Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Copper-catalyzed direct C-H arylation of pyridine *N*-oxides with arylboronic esters: one-pot synthesis of 2-arylpyridines.

Yan Shen, Jiuxi Chen,* Miaochang Liu, Jinchang Ding, Wenxia Gao, Xiaobo Huang and Huayue Wu*

College of Chemistry & Materials Engineering, Wenzhou University, Wenzhou 325035, P. R. China

Email: jiuxichen@wzu.edu.cn; huayuewu@wzu.edu.cn

List of Contents

1. General experimental details

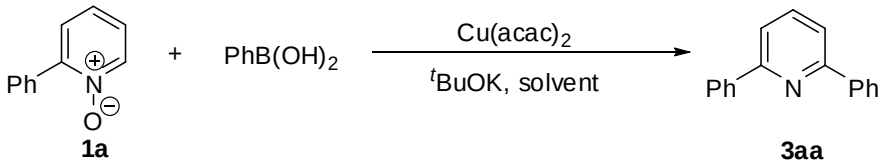
Chemicals were either purchased or purified by standard techniques without special instructions. ^{1}H NMR and ^{13}C NMR spectra were measured on a 500 MHz Bruker spectrometer, using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts are given in δ relative to TMS, the coupling constants J are given in Hz. All reactions were conducted under air atmosphere. Column chromatography was performed using EM Silica gel 60 (300-400 mesh). All products are known compounds and identified by comparison with authentic samples. Analytical data and spectra (^{1}H and ^{13}C NMR) of all compounds are supplied in the Supporting Information.

2. General procedure

Under air atmosphere, a Schlenk tube was charged with pyridine *N*-oxides (0.5 mmol), arylboronic acids or ester (1.0 mmol), $Cu(acac)_2$ (10 mol %) and dry ^{t}BuOK (1.5 mmol) in 5mL of toluene at room temperature. After that, the mixture was stirred constantly at 110 ^{o}C (oil bath temperature) for 2 h. After the completion of the reaction, as monitored by TLC and GC-MS analysis, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, then concentrated and purified by silica gel column chromatography with petroleum ether-ethyl acetate as eluent to afford the desired product **3**.

3. Screening optimal conditions

Table S1 *Screening optimal conditions*



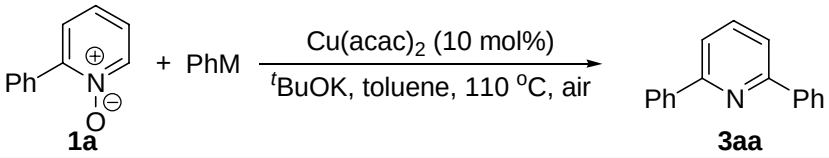
1a **3aa**

entry	N-oxide mmol	$PhB(OH)_2$ mmol	^tBuOK mmol	$Cu(acac)_2$ mmol	solvent	T (^oC)	yield (%)[b]
1	0.5	1.0	1.5	10%	xylene	110	48
2	0.5	1.0	1.5	10%	dioxane	110	trace
3	0.5	1.0	1.5	10%	THF	110	trace
4	0.5	1.0	1.5	10%	CH_3CN	110	trace
5	0.5	1.0	1.5	10%	DMF	110	trace
6	0.5	1.0	1.5	10%	DMSO	110	trace
7	0.5	1.0	1.5	10%	hexane	110	65
8	0.5	1.0	1.5	10%	toluene	110	79
9	1.0	0.5	0.5	10%	toluene	110	trace
10	1.0	0.5	1.0	10%	toluene	110	65
11	0.5	0.5	0.5	10%	toluene	110	trace
12	0.5	0.5	1.0	10%	toluene	110	67
13	0.5	1.0	0.5	10%	toluene	110	trace
14	0.5	1.0	1.0	10%	toluene	110	21
15	0.5	1.0	1.5	10%	toluene	110	79
16	0.5	1.0	2.0	10%	toluene	110	67
17	0.5	1.5	1.5	10%	toluene	110	53
18	0.5	1.5	2.0	10%	toluene	110	72
19	0.5	1.5	2.5	10%	toluene	110	76
20	0.5	1.5	3.0	10%	toluene	110	64
21	0.5	1.0	1.5	10%	toluene	50	23
22	0.5	1.0	1.5	10%	toluene	70	56
23	0.5	1.0	1.5	10%	toluene	90	64
24	0.5	1.0	1.5	10%	toluene	100	70
25	0.5	1.0	1.5	5%	toluene	110	59
26	0.5	1.0	1.5	10%	toluene	110	79
27	0.5	1.0	1.5	15%	toluene	110	63
28	0.5	1.0	1.5	20%	toluene	110	58
29	0.5	1.0	1.5	30%	toluene	110	56
30	0.5	1.0	1.5	40%	toluene	110	40

Reaction conditions: *N*-oxide, $PhB(OH)_2$, $Cu(acac)_2$, ^tBuOK, solvent (5 mL), 2 h, air. [b] Isolated yield.

4. The reaction of other organoborons with pyridine *N*-oxide

Table S2 *The arylation of organoboron reagents with pyridine N-oxide*[a]

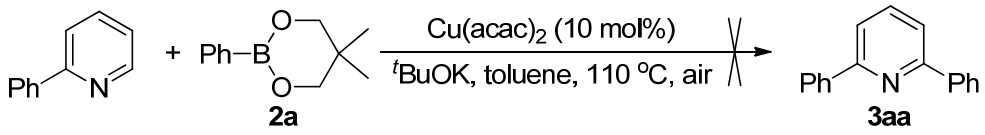


1a **3aa**

entry	PhM (equiv based on **1a**)	yield (%)[b]
1	$PhB(OH)_2$ (2)	79
2	$(PhBO)_3$ (0.7)	78
3	$NaBPh_4$ (0.5)	trace
4	$PhBF_3K$ (2)	trace
5	$PhB(OR)_2$ **2a** (2)	87
6	$^{i}BuB(OH)_2$ (2)	0
7	$PhCH_2B(OH)_2$ (2)	0

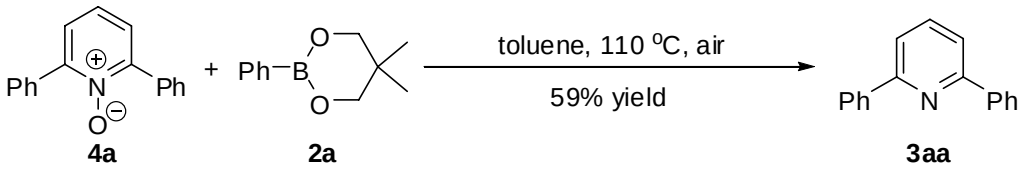
[a] *Reaction conditions*: **1a** (0.5 mmol), organoboron reagents, $Cu(acac)_2$ (10 mol %), ^{t}BuOK (1.5 mmol), toluene (5 mL), 110 ^{o}C, 2h, air. [b] Isolated yield.

5. Control experiments



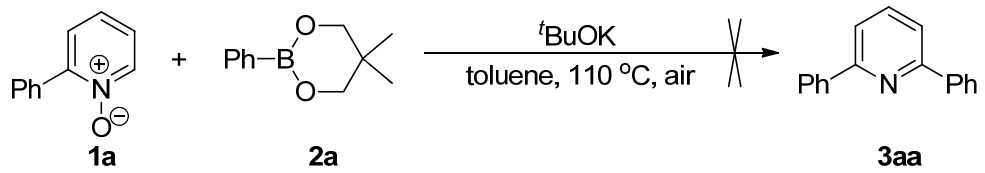
Scheme S1

Under air atmosphere, a Schlenk tube was charged with 2-phenylpyridine (0.5 mmol), **2a** (1.0mmol), $Cu(acac)_2$ (10 mol %) and dry ^tBuOK (1.5 mmol) in 5 mL of toluene at room temperature. After that, the mixture was stirred constantly at 110 ^oC (oil bath temperature) for 2 h. No target product was detected by GC/MS.



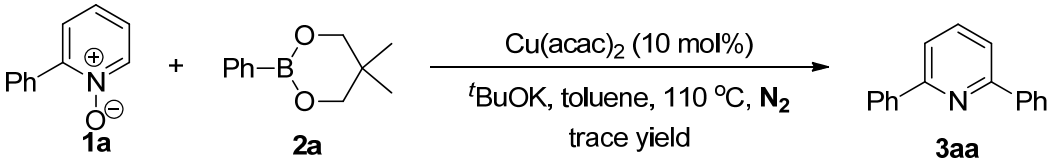
Scheme S2

Under air atmosphere, a Schlenk tube was charged with **4a** (0.5 mmol) and **2a** (1.0mmol) in 5 mL of toluene at room temperature. After that, the mixture was stirred constantly at 110 ^oC (oil bath temperature) for 2 h. The desired product **3aa** was obtained in 59% isolated yield.



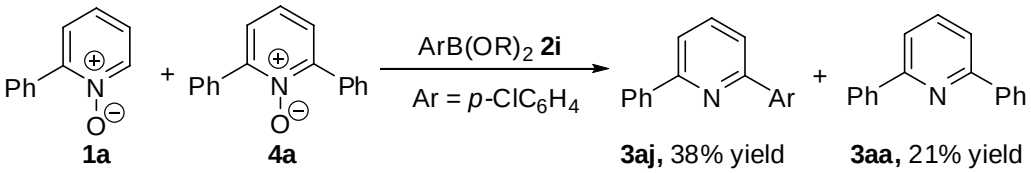
Scheme S3

Under air atmosphere, a Schlenk tube was charged with **1a** (0.5 mmol), **2a** (1.0mmol) and dry ^tBuOK (1.5 mmol) in 5 mL of toluene at room temperature. After that, the mixture was stirred constantly at 110 ^oC (oil bath temperature) for 2 h. No target product and trace deoxygenated starting material (2-phenylpyridine) was detected by GC/MS.



Scheme S4

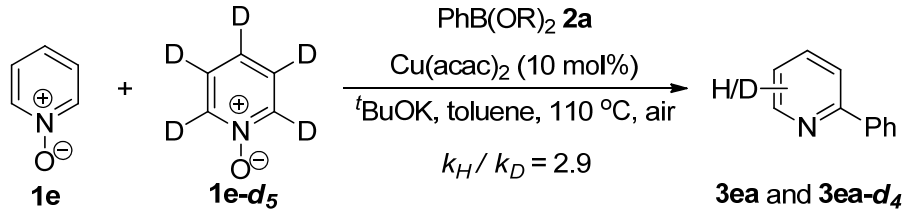
Under N_2 atmosphere, a Schlenk tube was charged with **1a** (0.5 mmol), **2a** (1.0mmol), $Cu(acac)_2$ (10 mol %) and dry ^tBuOK (1.5 mmol) in 5 mL of toluene at room temperature. After that, the mixture was stirred constantly at 110 ^oC (oil bath temperature) for 2 h. Trace target product **3aa** and trace deoxygenated starting material (2-phenylpyridine) was detected by GC/MS.



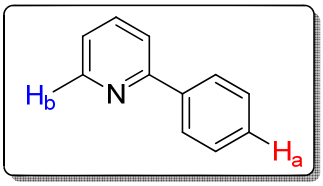
Scheme S5

Under air atmosphere, a Schlenk tube was charged with **1a** (0.5 mmol) and **4a** (0.5 mmol) and *p*-chlorophenylboronic ester (**2i**) (1.0 mmol), $Cu(acac)_2$ (10 mol %) and dry ^tBuOK (1.5 mmol) in 5 mL of toluene at room temperature. After that, the mixture was stirred constantly at 110 ^oC (oil bath temperature) for 2 h. After the completion of the reaction, the reaction mixture was cooled to room temperature. The result demonstrated that products **3aj** and **3aa** were observed by GC analysis in 38% and 21% yields, respectively.

6. Kinetic isotope competition experiment

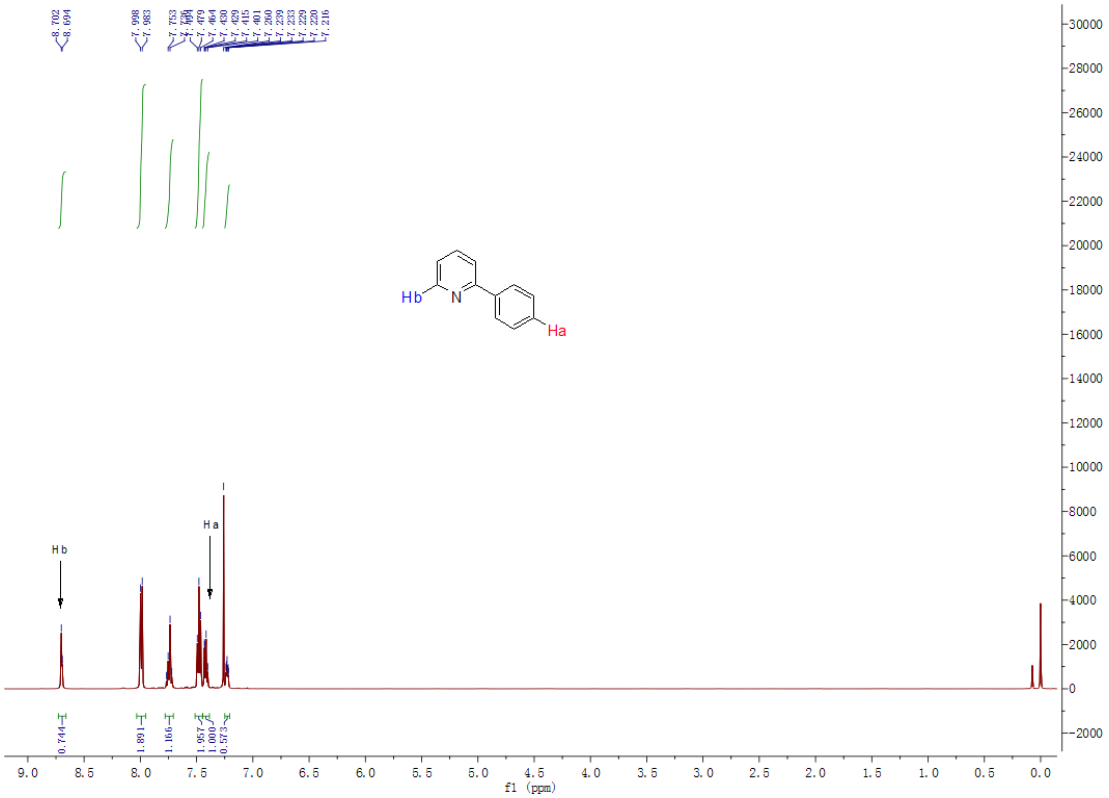


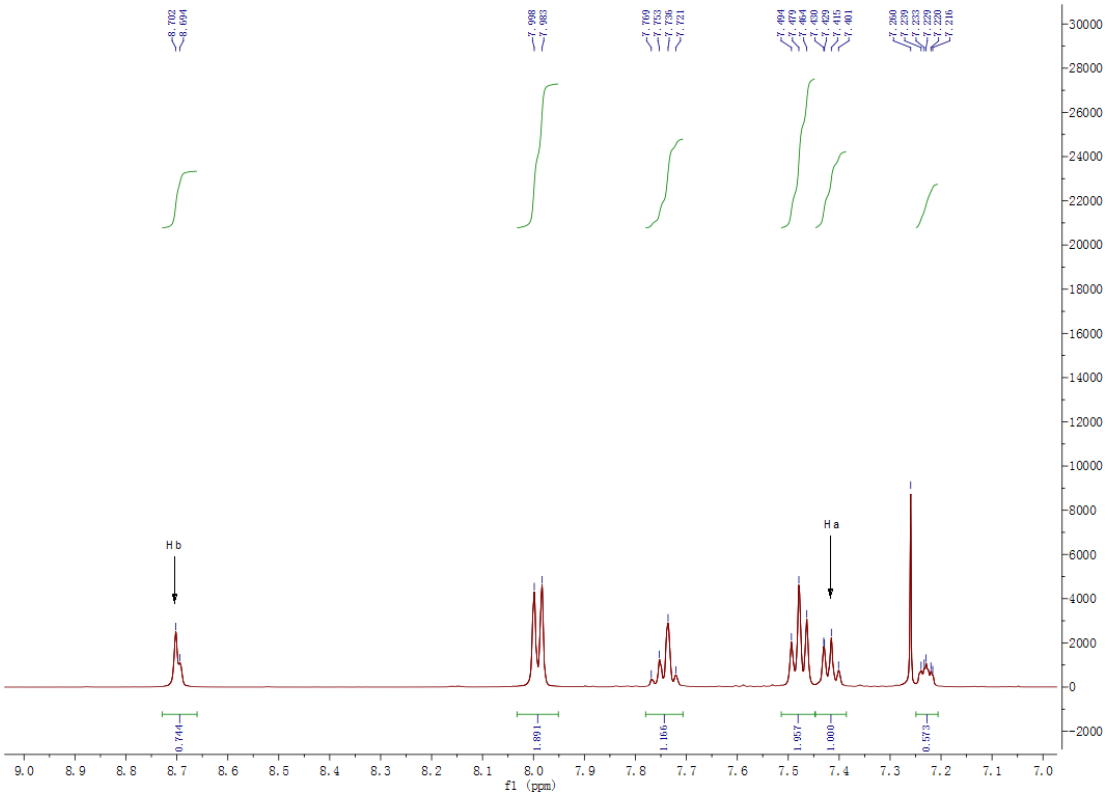
Scheme S6 *Kinetic isotope effect*



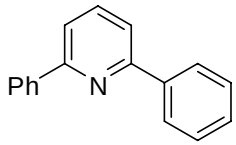
Under air atmosphere, a Schlenk tube was charged with **1e** (0.25 mmol) and **1e-*d*$_5$** (0.25 mmol) and **2a** (1.0 mmol), $Cu(acac)_2$ (10 mol %) and dry ^{t}BuOK (1.5 mmol) in 5mL of toluene at room temperature. After that, the mixture was stirred constantly at 110 ^{o}C (oil bath temperature) for 2 h. After the completion of the reaction, as monitored by TLC and GC-MS analysis, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, then concentrated and purified by silica gel column chromatography with petroleum ether-ethyl acetate as eluent to afford the corresponding product **3ea**/**3ea-*d*$_4$**. The integration value of the proton H_a is used for comparison with H_b.

Kinetic isotope competition experiment (^{1}H NMR)

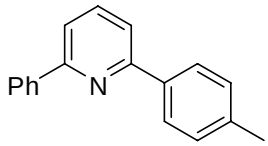




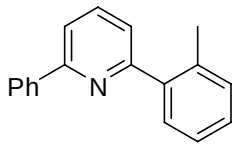
7. Analytical data for all products



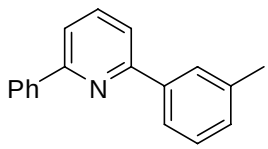
2,6-Diphenylpyridine (**3aa**): White solid, mp 81-82 °C (lit.[1] 79-80 °C). ^{1}H NMR (500Mz, $CDCl_3$) δ 8.24-8.22 (m, 4H), 7.81 (dd, *J* = 7.5, 8.5 Hz, 1H), 7.72 (d, *J* =7.5 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 4H), 7.49 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (125 Mz, $CDCl_3$) δ 156.7, 139.4, 137.4, 128.9, 128.6, 126.9, 118.5.



2-Phenyl-6-*p*-tolylpyridine (**3ab/3ba**): White solid, mp 91-92 °C (lit.[2] not reported). ^{1}H NMR (500Mz, $CDCl_3$) δ 8.18-8.16 (m, 2H), 8.07 (d, *J* = 8.0 Hz, 2H), 7.80 (t, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.53-7.50 (m, 2H), 7.46-7.43 (m, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 2.44(s, 3H). ^{13}C NMR (125 Mz, $CDCl_3$) δ 156.8, 156.7, 139.6, 138.9, 137.4, 136.7, 129.4, 128.9, 128.6, 127.0, 126.8, 118.3, 118.2, 21.3.



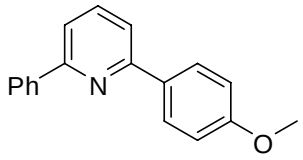
2-Phenyl-6-*o*-tolylpyridine (**3ac**): White solid, mp 63-64 °C (lit.[3] not reported). ^{1}H NMR (500Mz, $CDCl_3$) δ 8.12-8.10 (m, 2H), 7.83 (t, *J* = 8.0 Hz, 1H), 7.71 (dd, *J* =1.0, 8.0 Hz, 1H), 7.53-7.48 (m, 3H), 7.44-7.41 (m, 1H), 7.38 (dd, *J* = 1.0, 8.0 Hz, 1H), 7.35-7.30 (m, 3H), 2.52 (s, 3H). ^{13}C NMR (125 Mz, $CDCl_3$) δ 159.7, 156.5, 140.6, 139.5, 136.9, 136.1, 130.9, 129.8, 128.9, 128.6, 128.2, 127.0, 125.8, 122.3, 118.1, 20.7.



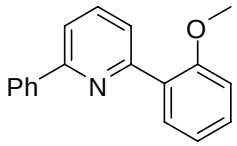
2-Phenyl-6-*m*-tolylpyridine (**3ad**): White solid, mp 66-67 °C. IR (KBr, cm^{-1}) 3042, 2961, 2365, 1567, 1451, 821, 795, 761, 697. ^{1}H NMR (500Mz, $CDCl_3$) δ 8.21-8.19

[1] Moreno-Manas, M.; Pleixats, R.; Serra-Muns, A. *Synlett.* **2006**, 3001.
[2] Wang, Y.; Toh, K.; Ng, E.; Chiba, S. *J. Am. Chem. Soc.* **2011**, *133*, 6411.
[3] Wei, Y.; Yoshikai, N. *J. Am. Chem. Soc.* **2013**, *135*, 3756.

