

Supporting Information

General Remarks

¹H-NMR were recorded at 400 MHz on a VarianMercury Plus 400. ¹³C-NMR were recorded at 100 MHz. IR spectra were recorded with a PerkinElmer Paragon 500 FT-IR. Mass spectra were performed on a GC/MS system by means of the EI technique (70 eV). Microanalyses were performed with a CHNS-O analyzer Model EA 1108 from Fisons Instruments.

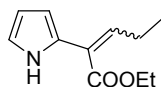
General Procedure for the preparation of compounds 4.

A mixture of β-nitroacrylate **1** (1 mmol) and pyrrole **2** (1 mmol) was stirred under solvent-free conditions, at room temperature, for three hours. Then, acetonitrile (4 mL) and TBD (2 mmol, 667 mg) were added and the solution was heated at 50°C and stirred for further 2 hours. Terminate the reaction (monitored by TLC), the promoter was filtered off and washed with EtOAc. Finally, after the evaporation of the solvent under vacuum, the crude product **4** was purified by flash chromatography column.

General Procedure for the preparation of compounds 5 or 6.

A mixture of β-nitroacrylate **1** (1 mmol) and pyrrole **2** (1 mmol) was stirred under solvent-free conditions, at room temperature, for three hours. Then, acetonitrile (4 mL) and TBD (2 mmol, 667 mg) were added and the solution was heated at 50°C and stirred for 2 hours. Terminate the reaction (monitored by TLC), the promoter was filtered off and washed with EtOAc. At that point, after the evaporation of the solvent under vacuum, the crude product was dissolved in EtOH (7 mL), treated with ammonium formate (HCOONH₄, 4 mmol), 10% Pd/C (100 mg) and stirred at 70°C for further two hours. Finally, the catalyst was removed by filtration and washed with EtOAc, then after the evaporation of the solvent under vacuum, the crude product **5** (or **6**) was purified by flash chromatography column.

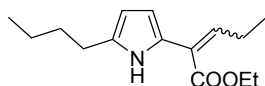
Spectroscopic data of compounds 4



Compound 4aa. Yield 75% (dr: *E/Z* = 80:20).

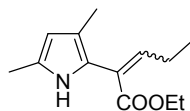
(*E*)-Diastereoisomer. Yellow oil. IR (cm⁻¹, neat): 721, 773, 805, 1118, 1207, 1445, 1614, 1696, 2949, 3411. ¹H-NMR (CDCl₃, 400MHz) δ: 1.17 (t, 3H, *J* = 7.5 Hz), 1.37 (t, 3H, *J* = 7.3 Hz), 2.44-2.61 (m, 2H), 4.30 (q, 2H, *J* = 7.3 Hz), 6.24-6.36 (m, 2H), 6.81 (t, 1H, *J* = 7.0 Hz), 6.83-6.88 (m, 1H), 9.88 (br s, 1H). ¹³C-NMR (CDCl₃, 100MHz) δ: 13.8, 14.4, 23.7, 61.2, 108.8, 110.8, 117.9, 123.4, 125.9, 143.1, 168.3. GC-MS (70 eV): *m/z*: 193 ([M⁺], 47), 164 (22), 146 (67), 132 (17), 118 (100), 104 (31), 92 (33), 91 (32), 77 (17), 65 (15), 51 (11), 39 (12), 29 (12). Anal. Calcd. for C₁₁H₁₅NO₂ (193.25): C, 68.37; H, 7.82; N, 7.25. Found: C, 68.46; H, 7.88; N, 7.19.

(*Z*)-Diastereoisomer. Yellow oil. IR (cm⁻¹, neat): 722, 771, 804, 1109, 1217, 1451, 1616, 1698, 2955, 3414. ¹H-NMR (CDCl₃, 400MHz) δ: 1.11 (t, 3H, *J* = 7.7 Hz), 1.38 (t, 3H, *J* = 7.3 Hz), 2.43-2.57 (m, 2H), 4.33 (q, 2H, *J* = 7.3 Hz), 6.16-6.37 (m, 3H), 6.74-6.79 (m, 1H), 9.27 (br s, 1H). ¹³C-NMR (CDCl₃, 100MHz) δ: 14.2, 14.5, 23.8, 61.2, 106.0, 109.3, 118.1, 124.5, 129.4, 139.6, 168.0. GC-MS (70 eV): *m/z*: 193 ([M⁺], 42), 164 (21), 146 (64), 132 (18), 118 (100), 104 (29), 92 (28), 91 (29), 77 (17), 65 (13), 51 (8), 39 (10), 29 (10). Anal. Calcd. for C₁₁H₁₅NO₂ (193.25): C, 68.37; H, 7.82; N, 7.25. Found: C, 68.43; H, 7.86; N, 7.21.



Compound 4ab. Yield 87% (dr: *E/Z* = 70:30; inseparable diastereomeric mixture).

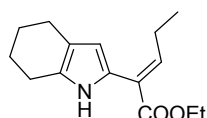
Yellow oil. IR (cm⁻¹, neat): 803, 1121, 1214, 1451, 1618, 1699, 2954, 3413. ¹H-NMR (CDCl₃, 400MHz) δ: 0.85-0.97 (m, 3H), 1.09 (t, 0.9H, *J* = 7.3), 1.15 (t, 2.1H, *J* = 7.7), 1.32-1.45 (m, 5H), 1.55-1.69 (m, 2H), 2.41-2.54 (m, 2H), 2.55-2.66 (m, 2H), 4.22-4.35 (m, 2H), 5.84-5.87 (m, 0.3H), 5.92-5.97 (m, 0.7H), 6.17-6.22 (m, 1H), 6.24 (t, 0.3H, *J* = 7.7), 6.71 (t, 0.7H, *J* = 7), 8.88 (br s, 0.3H), 9.67 (br s, 0.7H). ¹³C-NMR (CDCl₃, 100MHz) δ: 14.0, 14.1, 14.3, 14.4, 14.5, 22.6, 22.7, 23.6, 23.9, 27.7, 27.8, 31.9, 32.0, 61.1, 61.2, 105.8, 106.1, 106.2, 111.1, 123.1, 124.4, 124.7, 127.7, 133.4, 133.7, 137.6, 142.0, 168.2, 168.6. GC-MS (70 eV): *m/z*: (*E*)-Diastereoisomer: 249([M⁺], 50), 220 (31), 206 (49), 202 (76), 176 (25), 160 (100), 132 (81), 117 (60), 104 (56), 91 (22), 77 (28), 41 (24), 29 (44). (*Z*)-Diastereoisomer: 249([M⁺], 90), 220 (43), 206 (69), 202 (100), 176 (23), 160 (92), 132 (48), 117 (28), 104 (23), 91 (9), 77 (9), 41 (6), 29 (10). Anal. Calcd. for C₁₅H₂₃NO₂ (249.35): C, 72.25; H, 9.30; N, 5.62. Found: C, 72.32; H, 9.36; N, 5.59.



Compound 4ac. Yield 85% (dr: *E/Z* = 80:20).

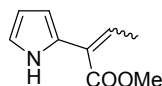
(*E*)-Diastereoisomer. Yellow oil. IR (cm⁻¹, neat): 777, 1041, 1156, 1420, 1445, 1620, 1698, 2963, 3377. ¹H-NMR (CDCl₃, 400MHz) δ: 1.03 (t, 3H, *J* = 7.5 Hz), 1.32 (t, 3H, *J* = 7.3), 1.80 (s, 3H), 2.11-2.22 (m, 2H), 2.25 (s, 3H), 4.23 (q, 2H, *J* = 7.3), 5.75 (s, 1H), 6.83 (t, 1H, *J* = 7.3), 8.07 (br s, 1H). ¹³C-NMR (CDCl₃, 100MHz) δ: 12.5, 13.3, 13.6, 14.5, 23.8, 61.1, 108.2, 119.1, 120.8, 124.3, 128.0, 144.2, 168.3. Anal. Calcd. for C₁₃H₁₉NO₂ (221.30): C, 70.56; H, 8.65; N, 6.33. Found: C, 70.49; H, 8.60; N, 6.37.

(*Z*)-Diastereoisomer. Yellow oil. IR (cm⁻¹, neat): 775, 1045, 1153, 1425, 1451, 1618, 1699, 2967, 3372. ¹H-NMR (CDCl₃, 400MHz) δ: 1.09 (t, 3H, *J* = 7.5 Hz), 1.35 (t, 3H, *J* = 7.3), 2.07 (s, 3H), 2.22 (s, 3H), 2.38-2.47 (m, 2H), 4.29 (q, 2H, *J* = 7.3), 5.72 (s, 1H), 5.95 (t, 1H, *J* = 7.7), 8.40 (br s, 1H). ¹³C-NMR (CDCl₃, 100MHz) δ: 11.2, 13.2, 14.0, 14.4, 23.8, 61.1, 108.8, 117.5, 125.6, 128.1, 142.4, 168.0. GC-MS (70 eV): *m/z*: 221 ([M⁺], 56), 207 (8), 192 (54), 174 (17), 160 (36), 148 (41), 146 (54), 132 (100), 118 (48), 104 (11), 91 (18), 77 (18), 65 (12), 51 (8), 42 (15), 29 (20). Anal. Calcd. for C₁₃H₁₉NO₂ (221.30): C, 70.56; H, 8.65; N, 6.33. Found: C, 70.61; H, 8.70; N, 6.29.



Compound 4ad. Yield 55% (isolated as single *E* diastereomer).

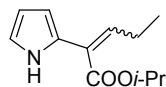
(*E*)-Diastereoisomer: Yellow oil. IR (cm⁻¹, neat): 732, 771, 1115, 1445, 1621, 1701, 2945, 3333. ¹H-NMR (CDCl₃, 400MHz) δ: 1.13 (t, 3H, *J* = 7.7 Hz), 1.34 (t, 3H, *J* = 7.3), 1.56-1.93 (m, 4H), 2.36-2.67 (m, 6H), 4.25 (q, 2H, *J* = 7.3 Hz), 6.02-6.08 (m, 1H), 6.67 (t, 1H, *J* = 7.3 Hz), 9.41 (br s, 1H). ¹³C-NMR (CDCl₃, 100MHz) δ: 14.0, 14.5, 23.0, 23.1, 23.6, 23.9, 24.0, 61.2, 110.1, 117.8, 123.2, 124.0, 127.7, 141.7, 168.6. GC-MS (70 eV): *m/z*: 247 ([M⁺], 65), 218 (46), 200 (100), 186 (27), 174 (38), 172 (71), 144 (50), 130 (55), 117 (35), 91 (20), 77 (21), 29 (28). Anal. Calcd. for C₁₅H₂₁NO₂ (247.34): C, 72.84; H, 8.56; N, 5.66. Found: C, 72.91; H, 8.60; N, 8.49.



Compound 4ba. Yield 62% (dr: *E/Z* = 70:30).

(*E*)-Diastereoisomer. Yellow oil. IR (cm⁻¹, neat): 722, 770, 802, 1114, 1212, 1435, 1615, 1699, 2950, 3417. ¹H-NMR (CDCl₃, 400MHz) δ: 2.08 (d, 3H, *J* = 7.3 Hz), 3.81 (s, 3H), 6.26-6.30 (m, 1H), 6.33-6.37 (m, 1H), 6.83-6.87 (m, 1H), 7.00 (q, 1H, *J* = 7.3 Hz), 9.87 (br s, 1H). ¹³C-NMR (CDCl₃, 100MHz) δ: 16.3, 52.1, 108.9, 111.0, 117.9, 124.8, 125.7, 136.2, 168.6. GC-MS (70 eV): *m/z*: 165 ([M⁺], 69), 133 (28), 106 (46), 105 (100), 104 (72), 91 (11), 79 (39), 77 (34), 51 (16), 39 (8). Anal. Calcd. for C₉H₁₁NO₂ (165.19): C, 65.44; H, 6.71; N, 8.48. Found: C, 65.38; H, 6.67; N, 8.53.

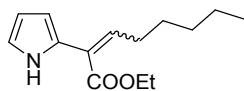
(*Z*)-Diastereoisomer. Yellow oil. IR (cm⁻¹, neat): 723, 769, 802, 1112, 1217, 1437, 1609, 1701, 2954, 3411. ¹H-NMR (CDCl₃, 400MHz) δ: 2.07 (d, 3H, *J* = 7.3 Hz), 3.87 (s, 3H), 6.16-6.20 (m, 1H), 6.26-6.32 (m, 1H), 6.50 (q, 1H, *J* = 7.3 Hz), 6.74-6.79 (m, 1H), 9.24 (br s, 1H). ¹³C-NMR (CDCl₃, 100MHz) δ: 16.2, 52.0, 106.1, 109.3, 118.1, 125.7, 133.6, 137.0, 168.3. GC-MS (70 eV): *m/z*: 165 ([M⁺], 84), 133 (38), 106 (53), 105 (100), 104 (75), 91 (10), 79 (34), 77 (34), 51 (14), 40 (9), 32 (51). Anal. Calcd. for C₉H₁₁NO₂ (165.19): C, 65.44; H, 6.71; N, 8.48. Found: C, 65.49; H, 6.75; N, 8.44.



