Supporting Information

Palladium-Catalyzed Carbenoid Based N-H Bond Insertions: Application to the Synthesis of Chiral α-Amino Esters

Gang Liu, Jian Li, Lin Qiu, Li Liu, Guangyang Xu, Bing Ma and Jiangtao Sun

School of Pharmaceutical Engineering and Life Science, Changzhou University, Changzhou 213164, China

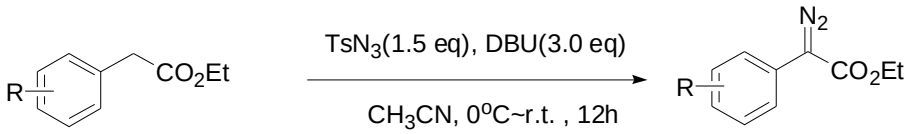
Supporting Information

Ⅰ General Information

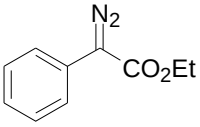
All experiments were reacted under an atmosphere of nitrogen unless otherwise indicated. Flasks were all flamed and cooled before use. All solvents were dried before use. ^{1}H NMR and ^{13}C NMR spectra were reported on a Bruker 300 MHz, 400 MHz, 500 MHz spectrometer. Melting points were determined on a SGW X-4B melting point apparatus. High-resolution mass spectra (HRMS) were performed on Bruker Daltonics, Inc. APEXⅢ 7.0 TESLA FTMS (Shanghai Mass Spectrometry Center, Shanghai Institute of Organic Chemistry). Optical rotations were determined on a Rudolph Autopol IV polarimeter.

Solid and liquid anilines were purchased from Aladdin, and they were sublimed or distilled before use.

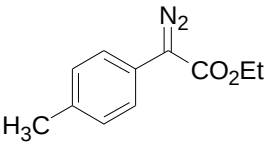
Ⅱ A) Preparation of the diazoesters[1]



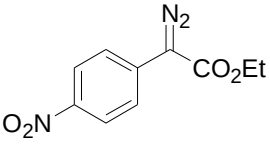
To a solution of ethyl phenyl acetate (25 mmol) and p-toluenesulfonyl azide (TsN_3) (7.39 g, 37.5 mmol) in MeCN (50 mL) was added DBU (11.4 g, 75 mmol) at 0 °C dropwisely. The reaction mixture was then stirred at room temperature for 12 hours. The resulting mixture was quenched with water, extracted with diethyl ether twice. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by a silica gel column chromatography with petroleum to give give the corresponding diazoacetate as yellow oil (3.56 g, 75%).



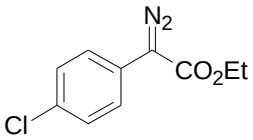
Ethyl 2-diazo-2-phenylacetate[1b]: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.53-7.49 (m, 2H), 7.43-7.38 (m, 2H), 7.23-7.18 (t, *J* = 7.5 Hz, 1H), 4.38-4.31 (q, *J* = 7.5 Hz, 2H), 1.39-1.34 (t, *J* = 7.5 Hz, 3H).



Ethyl 2-diazo-2-(4-tolyl)acetate: Yield: 65%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.40-7.37 (m, 2H), 7.23-7.20 (d, *J* = 9.0 Hz, 2H), 4.38-4.31 (q, *J* = 7.5 Hz, 2H), 2.36 (s, 3H), 1.38-1.33 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.5, 135.7, 129.7, 124.1, 122.3, 60.9, 21.0, 14.5.

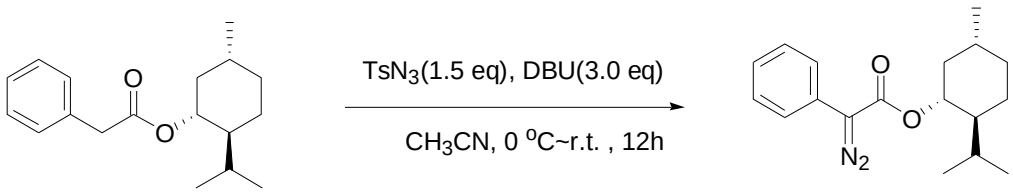


Ethyl 2-diazo-2-(4-nitrophenyl)acetate: Yield: 80%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.26-8.23 (m, 2H), 7.70-7.67 (m, 2H), 4.43-4.35 (q, *J* = 7.5 Hz, 2H), 1.41-1.36 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.8, 145.0, 134.1, 124.3, 123.1, 61.6, 14.5.

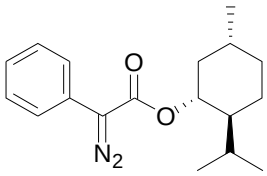


Ethyl 2-diazo-2-(4-chlorophenyl)acetate: Yield: 78%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.46-7.35 (m, 4H), 4.39-4.31 (q, *J* = 7.5 Hz, 2H), 1.38-1.33 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.0, 131.4, 129.1, 125.0, 124.3, 61.2, 14.5.

B) Preparation of phenylmenthyl aryldiazoacetates[2]

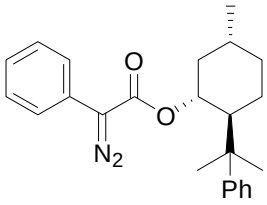


A 150 ml three-necked round bottom flask fitted with a magnetic stir bar was dried and cooled under nitrogen. A solution of menthyl ester[3] (3g, 10.9 mmol) and p-toluenesulfonyl azide (TsN_3) (3.24g, 16.35 mmol) in CH_3CN was added DBU (4.97 g, 32.7 mmol) at 0 °C. After the addition of DBU, the reaction mixture was stirred at room temperature for 12 hours. The reaction mixture was then added sat. NH_4Cl and the layers separated. The aqueous layer was extracted CH_2Cl_2 twice, while the organic layers were combined, washed with brine once, dried over Na_2SO_4 and evaporated in vacuo. The residue was purified by column chromatography on silica gel to get the final product as yellow oil.

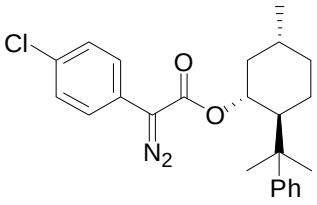


(*1R,2S,5R*)-8-menthyl 2-diazo-2-phenylacetate: Yield: 84%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.53-7.50 (m, 2H), 7.43-7.38 (t, *J* = 7.5 Hz, 2H), 7.22-7.17 (t, *J* = 7.5 Hz, 1H), 4.94-4.85 (m, 1H), 2.17-2.10 (m, 1H), 1.97-1.91 (m, 1H), 1.77-1.71 (m, 2H), 1.53-1.41 (m, 2H), 1.19-1.07 (m, 2H), 0.96-0.92 (m, 7H), 0.84-0.83 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.8, 128.9, 125.8,

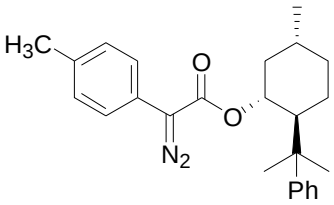
125.7, 123.9, 75.0, 47.1, 41.3, 34.2, 31.5, 26.5, 23.6, 22.1, 20.8, 16.6; $[\alpha]_D^{20}$ = -70.2 (c = 1.40, CH_2Cl_2).



(*1R,2S,5R*)-8-Phenylmenthyl 2-diazo-2-phenylacetate: Yield: 81%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.40-7.13 (m, 10H), 5.15-5.06 (m, 1H), 2.13-2.01 (m, 1H), 1.97-1.91 (m, 1H), 1.84-1.80 (m, 1H), 1.74-1.72 (m, 1H), 1.55-1.51 (m, 1H), 1.38 (s, 3H), 1.27 (s, 3H), 1.21-1.02 (m, 2H), 0.96-0.91 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.0, 151.4, 128.8, 128.0, 127.9, 125.5, 125.2, 125.0, 123.7, 74.3, 50.9, 42.3, 39.6, 34.5, 31.4, 28.3, 26.6, 24.4, 21.8; $[\alpha]_D^{20}$ = -107.4 (c = 1.32, CH_2Cl_2).

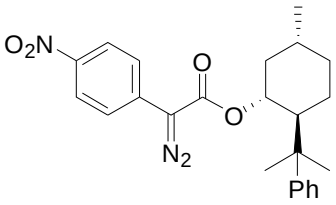


(*1R,2S,5R*)-8-Phenylmenthyl 2-diazo-2-(4-chlorophenyl)acetate: Yield: 86%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.36-7.10 (m, 10H), 5.13-5.04 (m, 1H), 2.12-2.03 (m, 1H), 1.94-1.81 (m, 2H), 1.73-1.68 (m, 1H), 1.36 (s, 3H), 1.27-1.21 (m, 4H), 1.10-1.00 (m, 1H), 0.95-0.85 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.8, 151.4, 131.0, 128.9, 127.9, 125.2, 125.0, 124.8, 124.6, 74.5, 50.9, 42.3, 39.5, 34.5, 31.4, 28.7, 26.5, 23.9, 21.8; $[\alpha]_D^{20}$ = -78.0 (c = 0.90, CH_2Cl_2).



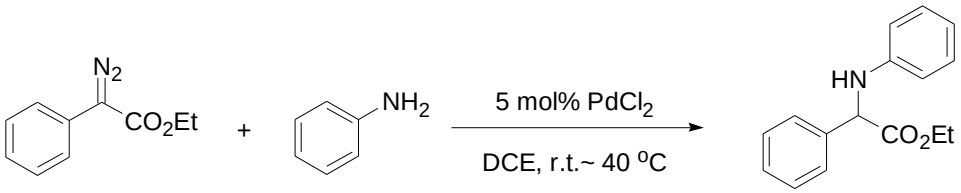
(*1R,2S,5R*)-8-Phenylmenthyl 2-diazo-2-(4-tolyl)acetate: Yield: 70%; ^{1}H NMR (300 MHz, $CDCl_3$): 7.29-7.14 (m, 9H), 5.13-5.01 (m, 1H), 2.36 (s, 3H), 2.11-2.02 (m, 1H), 1.98-1.11 (m, 1H), 1.81-1.67 (m, 2H), 1.55-1.49 (m, 1H), 1.37 (s, 3H), 1.26 (s, 3H), 1.16-0.82 (m, 6H); ^{13}C NMR

(125 MHz, $CDCl_3$) δ 164.3, 151.4, 135.2, 129.5, 128.0, 125.3, 125.0, 123.8, 122.7, 74.3, 51.1, 42.4, 39.6, 34.5, 31.4, 28.2, 26.7, 24.6, 21.8, 21.1; $[\alpha]_D^{20}$ = -80.4 (c = 0.90, CH_2Cl_2).



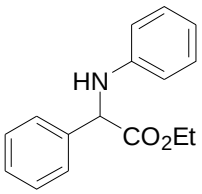
(*1R,2S,5R*)-8-Phenylmenthyl 2-diazo-2-(4-nitrophenyl)acetate: Yield: 75%; ^{1}H NMR (300 MHz, $CDCl_3$): 8.23-8.20 (d, *J* = 9.0 Hz, 2H), 7.53-7.50 (d, *J* = 9.0 Hz, 2H), 7.28-7.26 (m, 2H), 7.19-7.14 (m, 2H), 7.11-7.09 (m, 2H), 5.16-5.07 (m, 1H), 2.17-2.08 (m, 1H), 1.96-1.89 (m, 2H), 1.78-1.71 (m, 1H), 1.55-1.53 (m, 1H), 1.37 (s, 3H), 1.31-1.21 (m, 4H), 1.18-1.02 (m, 1H), 0.94-0.85 (m, 4H); $[\alpha]_D^{20}$ = -152.3 (c = 0.85, CH_2Cl_2).

Ⅲ General Procedure for the Pd catalyzed N-H Insertion Reactions

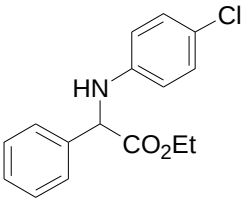


To a Schlenk tube was added aniline (1.1 mmol), $PdCl_2$ (0.05mmol) and $ClCH_2CH_2Cl$ (3 mL) under nitrogen atmosphere. Then the diazoeaster(phenylmenthyl aryldiazoacetates) (1 mmol) was added into the system, and the whole mixture was stirred at room temperature for 3h then at 40^{o}C for 6 hours. The reaction was quenched with water, extracted with dichloromethane twice, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (eluted with ethyl acetate/petroleum ether) to give the desired products.

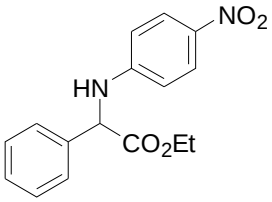
Data for the product



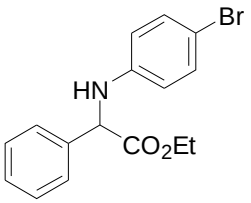
Ethyl 2-(phenylamino)-2-phenylacetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 100/1), mp 84-86 ^{o}C, yield: 82%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.54-7.52 (d, *J* = 6.0 Hz, 2H), 7.40-7.32 (m, 3H), 7.17-7.12 (t, *J* = 7.5 Hz, 2H), 6.74-6.70 (t, *J* = 6.0 Hz, 1H), 6.60-6.57 (d, *J* = 9.0 Hz, 2H), 5.10-4.99 (m, 2H), 4.32-4.10 (m, 2H), 1.26-1.22 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.8, 146.0, 137.7, 129.2, 128.8, 128.2, 127.2, 118.0, 133.4, 66.8, 60.8, 14.0; MS(ESI): 256 (M^{+}+1).



Ethyl 2-(4-chlorophenylamino)-2-phenylacetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 50/1), mp 85-87 ^{o}C, yield: 85%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.50-7.48 (d, *J* = 6.0 Hz, 2H), 7.40-7.33 (m, 3H), 7.09-7.06 (d, *J* = 9.0 Hz, 2H), 6.51-6.48 (d, *J* = 9.0 Hz, 2H), 5.01 (br, 2H), 4.32-4.10 (m, 2H), 1.26-1.21 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.5, 144.4, 137.2, 129.1, 128.9, 128.4, 127.2, 122.6, 114.5, 62.0, 60.7, 14.1; MS(ESI): 290 (M^{+}+1).

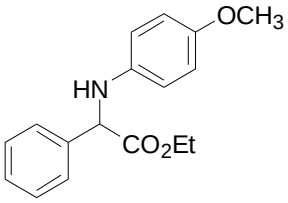


Ethyl 2-(4-nitrophenylamino)-2-phenylacetate: Yellow solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 40/1), mp 119-121 ^{o}C, yield: 93%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.06-8.03 (d, *J* = 9.0 Hz, 2H), 7.49-7.46 (m, 2H), 7.40-7.37 (m, 3H), 6.53-6.50 (d, *J* = 9.0 Hz, 2H), 5.87-5.86 (d, *J* = 3.0 Hz, 1H), 5.15-5.12 (d, *J* = 6.0 Hz, 1H), 4.33-4.15 (m, 2H), 1.27-1.23 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 150.8, 138.8, 136.1, 129.2, 128.8, 127.0, 126.2, 112.1, 62.5, 59.9, 14.0; MS(ESI): 323 (M^{+} +Na).

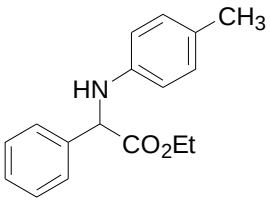


Ethyl 2-(4-bromophenylamino)-2-phenylacetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 50/1), mp 102-104 ^{o}C, yield: 90%; ^{1}H NMR (300 MHz,

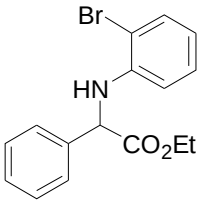
$CDCl_3$): δ (ppm) 7.50-7.47 (m, 2H), 7.38-7.33 (m, 3H), 7.23-7.16 (m, 2H), 6.46-6.43 (d, *J* = 9.0 Hz, 2H), 5.05-4.99 (m, 2H), 4.29-4.12 (m, 2H), 1.26-1.21 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.5, 144.8, 137.1, 132.0, 128.9, 128.4, 127.2, 115.0, 109.7, 62.0, 60.6, 14.1; MS(ESI): 334 (M^+ +1).



Ethyl 2-(4-methoxyphenylamino)-2-phenylacetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 40/1), mp 45-47 °C, yield: 84%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.53-7.50 (d, *J* = 9.0 Hz, 2H), 7.40-7.32 (m, 3H), 6.76-6.73 (m, 2H), 6.57-6.54 (m, 2H), 5.03-5.01 (d, *J* = 6.0 Hz, 1H), 4.71-4.69 (d, *J* = 6.0 Hz, 1H), 4.30-4.09 (m, 2H), 3.73 (s, 3H), 1.25-1.21 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.1, 152.4, 140.2, 137.8, 128.8, 128.2, 127.2, 114.8, 114.7, 61.4, 55.7, 51.0, 14.1; MS(ESI): 286 (M^+ +1).

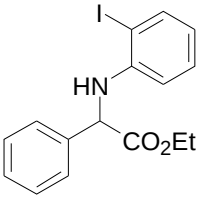


Ethyl 2-(p-toluidino)-2-phenylacetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 50/1), mp 86-88 °C, yield: 74%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.54-7.51 (d, *J* = 6.0 Hz, 2H), 7.40-7.32 (m, 3H), 6.97-6.94 (d, *J* = 9.0 Hz, 2H), 6.52-6.49 (m, 2H), 5.07-5.06 (d, *J* = 3.0 Hz, 1H), 4.86-4.84 (d, *J* = 6.0 Hz, 1H), 4.31-4.10 (m, 2H), 2.22 (s, 3H), 1.26-1.21 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.0, 143.7, 137.8, 129.7, 128.8, 128.2, 127.2, 113.5, 61.8, 61.1, 20.4, 14.1; MS(ESI): 292 (M^++Na).

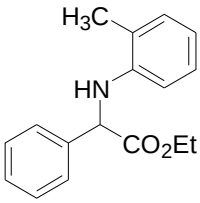


Ethyl 2-(2-bromophenylamino)-2-phenylacetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 100/1), mp 61-63 °C, yield: 78%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.55-7.52 (d, *J* = 9.0 Hz, 2H), 7.48-7.46 (d, *J* = 6.0 Hz, 1H), 7.42-7.34 (m, 3H), 7.07-7.02 (t, *J* = 7.5 Hz, 1H), 6.61-6.56 (t, *J* = 7.5 Hz, 1H), 6.39-6.37 (d, *J* = 6.0 Hz, 1H),

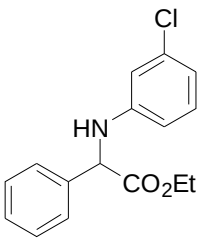
5.80-5.79 (d, J = 3.0 Hz, 1H), 5.13-5.11 (d, J = 6.0 Hz, 1H), 4.34-4.13 (m, 2H), 1.28-1.22 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.2, 142.9, 137.1, 132.5, 128.9, 128.4, 128.4, 127.1, 118.5, 112.2, 110.1, 62.1, 60.7, 14.1; MS(ESI): 334 (M^+ +1).`



Ethyl 2-(2-iodophenylamino)-2-phenylacetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 50/1), mp 71-74 °C, yield: 84%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.71-7.68 (d, J = 9.0 Hz, 1H), 7.53-7.50 (m, 2H), 7.41-7.33 (m, 3H), 7.09-7.04 (m, 1H), 6.47-6.42 (t, J = 7.5 Hz, 1H), 6.31-6.28 (m, 1H), 5.69-5.68 (d, J = 3.0 Hz, 1H), 5.11-5.09 (d, J = 6.0 Hz, 1H), 4.30-4.15 (m, 2H), 1.27-1.22 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.1, 145.2, 139.1, 137.0, 129.3, 128.9, 128.4, 127.1, 119.3, 111.5, 85.6, 62.1, 61.0, 14.0; MS(ESI): 382 (M^++1).

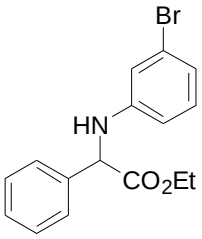


Ethyl 2-(2-toluidino)-2-phenylacetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate =100/1), mp 35-37 °C, yield: 78%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.47-7.45 (d, J = 6.0 Hz, 2H), 7.33-7.22 (m, 3H), 7.03-7.00 (d, J = 9.0 Hz, 1H), 6.95-6.89 (t, J = 9.0 Hz, 1H), 6.61-6.56 (t, J = 7.5 Hz, 1H), 6.29-6.26 (d, J = 9.0 Hz, 1H), 5.05-5.03 (d , J = 6.0 Hz, 1H), 4.87-4.85 (d, J = 6.0 Hz, 1H), 4.25-4.03 (m, 2H), 2.23 (s, 3H), 1.19-1.14 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.0, 144.0, 137.8, 130.2, 128.8, 128.2, 127.2, 127.0, 122.4, 117.6, 110.7, 61.8, 60.8, 17.5, 14.0; MS(ESI): 270 (M^+ +1).

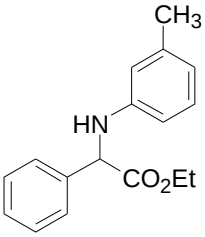


Ethyl 2-(3-chlorophenylamino)-2-phenylacetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 100/1), mp 86-88 °C, yield: 87%; ^{1}H NMR (300 MHz,

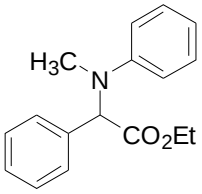
$CDCl_3$): δ (ppm) 7.51-7.47 (m, 2H), 7.42-7.33 (m, 3H), 7.06-7.01 (t, *J* = 7.5 Hz, 1H), 6.69-6.66 (m, 1H), 6.56-6.55 (m, 1H), 6.46-6.43 (d, *J* = 9.0 Hz, 1H), 5.12-5.10 (d, *J* = 6.0 Hz, 1H), 5.05-5.03 (d, *J* = 6.0 Hz, 1H), 4.30-4.12 (m, 2H), 1.26-1.22 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.5, 147.0, 137.1, 134.9, 130.2, 128.9, 128.4, 127.1, 117.9, 113.2, 111.6, 62.1, 60.4, 14.1; MS(ESI): 290 (M^+ +1).



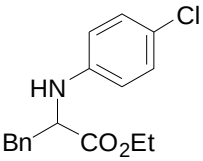
Ethyl 2-(3-bromophenylamino)-2-phenylacetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 50/1), mp 87-89 °C, yield: 85%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.51-7.49 (d, *J* = 6.0 Hz, 2H), 7.42-7.33 (m, 3H), 7.00-6.95 (t, *J* = 7.5 Hz, 1H), 6.83-6.81 (d, *J* = 6.0 Hz, 1H), 6.73-6.72 (m, 1H), 6.48-6.46 (d, *J* = 6.0 Hz, 1H), 5.11-5.09 (d, *J* = 6.0 Hz, 1H), 5.05-5.03 (d, *J* = 6.0 Hz, 1H), 4.30-4.12 (m, 2H), 1.26-1.22 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.4, 147.2, 137.1, 130.5, 129.0, 128.5, 127.1, 123.2, 120.8, 116.1, 111.9, 62.1, 60.4, 14.1; MS(ESI): 334 (M^+ +1).



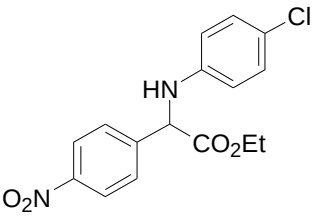
Ethyl 2-(m-toluidino)-2-phenylacetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 50/1), mp 108-110 °C, yield: 82%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.53-7.51 (d, *J* = 6.0 Hz, 2H), 7.40-7.32 (m, 3H), 7.05-7.00 (t, *J* = 7.5 Hz, 1H), 6.56-6.53 (d, *J* = 9.0 Hz, 1H), 6.44 (s, 1H), 6.38-6.36 (d, *J* = 6.0 Hz, 1H), 5.08 (s, 1H), 4.92 (s, 1H), 4.32-4.10 (m, 2H), 2.25 (s, 3H), 1.21 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.9, 146.0, 139.0, 137.8, 129.1, 128.8, 128.2, 127.2, 119.0, 114.3, 110.4, 61.8, 60.8, 21.6, 14.1; MS(ESI): 270 (M^++1).



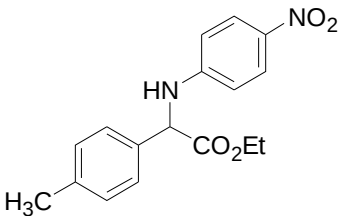
Ethyl 2-(methylphenylamino)-2-phenylacetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 50/1), mp 71-73 ^{o}C, yield: 86%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.43-7.28 (m, 7H), 6.92-6.89 (d, J = 6.0 Hz, 2H), 6.86-6.81 (t, J = 7.5 Hz, 1H), 5.67 (s, 1H), 4.35-4.23 (m, 2H), 2.82 (s, 3H), 1.32-1.27 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.9, 149.9, 136.0, 129.3, 128.6, 128.4, 128.0, 118.0, 113.4, 65.7, 61.1, 34.6, 14.3; MS(ESI): 270 (M^{+}+1).



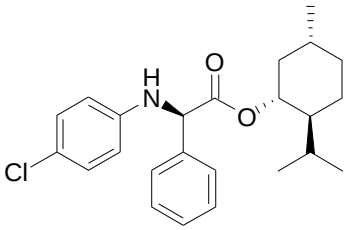
Ethyl 2-(4-chlorophenylamino)-2-benzylacetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 50/1), mp 53-55 ^{o}C, yield: 82%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.34-7.32 (m, 7H), 6.56-6.53 (d, J = 9.0 Hz, 2H), 4.33-4.28 (m, 1H), 4.21-4.11 (m, 3H), 3.20-3.08 (m, 2H), 1.23-1.18 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.9, 145.0, 136.1, 129.3, 129.2, 128.6, 127.1, 123.0, 114.7, 61.3, 57.8, 38.5, 14.2; MS(ESI): 305 (M^{+}+1).



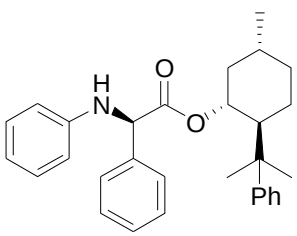
Ethyl 2-(4-chlorophenylamino)-2-(4-nitrophenyl)acetate: Yellow solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 30/1), mp 101-103 ^{o}C, yield: 84%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.26-8.23 (d, J = 9.0 Hz, 2H), 7.72-7.69 (d, J = 9.0 Hz, 2H), 7.10-7.07 (d, J = 9.0 Hz, 2H), 6.44-6.41 (d, J = 9.0 Hz, 2H), 5.20-5.18 (d, J = 6.0 Hz, 1H), 5.13-5.12 (d, J = 3.0 Hz, 1H), 4.34-4.13 (m, 2H), 1.27-1.22 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.0, 148.0, 144.8, 143.7, 129.3, 128.1, 124.1, 123.4, 114.5, 62.7, 60.3, 14.0; MS(ESI): 335 (M^{+}+1).



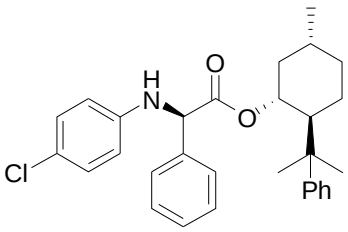
Ethyl 2-(4-nitrophenylamino)-2-(4-tolyl)acetate: Yellow solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 30/1), mp 125-127 ^{o}C, yield: 88%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.05-8.02 (d, *J* = 9.0 Hz, 2H), 7.36-7.34 (d, *J* = 6.0 Hz, 2H), 7.21-7.18 (d, *J* = 9.0 Hz, 2H), 6.53-6.50 (d, *J* = 9.0 Hz, 2H), 5.85-5.83 (d, *J* = 6.0 Hz, 1H), 5.11-5.09 (d, *J* = 6.0 Hz, 1H), 4.32-4.14 (m, 2H), 3.36 (s, 3H), 1.27-1.23 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.8, 150.9, 138.7, 138.7, 133.0, 129.8, 126.9, 126.2, 112.1, 62.4, 59.7, 21.2, 14.0; MS(ESI): 315 (M^{+}+1).



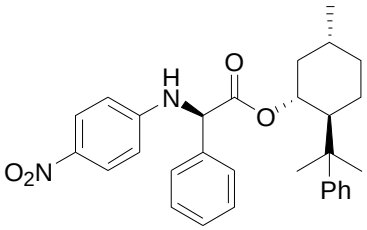
(*1R,2S,5R*)-8-menthyl (*R*)-2-(4-chlorophenylamino)-2-phenylacetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 100/1), mp 97-99 ^{o}C, yield: 78%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.49-7.46 (m, 2H), 7.37-7.34 (m, 3H), 7.09-7.06 (d, *J* = 9.0 Hz, 2H), 6.52-6.49 (d, *J* = 9.0 Hz, 2H), 5.02 (br, 2H), 4.79-4.70 (m, 1H), 1.94-1.84 (m, 1H), 1.71-1.64 (m, 3H), 1.45-1.36 (m, 3H), 1.12-1.02 (m, 1H), 0.94-0.91 (m, 3H), 0.84-0.73 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.1, 144.5, 137.2, 129.1, 128.8, 128.3, 127.1, 122.6, 114.5, 76.0, 60.8, 46.9, 39.9, 34.1, 31.3, 26.3, 23.3, 21.9, 20.8, 16.2; $[\alpha]_D^{20}$ = -10.6 (c = 0.70, CH_2Cl_2); HRMS (ESI) exact mass calcd. for $C_{24}H_{30}ClNO_2$: m/z 422.1857 ($[M + Na]^{+}$), found: m/z 422.1853 ($[M + Na]^{+}$).



(*1R,2S,5R*)-8-Phenylmenthyl (*R*)-2-(phenylamino)-2-phenylacetate: Colorless oil (Flash column chromatography eluent: petroleum ether/ethyl acetate = 100/1), yield: 75%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.52-7.50 (d, *J* = 6.0 Hz, 2H), 7.38-7.33 (t, *J* = 7.5 Hz, 2H), 7.25-7.20 (t, *J* = 7.5 Hz, 3H), 7.16-7.09 (m, 5H), 6.73-6.68 (t, *J* = 7.5 Hz, 1H), 6.57-6.54 (d, *J* = 9.0 Hz, 1H), 4.89-4.78 (m, 3H), 1.91-1.87 (m, 2H), 1.40-1.21 (m, 5H), 1.11-0.95 (m, 3H), 0.90-0.70 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 150.0, 146.0, 137.3, 129.1, 128.8, 128.4, 127.9, 127.8, 125.7, 125.4, 117.9, 113.5, 77.2, 61.6, 50.4, 41.6, 40.0, 34.4, 31.3, 29.7, 29.0, 27.2, 24.1, 21.7; $[\alpha]_D^{20}$ = -23.7 (c = 0.70, CH_2Cl_2); HRMS (ESI) exact mass calcd. for $C_{30}H_{35}NO_2$: m/z 464.2560 ($[M + Na]^+$), found: m/z 464.2549 ($[M + Na]^+$).

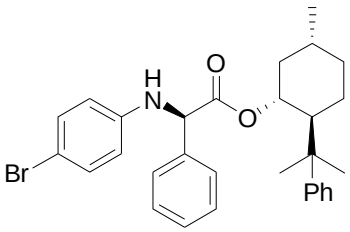


(*1R,2S,5R*)-8-Phenylmenthyl (*R*)-2-(4-chlorophenylamino)-2-phenylacetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 100/1), mp 100-102 ^{o}C, yield: 89%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.48-7.46 (d, *J* = 6.0 Hz, 2H), 7.35-7.19 (m, 7H), 7.13-7.05 (m, 5H), 6.46-6.43 (d, *J* = 9.0 Hz, 2H), 4.86-4.78 (m, 3H), 1.91-1.83 (m, 2H), 1.51-1.31 (m, 3H), 1.07-0.92 (m, 5H), 0.86-0.72 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.3, 150.1, 144.4, 136.8, 128.9, 128.9, 128.5, 127.9, 127.8, 125.6, 125.5, 114.6, 100.0, 77.3, 61.5, 50.4, 44.2, 41.6, 39.9, 34.3, 31.3, 28.6, 27.1, 24.5, 21.7; $[\alpha]_D^{20}$ = -52.14 (c = 0.80, CH_2Cl_2); HRMS (ESI) exact mass calcd. for $C_{30}H_{34}ClNO_2$: m/z 498.2170 ($[M + Na]^+$), found: m/z 498.2178 ($[M + Na]^+$).

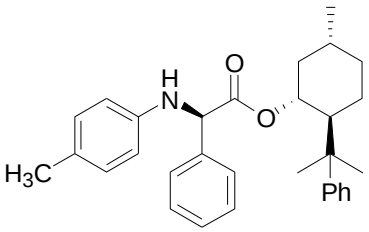


(*1R,2S,5R*)-8-Phenylmenthyl (*R*)-2-(4-nitrophenylamino)-2-phenylacetate: Yellow solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 40/1), mp 100-102 ^{o}C,

yield: 91%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.05-8.02 (d, *J* = 9.0 Hz, 2H), 7.46-7.43 (m, 2H), 7.40-7.31 (m, 3H), 7.25-7.20 (m, 2H), 7.14-7.11 (d, *J* = 9.0 Hz, 2H), 7.08-7.03 (t, *J* = 7.5 Hz, 1H), 6.48-6.45 (d, *J* = 9.0 Hz, 2H), 5.59-5.57 (d, *J* = 6.0 Hz, 1H), 4.89-4.82 (m, 2H), 1.96-1.86 (m, 2H), 1.54-1.37 (m, 3H), 1.16-1.04 (m, 4H), 0.92-0.73 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.3, 150.8, 150.0, 138.7, 135.8, 129.1, 128.9, 128.0, 127.6, 126.1, 125.6, 125.5, 112.2, 78.0, 60.8, 50.4, 41.6, 39.9, 34.3, 31.4, 27.9, 27.1, 25.1, 21.7; $[\alpha]_D^{20}$ = -68.3 (c = 0.86, CH_2Cl_2); HRMS (ESI) exact mass calcd. for $C_{30}H_{34}N_2O_4$: m/z 509.2411 ($[M + Na]^+$), found: m/z 509.2408 ($[M + Na]^+$).

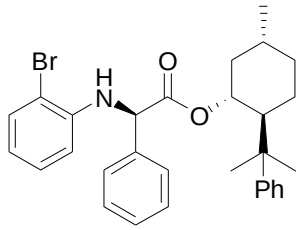


(*1R,2S,5R*)-8-Phenylmenthyl (*R*)-2-(4-bromophenylamino)-2-phenylacetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 100/1), mp 98-101 ^{o}C, yield: 86%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.47-7.45 (d, *J* = 6.0 Hz, 2H), 7.37-7.18 (m, 8H), 7.13-7.05 (m, 3H), 6.42-6.39 (d, *J* = 9.0 Hz, 2H), 4.85-4.79 (m, 3H), 1.92-1.88 (m, 2H), 1.45-1.38 (m, 3H), 1.03-1.00 (m, 3H), 0.93-0.80 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.3, 150.1, 144.8, 136.8, 131.8, 128.9, 128.5, 127.9, 127.7, 125.6, 125.5, 115.1, 109.6, 77.4, 61.4, 50.4, 41.6, 39.9, 34.3, 31.3, 28.5, 27.1, 24.6, 21.7; $[\alpha]_D^{20}$ = -44.2 (c = 1.00, CH_2Cl_2); HRMS (ESI) exact mass calcd. for $C_{30}H_{34}BrNO_2$: m/z 542.1665 ($[M + Na]^+$), found: m/z 542.1663 ($[M + Na]^+$).

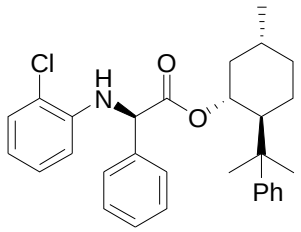


(*1R,2S,5R*)-8-Phenylmenthyl (*R*)-2-(p-toluidino)-2-phenylacetate: Colorless oil (Flash column chromatography eluent: petroleum ether/ethyl acetate = 100/1), yield: 82%; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.48-7.46(d, *J* = 10.0 Hz, 2H), 7.33-7.30 (t, *J* = 7.5 Hz, 2H), 7.25-7.22 (m, 1H),

7.21-7.18 (t, *J* = 7.5 Hz, 2H), 7.10-7.07 (m, 3H), 6.92-6.90 (d, *J* = 10 Hz, 2H), 6.46-6.45 (d, *J* = 5.0 Hz, 2H), 4.84 (s, 1H), 4.82-4.77 (m, 1H), 4.67 (br, 1H), 2.19 (s, 3H), 1.92-1.81 (m, 2H), 1.51-1.48 (m, 1H), 1.41-1.31 (m, 2H), 1.06-0.99 (m, 4H), 0.91-0.86 (m,1H), 0.83-0.82 (m, 6H), 0.78-0.70 (m, 1H);^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 150.1, 143.8, 137.5, 129.6, 128.8, 128.3, 127.9, 127.9, 127.1, 125.7, 125.4, 113.6, 61.9, 50.5, 41.7, 40.0, 34.4, 31.3, 29.1, 27.2, 24.2, 21.7, 20.4; $[\alpha]_D^{20}$ = -67.2 (c = 1.4, CH_2Cl_2); HRMS (ESI) exact mass calcd. for $C_{31}H_{37}NO_2$: m/z 478.2717 ($[M + Na]^+$), found: m/z 478.2715.

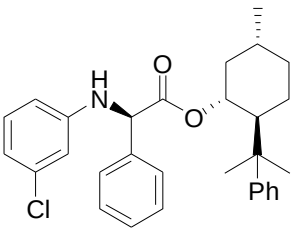


(*1R,2S,5R*)-8-Phenylmenthyl (*R*)-2-(2-bromophenylamino)-2-phenylacetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 100/1), mp 91-93 ^{o}C, yield: 74%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.54-7.12 (m, 12H), 6.60-6.55 (t, *J* = 7.5 Hz, 1H), 6.41-6.39 (d, *J* = 6.0 Hz, 1H), 5.74-5.73 (d, *J* = 3.0 Hz, 1H), 4.90-4.82 (m, 2H), 1.97-1.85 (m, 2H), 1.50-1.29 (m, 3H), 1.11-1.06 (m, 3H), 0.91-0.80 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.1, 149.9, 143.0, 136.7, 132.5, 128.9, 128.5, 128.3, 127.9, 127.8, 125.7, 125.4, 118.4, 112.2, 110.2, 61.4, 50.4, 41.7, 40.0, 34.3, 31.4, 29.2, 27.2, 23.9, 21.7; $[\alpha]_D^{20}$ = -19.5 (c = 0.67, CH_2Cl_2); HRMS (ESI) exact mass calcd. for $C_{30}H_{34}BrNO_2$: m/z 542.1665 ($[M + Na]^+$), found: m/z 542.1664 ($[M + Na]^+$).

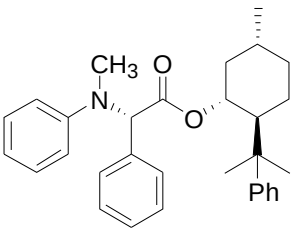


(*1R,2S,5R*)-8-Phenylmenthyl (*R*)-2-(2-chlorophenylamino)-2-phenylacetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 100/1), mp 89-92 ^{o}C, yield: 81%; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.50-7.48 (d, *J* = 10.0 Hz, 2H), 7.36-7.33 (t, *J* = 7.5 Hz, 2H), 7.28-7.24 (m, 2H), 7.20-7.17 (t, *J* = 7.5 Hz, 2H), 7.11-7.09 (m, 2H), 7.05-7.02 (t, *J* = 7.5

Hz, 1H), 7.00-6.97 (m, 1H), 6.63-6.60 (t, J = 7.5 Hz, 1H), 6.40-6.39 (d, J = 5.0 Hz, 1H), 5.64-5.63 (d, J = 5.0 Hz, 1H), 4.87-4.80 (m, 2H), 1.93-1.83 (m, 2H), 1.54-1.26 (m, 4H), 1.09-1.02 (m, 3H), 0.95-0.83 (m, 3H), 0.79-0.72 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.2, 149.9, 142.1, 136.8, 129.2, 128.9, 128.5, 127.9, 127.8, 127.6, 125.7, 125.3, 119.7, 117.9, 112.1, 77.4, 61.3, 50.5, 41.7, 40.0, 34.3, 31.4, 29.2, 27.2, 24.0, 21.7; $[\alpha]_D^{20}$ = -34.9 (c = 0.60, CH_2Cl_2); HRMS (ESI) exact mass calcd. for $C_{30}H_{34}ClNO_2$: m/z 498.2170 ($[M + Na]^+$), found: m/z 498.2167 ($[M + Na]^+$).

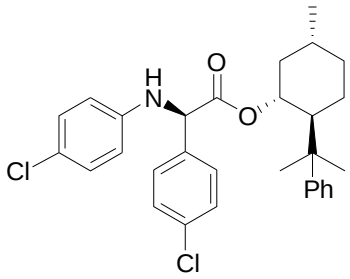


(*1R,2S,5R*)-8-Phenylmenthyl (*R*)-2-(3-chlorophenylamino)-2-phenylacetate: Colorless oil (Flash column chromatography eluent: petroleum ether/ethyl acetate = 100/1), yield: 84%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.50-7.47 (d, J = 9.0 Hz, 2H), 7.39-7.20 (m, 5H), 7.14-7.00 (m, 4H), 6.68-6.66 (d, J = 6.0 Hz, 1H), 6.53 (s, 1H), 6.42-6.40 (d, J = 6.0 Hz, 1H), 4.90-4.82 (m, 3H), 1.94-1.85 (m, 2H), 1.52-1.35 (m, 3H), 1.14-0.93 (m, 4H), 0.87-0.73 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 150.0, 147.1, 136.6, 134.8, 130.1, 128.9, 128.6, 127.9, 127.7, 125.6, 125.4, 117.8, 113.3, 111.8, 61.3, 50.4, 41.6, 39.9, 34.3, 31.3, 28.6, 27.1, 24.5, 21.7; $[\alpha]_D^{20}$ = -22.5 (c = 0.55, CH_2Cl_2); HRMS (ESI) exact mass calcd. for $C_{30}H_{34}ClNO_2$: m/z 498.2170 ($[M + Na]^+$), found: m/z 498.2170 ($[M + Na]^+$).