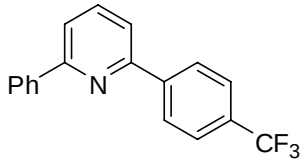
(m, 2H), 8.03 (s, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.81 (t, J = 8.0 Hz, 1H), 7.71-7.69 (m, 2H), 7.56-7.53 (m, 2H), 7.49-7.41 (m, 2H), 7.29 (d, J = 7.5 Hz, 1H), 2.51 (s, 3H). ^{13}C NMR (125 Mz, $CDCl_3$) δ 157.0, 156.8, 139.5, 139.4, 138.2, 137.3, 129.7, 128.9, 128.6, 128.5, 127.7, 127.0, 124.1, 118.7, 118.5, 21.6. HRMS (ESI) *m/z* calcd for $C_{18}H_{15}N$ $(M+H)^+$ 246.1277, Found 246.1281.



2-(4-Methoxyphenyl)-6-phenylpyridine (**3ae**/**3ca**): White solid, mp 132-133 °C (lit.[4] 133 °C). ^{1}H NMR (500Mz, $CDCl_3$) δ 8.17-8.11 (m, 4H), 7.78 (t, J = 8.0 Hz, 1H), 7.64 (dd, J = 3.0, 8.0 Hz, 2H), 7.52-7.49 (m, 2H), 7.45-7.42 (m, 1H), 7.05-7.02 (m, 2H), 3.88 (s, 3H). ^{13}C NMR (125 Mz, $CDCl_3$) δ 160.5, 156.6, 156.4, 139.6, 137.4, 132.1, 128.8, 128.6, 128.2, 126.9, 117.9, 117.8, 114.0, 55.3.



2-(2-methoxyphenyl)-6-phenylpyridine (**3af**): Oil[5]. ^{1}H NMR (500Mz, $CDCl_3$) δ 8.14-8.12 (m, 2H), 8.04 (dd, J = 1.5, 7.5 Hz, 1H), 7.86-7.85 (m, 1H), 7.78 (t, J = 7.5 Hz, 1H), 7.67 (d, J = 7.5 Hz, 1H), 7.51-7.48 (m, 2H), 7.44-7.39 (m, 2H), 7.16-7.13 (m, 1H), 7.03 (d, J = 8.0 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (125 Mz, $CDCl_3$) δ 157.2, 156.7, 155.5, 139.7, 136.3, 131.5, 129.9, 129.3, 128.7, 128.6, 127.0, 123.5, 121.1, 118.2, 111.5, 55.6.

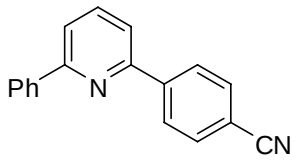


2-Phenyl-6-(4-(trifluoromethyl)phenyl)pyridine (**3ag**): White solid, mp 117-118 °C. IR (KBr, cm^{-1}) 3041, 2352, 1580, 1460, 1334, 1062, 866, 814, 745, 897. ^{1}H NMR (500Mz, $CDCl_3$) δ 8.26 (d, J = 8.0 Hz, 2H), 8.15 (d, J = 8.0 Hz, 2H), 7.85 (t, J = 8.0 Hz, 1H), 7.76-7.71 (m, 4H), 7.52 (t, J = 7.5 Hz, 2H), 7.46 (t, J=7.5 Hz, 1H). ^{13}C NMR (125 Mz, $CDCl_3$) δ 157.1, 155.2, 142.8, 139.1, 137.7, 130.7 (q, $^2J_{C\text{-}F}$ = 32.5 Hz), 129.2, 128.7, 127.2, 127.0, 125.6 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.2 (q, $^1J_{C\text{-}F}$ = 270.0 Hz), 119.4, 118.9. HRMS (ESI) *m/z* calcd for $C_{18}H_{12}NF_3$ $(M+H)^+$ 300.0995, Found 300.1005.

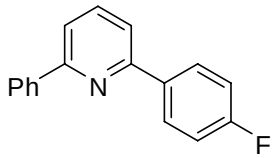
---

[4] Boivin, J.; Carpentier, F.; Jrad, R. *Synthesis*. **2006**, 1664.

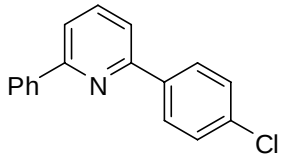
[5] Wang, Y.; Toh, K.; Ng, E.; Chiba, S. *J. Am. Chem. Soc.* **2011**, *133*, 6411



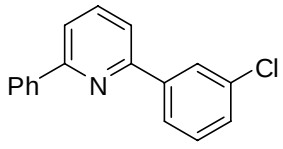
4-(6-Phenylpyridine-2-yl)-benzonitrile (**3ah**): White solid, mp 101-102 ^{o}C (lit.[6] not reported). ^{1}H NMR (500Mz, $CDCl_3$) δ 8.26 (d, J = 8.5 Hz, 2H), 8.14-8.13 (m, 2H), 7.87 (t, J = 8.0 Hz, 1H), 7.78-7.76 (m, 3H), 7.71 (d, J = 7.5 Hz, 1H), 7.53-7.50 (m, 2H), 7.47-7.45 (m, 1H). ^{13}C NMR (125 Mz, $CDCl_3$) δ 157.3, 154.5, 143.5, 138.9, 137.8, 132.5, 129.3, 128.8, 127.4, 126.9, 119.8, 119.0, 118.9, 112.4.



2-(4-Fluorophenyl)-6-phenylpyridine (**3ai/3da**): White solid, mp 94-95 ^{o}C (lit.[7] not reported). ^{1}H NMR (500 Mz, $CDCl_3$) δ 8.19-8.15 (m, 4H), 7.78 (t, J = 8.0 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.54 (t, J = 7.0 Hz, 2H), 7.47 (t, J = 7.0 Hz, 1H), 7.21 (t, J = 8.0 Hz, 2H). ^{13}C NMR (125 Mz, $CDCl_3$) δ 163.5 (d, $^{1}J_{C\text{-}F}$ = 247.5 Hz), 156.8, 156.7, 139.3, 137.5, 135.6 (d, $^{4}J_{C\text{-}F}$ = 3.7 Hz), 129.0, 128.7 (d, $^{3}J_{C\text{-}F}$ = 8.7 Hz), 128.6, 126.9, 118.5, 118.2, 115.5 (d, $^{2}J_{C\text{-}F}$ = 21.3 Hz).



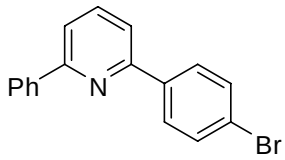
2-(4-Chlorophenyl)-6-phenylpyridine (**3aj**): White solid, mp 104-105 ^{o}C. IR (KBr, cm^{-1}) 3051, 2365, 1583, 1444, 1009, 809, 760, 695. ^{1}H NMR (500 Mz, $CDCl_3$) δ 8.15 (d, J = 7.0Hz, 2H), 8.11 (d, J = 7.5Hz, 2H), 7.80 (t, J = 7.5 Hz, 1H), 7.70 (d, J=7.5Hz, 1H), 7.65 (d, J = 7.5 Hz, 1H), 7.52 (t, J = 7.0 Hz, 2H,), 7.48-7.44 (m, 3H). ^{13}C NMR (125 Mz, $CDCl_3$) δ 156.9, 155.5, 139.3, 137.9, 137.6, 135.0, 129.1, 128.8, 128.7, 128.2, 126.9, 118.8, 118.3. HRMS (ESI) *m/z* calcd for $C_{17}H_{12}NCl$ $[M + H]^+$ 266.0731, found 266.0741.



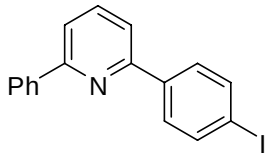
[6] Kumar, A.; Rhodes, R. A.; Spychala, J.; Wilson, W. D.; Boykin, D. W.; Tidwell, R. R.; Dykstra, C. C.; Hall, J. E.; Jones, S. K.; Schinazi, R. F. *Eur. J. Med. Chem.* **1995**, *30*, 99.

[7] Andersson, H.; Sainte-Luce, B.; Das, S.; Olsson, R.; Almqvist, F. *Chem. Commun.* **2010**, *46*, 3384.

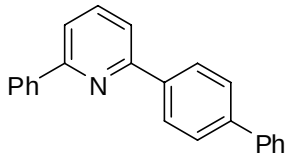
2-(3-Chlorophenyl)-6-phenylpyridine (**3ak**): White solid, mp 49-50 °C. IR (KBr, cm^{-1}) 3045, 2372, 1563, 1441, 1007, 821, 783, 760, 690. ^{1}H NMR (500Mz, $CDCl_3$) δ 8.20 (d, *J* = 2.0 Hz, 1H), 8.17-8.15 (m, 2H), 8.03-8.01 (m, 1H), 7.81 (t, *J* = 8.0 Hz, 1H), 7.72 (dd, *J* = 0.5, 8.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.54-7.51 (m, 2H), 7.48-7.45 (m, 1H), 7,43-7.41 (m, 2H). ^{13}C NMR (125 Mz, $CDCl_3$) δ 157.0, 155.3, 141.3, 139.2, 137.6, 134.8, 129.9, 129.1, 128.9, 128.7, 127.1, 127.0, 125.0, 119.1, 118.6. HRMS (ESI) *m/z* calcd for $C_{17}H_{12}NCl$ $(M+H)^+$ 266.0731, Found 266.0740.



2-(4-Bromophenyl)-6-phenylpyridine (**3al**): White solid, mp 115-116 °C (lit.[8] not reported). ^{1}H NMR (500Mz, $CDCl_3$) δ 8.14 (d, *J* = 8.0Hz, 2H), 8.04 (d, *J* = 8.5 Hz, 2H), 7.80 (t, *J* = 7.5 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.66-7.62 (m, 3H), 7.52 (t, *J* = 7.5 Hz, 2H), 7,45 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (125 Mz, $CDCl_3$) δ 157.0, 155.6, 139.2, 138.3, 137.6, 131.8, 129.1, 128.7, 128.5, 126.9, 123.4, 118.9, 118.3.



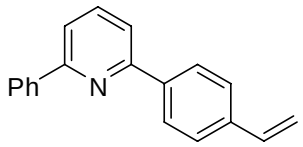
2-(4-Iodophenyl)-6-phenylpyridine (**3am**): White solid, mp 139-141 °C. IR (KBr, cm^{-1}) 3027, 2352, 1586, 1441, 1003, 803, 761, 692. ^{1}H NMR (500Mz, $CDCl_3$) δ 8.13 (d, *J* = 7.5 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.84-7.79 (m, 3H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.44 (t, *J* = 7.0 Hz, 1H). ^{13}C NMR (125 Mz, $CDCl_3$) δ 157.0, 155.7, 139.2, 138.9, 137.8, 137.6, 129.1, 128.7, 128.6, 126.9, 119.0, 118.3, 95.3. HRMS (ESI) *m/z* calcd for $C_{17}H_{12}NI$ $(M+H)^+$ 358.0087, Found 358.0083.



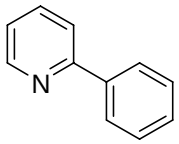
2-(Biphenyl-4-yl)-6-phenylpyridine (**3an**): White solid, mp 149-150 °C (lit.[9] 147-148 °C). ^{1}H NMR (500Mz, $CDCl_3$) δ 8.26 (d, *J* = 8.5Hz, 2H), 8.21-8.19 (m, 2H), 7.83 (t, *J* = 7.5 Hz, 1H), 7.76-7.69 (m, 6H), 7.55-7.44 (m, 5H), 7.39 (t, *J* = 7.0 Hz, 1H). ^{13}C

[8] Wang, Y.; Toh, K.; Ng, E.; Chiba, S. *J. Am. Chem. Soc.* **2011**, *133*, 6411.
[9] Gilman, H.; Weipert, E.; Soddy, T.; Hayes, F. *J. Org. Chem.* **1957**, *22*, 1169.

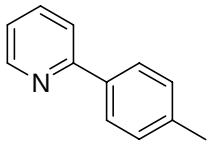
NMR (125 Mz, $CDCl_3$) δ 156.9, 156.4, 141.7, 140.7, 139.5, 138.4, 137.5, 129.0, 128.8, 128.7, 127.5, 127.4, 127.3, 127.1, 127.0, 118.6, 118.5.



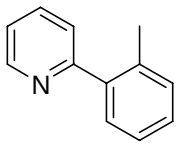
2-Phenyl-6-(4-vinylphenyl)pyridine (**3ao**): White solid, mp 101-102 °C. IR (KBr, cm^{-1}) 3052, 2346, 1639, 1537, 1507, 1407, 906, 814, 765, 750, 697. ^{1}H NMR (500Mz, $CDCl_3$) δ 8.20-8.16 (m, 4H), 7.80 (t, *J* = 7.5 Hz, 1H), 7.69 (d, *J* = 7.5 Hz, 2H), 7.57-7.52 (m, 4H), 7.48-7.45 (m, 1H), 6.82 (dd, *J* = 11.0, 17.5 Hz, 1H), 5.87 (d, *J* = 17.5 Hz, 1H), 5.34 (d, *J* = 11.0 Hz, 1H). ^{13}C NMR (125 Mz, $CDCl_3$) δ 156.8, 156.3, 139.5, 138.8, 138.2, 137.4, 136.5, 128.9, 128.6, 127.1, 126.9, 126.5, 118.6, 118.4, 114.3. HRMS (ESI) *m/z* calcd for $C_{19}H_{15}N$ $(M+H)^+$ 258.1277, Found 258.1264.



2-Phenylpyridine (**3ea**)[10]: Oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.5 Hz, 1H), 8.01-7.99 (m, 2H), 7.76-7.72 (m, 2H), 7.50-7.47 (m, 2H), 7.44-7.40 (m, 1H), 7.24-7.21 (m, 1H). ^{13}C NMR (125 Mz, $CDCl_3$) δ 157.4, 149.6, 139.4, 136.7, 128.9, 128.7, 126.9, 122.0, 120.5.



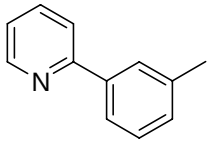
2-*p*-Tolylpyridine (**3eb**)[11]: Oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69-8.67 (m, 1H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.74-7.69(m, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.21-7.18 (m, 1H), 2.41 (s, 3H). ^{13}C NMR (125 Mz, $CDCl_3$) δ 157.5, 149.6, 138.9, 136.6, 136.5, 129.4, 126.8, 121.7, 120.2, 21.2.



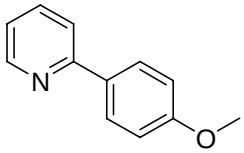
[10] Prokopcova, H.; Kappe, C. *J. Org. Chem.* **2007**, *72*, 4440.

[11] Yu, D.; Yu, M.; Guan, B.; Li, B.; Zheng, Y.; Wu, Z.; Shi, Z. *Org. Lett.* **2009**, *11*, 3374.

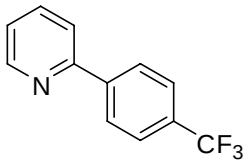
2-*o*-Tolylpyridine (**3ec**)[12]: Oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (d, J = 4.5 Hz, 1H), 7.73-7.70 (m, 1H), 7.37 (d, J = 8.0 Hz, 2H), 7.28-7.20 (m, 4H), 2.34 (s, 3H). ^{13}C NMR (125 Mz, $CDCl_3$) δ 160.0, 149.2, 140.4, 136.1, 135.7, 130.7, 129.6, 128.2, 125.8, 124.0, 121.6, 20.2.



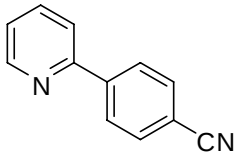
2-*m*-Tolylpyridine (**3ed**)[13]: Oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (d, J = 4.5 Hz, 1H), 7.83 (s, 1H), 7.76-7.70 (m, 3H), 7.37 (t, J = 7.5 Hz, 1H), 7.24-7.21 (m, 2H), 2.44 (s, 3H). ^{13}C NMR (125 Mz, $CDCl_3$) δ 157.6, 149.5, 139.2, 138.3, 136.7, 129.7, 128.6, 127.7, 124.0, 122.0, 120.7, 21.4.



2-(4-Methoxyphenyl)pyridine (**3ee**): White solid, mp 53-54 °C (lit.[14] 53-55 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (d, J = 5.0 Hz, 1H), 7.97-7.94 (m, 2H), 7.70-7.64 (m, 2H), 7.16-7.14 (m, 1H), 7.01-6.98 (m, 2H), 3.85 (s, 3H). ^{13}C NMR (125 Mz, $CDCl_3$) δ 160.4, 157.1, 149.5, 136.6, 132.0, 128.1, 121.3, 119.7, 114.1, 55.3.



2-(4-(Trifluoromethyl)phenyl)pyridine (**3eg**): White solid, mp 73-74 °C. (lit.[15] 70-72 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73-8.72 (m, 1H), 8.11 (d, J = 8.0 Hz, 2H), 7.81-7.78 (m, 1H), 7.77-7.75 (m, 1H), 7.73 (d, J = 8.0 Hz, 2H), 7.31-7.28 (m, 1H). ^{13}C NMR (125 Mz, $CDCl_3$) δ 155.9, 149.9, 142.7, 137.0, 130.7 (q, $^2J_{C\text{-}F}$ = 32.5 Hz), 127.2, 125.7 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.2 (q, $^1J_{C\text{-}F}$ = 270.0 Hz), 122.9, 120.8.



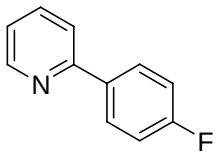
[12] Chen, X.; Li, J.; Hao, X.; Goodhue, C.; Yu, J. *J. Am. Chem. Soc.* **2006**, 128, 78.

[13] Liu, C.; Yang, W. *Chem Commun*. **2009**, *45*, 6267.

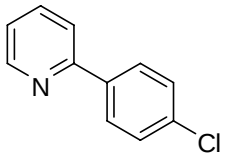
[14] Ackermann, L.; Kapdi, A.; Fenner, S.; Korhaass, C.; Schulzke, C. *Chem. Eur. J.* **2011**, *17*, 2965.

[15] Ackermann, L.; Potukuchi, H.; Kapdi, A.; Schulzke, C. *Chem. Eur. J.* **2010**, *16*, 3303.

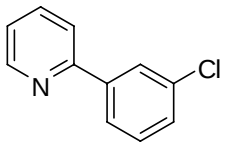
4-(Pyridine-2-yl)benzonitrile (**3eh**): White solid, mp 92-93 °C (lit.[16] 91-92 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73-8.72 (m, 1H), 8.11 (dd, *J* = 2.0, 7.0 Hz, 2H), 7.82-7.79 (m, 1H), 7.77-7.74 (m, 3H), 7.32-7.30 (m, 1H). ^{13}C NMR (125 Mz, $CDCl_3$) δ 155.2, 150.0, 143.5, 137.0, 132.5, 127.4, 123.3, 120.9, 118.8, 112.4.



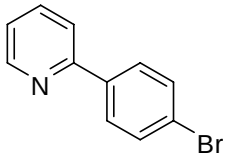
2-(4-Fluorophenyl)pyridine (**3ei**): White solid, mp 40-41 °C (lit.[17] 39-41 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (d, *J* = 5.0 Hz, 1H), 7.99-7.96 (m, 2H), 7.76-7.73 (m, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.23 (dd, *J* = 5.0, 7.0 Hz, 1H), 7.16(t, *J* = 9.0 Hz, 2H). ^{13}C NMR (125Mz, $CDCl_3$) δ 163.5 (d, $^1J_{C\text{-}F}$ = 247.0 Hz), 156.4, 149.6, 136.8, 135.5, 128.7 (d, $^3J_{C\text{-}F}$ = 8.1 Hz), 122.0, 120.2, 115.6 (d, $^2J_{C\text{-}F}$ = 21.5 Hz).



2-(4-Chlorophenyl)pyridine (**3ej**): White solid, mp 51-52 °C (lit.[18] 51-52 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.0 Hz, 1H), 7.95-7.93 (m, 2H), 7.77-7.74 (m, 1H), 7.70 (d, *J* = 7.5 Hz, 1H), 7.46-7.43 (m, 2H), 7.26-7.23 (m, 1H). ^{13}C NMR (125 Mz, $CDCl_3$) δ 156.2, 149.7, 137.8, 136.8, 135.1, 128.9, 128.2, 122.3, 120.3.



2-(3-Chlorophenyl)pyridine (**3ek**)[19]: Oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.5 Hz, 1H), 8.01 (d, *J* = 1.5 Hz, 1H), 7.87-7.85 (m, 1H), 7.79-7.75 (m, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.42-7.38 (m, 2H), 7.28-7.25 (m, 1H). ^{13}C NMR (125 Mz, $CDCl_3$) δ 156.0, 149.8, 141.2, 136.9, 134.9, 130.0, 128.9, 127.1, 124.9, 124.6, 120.6.



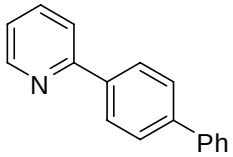
[16] Billingsley, K.; Buchwald, S. *Angew. Chem. Int. Ed.* **2008**, *47*, 4695.

[17] Ackermann, L.; Potukuchi, H.; Kapdi, A.; Schulzke, C. *Chem. Eur. J.* **2010**, *16*, 3303.

