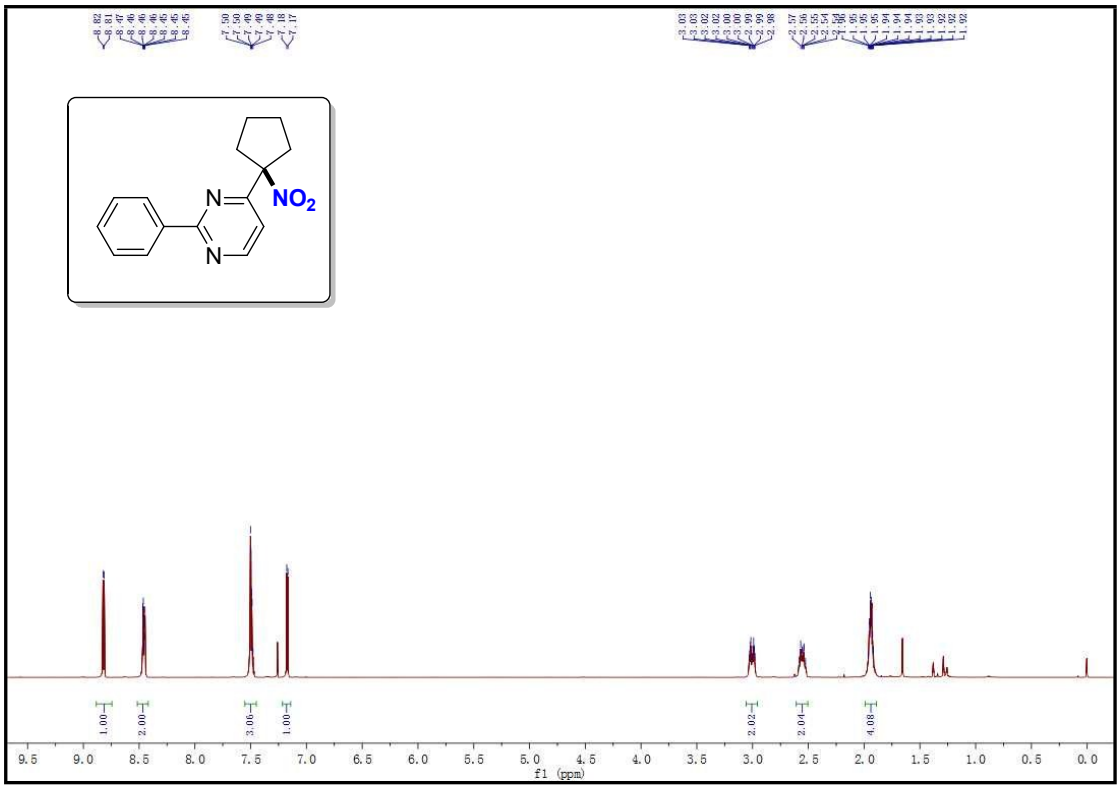


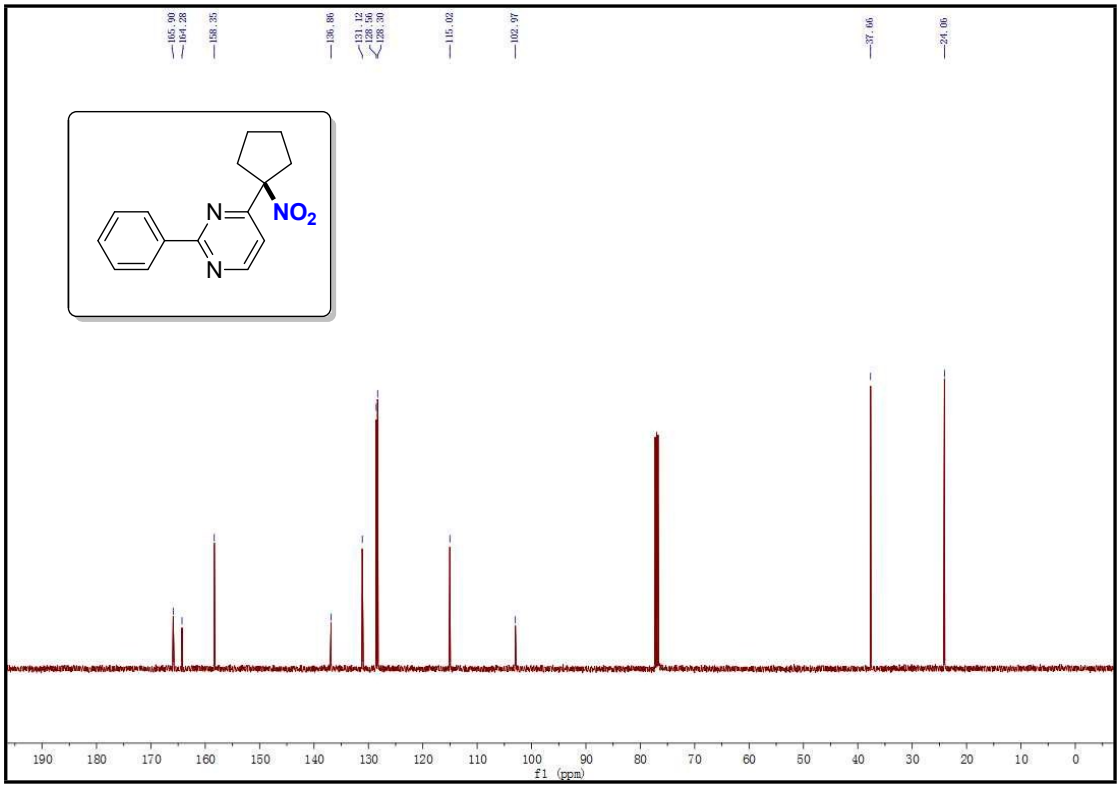
4-(1-nitrocyclohexyl)-2-