Supplementary Information

Divergent Synthesis of 1,3,5-Tri and 1,3-Disubstituted Pyrazoles under Transition Metal-Free Conditions

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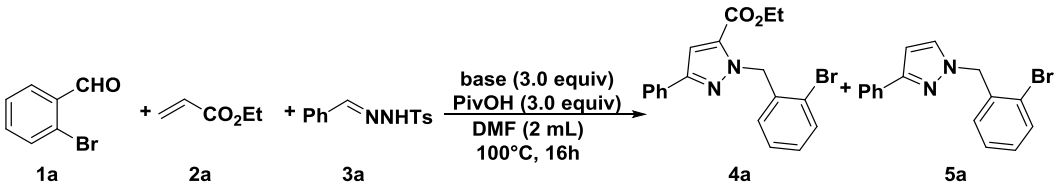
General information

Unless otherwise indicated, all glassware was oven dried by a heat gun before use and all reactions were performed under an atmosphere of Argon. All solvents were distilled from appropriate drying agents prior to use. All reagents were used as received from commercial suppliers unless otherwise stated. Arylvinyl N-tosylhydrazoneswere prepared according to the procedures reported in the literature. Reaction progress was monitored by thin layer chromatography (TLC). Visualization was achieved by ultraviolet light (254 nm). ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz and 101 MHz or spectrometer using $CDCl_3$ or as solvent and TMS as internal standard. The 1H NMR data are reported as the chemical shift in parts per million, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant in hertz, and number of protons. High resolution mass spectra were obtained using a high resolution ESI-TOF mass spectrometer.

Reaction Optimization

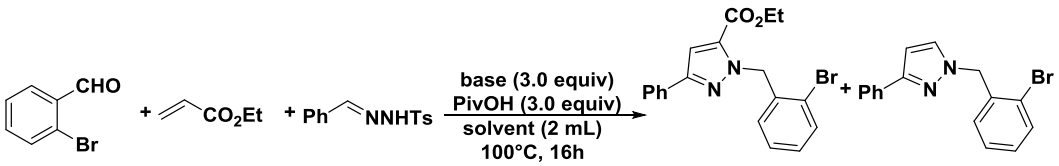


1a **2a** **3a** **4a** **5a**

1.0 equiv **2.0 equiv** **2.0 equiv**

entry	base	GC yield of **4a**[a]	GC yield of **5a**[a]
1	K_2CO_3	trace	54%
2	Na_2CO_3	22%	33%
3	Cs_2CO_3	trace	66%
4	K_3PO_4	46%	23%
5	NaO^tBu	36%	9%
6	LiOAc	39%	trace
7	CsOAc	58%	9%
8	CsF	61%	trace
9	NaOMe	50%	trace
10	NaOAc	52%	trace
11	KOAc	63%	trace
12	Et_3N	24%	0
13	DABCO	52%	0
14	DMAP	20%	0
15	DBU	54%	19%
16	pyridine	34%	0

[a]Yield determined by GC with decane as the internal standard, and isolated yields were indicated in parenthese.

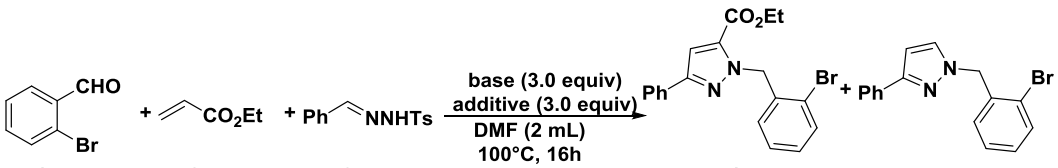


1a **2a** **3a** **4a** **5a**

1.0 equiv **2.0 equiv** **2.0 equiv**

entry	base	solvent	GC yield of **4a**[a]	GC yield of **5a**[a]
1	KOAc	DMA	60%	13%
2	KOAc	DME	16%	trace
3	KOAc	DMSO	39%	18%
4	KOAc	DMF	63%	9%
5	Cs_2CO_3	DMA	9%	60%
6	Cs_2CO_3	DME	12%	47%
7	Cs_2CO_3	DMSO	trace	42%
8	Cs_2CO_3	THF	9%	37%
9	Cs_2CO_3	CH_3CN	36%	27%
10	Cs_2CO_3	dioxane	trace	21%
11	Cs_2CO_3	DCE	10%	trace
12	Cs_2CO_3	toluene	trace	trace
13	Cs_2CO_3	CH_3OH	0	trace
14	Cs_2CO_3	DMF	trace	66%

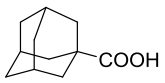
[a]Yield determined by GC with decane as the internal standard, and isolated yields were indicated in parenthese.



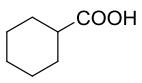
1a **2a** **3a** **4a** **5a**

1.0 equiv **2.0 equiv** **2.0 equiv**

entry	base	additive	GC yield of **4a**[a]	GC yield of **5a**[a]
1	K_2CO_3	--	trace	11%
2	K_2CO_3	A1	27%	20%
3	K_2CO_3	A2	21%	33%
4	K_2CO_3	A3	trace	trace
5	K_2CO_3	A4	trace	trace
6	K_2CO_3	PivOH	trace	54%
7	Cs_2CO_3	A2	12%	55%
8	Cs_2CO_3	PivOH	trace	66%
9[c]	Cs_2CO_3	PivOH	trace	69%
10[b]	Cs_2CO_3	HCOOH	14%	trace
11[b]	Cs_2CO_3	HOAc	8%	47%
12[b,c]	**Cs_2CO_3**	**PivOH**	**trace**	**73(71)%**
13	KOAc	A2	55%	9%
14[b]	KOAc	TsOH	trace	0
15[b]	KOAc	HCl	0	0
16[b]	KOAc	HCOOH	8%	0
17[b]	KOAc	HOAc	49%	trace
18	KOAc	PivOH	63%	9%
19[b]	**KOAc**	**PivOH**	**85(83)%**	**trace**



A1



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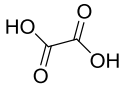

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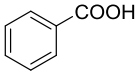


A4

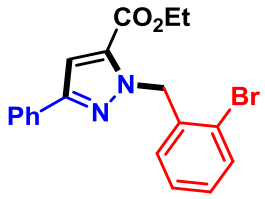
[a]Yield determined by GC with decane as the internal standard, and isolated yields were indicated in parenthese, [b]additive (4.0 equiv), [c]T=120°C.

General procedure

General procedure for preparation of 1,3,5-trisubstituted pyrazoles 4:

An oven-dried Schlenk tube under argon atmosphere was charged with 2-bromobenzaldehyde **1a** (0.2 mmol, 1.0 equiv), ethyl acrylate **2a** (0.4 mmol, 2.0 equiv), phenylhydrazone **3a** (0.4 mmol, 2.0 equiv), KOAc (0.60 mmol, 3.0 equiv), PivOH (0.8 mmol, 4.0 equiv) and DMF (2 mL). The mixture was stirred at 100 ℃ and the progress of the reaction was monitored by TLC. Upon completion, the resulting mixture was cooled to room temperature and added 10 mL of H_2O to quench the reaction, and then extracted with ethyl acetate (20 mL×3). The solvents were evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel to afford the products.

Ethyl 1-(2-bromobenzyl)-3-phenyl-1H-pyrazole-5-carboxylate (4a)



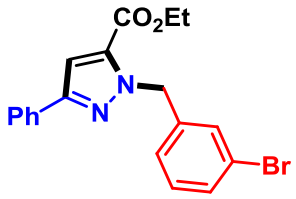
Yield：83% (63.7 mg); white solid; R_f = 0.25 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.85 (d, J = 7.6 Hz, 2H), 7.57 (dd, J_1 = 7.6 Hz, J_2 = 0.8 Hz, 1H), 7.42 (t, J = 7.2 Hz, 2H), 7.34 (t, J = 7.6 Hz, 1H), 7.28 (s, 1H), 7.17 – 7.09, (m, 2H), 6.47 (d, J = 7.6 Hz, 1H), 5.89 (s, 2H), 4.30 (q, J = 7.2 Hz, 2H), 1.31 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ= 159.2, 150.7, 137.1, 134.3, 132.5, 132.3, 128.73, 128.68, 128.2, 127.7, 126.9, 125.6, 121.6, 108.6, 61.3, 55.6, 14.1.

HRMS (ESI)：m/z calcd for $C_{19}H_{18}BrN_2O_2^+$ $(M+H)^+$ 385.05462, found 385.05481.

Ethyl 1-(3-bromobenzyl)-3-phenyl-1H-pyrazole-5-carboxylate (4b)



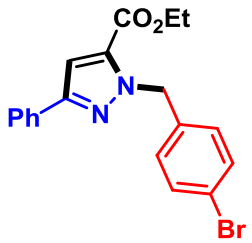
Yield: 48% (37.2 mg); yellow liquid; R_f = 0.33 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.83 (d, *J* = 7.2 Hz, 2H), 7.43-7.31 (m, 5H), 7.24 – 7.13 (m, 3H), 5.76 (s, 2H), 4.32 (q, *J* = 7.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=159.5, 150.5, 139.3, 133.4, 132.3, 130.8, 130.5, 130.0, 128.7, 128.2, 126.1, 125.6, 122.5, 108.6, 61.2, 54.4, 14.2.

HRMS (ESI)：m/z calcd for $C_{19}H_{18}BrN_2O_2^+$ $(M+H)^+$ 385.05462, found 385.05481.

Ethyl 1-(4-bromobenzyl)-3-phenyl-1H-pyrazole-5-carboxylate (4c)



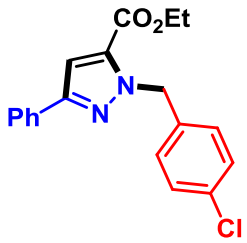
Yield 60% (45.7 mg); white solid; R_f = 0.33 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.83 (d, *J* = 7.6 Hz, 2H), 7.43 – 7.39 (m, 4H), 7.35 – 7.29 (m, 1H), 7.9-7.17 (m, 3H), 5.74 (s, 2H), 4.31 (q, *J* = 7.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=159.5, 150.4, 136.1, 133.3, 132.3, 131.6, 129.3, 128.7, 128.1, 125.6, 121.6, 108.5, 61.1, 54.4, 14.2.

HRMS (ESI)：m/z calcd for $C_{19}H_{18}BrN_2O_2^+$ $(M+H)^+$ 385.05462, found 385.05499.

Ethyl 1-(4-chlorobenzyl)-3-phenyl-1H-pyrazole-5-carboxylate (4d)

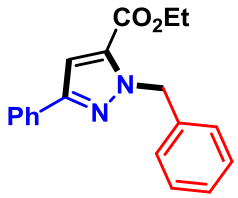


Yield 56% (38.4 mg); light yellow solid; R_f = 0.23 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.83 (d, *J* = 7.2 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.27 – 7.22 (m, 4H), 7.17 (s, 1H), 5.76 (s, 2H), 4.31 (q, *J* = 7.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=159.5, 150.4, 135.6, 133.5, 133.3, 132.3, 128.9, 128.7, 128.6, 128.1, 125.6, 108.5, 61.1, 54.3, 14.2.

Ethyl 1-benzyl-3-phenyl-1H-pyrazole-5-carboxylate (4e)

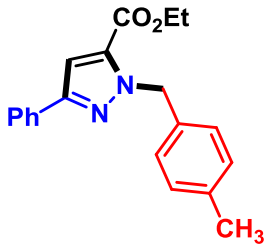


Yield 80% (49.1 mg); white solid; R_f = 0.30 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.84 (d, *J* = 7.2 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 2H), 7.35 – 7.25 (m, 6H), 7.18 (s, 1H), 5.81 (s, 2H), 4.31 (q, *J* = 7.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=159.6, 150.2, 137.2, 133.4, 132.5, 128.7, 128.5, 128.0, 127.6, 127.4, 125.6, 108.5, 61.1, 55.1, 14.2.

Ethyl 1-(4-methylbenzyl)-3-phenyl-1H-pyrazole-5-carboxylate (4f)

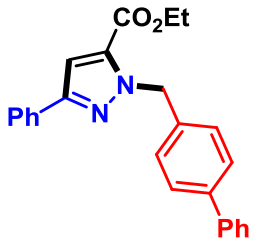


Yield 78% (50.2 mg); white solid; R_f = 0.23 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.84 (d, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.25 – 7.09 (m, 5H), 5.77 (s, 2H), 4.32 (q, *J* = 7.2 Hz, 2H), 2.30 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=159.6, 150.1, 137.3, 134.2, 133.3, 132.6, 129.1, 128.6, 128.0, 127.5, 125.6, 108.5, 61.0, 54.9, 21.1, 14.2.

Ethyl 1-([1,1'-biphenyl]-4-ylmethyl)-3-phenyl-1H-pyrazole-5-carboxylate (4g)



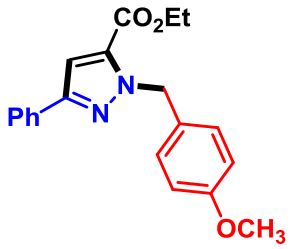
Yield 76% (58.0 mg); white solid; R_f = 0.23 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.86 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 8.0 Hz, 4H), 7.44 – 7.30 (m, 8H), 7.19 (s, 1H), 5.85 (s, 2H), 4.33 (q, *J* = 7.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=159.6, 150.3, 140.7, 140.5, 136.2, 133.4, 132.5, 128.70, 128.67, 128.1, 127.9, 127.2, 127.0, 125.6, 108.5, 61.1, 54.8, 27.0, 14.2.

HRMS (ESI)： m/z calcd for $C_{25}H_{23}N_2O_2^+$ $(M+H)^+$ 383.17540, found 383.17548.

ethyl 1-(4-methoxybenzyl)-3-phenyl-1H-pyrazole-5-carboxylate (4h)

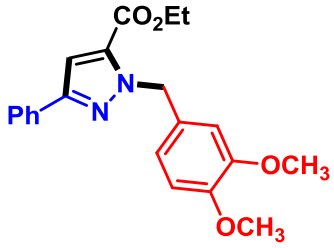


Yield 77% (51.5 mg); light yellow solid; R_f = 0.15 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.83 (d, *J* = 7.2 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.33 - 7.28 (m, 3H), 7.15 (s, 1H), 6.82 (d, *J* = 8.6 Hz, 2H), 5.73 (s, 2H), 4.32 (q, *J* = 7.2 Hz, 2H), 3.75 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=159.6, 159.0, 150.0, 133.1, 132.6, 129.3, 129.0, 128.6, 128.0, 125.6, 113.8, 108.4, 61.0, 55.2, 54.5, 14.2.

ethyl 1-(3,4-dimethoxybenzyl)-3-phenyl-1H-pyrazole-5-carboxylate (4i)



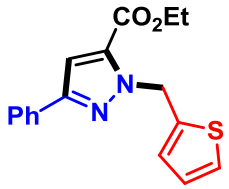
Yield 86% (63.2 mg); white solid; R_f = 0.1 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.82 (d, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.20 (s, 1H), 6.90 (t, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.35 (d, *J* = 8.0 Hz, 1H), 5.90 (s, 2H), 4.30 (q, *J* = 7.2 Hz, 2H), 3.93 (s, 3H), 3.83 (s, 3H), 1.33 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=159.4, 152.4, 150.1, 146.2, 133.9, 132.5, 131.5, 128.6, 127.9, 125.5, 124.0, 119.1, 111.6, 108.2, 61.0, 60.4, 55.7, 50.2, 14.1.

HRMS (ESI)：m/z calcd for $C_{21}H_{23}N_2O_4^+$ $(M+H)^+$ 367.16523, found 367.16525.

Ethyl 3-phenyl-1-(thiophen-2-ylmethyl)-1H-pyrazole-5-carboxylate (4j)



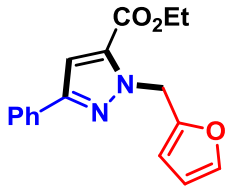
Yield 79% (62.4 mg); light yellow solid; R_f = 0.25 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.83 – 7.81 (m, 2H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.22 – 7.11 (m, 3H), 6.92 – 6.90 (m, 1H), 5.95 (s, 2H), 4.36 (q, *J* = 7.2 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=159.6, 150.4, 138.9, 132.9, 132.4, 128.6, 128.0, 126.9, 126.6, 125.8, 125.6, 108.4, 61.1, 49.7, 14.2.

HRMS (ESI)：m/z calcd for $C_{17}H_{17}N_2O_2S^+$ $(M+H)^+$ 313.10052, found 313.10046.

Ethyl 1-(furan-2-ylmethyl)-3-phenyl-1H-pyrazole-5-carboxylate (4k)



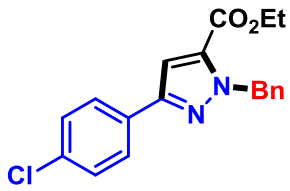
Yield 77% (45.4 mg); Brown liquid; R_f = 0.25 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.81 (d, *J* = 7.2 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.34 – 7.24 (m, 2H), 7.15 (s, 1H), 6.34 – 6.29 (m, 2H), 5.80 (s, 2H), 4.37 (q, *J* = 6.8 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=159.6, 150.4, 150.0, 142.5, 133.3, 132.4, 128.6, 128.0, 125.6, 110.3, 108.6, 108.4, 61.1, 48.1, 14.2.

HRMS (ESI)：m/z calcd for $C_{17}H_{17}N_2O_3^+$ $(M+H)^+$ 297.12337, found 297.12326.

Ethyl 1-benzyl-3-(4-chlorophenyl)-1H-pyrazole-5-carboxylate (4l)

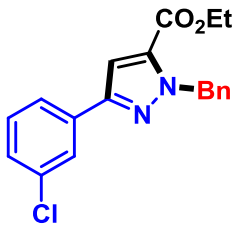


Yield 86% (58.7 mg); white solid; R_f = 0.35 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.76 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.32 – 7.20 (m, 5H), 7.14 (s, 1H), 5.79 (s, 2H), 4.31 (q, *J* = 7.2 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=159.4, 149.1, 137.0, 133.8, 133.5, 131.0, 128.8, 128.5, 127.6, 127.4, 126.8, 108.4, 61.1, 55.1, 14.2.

Ethyl 1-benzyl-3-(3-chlorophenyl)-1H-pyrazole-5-carboxylate (4m)



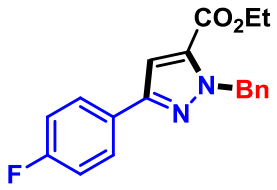
Yield 75% (51.1 mg); white solid; R_f = 0.35 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.84 (s, 1H), 7.69 (d, *J* = 7.2 Hz, 1H), 7.34 – 7.24 (m, 7H), 7.15 (s, 1H), 5.80 (s, 2H), 4.31 (q, *J* = 7.2 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=159.4, 148.8, 136.9, 134.7, 134.3, 133.6, 129.9, 128.5, 128.0, 127.7, 127.5, 125.6, 123.6, 108.6, 61.1, 55.1, 14.1.

HRMS (ESI)：m/z calcd for $C_{19}H_{18}ClN_2O_2^+$ $(M+H)^+$ 341.10513, found 341.10541.

Ethyl 1-benzyl-3-(4-fluorophenyl)-1H-pyrazole-5-carboxylate (4n)



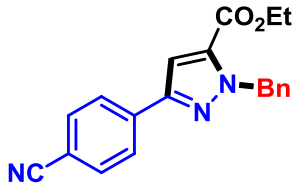
Yield 77% (49.6 mg); white solid; R_f = 0.35 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.82 – 7.77 (m, 2H), 7.30 – 7.23 (m, 5H), 7.11 – 7.06 (m, 3H), 5.79 (s, 2H), 4.31 (d, *J* = 7.2 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=163.2 (d, *J* = 248.0 Hz), 159.5, 149.3, 137.1, 133.5, 128.8,(d, *J* = 3.2 Hz), 128.5, 127.6, 127.4, 127.3 (d, *J* = 8.1 Hz), 115.5(d, *J* = 21.7 Hz), 108.2, 61.1, 55.0, 14.1.

^{19}F NMR (376 MHz, $CDCl_3$): δ= -113.9.

Ethyl 1-benzyl-3-(4-cyanophenyl)-1H-pyrazole-5-carboxylate (4o)



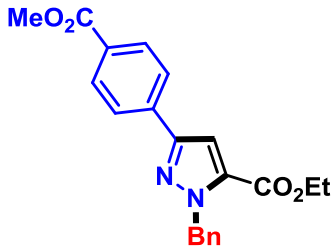
Yield 61% (40.3 mg); white solid; R_f = 0.12 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.93 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8. Hz, 2H), 7.33 – 7.26 (m, 5H), 7.22 (s, 1H), 5.82 (s, 2H), 4.34 (q, *J* = 7.2 Hz, 2H), 1.36 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=159.2, 148.2, 136.8, 136.6, 133.9, 132.5, 128.5, 127.8, 127.5, 125.9, 118.9, 111.3, 109.1, 61.3, 55.3, 14.1.

HRMS (ESI)： m/z calcd for $C_{20}H_{18}N_3O_2^+$ $(M+H)^+$ 332.13935, found 332.13925.

Ethyl 1-benzyl-3-(4-(methoxycarbonyl)phenyl)-1H-pyrazole-5-carboxylate (4p)



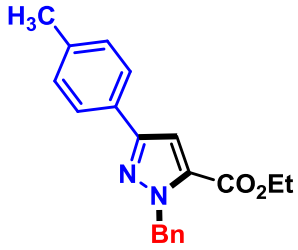
Yield 70% (49.7 mg); white solid; R_f = 0.11 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=8.08 (d, *J* = 8.4 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.23 (m, 6H), 5.82 (s, 2H), 4.32 (q, *J* = 7.2 Hz, 2H), 3.92 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=166.8, 159.4, 149.1, 136.9, 136.8, 133.7, 130.0, 129.4, 128.5, 127.7, 127.5, 125.3, 109.0, 61.2, 55.2, 52.1, 14.1.

HRMS (ESI)： m/z calcd for $C_{21}H_{21}N_2O_4^+$ $(M+H)^+$ 365.14958, found 365.14935.

Ethyl 1-benzyl-3-(p-tolyl)-1H-pyrazole-5-carboxylate (4q)

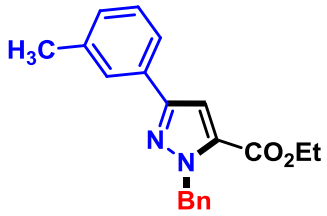


Yield 59% (37.9 mg); white solid; R_f = 0.3 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.73 (d, *J* = 8.0 Hz, 2H), 7.29 – 7.14 (m, 8H), 5.80 (s, 2H), 4.30 (q, *J* = 7.2 Hz, 2H), 2.37 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=159.6, 150.3, 137.9, 137.3, 133.3, 129.8, 129.3, 128.4, 127.5, 127.4, 125.5, 108.3, 61.0, 55.0, 21.3, 14.2.

Ethyl 1-benzyl-3-(m-tolyl)-1H-pyrazole-5-carboxylate (4r)



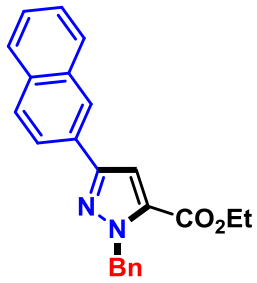
Yield 69% (44.4 mg); white solid; R_f = 0.27 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.68 (s, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.31 – 7.23 (m, 6H), 7.17 – 7.13 (m, 2H), 5.81 (s, 2H), 4.30 (q, *J* = 7.2 Hz, 2H), 2.40 (s, 3H), 1.34 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=159.6, 150.4, 138.3, 137.2, 133.3, 132.4, 128.8, 128.6, 128.4, 127.5, 127.4, 126.2, 122.8, 108.6, 61.0, 55.1, 21.4, 14.2.

HRMS (ESI)： m/z calcd for $C_{20}H_{21}N_2O_2^+$ $(M+H)^+$ 321.15975, found 321.15958.

Ethyl 1-benzyl-3-(naphthalen-2-yl)-1H-pyrazole-5-carboxylate (4s)



Yield 49% (35.2 mg); Pale yellow solid; R_f = 0.32 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=8.28 (s, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.84 – 7.80(m, 1H), 7.49 – 7.44 (m, 2H), 7.32 – 7.23 (m, 6H), 5.85 (s, 2H), 4.32 (q, *J* = 7,2Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H).

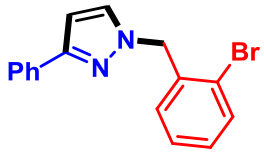
^{13}C NMR (101 MHz, $CDCl_3$): δ=159.6, 150.2, 137.2, 133.54, 133.50, 133.2, 129.9, 128.5, 128.3, 128.2, 127.7, 127.6, 127.4, 126.3, 126.0, 124.3, 123.8, 108.8, 61.1, 55.1, 14.2.

HRMS (ESI)：m/z calcd for $C_{23}H_{21}N_2O_2^+$ $(M+H)^+$ 357.15975, found 357.15970.

General procedure for preparation of 1,3-disubstituted pyrazoles 5:

An oven-dried Schlenk tube under argon atmosphere was charged with 2-bromobenzaldehyde **1a** (0.2 mmol, 1.0 equiv), ethyl acrylate **2a** (0.4 mmol, 2.0 equiv), phenylhydrazone **3a** (0.4 mmol, 2.0 equiv), Cs_2CO_3 (0.60 mmol, 3.0 equiv), PivOH (0.8 mmol, 4.0 equiv) and DMF (2 mL). The mixture was stirred at 120 ℃ and the progress of the reaction was monitored by TLC. Upon completion, the resulting mixture was cooled to room temperature and added 10 mL of H_2O to quench the reaction, and then extracted with ethyl acetate (20 mL×3). The solvents were evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel to afford the products.

1-(2-bromobenzyl)-3-phenyl-1H-pyrazole (5a)



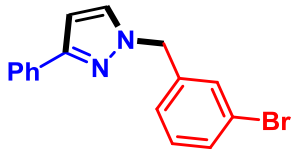
Yield 71% (44.4 mg); Pale yellow solid; R_f = 0.23 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.83 (d, *J* =8.0 Hz, 2H), 7.58 (d, *J* = 8.0 Hz,1H), 7.46 (d, *J* = 2.0 Hz, 1H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.17 – 7.14 (m, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.61 (d, *J* = 2.4 Hz, 1H), 5.46 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=151.9, 136.3, 133.4, 132.7, 131.3, 129.4, 129.2, 128.6, 127.9, 127.7, 125.6, 122.7, 103.4, 55.9.

HRMS (ESI)：m/z calcd for $C_{16}H_{14}BrN_2^+$ $(M+H)^+$ 313.03349, found 313.03329.

1-(3-bromobenzyl)-3-phenyl-1H-pyrazole (5b)



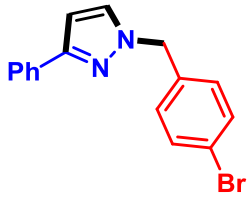
Yield 57% (35.8 mg); colorless liquid; R_f = 0.17 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.83 – 7.81 (m, 2H), 7.43 – 7.38 (m, 5H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.24 – 7.14 (m, 2H), 6.59 (d, *J* = 2.4 Hz, 1H), 5.31 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=151.9, 138.9, 133.3, 131.1, 130.7, 130.5, 130.3, 128.6, 127.7, 126.1, 125.6, 122.8, 103.6, 55.3.

HRMS (ESI)：m/z calcd for $C_{16}H_{14}BrN_2^+$ $(M+H)^+$ 313.03349, found 313.03333.

1-(4-bromobenzyl)-3-phenyl-1H-pyrazole (5c)



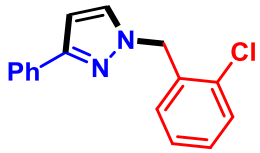
Yield 31% (19.1 mg); white solid; R_f = 0.16 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.82 – 7.80 (m, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.41 – 7.36 (m, 3H), 7.32 – 7.28 (m, 1H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.58 (d, *J* = 2.0 Hz, 1H), 5.30 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=151.8, 135.7, 133.3, 131.9, 130.6, 129.2, 128.6, 127.7, 125.6, 122.0, 103.5, 55.4.

HRMS (ESI)：m/z calcd for $C_{16}H_{14}BrN_2^+$ $(M+H)^+$ 313.03349, found 313.03360.

1-(2-chlorobenzyl)-3-phenyl-1H-pyrazole (5d)



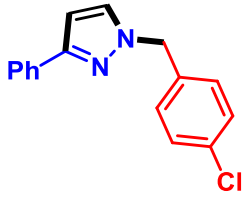
Yield 67% (35.8 mg); white solid; R_f = 0.20 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.82 (d, *J* = 7.2 Hz, 2H), 7.44 – 7.37 (m, 4H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.24 – 7.17 (m, 2H), 6.96 (dd, J_1 = 7.2 Hz, J_2 = 0.8 Hz, 1H), 6.60 (d, *J* = 2.4 Hz, 1H), 5.47 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=151.9, 134.6, 133.3, 132.7, 131.2, 129.4, 129.19, 129.17, 128.6, 127.6, 127.2, 125.6, 103.3, 53.4.

HRMS (ESI)： m/z calcd for $C_{16}H_{14}ClN_2^+$ $(M+H)^+$269.08400, found 269.08453.

1-(4-chlorobenzyl)-3-phenyl-1H-pyrazole (5e)

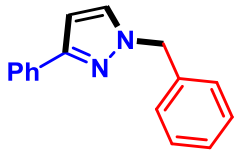


Yield 53% (28.2 mg); white solid; R_f = 0.16 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.81 (d, *J* = 7.6 Hz, 2H), 7.41 – 7.24 (m, 6H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.58 (d, *J* = 2.0 Hz, 1H), 5.31 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=151.8, 135.1, 133.8, 133.3, 130.6, 128.90, 128.89, 128.6, 127.7, 125.6, 103.5, 55.3.

1-benzyl-3-phenyl-1H-pyrazole (5f)

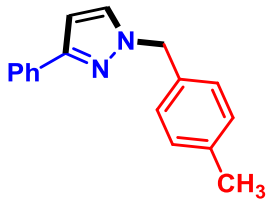


Yield 44% (20.6 mg); white solid; R_f = 0.33 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.82 (d, *J* = 7.6 Hz, 2H), 7.41 – 7.24 (m, 9H), 6.57 (d, *J* = 2.0 Hz, 1H), 5.36 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=151.6, 136.6, 133.5, 130.6, 128.8, 128.6, 128.0, 127.6, 127.5, 125.6, 103.3, 56.1.

1-(4-methylbenzyl)-3-phenyl-1H-pyrazole (5g)

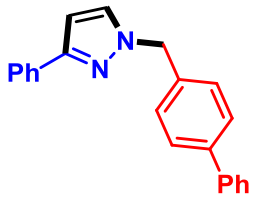


Yield 52% (25.9 mg); white solid; R_f = 0.34 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.81 (d, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 2.0 Hz, 1H), 7.30 – 7.24 (m, 1H), 7.18 – 7.13 (m, 4H), 6.55 (d, *J* = 2.4 Hz, 1H), 5.31 (s, 2H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=151.4, 137.8, 133.6, 133.5, 130.4, 129.4, 128.5, 127.8, 127.5, 125.6, 103.2, 55.9, 21.1.

1-([1,1'-biphenyl]-4-ylmethyl)-3-phenyl-1H-pyrazole (5h)



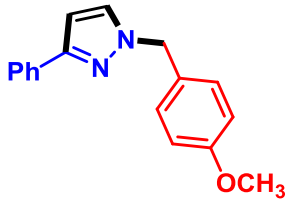
Yield 49% (30.4 mg); white solid; R_f = 0.15 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.83 (d, *J* = 7.2 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 4H), 7.44 – 7.27 (m, 9H), 6.59 (d, *J* = 2.0 Hz, 1H), 5.38 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=151.6, 140.9, 140.5, 135.5, 133.5, 130.6, 128.8, 128.6, 128.1, 127.6, 127.5, 127.4, 127.0, 125.6, 103.3, 55.7.

HRMS (ESI)： m/z calcd for $C_{22}H_{19}N_2^+$ $(M+H)^+$ 311.15428, found 311.15417.

1-(4-methoxybenzyl)-3-phenyl-1H-pyrazole (5i)

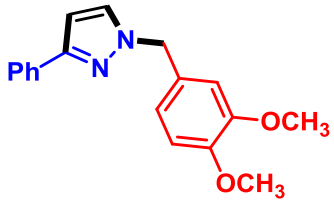


Yield 29% (15.2 mg); white solid; R_f = 0.20 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.81 (d, *J* = 7.2 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.21 (m, 4H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.55 (d, *J* = 2.0 Hz, 1H), 5.29 (s, 2H), 3.79 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=159.4, 151.4, 133.6, 130.3, 129.3, 128.55, 128.48, 127.5, 125.6, 114.1, 103.2, 55.6, 55.3.

1-(3,4-dimethoxybenzyl)-3-phenyl-1H-pyrazole (5j)



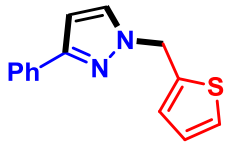
Yield 42% (24.6 mg); white solid; R_f = 0.25 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.82 (d, *J* = 7.2 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 2.0 Hz, 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 6.83 (d, *J* = 3.6 Hz, 3H), 6.56 (d, *J* = 2.0 Hz, 1H), 5.29 (s, 2H), 3.86 (s, 3H), 3.83 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=151.4, 149.2, 148.8, 133.5, 130.3, 128.8, 128.5, 127.5, 125.6, 120.4, 111.11, 111.05, 103.2, 55.89, 55.87, 55.8.

HRMS (ESI)：m/z calcd for $C_{18}H_{19}N_2O_2^+$ $(M+H)^+$ 295.14410, found 295.14413.

3-phenyl-1-(thiophen-2-ylmethyl)-1H-pyrazole (5k)



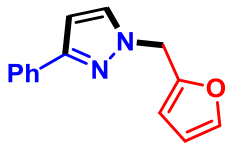
Yield 27% (13.4 mg); Pale yellow solid; R_f = 0.13 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.82 – 7.80 (m, 2H), 7.41 – 7.37 (m, 3H), 7.31 – 7.25 (m, 2H), 7.06 (d, J = 3.2 Hz, 1H), 6.99 – 6.97 (m, 1H), 6.56 (d, J = 2.4 Hz, 1H), 5.51 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=151.7, 138.3, 133.4, 130.1, 128.6, 127.6, 127.1, 127.0, 126.2, 125.6, 103.4, 50.7.

