

Copper-Catalyzed Annulation of α -Substituted Diazoacetates with 2-Ethynylanilines: The Direct Synthesis of C2-Functionalized Indoles

Gang Liu, Guangyang Xu, Jian Li, Dong Ding and Jiangtao Sun*

School of Pharmaceutical Engineering & Life Science, Changzhou University,

Changzhou 213164, P. R. 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. ^1H NMR and ^{13}C NMR spectra were reported on a Bruker 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 Agilent G6230A mass spectrometer.

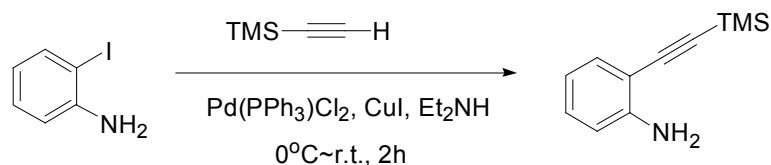
Solid and liquid anilines were purchased from Aladdin, and they were sublimed or distilled before use.

II A) Preparation of the diazoacetates¹

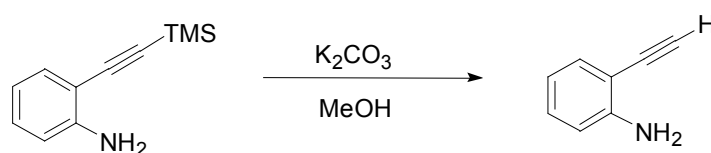
All α -diazoacetates were prepared by the same procedure in the literature.

B) Preparation of the 2-ethynylaniline substrates

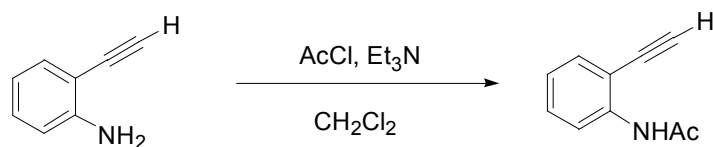
The following synthesis procedure is the general procedure used to prepare all substrates.



To a solution of 2-iodoaniline (3.30 g, 15.00 mmol), Pd(PPh₃)₂Cl₂ (210 mg, 0.30 mmol), CuI (114 mg, 0.60 mmol) in diethylamine (10 ml) was added a solution of trimethylsilylacetylene (2.94 g, 30.00 mmol) at 0 °C. The reaction was stirred at room temperature for about 2 hours. After the completion of the reaction, the mixture was quenched with sat.NH₄Cl and extracted with CH₂Cl₂ twice. The organic layers were combined, washed with brine once, dried over Na₂SO₄ and evaporated in vacuo. The residue was purified via column chromatography on silica gel (petroleum ether: ethyl acetate = 40: 1) to get the final product as oil (2.30 g, 81.0%).

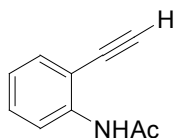


To a solution of 2-trimethylsilyl ethynyl-phenylamine (2.30 g, 12.16 mmol) and potassium carbonate (3.36 g, 24.33 mmol) in MeOH (15 mL) was stirred at room temperature for about 2 hours. The reaction was quenched with water and extracted with ethyl acetate three times. The organic layers were separated, combined, dried over Na₂SO₄ and evaporated in vacuo. The residue was purified via column chromatography on silica gel (petroleum ether: ethyl acetate = 20: 1) to give the final compound as oil (1.34 g, 94.1%).

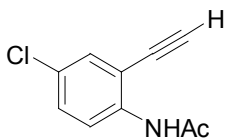


To a mixture of 2-ethynyl-phenylamine (1.34 g, 11.45 mmol), triethylamine (1.75 g, 17.30 mmol) in anhydrous dichloromethane (10 mL) was added acetyl chloride (0.99 g, 12.7 mmol) at room temperature for 1.5 hours. The reaction mixture was washed with water, extracted with ethyl acetate twice. The organic layers were separated, washed with brine twice, dried over Na₂SO₄ and evaporated in vacuo. The crude product was purified via column chromatography on silica gel (petroleum ether: ethyl acetate = 10: 1) to get the final amide as a white solid (1.60 g, 88.0%).

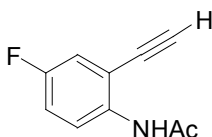
Data for the substrates



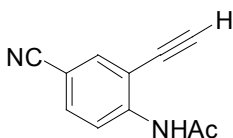
N-(2-Ethynylphenyl)-acetamide²: Yield: 63.5%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.39 (d, *J* = 8.0 Hz, 1H), 7.91 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.03 (t, *J* = 8.0 Hz, 1H), 3.50 (s, 1H), 2.22 (s, 3H);



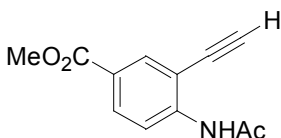
N-(4-Chloro-2-ethynylphenyl)-acetamide: Yield: 71.2%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.38 (d, *J* = 8.0 Hz, 1H), 7.84 (s, 1H), 7.42 (d, 1H), 7.33-7.30 (m, 1H), 3.55 (s, 1H), 2.23 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 168.3, 138.3, 131.6, 130.3, 128.1, 120.6, 112.0, 85.4, 78.0, 24.9;



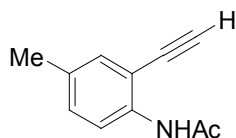
N-(4-Fluoro-2-ethynylphenyl)-acetamide³: Yield: 50.4%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.38-8.35 (m, 1H), 7.80 (s, 1H), 7.16-7.13 (m, 1H), 7.10-7.05 (m, 1H), 3.54 (s, 1H), 2.22 (s, 3H).



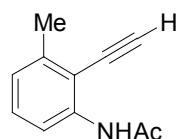
N-(4-Cyano-2-ethynylphenyl)-acetamide: Yield: 48.3%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.61 (d, *J* = 8.0 Hz, 1H), 8.05 (s, 1H), 7.74 (d, *J* = 4.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 3.63 (s, 1H), 2.27 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 168.6, 143.1, 135.9, 133.9, 119.4, 117.9, 111.2, 106.8, 100.0, 86.6, 25.0.



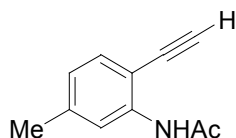
N-(4-Carboxylic acid methyl ester-2-ethynylphenyl)-acetamide: Yield: 62.5%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.52 (d, *J* = 8.0 Hz, 1H), 8.15 (d, 1H), 8.07 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 3.90 (s, 3H), 3.56 (s, 1H), 2.26 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 168.5, 165.8, 143.2, 133.8, 131.7, 124.9, 118.5, 110.3, 85.2, 78.3, 52.2, 25.0.



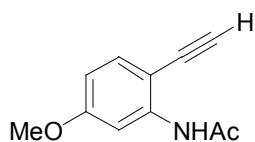
***N*-(4-Methyl-2-ethynyl-phenyl)-acetamide³**: Yield: 51.8%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.26 (d, *J* = 8.0 Hz, 1H), 7.82 (s, 1H), 7.26 (s, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 3.47 (s, 3H), 2.28 (s, 3H), 2.21 (s, 3H).



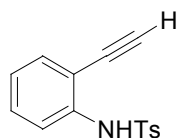
***N*-(3-Methyl-2-ethynyl-phenyl)-acetamide**: Yield: 62.0%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.24 (d, 1H), 7.96 (s, 1H), 7.26-7.22 (m, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 3.73 (s, 1H), 2.44 (s, 3H), 2.22 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 168.3, 141.2, 139.8, 129.5, 128.6, 124.5, 116.5, 88.4, 78.2, 25.0, 21.0.



***N*-(5-Methyl-2-ethynyl-phenyl)-acetamide**: Yield: 58%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.24 (s, 1H), 7.86 (s, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 3.46 (s, 1H), 2.36 (s, 3H), 2.22 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 168.3, 140.9, 139.5, 131.9, 124.3, 119.9, 107.6, 83.7, 79.5, 24.9, 22.0.



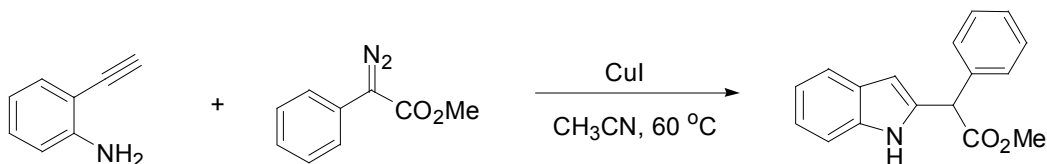
***N*-(5-Methoxy-2-ethynyl-phenyl)-acetamide**: Yield: 60%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.10 (s, 1H), 7.92 (s, 1H), 7.36 (d, *J* = 4.0 Hz, 1H), 6.59 (d, *J* = 4.0 Hz, 1H), 3.83 (s, 3H), 3.45 (s, 1H), 2.23 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 168.4, 161.1, 141.2, 133.1, 110.2, 104.3, 102.4, 83.2, 79.5, 55.5, 25.0.



***N*-(2-Ethynyl-phenyl)-4-methyl-benzenesulfonamide⁴**: Yield: 75%; ¹H NMR (400 MHz,

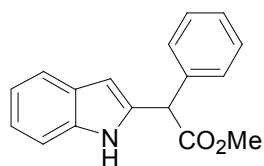
CDCl₃): δ (ppm) 7.69 (d, J = 8.0 Hz, 2H), 7.59 (d, J = 8.0 Hz, 1H), 7.35-7.20 (m, 5H), 7.03-6.99 (t, J = 8.0 Hz, 1H), 3.37 (s, 1H), 2.37 (s, 3H).

III General Procedure for the CuI catalyzed synthesis of C2-substituted indoles

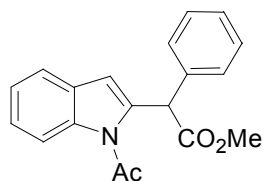


To a Schlenk tube was added 2-ethynyl-phenylamine (1.0 mmol), CuI (0.05 mmol) and CH₃CN (2 mL) under nitrogen atmosphere. Then the diazoacetate (1.0 mmol) in CH₃CN (1 mL) was added into the system and the whole solution was stirred at 60 °C for 4 hours. The completion of the reaction was monitored by TLC analysis. After cooling to room temperature, the reaction mixture was filtered through a pad of celite. The filtrate was concentrated under vacuum and the residue was purified by flash column chromatography (eluted with ethyl acetate/petroleum ether) to give the desired C2-substituted indole product.

Data for the product

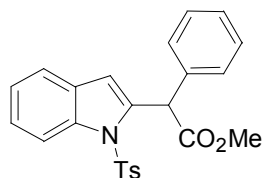


Methyl 2-(1H-indol-2-yl)-2-phenylacetate¹: Red oil (Flash column chromatography eluent: petroleum ether/ethyl acetate = 50/1), yield: 50%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.72 (br, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.32-7.25 (m, 6H), 7.15 (t, J = 8.0 Hz, 1H), 7.09-7.05 (m, 1H), 6.39 (s, 1H), 5.21 (s, 1H), 3.77 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 172.4, 137.4, 136.3, 134.5, 128.8, 128.0, 127.8, 121.9, 120.4, 119.9, 111.0, 102.2, 52.7, 50.6; HRMS (ESI) exact mass calcd. for C₁₇H₁₅NNaO₂ ([M + Na]⁺) 288.1178, found: 288.1175.

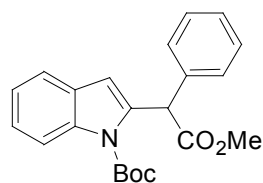


Methyl 2-(1-acetyl-1H-indol-2-yl)-2-phenylacetate: White solid (Flash column chromatography

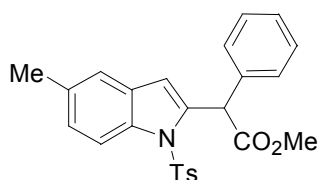
eluent: petroleum ether/ethyl acetate = 50/1), mp 99-101 °C, yield: 72%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.62 (d, *J* = 8.0 Hz, 1H), 7.41-7.35 (m, 6H), 7.29-7.25 (m, 1H), 7.19 (t, *J* = 8.0 Hz, 1H), 6.02 (s, 1H), 5.62 (s, 1H), 3.74 (s, 3H), 2.80 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 172.1, 170.8, 140.4, 136.7, 136.0, 129.6, 129.1, 128.9, 127.9, 124.2, 123.1, 121.4, 114.2, 112.6, 53.3, 52.4, 27.6; HRMS (ESI) exact mass calcd. for C₁₉H₁₇NNaO₃ ([M + Na]⁺) 330.1089, found: 330.1097.



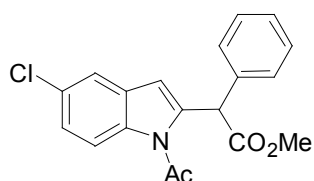
Methyl 2-(1-(toluene-4-sulfonyl)-1H-indol-2-yl)-2-phenylacetate: Colorless oil (Flash column chromatography eluent: petroleum ether/ethyl acetate = 50/1), yield: 70%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.02 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.37-7.32 (m, 6H), 7.25-7.22 (m, 1H), 7.16 (t, *J* = 6.0 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.33 (s, 1H), 5.80 (s, 1H), 3.74 (s, 3H), 2.28 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 171.8, 144.9, 138.6, 137.1, 136.6, 135.9, 129.8, 129.1, 129.0, 128.9, 128.0, 126.6, 124.8, 123.6, 121.0, 114.8, 112.9, 52.7, 51.1, 21.6; HRMS (ESI) exact mass calcd. for C₂₄H₂₁NNaO₄S ([M + Na]⁺) 442.1082, found: 442.1078.



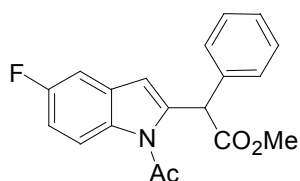
Methyl 2-(1-carboxylic acid tert-butyl ester-1H-indol-2-yl)-2-phenylacetate: Colorless oil (Flash column chromatography eluent: petroleum ether/ethyl acetate = 50/1), yield: 54%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.02 (d, *J* = 8.0 Hz, 1H), 7.41-7.34 (m, 6H), 7.27-7.23 (m, 1H), 7.16 (t, *J* = 6.0 Hz, 1H), 5.96 (s, 1H), 5.65 (s, 1H), 3.73 (s, 3H), 1.67 (s, 9H); ¹³C NMR (125 MHz, CDCl₃): δ 172.1, 150.9, 139.0, 136.9, 136.6, 129.2, 128.8, 128.6, 127.8, 124.1, 122.7, 120.5, 115.7, 111.2, 84.5, 52.7, 52.4, 28.2; HRMS (ESI) exact mass calcd. for C₂₂H₂₃NNaO₄ ([M + Na]⁺) 388.1508, found: 388.1513.



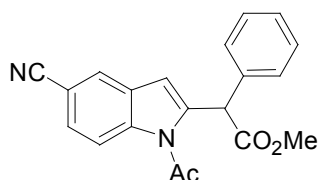
Methyl 2-(5-methyl-1-(toluene-4-sulfonyl)-1*H*-indol-2-yl)-2-phenylacetate: Colorless oil (Flash column chromatography eluent: petroleum ether/ethyl acetate = 40/1), yield: 73%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.89 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.35-7.20 (m, 5H), 7.14 (t, *J* = 10.0 Hz, 3H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.27 (s, 1H), 5.78 (s, 1H), 3.75 (s, 3H), 2.35 (s, 3H), 2.31 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 171.8, 144.7, 138.5, 136.5, 135.9, 135.3, 133.2, 129.7, 129.3, 129.0, 128.8, 127.9, 126.6, 126.1, 120.8, 114.5, 112.7, 52.7, 51.0, 21.5, 21.2; HRMS (ESI) exact mass calcd. for C₂₅H₂₃NNaO₄S ([M + Na]⁺) 456.1231, found: 456.1237.



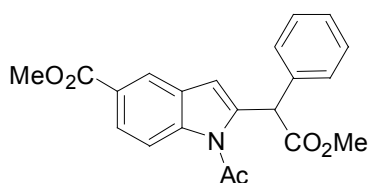
Methyl 2-(5-chloro-1-acetyl-1*H*-indol-2-yl)-2-phenylacetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 40/1), mp 112-114 °C, yield: 62%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.55 (d, *J* = 8.0 Hz, 1H), 7.43-7.34 (m, 6H), 7.25-7.22 (m, 1H), 5.96 (s, 1H), 5.59 (s, 1H), 3.74 (s, 3H), 2.80 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 171.9, 170.5, 141.9, 136.3, 134.4, 130.9, 129.1, 129.0, 128.8, 128.1, 124.2, 120.9, 115.1, 111.8, 53.3, 52.5, 27.5; HRMS (ESI) exact mass calcd. for C₁₉H₁₆ClNNaO₃ ([M + Na]⁺) 364.0701, found: m/z 364.0705.



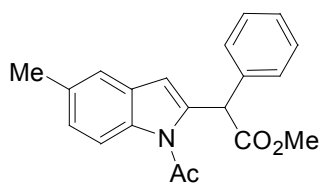
Methyl 2-(5-fluoro-1-acetyl-1*H*-indol-2-yl)-2-phenylacetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 40/1), mp 122-123 °C, yield: 55%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.58-7.55 (m, 1H), 7.43-7.38 (m, 3H), 7.36-7.34 (m, 2H), 7.08-7.05 (m, 1H), 7.03-6.98 (m, 1H), 5.98 (s, 1H), 5.59 (s, 1H), 3.74 (s, 3H), 2.80 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 172.0, 170.5, 160.2, 158.3, 142.1, 136.4, 132.4, 130.8, 130.7, 129.1, 129.0, 128.0, 115.1, 115.0, 112.3, 111.90, 111.7, 106.9, 106.8, 53.3, 52.5, 27.5; HRMS (ESI) exact mass calcd. for C₁₉H₁₆FNNaO₃ ([M + Na]⁺) 348.1005, found: 348.1002.



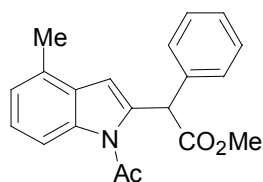
Methyl 2-(5-cyano-1-acetyl-1*H*-indol-2-yl)-2-phenylacetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 30/1), mp 129-131 °C, yield: 45%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.73 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.43-7.42 (m, 4H), 7.34 (d, *J* = 8.0 Hz, 1H), 6.08 (s, 1H), 5.60 (s, 1H), 3.75 (s, 3H), 2.84 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 171.7, 170.6, 142.9, 137.8, 136.0, 129.6, 129.1, 129.0, 128.3, 127.3, 125.9, 119.3, 114.8, 111.8, 106.6, 53.1, 52.6, 27.6; HRMS (ESI) exact mass calcd. for C₂₀H₁₆N₂NaO₃ ([M + Na]⁺) 355.1048, found: 355.1052.



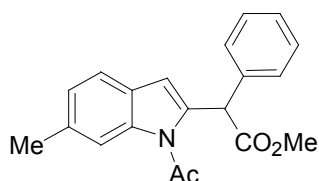
Methyl 2-(5-carboxylic acid methyl ester-1-acetyl-1*H*-indol-2-yl)-2-phenylacetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 30/1), mp 143-145 °C, yield: 45%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.13 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.42-7.35 (m, 5H), 6.09 (s, 1H), 5.61 (s, 1H), 3.91 (s, 3H), 3.75 (s, 3H), 2.85 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 172.0, 170.8, 167.0, 141.8, 138.6, 136.3, 129.4, 129.1, 129.0, 128.1, 125.5, 125.1, 123.5, 113.8, 112.7, 53.2, 52.5, 52.1, 27.6; HRMS (ESI) exact mass calcd. for C₂₁H₁₉NNaO₅ ([M + Na]⁺) 388.1147, found: 388.1153.



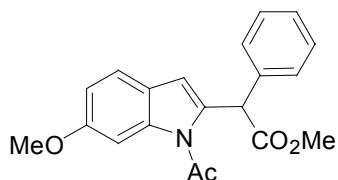
Methyl 2-(5-methyl-1-acetyl-1*H*-indol-2-yl)-2-phenylacetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 100/1), mp 160-161 °C, yield: 79%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.49 (d, *J* = 8.0 Hz, 1H), 7.42-7.35 (m, 5H), 7.19 (br, 1H), 7.10-7.07 (m, 1H), 5.95 (s, 1H), 5.60 (s, 1H), 3.74 (s, 3H), 2.79 (s, 3H), 2.38 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 172.2, 170.7, 140.4, 136.8, 134.3, 132.7, 129.9, 129.2, 128.9, 127.9, 125.5, 121.3, 113.9, 112.4, 53.4, 52.4, 27.5, 21.0; HRMS (ESI) exact mass calcd. for C₂₀H₁₉NNaO₃ ([M + Na]⁺) 344.1248, found: 344.1255.



Methyl 2-(4-methyl-1-acetyl-1H-indol-2-yl)-2-phenylacetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 40/1), mp 122-123 °C, yield: 82%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.47-7.36 (m, 6H), 7.18 (t, *J* = 8.0 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.06 (s, 1H), 5.63 (s, 1H), 3.74 (s, 3H), 2.81 (s, 3H), 2.36 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 172.3, 171.0, 139.6, 136.7, 135.9, 130.9, 129.2, 129.1, 128.9, 127.9, 124.2, 123.6, 111.7, 110.7, 53.3, 52.4, 27.6, 18.4; HRMS (ESI) exact mass calcd. for C₂₀H₁₉NNaO₃ ([M + Na]⁺) 344.1246, found: 344.1253.

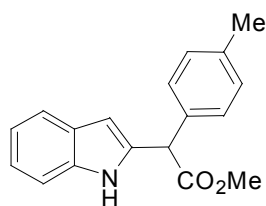


Methyl 2-(6-methyl-1-acetyl-1H-indol-2-yl)-2-phenylacetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 40/1), mp 108-110 °C, yield: 83%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.43-7.35 (m, 6H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 5.96 (s, 1H), 5.59 (s, 1H), 3.74 (s, 3H), 2.81 (s, 3H), 2.48 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 172.2, 170.9, 139.7, 136.8, 136.5, 134.1, 129.1, 128.8, 127.8, 127.4, 124.4, 120.9, 114.6, 112.4, 53.3, 52.4, 27.7, 22.3; HRMS (ESI) exact mass calcd. for C₂₀H₁₉NNaO₃ ([M + Na]⁺) 344.1247, found: 344.1256.

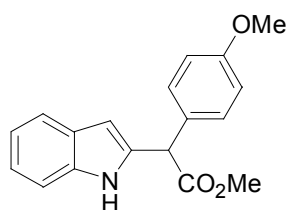


Methyl 2-(6-methoxy-1-acetyl-1H-indol-2-yl)-2-phenylacetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 40/1), mp 110-111 °C, yield: 76%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.44-7.35 (m, 5H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.17 (s, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 5.93 (s, 1H), 5.58 (s, 1H), 3.86 (s, 3H), 3.74 (s, 3H), 2.79 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 172.3, 170.8, 157.5, 139.2, 137.0, 136.8, 129.1, 128.9, 127.9, 123.7, 121.7, 112.3, 110.3, 100.9, 55.9, 53.3, 52.4, 27.5; HRMS (ESI) exact mass calcd. for C₂₀H₁₉NNaO₄ ([M +

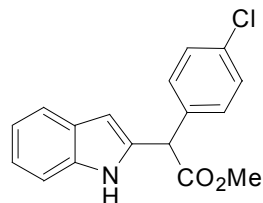
$[\text{Na}]^+$) 360.1198, found: 360.1202.



Methyl 2-(1*H*-indol-2-yl)-2-*p*-tolylacetate¹: Red oil (Flash column chromatography eluent: petroleum ether/ethyl acetate = 50/1), yield: 53%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.71 (s, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.23-7.19 (m, 2H), 7.16-7.11 (m, 3H), 7.07 (t, *J* = 8.0 Hz, 1H), 6.38 (s, 1H), 5.37 (s, 1H), 3.77 (s, 3H), 2.31 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 172.5, 137.6, 136.3, 134.7, 134.4, 129.5, 128.1, 127.9, 121.9, 120.4, 119.9, 111.0, 102.1, 52.7, 50.3, 21.0; HRMS (ESI) exact mass calcd. for C₁₈H₁₇NNaO₂ ([M + Na]⁺) 302.1335, found: 302.1331.

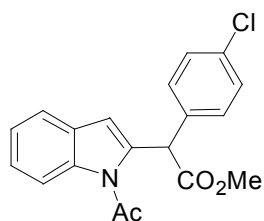


Methyl 2-(1*H*-indol-2-yl)-2-(4-methoxyphenyl)acetate¹: Red oil (Flash column chromatography eluent: petroleum ether/ethyl acetate = 50/1), yield: 58%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.71 (s, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 8.0 Hz, 1H), 7.07 (t, *J* = 8.0 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 2H), 6.37 (s, 1H), 5.15 (s, 1H), 3.76 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 172.6, 159.1, 136.3, 134.9, 129.5, 129.1, 128.1, 128.0, 121.9, 120.3, 119.9, 114.2, 111.0, 102.0, 55.3, 52.6, 49.8; HRMS (ESI) exact mass calcd. for C₁₈H₁₇NNaO₃ ([M + Na]⁺) 318.1286, found: 318.1283.

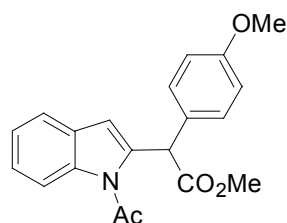


Methyl 2-(1*H*-indol-2-yl)-2-(4-chlorophenyl)acetate¹: Red oil (Flash column chromatography eluent: petroleum ether/ethyl acetate = 50/1), yield: 61%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.69 (s, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.30-7.20 (m, 5H), 7.18-7.12 (m, 1H), 7.07 (t, *J* = 8.0 Hz, 1H), 6.36 (s, 1H), 5.14 (s, 1H), 3.75 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 172.0, 136.3, 135.9, 133.9, 133.7, 129.4, 128.9, 128.0, 122.1, 120.4, 120.0, 111.0, 102.4, 52.8, 49.9; HRMS (ESI)

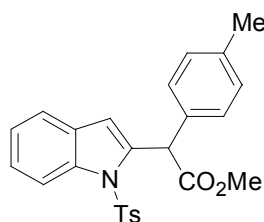
exact mass calcd. for $C_{17}H_{14}ClNNaO_2$ ($[M + Na]^+$) 322.0789, found: 322.0785.



Methyl 2-(1-acetyl-1H-indol-2-yl)-2-(4-chlorophenyl)acetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 100/1), mp 115-116 °C, yield: 80%; 1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.63 (d, $J = 8.0$ Hz, 1H), 7.44 (d, $J = 8.0$ Hz, 1H), 7.38 (d, $J = 8.0$ Hz, 2H), 7.31-7.20 (m, 4H), 6.06 (s, 1H), 5.61 (s, 1H), 3.74 (s, 3H), 2.81 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.8, 170.8, 139.7, 136.0, 135.2, 133.9, 130.5, 129.5, 129.1, 124.4, 123.2, 121.5, 114.2, 112.5, 52.6, 52.5, 27.6; HRMS (ESI) exact mass calcd. for $C_{19}H_{16}ClNNaO_3$ ($[M + Na]^+$) 364.0702, found: 364.0709.

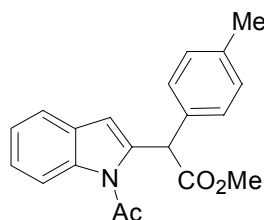


Methyl 2-(1-acetyl-1H-indol-2-yl)-2-(4-methoxyphenyl)acetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 100/1), mp 90-92 °C, yield: 78%; 1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.63 (d, $J = 8.0$ Hz, 1H), 7.42 (d, $J = 8.0$ Hz, 1H), 7.30-7.26 (m, 3H), 7.20 (t, $J = 8.0$ Hz, 1H), 6.94 (d, $J = 8.0$ Hz, 2H), 6.05 (s, 1H), 5.55 (s, 1H), 3.84 (s, 3H), 3.74 (s, 3H), 2.82 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.4, 170.8, 159.3, 140.8, 136.1, 130.2, 129.7, 128.7, 124.2, 123.1, 121.4, 114.3, 114.2, 112.5, 55.3, 52.5, 52.4, 27.6; HRMS (ESI) exact mass calcd. for $C_{20}H_{19}NNaO_4$ ($[M + Na]^+$) 360.1199, found: 360.1204.

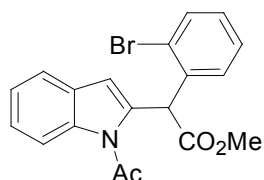


Methyl 2-(1-(toluene-4-sulfonyl)-1H-indol-2-yl)-2-(4-methylphenyl)acetate: Colorless oil (Flash column chromatography eluent: petroleum ether/ethyl acetate = 50/1), yield: 73%; 1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.01 (d, $J = 8.0$ Hz, 1H), 7.57 (d, $J = 8.0$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz,

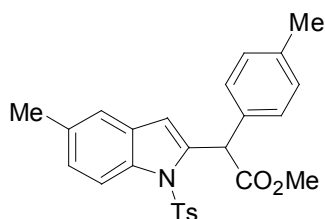
1H), 7.25-7.10 (m, 8H), 6.32 (s, 1H), 5.75 (s, 1H), 3.73 (s, 3H), 2.35 (s, 3H), 2.29 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 171.9, 144.8, 138.8, 137.7, 137.1, 135.9, 133.5, 129.7, 129.5, 129.0, 128.8, 126.6, 124.6, 123.6, 120.9, 114.7, 112.8, 52.6, 50.7, 21.5, 21.1; HRMS (ESI) exact mass calcd. for C₂₅H₂₃NNaO₄S ([M + Na]⁺) 456.1230, found: 456.1235.



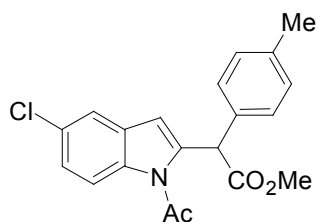
Methyl 2-(1-acetyl-1H-indol-2-yl)-2-(4-methylphenyl)acetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 40/1), mp 100-102 °C, yield: 82%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.64 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.29-7.21 (m, 6H), 6.06 (s, 1H), 5.59 (s, 1H), 3.75 (s, 3H), 2.83 (s, 3H), 2.40 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 172.3, 170.8, 140.6, 137.6, 136.1, 133.6, 129.7, 129.6, 129.0, 124.2, 123.1, 121.4, 114.2, 112.5, 52.9, 52.4, 27.6, 21.2; HRMS (ESI) exact mass calcd. for C₂₀H₁₉NNaO₃ ([M + Na]⁺) 344.1246, found: 344.1252.



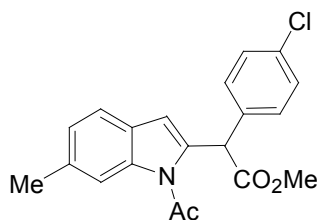
Methyl 2-(1-acetyl-1H-indol-2-yl)-2-(2-bromophenyl)acetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 40/1), mp 146-147 °C, yield: 82%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.68-7.65 (m, 2H), 7.44 (d, *J* = 4.0 Hz, 1H), 7.37-7.29 (m, 3H), 7.24-7.20 (m, 2H), 6.10 (s, 1H), 5.97 (s, 1H), 3.78 (s, 3H), 2.84 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 171.8, 170.7, 138.5, 136.7, 136.1, 133.5, 129.6, 129.6, 129.4, 127.8, 125.5, 124.3, 123.1, 121.4, 114.3, 112.2, 52.9, 52.6, 27.6; HRMS (ESI) exact mass calcd. for C₁₉H₁₆BrNNaO₃ ([M + Na]⁺) 408.0206, found: 408.0203.



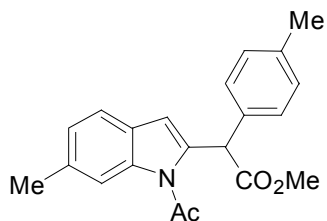
Methyl 2-(5-methyl-1-(toluene-4-sulfonyl)-1*H*-indol-2-yl)-2-(4-methylphenyl)acetate: Colorless oil (Flash column chromatography eluent: petroleum ether/ethyl acetate = 50/1), yield: 76%; ¹H NMR (400MHz, CDCl₃): δ (ppm) 7.89 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.20-7.09 (m, 7H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.27 (s, 1H), 5.73 (s, 1H), 3.72 (s, 3H), 2.34 (s, 3H), 2.33 (s, 3H), 2.28 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 171.9, 144.6, 138.8, 137.6, 135.9, 135.3, 133.6, 133.2, 129.6, 129.5, 129.3, 128.8, 126.5, 126.0, 120.8, 114.4, 112.7, 52.6, 50.6, 21.5, 21.1; HRMS (ESI) exact mass calcd. for C₂₆H₂₅NNaO₄S ([M + Na]⁺) 470.1392, found: 470.1397.



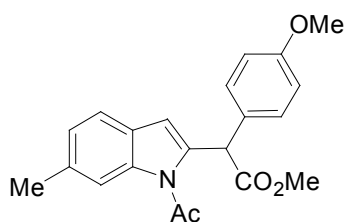
Methyl 2-(5-chloro-1-acetyl-1*H*-indol-2-yl)-2-(4-methylphenyl)acetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 40/1), mp 118-120 °C, yield: 75%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.54 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 4.0 Hz, 1H), 7.24-7.21 (m, 5H), 5.99 (s, 1H), 5.55 (s, 1H), 3.73 (s, 3H), 2.79 (s, 3H), 2.39 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 172.1, 170.5, 142.1, 137.8, 134.4, 133.3, 130.9, 129.7, 128.9, 128.8, 124.2, 120.8, 115.1, 111.7, 52.9, 52.4, 27.5, 21.2; HRMS (ESI) exact mass calcd. for C₂₀H₁₈ClNNaO₃ ([M + Na]⁺) 378.0855, found: 378.0860.



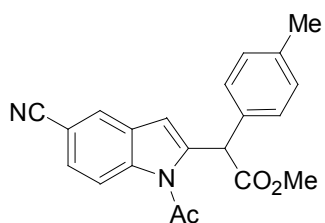
Methyl 2-(6-methyl-1-acetyl-1*H*-indol-2-yl)-2-(4-chlorophenyl)acetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 40/1), mp 143-144 °C, yield: 81%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.42 (s, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.32-7.28 (m, 3H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.00 (s, 1H), 5.58 (s, 1H), 3.74 (s, 3H), 2.80 (s, 3H), 2.48 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 171.9, 170.9, 139.0, 136.4, 135.3, 134.3, 133.8, 130.5, 129.0, 127.3, 124.6, 121.0, 114.6, 112.4, 52.6, 52.5, 27.7, 22.3; HRMS (ESI) exact mass calcd. for C₂₀H₁₈ClNNaO₃ ([M + Na]⁺) 378.0858, found: 378.0862.



Methyl 2-(6-methyl-1-acetyl-1*H*-indol-2-yl)-2-(4-methylphenyl)acetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 40/1), mp 122-124 °C, yield: 88%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.43 (s, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.26-7.19 (m, 4H), 7.03 (d, *J* = 8.0 Hz, 1H), 5.99 (s, 1H), 5.55 (s, 1H), 3.73 (s, 3H), 2.81 (s, 3H), 2.48 (s, 3H), 2.38 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 172.4, 170.9, 139.9, 137.6, 136.5, 134.0, 133.8, 129.6, 129.0, 127.4, 124.4, 120.9, 114.6, 112.4, 52.9, 52.3, 27.7, 22.3, 21.2; HRMS (ESI) exact mass calcd. for C₂₁H₂₁NNaO₃ ([M + Na]⁺) 358.1408, found: 358.1411.

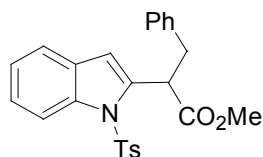


Methyl 2-(6-methyl-1-acetyl-1*H*-indol-2-yl)-2-(4-methoxyphenyl)acetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 40/1), mp 161-162 °C, yield: 85%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.42 (s, 1H), 7.30-7.26 (m, 3H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.00 (s, 1H), 5.53 (s, 1H), 3.83 (s, 3H), 3.73 (s, 3H), 2.80 (s, 3H), 2.48 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 172.4, 170.9, 159.2, 140.1, 136.5, 134.0, 130.2, 128.8, 127.4, 124.4, 120.9, 114.6, 114.3, 112.3, 55.3, 52.5, 52.3, 27.7, 22.3; HRMS (ESI) exact mass calcd. for C₂₁H₂₁NNaO₄ ([M + Na]⁺) 374.1350, found: 374.1358.

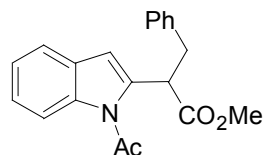


Methyl 2-(5-cyano-1-acetyl-1*H*-indol-2-yl)-2-(4-methylphenyl)acetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 40/1), mp 152-153 °C, yield: 55%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.73 (d, *J* = 8.0 Hz, 2H), 7.56-7.53 (m, 1H), 7.23-7.21 (m, 4H), 6.10 (s, 1H), 5.56 (s, 1H), 3.74 (s, 3H), 2.84 (s, 3H), 2.40 (s, 3H); ¹³C NMR (125 MHz,

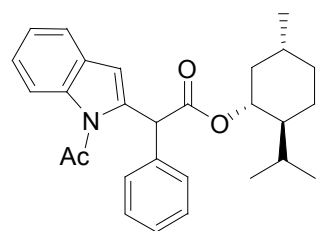
CDCl₃) δ 171.9, 170.5, 143.1, 138.1, 137.8, 132.9, 129.8, 129.6, 128.9, 127.2, 125.9, 119.3, 114.8, 111.7, 106.6, 52.7, 52.6, 27.6, 21.2; HRMS (ESI) exact mass calcd. for C₂₁H₁₈N₂NaO₃ ([M + Na]⁺) 369.1209, found: 369.1211.



Methyl 2-(1-(toluene-4-sulfonyl)-1H-indol-2-yl)-2-benzylacetate: Yellow oil (Flash column chromatography eluent: petroleum ether/ethyl acetate = 50/1), yield: 67%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.12 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.29-7.20 (m, 7H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.72 (s, 1H), 4.98 (t, *J* = 8.0 Hz, 1H), 3.61 (s, 3H), 3.34-3.31 (m, 2H), 2.32 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 172.4, 144.8, 138.7, 138.4, 137.0, 135.8, 129.7, 129.3, 129.1, 128.4, 126.6, 126.5, 124.7, 123.7, 120.8, 115.1, 110.6, 52.2, 46.5, 39.7, 21.5; HRMS (ESI) exact mass calcd. for C₂₅H₂₃NNaO₄S ([M + Na]⁺) 456.1235, found: 456.1239.

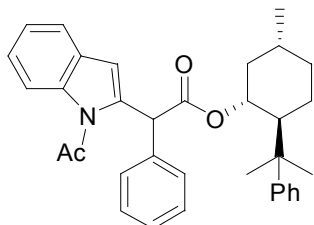


Methyl 2-(1-acetyl-1H-indol-2-yl)-2-benzylacetate: Yellow oil (Flash column chromatography eluent: petroleum ether/ethyl acetate = 100/1), yield: 73%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.63 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 4.0 Hz, 1H), 7.30-7.19 (m, 7H), 6.62 (s, 1H), 4.73 (t, *J* = 6.0 Hz, 1H), 3.65 (s, 3H), 3.48-3.43 (m, 1H), 3.30-3.25 (m, 1H), 2.80 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 172.8, 170.5, 139.0, 139.0, 135.7, 129.7, 128.9, 128.3, 126.4, 124.1, 123.1, 121.3, 114.1, 110.5, 52.1, 48.0, 38.1, 27.6; HRMS (ESI) exact mass calcd. for C₂₀H₁₉NNaO₃ ([M + Na]⁺) 344.1250, found: 344.1253.



