

Supporting Information for

Efficient Method for the Synthesis of Functionalized Pyrazoles by Catalyst-Free One-Pot Tandem Reaction of Nitroalkenes with Ethyl Diazoacetate

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1. General methods

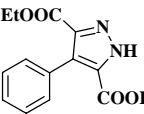
2. 1, 3-dipolar cycloaddition of the ethyl diazoacetate with conjugated nitroalkenes

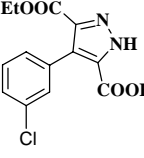
1. General Methods:

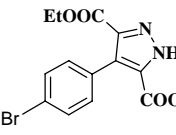
NMR spectra were recorded with tetramethylsilane as the internal standard. TLC was performed on glass-backed silica plates. Column chromatography was performed using silica gel (200-300 mesh) eluting with ethyl acetate and petroleum ether. ¹H NMR spectra were recorded at 400 MHz, and ¹³C NMR spectra were recorded at 100 MHz (Bruker Avance). Chemical shifts (δ) are reported in ppm downfield from CDCl₃ (δ = 7.26 ppm) for ¹H NMR and relative to the central CDCl₃ resonance (δ = 77.0 ppm) for ¹³C NMR spectroscopy. Coupling constants (J) are given in Hz. IR spectra were recorded using a Perkin-Elmer 1600 Series FTIR. ESI-HRMS spectrometer was measured with a Finnigan LCQ^{DECA} ion trap mass spectrometer. Conjugated nitroalkenes **1a-1f**¹, **3a-3g**¹ and **5a-5c**² were prepared according to literature procedures.

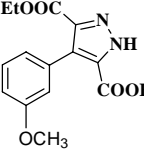
2. 1, 3-dipolar cycloaddition of the ethyl diazoacetate with conjugated nitroalkenes

General procedure: α -carbethoxy-1-nitrostyrene **1a** (0.5 mmol, 1 equiv.) and ethyl diazoacetate (2.5 mmol, 5 equiv.) were stirred at room temperature in THF (2ml) for 72h. The end of reaction was detected by TLC (20% ethyl acetate/petroleum ether). The solvent was removed and flash chromatography on silica gel (20% ethyl acetate/petroleum ether) or washed with 20% DCM/petroleum ether gave **2a** as a yellow solid **2a**.

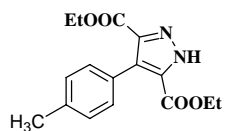
 **2a** $^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm) 15.6 (s, 1H), 7.35-7.28 (m, 5H), 4.24-4.19 (m, 4H), 1.16-1.11 (m, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ (ppm) 160.4, 160.4, 135.7, 135.6, 130.7, 130.3, 130.3, 127.7, 127.6, 127.2, 127.2, 61.2, 61.2, 13.7, 13.7. IR (KBr) cm^{-1} 2925, 1732, 1510; ESI-HRMS: calcd. for $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_4+\text{Na}$ 311.10036, found 311.10023;

 **2b** $^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm) 15.6 (s, 1H), 7.33-7.17 (m, 4H), 4.24-4.18 (m, 4H), 1.24-1.12 (m, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ (ppm) 160.2, 160.2, 133.0, 132.4, 130.1, 130.1, 128.7, 128.4, 128.4, 127.8, 127.8, 61.4, 61.4, 13.7, 13.7. IR (KBr) cm^{-1} 3108, 1741, 1447; ESI-HRMS: calcd. for $\text{C}_{15}\text{H}_{15}\text{ClN}_2\text{O}_4+\text{Na}$ 345.06127, found 345.06126;

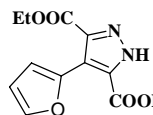
 **2c** $^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm) 13.7 (s, 1H), 7.44 (d, $J = 1.9$ Hz, 2H), 7.21 (dd, $J = 8.4, 2.1$ Hz, 2H), 7.26 (dd, $J = 13.8, 7.1$ Hz, 2H), 1.20 (t, $J = 7.1$ Hz, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ (ppm) 160.2, 160.2, 132.0, 131.8, 131.8, 130.8, 130.5, 130.5, 128.5, 126.6, 122.1, 61.5, 61.5, 13.8, 13.8. IR (KBr) cm^{-1} 3213, 1749, 1453; ESI-HRMS: calcd. for $\text{C}_{15}\text{H}_{15}\text{BrN}_2\text{O}_4+\text{Na}$ 389.01205, found 389.01074

 **2d** $^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm) 12.7 (s, 1H), 7.27 (t, $J = 6.8$ Hz, 1H), 7.27 (t, $J = 5.5$ Hz, 3H), 4.23 (dd, $J = 14.2, 7.0$ Hz, 4H), 3.78 (s, 3H), 1.16 (t, $J = 7.0$ Hz, 6H); $^{13}\text{C NMR}$ (100 MHz,

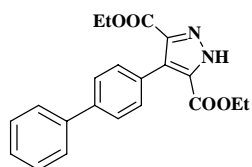
CDCl₃) δ (ppm) 160.4, 160.4, 158.6, 135.1, 135.0, 131.8, 128.3, 127.7, 122.8, 116.0, 113.4, 61.3, 61.3, 55.4, 13.8, 13.8. IR (KBr) cm⁻¹ 3104, 1769, 1518; ESI-HRMS: calcd. for C₁₆H₁₈N₂O₅+Na 341.11130, found 341.11079;



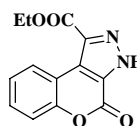
2e ¹H NMR (400 MHz, CDCl₃) δ (ppm) 15.6 (s, 1H), 7.28-7.17 (m, 4H), 4.40-4.23 (m, 4H), 2.38 (s, 3H), 1.20-1.17 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 160.4, 160.4, 137.4, 135.6, 130.7, 130.1, 130.1, 128.0, 128.0, 127.4, 127.4, 61.2, 61.2, 21.3, 13.9, 13.9. IR (KBr) cm⁻¹ 3233, 1749, 1492; ESI-HRMS: calcd. for C₁₆H₁₈N₂O₄+Na 325.11614, found 325.11588;



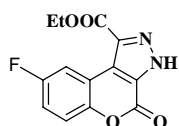
2f ¹H NMR (400 MHz, CDCl₃) δ (ppm) 13.7 (s, 1H), 7.51 (dd, *J* = 1.9, 0.7 Hz, 1H), 6.70 (dd, *J* = 3.3, 1.2 Hz, 1H), 6.49 (dd, *J* = 7.3, 1.9 Hz, 1H), 4.35-4.28 (m, 4H), 1.28-1.25 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 160.1, 160.1, 154.0, 142.8, 142.7, 137.7, 116.6, 111.8, 110.7, 61.8, 61.5, 14.0, 13.8. IR (KBr) cm⁻¹ 3102, 1732, 1531; ESI-HRMS: calcd. for C₁₃H₁₄N₂O₅+Na 301.07982, found 301.07949;



2g ¹H NMR (400 MHz, CDCl₃) δ (ppm) 13.7 (s, 1H), 7.65-7.58 (m, 4H), 7.44 (dd, *J* = 15.2, 7.4 Hz, 4H), 4.27 (dd, *J* = 14.2, 7.1 Hz, 4H), 1.18 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 160.5, 160.5, 154.0, 140.8, 140.5, 130.8, 128.9, 128.8, 128.7, 128.7, 128.6, 127.4, 127.3, 127.1, 127.1, 127.0, 125.9, 61.4, 61.4, 13.6, 13.6. IR (KBr) cm⁻¹ 3113, 1738, 1491; ESI-HRMS: calcd. for C₂₁H₂₀N₂O₄+Na 387.13183, found 387.13153;

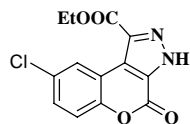


4a ¹H NMR (400 MHz, DMSO) δ (ppm) 15.5 (s, 1H), 8.86 (d, *J* = 3.1 Hz, 1H), 7.56-7.38 (m, 3H), 4.44 (dd, *J* = 14.1, 7.2 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, DMSO) δ (ppm) 167.9, 162.8, 151.7, 135.1, 132.7, 130.3, 127.1, 125.1, 117.5, 117.4, 115.2, 62.0, 14.5. IR (KBr) cm⁻¹ 3213, 1751, 1725, 1467; ESI-HRMS: calcd. for C₁₃H₁₀N₂O₄+H 259.07057, found 259.07133;

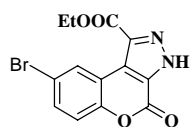


4b ¹H NMR (400 MHz, DMSO) δ (ppm) 15.6 (s, 1H), 8.62 (d, *J* = 8.4 Hz, 1H), 7.53-7.50

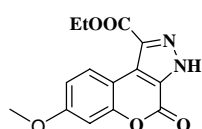
(m, 1H), 7.42-7.37 (d, $J = 8.8$ Hz, 1H), 4.46 (dd, $J = 14.2, 7.1$ Hz, 2H), 1.42 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, DMSO) δ (ppm) 167.9, 162.8, 150.4, 135.1, 132.7, 129.9, 128.9, 126.3, 119.4, 117.3, 116.8, 62.3, 14.5. IR (KBr) cm^{-1} 3105, 1754, 1739, 1510; ESI-HRMS: calcd. for $\text{C}_{13}\text{H}_9\text{FN}_2\text{O}_4+\text{H}$ 277.06227, found 277.06191;



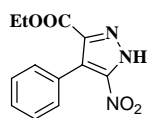
4c ^1H NMR (400 MHz, DMSO) δ (ppm) 15.6 (s, 1H), 8.99 (s, 1H), 7.64-7.67 (m, 1H), 7.39 (d, $J = 8.8$ Hz, 1H), 4.45 (dd, $J = 14.2, 7.1$ Hz, 2H), 1.41 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, DMSO) δ (ppm) 167.9, 162.8, 150.1, 135.1, 132.7, 129.2, 127.8, 126.3, 119.7, 117.3, 116.9, 62.3, 14.5. IR (KBr) cm^{-1} 3217, 1757, 1729, 1476; ESI-HRMS: calcd. for $\text{C}_{13}\text{H}_9\text{ClN}_2\text{O}_4+\text{H}$ 293.03271, found 293.03236;



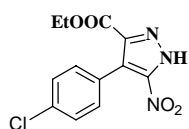
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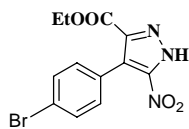
4e ^1H NMR (400 MHz, DMSO) δ (ppm) 15.3 (s, 1H), 8.63 (d, $J = 8.6$ Hz, 1H), 6.89 (t, $J = 11.9$ Hz, 2H), 4.41 (dd, $J = 13.9, 6.9$ Hz, 2H), 3.81 (s, 3H), 1.38 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, DMSO) δ (ppm) 167.9, 162.8, 160.8, 153.1, 135.1, 135.1, 127.9, 125.1, 112.2, 107.9, 102.0, 61.9, 56.1, 14.5. IR (KBr) cm^{-1} 3107, 1761, 1743, 1493; ESI-HRMS: calcd. for $\text{C}_{14}\text{H}_{13}\text{N}_2\text{O}_5+\text{H}$ 289.08204, found 289.08190;



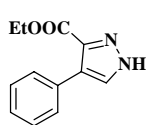
6a ^1H NMR (400 MHz, CDCl_3) δ (ppm) 13.7 (s, 1H), 7.44-7.33 (m, 5H), 4.26 (dd, $J = 14.2, 7.2$ Hz, 2H), 1.14 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 158.3, 135.4, 133.6, 130.4, 130.2, 128.7, 127.8, 127.4, 125.4, 120.8, 62.3, 13.7. IR (KBr) cm^{-1} 2922, 1724, 1533; ESI-HRMS: calcd. for $\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}_4+\text{Na}$ 284.06470, found 284.06418;



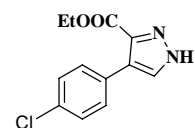
6b ^1H NMR (400 MHz, CDCl_3) δ (ppm) 13.7 (s, 1H), 7.41 (d, $J = 8.5$ Hz, 2H), 7.29 (d, $J = 8.4$ Hz, 2H), 4.29 (dd, $J = 14.2, 7.2$ Hz, 2H), 1.19 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 158.0, 135.0, 131.5, 131.4, 131.2, 128.2, 128.2, 126.2, 125.0, 119.8, 62.5, 13.7. IR (KBr) cm^{-1} 3116, 1765, 1497; ESI-HRMS: calcd. for $\text{C}_{12}\text{H}_{10}\text{ClN}_3\text{O}_4 + \text{Na}$ 318.02561, found 318.02520;



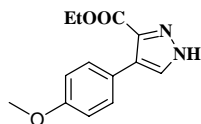
6c ^1H NMR (400 MHz, CDCl_3) δ (ppm) 13.7 (s, 1H), 7.57 (d, $J = 8.4$ Hz, 2H), 7.23 (d, $J = 8.4$ Hz, 2H), 4.29 (dd, $J = 14.2, 7.2$ Hz, 2H), 1.19 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 157.9, 135.1, 131.8, 131.7, 131.2, 131.2, 126.7, 125.0, 123.3, 119.8, 62.5, 13.7. IR (KBr) cm^{-1} 2914, 1774, 1485; ESI-HRMS: calcd. for $\text{C}_{12}\text{H}_{10}\text{BrN}_3\text{O}_4 + \text{Na}$ 361.97545, found 361.97469;



