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NIS/CHP Mediated Reaction of Isocyanides with Hydrazones: Access to Aminopyrazoles

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Table of Contents

Experimental Section

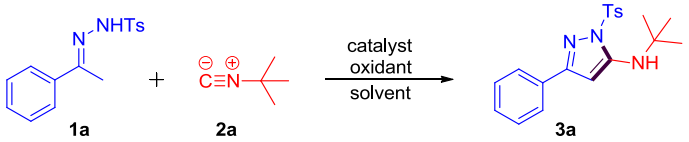
General experimental: All chemicals were commercially available. Progresses of reactions were monitored by Thin Layer Chromatography while purification was

performed using silicagel column chromatography. IR spectra were recorded on a Bruker spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 300/75 or 400/100 MHz spectrometer using $CDCl_3$, as solvent and TMS as internal standard. High resolution mass spectra were obtained using GCT-TOF instrument with CI source. X-ray diffraction data were recorded on a Rigaku Mercury CCD area detector with graphite monochromated Mo Kα radiation.

General procedures for reactions

N-Iodosuccinimide (NIS) (0.02 mmol) and hydrazones (0.5 mmol) were added to test tube. 1,4-dioxane (3.0 mL)、Cumene Hydroperoxide (CHP) (0.5 mmol)、isocyanides (0.6 mmol) were added via syringe. The test tube was closed. The reaction mixture was stirred at 100 ^{o}C for 12 or 24 h. Then the reactions were cooled to room temperature. Removal of solvent followed by flash column chromatographic purification afforded products using petroleum and acetone.

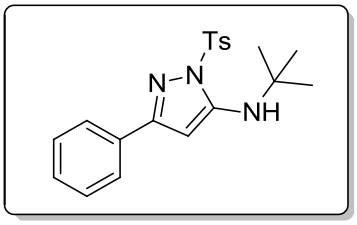
Table 1: Condition Screening for Reaction of hydrazones **1a** with *tert*-butyl isocyanide **2a**.[a]



entry	catalyst (mol%)	oxidant (eq.)	solvent	yield[b] (%)
1	----	TBPB[g] (2)	1,4-dioxane	trace
2	I_2 (20)	TBPB (2)	1,4-dioxane	59
3	TBAI[c] (20)	TBPB (2)	1,4-dioxane	43
4	TBAB[d] (20)	TBPB (2)	1,4-dioxane	trace
5	TBAC[e] (20)	TBPB (2)	1,4-dioxane	trace
6	KI (20)	TBPB (2)	1,4-dioxane	57
7	**NIS**[f] (20)	TBPB (2)	1,4-dioxane	63
8	NIS (20)	Ar	1,4-dioxane	trace
9	NIS (20)	**CHP**[h] (2)	**1,4-dioxane**	74
10	NIS (20)	DTBP[i] (2)	1,4-dioxane	56
11	NIS (20)	O_2	1,4-dioxane	51
12	NIS (20)	$K_2S_2O_8$ (2)	1,4-dioxane	trace
13	NIS (20)	TEMPO (2)	1,4-dioxane	6
14	NIS (20)	CHP (2)	DME[j]	66
15	NIS (20)	CHP (2)	DCE[k]	63
16	NIS (20)	CHP (2)	THF[l]	70
17	NIS (20)	CHP (2)	toluene	62
18	NIS (20)	CHP (2)	DMSO[m]	52
19	NIS (30)	CHP (2)	1,4-dioxane	71
20	NIS (10)	CHP (2)	1,4-dioxane	75
21	NIS (5)	CHP (2)	1,4-dioxane	76
22	NIS 4)	CHP (2)	1,4-dioxane	80
23	NIS (3)	CHP (2)	1,4-dioxane	70
24	NIS (4)	CHP (3)	1,4-dioxane	79
25	**NIS (4)**	**CHP (1)**	**1,4-dioxane**	**81**
26[n]	NIS (4)	CHP (1)	1,4-dioxane	79
27[o]	NIS (4)	CHP (1)	1,4-dioxane	75
27[p]	NIS (4)	CHP (1)	1,4-dioxane	31

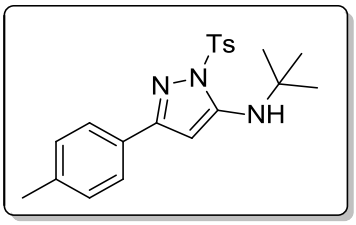
[a]Reaction condition: *N*-tosylhydrazone **1a** (0.5 mmol), *tert*-butyl isonitrile **2a** (1.2 equiv, 0.6 mmol), catalyst, and oxidant in 3 mL of solvent at 100 ℃ for 12 h. [b]Yields were determined by HPLC analysis with biphenyl as the internal standard. [c]TBAC = Tertabutyl ammonium chloride. [d]TBAB = Tertabutyl ammonium bromide. [e]TBAI = Tertabutyl ammonium

iodide. [f]NIS = N-Iodosuccinimide. [g]TBPB = Tert-Buytl Peroxybenzoate. [i]CHP = Cumene Hydroperoxide. [i]DTBP = Di-tert-butyl peroxide. [j]DME = Ethyleneglycol dimethyl ether. [k]DCE = 1,2-Dichloroethane. [l]THF = Trahydrofuran. [m]DMSO = Dimethyl sulfoxide. [j]The system was at 80 ℃. [k]The system was carried out at 110 ℃. [l]The system was carried out at room temperature.



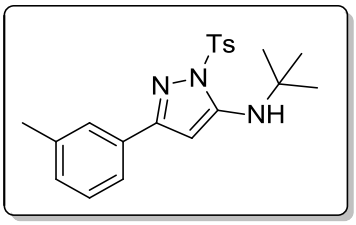
***N*-(*tert*-butyl)-3-phenyl-1-tosyl-1*H*-pyrazol-5-amine (3aa)**

White solid, 79% yield (146 mg), IR (ν, cm^{-1}): 3408, 1365, 1171. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.3 Hz, 2H, -ArH), 7.76 (d, J = 6.5 Hz, 2H, -ArH), 7.37 – 7.30 (m, 3H, -ArH), 7.24 (d, J = 8.2 Hz, 2H, -ArH), 6.01 (s, 1H, -NH), 5.63 (s, 1H, -HetH), 2.33 (s, 3H, $-CH_3$), 1.36 (s, 9H, $-C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.68, 150.69, 145.23, 134.71, 132.13, 129.74, 129.06, 128.41, 127.61, 126.41, 85.89, 51.71, 28.92, 21.65. HRMS (CI^+) m/z: Found: 370.1595. Calcd for $C_{20}H_{24}N_3O_2S$: $(M+H)^+$ 370.1589.



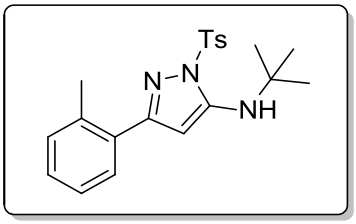
***N*-(*tert*-butyl)-3-(*p*-tolyl)-1-tosyl-1*H*-pyrazol-5-amine (3ba)**

White solid, 87% yield (167 mg), IR (ν, cm^{-1}): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.4 Hz, 2H, -ArH), 7.66 (d, J = 8.1 Hz, 2H, -ArH), 7.23 (d, J = 8.0 Hz, 2H, -ArH), 7.15 (d, J = 8.0 Hz, 2H, -ArH), 5.99 (s, 1H, -NH), 5.60 (s, 1H, -HetH), 2.32 (s, 6H, $-CH_3$), 1.36 (s, 9H, $-C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.81, 150.67, 145.15, 139.02, 134.72, 129.71, 129.32, 129.11, 127.58, 126.32, 85.85, 51.68, 28.92, 21.64, 21.37. HRMS (CI^+) m/z: Found: 383.1658. Calcd for $C_{21}H_{25}N_3O_2S$: $(M)^+$ 383.1667.



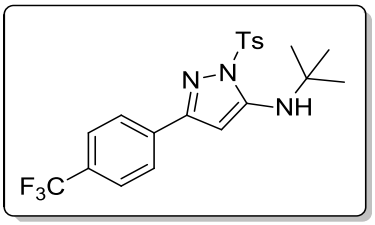
***N*-(*tert*-butyl)-3-(*m*-tolyl)-1-tosyl-1*H*-pyrazol-5-amine (3ca)**

White solid, 67% yield (129 mg), IR (ν, cm^{-1}): 3409, 1359, 1170. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.3 Hz, 2H, -ArH), 7.61 (s, 1H, -ArH), 7.54 (d, J = 7.6 Hz, 1H, -ArH), 7.24 (d, J = 8.0 Hz, 2H, -ArH), 7.23 (d, J = 12.0 Hz, 1H, -ArH), 7.13 (d, J = 7.5 Hz, 1H, -ArH), 5.99 (s, 1H, -NH), 5.62 (s, 1H, -HetH), 2.35 (s, 3H, $-CH_3$), 2.33 (s, 3H, $-CH_3$), 1.36 (s, 9H, $-C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.88, 150.63, 145.19, 138.07, 134.72, 132.00, 129.87, 129.74, 128.31, 127.57, 126.97, 123.60, 86.02, 51.70, 28.92, 21.65, 21.38. HRMS (CI^+) m/z: Found: 384.1747. Calcd for $C_{21}H_{26}N_3O_2S$: $(M+H)^+$ 384.1746.



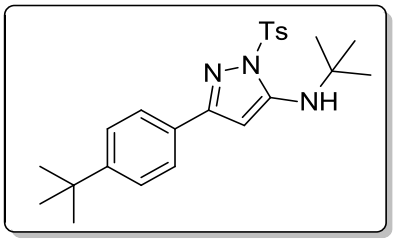
***N*-(*tert*-butyl)-3-(*o*-tolyl)-1-tosyl-1*H*-pyrazol-5-amine (3da)**

White solid, 57% yield (109 mg), IR (ν, cm^{-1}): 3410, 1360, 1166. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.3 Hz, 2H, -ArH), 7.39 (d, J = 7.4 Hz, 1H, ArH), 7.29 (d, J = 8.1 Hz, 2H, ArH), 7.22 – 7.14 (m, 3H, ArH), 6.00 (s, 1H, -NH), 5.46 (s, 1H, -HetH), 2.40 (s, 3H, $-CH_3$), 2.32 (s, 3H, $-CH_3$), 1.37 (s, 9H, $-C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.86, 149.97, 145.17, 136.55, 134.78, 132.14, 130.72, 129.66, 129.28, 128.55, 127.68, 125.59, 88.99, 51.67, 28.90, 21.69, 21.00. HRMS (CI^+) m/z: Found: 384.1761. Calcd for $C_{21}H_{26}N_3O_2S$: $(M+H)^+$ 384.1746.



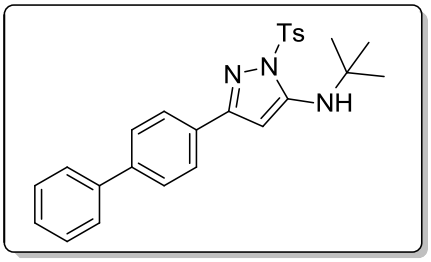
***N*-(*tert*-butyl)-1-tosyl-3-(4-(trifluoromethyl)phenyl)-1*H*-pyrazol-5-amine (3ea)**

White solid, 80% yield (175 mg), IR (ν, cm^{-1}): 3410, 1368, 1174. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, J = 10.3, 8.4 Hz, 4H, -ArH), 7.59 (d, J = 8.3 Hz, 2H, -ArH), 7.28 (d, J = 8.3 Hz, 2H, -ArH), 6.06 (s, 1H, -NH), 5.67 (s, 1H, -HetH), 2.37 (s, 3H, $-CH_3$), 1.39 (s, 9H, $-C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.99, 150.79, 145.50, 135.61, 134.55, 130.66 (q, J = 32.5 Hz), 129.82, 127.63, 126.61, 125.32 (q, J = 3.5 Hz), 124.12 (q, J = 271.0 Hz), 85.73, 51.79, 28.87, 21.64. HRMS (CI^+) m/z: Found: 438.1447. Calcd for $C_{21}H_{23}N_3O_2F_3S$: $(M+H)^+$ 438.1463.



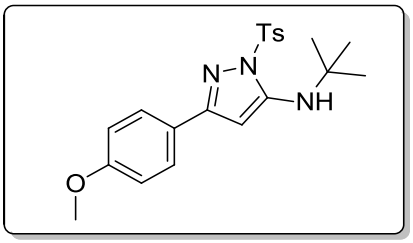
***N*-(*tert*-butyl)-3-(4-(*tert*-butyl)phenyl)-1-tosyl-1*H*-pyrazol-5-amine (3fa)**

Light yellow solid, 60% yield (127 mg), IR (ν, cm^{-1}): 3398, 1361, 1170. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.3 Hz, 2H, -ArH), 7.71 (d, J = 8.4 Hz, 2H, -ArH), 7.37 (d, J = 8.5 Hz, 2H, -ArH), 7.22 (d, J = 8.1 Hz, 2H, -ArH), 5.99 (s, 1H, -NH), 5.61 (s, 1H, -HetH), 2.32 (s, 3H, $-CH_3$), 1.36 (s, 9H, $-C(CH_3)_3$), 1.30 (s, 9H, $-C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.78, 152.24, 150.70, 145.11, 134.74, 129.70, 129.35, 127.58, 126.17, 125.34, 85.96, 51.69, 34.71, 31.29, 28.93, 21.64. HRMS (CI^+) m/z: Found: 426.2207. Calcd for $C_{24}H_{32}N_3O_2S$: $(M+H)^+$ 426.2215.



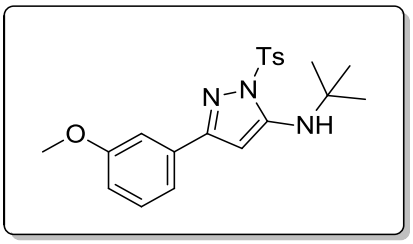
3-([1,1'-biphenyl]-4-yl)-*N*-(*tert*-butyl)-1-tosyl-1*H*-pyrazol-5-amine (3ga)

Light yellow solid, 61% yield (136 mg), IR (ν, cm^{-1}): 3417, 1358, 1170. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.3 Hz, 4H, -ArH), 7.59 (d, *J* = 8.4 Hz, 4H, -ArH), 7.41 (t, *J* = 7.6 Hz, 2H, -ArH), 7.32 (t, *J* = 7.3 Hz, 1H, -ArH), 7.25 (d, *J* = 8.2 Hz, 2H, -ArH), 6.02 (s, 1H, -NH), 5.66 (s, 1H, -HetH), 2.34 (s, 3H, $-CH_3$), 1.37 (s, 9H, $-C(CH_{3)3}$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.34, 150.75, 145.25, 141.79, 140.59, 134.73, 131.11, 129.78, 128.85, 127.64, 127.55, 127.11, 127.05, 126.85, 85.92, 51.75, 28.95, 21.69. HRMS (CI^+) m/z: Found: 446.1884. Calcd for $C_{26}H_{28}N_3O_2S$: $(M+H)^+$ 446.1902.



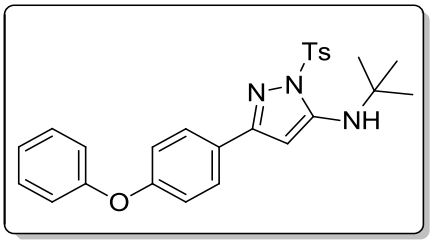
***N*-(*tert*-butyl)-3-(4-methoxyphenyl)-1-tosyl-1*H*-pyrazol-5-amine (3ha)**

White solid, 51% yield (102 mg), IR (ν, cm^{-1}): 3412, 1354, 1275, 1172. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H, -ArH), 7.70 (d, *J* = 8.8 Hz, 2H, -ArH), 7.25 (d, *J* = 8.2 Hz, 2H, -ArH), 6.88 (d, *J* = 8.8 Hz, 2H, -ArH), 5.99 (s, 1H, -NH), 5.56 (s, 1H, -HetH), 3.80 (s, 3H, $-OCH_{3)}$, 2.36 (s, 3H, $-CH_3$), 1.36 (s, 9H, $-C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.37, 156.55, 150.68, 145.08, 134.72, 129.68, 127.76, 127.58, 124.79, 113.76, 85.64, 55.30, 51.66, 28.91, 21.65. HRMS (CI^+) m/z: Found: 400.1710. Calcd for $C_{21}H_{26}N_3O_3S$: $(M+H)^+$ 400.1695.



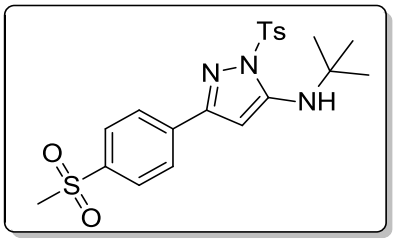
***N*-(*tert*-butyl)-3-(3-methoxyphenyl)-1-tosyl-1*H*-pyrazol-5-amine (3ia)**

White solid, 73% yield (146 mg), IR (ν, cm^{-1}): 3383, 1363,1284, 1165. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.3 Hz, 2H, -ArH), 7.35 – 7.31 (m, 2H, -ArH), 7.28 – 7.23 (m, 3H, -ArH), 6.90 – 6.84 (m, 1H, -ArH), 6.00 (s, 1H, -NH), 5.61 (s, 1H, -HetH), 3.81 (s, 3H, $-OCH_3$), 2.35 (s, 3H, $-CH_3$), 1.36 (s, 9H, $-C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.70, 156.56, 150.64, 145.23, 134.68, 133.51, 129.73, 129.43, 127.60, 119.02, 114.85, 111.68, 86.05, 55.40, 51.70, 28.90, 21.64. HRMS (CI^+) m/z: Found: 400.1711. Calcd for $C_{21}H_{26}N_3O_3S$: $(M+H)^+$ 400.1695.



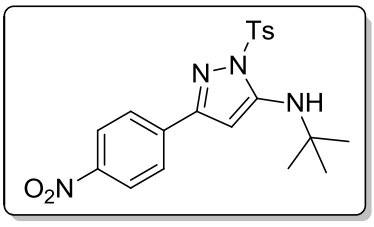
***N*-(*tert*-butyl)-3-(4-phenoxyphenyl)-1-tosyl-1*H*-pyrazol-5-amine (3ja)**

White solid, 46% yield (106 mg), IR (ν, cm^{-1}): 3406, 1358, 1237, 1168. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.3 Hz, 2H, -ArH), 7.73 (d, J = 8.5 Hz, 2H, -ArH), 7.32 (t, J = 7.9 Hz, 2H, -ArH), 7.26 (d, J = 8.2 Hz, 2H, -ArH), 7.10 (t, J = 7.4 Hz, 1H, -ArH), 7.01 – 6.96 (m, 4H, -ArH), 6.01 (s, 1H, -NH), 5.59 (s, 1H, -HetH), 2.36 (s, 3H, $-CH_3$), 1.37 (s, 9H, $-C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.10, 156.88, 156.16, 150.73, 145.21, 134.72, 129.84, 129.75, 128.00, 127.62, 127.26, 123.56, 119.06, 118.58, 85.72, 51.72, 28.93, 21.68. HRMS (CI^+) m/z: Found: 462.1855. Calcd for $C_{26}H_{28}N_3O_3S$: $(M+H)^+$ 462.1851.



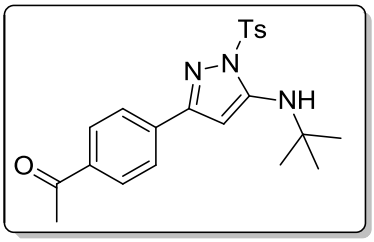
***N*-(*tert*-butyl)-3-(4-(methylsulfonyl)phenyl)-1-tosyl-1*H*-pyrazol-5-amine (3ka)**

Light yellow solid, 89% yield (199 mg), IR (ν, cm^{-1}): 3404, 1361, 1288, 1172. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, J = 16.7, 8.1 Hz, 4H, -ArH), 7.85 (d, J = 7.9 Hz, 2H, -ArH), 7.31 (d, J = 7.9 Hz, 2H, -ArH), 6.07 (s, 1H, -NH), 5.70 (s, 1H, -HetH), 3.06 (s, 3H, $-CH_3$), 2.40 (s, 3H, $-CH_3$), 1.40 (s, 9H, $-C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.32, 150.80, 145.66, 140.36, 137.42, 134.38, 129.89, 127.62, 127.52, 127.10, 85.79, 51.84, 44.50, 28.87, 21.69. HRMS (CI^+) m/z: Found: 448.1361. Calcd for $C_{21}H_{26}N_3O_4S_2$: $(M+H)^+$ 448.1365.



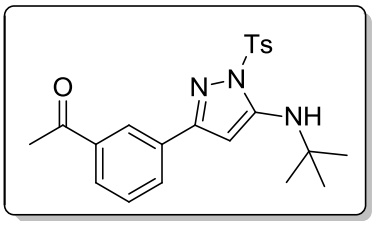
***N*-(*tert*-butyl)-3-(4-nitrophenyl)-1-tosyl-1*H*-pyrazol-5-amine (3la)**

Yellow solid, 63% yield (130 mg), IR (ν, cm^{-1}): 3400, 1364, 1168. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.5 Hz, 2H, -ArH), 7.93 (d, J = 8.5 Hz, 2H, -ArH), 7.87 (d, J = 8.1 Hz, 2H, -ArH), 7.32 (d, J = 8.0 Hz, 2H, -ArH), 6.09 (s, 1H, -NH), 5.72 (s, 1H, -HetH), 2.40 (s, 3H, $-CH_3$), 1.40 (s, 9H, $-C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.91, 150.81, 147.88, 145.73, 138.36, 134.41, 129.92, 127.67, 127.02, 123.71, 85.80, 51.86, 28.87, 21.70. HRMS (CI^+) m/z: Found: 415.1450. Calcd for $C_{20}H_{23}N_4O_4S$: $(M+H)^+$ 415.1440.



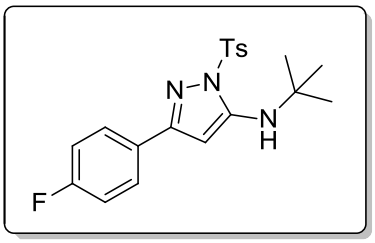
1-(4-(5-(*tert*-butylamino)-1-tosyl-1*H*-pyrazol-3-yl)phenyl)ethanone (3ma)

Light yellow solid, 57% yield (103 mg), IR (ν, cm^{-1}): 3406, 1770, 1366, 1172. ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.4 Hz, 2H, -ArH), 7.86 (d, J = 8.5 Hz, 4H, -ArH), 7.30 (d, J = 8.2 Hz, 2H, -ArH), 6.04 (s, 1H, -NH), 5.67 (s, 1H, -HetH), 2.60 (s, 3H, $-CH_3$), 2.39 (s, 3H, $-CH_3$), 1.39 (s, 9H, $-C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.69, 155.18, 150.70, 145.44, 137.15, 136.54, 134.59, 129.81, 128.49, 127.66, 126.44, 85.87, 51.78, 28.91, 26.68, 21.69. HRMS (CI^+) m/z: Found: 412.1687. Calcd for $C_{22}H_{26}N_3O_3S$: $(M+H)^+$ 412.1695.



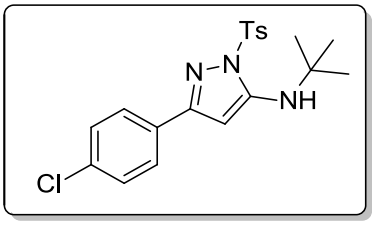
1-(3-(5-(*tert*-butylamino)-1-tosyl-1*H*-pyrazol-3-yl)phenyl)ethanone (3na)

Light yellow solid, 57% yield (113 mg), IR (ν, cm^{-1}): 3415, 1677, 1365, 1172. ^1H NMR (400 MHz, $CDCl_3$) δ 8.26 (t, J = 1.4 Hz, 1H, -ArH), 8.03 (d, J = 7.8 Hz, 1H, -ArH), 7.91 (d, J = 7.8 Hz, 1H, -ArH), 7.85 (d, J = 8.3 Hz, 2H, -ArH), 7.46 (t, J = 7.8 Hz, 1H, -ArH), 7.29 (d, J = 8.3 Hz, 2H, -ArH), 6.05 (s, 1H, -NH), 5.69 (s, 1H, -HetH), 2.63 (s, 3H, $-CH_3$), 2.38 (s, 3H, $-CH_3$), 1.39 (s, 9H, $-C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.05, 155.61, 150.78, 145.36, 137.27, 134.61, 132.77, 130.97, 129.79, 128.90, 128.73, 127.62, 126.01, 85.75, 51.77, 28.90, 26.81, 21.68. HRMS (CI^+) m/z: Found: 412.1700. Calcd for $C_{22}H_{26}N_3O_3S$: $(M+H)^+$ 412.1695.



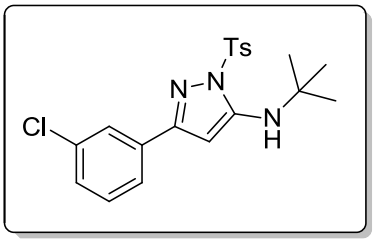
***N*-(*tert*-butyl)-3-(4-fluorophenyl)-1-tosyl-1*H*-pyrazol-5-amine (3oa)**

White solid, 90% yield (174 mg), IR (ν, cm^{-1}): 3394, 1360, 1181. ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.3 Hz, 2H, -ArH), 7.78 – 7.70 (m, 2H, -ArH), 7.26 (d, J = 8.2 Hz, 2H, -ArH), 7.02 (t, J = 8.7 Hz, 2H, -ArH), 6.03 (s, 1H, -NH), 5.59 (s, 1H, -HetH), 2.35 (s, 3H, $-CH_3$), 1.37 (s, 9H, $-C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.29 (d, J = 248.2 Hz), 155.67, 150.74, 145.32, 134.64, 129.77, 128.37 (d, J = 3.2 Hz), 128.23 (d, J = 8.3 Hz), 127.59, 115.34 (d, J = 21.6 Hz), 85.62, 51.72, 28.88, 21.64. HRMS (CI^+) m/z: Found: 388.1494. Calcd for $C_{20}H_{23}N_3O_2SF$: $(M+H)^+$ 388.1495.



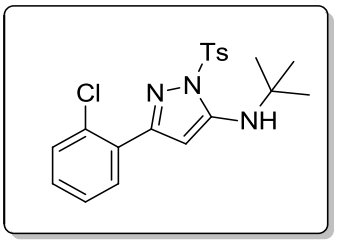
***N*-(*tert*-butyl)-3-(4-chlorophenyl)-1-tosyl-1*H*-pyrazol-5-amine (3pa)**

White solid, 96% yield (194 mg), IR (ν, cm^{-1}): 3411, 1365, 1172. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.3 Hz, 2H，-ArH), 7.69 (d, J = 8.5 Hz, 2H，-ArH), 7.29 (dd, J = 15.7, 8.4 Hz, 4H, -ArH), 6.03 (s, 1H, -NH), 5.59 (s, 1H, -HetH), 2.36 (s, 3H, $-CH_3$), 1.37 (s, 9H, $-C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.44, 150.73, 145.35, 134.82, 134.62, 130.67, 129.79, 128.58, 127.68, 127.61, 85.60, 51.74, 28.90, 21.67. HRMS (CI^+) m/z: Found: 404.1208. Calcd for $C_{20}H_{23}N_3O_2SCl$: $(M+H)^+$ 404.1170.



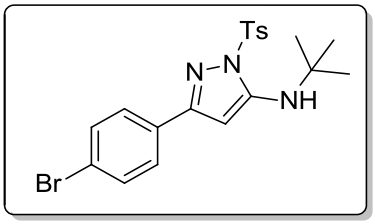
***N*-(*tert*-butyl)-3-(3-chlorophenyl)-1-tosyl-1*H*-pyrazol-5-amine (3qa)**

White solid, 81% yield (164 mg), IR (ν, cm^{-1}): 3411, 1363, 1171. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.4 Hz, 2H, -ArH), 7.76 (s, 1H, -ArH), 7.66 – 7.61 (m, 1H, -ArH), 7.30 – 7.25 (m, 4H, -ArH), 6.03 (s, 1H, -NH), 5.60 (s, 1H, -NetH), 2.37 (s, 3H, $-CH_3$), 1.37 (s, 9H, $-C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.18, 150.70, 145.40, 134.59, 134.40, 133.97, 129.81, 129.69, 128.95, 127.62, 126.38, 124.54, 85.68, 51.76, 28.90, 21.68. HRMS (CI^+) m/z: Found: 404.1215. Calcd for $C_{20}H_{23}N_3O_2SCl$: $(M+H)^+$ 404.1170.



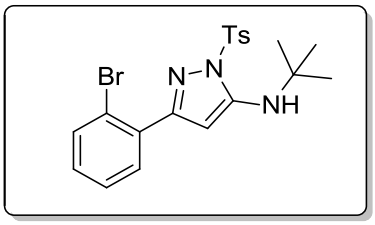
***N*-(*tert*-butyl)-3-(2-chlorophenyl)-1-tosyl-1*H*-pyrazol-5-amine (3ra)**

White solid, 91% yield (184 mg), IR (ν, cm^{-1}): 3409, 1371, 1167. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.3 Hz, 2H, -ArH), 7.69 (dd, J = 6.0, 3.5 Hz, 1H, -ArH), 7.41 – 7.36 (m, 1H, -ArH), 7.31 (d, J = 8.1 Hz, 2H, -ArH), 7.27 (dd, J = 5.7, 3.5 Hz, 2H, -ArH), 5.99 (s, 1H, -NH), 5.82 (s, 1H, -HetH), 2.41 (s, 3H, $-CH_3$), 1.38 (s, 9H, $-C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.11, 149.72, 145.33, 134.71, 132.64, 131.51, 131.00, 130.11, 129.86, 129.76, 127.63, 126.75, 89.86, 51.72, 28.90, 21.69. HRMS (CI^+) m/z: Found: 404.1208. Calcd for $C_{20}H_{23}N_3O_2SCl$: $(M+H)^+$ 404.1170.



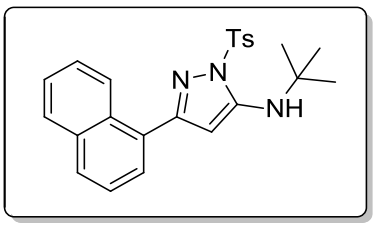
3-(4-bromophenyl)-*N*-(*tert*-butyl)-1-tosyl-1*H*-pyrazol-5-amine (3sa)

White solid, 97% yield (217 mg), IR (ν, cm^{-1}): 3394, 1360, 1168. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.3 Hz, 2H, -ArH), 7.63 (d, J = 8.5 Hz, 2H, -ArH), 7.46 (d, J = 7.9 Hz, 2H, -ArH), 7.27 (d, J = 7.6 Hz, 2H, -ArH), 6.03 (s, 1H, -NH), 5.60 (s, 1H, -HetH), 2.36 (s, 3H, $-CH_3$), 1.37 (s, 9H, $-C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.46, 150.73, 145.37, 134.60, 131.53, 131.11, 129.79, 127.95, 127.61, 123.11, 85.57, 51.74, 28.91, 21.68. HRMS (CI^+) m/z: Found: 448.0700. Calcd for $C_{20}H_{23}N_3O_2SBr$: $(M+H)^+$ 448.0694.



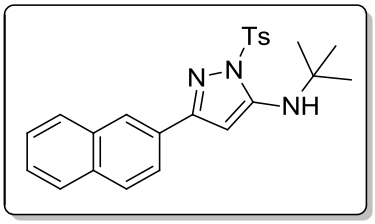
3-(2-bromophenyl)-*N*-(*tert*-butyl)-1-tosyl-1*H*-pyrazol-5-amine (3ta)

White solid, 74% yield (166 mg), IR (ν, cm^{-1}): 3409, 1371, 1167. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.2 Hz, 2H, -ArH), 7.62 – 7.51 (m, 2H, -ArH), 7.33 – 7.25 (m, 3H, -ArH), 7.17 (t, J = 7.6 Hz, 1H, -ArH), 5.96 (s, 1H, -NH), 5.75 (s, 1H, -HetH), 2.40 (s, 3H, $-CH_3$), 1.36 (s, 9H, $-C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.65, 149.65, 145.29, 134.74, 133.69, 133.28, 131.31, 130.07, 129.75, 127.64, 127.28, 122.13, 89.96, 51.73, 28.90, 21.71. HRMS (CI^+) m/z: Found: 448.0700. Calcd for $C_{20}H_{23}N_3O_2SBr$: $(M+H)^+$ 448.0694.



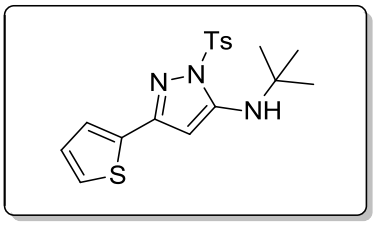
***N*-(*tert*-butyl)-3-(naphthalen-1-yl)-1-tosyl-1*H*-pyrazol-5-amine (3ua)**

Light yellow solid, 53% yield (111 mg), IR (ν, cm^{-1}): 3395, 1362, 1163. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.4 Hz, 1H, -ArH), 7.91 (d, J = 8.3 Hz, 2H, -ArH), 7.82 (d, J = 8.1 Hz, 2H, -ArH), 7.59 (d, J = 7.0 Hz, 1H, -ArH), 7.48 – 7.38 (m, 3H, -ArH), 7.31 (d, J = 8.1 Hz, 2H, -ArH), 6.09 (s, 1H, -NH), 5.61 (s, 1H, -HetH), 2.40 (s, 3H, $-CH_3$), 1.39 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.23, 150.15, 145.33, 134.87, 133.76, 131.17, 130.36, 129.78, 129.29, 128.28, 127.77, 127.33, 126.34, 126.01, 125.84, 125.10, 89.77, 51.76, 28.94, 21.73. HRMS (CI^+) m/z: Found: 420.1738. Calcd for $C_{24}H_{26}N_3O_2S$: $(M+H)^+$ 420.1746.



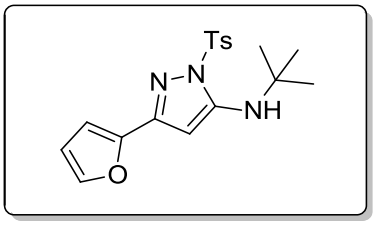
***N*-(*tert*-butyl)-3-(naphthalen-2-yl)-1-tosyl-1*H*-pyrazol-5-amine (3va)**

Light yellow solid, 98% yield (206 mg), IR (ν, cm^{-1}): 3408, 1374, 1165. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H, -ArH), 7.95 (d, J = 8.4 Hz, 1H, -ArH), 7.89 – 7.74 (m, 5H, -ArH), 7.48 – 7.38 (m, 2H, -ArH), 7.23 (d, J = 7.8 Hz, 2H, -ArH), 6.04 (s, 1H, -NH), 5.77 (s, 1H, -HetH), 2.30 (s, 3H, $-CH_3$), 1.39 (s, 9H, $-C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.67, 150.79, 145.28, 134.71, 133.73, 133.22, 129.78, 129.57, 128.37, 128.10, 127.75, 127.64, 126.44, 126.32, 125.67, 124.19, 86.02, 51.77, 28.98, 21.66. HRMS (CI^+) m/z: Found: 420.1741. Calcd for $C_{24}H_{26}N_3O_2S$: $(M+H)^+$ 420.1746.