phenylpyrimidine (2q)



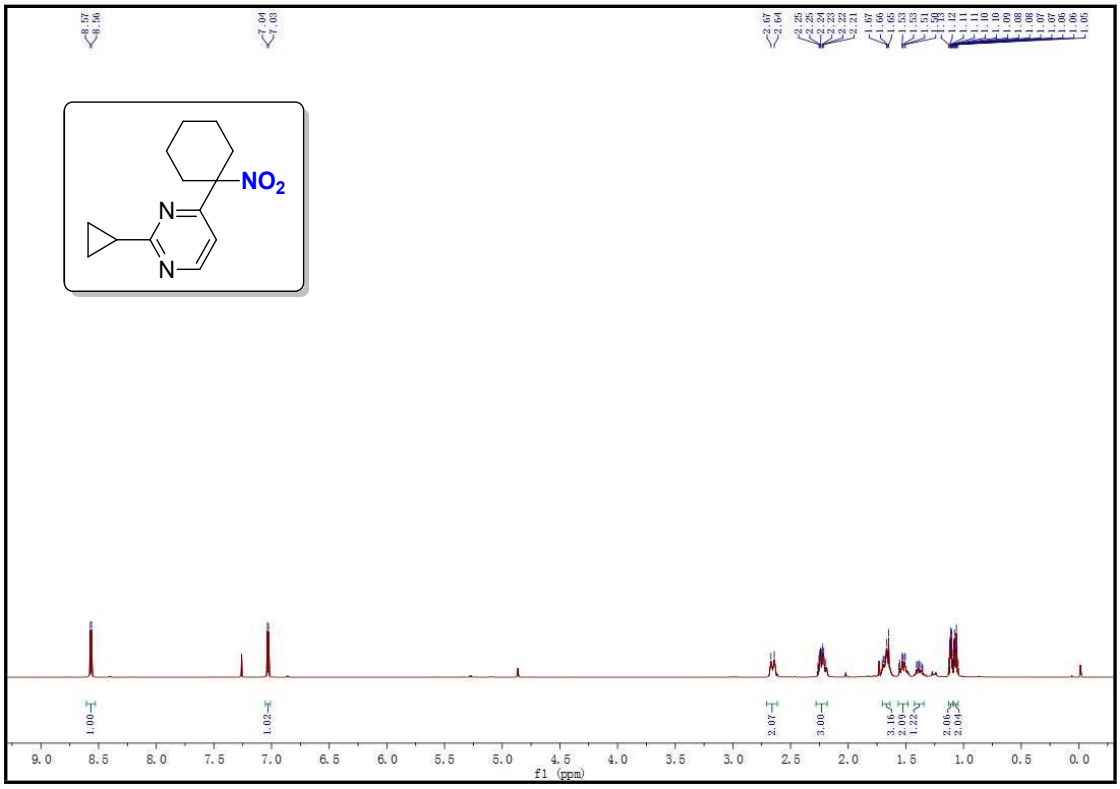


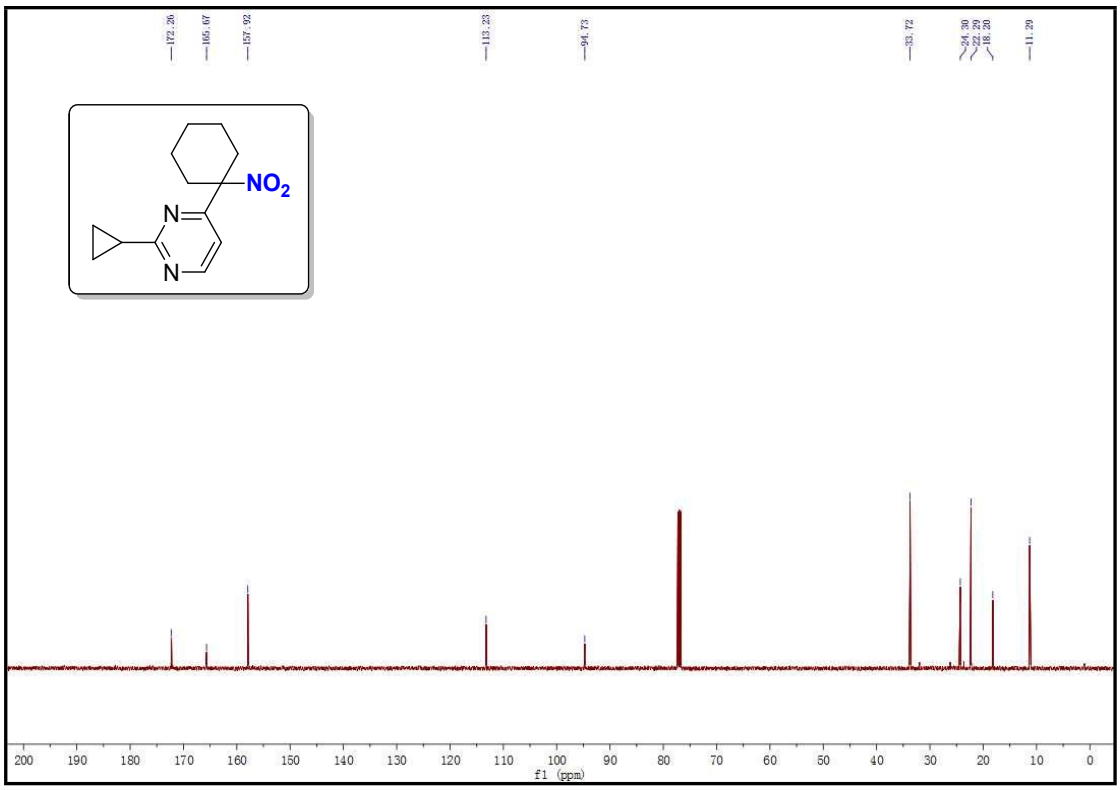