(1R,2S,5R)-8-menthyl-2-(1-acetyl-1H-indol-2-yl)-2-phenylacetate: Colorless oil (Flash column chromatography eluent: petroleum ether/ethyl acetate = 50/1), yield: 71% (d.r.: 1:1); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.63 (d, *J* = 8.0 Hz, 1H), 7.43-7.35 (m, 6H), 7.30-7.26 (m, 1H), 7.20

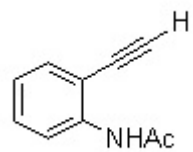
(t, $J = 8.0$ Hz, 1H), 6.08 (s, 1H), 5.57 (s, 1H), 4.71-4.64 (m, 1H), 2.83 (s, 3H), 2.20-2.17 (m, 1H), 1.67-1.57 (m, 1H), 1.51-1.49 (m, 1H), 1.13-1.28 (m, 2H), 1.18-1.10 (m, 1H), 0.95 (d, $J = 4.0$ Hz, 3H), 0.64-0.62 (d, $J = 8.0$ Hz, 3H), 0.54-0.52 (d, $J = 8.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 171.2, 170.7, 140.6, 136.9, 136.1, 129.7, 129.3, 128.6, 127.7, 124.0, 123.0, 121.3, 114.1, 112.3, 75.1, 53.8, 47.0, 40.6, 34.3, 31.5, 27.6, 25.5, 23.2, 22.1, 20.5, 15.9; HRMS (ESI) exact mass calcd. for $\text{C}_{28}\text{H}_{33}\text{NNaO}_3$ ($[\text{M} + \text{Na}]^+$) 454.2348, found: 454.2351.



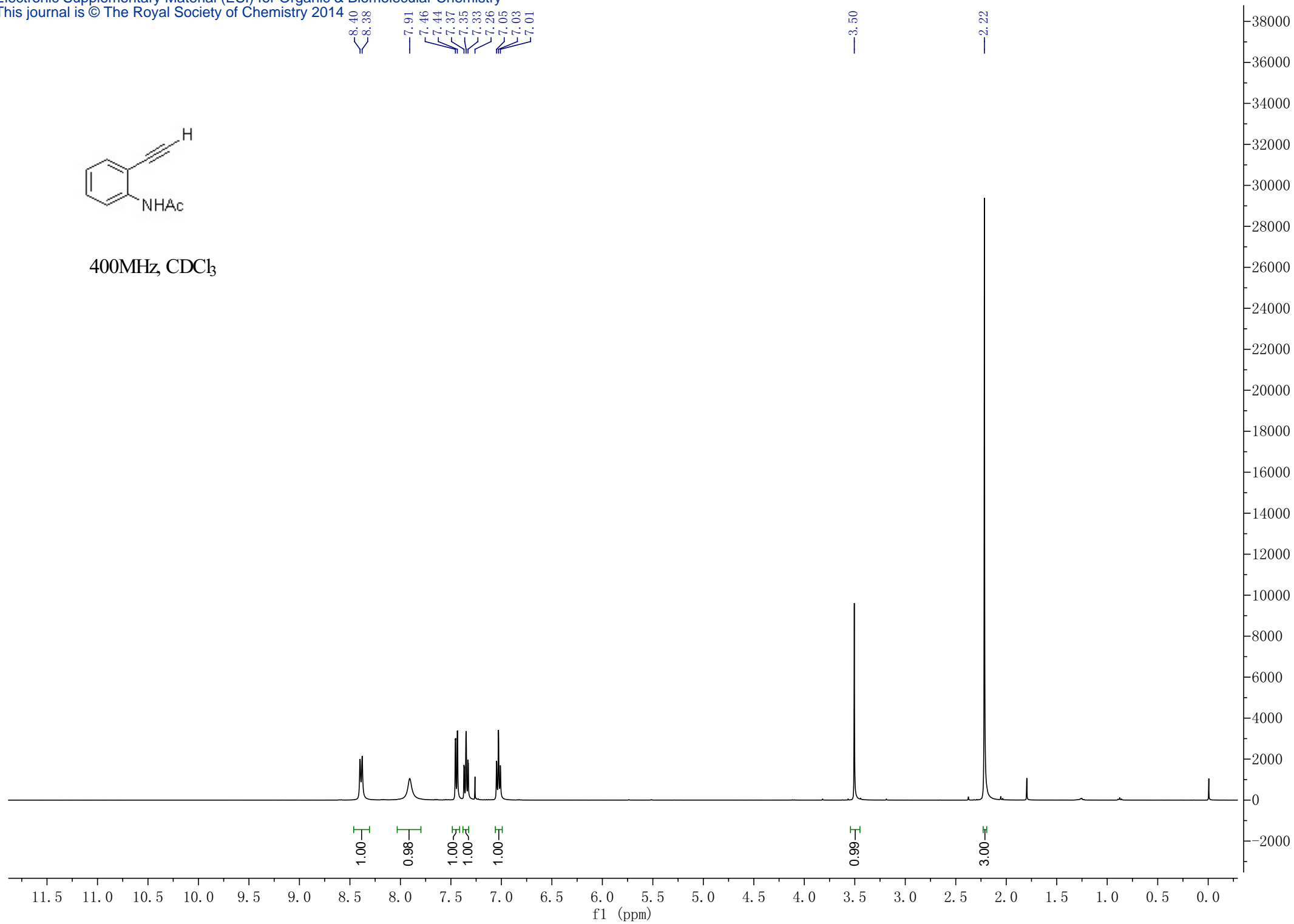
(1R,2S,5R)-8-Phenylmenthyl-2-(1-acetyl-1H-indol-2-yl)-2-phenylacetate: White solid (Flash column chromatography eluent: petroleum ether/ethyl acetate = 40/1), mp 114-115 °C, yield: 76% (d.r.: 1:1.5); ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.64 (d, $J = 8.0$ Hz, 1H), 7.45-7.35 (m, 5H), 7.32-7.28 (m, 2H), 7.24-7.19 (m, 3H), 7.13-7.10 (m, 3H), 6.18 (s, 1H), 5.88 (s, 1H), 4.81-4.74 (m, 1H), 2.80 (s, 3H), 2.23 (d, $J = 12.0$ Hz, 1H), 1.90-1.83 (m, 1H), 1.48-1.45 (m, 2H), 1.16 (t, $J = 12.0$ Hz, 2H), 1.00 (s, 3H), 0.89 (d, $J = 8.0$ Hz, 1H), 0.86-0.70 (m, 5H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.8, 170.5, 150.7, 140.2, 136.1, 129.7, 129.6, 128.7, 127.9, 125.7, 125.1, 124.1, 123.0, 121.3, 114.2, 112.3, 53.6, 50.6, 41.2, 40.1, 34.6, 31.4, 29.7, 27.6, 22.9, 21.9; HRMS (ESI) exact mass calcd. for $\text{C}_{34}\text{H}_{37}\text{NNaO}_3$ ($[\text{M} + \text{Na}]^+$) 530.2650, found: 530.2660.

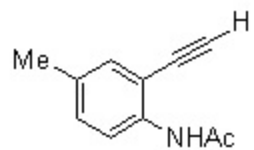
References

- 1) Chan, W.-W.; Yeung, S.-H.; Zhou, Z.; Chan, A.; Yu, W.-Y. *Org. Lett.* **2010**, *12*, 604-607.
- 2) Sakai, N.; Annaka, K.; Fujita, A.; Sato, A.; Konakahara, T. *J. Org. Chem.* **2008**, *73*, 4160-4165.
- 3) Chen, Z.-Y.; Zheng, D.-Q.; Wu, J. *Org. Lett.* **2011**, *13*, 848-851.
- 4) Shu, C.; Liu, M.-Q.; Wang, S.-S.; Li, L.; Ye, L.-W. *J. Org. Chem.* **2008**, *73*, 3292-3299.