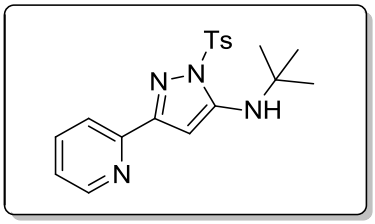
***N*-(*tert*-butyl)-3-(thiophen-2-yl)-1-tosyl-1*H*-pyrazol-5-amine (3wa)**

Light yellow solid, 52% yield (98 mg), IR (ν, cm^{-1}): 3398, 1361, 1169. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.3 Hz, 2H, -ArH), 7.34 (dd, J = 3.6, 1.1 Hz, 1H, -ArH), 7.29 – 7.22 (m, 3H, -ArH), 7.00 (dd, J = 4.9, 3.7 Hz, 1H), 6.01 (s, 1H, -NH), 5.51 (s, 1H, -HetH), 2.36 (s, 3H, $-CH_3$), 1.36 (s, 9H, $-C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.05, 150.60, 145.28, 135.33, 134.50, 129.73, 127.65, 127.30, 126.33, 125.92, 85.94, 51.72, 28.87, 21.66. HRMS (CI^+) m/z: Found: 376.1154. Calcd for $C_{18}H_{22}N_3O_2S_2$: $(M+H)^+$ 376.1153.



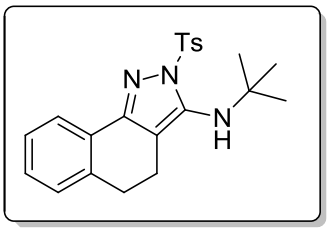
***N*-(*tert*-butyl)-3-(furan-2-yl)-1-tosyl-1*H*-pyrazol-5-amine (3xa)**

Light yellow solid, 45% yield (81 mg), IR (ν, cm^{-1}): 3402, 1358, 1172. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.3 Hz, 2H, -ArH), 7.42 (d, J = 1.0 Hz, 1H, -ArH), 7.27 (d, J = 8.2 Hz, 2H, -ArH), 6.79 (d, J = 3.4 Hz, 1H, -ArH), 6.42 (dd, J = 3.3, 1.8 Hz, 1H, -ArH), 6.01 (s, 1H, -NH), 5.58 (s, 1H, -HetH), 2.37 (s, 3H, $-CH_3$), 1.36 (s, 9H, $-C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.26, 149.00, 147.59, 145.30, 142.74, 134.53, 129.76, 127.58, 111.47, 108.44, 85.52, 51.72, 28.83, 21.64. HRMS (CI^+) m/z: Found: 360.1389. Calcd for $C_{18}H_{22}N_3O_3S$: $(M+H)^+$ 360.1382.



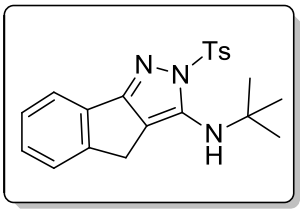
***N*-(*tert*-butyl)-3-(pyridin-2-yl)-1-tosyl-1*H*-pyrazol-5-amine (3ya)**

Light yellow solid, 73% yield (135 mg), IR (ν, cm^{-1}): 3411, 1364, 1172. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, J = 4.7 Hz, 1H, -ArH), 8.07 (d, J = 8.0 Hz, 1H, -ArH), 7.84 (d, J = 8.2 Hz, 2H, -ArH), 7.68 (t, J = 7.7 Hz, 1H, -ArH), 7.27 (d, J = 8.1 Hz, 2H, -ArH), 7.24 – 7.19 (m, 1H, -ArH), 6.04 (s, 1H, -HetH), 6.02 (s, 1H, -NH), 2.36 (s, 3H, $-CH_3$), 1.38 (s, 9H, $-C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.86, 151.05, 150.68, 149.05, 145.34, 136.40, 134.63, 129.76, 127.58, 123.63, 120.96, 86.53, 51.74, 28.88, 21.63. HRMS (CI^+) m/z: Found: 371.1555. Calcd for $C_{19}H_{23}N_4O_2S$: $(M+H)^+$ 371.1542.



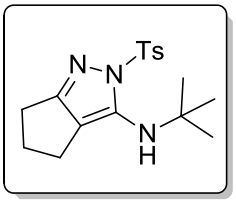
***N*-(*tert*-butyl)-2-tosyl-4,5-dihydro-2*H*-benzo[g]indazol-3-amine (5aa)**

Light yellow solid, 46% yield (91 mg), IR (ν, cm^{-1}): 3368, 1361, 1170. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, J = 5.2, 3.8 Hz, 1H, -ArH), 7.82 (d, J = 8.4 Hz, 2H, -ArH), 7.23 (dd, J = 8.5, 4.6 Hz, 4H, -ArH), 7.17 (dd, J = 3.5, 1.9 Hz, 1H, -ArH), 4.89 (s, 1H, -NH), 2.79 (t, J = 6.9 Hz, 2H, $-CH_2$), 2.67 (t, J = 6.8 Hz, 2H, $-CH_2$), 2.34 (s, 3H, $-CH_3$), 1.27 (s, 9H, $-C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.73, 146.00, 145.06, 137.89, 135.16, 129.70, 129.16, 128.69, 128.16, 127.71, 126.80, 123.72, 108.36, 55.60, 30.37, 29.42, 21.64, 21.44. HRMS (CI^+) m/z: Found: 396.1753. Calcd for $C_{22}H_{26}N_3O_2S$: $(M+H)^+$ 396.1746.



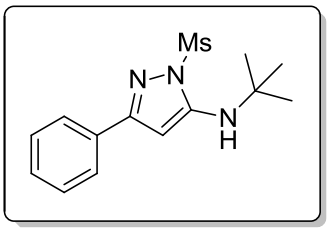
***N*-(*tert*-butyl)-2-tosyl-2,4-dihydroindeno[1,2-c]pyrazol-3-amine (5ba)**

Light yellow solid, 35% yield (67 mg), IR (ν, cm^{-1}): 3386, 1365, 1170. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.2 Hz, 3H, -ArH), 7.41 – 7.37 (m, 1H, -ArH), 7.31 (dd, J = 5.5, 3.0 Hz, 2H, -ArH), 7.24 (d, J = 8.2 Hz, 2H, -ArH), 6.21 (s, 1H, -NH), 3.67 (s, 2H, $-CH_2$), 2.35 (s, 3H, $-CH_3$), 1.36 (s, 9H, $-C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.83, 148.99, 145.32, 144.99, 134.85, 132.96, 129.68, 128.81, 127.49, 127.15, 125.45, 121.86, 102.96, 51.62, 32.61, 30.58, 21.63. HRMS (CI^+) m/z: Found: 382.1599. Calcd for $C_{21}H_{24}N_3O_2S$: $(M+H)^+$ 382.1589.



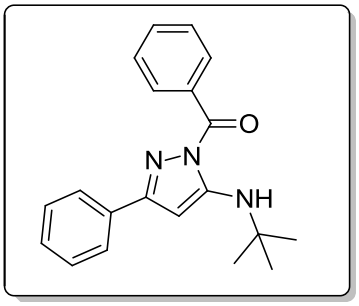
***N*-(*tert*-butyl)-2-tosyl-2,4,5,6-tetrahydrocyclopenta[c]pyrazol-3-amine (5da)**

White solid, 31% yield (52 mg), IR (ν, cm^{-1}): 3410, 1349, 1160. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.1 Hz, 2H, -ArH), 7.28 (d, J = 8.2 Hz, 2H, -ArH), 5.99 (s, 1H, -NH), 2.61 (t, J = 7.0 Hz, 2H, $-CH_2$), 2.54 (t, J = 7.5 Hz, 2H, $-CH_2$), 2.40 (s, 3H, $-CH_3$), 2.28 – 2.20 (m, 2H, $-CH_2$), 1.28 (s, 9H, $-C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.68, 144.76, 144.62, 135.08, 129.63, 127.50, 105.37, 51.54, 30.42, 28.93, 27.11, 24.89, 21.66. HRMS (CI^+) m/z: Found: 334.1599. Calcd for $C_{17}H_{24}N_3O_2S$: $(M+H)^+$ 334.1589.



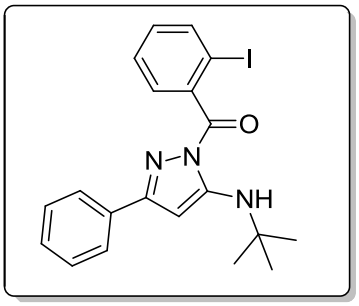
***N*-(*tert*-butyl)-1-(methylsulfonyl)-3-phenyl-1*H*-pyrazol-5-amine (7aa)**

White solid, 54% yield (79 mg), IR (ν, cm^{-1}): 3411, 1367, 1166. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, J = 8.0, 1.6 Hz, 2H, -ArH), 7.43 – 7.36 (m, 3H, -ArH), 5.85 (s, 1H, -NH), 5.72 (s, 1H, -HetH), 3.23 (s, 3H, $-CH_3$), 1.39 (s, 9H, $-C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.51, 150.43, 131.96, 129.23, 128.55, 126.42, 85.57, 51.83, 40.70, 28.87. HRMS (CI^+) m/z: Found: 293.1203. Calcd for $C_{14}H_{19}N_3O_2S$: $(M)^+$ 293.1198.



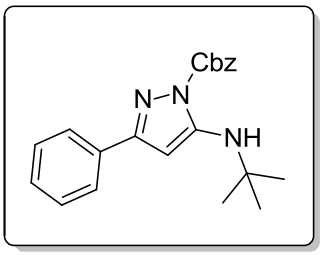
(5-(*tert*-butylamino)-3-phenyl-1*H*-pyrazol-1-yl)(phenyl)methanone (7ba)

Yellow solid, 56% yield (89 mg), IR (ν, cm^{-1}): 3365, 1661, 1356. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.3 Hz, 2H, -ArH), 7.81 (d, J = 8.1 Hz, 2H, -ArH), 7.64 (s, 1H, -NH), 7.53 (t, J = 7.4 Hz, 1H, -ArH), 7.45 (t, J = 7.6 Hz, 2H, -ArH), 7.40 – 7.32 (m, 3H, -ArH), 5.78 (s, 1H, -HetH), 1.45 (s, 9H, $-C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.16, 155.06, 152.22, 133.77, 132.61, 132.23, 131.41, 129.07, 128.57, 127.74, 126.45, 84.49, 51.36, 28.85. HRMS (CI^+) m/z: Found: 320.1761. Calcd for $C_{20}H_{22}N_3O_2$: $(M+H)^+$ 320.1763.



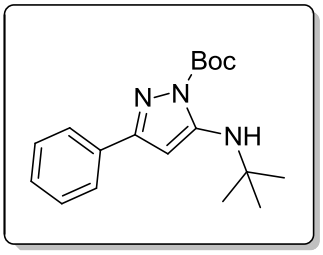
(5-(*tert*-butylamino)-3-phenyl-1*H*-pyrazol-1-yl)(2-iodophenyl)methanone (7ca)

Yellow solid, 57% yield (127 mg), IR (ν, cm^{-1}): 3376, 1679, 1357. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.0 Hz, 1H, -ArH), 7.70 (dd, J = 4.9, 1.8 Hz, 2H, -ArH), 7.48 – 7.39 (m, 3H, -ArH), 7.35 – 7.29 (s+m, 3H, -NH+-ArH), 7.14 (td, J = 7.9, 1.8 Hz, 1H, -ArH), 5.76 (s, 1H, -HetH), 1.47 (s, 9H, $-C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.81, 155.91, 151.59, 141.08, 139.07, 132.44, 131.10, 129.16, 129.10, 128.47, 127.49, 126.54, 93.17, 84.91, 51.57, 28.87. HRMS (CI^+) m/z: Found: 446.0728. Calcd for $C_{20}H_{21}N_3O_2I$: $(M+H)^+$ 446.0729.



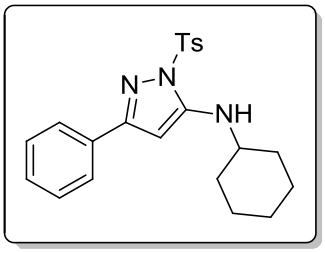
benzyl 5-(*tert*-butylamino)-3-phenyl-1*H*-pyrazole-1-carboxylate (7da)

Light yellow solid, 57% yield (100 mg), IR (ν, cm^{-1}): 3364, 1717, 1354. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 7.3 Hz, 2H, -ArH), 7.49 (d, J = 6.9 Hz, 2H, -ArH), 7.40 – 7.31 (m, 6H, -ArH), 6.86 (s, 1H, -NH), 5.70 (s, 1H, -HetH), 5.44 (s, 2H, $-CH_2$), 1.38 (s, 9H, $-C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.36, 152.73, 151.12, 135.14, 132.56, 129.00, 128.67, 128.64, 128.53, 128.49, 126.61, 84.79, 68.91, 51.34, 28.82. HRMS (CI^+) m/z: Found: 350.1855. Calcd for $C_{21}H_{24}N_3O_2$: $(M+H)^+$ 350.1869.



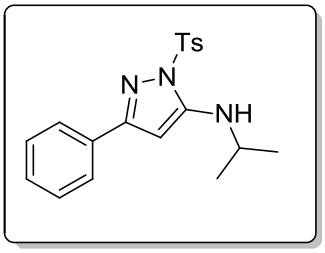
***tert*-butyl 5-(*tert*-butylamino)-3-phenyl-1*H*-pyrazole-1-carboxylate (7ea)**

Light yellow solid, 32% yield (50 mg), IR (ν, cm^{-1}): 3373, 1708, 1356. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.82 (m, 2H, -ArH), 7.41 – 7.32 (m, 3H, -ArH), 6.87 (s, 1H, -NH), 5.71 (s, 1H, -HetH), 1.66 (s, 9H, $-C(CH_3)_3$), 1.41 (s, 9H, $-C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.28, 151.52, 150.99, 132.75, 128.72, 128.38, 126.40, 84.83, 84.66, 51.23, 28.87, 28.11. HRMS (CI^+) m/z: Found: 316.2021. Calcd for $C_{18}H_{26}N_3O_2$: $(M+H)^+$ 316.2025.



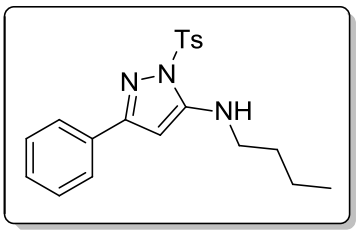
***N*-cyclohexyl-3-phenyl-1-tosyl-1*H*-pyrazol-5-amine (8ab)**

White solid, 30% yield (59 mg), IR (ν, cm^{-1}): 3396, 1362, 1168. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.3 Hz, 2H, -ArH), 7.79 (dd, J = 7.8, 1.6 Hz, 2H, -ArH), 7.39 – 7.34 (m, 3H, -ArH), 7.29 (d, J = 8.1 Hz, 2H, -ArH), 5.80 (d, J = 7.8 Hz, 1H, -NH), 5.53 (s, 1H, -Heth), 3.17 (dd, J = 10.4, 6.6 Hz, 1H, -CH), 2.40 (s, 3H, $-CH_3$), 2.07 (d, J = 11.0 Hz, 2H, $-CH_2$), 1.81 (dd, J = 8.8, 3.4 Hz, 2H, $-CH_2$), 1.70 – 1.64 (m, 1H, $-CH_2$), 1.42 – 1.29 (m, 5H, $-CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.76, 152.04, 145.18, 134.68, 132.13, 129.75, 129.01, 128.37, 127.65, 126.39, 83.89, 53.97, 32.78, 25.65, 24.65, 21.67. HRMS (CI^+) m/z: Found: 396.1758. Calcd for $C_{22}H_{26}N_3O_2S$: $(M+H)^+$ 396.1746.



***N*-isopropyl-3-phenyl-1-tosyl-1*H*-pyrazol-5-amine (8ac)**

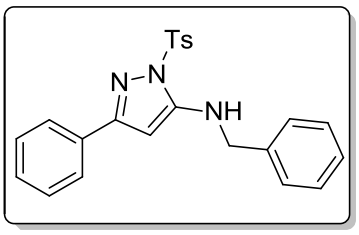
White solid, 42% yield (75 mg), IR (ν, cm^{-1}): 3401, 1366, 1170. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.4 Hz, 2H, -ArH), 7.75 (dd, J = 7.9, 1.7 Hz, 2H, -ArH), 7.37 – 7.29 (m, 3H, -ArH), 7.25 (d, J = 8.3 Hz, 2H, -ArH), 5.66 (d, J = 7.8 Hz, 1H, -NH), 5.51 (s, 1H, -HetH), 3.47 (dq, J = 12.8, 6.4 Hz, 1H, -CH), 2.35 (s, 3H, $-CH_3$), 1.27 (d, J = 6.4 Hz, 6H, $-CH\ (CH_3)_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.75, 152.12, 145.25, 134.65, 132.10, 129.77, 129.05, 128.40, 127.65, 126.38, 84.14, 47.00, 22.65, 21.67. HRMS (CI^+) m/z: Found: 356.1447. Calcd for $C_{19}H_{22}N_3O_2S$: $(M+H)^+$ 356.1433.



***N*-butyl-3-phenyl-1-tosyl-1*H*-pyrazol-5-amine (8ad)**

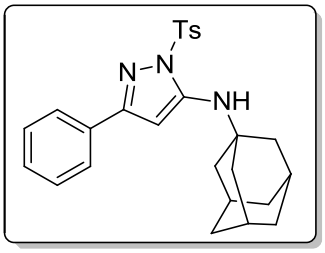
White solid, 22% yield (41 mg), IR (ν, cm^{-1}): 3406, 1362, 1172. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, J = 8.3 Hz, 2H, -ArH), 7.76 (dd, J = 7.3, 1.8 Hz, 2H, -ArH), 7.42 – 7.32 (m, 3H, -ArH), 7.28 (d, J = 9.4 Hz, 2H, -ArH), 5.75 (t, J = 5.2 Hz, 1H, -NH), 5.52 (s, 1H, HetH), 3.16 (dd, J = 12.8, 6.7 Hz, 2H, $-CH_2$), 2.39 (s, 3H, $-CH_3$), 1.69 – 1.62 (m, 2H, $-CH_2$), 1.44 (dq, J = 14.4, 7.3 Hz, 2H, $-CH_2$), 0.98 (t, J = 7.3 Hz, 3H, $-CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.60, 152.95, 145.22, 134.69, 132.09, 129.78, 129.03, 128.39, 127.67, 126.37, 83.86, 45.16, 31.11, 21.67, 20.13, 13.79. HRMS (CI^+) m/z: Found: 370.1601.

Calcd for $C_{20}H_{24}N_3O_2S$: $(M+H)^+$ 370.1589.



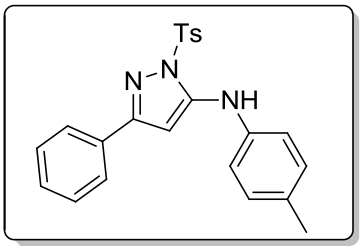
***N*-benzyl-3-phenyl-1-tosyl-1*H*-pyrazol-5-amine (8ae)**

Light yellow solid, 56% yield (113 mg), IR (ν, cm^{-1}): 3406, 1352, 1166. ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.3 Hz, 2H, -ArH), 7.71 (dd, *J* = 7.6, 1.7 Hz, 2H, -ArH), 7.37 – 7.26 (m, 8H, -ArH), 7.23 (d, *J* = 8.2 Hz, 2H, -ArH), 6.20 (t, *J* = 5.1 Hz, 1H, -NH), 5.51 (s, 1H, -HetH), 4.34 (d, *J* = 5.7 Hz, 2H, $-CH_2$), 2.34 (s, 3H, $-CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.54, 152.62, 145.40, 137.62, 134.60, 131.97, 129.87, 129.12, 128.85, 128.43, 127.76, 127.73, 127.22, 126.41, 84.92, 49.31, 21.70. HRMS (CI^+) m/z: Found: 404.1447. Calcd for $C_{23}H_{22}N_3O_2S$: $(M+H)^+$ 404.1433.



***N*-adamantan-1-yl)-3-phenyl-1-tosyl-1*H*-pyrazol-5-amine (8af)**

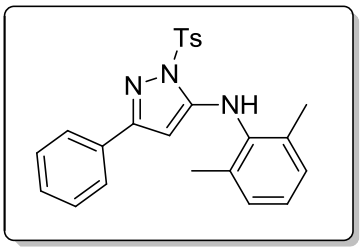
Light yellow solid, 45% yield (101 mg), IR (ν, cm^{-1}): 3403, 1365, 1166. ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.3 Hz, 2H, -ArH), 7.76 (d, *J* = 6.5 Hz, 2H, -ArH), 7.37 – 7.30 (m, 3H, -ArH), 7.25 (d, *J* = 8.1 Hz, 2H, -ArH), 5.96 (s, 1H, -NH), 5.66 (s, 1H, -HetH), 2.35 (s, 3H, $-CH_3$), 2.14 (s, 3H, -CH), 1.93 (s, 6H, $-CH_2$), 1.74 – 1.66 (t, J = 16.0 Hz, 6H, $-CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.61, 149.91, 145.16, 134.76, 132.17, 129.72, 129.01, 128.38, 127.64, 126.42, 86.42, 52.17, 42.02, 36.30, 29.51, 21.67. HRMS (CI^+) m/z: Found: 448.2056. Calcd for $C_{26}H_{30}N_3O_2S$: $(M+H)^+$ 448.2059.



3-phenyl-*N*-(p-tolyl)-1-tosyl-1*H*-pyrazol-5-amine (8ag)

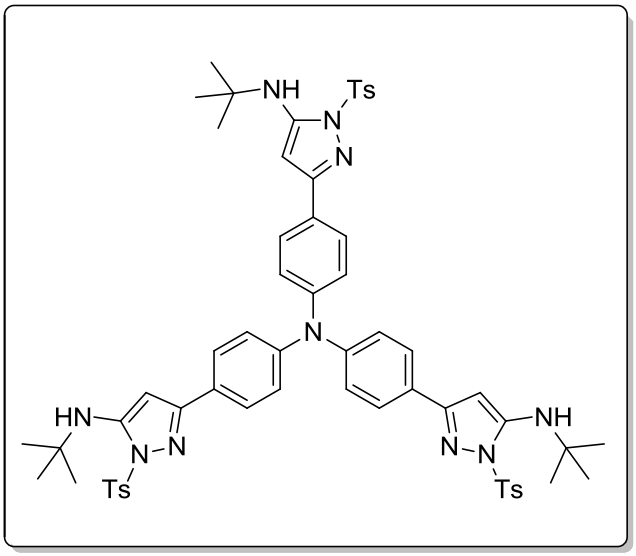
Light yellow solid, 21% yield (42 mg), IR (ν, cm^{-1}): 3383, 1371, 1167. ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 2H, -ArH), 7.75 (dd, *J* = 7.6, 1.7 Hz, 2H, -ArH), 7.72 (s, 1H, -NH), 7.36 – 7.32 (m, 3H, -ArH), 7.27 (d, *J* = 8.3 Hz, 2H, -ArH), 7.16 (d, *J* = 8.3 Hz, 2H, -ArH), 7.08 (d, *J* = 8.3 Hz, 2H, -ArH), 6.06 (s, 1H, -HetH), 2.36 (s, 3H, $-CH_3$), 2.33 (s, 3H, $-CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.33, 148.68, 145.60, 137.72, 134.48, 133.13, 131.79, 130.13, 129.96, 129.24, 128.49, 127.81,

126.39, 119.58, 87.36, 21.72, 20.82. HRMS (CI^+) m/z: Found: 404.1432. Calcd for $C_{23}H_{22}N_3O_2S$: $(M+H)^+$ 404.1433.



_N_-(2,6-dimethylphenyl)-3-phenyl-1-tosyl-1_H_-pyrazol-5-amine (8ah)

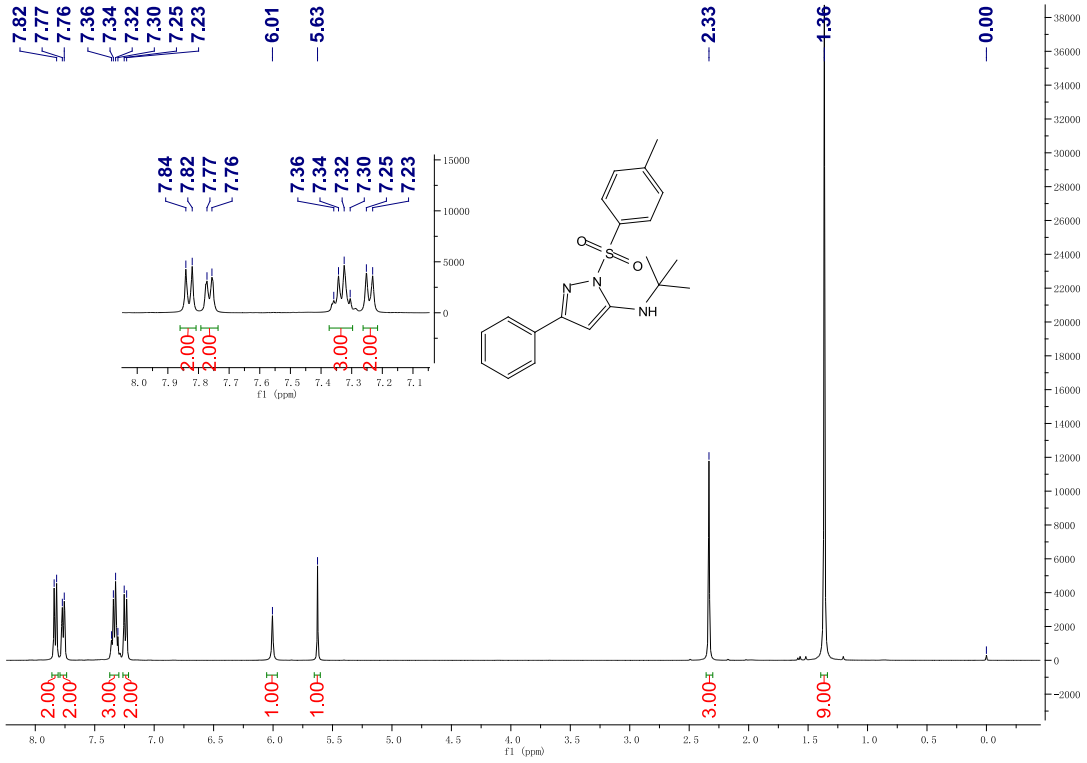
Light yellow solid, 19% yield (40 mg), IR (ν, cm^{-1}): 3400, 1365, 1169. ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.3 Hz, 2H, -ArH), 7.68 (dd, *J* = 6.5, 3.1 Hz, 2H, -ArH), 7.37 – 7.27 (m, 6H, -ArH), 7.14 (s, 1H, -NH), 7.13 (s, 2H, -ArH), 5.13 (s, 1H, -HetH), 2.41 (s, 3H, $-CH_3$), 2.21 (s, 6H, $-CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.26, 150.46, 145.53, 136.72, 135.61, 134.64, 131.82, 129.88, 129.09, 128.83, 128.37, 127.89, 127.16, 126.33, 85.90, 21.73, 18.11. HRMS (CI^+) m/z: Found: 418.1598. Calcd for $C_{24}H_{24}N_3O_2S$: $(M+H)^+$ 418.1589.

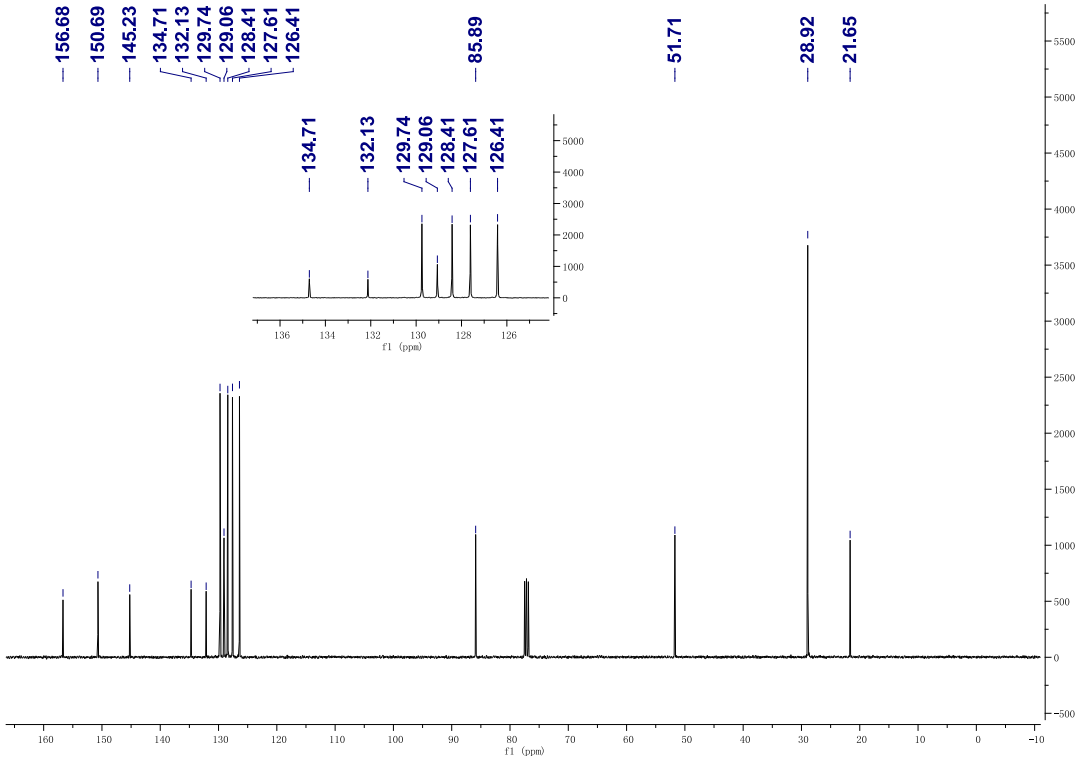


3-(4-(bis(4-(5-(*tert*-butylamino)-1-tosyl-1*H*-pyrazol-3-yl)phenyl)amino)phenyl)-*N*-(*tert*-butyl)-1-tosyl-1*H*-pyrazol-5-amine (10aa)

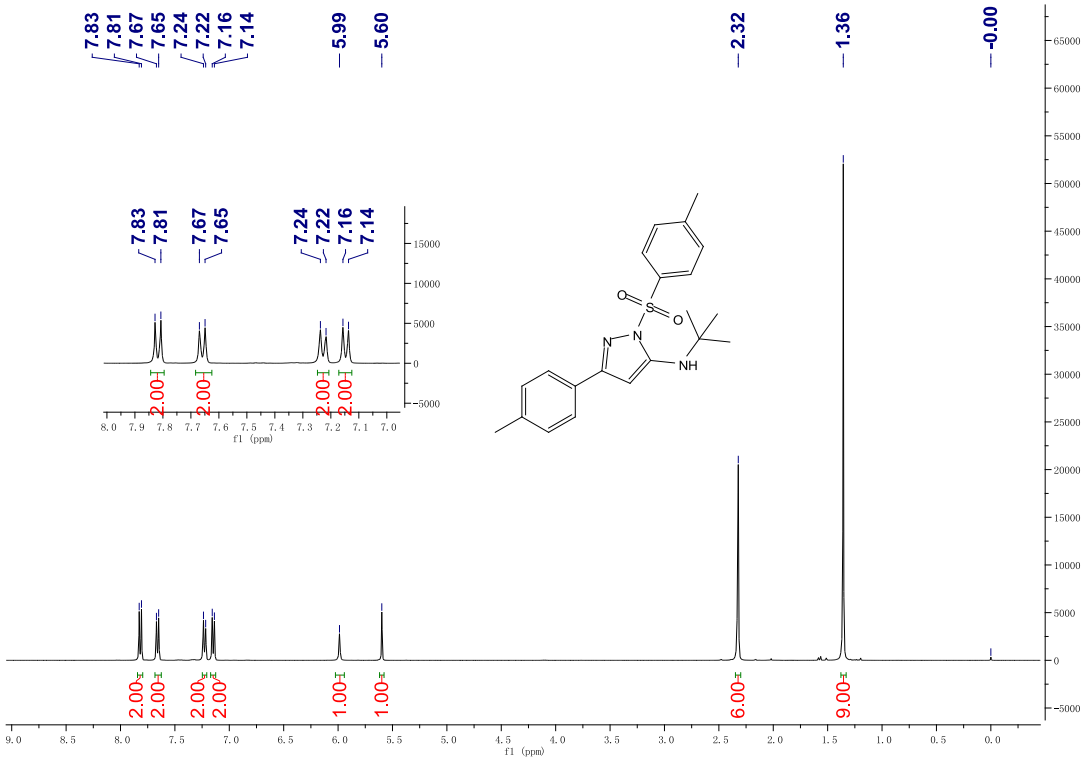
Light yellow solid, 33% yield (185 mg),IR (ν, cm^{-1}): 3403, 1365, 1168. ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.83 (d, *J* = 8.3 Hz, 6H, -ArH), 7.63 (d, *J* = 8.6 Hz, 6H, -ArH), 7.29 (d, *J* = 8.1 Hz, 6H, -ArH), 7.04 (d, *J* = 8.6 Hz, 6H, -ArH), 6.00 (s, 3H, -NH), 5.57 (s, 3H, -HetH), 2.40 (s, 9H, $-CH_3$), 1.37 (s, 27H, $-C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 156.22, 150.66, 147.77, 145.15, 134.71, 129.73, 127.62, 127.46, 126.91, 123.91, 85.70, 51.70, 28.92, 21.69.