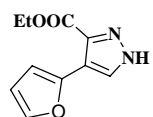
8a ^1H NMR (400 MHz, CDCl_3) δ (ppm) 13.7 (s, 1H), 7.47-7.41 (m, 1H), 7.73 (s, 1H), 7.55 (dd, $J = 8.4, 1.5$ Hz, 2H), 7.40-7.20 (m, 3H), 4.35 (dd, $J = 14.2, 7.1$ Hz, 2H), 1.32 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 161.7, 138.6, 136.4, 131.9, 129.3, 127.9, 127.8, 129.4, 127.4, 125.4, 61.1, 14.1. IR (KBr) cm^{-1} 2925, 1687, 1513; ESI-HRMS: calcd. for $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_2 + \text{Na}$ 239.07945, found 239.07910;



8b ^1H NMR (400 MHz, CDCl_3) δ (ppm) 13.6 (s, 1H), 8.1 (s, 1H), 7.62-7.42 (m, 4H), 4.29-4.21 (m, 2H), 1.27-1.21 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 162.9, 140.6, 139.5, 132.4, 131.5, 130.9, 130.2, 128.2, 124.1, 123.1, 61.3, 14.5. IR (KBr) cm^{-1} 2900, 1694, 1563; ESI-HRMS: calcd. for $\text{C}_{12}\text{H}_{11}\text{N}_2\text{O}_2 + \text{Na}$ 273.04040, found 273.04013;



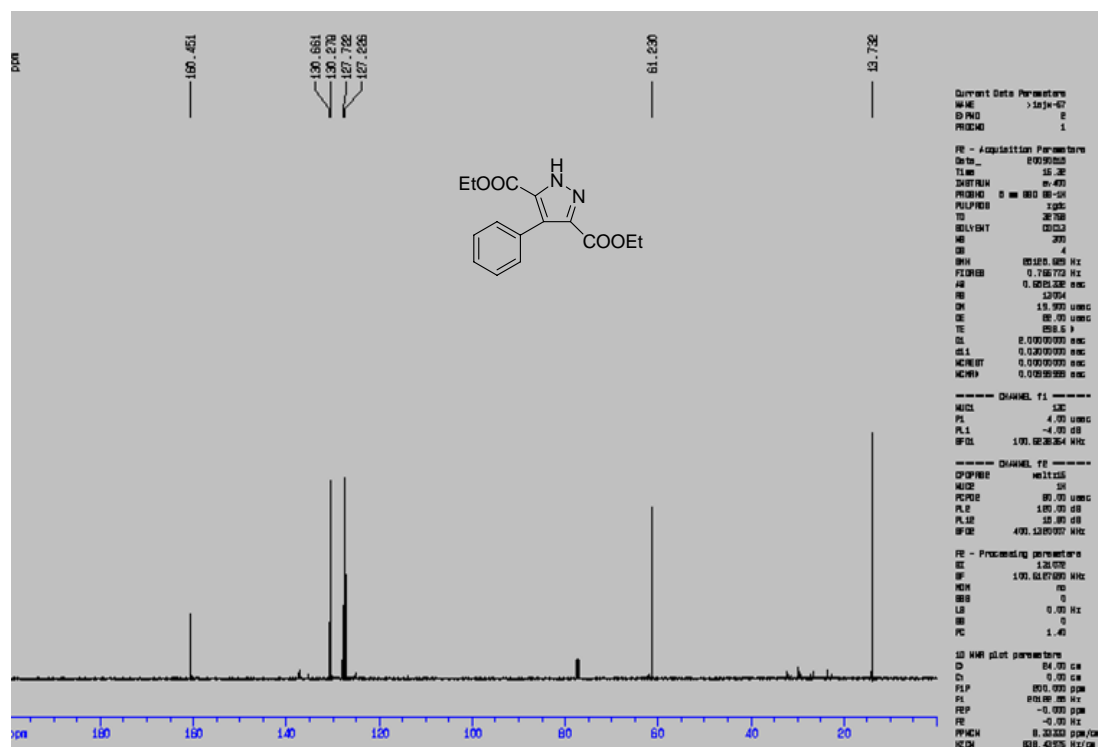
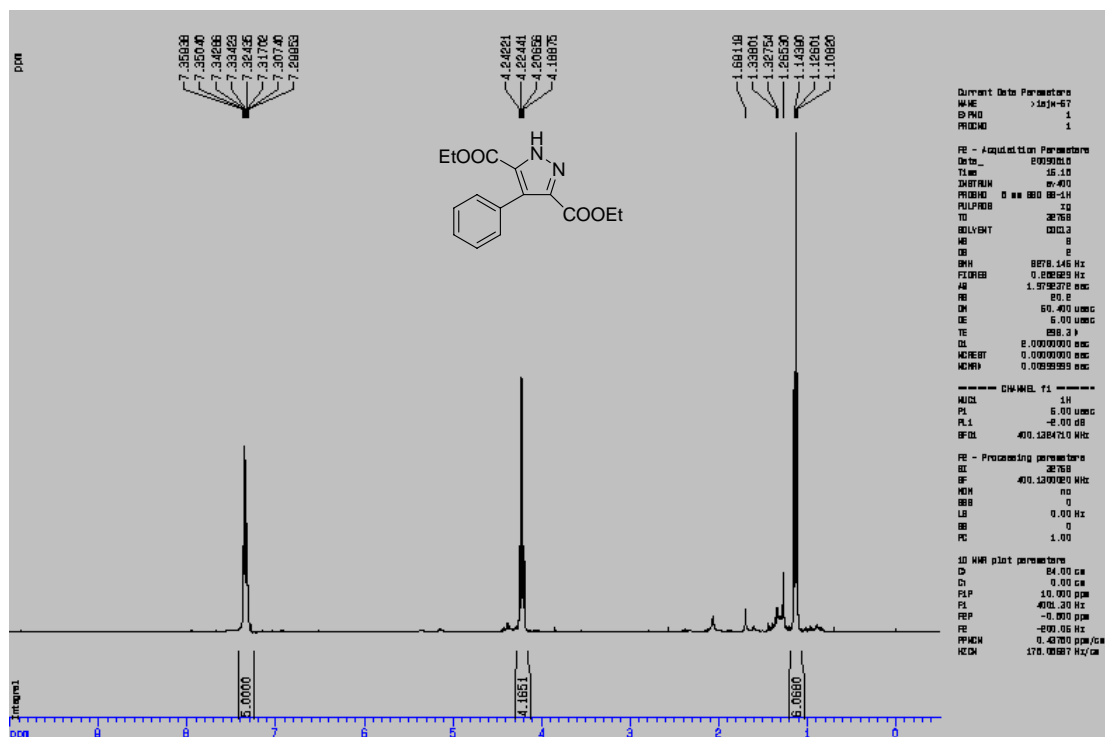
8c ^1H NMR (400 MHz, CDCl_3) δ (ppm) 13.7 (s, 1H), 7.75 (s, 1H), 7.49 (d, $J = 7.0$ Hz, 2H), 6.65 (dd, $J = 6.8, 2.0$ Hz, 2H), 4.36 (dd, $J = 14.3, 7.1$ Hz, 2H), 3.86 (s, 3H), 1.32 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 161.7, 158.7, 142.7, 141.6, 136.4, 131.9, 127.8, 125.4, 115.6, 110.6, 61.1, 55.9, 14.1. IR (KBr) cm^{-1} 2929, 1683, 1542; ESI-HRMS: calcd. for $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_3 + \text{Na}$ 269.09022, found 269.08966;



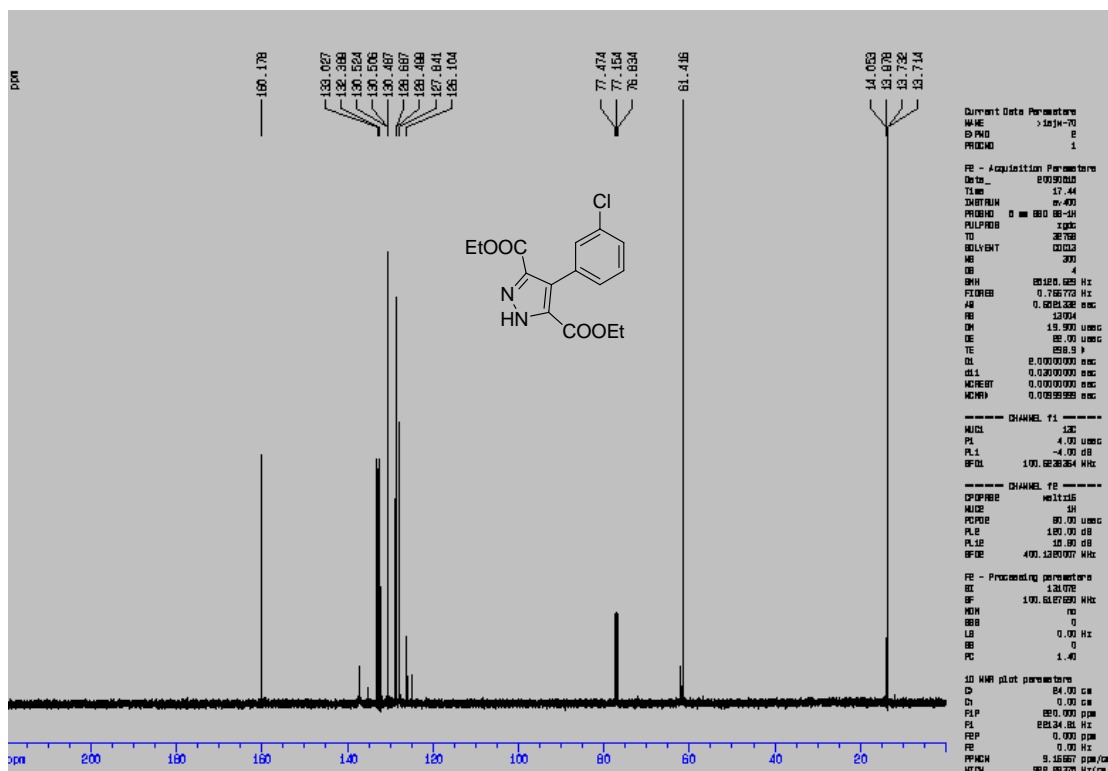
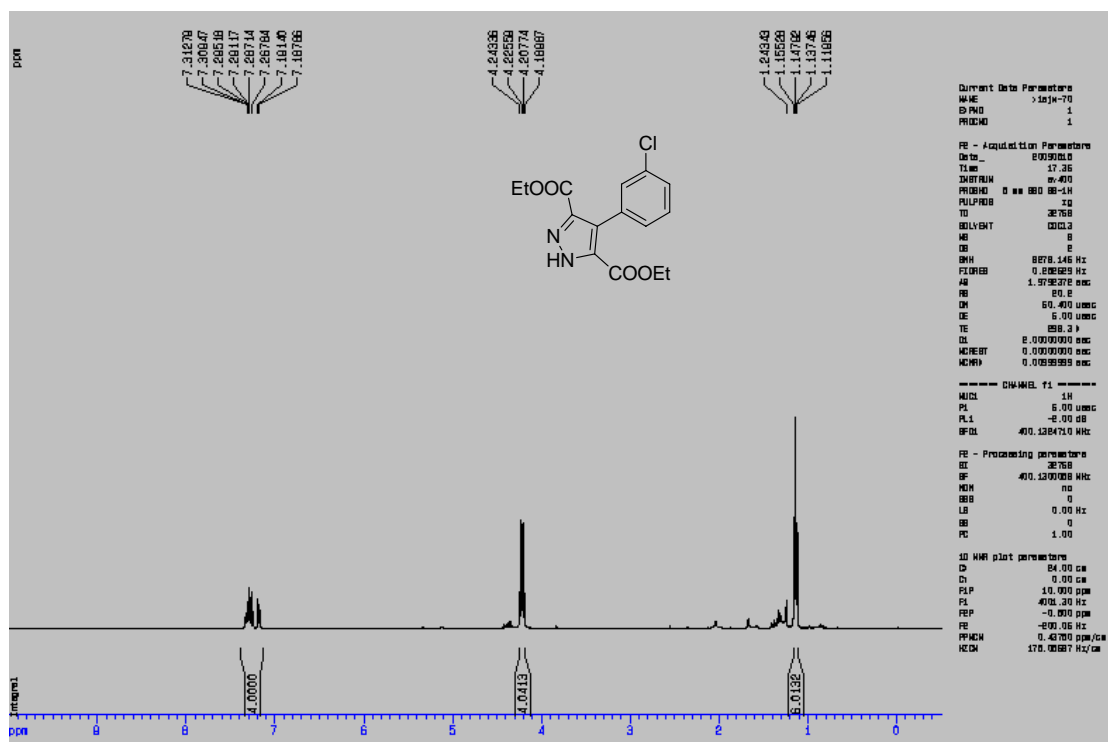
8d ^1H NMR (400 MHz, CDCl_3) δ (ppm) 13.7 (s, 1H), 8.04 (s, 1H), 7.45 (s, 1H), 7.13 (d, $J = 3.2$ Hz, 1H), 6.48 (dd, $J = 3.0, 1.7$ Hz, 1H), 4.47 (dd, $J = 14.2, 7.1$ Hz, 2H), 1.44 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 161.5, 154.0, 142.9, 141.0, 133.2, 108.0, 107.2, 105.0, 61.1, 14.1. IR (KBr) cm^{-1} 2894, 1680, 1540; ESI-HRMS: calcd. for $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}_3 + \text{Na}$ 229.05868, found 229.05836.

