Electronic Supplementary Information

Oxidative ring-opening of ferrocenylcyclopropylamines to *N*-ferrocenylmethyl β-hydroxyamides

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General experimental details

Unless stated specifically, all chemicals were purchased from commercial suppliers and used without purification. All reactions were conducted in oven-dried glassware under nitrogen atmosphere. Reaction solvents were dried by passing through a column of activated alumina and then stored over 4Å molecular sieves. Progress of reactions was tracked by TLC and was performed on aluminium backed silica gel sheets (Grace Davison, UV254). TLC plates were visualised under UV lamp at 254 nm and/or by treatment with one of the following TLC stains: Phosphomolybdic acid (PMA) stain: PMA (10 g), absolute EtOH (100 mL); Potassium permanganate stain: $KMnO_4$ (1.5 g), 10% NaOH (1.25 mL), water (200 mL); Vanillin stain: Vanillin (15 g), concentrated H_2SO_4 (2.5 mL), EtOH (250 mL). Preparative TLC was carried out on glass backed TLC plates with silica matrix. Column chromatography was performed using silica gel (40 – 75 μm) as the solid phase. For NMR spectroscopy analytes were dissolved in deuterated chloroform or stated otherwise. NMR spectra for each compound were collected from one of the following instrument: Mercury 2000 spectrometer operates at 500 and 125 MHz for ^{1}H and ^{13}C NMR respectively, or Varian spectrometer operates at 300 and 75 MHz for ^{1}H and ^{13}C NMR respectively. NMR data are expressed in parts per million (ppm) and referenced to the solvent (7.26 ppm for ^{1}H NMR and 77.16 ppm for ^{13}C NMR). The following abbreviations are used to assign the multiplicity of the ^{1}H NMR signal: s = singlet; bs = broad singlet; d = doublet; t = triplet; q = quartet; quin = quintet; dd = doublet of doublets; m = multiplet. For mass spectroscopy analytes were dissolved in HPLC grade methanol. Spectra of low-resolution mass spectroscopy were obtained from a Shimadzu LC-2010 mass spectrometer (ESI) or a Shimadzu QP5050 mass spectrometer (EI). High-resolution mass spectra were collected from a Waters Xevo G1 QTOF mass spectrophotometer (ESI or ASAP) or Thermo Scientific LTQ Orbitrap XL (ESI). Infrared spectra were obtained from a Shimadzu IRAffinity-1 Fourier transform infrared spectrophotometer with ATR attachment. Melting point measurements were taken on a Buchi M-560.

X-ray Crystallography

Crystals of **7d** were obtained from recrystallisation in ethyl acetate/hexanes. CCDC reference number 1434659. Data for **7d** were collected at -173 °C on crystals mounted on a Hampton

Scientific cryoloop at the MX1 beamline of the Australian Synchrotron.[1] The structures were solved by direct methods with SHELXS-97, refined using full-matrix least-squares routines against F^2 with SHELXL-97,[2] and visualised using X-SEED.[3] All non-hydrogen atoms were refined anisotropically. All protons were clearly visible in difference maps during the refinement, including the amide N-H and alcohol O-H, but all were later placed in calculated positions and refined using a riding model with fixed C–H distances of 0.95 Å (sp^2CH), 1.00 Å (sp^3CH), 0.99 Å (CH_2), 0.98 Å (CH_3), N–H distances of 0.88 Å and O–H distances of 0.84 Å The thermal parameters of all hydrogen atoms were estimated as $U_{iso}(H) = 1.2U_{eq}(C)$ except for CH_3 where $U_{iso}(H) = 1.5U_{eq}(C)$. A summary of crystallographic data given below.

Crystal data for **7d**: $C_{20}H_{20}FFeNO_2$, M = 381.22, monoclinic, a = 10.5080(11), b = 35.761(4), c = 9.5150(16) Å, β = 107.758(6) °, U = 3405.2(8) Å^3, T = 100 K, space group $P2_1/n$ (no. 14), Z = 8, 31981 reflections measured, 7745 unique (R_{int} = 0.0460), 6200 > 4s(F), R = 0.0624 (observed), R_w = 0.1474 (all data).

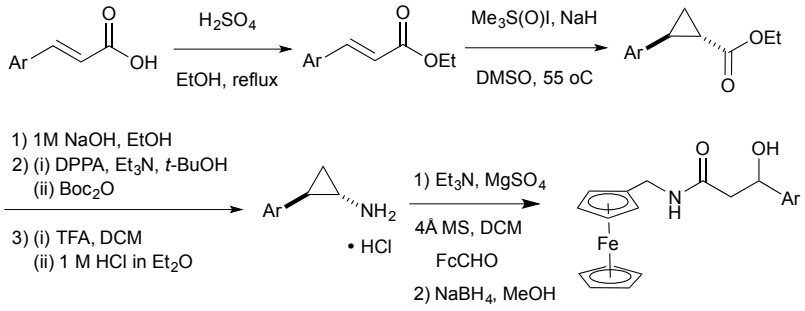
Acknowledgement

Data for the structure of complex **7d** were obtained on the MX1 beamline at the Australian Synchrotron, Victoria, Australia.

[1] T. M. McPhillips, S. E. McPhillips, H. J. Chiu, A. E. Cohen, A. M. Deacon, P. J. Ellis, E. Garman, A. Gonzalez, N. K. Sauter, R. P. Phizackerley, S. M. Soltis and P. Kuhn, *J. Synchrotron Radiat*., 2002, **9**, 401.
[2] G. M. Sheldrick, *SHELX97, Programs for Crystal Structure Analysis*; Universität Göttingen: Germany, 1998.
[3] L. J. Barbour, *J. Supramol. Chem*., 2001, **1**, 189.

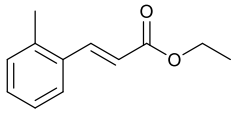
Preparation and characterisation of synthesised compounds

General Synthetic Scheme:



Esterification

Ethyl (*E*)-3-(*o*-tolyl)-2-propenoate 9b

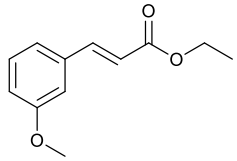


Concentrated sulphuric acid (approximately 1 mL) was added to a solution of 2-methylcinnamic acid (2.0098 g, 12.4 mmol) in ethanol (40 mL). After heating to reflux for 24 h, the reaction solution was concentrated *in vacuo* and diluted with ethyl acetate (40 mL). The solution was washed with 5% by mass $NaHCO_3$ aqueous solution (3 × 30 mL) and water (3 × 30 mL). After drying the solution with magnesium sulphate, the solution was concentrated under reduced pressure to give the title compound as a pale yellow oil (2.1168 g, 11.1 mmol) in 90% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, J = 16 Hz, 1H), 7.55 (d, J = 7.5 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.21 (t, J = 6.5 Hz, 2H), 6.36 (d, J = 16 Hz, 1H), 4.27 (q, J = 7 Hz, 2H), 2.44 (s, 3H), 1.34 (t, J = 7 Hz, 3H) ppm

^{1}H NMR data consistent with literature and the material is commercially available.[1,2]

Ethyl (*E*)-3-(*m*-methoxyphenyl)-2-propenoate 9c

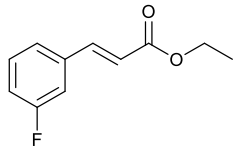


Concentrated sulphuric acid (approximately 1 mL) was added to a solution of 3-methoxycinnamic acid (2.0012 g, 11.2 mmol) in ethanol (38 mL). After heating to reflux for 24 h, the reaction solution was concentrated *in vacuo* and diluted with ethyl acetate (38 mL). The solution was washed with 5% by mass $NaHCO_3$ aqueous solution (3 × 30 mL) and water (3 × 35 mL). After drying the solution with magnesium sulphate, the solution was concentrated under reduced pressure to give the title compound as a pale yellow oil (2.0874 g, 10.1 mmol) in 90% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65 (d, *J* = 16 Hz, 1H), 7.30 (t, *J* = 8 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.05 (s, 1H), 6.93 (d, *J* = 8.5 Hz, 1H), 6.43 (d, *J* = 16 Hz, 1H), 4.27 (q, *J* = 7 Hz, 2H), 3.83 (s, 3H), 1.34 (t, *J* = 7 Hz, 3H) ppm

^{1}H NMR data consistent with literature and the compound is commercially available.[3]

Ethyl (*E*)-3-(*m*-fluorophenyl)-2-propenoate 9d



Concentrated sulphuric acid (approximately 1 mL) was added to a solution of 3-fluorocinnamic acid (1.5063 g, 9.07 mmol) in ethanol (30 mL). After the solution was heated to reflux for 24 h, the reaction solution was concentrated in vacuo and diluted with ethyl acetate (30 mL). The solution was washed with 5% by mass $NaHCO_3$ aqueous solution (3 × 30 mL) and water (3 × 30 mL). After drying the solution with magnesium sulphate, the solution was concentrated under reduced pressure to give the title compound as a pale yellow oil (1.4151 g, 7.29 mmol) in 80% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, *J* = 15 Hz, 1H), 7.40 – 7.20 (m, 3H), 7.08 (t, *J* = 11.5 Hz, 1H), 6.43 (d, *J* = 18 Hz, 1H), 4.27 (q, *J* = 11.5 Hz, 2H), 1.34 (t, *J* = 12 Hz, 3H) ppm

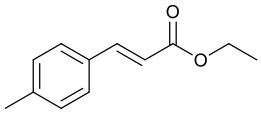
^{13}C NMR (75 MHz, $CDCl_3$): δ 166.6, 163.0 (d, *J* = 247.5 Hz), 143.2 (d, *J* = 2.25 Hz), 136.7 (d, *J* = 0.75 Hz), 130.4 (d, *J* = 8.25 Hz), 124.0 (d, *J* = 1.5 Hz), 119.7, 117.1 (d, *J* = 21 Hz), 114.3 (d, *J* = 21.8 Hz), 60.7, 14.3 ppm

IR (Neat): 1708 cm^{-1}

HRMS (ASAP) Found: (M+H)+, 195.0821. $C_{11}H_{11}O_2F$ requires (M+H)+, 195.0821

^{1}H NMR data consistent with literature and the compound is commercially available.[10]

Ethyl (*E*)-3-(*p*-tolyl)-2-propenoate 9e

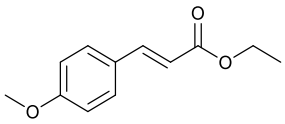


Concentrated sulphuric acid (approximately 1 mL) was added to a solution of 4-methylcinnamic acid (1.5024 g, 9.26 mmol) in ethanol (31 mL). After heating to reflux for 24 h, the reaction solution was concentrated *in vacuo* and diluted with ethyl acetate (30 mL). The solution was washed with 5% by mass $NaHCO_3$ aqueous solution (3 × 30 mL) and water (3 × 30 mL). After drying the solution with magnesium sulphate, the solution was concentrated under reduced pressure to give the title compound as a colourless oil (1.4955 g, 7.86 mmol) in 85% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, *J* = 16 Hz, 1H), 7.43 (d, *J* = 8 Hz, 2H), 7.19 (d, *J* = 8 Hz, 2H), 6.39 (d, *J* = 16 Hz, 1H), 4.26 (q, *J* = 7 Hz, 2H), 2.37 (s, 3H), 1.34 (s, 3H) ppm

^{1}H NMR data consistent with literature.[4]

Ethyl (*E*)-3-(*p*-methoxyphenyl)-2-propenoate 9f

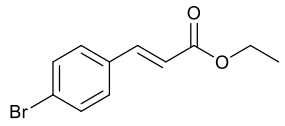


Concentrated sulphuric acid (approximately 1 mL) was added to a solution of 4-methoxycinnamic acid (2.0060 g, 11.3 mmol) in ethanol (35 mL). After heating to reflux for 24 h, the reaction solution was concentrated *in vacuo* and diluted with ethyl acetate (35 mL). The solution was washed with 5% by mass $NaHCO_3$ aqueous solution (3 × 30 mL) and water (3 × 30 mL). After drying the solution with magnesium sulphate, the solution was concentrated under reduced pressure to give the title compound as a colourless oil (2.2047 g, 10.7 mmol) in 95% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, *J* = 16 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 6.31 (d, *J* = 16 Hz, 1H), 4.25 (q, *J* = 7.5 Hz, 2H), 3.84 (s, 3H), 1.33 (t, *J* = 7 Hz, 3H) ppm

^{1}H NMR data are consistent with literature.[5]

Ethyl (*E*)-3-(*p*-bromophenyl)-2-propenoate 9g



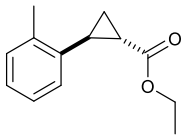
Concentrated sulphuric acid (approximately 1 mL) was added to a solution of 4-bromocinnamic acid (3.3966 g, 15.0 mmol) in ethanol (50 mL). After heating to reflux for 24 h, the reaction solution was concentrated *in vacuo* and diluted with ethyl acetate (50 mL). The solution was washed with 5% by mass $NaHCO_3$ aqueous solution (3 × 30 mL) and water (3 × 30 mL). After drying the solution with magnesium sulphate, the solution was concentrated under reduced pressure to give a mixture of colourless oil and white precipitate. After hexane was added to the mixture, the colourless oil was dissolved in the solvent while the precipitate remained insoluble. After filtering the suspension, the filtrate was concentrated in vacuo to give the title compound as a pale yellow oil (3.4818 g, 13.6 mmol) in 91% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61 (d, *J* = 15.9 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 6.42 (d, *J* = 16.2 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 3H) ppm

^{1}H NMR data are consistent with literature.[6]

Corey–Chaykovsky Cyclopropanation

Ethyl 2-(*o*-tolyl)cyclopropane-1-carboxylate 10b



A suspension of trimethylsulfoxonium iodide (2.9402 g, 13.4 mmol, 1.2 equiv) and sodium hydride (60% in mineral oil, 544.2 mg, 13.6 mmol, 1.2 equiv) in anhydrous DMSO (10 mL) were stirred for 1 h before the addition of ethyl (*E*)-3-(*o*-tolyl)-2-propenoate (2.117 g, 11.1 mmol, 1 equiv) in anhydrous DMSO (10 mL). After the reaction was heated at 55°C for 24 h, another suspension of trimethylsulfoxonium iodide (0.7503 g, 3.41 mmol, 0.3 equiv) and sodium hydride (60% in mineral oil, 137.1 mg, 3.43 mmol, 0.3 equiv) in anhydrous DMSO (2.5 mL) was stirred for 1 h and added to the reaction solution. The reaction was then heated at 65°C overnight before it was poured into brine solution (50 mL) and extracted with ethyl acetate (4 × 30 mL). The combined organic extracts were washed with water (50 mL) and brine solution (50 mL). After drying with magnesium sulphate, the solution was concentrated under reduced pressure to give a mixture of yellow oil and brown precipitate which was later subjected to column chromatography twice (5% ethyl acetate in hexane). The title compound was collected as a pale yellow oil (1.3852 g, 6.78 mmol) in 61% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.15 – 7.11 (m, 3H), 7.00 (d, *J* = 6 Hz, 1H), 4.25 – 4.15 (m, 2H), 2.53 – 2.49 (m, 1H), 2.38 (s, 3H), 1.78 (ddd, *J* = 8.6, 4.5, 4.5 Hz, 1H), 1.59 – 1.56 (m, 1H), 1.32 – 1.28 (m, 4H) ppm

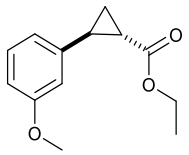
^{13}C NMR (75 MHz, $CDCl_3$): δ 174, 138.1, 138.0, 130.0, 126.8, 126.0, 126.0, 60.8, 24.8, 22.5, 19.7, 15.5, 14.5 ppm

IR (Neat): 2923, 1724 cm^{-1}

HRMS (ASAP) Found: (M+H)+, 205.1230. $C_{13}H_{16}O_2$ requires (M+H)+, 205.1229

^1H and ^{13}C NMR data are consistent with literature.[7]

Ethyl 2-(*m*-methoxyphenyl)cyclopropane-1-carboxylate 10c

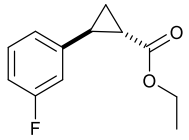


A suspension of trimethylsulfoxonium iodide (2.6871 g, 12.2 mmol, 1.2 equiv) and sodium hydride (60% in mineral oil, 497.8 mg, 12.4 mmol, 1.2 equiv) in anhydrous DMSO (10 mL) were stirred for 1 h before the addition of ethyl (*E*)-3-(*m*-methoxyphenyl)-2-propenoate (2.0848 g, 10.1 mmol, 1 equiv) in anhydrous DMSO (10 mL). After the reaction was heated at 55°C for 24 h, the reaction solution was poured into brine solution (50 mL) and extracted with ethyl acetate (3 × 30 mL). The combined organic extracts were washed with water (2 × 20 mL) and brine solution (2 × 20 mL). After drying with magnesium sulphate, the solution was concentrated under reduced pressure to give a yellow oil crude which was later subjected to column chromatography (10% ethyl acetate in hexane). The title compound was collected as a colourless oil (809.3 mg, 3.67 mmol) in 36% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.19 (t, *J* = 8 Hz, 1H), 6.74 (d, *J* = 8 Hz, 1H), 6.69 (d, *J* = 7.5 Hz, 1H), 6.65 (s, 1H), 4.17 (q, *J* = 7 Hz, 2H), 3.79 (s, 3H), 2.51 – 2.47 (m, 1H), 1.90 (ddd, *J* = 8.4, 4.5, 4.5 Hz, 1H), 1.60 – 1.57 (m, 1H), 1.32 – 1.26 (m, 4H) ppm

^1H NMR data are consistent with literature.[8]

Ethyl 2-(*m*-fluorophenyl)cyclopropane-1-carboxylate 10d



A suspension of trimethylsulfoxonium iodide (1.9331 g, 8.78 mmol, 1.2 equiv) and sodium hydride (60% in mineral oil, 355 mg, 8.87 mmol, 1.2 equiv) in anhydrous DMSO (7.5 mL) were stirred for 1 h before the addition of ethyl (*E*)-3-(*m*-fluorophenyl)-2-propenoate (1.415 g, 7.29 mmol, 1 equiv) in anhydrous DMSO (7.5 mL). After heating at 55°C for 24 h, the reaction solution was poured into brine solution (45 mL) and extracted with ethyl acetate (3 × 30 mL). The combined organic extracts were washed with water (4 × 20 mL) and brine solution (2 × 20 mL). After drying the solution with magnesium sulphate, the solution was concentrated under reduced pressure to give a yellow oil crude which was later subjected to column chromatography (5% ethyl acetate in hexane). The title compound was collected as a colourless oil (649.8 mg, 3.12 mmol) in 43% yield.

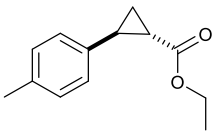
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26 – 7.21 (m, 1H), 6.91 – 6.87 (m, 2H), 6.78 (d, *J* = 10 Hz, 1H), 4.17 (q, *J* = 7 Hz, 2H), 2.52 – 2.48 (m, 1H), 1.92 – 1.88 (m, 1H), 1.63 – 1.59 (m, 1H), 1.28 (t, *J* = 7 Hz, 4H) ppm

^{13}C NMR (125 MHz, $CDCl_3$): δ 172.7, 162.8 (d, *J* = 245 Hz), 142.8 (d, *J* = 7.5 Hz), 129.7 (d, *J* = 8.8 Hz), 121.8 (d, *J* = 2.5 Hz), 113.1 (d, *J* = 21.3 Hz), 112.7 (d, *J* = 22.5 Hz), 60.5, 25.5 (d, *J* = 1.3 Hz), 24.1, 16.9, 14.0 ppm

IR (Neat): 1718 cm^{-1}

HRMS (ESI) Found: (M+H)+, 209.09770. $C_{12}H_{13}FO_2$ requires (M+H)+, 209.09778

Ethyl 2-(*p*-tolyl)cyclopropane-1-carboxylate 10e



A suspension of trimethylsulfoxonium iodide (1.2960 g, 5.89 mmol, 1.2 equiv) and sodium hydride (60% in mineral oil, 242.8 mg, 6.07 mmol, 1.2 equiv) in anhydrous DMSO (5 mL) were stirred for 1 h before the addition of ethyl (*E*)-3-(*p*-tolyl)-2-propenoate (932.4 mg, 4.90 mmol, 1 equiv) in anhydrous DMSO (5 mL). After the reaction was heated at 55°C for 5 h, the reaction solution was poured into brine solution (30 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic extracts were washed with water (2 × 30 mL) and brine

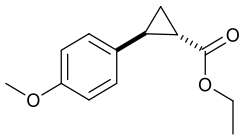
solution (30 mL). After drying the solution with magnesium sulphate, the solution was concentrated under reduced pressure to give a yellow oil crude which was later subjected to column chromatography (5% ethyl acetate in hexane). The title compound was collected as a colourless oil (480.5 mg, 2.35 mmol) in 48% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.09 (d, *J* = 7.8 Hz, 2H), 6.99 (d, *J* = 8.1 Hz, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 2.52 – 2.45 (m, 1H), 2.31 (s, 3H), 1.86 (ddd, *J* = 8.7, 4.7, 4.2 Hz, 1H), 1.60 – 1.53 (m, 1H), 1.27 (t, *J* = 7.2 Hz, 4H) ppm

HRMS (ASAP) Found: (M+H)+, 205.1228. $C_{13}H_{16}O_2$ requires (M+H)+, 205.1229

^{1}H NMR data are consistent with literature.[8]

Ethyl 2-(*p*-methoxyphenyl)cyclopropane-1-carboxylate 10f



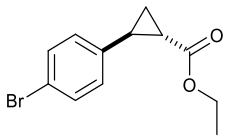
A suspension of trimethylsulfoxonium iodide (2.8271 g, 12.8 mmol, 1.2 equiv) and sodium hydride (60% in mineral oil, 537.4 mg, 13.4 mmol, 1.3 equiv) in anhydrous DMSO (10 mL) were stirred for 1 h before the addition of ethyl (*E*)-3-(*p*-methoxyphenyl)-2-propenoate (2.205 g, 10.7 mmol, 1 equiv) in anhydrous DMSO (10 mL). After the reaction was heated at 55°C for 24 h, another suspension of trimethylsulfoxonium iodide (0.7503 g, 3.41 mmol, 0.3 equiv) and sodium hydride (60% in mineral oil, 137.1 mg, 3.43 mmol, 0.3 equiv) in anhydrous DMSO (2.5 mL) was stirred for 1 h and added to the reaction solution. The reaction was then heated at 65°C for 84 h before it was poured into brine solution (60 mL) and extracted with ethyl acetate (4 × 30 mL). The combined organic extracts were washed with water (50 mL) and brine solution (50 mL). After drying the solution with magnesium sulphate, the solution was concentrated under reduced pressure to give an orange-yellow solid crude which was later subjected to column chromatography (10% ethyl acetate in hexane). The title compound was collected as a white solid (919 mg, 4.17 mmol) in 39% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.03 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 9 Hz, 2H), 4.16 (q, *J* = 7 Hz, 2H), 3.78 (s, 3H), 2.50 – 2.46 (m, 1H), 1.82 (ddd, *J* = 8.5, 4.8, 5 Hz, 1H), 1.57 – 1.53 (m, 1H), 1.29 – 1.23 (m, 4H) ppm

HRMS (ASAP) Found: (M+H)+, 221.1179. $C_{13}H_{16}O_3$ requires (M+H)+, 221.1178

^{1}H NMR data are consistent with literature.[8]

Ethyl 2-(*p*-bromophenyl)cyclopropane-1-carboxylate 10g



A suspension of trimethylsulfoxonium iodide (3.6085 g, 16.4 mmol, 1.2 equiv) and sodium hydride (60% in mineral oil, 664.1 mg, 16.6 mmol, 1.2 equiv) in anhydrous DMSO (12 mL) were stirred for 1 h before the addition of ethyl (*E*)-3-(*p*-bromophenyl)-2-propenoate (3.482 g, 13.6 mmol, 1 equiv) in anhydrous DMSO (12 mL). After the reaction was heated at 60°C for 36 h, the reaction solution was poured into brine solution (50 mL) and extracted with ethyl acetate (4 × 30 mL). The combined organic extracts were washed with water (50 mL) and brine solution (50 mL). After drying the solution with magnesium sulphate, the solution was concentrated under reduced pressure to give a brown oil crude which was later subjected to column chromatography (10% ethyl acetate in hexane). The title compound was collected as a colourless oil (1.5181 g, 5.64 mmol) in 41% yield.

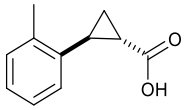
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8 Hz, 2H), 6.97 (d, *J* = 8 Hz, 2H), 4.17 (q, *J* = 7 Hz, 2H), 2.49 – 2.45 (m, 1H), 1.86 (ddd, *J* = 8.4, 4.5, 4.5 Hz, 1H), 1.60 (ddd, *J* = 9.3, 4.8, 5 Hz, 1H), 1.29 – 1.25 (m, 4H) ppm

HRMS (ASAP) Found: (M+H)+, 269.0164. $C_{12}H_{13}O_2Br$ requires (M+H)+, 269.0177

^{1}H NMR data are consistent with literature.[8]

Basic hydrolysis

2-(*o*-tolyl)cyclopropane-1-carboxylic acid



Sodium hydroxide solution (1 M, 9.5 mL, 9.5 mmol, 2 equiv) was added to a solution of ethyl 2-(*o*-tolyl)cyclopropane-1-carboxylate (1.0022 g, 4.91 mmol, 1 equiv) in ethanol (18 mL). After the solution was left stirring overnight at room temperature, hydrochloric acid solution (2 M, 7.1 mL, 14.2 mmol, 3 equiv) and water (5 mL) were added at 0°C. The solution was extracted with ethyl acetate (50 mL + 2 × 30 mL) and washed with brine solution (2 × 30 mL). After drying the solution with magnesium sulphate, the solution was concentrated under reduced pressure to give the title compound as a white solid (816.3 mg, 4.63 mmol) in 94% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.18 – 7.12 (m, 3H), 7.01 (d, *J* = 7 Hz, 1H), 2.63 – 2.59 (m, 1H), 2.41 (s, 3H), 1.81 – 1.77 (m, 1H), 1.65 (ddd, *J* = 9.1, 4.5, 5.0 Hz, 1H), 1.43 – 1.39 (m, 1H) ppm

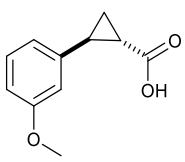
^{13}C NMR (125 MHz, $CDCl_3$): δ 180.4, 138.1, 137.3, 130.0, 127.0, 126.0, 126.0, 25.6, 22.3, 19.6, 16.0 ppm

IR (Neat): 2926, 1685 cm^{-1}

HRMS (ASAP) Found: (M+H)+, 177.0944. $C_{11}H_{12}O_2$ requires (M+H)+, 177.0916

Melting point: 67.3 – 69.7 °C

2-(*m*-methoxyphenyl)cyclopropane-1-carboxylic acid



Sodium hydroxide solution (1 M, 7.35 mL, 7.35 mmol, 2 equiv) was added to a solution of ethyl 2-(*m*-methoxyphenyl)cyclopropane-1-carboxylate (807.7 mg, 3.67 mmol, 1 equiv) in ethanol (14 mL). After the solution was left stirring overnight at room temperature, hydrochloric acid solution (2 M, 5.5 mL, 11 mmol, 3 equiv) and water (8.5 mL) were added to the reaction solution at 0°C. The solution was extracted with ethyl acetate (55 mL + 2 × 30 mL) and washed with brine solution (2 × 30 mL). After drying the solution with magnesium sulphate, the solution was concentrated under reduced pressure to give the title compound as a white solid (689.6 mg, 3.59 mmol) in 98% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.20 (t, *J* = 8 Hz, 1H), 6.76 (d, *J* = 8 Hz, 1H), 6.69 (d, *J* = 7.5 Hz, 1H), 6.65 (s, 1H), 3.79 (s, 3H), 2.60 – 2.56 (m, 1H), 1.90 (ddd, *J* = 8.4, 4.5, 4.5 Hz, 1H), 1.65 (ddd, *J* = 9.5, 4.5, 5.0 Hz, 1H), 1.41 – 1.37 (m, 1H) ppm

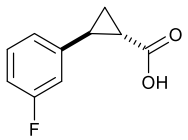
^{13}C NMR (125 MHz, $CDCl_3$): δ 179.7, 159.8, 141.2, 129.6, 118.6, 112.3, 112.0, 56.2, 27.1, 24.0, 17.5 ppm

IR (Neat): 2934, 1684 cm^{-1}

HRMS (ESI) Found: (M-H)-, 191.0699. $C_{11}H_{12}O_3$ requires (M-H)-, 191.0708

Melting point: 94.3 – 95.1 °C

2-(*m*-fluorophenyl)cyclopropane-1-carboxylic acid



Sodium hydroxide solution (1 M, 5.1 mL, 5.1 mmol, 2 equiv) was added to a solution of ethyl 2-(*m*-fluorophenyl)cyclopropane-1-carboxylate (529.2 mg, 2.54 mmol, 1 equiv) in ethanol (45 mL). After the solution was left stirring overnight at room temperature, hydrochloric acid solution (2 M, 3.8 mL, 7.6 mmol, 3 equiv) and water (5 mL) were added to the reaction solution at 0°C. The solution was extracted with ethyl acetate (80 mL + 2 × 20 mL) and washed with brine solution (2 × 40 mL). After drying the solution with magnesium

sulphate, the solution was concentrated under reduced pressure to give the title compound as a white solid (367.1 mg) in 80% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24 (d, *J* = 6.5 Hz, 1H), 6.92 – 6.89 (m, 2H), 6.79 (d, *J* = 10 Hz, 1H), 2.61 – 2.57 (m, 1H), 1.90 (ddd, *J* = 8.4, 4.5, 4.5 Hz, 1H), 1.67 (ddd, *J* = 9.6, 4.8, 5.0 Hz, 1H), 1.40 – 1.36 (m, 1H) ppm

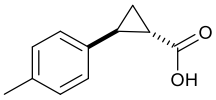
^{13}C NMR (125 MHz, $CDCl_3$): δ 179.5, 163.0 (d, *J* = 244 Hz), 142.2 (d, *J* = 7.5 Hz), 130.0 (d, *J* = 7.5 Hz), 122.1 (d, *J* = 3.8 Hz), 113.7 (d, *J* = 21.3 Hz), 113.2 (d, *J* = 22.5 Hz), 26.6 (d, *J* = 2.5 Hz), 24.1, 17.5 ppm

IR (Neat): 1685 cm^{-1}

HRMS (ESI) Found: (M-H)-, 179.05068. $C_{10}H_9FO_2$ requires (M-H)-, 179.05083

Melting point: 78.9 – 79.9 °C

2-(*p*-tolyl)cyclopropane-1-carboxylic acid



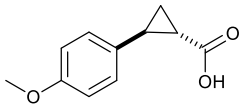
Sodium hydroxide solution (1 M, 4.7 mL, 4.7 mmol, 2 equiv) was added to a solution of ethyl 2-(*p*-tolyl)cyclopropane-1-carboxylate (476.6 mg, 2.3 mmol) in ethanol (43 mL). After the solution was left stirring overnight at room temperature, hydrochloric acid solution (2 M, 3.6 mL, 7.2 mmol) and water (21 mL) were added to the reaction solution at 0°C. The solution was extracted with ethyl acetate (80 mL + 2 × 40 mL) and washed with brine solution (30 mL). After drying the solution with magnesium sulphate, the solution was concentrated under reduced pressure to give the title compound as a white solid (343.9 mg, 1.95 mmol) in 84% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.10 (d, *J* = 7.5 Hz, 2H), 7.01 (d, *J* = 8 Hz, 2H), 2.59 – 2.55 (m, 1H), 2.32 (s, 3H), 1.87 (ddd, *J* = 8.4, 4.5, 4.5 Hz, 1H), 1.63 (ddd, *J* = 9.3, 4.8, 5 Hz, 1H), 1.39 – 1.35 (m, 1H) ppm

Melting point: 113.0 – 116.4 °C

^{1}H NMR data are consistent with literature.[9]

2-(*p*-methoxyphenyl)cyclopropane-1-carboxylic acid



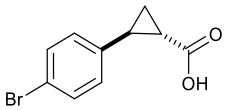
Sodium hydroxide solution (1 M, 8.5 mL, 8.5 mmol, 2 equiv) was added to a solution of ethyl 2-(*p*-methoxyphenyl)cyclopropane-1-carboxylate (917.9 mg, 4.17 mmol, 1 equiv) in ethanol (15 mL). After the solution was left stirring overnight at room temperature, hydrochloric acid solution (2 M, 6.4 mL, 12.8 mmol, 3 quiv) and water (9 mL) were added at 0°C. The solution was extracted with ethyl acetate (50 mL + 2 × 30 mL) and washed with brine solution (2 × 30 mL). After drying the solution with magnesium sulphate, the solution was concentrated under reduced pressure to give the title compound as a white solid (791.4 mg, 4.12 mmol) in 99% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.05 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 9 Hz, 2H), 3.79 (s, 3H), 2.59 – 2.55 (m, 1H), 1.83 (ddd, *J* = 8.4, 4.5, 4.5 Hz, 1H), 1.62 (ddd, *J* = 9.5, 4.8, 4.5 Hz, 1H), 1.37 – 1.34 (m, 1H) ppm

Melting point: 109.9 – 113.3 °C

^{1}H NMR data are consistent with literature.[9]

2-(*p*-bromophenyl)cyclopropane-1-carboxylic acid[12]



Sodium hydroxide solution (1 M, 6.9 mL, 6.9 mmol, 2 equiv) was added to a solution of ethyl 2-(*p*-bromophenyl)cyclopropane-1-carboxylate (922.3 mg, 3.43 mmol, 1 equiv) in ethanol (12 mL). After the solution was left stirring overnight at room temperature, hydrochloric acid solution (2 M, 5.2 mL, 10.4 mmol, 3 equiv) and water (5 mL) were added

to the reaction solution at 0°C. The solution was extracted with ethyl acetate (3 × 30 mL) and washed with brine solution (2 × 30 mL). After drying the solution with magnesium sulphate, the solution was concentrated under reduced pressure to give the title compound as a white solid (823.1 mg, 3.41 mmol) in 100% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 8 Hz, 2H), 2.57 – 2.53 (m, 1H), 1.88 (ddd, *J* = 8.2, 4.2, 4.0 Hz, 1H), 1.66 (ddd, *J* = 9.2, 4.8, 5.0 Hz, 1H), 1.39 – 1.35 (m, 1H) ppm

^{13}C NMR (75 MHz, $CDCl_3$): δ 179.3, 138.8, 131.7, 128.2, 120.5, 26.5, 24.2, 17.5 ppm

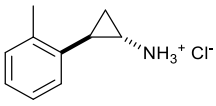
IR (Neat): 2923, 1681 cm^{-1}

HRMS (ASAP) Found: (M+H)+, 240.9865. $C_{10}H_9O_2Br$ requires (M+H)+, 240.9864

Melting point: 118.5 – 122.4 °C

Curtius rearrangement + Deprotection

2-(*o*-tolyl)cyclopropylamine hydrochloride 11b



Diphenyl phosphoryl azide (1.1 mL, 1.381 g, 5.02 mmol, 1.2 equiv), triethylamine (0.95 mL, 0.692 g, 6.84 mmol, 1.6 equiv) and *tert*-butanol (8.8 mL, 6.763 g, 91.24 mmol, 21 equiv) were added to a solution of 2-(*o*-tolyl)cyclopropane-1-carboxylic acid (748.8 mg, 4.25 mmol, 1 equiv) in dry toluene (25 mL). After the reaction was heated at 82°C for 24 h, di-*tert*-butyl dicarbonate (1.1540 g, 5.29 mmol, 1.2 equiv) was added and the reaction solution was allowed to stir for another 1.5 h before concentrating it under reduced pressure. The crude mixture was subjected to column chromatography (15% ethyl acetate in hexane) to give the intermediate *tert*-butyl (2-(*o*-tolyl)cyclopropyl)carbamate as a yellowish white solid (502.2 mg, 2.03 mmol).**^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.12 – 7.05 (m, 4H), 4.82 (bs, 1H), 2.78 (bs, 1H), 2.41 (s, 3H), 2.02 – 1.97 (m, 1H), 1.47 (s, 9H), 1.15 – 1.11 (m, 2H) ppm. Trifluoroacetic acid (5 mL) was added to a solution of *tert*-butyl (2-(*o*-tolyl)cyclopropyl)carbamate (494.9 mg, 2 mmol) in dichloromethane (1 mL). After the solution was stirred for 30 mins, solvent

was removed under reduced pressure and ethereal HCl (1 M, 7 mL, 7 mmol, 3.5 equiv) was added to precipitate the product. Solvent was carefully removed by a glass Pasteur pipette and the precipitate was washed with diethyl ether (3 × 10 mL). The title compound was collected as a yellow solid (343.6 mg, 1.87 mmol) in 45% yield after two consecutive steps.