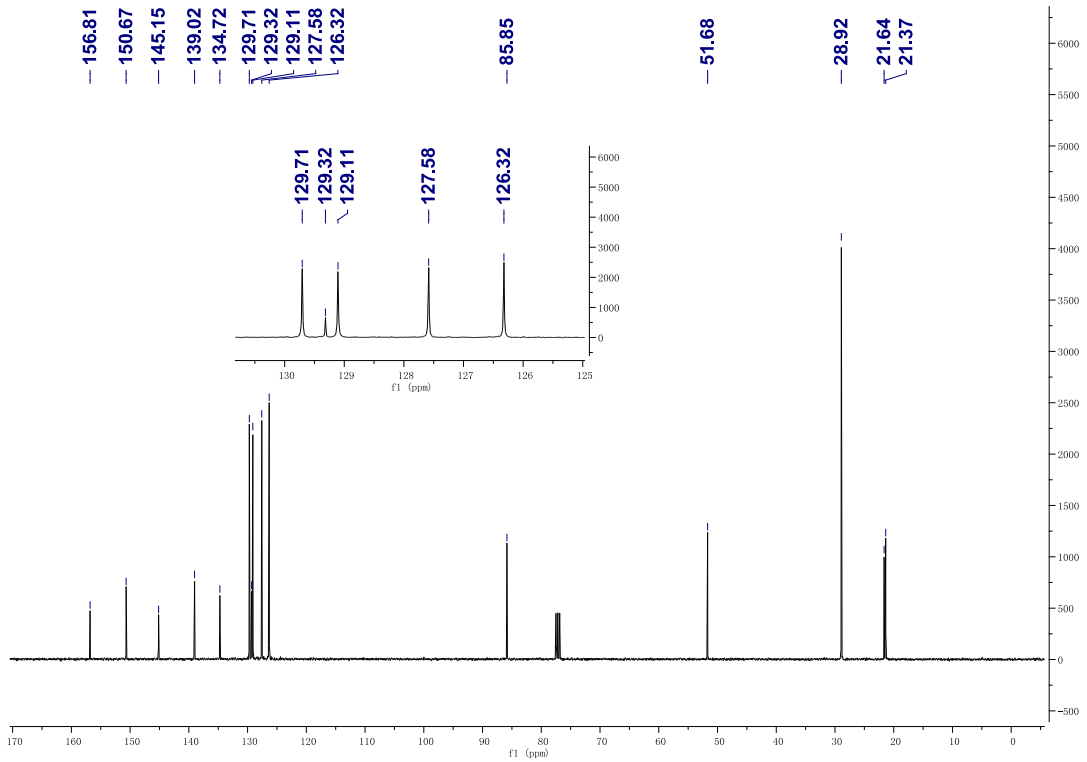
N-(*tert*-butyl)-3-phenyl-1-tosyl-1*H*-pyrazol-5-amine (3aa)



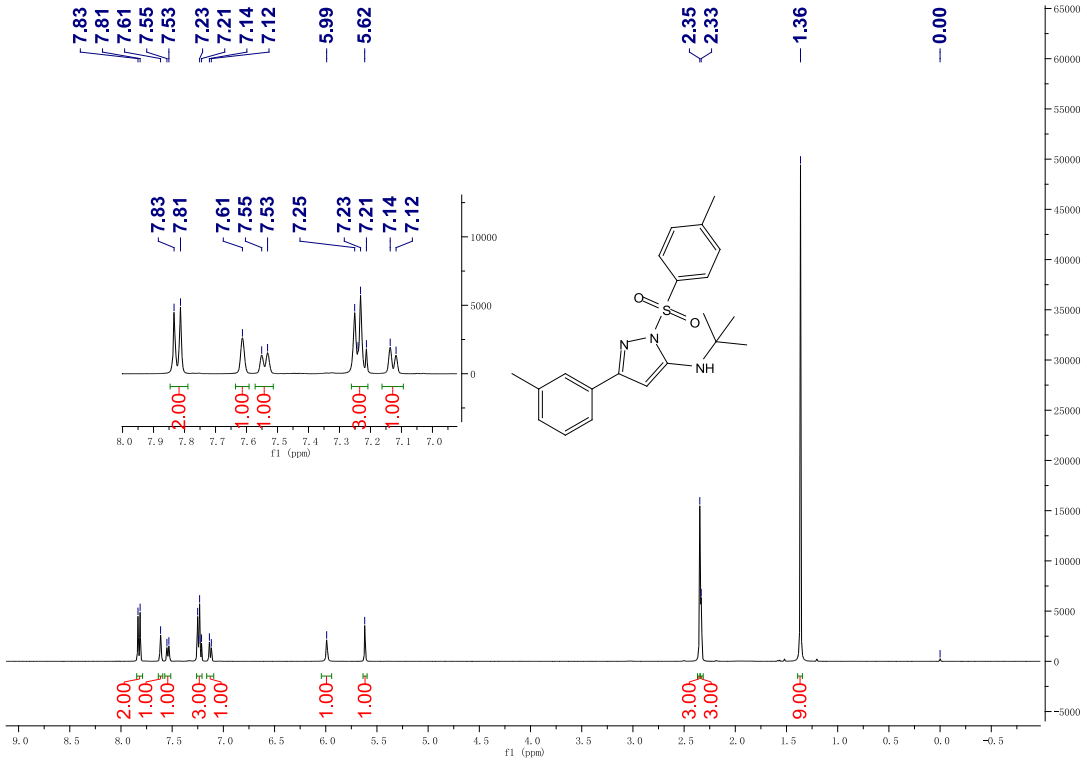


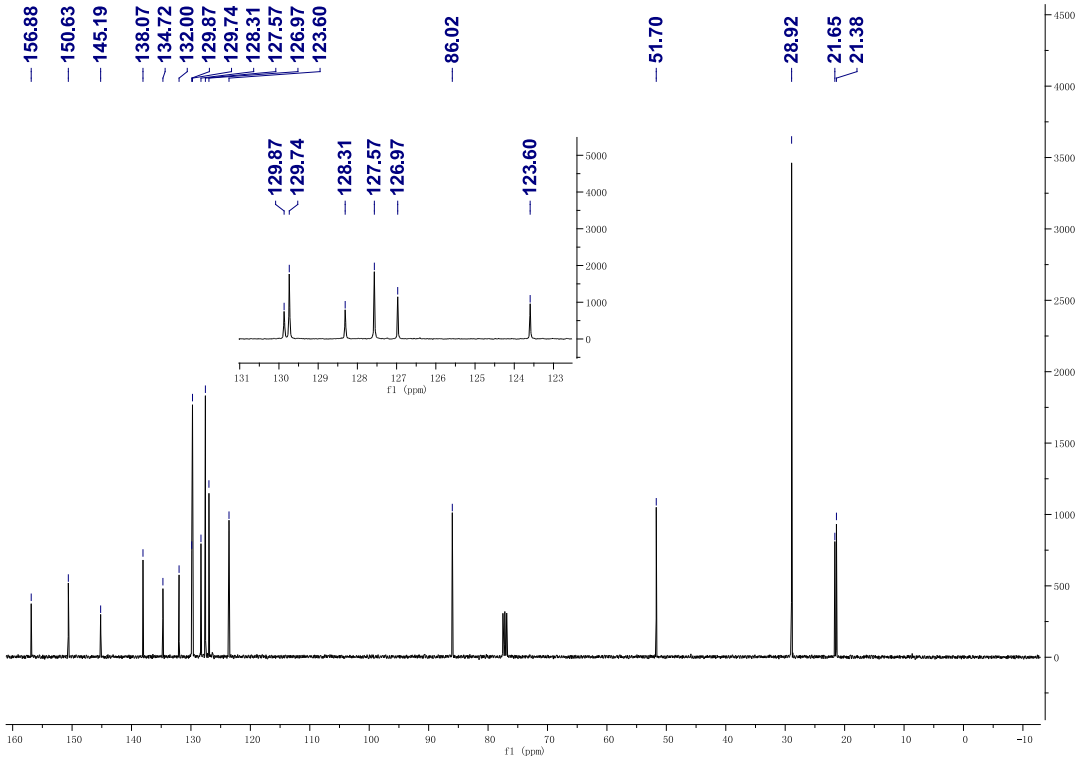
***N*-(*tert*-butyl)-3-(*p*-tolyl)-1-tosyl-1*H*-pyrazol-5-amine (3ba)**



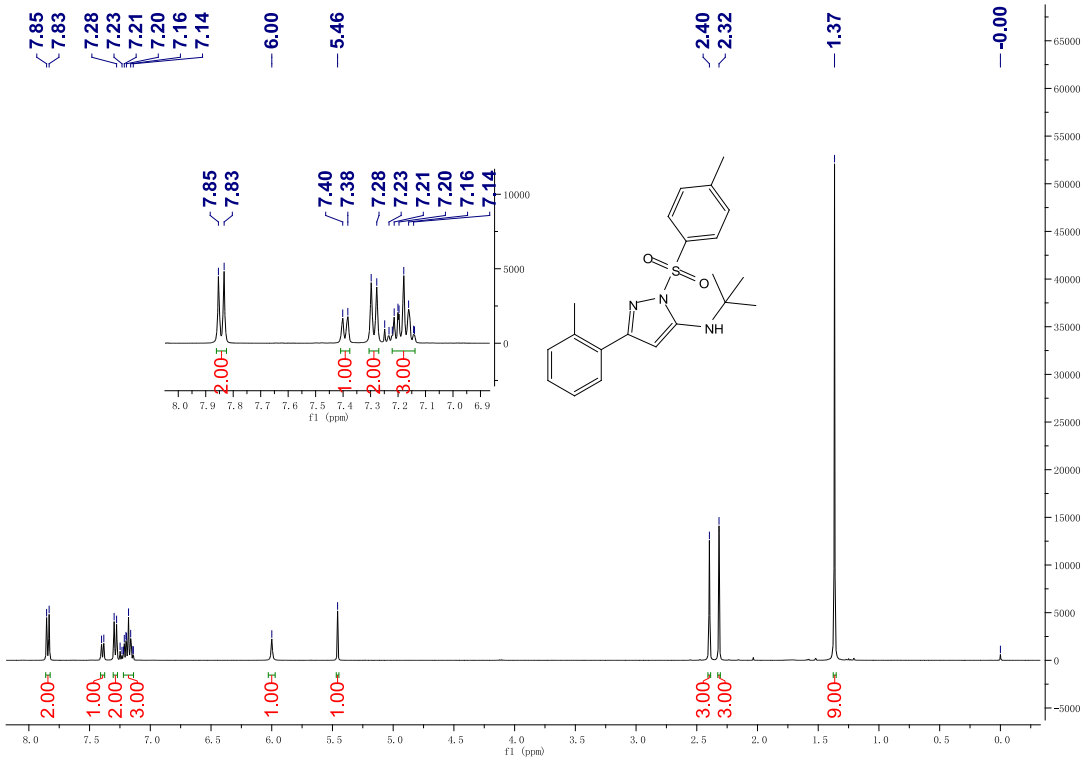


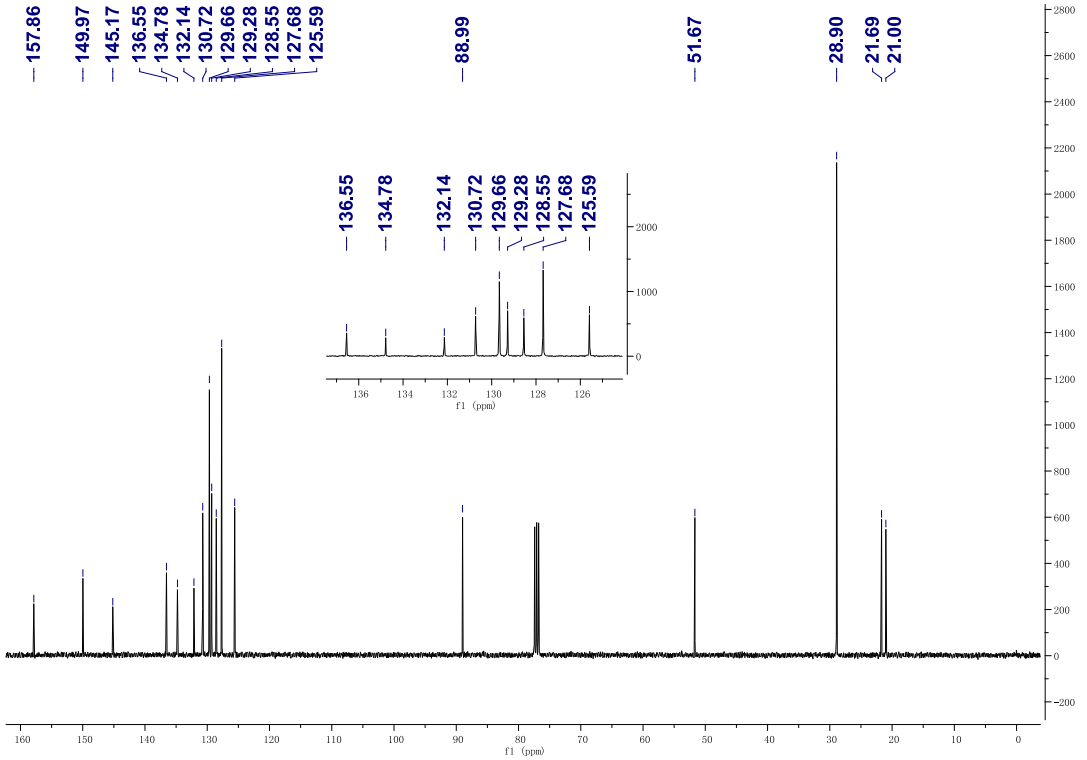
_N_-(_tert_-butyl)-3-(_m_-tolyl)-1-tosyl-1_H_-pyrazol-5-amine (3ca)



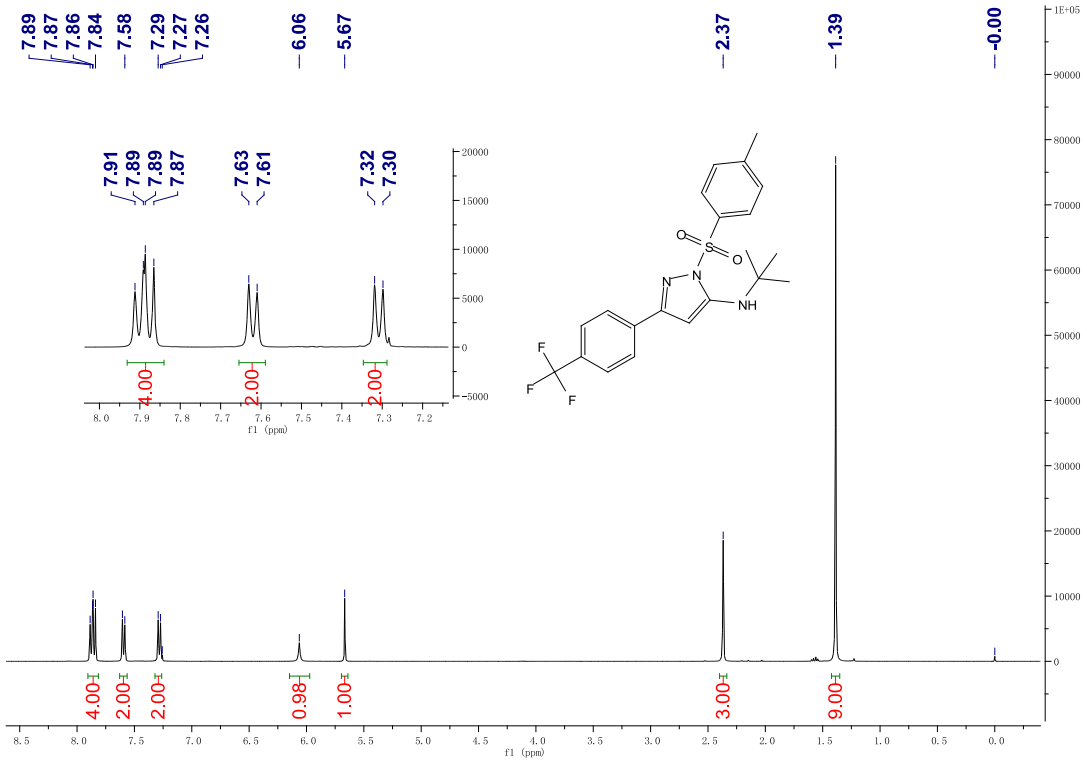


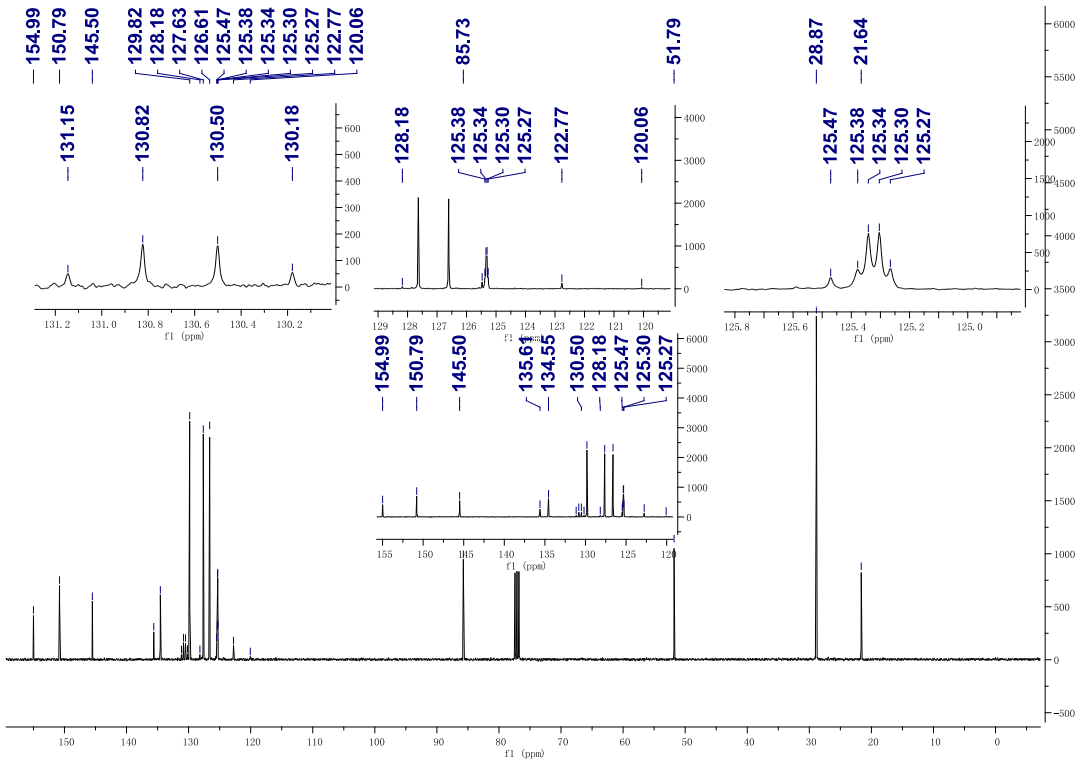
***N*-(*tert*-butyl)-3-(*o*-tolyl)-1-tosyl-1*H*-pyrazol-5-amine (3da)**



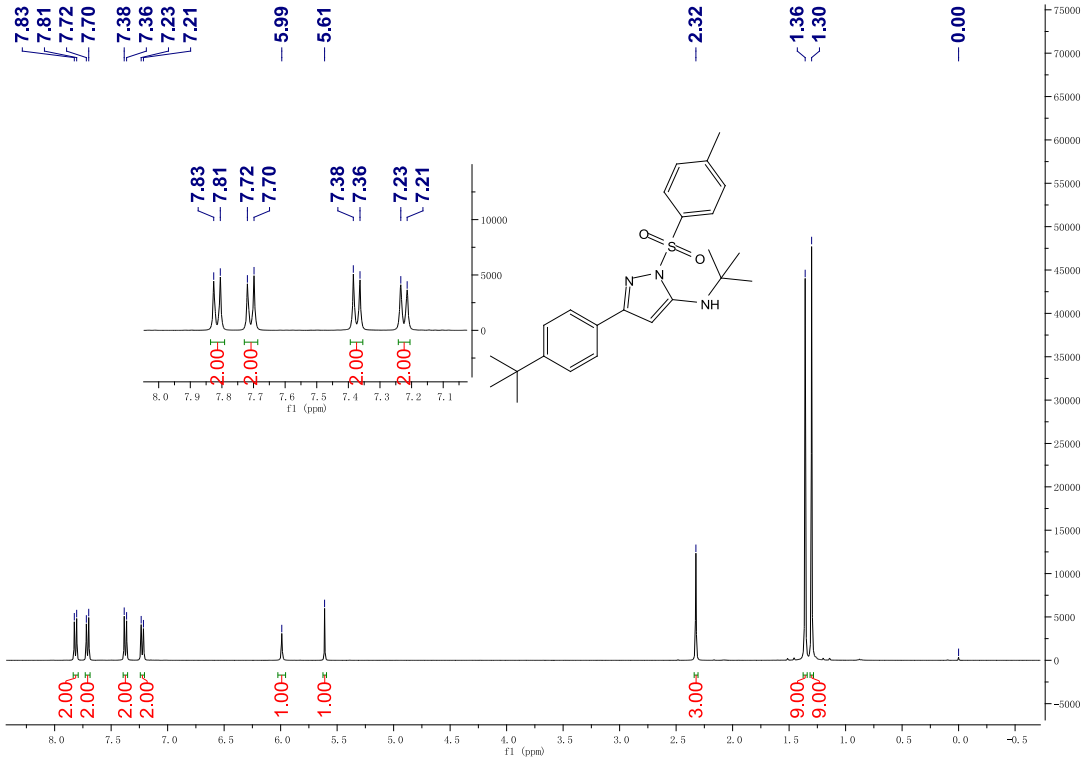


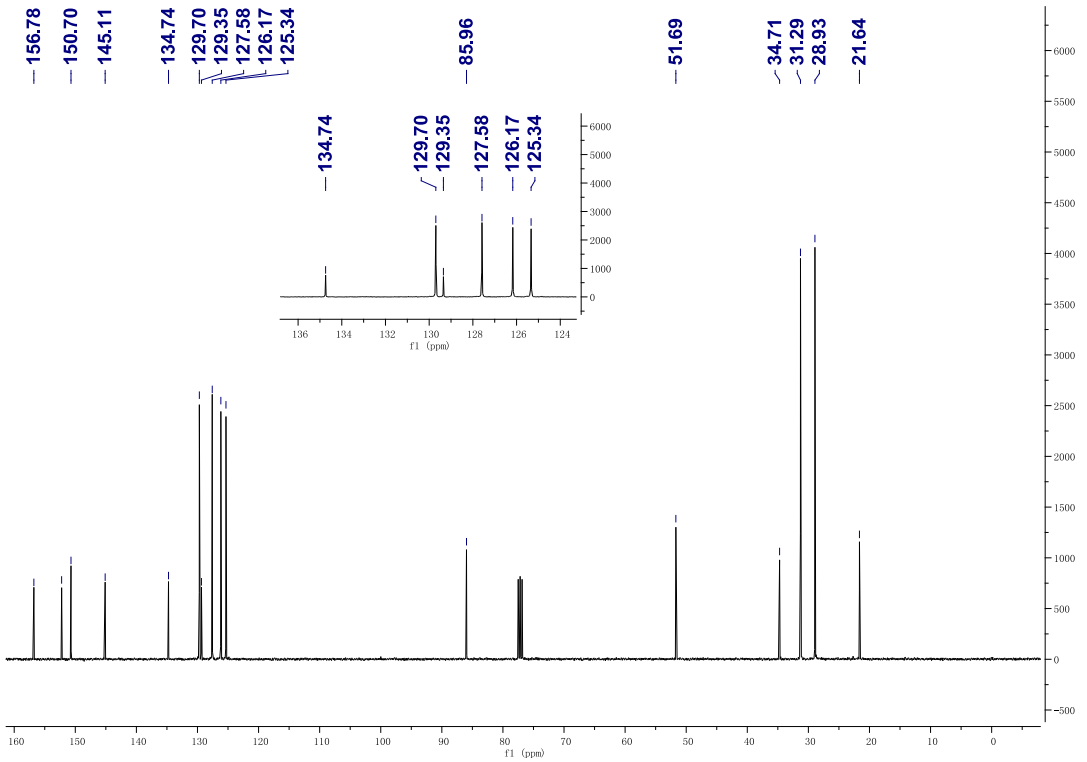
_N_-(_tert_-butyl)-1-tosyl-3-(4-(trifluoromethyl)phenyl)-1_H_-pyrazol-5-amine (3ea)



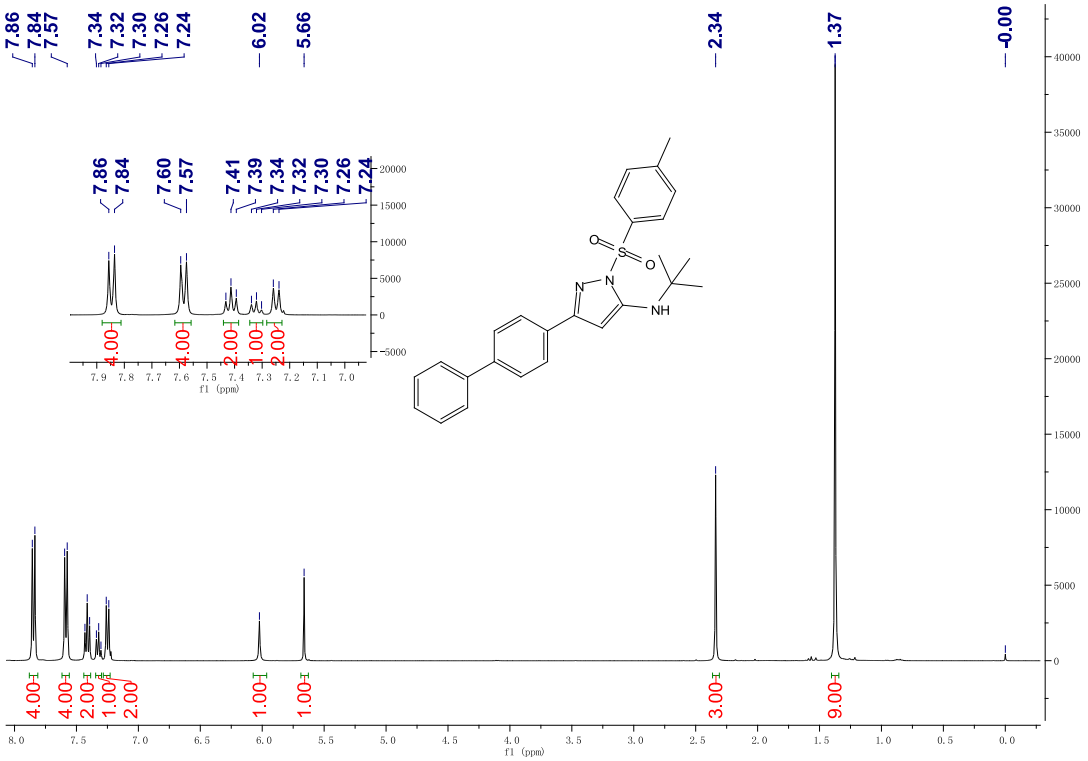


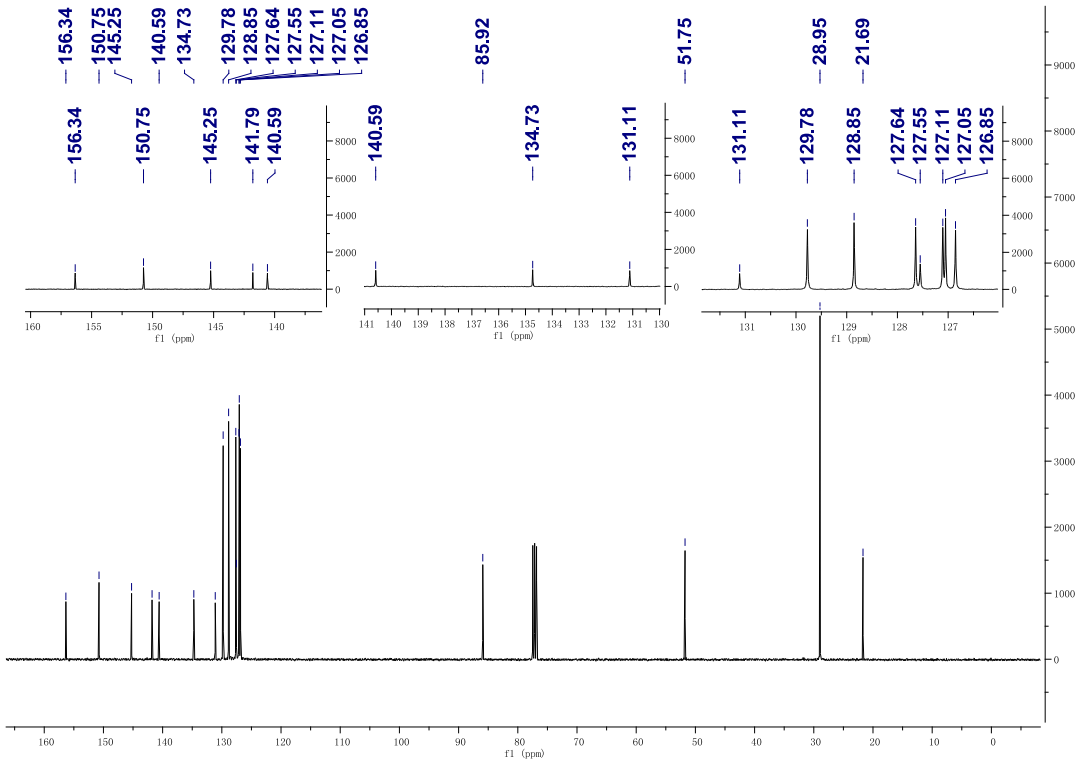
***N*-(*tert*-butyl)-3-(4-(*tert*-butyl)phenyl)-1-tosyl-1*H*-pyrazol-5-amine (3fa)**



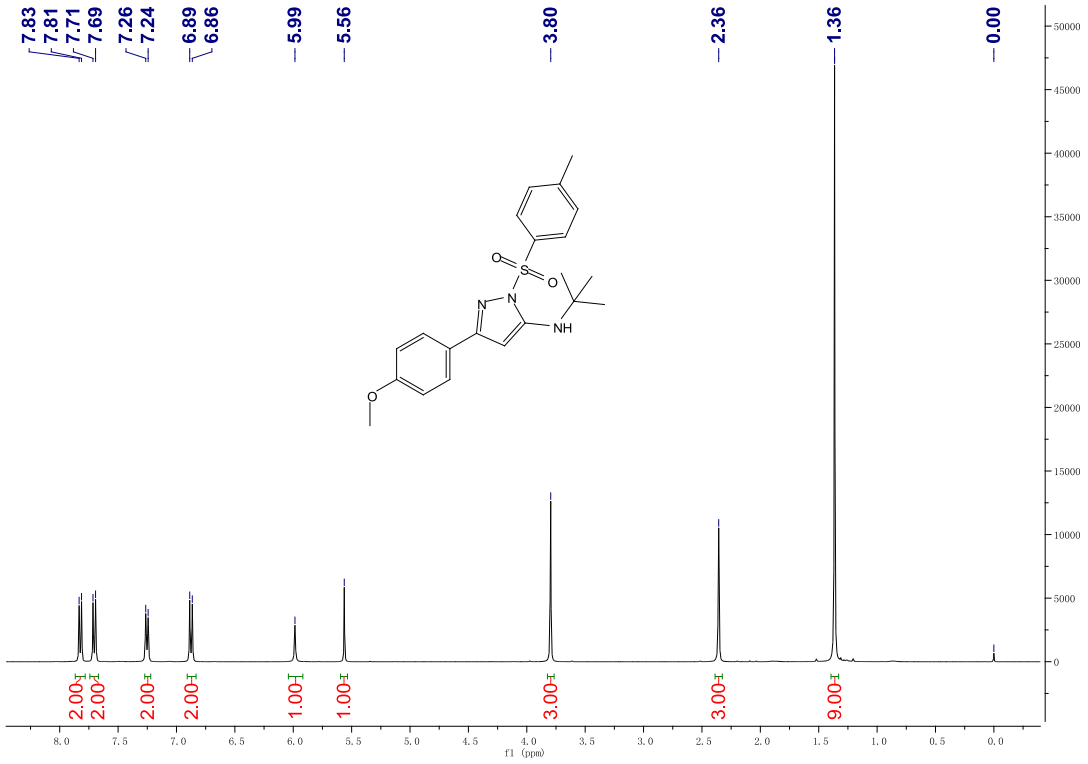


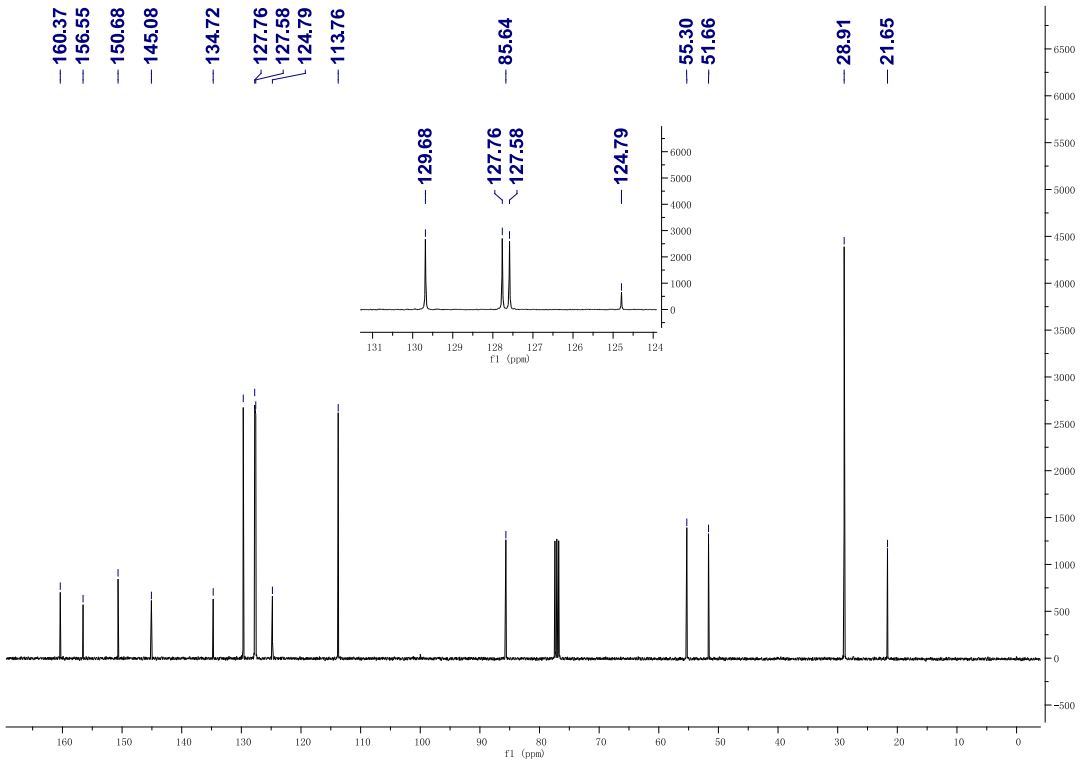
3-([1,1'-biphenyl]-4-yl)-*N*-(*tert*-butyl)-1-tosyl-1*H*-pyrazol-5-amine (3ga)



