Supporting information

Rhodium/Bisphosphine-Thiourea-Catalyzed Highly Enantioselective Hydrogenation of α,β-Unsaturated *N*-Acylpyrazoles

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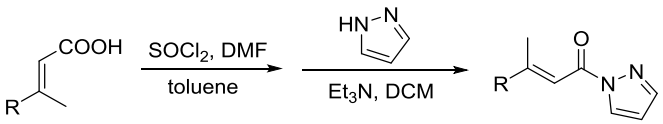
Content

I. General Remarks

All the reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under a positive pressure of nitrogen or in the nitrogen-filled glovebox. Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers without further purification. Anhydrous solvents were purchased from Sigma-Aldrich and transferred by syringe. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded on a Bruker ADVANCE III (400 MHz) spectrometer with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts are reported in parts per million (ppm, δ scale) downfield from TMS at 0.00 ppm and referenced to the $CDCl_3$ at 7.26 ppm (for ^{1}H NMR) or 77.0 ppm (for euteriochloroform). Data are reported as: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in hertz (Hz) and signal area integration in natural numbers. ^{13}C NMR and ^{31}P NMR analyses were run with decoupling. Enantiomeric excess values were determined by Daicel chiral column on an Agilent 1260 Series HPLC instrument. Optical rotations $[\alpha]_D$ were measured on a PERKIN ELMER polarimeter 343 instrument.

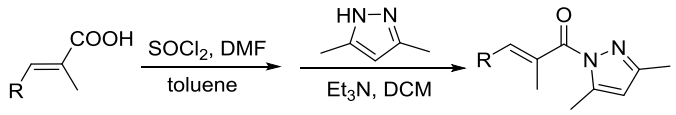
II. General procedure for the synthesis of compounds 1and 3

General Procedure for (*E*)-3,5-dimethyl-1-(3-butanonyl)pyrazoles:



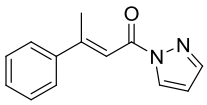
To a solution of the carboxylic acid [1] in toluene at room temperature under N_2 was added dropwise of $SOCl_2$ (200 mmol) followed by a catalytic amount of dry DMF. The reaction was allowed to stir at 80 ^{o}Cfor 2h. Toluene and excess sulfoxide chloride was removed by distillation and the result acid chloride was used immediately without further purification. To a solution of acid chloride in DCM, pryzole (22 mmol) and Et_3N (40 mmol) were added to the solution at 0 ^{o}C. After stirring at room temperature for 1 h, the reaction mixture was poured into water and extracted with dichloromethane. The combined extracts were washed with brine, dried with magnesium sulfate, and evaporated in vacuo. The residue was purified by FC (silica gel, petroleum ether/ethyl acetate = 20:1) to provide pure (*E*)-β-arylbut-2-enoic pyrazolamide.

General Procedure for (*E*)-β-substituted methacrylic pyrazolamide:



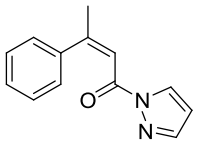
To a solution of the carboxylic acid [2] in toluene at rt under an atmosphere of N_2 was added dropwise of $SOCl_2$ (200 mmol) followed by a catalytic amount of dry DMF. The reaction was allowed to stir at 80 °C for 2h. Toluene and excess sulfoxide chloride was removed by distillation and the result acid chloride was used immediately without further purification. To a solution of acid chloride in DCM, pryzole (22 mmol) and Et_3N (40 mmol)were added to the solution at 0°C. After stirring at room temperature for 1 h, the reaction mixture was poured into water and extracted with dichloromethane. The combined extracts were washed with brine, dried with magnesium sulfate, and evaporated in vacuo. The residue was purified by FC(silicagel, petroleum ether/ethyl acetate = 20:1) to provide analytically (*E*)-β-substituted methacrylic pyrazolamide.

(*E*)-3-phenyl-1-(1H-pyrazol-1-yl)but-2-en-1-one **1a**



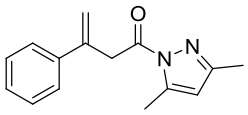
Light yellow solid; yield: 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.38 (s, 1H), 7.73 (s, 1H), 7.62-7.60 (m, 3H), 7.42-7.41 (m, 3H), 6.47-6.46 (m, 1H), 2.74 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.3, 160.5, 143.4, 142.2, 129.7, 128.6, 128.5, 126.7, 114.8, 109.4, 19.0; ESI-HRMS Calculated for $C_{13}H_{13}N_2O^+$([M+H]$^+$): 213.1022, found 213.1018.

(*Z*)-3-phenyl-1-(1H-pyrazol-1-yl)but-2-en-1-one **1a-1**



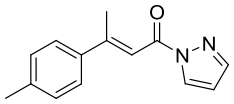
Yellow oil; yield: 10%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.13 (s, 1H), 7.66 (s, 1H), 7.33-7.27 (m, 3H), 7.21-7.18 (m, 3H), 6.33 (s, 1H), 2.27(s, 3H).

1-(3,5-dimethyl-1H-pyrazol-1-yl)-3-phenylbut-3-en-1-one **1a-2**



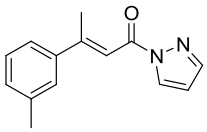
Yellow oil; yield: 10%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50-7.48 (m, 2H), 7.35-7.29 (m, 3H), 5.97 (s, 1H), 5.63 (s, 1H), 5.26 (s, 1H), 4.37 (s, 2H), 2.49 (s, 3H), 2.27 (s, 3H).

(*E*)-1-(1H-pyrazol-1-yl)-3-p-tolylbut-2-en-1-one **1b**



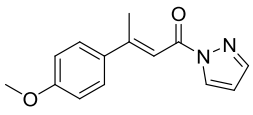
White solid; yield: 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.38 (d, *J* = 4.0 Hz, 1H), 7.73 (s, 1H), 7.61 (s, 1H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.46-6.45 (m, 1H), 2.72 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.3, 160.5, 143.3, 140.1, 139.2, 129.3, 128.5, 126.6, 113.8, 109.3, 21.3, 18.8; ESI-HRMS Calculated for $C_{14}H_{15}N_2O^+$([M+H]$^+$): 227.1179, found 227.1175.

(*E*)-1-(1H-pyrazol-1-yl)-3-m-tolylbut-2-en-1-one **1c**



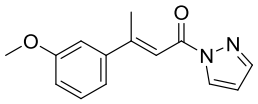
Colorless oil; yield: 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.38 (s, 1H), 7.73 (s, 1H), 7.59 (s, 1H), 7.42 (m, 2H), 7.30-7.23 (m, 2H), 6.46-6.45 (m, 1H), 2.72 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.3, 160.9, 143.3, 142.2, 138.3, 130.5, 128.5, 127.3, 123.8, 114.5, 109.4, 21.5, 19.1; ESI-HRMS Calculated for $C_{14}H_{15}N_2O^+$([M+H]$^+$): 227.1179, found 227.1175.

(*E*)-3-(4-methoxyphenyl)-1-(1H-pyrazol-1-yl)but-2-en-1-one **1d**



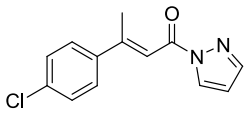
Colorless solid; yield: 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ =8.38 (d, *J* = 4.0 Hz, 1H), 7.72 (s, 1H), 7.63-7.59 (m, 3H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.46-6.45 (m, 1H), 3.85 (s, 3H), 2.73 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.4, 161.1, 160.0, 143.2, 134.2, 128.5, 128.2, 114.0, 112.7, 109.2, 55.4, 18.6; ESI-HRMS Calculated for $C_{14}H_{15}N_2O_2^+$([M+H]$^+$): 243.1128, found 243.1125.

(*E*)-3-(3-methoxyphenyl)-1-(1H-pyrazol-1-yl)but-2-en-1-one **1e**



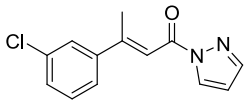
White solid; yield: 72%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.38 (s, 1H), 7.73 (s, 1H), 7.60 (s, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.12 (s, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.46 (s, 1H), 3.86 (s, 3H), 2.72 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.2, 160.4, 159.7, 143.7, 143.4, 129.6, 128.5, 119.2, 115.0, 114.9, 112.5, 109.4, 55.4, 19.1;ESI-HRMS Calculated for $C_{14}H_{15}N_2O_2^+$([M+H]$^+$): 243.1128, found 243.1124.

(*E*)-3-(4-chlorophenyl)-1-(1H-pyrazol-1-yl)but-2-en-1-one **1f**



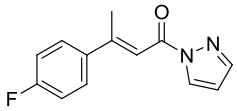
White solid; yield: 72%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.38 (d, *J* = 4.0 Hz, 1H), 7.74 (s, 1H), 7.59-7.55 (m, 3H), 7.39 (d, *J* = 8.0 Hz, 2H), 6.48-6.47 (m, 1H), 2.71 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.1, 158.9, 143.5, 140.5, 135.8, 128.8, 128.6, 128.0, 115.1, 109.6, 18.8; ESI-HRMS Calculated for $C_{13}H_{12}N_2OCl^+$([M+H]$^+$): 247.0633, found 247.0630.

(*E*)-3-(3-chlorophenyl)-1-(1H-pyrazol-1-yl)but-2-en-1-one **1g**



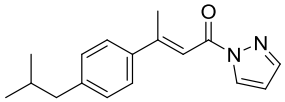
White solid; yield: 51%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.38 (d, *J* = 4.0Hz, 1H), 7.74 (s, 1H), 7.58-7.57 (m, 2H), 7.50-7.47 (m, 1H), 7.39-7.33 (m, 2H), 6.48-6.47 (m, 1H), 2.70 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.0, 158.6, 144.0, 143.5, 129.9, 129.6, 128.6, 126.8, 124.8, 115.8, 109.6, 18.9; ESI-HRMS Calculated for $C_{13}H_{12}N_2OCl^+$([M+H]$^+$): 247.0633, found 247.0630.

(*E*)-3-(4-fluorophenyl)-1-(1H-pyrazol-1-yl)but-2-en-1-one **1h**



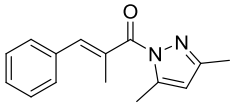
White solid; yield: 47%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.38 (d, *J* = 4.0 Hz, 1H), 7.74 (s, 1H), 7.62-7.57 (m, 3H), 7.13-7.09 (m, 2H), 6.47 (s, 1H), 2.72 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ =163.7 (d, *J* = 249.0 Hz), 163.1, 159.1, 143.4, 138.1 (d, *J* = 3.0 Hz), 128.7, 128.6 (d, *J* = 4.0 Hz), 115.6 (d, *J* = 22.0 Hz), 114.6, 109.5, 18.9; ESI-HRMS Calculated for $C_{13}H_{12}N_2OF^+$([M+H]$^+$): 213.0928, found 213.0925.

(*E*)-3-(4-isobutylphenyl)-1-(1H-pyrazol-1-yl)but-2-en-1-one **1i**



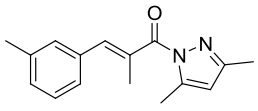
Dark yellow oil; yield: 47%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.39-8.38 (m, 1H), 7.73 (s, 1H), 7.62 (s, 1H), 7.56 (d, *J* = 4.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.46 (s, 1H), 2.74 (s, 3H), 2.51 (d, *J* = 8.0 Hz, 2H), 1.94-1.84 (m, 1H), 0.92 (d, *J* = 8.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.3, 160.7, 143.9, 143.3, 139.4, 129.4, 128.5, 126.5, 113.8, 109.3, 45.2, 30.2, 22.4, 18.8; ESI-HRMS Calculated for $C_{17}H_{21}N_2O^+$([M+H]$^+$): 269.1548, found 269.1641.

(*E*)-1-(3,5-dimethyl-1H-pyrazol-1-yl)-2-methyl-3-phenylprop-2-en-1-one **3a**



Colorless solid; yield: 75%; ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.48-7.46 (m, 2H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.34-7.31 (m, 2H), 6.02 (s, 1H), 2.57 (s, 3H), 2.30 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 171.2, 151.7, 144.6, 139.9, 135.8, 131.8, 129.8, 128.3, 110.7, 16.4, 14.1, 13.9;ESI-HRMS Calculated for $C_{15}H_{17}N_2O^+$([M+H]$^+$): 241.1335, found 241.1328.

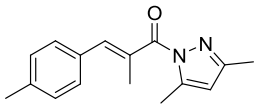
(*E*)-1-(3,5-dimethyl-1H-pyrazol-1-yl)-2-methyl-3-m-tolylprop-2-en-1-one **3e**



Colorless oil; yield: 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30-7.27 (m, 4H), 7.14 (d, *J* = 8.0 Hz), 6.02 (s, 1H), 2.56 (s, 3H), 2.38 (s, 3H), 2.29 (s, 3H), 2.25 (s, 3H);^{13}C NMR (101 MHz,

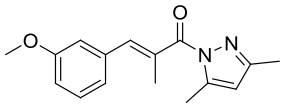
$CDCl_3$) δ = 171.2, 151.7, 144.6, 140.3, 137.9, 135.7, 131.6, 130.6, 129.1, 128.2, 126.9, 110.7, 31.0, 21.5, 16.4, 14.1, 13.9; ESI-HRMS Calculated for $C_{16}H_{19}N_2O^+$([M+H]$^+$): 255.1492, found 255.1486.

(*E*)-1-(3,5-dimethyl-1H-pyrazol-1-yl)-2-methyl-3-p-tolylprop-2-en-1-one **3f**



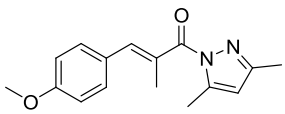
Colorless solid; yield: 75%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.01 (s, 1H), 2.56 (s, 3H), 2.37 (s, 3H), 2.29 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 171.3, 151.6, 144.6, 140.4, 138.5, 132.9, 130.8, 129.9, 129.1, 110.6, 21.4, 16.4, 14.1, 13.9;ESI-HRMS Calculated for $C_{16}H_{19}N_2O^+$([M+H]$^+$): 255.1492, found 255.1484.

(*E*)-1-(3,5-dimethyl-1H-pyrazol-1-yl)-3-(3-methoxyphenyl)-2-methylprop-2-en-1-one **3g**



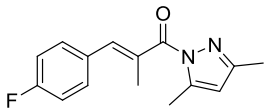
Colorless oil, yield: 66%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34-7.27 (m, 2H), 7.06 (d, *J* = 8.0 Hz, 1H), 7.00 (s, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.02 (s, 1H), 3.83 (s, 3H), 2.57 (s, 3H), 2.29 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 171.1, 159.4, 151.8, 144.6, 139.7, 137.1, 132.2, 129.3, 122.3, 115.1, 114.0, 110.8, 55.3, 16.4, 14.1, 13.9; ESI-HRMS Calculated for $C_{16}H_{19}N_2O_2^+$([M+H]$^+$): 271.1441, found 271.1434.

(*E*)-1-(3,5-dimethyl-1H-pyrazol-1-yl)-3-(4-methoxyphenyl)-2-methylprop-2-en-1-one **3h**



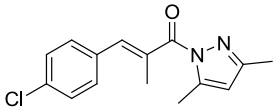
Colorless solid; yield: 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45 (d, *J* = 8.0 Hz, 2H), 7.31 (s, 1H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.01 (s, 1H), 3.84 (s, 3H), 2.55 (s, 3H), 2.30 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 171.3, 159.7, 151.5, 144.5, 140.5, 131.7, 129.4, 128.4, 113.8, 110.5, 55.3, 16.4, 14.0, 13.9; ESI-HRMS Calculated for $C_{16}H_{19}N_2O_2^+$([M+H]$^+$): 271.1441, found 271.1434.

(*E*)-1-(3,5-dimethyl-1H-pyrazol-1-yl)-3-(4-fluorophenyl)-2-methylprop-2-en-1-one **3i**



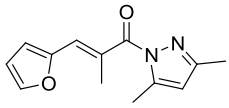
White solid; yield: 54%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47-7.44 (m, 2 H), 7.27 (s, 1H), 7.12-7.07 (m, 2H), 6.02 (s, 1H), 2.57 (s, 3H), 2.28 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 171.0, 162.5 (d, *J* = 248.0 Hz), 151.8, 144.7, 138.6, 131.7, 131.6, 115.5, 115.3, 110.8, 16.3, 14.1, 13.9; ESI-HRMS Calculated for $C_{15}H_{16}N_2OF^+$([M+H]$^+$): 259.1241, found 259.1236.

(*E*)-3-(4-chlorophenyl)-1-(3,5-dimethyl-1H-pyrazol-1-yl)-2-methylprop-2-en-1-one **3j**



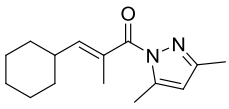
White solid; yield: 54%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41-7.35 (m, 4H), 7.25-7.24 (m, 1H), 6.02 (s, 1H), 2.57 (s, 3H), 2.27 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.1, 151.9, 144.7, 138.2, 134.19, 134.15, 132.6, 131.1, 128.6, 110.9, 16.4, 14.1, 13.9; ESI-HRMS Calculated for $C_{15}H_{16}N_2OCl^+$ ([M+H]$^+$): 275.0946, found 275.0939.

(*E*)-1-(3,5-dimethyl-1H-pyrazol-1-yl)-3-(furan-2-yl)-2-methylprop-2-en-1-one **3k**



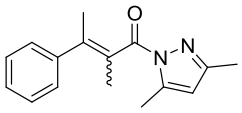
Dark yellow solid; yield: 30%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.55 (d, *J* = 4.0 Hz, 1H); 7.23 (s, 1H), 6.65 (d, *J* = 4.0 Hz, 1H); 6.52-6.50(m, 1H), 6.02 (s, 1H), 2.54 (s, 3H), 2.35 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.6, 151.8, 151.5, 144.6, 144.1, 128.5, 127.9, 115.1, 112.2, 110.6, 16.4, 14.0, 13.9; ESI-HRMS Calculated for $C_{13}H_{15}N_2O_2^+$([M+H]$^+$): 231.1128, found 231.1123.

(*E*)-3-cyclohexyl-1-(3,5-dimethyl-1H-pyrazol-1-yl)-2-methylprop-2-en-1-one **3l**



Colorless oil; yield: 10%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.99 (s, 1H), 5.52 (d, *J* = 8.0 Hz, 1H), 2.58 (s, 3H), 2.24 (s, 3H), 2.04 (s, 3H), 1.70-1.02 (m, 11H).

1-(3,5-dimethyl-1H-pyrazol-1-yl)-2-methyl-3-phenylbut-2-en-1-one **3m**



Yellow oil; yield: 45%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40-7.36 (m, 2H), 7.32-7.26 (m, 3H), 6.00 (s, 1H), 2.61 (s, 3H), 2.25 (s, 3H), 1.96 (s, 3H), 1.91 (s, 3H).

III. General procedure for asymmetric hydrogenation of compounds 1 and 3

General procedure for asymmetric hydrogenation of compound 1

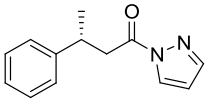
In the nitrogen-filled glovebox,a solution of **L3** (1.1 eqv.) and $Rh(COD)_2BF_4$ (4.9 mg, 0.006 mmol) in 1.2 mL anhydrous EtOH / CH_2Cl_2 (5:1 v/v) was stirred at room temperature for 30 min. 0.4 mL (for substrates **1**) of the resulting solution was transferred by syringeinto a vial charged with **1** (0.1 mmol) in 0.6 mL anhydrous EtOH/CH_2Cl_2 (5:1 v/v). The vials were transferred to an autoclave, which was then charged with 50atm of H_2 and stirred at room temperature for 24 h. The hydrogen gas was released slowly and the solution was concentrated and passed through a short column of silica gel to remove the metal complex. The product was analyzed by NMR spectroscopy for conversion and chiral HPLC for ee values. The absolute configuration was assigned by comparison of the corresponding chiral carboxylic acid with the $[\alpha]_D^{20}$ that reported in the literature.[3]

General procedure for asymmetric hydrogenation of compound 3

In the nitrogen-filled glovebox,a solution of **L3** (1.1 eqv.) and $Rh(NBD)_2BF_4$ (4.9 mg, 0.006 mmol) in 1.2 mL anhydrous CH_2Cl_2 was stirred at room temperature for 30 min. 0.2 mL (for substrates **3**) of the resulting solution was transferred by syringeinto a vial charged with **3** (0.1 mmol) in 0.8 mL anhydrous CH_2Cl_2. The vials were transferred to an autoclave, which was then charged with 50atm of H_2 and stirred at room temperature for 12 h. The hydrogen gas was released slowly and the solution was concentrated and passed through a short column of silica gel to remove the metal complex. The product was analyzed by NMR spectroscopy for conversion

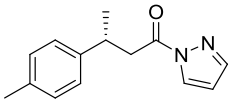
and chiral HPLC for ee values. The absolute configuration was assigned by comparison of the corresponding chiral carboxylic acid with the $[\alpha]_D^{20}$ that reported in the literature.[4]

(*R*)-3-phenyl-1-(1H-pyrazol-1-yl)butan-1-one **2a**



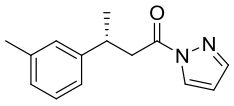
The title compound was purified by flash silica gel chromatography to afford the product. The eluent was petroleum ether: ethyl acetate = 10:1(V/V). Colorless oil; >99% conversion; 20.1 mg, 94% yield; 96% ee; $[\alpha]_D^{25}$ = 5.25 (c = 0.4, $CHCl_3$); The enantiomeric excess was determinedby HPLC on Chiralpak OJ-H column, hexane: isopropanol = 95:5; flow rate = 1.0 mL/min; UVdetection at 240 nm; t_R= 16.77 min (major), 18.71 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.21 (d, *J* = 4.0 Hz, 1H), 7.70 (s, 1H), 7.30-7.20 (m, 5H), 6.42 (s, 1H), 3.53-3.47 (m, 1H), 3.43-3.38 (m, 1H), 1.38 (d, *J* = 4.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.9, 145.6, 143.9, 128.6, 128.3, 126.9, 126.5, 109.6, 42.1, 35.9, 22.1; ESI-HRMS Calculated for $C_{13}H_{15}N_2O^+$([M+H]$^+$): 215.1176; found 215.1179.

(*R*)-1-(1H-pyrazol-1-yl)-3-p-tolylbutan-1-one **2b**



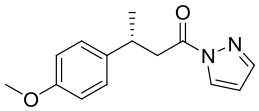
The title compound was purified by flash silica gel chromatography to afford the product. The eluent was petroleum ether: ethyl acetate = 10:1(V/V). Colorless oil; >99% conversion; 21.7 mg, 95% yield; 92% ee; $[\alpha]_D^{25}$ = 2.00 (c = 0.4, $CHCl_3$); The enantiomeric excess was determinedby HPLC on Chiralpak OJ-H column, hexane: isopropanol = 90:10; flow rate = 0.6 mL/min; UVdetection at 240 nm; t_R= 20.93 min (minor), 22.02 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.22 (d, *J* = 4.0 Hz, 1H), 7.70 (s, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.11(d, *J* = 8.0 Hz, 2H), 6.42 (d, *J* = 4.0 Hz, 1H), 3.51-3.45(m, 2H), 3.41-3.34 (m, 1H), 2.31 (s, 3H), 1.35 (d, *J* = 8.0 Hz, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.9, 143.9, 142.6, 136.0, 129.2, 128.3, 126.8, 109.6, 42.1, 35.5, 22.3, 21.1; ESI-HRMS Calculated for $C_{14}H_{17}N_2O^+$ ([M+H]$^+$): 229.1331, found 229.1335.

(*R*)-1-(1H-pyrazol-1-yl)-3-m-tolylbutan-1-one **2c**



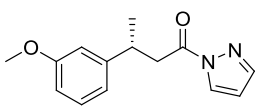
The title compound was purified by flash silica gel chromatography to afford the product. The eluent was petroleum ether: ethyl acetate = 10:1(V/V). Colorless oil; >99% conversion; 22.1 mg, 97% yield; 93% ee; $[\alpha]_D^{25}$ = 2.00 (c = 0.4, $CHCl_3$); The enantiomeric excess was determinedby HPLC on Chiralpak OJ-H column, hexane: isopropanol = 90:10; flow rate = 0.6 mL/min; UVdetection at 240 nm; t_R= 14.73 min (major), 15.74 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.23 (d, *J* = 4.0 Hz, 1H), 7.71 (s, 1H), 7.19-7.17 (m, 1H), 7.10-7.01 (m, 3H), 6.43-6.42 (m,1H), 3.51-3.45 (m, 2H), 3.42-3.38 (m, 1H), 2.33 (s, 3H), 1.36 (d, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.9, 145.6, 143.9, 138.1, 128.4, 128.3, 127.7, 127.2, 123.9, 109.6, 42.0, 35.8, 22.2, 21.5; ESI-HRMS Calculated for $C_{14}H_{17}N_2O^+$([M+H]$^+$): 229.1332, found 229.1335.