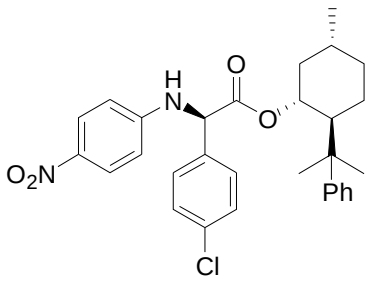


(*1R,2S,5R*)-8-Phenylmenthyl (*S*)-2-(methylphenylamino)-2-phenylacetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 100/1), mp 77-79 ^{o}C, yield: 86%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.40-7.11 (m, 12H), 6.82-6.77 (t, J = 7.5 Hz, 1H), 6.70-6.67 (d, J = 9.0 Hz, 2H), 4.93-4.84 (m, 1H), 4.75 (s, 1H), 2.78 (s, 3H), 2.07-1.99 (m, 1H), 1.79-1.62 (m, 3H), 1.44-1.09 (m, 8H), 0.91-0.83 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 151.6, 149.5,

135.5, 129.0, 128.4, 128.3, 128.0, 127.7, 125.4, 125.1, 117.7, 113.5, 75.6, 65.8, 50.3, 41.4, 39.7, 35.2, 34.5, 31.2, 27.7, 26.6, 25.1, 21.8; $[\alpha]_D^{20}$ = +36.5 (c = 0.70, CH_2Cl_2); HRMS (ESI) exact mass calcd. for $C_{31}H_{37}NO_2$: m/z 478.2717 ($[M + Na]^+$), found: m/z 478.2729 ($[M + Na]^+$).

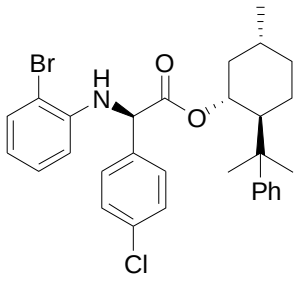


(*1R,2S,5R*)-8-Phenylmenthyl (*R*)-2-(4-chlorophenylamino)-2-(4-chlorophenyl)acetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 100/1), mp 170-172 ^oC, yield: 75%; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.42-7.39 (d, *J* = 9.0 Hz, 2H), 7.34-7.31 (d, *J* = 9.0 Hz, 2H), 7.25-7.21 (m, 2H), 7.17-7.15 (m, 2H), 7.08-7.05 (m, 3H), 6.41-6.38 (d, *J* = 9.0 Hz, 2H), 4.90-4.81 (m, 1H), 4.73 (br, 2H), 1.97-1.83 (m, 2H), 1.54-1.33 (m, 3H), 1.12-1.01 (m, 4H), 1.00-0.91 (m, 4H), 0.87-0.77 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8, 150.2, 144.2, 135.6, 134.3, 129.0, 128.0, 125.6, 125.5, 122.9, 114.7, 77.5, 60.9, 50.3, 41.6, 39.9, 34.3, 31.4, 27.9, 27.1, 25.1, 21.7; $[\alpha]_D^{20}$ = -32.9 (c = 0.84, CH_2Cl_2); HRMS (ESI) exact mass calcd. for $C_{30}H_{33}Cl_2NO_2$: m/z 532.1781 ($[M + Na]^+$), found: m/z 532.1761 ($[M + Na]^+$).

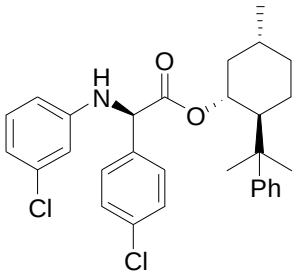


(*1R,2S,5R*)-8-Phenylmenthyl (*R*)-2-(4-nitrophenylamino)-2-(4-chlorophenyl)acetate: Yellow solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 100/1), mp 171-173 ^oC, yield: 83%; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.05-8.02 (d, *J* = 9.0 Hz, 2H), 7.39-7.36 (m, 4H), 7.23-7.16 (m, 4H), 7.06-7.02 (t, *J* = 6.0 Hz, 1H), 6.44-6.41 (d, *J* = 9.0 Hz, 2H), 5.45-5.43 (d, *J* = 6.0 Hz, 1H), 4.93-4.84 (m, 1H), 4.80-4.79 (d, *J* = 3.0 Hz, 1H), 1.97-1.93 (m, 1H), 1.85-1.81 (m, 1H), 1.65-1.51 (m, 3H), 1.45-1.35 (m, 1H), 1.16-0.99 (m, 4H), 0.94-0.80 (m, 7H); ^{13}C NMR

(125 MHz, $CDCl_3$) δ 168.8, 150.5, 150.2, 134.8, 134.5, 129.3, 128.8, 128.0, 126.1, 125.6, 125.5, 112.3, 78.3, 60.2, 50.3, 41.6, 39.8, 34.3, 31.4, 27.3, 27.0, 25.7, 21.7; $[\alpha]_D^{20}$ = -76.7 (c = 0.67, CH_2Cl_2); HRMS (ESI) exact mass calcd. for $C_{30}H_{33}ClN_2O_4$: m/z 543.2021 ($[M + Na]^+$), found: m/z 543.2017 ($[M + Na]^+$).

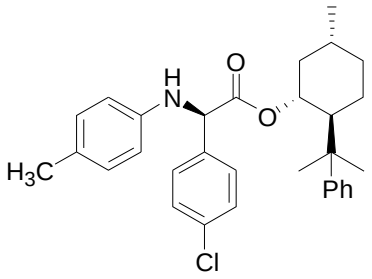


(*1R,2S,5R*)-8-Phenylmenthyl (*R*)-2-(2-bromophenylamino)-2-(4-chlorophenyl)acetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 100/1), mp 173-175 ^oC, yield: 65%; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.47-7.45 (d, *J* = 6.0 Hz, 1H), 7.37-7.35 (m, 2H), 7.26-7.18 (m, 5H), 7.09-6.98 (m, 4H), 6.60-6.55 (t, *J* = 7.5 Hz, 1H), 5.98-5.95 (d, *J* = 9.0 Hz, 1H), 5.72-5.70 (d, *J* = 6.0 Hz, 1H), 4.89-4.80 (m, 1H), 3.75-3.74 (d, *J* = 3.0 Hz, 1H), 2.16-1.95 (m, 1H), 1.73-1.68 (m, 1H), 1.48-1.19 (m, 9H), 0.97-0.80 (m, 4H), 0.69-0.56 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7, 152.4, 142.6, 135.7, 133.6, 132.5, 128.6, 128.3, 128.1, 128.1, 125.4, 125.2, 118.3, 112.3, 109.9, 75.9, 59.0, 50.5, 40.6, 39.3, 34.4, 31.2, 30.5, 26.1, 21.8, 21.7; $[\alpha]_D^{20}$ = -52.4 (c = 0.65, CH_2Cl_2); HRMS (ESI) exact mass calcd. for $C_{30}H_{33}BrClNO_2$: m/z 576.1275 ($[M + Na]^+$), found: m/z 576.1251 ($[M + Na]^+$).

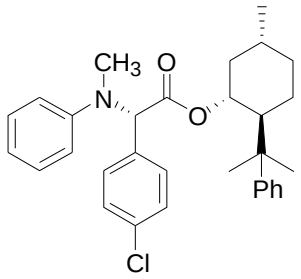


(*1R,2S,5R*)-8-Phenylmenthyl (*R*)-2-(3-chlorophenylamino)-2-(4-chlorophenyl)acetate: Colorless oil (Flash column chromatography eluent: petroleum ether/ethyl acetate = 100/1), yield: 73%; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.43-7.40 (d, *J* = 9.0 Hz, 2H), 7.35-7.32 (d, *J* = 9.0 Hz, 2H), 7.25-7.21 (m, 2H), 7.18-7.11 (m, 2H), 7.10-7.00 (m, 2H), 6.70-6.67 (m, 1H), 6.48-6.47 (m, 1H),

6.37-6.33 (m, 1H), 4.90-4.79 (m, 2H), 4.75-4.74 (d, *J* = 3.0 Hz, 1H), 1.98-1.84 (m, 2H), 1.49-1.28 (m, 5H), 1.13-1.05 (m, 3H), 0.95-0.83 (m, 7H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7, 150.1, 146.8, 135.4, 134.8, 134.4, 130.1, 129.1, 129.0, 128.0, 125.6, 125.5, 118.1, 113.4, 111.8, 60.7, 50.3, 41.6, 39.9, 34.3, 31.4, 28.0, 27.1, 25.1, 21.7; $[\alpha]_D^{20}$ = -36.7 (c = 0.60, CH_2Cl_2); HRMS (ESI) exact mass calcd. for $C_{30}H_{33}Cl_2NO_2$: m/z 532.1781 ($[M + Na]^+$), found: m/z 532.1760 ($[M + Na]^+$).

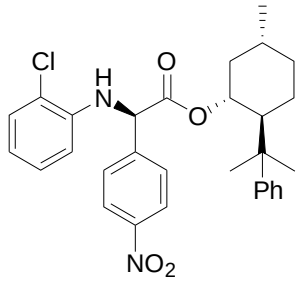


(*1R,2S,5R*)-8-Phenylmenthyl (*R*)-2-(p-toluidino)-2-(4-chlorophenyl)acetate: Colorless oil (Flash column chromatography eluent: petroleum ether/ethyl acetate = 100/1), yield: 49%;^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.51-7.49 (d, *J* = 6.0 Hz, 2H), 7.37-7.32 (t, *J* = 7.5 Hz, 2H), 7.25-7.20 (m, 2H), 7.13-7.07 (m, 3H), 6.96-6.93 (d, *J* = 9.0 Hz, 2H), 6.50-6.47 (d, *J* = 9.0 Hz, 2H), 4.87-4.72 (m, 3H), 2.22 (s, 3H), 1.94-1.82 (m, 2H), 1.55-1.49 (m, 2H), 1.38-1.22 (m, 3H), 1.07-0.99 (m, 3H), 0.90-0.74 (m, 7H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.9, 150.0, 143.8, 137.4, 129.6, 128.7, 128.3, 127.9, 127.1, 125.7,125.4, 113.7, 61.9, 50.5, 41.6, 40.0, 34.4, 31.3, 29.0, 27.2, 24.1, 21.7, 20.4; $[\alpha]_D^{20}$ = -35.4 (c = 0.65, CH_2Cl_2); HRMS (ESI) exact mass calcd. for $C_{31}H_{36}ClNO_2$: m/z 512.2328 ($[M + Na]^+$), found: m/z 512.2322 ($[M + Na]^+$).

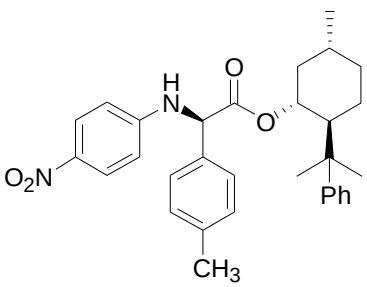


(*1R,2S,5R*)-8-Phenylmenthyl (*S*)-2-(methylphenylamino)-2-(4-chlorophenyl)acetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 100/1), mp 154-156 ^{o}C, yield: 79%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.36-7.33 (d, *J* = 9.0 Hz, 2H), 7.24-7.16 (m,

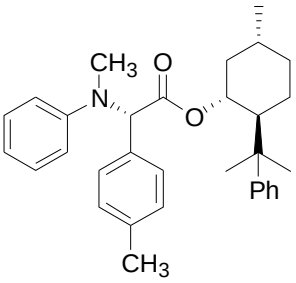
8H), 7.11-7.07 (t, *J* = 6.0 Hz, 1H), 6.81-6.76 (t, *J* = 7.5 Hz, 1H), 6.62-6.59 (d, *J* = 9.0 Hz, 2H), 4.90-4.81 (m, 1H), 4.48 (s, 1H), 2.72 (s, 3H), 2.07-1.99 (m, 1H), 1.79-1.73 (m, 1H), 1.66-1.62 (m, 2H), 1.47-1.38 (m, 1H), 1.25 (s, 3H), 1.18-1.06 (m, 4H), 0.91-0.74 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8, 151.8, 149.2, 134.2, 133.5, 129.7, 128.9, 128.4, 128.0, 125.3, 125.0, 118.0, 113.7, 75.5, 65.3, 50.2, 41.4, 39.6, 35.4, 34.4, 31.2, 28.6, 26.4, 24.1, 21.7; $[\alpha]_D^{20}$ = +63.4 (c = 0.83, CH_2Cl_2); HRMS (ESI) exact mass calcd. for $C_{31}H_{36}ClNO_2$: m/z 512.2327 ($[M + Na]^+$), found: m/z 512.2322 ($[M + Na]^+$).



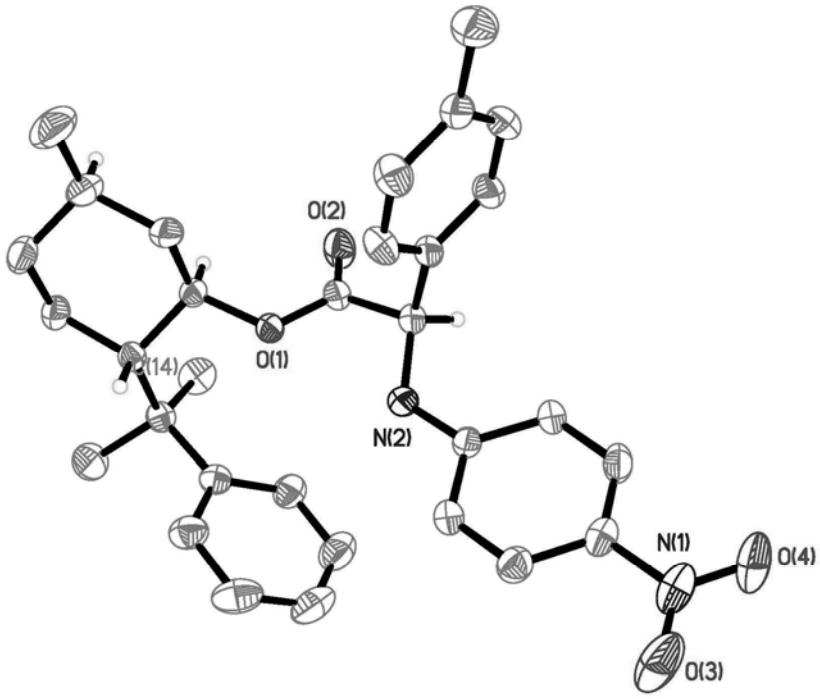
(*1R,2S,5R*)-8-Phenylmenthyl (*R*)-2-(2-chlorophenylamino)-2-(4-nitrophenyl)acetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 100/1), mp 150-152 ^{o}C, yield: 65%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.10-8.08 (d, *J* = 6.0 Hz, 2H), 7.40-7.37 (d, *J* = 9.0 Hz, 2H), 7.33-7.26 (m, 4H), 7.22-7.19 (d, *J* = 9.0 Hz, 2H), 7.11-7.06 (t, *J* = 7.5 Hz, 1H), 6.98-6.93 (t, *J* = 7.5 Hz, 1H), 6.69-6.64 (t, *J* = 7.5 Hz, 1H), 5.89-5.87 (d, *J* = 6.0 Hz, 1H), 5.75-5.73 (d, *J* = 6.0 Hz, 1H), 4.92-4.83 (m, 1H), 3.81-3.79 (d, *J* = 6.0 Hz, 1H), 2.19-2.00 (m, 2H), 1.76-1.70 (m, 1H), 1.46-1.34 (m, 5H), 1.26-1.16 (m, 4H), 0.99-0.97 (m, 1H), 0.85-0.79 (m, 3H), 0.65-0.53 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.7, 152.6, 144.8, 141.2, 129.4, 128.2, 127.9, 127.5, 125.5, 125.2, 123.7, 118.3, 112.1, 76.2, 59.1, 50.5, 40.6, 39.3, 34.4, 31.2, 30.9, 26.0, 21.6, 21.2; $[\alpha]_D^{20}$ = -26.5 (c = 0.40, CH_2Cl_2); HRMS (ESI) exact mass calcd. for $C_{30}H_{33}ClN_2O_4$: m/z 543.2021 ($[M + Na]^+$), found: m/z 543.2036 ($[M + Na]^+$).



(*1R,2S,5R*)-8-Phenylmenthyl (*R*)-2-(4-nitrophenylamino)-2-(4-tolyl)acetate: Yellow solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 100/1), mp 159-161 ^{o}C, yield: 81%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.04-8.01 (d, *J* = 9.0 Hz, 2H), 7.33-7.31 (d, *J* = 6.0 Hz, 2H), 7.23-7.12 (m, 6H), 7.08-7.04 (t, *J* = 6.0 Hz, 1H), 6.47-6.44 (d, *J* = 9.0 Hz, 2H), 5.55-5.53 (d, *J* = 6.0 Hz, 1H), 4.88-4.79 (m, 2H), 2.31 (s, 3H), 1.95-1.86 (m, 2H), 1.55-1.31 (m, 3H), 1.15-0.99 (m, 5H), 0.95-0.74 (m, 7H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5, 150.9, 150.1, 138.8, 138.6, 132.8, 129.8, 128.0, 127.5, 126.1, 125.6, 125.5, 112.2, 78.0, 60.5, 50.4, 41.6, 39.9, 34.3, 31.4, 28.0, 27.1, 25.2, 21.7, 21.1; $[\alpha]_D^{20}$ = -119.7 (c = 1.17, CH_2Cl_2); HRMS (ESI) exact mass calcd. for $C_{31}H_{36}N_2O_4$: m/z 523.2567 ($[M + Na]^+$), found: m/z 523.2578 ($[M + Na]^+$).



(*1R,2S,5R*)-8-Phenylmenthyl (*S*)-2-(methylphenylamino)-2-(4-tolyl)acetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 100/1), mp 157-159 ^{o}C, yield: 77%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.25-7.15 (m, 10H), 7.12-7.07 (m, 1H), 6.79-6.74 (t, *J* = 7.5 Hz, 1H), 6.88-6.86 (d, *J* = 6.0 Hz, 2H), 4.90-4.82 (m, 1H), 4.74 (s, 1H), 2.76 (s, 3H), 2.38 (s, 3H), 2.00-1.96 (m, 1H), 1.79-1.74 (m, 1H), 1.68-1.60 (m, 2H), 1.45-1.39 (m, 1H), 1.20-1.18 (d, 6H), 1.10-1.00 (m, 1H), 0.90-0.82 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.5, 151.5, 149.5, 137.4, 132.4, 129.0, 128.9, 128., 127.9, 125.4, 125.0, 117.6, 113.5, 75.6, 65.6, 50.4, 41.5, 39.7, 35.0, 34.5, 31.2, 27.3, 26.7, 25.5, 21.7, 21.1; $[\alpha]_D^{20}$ = +54.1 (c = 0.67, CH_2Cl_2); HRMS (ESI) exact mass calcd. for $C_{32}H_{39}NO_2$: m/z 492.2172 ($[M + Na]^+$), found: m/z 492.2180 ($[M + Na]^+$).



The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 939059). The data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/conts/retrieving.html.

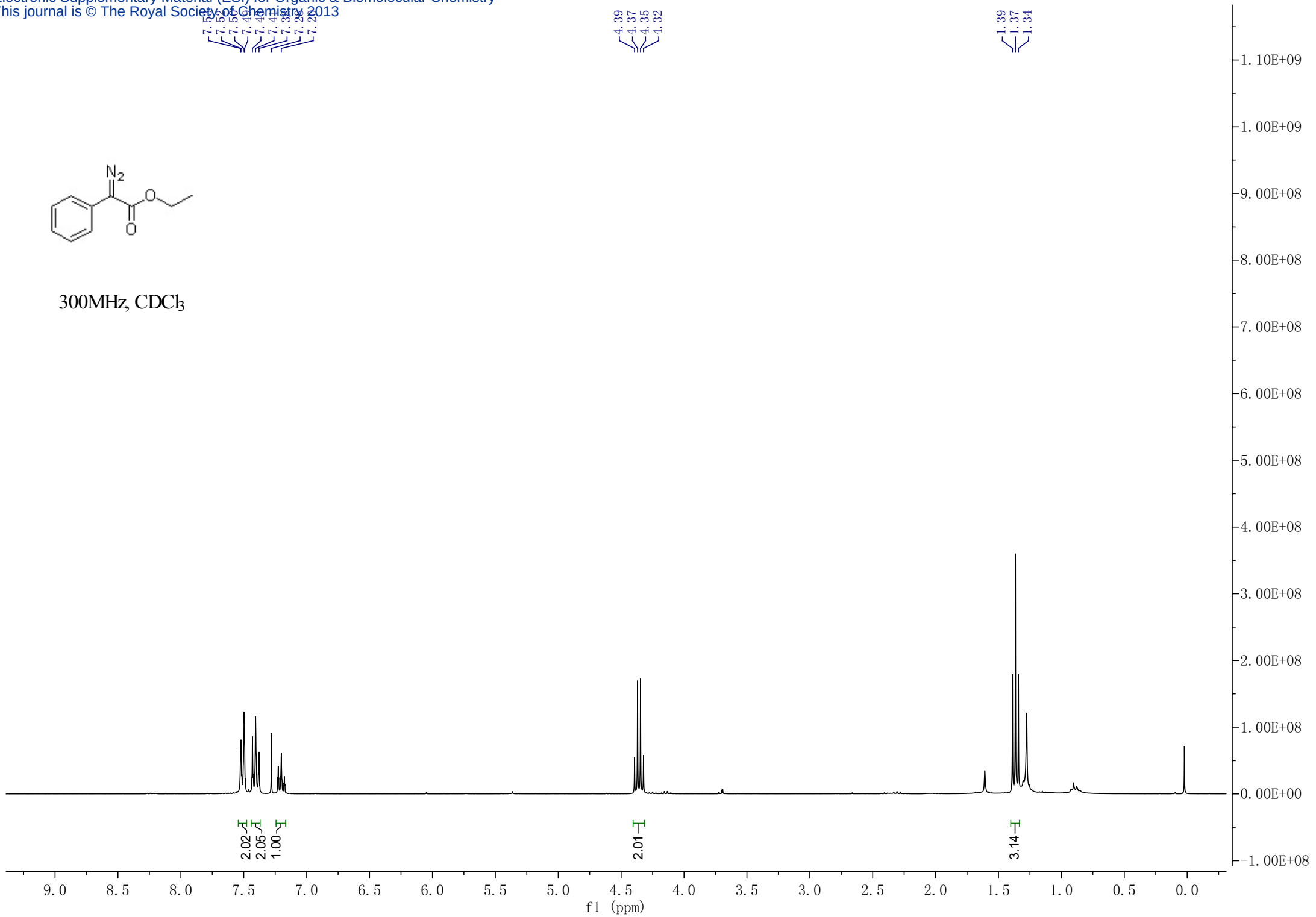
References

1) (a) Qu, Z.; Shi, W.; Wang, J. *J. Org. Chem.* **2001**, *66*, 8139-8144; (b) Bachmann, S.; Fielenbach, D.; Jørgensen, K. A. *Org. Biomol. Chem.* **2004**, *2*, 3044-3049.

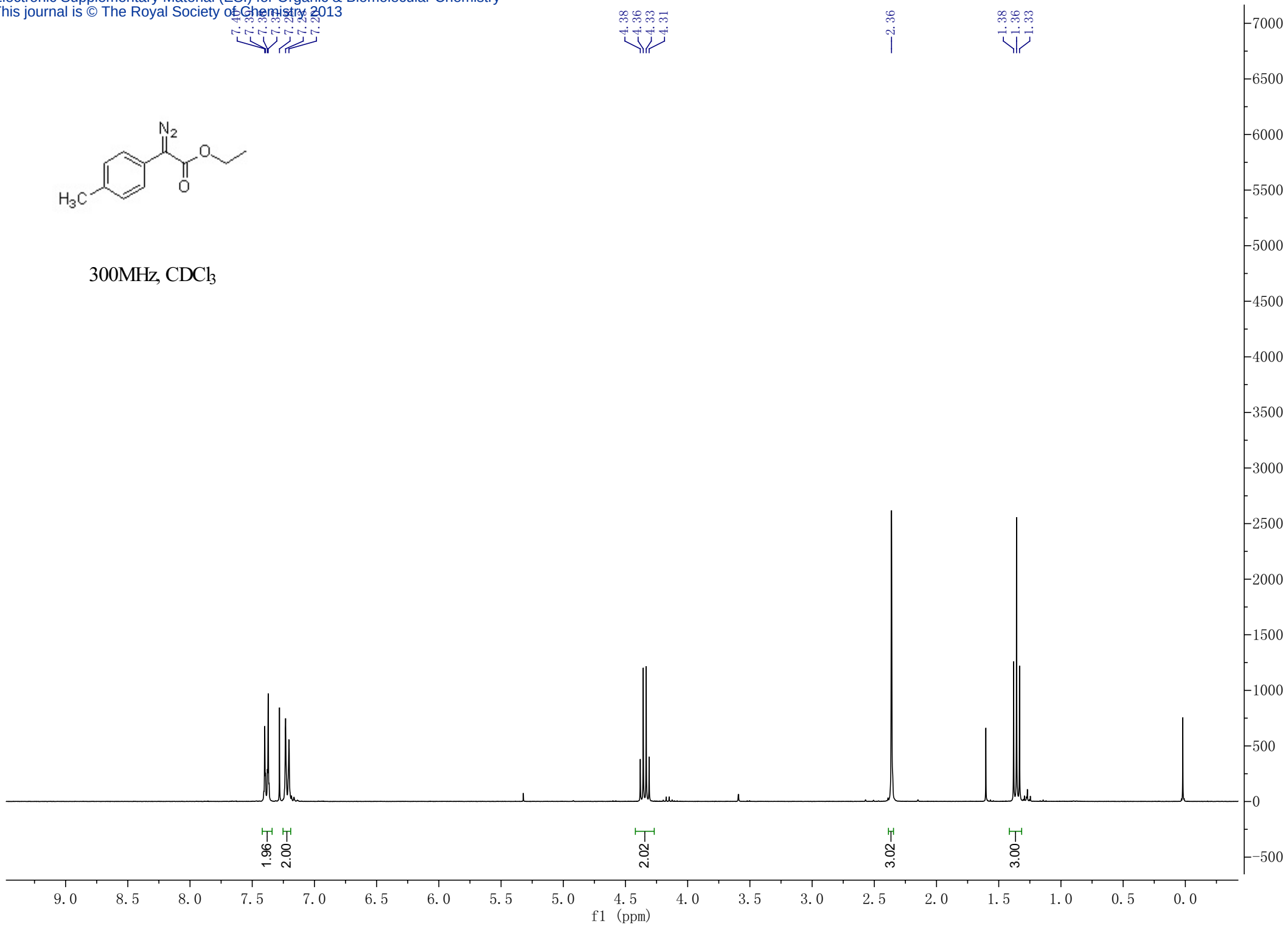
2) Hashimoto, T.; Uchiyama, N.; Maruoka, K. *J. Am. Chem. Soc.* **2008**, *130*, 2434-2435.

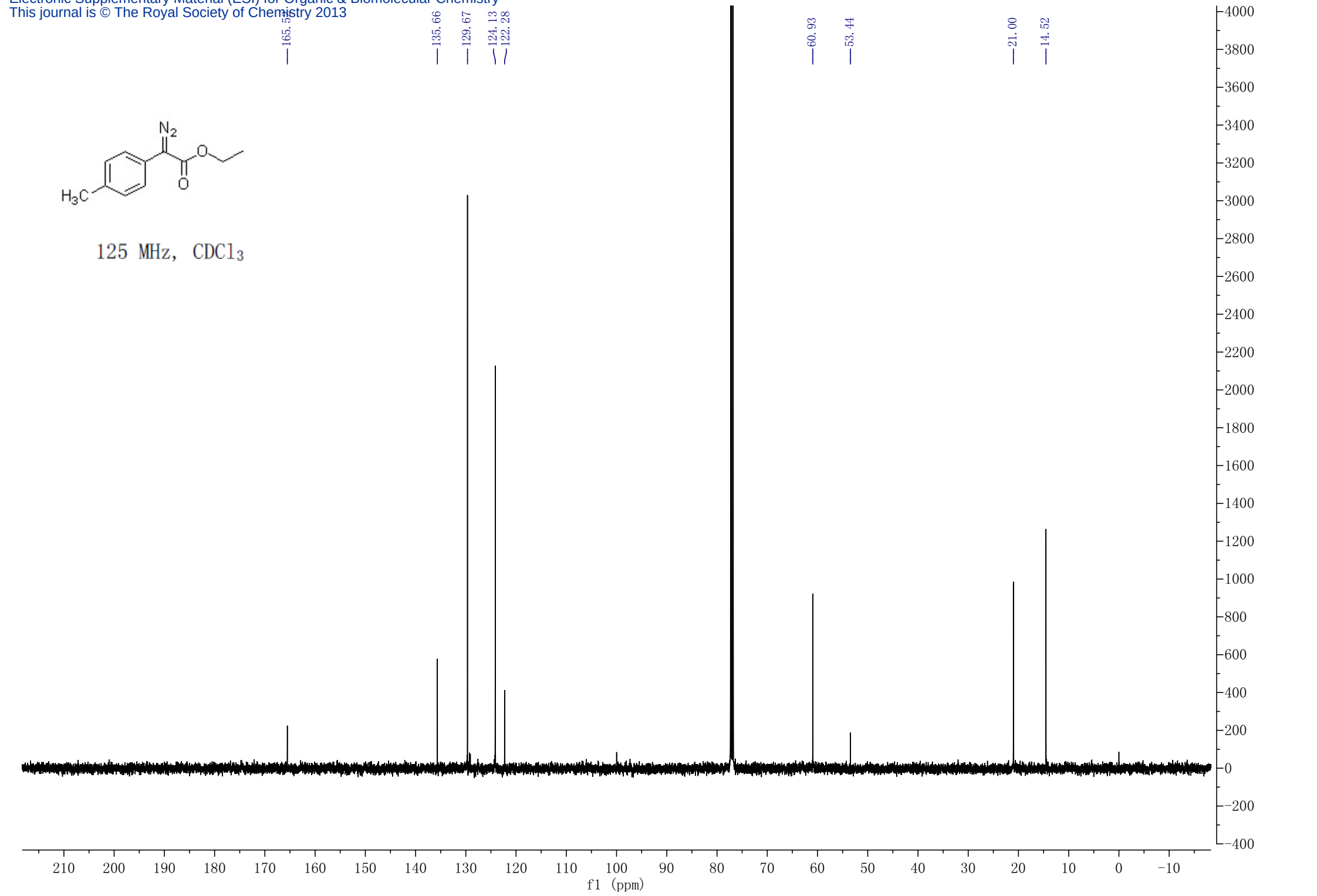
3) Cavallo, A.; Csaky, Au.; Suffert, J. *J. Org. Chem*. **1994**, *59,* 5343-5346.