Compound 4ca. Yield 53% (dr: *E/Z* = 70:30).

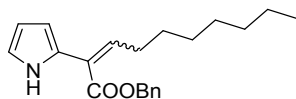
(*E*)-Diastereoisomer. Yellow oil. IR (cm⁻¹, neat): 721, 767, 802, 1090, 1105, 1212, 1271, 1464, 1612, 1693, 2977, 3418. ¹H-NMR (CDCl₃, 400MHz) δ: 1.15 (t, 3H, *J* = 7.5 Hz), 1.33 (d, 6H, *J* = 6.4 Hz), 2.45-2.55 (m, 2H), 5.08-5.19 (m, 1H), 6.24-6.27 (m, 1H), 6.29-6.33 (m, 1H), 6.75 (t, 1H, *J* = 6.8 Hz), 6.81-6.87 (m, 1H), 9.94 (br s, 1H). ¹³C-NMR (CDCl₃, 100MHz) δ: 13.9, 22.1, 23.8, 68.8, 108.7, 110.7, 117.9, 123.5, 126.1, 142.9, 168.0. GC-MS (70 eV): *m/z*: 207 ([M⁺], 38), 164 (28), 146 (44), 132 (22), 120 (42), 119 (45), 118 (100), 104 (26), 91 (24), 77 (13), 65 (9), 43 (12). Anal. Calcd. for C₁₂H₁₇NO₂ (207.27): C, 69.54; H, 8.27; N, 6.76. Found: C, 69.60; H, 8.33; N, 6.72.

(*Z*)-Diastereoisomer. Yellow oil. IR (cm⁻¹, neat): 720, 769, 802, 1097, 1110, 1213, 1269, 1458, 1614, 1698, 2977, 3416. ¹H-NMR (CDCl₃, 400MHz) δ: 1.10 (t, 3H, *J* = 7.5 Hz), 1.35 (d, 6H, *J* = 6.4 Hz), 2.41-2.53 (m, 2H), 5.16-5.26 (m, 1H), 6.15-6.21 (m, 1H), 6.27-6.34 (m, 2H), 6.73-6.78 (m, 1H), 9.28 (br s, 1H). ¹³C-NMR (CDCl₃, 100MHz) δ: 14.2, 22.2, 23.5, 69.0, 105.8, 109.3, 118.0, 124.8, 136.6, 138.8, 167.6. GC-MS (70 eV): *m/z*: 207 ([M⁺], 57), 164 (34), 146 (51), 132 (23), 120 (46), 119 (44), 118 (100), 104 (26), 91 (23), 77 (11), 65 (8), 43 (8). Anal. Calcd. for C₁₂H₁₇NO₂ (207.27): C, 69.54; H, 8.27; N, 6.76. Found: C, 69.60; H, 8.30; N, 6.72.



Compound 4da. Yield 54% (dr: *E/Z* = 80:20; inseparable diastereomeric mixture).

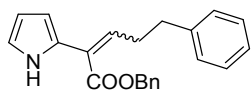
Yellow oil. IR (cm⁻¹, neat): 724, 772, 803, 1104, 1221, 1457, 1615, 1697, 2961, 3402. ¹H-NMR (CDCl₃, 400MHz) δ: 0.83-0.95 (m, 3H), 1.22-1.41 (m, 7H), 1.43-1.63 (m, 2H), 2.38-2.53 (m, 2H), 4.23-4.37 (m, 2H), 6.14-6.21 (m, 0.2H), 6.24-6.39 (m, 2H), 6.74-6.79 (m, 0.2H), 6.80-6.87 (m, 1.6H), 9.25 (br s, 0.2H), 9.89 (br s, 0.8). ¹³C-NMR (CDCl₃, 100MHz) δ: 14.2, 14.4, 14.5, 22.7, 29.2, 29.4, 30.2, 30.5, 31.8, 31.9, 61.1, 61.3, 105.9, 108.8, 109.3, 110.8, 118.0, 118.1, 123.5, 124.8, 126.0, 129.3, 138.3, 142.1, 168.3, 168.4. GC-MS (70 eV): *m/z*: (*E*)-Diastereoisomer: 235 ([M⁺], 77), 210 (24), 188 (39), 165 (28), 162 (42), 146 (28), 132 (100), 118 (46), 106 (23), 104 (47), 92 (20), 79 (17), 77 (17), 41 (6), 29 (7). (*Z*)-Diastereoisomer: 235 ([M⁺], 69), 210 (21), 188 (36), 165 (27), 162 (40), 146 (27), 132 (100), 118 (44), 106 (23), 104 (48), 92 (21), 79 (17), 77 (18), 41 (7), 29 (8). Anal. Calcd. for C₁₄H₂₁NO₂ (235.33): C, 71.46; H, 9.00; N, 5.95. Found: C, 71.52; H, 9.07; N, 5.92.



Compound 4ea. Yield 56% (dr: *E/Z* = 70:30).

(*E*)-Diastereoisomer. Yellow oil. IR (cm⁻¹, neat): 697, 723, 1095, 1205, 1455, 1609, 1699, 2924, 3029, 3423. ¹H-NMR (CDCl₃, 400MHz) δ: 0.89 (t, 3H, *J* = 6.8 Hz), 1.18-1.41 (m, 8H), 1.48-1.59 (m, 2H), 2.42-2.53 (m, 2H), 5.27 (s, 2H), 6.24-6.29 (m, 1H), 6.30-6.35 (m, 1H), 6.82-6.85 (m, 1H), 6.90 (t, 1H, *J* = 7.3 Hz), 7.17-7.48 (m, 5H), 9.86 (br s, 1H). ¹³C-NMR (CDCl₃, 100MHz) δ: 14.3, 22.9, 29.4, 29.5, 29.7, 30.6, 32.0, 67.0, 108.8, 110.9, 118.0, 123.3, 128.3, 128.5, 128.8, 128.9, 136.2, 142.8, 168.1. GC-MS (70 eV): *m/z*: 325([M⁺], 6), 234 (32), 216 (28), 132 (9), 118 (9), 106 (14), 91 (100), 80 (10), 65 (9), 41 (5). Anal. Calcd. for C₂₁H₂₇NO₂ (325.45): C, 77.50; H, 8.36; N, 4.30. Found: C, 77.43; H, 8.31; N, 4.32.

(*Z*)-Diastereoisomer. Yellow oil. IR (cm⁻¹, neat): 698, 721, 1099, 1212, 1453, 1610, 1698, 2928, 3027, 3421. ¹H-NMR (CDCl₃, 400MHz) δ: 0.84 (t, 3H, *J* = 7.3 Hz), 0.97-1.54 (m, 10H), 2.36-2.52 (m, 2H), 5.30 (s, 2H), 6.14-6.19 (m, 1H), 6.27-6.30 (m, 1H), 6.38 (t, 1H, *J* = 7.7 Hz), 6.72-6.76 (m, 1H), 7.23-7.47 (m, 5H), 9.22 (br s, 1H). ¹³C-NMR (CDCl₃, 100MHz) δ: 14.3, 22.8, 29.3, 29.6, 29.7, 30.3, 32.0, 67.0, 106.0, 109.9, 118.1, 124.8, 128.3, 128.7, 128.8, 128.9, 139.1, 142.8, 164.5. GC-MS (70 eV): *m/z*: 325([M⁺], 6), 234 (34), 216 (29), 132 (9), 118 (9), 106 (12), 91 (100), 80 (10), 65 (9), 41 (6). Anal. Calcd. for C₂₁H₂₇NO₂ (325.45): C, 77.50; H, 8.36; N, 4.30. Found: C, 77.56; H, 8.39; N, 4.28.

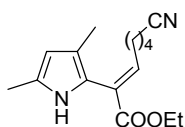


Compound 4fa. Yield 68% (dr: *E/Z* = 80:20).

(*E*)-Diastereoisomer. Yellow oil. IR (cm⁻¹, neat): 698, 728, 1029, 1101, 1208, 1454, 1603, 1698, 2926, 3028, 3422. ¹H-NMR (CDCl₃, 400MHz) δ: 2.82-2.93 (m, 4H), 5.30 (s, 2H), 6.28-6.33 (m, 1H), 6.35-6.40 (m, 1H), 6.84-6.88 (m, 1H), 6.99 (t, 1H, *J* = 6.7 Hz), 7.23-7.31 (m, 3H), 7.32-7.38 (m, 2H), 7.39-7.48 (m, 5H), 9.84 (br s, 1H). ¹³C-NMR (CDCl₃, 100MHz) δ: 32.3, 35.5, 67.1, 109.0, 111.2, 118.3, 123.9, 125.6, 126.5, 128.3, 128.6, 128.7, 128.8, 128.9, 136.2, 141.0, 141.4, 168.0. GC-MS (70 eV): *m/z*: 331 ([M⁺], 3), 240 (30), 91 (100), 65 (9). Anal. Calcd. for C₂₂H₂₁NO₂ (331.41): C, 79.73; H, 6.39; N, 4.23. Found: C, 79.77; H, 6.43; N, 4.19.

(*Z*)-Diastereoisomer. Yellow oil. IR (cm⁻¹, neat): 697, 731, 1035, 1104, 1209, 1454, 1607, 1699, 2929, 3026, 3420. ¹H-NMR (CDCl₃, 400MHz) δ: 2.68-2.81 (m, 4H), 5.28 (s, 2H), 6.14-6.19 (m, 1H), 6.25-6.30 (m, 1H), 6.40 (t, 1H, *J* = 6.8 Hz), 6.71-6.76 (m, 1H), 7.03-7.11 (m, 2H), 7.14-7.44 (m, 8H), 9.22 (br s, 1H). ¹³C-NMR (CDCl₃, 100MHz) δ: 31.8, 35.7, 67.1, 106.4, 109.3, 118.3, 126.2, 126.3, 128.4, 128.6, 128.7, 128.9, 129.1, 135.7, 137.1, 140.1, 141.3, 167.5. GC-MS (70 eV): *m/z*: 331 ([M⁺], 4), 240 (28), 91 (100), 65 (12).

Anal. Calcd. for C₂₂H₂₁NO₂ (331.41): C, 79.73; H, 6.39; N, 4.23. Found: C, 79.79; H, 6.43; N, 4.20.

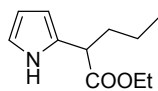


Compound 4gc Yield 75% (isolated as single *E* diastereomer).

(*E*)-Diastereoisomer. Yellow oil. IR (cm⁻¹, neat): 778, 1043, 1248, 1627, 1705, 2245, 2932, 3374. ¹H-NMR (CDCl₃, 400MHz) δ: 1.31 (t, 3H, *J* = 7.3 Hz), 1.53-1.67 (m, 4H), 1.88 (s, 3H), 2.14-2.28 (m, 4H), 2.24 (s, 3H), 4.22 (q, 2H, *J* = 7.3 Hz), 5.71-5.77 (m, 1H), 6.80 (t, 1H, *J* = 7.7 Hz), 8.13 (br s, 1H). ¹³C-NMR (CDCl₃, 100MHz) δ: 12.6, 13.3, 14.5, 17.0, 25.0, 27.9, 29.2, 61.3, 108.3, 119.2, 119.8, 120.2, 126.0, 128.4, 142.7, 168.0. GC-MS (70 eV): *m/z*: 274 ([M⁺], 90), 245 (50), 206 (45), 201 (87), 160 (100), 132 (67), 118 (36), 91 (13). Anal. Calcd. for C₁₆H₂₂N₂O₂ (274.36): C, 70.04; H, 8.08; N, 10.21. Found: C, 70.11; H, 8.11; N, 10.17.

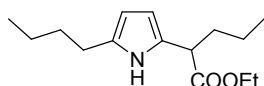
181 ($[M^+]$, 46), 152 (47), 136 (100), 134 (90), 121 (36), 83 (16), 43 (54). Anal. Calcd. for $C_{10}H_{15}NO_2$ (181.23): C, 66.27; H, 8.34; N, 7.73. Found: C, 66.32; H, 8.30; N, 7.76.

Spectroscopic data of compounds 6



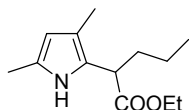
Compound 6aa. Yield 62%.

Colourless oil. IR (cm^{-1} , neat): 722, 1161, 1442, 1718, 2961, 3393. 1H -NMR ($CDCl_3$, 400MHz) δ : 0.92 (t, 3H, $J = 7.7$ Hz), 1.23-1.38 (m, 2H), 1.27 (t, 3H, $J = 7.3$ Hz), 1.69-1.82 (m, 1H), 1.88-2.00 (m, 1H), 3.67 (t, 1H, $J = 7.7$ Hz), 4.09-4.24 (m, 2H), 5.99-6.05 (m, 1H), 6.10-6.15 (m, 1H), 6.71-6.75 (m, 1H), 8.66 (br s, 1H). ^{13}C -NMR ($CDCl_3$, 100MHz) δ : 13.9, 14.4, 20.8, 36.2, 44.7, 61.1, 106.7, 108.2, 117.7, 128.7, 174.5. GC-MS (70 eV): m/z : 195 ($[M^+]$, 42), 152 (23), 122 (100), 106 (38), 93 (24), 80 (99), 29 (10). Anal. Calcd. for $C_{11}H_{17}NO_2$ (195.26): C, 67.66; H, 8.78; N, 7.17. Found: C, 67.73; H, 8.81; N, 7.13.