(*R*)-3-(4-methoxyphenyl)-1-(1H-pyrazol-1-yl)butan-1-one **2d**



The title compound was purified by flash silica gel chromatography to afford the product. The eluent was petroleum ether: ethyl acetate = 10:1(V/V). Colorless oil; >99% conversion; 22.9 mg, 94% yield; 93% ee; $[\alpha]_D^{25}$ = 1.50 (c = 0.4, $CHCl_3$); The enantiomeric excess was determinedby HPLC on Chiralpak AD-H column, hexane: isopropanol = 90:10; flow rate = 0.6 mL/min; UVdetection at 240 nm; t_R= 32.97 min (major), 36.70 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.21 (s, 1H), 7.70 (s, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.0 Hz, 2H), 6.42 (d, *J* = 4.0 Hz, 1H), 3.78 (s, 3H), 3.48-3.43 (m, 2H), 3.39-3.32 (m, 1H), 1.35 (d, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.9, 158.1, 143.9, 137.7, 128.3, 127.8, 113.9, 109.6, 55.2, 42.3, 35.1, 22.3; ESI-HRMS Calculated for $C_{14}H_{17}N_2O_2^+$ ([M+H]$^+$): 245.1281, found 245.1285.

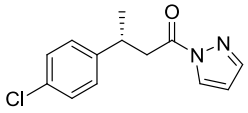
(*R*)-3-(3-methoxyphenyl)-1-(1H-pyrazol-1-yl)butan-1-one **2e**



The title compound was purified by flash silica gel chromatography to afford the product. The eluent was petroleum ether: ethyl acetate = 10:1(V/V). Colorless oil; >99% conversion; 22.7 mg, 93%

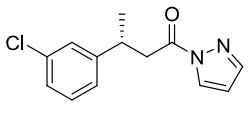
yield; 94% ee; $[\alpha]_D^{25}$ = 4.00 (c = 0.4, $CHCl_3$); The enantiomeric excess was determinedby HPLC on Chiralpak OJ-H column, hexane: isopropanol = 90:10; flow rate = 0.6 mL/min; UVdetection at 240 nm; t_R= 22.64 min (major), 26.43 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.22 (s, 1H), 7.70 (s, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 6.90-6.88 (m, 1H), 6.83 (s, 1H), 6.76-6.73 (m, 1H), 6.42 (s, 1H), 3.79 (s, 3H), 3.52-3.47 (m, 2H), 3.41-3.34 (m, 1H), 1.37 (d, *J* = 4.0 Hz, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.8, 159.7, 147.3, 143.9, 129.5, 128.3, 119.3, 112.8, 111.6, 109.6, 55.2, 42.0, 35.9, 22.1; ESI-HRMS Calculated for $C_{14}H_{17}N_2O_2^+$ ($[M+H]^+$): 245.1279, found 245.1284.

(*R*)-3-(4-chlorophenyl)-1-(1H-pyrazol-1-yl)butan-1-one **2f**



The title compound was purified by flash silica gel chromatography to afford the product. The eluent was petroleum ether: ethyl acetate = 10:1(V/V). Colorless oil; >99% conversion; 23.9 mg, 96% yield; 90% ee; $[\alpha]_D^{25}$ = 5.75 (c = 0.4, $CHCl_3$); The enantiomeric excess was determinedby HPLC on Chiralpak OJ-H column, hexane: isopropanol = 90:10; flow rate = 0.6 mL/min; UVdetection at 240 nm; t_R= 14.08 min (minor), 15.40 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.21 (d, *J* = 4.0 Hz, 1H), 7.70 (s, 1H), 7.27-7.23 (m, 4H), 6.43 (t, *J* = 4.0 Hz, 1H), 3.52-3.45 (m, 2H), 3.40-3.33 (m, 1H), 1.36 (d, *J* = 4.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.6, 144.0, 132.1, 128.7, 128.28, 128.31, 109.7, 89.7, 41.9, 35.3, 22.1; ESI-HRMS Calculated for $C_{13}H_{14}N_2OCl^+$($[M+H]^+$): 249.0783, found 249.0789.

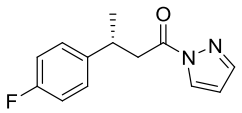
(*R*)-3-(3-chlorophenyl)-1-(1H-pyrazol-1-yl)butan-1-one **2g**



The title compound was purified by flash silica gel chromatography to afford the product. The eluent was petroleum ether: ethyl acetate = 10:1(V/V). Colorless oil; >99% conversion; 23.4 mg, 94% yield; 95% ee; $[\alpha]_D^{25}$ = 3.00 (c = 0.4, $CHCl_3$); The enantiomeric excess was determinedby HPLC on Chiralpak OJ-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UVdetection at 240 nm; t_R= 4.73 min (major), 5.29 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.13 (s, 1H), 7.62 (s, 1H), 7.19-7.15 (m, 4H), 6.35 (s, 1H), 3.42-3.38 (m, 2H), 3.32-3.25 (m, 1H), 1.28 (d, *J* = 8.0 Hz, 3H);

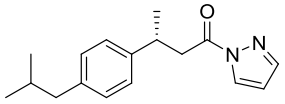
^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.5, 147.7, 144.0, 134.3, 129.8, 128.3, 127.2, 126.7, 125.2, 109.7, 41.8, 35.6, 22.0; ESI-HRMS Calculated for $C_{13}H_{14}N_2OCl^+$([M+H]$^+$): 249.0783, found 249.0789.

(*R*)-3-(4-fluorophenyl)-1-(1H-pyrazol-1-yl)butan-1-one **2h**



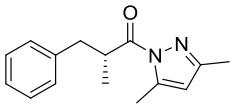
The title compound was purified by flash silica gel chromatography to afford the product. The eluent was petroleum ether: ethyl acetate = 10:1(V/V). Colorless oil; >99% conversion; 22.0 mg, 95% yield; 92% ee; $[\alpha]_D^{25}$ = 6.50 (c = 0.4, $CHCl_3$); The enantiomeric excess was determinedby HPLC on Chiralpak OJ-H column, hexane: isopropanol = 98:2; flow rate = 0.6 mL/min; UVdetection at 240 nm; t_R= 24.63 min (minor), 27.02 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.21 (d, *J* = 4.0 Hz, 1H), 7.70 (s, 1H), 7.27-7.23 (m, 2H), 6.99 (t, *J* = 8.0 Hz, 2H), 6.43-6.42 (m, 1H), 3.55-3.45 (m, 2H), 3.39-3.32 (m, 1H), 1.36 (d, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.7, 161.5 (d, *J* = 242.0 Hz), 144.0, 141.2, 128.2 (d, *J* = 8.1 Hz), 115.3 (d, *J* = 21.2 Hz), 109.7, 42.2, 35.2, 22.3; ESI-HRMS Calculated for $C_{13}H_{14}N_2OF^+$([M+H]$^+$): 233.1075, found 233.1085.

(*R*)-3-(4-isobutylphenyl)-1-(1H-pyrazol-1-yl)butan-1-one **2i**



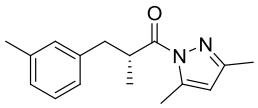
The title compound was purified by flash silica gel chromatography to afford the product. The eluent was petroleum ether: ethyl acetate = 10:1(V/V). Colorless oil; >99% conversion; 25.9 mg, 96% yield; 89% ee; $[\alpha]_D^{25}$ = 3.25 (c = 0.4, $CHCl_3$); The enantiomeric excess was determinedby HPLC on Chiralpak OJ-H column, hexane: isopropanol = 95:5; flow rate = 0.6 mL/min; UVdetection at 240 nm; t_R= 9.07 min (minor), 10.33 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.26 (d , *J* = 4.0 Hz, 1H), 7.72 (s, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.45-6.44 (m, 1 H), 3.55-3.48 (m, 2H), 3.44-3.37 (m, 1H), 2.46 (d, *J* = 8.0 Hz, 2H), 1.88-1.84 (m, 1H), 1.40 (d, *J* = 4.0 Hz, 1H), 0.92 (d, *J* = 8.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 171.0, 143.9, 142.8, 139.8, 129.2, 128.3, 126.6, 109.5, 45.1, 42.2, 35.5, 30.2, 22.4, 22.1; ESI-HRMS Calculated for $C_{17}H_{23}N_2O^+$([M+H]$^+$): 271.1798, found 271.1805.

(*R*)-1-(3,5-dimethyl-1H-pyrazol-1-yl)-2-methyl-3-phenylpropan-1-one **4a**



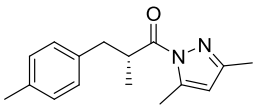
The title compound was purified by flash silica gel chromatography to afford the product. The eluent was petroleum ether: ethyl acetate = 10:1(V/V). Colorless oil; >99% conversion; 22.7 mg, 94% yield; 97% ee; $[\alpha]_D^{25}$ = -26.50 (c = 0.4, $CHCl_3$); The enantiomeric excess was determinedby HPLC on Chiralpak OJ-H column, hexane: isopropanol = 98:2; flow rate = 1.0 mL/min; UVdetection at 240 nm; t_R= 5.28 min (minor), 7.00 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29-7.17 (m, 5H), 5.94 (s, 1H), 4.20-4.11 (m, 1H), 3.20-3.15 (m, 1H), 2.73-2.68 (m, 1H), 2.51 (s, 3H), 2.23 (s, 3H), 1.22 (d, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 177.0, 151.7, 144.1, 139.6, 129.3, 128.3, 126.2, 111.1, 40.0, 39.4, 16.8, 14.7, 13.9; ESI-HRMS Calculated for $C_{15}H_{19}N_2O^+$([M+H]$^+$): 243.1490, found 243.1492.

(*R*)-1-(3,5-dimethyl-1H-pyrazol-1-yl)-2-methyl-3-m-tolylpropan-1-one **4e**



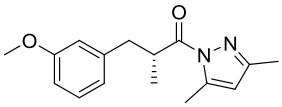
The title compound was purified by flash silica gel chromatography to afford the product. The eluent was petroleum ether: ethyl acetate = 10:1 (V/V). Colorless oil; >99% conversion; 23.8 mg, 93% yield; 94% ee; $[\alpha]_D^{25}$ = -17.75 (c = 0.4, $CHCl_3$); The enantiomeric excess was determinedby HPLC on Chiralpak OJ-H column, hexane: isopropanol = 98:2; flow rate = 1.0 mL/min; UVdetection at 240 nm; t_R= 4.65 min (minor), 5.66 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.17-7.14 (m, 1H), 7.04-6.99 (m, 3H), 5.94 (s, 1H), 4.18-4.10 (m, 1H), 3.16-3.11 (m, 1H), 2.69-2.64 (m, 1H), 2.52 (s, 3H), 2.32 (s, 3H), 2.24 (s, 3H), 1.22 (d, *J* = 4.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 177.1, 151.7, 144.1, 139.4, 137.8, 130.0, 128.1, 126.9, 126.3, 39.9, 39.3, 21.4, 16.8, 14.7, 13.9; ESI-HRMS Calculated for $C_{16}H_{21}N_2O^+$([M+H]$^+$): 257.1642, found 257.1648.

(*R*)-1-(3,5-dimethyl-1H-pyrazol-1-yl)-2-methyl-3-p-tolylpropan-1-one **4f**



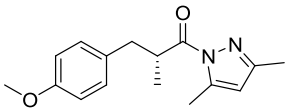
The title compound was purified by flash silica gel chromatography to afford the product. The eluent was petroleum ether: ethyl acetate = 10:1(V/V). Colorless oil; >99% conversion; 24.1 mg, 94% yield; 92% ee; $[\alpha]_D^{25}$ = -24.00 (c = 0.4, $CHCl_3$); The enantiomeric excess was determinedby HPLC on Chiralpak OJ-H column, hexane: isopropanol = 98:2; flow rate = 1.0 mL/min; UVdetection at 240 nm; t_R= 5.16 min (minor), 6.91 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.13-7.06 (m, 4H), 5.94 (s, 1H), 4.17-4.08 (m, 1H), 3.16-3.11 (m, 1H), 2.69-2.62 (m, 1H), 2.51 (s, 3H), 2.30 (s, 3H), 2.23 (s, 3H), 1.21 (d, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 177.1, 151.7, 144.1, 136.4, 135.6, 129.1, 128.9, 111.1, 40.0, 38.9, 21.1, 16.8, 14.7, 13.9; ESI-HRMS Calculated for $C_{16}H_{21}N_2O^+$([M+H]$^+$): 257.1643, found 257.1648.

(*R*)-1-(3,5-dimethyl-1H-pyrazol-1-yl)-3-(3-methoxyphenyl)-2-methylpropan-1-one **4g**



The title compound was purified by flash silica gel chromatography to afford the product. The eluent was petroleum ether: ethyl acetate = 10:1(V/V). Colorless oil; >99% conversion; 26.1 mg, 96% yield; 93% ee; $[\alpha]_D^{25}$ = -19.75 (c = 0.4, $CHCl_3$); The enantiomeric excess was determinedby HPLC on Chiralpak OJ-H column, hexane: isopropanol = 98:2; flow rate = 1.0 mL/min; UVdetection at 240 nm; t_R= 6.97 min (minor), 8.69 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.18 (t, *J* = 8.0 Hz, 1H), 6.83-6.80 (m, 2H), 6.75-6.72 (m, 1H), 5.94 (s, 1H), 4.19-4.11 (m, 1H), 3.78 (s, 3H), 3.18-3.13 (m, 1H), 2.71-2.65 (m, 1H), 2.52 (s, 3H), 2.23 (s, 3H), 1.23 (d, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 177.0, 159.5, 151.8, 144.1, 141.2, 129.2, 121.7, 114.8, 111.6, 111.1, 55.1, 39.9, 39.4, 16.9, 14.7, 13.9; ESI-HRMS Calculated for $C_{16}H_{21}N_2O_2^+$([M+H]$^+$): 273.1591, found 273.1598.

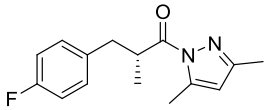
(*R*)-1-(3,5-dimethyl-1H-pyrazol-1-yl)-3-(4-methoxyphenyl)-2-methylpropan-1-one **4h**



The title compound was purified by flash silica gel chromatography to afford the product. The eluent was petroleum ether: ethyl acetate = 10:1(V/V). Colorless oil; >99% conversion; 25.0 mg, 92%

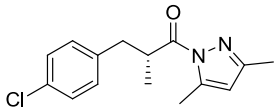
yield; 91% ee; $[\alpha]_D^{25}$ = -3.50 (c = 0.4, $CHCl_3$); The enantiomeric excess was determinedby HPLC on Chiralpak OJ-H column, hexane: isopropanol = 98:2; flow rate = 1.0 mL/min; UVdetection at 240 nm; t_R= 8.75 min (minor), 10.14 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.14 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 5.94 (s, 1H), 4.15-4.06 (m, 1H), 3.77 (s, 3H), 3.13-3.08 (m, 1H), 2.68-2.61 (m, 1H), 2.51 (s, 3H), 2.23 (s, 3H), 1.21 (d, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 177.1, 158.0, 151.7, 144.1, 131.6, 130.2, 113.6, 111.1, 55.2, 40.2, 38.5, 16.8, 14.7, 13.9; ESI-HRMS Calculated for $C_{16}H_{21}N_2O_2^+$([M+H]$^+$): 273.1591, found 273.1598.

(*R*)-1-(3,5-dimethyl-1H-pyrazol-1-yl)-3-(4-fluorophenyl)-2-methylpropan-1-one **4i**



The title compound was purified by flash silica gel chromatography to afford the product. The eluent was petroleum ether: ethyl acetate = 10:1 (V/V). Colorless oil; >99% conversion; 22.7 mg, 94% yield; 98% ee; $[\alpha]_D^{25}$ = -19.00 (c = 0.4, $CHCl_3$); The enantiomeric excess was determinedby HPLC on Chiralpak AD-H column, hexane: isopropanol = 99:1; flow rate = 1.0 mL/min; UVdetection at 240 nm; t_R= 4.17 min (minor), 4.57 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.23 (d, *J* = 12.0 Hz, 2H), 7.16 (d, *J* = 12.0 Hz, 2H), 5.94 (s, 1H), 4.17-4.08 (m, 1H), 3.16-3.11 (m, 1H), 2.71-2.66 (m, 1H), 2.51 (s, 3H), 2.23 (s, 3H), 1.22 (d, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 176.8, 151.8, 144.1, 135.2, 130.6 (d, *J* = 7.07Hz), 114.8 (d, *J* = 11.11Hz), 111.2, 40.1, 38.6, 16.9, 14.7, 13.9; ESI-HRMS Calculated for $C_{15}H_{18}N_2OF^+$([M+H]$^+$): 261.1393, found 261.1398.

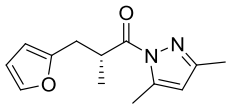
(*R*)-3-(4-chlorophenyl)-1-(3,5-dimethyl-1H-pyrazol-1-yl)-2-methylpropan-1-one **4j**



The title compound was purified by flash silica gel chromatography to afford the product. The eluent was petroleum ether: ethyl acetate = 10:1 (V/V). Colorless oil; >99% conversion; 26.8 mg, 97% yield; 98% ee; $[\alpha]_D^{25}$ = -22.50 (c = 0.4, $CHCl_3$); The enantiomeric excess was determinedby HPLC on Chiralpak OJ-H column, hexane: isopropanol = 98:2; flow rate = 1.0 mL/min; UVdetection at 240 nm; t_R= 5.13 min (minor), 5.69 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.20-7.16 (m, 2H), 6.96-6.92 (m, 2H), 5.94 (s, 1H), 4.17-4.08 (m, 1H), 3.16-3.11 (m, 1H), 2.71-2.66 (m, 1H), 2.51 (s,

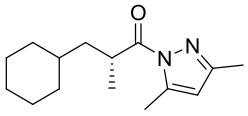
3H), 2.23 (s, 3H), 1.22 (d, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 176.6, 151.9, 144.1, 138.1, 132.0, 130.6, 128.4, 111.3, 39.9, 38.8, 38.7, 17.0, 14.7, 13.9; ESI-HRMS Calculated for $C_{15}H_{18}N_2OCl^+$([M+H]$^+$): 276.7611, found 276.7612.

(*R*)-1-(3,5-dimethyl-1H-pyrazol-1-yl)-3-(furan-2-yl)-2-methylpropan-1-one **4k**



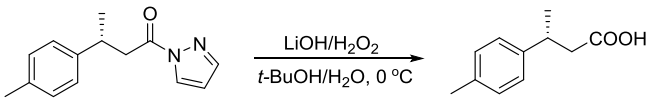
The title compound was purified by flash silica gel chromatography to afford the product. The eluent was petroleum ether: ethyl acetate = 10:1 (V/V). Colorless oil; >99% conversion; 22.0 mg, 95% yield; 99% ee; $[\alpha]_D^{25}$ = -7.00 (c = 0.4, $CHCl_3$); The enantiomeric excess was determinedby HPLC on Chiralpak OJ-H column, hexane: isopropanol = 98:2; flow rate = 1.0 mL/min; UVdetection at 240 nm; t_R= 5.68 min (minor), 7.44 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29-7.28 (m, 1H), 6.25-6.24 (m, 1H), 6.03 (m, 1H), 5.96 (s, 1H), 4.24-4.19 (m, 1H), 3.17-3.11 (m, 1H), 2.86-2.81 (m, 1H), 2.53 (s, 3H), 2.24 (s, 3H), 1.27 (d, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 176.6, 153.4, 151.9, 144.2, 141.3, 111.2, 110.1, 106.5, 37.7, 31.5, 17.4, 14.7, 13.9; ESI-HRMS Calculated for $C_{13}H_{17}N_2O_2^+$([M+H]$^+$): 233.1282, found 233.1285.

(*R*)-3-cyclohexyl-1-(3,5-dimethyl-1H-pyrazol-1-yl)-2-methylpropan-1-one **4l**



The title compound was purified by flash silica gel chromatography to afford **4l** (>99% conversion, 92% yield). The product **4l** was transformed to the corresponding acid by the procedure IV, and then the acid was methyl esterified by diazomethane. The enantiomeric excess (33% ee) of the resulted methyl ester was determined by Supelco's Beta Dex 120 column Temperature program: 80 ℃, 0.5 ℃/min to 150 ℃, stay 10 mins, Flow rate = 1.0 mL/min, t_R= 55.3 min (major), 56.0 min (minor). **4l**: $[\alpha]_D^{25}$ = -1.25 (c = 0.4, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.89 (s, 1H), 2.46 (s, 3H), 2.17 (s, 3H), 1.66-1.59 (m, 8H), 1.26-1.21 (m, 6H), 1.14 (d, *J* = 8.0 Hz, 3H).

