Supporting Information

Palladium-Catalyzed Tandem Reaction of *o*-Aminophenols, Bromoalkynes and Isocyanides to 4-Amine-benzo[b][1,4]oxazepines

Bifu Liu, Yibiao Li, Meizhou Yin, Wanqing Wu and Huanfeng Jiang*

School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, PR China

jianghf@scut.edu.cn

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I. General method

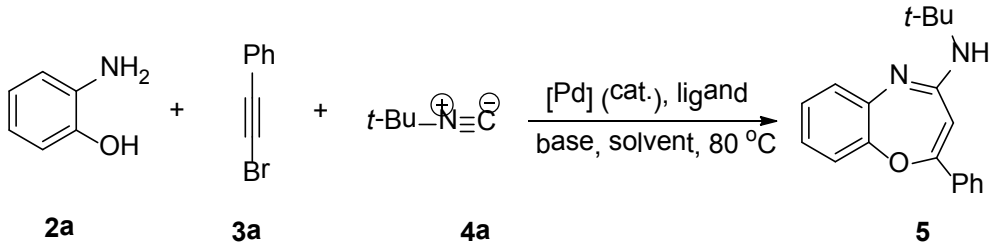
Melting points were measured with a BÜCHI B-545 melting point instrument and were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance 400 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.24 and 77.0 ppm, respectively, and chloroform is solvent with TMS as the internal standard. IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker Vector 22 spectrometer. GC–MS was obtained using electron ionization. HRMS (ESI) was carried out on a MAT 95XP (Thermo). TLC was performed by using commercially prepared 100–400 mesh silica gel plates (GF254) and visualization was effected at 254 nm. All the other chemicals were purchased from Aldrich Chemicals. Unless otherwise noted, all commercial material s and solvents were used without further purification.

II. Optimization of the reaction conditions

To test our hypothesis on the palladium-catalyzed tandem reaction to the synthesis of 4-amine-benzo[b][1,4]oxazepines, 2-aminophenol (**2a**), phenylethynyl bromide (**3a**) and *tert*-butylisocyanide (**4a**) were used as the starting materials for the model reaction (Table 1). Initially, we preformed the model reaction under the conditions similar to our previous work (Table 1, entry 1). Fortunately, the reaction proceeded as expected, albeit in low yield. With this promising preliminary result in hand, different catalysts, ligands, solvents, and bases were screened, and the results are summarized in Table 1. The screening of various bases showed that the identity of the base was proved critical to the success of palladium-catalyzed tandem reaction (entries 2-7). No desired product was detected in the absence of base (entry 2) and only trace amount of **5** was detected when Et_3N, K_2CO_3, DABCO, and *t*-BuOK were used as bases (entries 4-7). To our delight, the yield of **5** was improved to 68% by replacing CsF with Cs_2CO_3 as the base (entry 3). Further screening of the catalytic reaction conditions

revealed that dioxane was the solvent of choice for the reaction. It is worthy to note that non-polar solvent (entry 11) was much inferior to polar solvents (entries 8-10). Testing different palladium precursors and ligands are also listed in Table 1 (entries 12-17). The results show that $Pd_2(dba)_3$ (entry 12), $Pd_3(PPh_3)_4$ (entry 13) and Pd_2Cl_2/PPh_3 (entry 15) were also effective for this catalytic reaction system, but gave the desired product in a lower yield than $Pd(PPh_3)_2Cl_2/PPh_3$ (entry 8). Further optimization revealed that phosphine as ligand was essential in this reaction as well (entries 14, 16 and 17). Without phosphine, the yield of **5** dramatically decreased to 35% (entry 14). Notably, the reaction completed within 2 h and **5** was obtained in 86% isolated yield (entry 18). However, lower temperature disfavored the reaction and only gave 70% yield of **5** at 60 °C for 10 h (entry 19).

Table 1 Optimization of the Reaction Conditions[a]



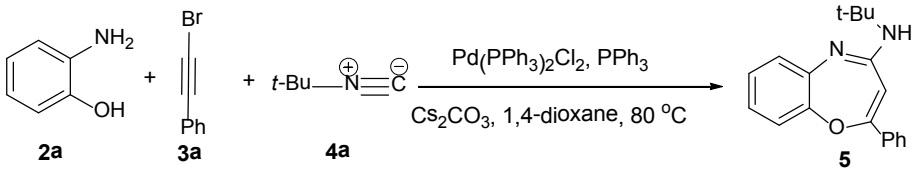
2a **3a** **4a** **5**

Entry	Pd source/Ligand	Base	Solvent	Yield (%)[b]
1	$Pd(PPh_3)_2Cl_2/PPh_3$	CsF	DMSO	17
2	$Pd(PPh_3)_2Cl_2/PPh_3$	-	DMSO	n.d.
3	$Pd(PPh_3)_2Cl_2/PPh_3$	Cs_2CO_3	DMSO	68
4	$Pd(PPh_3)_2Cl_2/PPh_3$	Et_3N	DMSO	trace
5	$Pd(PPh_3)_2Cl_2/PPh_3$	K_2CO_3	DMSO	trace
6	$Pd(PPh_3)_2Cl_2/PPh_3$	DABCO	DMSO	trace
7	$Pd(PPh_3)_2Cl_2/PPh_3$	*t*-BuOK	DMSO	trace
8	$Pd(PPh_3)_2Cl_2/PPh_3$	Cs_2CO_3	dioxane	88
9	$Pd(PPh_3)_2Cl_2/PPh_3$	Cs_2CO_3	DMF	79
10	$Pd(PPh_3)_2Cl_2/PPh_3$	Cs_2CO_3	CH_3CN	72
11	$Pd(PPh_3)_2Cl_2/PPh_3$	Cs_2CO_3	toulene	23
12	$Pd_2(dba)_3$	Cs_2CO_3	1,4-dioxane	78
13	$Pd_3(PPh_3)_4$	Cs_2CO_3	1,4-dioxane	81
14	$Pd(PPh_3)_2Cl_2$	Cs_2CO_3	1,4-dioxane	35
15	$PdCl_2/PPh_3$	Cs_2CO_3	1,4-dioxane	76
16	$Pd(PPh_3)_2Cl_2$/DPPP	Cs_2CO_3	1,4-dioxane	78

17	$Pd(PPh_3)_2Cl_2$/TCHP	Cs_2CO_3	1,4-dioxane	73
18[c]	**$Pd(PPh_3)_2Cl_2$/PPh_3**	**Cs_2CO_3**	**1,4-dioxane**	**90 (86)**
19[d]	$Pd(PPh_3)_2Cl_2$/PPh_3	Cs_2CO_3	1,4-dioxane	70

[a] Reaction conditions: **2a** (0.5 mmol), **3a** (0.5 mmol), **4a** (0.6 mmol), catalysts (5 mol %), ligands (10 mol %), base (2.0 equiv.), and solvent (2.0 mL) at 80 °C for 4 h. n.d. = not detected. DPPP = 1,3-bis(diphenylphosphino)propane. TCHP = tricyclohexylphosphine. [b] Yields are based on **3a**, detected by GC-MS. Number in parentheses is isolated yield. [c] Reaction at 80 °C for 2 h. [d] Reaction at 60 °C for 10 h.

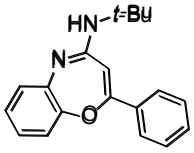
III. General procedure for the synthesis of 5



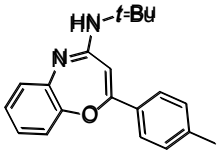
2a **3a** **4a** **5**

To the mixture of 2-aminophenol (**2a**) (0.5 mmol), $Pd(PPh_3)_2Cl_2$ (5 mol %) and PPh_3 (10 mol %) in 1,4-dioxane (1.0 mL) solvent, Cs_2CO_3 (2.0 equiv.) and phenylethynyl bromide (**3a**) were added successively in Schlenk tube, stirred for five minutes at the room temperature, *tert*-butylisocyanide (**4a**) (0.6 mmol) were added, then the mixture was stirred at 80 °C for 2 hours. Upon completion, the reaction mixture was extracted with ethyl acetate (3×10 mL), and the organic layers were combined, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure, and the residue was separated by column chromatography (hexane/EtOAc 10:1) to give the pure product **5**.

IV. Analytical data for compounds 5-36

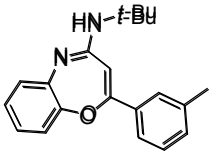


***N-tert*-butyl-2-phenylbenzo[b][1,4]oxazepin-4-amine (5)**
Yellow solid; MP = 109-111 °C; IR (KBr): 3437, 3060, 2964, 1599, 1545, 1563, 1515, 1357, 1272, 1228, 1122, 923, 752, 692; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.67 (d, J = 8.0 Hz, 2H), 7.28-7.24 (m, 2H), 7.15-7.10 (m, 2H), 6.94-6.83 (m, 3H), 5.73 (s, 1H), 4.48 (br. s, 1H), 1.43 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.7, 143.4, 139.2, 134.2, 133.1, 129.1, 128.4, 127.1, 125.2, 123.6,123.2, 114.2, 103.4, 52.3, 29.0; ESI-HRMS calcd for $C_{19}H_{21}N_2O$ $(M + H)^+$ 293.1648, found 293.1646.



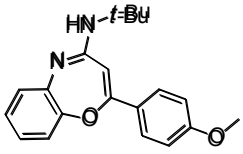
***N-tert*-butyl-2-*p*-tolylbenzo[b][1,4]oxazepin-4-amine (6)**
Yellow solid; MP = 99-101 °C; IR (KBr): 3433, 2963, 2923, 1599, 1564, 1514, 1355, 1273, 1227, 1123, 928, 833, 749. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.68 (d, J = 8.0 Hz, 2H), 7.21-7.17 (m, 3H), 7.03-6.93 (m, 3H), 5.82 (s,

1H), 4.58 (br. s, 1H), 2.35 (s, 3H), 1.53 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.9, 143.5, 138.7, 137.1, 133.2, 131.3, 129.1, 129.0, 125.1, 123.5,123.1, 114.2, 103.5, 52.3, 29.0, 21.3; ESI-HRMS calcd for $C_{20}H_{23}N_2O$ $(M + H)^+$ 307.1805, found 307.1808.



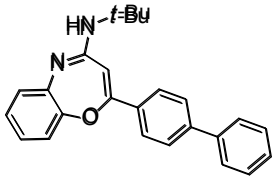
***N-tert*-butyl-2-*m*-tolylbenzo[b][1,4]oxazepin-4-amine (7)**

Yellow thickened liquid; IR (KBr): 3433, 2962, 2922, 1598, 1563, 1515, 1353, 1272, 1225, 1122, 749. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62 (d, J = 7.6 Hz, 1H), 7.56 (s, 1H), 7.28-7.18 (m, 2H), 7.07-6.93 (m, 4H), 5.81 (s, 1H), 4.58 (br. s, 1H), 2.37 (s, 3H), 1.53 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.8, 143.4, 139.1, 137.8, 134.1, 133.1, 129.9, 128.3, 128.0, 126.2, 125.2,123.6, 123.2, 114.2, 103.5, 52.3, 29.1, 21.6; ESI-HRMS calcd for $C_{20}H_{23}N_2O$ $(M + H)^+$ 307.1805, found 307.1807.



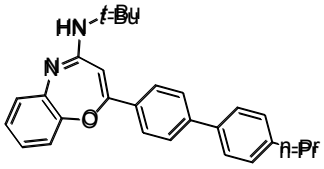
***N-tert*-butyl-2-(4-methoxyphenyl)benzo[b][1,4]oxazepin-4-amine (8)**

Yellow thickened liquid; IR (KBr): 3430, 2964, 1602, 1563, 1511, 1356, 1250, 1178, 1122, 1032, 928, 838, 750. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 7.2 Hz, 1H), 7.04-6.92 (m, 5H), 5.83 (s, 1H), 4.57 (br. s, 1H), 3.83 (s, 3H), 1.55 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.7, 149.1, 143.6, 137.9, 134.0, 130.4, 126.9, 125.1, 123.5, 123.1, 114.1, 113.9, 103.3, 55.2, 52.3, 29.1; ESI-HRMS calcd for $C_{20}H_{23}N_2O_2$ $(M + H)^+$ 323.1754, found 323.1751.



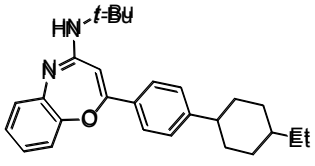
***N-tert*-butyl-2-(biphenyl-4-yl)benzo[b][1,4]oxazepin-4-amine (9)**

Yellow solid; MP = 59-61 ^{o}C; IR (KBr): 3437, 3060, 2963, 1597, 1562, 1516, 1484, 1357, 1273, 1229, 1125, 927, 847, 753, 697. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86 (d, J = 8.0 Hz, 2H), 7.63-7.61 (m, 4H), 7.45-7.41 (m, 2H), 7.35-7.31 (m, 1H), 7.23 (d, J = 7.6 Hz, 1H), 7.07 (d, J = 7.2 Hz, 1H), 7.02-6.92 (m, 2H), 5.87 (s, 1H), 4.61 (br. s, 1H), 1.55 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.3, 140.6, 139.6, 139.2, 133.3, 133.1, 129.5, 128.8, 127.3, 127.0, 126.9, 125.2, 123.7, 123.3, 52.3, 29.0; ESI-HRMS calcd for $C_{25}H_{25}N_2O$ $(M + H)^+$ 369.1961, found 369.1957.



***N-tert*-butyl-2-(4'-propylbiphenyl-4-yl)benzo[b][1,4]oxazepin-4-amine (10)**

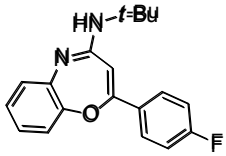
Yellow thickened liquid; IR (KBr): 3781, 3696, 3660, 3432, 1595, 1564, 1383, 1231, 802, 748. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.85 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.0 Hz, 2H), 7.27-7.21 (m, 3H), 7.09-6.96 (m, 3H), 5.89 (s, 1H), 4.62 (br. s, 1H), 2.63 (t, J = 7.8 Hz, 2H), 1.71-1.64 (m, 2H), 1.56 (s, 9H), 0.98 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.8, 143.4, 142.0, 139.7, 137.9, 133.2, 133.0, 129.5, 128.9, 126.8, 126.7, 125.2, 123.7, 123.3, 114.3, 103.1, 52.4, 37.7, 29.1, 24.5, 13.9; ESI-HRMS calcd for $C_{28}H_{31}N_2O$ $(M + H)^+$ 411.2431, found 411.2437.



***N-tert*-butyl-2-(4-(4-ethylcyclohexyl)phenyl)benzo[b][1,4]oxazepin-4-amine (11)**

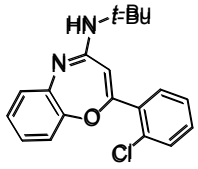
Yellow thickened liquid; IR (KBr): 3430, 2962, 2922, 2852, 1597,

1563, 1515, 1454, 1357, 1274, 1228, 1123, 927, 842, 750. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.72 (d, J = 8.4 Hz, 2H), 7.24-7.17 (m, 3H), 7.05-6.94 (m, 3H), 5.84 (s, 1H), 4.59 (br. s, 1H), 2.54-2.44 (m, 1H), 1.94-1.85 (m, 5H), 1.55 (s, 9H), 1.30-1.25 (m, 4H), 1.07-1.04 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.8, 143.4, 142.0, 139.7, 137.9, 133.2, 133.0, 129.5, 128.9, 126.8, 126.7, 125.2, 123.7, 123.3, 114.3, 103.1, 52.4, 37.7, 29.1, 24.5, 13.9; ESI-HRMS calcd for $C_{27}H_{35}N_2O$ $(M + H)^+$ 403.2744, found 403.2746.



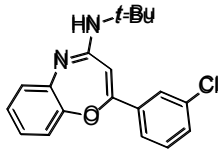
N-tert-butyl-2-(4-fluorophenyl)benzo[b][1,4]oxazepin-4-amine (12)

Yellow solid; MP = 71-73 °C; IR (KBr): 3780, 3698, 3442, 2961, 2924, 1597, 1564, 1511, 1356, 1230, 1125, 929, 842, 749. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.78-7.74 (m, 2H), 7.22-7.20 (m, 1H), 7.09-6.95 (m, 5H), 5.82 (s, 1H), 4.57 (br. s, 1H), 1.54 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.2 (d, J = 246.3 Hz), 148.6, 143.2, 138.8, 133.1, 130.7 (d, J = 7.9 Hz), 130.4 (d, J = 3.4 Hz), 125.3, 123.7, 123.3, 115.4 (d, J = 21.3 Hz), 114.2, 102.3, 52.4, 29.0; ESI-HRMS calcd for $C_{19}H_{20}FN_2O$ $(M + H)^+$ 311.1554, found 311.1555.



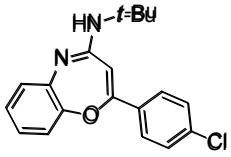
N-tert-butyl-2-(2-chlorophenyl)benzo[b][1,4]oxazepin-4-amine (13)

Yellow solid; MP = 64-66 °C; IR (KBr): 3442, 2961, 2923, 1595, 1563, 1517, 1480, 1355, 1231, 1226, 884, 749. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40 (d, J = 8.0 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.24-7.22 (m, 1H), 7.13 (t, J = 7.6 Hz, 1H), 7.03-6.94 (m, 3H), 6.24 (s, 1H), 4.68 (br. s, 1H), 1.55 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.4, 143.0, 140.1, 133.1, 133.0, 132.0, 130.2, 129.4, 128.1, 126.7, 125.3, 123.7, 123.4, 114.2, 98.8, 52.4, 29.0; ESI-HRMS calcd for $C_{19}H_{20}N_2ClO$ $(M + H)^+$ 327.1259, found 327.1261.



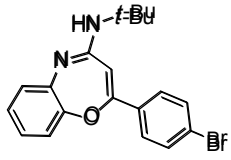
N-tert-butyl-2-(3-chlorophenyl)benzo[b][1,4]oxazepin-4-amine (14)

Yellow thickened liquid; IR (KBr): 3442, 2963, 2924, 1598, 1565, 1517, 1480, 1360, 1270, 1228, 1119, 1033, 942, 751. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.89 (s, 1H), 7.66 (d, J = 7.6 Hz, 1H), 7.35-7.31 (m, 1H), 7.28-7.24 (m, 2H), 7.11-7.00 (m, 3H), 5.81 (s, 1H), 4.62 (br. s, 1H), 1.58 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.2, 143.0, 140.0, 136.1, 134.2, 132.9, 129.5, 128.8, 127.1, 127.0, 125.3, 123.8, 123.5, 114.3, 101.9, 52.4, 29.0; ESI-HRMS calcd for $C_{19}H_{20}N_2ClO$ $(M + H)^+$ 327.1259, found 327.1257.



N-tert-butyl-2-(4-chlorophenyl)benzo[b][1,4]oxazepin-4-amine (15)

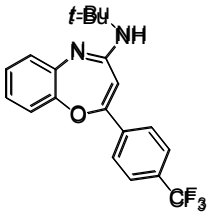
Yellow thickened liquid; IR (KBr): 3785, 3439, 2964, 1598, 1563, 1516, 1484, 1384, 1271, 1127, 1093, 836, 749. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.71 (d, J = 8.8 Hz, 2H), 7.34 (d, J = 8.8 Hz, 2H), 7.23-7.21 (m, 1H), 7.04-6.96 (m, 3H), 5.79 (s, 1H), 4.58 (br. s, 1H), 1.54 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.4, 143.1, 139.5, 133.0, 132.8, 132.6, 130.2, 128.6, 125.3, 123.8, 123.4, 114.2, 102.1, 52.4, 29.0; ESI-HRMS calcd for $C_{19}H_{20}N_2ClO$ $(M + H)^+$ 327.1259, found 327.1258.



N-tert-butyl-2-(4-bromophenyl)benzo[b][1,4]oxazepin-4-amine (16)

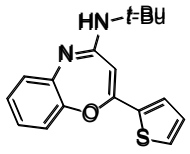
Yellow solid; MP = 94-96 °C; IR (KBr): 3439, 2964, 1597, 1562, 1515, 1482, 1355, 1271, 1226, 1128, 836, 748. ^{1}H NMR (400 MHz, $CDCl_3$) δ =

7.64 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.8 Hz, 1H), 7.04-6.96 (m, 3H), 5.76 (s, 1H), 4.57 (br. s, 1H), 1.55 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.3, 143.1, 139.5, 133.2, 132.9, 131.5, 130.5, 125.3, 123.7, 123.4, 120.7, 114.2, 102.1, 52.4, 29.0; ESI-HRMS calcd for $C_{19}H_{20}BrN_2O$ $(M + H)^+$ 371.0754, found 371.0759.



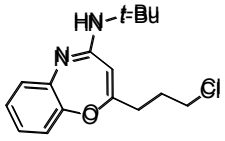
***N-tert*-butyl-2-(4-(trifluoromethyl)phenyl)benzo[b][1,4]oxazepin-4-amine (17)**

Yellow thickened liquid; IR (KBr): 3780, 3442, 2963, 1764, 1598, 1564, 1383, 1322, 1238, 1127, 1065, 850, 750. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H), 7.24-7.23 (m, 1H), 7.05-6.97 (m, 3H), 5.83 (s, 1H), 4.60 (br. s, 1H), 1.54 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.07, 142.9, 140.6, 137.9, 132.9, 129.0, 128.5 (q, J = 32.3 Hz), 125.3 (q, J = 3.8 Hz), 124.2 (q, J = 270.2 Hz), 123.9, 123.6, 114.3, 101.7, 52.5, 29.0; ESI-HRMS calcd for $C_{20}H_{20}N_2F_3O$ $(M + H)^+$ 361.1522, found 361.1506.



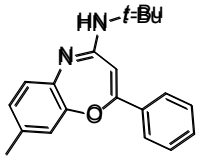
***N-tert*-butyl-2-(thiophen-2-yl)benzo[b][1,4]oxazepin-4-amine (18)**

Reddish-brown thickened liquid; IR (KBr): 3783, 3432, 2964, 2924, 1595, 1562, 1515, 1360, 1230, 1111, 832, 750, 696. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34 (d, J = 4.8 Hz, 1H), 7.22-7.21 (m, 2H), 7.15-7.11 (m, 1H), 7.06-7.04 (m, 1H), 7.02-6.96 (m, 2H), 6.23 (s, 1H), 4.50 (br. s, 1H), 1.53 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.4, 143.5, 136.9, 136.8, 133.2, 127.2, 126.6, 126.3, 125.3, 123.7, 123.3, 114.4, 98.4, 52.3, 29.1; ESI-HRMS calcd for $C_{17}H_{19}N_2OS$ $(M + H)^+$ 299.1213, found 299.1202.



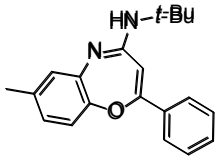
***N-tert*-butyl-2-(3-chloropropyl)benzo[b][1,4]oxazepin-4-amine (19)**

Yellow thickened liquid; IR (KBr): 3784, 3699, 2962, 1764, 1568, 1239, 1056, 750. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.15 (d, J = 6.4 Hz, 1H), 6.95-6.87 (m, 3H), 4.96 (s, 1H), 4.40 (br. s, 1H), 3.57 (t, J = 6.6 Hz, 2H), 2.46-2.40 (m, 2H), 1.96-1.89 (m, 2H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.3, 144.0, 140.3, 133.2, 125.0, 123.5, 122.8, 114.0, 102.9, 52.1, 44.5, 32.0, 29.0, 21.8; ESI-HRMS calcd for $C_{16}H_{22}N_2OCl$ $(M + H)^+$ 293.1415, found 293.1406.



***N-tert*-butyl-8-methyl-2-phenylbenzo[b][1,4]oxazepin-4-amine (20)**

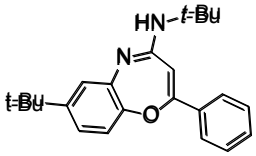
Yellow thickened liquid; IR (KBr): 3435, 2962, 2922, 2360, 1604, 1567, 1502, 1355, 1274, 1158, 1122, 811, 749, 690. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.78 (d, J = 8.0 Hz, 2H), 7.37 (t, J = 7.6 Hz, 2H), 7.24 (t, J = 7.2 Hz, 1H), 7.09 (d, J = 8.0 Hz, 1H), 6.87 (s, 1H), 6.80 (d, J =7.6 Hz, 1H), 5.82 (s, 1H), 4.52 (br. s, 1H), 2.31 (s, 3H), 1.53 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.2, 143.0, 139.3, 134.4, 133.7, 130.6, 129.0, 128.4, 127.0, 124.8, 123.9, 114.7, 103.1, 52.2, 29.1, 21.0; ESI-HRMS calcd for $C_{20}H_{23}N_2O$ $(M + H)^+$ 307.1805, found 307.1800.



***N-tert*-butyl-7-methyl-2-phenylbenzo[b][1,4]oxazepin-4-amine (21)**

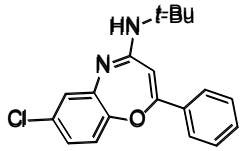
Yellow thickened liquid; IR (KBr): 3436, 2962, 2922, 1599, 1564, 1517, 1357, 1269, 1227, 1119, 803, 753, 692. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.78 (d, J = 8.0 Hz, 2H), 7.37 (t, J = 7.6 Hz, 2H), 7.27-7.22 (m, 1H), 7.04 (s,

1H), 6.93 (d, J = 8.4 Hz, 1H), 6.79-6.76 (m, 1H), 5.82 (s, 1H), 4.58 (br. s, 1H), 2.30 (s, 3H), 1.54 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.8, 141.2, 139.4, 134.4, 132.7, 132.7, 129.0, 128.4, 127.0, 125.6, 124.2, 113.8, 103.1, 52.3, 29.0, 20.7; ESI-HRMS calcd for $C_{20}H_{23}N_2O$ $(M + H)^+$ 307.1805, found 307.1803.



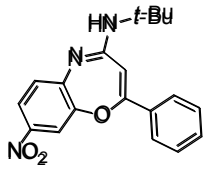
***N,7-di-tert*-butyl-2-phenylbenzo[b][1,4]oxazepin-4-amine (22)**

Yellow thickened liquid; IR (KBr): 3437, 2961, 16009, 1565, 1517, 1452, 1359, 1236, 1137, 811, 753, 693. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.76 (d, J = 7.6 Hz, 2H), 7.35 (t, J = 7.8 Hz, 2H), 7.22-7.21 (m, 2H), 7.00-6.94 (m, 2H), 5.81 (s, 1H), 4.56 (br. s, 1H), 1.54 (s, 9H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.8, 146.3, 141.1, 139.5, 134.4, 132.4, 129.0, 128.4, 127.0, 122.2, 120.7, 113.6, 103.1, 52.3, 34.3, 31.5, 29.1; ESI-HRMS calcd for $C_{23}H_{29}N_2O$ $(M + H)^+$ 349.2274, found 349.2288.



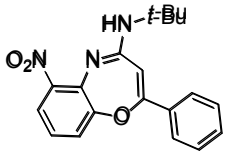
***N-tert*-butyl-7-chloro-2-phenylbenzo[b][1,4]oxazepin-4-amine (23)**

Yellow solid; MP = 124-126 ^{o}C; IR (KBr): 3435, 2963, 1597, 1558, 1479, 1358, 1253, 1227, 1071, 954, 802, 753. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75 (d, J = 8.0 Hz, 2H), 7.38 (t, J = 7.6 Hz, 2H), 7.26 (t, J = 8.2 Hz, 1H), 7.19 (s, 1H), 6.95-6.88 (m, 2H), 5.87 (s, 1H), 4.71 (br. s, 1H), 1.53 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.3, 142.0, 138.7, 134.3, 133.9, 129.2, 128.5, 127.9, 127.4, 124.7, 123.1, 115.1, 104.2, 52.6, 29.0; ESI-HRMS calcd for $C_{19}H_{20}N_2ClO$ $(M + H)^+$ 327.1259, found 327.1273.



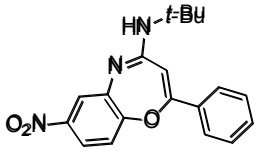
***N-tert*-butyl-8-nitro-2-phenylbenzo[b][1,4]oxazepin-4-amine (24)**

Yellow-brown solid; MP = 124-126 ^{o}C; IR (KBr): 3434, 2923, 2855, 2362, 1529, 1382, 1313, 1246, 1074, 846, 748, 684. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.90 (d, J = 7.2 Hz, 2H), 7.75 (d, J = 8.0 Hz, 2H), 7.41 (t, J = 7.6 Hz, 2H), 7.31 (t, J = 7.4 Hz, 1H), 7.19 (d, J = 9.2 Hz, 1H), 5.97 (s, 1H), 5.04 (br. s, 1H), 1.56 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 150.9, 142.7, 142.7, 140.0, 137.7, 133.1, 129.4, 128.7, 128.1, 124.5, 119.6, 110.2, 106.1, 53.2, 28.9; ESI-HRMS calcd for $C_{19}H_{20}N_3O_3$ $(M + H)^+$ 339.1577, found 339.1581.



***N-tert*-butyl-6-nitro-2-phenylbenzo[b][1,4]oxazepin-4-amine (25)**

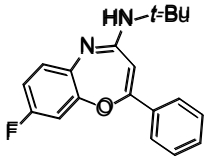
Yellow-brown solid; MP = 130-132 ^{o}C; IR (KBr): 3422, 2965, 1530, 1454, 1381, 1268, 1125, 737, 693. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.74 (d, J = 7.6 Hz, 2H), 7.38 (t, J = 7.4 Hz, 3H), 7.29 (t, J = 7.2 Hz, 1H), 7.16 (d, J = 8.0 Hz, 1H), 6.93 (t, J = 8.0 Hz, 1H), 5.98 (s, 1H), 5.04 (br. s, 1H), 1.52 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 150.1, 144.1, 137.5, 133.2, 129.3, 128.5, 127.9, 121.7, 118.2, 117.6, 105.8, 53.2, 28.8; ESI-HRMS calcd for $C_{19}H_{20}N_3O_3$ $(M + H)^+$ 339.1577, found 339.1588.



***N-tert*-butyl-7-nitro-2-phenylbenzo[b][1,4]oxazepin-4-amine (26)**

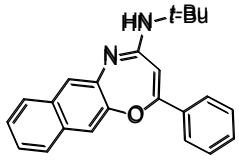
Yellow-brown solid; MP = 134-136 ^{o}C; IR (KBr): 3429, 2965, 1589, 1556, 1518, 1332, 1262, 1226, 1120, 891, 749, 692. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02 (d, J = 2.8 Hz, 1H), 7.82 (dd, J_1 = 2.4 Hz, J_2 = 8.8 Hz, 1H), 7.73 (d, J = 7.6 Hz, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.29 (t, J = 7.4 Hz, 1H), 7.04 (t, J = 8.8 Hz, 1H), 5.97 (s, 1H), 4.87 (br. s, 1H), 1.55 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.6, 148.2,

143.6, 137.6, 133.8, 133.1, 129.4, 128.5, 128.0, 120.3, 119.1, 114.3, 105.9, 52.9, 28.9; ESI-HRMS calcd for $C_{19}H_{20}N_3O_3$ $(M + H)^+$ 339.1577, found 339.1571.



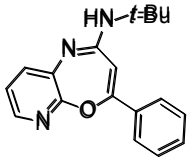
***N-tert*-butyl-8-fluoro-2-phenylbenzo[b][1,4]oxazepin-4-amine (27)**

Yellow thickened liquid; IR (KBr): 3445, 2965, 1604, 1570, 1495, 1356, 1227, 1104, 980, 841, 689. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.76 (d, J = 7.6 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.28 (t, J = 7.4 Hz, 1H), 7.17-7.14 (m, 1H), 6.80 (dd, J_1 = 2.4 Hz, J_2 = 8.8 Hz, 1H), 6.76-6.71 (m, 1H), 5.89 (s, 1H), 4.58 (br. s, 1H), 1.56 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.0 (d, J = 240.7 Hz), 148.0, 143.5, 143.4, 138.5, 133.9, 129.1, 128.4, 127.4, 125.4 (d, J = 9.3 Hz), 109.8 (d, J = 22.1 Hz), 104.1, 102.1 (d, J = 26.6 Hz), 52.3, 29.0; ESI-HRMS calcd for $C_{19}H_{20}FN_2O$ $(M + H)^+$ 311.1554, found 311.1557.



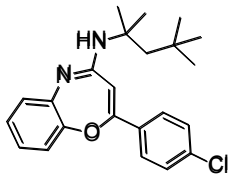
***N-tert*-butyl-2-phenylnaphtho[2,3-b][1,4]oxazepin-4-amine (28)**

Yellow solid; MP = 129-131 ^{o}C; IR (KBr): 3433, 3056, 2965, 1567, 1518, 1358, 1237, 1186, 869, 746. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.81 (d, J = 8.0 Hz, 2H), 7.70-7.58 (m, 2H), 7.58 (s, 1H), 7.40-7.35 (m, 3H), 7.30-7.26 (m, 3H), 5.89 (s, 1H), 4.63 (br. s, 1H), 1.55 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.2, 143.1, 138.8, 133.9, 133.2, 131.1, 131.0, 129.3, 128.4, 127.5, 127.1, 126.5, 124.7, 124.1, 121.7, 109.6, 105.0, 52.4, 29.1; ESI-HRMS calcd for $C_{23}H_{23}N_2O$ $(M + H)^+$ 343.1805, found 343.1809.



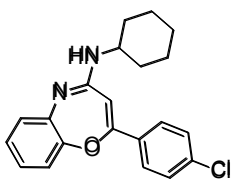
***N-tert*-butyl-4-phenylpyrido[2,3-b][1,4]oxazepin-2-amine (29)**

Yellow solid; MP = 89-91 ^{o}C; IR (KBr): 3358, 3061, 2967, 1586, 1545, 1434, 1358, 1257, 1210, 1126, 797, 754, 692. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86-7.83 (m, 3H), 7.45-7.43 (m, 1H), 7.34 (t, J = 7.8 Hz, 2H), 7.24-7.19 (m, 1H), 6.98-6.94 (m, 1H), 5.95 (s, 1H), 4.92 (br. s, 1H), 1.52 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 150.5, 149.1, 140.9, 139.3, 133.3, 132.1, 129.4, 128.5, 127.6, 120.2, 105.6, 52.5, 28.8; ESI-HRMS calcd for $C_{18}H_{20}N_3O$ $(M + H)^+$ 294.1601, found 294.1602.



2-(4-chlorophenyl)-*N*-(2,4,4-trimethylpentan-2-yl)benzo[b][1,4]oxazepin-4-amine (32)

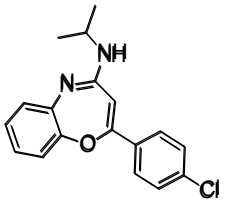
Yellow solid; MP = 95-97 ^{o}C; IR (KBr): 3442, 2955, 1598, 1564, 1518, 1483, 1356, 1272, 1227, 1130, 924, 839, 750. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.68 (d, J = 8.8 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 6.4 Hz, 1H), 7.02-6.93 (m, 3H), 5.74 (s, 1H), 4.58 (br. s, 1H), 1.94 (s, 2H), 1.57 (s, 6H), 1.03 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.2, 143.1, 139.7, 133.0, 132.9, 132.6, 130.2, 128.6, 125.3, 123.6, 123.4, 114.2, 102.2, 56.3, 51.6, 31.8, 31.6, 29.4; ESI-HRMS calcd for $C_{23}H_{28}N_2ClO$ $(M + H)^+$ 383.1885, found 383.1871.



2-(4-chlorophenyl)-*N*-cyclohexylbenzo[b][1,4]oxazepin-4-amine (33)

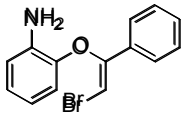
Yellow thickened liquid; IR (KBr): 3784, 3699, 3410, 2930, 2854, 1647, 1582, 1488, 1351, 1214, 1095, 1010, 821, 752. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 7.6 Hz, 2H), 7.13 (d, J = 8.0 Hz, 1H), 7.07 (t, J = 7.4 Hz, 1H), 7.01-6.90 (m, 2H), 5.85 (s, 1H), 3.92 (br. s, 1H), 2.10-2.08 (m, 2H), 1.80-1.68 (m, 3H), 1.27-1.16 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ =

150.5, 136.2, 132.0, 128.9, 127.2, 125.8, 123.8, 123.7, 120.6, 120.3, 116.2, 108.6, 52.0, 33.3, 25.7, 24.9; ESI-HRMS calcd for $C_{21}H_{22}ClN_2O$ $(M + H)^+$ 353.1415, found 353.1423.



2-(4-chlorophenyl)-*N*-isopropylbenzo[b][1,4]oxazepin-4-amine (34)

Yellow thickened liquid; IR (KBr): 3436, 2965, 1597, 1557, 1515, 1484, 1355, 1267, 1225, 837, 748,691. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.20 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 7.24-7.21 (m, 1H), 7.05-6.96 (m, 3H), 5.82 (s, 1H), 4.59 (br. s, 1H), 4.43-4.34 (m, 1H), 1.29 (d, J = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.8, 143.2, 139.2, 133.1, 132.7, 132.7, 130.2, 128.6, 125.0, 123.9, 123.5, 114.3, 102.4, 42.6, 22.8; ESI-HRMS calcd for $C_{18}H_{18}ClN_2O$ $(M + H)^+$ 313.1102, found 313.1102.

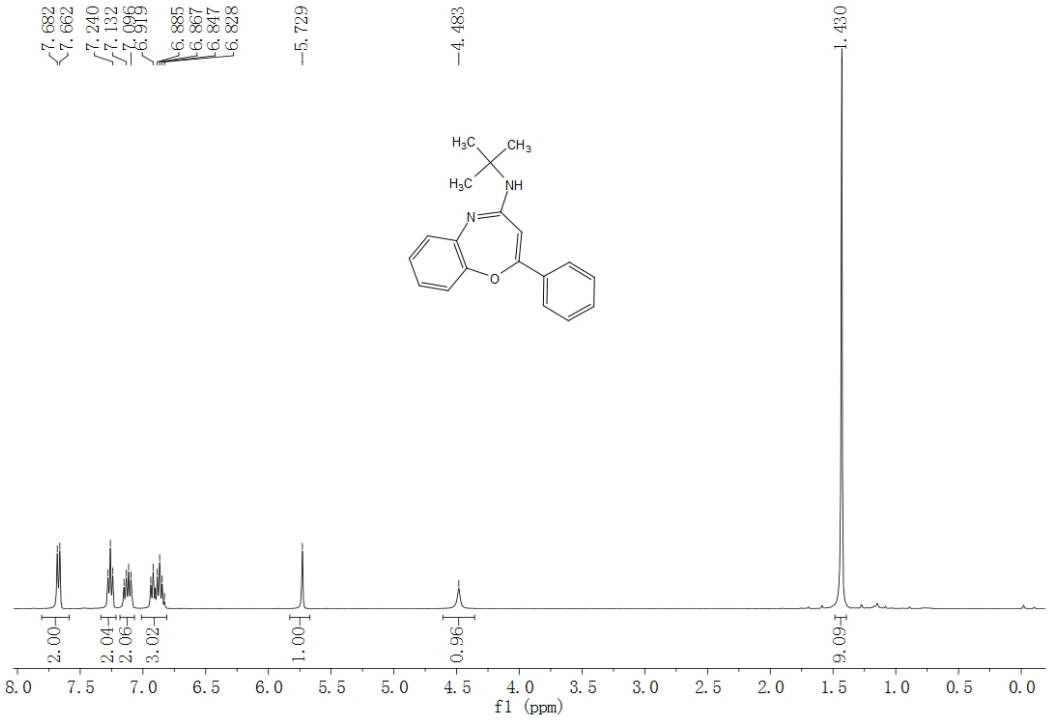


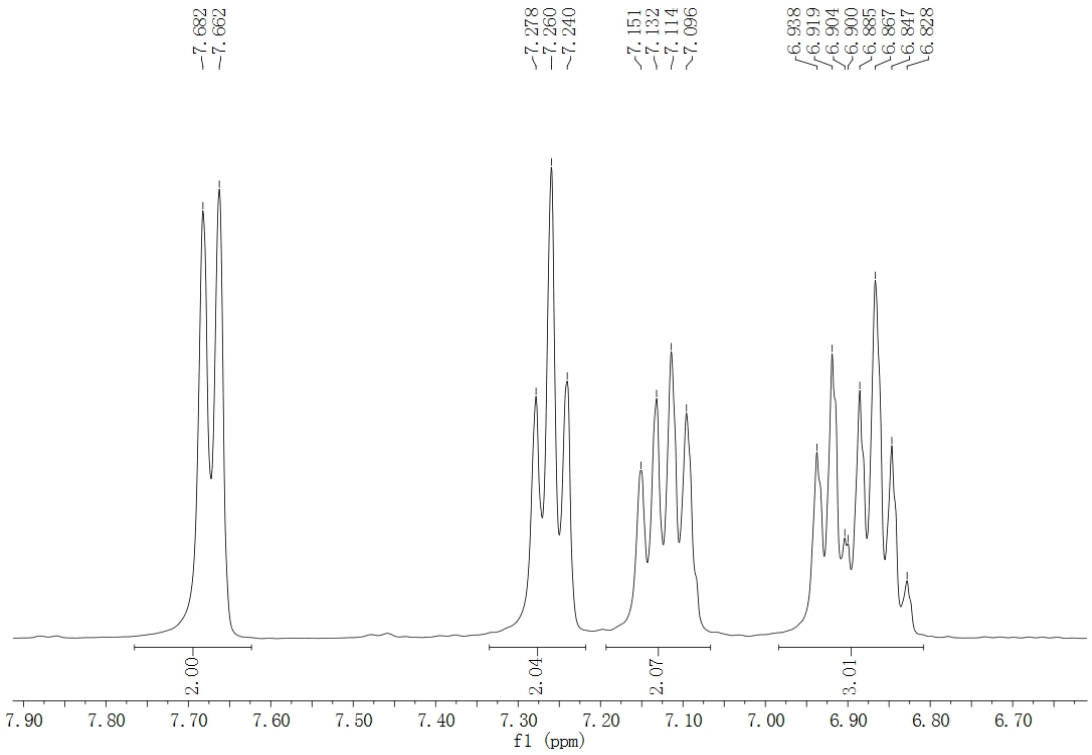
(*Z*)-2-((2-bromo-1-phenylvinyl)oxy)aniline (36)

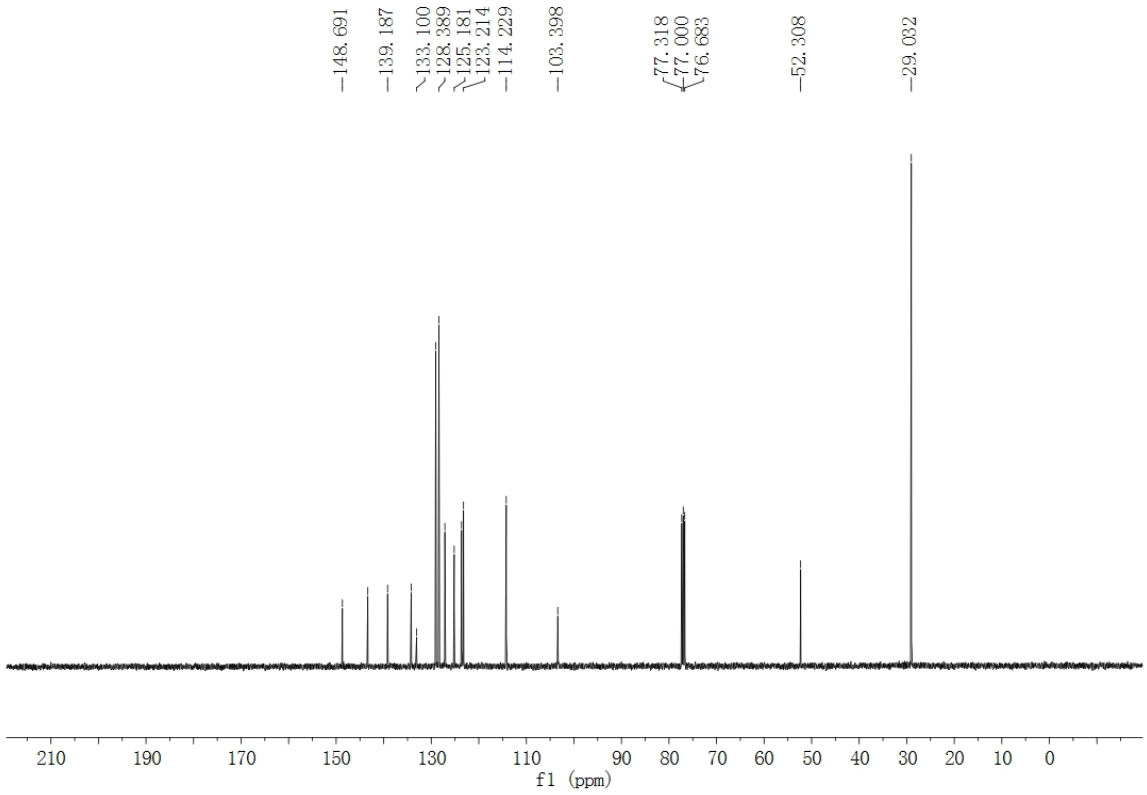
Yellow thickened liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47-7.45 (m, 2H), 7.31-7.30 (m, 3H), 6.83-6.75 (m, 2H), 6.61 (d, J = 8.0 Hz, 1H), 6.54 (d, J = 7.4 Hz, 1H), 6.47 (s, 1H), 3.76 (br. s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.6, 143.2, 136.2, 133.4, 129.2, 128.7, 125.6, 123.0, 118.3, 116.0, 14.7, 94.7; ESI-HRMS calcd for $C_{14}H_{13}BrNO$ $(M + H)^+$ 290.0175, found 290.0173.