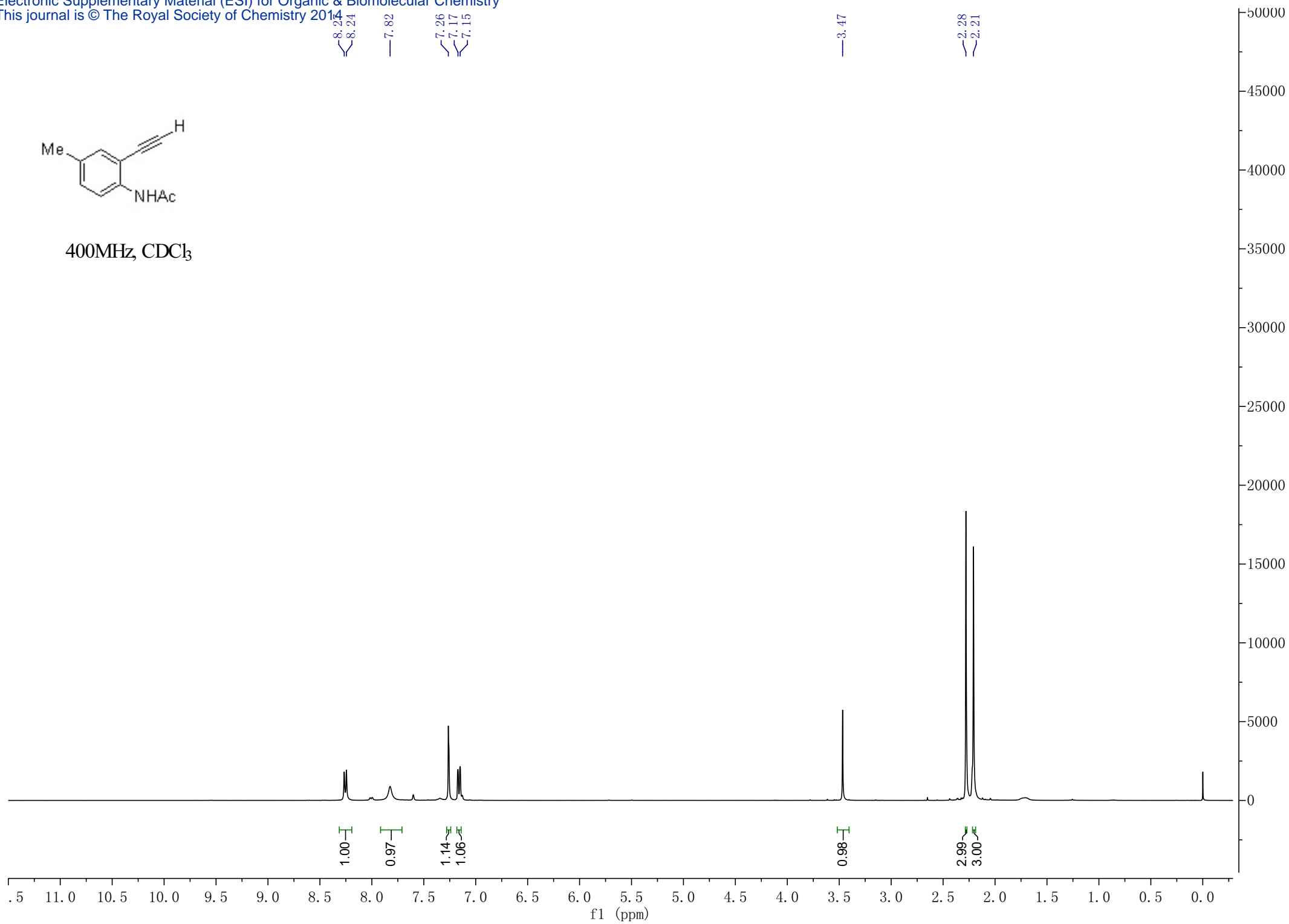


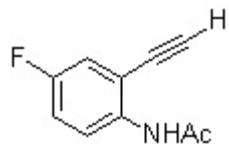
400MHz, CDCl₃





400MHz, CDCl₃



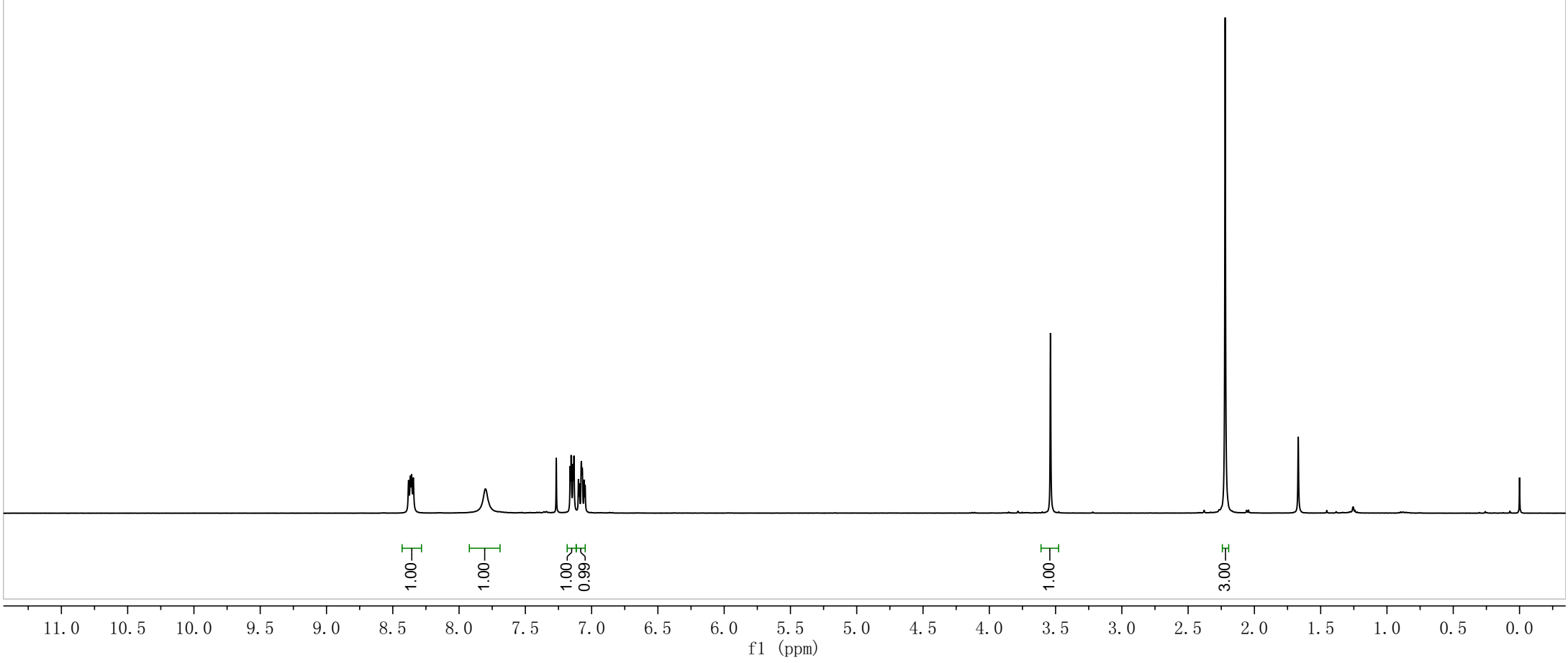


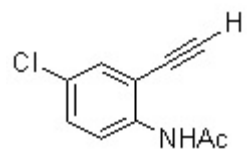
400MHz, CDCl₃

8.334
8.334
8.336
8.335
7.80
7.16
7.15
7.14
7.13
7.10
7.09
7.08
7.07
7.06
7.05

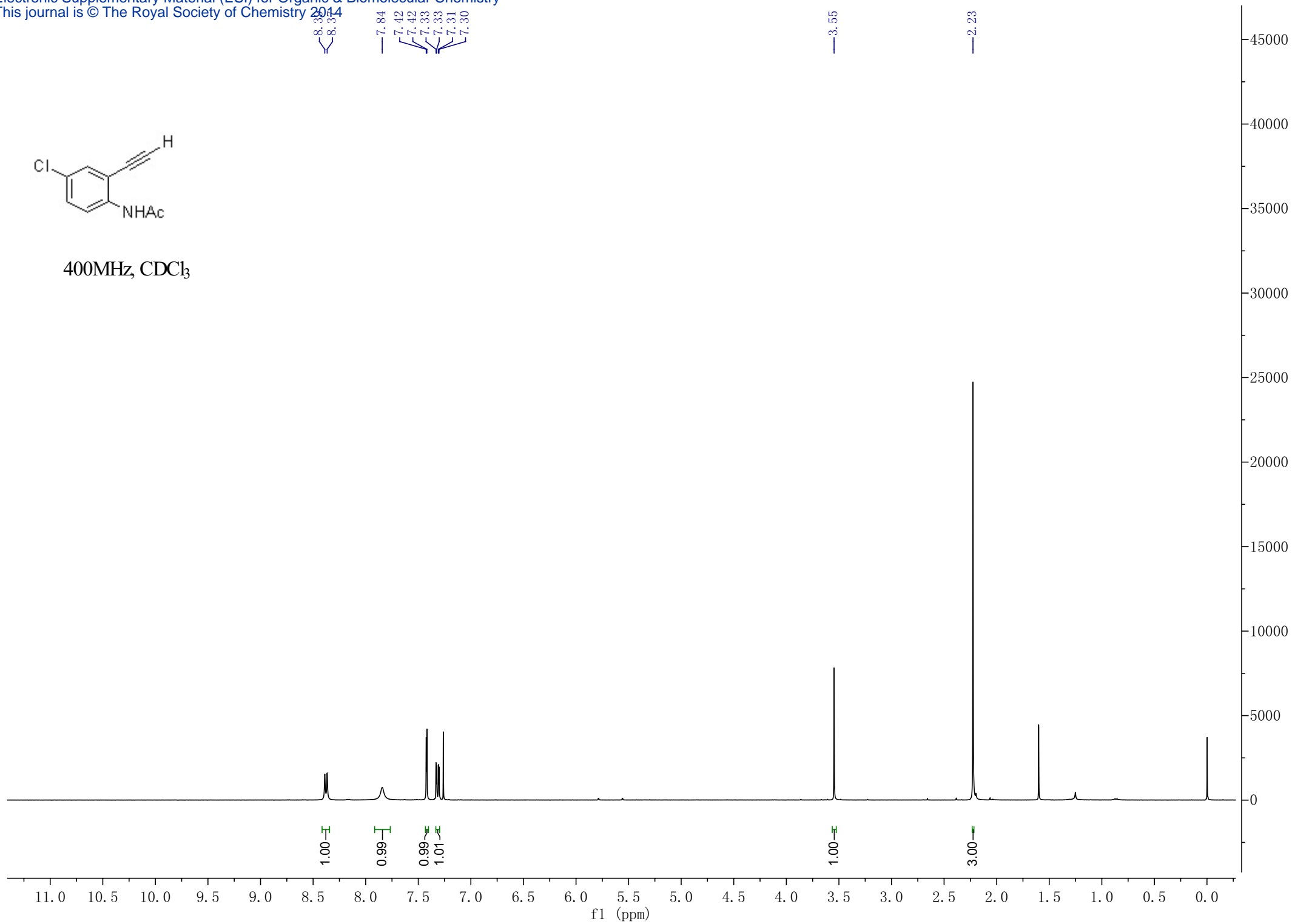
3.54

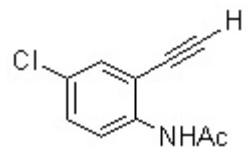
2.22



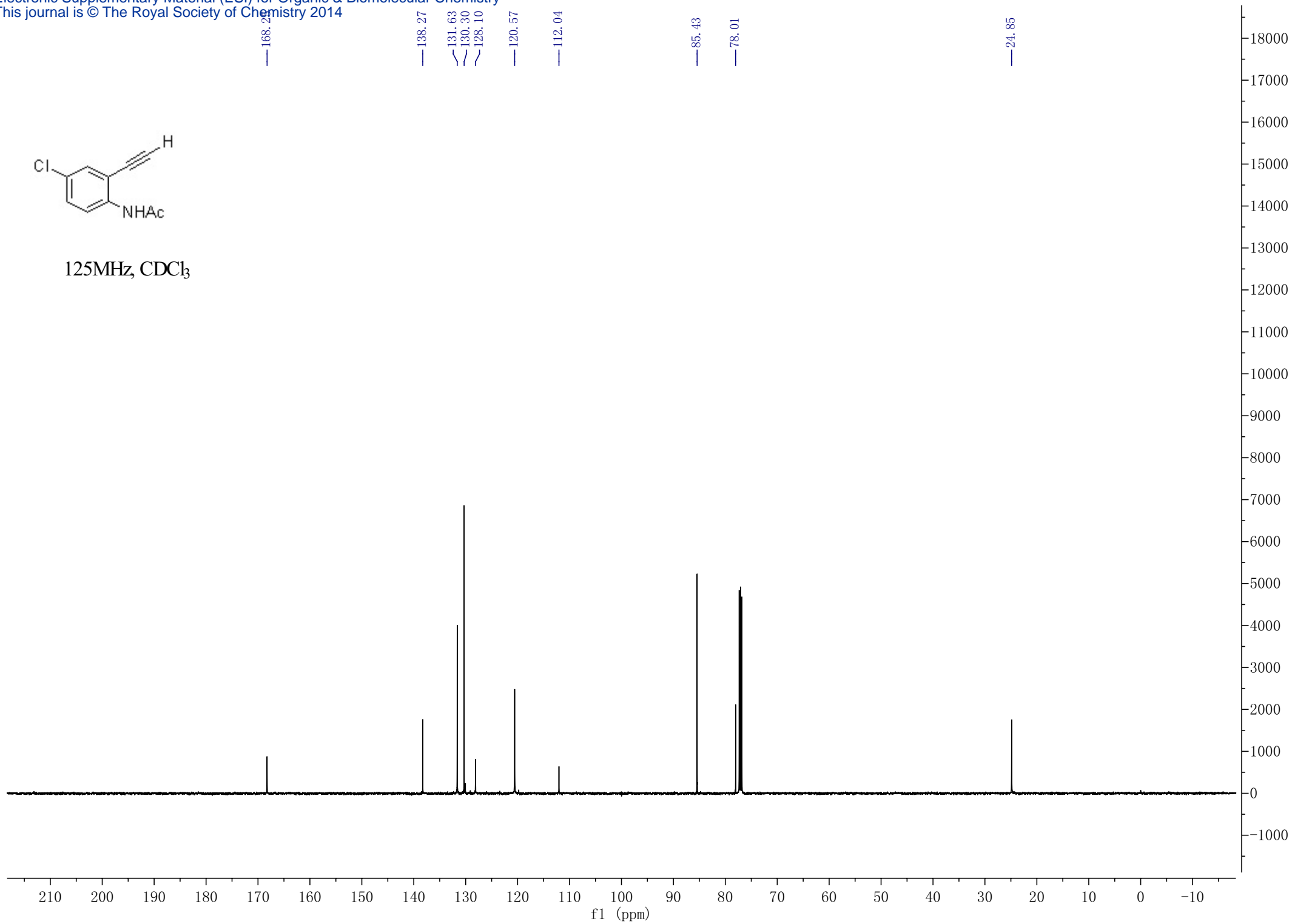


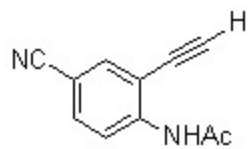
400MHz, CDCl₃



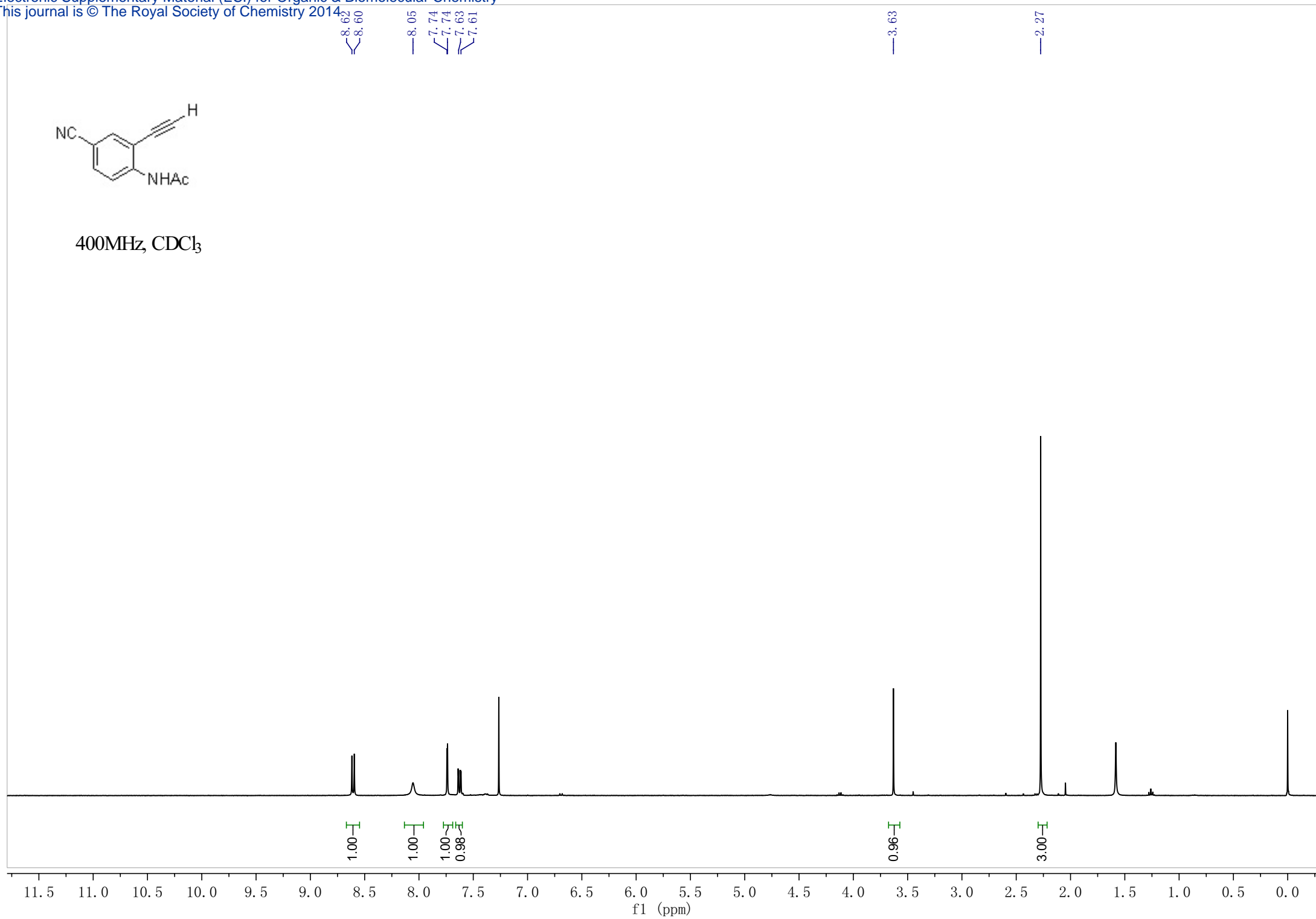


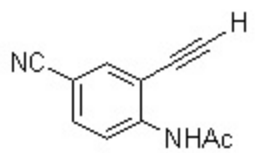
125MHz, CDCl₃



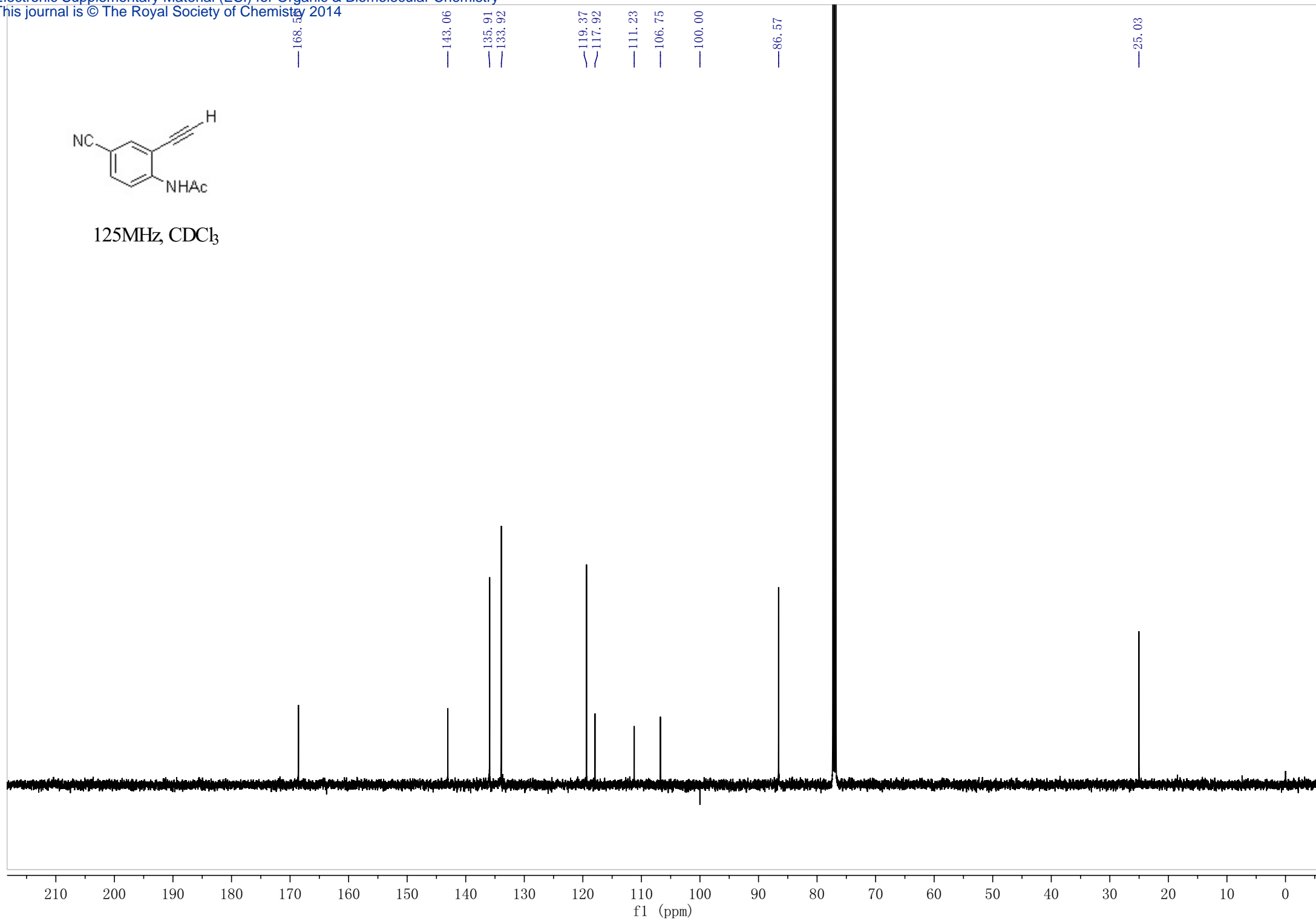


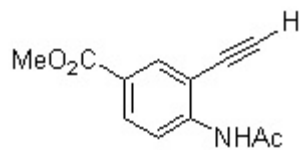
400MHz, CDCl₃



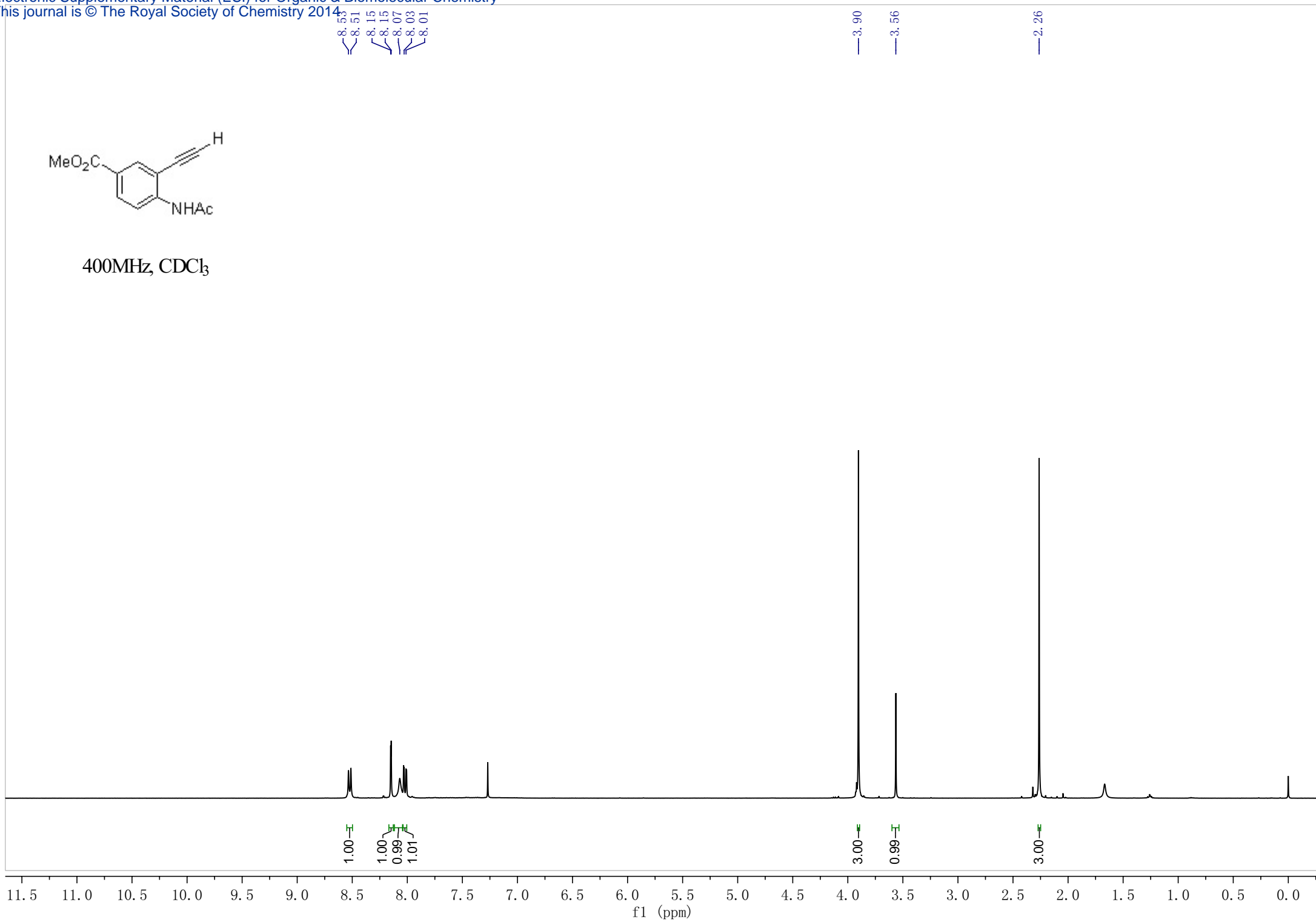


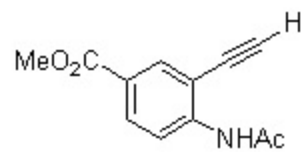
125MHz, CDCl₃



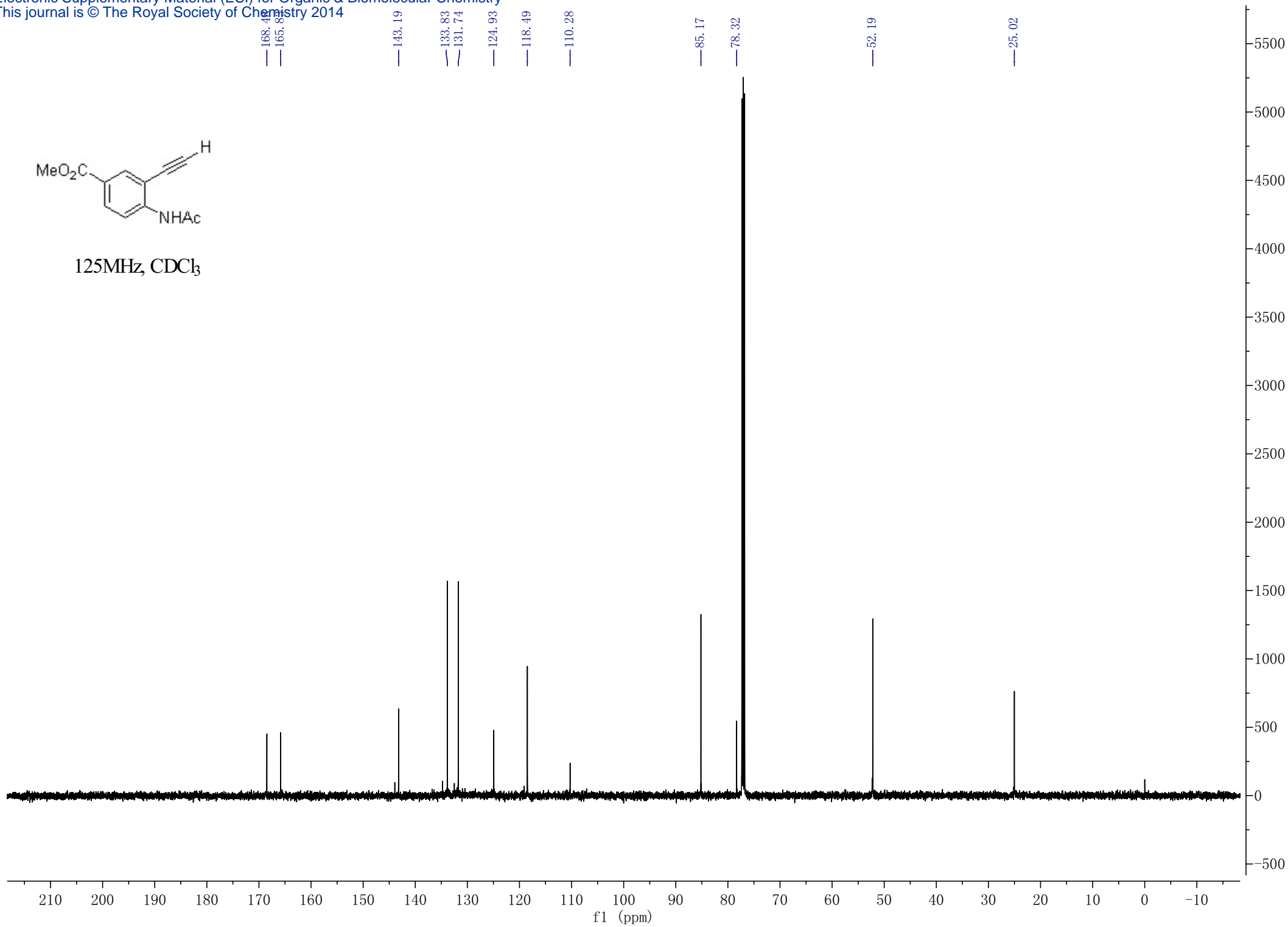


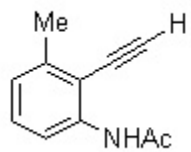
400MHz, CDCl₃



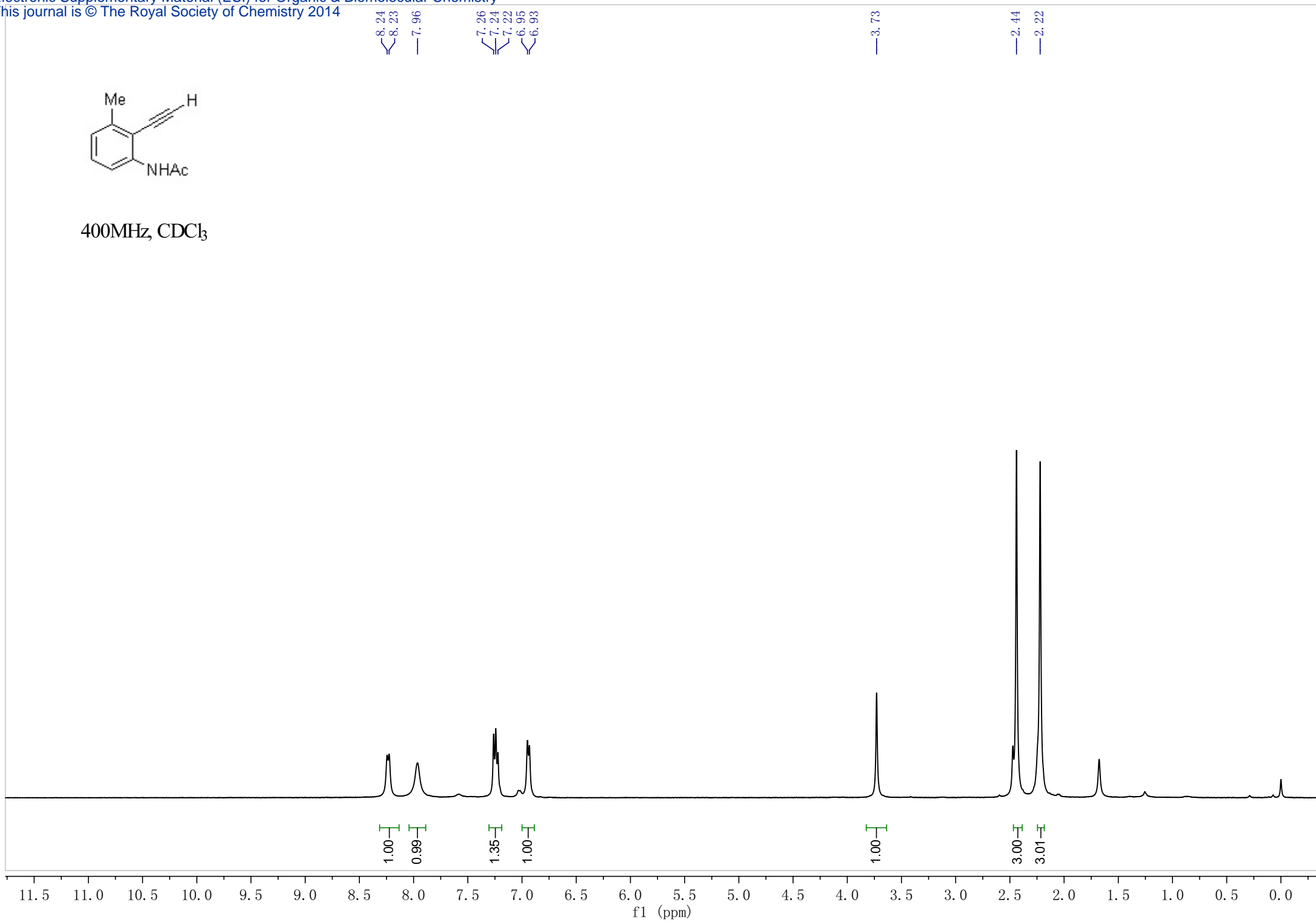


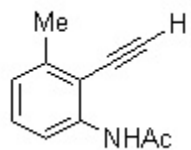
125MHz, CDCl₃



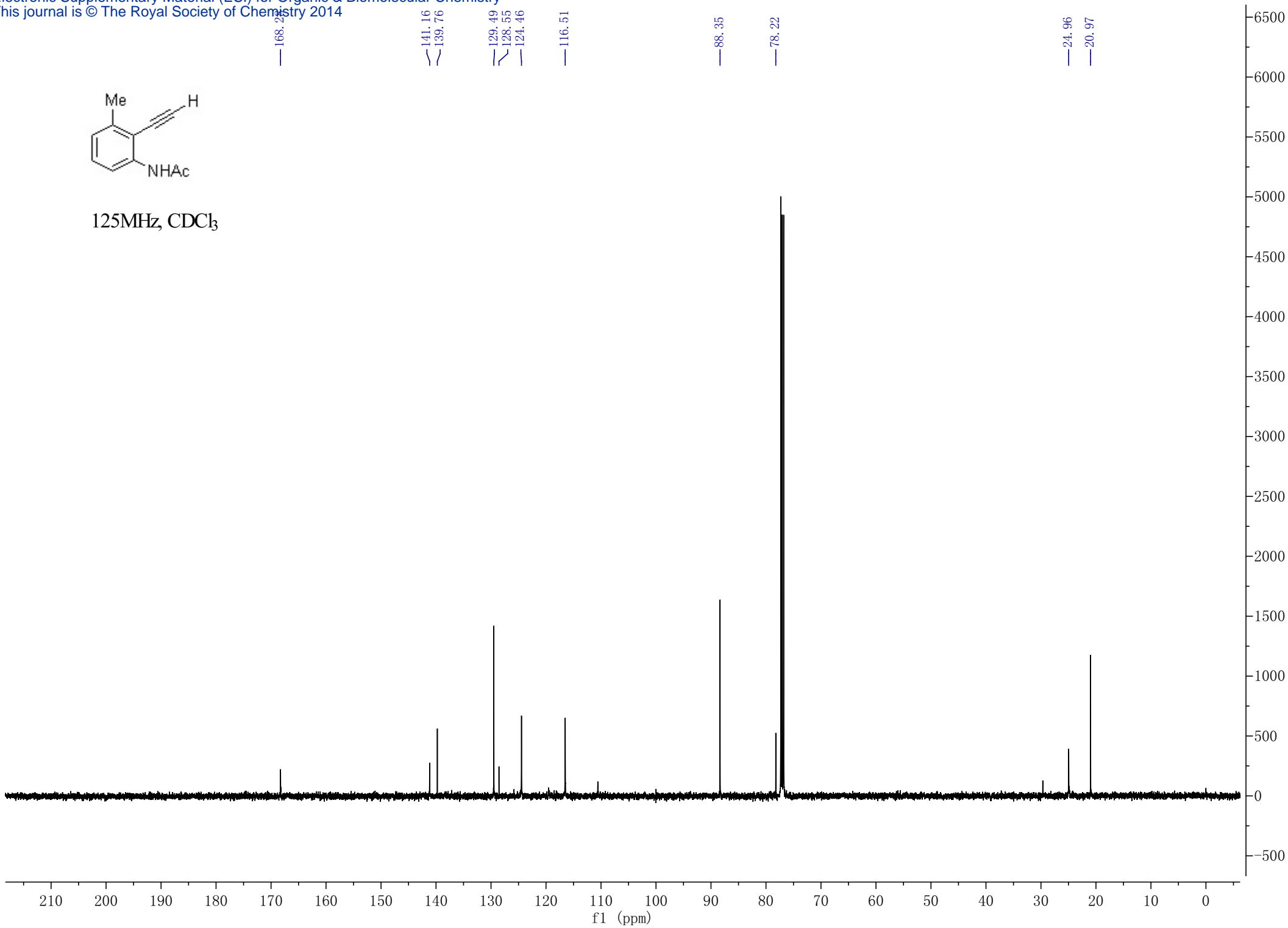


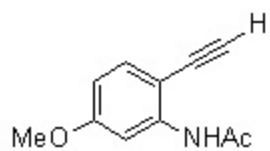
400MHz, CDCl₃



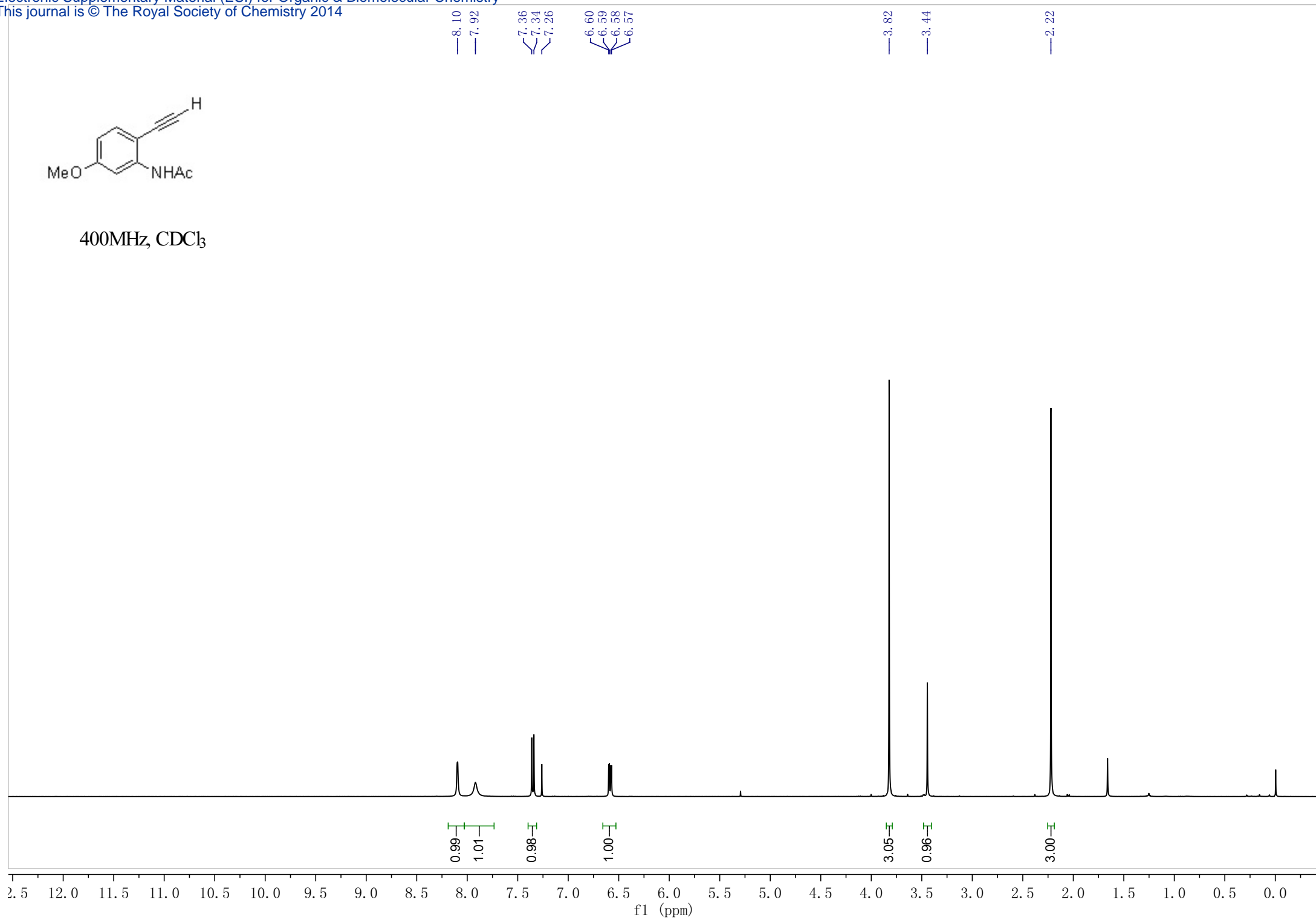


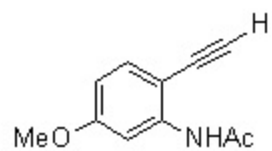
125MHz, CDCl₃



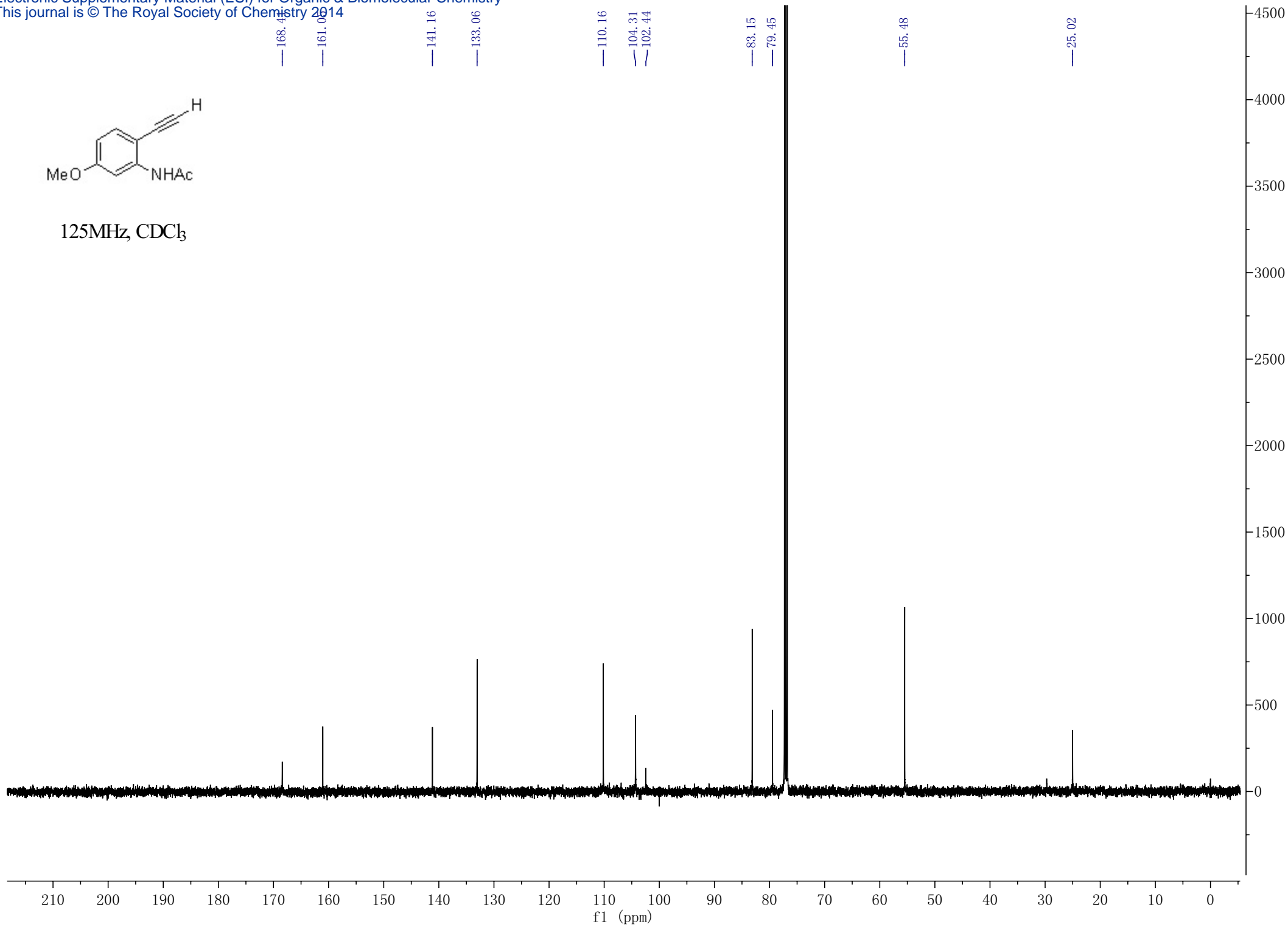


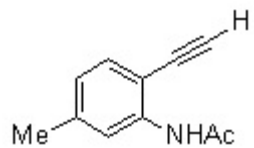
400MHz, CDCl₃



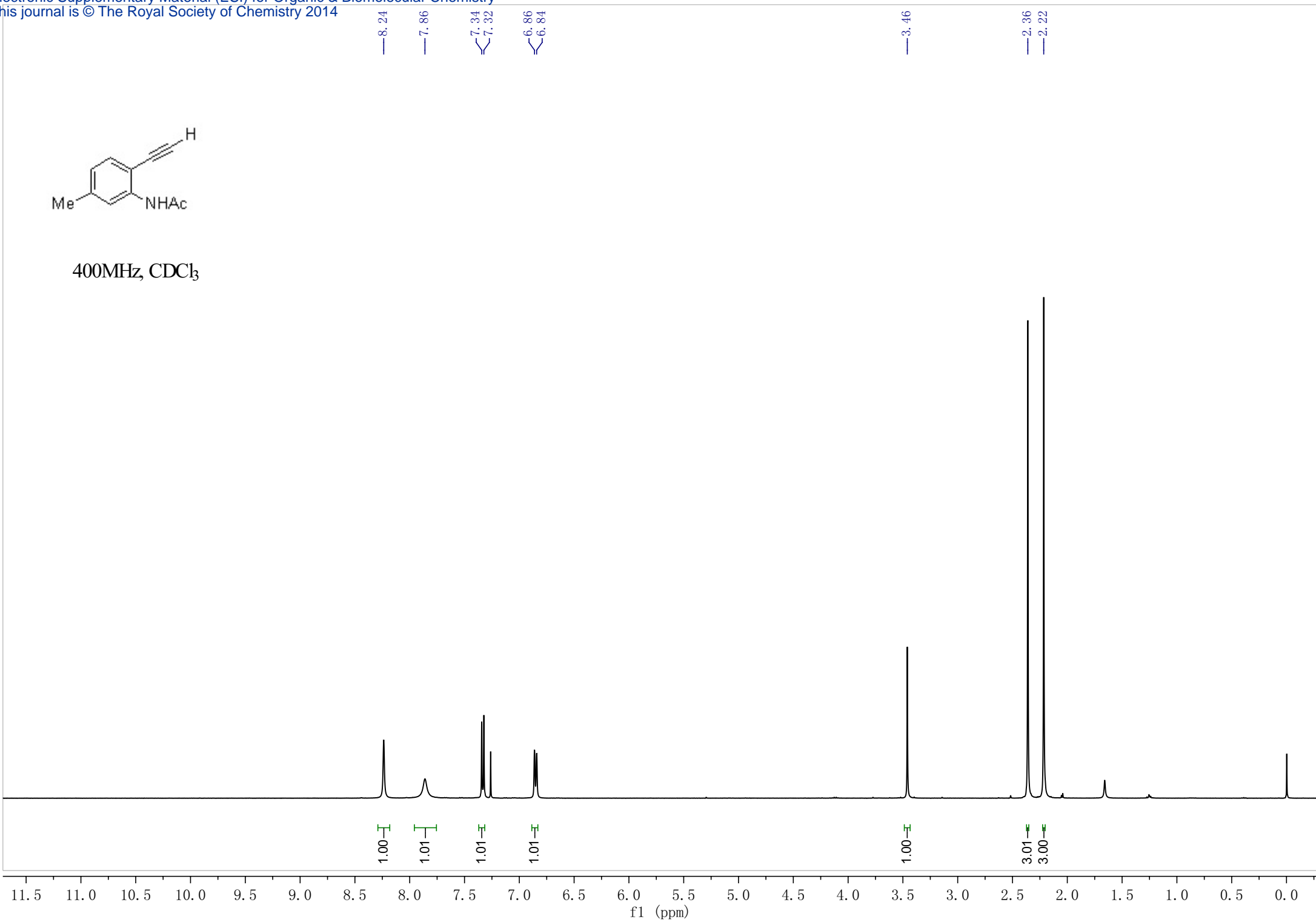


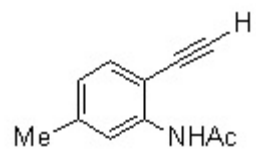
125MHz, CDCl₃



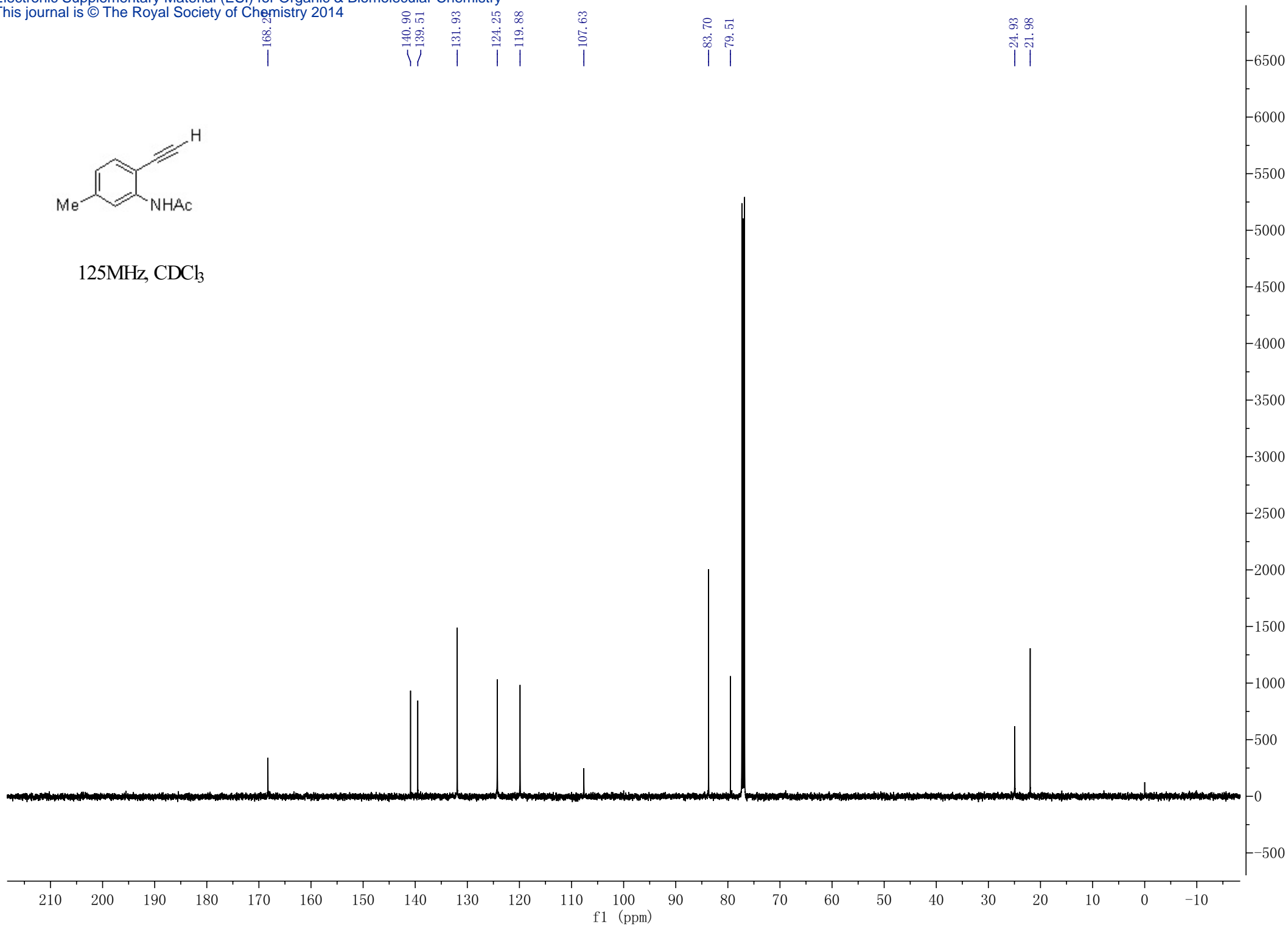


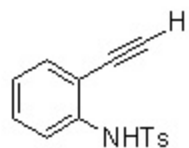
400MHz, CDCl₃



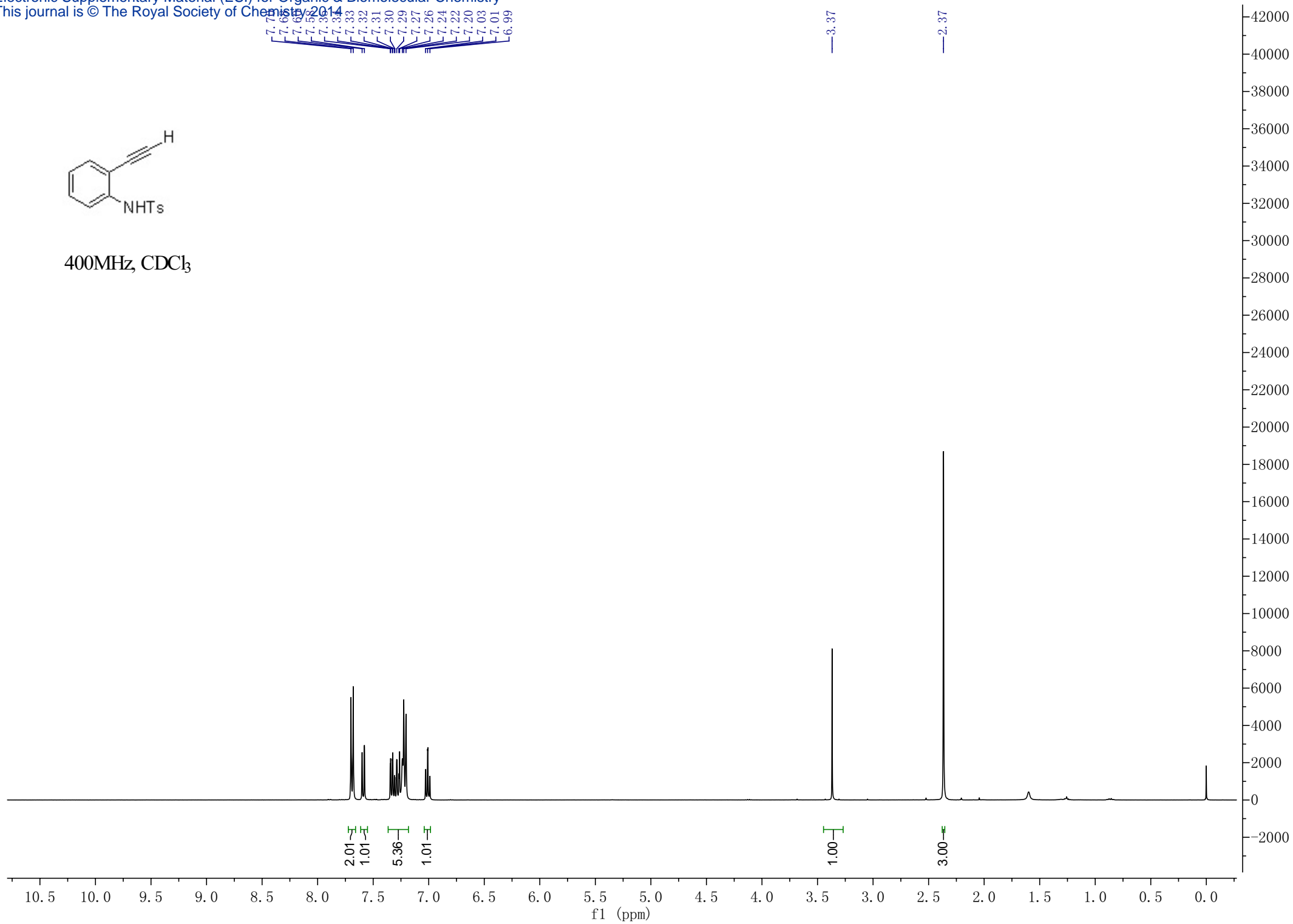