4-(1-nitrocyclopentyl)-2-phenylpyrimidine (2r)



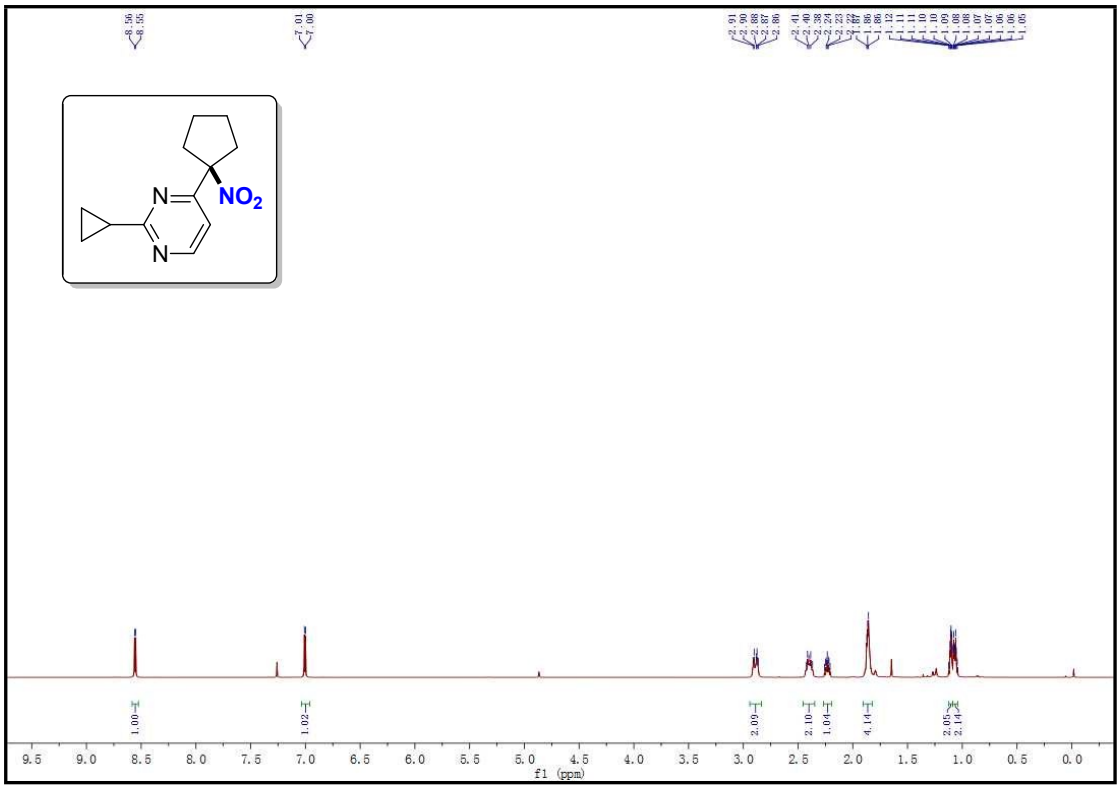