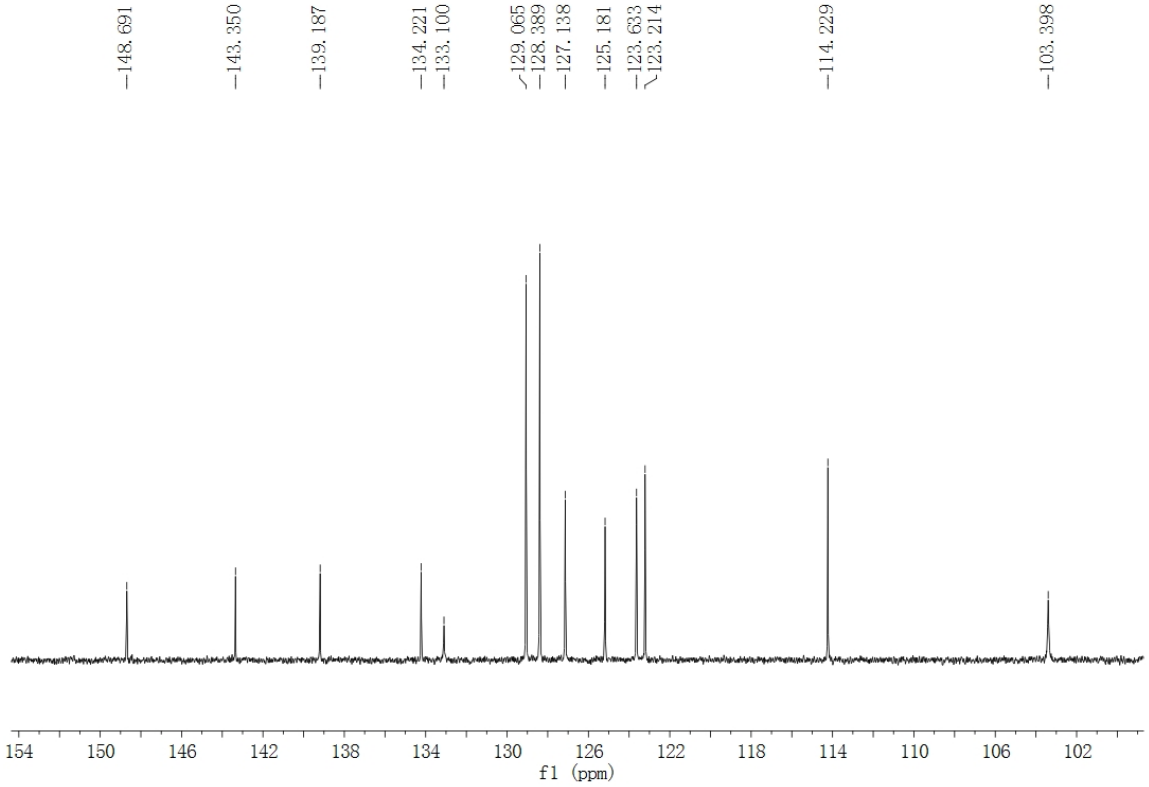
V. ^{1}H and ^{13}C NMR spectra of compounds 5-36

^{1}H NMR and ^{13}C NMR of *N-tert*-butyl-2-phenylbenzo[b][1,4]oxazepin-4-amine (5)

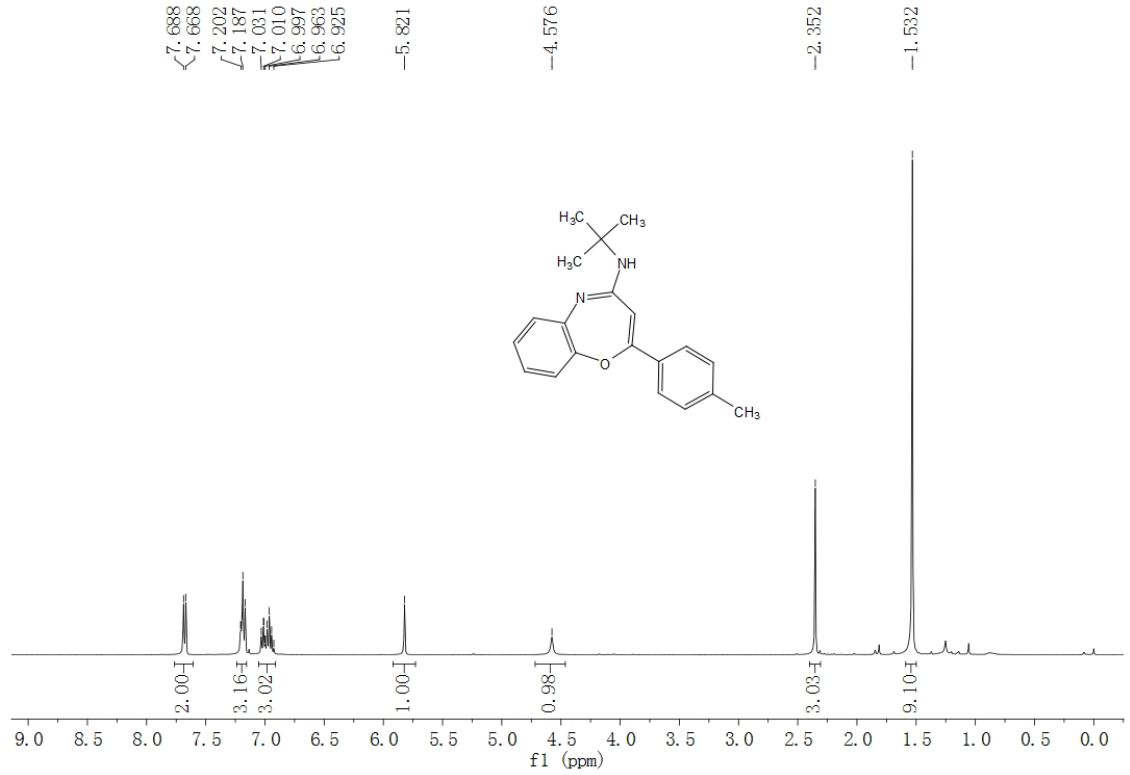


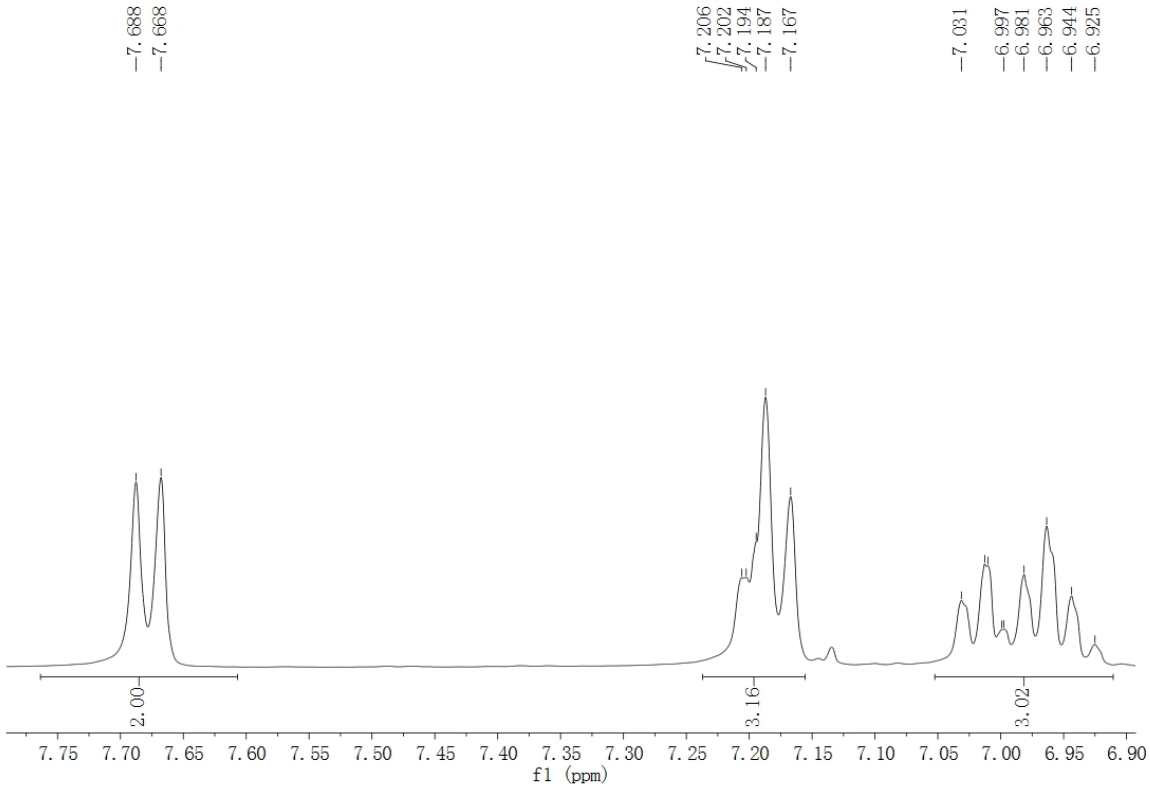

7.682
7.662
7.278
7.260
7.240
7.151
7.132
7.114
7.096
6.938
6.919
6.904
6.900
6.885
6.867
6.847
6.828
2.00
2.04
2.07
3.01
7.90 7.80 7.70 7.60 7.50 7.40 7.30 7.20 7.10 7.00 6.90 6.80 6.70
f1 (ppm)

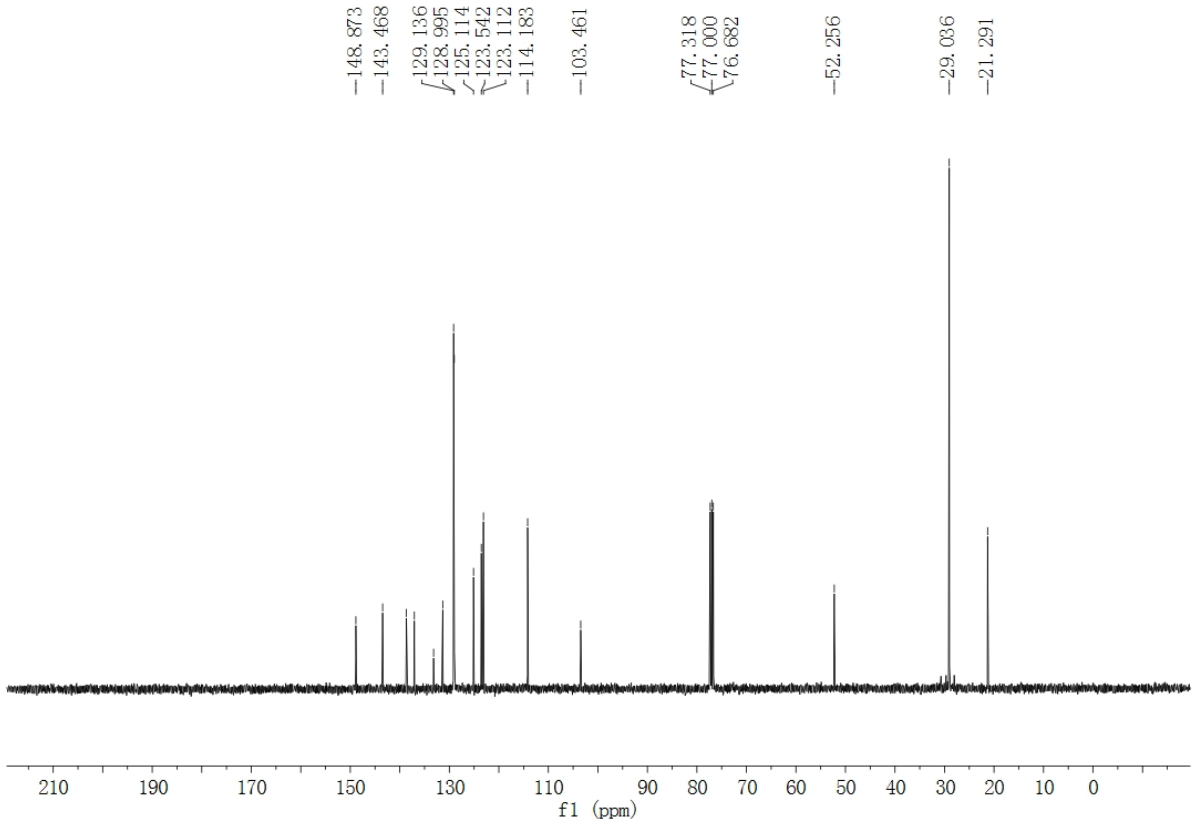

148.691
139.187
133.100
128.389
125.181
123.214
114.229
103.398
77.318
77.000
76.683
52.308
29.032
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

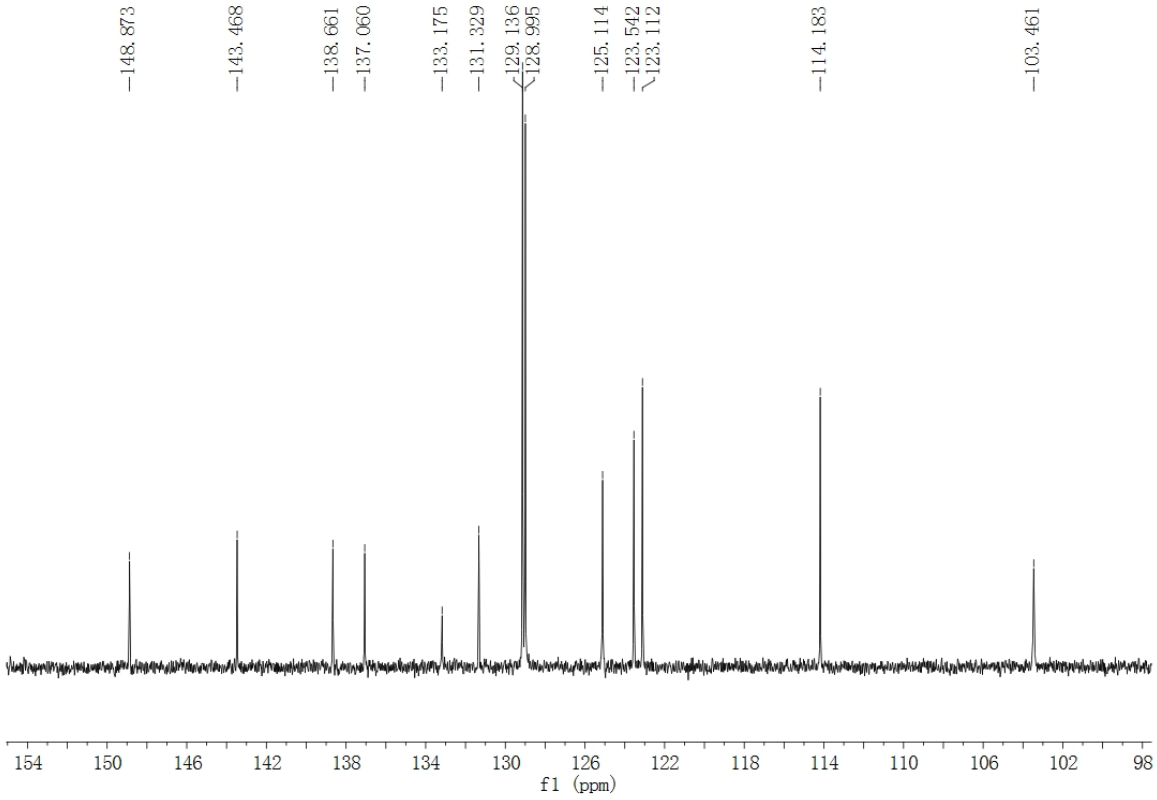


^{1}H NMR and ^{13}C NMR of *N-tert*-butyl-2-*p*-tolylbenzo[b][1,4]oxazepin-4-amine (6)

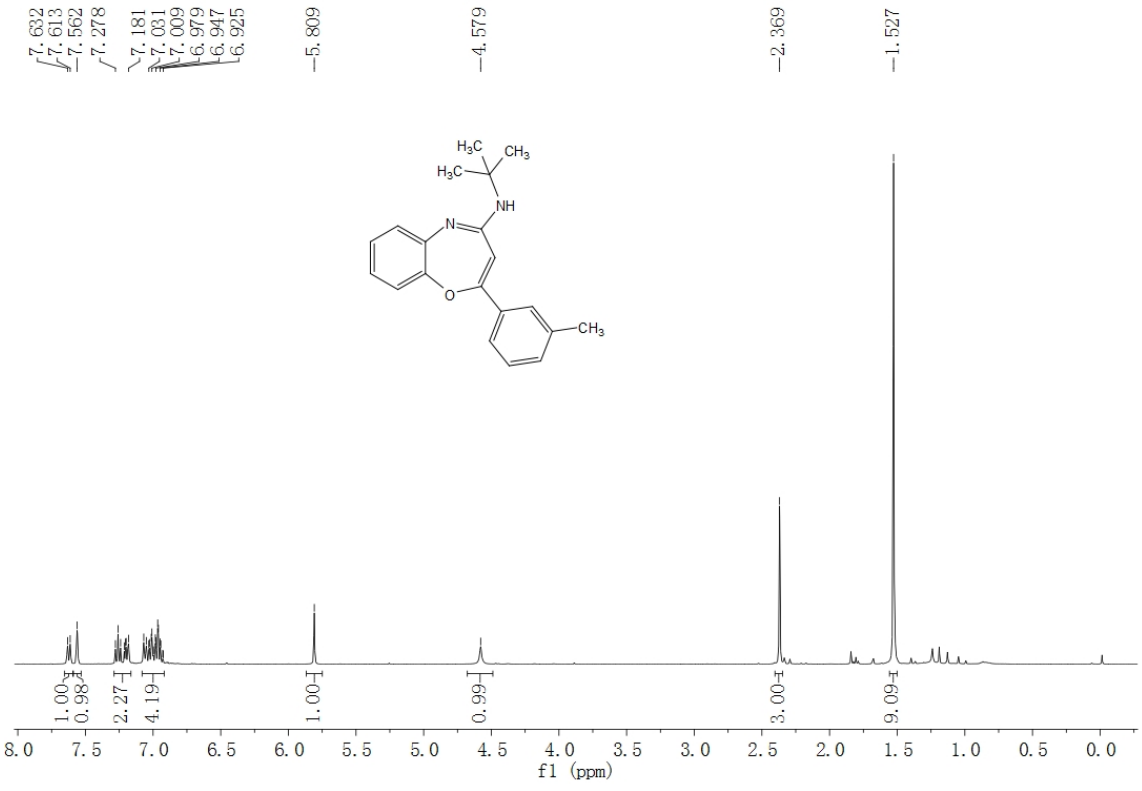


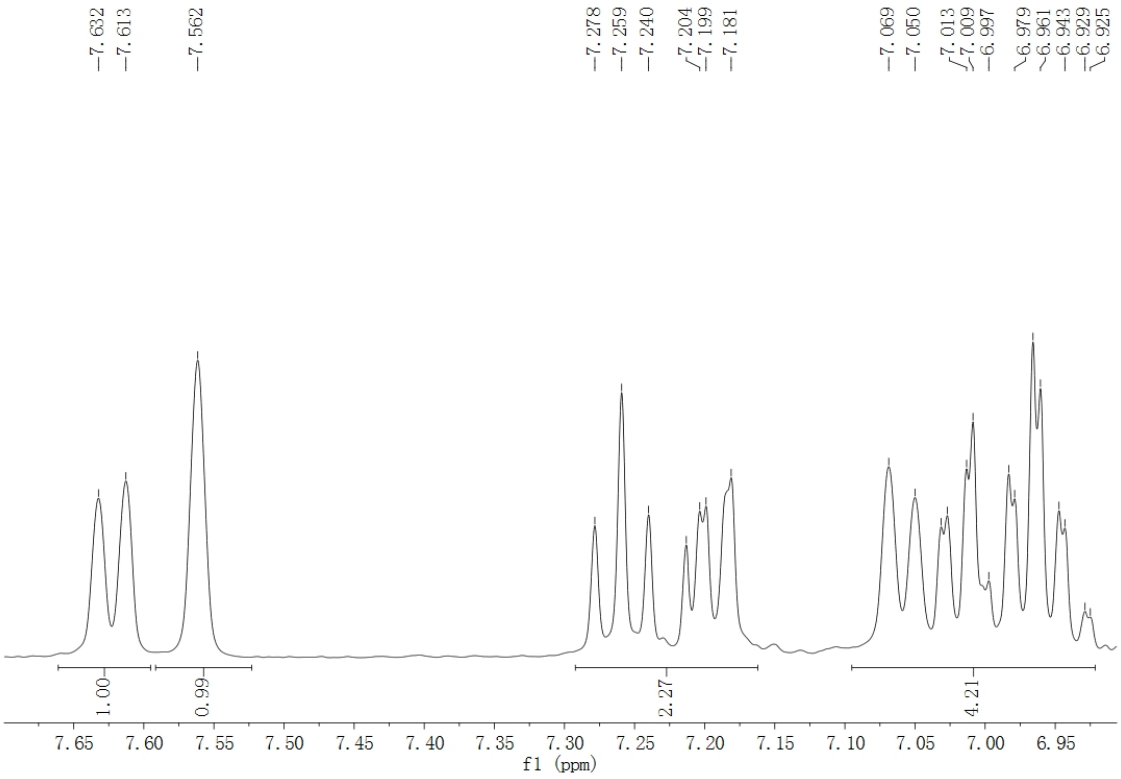

7.688
7.668
7.206
7.202
7.194
7.187
7.167
7.031
6.997
6.981
6.963
6.944
6.925
2.00
3.16
3.02
7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90
f1 (ppm)

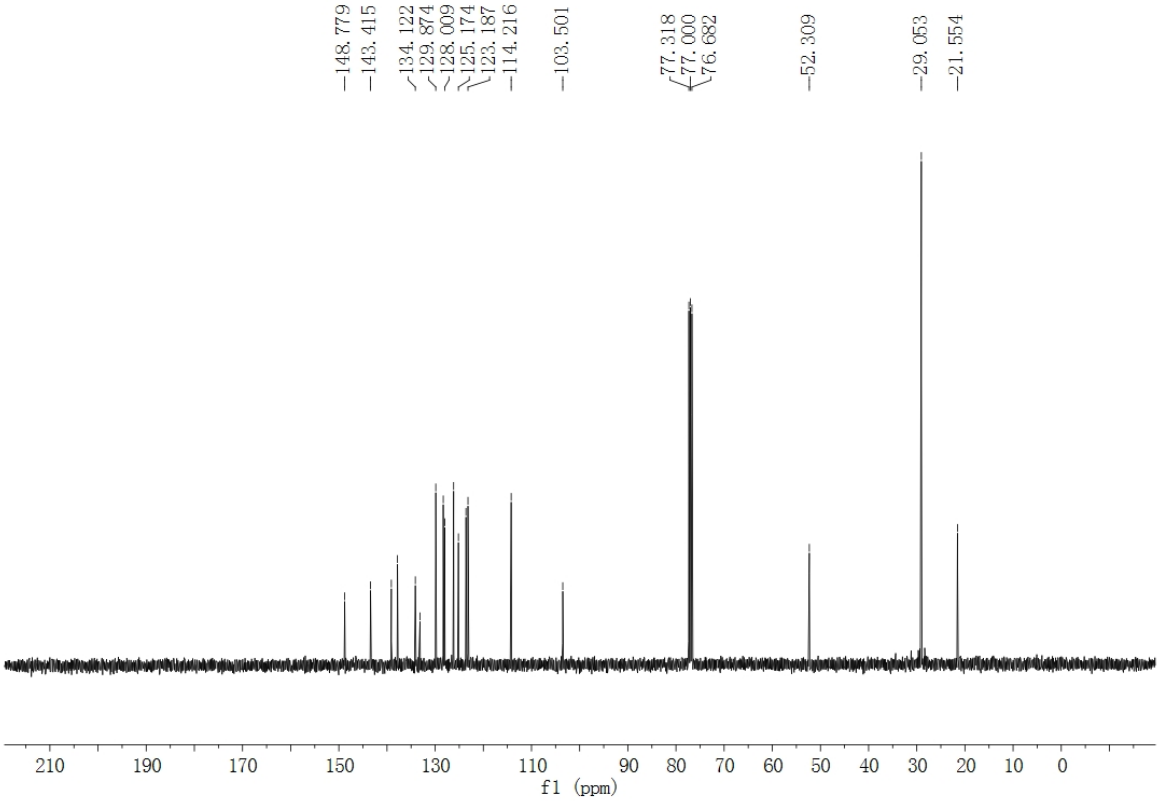

148.873
143.468
129.136
128.995
125.114
123.542
123.112
114.183
103.461
77.318
77.000
76.682
52.256
29.036
21.291
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

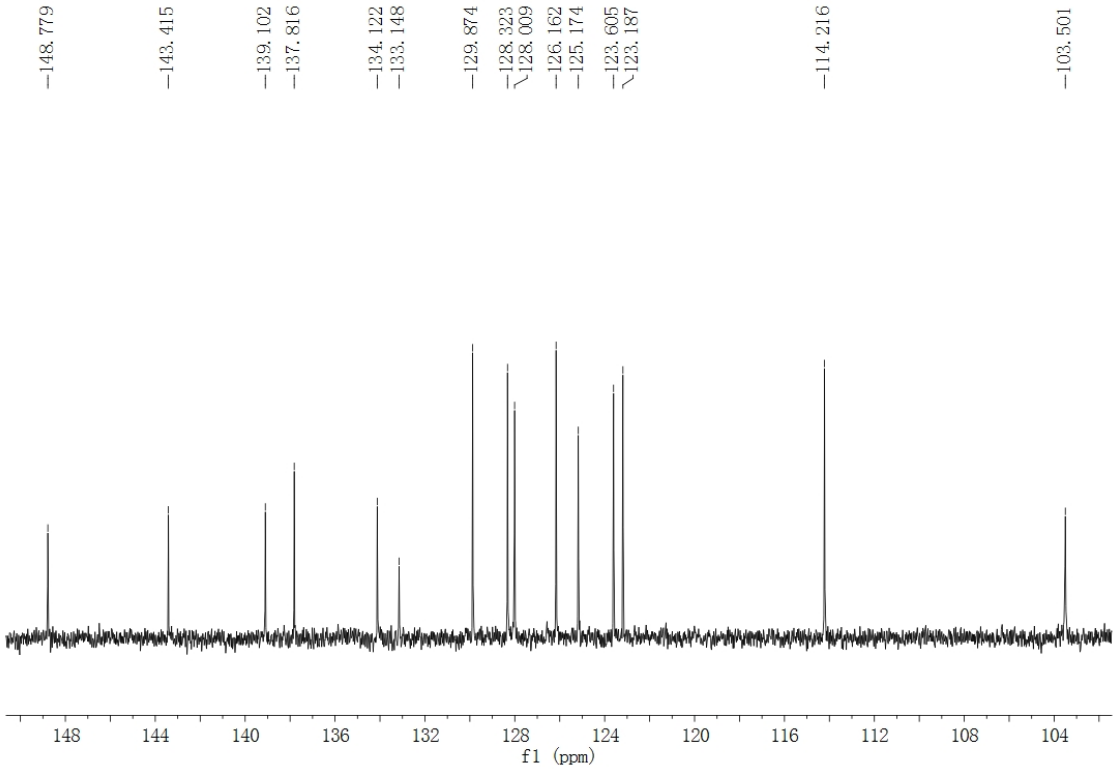


^{1}H NMR and ^{13}C NMR of *N-tert*-butyl-2-*m*-tolylbenzo[b][1,4]oxazepin-4-amine (7)

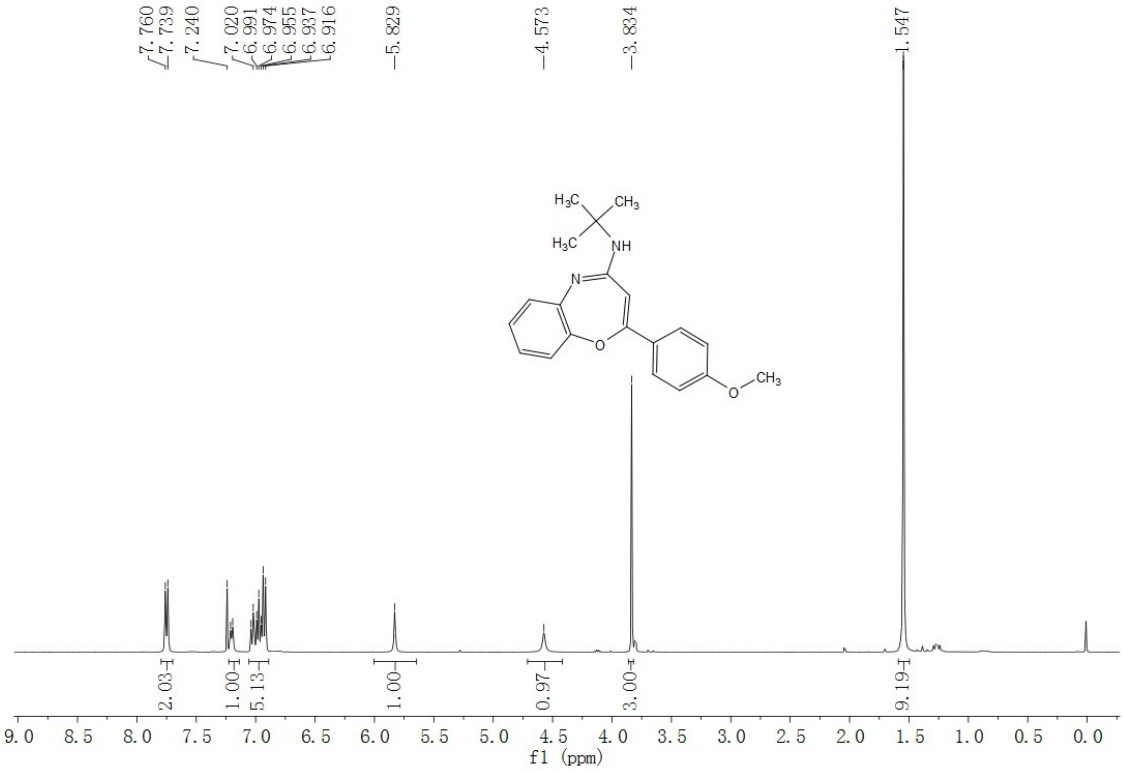


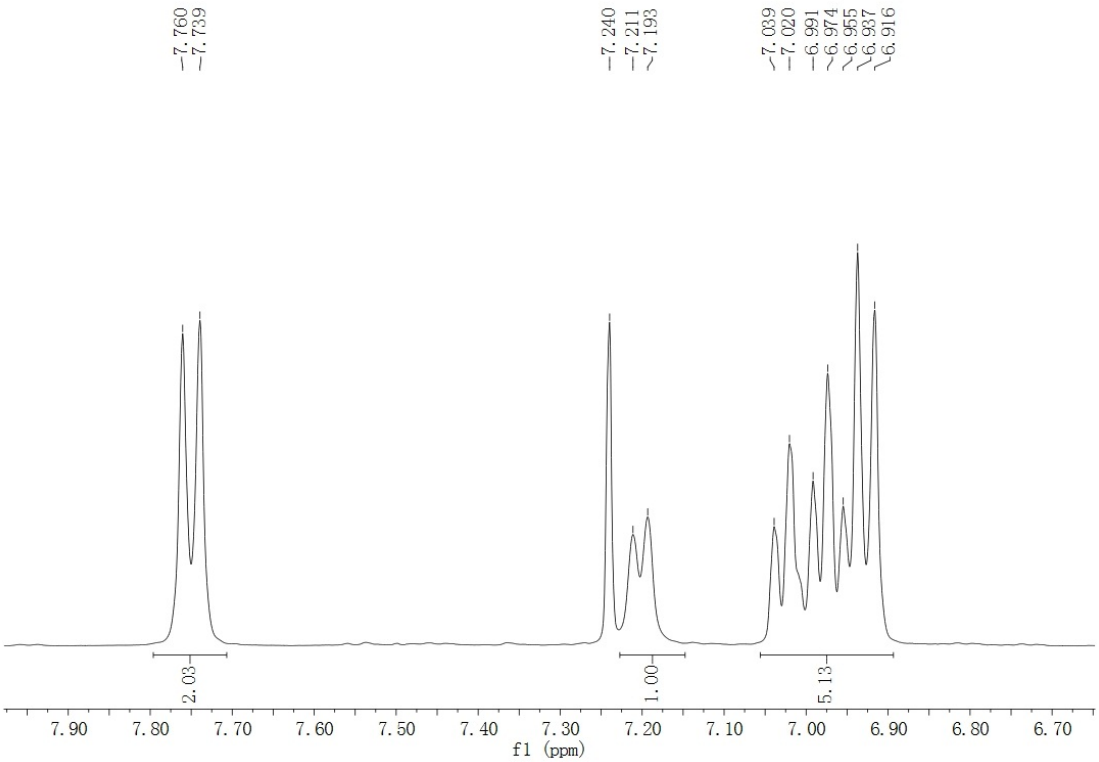

7.632
7.613
7.562
7.278
7.259
7.240
7.204
7.199
7.181
7.069
7.050
7.013
7.009
6.997
6.979
6.961
6.943
6.929
6.925
1.00
0.99
2.27
4.21
7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95
f1 (ppm)

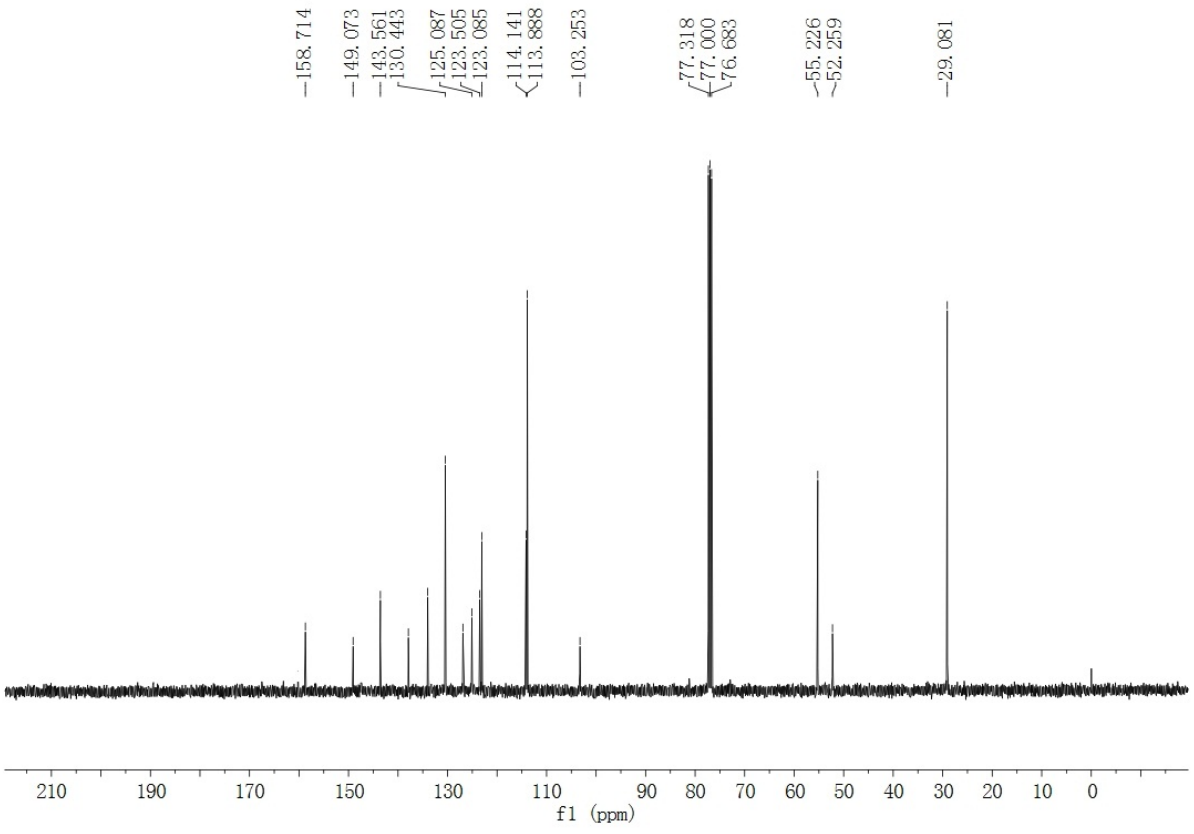

148.779
143.415
134.122
129.874
128.009
125.174
123.187
114.216
103.501
77.318
77.000
76.682
52.309
29.053
21.554
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

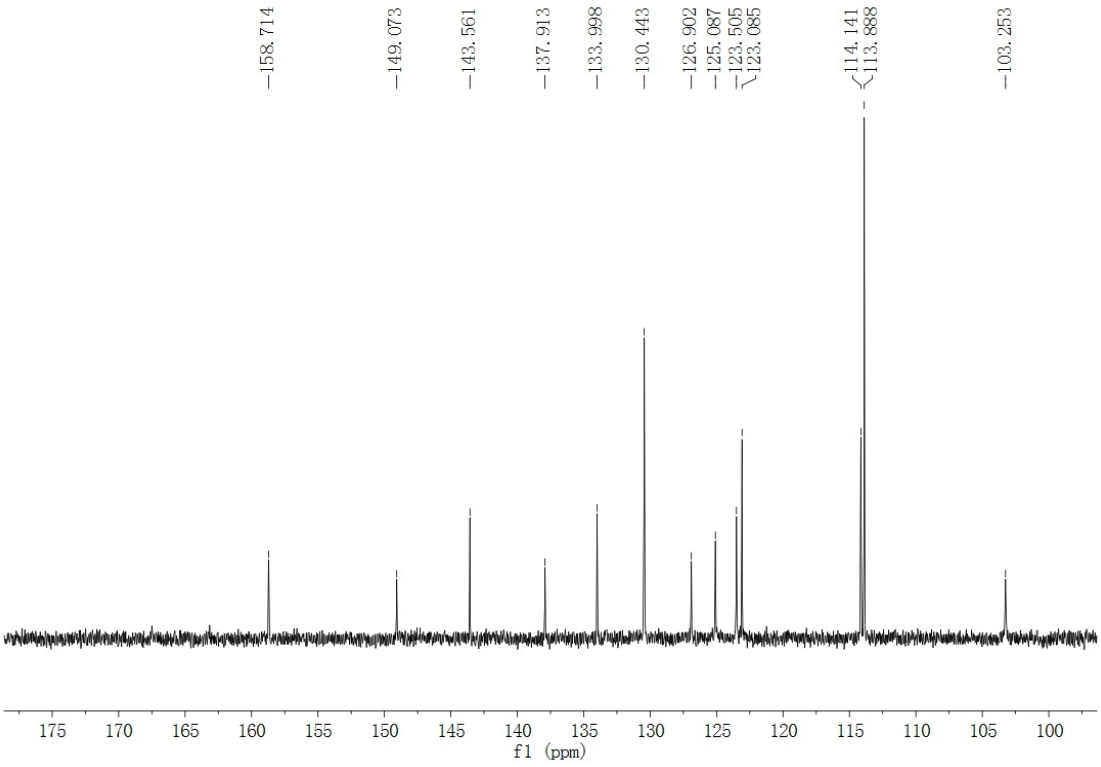


^{1}H NMR and ^{13}C NMR of *N-tert*-butyl-2-(4-methoxyphenyl)benzo[b][1,4]oxazepin-4-amine (8)

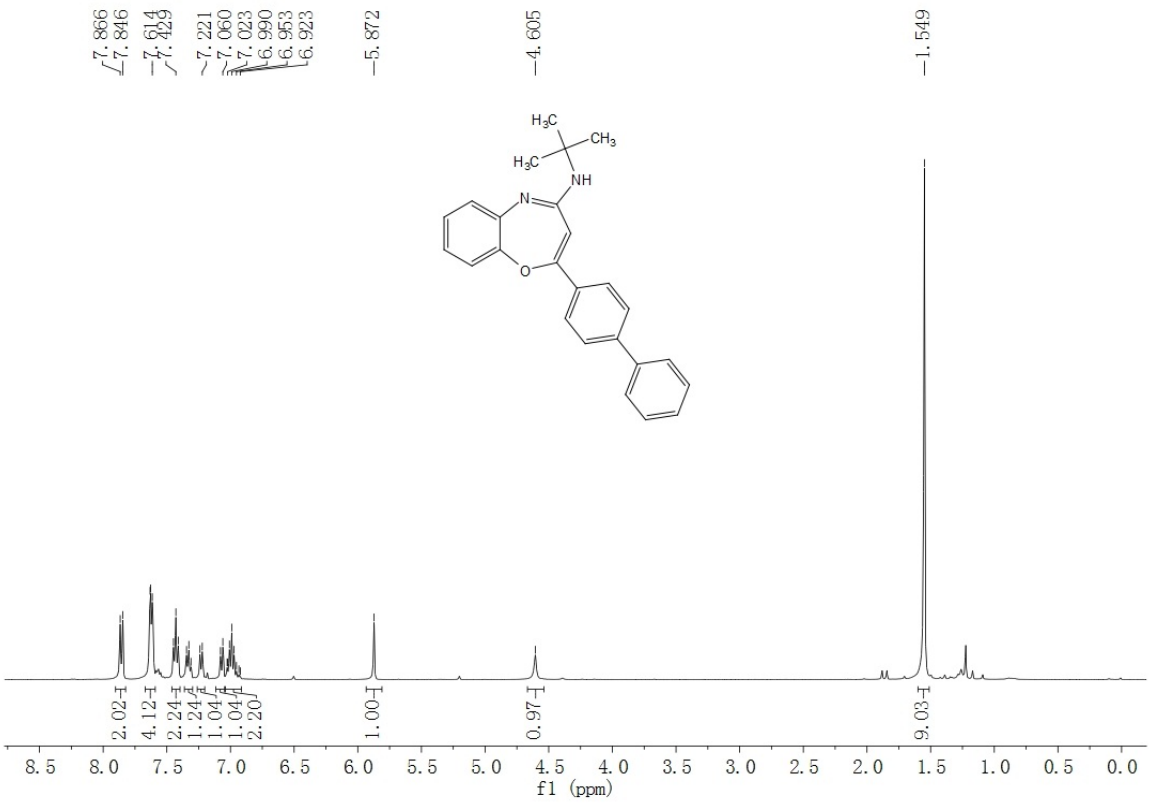


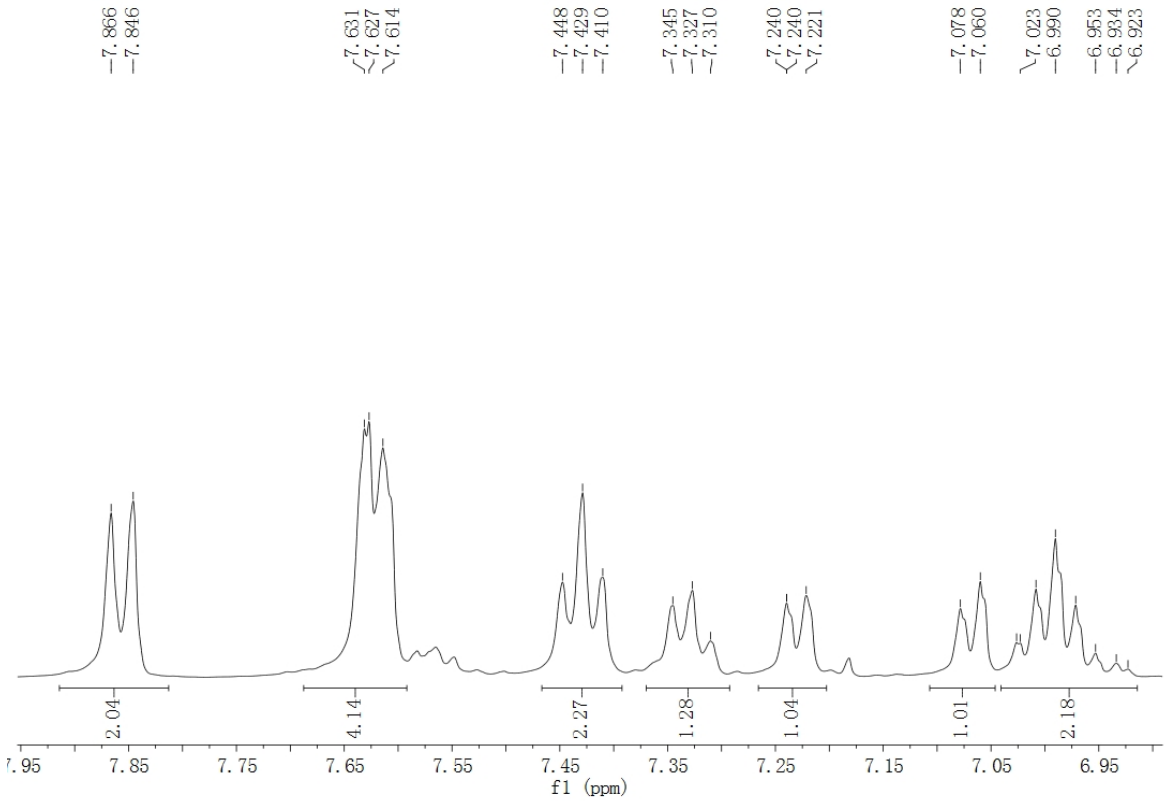

7.760
7.739
7.240
7.211
7.193
7.039
7.020
6.991
6.974
6.955
6.937
6.916
2.03
1.00
5.13
7.90
7.80
7.70
7.60
7.50
7.40
7.30
7.20
7.10
7.00
6.90
6.80
6.70
f1 (ppm)

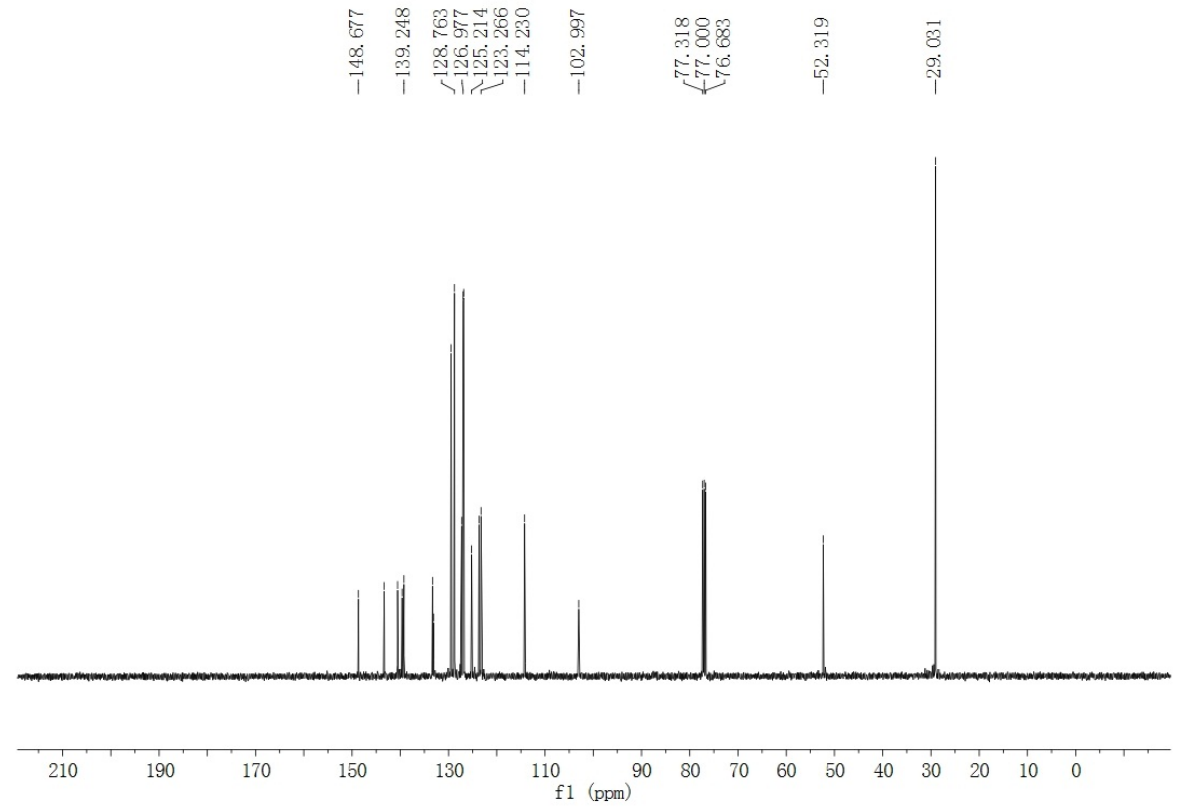

158.714
149.073
143.561
130.443
125.087
123.505
123.085
114.141
113.888
103.253
77.318
77.000
76.683
55.226
52.259
29.081
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

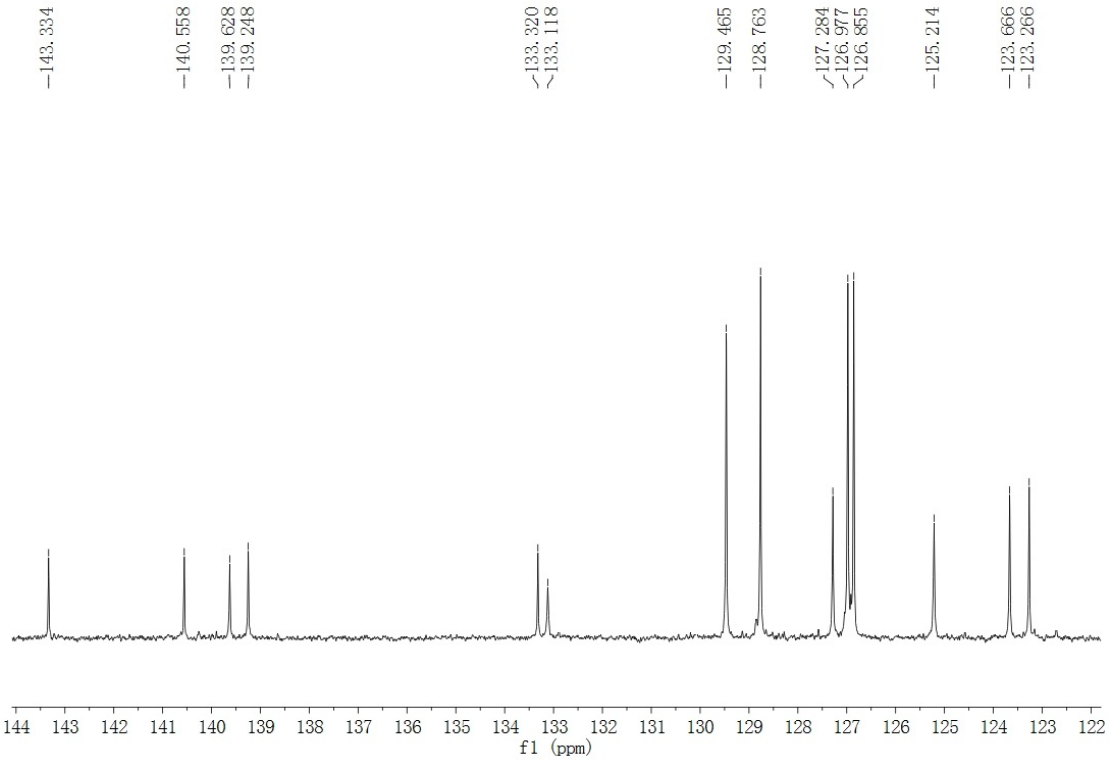


^{1}H NMR and ^{13}C NMR of *N-tert*-butyl-2-(biphenyl-4-yl)benzo[b][1,4]oxazepin-4-amine (9)