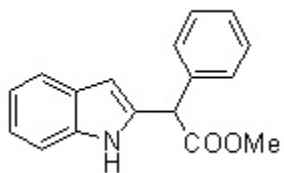
125MHz, CDCl₃



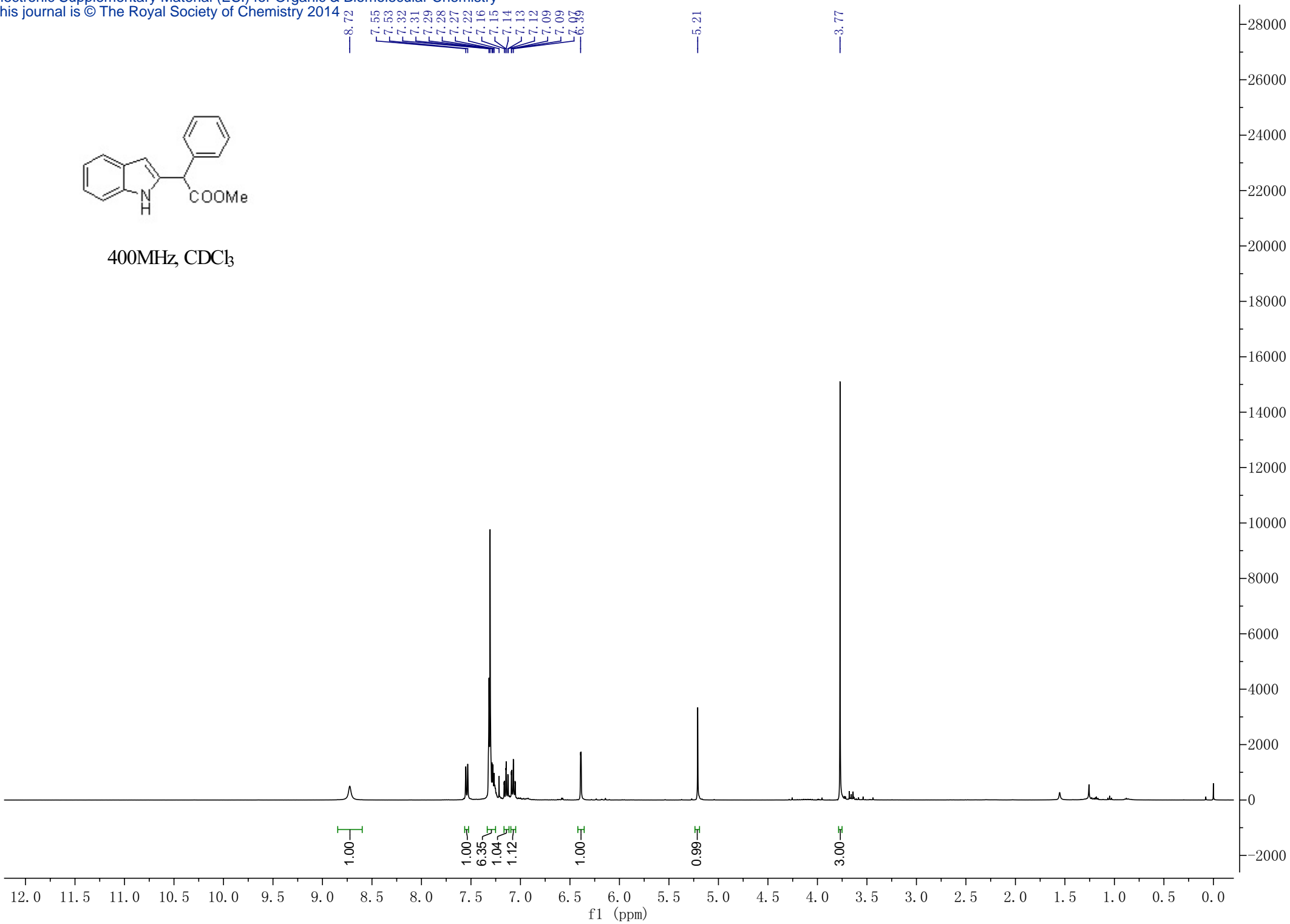


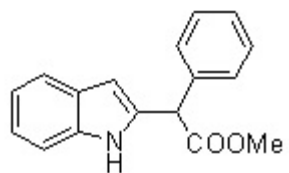
400MHz, CDCl₃



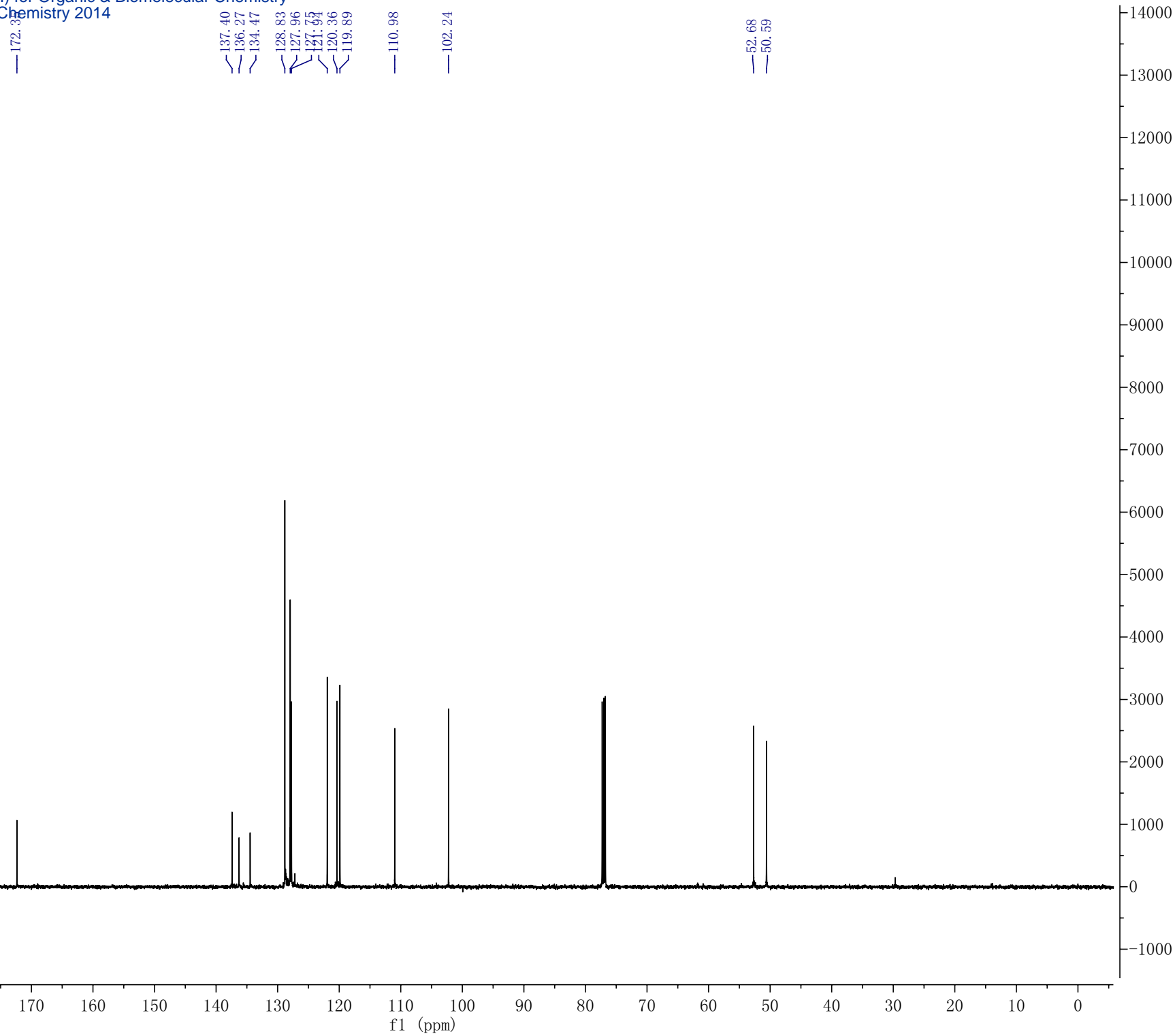


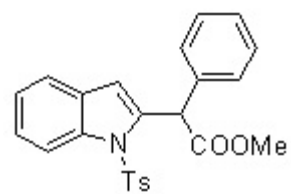
400MHz, CDCl₃



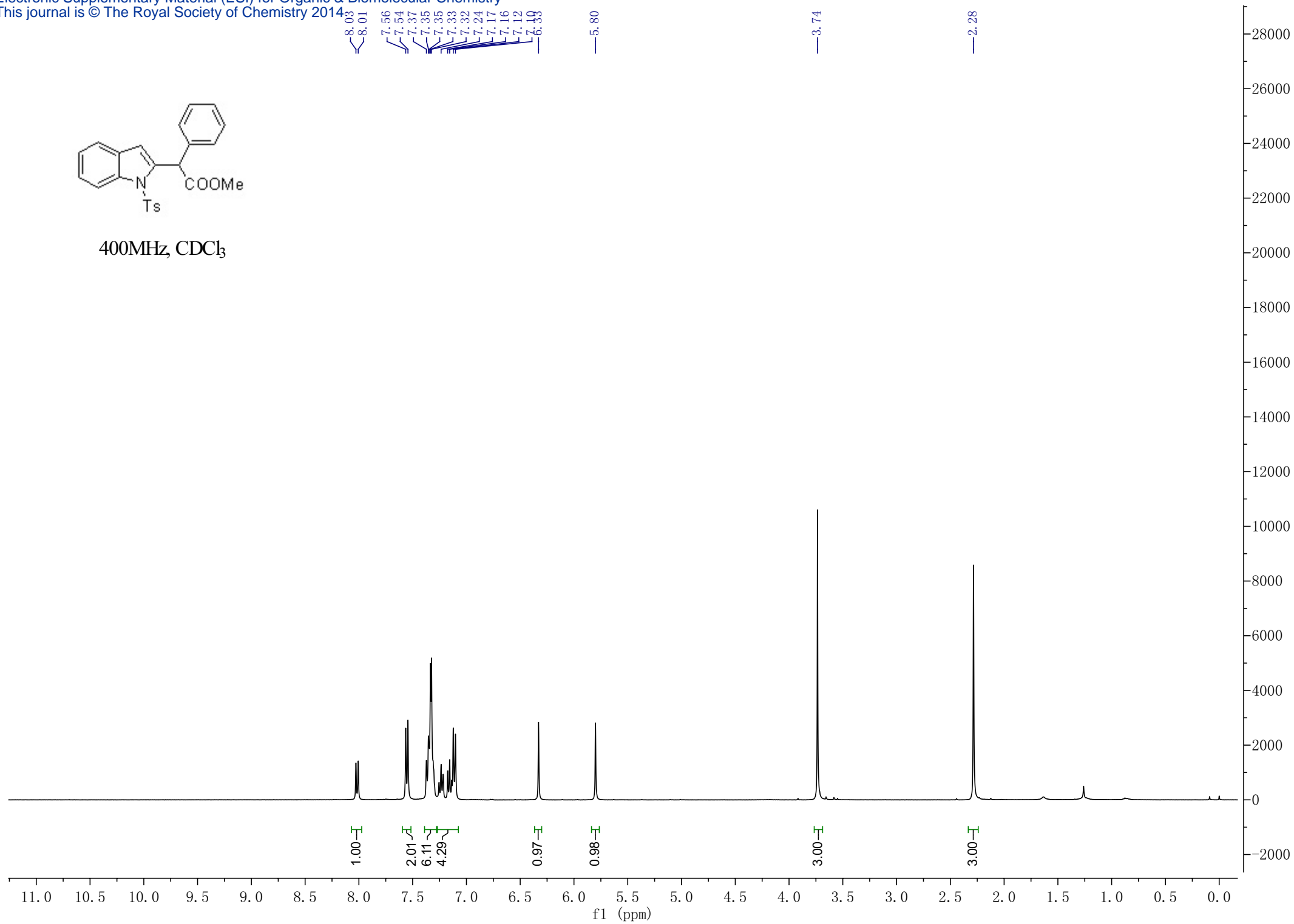


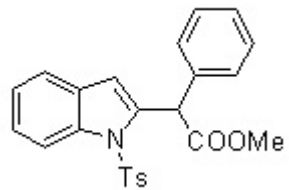
125MHz, CDCl₃



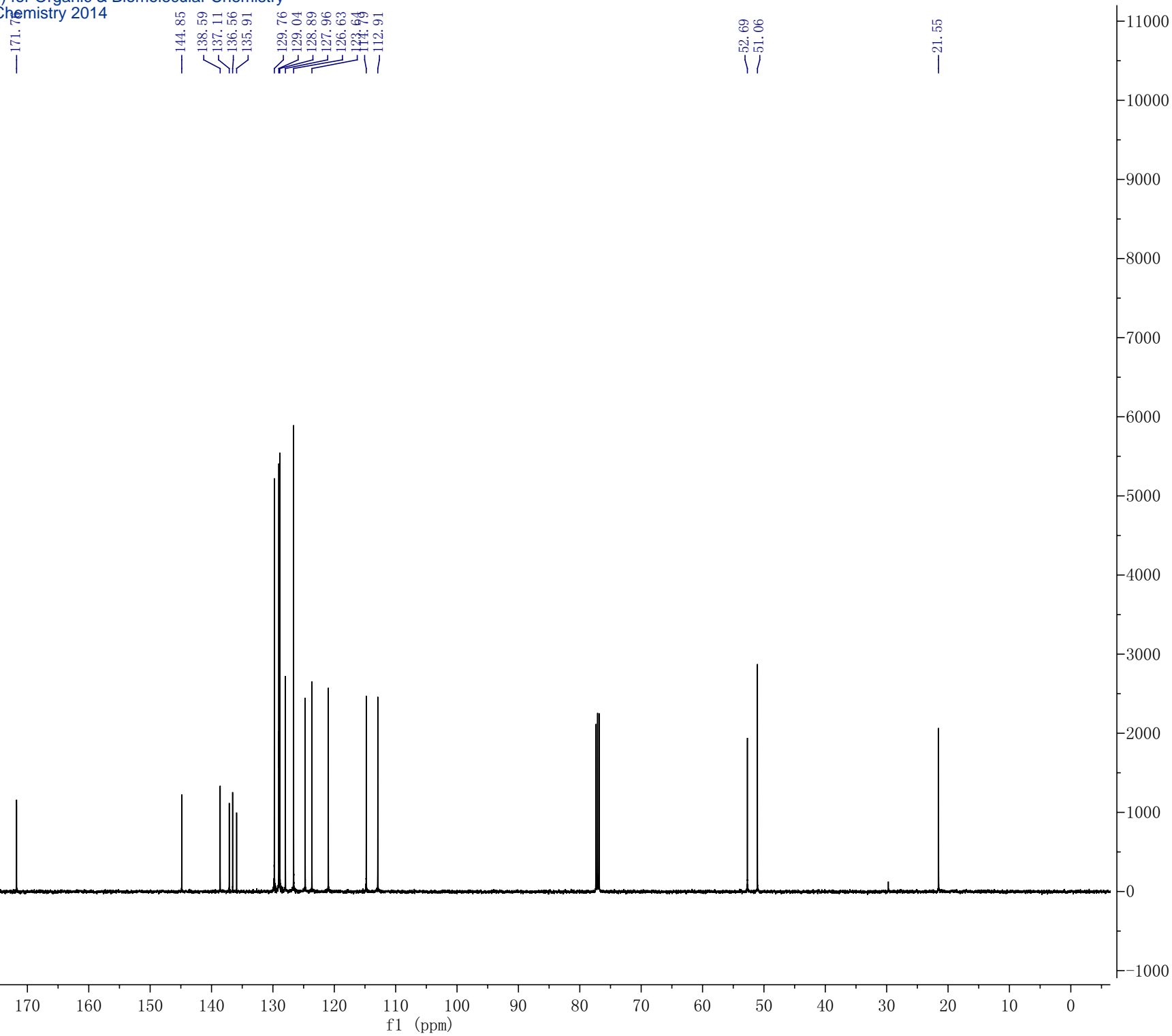


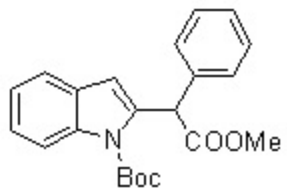
400MHz, CDCl₃



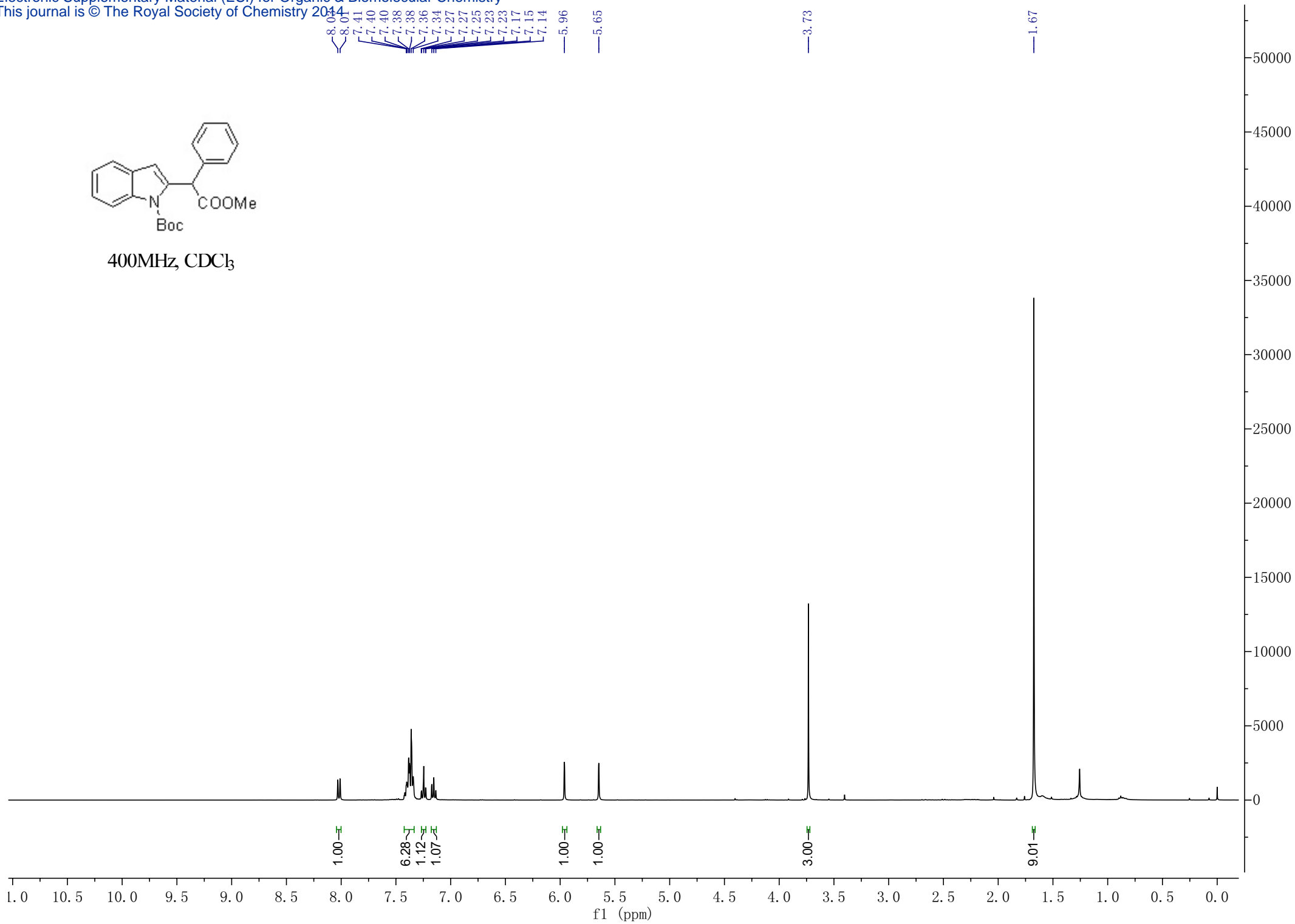


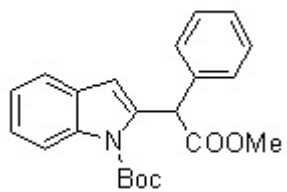
125MHz, CDCl₃



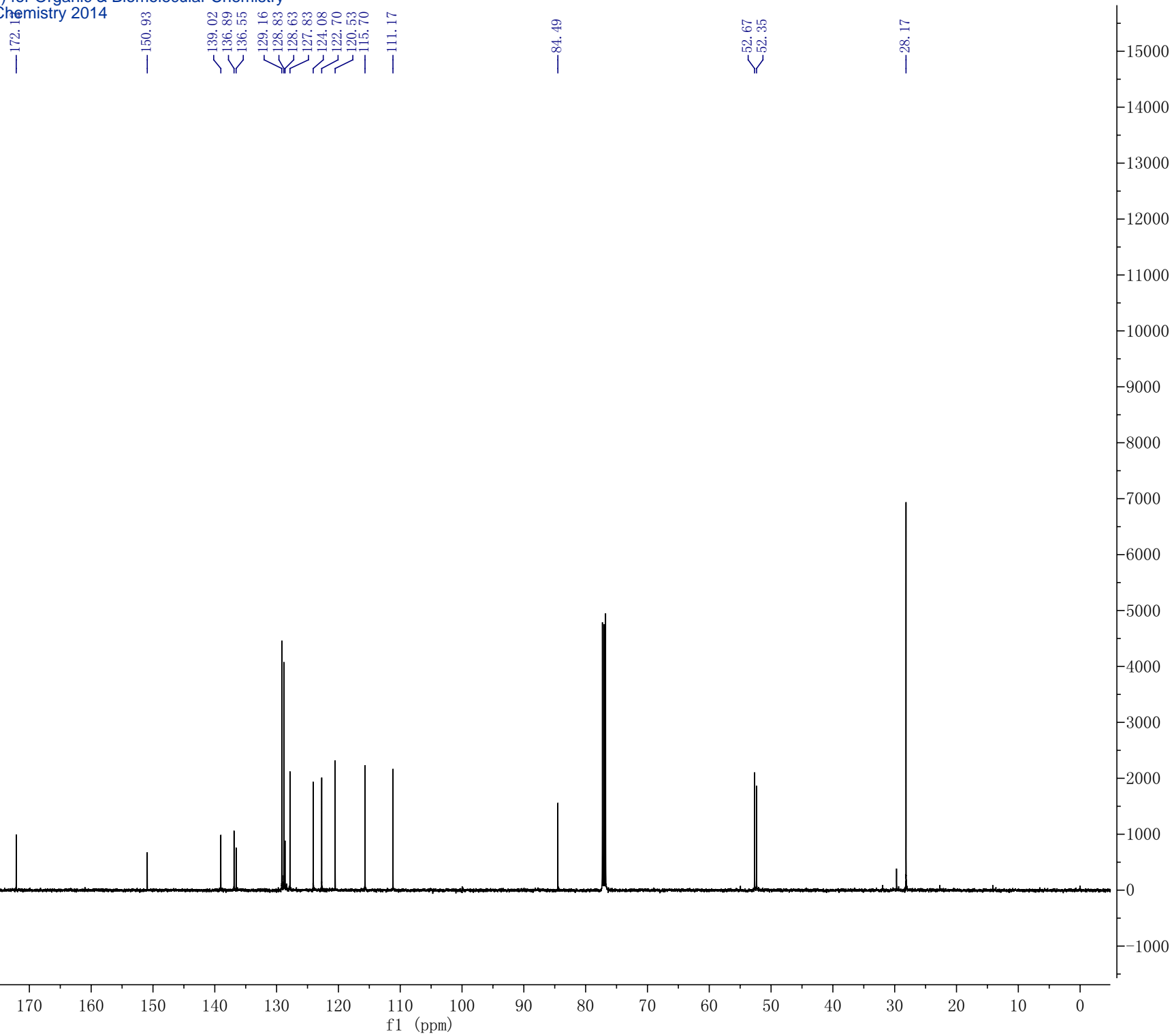


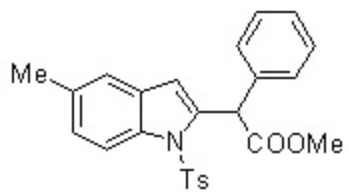
400MHz, CDCl₃



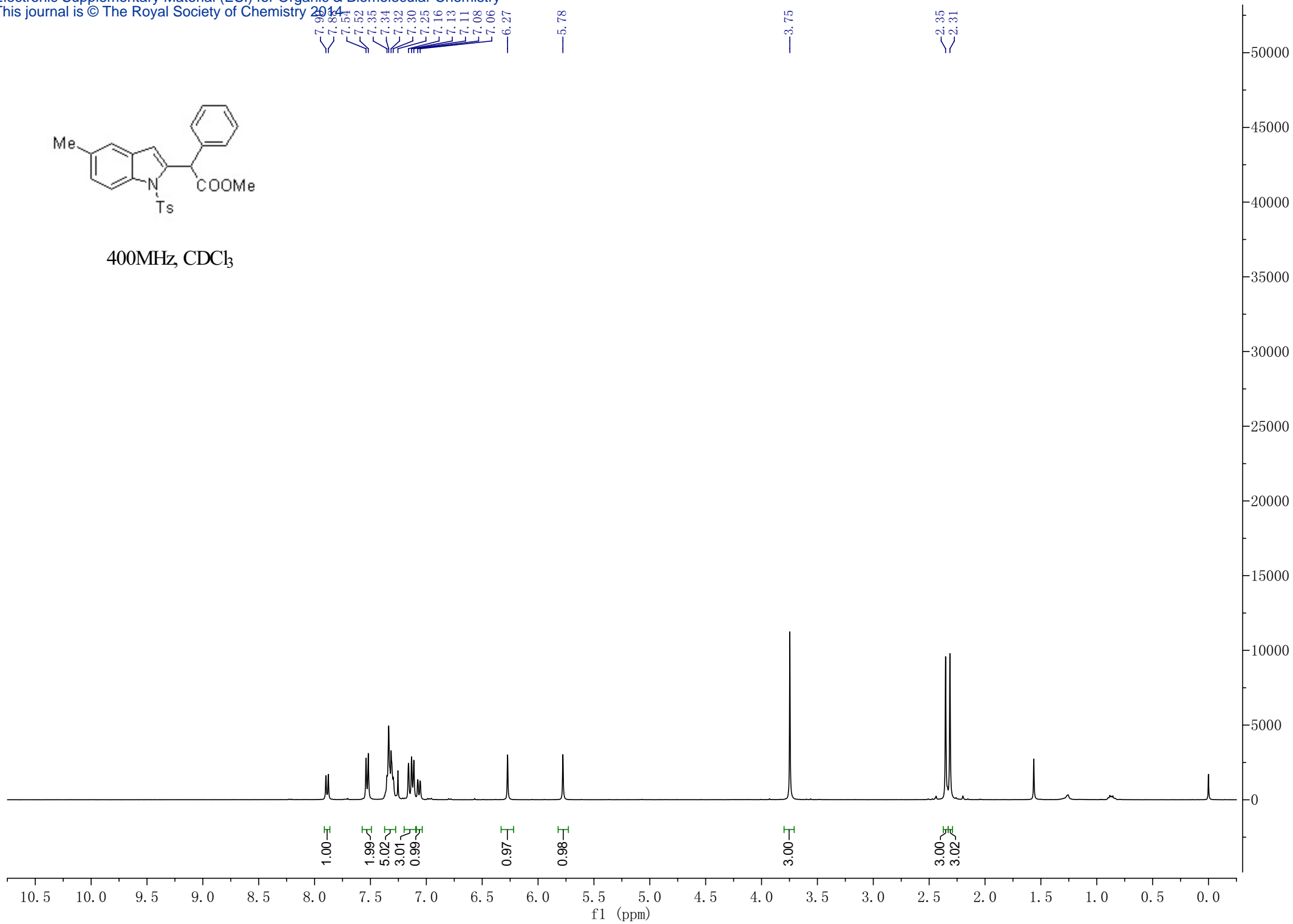


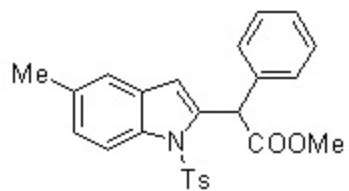
125MHz, CDCl₃



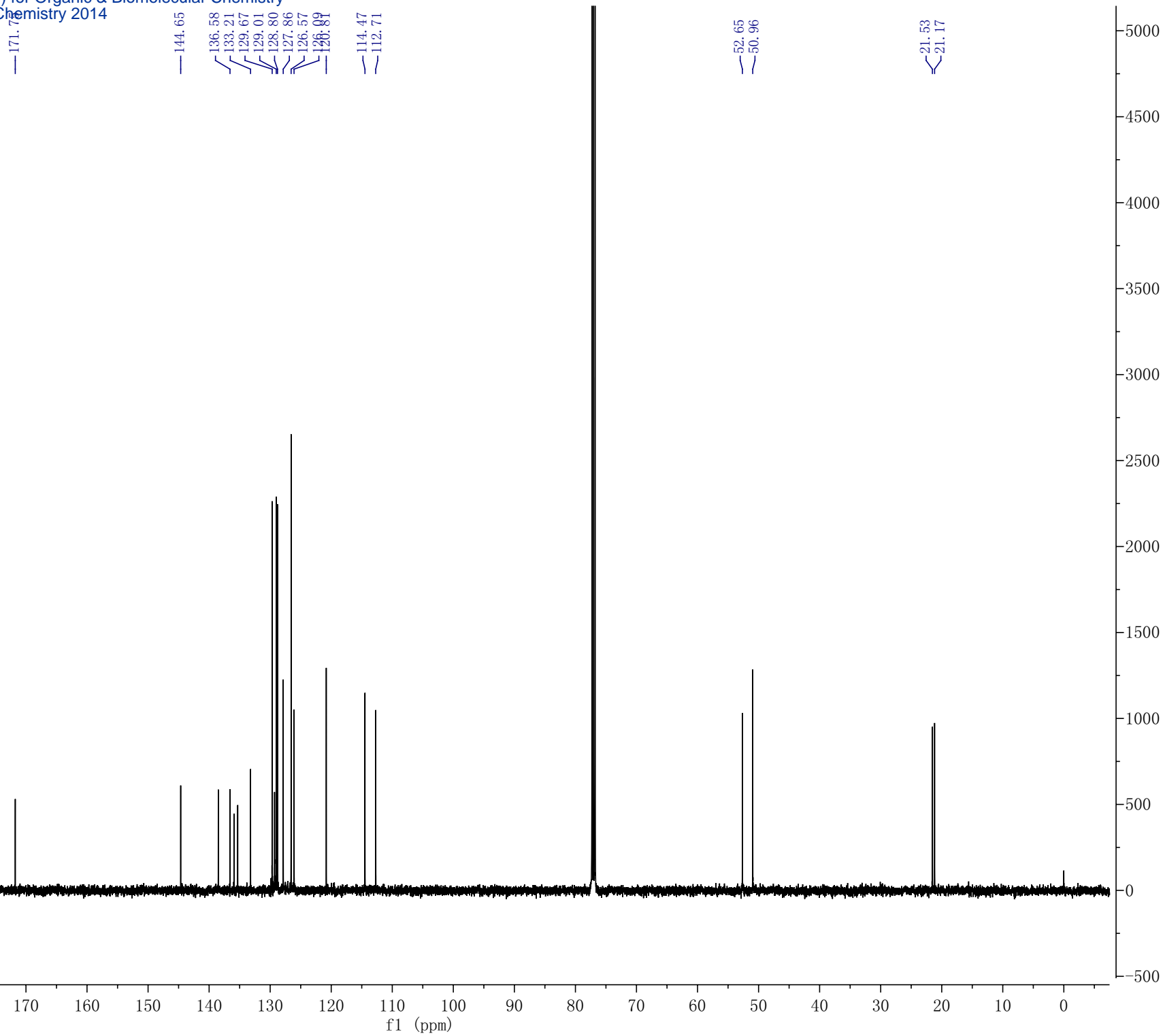


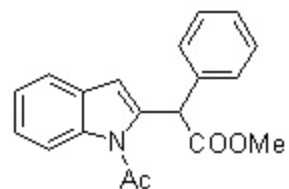
400MHz, CDCl₃



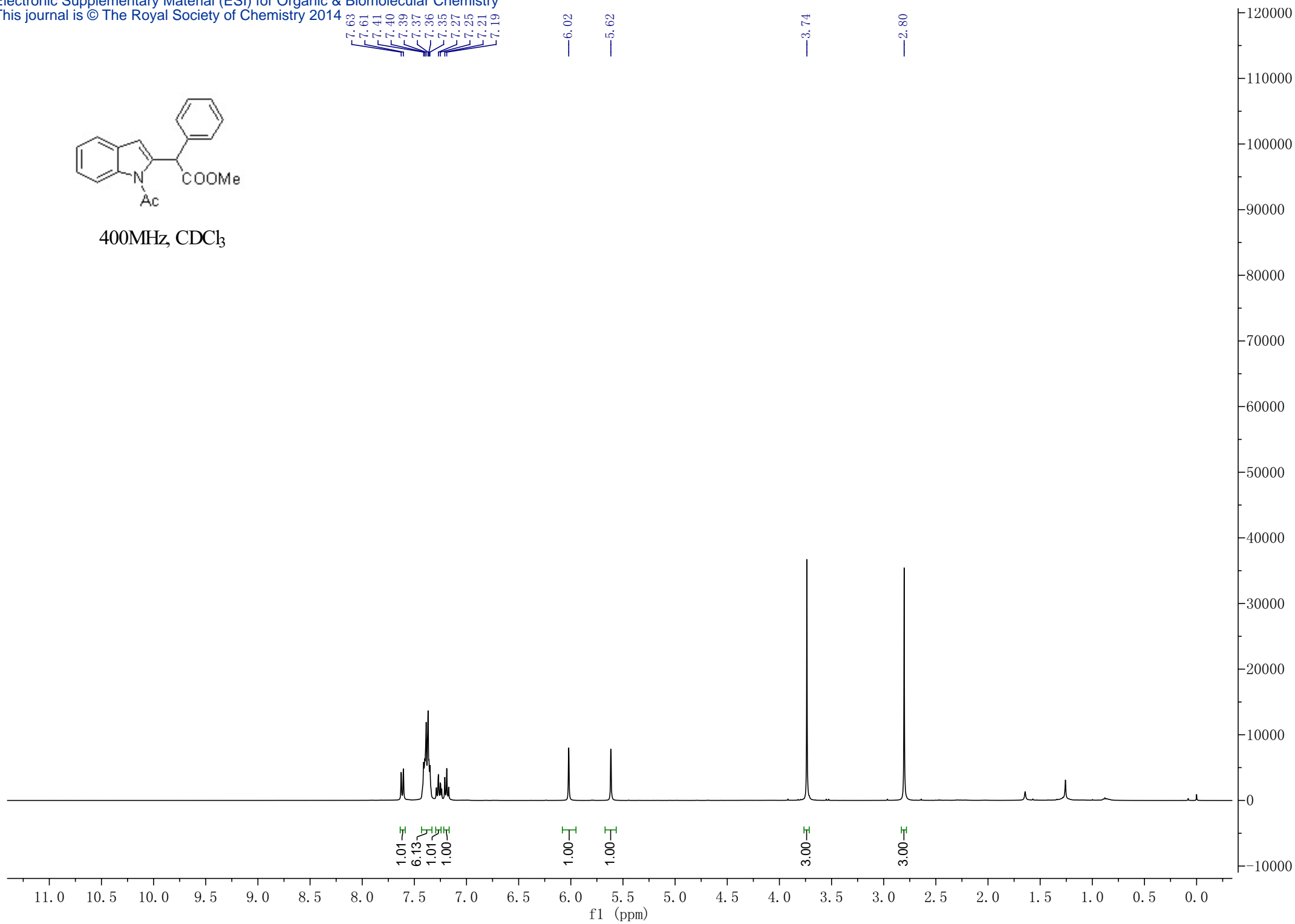


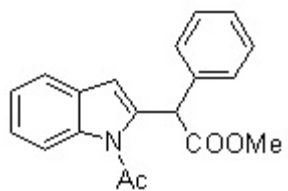
125MHz, CDCl₃



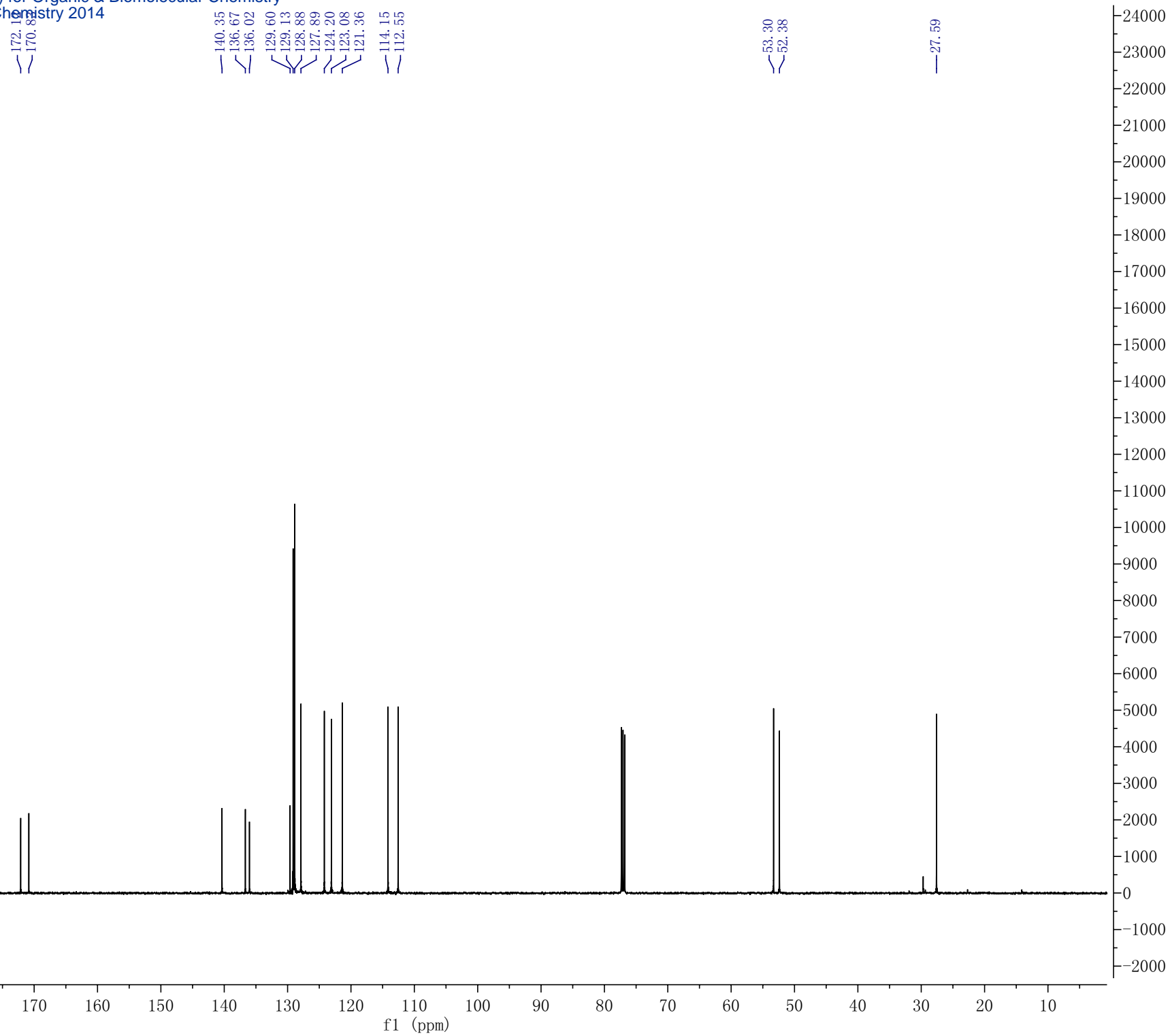


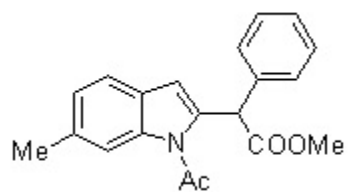
400MHz, CDCl₃



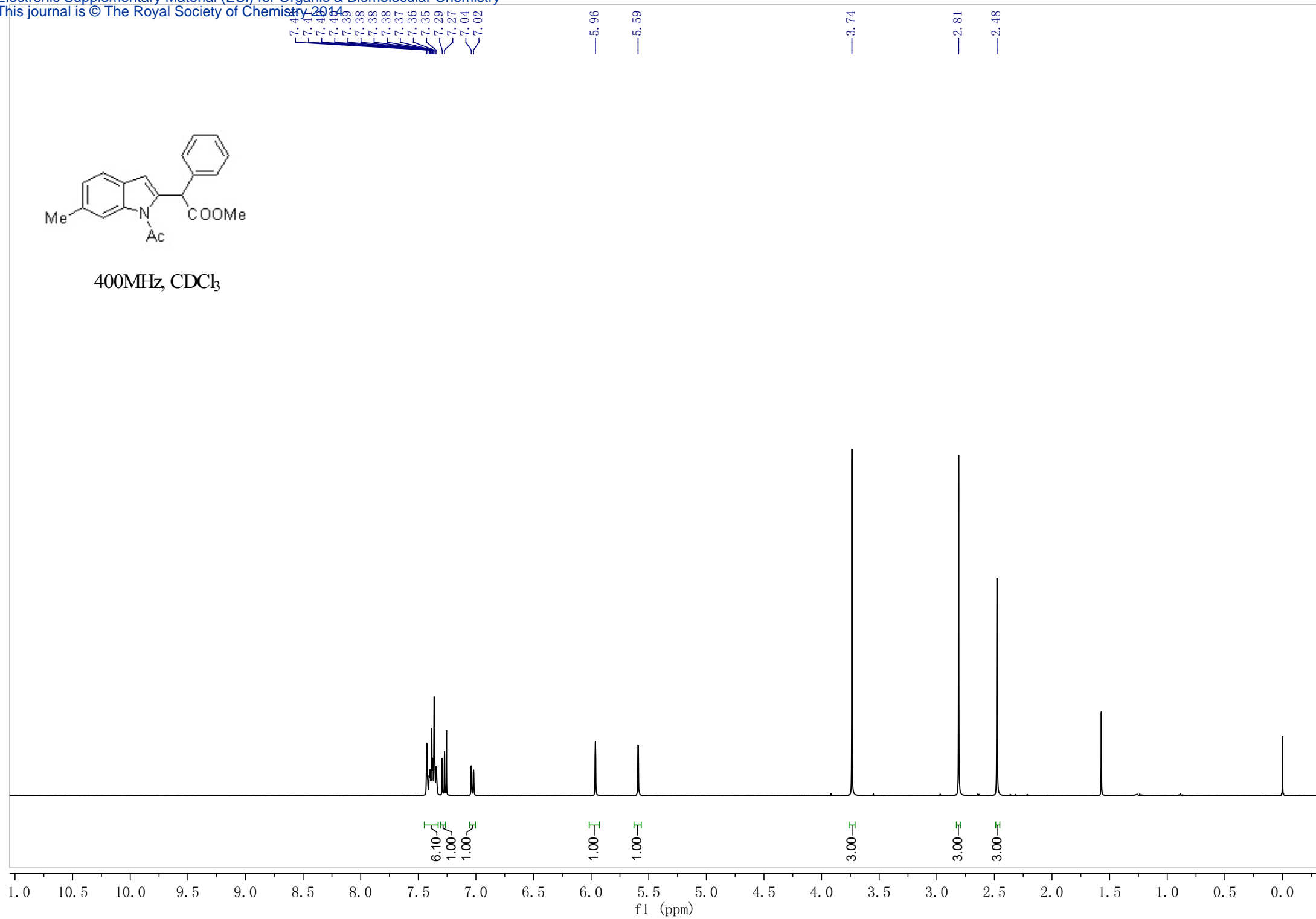


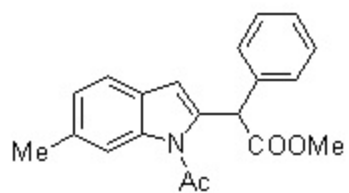
125MHz, CDCl₃





400MHz, CDCl₃



125MHz, CDCl₃

172.23
170.81
139.66
136.78
136.45
134.08
129.14
128.84
127.84
127.36
124.44
120.93
114.60
112.43

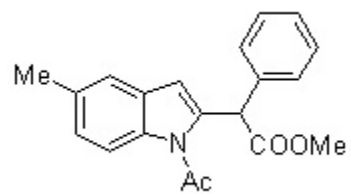
53.31
52.36

27.66

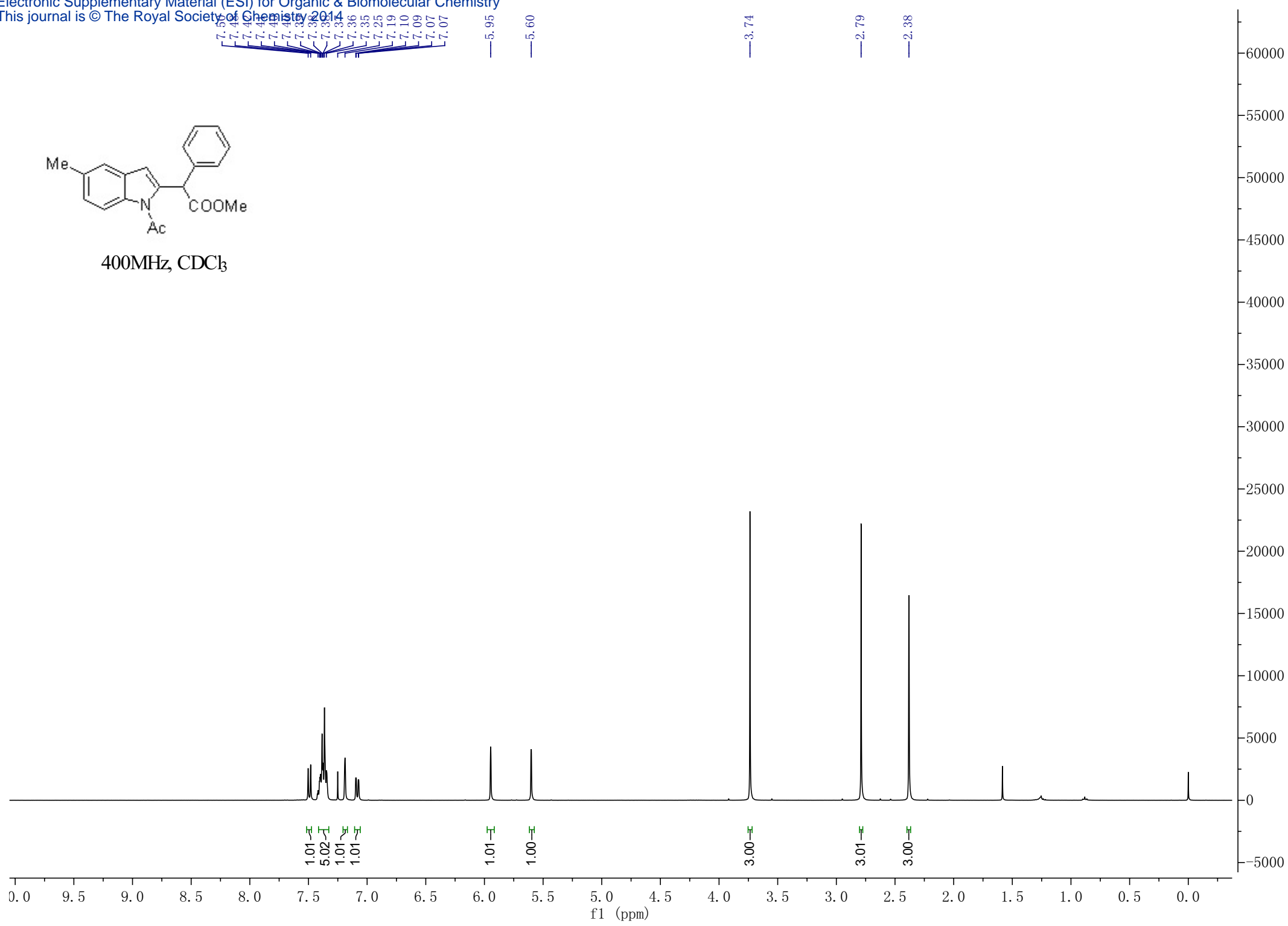
22.25

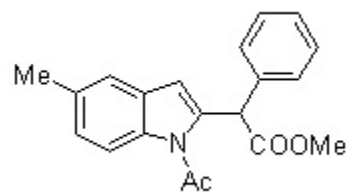
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

