Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Nickel(II)-Catalyzed C-C, N-C Cascade Coupling of Ketonitriles into Substituted Pyrroles and Pyridines

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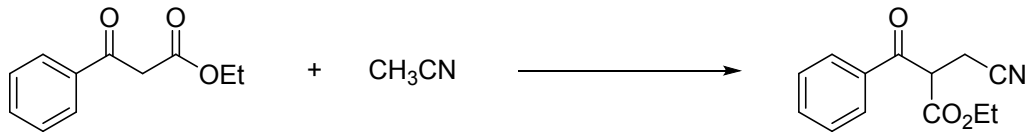
1. General Information

Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were measured on a 500 MHz spectrometer using DMSO-d_6 or $CDCl_3$ as the solvent with tetramethylsilane (TMS) as an internal standard at room temperature. Chemical shifts are given in δ relative to TMS, and the coupling constants J are given in hertz. High-resolution mass spectrometry (HRMS) was recorded on an ESI-Q-TOF mass spectrometer. 2-(Cyanomethyl)benzonitriles and methyl 2-(cyanomethyl)benzoates were synthesized according to the literature procedures. Other commercially obtained reagents were used without further purification. Column chromatography was performed using EM silica gel 60 (300−400 mesh).

2. Experimental Section

2.1 Preparation of reactant

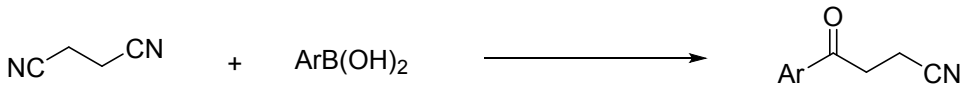
2.1.1 General Procedure for the Synthesis of 3-benzoyl-4-oxopentanenitrile diverties[a]



1

To a reaction tube equipped with a magnetic stirring bar were added $FeCl_3$ (20 mmol %) and PPh_3 (20 mmol %). Under a nitrogen atmosphere, 1,3-Dicarbonyls (10 mmol), DTBP (3.0 equiv), CH_3CN (80 mL) were added. The resulting mixture was heated at 100 ^oC for 36 h. The reaction mixture was concentrated under vacuum and the crude product was purified by column chromatography on silica gel (300-400 mesh) with PE - EtOAc (8:1) as eluent to give the desired product **1**.

2.1.2 General Procedure for the Synthesis of 4-oxo-4-phenylbutanenitrile diverties



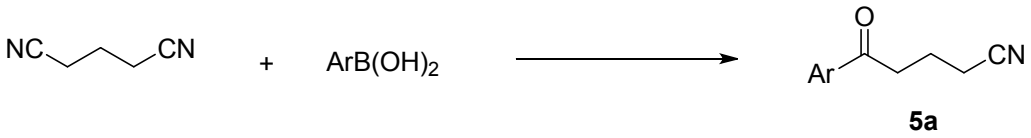
4a

A sealed reaction tube was charged with succinonitrile (40 mmol) and Aryl boric acid (20 mmol) , $Pd(acac)_2$ (5 mmol %), bpy (10 mmol %), TsOH-H_2O (2 equiv) were stirred at tolune (100 mL), H_2O (20 mL), 80 ^oC for 24 h. The reaction mixture was added to brine (20 mL) and extracted with ethyl acetate (5×10 mL). The reaction mixture was concentrated under vacuum and the crude product was purified by column chromatography

[a] C. Wang, Y. Li, M. Gong, Q. Wu, J. Zhang, J. K. Kim, M. Huang, Y. Wu. *Org. Lett*. **2016**, 18, 4151-4153.

on silica gel (300-400 mesh) with PE - EtOAc (5:1) as eluent to give the desired product **4a**.

2.1.3 General Procedure for the Synthesis of 5-oxo-5-phenylpentanenitrile diverties

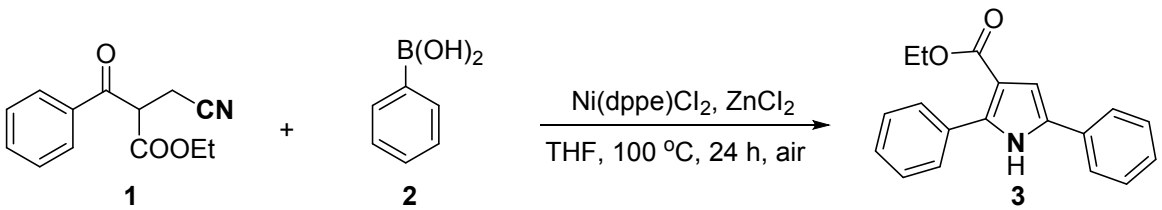


5a

A sealed reaction tube was charged with glutaronitrile (40 mmol) and Aryl boric acid (20 mmol), $Pd(acac)_2$ (5 mmol %), bpy (10 mmol %), TsOH-H_2O (2 equiv) were stirred at tolune (100 mL), H_2O (20 mL), 80 ^oC for 24 h. The reaction mixture was added to brine (20 mL) and extracted with ethyl acetate (5×10 mL). The reaction mixture was concentrated under vacuum and the crude product was purified by column chromatography on silica gel (300-400 mesh) with PE - EtOAc (10:1) as eluent to give the desired product **5a**.

2.2 Typical Procedure

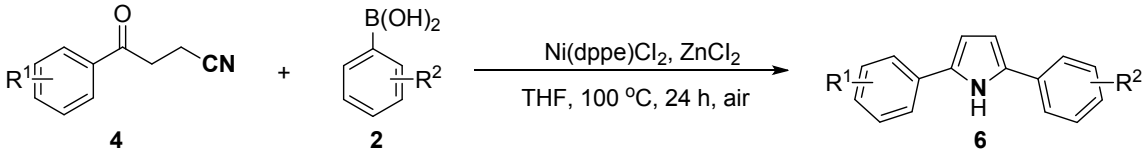
2.2.1 General Procedure for the Synthesis of 3



Ethyl 2-(cyanomethyl)-3-oxo-3-phenylpropanoate **1** (0.4mmol), arylboronic acid **2** (1.2 mmol), $Ni(dppe)Cl_2$ (10 mol %), $ZnCl_2$ (0.8 mmol), and THF (1.5 mL) were successively added in to a Schlenk reaction tube under air. The reaction mixture was stirred vigorously at 100 °C for 24 h. After the reaction equilibrium, the mixture was poured into ethyl acetate, which was washed with saturated $NaHCO_3$ (2×10 mL). After the aqueous layer was extracted with ethyl acetate, the combined organic layers were dried over

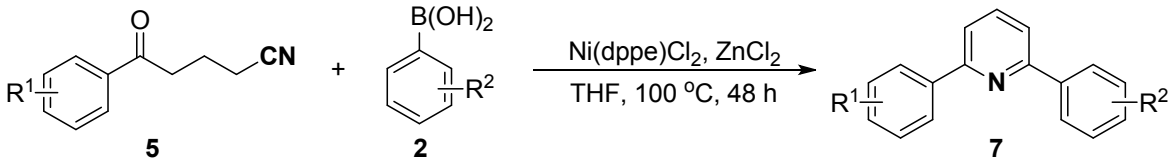
anhydrous Na_2SO_4 and evaporated under a vacuum. The residue was purified by flash column chromatography PE - EtOAc (8:1) to afford the desired products **3**.

2.2.2 General Procedure for the Synthesis of 6



4-oxo-4-phenylbutanenitrile **4** (0.4mmol), arylboronic acid **2** (0.8 mmol), Ni(dppe)Cl_2 (10 mol %), $ZnCl_2$ (0.8 mmol), and THF (1.5 mL) were successively added in to a Schlenk reaction tube under air. The reaction mixture was stirred vigorously at 100 °C for 24 h. After the reaction equilibrium, the mixture was poured into ethyl acetate, which was washed with saturated $NaHCO_3$ (2×10 mL). After the aqueous layer was extracted with ethyl acetate, the combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under a vacuum. The residue was purified by flash column chromatography PE - EtOAc (10:1) to afford the desired products **6**.

2.2.3 General Procedure for the Synthesis of 7

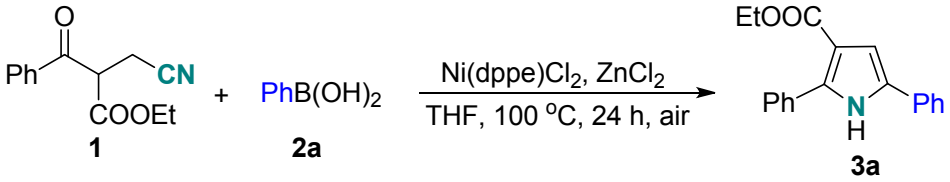


5-oxo-5-phenylpentanenitrile **5** (0.4mmol), arylboronic acid **2** (0.8 mmol), Ni(dppe)Cl_2 (10 mol %), $ZnCl_2$ (1.2 mmol), and THF (2.0 mL) were successively added in to a Schlenk reaction tube under air. The reaction mixture was stirred vigorously at 100 °C for 48 h. After the reaction equilibrium, the mixture was poured into ethyl acetate, which was washed with saturated $NaHCO_3$ (2×10 mL) After the aqueous layer was extracted with

ethyl acetate, the combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under a vacuum. The residue was purified by flash column chromatography PE - EtOAc (15:1) to afford the desired products **7**.

2.3 Optimization of the amount of arylboronic acid

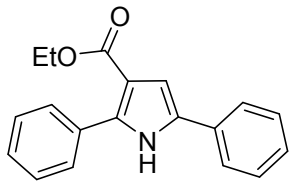
Table S1 Optimization of the amount of arylboronic acid



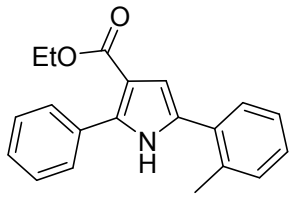
Entry	**2a** (equiv.)	Yeild (%)[b]
1	1	81
2	2	98
3	3	95

[a]Reaction conditions: **1a** (0.4 mmol), **2a,** Ni(dppe)Cl_2 (10 mol%), $ZnCl_2$ (1.0 equiv), THF (1.5 mL), air, 100 °C, 24 h.
[b]Isolated yield.

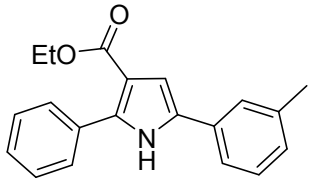
3. Analytical Data for All Products



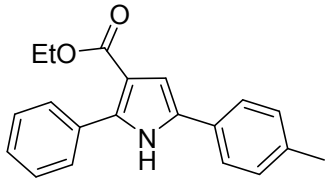
*ethyl 2,5-diphenyl-1H-pyrrole-3-carboxylate (**3a**)*: White solid (114.1 mg, 98%), mp 159.4-161.2°C (lit.[1] 167-170 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 (s, 1H), 7.66-7.64 (m, 2H), 7.53-7.52 (m, 2H), 7.45-7.39 (m, 5H), 7.29-7.26 (m, 1H), 7.03-7.02 (m, 1H), 4.24 (q, *J* = 7.0 Hz, 2H), 1.28 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 137.7, 132.0, 131.8, 131.6, 129.1, 129.0, 128.4, 128.2, 127.1, 124.0, 113.9, 109.2, 59.8, 14.3.



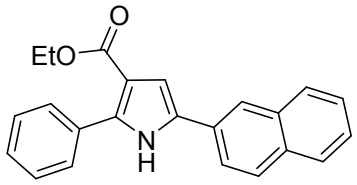
*ethyl 5-phenyl-2-(o-tolyl)-1H-pyrrole-3-carboxylate (**3b**)*: White solid (98.8 mg, 81%), mp 140.1-142.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.60-7.58 (m, 2H), 7.37-7.30 (m, 4H), 7.25-7.19 (m, 3H), 6.77-6.76 (m, 1H), 4.16 (q, *J* = 7.0 Hz, 2H), 2.46 (s, 3H), 1.22 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0, 136.9, 135.4, 131.9, 131.5, 131.0, 131.0, 128.9, 128.1, 128.0, 127.4, 126.0, 112.9, 112.0, 59.7, 21.0, 14.3. HRMS calcd for $C_{20}H_{20}NO_2$ $[M+H]^+$: 306.1489, found 306.1496.



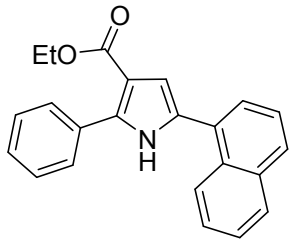
*ethyl 5-phenyl-2-(m-tolyl)-1H-pyrrole-3-carboxylate (**3c**)*: White solid (108.7 mg, 89%), mp 140.6-141.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.66-7.65 (m, 2H), 7.43-7.29 (m, 6H), 7.10-7.08 (m, 1H), 7.01-7.00 (m, 1H), 4.24 (q, *J* = 7.0 Hz, 2H), 2.40 (s, 3H), 1.28 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 138.7, 137.5, 132.0, 131.9, 131.5, 129.0, 129.0, 128.4, 128.2, 127.9, 124.8, 121.2, 113.8, 109.1, 59.8, 21.5, 14.3. HRMS calcd for $C_{20}H_{20}NO_2$ $[M+H]^+$: 306.1489, found 306.1496.



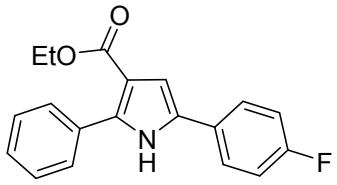
*ethyl 5-phenyl-2-(p-tolyl)-1H-pyr*role-3-c*arboxylate (**3d**)*: White solid (109.9 mg, 90%), mp 166.0-167.3 °C (lit.[1] 173-175 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.88 (s, 1H), 7.63-7.61 (m, 2H), 7.44-7.34 (m, 5H), 7.21-7.19 (m, 2H), 6.96-6.95 (m, 1H), 4.19 (q, *J* = 8.0 Hz, 2H), 2.37 (s, 3H), 1.26 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0, 137.4, 136.7, 132.0, 131.9, 129.6, 129.0, 128.8, 128.1, 128.0, 124.0, 113.5, 108.5, 59.7, 21.1, 14.2. HRMS calcd for $C_{20}H_{20}NO_2$ $[M+H]^+$: 306.1489, found 306.1496.



*ethyl 2-(naphthalen-2-yl)-5-phenyl-1H-pyrrole-3-carboxylate (**3e**)*: White solid (112.0 mg, 82%), mp 164.1-165.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.84 (s, 1H), 7.90-7.86 (m, 2H), 7.83-7.81 (m, 2H), 7.70-7.67 (m, 3H), 7.50-7.38 (m, 5H), 7.15-7.14 (m, 1H), 4.25 (q, *J* = 7.0 Hz, 2H), 1.30 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 138.1, 133.7, 132.5, 131.9, 131.8, 129.1, 128.9, 128.8, 128.5, 128.2, 127.8, 127.8, 126.7, 125.9, 123.0, 121.6, 114.0, 109.8, 59.9, 14.3. HRMS calcd for $C_{23}H_{20}NO_2$ $[M+H]^+$: 342.1489, found 342.1491.

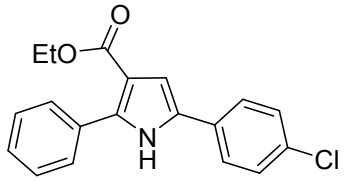


*ethyl 2-(naphthalen-1-yl)-5-phenyl-1H-pyrrole-3-carboxylate (**3f**)*: White solid (117.4 mg, 86%), mp 163.3-164.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.31-8.30 (m, 1H), 7.91-7.83 (m, 2H), 7.67-7.66 (m, 2H), 7.54-7.47 (m, 4H), 7.41-7.35 (m, 3H), 6.98 (s, 1H), 4.22 (q, *J* = 8.0 Hz, 2H), 1.28 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0, 137.4, 133.9, 131.9, 131.3, 130.3, 130.1, 129.0, 128.5, 128.2, 128.2, 128.1, 126.6, 126.4, 126.1, 125.3, 125.3, 113.2, 112.7, 59.7, 14.2. HRMS calcd for $C_{23}H_{20}NO_2$ $[M+H]^+$: 342.1489, found 342.1491.

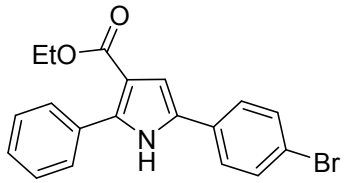


*ethyl 2-(4-fluorophenyl)-5-phenyl-1H-pyrrole-3-carboxylate (**3g**)*: White solid (79.2 mg, 64%), mp 147.8-148.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.03 (s, 1H), 7.58-7.57 (m, 2H), 7.49-7.46 (m, 2H), 7.36-7.31 (m, 3H), 7.08-7.04 (m, 2H), 6.89-6.88 (m, 1H), 4.15 (q, *J* = 7.0 Hz, 2H), 1.23 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0, 161.9 (d, *J* = 246.6 Hz), 137.9, 131.8, 131.0, 129.0, 128.2, 128.0, 125.8 (d, J_{CF} = 8.0 Hz), 124.0, 115.8

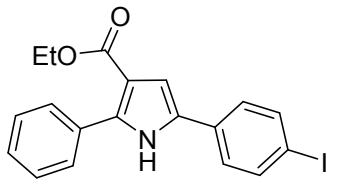
(d, J_{CF} = 21.8 Hz), 113.6, 108.9, 59.8, 14.2. HRMS calcd for $C_{19}H_{17}FNO_2$ $[M+H]^+$: 310.1238, found 310.1238.



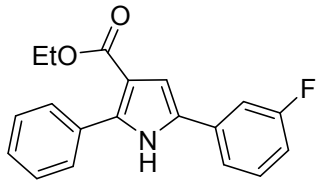
*ethyl 2-(4-chlorophenyl)-5-phenyl-1H-pyrrole-3-carboxylate (**3h**)*: White solid (82.1 mg, 63%), mp 205.0-206.3 °C (lit.[1] 203-205 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.63-7.61 (m, 2H), 7.45-7.35 (m, 7H), 6.99-6.98 (m, 1H), 4.22 (q, J = 8.0 Hz, 2H), 1.27 (t, J = 8.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.7, 138.0, 132.7, 131.8, 130.6, 130.1, 129.2, 129.0, 128.5, 128.2, 125.2, 124.0, 114.0, 109.6, 59.9, 14.3. HRMS calcd for $C_{19}H_{17}ClNO_2$ $[M+H]^+$: 326.0948 and 328.0918, found 326.0943 and 328.0913.



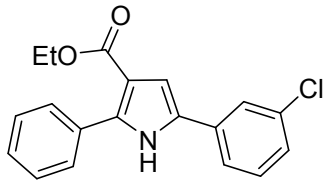
*ethyl 2-(4-bromophenyl)-5-phenyl-1H-pyrrole-3-carboxylate (**3i**)*: White solid (88.6 mg, 60%), mp 213.5-213.7 °C (lit.[1] 213-215 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (s, 1H), 7.63-7.62 (m, 2H), 7.52-7.51 (m, 2H), 7.44-7.38 (m, 5H), 7.01-7.00 (m, 1H), 4.22 (q, J = 7.0 Hz, 2H), 1.27 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.6, 138.1, 132.1, 131.8, 130.6, 130.5, 129.0, 128.5, 128.2, 125.5, 120.7, 114.1, 109.7, 59.9, 14.3. HRMS calcd for $C_{19}H_{17}BrNO_2$ $[M+H]^+$:370.0443 and 372.0422, found 370.0443 and 372.0422.



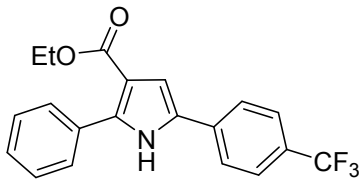
*ethyl 2-(4-iodophenyl)-5-phenyl-1H-pyrrole-3-carboxylate (**3j**)*: White solid (83.4 mg, 50%), mp 204.7-206.2 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.71-7.69 (m, 2H), 7.62-7.60 (m, 2H), 7.41-7.36 (m, 3H), 7.28-7.27 (m, 2H), 7.00-3.99 (m, 1H), 4.20 (q, J = 8.0 Hz, 2H), 1.27 (t, J = 8.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.7, 138.2, 138.0, 131.7, 131.0, 130.7, 129.0, 128.5, 128.2, 125.7, 124.0, 113.9, 109.7, 91.8, 59.9, 14.3. HRMS calcd for $C_{19}H_{16}INO_2Na$ $[M+Na]^+$: 440.0124, found 440.0131.



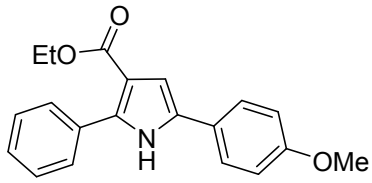
*ethyl 2-(3-fluorophenyl)-5-phenyl-1H-pyrrole-3-carboxylate (**3k**)*: White solid (70.5 mg, 57%), mp 170.1-170.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.90 (s, 1H), 7.60-7.58 (m, 2H), 7.39-7.28 (m, 5H), 7.23-7.21 (m, 1H), 7.00-6.99 (m, 1H), 6.96-6.92 (m, 1H), 4.19 (q, J = 8.0 Hz, 2H), 1.25 (t, J = 8.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 164.3 (d, J_{CF} = 245.8 Hz), 138.3, 133.7 (d, J_{CF} = 8.3 Hz), 131.7, 130.5, 130.5, 129.1, 128.5, 128.1, 119.6 (d, J_{CF} = 2.7 Hz), 113.8, 113.7 (d, J_{CF} = 21.3 Hz), 111.0 (d, J_{CF} = 22.9 Hz), 110.0, 59.9, 14.2. HRMS calcd for $C_{19}H_{17}FNO_2$ $[M+H]^+$: 310.1238, found 310.1238.



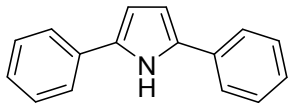
*ethyl 2-(3-chlorophenyl)-5-phenyl-1H-pyrrole-3-carboxylate (**3l**)*: White solid (52.0 mg, 40%), mp 118.3-119.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.25 (s, 1H), 7.67-7.66 (m, 2H), 7.62-7.60 (m, 1H), 7.45-7.37 (m, 4H), 7.32-7.29 (m, 1H), 7.23-7.20 (m, 1H), 7.09-7.08 (m, 1H), 4.25 (q, J = 7.0 Hz, 2H), 1.29 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.7, 137.5, 131.8, 130.8, 130.2, 129.9, 129.5, 129.0, 128.9, 128.5, 128.2, 127.4, 113.1, 112.8, 59.8, 14.3. HRMS calcd for $C_{19}H_{17}ClNO_2$ $[M+H]^+$: 326.0948 and 328.0918, found 326.0943 and 328.0913.



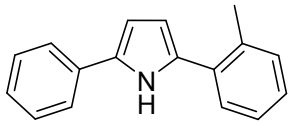
*ethyl 5-phenyl-2-(4-(trifluoromethyl)phenyl)-1H-pyrrole-3-carboxylate (**3m**)*: Yellow Oil (44.5 mg, 31%), ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.21 (s, 1H), 7.60-7.55 (m, 6H), 7.35-7.32 (m, 3H), 7.05-7.04 (m, 1H), 4.15 (q, J = 7.0 Hz, 2H), 1.23 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.9, 138.9, 134.8, 131.5, 130.3, 129.1, 128.6, 128.1, 125.9 (q, J_{CF} = 3.7Hz), 125.3, 124.0, 123.1, 114.0, 110.7, 60.0, 14.2. HRMS calcd for $C_{20}H_{16}F_3NO_2Na$ $[M+Na]^+$: 382.1031, found 382.1029.



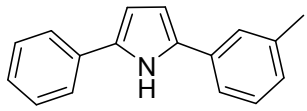
*ethyl 2-(4-methoxyphenyl)-5-phenyl-1H-pyrrole-3-carboxylate (**3n**)*: White solid (109.3 mg, 85%), mp 155.0-156.0 °C (lit.[1] 158-160 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.64-7.63 (m, 2H), 7.46-7.40 (m, 4H), 7.38-7.35 (m, 1H), 6.95-6.6.93 (m, 2H), 6.90-6.89 (m, 1H), 4.23 (q, *J* = 7.0 Hz, 2H), 3.83 (s, 3H), 1.27 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.9, 158.9, 137.2, 132.1, 131.8, 129.0, 128.3, 128.2, 125.5, 124.5, 114.5, 113.7, 108.1, 59.7, 55.4, 14.3. HRMS calcd for $C_{20}H_{20}NO_3$ $[M+H]^+$: 322.1438, found 322.1442.



*2,5-diphenyl-1H-pyrrole (**6a**)*: White solid (78.8 mg, 90%), mp 139.7-140.2 °C (lit.[2] 143 °C). ^{1}H NMR (500 MHz, DMSO) δ 11.25 (s, 1H), 7.77-7.76 (m, 4H), 7.39-7.36 (m, 4H), 7.20-7.17 (m, 2H), 6.61-6.60 (m, 2H); ^{13}C NMR (125 MHz, DMSO) δ 133.0, 132.5, 128.5, 125.7, 123.9, 107.6.

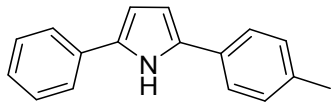


*2-phenyl-5-(o-tolyl)-1H-pyrrole (**6b**)*: White solid (84.8 mg, 91%; 81.2 mg, 87%), mp 126.5-127.7 °C (lit.[3] 125-127 °C).^{1}H NMR (500 MHz, DMSO) δ 11.22 (s, 1H), 7.78-7.76 (m, 2H), 7.62 (s, 1H), 7.57-7.56 (m, 1H), 7.39-7.35 (m, 2H), 7.27-7.24 (m, 1H), 7.1-7.16 (m, 1H), 7.01-6.99 (m, 1H), 6.60-6.58 (m, 2H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, DMSO) δ 137.6, 133.1, 132.9, 132.6, 132.5, 128.5, 128.4, 126.4, 125.7, 124.5, 123.9, 121.2, 107.6, 107.5, 21.1.

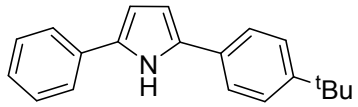


*2-phenyl-5-(m-tolyl)-1H-pyrrole (**6c**)*: White solid (80.2 mg, 86%; 80.3 mg, 81%), mp 124.4-124.5 °C (lit.[3] 132-133 °C).^{1}H NMR (500 MHz, DMSO) δ 11.22 (s, 1H), 7.78-7.77 (m, 2H), 7.62-7.56 (m, 2H), 7.39-7.36 (m, 2H), 7.28-7.17 (m, 2H), 7.01-7.00 (m, 1H),

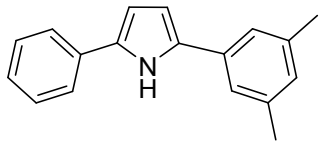
6.59-6.58 (m, 2H), 2.35 (s, 3H) ; ^{13}C NMR (125 MHz, DMSO) δ 137.6, 133.1, 132.9, 132.6, 132.5, 128.5, 128.4, 126.4, 125.7, 124.5, 123.9, 121.2, 107.6, 107.5, 21.1.



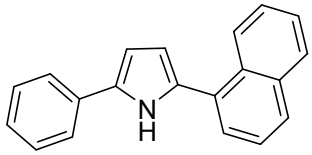
*phenyl-5-(p-tolyl)-1H-pyrrole (**6d**)*: White solid (72.8 mg, 78%; 68.1 mg, 73%), mp 144.3-144.9 °C (lit.[3] 142-143 °C).^{1}H NMR (500 MHz, DMSO) δ 11.18 (s, 1H), 7.75 (d, *J* = 7.5 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.38-7.35 (m, 2H), 7.19-7.15 (m, 3H), 6.58-6.53 (m, 2H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, DMSO) δ134.8, 133.1, 132.6, 132.5, 129.8, 129.0, 128.5, 125.5, 123.8, 123.8, 107.5, 107.0, 20.6.



*2-(4-(tert-butyl)phenyl)-5-phenyl-1H-pyrrole (**6e**)*: White solid (85.8 mg, 78%; 82.6 mg, 75%), mp 141.2-142.0 °C. ^{1}H NMR (500 MHz, DMSO) δ 11.20 (s, 1H), 7.76-7.67 (m, 4H), 7.40-7.35 (m, 4H), 7.18-7.15 (m, 1H), 6.58-6.52 (m, 2H), 1.30 (s, 9H); ^{13}C NMR (125 MHz, DMSO) δ 148.2, 133.1, 132.7, 132.6, 129.9, 128.5, 125.6, 125.2, 123.9, 123.8, 107.5, 107.1, 34.2, 31.1. HRMS calcd for $C_{20}H_{22}N$ $[M+H]^+$: 276.1747, found 276.1748.

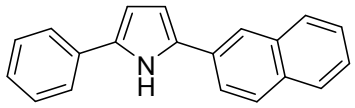


*2-(3,5-dimethylphenyl)-5-phenyl-1H-pyrrole (**6f**)*: White solid (47.5 mg, 48%; 68.3 mg, 69%), mp 120.4-123.0 °C. ^{1}H NMR (500 MHz, DMSO) δ 11.17 (s, 1H), 7.77-7.76 (m, 2H), 7.40-7.35 (m, 4H), 7.19-7.16 (m, 1H), 6.82 (s, 1H), 6.58-6.54 (m, 2H), 2.30 (s, 6H); ^{13}C NMR (125 MHz, DMSO) δ 137.4, 133.2, 132.7, 132.6, 132.4, 128.5, 127.3, 125.6, 123.9, 121.8, 107.5, 107.4, 21.0. HRMS calcd for $C_{18}H_{18}N$ $[M+H]^+$: 248.1434, found 248.1429.

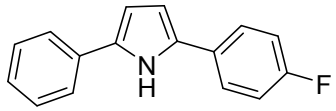


*(naphthalen-1-yl)-5-phenyl-1H-pyrrole (**6g**)*: White solid (91.5 mg, 85%; 85.1 mg, 79%), mp 160.3-161.9 °C. ^{1}H NMR (500 MHz, DMSO) δ 11.41 (s, 1H), 8.31-8.30 (m, 1H), 7.95-7.81 (m, 6H), 7.52-7.49 (m, 1H), 7.45-7.39 (m, 3H), 7.22-7.19 (m, 1H), 6.76 (s, 1H), 6.66

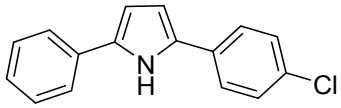
(s, 1H); ^{13}C NMR (126 MHz, DMSO) δ 133.6, 132.7, 132.5, 131.3, 131.1, 130.8, 128.6, 128.3, 127.0, 126.4, 126.3, 125.9, 125.6, 125.4, 123.8, 111.0, 106.9. HRMS calcd for $C_{20}H_{16}N$ $[M+H]^+$: 270.1277, found 270.1276.