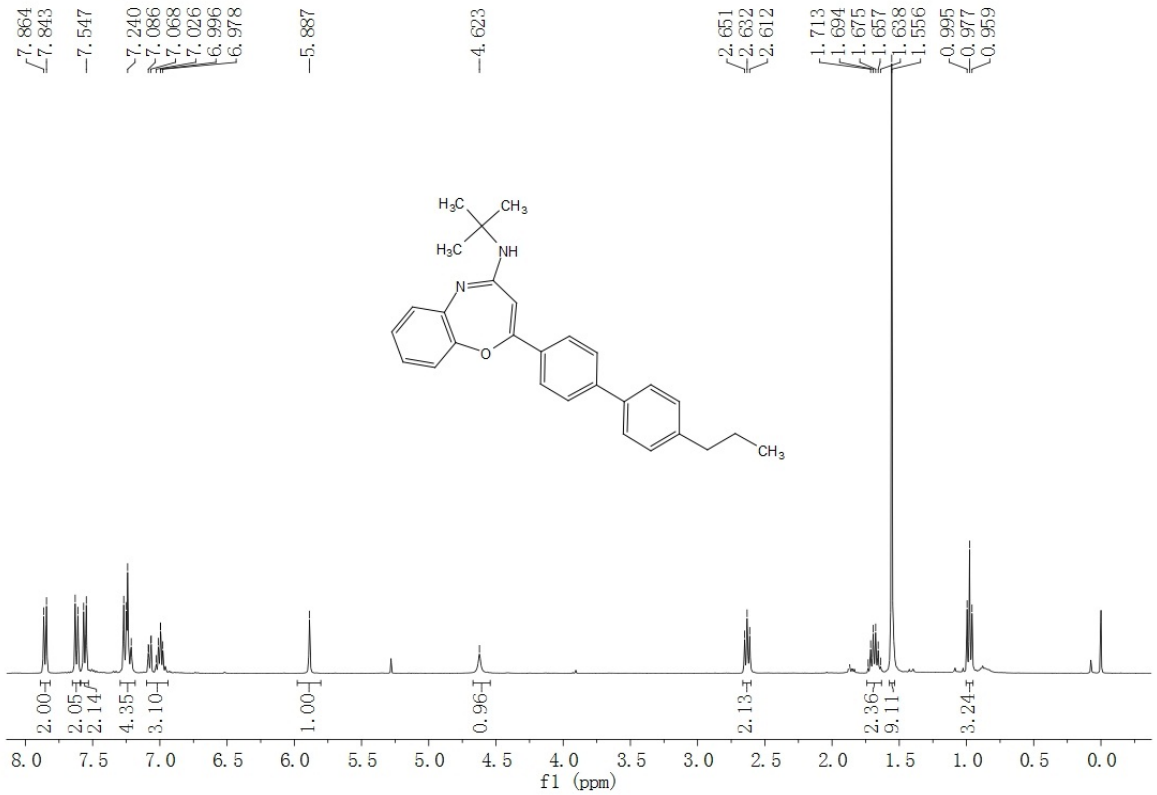


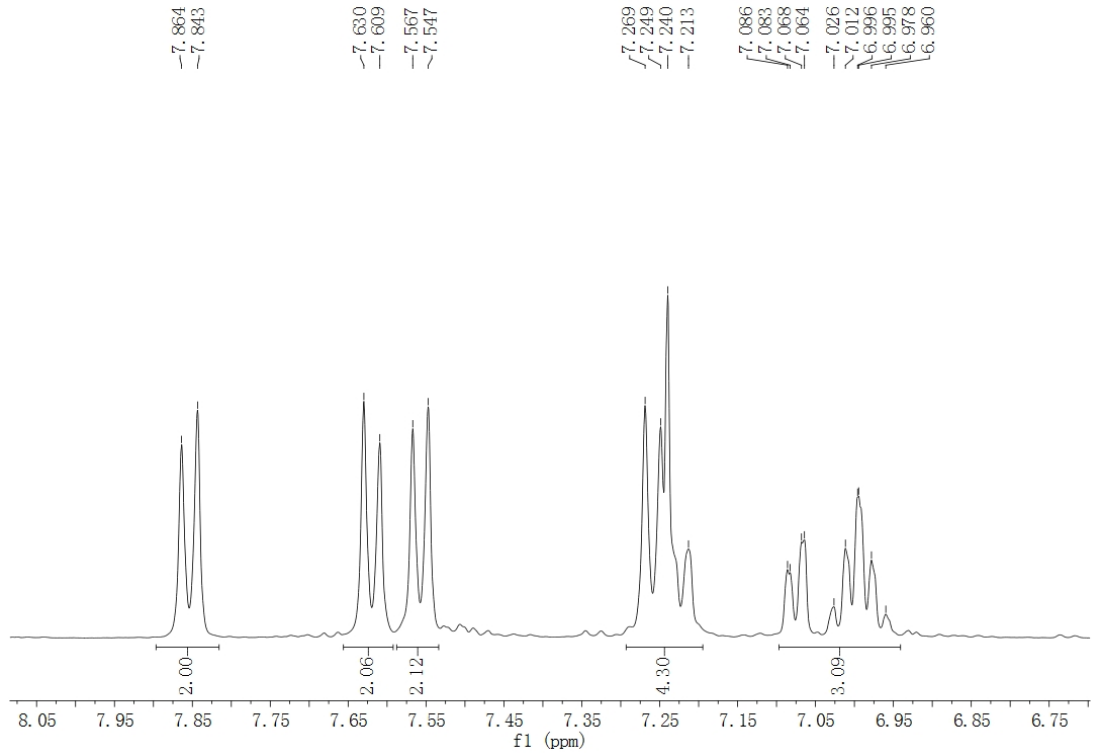

7.866
7.846
7.631
7.627
7.614
7.448
7.429
7.410
7.345
7.327
7.310
7.240
7.240
7.221
7.078
7.060
7.023
6.990
6.953
6.934
6.923
2.04
4.14
2.27
1.28
1.04
1.01
2.18
7.95
7.85
7.75
7.65
7.55
7.45
7.35
7.25
7.15
7.05
6.95
f1 (ppm)

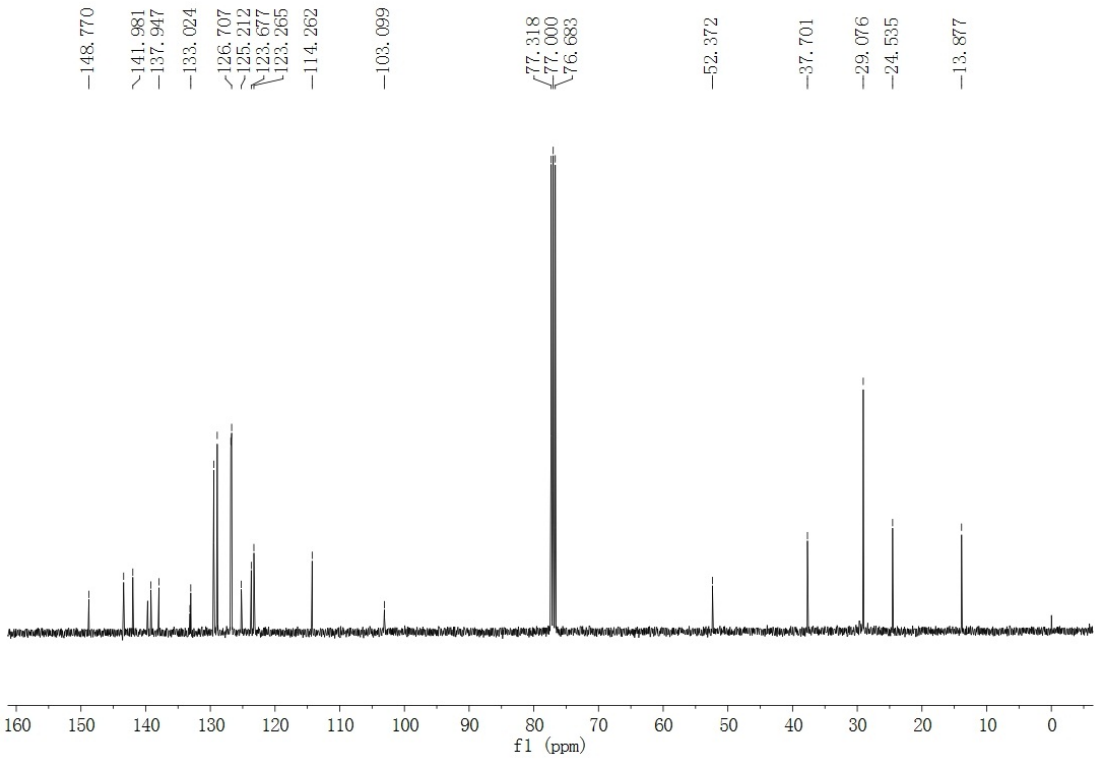

148.677
139.248
128.763
126.977
125.214
123.266
114.230
102.997
77.318
77.000
76.683
52.319
29.031
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

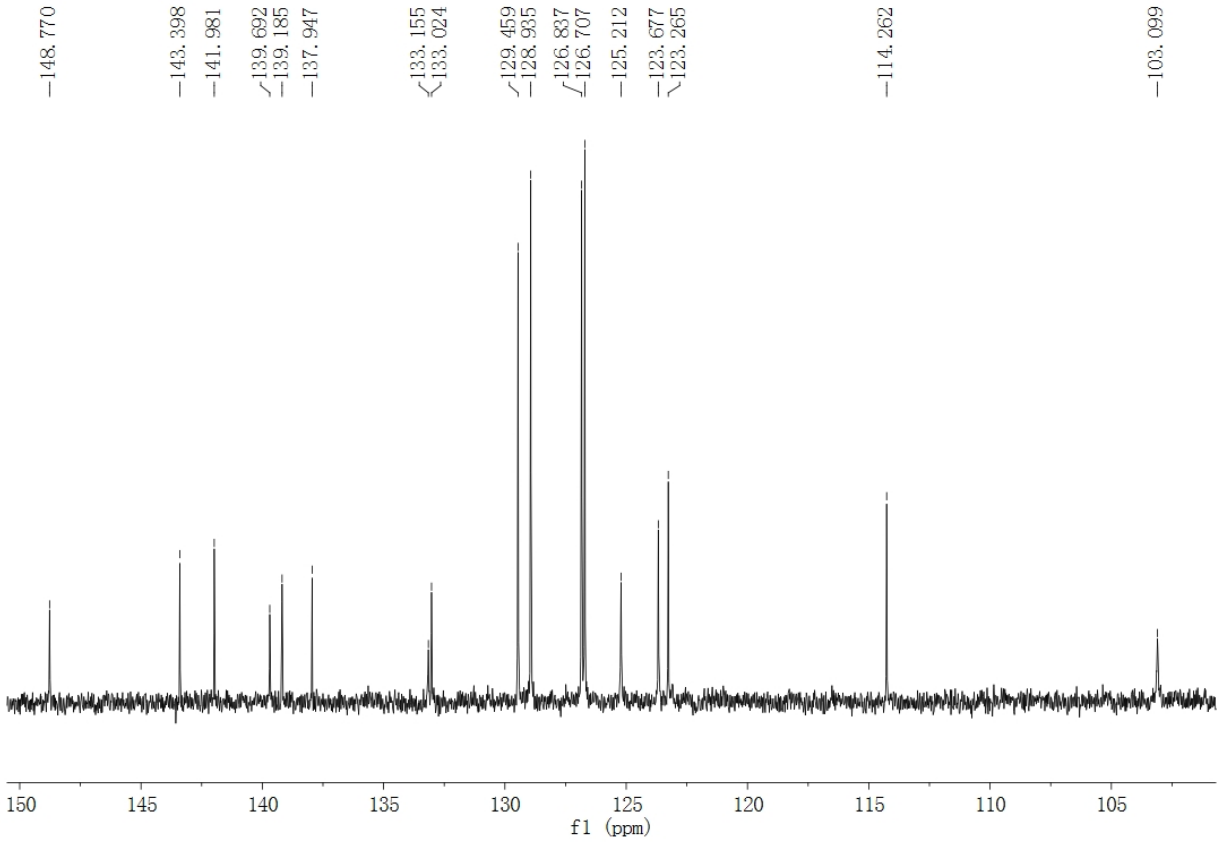


^{1}H NMR and ^{13}C NMR of *N-tert*-butyl-2-(4'-propylbiphenyl-4-yl)-benzo[b][1,4]oxazepin-4-amine (10)

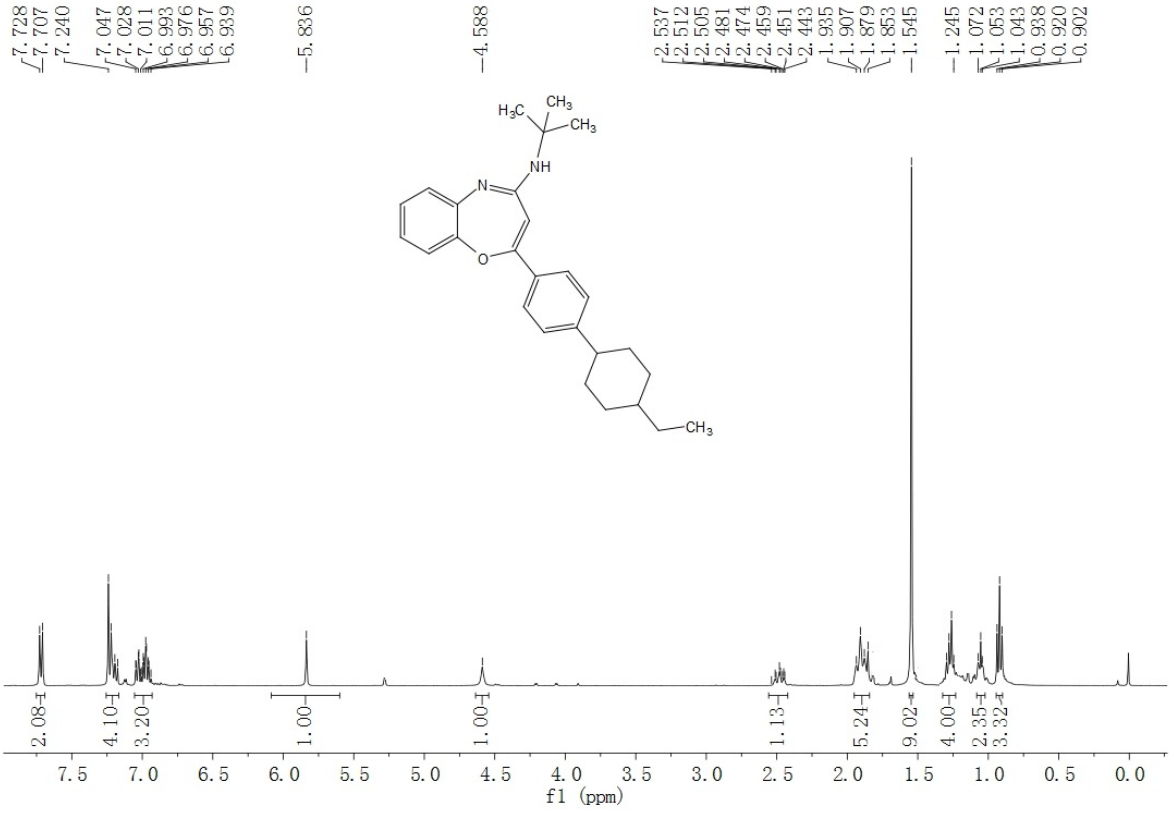

7.864
7.843
7.547
7.240
7.086
7.068
7.026
6.996
6.978
5.887
4.623
2.651
2.632
2.612
1.713
1.694
1.675
1.657
1.638
1.556
0.995
0.977
0.959
H3C
CH3
H3C
NH
N
O
CH3
2.00
2.05
2.14
4.35
3.10
1.00
0.96
2.13
2.36
9.11
3.24
f1 (ppm)

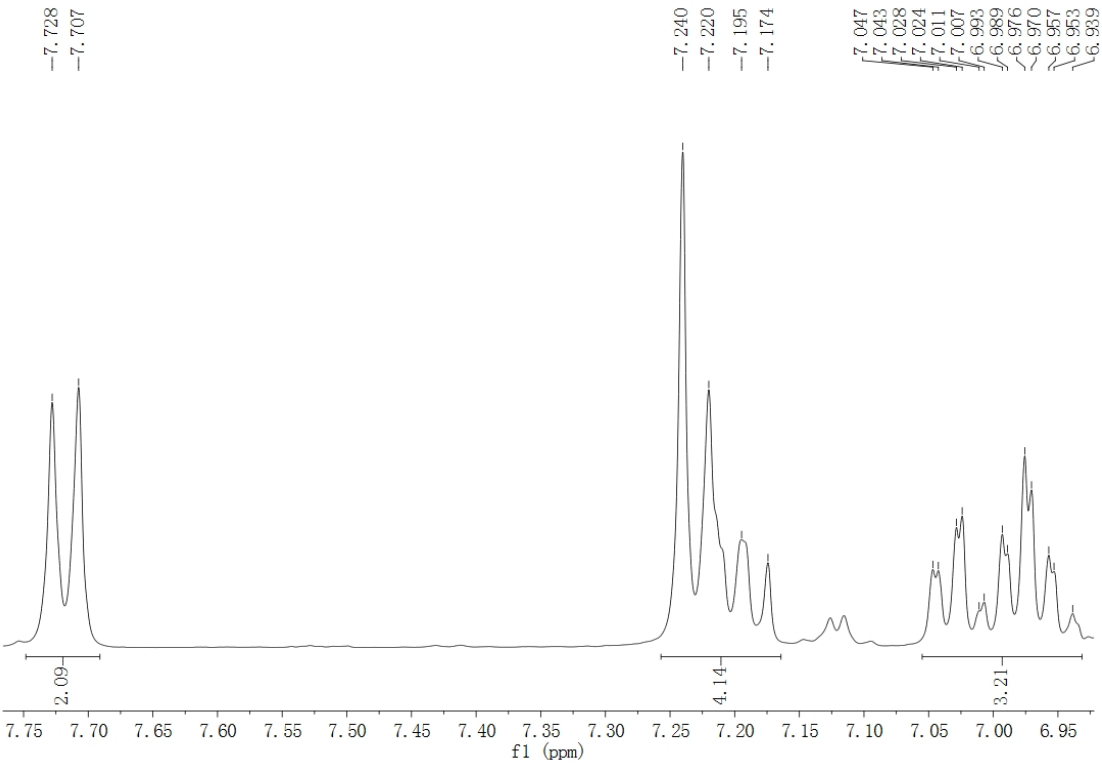

7.864
7.843
7.630
7.609
7.567
7.547
7.269
7.249
7.240
7.213
7.086
7.083
7.068
7.064
7.026
7.012
6.996
6.995
6.978
6.960
2.00
2.06
2.12
4.30
3.09
f1 (ppm)

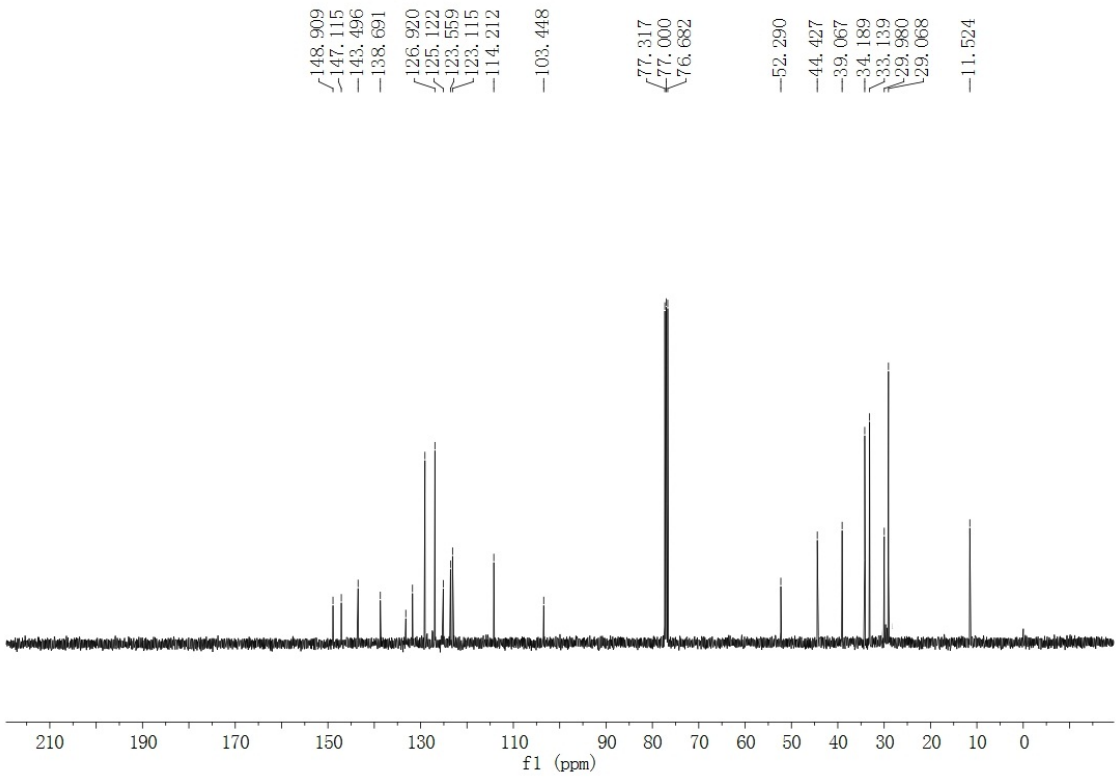

148.770
141.981
137.947
133.024
126.707
125.212
123.677
123.265
114.262
103.099
77.318
77.000
76.683
52.372
37.701
29.076
24.535
13.877
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

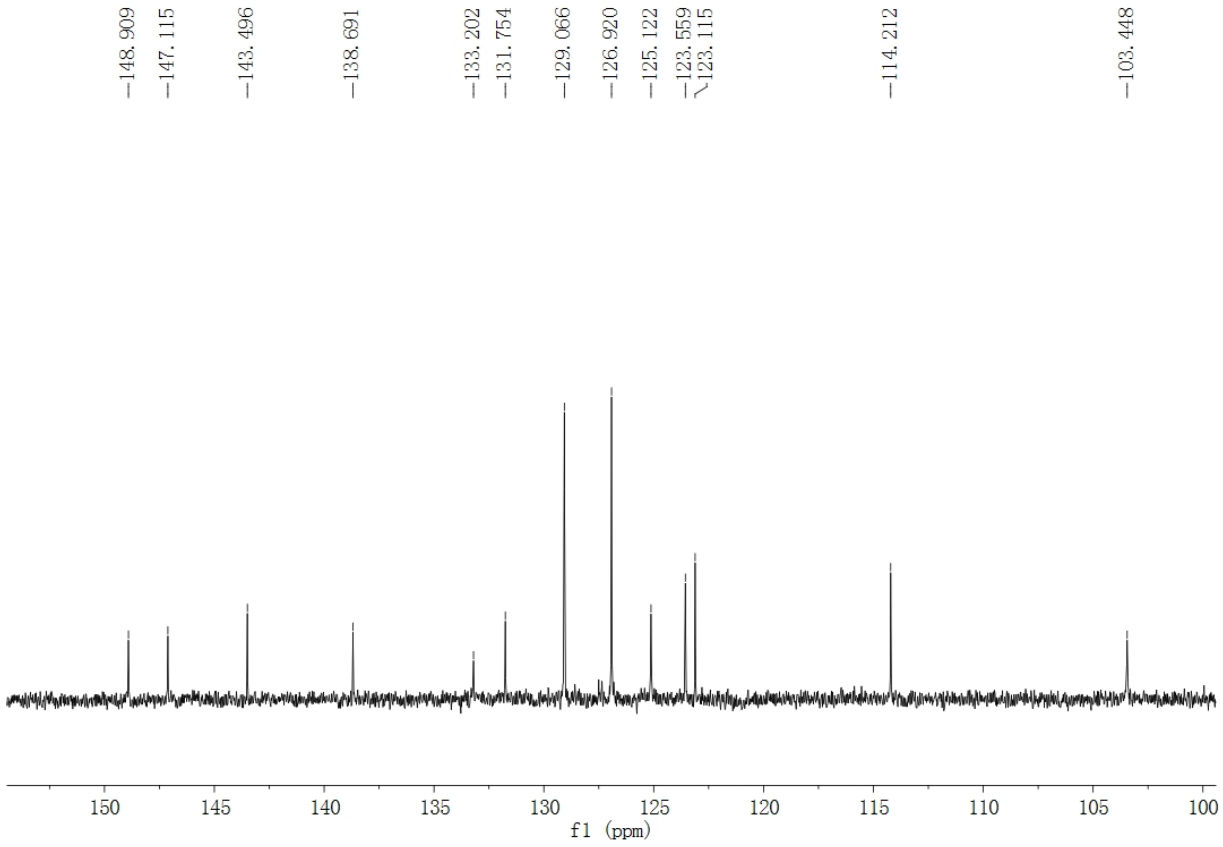

148.770
143.398
141.981
139.692
139.185
137.947
133.155
133.024
129.459
128.935
126.837
126.707
125.212
123.677
123.265
114.262
103.099
150 145 140 135 130 125 120 115 110 105
f1 (ppm)

^{1}H NMR and ^{13}C NMR of *N-tert*-butyl-2-(4-(4-ethylcyclohexyl)phenyl)-benzo[b][1,4]oxazepin-4-amine (11)

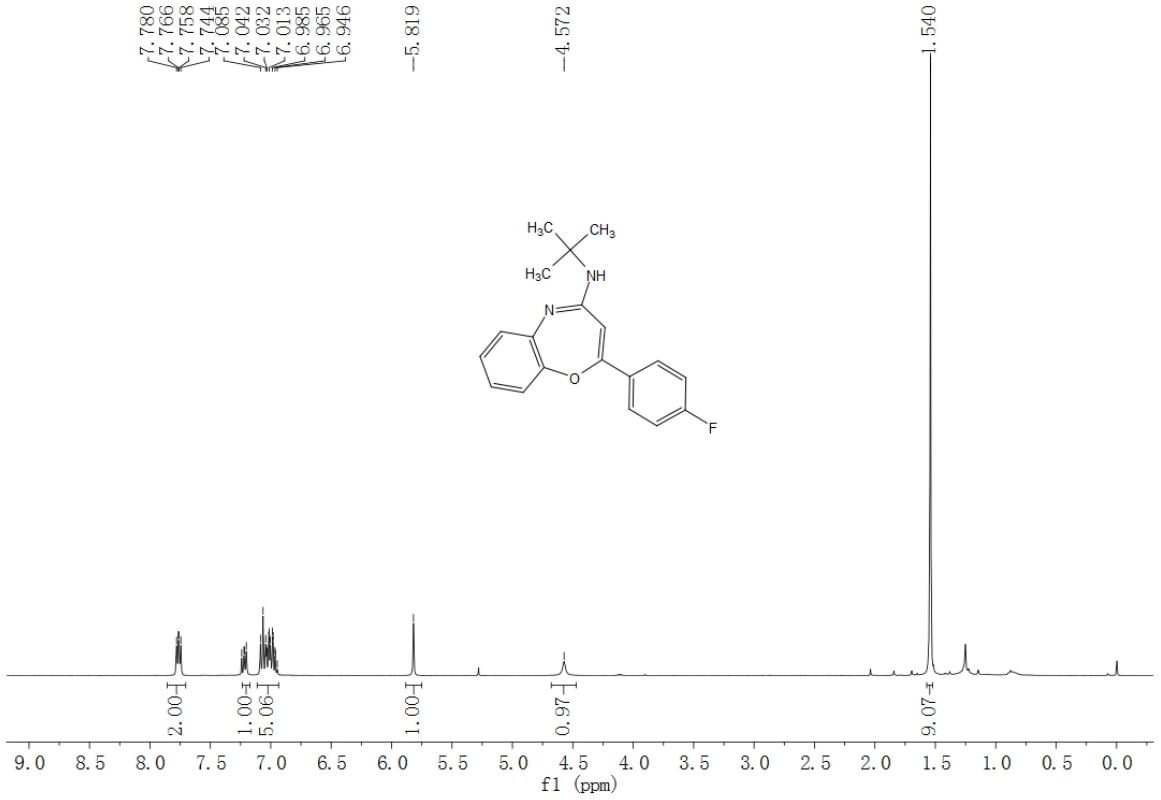


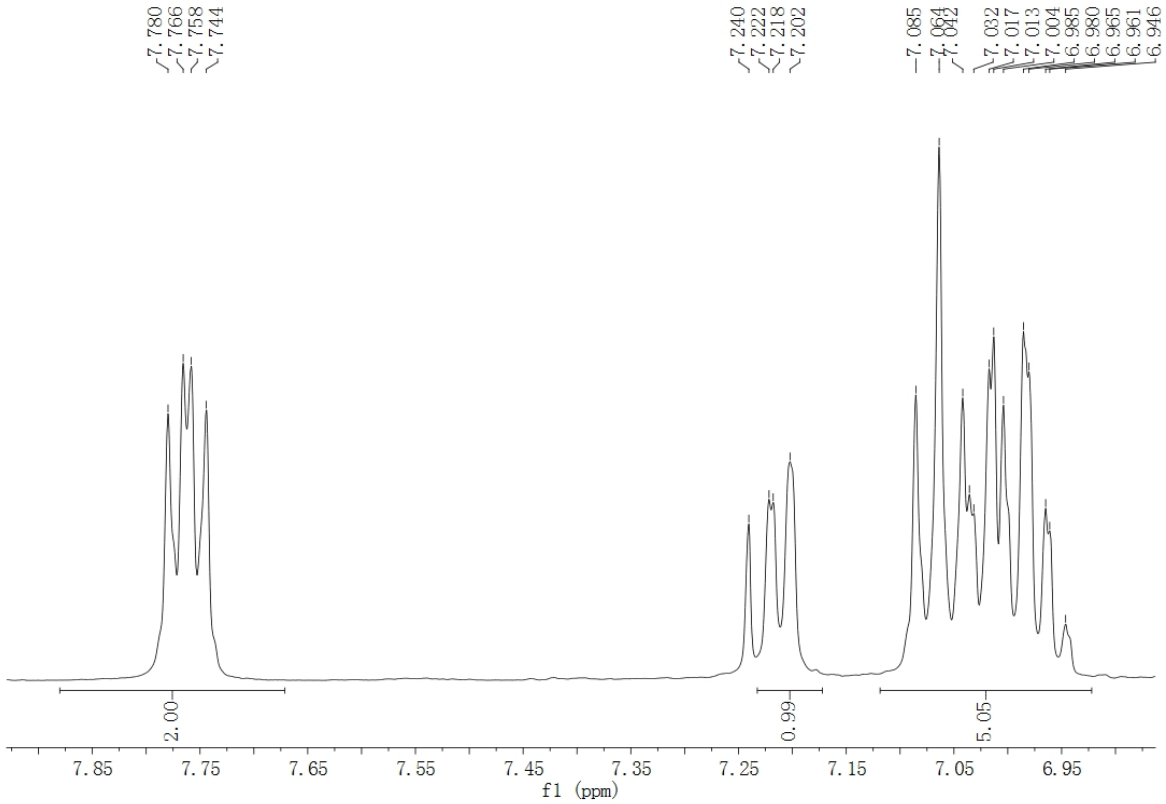


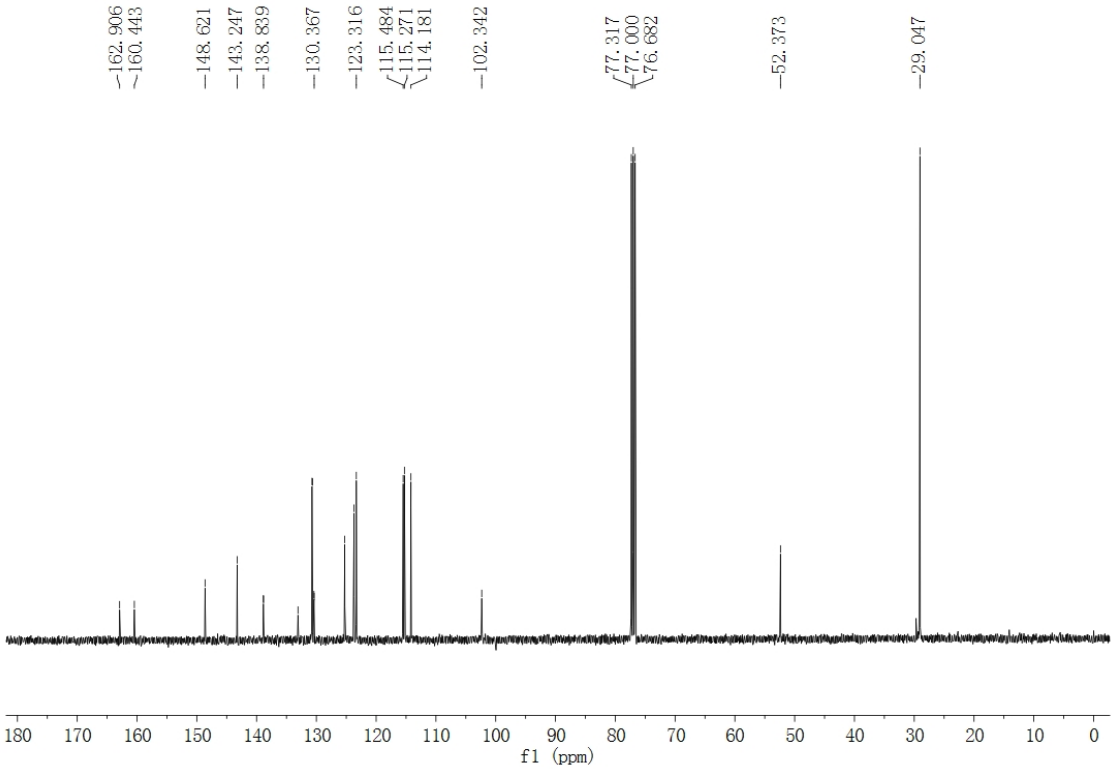

148.909
147.115
143.496
138.691
126.920
125.122
123.559
123.115
114.212
103.448
77.317
77.000
76.682
52.290
44.427
39.067
34.189
33.139
29.980
29.068
11.524
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

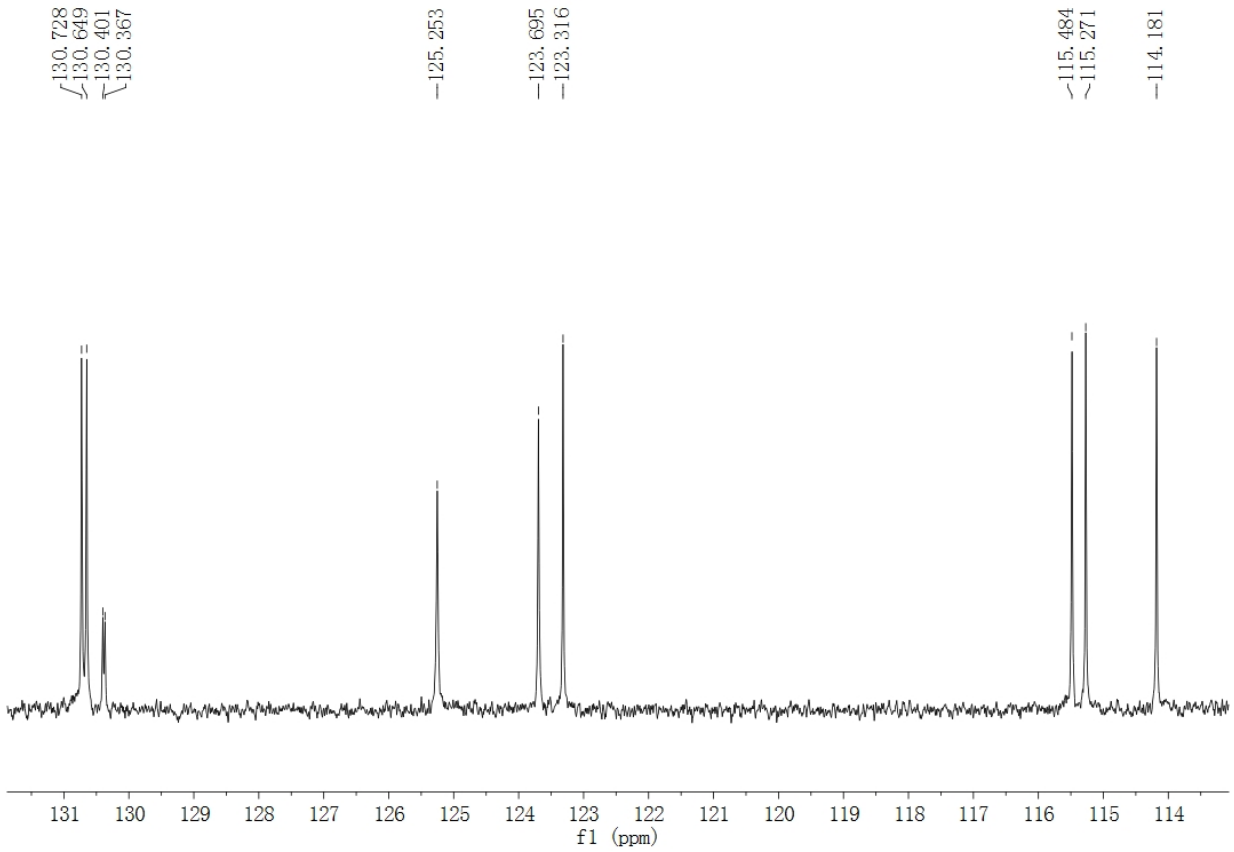

148.909
147.115
143.496
138.691
133.202
131.754
129.066
126.920
125.122
123.559
123.115
114.212
103.448
150
145
140
135
130
125
120
115
110
105
100
f1 (ppm)

^{1}H NMR and ^{13}C NMR of *N-tert*-butyl-2-(4-fluorophenyl)benzo[b][1,4]oxazepin-4-amine (12)

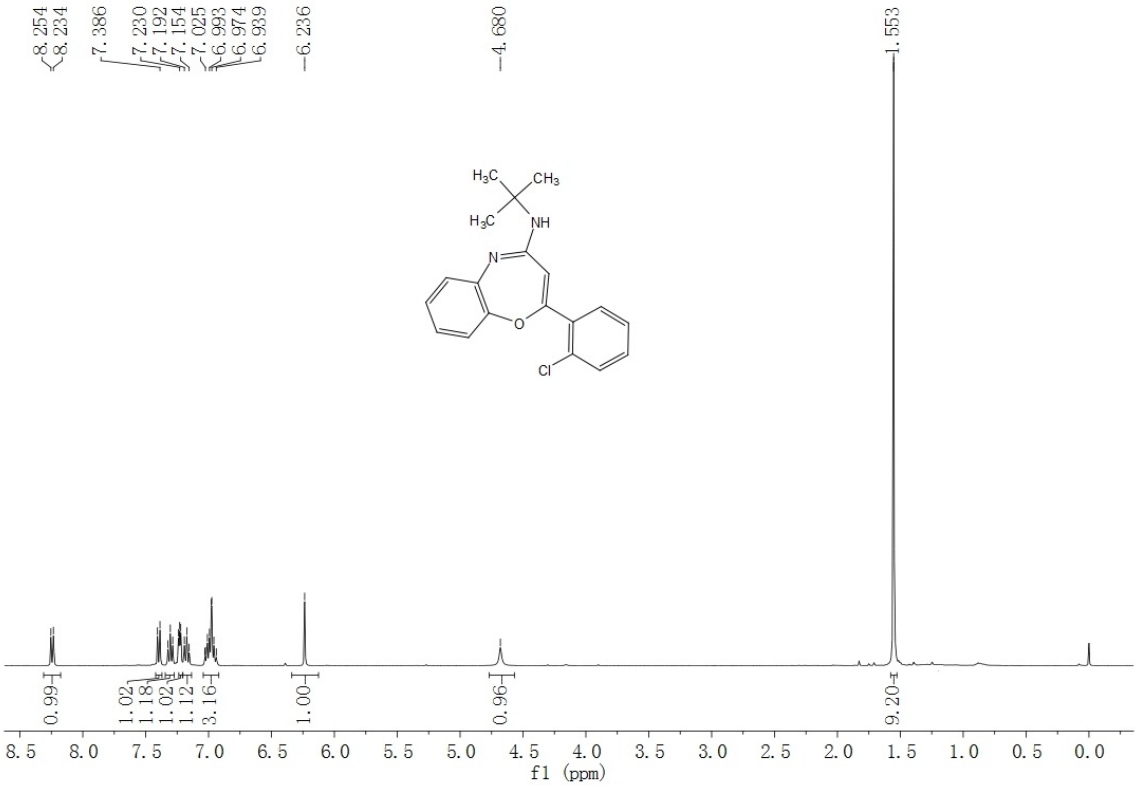


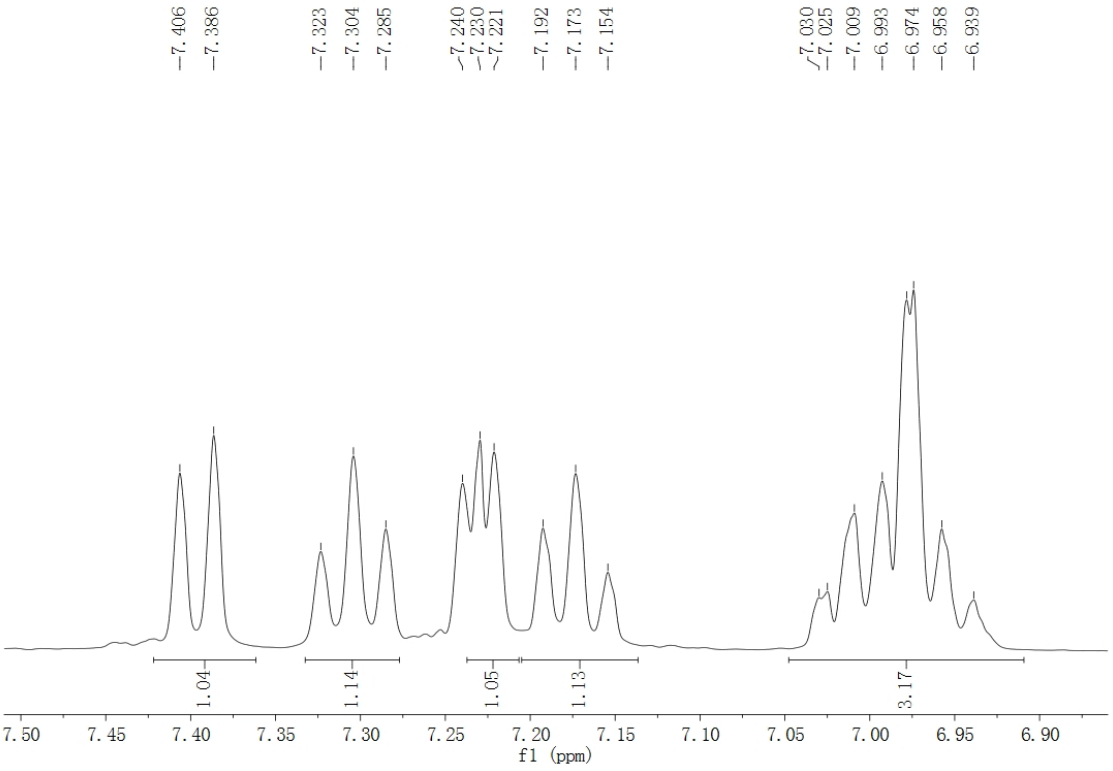


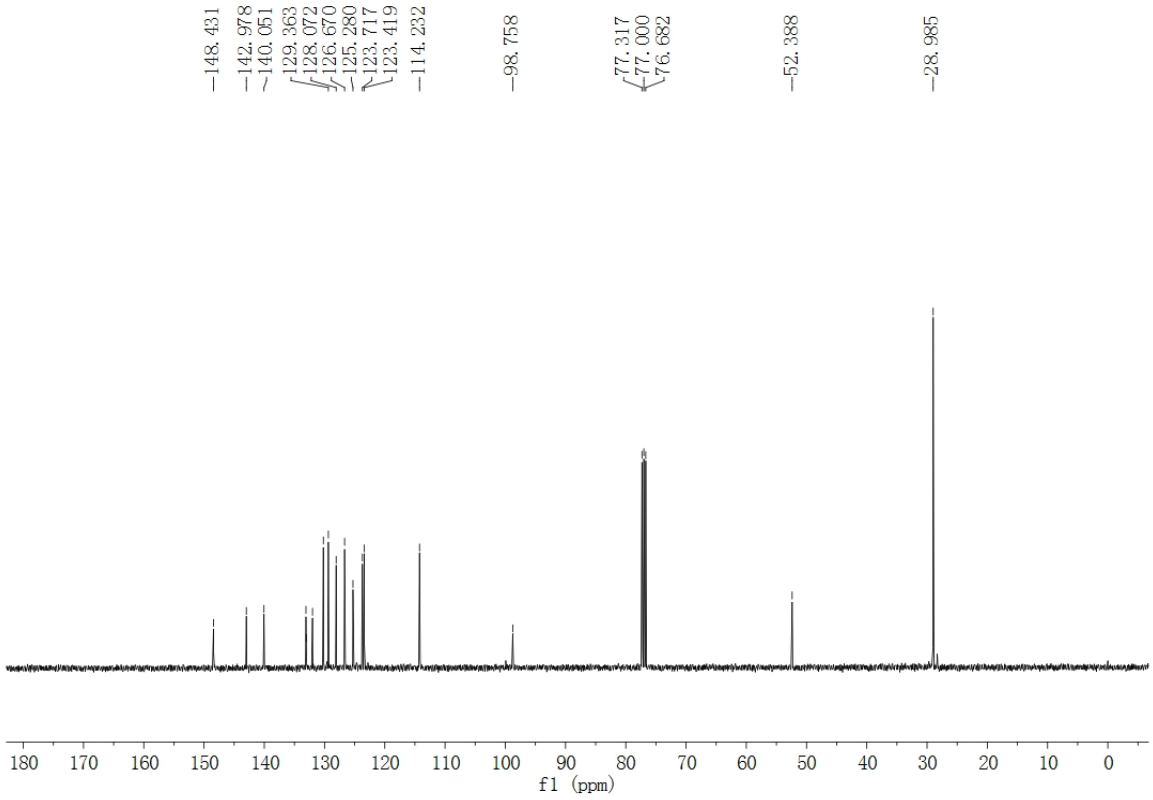

162.906
160.443
148.621
143.247
138.839
130.367
123.316
115.484
115.271
114.181
102.342
77.317
77.000
76.682
52.373
29.047
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