1. Daniel Dauzonne, Rene Royer, synthesis, 1983, 836-837;
2. Madhu Ganesh and Irishi N. N. Namboothiri, Tetrahedron 63 (2007) 11973–11983

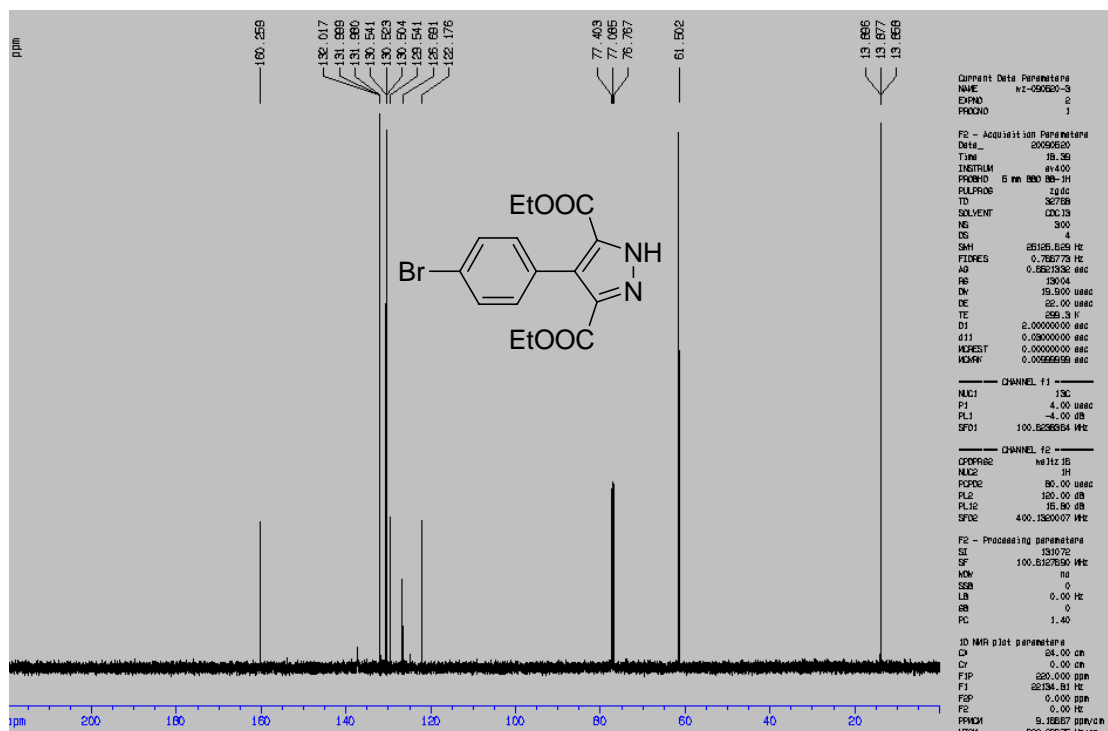
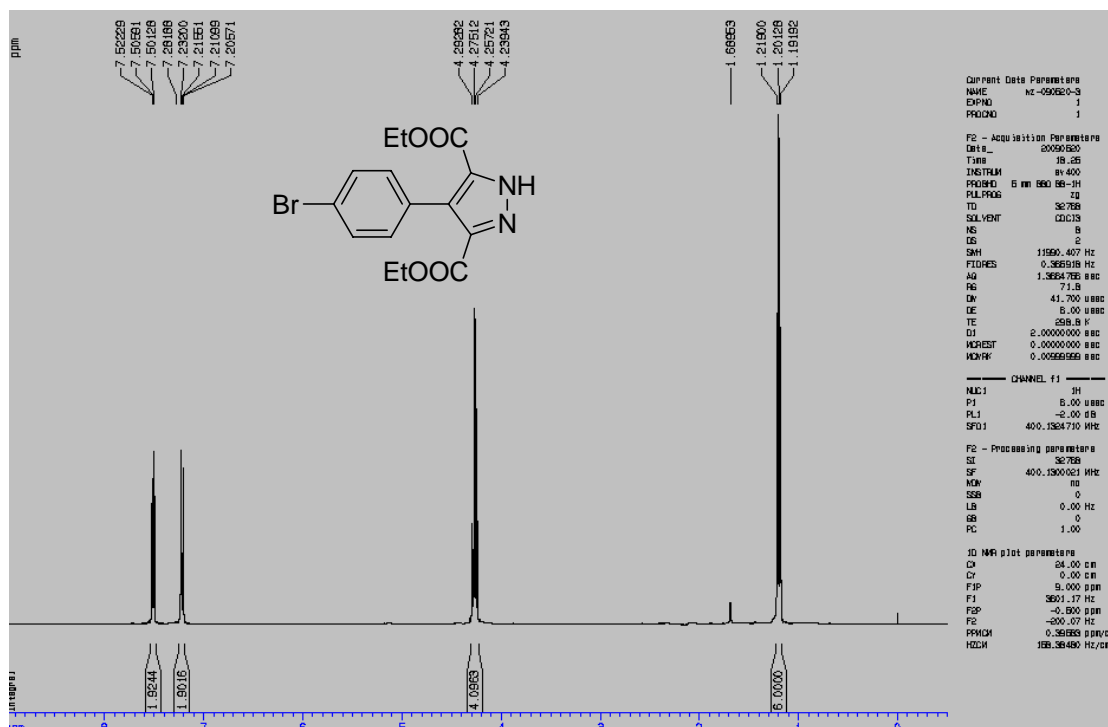
2a



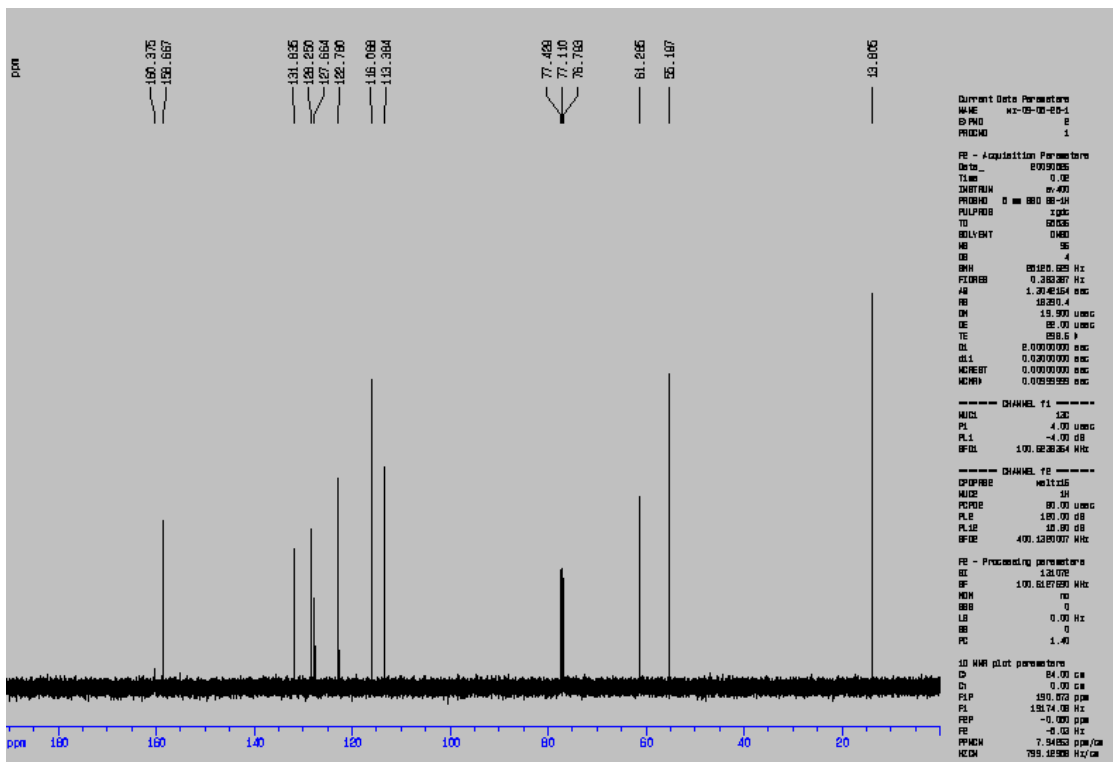
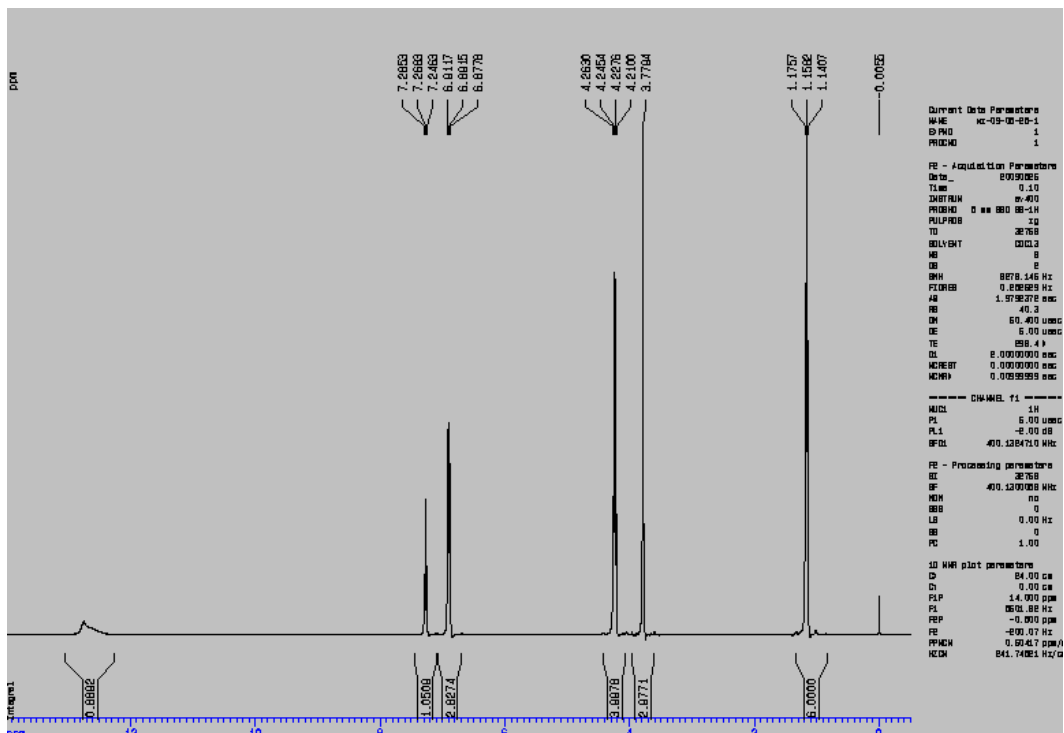
2b

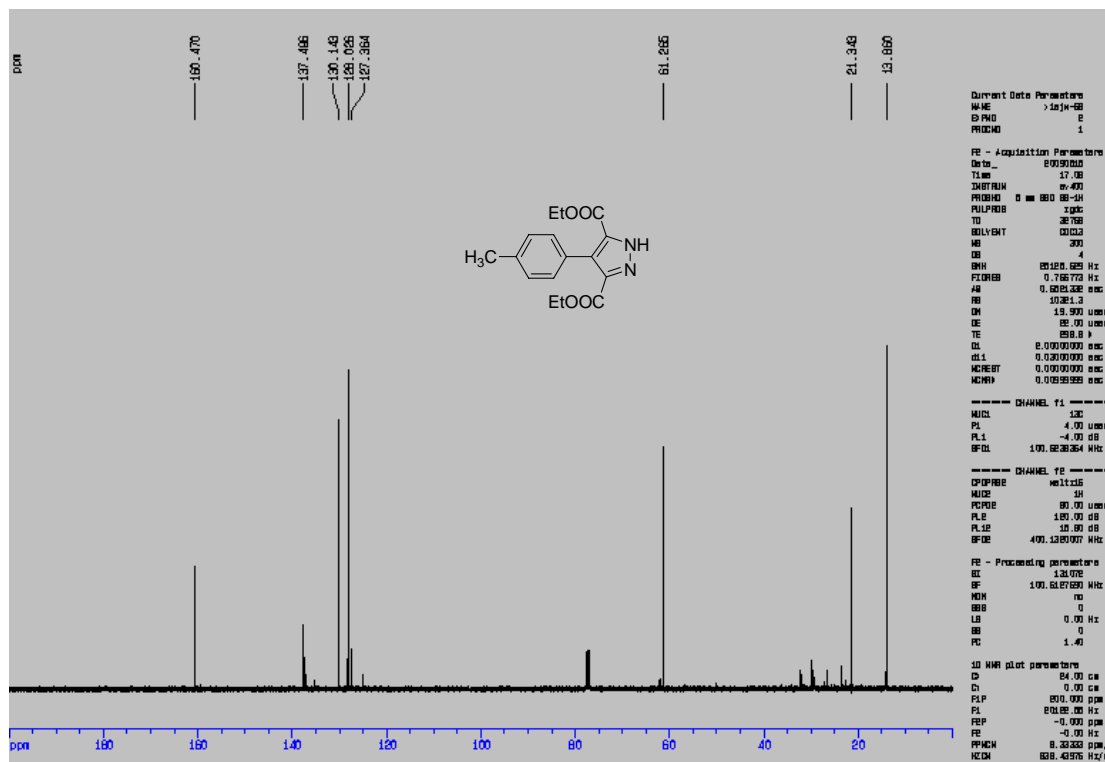
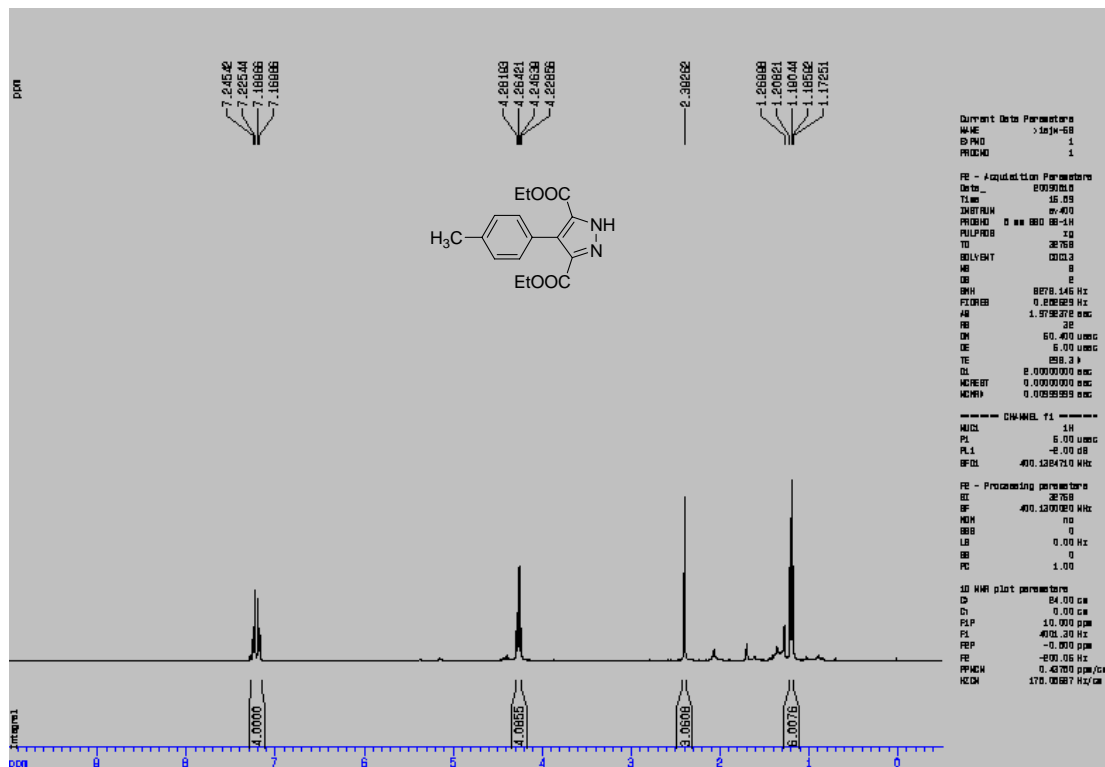