HRMS (ESI)：m/z calcd for $C_{14}H_{13}N_2S^+$ $(M+H)^+$ 241.07940, found 241.07910.

1-(furan-2-ylmethyl)-3-phenyl-1H-pyrazole (5l)



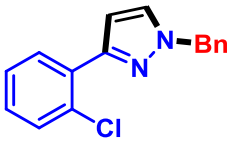
Yield 33% (14.7 mg); Brown solid; R_f = 0.15 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.80 (d, J = 7.6 Hz, 2H), 7.41 – 7.36 (m, 4H), 7.31 – 7.25, (m, 1H), 6.56 (d, J = 2.0 Hz, 1H), 6.39 – 6.36 (m, 2H), 5.33 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=151.6, 149.2, 143.0, 133.4, 130.3, 128.5, 127.6, 125.6, 110.6, 109.3, 103.3, 48.8.

HRMS (ESI)：m/z calcd for $C_{14}H_{13}N_2O^+$ $(M+H)^+$ 225.10224, found 225.10175.

1-benzyl-3-(2-chlorophenyl)-1H-pyrazole (5m)



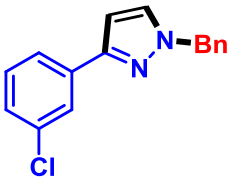
Yield 50% (26.7 mg); Pale yellow liquid; R_f = 0.22 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.83 (d, *J* = 7.6 Hz, 1H), 7.44 – 7.21 (m, 9H), 6.80 (d, *J* = 1.6 Hz, 1H), 5.37 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=149.0, 136.4, 132.4, 132.2, 130.6, 130.2, 129.7, 128.8, 128.6, 128.0, 127.7, 126.8, 107.3, 56.1.

HRMS (ESI)：m/z calcd for $C_{16}H_{14}ClN_2^+$ $(M+H)^+$ 269.08400, found 269.08392.

1-benzyl-3-(3-chlorophenyl)-1H-pyrazole (5n)



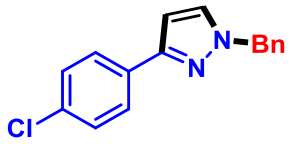
Yield 65% (34.6 mg); colorless liquid; R_f = 0.23 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.82 (s, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.37 – 7.24 (m, 8H), 6.56 (s, 1H), 5.35 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=150.2, 136.3, 135.3, 134.5, 130.8, 129.8, 128.8, 128.1, 127.7, 127.5, 125.7, 123.7, 103.5, 56.2.

HRMS (ESI)：m/z calcd for $C_{16}H_{14}ClN_2^+$ $(M+H)^+$ 269.08400, found 269.08426.

1-benzyl-3-(4-chlorophenyl)-1H-pyrazole (5o)



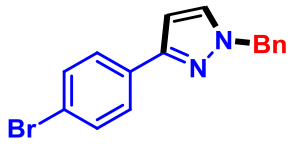
Yield 67% (34.0 mg); Pale yellow liquid; R_f = 0.26 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.75 – 7.73 (m, 2H), 7.36 – 7.30 (m, 6H), 7.24 (d, *J* = 6.4 Hz, 2H), 6.54 (d, *J* = 2.4 Hz, 1H), 5.34 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=150.4, 136.3, 133.2, 132.0, 130.8, 128.8, 128.7, 128.0, 127.6, 126.8, 103.2, 56.1.

HRMS (ESI)：m/z calcd for $C_{16}H_{14}ClN_2^+$ $(M+H)^+$ 269.08400, found 269.08408.

1-benzyl-3-(4-bromophenyl)-1H-pyrazole (5p)



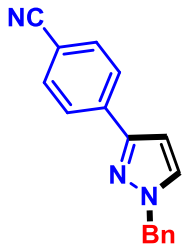
Yield 60% (37.3 mg); white solid; R_f = 0.21 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.68 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.36 – 7.22 (m, 6H), 6.53 (d, *J* = 2.4 Hz, 1H), 5.33 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=150.4, 136.3, 132.5, 131.6, 130.8, 128.8, 128.0, 127.6, 127.1, 121.4, 103.3, 56.1.

HRMS (ESI)：m/z calcd for $C_{16}H_{14}BrN_2$+ $(M+H)^+$ 313.03349, found 313.03357.

4-(1-benzyl-1H-pyrazol-3-yl)benzonitrile (5q)



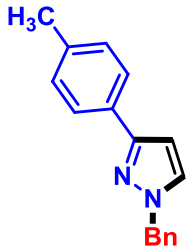
Yield 56% (29.1 mg); white solid; R_f = 0.10 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.91 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.41 – 7.25 (m, 6H), 6.63 (d, *J* = 2.4 Hz, 1H), 5.36 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=149.5, 137.9, 136.0, 132.4, 131.1, 128.8, 128.2, 127.7, 125.9, 119.1, 110.7, 104.0, 56.3.

HRMS (ESI)：m/z calcd for $C_{17}H_{14}N_3^+$ $(M+H)^+$ 260.11822, found 260.11801.

1-benzyl-3-(p-tolyl)-1H-pyrazole (5r)



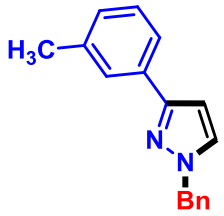
Yield 55% (27.2 mg); Pale yellow solid; R_f = 0.14 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.71 (d, *J* = 8.0 Hz, 2H), 7.35 – 7.18 (m, 8H), 6.53 (d, *J* = 2.0 Hz, 1H), 5.34 (s, 2H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=151.6, 137.2, 136.6, 130.7, 130.5, 129.2, 128.7, 127.9, 127.6, 125.5, 103.0, 56.0, 21.2.

HRMS (ESI)：m/z calcd for $C_{17}H_{17}N_2^+$ $(M+H)^+$ 249.13862, found 249.13832.

1-benzyl-3-(m-tolyl)-1H-pyrazole (5s)



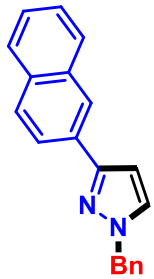
Yield 47% (23.1 mg); Pale yellow liquid; R_f = 0.20 (petroleum ether : ethyl acetate = 50 : 1)

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.68 (s, 1H), 7.61 – 7.59 (m, 1H), 7.34 – 7.23 (m, 7H), 7.12 – 7.11 (m, 1H), 6.564 – 6.556 (m, 1H), 5.36 (d, *J* = 3.2 Hz, 2H), 2.39 (d, *J* = 2.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=151.7, 138.2, 136.6, 133.4, 130.5, 128.7, 128.5, 128.3, 127.9, 127.6, 126.2, 122.8, 103.3, 56.0, 21.4.

HRMS (ESI)：m/z calcd for $C_{17}H_{17}N_2^+$ $(M+H)^+$ 249.13862, found 249.13837.

1-benzyl-3-(naphthalen-2-yl)-1H-pyrazole (5t)

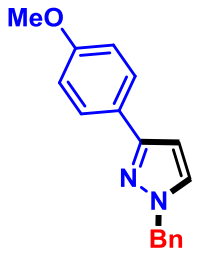


Yield 51% (30.7 mg); white solid; R_f = 0.20 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=8.26 (s, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.87 – 7.80 (m, 3H), 7.47 – 7.22 (m, 8H), 6.69 (d, *J* = 2.4 Hz, 1H), 5.38 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=151.5, 136.5, 133.6, 133.0, 130.9, 130.7, 128.8, 128.2, 128.1, 128.0, 127.7, 126.1, 125.7, 124.1, 124.0, 103.6, 56.1.

1-benzyl-3-(4-methoxyphenyl)-1H-pyrazole (5u)



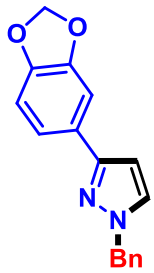
Yield 43% (22.9 mg); Pale yellow solid; R_f = 0.05 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.74 (d, *J* = 8.4 Hz, 2H), 7.34 – 7.23 (m, 6H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.50 (d, *J* = 2.0 Hz, 1H), 5.34 (s, 2H), 3.83 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=159.2, 151.4, 136.7, 130.5, 128.7, 127.9, 127.6, 126.9, 126.4, 114.0, 102.8, 56.0, 55.3.

HRMS (ESI)：m/z calcd for $C_{17}H_{17}N_2O^+$ $(M+H)^+$ 265.13354, found 265.13315.

3-(benzo[d][1,3]dioxol-5-yl)-1-benzyl-1H-pyrazole (5v)



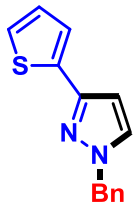
Yield 44% (24.4 mg); white solid; R_f = 0.18 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.36 – 7.23 (m, 8H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.46 (d, *J* = 2.0 Hz, 1H), 5.95 (s, 2H), 5.32 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=151.3, 147.9, 147.1, 136.6, 130.6, 128.7, 127.95, 127.90, 127.6, 119.2, 108.4, 106.3, 102.9, 100.9, 56.0.

HRMS (ESI)：m/z calcd for $C_{17}H_{15}N_2O_2^+$ $(M+H)^+$ 279.11280, found 279.11264.

1-benzyl-3-(thiophen-2-yl)-1H-pyrazole (5w)

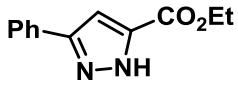


Yield 49% (23.7 mg), yellow solid; R_f = 0.19 (petroleum ether : ethyl acetate = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=7.36 – 7.21 (m, 8H), 7.05 – 7.03 (m, 1H), 6.47 (d, *J* = 2.4 Hz, 1H), 5.32 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ=146.7, 136.7, 136.3, 130.6, 128.8, 128.0, 127.7, 127.4, 124.2, 123.5, 103.4, 56.0.

ethyl 3-phenyl-1H-pyrazole-5-carboxylate (6)

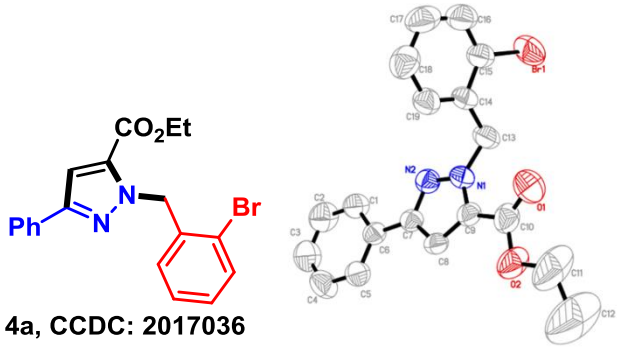


Yield 51% (43.8 mg); white solid; R_f = 0.23 (petroleum ether : ethyl acetate = 5 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ=12.25 (s, 1H), 7.74 (d, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.06 (s, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ= 161.0, 147.9, 140.2, 130.1, 128.8, 128.5, 125.6, 105.1, 61.0, 14.0.

Crystal data of product 4a



Bond precision: C-C = 0.0067 A Wavelength=0.71073

Cell: a=10.495(2) b=21.897(4) c=7.8420(16)
alpha=90 beta=96.57(3) gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	1790.3(6)	1790.3(6)
Space group	P 21/c	P21/c
Hall group	-P 2ybc	?
Moiety formula	C19 H17 Br N2 O2	?
Sum formula	C19 H17 Br N2 O2	C19 H17 Br N2 O2
Mr	385.25	385.26
Dx,g cm-3	1.429	1.429
Z	4	4
Mu (mm-1)	2.309	2.309
F000	784.0	784.0
F000'	783.15	
h,k,lmax	13,28,10	13,28,10
Nref	4104	4093
Tmin,Tmax	0.343,0.500	0.632,1.000
Tmin'	0.152	

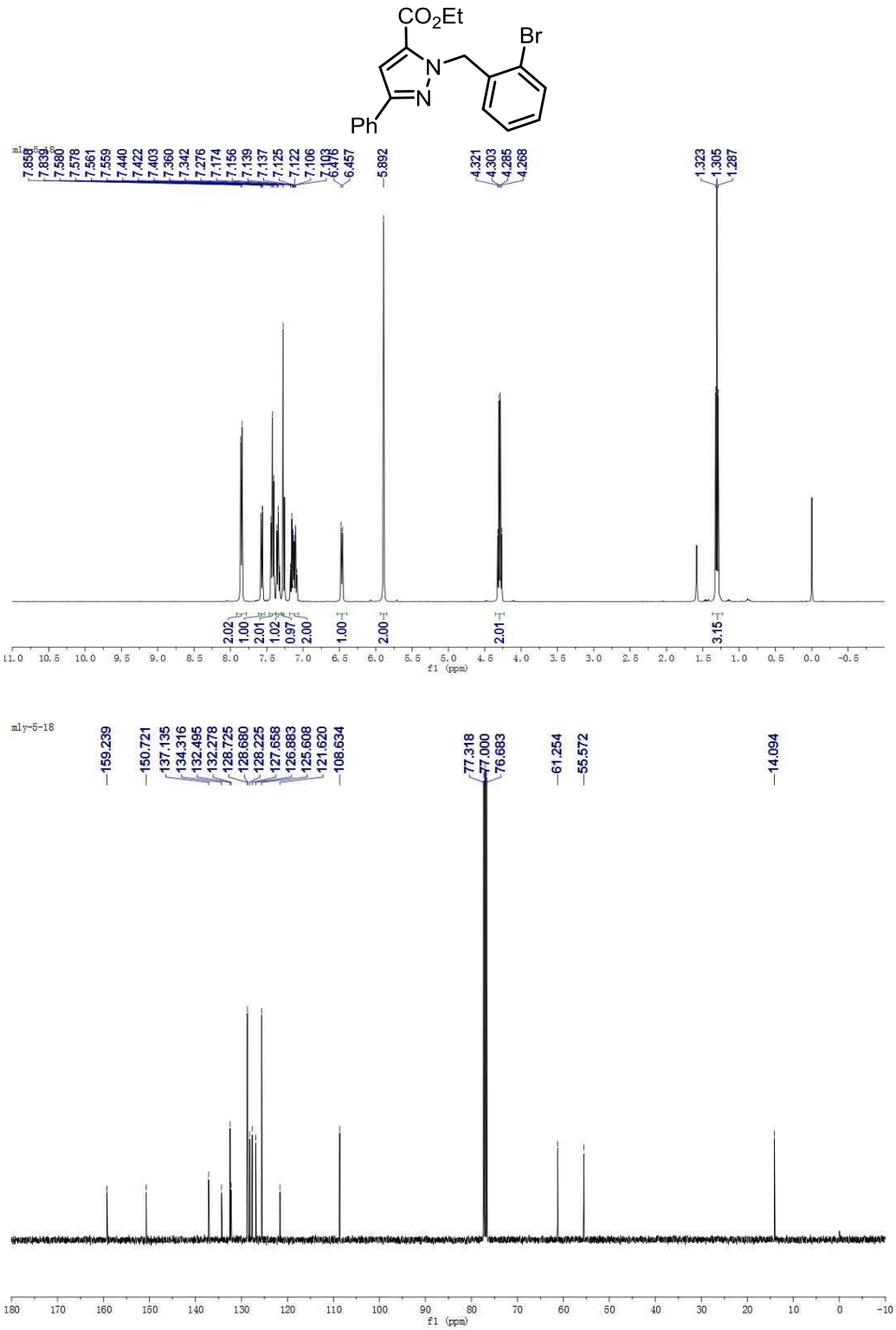
Correction method= # Reported T Limits: Tmin=0.632 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.997 Theta(max)= 27.480

R(reflections)= 0.0709(2584) wR2(reflections)= 0.2131(4093)

S = 1.198 Npar= 218

NMR Spectra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N
Ph
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7.422
7.403
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7.342
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7.174
7.156
7.139
7.137
7.125
7.122
7.106
6.457
5.892
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4.268
1.323
1.305
1.287
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1.00
2.01
1.02
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2.00
1.00
2.00
2.01
3.15
f1 (ppm)
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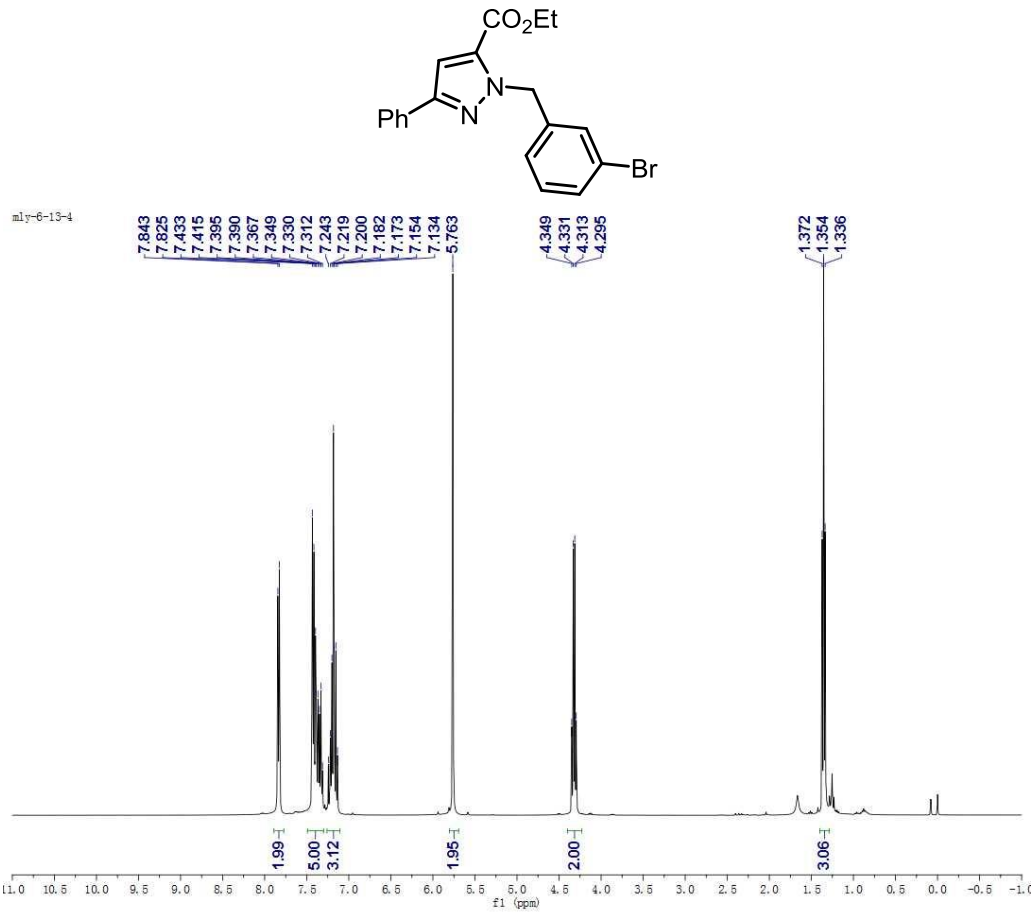
f1 (ppm)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Br
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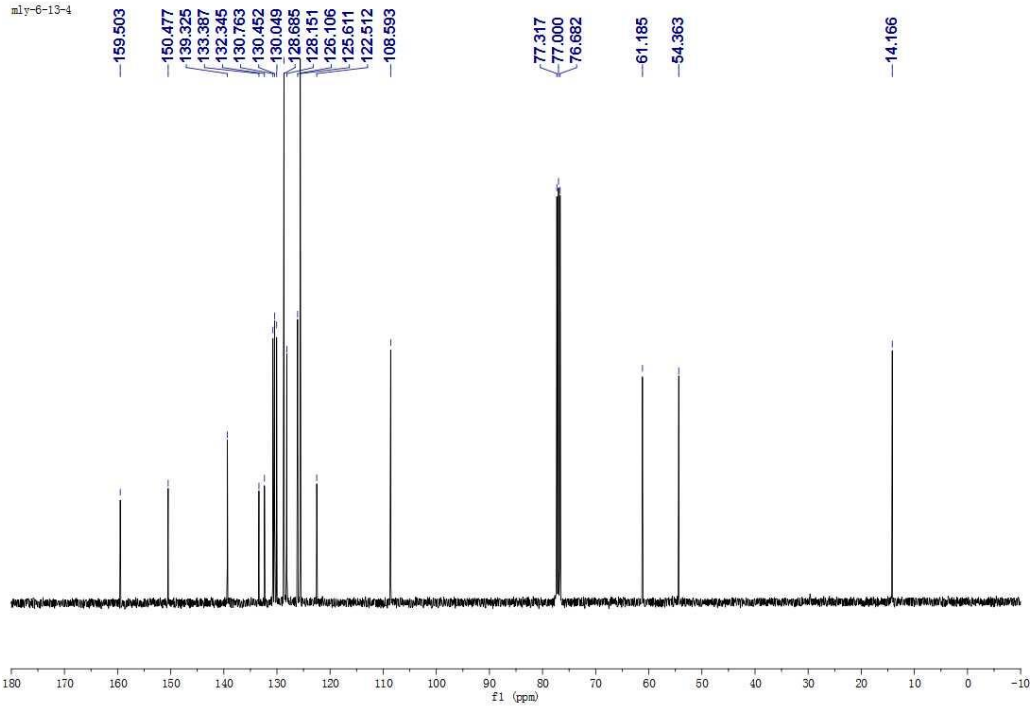
3.06
f1 (ppm)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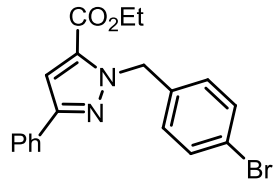
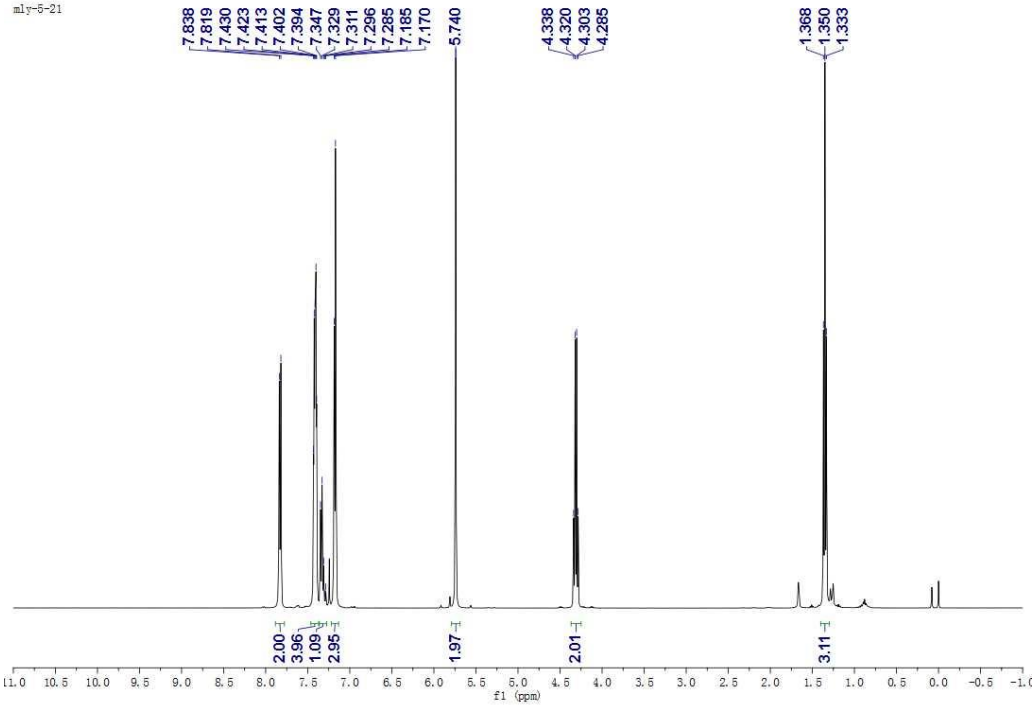
f1 (ppm)


CO2Et
N
N
Ph
Br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7.413
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7.347
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7.296
7.285
7.185
7.170
5.740
4.338
4.320
4.303
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2.95
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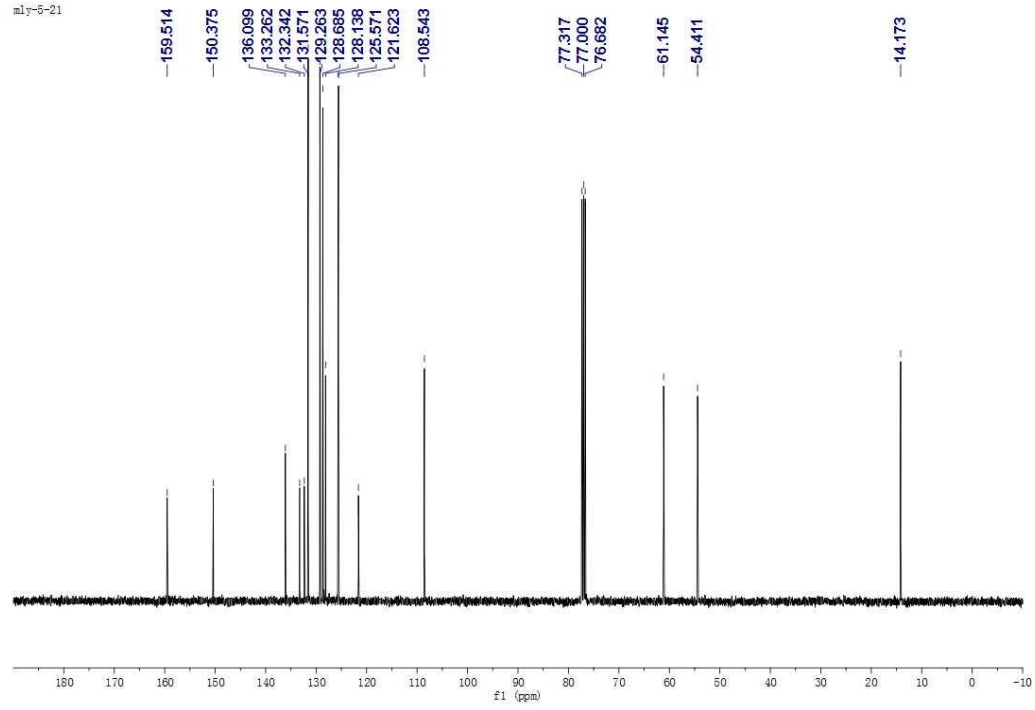
3.11
f1 (ppm)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132.342
131.571
129.263
128.685
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121.623
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77.000
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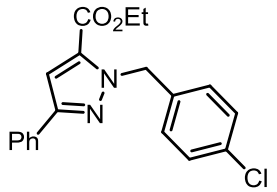
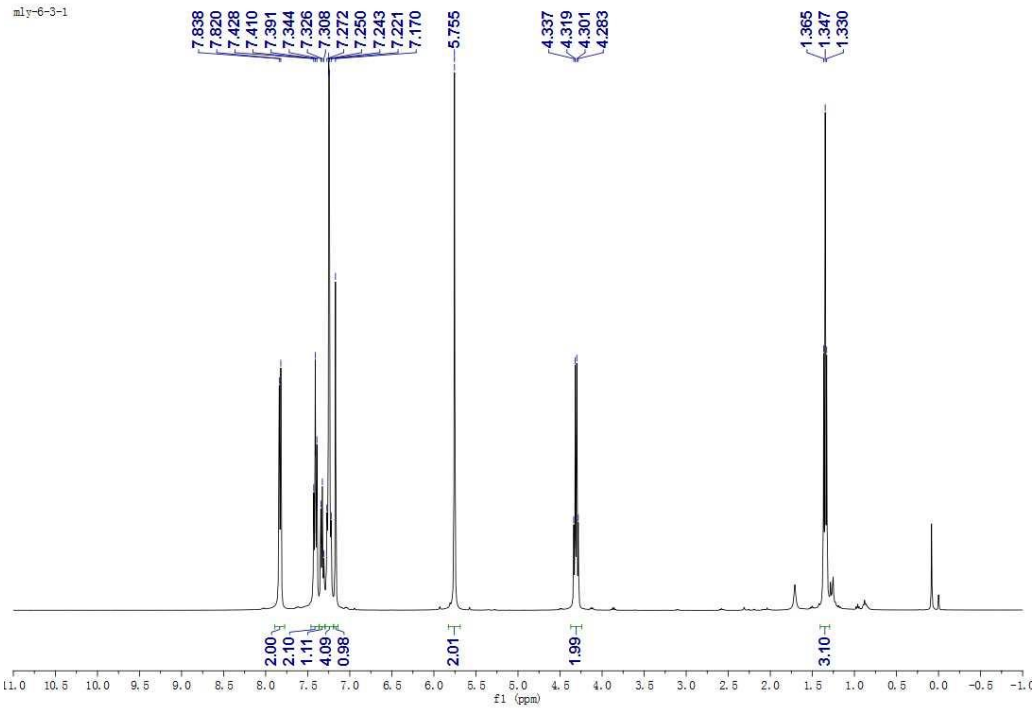
61.145
54.411
14.173
f1 (ppm)