300MHz, $CDCl_3$

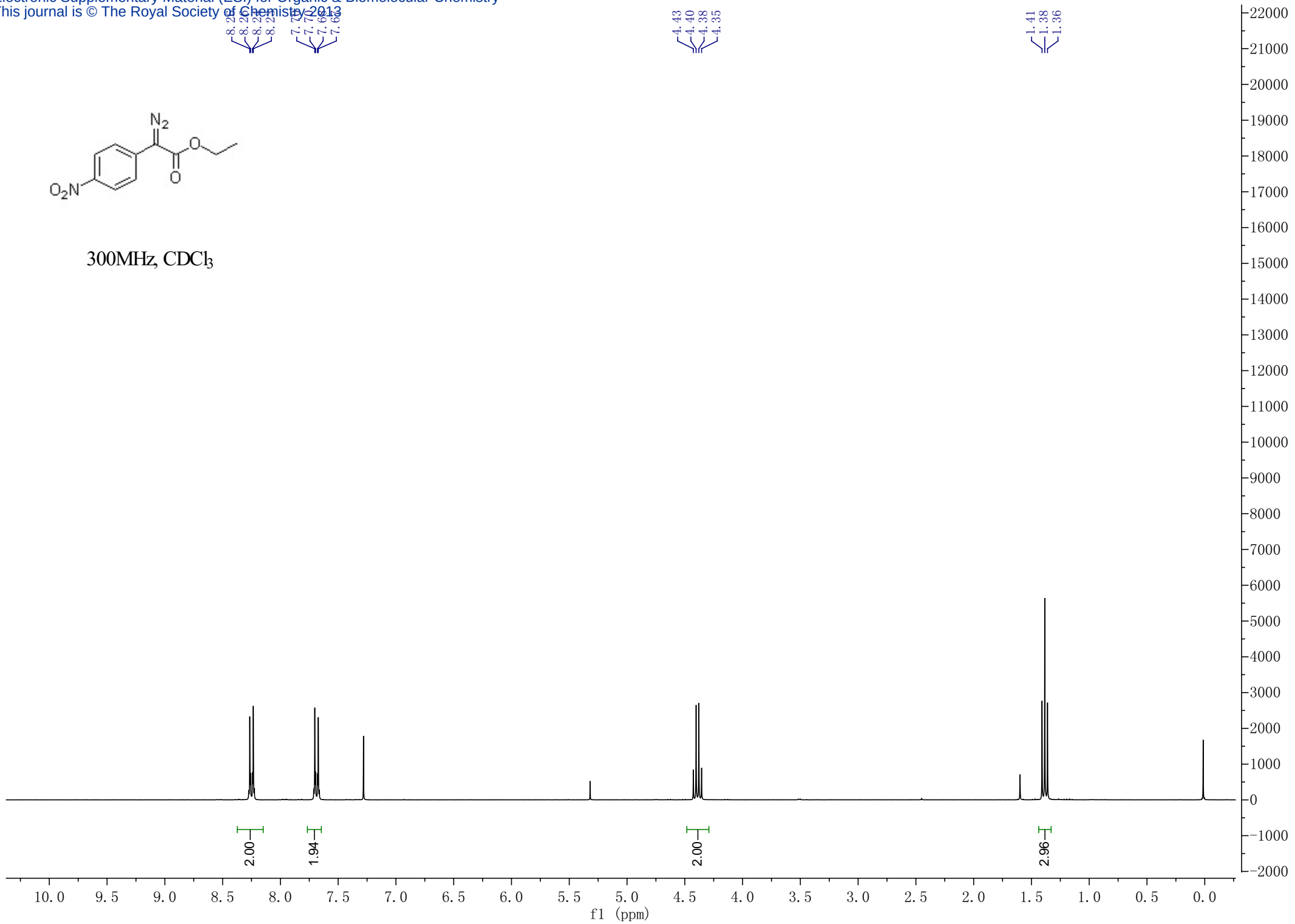


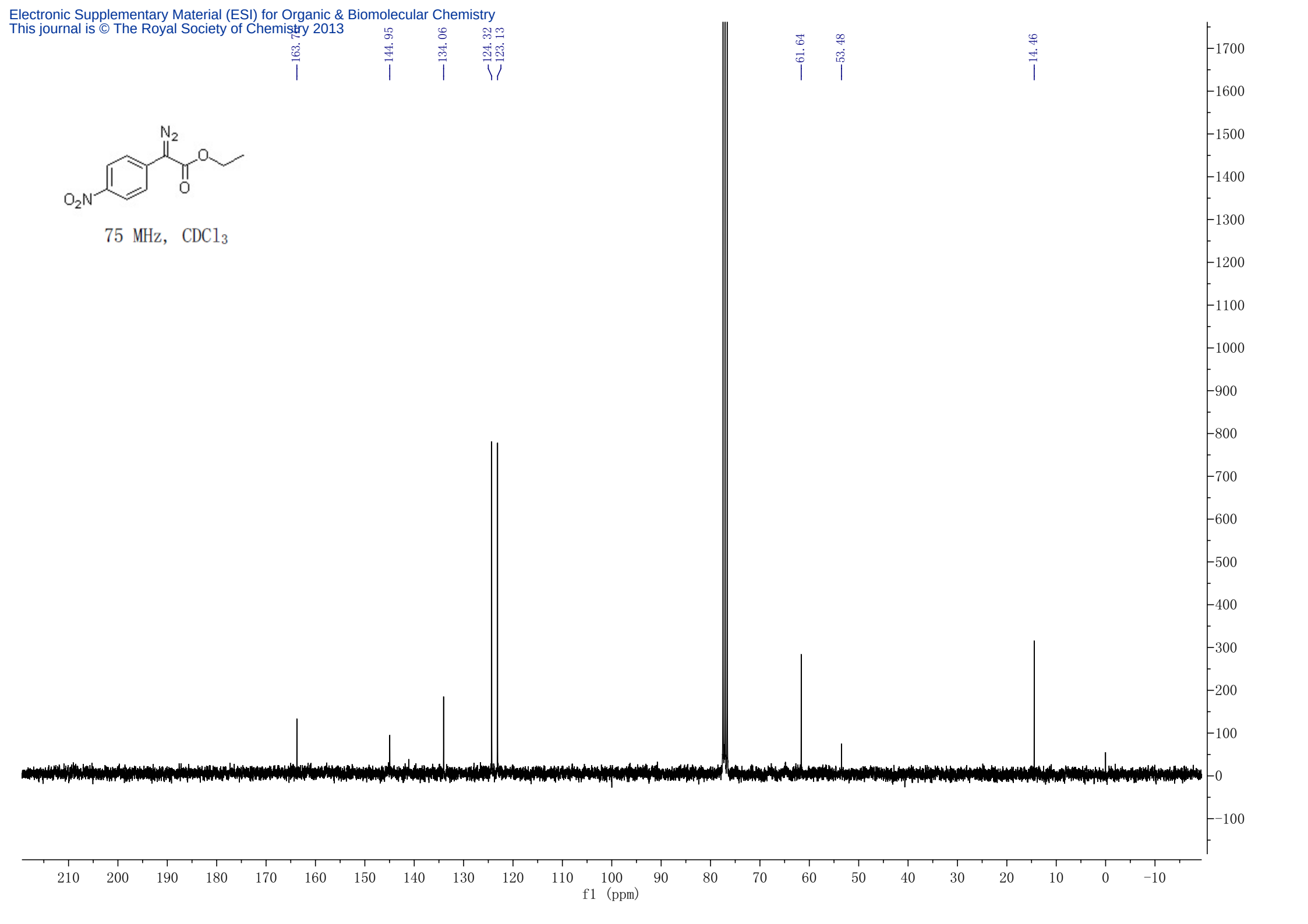
300MHz, $CDCl_3$



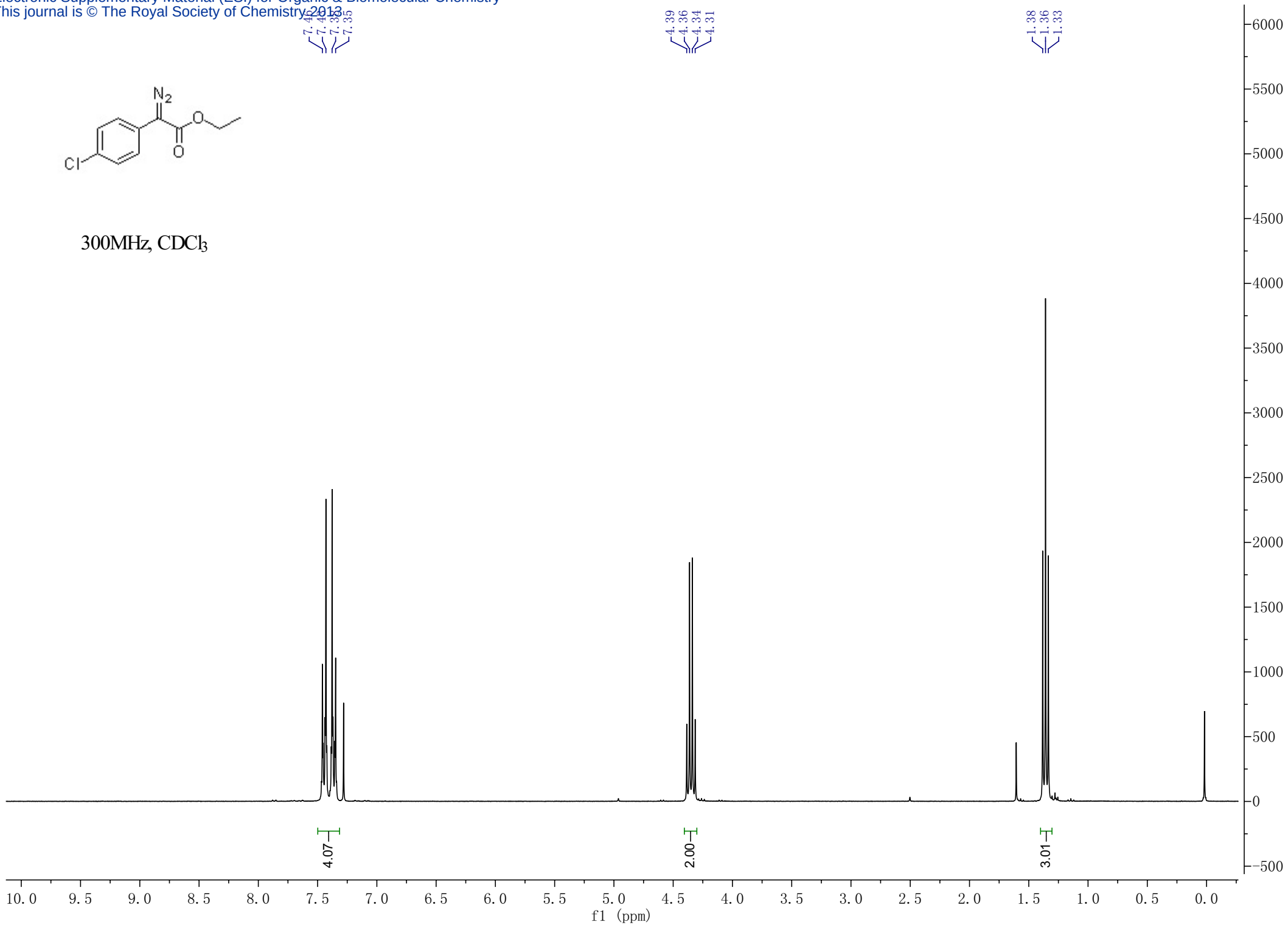


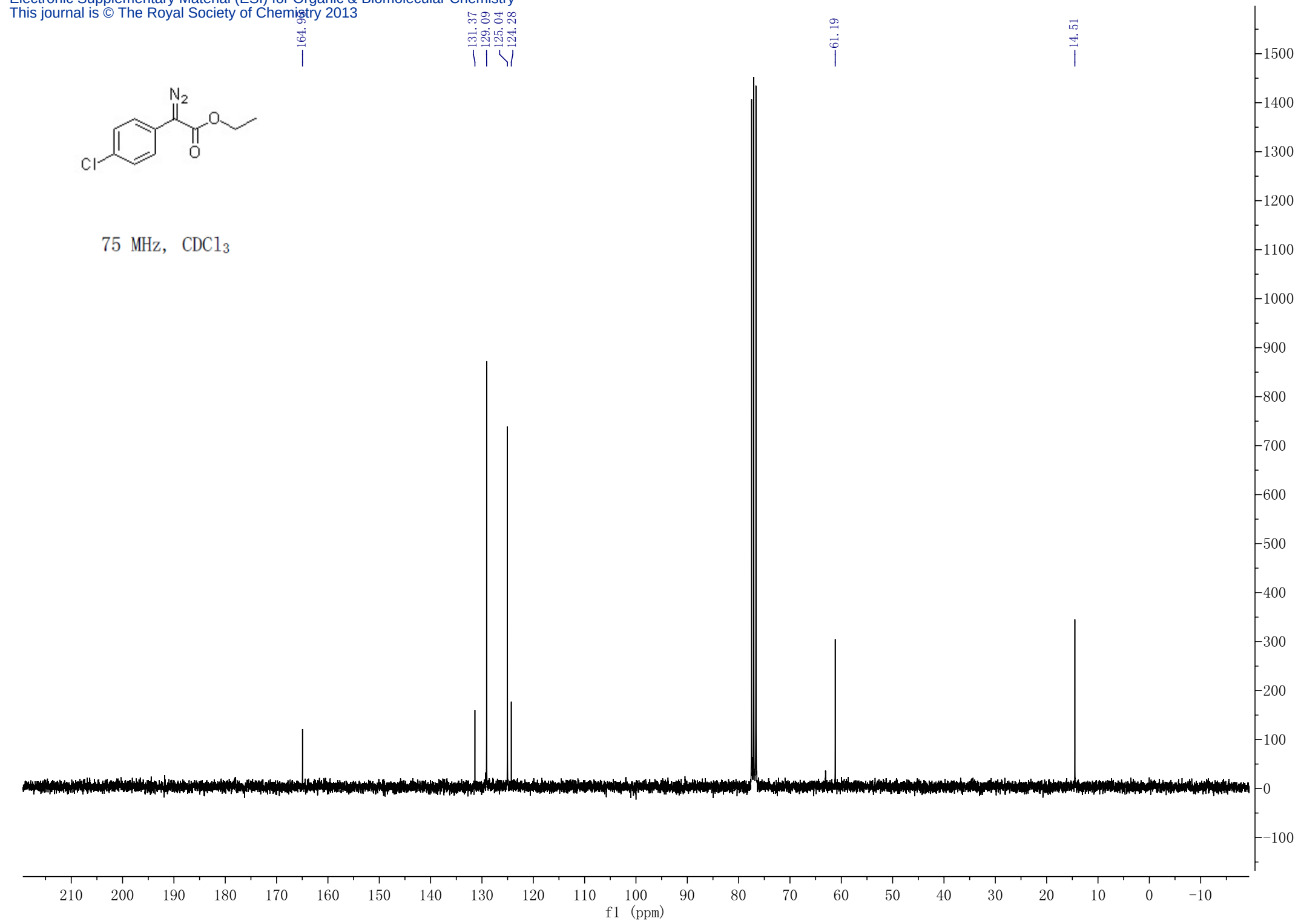
300MHz, $CDCl_3$



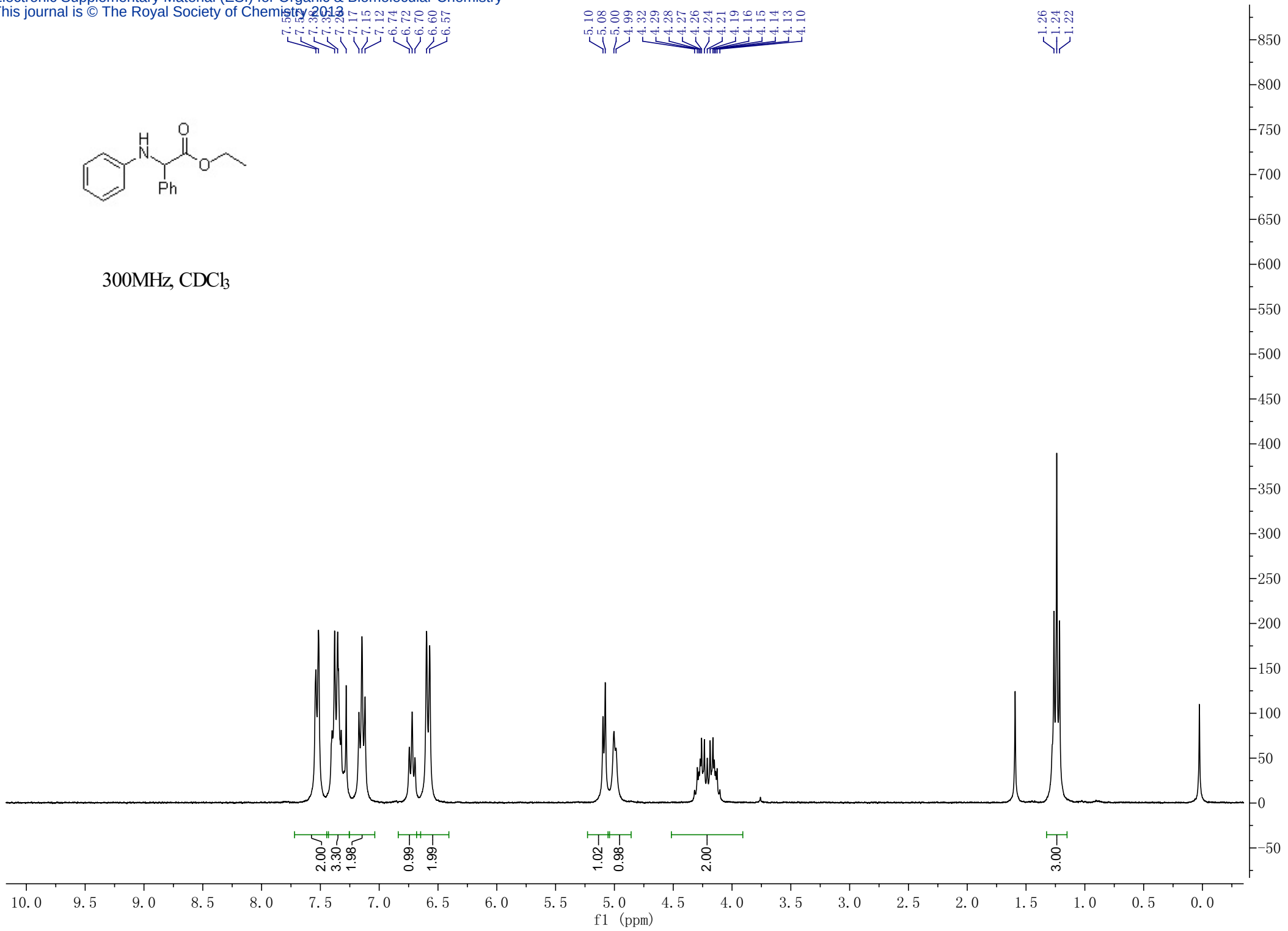


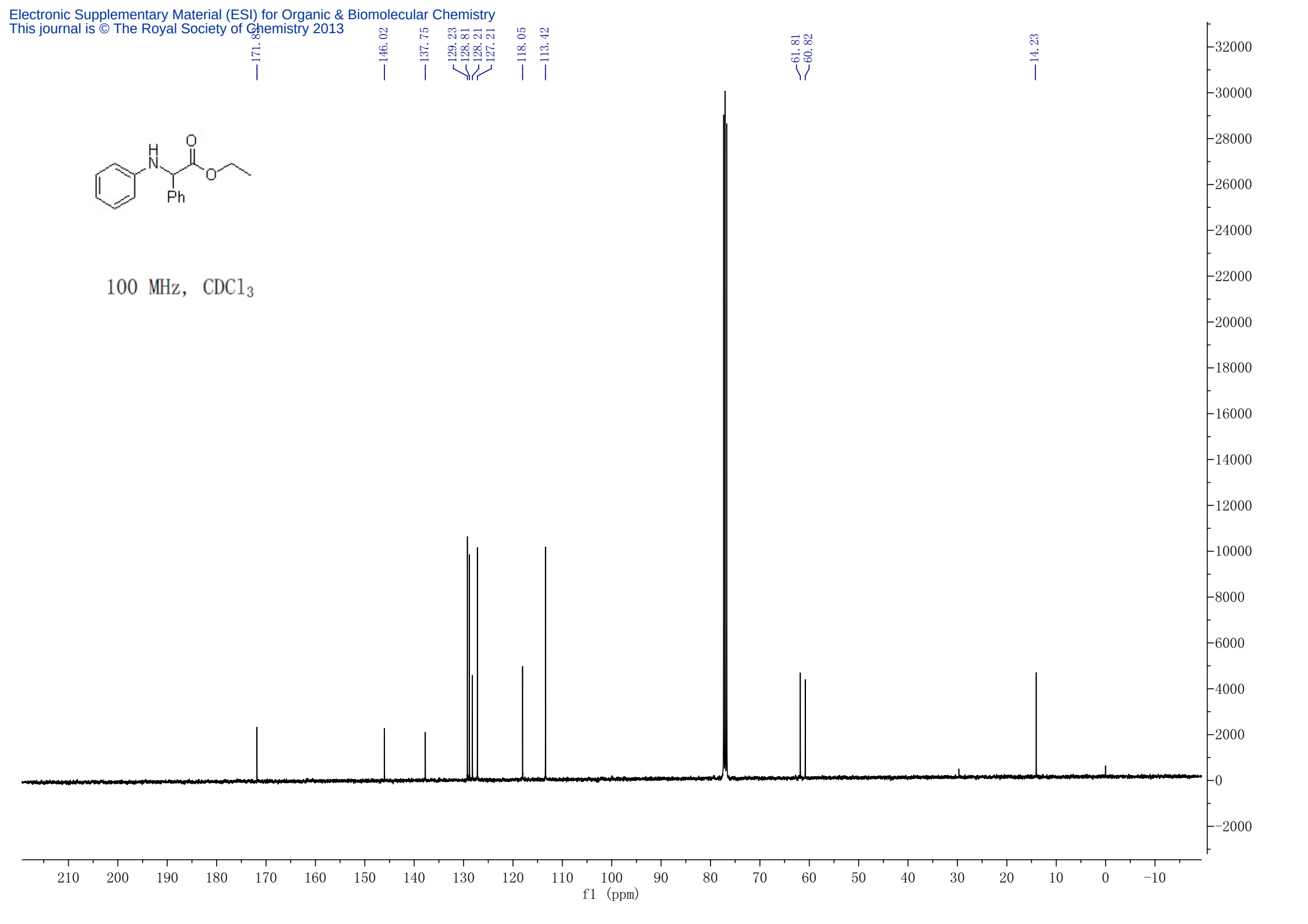
300MHz, $CDCl_3$



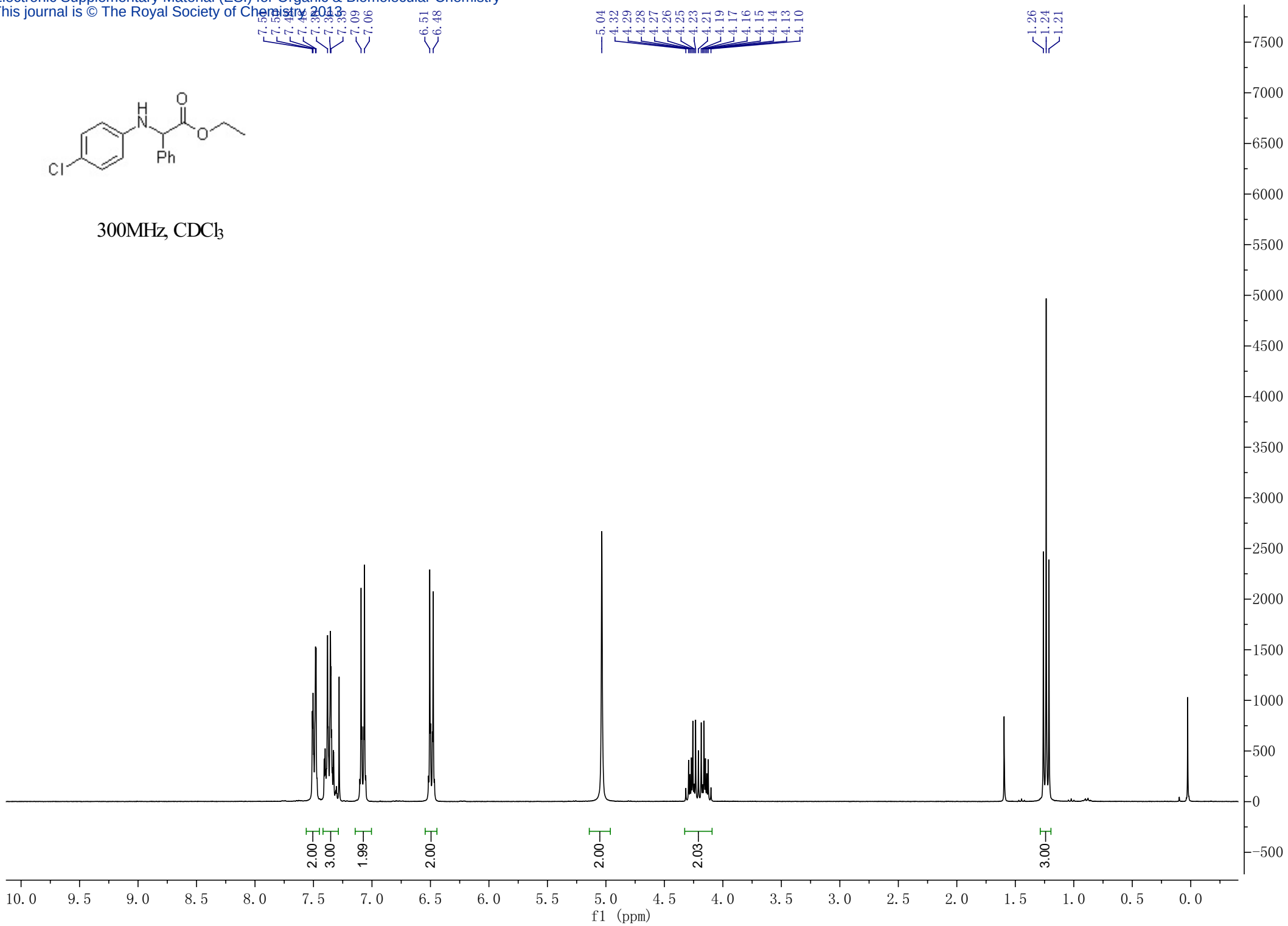


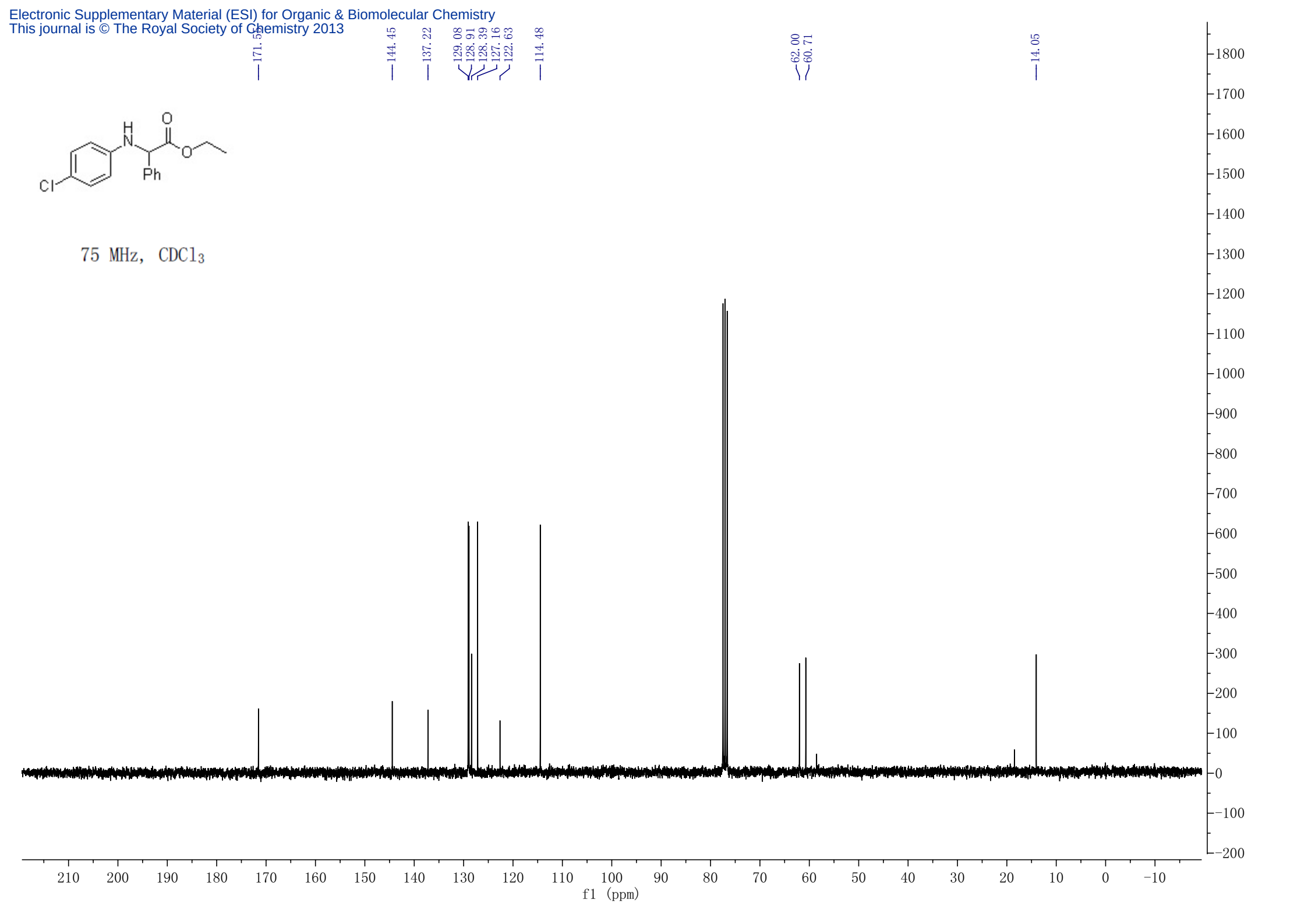
300MHz, $CDCl_3$



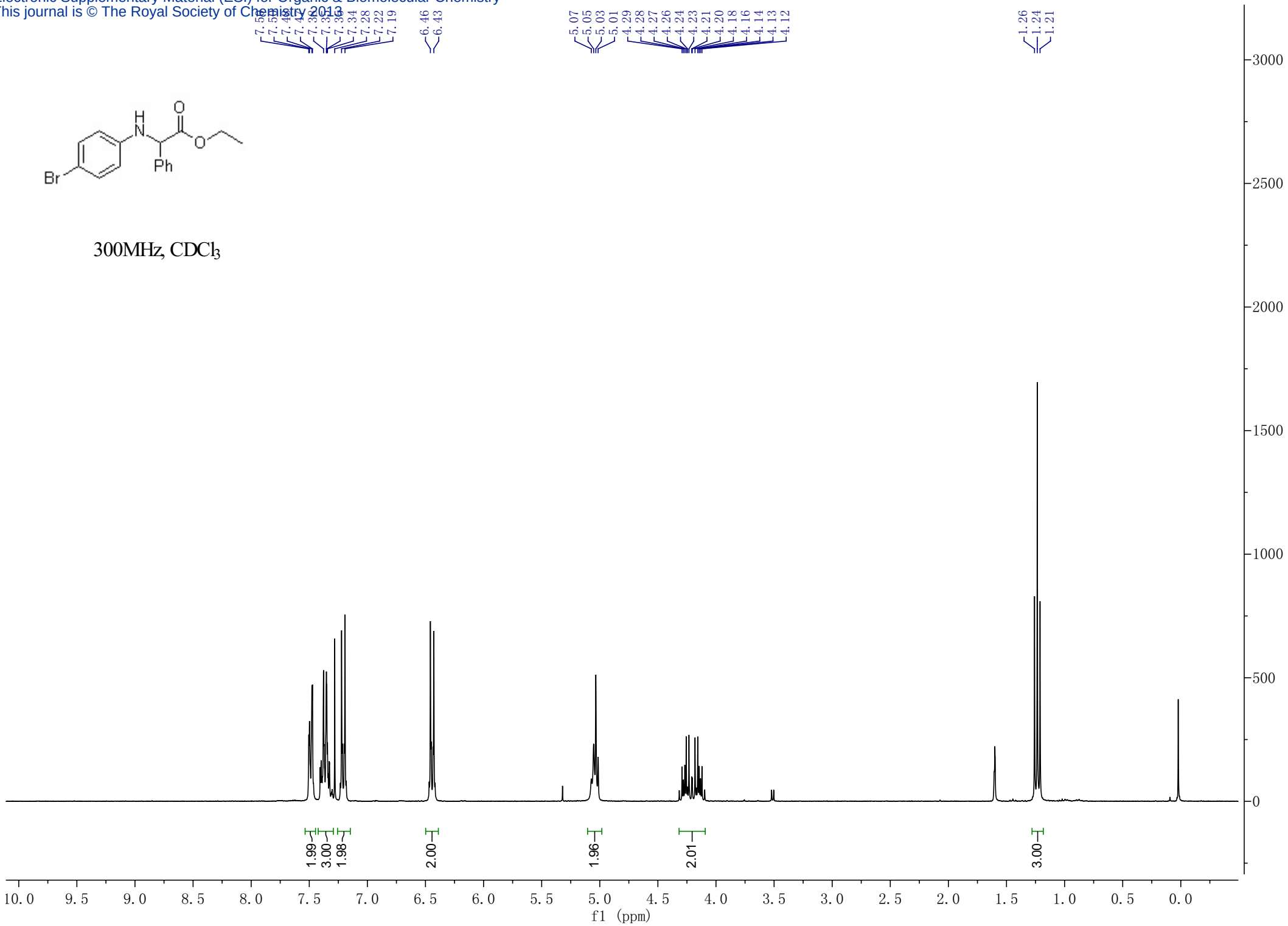


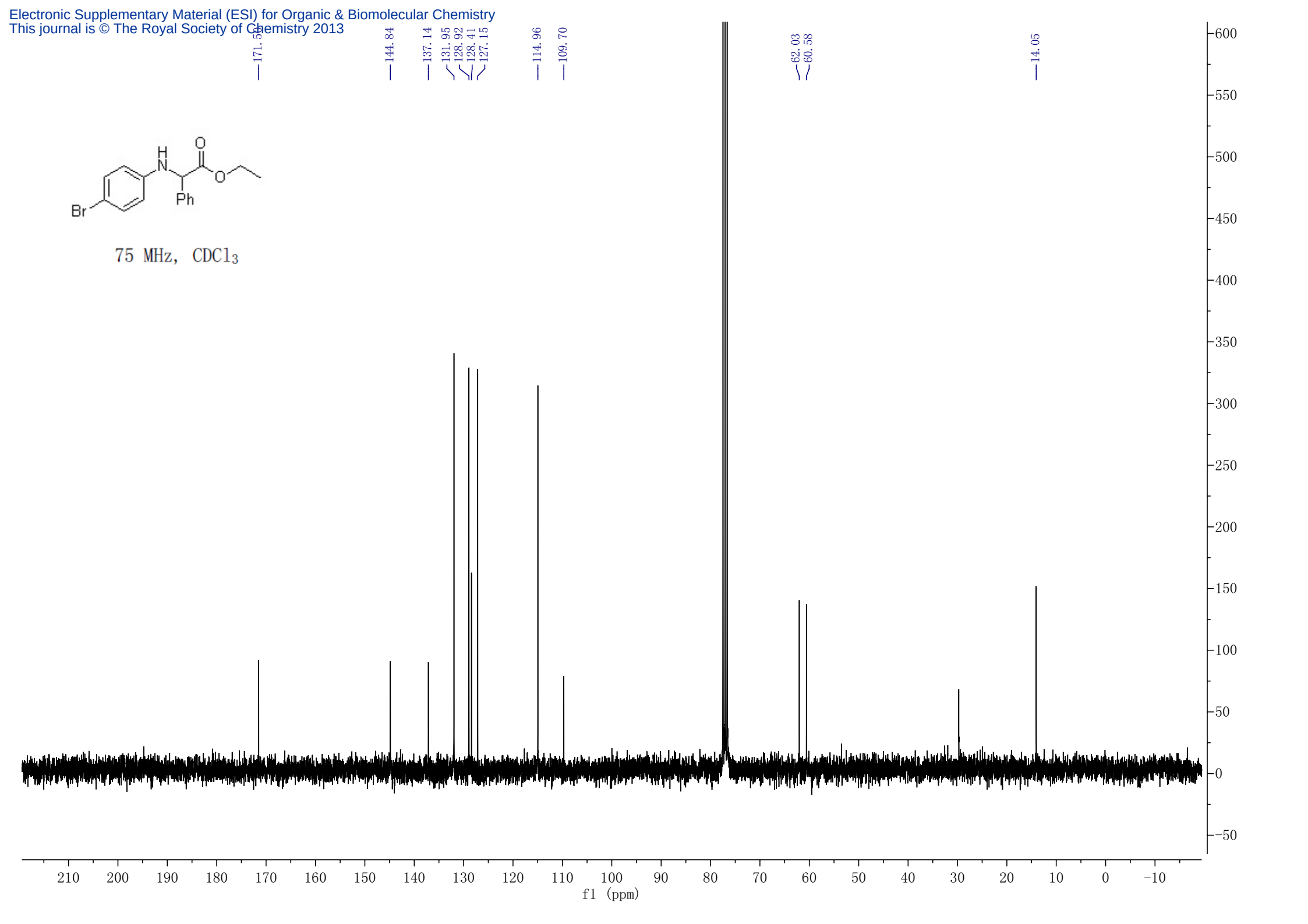
300MHz, $CDCl_3$



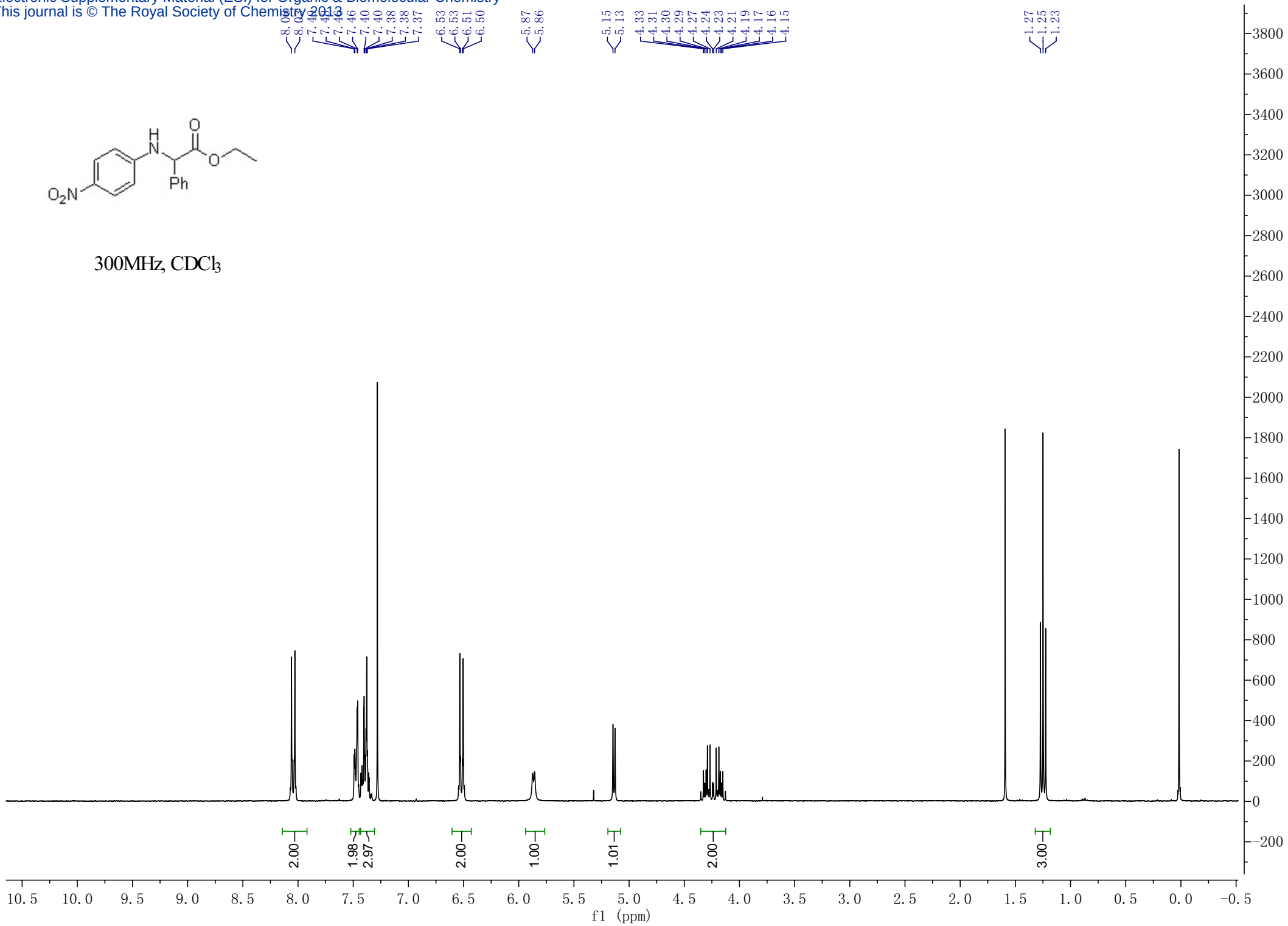


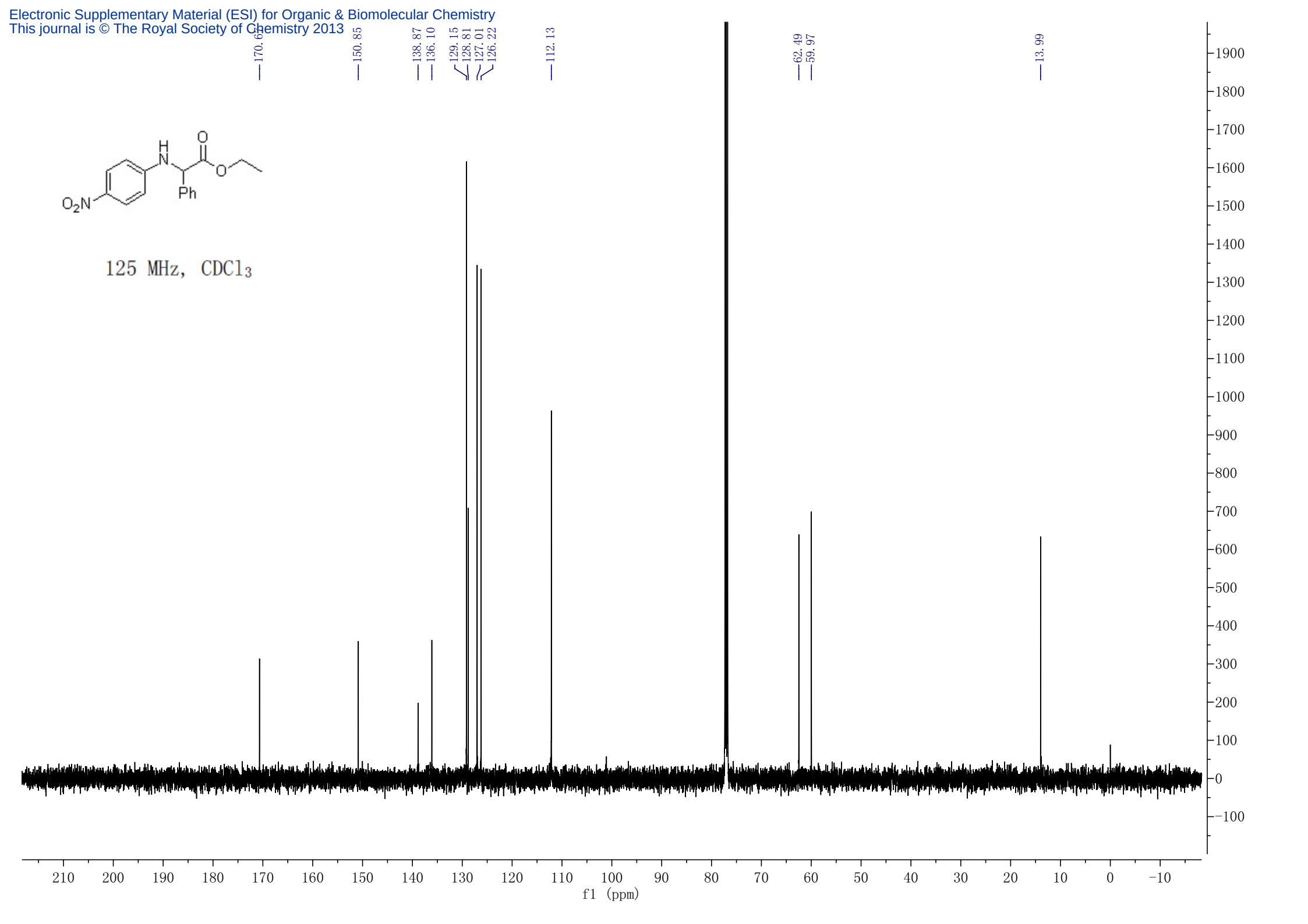
300MHz, $CDCl_3$



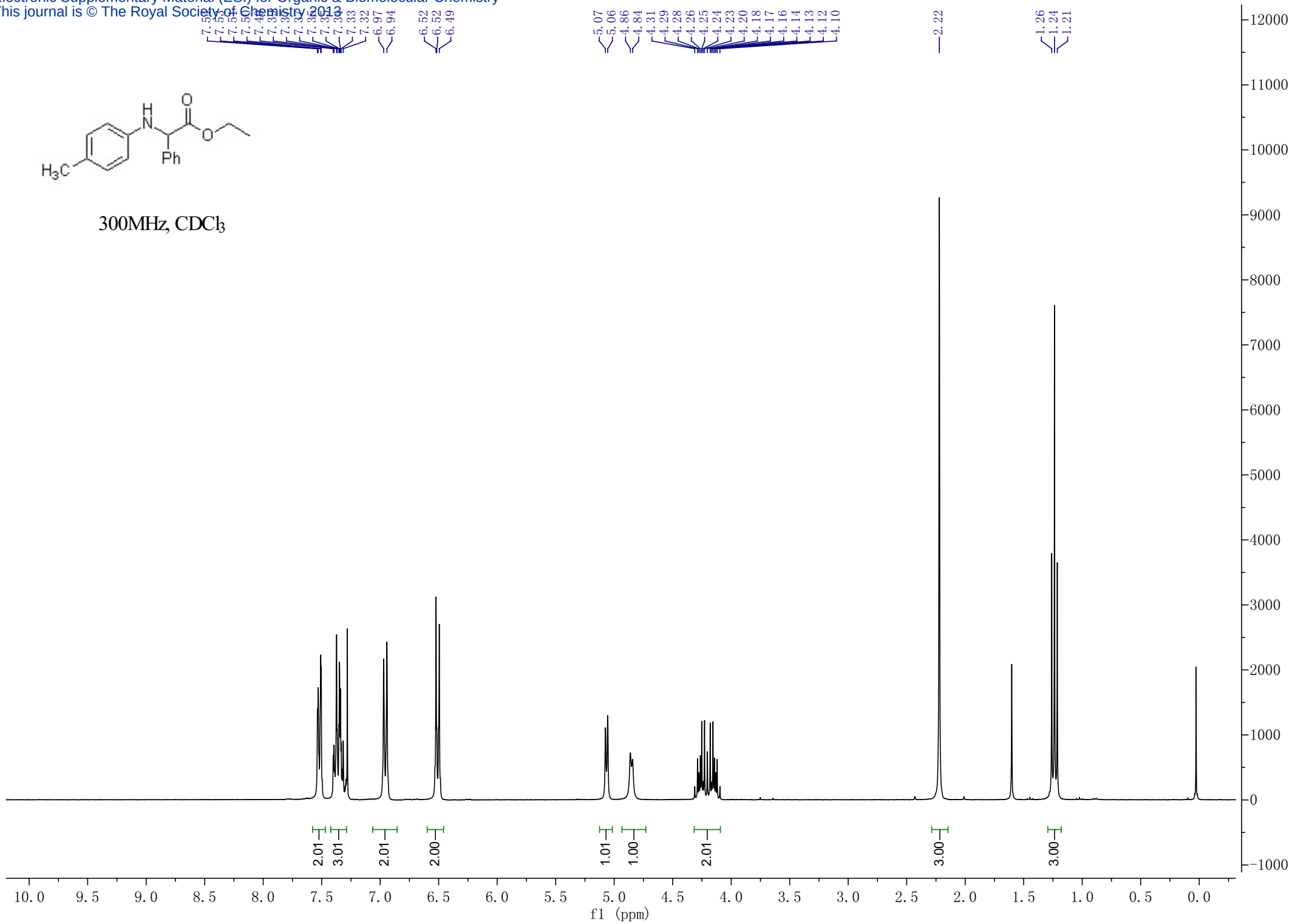


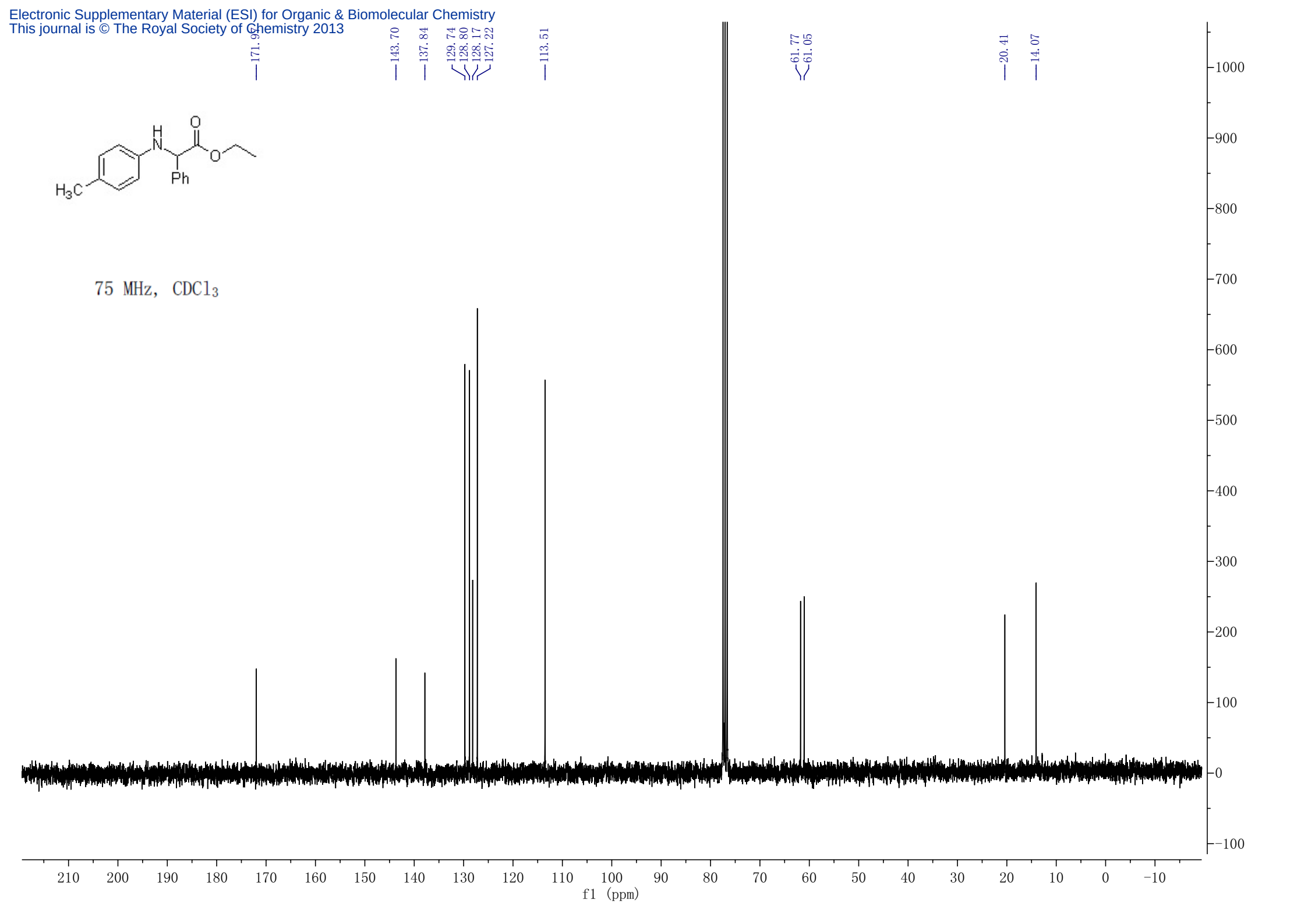
