Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Unexpected TFA-catalyzed tandem reaction of benzo[*d*]oxazoles with 2-oxo-2-arylacetic acids: synthesis of 3-aryl-2*H*-benzo[*b*][1,4]oxazin-2-ones and cephalandole A

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

List of Contents:

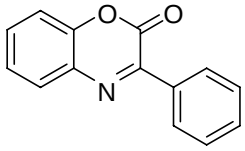
1. General experimental details

Chemicals and solvents were either purchased or purified by standard techniques. Melting points were uncorrected and recorded on Digital Melting Point Apparatus WRS-1B. IR spectra were recorded on an AVATAR 370 FI-Infrared Spectrophotometer. NMR spectroscopy was performed on both a Bruck spectrometer operating at 500 MHz (^{1}H NMR) and 125 MHz (^{13}C NMR). TMS (tetramethylsilane) was used as an internal standard and $CDCl_3$ or DMSO-d_6 was used as the solvent. IR spectra were obtained using a Nicolet iS10 spectrophotometer (Thermo Scientific). High-resolution mass spectra (HRMS) were recorded on Bruker micro TOF QII ESI-Q-TOF mass spectrometer. Column chromatography was performed using EM silica gel 60 (300−400 mesh).

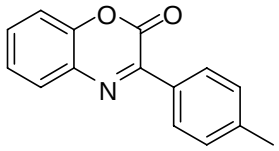
2. Typical procedure for the synthesis of 2-aryl-2*H*-benzo[*b*][1,4]oxazin-2-ones

Under air atmosphere, a Schlenk tube was charged with 2- benzo[*d*]oxazoles (0.2 mmol), oxo-2-arylacetic acids (0.3 mmol), and TFA (20 mol %) in 2 mL of isopropanol at room temperature. After that, the mixture was stirred constantly at 70 ^{o}C (oil bath temperature) for 18 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**.

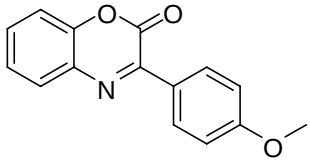
3. Experimental characterization data for compounds



3-Phenyl-2*H*-benzo[*b*][1,4]oxazin-2-one (**3a**): White solid, mp 119-120 ^{o}C (lit.[1] 121-122 ^{o}C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35-8.32 (m, 2H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.55-7.48 (m, 4H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.3, 150.9, 146.5, 134.2, 131.7, 131.4, 131.1, 129.5, 128.4, 125.6, 116.2. One peak was missing due to overlapping.



3-*p*-Tolyl-2*H*-benzo[*b*][1,4]oxazin-2-one (**3b**): White solid, mp 134-135 ^{o}C (lit.[2] not reported). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.5 Hz, 2H), 7.84-7.82 (m, 1H), 7.51-7.47 (m, 1H), 7.39-7.36 (m, 1H), 7.31 (t, *J* = 8.5 Hz, 3H), 2.42 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.3, 150.6, 146.4, 142.0, 131.7, 131.4, 130.8, 129.4, 129.3, 129.1, 125.4, 116.1, 21.5.

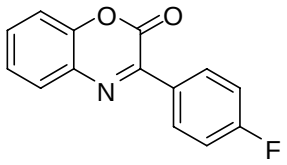


3-(4-Methoxyphenyl)-2*H*-benzo[*b*][1,4]oxazin-2-one (**3c**): Yellow solid, mp 131-132 ^{o}C (lit.[3] not reported). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.40 (d, *J* = 6.0 Hz, 2H), 7.81 (dd, *J* = 1.5, 7.8 Hz, 1H), 7.49-7.44 (m, 1H), 7.39-7.29 (m, 2H), 7.00 (d, *J* = 9.0 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4, 152.4, 149.8, 146.3, 131.8, 131.4, 130.4, 129.1, 126.8, 125.4, 116.0, 113.8, 55.4.

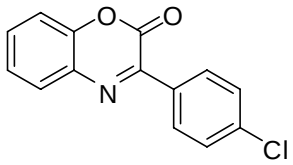
[1] Miyabe, H.; Yamaoka, Y.; Takemoto, Y. *J. Org. Chem*. **2006**, *71*, 2099 .

[2] Xue, Z.; Jiang, Y.; Peng, X.; Yuan, W.; Zhang, X. *Adv. Synth. Catal*. **2010**, *352*, 2132.

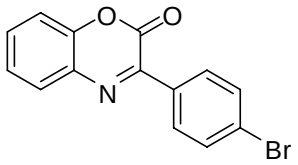
[3] Lemp, E.; Canete, A.; Guenther, G.; Pizarro, N.; Zanocco, A. *J. Photochem. Photobiol. A: Chem.* **2008**, *199*, 345.



3-(4-Fluorophenyl)-2*H*-benzo[*b*][1,4]oxazin-2-one (**3d**): White solid, mp 154-156 ^{o}C(lit.[4] not reported). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43-8.40 (m, 2H), 7.84 (dd, *J* = 1.5, 8.0 Hz, 1H), 7.54-7.50 (m, 1H), 7.42-7.38 (m, 1H), 7.34-7.32 (m, 1H), 7.20-7.15 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.9 (d, $^{1}J_{C\text{-}F}$ = 252.5 Hz, 1C), 152.2, 149.5, 146.4, 131.8 (d, $^{3}J_{C\text{-}F}$ = 8.75 Hz, 1C), 131.6, 131.2, 130.3 (d, $^{4}J_{C\text{-}F}$ = 2.5 Hz, 1C), 129.4, 125.6, 116.2, 115.5 (d, $^{2}J_{C\text{-}F}$ = 22.5 Hz, 1C).



3-(4-Chlorophenyl)-2*H*-benzo[*b*][1,4]oxazin-2-one (**3e**): White solid, mp 141-142 ^{o}C (lit.[5] not reported). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.5 Hz, 2H), 7.84 (d, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.1, 149.5, 146.5, 137.9, 132.5, 131.6, 131.4, 130.8, 129.5, 128.7, 125.7, 116.2.

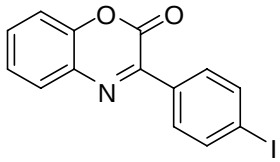


3-(4-Bromophenyl)-2*H*-benzo[*b*][1,4]oxazin-2-one (**3f**): White solid, mp 134-135 ^{o}C (lit.[6] not reported). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 9.0 Hz, 2H), 7.84 (dd, *J* = 1.5, 8.0 Hz, 1H), 7.64-7.61 (m, 2H), 7.55-7.51 (m, 1H), 7.42-7.39 (m, 1H), 7.34-7.33 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.1, 149.6, 146.5, 132.9, 131.6, 131.6, 131.4, 131.0, 129.5, 126.5, 125.7, 116.2.

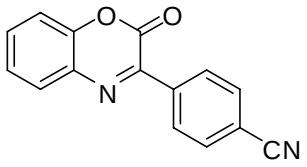
[4] Chen, Q.; Gao, K.; Duan, Y.; Ye, Z.; Shi, L.; Yang, Y.; Zhou, Y. *J. Am. Chem. Soc*. **2012**, *134*, 2442.

[5] Xue, Z.; Jiang, Y.; Peng, X.; Yuan, W.; Zhang, X. *Adv. Synth. Catal*. **2010**, *352*, 2132.

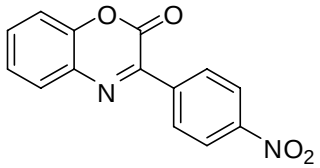
[6] Chen, Q.; Gao, K.; Duan, Y.; Ye, Z.; Shi, L.; Yang, Y.; Zhou, Y. *J. Am. Chem. Soc*. **2012**, *134*, 2442.



3-(4-Iodophenyl)-2*H*-benzo[*b*][1,4]oxazin-2-one (**3g**): Yellow, mp 124-125 ^{o}C. IR (KBr, cm^{-1}) 2365, 1734, 1610, 1394, 1123, 975, 917, 824, 76,1 697, 521. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.5 Hz, 2H), 7.84 (d, *J* = 8.5 Hz, 3H), 7.53 (t, *J* = 8.5 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.0, 149.8, 146.5, 137.6, 133.5, 131.6, 131.4, 130.9, 129.5, 125.7, 116.2, 98.9. HRMS (ESI) *m/z* calcd for $C_{14}H_9INO_2$ $[M+H]^+$ 249.9672, Found 249.9675.

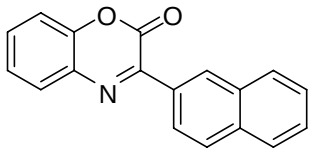


4-(2-Oxo-2*H*-benzo[*b*][1,4]oxazin-3-yl)benzonitrile (**3h**): White solid, mp 191-192 ^{o}C. IR (KBr, cm^{-1}) 3418, 2352, 1729, 1606, 1450, 1129, 978, 847, 771, 567. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (d, *J* = 7.5 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 9.0 Hz, 2H), 7.60-7.57 (m, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.9, 148.7, 146.5, 137.9, 132.3, 132.0, 131.4, 129.9, 128.9, 125.9, 118.3, 116.3, 114.6. HRMS (ESI) *m/z* calcd for $C_{15}H_9N_2O_2$ $[M+H]^+$ 249.0659, Found 249.0682.

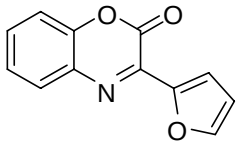


3-(4-Nitrophenyl)-2*H*-benzo[*b*][1,4]oxazin-2-one (**3i**): Yellow solid, mp 158-159 ^{o}C. IR (KBr, cm^{-1}) 3438, 3086, 1733, 1597, 1517, 1355, 1106, 983, 917, 866, 766, 690, 618. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 9.0 Hz, 2H), 8.32 (d, *J* = 9.0 Hz, 2H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.9, 149.2, 148.4, 146.6, 139.5, 132.5, 131.4, 130.4, 129.9, 126.0, 123.4, 116.3. HRMS (ESI) *m/z* calcd for $C_{14}H_9N_2O_4$

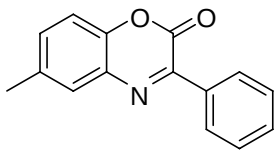
$[M+H]^+$ 269.0577, Found 269.0577.



3-(Naphthalen-2-yl)-2*H*-benzo[*b*][1,4]oxazin-2-one (**3j**): Yellow solid, mp 171-172 ^oC. IR (KBr, cm^{-1}) 2352, 1739, 1603, 1103, 980, 939, 821, 750, 650. ^1H NMR (500 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.42-8.39 (m, 1H), 8.00 (t, *J* = 7.5 Hz, 1H), 7.93 (d, *J* = 9.0 Hz, 1H), 7.88 (t, *J* = 9.0 Hz, 2H), 7.59-7.51 (m, 3H), 7.42-7.39 (m, 1H), 7.35 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.3, 150.2, 146.4, 134.7, 132.8, 131.8, 131.4, 131.1, 131.1, 129.6, 129.4, 128.0, 127.9, 127.6, 126.5, 125.6, 125.3, 116.1. HRMS (ESI) *m/z* calcd for $C_{18}H_{12}NO_2$ $[M+H]^+$ 274.0863, Found 274.0881.



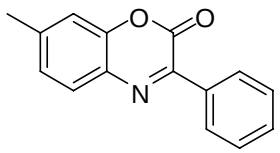
3-(Furan-2-yl)-2*H*-benzo[*b*][1,4]oxazin-2-one (**3k**): Brown solid, mp 109-111 ^oC. IR (KBr, cm^{-1}) 3106, 2921, 1757, 1613, 1454, 1222, 1033, 985, 917, 887, 759, 633, 591. ^1H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 3.5 Hz, 1H), 7.75 (s, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.5, 1H), 6.64 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.9, 148.0, 147.0, 145.7, 141.1, 131.4, 130.7, 129.2, 125.9, 120.6, 116.3, 113.0. HRMS (ESI) *m/z* calcd for $C_{12}H_8NO_3$ $[M+H]^+$ 214.0499, Found 214.0498.



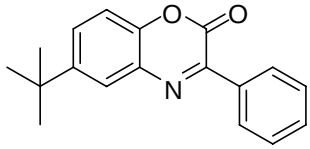
6-Methyl-3-phenyl-2*H*-benzo[*b*][1,4]oxazin-2-one (**3l**): Yellow solid, mp 130-132 ^oC (lit.[7] 135 ^oC). ^1H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 6.5 Hz, 2H), 7.65 (s, 1H),

[7] Biekert, E.; Hoffmann, D.; Meyer, F. *Chem. Ber*. **1961**, *94*, 1664

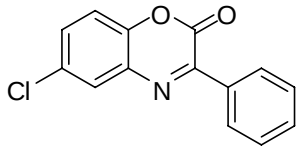
7.53-7.48 (m, 3H), 7.32 (d, J = 8.5 Hz, 1H), 7.22 (d, J = 8.5Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.5, 150.7, 144.5, 135.5, 134.3, 132.1, 131.4, 131.3, 129.4, 129.3, 128.4, 115.7, 20.8.



7-Methyl-3-phenyl-2*H*-benzo[*b*][1,4]oxazin-2-one (**3m**): Yellow solid, mp 136-137 ^{o}C(lit.[8] not reported). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32-8.34 (m, 2H), 7.71 (d, J = 8.0 Hz, 1H), 7.52-7.47 (m, 3H), 7.19 (d, J = 8.0 Hz, 1H), 7.12 (s, 1H), 2.47 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.5, 149.6, 146.4, 142.5, 134.3, 131.1, 129.7, 129.3, 129.0, 128.3, 126.7, 116.2, 21.7.