CO2Et
N
N
Ph
Cl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7.272
7.250
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5.755
4.337
4.319
4.301
4.283
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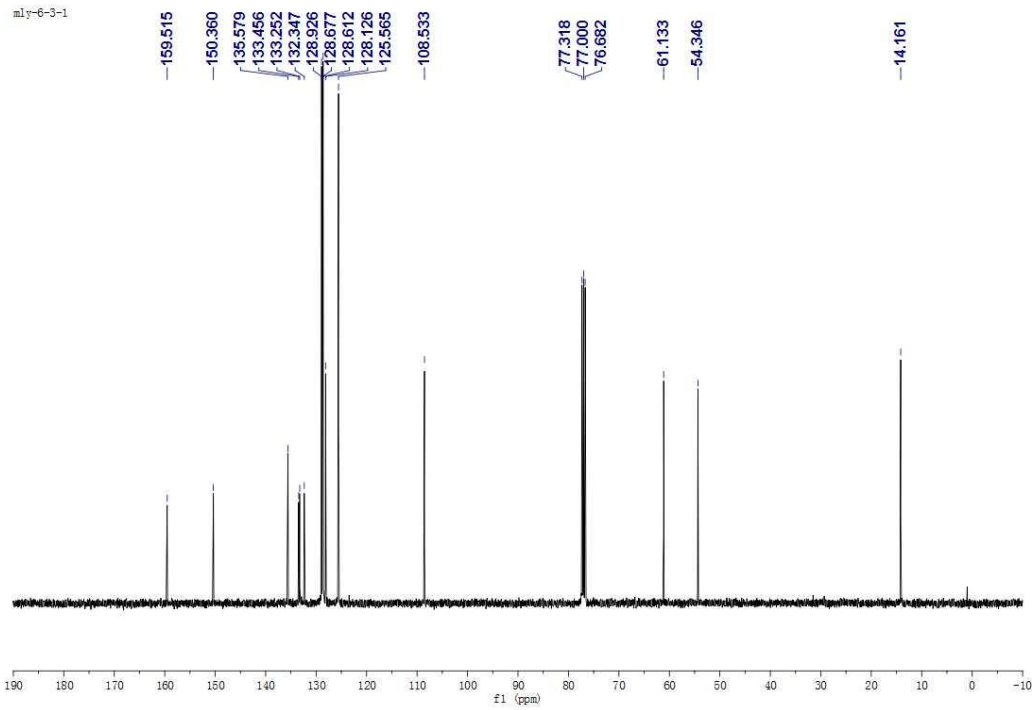
1.347
1.330
2.00
2.10
1.11
4.09
0.98
2.01
1.99
3.10
f1 (ppm)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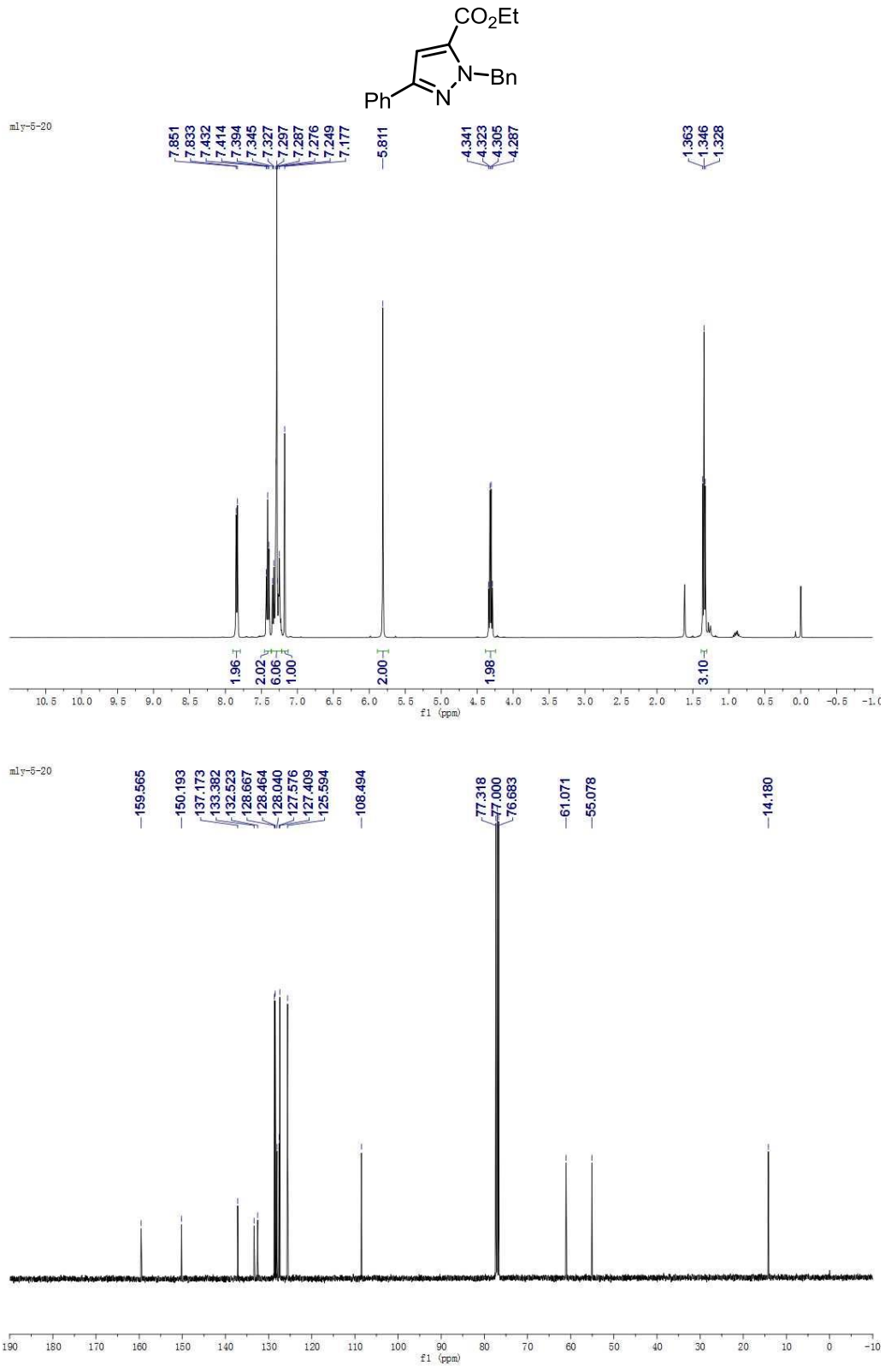
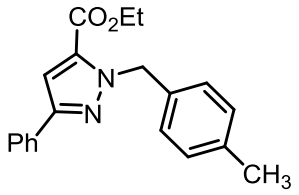
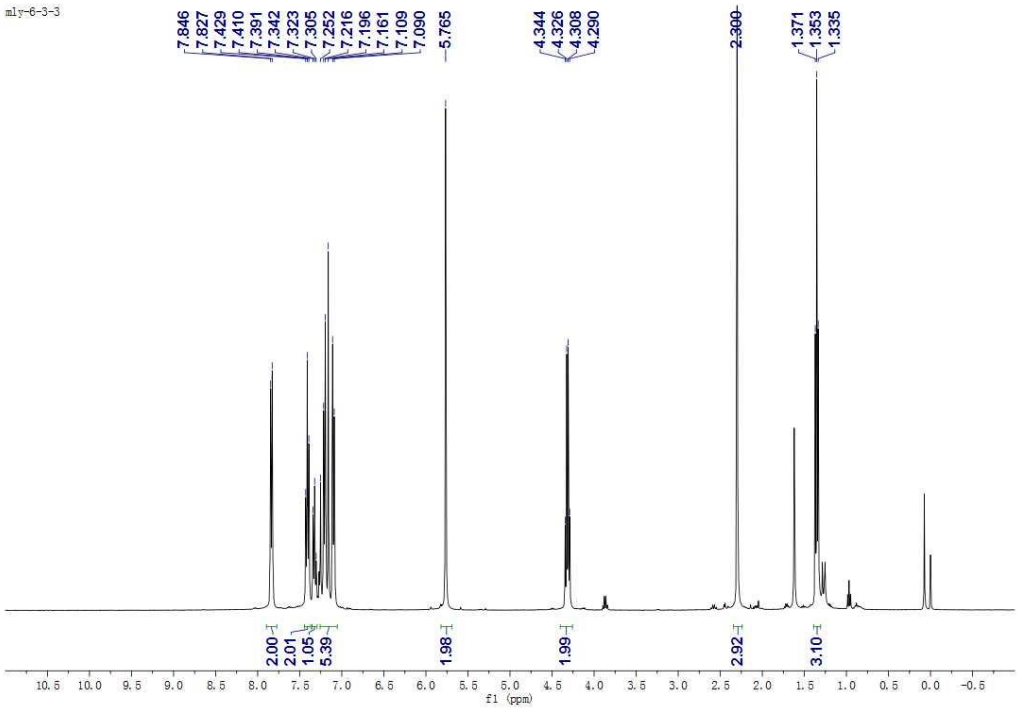
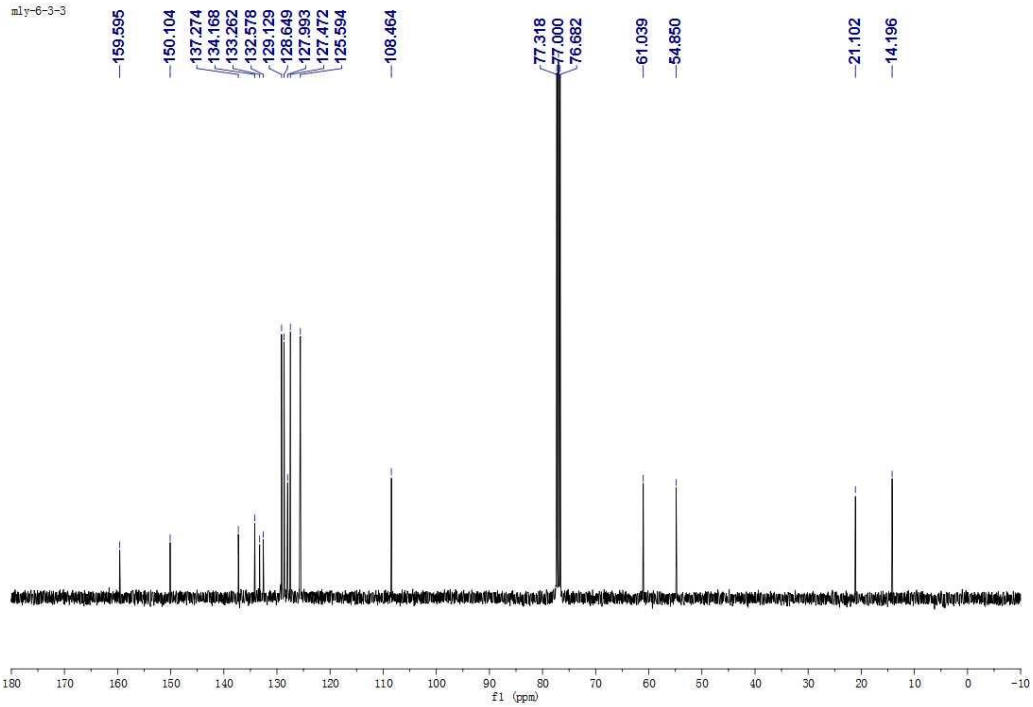
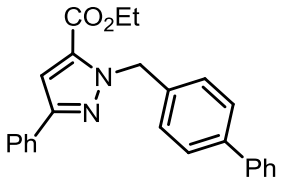
77.000
76.682
61.133
54.346
14.161
f1 (ppm)

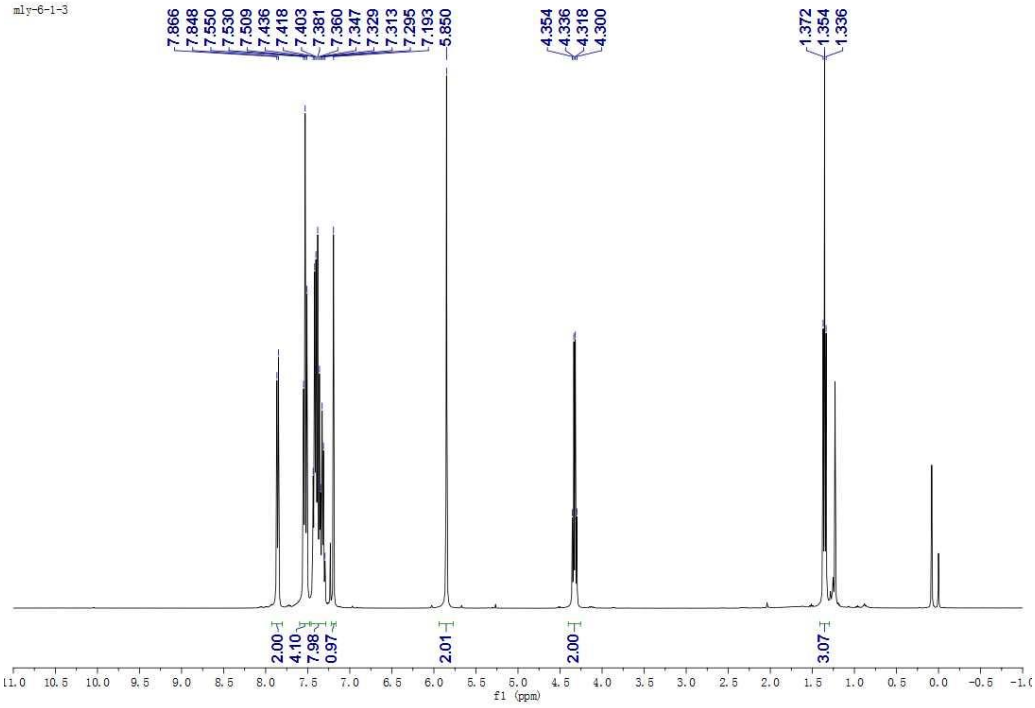

CO2Et
N
Bn
Ph
N
mly-5-20
7.851
7.833
7.432
7.414
7.394
7.345
7.327
7.297
7.287
7.276
7.249
7.177
5.811
4.341
4.323
4.305
4.287
1.363
1.346
1.328
1.96
2.02
6.06
1.00
2.00
1.98
3.10
f1 (ppm)
mly-5-20
159.565
150.193
137.173
133.382
132.523
128.667
128.464
128.040
127.576
127.409
125.594
108.494
77.318
77.000
76.683
61.071
55.078
14.180
f1 (ppm)

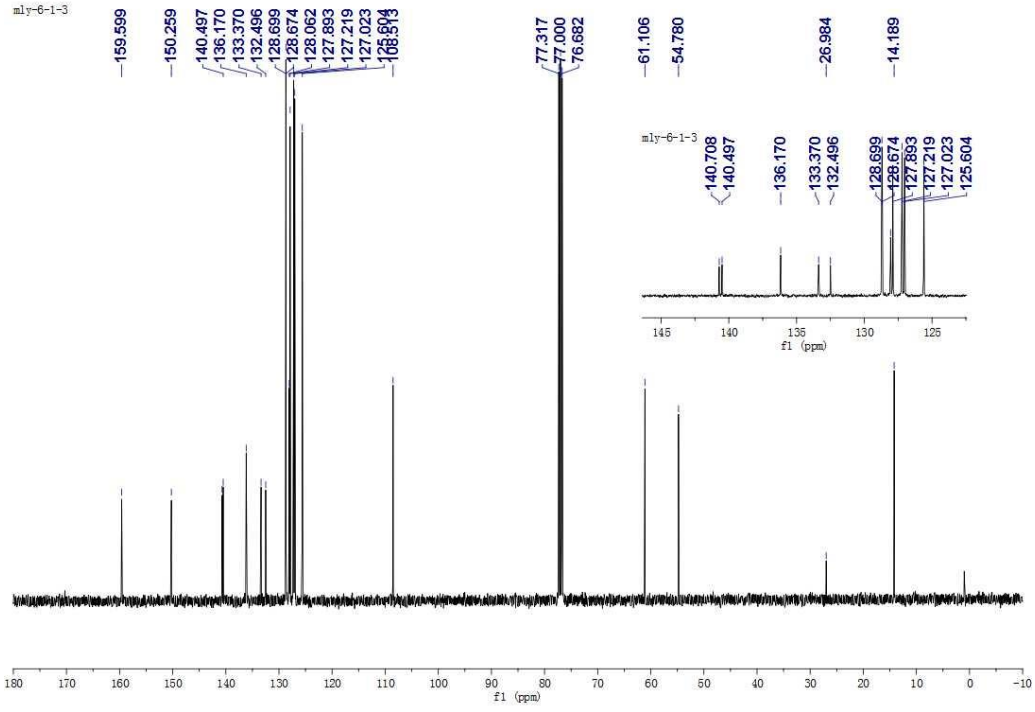

CO2Et
N
N
Ph
CH3

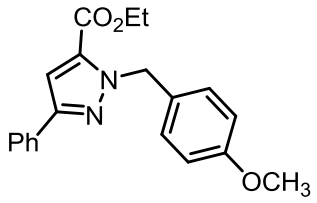

mly-6-3-3
7.846
7.827
7.429
7.410
7.391
7.342
7.323
7.305
7.252
7.216
7.196
7.161
7.109
7.090
5.765
4.344
4.326
4.308
4.290
2.300
1.371
1.353
1.335
2.00
2.01
1.05
5.39
1.98
1.99
2.92
3.10
f1 (ppm)

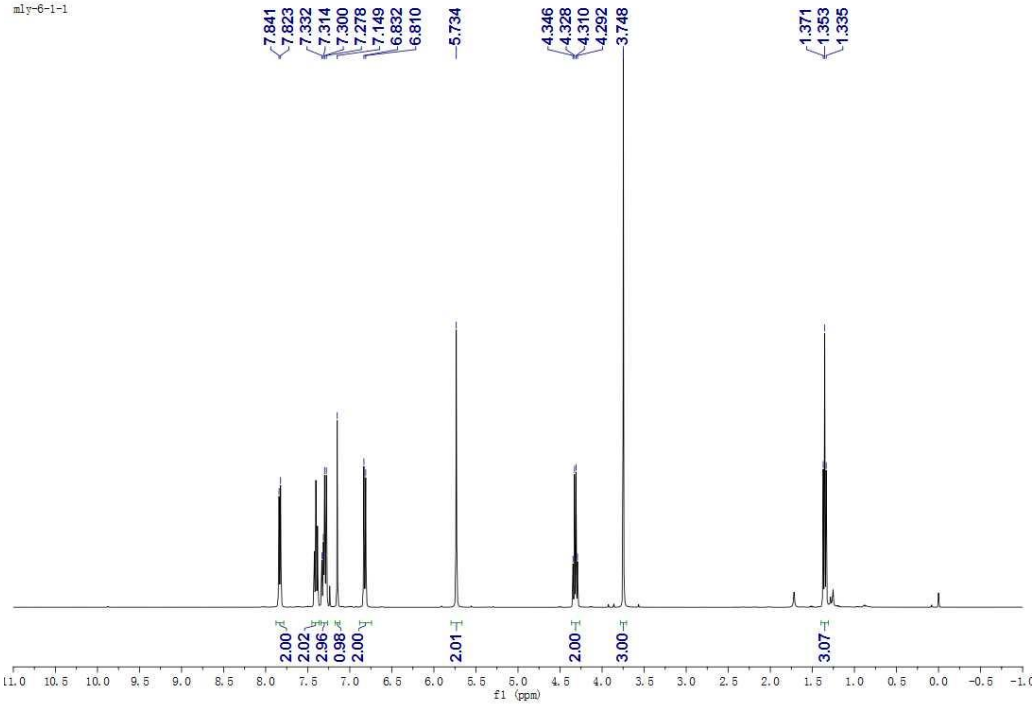

mly-6-3-3
159.595
150.104
137.274
134.168
133.262
132.578
129.129
128.649
127.993
127.472
125.594
108.464
77.318
77.000
76.682
61.039
54.850
21.102
14.196
f1 (ppm)

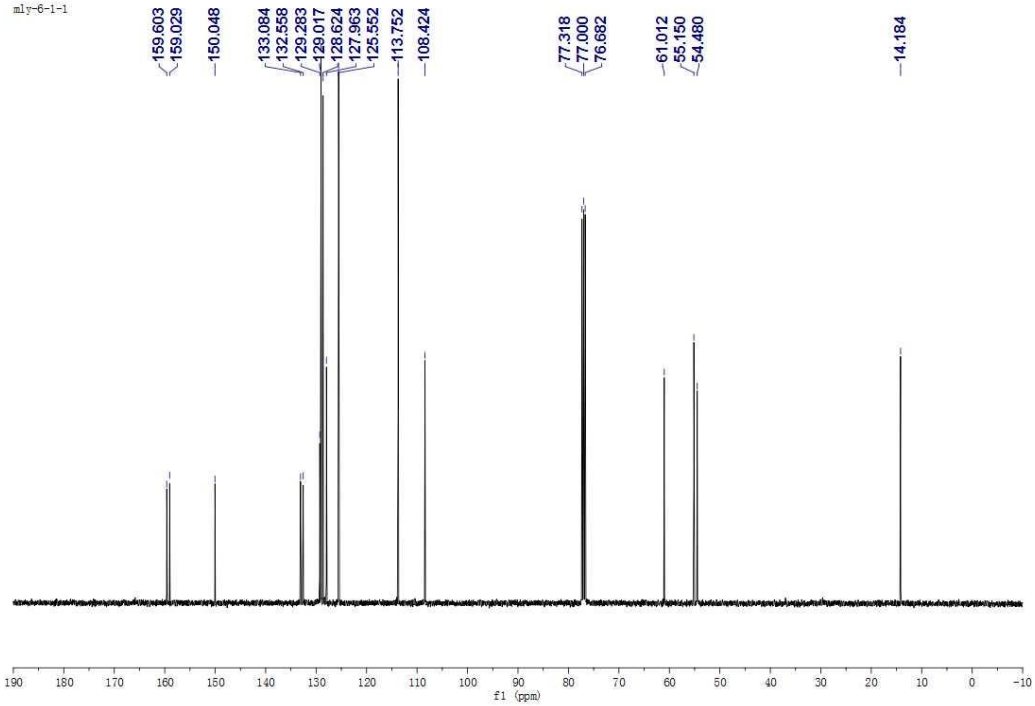

CO2Et
N
N
Ph
Ph

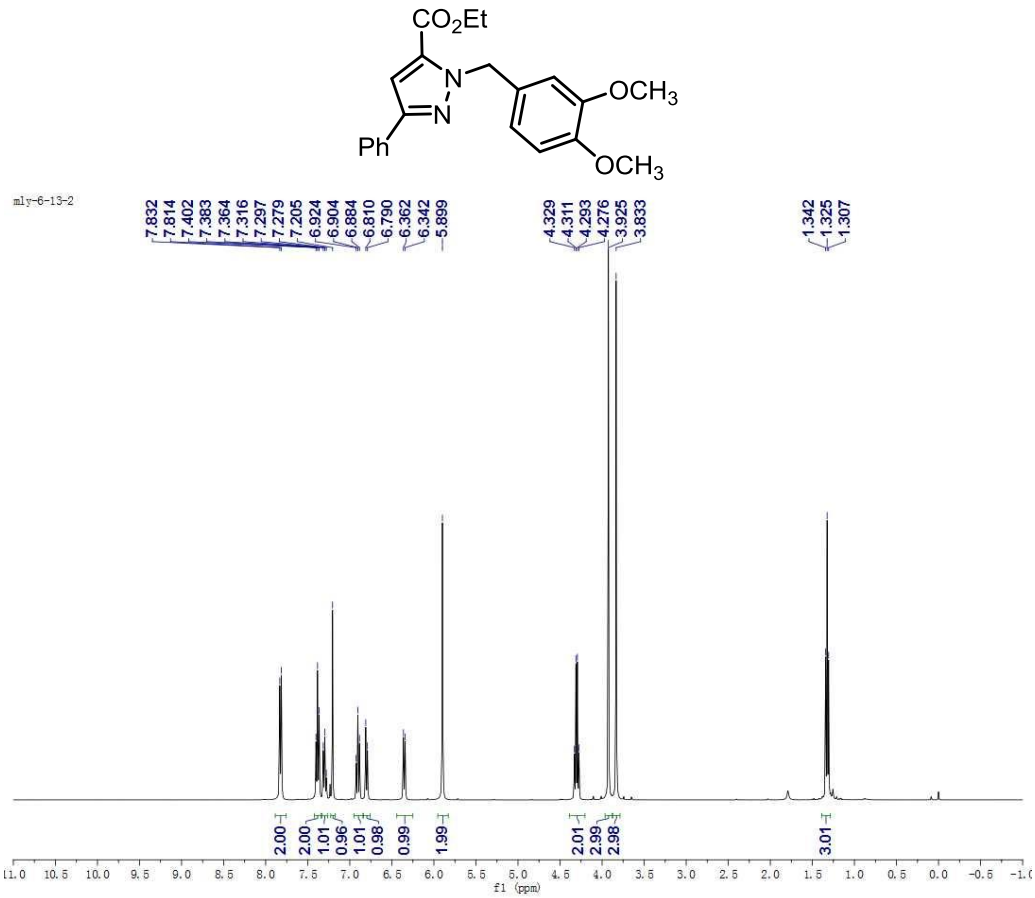

mly-6-1-3
7.866
7.848
7.550
7.530
7.509
7.436
7.418
7.403
7.381
7.360
7.347
7.329
7.313
7.295
7.193
5.850
4.354
4.336
4.318
4.300
1.372
1.354
1.336
2.00
4.10
7.98
0.97
2.01
2.00
3.07
f1 (ppm)

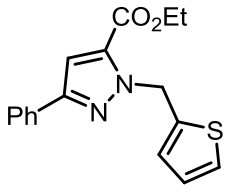

mly-6-1-3
159.599
150.259
140.497
136.170
133.370
132.496
128.699
128.674
128.062
127.893
127.219
127.023
125.604
108.513
77.317
77.000
76.682
61.106
54.780
26.984
14.189
mly-6-1-3
140.708
140.497
136.170
133.370
132.496
128.699
128.674
127.893
127.219
127.023
125.604
f1 (ppm)
f1 (ppm)

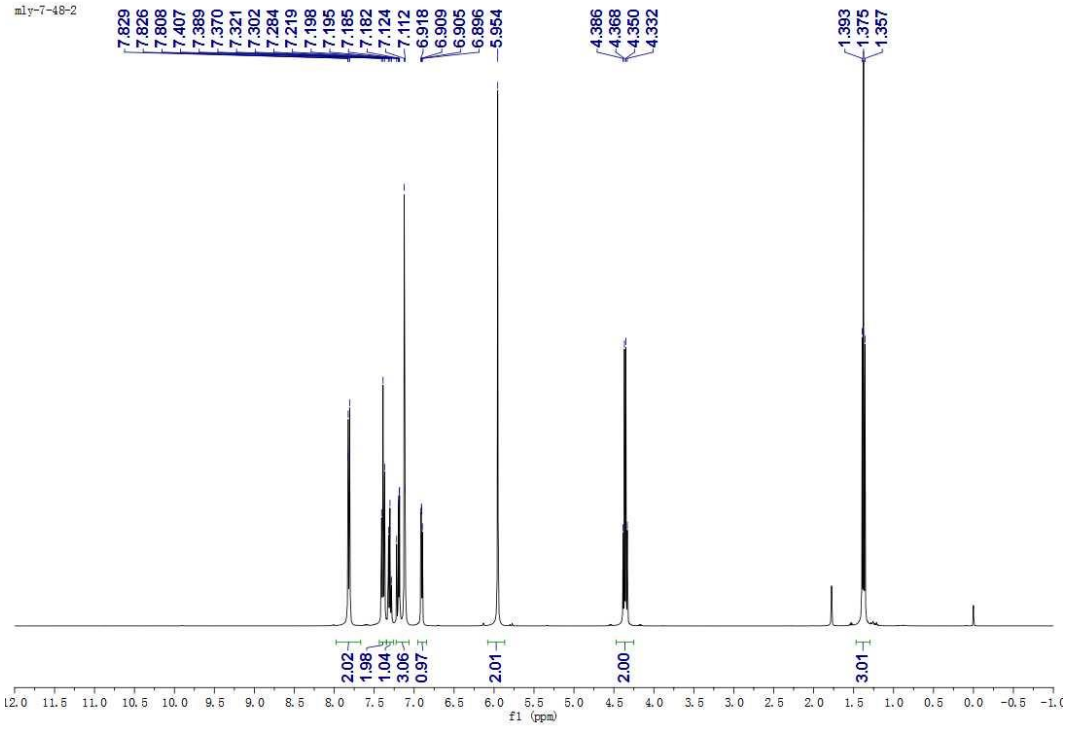

CO2Et
N
N
Ph
OCH3

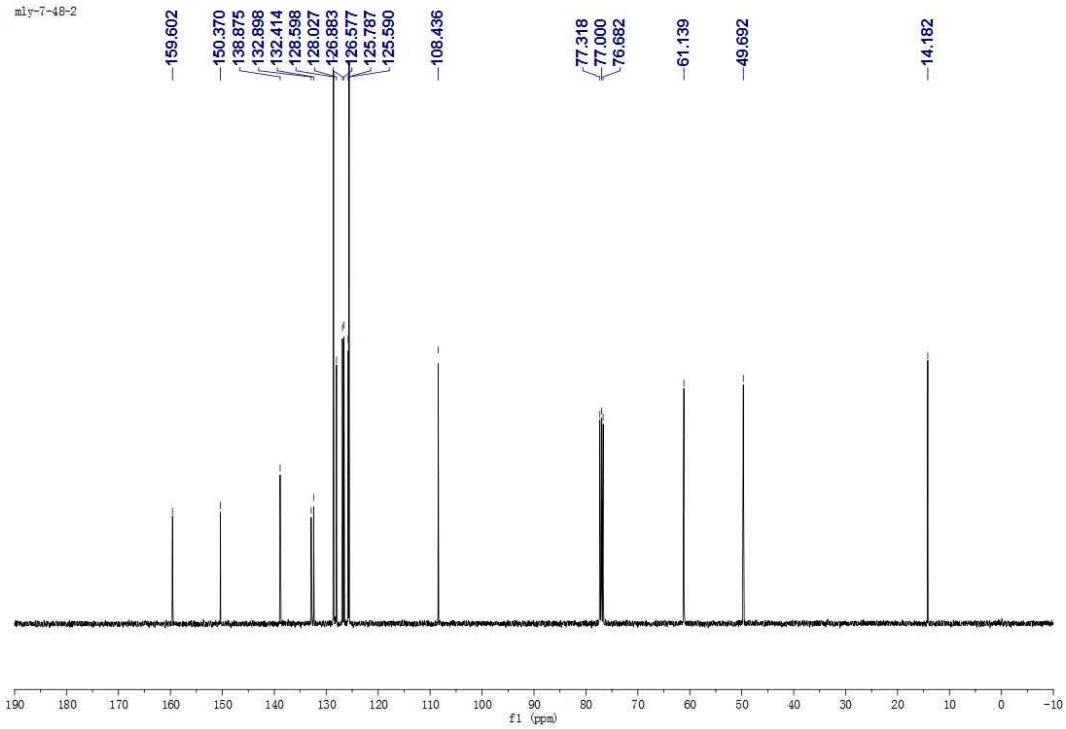

mly-6-1-1
7.841
7.823
7.332
7.314
7.300
7.278
7.149
6.832
6.810
5.734
4.346
4.328
4.310
4.292
3.748
1.371
1.353
1.335
2.00
2.02
2.96
0.98
2.00
2.01
2.00
3.00
3.07
f1 (ppm)

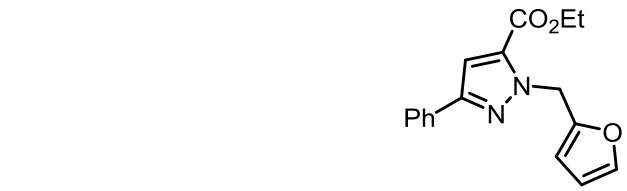

mly-6-1-1
159.603
159.029
150.048
133.084
132.558
129.283
129.017
128.624
127.963
125.552
113.752
108.424
77.318
77.000
76.682
61.012
55.150
54.480
14.184
f1 (ppm)

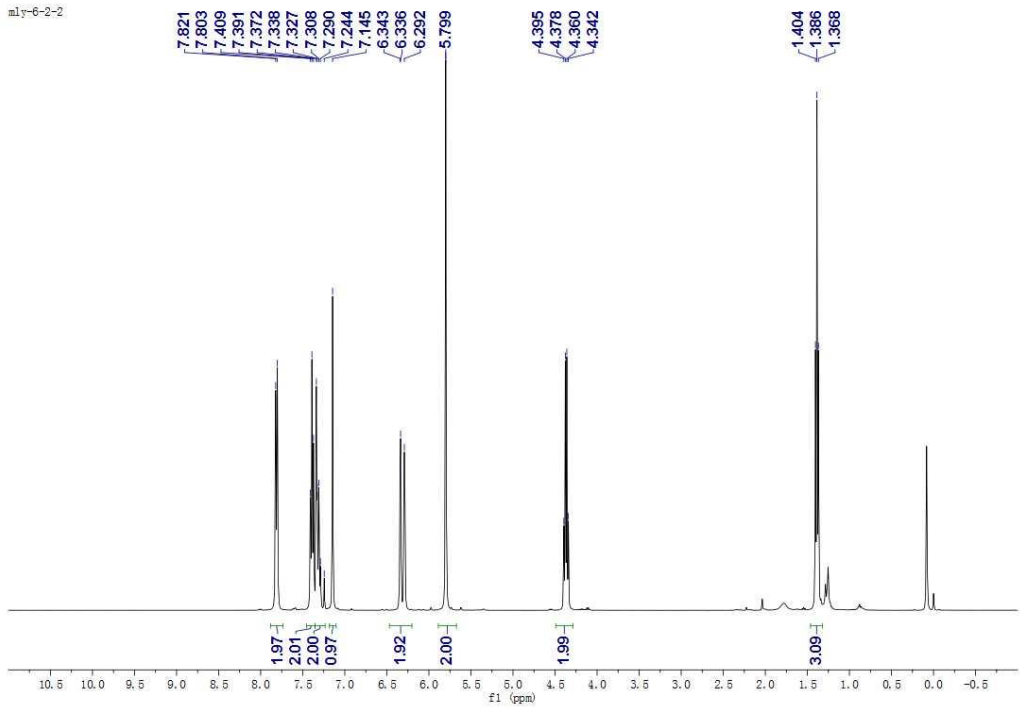

CO2Et
N
N
Ph
OCH3
OCH3
mly-6-13-2
7.832
7.814
7.402
7.383
7.364
7.316
7.297
7.279
7.205
6.924
6.904
6.884
6.810
6.790
6.362
6.342
5.899
4.329
4.311
4.293
4.276
3.925
3.833
1.342
1.325
1.307
2.00
2.00
1.01
0.96
1.01
0.98
0.99
1.99
2.01
2.99
2.98
3.01
f1 (ppm)
mly-6-13-2
159.411
152.385
150.146
146.157
133.949
132.494
131.540
128.575
127.930
125.496
123.966
119.116
111.560
108.196
77.318
77.000
76.682
60.978
60.442
55.655
50.209
14.105
f1 (ppm)

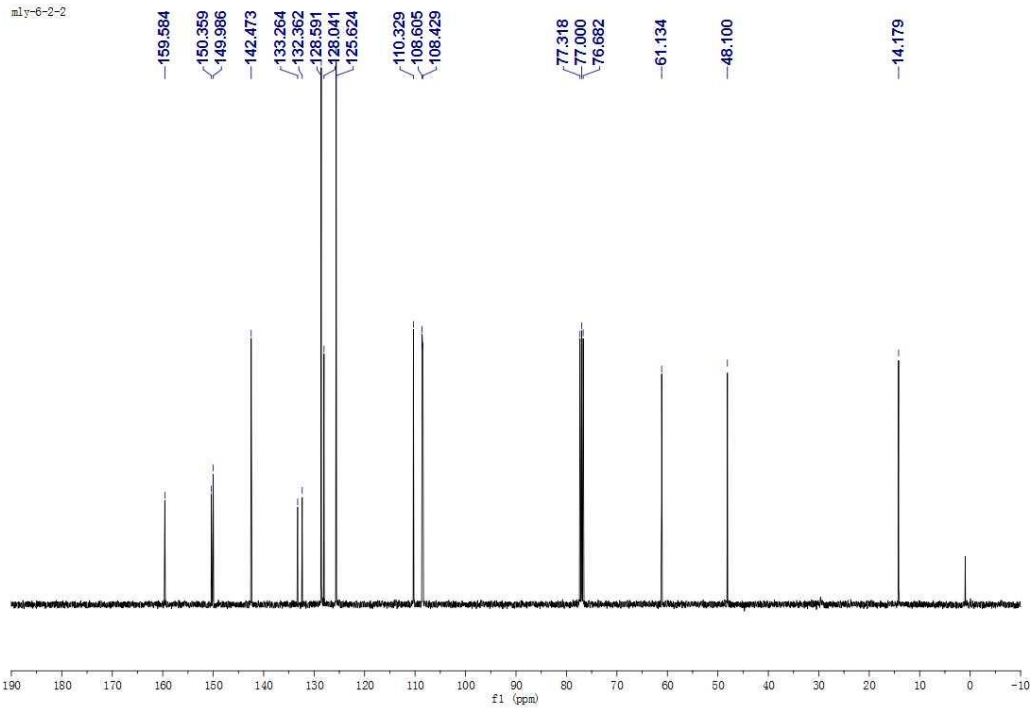

CO2Et
Ph
N
N
S

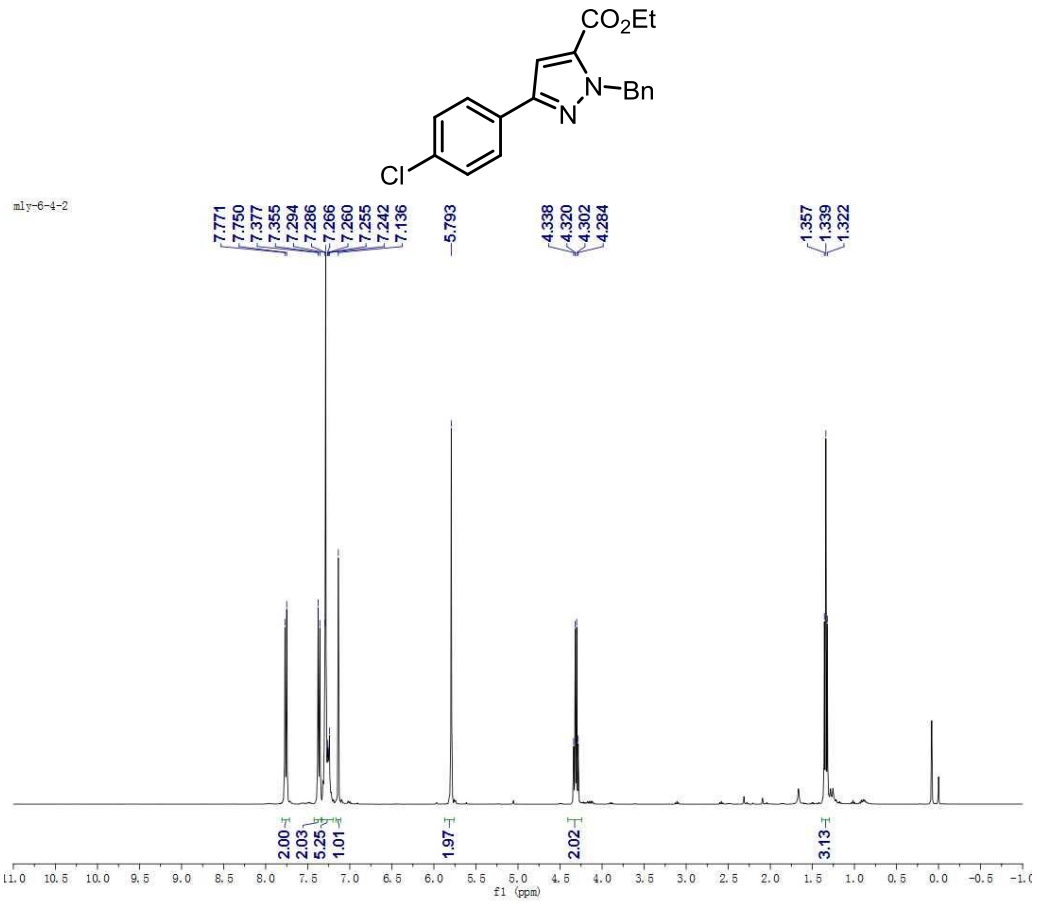

mly-7-48-2
7.829
7.826
7.808
7.407
7.389
7.370
7.321
7.302
7.284
7.219
7.198
7.195
7.185
7.182
7.124
7.112
6.918
6.909
6.905
6.896
5.954
4.386
4.368
4.350
4.332
1.393
1.375
1.357
2.02
1.98
1.04
3.06
0.97
2.01
2.00
3.01
f1 (ppm)