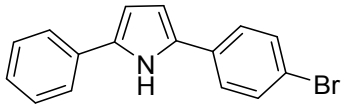
*2-(naphthalen-2-yl)-5-phenyl-1H-pyrrole (**6h**)*: White solid (99.0 mg, 92%; 86.2 mg, 80%), mp 157.9-158.2 °C (lit.[3] 162-163 °C). ^{1}H NMR (500 MHz, DMSO) δ 11.43 (s, 1H), 8.32 (s, 1H), 7.95-7.82 (m, 6H), 7.52-7.39 (m, 4H), 7.22-7.19 (m, 1H), 6.77 (s, 1H), 6.66 (s, 1H); ^{13}C NMR (126 MHz, DMSO) δ 133.5, 133.5, 133.0, 132.5, 131.5, 130.0, 128.6, 128.0, 127.6, 127.5, 126.4, 125.9, 125.1, 124.0, 123.5, 120.9, 108.6, 107.9.



*2-(4-fluorophenyl)-5-phenyl-1H-pyrrole (**6i**)*: Yellow solid (71.1 mg, 75%; 77.8 mg, 82%), mp 150.2-150.6 °C (lit.[3] 148-149 °C). ^{1}H NMR (500 MHz, DMSO) δ 11.25 (s, 1H), 7.81-7.75 (m, 4H), 7.39-7.36 (m, 2H), 7.24-7.17 (m, 3H), 6.60-6.56 (m, 2H); ^{13}C NMR (125 MHz, DMSO) δ 160.2 (d, J = 237.5 Hz), 133.0, 132.5, 132.1, 129.2, 128.6, 125.8, 125.7 (d, J = 12.5 Hz), 123.9, 115.4 (d, J_{CF} = 25.0 Hz), 107.6, 107.6.

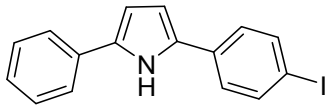


*2-(4-chlorophenyl)-5-phenyl-1H-pyrrole (**6j**)*: Yellow solid (72.8 mg, 73%; 73.8 mg, 74%), mp 155.1-156.1 °C (lit.[3] 153-154 °C). ^{1}H NMR (500 MHz, DMSO) δ 11.31 (s, 1H), 7.81-7.76 (m, 4H), 7.44-7.36 (m, 4H), 7.21-7.18 (m, 1H), 6.65-6.60 (m, 2H); ^{13}C NMR (125 MHz, DMSO) δ 133.5, 132.4, 131.7, 131.4, 129.9, 128.6, 128.5, 125.9, 125.5, 124.0, 108.3, 107.8.

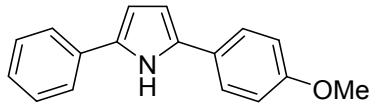


*2-(4-bromophenyl)-5-phenyl-1H-pyrrole (**6k**)*: White solid (59.6 mg, 50%; 79.9 mg, 67%), mp 161.9-162.3 °C. ^{1}H NMR (500 MHz, DMSO) δ 11.31 (s, 1H), 7.77-7.73 (m, 4H), 7.56-7.55 (m, 2H), 7.39-7.36 (m, 2H), 7.21-7.18 (m, 1H), 6.66-6.60 (m, 2H); ^{13}C NMR (125 MHz, DMSO) δ 133.5, 132.3, 131.7, 131.3, 128.5, 125.9, 125.7, 124.0, 118.3, 108.3, 107.8.

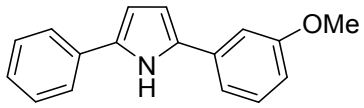
HRMS calcd for $C_{16}H_{13}BrN$ $[M+H]^+$: 298.0231 and 300.0211, found 298.0230 and 300.0210.



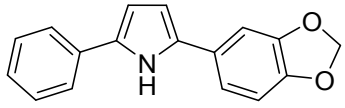
2-(4-iodophenyl)-5-phenyl-1H-pyrrole ***(6l)***: White solid (67.6 mg, 49%; 85.6 mg, 62%), mp 179.0-181.4 °C. ^{1}H NMR (500 MHz, DMSO) δ 11.30 (s, 1H), 7.77-7.71 (m, 4H), 7.61-6.59 (m, 2H), 7.39-7.36 (m, 2H), 7.21-7.18 (m, 1H), 6.65-6.60 (m, 2H); ^{13}C NMR (125 MHz, DMSO) δ 137.2, 133.5, 132.3, 132.0, 131.8, 128.5, 125.9, 124.0, 108.3, 107.8, 90.6. HRMS calcd for $C_{16}H_{13}IN$ $[M+H]^+$: 346.0087, found 346.0087.



2-(4-methoxyphenyl)-5-phenyl-1H-pyrrole ***(6m)***: White solid (69.8 mg, 70%; 57.8 mg, 58%), mp 163.4-164.5 °C (lit.[3] 162-163 °C). ^{1}H NMR (500 MHz, DMSO) δ 11.13 (s, 1H), 7.75-7.69 (m, 4H), 7.37-7.34 (m, 2H), 7.17-7.14 (m, 1H), 6.96 (d, *J* = 7.5 Hz, 2H), 6.57-6.56 (m, 1H), 6.46-6.45 (m, 1H), 3.78 (s, 3H); ^{13}C NMR (125 MHz, DMSO) δ 157.6, 133.1, 132.7, 132.1, 128.5, 125.5, 125.4, 125.3, 123.7, 114.0, 107.4, 106.3, 55.0.

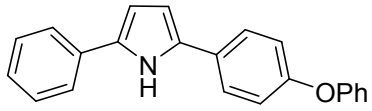


2-(3-methoxyphenyl)-5-phenyl-1H-pyrrole ***(6n)***: White solid (62.7 mg, 63%; 55.9 mg, 56%), mp 134.9-135.9 °C. ^{1}H NMR (500 MHz, DMSO) δ 11.49 (s, 1H), 8.40 (s, 1H), 8.04-8.02 (m, 1H), 7.81-7.86 (m, 3H), 7.53-7.50 (m, 1H), 7.40-7.37 (m, 2H), 6.70-6.63 (m, 2H), 3.90 (s, 3H); ^{13}C NMR (125 MHz, DMSO) δ 166.4, 133.7, 133.1, 132.4, 131.9, 130.2, 129.0, 128.5, 126.2, 126.0, 124.2, 124.1, 108.5, 107.9, 52.1. HRMS calcd for $C_{17}H_{16}NO$ $[M+H]^+$: 250.1227, found 250.1225.

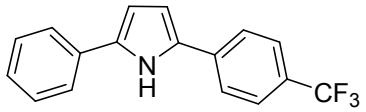


2-(benzo[d][1,3]dioxol-5-yl)-5-phenyl-1H-pyrrole ***(6o)***: White solid (70.5 mg, 67%), mp 146.1-147.3 °C. ^{1}H NMR (500 MHz, DMSO) δ 11.10 (s, 1H), 7.75-7.74 (m, 2H), 7.39-7.35 (m, 3H), 7.28-7.26 (m, 1H), 7.18-7.15 (m, 1H), 6.95-6.93 (m, 1H), 6.56-6.49 (m, 2H), 6.03 (s, 2H); ^{13}C NMR (125 MHz, DMSO) δ 147.6, 145.4, 133.0, 132.6, 132.4, 128.5, 127.1,

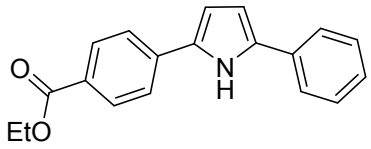
125.5, 123.8, 117.5, 108.5, 107.5, 107.0, 104.8, 100.8. HRMS calcd for $C_{17}H_{14}NO_2$ $[M+H]^+$: 264.1019, found 264.1028.



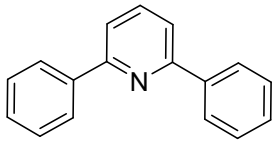
*2-(4-phenoxyphenyl)-5-phenyl-1H-pyrrole (**6p**)*: White solid (58.5 mg, 47%; 99.6 mg, 80%), mp 157.1-158.1 °C. ^{1}H NMR (500 MHz, DMSO) δ 11.23 (s, 1H), 7.80-7.75 (m, 4H), 7.42-7.36 (m, 4H), 7.19-7.13 (m, 2H), 7.06-7.03 (m, 4H), 6.59-6.54 (m, 2H); ^{13}C NMR (125 MHz, DMSO) δ 157.0, 154.5, 132.8, 132.6, 130.0, 128.5, 128.4, 125.6, 123.8, 123.2, 119.1, 118.2, 107.6, 107.3. HRMS calcd for $C_{22}H_{18}NO$ $[M+H]^+$: 312.1383, found 312.1385.



*2-phenyl-5-(4-(trifluoromethyl)phenyl)-1H-pyrrole (**6q**)*: White solid (46.0 mg, 40%), mp 167.6-168.4 °C (lit.[3] 168-169 °C). ^{1}H NMR (500 MHz, DMSO) δ 11.47 (s, 1H), 7.99-7.98 (m, 2H), 7.81-7.79 (m, 2H), 7.72-7.70 (m, 2H), 7.42-7.38 (m, 2H), 7.24-7.21 (m, 1H), 6.80-6.79 (m, 1H), 6.66-6.65 (m, 1H); ^{13}C NMR (125 MHz, DMSO) δ 136.2, 134.4, 132.1, 131.3, 128.6, 126.2, 125.6, 125.5 (q, J_{CF} = 3.8 Hz), 125.3, 124.2, 123.9, 109.7, 108.1. HRMS calcd for $C_{17}H_{13}F_3N$ $[M+H]^+$: 288.0995, found 288.0989.

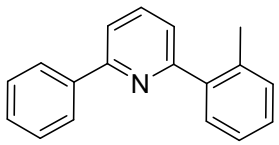


*ethyl 4-(5-phenyl-1H-pyrrol-2-yl)benzoate (**6r**)*: White solid (87.3 mg, 75%), mp 139.7-140.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.05-8.04 (m, 2H), 7.58-7.57 (m, 4H), 7.42-7.39 (m, 2H), 7.27-7.25 (m, 1H), 6.72 (s, 1H), 6.62 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 136.4, 134.5, 132.1, 131.9, 130.3, 129.0, 127.7, 126.8, 124.1, 123.0, 109.8, 108.4, 60.9, 14.3. HRMS calcd for $C_{19}H_{17}NO_2$ $[M+H]^+$: 292.1332, found 292.1332.

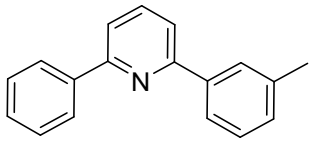


*3,5-diphenylpyridine (**7a**)*: Yellow solid (74.9 mg, 81%), mp 78.9-79.6 °C (lit.[4] 79-80 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17-8.15 (m, 4H), 7.84-7.81 (m, 1H), 7.71-7.69 (m, 2H),

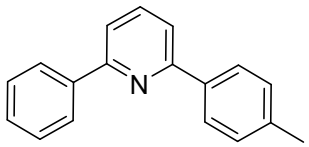
7.52-7.49 (m, 4H), 7.45-7.42 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.9, 139.5, 137.5, 129.0, 128.7, 127.0, 118.6.



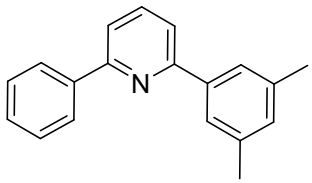
*3-phenyl-5-(o-tolyl)pyridine (**7b**)*: Yellow oil (54.0 mg, 55%; 52.0 mg, 53%), mp 62.7-62.9 °C (lit.[4] 63-64 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09-8.07 (m, 2H), 7.84-7.81 (m, 1H), 7.71-7.69 (m, 1H), 7.50-7.46 (m, 3H), 7.42-7.39 (m, 1H), 7.37-7.36 (m, 1H), 7.31-7.29 (m, 3H), 2.49 (s, 3H); ^{1}C NMR (125 MHz, $CDCl_3$) δ 159.8, 156.5, 140.5, 139.4, 137.0, 136.2, 130.9, 129.8, 128.9, 128.7, 128.3, 127.1, 125.9, 122.4, 118.3, 20.7.



*3-phenyl-5-(m-tolyl)pyridine (**7c**)*: Yellow oil (65.7 mg, 67%; 58.9, 60%) mp 66.1-66.5 °C (lit.[4] 66-67 °C). ^{1}H NMR (500 MHz, DMSO) δ 8.21-8.20 (m, 2H), 8.12-8.00 (m, 2H), 7.95-7.89 (m, 3H), 7.54-7.45 (m, 3H), 7.34-7.33 (m, 2H), 2.37 (s, 3H); ^{1}C NMR (125 MHz, $CDCl_3$) δ 155.6, 155.5, 138.8, 138.7, 138.2, 135.9, 129.3, 129.1, 128.7, 126.6, 126.5, 118.8, 118.5, 118.4, 20.8.

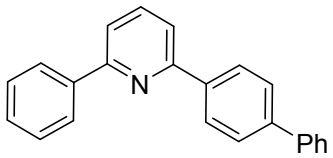


*3-phenyl-5-(p-tolyl)pyridine (**7d**)*: White solid (73.6 mg, 75%; 65.8 mg, 67%), mp 88.6-89.5 °C (lit.[4] 91-92 °C). ^{1}H NMR (500 MHz, DMSO) δ 8.21-8.20 (m, 2H), 8.02-7.89 (m, 5H), 7.55-7.52 (m, 2H), 7.48-7.45 (m, 1H), 7.43-7.40 (m, 1H), 7.28-7.27 (m, 1H), 2.43 (s, 3H); ^{1}C NMR (125 MHz, $CDCl_3$) δ 155.8, 155.6 , 138.7, 138.2, 137.9, 129.8, 129.1, 128.7, 128.6, 127.1, 126.6, 126.5, 123.8, 118.9, 118.8, 21.2.

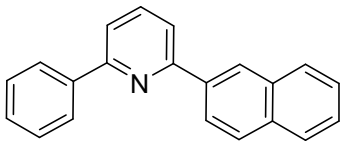


*3-(3,5-dimethylphenyl)-5-phenylpyridine (**7e**)*: White solid (68.5 mg, 66%; 70.5 mg, 68%),

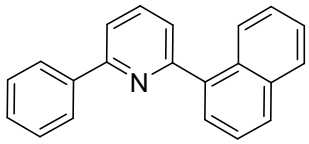
mp 86.5-87.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15-8.13 (m, 2H), 7.79 (t, *J* = 8.0 Hz, 1H), 7.75 (s, 2H), 7.67-7.65 (m, 2H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.44-7.41 (m, 1H), 7.07 (s, 1H), 2.42 (s, 6H); ^{1}C NMR (125 MHz, $CDCl_3$) δ 157.3, 156.8, 139.6, 139.5, 138.2, 137.4, 130.7, 128.9, 128.7, 127.1, 124.9, 118.8, 118.6, 21.5. HRMS calcd for $C_{19}H_{18}N$ $[M+H]^+$: 260.1434, found 260.1434.



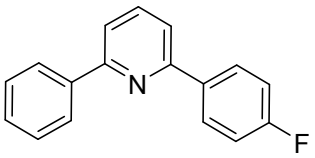
*3-([1,1'-biphenyl]-4-yl)-5-phenylpyridine (**7f**)*: White solid (62.7 mg, 51%; 76.2 mg, 62%), mp 146.9-147.1 °C (lit.[4] 149-150 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26-8.24 (m, 2H), 8.20-8.18 (m, 2H), 7.86-7.82 (m, 1H), 7.76-7.72 (m, 4H), 7.70-7.68 (m, 2H), 7.54-7.43 (m, 5H), 7.40-7.37 (m, 1H); ^{1}C NMR (125 MHz, $CDCl_3$) δ 156.9, 156.5, 141.8, 140.8, 139.5, 138.4, 137.5, 129.0, 128.8, 128.7, 127.5, 127.4, 127.4, 127.1, 127.0, 118.6, 118.5.



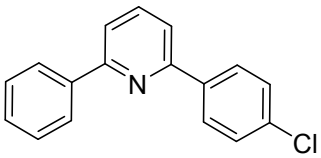
*3-(naphthalen-2-yl)-5-phenylpyridine (**7g**)*: Colorless oil (68.6 mg, 61%; 72.0 mg, 64%) (lit.[4] Oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27-8.25 (m, 1H), 8.14-8.12 (m, 2H), 7.95-7.89 (m, 3H), 7.81-7.80 (m, 1H), 7.72-7.70 (m, 1H), 7.60-7.47 (m, 6H), 7.44-7.42 (m, 1H); ^{1}C NMR (125 MHz, $CDCl_3$) δ 158.9, 156.9, 139.2, 138.5, 137.3, 134.0, 131.3, 129.0, 128.9, 128.7, 128.3, 127.9, 127.7, 127.1, 126.3, 125.9, 125.8, 125.3, 123.5, 118.7.



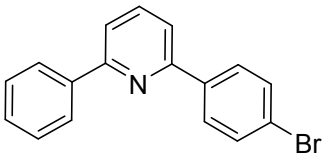
*3-(naphthalen-1-yl)-5-phenylpyridine (**7h**)*: Colorless oil (78.8 mg, 70%; 65.3 mg, 58%) (lit.[5] Oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34-8.34 (m, 1H), 8.19-8.17 (m, 2H), 7.98-7.96 (m, 2H), 7.91-7.87 (m, 1H), 7.82-7.80 (m, 1H), 7.75-7.73 (m, 1H), 7.63-7.60 (m, 1H), 7.58-7.50 (m, 5H), 7.47-7.44 (m, 1H); ^{1}C NMR (125 MHz, $CDCl_3$) δ 159.0, 156.8, 139.4, 138.7, 137.1, 134.0, 131.3, 128.9, 128.8, 128.7, 128.3, 127.6, 127.0, 126.3, 125.9, 125.8, 125.3, 123.3, 118.5.



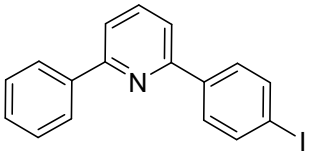
*3-(4-fluorophenyl)-5-phenylpyridine (**7i**)*: Yellow solid (56.8 mg, 57%; 62.8 mg, 63%), mp 84.4-86.1 °C (lit.[4] 94-95 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17-8.13 (m, 4H), 7.84-7.80 (m,1H), 7.71-7.68 (m, 1H), 7.66-7.64 (m, 1H), 7.53-7.49 (m, 2H), 7.46-7.42 (m, 1H), 7.20-7.16 (m, 2H); ^{1}C NMR (125 MHz, $CDCl_3$) δ 163.7 (d, J_{CF} = 248.4 Hz), 156.9, 155.9, 139.3, 137.7, 135.6, 129.1, 128.8 (d, J_{CF} = 8.4 Hz), 128.7, 127.1, 127.0, 118.4 (d, J_{CF} = 37.5 Hz), 115.6 (d, J_{CF} = 21.5 Hz).



*3-(4-chlorophenyl)-5-phenylpyridine (**7j**)*: Yellow solid (65.9 mg, 62%; 61.7 mg, 58%), mp 105.8-106.2 °C (lit.[4] 104-105 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17-8.10 (m, 4H), 7.84-7.81 (m, 1H), 7.72-7.66 (m, 2H), 7.52-7.43 (m, 5H); ^{1}C NMR (125 MHz, $CDCl_3$) δ 157.0, 155.6, 139.2, 137.9, 137.7, 135.2, 129.1, 129.1, 128.9, 128.7, 128.3, 127.1, 127.0, 119.0, 118.8, 118.4.

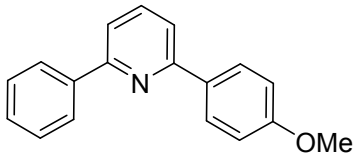


*3-(4-bromophenyl)-5-phenylpyridine (**7k**)*: Yellow solid (65.8 mg, 53%; 63.3 mg, 51%), mp 112.9-113.2 °C (lit.[4] 115-116 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15-8.12 (m, 2H), 8.05-8.02 (m, 2H), 7.85-7.81 (m, 1H), 7.72-7.70 (m, 1H), 7.68-7.61 (m, 3H), 7.53-7.49 (m, 2H), 7.46-7.42 (m, 1H); ^{1}C NMR (125 MHz, $CDCl_3$) δ 157.1, 155.7, 139.3, 138.4, 137.7, 131.8, 129.1, 128.7, 128.7, 128.6, 127.1, 127.0, 123.5, 119.0, 118.4.

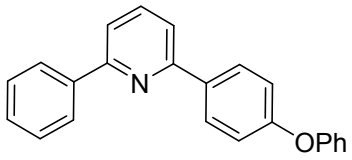


*3-(4-iodophenyl)-5-phenylpyridine (**7l**)*: Yellow solid (42.9 mg, 30%; 40.0 mg, 28%), mp 138.7-139.4 °C (lit.[4] 139-141 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, J = 8.0 Hz, 2H), 7.88-7.87 (m, 2H), 7.82-7.77 (m, 3H), 7.69-7.68 (m, 1H), 7.63-7.62 (m, 1H), 7.51-7.48 (m,

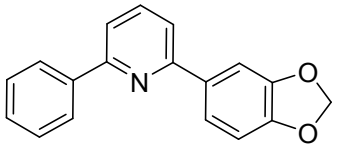
2H), 7.44-7.41 (m, 1H); ^{1}C NMR (125 MHz, $CDCl_3$) δ 157.0, 155.7, 139.2, 138.9, 137.8, 137.6, 129.1, 128.7, 128.7, 127.1, 127.0, 119.0, 118.3, 95.3 .



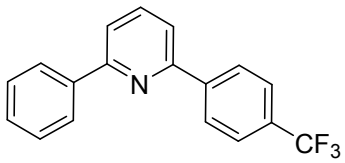
*3-(4-methoxyphenyl)-5-phenylpyridine (**7m**)*: White solid (62.7 mg, 60%; 45.0 mg, 43%), mp 131.5-131.9 °C (lit.[4] 132-133 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17-8.12 (m, 4H), 7.79-7.75 (m, 1H), 7.65-7.62 (m, 2H),7.53-7.49 (m, 2H), 7.45-7.42 (m, 1H), 7.05-7.02 (m, 2H), 3.88 (s, 3H); ^{1}C NMR (125 MHz, $CDCl_3$) δ 160.6, 156.7, 156.5, 139.6, 137.4, 132.2, 128.9, 128.6, 128.3, 127.0, 117.9, 117.9, 114.1, 55.4.



*3-(4-phenoxyphenyl)-5-phenylpyridine (**7n**)*: Yellow oil (58.2 mg, 45%; 64.7 mg, 50%). ^{1}H NMR (500 MHz, DMSO) δ 8.25-8.20 (m, 3H), 7.95-7.89 (m, 2H), 7.54-7.42 (m, 4H), 7.21-7.09 (m, 4H); ^{1}C NMR (125 MHz, DMSO) δ 157.8, 156.2, 155.6, 155.0, 138.7, 138.3, 133.8, 130.1, 129.1, 128.7, 128.4, 126.6, 123.8, 119.0, 118.4, 118.5, 118.4. HRMS calcd for $C_{23}H_{18}NO$ $[M+H]^+$: 324.1383, found 324.1386.



*3-(benzo[d][1,3]dioxol-5-yl)-5-phenylpyridine (**7o**)*: Colorless oil (69.4 mg, 63%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16-8.14 (m, 2H), 7.79-7.74 (m, 2H), 7.66-7.64 (m, 2H), 7.60-7.58 (m, 1H), 7.52-7.48 (m, 2H), 7.45-7.41 (m, 1H), 6.94-6.92 (m, 1H), 6.03 (s, 2H); ^{1}C NMR (125 MHz, $CDCl_3$) δ 156.7, 156.3, 148.5, 148.3, 139.5, 137.4, 134.0, 129.0, 128.7, 127.0, 121.0, 118.2, 118.0, 108.4, 107.5, 101.3. HRMS calcd for $C_{18}H_{14}NO_2$ $[M+H]^+$: 276.1019, found 276.1021.



*3-phenyl-5-(4-(trifluoromethyl)phenyl)pyridine (**7p**)*: Yellow solid (57.5 mg, 48%), mp

109.0-110.2 °C (lit.[4] 117-118 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27-8.25 (m, 2H), 8.15-8.13 (m, 2H), 7.87-7.83 (m, 1H), 7.76-7.71 (m, 4H), 7.53-7.43 (m, 3H); ^{1}C NMR (125 MHz, $CDCl_3$) δ 157.2, 155.3, 142.8, 139.2, 137.7, 129.2, 128.8, 127.3, 127.0, 125.6 (q, J = 3.8Hz), 125.4, 123.2, 119.5, 118.9.

Reference

(1) N. Naresh Kumar Reddy, D. Rawat, S. Adimurthy. *J. Org. Chem*., 2018, **83**, 9412−9421.

(2) H. Rao, S. Jothilingam, H. Scheeren. *Tetrahedron*., 2004, **60**, 1625–1630.

(3) J. Cen, Y. Wu, J. Li, L. Huang, W. Wu, Z. Zhu, S. Yang, H. Jiang, *Org. Lett*., 2019, **21**, 2090−2094.

(4) Y. Shen, J. Chen, M. Liu, J. Ding, W. Gao, X. Huang, H. Wu, *Chem. Commun.,* 2014, **50**, 4292−4295.

(5) J. Zhan, M. Wu, D. Wei, B. Wei, Y. Jiang, W. Yu, B. Han, *ACS Catal*., 2019, **9**, 4179-4188.

4. NMR Spectra for All Products

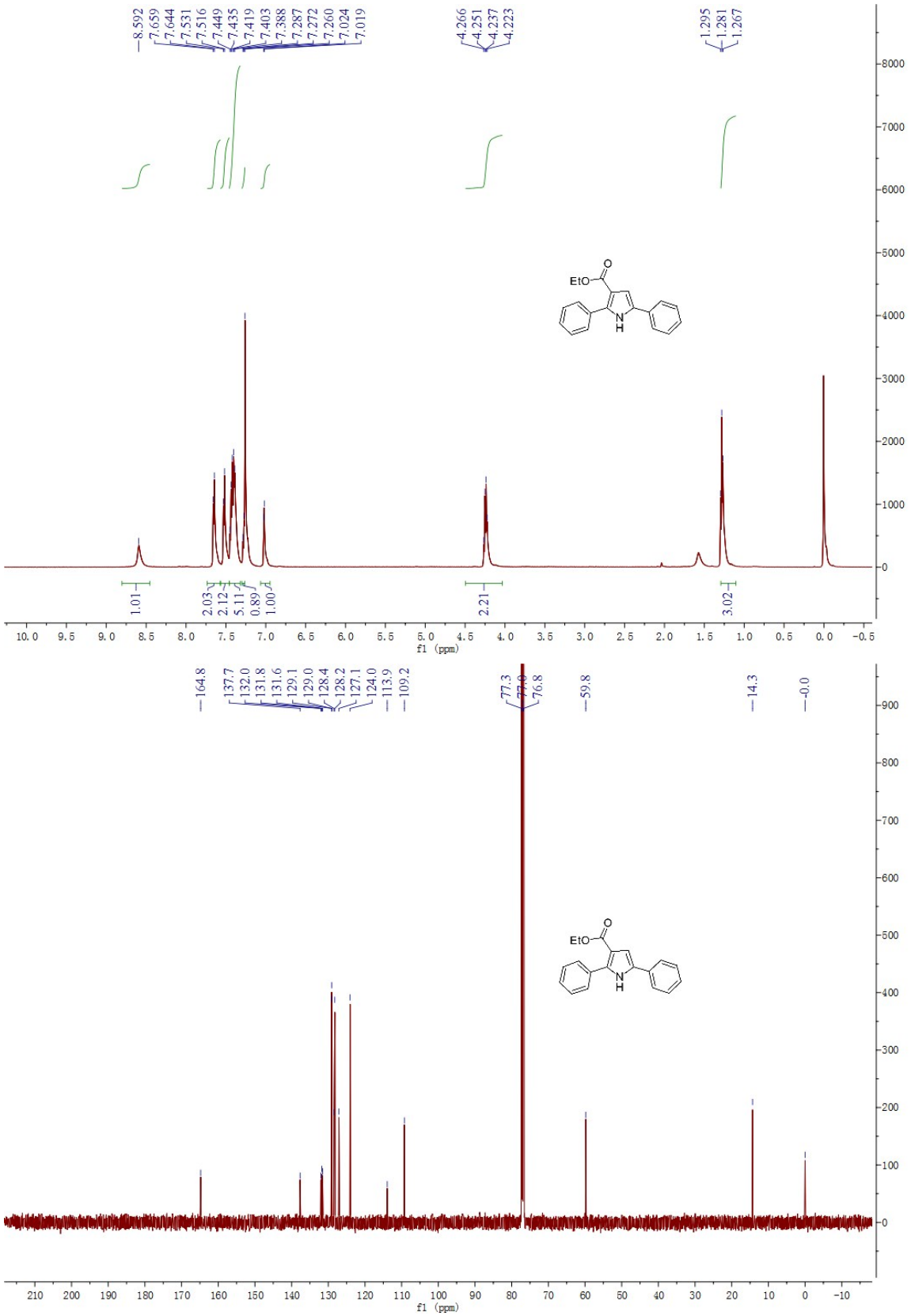


Figure S1. ^{1}H NMR of **3a** (500 MHz,$CDCl_3$) and ^{13}C NMR of **3a** (125 MHz, $CDCl_3$)