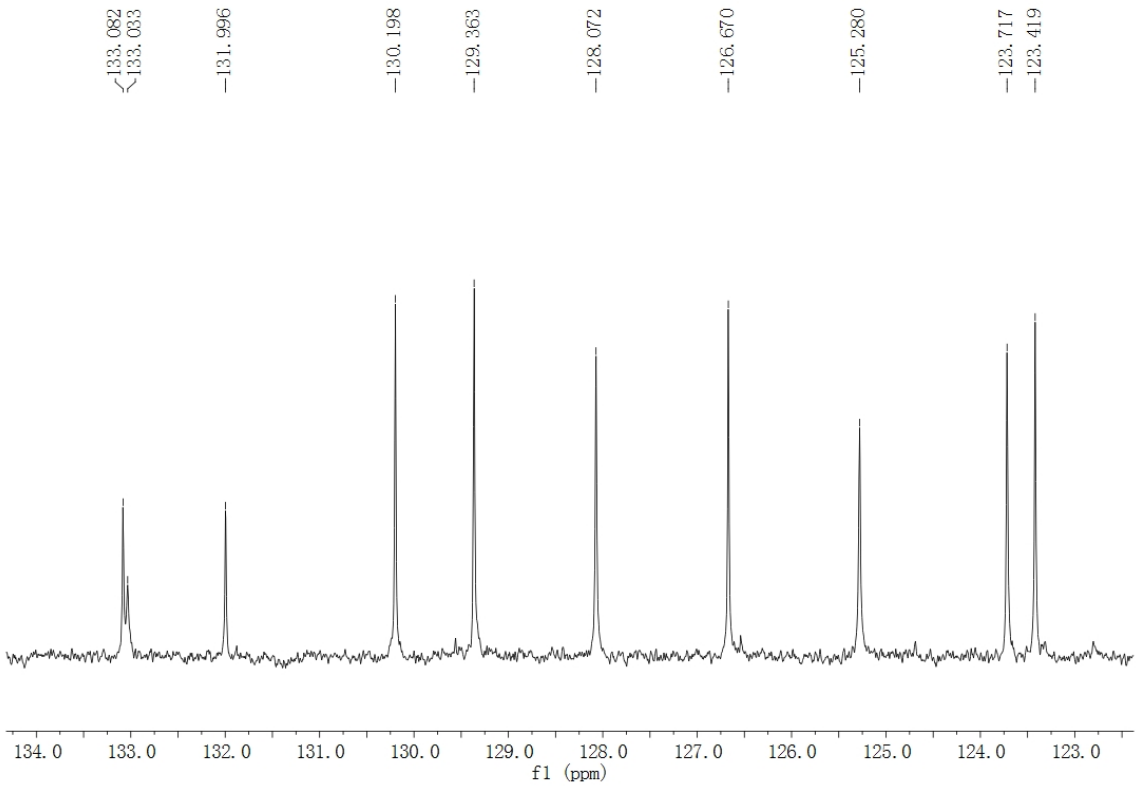

130.728
130.649
130.401
130.367
125.253
123.695
123.316
115.484
115.271
114.181
131 130 129 128 127 126 125 124 123 122 121 120 119 118 117 116 115 114
f1 (ppm)

^{1}H NMR and ^{13}C NMR of *N-tert*-butyl-2-(2-chlorophenyl)benzo-[b][1,4]oxazepin-4-amine (13)

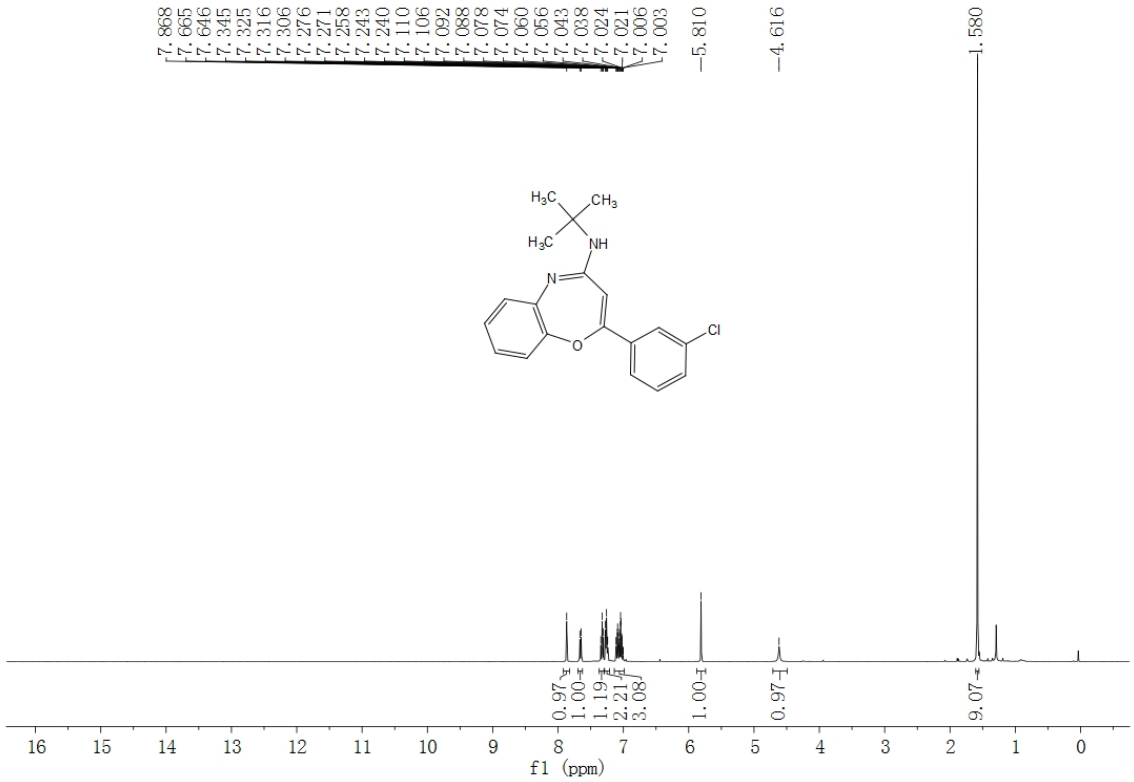


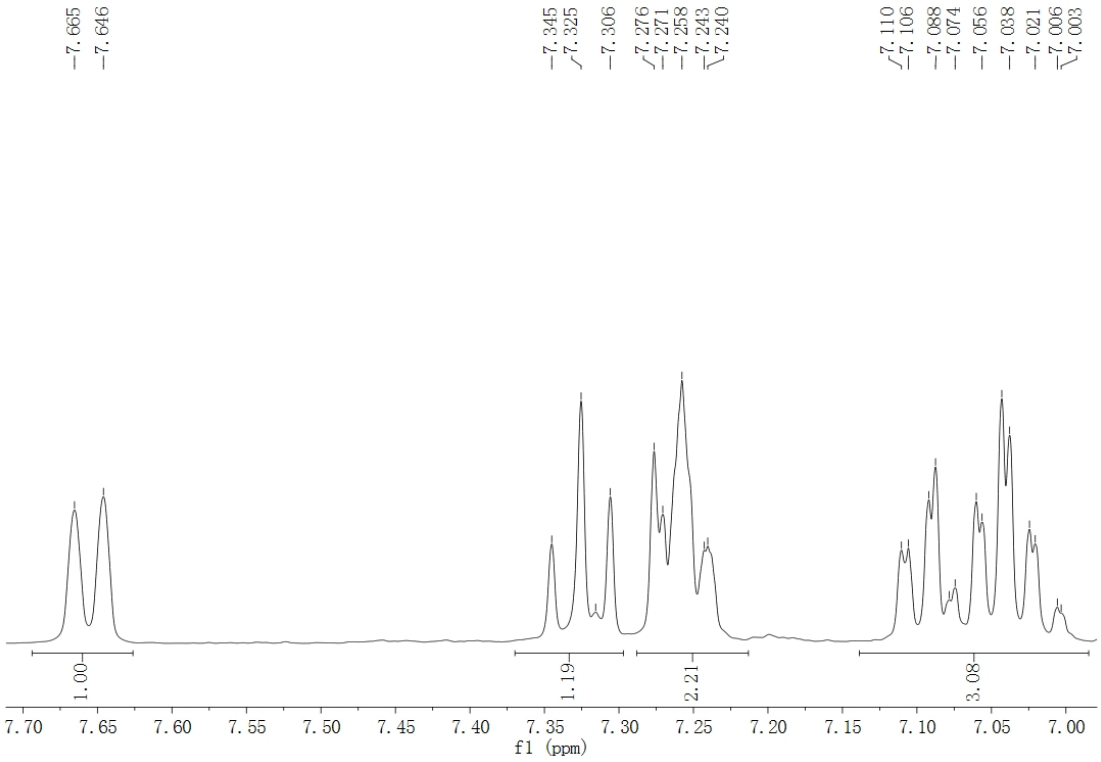


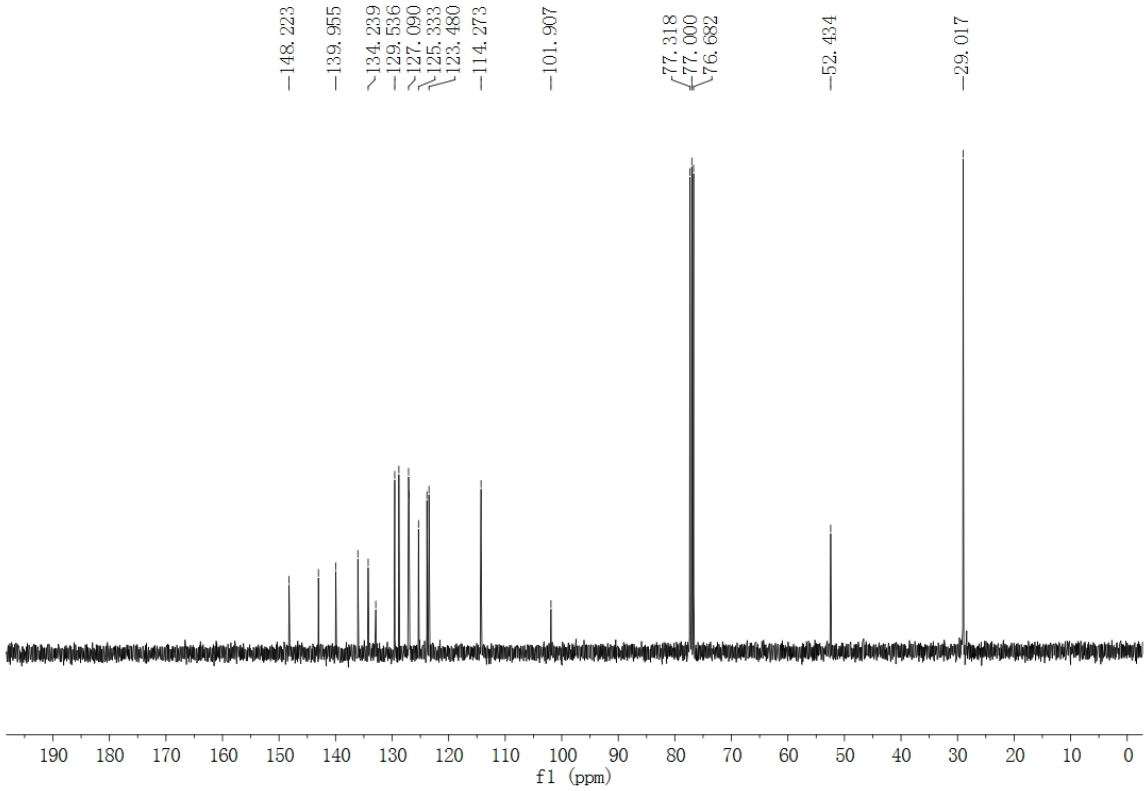

148.431
142.978
140.051
129.363
128.072
126.670
125.280
123.717
123.419
114.232
98.758
77.317
77.000
76.682
52.388
28.985
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

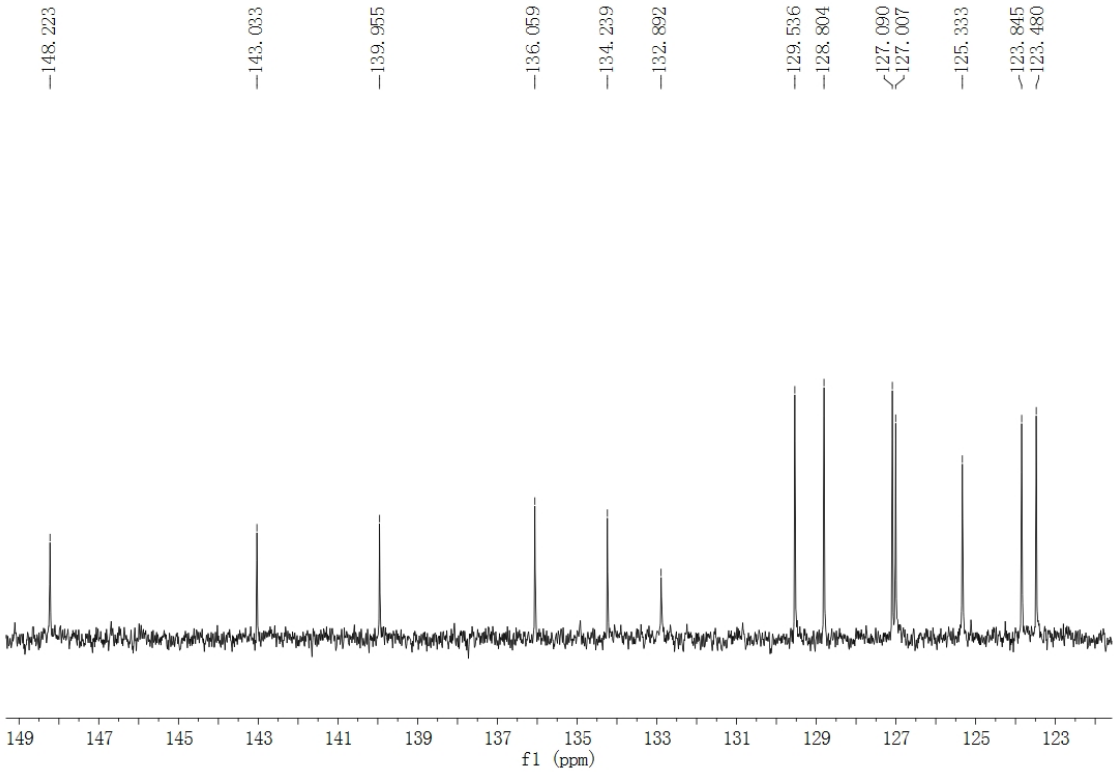

133.082
133.033
131.996
130.198
129.363
128.072
126.670
125.280
123.717
123.419
134.0 133.0 132.0 131.0 130.0 129.0 128.0 127.0 126.0 125.0 124.0 123.0
f1 (ppm)

^{1}H NMR and ^{13}C NMR of *N-tert*-butyl-2-(3-chlorophenyl)-benzo[b][1,4]oxazepin-4-amine (14)

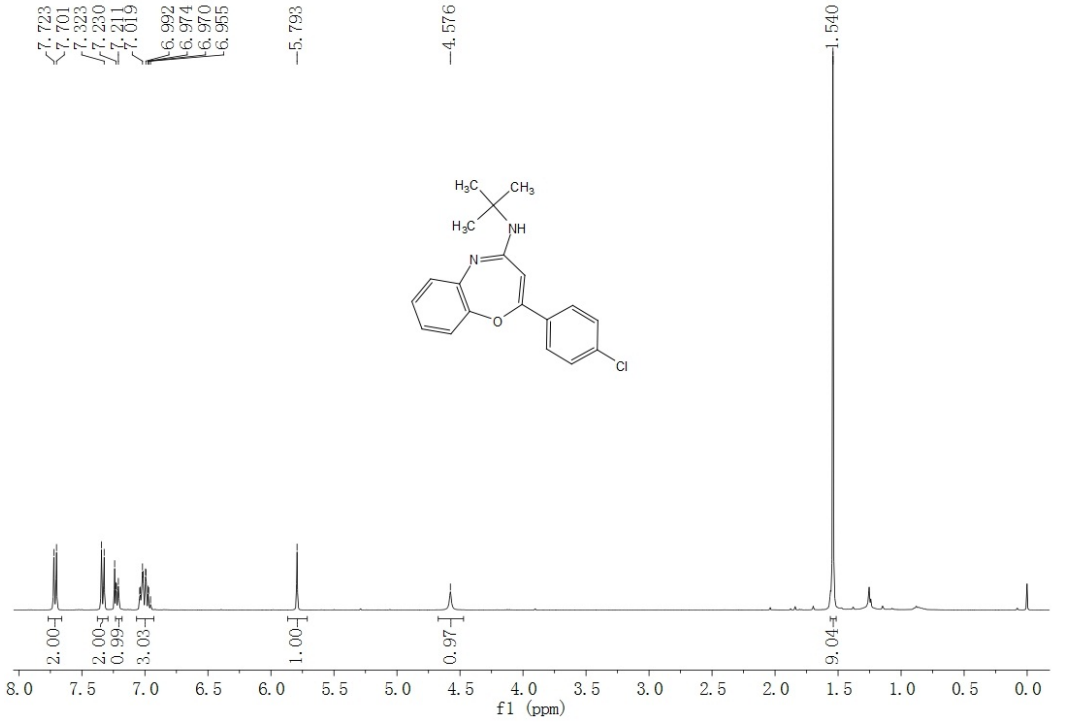


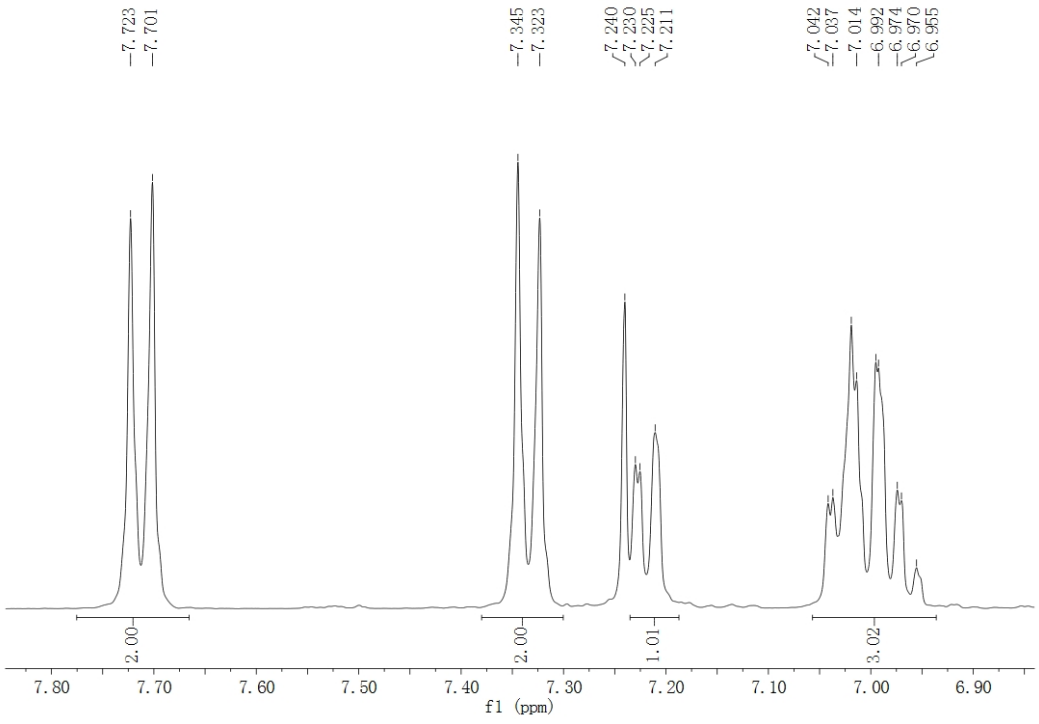


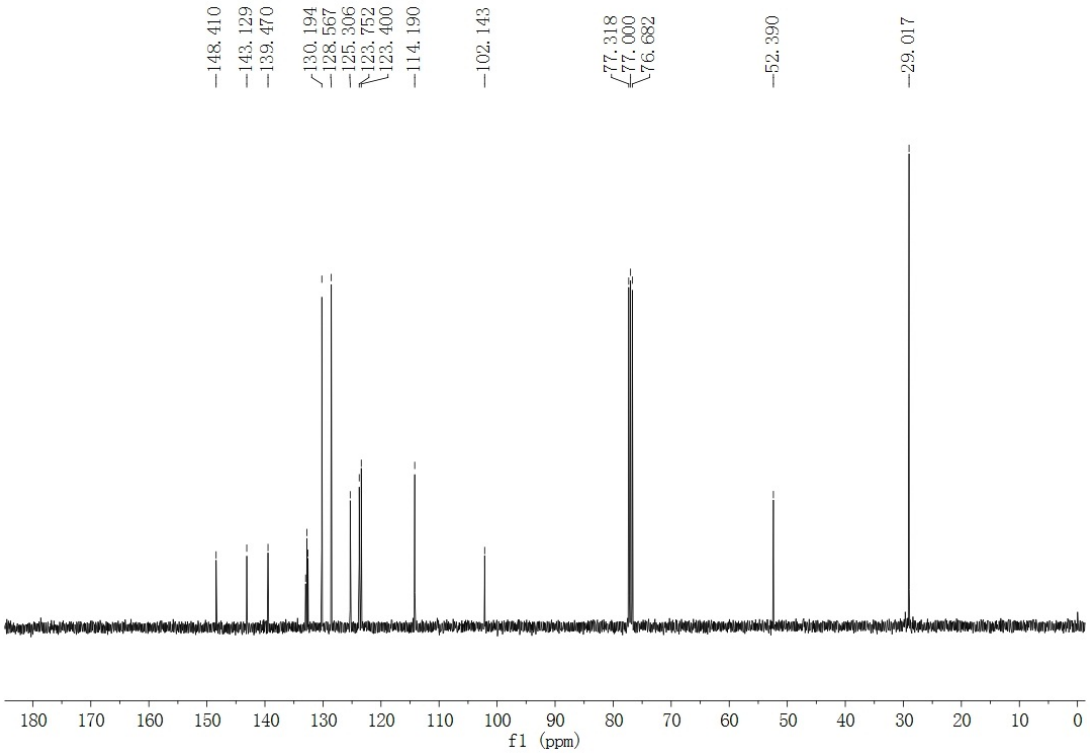

148.223
139.955
134.239
129.536
127.090
125.333
123.480
114.273
101.907
77.318
77.000
76.682
52.434
29.017
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

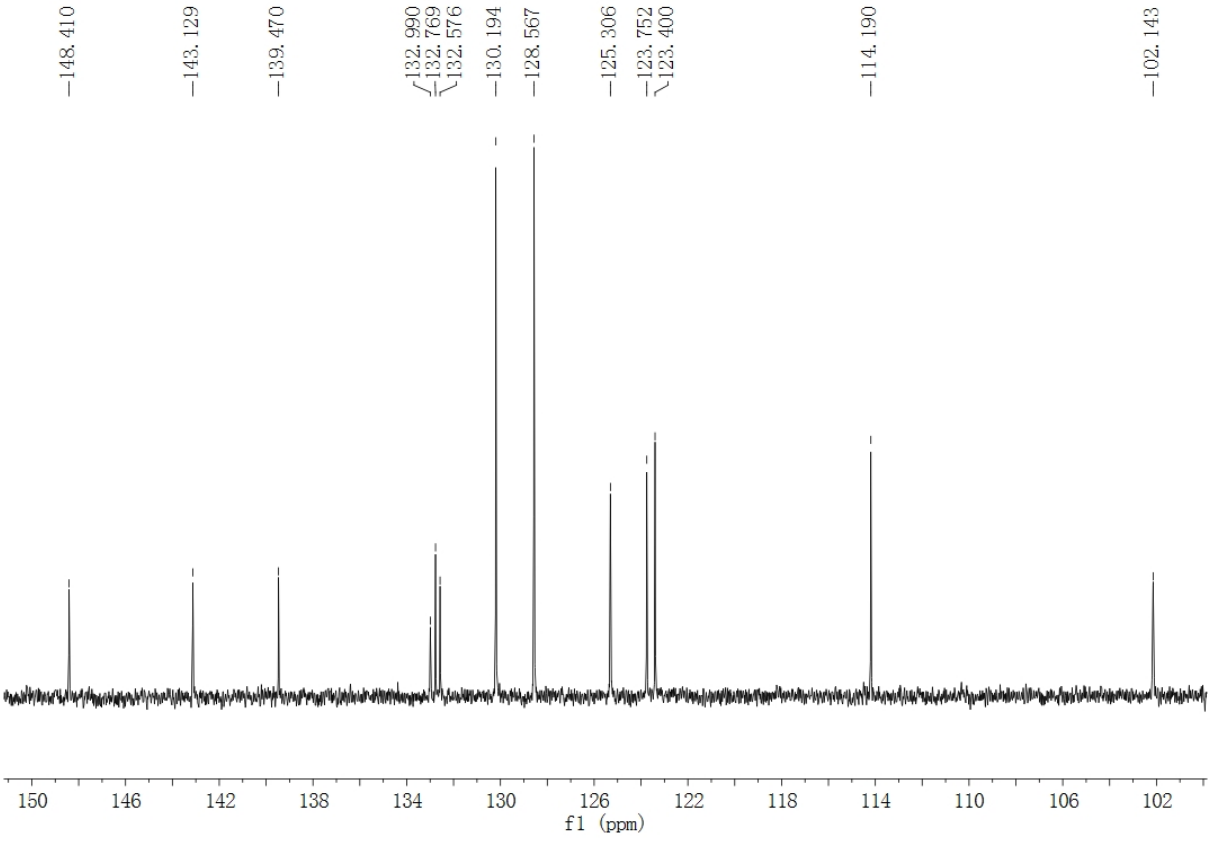

148.223
143.033
139.955
136.059
134.239
132.892
129.536
128.804
127.090
127.007
125.333
123.845
123.480
149 147 145 143 141 139 137 135 133 131 129 127 125 123
f1 (ppm)

^{1}H NMR and ^{13}C NMR of *N-tert*-butyl-2-(4-chlorophenyl)benzo-[b][1,4]oxazepin-4-amine (15)

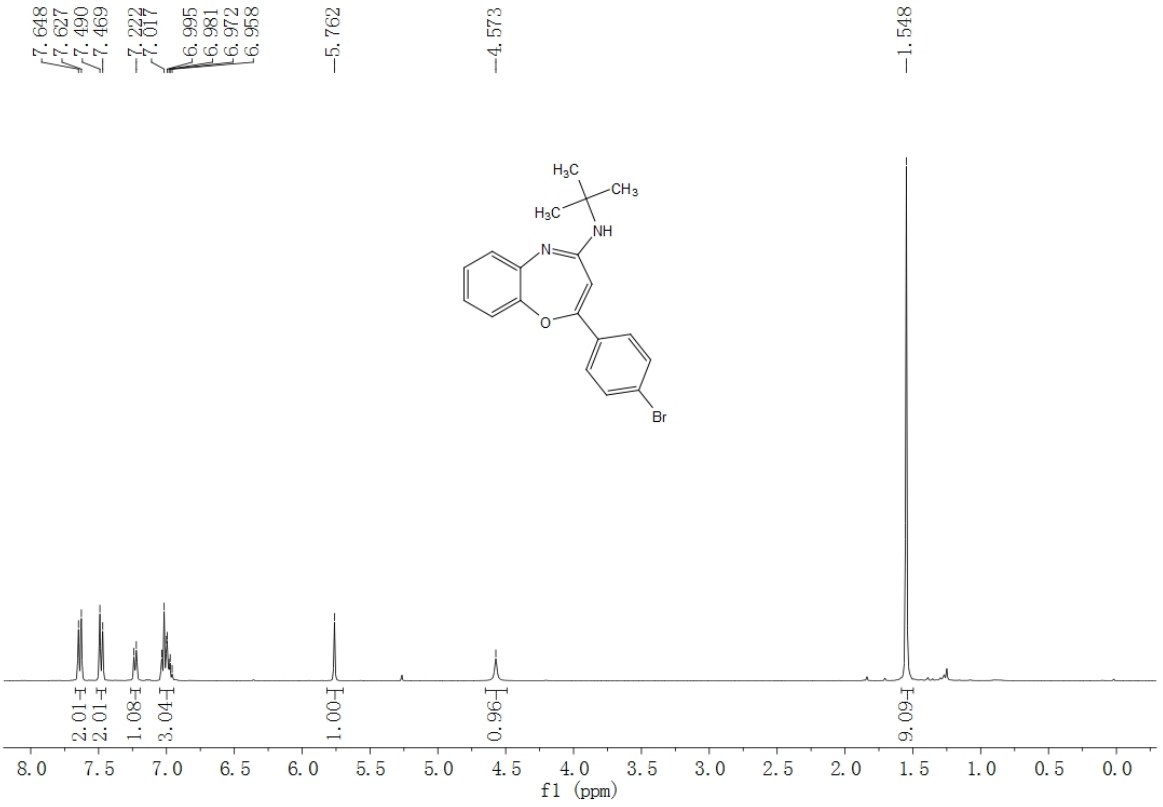


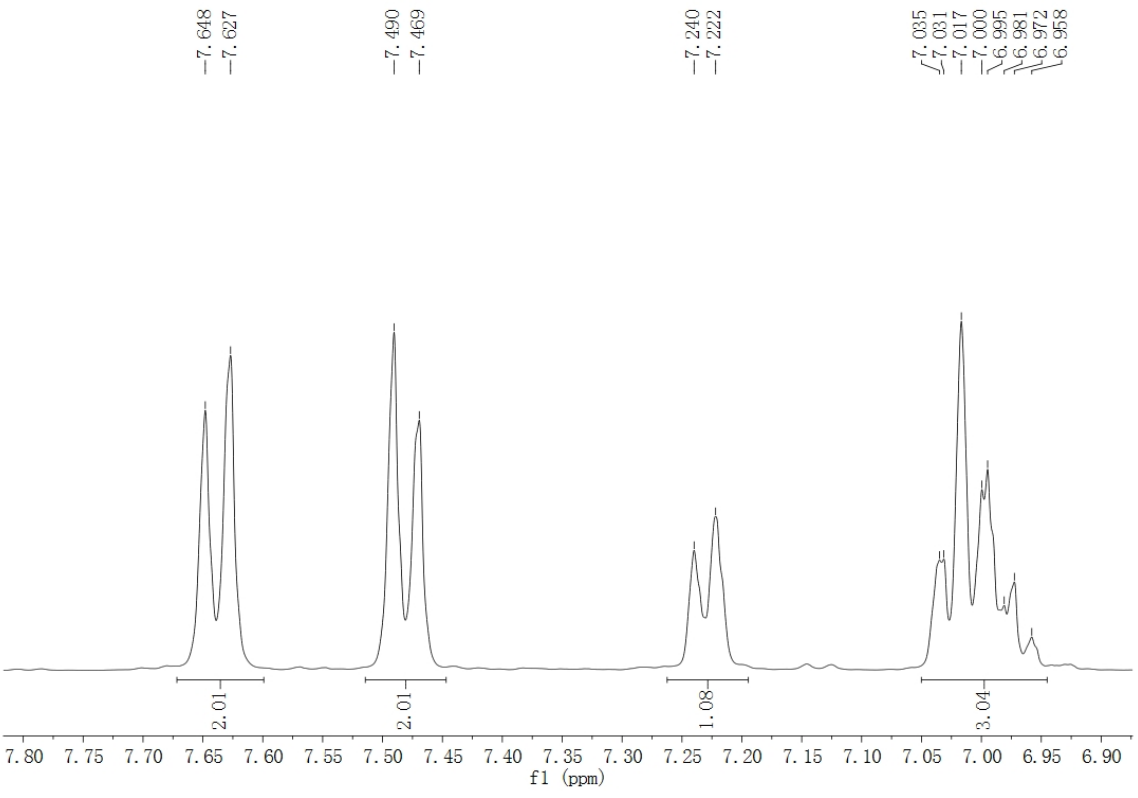


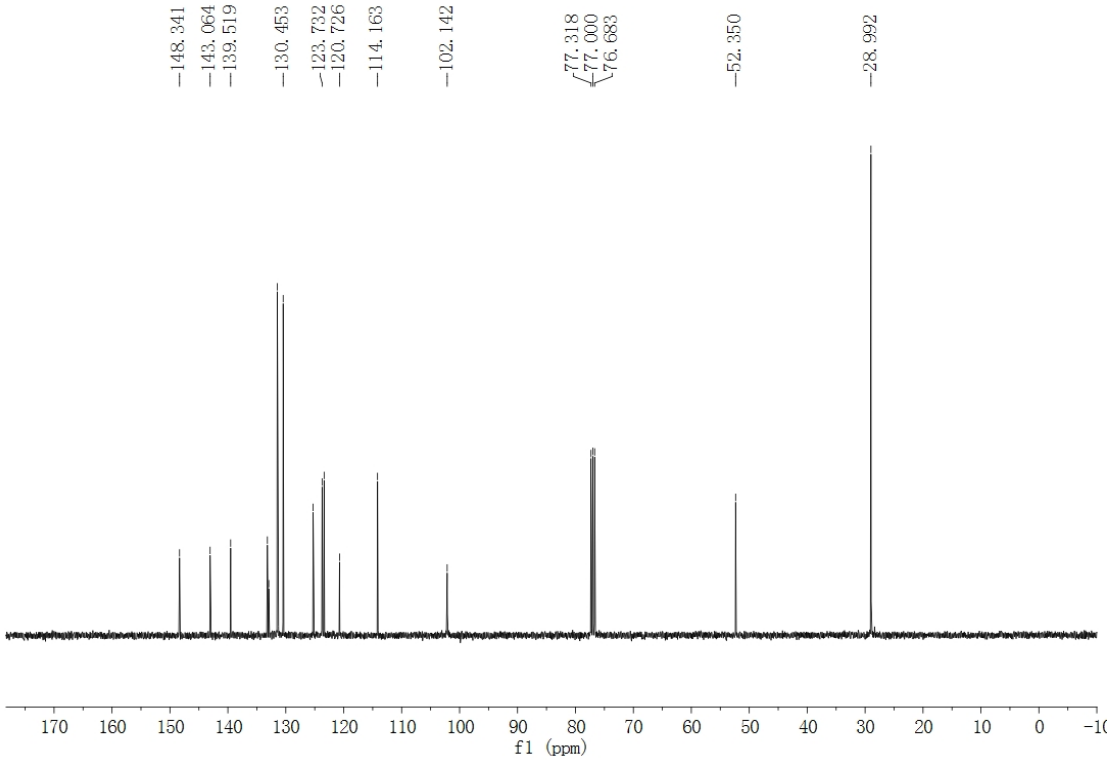

148.410
143.129
139.470
130.194
128.567
125.306
123.752
123.400
114.190
102.143
77.318
77.000
76.682
52.390
29.017
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

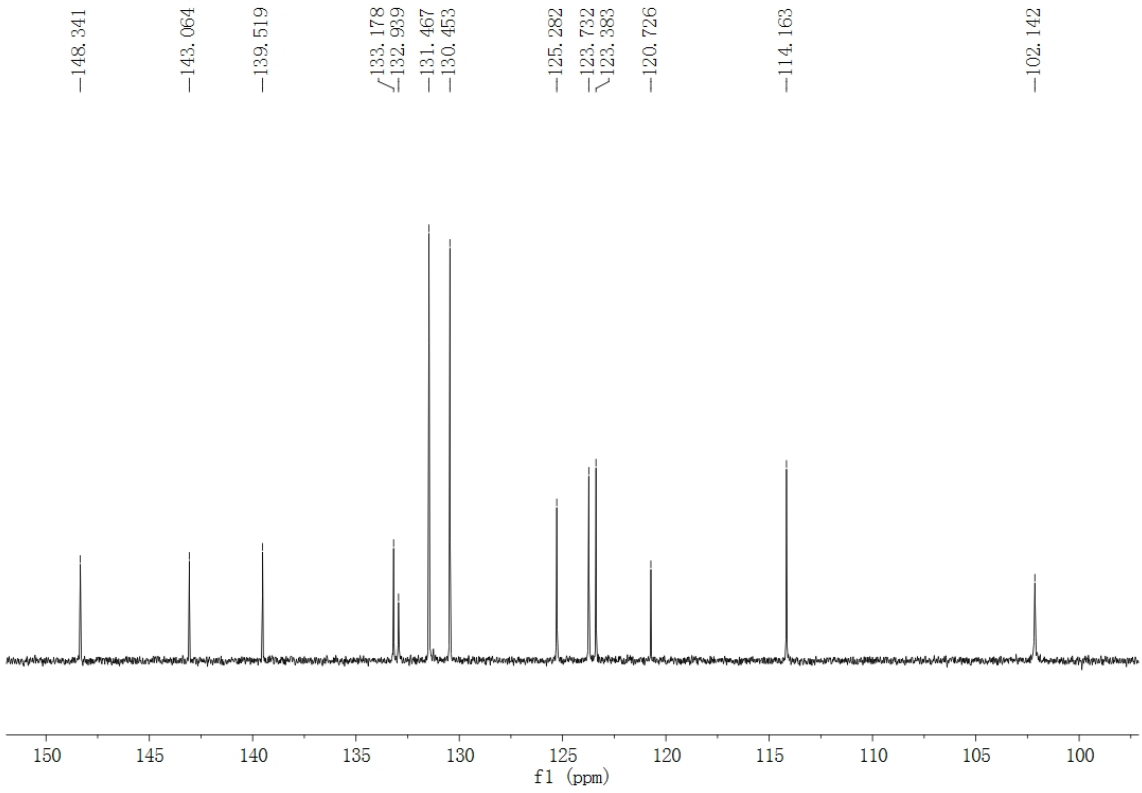

148.410
143.129
139.470
132.990
132.769
132.576
130.194
128.567
125.306
123.752
123.400
114.190
102.143
150 146 142 138 134 130 126 122 118 114 110 106 102
f1 (ppm)

^{1}H NMR and ^{13}C NMR of *N-tert*-butyl-2-(4-bromophenyl)benzo-[b][1,4]oxazepin-4-amine (16)

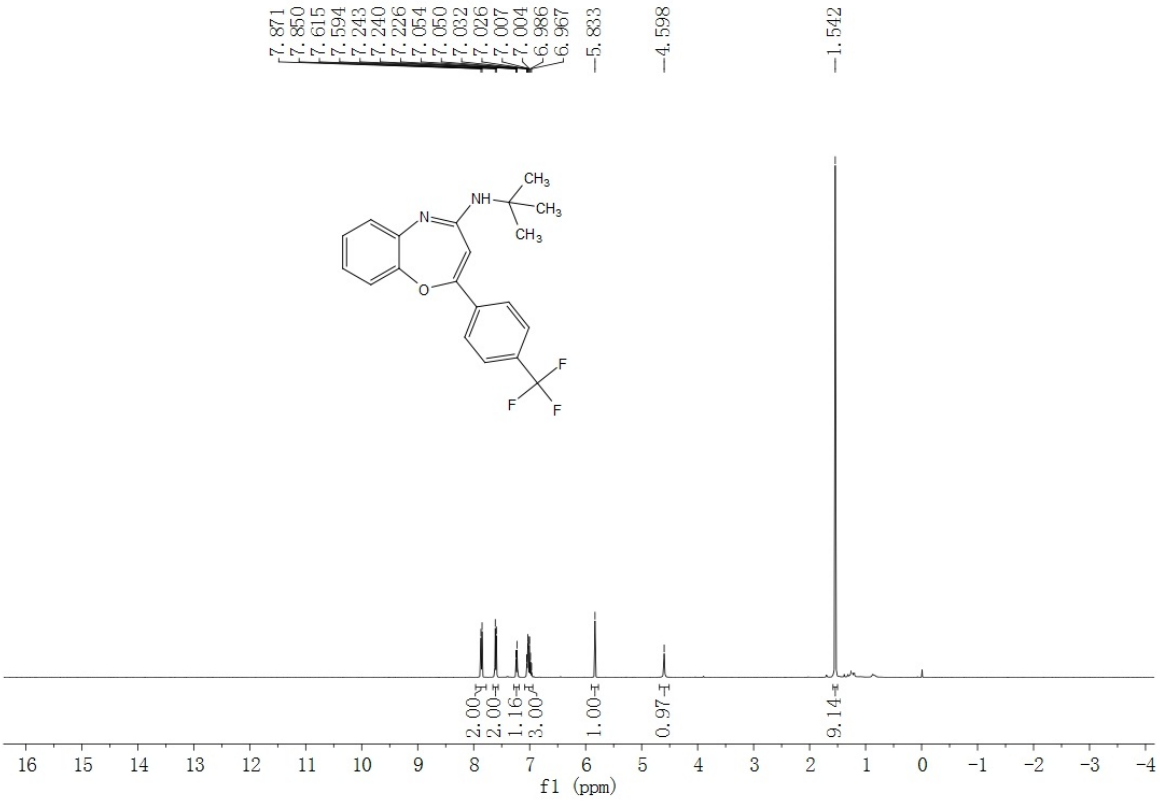


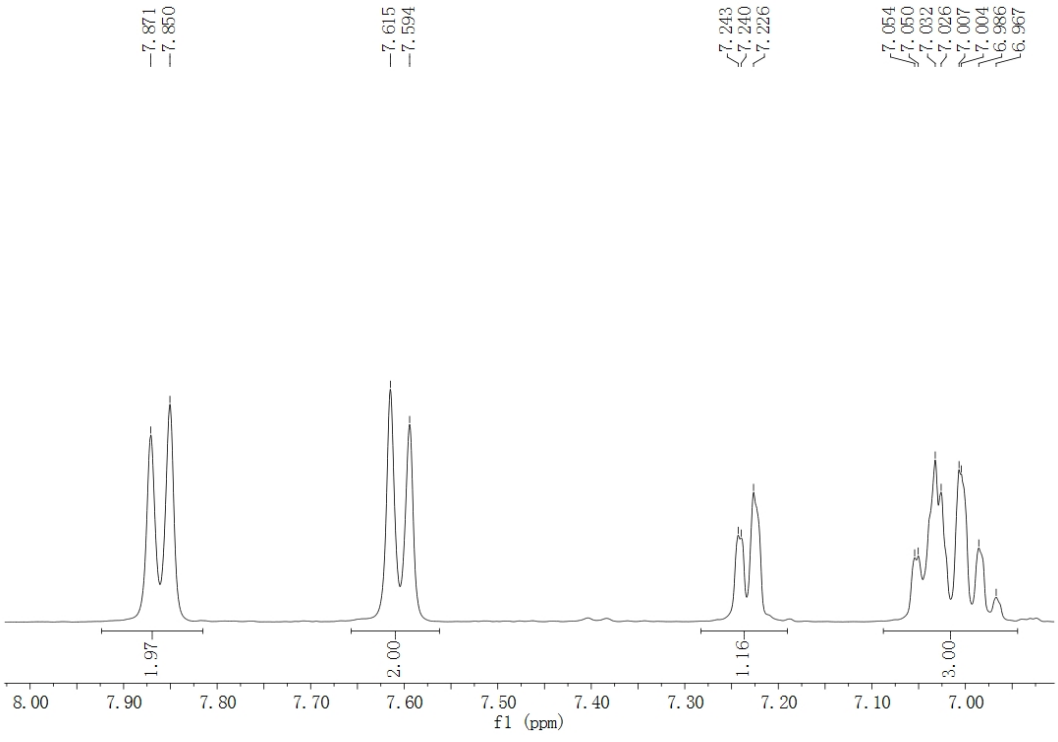


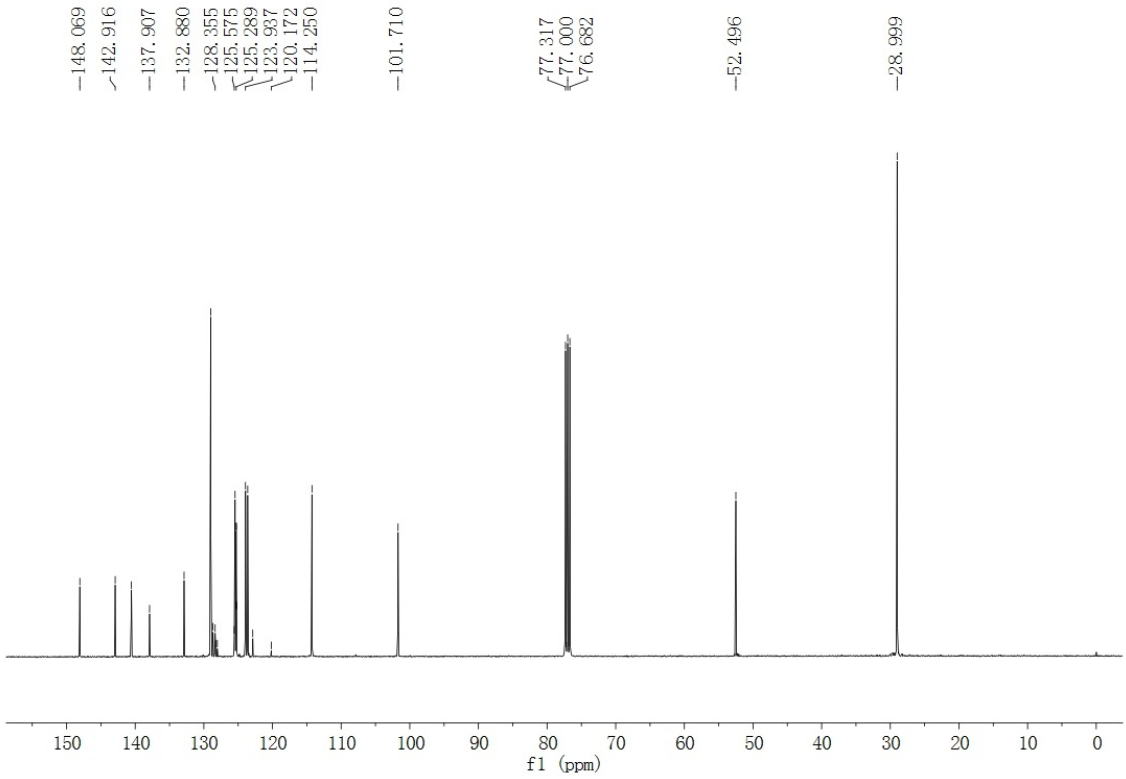

148.341
143.064
139.519
130.453
123.732
120.726
114.163
102.142
77.318
77.000
76.683
52.350
28.992
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

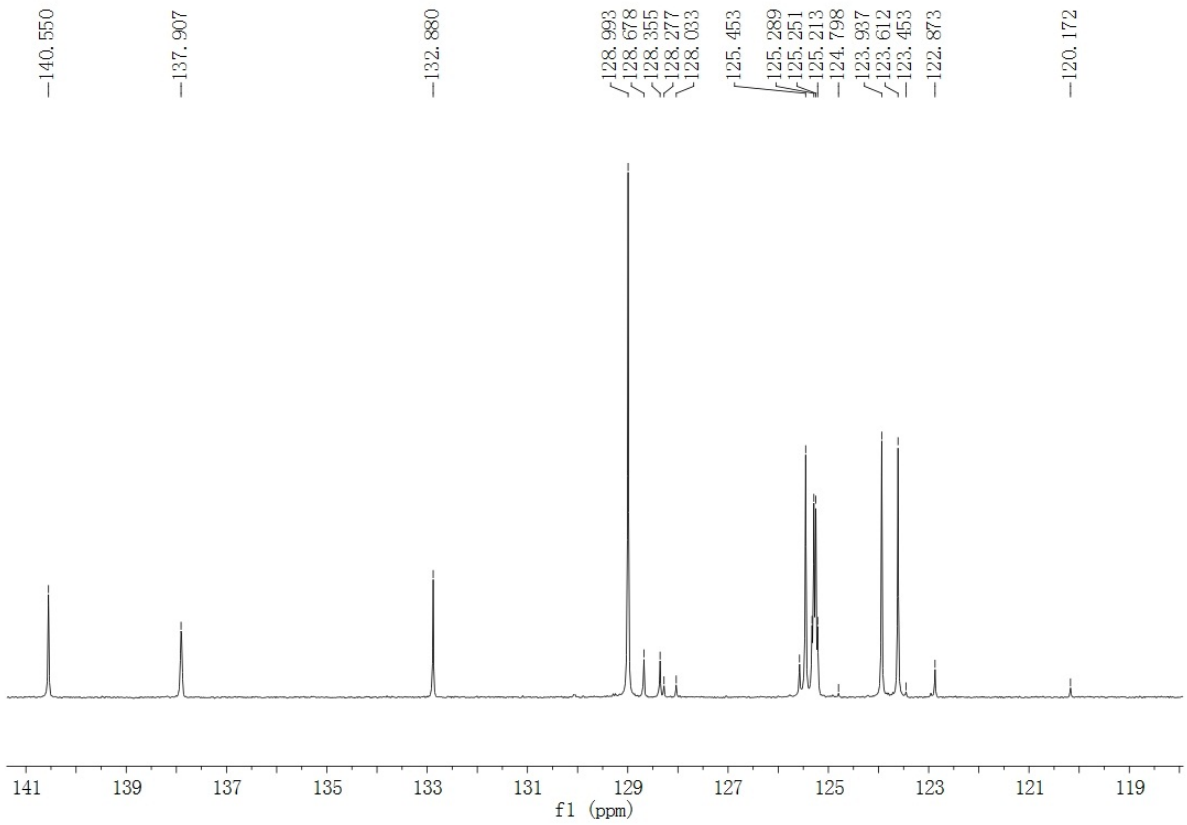

148.341
143.064
139.519
133.178
132.939
131.467
130.453
125.282
123.732
123.383
120.726
114.163
102.142
150 145 140 135 130 125 120 115 110 105 100
f1 (ppm)