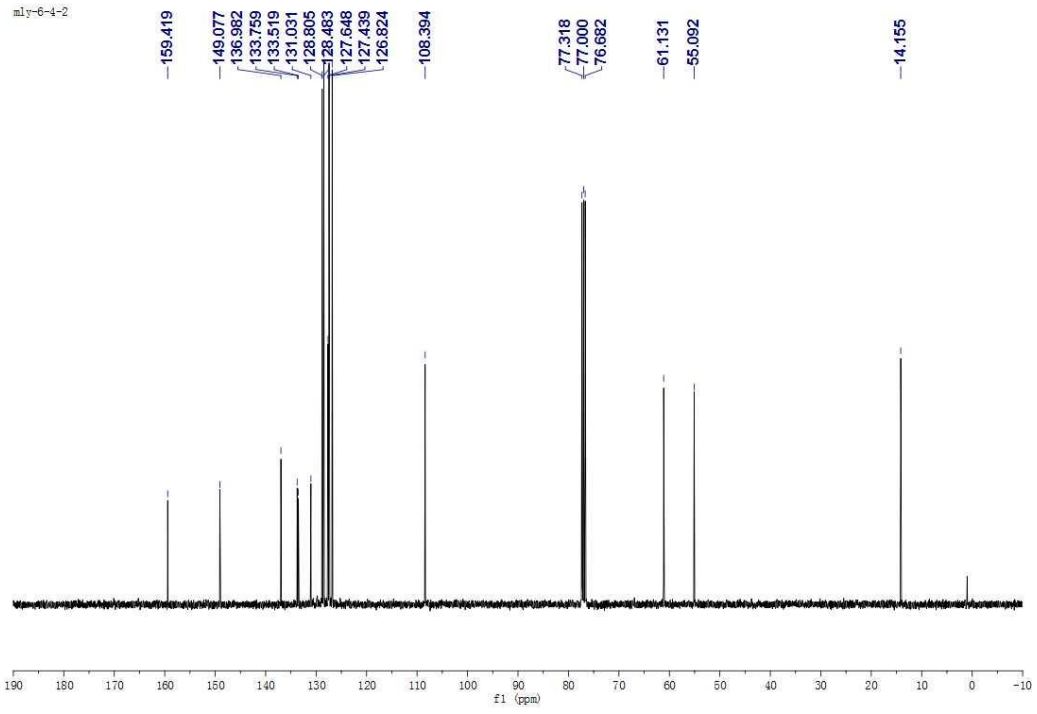

mly-7-48-2
159.602
150.370
138.875
132.898
132.414
128.598
128.027
126.883
126.577
125.787
125.590
108.436
77.318
77.000
76.682
61.139
49.692
14.182
f1 (ppm)


CO2Et
Ph
N
N
O


mly-6-2-2
7.821
7.803
7.409
7.391
7.372
7.338
7.327
7.308
7.290
7.244
7.145
6.343
6.336
6.292
5.799
4.395
4.378
4.360
4.342
1.404
1.386
1.368
1.97
2.01
2.00
0.97
1.92
2.00
1.99
3.09
f1 (ppm)


mly-6-2-2
159.584
150.359
149.986
142.473
133.264
132.362
128.591
128.041
125.624
110.329
108.605
108.429
77.318
77.000
76.682
61.134
48.100
14.179
f1 (ppm)


CO2Et
N
N
Bn
Cl
mly-6-4-2
7.771
7.750
7.377
7.355
7.294
7.286
7.266
7.260
7.255
7.242
7.136
5.793
4.338
4.320
4.302
4.284
1.357
1.339
1.322
2.00
2.03
5.25
1.01
1.97
2.02
3.13
f1 (ppm)


mly-6-4-2
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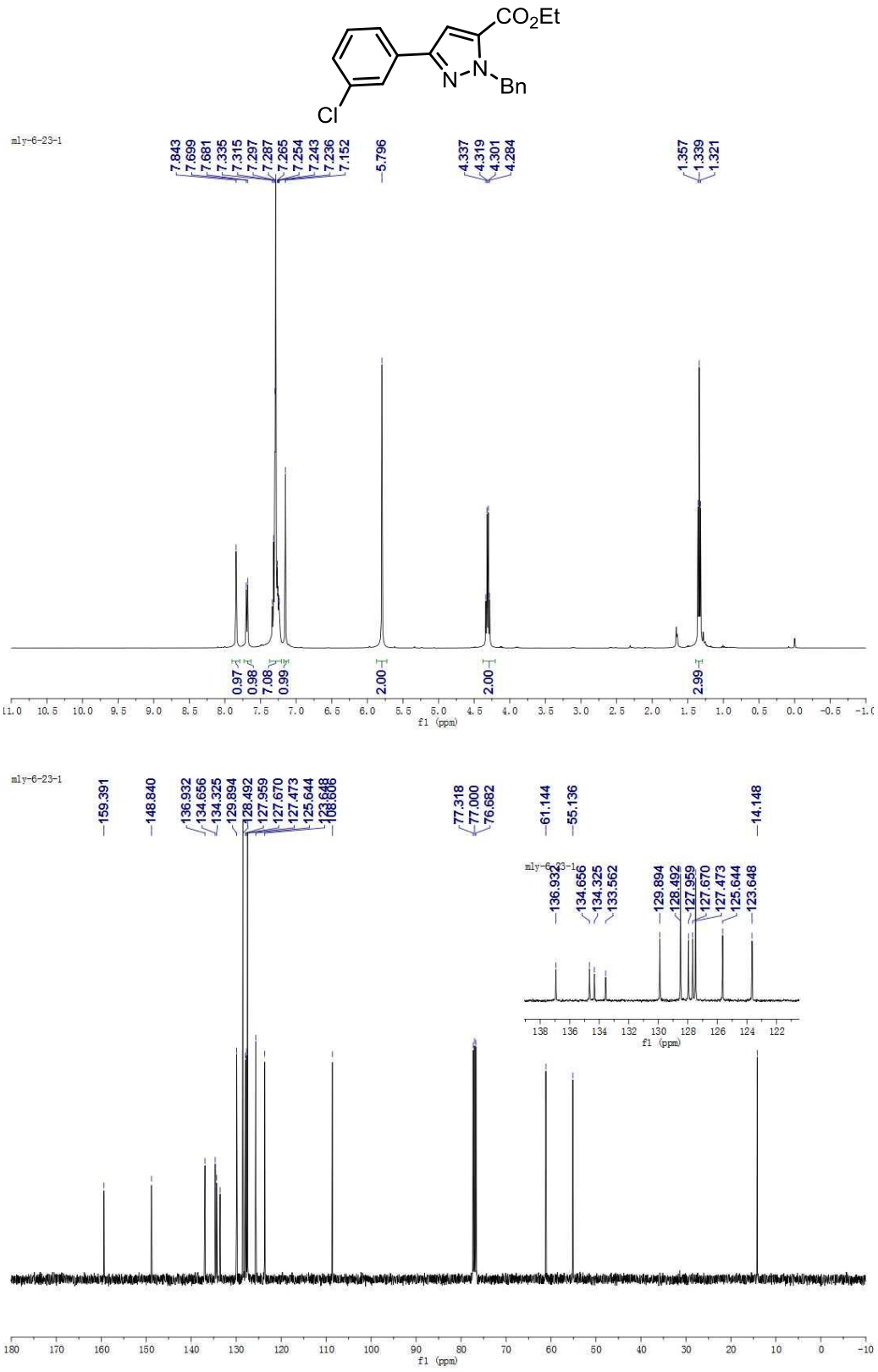
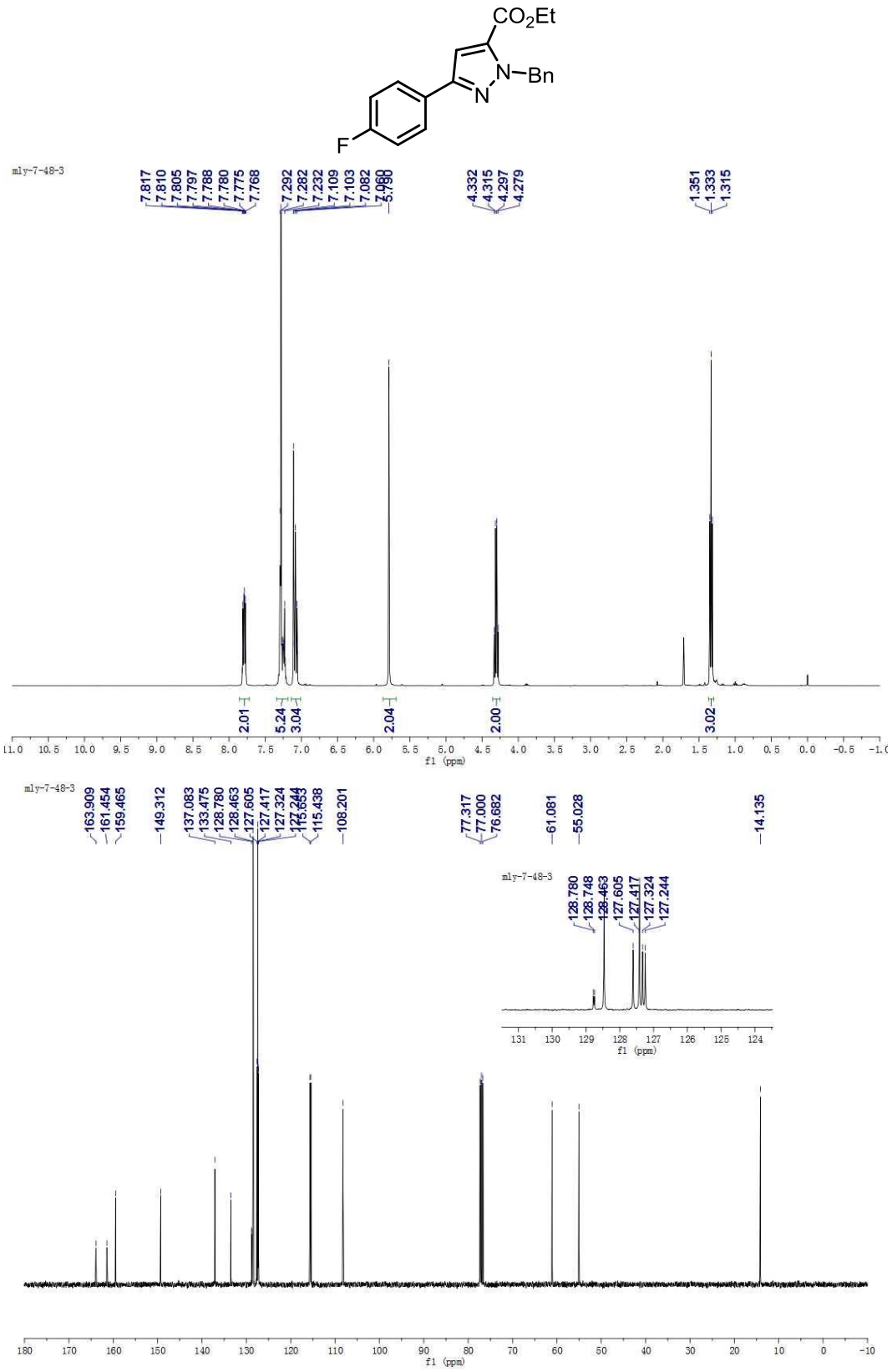
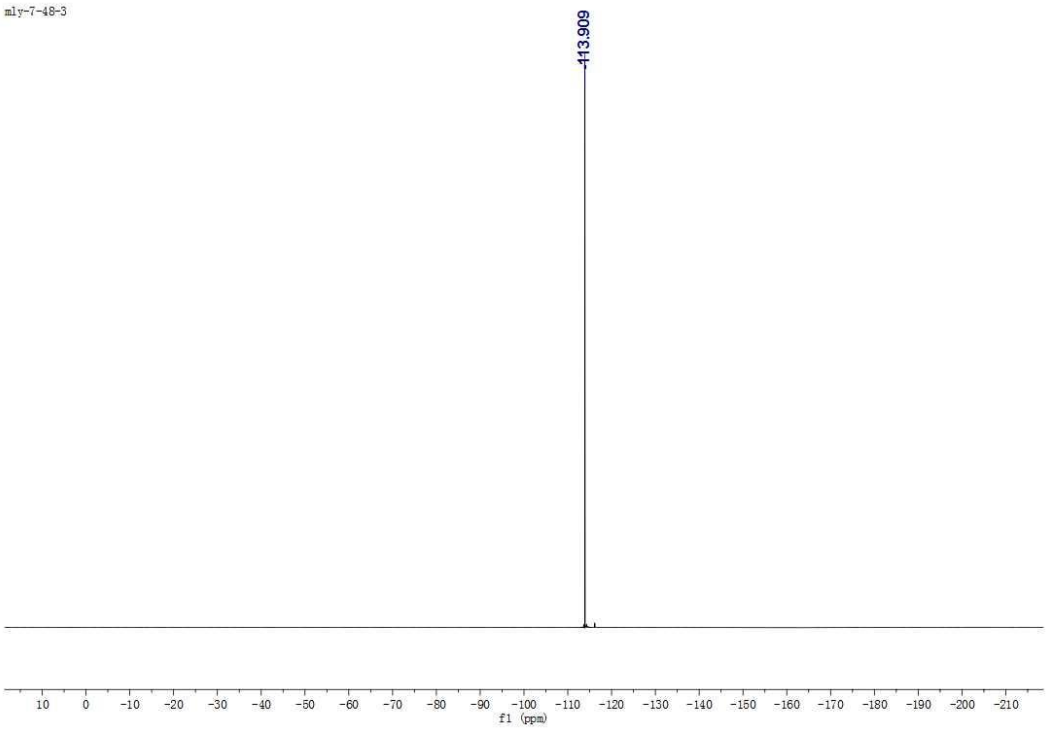
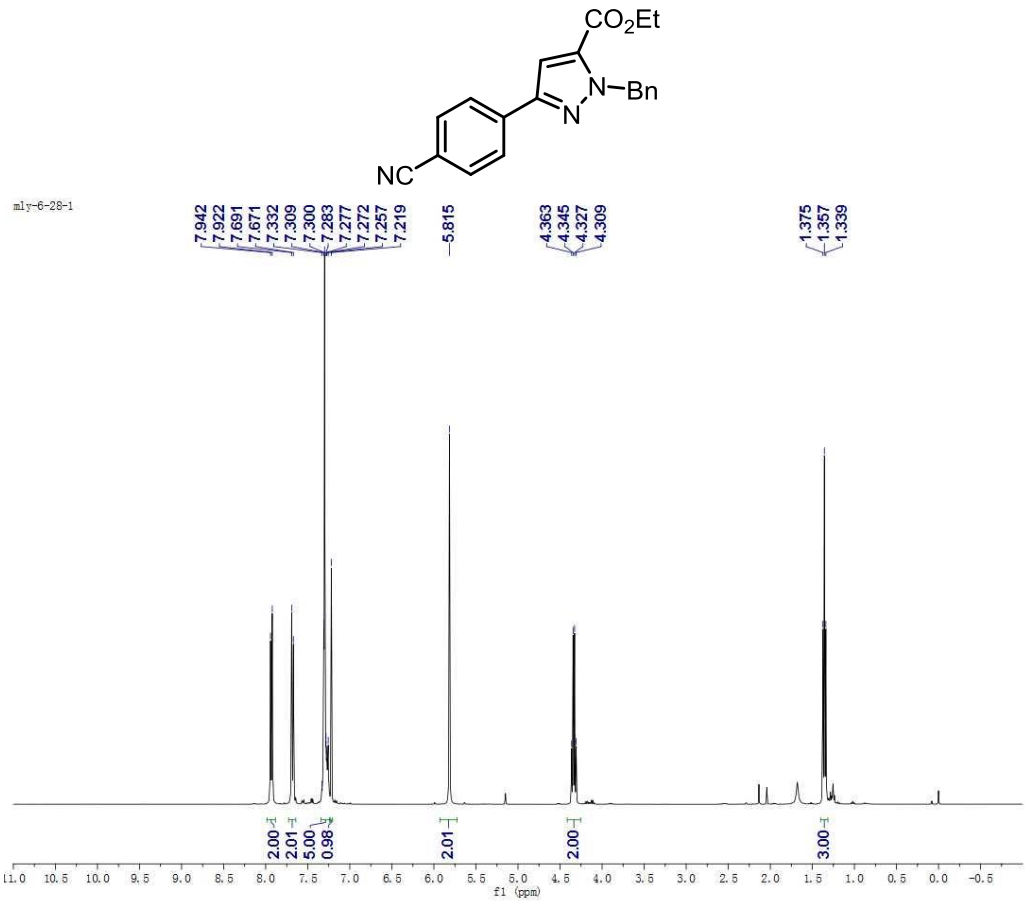
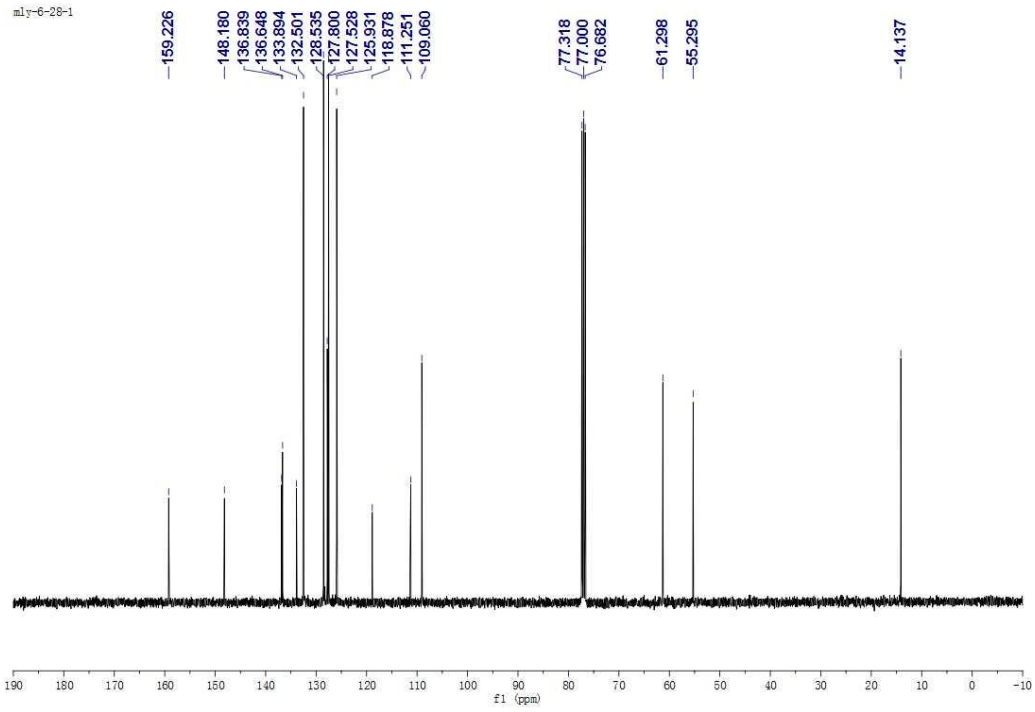
149.077
136.982
133.759
133.519
131.031
128.805
128.483
127.648
127.439
126.824
108.394
77.318
77.000
76.682
61.131
55.092
14.155
f1 (ppm)

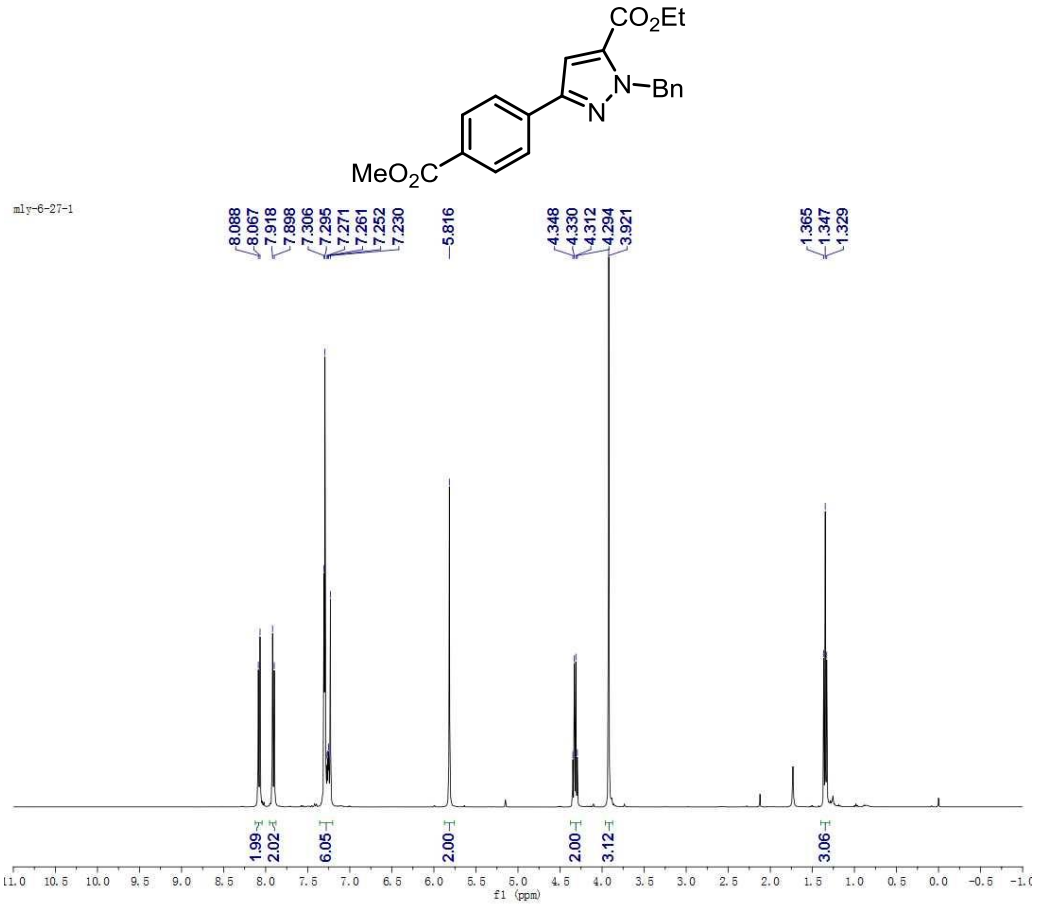

CO2Et
N
N
Bn
Cl
mly-6-23-1
7.843
7.699
7.681
7.335
7.315
7.297
7.287
7.265
7.254
7.243
7.236
7.152
5.796
4.337
4.319
4.301
4.284
1.357
1.339
1.321
0.97
0.98
7.08
0.99
2.00
2.00
2.99
f1 (ppm)
mly-6-23-1
159.391
148.840
136.932
134.656
134.325
129.894
128.492
127.959
127.670
127.473
125.644
123.648
77.318
77.000
76.682
61.144
55.136
14.148
f1 (ppm)

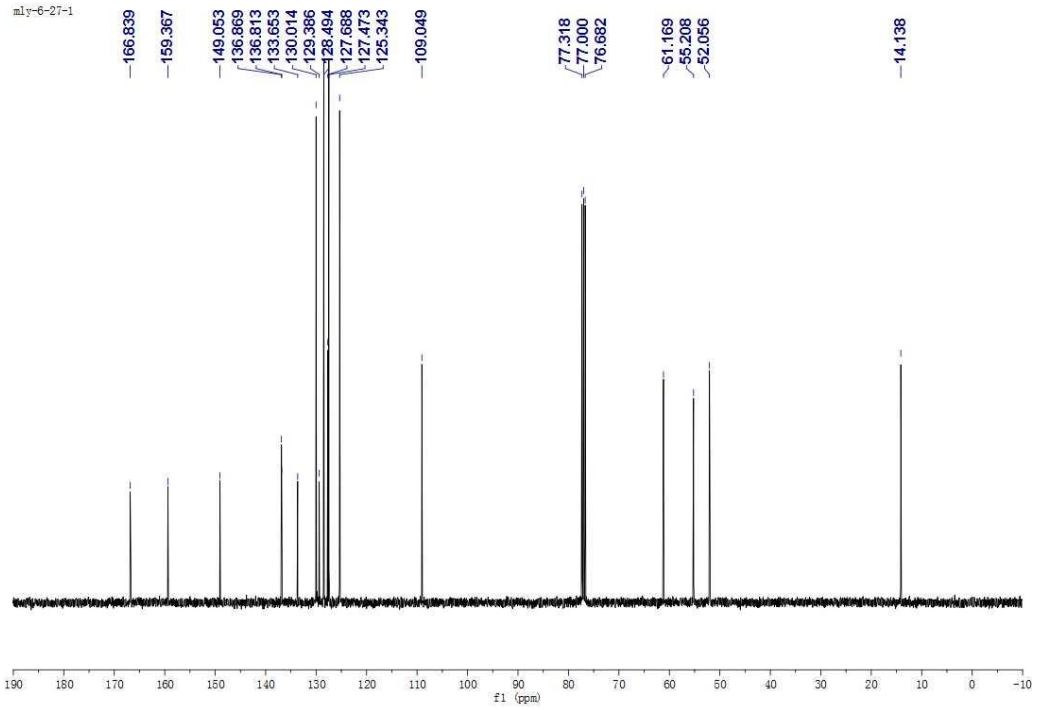

CO2Et
N
Bn
N
F
mly-7-48-3
7.817
7.810
7.805
7.797
7.788
7.780
7.775
7.768
7.292
7.282
7.232
7.109
7.103
7.082
4.332
4.315
4.297
4.279
1.351
1.333
1.315
2.01
5.24
3.04
2.04
2.00
3.02
f1 (ppm)
mly-7-48-3
163.909
161.454
159.465
149.312
137.083
133.475
128.780
128.463
127.605
127.417
127.324
115.438
108.201
77.317
77.000
76.682
61.081
55.028
14.135
mly-7-48-3
128.780
128.748
128.463
127.605
127.417
127.324
127.244
f1 (ppm)
f1 (ppm)

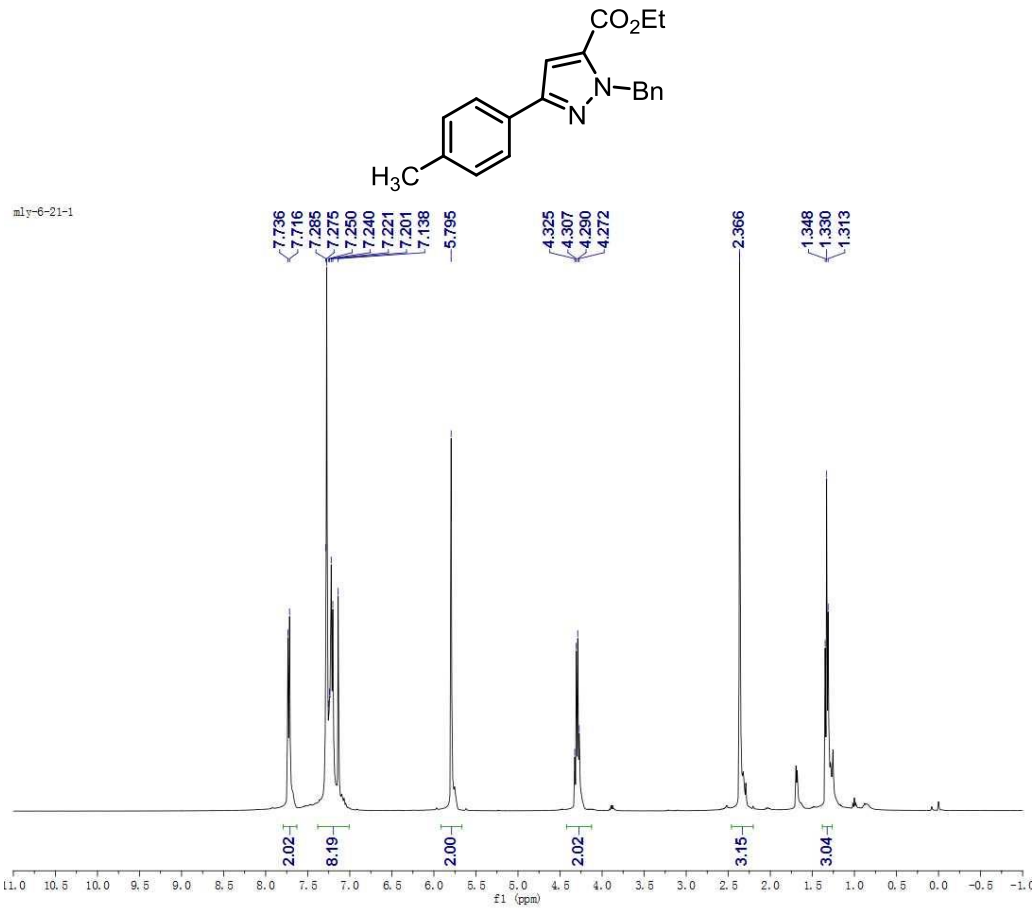

mly-7-48-3
-113.909
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

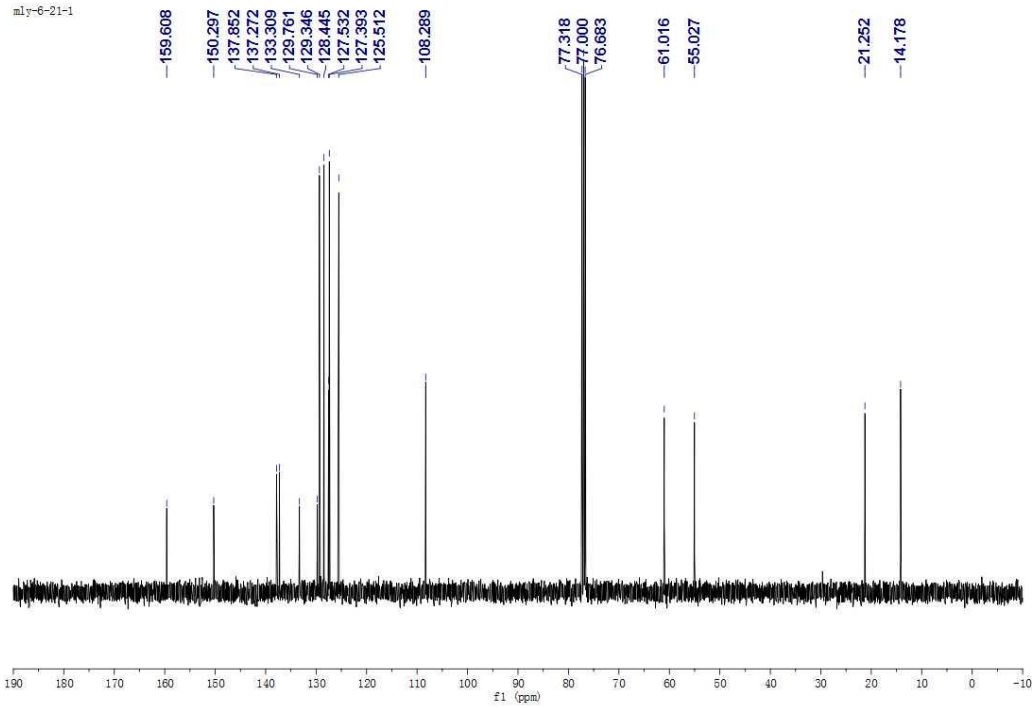

CO2Et
N
N
Bn
NC
mly-6-28-1
7.942
7.922
7.691
7.671
7.332
7.309
7.300
7.283
7.277
7.272
7.257
7.219
5.815
4.363
4.345
4.327
4.309
1.375
1.357
1.339
2.00
2.01
5.00
0.98
2.01
2.00
3.00
f1 (ppm)