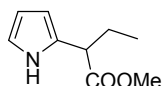
Compound 6ab. Yield 53%.

Colourless oil. IR (cm^{-1} , neat): 724, 1159, 1447, 1721, 2959, 3389. 1H -NMR ($CDCl_3$, 400MHz) δ : 0.89-0.95 (m, 6H), 1.27 (t, 3H, $J = 7.3$ Hz), 1.28-1.42 (m, 4H), 1.54-1.64 (m, 2H), 1.67-1.78 (m, 1H), 1.86-1.98 (m, 1H), 2.53-2.58 (m, 2H), 3.60 (t, 1H, $J = 7.7$ Hz), 4.06-4.24 (m, 2H), 5.76-5.80 (m, 1H), 5.87-5.90 (m, 1H), 8.27 (br s, 1H). ^{13}C -NMR ($CDCl_3$, 100MHz) δ : 14.0, 14.1, 14.4, 20.9, 22.7, 27.8, 31.9, 36.2, 44.8, 61.1, 104.6, 106.5, 126.9, 133.0, 174.7. GC-MS (70 eV): m/z : 251 ($[M^+]$, 21), 208 (40), 178 (100), 136 (18), 106 (25). Anal. Calcd. for $C_{15}H_{25}NO_2$ (251.19): C, 71.67; H, 10.03; N, 5.57. Found: C, 71.71; H, 10.09; N, 5.54.



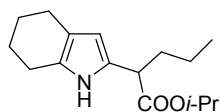
Compound 6ac. Yield 51%.

Colourless oil. IR (cm^{-1} , neat): 639, 780, 1029, 1177, 1464, 1603, 1715, 2960, 3391. 1H -NMR ($CDCl_3$, 400MHz) δ : 0.92 (t, 3H, $J = 7.7$ Hz), 1.23-1.36 (m, 5H), 1.59-1.75 (m, 1H), 1.82-1.94 (m, 1H), 2.01 (s, 3H), 2.22 (s, 3H), 3.66 (t, 1H, $J = 7.7$ Hz), 4.04-4.25 (m, 2H), 5.46-5.78 (m, 1H), 8.20 (br s, 1H). ^{13}C -NMR ($CDCl_3$, 100MHz) δ : 11.0, 13.3, 14.0, 14.4, 20.8, 36.8, 42.4, 61.0, 107.8, 125.5, 128.5, 129.3, 175.0. GC-MS (70 eV): m/z : 223 ($[M^+]$, 34), 180 (35), 150 (100), 134 (32), 108 (28). Anal. Calcd. for $C_{13}H_{21}NO_2$ (223.32): C, 69.92; H, 9.48; N, 6.27. Found: C, 69.99; H, 9.52; N, 6.24.



Compound 6ba. Yield 52%.

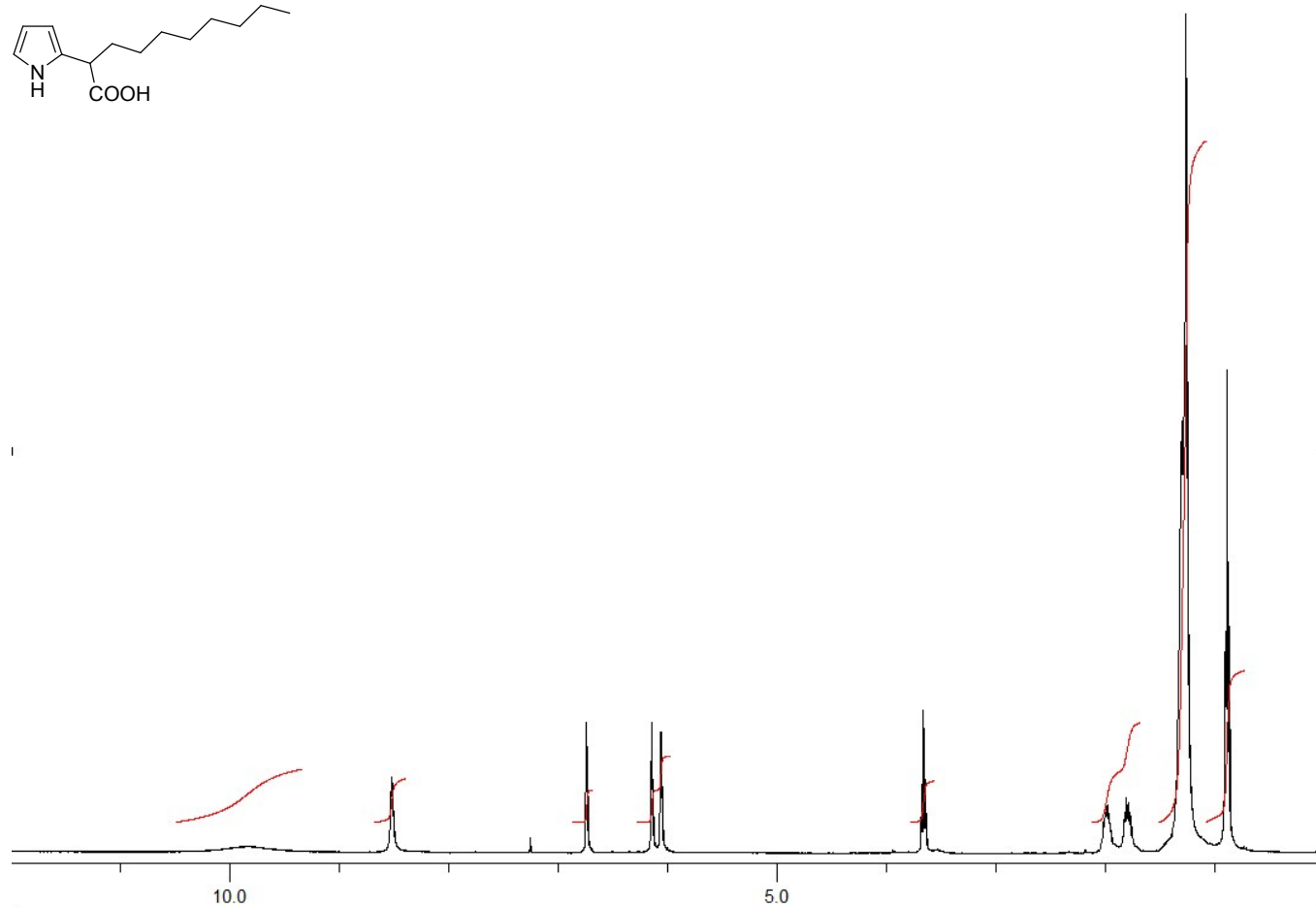
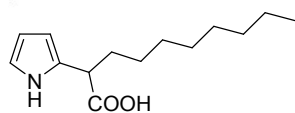
Colourless oil. IR (cm^{-1} , neat): 720, 1163, 1435, 1720, 2964, 3385. 1H -NMR ($CDCl_3$, 400MHz) δ : 0.91 (t, 3H, $J = 7.7$ Hz), 1.72-1.88 (m, 1H), 1.93-2.07 (m, 1H), 3.59 (t, 1H, $J = 7.7$ Hz), 3.71 (s, 3H), 6.00-6.06 (m, 1H), 6.10-6.16 (m, 1H), 6.72-6.77 (m, 1H), 8.63 (br s, 1H). ^{13}C -NMR ($CDCl_3$, 100MHz) δ : 12.2, 27.2, 46.5, 52.3, 106.9, 108.3, 117.8, 128.4, 174.8. GC-MS (70 eV): m/z : 167 ($[M^+]$, 29), 138 (16), 108 (100), 106 (33), 93 (18), 80 (26). Anal. Calcd. for $C_9H_{13}NO_2$ (167.21): C, 64.65; H, 7.84; N, 8.38. Found: C, 64.71; H, 7.90; N, 8.33.



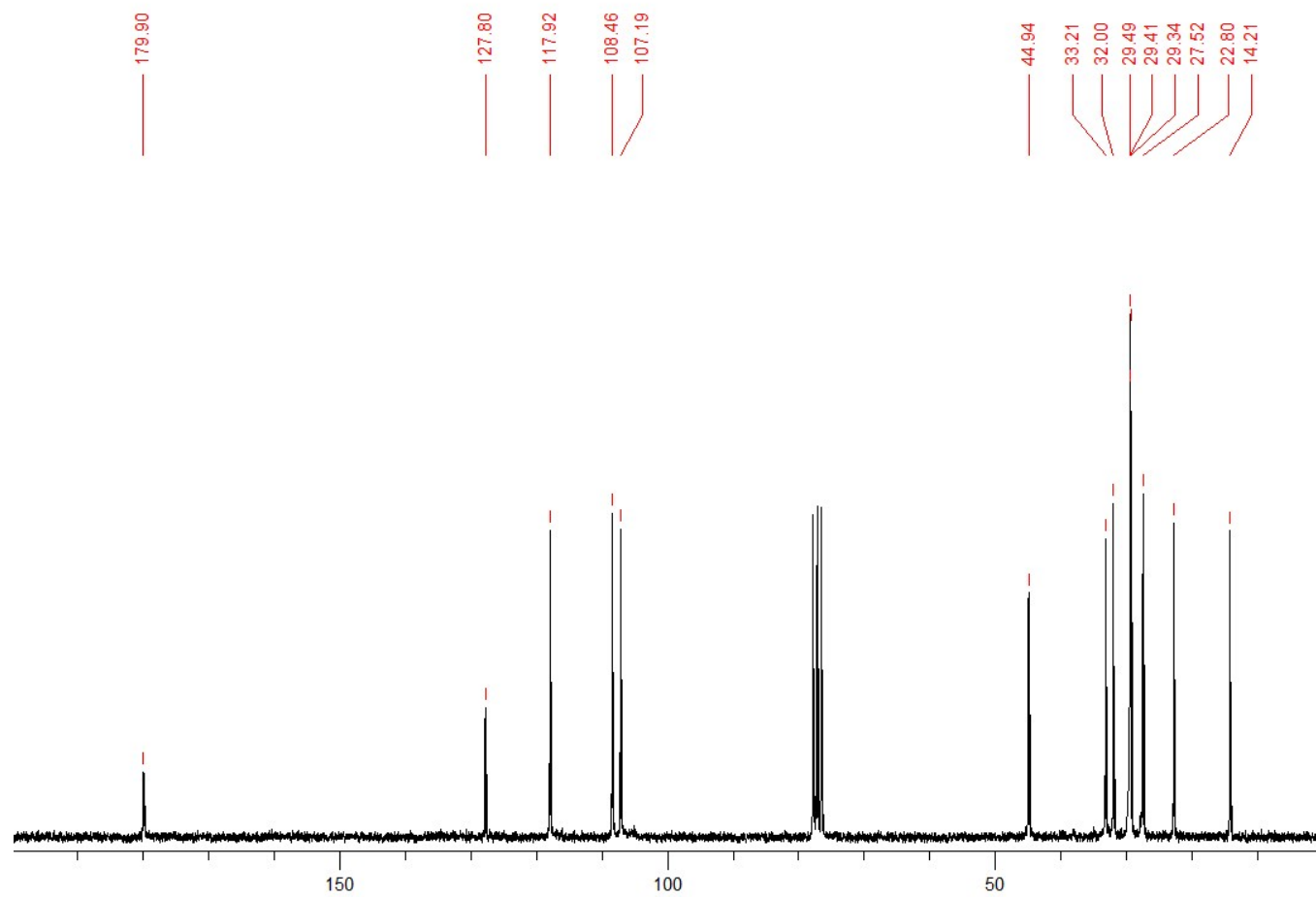
Compound 6cd. Yield 64%.

Colourless oil. IR (cm^{-1} , neat): 730, 784, 1105, 1175, 1455, 1602, 1713, 2927, 3386. 1H -NMR ($CDCl_3$, 400MHz) δ : 0.92 (t, 3H, $J = 7.7$ Hz), 1.23 (d, 3H, $J = 6.4$ Hz), 1.26 (d, 3H, $J = 6.0$ Hz), 1.28-1.39 (m, 2H), 1.63-1.83 (m, 5H), 1.85-1.97 (m, 1H), 2.42-2.49 (m, 2H), 2.50-2.57 (m, 2H), 3.54 (t, 1H, $J = 7.7$ Hz), 4.95-5.07 (m, 1H), 5.73 (s, 1H), 8.11 (br s, 1H). ^{13}C -NMR ($CDCl_3$, 100MHz) δ : 14.0, 20.9, 22.0, 22.1, 23.0, 23.1, 23.6, 24.0, 36.8, 45.0, 68.5, 105.7, 116.7, 125.5, 126.8, 174.2. GC-MS (70 eV): m/z : 263 ($[M^+]$, 32), 220 (14), 176 (100), 160 (16), 134 (22), 119 (22). Anal. Calcd. for $C_{16}H_{25}NO_2$ (263.38): C, 72.97; H, 9.57; N, 5.32. Found: C, 73.02; H, 9.61; N, 5.29.