300MHz, $CDCl_3$



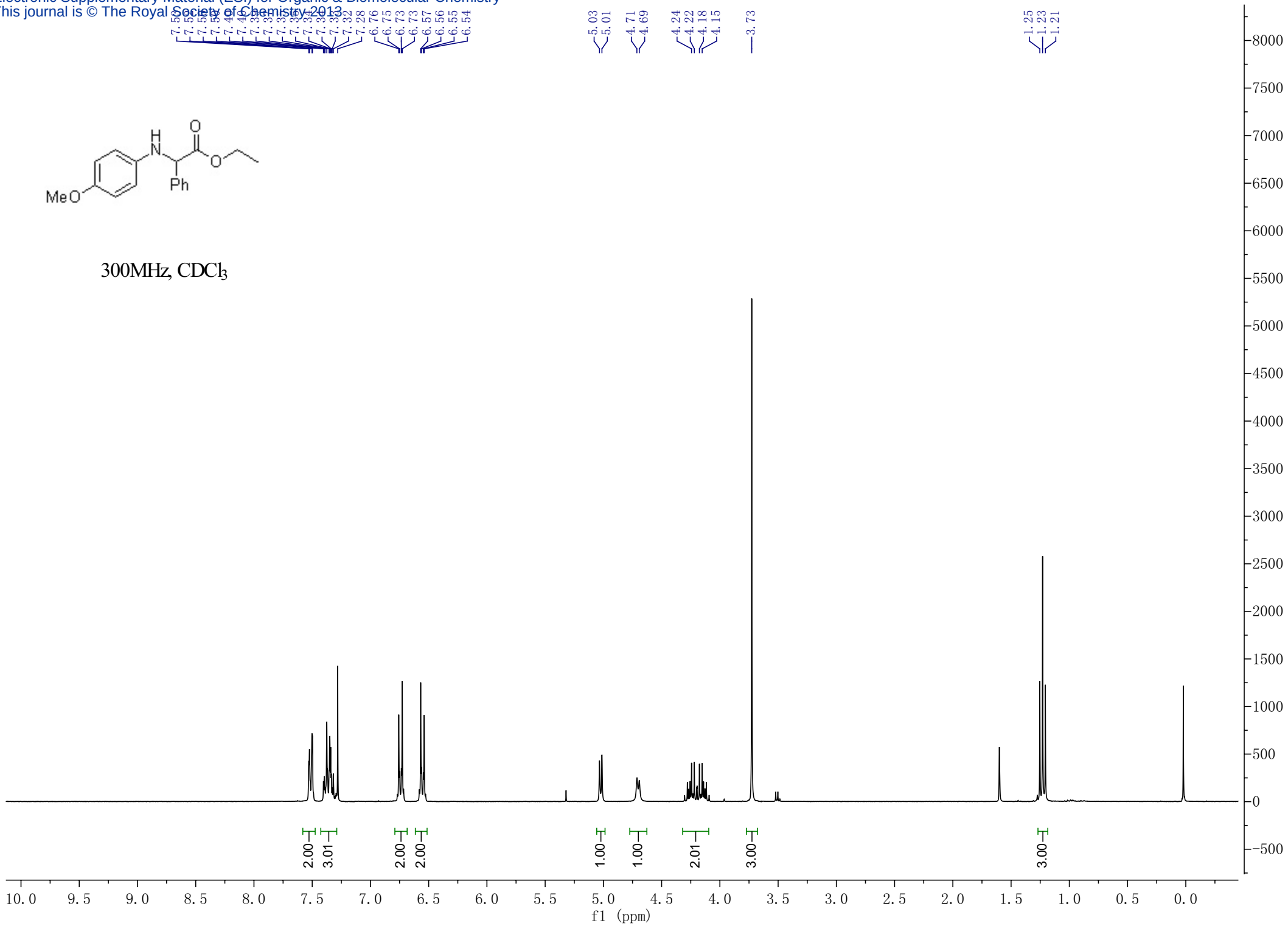


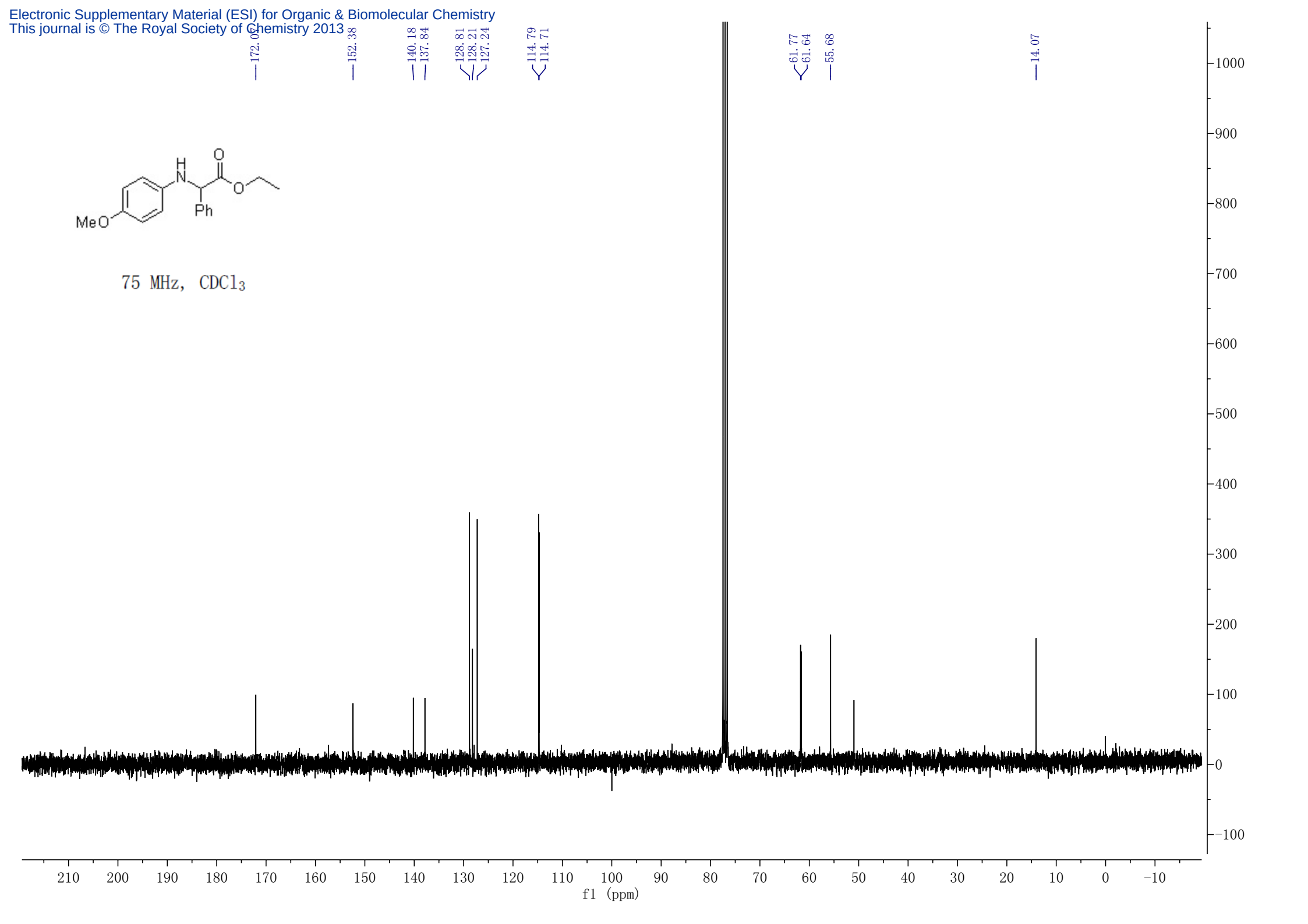
300MHz, $CDCl_3$



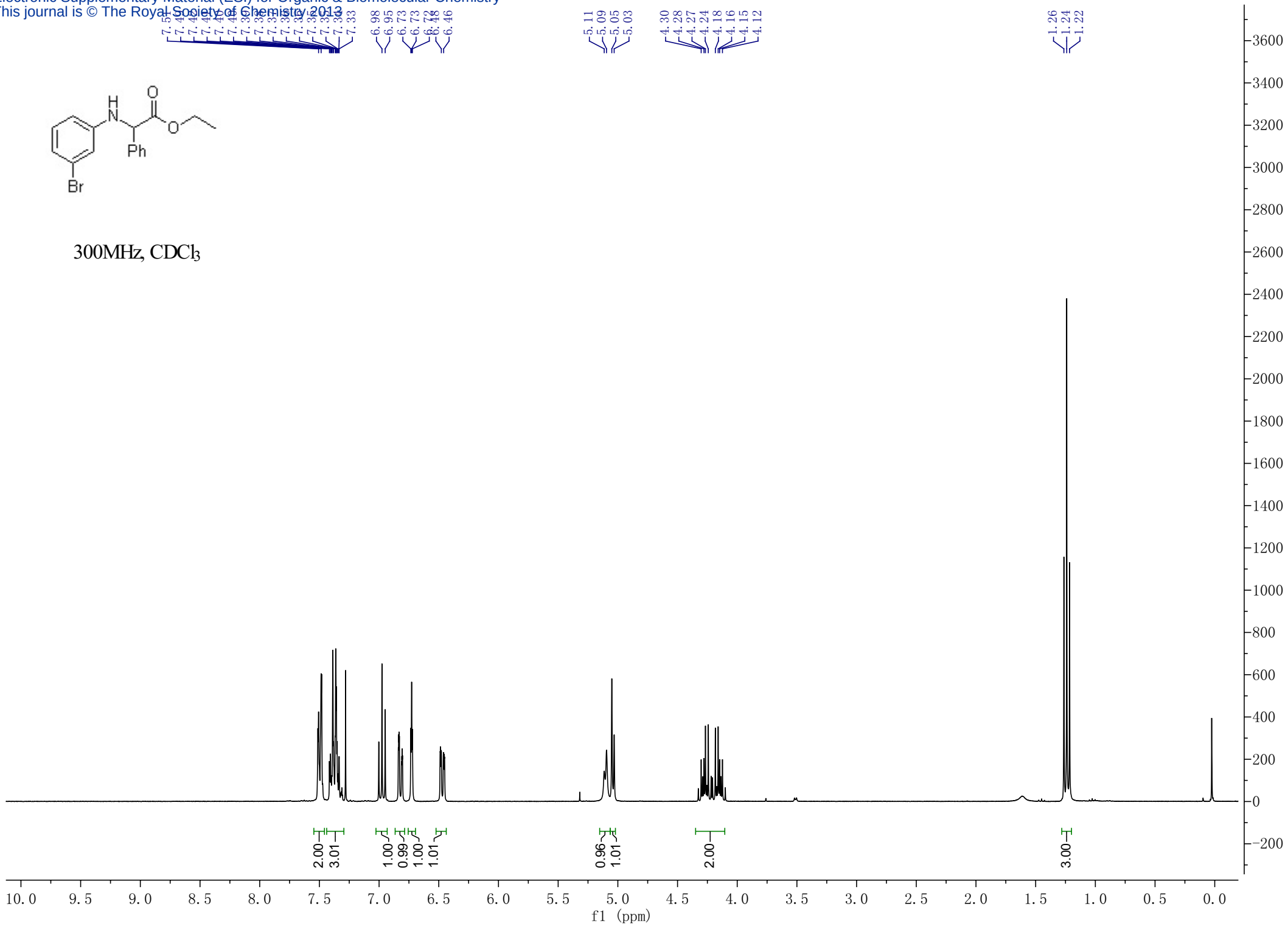


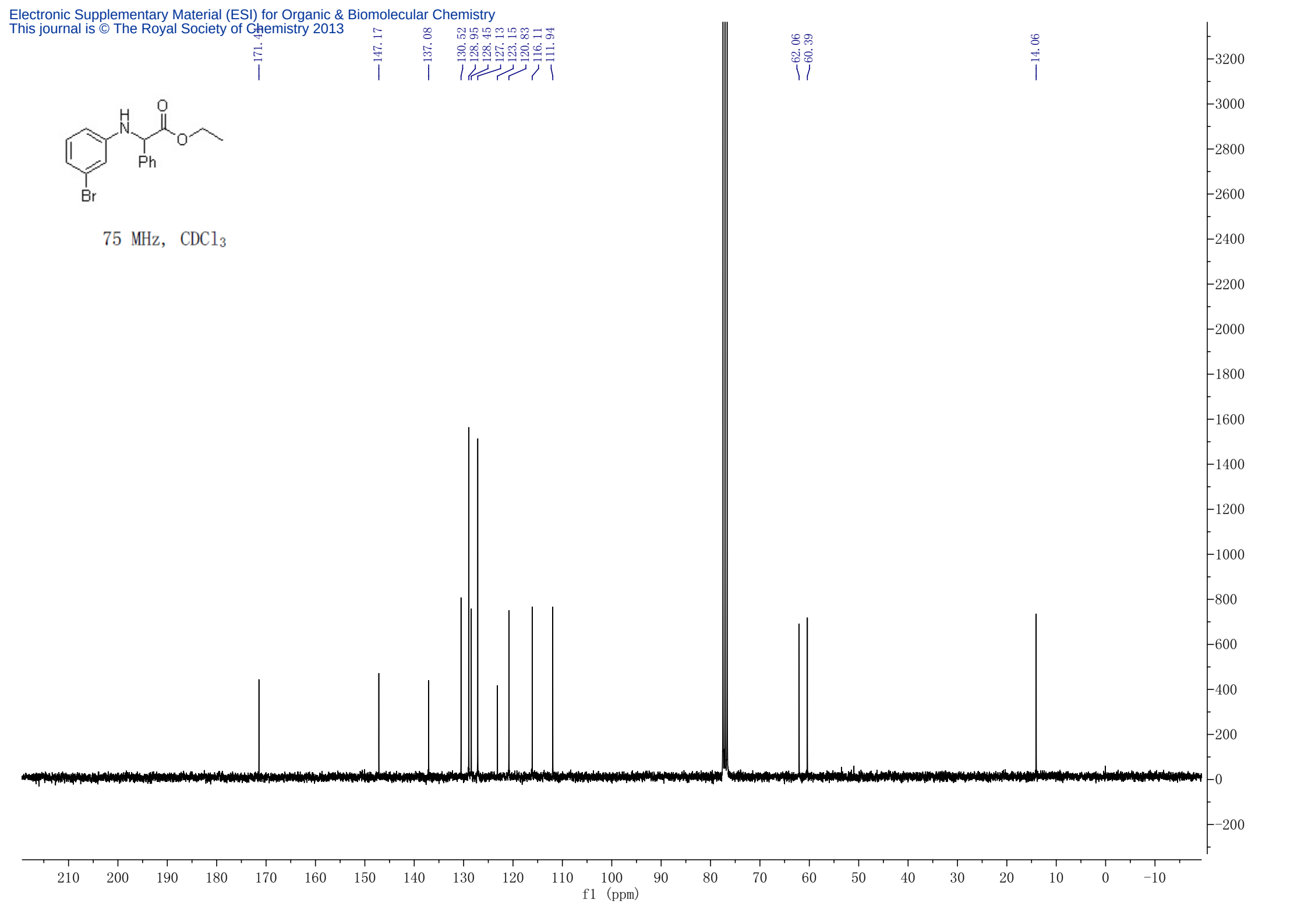
300MHz, $CDCl_3$



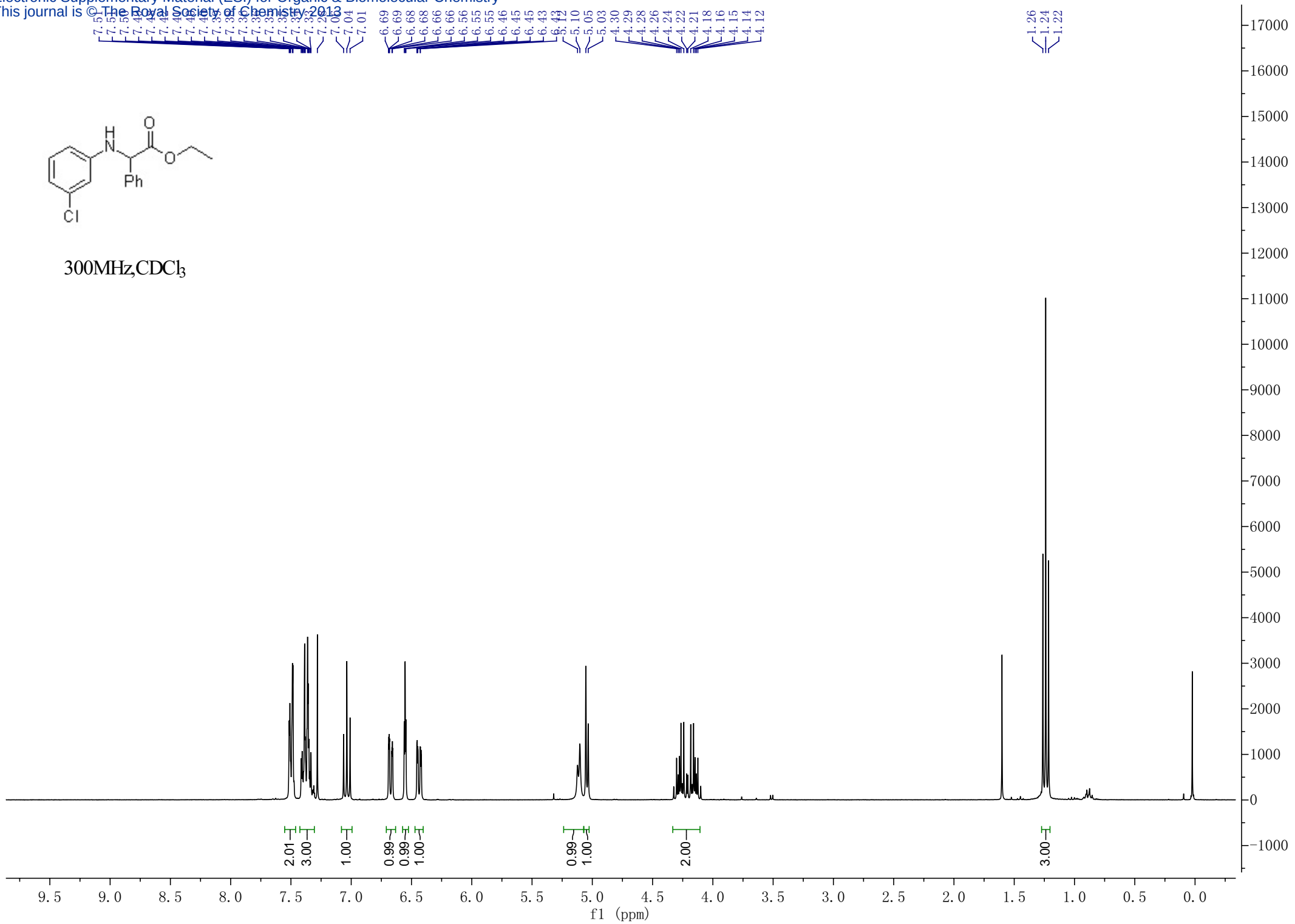


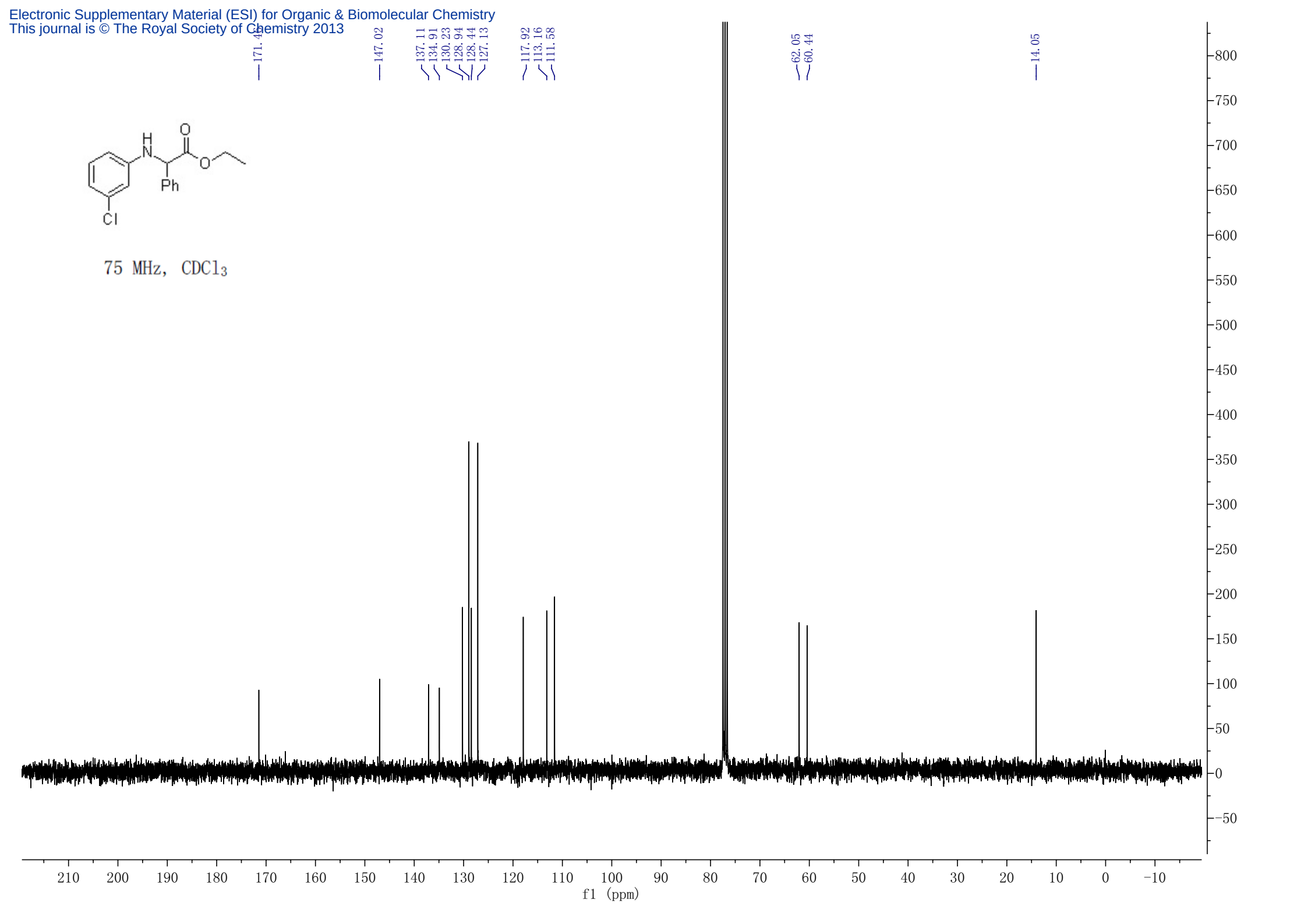
300MHz, $CDCl_3$



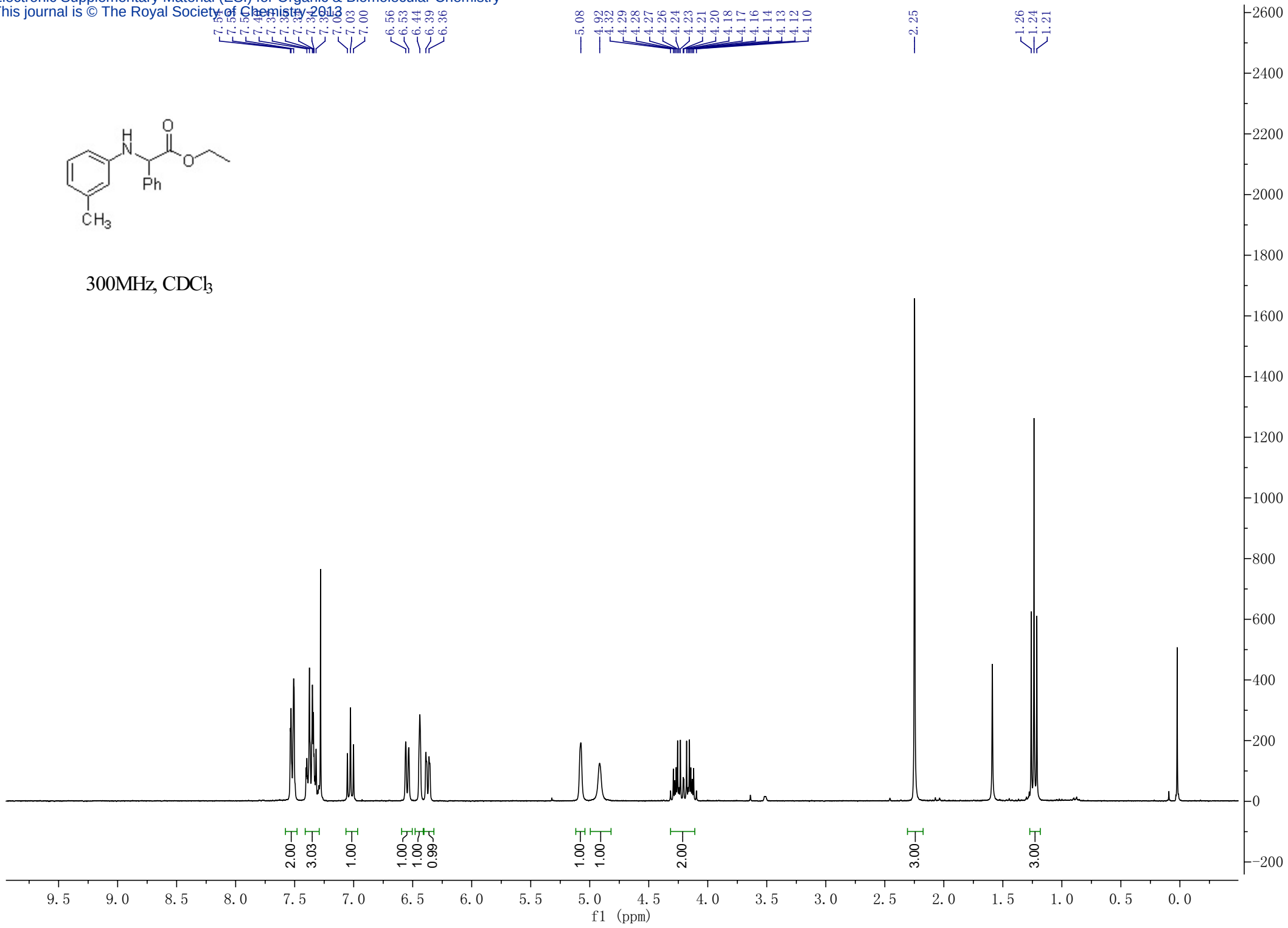


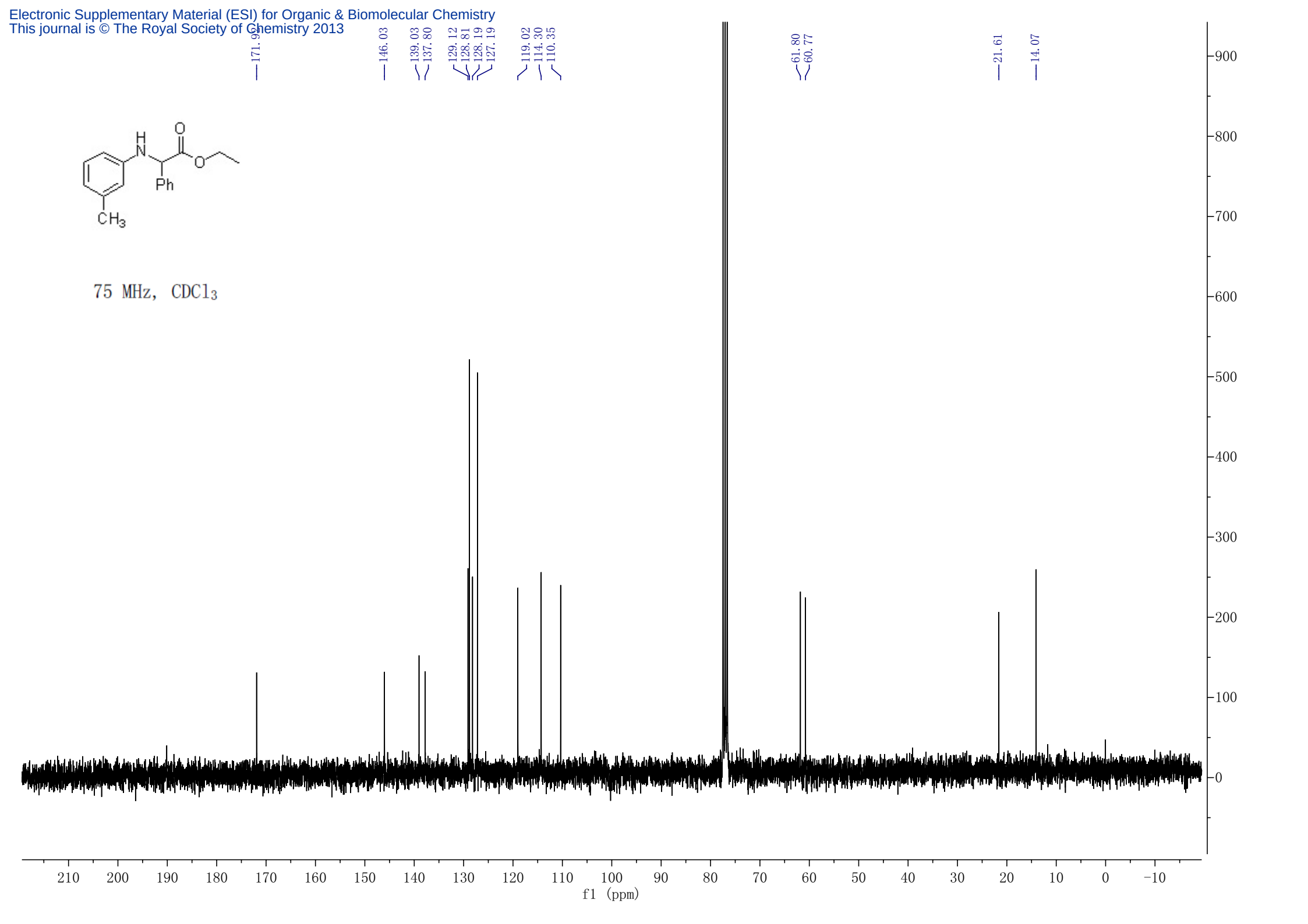
300MHz,$CDCl_3$



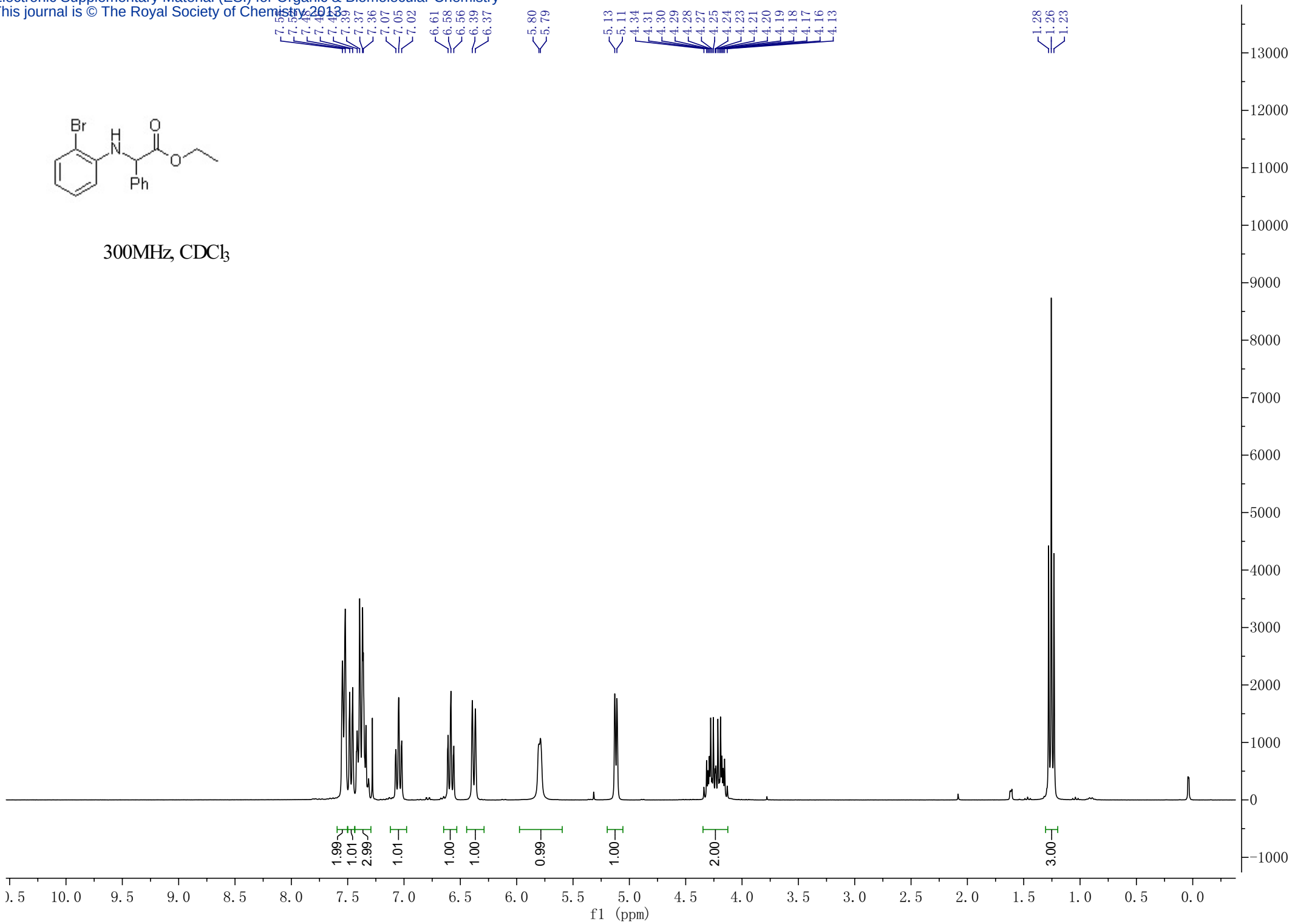


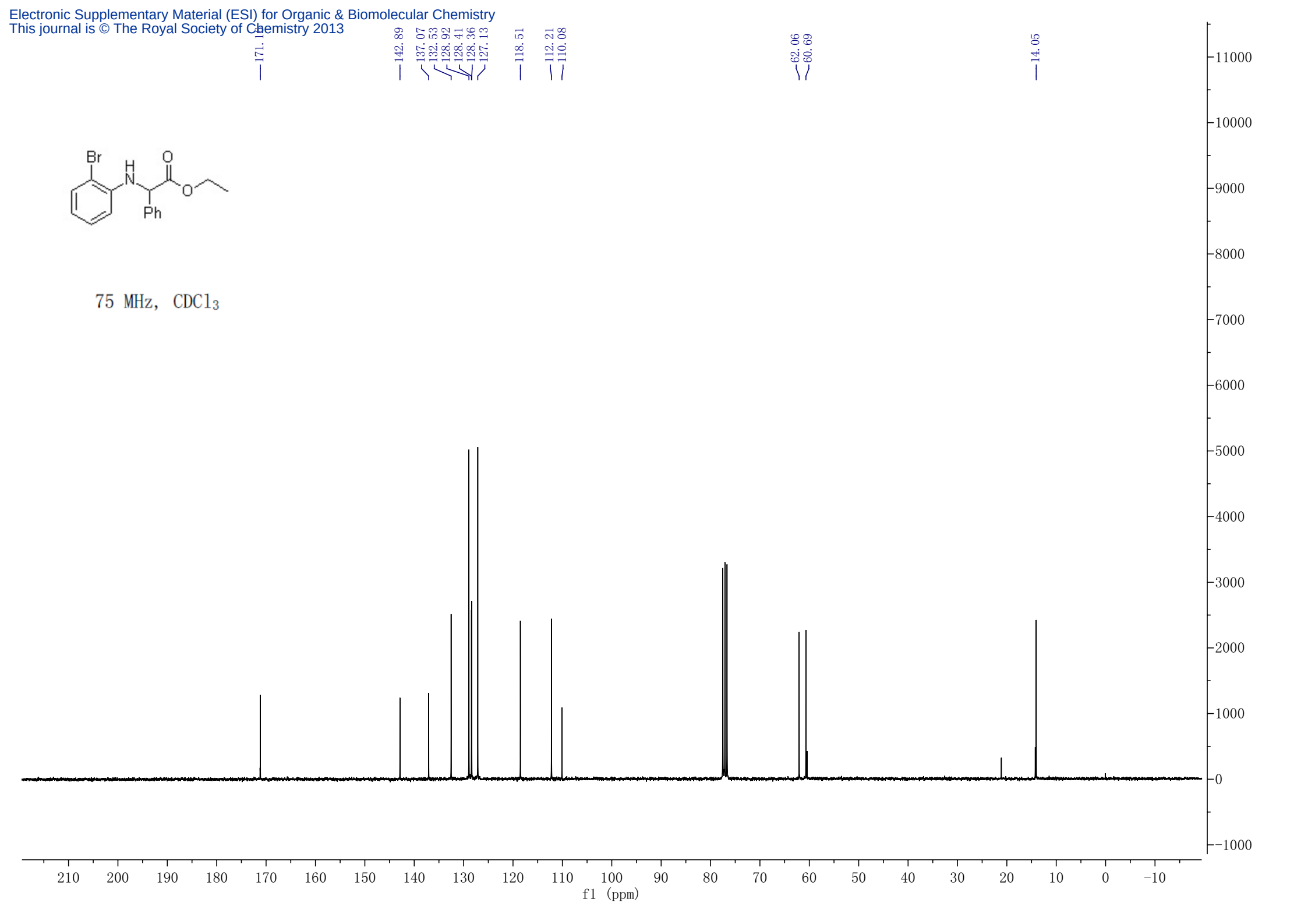
300MHz, $CDCl_3$



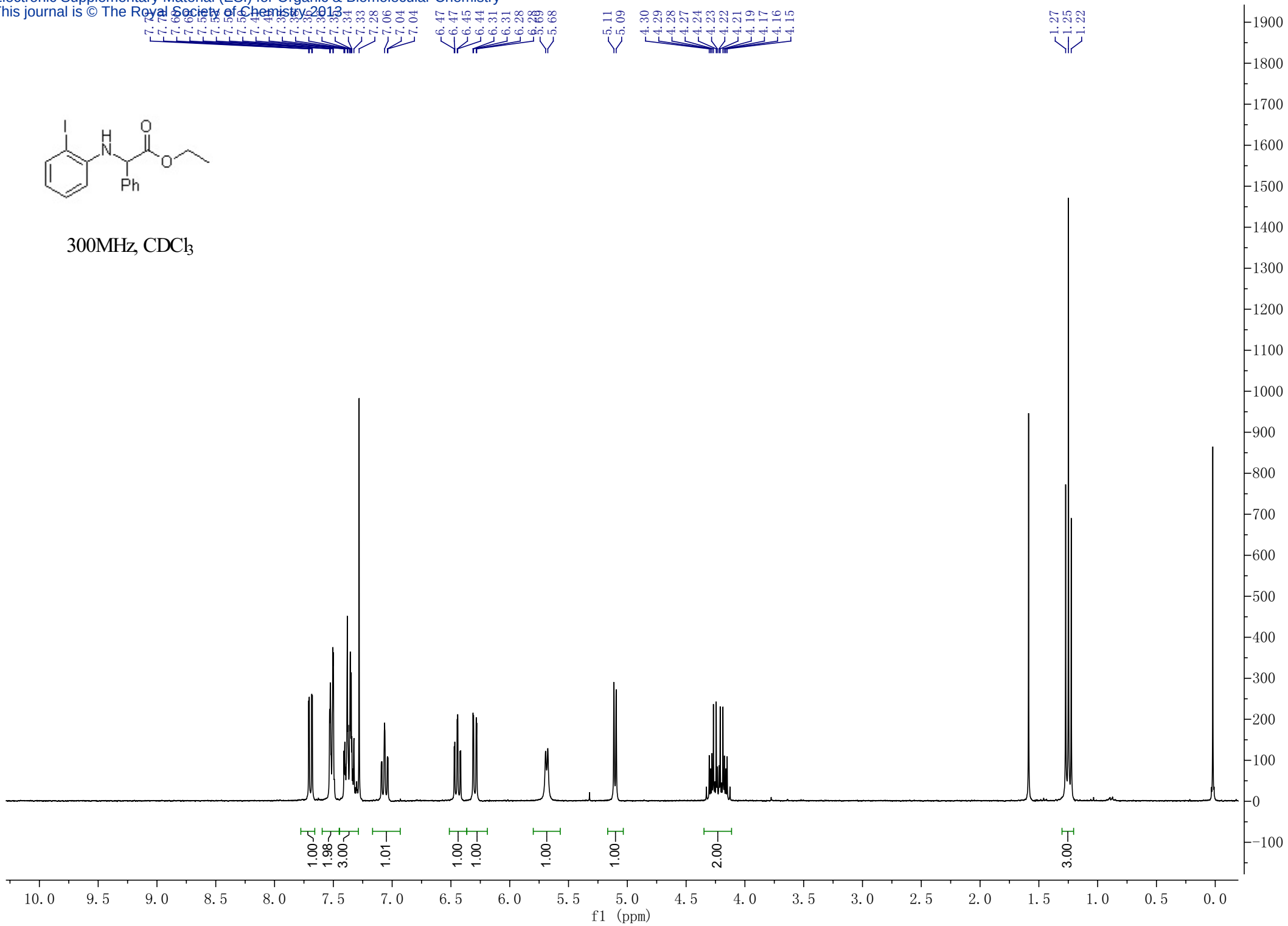


300MHz, $CDCl_3$

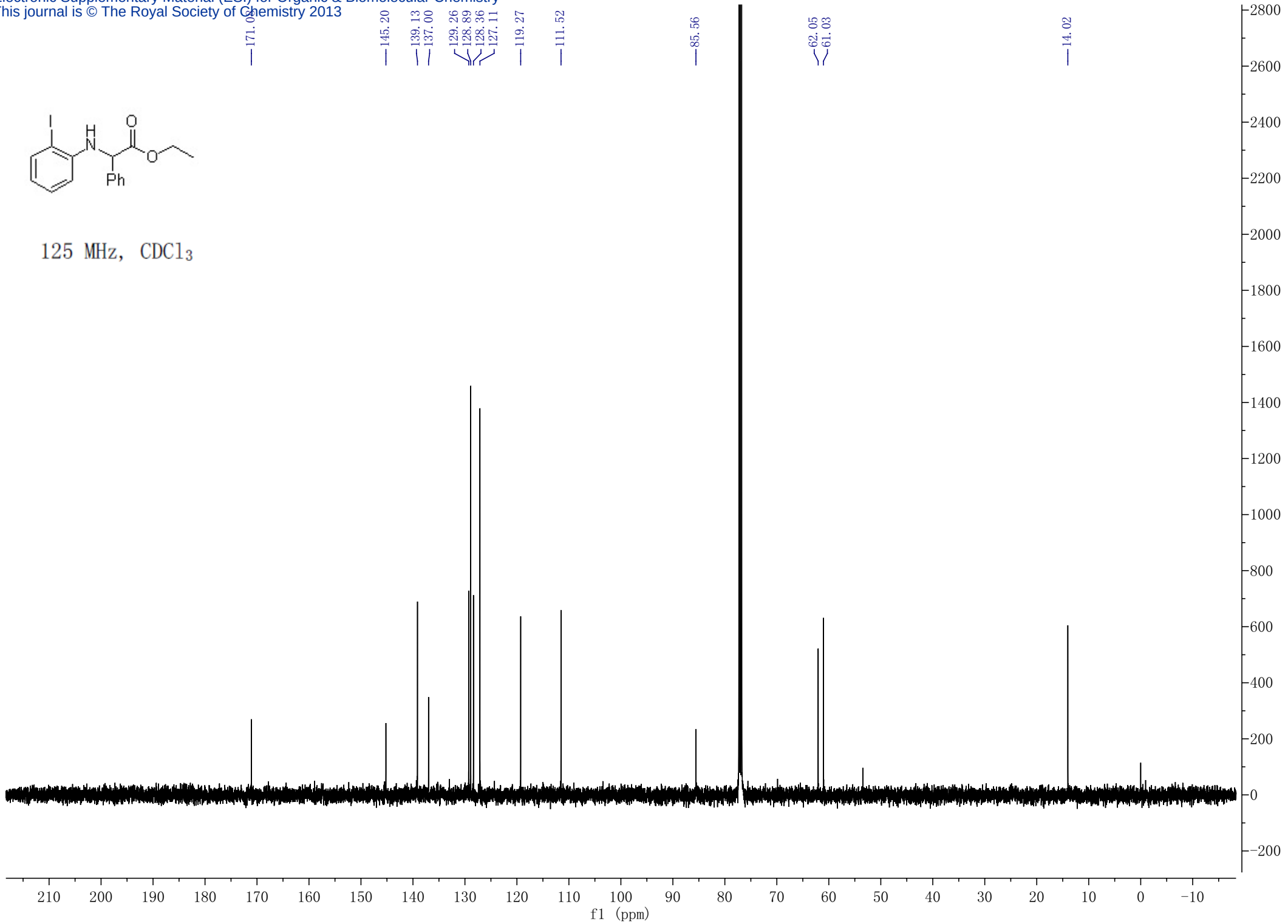




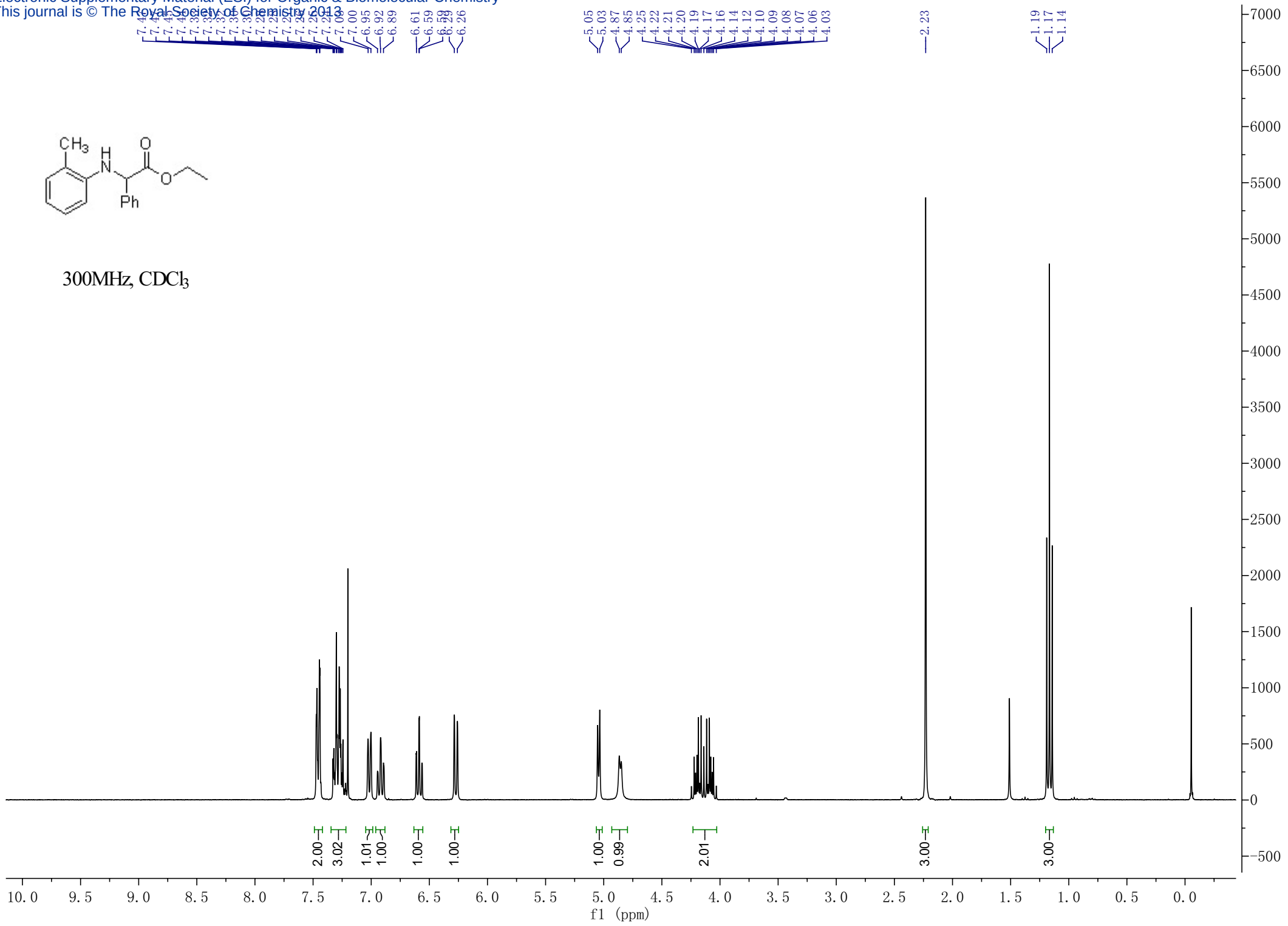