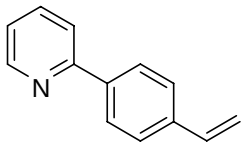
[18] Beadle, J.; Korzeniowaki, S.; Rosenberg, D.; Garcia-Slanga, B.; Gokel, G. *J. Org. Chem.* **1984**, *49*, 1594.

[19] Chaitanya, M.; Yadagiri, D.; Anbarasan, P. *Org. Lett.* **2013,** *15,* 4960.

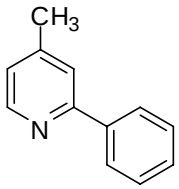
2-(4-Bromophenyl)pyridine (**3el**): White solid, mp 60-61 °C (lit.[20] 60-62 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.5 Hz, 1H), 7.89-7.86 (m, 2H), 7.77-7.74 (m, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.61-7.59 (m, 2H), 7.26-7.24 (m, 1H). ^{13}C NMR (125 Mz, $CDCl_3$) δ 156.3, 149.8, 138.3, 136.9, 131.9, 128.5, 123.4, 122.4, 120.3.



2-(Biphenyl-4-yl)pyridine (**3en**): White solid, mp 138-139 °C (lit.[21] 139-142 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73-8.72 (m, 1H), 8.10-8.08 (m, 2H), 7.79-7.76 (m, 2H), 7.75-7.72 (m, 2H), 7.68-7.66 (m, 2H), 7.49-7.46 (m, 2H), 7.40-7.36 (m, 1H), 7.26-7.23 (m, 1H). ^{13}C NMR (125 Mz, $CDCl_3$) δ 157.0, 149.7, 141.7, 140.6, 138.3, 136.7, 128.8, 127.5, 127.4, 127.3, 127.1, 122.1, 120.4.



2-(4-Vinylphenyl)pyridine (**3eo**)[22]: Oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70-8.68 (m, 1H), 7.99-7.97 (m, 2H), 7.72-7.71 (m, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.26-7.19 (m, 1H), 6.77 (dd, *J* = 11.0, 17.5 Hz, 1H), 5.83 (d, *J* = 17.5 Hz, 1H), 5.30 (d, *J* = 11.0Hz, 1H). ^{13}C NMR (125 Mz, $CDCl_3$) δ 156.9, 149.6, 138.7, 138.1, 136.6, 136.4, 127.0, 126.6, 122.0, 120.3, 114.4.



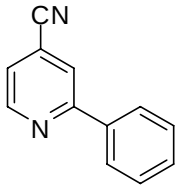
4-Methyl-2-phenylpyridine (**3fa**)[23]: Oil. ^{1}H NMR (500Mz, $CDCl_3$) δ 8.55 (d, *J* = 5.0 Hz, 1H), 7.99-7.97 (m, 2H), 7.54 (d, *J* = 0.5 Hz, 1H), 7.48-7.45 (m, 2H), 7.42-7.39 (m, 1H), 7.05 (d, *J* = 5.0 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (125 Mz, $CDCl_3$) δ 157.3, 149.4, 147.7, 139.5, 128.7, 128.6, 126.9, 123.1, 121.5, 21.2.

[20] Ono, K.; Joho, M.; Satio, K.; Tomura, M.; Matsushita, Y.; Naka, S.; Okada, H.; Onnagawa, H. *Eur. J. Inorg. Chem.* **2006**, 3676.

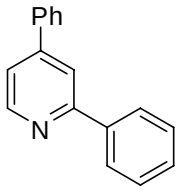
[21] Kumar, M.; Park, K.; Lee, S. *Adv. Synth. Catal.* **2010**, *352*, 3255.

[22] Mizuno, H.; Takaya, J.; Iwasawa, N. *J. Am. Chem. Soc.* **2011**, *133*, 1251.

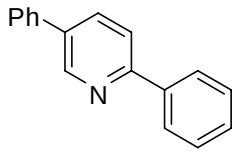
[23] Ohashi, M.; Takeda, I.; Ikawa, M.; Ogoshi, S. *J. Am. Chem. Soc.* **2011**, *133*, 18018.



2-Phenylisonicotinonitrile (**3ga**): White solid, mp 76-77 ^{o}C (lit.[24] not reported). ^{1}H NMR (500 Mz, $CDCl_3$) δ 8.85 (1H, d, J = 5.0 Hz), 8.01-7.99 (2H, m), 7.94 (1H, d, J = 0.5 Hz), 7.53-7.48 (3H, m), 7.45-7.43 (1H, m). ^{13}C NMR (125 Mz, $CDCl_3$) δ 158.7, 150.6, 137.3, 130.2, 129.0, 126.9, 123.1, 122.0, 121.2, 116.7.



2,4-Diphenylpyridine (**3ha**): White solid, mp 67-68 ^{o}C (lit.[25] 80 ^{o}C). ^{1}H NMR (500Mz, $CDCl_3$) δ 8.75 (d, J = 5.0 Hz, 1H), 8.08-8.07 (m, 2H), 7.94 (d, J = 1.0 Hz, 1H), 7.71-7.69 (m, 2H), 7.53-7.50 (m, 4H), 7.49-7.44 (m, 3H). ^{13}C NMR (125 Mz, $CDCl_3$) δ 158.0, 150.0, 149.2, 139.4, 138.5, 129.1, 129.0, 128.9, 128.7, 127.0, 126.9, 120.2, 118.7.



2,5-Diphenylpyridine (**3ia**): White solid, mp 171-172 ^{o}C (lit.[26] 170-172 ^{o}C). ^{1}H NMR (500 Mz, $CDCl_3$) δ 8.95 (d, J = 2.0Hz, 1H), 8.07-8.05 (m, 2H), 7.96 (dd, J = 2.5, 8.0 Hz, 1H), 7.81 (d, J = 8.5Hz, 1H), 7.66-7.64 (m, 2H), 7.52-7.49 (m, 4H), 7.46-7.41 (m, 2H). ^{13}C NMR (125 Mz, $CDCl_3$) δ 156.1, 148.1, 139.0, 137.6, 135.1, 134.9, 129.1, 129.0, 128.8, 128.0, 127.0, 126.8, 120.3.

[24] Wang, J.; Wang, S.; Wang, G.; Zhang, J.; Yu, X. *Chem. Commun*. **2012**, *48*, 11769.

[25] Kleine, T.; Froehlich, R.; Wibbeling, B.; Wuerthwein, E. *J. Org. Chem.* **2011**, *76*, 4591.

[26] Prokopcova, H.; Kappe, C. *J. Org. Chem*. **2007**, *72*, 4440.

8. ^{1}H NMR and ^{13}C NMR spectra for all products

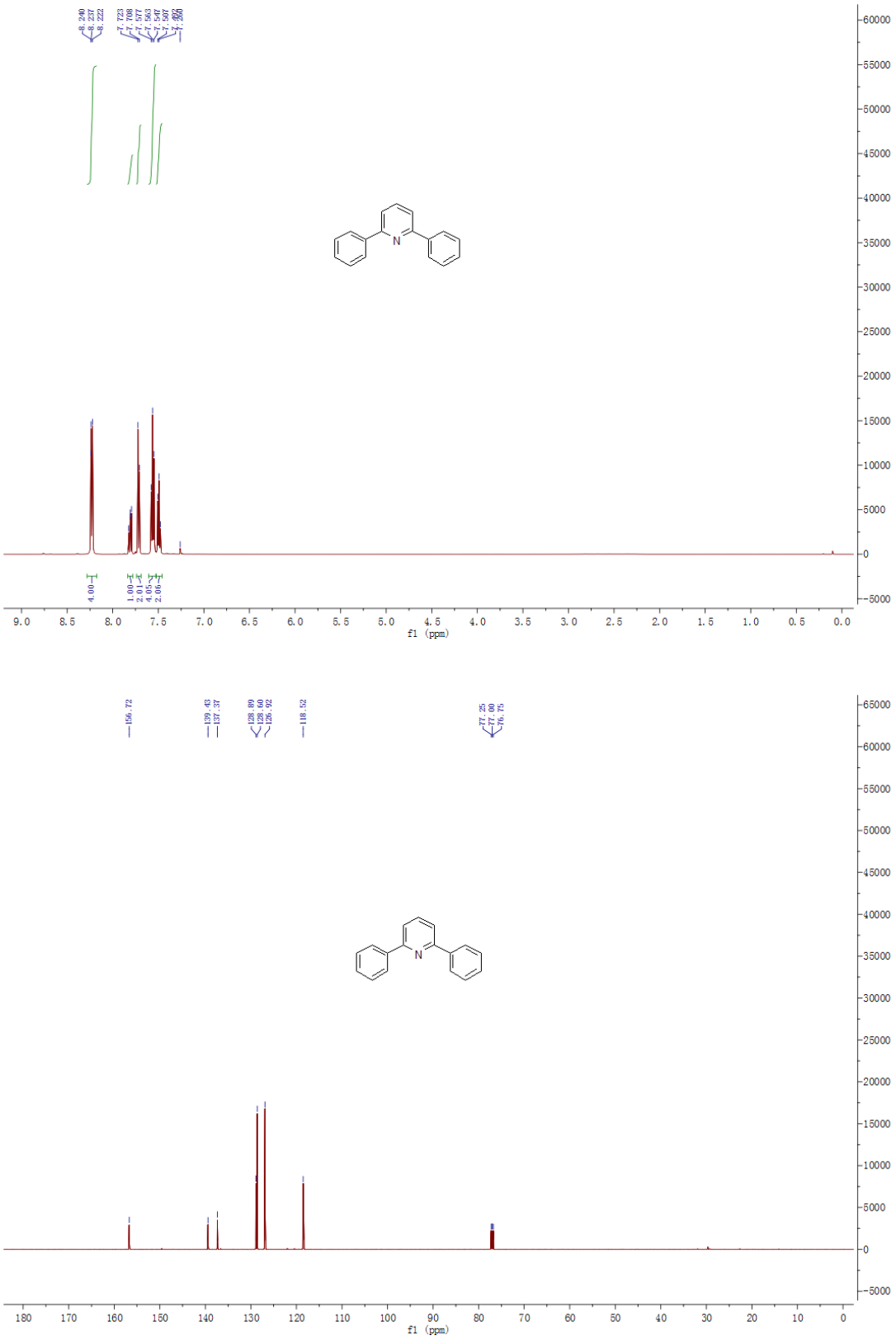


Figure S1. ^{1}H NMR of **3aa** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3aa** (125 MHz, $CDCl_3$).

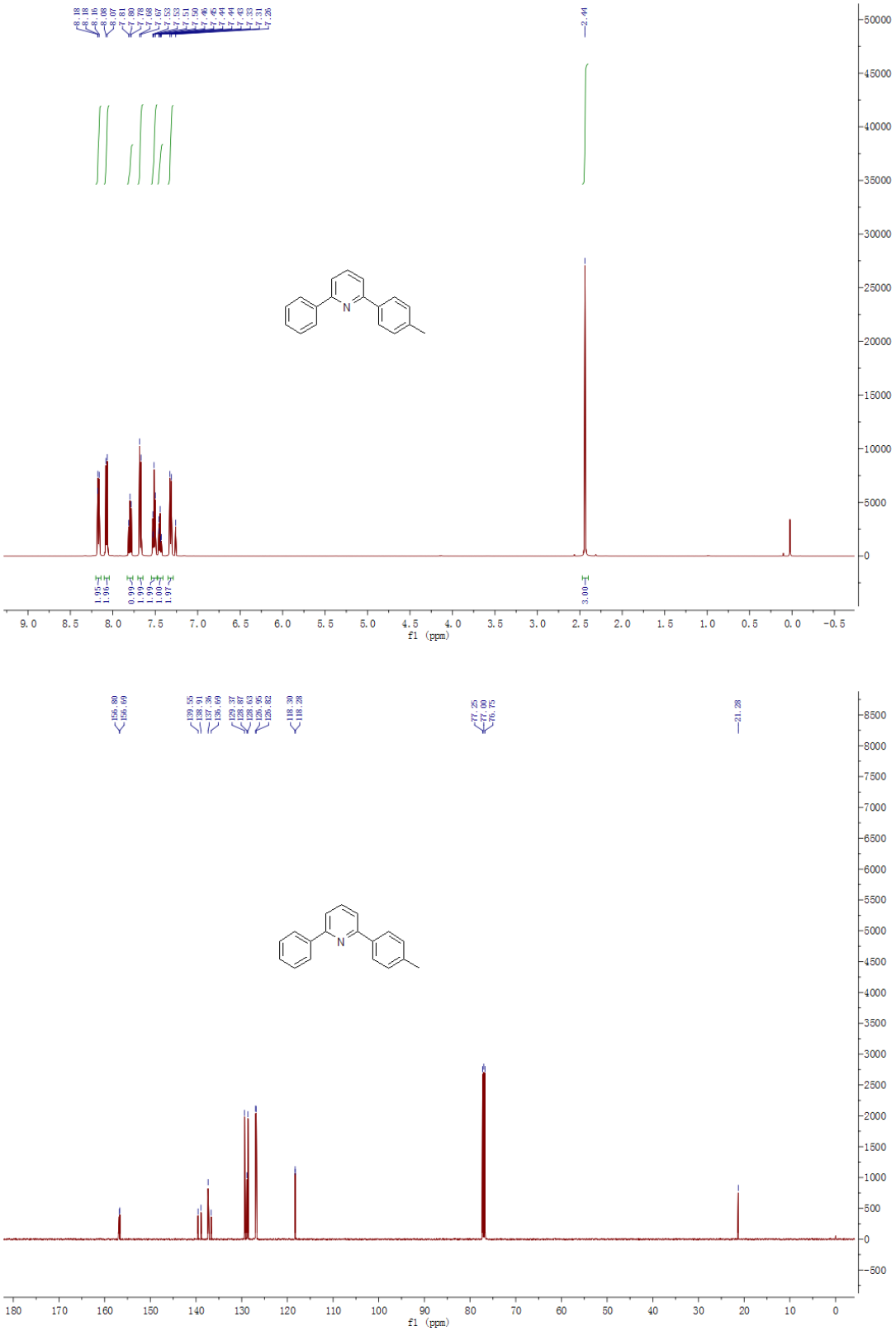


Figure S2. ^{1}H NMR of **3ab** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ab** (125 MHz, $CDCl_3$).

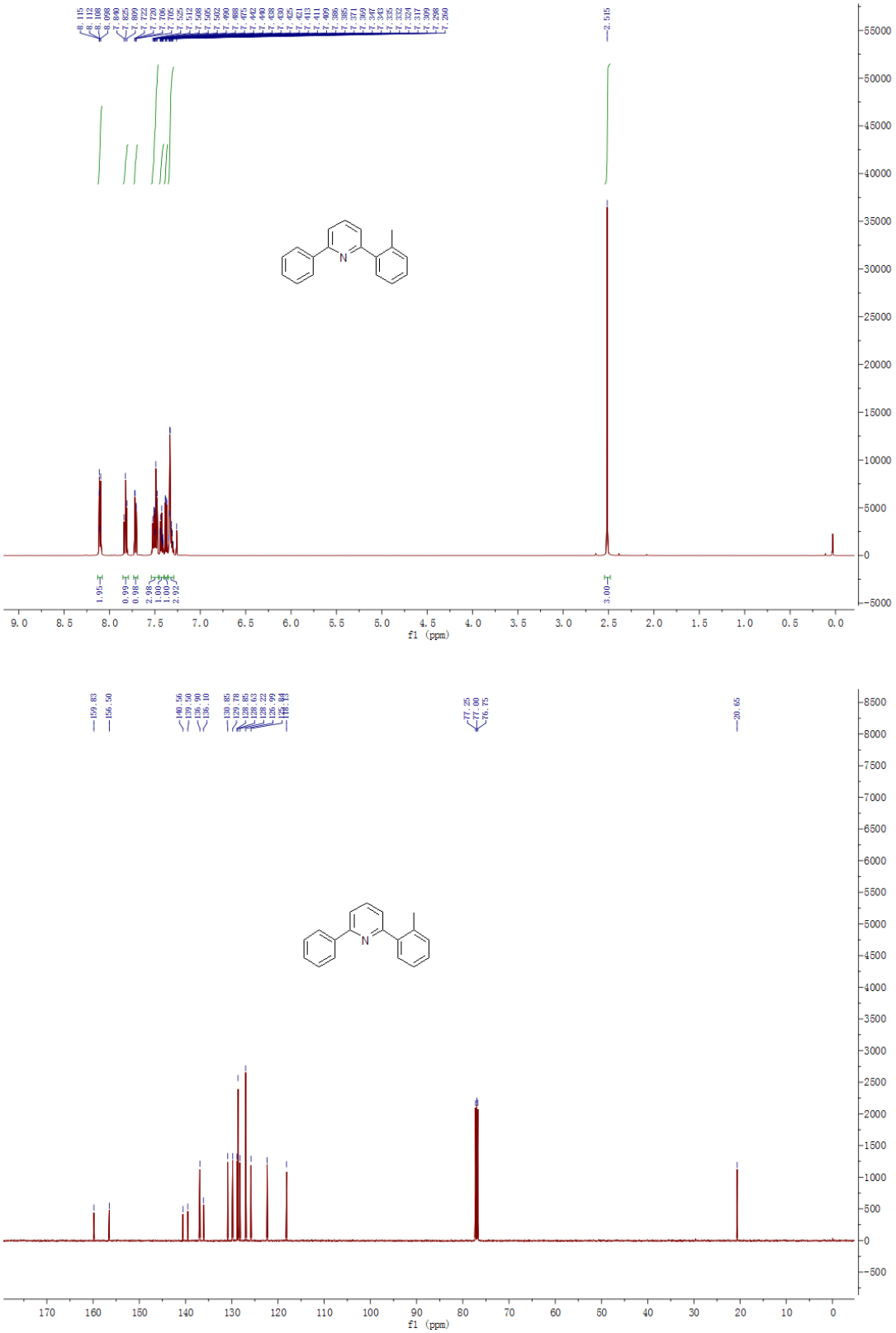


Figure S3. ^{1}H NMR of **3ac** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ac** (125 MHz, $CDCl_3$).

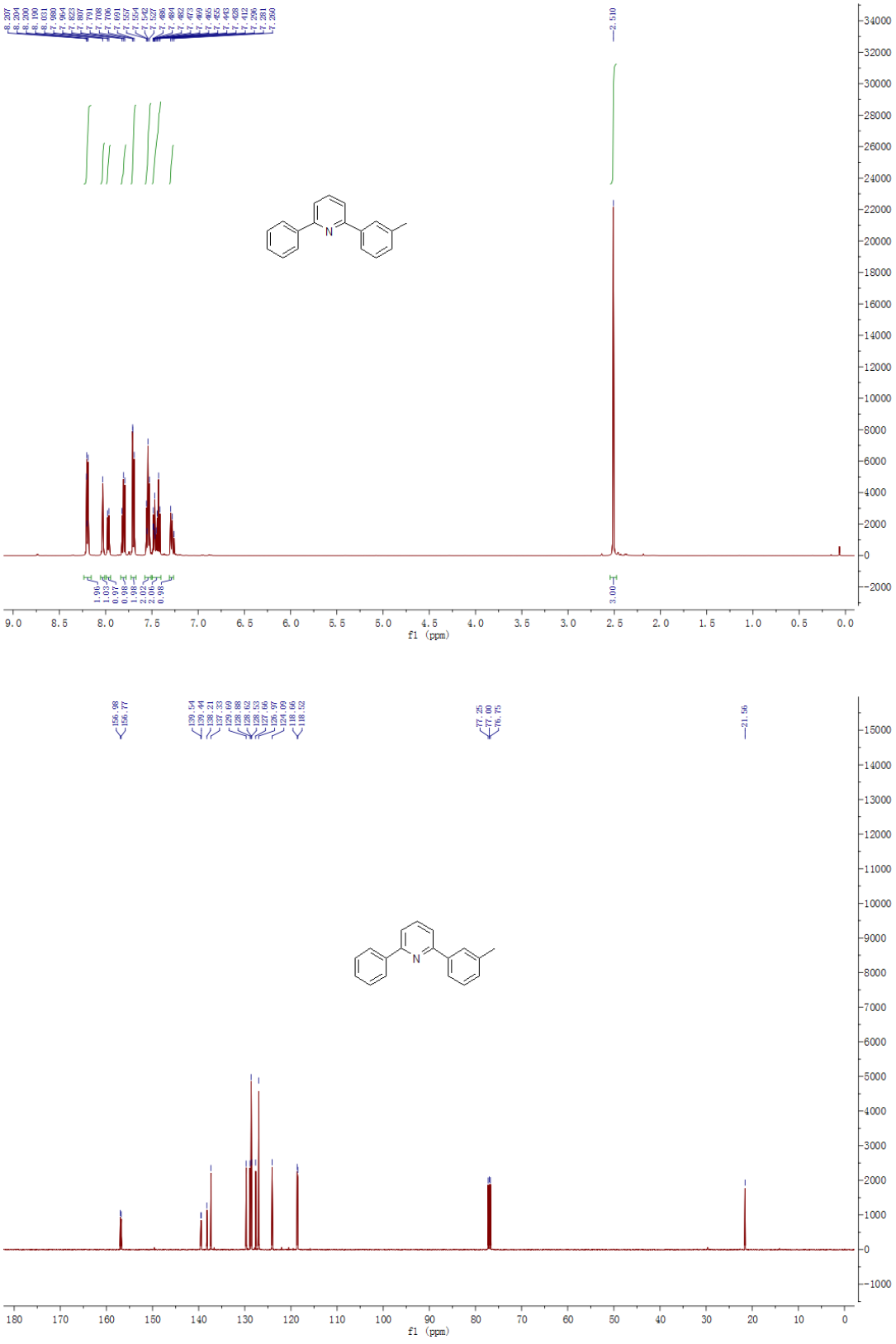


Figure S4. ^{1}H NMR of **3ad** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ad** (125 MHz, $CDCl_3$).