^{1}H NMR and ^{13}C NMR of *N-tert*-butyl-2-(4-(trifluoromethyl)phenyl)benzo-[b][1,4]oxazepin-4-amine (17)

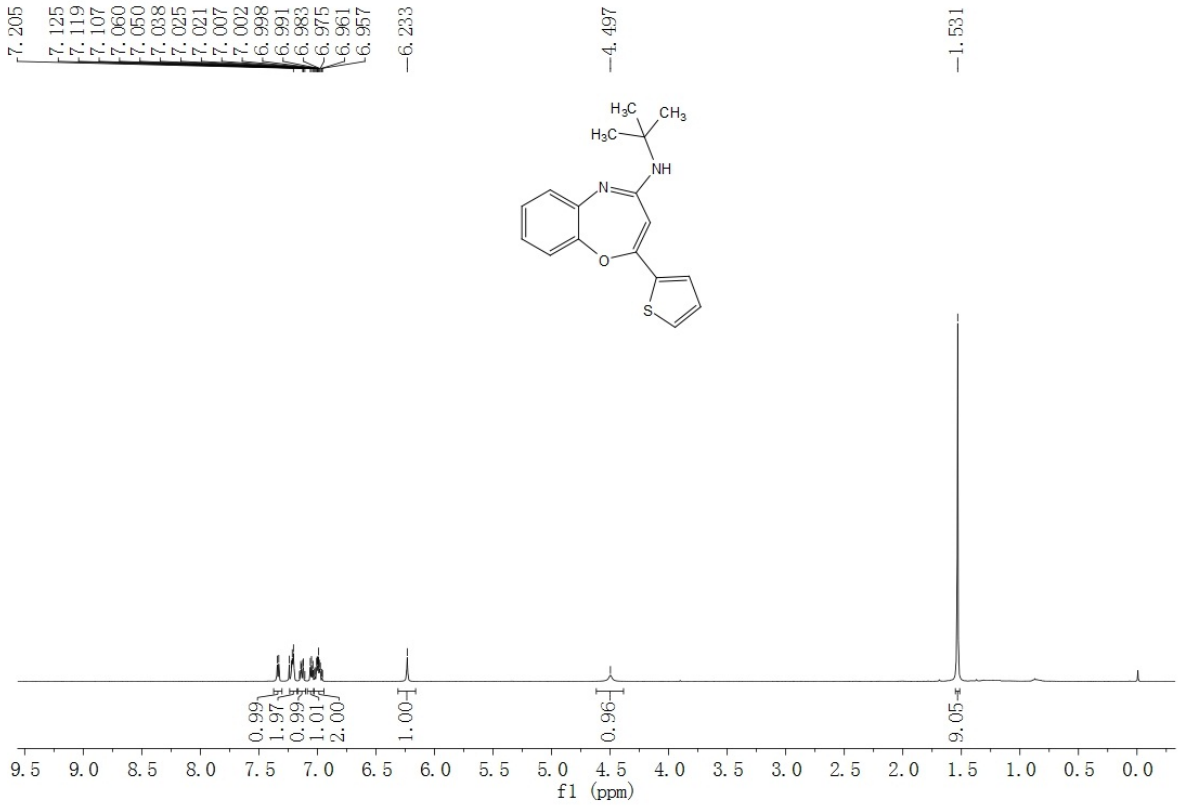


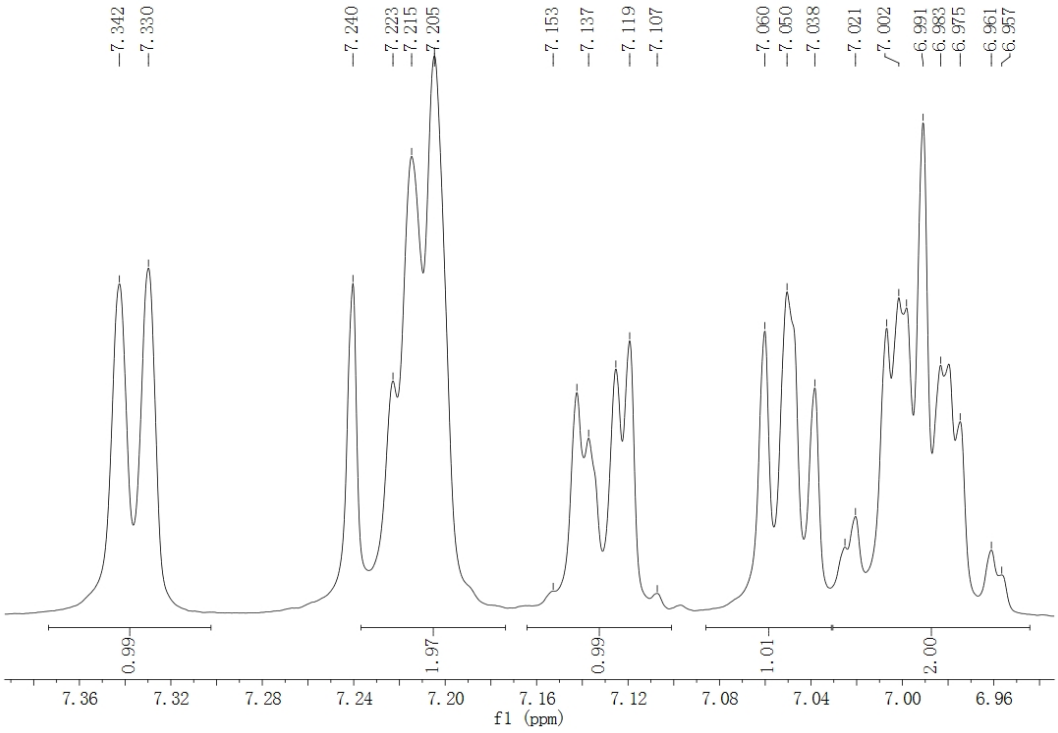


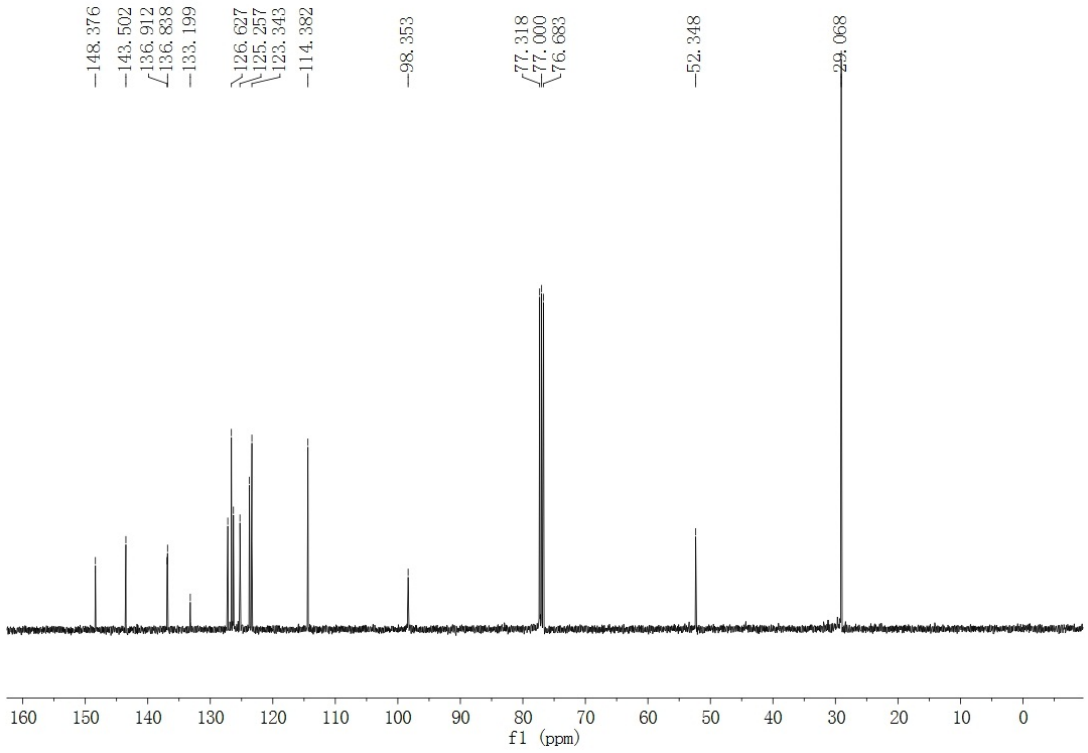

148.069
142.916
137.907
132.880
128.355
125.575
125.289
123.937
120.172
114.250
101.710
77.317
77.000
76.682
52.496
28.999
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

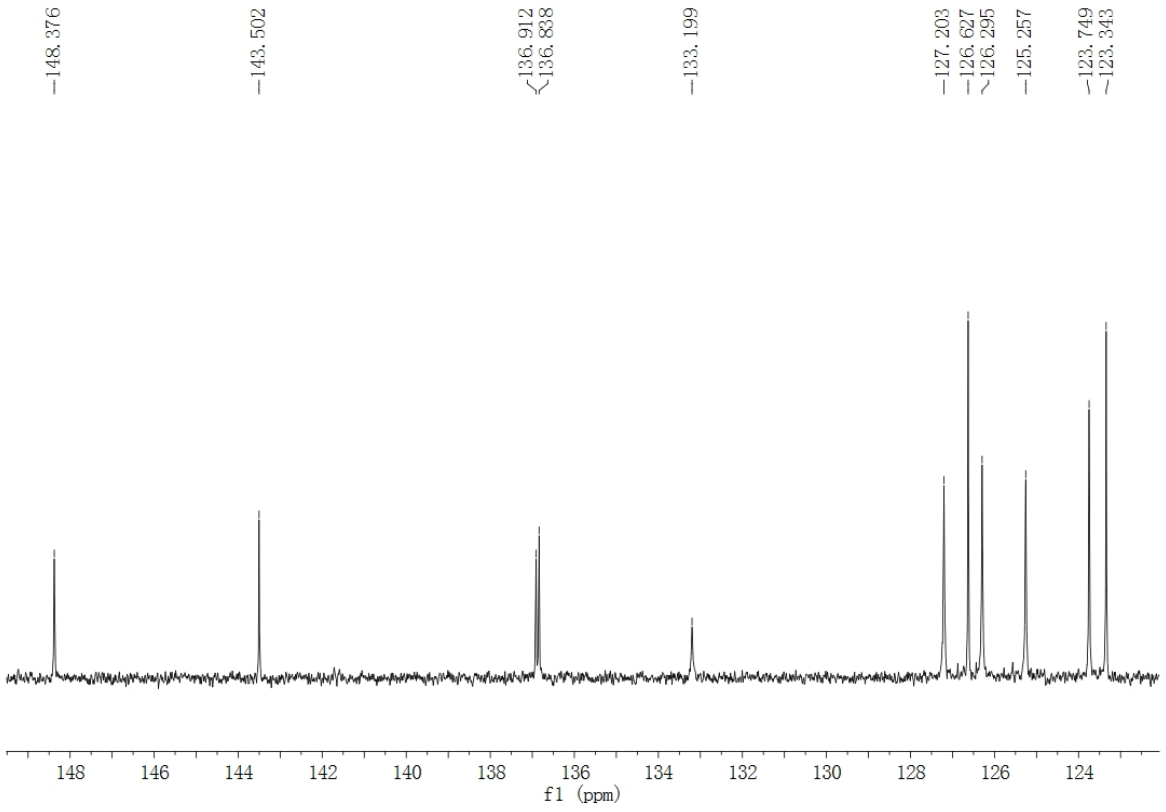

140.550
137.907
132.880
128.993
128.678
128.355
128.277
128.033
125.453
125.289
125.251
125.213
124.798
123.937
123.612
123.453
122.873
120.172
141 139 137 135 133 131 129 127 125 123 121 119
f1 (ppm)

^{1}H NMR and ^{13}C NMR of *N-tert*-butyl-2-(thiophen-2-yl)benzo-[b][1,4]oxazepin-4-amine (18)

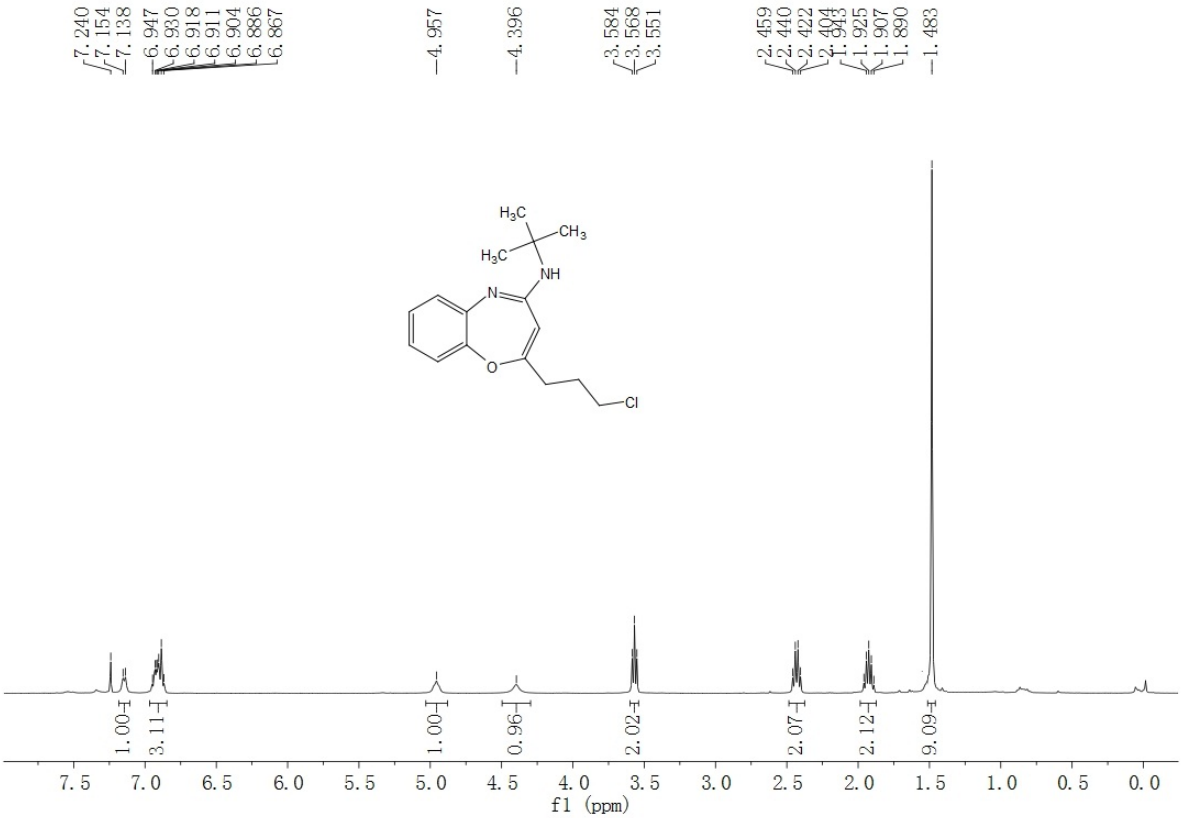


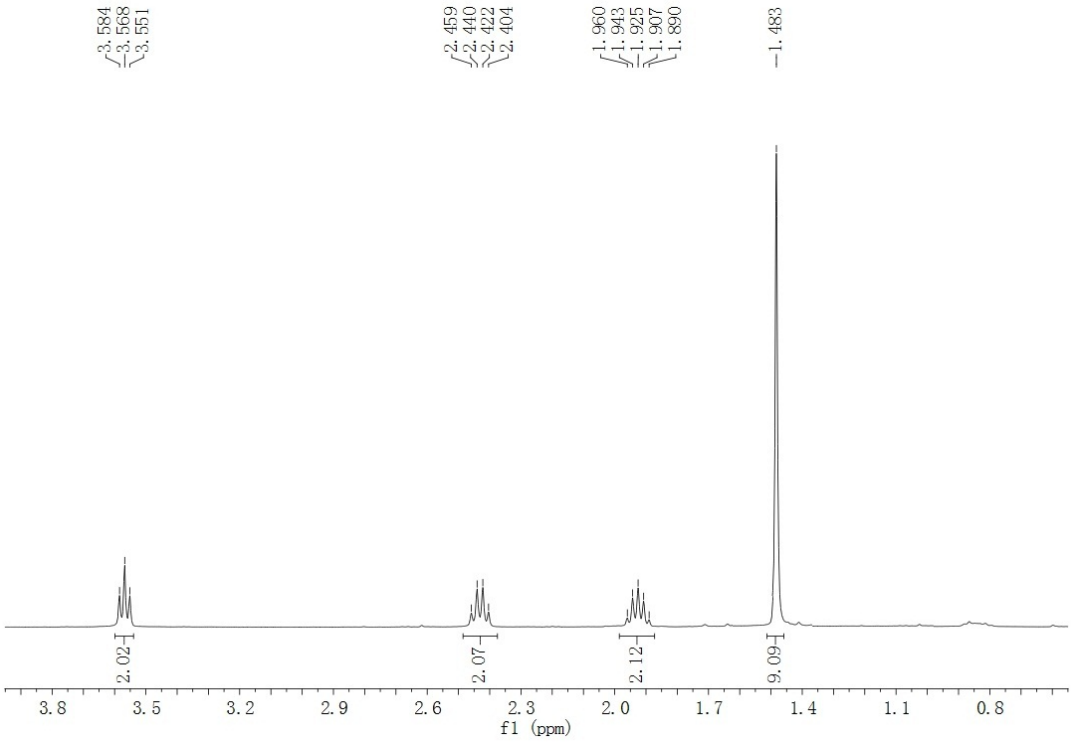


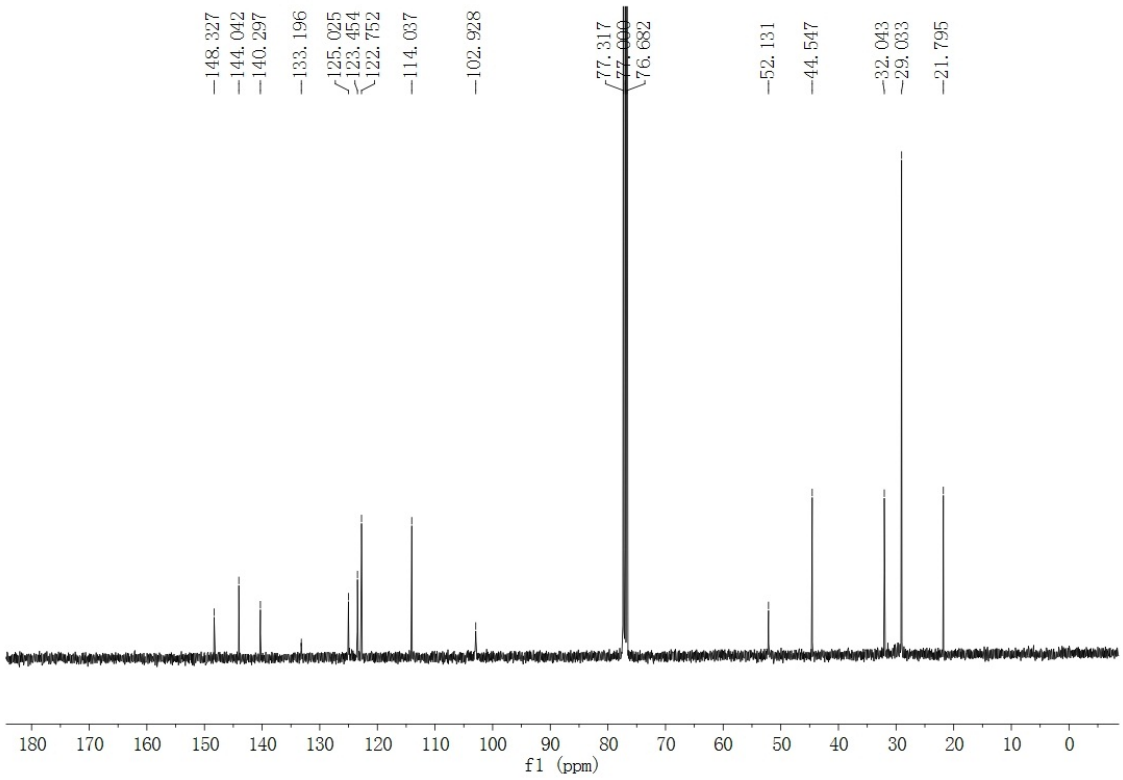

148.376
143.502
136.912
136.838
133.199
126.627
125.257
123.343
114.382
98.353
77.318
77.000
76.683
52.348
29.068
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


148.376
143.502
136.912
136.838
133.199
127.203
126.627
126.295
125.257
123.749
123.343
148 146 144 142 140 138 136 134 132 130 128 126 124
f1 (ppm)

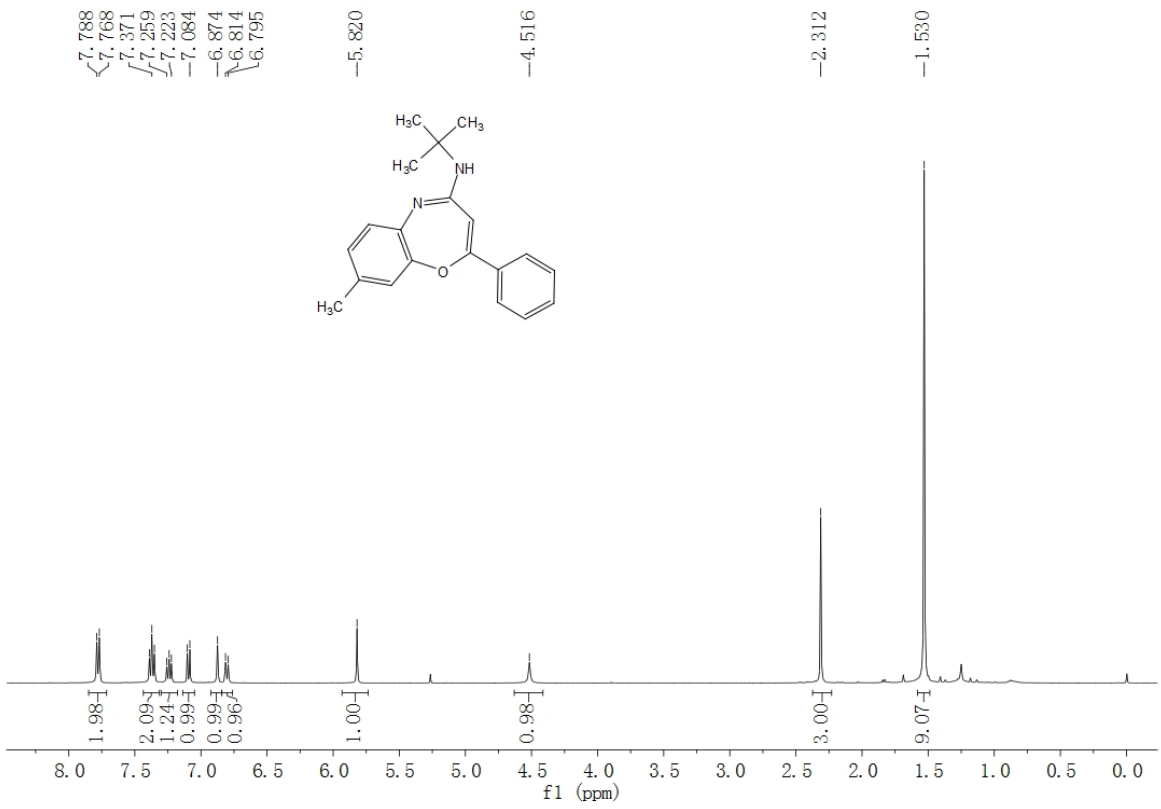
^{1}H NMR and ^{13}C NMR of *N-tert*-butyl-2-(3-chloropropyl)benzo-[b][1,4]oxazepin-4-amine (19)

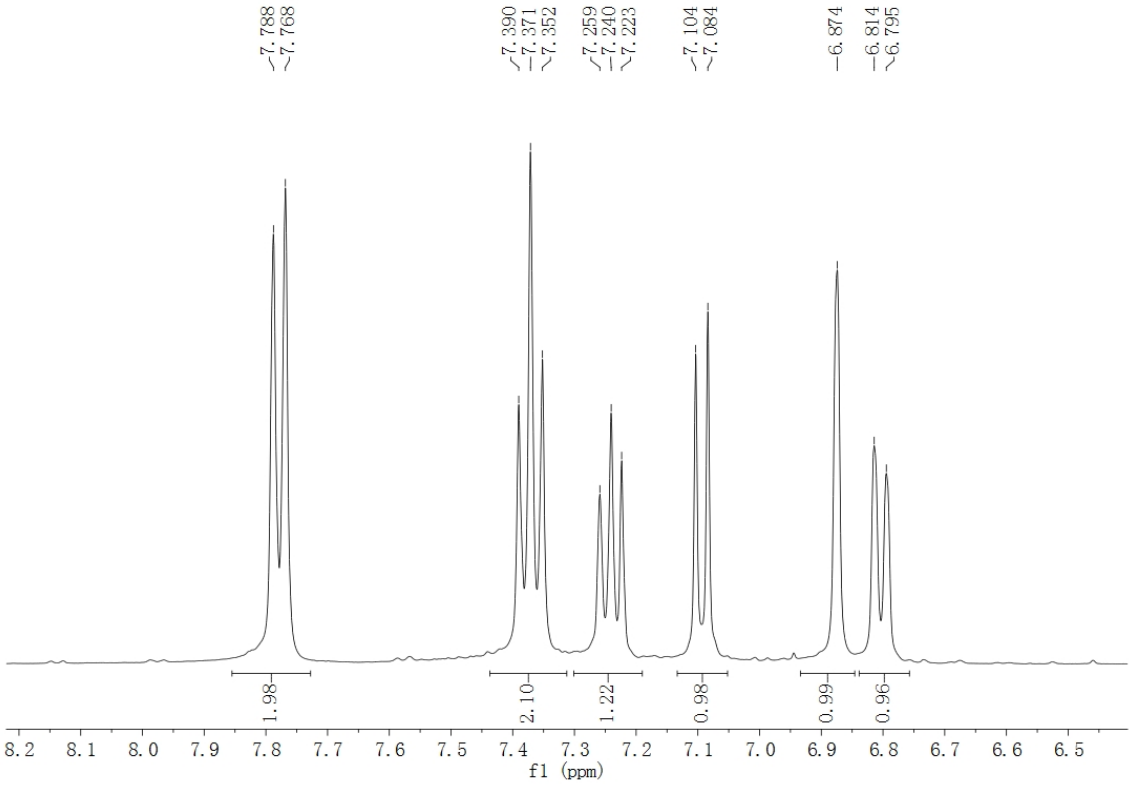


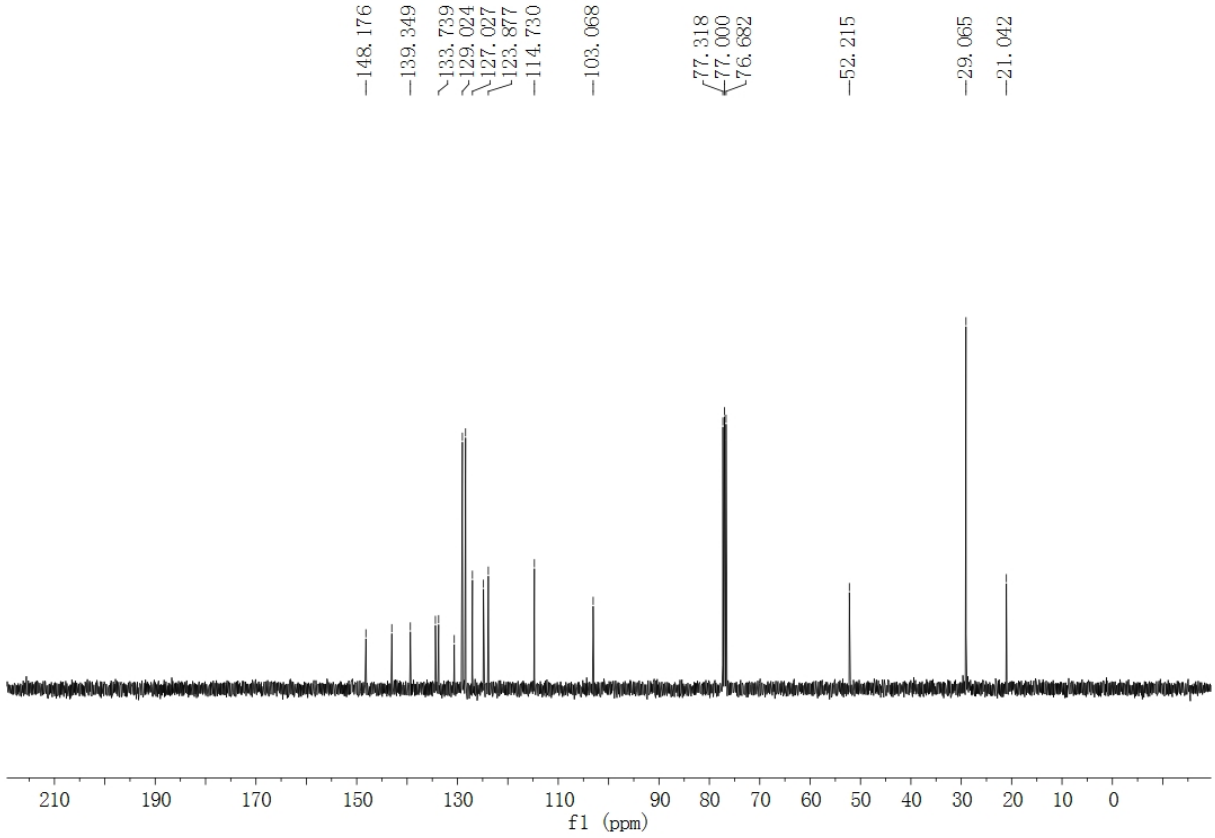


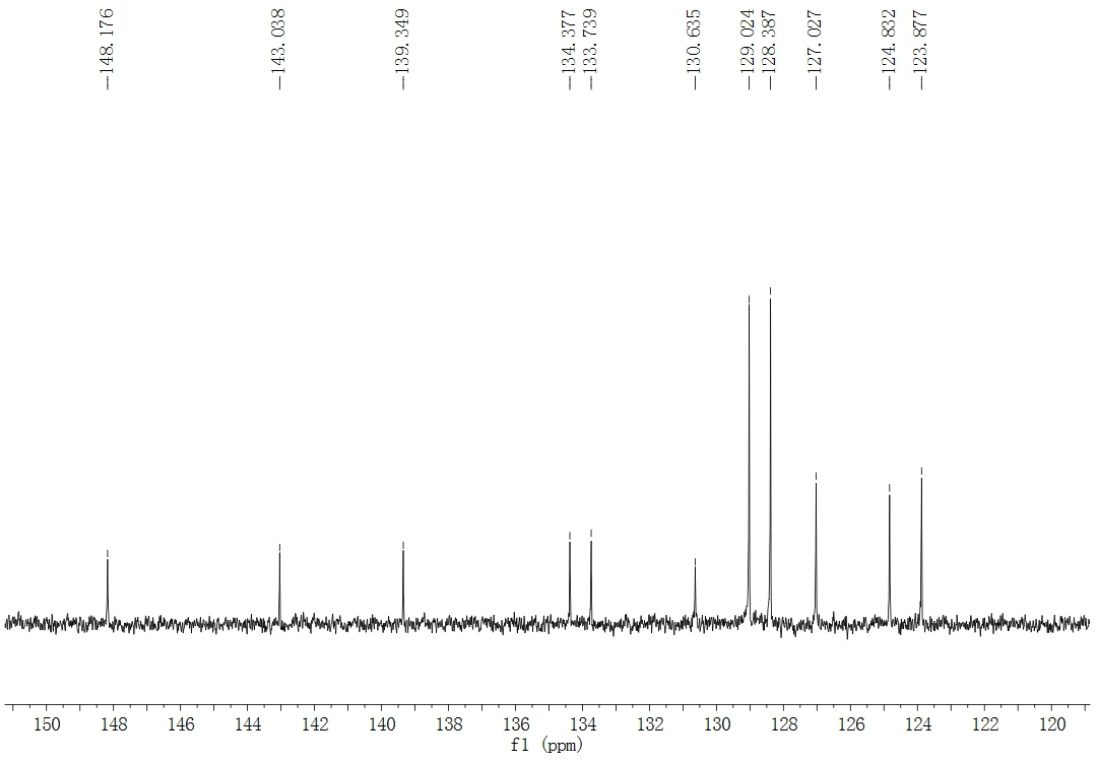


^{1}H NMR and ^{13}C NMR of *N-tert*-butyl-8-methyl-2-phenylbenzo[b][1,4]oxazepin-4-amine (20)

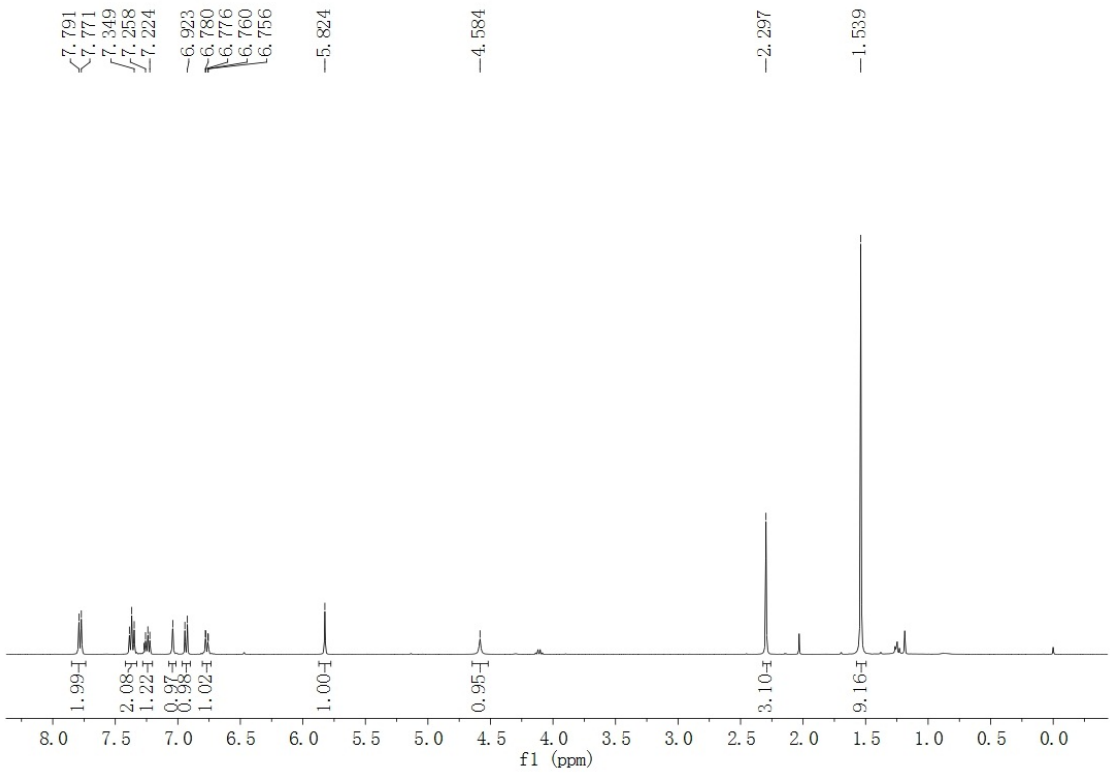


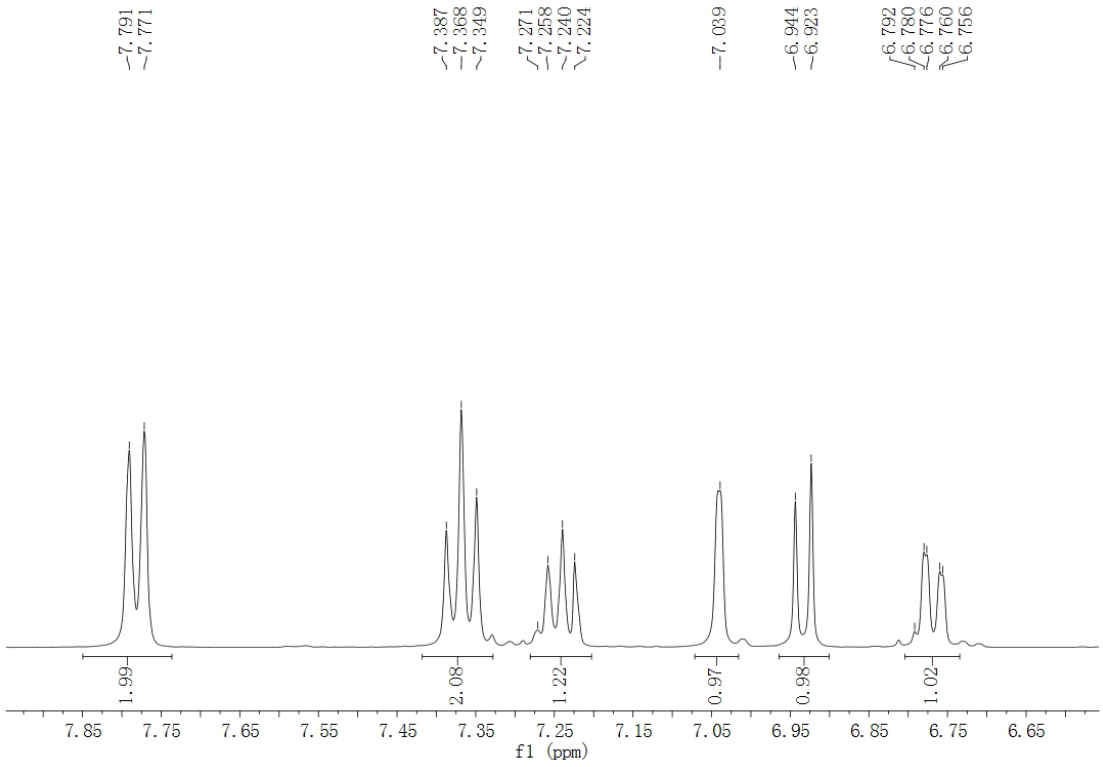

7.788
7.768
7.390
7.371
7.352
7.259
7.240
7.223
7.104
7.084
6.874
6.814
6.795
1.98
2.10
1.22
0.98
0.99
0.96
f1 (ppm)

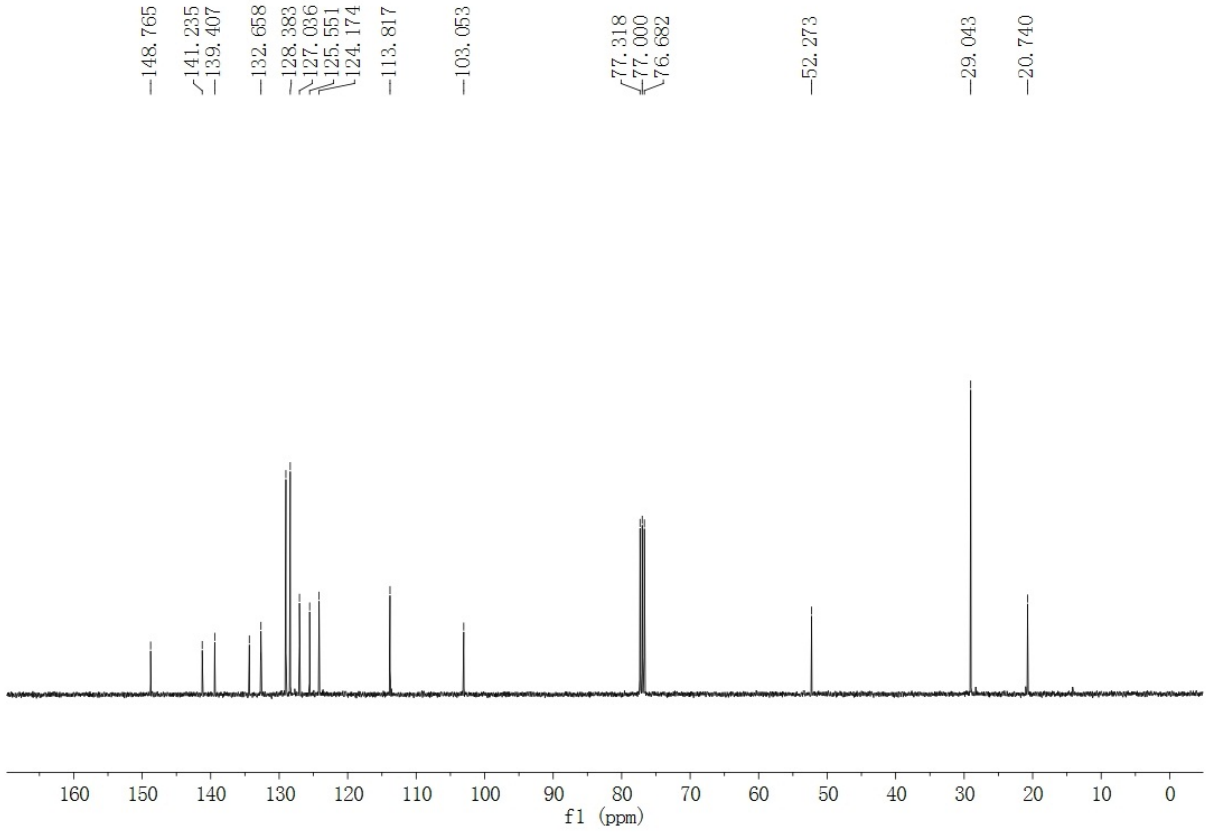

148.176
139.349
133.739
129.024
127.027
123.877
114.730
103.068
77.318
77.000
76.682
52.215
29.065
21.042
f1 (ppm)

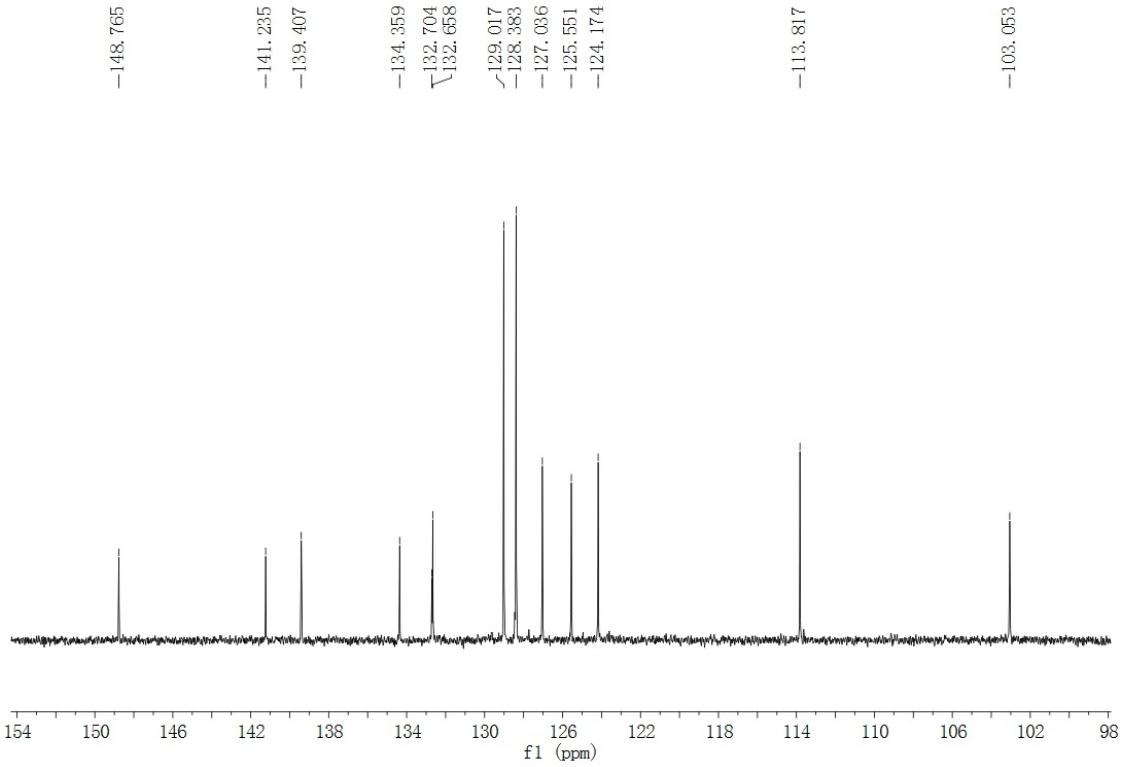


^{1}H NMR and ^{13}C NMR of *N-tert*-butyl-7-methyl-2-phenylbenzo[b][1,4]oxazepin-4-amine (21)