IV. Procedure for the transformation of hydrogenation product 2b



2b

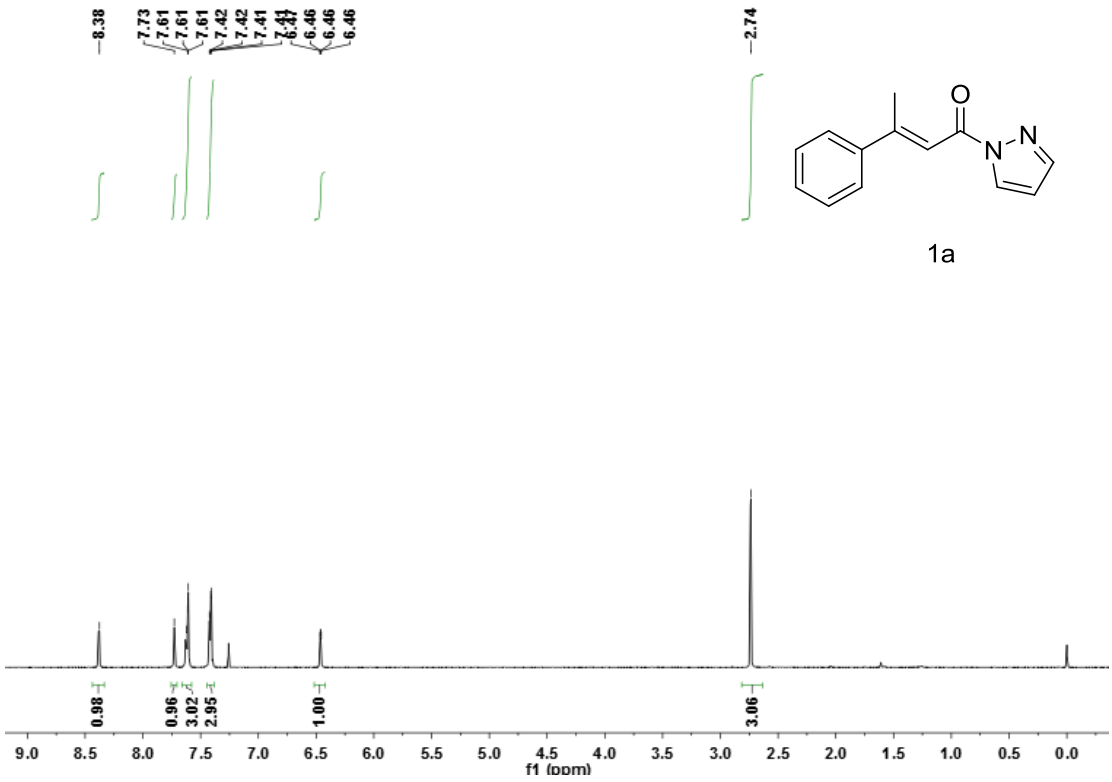
ee: 95%

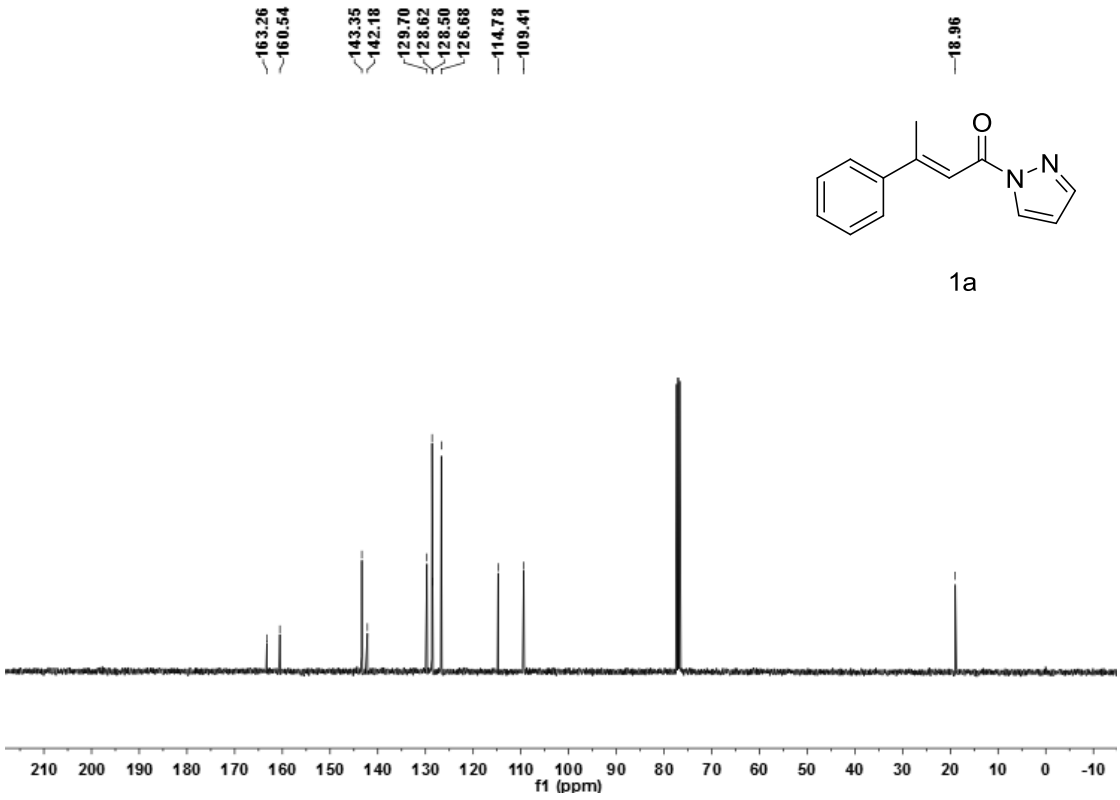
9

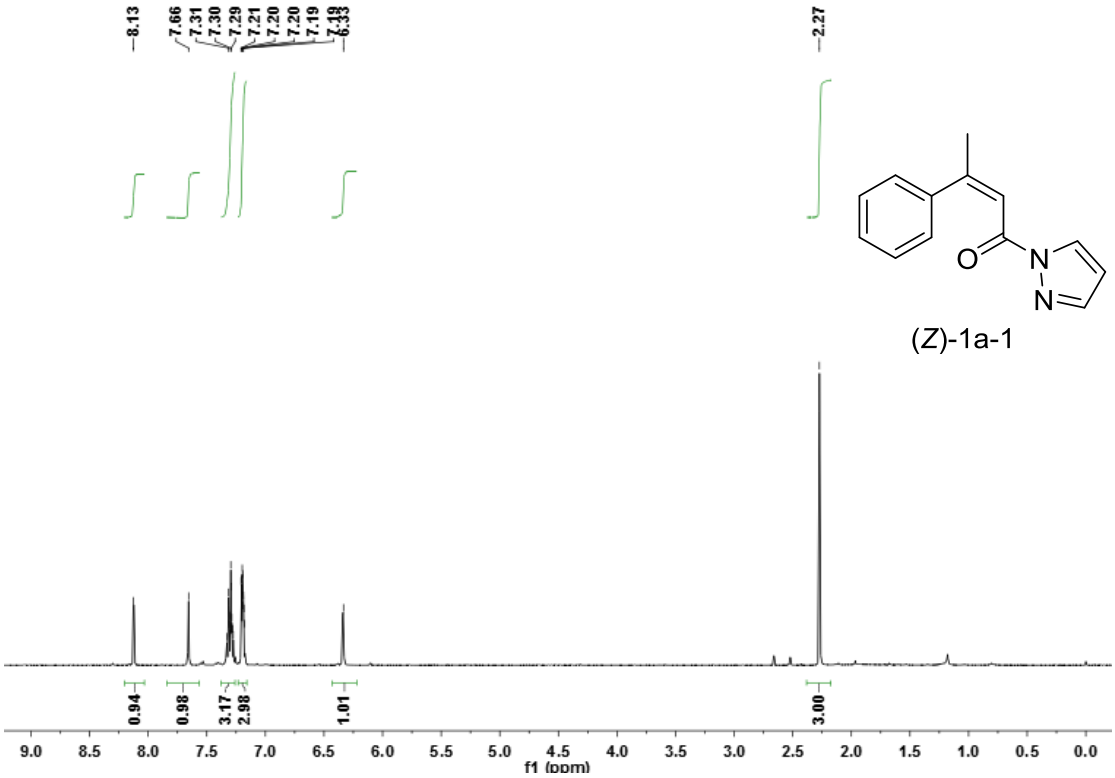
yield: 90%
ee: 95%

To the solution of 30 % H_2O_2 (0.05 mL) in water (0.16 mL)/*t*-BuOH (0.16 mL) was added LiOH/H_2O (6.4 mg, 0.15 mmol) at 0 ℃. The reaction mixture was stirred at 0 ℃ for 5 min, and (*R*)-1-(1H-pyrazol-1-yl)-3-p-tolylbutan-1-one **2b** (90.6 mg, 0.1 mmol) was added. After completion monitored by TLC then carefully treated with a saturated aqueous solution of $Na_2S_2O_3$ (0.3 mL) followed by 2 M aqueous solution off HCl (1 mL). The mixture was extracted with EtOAc (3 x 5 mL), dried over MgSO4, and removed under reduced pressure to give the crude carboxylic acid product **9**.[5] White solid; yield: 90%; $[\alpha]_D^{20}$= -35.0 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.11 (s, 4 H), 3.26-3.12 (m, 1H), 2.64 (dd, *J* = 8.0, 16.0 Hz, 1H), 2.55 (dd, *J* = 8.0, 16.0 Hz, 1H); ^{13}C HNMR (101 MHz, $CDCl_3$) δ = 21.0, 22.0, 35.8, 42.8, 126.6, 129.2, 136.0, 142.5, 178.3. The enantiomeric excess was determined with its diazomethane esterifying methyl derivative by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 95:5; flow rate = 0.6 mL/min; UVdetection at 210 nm; t_R= 15.4 min (major), 16.5 min (minor).

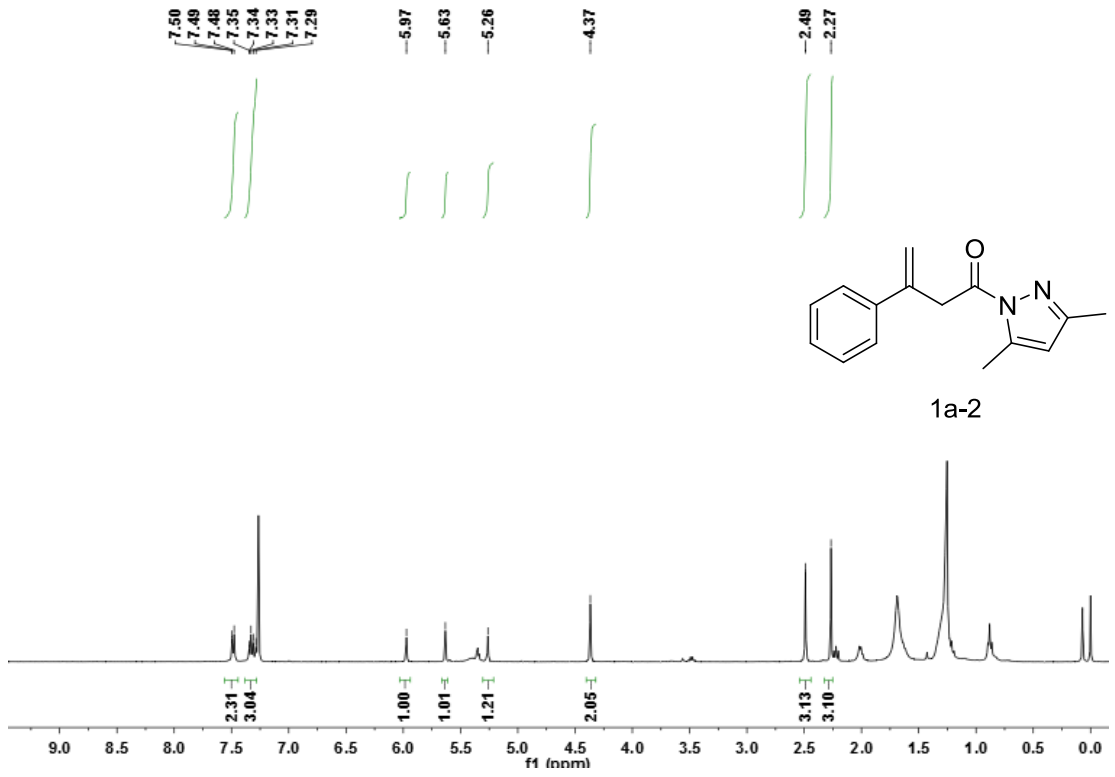
V. NMR spectra






8.13
7.66
7.31
7.30
7.29
7.21
7.20
7.20
7.19
7.19
6.33
2.27
O
N
N
0.94
0.98
3.17
2.98
1.01
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

(*Z*)-1a-1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7.49
7.48
7.35
7.34
7.33
7.31
7.29
5.97
5.63
5.26
4.37
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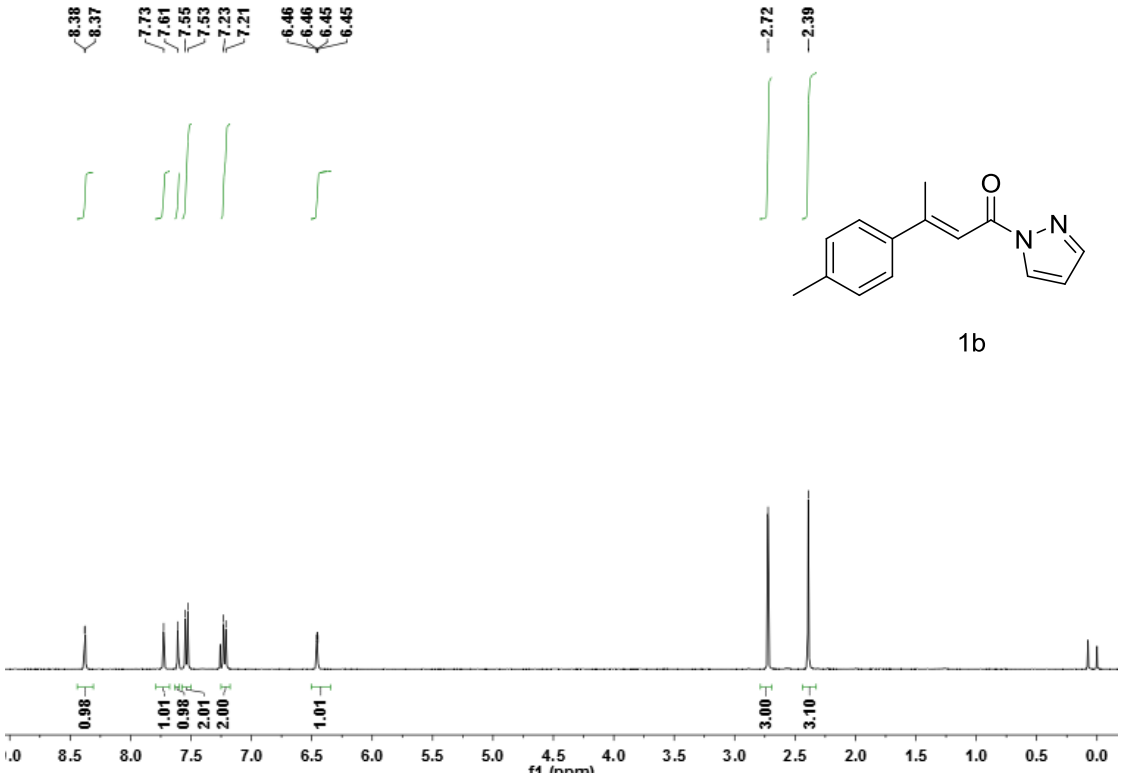
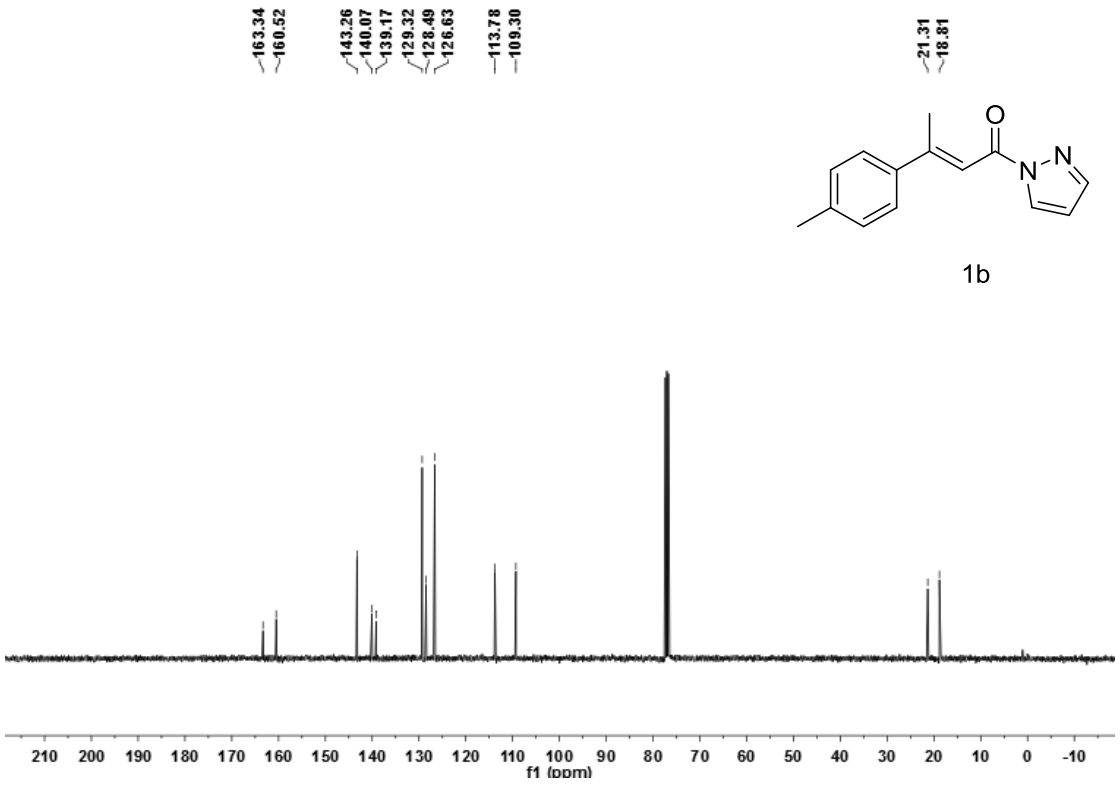
2.27
O
N
N
2.31
3.04
1.00
1.01
1.21
2.05
3.13
3.10
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

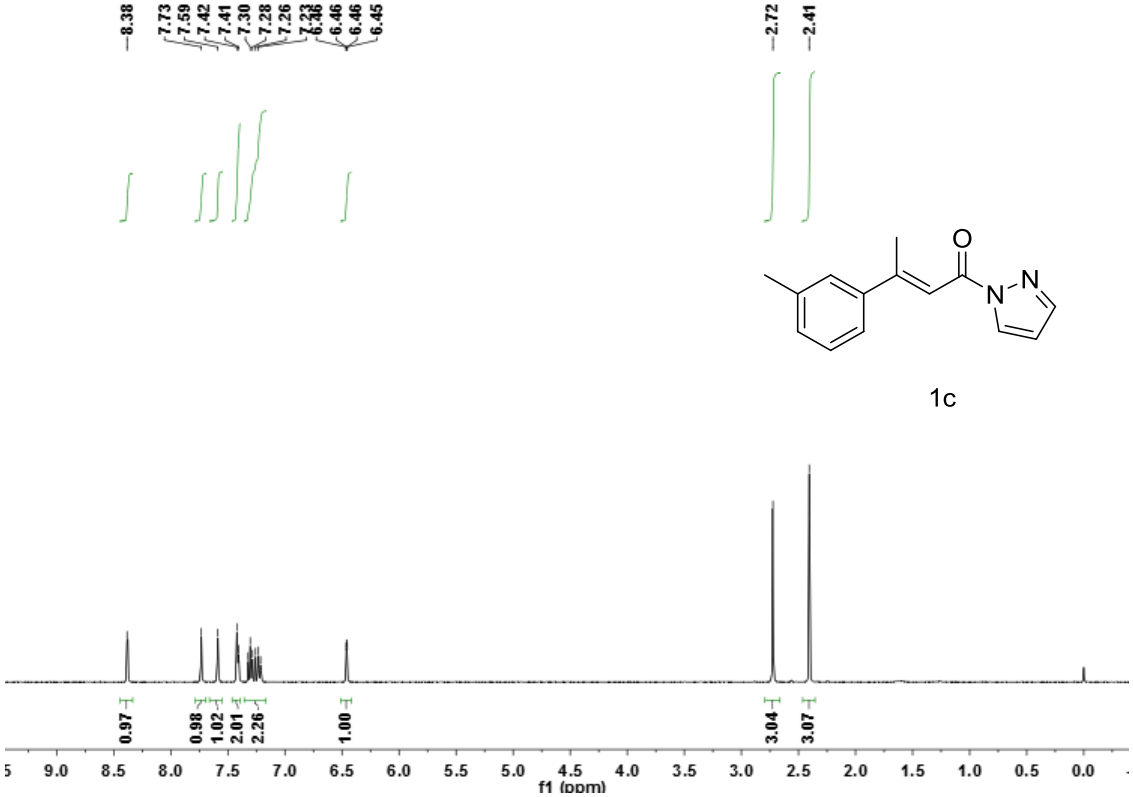
1a-2


8.38
8.37
7.73
7.61
7.55
7.53
7.23
7.21
6.46
6.46
6.45
6.45
2.72
2.39
O
N
N
0.98
1.01
0.98
2.01
2.00
1.01
3.00
3.10
f1 (ppm)

1b


163.34
160.52
143.26
140.07
139.17
129.32
128.49
126.63
113.78
109.30
21.31
18.81
O
N
N
f1 (ppm)