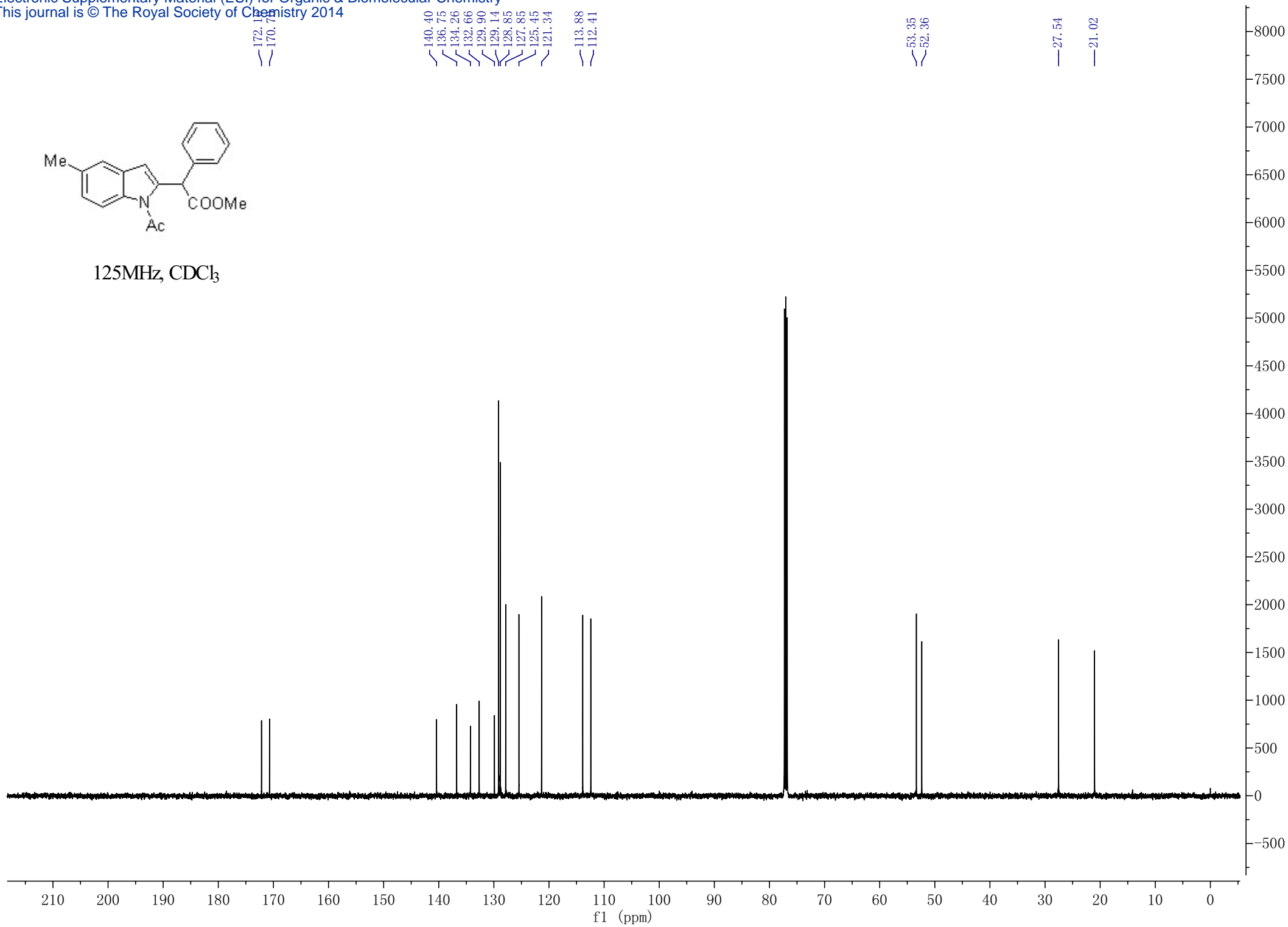


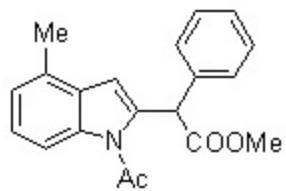
400MHz, CDCl₃



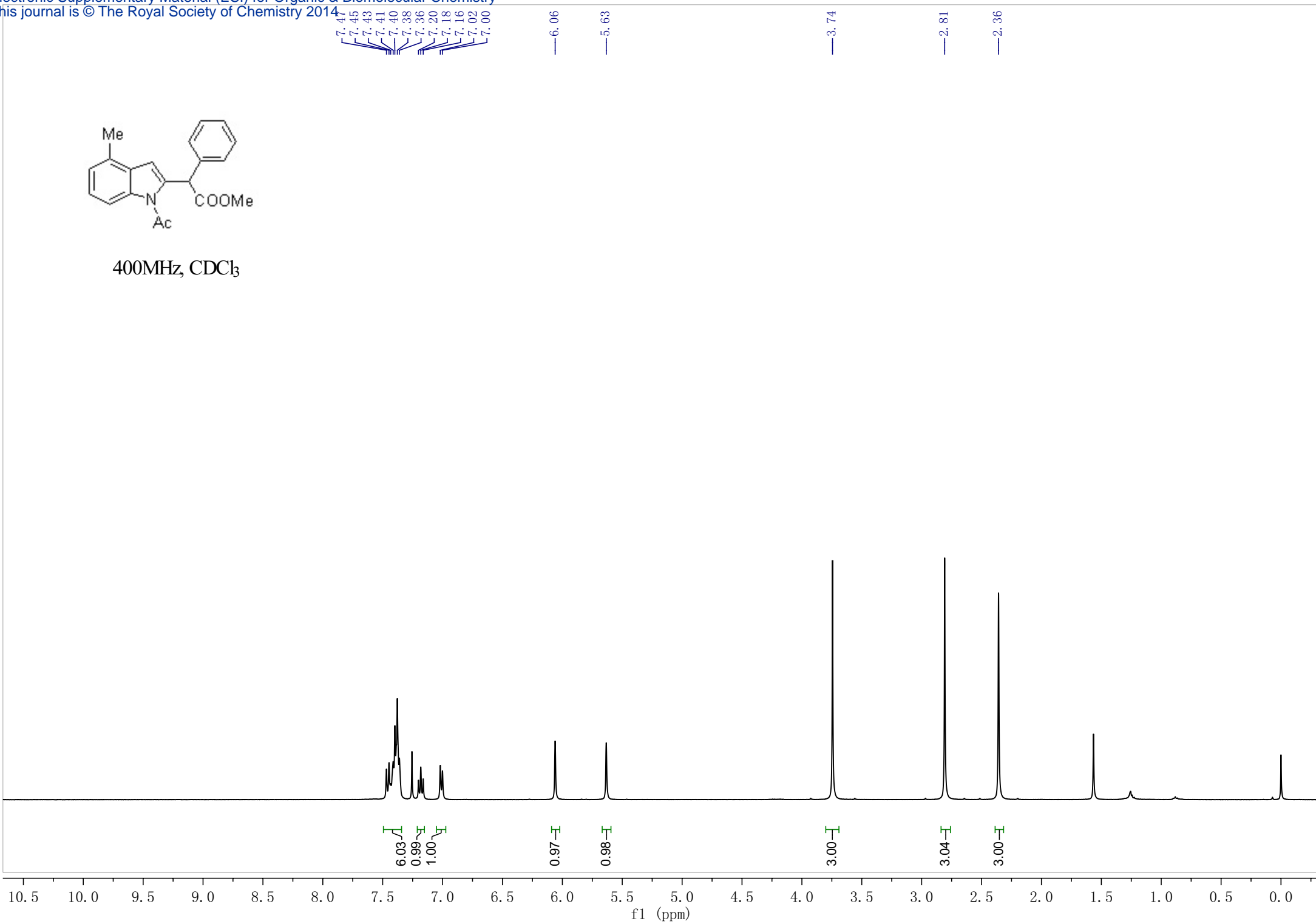


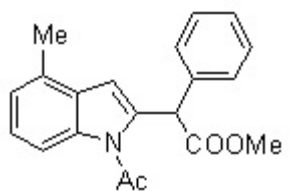
125MHz, CDCl₃



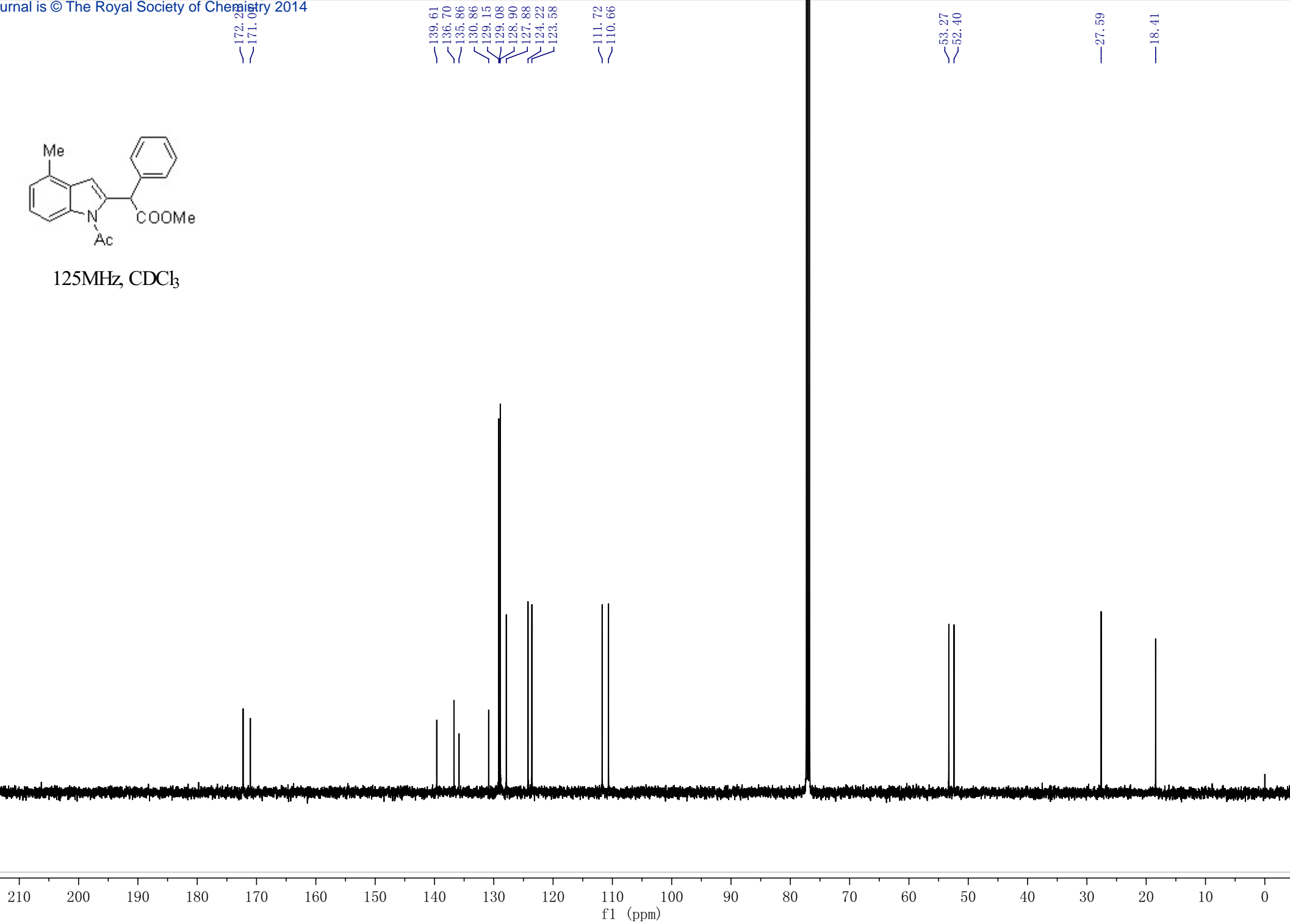


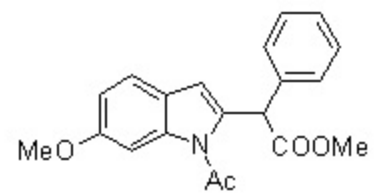
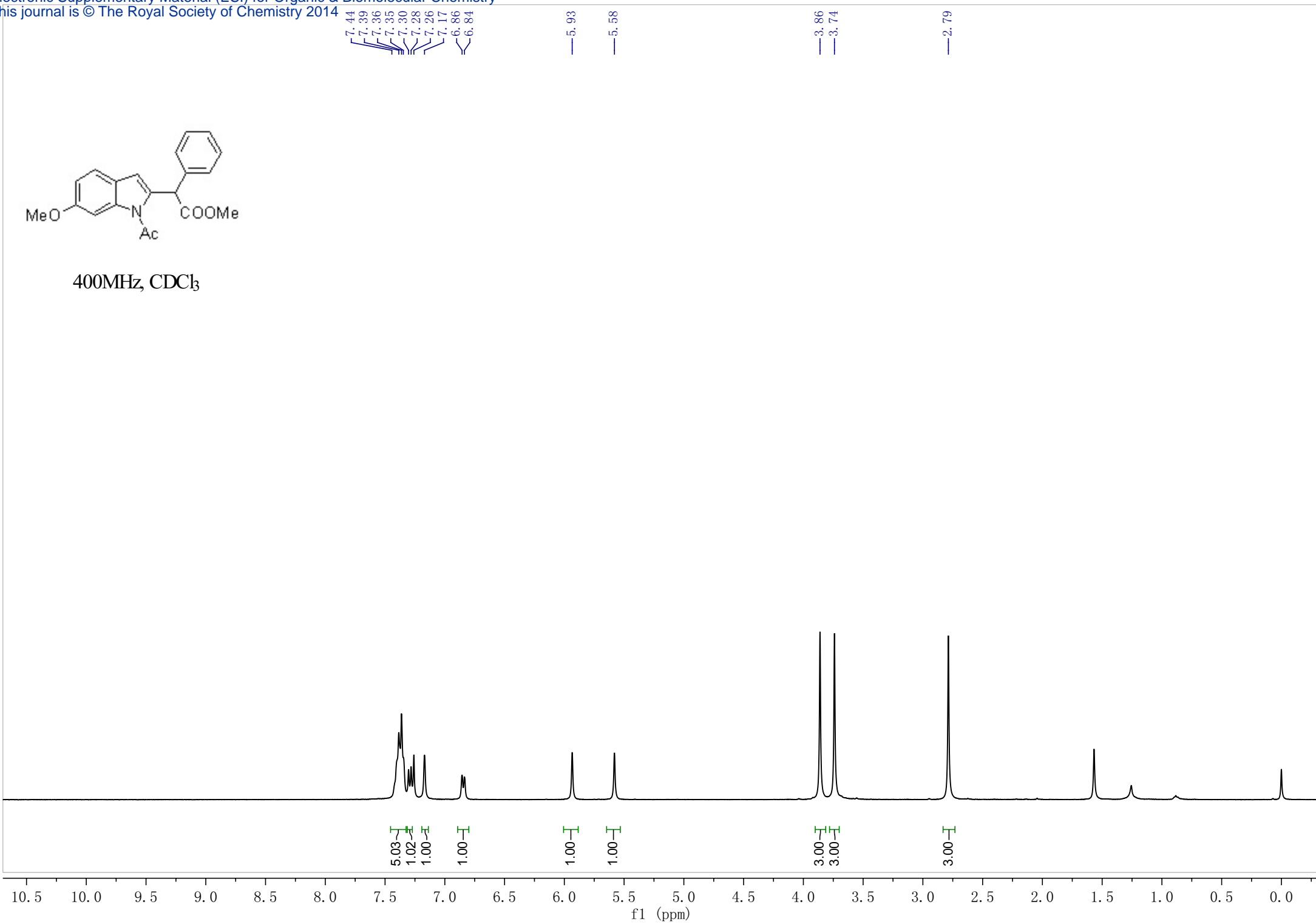
400MHz, CDCl₃

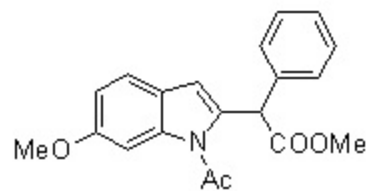




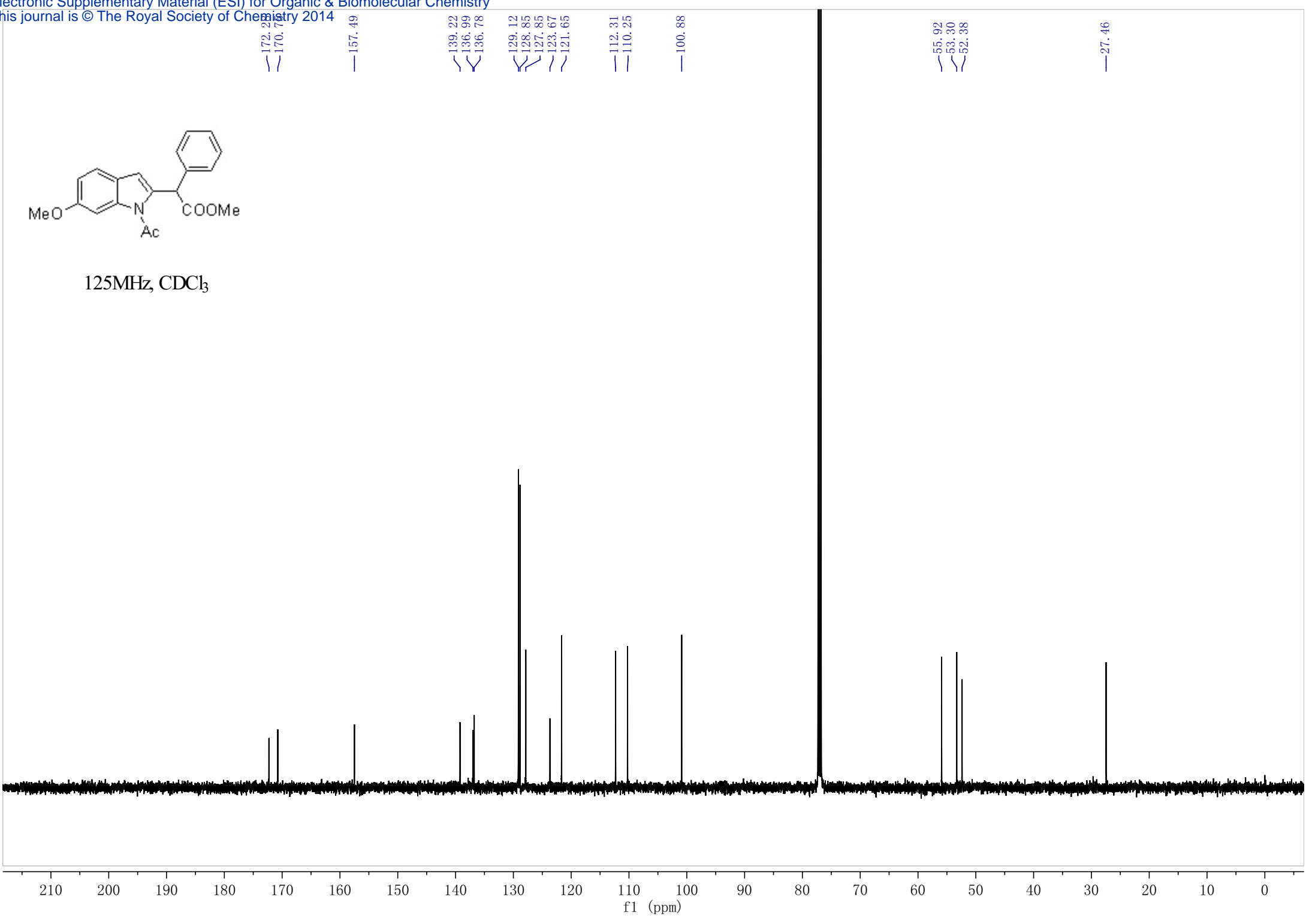
125MHz, CDCl₃

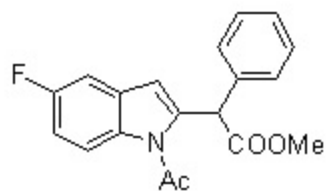


400MHz, CDCl₃

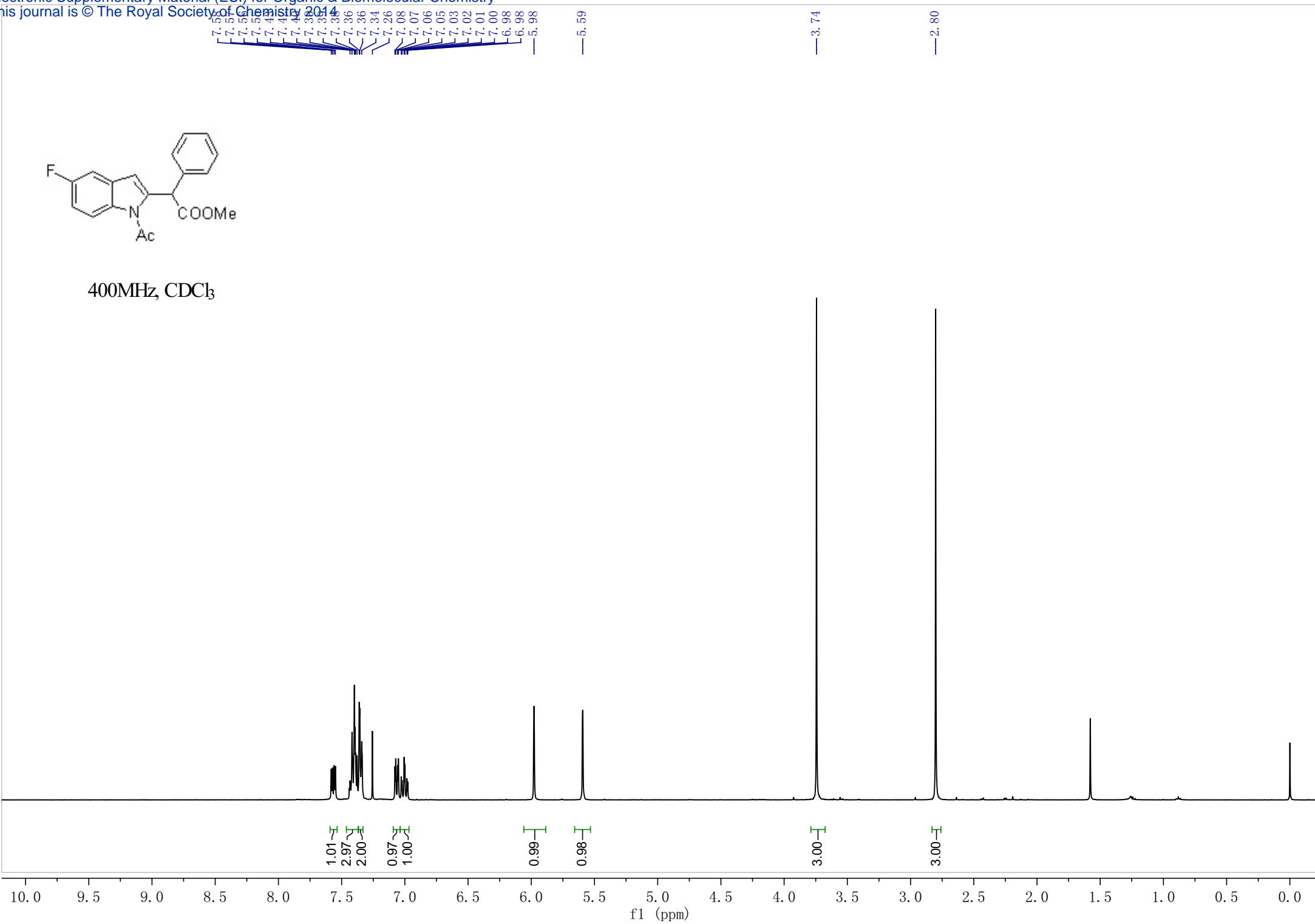


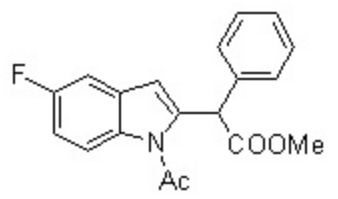
125MHz, CDCl₃



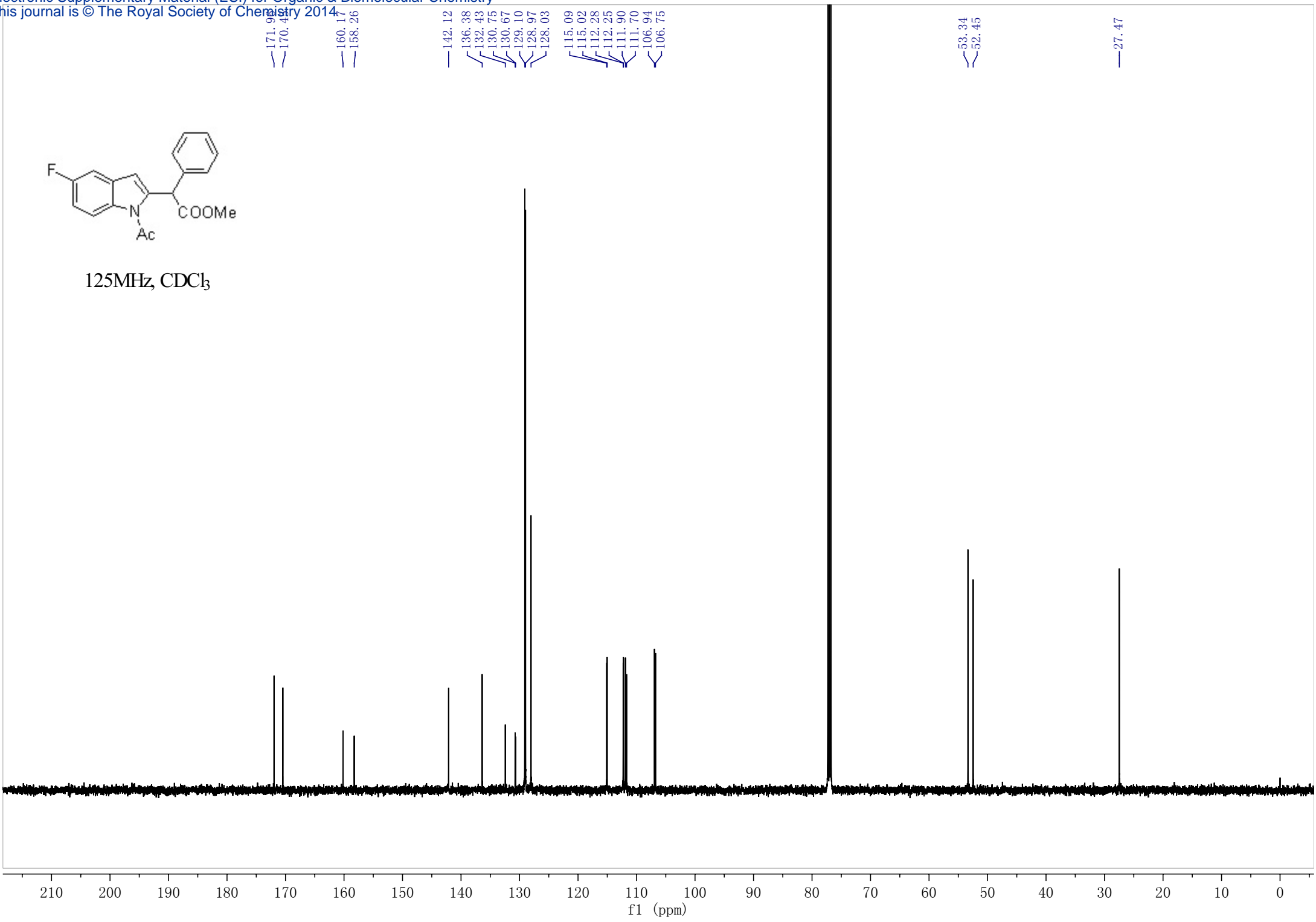


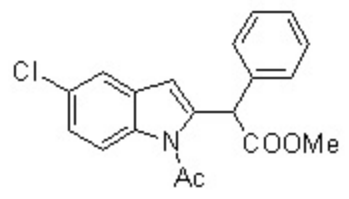
400MHz, CDCl₃



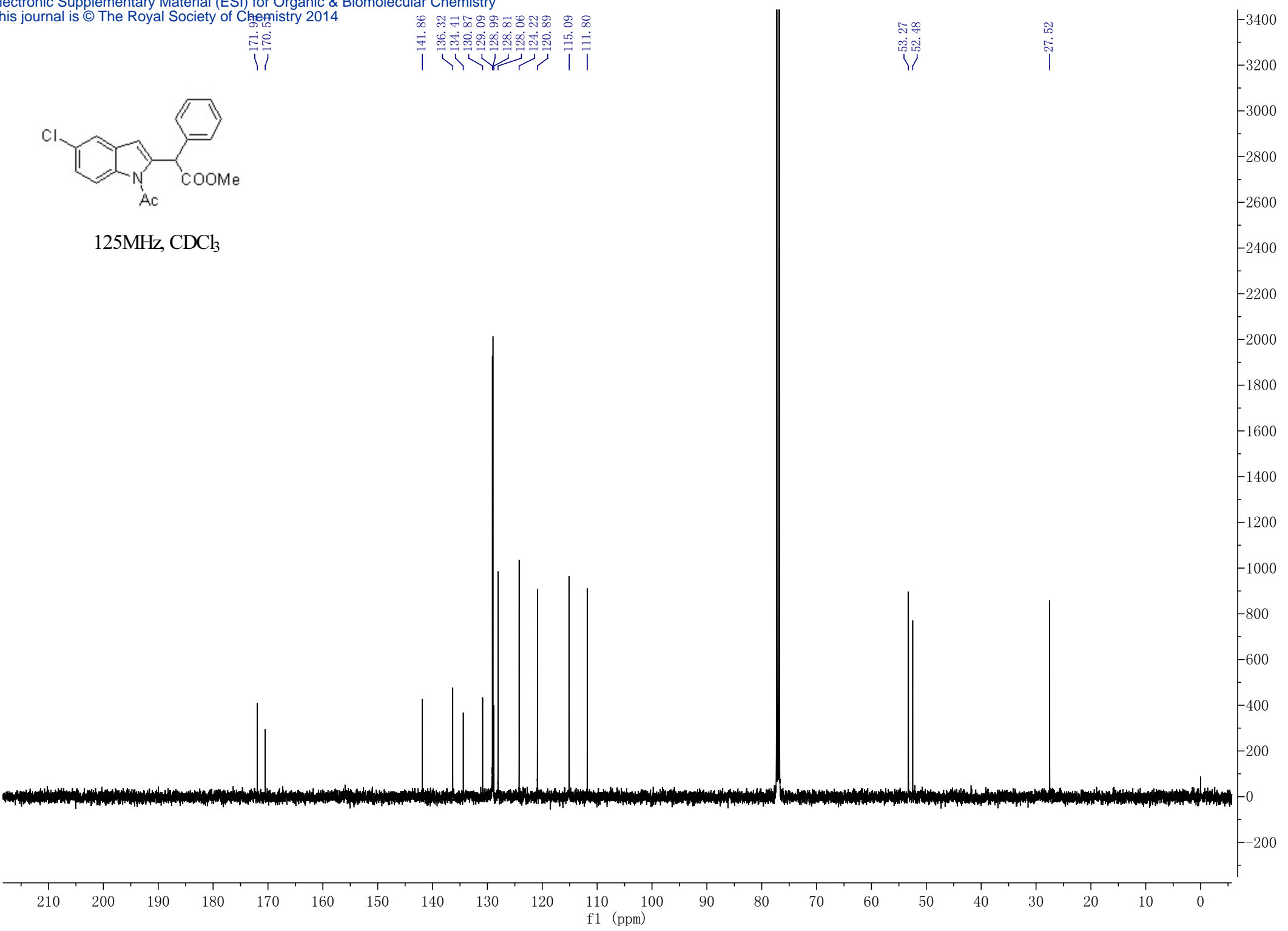


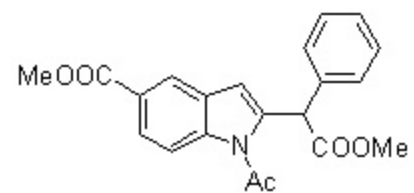
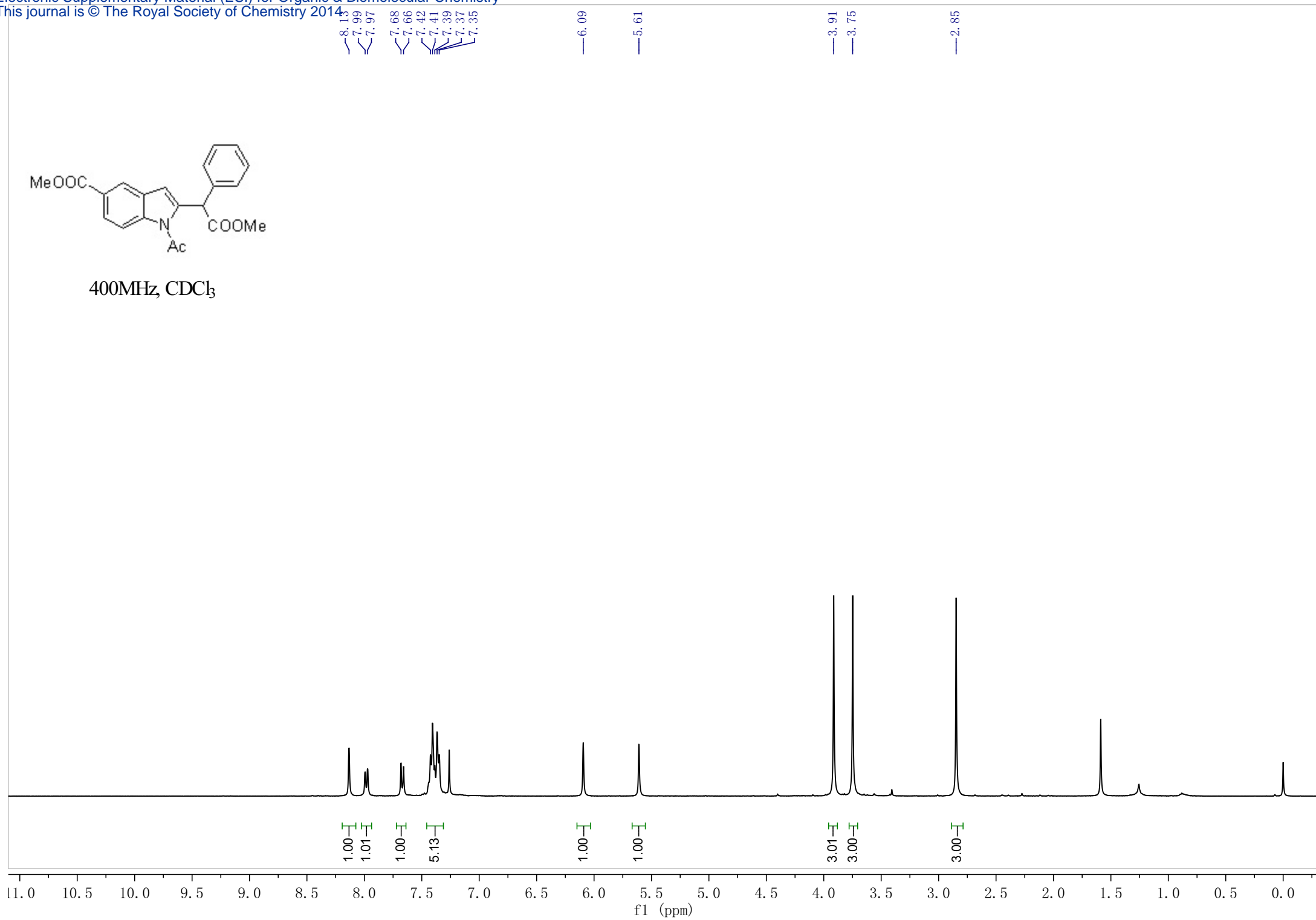
125MHz, CDCl₃

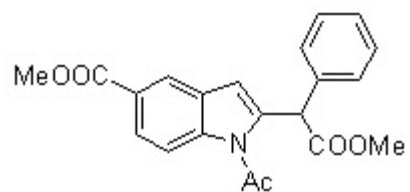
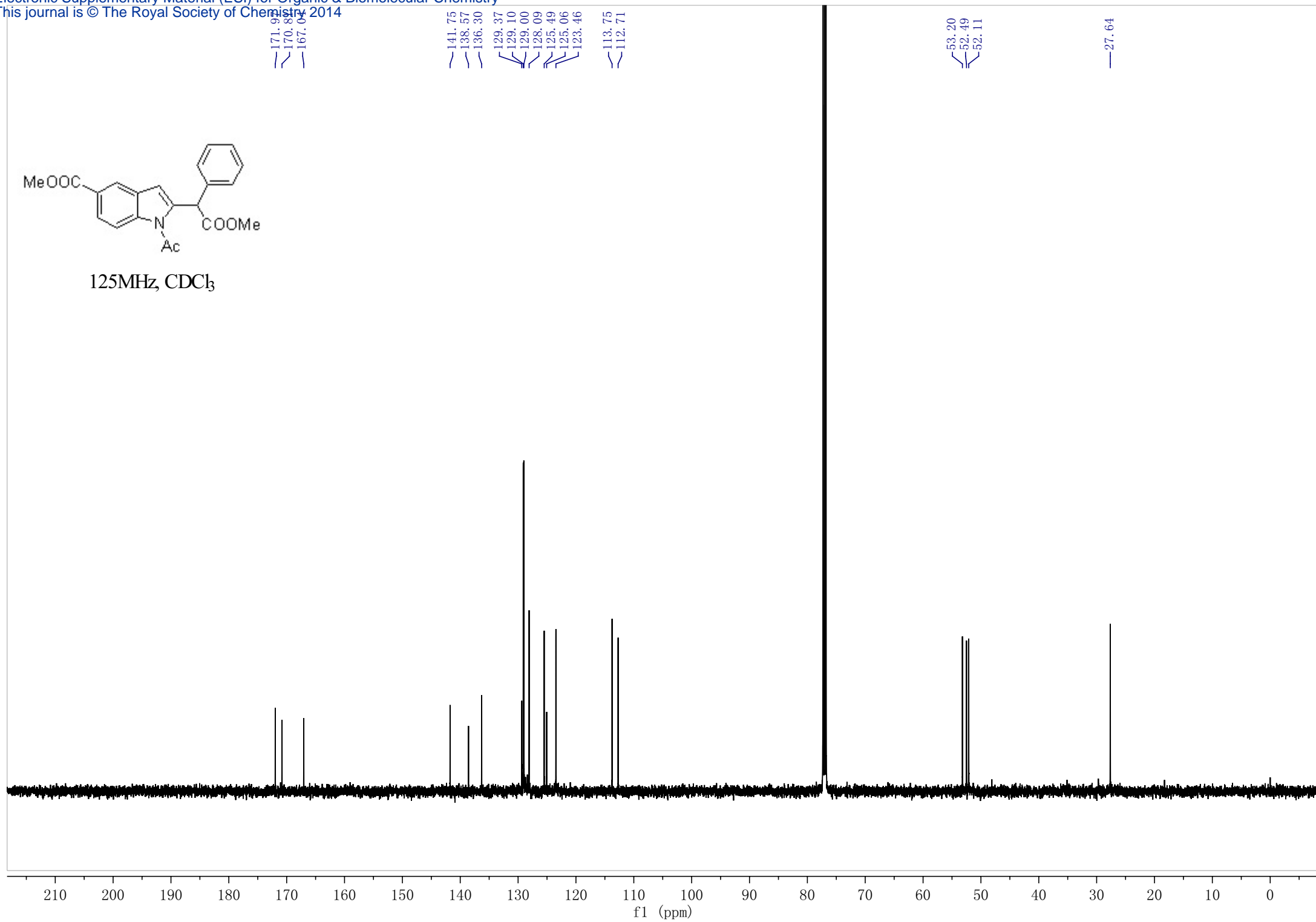