6-*Tert*-butyl-3-phenyl-2*H*-benzo[*b*][1,4]oxazin-2-one (**3n**): Yellow solid, mp 98-99 ^{o}C (lit.[9] not reported). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, J = 7.0 Hz, 2H), 7.86 (s, 1H), 7.57-7.46 (m, 4H), 7.26 (d, J = 9.0 Hz, 1H), 1.40 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.5, 150.6, 149.0, 144.2, 134.3, 131.2, 131.1, 129.3, 128.7, 128.3, 126.0, 115.5, 34.6, 31.3.



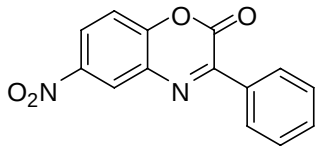
6-Chloro-3-phenyl-2*H*-benzo[*b*][1,4]oxazin-2-one (**3o**): Yellow solid, mp 138-139 ^{o}C. (lit.[10] not reported). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, J = 7.5 Hz, 2H), 7.85 (s, 1H), 7.57-7.45 (m, 4H), 7.27 (d, J = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ

[8] Chen, Q.; Gao, K.; Duan, Y.; Ye, Z.; Shi, L.; Yang, Y.; Zhou, Y. *J. Am. Chem. Soc.* **2012**, *134*, 2442.

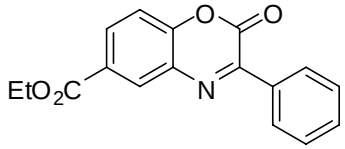
[9] Núñez-Rico, J. L.; Vidal-Ferran, A. *Org. Lett.* **2013**, *15*, 2066.

[10] Núñez-Rico, J. L.; Vidal-Ferran, A. *Org. Lett.* **2013**, *15*, 2066.

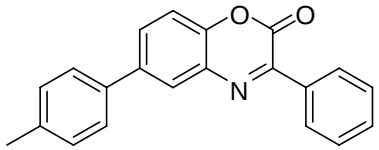
151.8, 151.7, 145.0, 133.7, 132.2, 131.9, 130.9, 130.7, 129.6, 128.8, 128.5, 117.3.



6-Nitro-3-phenyl-2*H*-benzo[*b*][1,4]oxazin-2-one (**3p**): White solid, mp 183-184 ^{o}C (lit.[11] 180-182 ^{o}C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (d, *J* = 3.0 Hz, 1H), 8.40-8.37 (m, 3H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 9.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.7, 150.6, 150.4, 145.1, 133.1, 132.5, 131.1, 129.7, 128.6, 125.6, 125.1, 117.1.



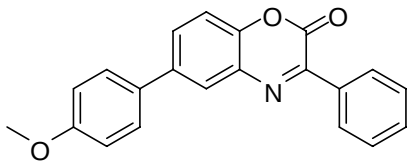
Ethyl 2-oxo-3-phenyl-2*H*-benzo[*b*][1,4]oxazine-6-carboxylate (**3q**): White solid, mp 140-141 ^{o}C. IR (KBr, cm^{-1}) 3458, 2981, 1752, 1610, 1305, 1215, 1083, 973, 882, 801, 761, 688. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 2.0 Hz, 1H), 8.34-8.32 (m, 2H), 8.17 (dd, *J* = 2.0, 8.5 Hz, 1H), 7.54-7.48 (m, 3H), 7.35 (d, *J* = 8.5 Hz, 1H), 4.41 (q, *J* = 7.5 Hz, 2H), 1.42 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0, 151.4, 151.3, 149.3, 133.6, 131.9, 131.8, 131.1, 131.0, 129.5, 128.4, 128.1, 116.2, 61.5, 14.2. HRMS (ESI) *m/z* calcd for $C_{17}H_{14}NO_4$ $[M+H]^+$ 296.0917, Found 269.0911.



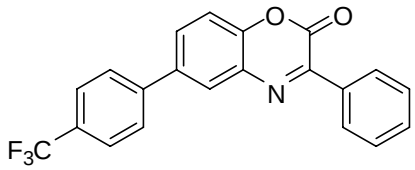
3-Phenyl-6-*p*-tolyl-2*H*-benzo[*b*][1,4]oxazin-2-one (**3r**): Yellow solid, mp 135-136 ^{o}C. IR (KBr, cm^{-1}) 3457, 2365, 1736, 1481, 1129, 970, 806, 700, 509. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.0 Hz, 2H), 8.05 (s, 1H), 7.72 (dd, *J* = 2.0, 8.5 Hz, 1H), 7.57-7.50 (m, 5H), 7.37 (d, *J* = 8.5 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 2H), 2.43 (s, 3H). ^{13}C

[11] Moffet, R. B. *J. Med. Chem.* **1966**, 9, 475.

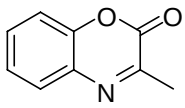
NMR (125 MHz, $CDCl_3$) δ 152.2, 151.0, 145.5, 138.9, 137.8, 136.2, 134.1, 131.8, 131.4, 129.7, 129.7, 129.5, 128.4, 127.2, 126.8, 116.3, 21.1. HRMS (ESI) *m/z* calcd for $C_{21}H_{16}NO_2$ $[M+H]^+$ 314.1176, Found 314.1187.



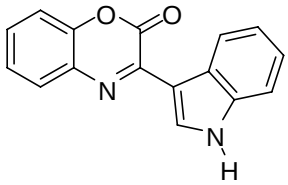
6-(4-Methoxyphenyl)-3-phenyl-2*H*-benzo[*b*][1,4]oxazin-2-one (**3s**): Yellow solid, mp 144-145 ^oC. IR (KBr, cm^{-1}) 3473, 2365, 1733, 1603, 1484, 1249, 1040, 973, 819, 692. ^1H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.5 Hz, 2H), 8.01 (s, 1H), 7.70-7.68 (m, 1H), 7.57-7.50 (m, 5H), 7.36 (d, *J* = 9.0 Hz, 1H), 7.01 (d, *J* = 8.5 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6, 152.3, 151.0, 145.3, 138.6, 134.2, 131.8, 131.6, 131.4, 129.5, 128.4, 128.1, 126.9, 116.3, 114.5, 55.4. One peak was missing due to overlapping. HRMS (ESI) *m/z* calcd for $C_{21}H_{16}NO_3$ $[M+H]^+$ 330.1125, Found 330.1144.



3-Phenyl-6-(4-(trifluoromethyl)phenyl)-2*H*-benzo[*b*][1,4]oxazin-2-one (**3t**): Yellow solid, mp 146-147 ^oC. IR (KBr, cm^{-1}) 2359, 1743, 1484, 1252, 1119, 972, 816, 69,5 519. ^1H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.5 Hz, 2H), 8.05 (s, 1H), 7.75-7.74 (m, 5H), 7.55-7.50 (m, 3H), 7.43 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.0, 151.5, 146.3, 142.7, 137.4, 133.9, 131.8, 131.7, 130.0 (q, $^2J_{C\text{-}F}$ = 32.5 Hz, 1C), 129.8, 129.5, 128.5, 127.8, 127.4, 126.0 (q, $^3J_{C\text{-}F}$ = 3.75 Hz), 124.1 (q, $^1J_{C\text{-}F}$ = 270.5 Hz, 1C), 116.8. HRMS (ESI) *m/z* calcd for $C_{21}H_{13}F_3NO_2$ $[M+H]^+$ 368.0893, Found 368.0881.



3-Methyl-2*H*-benzo[*b*][1,4]oxazin-2-one (**3u**): White solid, mp 102-103 °C (lit.[12] 102-104 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 1.5, 8.0 Hz, 1H), 7.49-7.45 (m, 1H), 7.37-7.34 (m, 1H), 7.29-7.28 (m, 1H), 2.57 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.1, 153.3, 146.6, 131.1, 130.5, 128.6, 125.4, 116.4, 21.3.



3-(1*H*-indol-3-yl)-2*H*-benzo[*b*][1,4]oxazin-2-one (**cephalandole A**): Yellow solid, mp 237-238 °C (lit.[13] 236-237 °C). ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.00 (s, 1H), 8.78-8.76 (m, 1H), 8.71 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.55-7.54 (m, 1H), 7.50-7.46 (m, 1H), 7.42 (t, *J* = 7.0 Hz, 2H), 7.30-7.25 (m, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 152.0, 147.9, 144.8, 136.6, 133.7, 131.9, 128.6, 127.7, 126.0, 125.3, 123.0, 122.8, 121.5, 115.9, 112.2, 110.6.

[12] Yavari, I.; Souri, S.; Sirouspour, M.; Djahaniani, H. *Synthesis* **2006**, 3243.

[13] Mason, J.; Bergman, J.; Janosik, T.; *J. Nat. Prod*. **2008**, *8*, 1447.

2. ^{1}H NMR and ^{13}C NMR spectra for all products

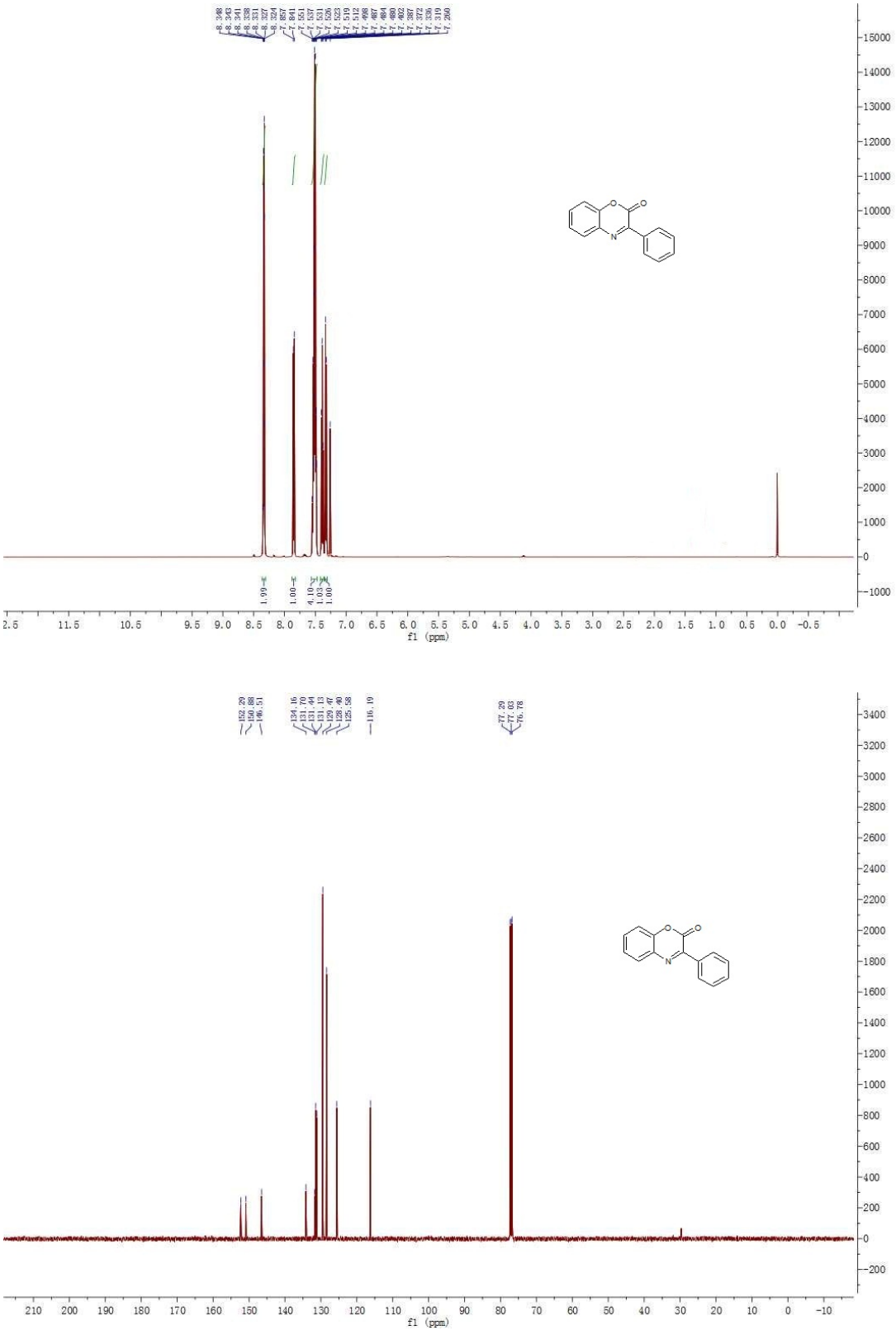


Figure S1. ^{1}H NMR of **3a** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3a** (125 MHz, $CDCl_3$).