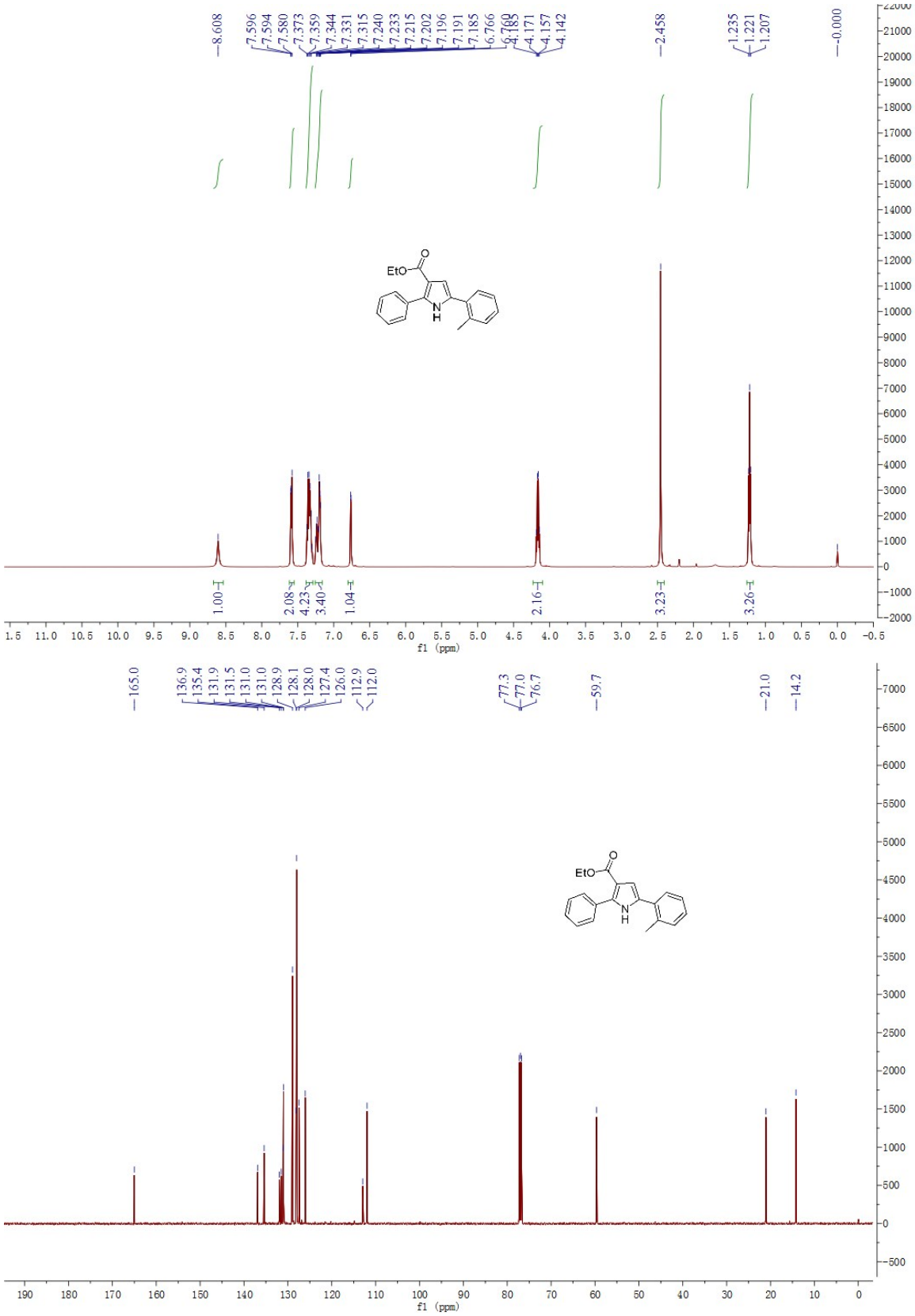


Figure S2. ^{1}H NMR of **3b** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3b** (125 MHz, $CDCl_3$)

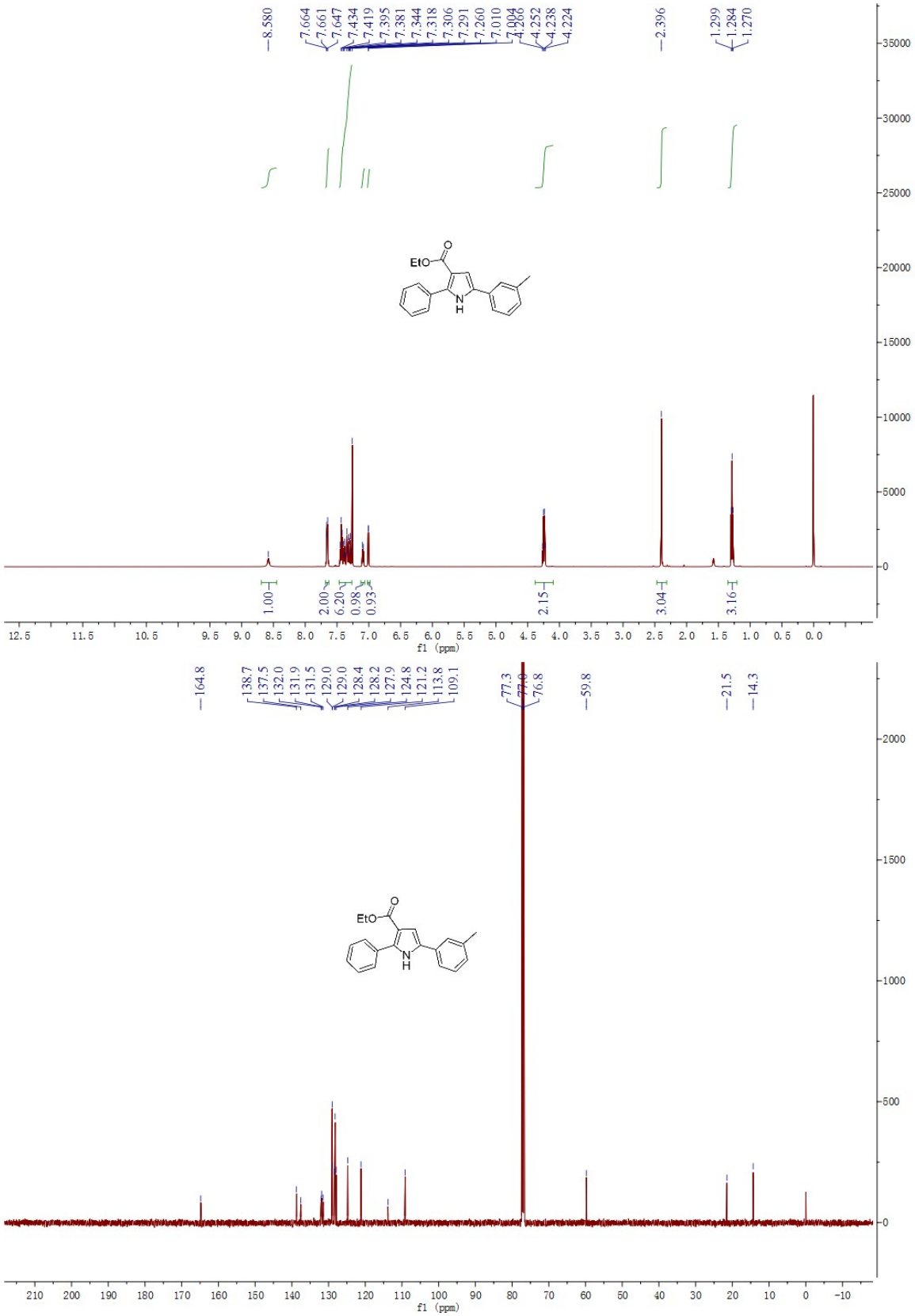


Figure S3. ^{1}H NMR of **3c** (500 MHz,$CDCl_3$) and ^{13}C NMR of **3c** (125 MHz, $CDCl_3$)

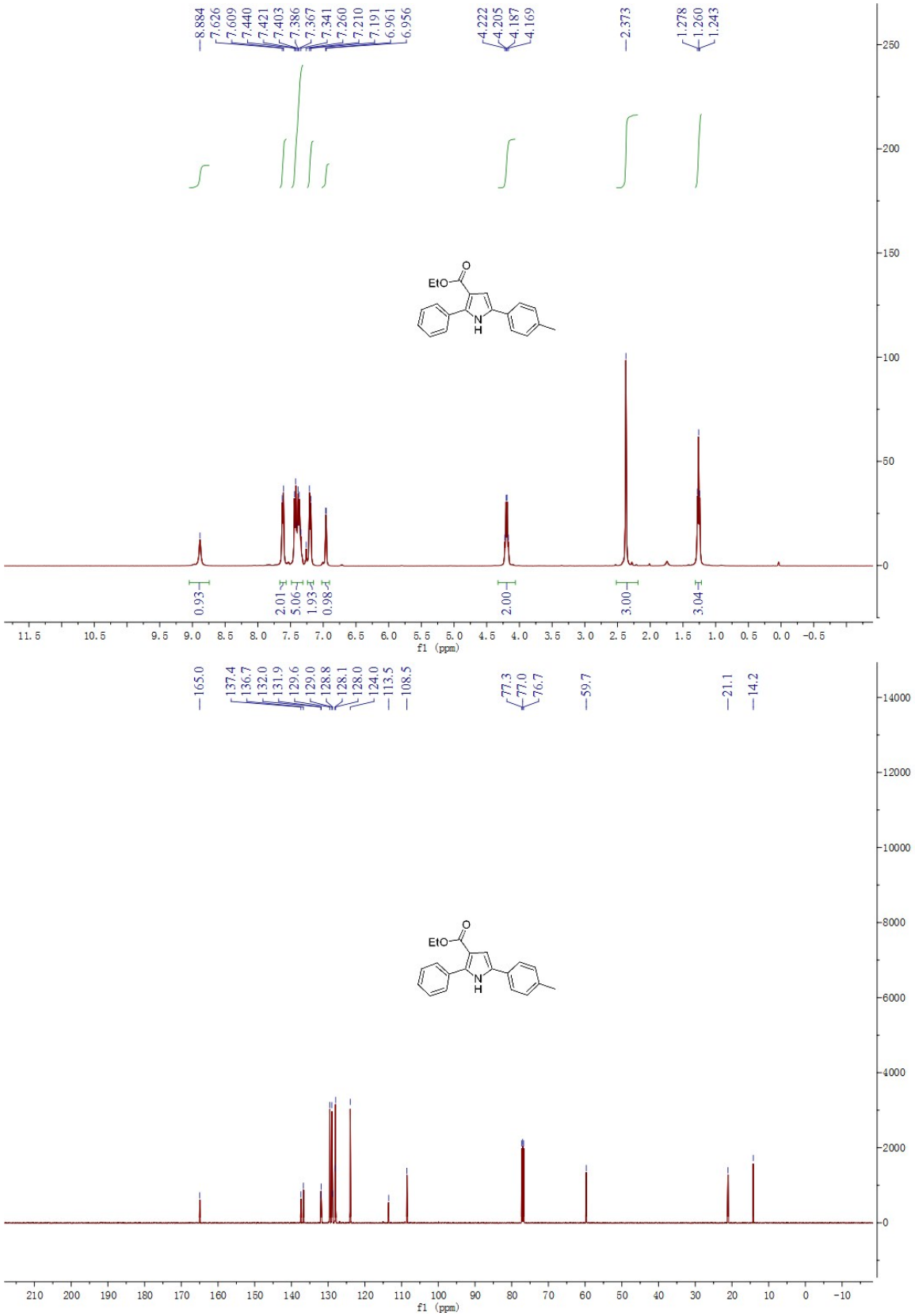


Figure S4. ^{1}H NMR of **3d** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3d** (125 MHz, $CDCl_3$)

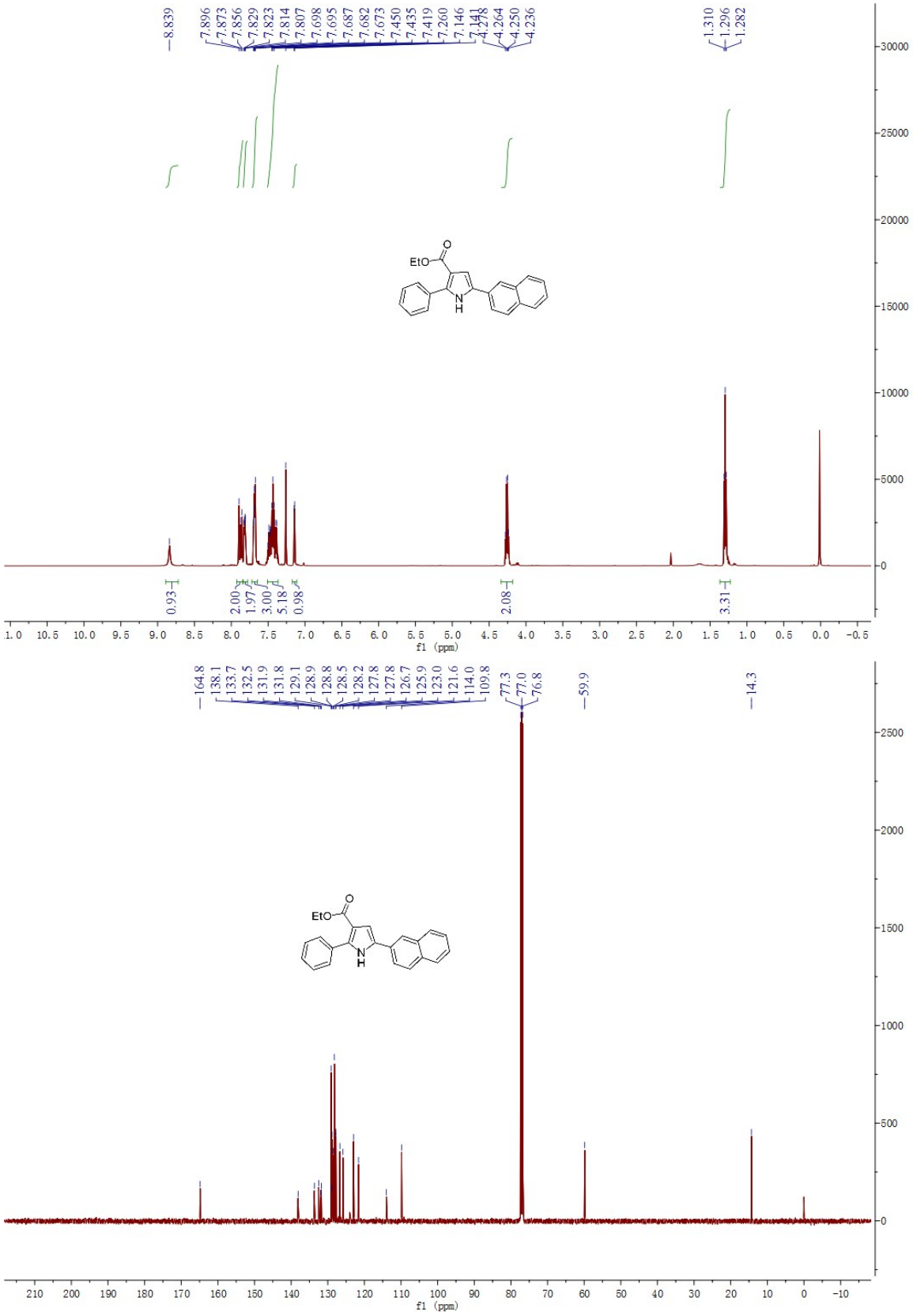


Figure S5. ^{1}H NMR of **3e** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3e** (125 MHz, $CDCl_3$)

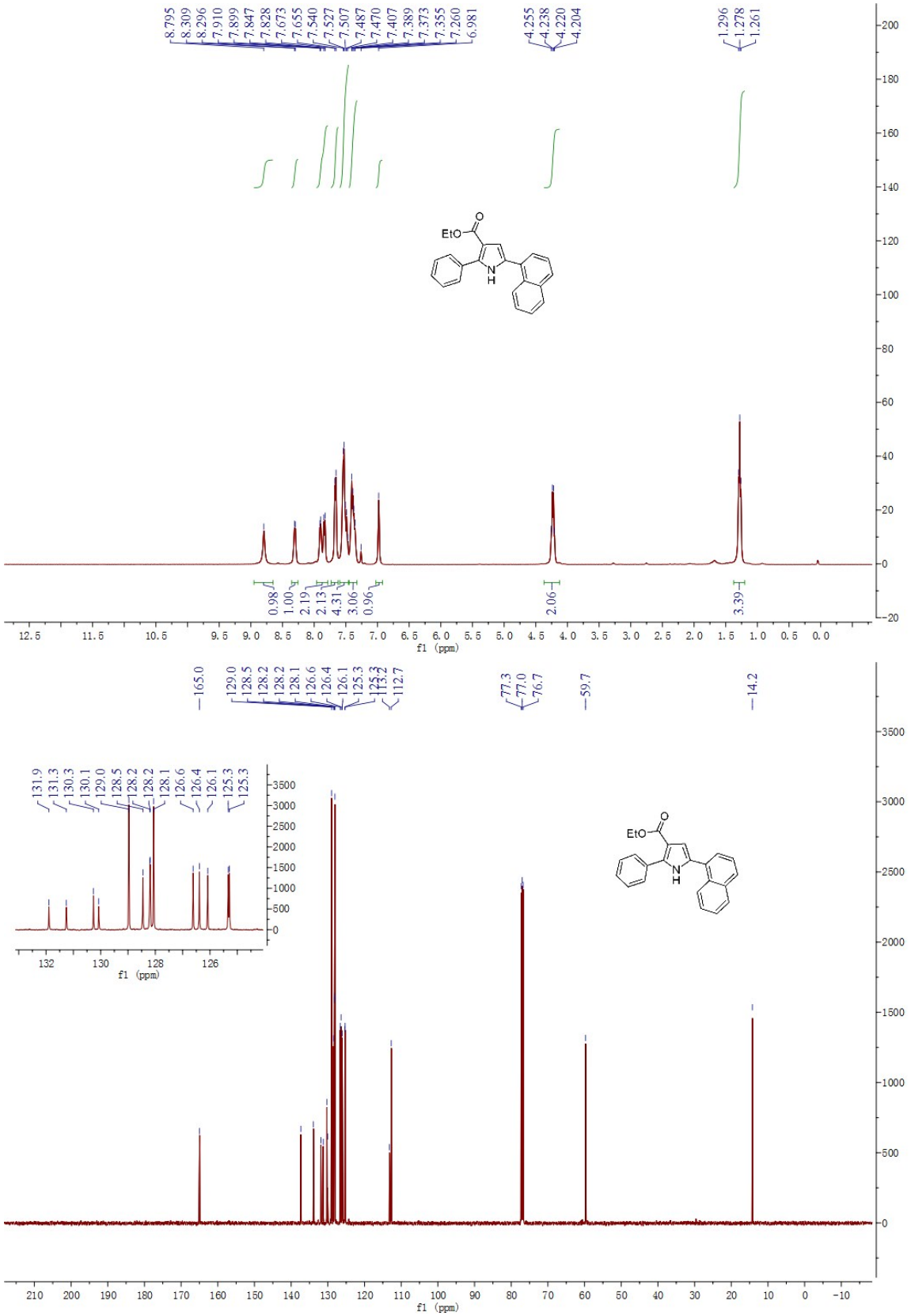


Figure S6. ^{1}H NMR of **3f** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3f** (125 MHz,$CDCl_3$)

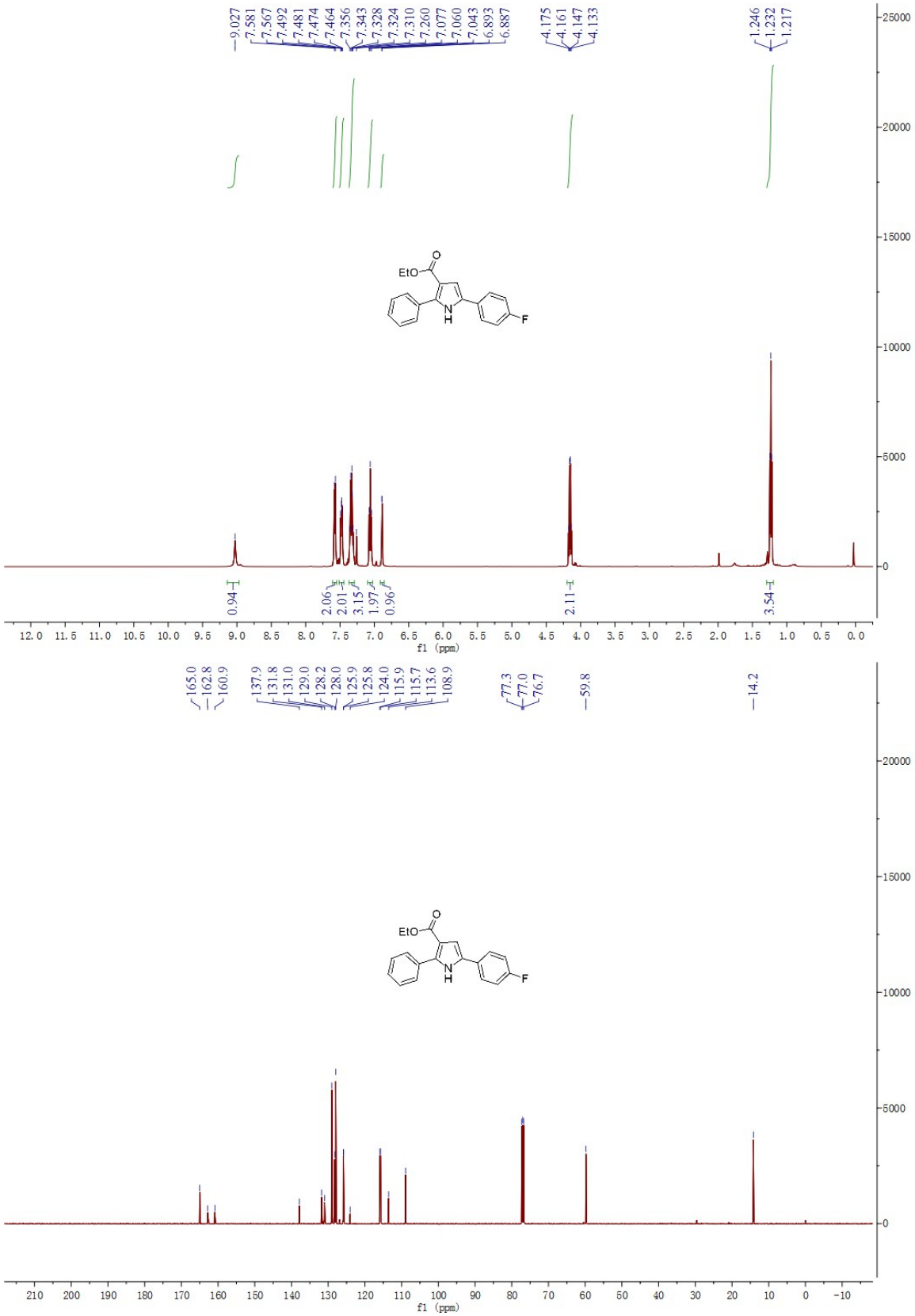


Figure S7. ^{1}H NMR of **3g** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3g** (125 MHz,$CDCl_3$)

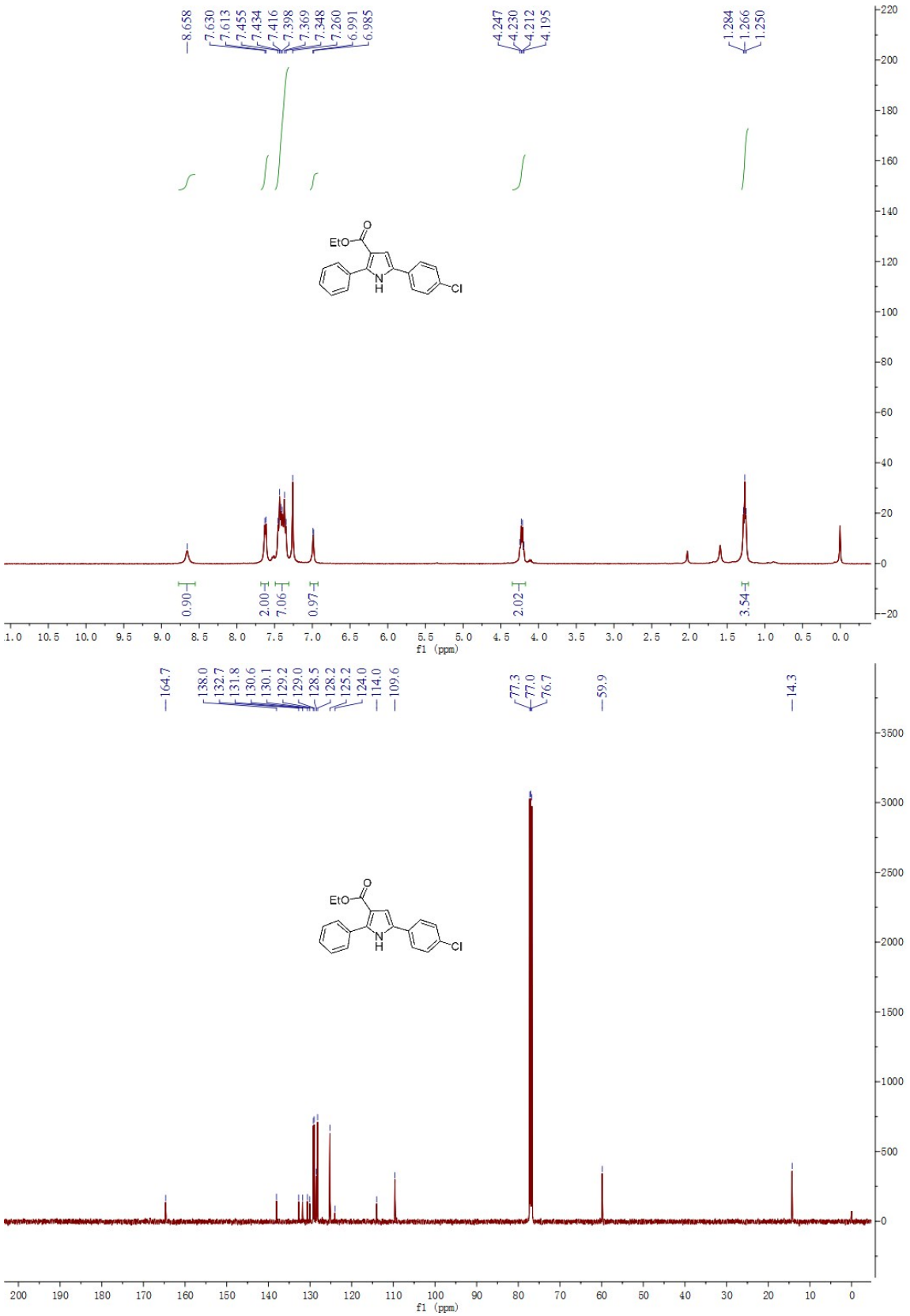


Figure S8. ^{1}H NMR of **3h** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3h** (125 MHz, $CDCl_3$)

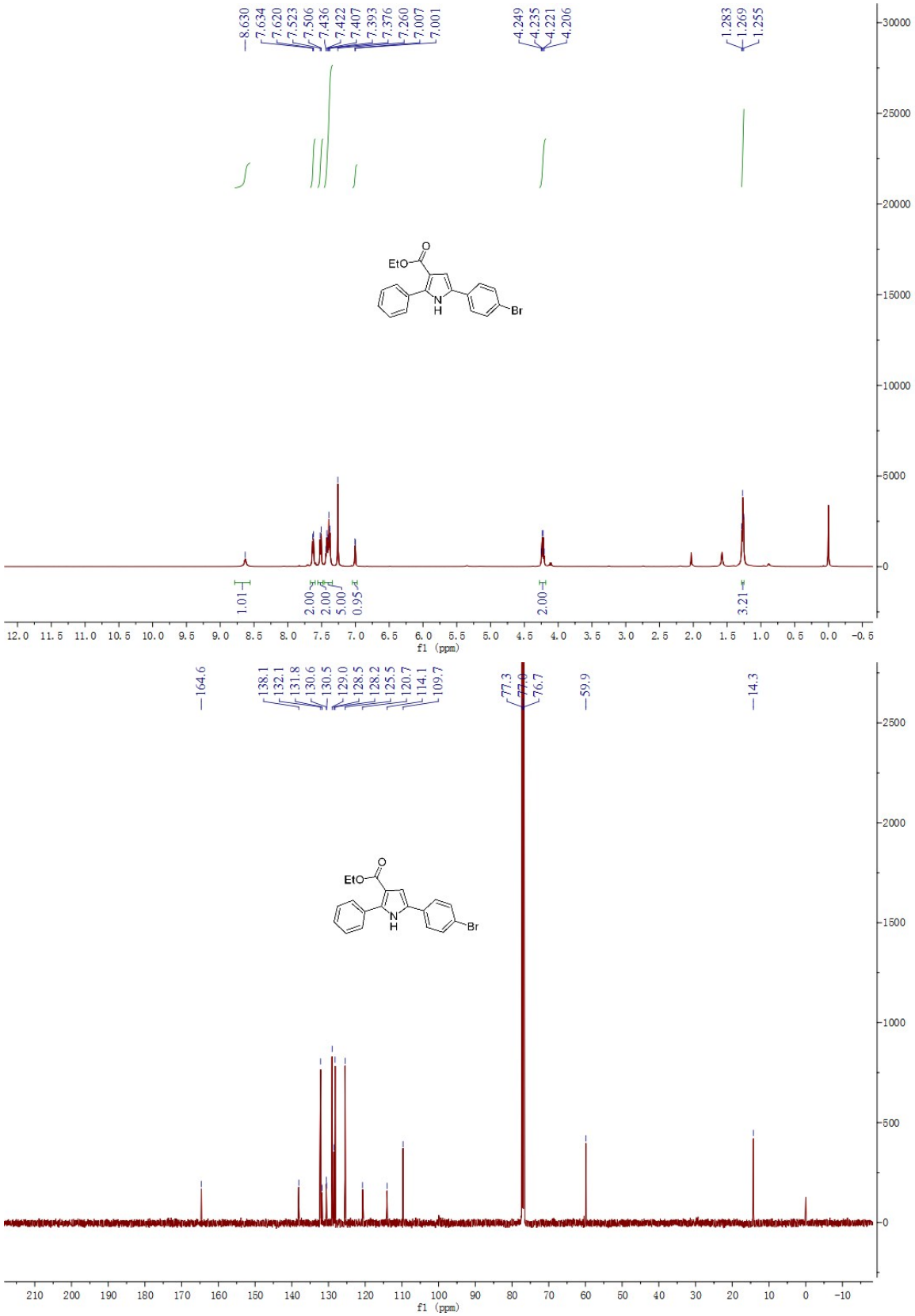


Figure S9. ^{1}H NMR of **3i** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3i** (125 MHz, $CDCl_3$)