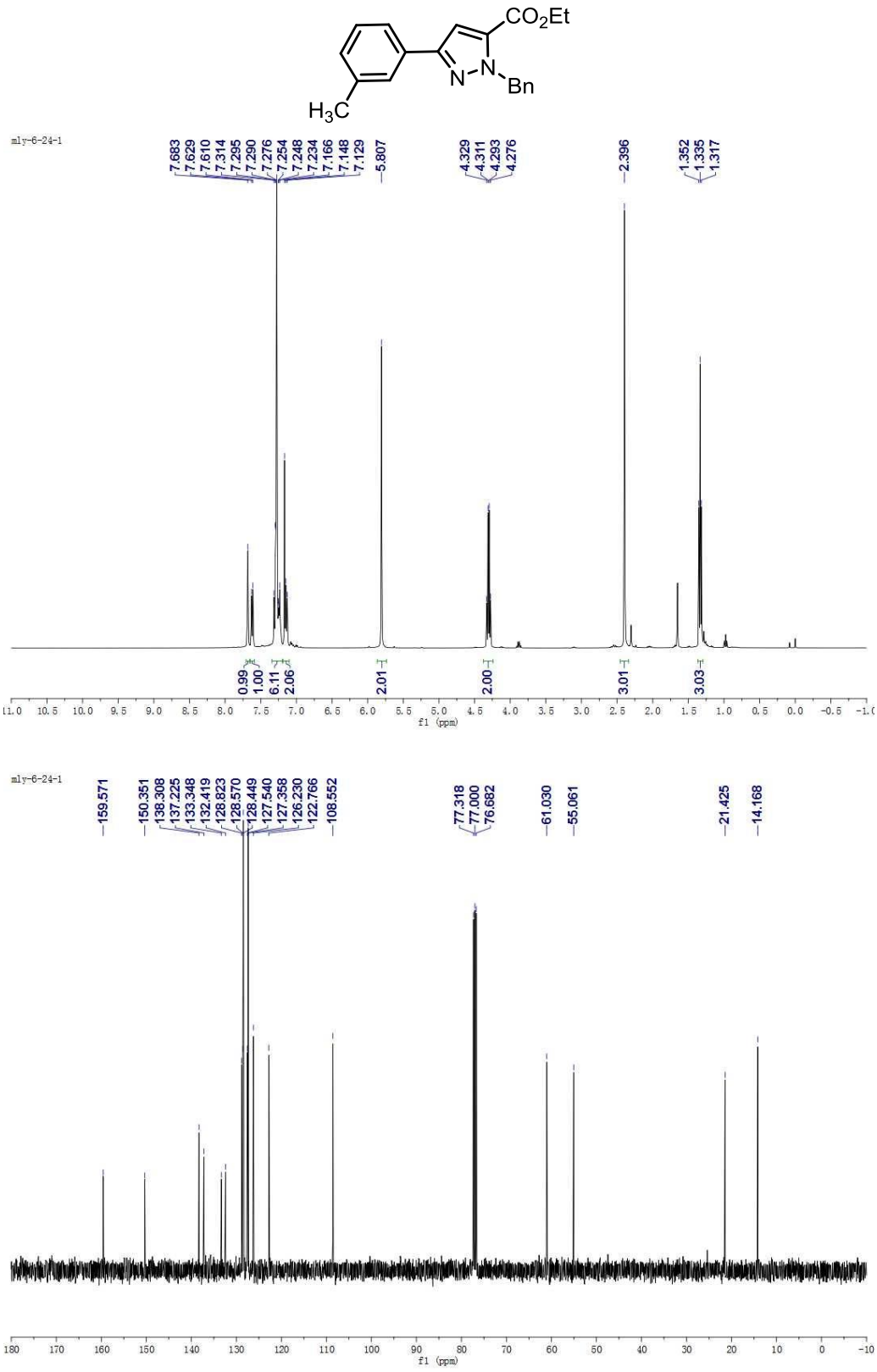

mly-6-28-1
159.226
148.180
136.839
136.648
133.894
132.501
128.535
127.800
127.528
125.931
118.878
111.251
109.060
77.318
77.000
76.682
61.298
55.295
14.137
f1 (ppm)


mly-6-27-1
8.088
8.067
7.918
7.898
7.306
7.295
7.271
7.261
7.252
7.230
5.816
4.348
4.330
4.312
4.294
3.921
1.365
1.347
1.329
1.99
2.02
6.05
2.00
2.00
3.12
3.06
f1 (ppm)

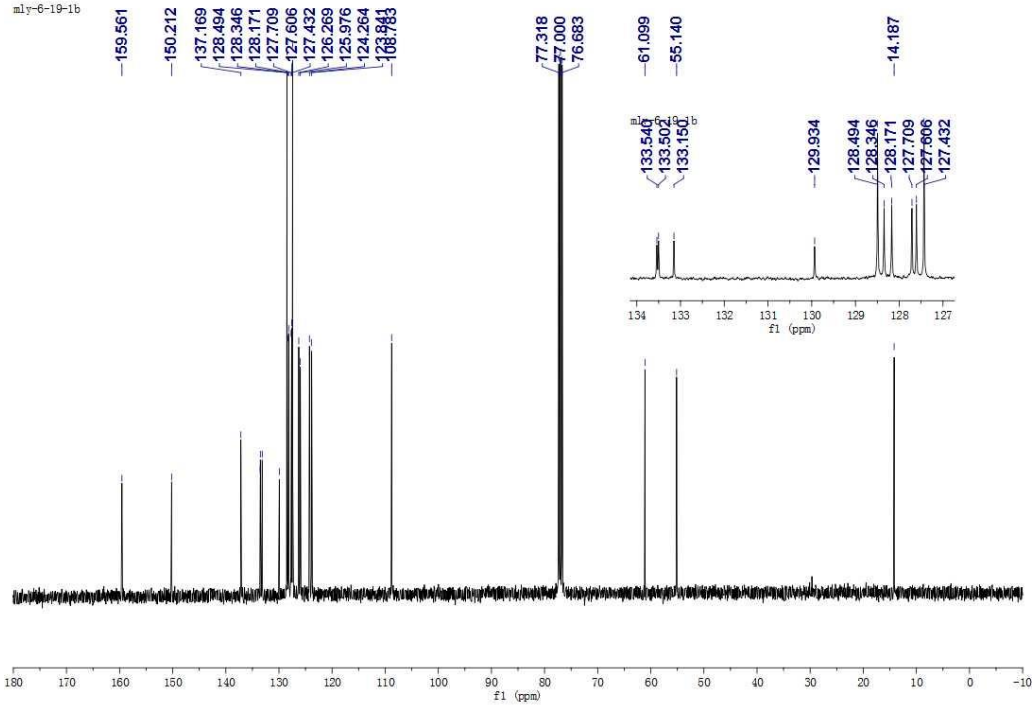

mly-6-27-1
166.839
159.367
149.053
136.869
136.813
133.653
130.014
129.386
128.494
127.688
127.473
125.343
109.049
77.318
77.000
76.682
61.169
55.208
52.056
14.138
f1 (ppm)

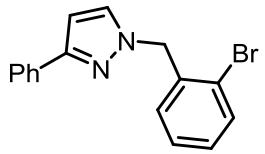

mly-6-21-1
7.736
7.716
7.285
7.275
7.250
7.240
7.221
7.201
7.138
5.795
4.325
4.307
4.290
4.272
2.366
1.348
1.330
1.313
2.02
8.19
2.00
2.02
3.15
3.04
f1 (ppm)

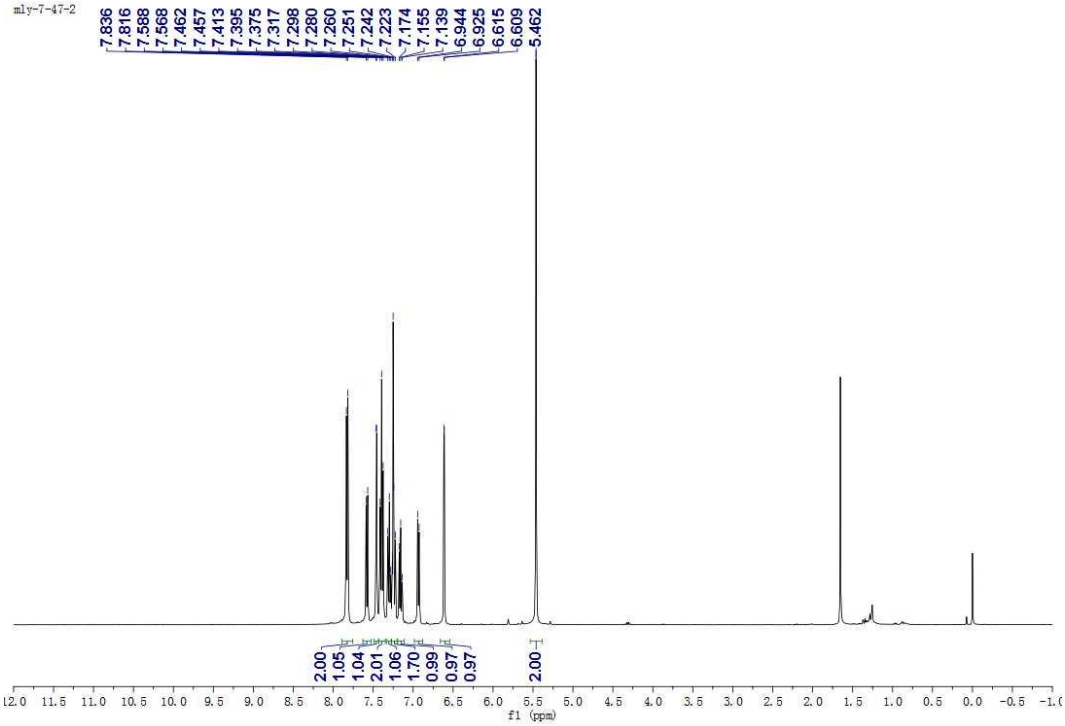

mly-6-21-1
159.608
150.297
137.852
137.272
133.309
129.761
129.346
128.445
127.532
127.393
125.512
108.289
77.318
77.000
76.683
61.016
55.027
21.252
14.178
f1 (ppm)

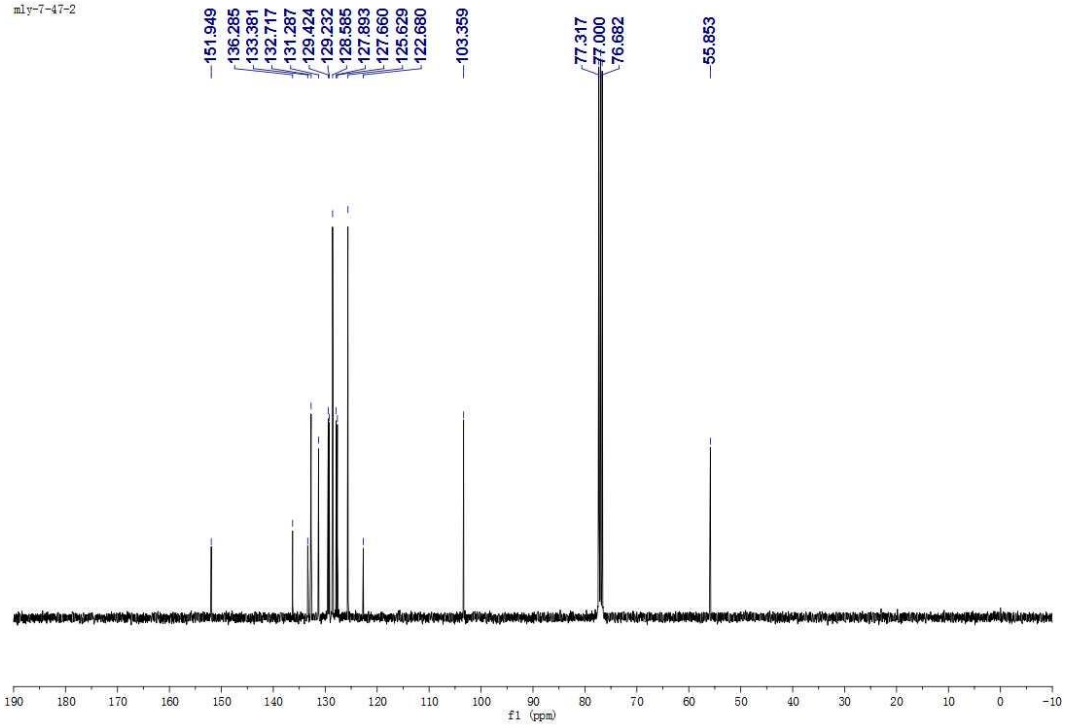

CO2Et
N
N
Bn
H3C
mly-6-24-1
7.683
7.629
7.610
7.314
7.295
7.290
7.276
7.254
7.248
7.234
7.166
7.148
7.129
5.807
4.329
4.311
4.293
4.276
2.396
1.352
1.335
1.317
0.99
1.00
6.11
2.06
2.01
2.00
3.01
3.03
f1 (ppm)
mly-6-24-1
159.571
150.351
138.308
137.225
133.348
132.419
128.823
128.570
128.449
127.540
127.358
126.230
122.766
108.552
77.318
77.000
76.682
61.030
55.061
21.425
14.168
f1 (ppm)

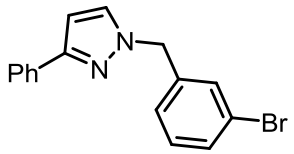

CO2Et
N
N
Bn
8.284
8.008
7.987
7.886
7.865
7.837
7.820
7.816
7.481
7.476
7.472
7.465
7.457
7.453
7.318
7.311
7.305
7.283
7.268
7.262
7.255
7.247
5.846
4.350
4.333
4.315
4.297
1.370
1.353
1.335
1.04
1.10
2.06
1.00
2.14
5.95
2.05
2.00
3.05
f1 (ppm)

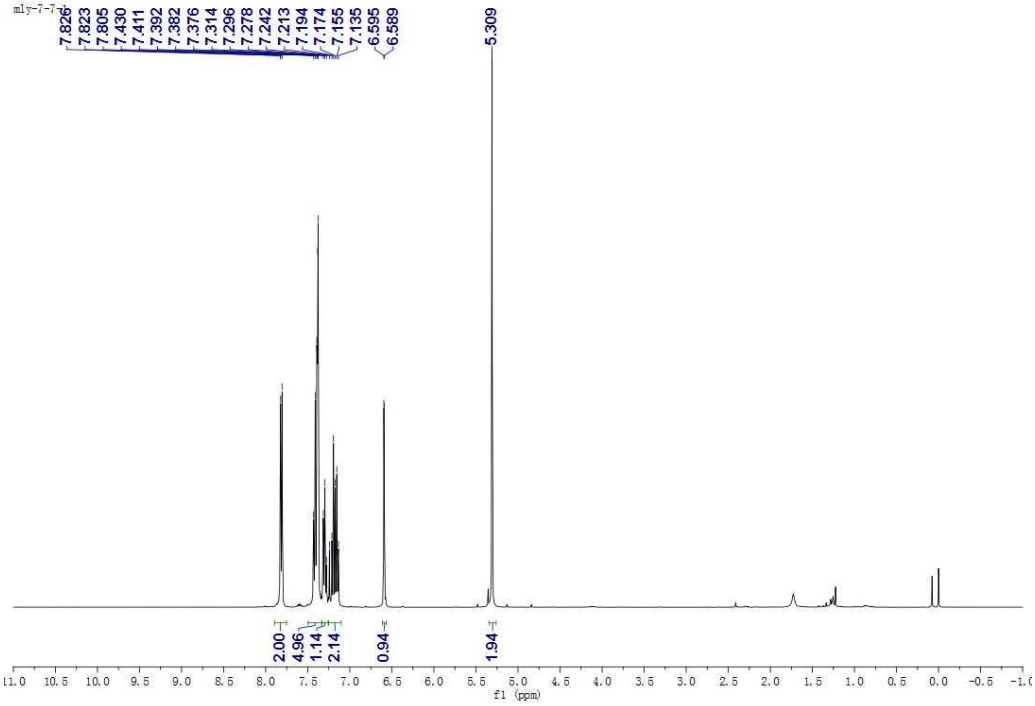

mly-6-19-1b
159.561
150.212
137.169
128.494
128.346
128.171
127.709
127.606
127.432
126.269
125.976
124.264
77.318
77.000
76.683
61.099
55.140
14.187
133.540
133.502
133.150
129.934
128.494
128.346
128.171
127.709
127.606
127.432
f1 (ppm)

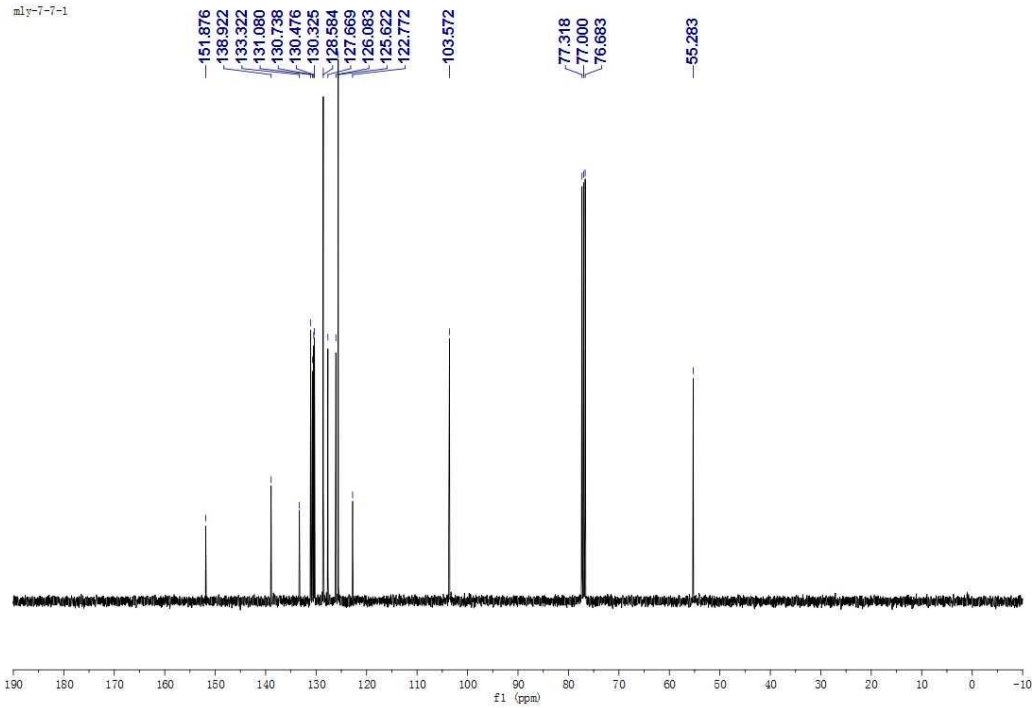

Ph
N
N
Br


mly-7-47-2
7.836
7.816
7.588
7.568
7.462
7.457
7.413
7.395
7.375
7.317
7.298
7.280
7.260
7.251
7.242
7.223
7.174
7.155
7.139
6.944
6.925
6.615
6.609
5.462
2.00
1.05
1.04
2.01
1.06
1.70
0.99
0.97
0.97
2.00
f1 (ppm)

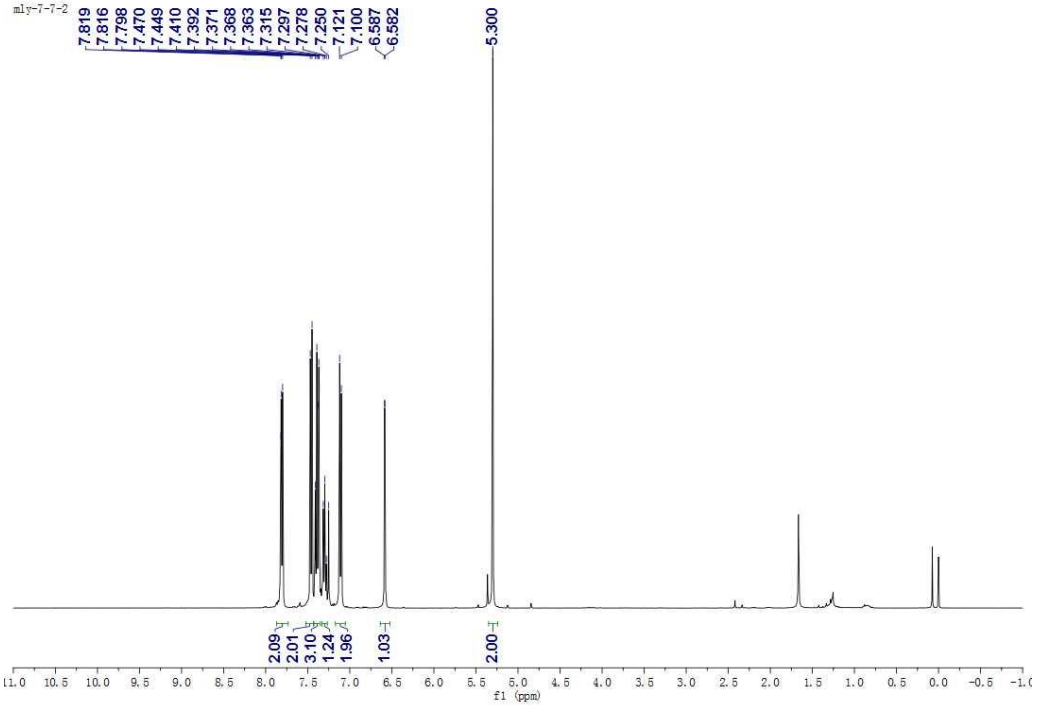

mly-7-47-2
151.949
136.285
133.381
132.717
131.287
129.424
129.232
128.585
127.893
127.660
125.629
122.680
103.359
77.317
77.000
76.682
55.853
f1 (ppm)

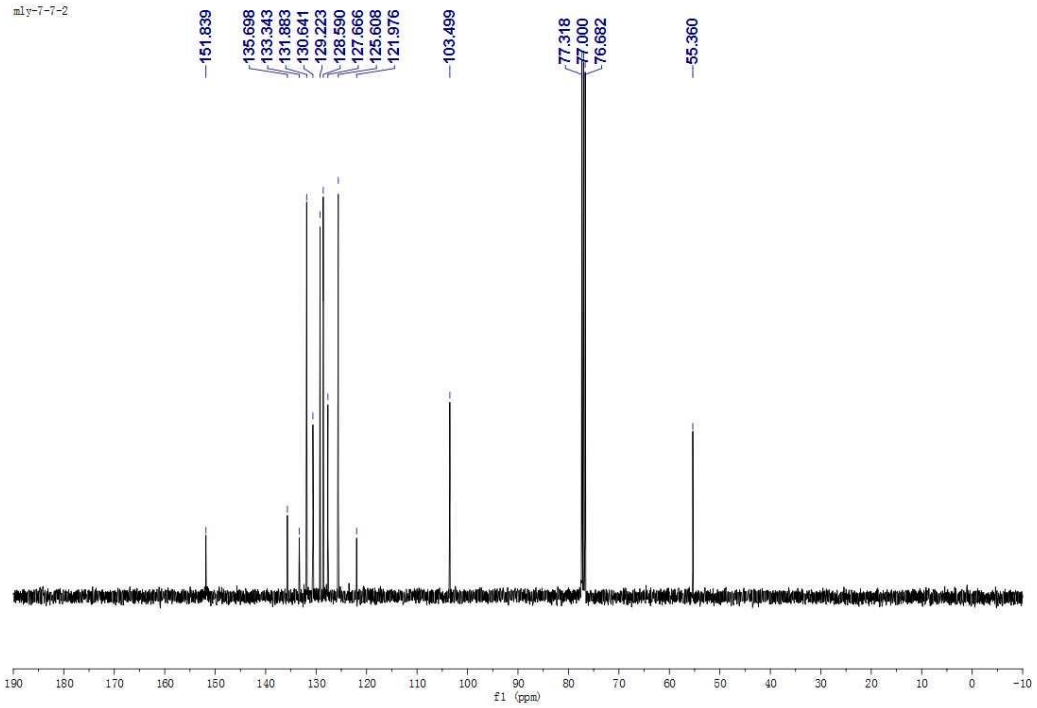

Ph
N
N
Br


mly-7-7-1
7.826
7.823
7.805
7.430
7.411
7.392
7.382
7.376
7.314
7.296
7.278
7.242
7.213
7.194
7.174
7.155
7.135
6.595
6.589
5.309
2.00
4.96
1.14
2.14
0.94
1.94
f1 (ppm)


mly-7-7-1
151.876
138.922
133.322
131.080
130.738
130.476
130.325
128.584
127.669
126.083
125.622
122.772
103.572
77.318
77.000
76.683
55.283
f1 (ppm)


Ph
N
N
Br


mly-7-7-2
7.819
7.816
7.798
7.470
7.449
7.410
7.392
7.371
7.368
7.363
7.315
7.297
7.278
7.250
7.121
7.100
6.587
6.582
5.300
2.09
2.01
3.10
1.24
1.96
1.03
2.00
f1 (ppm)


mly-7-7-2
151.839
135.698
133.343
131.883
130.641
129.223
128.590
127.666
125.608
121.976
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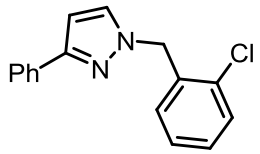
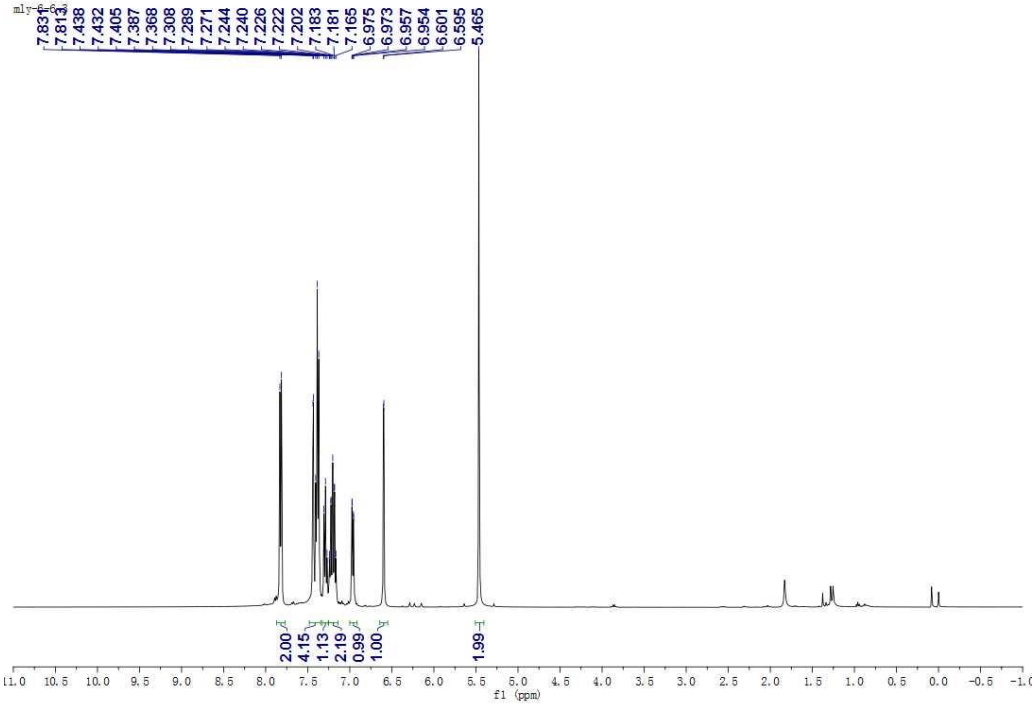
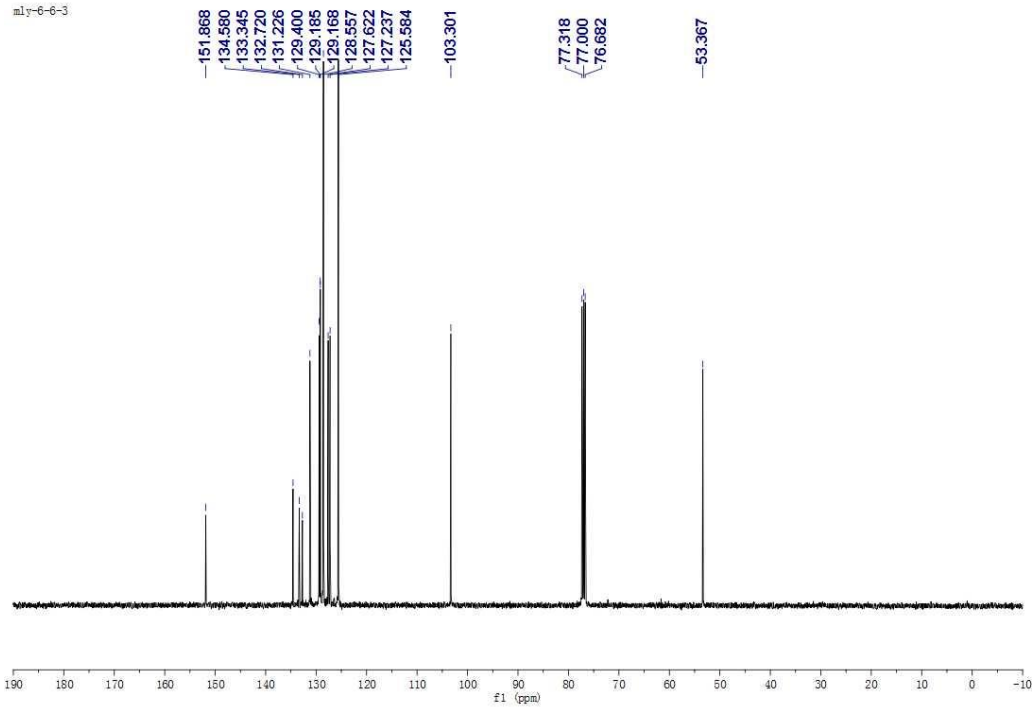
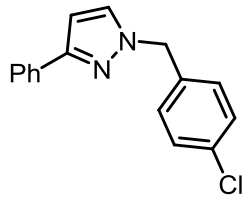
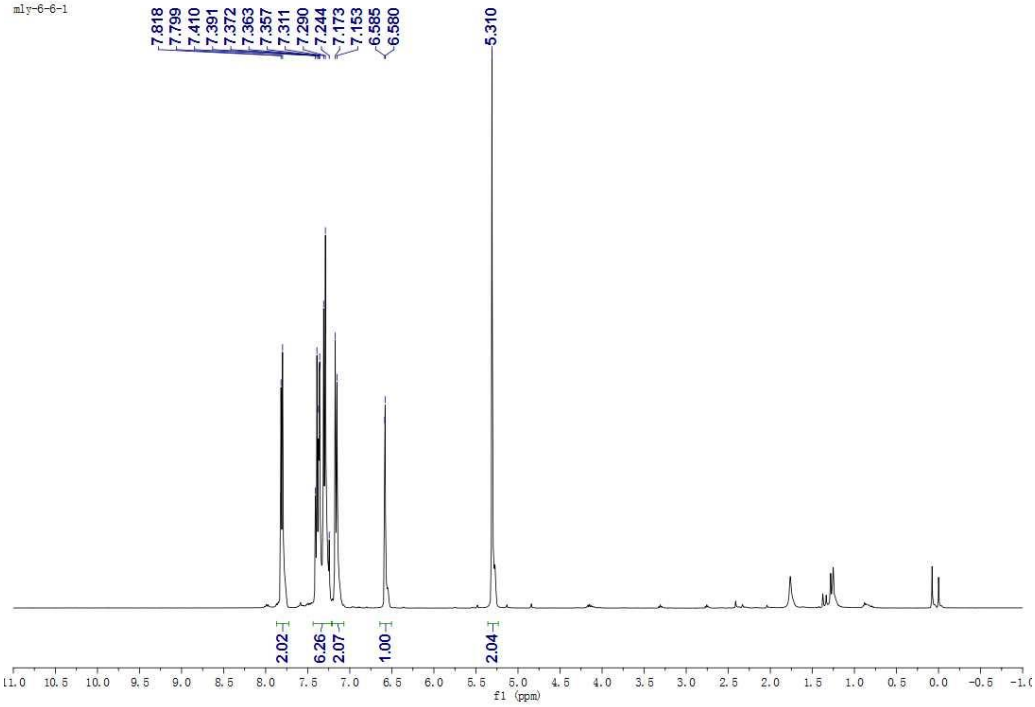
77.318
77.000
76.682
55.360
f1 (ppm)

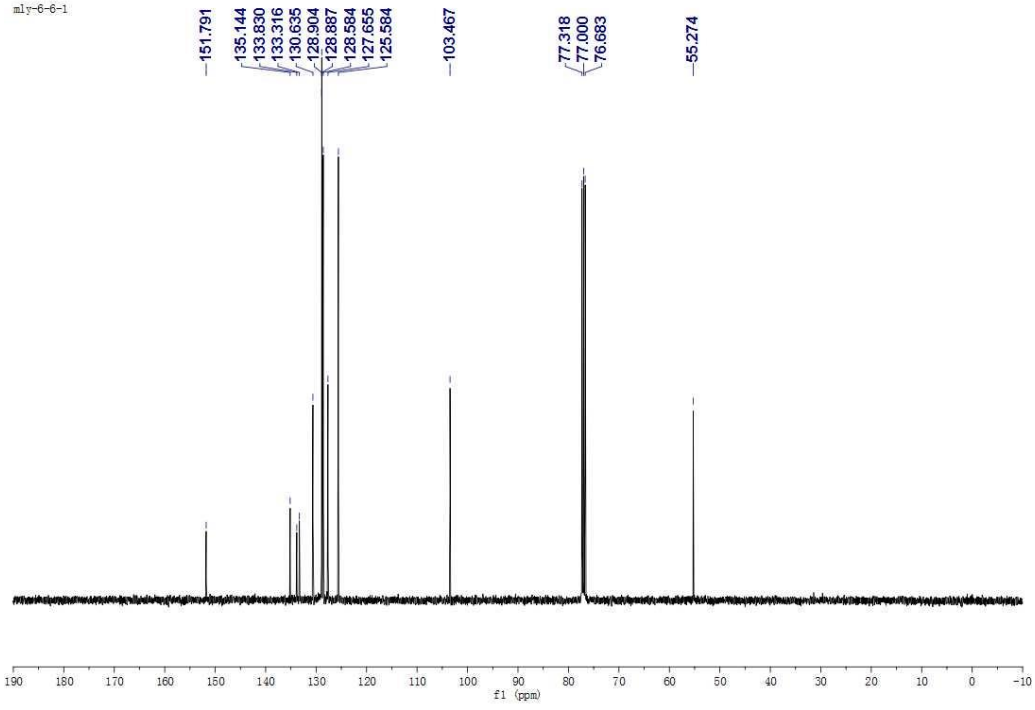

Ph
N
N
Cl


mly-6-6
7.831
7.813
7.438
7.432
7.405
7.387
7.368
7.308
7.289
7.271
7.244
7.240
7.226
7.222
7.202
7.183
7.181
7.165
6.975
6.973
6.957
6.954
6.601
6.595
5.465
2.00
4.15
1.13
2.19
0.99
1.00
1.99
f1 (ppm)