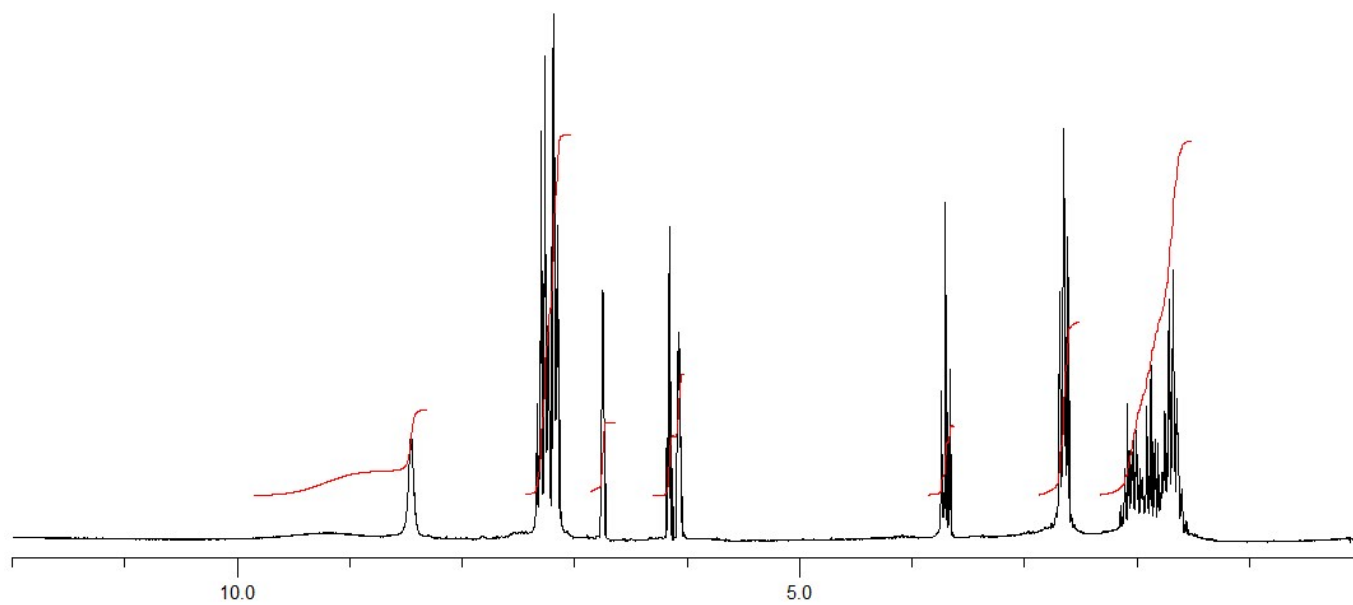
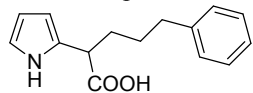
¹H-NMR Spectra of compounds **5ea**



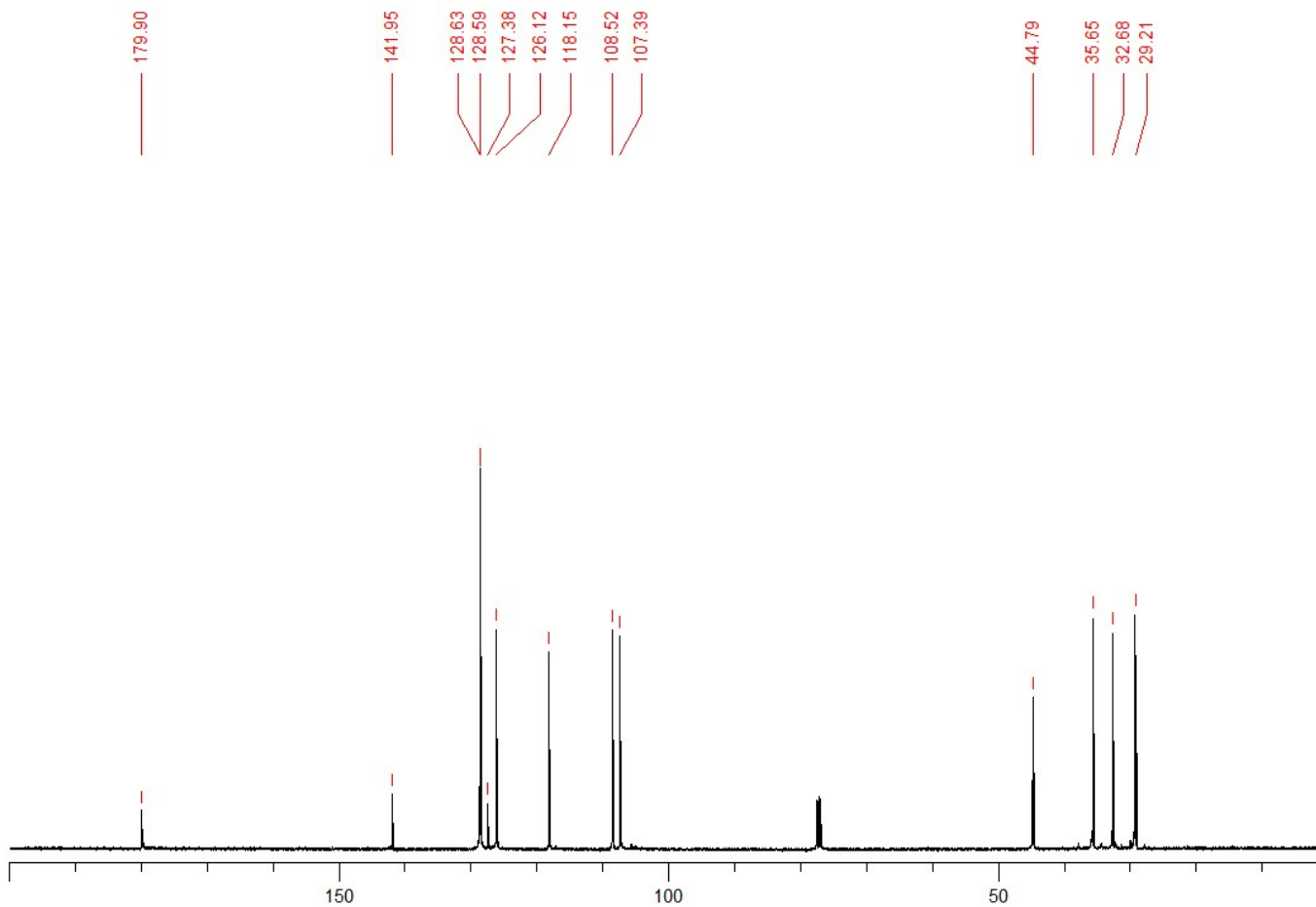
¹³C-NMR Spectra of compounds **5ea**



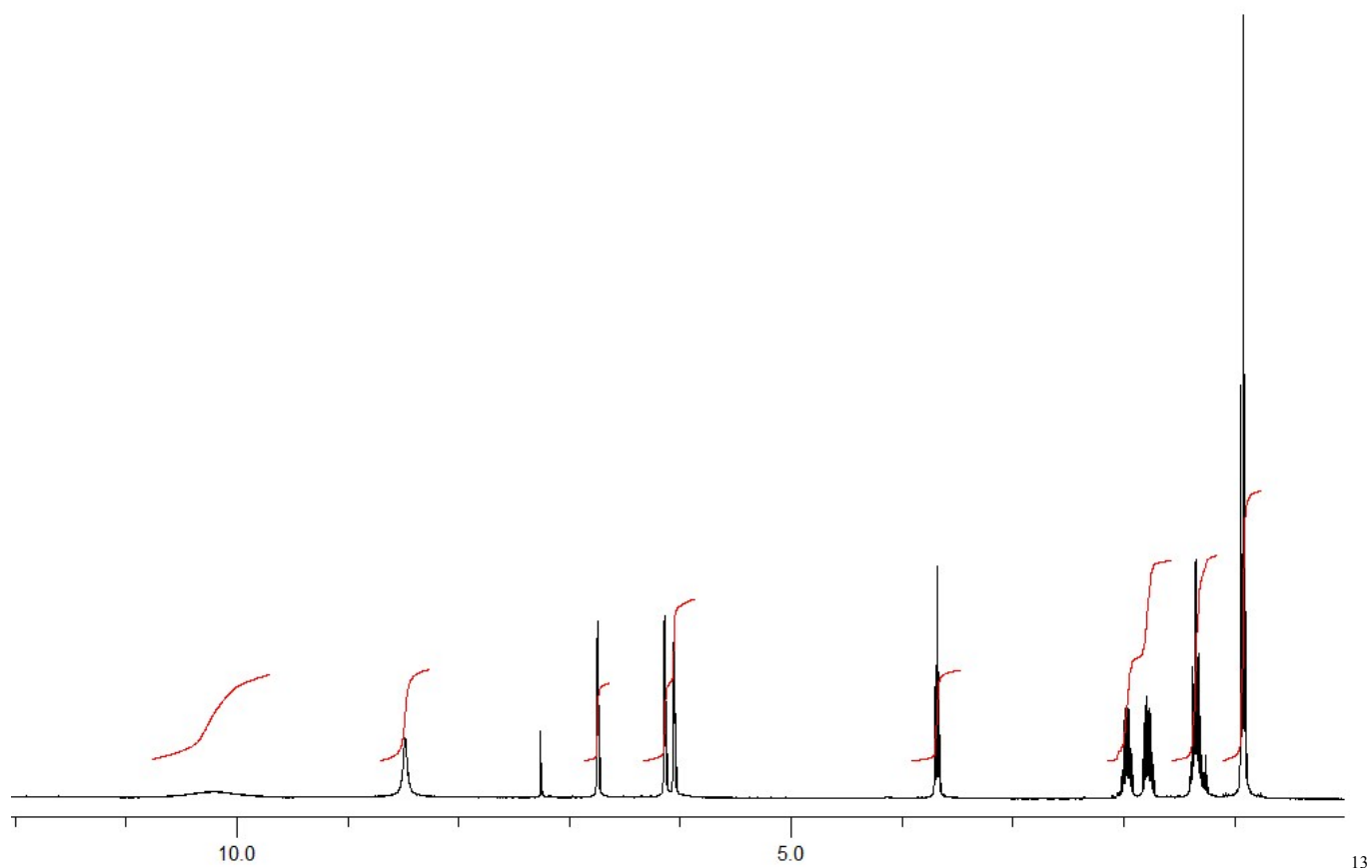
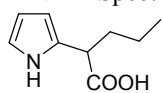
¹H-NMR Spectra of compounds **5fa**