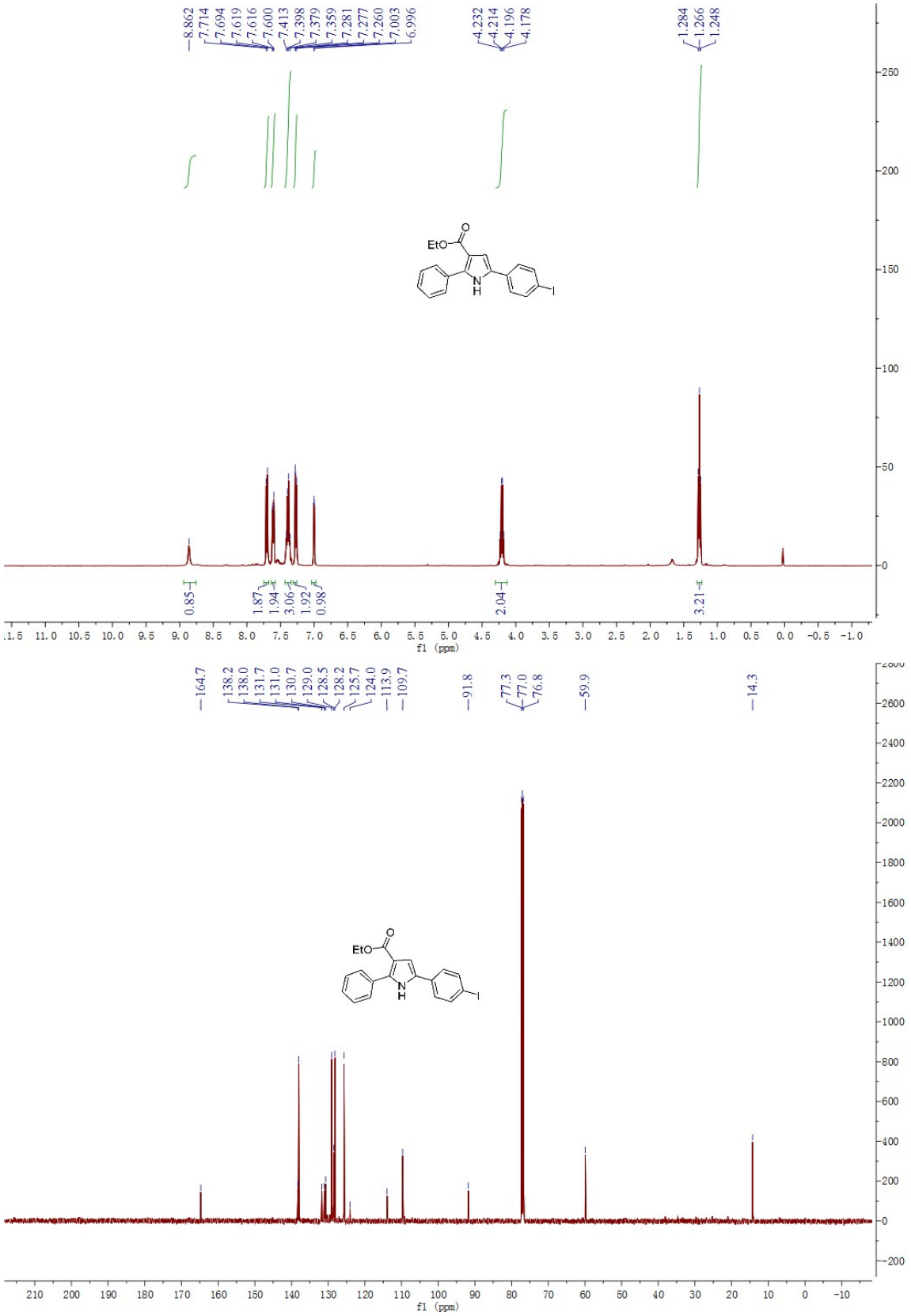


Figure S10. ^{1}H NMR of **3j** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3j** (125 MHz, $CDCl_3$)

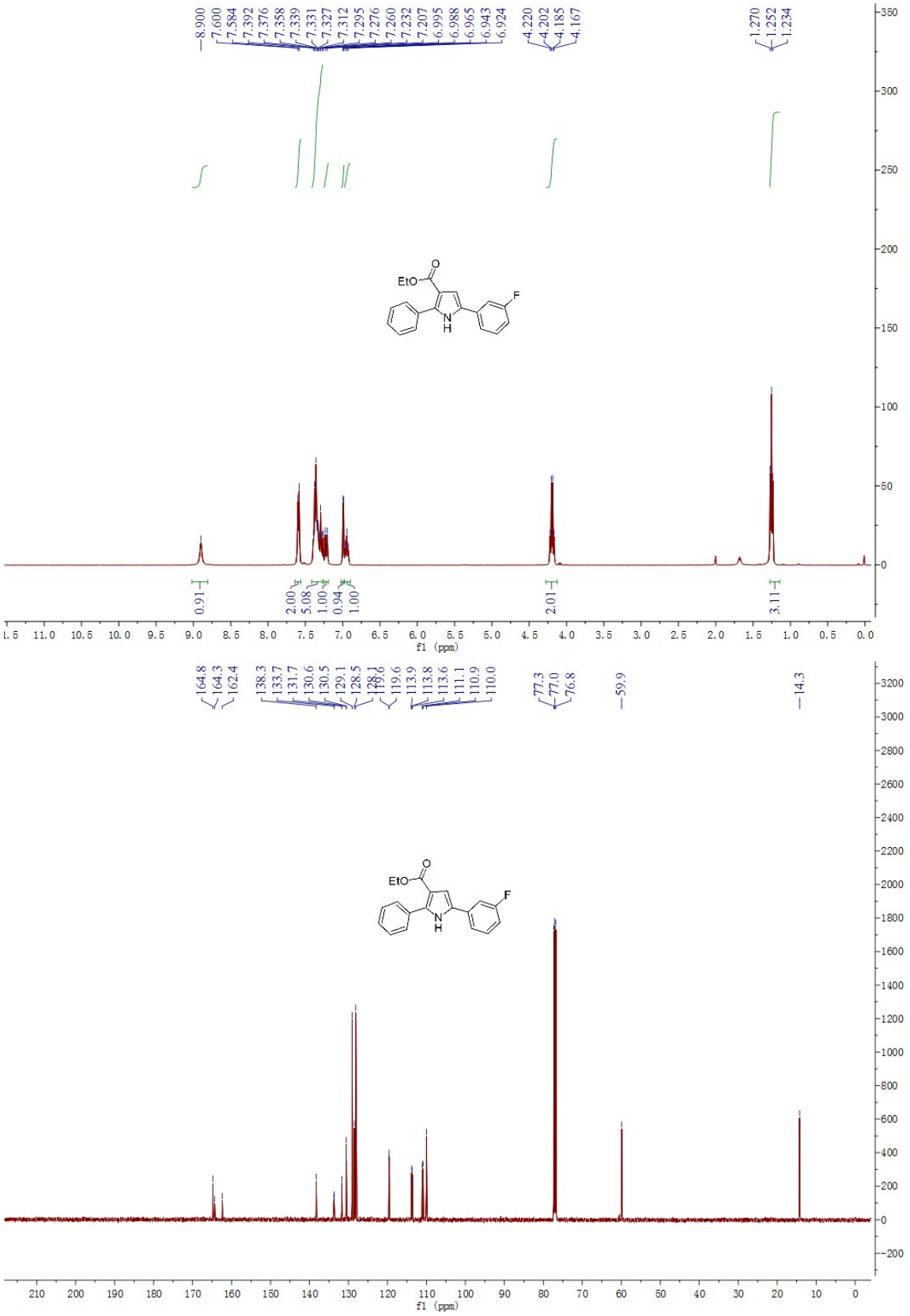


Figure S11. ^{1}H NMR of **3k** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3k** (125 MHz, $CDCl_3$)

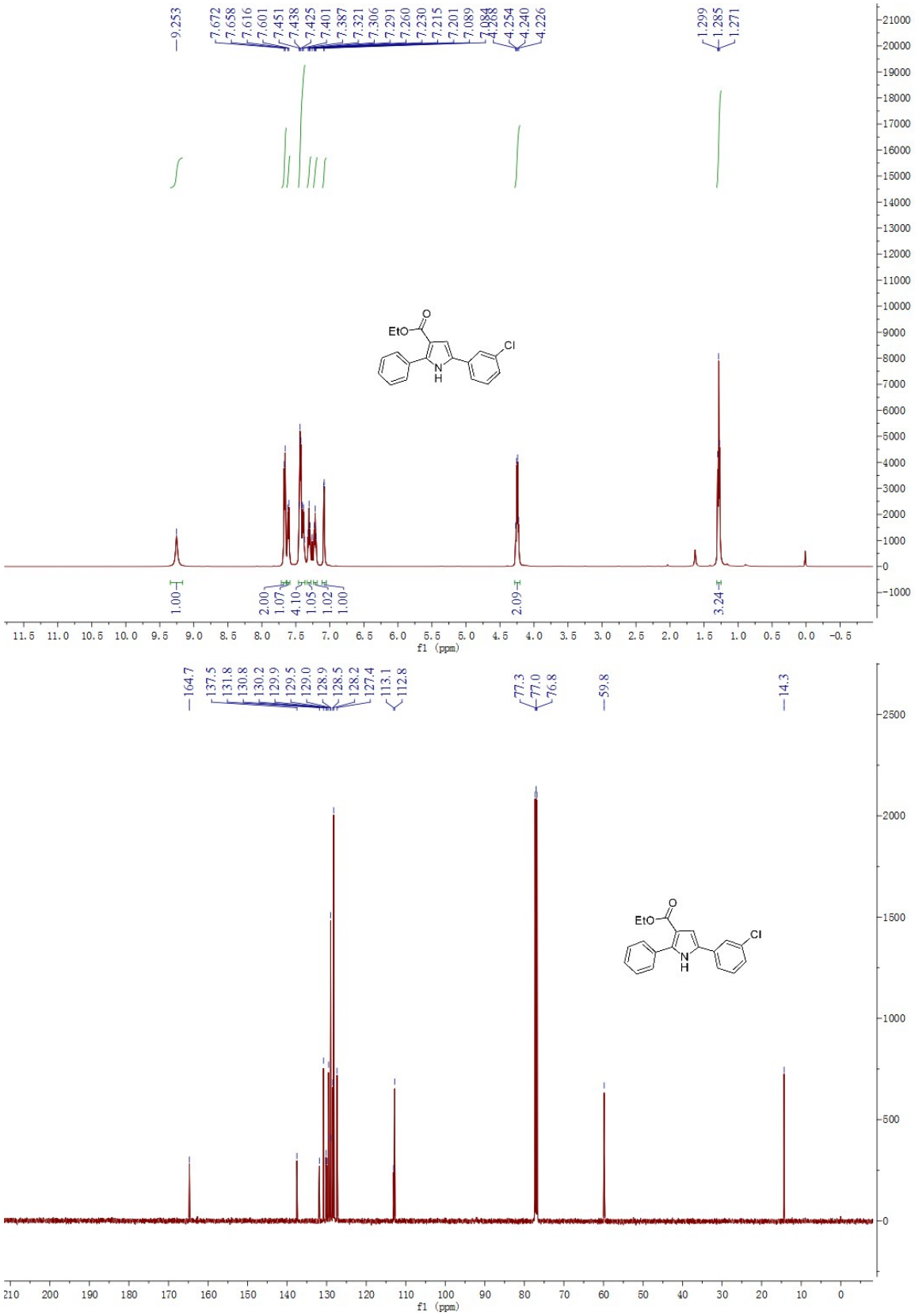


Figure S12. ^{1}H NMR of **3l** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3l** (125 MHz, $CDCl_3$)

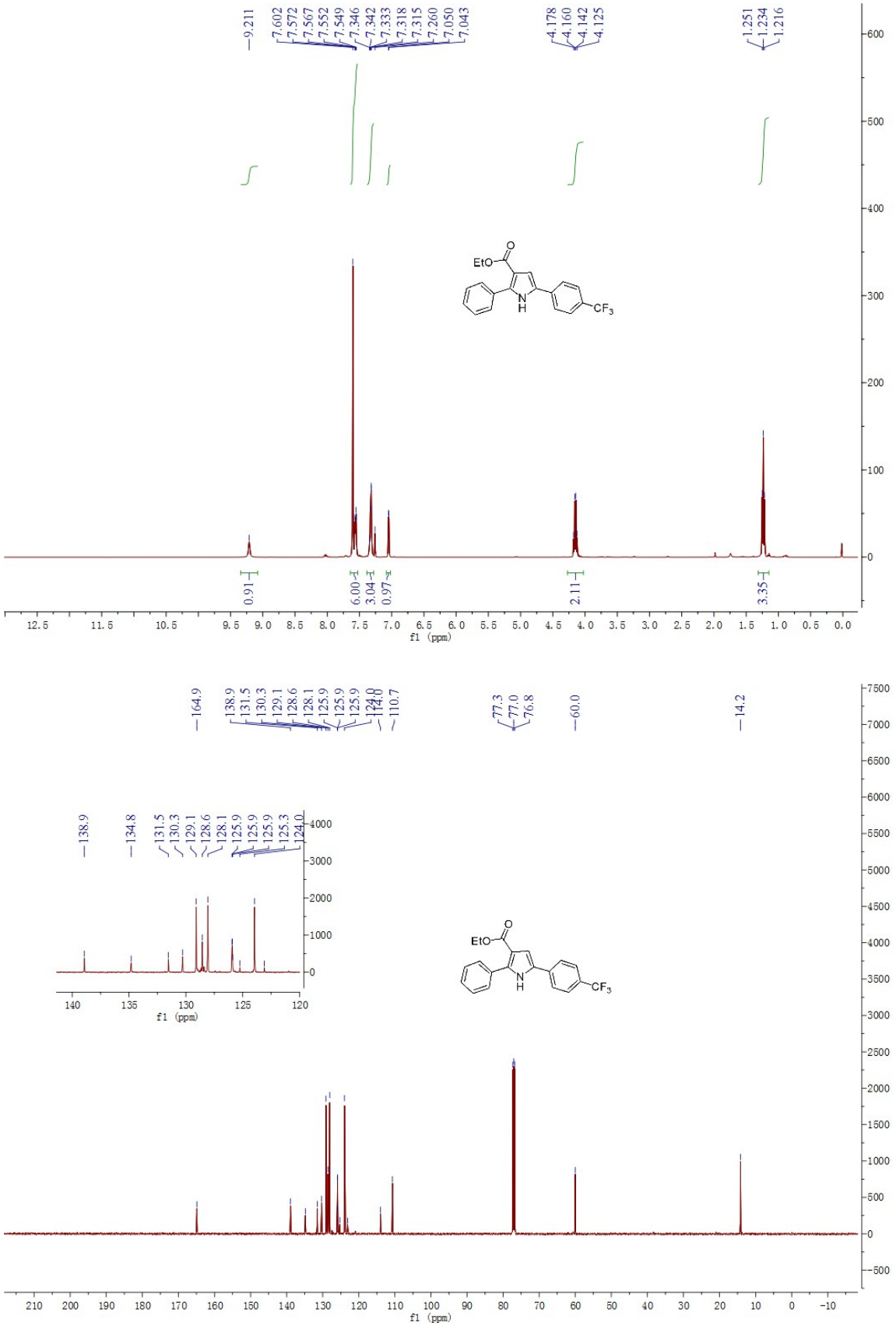


Figure S13. ^{1}H NMR of **3m** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3m** (125 MHz, $CDCl_3$)

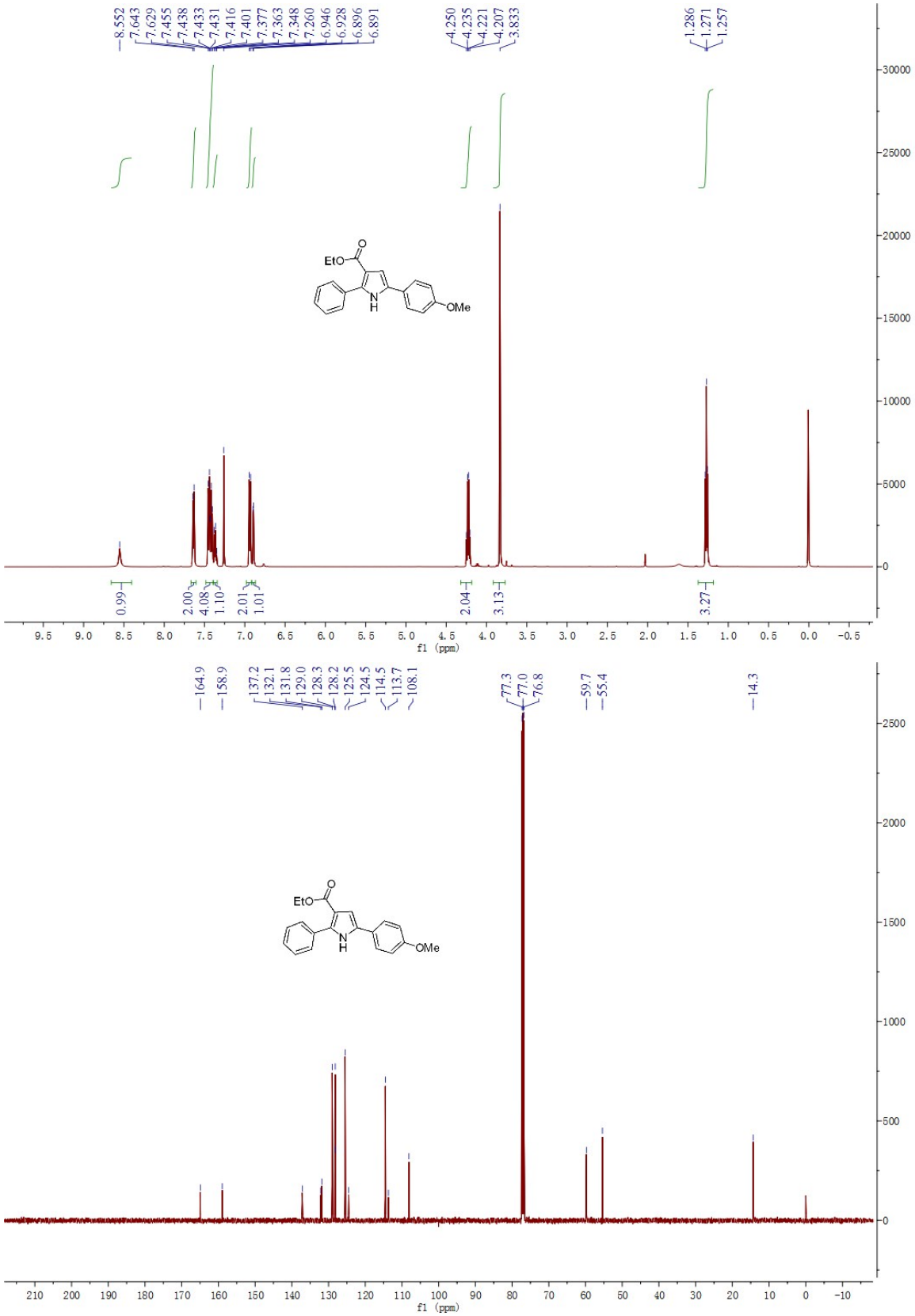


Figure S14. ^{1}H NMR of **3n** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3n** (125 MHz, $CDCl_3$)

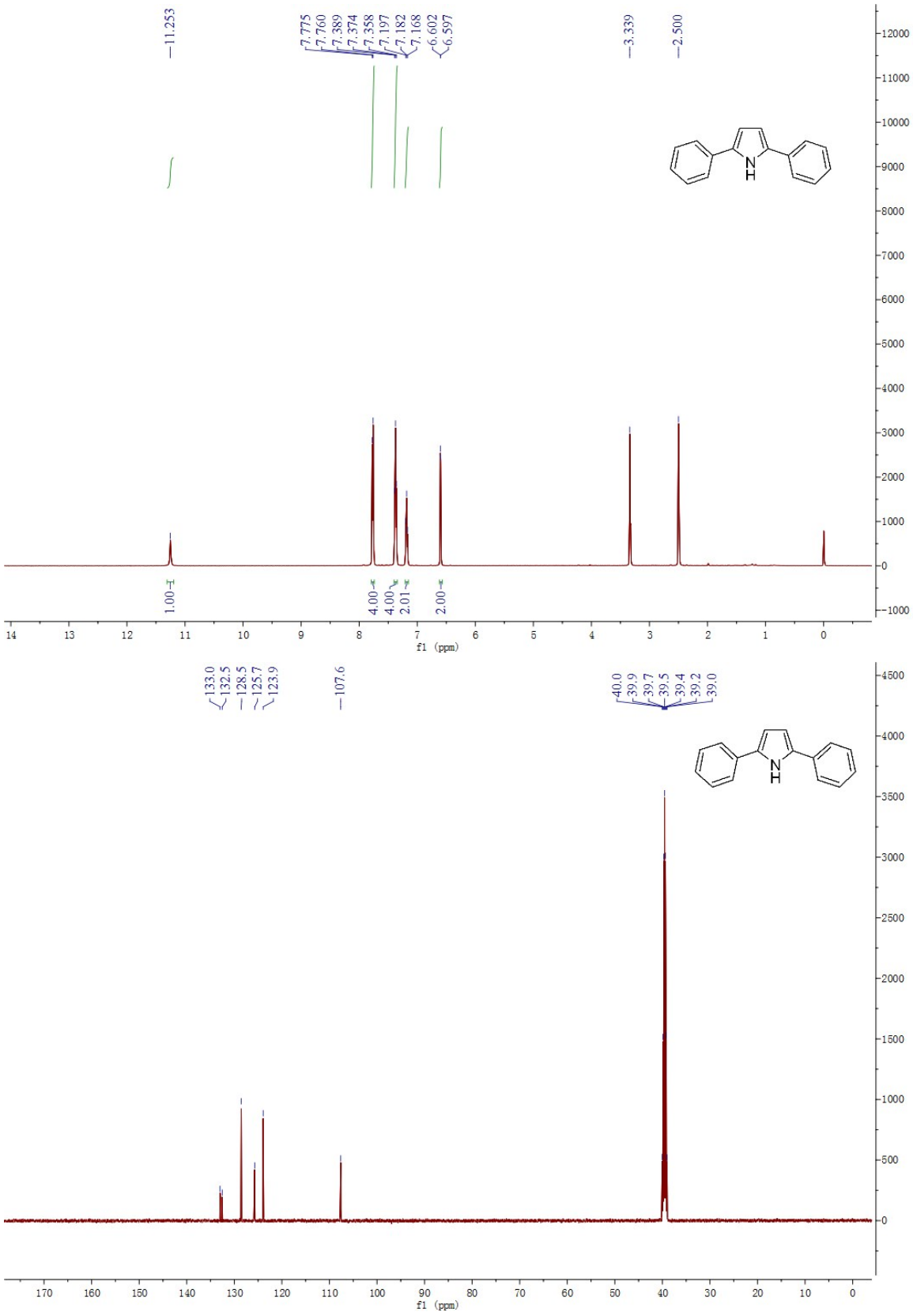


Figure S15. ^{1}H NMR of **5a** (500 MHz, DMSO) and ^{13}C NMR of **5a** (125 MHz, DMSO)

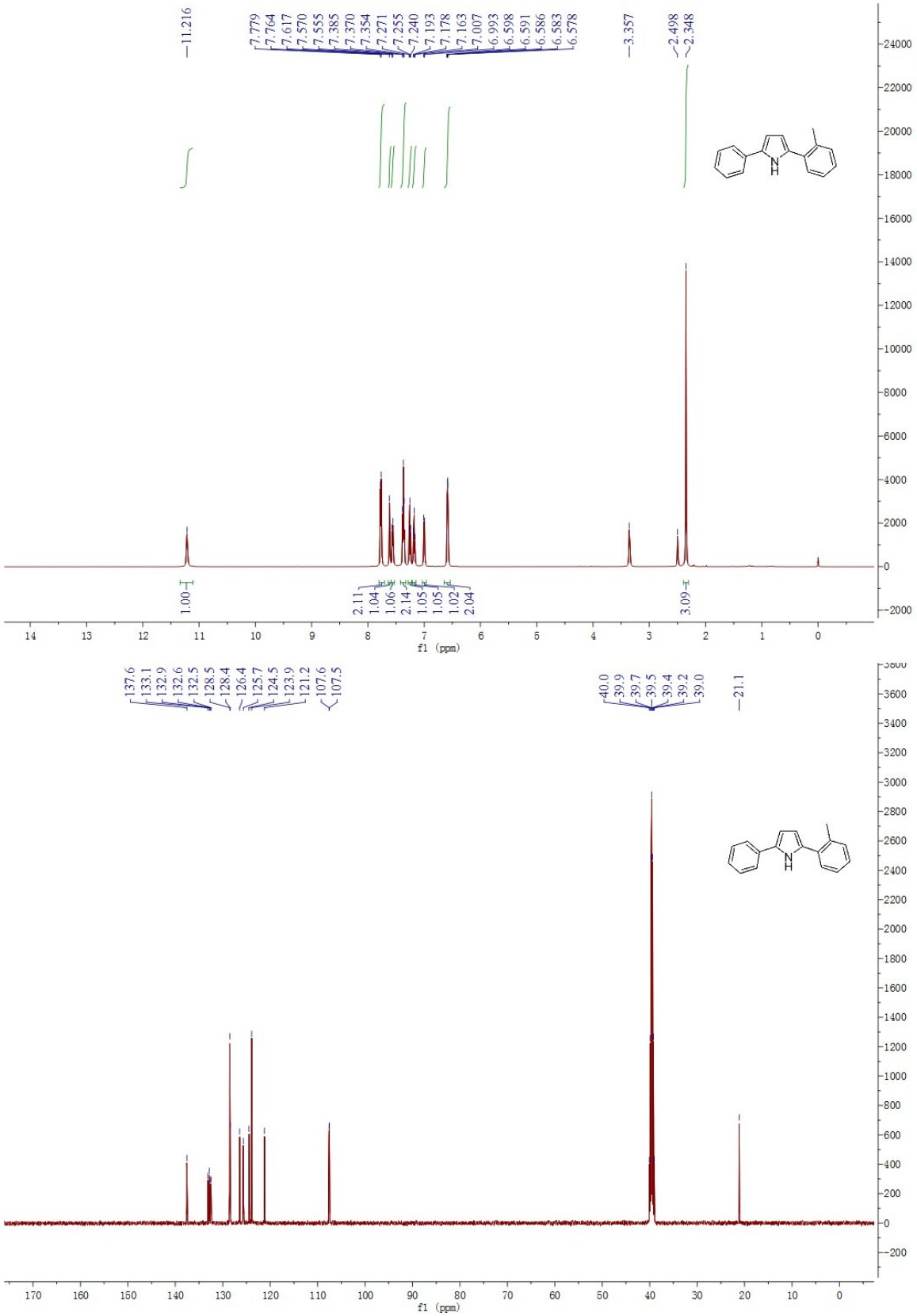


Figure S16. ^{1}H NMR of **5b** (500 MHz, DMSO) and ^{13}C NMR of **5b** (125 MHz, DMSO)

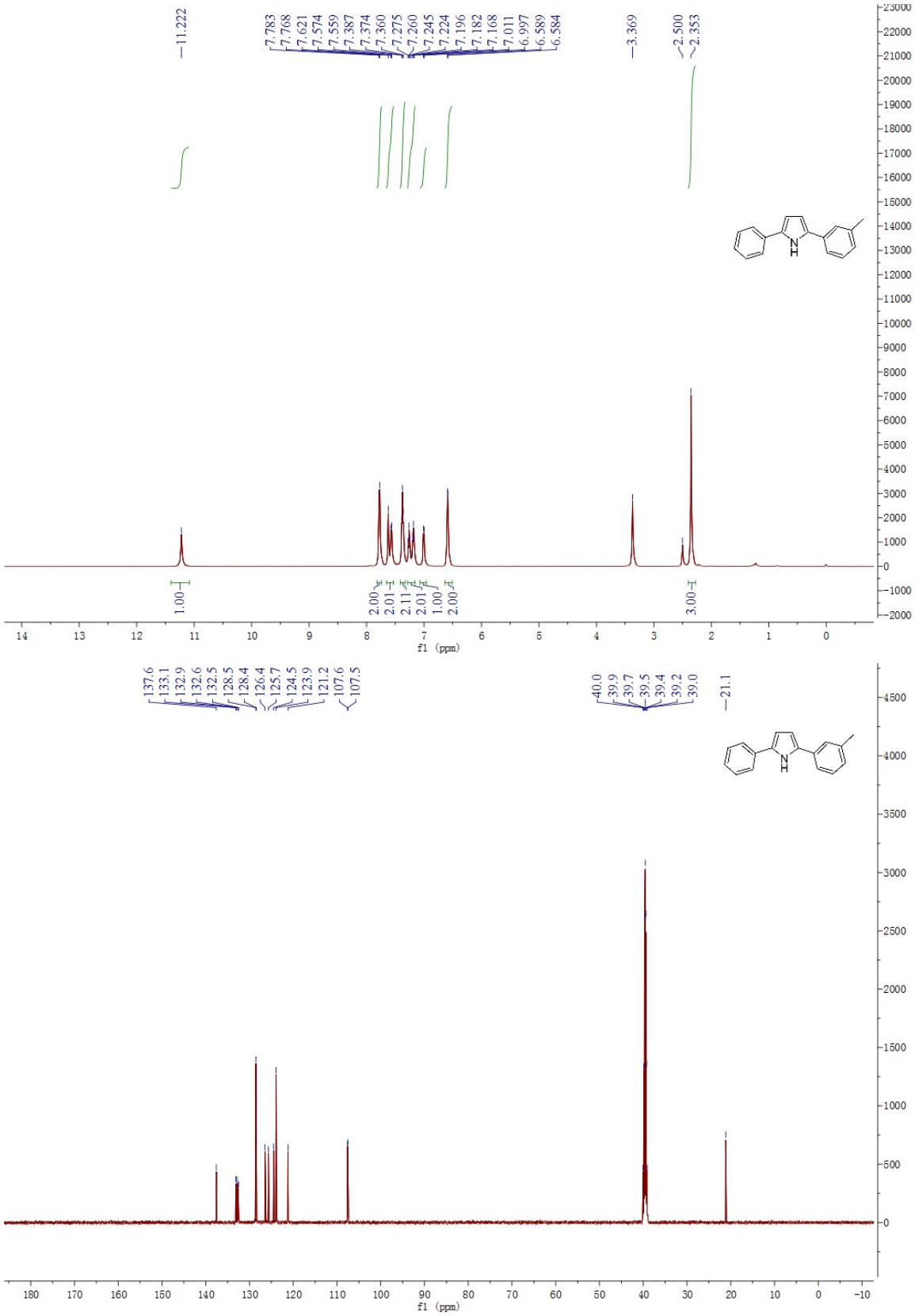


Figure S17. ^{1}H NMR of **5c** (500 MHz, DMSO) and ^{13}C NMR of **5c** (125 MHz, DMSO)