1b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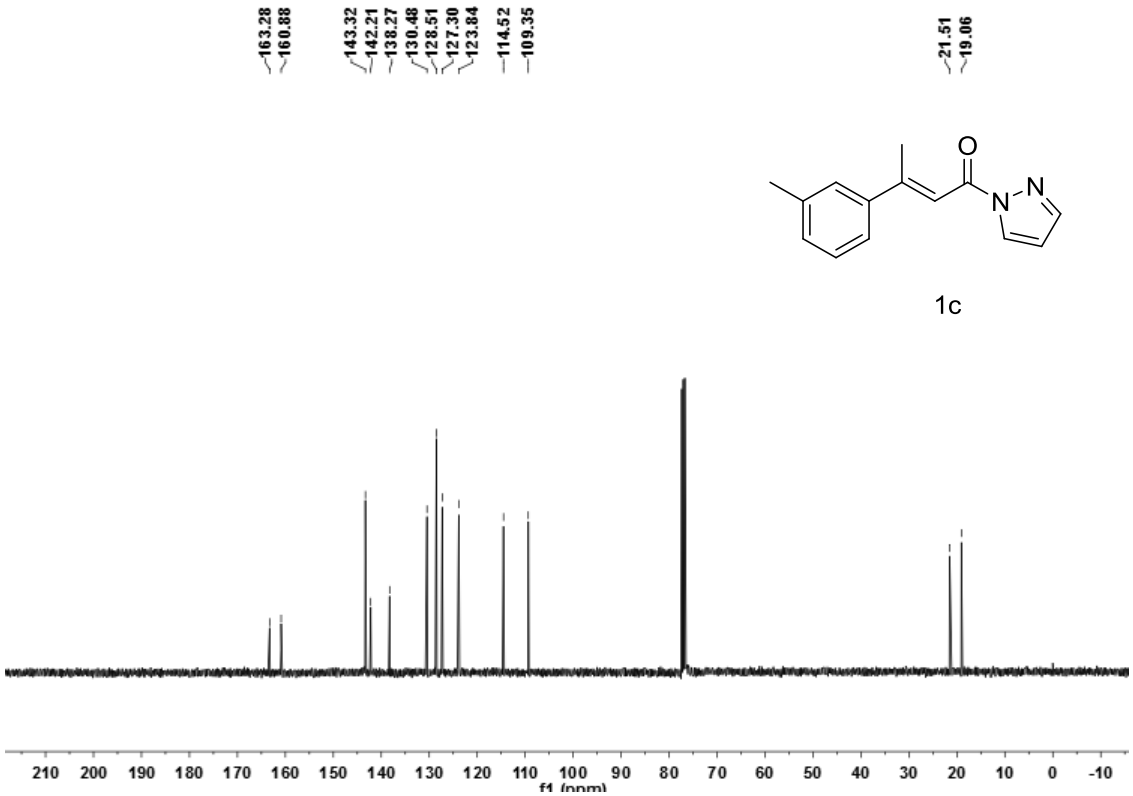
7.73
7.59
7.42
7.41
7.30
7.28
7.26
6.46
6.46
6.45
2.72
2.41
O
N
N
1c
0.97
0.98
1.02
2.01
2.26
1.00
3.04
3.07
f1 (ppm)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160.88
143.32
142.21
138.27
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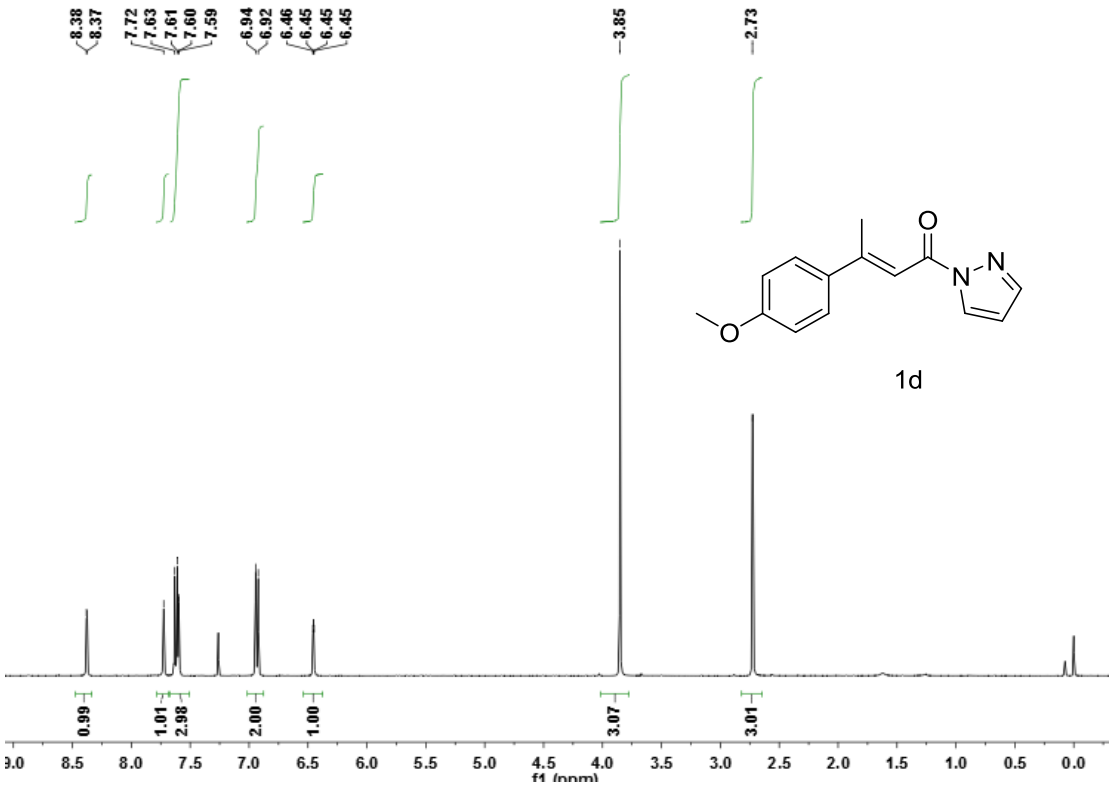
128.51
127.30
123.84
114.52
109.35
21.51
19.06
O
N
N
1c
f1 (ppm)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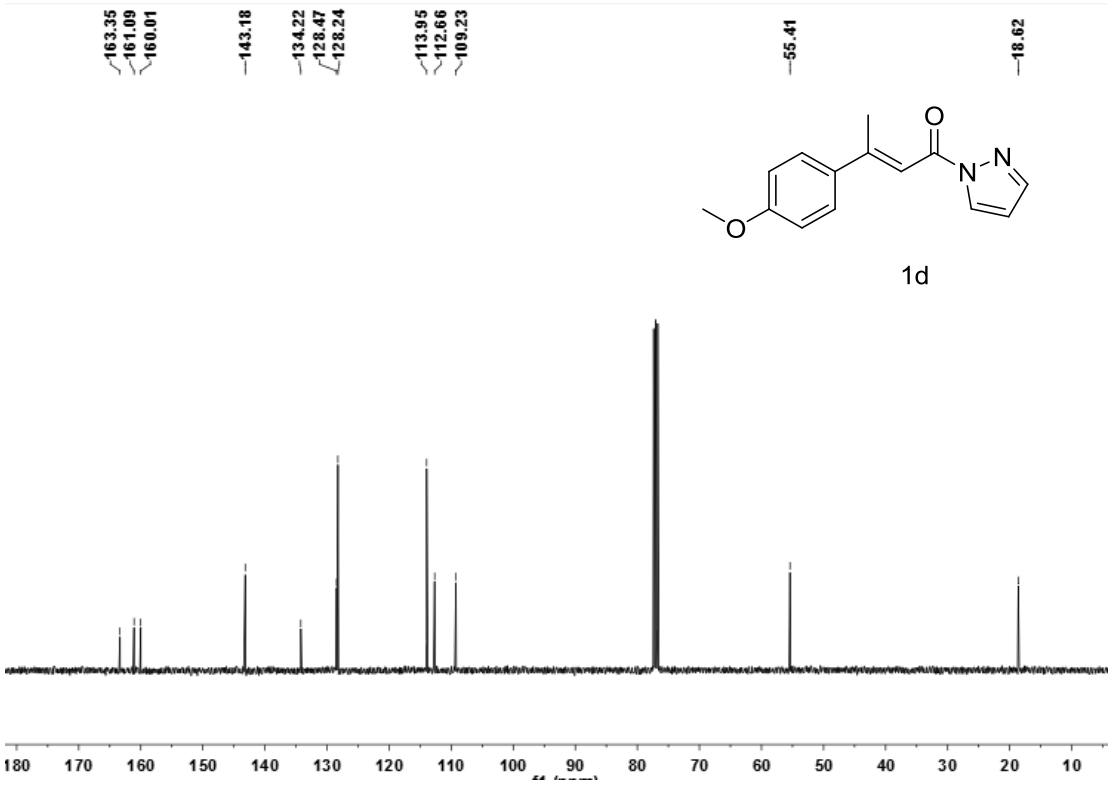
7.63
7.61
7.60
7.59
6.94
6.92
6.46
6.45
6.45
6.45
3.85
2.73
O
N
N
O
1d
0.99
1.01
2.98
2.00
1.00
3.07
3.01
f1 (ppm)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161.09
160.01
143.18
134.22
128.47
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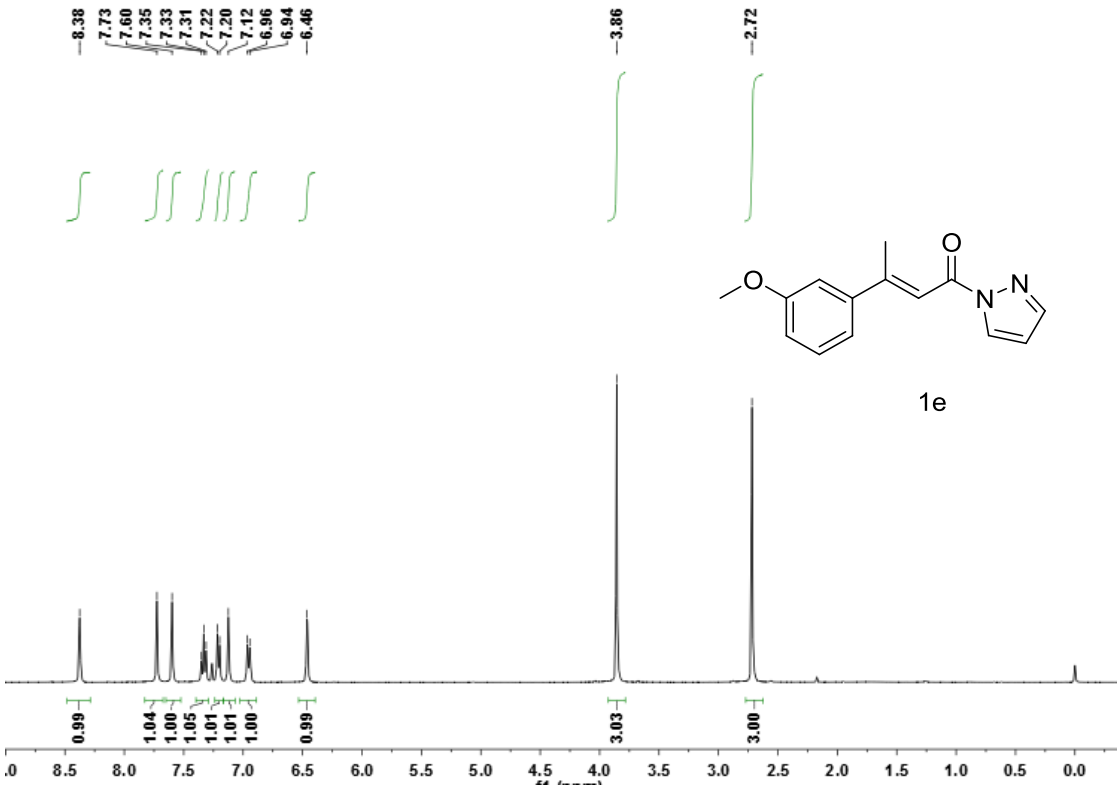
113.95
112.66
109.23
55.41
18.62
O
N
N
O
1d
f1 (ppm)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7.60
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7.31
7.22
7.20
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6.96
6.94
6.46
3.86
2.72
O
O
N
N
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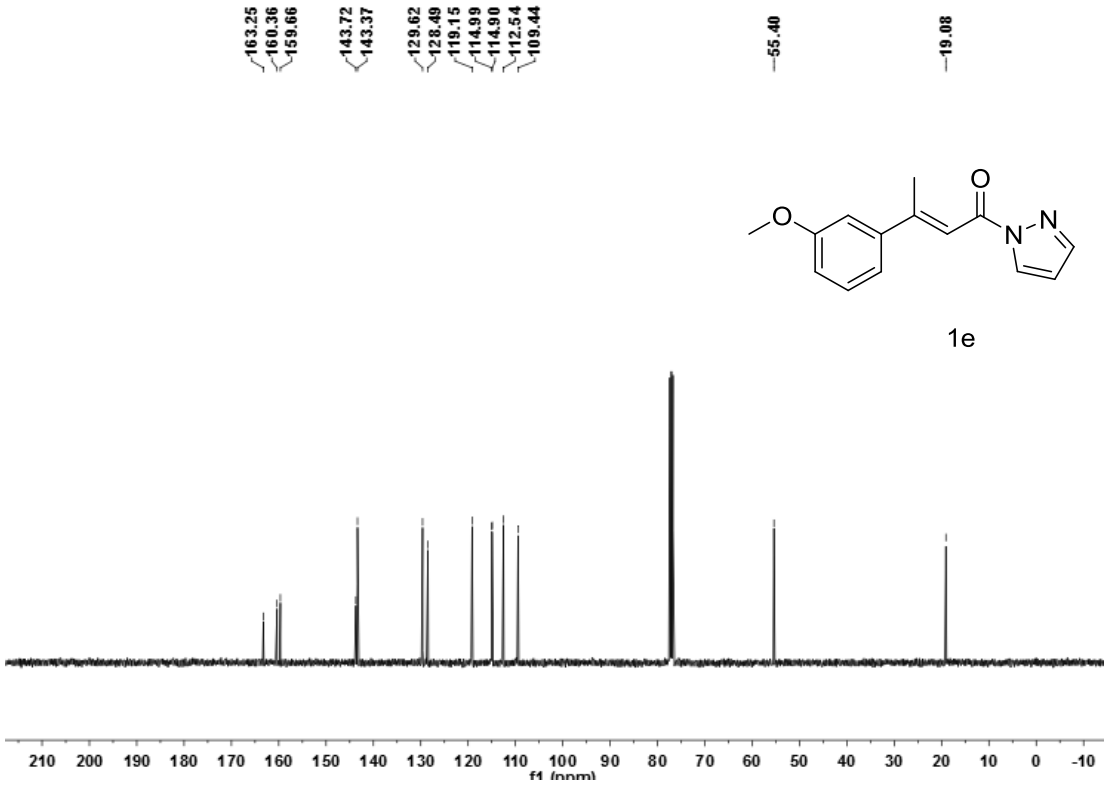
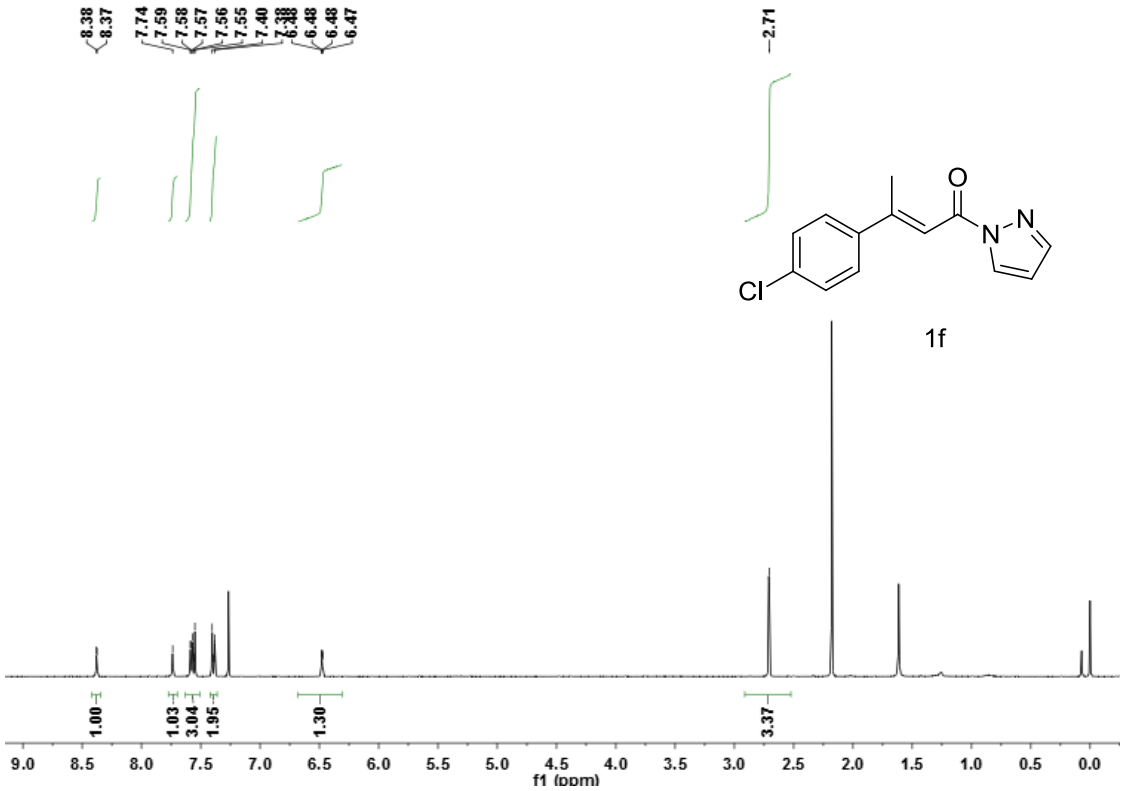
1.04
1.00
1.05
1.01
1.01
1.00
0.99
3.03
3.00


163.25
160.36
159.66
143.72
143.37
129.62
128.49
119.15
114.99
114.90
112.54
109.44
55.40
19.08
O
O
N
N
1e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8.37
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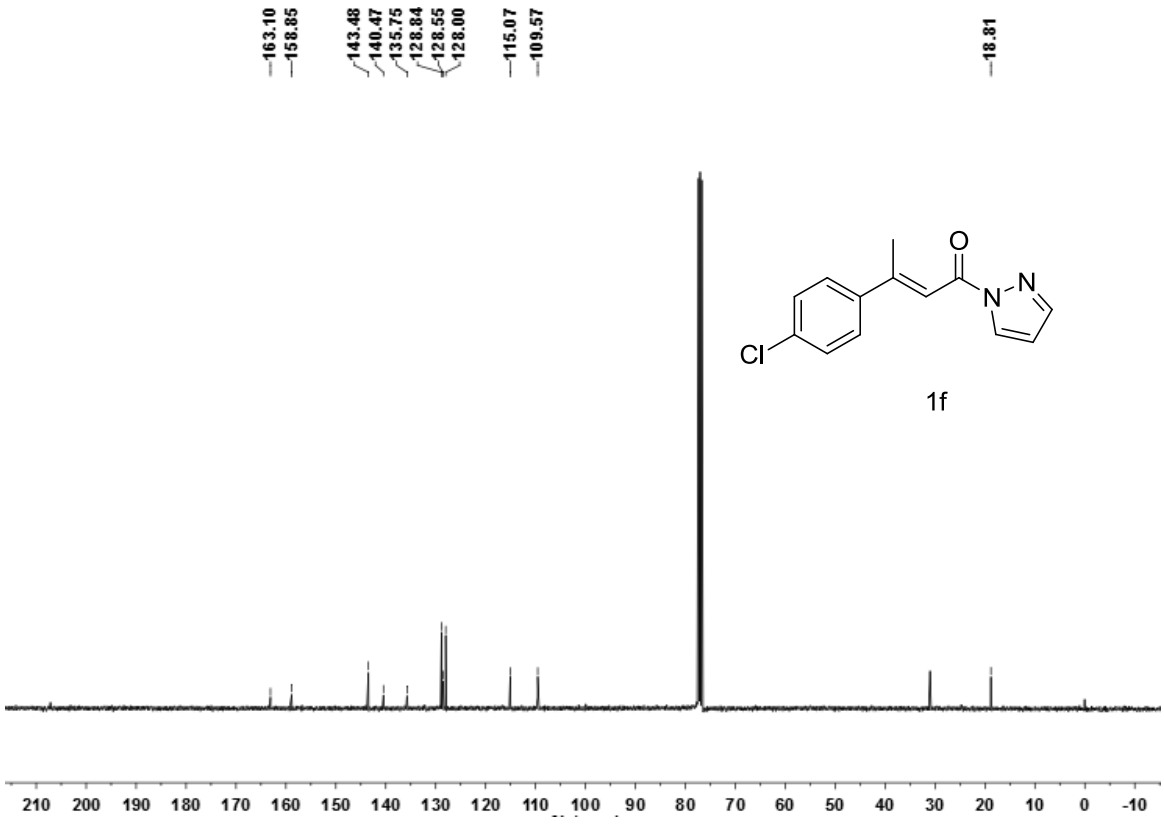
6.47
2.71
O
N
N
Cl
1f
1.00
1.03
3.04
1.95
1.30
3.37
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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140.47
135.75
128.84
128.55
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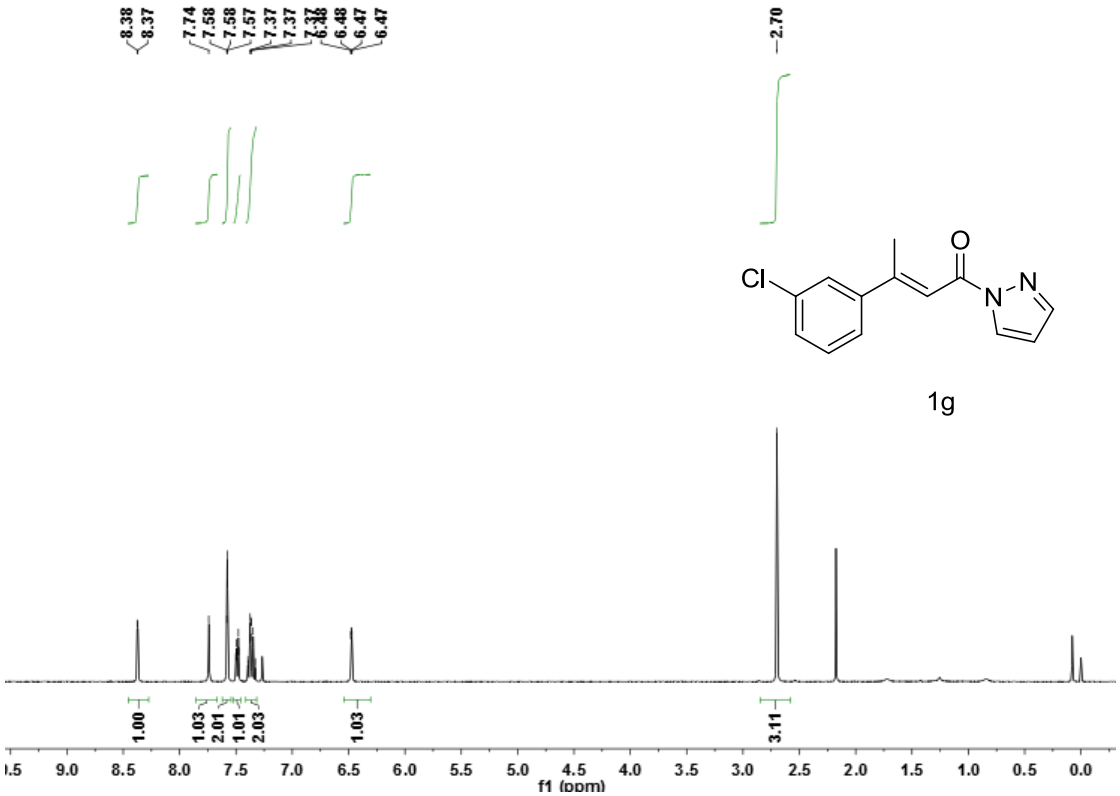
115.07
109.57
18.81
O
N
N
Cl
1f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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8.37
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7.58
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7.57
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7.37
6.48
6.47
6.47
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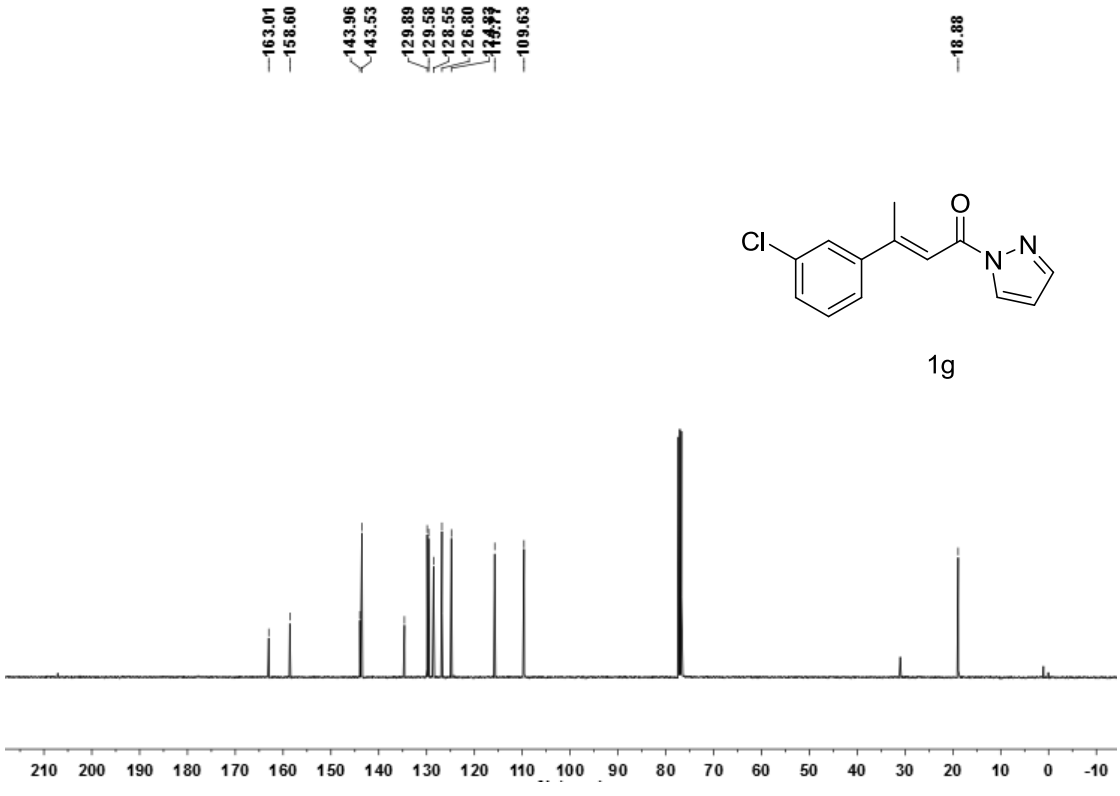
1.01
2.03
1.03
3.11
f1 (ppm)


163.01
158.60
143.96
143.53
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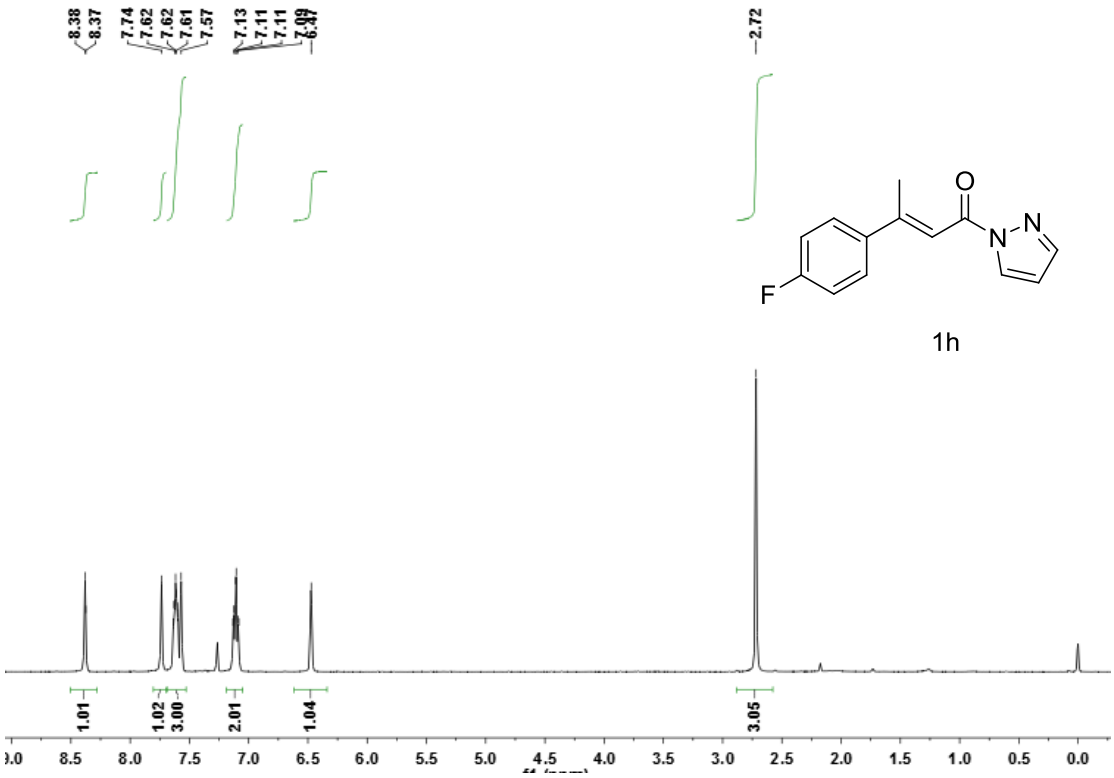
129.58
128.55
126.80
109.63
18.88
Cl
O
N
N
1g
f1 (ppm)