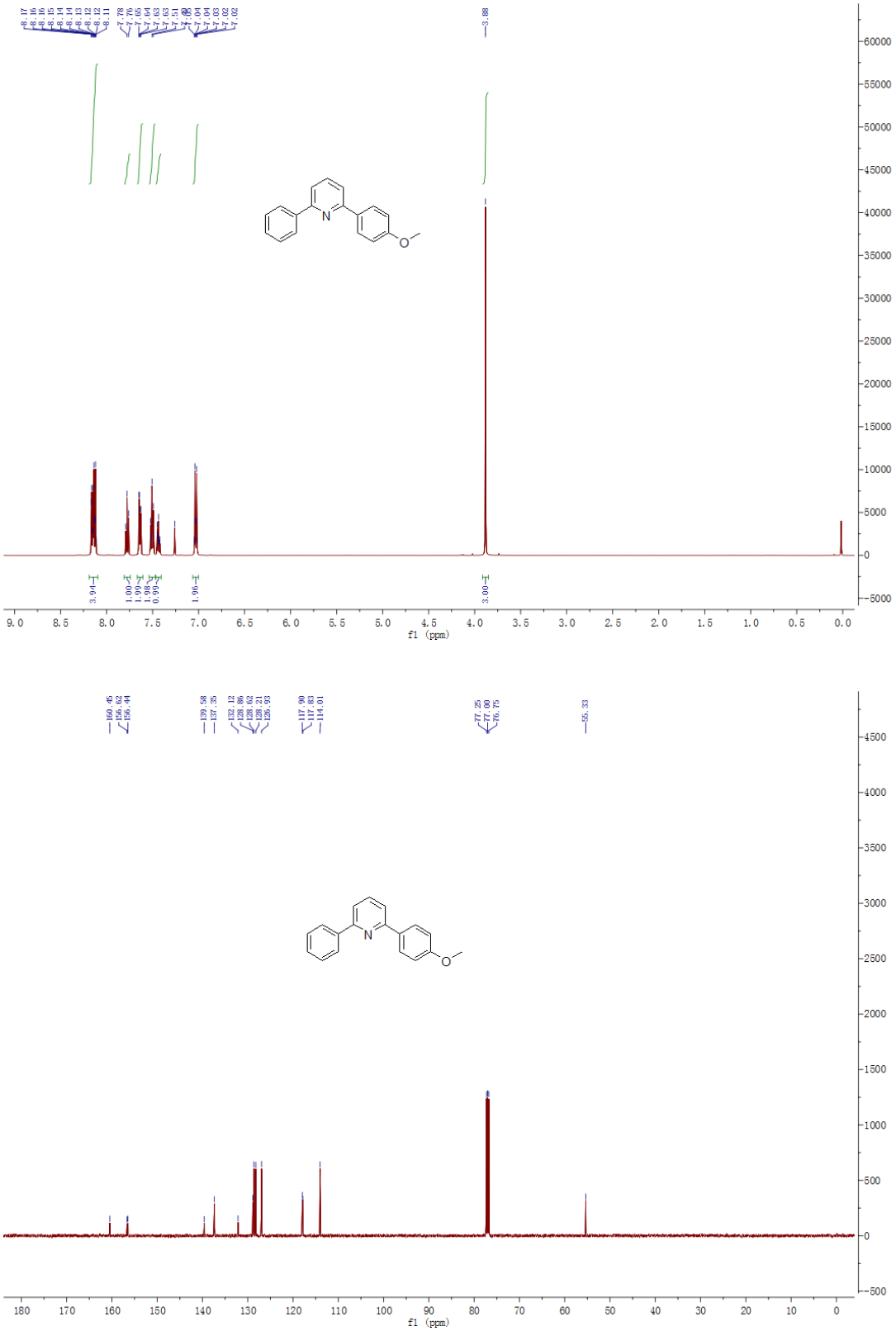


Figure S5. ^{1}H NMR of **3ae** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ae** (125 MHz, $CDCl_3$).

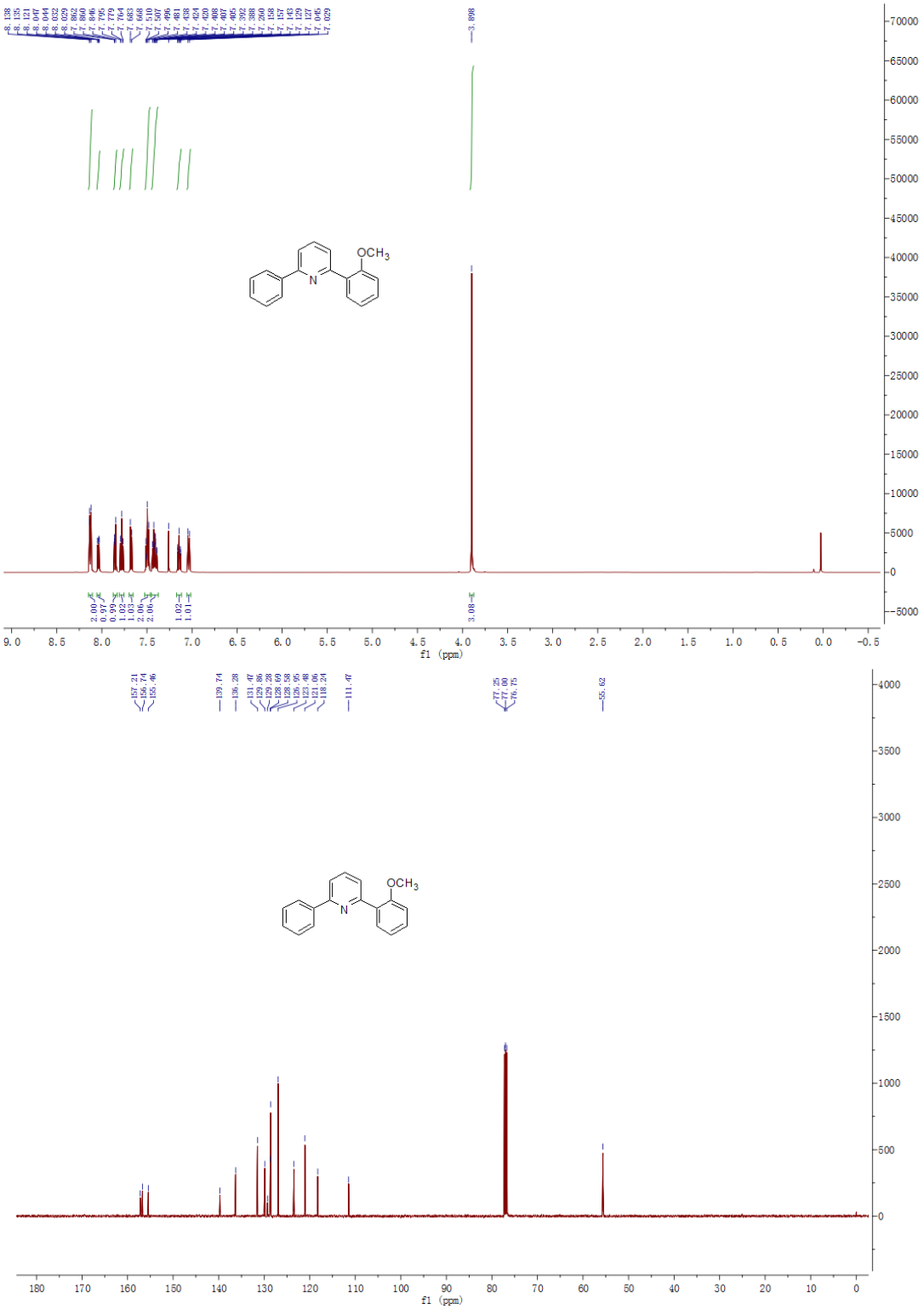


Figure S6. ^{1}H NMR of **3af** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3af** (125 MHz, $CDCl_3$).

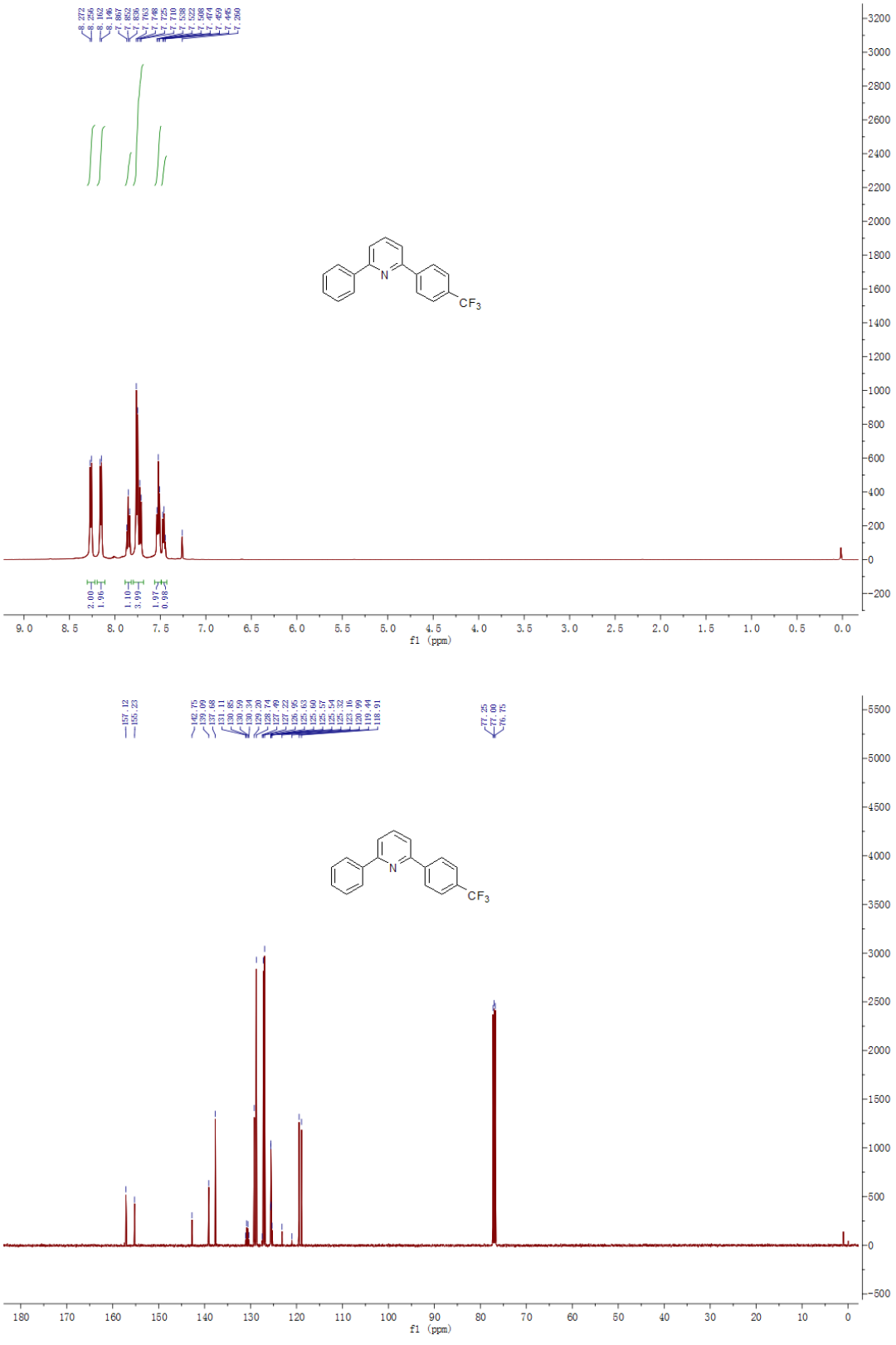


Figure S7. ^{1}H NMR of **3ag** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ag**(125 MHz, $CDCl_3$).

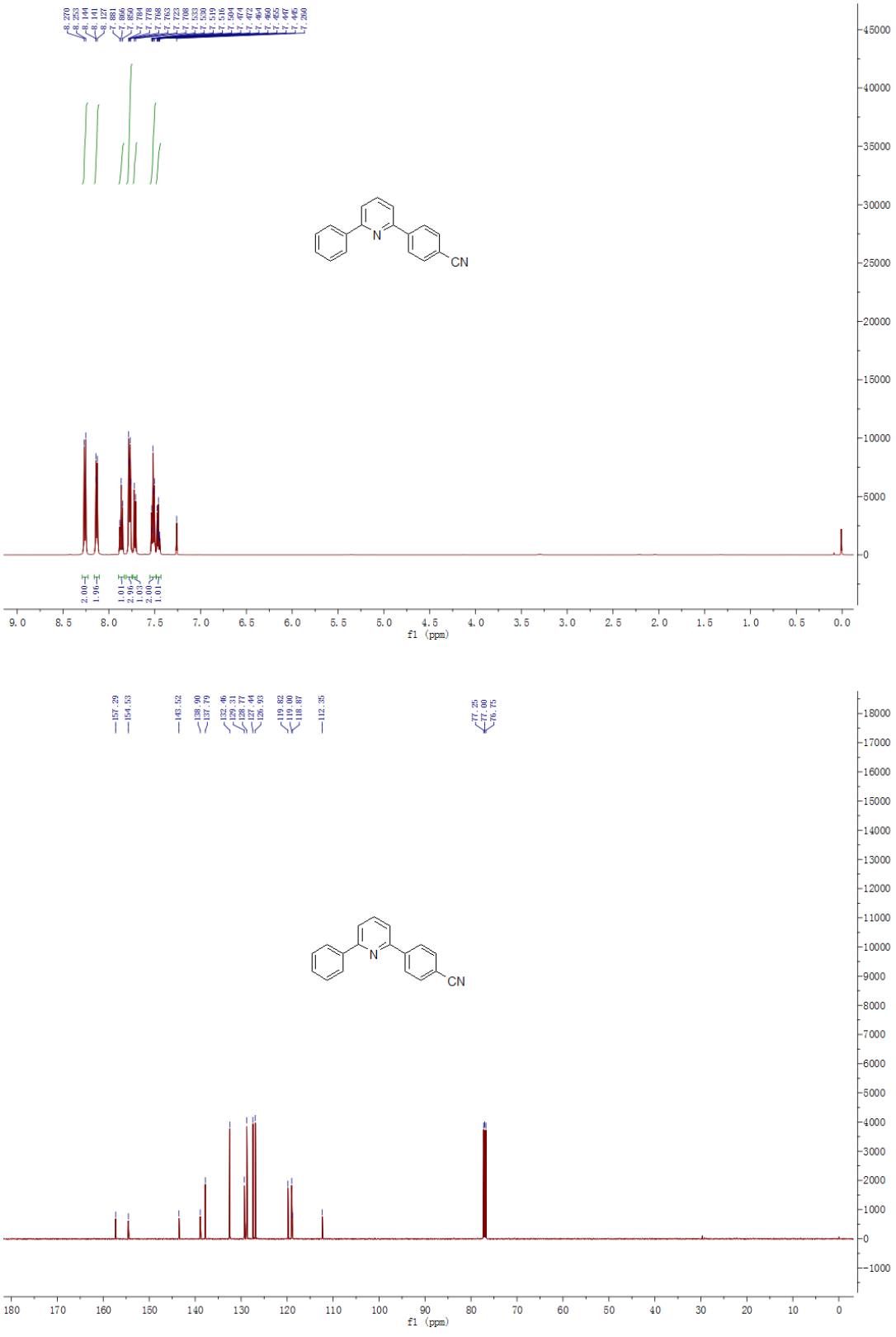


Figure S8. ^{1}H NMR of **3ah** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ah** (125 MHz, $CDCl_3$).

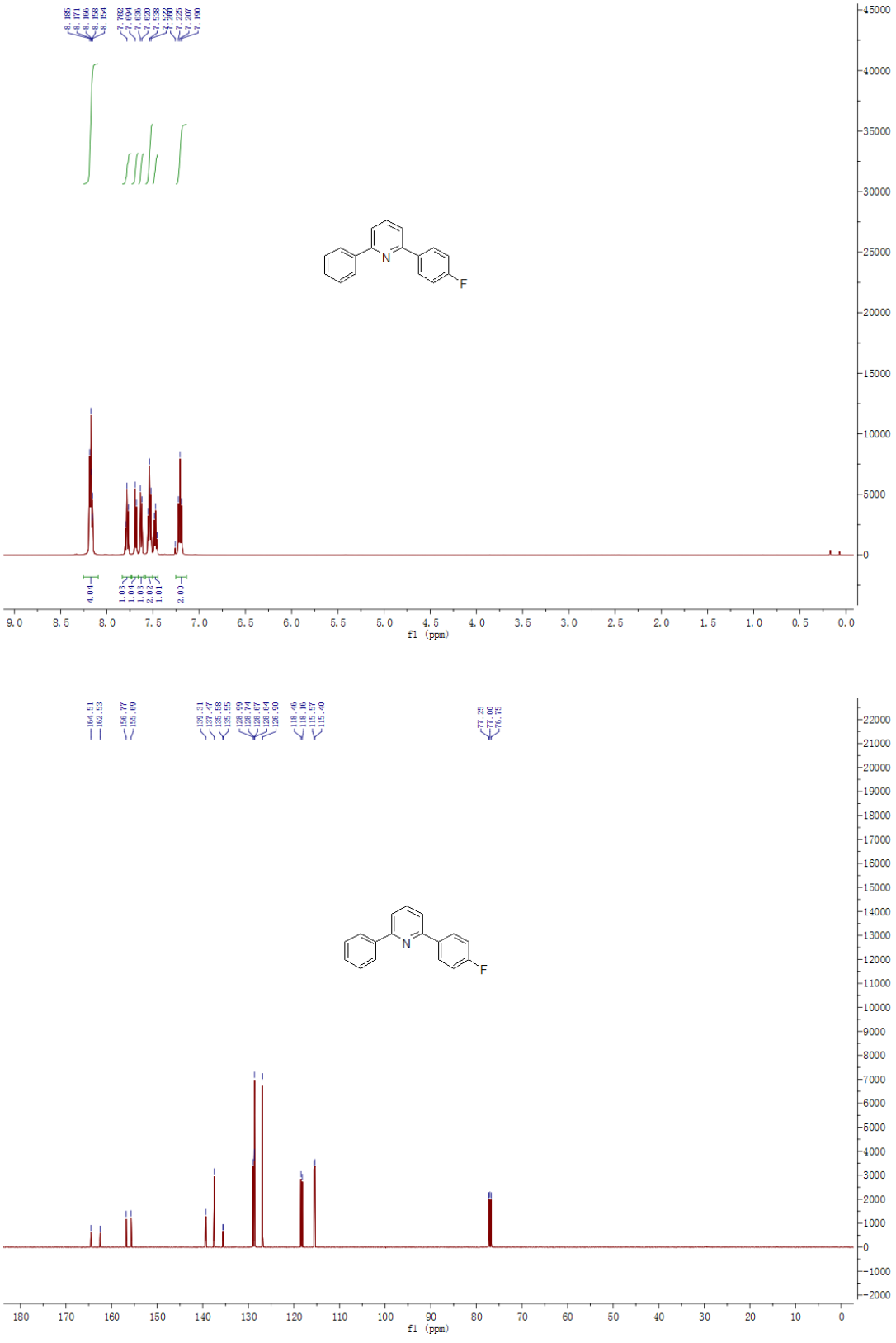


Figure S9. ^{1}H NMR of **3ai** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ai** (125 MHz, $CDCl_3$).

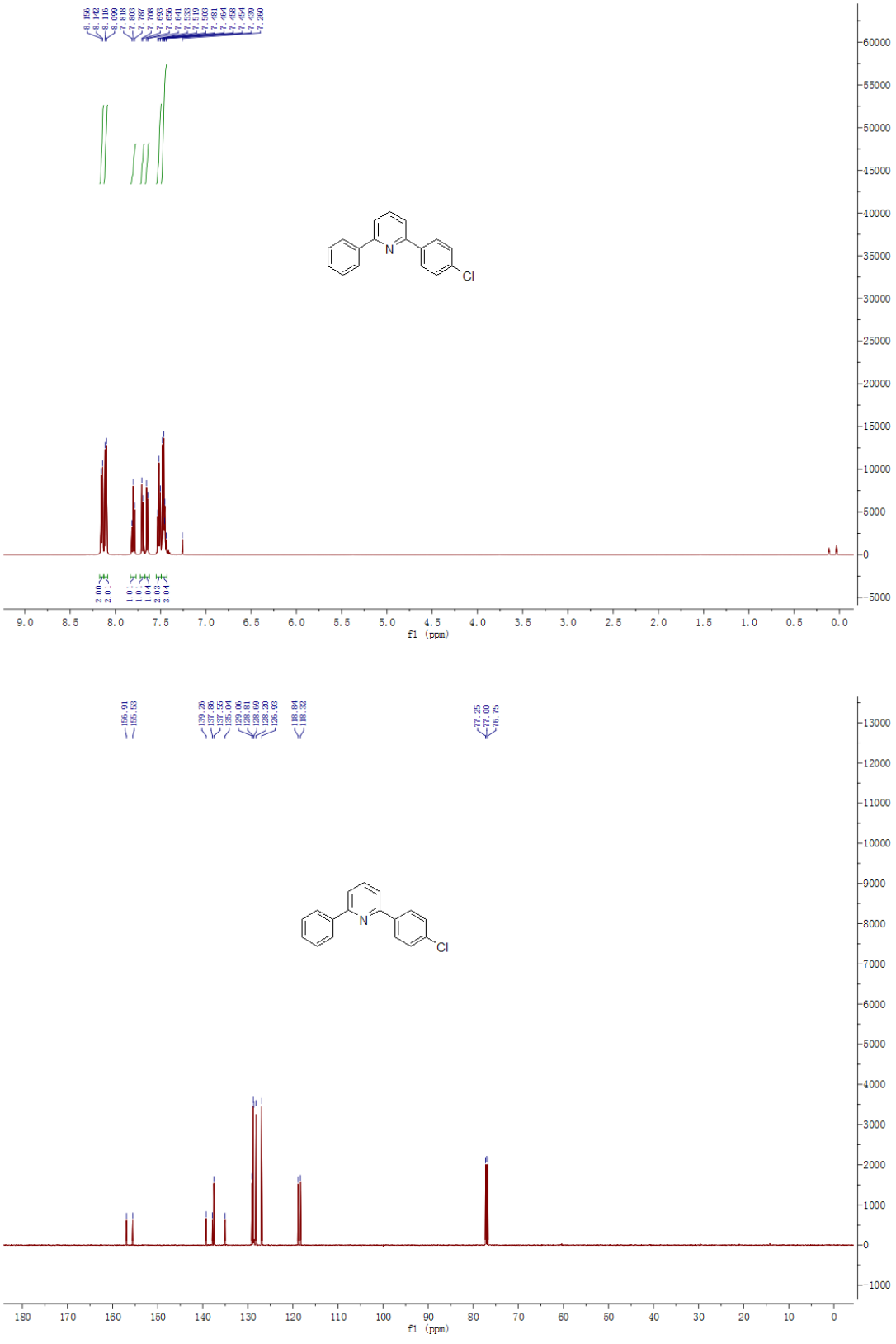


Figure S10. ^{1}H NMR of **3aj** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3aj** (125 MHz, $CDCl_3$).