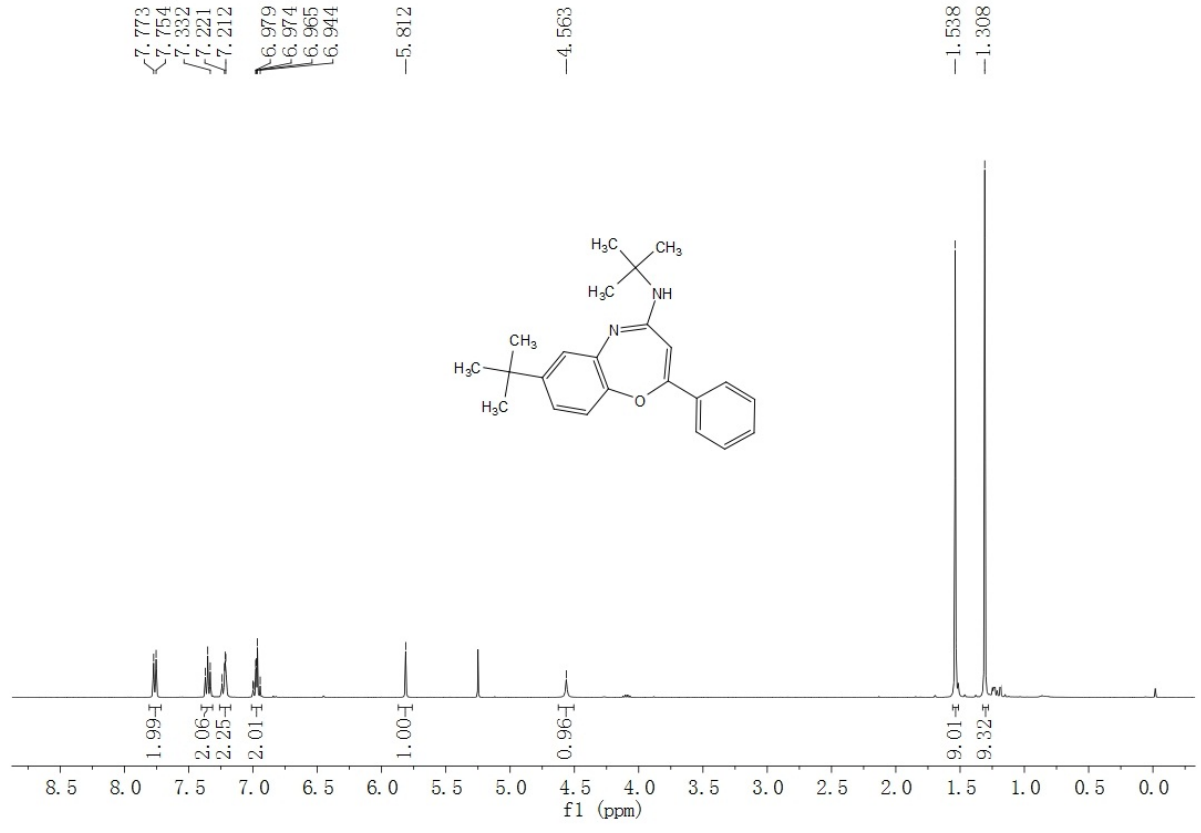


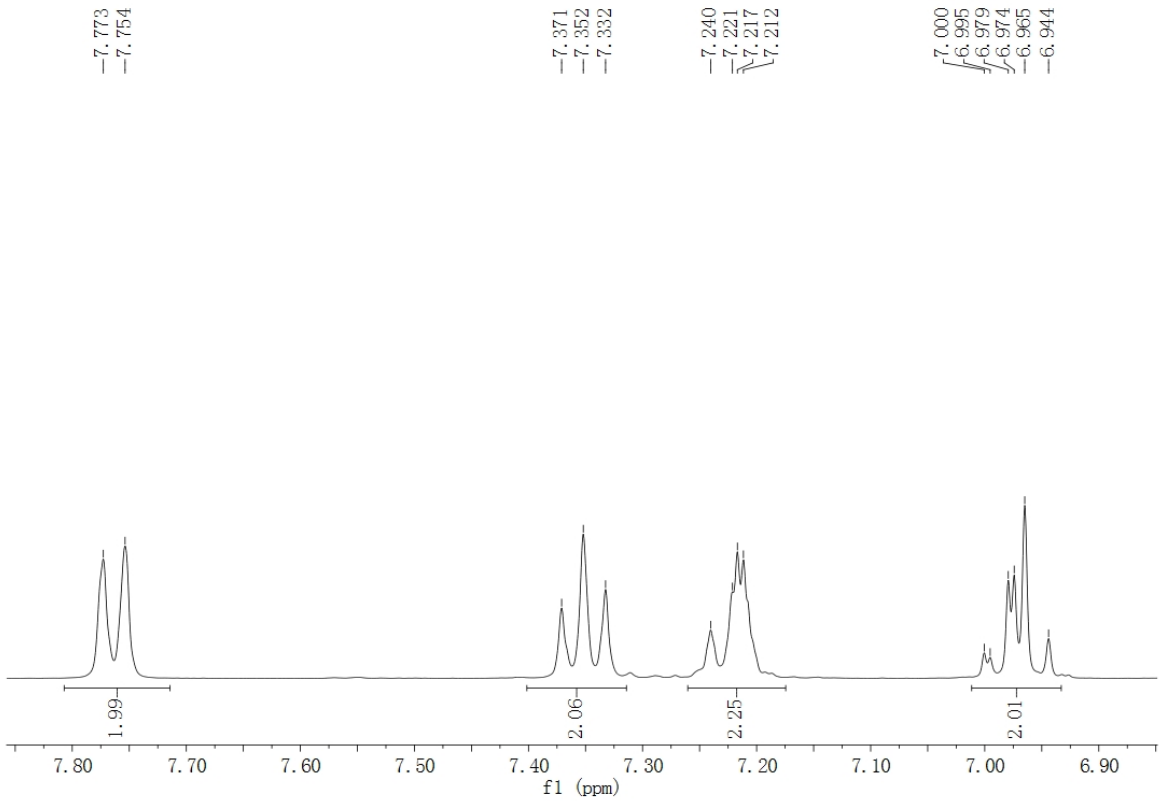

7.791
7.771
7.387
7.368
7.349
7.271
7.258
7.240
7.224
7.039
6.944
6.923
6.792
6.780
6.776
6.760
6.756
1.99
2.08
1.22
0.97
0.98
1.02
7.85
7.75
7.65
7.55
7.45
7.35
7.25
7.15
7.05
6.95
6.85
6.75
6.65
f1 (ppm)

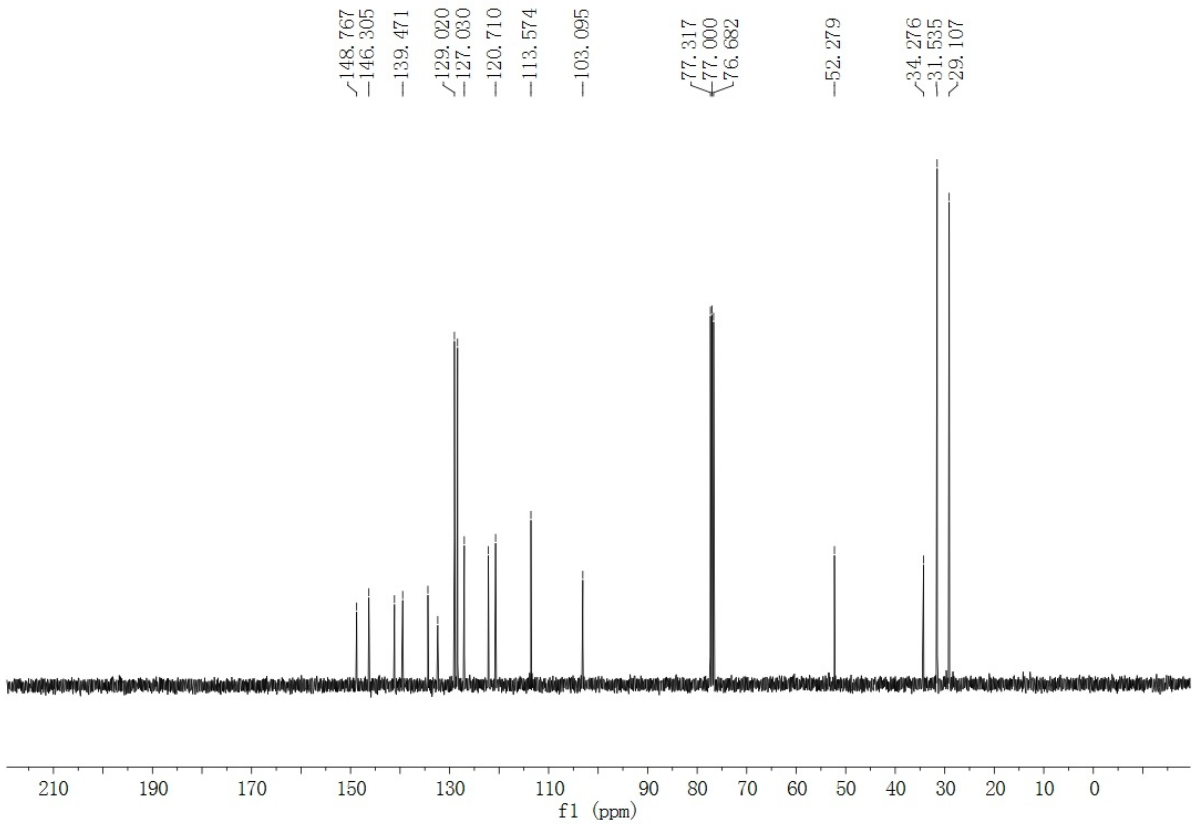

148.765
141.235
139.407
132.658
128.383
127.036
125.551
124.174
113.817
103.053
77.318
77.000
76.682
52.273
29.043
20.740
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

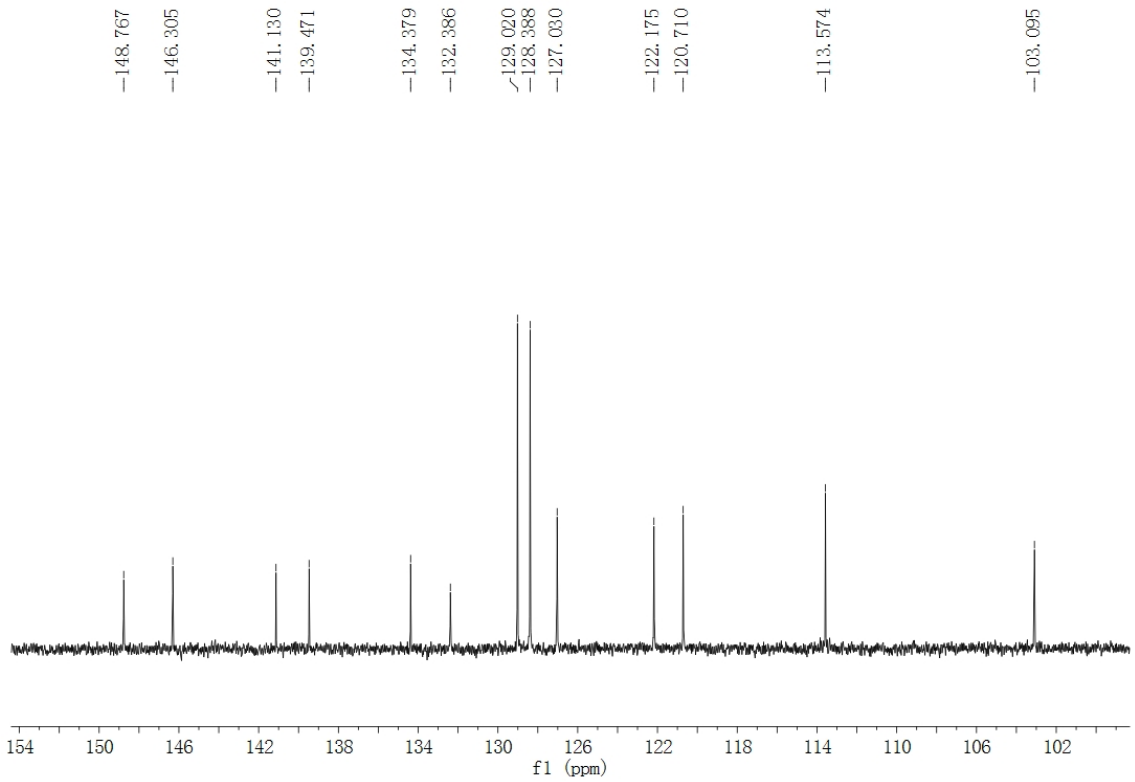


^{1}H NMR and ^{13}C NMR of *N,7-di-tert*-butyl-2-phenylbenzo[b][1,4]oxazepin-4-amine (22)

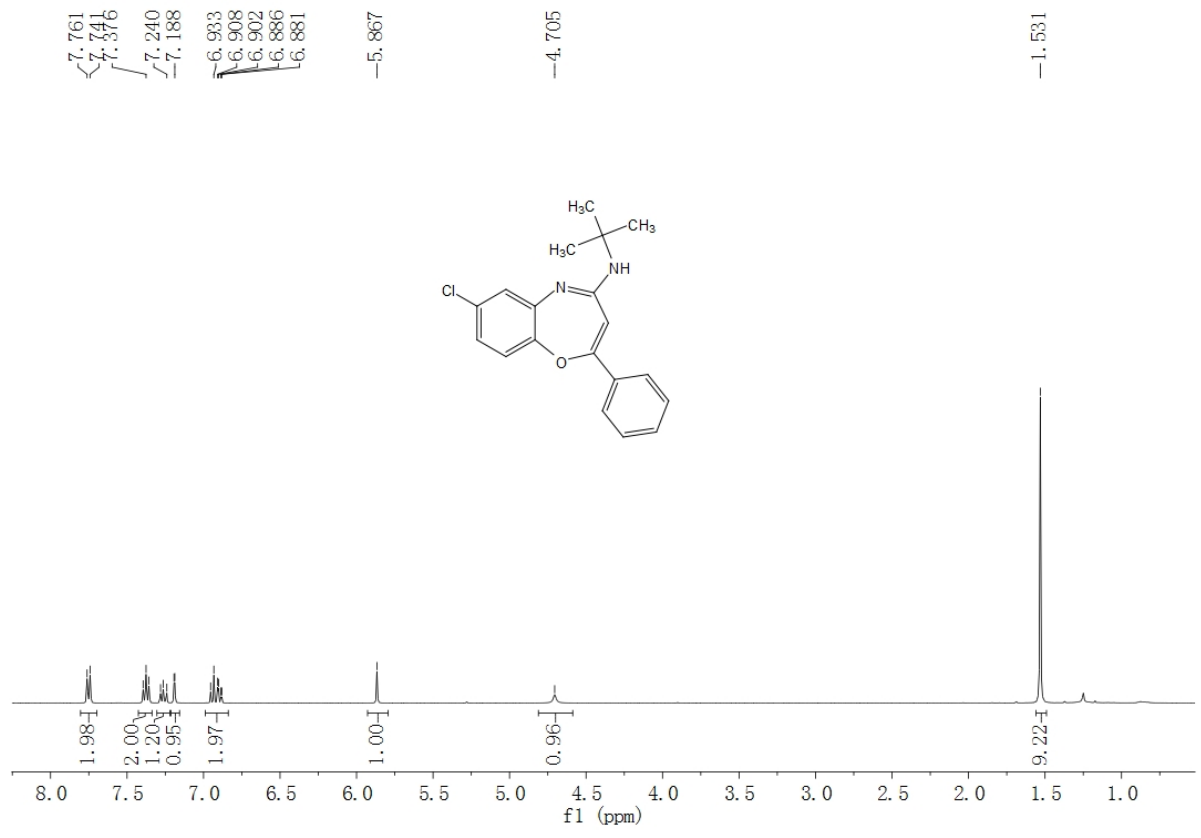


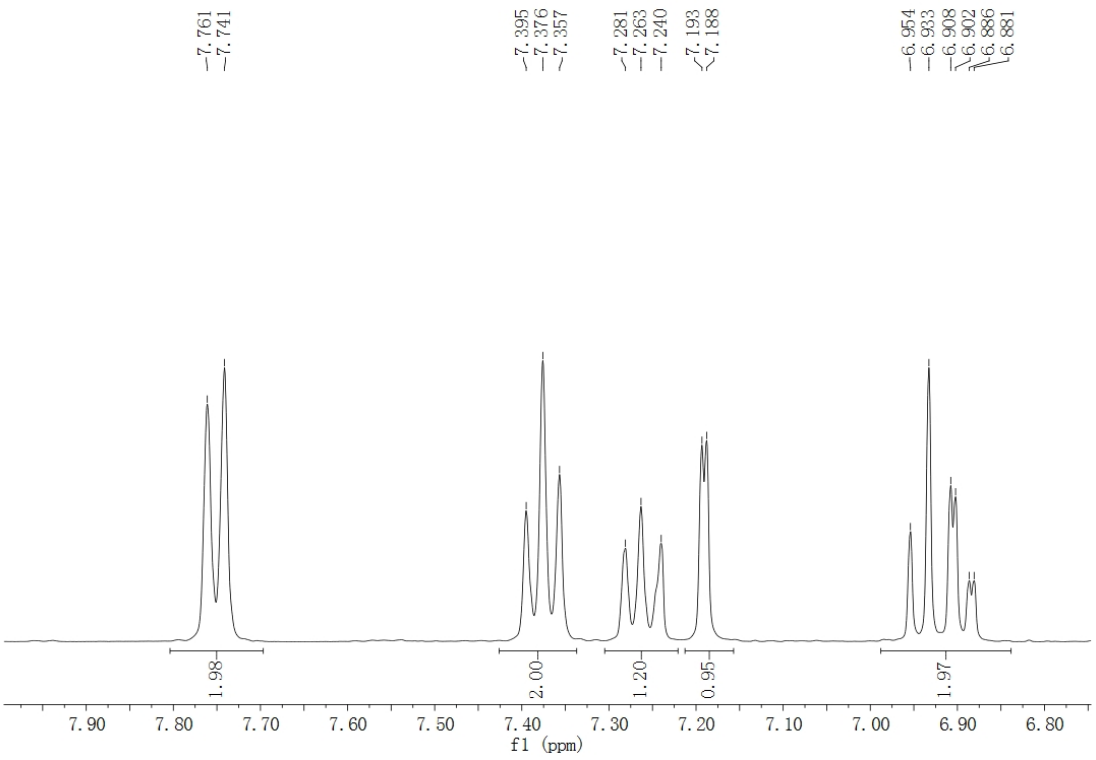

7.773
7.754
7.371
7.352
7.332
7.240
7.221
7.217
7.212
7.000
6.995
6.979
6.974
6.965
6.944
1.99
2.06
2.25
2.01
7.80
7.70
7.60
7.50
7.40
7.30
7.20
7.10
7.00
6.90
f1 (ppm)

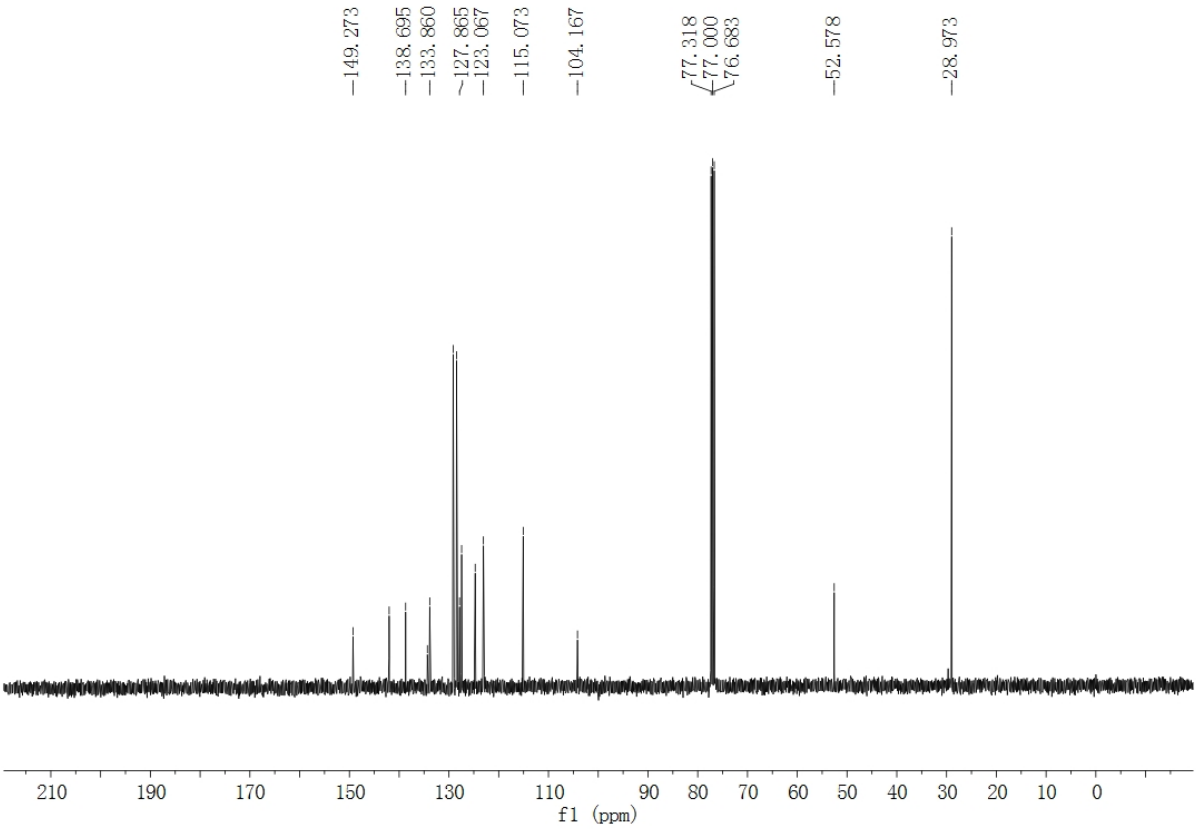

148.767
146.305
139.471
129.020
127.030
120.710
113.574
103.095
77.317
77.000
76.682
52.279
34.276
31.535
29.107
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

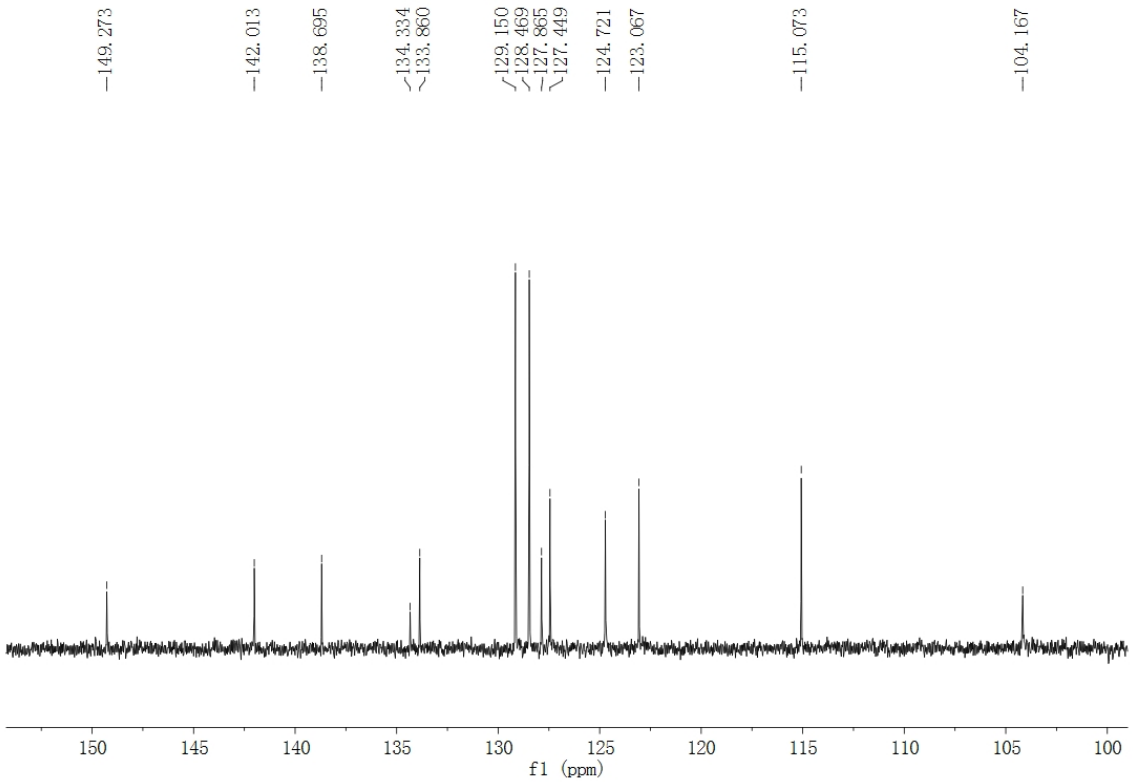


^{1}H NMR and ^{13}C NMR of *N-tert*-butyl-7-chloro-2-phenylbenzo[b][1,4]oxazepin-4-amine (23)

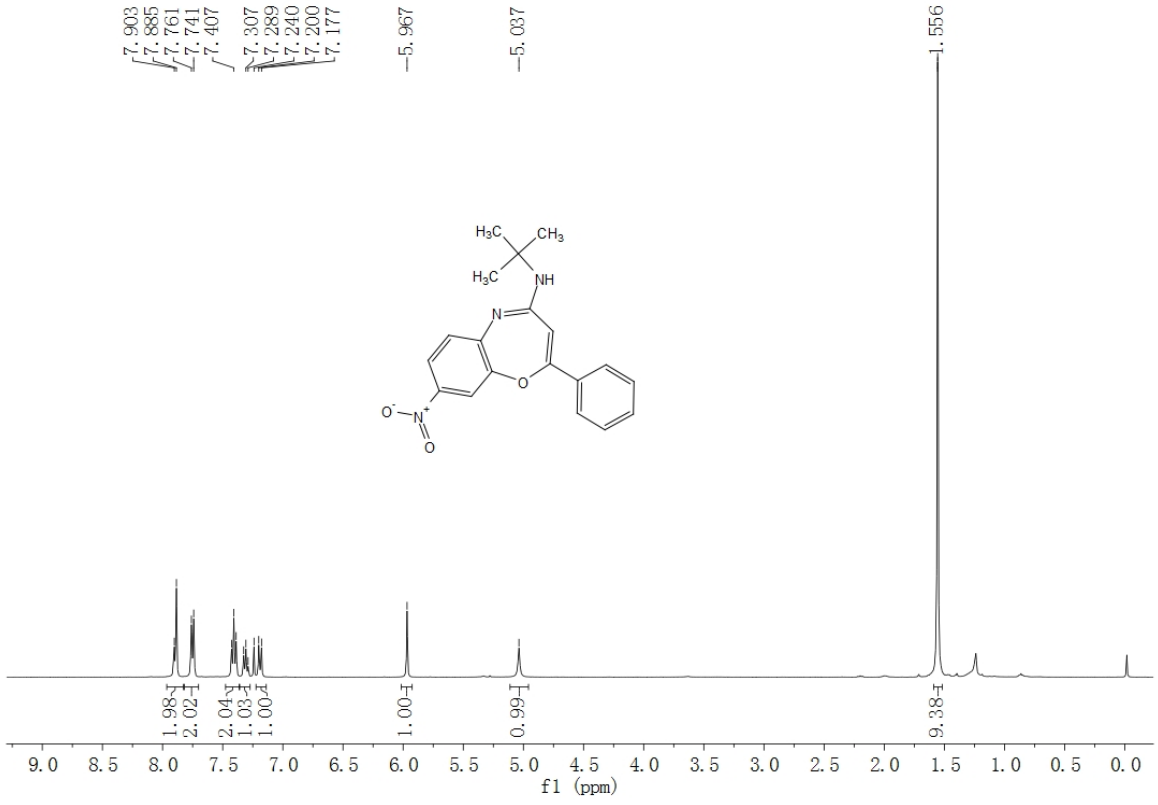


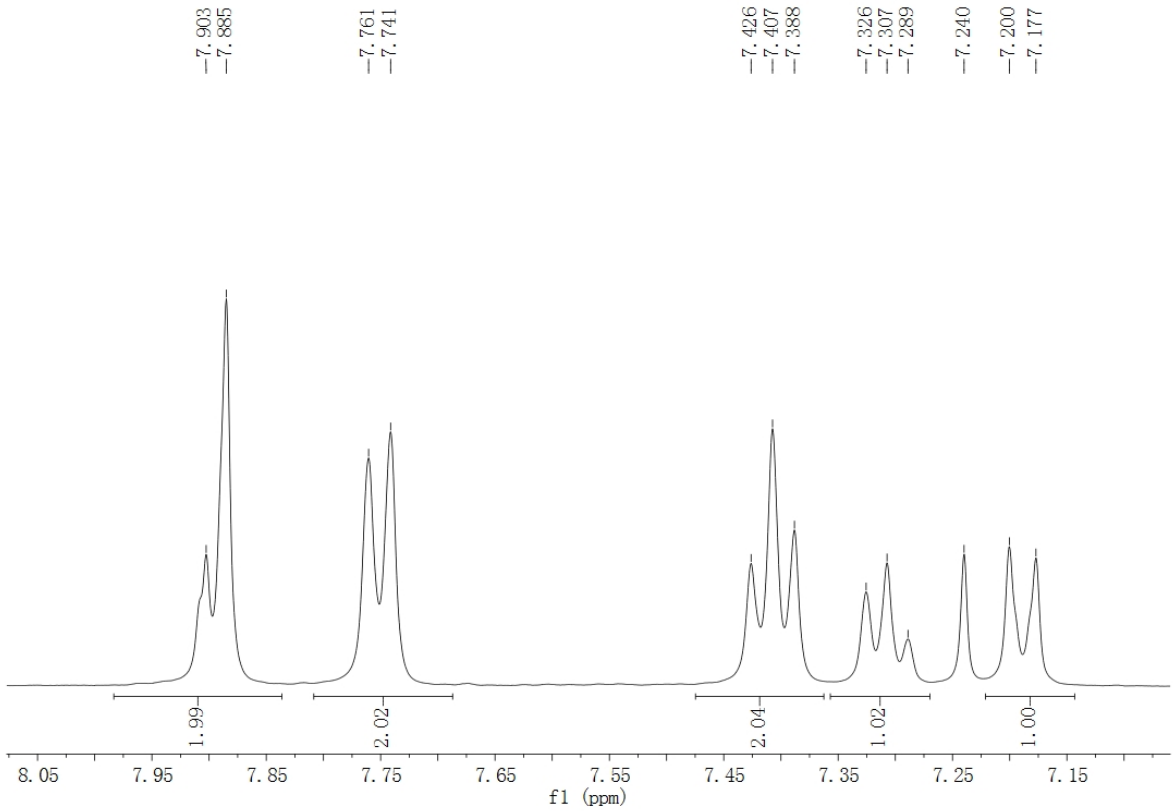

7.761
7.741
7.395
7.376
7.357
7.281
7.263
7.240
7.193
7.188
6.954
6.933
6.908
6.902
6.886
6.881
1.98
2.00
1.20
0.95
1.97
7.90
7.80
7.70
7.60
7.50
7.40
7.30
7.20
7.10
7.00
6.90
6.80
f1 (ppm)

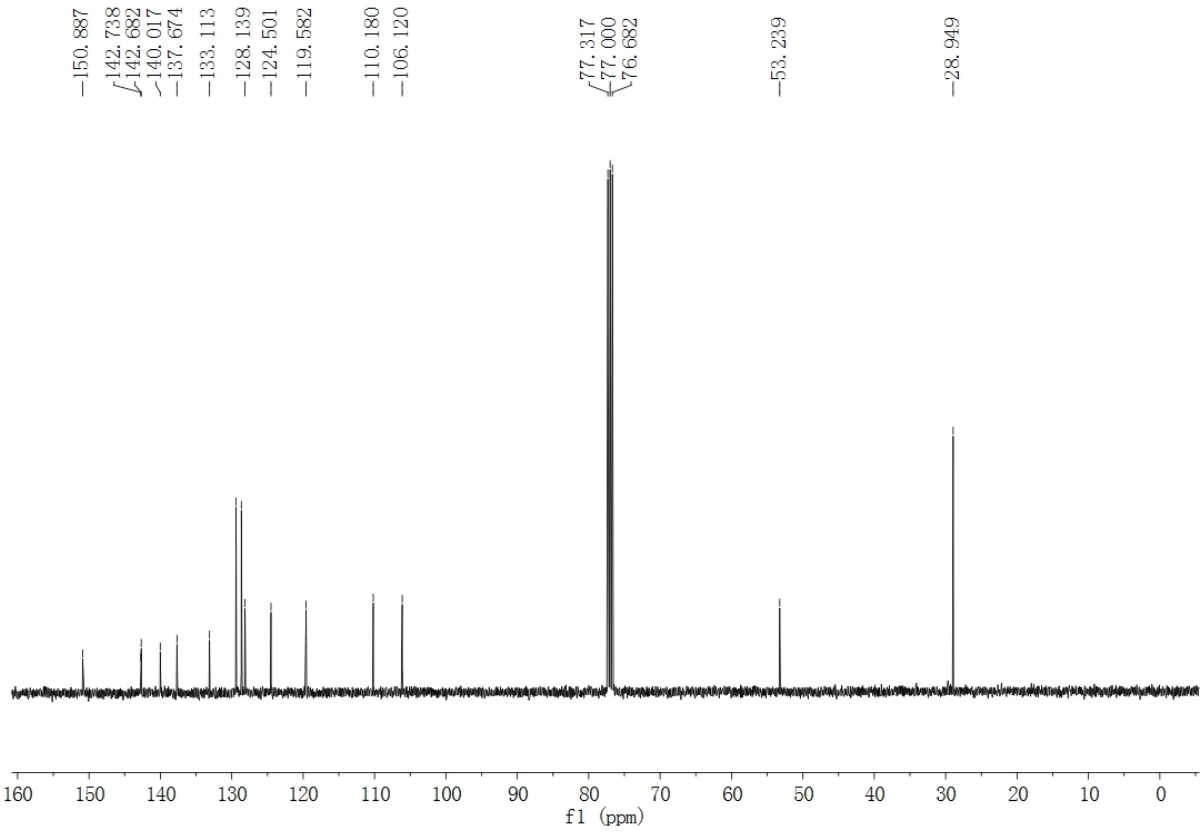

149.273
138.695
133.860
127.865
123.067
115.073
104.167
77.318
77.000
76.683
52.578
28.973
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

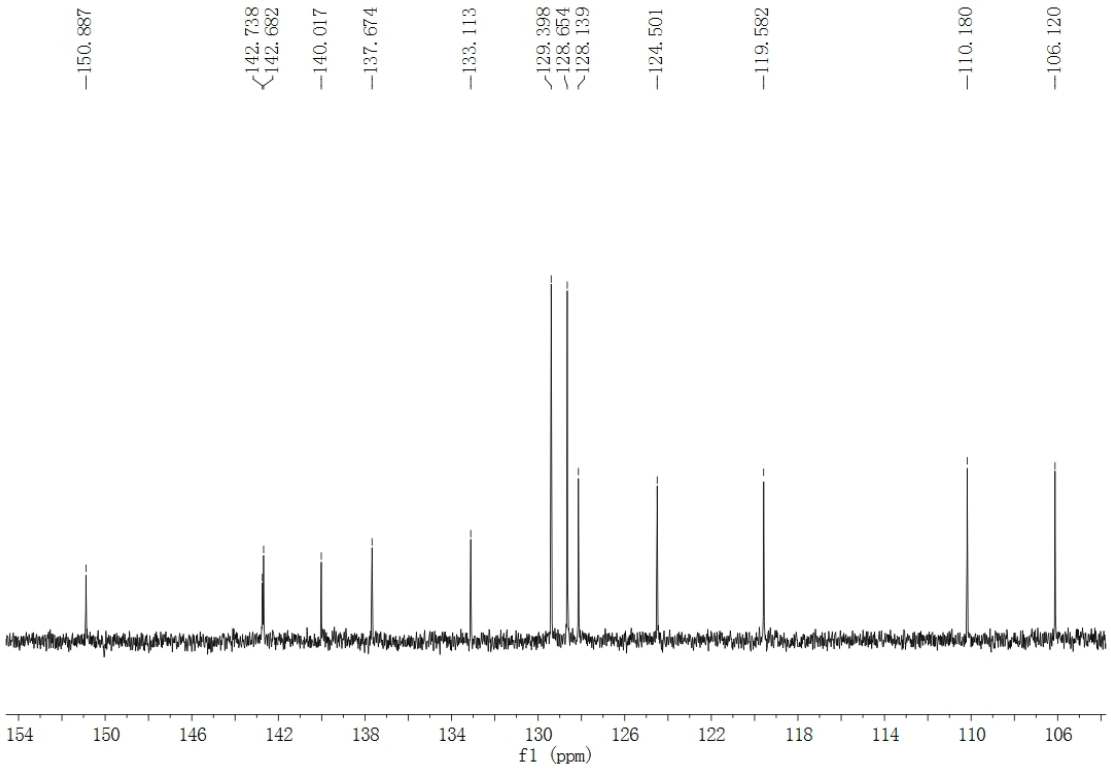


^{1}H NMR and ^{13}C NMR of *N-tert*-butyl-8-nitro-2-phenylbenzo[b][1,4]oxazepin-4-amine (24)

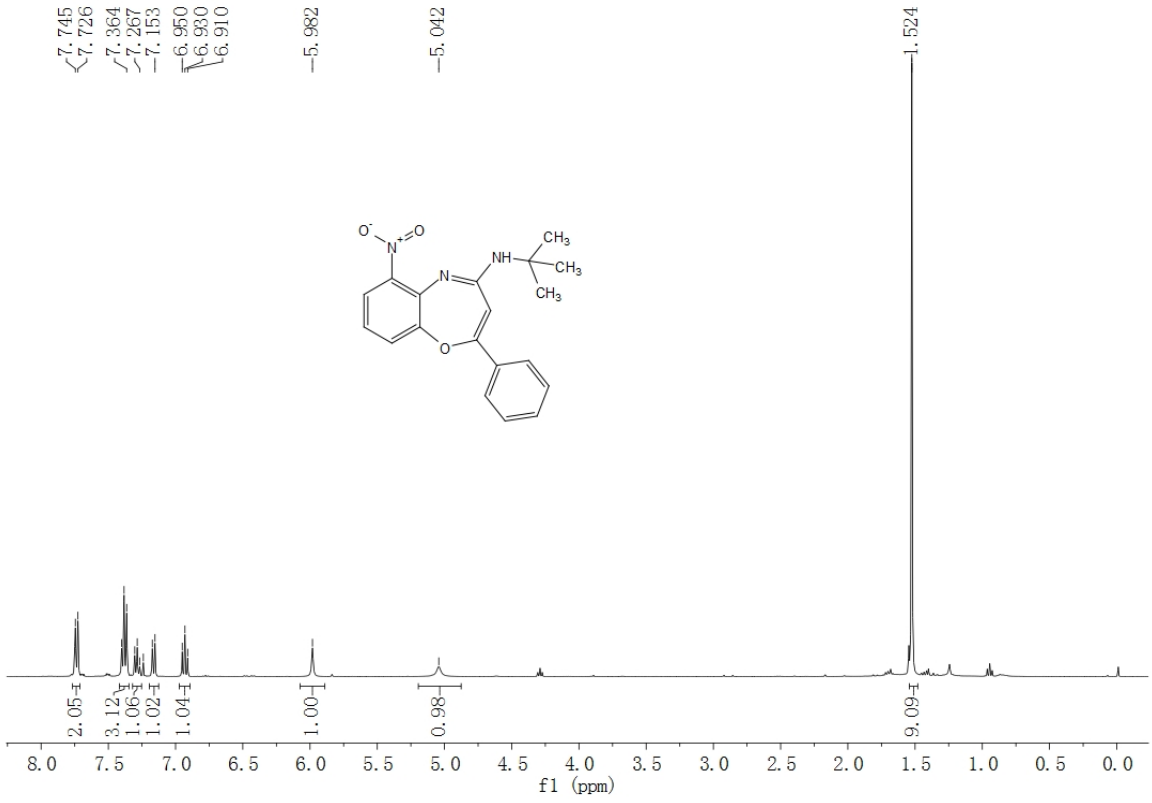


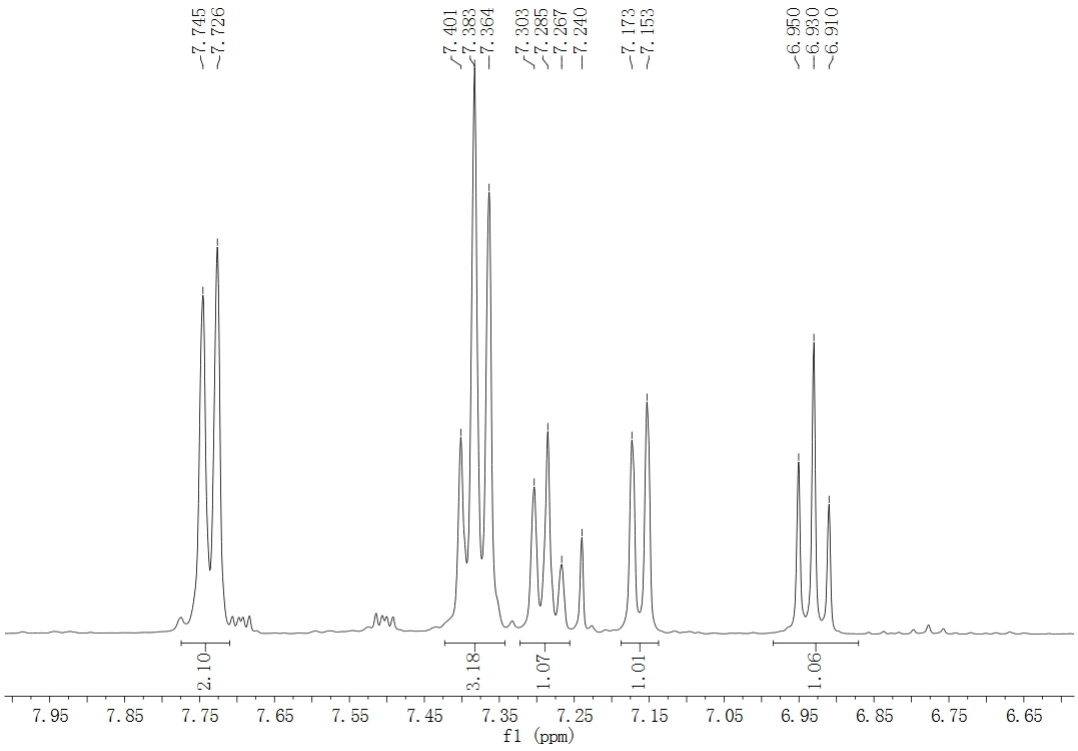

7.903
7.885
7.761
7.741
7.426
7.407
7.388
7.326
7.307
7.289
7.240
7.200
7.177
1.99
2.02
2.04
1.02
1.00
8.05
7.95
7.85
7.75
7.65
7.55
7.45
7.35
7.25
7.15
f1 (ppm)

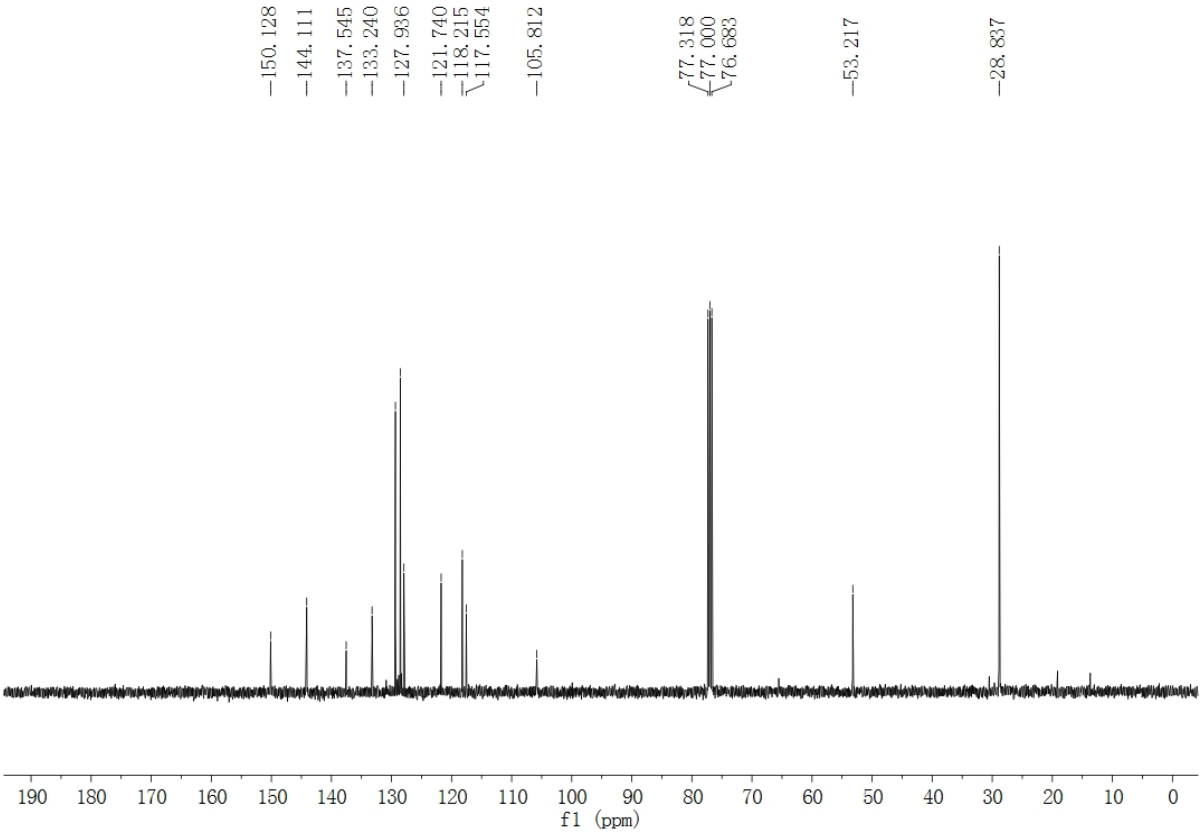

150.887
142.738
142.682
140.017
137.674
133.113
128.139
124.501
119.582
110.180
106.120
77.317
77.000
76.682
53.239
28.949
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

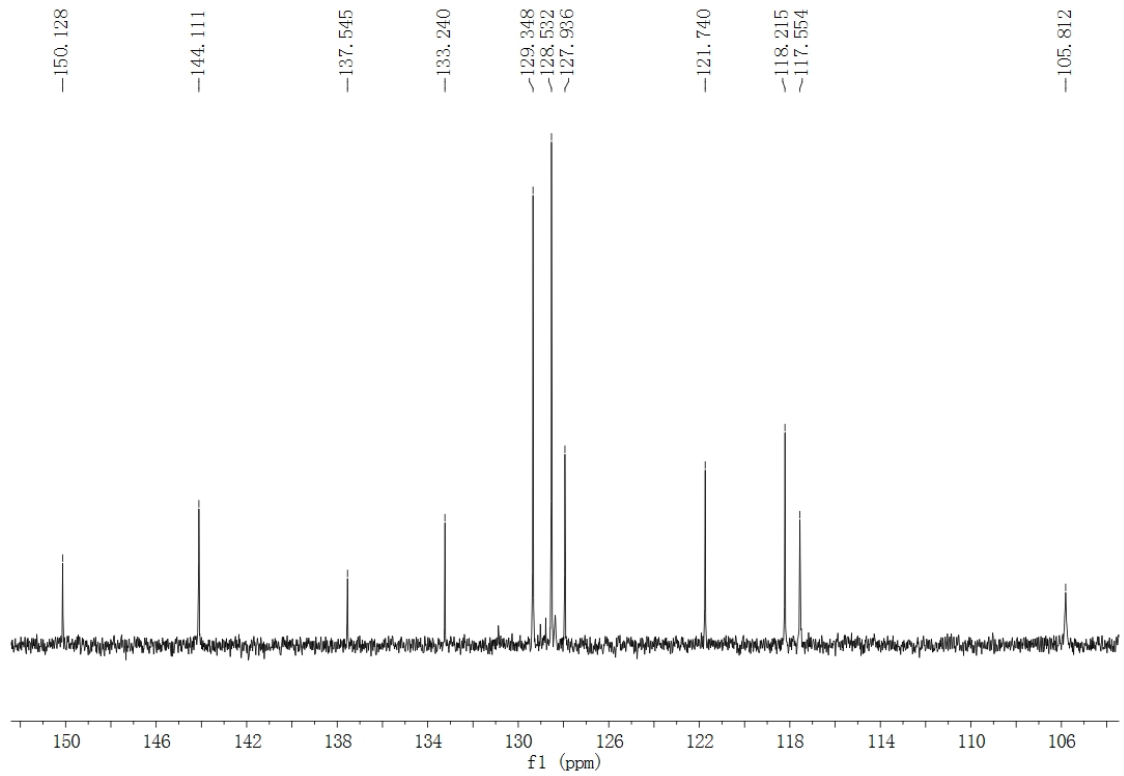


^{1}H NMR and ^{13}C NMR of *N-tert*-butyl-6-nitro-2-phenylbenzo[b][1,4]oxazepin-4-amine (25)