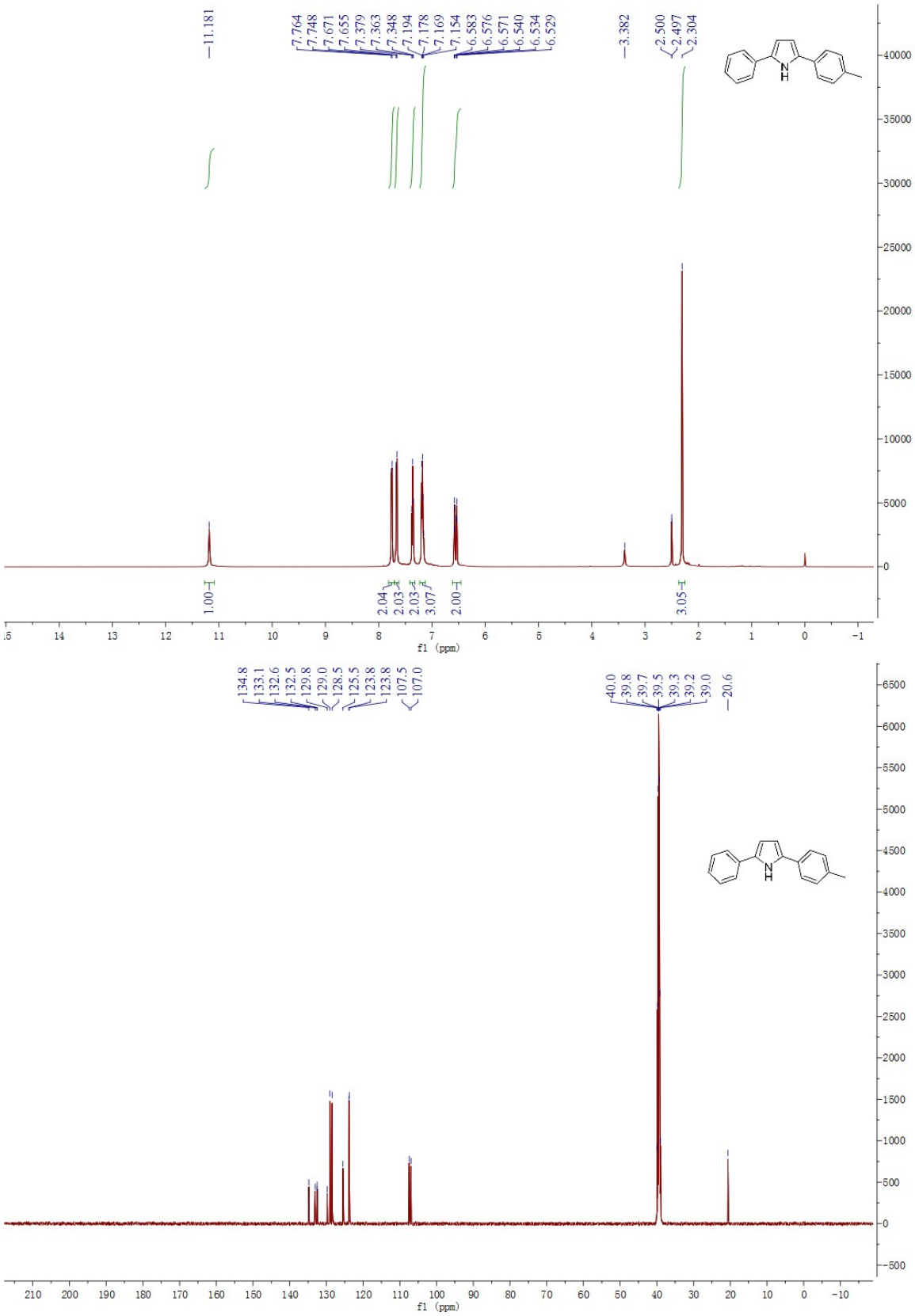


Figure S18. ^{1}H NMR of **5d** (500 MHz, DMSO) and ^{13}C NMR of **5d** (125 MHz, DMSO)

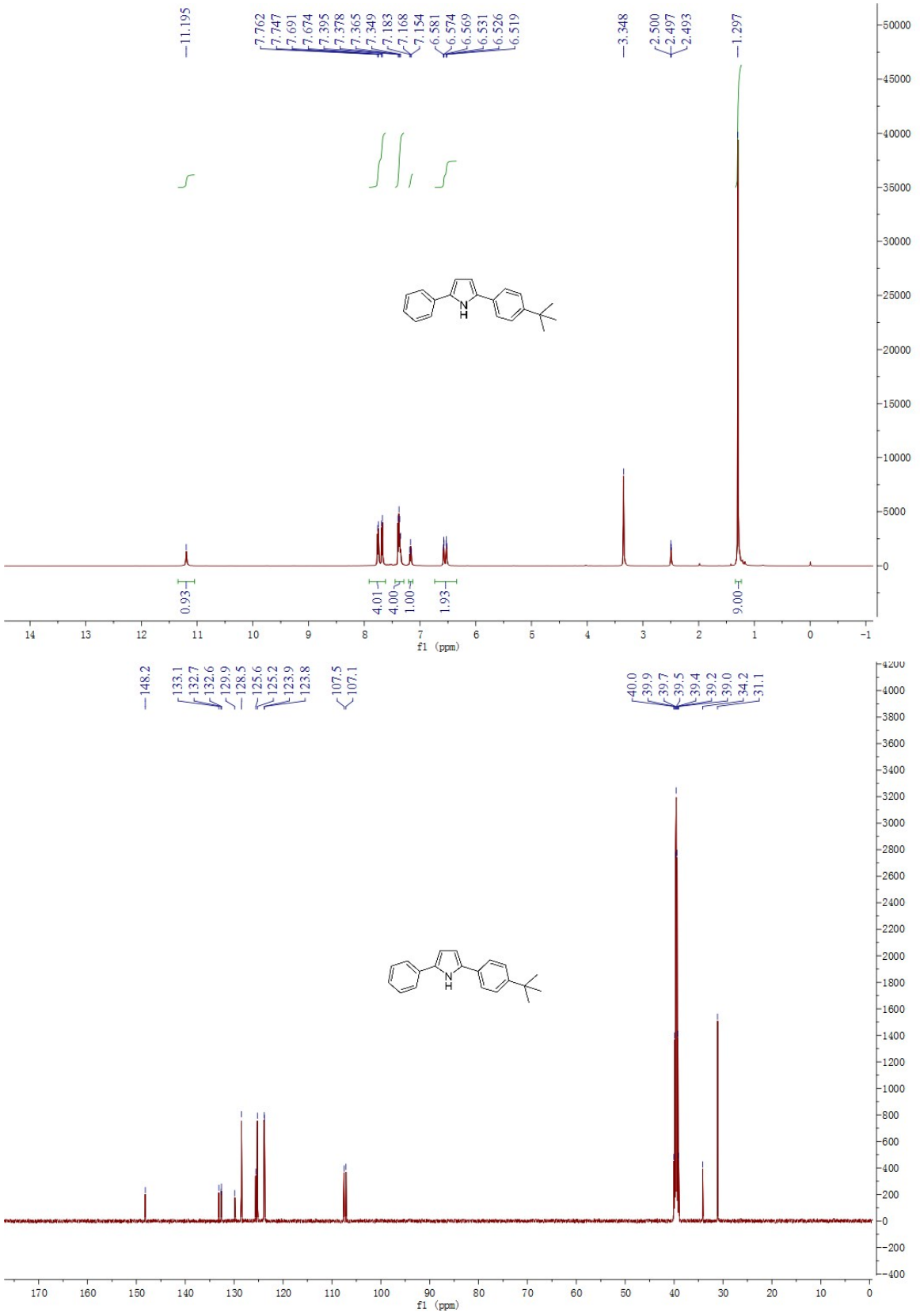


Figure S19. ^{1}H NMR of **5e** (500 MHz, DMSO) and ^{13}C NMR of **5e** (125 MHz, DMSO)

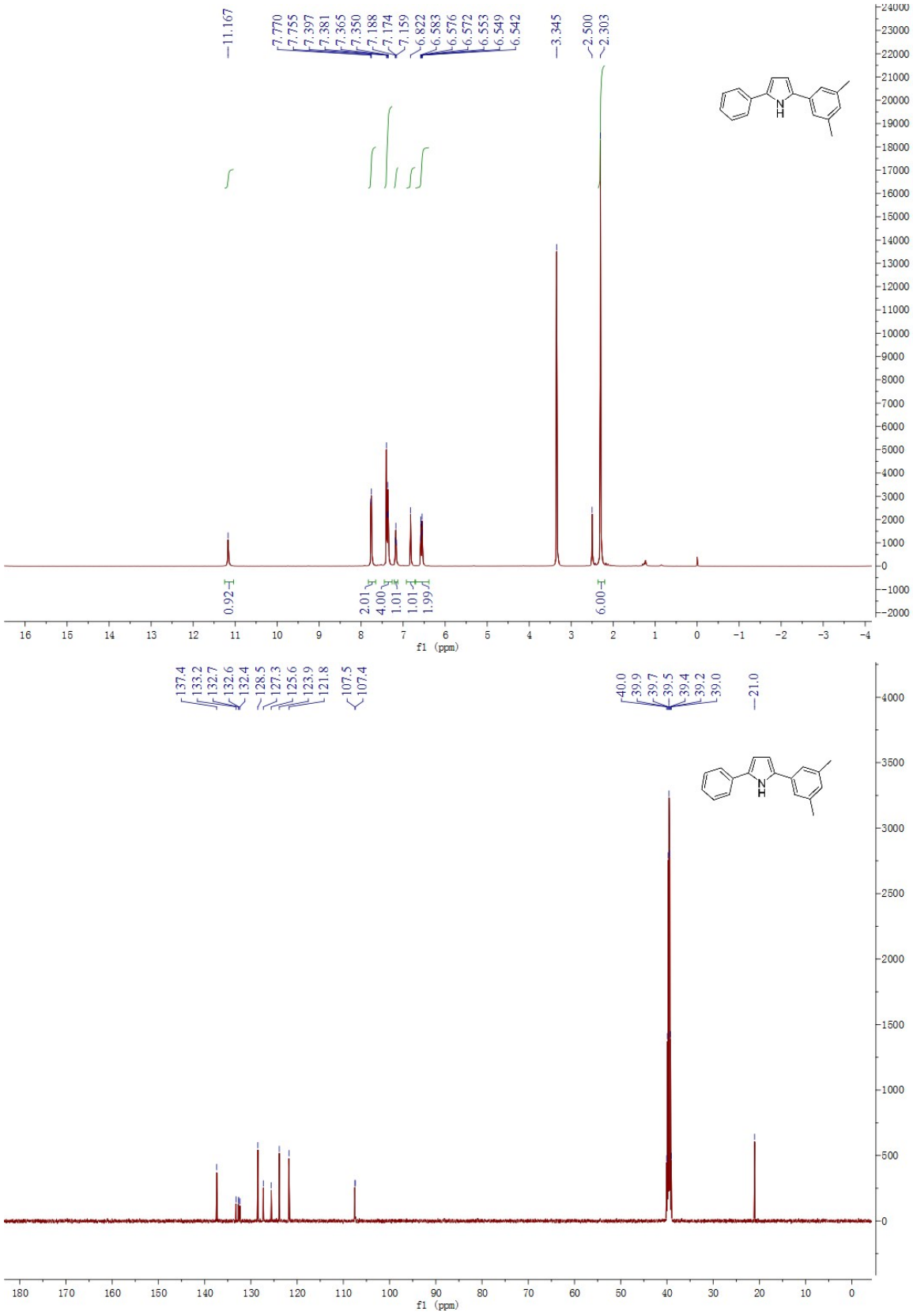


Figure S20. ^{1}H NMR of **5f** (500 MHz, DMSO) and ^{13}C NMR of **5f** (125 MHz, DMSO)

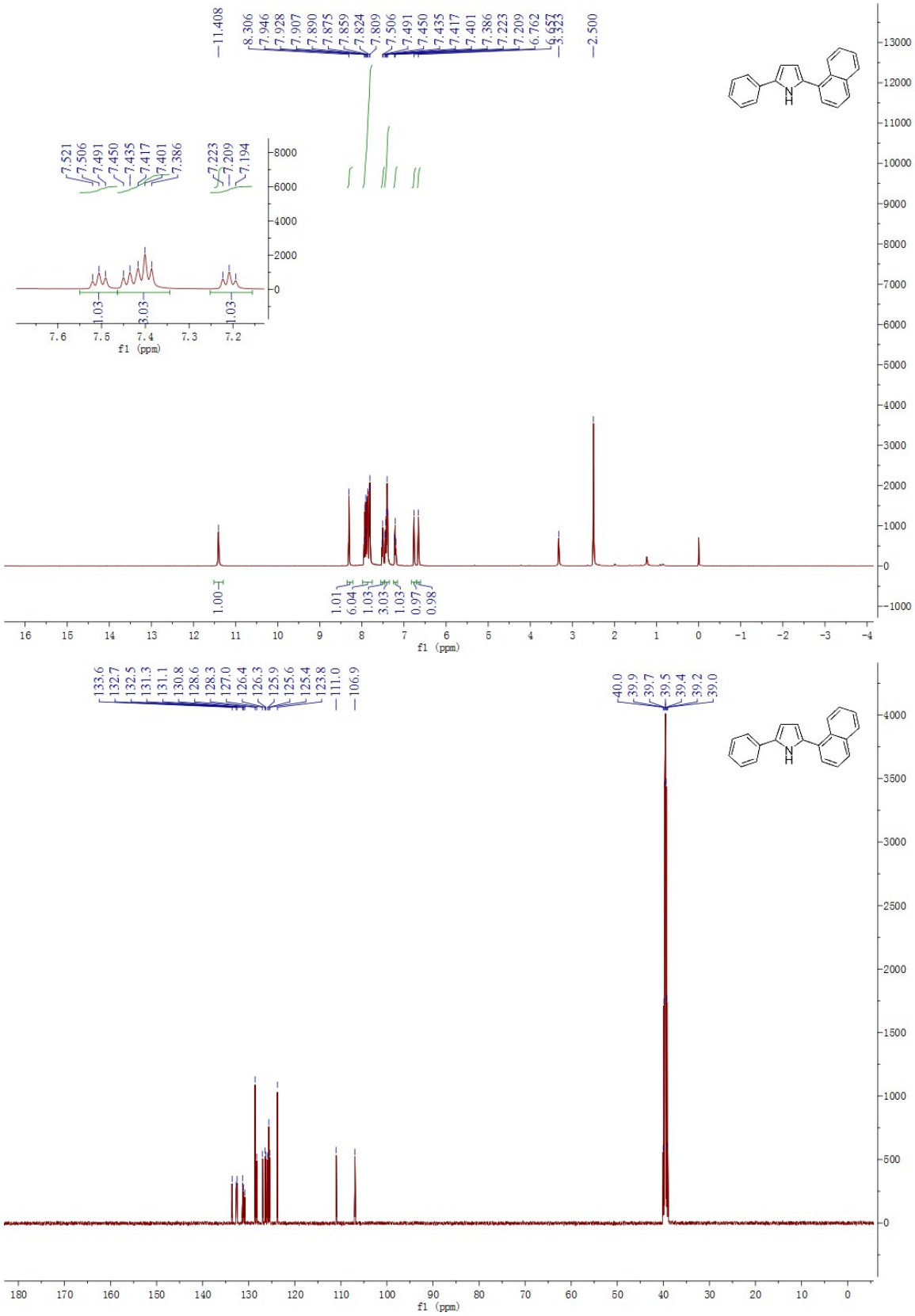


Figure S21. ^{1}H NMR of **5g** (500 MHz, DMSO) and ^{13}C NMR of **5g** (125 MHz, DMSO)

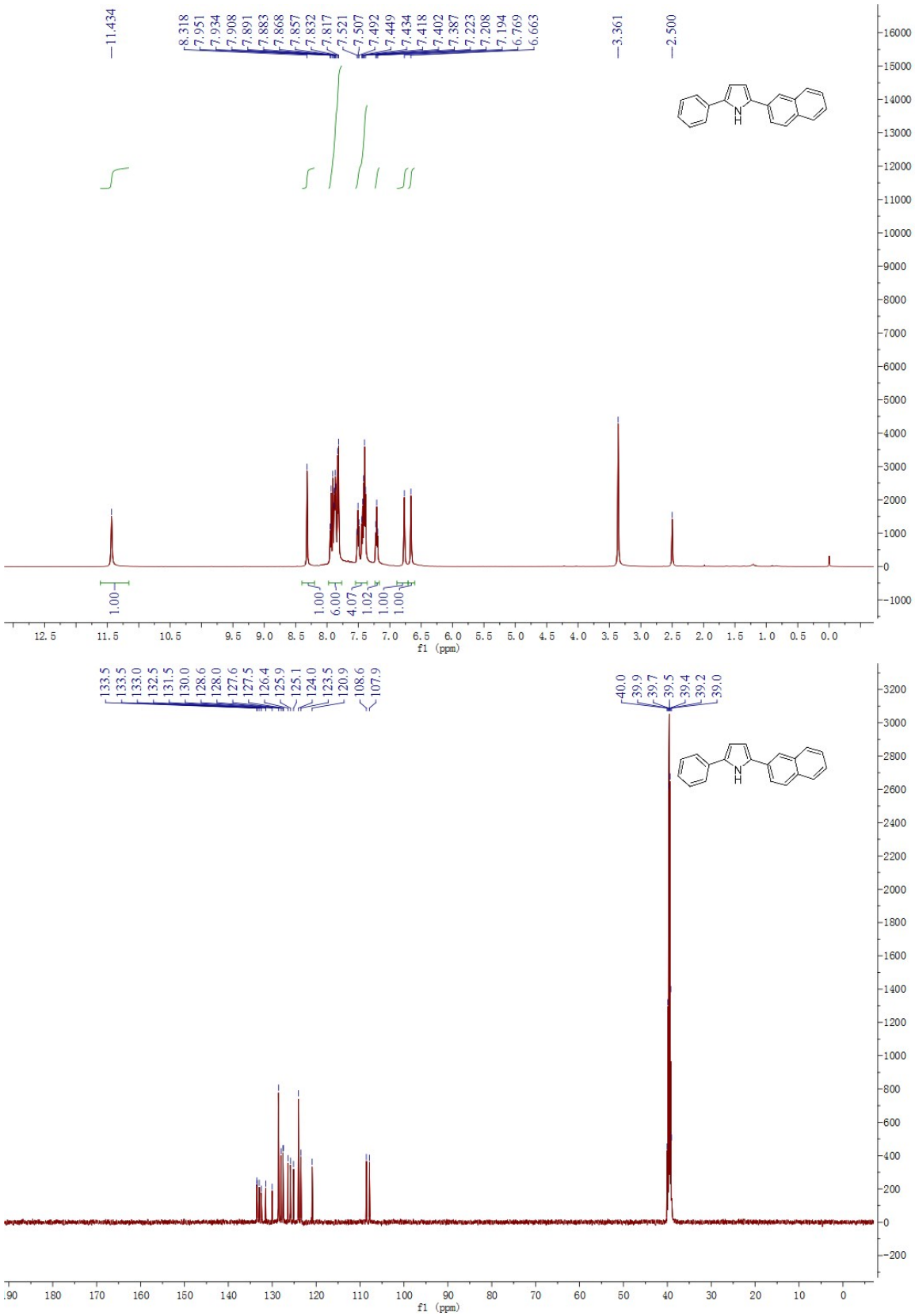


Figure S22. ^{1}H NMR of **5h** (500 MHz, DMSO) and ^{13}C NMR of **5h** (125 MHz, DMSO)

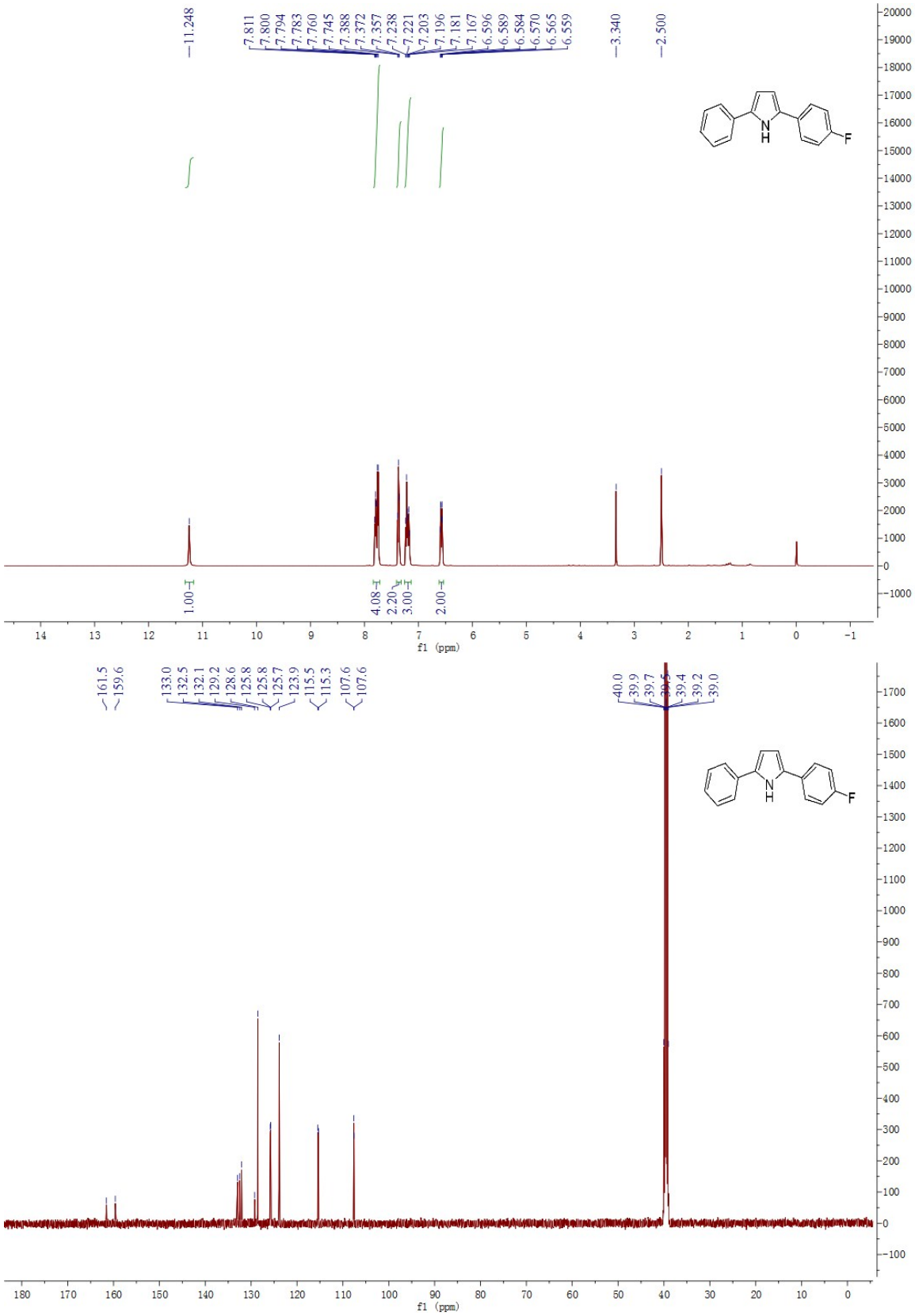


Figure S23. ^{1}H NMR of **5i** (500 MHz, DMSO) and ^{13}C NMR of **5i** (125 MHz, DMSO)

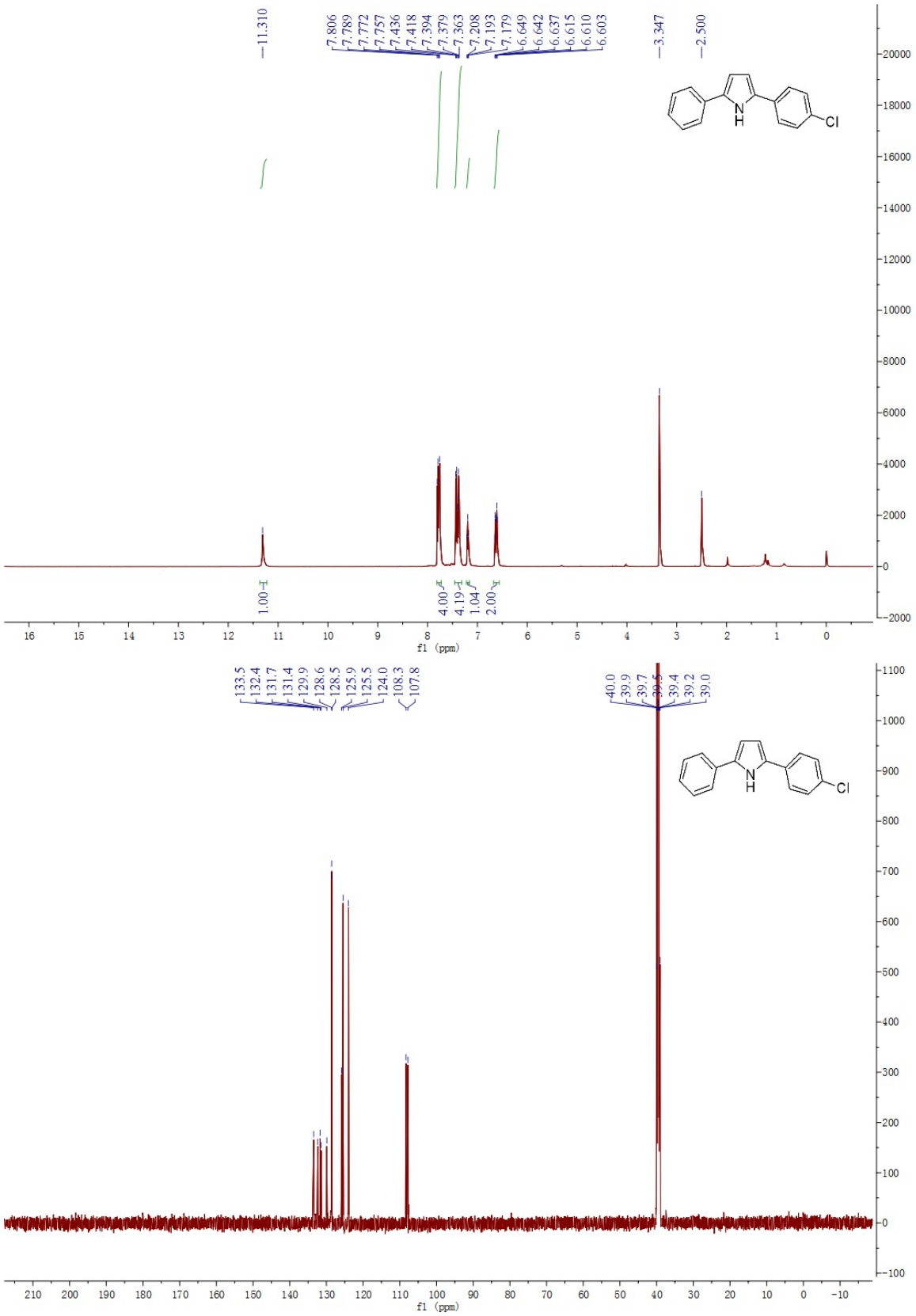


Figure S24. ^{1}H NMR of **5j** (500 MHz, DMSO) and ^{13}C NMR of **5j** (125 MHz, DMSO)

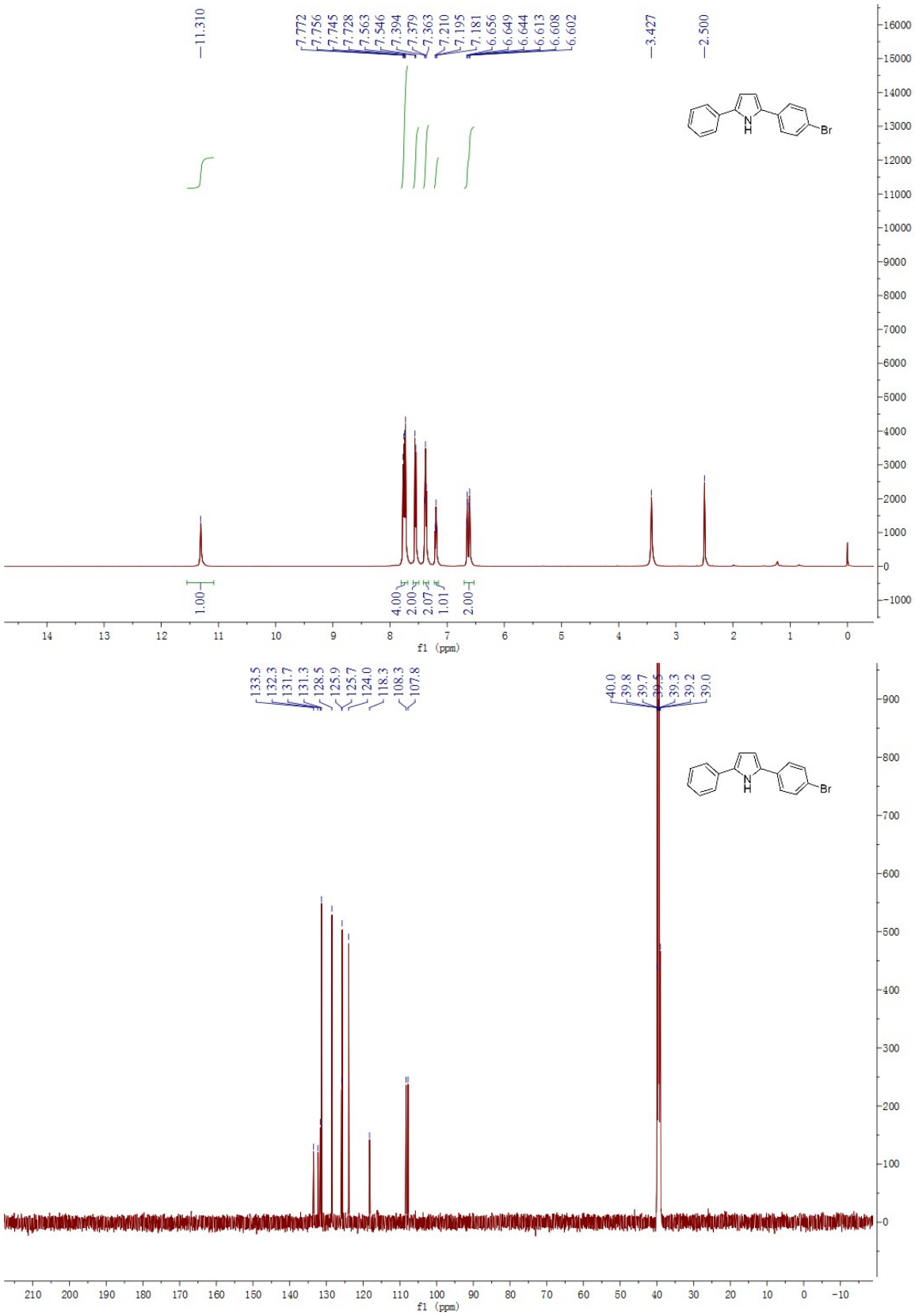


Figure S25. ^{1}H NMR of **5k** (500 MHz, DMSO) and ^{13}C NMR of **5k** (125 MHz, DMSO)