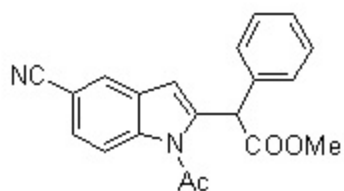


125MHz, CDCl₃



400MHz, CDCl₃

125MHz, CDCl₃



400MHz, CDCl₃

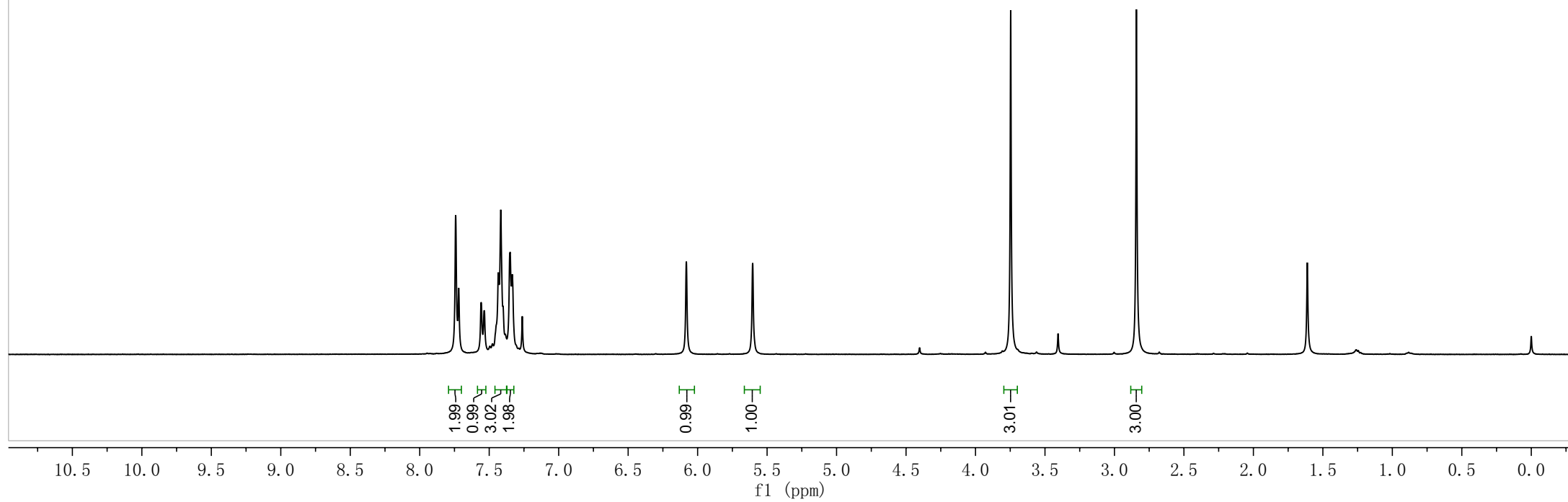
7.74
7.72
7.56
7.54
7.43
7.42
7.35
7.33

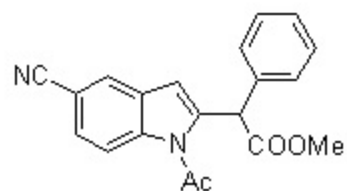
6.08

5.60

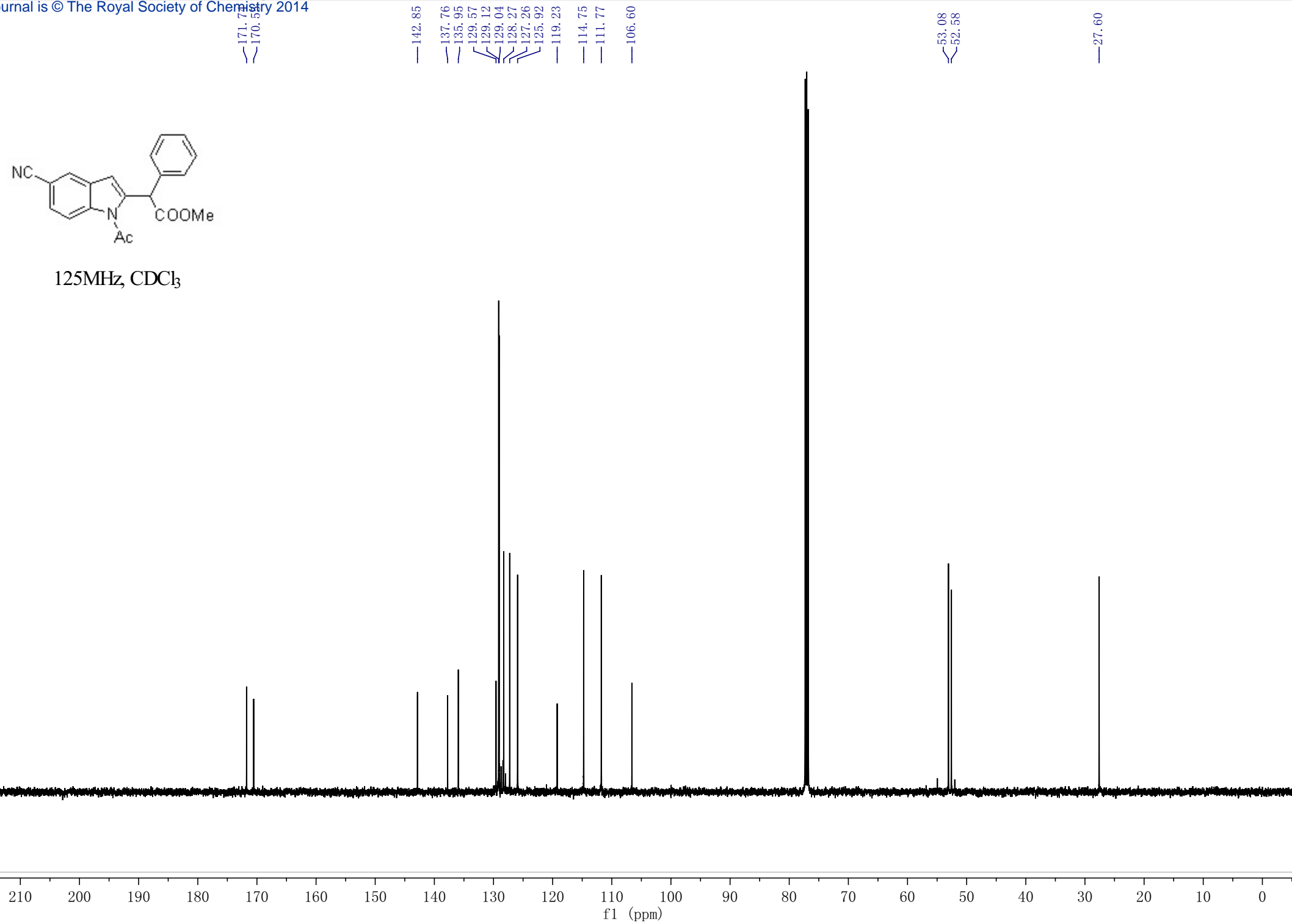
3.75

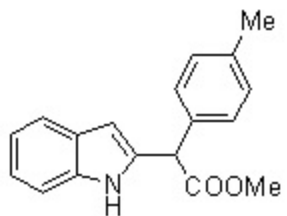
2.84



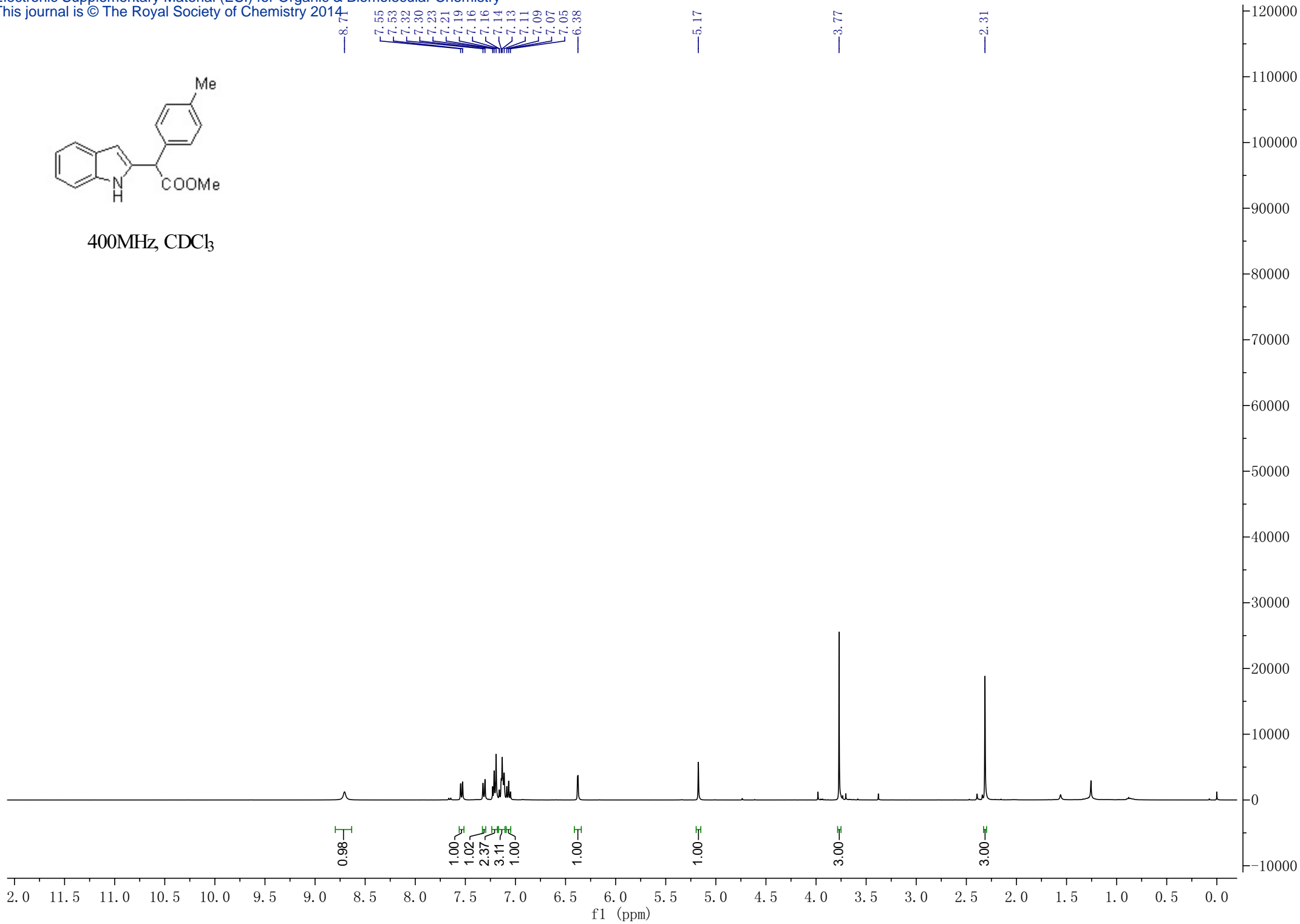


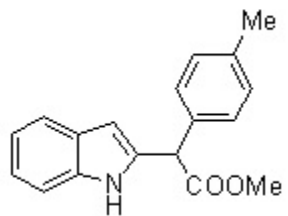
125MHz, CDCl₃



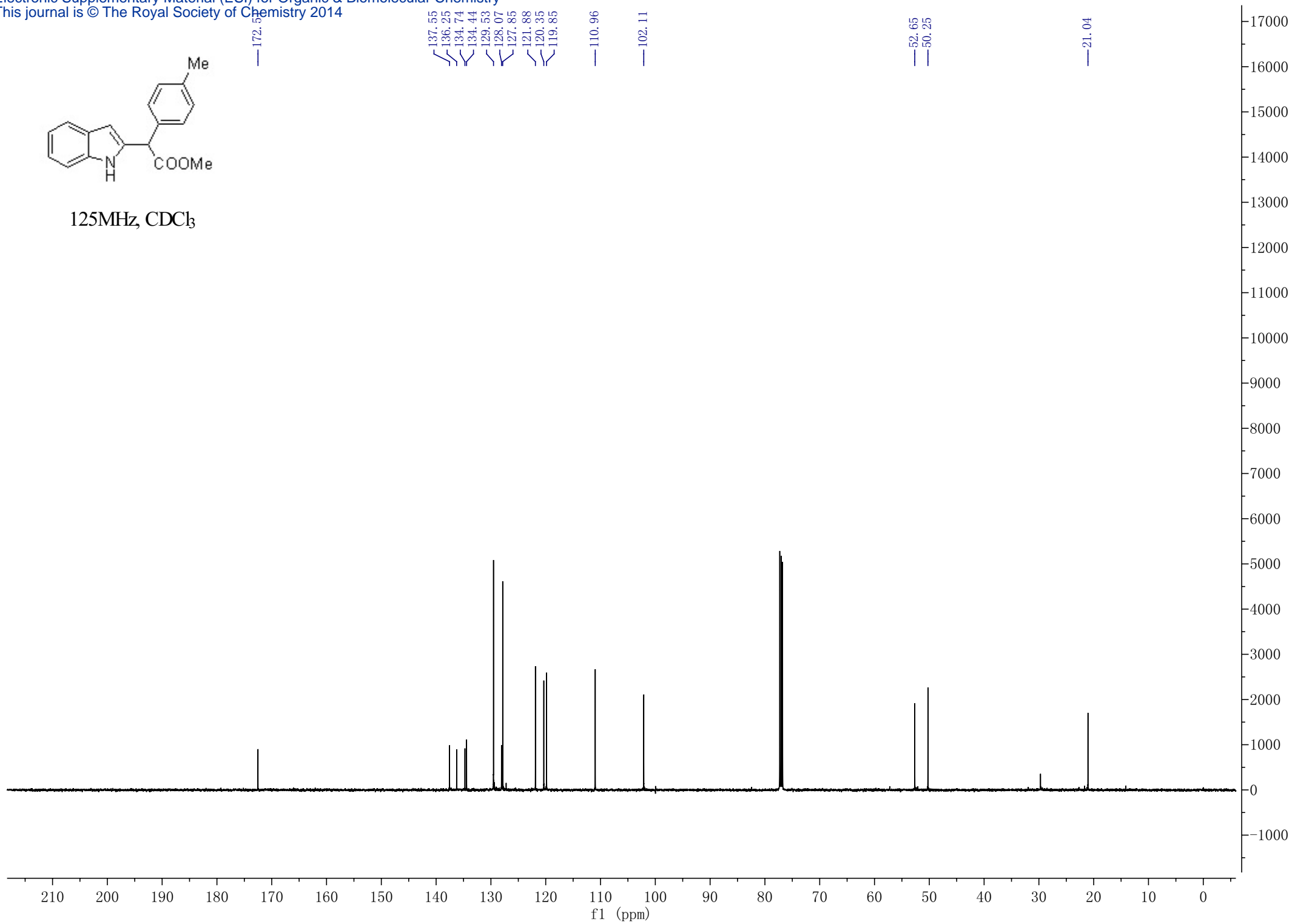


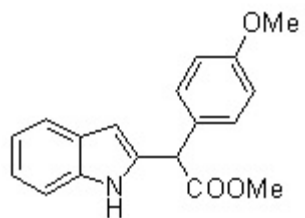
400MHz, CDCl₃



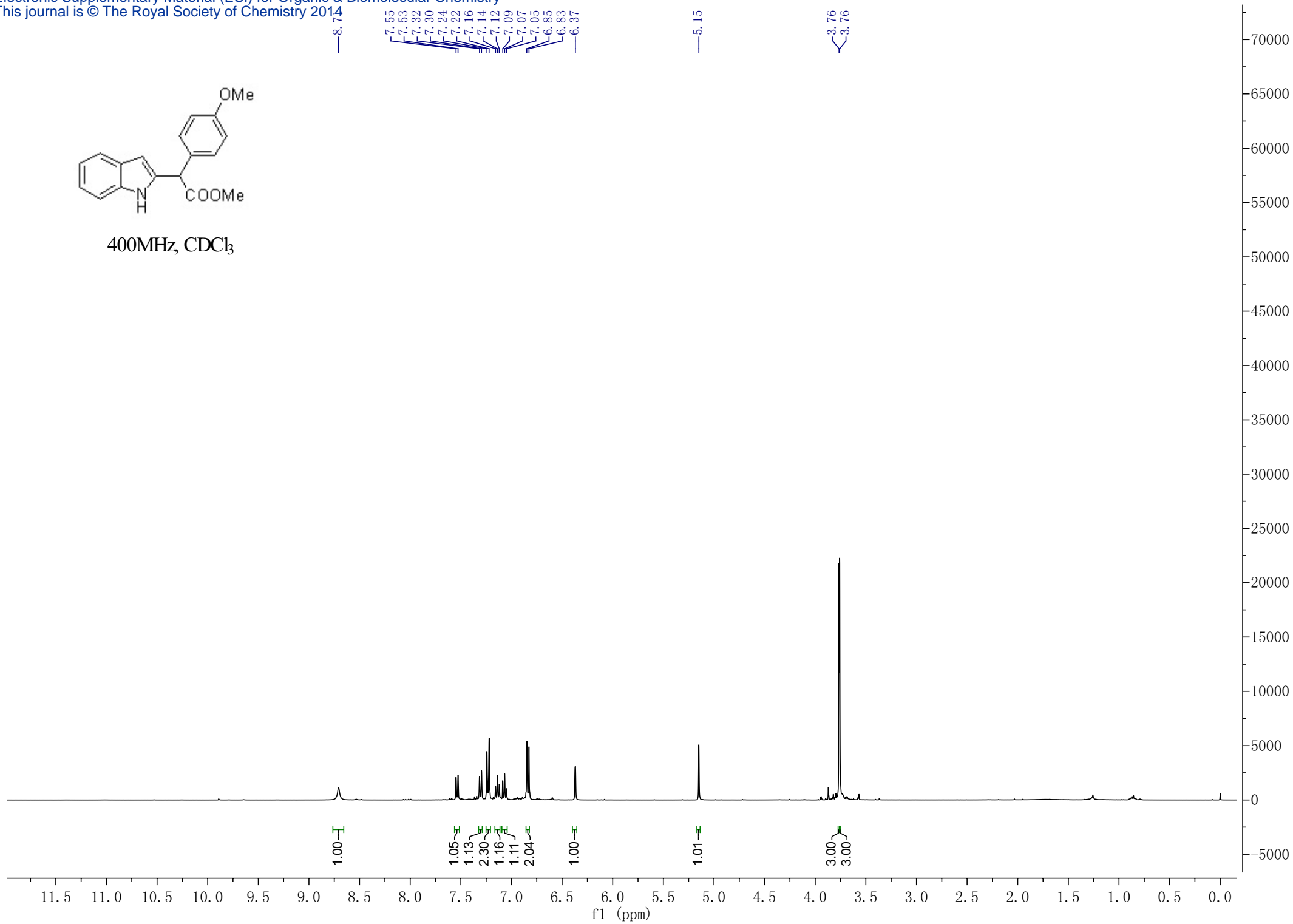


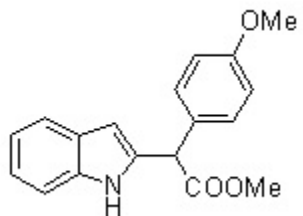
125MHz, CDCl₃



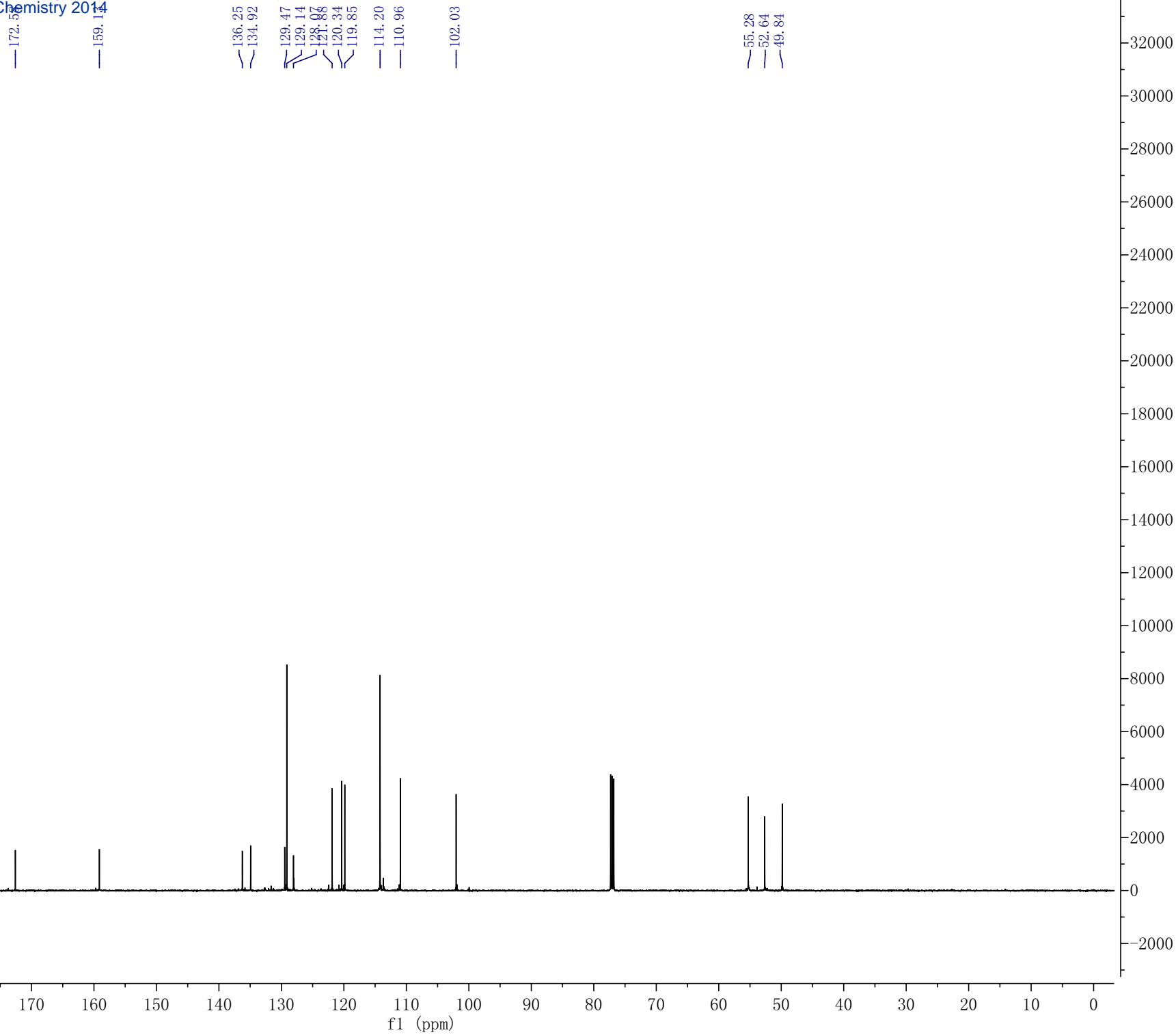


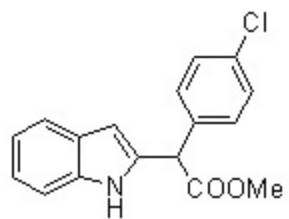
400MHz, CDCl₃



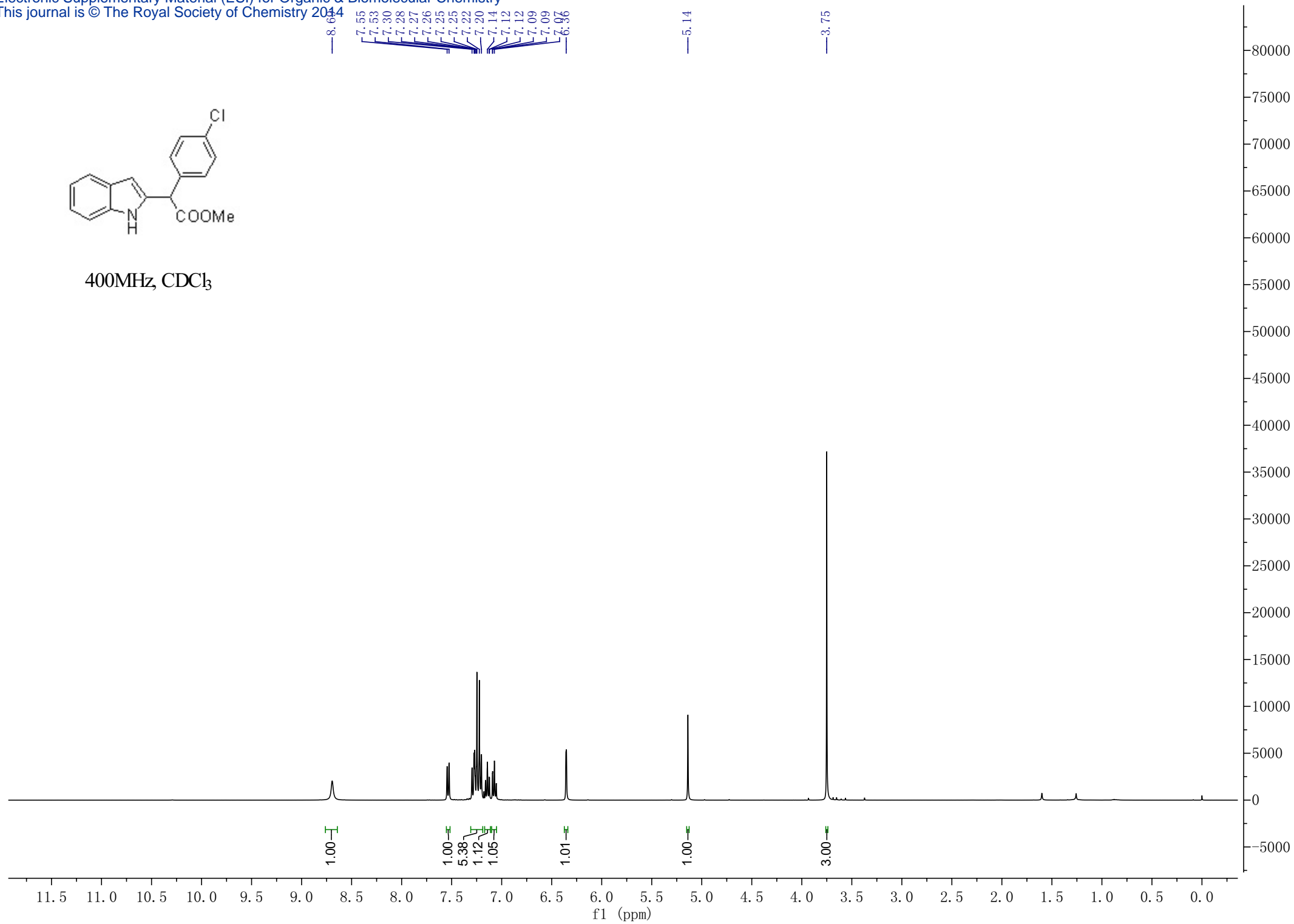


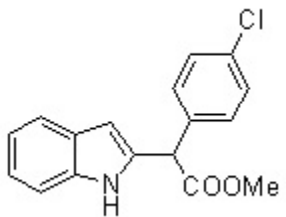
125MHz, CDCl₃



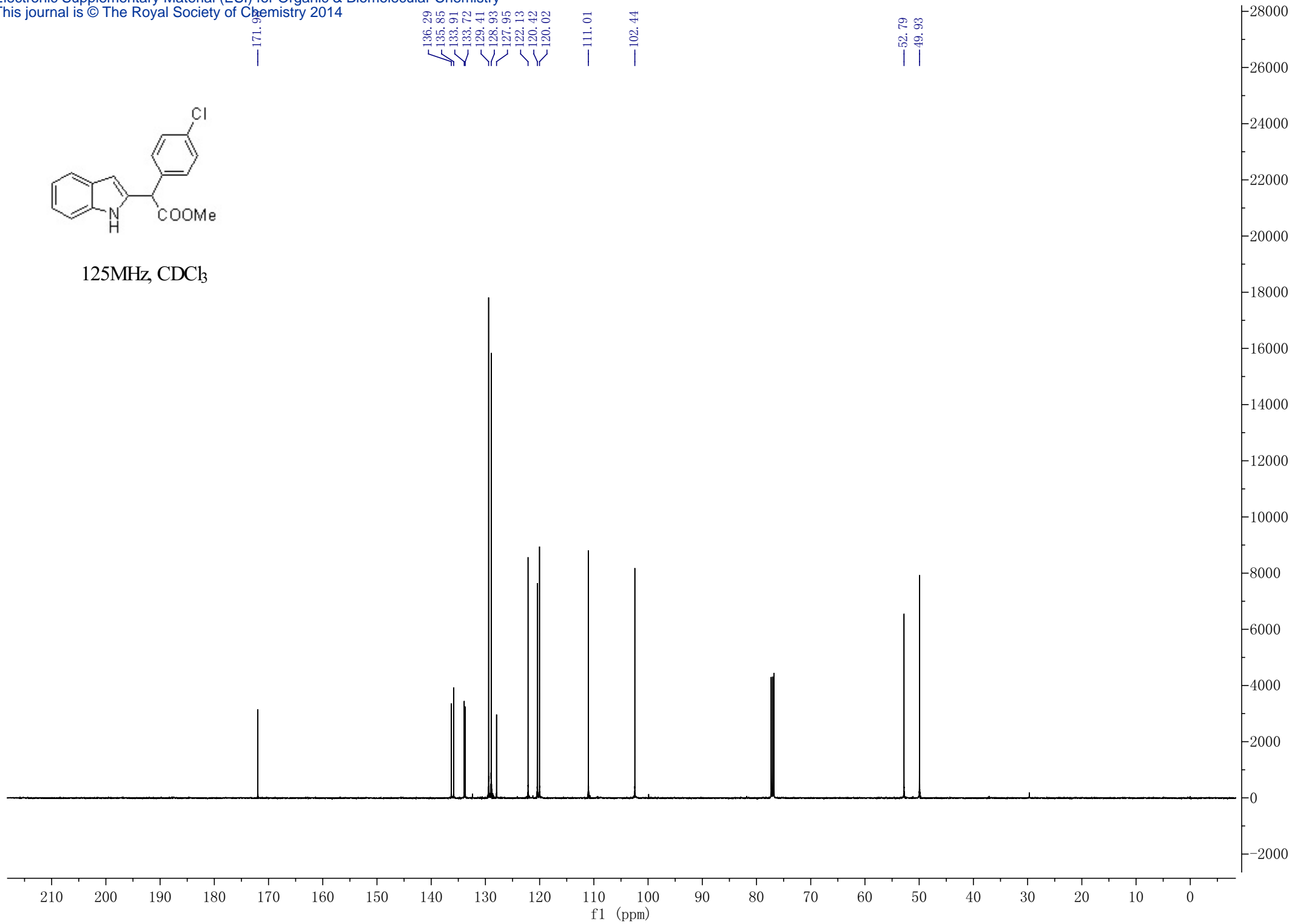


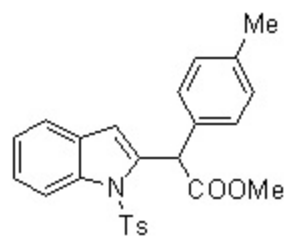
400MHz, CDCl₃



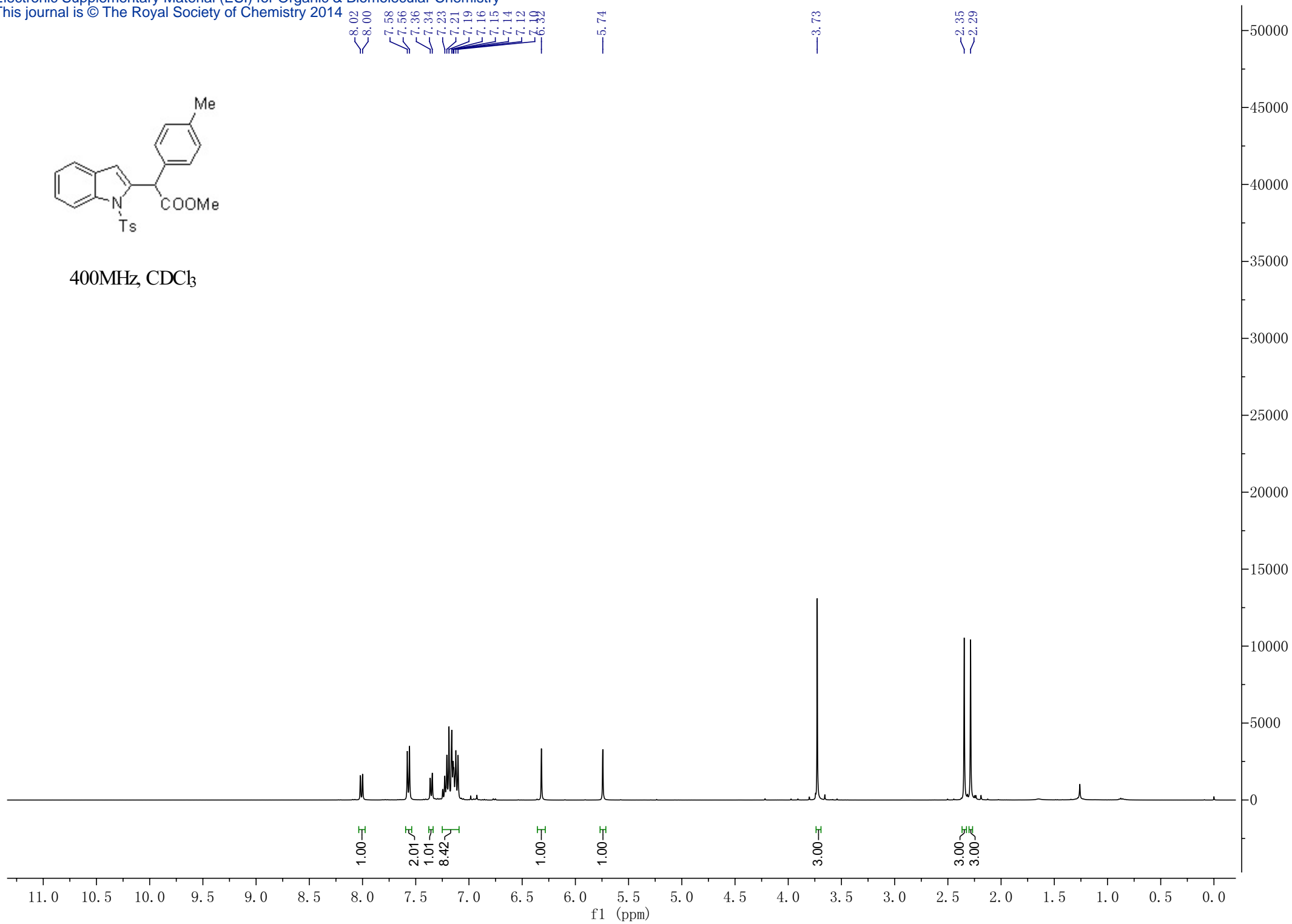


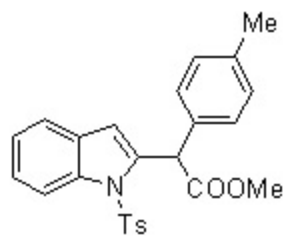
125MHz, CDCl₃



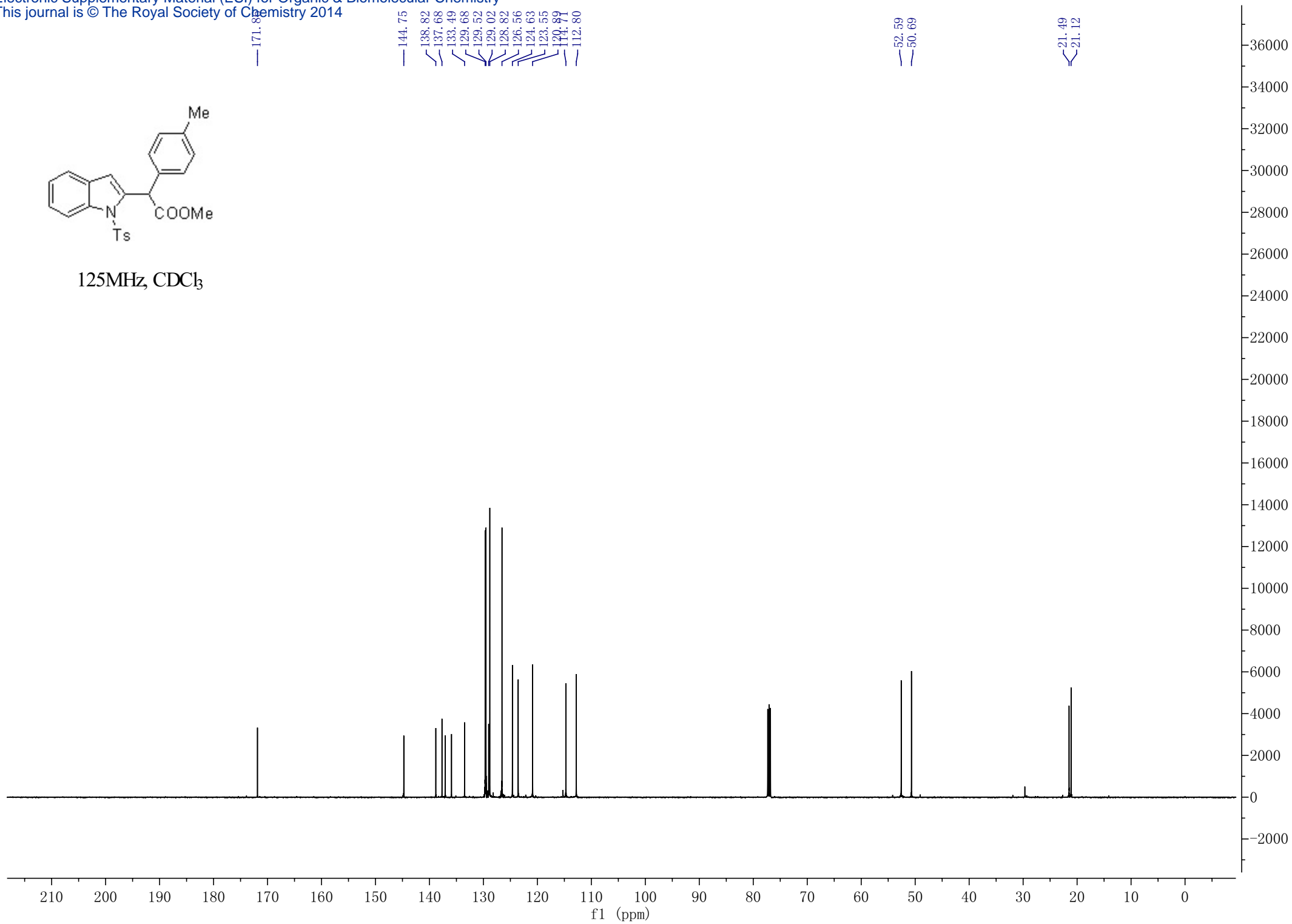


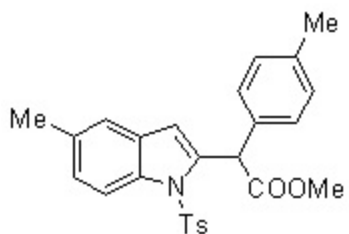
400MHz, CDCl₃



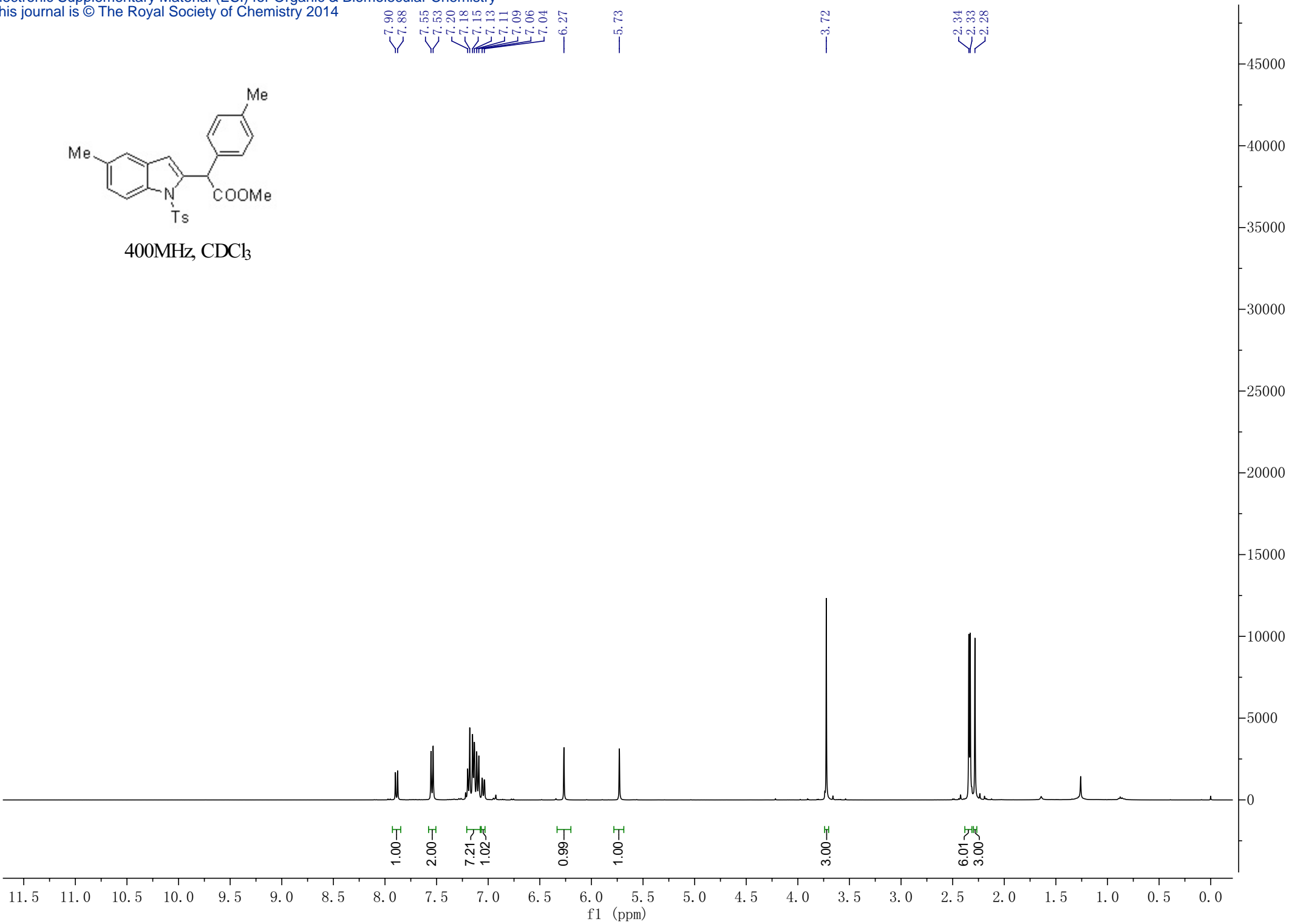


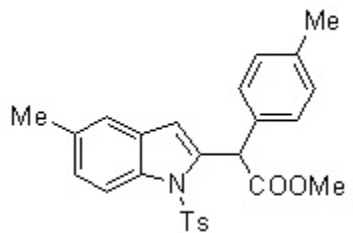
125MHz, CDCl₃



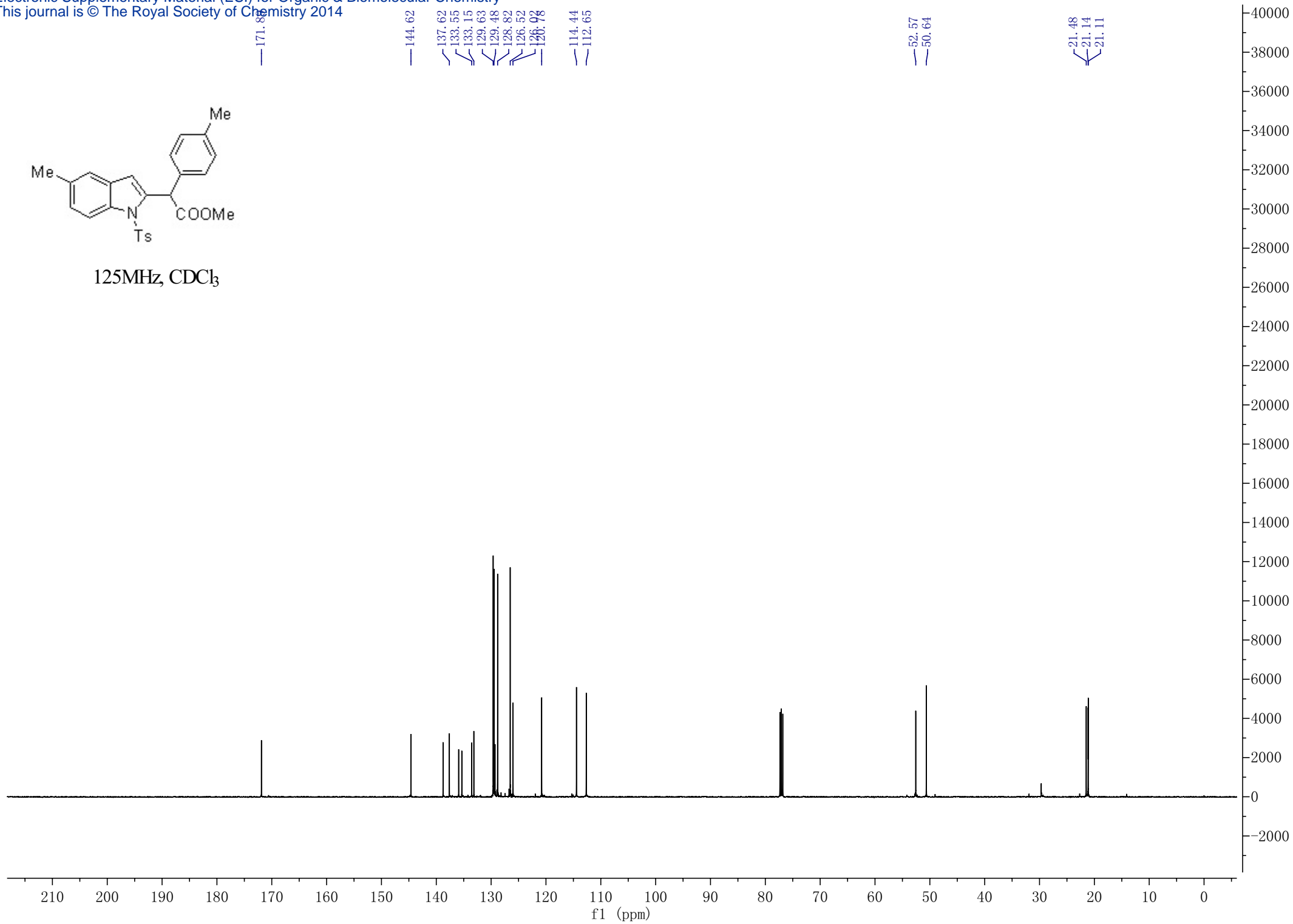


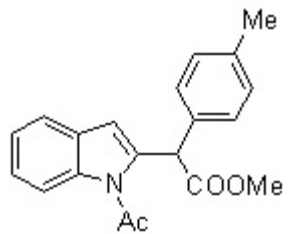
400MHz, CDCl₃



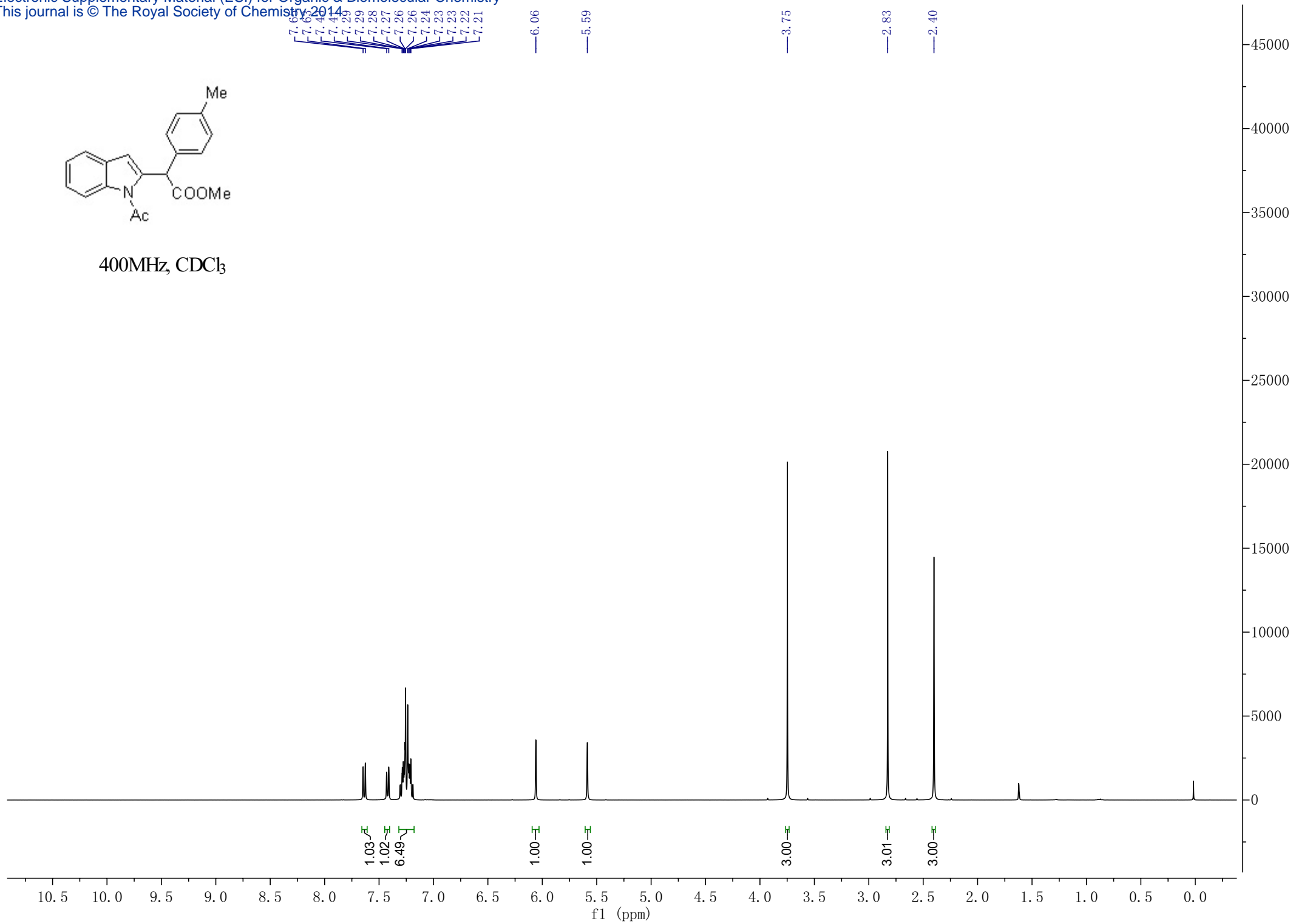