300MHz, $CDCl_3$

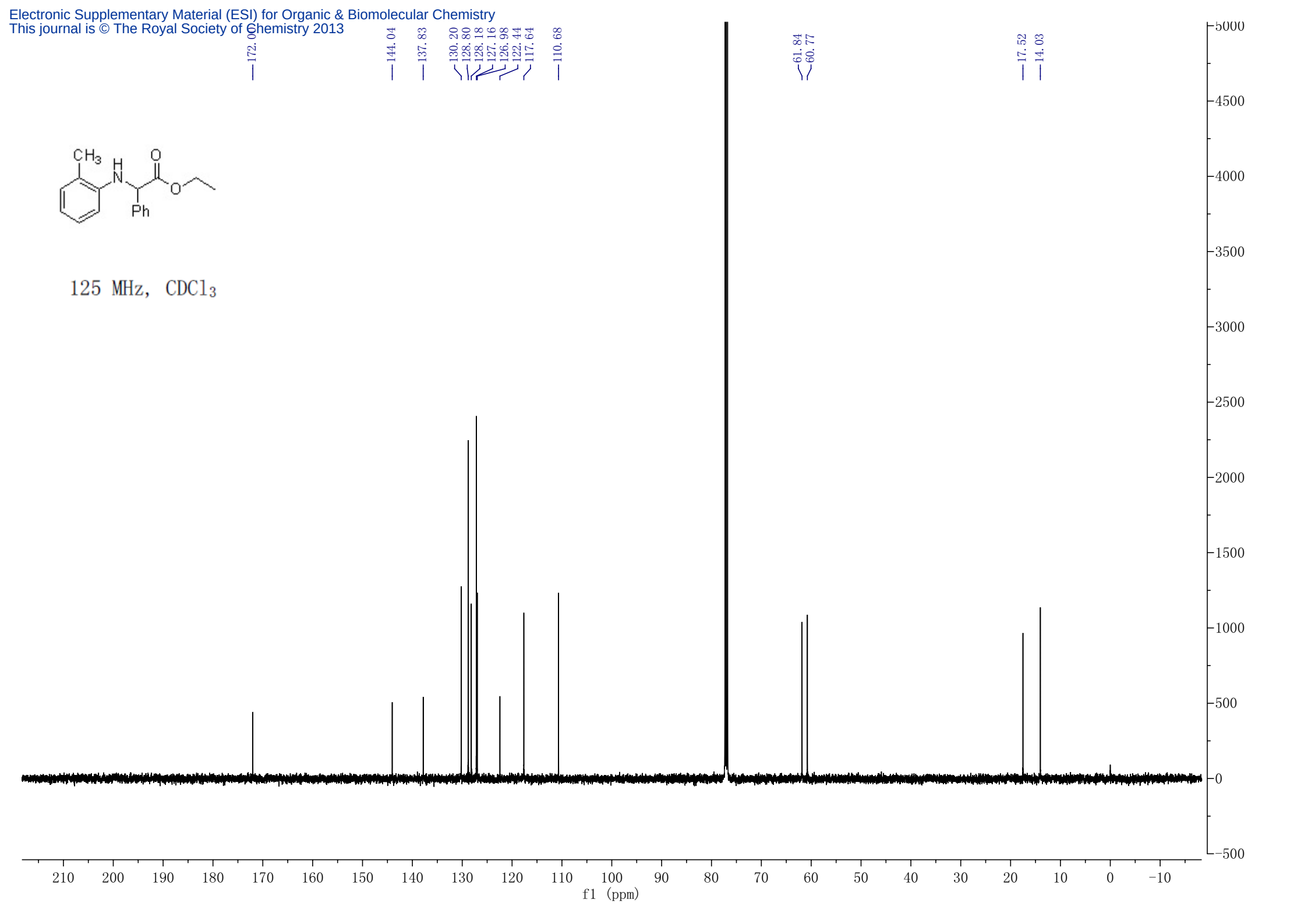


125 MHz, $CDCl_3$

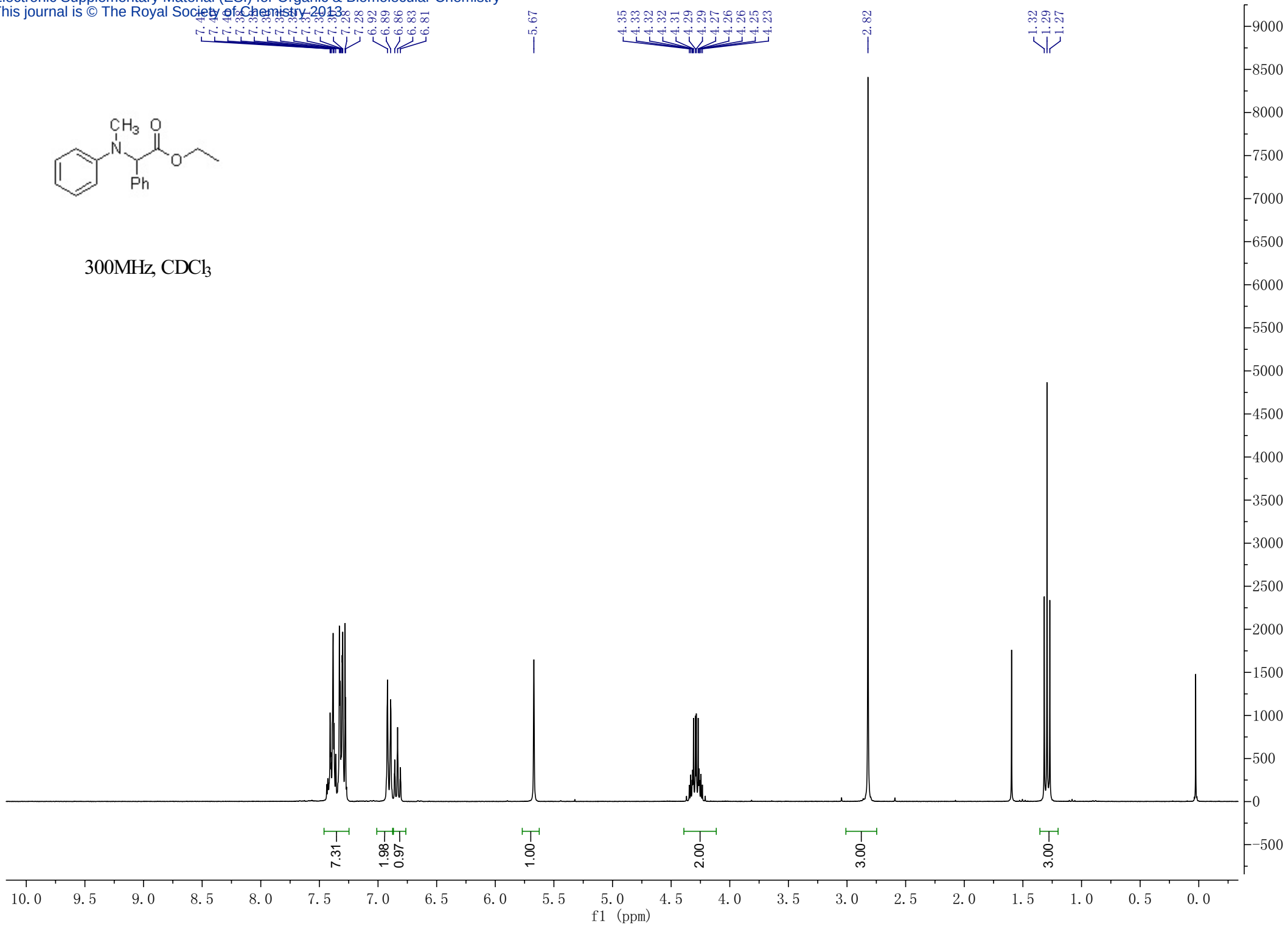


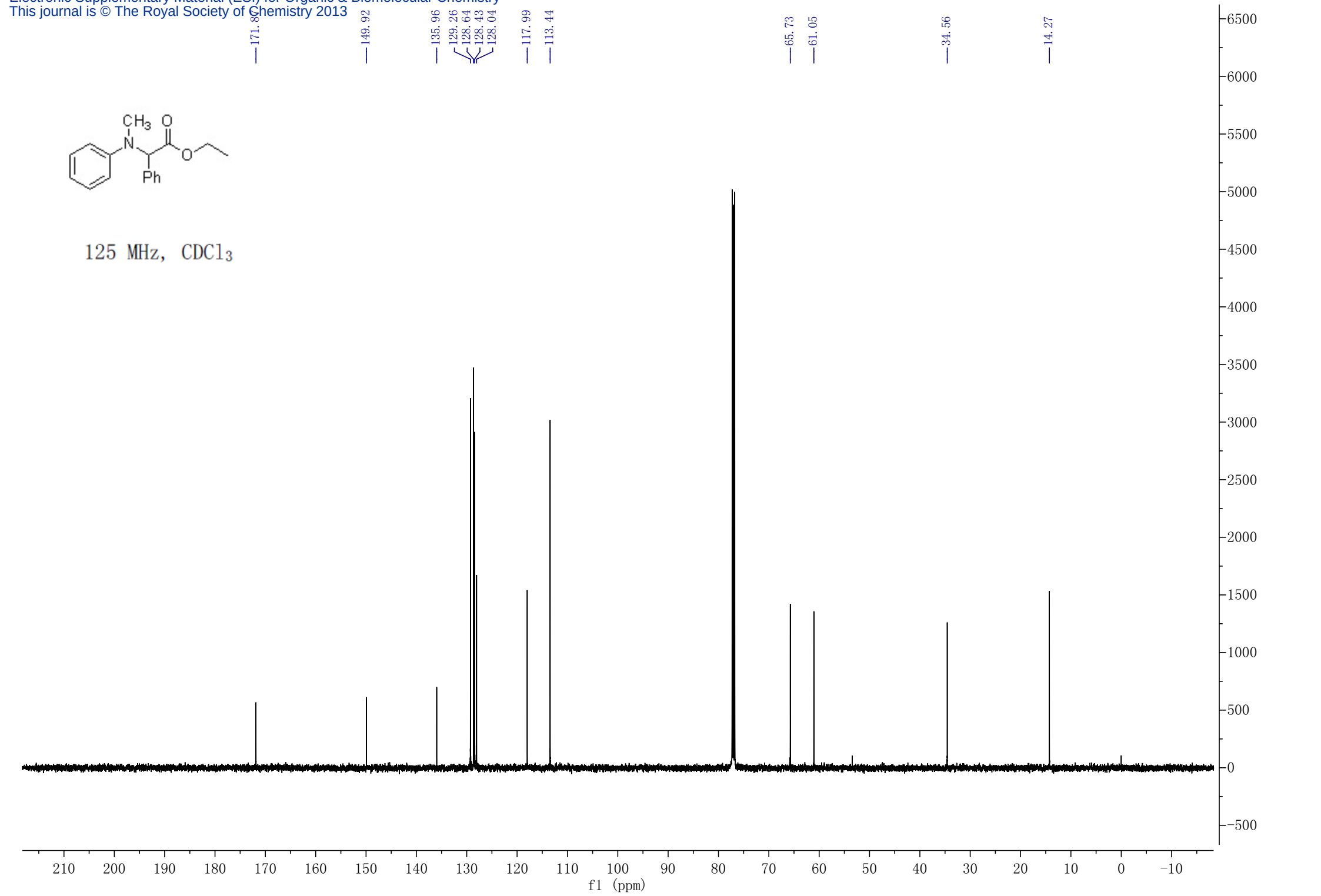
300MHz, $CDCl_3$



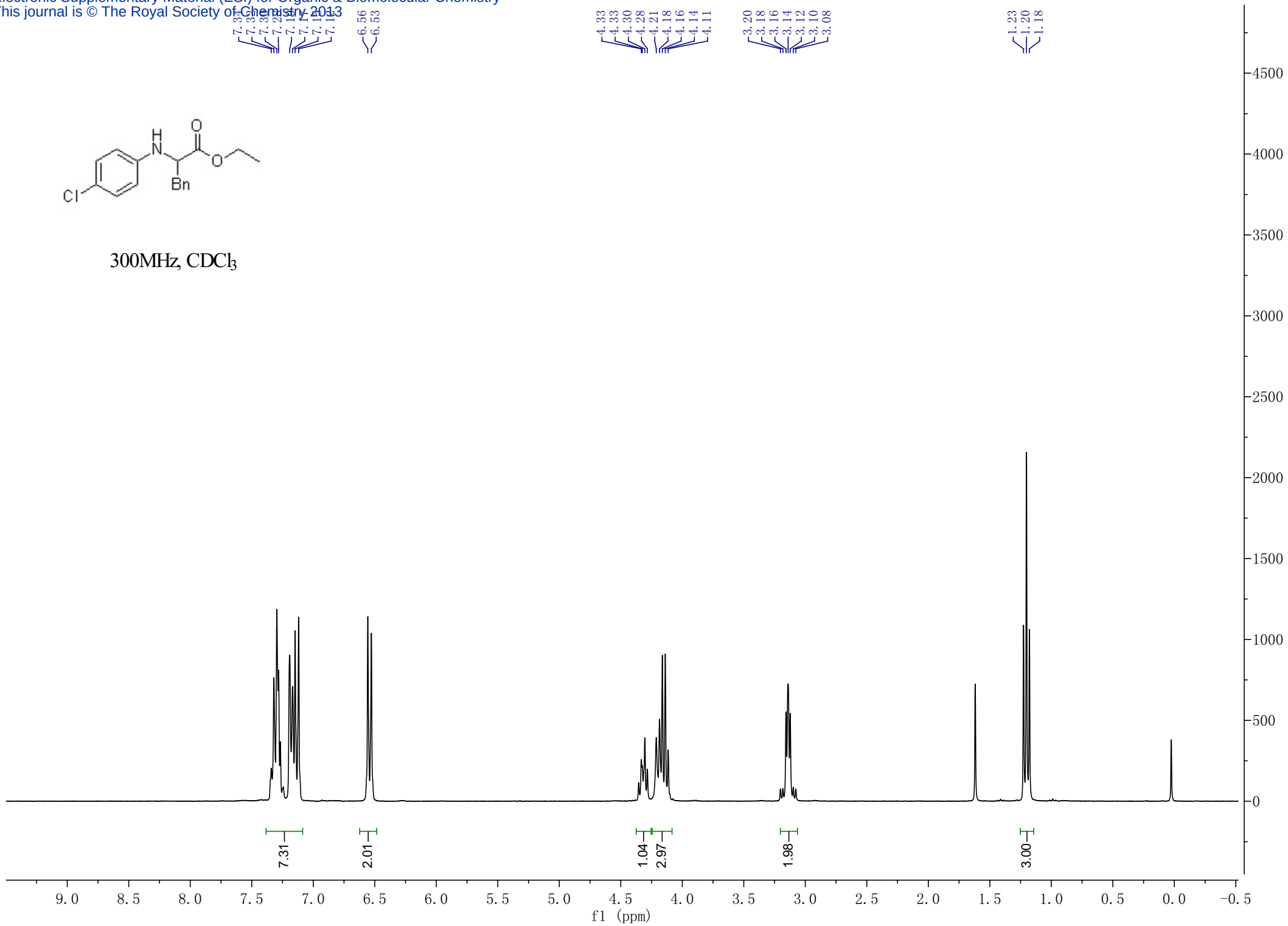


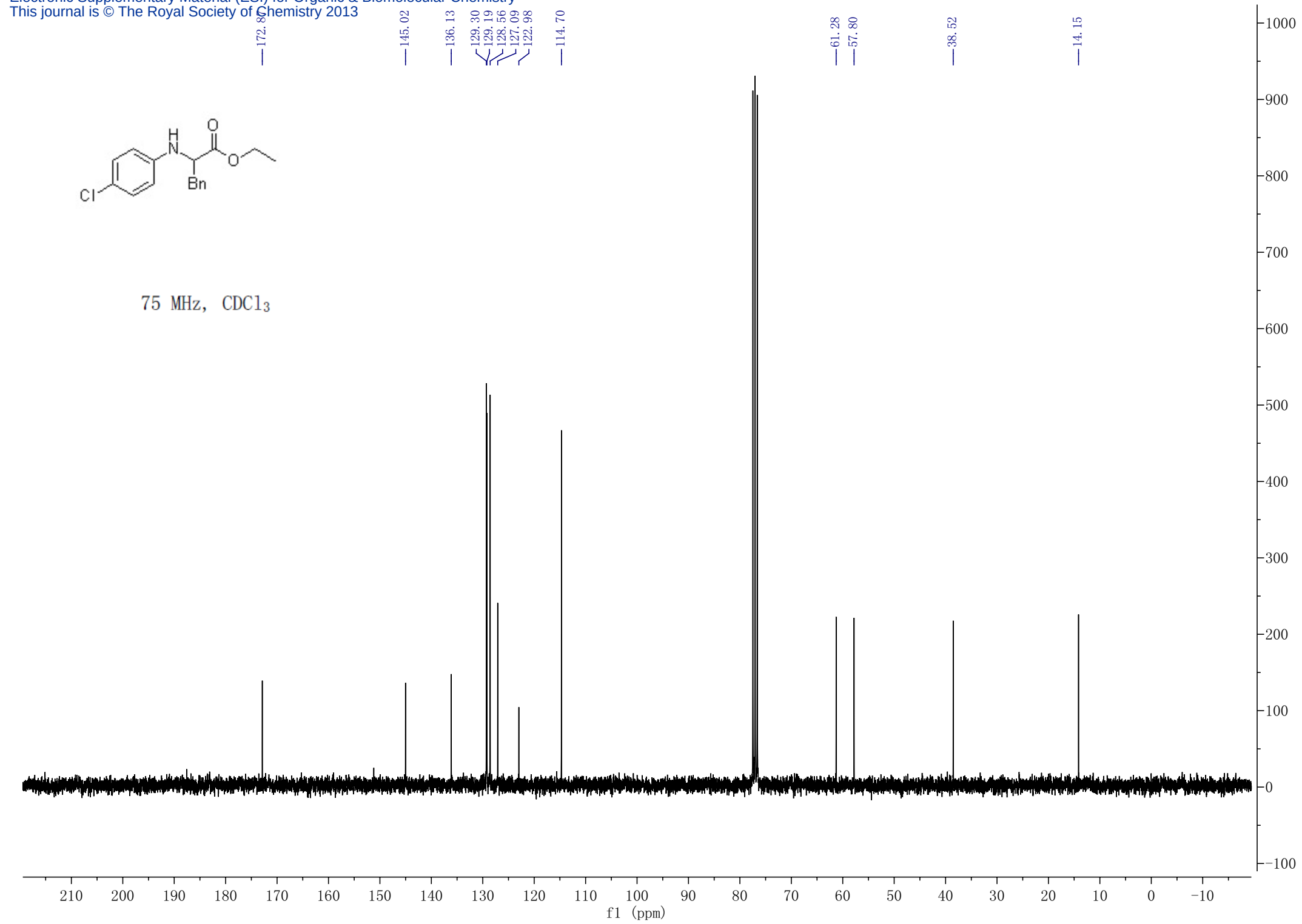
300MHz, $CDCl_3$



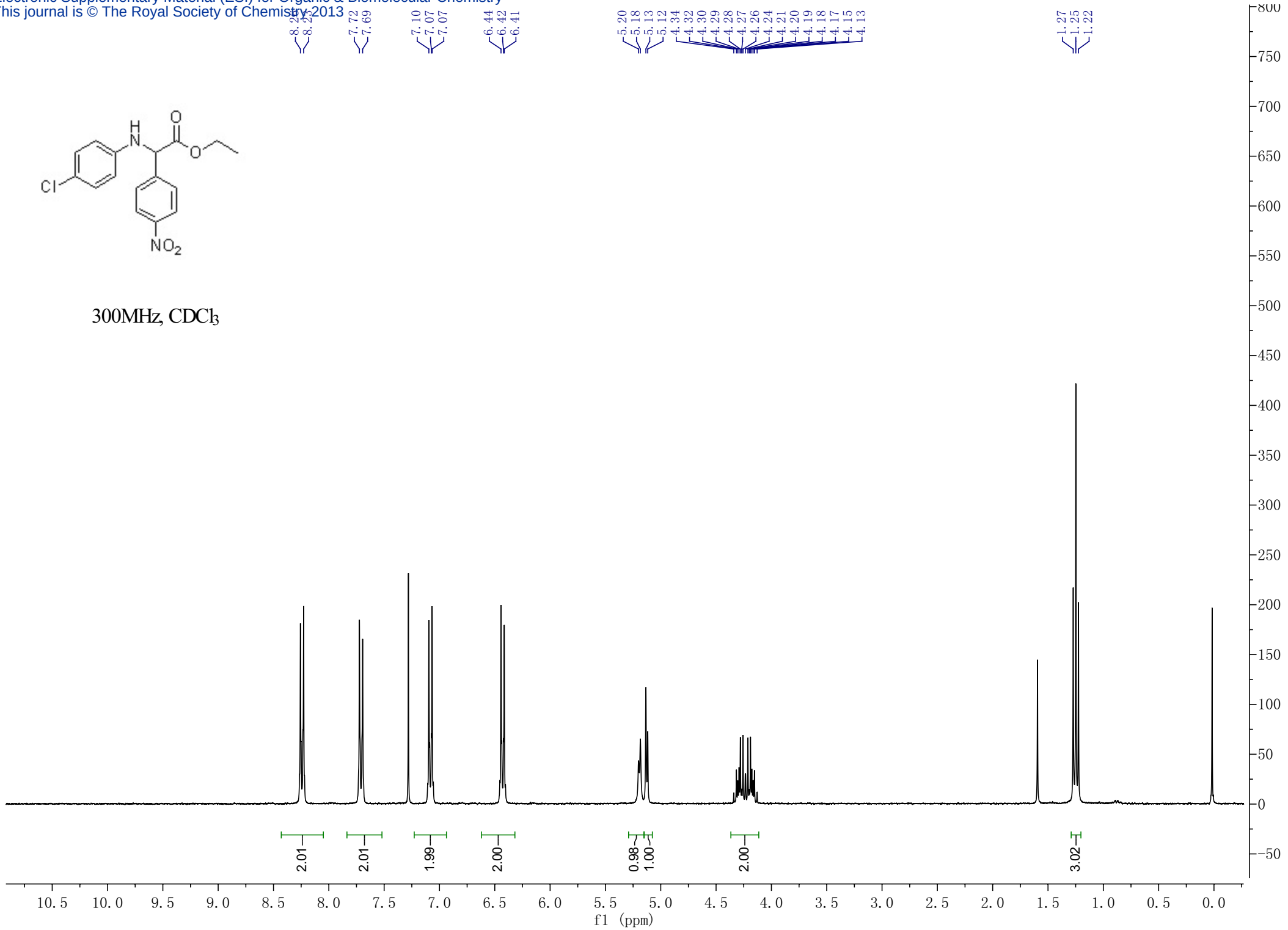


300MHz, $CDCl_3$

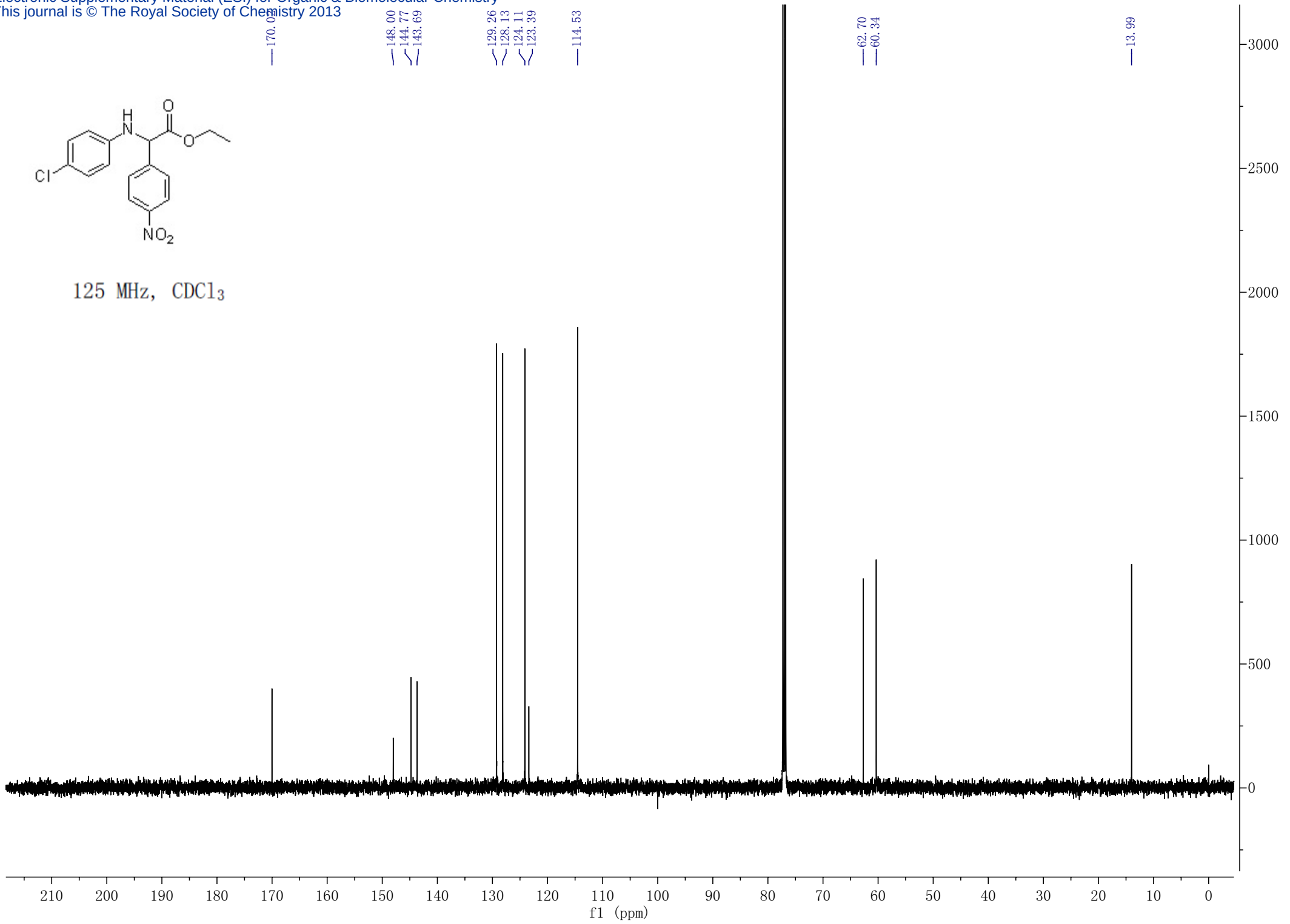




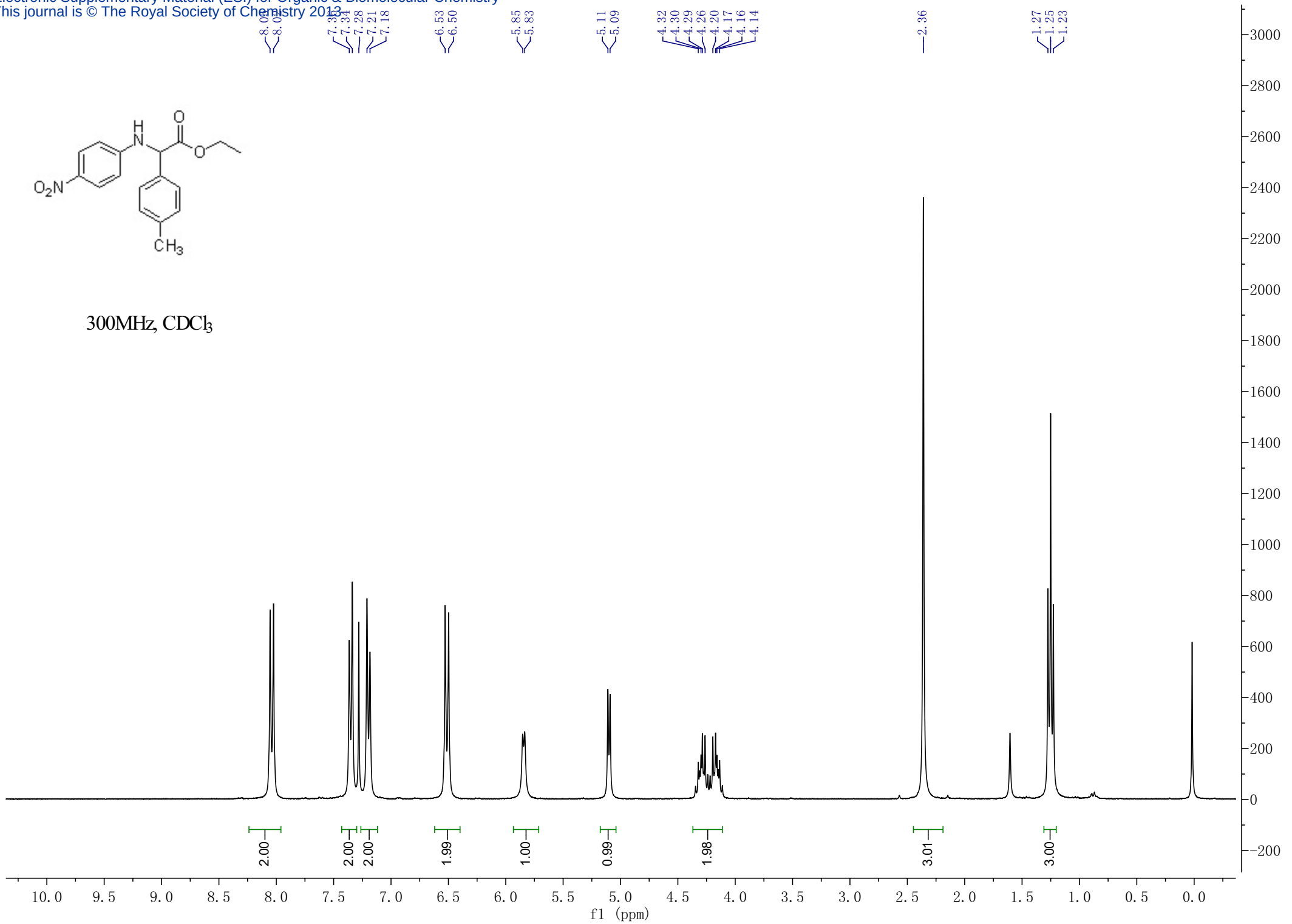
300MHz, $CDCl_3$



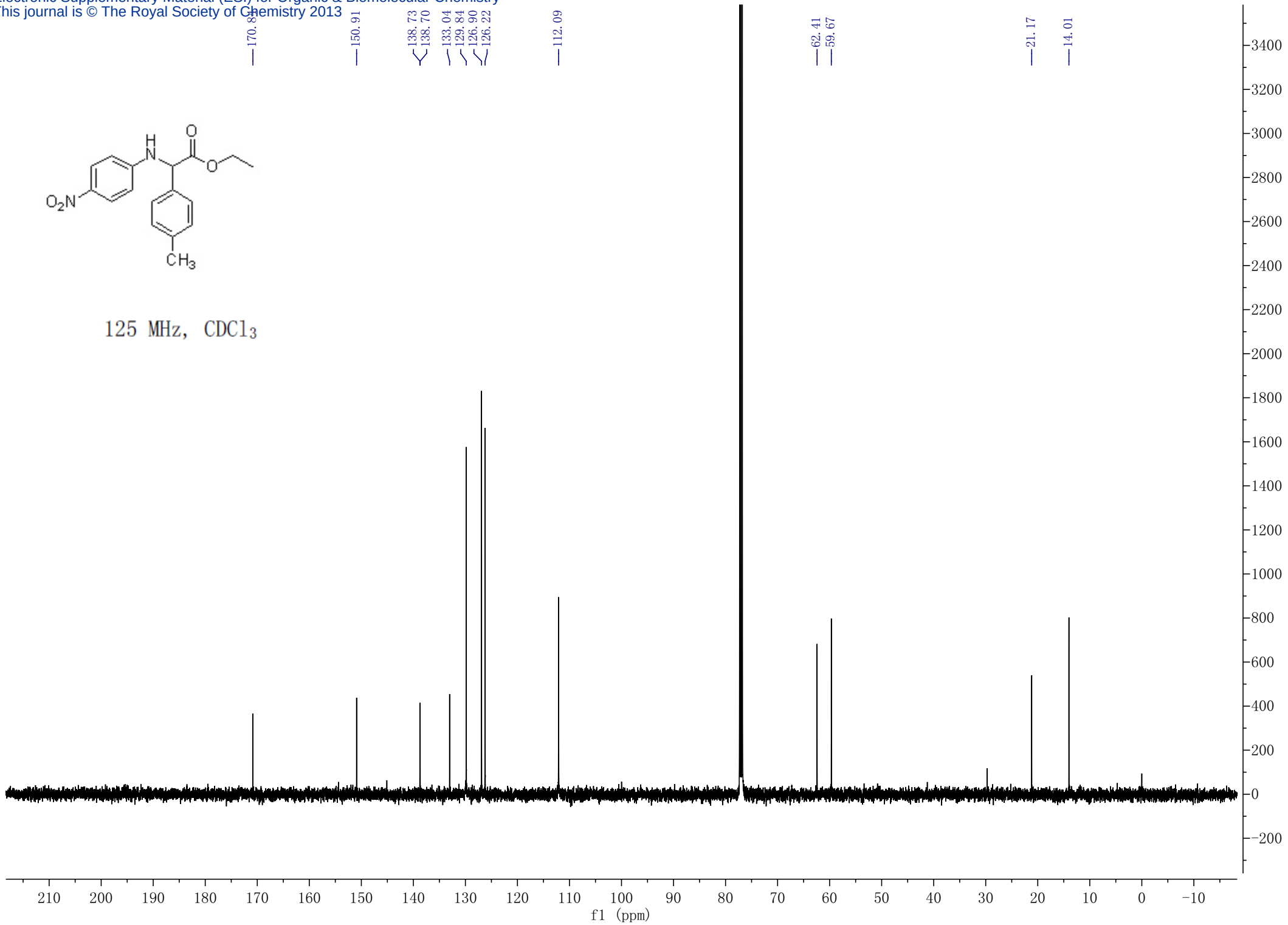
125 MHz, $CDCl_3$



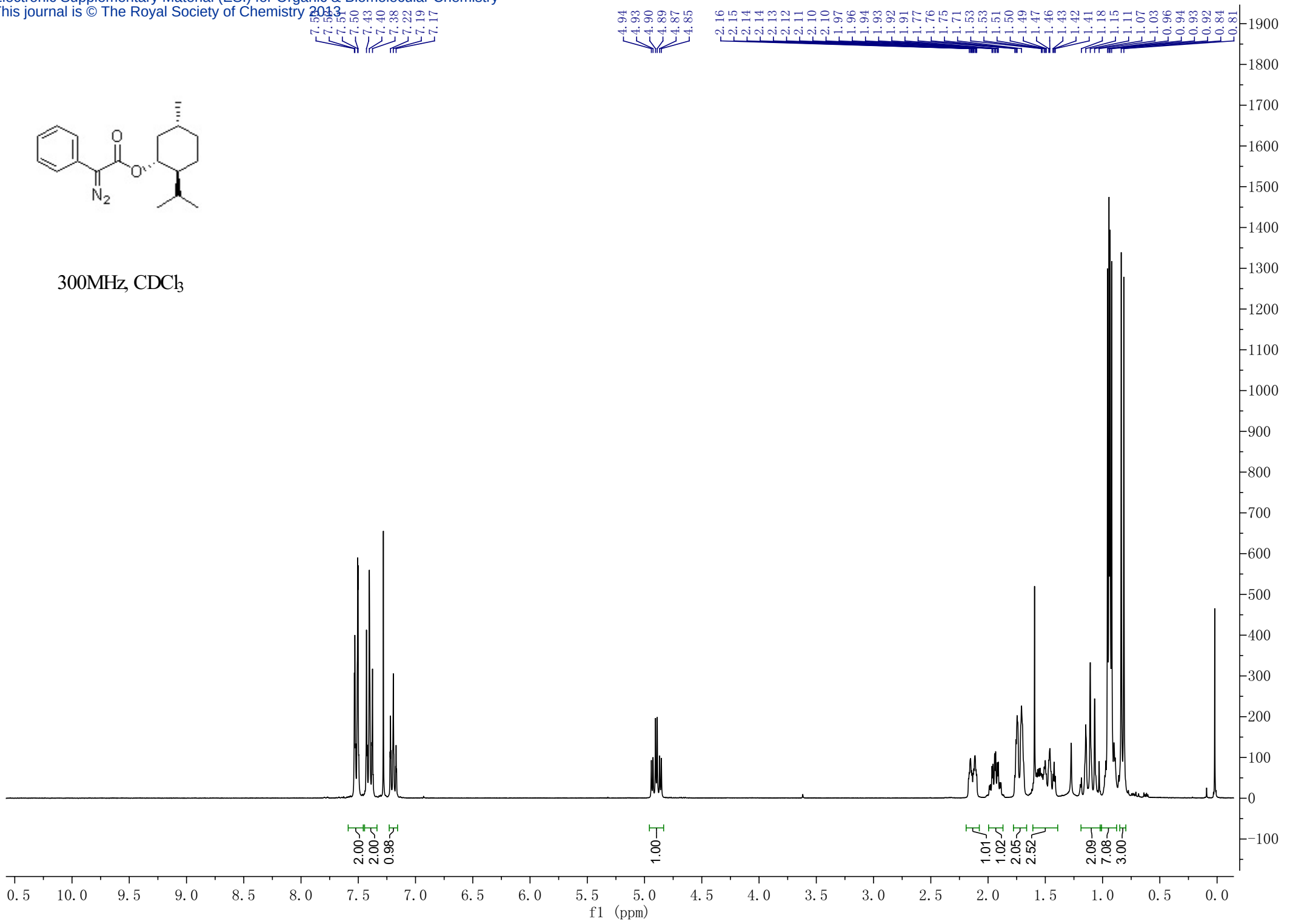
300MHz, $CDCl_3$

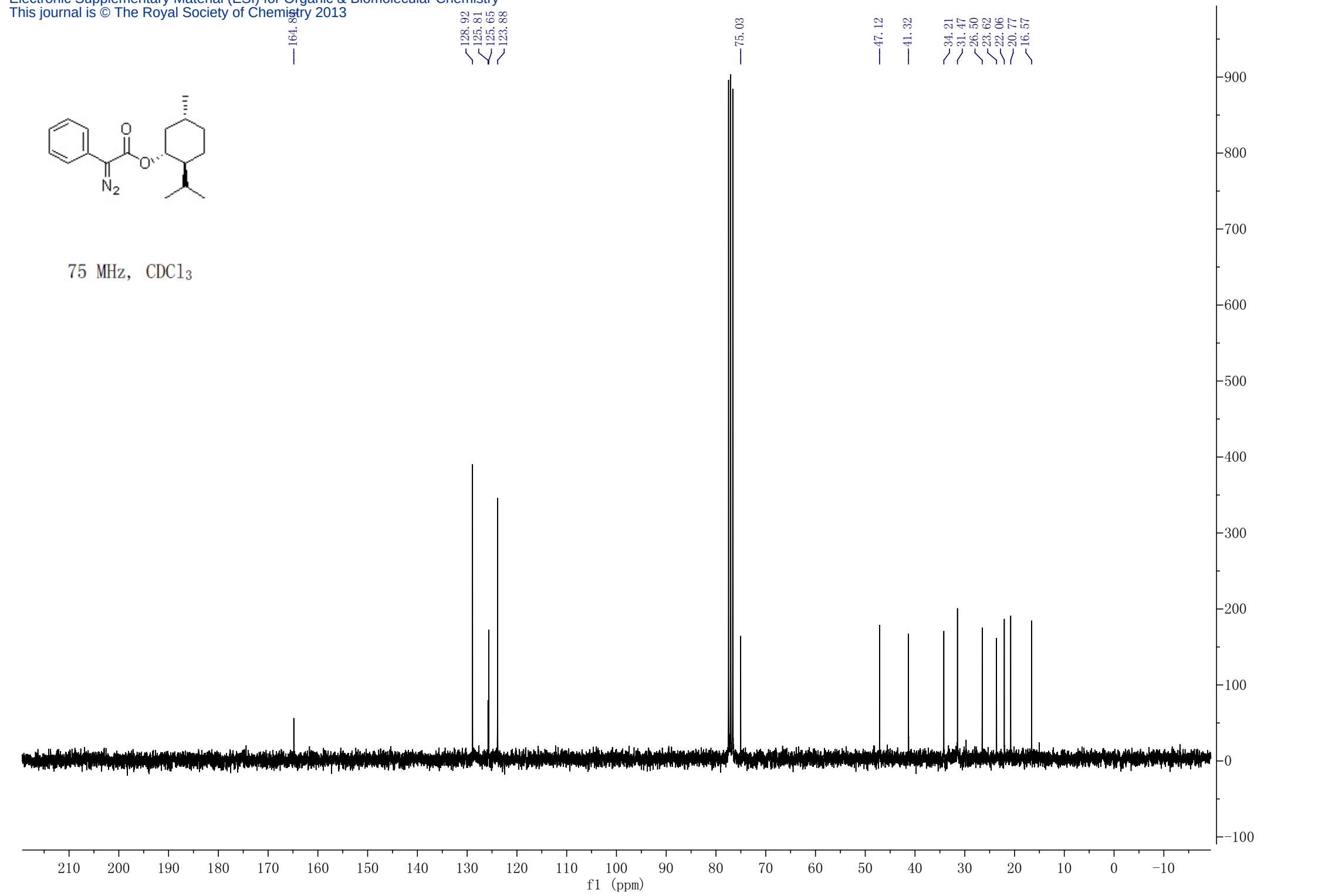


125 MHz, $CDCl_3$

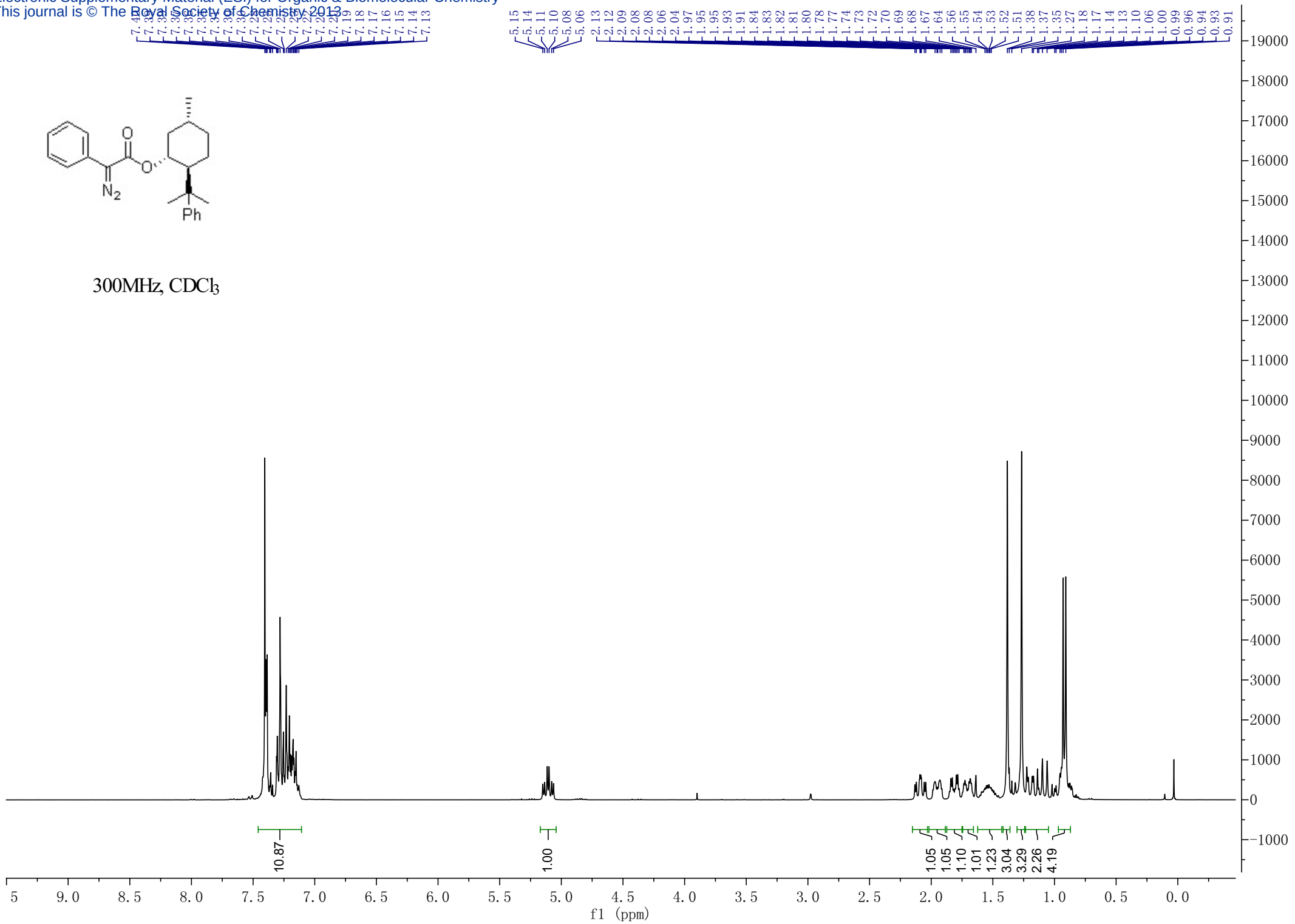


300MHz, $CDCl_3$