^{1}H NMR (500 MHz, DMSO): δ 8.72 (br s, 3H), 7.16 (bs, 1H), 7.12 – 7.09 (m, 2H), 6.98 (d, *J* = 6 Hz, 1H), 2.68 (bs, 1H), 2.46 (m, 1H), 2.38 (s, 3H), 1.39 – 1.35 (m, 1H), 1.20 – 1.16 (m, 1H) ppm

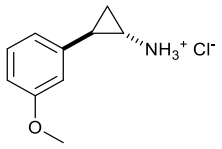
^{13}C NMR (125 MHz, DMSO): δ 137.2, 136.9, 129.6, 126.5, 125.9, 125.6, 29.6, 19.5, 18.9, 11.4 ppm

IR (Neat): 2898 cm^{-1}

HRMS (ESI) Found: (M+H)+, 148.1130. $C_{10}H_{13}N$ requires (M+H)+, 148.1126

Melting point: 173.7 – 175.4 °C

2-(*m*-methoxyphenyl)cyclopropylamine hydrochloride 11c[13]



Diphenyl phosphoryl azide (0.85 mL, 1.086 g, 3.95 mmol, 1.2 equiv), triethylamine (0.75 mL, 0.545 g, 5.38 mmol, 1.7 equiv) and *tert*-butanol (7 mL, 5.425 g, 73.2 mmol, 22 mmol) were added to a solution of 2-(*m*-methoxyphenyl)cyclopropane-1-carboxylic acid (626.8 mg, 3.26 mmol, 1 equiv) in dry toluene (20 mL). After the reaction was heated at 82°C for 24 h, di-*tert*-butyl dicarbonate (1.0649 g, 4.88 mmol, 1.5 equiv) was added and the reaction solution was allowed to stir for another 2 h before concentrating it under reduced pressure. The crude mixture was subjected to rapid column chromatography (20% ethyl acetate in hexane) to give the intermediate *tert*-butyl (2-(*m*-methoxyphenyl)cyclopropyl)carbamate as a white solid (459 mg, 1.74 mmol). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.17 (t, *J* = 8 Hz, 1H), 6.72 (d, *J* = 8 Hz, 2H), 6.65 (bs, 1H), 4.82 (bs, 1H), 3.78 (s, 3H), 2.74 (bs, 1H), 2.03 – 1.99 (m, 1H), 1.45 (s, 9H), 1.17 – 1.15 (m, 2H) ppm. Trifluoroacetic acid (3 mL) was added to a

solution of *tert*-butyl (2-(*m*-methoxyphenyl)cyclopropyl)carbamate (457.9 mg, 1.74 mmol, 1 equiv) in dichloromethane (2 mL). After the solution was stirred for 50 mins, solvent was removed under reduced pressure and ethereal HCl (1 M, 6 mL, 6 mmol, 3.4 equiv) was added to precipitate the product. Solvent was carefully removed by a glass pasteur pipette and the precipitate was washed with diethyl ether (4 × 10 mL). The title compound was collected as a sandy brown solid (329.6 mg, 1.65 mmol) in 50% yield after two consecutive steps.

^{1}H NMR (300 MHz, DMSO): δ 8.68 (br s, 3H), 7.19 (t, *J* = 7.8 Hz, 1H), 6.77 – 6.70 (m, 3H), 3.73 (s, 3H), 2.77 (bs, 1H), 2.35 (bs, 1H), 1.45 – 1.39 (m, 1H), 1.22 – 1.15 (m, 1H) ppm

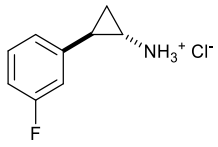
^{13}C NMR (75 MHz, DMSO): δ 159.4, 140.9, 129.4, 118.5, 111.9, 111.8, 55.0, 30.5, 20.8, 13.2 ppm

IR (Neat): 3065, 2958, 2870 cm^{-1}

HRMS (ESI) Found: (M+H)+, 164.1076. $C_{10}H_{13}ON$ requires (M+H)+, 164.1075

Melting point: 146.5 – 147.8 °C

2-(*m*-fluorophenyl)cyclopropylamine hydrochloride 11d



Diphenyl phosphoryl azide (0.5 mL, 613.2 mg, 2.23 mmol, 1.2 equiv), triethylamine (0.42 mL, 307.5 mg, 3.04 mmol, 1.6 equiv) and *tert*-butanol (3.9 mL, 3.003 g, 40.5 mmol,m 22 equiv) were added to a solution of 2-(*m*-fluorophenyl)cyclopropane-1-carboxylic acid (339.3 mg, 1.88 mmol, 1 equiv) in dry toluene (11 mL). After the reaction was heated at 82°C for 22 h, di-*tert*-butyl dicarbonate (669.9 mg, 3.07 mmol, 1.6 equiv) was added and the reaction solution was allowed to stir for another 2 h before concentrating it under reduced pressure. The crude mixture was subjected to column chromatography (15% ethyl acetate in hexane) to give the intermediate *tert*-butyl (2-(*m*-fluorophenyl)cyclopropyl)carbamate as a white solid (203.3 mg, 0.809 mmol). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.21 (q, *J* = 6.5 Hz, 1H), 6.92 (d, *J* = 7.5 Hz, 1H), 6.87 – 6.80 (m, 2H), 4.84 (bs, 1H), 2.71 (bs, 1H), 2.05 – 2.02 (m, 1H), 1.45 (s,

9H), 1.16 (t, *J* = 7.5 Hz, 2H) ppm. Trifluoroacetic acid (2 mL) was added to a solution of *tert*-butyl (2-(*m*-fluorophenyl)cyclopropyl)carbamate (203.3 mg, 0.809 mmol, 1 equiv) in dichloromethane (3 mL). After the solution was stirred for 30 mins, solvent was removed under reduced pressure and ethereal HCl (1 M, 4 mL, 4 mmol, 4.9 equiv) was added to precipitate the product. Solvent was carefully removed by a glass pasteur pipette and the precipitate was washed with diethyl ether (3 × 10 mL). The title compound was collected as a white solid (145.6 mg, 0.78 mmol) in 41% yield after two consecutive steps.

^{1}H NMR (300 MHz, DMSO): δ 8.72 (br s, 3H), 7.32 (q, *J* = 6 Hz, 1H), 7.02 (t, *J* = 6.9 Hz, 3H), 2.84 – 2.79 (m, 1H), 2.45 – 2.38 (m, 1H), 1.50 – 1.43 (m, 1H), 1.23 (m, 1H) ppm

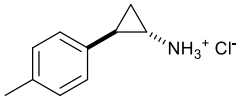
^{13}C NMR (125 MHz, DMSO): δ 162.3 (d, *J* = 241.3 Hz), 142.5 (d, *J* = 7.5 Hz), 130.2 (d, *J* = 8.8 Hz), 122.7 (d, *J* = 2.5 Hz), 113.0 (d, *J* = 17.5 Hz), 112.9 (d, *J* = 18.8 Hz), 30.7, 20.5 (d, *J* = 2.5 Hz), 13.5 ppm

IR (Neat): 2990, 2945, 2863, cm^{-1}

HRMS (ASAP) Found: (M+H)+, 152.0906. $C_9H_{10}NF$ requires (M+H)+, 152.0876

Melting point: 173.8 – 175.4 °C

2-(*p*-tolyl)cyclopropylamine hydrochloride 11e



Diphenyl phosphoryl azide (0.5 mL, 640 mg, 2.33 mmol, 1.2 equiv), triethylamine (0.41 mL, 297.7 mg, 2.94 mmol, 1.6 equiv) and *tert*-butanol (3.8 mL, 2.945 g, 39.7 mmol, 21 equiv) were added to a solution of 2-(*p*-tolyl)cyclopropane-1-carboxylic acid (331.1 mg, 1.88 mmol, 1 equiv) in dry toluene (11 mL). After the reaction was heated at 82°C for 24 h, di-*tert*-butyl dicarbonate (646.5 mg, 2.96 mmol, 1.6 equiv) was added and the reaction solution was allowed to stir for another 2 h before concentrating it under reduced pressure. The crude mixture was subjected to column chromatography (15% ethyl acetate in hexane) to give the intermediate *tert*-butyl (2-(*p*-tolyl)cyclopropyl)carbamate as a white solid (227.8 mg, 0.92 mmol). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.07 (d, *J* = 8 Hz, 2H), 7.02 (d, *J* = 7.5 Hz, 2H), 4.84

(bs, 1H), 2.69 (bs, 1H), 2.30 (s, 3H), 2.02 – 1.98 (m, 1H), 1.45 (s, 9H), 1.14 – 1.12 (m, 2H) ppm. Trifluoroacetic acid (2 mL) was added to a solution of *tert*-butyl (2-(*p*-tolyl)cyclopropyl)carbamate (215.6 mg, 0.87 mmol, 1 equiv) in dichloromethane (2 mL). After the solution was stirred for 30 mins, solvent was removed under reduced pressure and ethereal HCl (1 M, 4 mL, 4 mmol, 4.6 equiv) was added to precipitate the product. Solvent was carefully removed by a glass pasteur pipette and the precipitate was washed with diethyl ether (2 × 10 mL). The title compound was collected as a yellow solid (123.9 mg, 0.67 mmol) in 38% yield after two consecutive steps.

^{1}H NMR (500 MHz, DMSO): δ 8.67 (br s, 3H), 7.09 (d, *J* = 7.5 Hz, 2H), 7.03 (d, *J* = 8 Hz, 2H), 2.70 (bs, 1H), 2.34 (bs, 1H), 2.25 (s, 3H), 1.41 – 1.37 (m, 1H), 1.14 – 1.11 (m, 1H) ppm

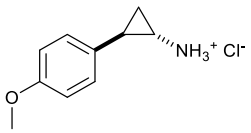
^{13}C NMR (125 MHz, DMSO): δ 136.2, 135.3, 128.9, 126.1, 30.4, 20.6, 20.4, 13.0 ppm

IR (Neat): 2903 cm^{-1}

HRMS (ESI) Found: (M+H)+, 148.11215. $C_{10}H_{13}N$ requires (M+H)+, 148.11262

Melting point: 150.2 – 155.5 °C

2-(*p*-methoxyphenyl)cyclopropylamine hydrochloride 11f



Diphenyl phosphoryl azide (0.97 mL, 1.237 g, 4.5 mmol, 1.2 equiv), triethylamine (0.85 mL, 620.3 mg, 6.13 mmol, 1.6 equiv) and *tert*-butanol (7.8 mL, 6.0605 g, 81.8 mmol, 21 equiv) were added to a solution of 2-(*p*-methoxyphenyl)cyclopropane-1-carboxylic acid (746 mg, 3.9 mmol, 1 equiv) in dry toluene (24 mL). After the reaction was heated at 82°C for 24 h, di-*tert*-butyl dicarbonate (990.5 mg, 4.54 mmol, 1.2 equiv) was added and the reaction solution was allowed to stir for another 2 h before concentrating it under reduced pressure. The crude mixture was subjected to column chromatography (20% ethyl acetate in hexane) to give the intermediate *tert*-butyl (2-(*p*-methoxyphenyl)cyclopropyl)carbamate as a white solid (607.8 mg, 2.31 mmol). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.08 (d, *J* = 8 Hz, 2H), 6.81 (d, *J* = 8 Hz, 2H), 4.81 (bs, 1H), 3.77 (s, 3H), 2.65 (bs, 1H), 2.00 (bs, 1H), 1.46 (s, 9H), 1.11 – 1.08 (m,

2H) ppm. Trifluoroacetic acid (2 mL) was added to a solution of *trans-tert*-Butyl-2-(*p*-methoxyphenyl)cyclopropylcarbamate (0.371 g, 1.4 mmol) in dichloromethane (2 mL). After the solution was stirred for 30 mins, solvent was removed under reduced pressure and ethereal HCl (1 M, 4 mL, 4 mmol, 2.9 equiv) was added to precipitate the product. Solvent was carefully removed by a glass pasteur pipette and the precipitate was washed with diethyl ether (5 × 10 mL). The title compound was collected as pale yellow powder (225 mg, 1.13 mmol) in 41% yield after two consecutive steps.

^{1}H NMR (500 MHz, CD_3OD): δ 7.10 (d, J = 8 Hz, 2H), 6.86 (d, J = 8 Hz, 2H), 3.76 (s, 3H), 2.76 – 2.75 (m, 1H), 2.35 (bs, 1H), 1.39 – 1.36 (m, 1H), 1.25 (q, J = 7 Hz, 1H) ppm

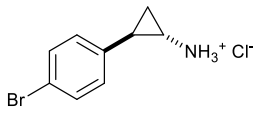
^{13}C NMR (125 MHz, CD_3OD): δ 160.1, 131.6, 128.6, 115.1, 55.7, 31.8, 21.9, 13.4 ppm

IR (Neat): 3128, 3037, 2884 cm^{-1}

Melting point: 176.4 – 179.4°C

^{1}H NMR data are consistent with literature.[10]

2-(*p*-bromophenyl)cyclopropylamine hydrochloride 11g



Diphenyl phosphoryl azide (0.8 mL, 1.024 g, 3.72 mmol, 1.5 equiv), triethylamine (0.7 mL, 508.2 mg, 5.02 mmol, 2 equiv) and *tert*-butanol (6.4 mL, 4.96 g, 66.9 mmol, 26 equiv) were added to a solution of 2-(*p*-bromophenyl)cyclopropane-1-carboxylic acid (611.5 mg, 2.54 mmol, 1 equiv) in dry toluene (20 mL). After the reaction was heated at 82°C for 24 h, di-*tert*-butyl dicarbonate (840.8 mg, 3.85 mmol, 1.5 equiv) was added and the reaction solution was allowed to stir for another 1 h before concentrating it under reduced pressure. The crude mixture was subjected to column chromatography (15% ethyl acetate in hexane) to give the intermediate *tert*-butyl (2-(*p*-bromophenyl)cyclopropyl)carbamate as a white solid (372.4 mg, 1.19 mmol). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.37 (d, J = 7.5 Hz, 2H), 7.02 (d, J = 7.5 Hz, 2H), 4.81 (bs, 1H), 2.67 (bs, 1H), 2.00 (bs, 1H), 1.45 (s, 9H), 1.15 – 1.12 (bs, 2H) ppm. Trifluoroacetic acid (4 mL) was added to a solution of *tert*-butyl (2-(*p*-

bromophenyl)cyclopropyl)carbamate (371.9 mg, 1.19 mmol, 1 equiv) in dichloromethane (3 mL). After the solution was stirred for 30 mins, solvent was removed under reduced pressure and ethereal HCl (1 M, 5 mL, 5 mmol, 4.2 equiv) was added to precipitate the product. Solvent was carefully removed by a glass pasteur pipette and the precipitate was washed with diethyl ether (2 × 10 mL). The title compound was collected as an off white solid (287.4 mg, 1.16 mmol) in 46% yield after two consecutive steps.

^{1}H NMR (500 MHz, CD_3OD): δ 7.45 (d, *J* = 8 Hz, 2H), 7.11 (d, *J* = 8 Hz, 2H), 2.85 (ddd, *J* =7.6, 4, 4 Hz, 1H), 2.38 – 2.34 (m, 1H), 1.46 – 1.42 (m, 1H), 1.33 (q, *J* = 7 Hz, 1H) ppm

^{13}C NMR (125 MHz, CD_3OD): δ 139.1, 132.7, 129.4, 121.5, 32.0, 22.1, 13.9 ppm

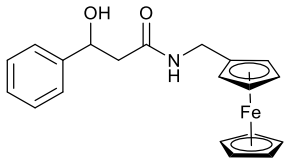
IR (Neat): 3013, 2884 cm^{-1}

Melting point: 191.0 – 194.7 °C

^{1}H NMR data are consistent with literature.[10]

Reductive amination

_N_-(Ferrocenylmethyl)-3-hydroxy-3-phenylpropanamide 7a



Triethylamine (0.13 mL, 94.4 mg, 0.93 mmol, 1.9 equiv) was added to a suspension of *trans*-2-Phenylcyclopropylamine hydrochloride (82.2 mg, 0.48 mmol, 1 equiv) and magnesium sulphate (219.1 mg, 1.82 mmol, 3.8 equiv) in dry dichloromethane (4 mL). This mixture was stirred for 10 minutes before ferrocenecarboxaldehyde (123.1 mg, 0.58 mmol, 1.2 equiv) was added. After 3 hours of stirring, another portion of ferrocenecarboxaldehyde (20 mg, 93.4 µmol, 0.2 equiv) and one spatula of magnesium sulphate were added. The mixture was allowed to stir overnight after which another portion of ferrocenecarboxaldehyde (14.4 mg, 67.3 µmol, 0.1 equiv) and a spatula of magnesium sulphate were added. After 2 hours of stirring, dry toluene (8 mL) was added to precipitate triethylamine hydrochloride and the mixture was filtered. After removal of solvents under reduced pressure, more triethylamine

hydrochloride precipitated out, therefore dry toluene (10 mL) was added and the mixture was filtered again. After removal of solvents, sodium borohydride (45.2 mg, 2.07 mmol, 4.3 equiv) was added to the solution of crude imine mixture (213.4 mg) in dry methanol (5 mL) at -10 °C. After stirring for 15 minutes at -10 °C, the reaction was left stirring at room temperature. Another portion of sodium borohydride (17.1 mg, 0.78 mmol, 1.6 equiv) was added after 45 mins at -10 °C. After stirring for 15 minutes at -10 °C, the reaction solution was left stirring overnight at room temperature. The reaction was quenched with water (5 mL) and methanol was evaporated under reduced pressure. After the aqueous layer was extracted with ethyl acetate (3 × 10 mL), the combined organic extracts were washed with brine (10 mL) and dried over magnesium sulphate. This crude mixture was subjected to column chromatography (40-80% ethyl acetate in hexane) which yielded the title compound as a yellowish orange solid (77.8 mg, 0.21 mmol) in a 44% overall yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 – 7.25 (m, 5H), 6.08 (s, 1H), 5.09 (dd, *J* = 8.75, 3.5 Hz, 1H), 4.14 – 4.12 (m, 11H), 2.59 – 2.50 (m, 2H) ppm

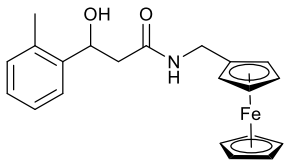
^{13}C NMR (125 MHz, $CDCl_3$): δ 171.1, 143.1, 128.5, 127.7, 125.6, 84.4, 70.9, 68.6, 68.2, 68.1, 44.7, 38.8 ppm

IR (Neat): 3300, 1646 cm^{-1}

HRMS (ASAP) Found: M, 363.0914. $C_{20}H_{21}FeNO_2$ requires M, 363.0922

Melting point: 114.7 – 116.9 °C

***N*-(ferrocenylmethyl)-3-hydroxy-3-(*o*-methylphenyl)propanamide 7b**



Triethylamine (0.15 mL, 108.9 mg, 1.08 mmol, 2 equiv) was added to a suspension of *trans*-2-(*o*-methylphenyl)cyclopropylamine hydrochloride (100.9 mg, 0.55 mmol, 1 equiv) and magnesium sulphate (234.5 mg) in dry dichloromethane (4 mL). This mixture was stirred for

10 minutes before ferrocenecarboxaldehyde (139.3 mg, 0.65 mmol, 1.2 equiv) was added. After 3 hours of stirring, another portion of ferrocenecarboxaldehyde (25.8 mg, 0.12 mmol, 0.2 equiv) and one spatula of magnesium sulphate were added. The mixture was allowed to stir overnight after which another portion of ferrocenecarboxaldehyde (12.1 mg, 56.5 μmol, 0.1 equiv) and a spatula of magnesium sulphate were added. After 2 hours of stirring, dry toluene (8 mL) was added to precipitate triethylamine hydrochloride and the mixture was filtered. After removal of solvents under reduced pressure, more triethylamine hydrochloride precipitated out, therefore dry toluene (10 mL) was added and the mixture was filtered again. After removal of solvents, sodium borohydride (50.1 mg, 2.3 mmol, 4.2 equiv) was added to the solution of crude imine mixture (251.5 mg) in dry methanol (7 mL) at -10 °C. After stirring for 15 minutes at -10 °C, the reaction was left stirring at room temperature. Another portion of sodium borohydride (20.9 mg, 0.96 mmol, 1.7 equiv) was added after 4 h 30 mins at -10 °C. After stirring for 15 minutes at -10 °C, the reaction solution was left stirring overnight at room temperature. The reaction was quenched with water (4 mL) and methanol was evaporated under reduced pressure. After the aqueous layer was extracted with ethyl acetate (3 × 10 mL), the combined organic extracts were washed with brine (10 mL) and dried over magnesium sulphate. This crude mixture was subjected to column chromatography (40-80% ethyl acetate in hexane) which yielded the title compound as a brownish orange solid (46.1 mg, 0.12 mmol) in a 22% overall yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 (d, *J* = 7.5 Hz, 1H), 7.21 – 7.14 (m, 2H), 7.10 – 7.09 (m, 1H), 6.29 (bs, 1H), 5.27 (d, *J* = 9 Hz, 1H), 4.14 – 4.12 (m, 11H), 2.50 – 2.40 (m, 2H), 2.29 (s, 3H) ppm

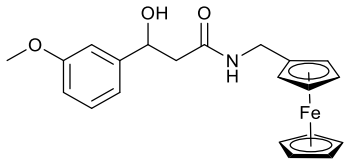
^{13}C NMR (125 MHz, $CDCl_3$): δ 171.3, 141.1, 134.1, 130.5, 127.5, 126.5, 125.3, 84.5, 68.7, 68.3, 68.3, 67.5, 43.4, 38.9, 19.1 ppm

IR (Neat): 3305, 1636 cm^{-1}

HRMS (ESI) Found: M+, 377.10726. $C_{21}H_{23}FeNO_2$ requires M+, 317.10782

Melting point: 103.2 – 107.3 °C

***N*-(ferrocenylmethyl)-3-hydroxy-3-(*m*-methoxyphenyl)propanamide 7c**



Magnesium sulphate (230.6 mg, 1.92mmol, 3.8 equiv) was added to a solution of *trans*-2-(*m*-methoxyphenyl)cyclopropylamine hydrochloride (101.2 mg, 0.51 mmol, 1 equiv) and triethylamine (0.21 ml, 1.5 mmol, 3 equiv) in dry dichloromethane (5 mL). This mixture was stirred for 15 mins before ferrocenecarboxaldehyde (130.2 mg, 0.61 mmol, 1.2 equiv) was added. After 4 h of stirring, another portion of ferrocenecarboxaldehyde (19.7 mg, 0.092 mmol, 0.2 equiv) and magnesium sulphate (103.4 mg, 0.86 mmol, 1.7 equiv) were added. The mixture was allowed to stir overnight after which another portion of ferrocenecarboxaldehyde (14.3 mg, 0.067mmol, 0.1 equiv) and a spatula of 4 Å molecular sieves were added. After 2 h of stirring, dry toluene (10 mL) was added to precipitate triethylamine hydrochloride and the mixture was filtered. After removal of solvents under reduced pressure, more triethylamine hydrochloride precipitated out, therefore dry toluene (4 mL) was added and the mixture was filtered again. After removal of solvents, sodium borohydride (41.1 mg, 1.09 mmol, 2.2 equiv) was added to the solution of crude imine mixture (239.6 mg) in dry methanol (3 mL) at -10 °C. After stirring for 15 mins at -10 °C, the reaction solution was left stirring overnight at room temperature. The reaction was quenched with water (5 mL) and methanol was evaporated by purging nitrogen gas through the flask. After the aqueous layer was extracted with ethyl acetate (3 × 15 mL), the combined organic extracts were washed with brine (5 mL) and dried over magnesium sulphate. This crude mixture was subjected to column chromatography (40-80% ethyl acetate in hexane) which yielded the title compound as a brownish orange solid (111.5 mg, 0.28 mmol) in a 56% overall yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26 – 7.23 (m, 1H), 6.94 – 6.91 (m, 2H), 6.81 (d, J = 8 Hz, 1H), 6.05 (bs, 1H), 5.08 – 5.07 (m, 1H), 4.15 – 4.13 (m, 11H), 3.80 (s, 3H), 2.56-2.54 (m, 2H) ppm

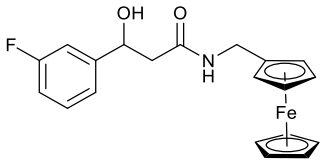
^{13}C NMR (125 MHz, $CDCl_3$): δ 171.2, 160.0, 145.0, 129.8, 118.0, 113.5, 111.3, 84.6, 71.1, 68.8, 68.4, 68.4, 68.4, 55.5, 44.9, 39.0 ppm

IR (Neat): 3310, 1647 cm^{-1}

HRMS (ESI) Found: (M+Na)+, 416.0918. $C_{21}H_{23}NO_3Fe$ requires (M+Na)+, 416.0925

Melting point: 83.2 – 86.8 °C

***N*-(ferrocenylmethyl)-3-hydroxy-3-(*m*-fluorophenyl)propanamide 7d**



Magnesium sulphate (134.0 mg, 1.11 mmol, 5.8 equiv) was added to a solution of *trans*-2-(m-fluorophenyl)cyclopropylamine hydrochloride (35.4 mg, 0.19 mmol, 1 equiv) and triethylamine (0.08 ml, 0.6 mmol, 3 equiv) in dry dichloromethane (2.0 mL). This mixture was stirred for 15 mins before ferrocenecarboxaldehyde (43.7 mg, 0.20 mmol, 1.1 equiv) was added. After 4 h of stirring, another portion of ferrocenecarboxaldehyde (4.5 mg, 0.021 mmol, 0.1 equiv) and magnesium sulphate (100.6 mg, 0.84 mmol, 4.4 equiv) were added. The mixture was allowed to stir overnight after which another portion of ferrocenecarboxaldehyde (2.8 mg, 0.013 mmol, 0.1 equiv) and a spatula of 4Å molecular sieves were added. After 2 h of stirring, dry toluene (5.0 mL) was added to precipitate triethylamine hydrochloride and the mixture was filtered. After removal of solvents under reduced pressure, more triethylamine hydrochloride salt precipitated out, so dry toluene (2.0 mL) was added and the mixture filtered again. After removal of solvents, sodium borohydride (11.6 mg, 0.31 mmol, 1.6 equiv) was added to the solution of crude imine mixture in dry methanol (1.0 mL) at -10 °C. After stirring for 15 mins at -10 °C, the reaction solution was left stirring overnight at room temperature. The reaction was quenched with water (5 mL) and methanol was evaporated by purging nitrogen gas through the flask. After the aqueous layer was extracted with ethyl acetate (3 × 10 mL), the combined organic extracts were washed with brine (3 mL) and dried over magnesium sulphate. This crude mixture was subjected to column chromatography (40-70% ethyl acetate in hexane) which yielded the title compound as a brown solid (35.2 mg, 0.09 mmol) in a 49% overall yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33 – 7.26 (m, 1H), 7.13 – 7.10 (m, 2H), 6.99 – 6.93 (m, 1H), 5.93 (bs, 1H), 5.11 (t, J = 6.3 Hz, 1H), 4.15 – 4.14 (m, 11H), 2.53 (d, J = 6 Hz, 2H) ppm

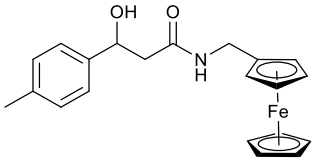
^{13}C NMR (125 MHz, $CDCl_3$): δ 171.0, 163.0 (d, *J* = 245 Hz), 145.9 (d, *J* = 7.5 Hz), 130.1 (d, *J* = 8.75 Hz), 121.2 (d, *J* = 3.75 Hz), 114.5 (d, *J* = 21.25 Hz), 112.7 (d, *J* = 22.5 Hz), 84.3, 70.3, 68.7, 68.3, 68.3, 68.3, 44.5, 38.9 ppm

IR (Neat): 3238, 1650 cm^{-1}

HRMS (ESI) Found: (M+Na)+, 404.0710. $C_{20}H_{20}NO_2FFe$ requires (M+Na)+, 404.0725

Melting point: 112.3 – 116.3 °C

***N*-(ferrocenylmethyl)-3-hydroxy-3-(*p*-methylphenyl)propanamide 7e**



Magnesium sulphate (251.6 mg, 2.1 mmol, 3.8 equiv) was added to a solution of *trans*-2-(*p*-methylphenyl)cyclopropylamine hydrochloride (101.0 mg, 0.55 mmol, 1 equiv) and triethylamine (0.23 ml, 1.7 mmol, 3 equiv) in dry dichloromethane (5 mL). This mixture was stirred for 15 mins before ferrocenecarboxaldehyde (139.1 mg, 0.65 mmol, 1.2 equiv) was added. After stirring overnight, another portion of ferrocenecarboxaldehyde (23.1 mg, 0.11 mmol, 0.2 equiv) and magnesium sulphate (135.6 mg, 1.1mmol, 2 equiv) were added. The mixture was allowed to stir for 2 more h after which another portion of ferrocenecarboxaldehyde (11.7 mg, 0.055 mmol, 0.1 equiv) and a spatula of 4Å molecular sieves were added. After stirring overnight, dry toluene (10 mL) was added to precipitate triethylamine hydrochloride and the mixture was filtered. After removal of solvents under reduced pressure, more triethylamine hydrochloride precipitated out, so dry toluene (4.0 mL) was added and the mixture was filtered again. After removal of solvent, sodium borohydride (62.4 mg, 1.65 mmol, 3 equiv) was added to the solution of crude imine mixture (251.2 mg) in dry methanol (3 mL) at -10 °C. After stirring for 15 mins at -10 °C, the reaction solution was left stirring overnight at room temperature. The reaction was quenched with water (5 mL) and methanol was evaporated by purging nitrogen gas through the flask. After the aqueous layer was extracted with ethyl acetate (3 × 15 mL), the combined organic extracts were washed with brine (5 mL) and dried over sodium sulphate. This crude mixture was subjected to column chromatography (40-80% ethyl acetate in hexane) which yielded the title compound as a yellow oil (118.8 mg, 0.32 mmol) in 58% overall yield.