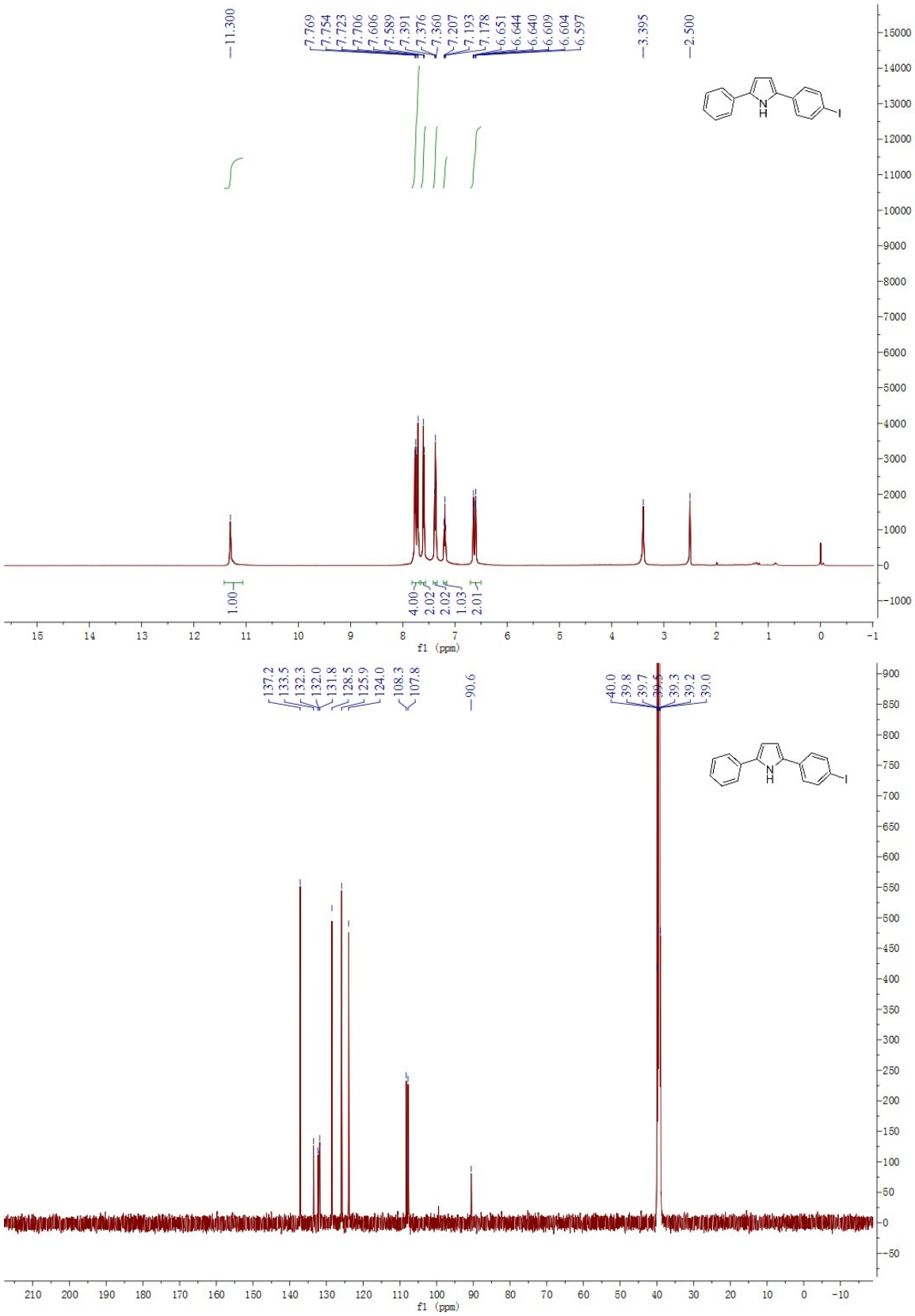


Figure S26. ^{1}H NMR of **5l** (500 MHz, DMSO) and ^{13}C NMR of **5l** (125 MHz, DMSO)

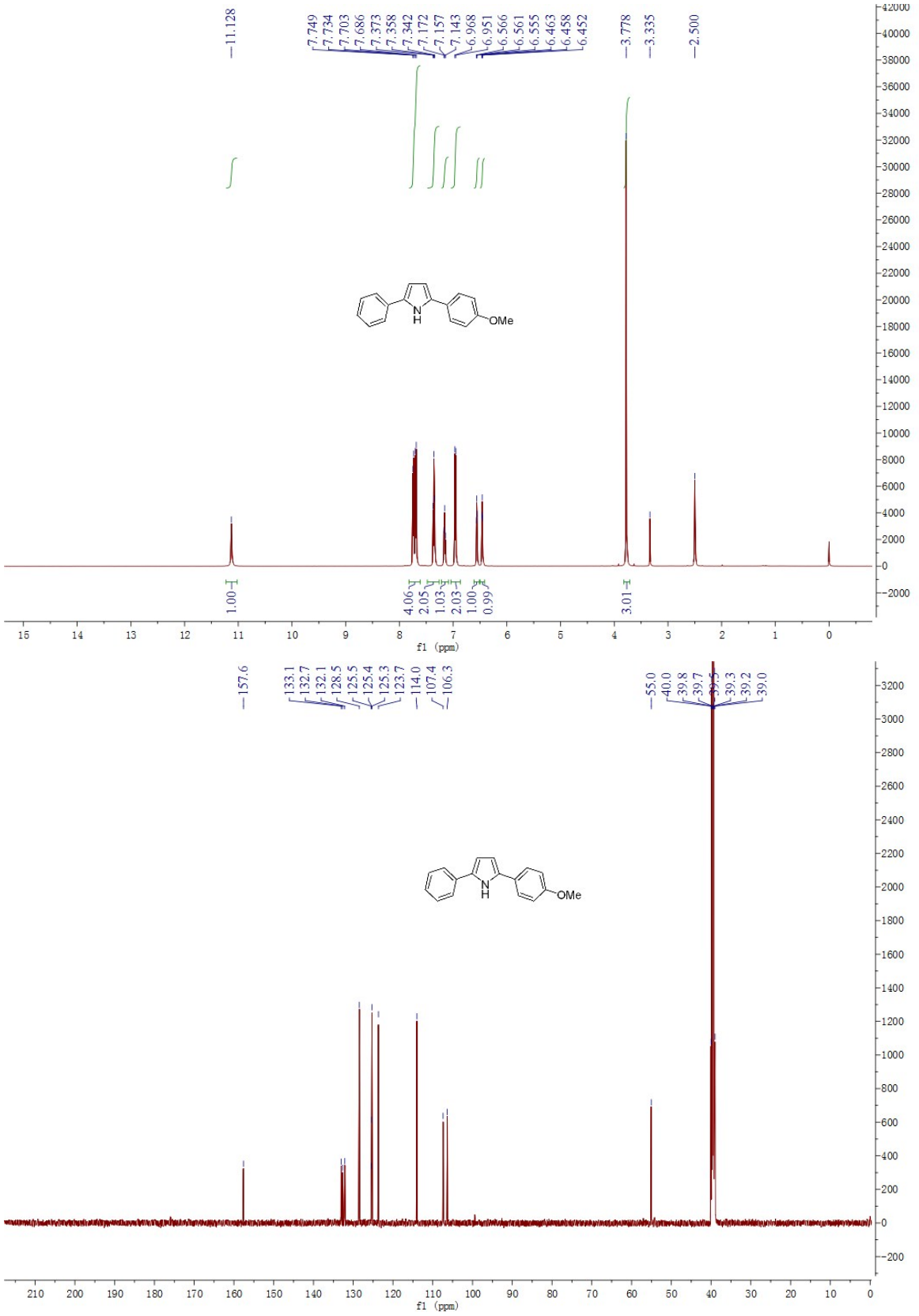


Figure S27. ^{1}H NMR of **5m** (500 MHz, DMSO) and ^{13}C NMR of **5m** (125 MHz, DMSO)

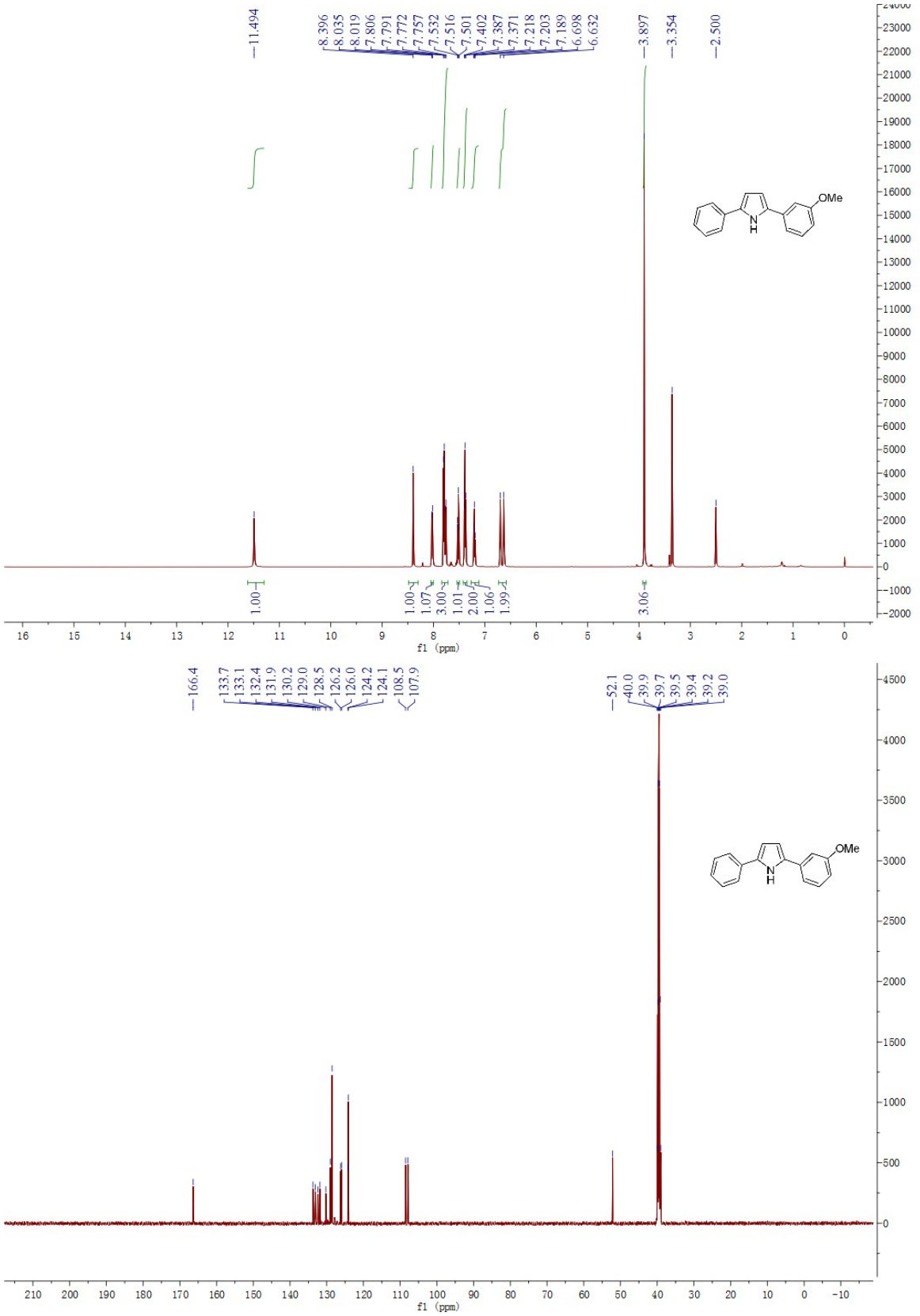


Figure S28. ^{1}H NMR of **5n** (500 MHz, DMSO) and ^{13}C NMR of **5n** (125 MHz, DMSO)

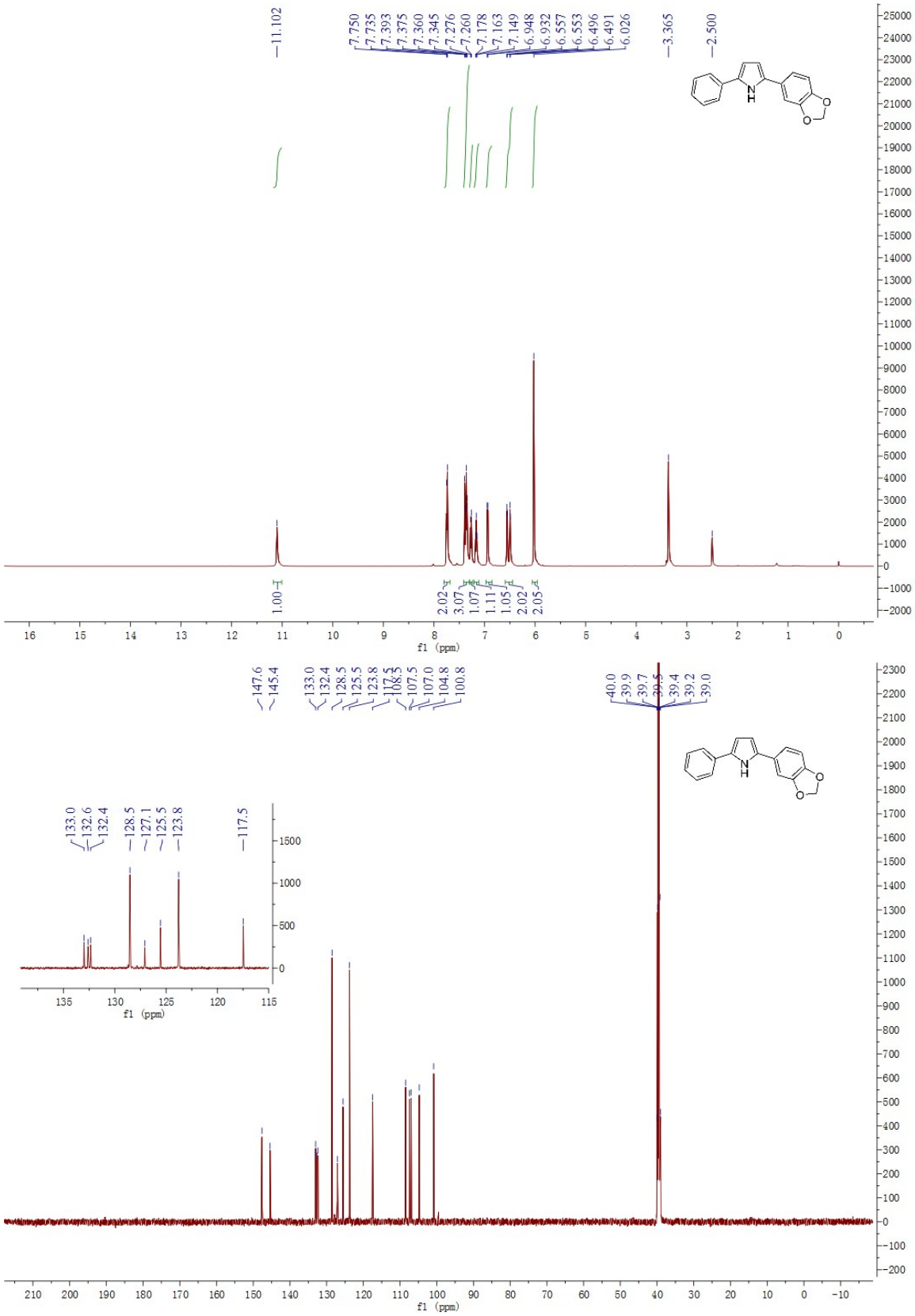


Figure S29. ^{1}H NMR of **5o** (500 MHz, DMSO) and ^{13}C NMR of **5o** (125 MHz, DMSO)

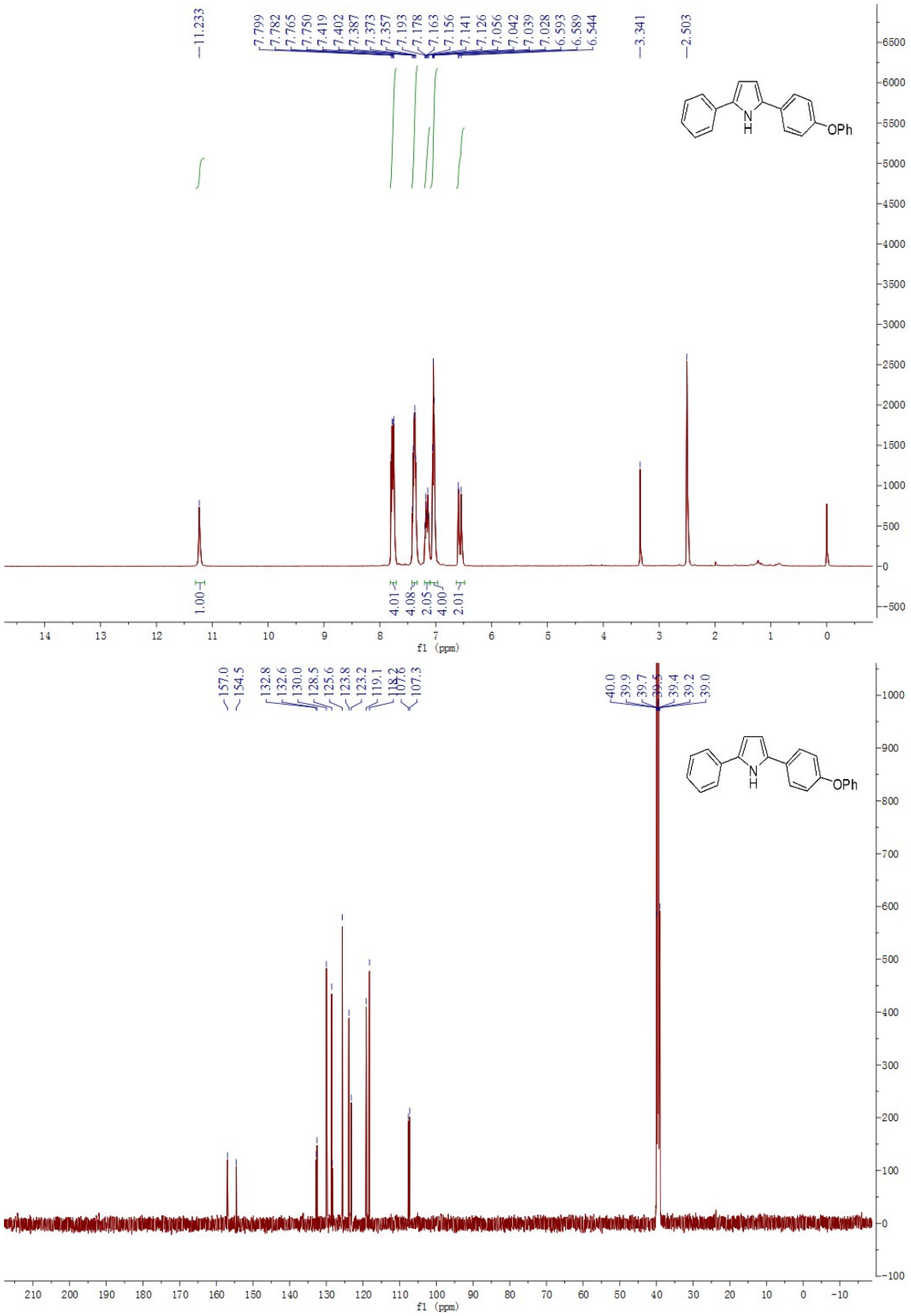


Figure S30. ^{1}H NMR of **5p** (500 MHz, DMSO) and ^{13}C NMR of **5p** (125 MHz, DMSO)

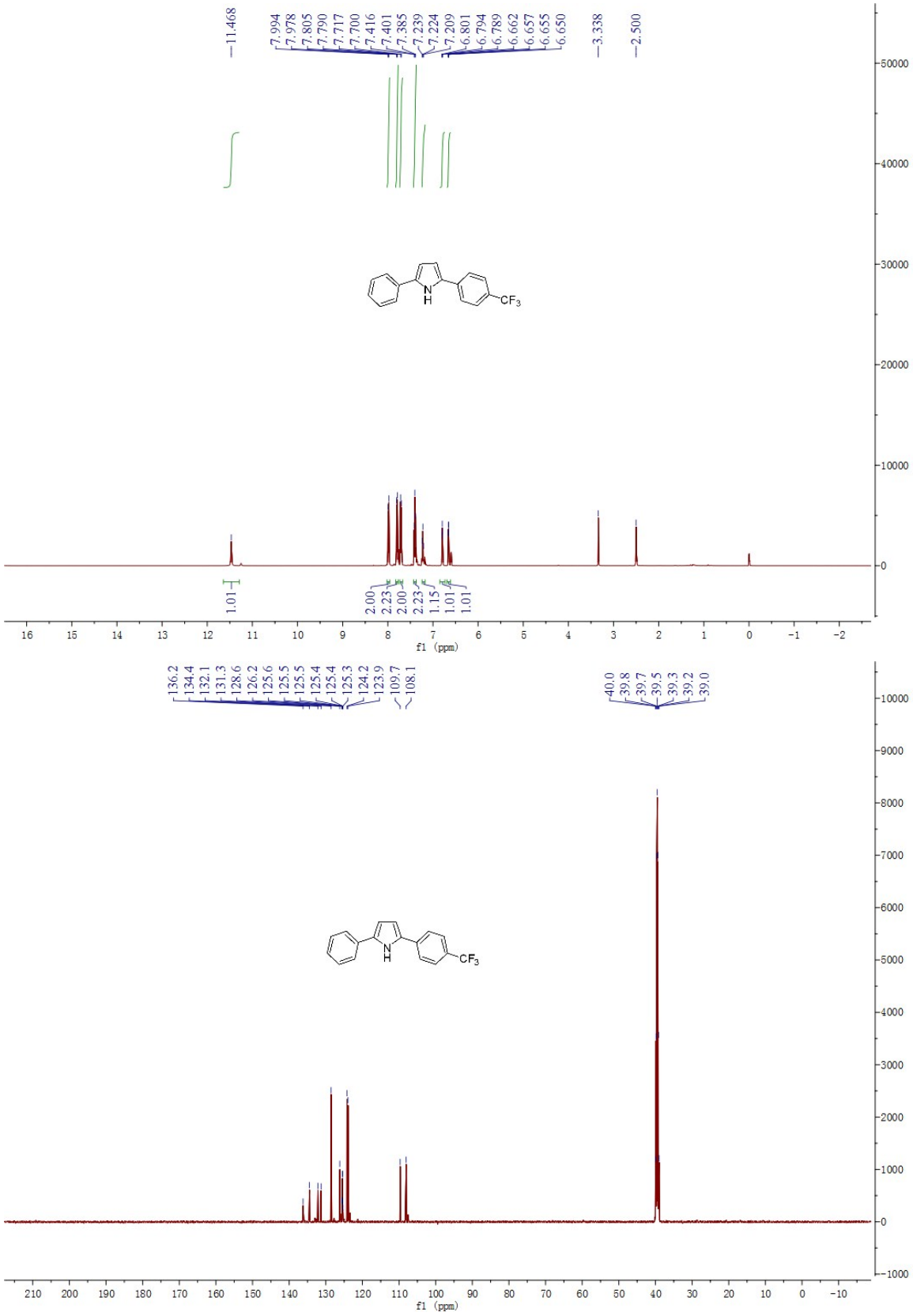


Figure S31. ^{1}H NMR of **5q** (500 MHz, DMSO) and ^{13}C NMR of **5q** (125 MHz, DMSO)

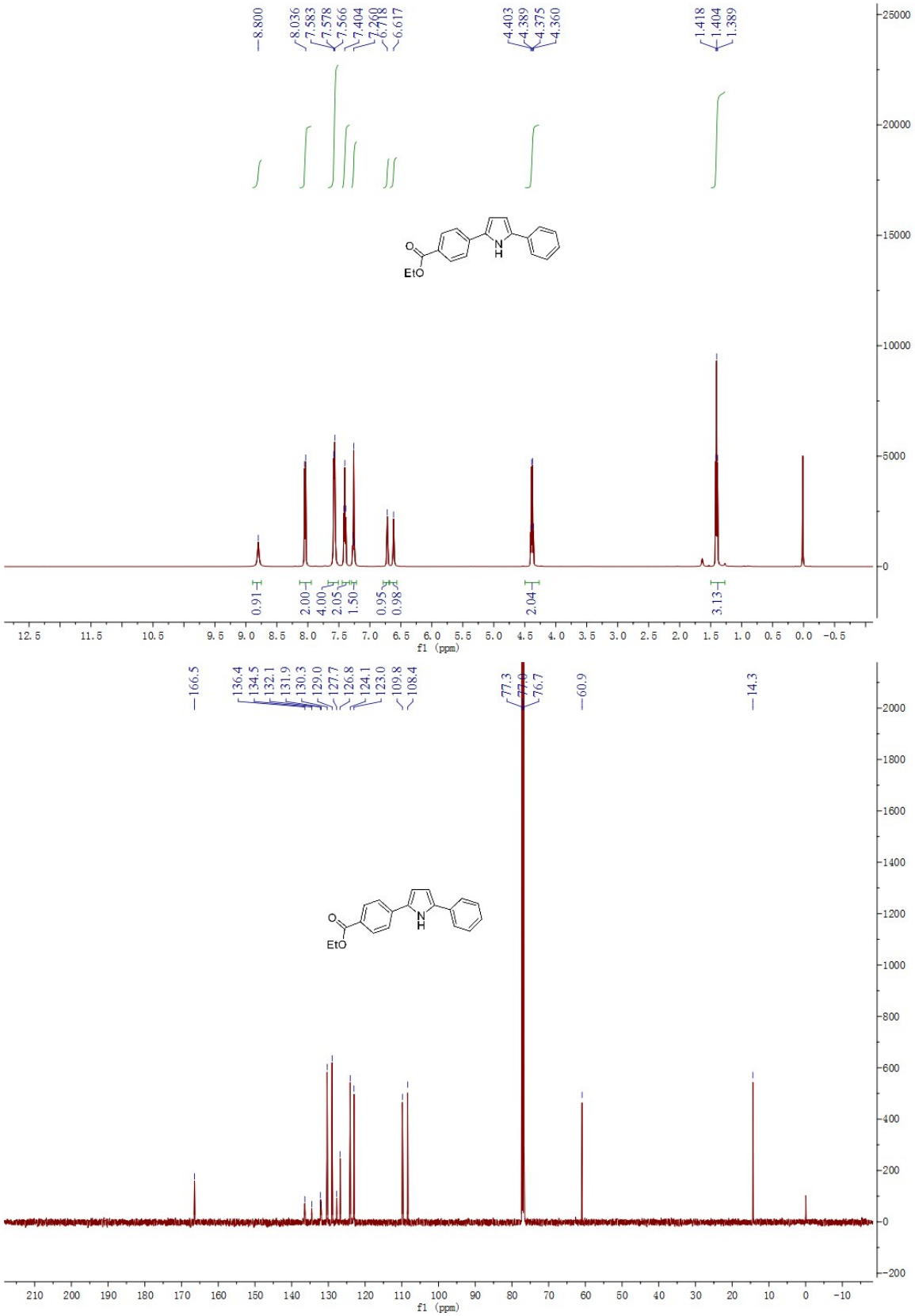


Figure S32. ^{1}H NMR of **6r** (500 MHz, $CDCl_3$) and ^{13}C NMR of **6r** (125 MHz, $CDCl_3$)