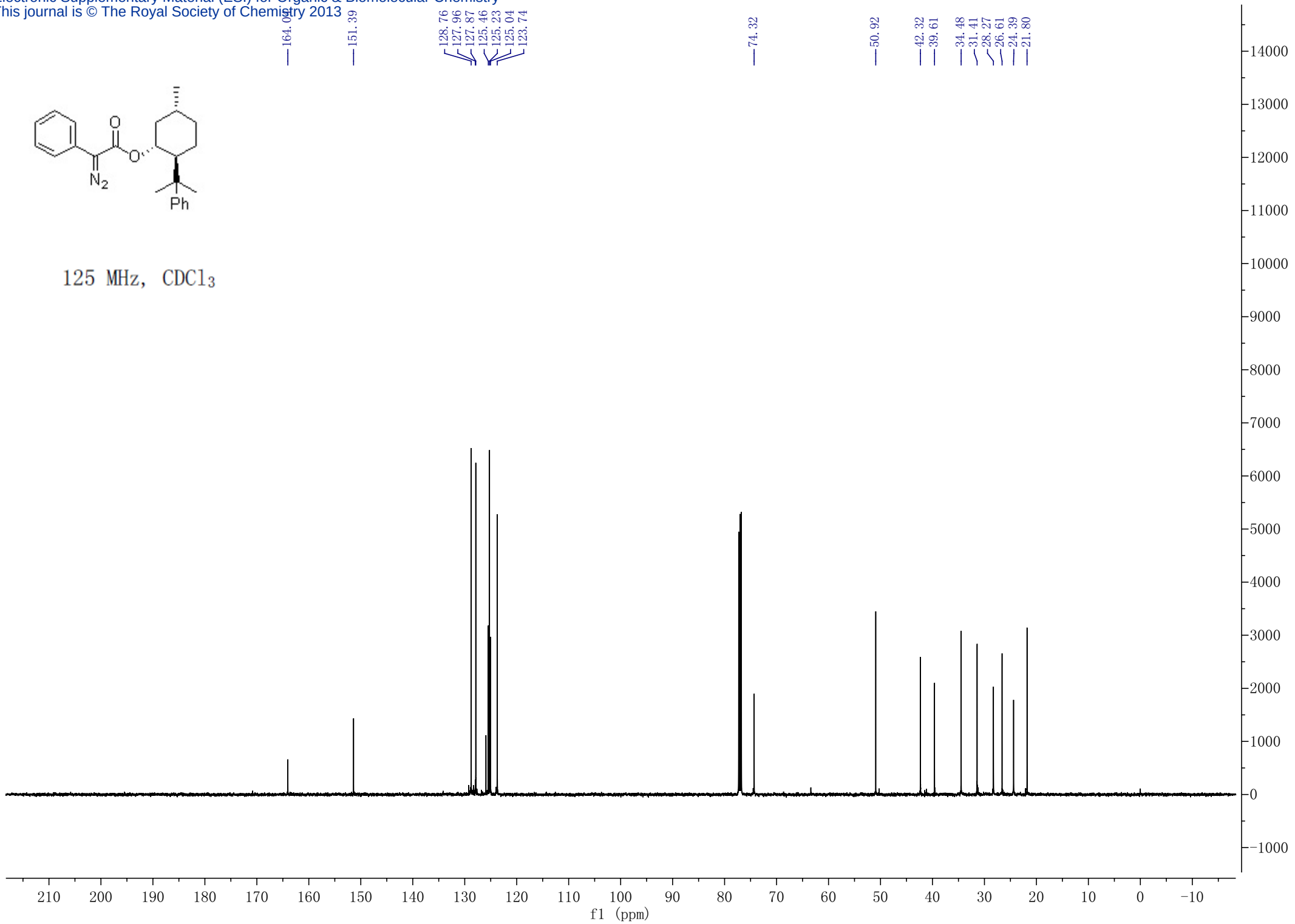




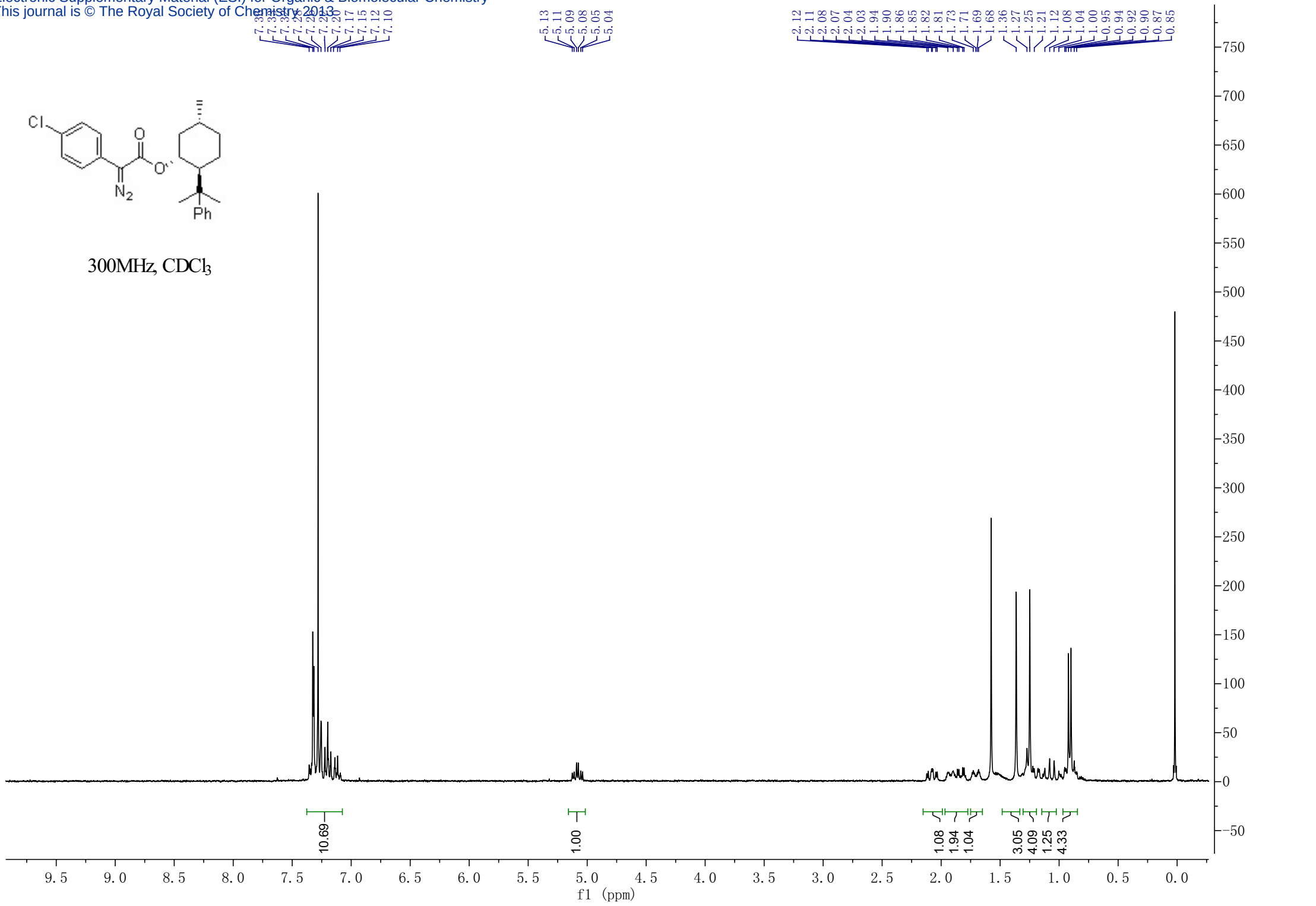
300MHz, $CDCl_3$



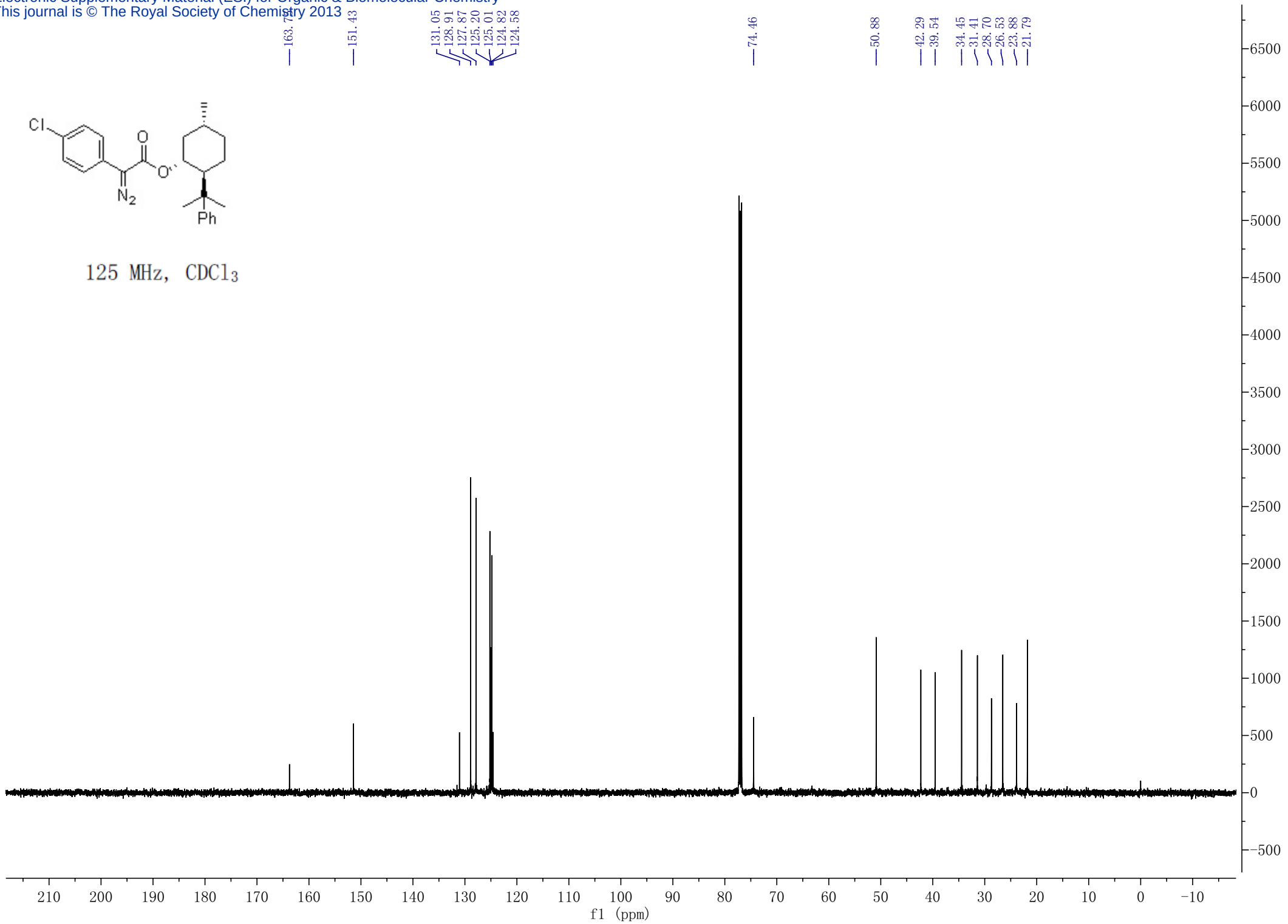
125 MHz, $CDCl_3$



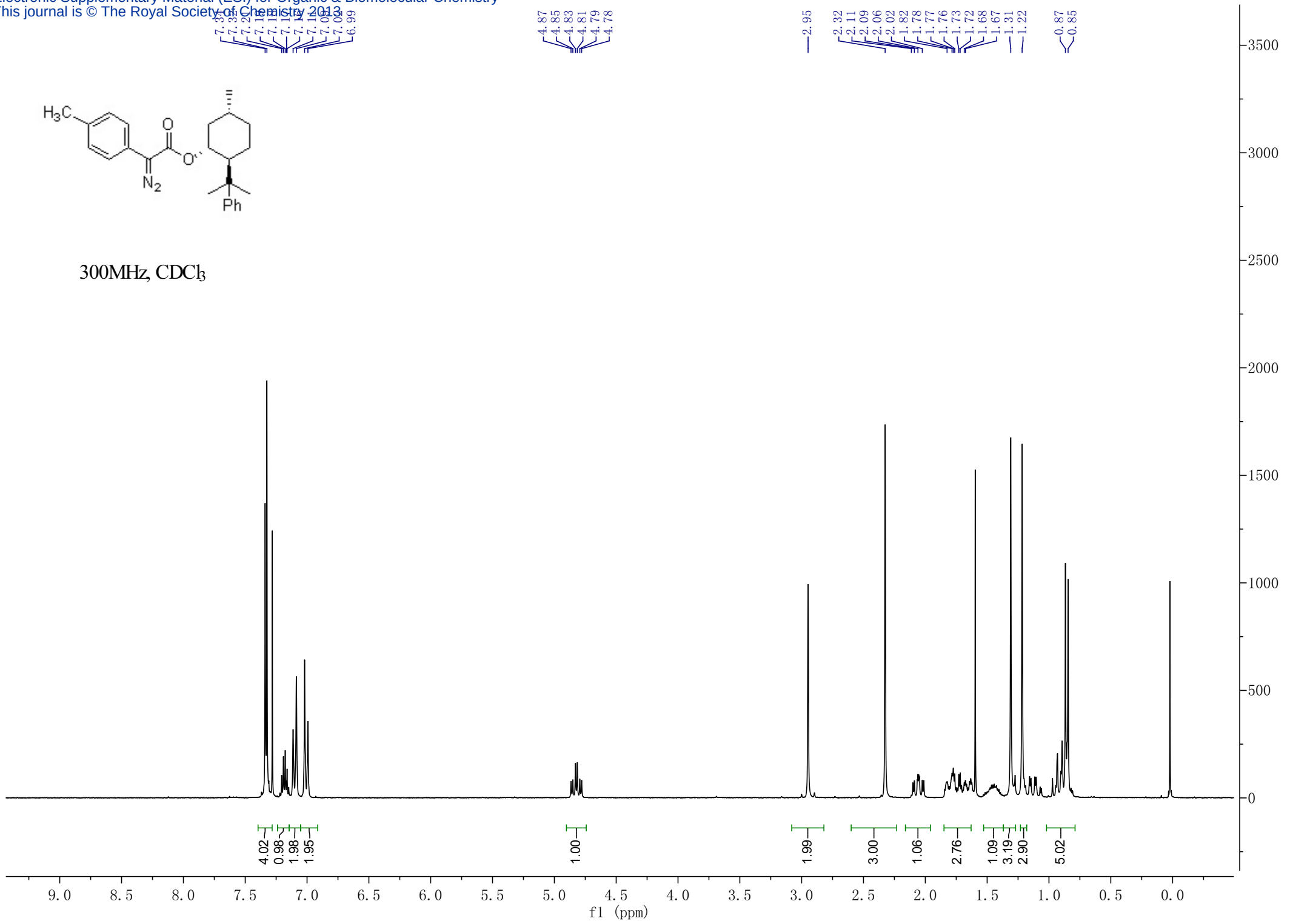
300MHz, $CDCl_3$

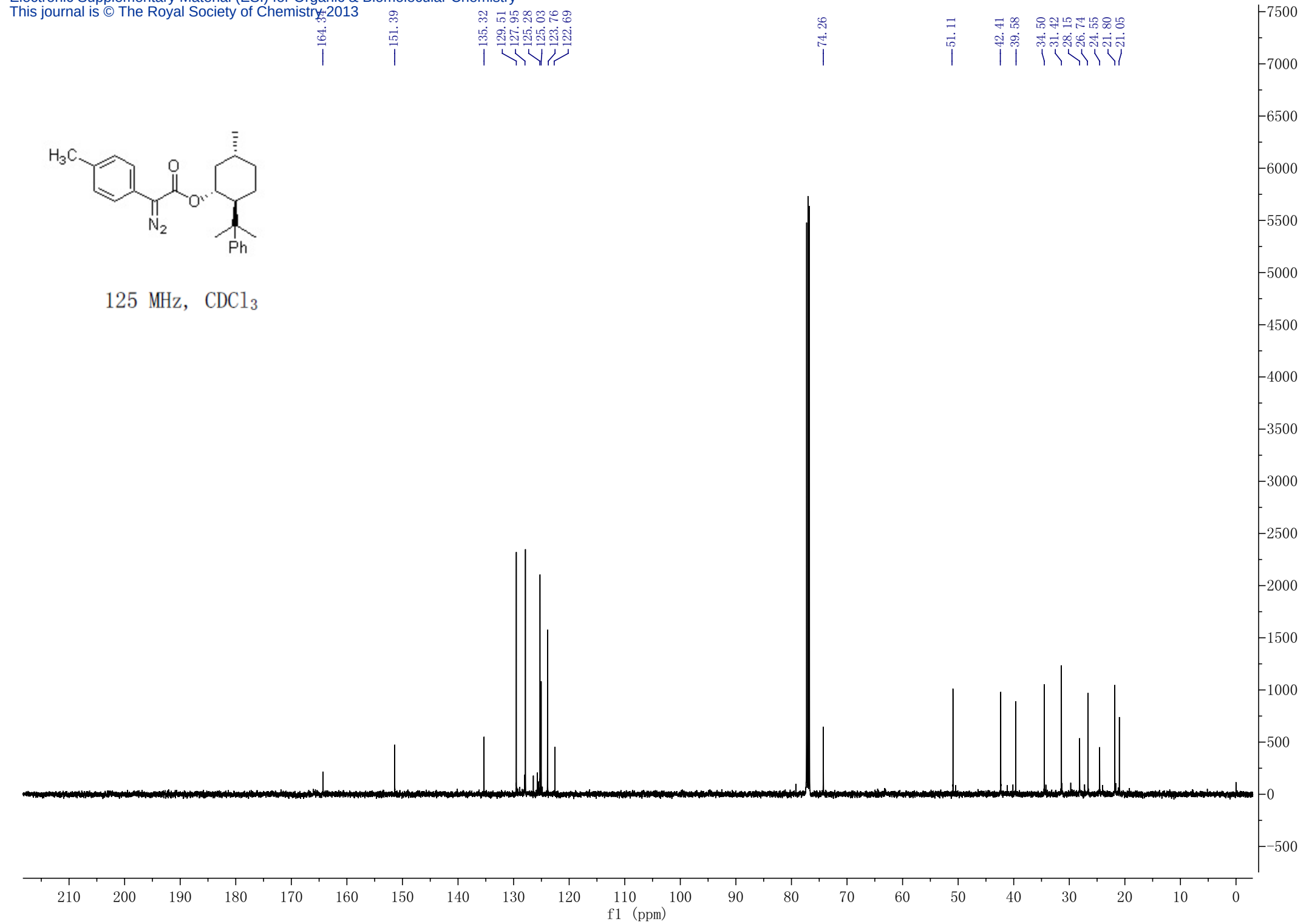


125 MHz, $CDCl_3$

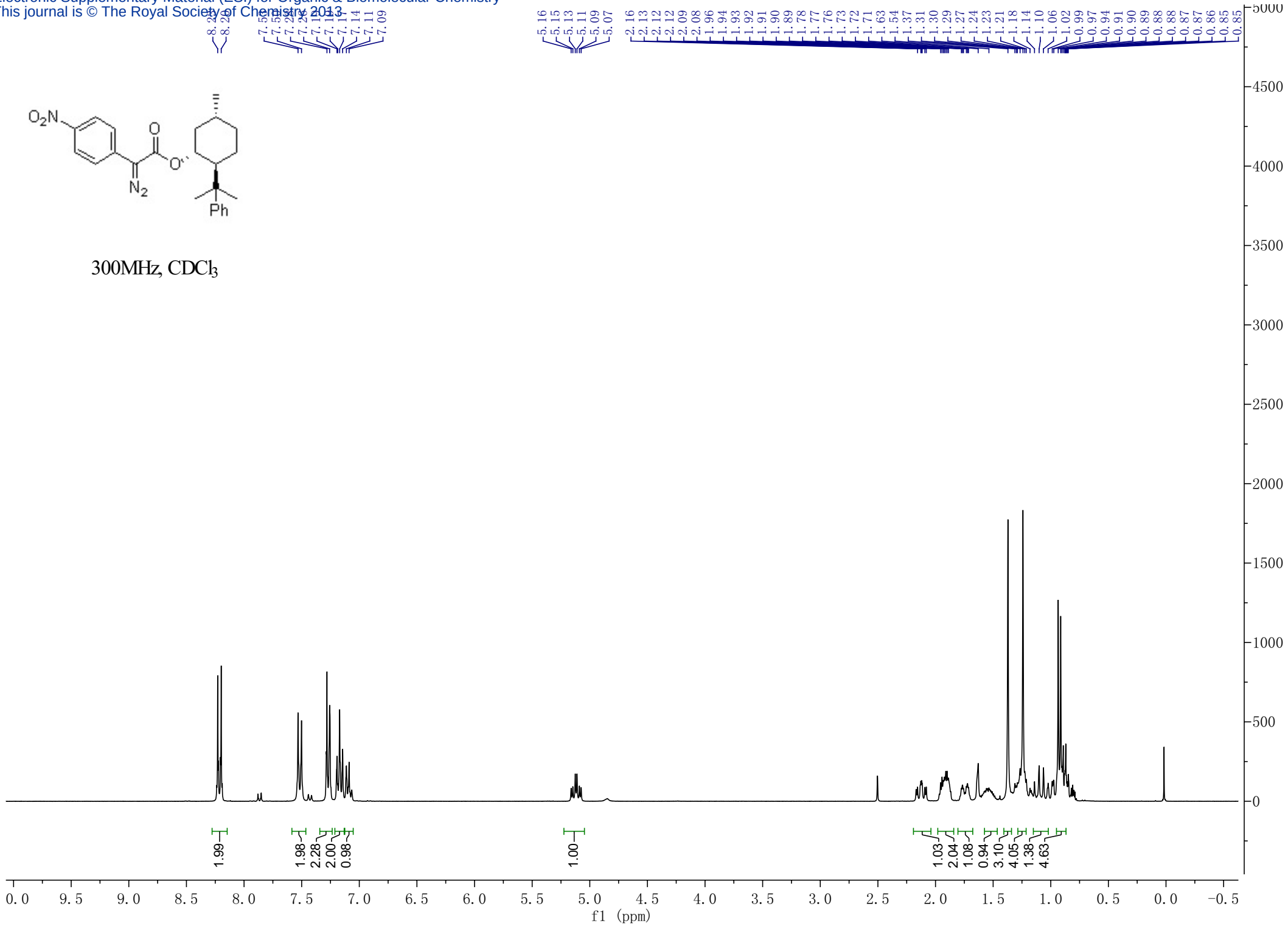


300MHz, $CDCl_3$

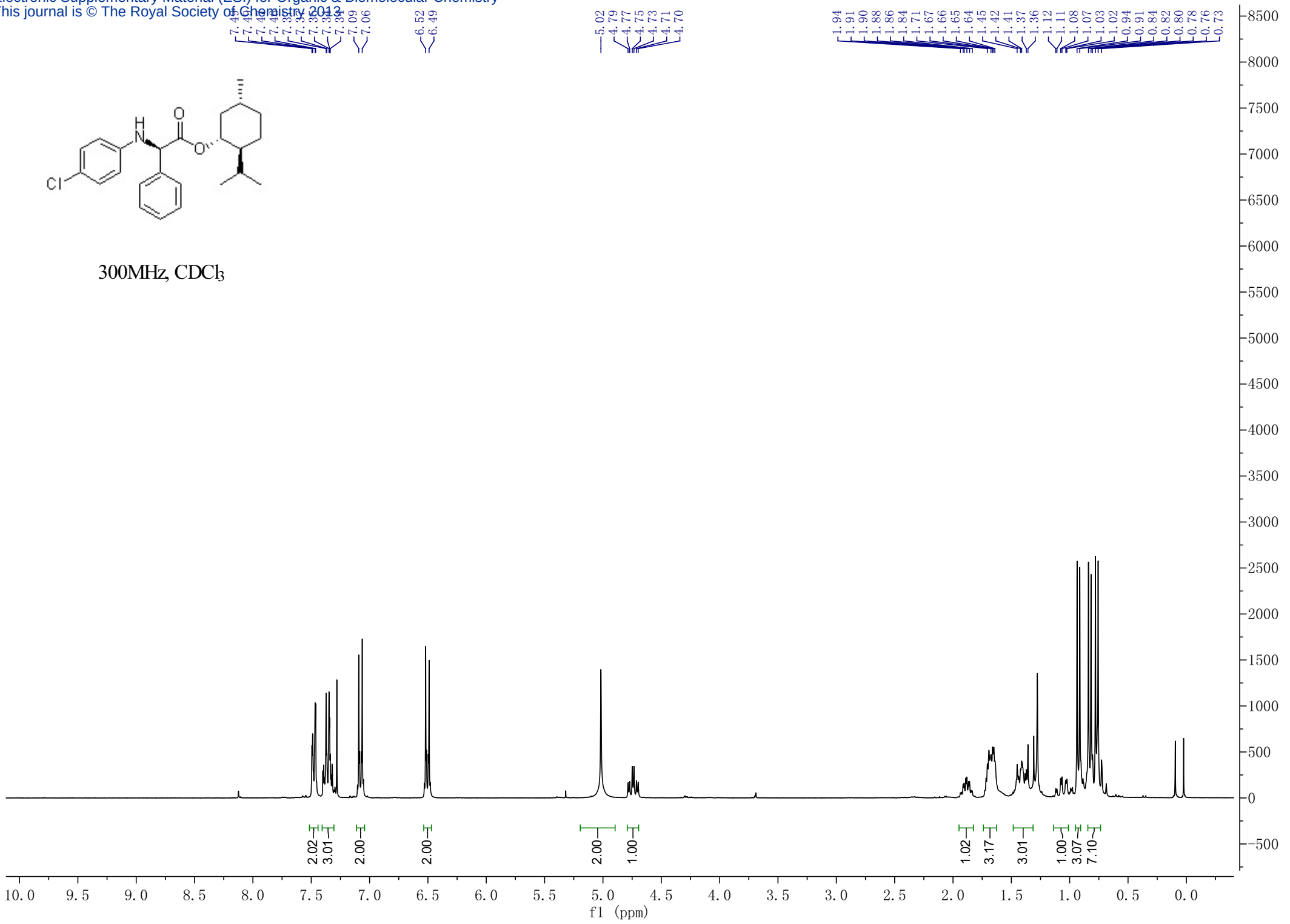


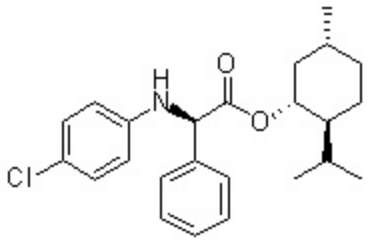


300MHz, $CDCl_3$



300MHz, $CDCl_3$



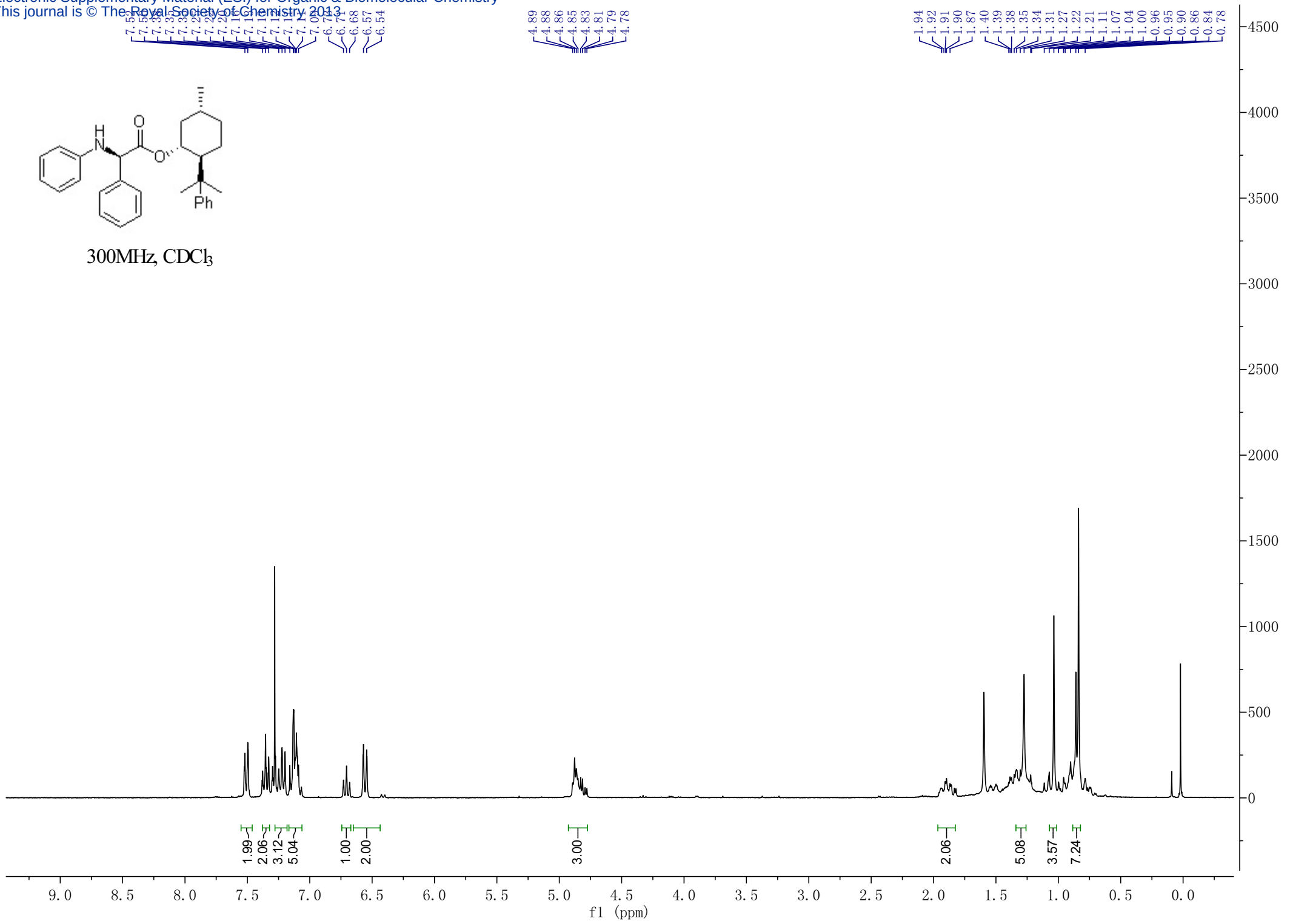


75 MHz, $CDCl_3$

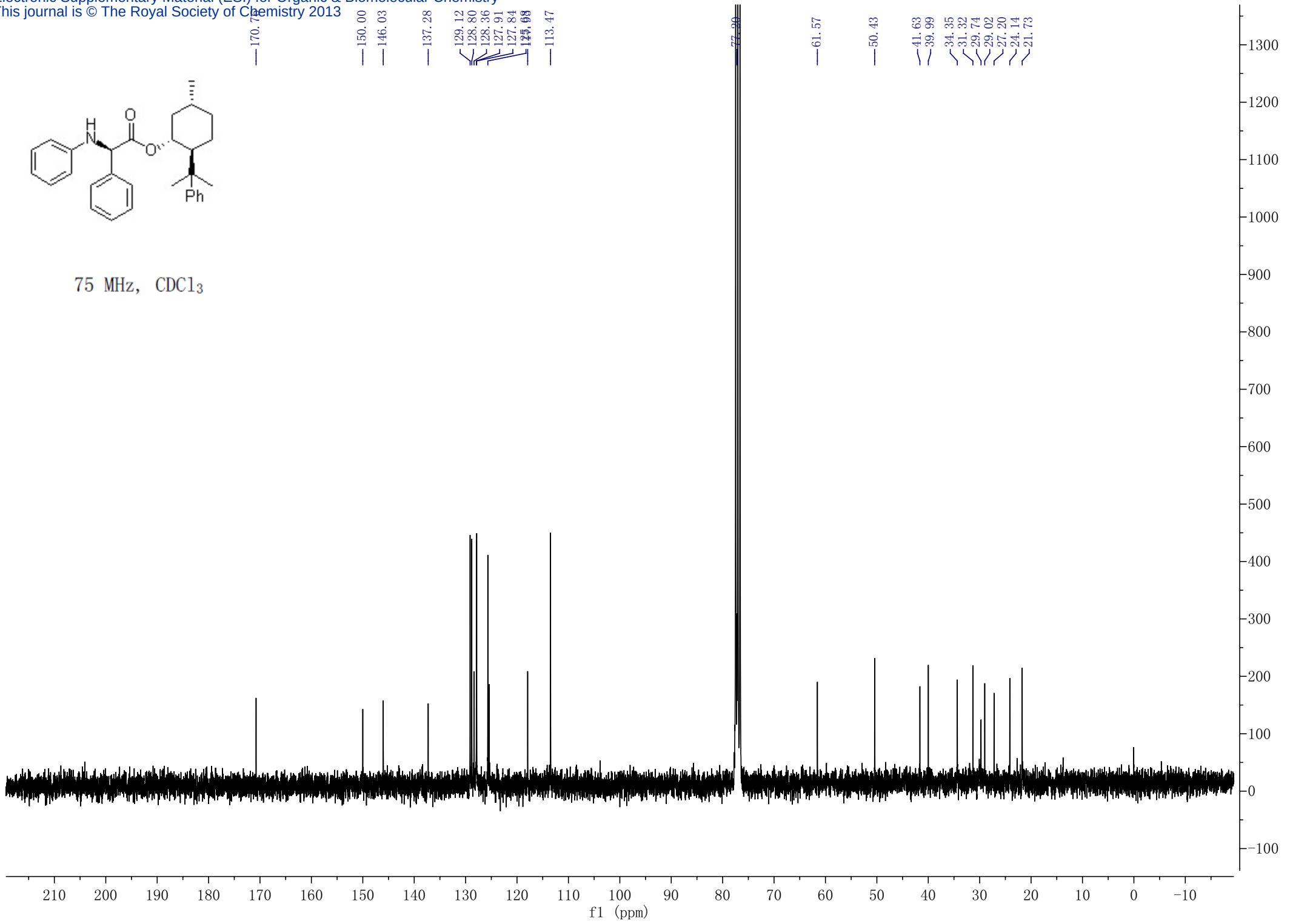
171.12
144.50
137.19
129.05
128.81
128.30
127.07
122.60
114.54
78.03
60.77
46.86
39.93
34.05
31.28
26.28
23.25
21.91
20.78
16.22

f1 (ppm)