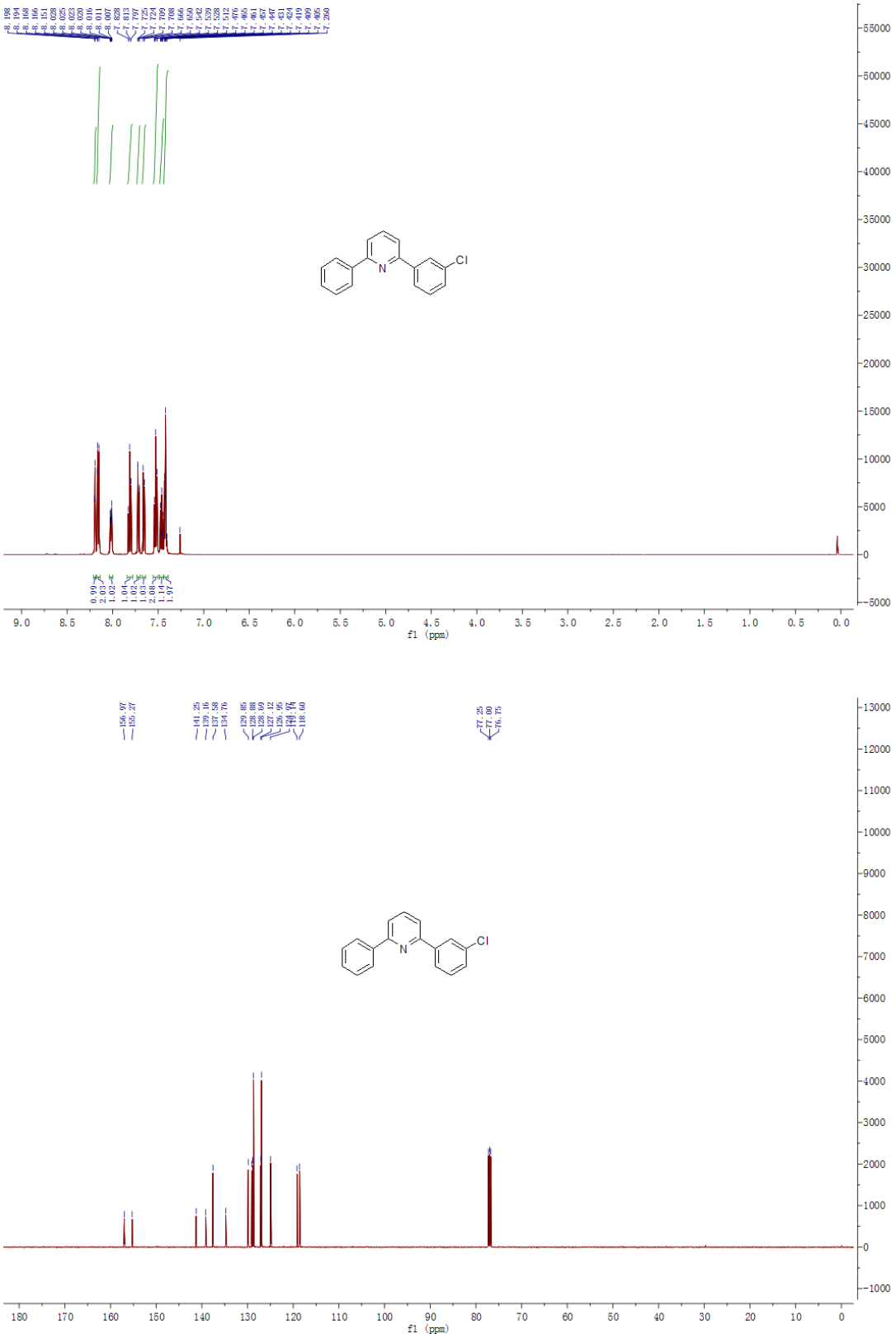


Figure S11. ^{1}H NMR of **3ak** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ak** (125 MHz, $CDCl_3$).

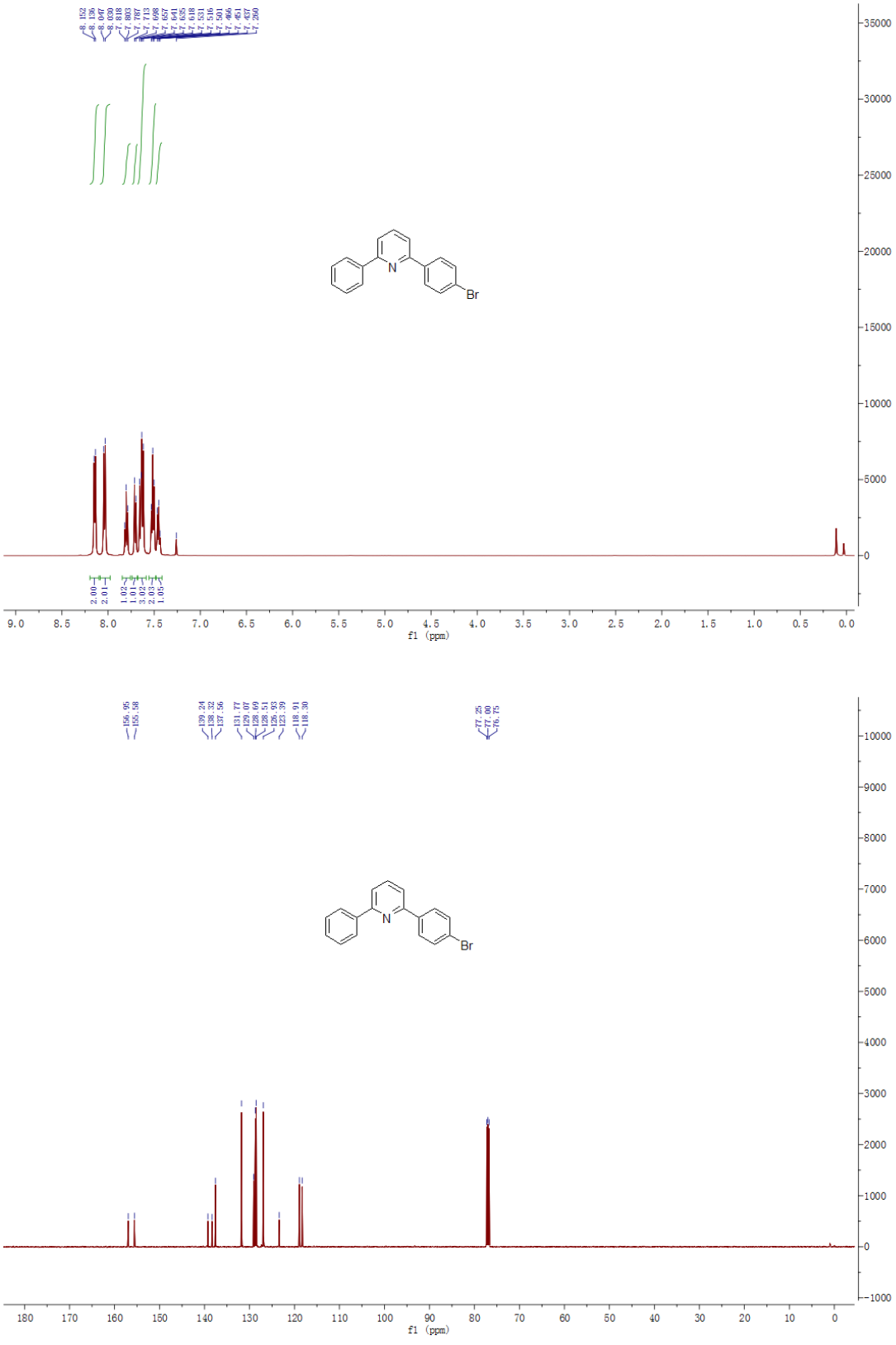


Figure S12. ^{1}H NMR of **3al** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3al** (125 MHz, $CDCl_3$).

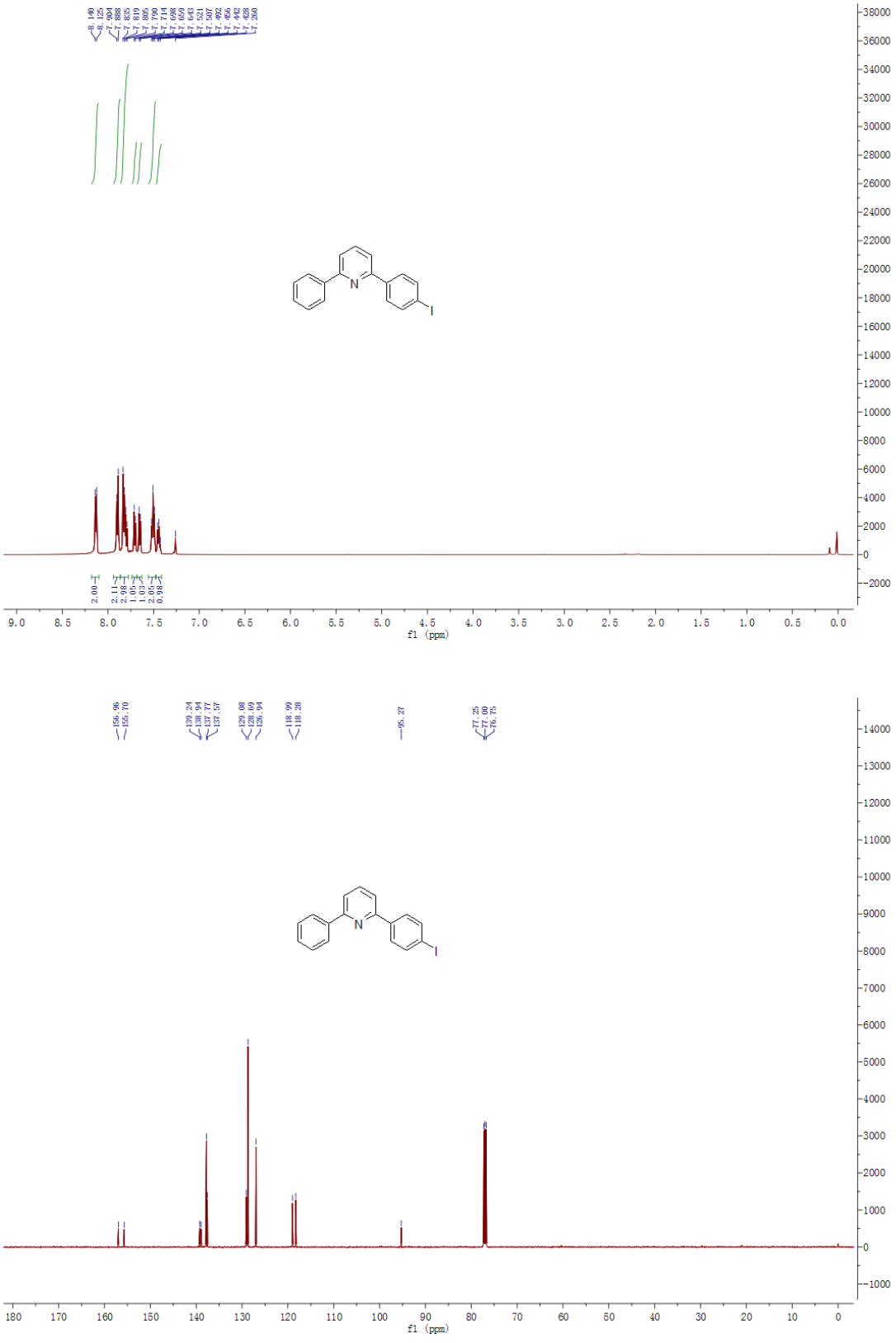


Figure S13. ^{1}H NMR of **3am** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3am** (125 MHz, $CDCl_3$).

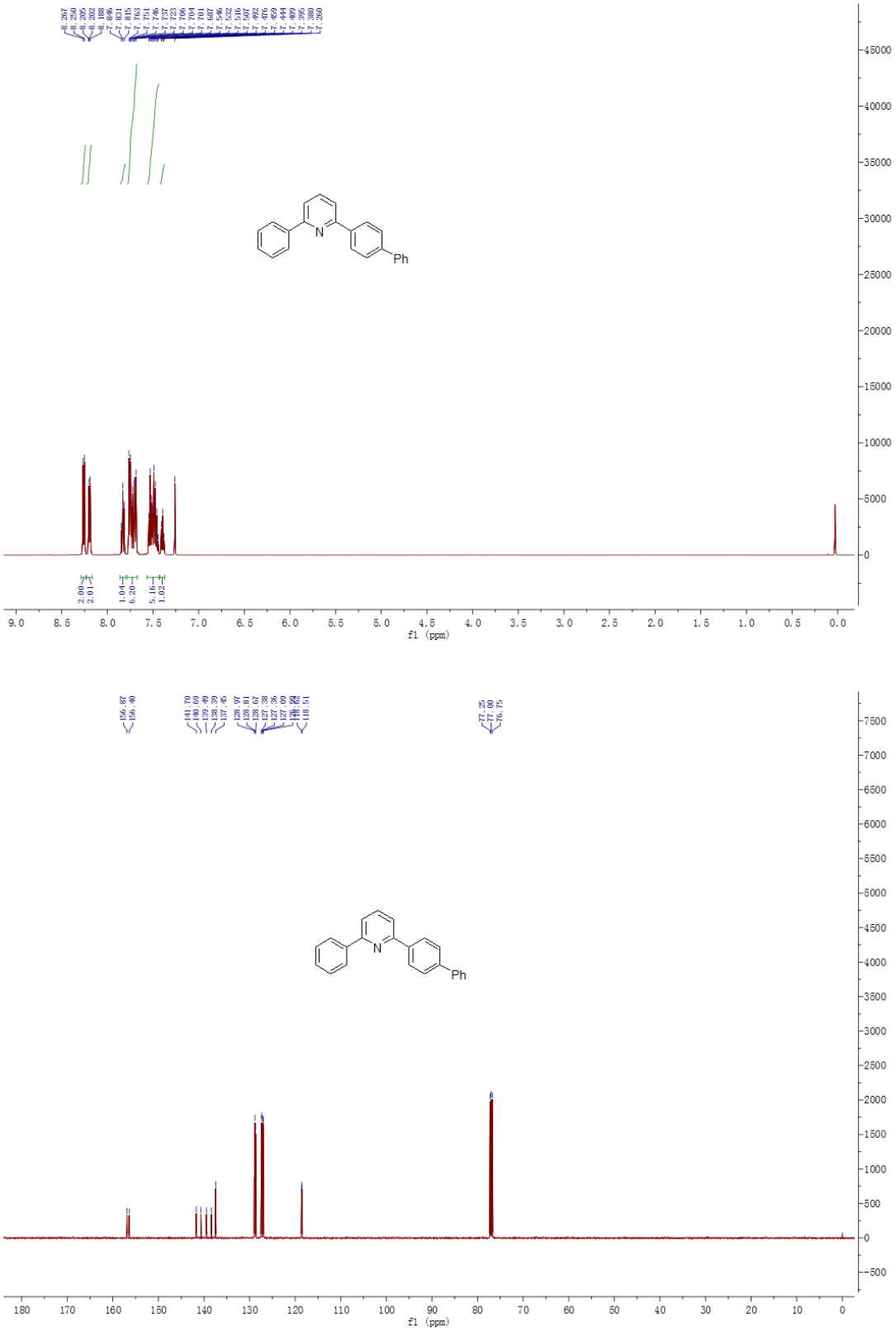


Figure S14. ^{1}H NMR of **3an** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3an** (125 MHz, $CDCl_3$).

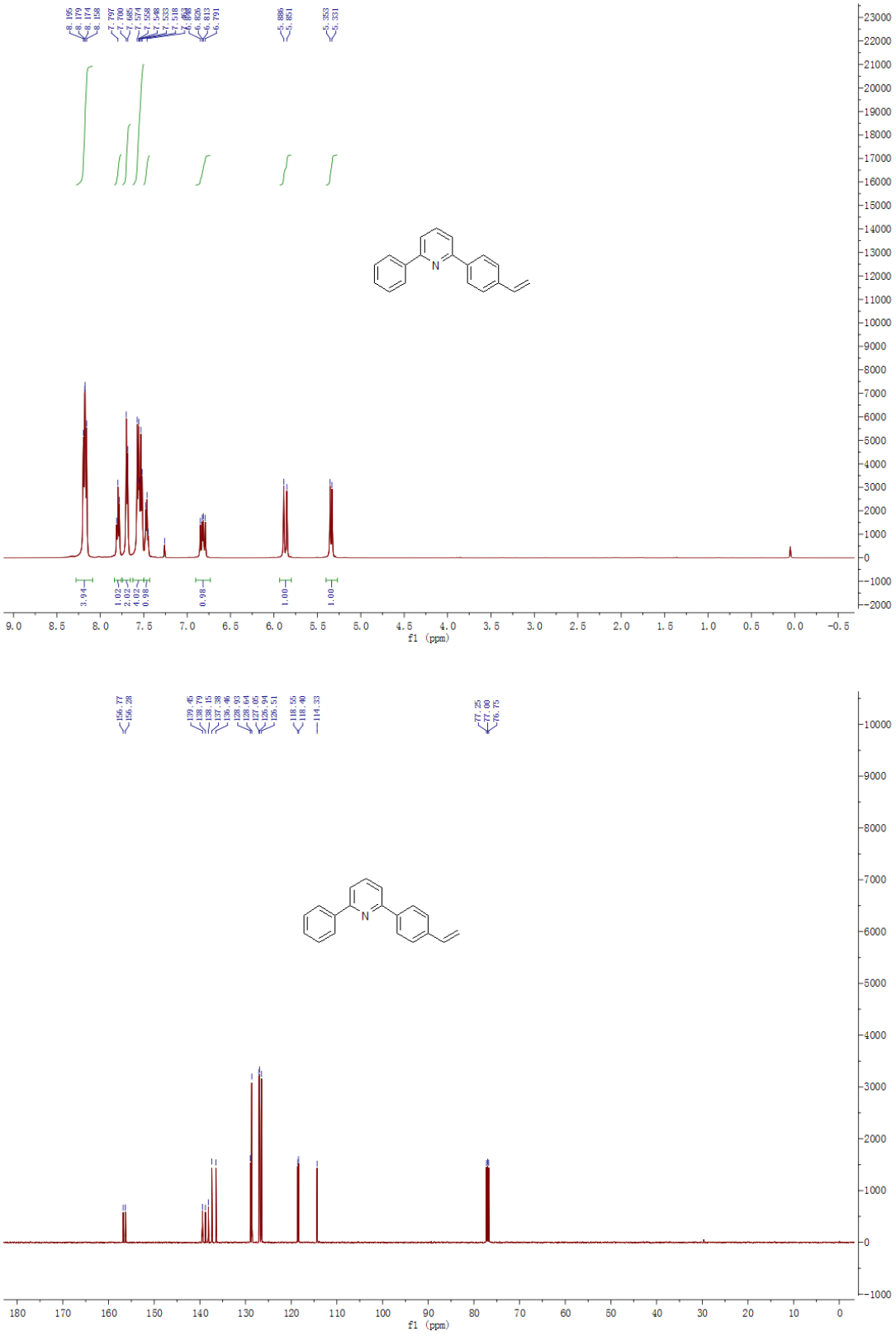


Figure S15. ^{1}H NMR of **3ao** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ao** (125 MHz, $CDCl_3$).