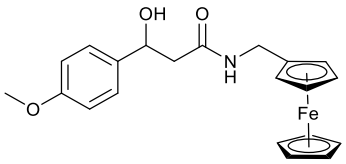
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25 (d, *J* = 7.5 Hz, 2H), 7.15 (d, *J* = 8 Hz, 2H), 5.99 (bs, 1H), 5.08 (d, *J* = 8.5 Hz, 1H), 4.15 – 4.13 (m, 11H), 3.92 (bs, 1H), 2.61 – 2.50 (m, 2H), 2.34 (s, 3H) ppm

^{13}C NMR (125 MHz, $CDCl_3$): δ 171.1, 140.1, 137.4, 129.2, 125.5, 84.4, 70.9, 68.6, 68.2, 68.2, 44.8, 38.8, 21.1 ppm

IR (Neat): 3299, 1636 cm^{-1}

HRMS (ESI) Found: (M+Na)+, 400.0979. $C_{21}H_{23}NO_2Fe$ requires (M+Na)+, 400.0976

***N*-(ferrocenylmethyl)-3-hydroxy-3-(*p*-methoxyphenyl)propanamide 7f**



Sodium sulphate (283.0 mg, 1.99 mmol, 3.7 equiv) was added to a solution of *trans*-2-(*p*-methoxyphenyl)cyclopropylamine hydrochloride (107.4 mg, 0.54 mmol, 1.0 equiv) and triethylamine (0.23 ml, 1.6 mmol, 3.0 equiv) in dry dichloromethane (5.0 mL). The mixture was stirred for 15 mins before ferrocenecarboxaldehyde (138.4 mg, 0.65 mmol, 1.2 equiv) was added. After stirring overnight, another portion of ferrocenecarboxaldehyde (23.0 mg, 0.11 mmol, 0.2 equiv) and sodium sulphate (150.0 mg, 1.06 mmol) were added. The mixture was stirred for 3 h after which another portion of ferrocenecarboxaldehyde (11.4 mg, 0.055mmol, 0.1 equiv) and a spatula of 4Å molecular sieves were added. After 2 h of stirring, dry toluene (10.0 mL) was added to precipitate triethylamine hydrochloride and the mixture was filtered. After removal of solvents under reduced pressure, more triethylamine hydrochloride precipitated out, therefore dry toluene (5.0 mL) was added and the mixture was filtered again. After removal of solvents, sodium borohydride (32.7 mg, 0.86 mmol, 1.6 equiv) was added to a solution of the crude imine mixture (239.6 mg) in dry methanol (3 mL) at -10 °C. After stirring for 15 mins at -10 °C, the mixture was stirred overnight at room temperature. The reaction was quenched with water (5 mL) and methanol was evaporated by purging nitrogen gas through the flask. After the aqueous layer was extracted with ethyl acetate (3 × 15 mL), the combined organic extracts were washed with brine (5 mL) and dried over sodium sulphate. The crude mixture was subjected to column chromatography (40-80% ethyl acetate/hexanes) which yielded a 65.0 mg mixture of the title compound and an

unknown impurity that was not removable by column chromatography (using either 50% ethyl acetate/hexanes or 5% methanol/dichloromethane), therefore preparative TLC was used to obtain the title compound (52.0 mg, 0.13 mmol) as a yellowish orange solid in 25% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27 (d, *J* = 8.1 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 6.13 (bs, 1H), 5.04 (d, *J* = 8.4 Hz, 1H), 4.15 – 4.14 (m, 11H), 3.79 (s, 3H), 2.61 – 2.46 (m, 2H) ppm

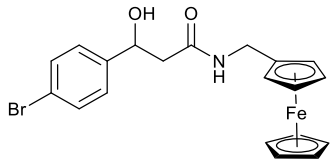
^{13}C NMR (75 MHz, $CDCl_3$): δ 171.3, 159.2, 135.4, 127.0, 114.0, 84.5, 70.7, 68.8, 68.7, 68.3, 55.4, 44.9, 38.9 ppm

IR (Neat): 3301, 1636 cm^{-1}

HRMS (ESI) Found: (M+Na)+, 416.0937. $C_{21}H_{23}FeNO_3$ requires (M+Na)+, 416.0925

Melting point: 80.5 – 83.8 °C

***N*-(ferrocenylmethyl)-3-hydroxy-3-(*p*-bromophenyl)propanamide 7g**



Triethylamine (0.11 mL, 81.4 mg, 0.80 mmol, 1.9 equiv) was added to a suspension of *trans*-2-(*p*-bromophenyl)cyclopropylamine hydrochloride (105.8 mg, 0.43 mmol, 1 equiv) and magnesium sulphate (196.5 mg, 1.63 mmol, 3.8 equiv) in dry dichloromethane (4 mL). This mixture was stirred for 10 minutes before ferrocenecarboxaldehyde (104.3 mg, 0.49 mmol, 1.1 equiv) was added. After 3 hours of stirring, another portion of ferrocenecarboxaldehyde (18.0 mg, 0.08 mmol, 0.2 equiv) and one spatula of magnesium sulphate were added. The mixture was allowed to stir overnight after which another portion of ferrocenecarboxaldehyde (9.6 mg, 0.04 mmol, 0.1 equiv) and a spatula of magnesium sulphate were added. After 2 hours of stirring, dry toluene (8 mL) was added to precipitate triethylamine hydrochloride and the mixture was filtered. After removal of solvents under reduced pressure, more triethylamine hydrochloride precipitated out, therefore dry toluene (5 mL) was added and the mixture was filtered again. After removal of solvents, sodium borohydride (65.4 mg, 3.00 mmol, 7 equiv) was added to the solution of crude imine mixture (232.9 mg) in dry methanol

(5 mL) at -10 °C. After stirring for 15 minutes at -10 °C, the reaction was left stirring at room temperature. Another portion of sodium borohydride (28.7 mg, 1.32 mmol, 3.06 equiv) was added after 45 mins at -10 °C. After stirring for 15 minutes at -10 °C, the reaction solution was left stirring overnight at room temperature. The reaction was quenched with water (3 mL) and methanol was evaporated under reduced pressure. After the aqueous layer was extracted with ethyl acetate (3 × 10 mL), the combined organic extracts were washed with brine (10 mL) and dried over magnesium sulphate. This crude mixture was subjected to column chromatography (40-80% ethyl acetate in hexane) which yielded the title compound as a yellowish orange (82.5 mg, 0.19 mmol) in a 44% overall yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 6.13 (bs, 1H), 5.03 – 5.00 (m, 1H), 4.14 – 4.09 (m, 11H), 2.48 – 2.47 (m, 2H) ppm

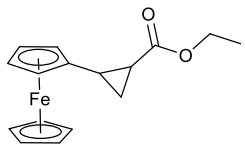
^{13}C NMR (125 MHz, $CDCl_3$): δ 170.9, 142.2, 131.7, 127.4, 121.5, 84.2, 70.3, 68.7, 68.4, 68.3, 68.3, 44.5, 38.9 ppm

IR (Neat): 3302, 1636 cm^{-1}

HRMS (ESI) Found: (M+Na)+, 463.9934. $C_{20}H_{20}BrFeNO_2$ requires (M+Na)+, 463.9925

Melting point: 113.6 – 115.1 °C

Ethyl 2-ferrocenylcyclopropane-1-carboxylate



Vinylferrocene (130.4 mg, 0.61 mmol, 1 equiv) and rhodium(II) acetate dimer (11.8 mg, 26.7 μmol, 4.3 mol%) were dissolved in dry dichloromethane (3 mL). To this mixture, a solution of ethyl diazoacetate (0.22 mL, 1.84 mmol, 3 equiv) in dry dichloromethane was added dropwise over 3 h. The resulting solution was left stirring at room temperature overnight. After this time, the reaction solution was concentrated under reduced pressure and filtered

through a small plug of silica gel using dichloromethane to elute. The filtrate was evaporated under reduced pressure to give a dark brown oil which was purified by column chromatography (10% diethyl ether in hexane). The title compound was obtained as yellow oil (36.8 mg, 0.12 mmol) in 20% yield.

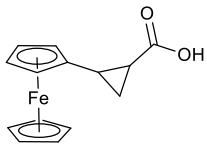
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.19 – 4.15 (m, 7H), 4.05 – 4.03 (m, 4H), 2.19 – 2.15 (m, 1H), 1.75 (ddd, *J* = 8.4, 4.2, 4.0 Hz, 1H), 1.49 (ddd, *J* = 9.1, 4.8, 4.5 Hz, 1H), 1.28 (t, *J* = 7 Hz, 3H), 1.12 – 1.08 (m, 1H) ppm

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.5, 88.3, 68.6, 67.4, 67.1, 66.6, 66.6, 60.5, 24.6, 22.2, 17.8, 14.3 ppm

IR (Neat): 1719 cm^{-1}

HRMS Found: M+, 298.0653. $C_{16}H_{18}FeO_2$ requires M+, 298.0656

2-Ferrocenylcyclopropane-1-carboxylic acid (17)



Ethyl 2-ferrocenylcyclopropane-1-carboxylate (36.8 mg, 0.12 mmol) was dissolved in ethanol (0.45 mL) and sodium hydroxide (1 M, 0.25 mL, 0.25 mmol, 2 equiv) added to this solution. The solution was left stirring at room temperature for 2 days after which time the reaction was quenched with hydrochloric acid (2 M, 0.19 mL, 0.37 mmol, 3 equiv) and water (0.43 mL) at 0°C. The solution was stirred for 5 min then extracted with ethyl acetate (3 × 4 mL). The collected organic extracts were washed with water (2 mL) and brine (2 mL). The organic extracts were dried with magnesium sulphate and the solvent evaporated under

reduced pressure to yield the product as a yellow solid that required no further purification (34.6 mg, 0.13 mmol) in 100% yield.

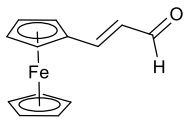
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.16 (bs, 5H), 4.07 (bs, 4H), 2.27 (bs, 1H), 1.77 (bs, 1H), 1.57 – 1.56 (m, 1H), 1.22 – 1.19 (m, 1H) ppm

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.8, 87.8, 68.7, 67.6, 67.3, 66.7, 66.7, 24.5, 23.3, 18.5 ppm

IR (Neat): 3094, 1678 cm^{-1}

HRMS Found: M+, 270.0338. $C_{14}H_{14}FeO_2$ requires M+, 270.0343

(*E*)-3-Ferrocenylacrylaldehyde (21)



Triethylamine (0.03 mL, 19.4 mg, 0.19 mmol, 1.5 equiv) and diphenylphosphoryl azide (0.04 mL, 52.7 mg, 0.19 mmol, 1.5 equiv) were added to a solution of 2-ferrocenylcyclopropane-1-carboxylic acid **17** (34.6 mg, 0.13 mmol, 1 equiv) in dry toluene (0.74 mL) at room temperature. The solution was left stirring at reflux for 2 h before *tert*-butanol (0.74 mL) was added. The resulting solution was refluxed for an additional 17 h, and then cooled down to room temperature. The reaction solution was diluted with ethyl acetate (3 mL) and washed with 5% citric acid (0.6 mL), water (0.6 mL), saturated sodium bicarbonate solution (0.6 mL), water (0.6 mL) and brine (0.6 mL). The organic layer was dried with magnesium sulphate and after the removal of solvent under reduced pressure, the crude product was purified by column chromatography (20% ethyl acetate in hexane). The title compound was obtained as a dark red oil (12.6 mg, 52.5 μmol) in 41% yield.

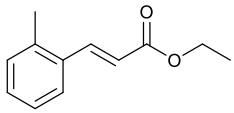
^{1}H NMR (300 MHz, $CDCl_3$) δ 9.56 (d, *J* = 8.1 Hz, 1H), 7.43 (d, *J* = 15.6 Hz, 1H), 6.35 (dd, *J* = 15.6. 7.8 Hz, 1H), 4.56 (bs, 2H), 4.53 (bs, 2H), 4.18 (bs, 5H) ppm

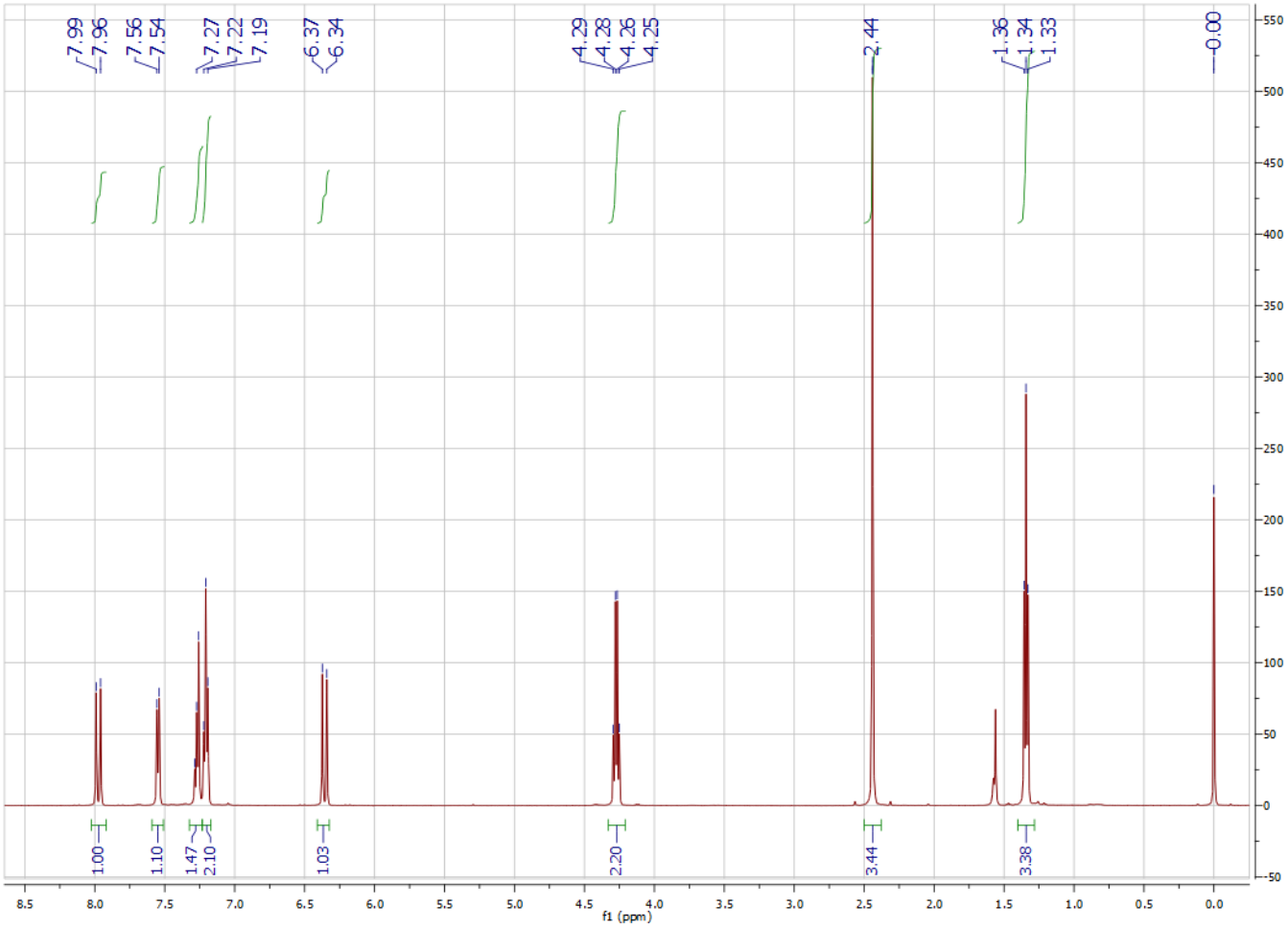
^{13}C NMR (75 MHz, $CDCl_3$) δ 193.2, 155.1, 126.4, 77.8, 71.9, 70.0, 69.2 ppm

^{1}H NMR data are consistent with literature.[14]

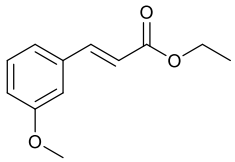
^{1}H and ^{13}C NMR spectra

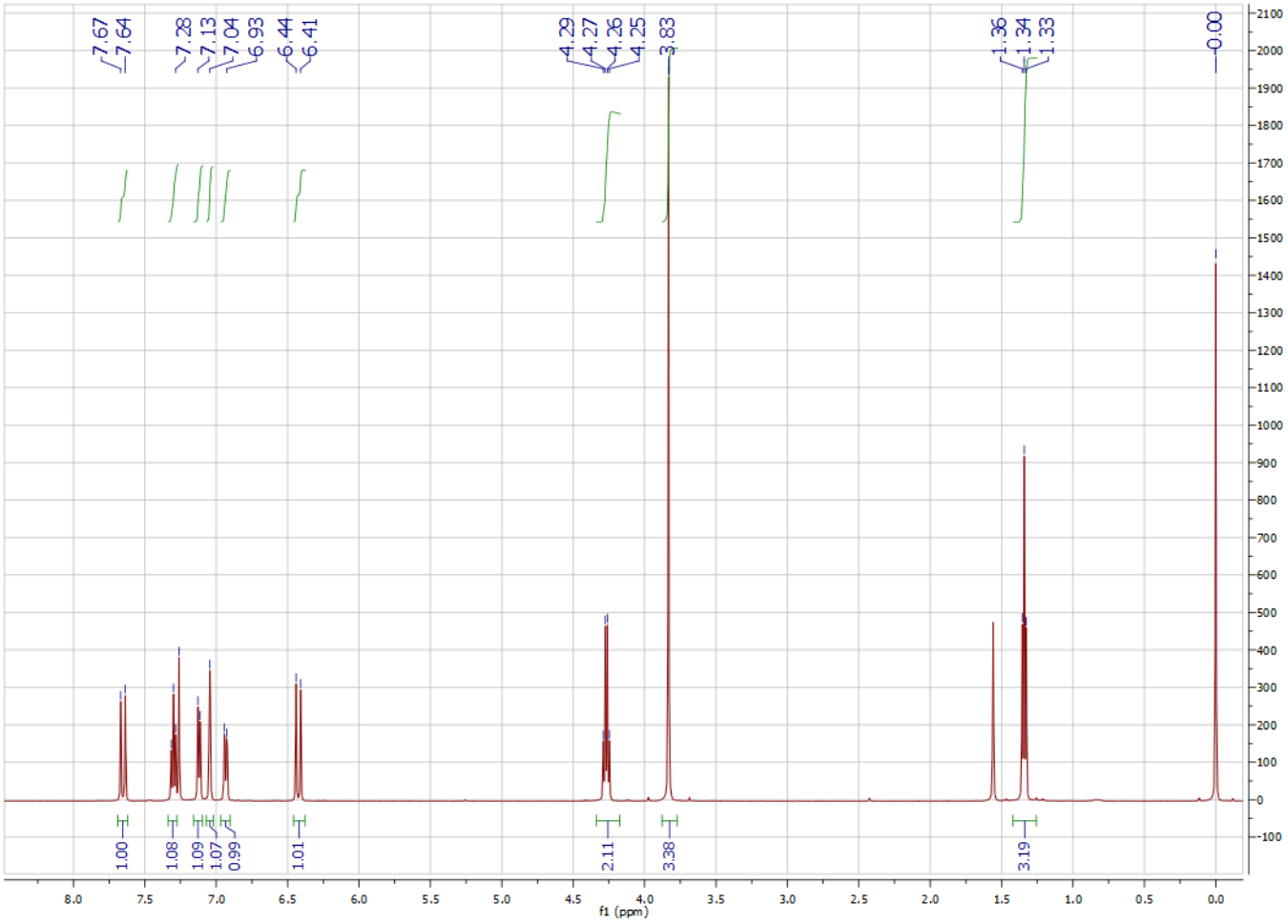
Ethyl (*E*)-3-(*o*-tolyl)-2-propenoate 9b



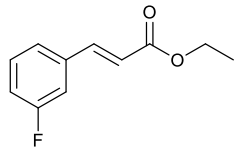


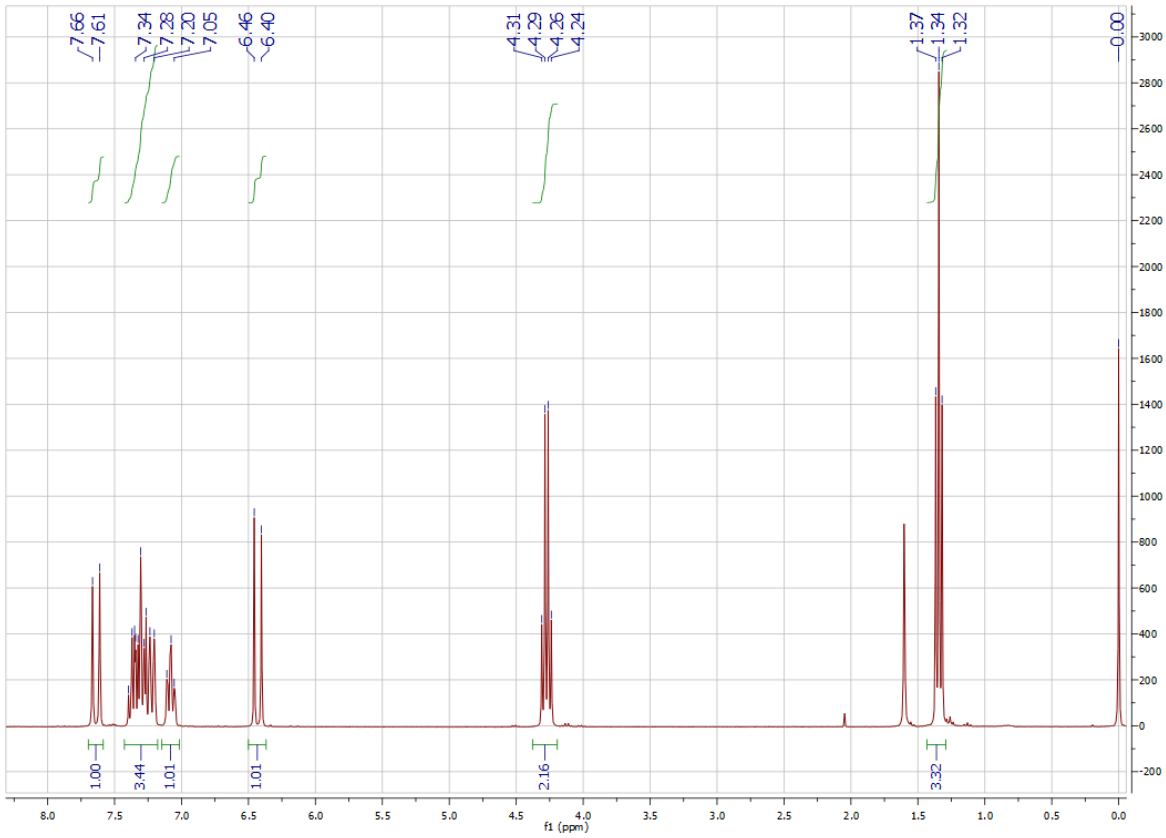
Ethyl (*E*)-3-(*m*-methoxyphenyl)-2-propenoate 9c

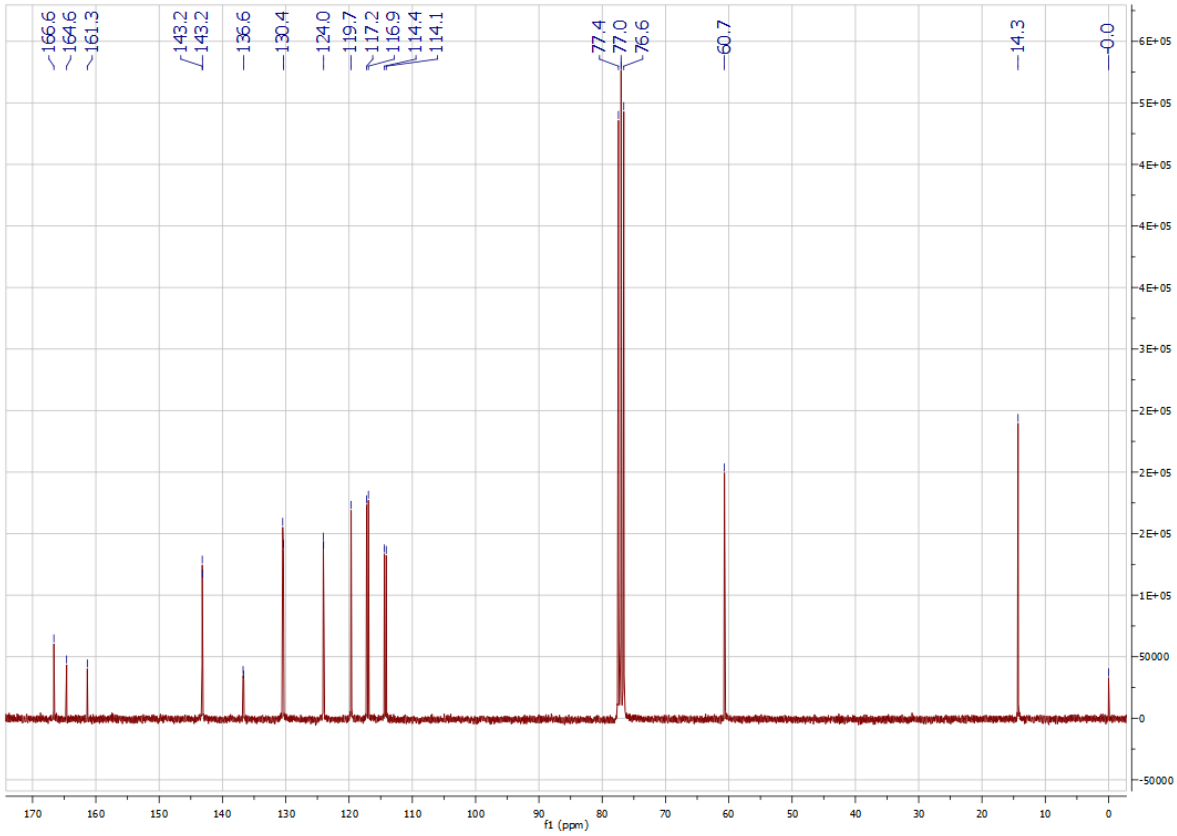




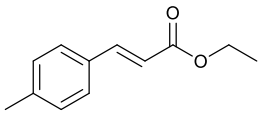
Ethyl (*E*)-3-(*m*-fluorophenyl)-2-propenoate 9d

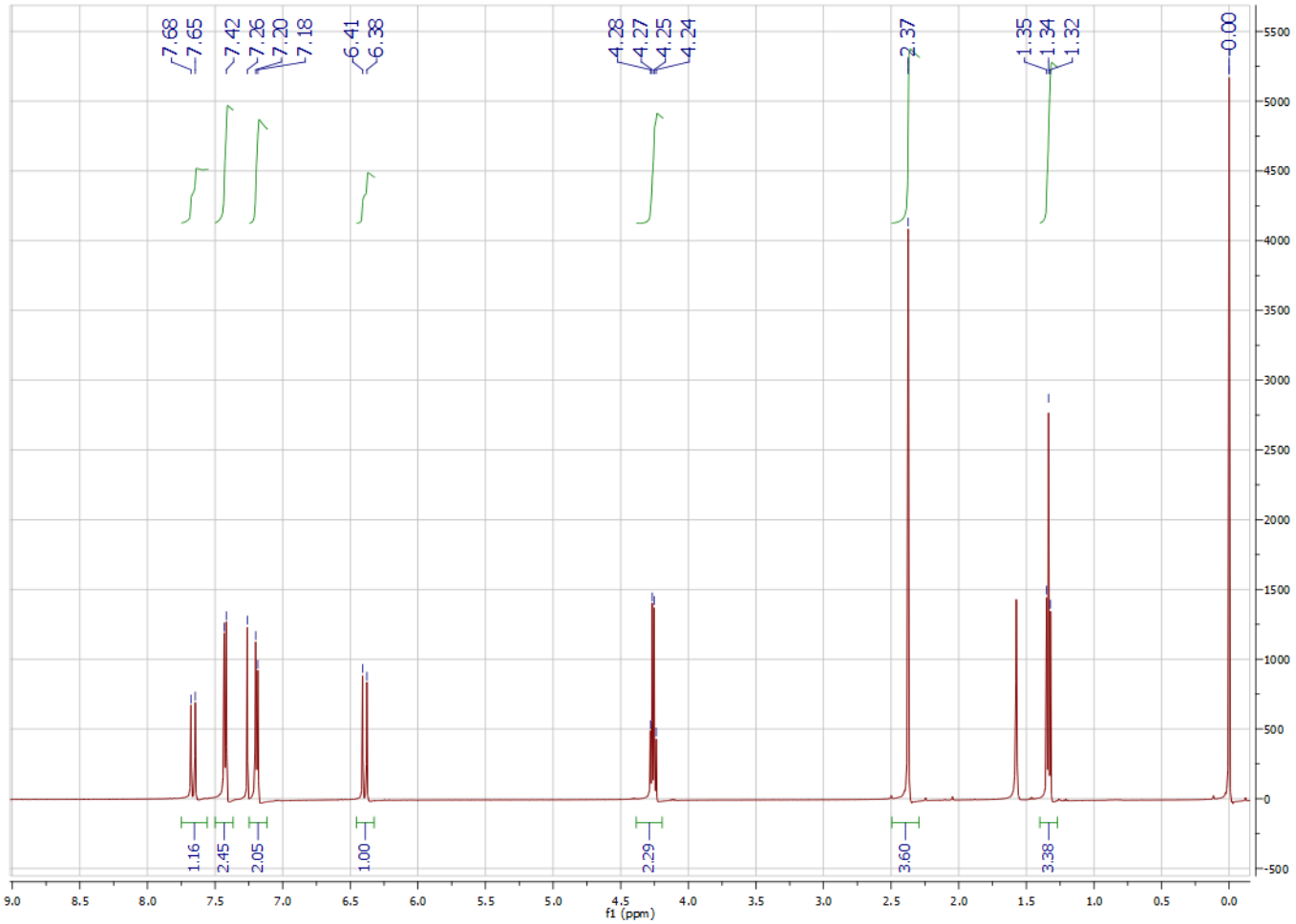




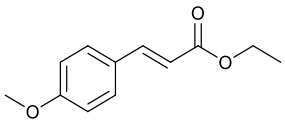


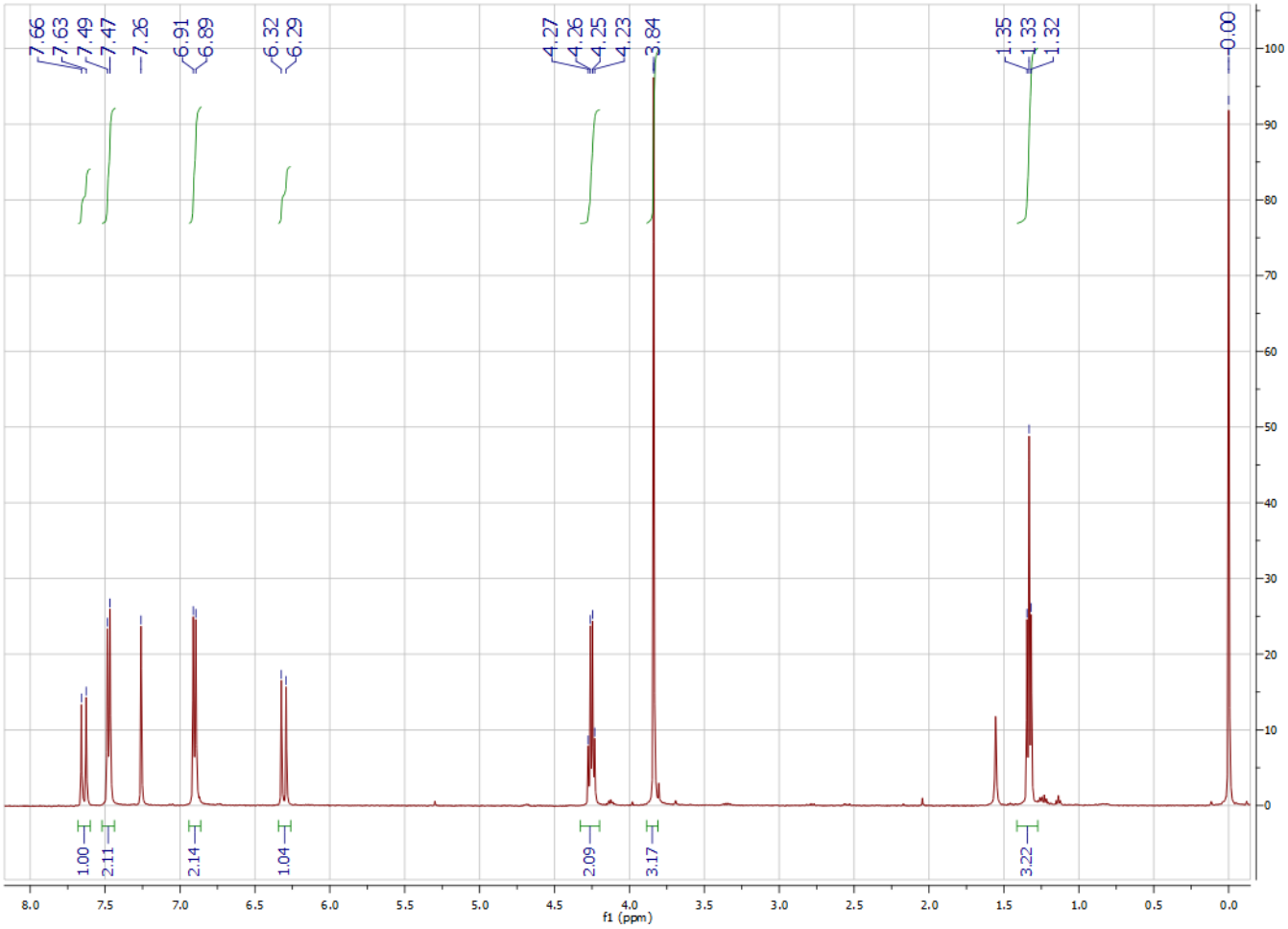
Ethyl (*E*)-3-(*p*-tolyl)-2-propenoate 9e



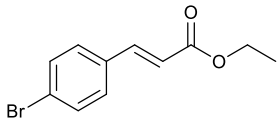


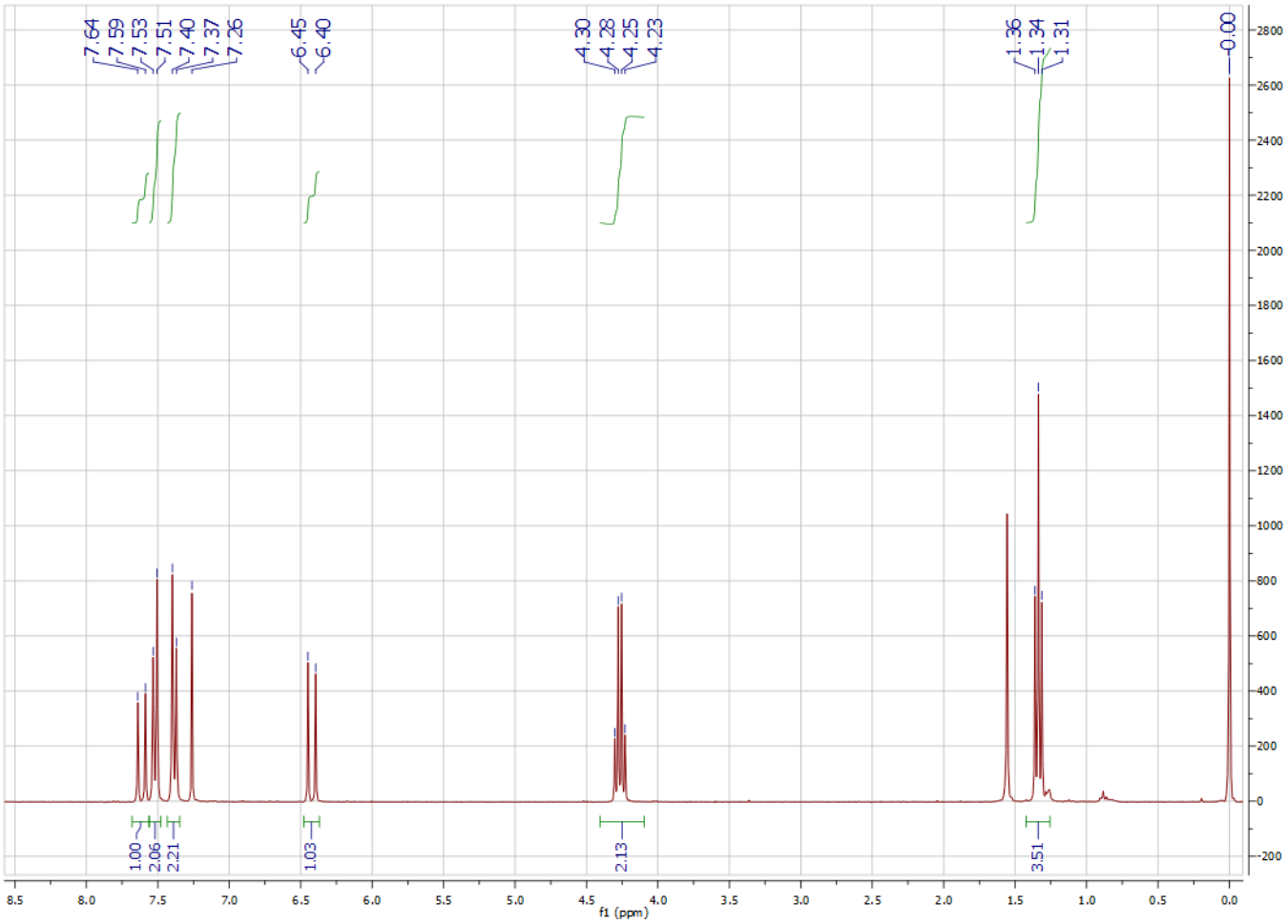
Ethyl (*E*)-3-(*p*-methoxyphenyl)-2-propenoate 9f