¹³C-NMR Spectra of compounds **5fa**

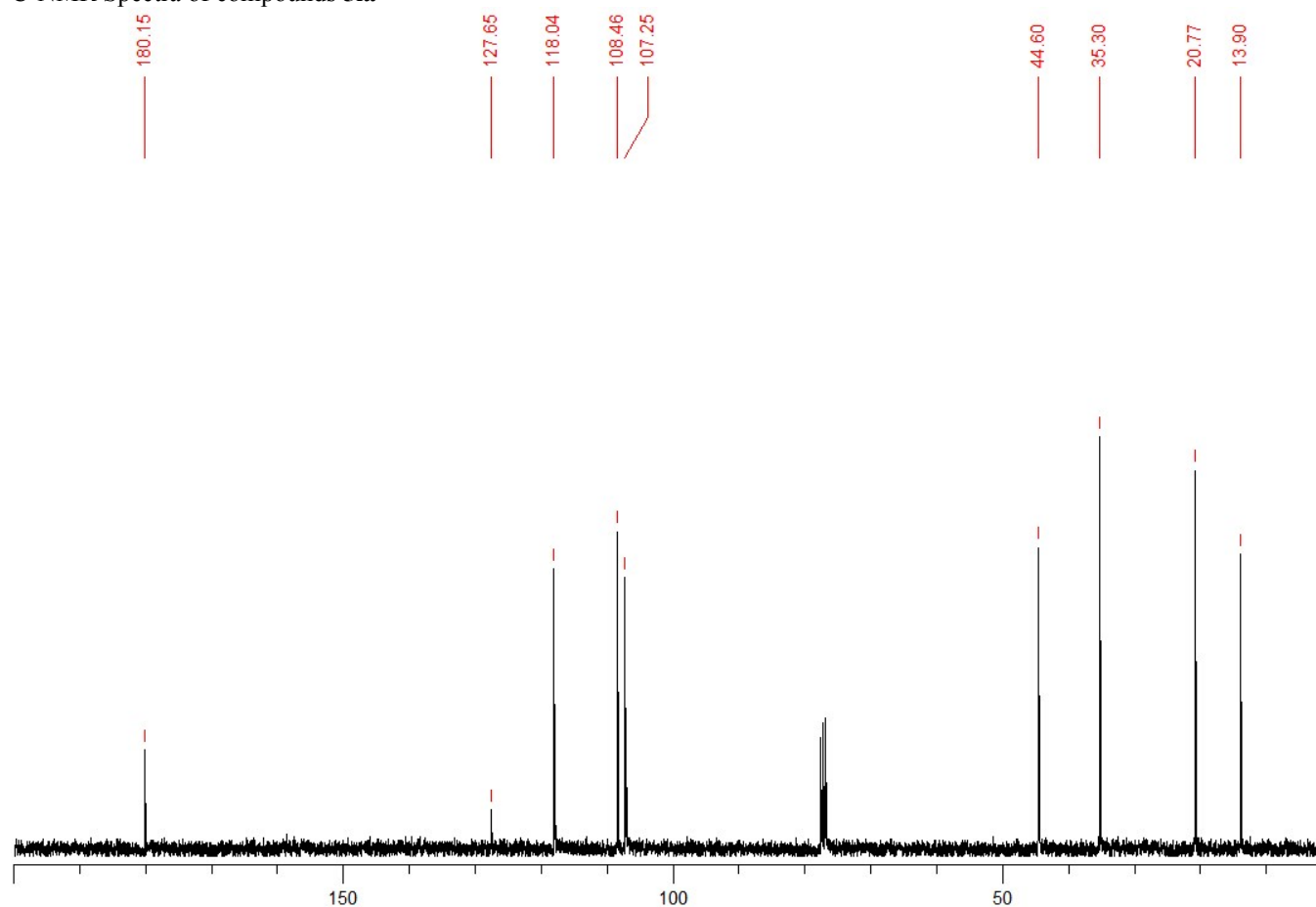


¹H-NMR Spectra of compounds **5ia**

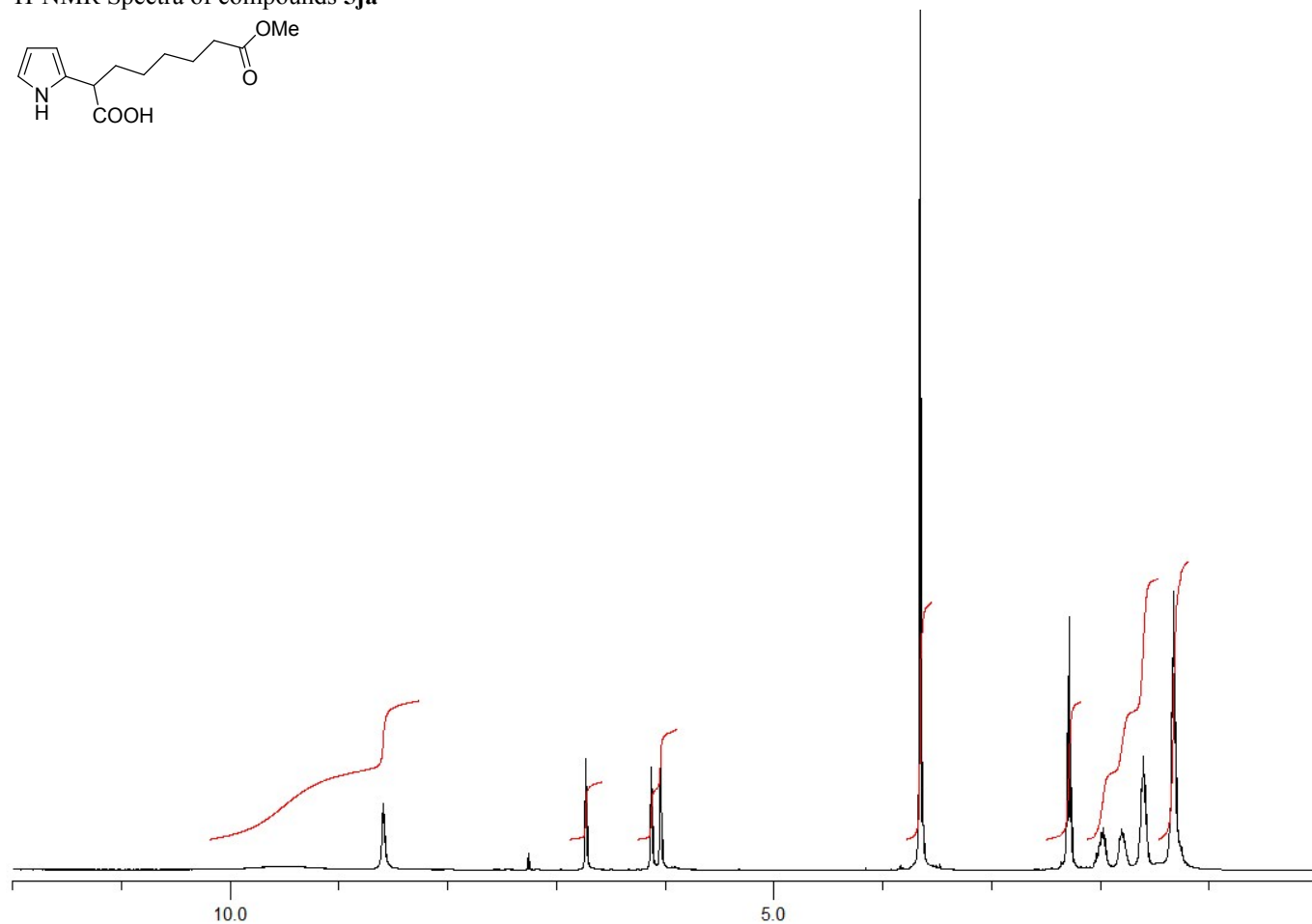
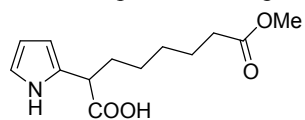


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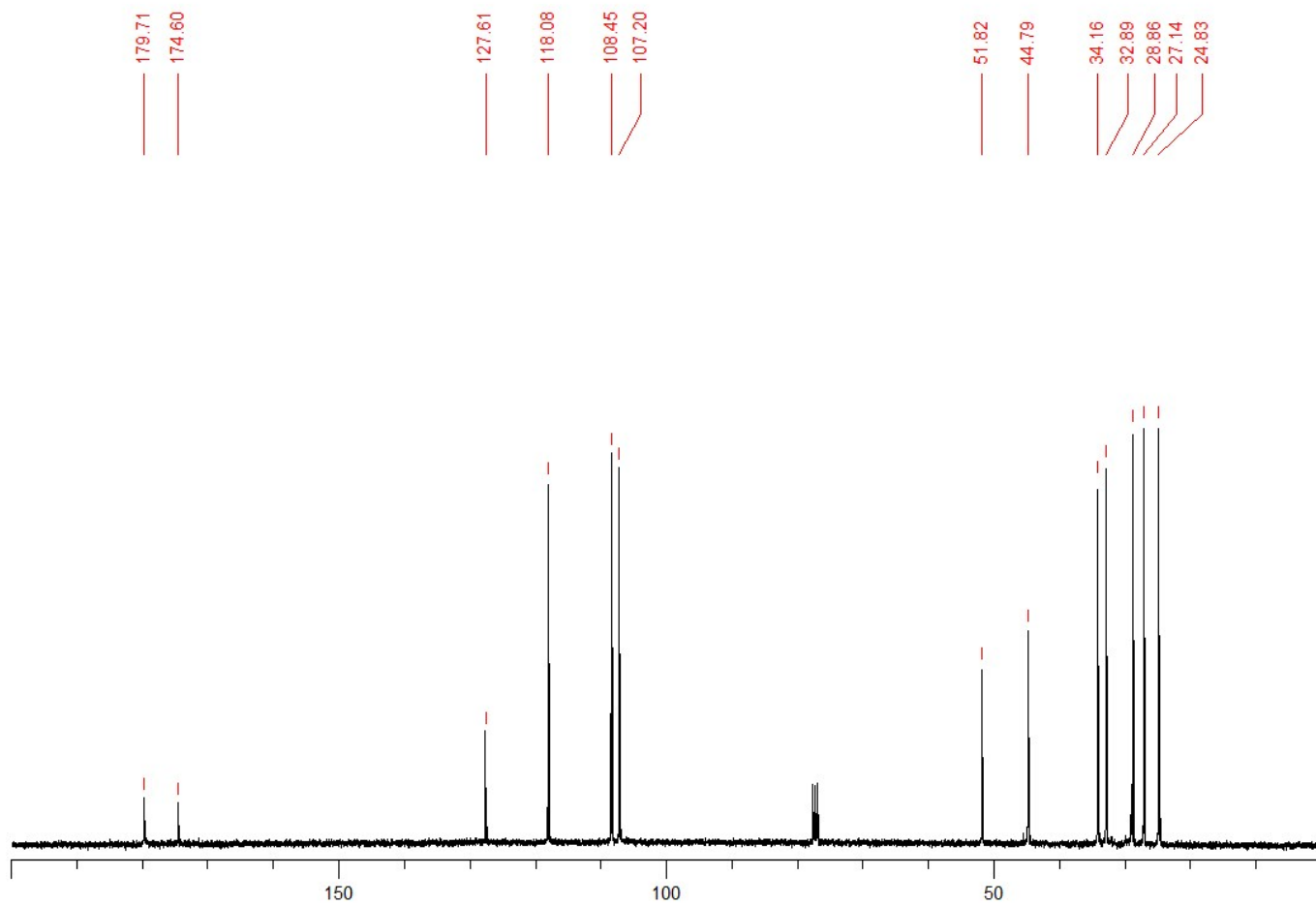
C-NMR Spectra of compounds **5ia**



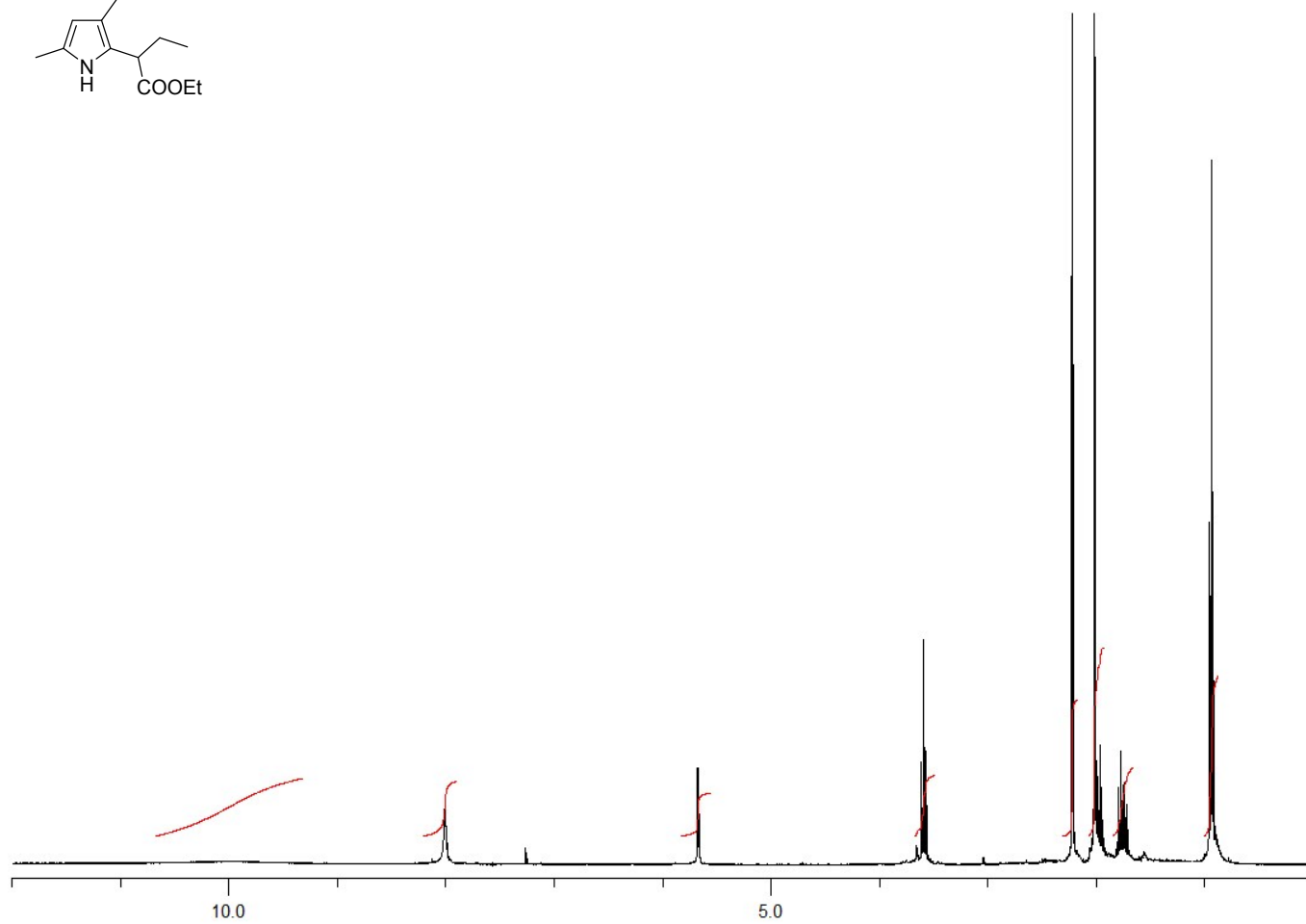
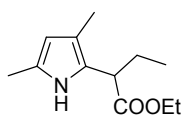
¹H-NMR Spectra of compounds **5ja**