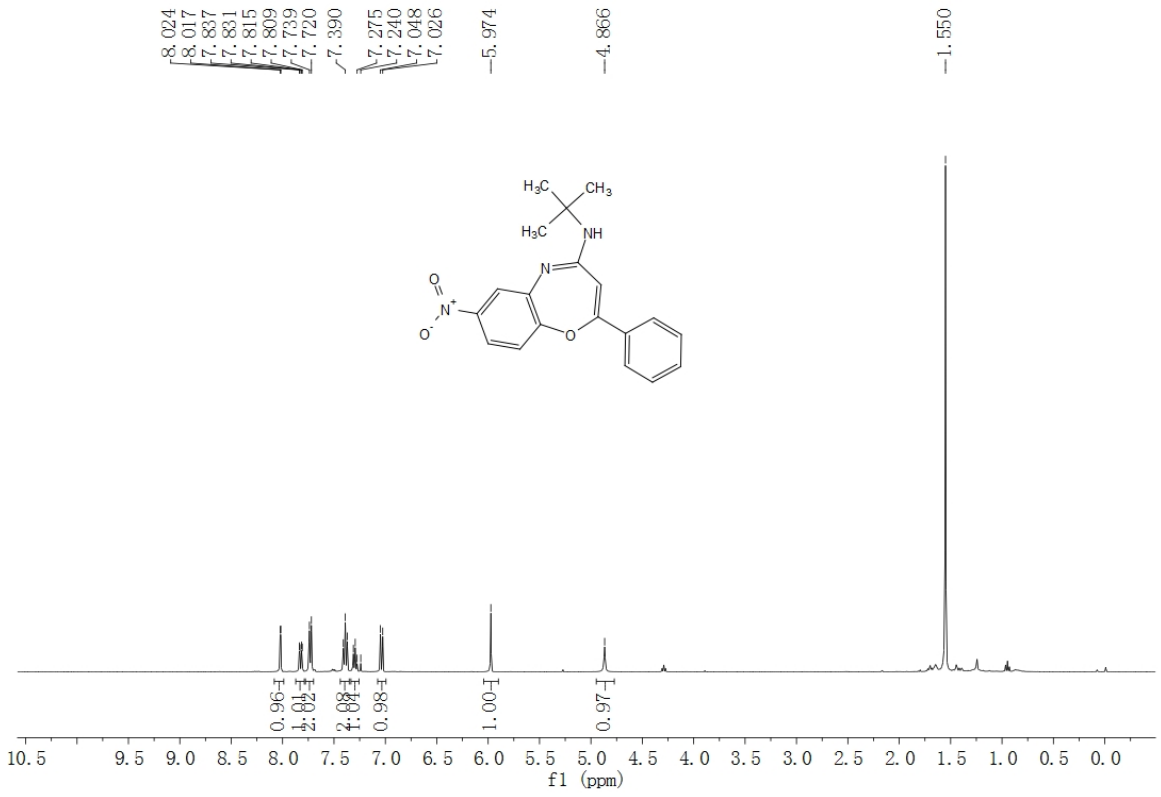


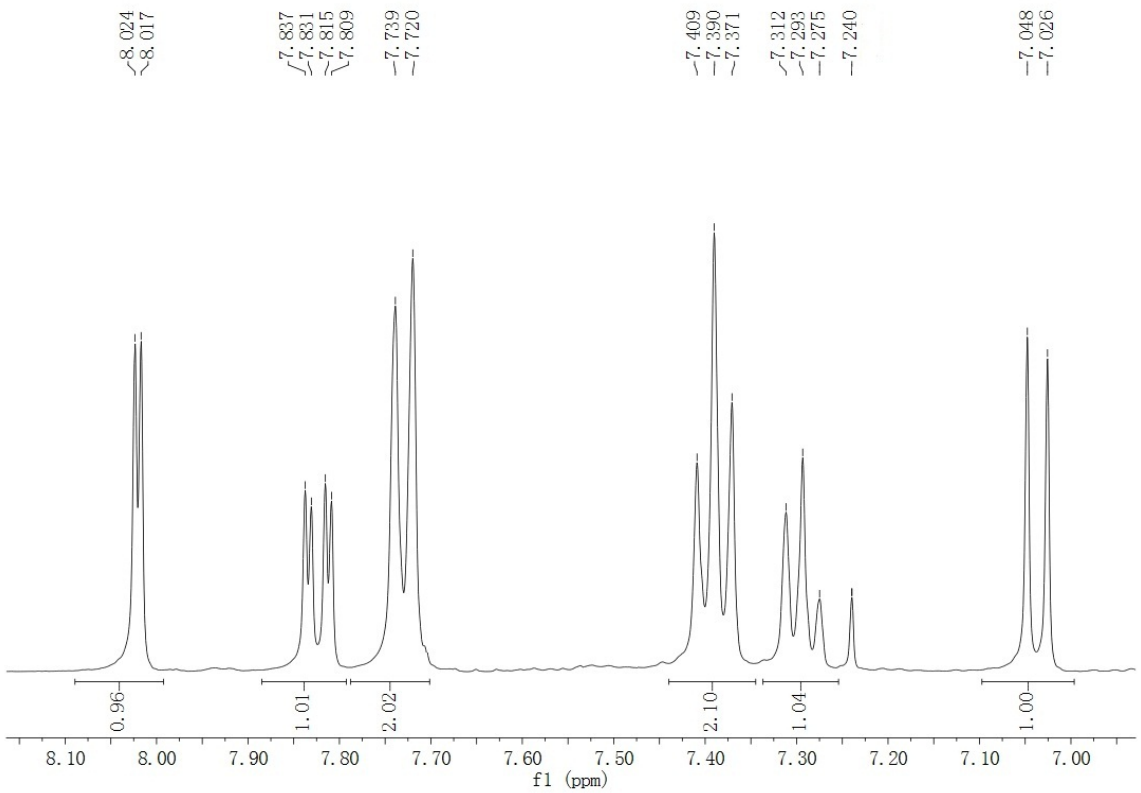

7.745
7.726
7.401
7.383
7.364
7.303
7.285
7.267
7.240
7.173
7.153
6.950
6.930
6.910
2.10
3.18
1.07
1.01
1.06
7.95
7.85
7.75
7.65
7.55
7.45
7.35
7.25
7.15
7.05
6.95
6.85
6.75
6.65
f1 (ppm)

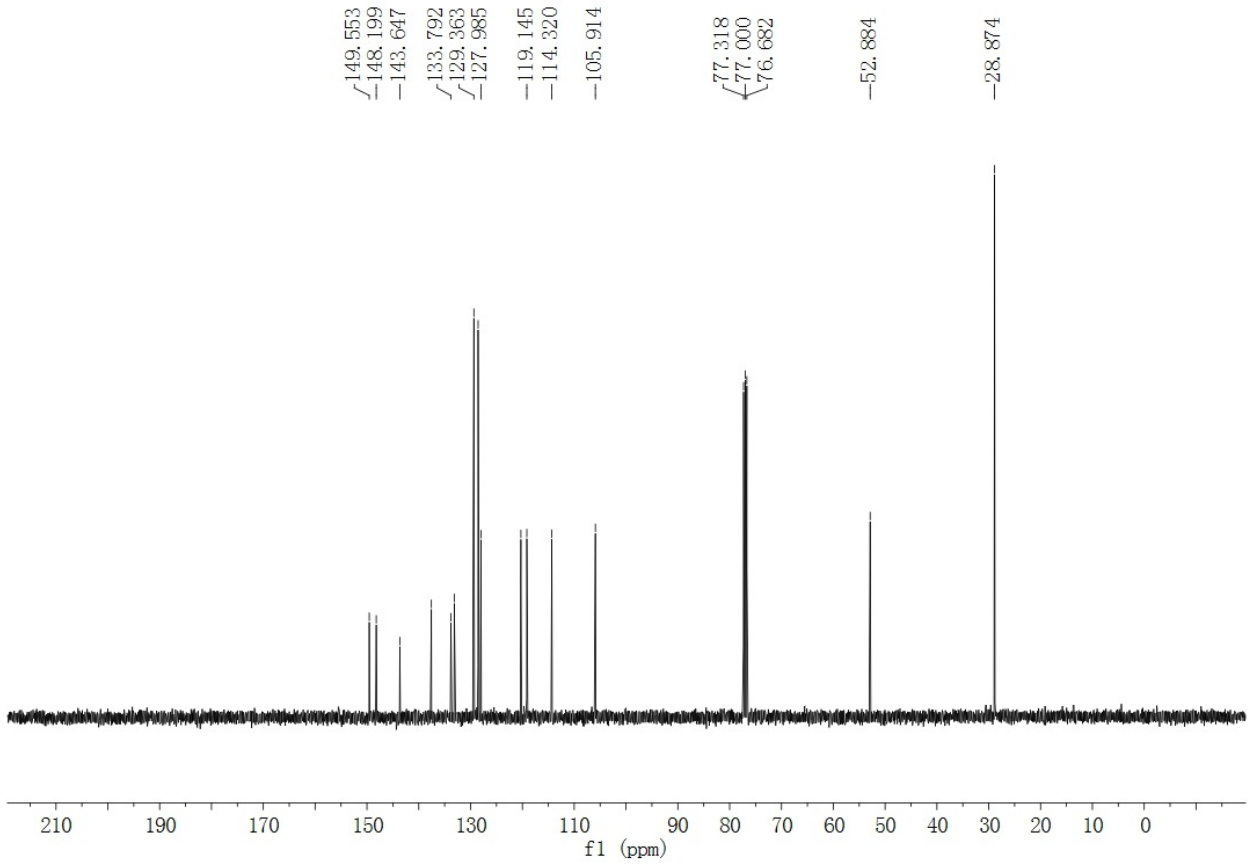

150.128
144.111
137.545
133.240
127.936
121.740
118.215
117.554
105.812
77.318
77.000
76.683
53.217
28.837
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

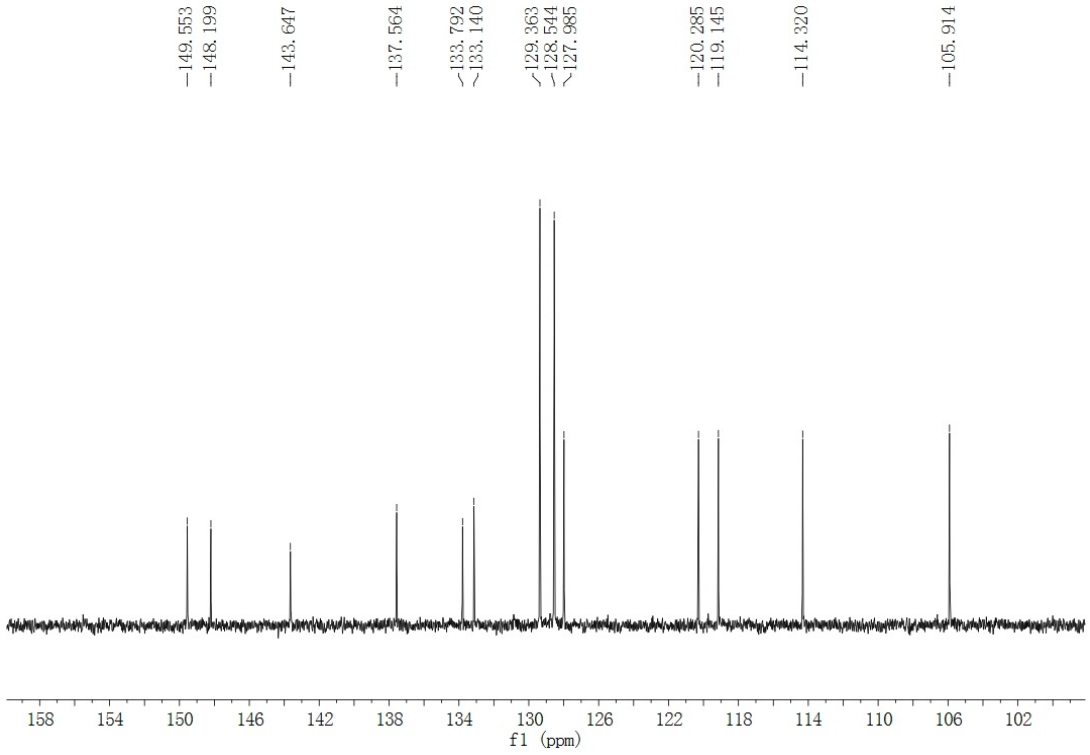


^{1}H NMR and ^{13}C NMR of *N-tert*-butyl-7-nitro-2-phenylbenzo[b][1,4]oxazepin-4-amine (26)

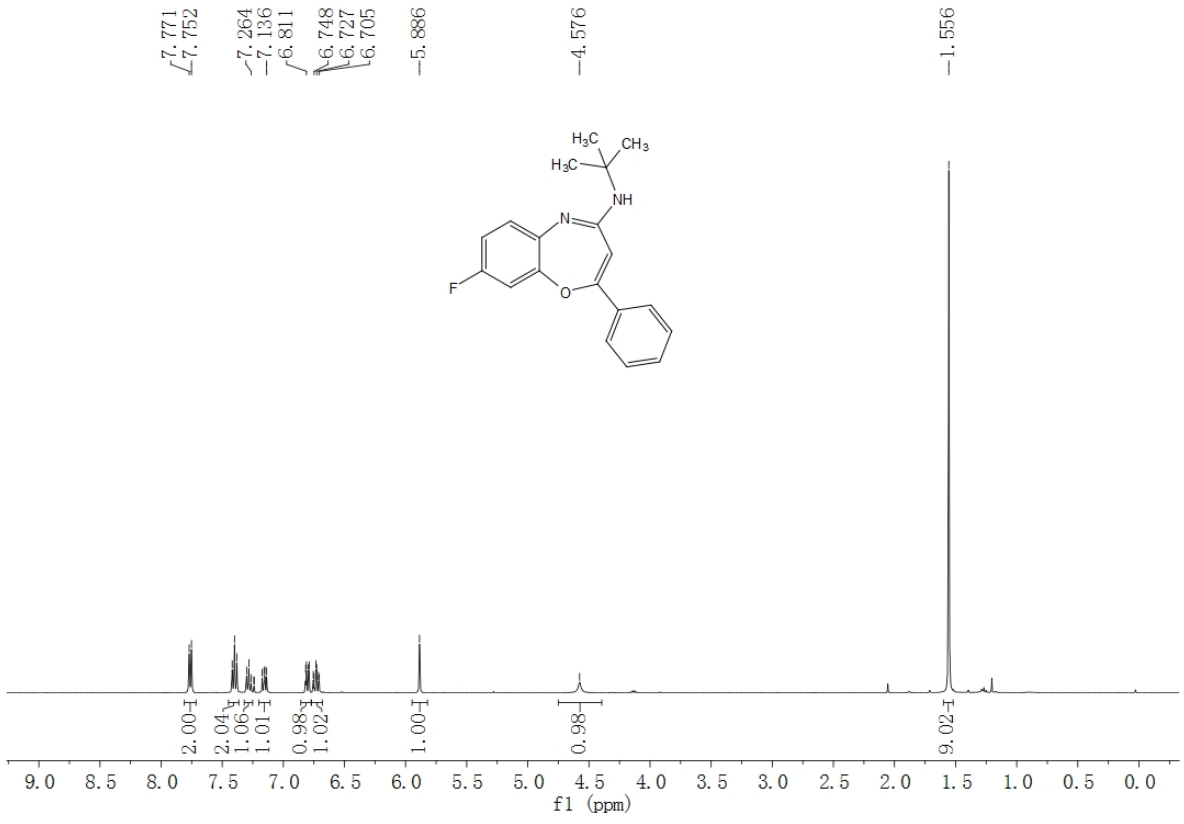


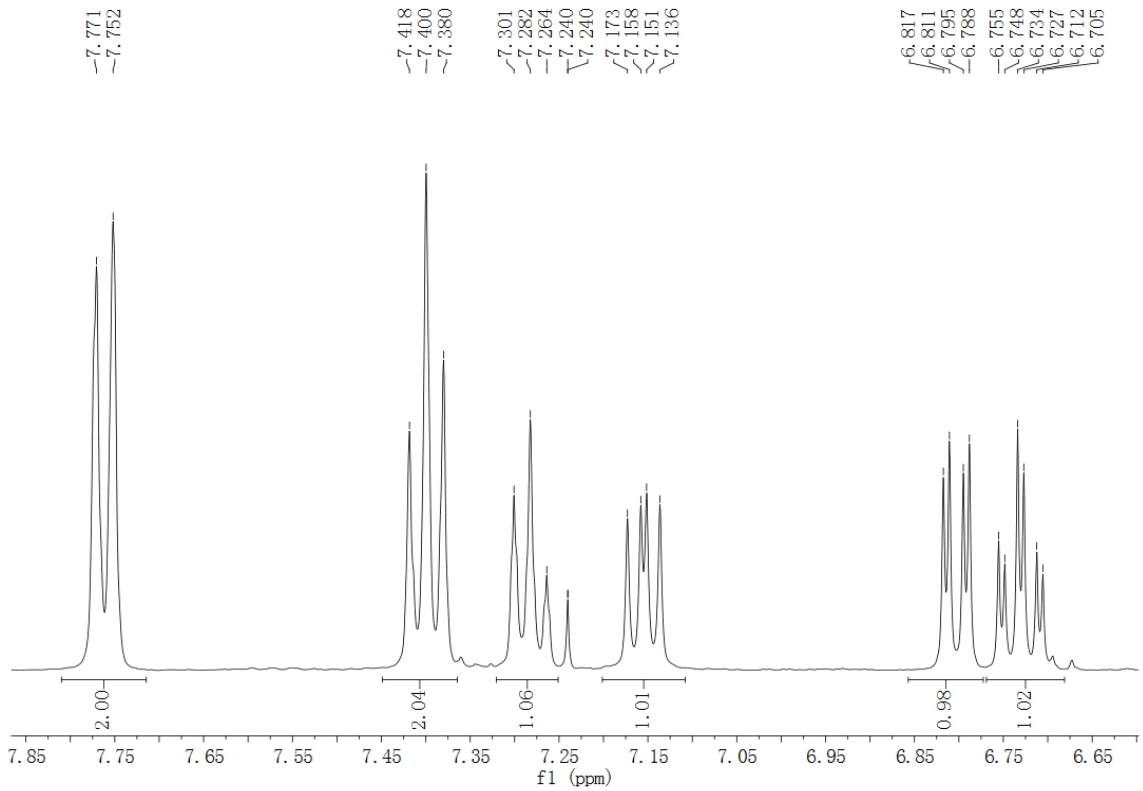

8.024
8.017
7.837
7.831
7.815
7.809
7.739
7.720
7.409
7.390
7.371
7.312
7.293
7.275
7.240
7.048
7.026
0.96
1.01
2.02
2.10
1.04
1.00
8.10
8.00
7.90
7.80
7.70
7.60
7.50
7.40
7.30
7.20
7.10
7.00
f1 (ppm)

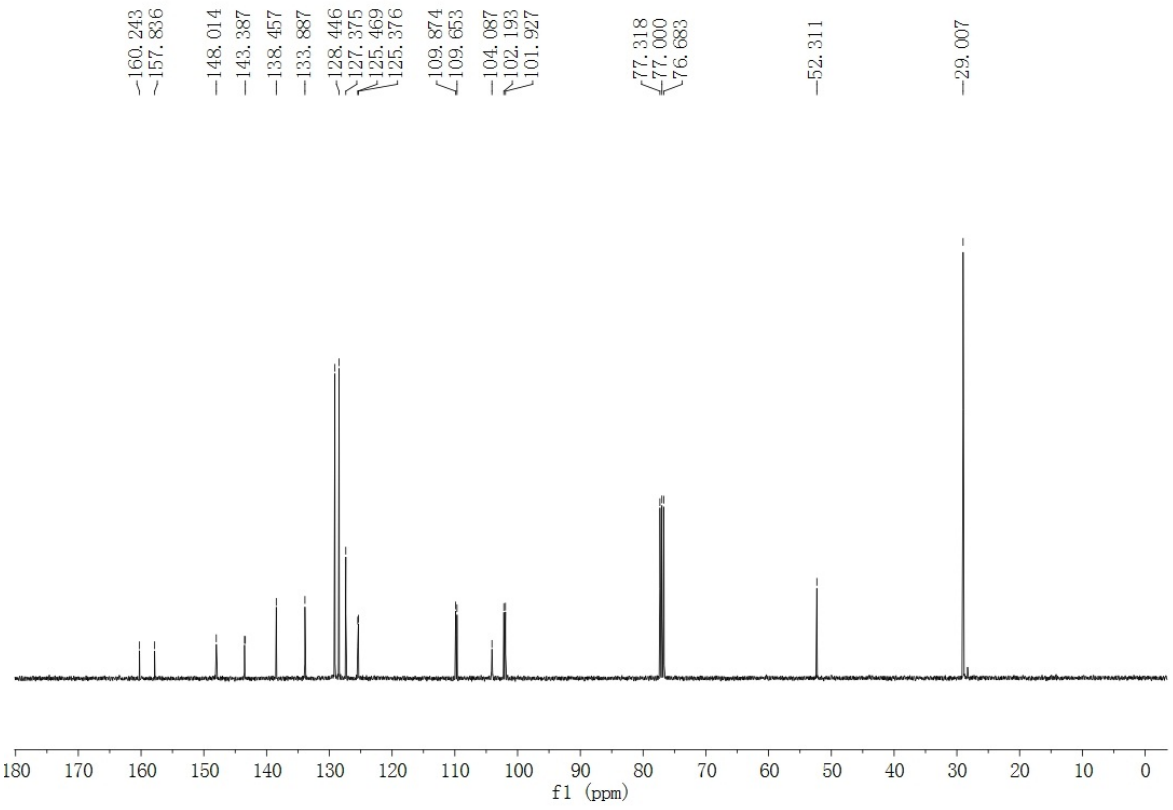

149.553
148.199
143.647
133.792
129.363
127.985
119.145
114.320
105.914
77.318
77.000
76.682
52.884
28.874
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

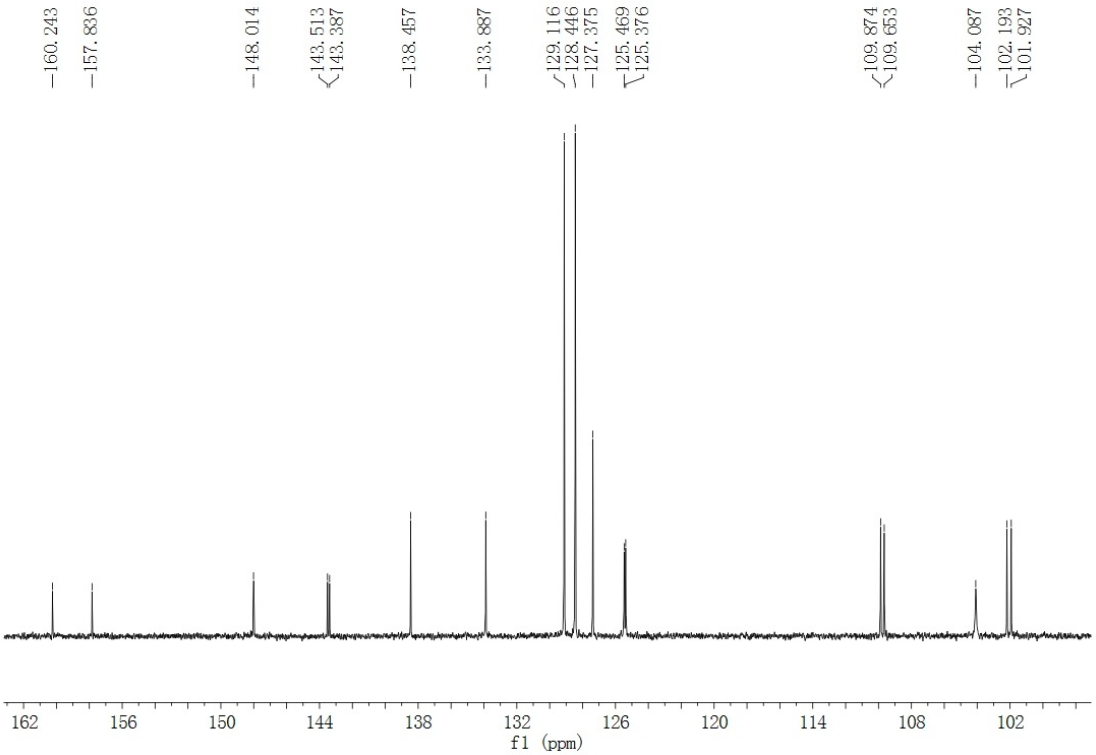


^{1}H NMR and ^{13}C NMR of *N-tert*-butyl-8-fluoro-2-phenylbenzo[b][1,4]oxazepin-4-amine (27)

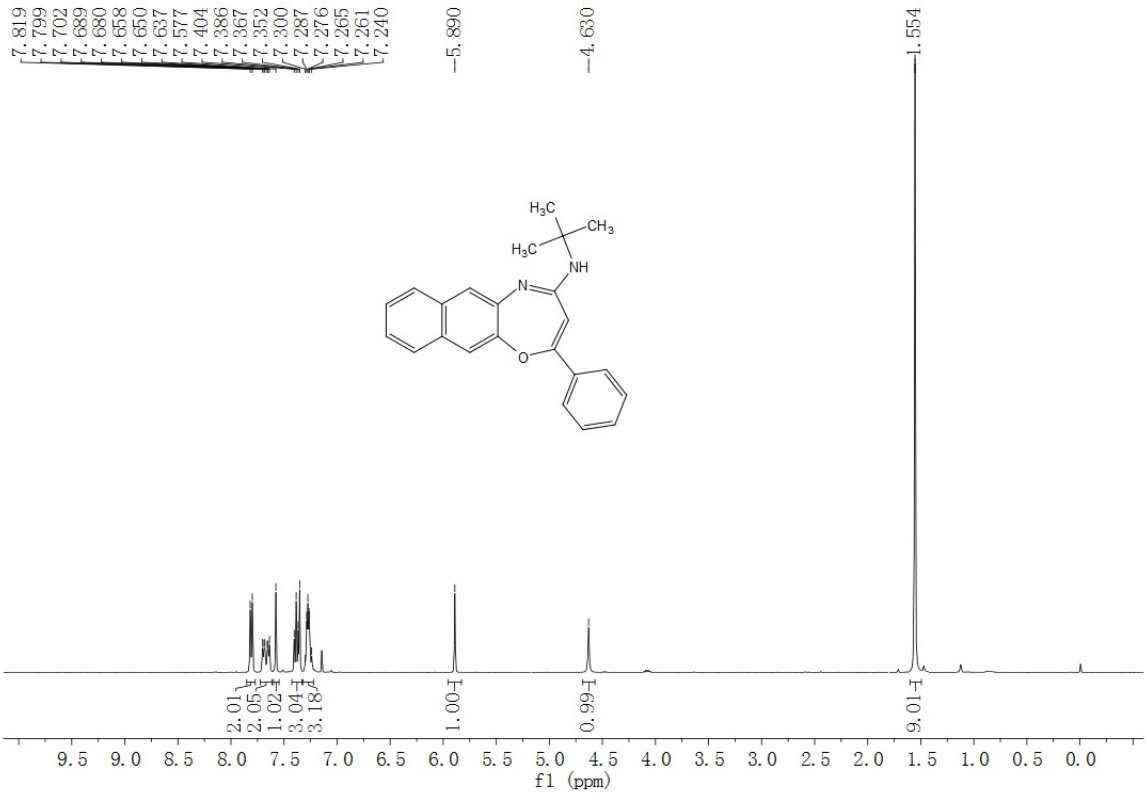


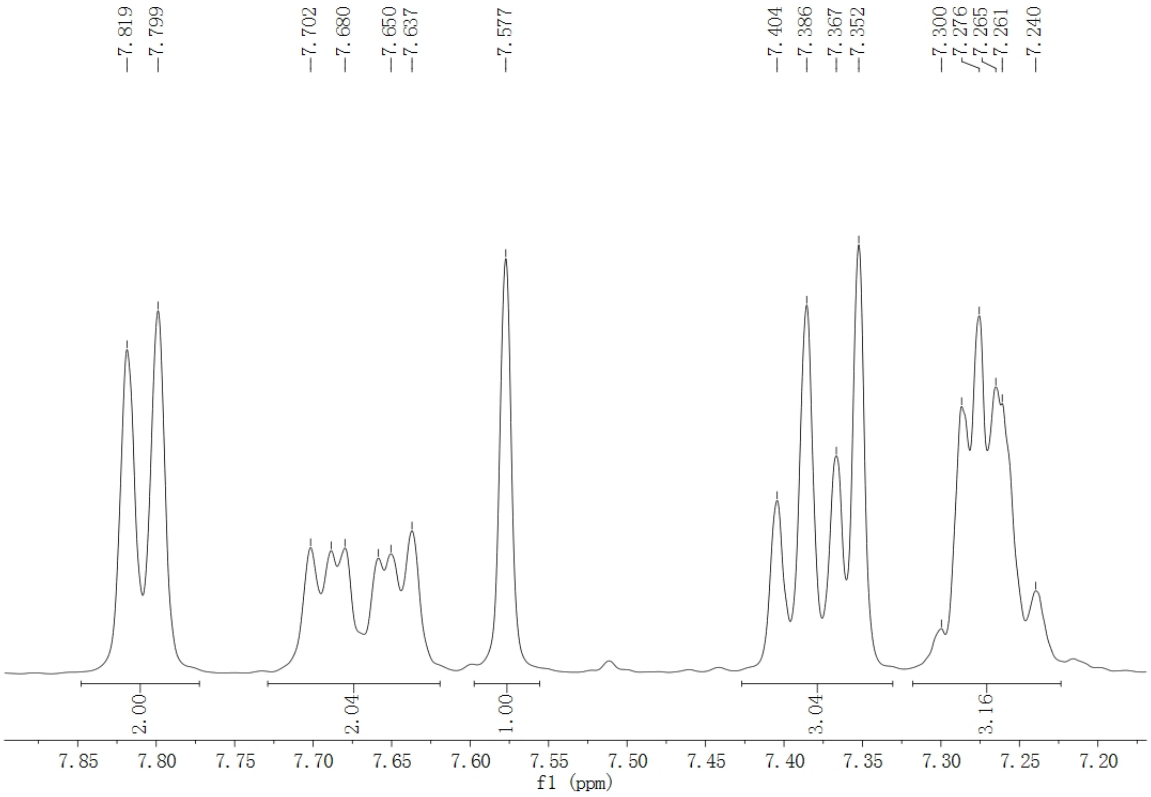

7.771
7.752
7.418
7.400
7.380
7.301
7.282
7.264
7.240
7.240
7.173
7.158
7.151
7.136
6.817
6.811
6.795
6.788
6.755
6.748
6.734
6.727
6.712
6.705
2.00
2.04
1.06
1.01
0.98
1.02
7.85 7.75 7.65 7.55 7.45 7.35 7.25 7.15 7.05 6.95 6.85 6.75 6.65
f1 (ppm)

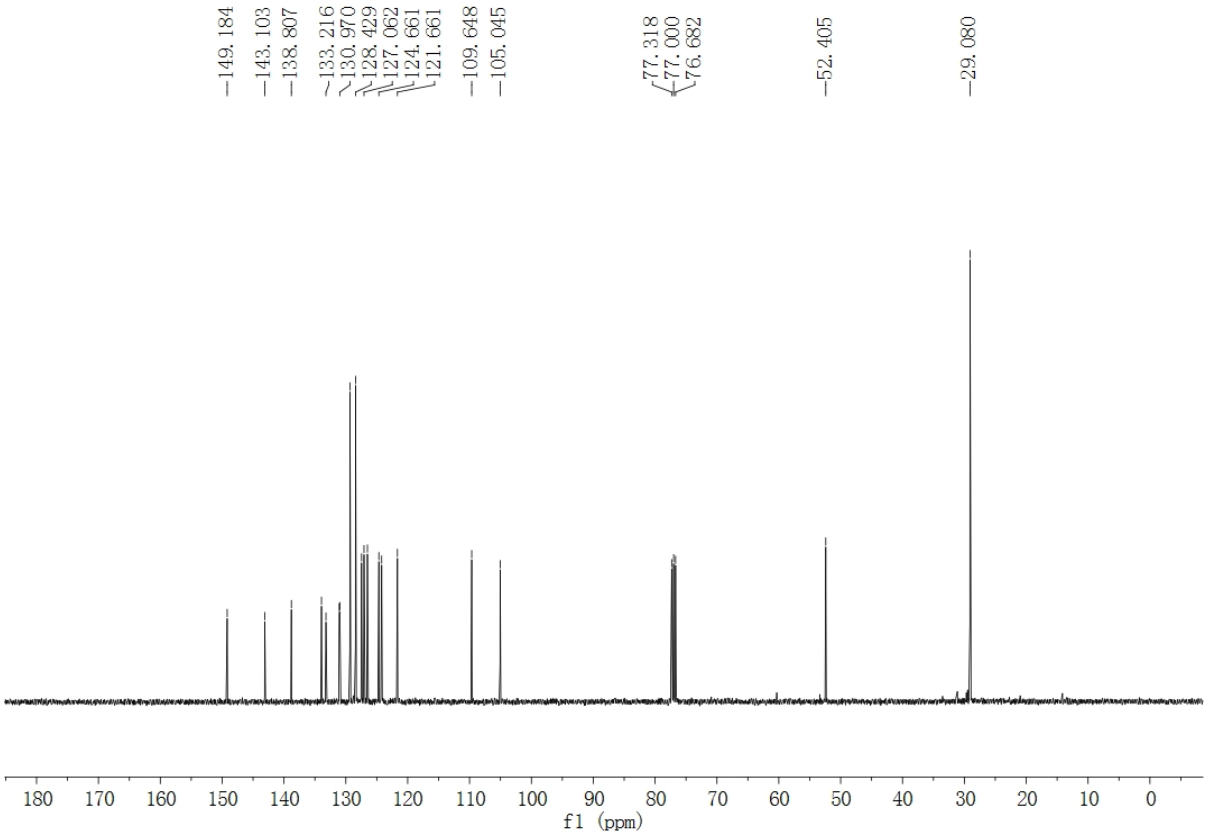

160.243
157.836
148.014
143.387
138.457
133.887
128.446
127.375
125.469
125.376
109.874
109.653
104.087
102.193
101.927
77.318
77.000
76.683
52.311
29.007
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

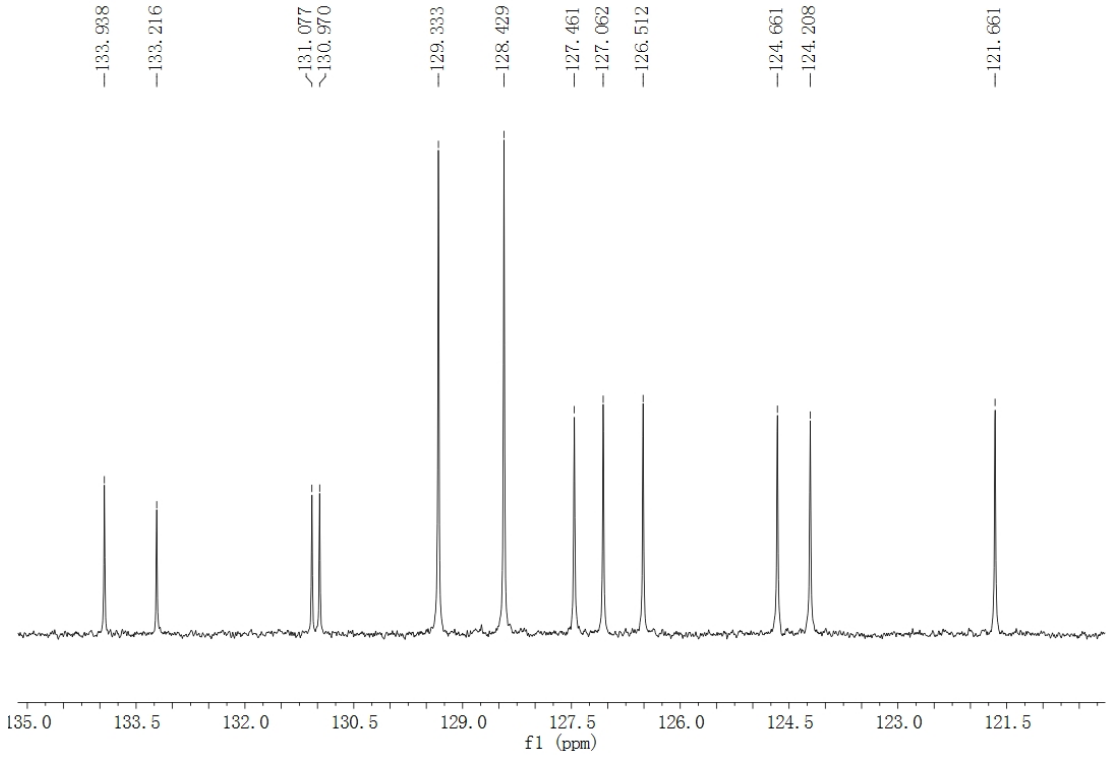


^{1}H NMR and ^{13}C NMR of *N-tert*-butyl-2-phenylnaphtho[2,3-b][1,4]oxazepin-4-amine (28)

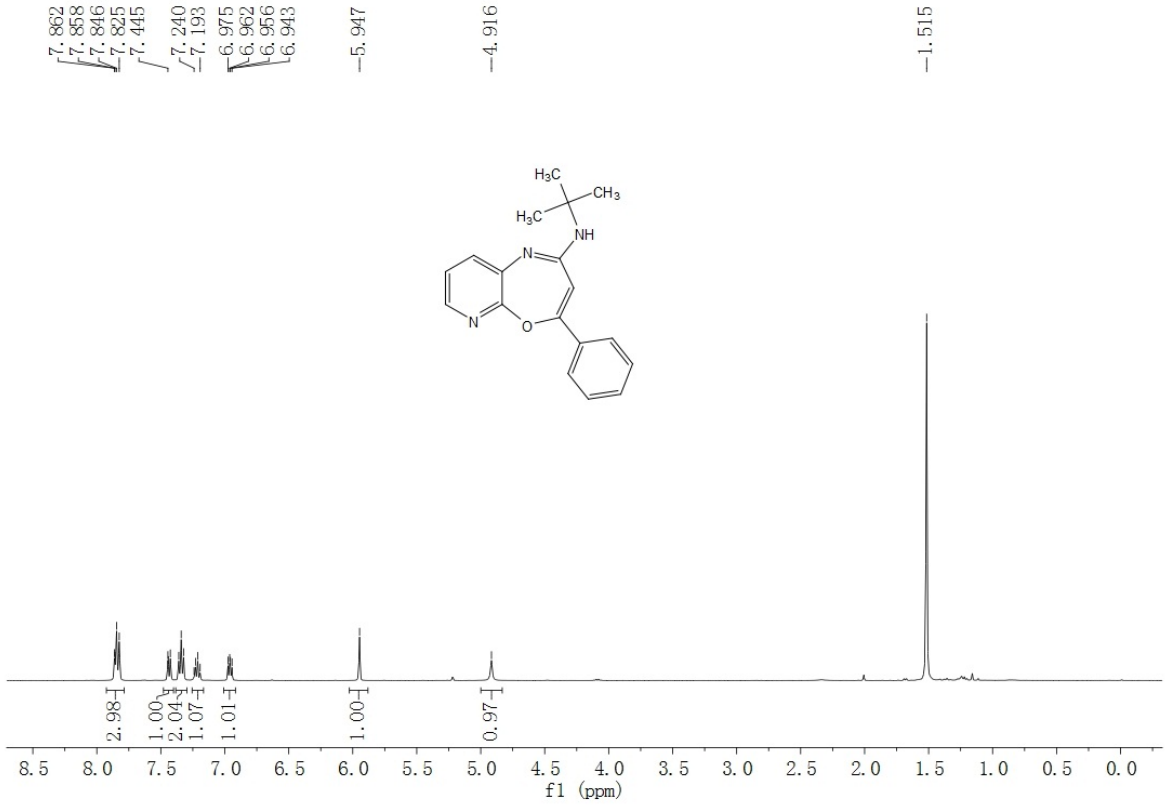


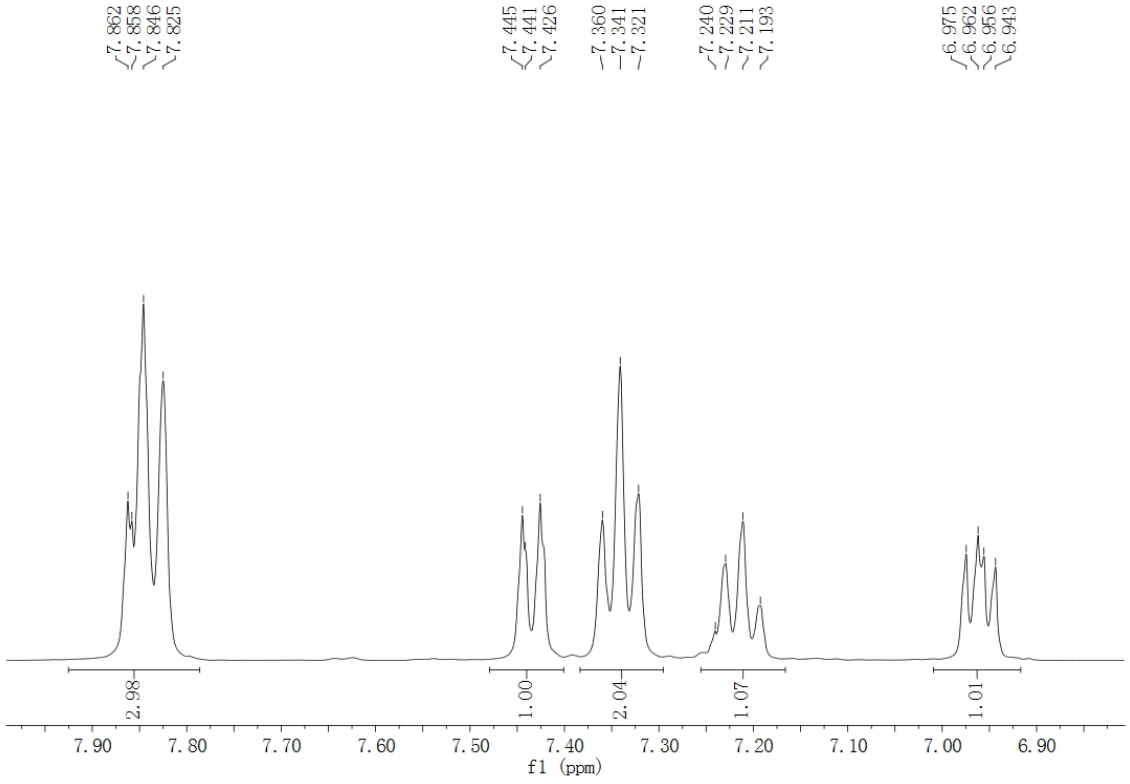

7.819
7.799
7.702
7.680
7.650
7.637
7.577
7.404
7.386
7.367
7.352
7.300
7.276
7.265
7.261
7.240
2.00
2.04
1.00
3.04
3.16
7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20
f1 (ppm)

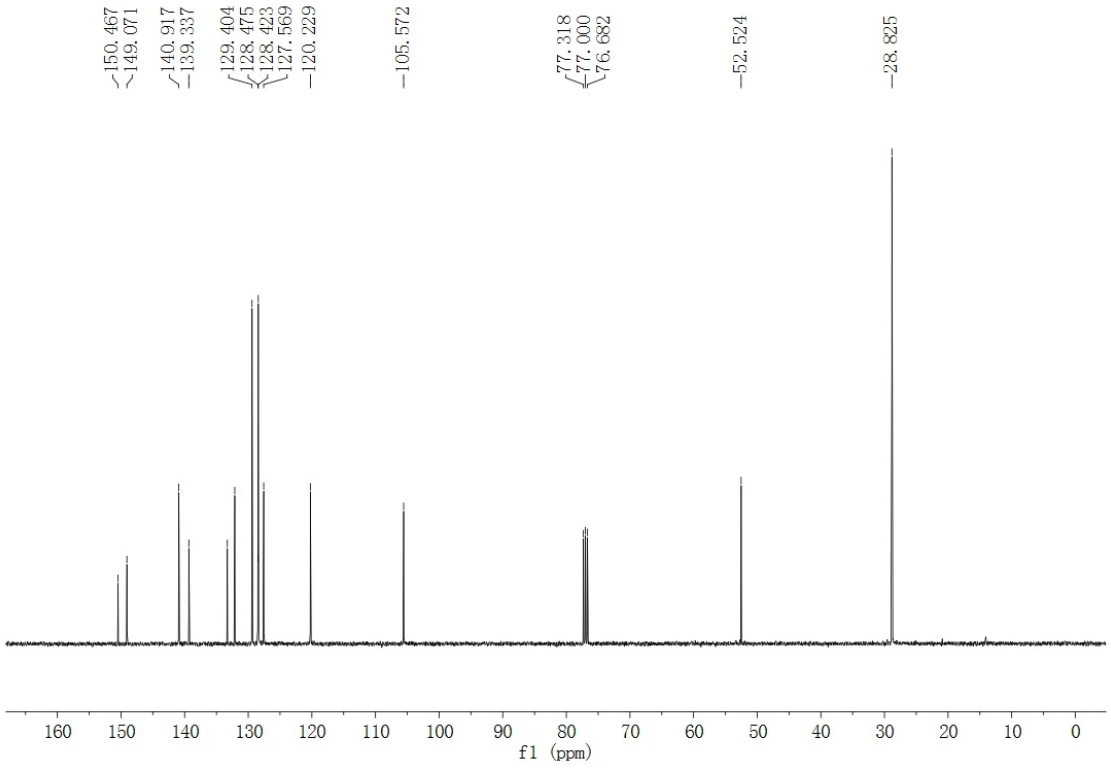

149.184
143.103
138.807
133.216
130.970
128.429
127.062
124.661
121.661
109.648
105.045
77.318
77.000
76.682
52.405
29.080
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

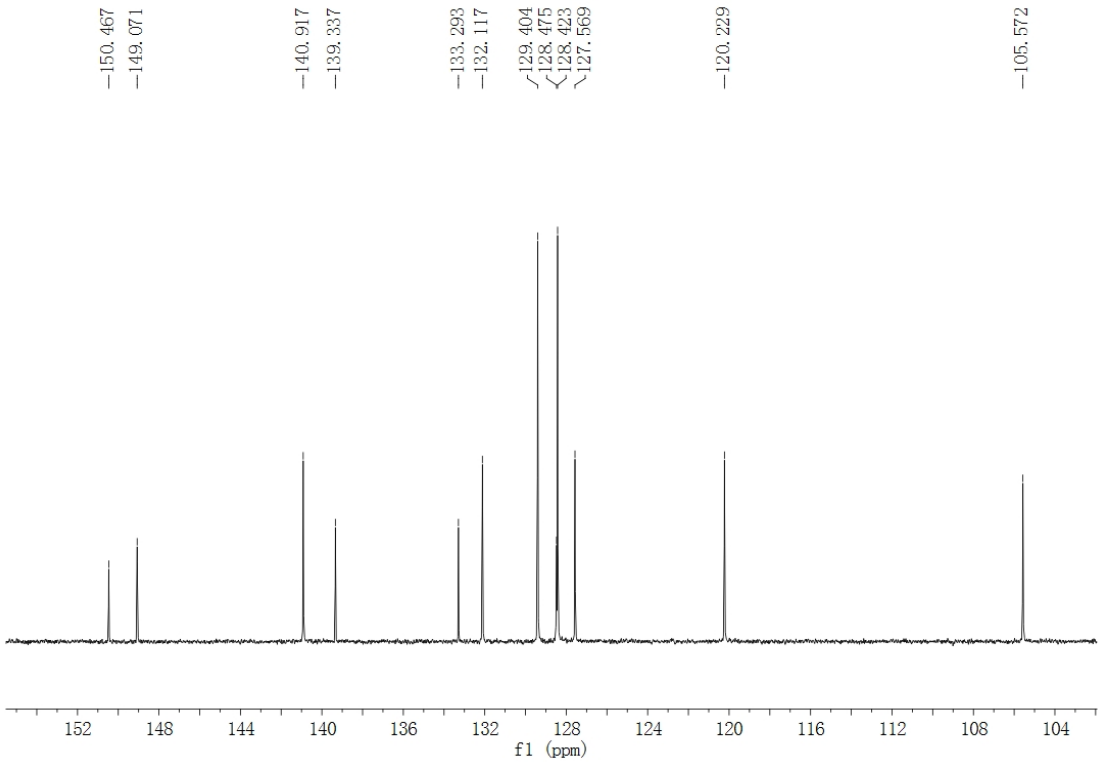


^{1}H NMR and ^{13}C NMR of *N-tert*-butyl-4-phenylpyrido[2,3-b][1,4]oxazepin-2-amine (29)