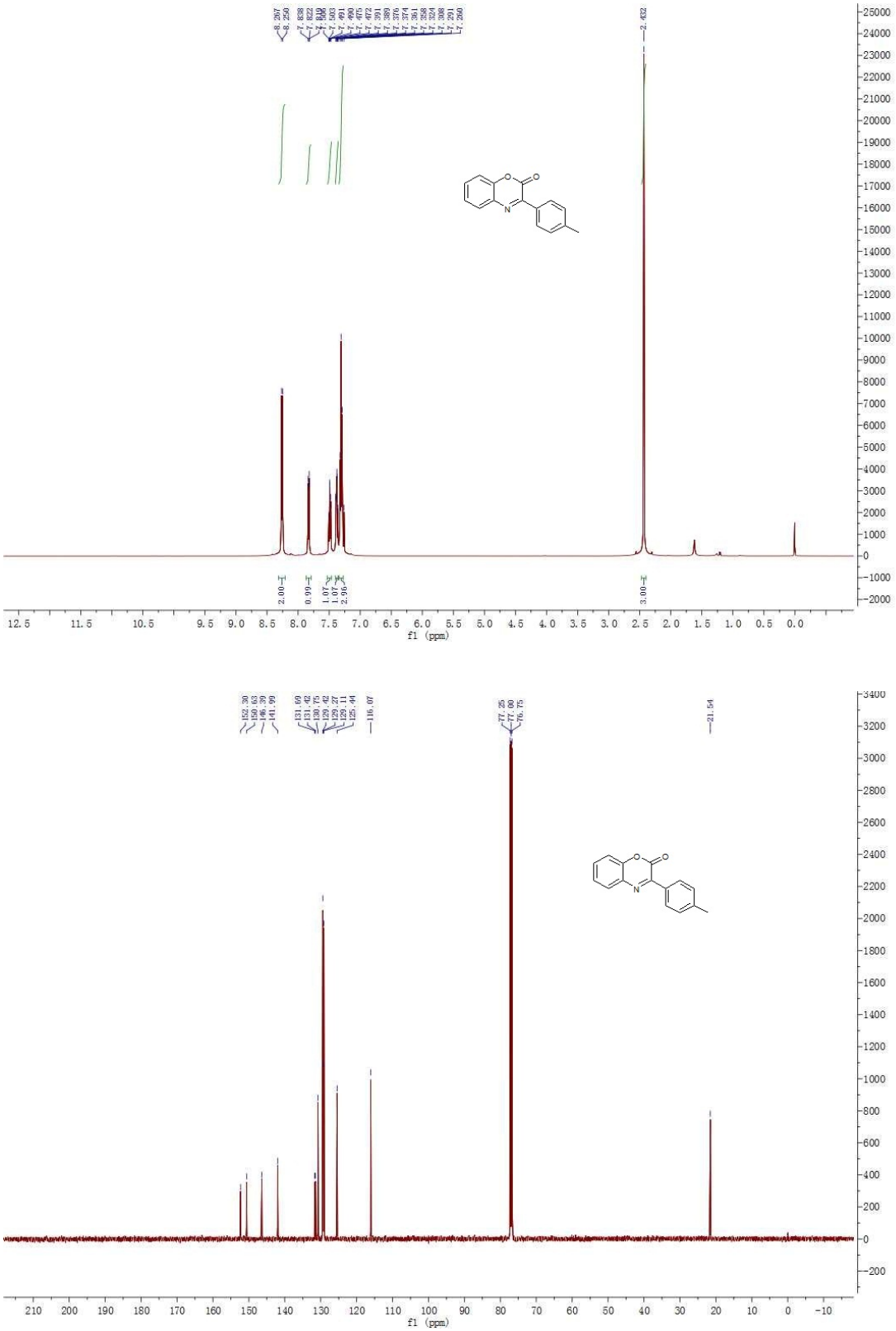


Figure S2. ^{1}H NMR of **3b** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3b** (125 MHz, $CDCl_3$)

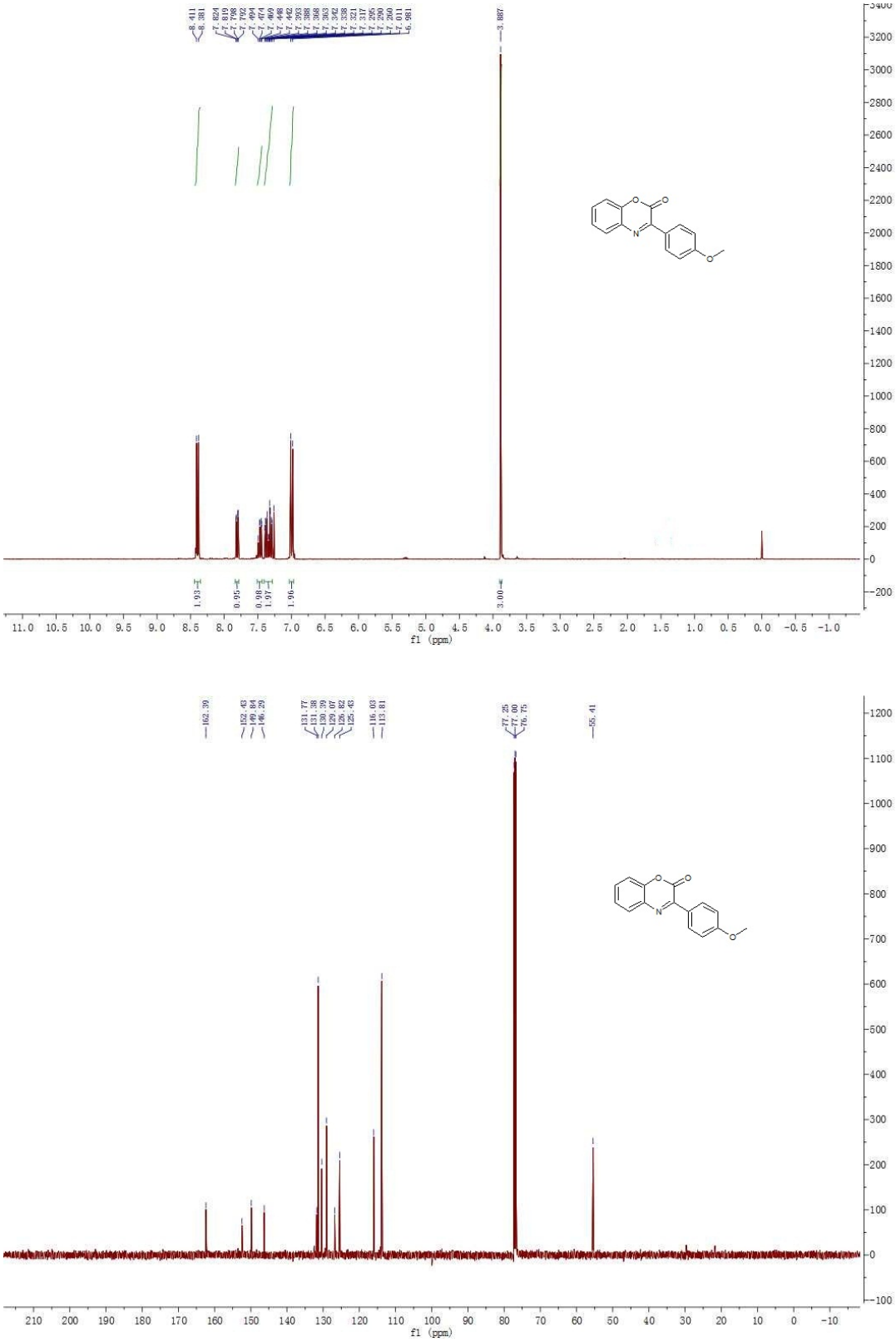


Figure S3. ^{1}H NMR of **3c** (300 MHz, $CDCl_3$) and ^{13}C NMR of **3c** (125 MHz, $CDCl_3$)

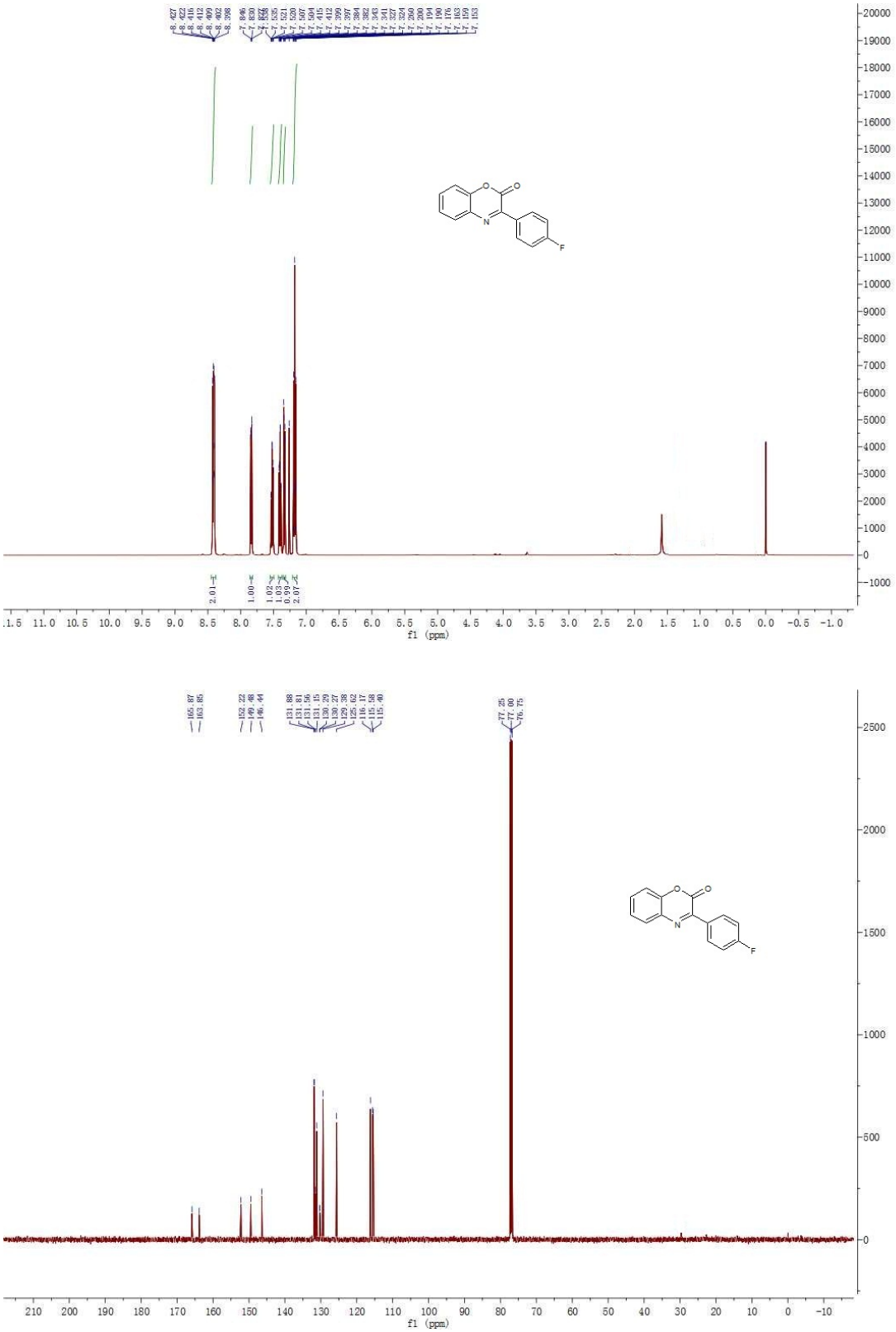


Figure S4. ^{1}H NMR of **3d** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3d** (125 MHz, $CDCl_3$)

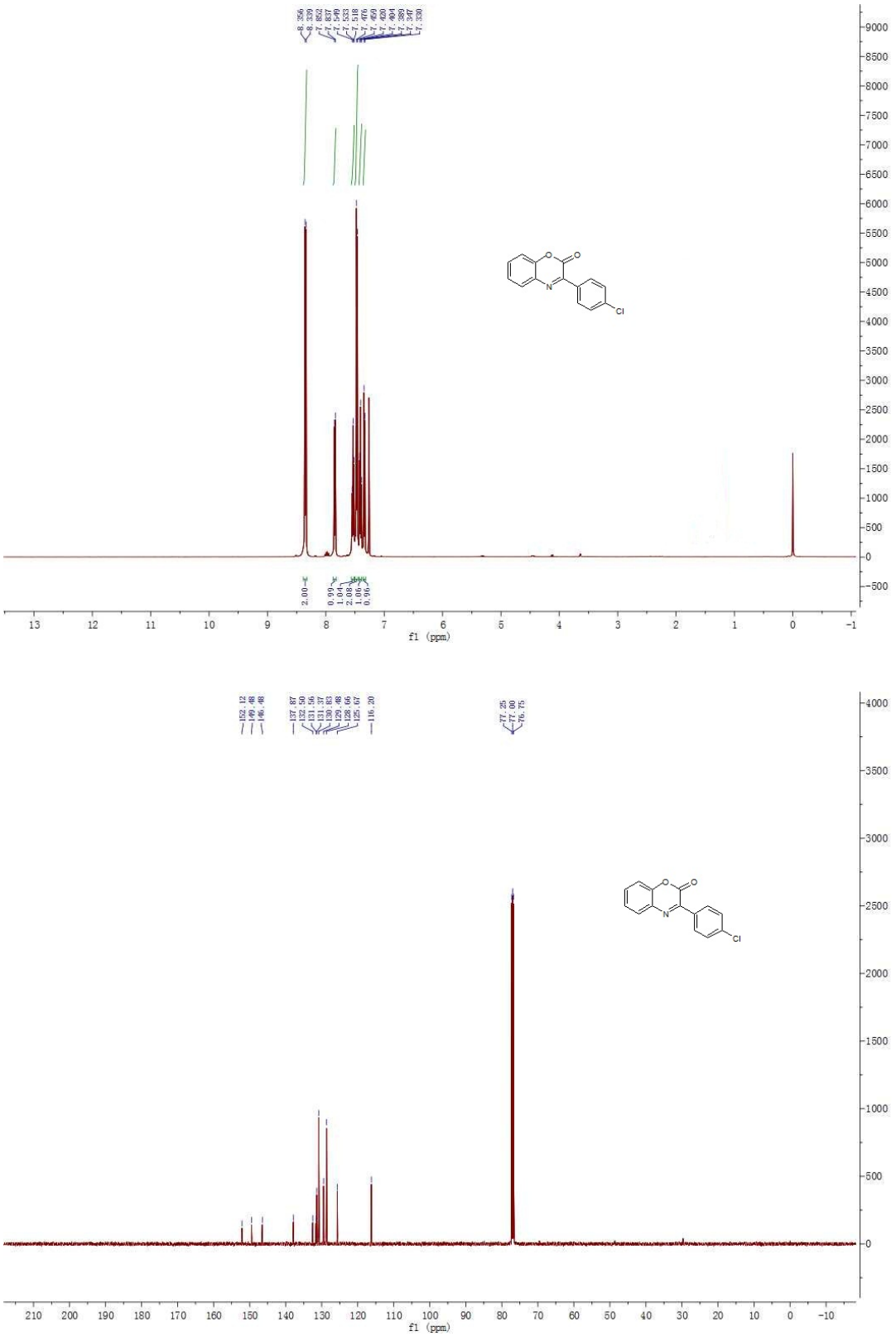


Figure S5. ^{1}H NMR of **3e** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3e** (125 MHz, $CDCl_3$)