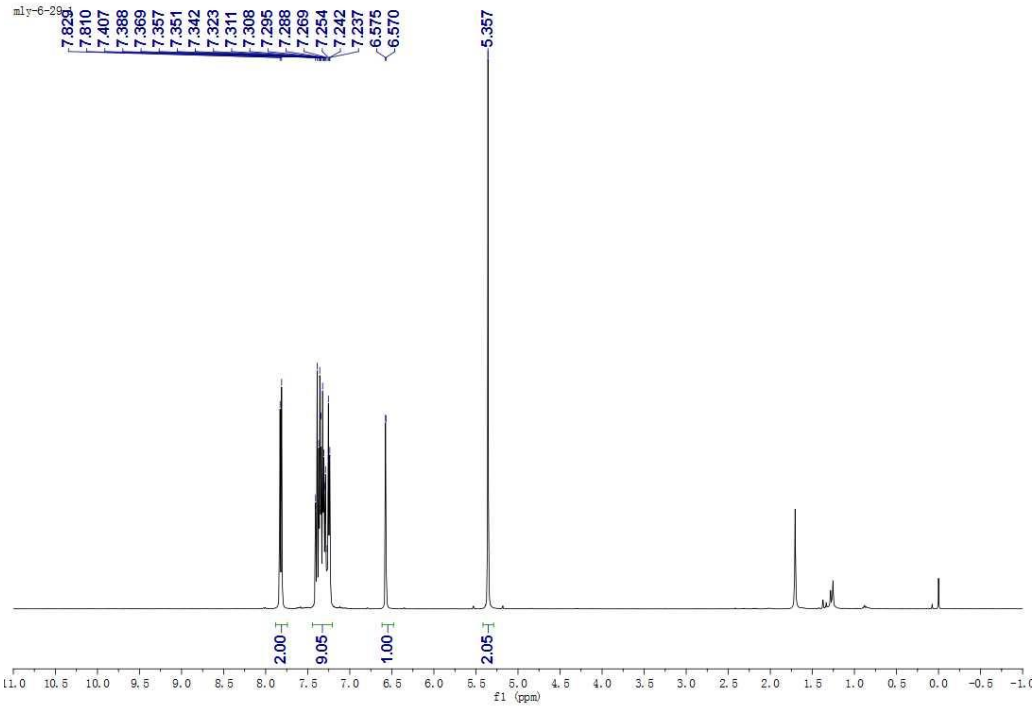

mly-6-6-3
151.868
134.580
133.345
132.720
131.226
129.400
129.185
129.168
128.557
127.622
127.237
125.584
103.301
77.318
77.000
76.682
53.367
f1 (ppm)

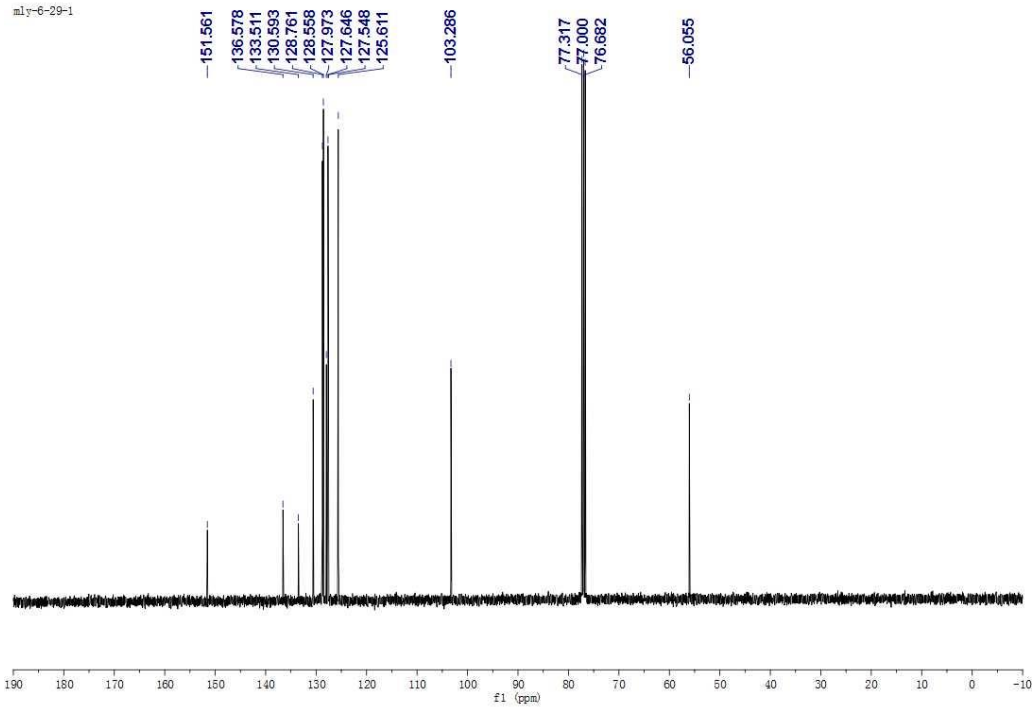

Ph
N
N
Cl

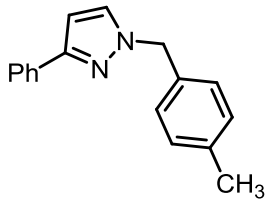

mly-6-6-1
7.818
7.799
7.410
7.391
7.372
7.363
7.357
7.311
7.290
7.244
7.173
7.153
6.585
6.580
5.310
2.02
6.26
2.07
1.00
2.04
f1 (ppm)

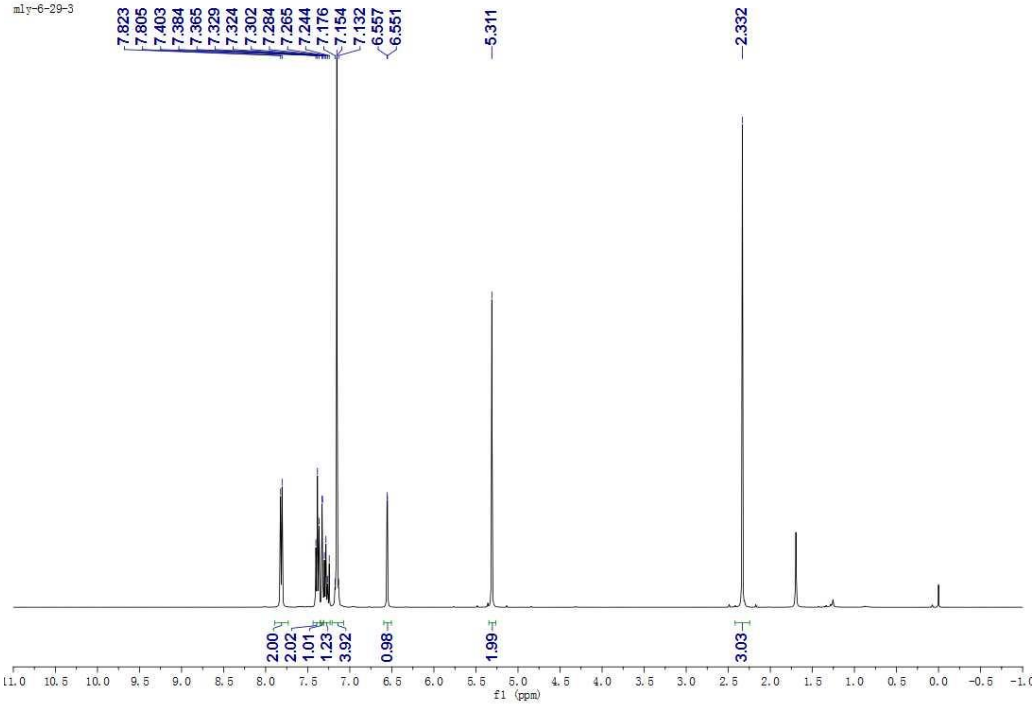

mly-6-6-1
151.791
135.144
133.830
133.316
130.635
128.904
128.887
128.584
127.655
125.584
103.467
77.318
77.000
76.683
55.274
f1 (ppm)


Ph
N
N


mly-6-29-1
7.829
7.810
7.407
7.388
7.369
7.357
7.351
7.342
7.323
7.311
7.308
7.295
7.288
7.269
7.254
7.242
7.237
6.575
6.570
5.357
2.00
9.05
1.00
2.05
f1 (ppm)


mly-6-29-1
151.561
136.578
133.511
130.593
128.761
128.558
127.973
127.646
127.548
125.611
103.286
77.317
77.000
76.682
56.055
f1 (ppm)


Ph
N
N
CH3


mly-6-29-3
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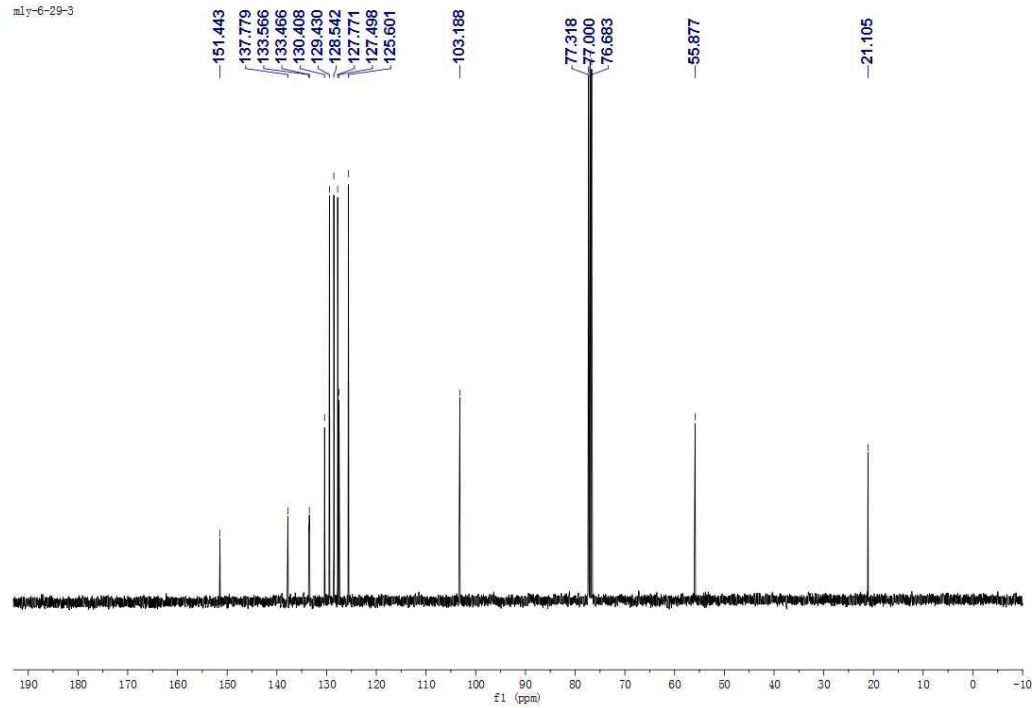
7.805
7.403
7.384
7.365
7.329
7.324
7.302
7.284
7.265
7.244
7.176
7.154
7.132
6.557
6.551
5.311
2.332
2.00
2.02
1.01
1.23
3.92
0.98
1.99
3.03
f1 (ppm)


mly-6-29-3
151.443
137.779
133.566
133.466
130.408
129.430
128.542
127.771
127.498
125.601
103.188
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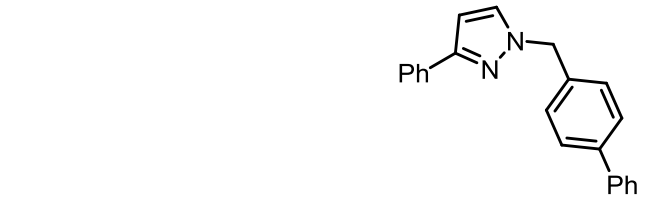
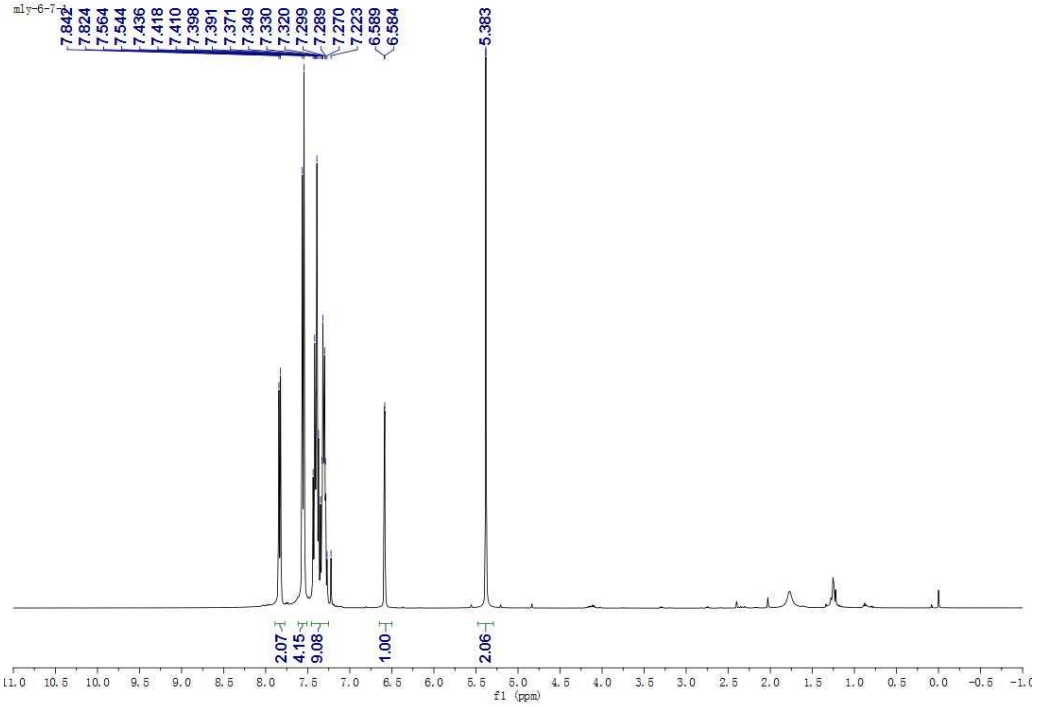
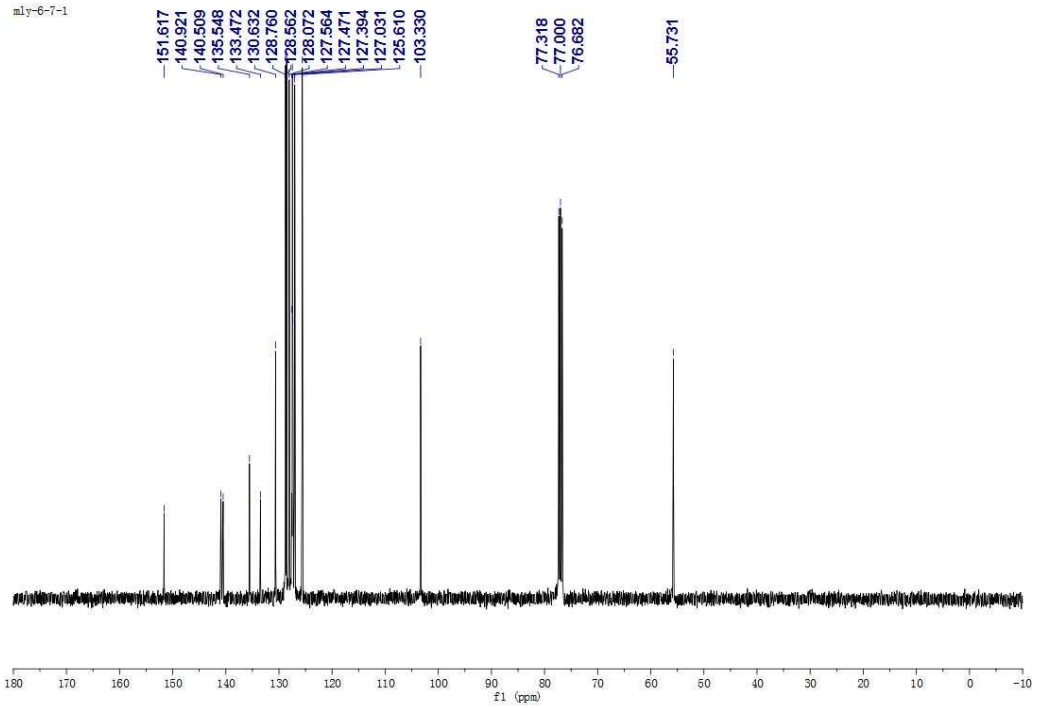
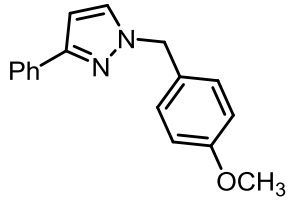
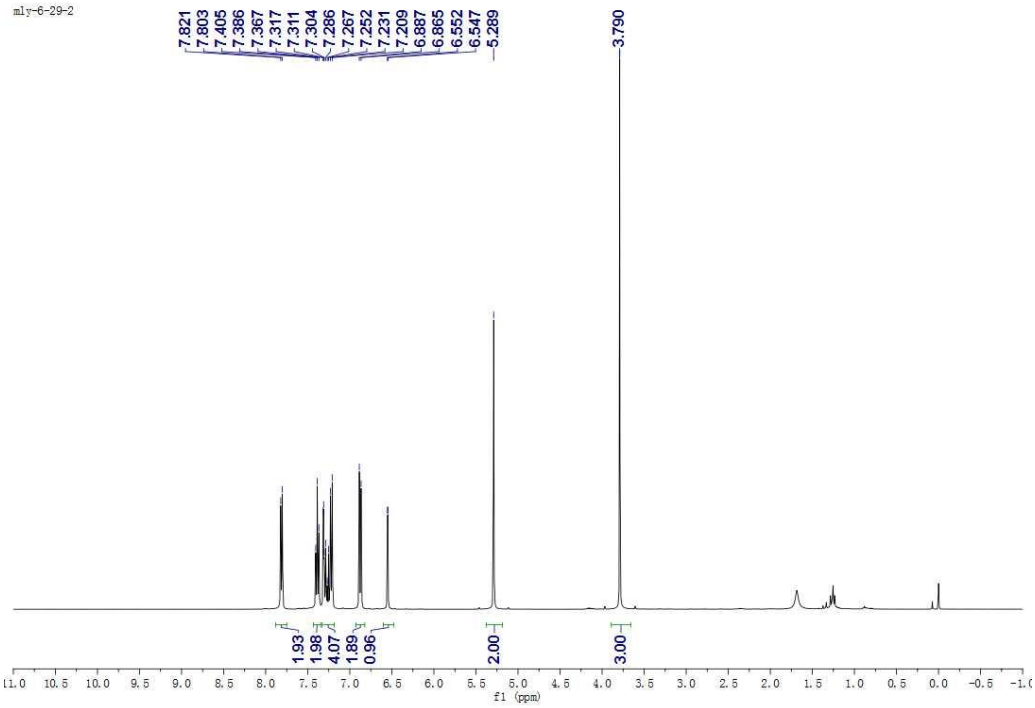
77.000
76.683
55.877
21.105
f1 (ppm)

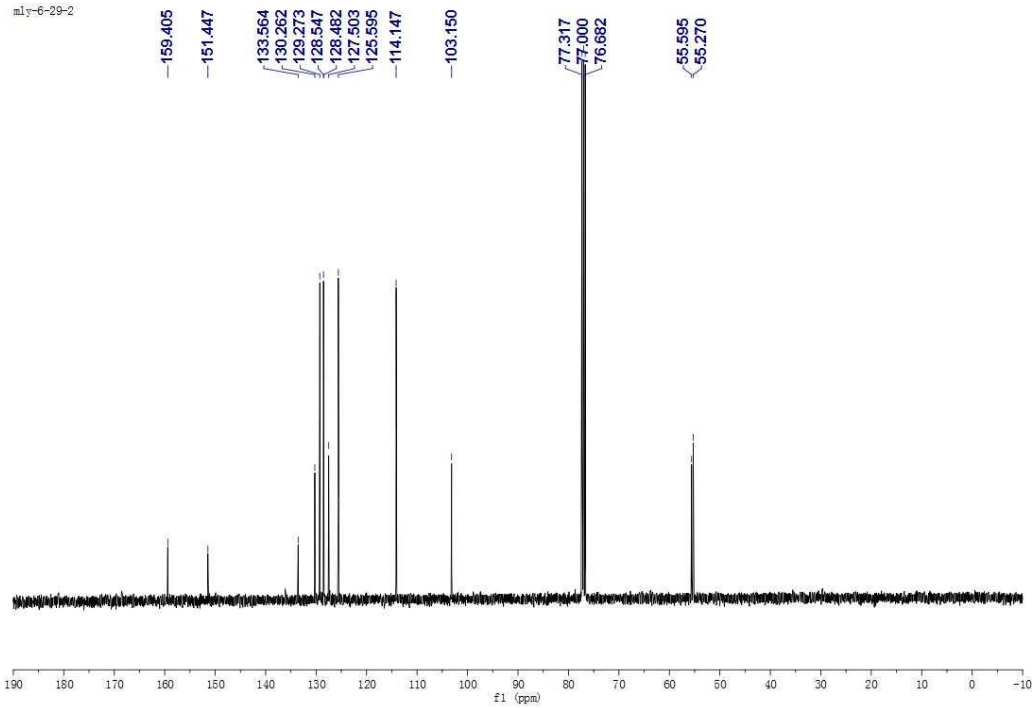

Ph
N
N
Ph


mly-6-7-1
7.842
7.824
7.564
7.544
7.436
7.418
7.410
7.398
7.391
7.371
7.349
7.330
7.320
7.299
7.289
7.270
7.223
6.589
6.584
5.383
2.07
4.15
9.08
1.00
2.06
f1 (ppm)


mly-6-7-1
151.617
140.921
140.509
135.548
133.472
130.632
128.760
128.562
128.072
127.564
127.471
127.394
127.031
125.610
103.330
77.318
77.000
76.682
55.731
f1 (ppm)


Ph
N
N
OCH3


mly-6-29-2
7.821
7.803
7.405
7.386
7.367
7.317
7.311
7.304
7.286
7.267
7.252
7.231
7.209
6.887
6.865
6.552
6.547
5.289
3.790
1.93
1.98
4.07
1.89
0.96
2.00
3.00
f1 (ppm)


mly-6-29-2
159.405
151.447
133.564
130.262
129.273
128.547
128.482
127.503
125.595
114.147
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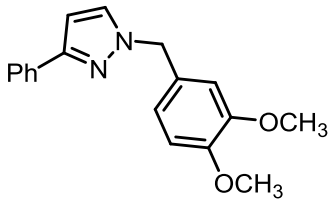
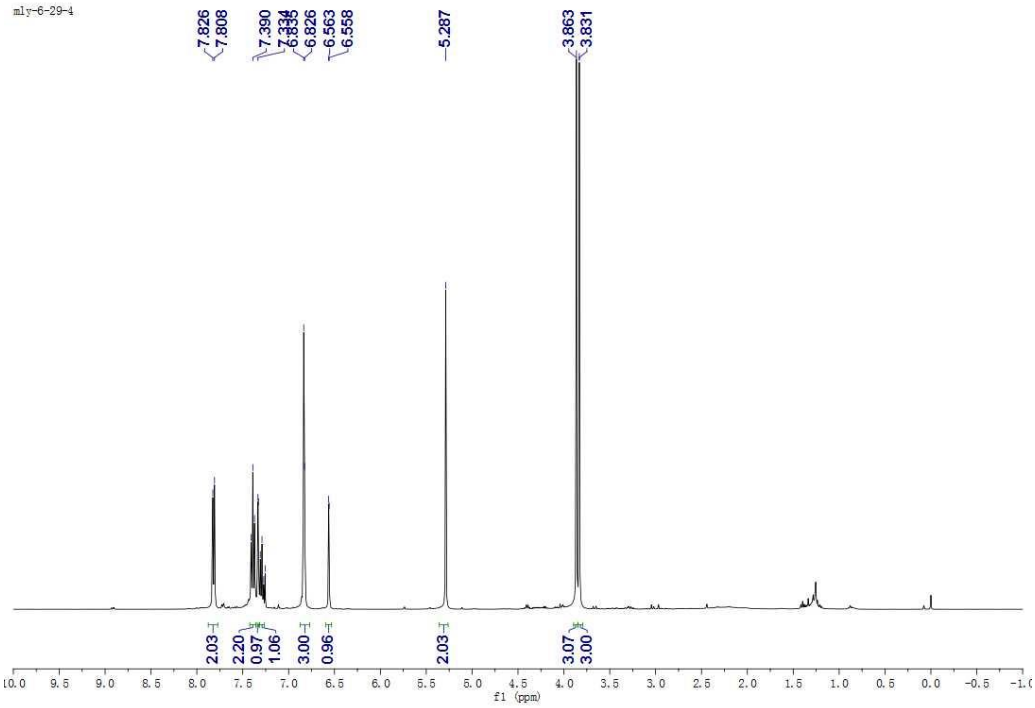
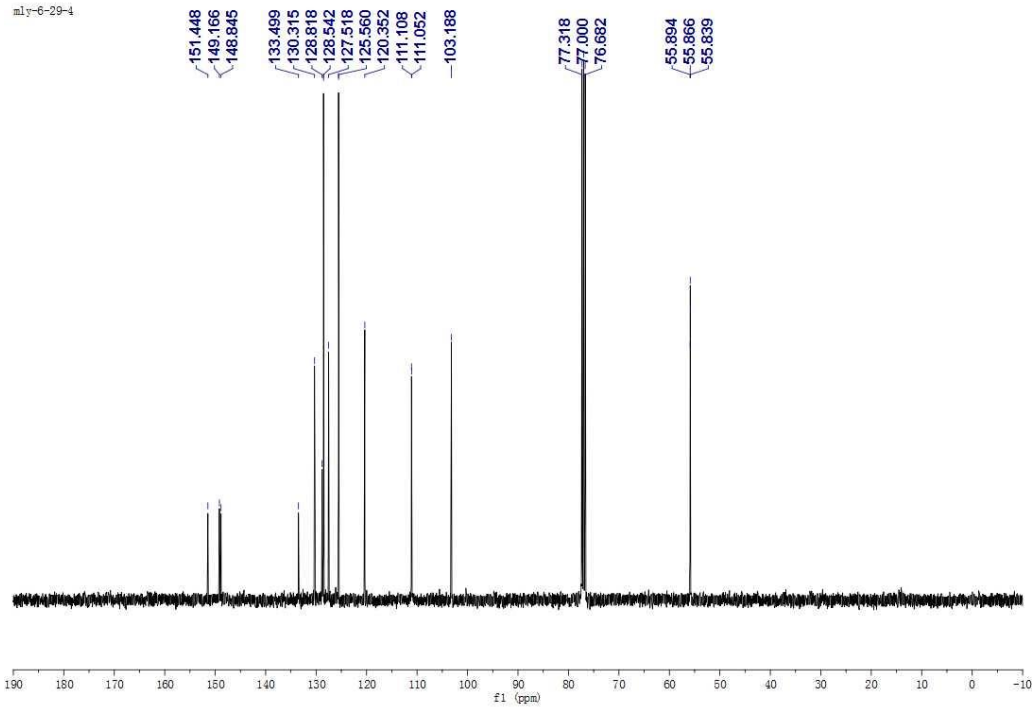
77.317
77.000
76.682
55.595
55.270
f1 (ppm)


Ph
N
N
OCH3
OCH3


mly-6-29-4
7.826
7.808
7.390
7.334
6.835
6.826
6.563
6.558
5.287
3.863
3.831
2.03
2.20
0.97
1.06
3.00
0.96
2.03
3.07
3.00
f1 (ppm)


mly-6-29-4
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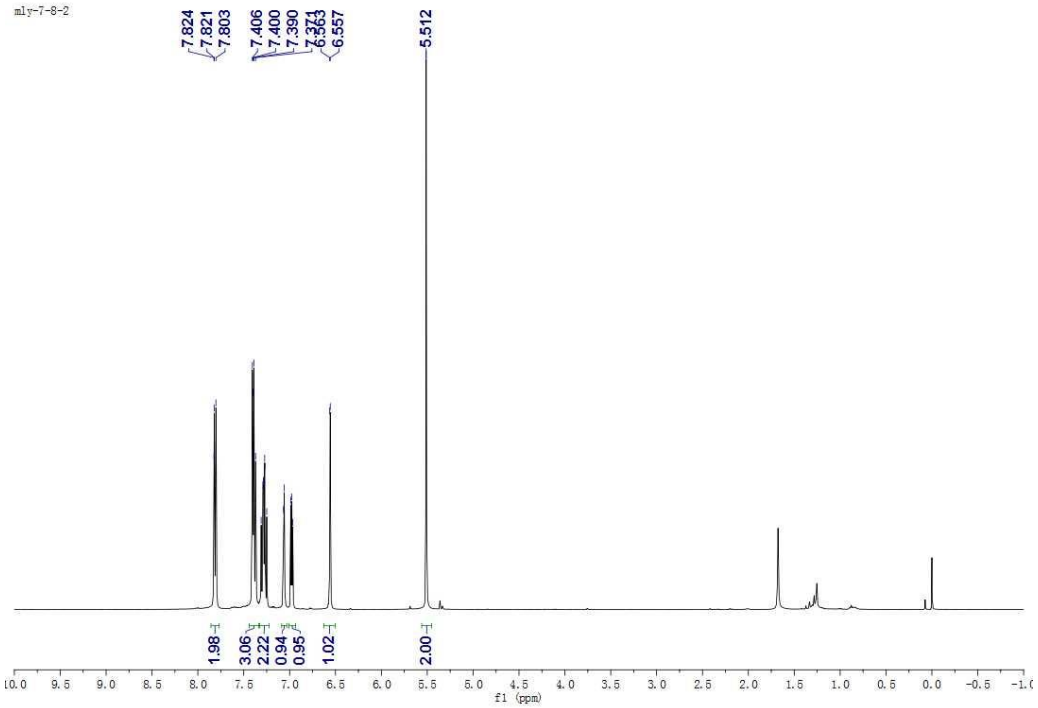
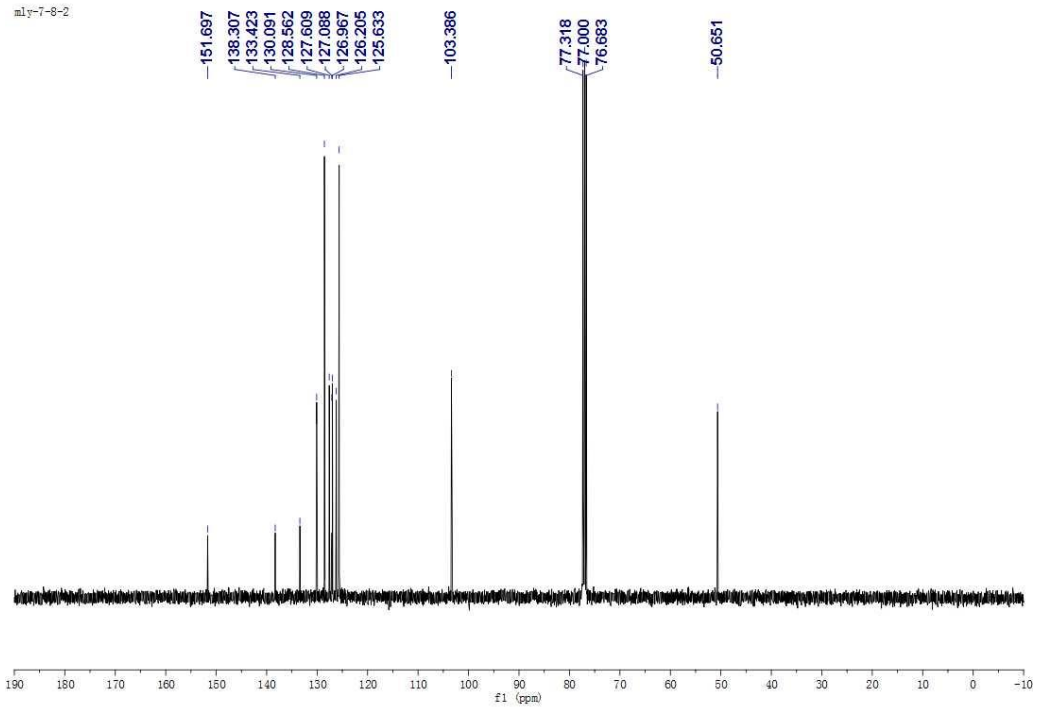
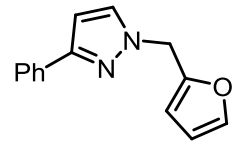
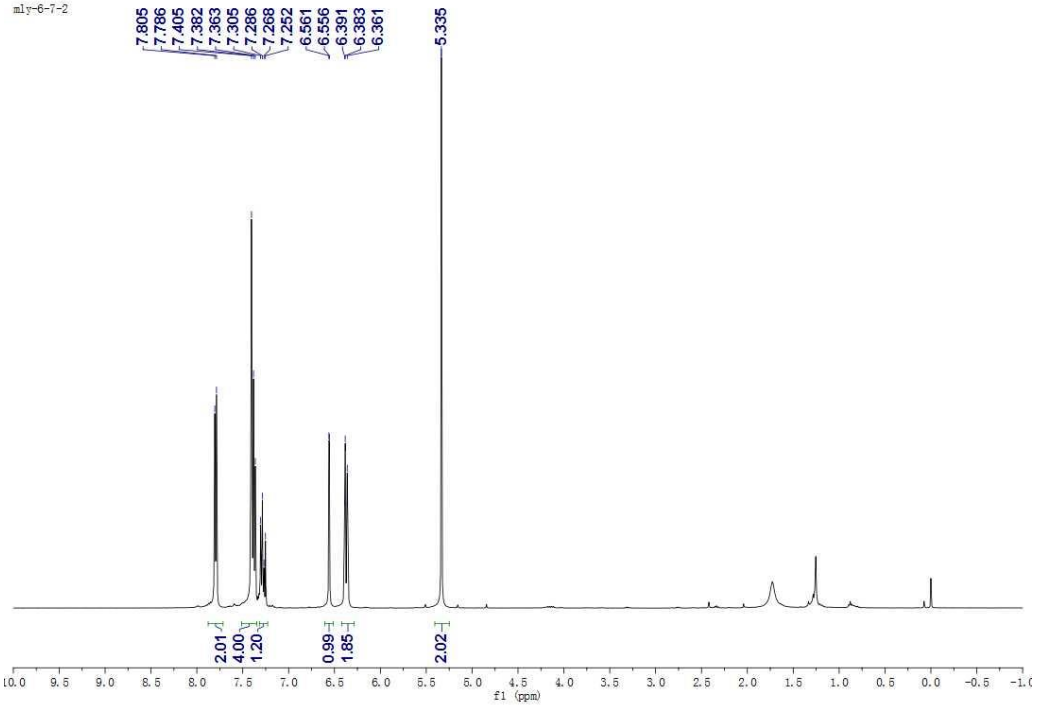
149.166
148.845
133.499
130.315
128.818
128.542
127.518
125.560
120.352
111.108
111.052
103.188
77.318
77.000
76.682
55.894
55.866
55.839
f1 (ppm)