8.38
8.37
7.74
7.62
7.62
7.61
7.57
7.13
7.11
7.11
2.72
O
N
N
F
1h
1.01
1.02
3.00
2.01
1.04
3.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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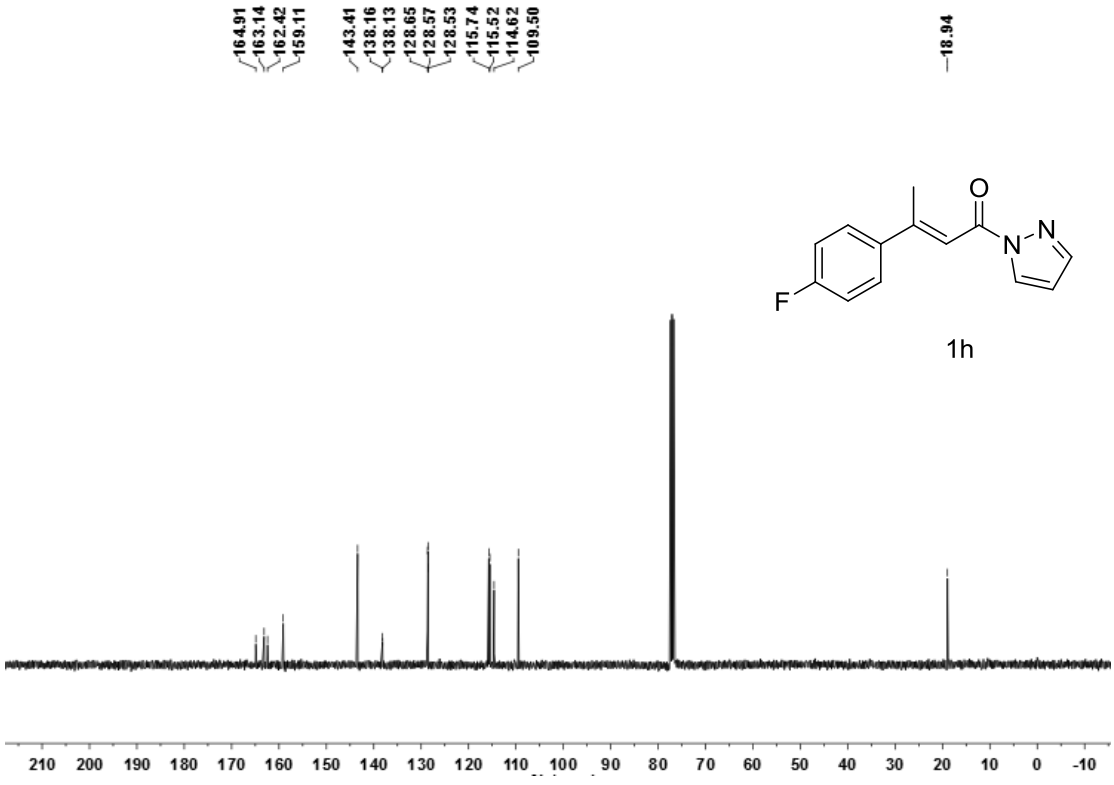
0.0


164.91
163.14
162.42
159.11
143.41
138.16
138.13
128.65
128.57
128.53
115.74
115.52
114.62
109.50
18.94
O
N
N
F
1h
210
200
190
180
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160
150
140
130
120
110
100
90
80
70
60
50
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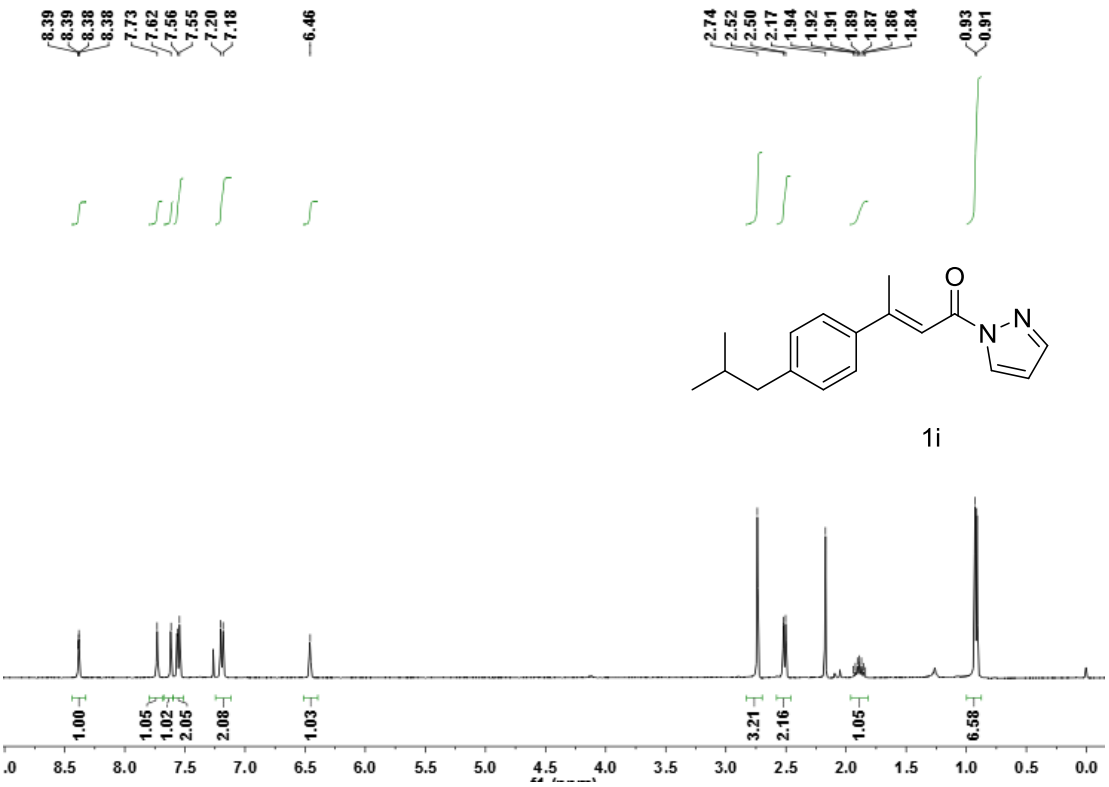
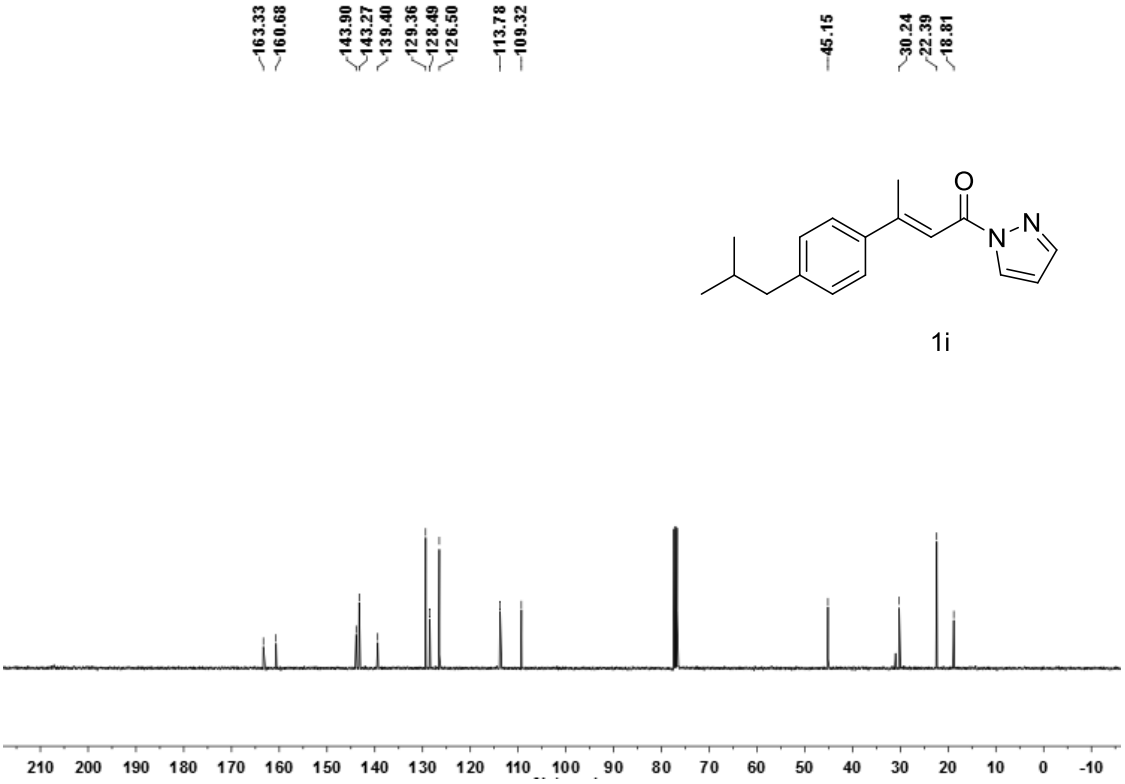
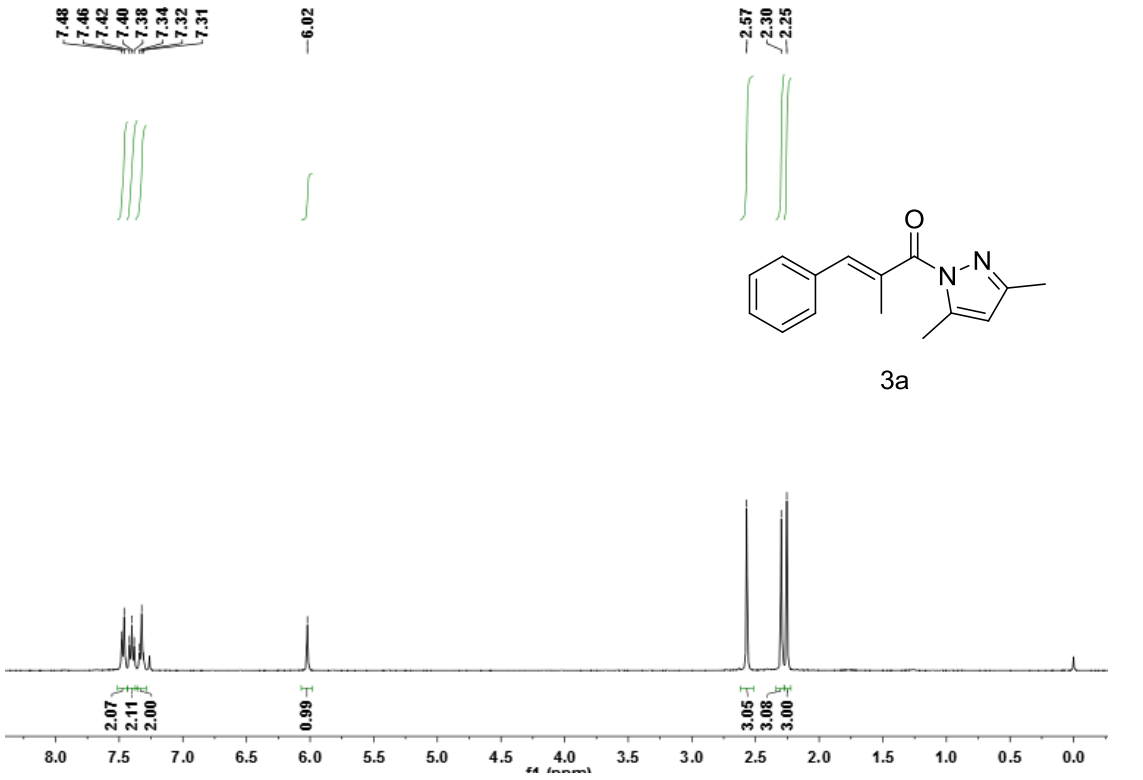
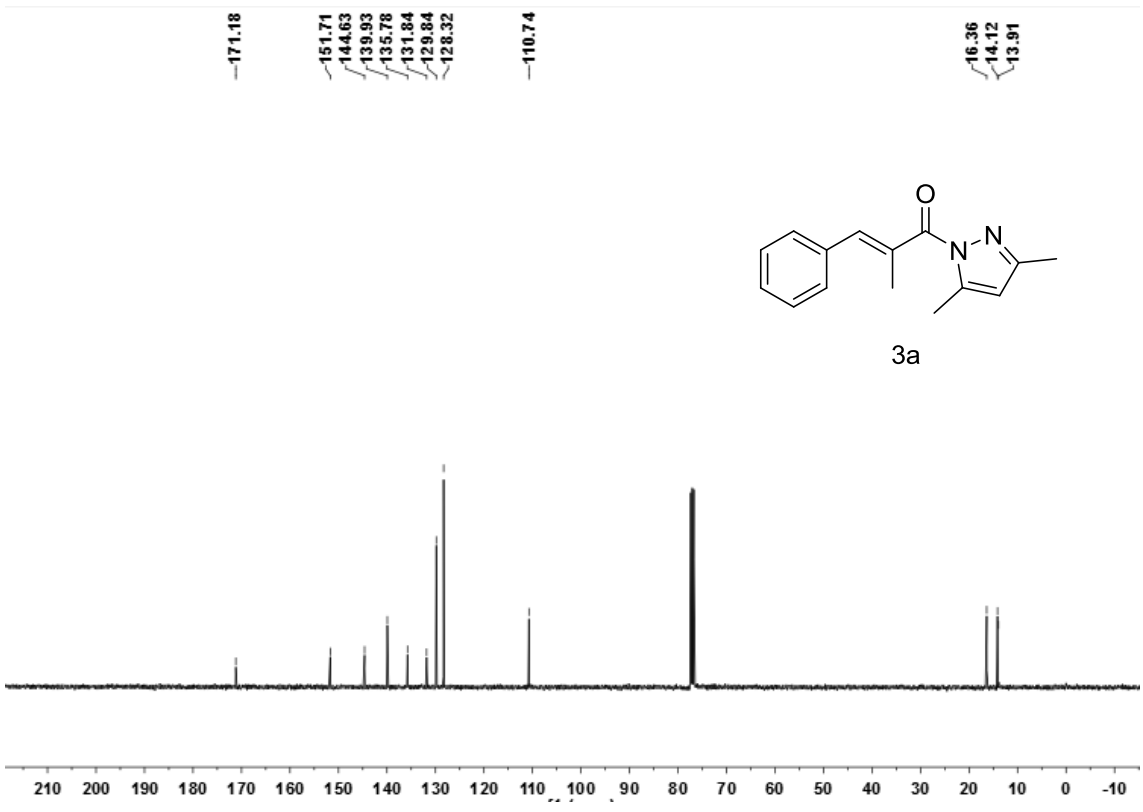
30
20
10
0
-10


8.39
8.39
8.38
8.38
7.73
7.62
7.56
7.55
7.20
7.18
6.46
2.74
2.52
2.50
2.17
1.94
1.92
1.91
1.89
1.87
1.86
1.84
0.93
0.91
O
N
N
1i
1.00
1.05
1.02
2.05
2.08
1.03
3.21
2.16
1.05
6.58
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


163.33
160.68
143.90
143.27
139.40
129.36
128.49
126.50
113.78
109.32
45.15
30.24
22.39
18.81
O
N
N
1i
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


7.48
7.46
7.42
7.40
7.38
7.34
7.32
7.31
6.02
2.57
2.30
2.25
O
N
N
2.07
2.11
2.00
0.99
3.05
3.08
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

3a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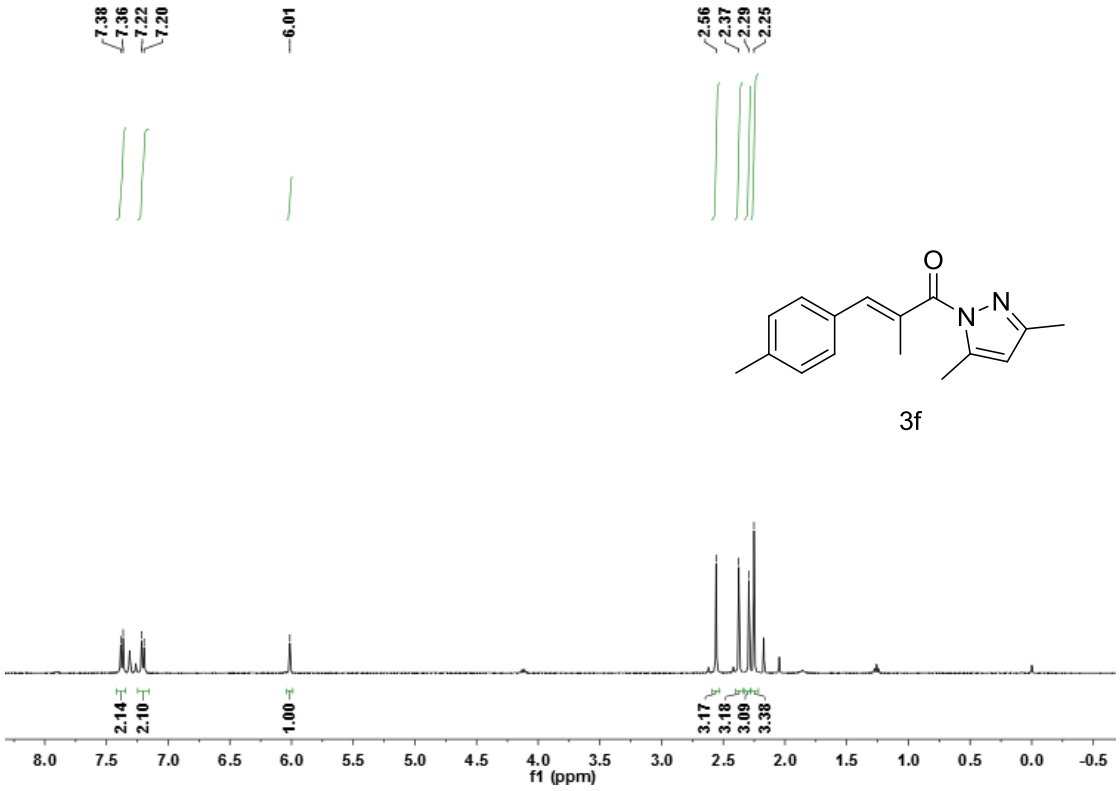
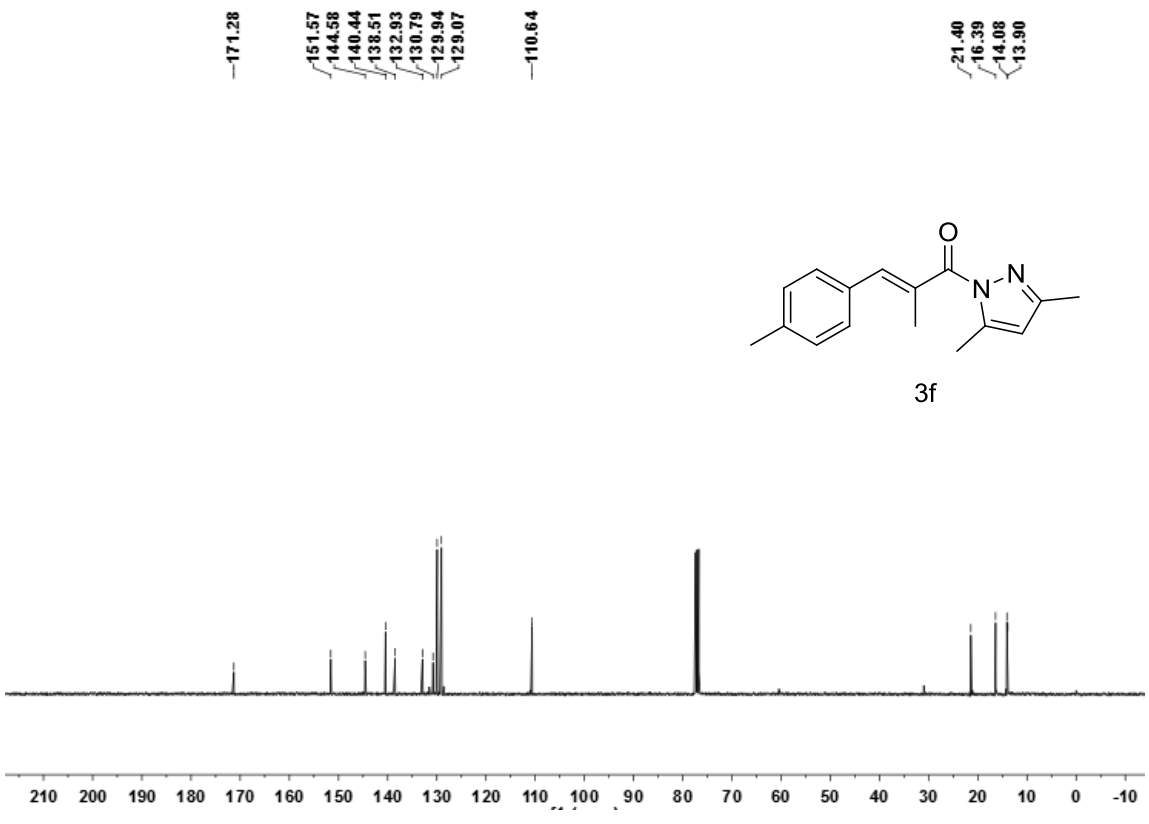
151.71
144.63
139.93
135.78
131.84
129.84
128.32
110.74
16.36
14.12
13.91
O
N
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

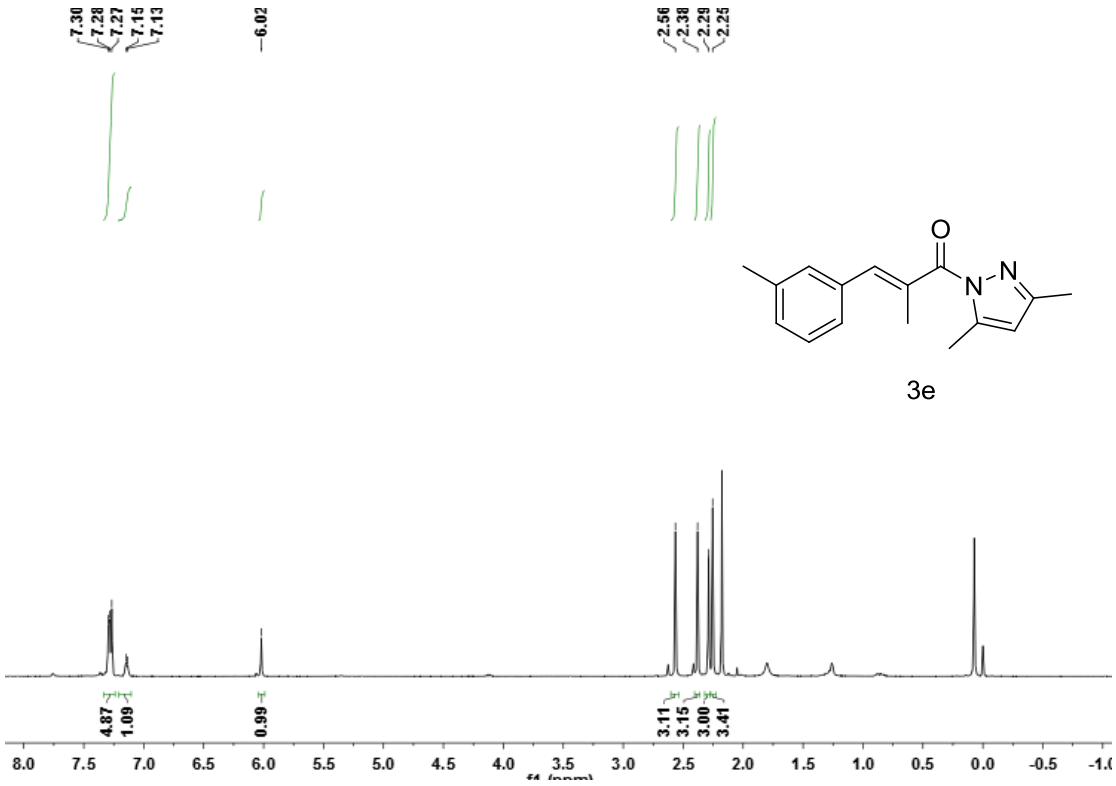
3a


7.38
7.36
7.22
7.20
6.01
2.56
2.37
2.29
2.25
O
N
N
2.14
2.10
1.00
3.17
3.18
3.09
3.38
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