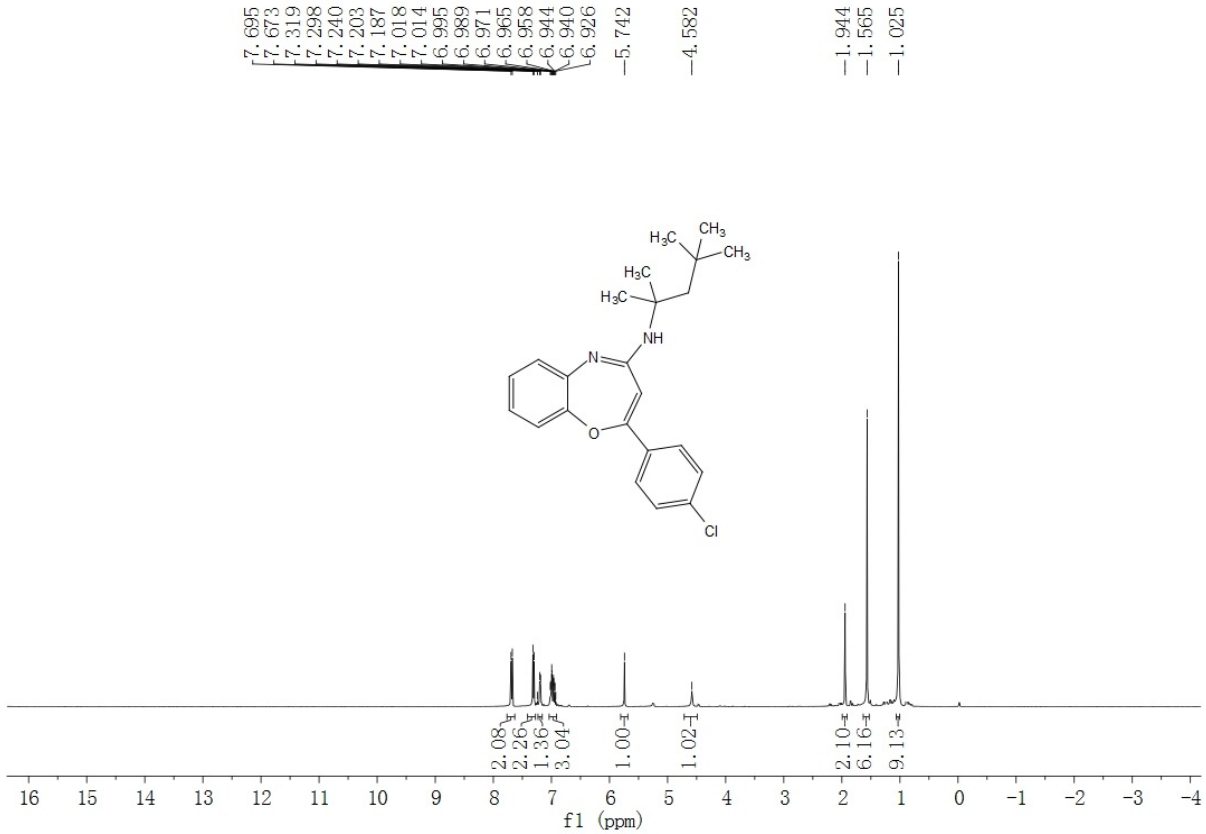


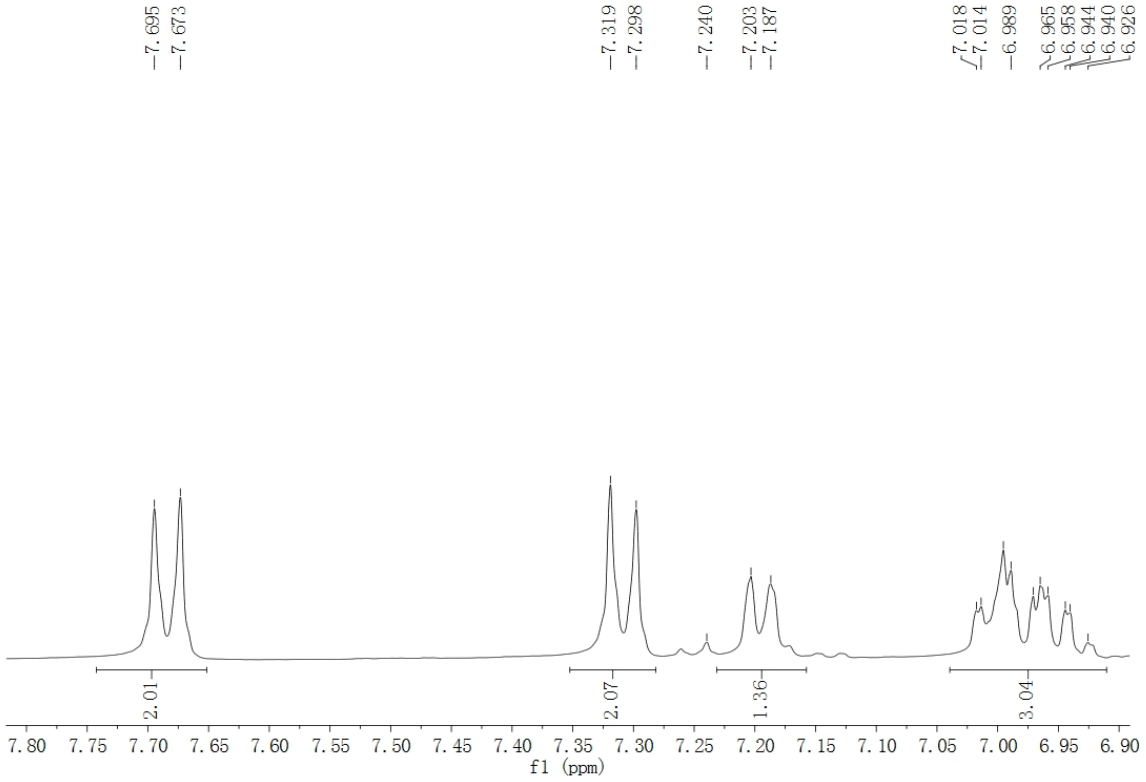

7.862
7.858
7.846
7.825
7.445
7.441
7.426
7.360
7.341
7.321
7.240
7.229
7.211
7.193
6.975
6.962
6.956
6.943
2.98
1.00
2.04
1.07
1.01
7.90
7.80
7.70
7.60
7.50
7.40
7.30
7.20
7.10
7.00
6.90
f1 (ppm)

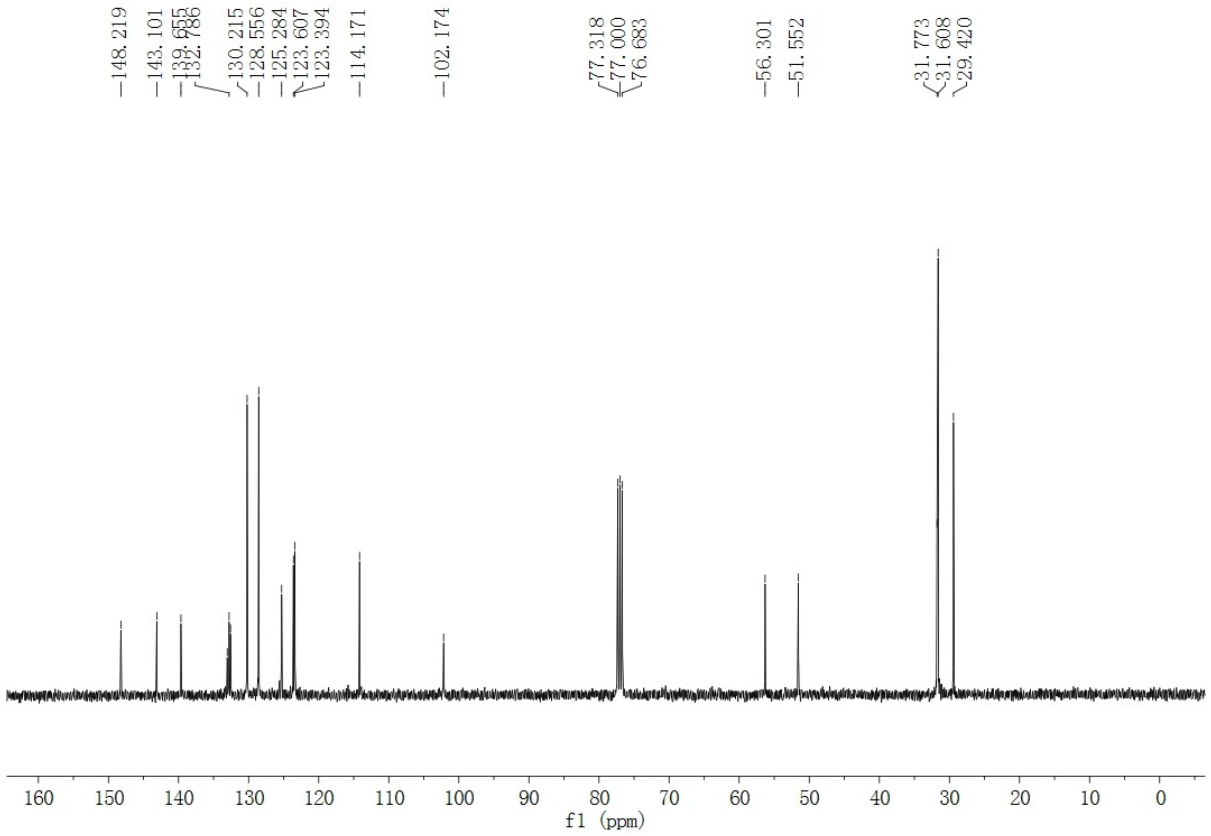

150.467
149.071
140.917
139.337
129.404
128.475
128.423
127.569
120.229
105.572
77.318
77.000
76.682
52.524
28.825
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

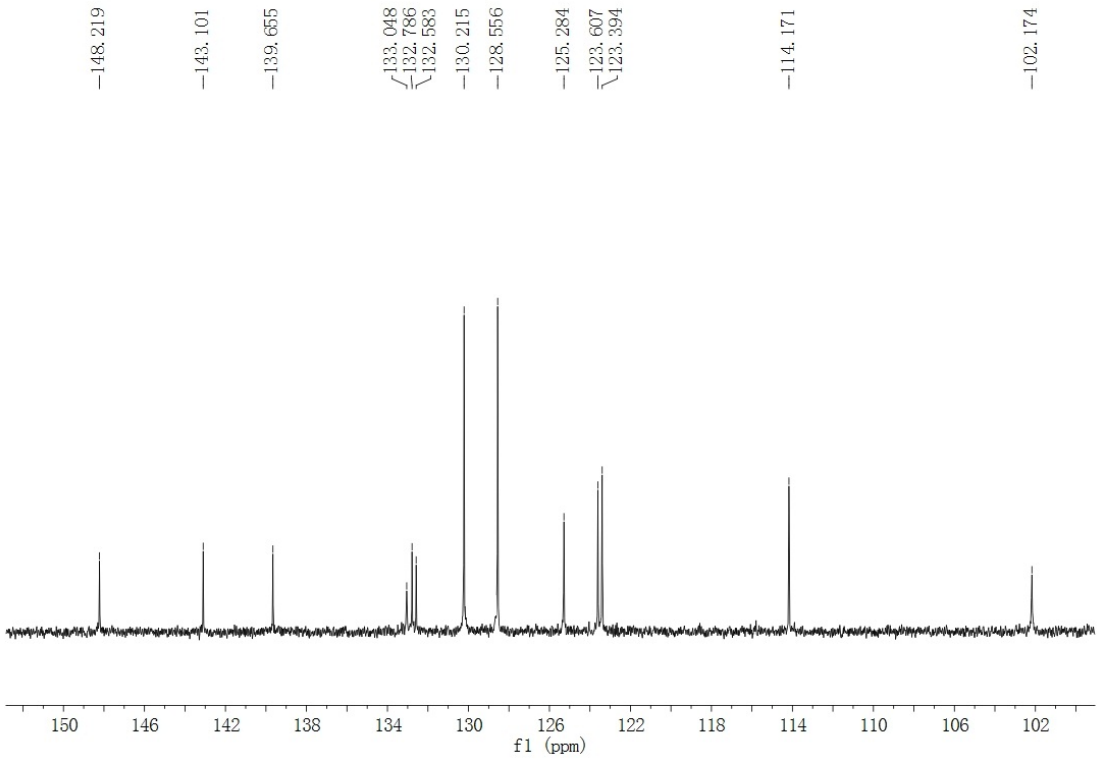


^{1}H NMR and ^{13}C NMR of 2-(4-chlorophenyl)-*N*-(2,4,4-trimethylpentan-2-yl)benzo-[b][1,4]oxazepin-4-amine (32)

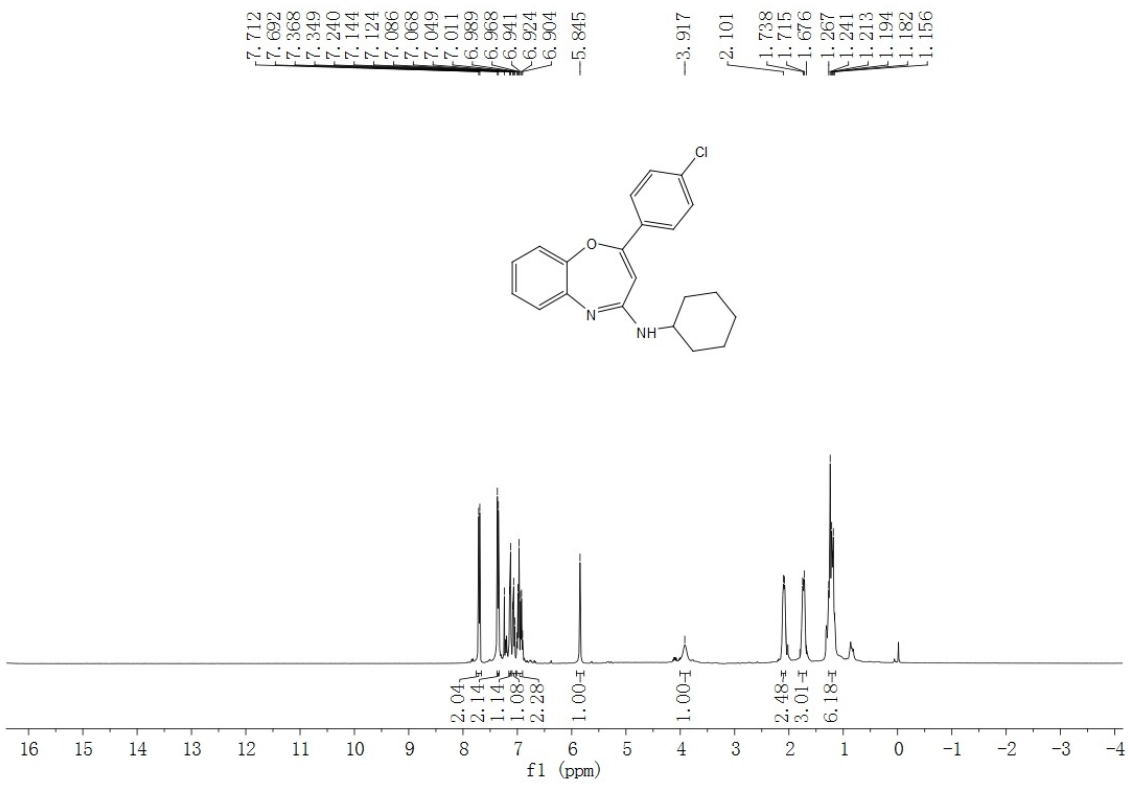


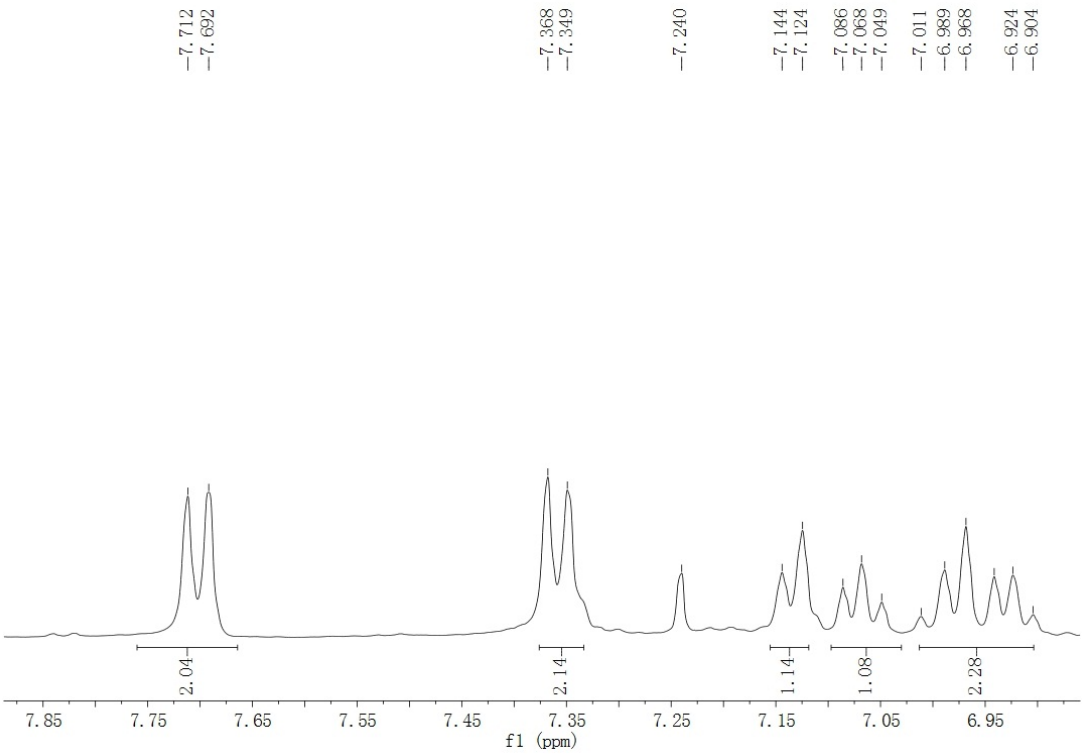

7.695
7.673
7.319
7.298
7.240
7.203
7.187
7.018
7.014
6.989
6.965
6.958
6.944
6.940
6.926
2.01
2.07
1.36
3.04
7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90
f1 (ppm)

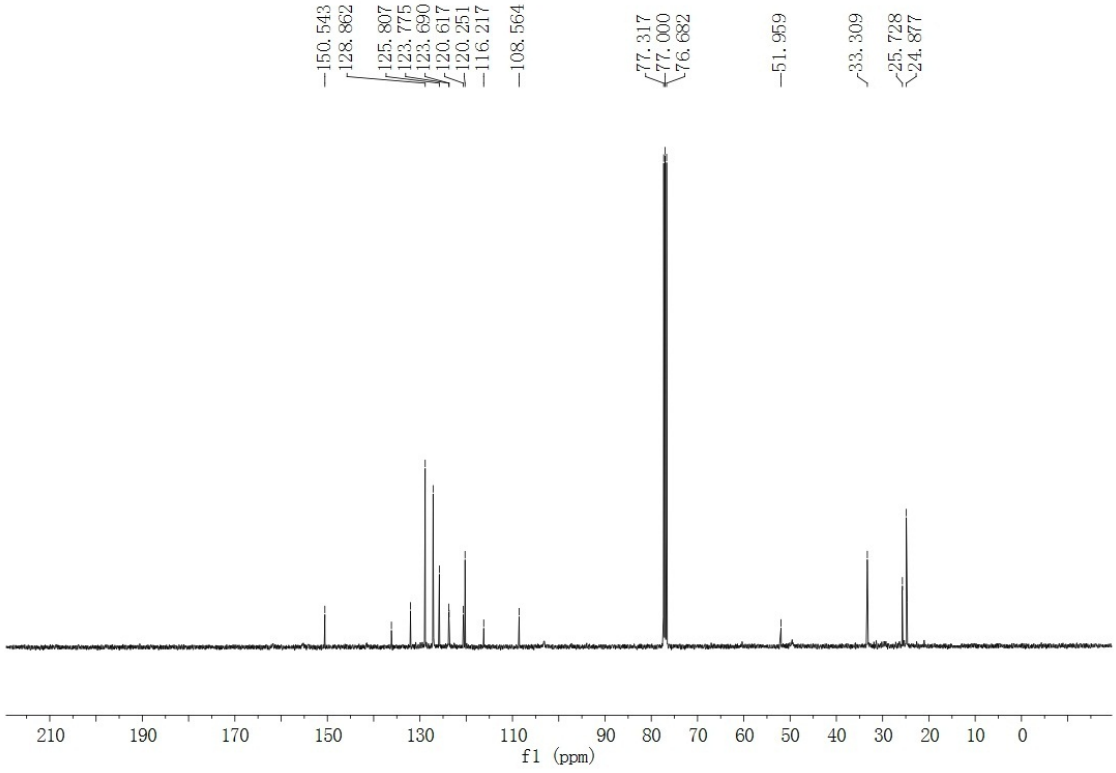

148.219
143.101
139.655
132.786
130.215
128.556
125.284
123.607
123.394
114.171
102.174
77.318
77.000
76.683
56.301
51.552
31.773
31.608
29.420
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

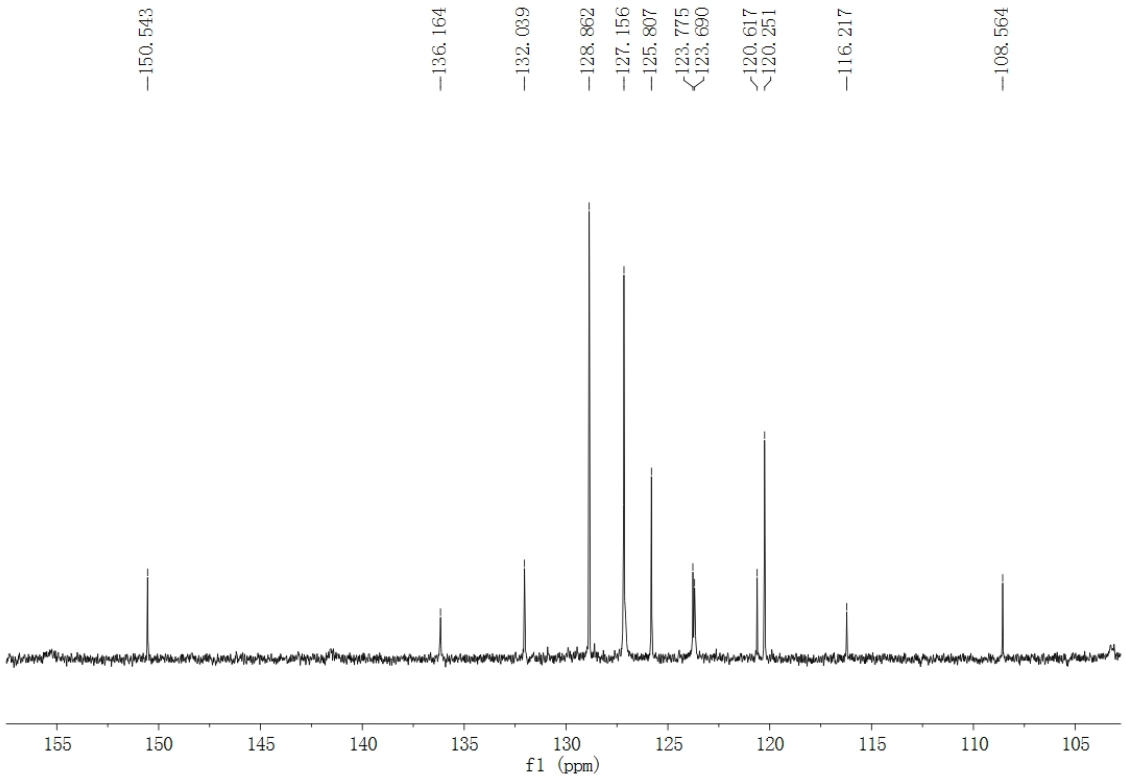


^{1}H NMR and ^{13}C NMR of 2-(4-chlorophenyl)-*N*-cyclohexylbenzo-[b][1,4]oxazepin-4-amine (33)

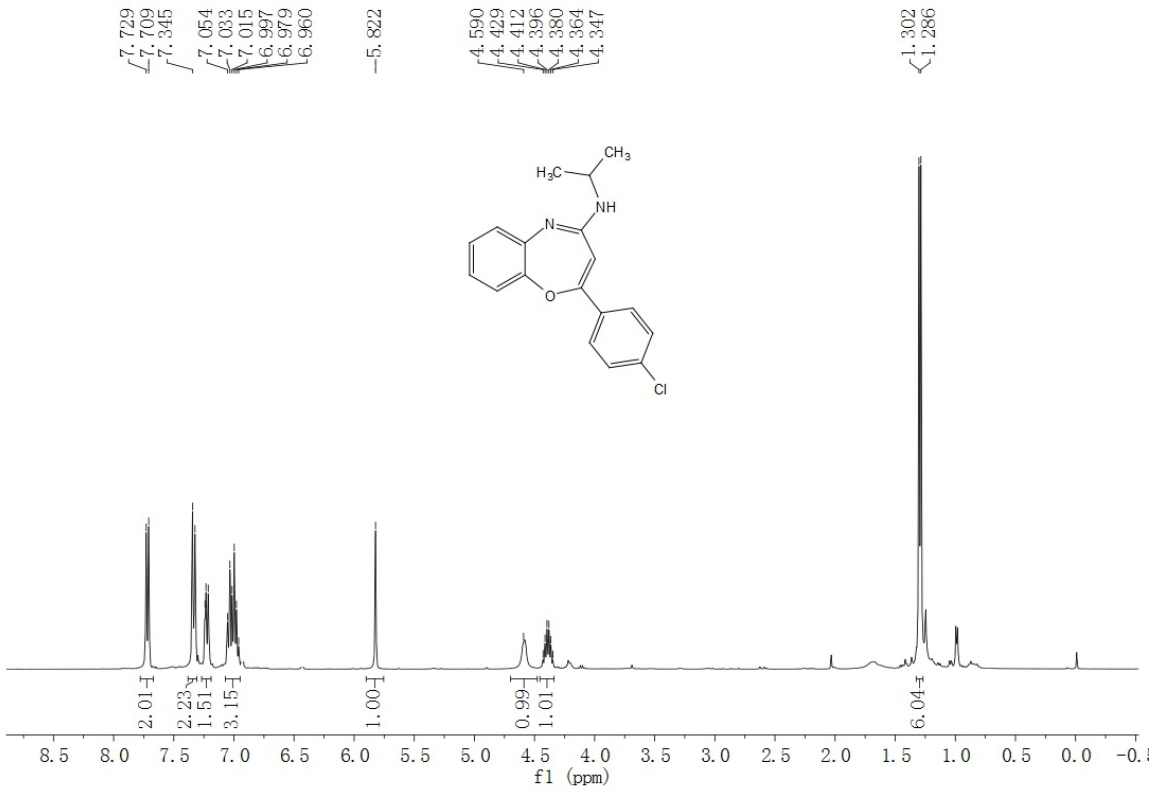


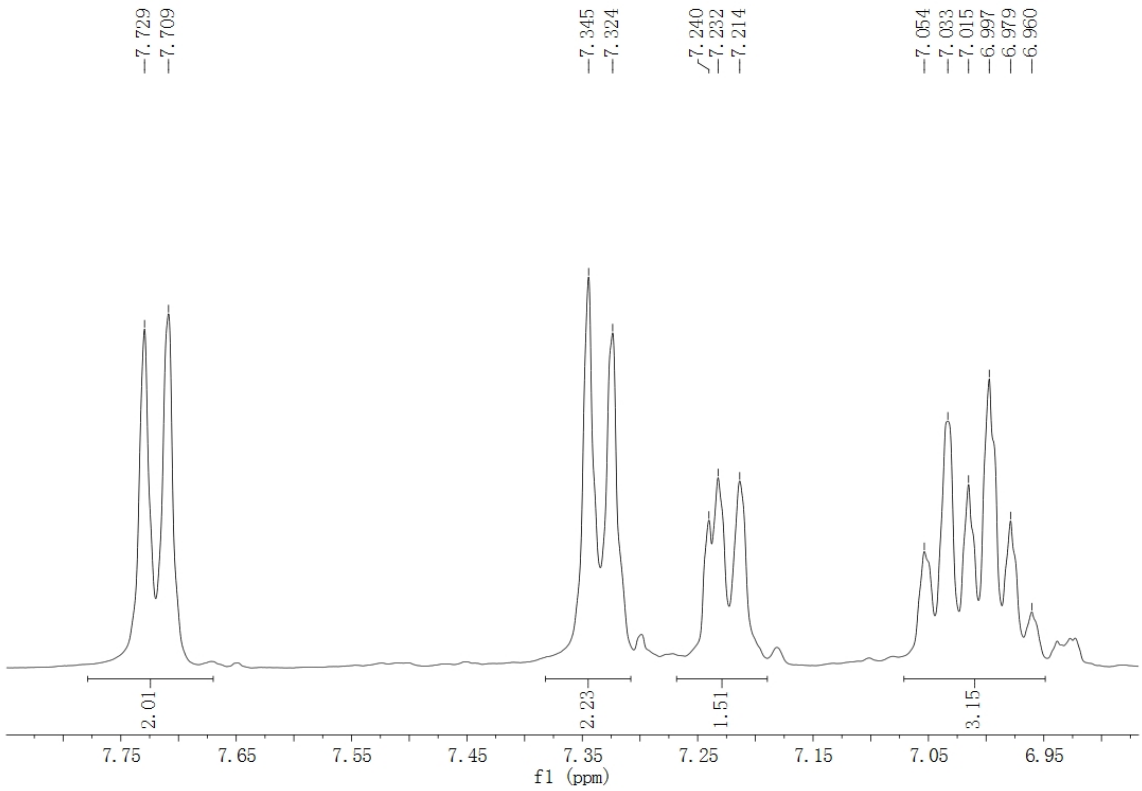

7.712
7.692
7.368
7.349
7.240
7.144
7.124
7.086
7.068
7.049
7.011
6.989
6.968
6.924
6.904
2.04
2.14
1.14
1.08
2.28
7.85
7.75
7.65
7.55
7.45
7.35
7.25
7.15
7.05
6.95
f1 (ppm)

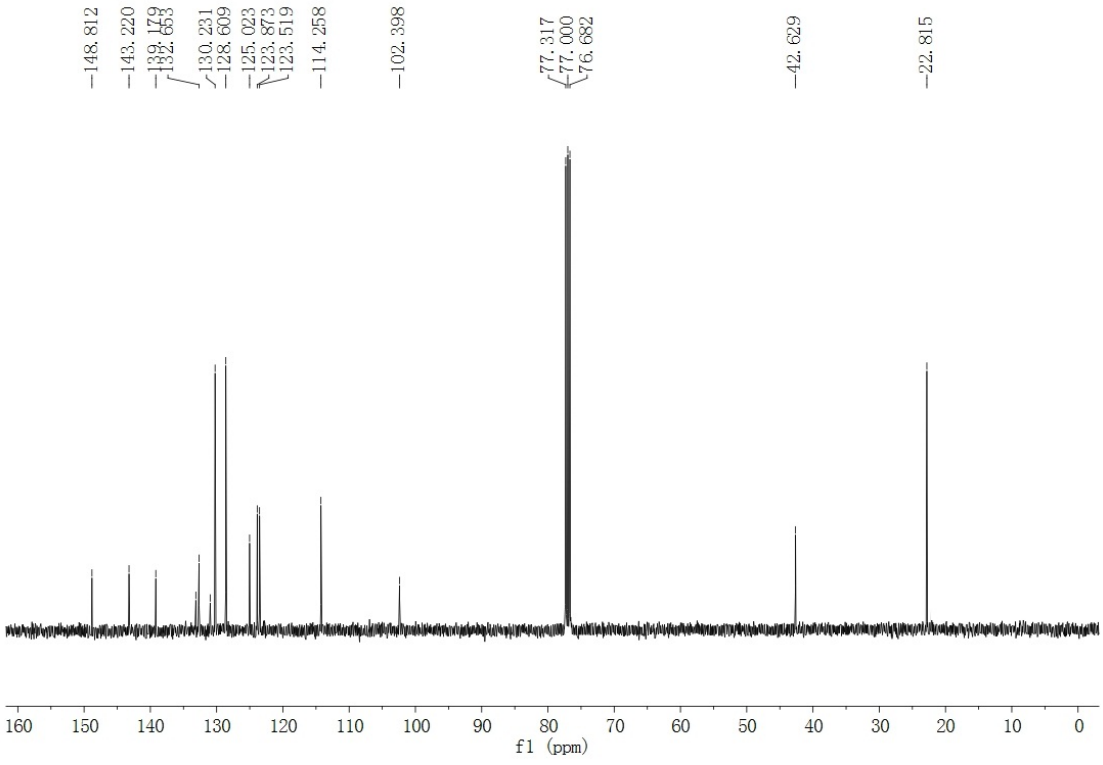

150.543
128.862
125.807
123.775
123.690
120.617
120.251
116.217
108.564
77.317
77.000
76.682
51.959
33.309
25.728
24.877
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

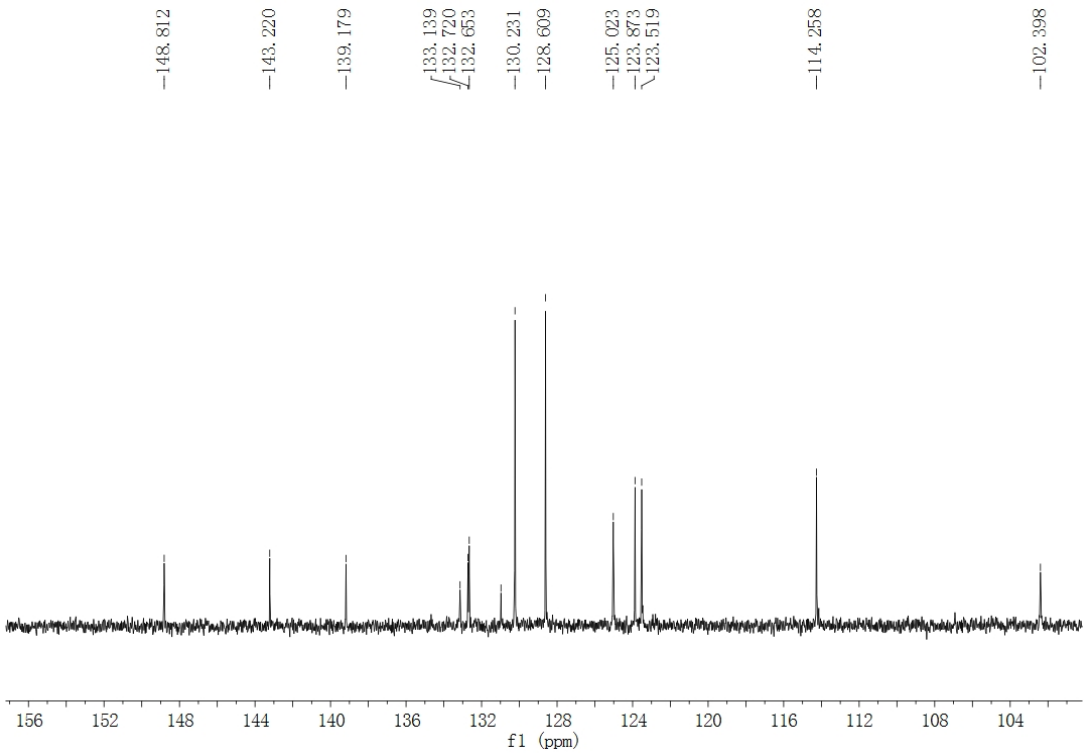


^{1}H NMR and ^{13}C NMR of 2-(4-chlorophenyl)-*N*-isopropylbenzo-[b][1,4]oxazepin-4-amine (34)

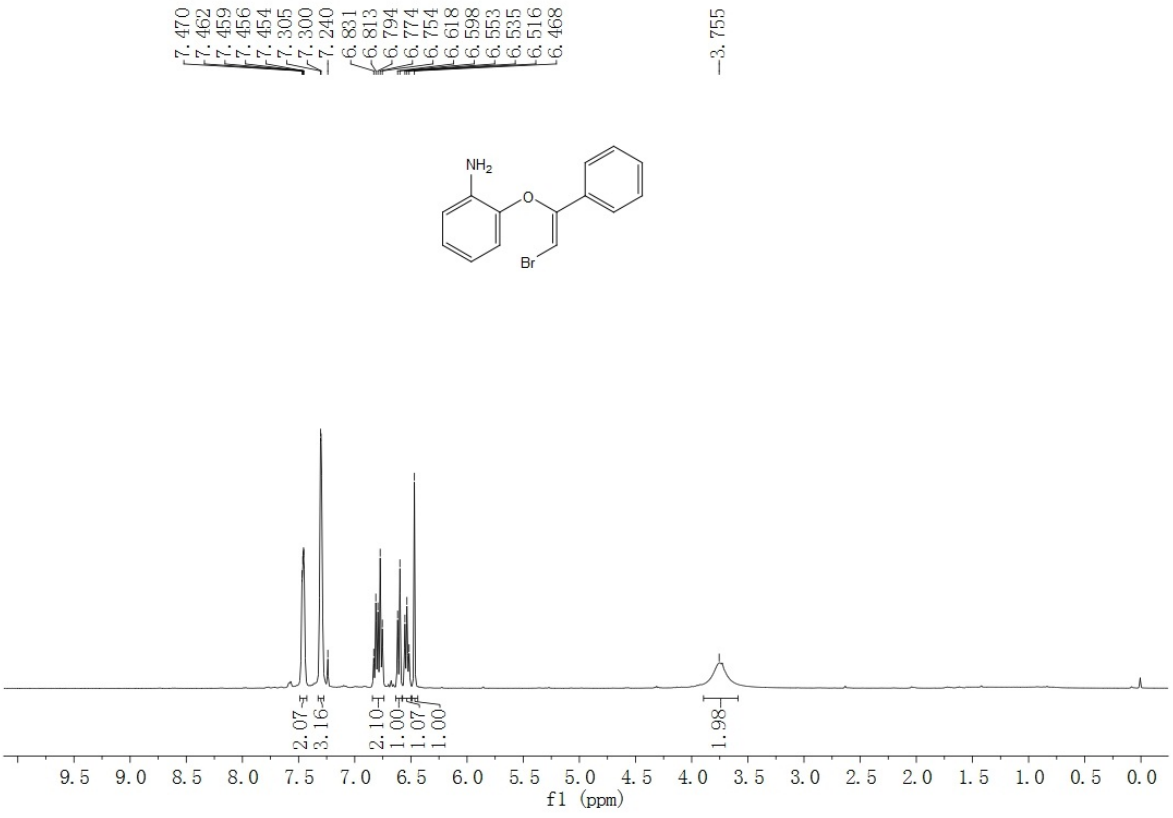


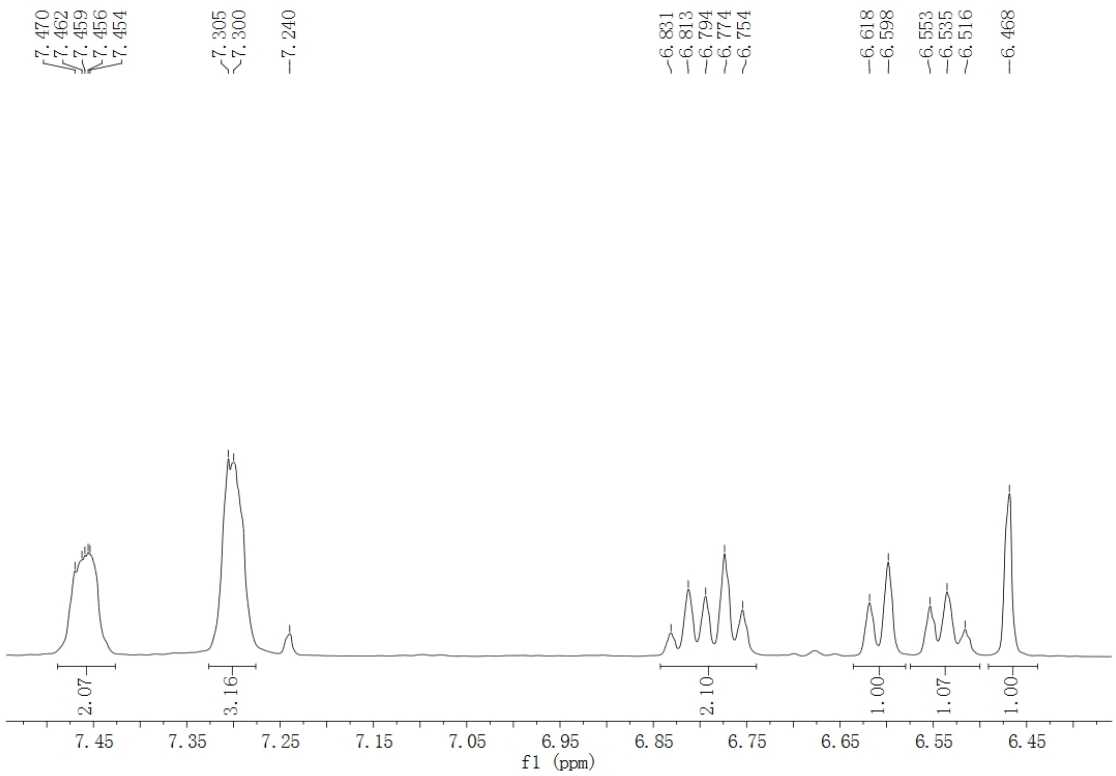

7.729
7.709
7.345
7.324
7.240
7.232
7.214
7.054
7.033
7.015
6.997
6.979
6.960
2.01
2.23
1.51
3.15
7.75
7.65
7.55
7.45
7.35
7.25
7.15
7.05
6.95
f1 (ppm)

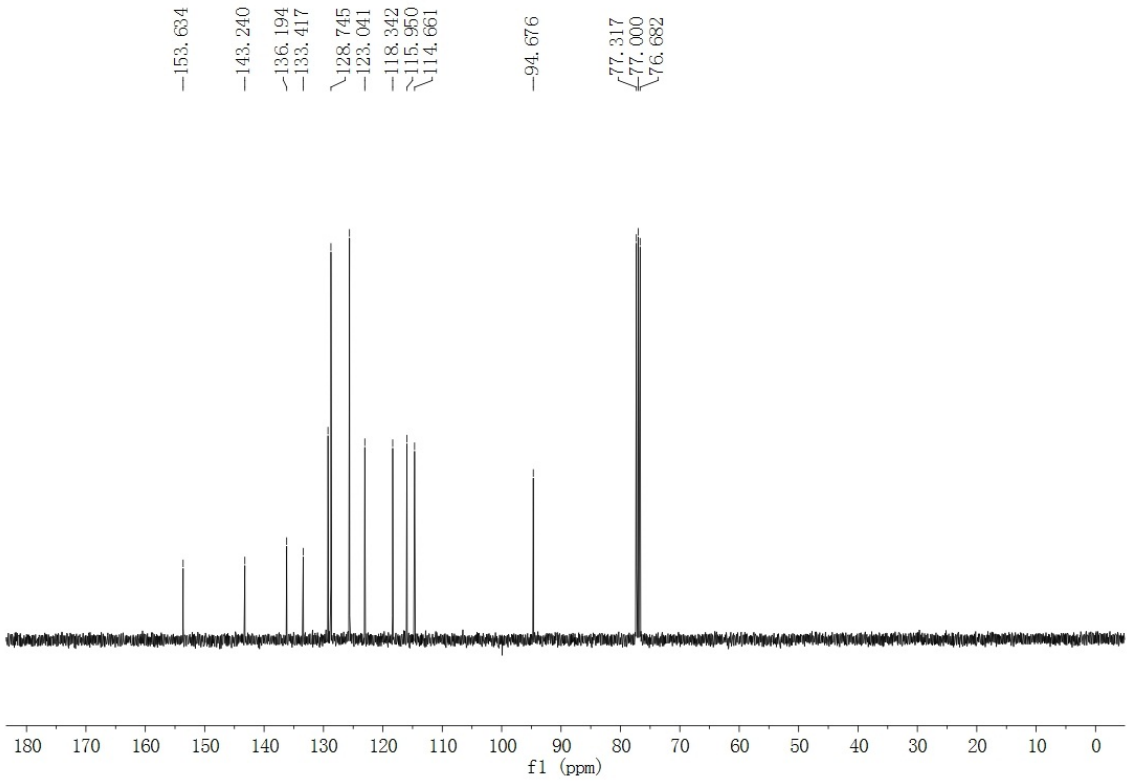

148.812
143.220
139.179
132.653
130.231
128.609
125.023
123.873
123.519
114.258
102.398
77.317
77.000
76.682
42.629
22.815
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

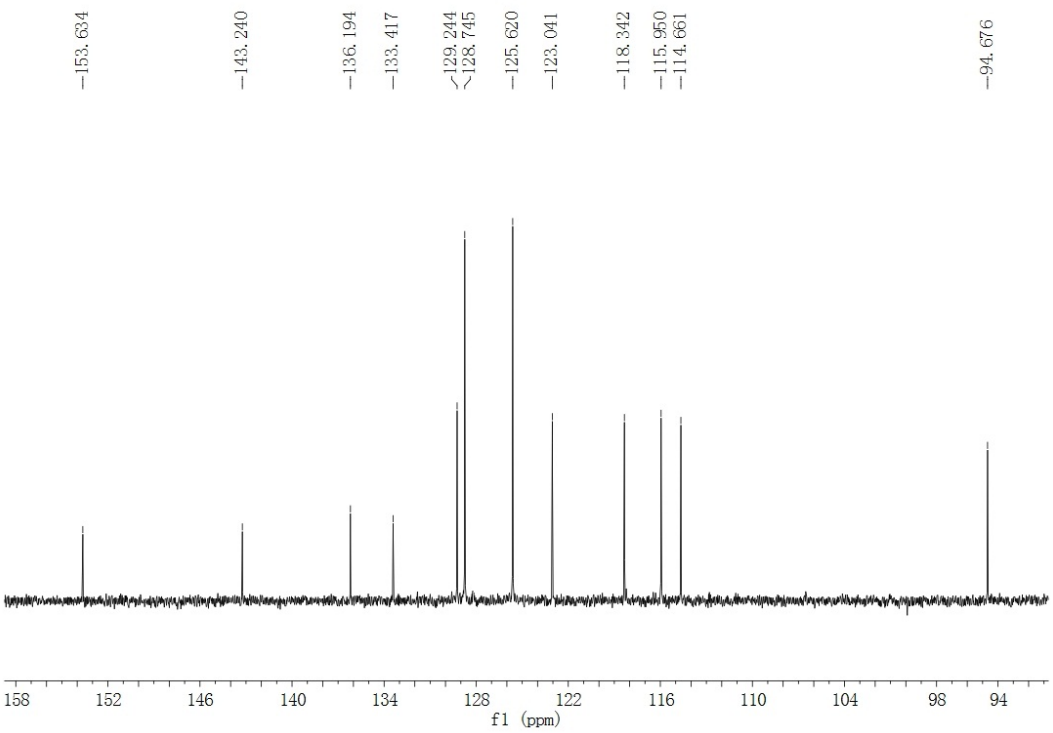


^{1}H NMR and ^{13}C NMR of (*Z*)-2-((2-bromo-1-phenylvinyl)oxy)aniline (36)




7.470
7.462
7.459
7.456
7.454
7.305
7.300
7.240
6.831
6.813
6.794
6.774
6.754
6.618
6.598
6.553
6.535
6.516
6.468
2.07
3.16
2.10
1.00
1.07
1.00
7.45
7.35
7.25
7.15
7.05
6.95
6.85
6.75
6.65
6.55
6.45
f1 (ppm)


153.634
143.240
136.194
133.417
128.745
123.041
118.342
115.950
114.661
94.676
77.317
77.000
76.682
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


153.634
143.240
136.194
133.417
129.244
128.745
125.620
123.041
118.342
115.950
114.661
94.676
158
152
146
140
134
128
122
116
110
104
98
94
f1 (ppm)