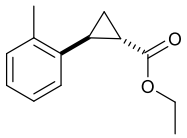


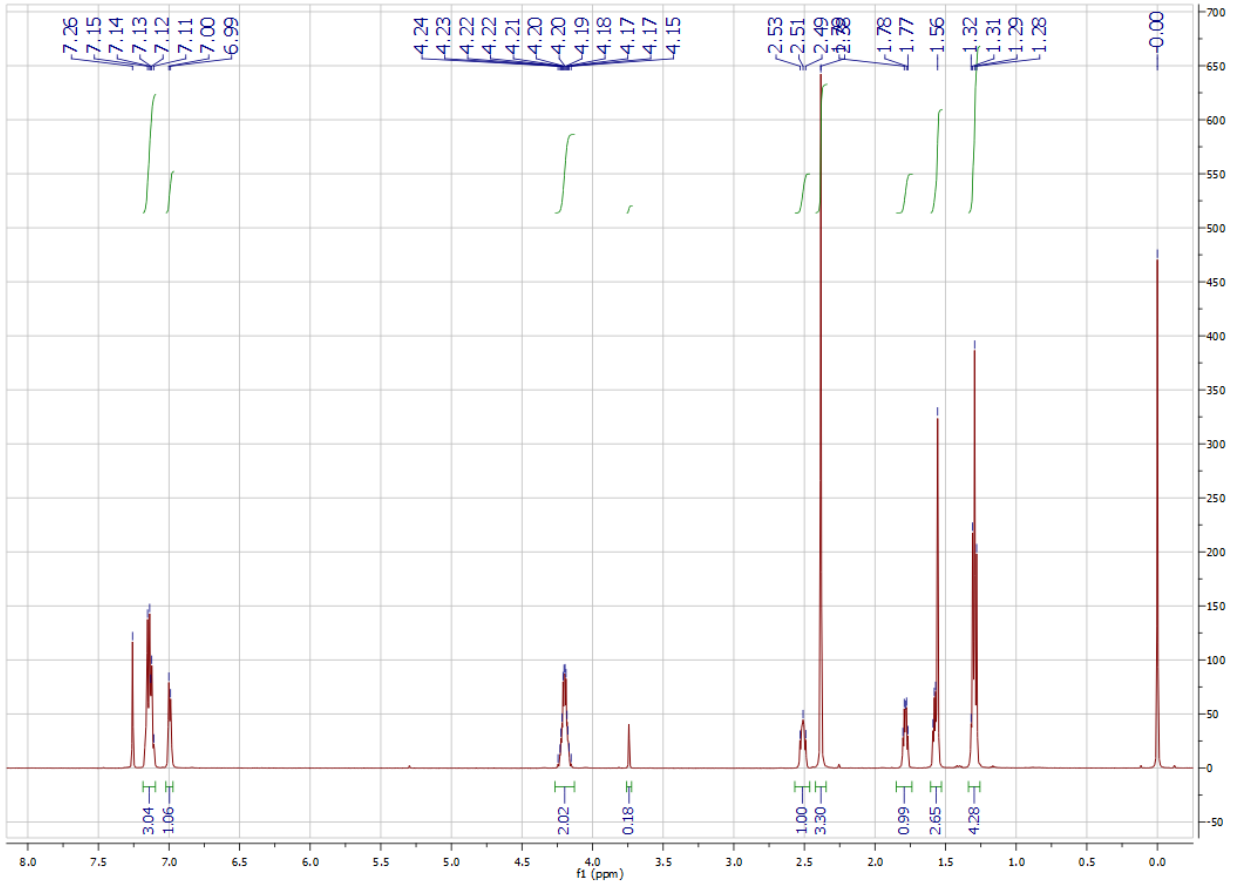
Ethyl (*E*)-3-(*p*-bromophenyl)-2-propenoate 9g

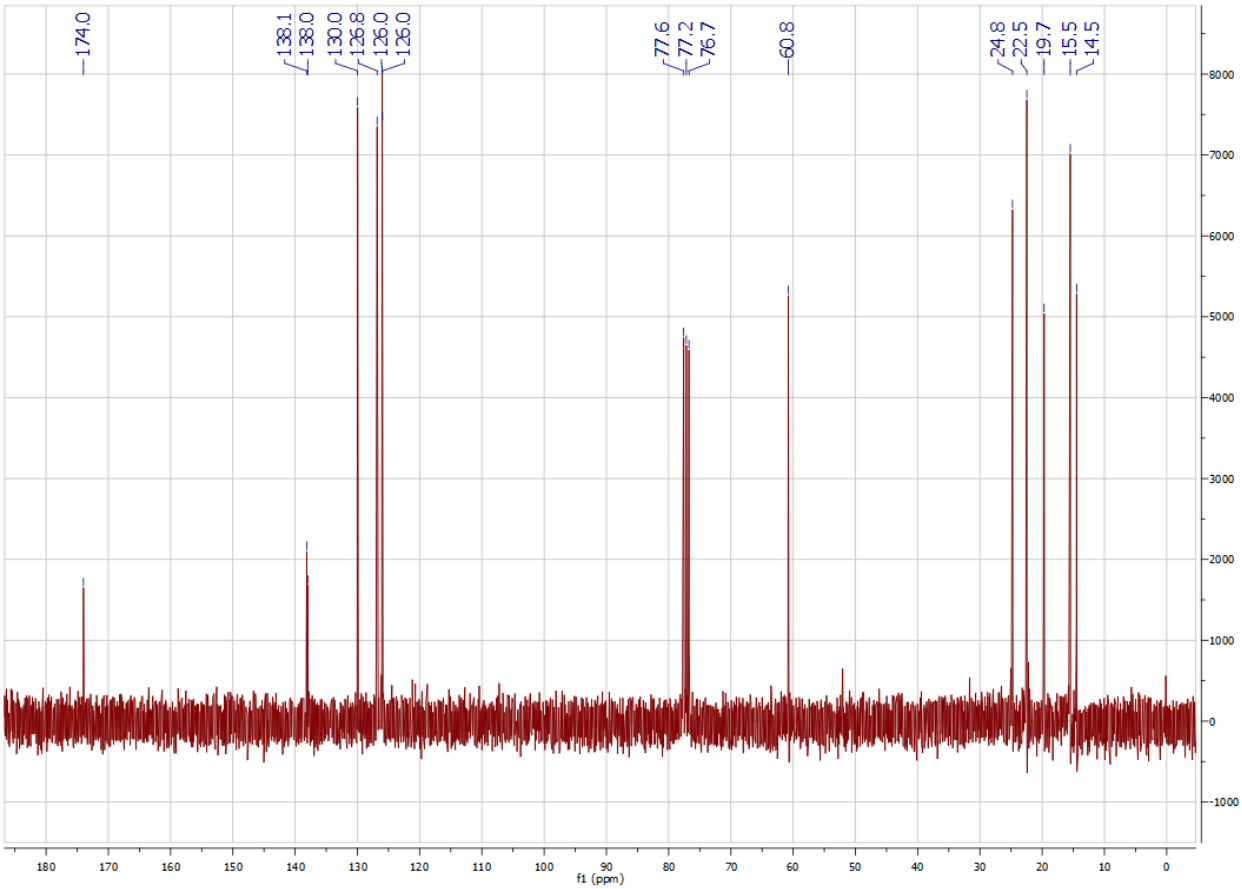




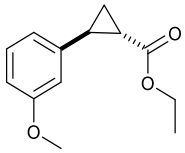
Ethyl 2-(*o*-tolyl)cyclopropane-1-carboxylate 10b

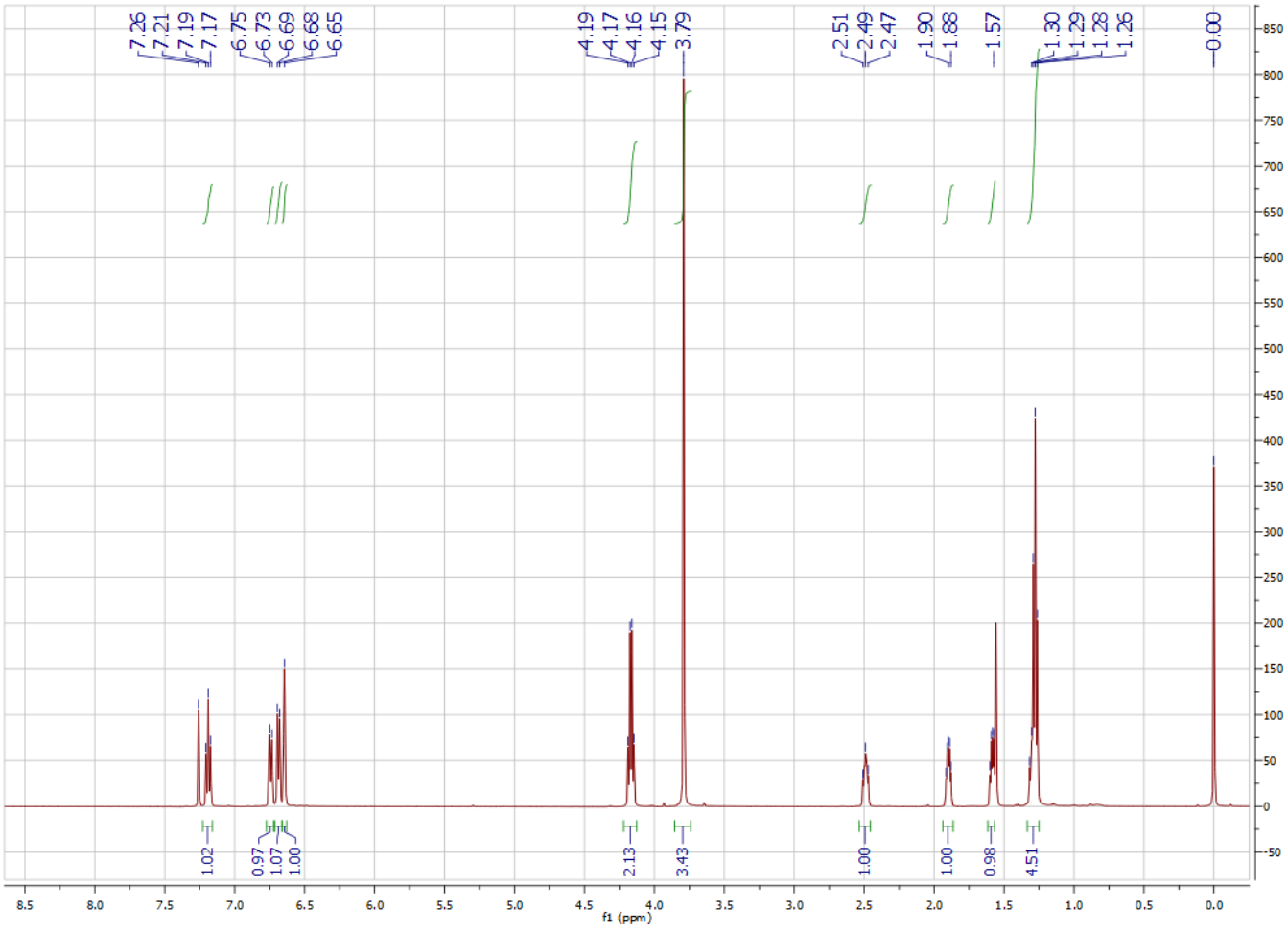




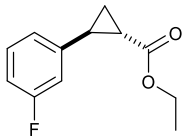


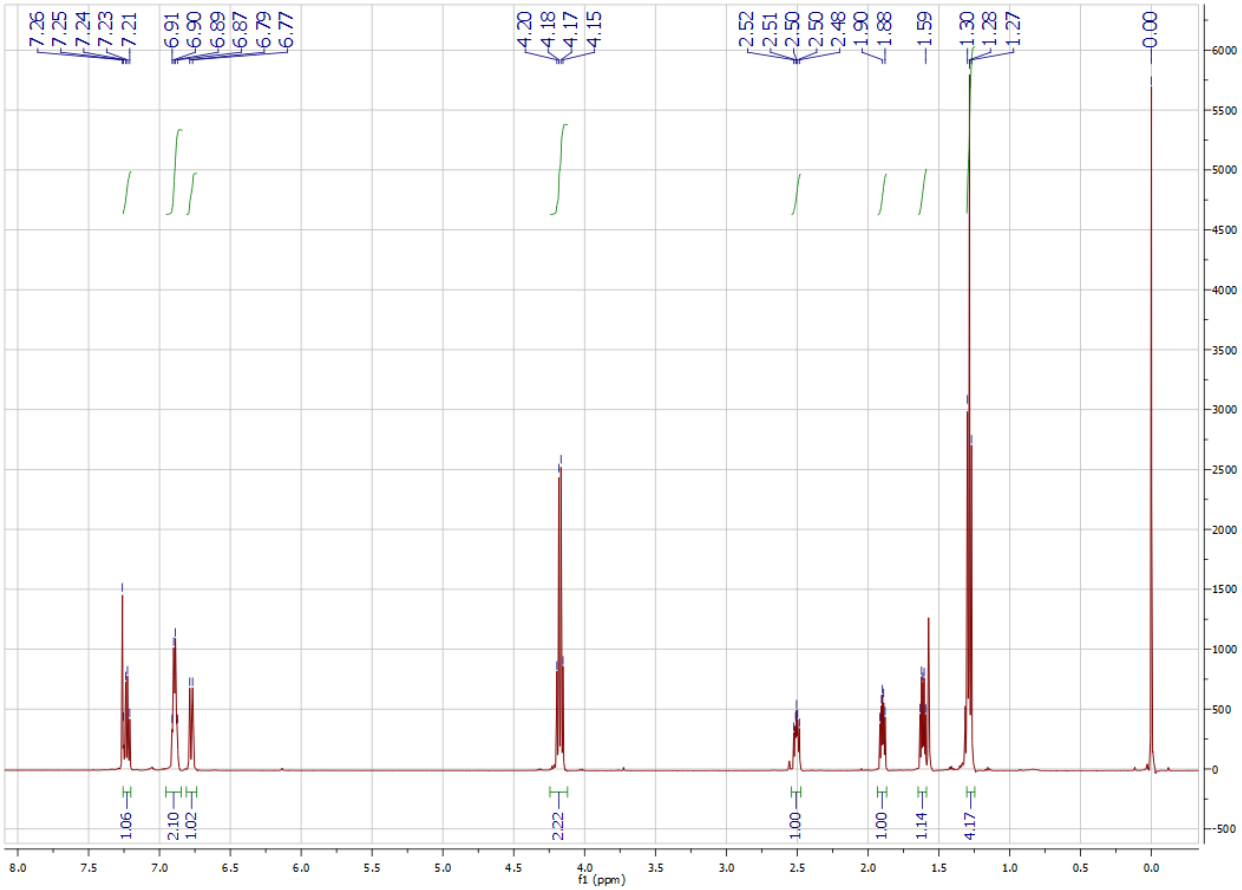
Ethyl 2-(*m*-methoxyphenyl)cyclopropane-1-carboxylate 10c

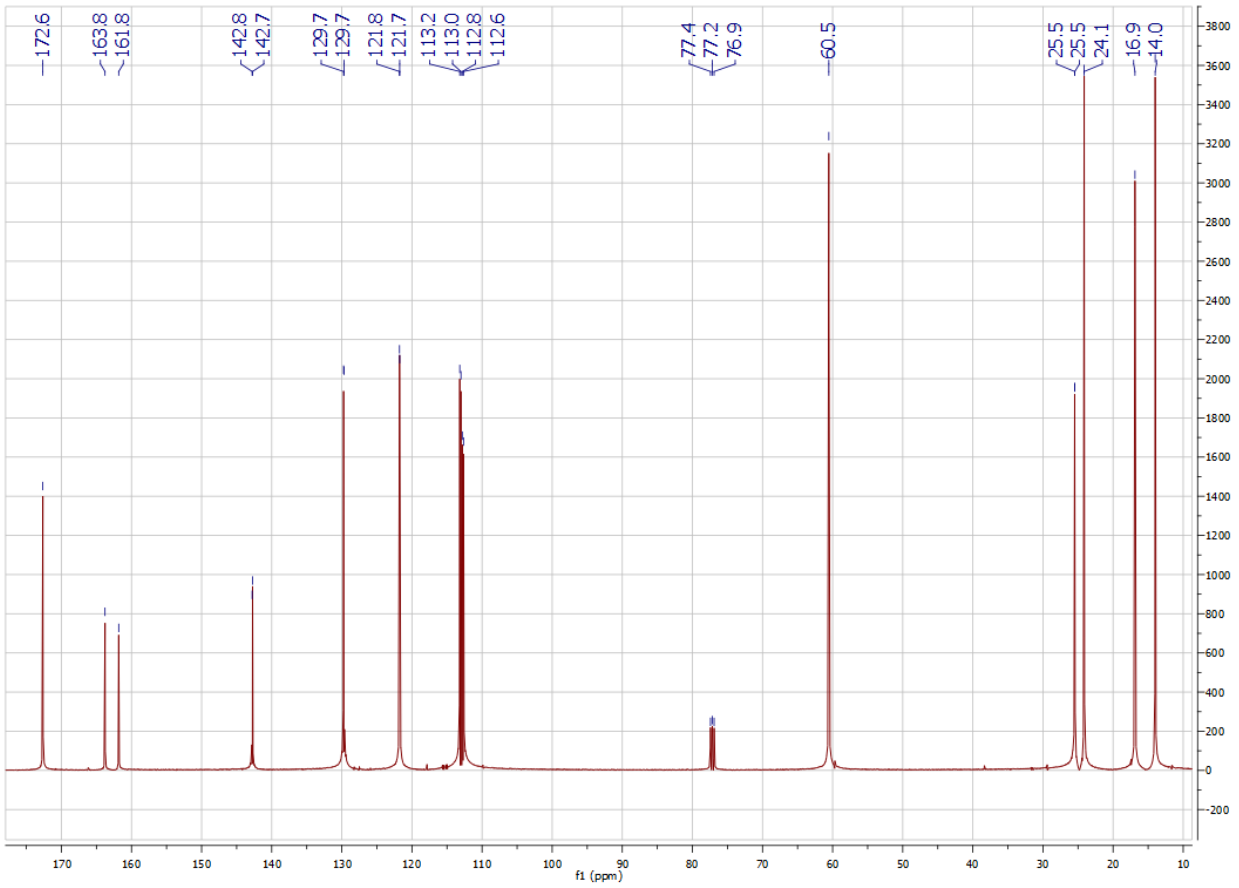




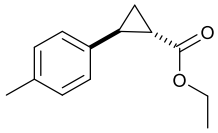
Ethyl 2-(*m*-fluorophenyl)cyclopropane-1-carboxylate 10d

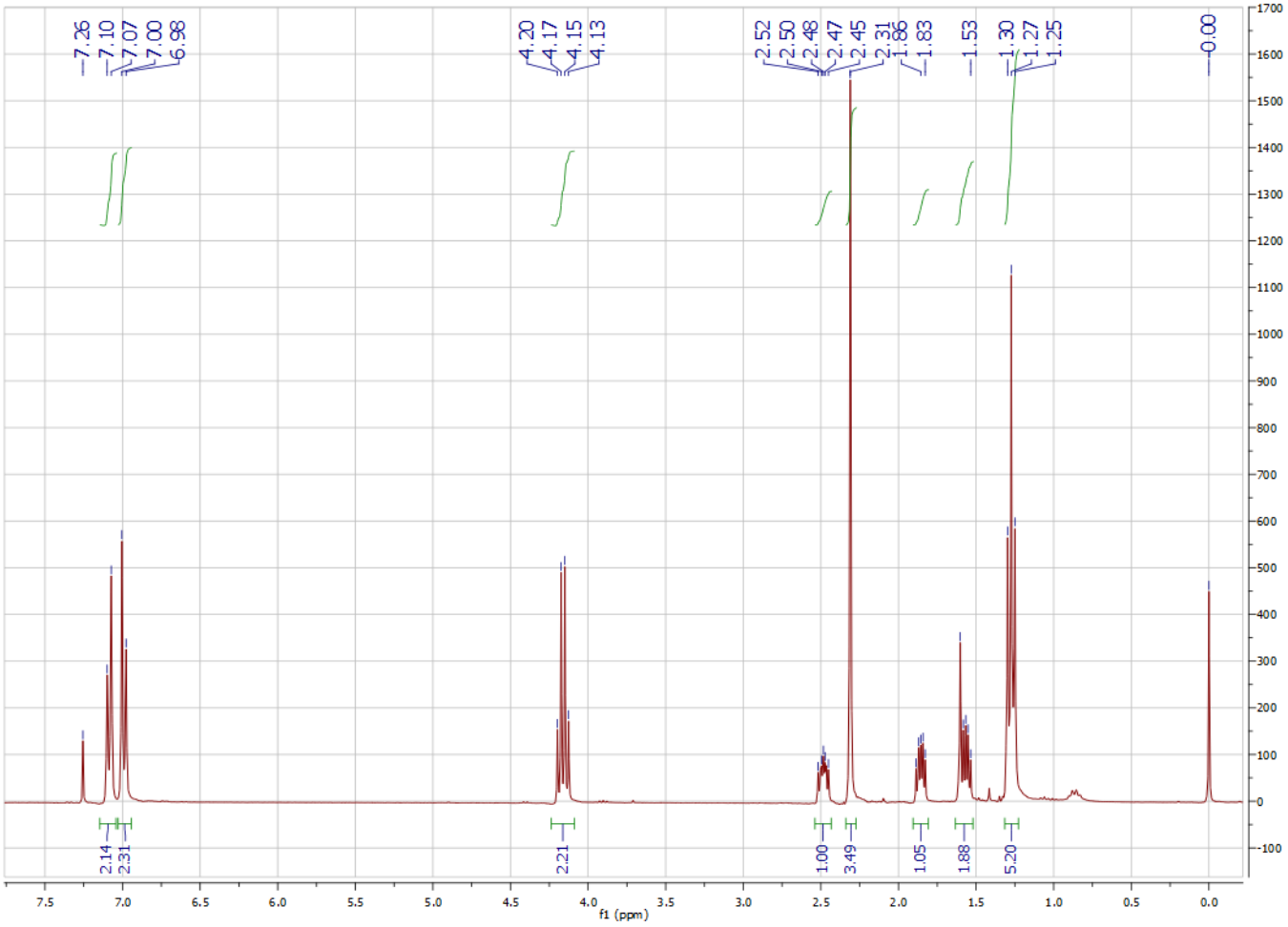




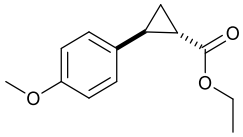


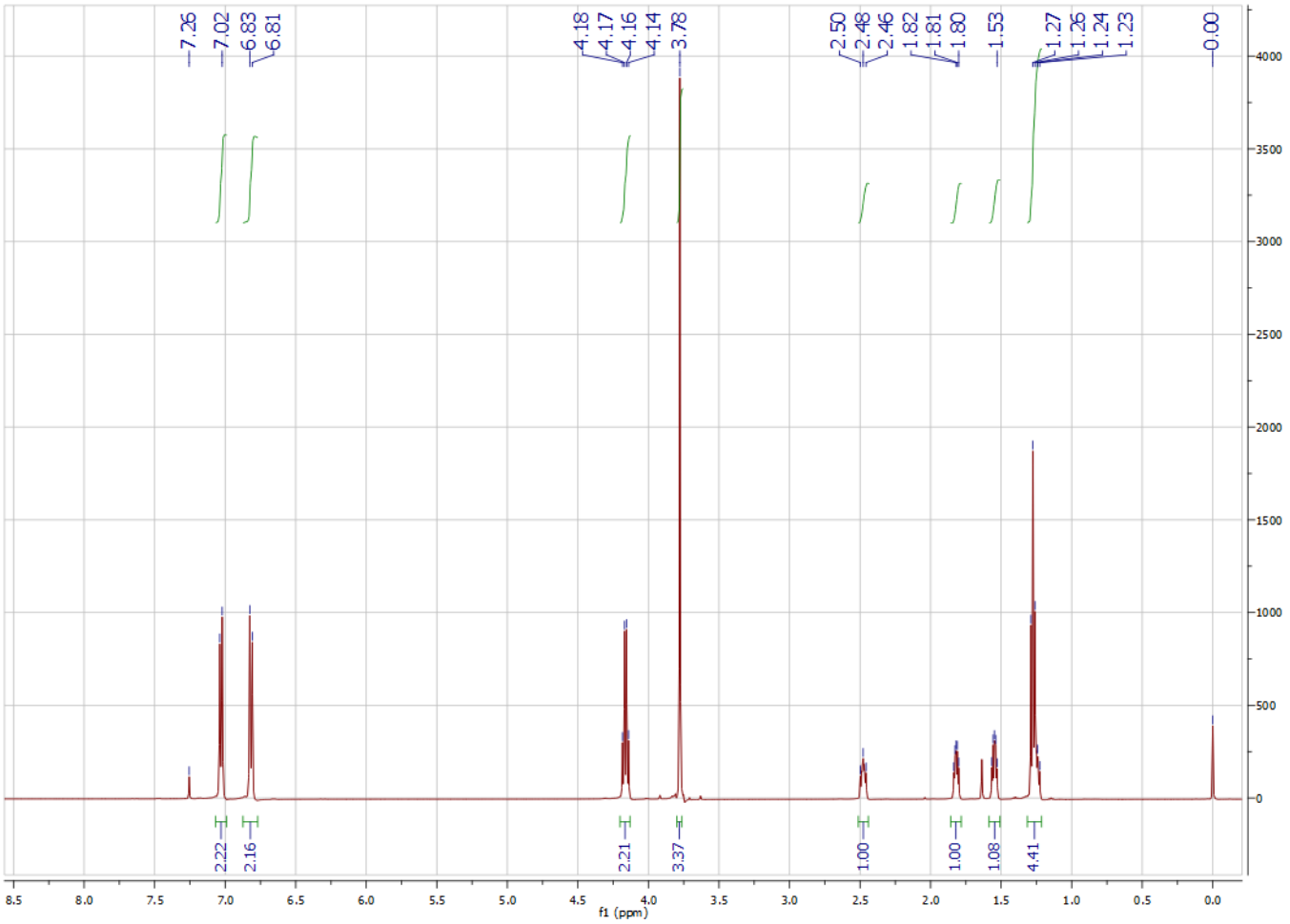
Ethyl 2-(*p*-tolyl)cyclopropane-1-carboxylate 10e



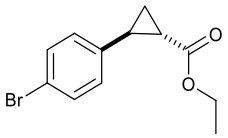


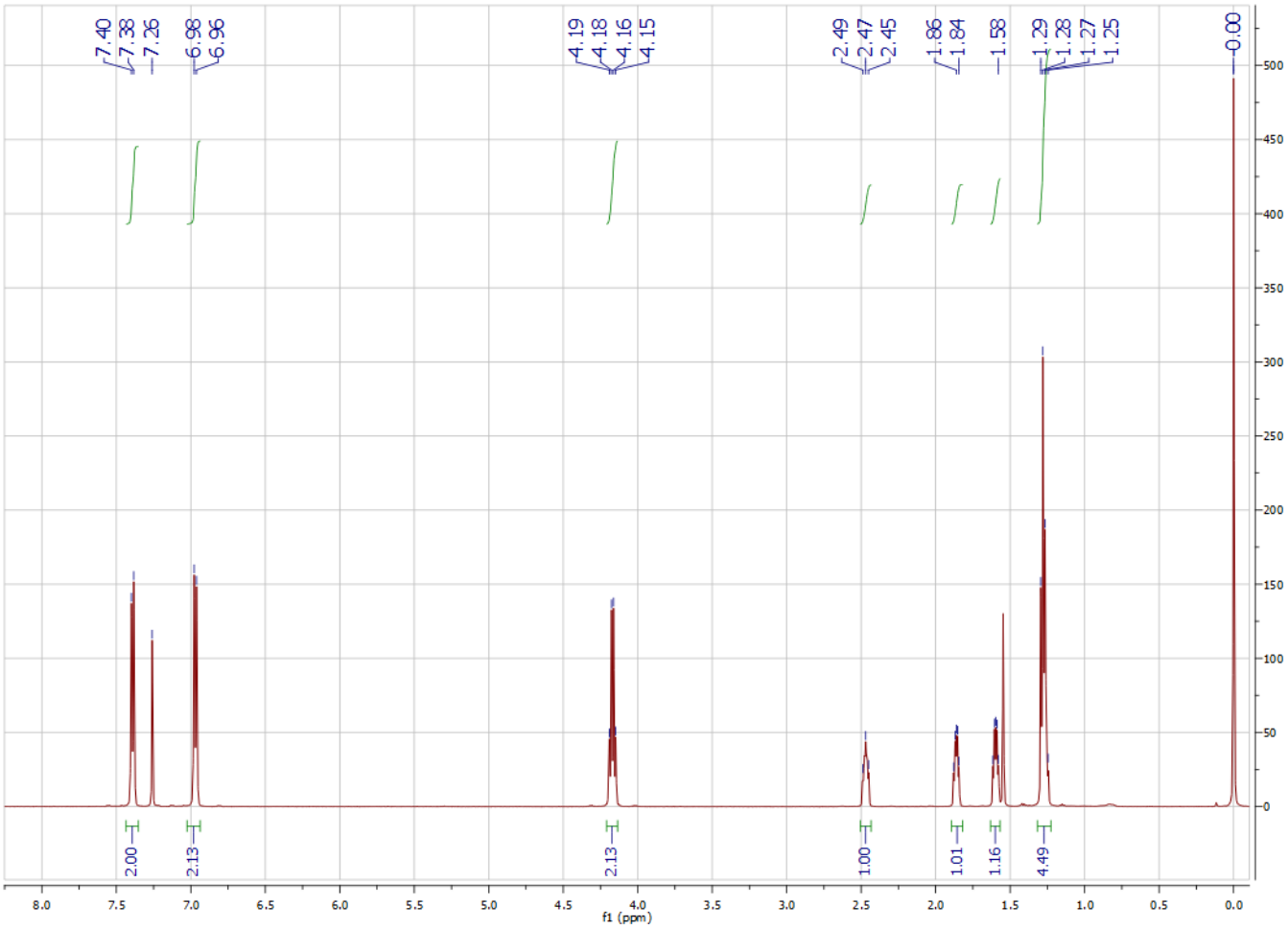
Ethyl 2-(*p*-methoxyphenyl)cyclopropane-1-carboxylate 10f



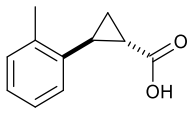


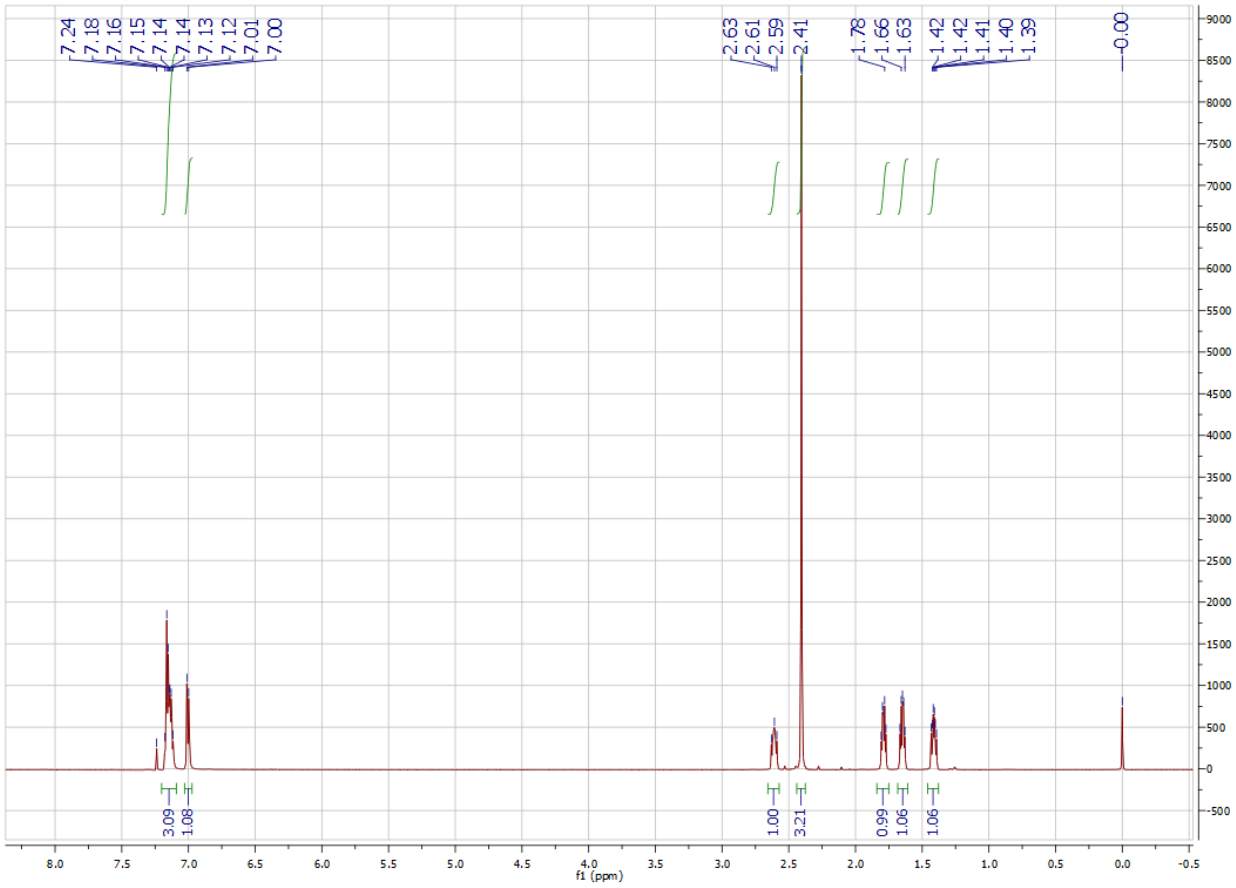
Ethyl 2-(*p*-bromophenyl)cyclopropane-1-carboxylate 10g