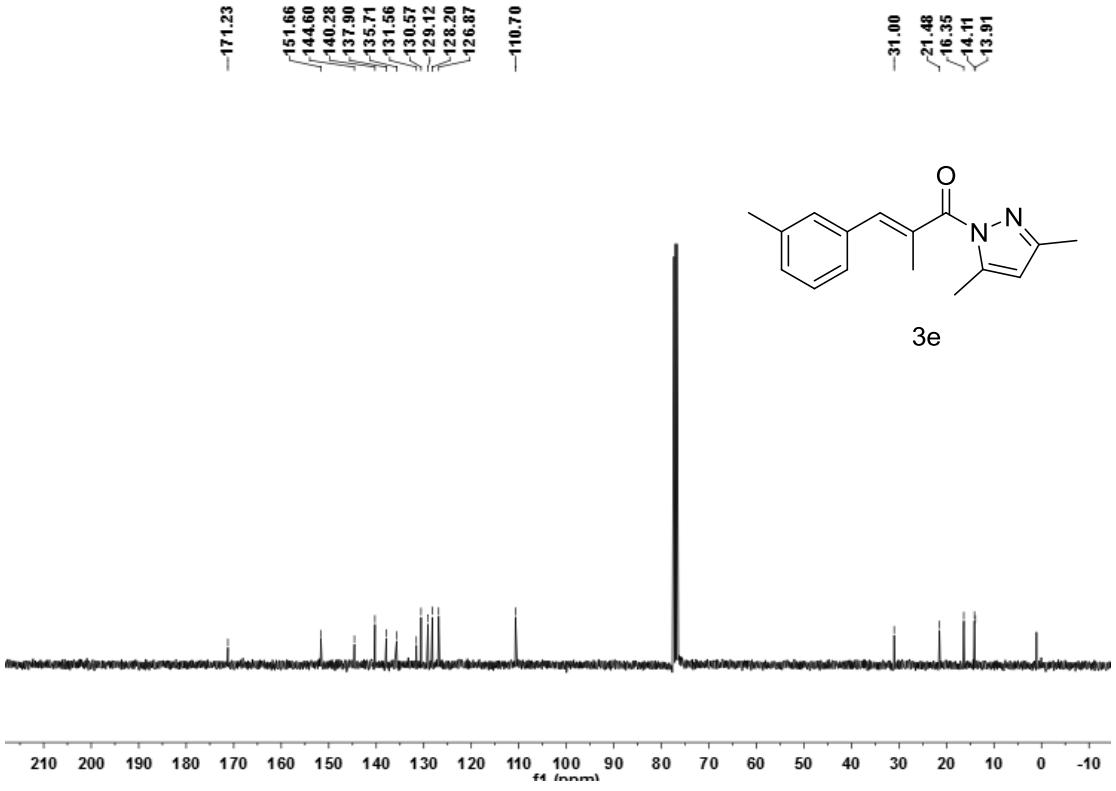
3f


171.28
151.57
144.58
140.44
138.51
132.93
130.79
129.94
129.07
110.64
21.40
16.39
14.08
13.90
O
N
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

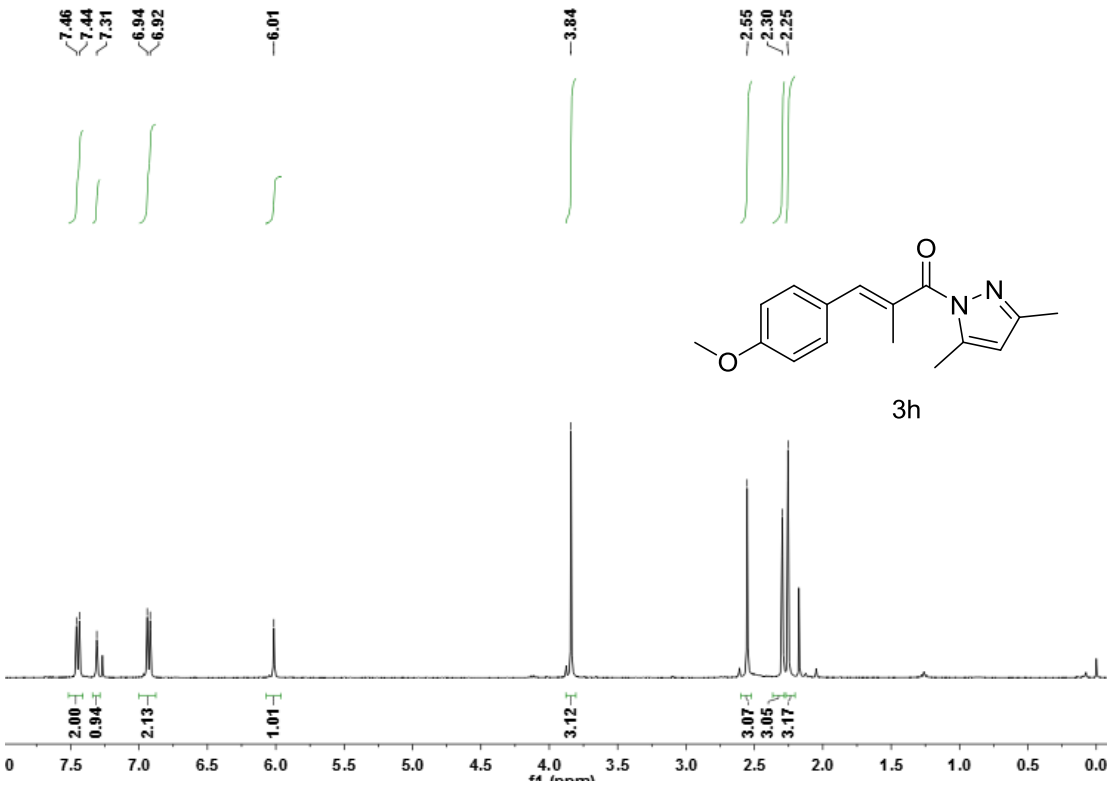
3f

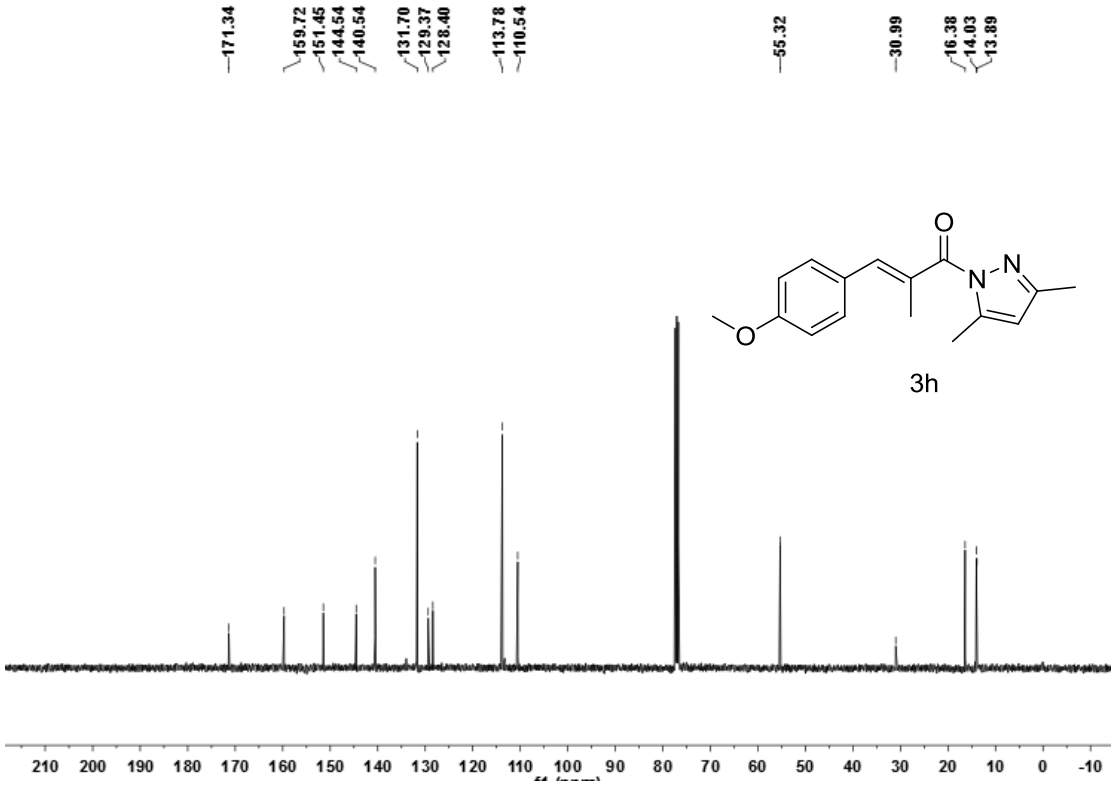

7.30
7.28
7.27
7.15
7.13
6.02
2.56
2.38
2.29
2.25
O
N
N
4.87
1.09
0.99
3.11
3.15
3.00
3.41
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

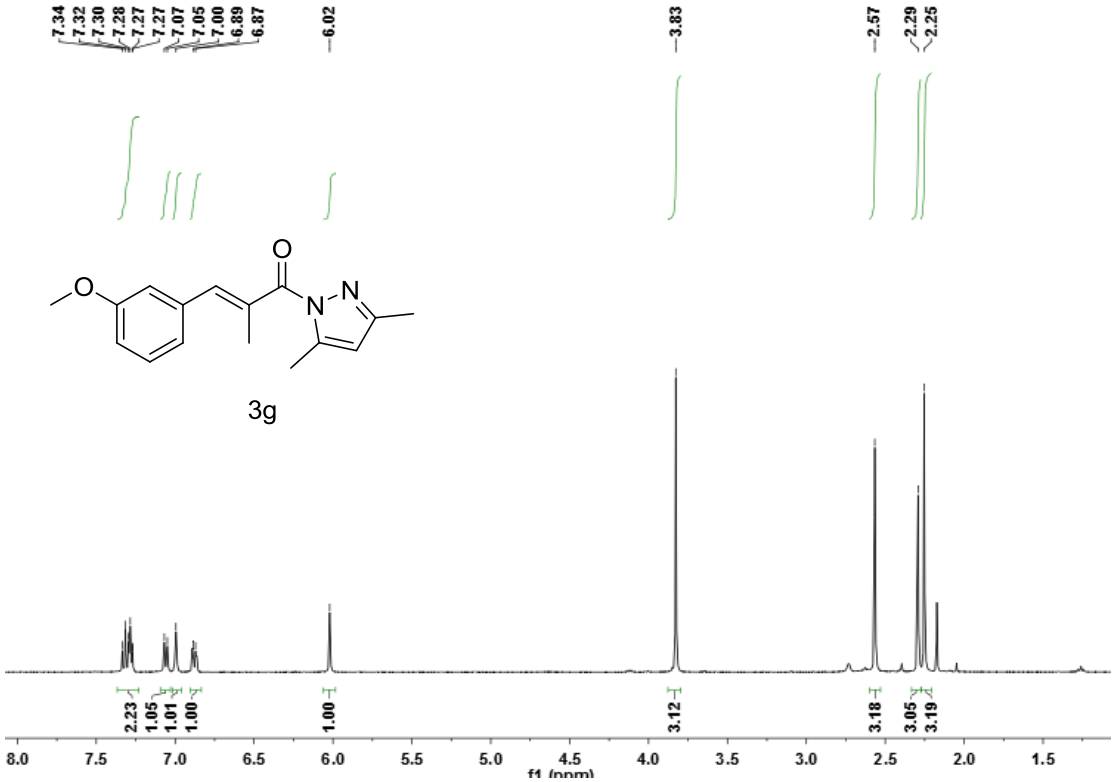
3e


171.23
151.66
144.60
140.28
137.90
135.71
131.56
130.57
129.12
128.20
126.87
110.70
31.00
21.48
16.35
14.11
13.91
O
N
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

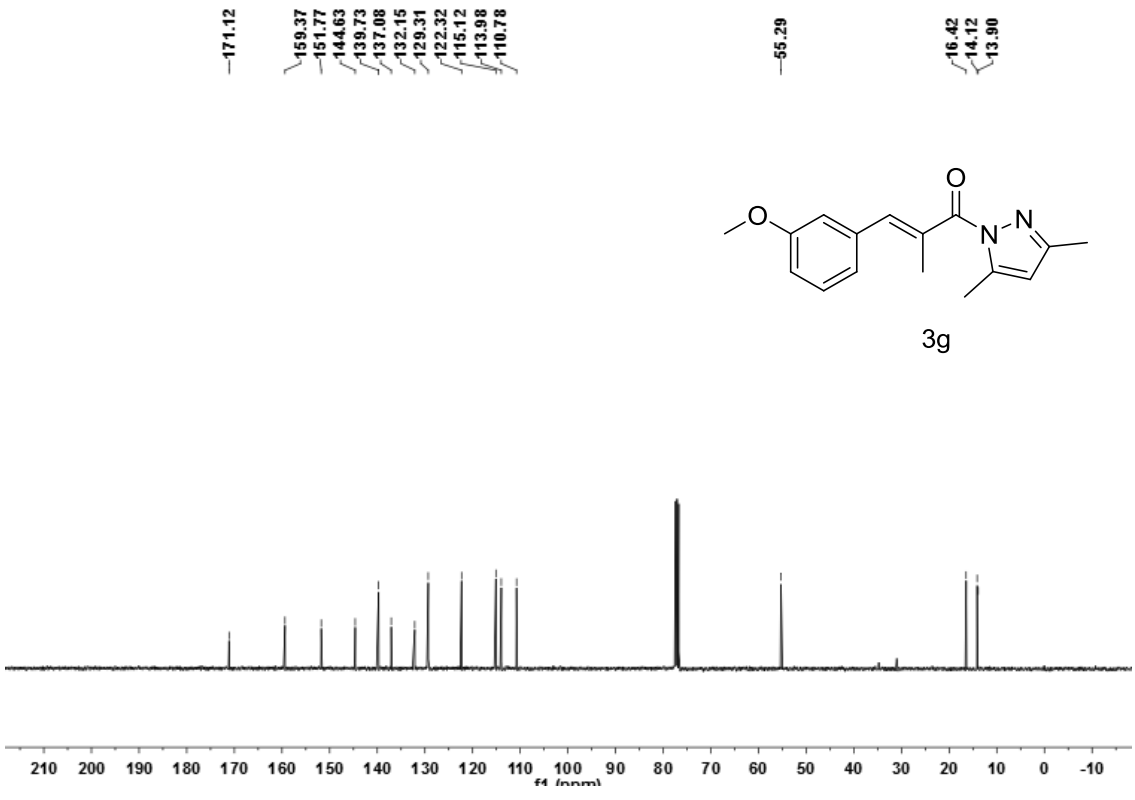
3e


7.46
7.44
7.31
6.94
6.92
6.01
3.84
2.55
2.30
2.25
O
N
N
O
3h
2.00
0.94
2.13
1.01
3.12
3.07
3.05
3.17
0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

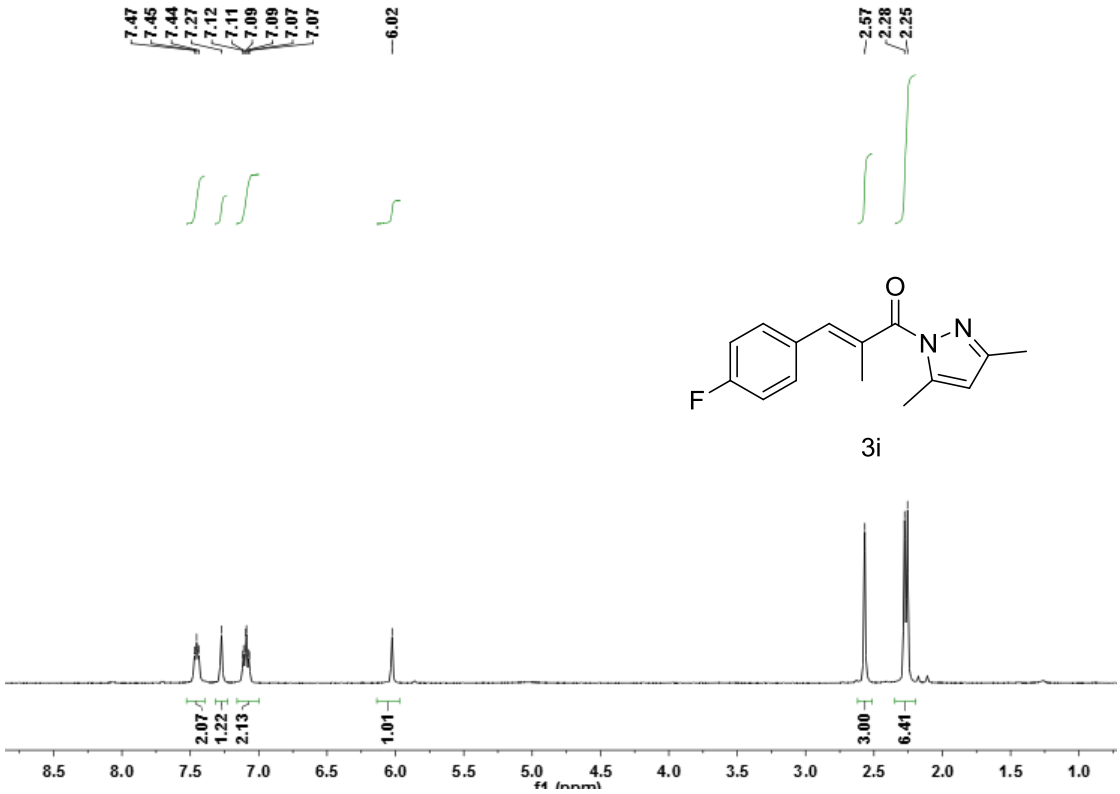

171.34
159.72
151.45
144.54
140.54
131.70
129.37
128.40
113.78
110.54
55.32
30.99
16.38
14.03
13.89
O
N
N
O
3h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


7.34
7.32
7.30
7.28
7.27
7.27
7.07
7.05
7.00
6.89
6.87
6.02
3.83
2.57
2.29
2.25
O
O
N
N
2.23
1.05
1.01
1.00
1.00
3.12
3.18
3.05
3.19
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

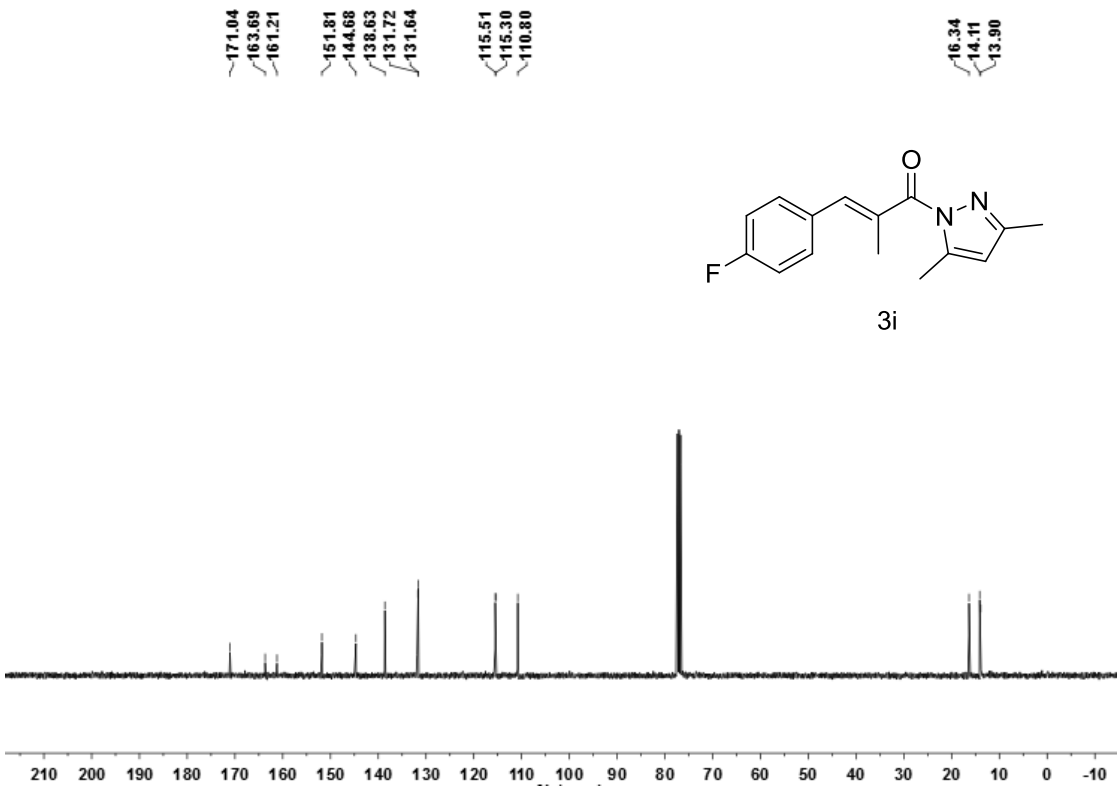
3g


171.12
159.37
151.77
144.63
139.73
137.08
132.15
129.31
122.32
115.12
113.98
110.78
55.29
16.42
14.12
13.90
O
O
N
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

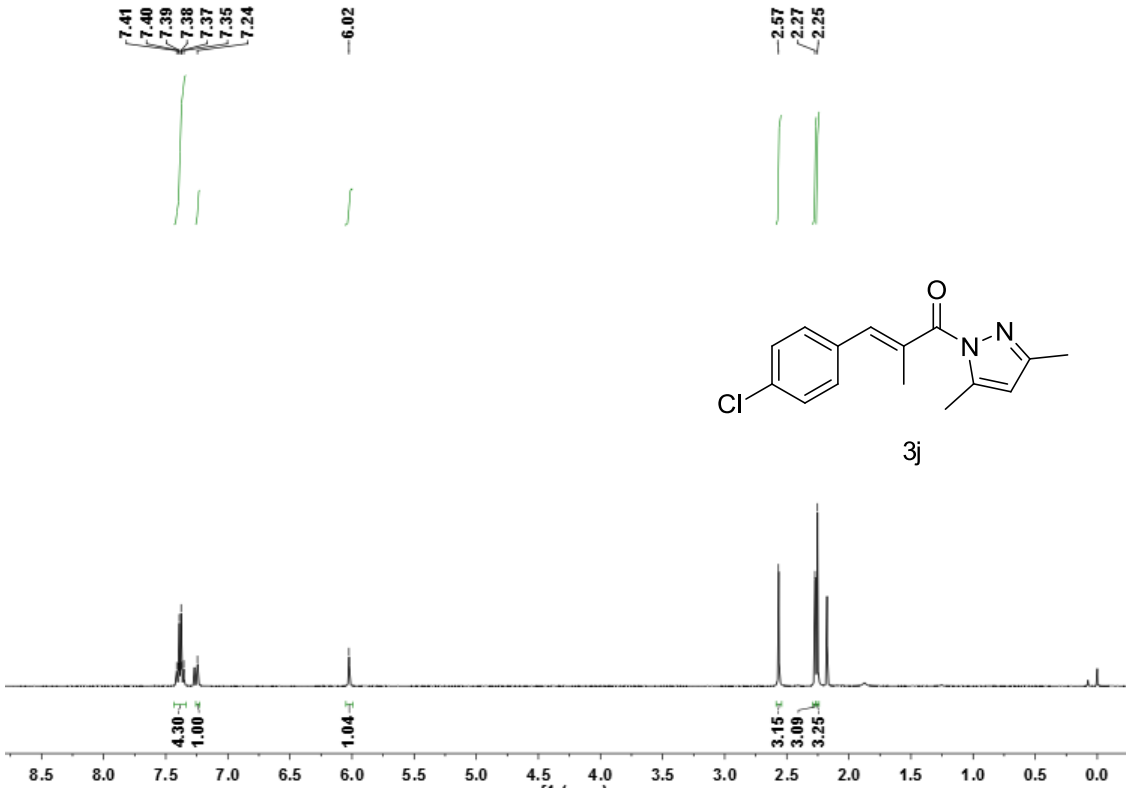
3g


7.47
7.45
7.44
7.27
7.12
7.11
7.09
7.09
7.07
7.07
6.02
2.57
2.28
2.25
O
N
N
F
2.07
1.22
2.13
1.01
3.00
6.41
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