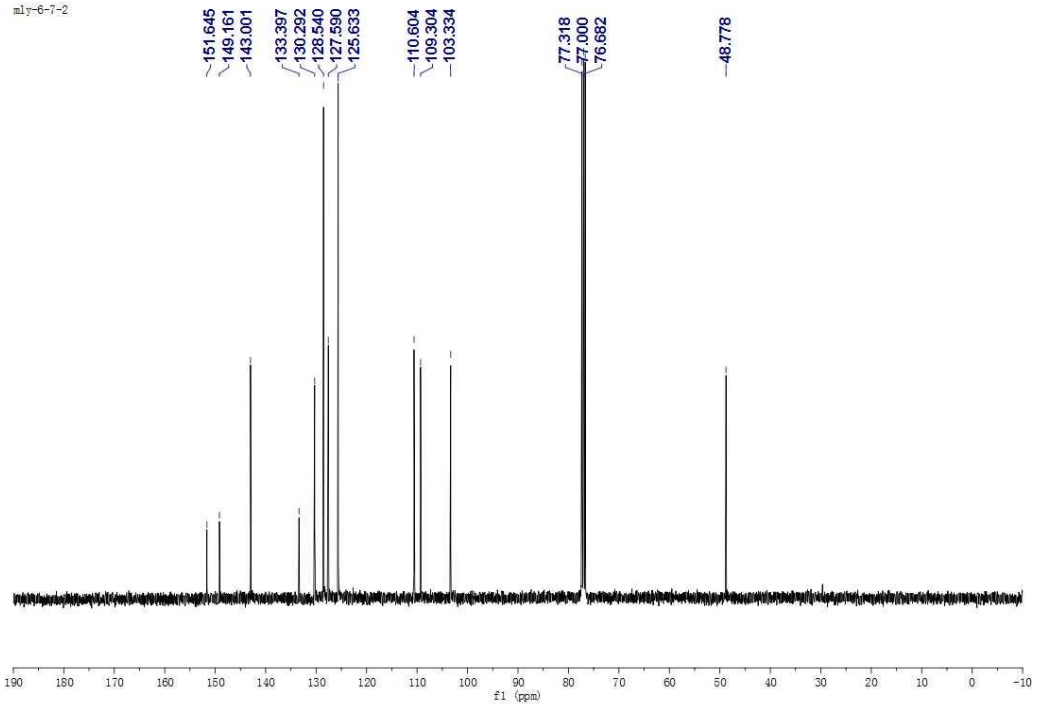

Ph
N
N
S

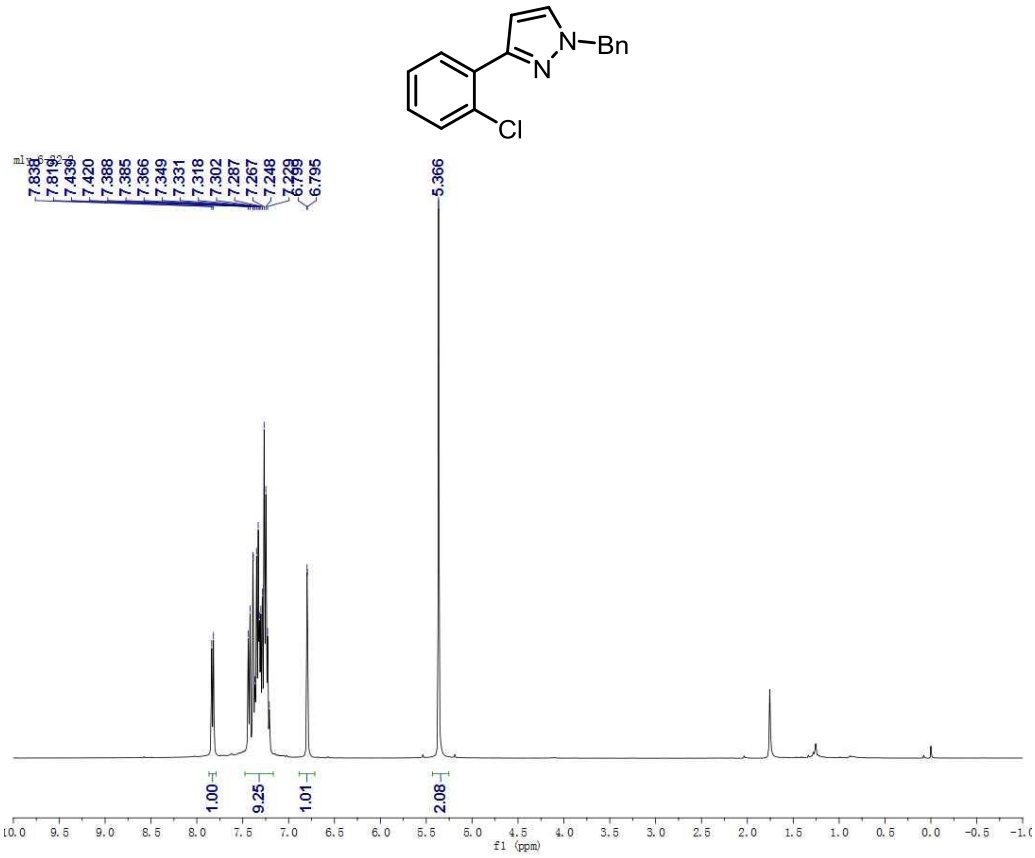

mly-7-8-2
7.824
7.821
7.803
7.406
7.400
7.390
6.563
6.557
5.512
1.98
3.06
2.22
0.94
0.95
1.02
2.00
f1 (ppm)

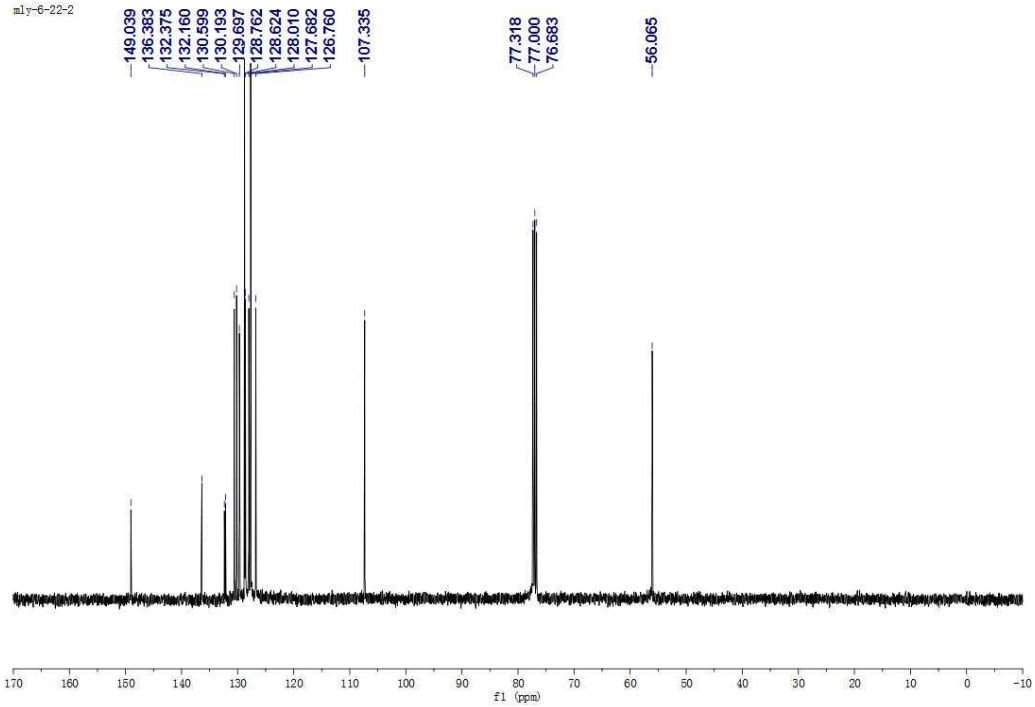

mly-7-8-2
151.697
138.307
133.423
130.091
128.562
127.609
127.088
126.967
126.205
125.633
103.386
77.318
77.000
76.683
50.651
f1 (ppm)

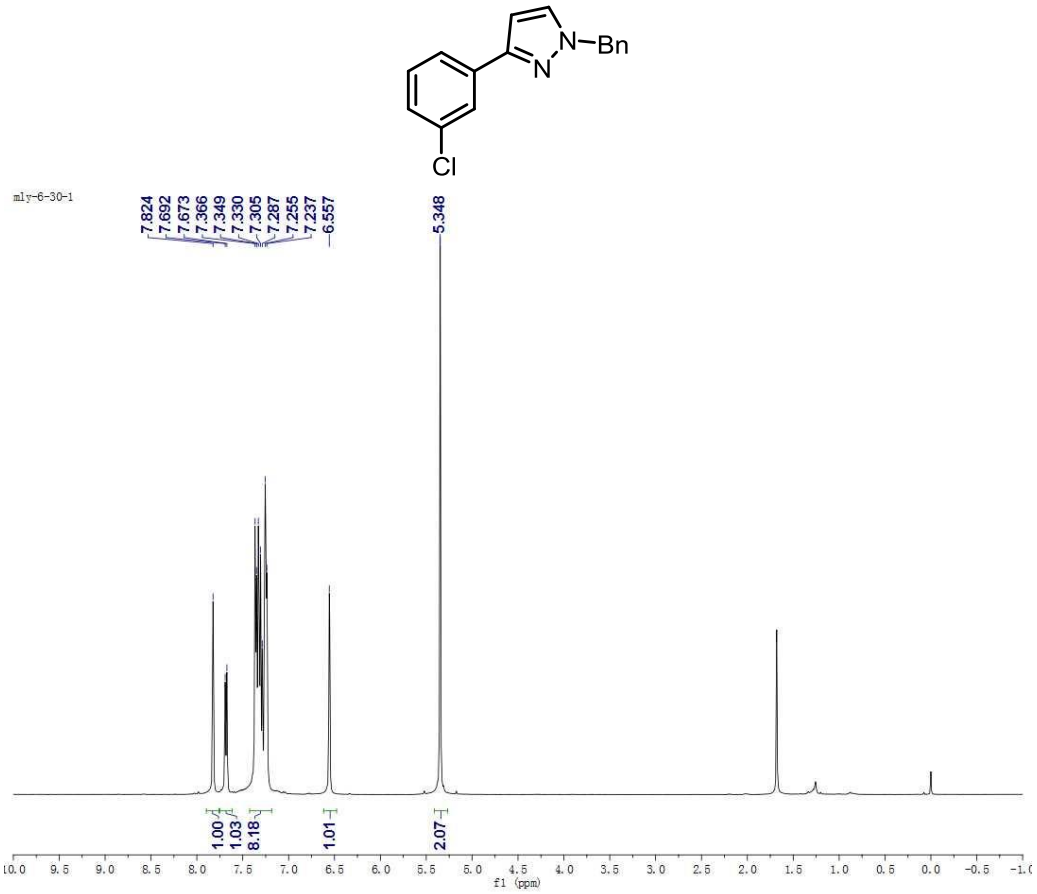

Ph
N
N
O

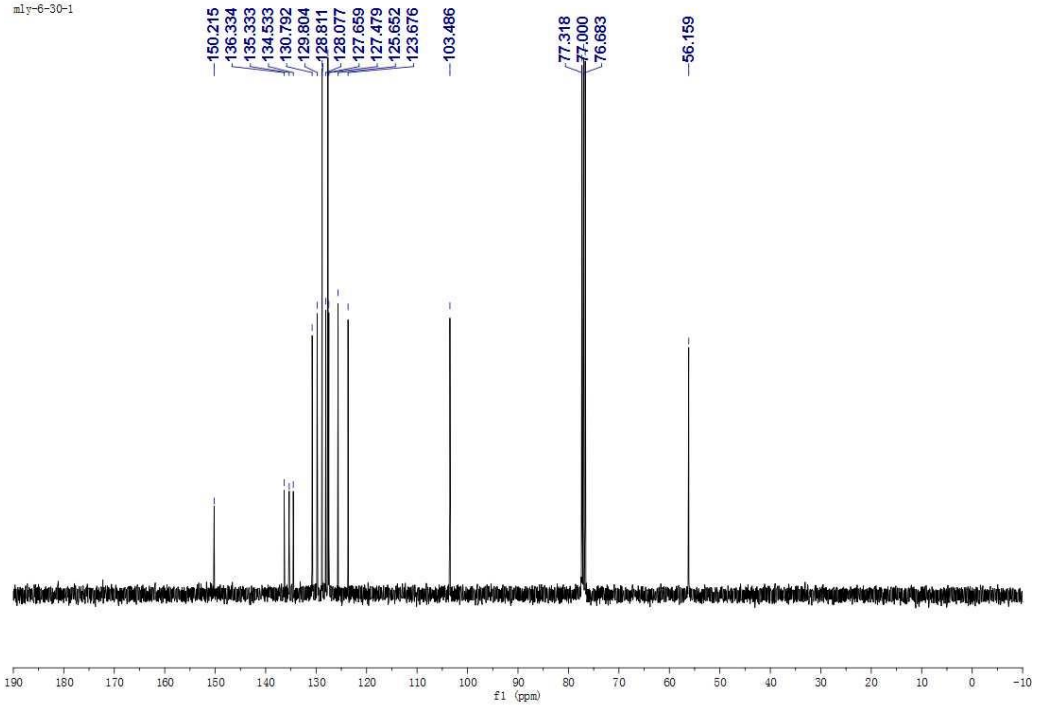

mly-6-7-2
7.805
7.786
7.405
7.382
7.363
7.305
7.286
7.268
7.252
6.561
6.556
6.391
6.383
6.361
5.335
2.01
4.00
1.20
0.99
1.85
2.02
f1 (ppm)

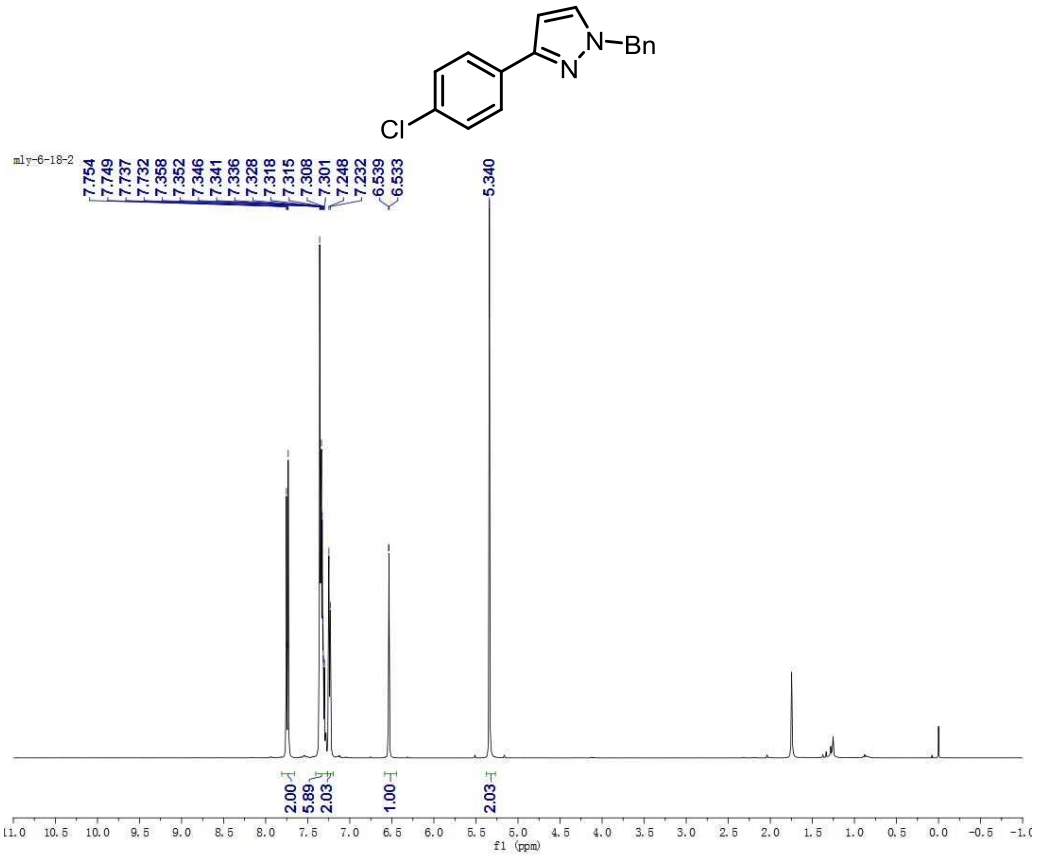

mly-6-7-2
151.645
149.161
143.001
133.397
130.292
128.540
127.590
125.633
110.604
109.304
103.334
77.318
77.000
76.682
48.778
f1 (ppm)

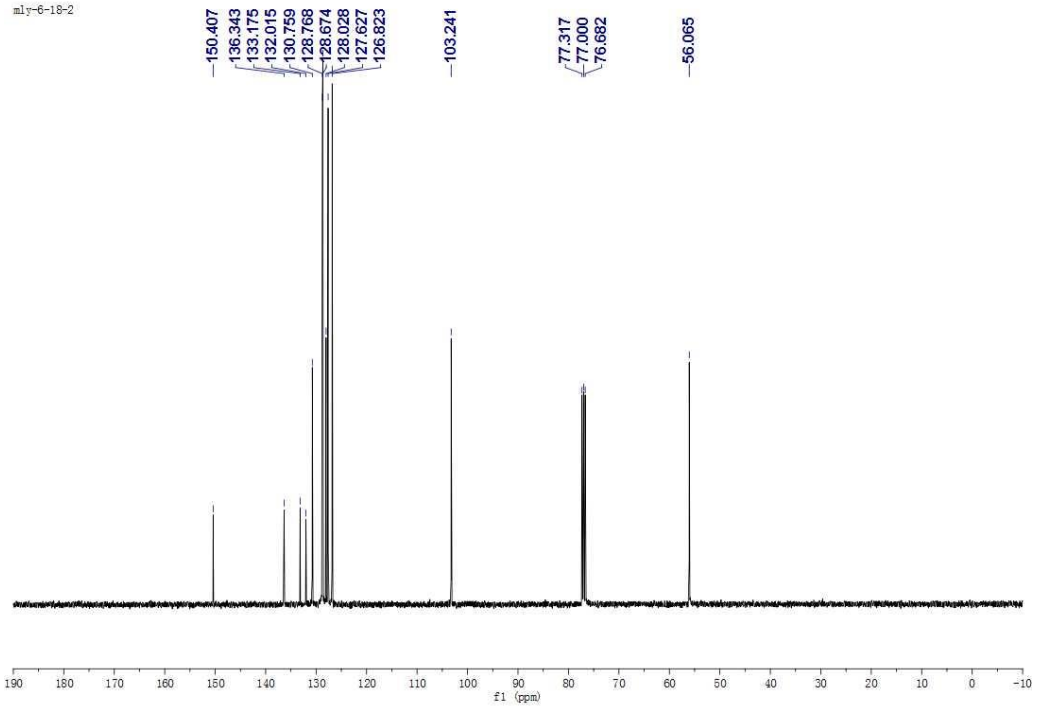

N
N
Bn
Cl
7.838
7.819
7.439
7.420
7.388
7.385
7.366
7.349
7.331
7.318
7.302
7.287
7.267
7.248
7.229
6.799
6.795
5.366
1.00
9.25
1.01
2.08
f1 (ppm)


mly-6-22-2
149.039
136.383
132.375
132.160
130.599
130.193
129.697
128.762
128.624
128.010
127.682
126.760
107.335
77.318
77.000
76.683
56.065
f1 (ppm)

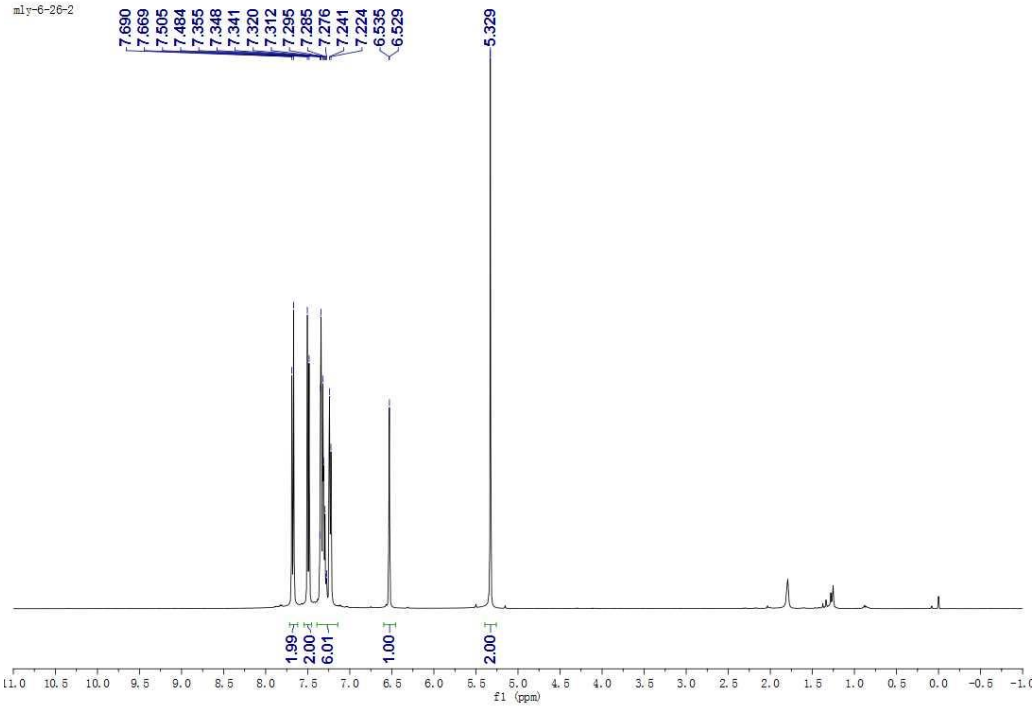

N–Bn
N
Cl
mly-6-30-1
7.824
7.692
7.673
7.366
7.349
7.330
7.305
7.287
7.255
7.237
6.557
5.348
1.00
1.03
8.18
1.01
2.07
f1 (ppm)

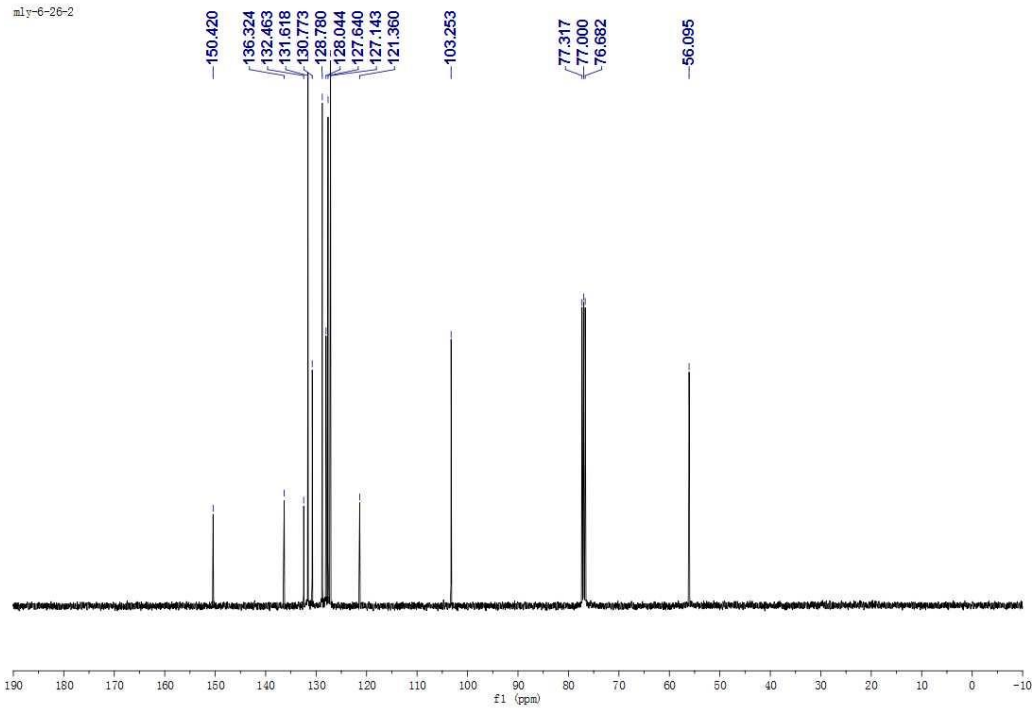

mly-6-30-1
150.215
136.334
135.333
134.533
130.792
129.804
128.811
128.077
127.659
127.479
125.652
123.676
103.486
77.318
77.000
76.683
56.159
f1 (ppm)

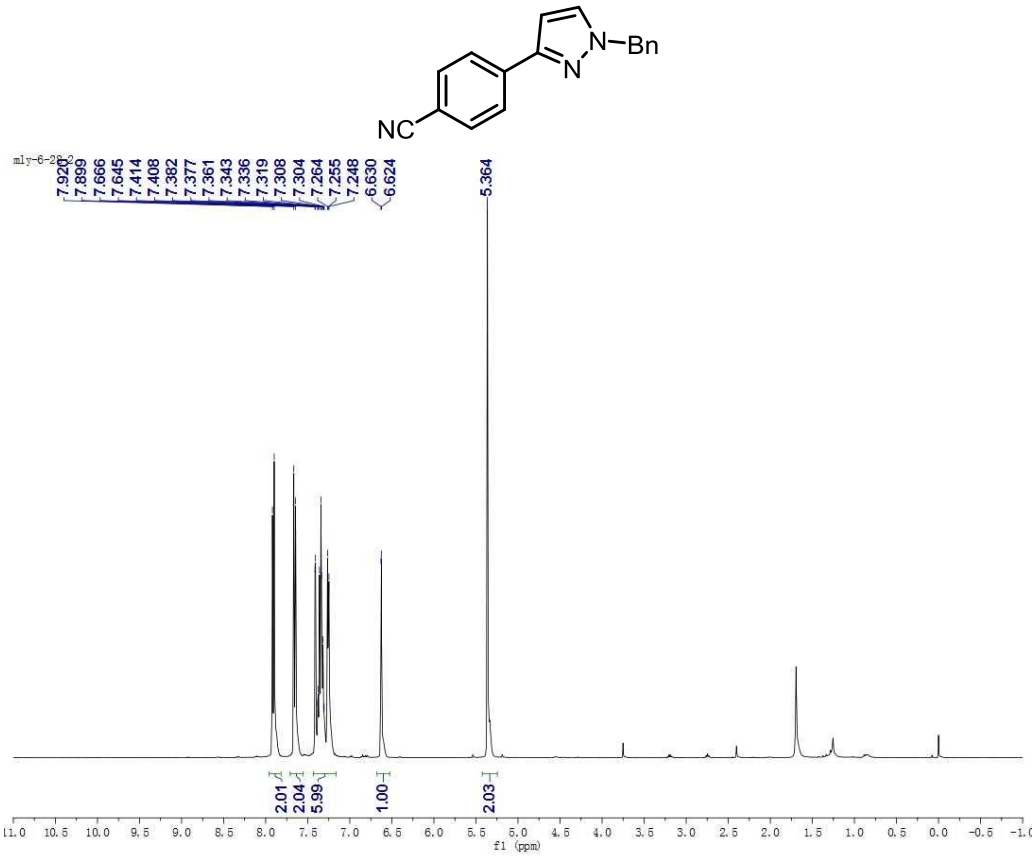

mly-6-18-2
7.754
7.749
7.737
7.732
7.358
7.352
7.346
7.341
7.336
7.328
7.318
7.315
7.308
7.301
7.248
7.232
6.539
6.533
5.340
2.00
5.89
2.03
1.00
2.03
f1 (ppm)

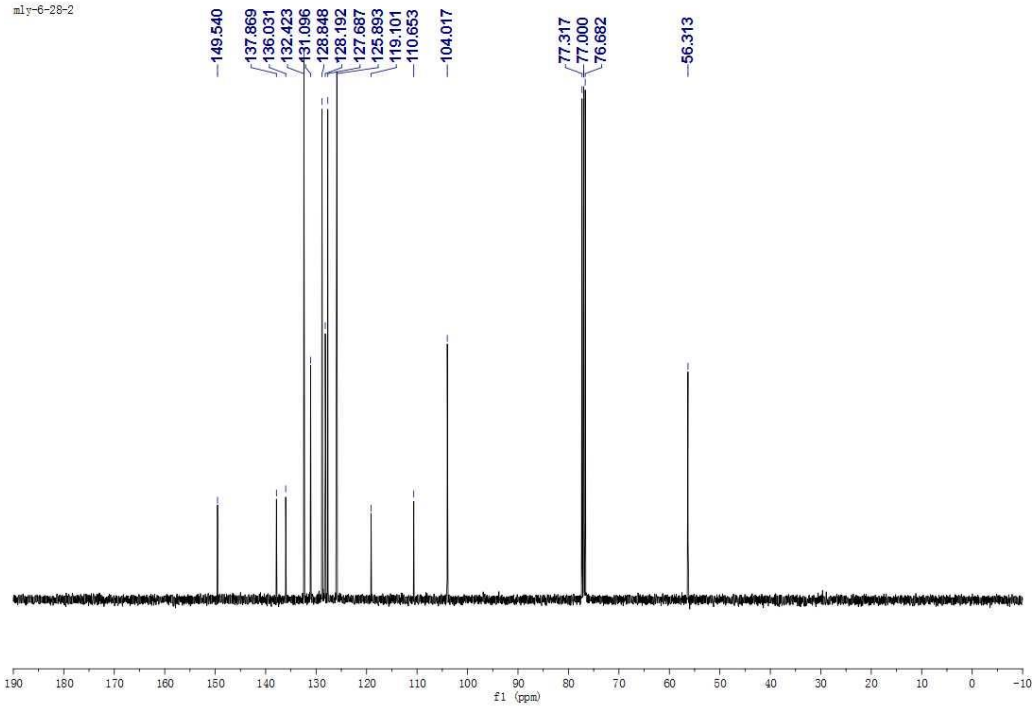

mly-6-18-2
150.407
136.343
133.175
132.015
130.759
128.768
128.674
128.028
127.627
126.823
103.241
77.317
77.000
76.682
56.065
f1 (ppm)

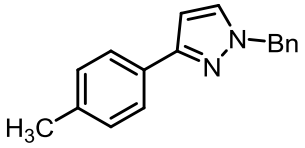

N
N
Bn
Br

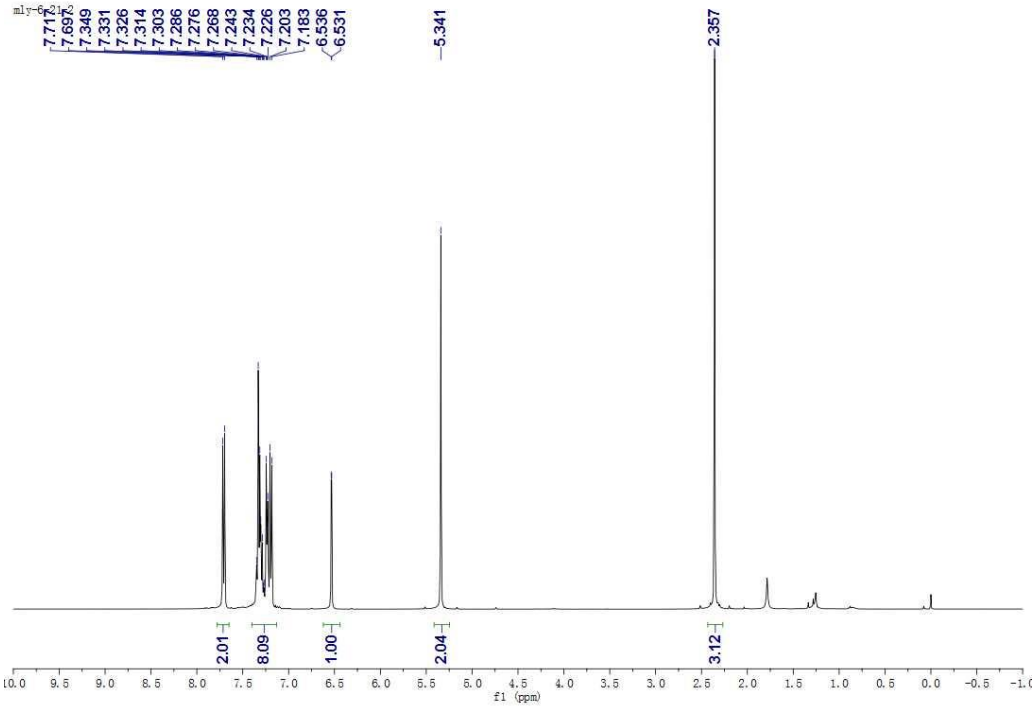

mly-6-26-2
7.690
7.669
7.505
7.484
7.355
7.348
7.341
7.320
7.312
7.295
7.285
7.276
7.241
7.224
6.535
6.529
5.329
1.99
2.00
6.01
1.00
2.00
f1 (ppm)

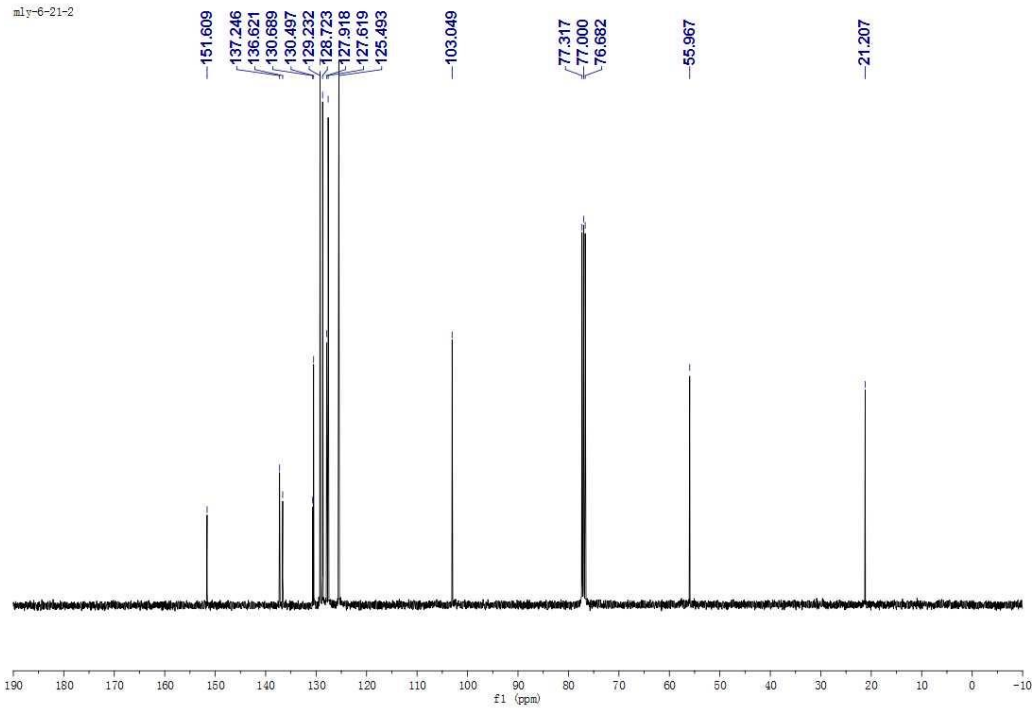

mly-6-26-2
150.420
136.324
132.463
131.618
130.773
128.780
128.044
127.640
127.143
121.360
103.253
77.317
77.000
76.682
56.095
f1 (ppm)