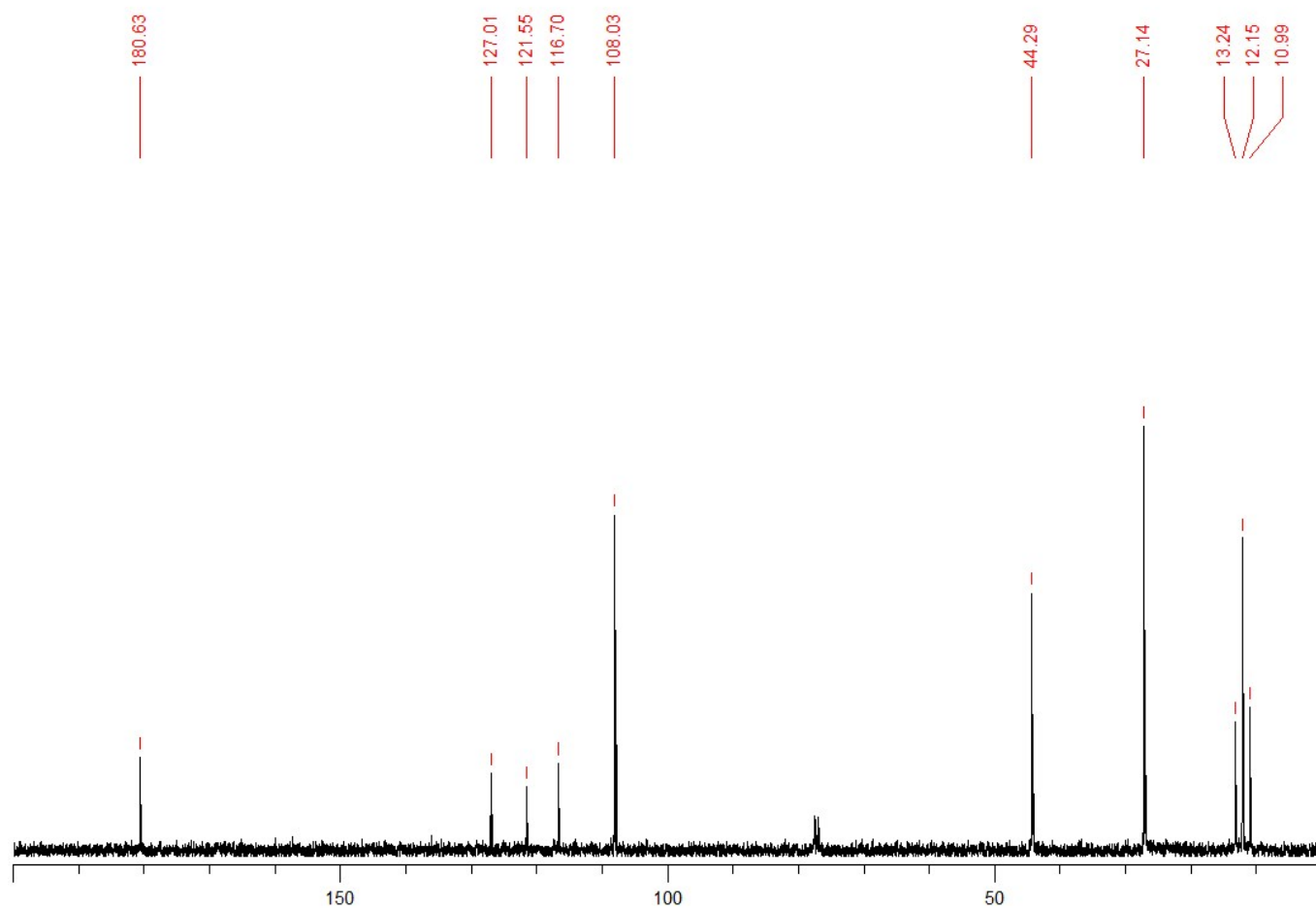
¹³C-NMR Spectra of compounds **5ja**



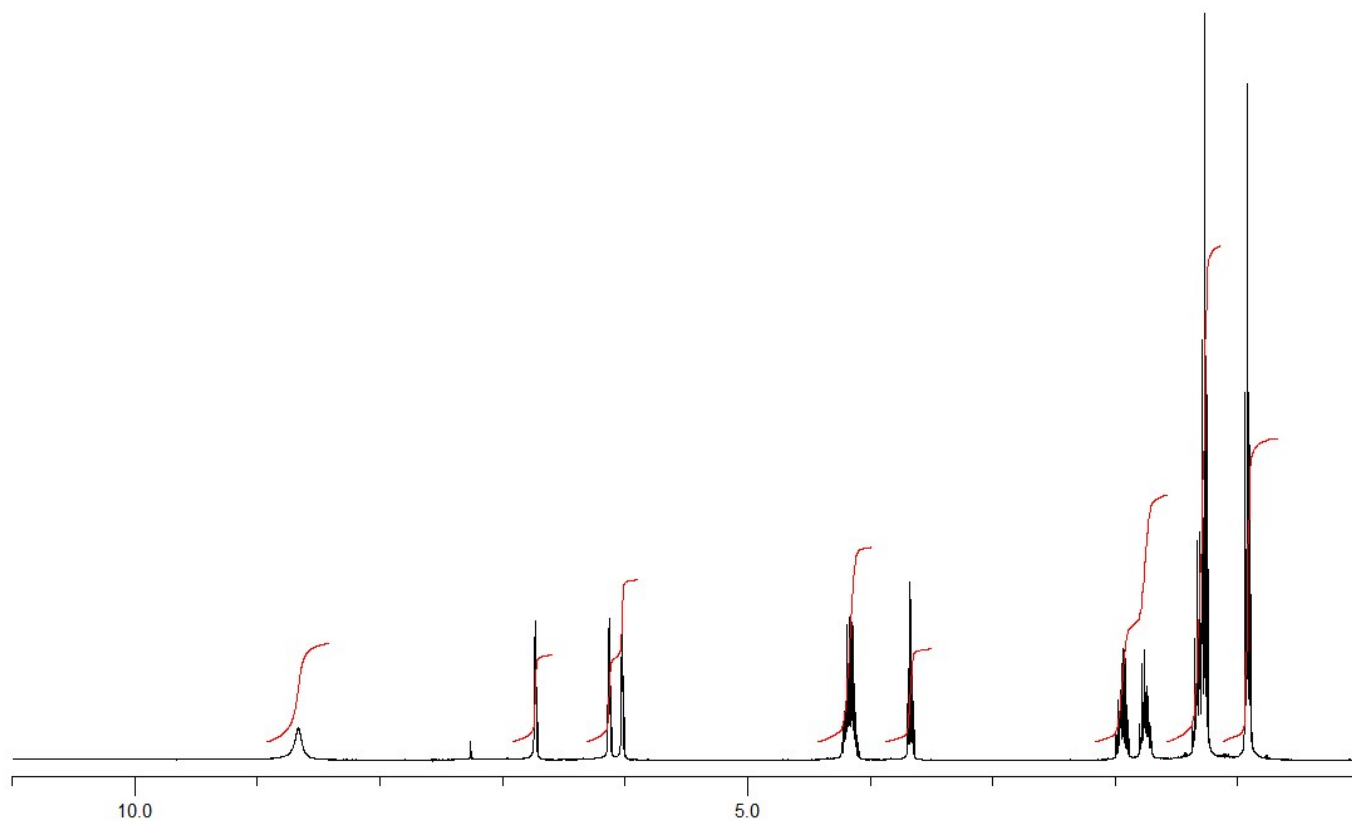
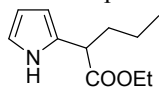
¹H-NMR Spectra of compounds **5kc**