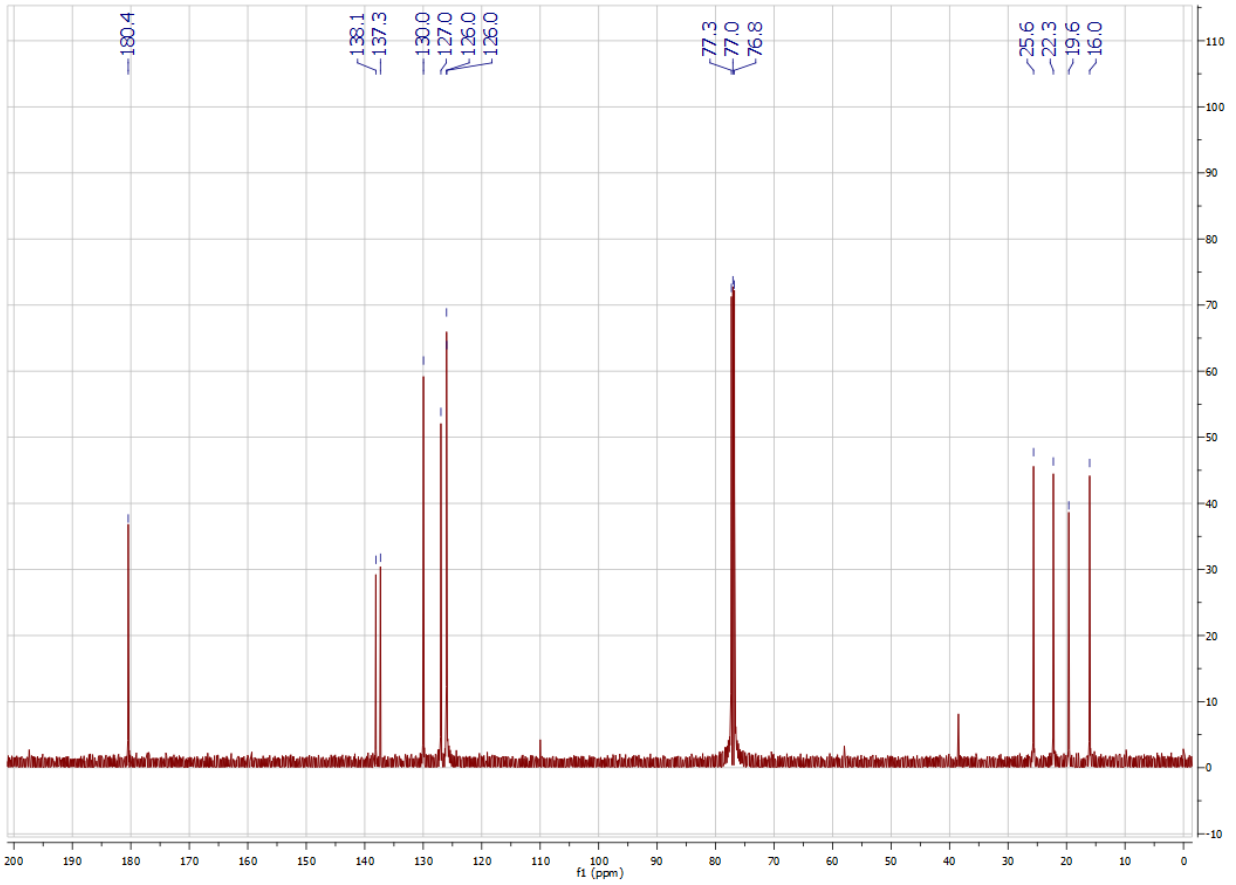




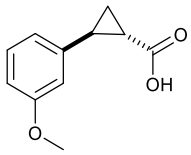
2-(*o*-tolyl)cyclopropane-1-carboxylic acid

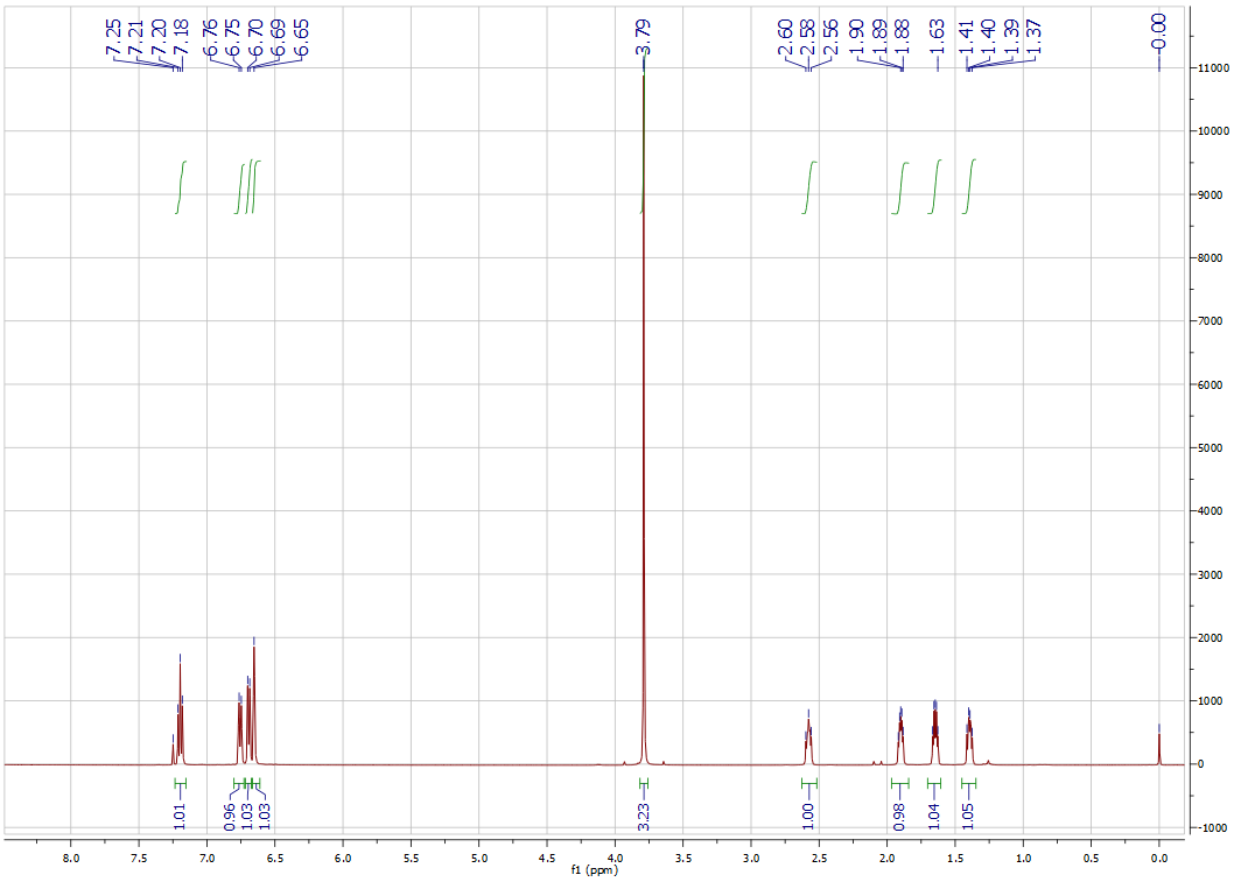


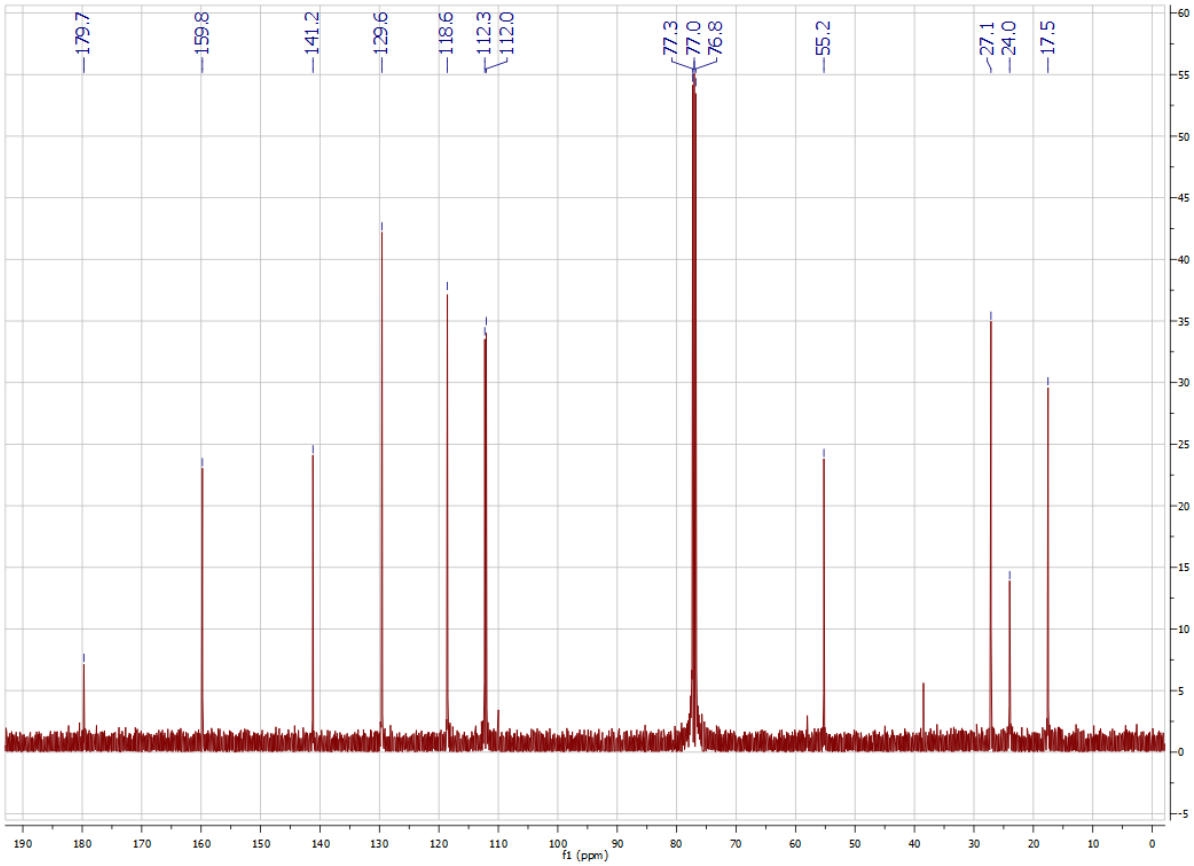




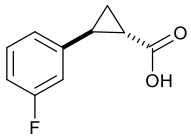
2-(*m*-methoxyphenyl)cyclopropane-1-carboxylic acid

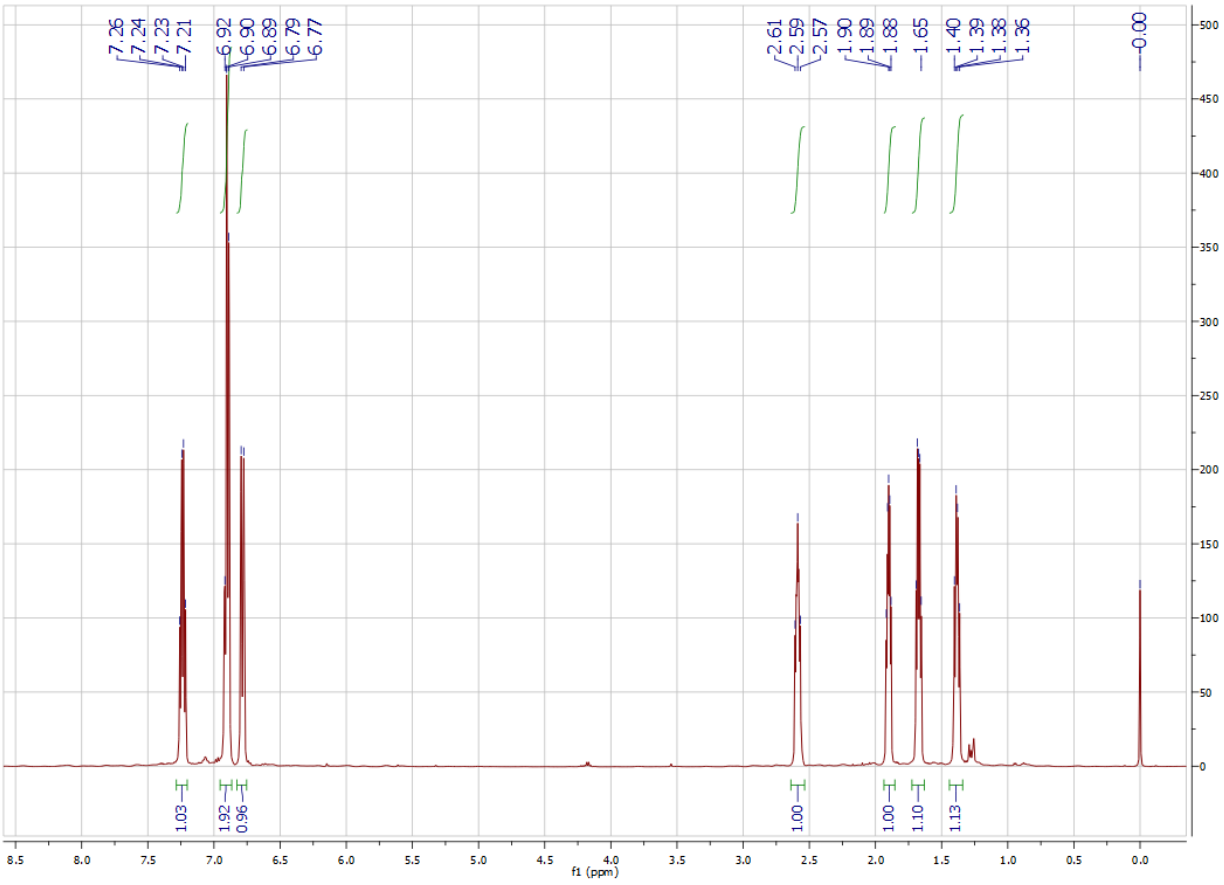


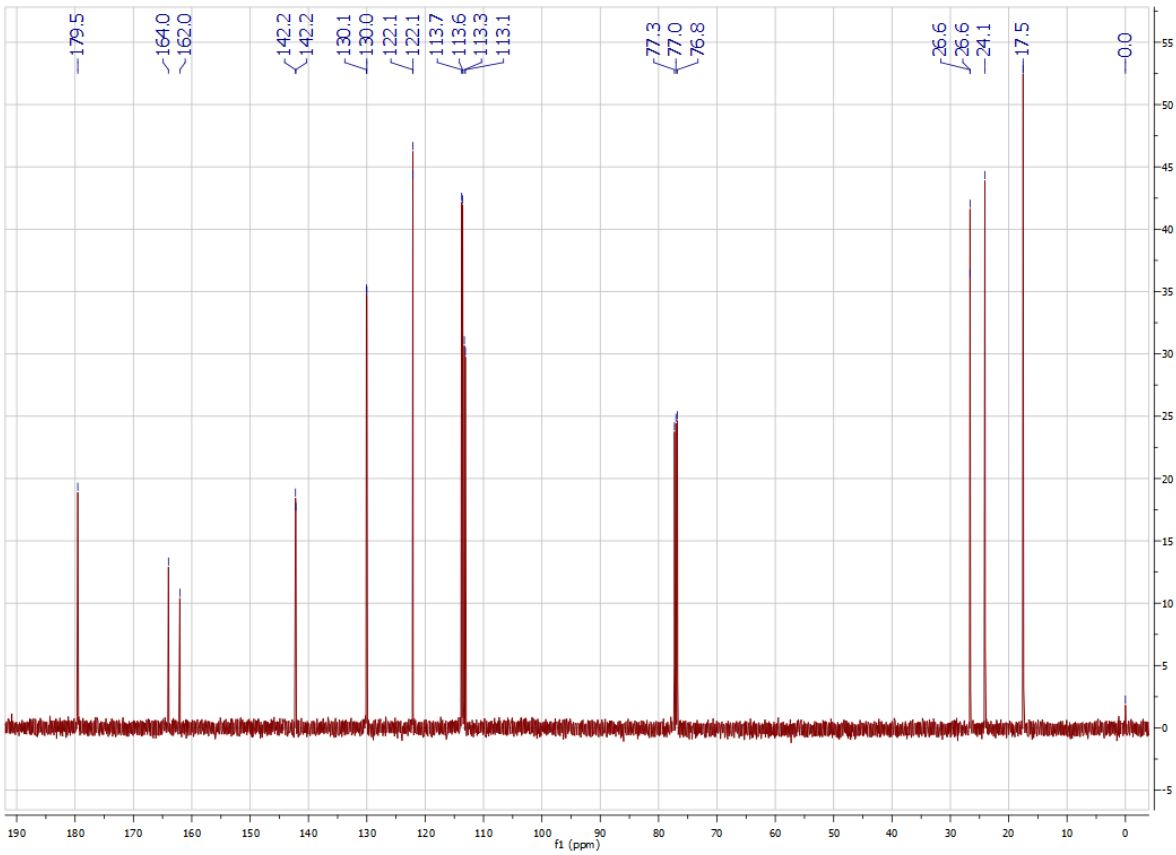




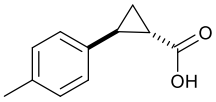
2-(*m*-fluorophenyl)cyclopropane-1-carboxylic acid

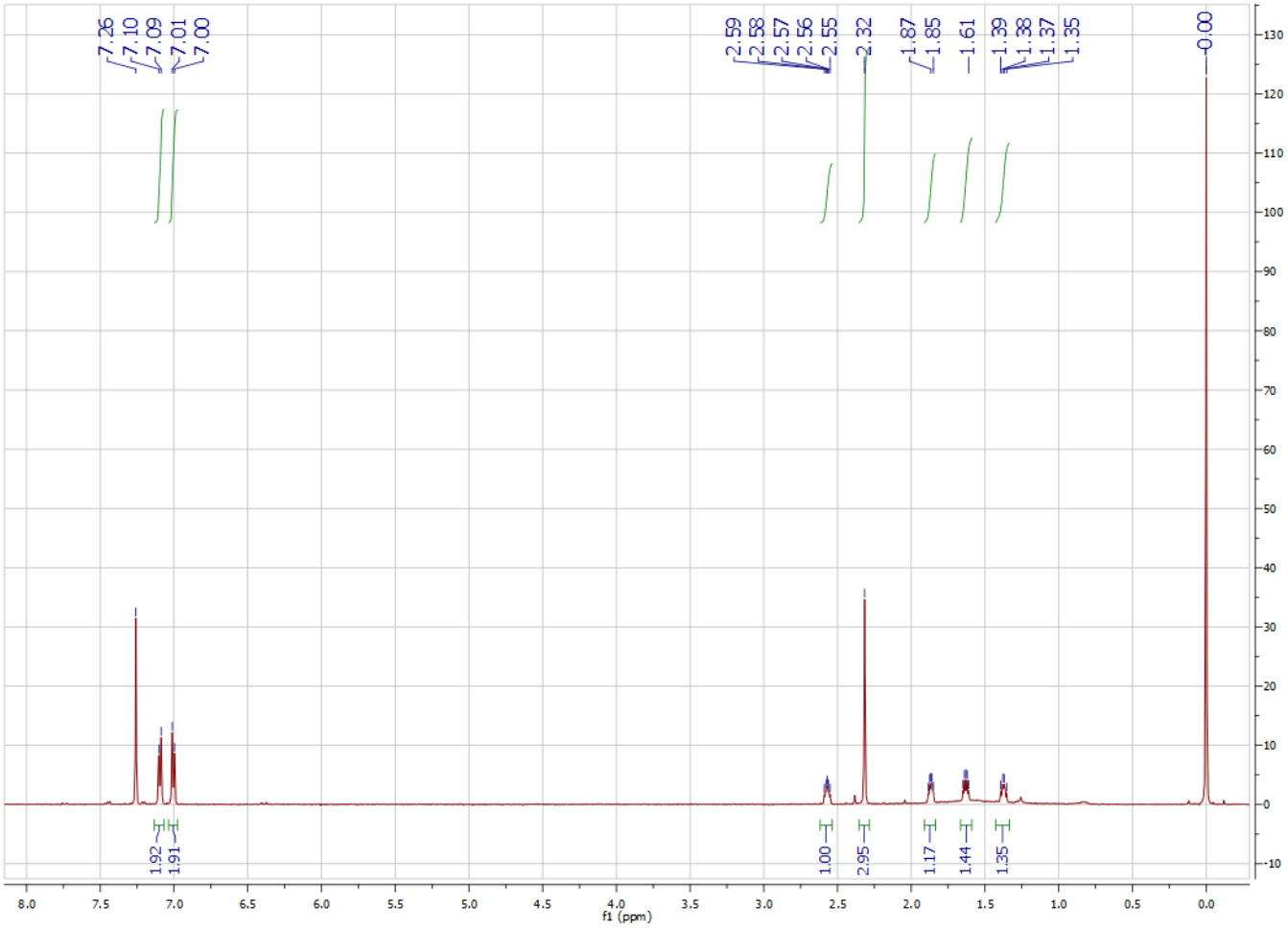




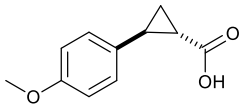


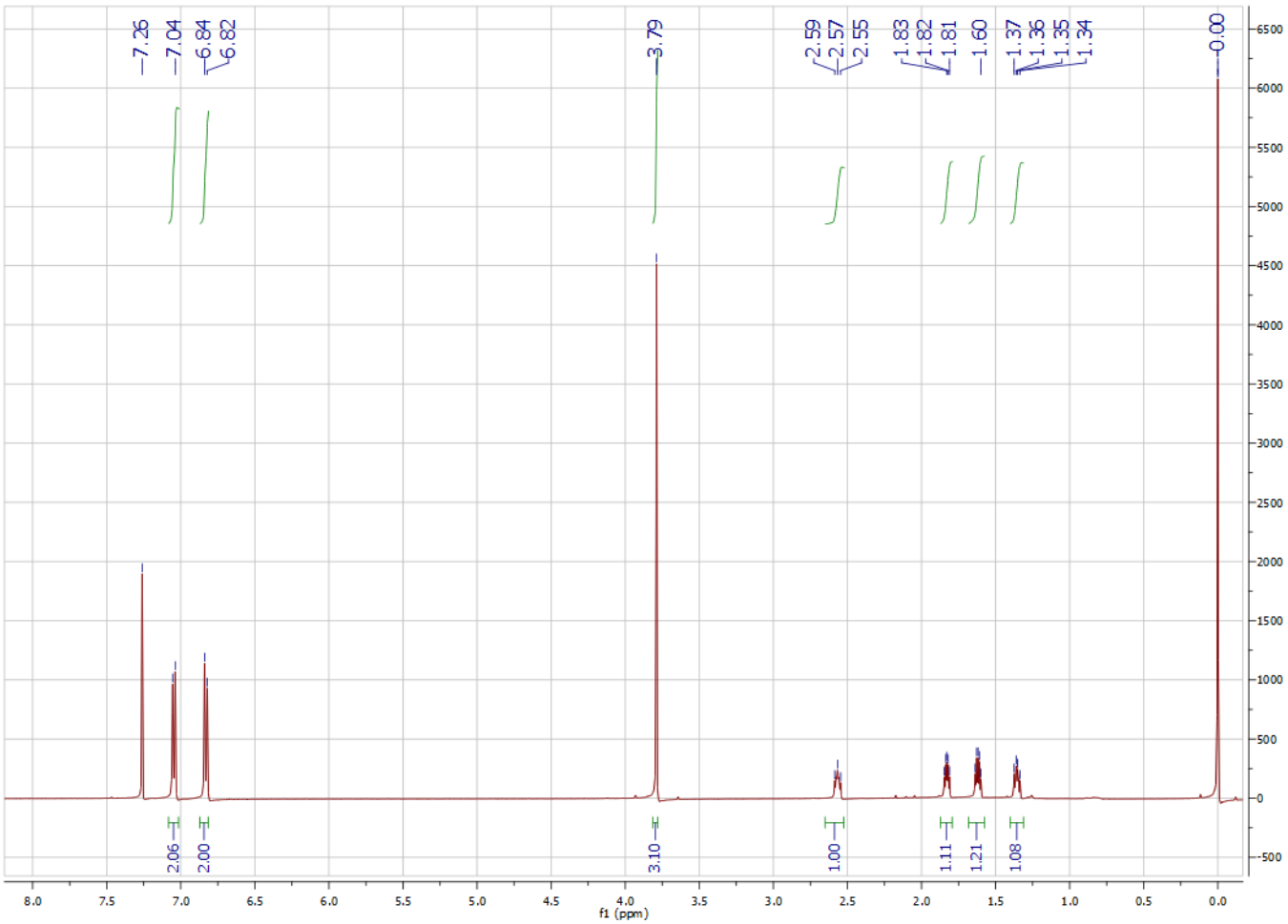
2-(*p*-tolyl)cyclopropane-1-carboxylic acid



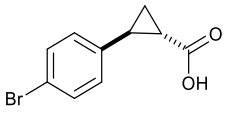


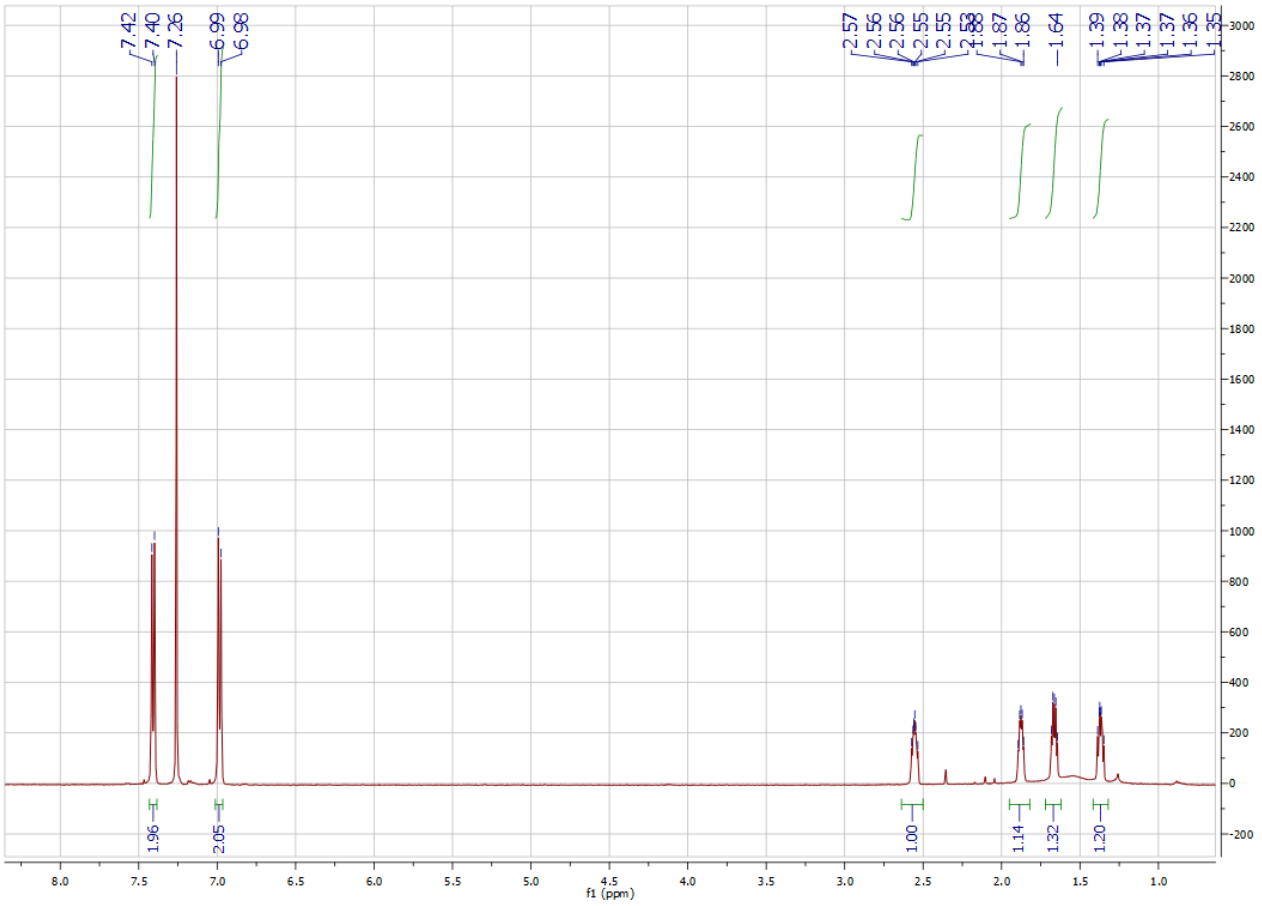
2-(*p*-methoxyphenyl)cyclopropane-1-carboxylic acid

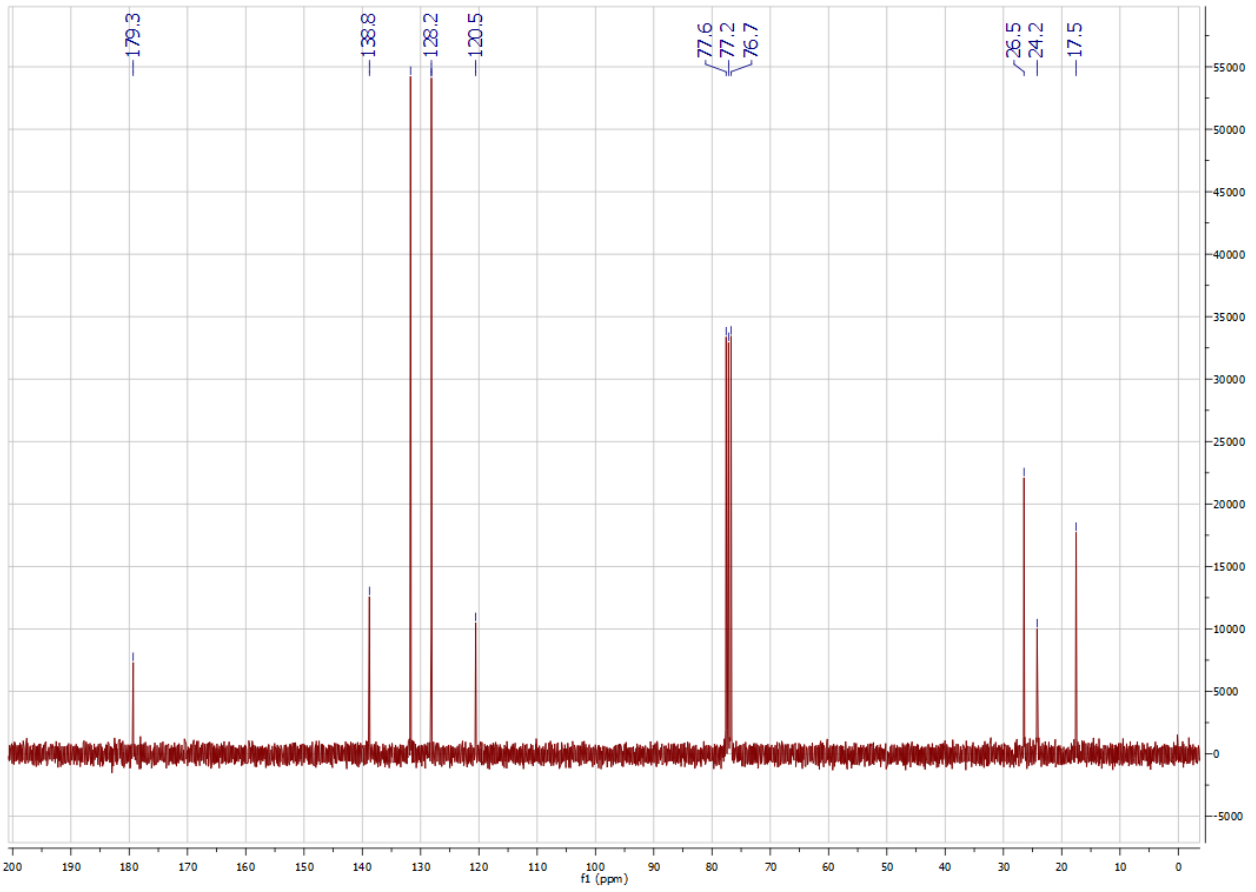




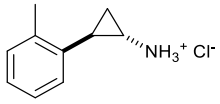
2-(*p*-bromophenyl)cyclopropane-1-carboxylic acid