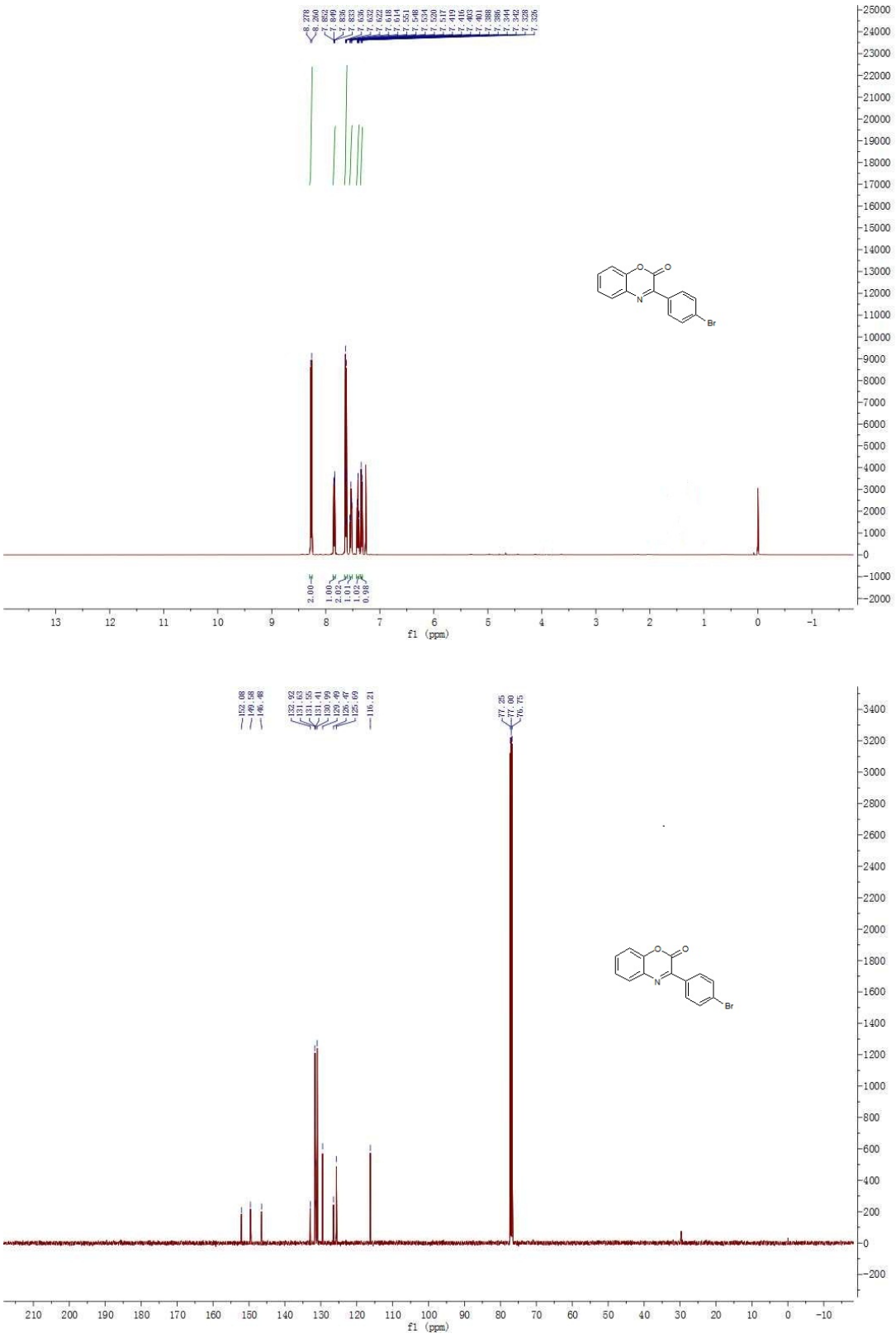


Figure S6. ^{1}H NMR of **3f** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3f** (125 MHz, $CDCl_3$)

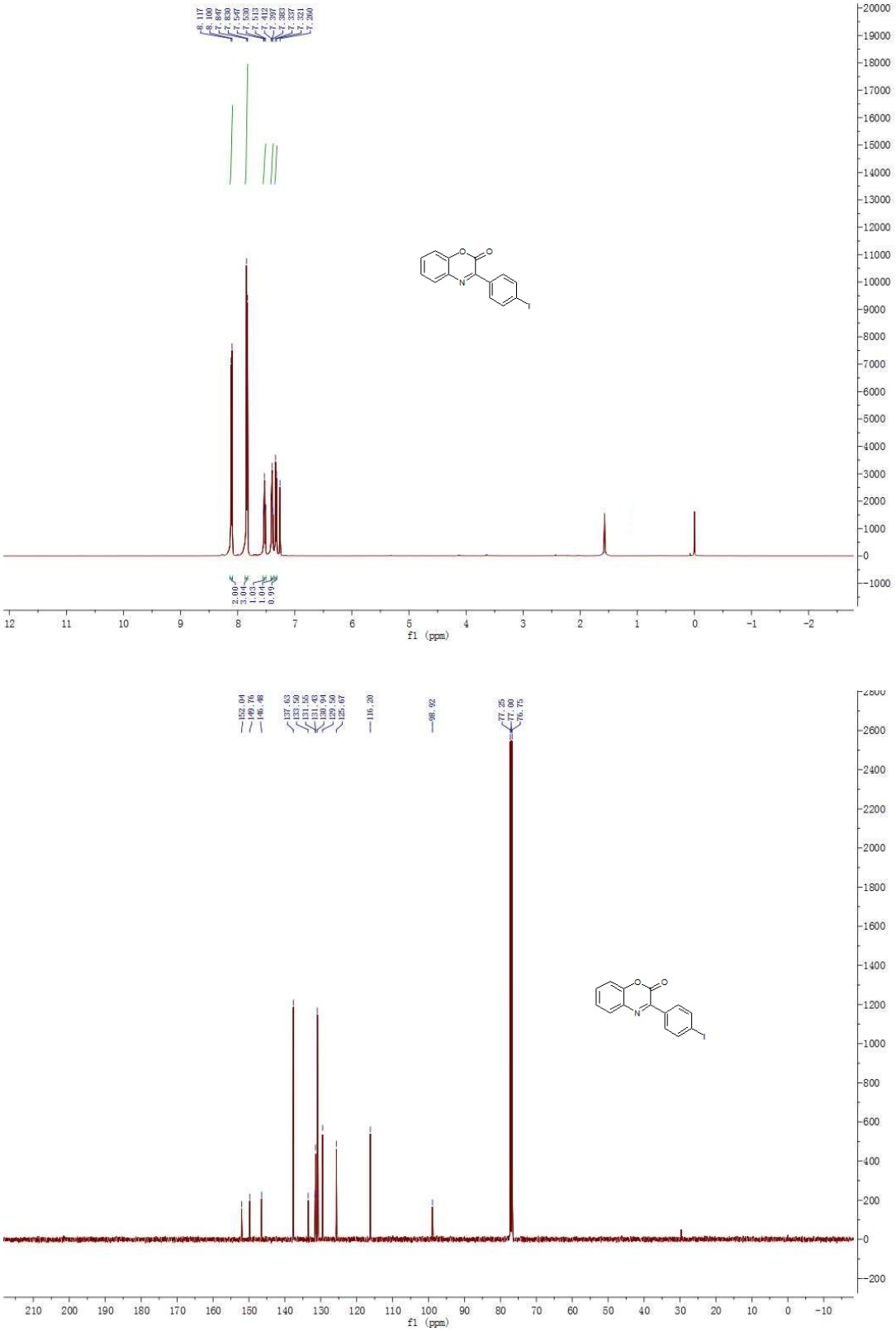


Figure S7. ^{1}H NMR of **3g** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3g** (125 MHz, $CDCl_3$)

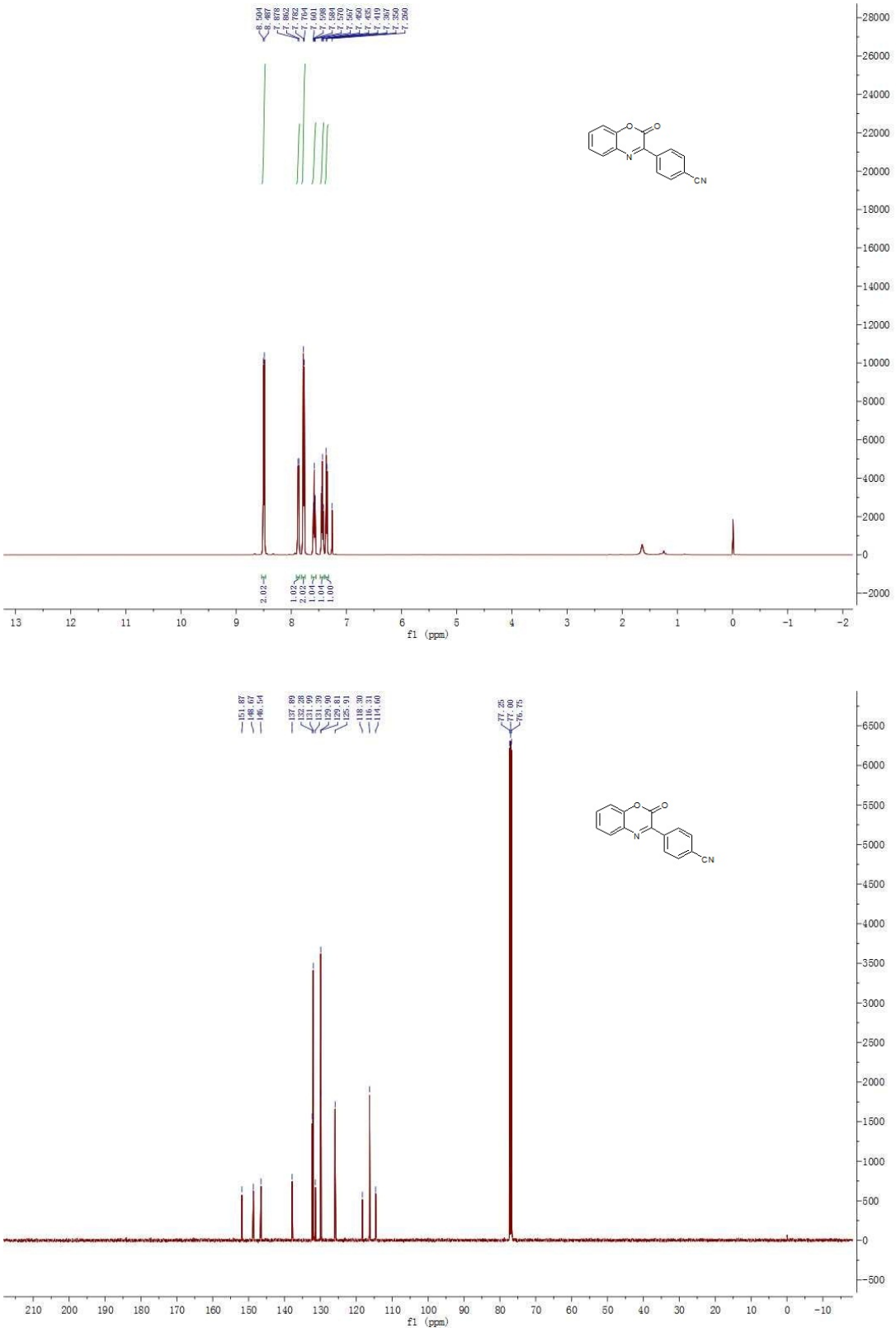


Figure S8. ^{1}H NMR of **3h** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3h** (125 MHz, $CDCl_3$)