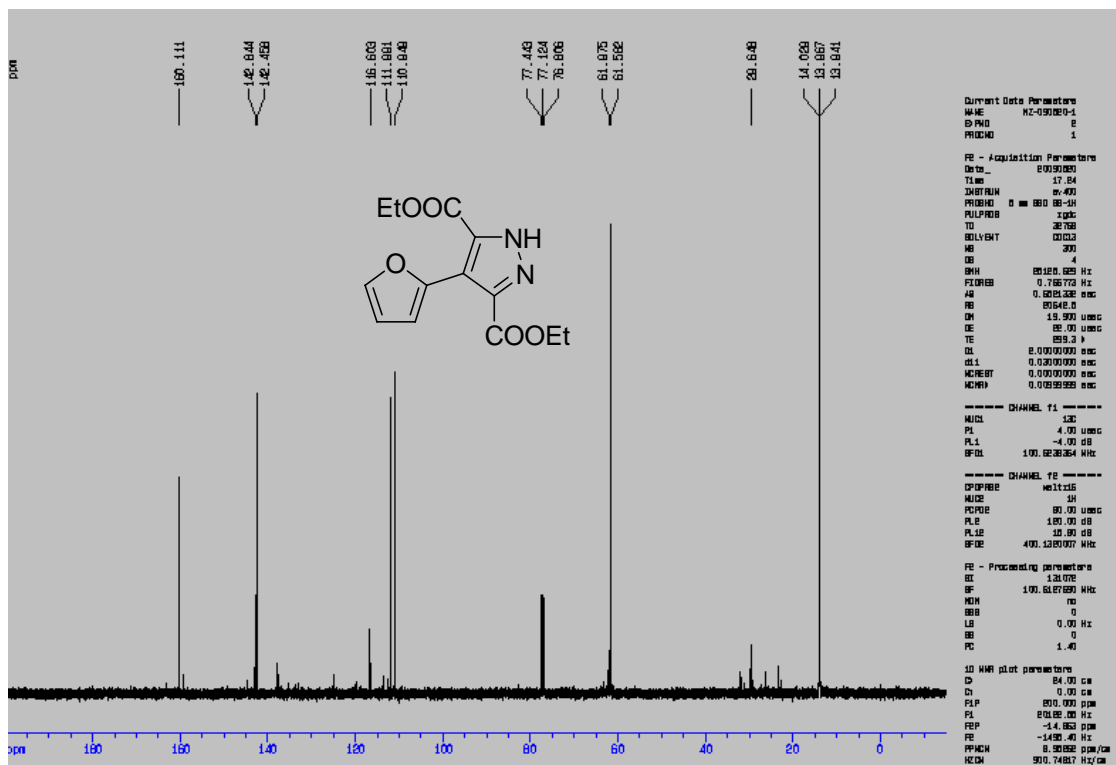
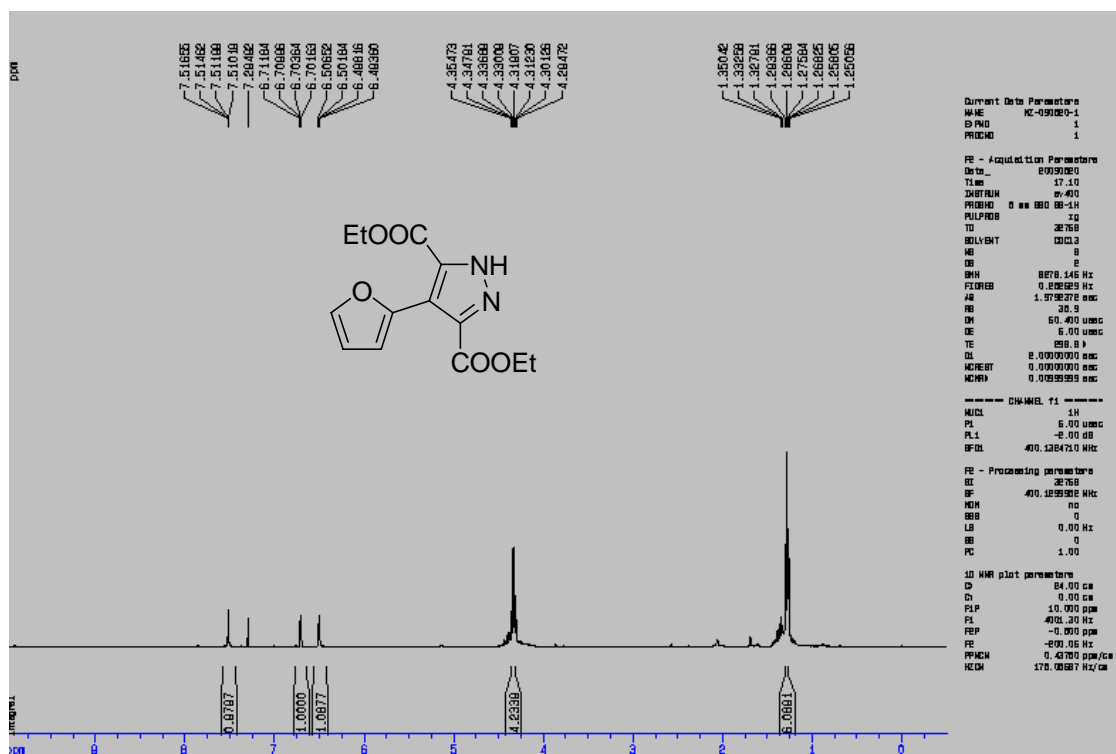
2c

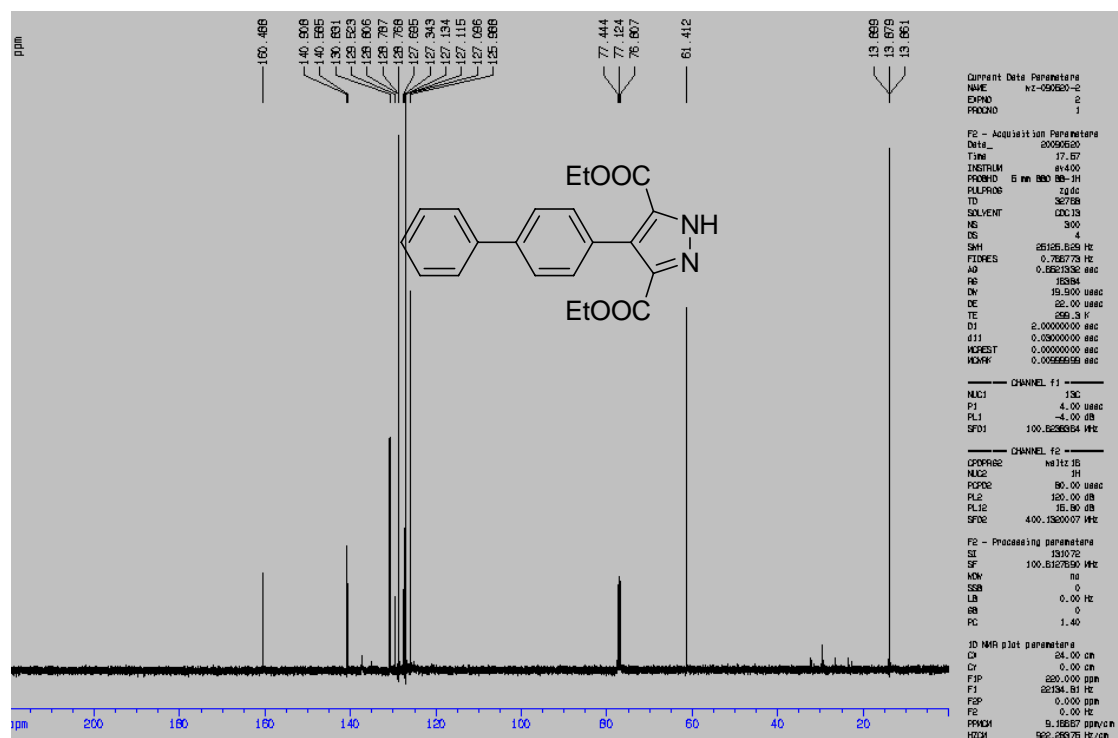
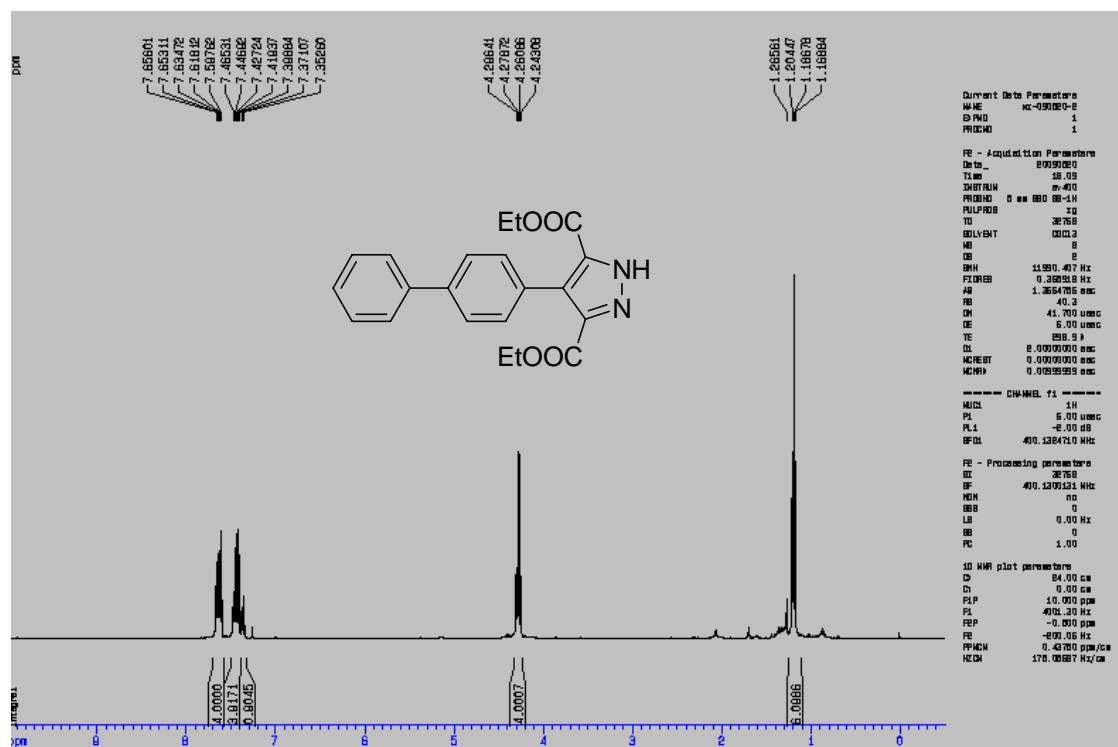