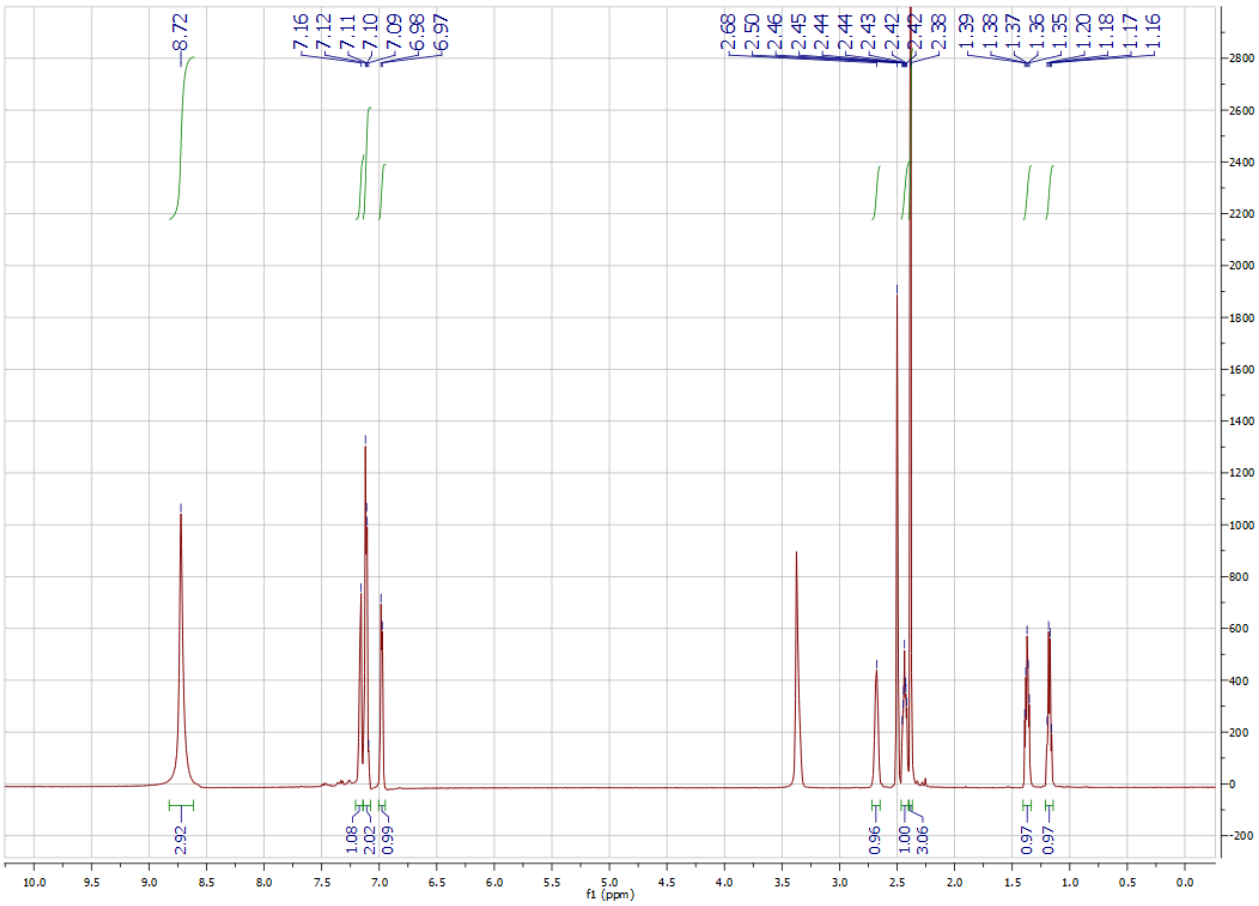


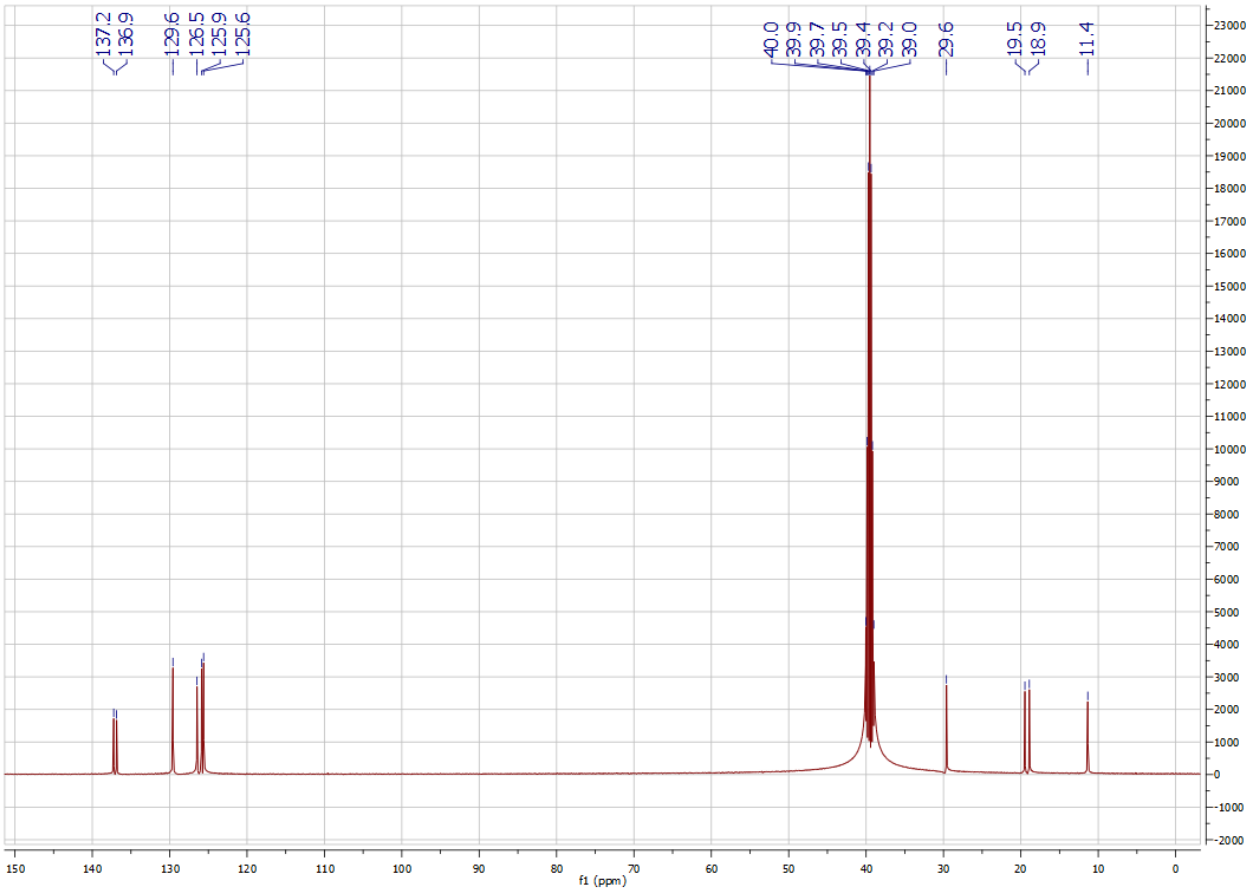




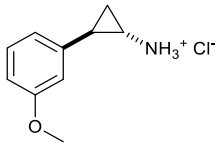
2-(*o*-tolyl)cyclopropylamine hydrochloride 11b

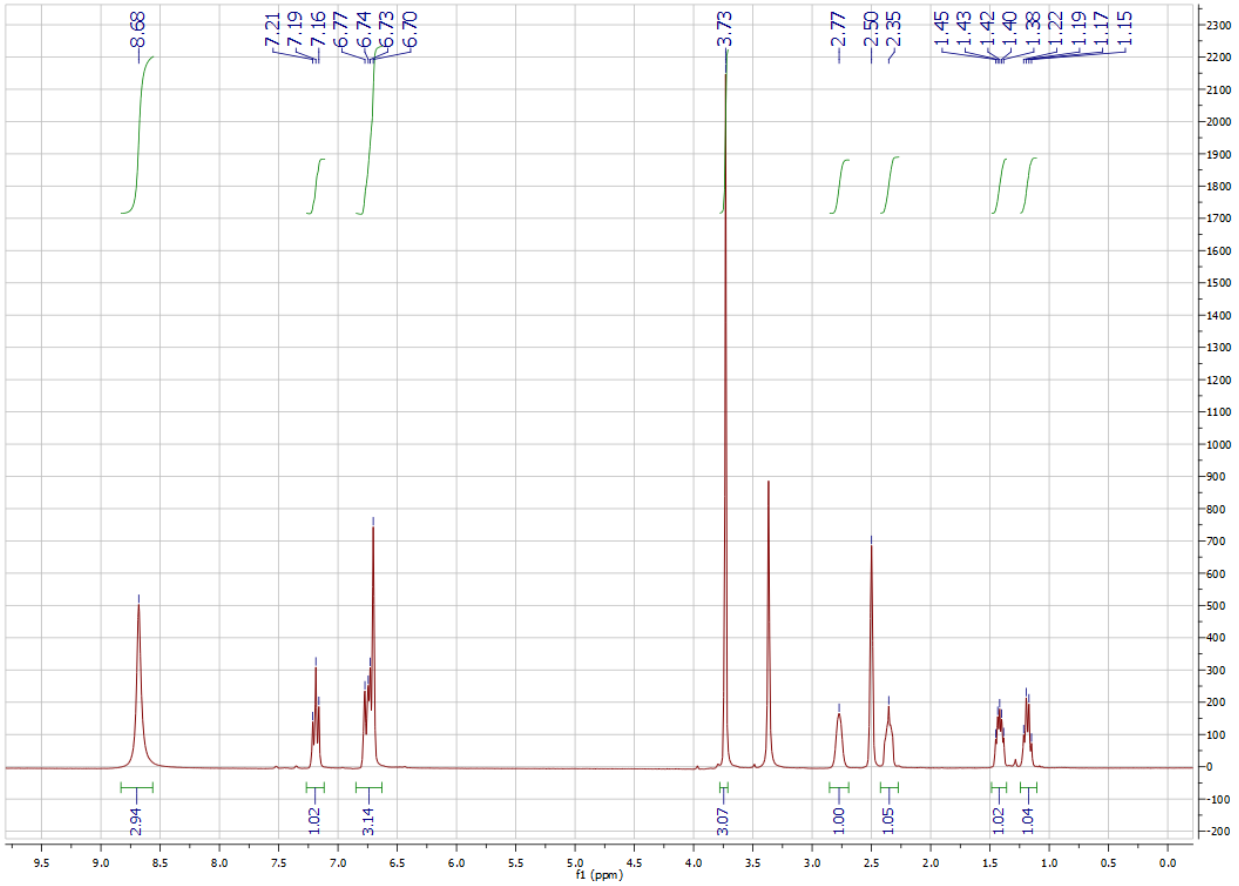


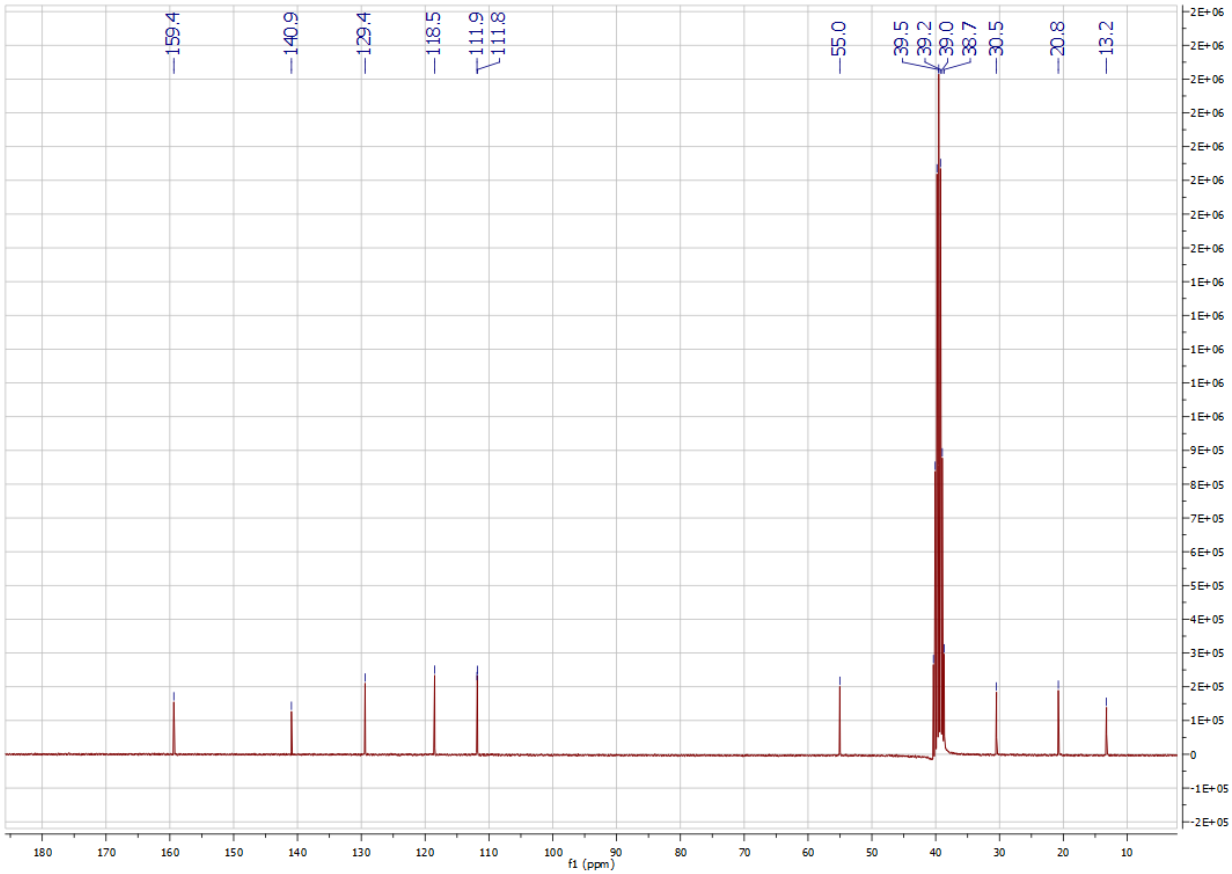




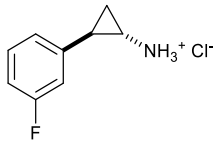
2-(*m*-methoxyphenyl)cyclopropylamine hydrochloride 11b

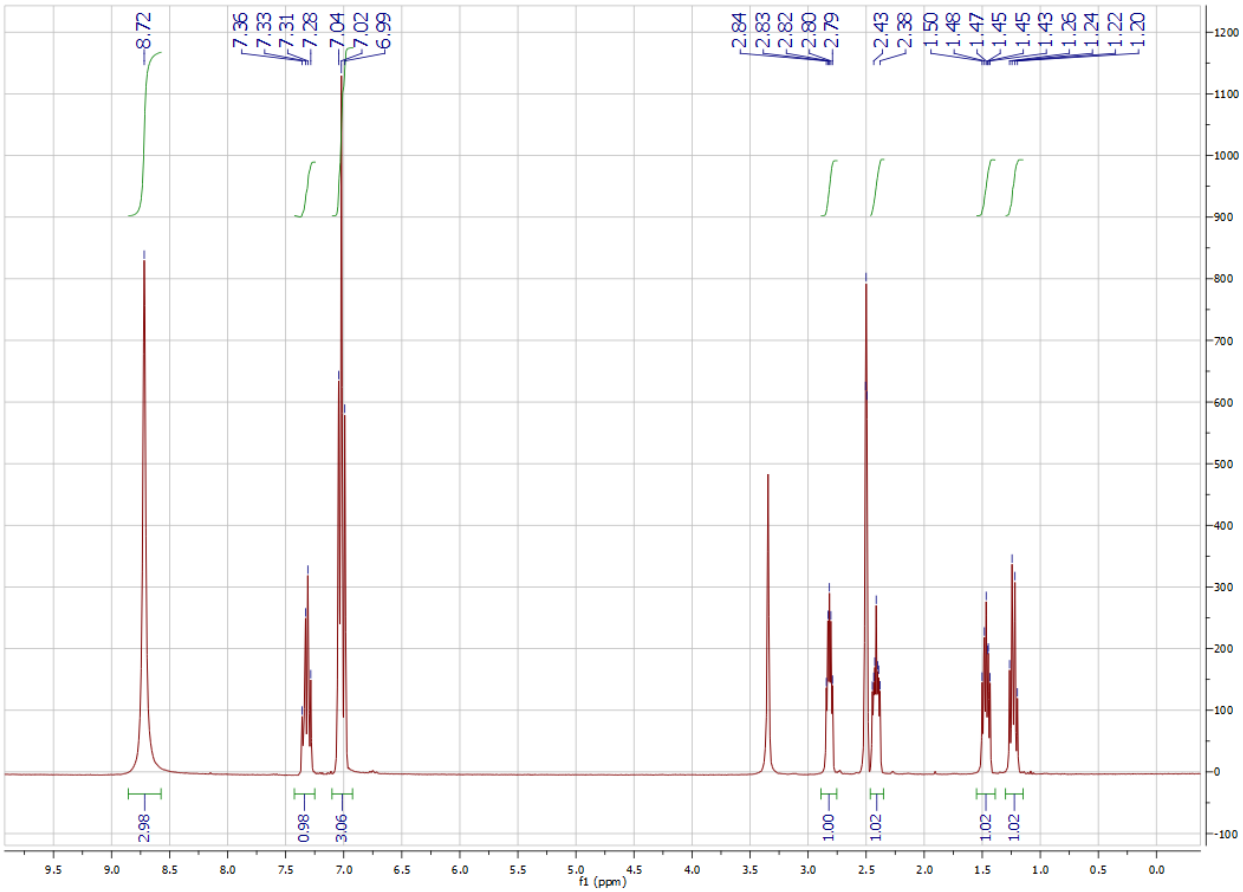


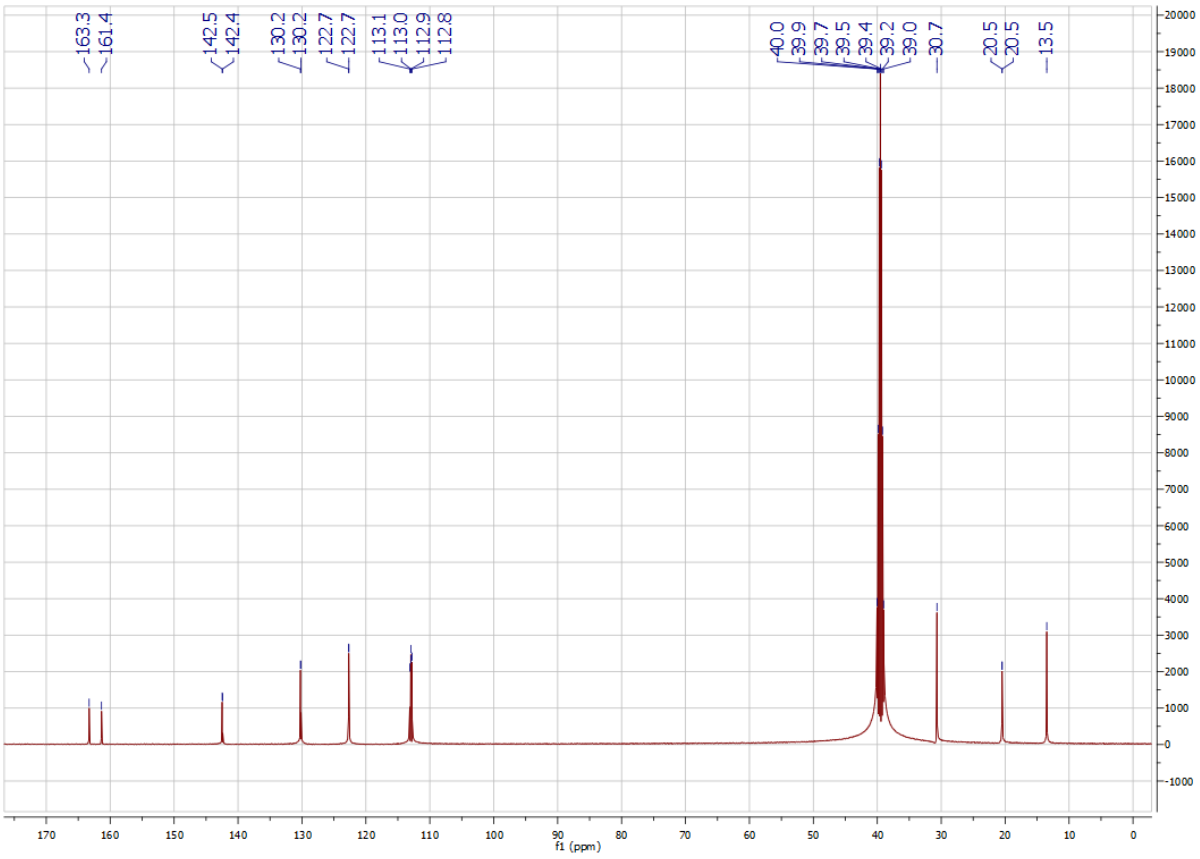




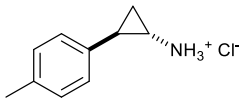
2-(*m*-fluorophenyl)cyclopropylamine hydrochloride 11d

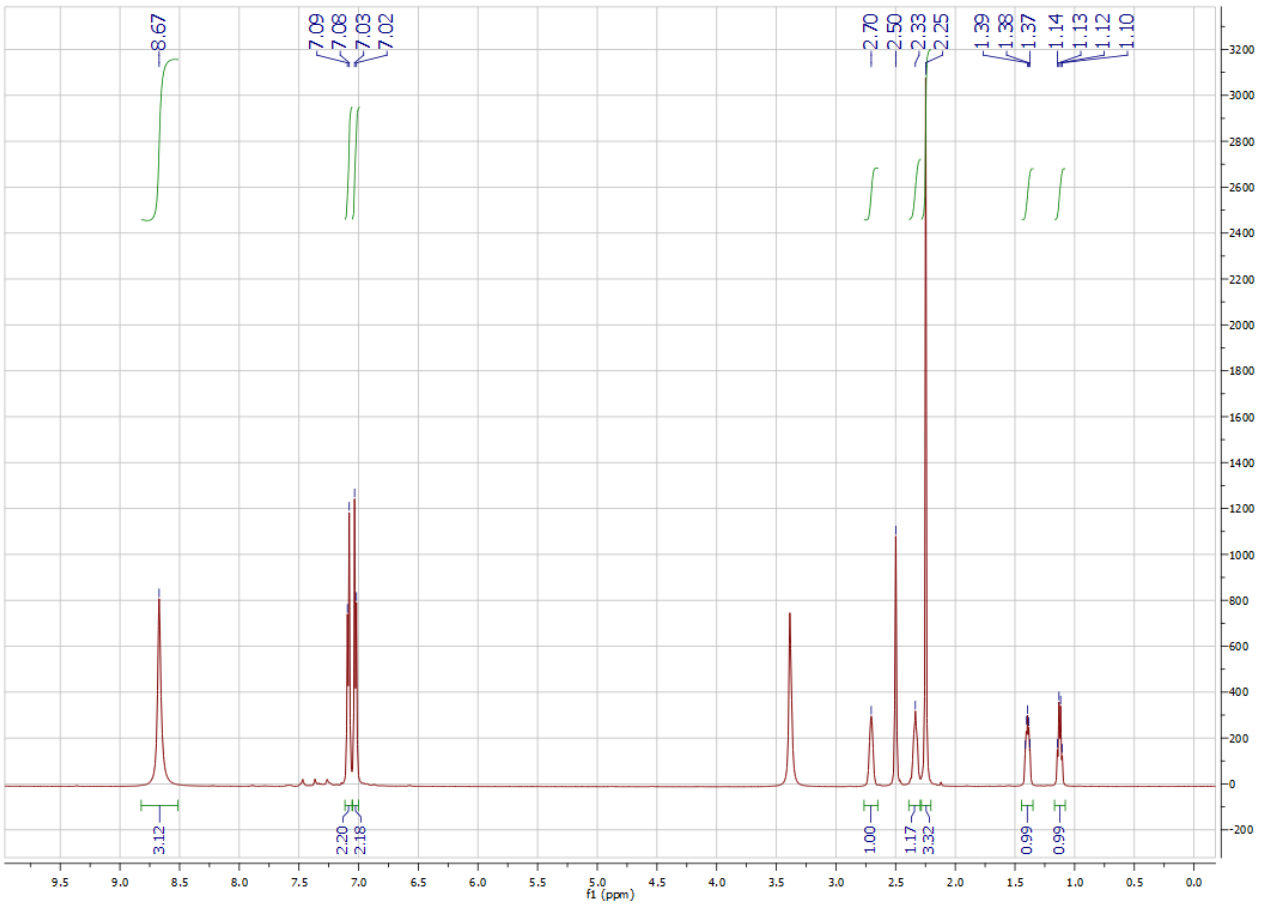


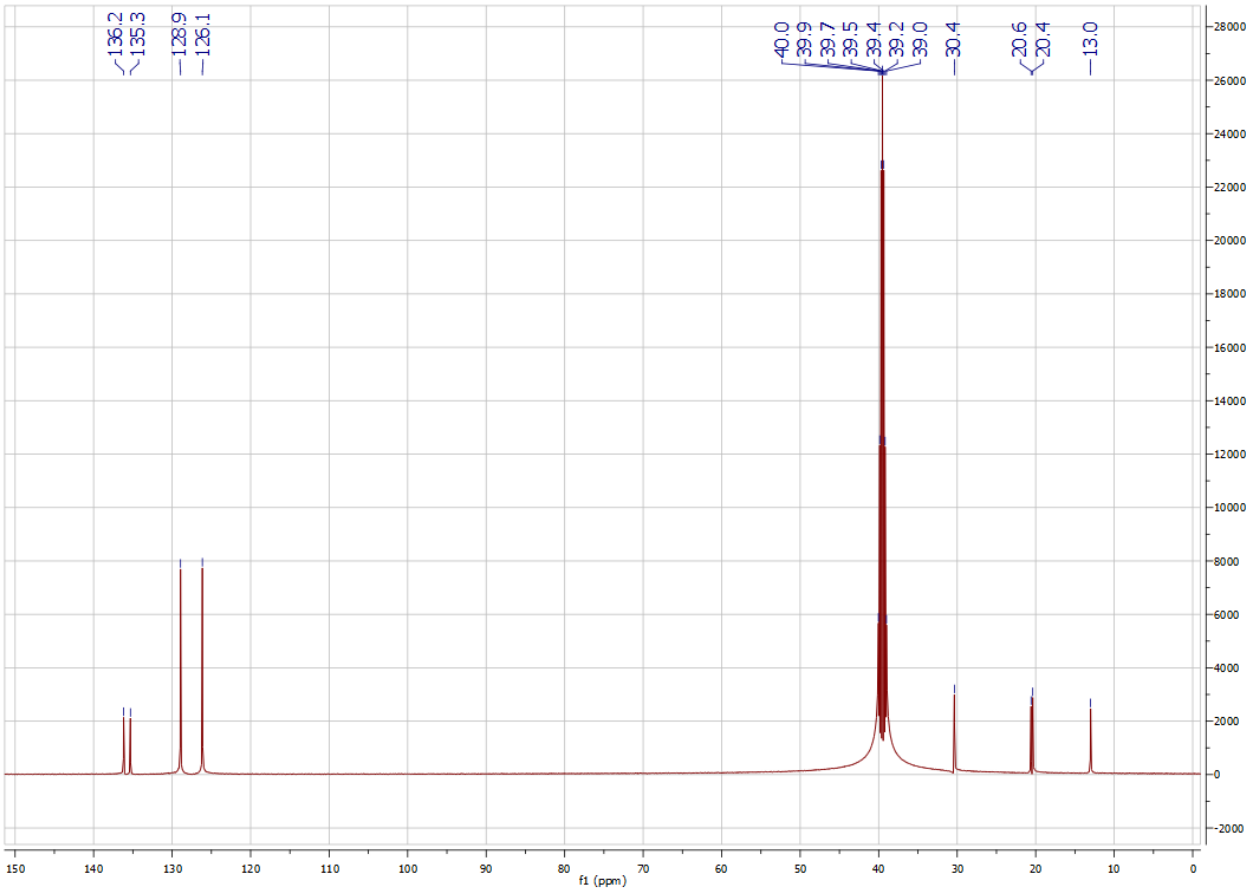




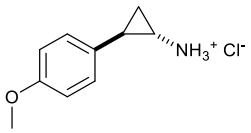
2-(*p*-tolyl)cyclopropylamine hydrochloride 11e

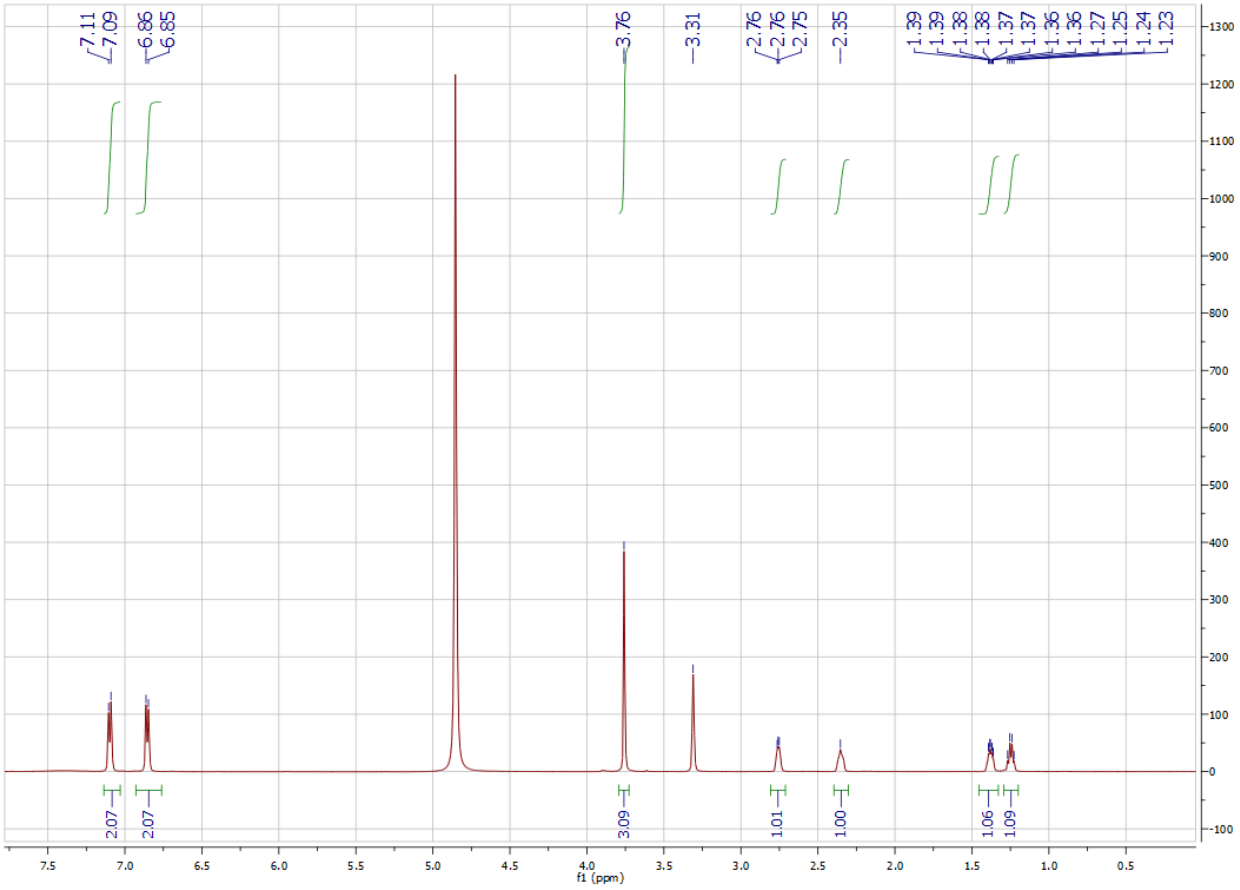


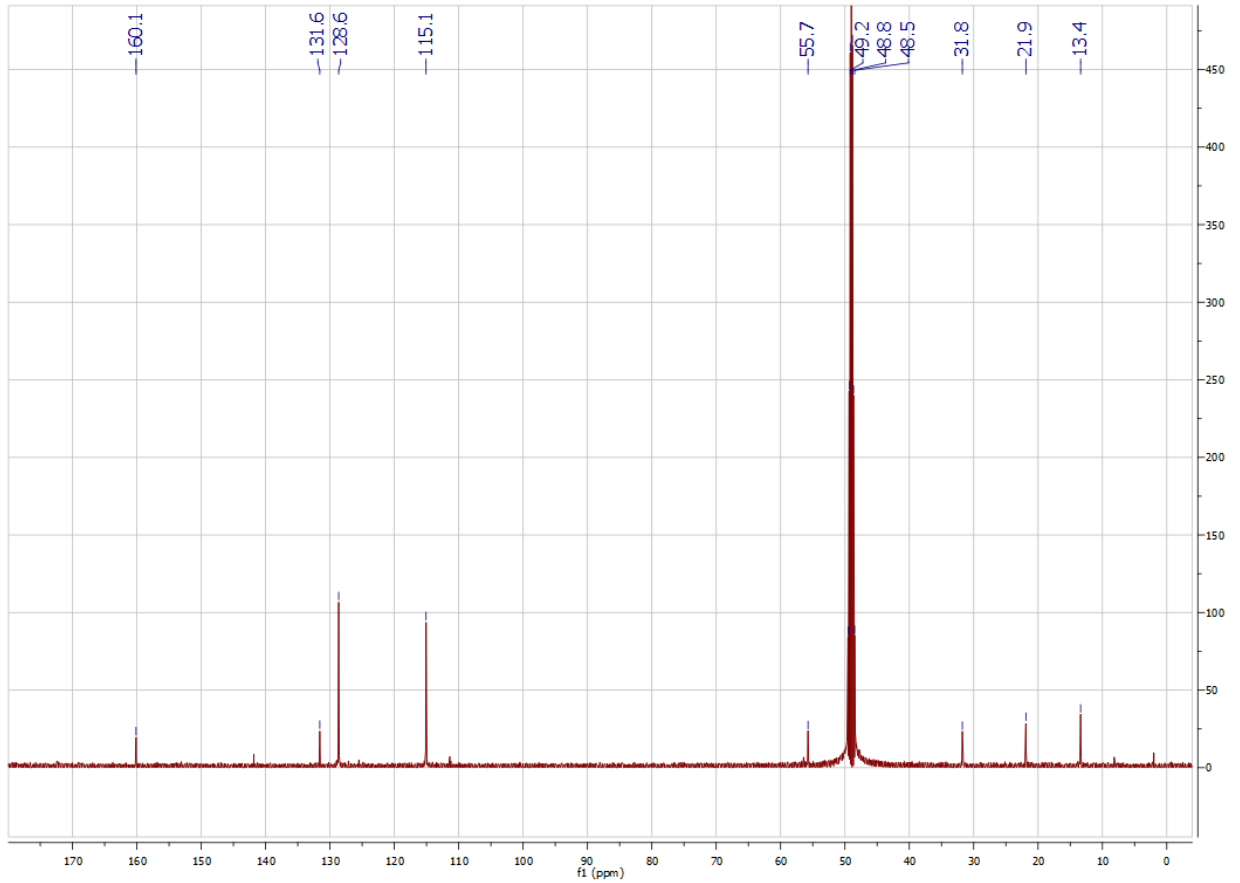




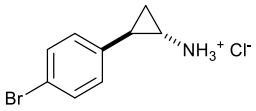
2-(*p*-methoxyphenyl)cyclopropylamine hydrochloride 11f