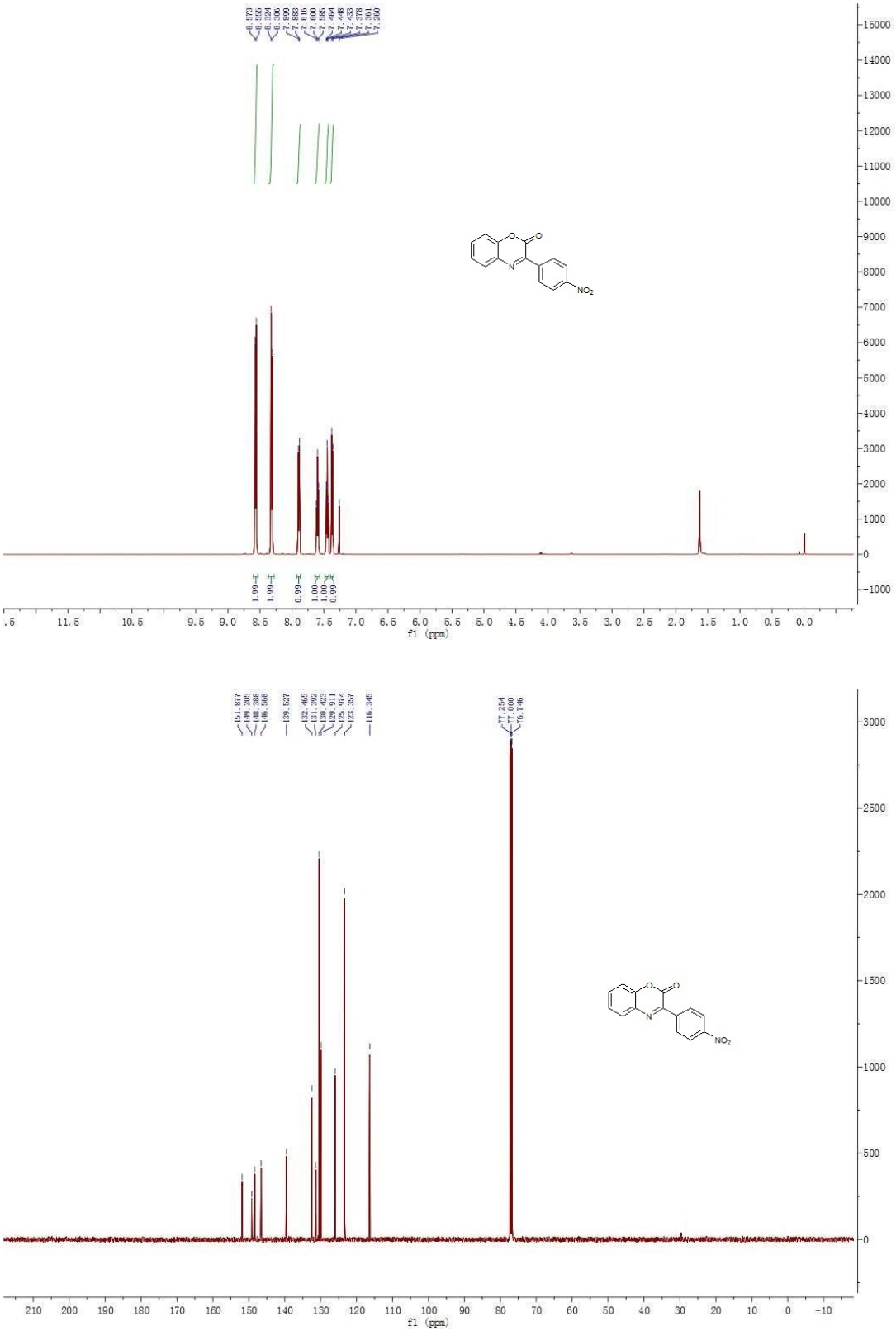


Figure S9. ^{1}H NMR of **3i** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3i** (125 MHz, $CDCl_3$)

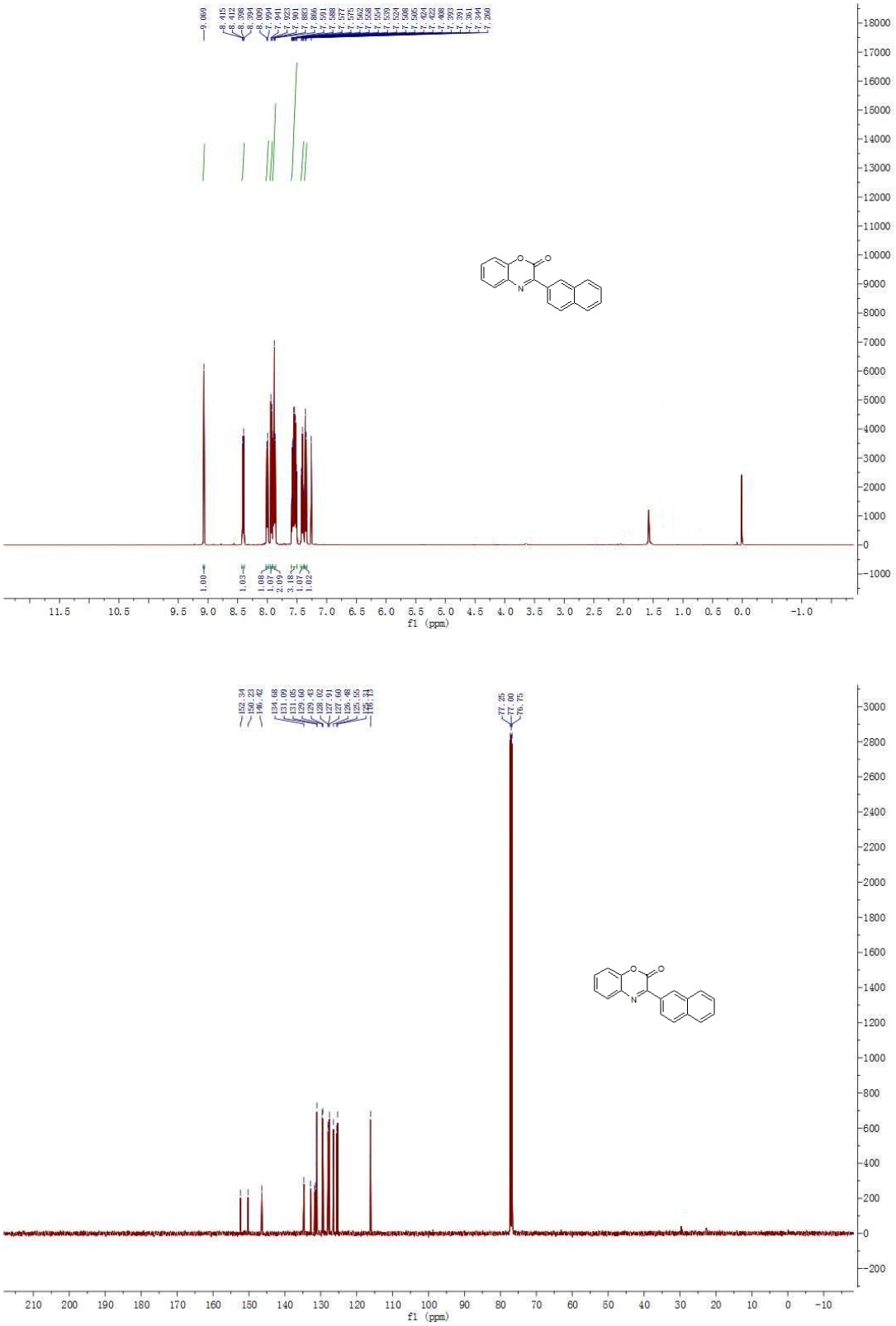


Figure S10. ^{1}H NMR of **3j** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3j** (125 MHz, $CDCl_3$)

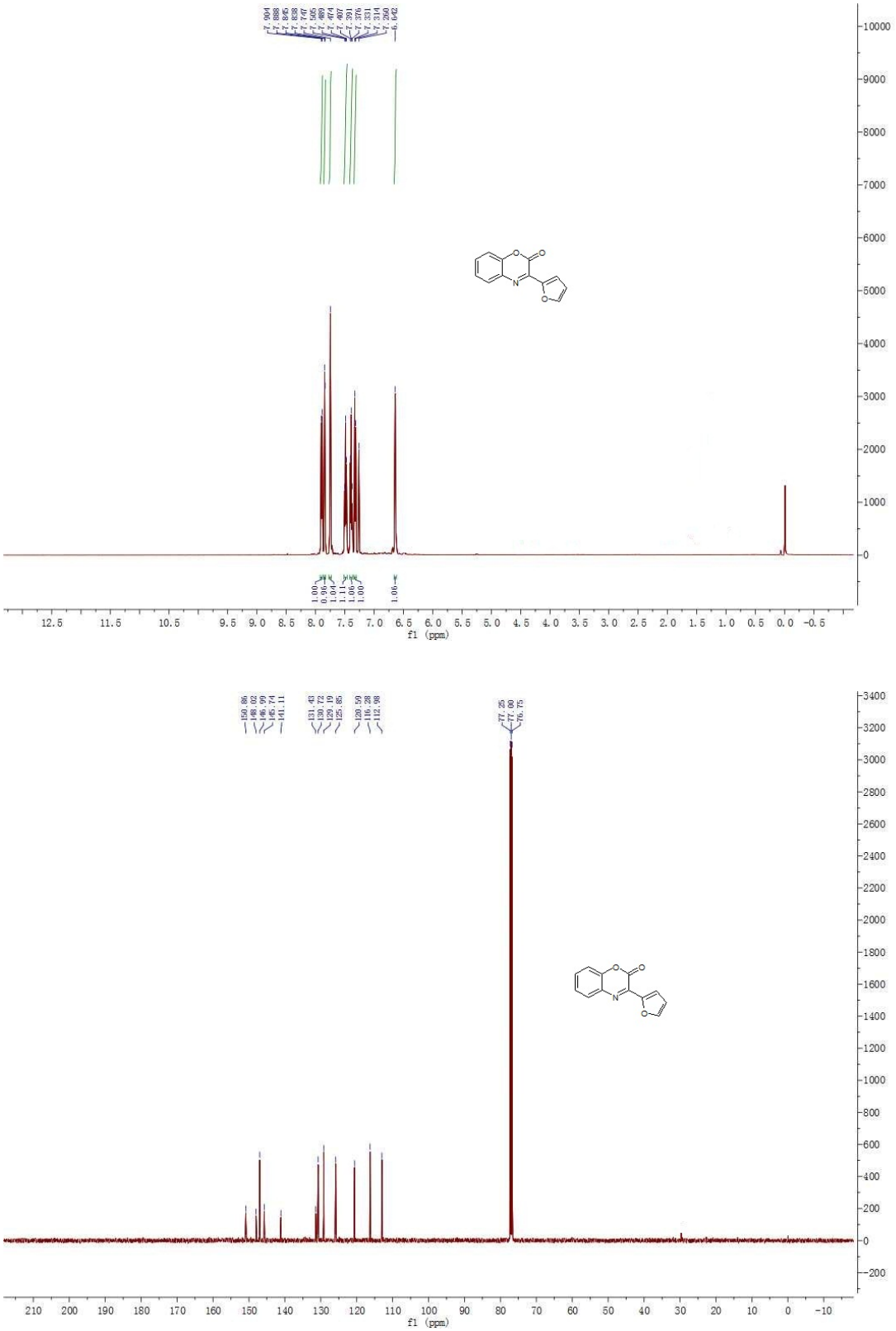


Figure S11. ^{1}H NMR of **3k** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3k** (125 MHz, $CDCl_3$)

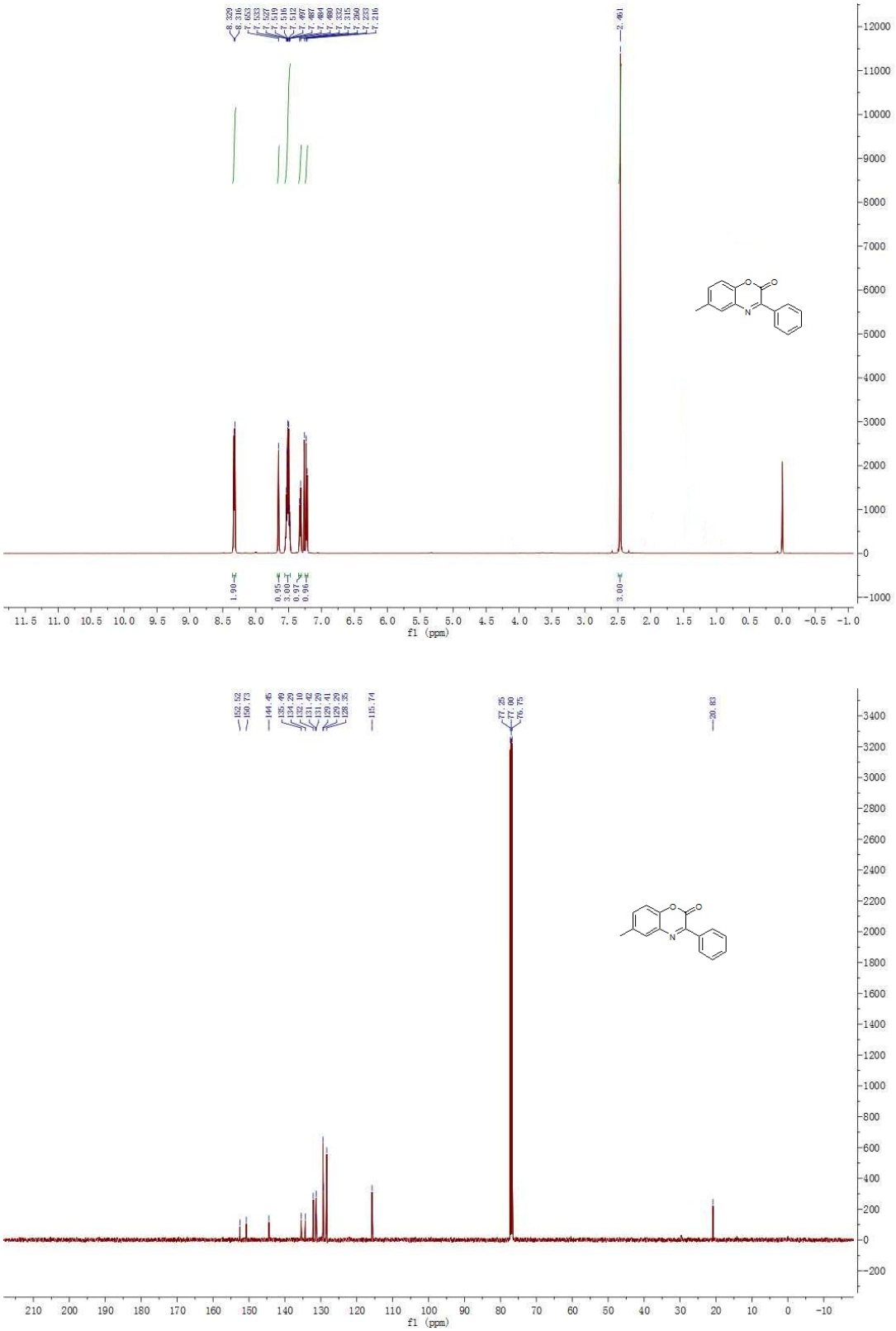


Figure S12. ^{1}H NMR of **3l** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3l** (125 MHz, $CDCl_3$)