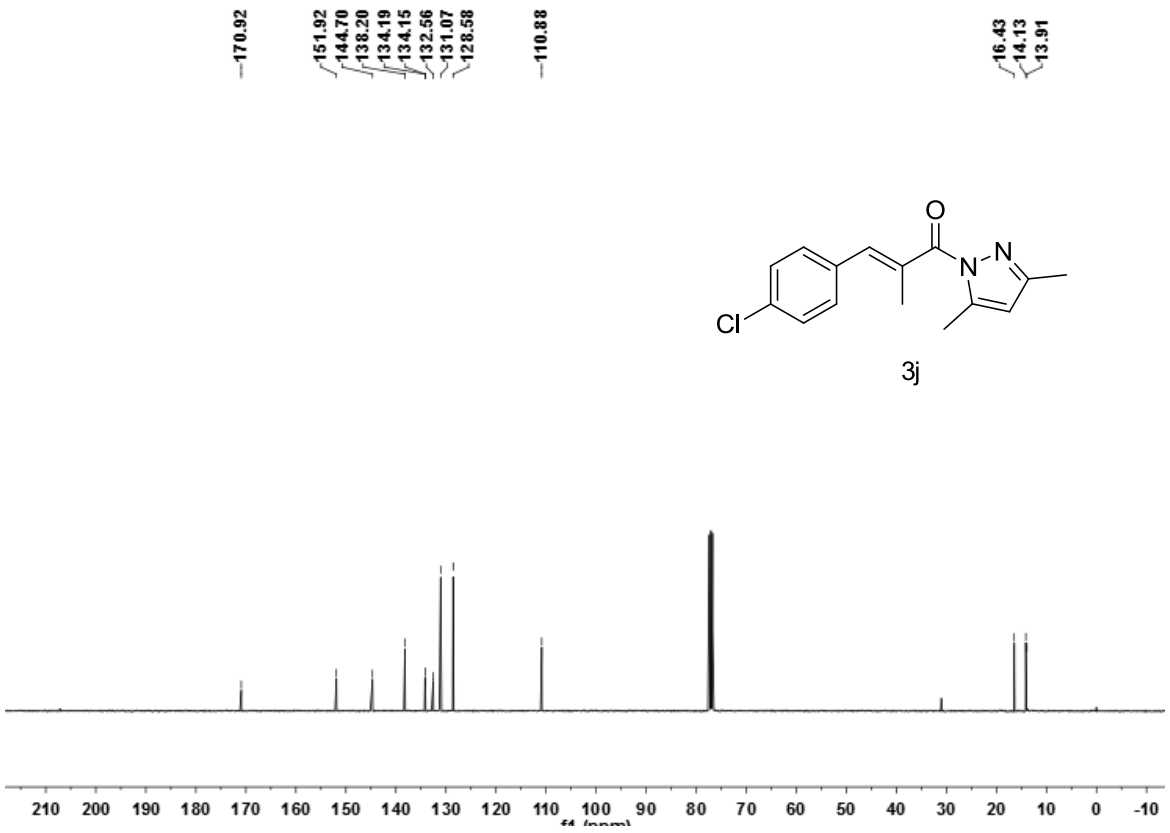
3i


171.04
163.69
161.21
151.81
144.68
138.63
131.72
131.64
115.51
115.30
110.80
16.34
14.11
13.90
O
N
N
F
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

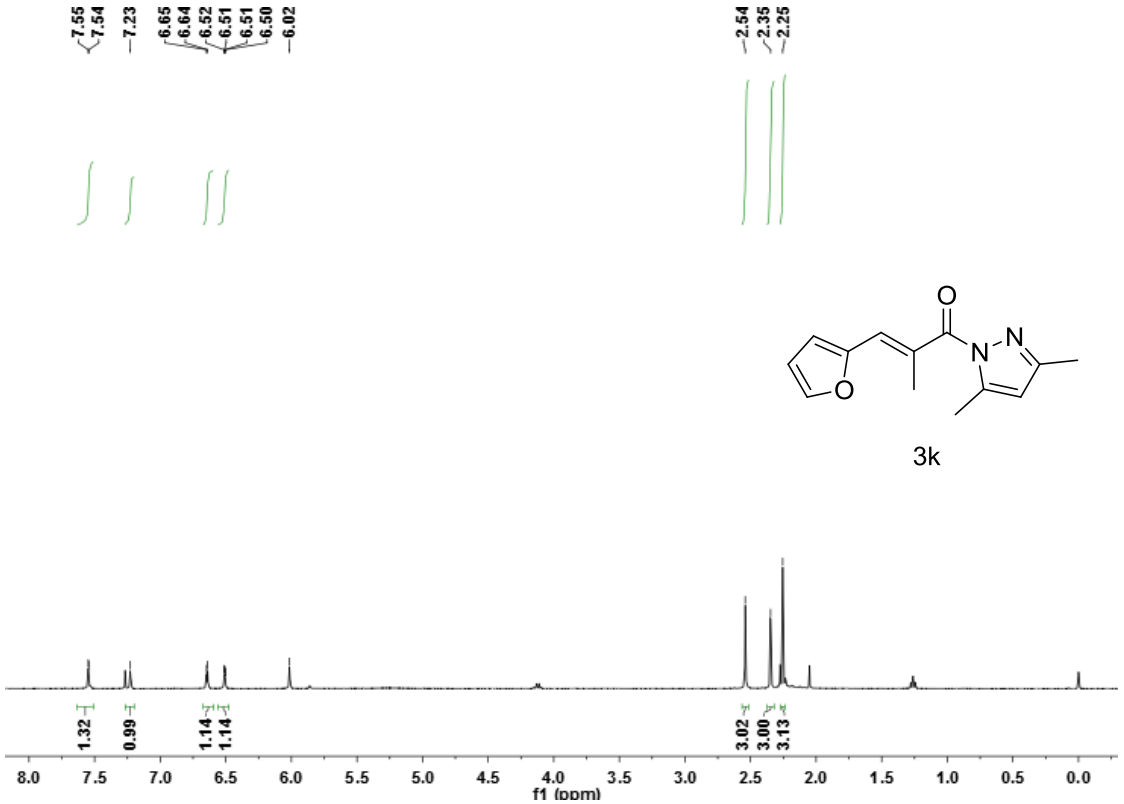
3i


7.41
7.40
7.39
7.38
7.37
7.35
7.24
6.02
2.57
2.27
2.25
O
N
N
Cl
4.30
1.00
1.04
3.15
3.09
3.25
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

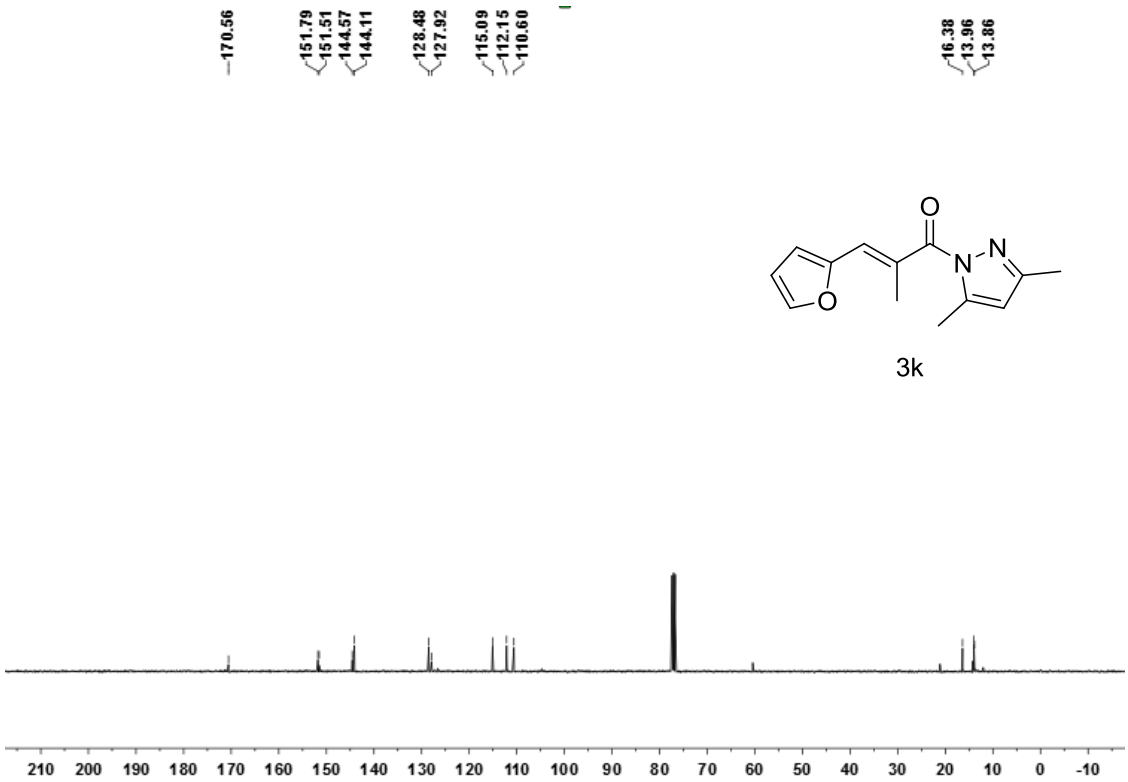
3j


170.92
151.92
144.70
138.20
134.19
134.15
132.56
131.07
128.58
110.88
16.43
14.13
13.91
O
N
N
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

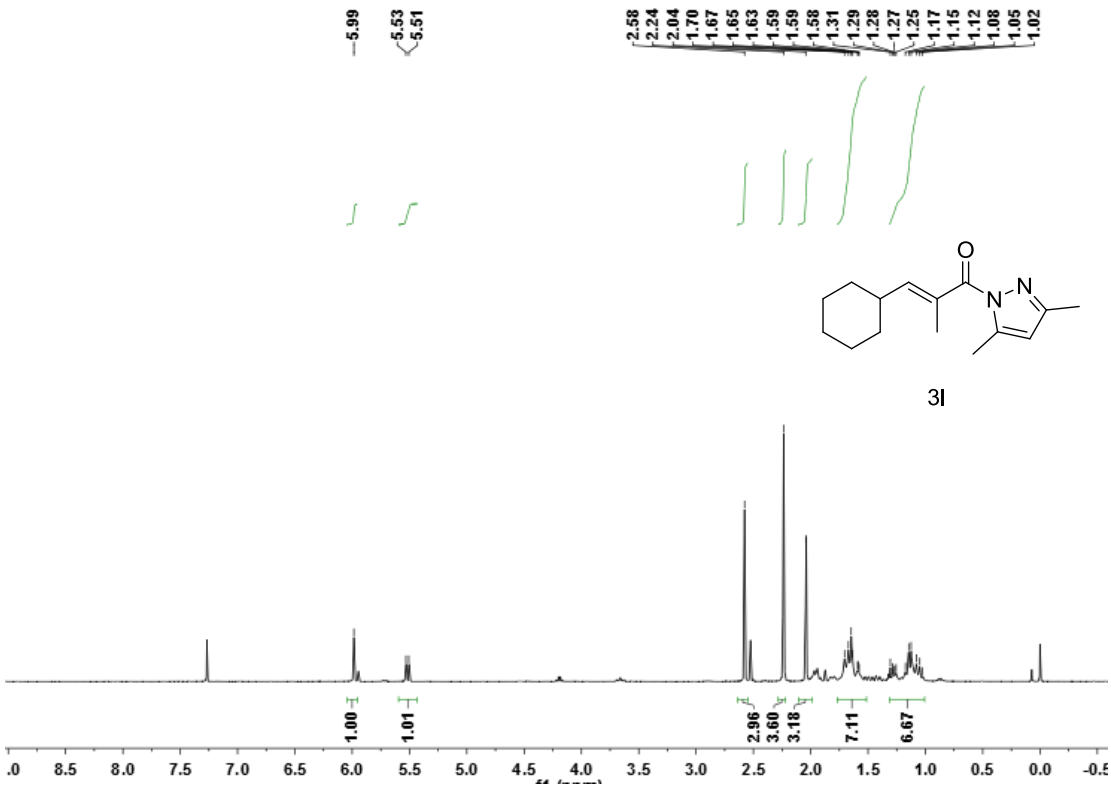
3j


7.55
7.54
7.23
6.65
6.64
6.52
6.51
6.51
6.50
6.02
2.54
2.35
2.25
O
N
N
O
1.32
0.99
1.14
1.14
3.02
3.00
3.13
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

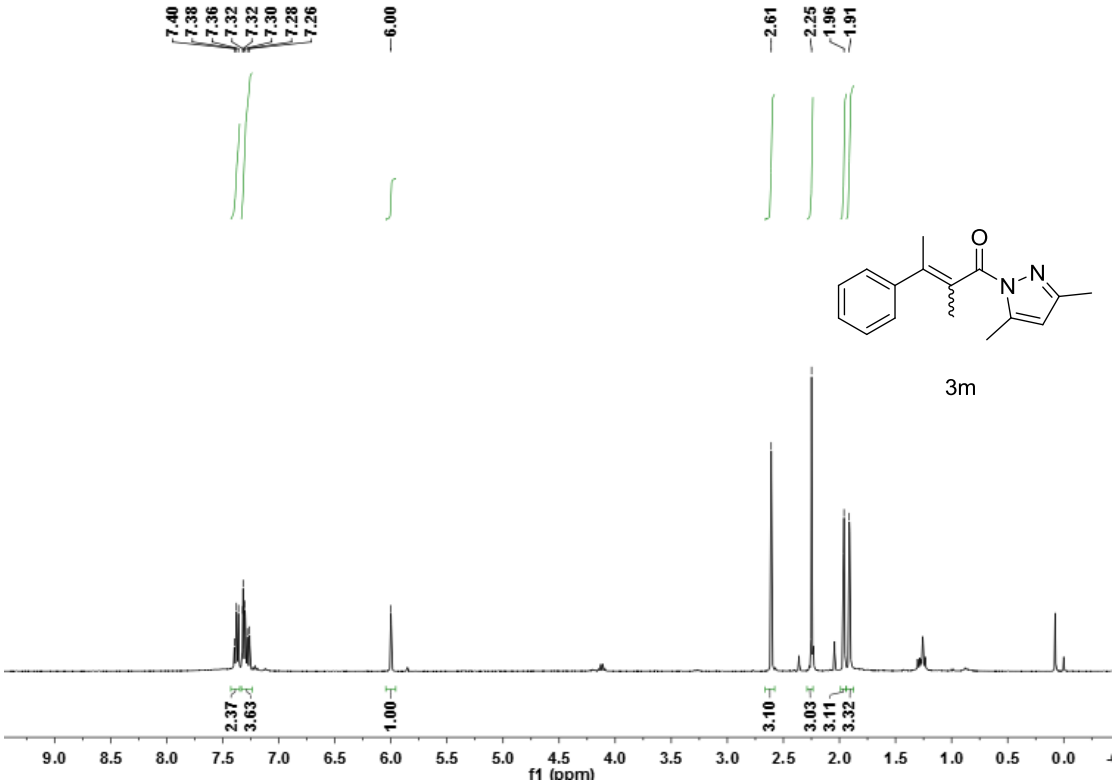
3k


170.56
151.79
151.51
144.57
144.11
128.48
127.92
115.09
112.15
110.60
16.38
13.96
13.86
O
N
N
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

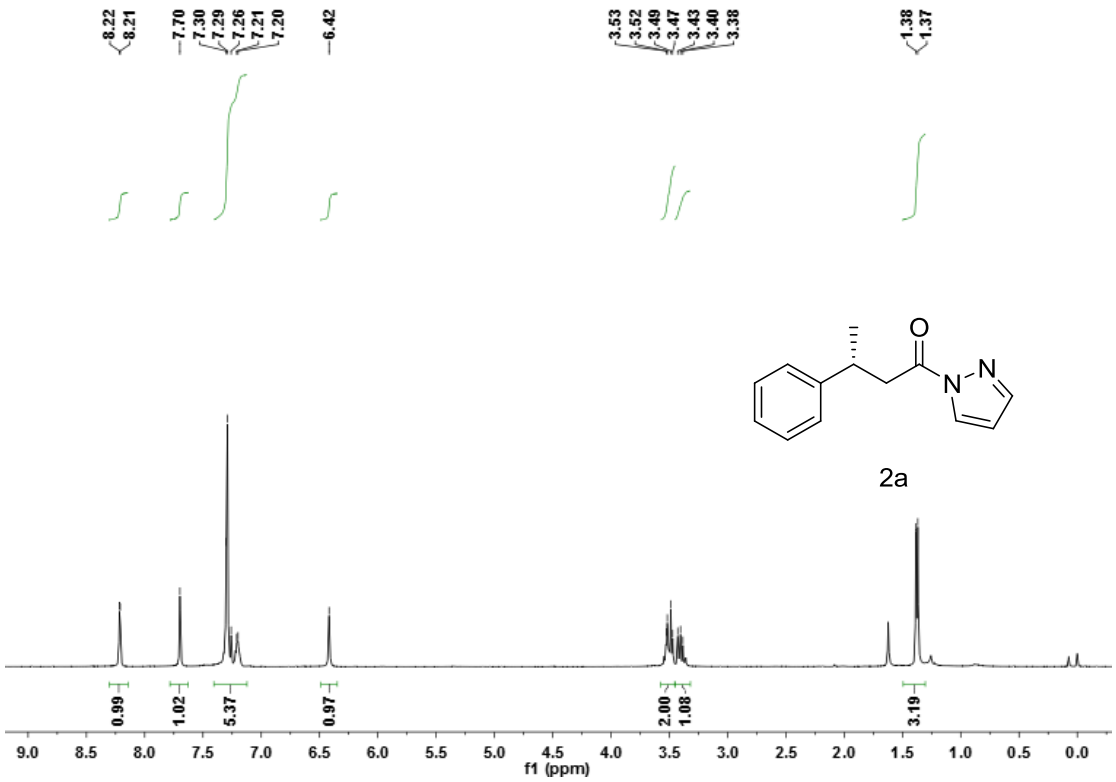
3k


5.99
5.53
5.51
2.58
2.24
2.04
1.70
1.67
1.65
1.63
1.59
1.59
1.58
1.31
1.29
1.28
1.27
1.25
1.17
1.15
1.12
1.08
1.05
1.02
O
N
N
1.00
1.01
2.96
3.60
3.18
7.11
6.67

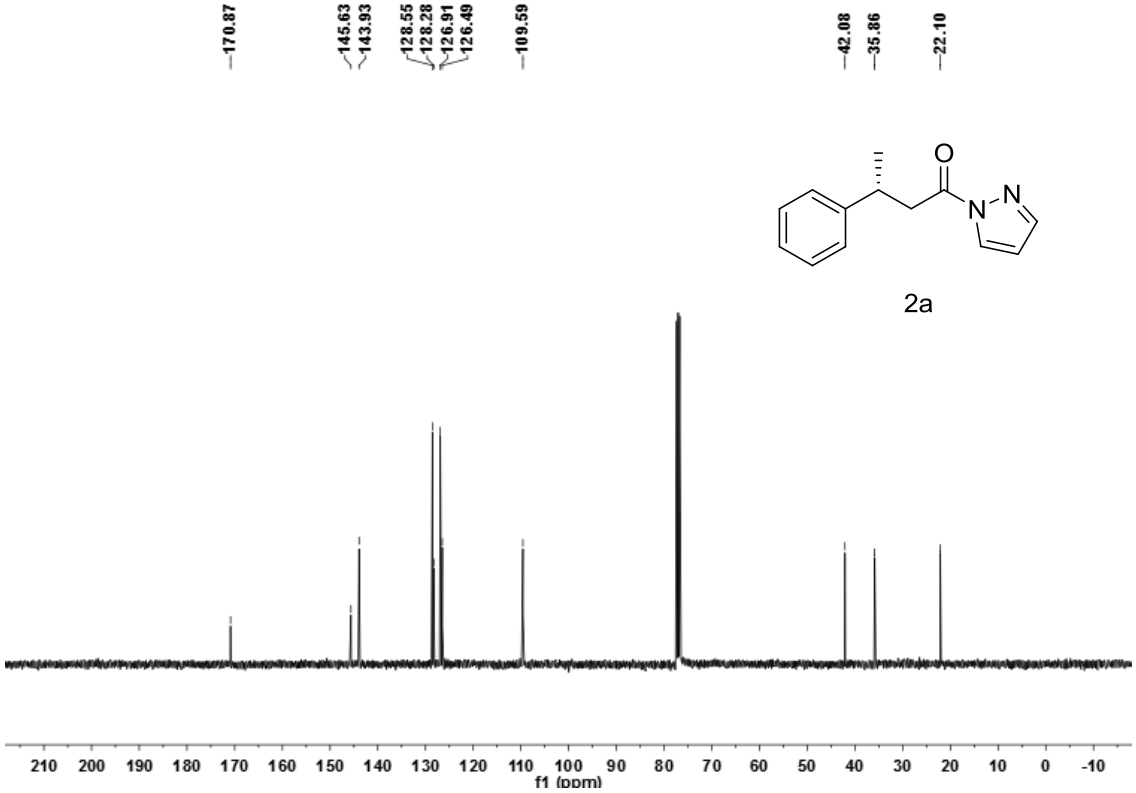
3l


7.40
7.38
7.36
7.32
7.32
7.30
7.28
7.26
6.00
2.61
2.25
1.96
1.91
O
N
N
2.37
3.63
1.00
3.10
3.03
3.11
3.32
f1 (ppm)

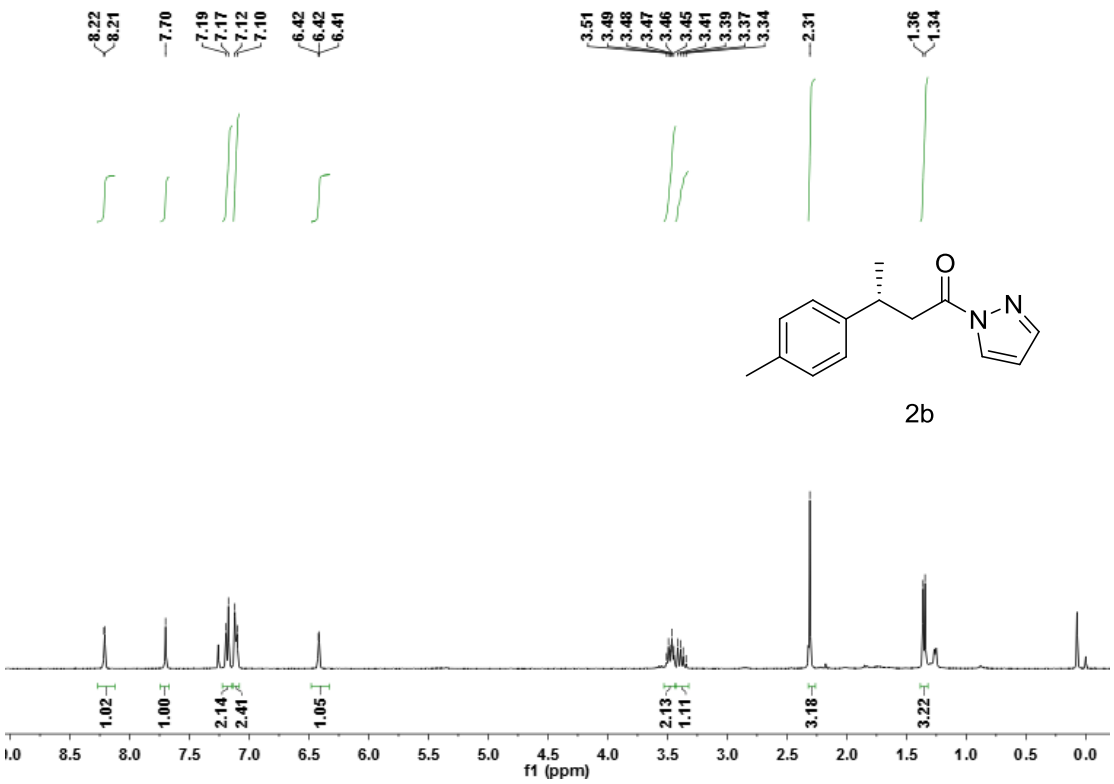
3m


8.22
8.21
7.70
7.30
7.29
7.26
7.21
7.20
6.42
3.53
3.52
3.49
3.47
3.43
3.40
3.38
1.38
1.37
O
N
N
0.99
1.02
5.37
0.97
2.00
1.08
3.19
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