2d

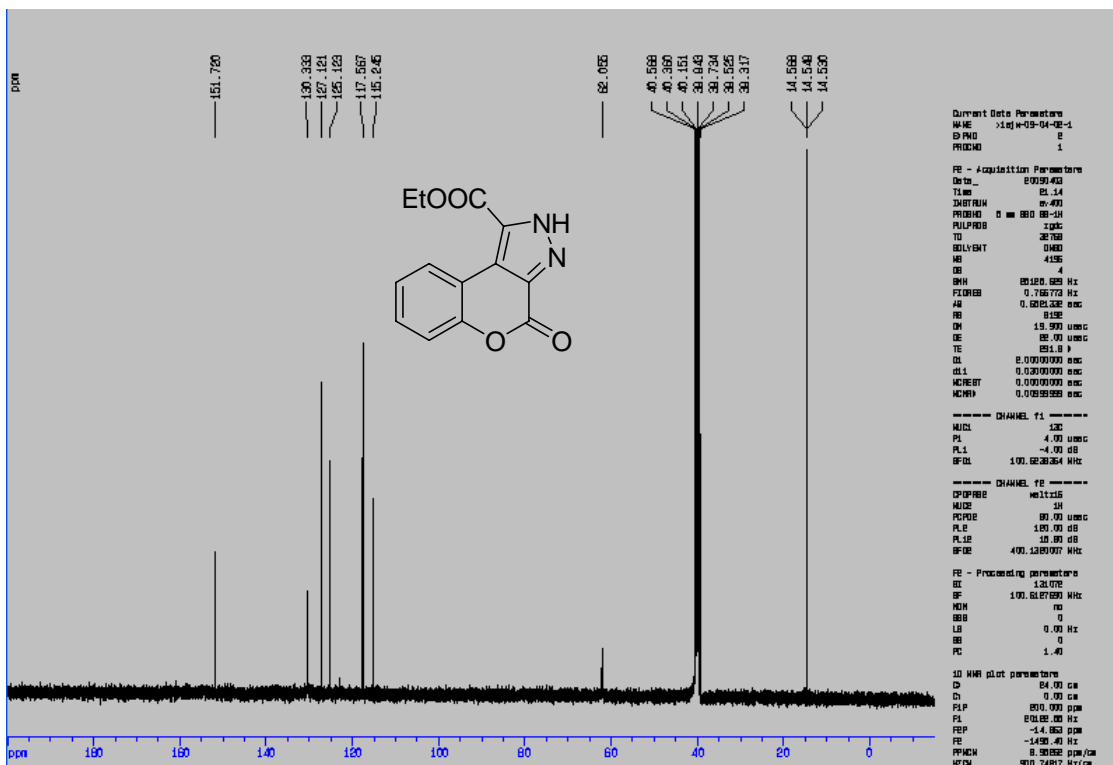
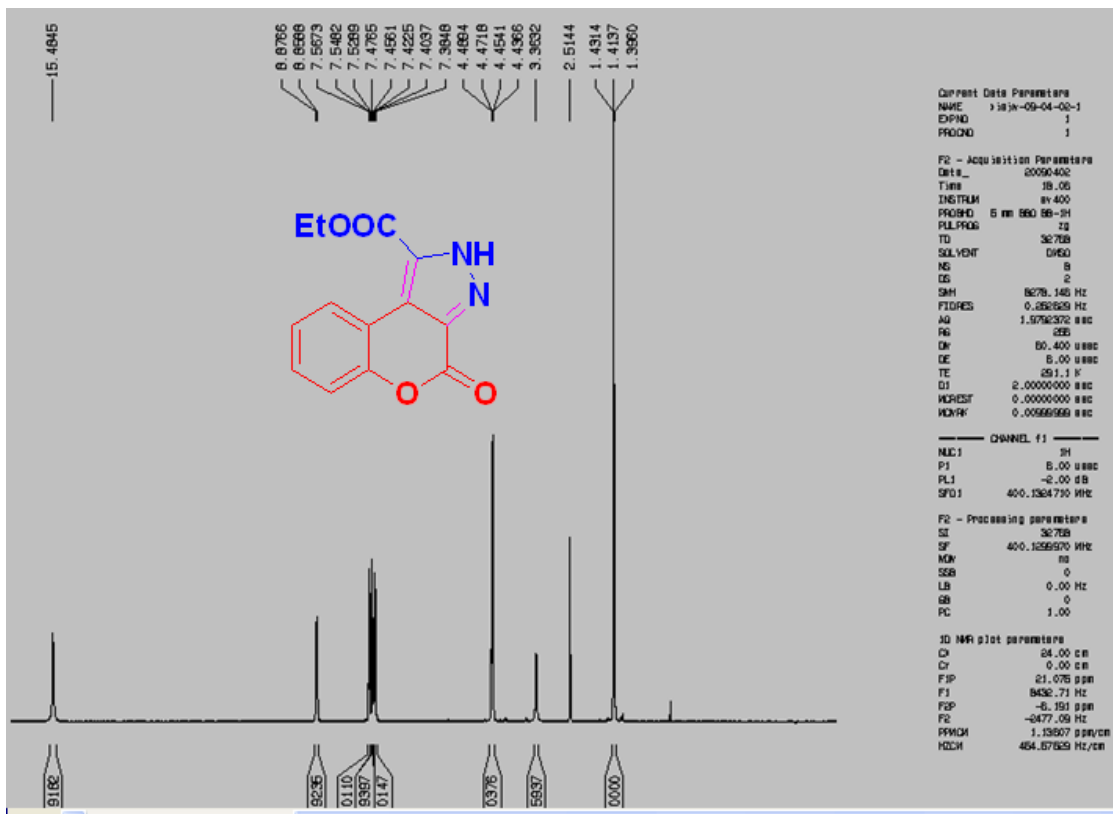




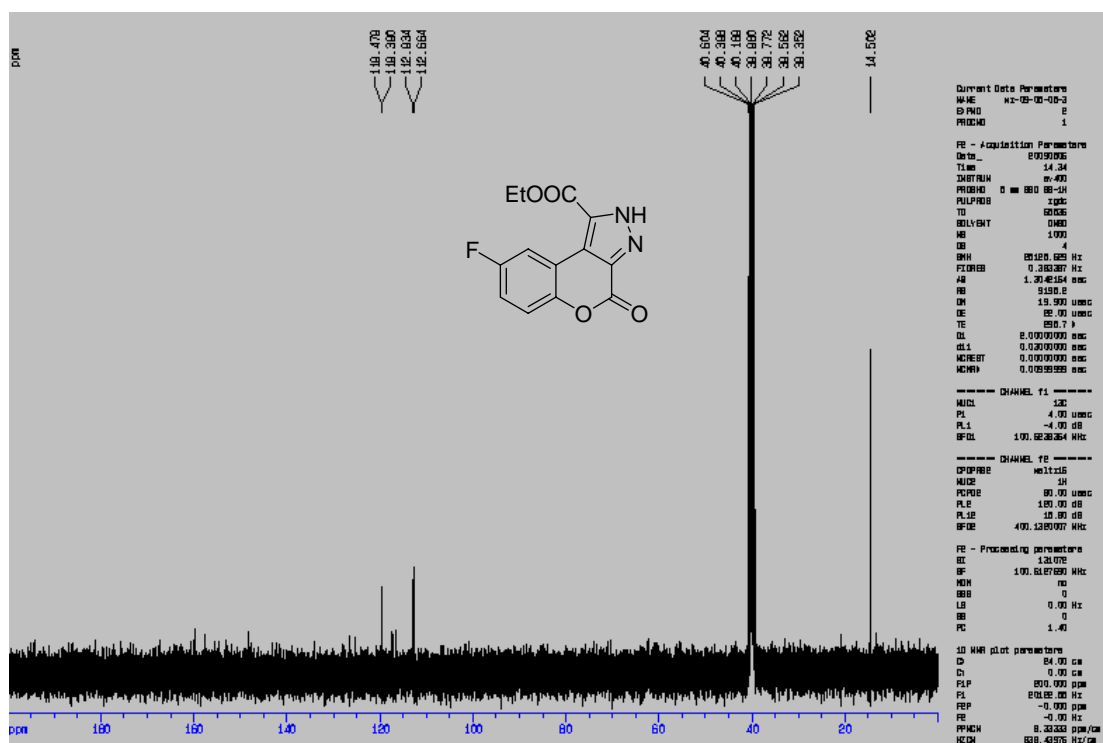
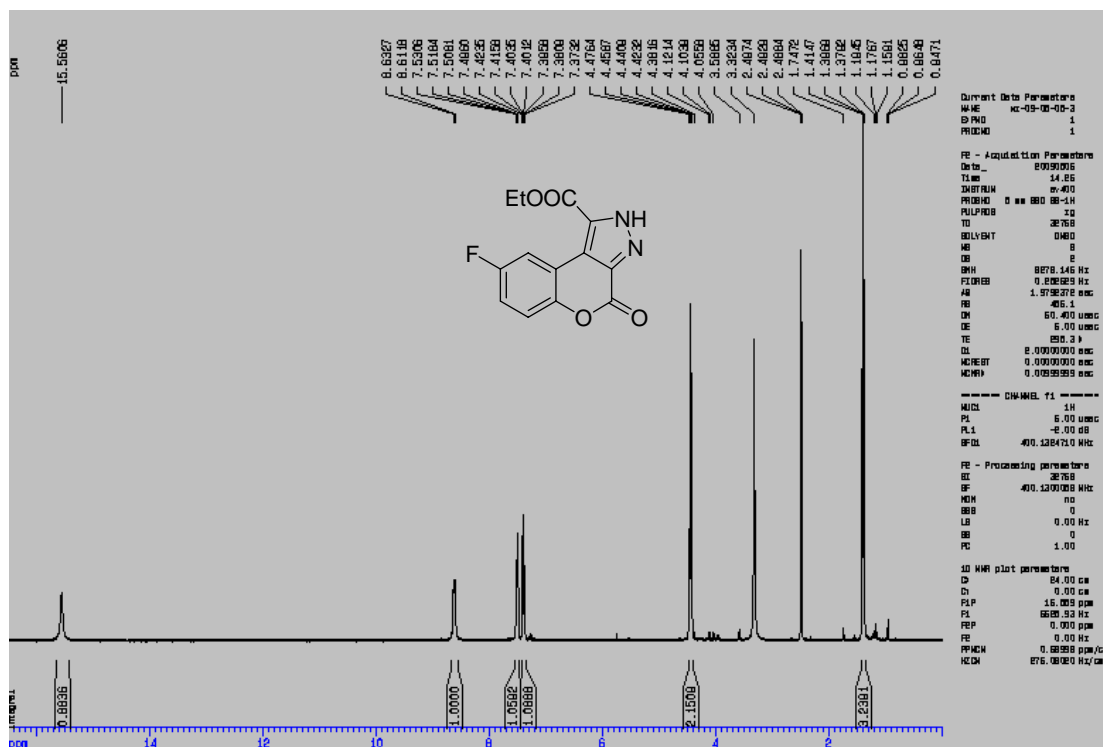