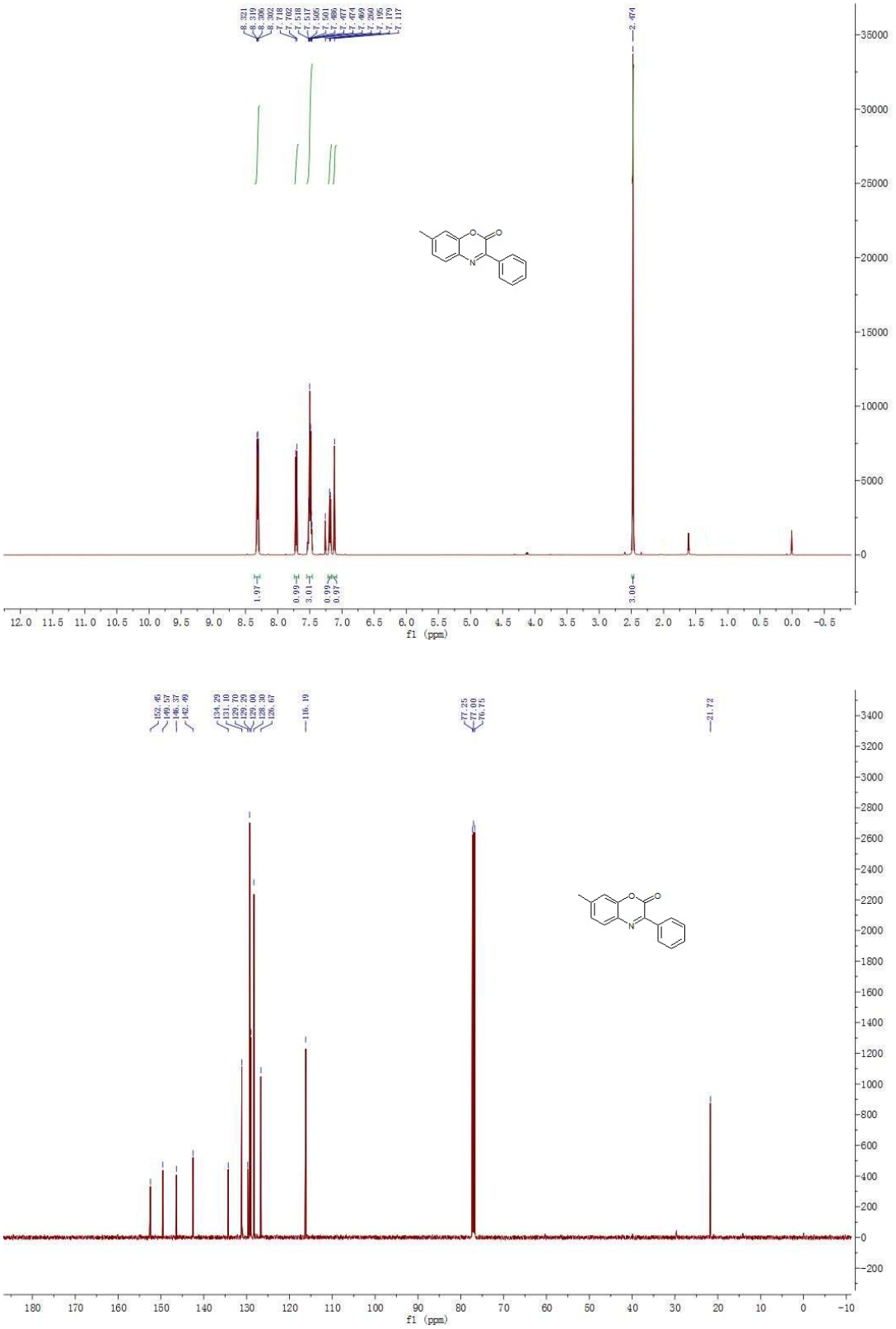


Figure S13. ^{1}H NMR of **3m** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3m** (125 MHz, $CDCl_3$)

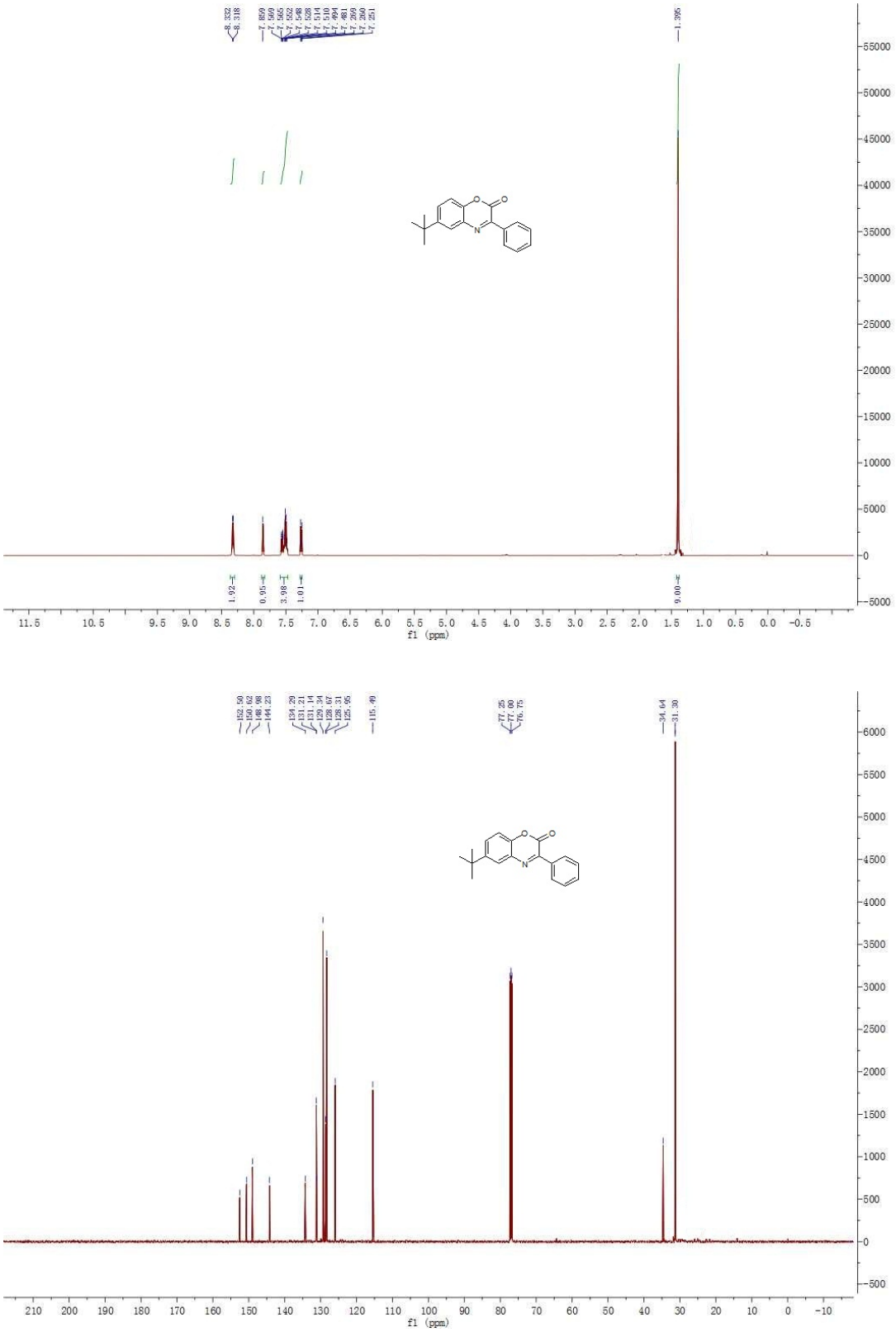


Figure S14. ^{1}H NMR of **3n** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3n** (125 MHz, $CDCl_3$)

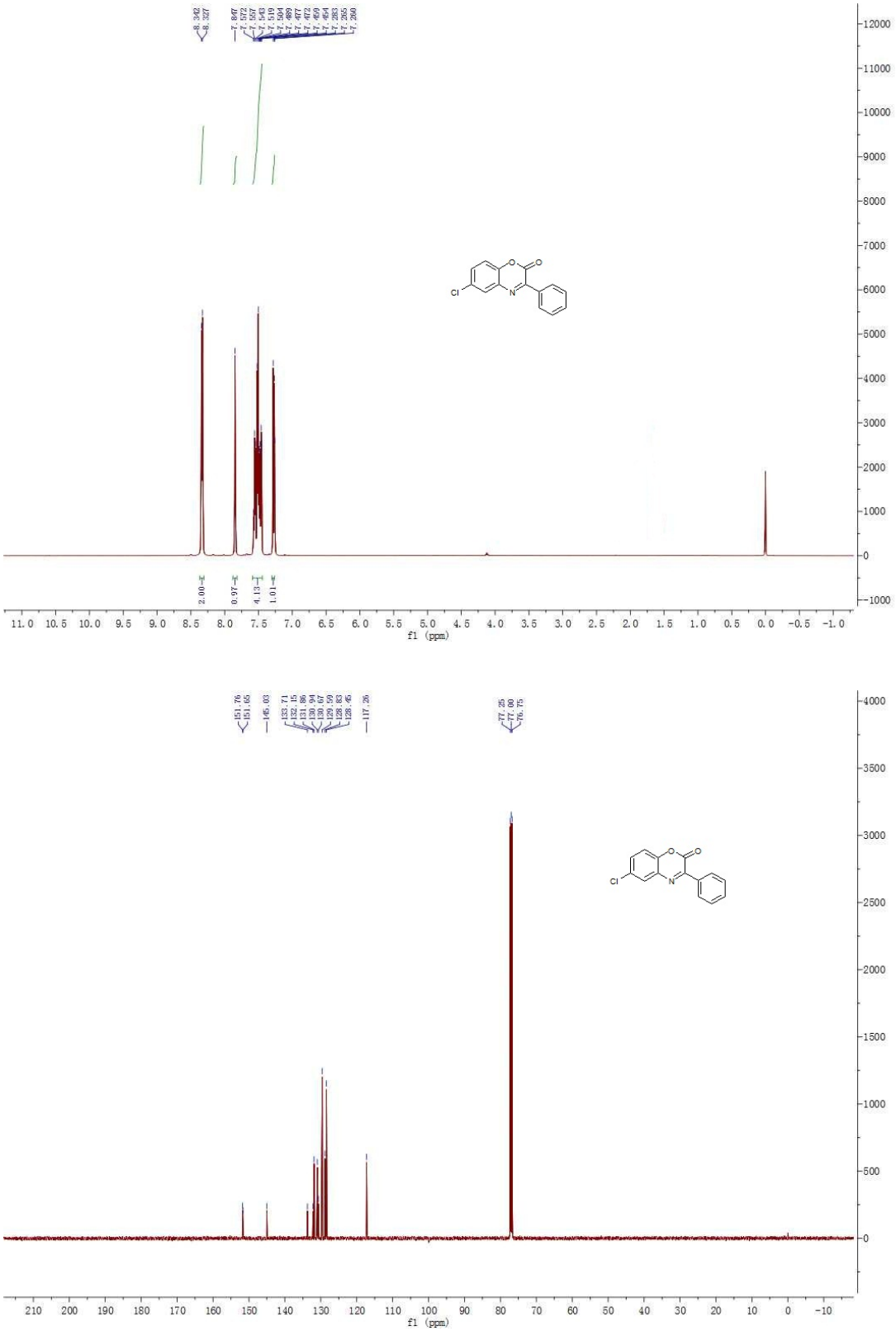


Figure S15. ^{1}H NMR of **3o** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3o** (125 MHz, $CDCl_3$)