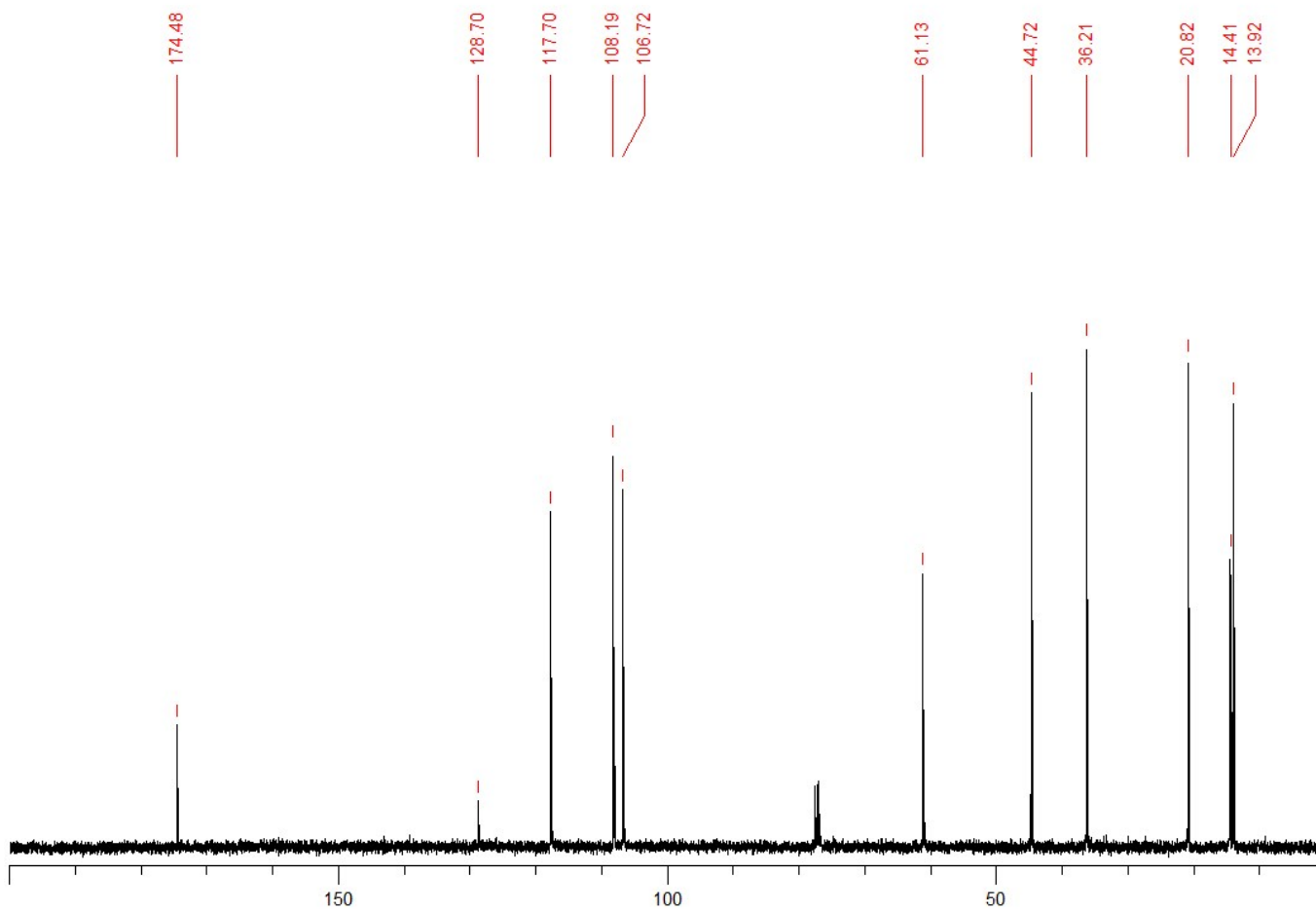
¹³C-NMR Spectra of compounds **5kc**



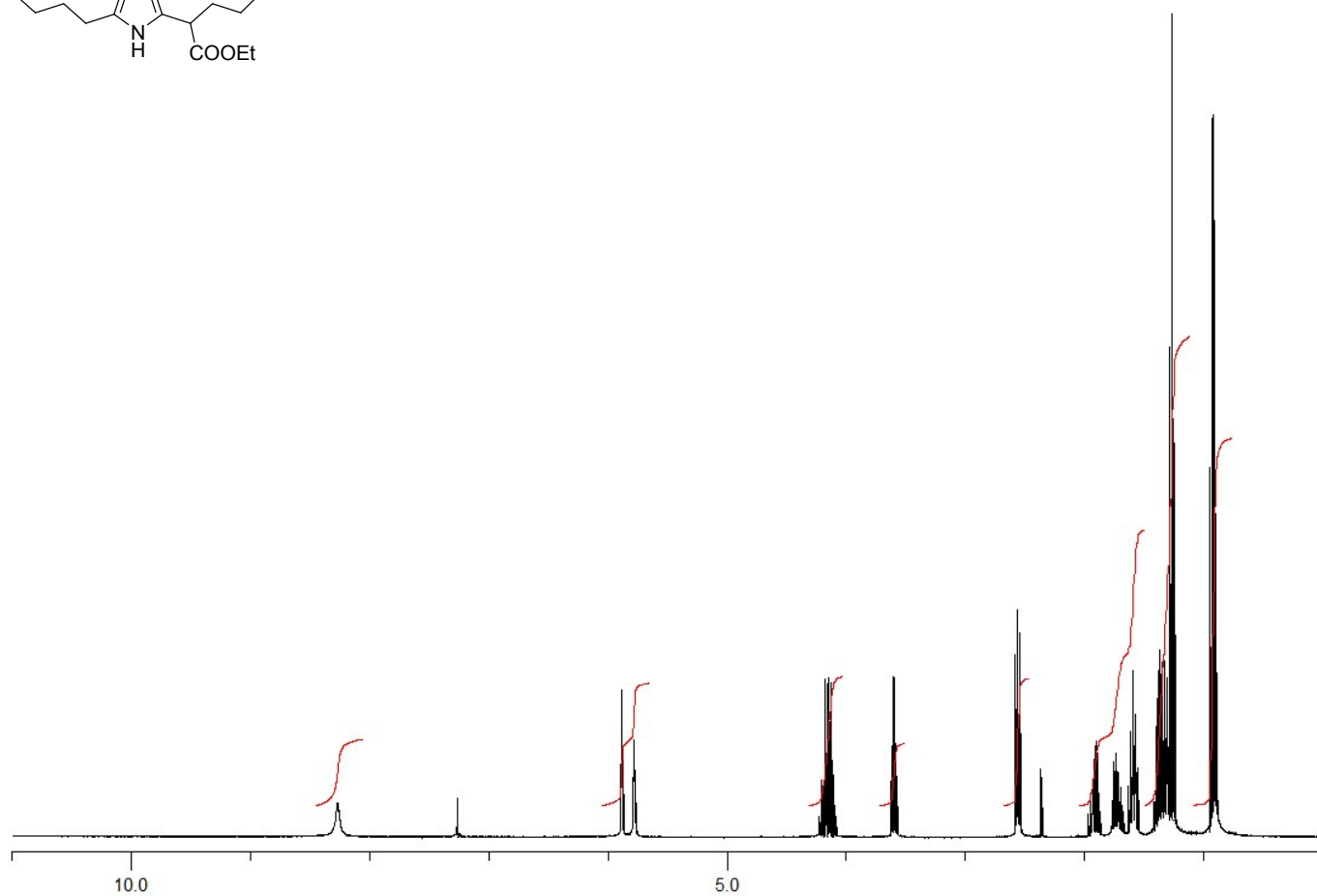
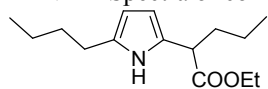
¹H-NMR Spectra of compounds **6aa**



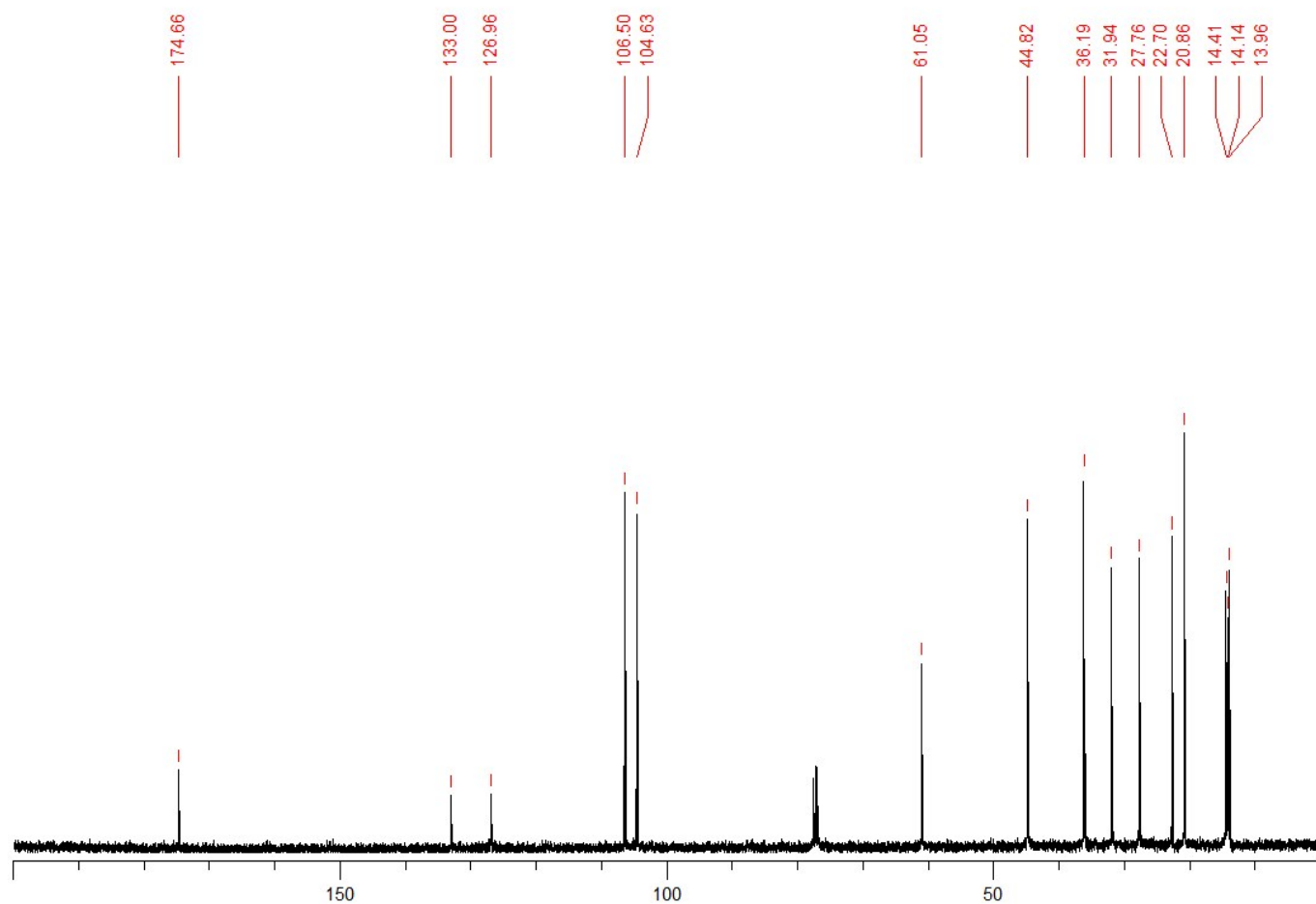
¹³C-NMR Spectra of compounds **6aa**



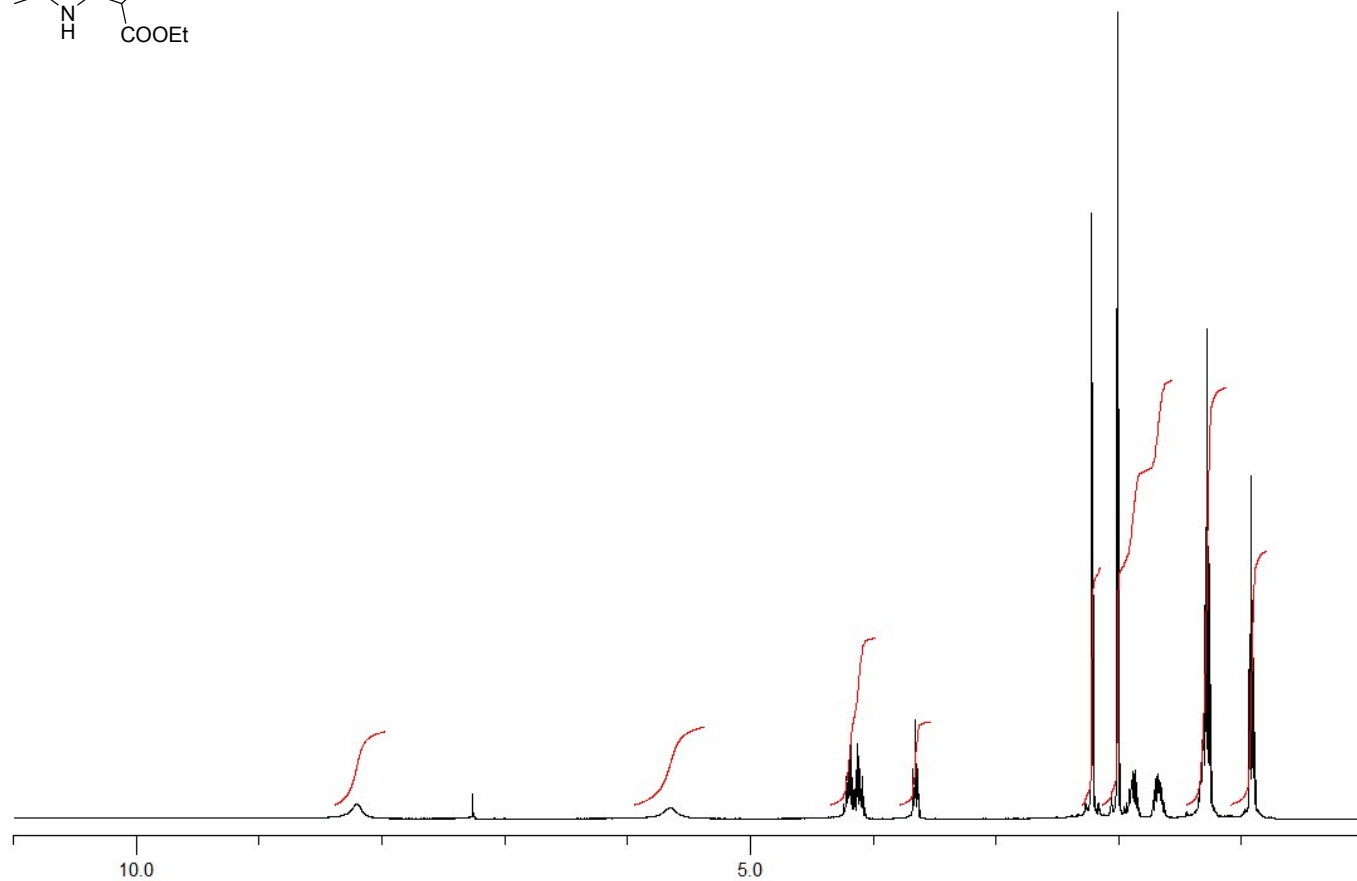
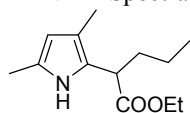
¹H-NMR Spectra of compounds **6ab**