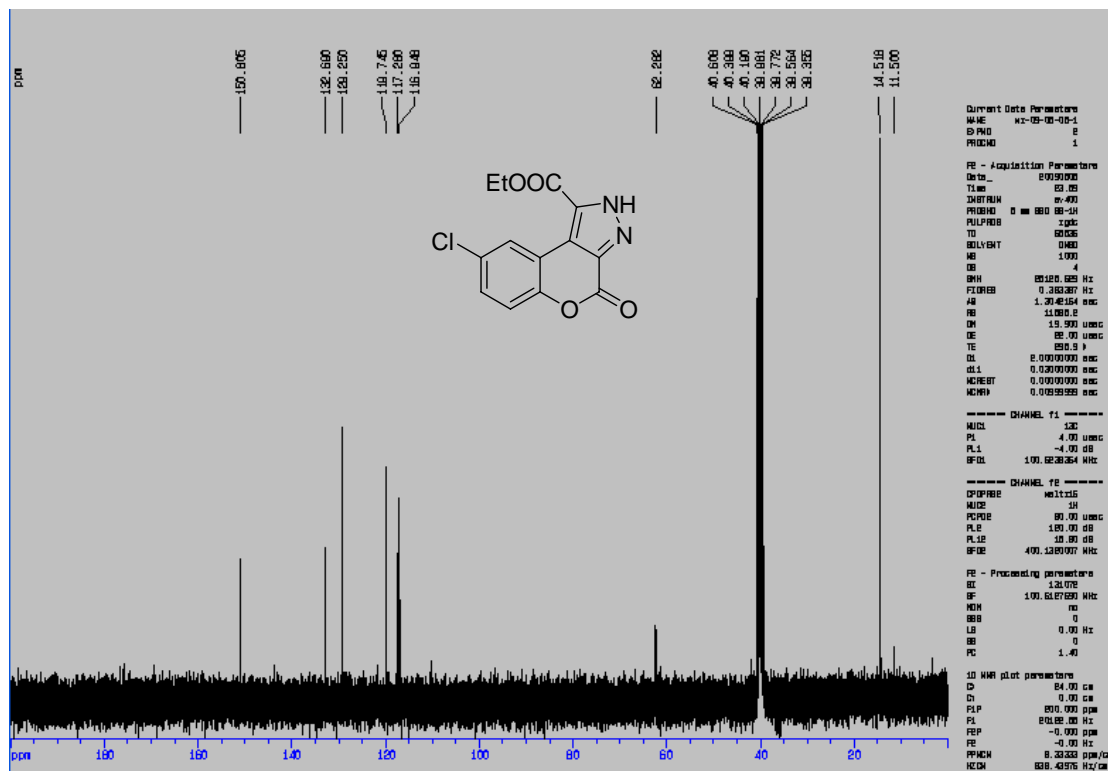
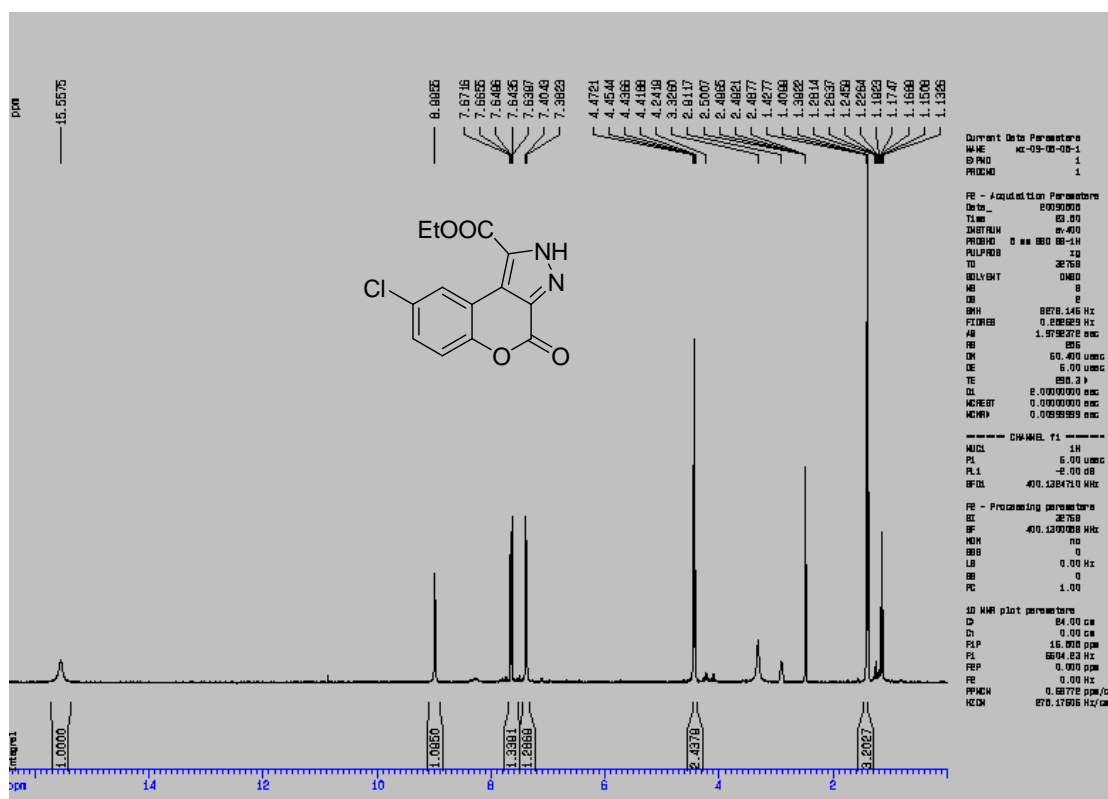
4a