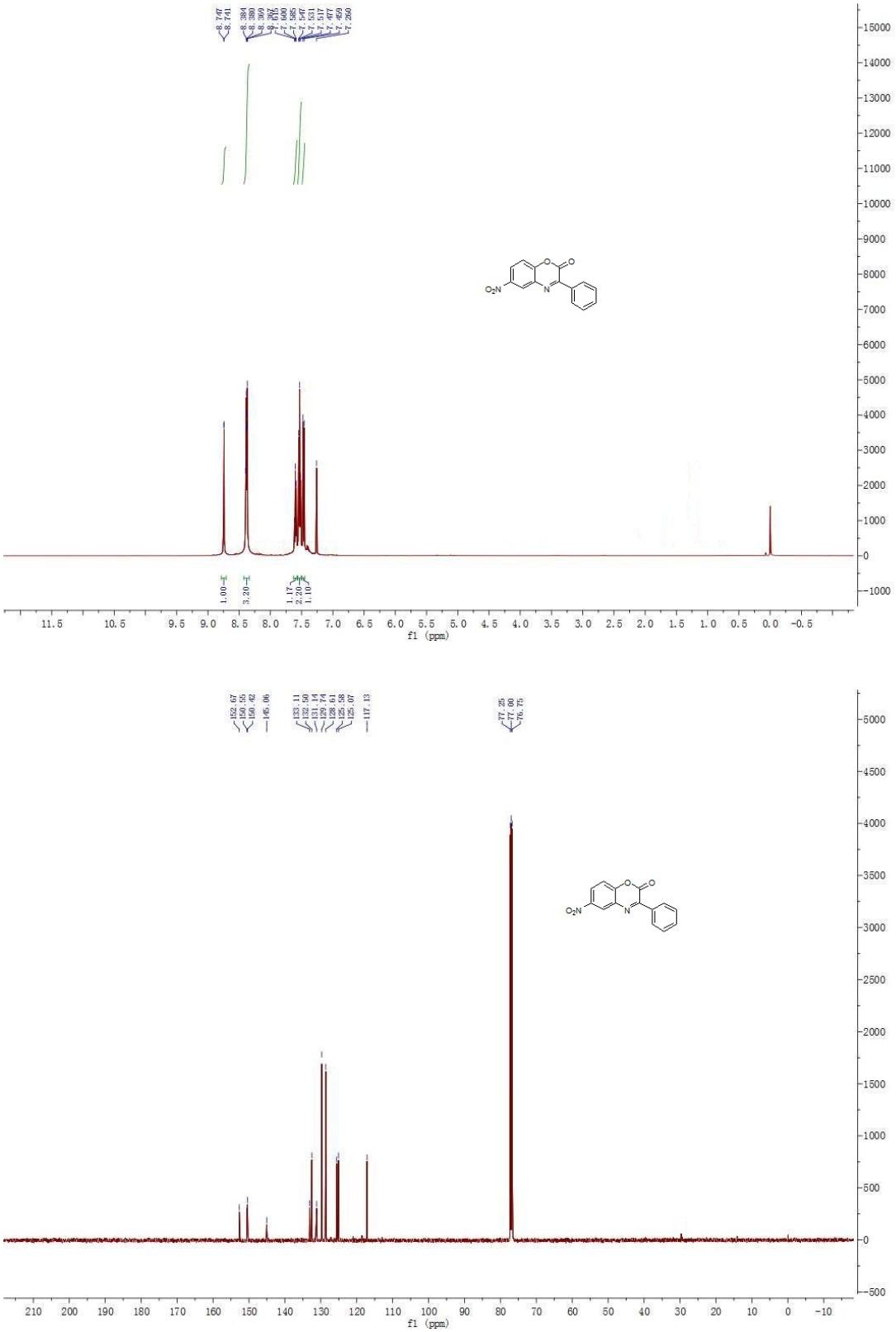


Figure S16. ^{1}H NMR of **3p** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3p** (125 MHz, $CDCl_3$)

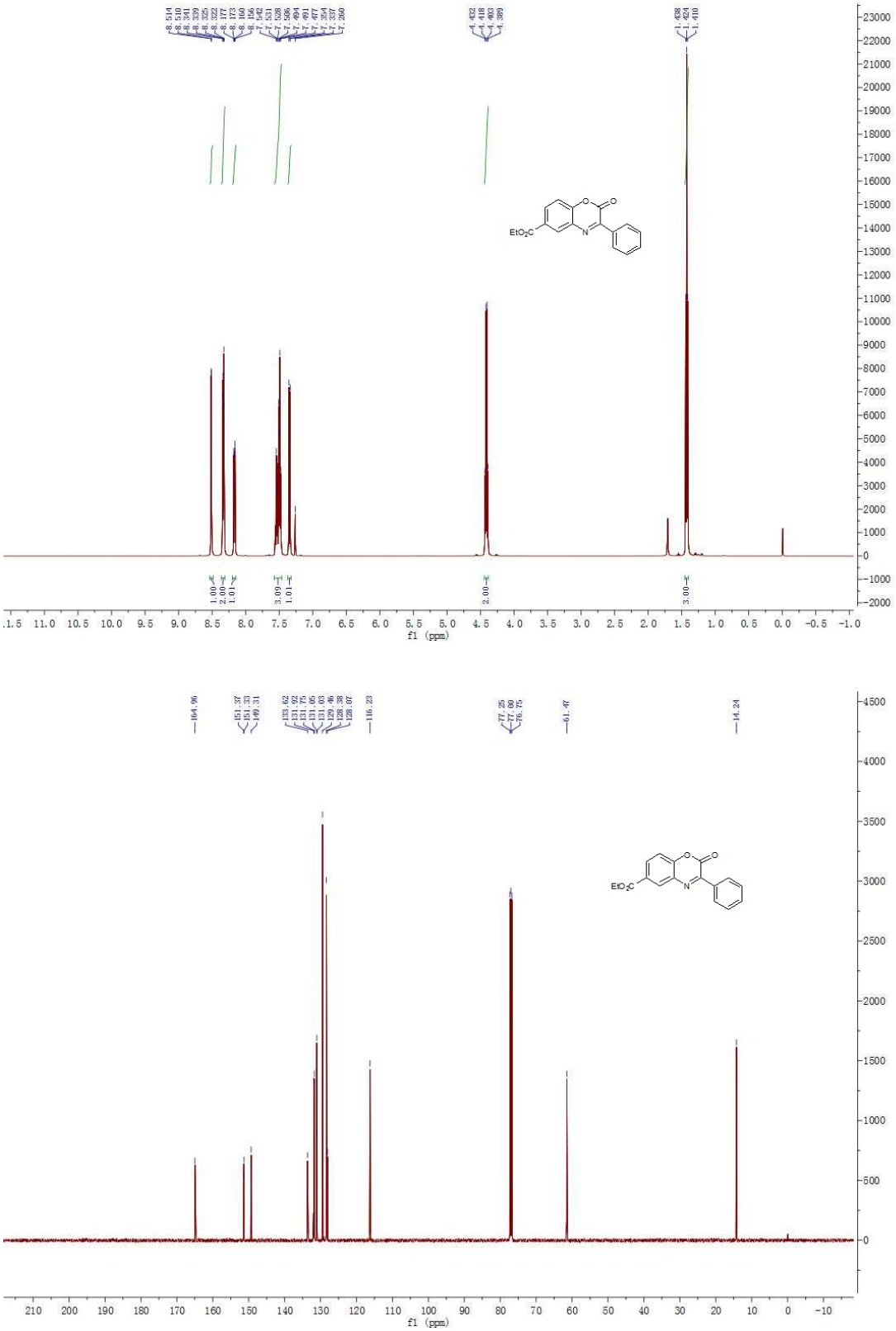


Figure S17. ^{1}H NMR of **3q** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3q** (125 MHz, $CDCl_3$)

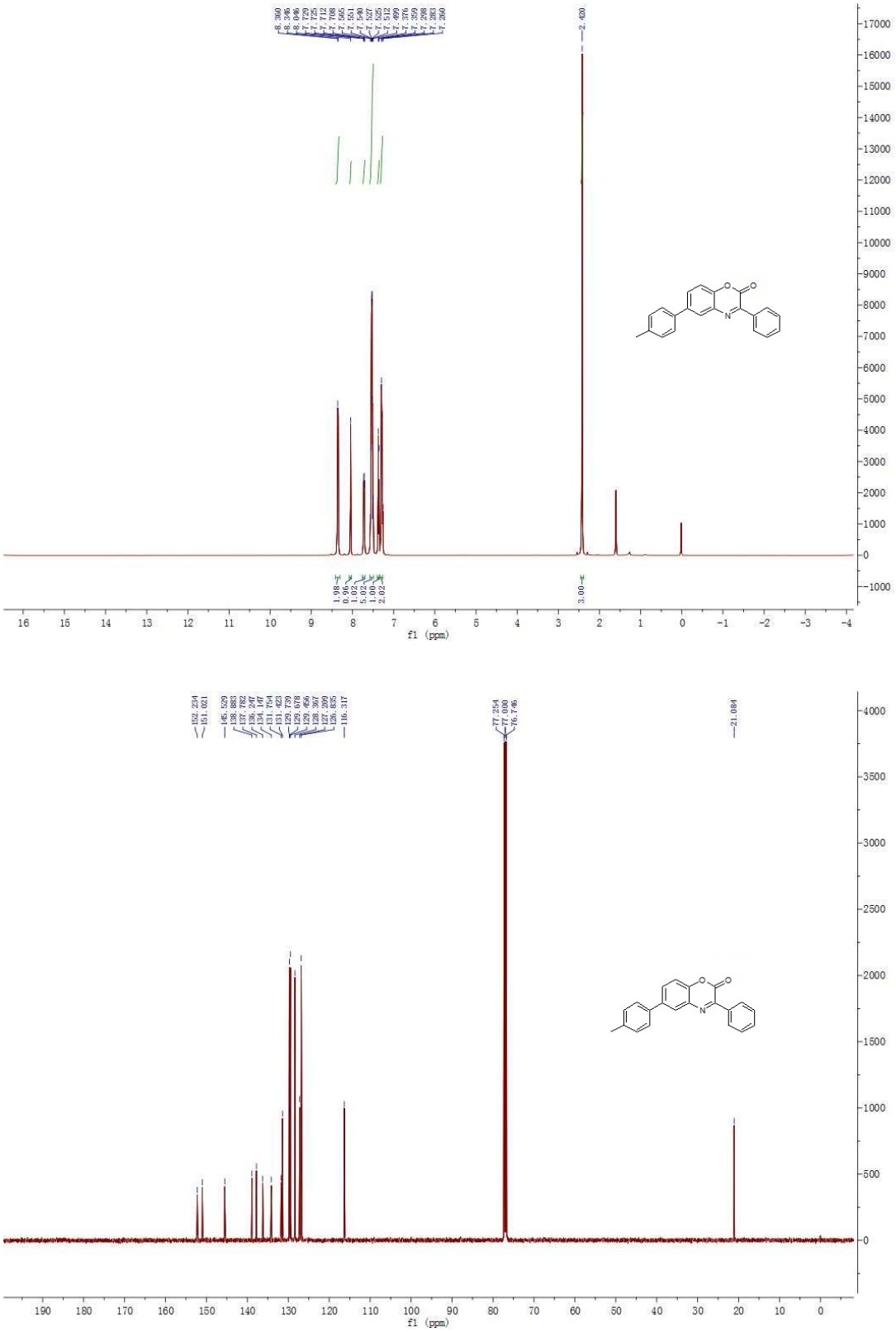


Figure S18. ^{1}H NMR of **3r** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3r** (125 MHz, $CDCl_3$)

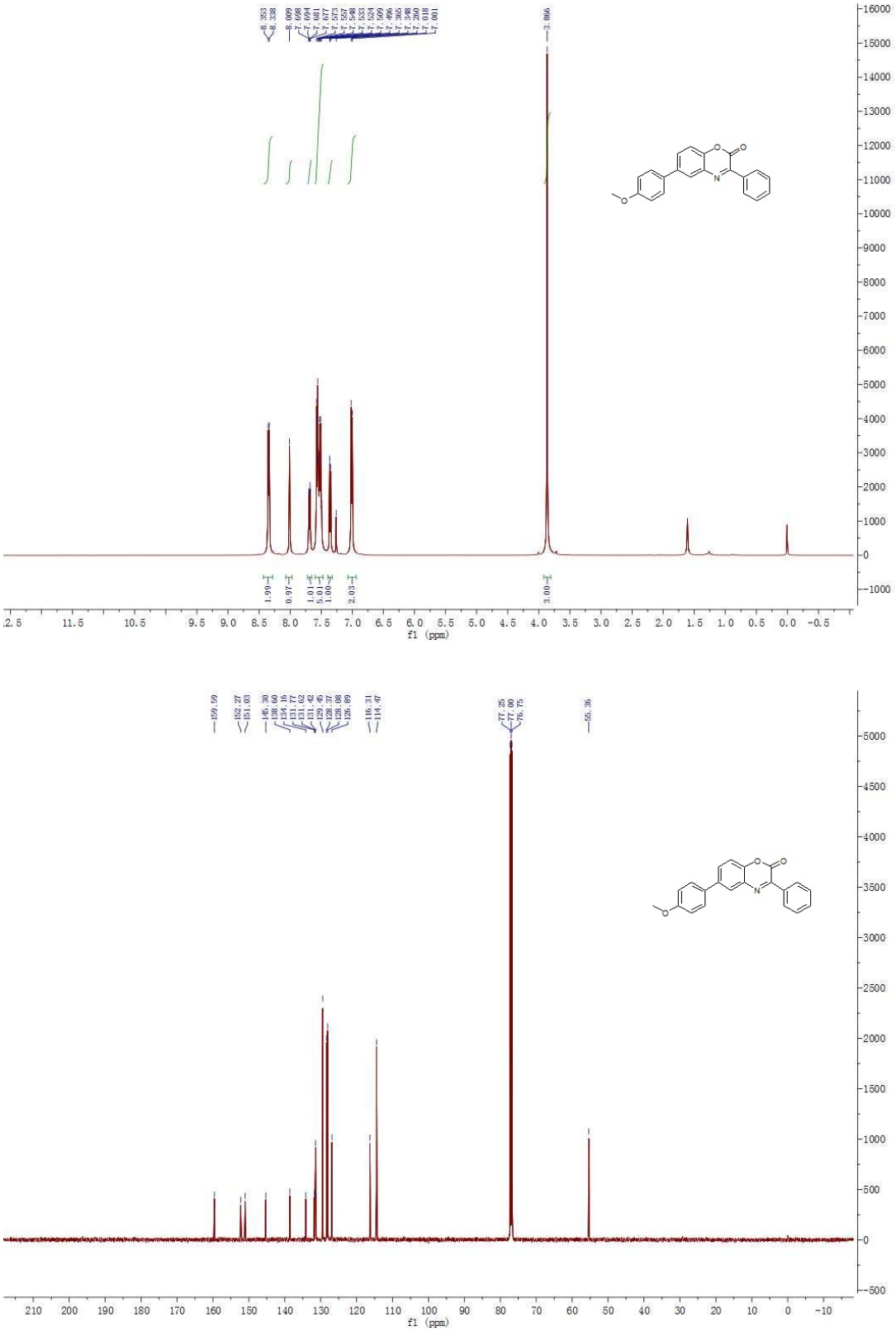


Figure S19. ^{1}H NMR of **3s** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3s** (125 MHz, $CDCl_3$)