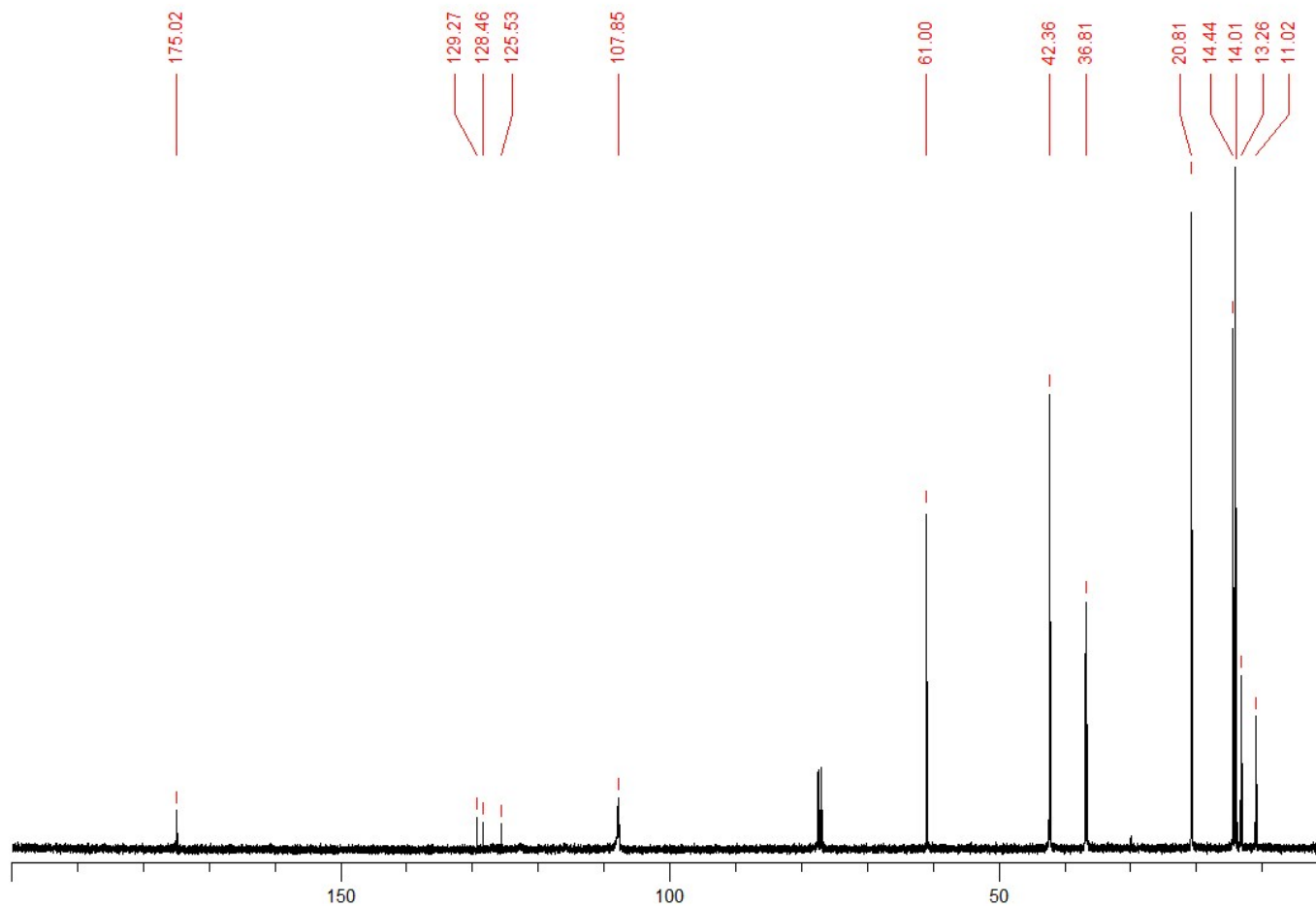
¹³C-NMR Spectra of compounds **6ab**



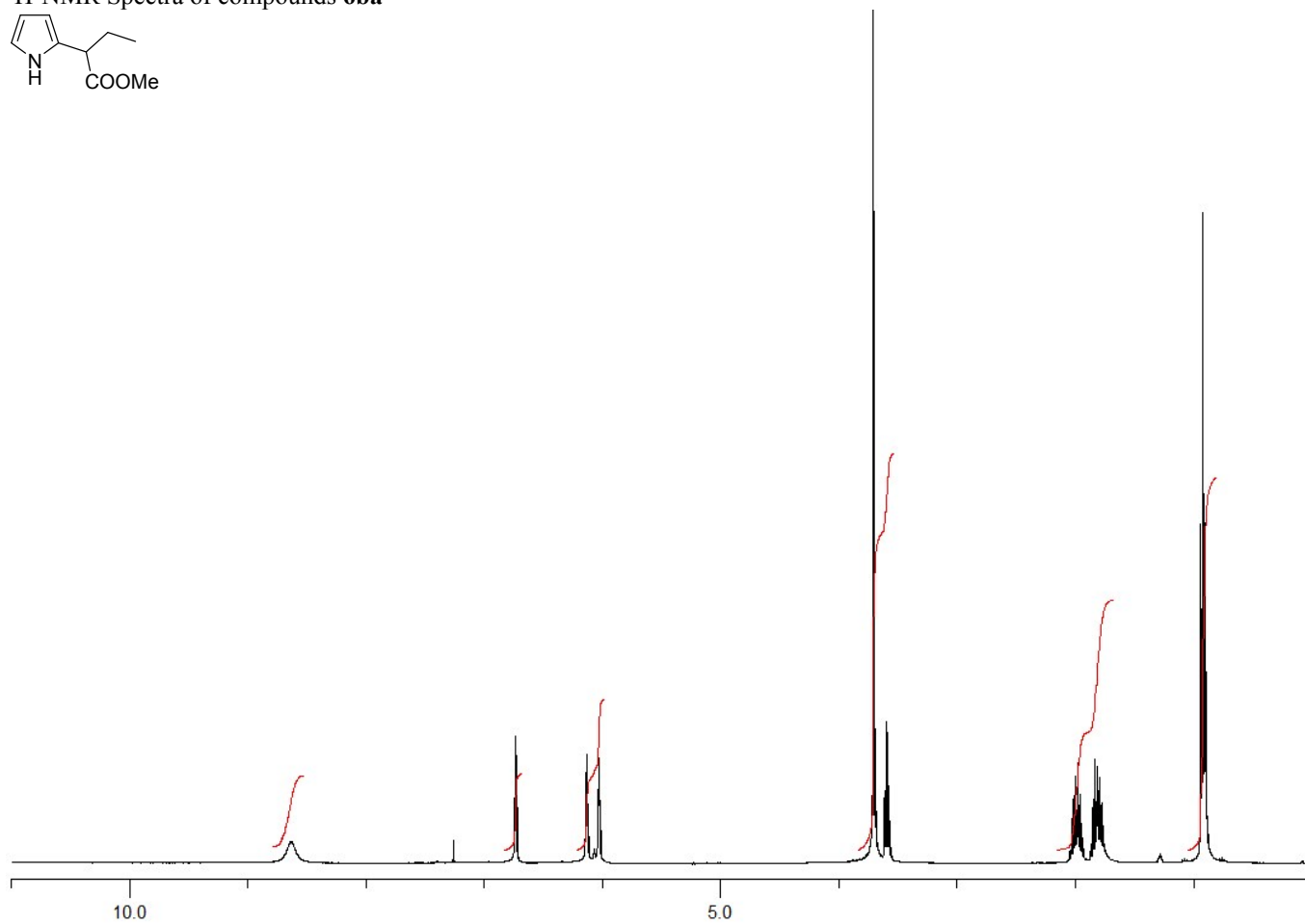
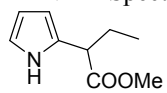
¹H-NMR Spectra of compounds **6ac**



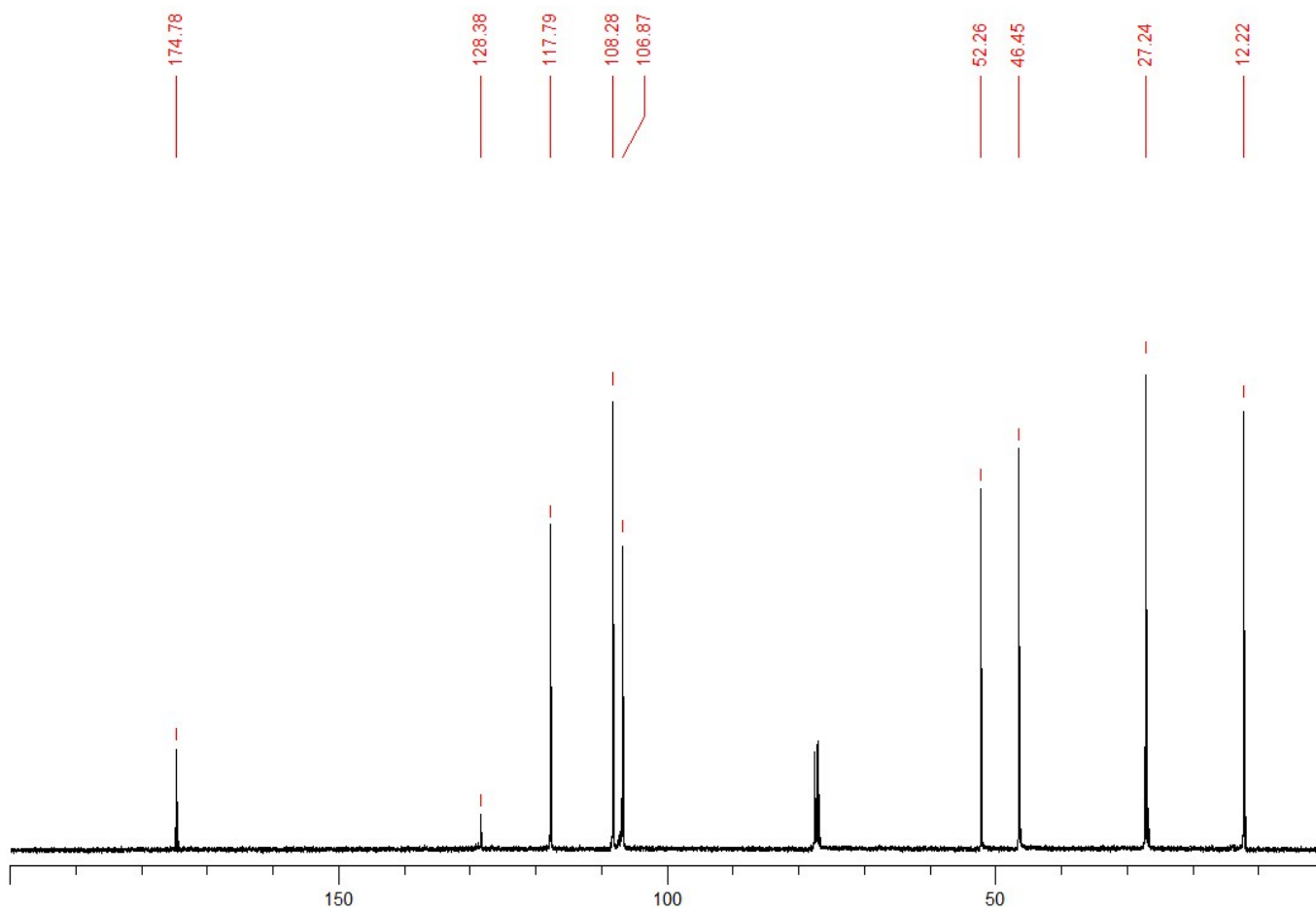
¹³C-NMR Spectra of compounds **6ac**



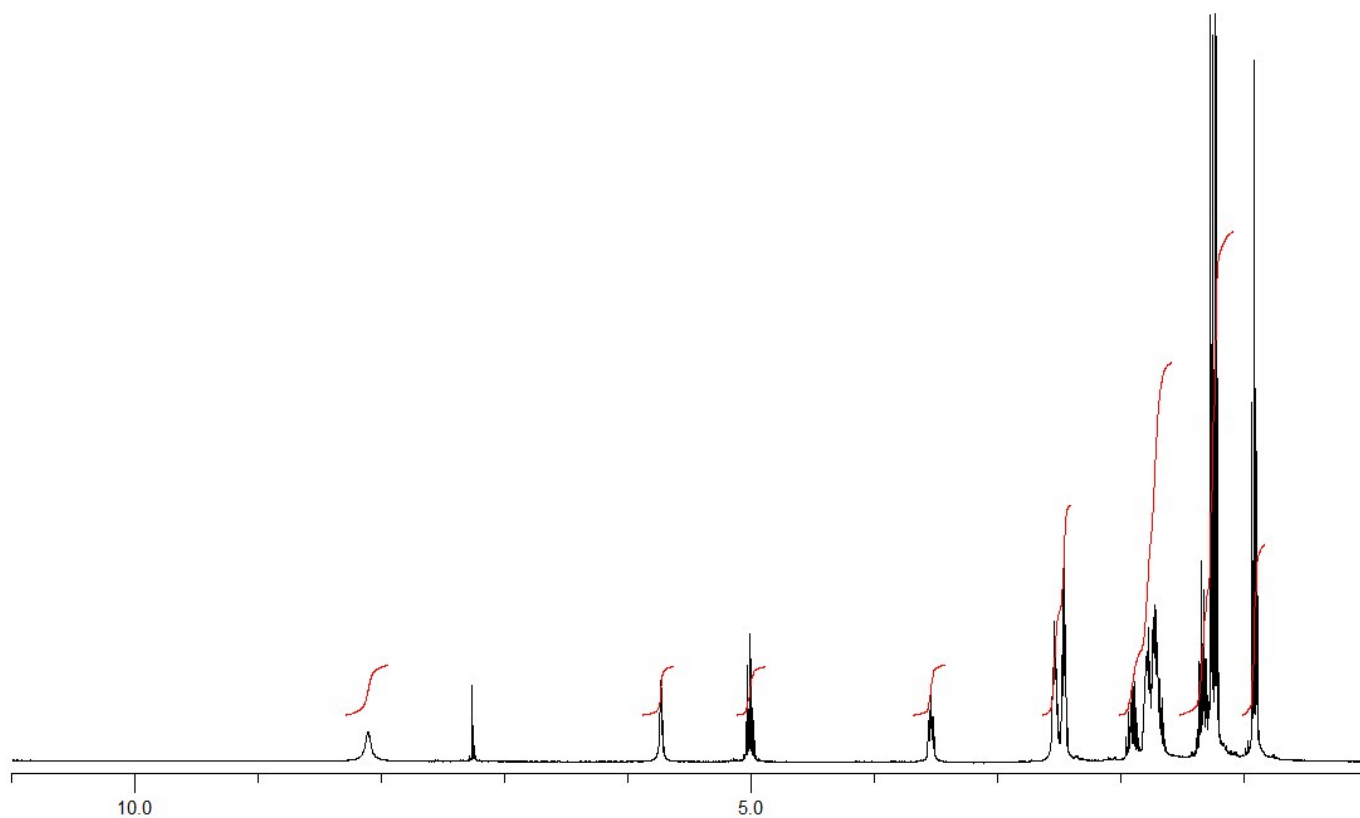
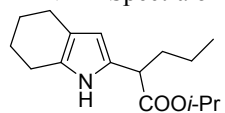
¹H-NMR Spectra of compounds **6ba**



¹³C-NMR Spectra of compounds **6ba**



¹H-NMR Spectra of compounds **6cd**



¹³C-NMR Spectra of compounds **6cd**