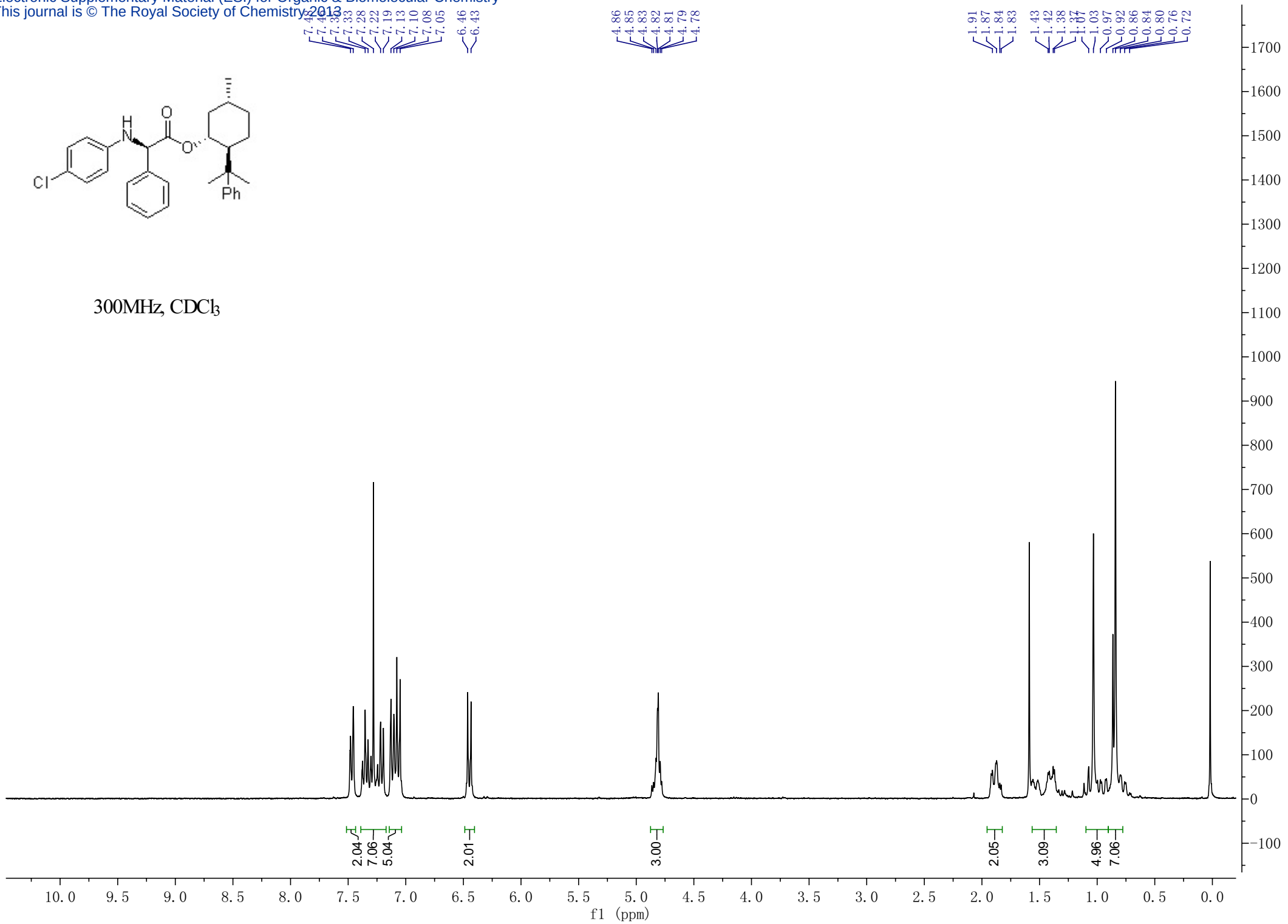
300MHz, $CDCl_3$

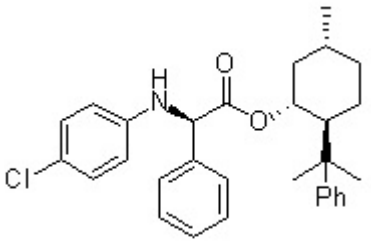


75 MHz, $CDCl_3$



300MHz, $CDCl_3$



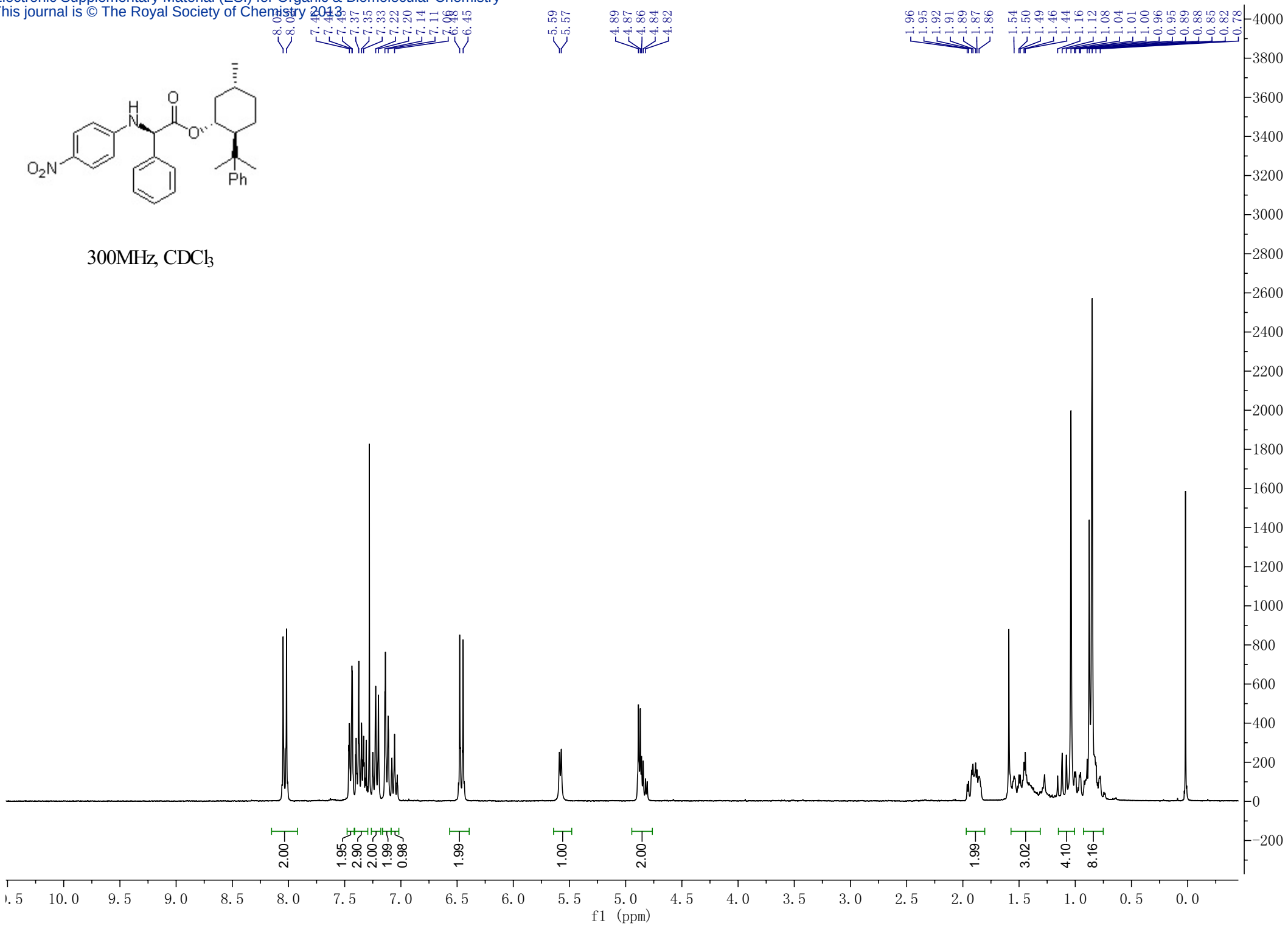


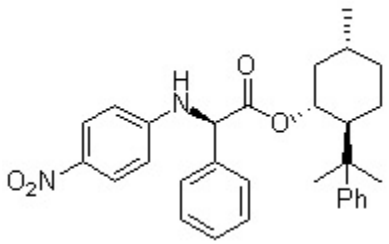
75 MHz, $CDCl_3$

170.38
150.05
144.42
136.80
128.94
128.87
128.52
127.91
127.76
125.64
125.45
114.64
99.99
77.24
61.53
50.39
41.62
39.93
34.32
31.33
28.55
27.14
24.54
21.73

f1 (ppm)

300MHz, $CDCl_3$

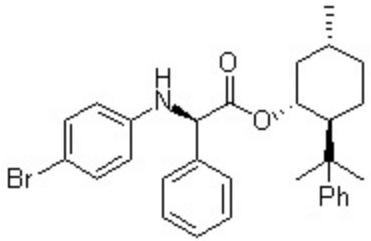




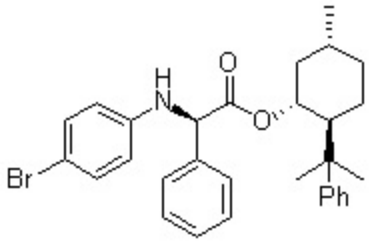
75 MHz, $CDCl_3$

169.29
150.82
150.02
138.67
135.77
129.13
128.93
127.95
127.57
126.09
125.61
125.52
112.22
77.96
60.77
50.35
41.61
39.86
34.26
31.37
27.92
27.05
25.11
21.71

f1 (ppm)



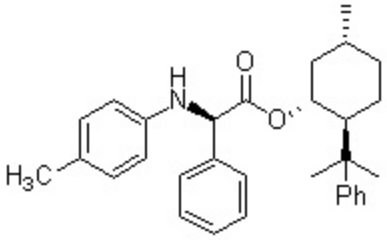
300MHz, $CDCl_3$



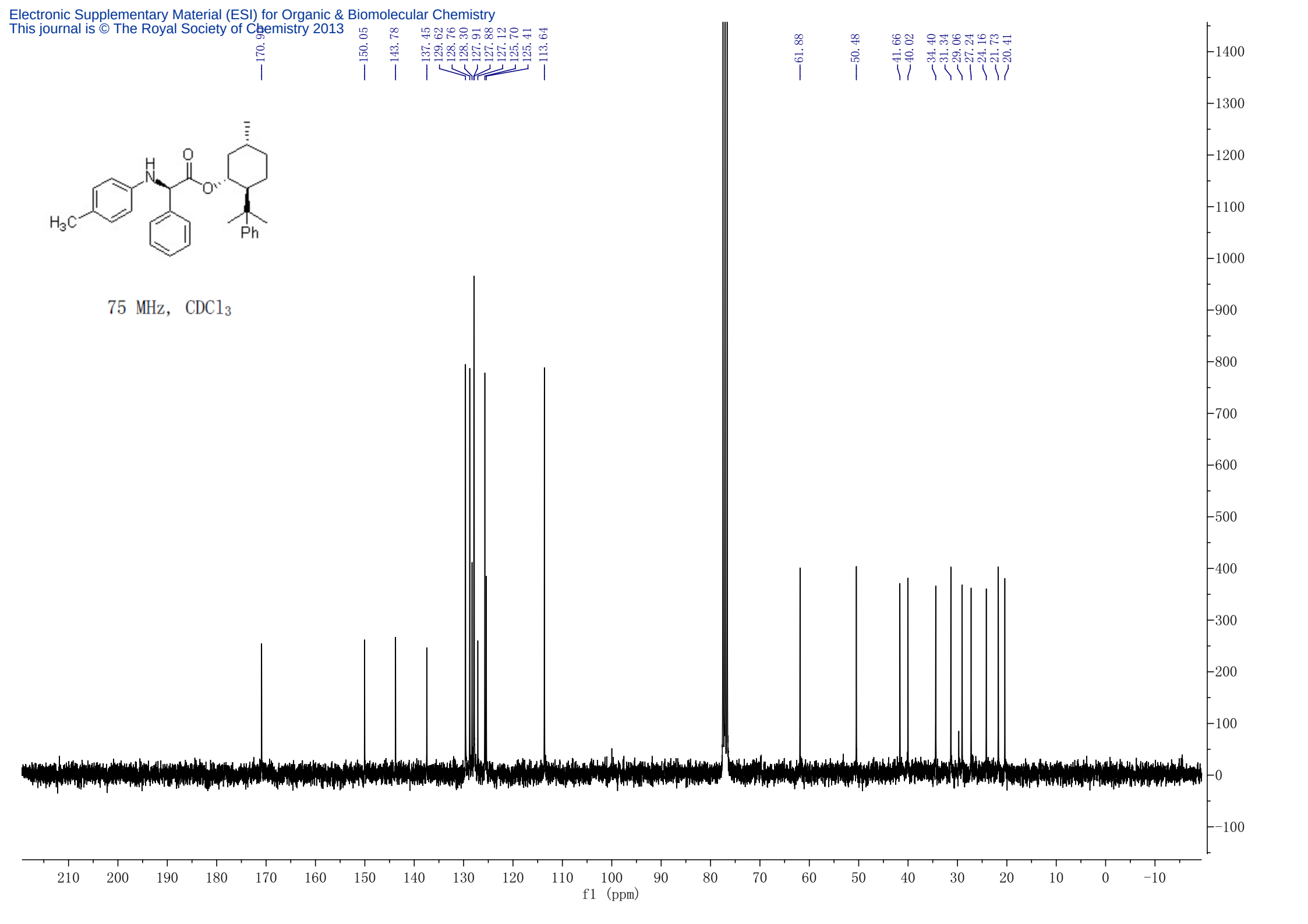
75 MHz, $CDCl_3$

170.38
150.05
144.87
136.77
131.80
128.87
128.52
127.91
127.74
125.64
125.45
115.11
109.62
77.36
61.41
50.40
41.63
39.93
34.33
31.33
28.51
27.13
24.58
21.73

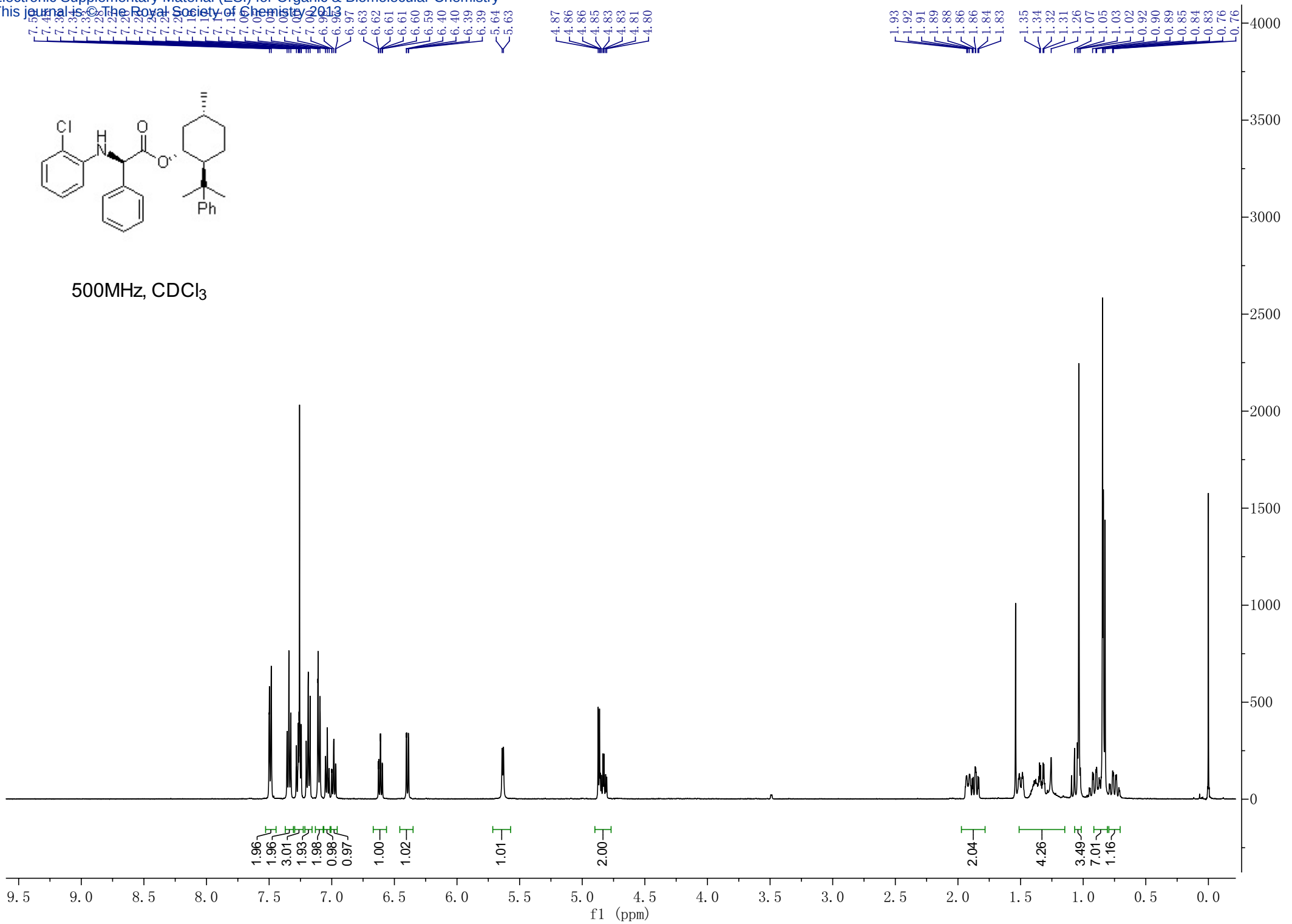
f1 (ppm)

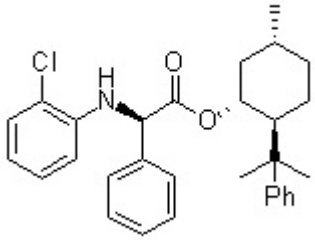


500MHz, $CDCl_3$



500MHz, $CDCl_3$



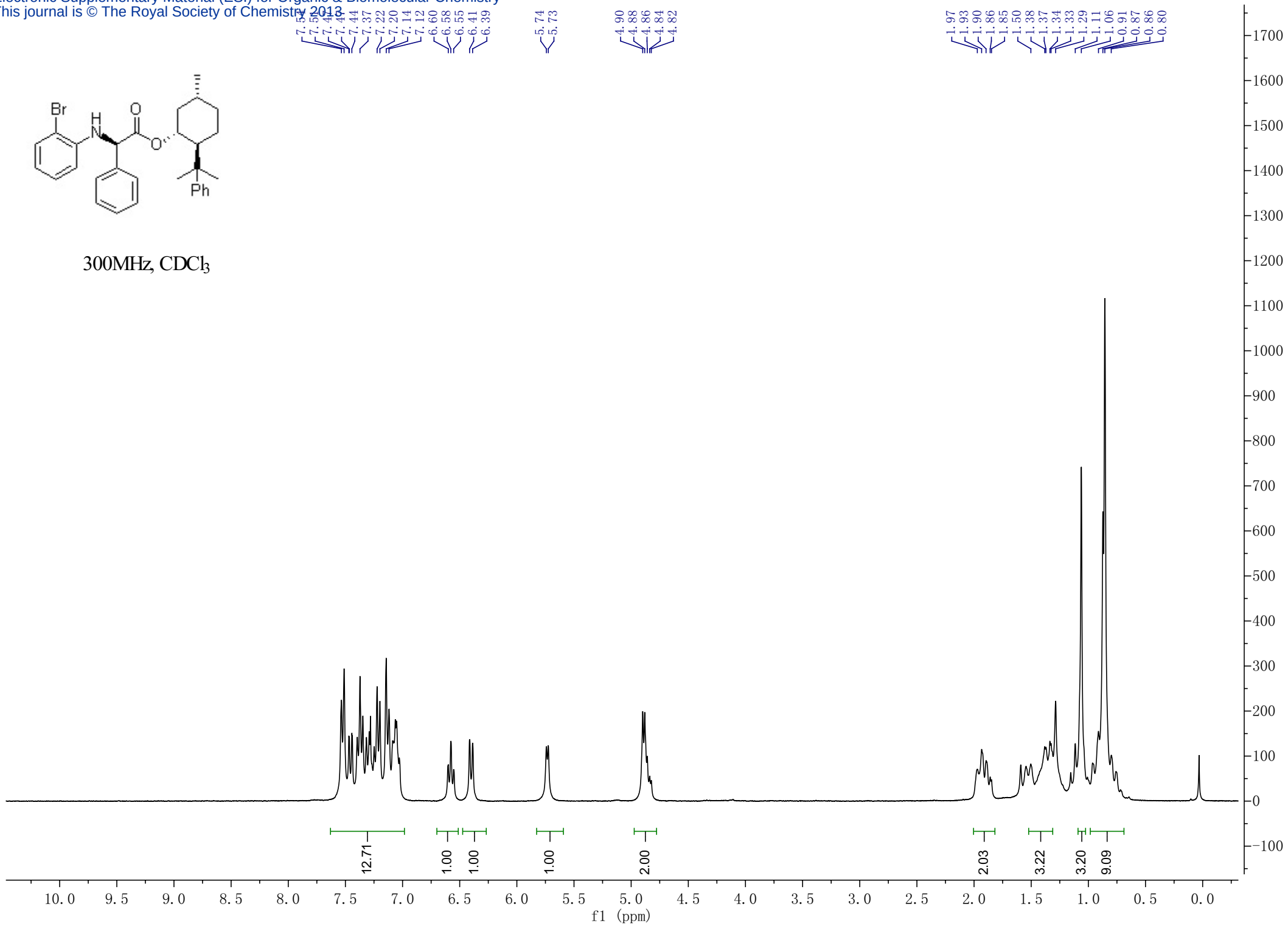


125 MHz, $CDCl_3$

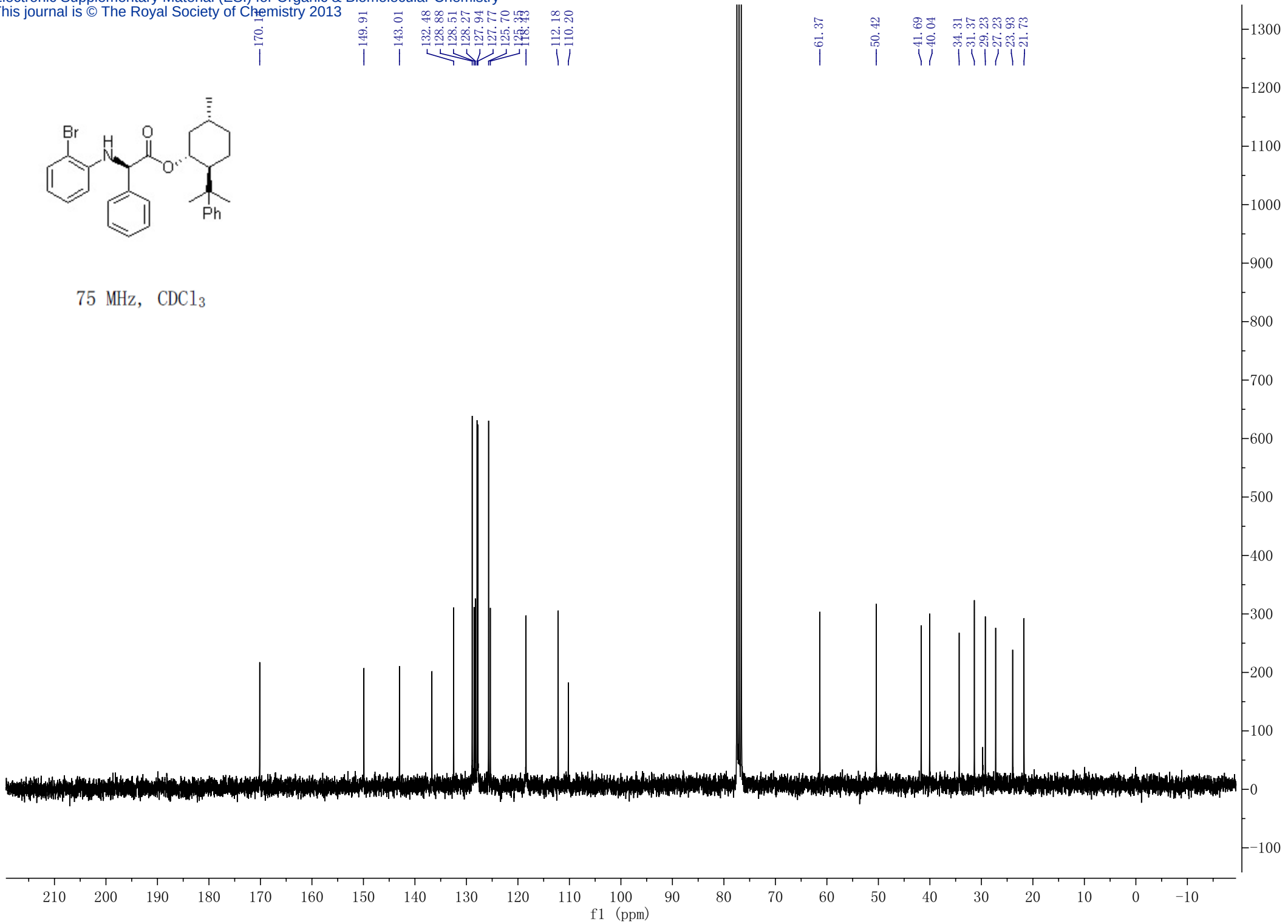
170.12
149.90
142.06
136.77
129.20
128.86
127.91
127.75
125.68
119.71
117.92
112.10
77.43
61.25
50.46
41.67
40.04
34.33
31.36
29.22
27.24
23.95
21.69

f1 (ppm)

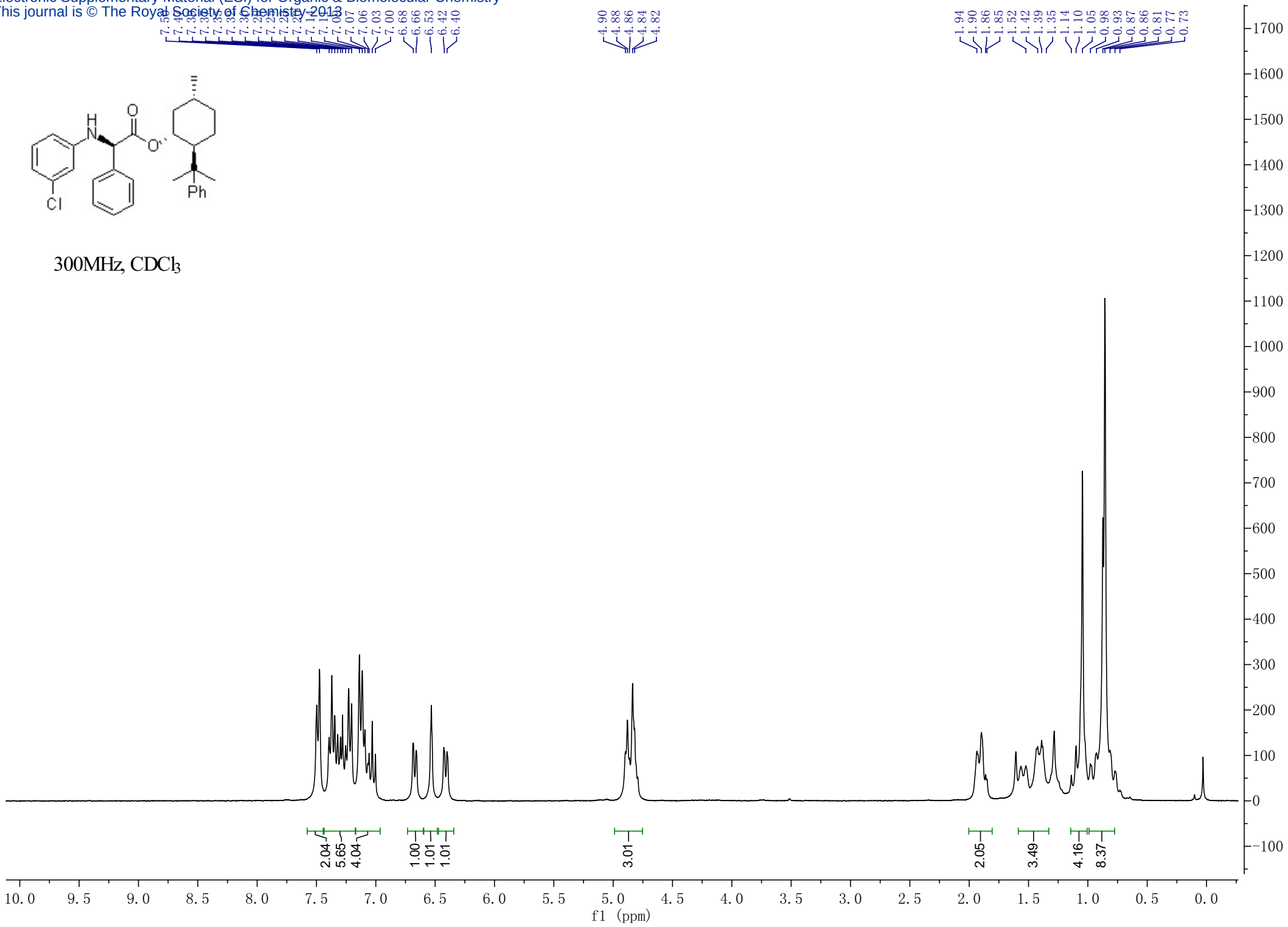
300MHz, $CDCl_3$

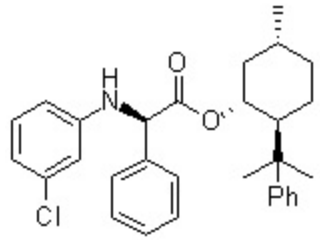


75 MHz, $CDCl_3$



300MHz, $CDCl_3$



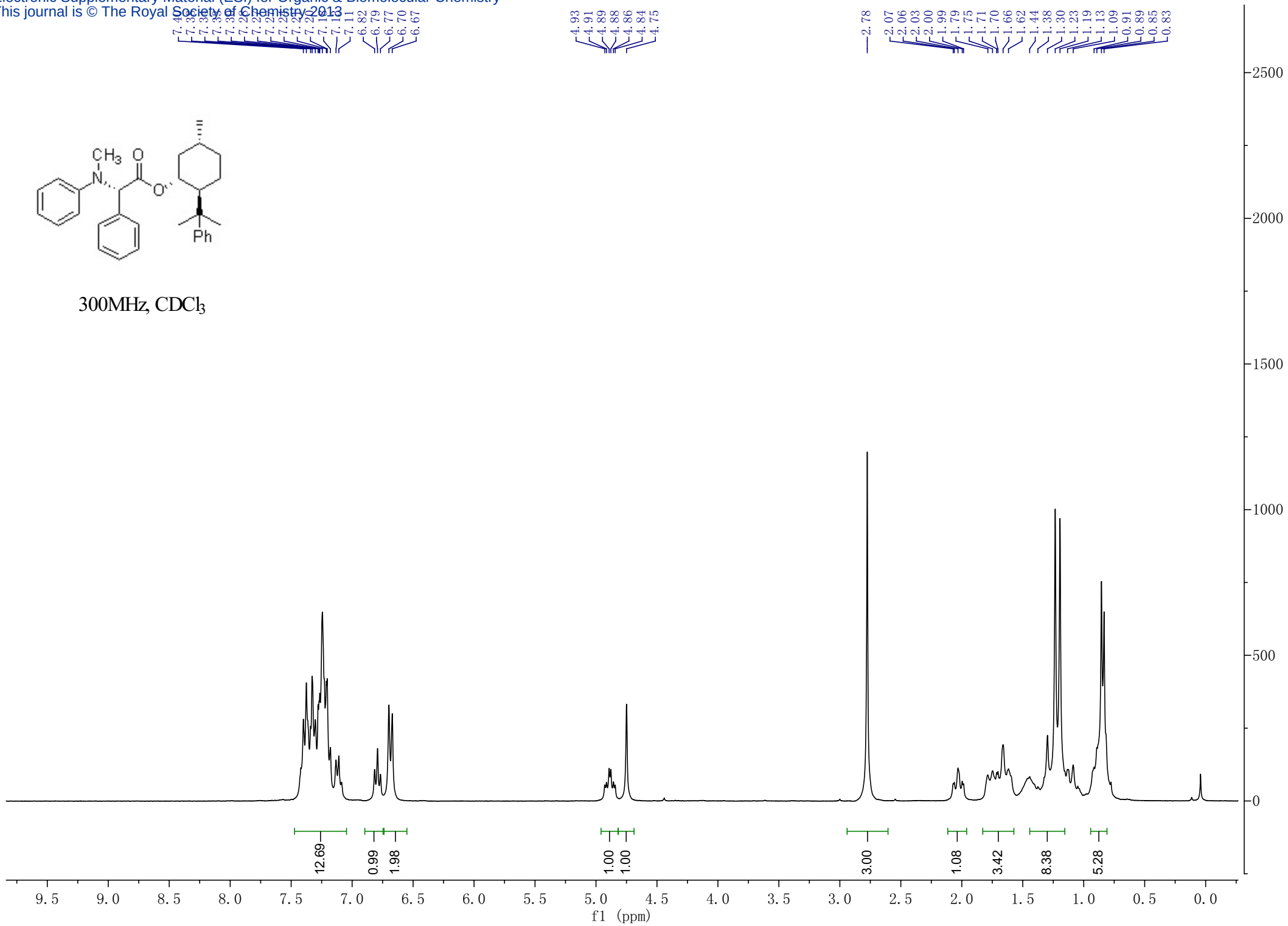


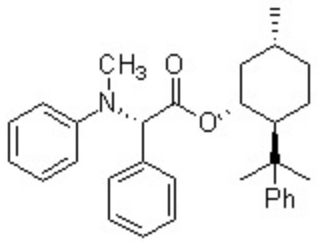
75 MHz, $CDCl_3$

170.34
150.01
147.08
136.64
134.79
130.06
128.88
128.55
127.90
127.74
125.63
125.41
117.82
113.26
111.77
61.29
50.38
41.62
39.93
34.32
31.31
28.58
27.13
24.52
21.68

f1 (ppm)

300MHz, $CDCl_3$



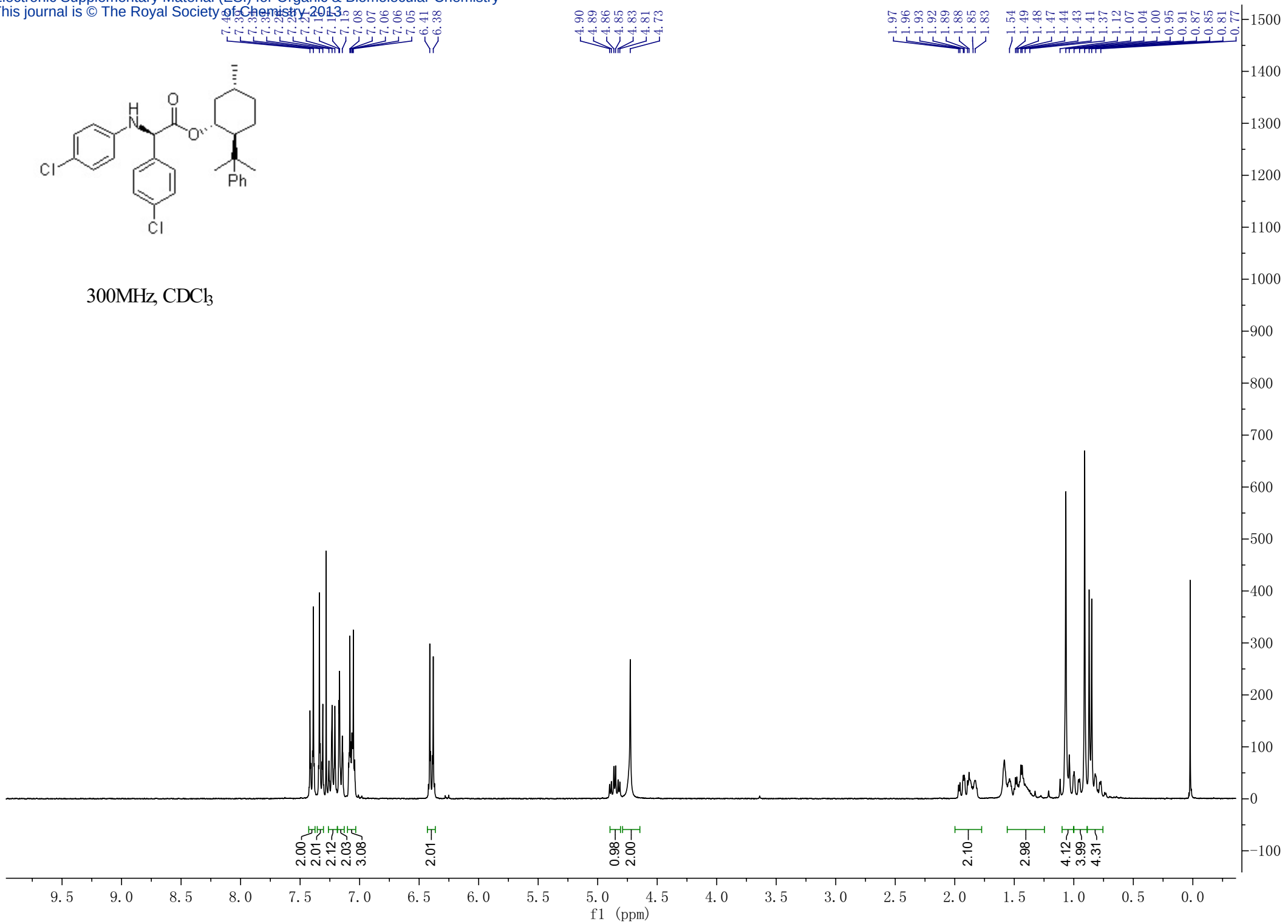


75 MHz, $CDCl_3$

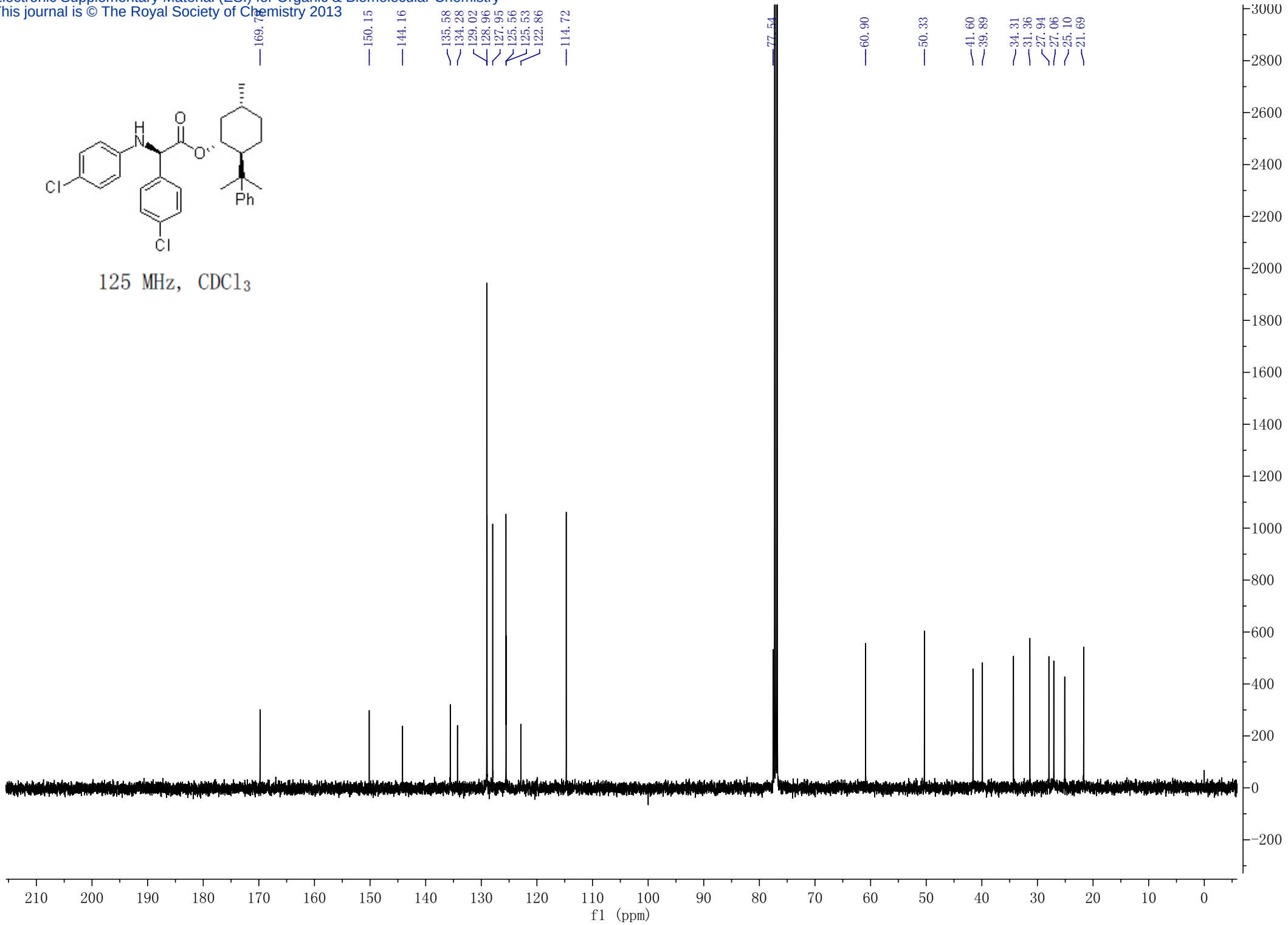
170.38
151.64
149.46
135.52
128.95
128.38
128.29
127.96
127.71
113.52
75.61
65.76
50.33
41.42
39.66
35.21
34.48
31.24
27.66
26.61
25.07
21.77

f1 (ppm)