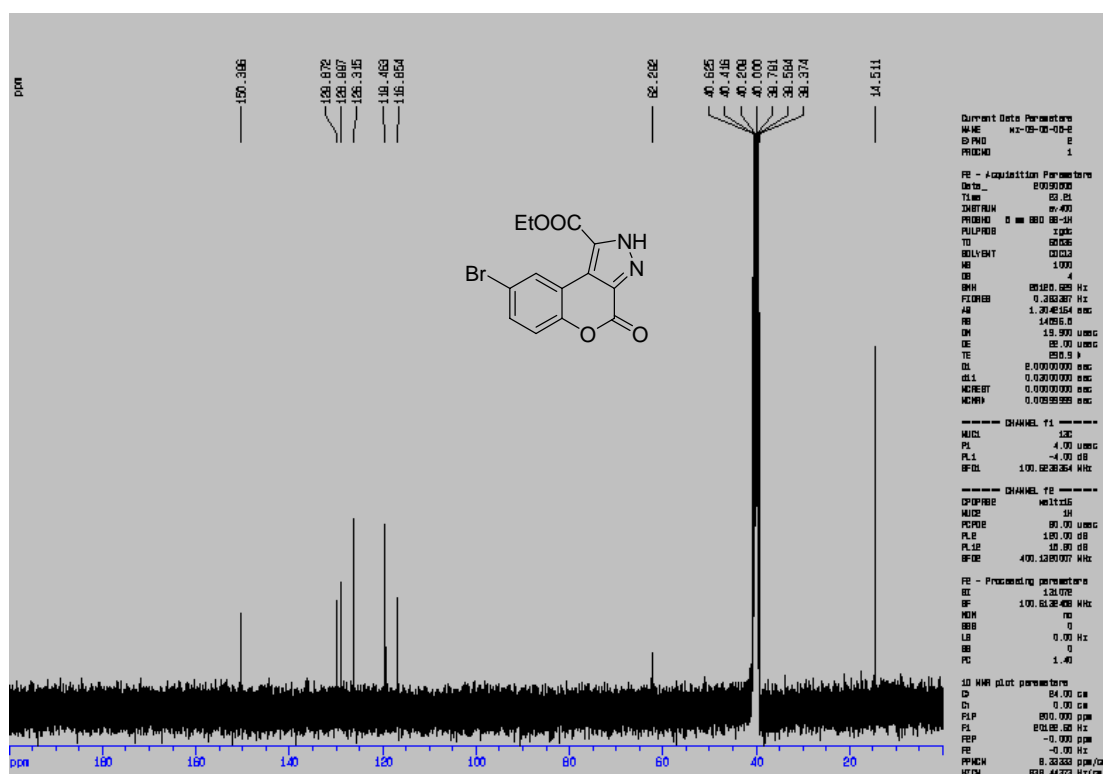
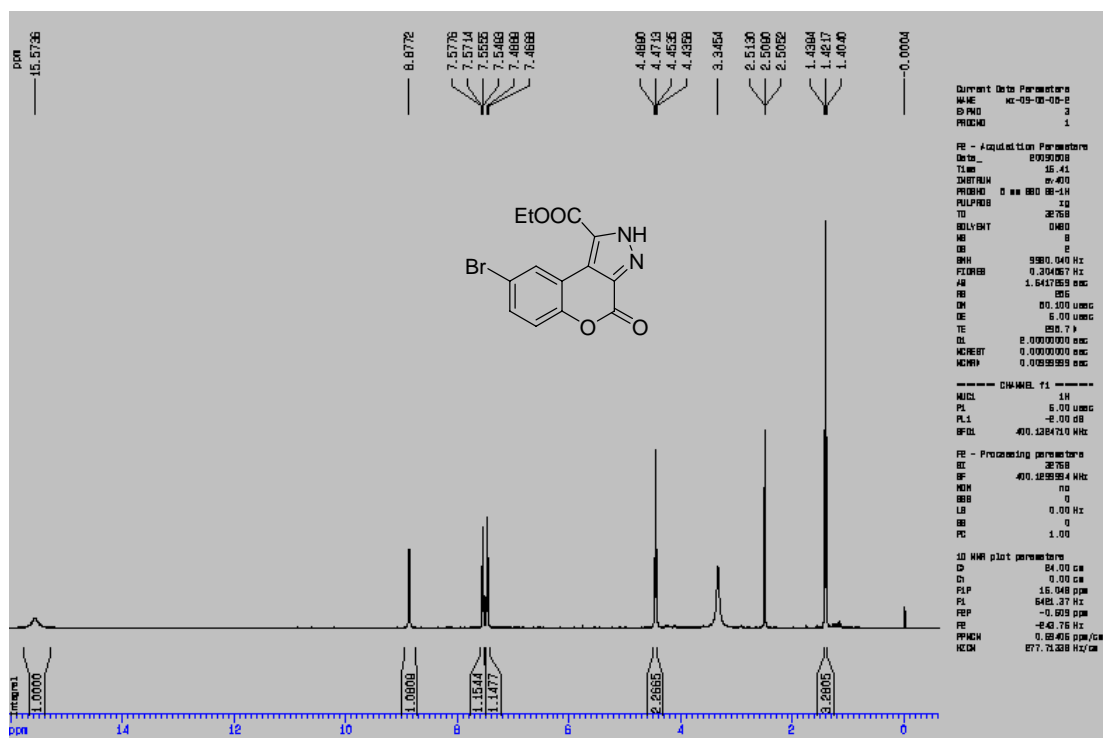
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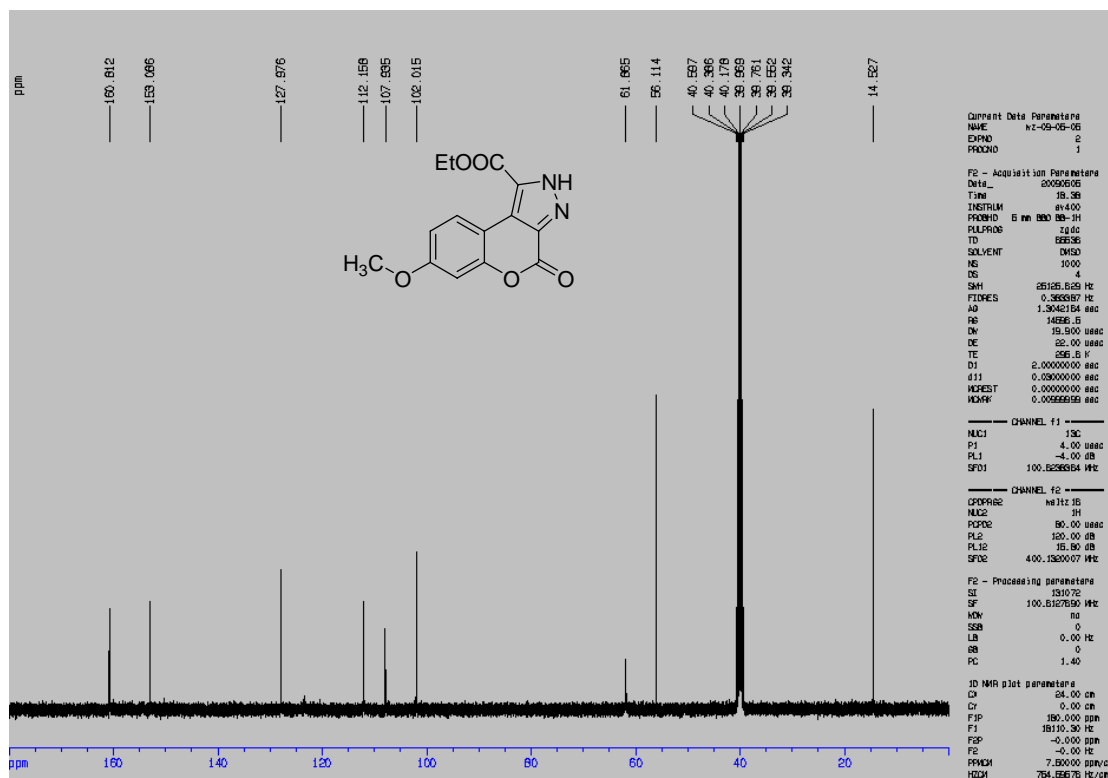
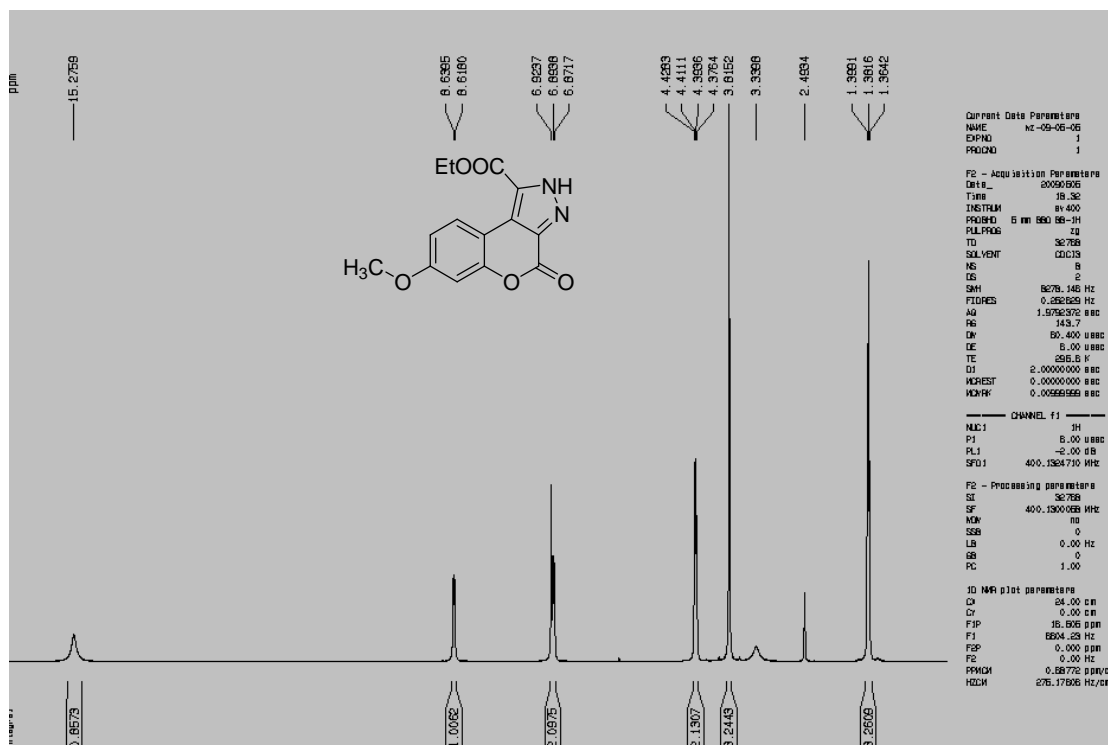
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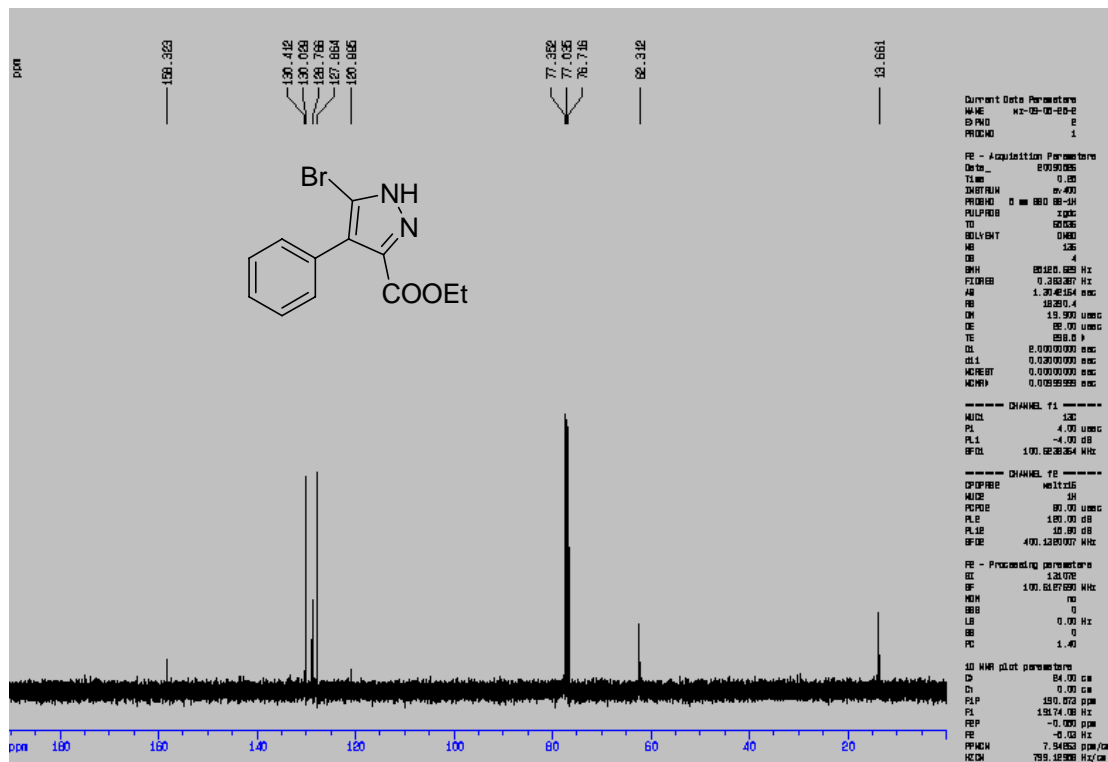
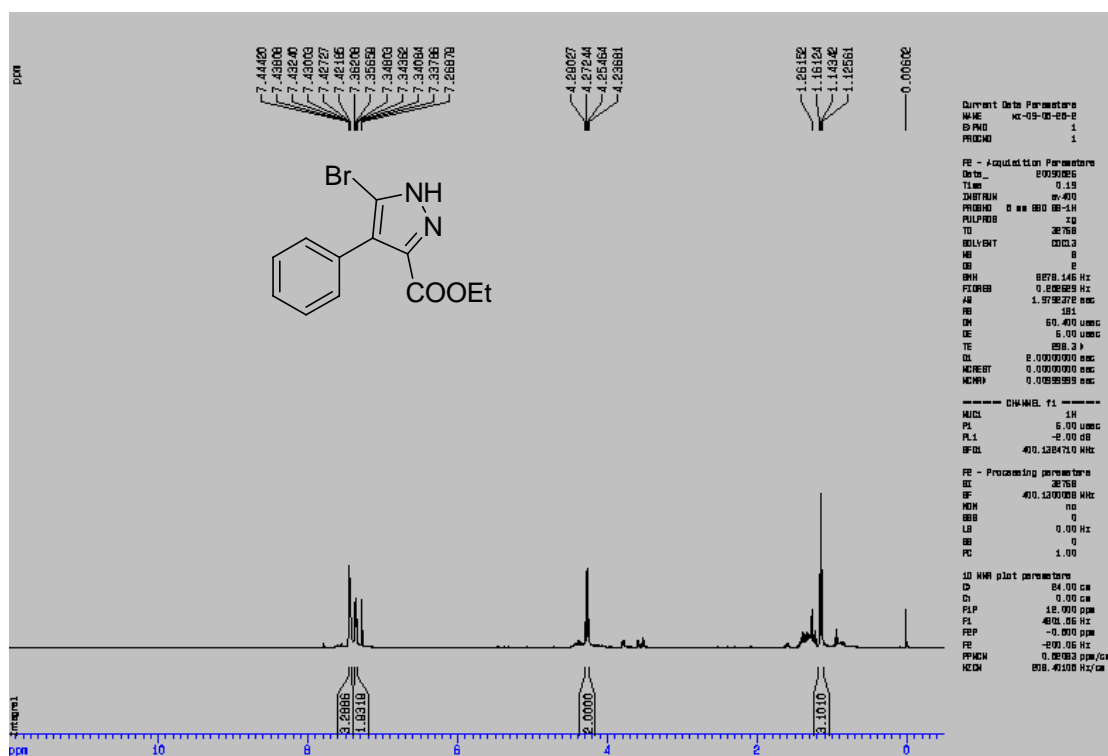
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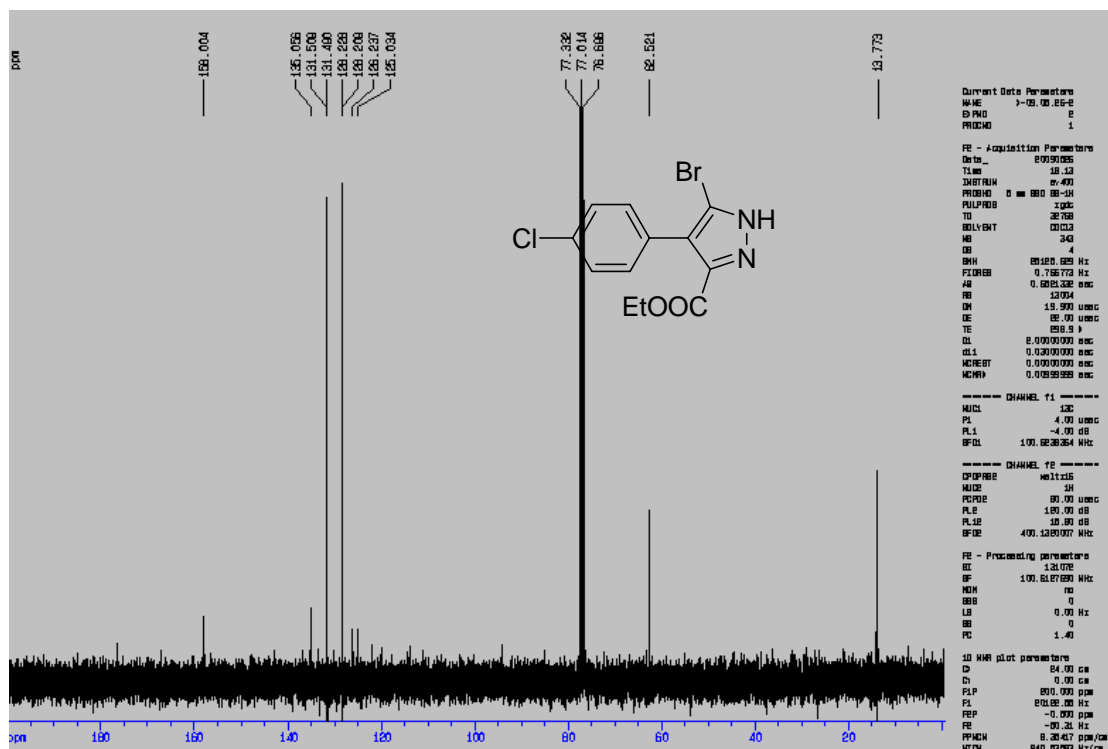
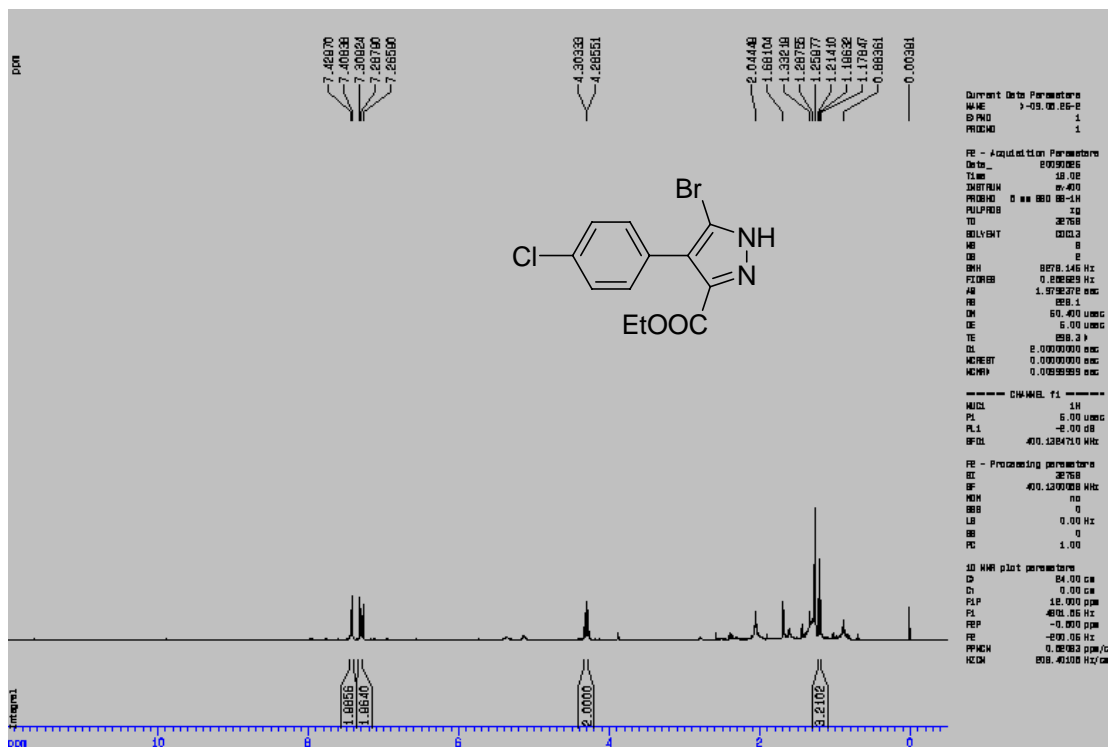
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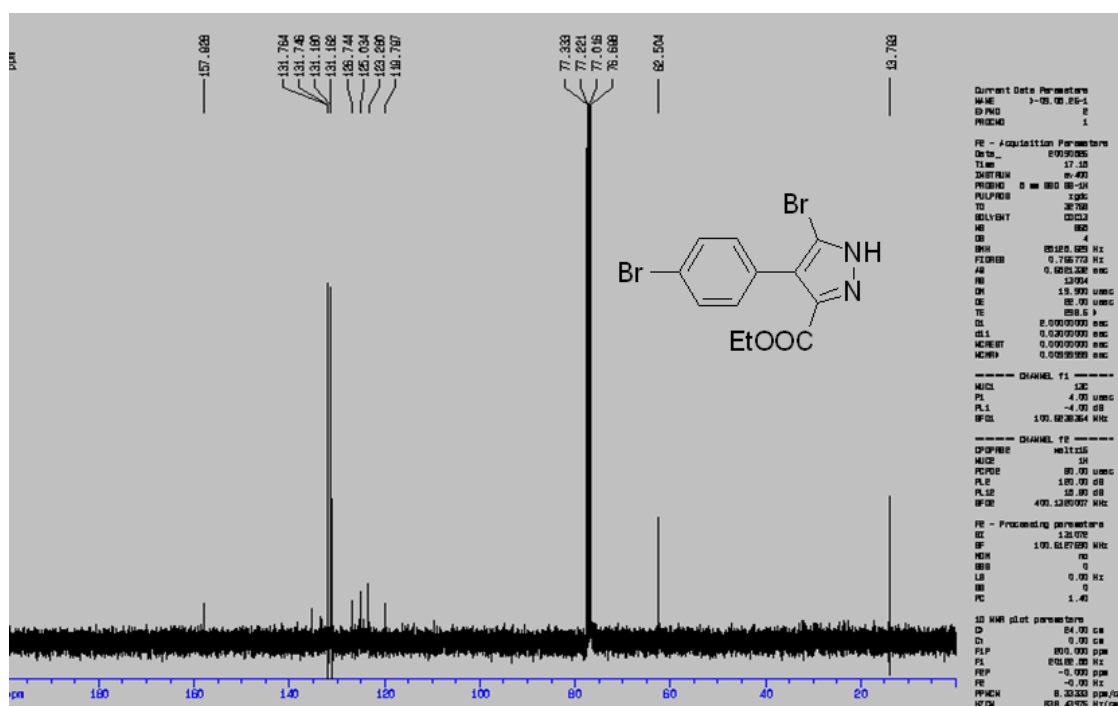
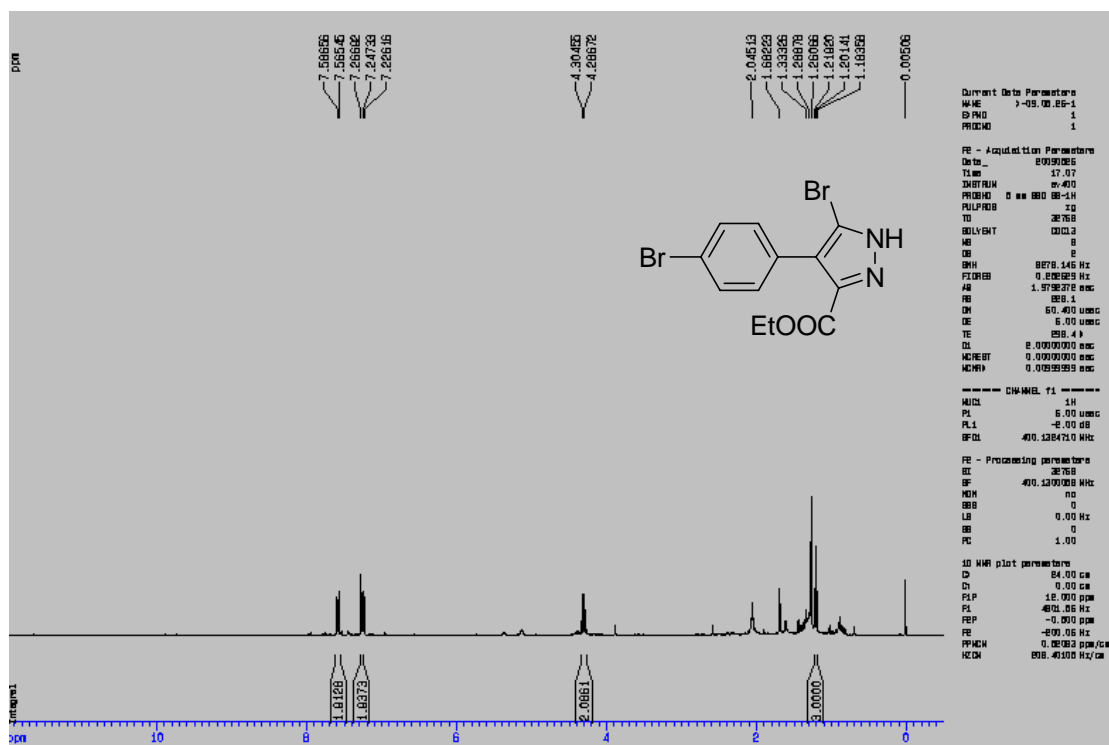