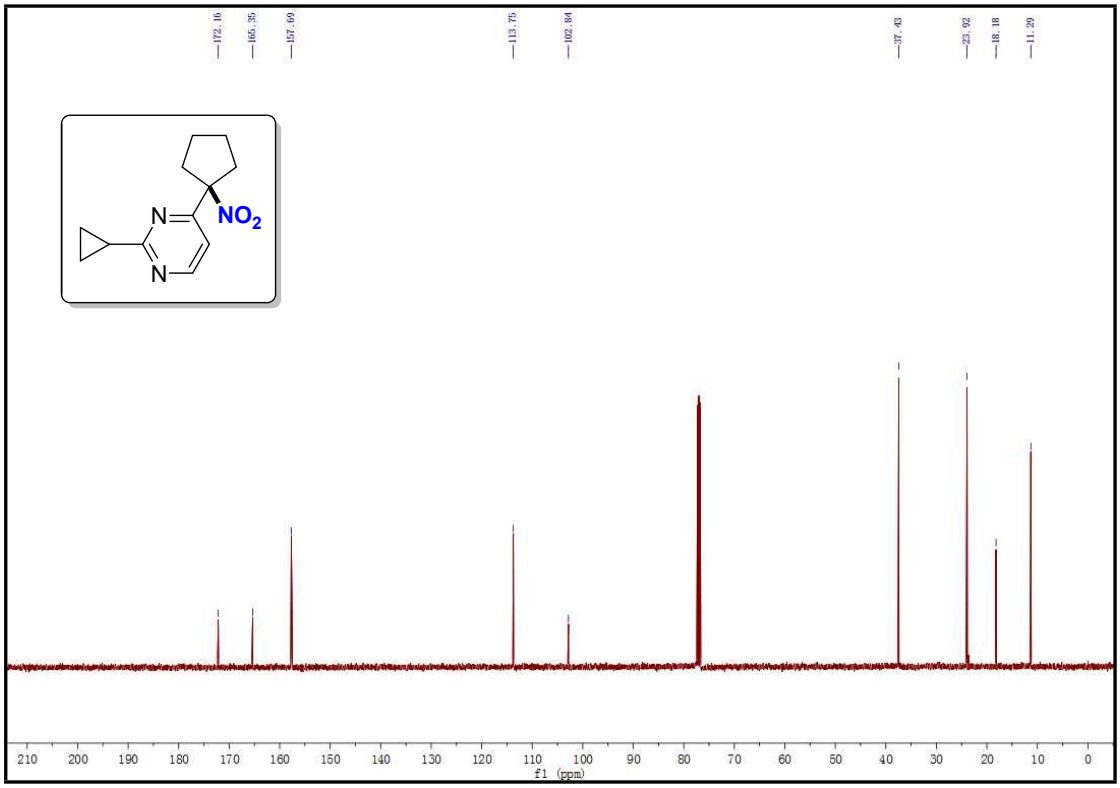
2-cyclopropyl-4-(1-nitrocyclohexyl)pyrimidine (2u)



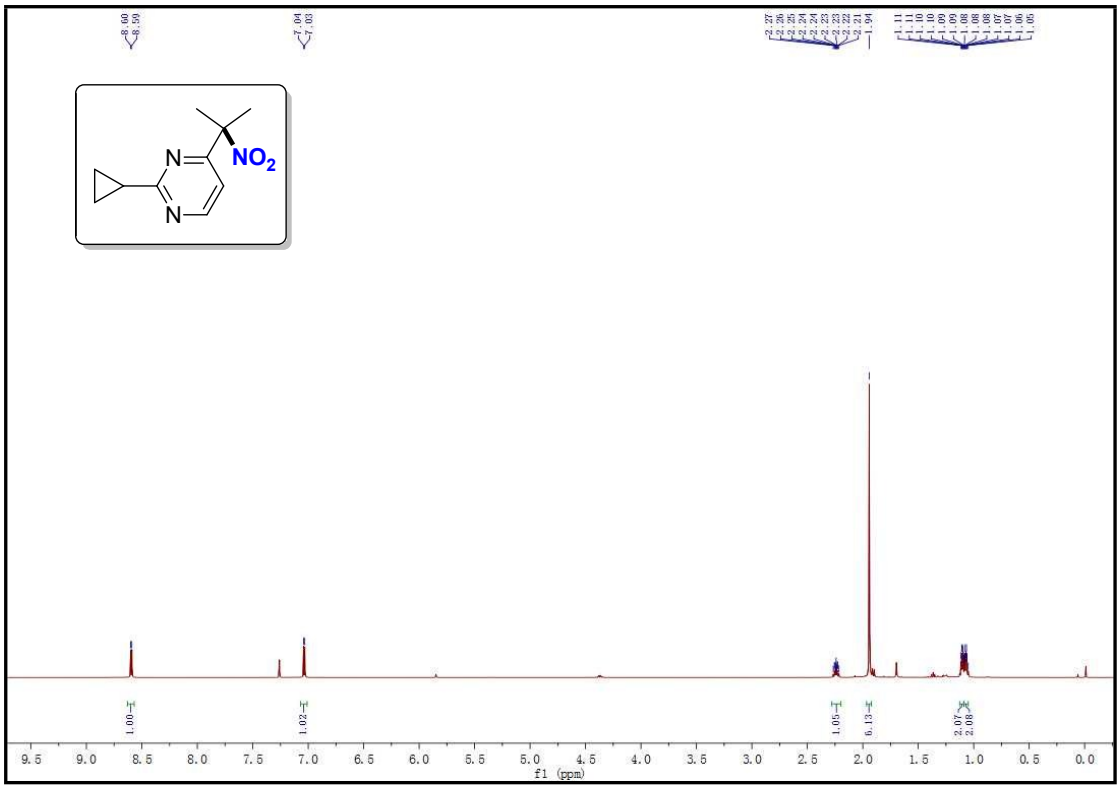