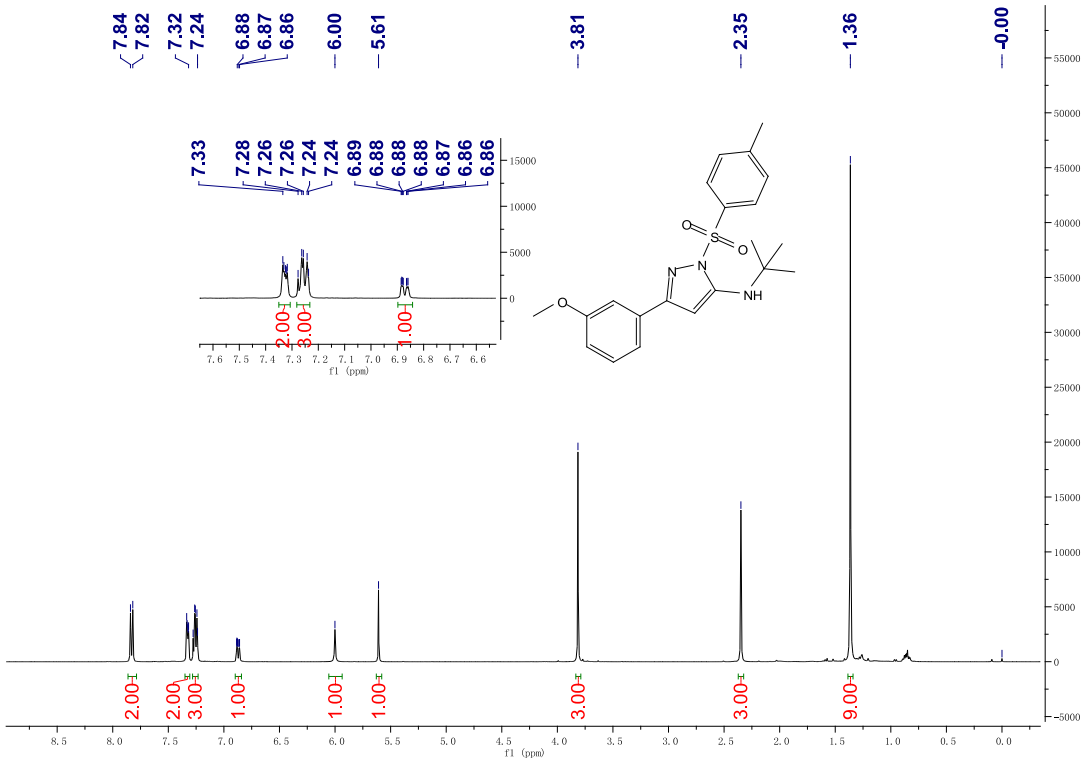


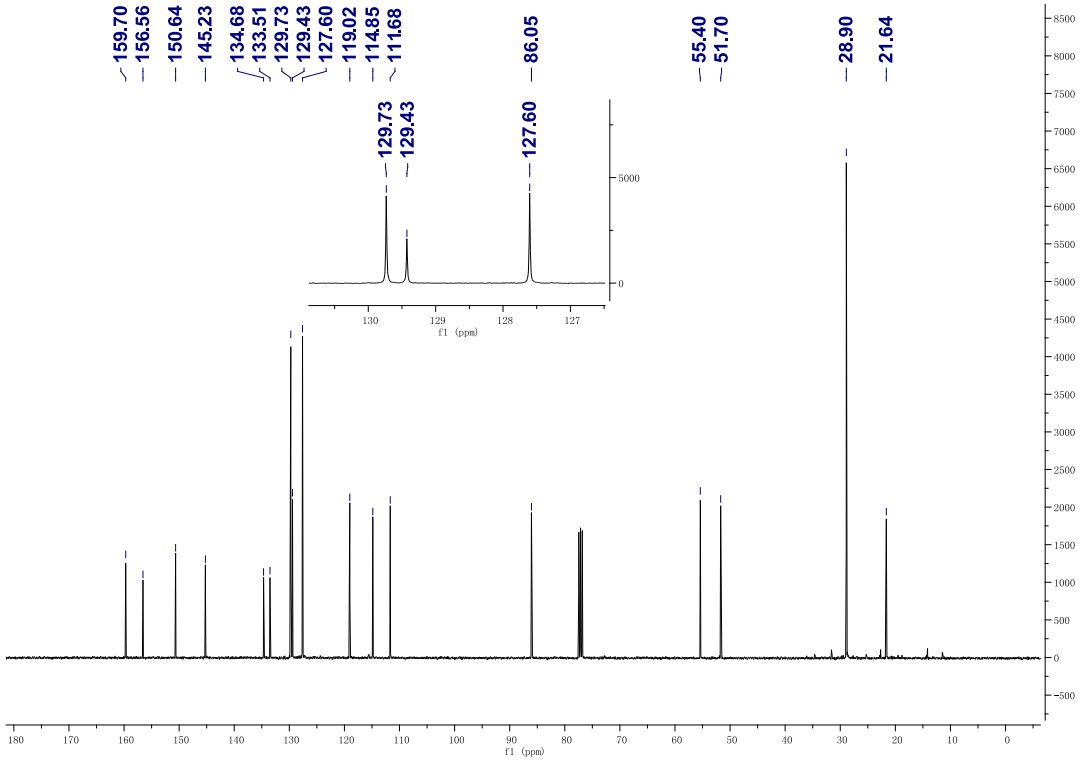
***N*-(*tert*-butyl)-3-(4-methoxyphenyl)-1-tosyl-1*H*-pyrazol-5-amine (3ha)**



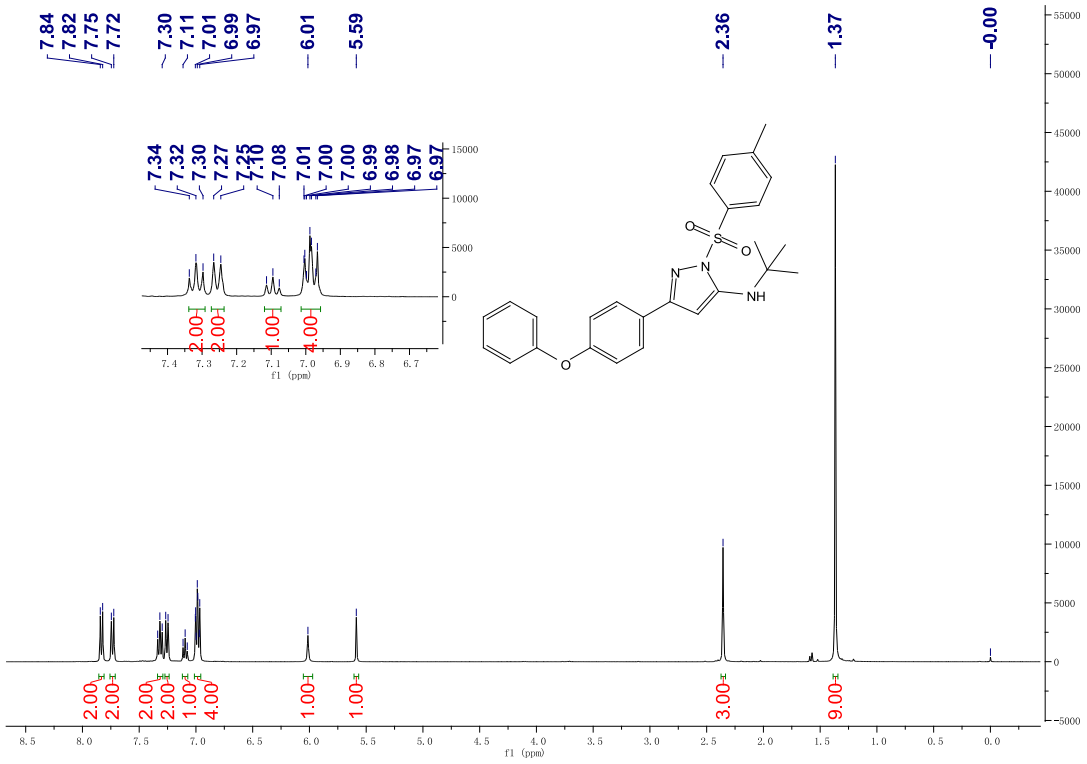


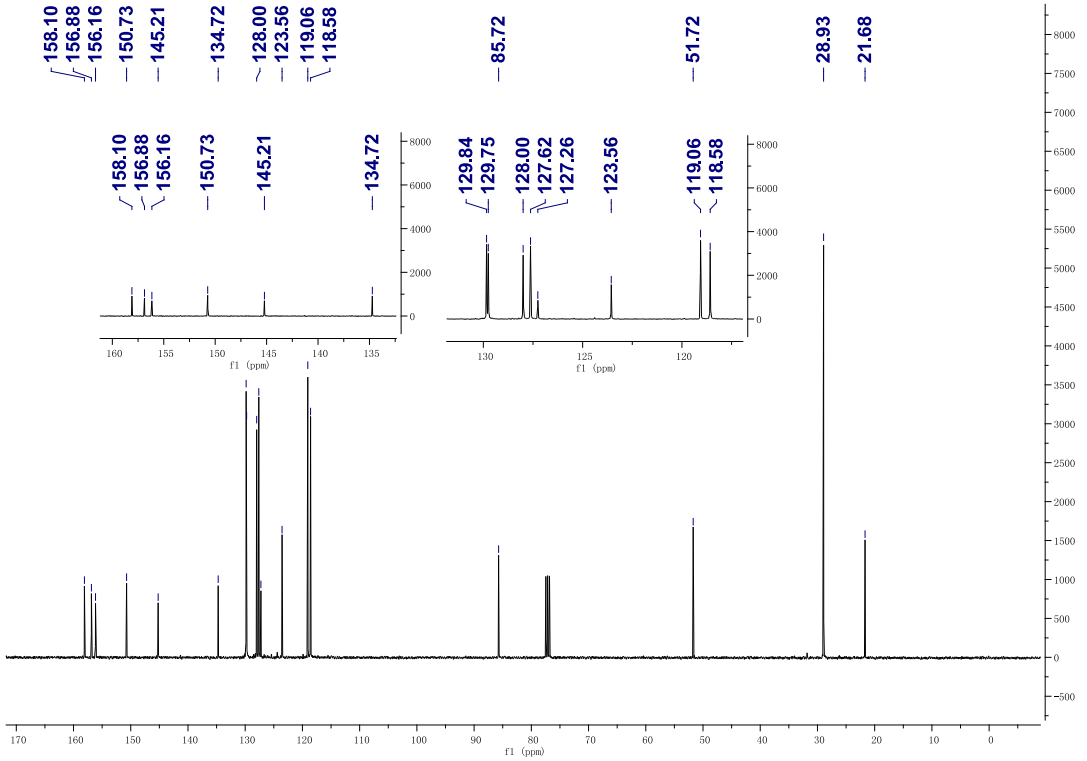
***N*-(*tert*-butyl)-3-(3-methoxyphenyl)-1-tosyl-1*H*-pyrazol-5-amine (3ia)**



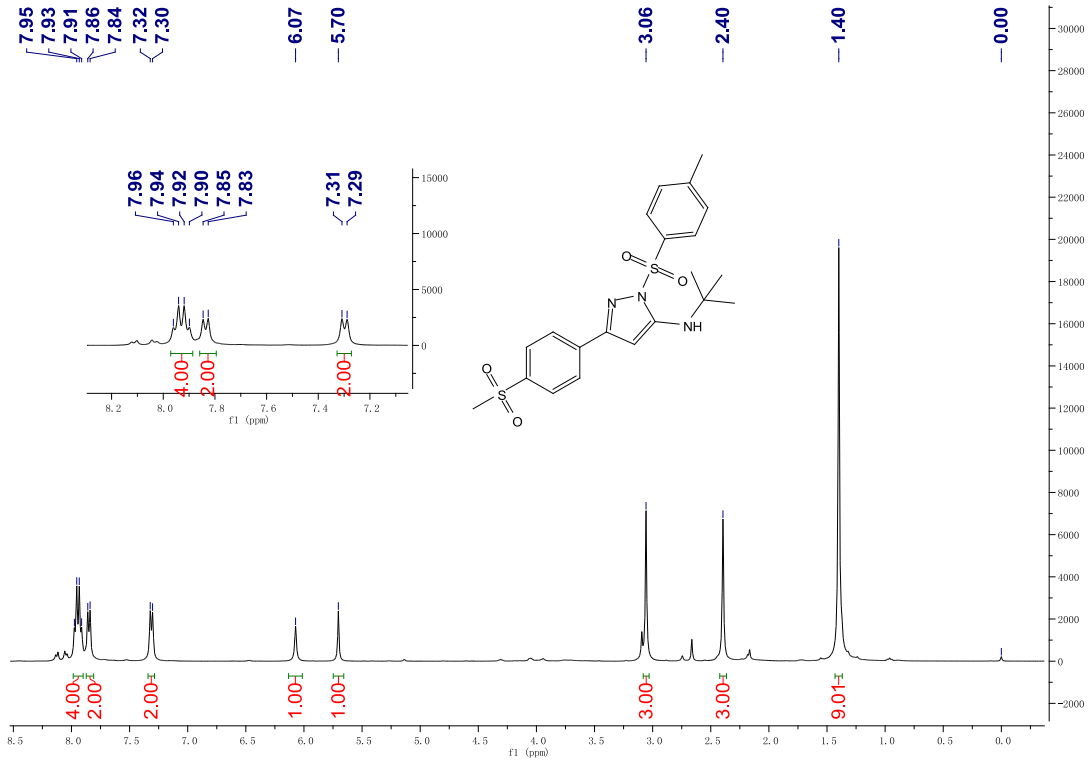


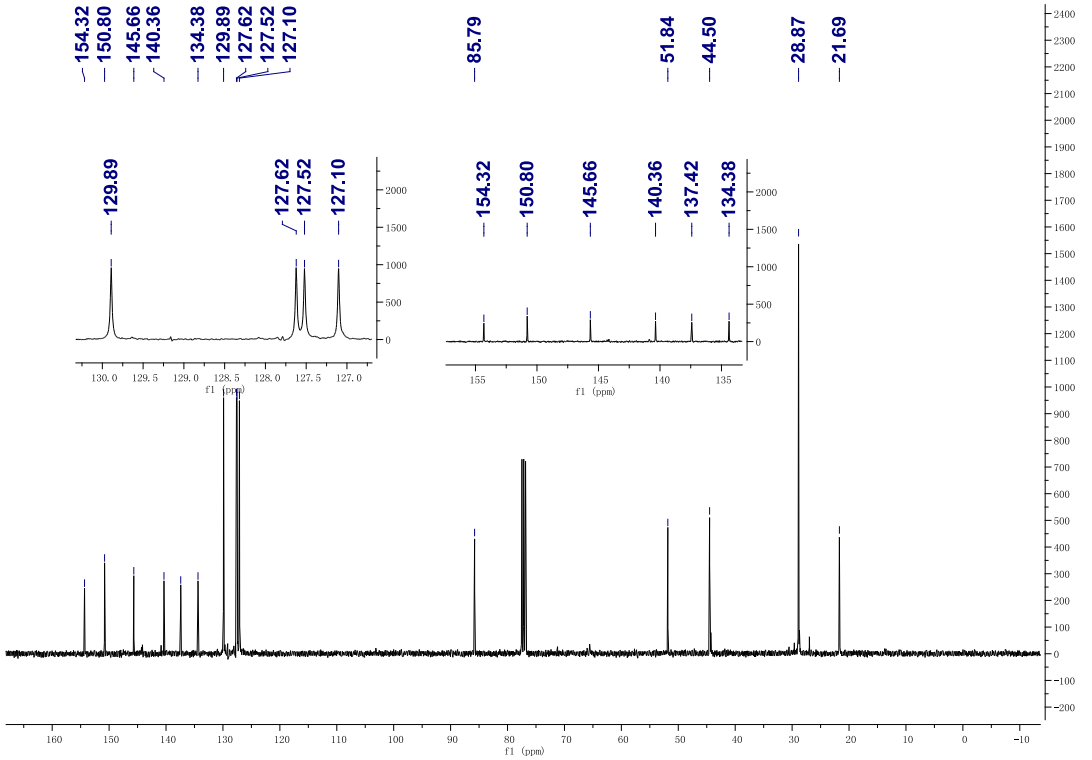
***N*-(*tert*-butyl)-3-(4-phenoxyphenyl)-1-tosyl-1*H*-pyrazol-5-amine (3ja)**



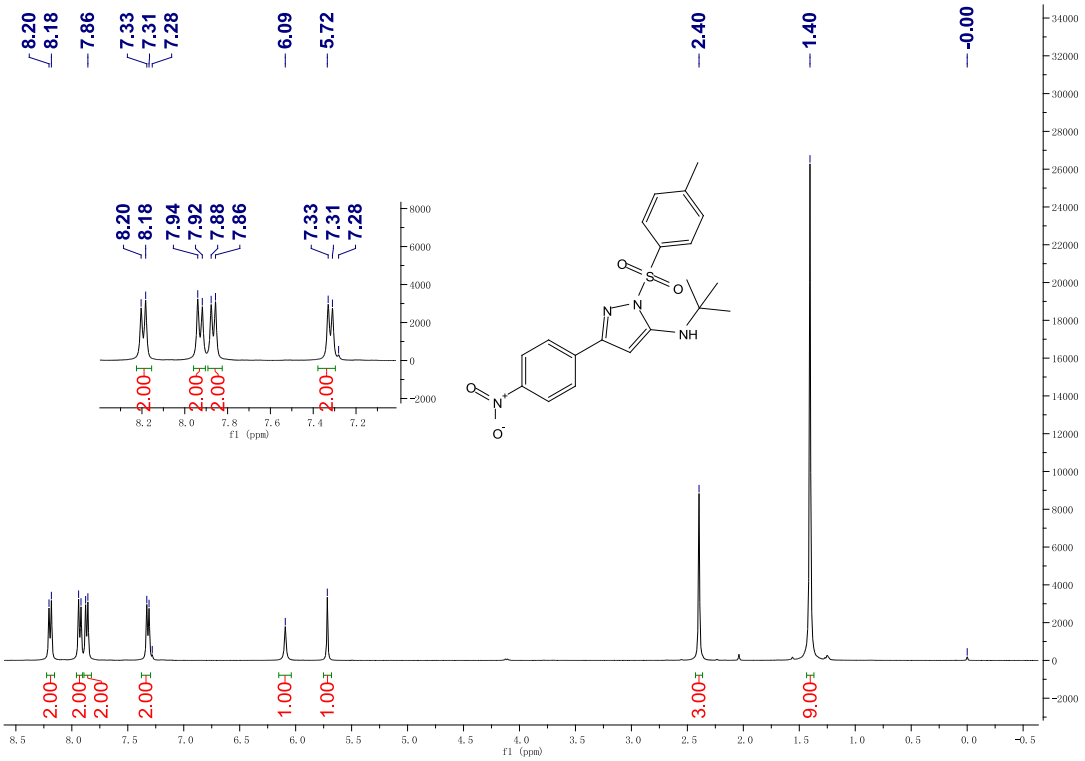


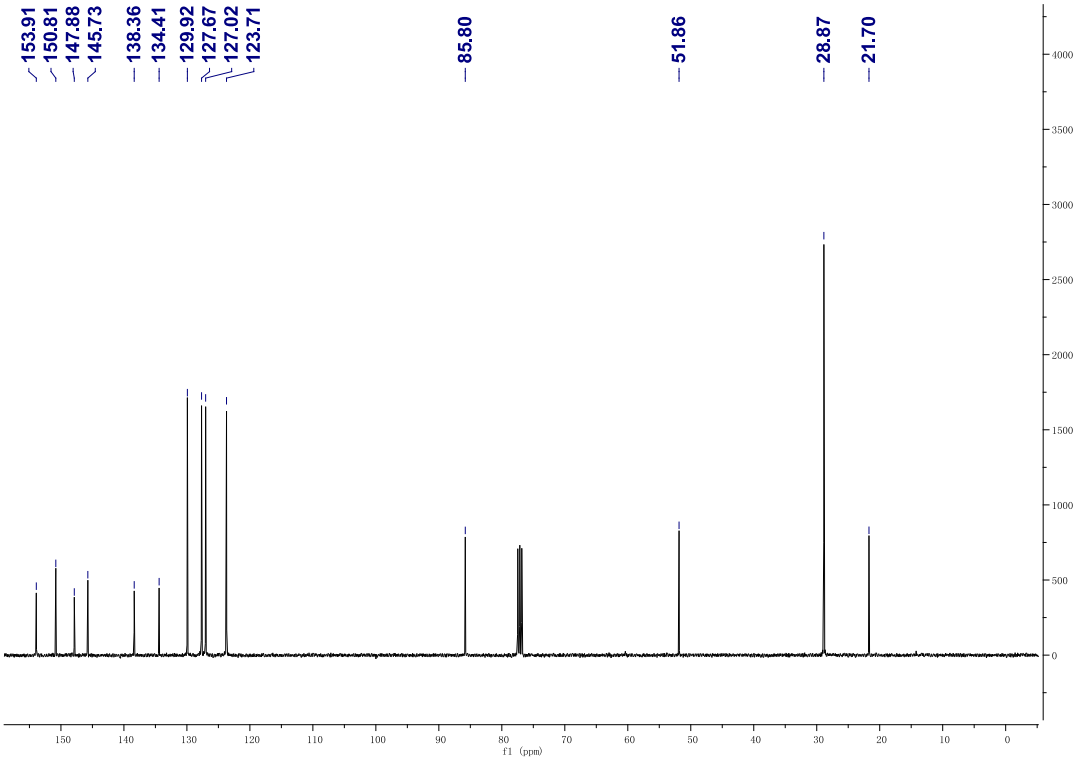
_N_-(_tert_-butyl)-3-(4-(methylsulfonyl)phenyl)-1-tosyl-1_H_-pyrazol-5-amine (3ka)



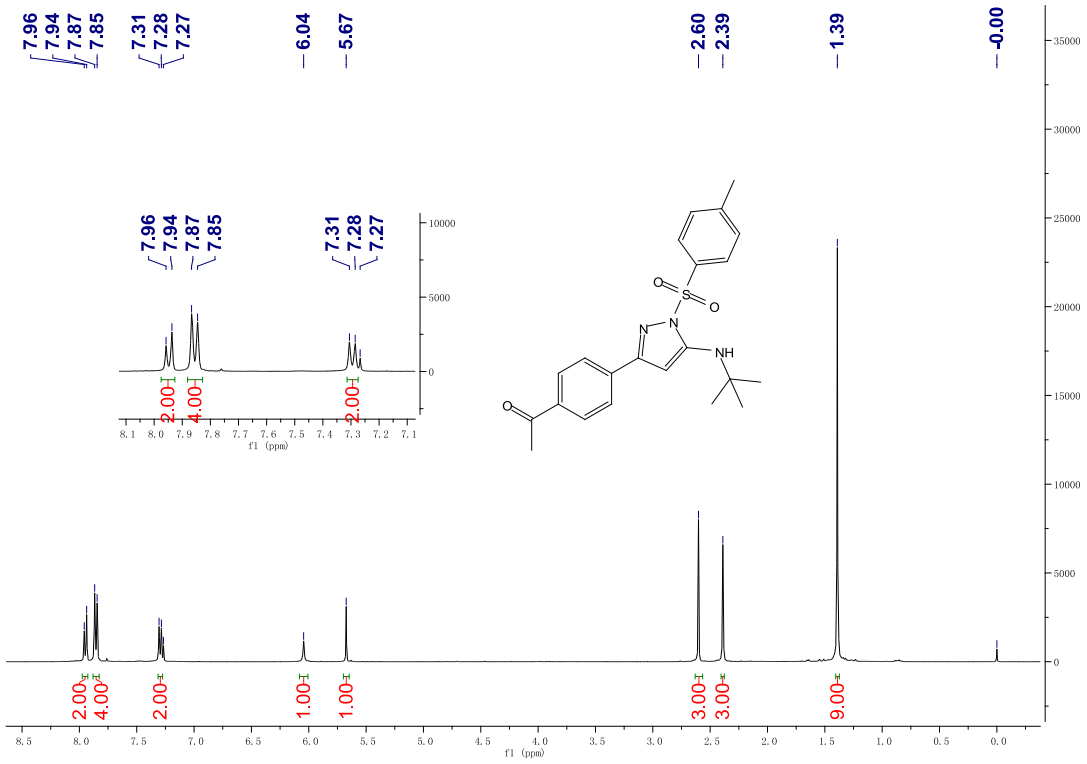


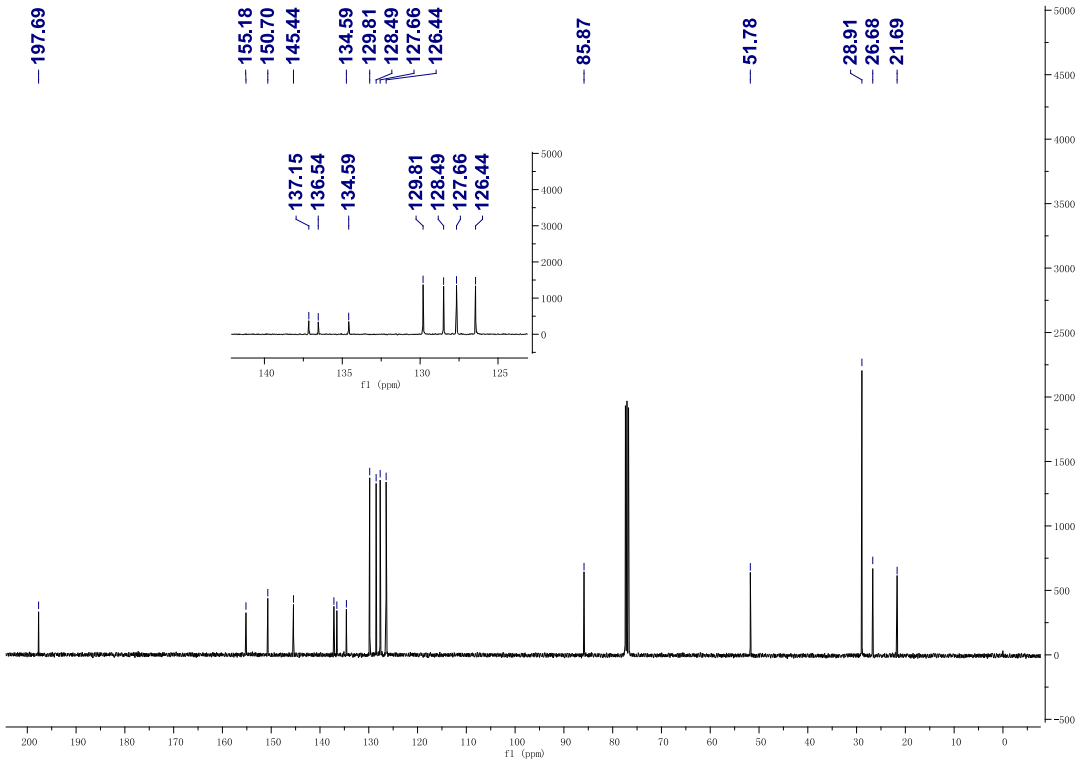
***N*-(*tert*-butyl)-3-(4-nitrophenyl)-1-tosyl-1*H*-pyrazol-5-amine (3la)**



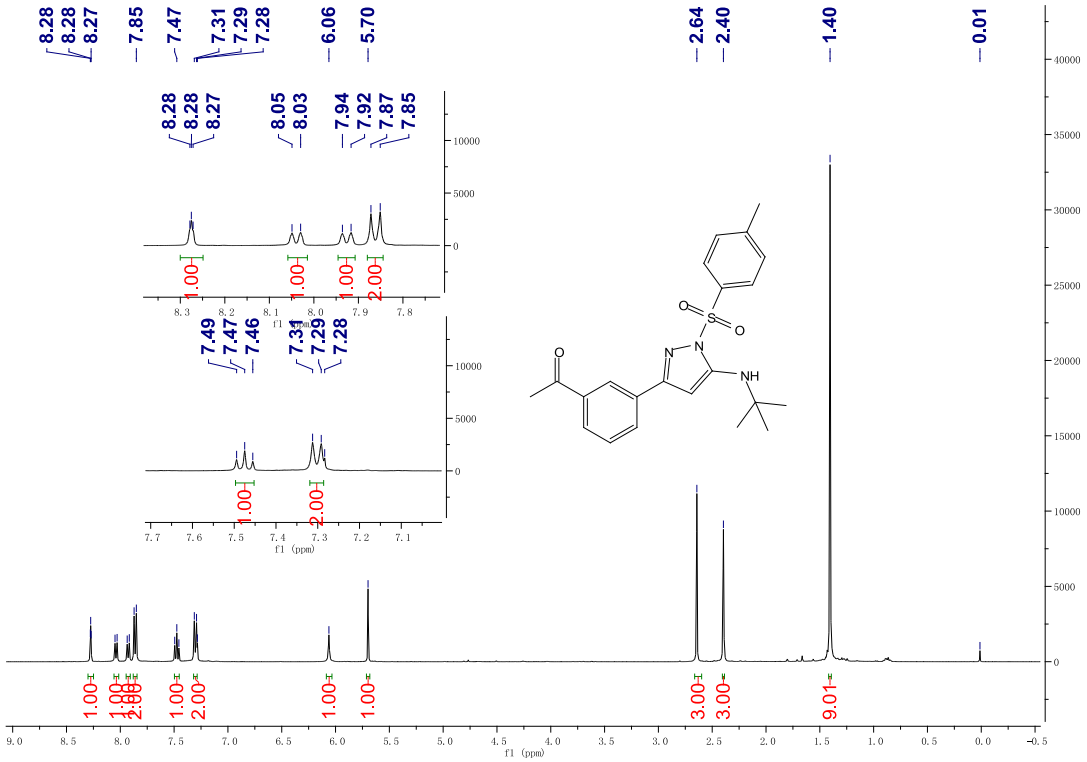


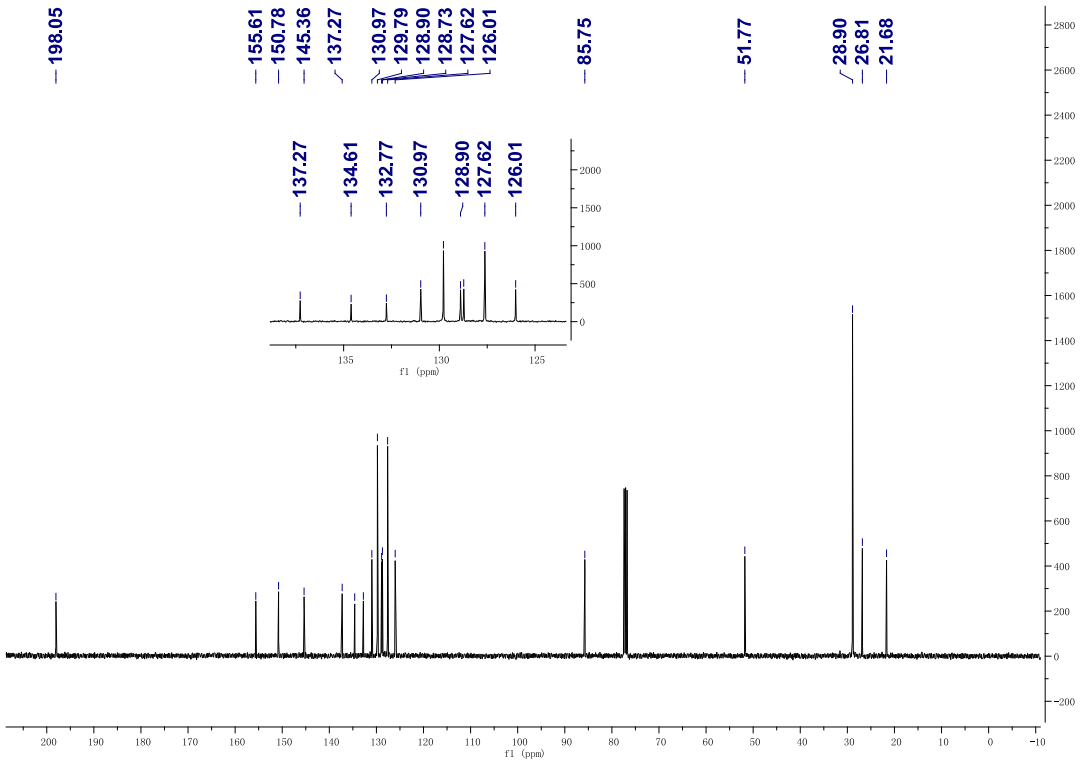
1-(4-(5-(*tert*-butylamino)-1-tosyl-1*H*-pyrazol-3-yl)phenyl)ethanone (3ma)