6a

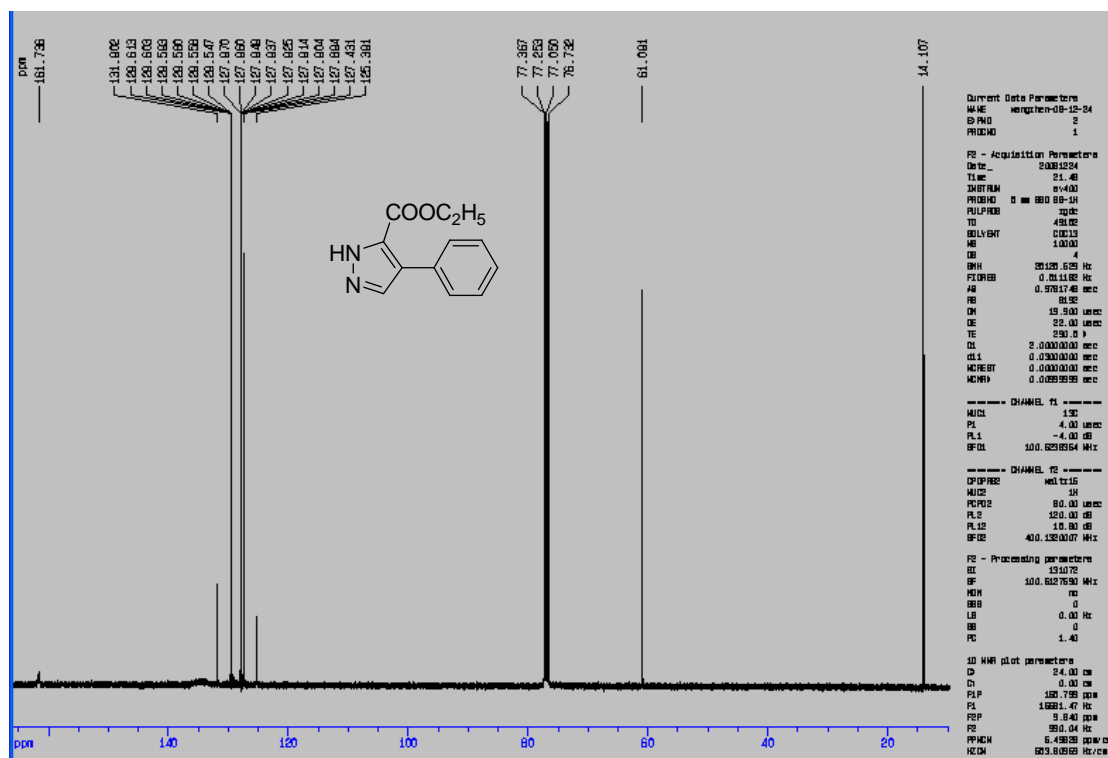
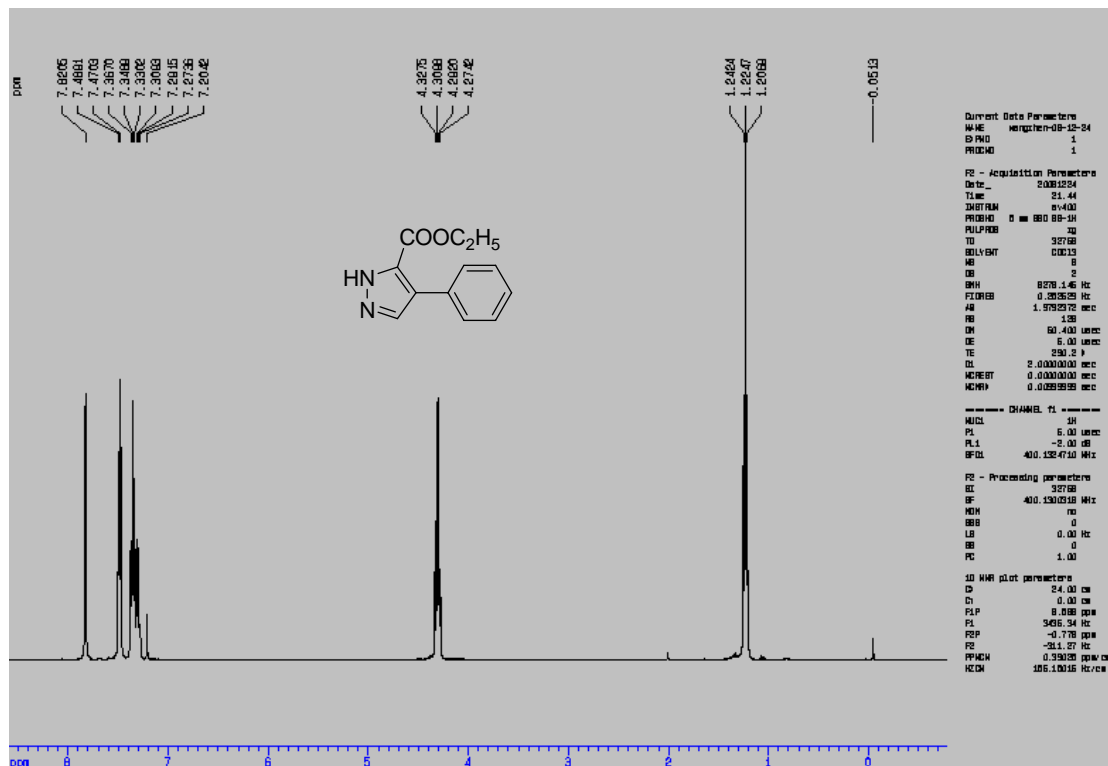


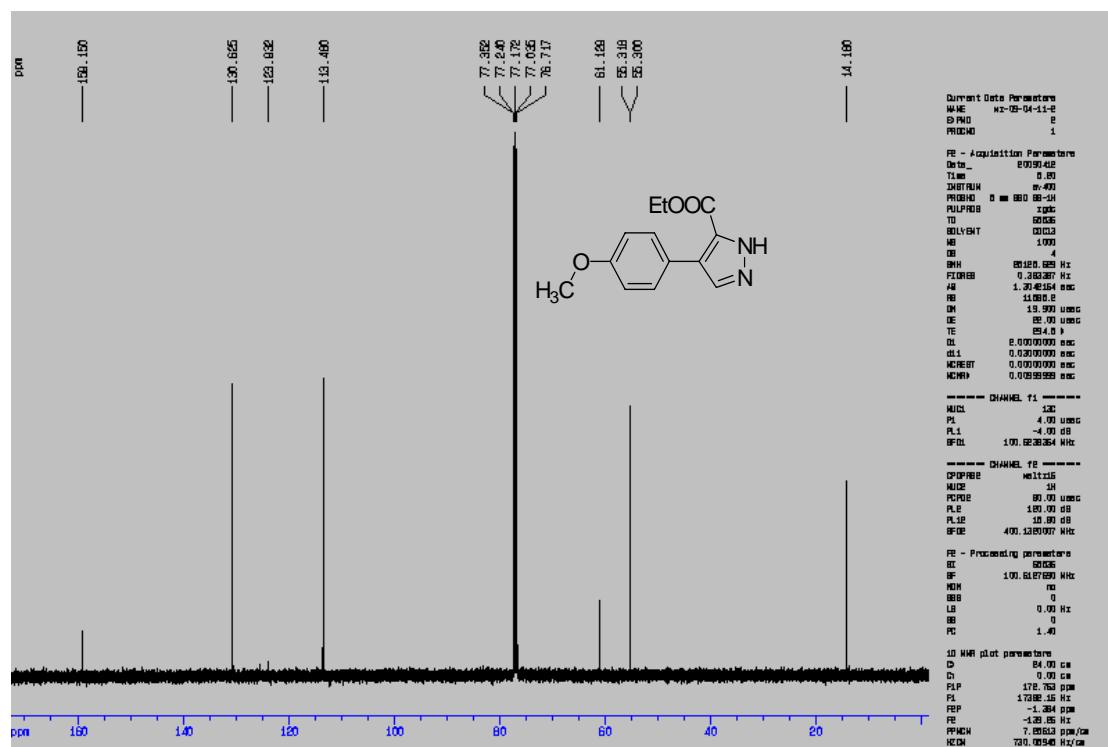
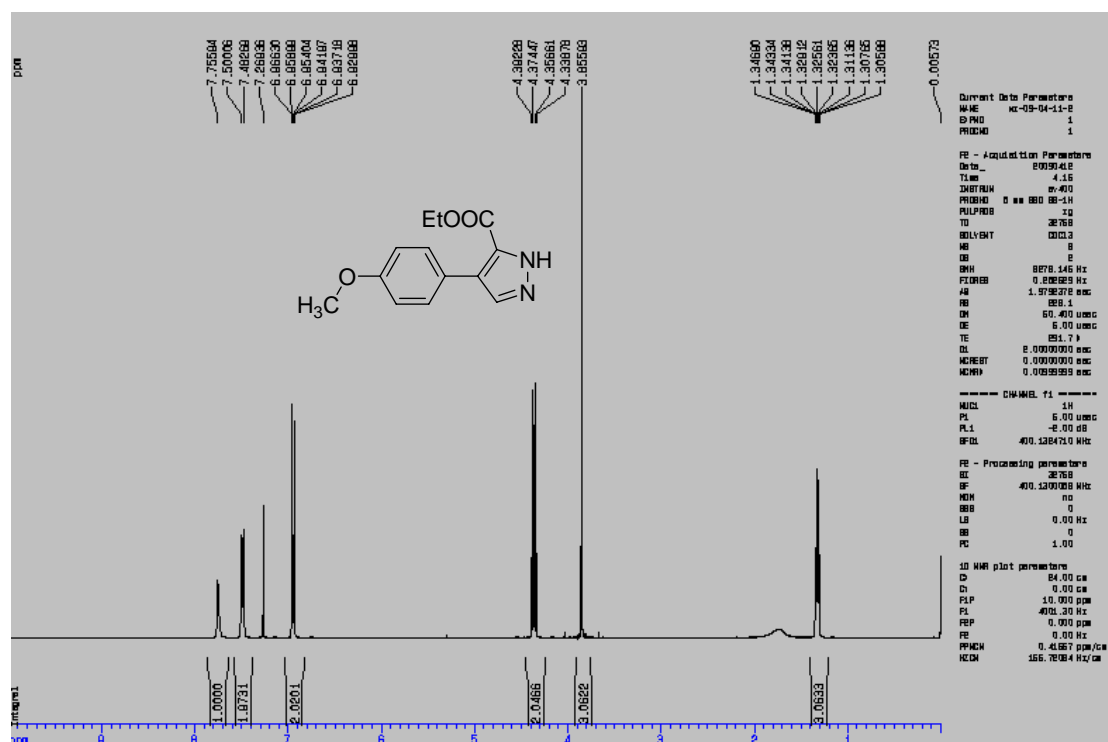
6b





8a





8d