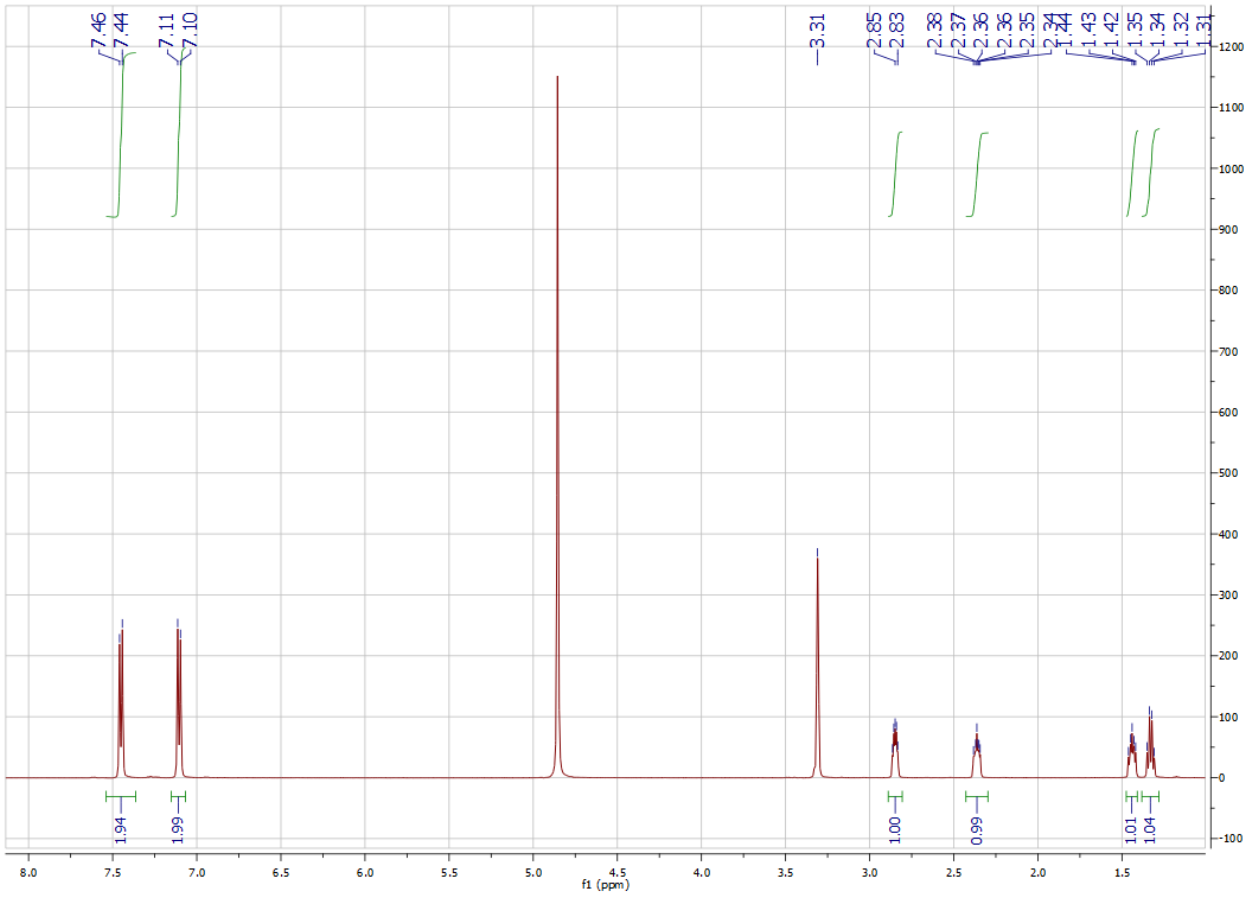


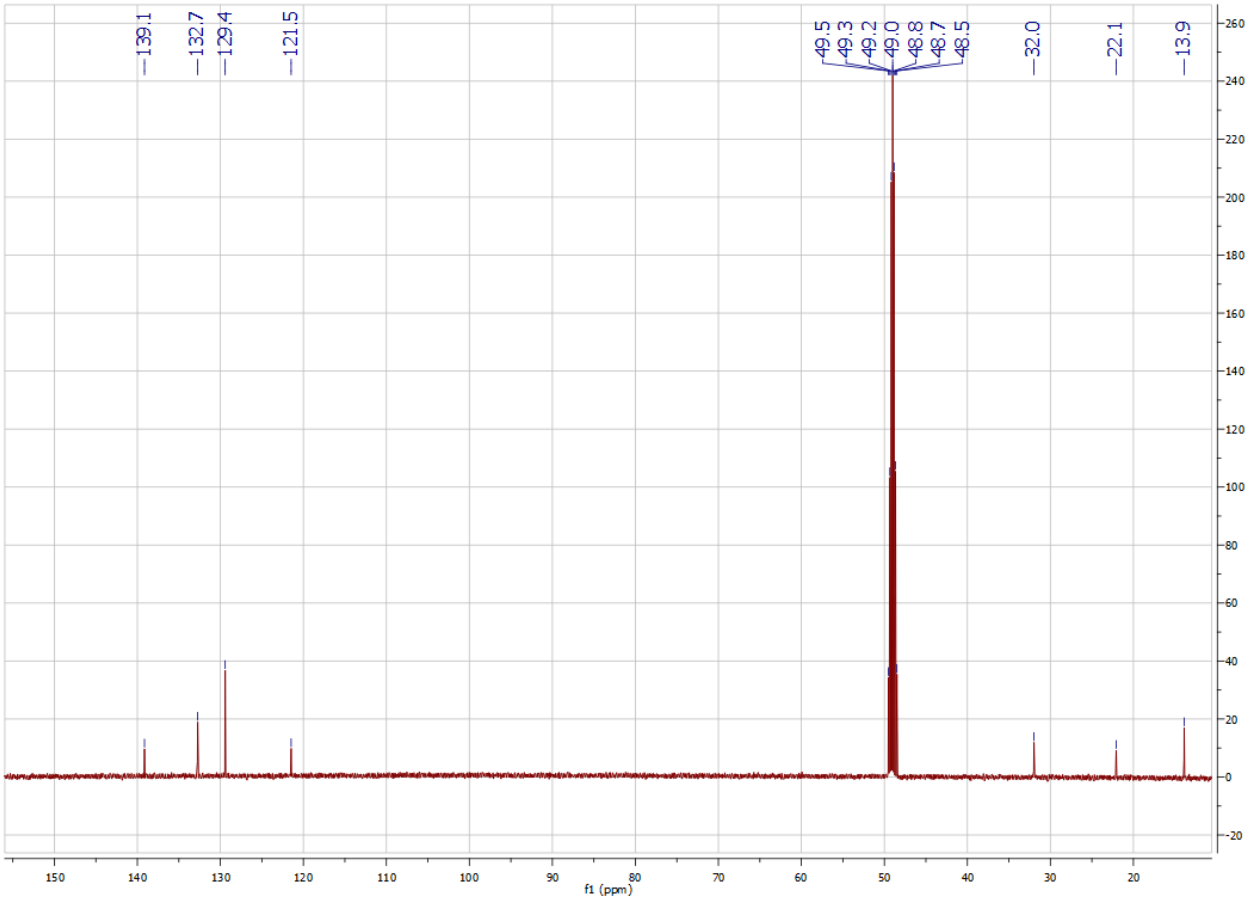




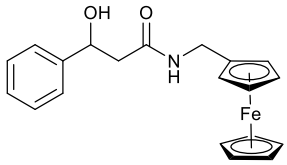
2-(*p*-bromophenyl)cyclopropylamine hydrochloride 11g

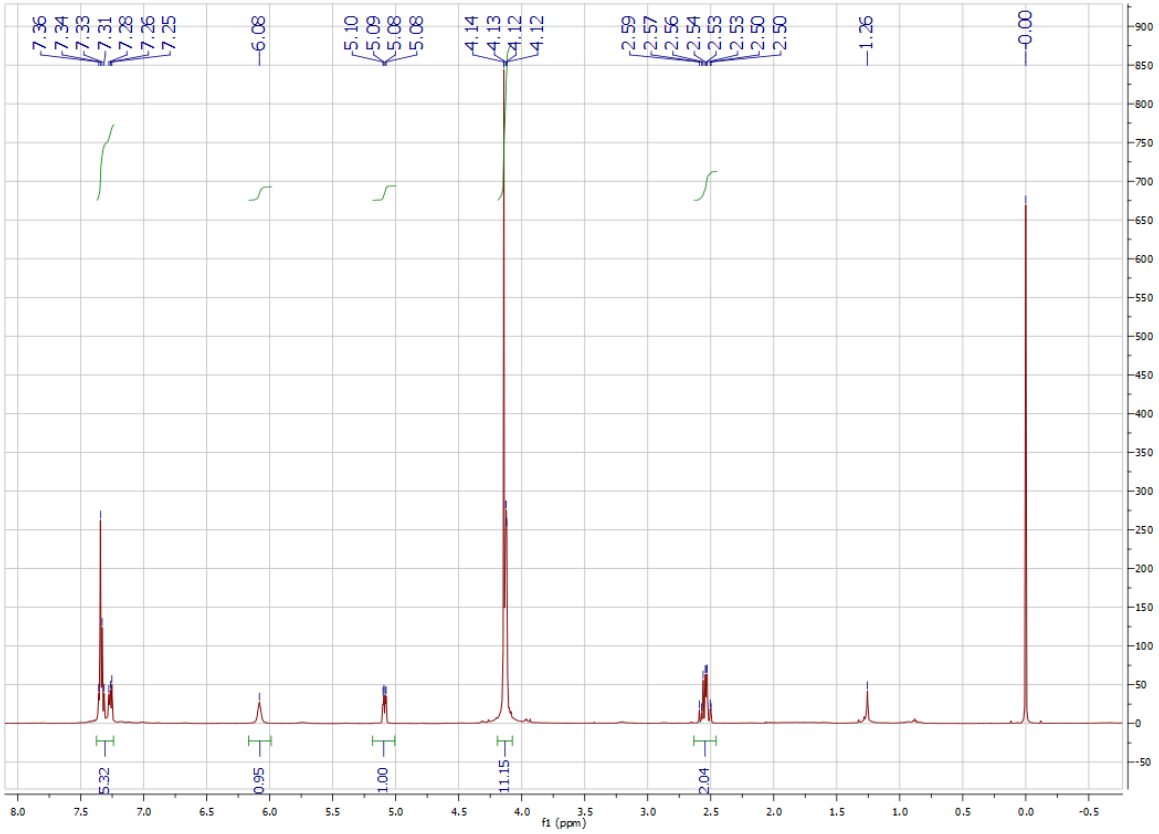


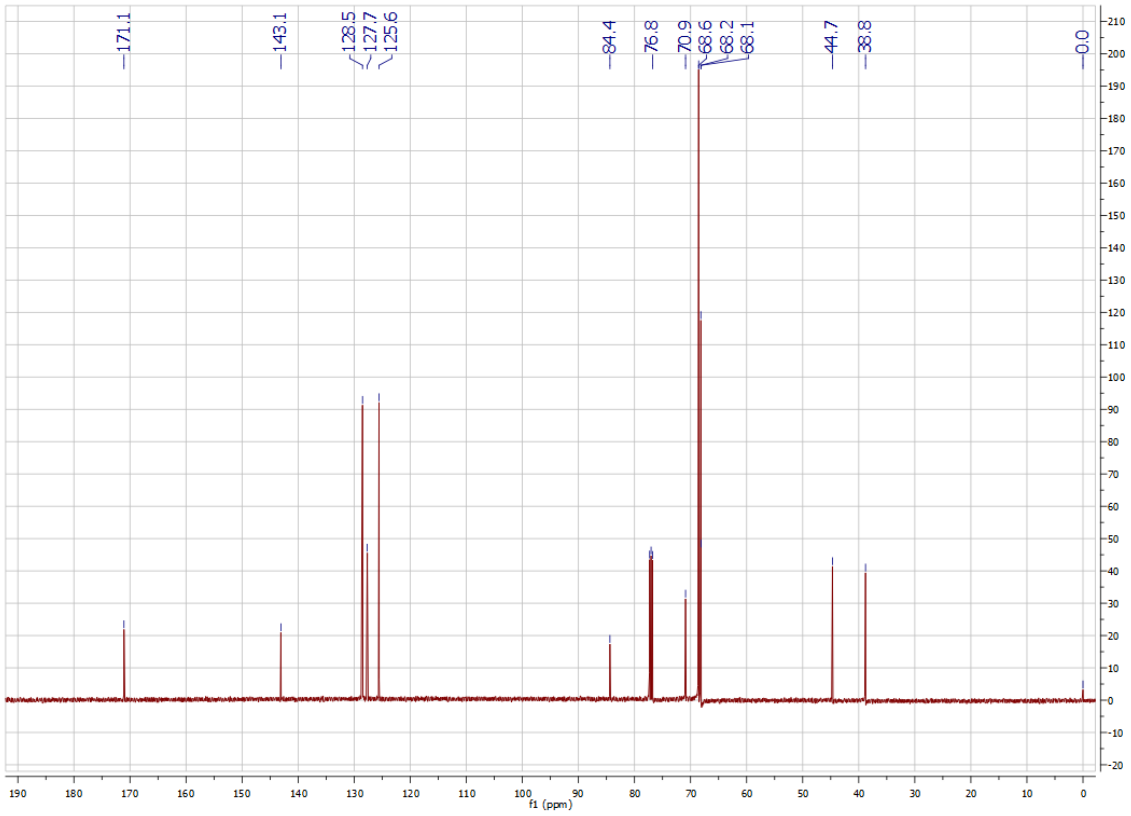




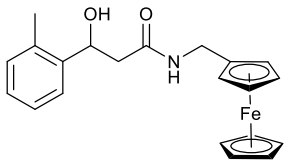
N-(Ferrocenylmethyl)-3-hydroxy-3-phenylpropanamide 7a

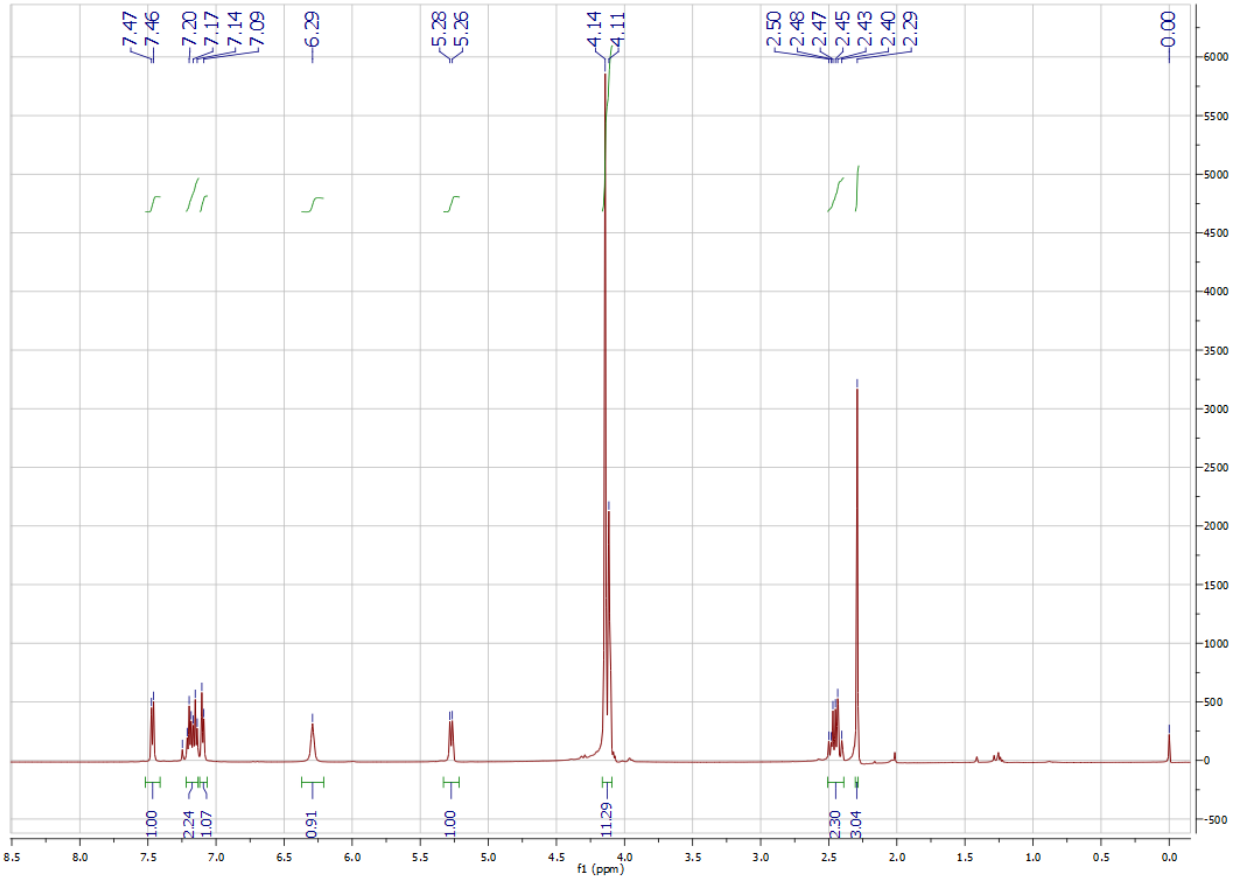


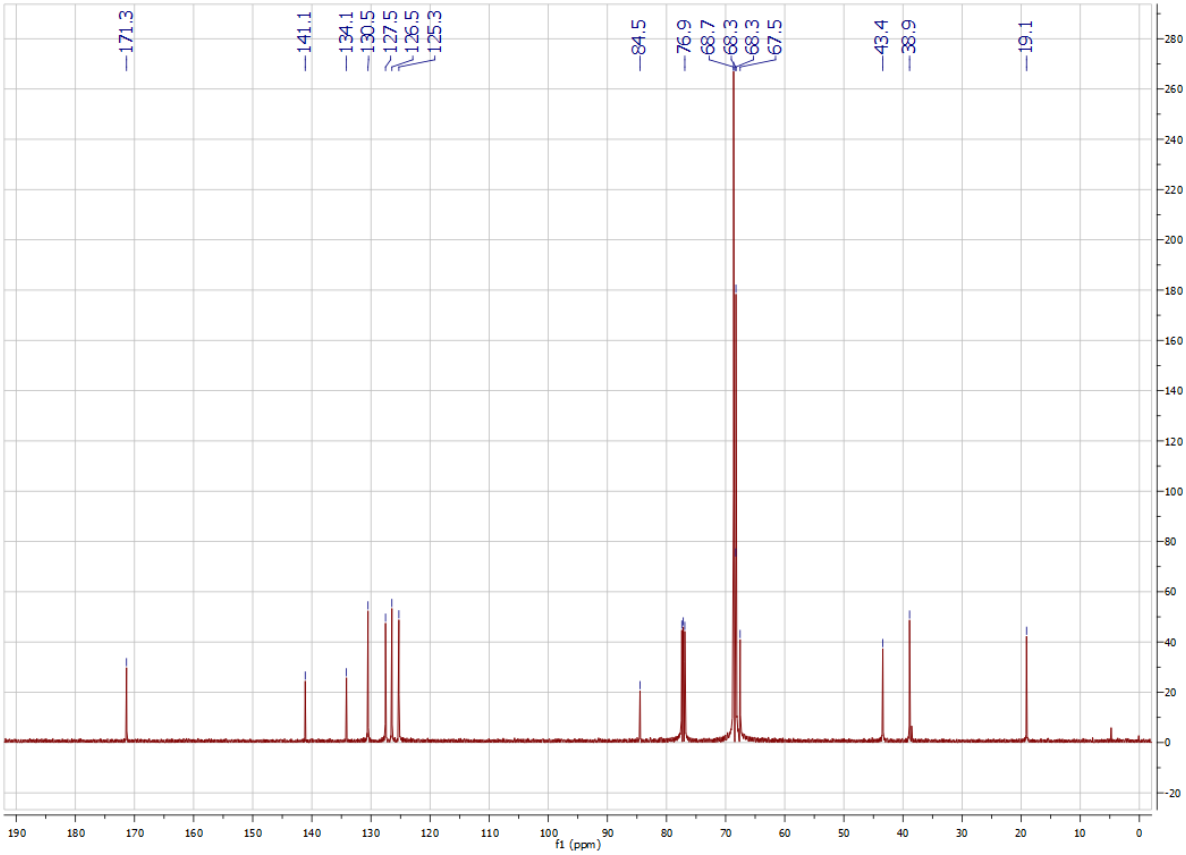




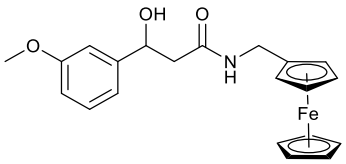
***N*-(ferrocenylmethyl)-3-hydroxy-3-(*o*-methylphenyl)propanamide 7b**

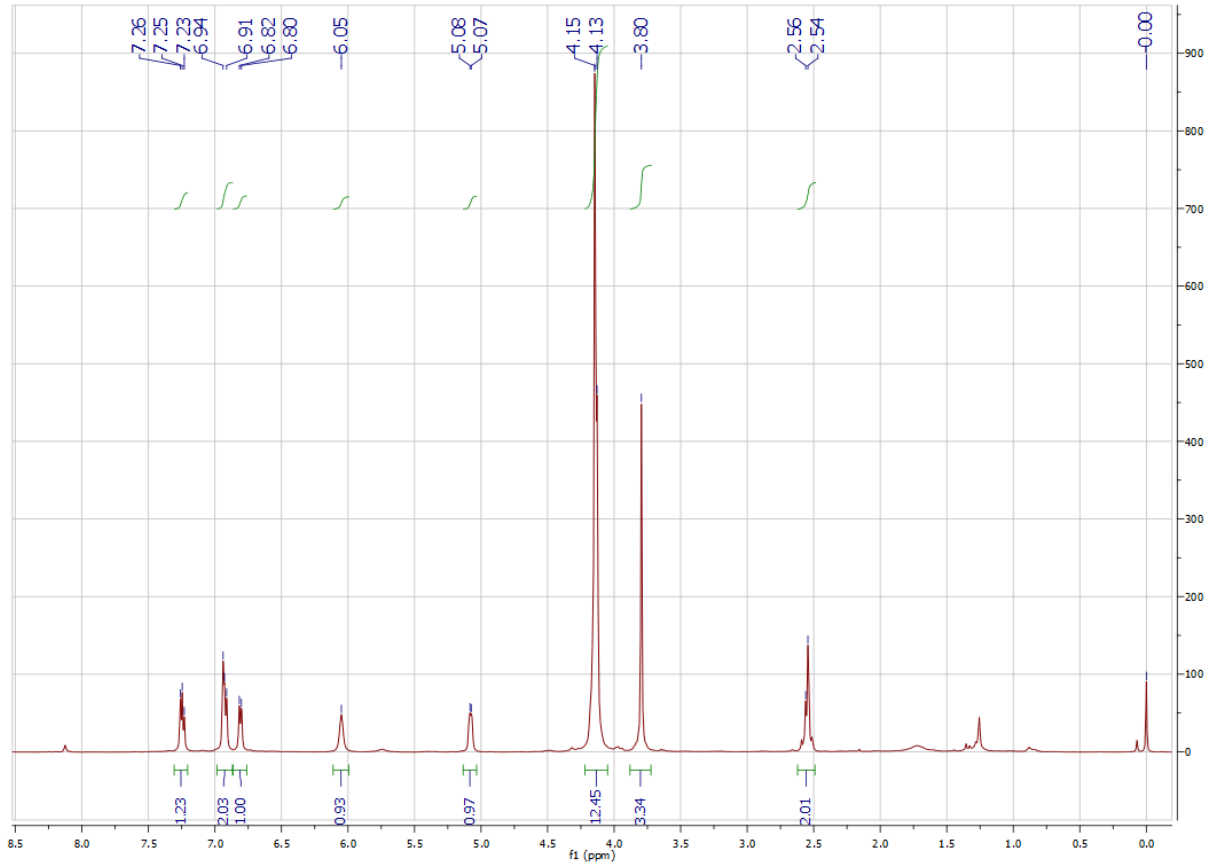


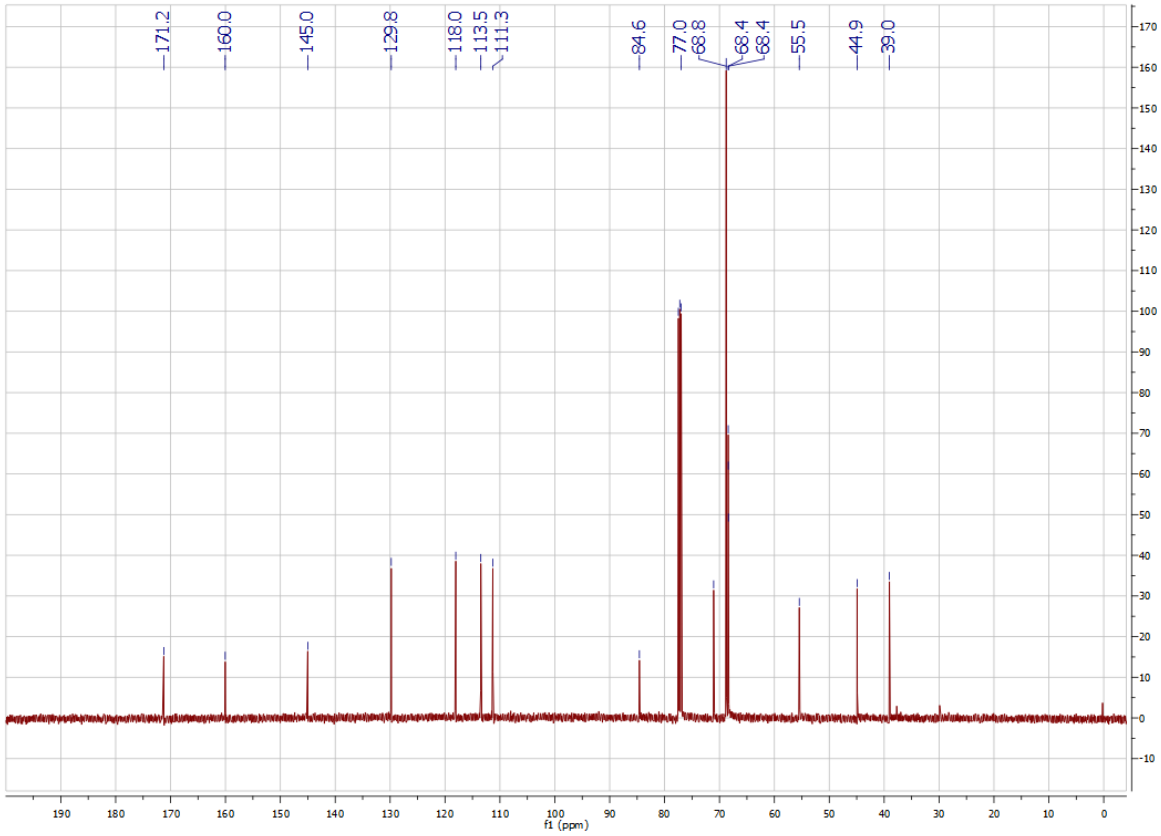




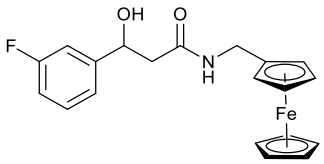
***N*-(ferrocenylmethyl)-3-hydroxy-3-(*m*-methoxyphenyl)propanamide 7c**

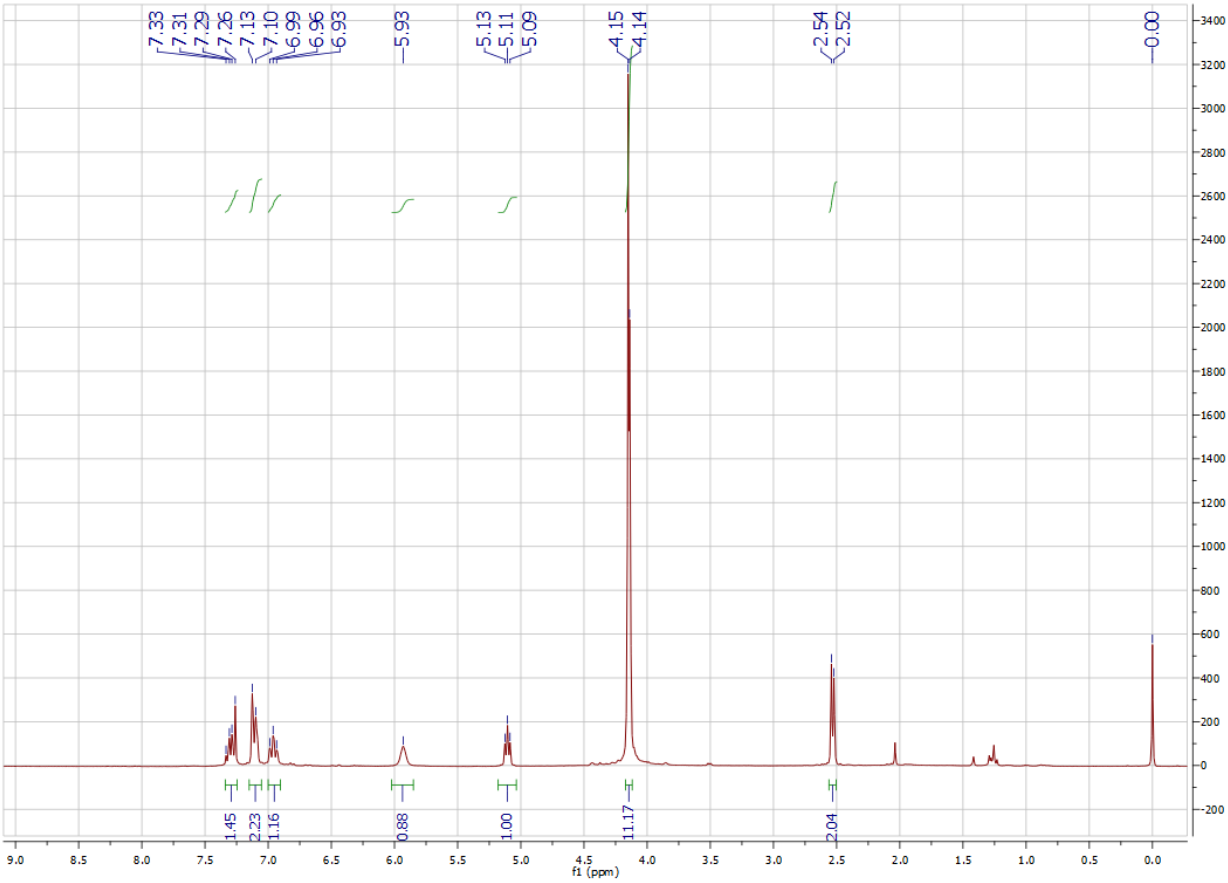


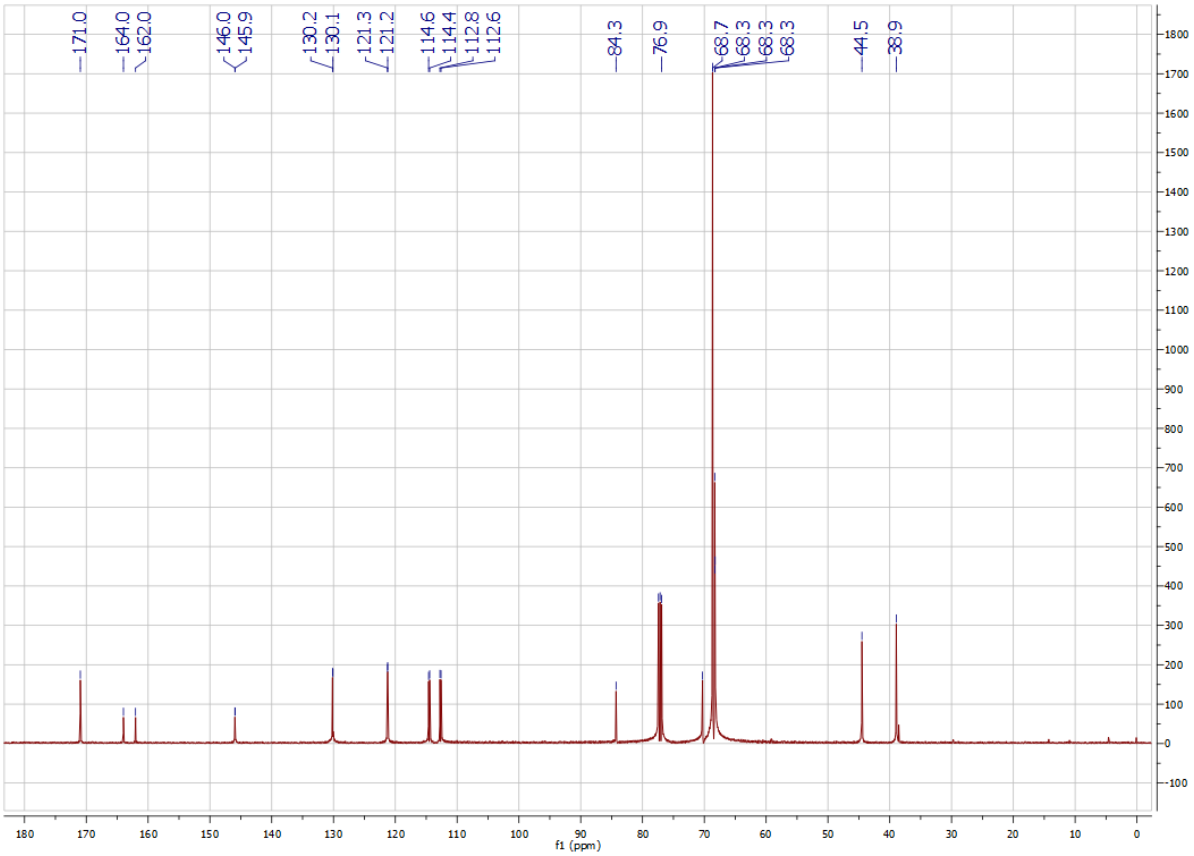




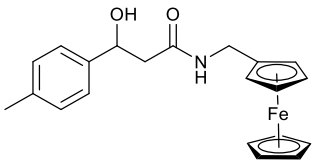
_N_-(ferrocenylmethyl)-3-hydroxy-3-(_m_-fluorophenyl)propanamide 7d