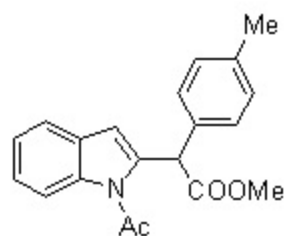
125MHz, CDCl₃



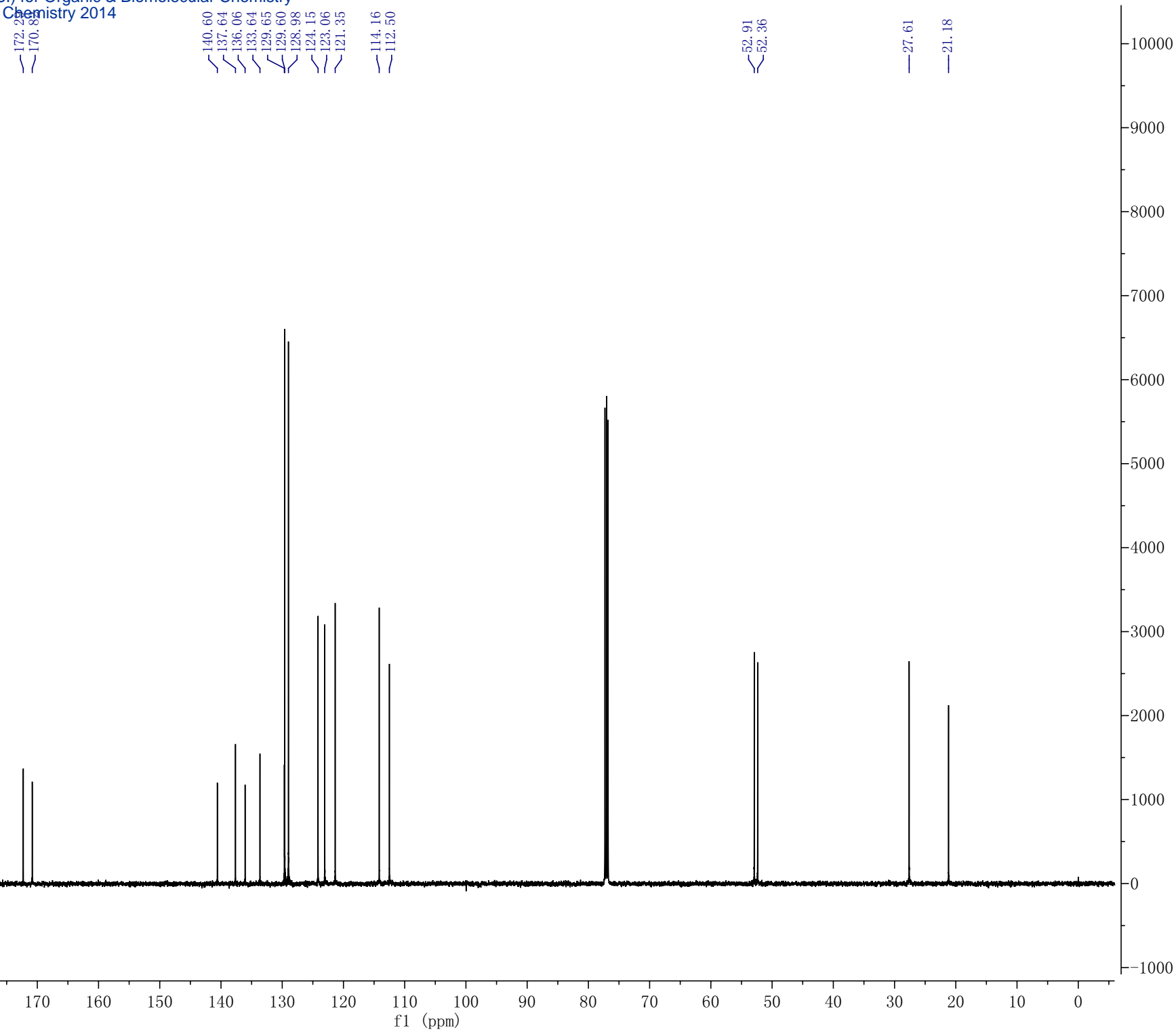


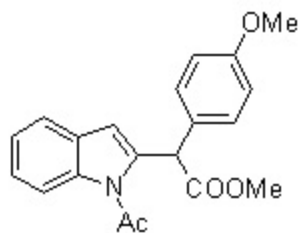
400MHz, CDCl₃



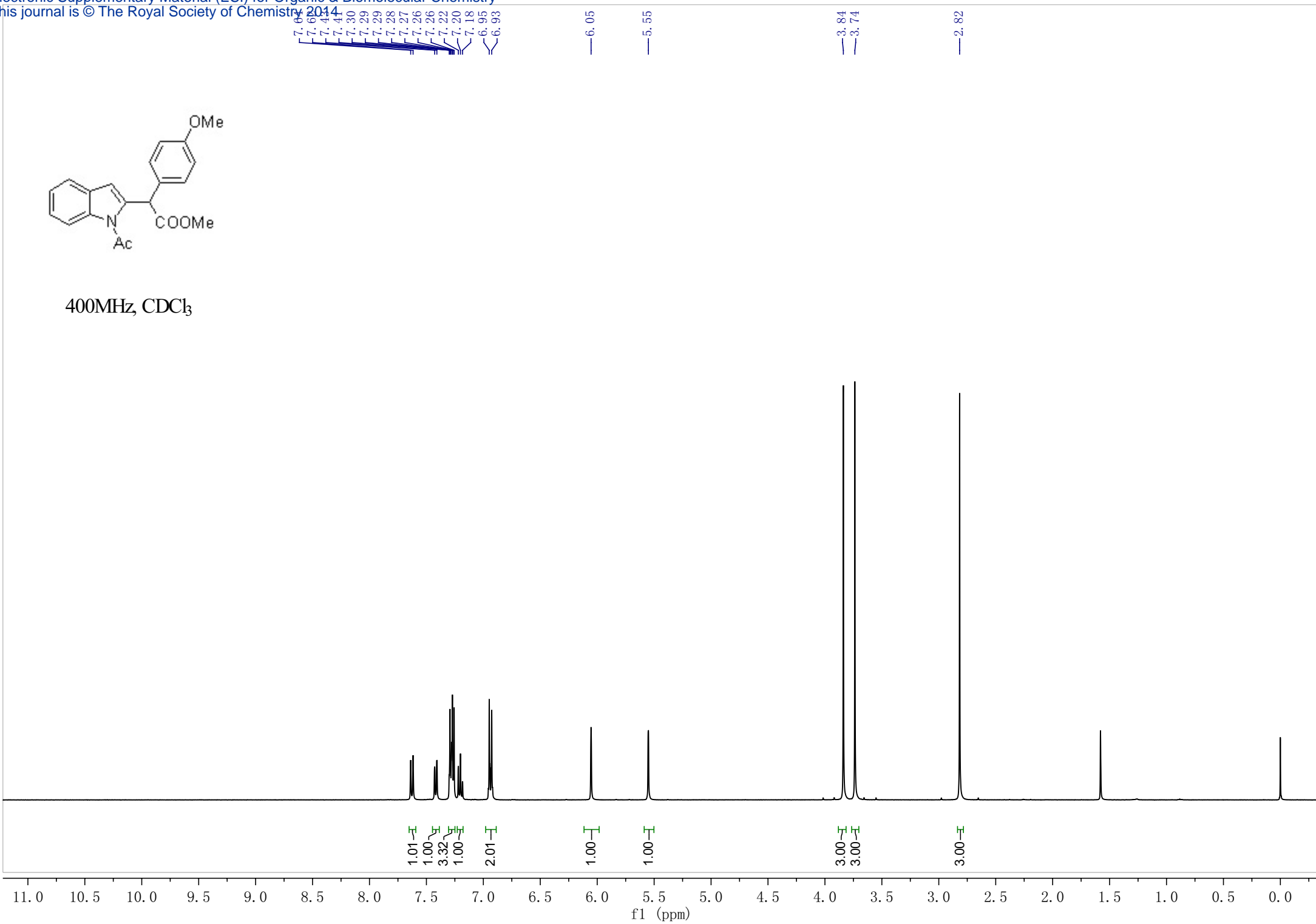


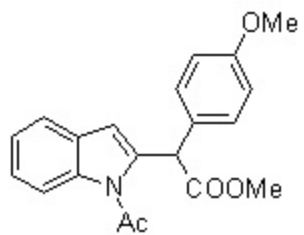
125MHz, CDCl₃



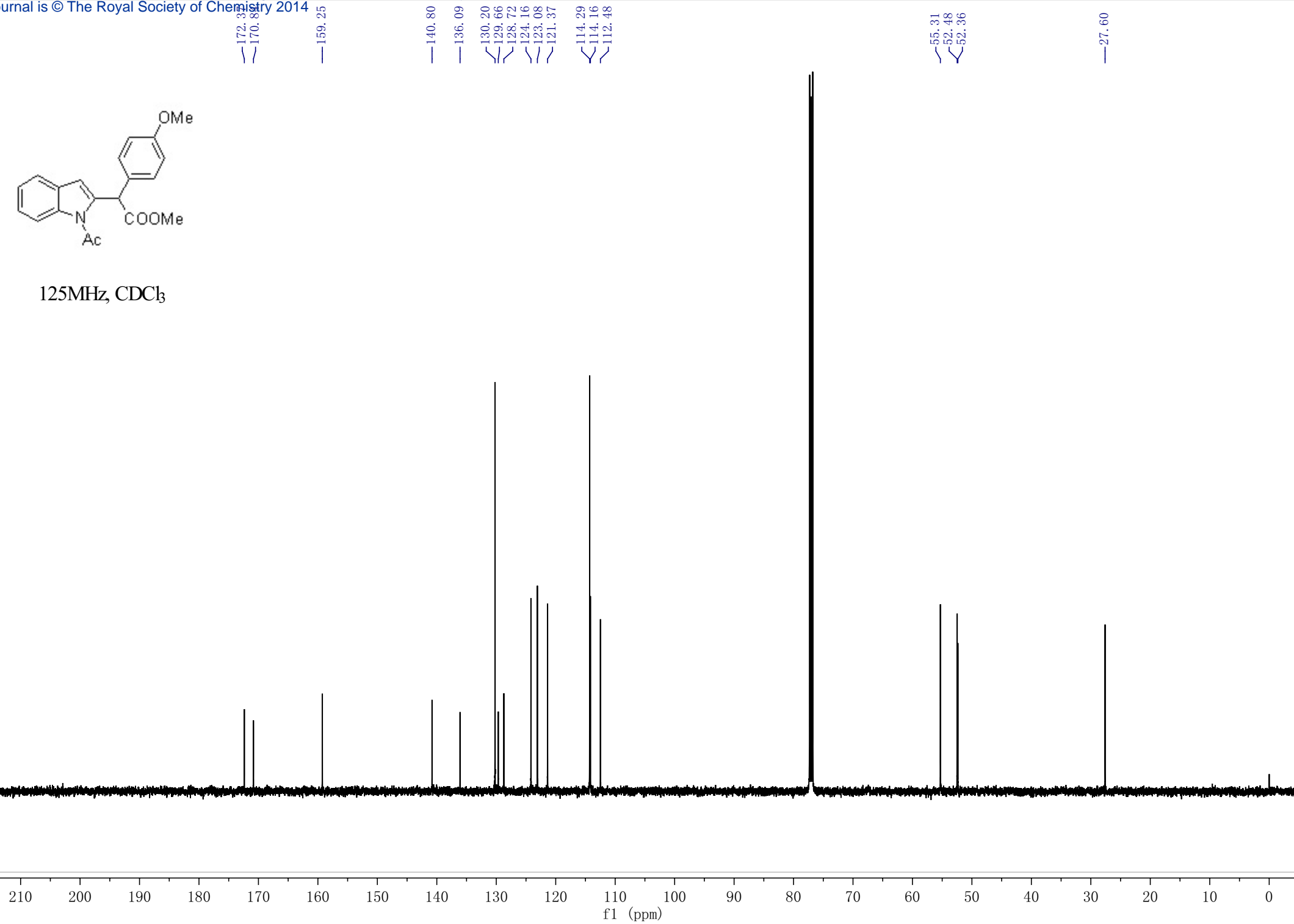


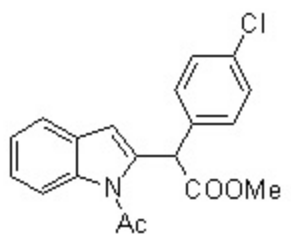
400MHz, CDCl₃



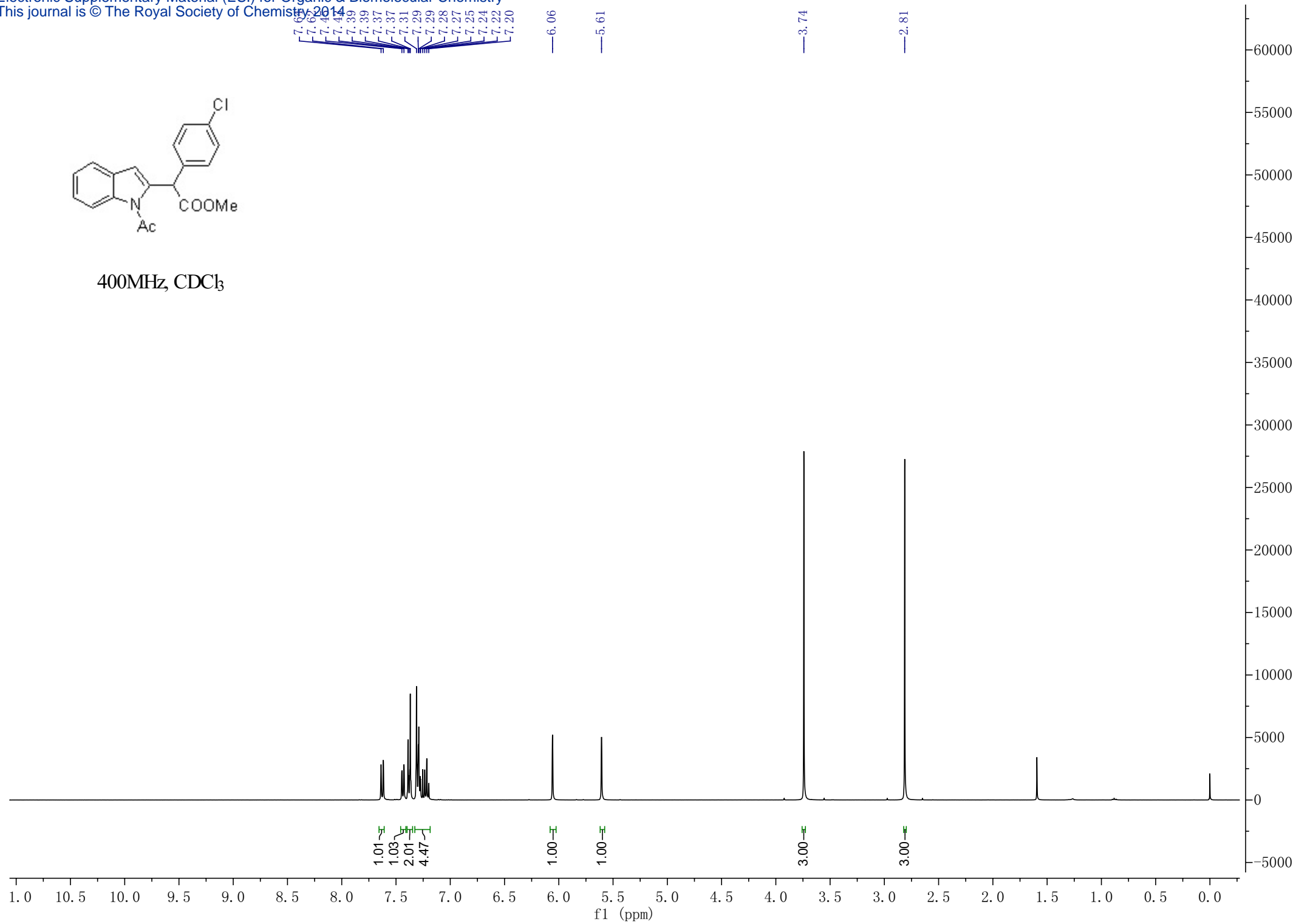


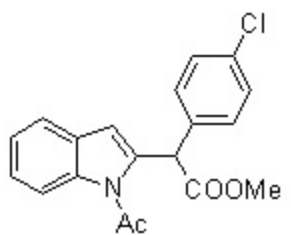
125MHz, CDCl₃



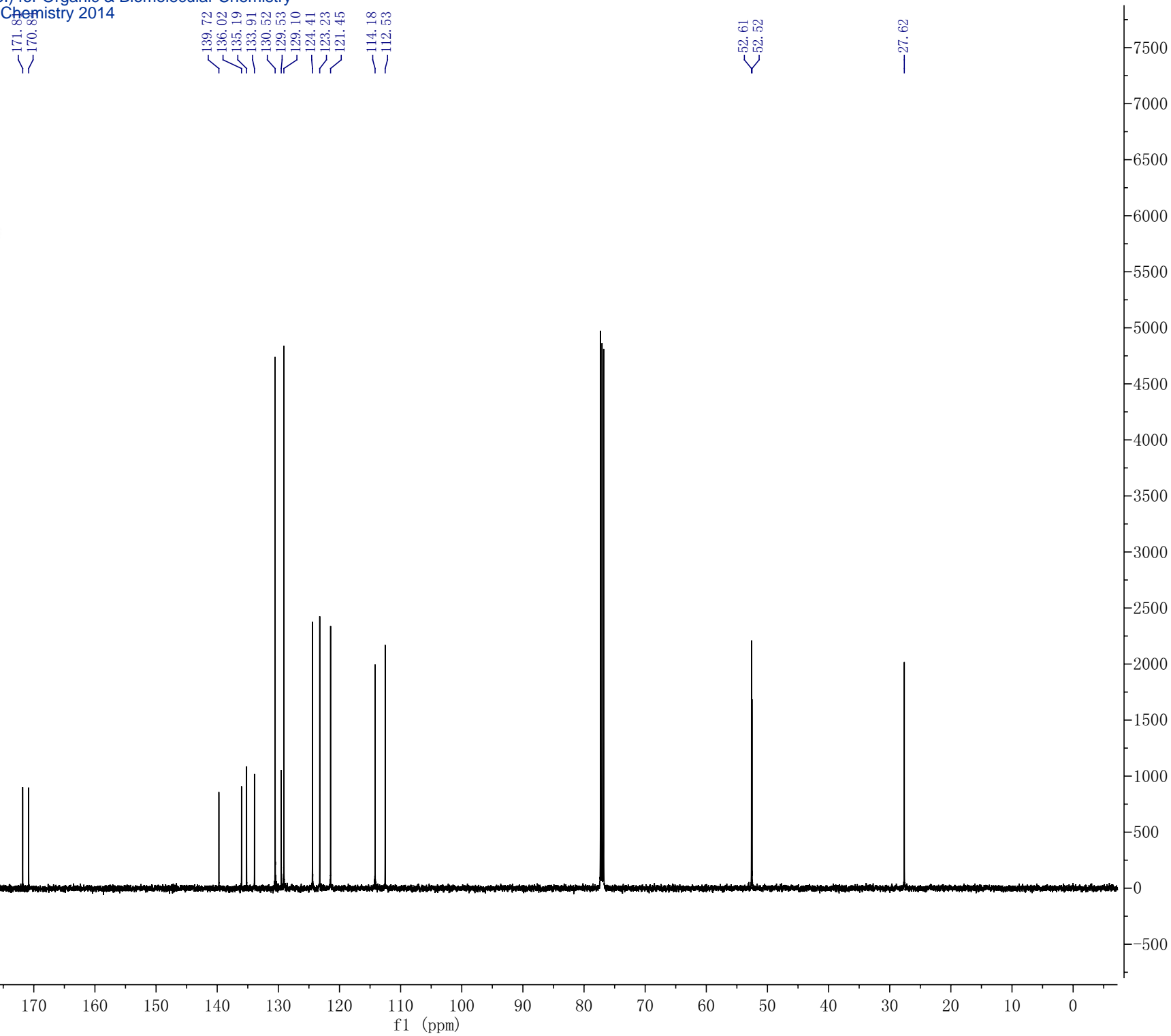


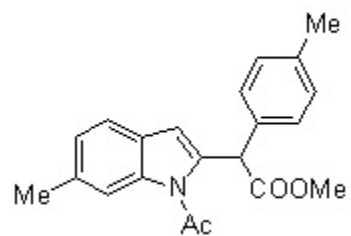
400MHz, CDCl₃





125MHz, CDCl₃





400MHz, CDCl₃

7.42
7.29
7.27
7.26
7.23
7.21
7.19
7.04
7.02

5.99

5.55

3.73

2.81

2.48

2.38

10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

f1 (ppm)

1.01
0.98
4.20
1.01

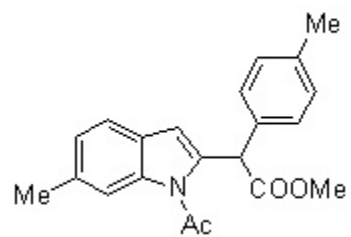
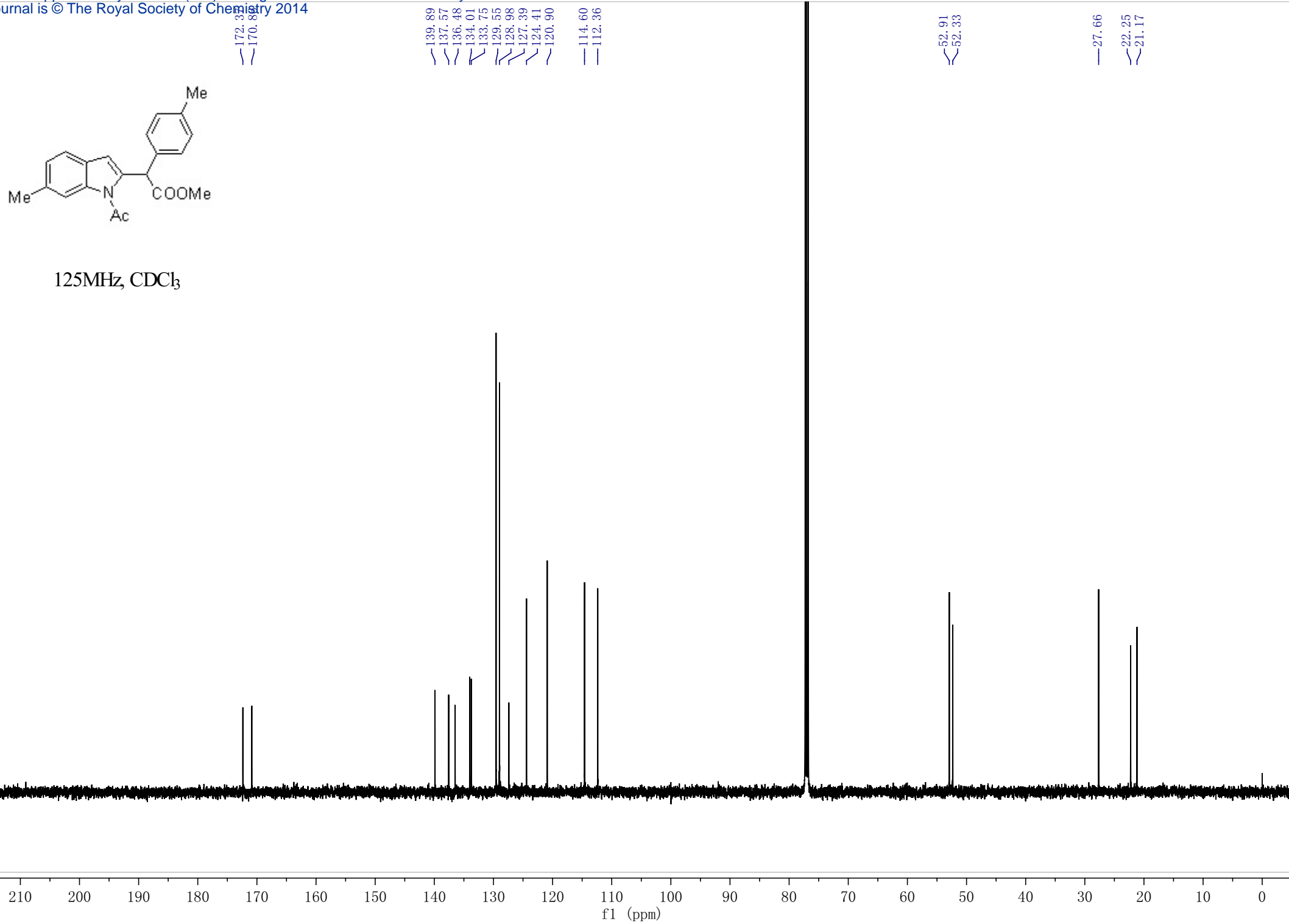
0.95

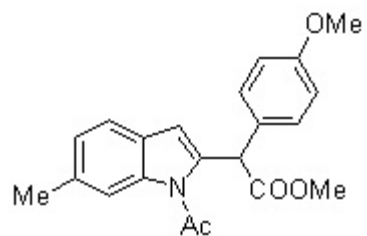
0.97

3.00

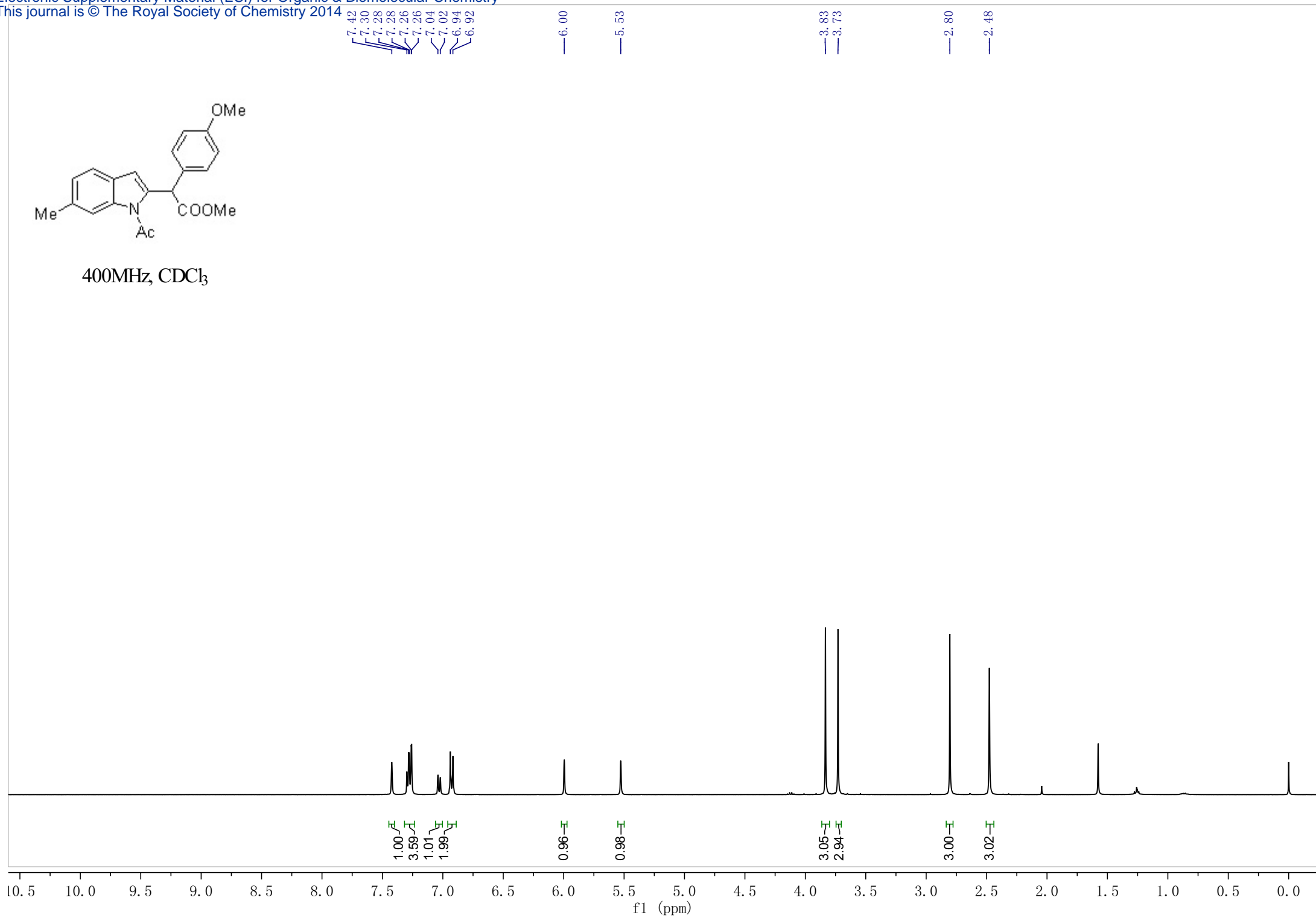
3.00

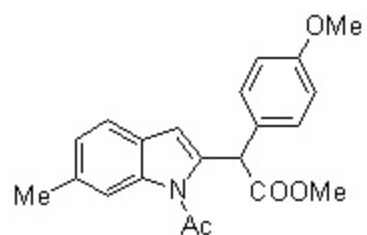
3.00
3.00

125MHz, CDCl₃

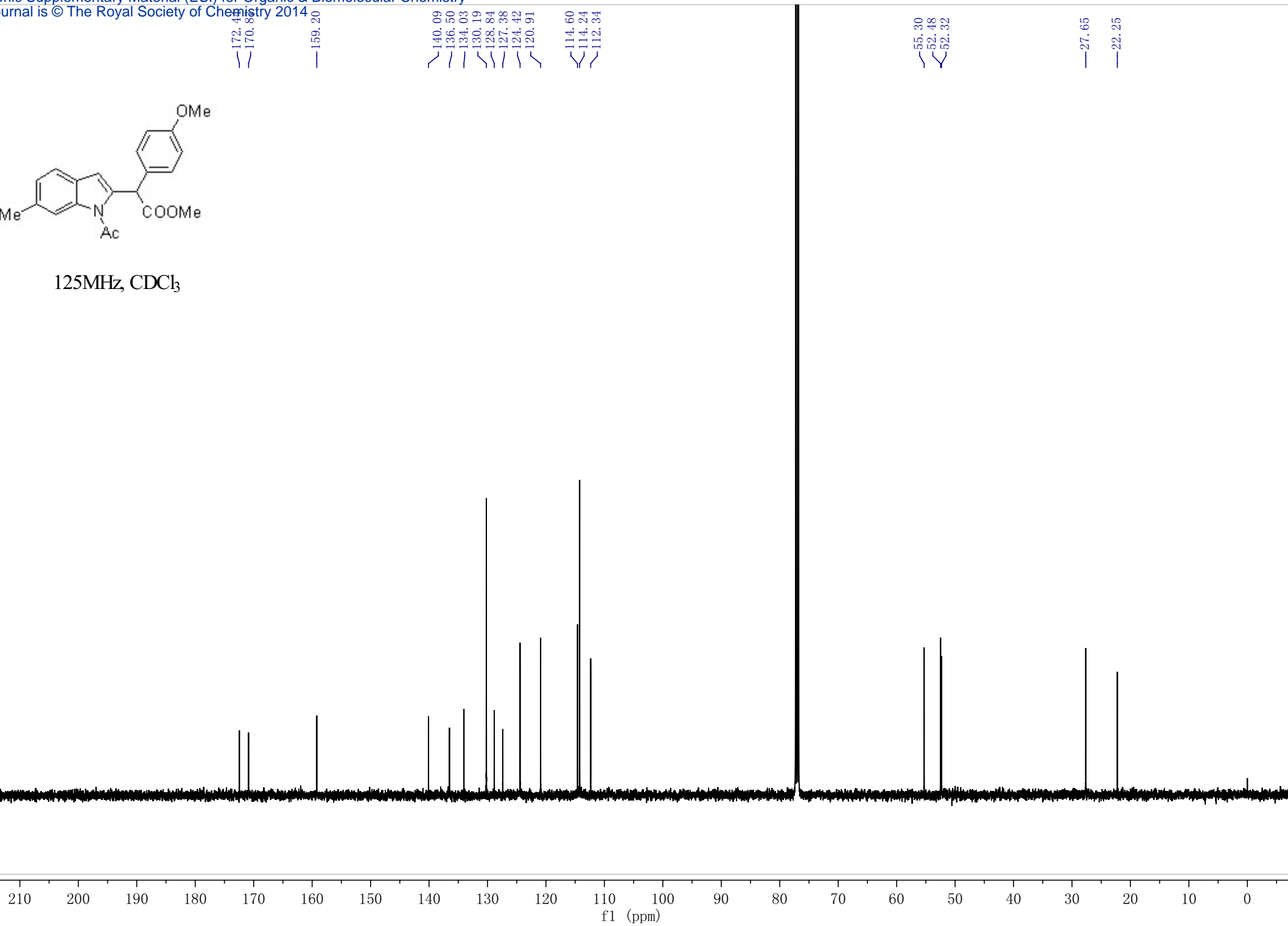


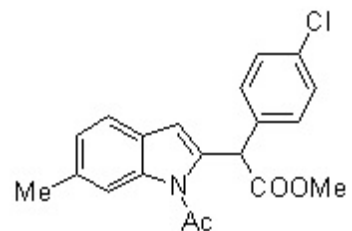
400MHz, CDCl₃



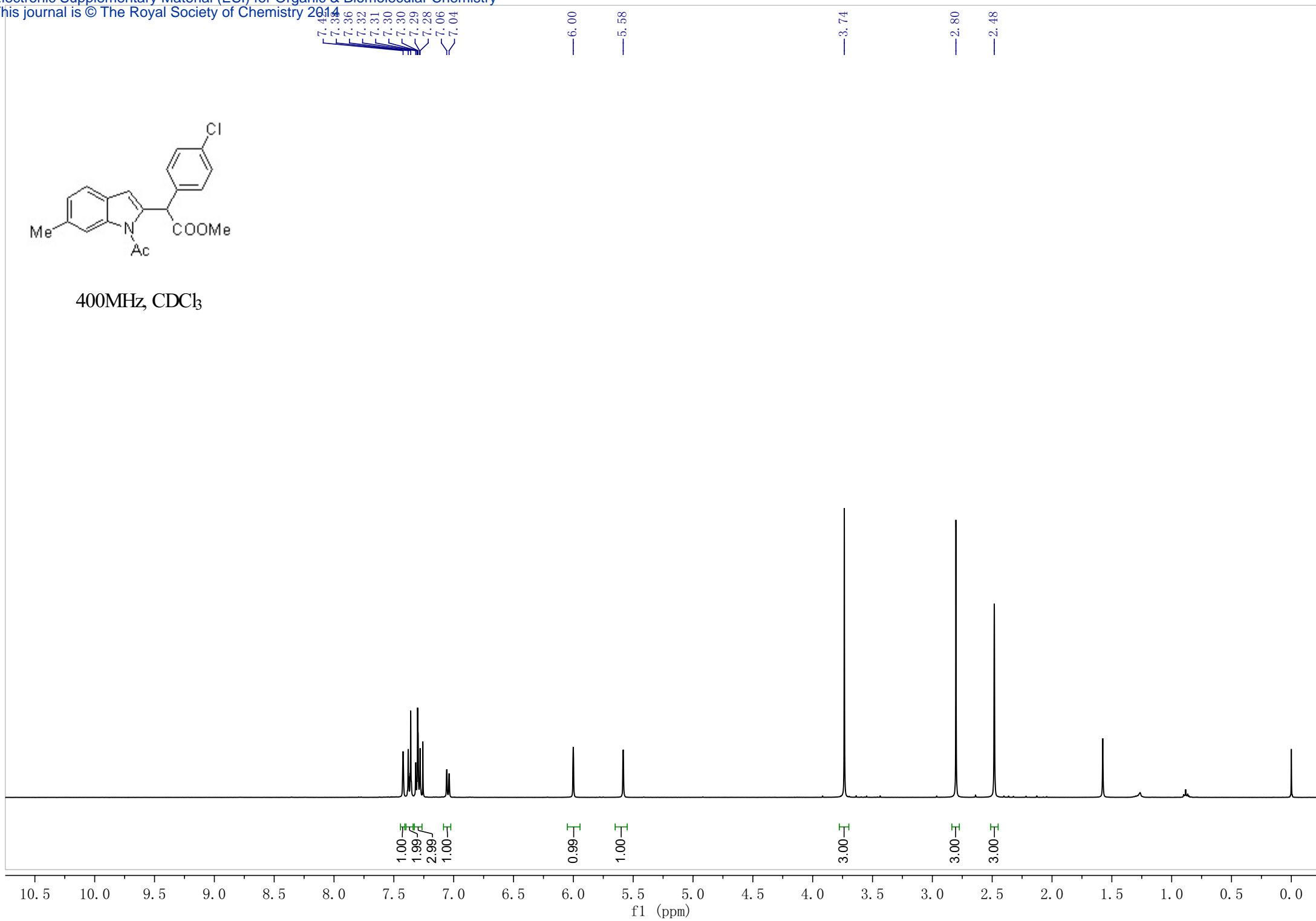


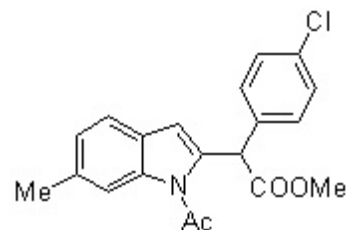
125MHz, CDCl₃





400MHz, CDCl₃





125MHz, CDCl₃

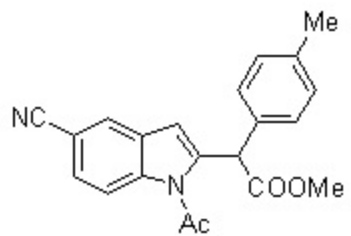
171.80
170.80
139.00
136.43
135.30
134.31
133.82
130.51
129.03
127.25
124.57
120.99
114.59
112.38