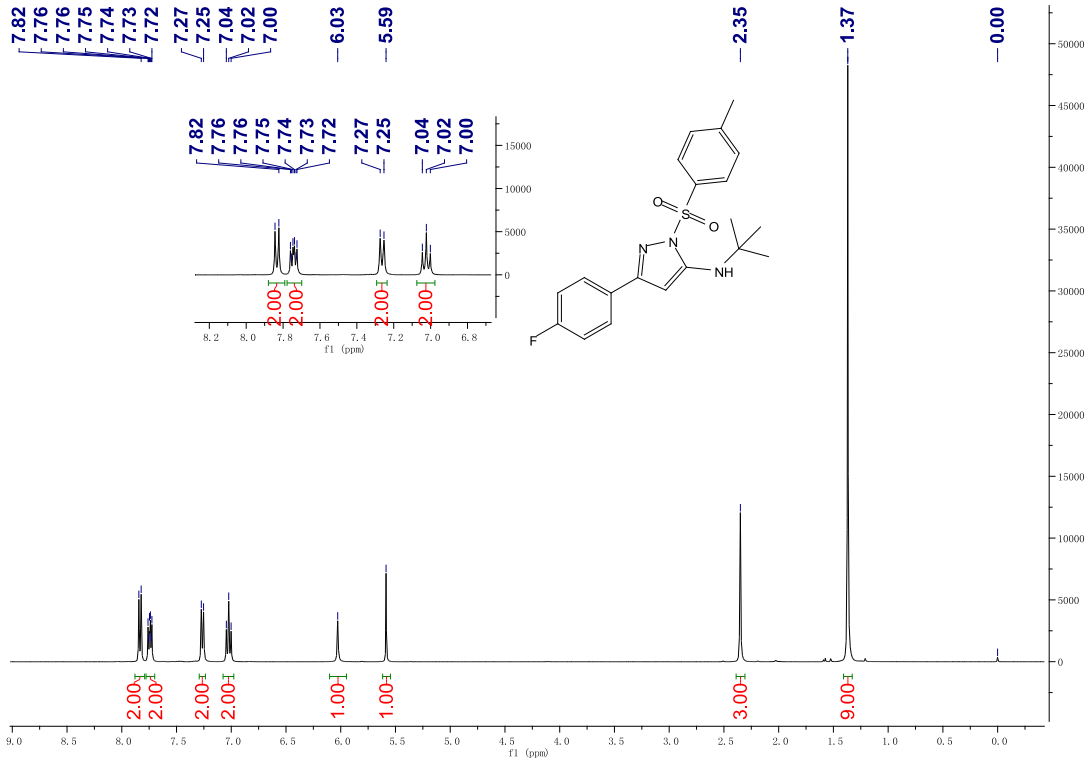


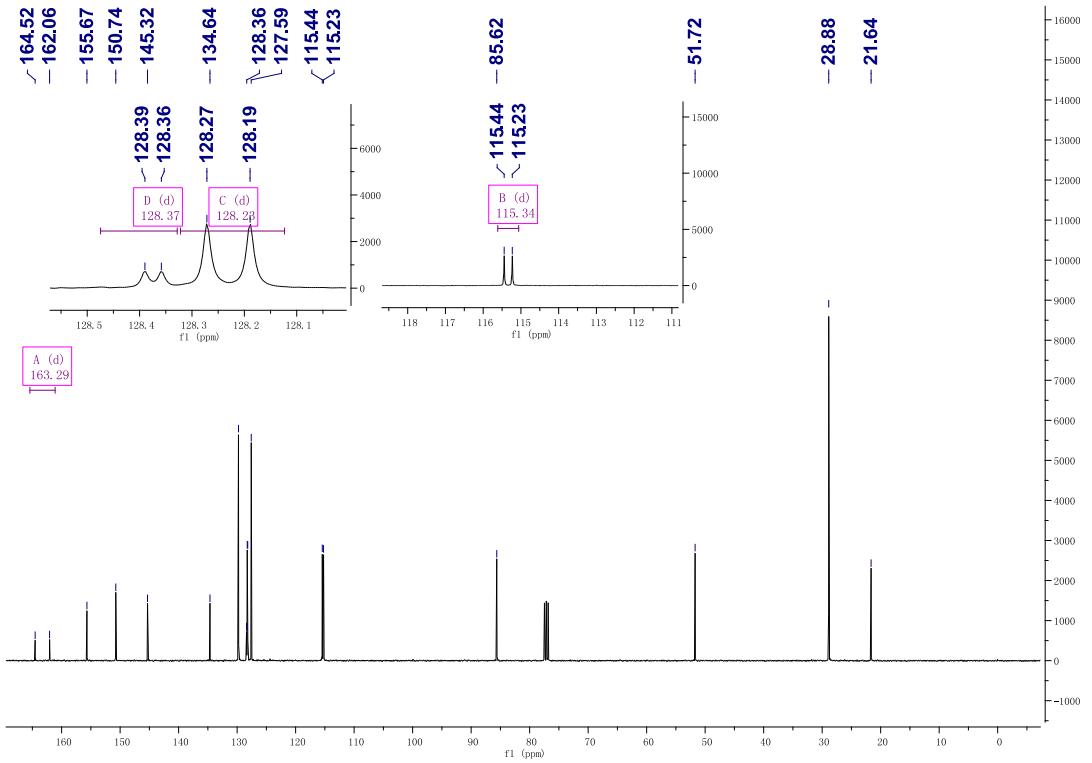
1-(3-(5-(*tert*-butylamino)-1-tosyl-1*H*-pyrazol-3-yl)phenyl)ethanone (3na)



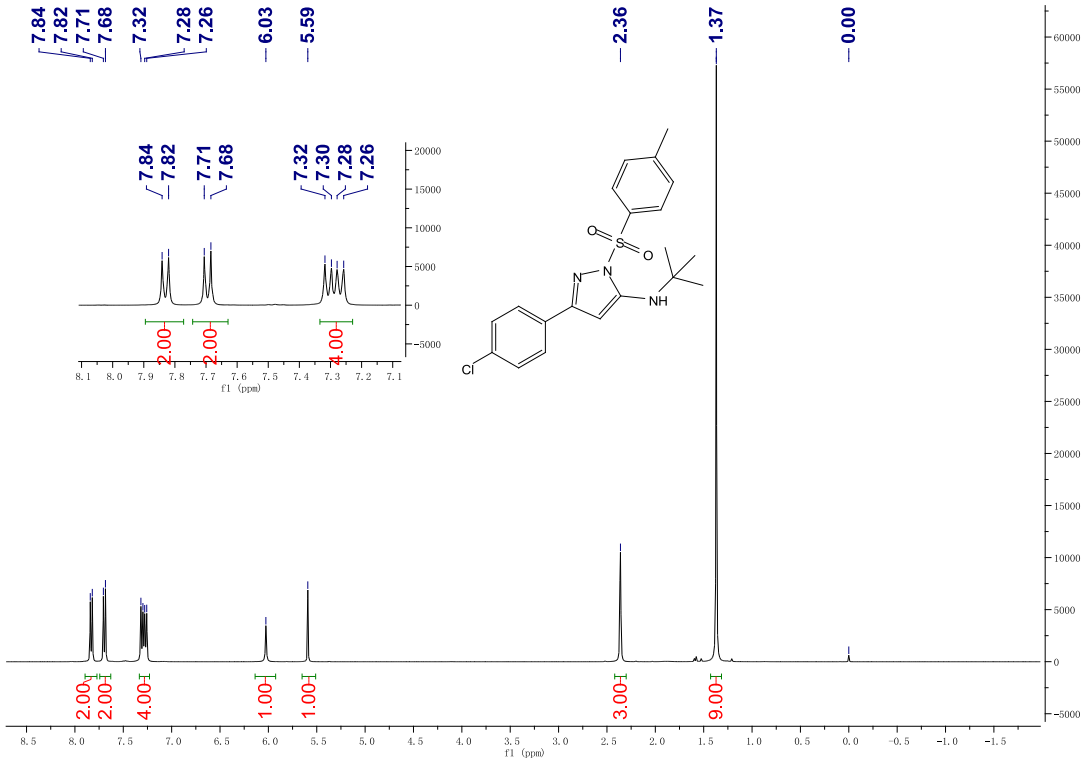


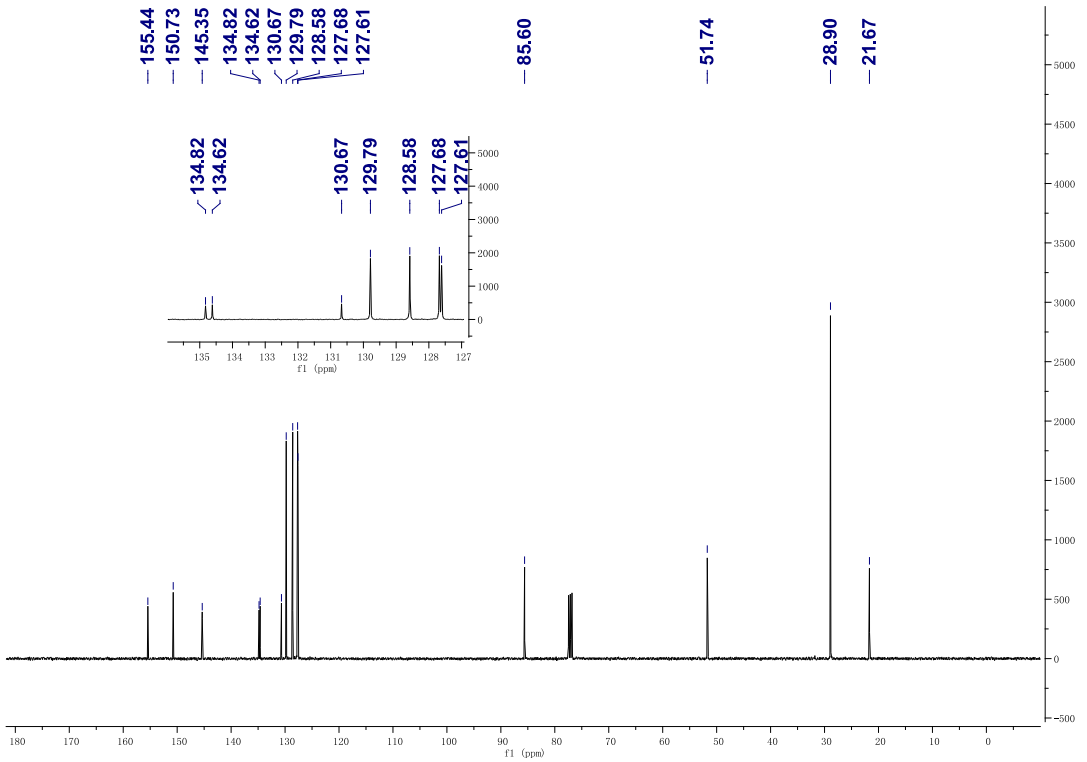
N-(*tert*-butyl)-3-(4-fluorophenyl)-1-tosyl-1*H*-pyrazol-5-amine (3oa)



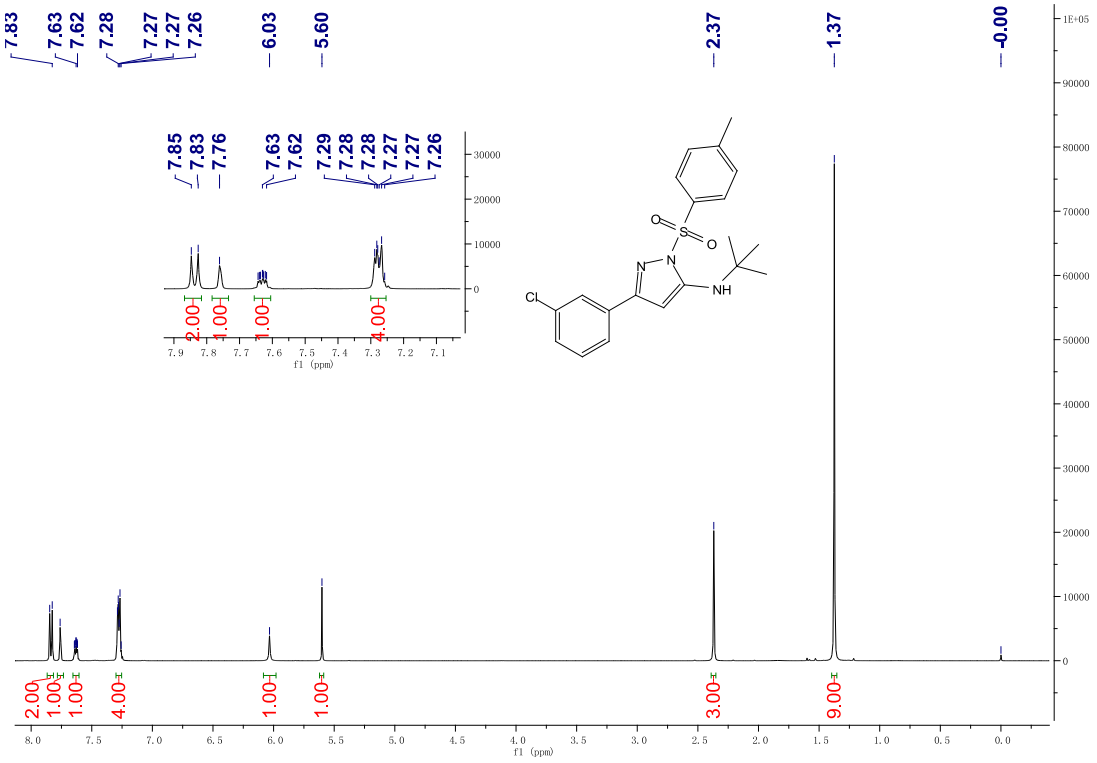


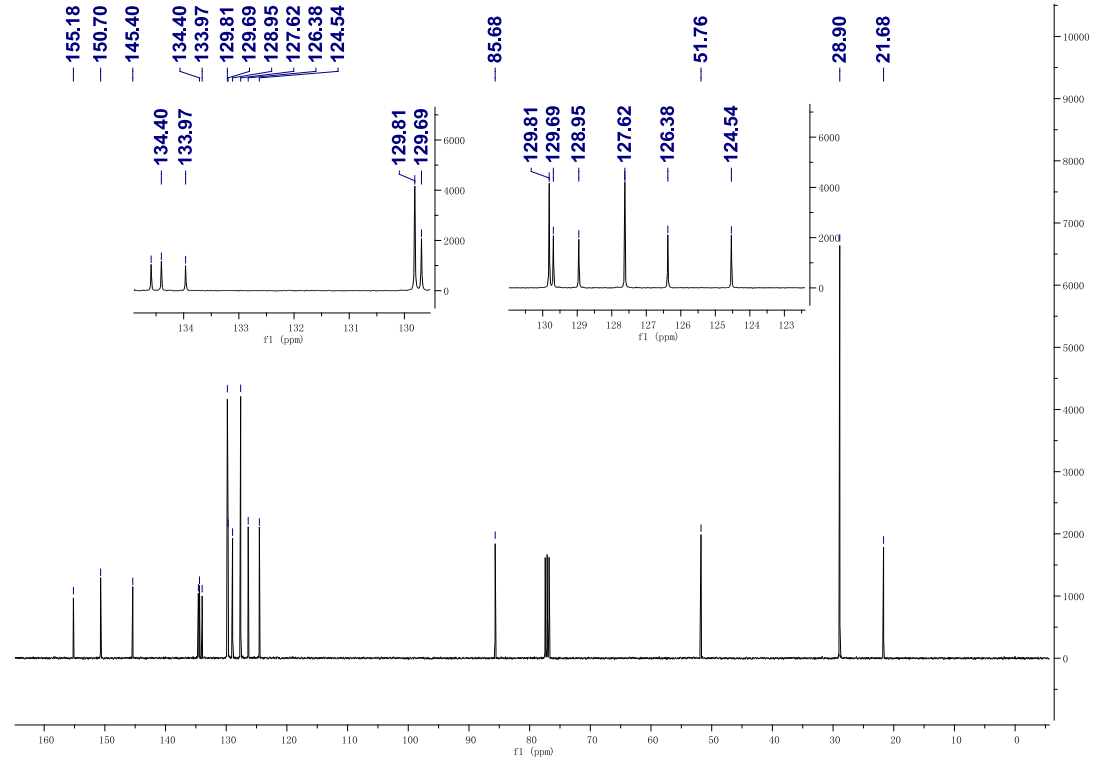
N-(*tert*-butyl)-3-(4-chlorophenyl)-1-tosyl-1*H*-pyrazol-5-amine (3pa)



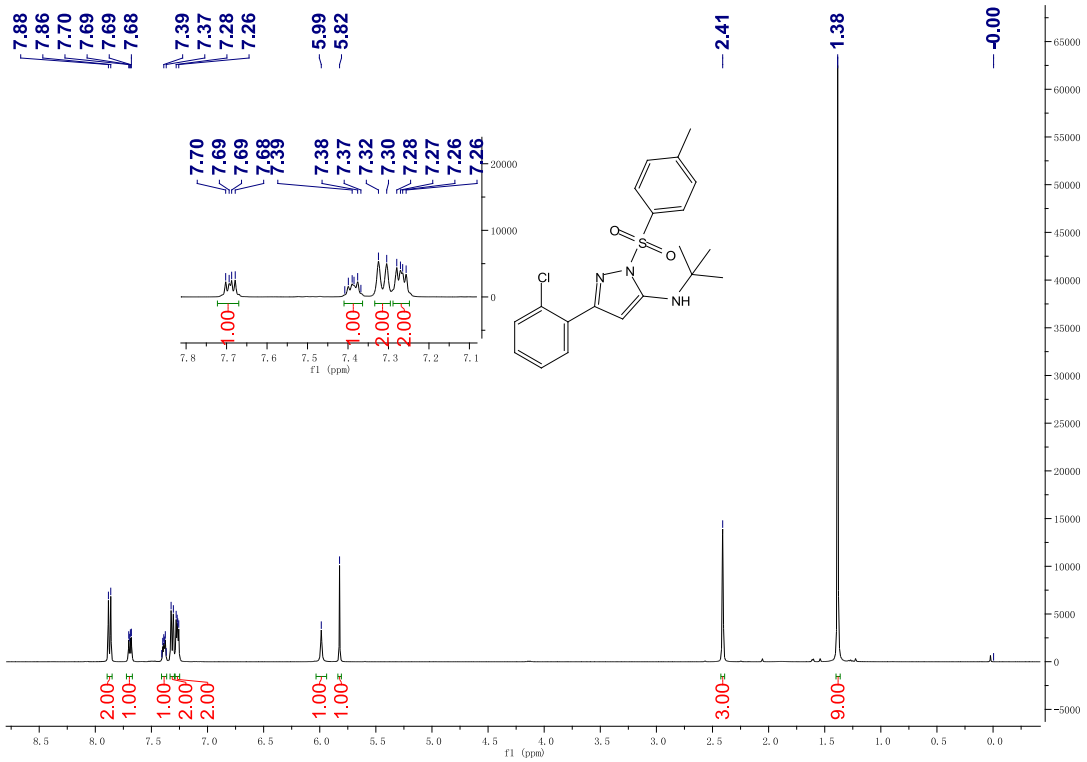


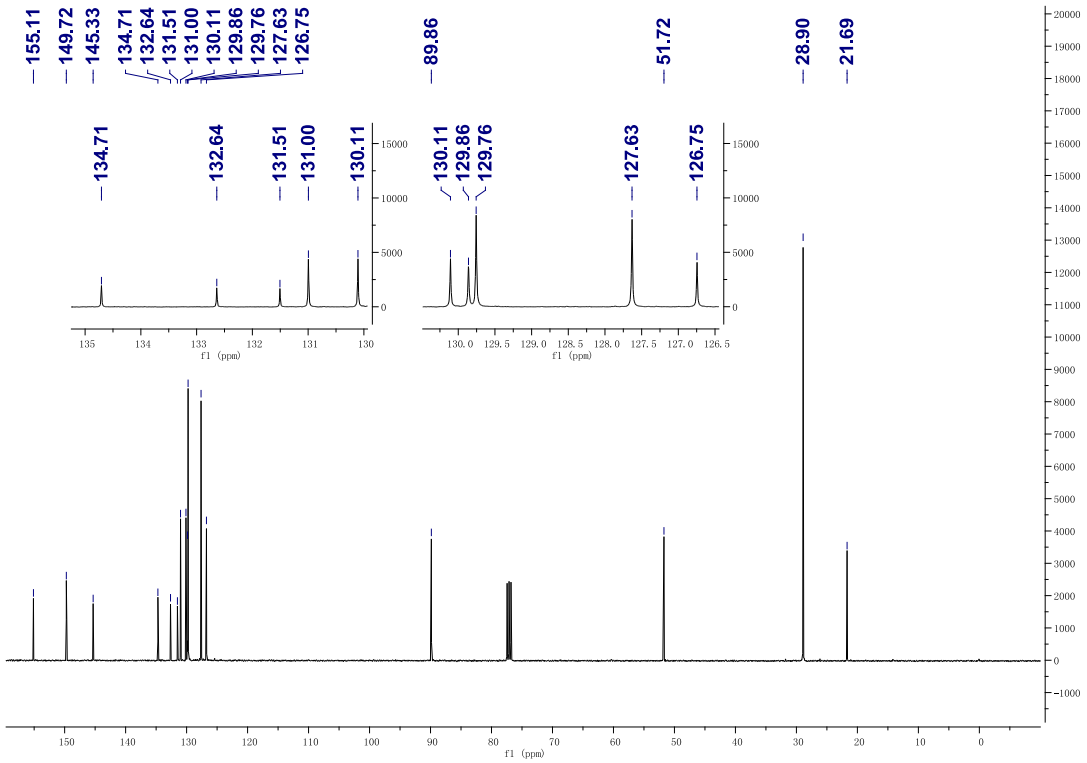
***N*-(*tert*-butyl)-3-(3-chlorophenyl)-1-tosyl-1*H*-pyrazol-5-amine (3qa)**



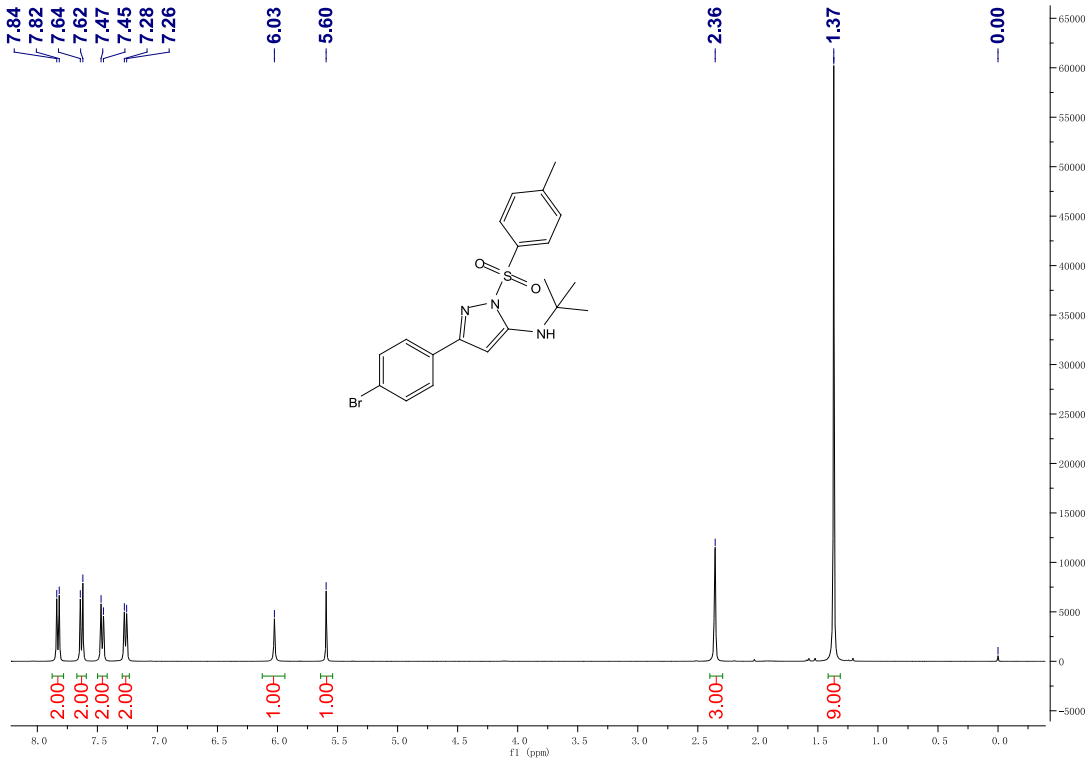


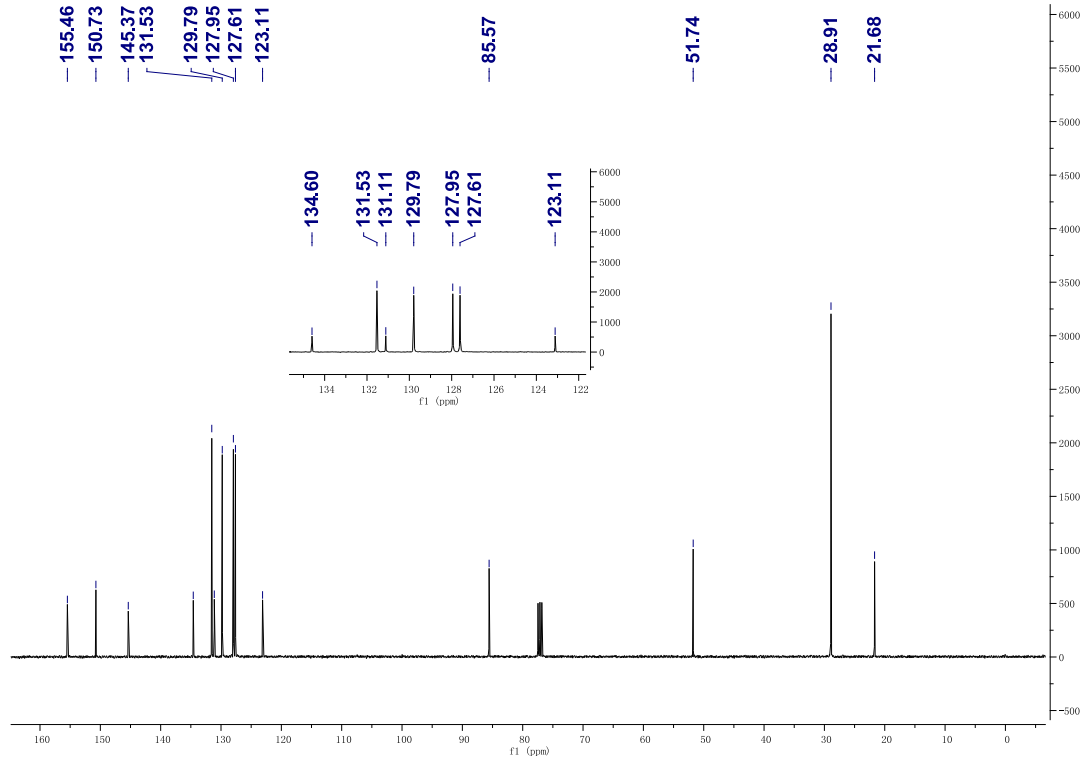
N-(*tert*-butyl)-3-(2-chlorophenyl)-1-tosyl-1*H*-pyrazol-5-amine (3ra)



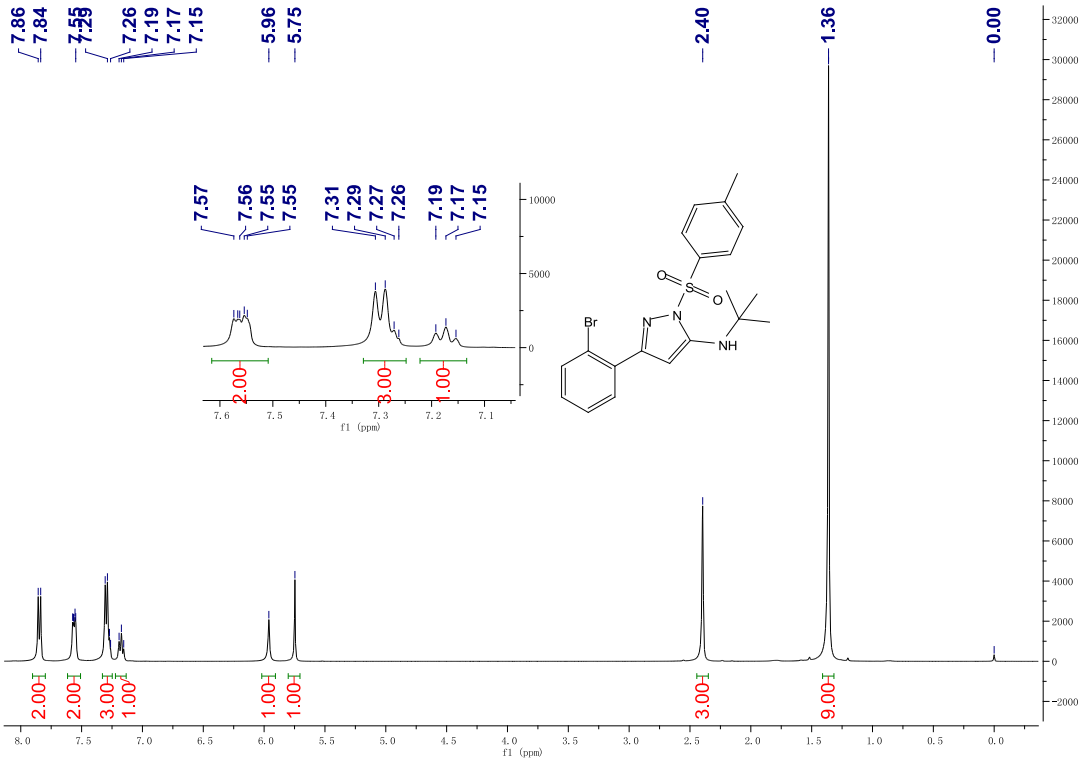


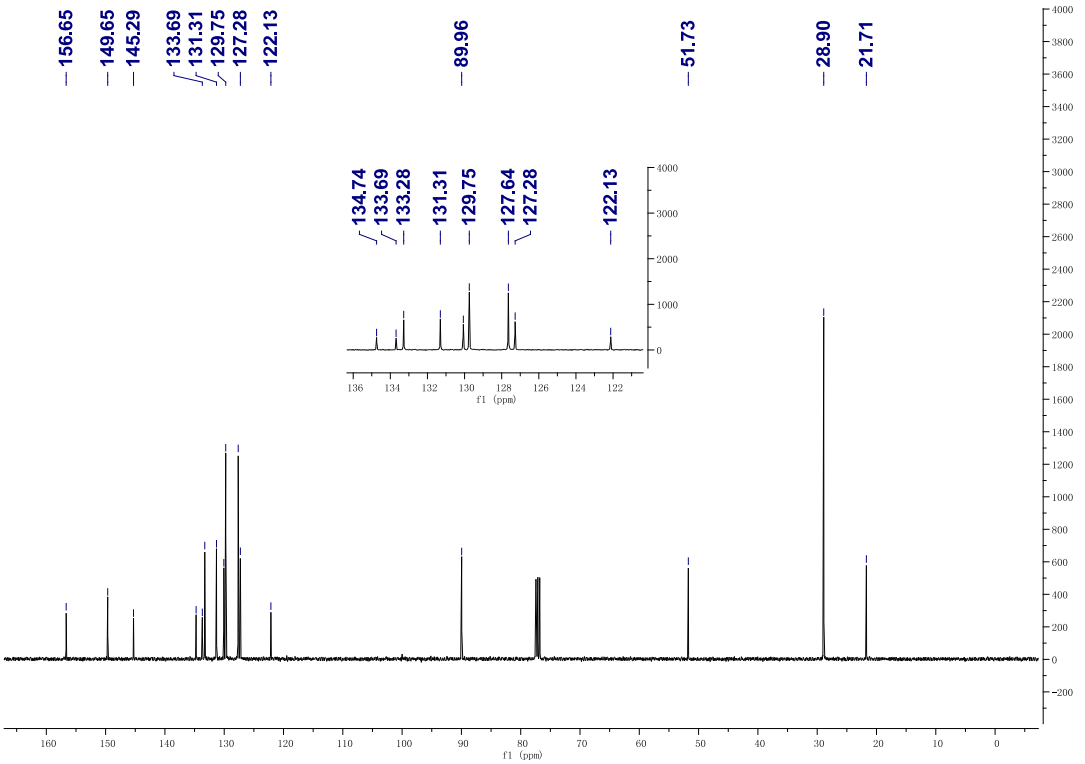
3-(4-bromophenyl)-*N*-(*tert*-butyl)-1-tosyl-1*H*-pyrazol-5-amine (3sa)



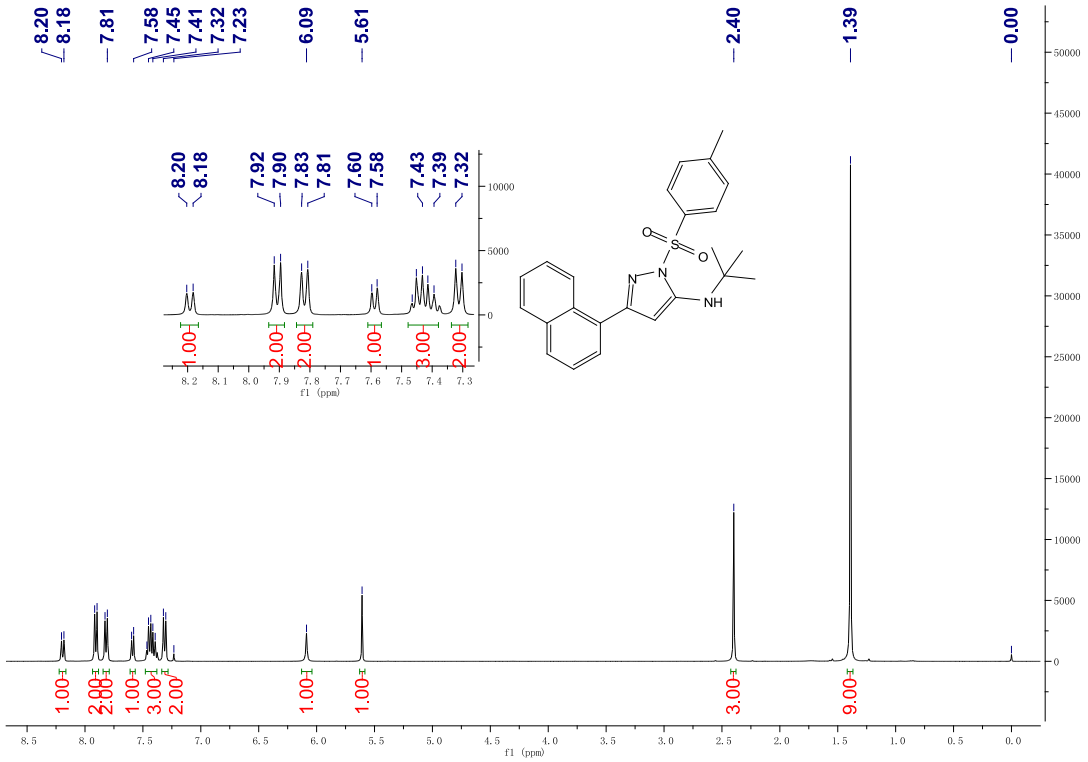


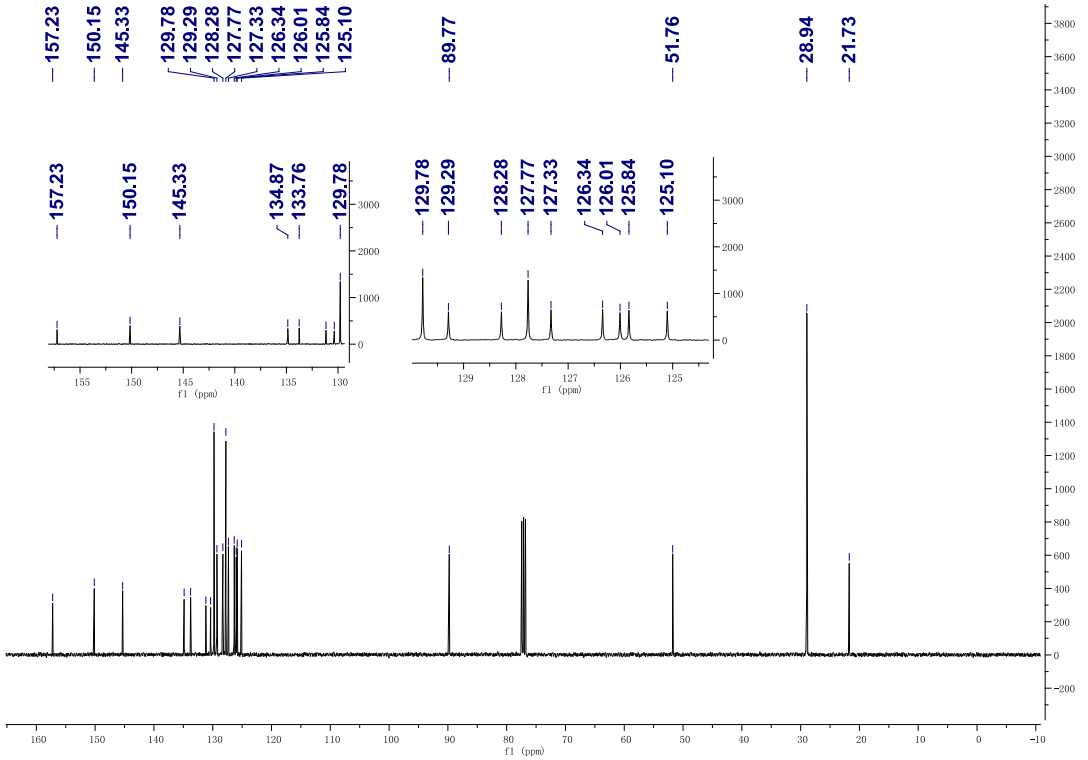
3-(2-bromophenyl)-*N*-(*tert*-butyl)-1-tosyl-1*H*-pyrazol-5-amine (3ta)