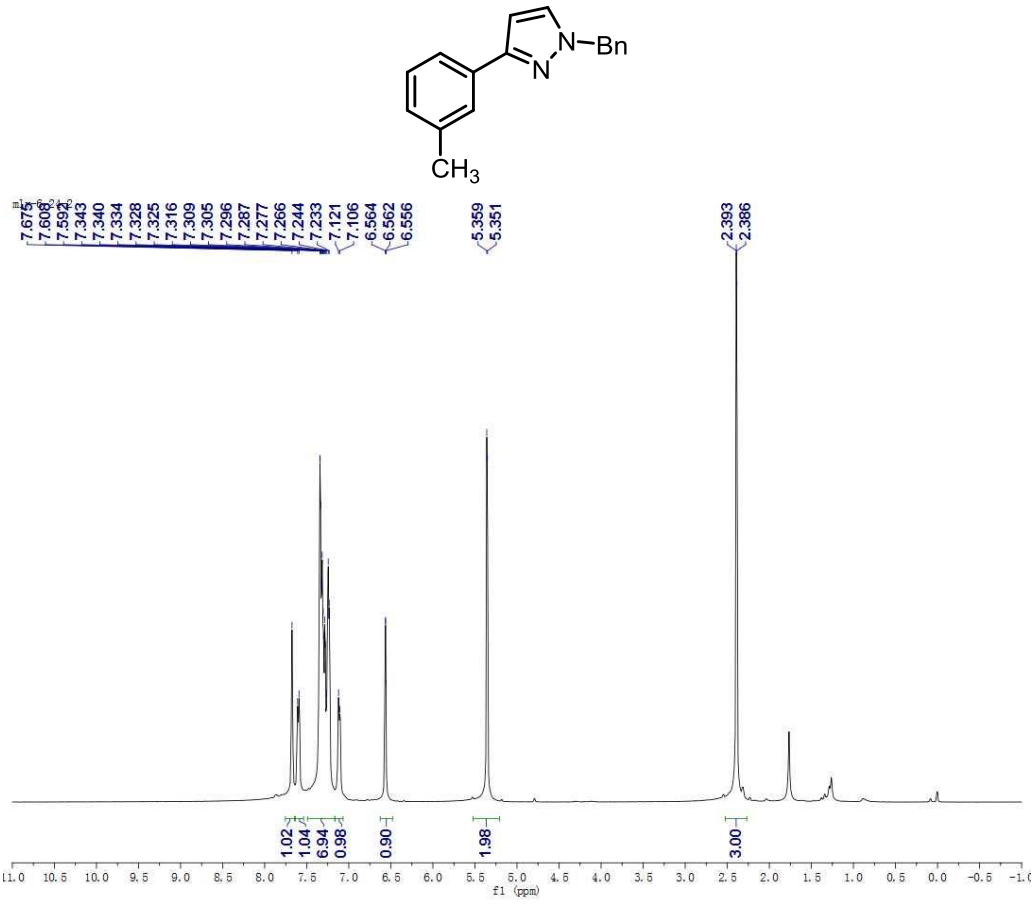

N
N
Bn
NC
mly-6-28-2
7.920
7.899
7.666
7.645
7.414
7.408
7.382
7.377
7.361
7.343
7.336
7.319
7.308
7.304
7.264
7.255
7.248
6.630
6.624
5.364
2.01
2.04
5.99
1.00
2.03
f1 (ppm)

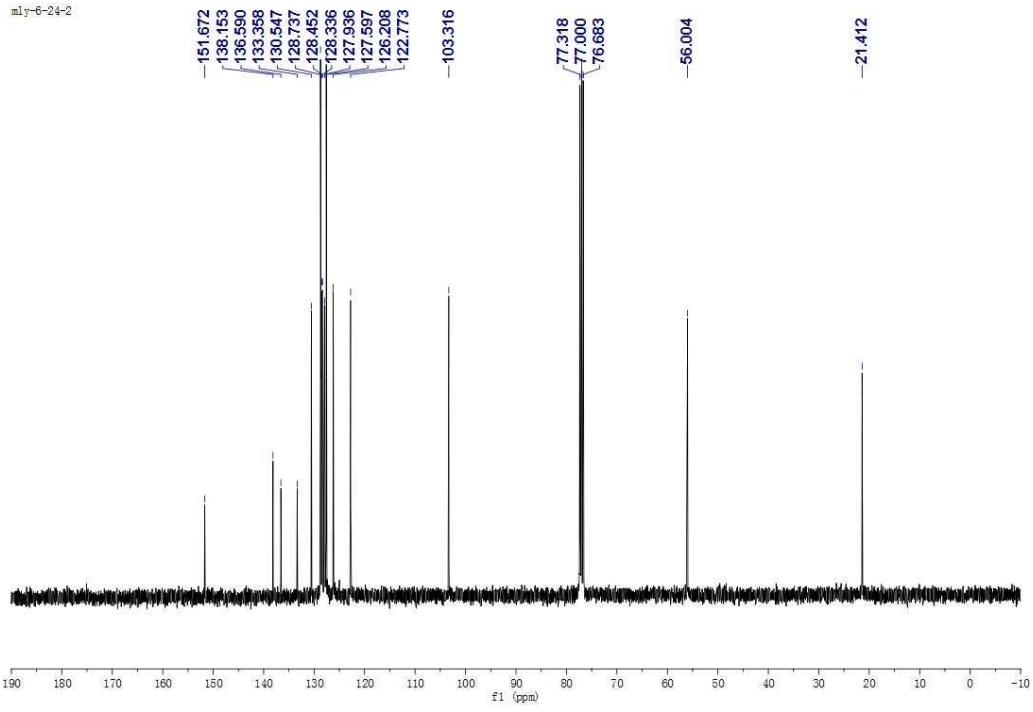

mly-6-28-2
149.540
137.869
136.031
132.423
131.096
128.848
128.192
127.687
125.893
119.101
110.653
104.017
77.317
77.000
76.682
56.313
f1 (ppm)

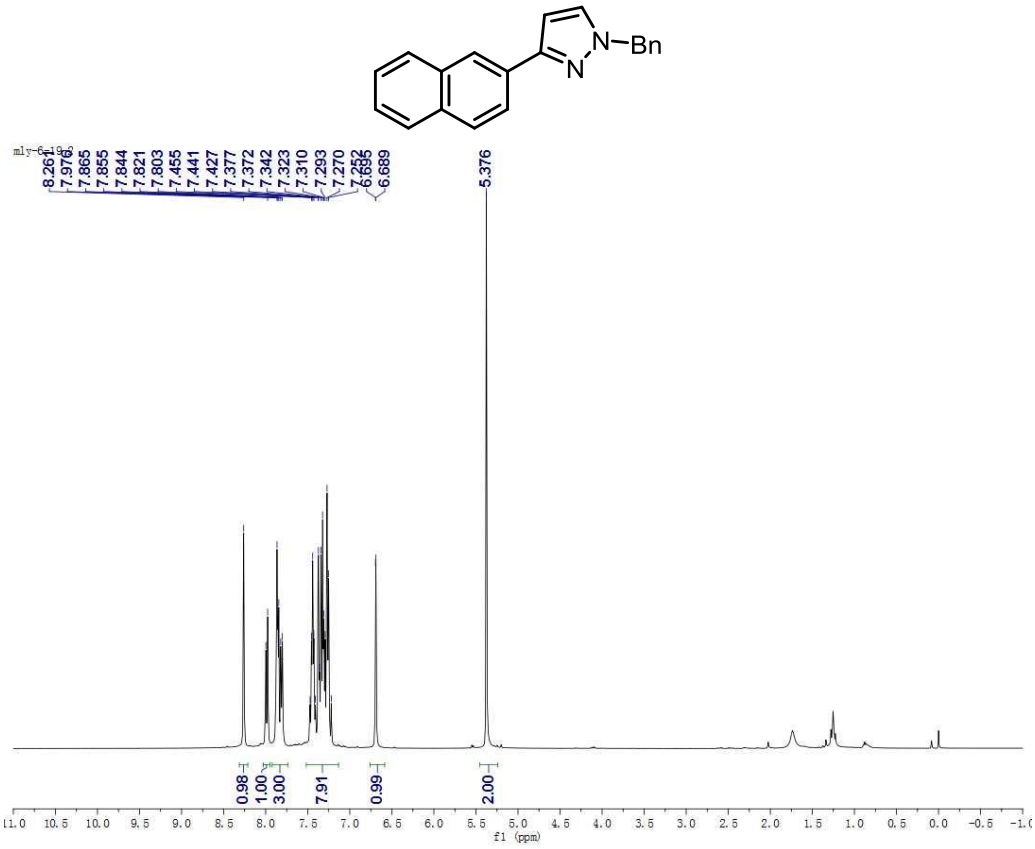

N
Bn
N
H3C

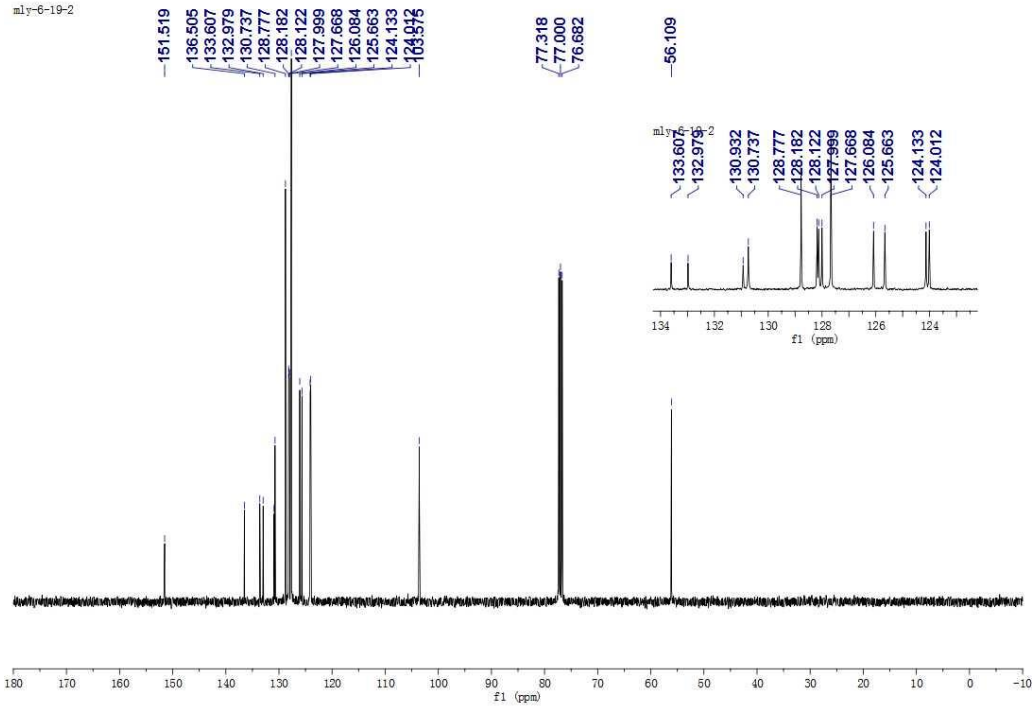

mly-6-21-2
7.711
7.697
7.349
7.331
7.326
7.314
7.303
7.286
7.276
7.268
7.243
7.234
7.226
7.203
7.183
6.536
6.531
5.341
2.357
2.01
8.09
1.00
2.04
3.12
f1 (ppm)

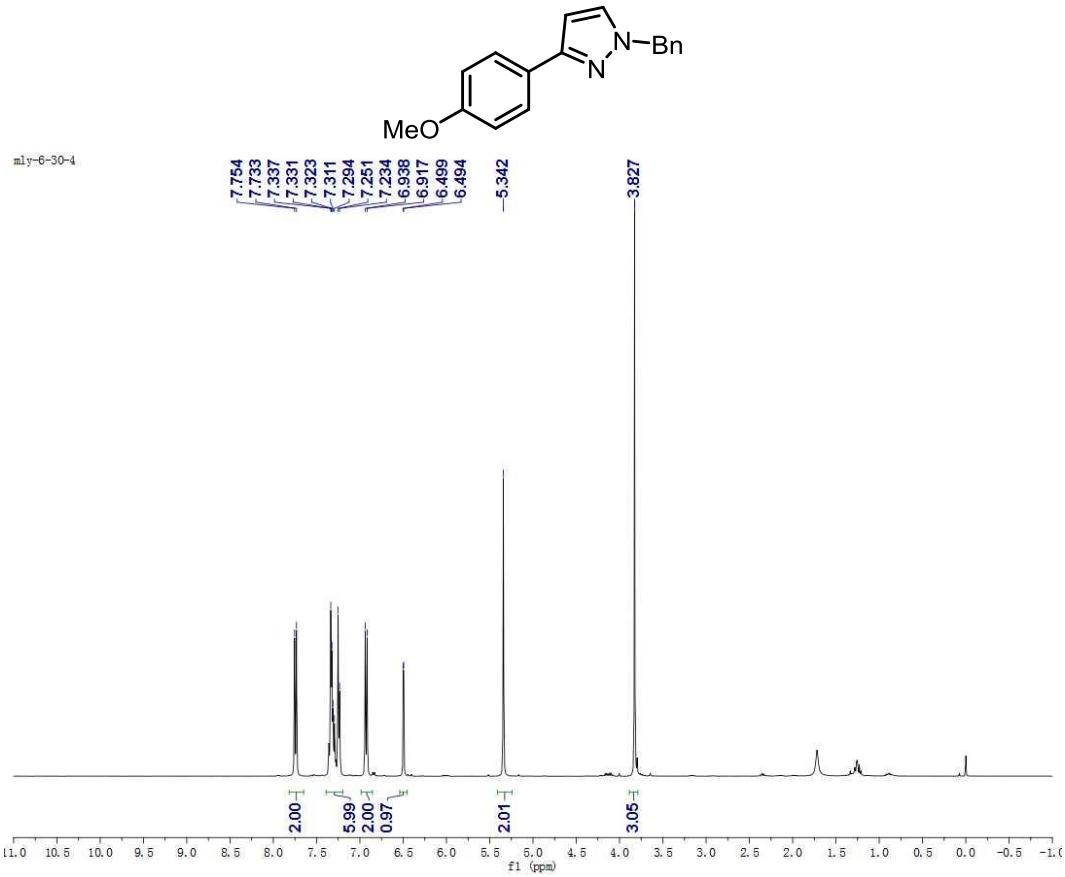

mly-6-21-2
151.609
137.246
136.621
130.689
130.497
129.232
128.723
127.918
127.619
125.493
103.049
77.317
77.000
76.682
55.967
21.207
f1 (ppm)

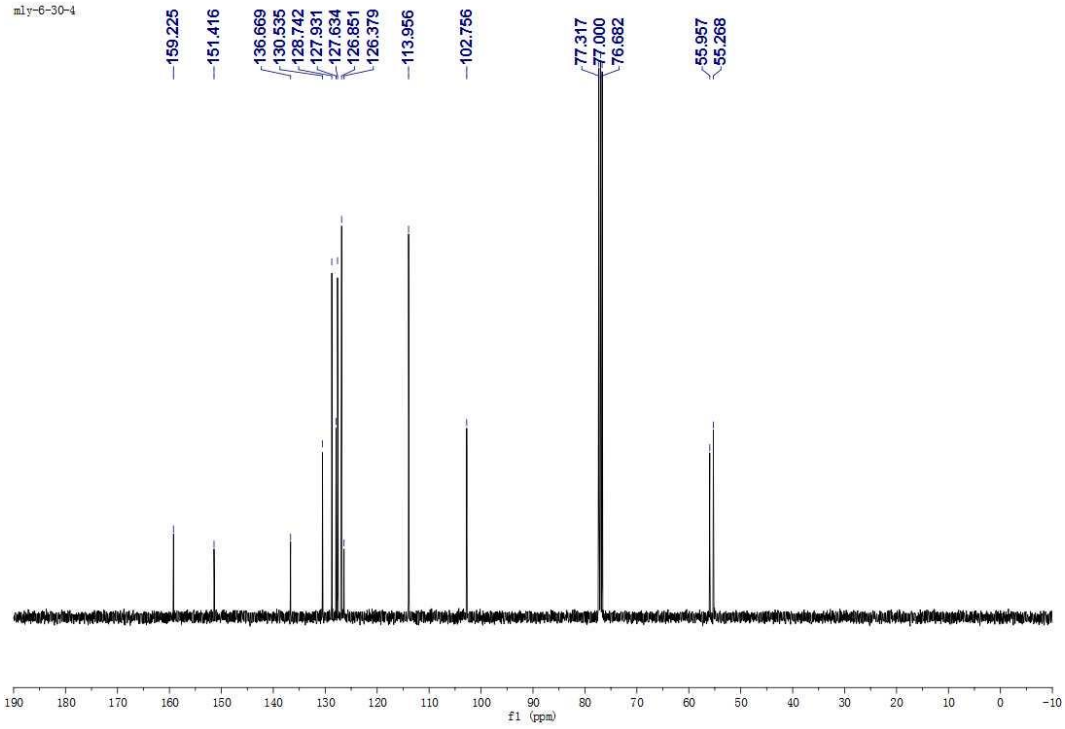

N–Bn
N
CH3
7.675
7.606
7.592
7.343
7.340
7.334
7.328
7.325
7.316
7.309
7.305
7.296
7.287
7.277
7.266
7.244
7.233
7.121
7.106
6.564
6.562
6.556
5.359
5.351
2.393
2.386
1.02
1.04
6.94
0.98
0.90
1.98
3.00
f1 (ppm)

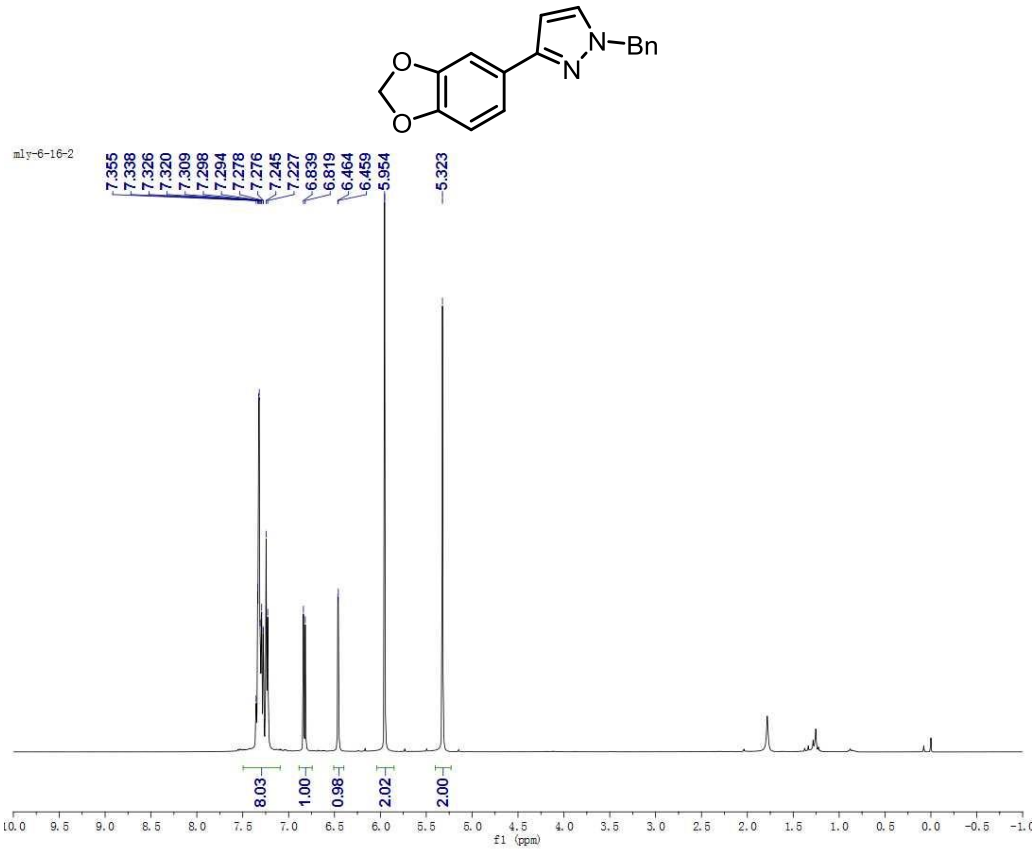

mly-6-24-2
151.672
138.153
136.590
133.358
130.547
128.737
128.452
128.336
127.936
127.597
126.208
122.773
103.316
77.318
77.000
76.683
56.004
21.412
f1 (ppm)

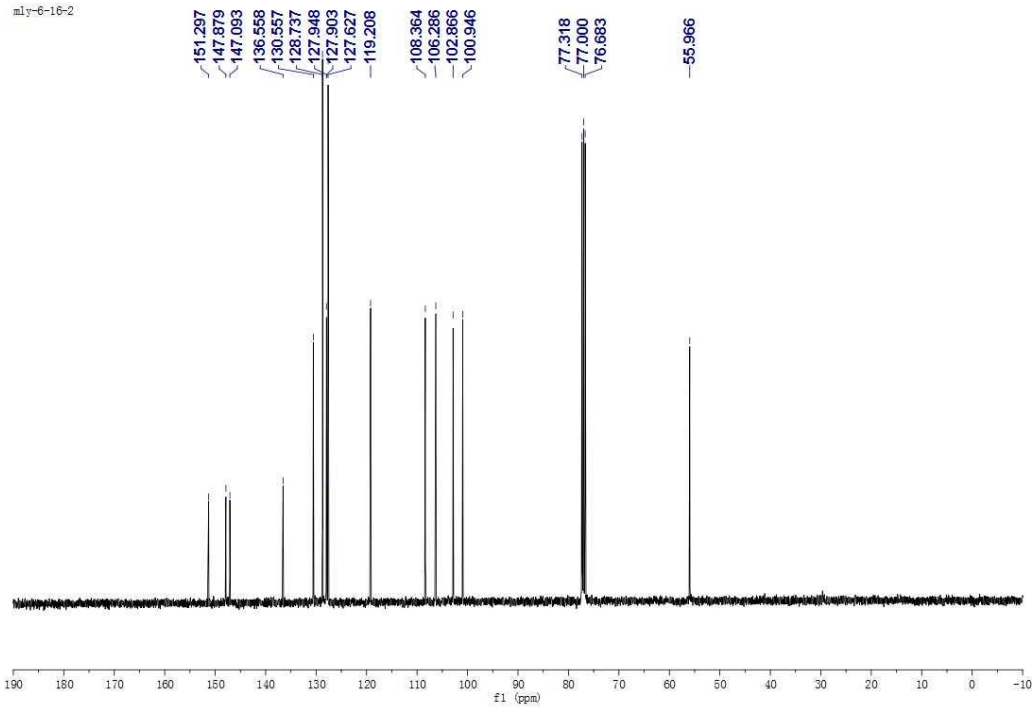

N–Bn
N
8.264
7.976
7.865
7.855
7.844
7.821
7.803
7.455
7.441
7.427
7.377
7.372
7.342
7.323
7.310
7.293
7.270
7.252
6.695
6.689
5.376
0.98
1.00
3.00
7.91
0.99
2.00
f1 (ppm)


mly-6-19-2
151.519
136.505
133.607
132.979
130.737
128.777
128.182
128.122
127.999
127.668
126.084
125.663
124.133
124.012
103.575
77.318
77.000
76.682
56.109
mly-6-19-2
133.607
132.979
130.932
130.737
128.777
128.182
128.122
127.999
127.668
126.084
125.663
124.133
124.012
f1 (ppm)
f1 (ppm)

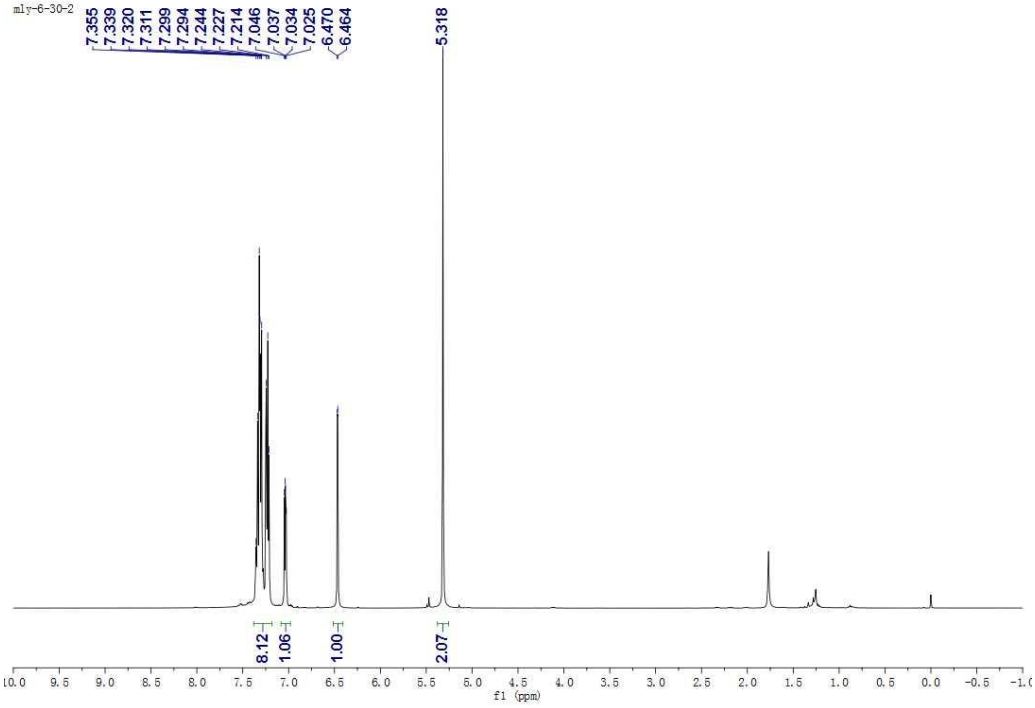

MeO
N
N
Bn
mly-6-30-4
7.754
7.733
7.337
7.331
7.323
7.311
7.294
7.251
7.234
6.938
6.917
6.499
6.494
5.342
3.827
2.00
5.99
2.00
0.97
2.01
3.05
f1 (ppm)

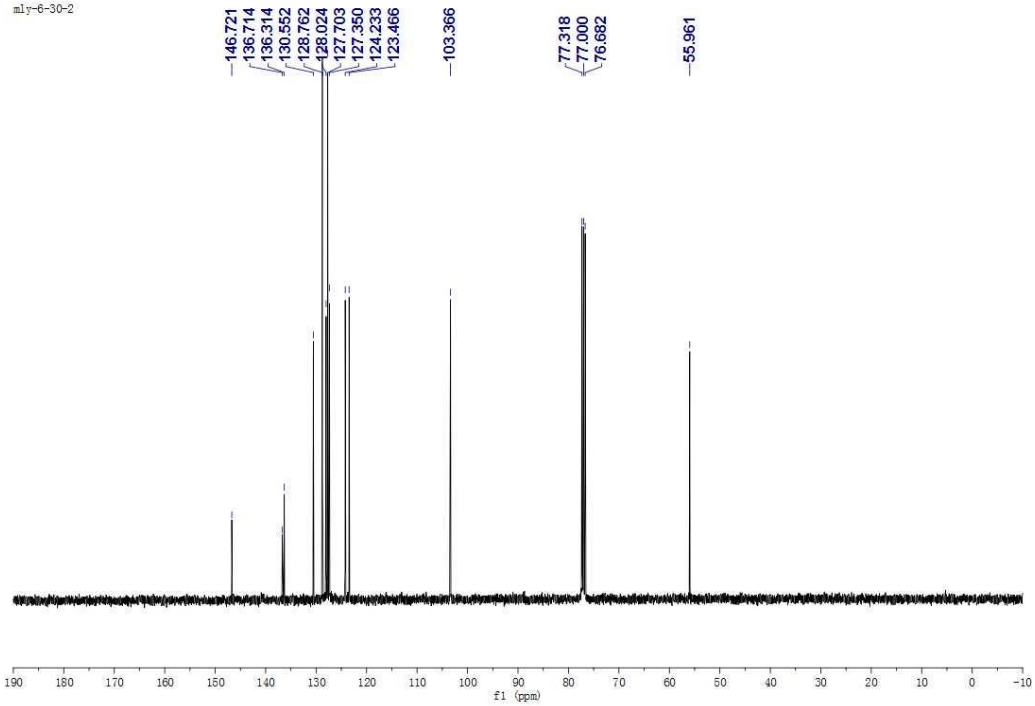

mly-6-30-4
159.225
151.416
136.669
130.535
128.742
127.931
127.634
126.851
126.379
113.956
102.756
77.317
77.000
76.682
55.957
55.268
f1 (ppm)

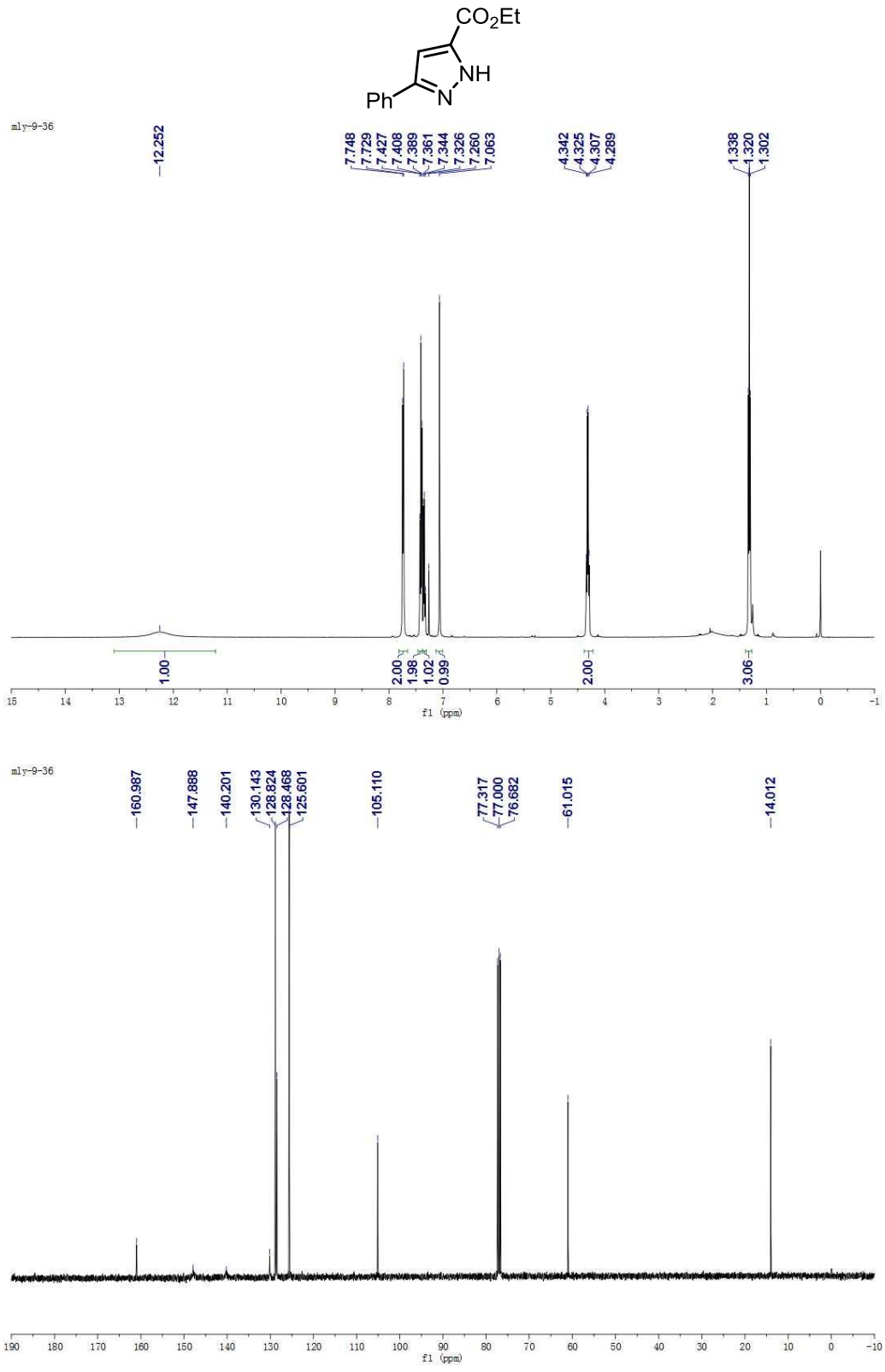

mly-6-16-2
7.355
7.338
7.326
7.320
7.309
7.298
7.294
7.278
7.276
7.245
7.227
6.839
6.819
6.464
6.459
5.954
5.323
8.03
1.00
0.98
2.02
2.00
f1 (ppm)


mly-6-16-2
151.297
147.879
147.093
136.558
130.557
128.737
127.948
127.903
127.627
119.208
108.364
106.286
102.866
100.946
77.318
77.000
76.683
55.966
f1 (ppm)


N
Bn
N
S


mly-6-30-2
7.355
7.339
7.320
7.311
7.299
7.294
7.244
7.227
7.214
7.046
7.037
7.034
7.025
6.470
6.464
5.318
8.12
1.06
1.00
2.07
f1 (ppm)


mly-6-30-2
146.721
136.714
136.314
130.552
128.762
128.024
127.703
127.350
124.233
123.466
103.366
77.318
77.000
76.682
55.961
f1 (ppm)


CO2Et
NH
N
Ph
mly-9-36
12.252
7.748
7.729
7.427
7.408
7.389
7.361
7.344
7.326
7.260
7.063
4.342
4.325
4.307
4.289
1.338
1.320
1.302
1.00
2.00
1.98
1.02
0.99
2.00
3.06
f1 (ppm)
mly-9-36
160.987
147.888
140.201
130.143
128.824
128.468
125.601
105.110
77.317
77.000
76.682
61.015
14.012
f1 (ppm)