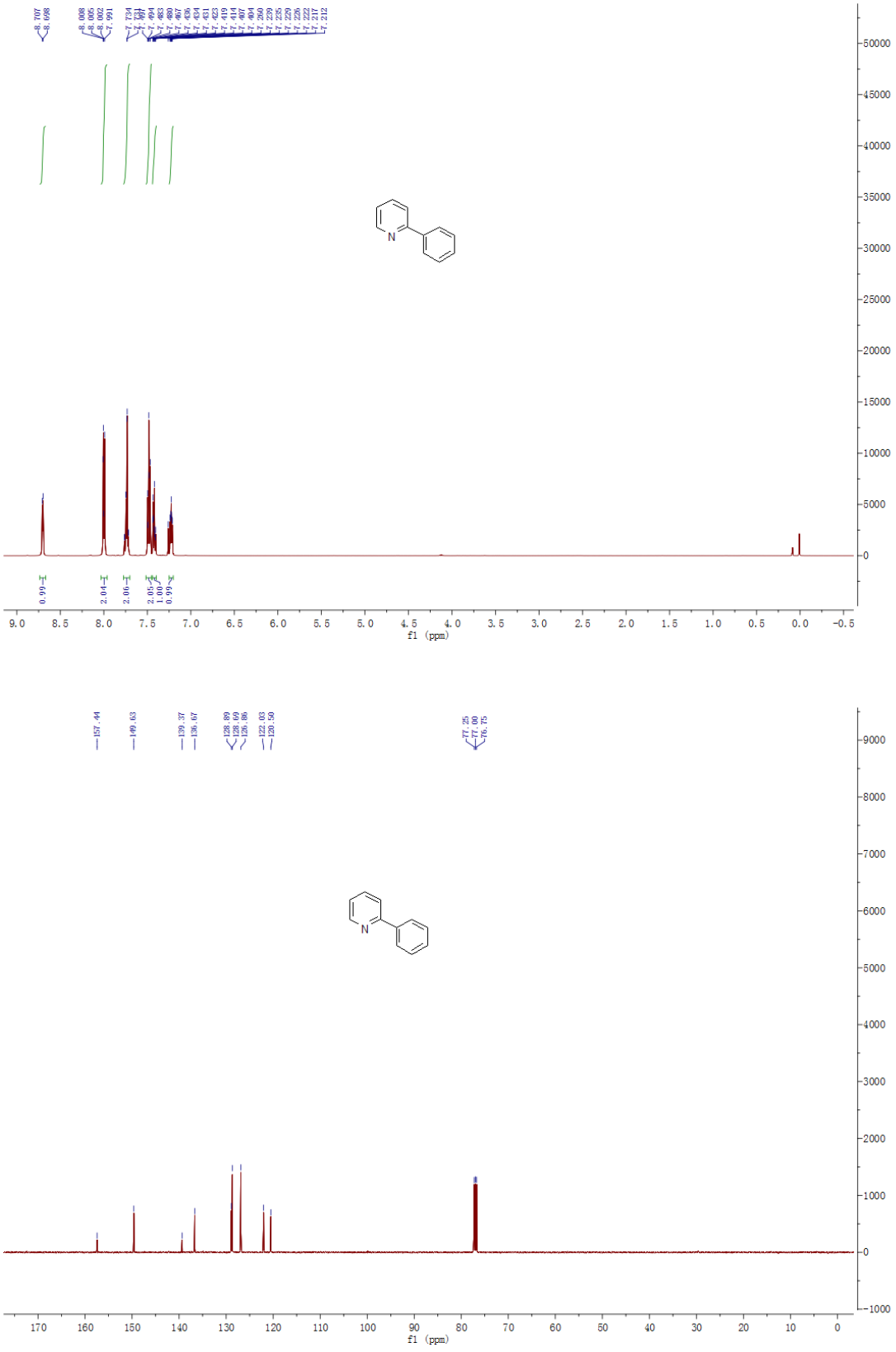


Figure 16. ^{1}H NMR of **3ea** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ea** (125 MHz, $CDCl_3$).

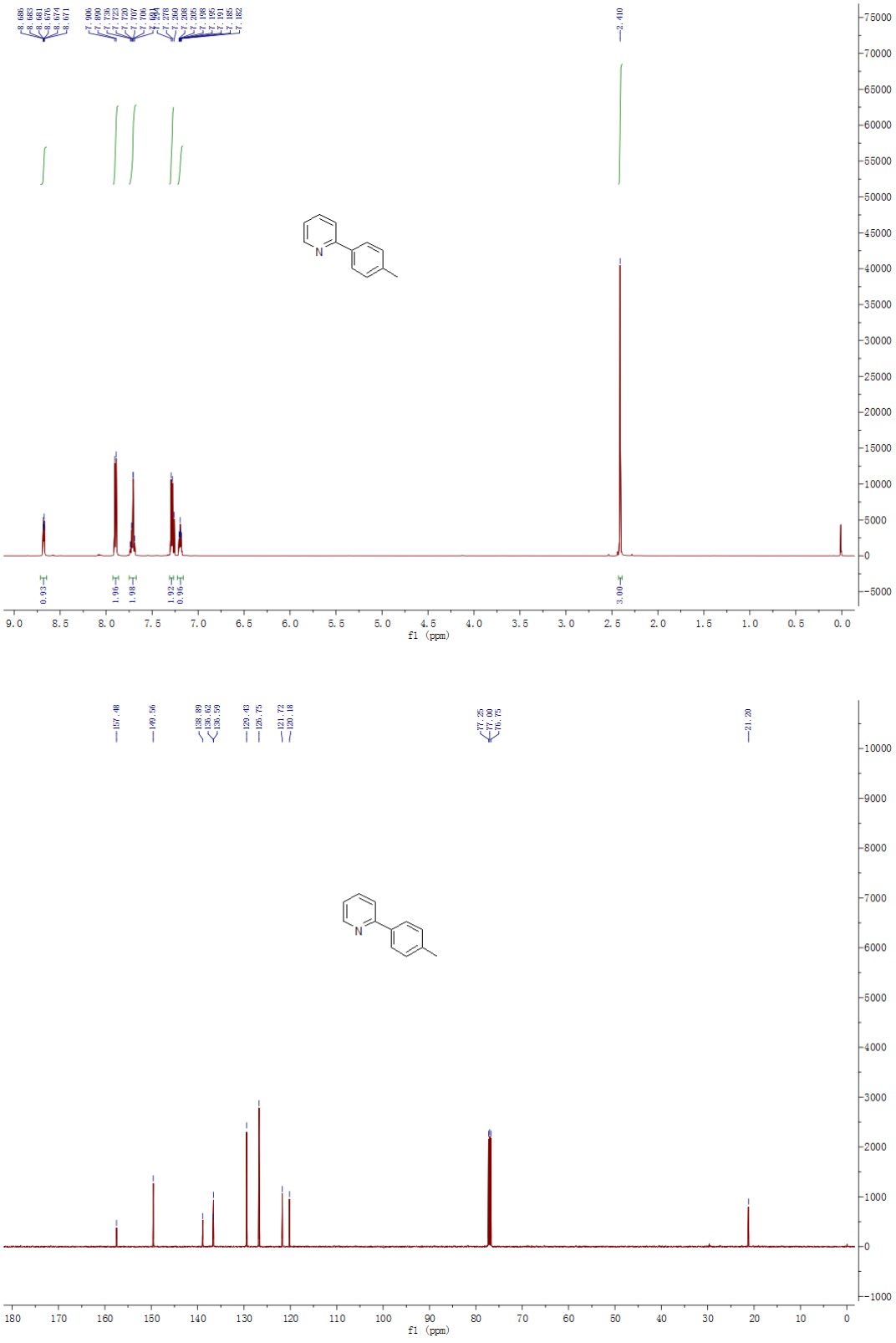


Figure S17. ^{1}H NMR of **3eb** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3eb** (125 MHz, $CDCl_3$).

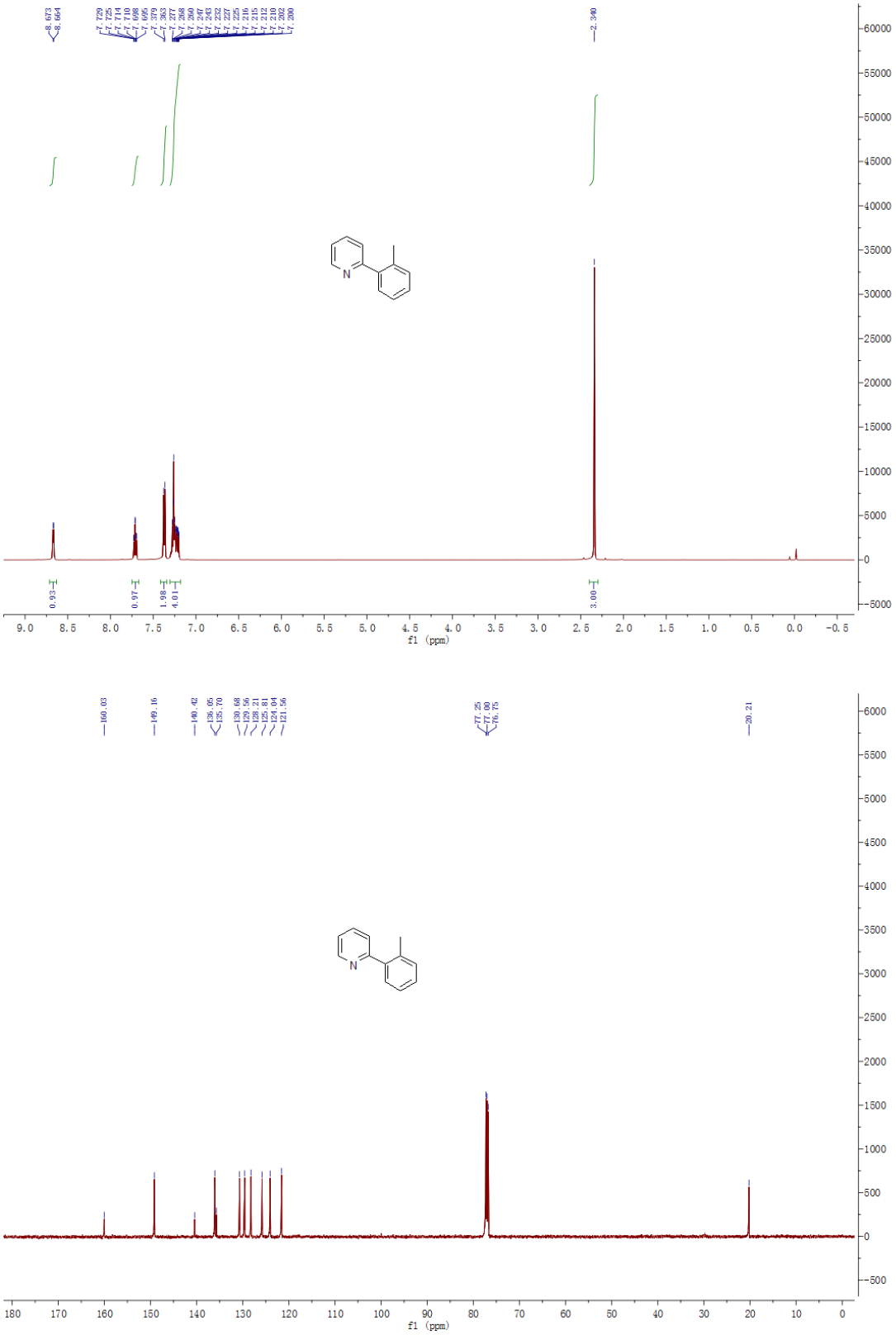


Figure 18. ^{1}H NMR of **3ec** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ec** (125 MHz, $CDCl_3$).

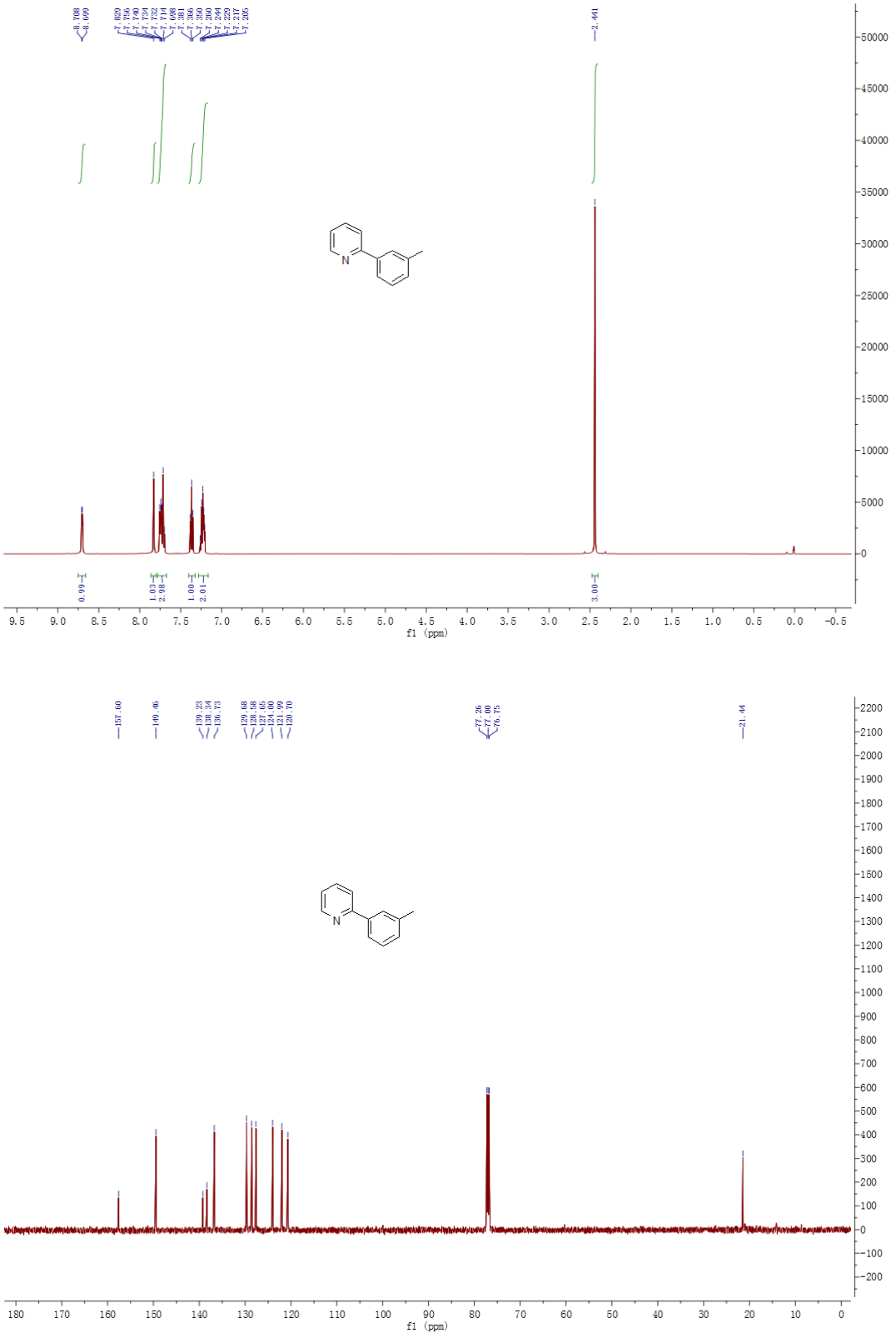


Figure S19. ^{1}H NMR of **3ed** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ed** (125 MHz, $CDCl_3$).

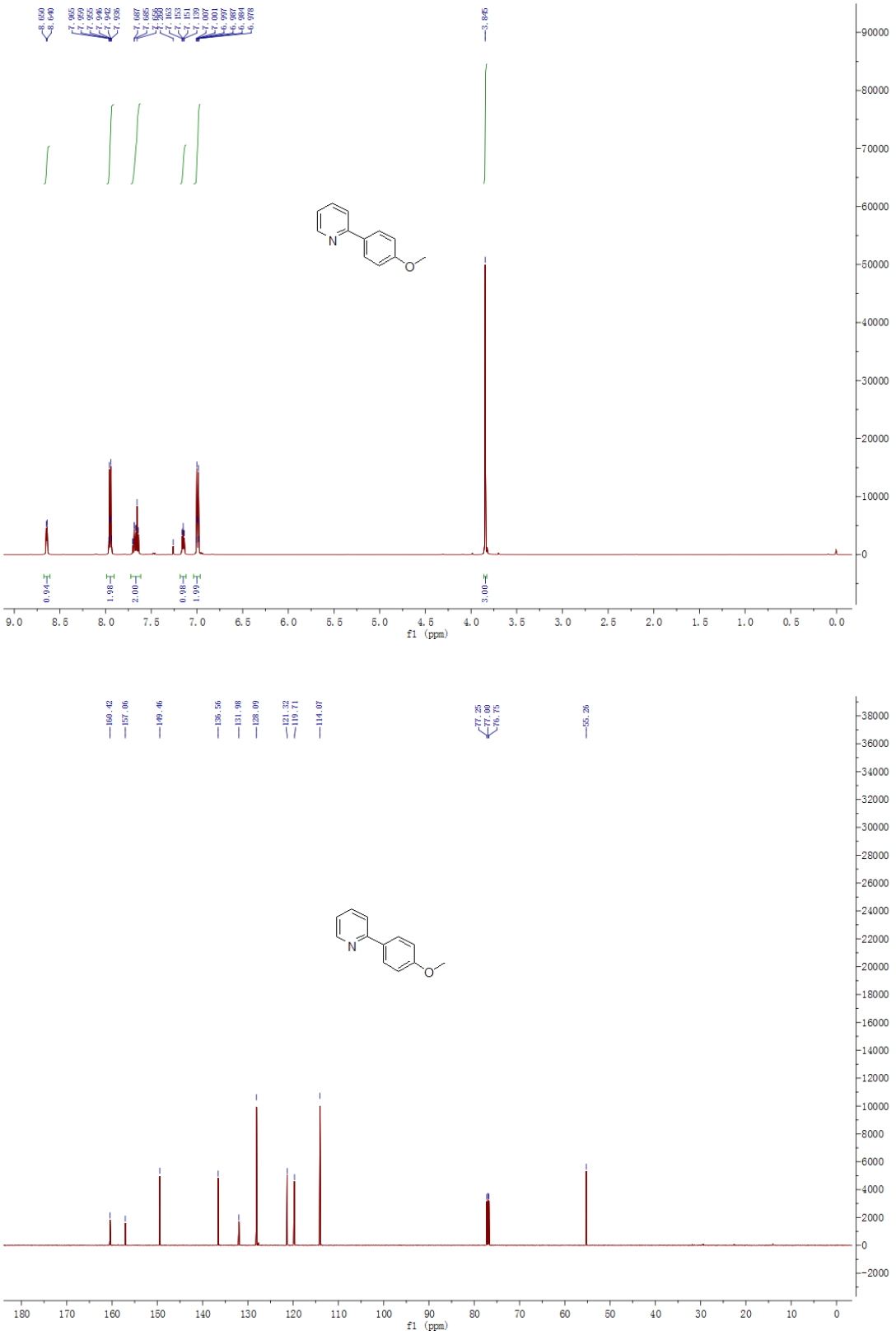


Figure S20. ^{1}H NMR of **3ee** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ee** (125 MHz, $CDCl_3$).

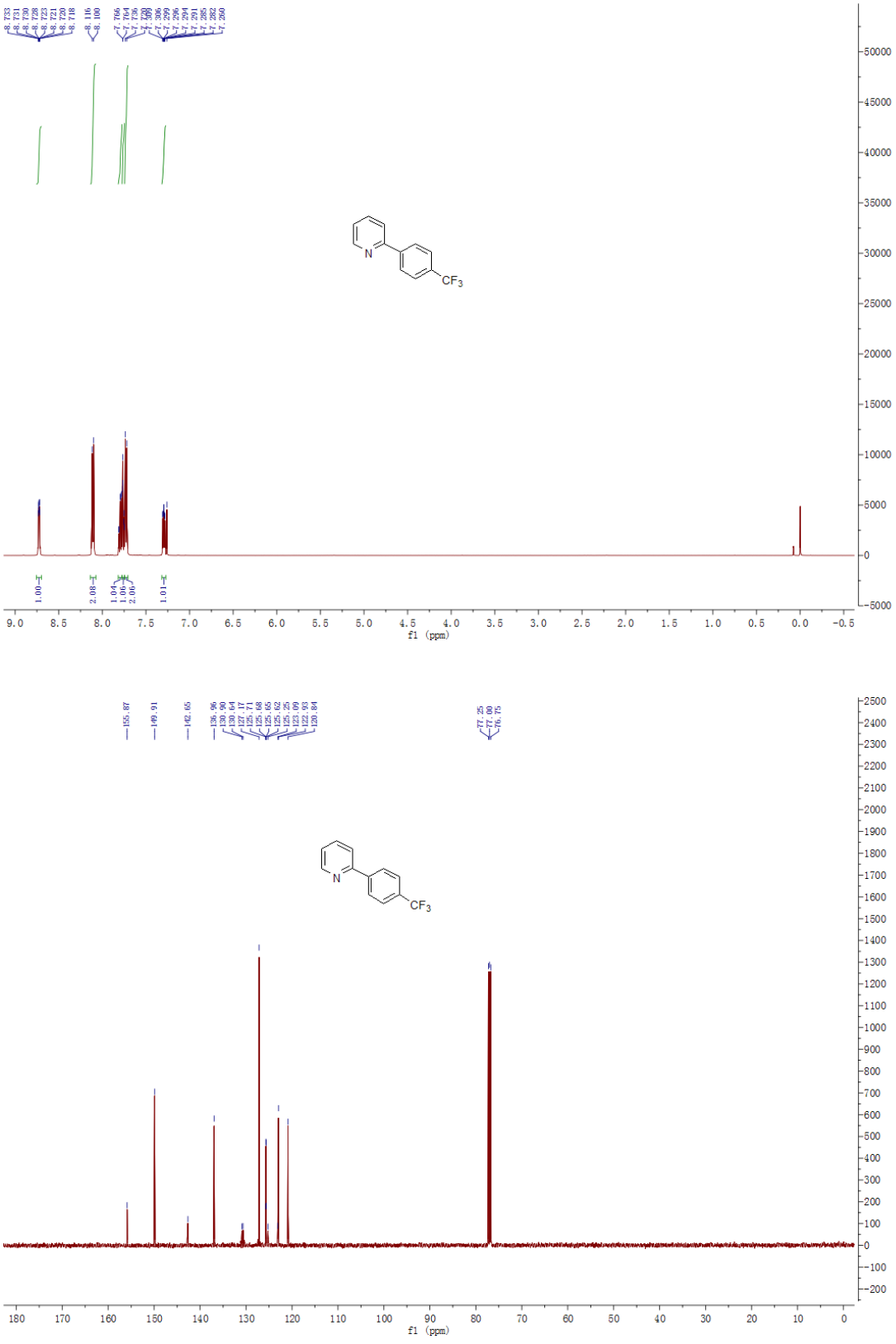


Figure S21. ^{1}H NMR of **3eg** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3eg** (125 MHz, $CDCl_3$).