52.60
52.47

27.65
22.26

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)



400MHz, CDCl₃

7.74
7.72
7.56
7.53
7.54
7.53
7.23
7.21

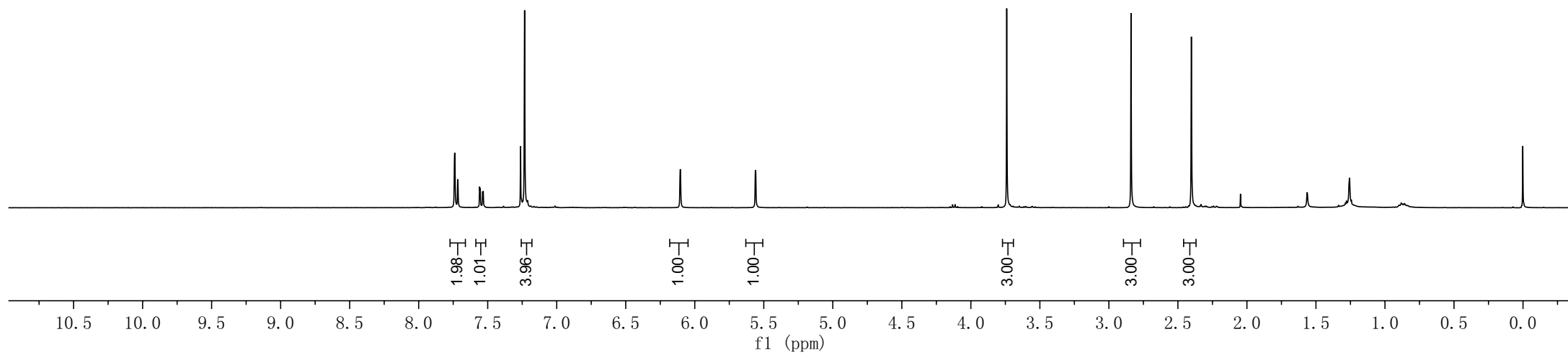
6.10

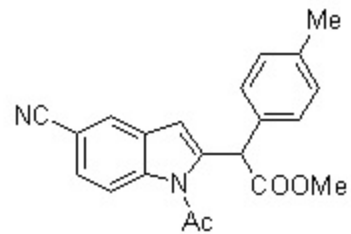
5.56

3.74

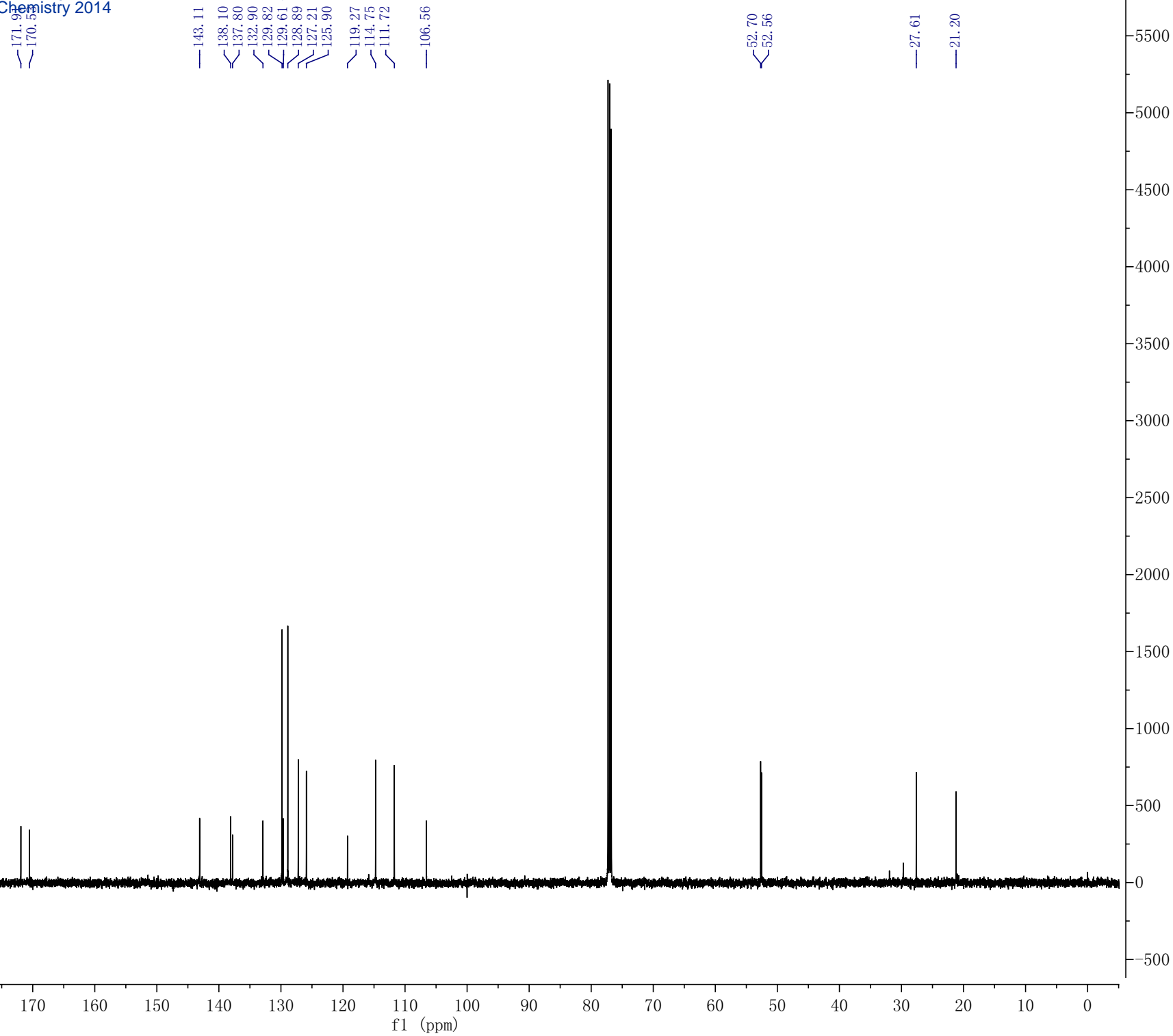
2.84

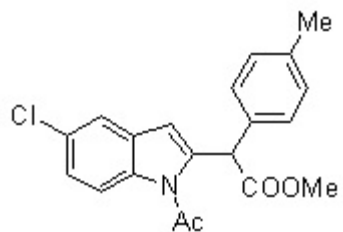
2.40



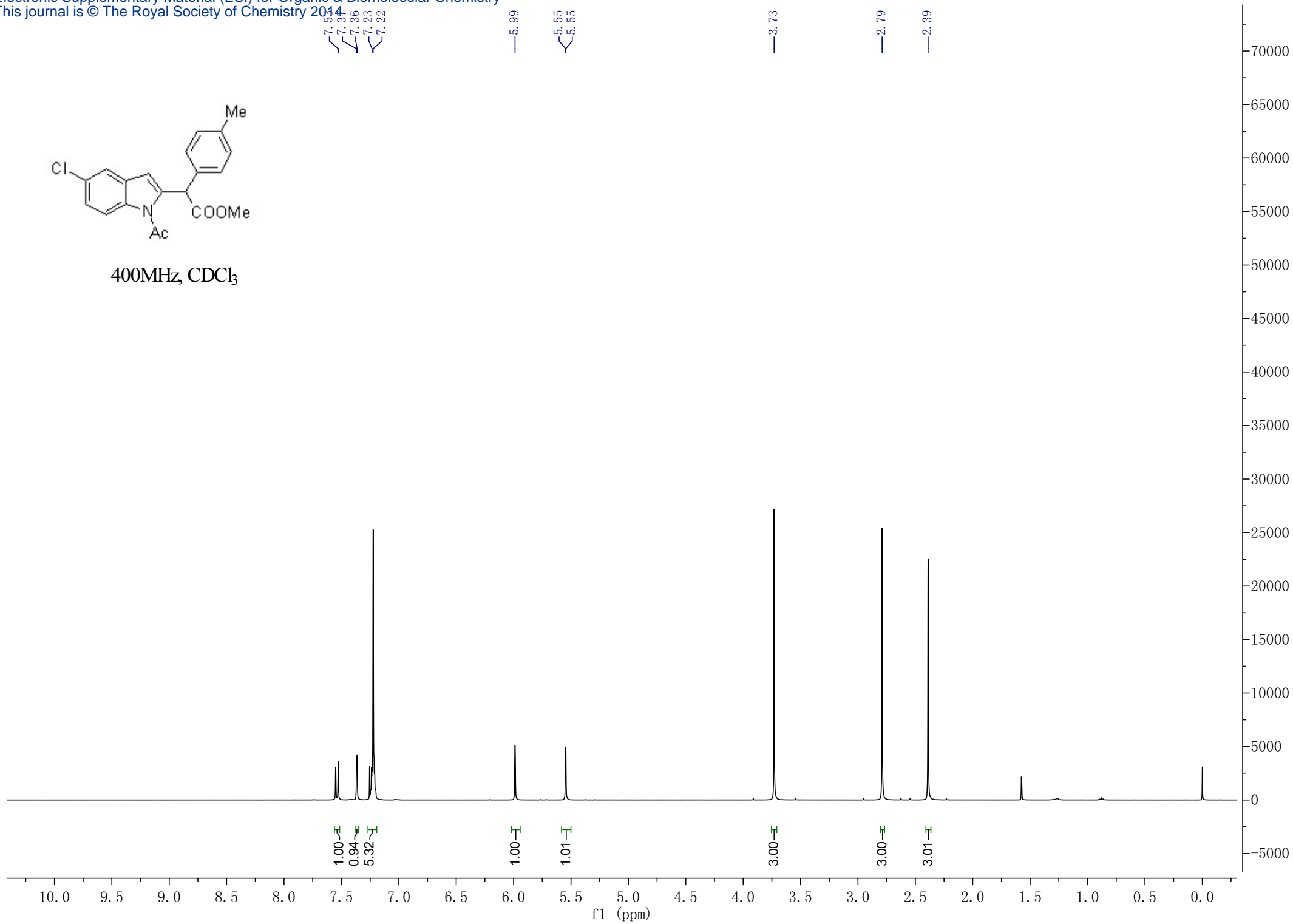


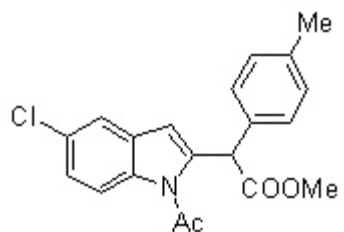
125MHz, CDCl₃



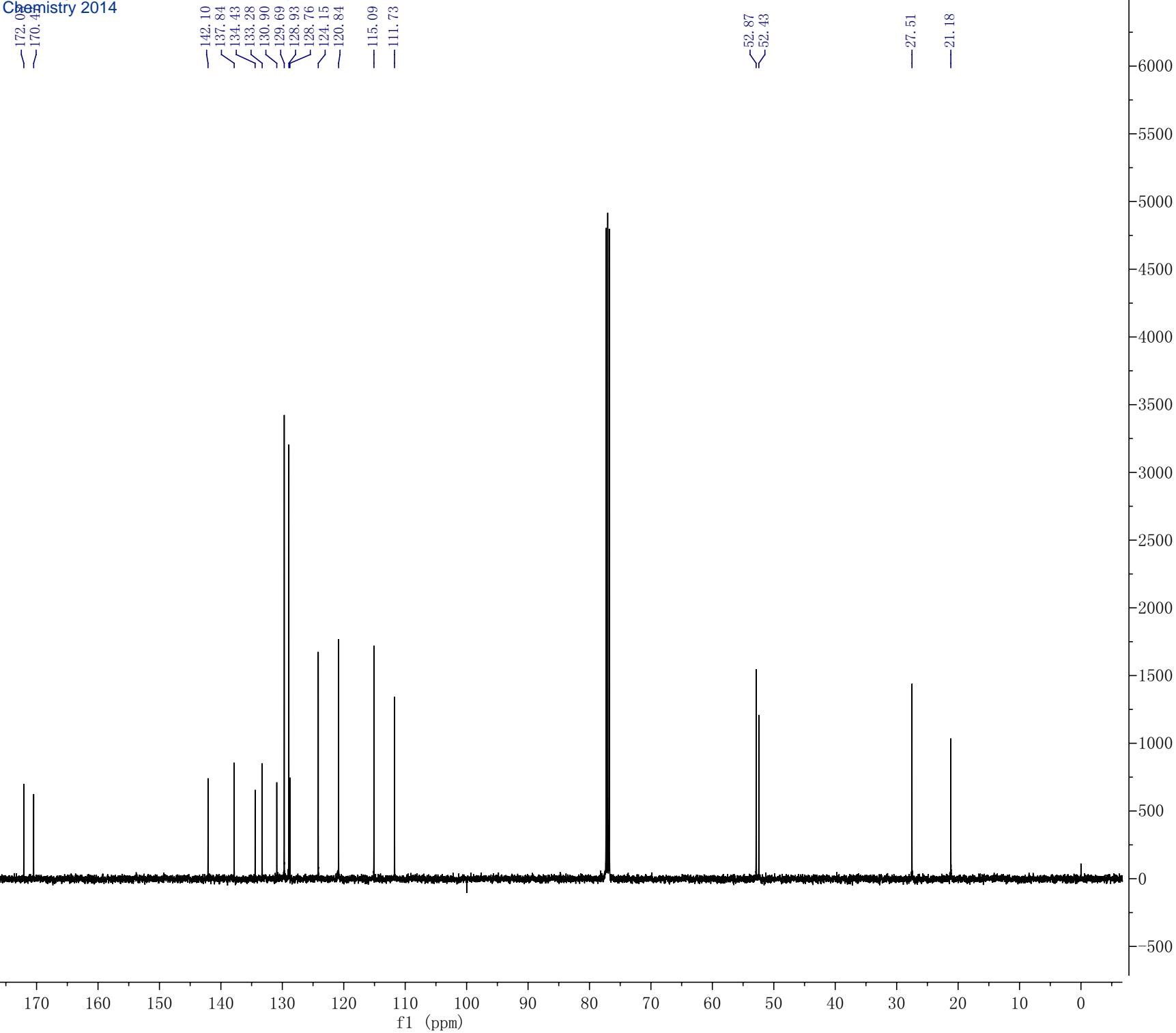


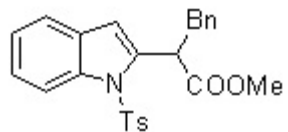
400MHz, CDCl₃



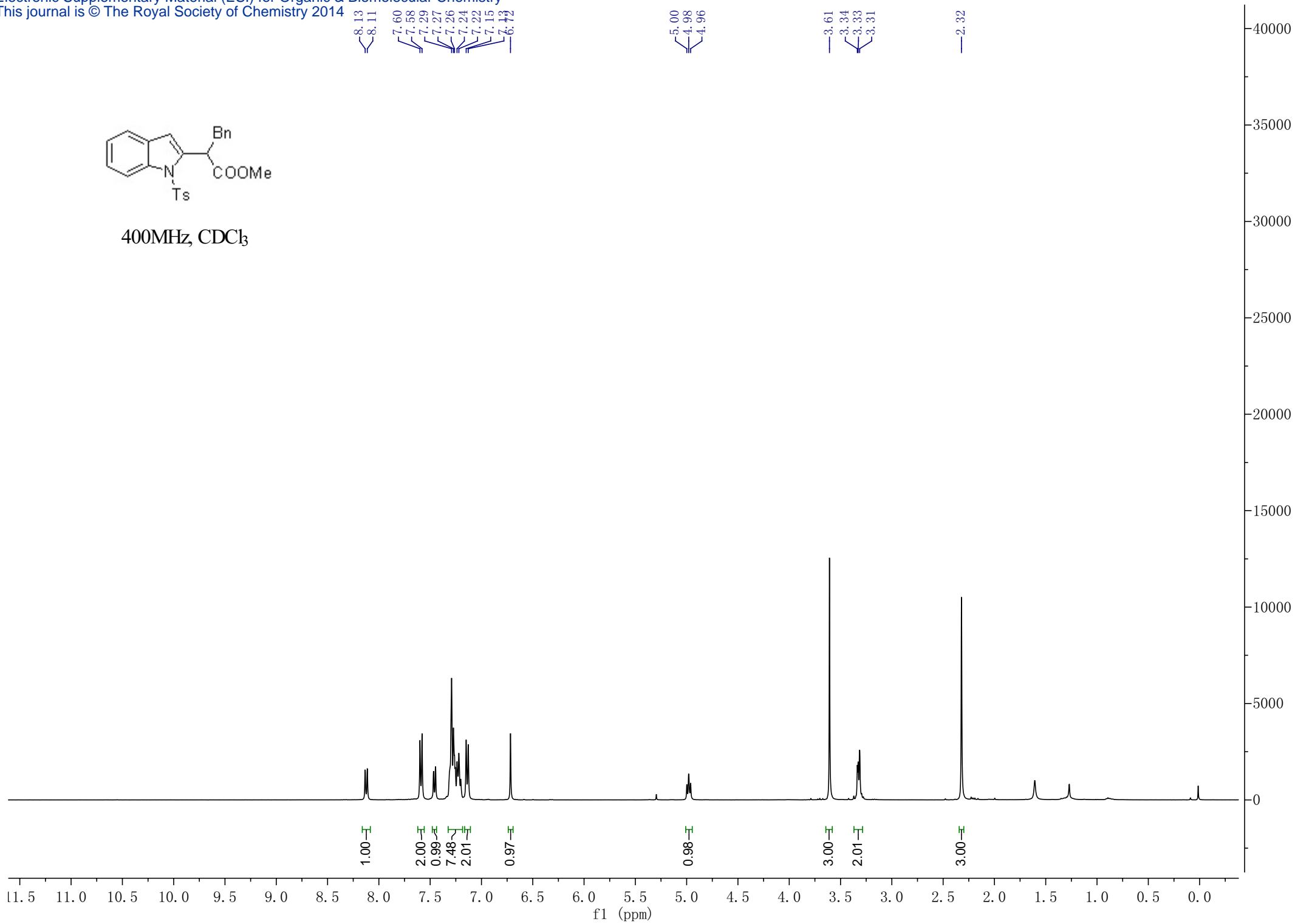


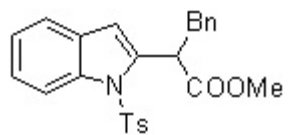
125MHz, CDCl₃



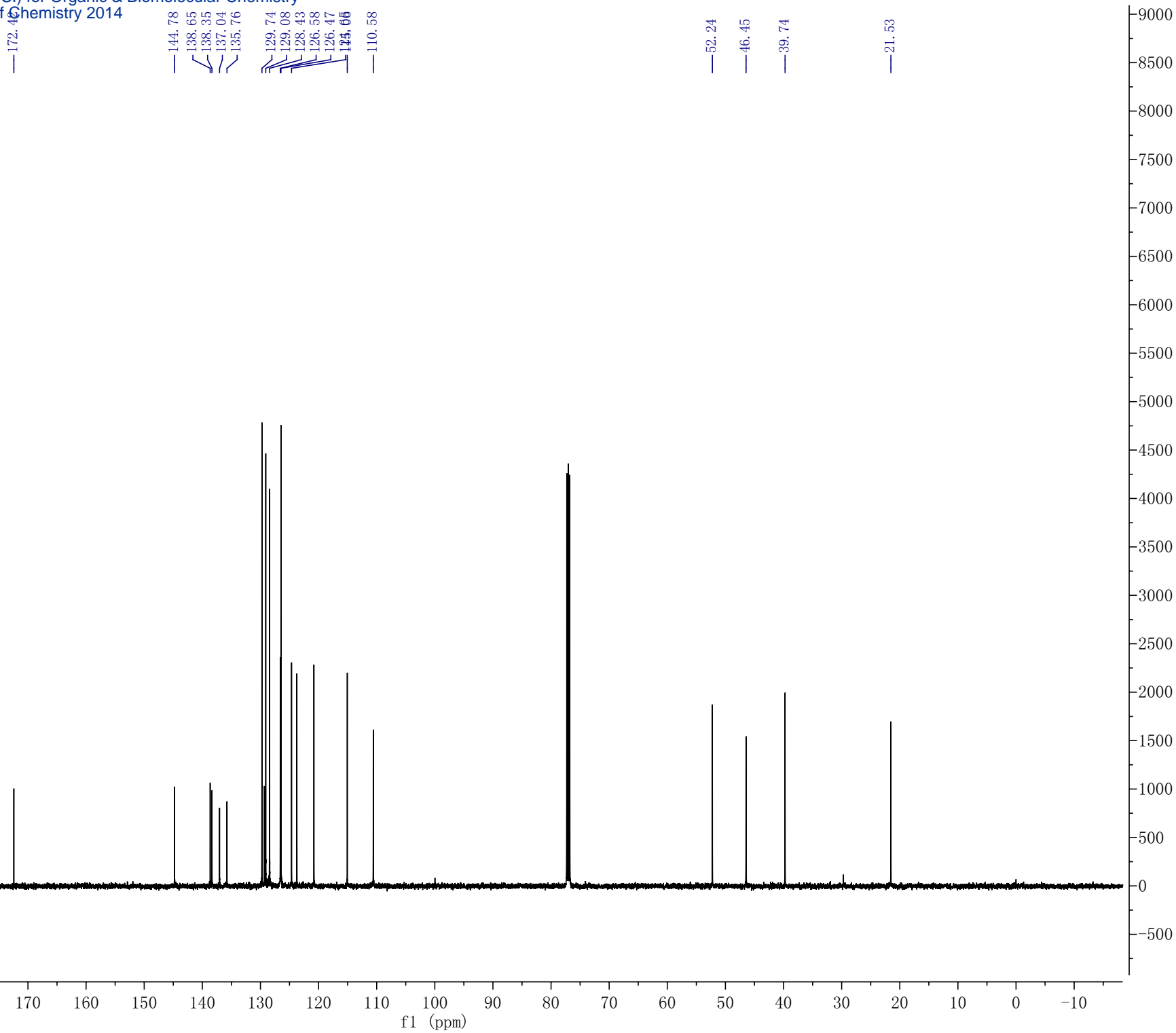


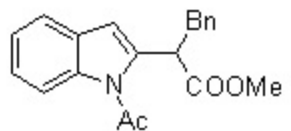
400MHz, CDCl₃



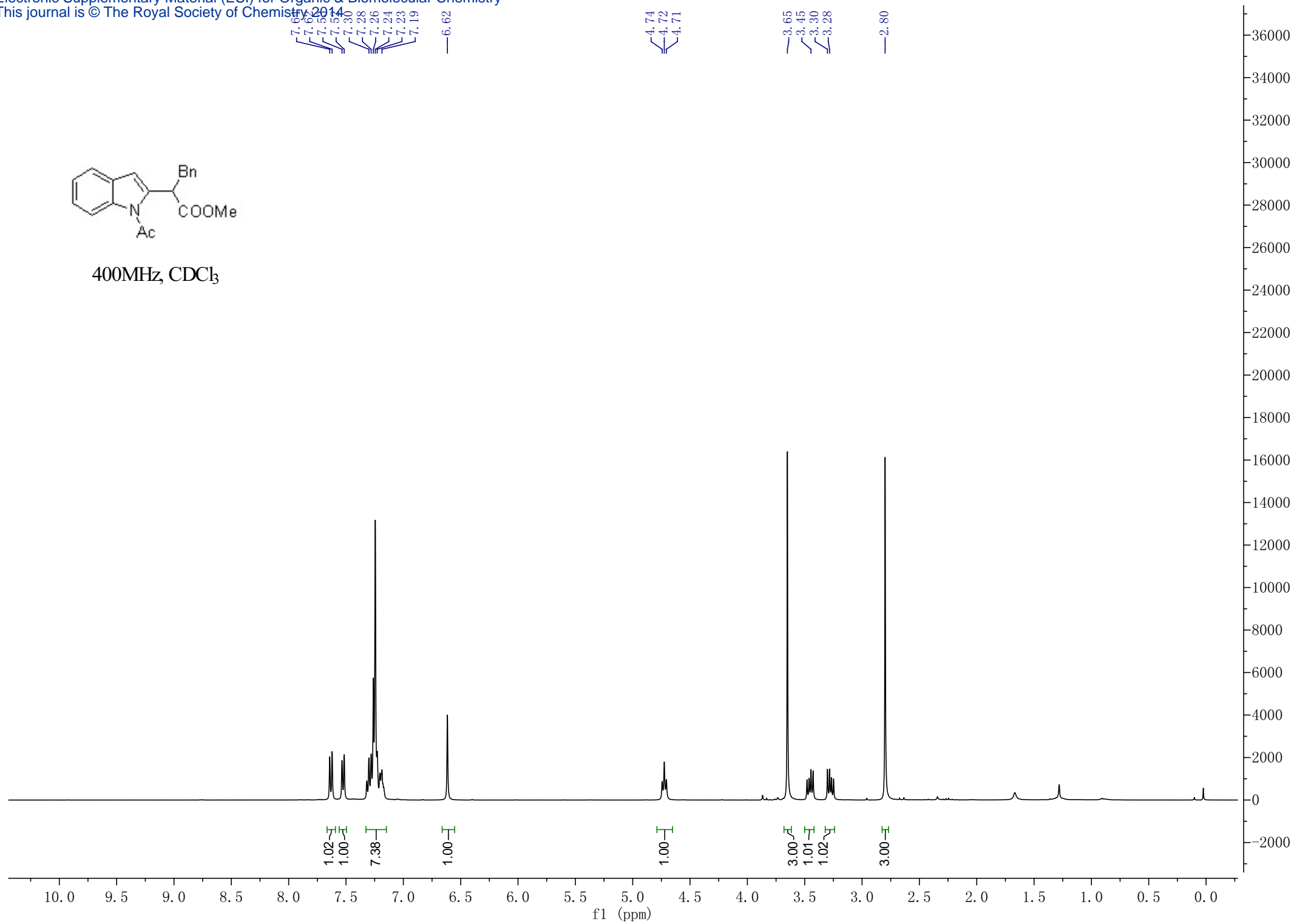


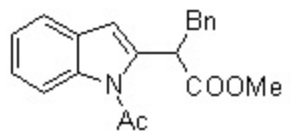
125MHz, CDCl₃



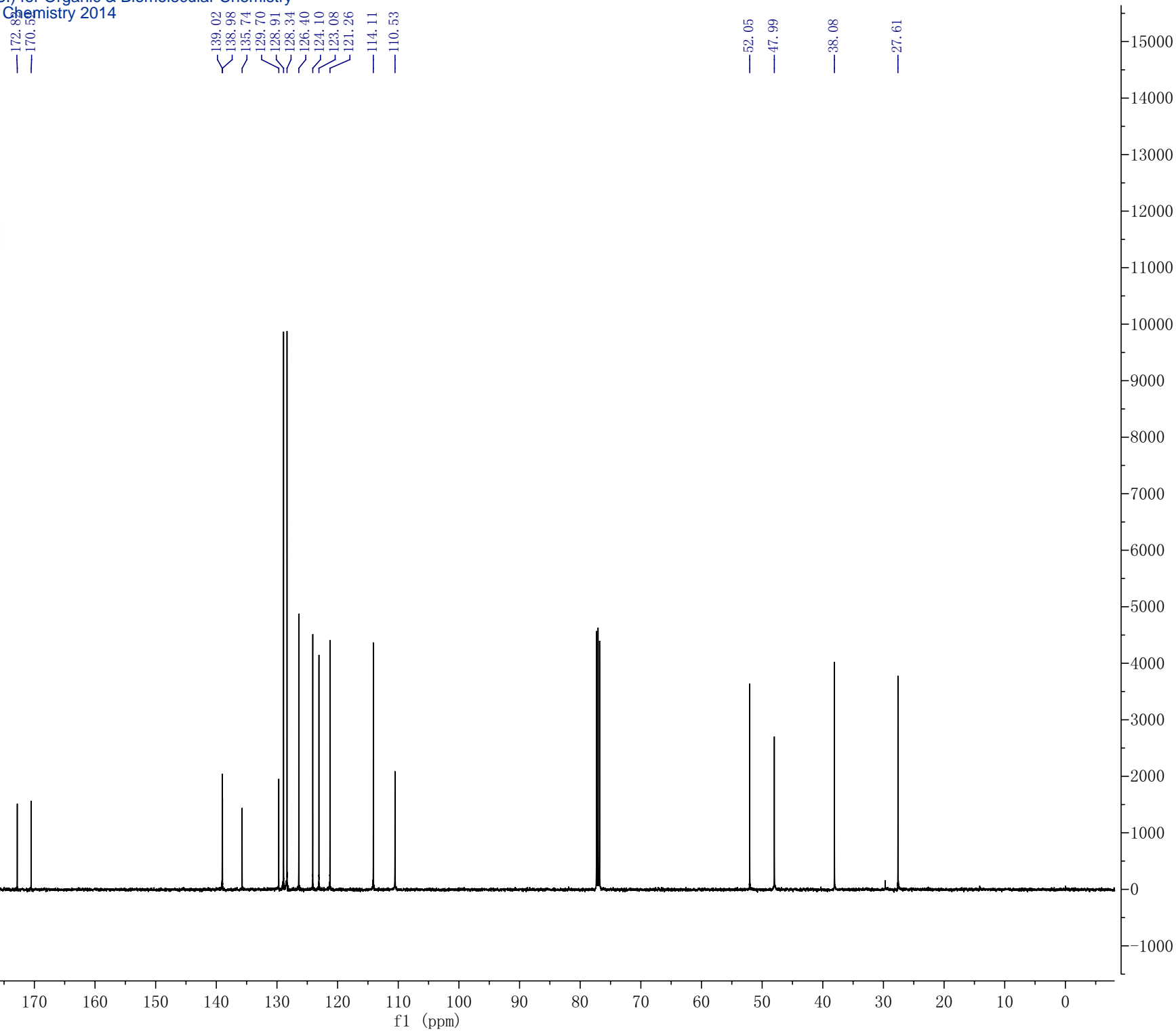


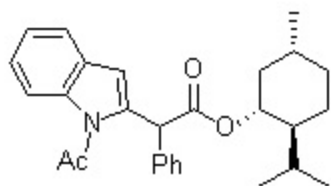
400MHz, CDCl₃



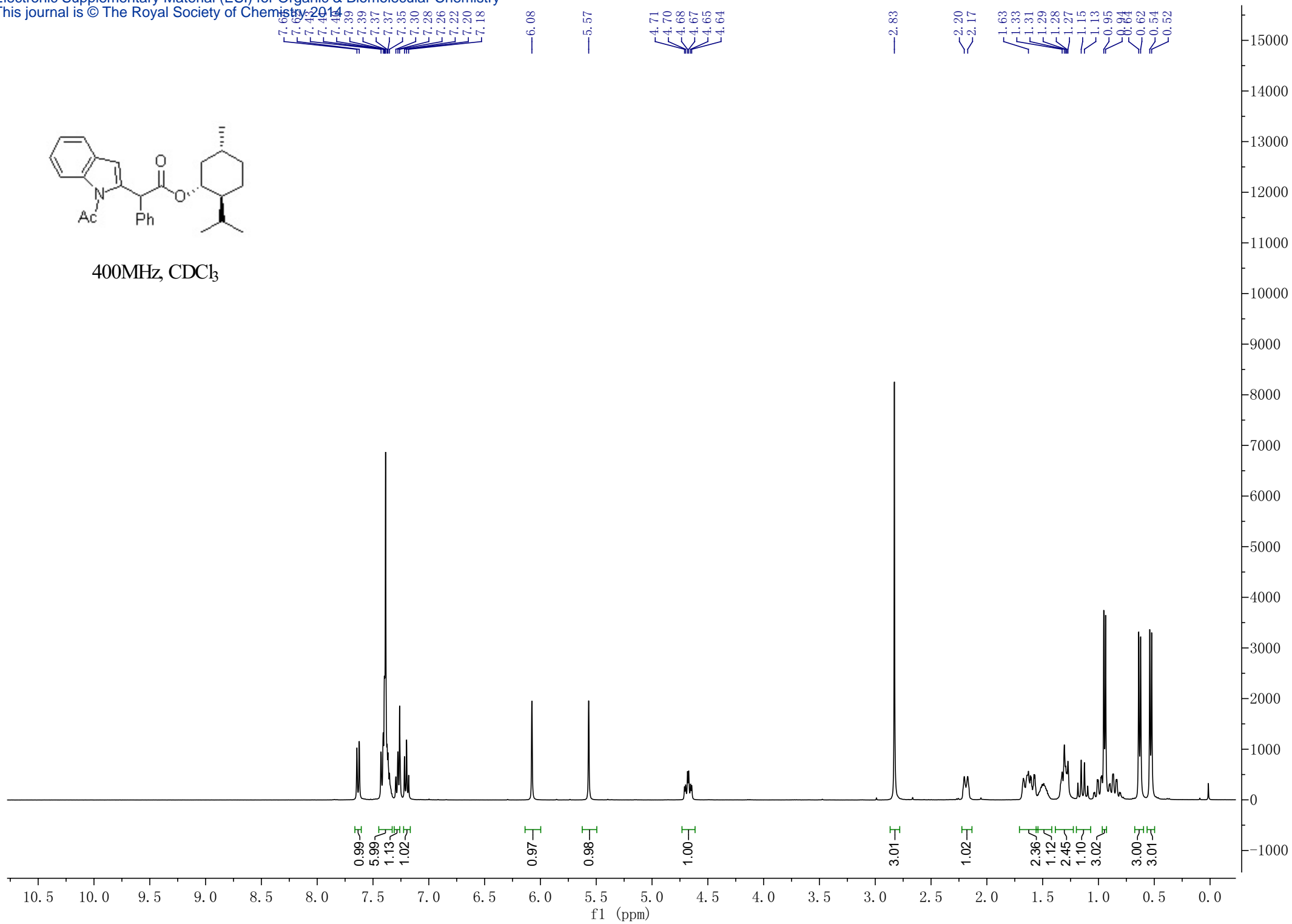


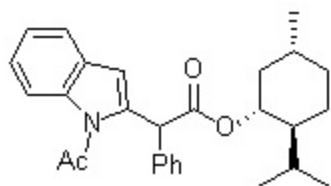
125MHz, CDCl₃



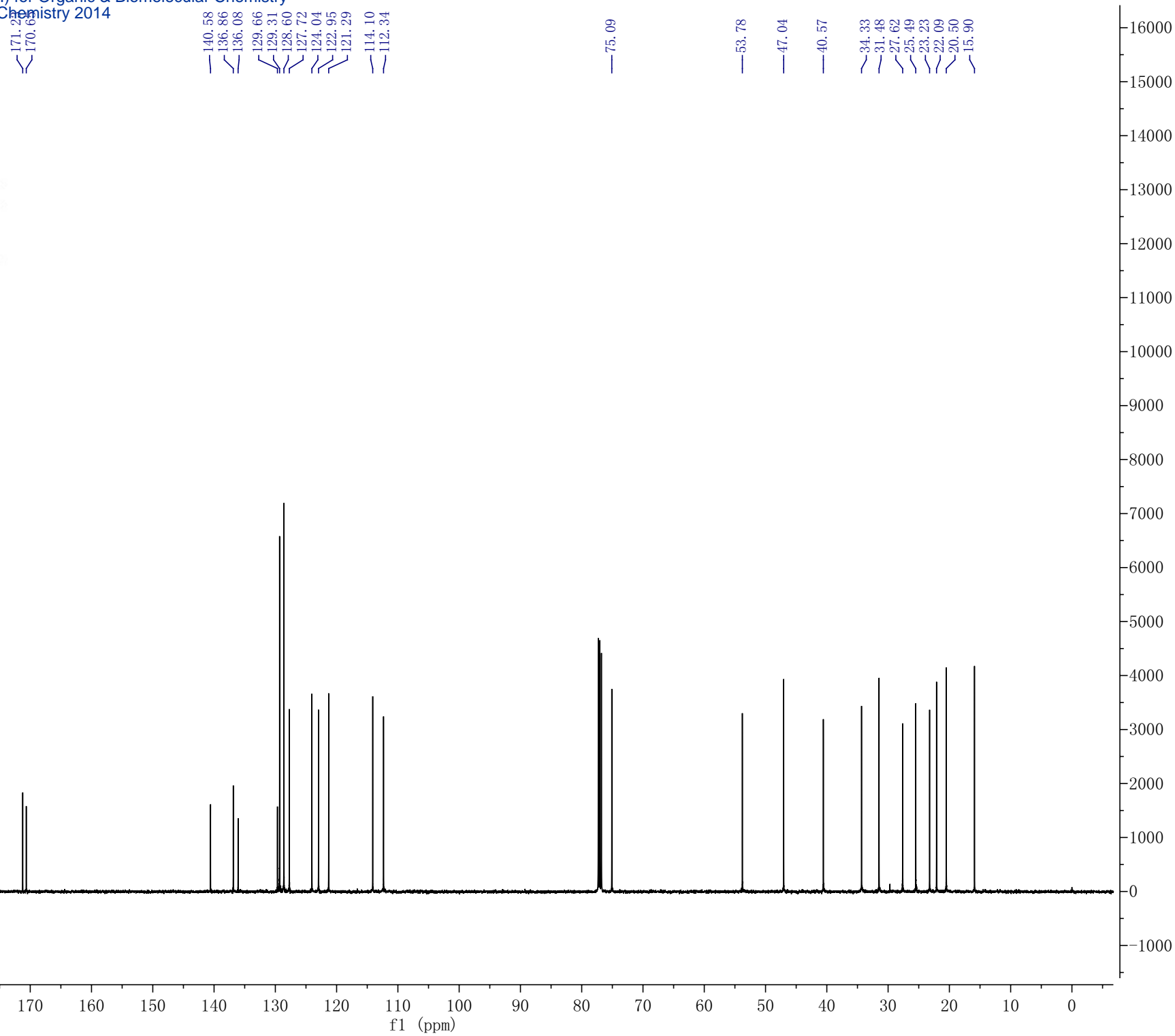


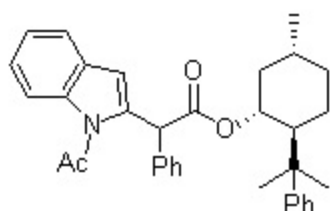
400MHz, CDCl₃





125MHz, CDCl₃





400MHz, CDCl₃