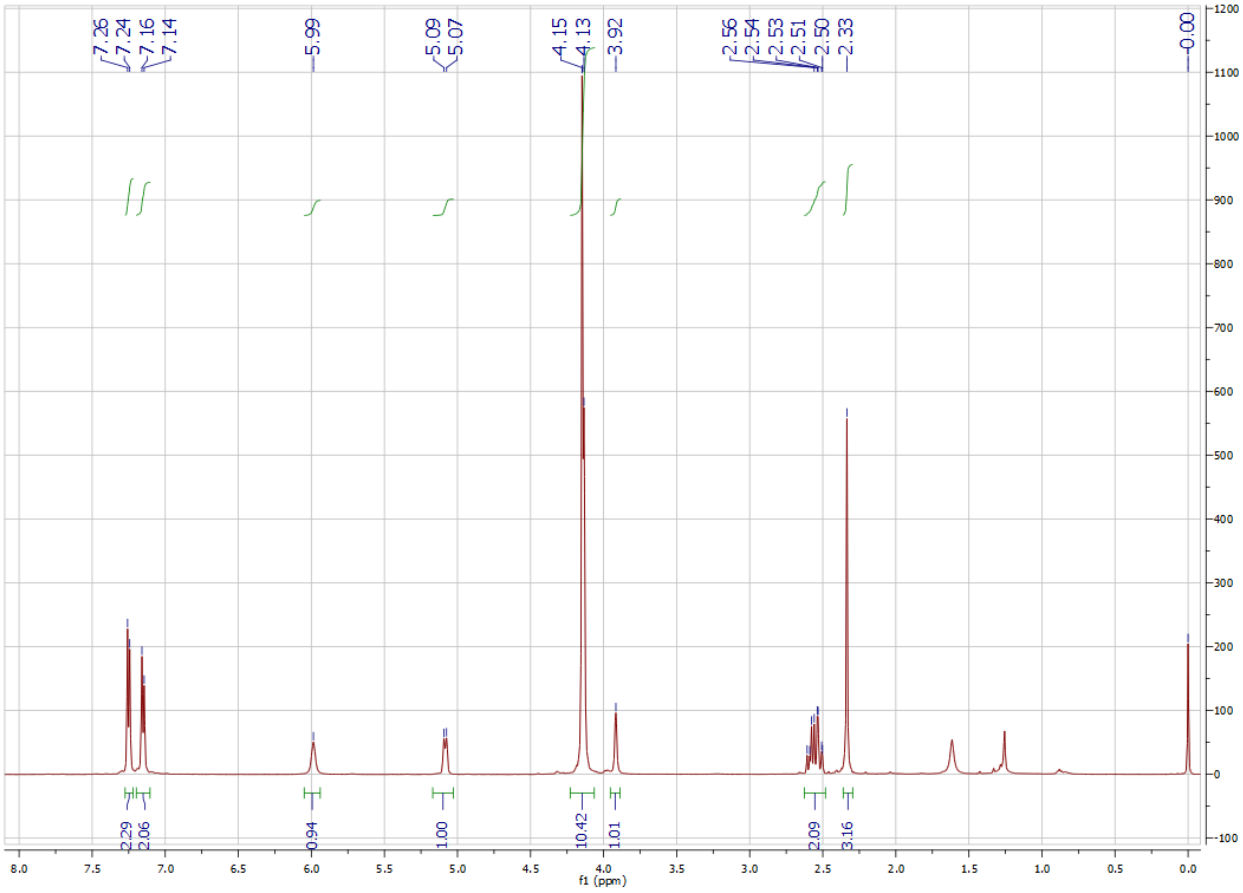


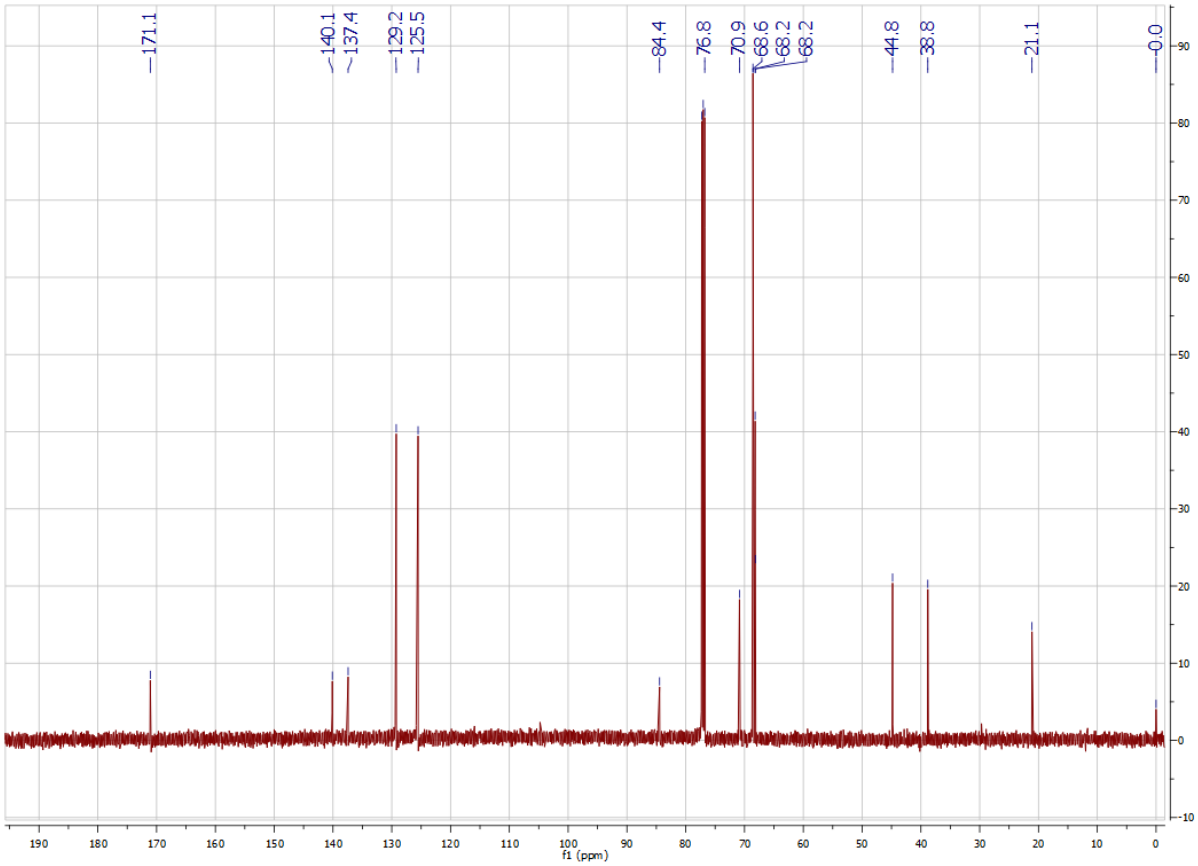




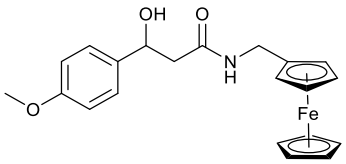
***N*-(ferrocenylmethyl)-3-hydroxy-3-(*p*-methylphenyl)propanamide 7e**

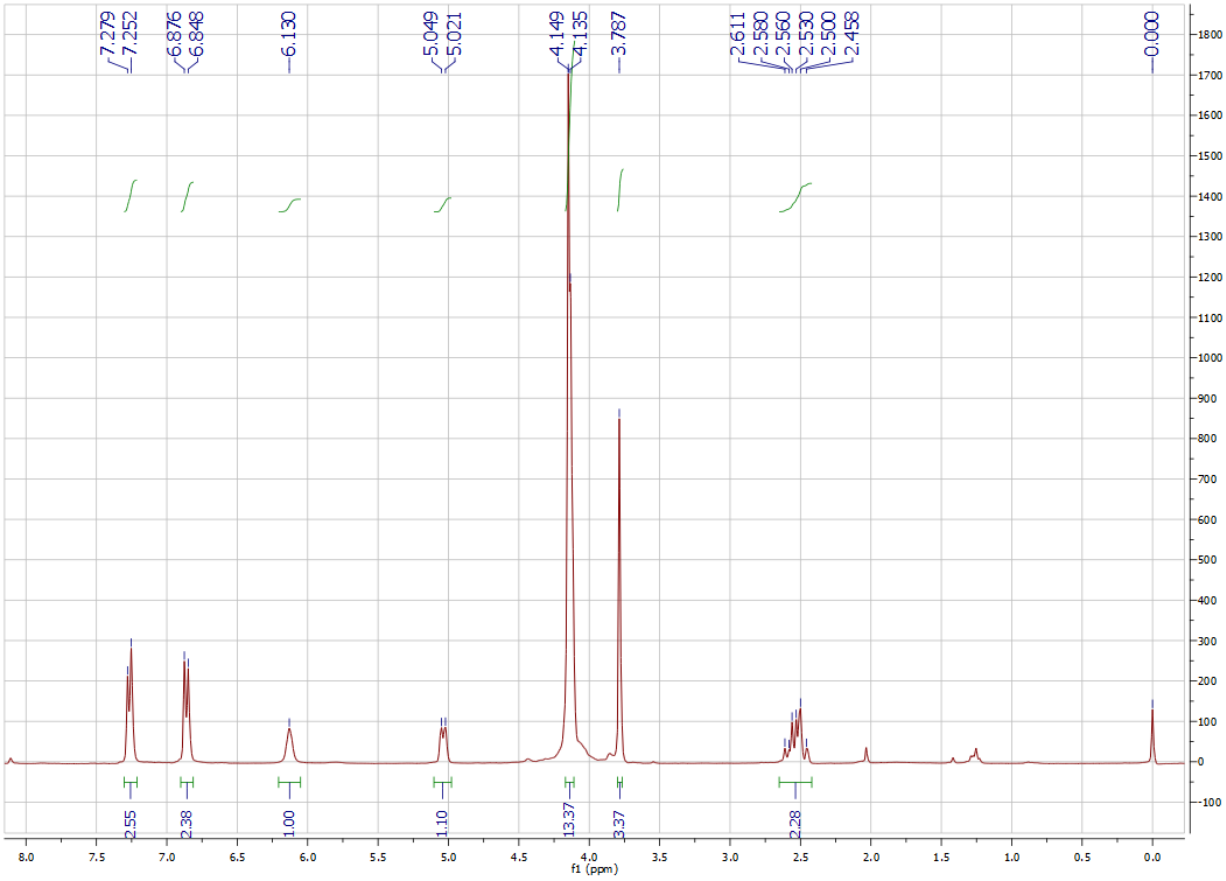


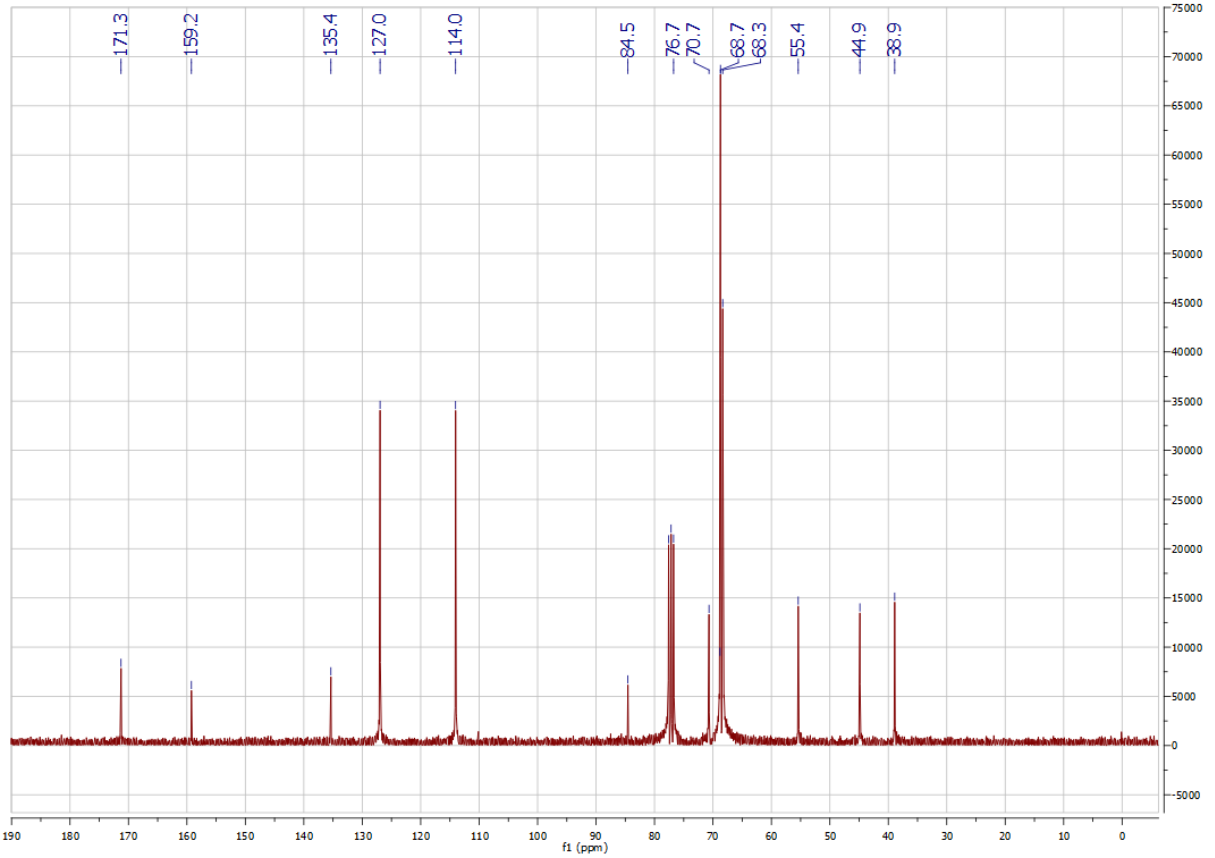




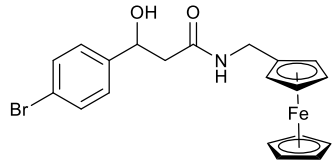
***N*-(ferrocenylmethyl)-3-hydroxy-3-(*p*-methoxyphenyl)propanamide 7f**

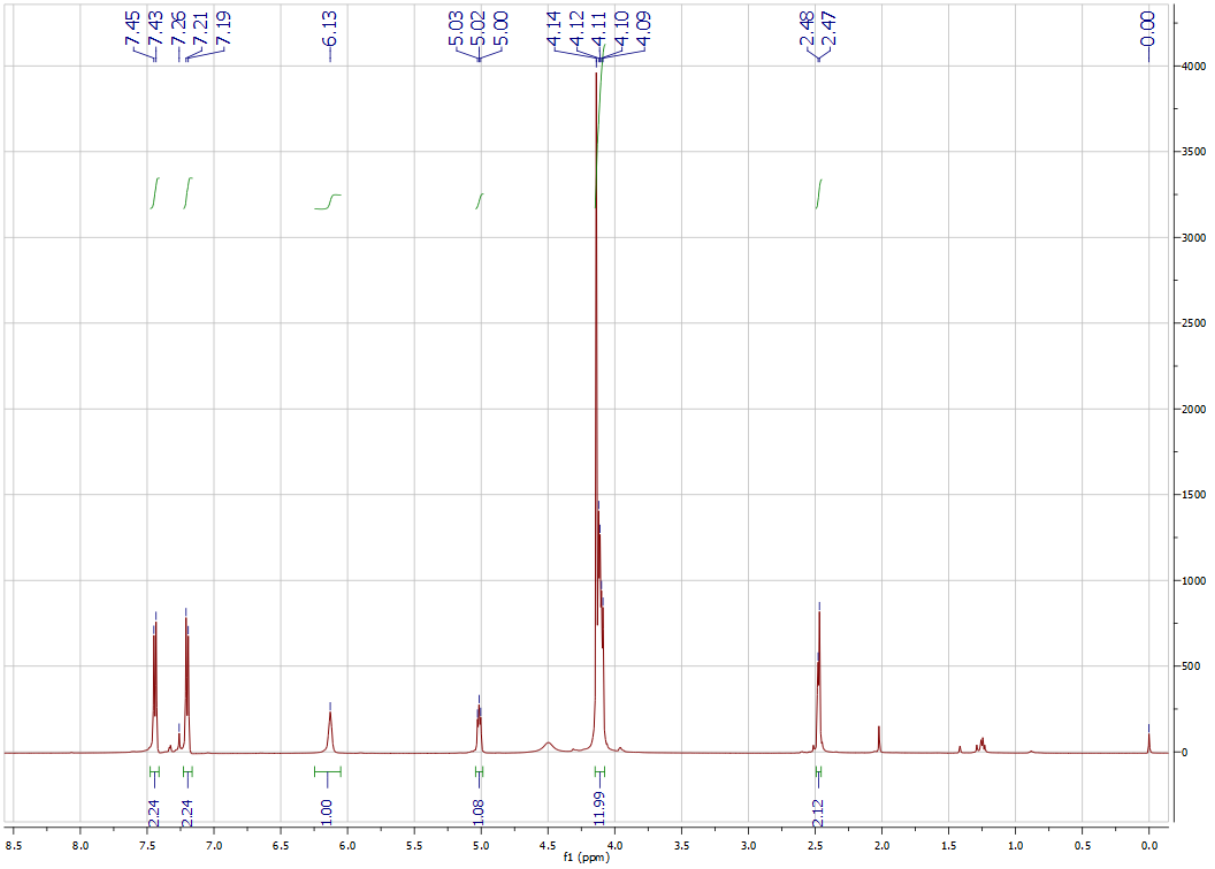


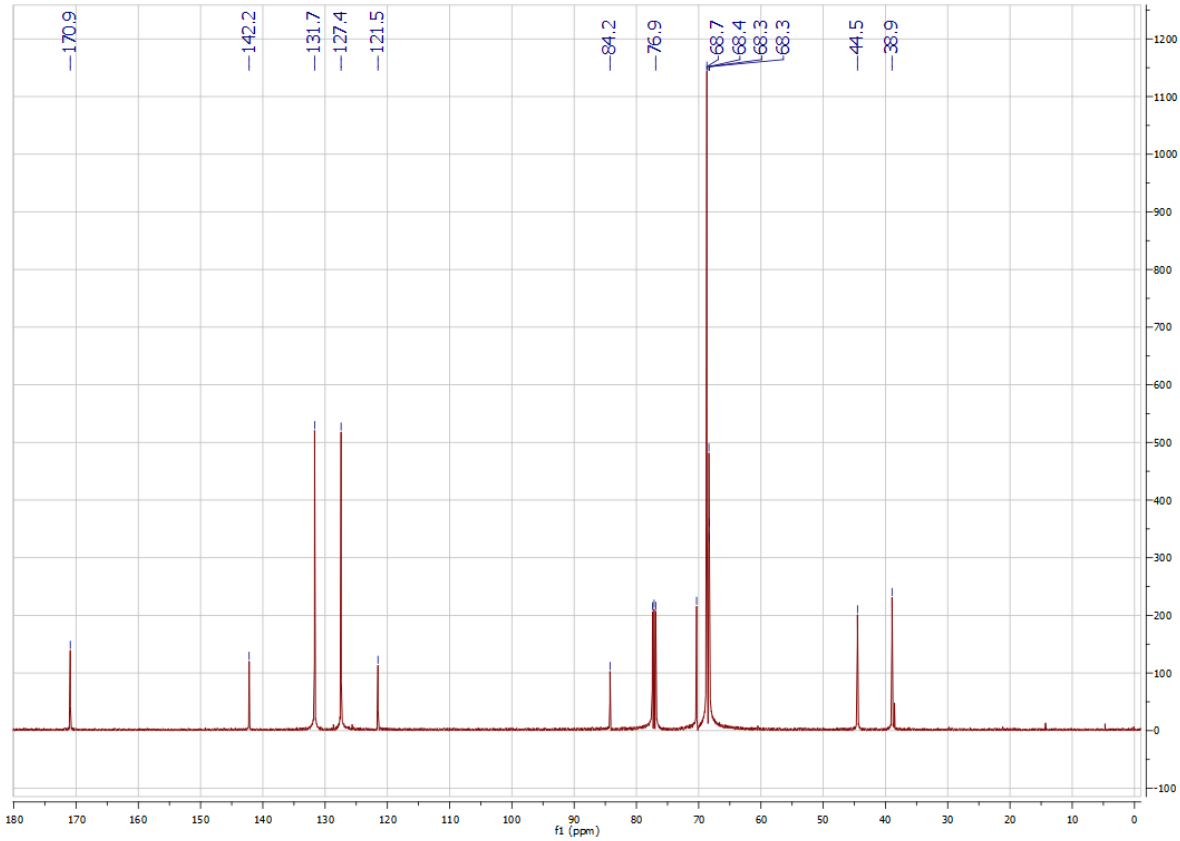




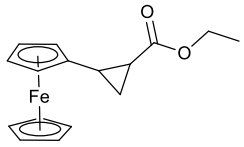
_N_-(ferrocenylmethyl)-3-hydroxy-3-(_p_-bromophenyl)propanamide 7g

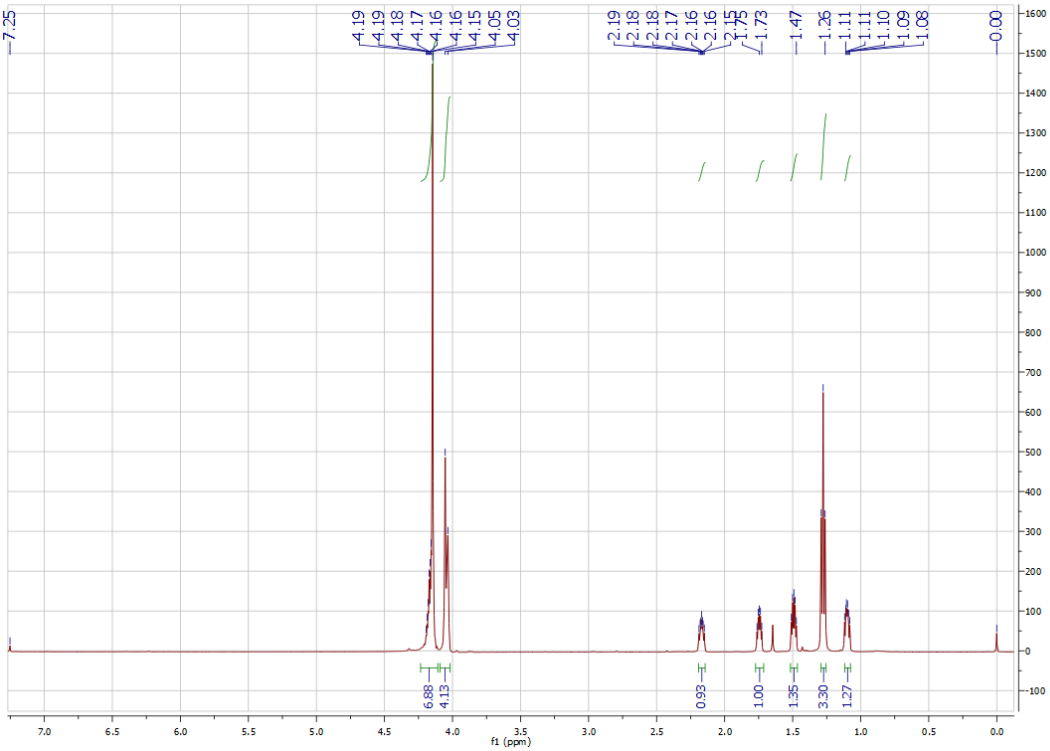


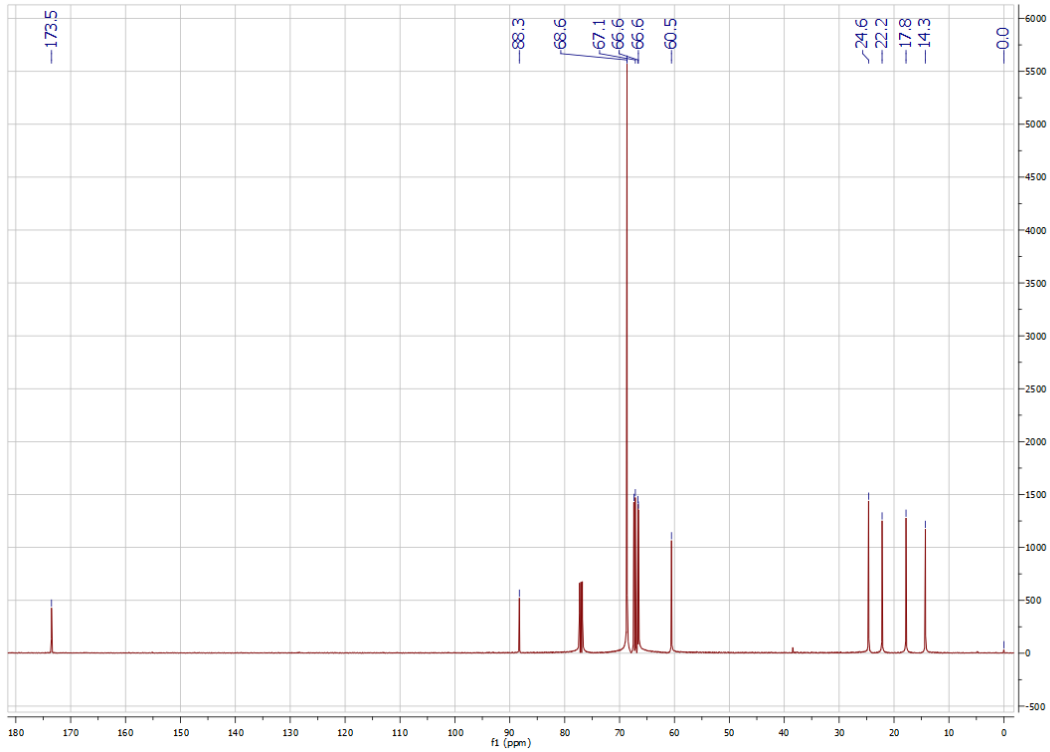




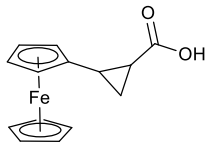
Ethyl 2-ferrocenylcyclopropane-1-carboxylate

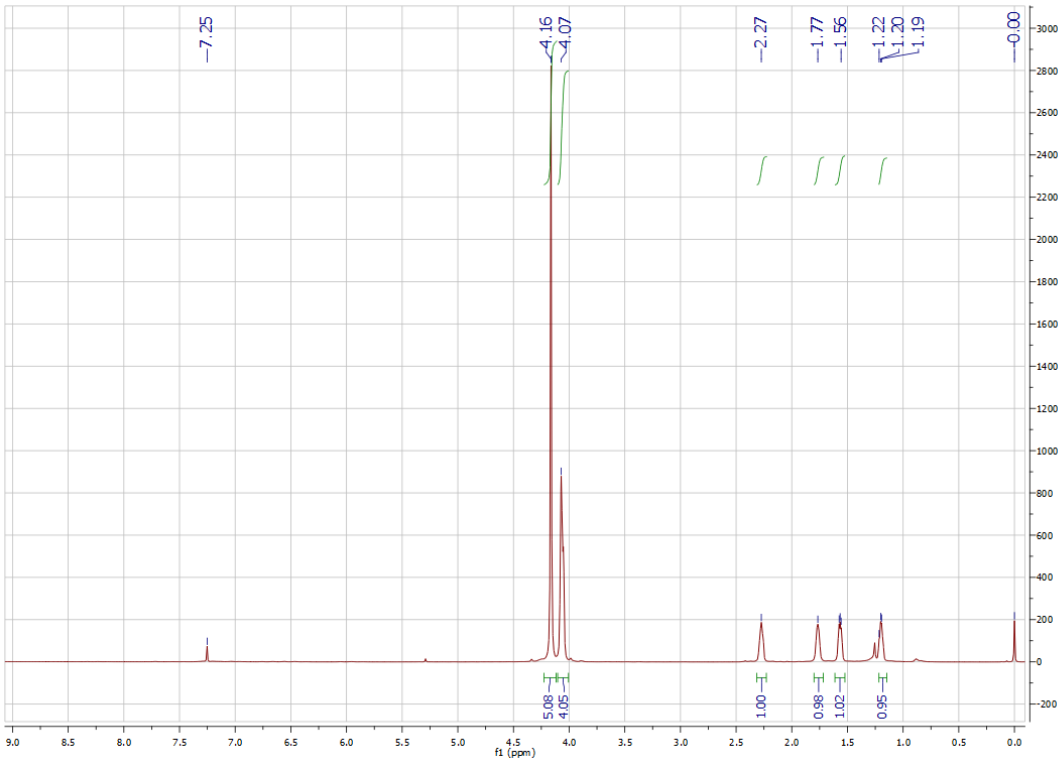


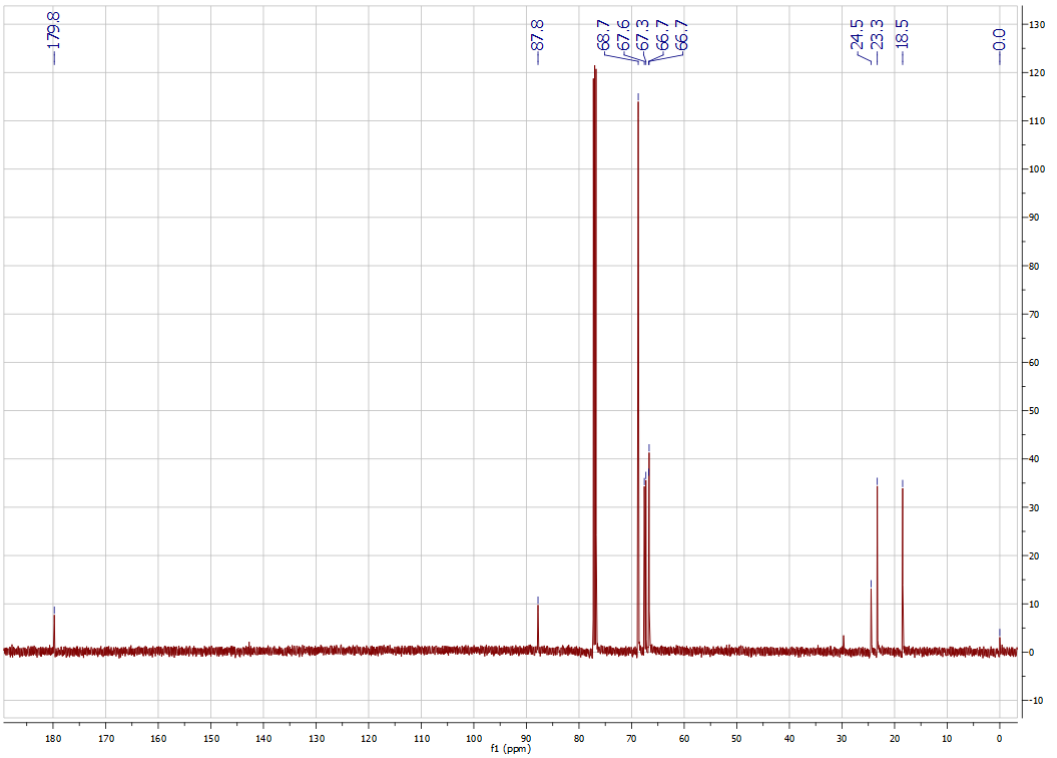




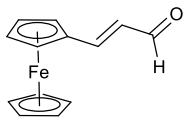
2-Ferrocenylcyclopropane-1-carboxylic acid (17)

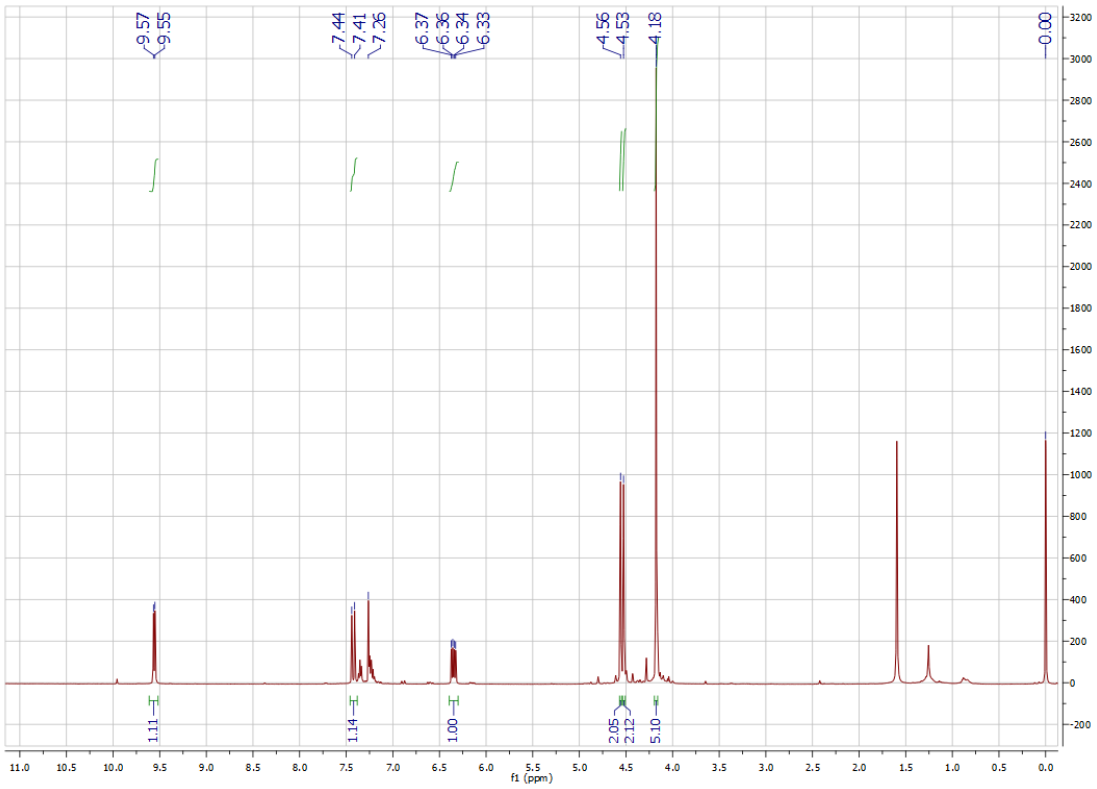


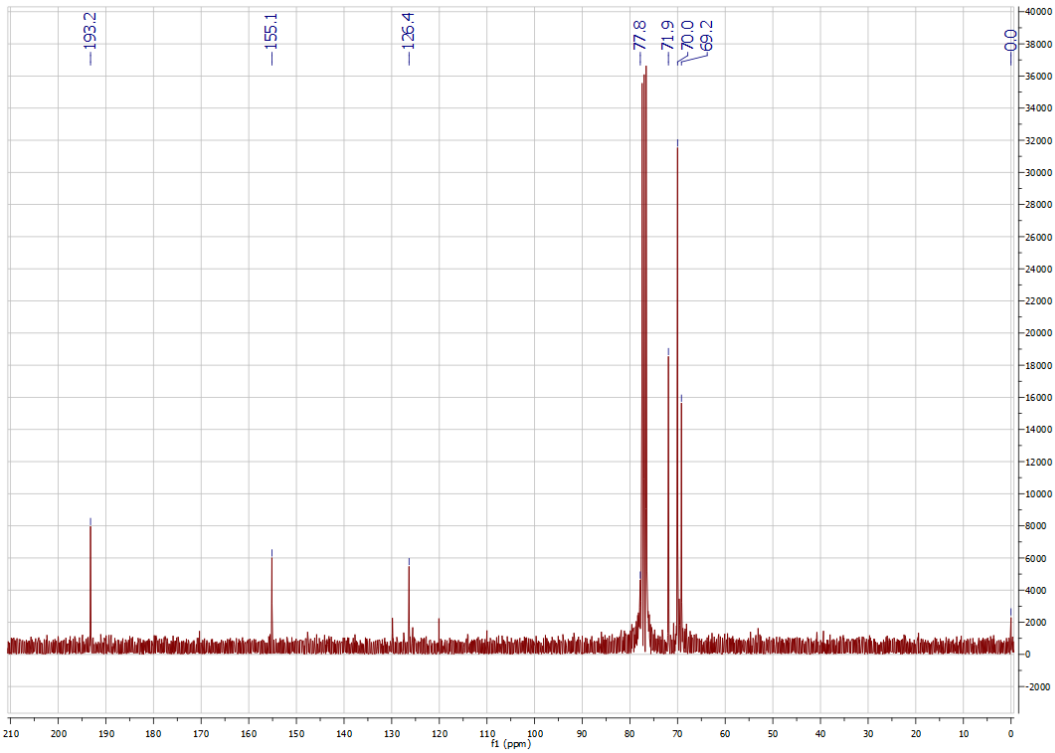




(*E*)-3-Ferrocenylacrylaldehyde (21)







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