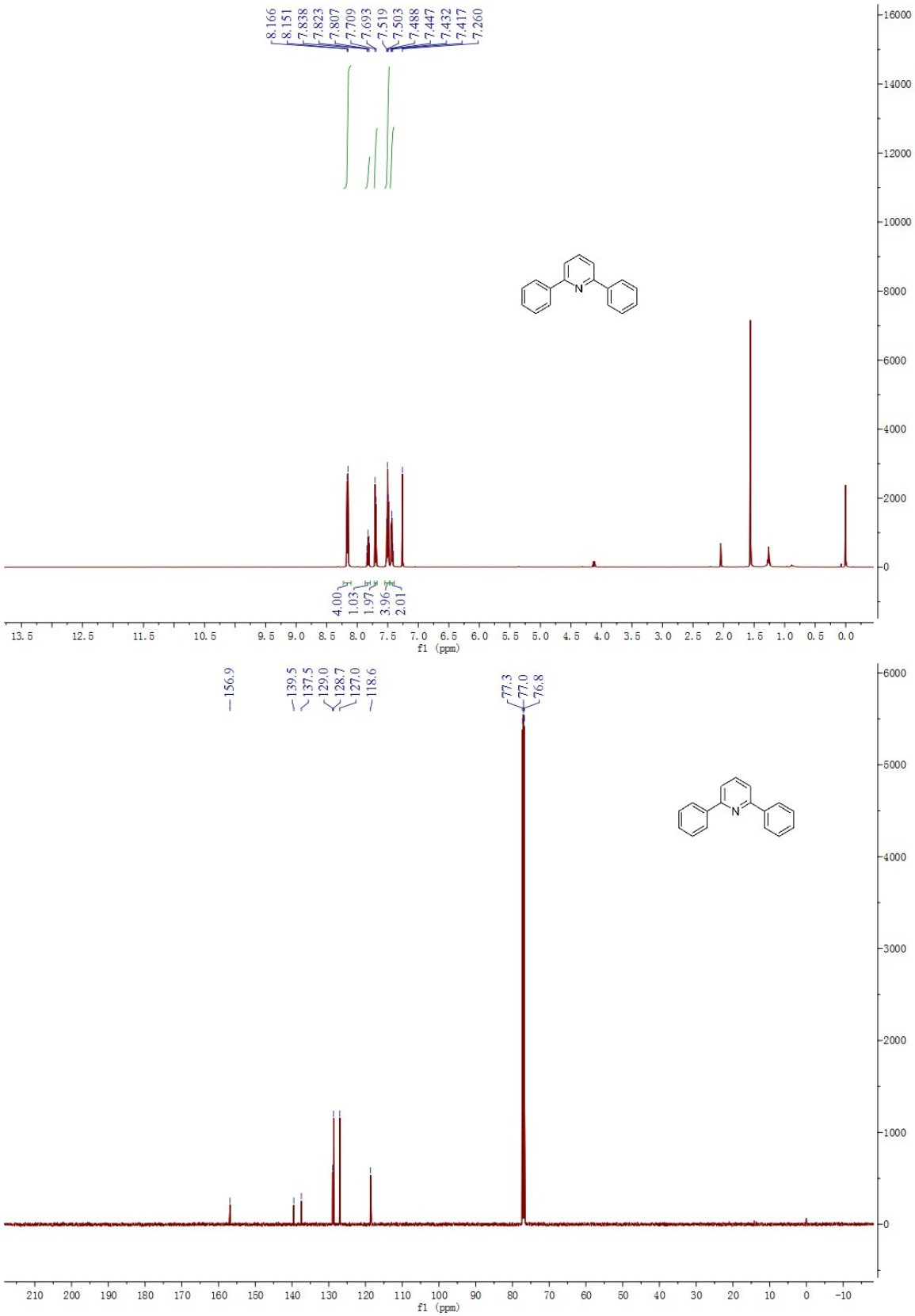


Figure S33. ^{1}H NMR of **7a** (500 MHz, $CDCl_3$) and ^{13}C NMR of **7a** (125 MHz, $CDCl_3$)

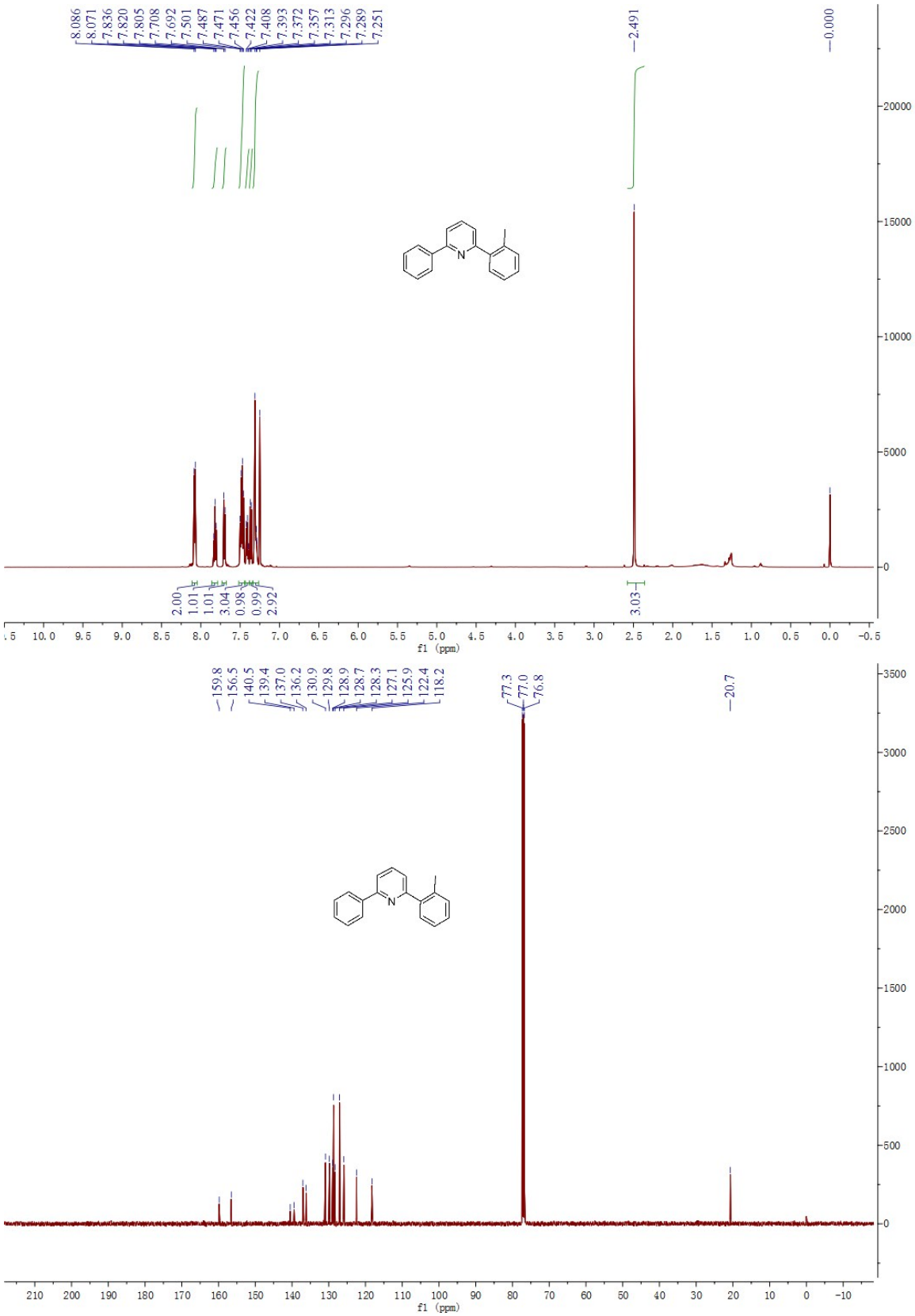


Figure S34. ^{1}H NMR of **7b** (500 MHz, $CDCl_3$) and ^{13}C NMR of **7b** (125 MHz, $CDCl_3$)

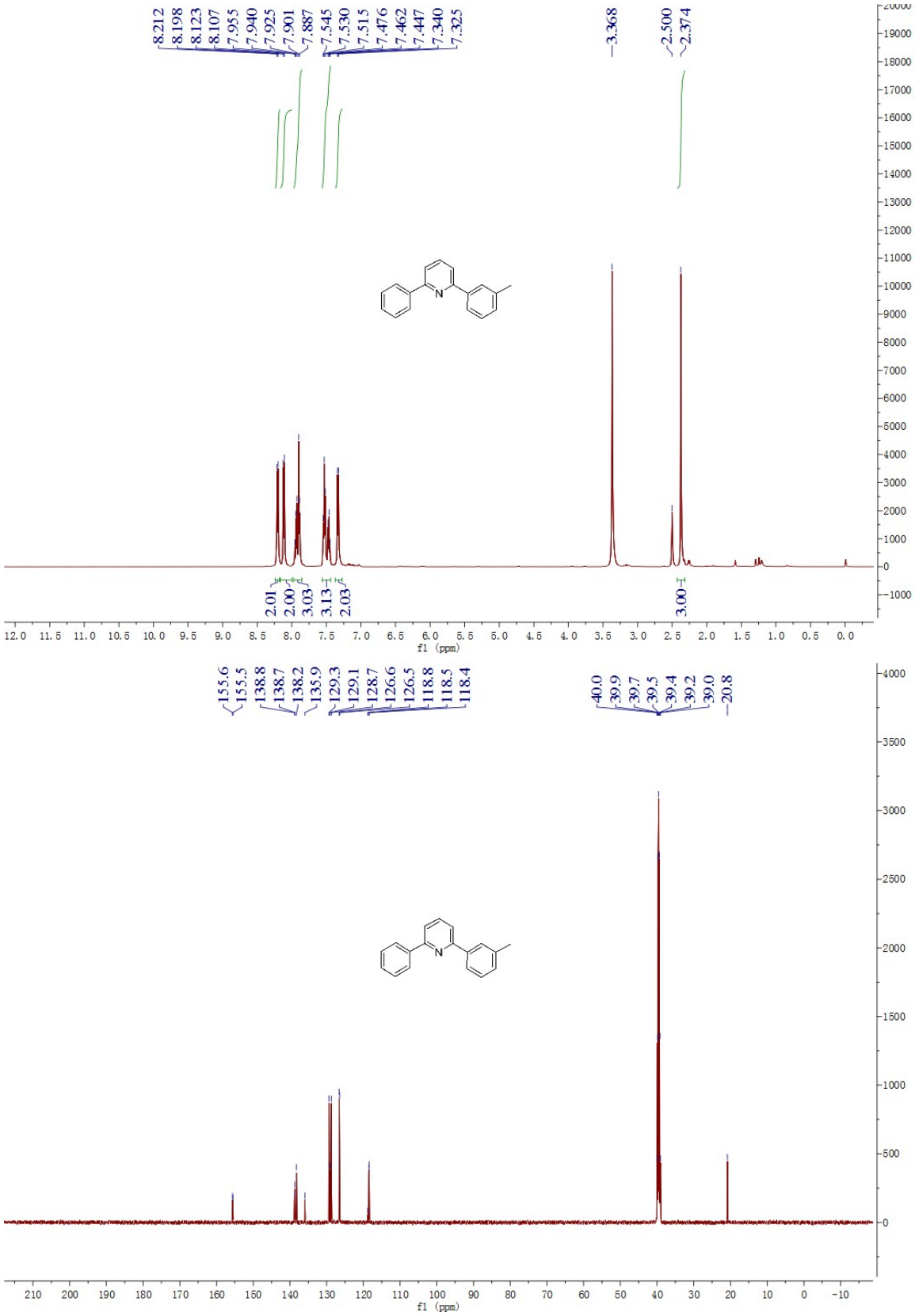


Figure S35. ^{1}H NMR of **7c** (500 MHz, DMSO) and ^{13}C NMR of **7c** (125 MHz, DMSO)

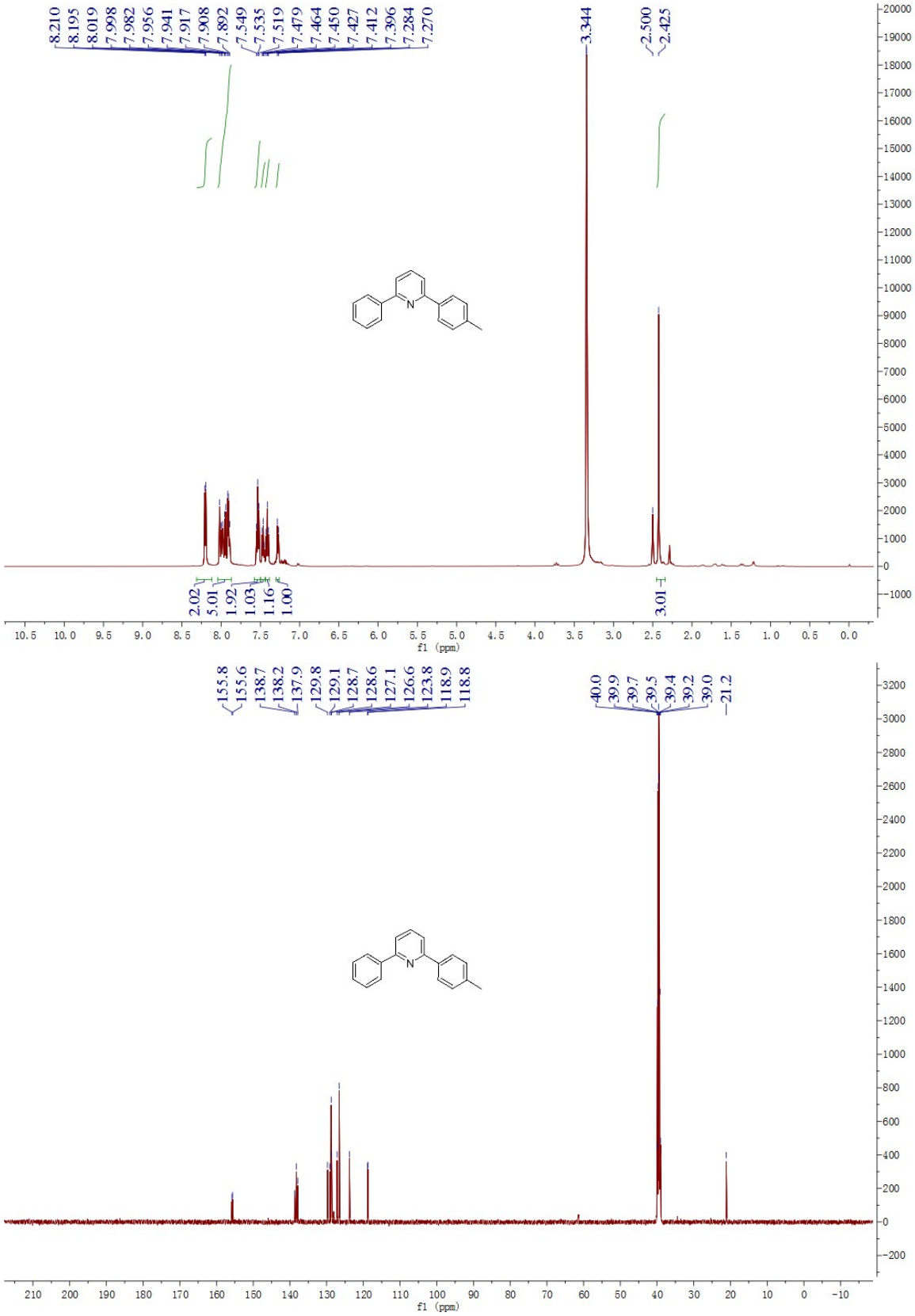


Figure S36. ^{1}H NMR of **7d** (500 MHz, DMSO) and ^{13}C NMR of **7d** (125 MHz, DMSO)

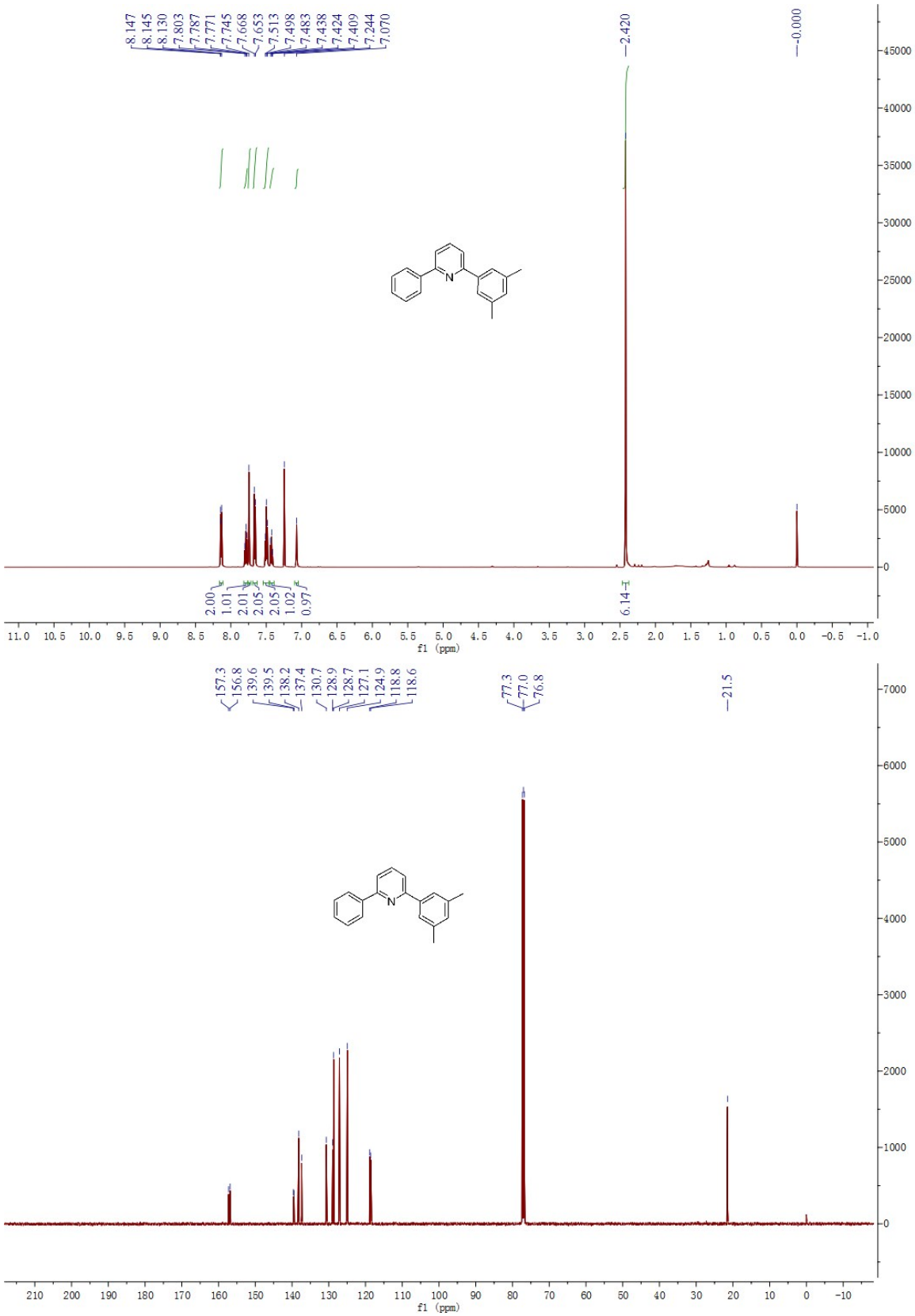


Figure S37. ^{1}H NMR of **7e** (500 MHz, $CDCl_3$) and ^{13}C NMR of **7e** (125 MHz, $CDCl_3$)

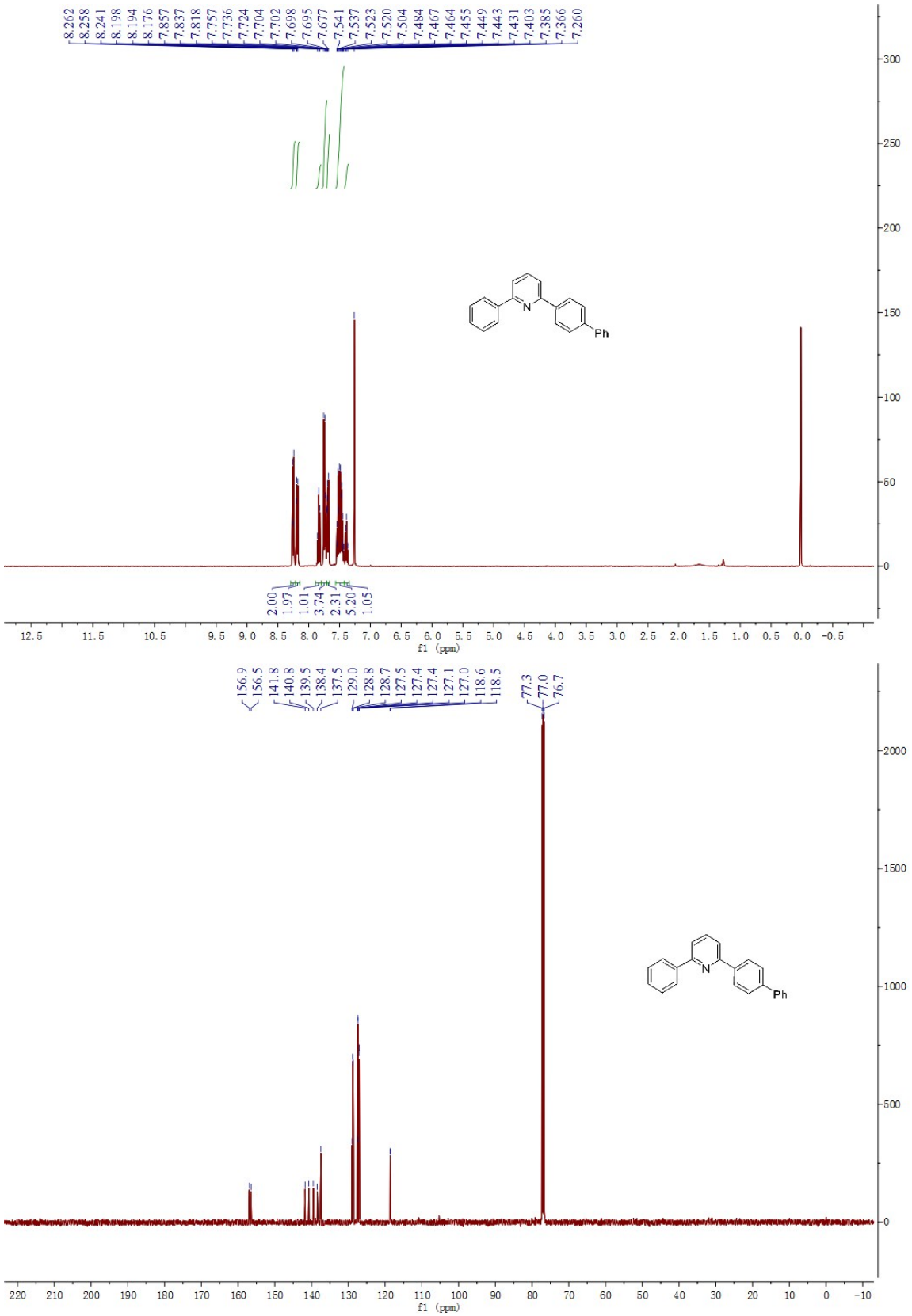


Figure S38. ^{1}H NMR of **7f** (500 MHz, $CDCl_3$) and ^{13}C NMR of **7f** (125 MHz, $CDCl_3$)

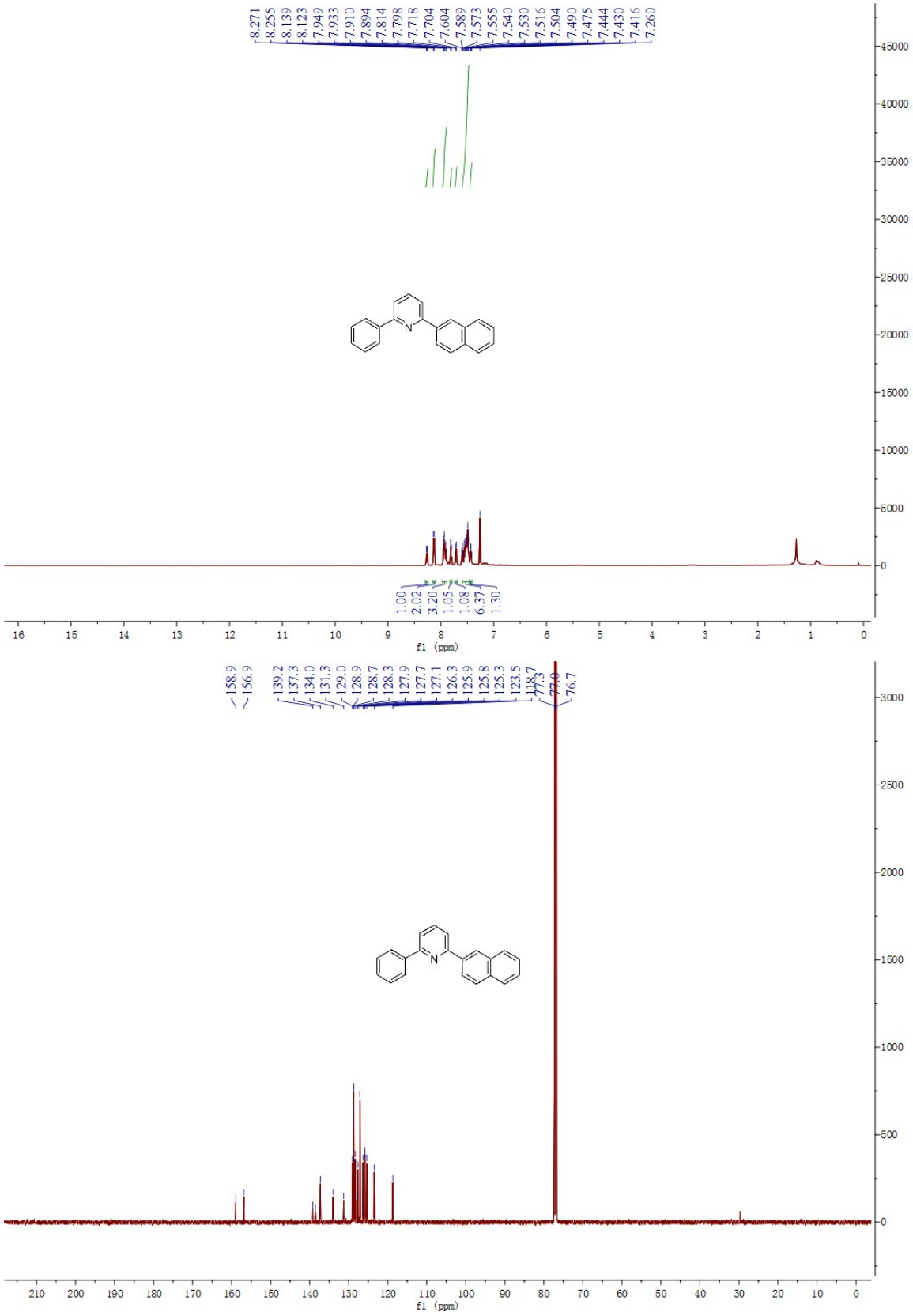


Figure S39. ^{1}H NMR of **7g** (500 MHz, $CDCl_3$) and ^{13}C NMR of **7g** (125 MHz, $CDCl_3$)

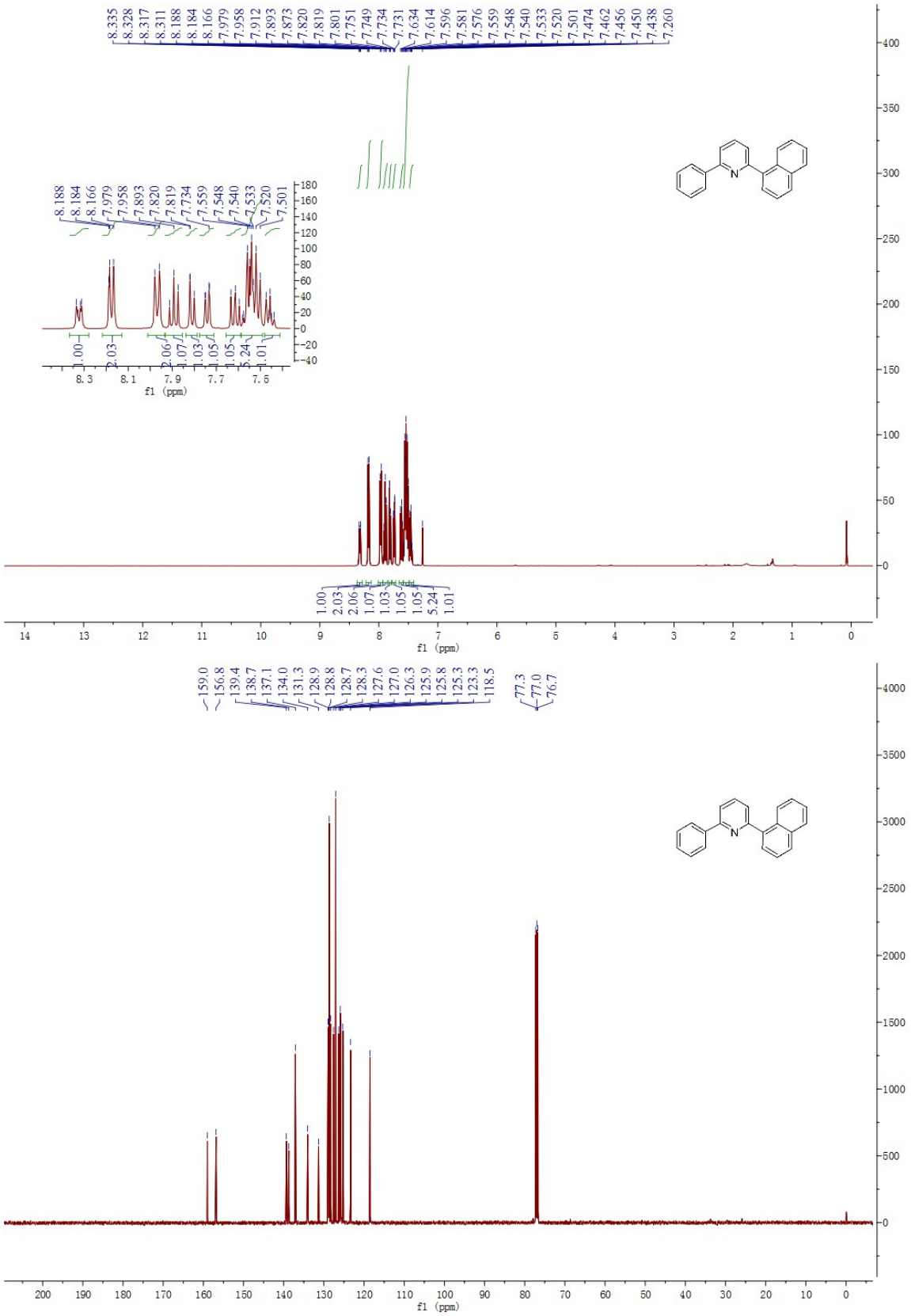


Figure S40. ^{1}H NMR of **7h** (500 MHz, $CDCl_3$) and ^{13}C NMR of **7h** (125 MHz, $CDCl_3$)