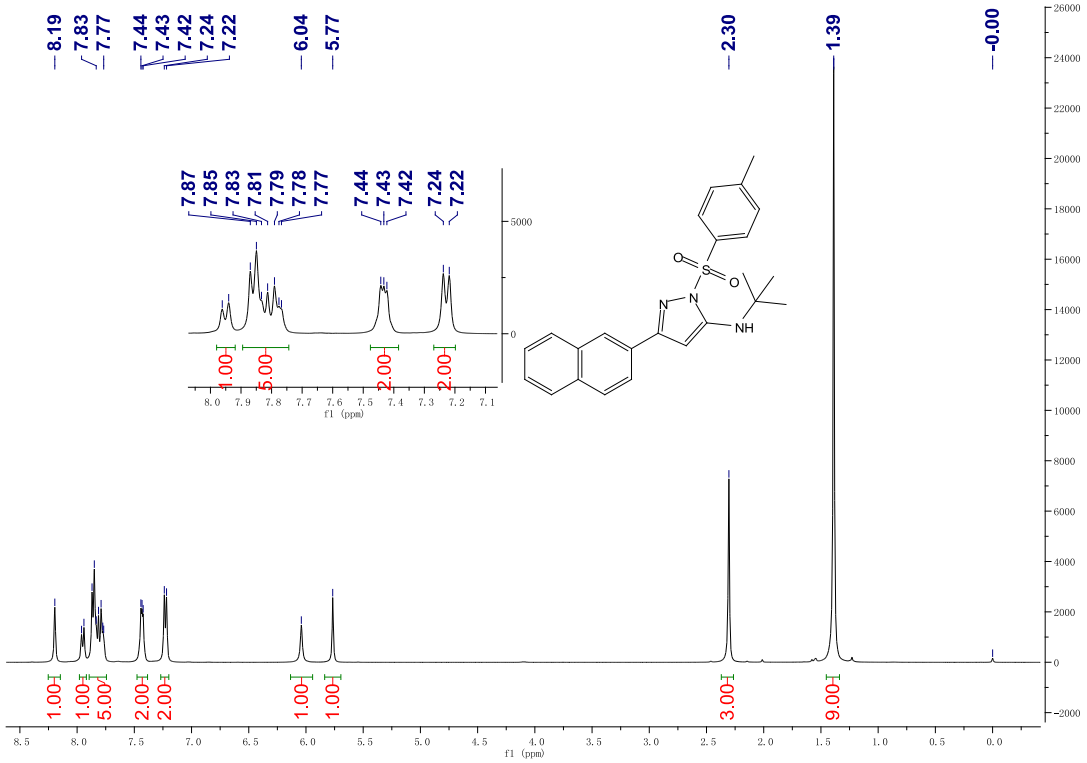


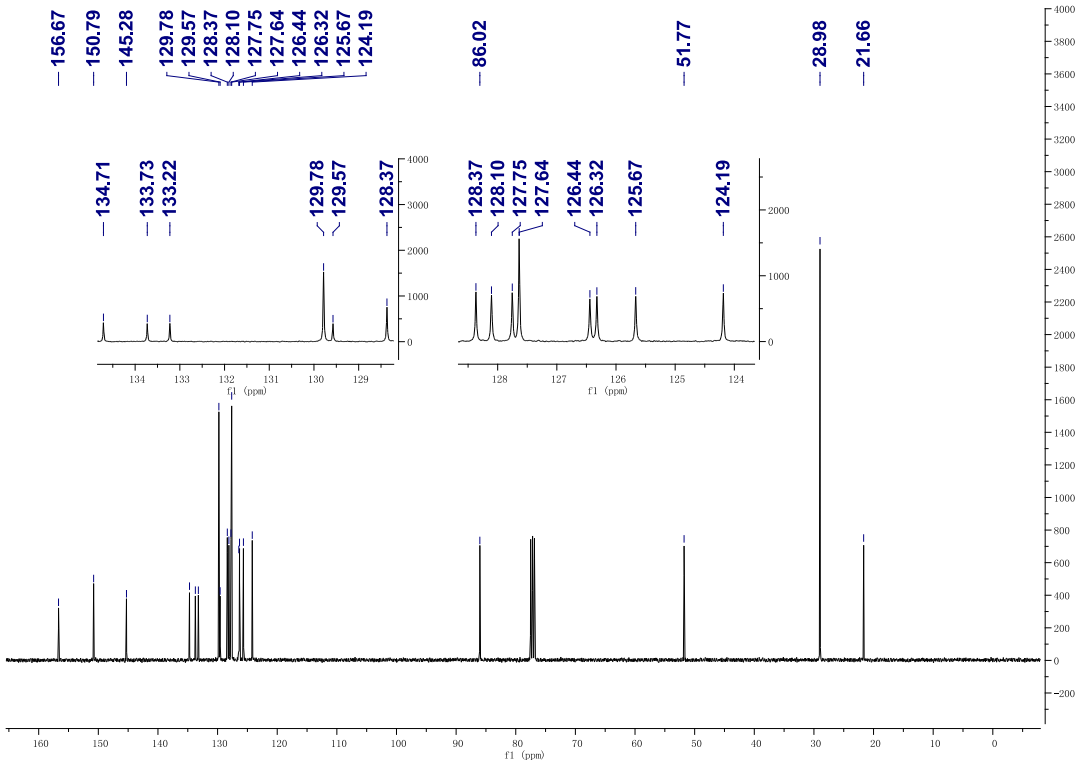
***N*-(*tert*-butyl)-3-(naphthalen-1-yl)-1-tosyl-1*H*-pyrazol-5-amine (3ua)**



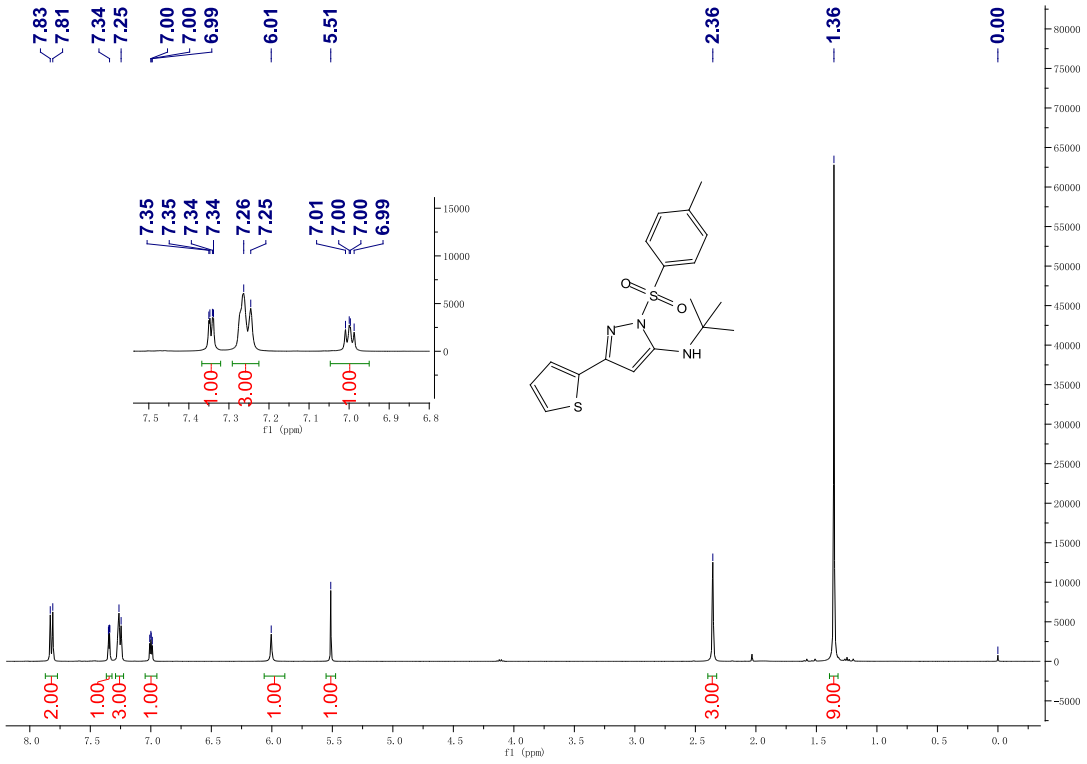


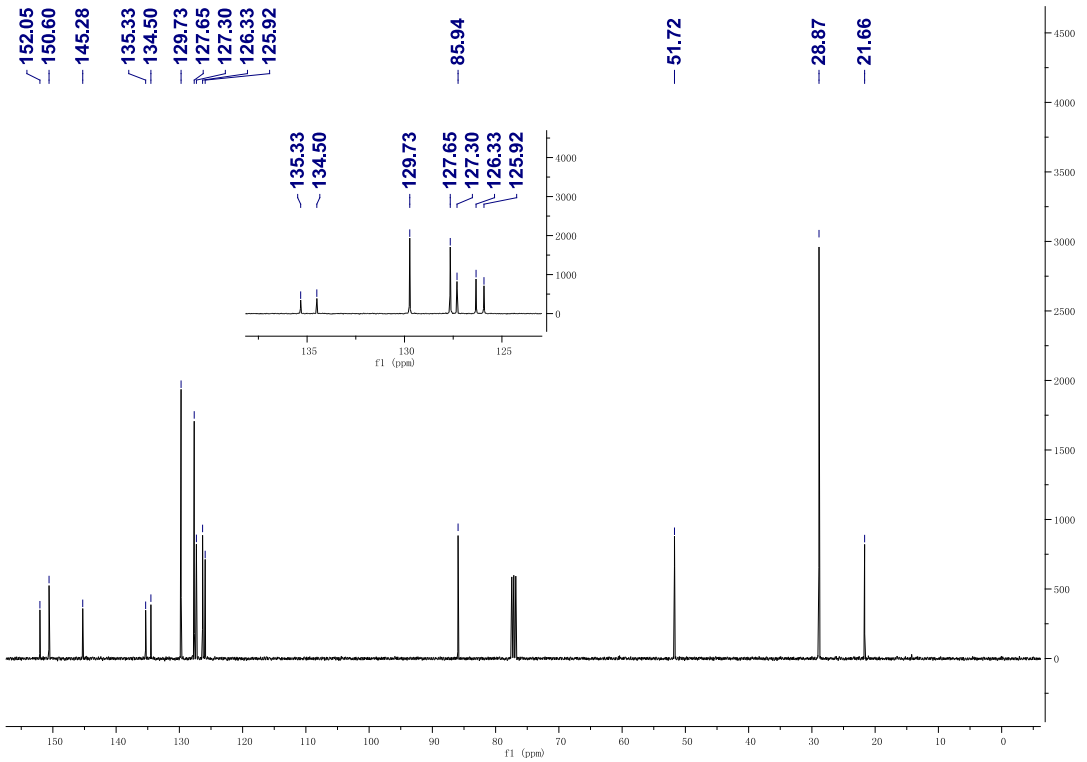
N-(tert-butyl)-3-(naphthalen-2-yl)-1-tosyl-1H-pyrazol-5-amine (3va)



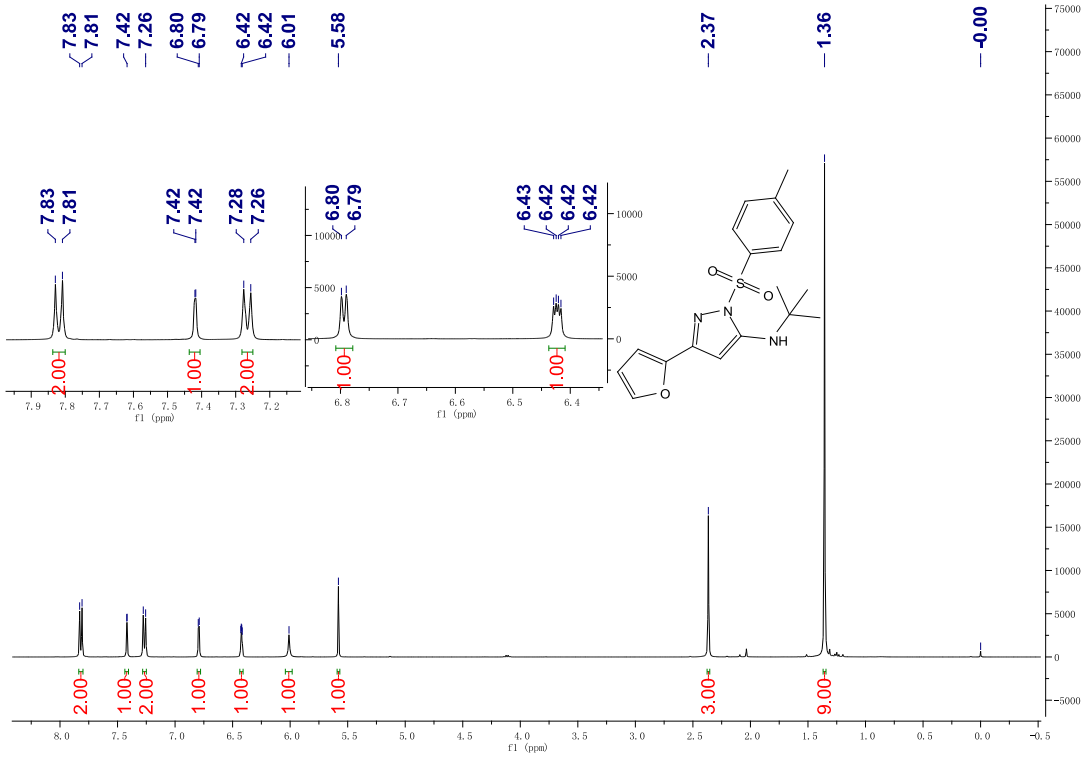


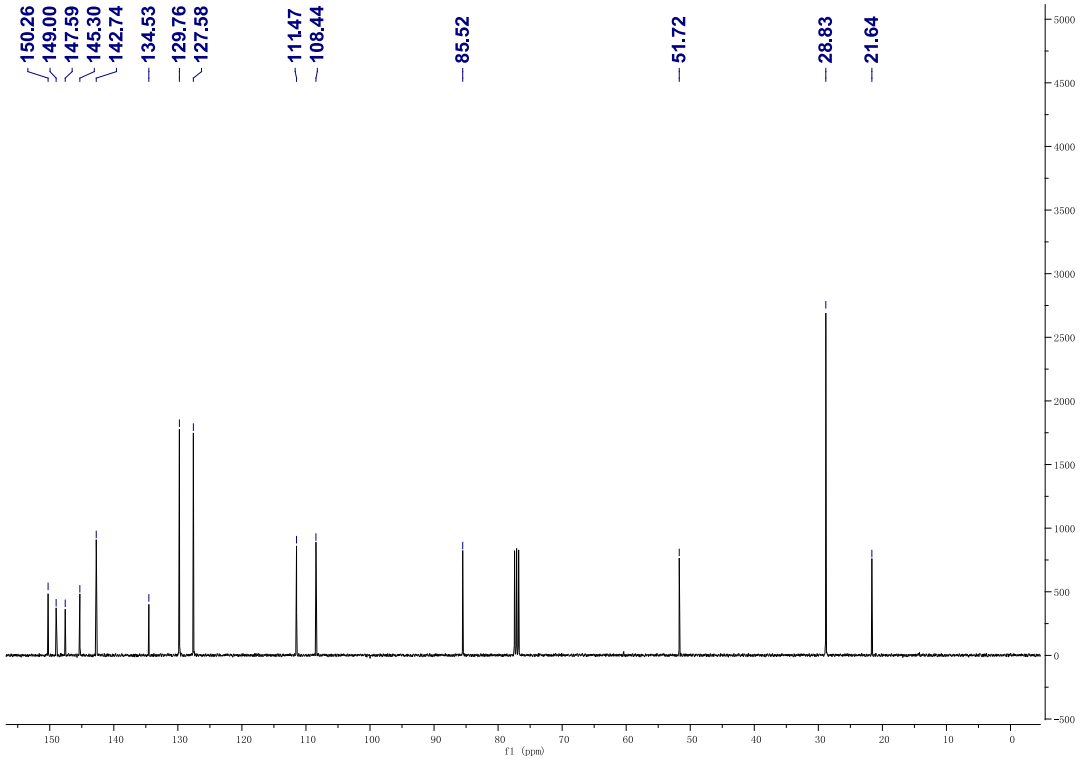
***N*-(*tert*-butyl)-3-(thiophen-2-yl)-1-tosyl-1*H*-pyrazol-5-amine (3wa)**



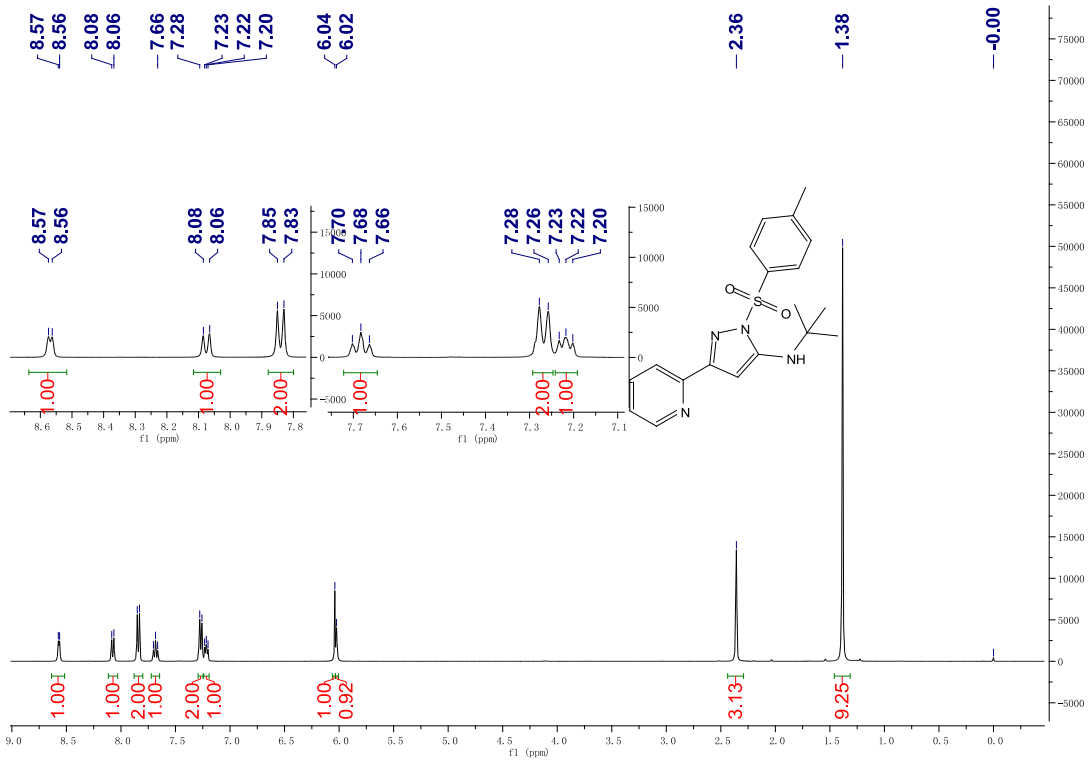


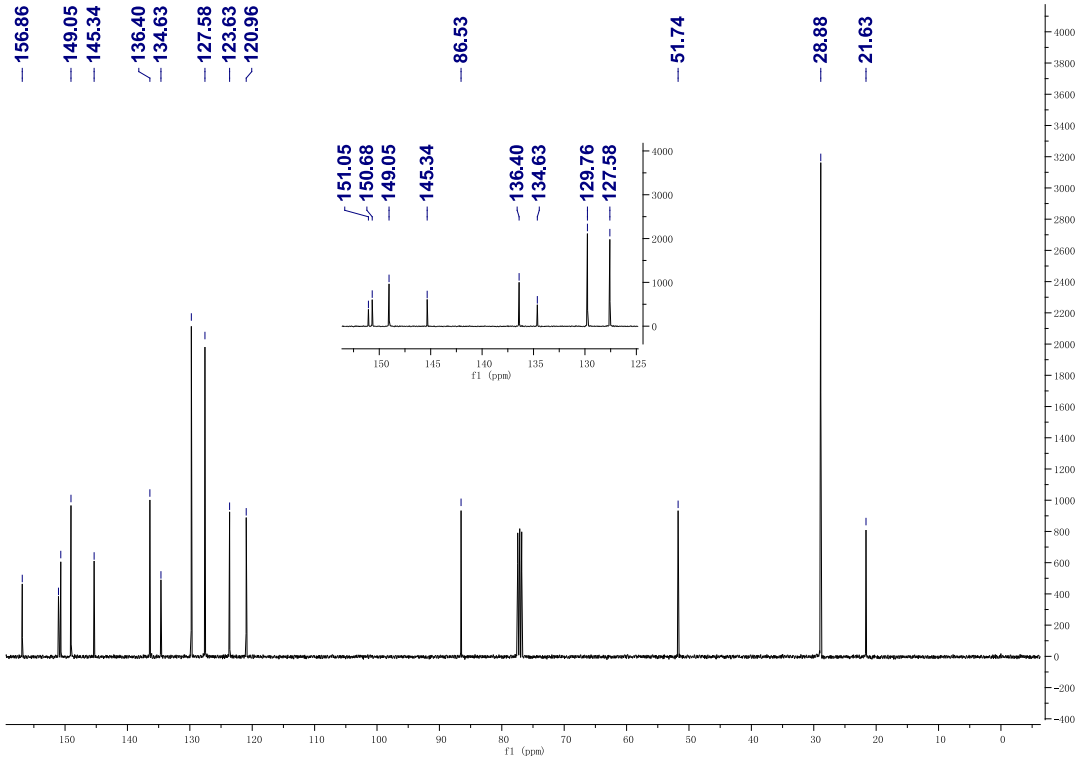
***N*-(*tert*-butyl)-3-(furan-2-yl)-1-tosyl-1*H*-pyrazol-5-amine (3xa)**



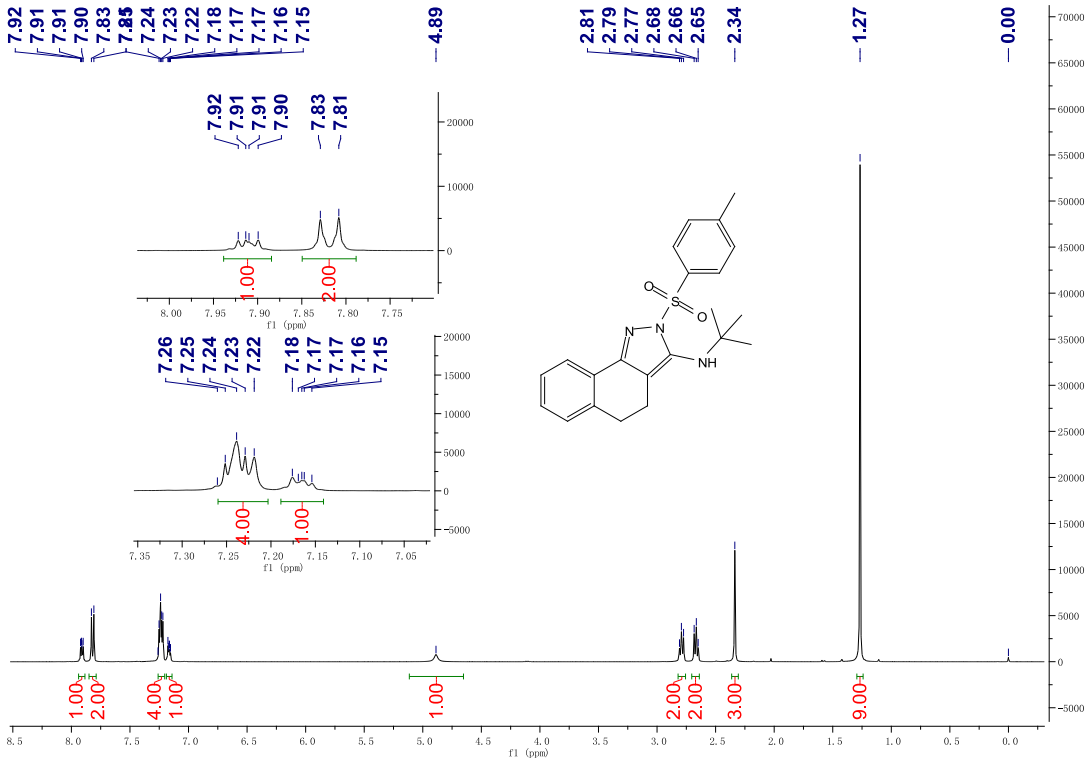


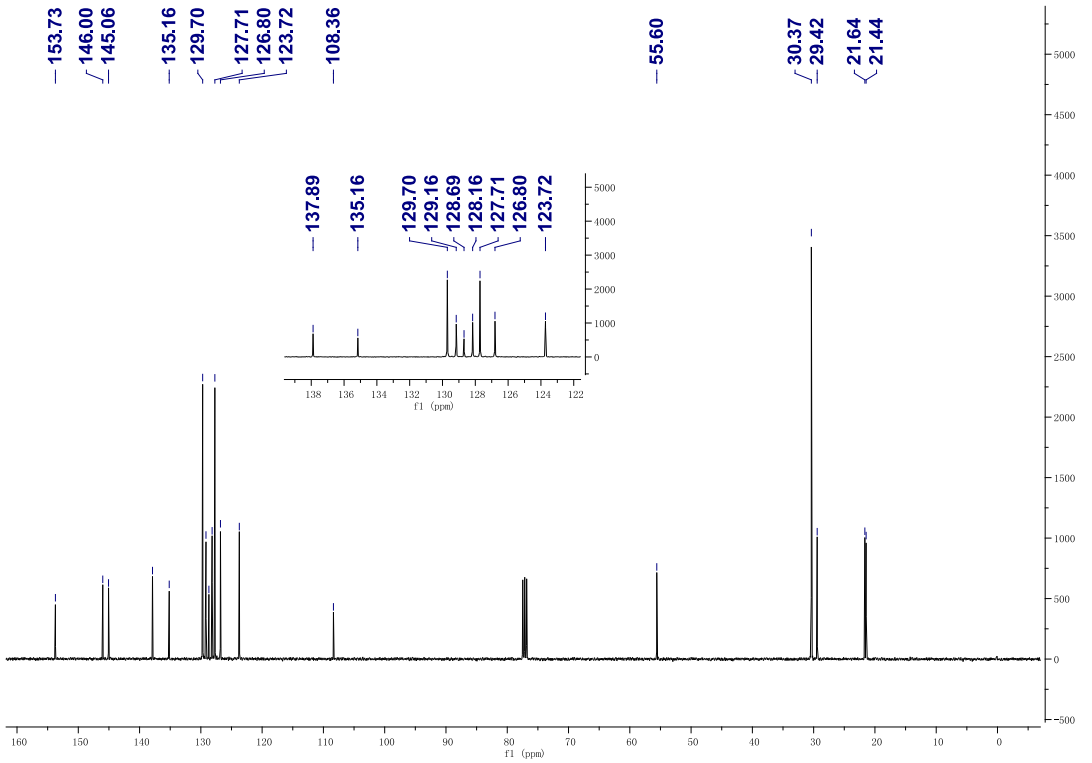
***N*-(*tert*-butyl)-3-(pyridin-2-yl)-1-tosyl-1*H*-pyrazol-5-amine (3ya)**



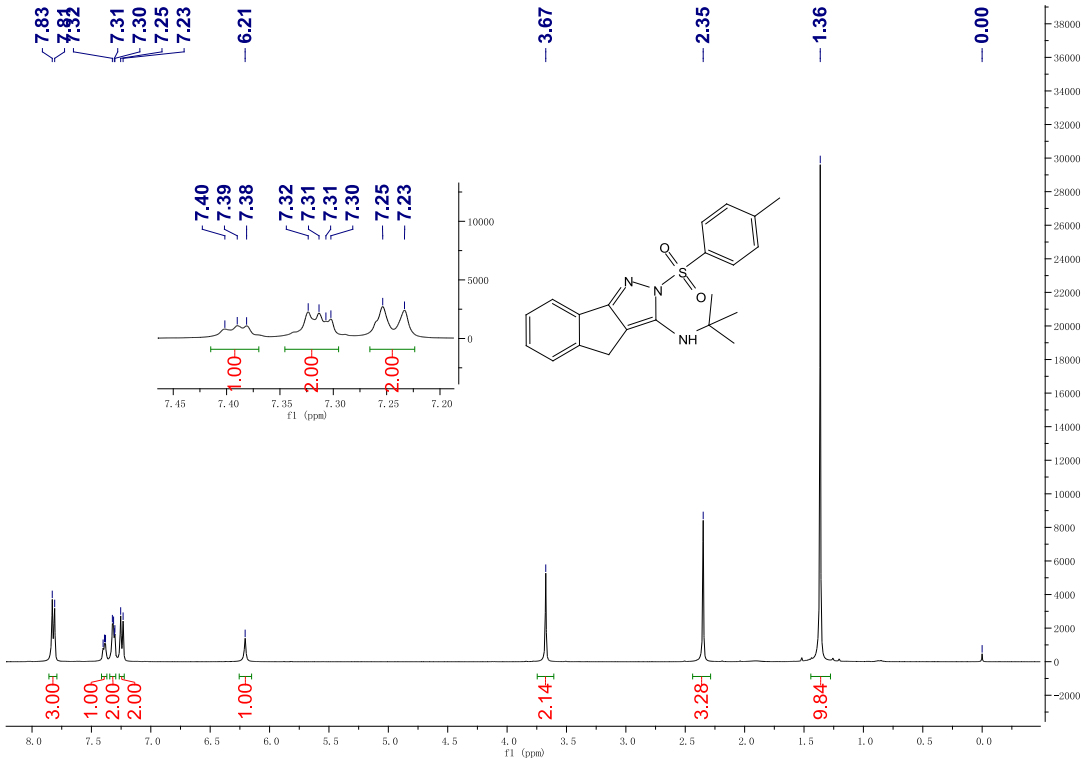


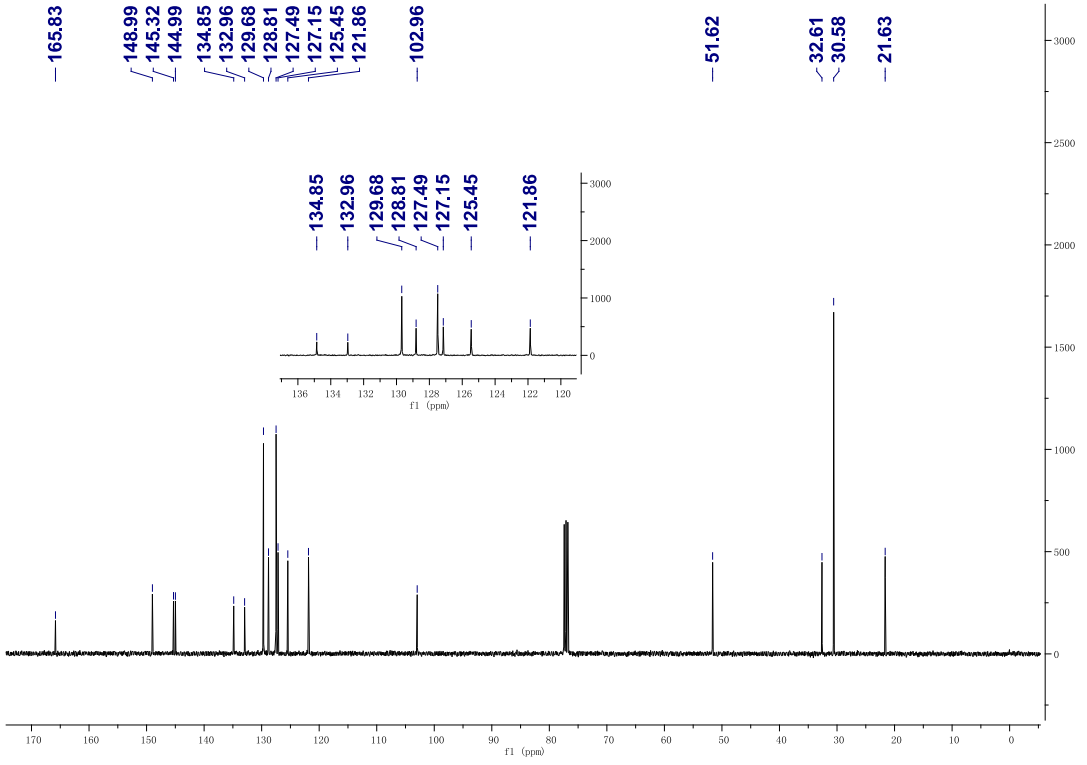
***N*-(*tert*-butyl)-2-tosyl-4,5-dihydro-2*H*-benzo[g]indazol-3-amine (5aa)**