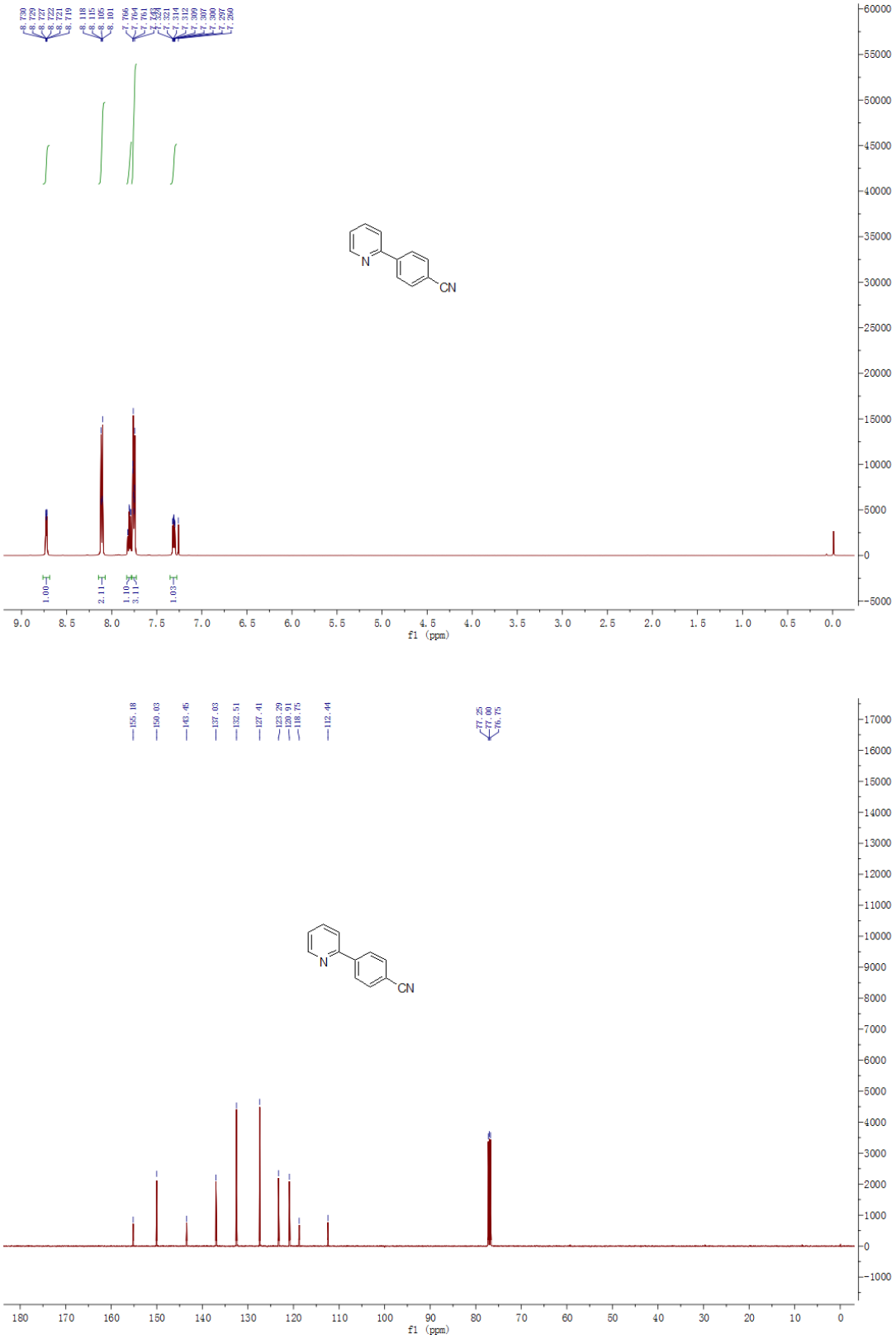


Figure S22. ^{1}H NMR of **3eh** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3eh** (125 MHz, $CDCl_3$).

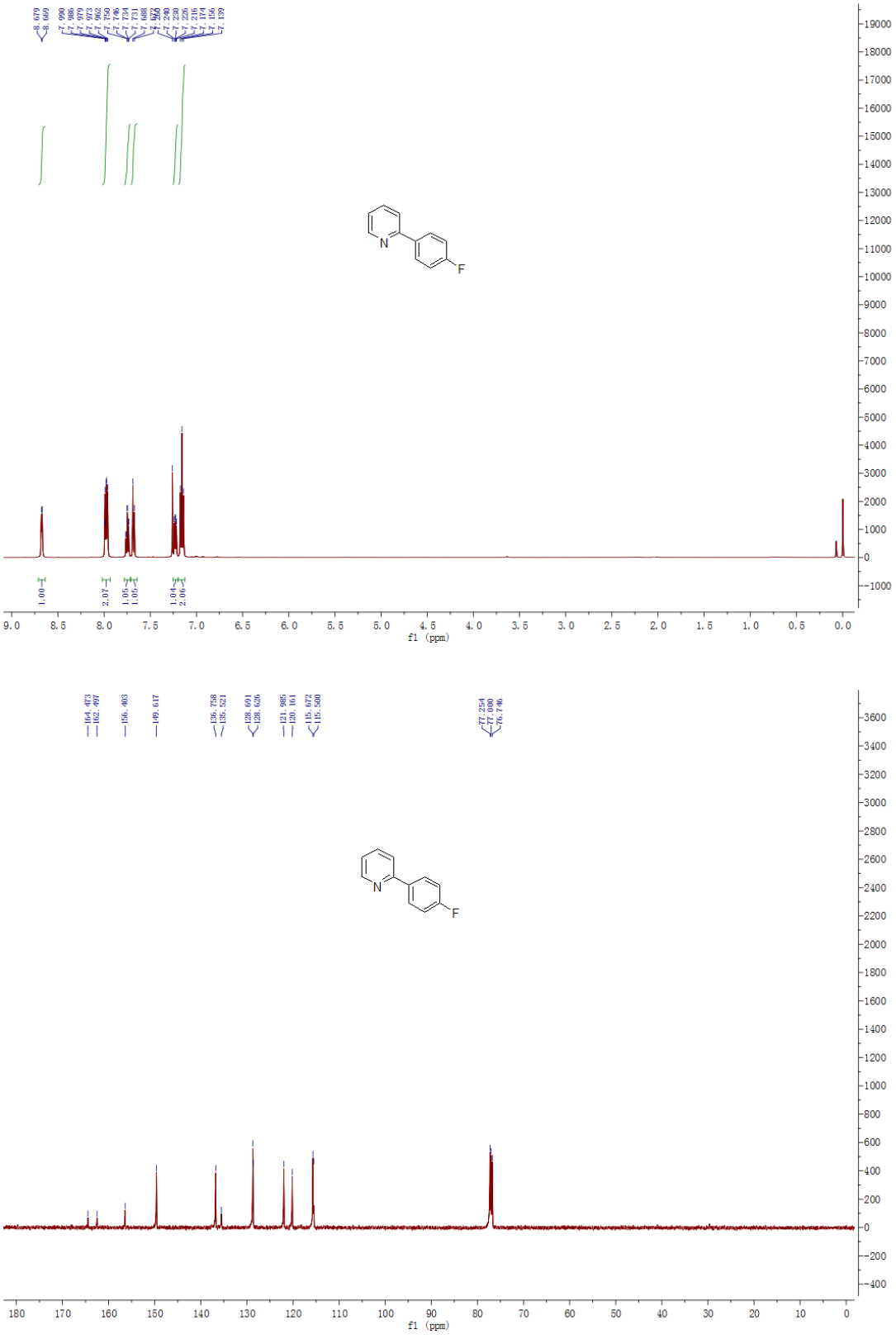


Figure S23. ^{1}H NMR of **3ei** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ei** (125 MHz, $CDCl_3$).

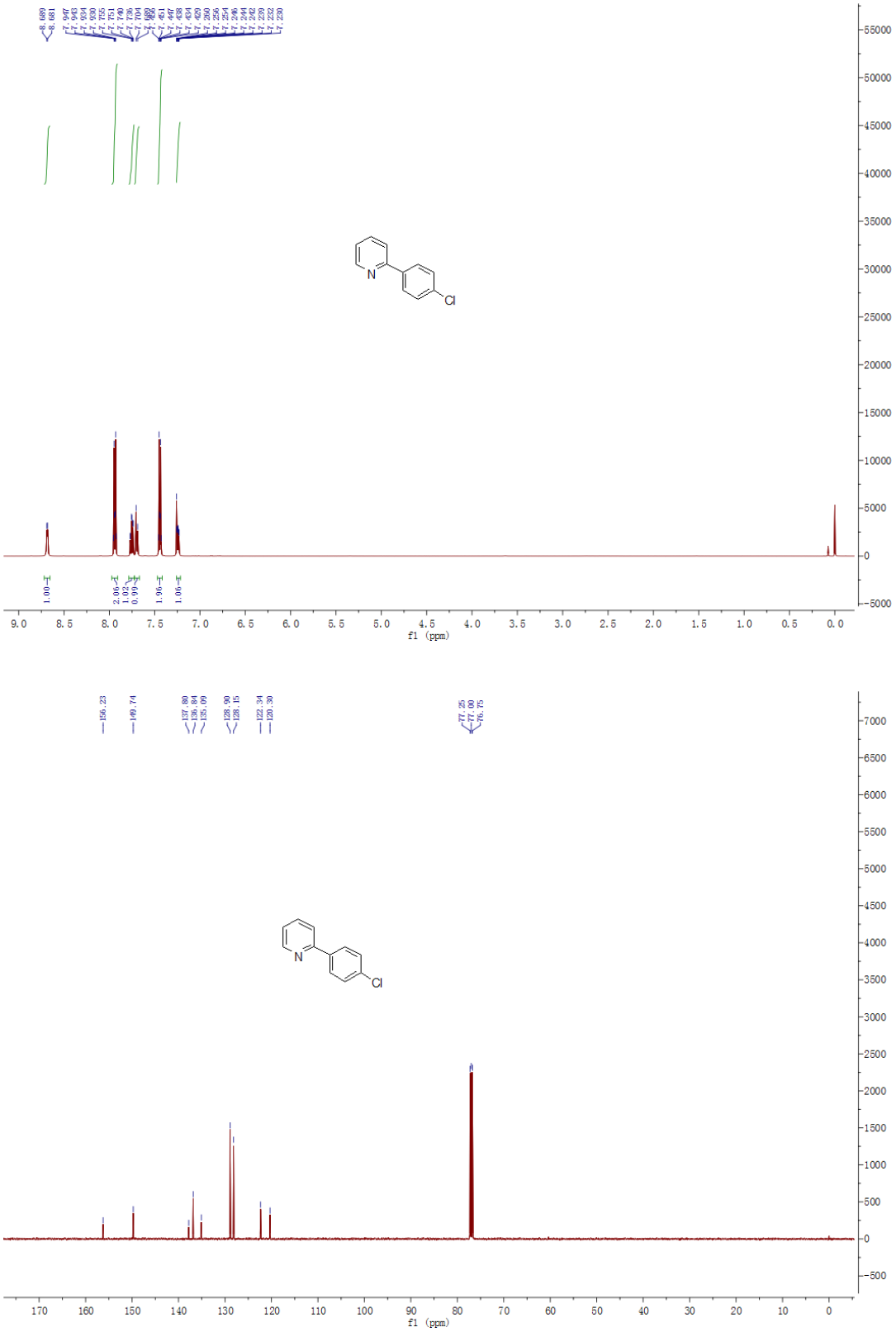


Figure S24. ^{1}H NMR of **3ej** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ej** (125 MHz, $CDCl_3$).

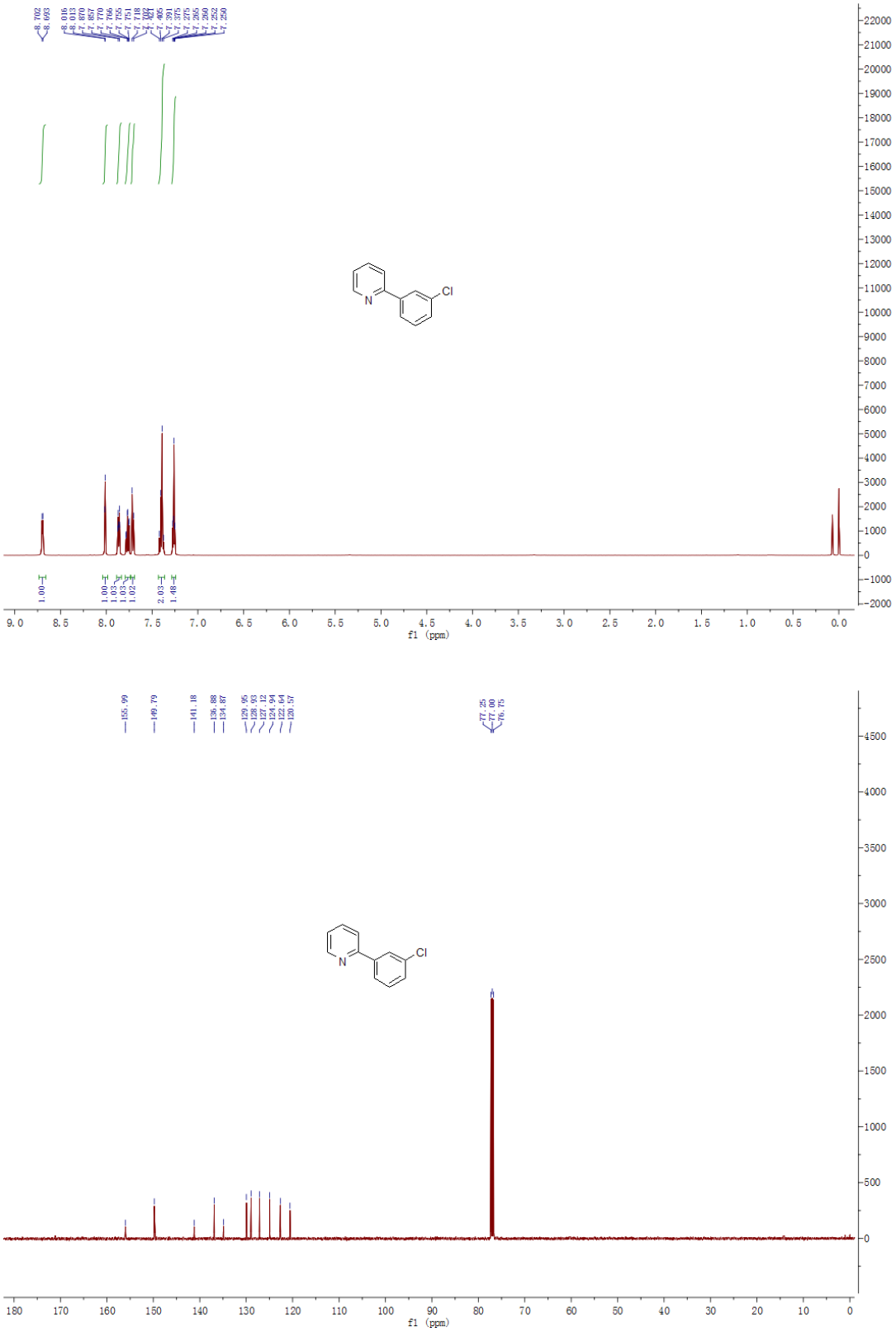


Figure S25. ^{1}H NMR of **3ek** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ek** (125 MHz, $CDCl_3$).

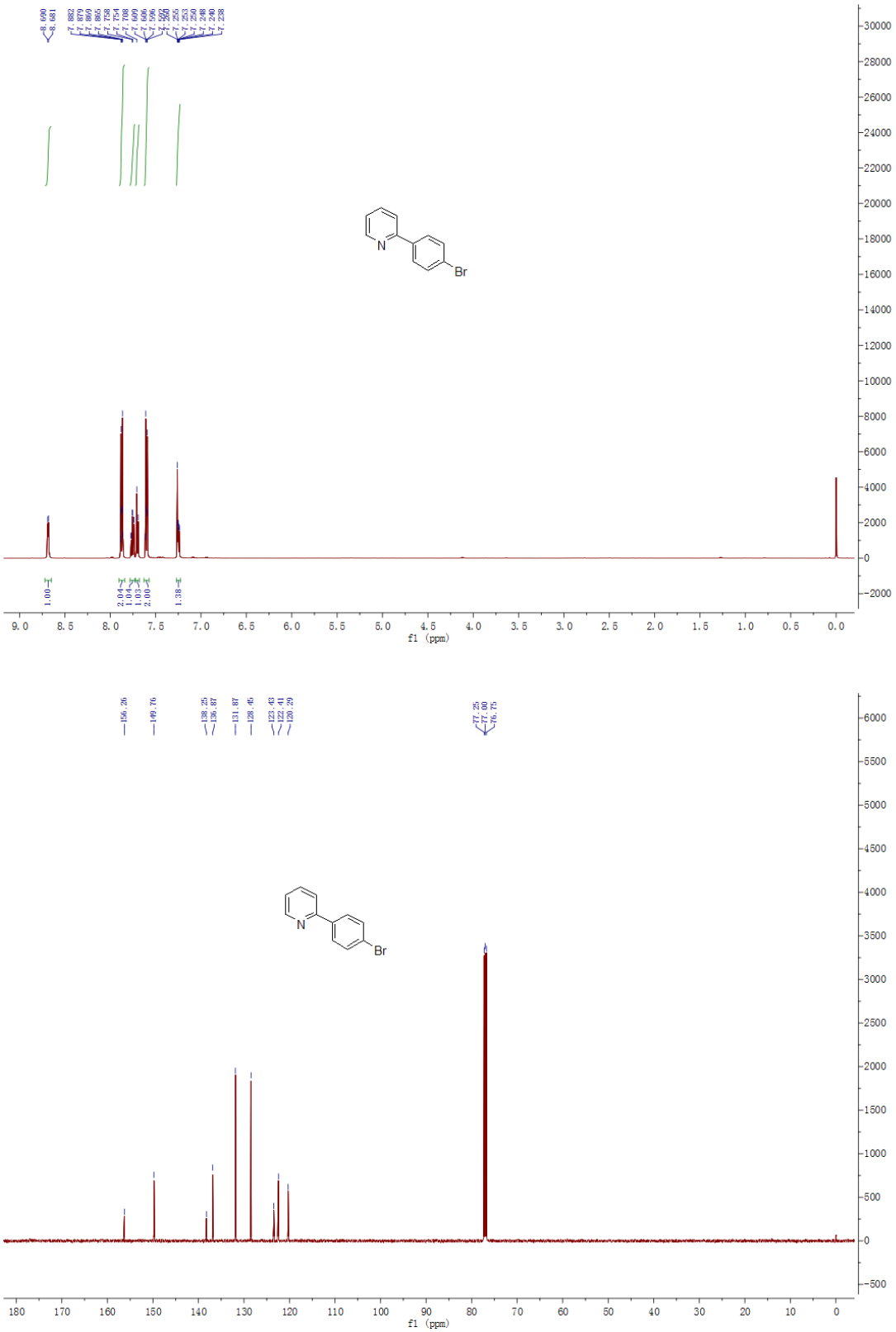


Figure S26. ^{1}H NMR of **3el** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3el** (125 MHz, $CDCl_3$).