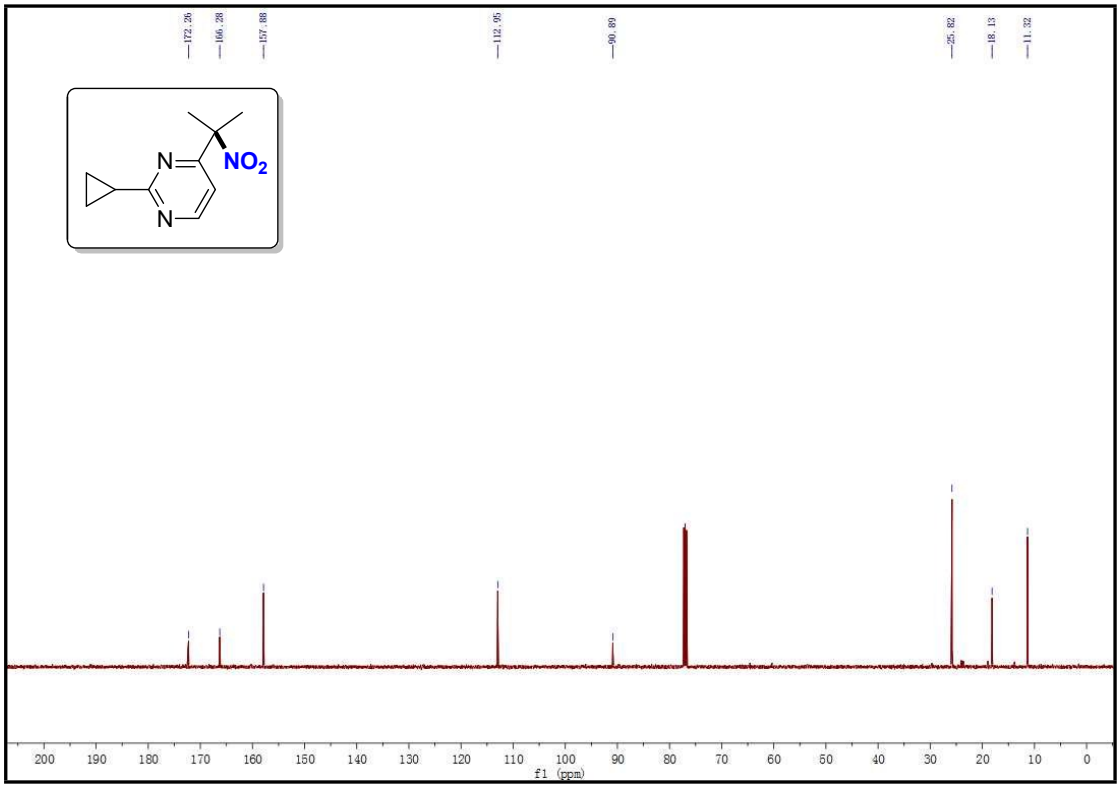
2-cyclopropyl-4-(1-nitrocyclopentyl)pyrimidine (2v)





2-cyclopropyl-4-(2-nitropropan-2-yl)pyrimidine(2w)





2-(2-cyclopropylpyrimidin-4-yl)propan-2-amine (6)