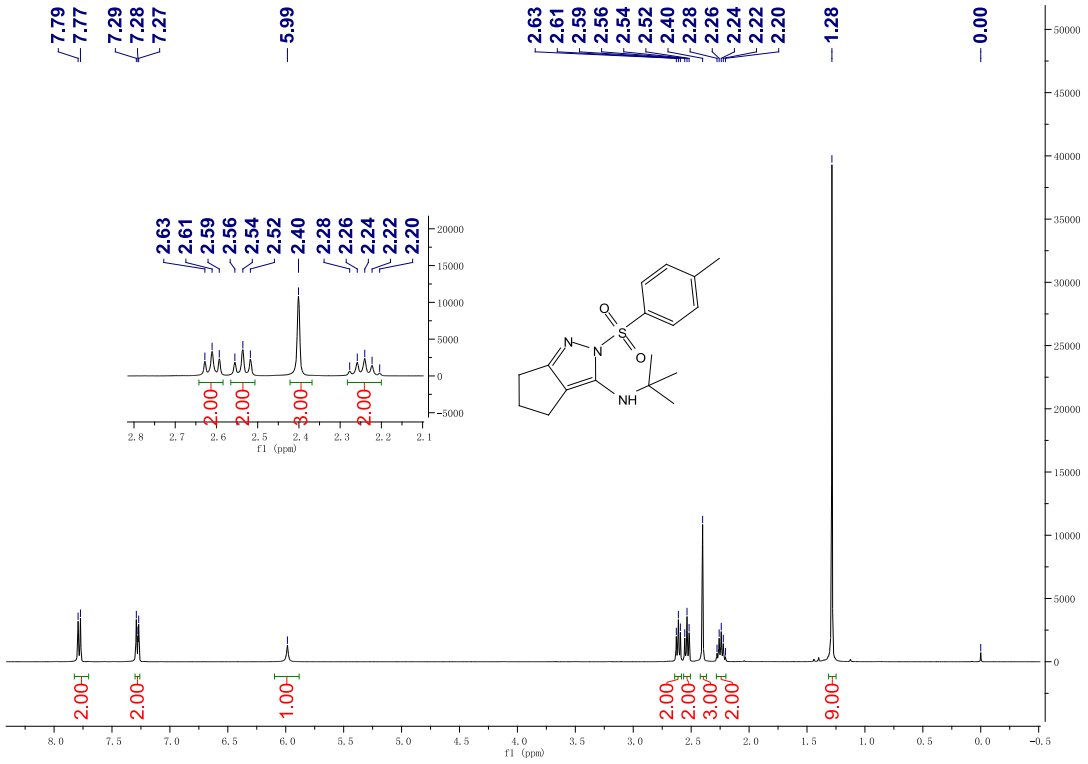


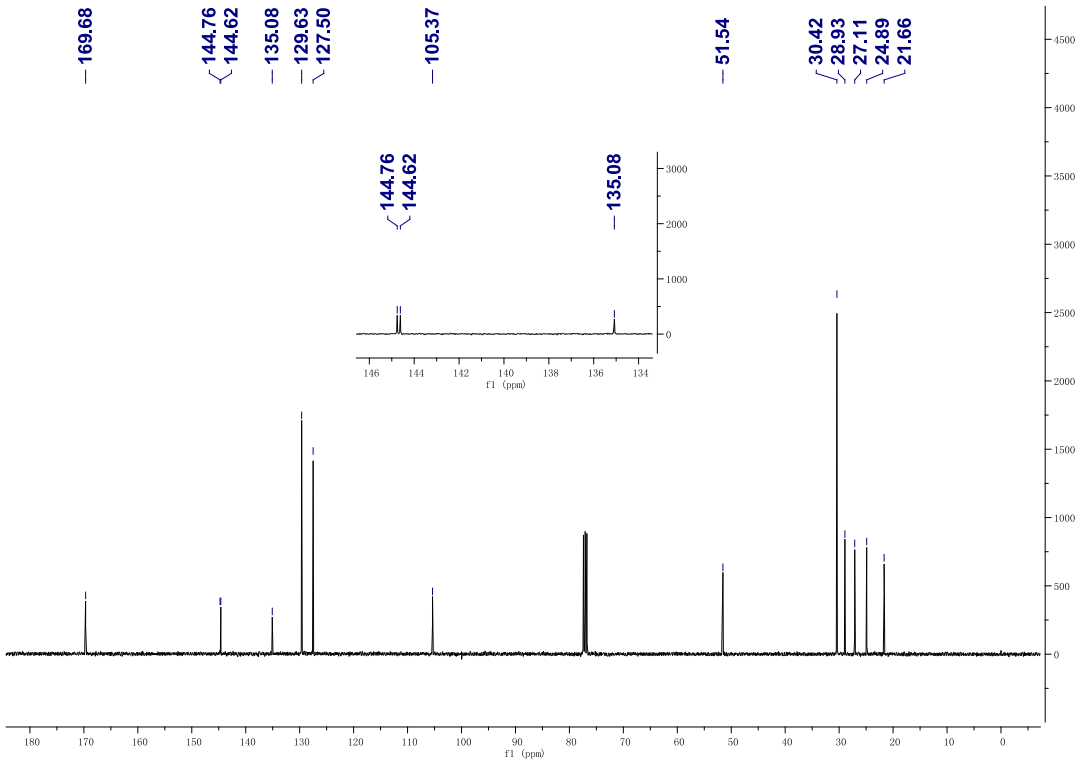
***N*-(*tert*-butyl)-2-tosyl-2,4-dihydroindeno[1,2-c]pyrazol-3-amine (5ba)**



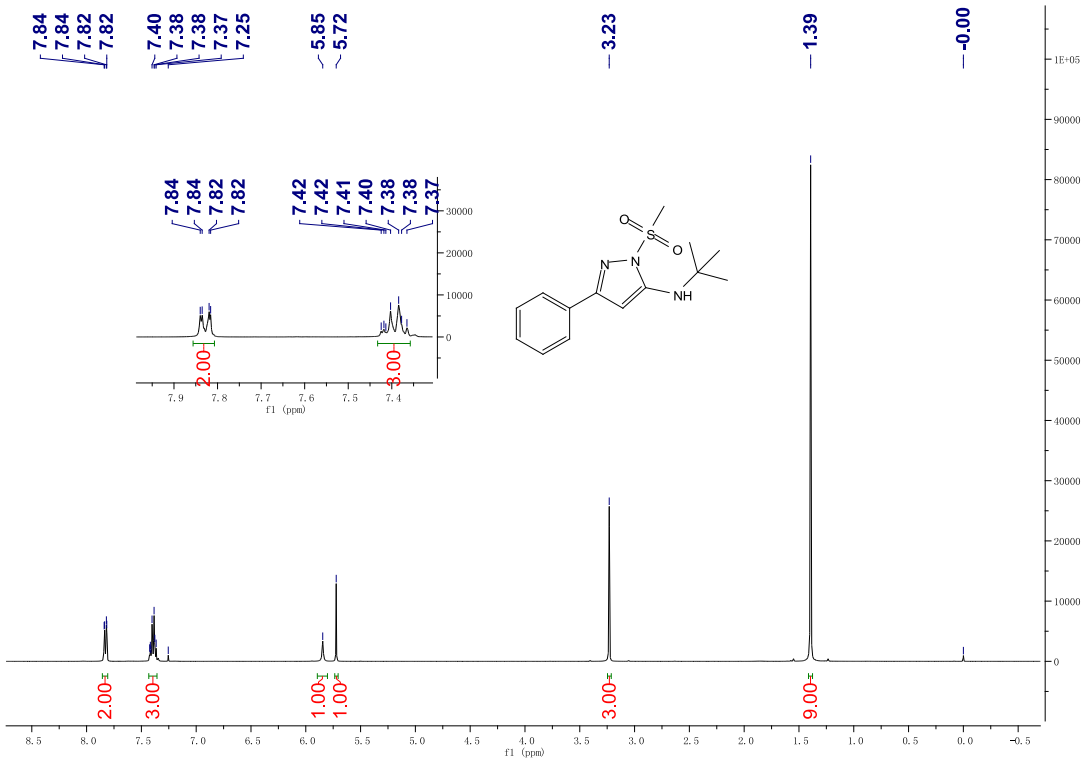


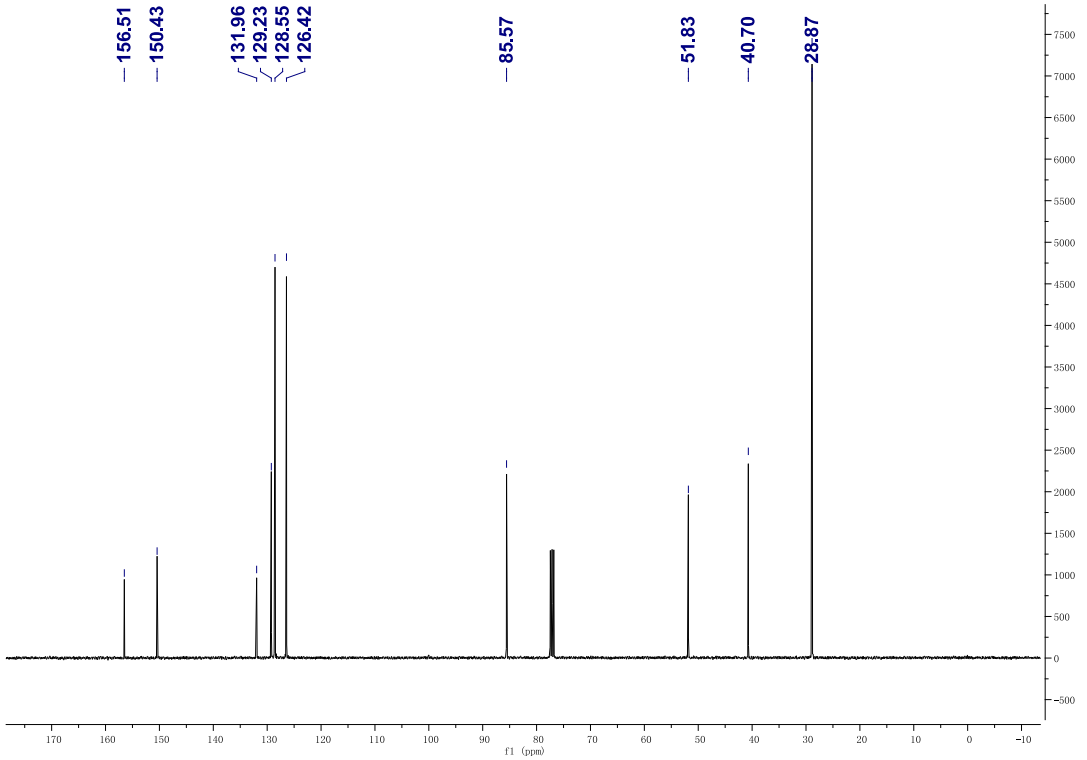
_N_-(_tert_-butyl)-2-tosyl-2,4,5,6-tetrahydrocyclopenta[c]pyrazol-3-amine (5da)



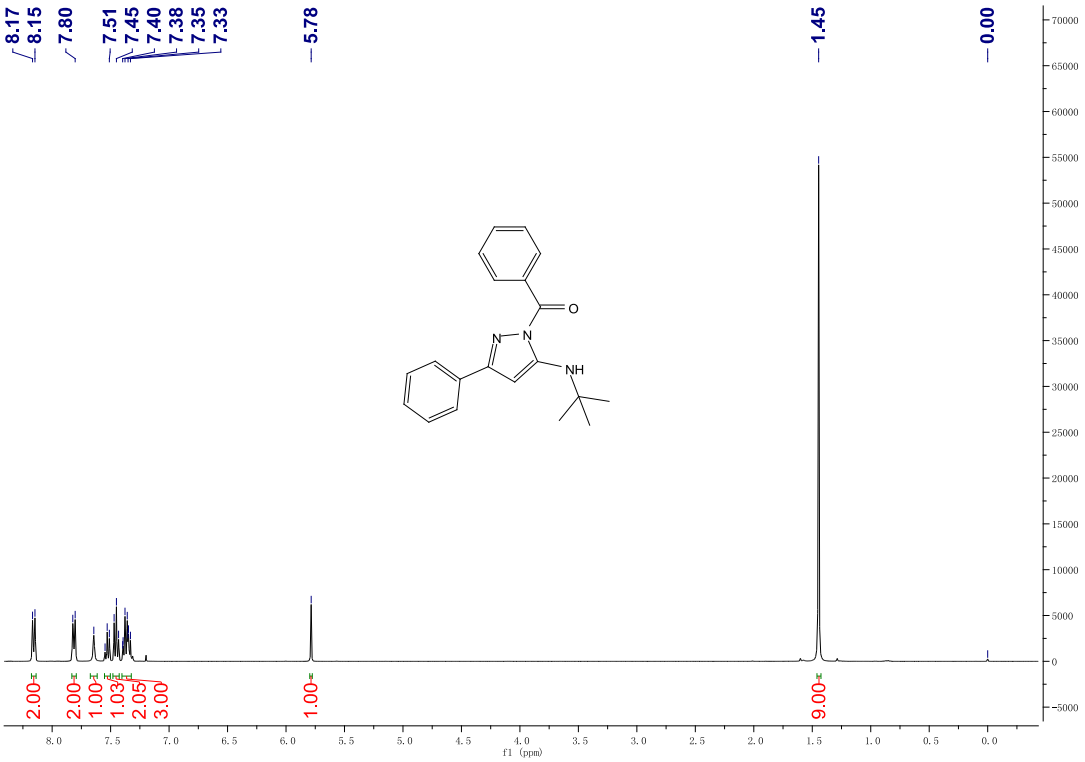


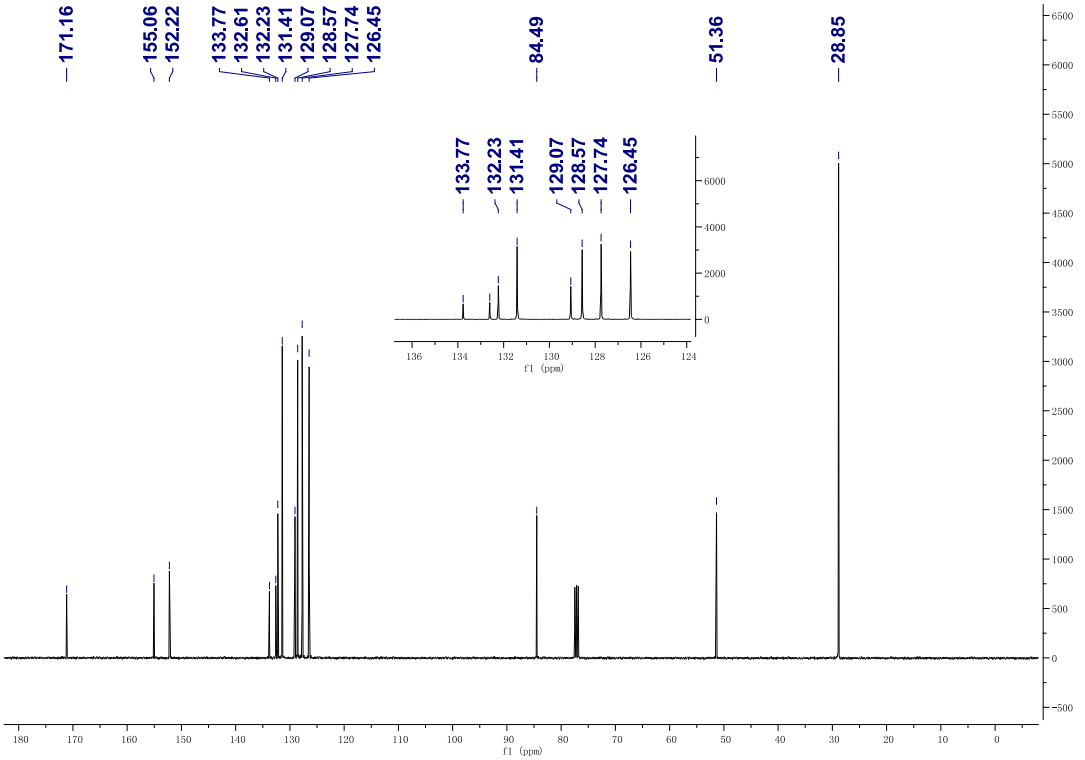
***N*-(*tert*-butyl)-1-(methylsulfonyl)-3-phenyl-1*H*-pyrazol-5-amine (7aa)**



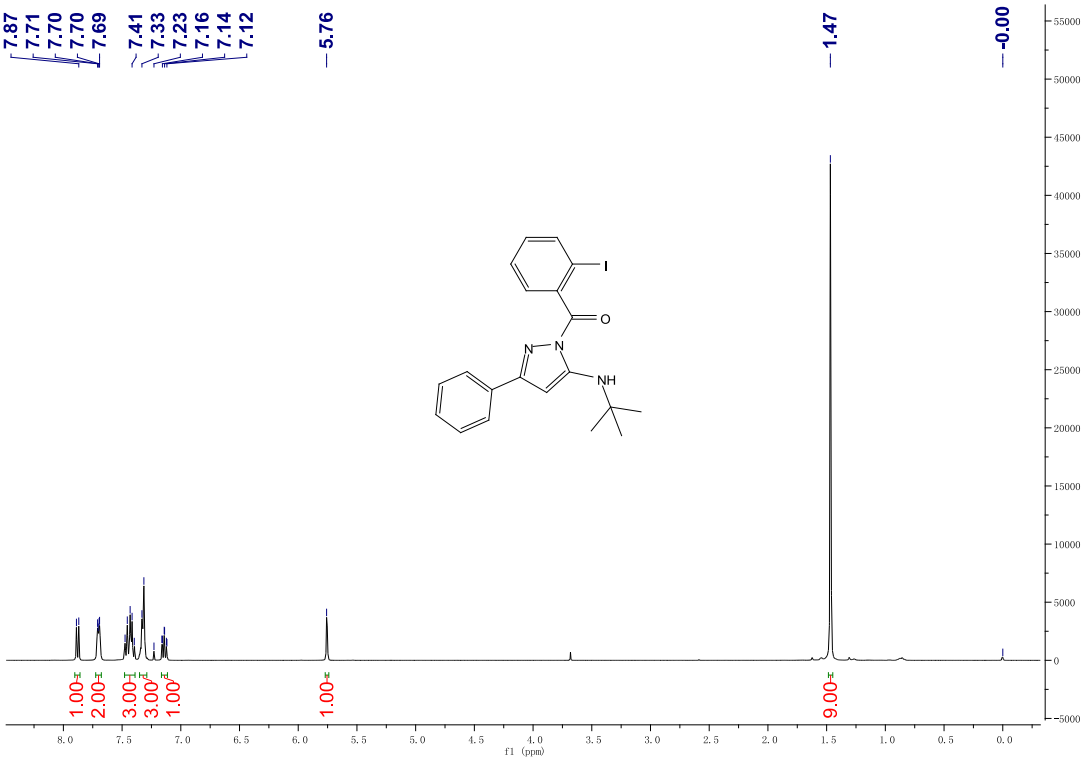


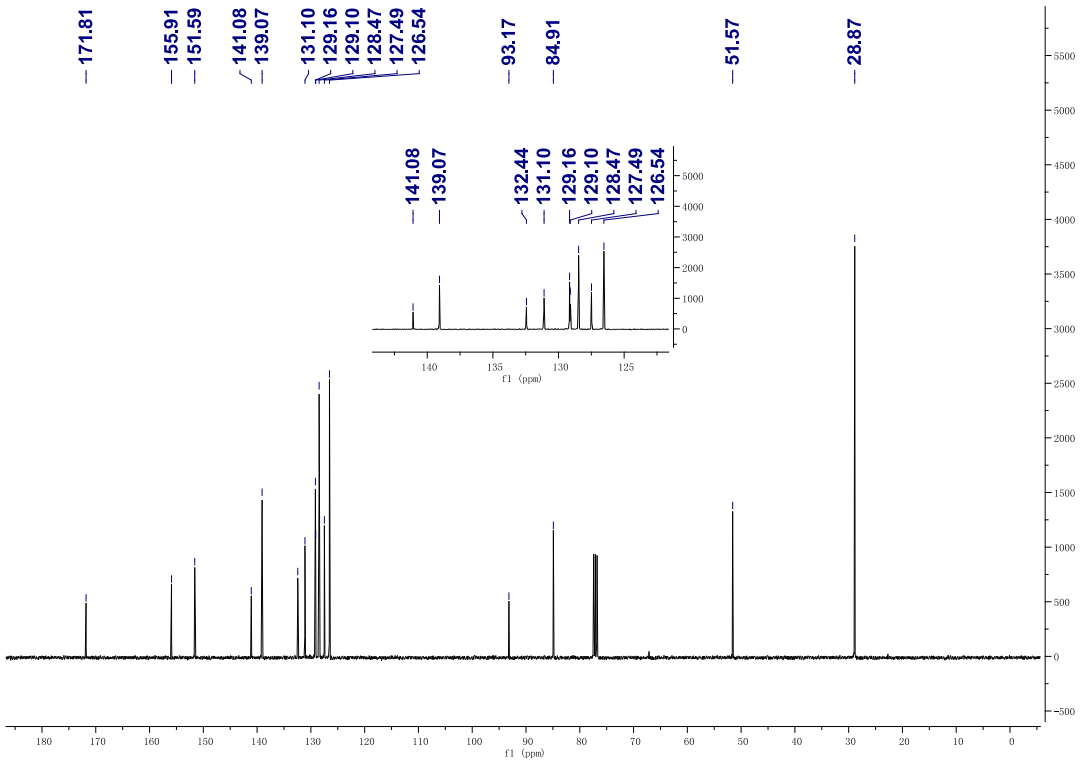
(5-(*tert*-butylamino)-3-phenyl-1*H*-pyrazol-1-yl)(phenyl)methanone (7ba)



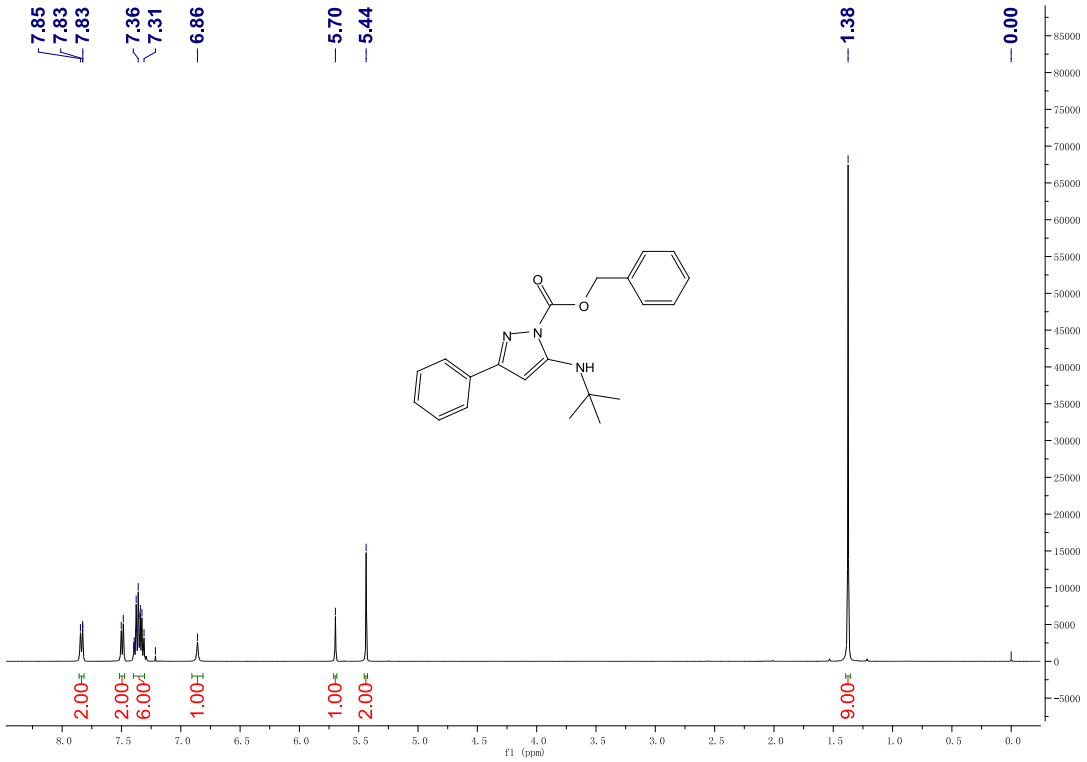


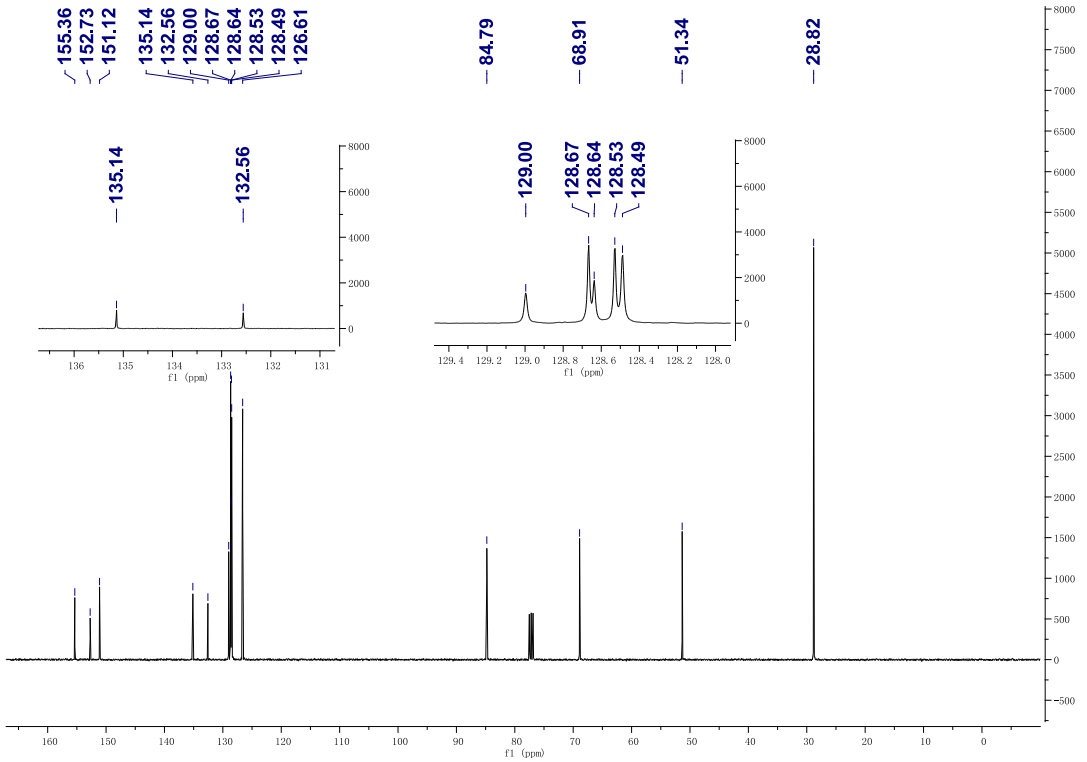
(5-(*tert*-butylamino)-3-phenyl-1*H*-pyrazol-1-yl)(2-iodophenyl)methanone (7ca)



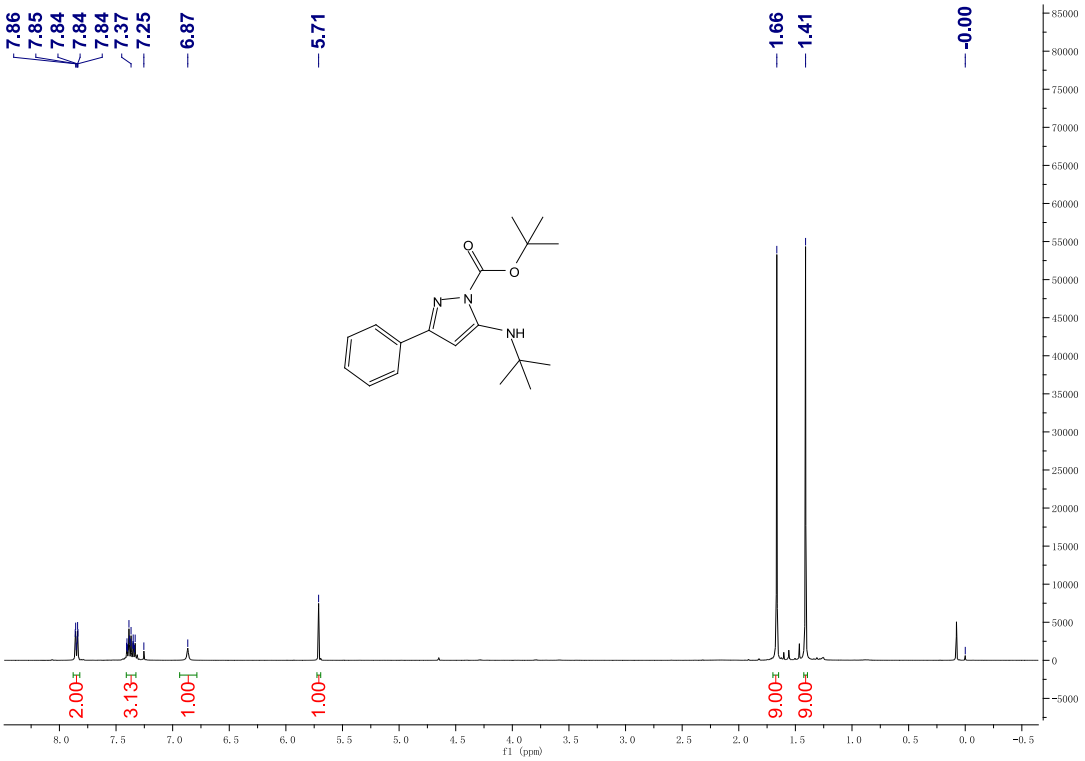


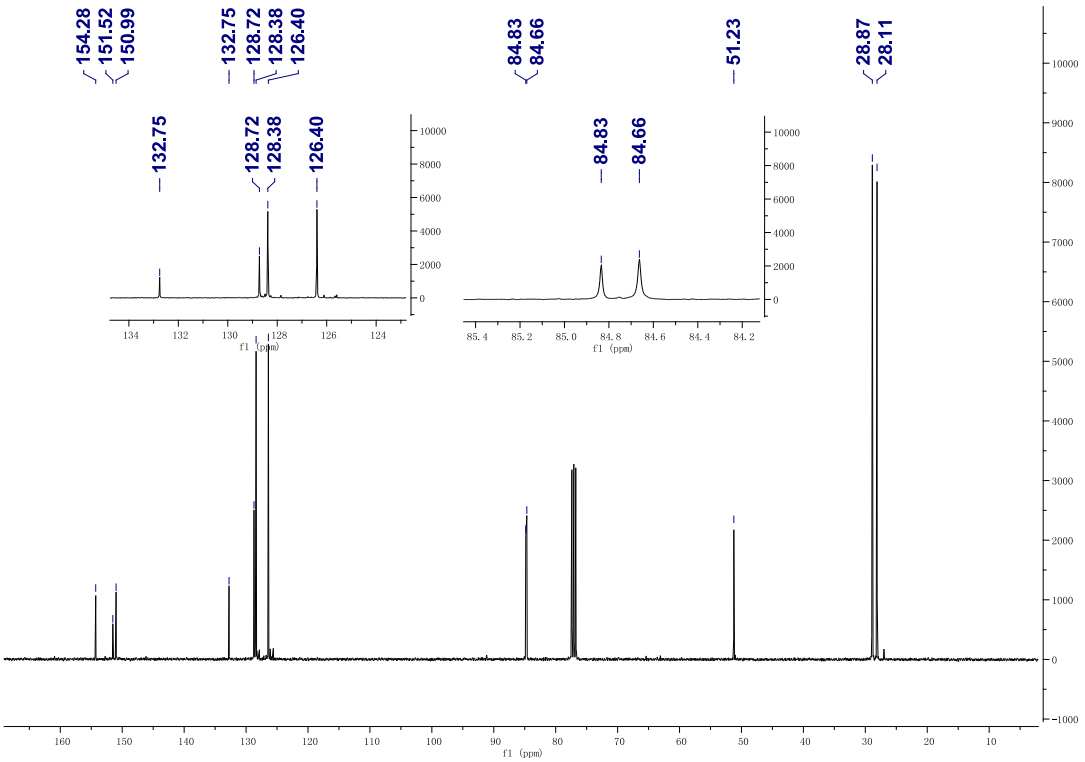
benzyl 5-(*tert*-butylamino)-3-phenyl-1*H*-pyrazole-1-carboxylate (7da)



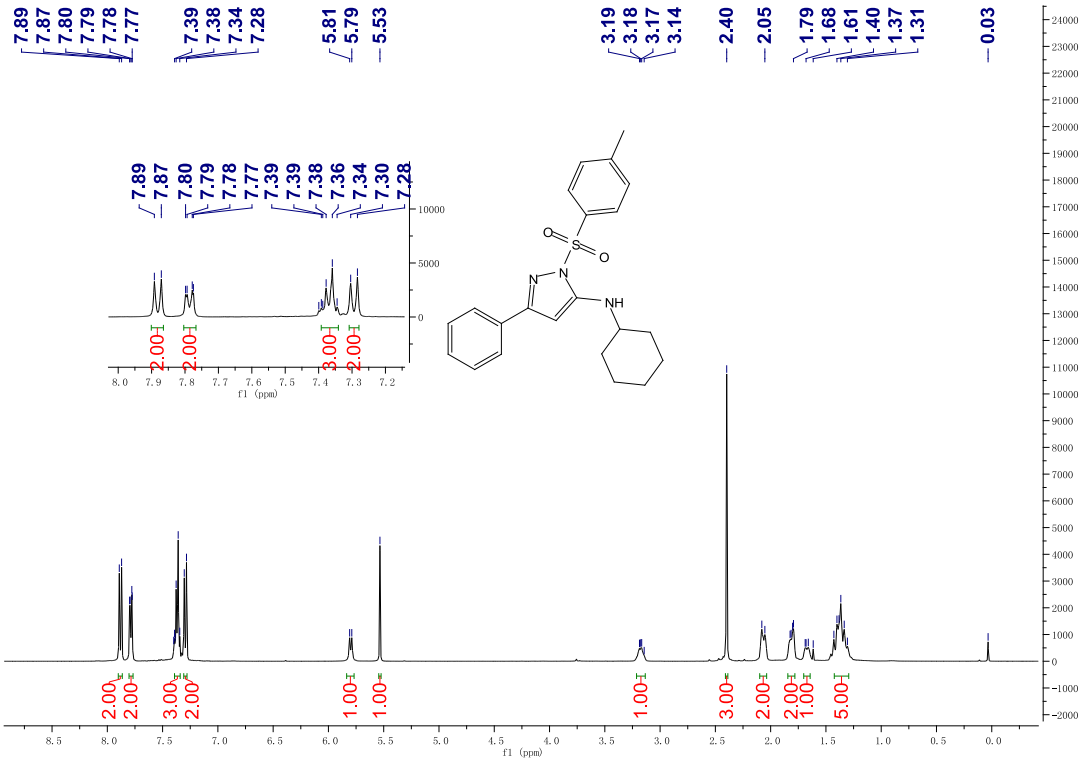


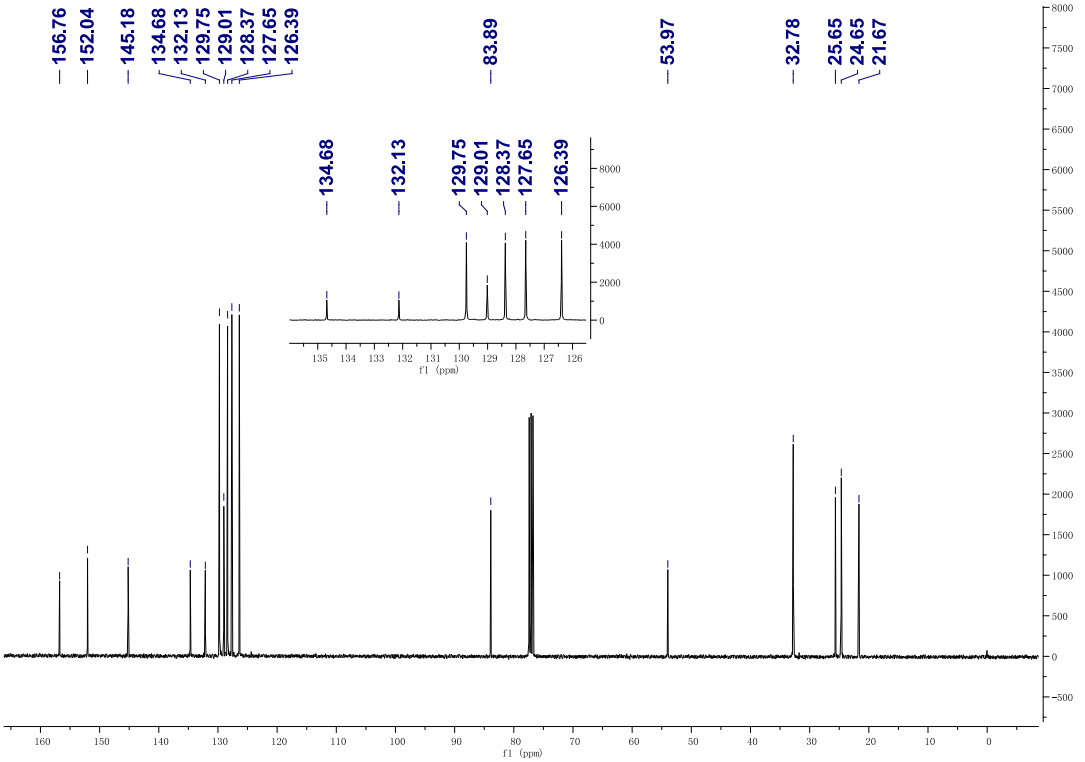
***tert*-butyl 5-(*tert*-butylamino)-3-phenyl-1*H*-pyrazole-1-carboxylate (7ea)**