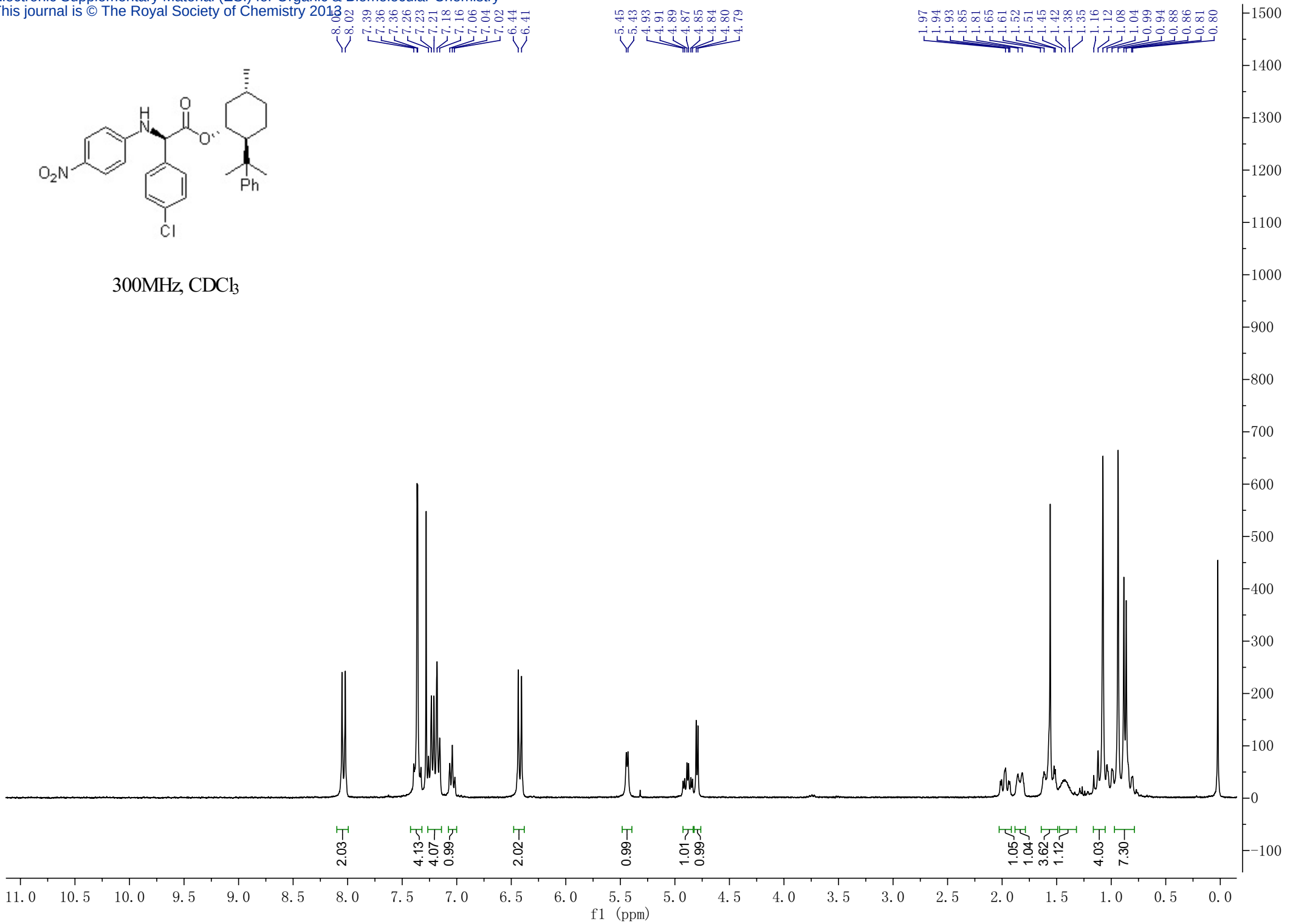
300MHz, $CDCl_3$

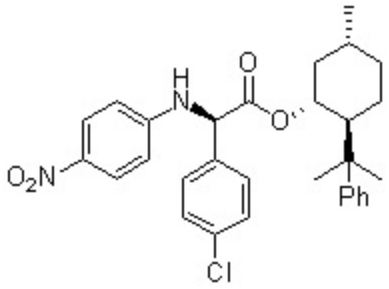


125 MHz, $CDCl_3$



300MHz, $CDCl_3$



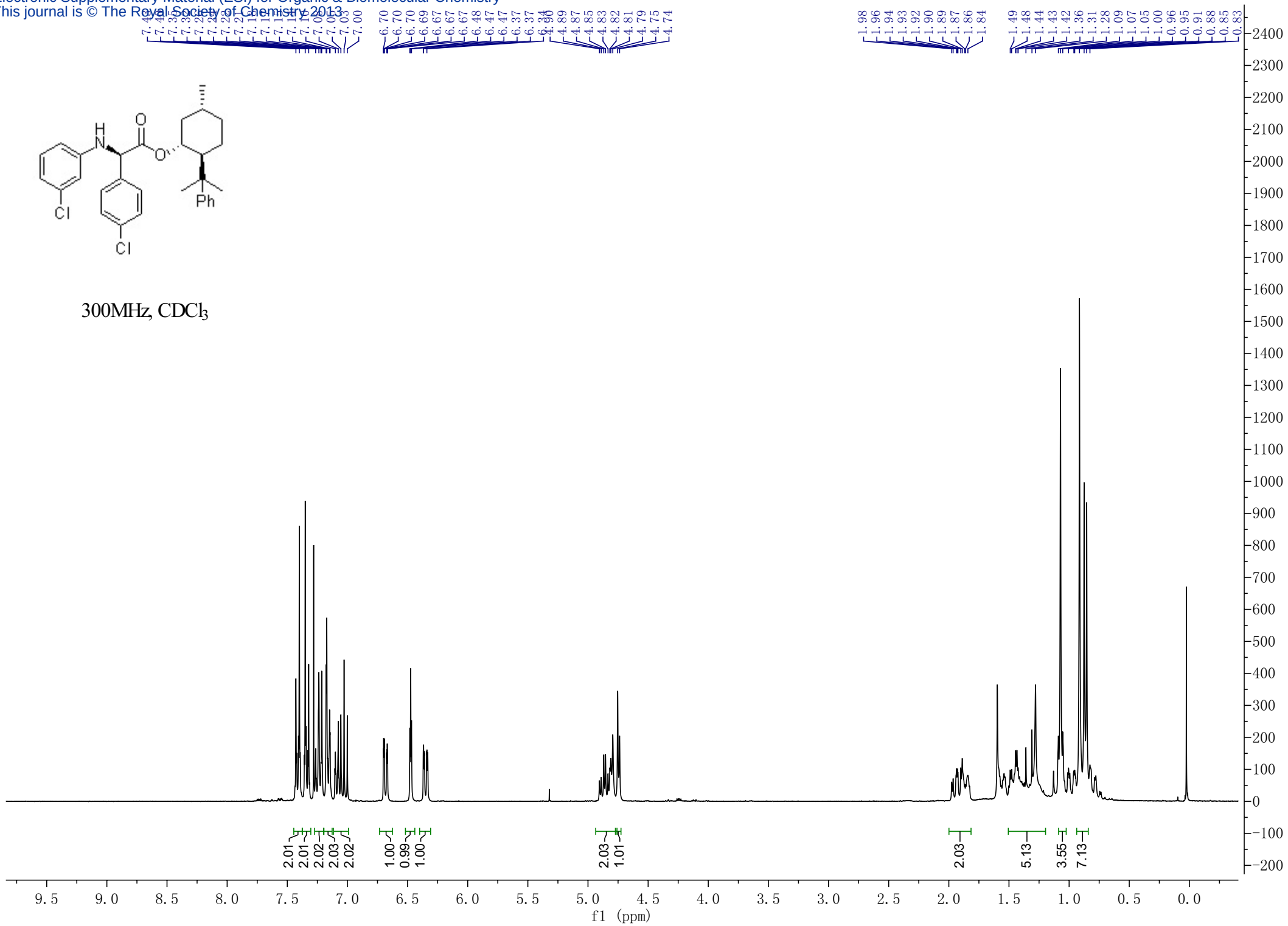


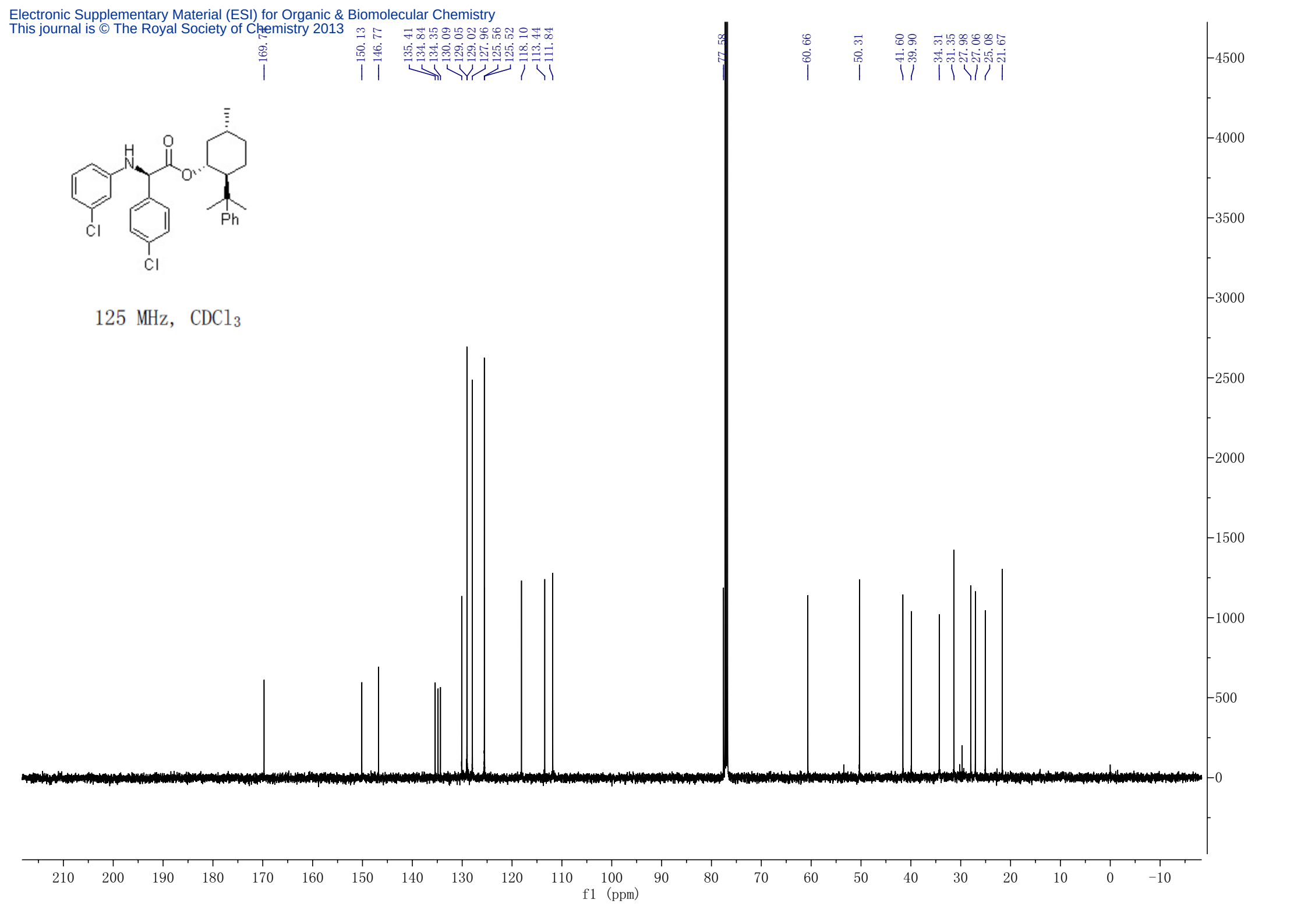
125 MHz, $CDCl_3$

168.76
150.51
150.17
134.82
134.47
129.31
128.82
128.00
126.05
125.59
125.54
112.34
78.28
60.15
50.27
41.57
39.83
34.25
31.40
27.30
26.99
25.67
21.69

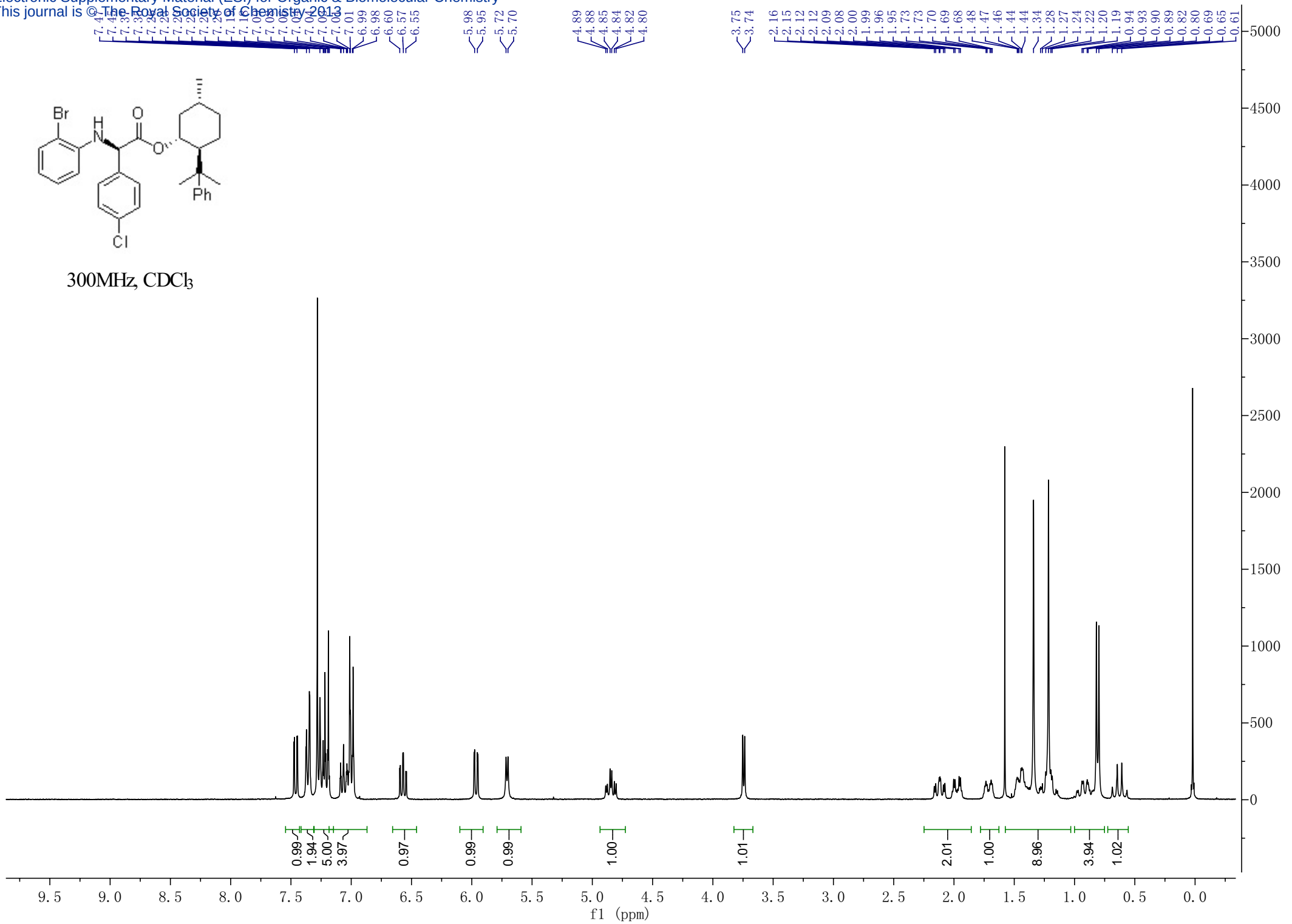
f1 (ppm)

300MHz, $CDCl_3$

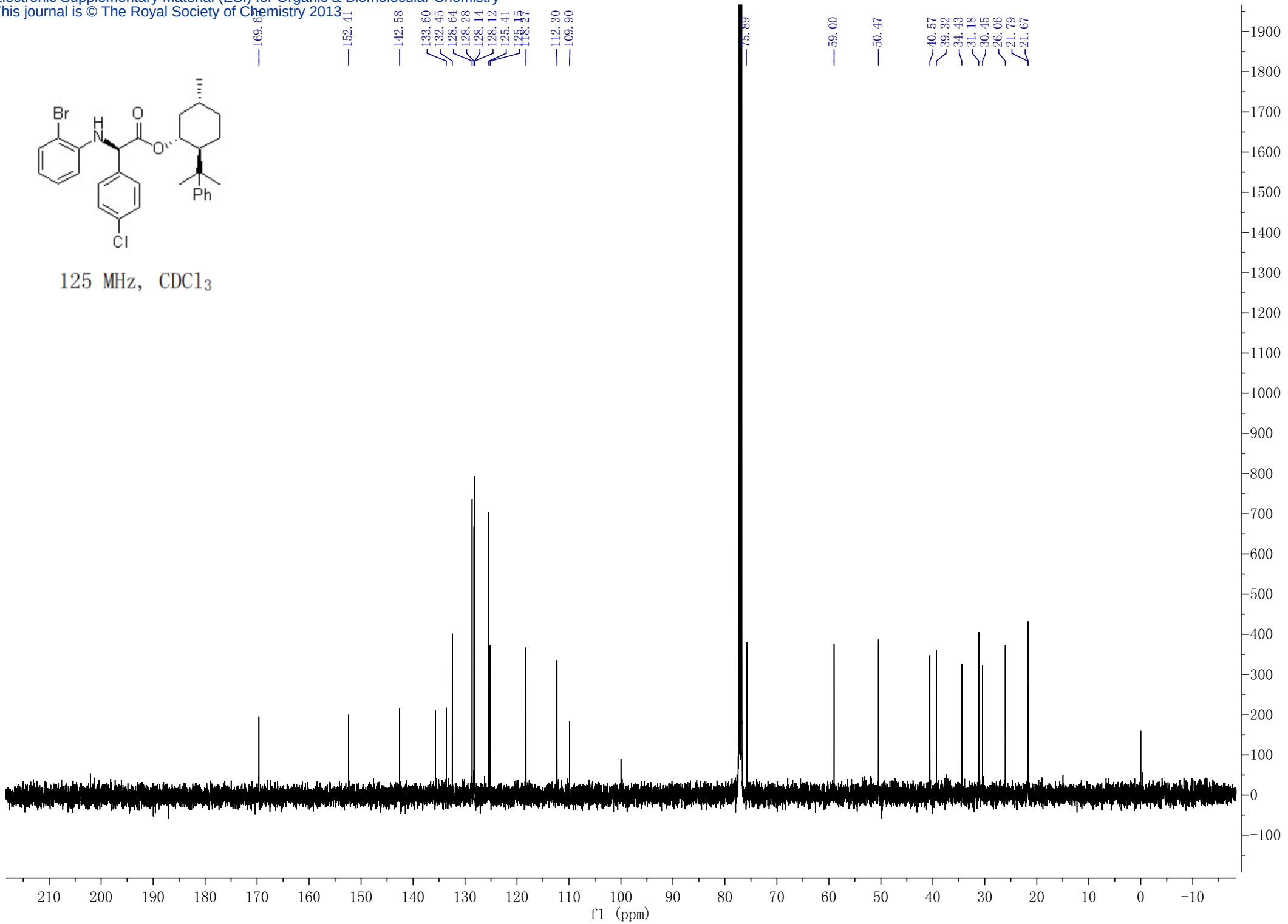


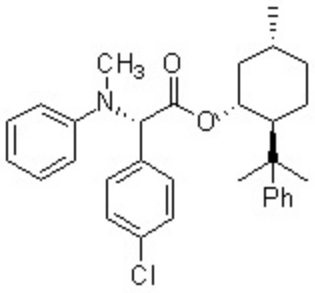


300MHz, $CDCl_3$

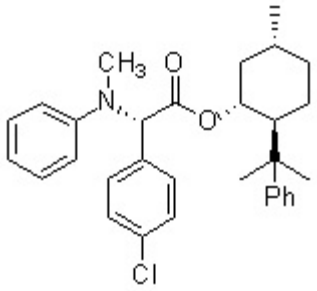


125 MHz, $CDCl_3$





300MHz, $CDCl_3$

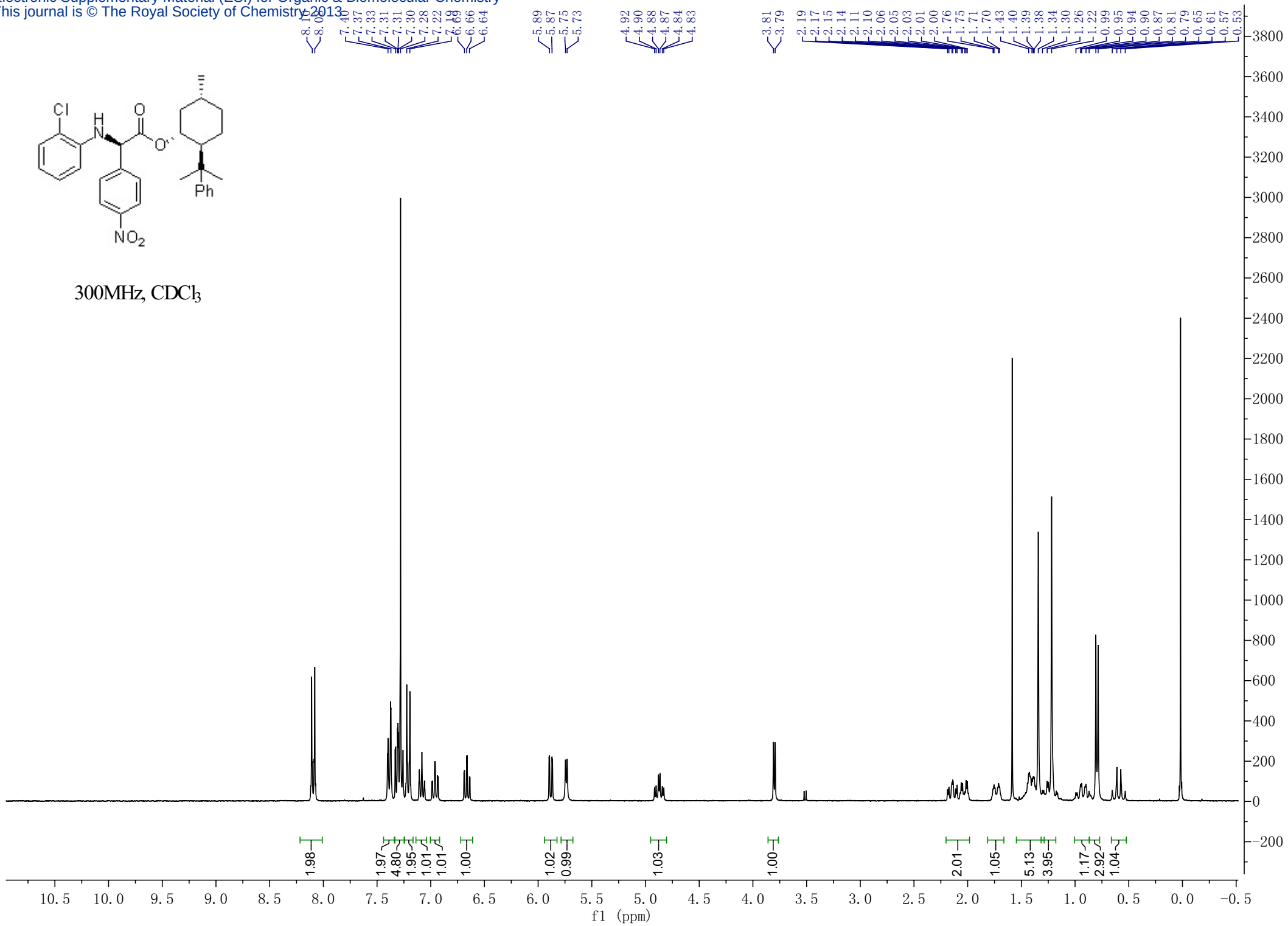


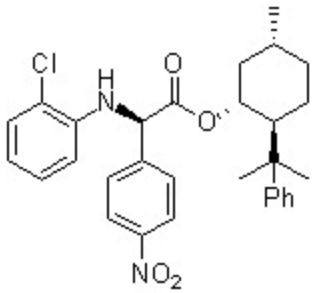
125 MHz, $CDCl_3$

169.72
151.81
149.15
134.16
133.50
129.65
128.93
128.39
127.96
125.33
125.04
117.98
113.73
75.47
65.31
50.20
41.37
39.55
35.40
34.42
31.20
28.55
26.42
24.11
21.72

f1 (ppm)

300MHz, $CDCl_3$



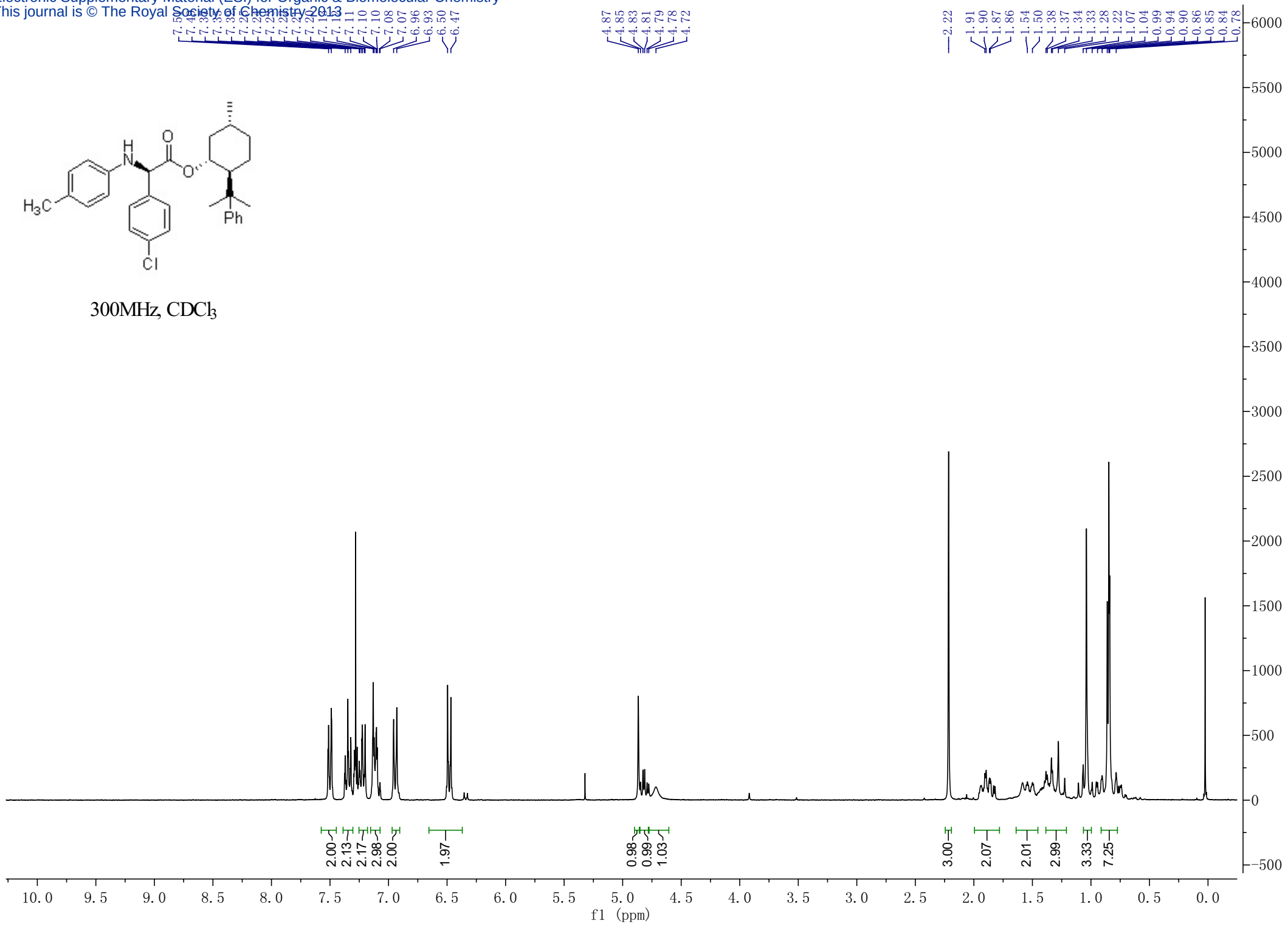


125 MHz, $CDCl_3$

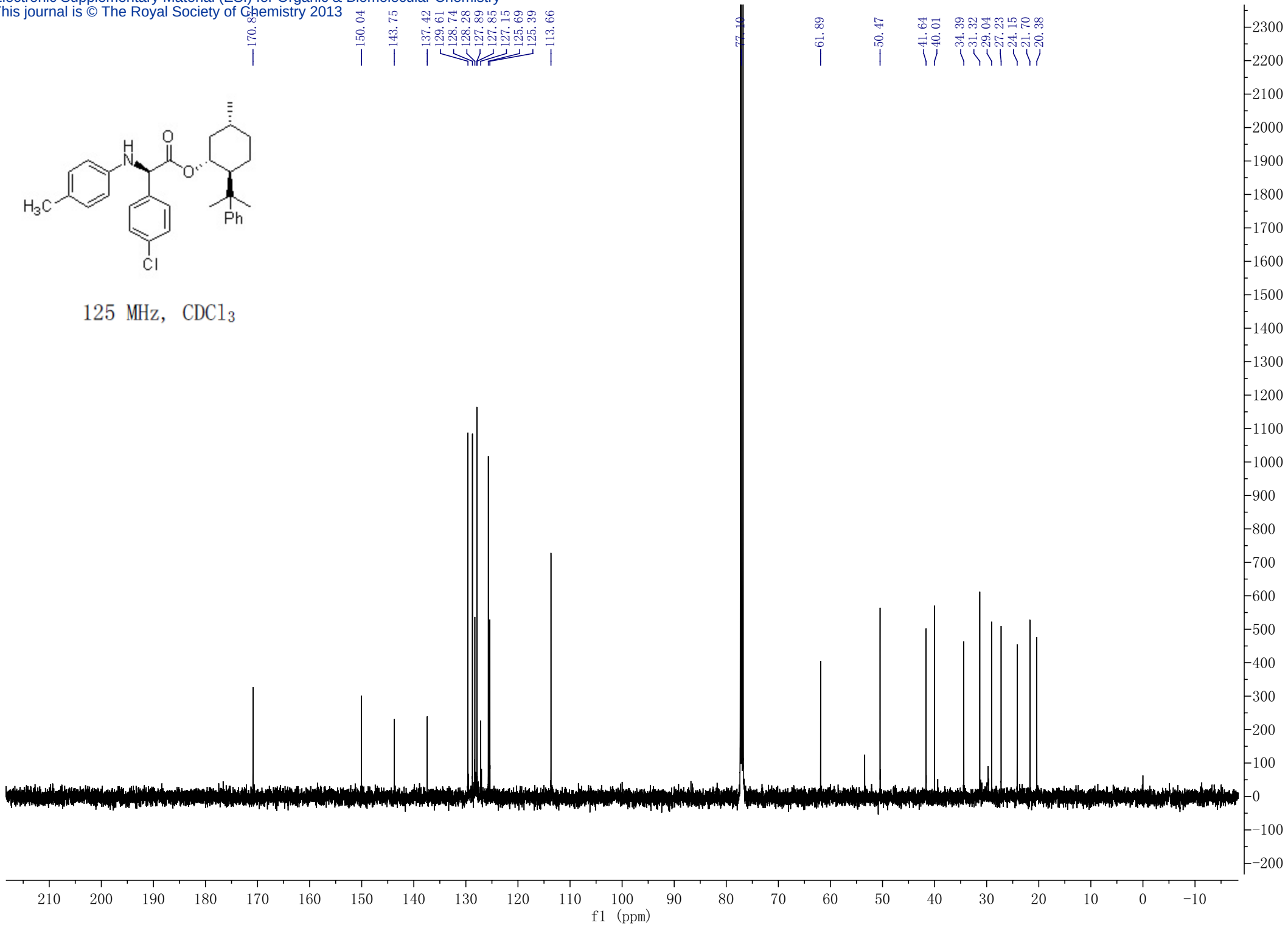
168.62
152.64
144.81
141.24
129.38
128.19
127.90
127.53
125.47
125.23
123.69
118.26
112.05
78.19
59.09
50.49
40.63
39.29
34.37
31.17
30.92
25.97
21.64
21.20

f1 (ppm)

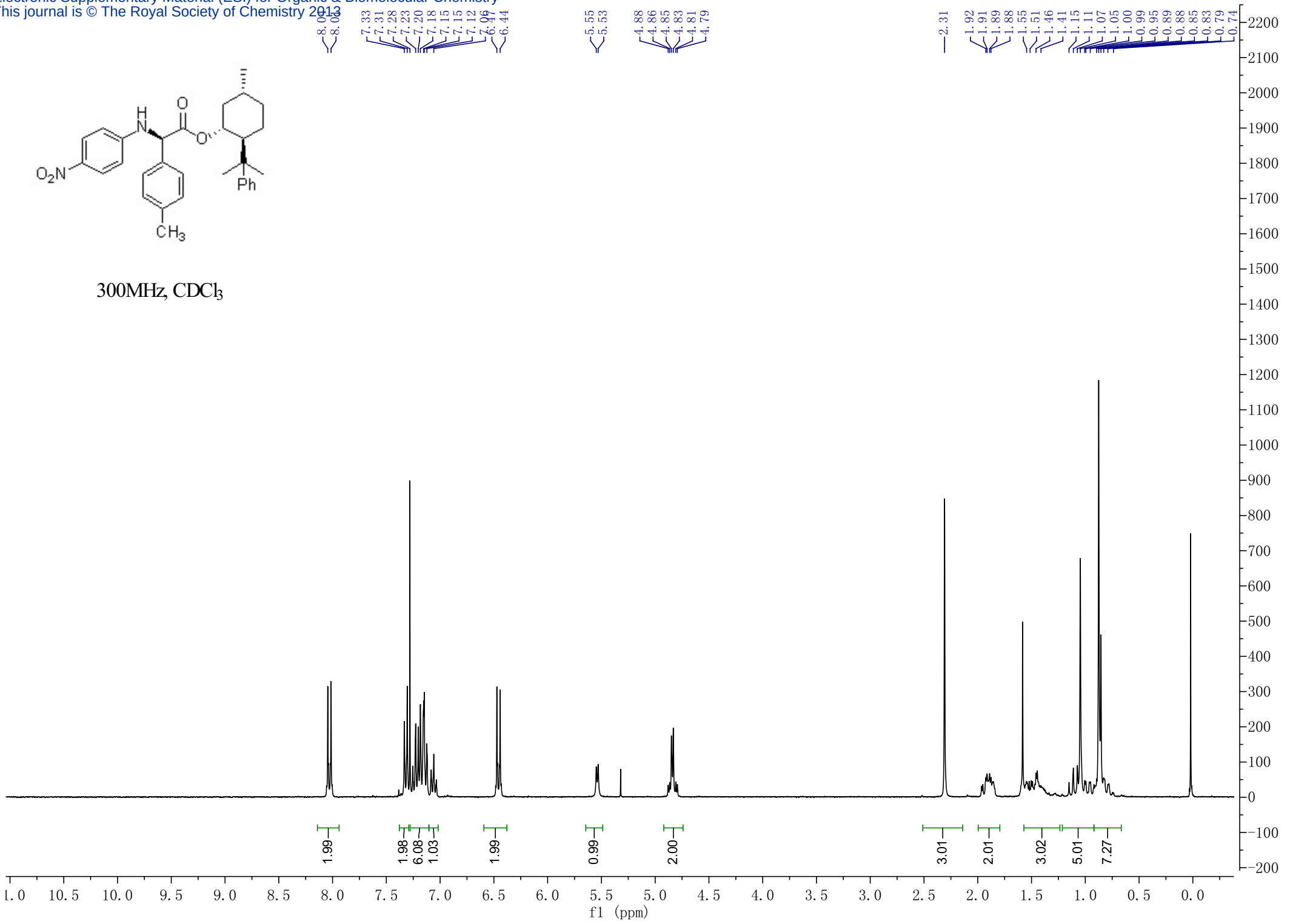
300MHz, $CDCl_3$

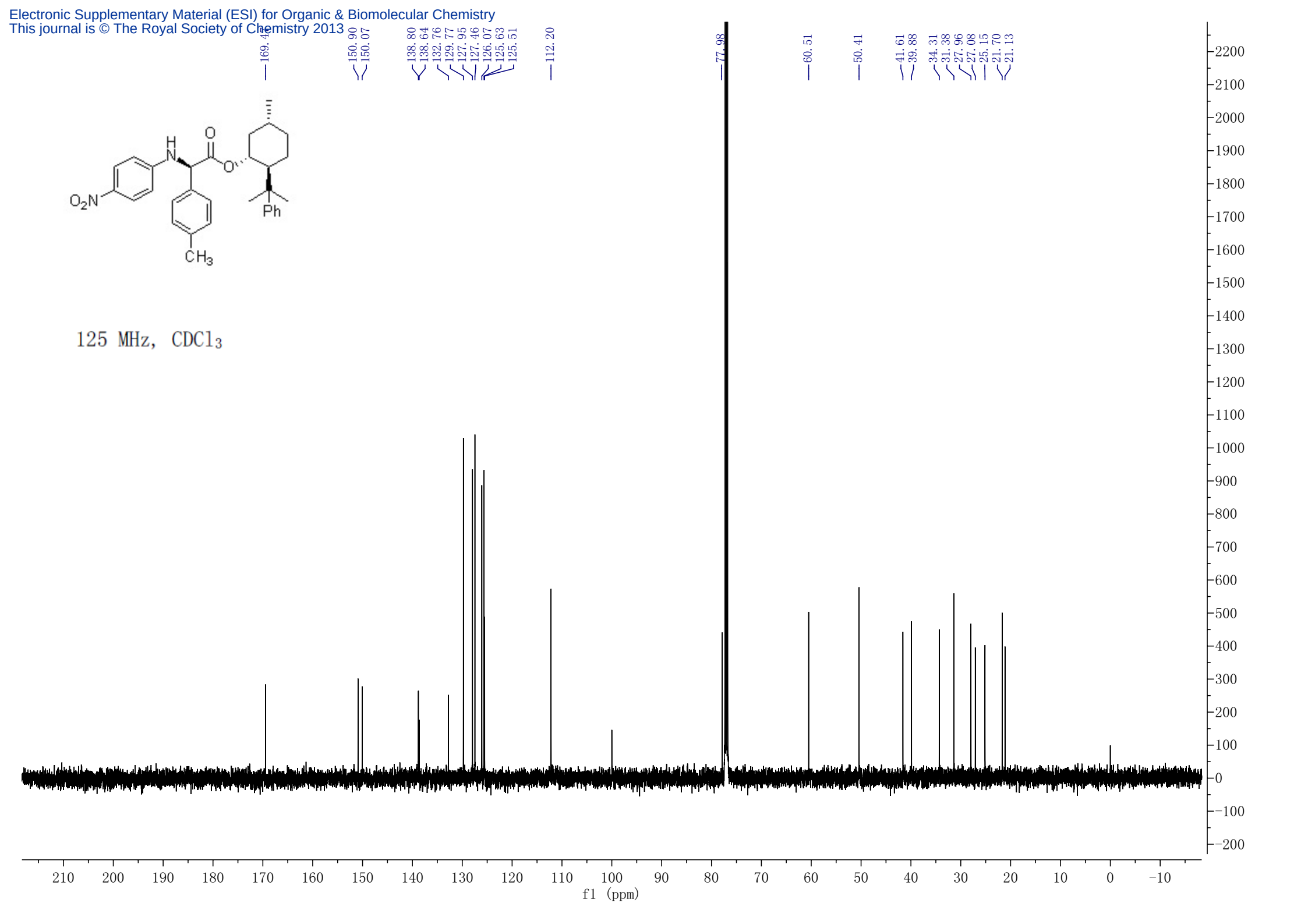


125 MHz, $CDCl_3$



300MHz, $CDCl_3$





300MHz, $CDCl_3$