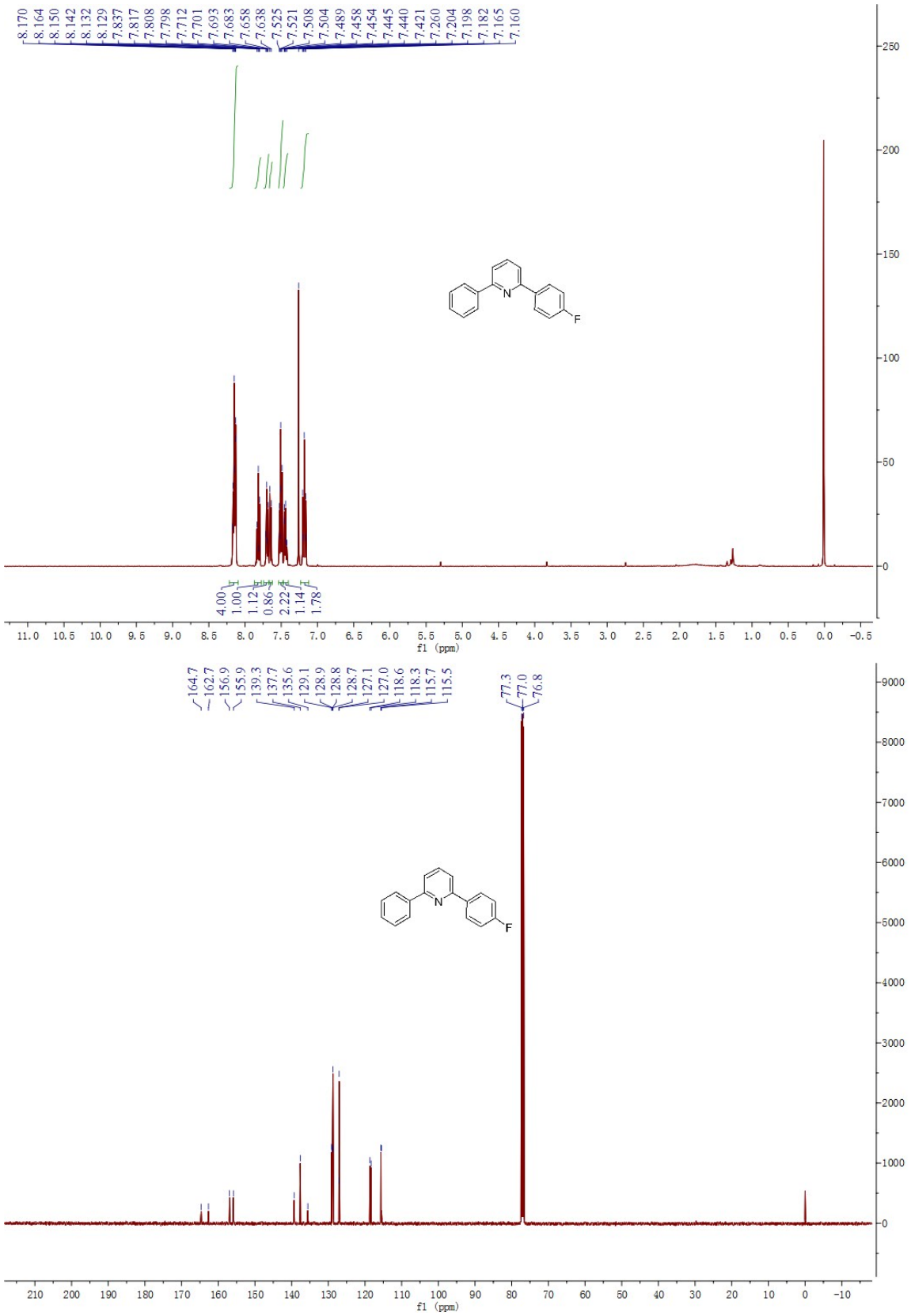


Figure S41. ^{1}H NMR of **7i** (500 MHz, $CDCl_3$) and ^{13}C NMR of **7i** (125 MHz, $CDCl_3$)

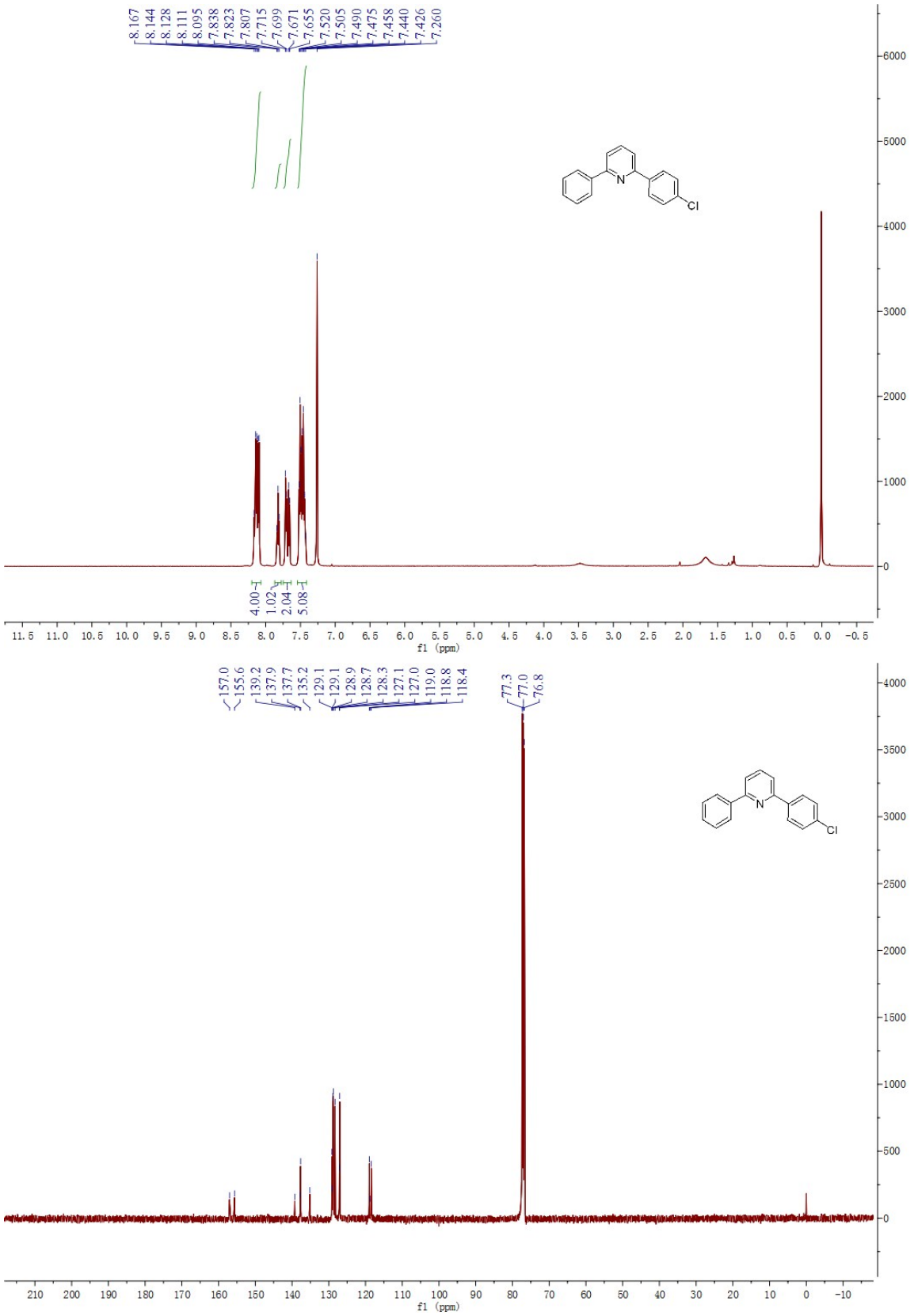


Figure S42. ^{1}H NMR of **7j** (500 MHz, $CDCl_3$) and ^{13}C NMR of **7j** (125 MHz, $CDCl_3$)

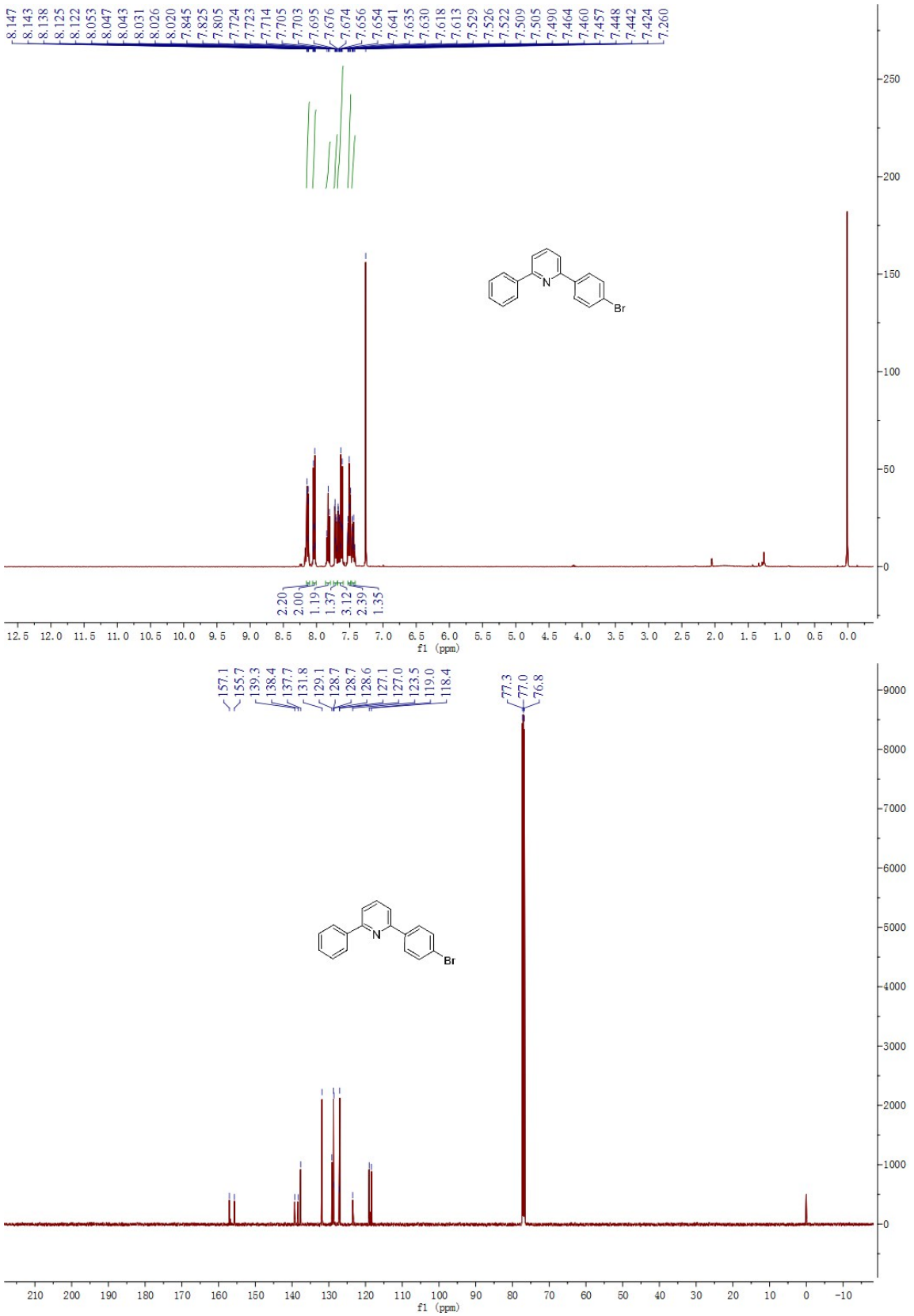


Figure S43. ^{1}H NMR of **7k** (500 MHz, $CDCl_3$) and ^{13}C NMR of **7k** (125 MHz, $CDCl_3$)

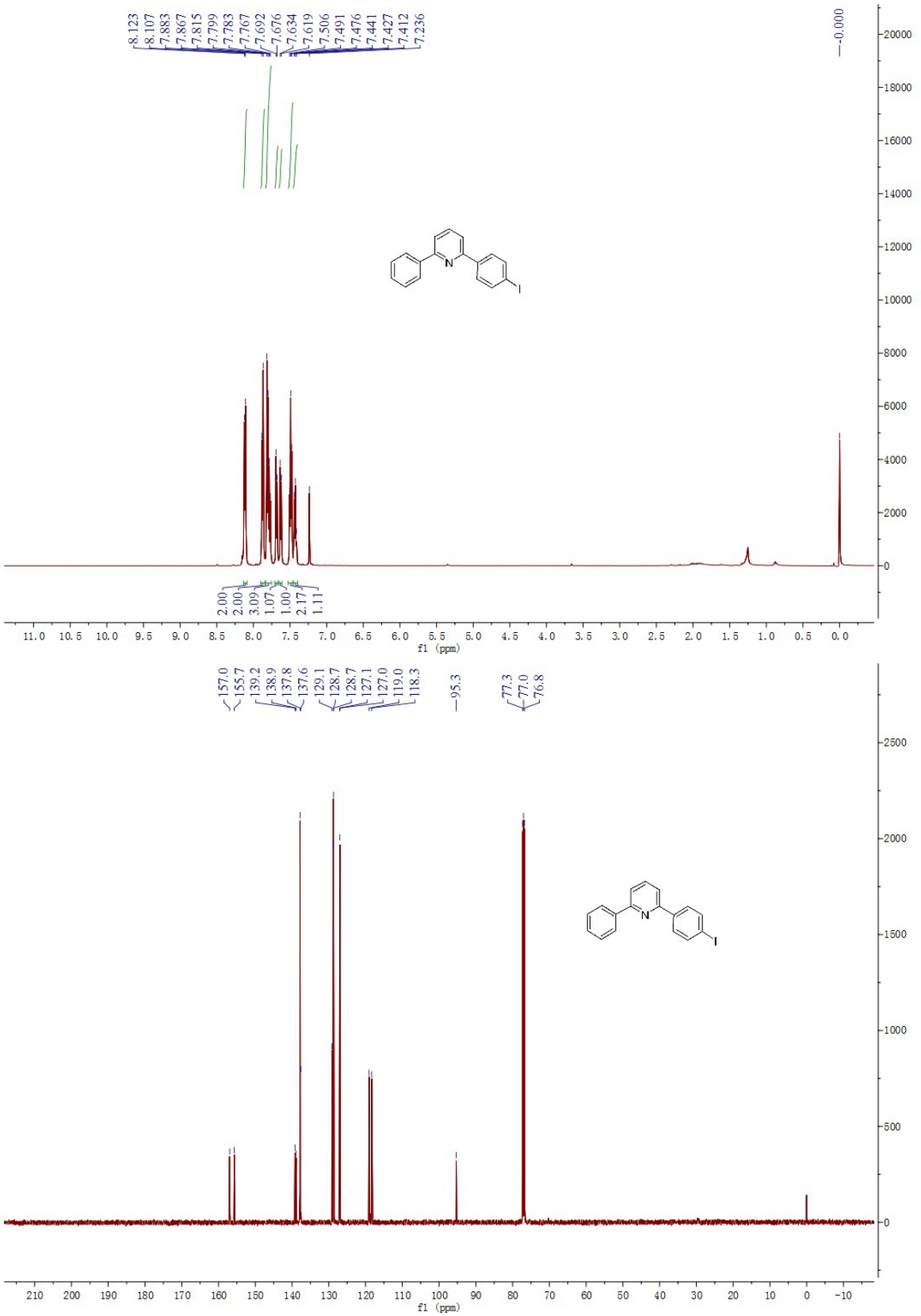


Figure S44. ^{1}H NMR of **7l** (500 MHz, $CDCl_3$) and ^{13}C NMR of **7l** (125 MHz, $CDCl_3$)

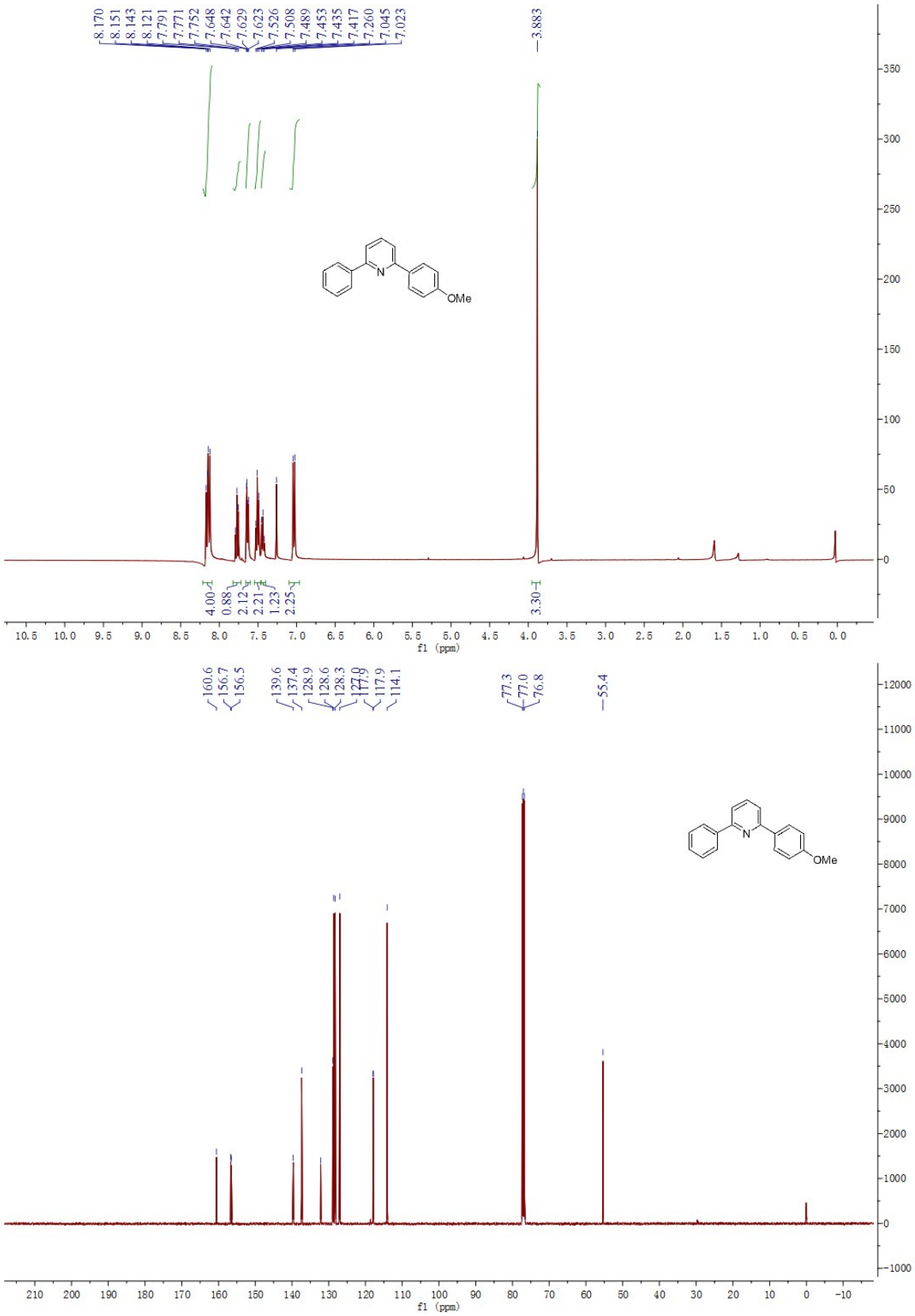


Figure S45. ^{1}H NMR of **7m** (500 MHz, $CDCl_3$) and ^{13}C NMR of **7m** (125 MHz, $CDCl_3$)

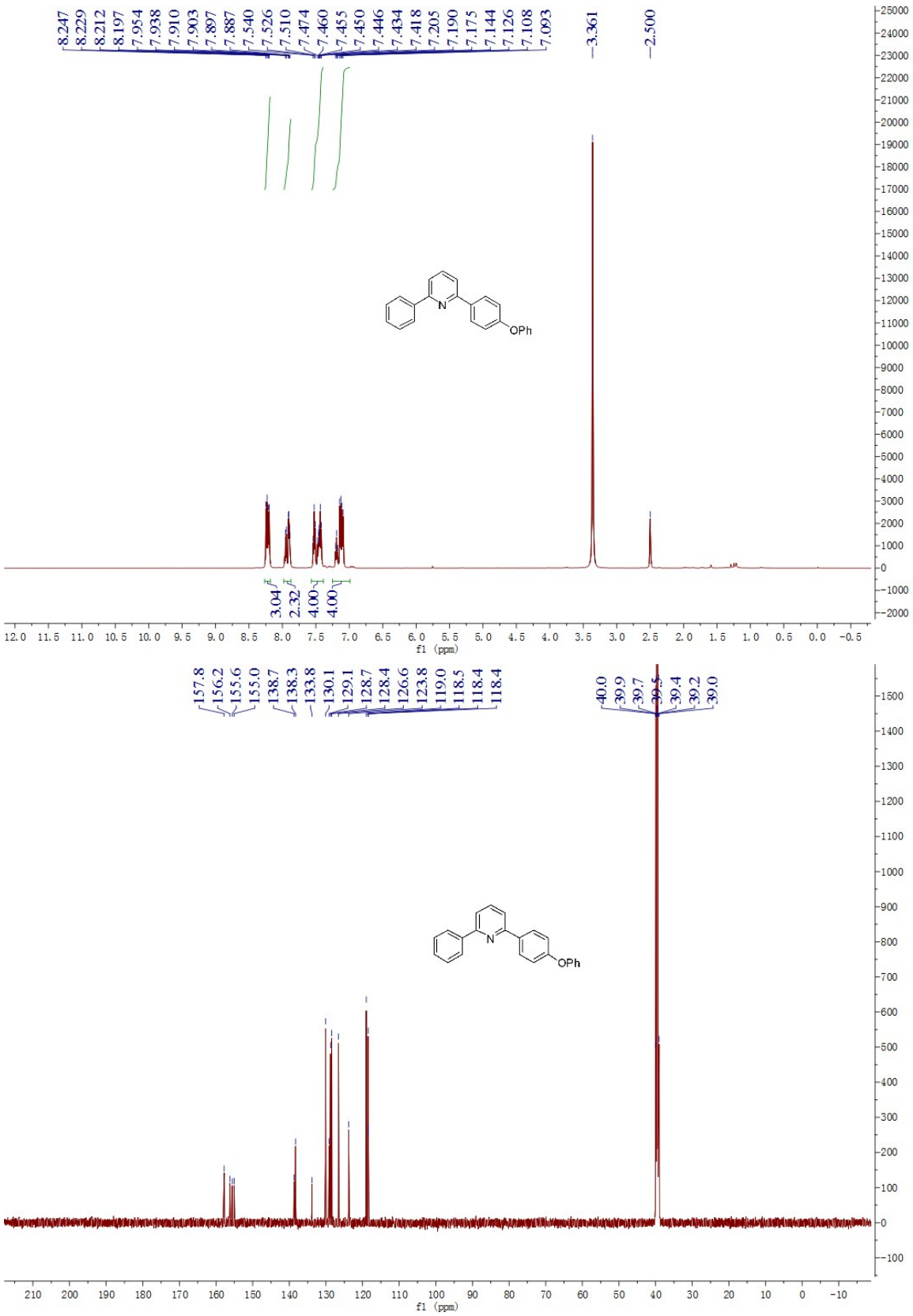


Figure S46. ^{1}H NMR of **7n** (500 MHz, DMSO) and ^{13}C NMR of **7n** (125 MHz, DMSO)

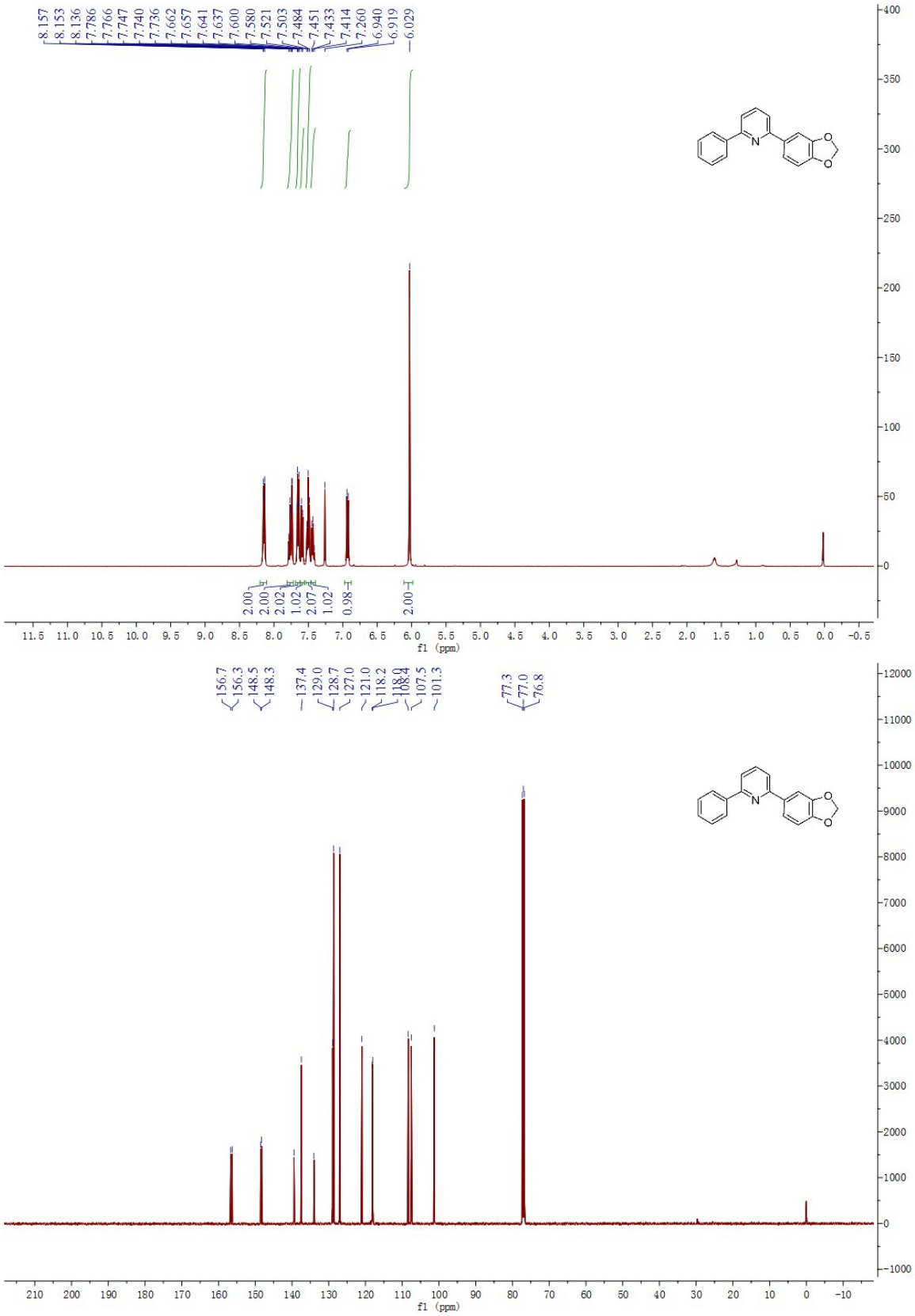


Figure S47. ^{1}H NMR of **7o** (500 MHz, $CDCl_3$) and ^{13}C NMR of **7o** (125 MHz, $CDCl_3$)

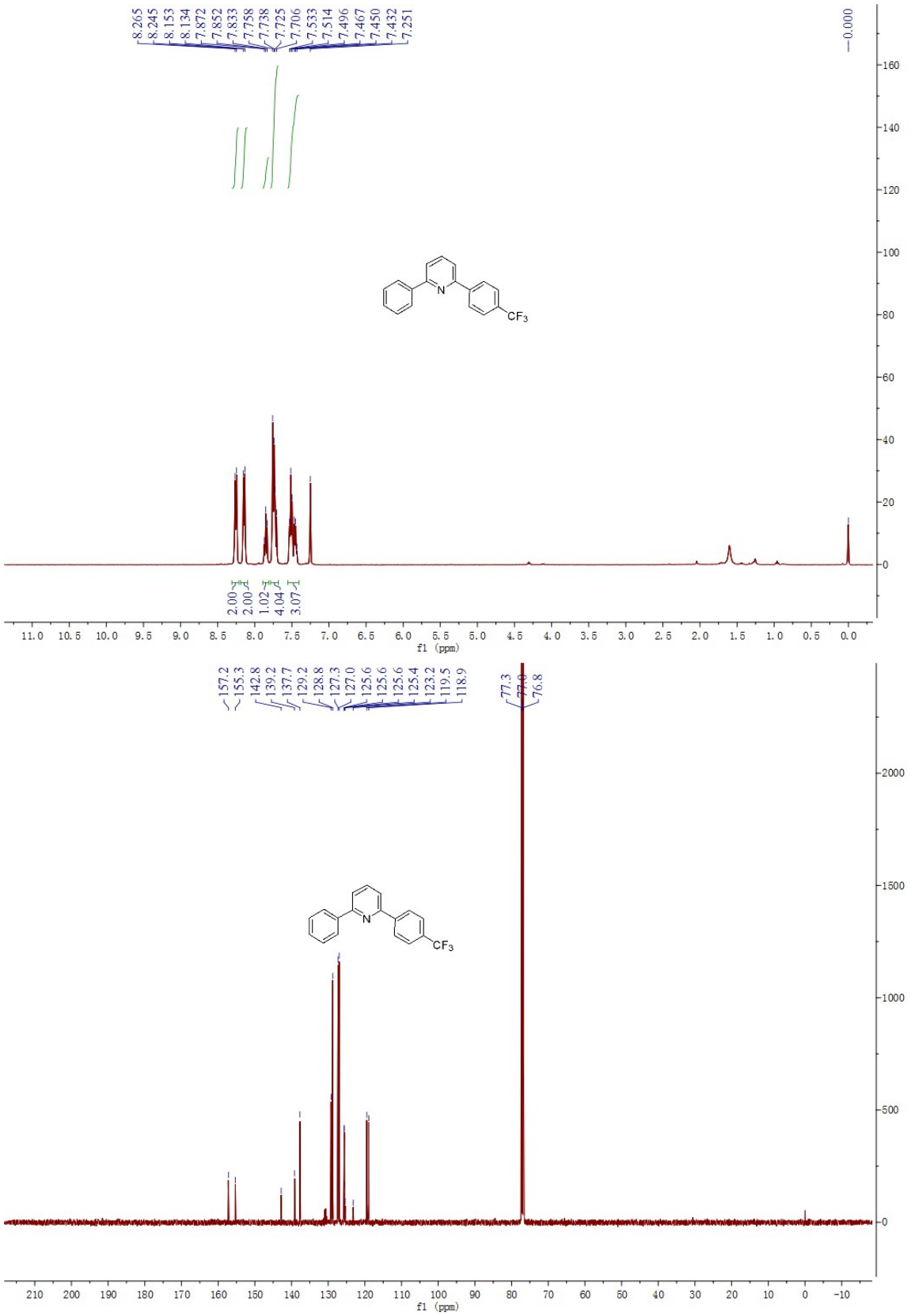


Figure S48. ^{1}H NMR of **7p** (500 MHz, $CDCl_3$) and ^{13}C NMR of **7p** (125 MHz, $CDCl_3$)