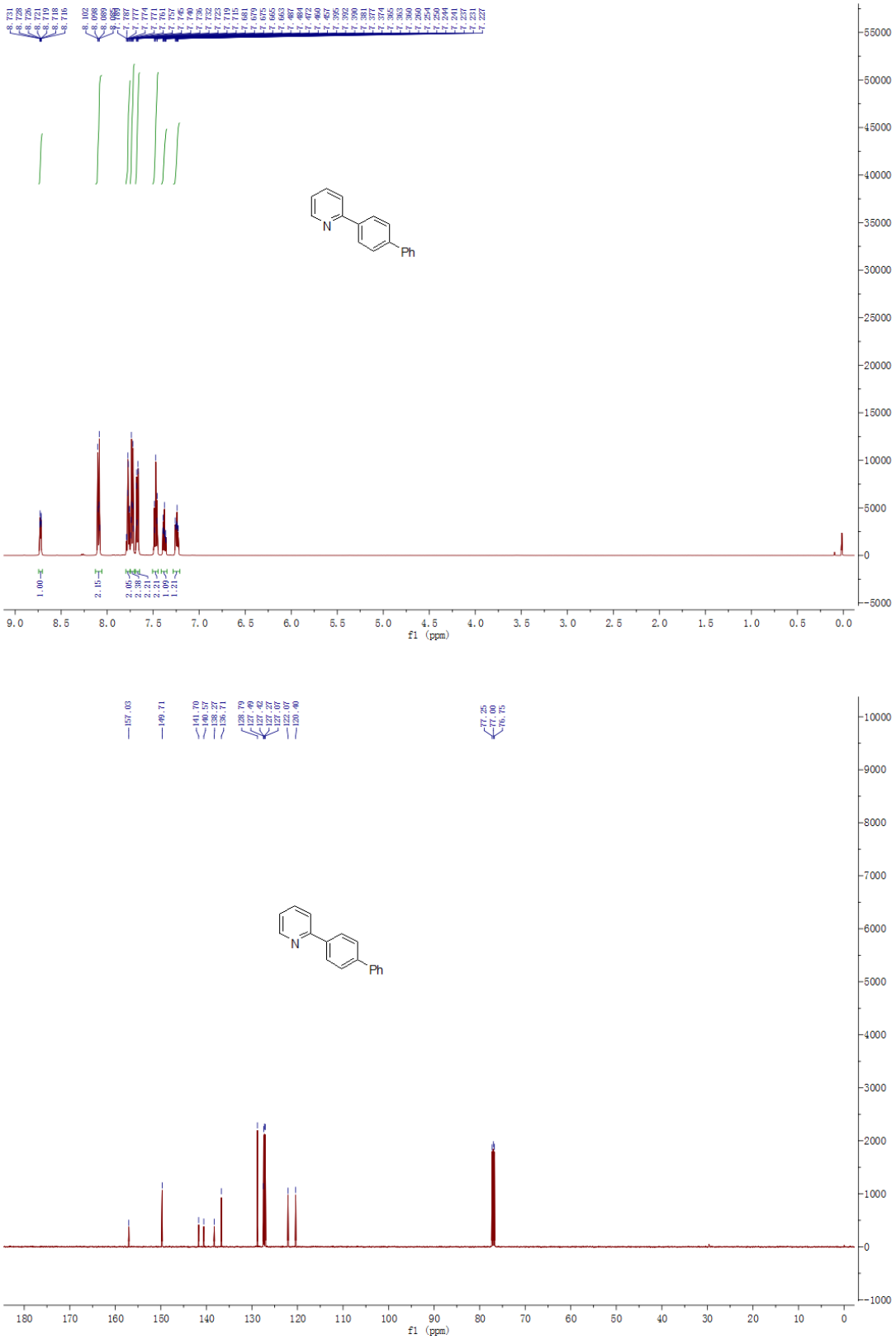


Figure S27. ^{1}H NMR of **3en** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3en** (125 MHz, $CDCl_3$).

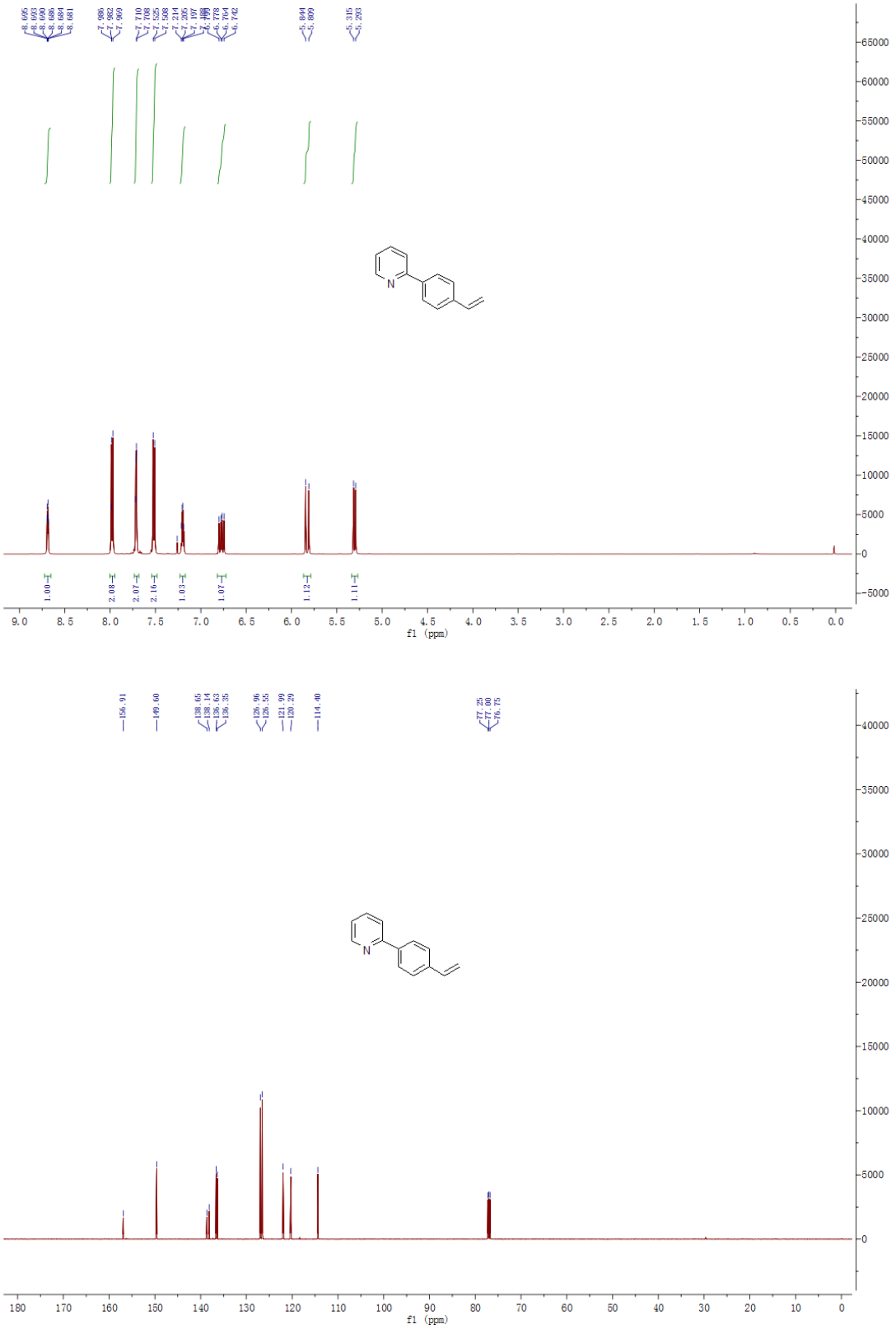


Figure S28. ^{1}H NMR of **3eo** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3eo** (125 MHz, $CDCl_3$).

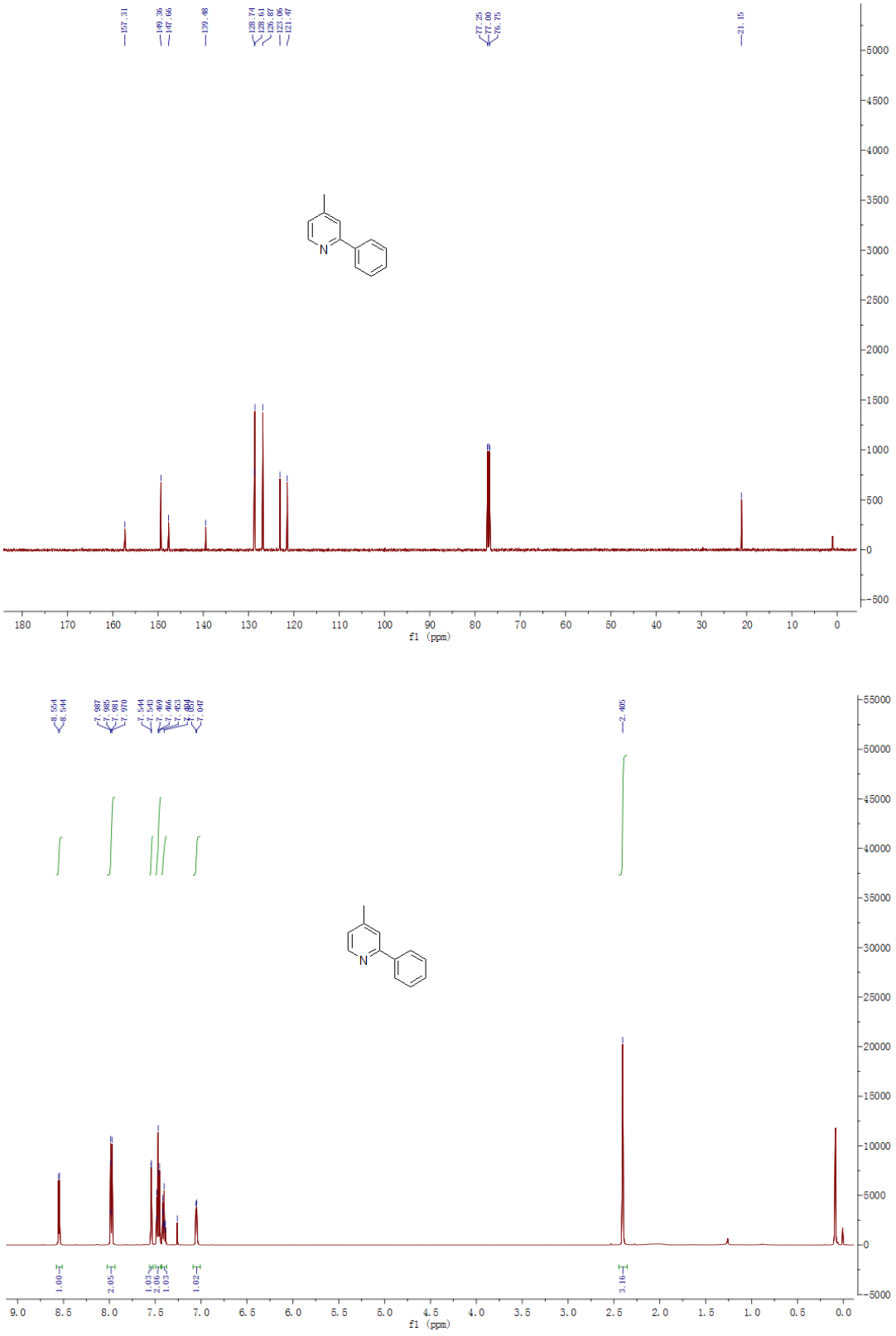


Figure S29. ^{1}H NMR of **3fa** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3fa** (125 MHz, $CDCl_3$).

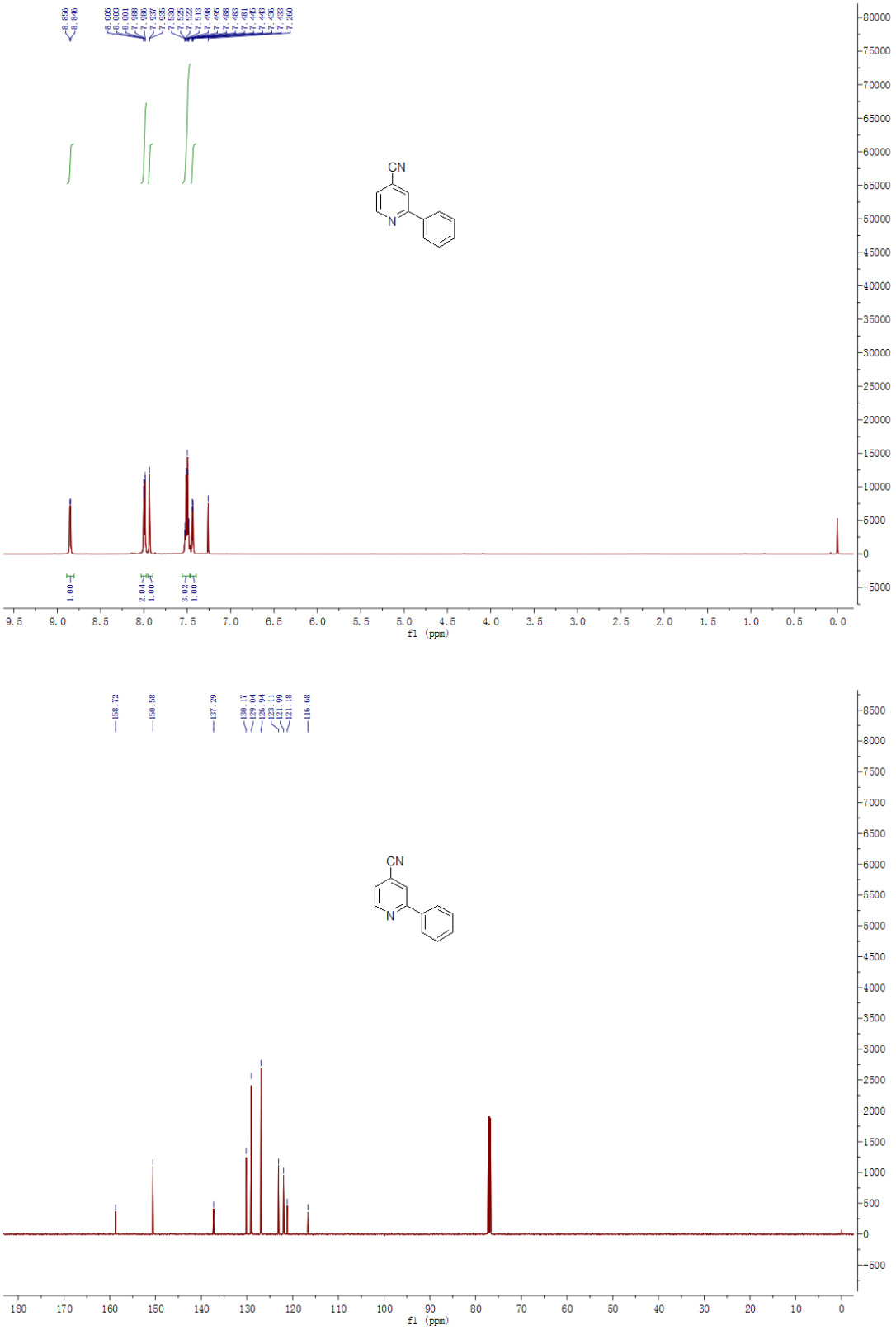


Figure S30. ^{1}H NMR of **3ga** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ga** (125 MHz, $CDCl_3$).

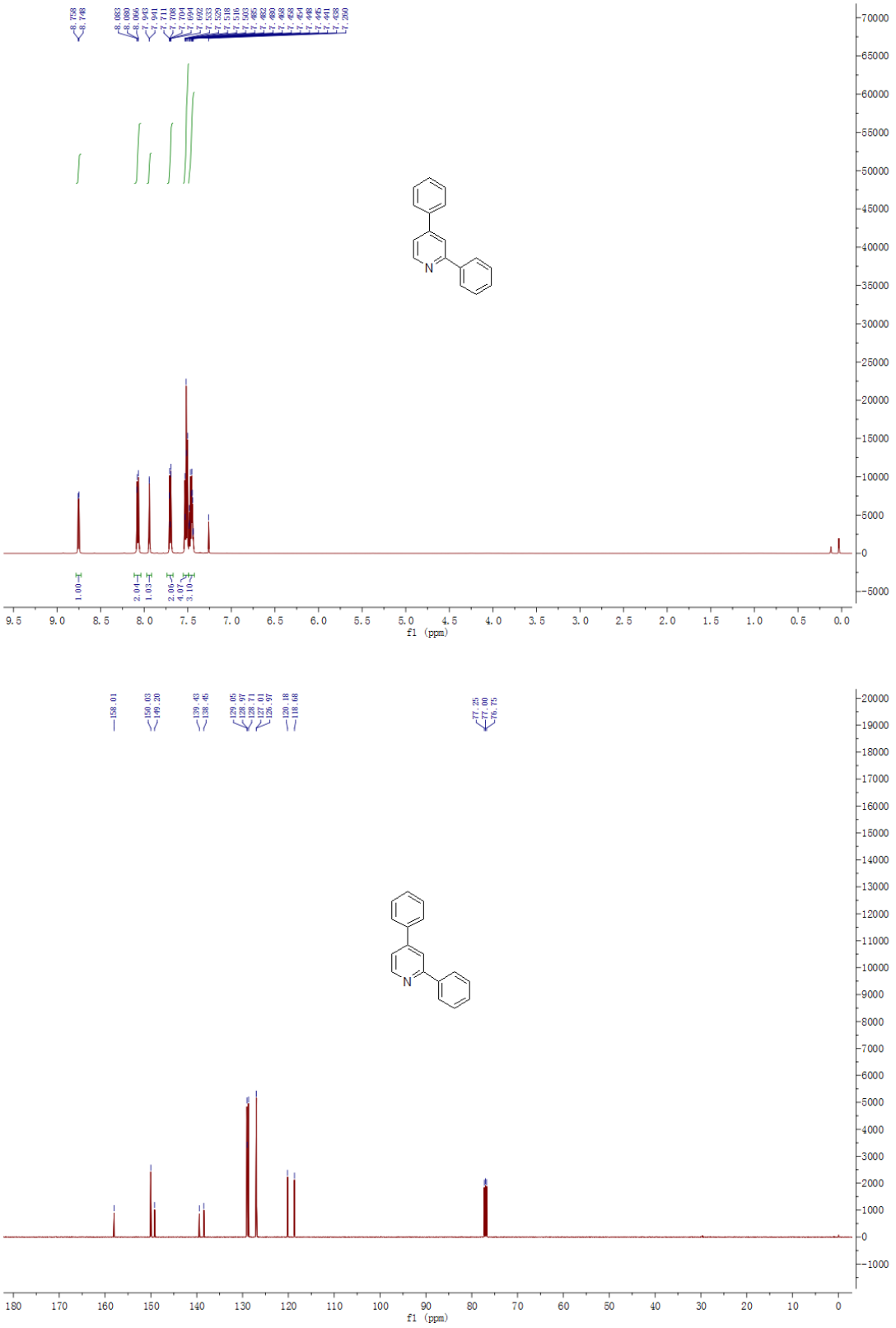


Figure S31. ^{1}H NMR of **3ha** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ha** (125 MHz, $CDCl_3$).

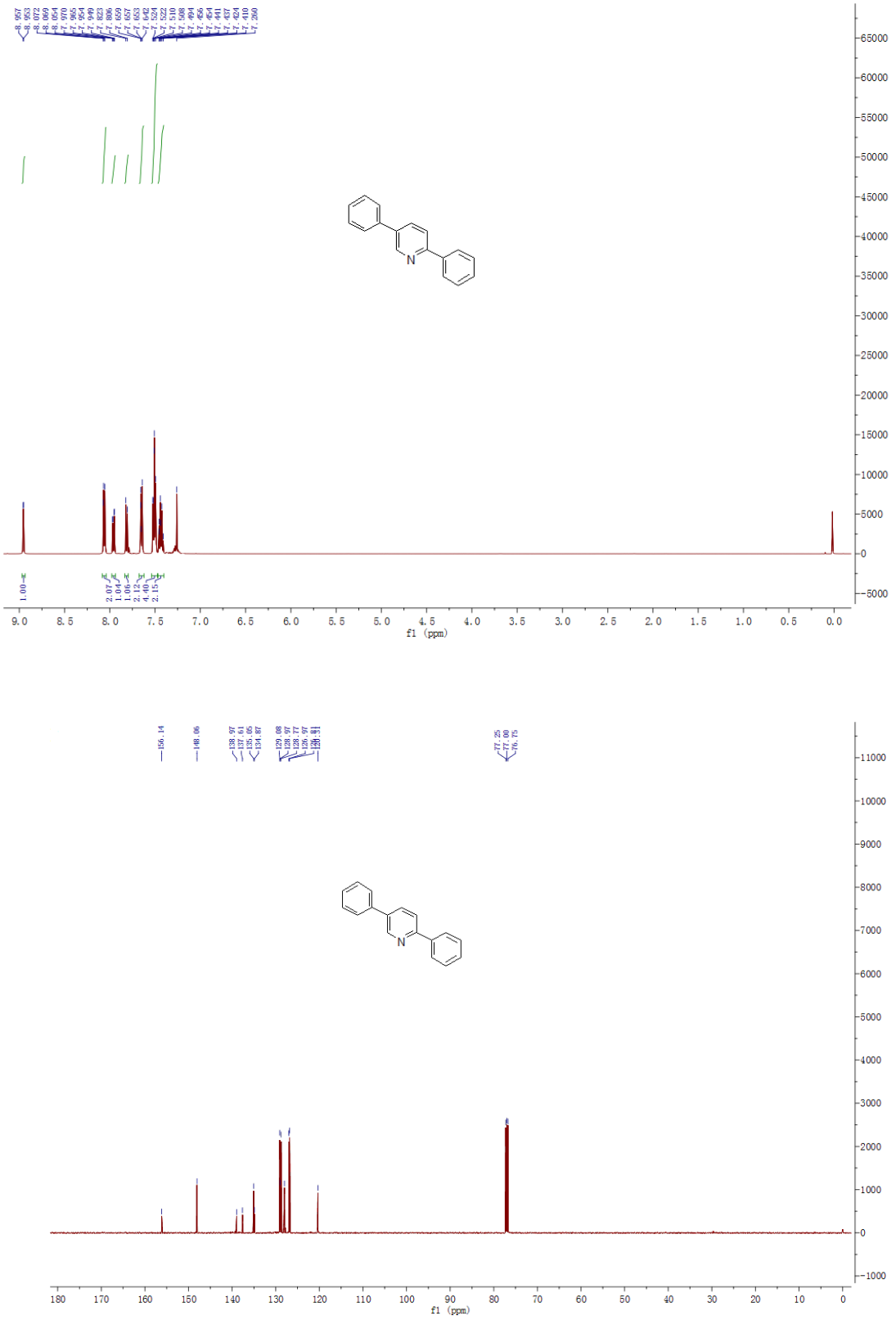


Figure S32. ^{1}H NMR of **3ia** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3ia** (125 MHz, $CDCl_3$).