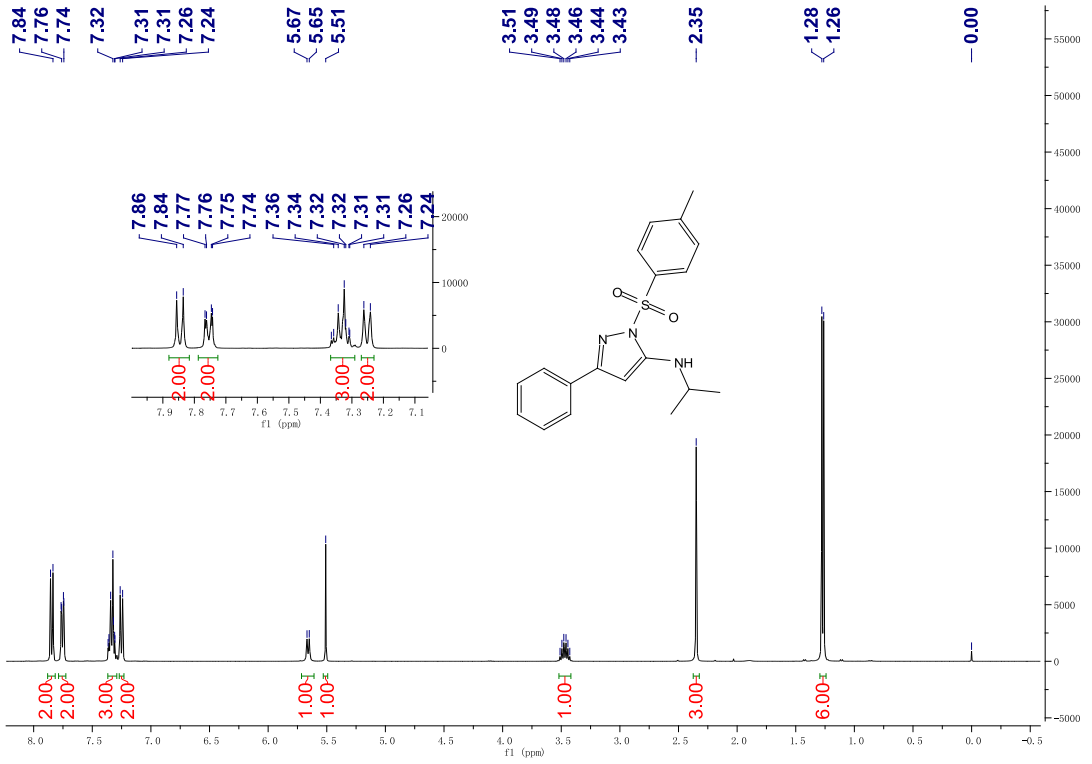


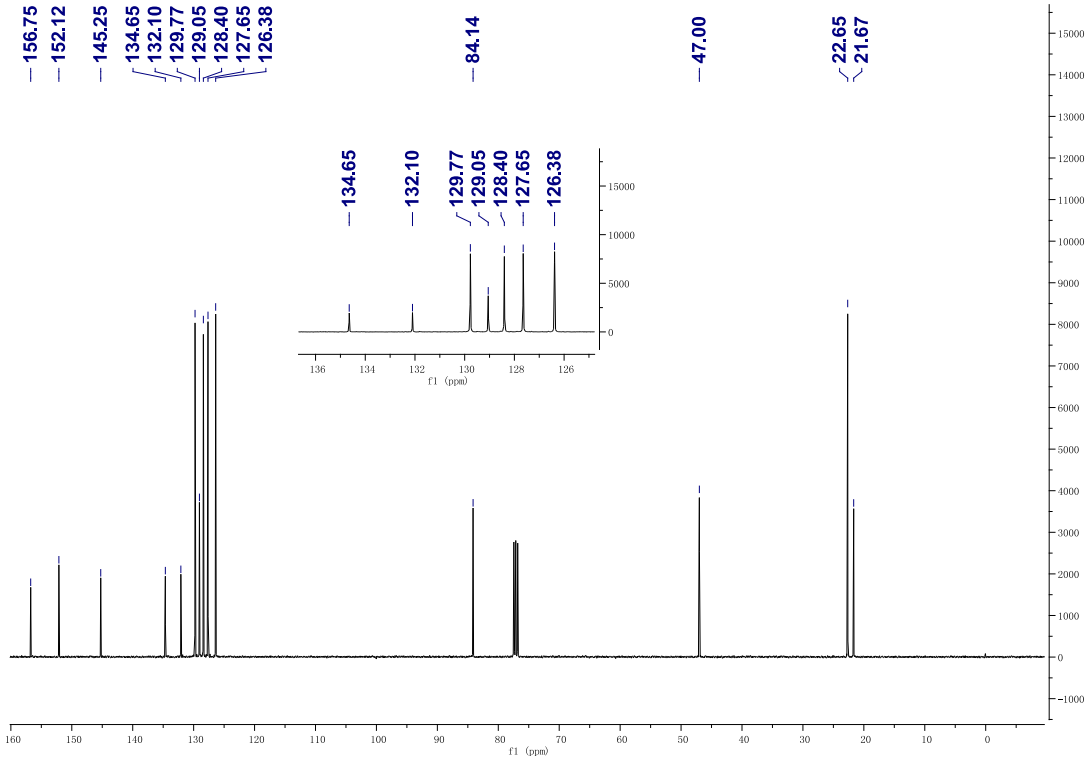
N-cyclohexyl-3-phenyl-1-tosyl-1*H*-pyrazol-5-amine (8ab)



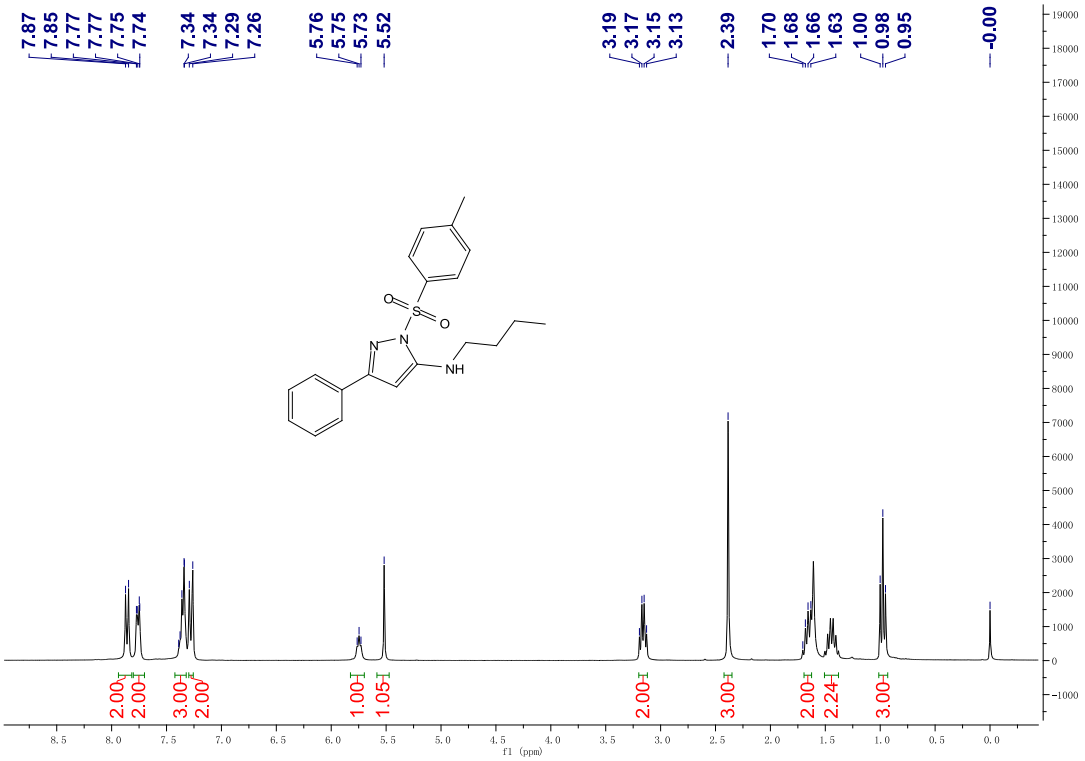


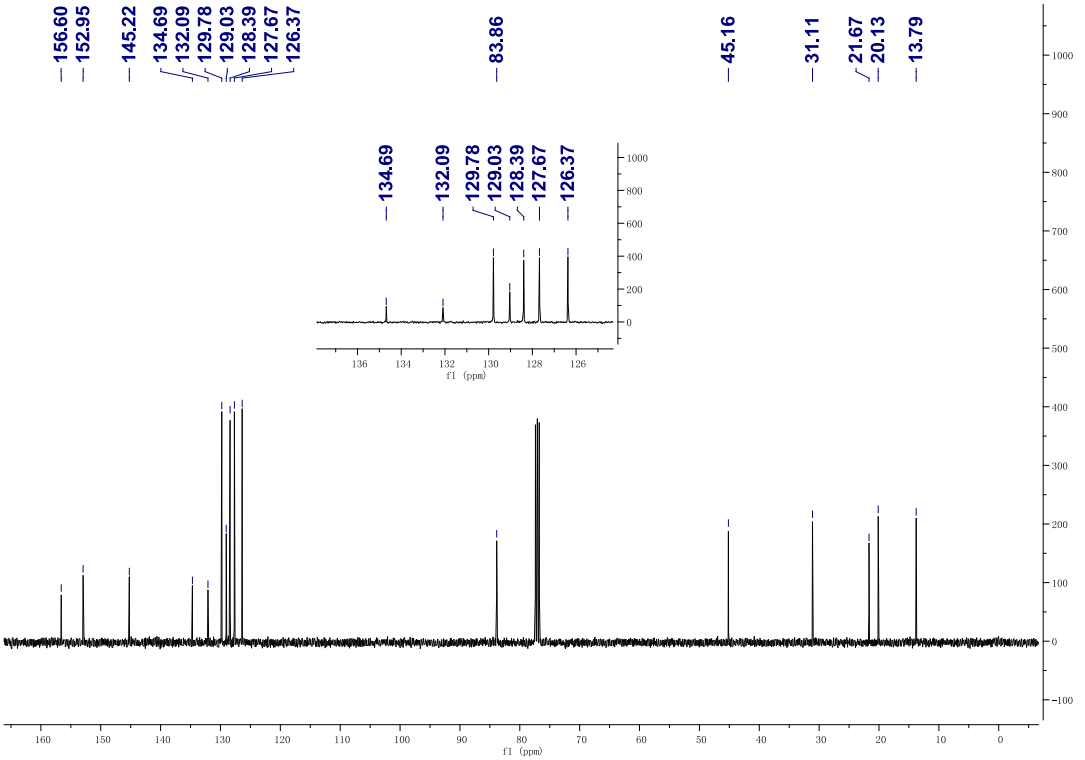
N-isopropyl-3-phenyl-1-tosyl-1*H*-pyrazol-5-amine (8ac)



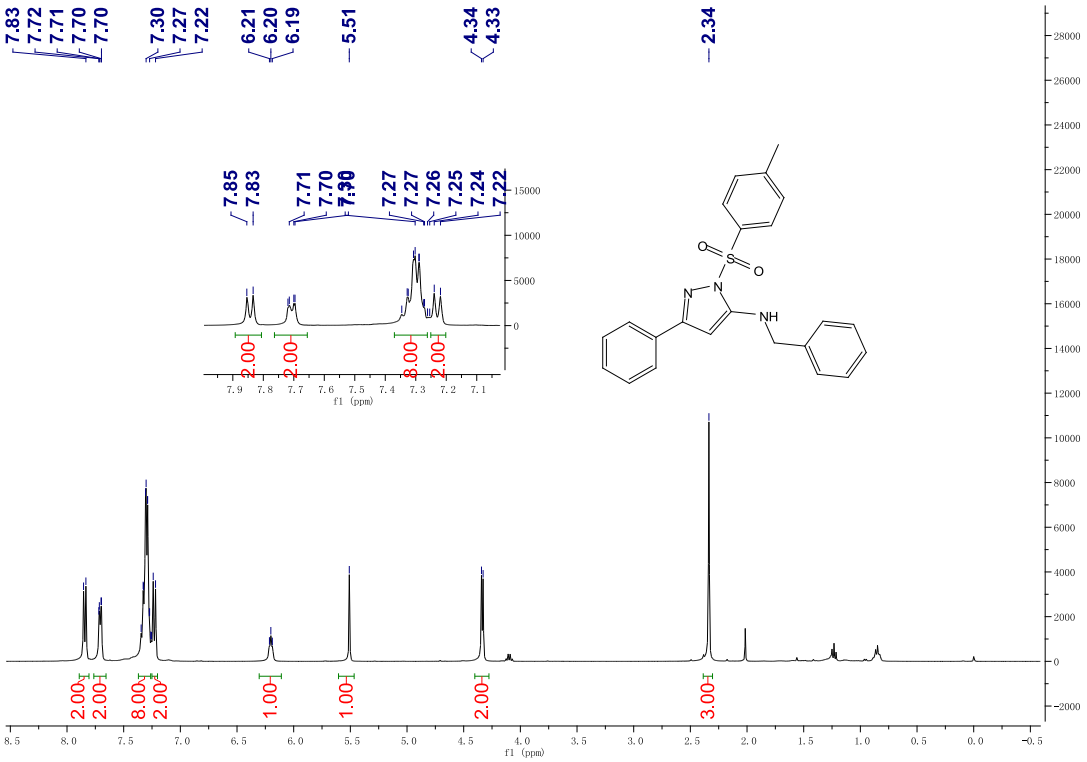


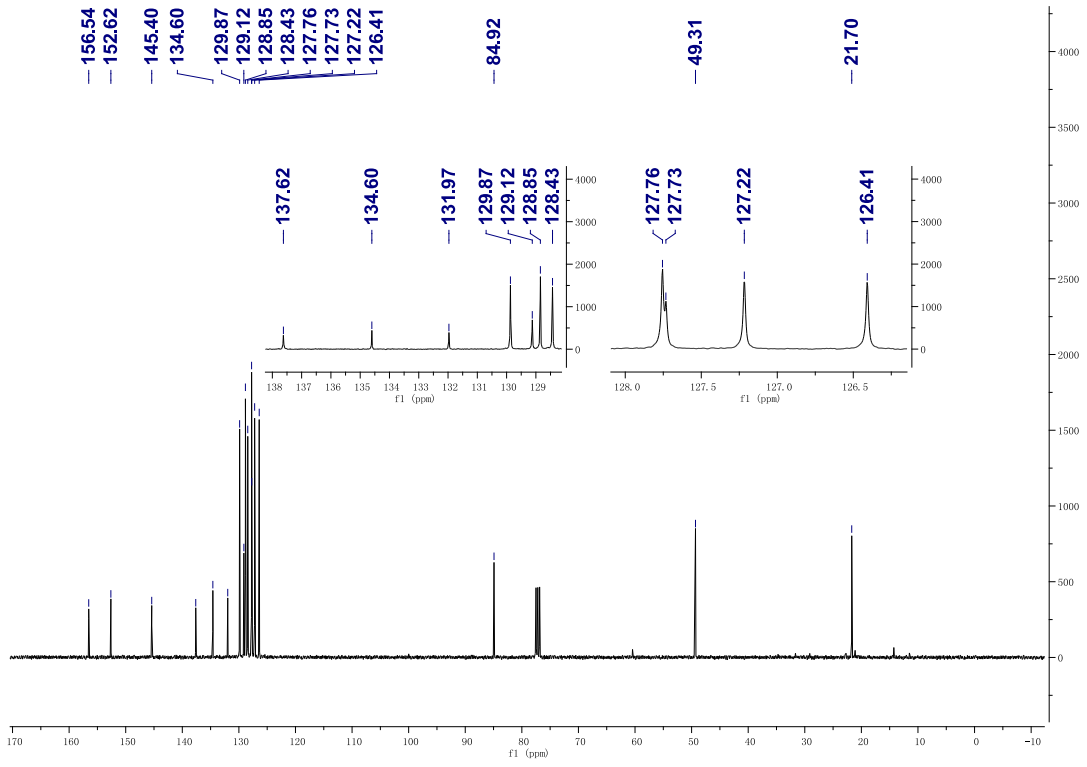
***N*-butyl-3-phenyl-1-tosyl-1*H*-pyrazol-5-amine (8ad)**



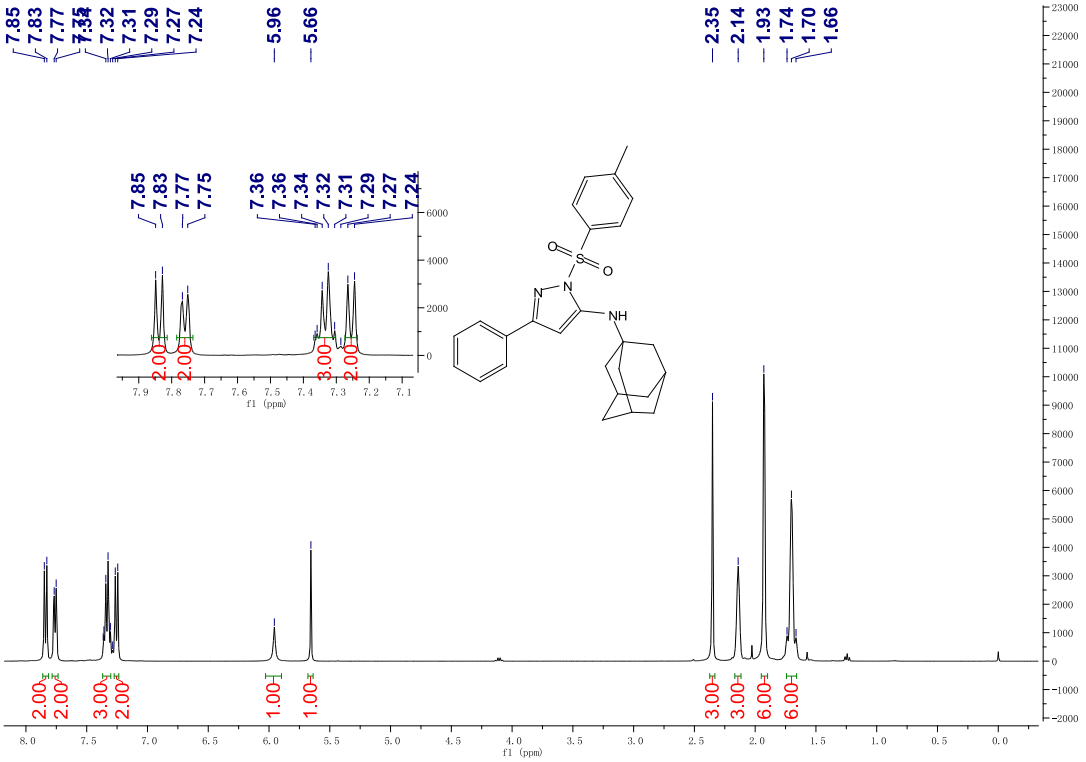


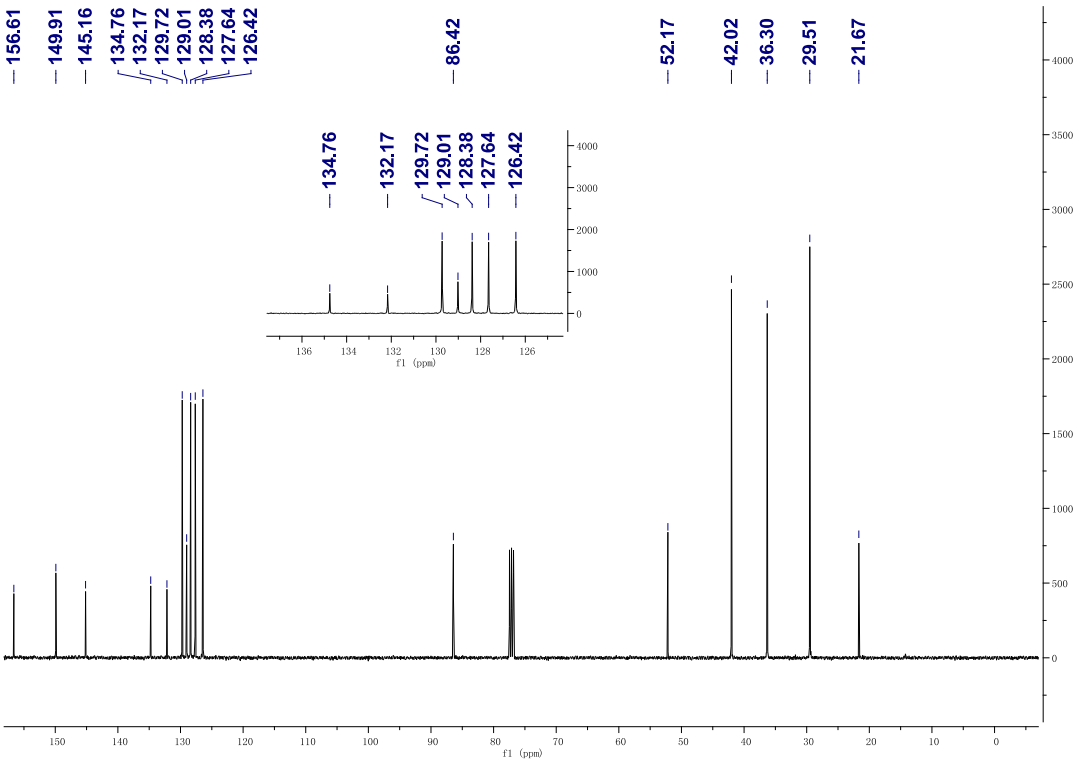
N-benzyl-3-phenyl-1-tosyl-1*H*-pyrazol-5-amine (8ae)



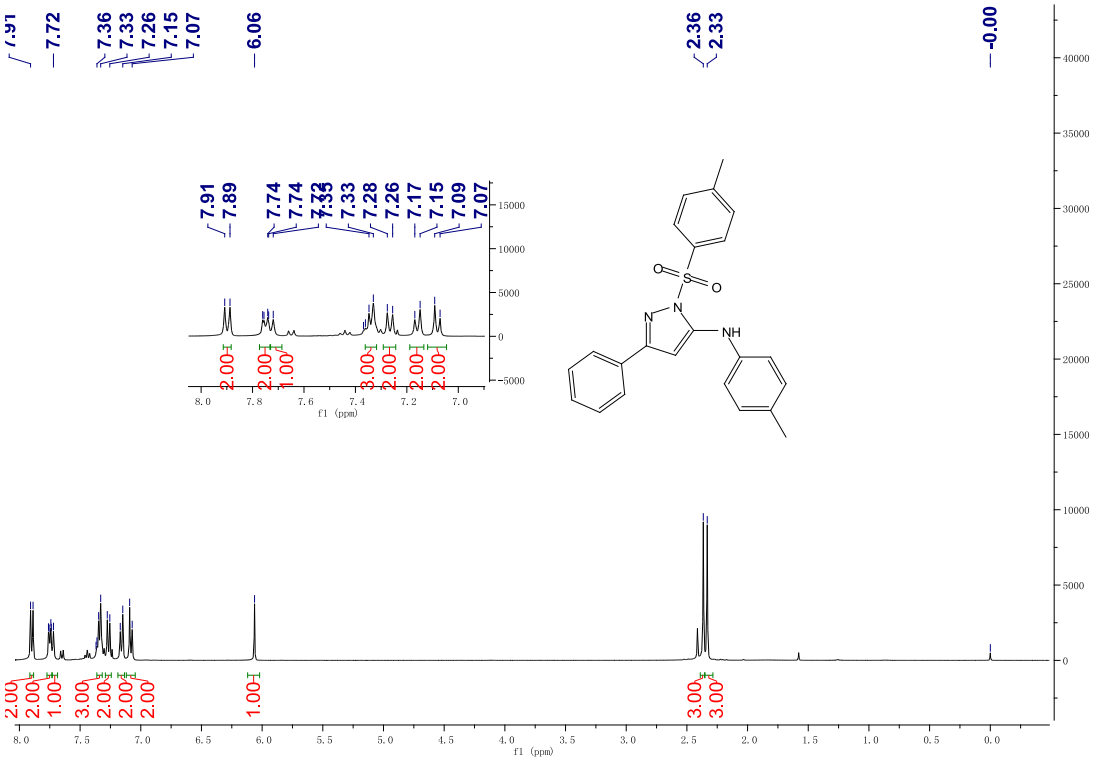


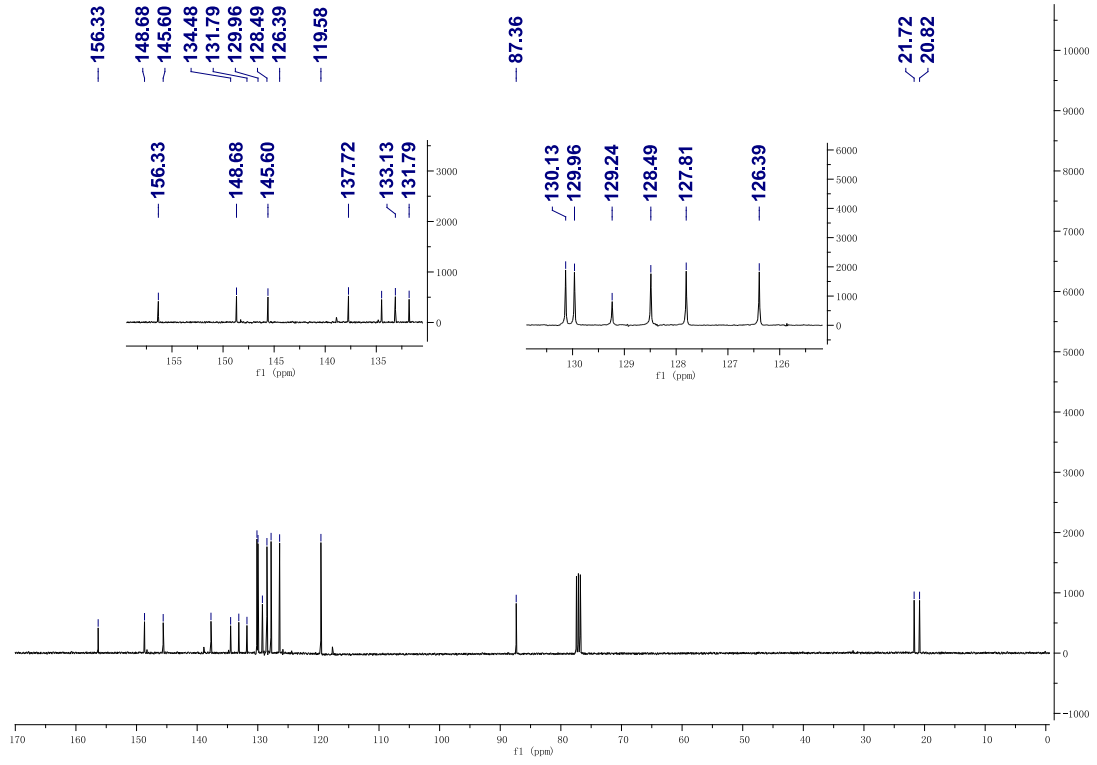
***N*-((1S,3s)-adamantan-1-yl)-3-phenyl-1-tosyl-1*H*-pyrazol-5-amine (8af)**



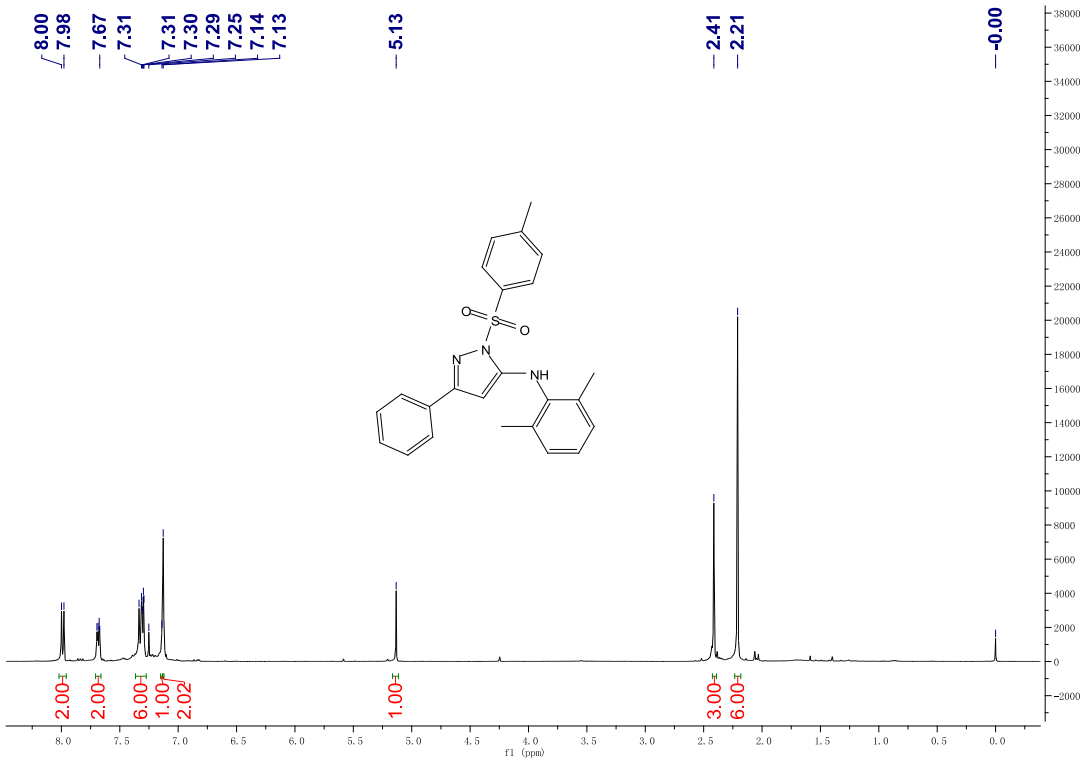


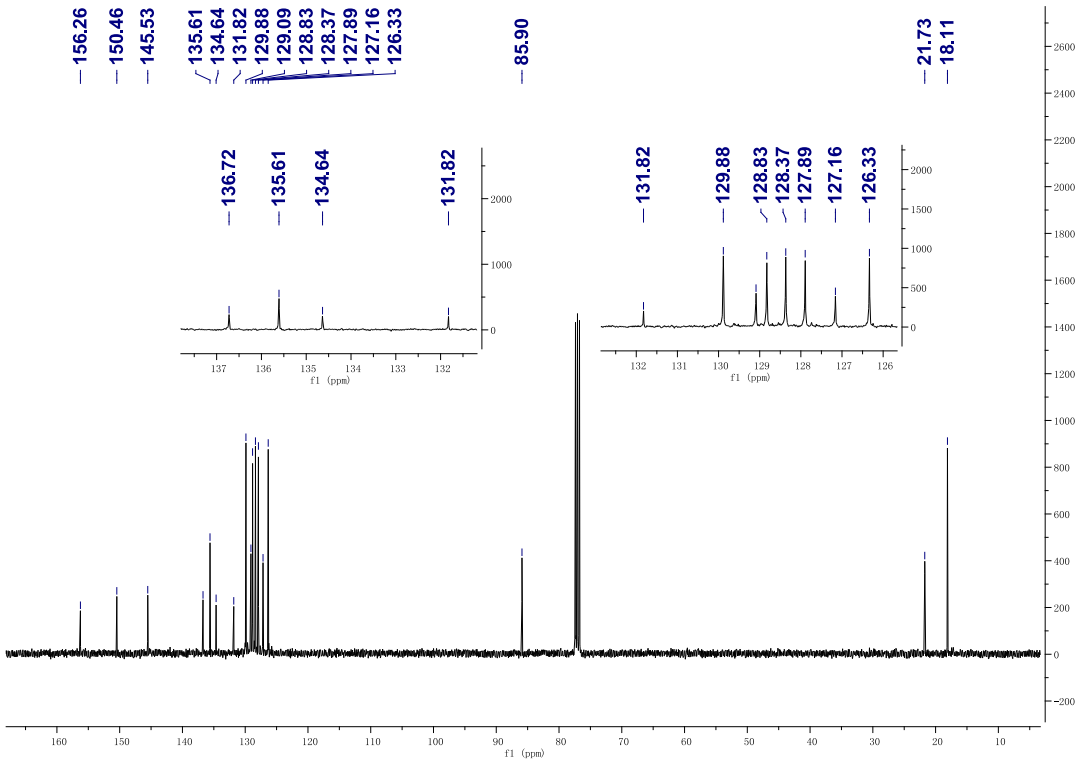
3-phenyl-*N*-(p-tolyl)-1-tosyl-1*H*-pyrazol-5-amine (8ag)





_N_-(2,6-dimethylphenyl)-3-phenyl-1-tosyl-1_H_-pyrazol-5-amine (8ah)





3-(4-(bis(4-(5-(*tert*-butylamino)-1-tosyl-1*H*-pyrazol-3-yl)phenyl)amino)phenyl)-*N*-(*tert*-butyl)-1-tosyl-1*H*-pyrazol-5-amine (10aa)