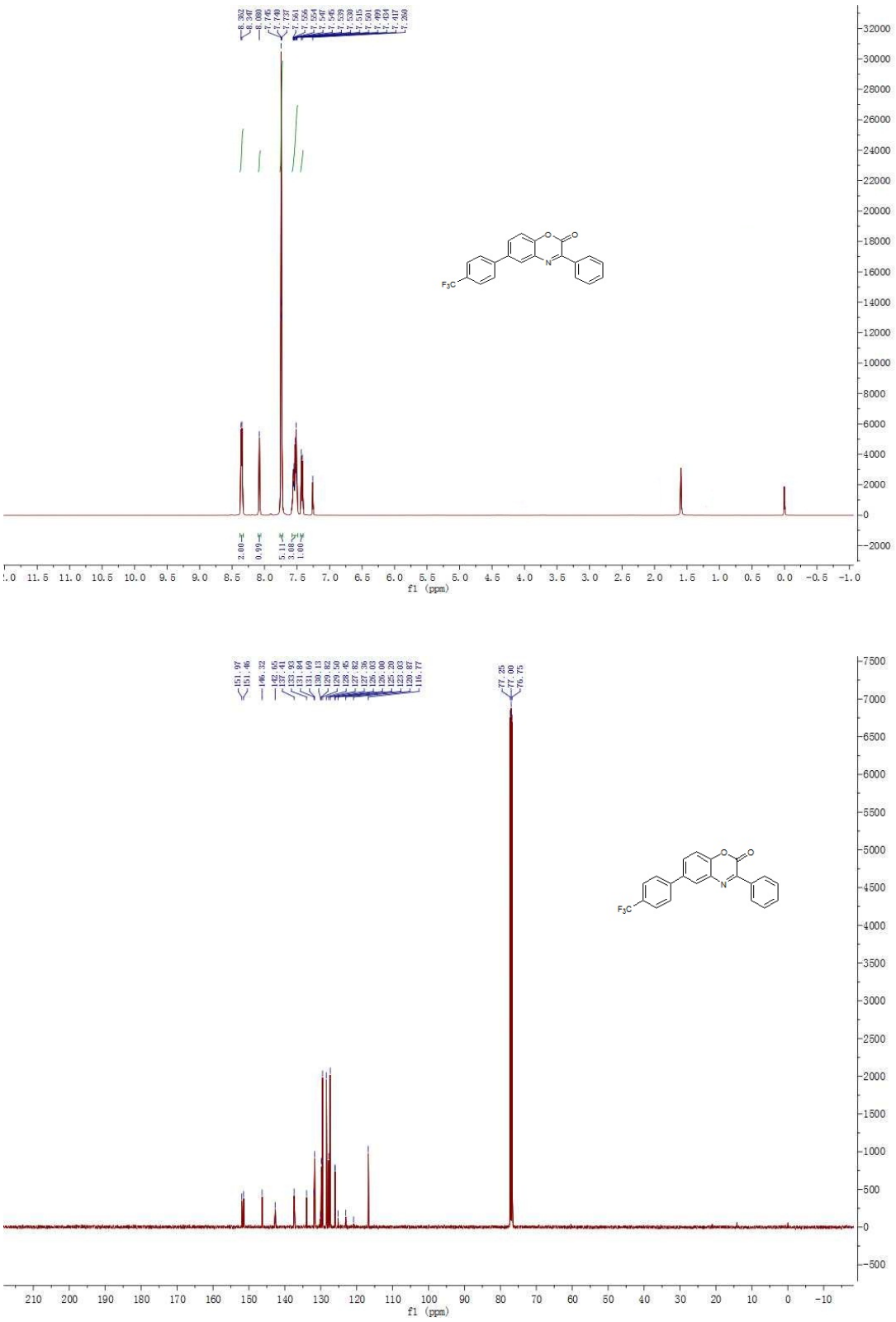


Figure S20. ^{1}H NMR of **3t** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3t** (125 MHz, $CDCl_3$)

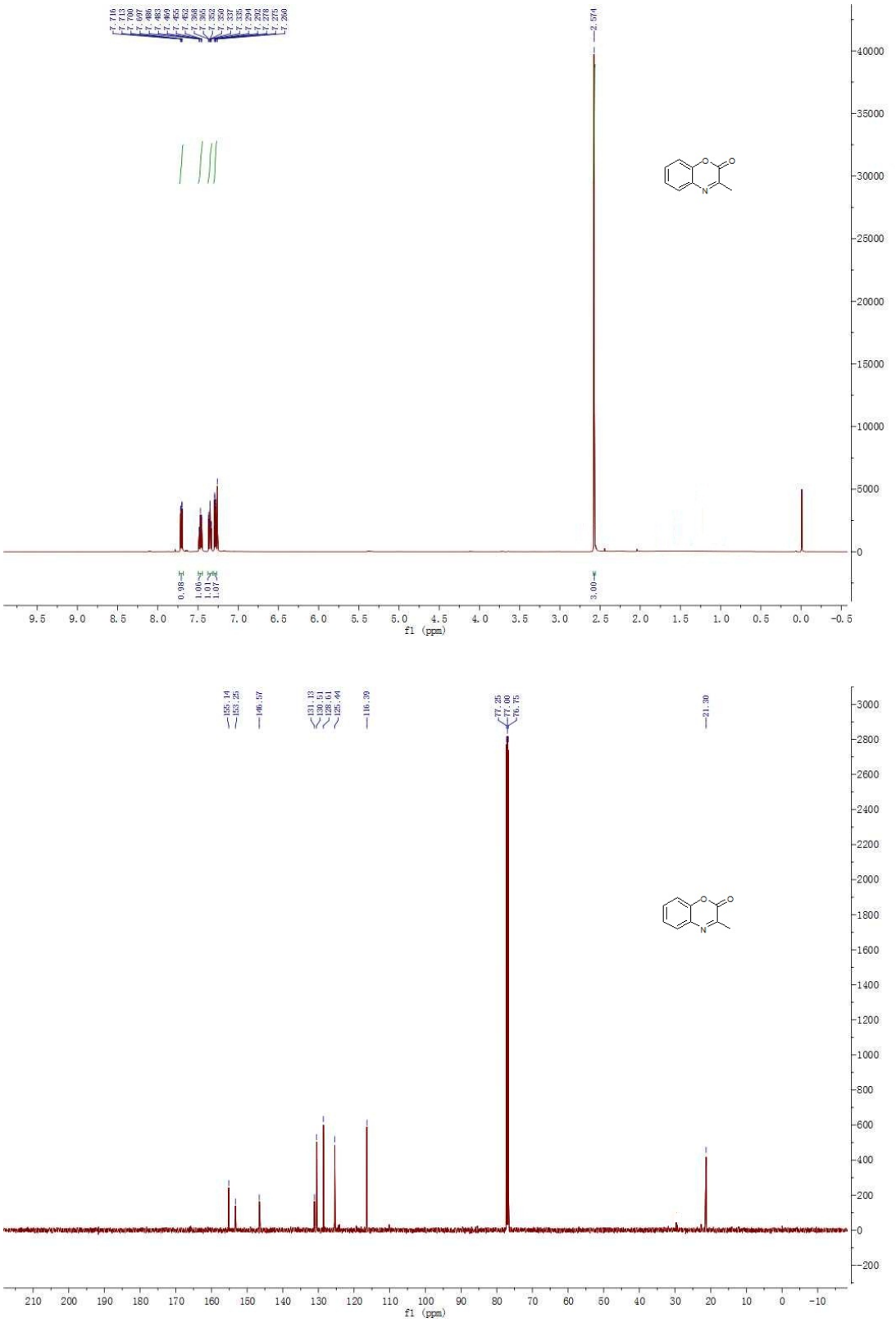


Figure S21. ^{1}H NMR of **3u** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3u** (125 MHz, $CDCl_3$)

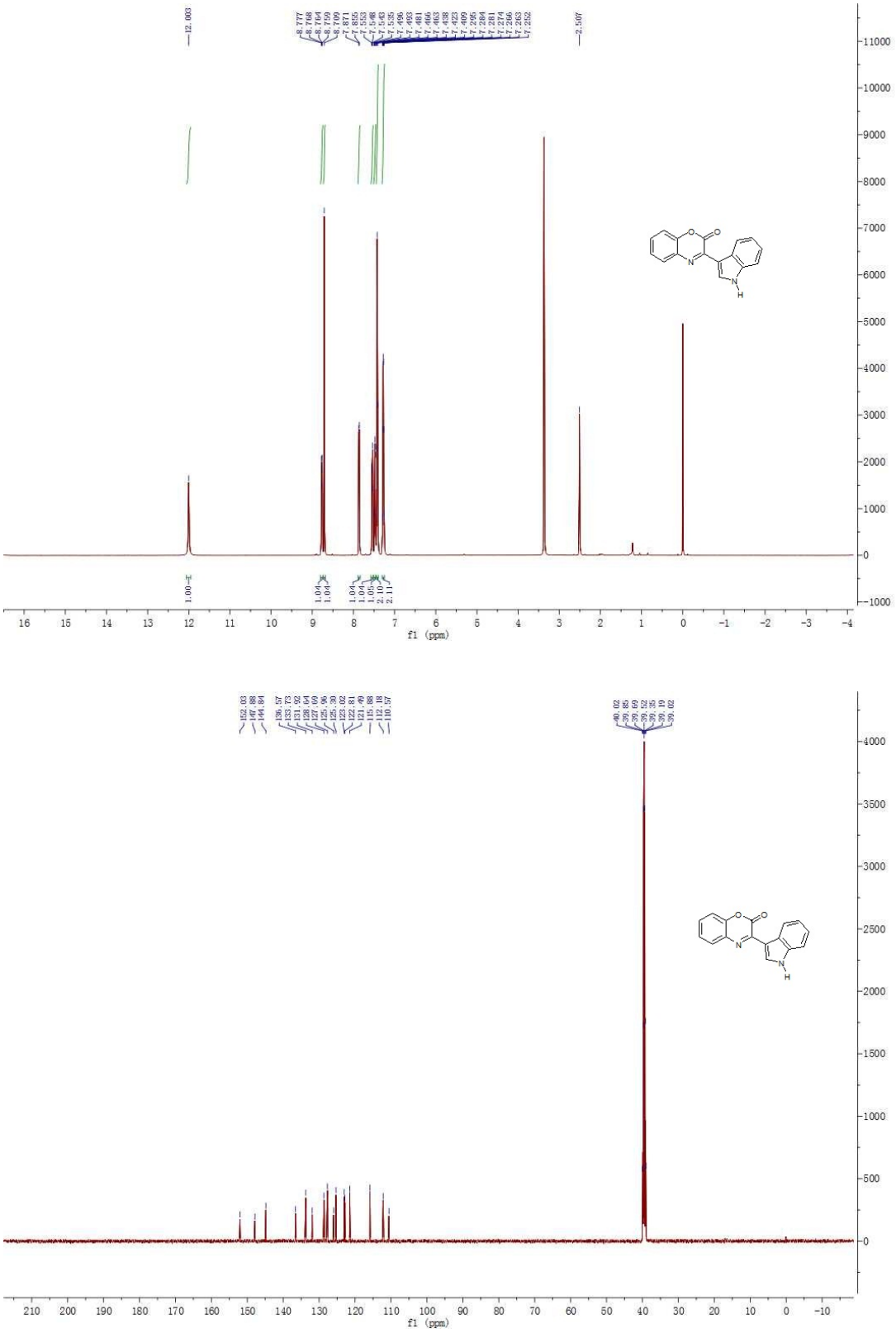


Figure S22. ^{1}H NMR of **cephalandole A** (500 MHz, $CDCl_3$) and ^{13}C NMR of **cephalandole A** (125 MHz, $CDCl_3$)