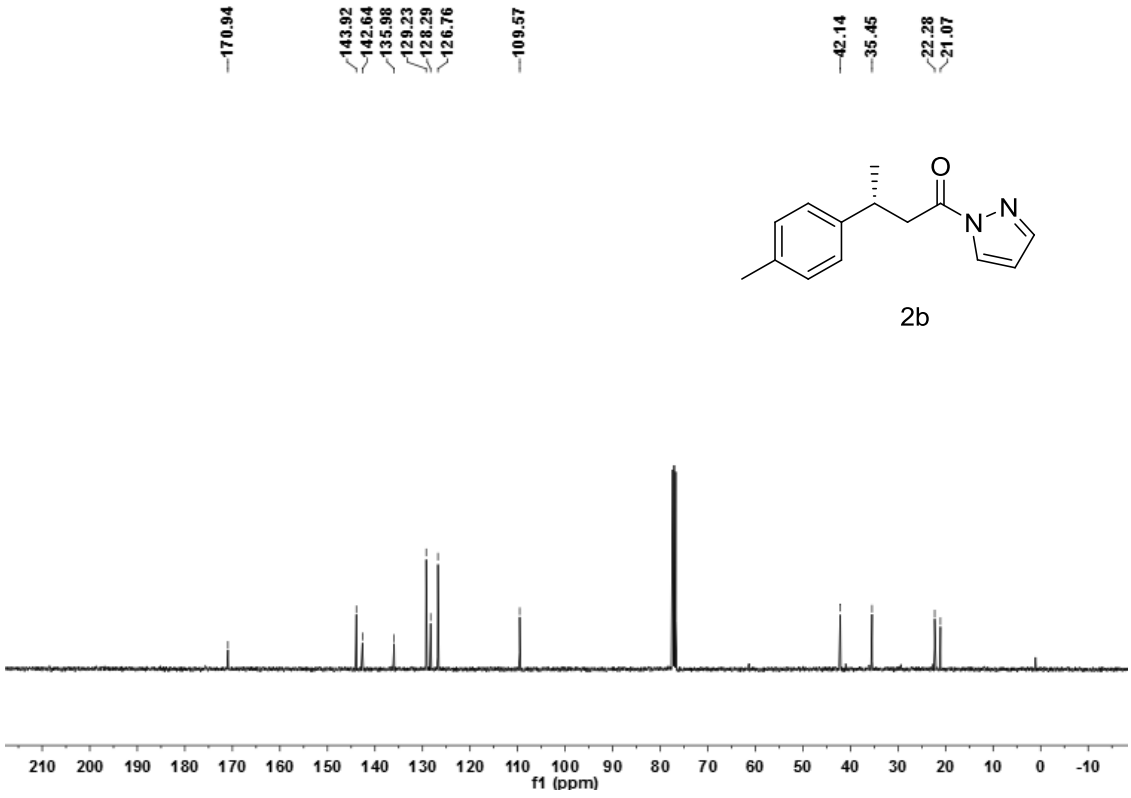
2a


170.87
145.63
143.93
128.55
128.28
126.91
126.49
109.59
42.08
35.86
22.10
O
N
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

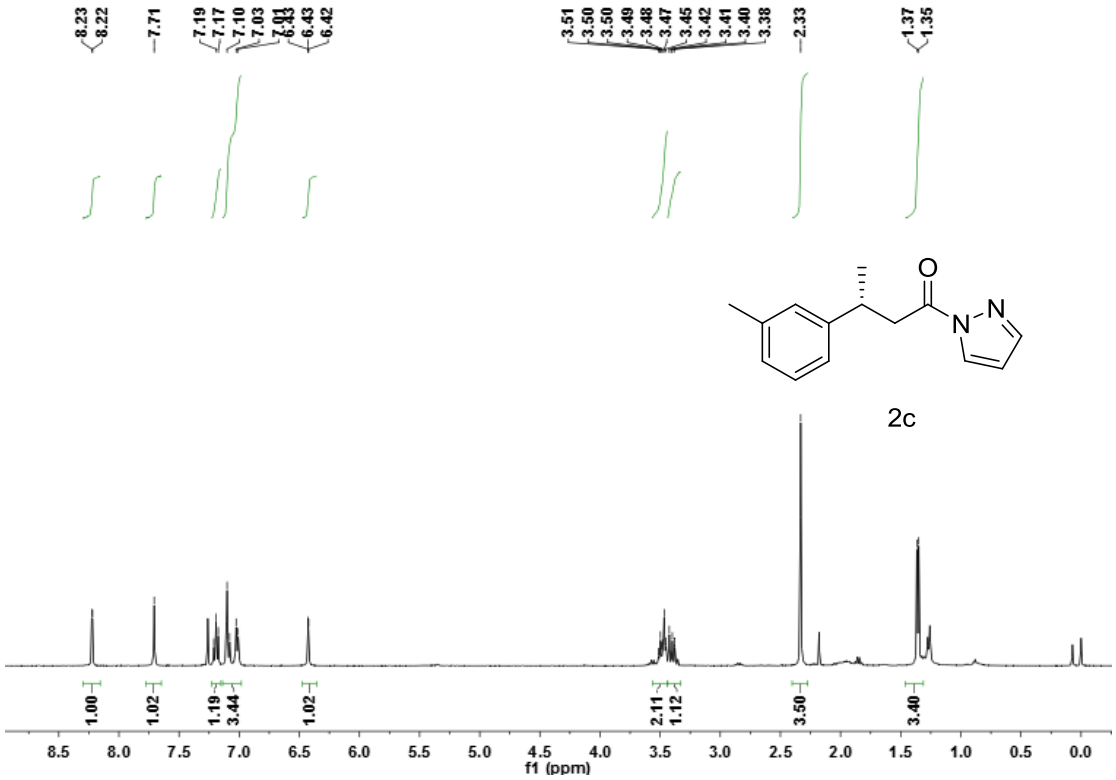
2a

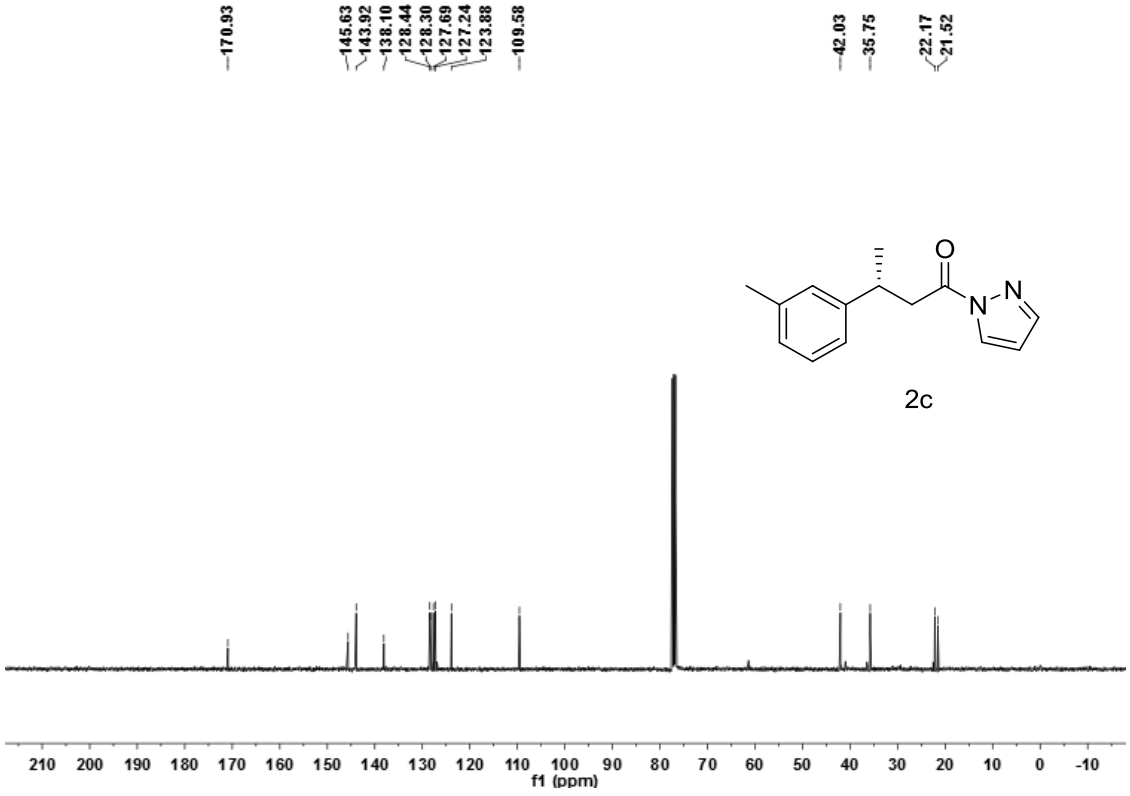

8.22
8.21
7.70
7.19
7.17
7.12
7.10
6.42
6.42
6.41
3.51
3.49
3.48
3.47
3.46
3.45
3.41
3.39
3.37
3.34
2.31
1.36
1.34
O
N
N
1.02
1.00
2.14
2.41
1.05
2.13
1.11
3.18
3.22
f1 (ppm)

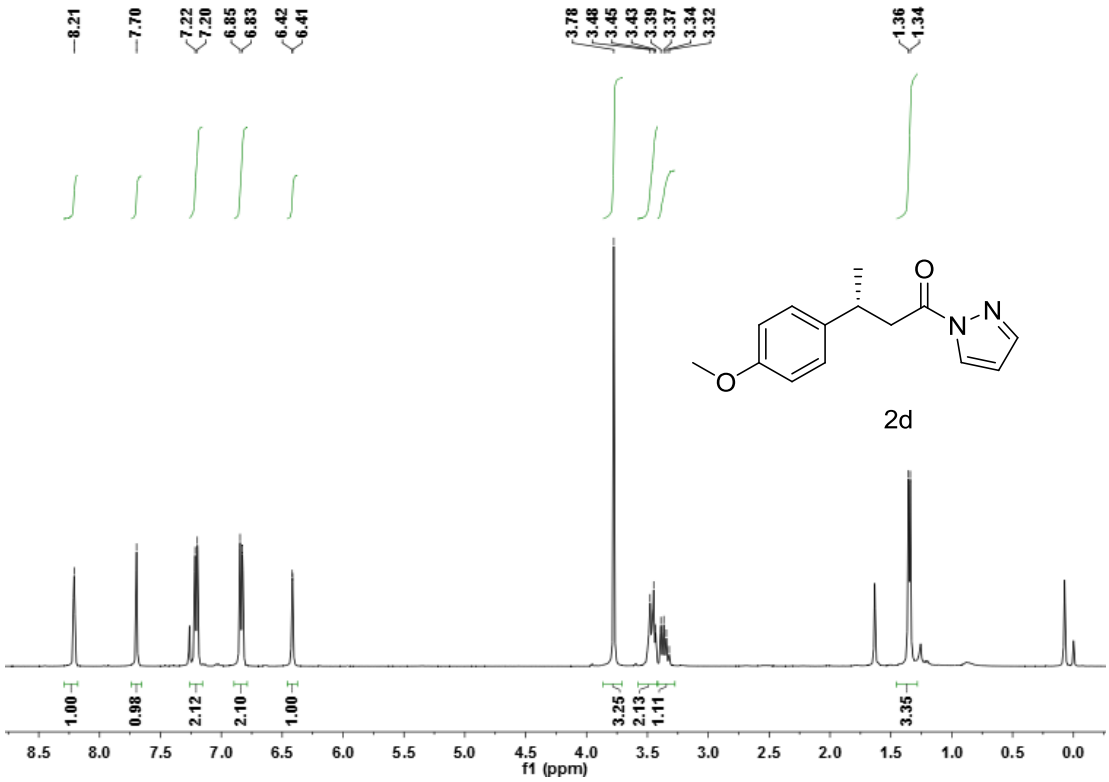
2b


170.94
143.92
142.64
135.98
129.23
128.29
126.76
109.57
42.14
35.45
22.28
21.07
O
N
N
f1 (ppm)

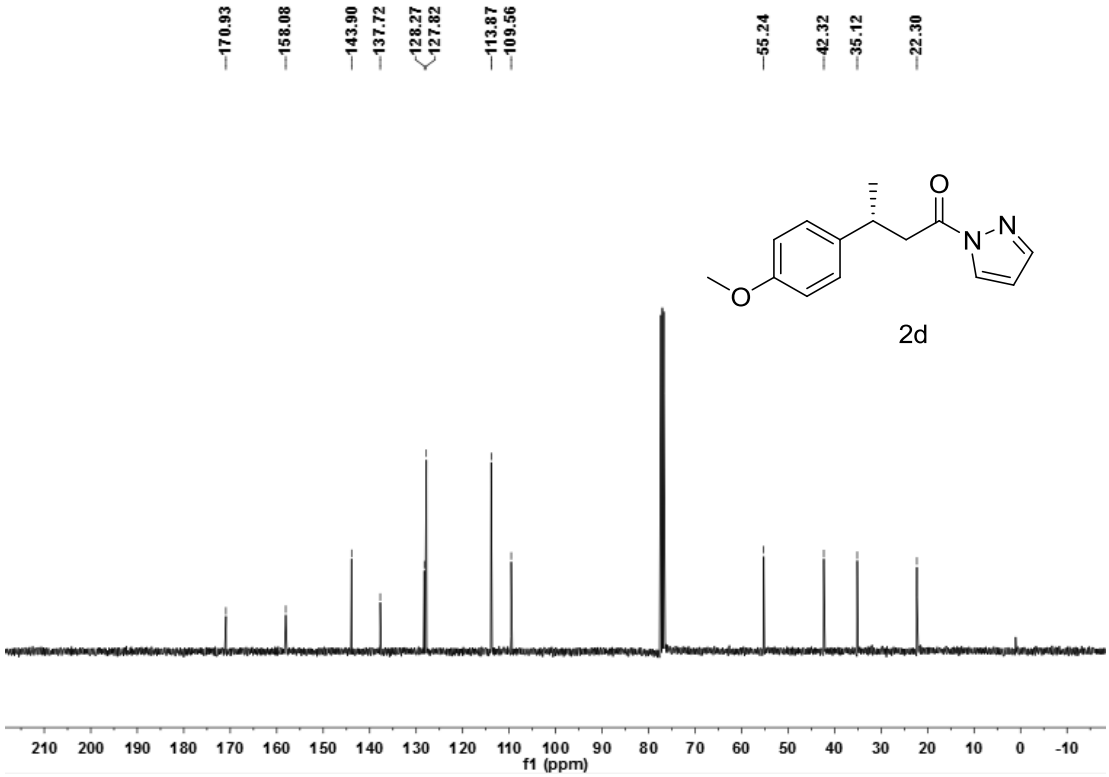
2b


8.23
8.22
7.71
7.19
7.17
7.10
7.03
6.43
6.42
3.51
3.50
3.50
3.49
3.48
3.47
3.45
3.42
3.41
3.40
3.38
2.33
1.37
1.35
O
N
N
2c
1.00
1.02
1.19
3.44
1.02
2.11
1.12
3.50
3.40
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

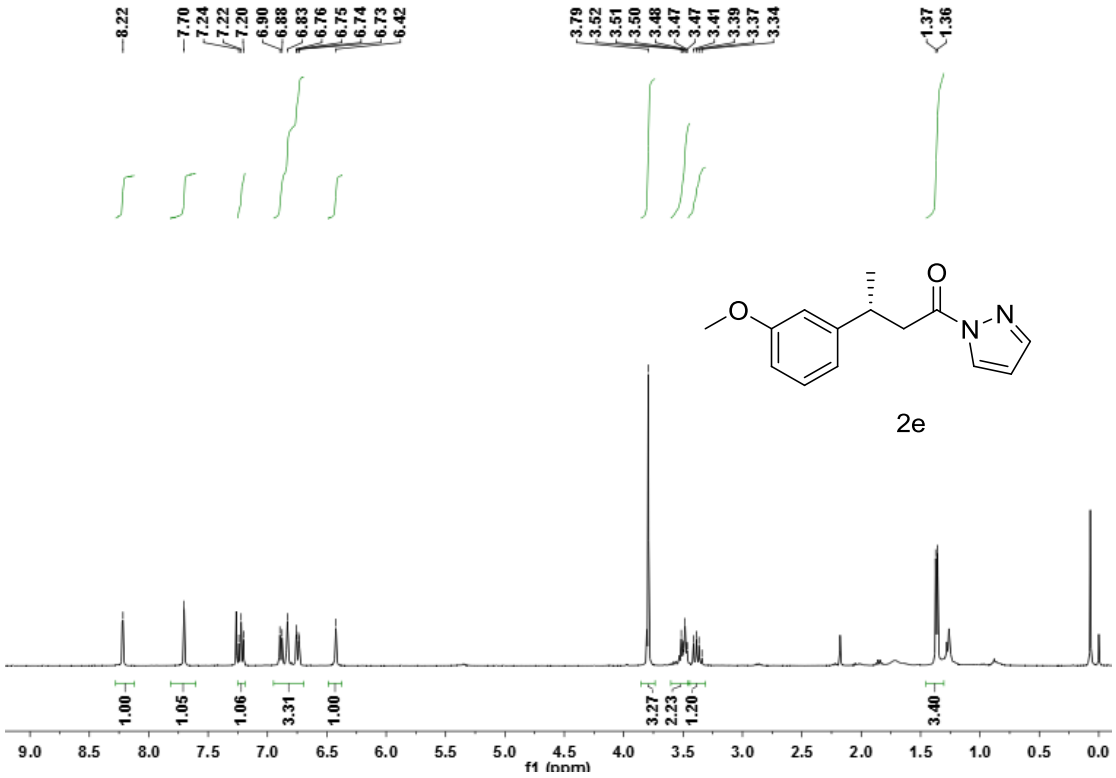

170.93
145.63
143.92
138.10
128.44
128.30
127.69
127.24
123.88
109.58
42.03
35.75
22.17
21.52
O
N
N
2c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

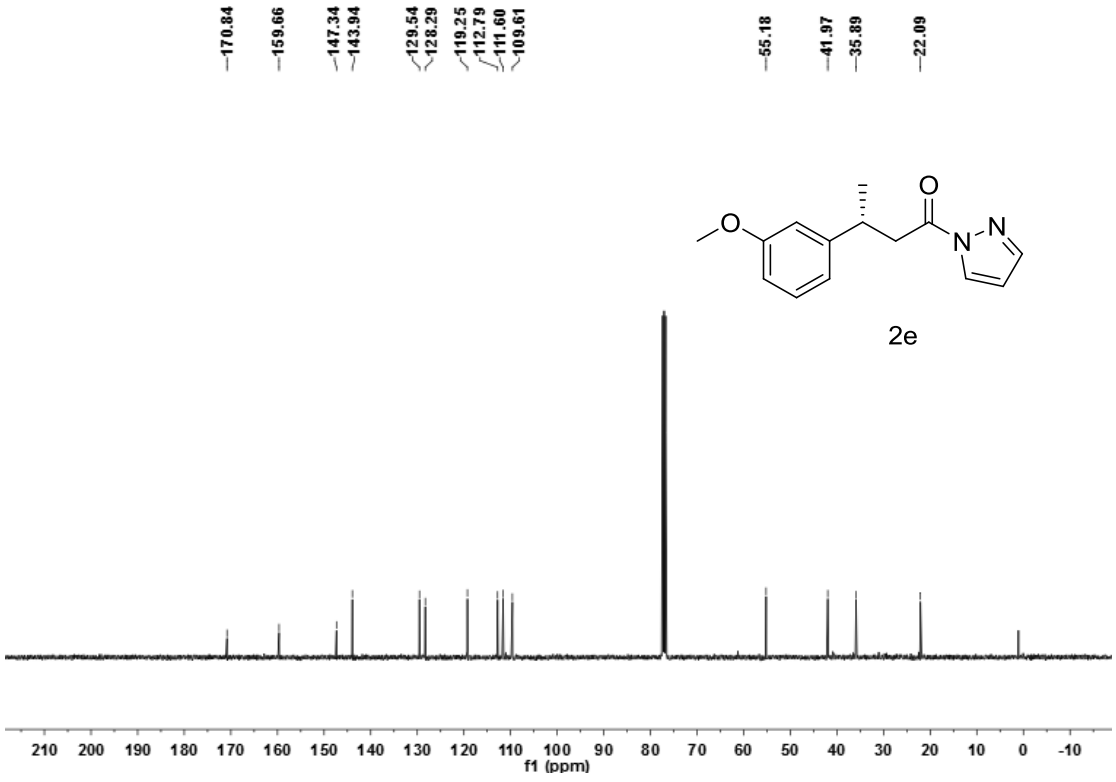

8.21
7.70
7.22
7.20
6.85
6.83
6.42
6.41
3.78
3.48
3.45
3.43
3.39
3.37
3.34
3.32
1.36
1.34
1.00
0.98
2.12
2.10
1.00
3.25
2.13
1.11
3.35
f1 (ppm)

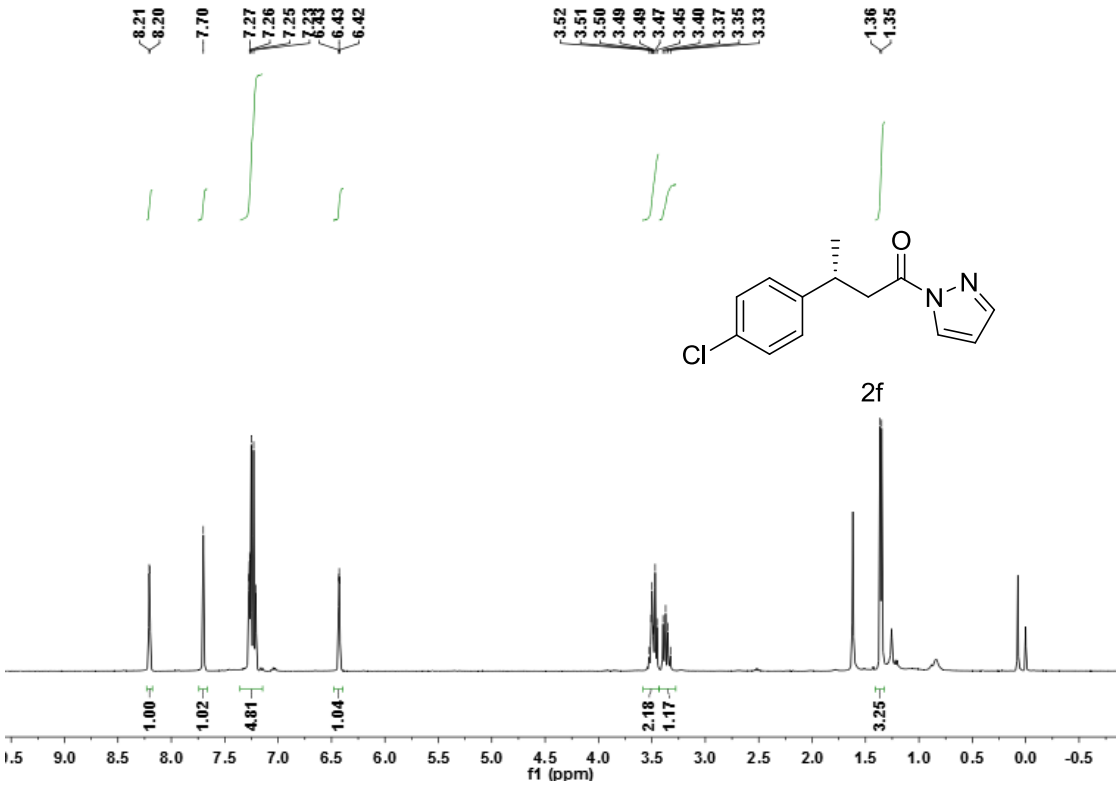
2d

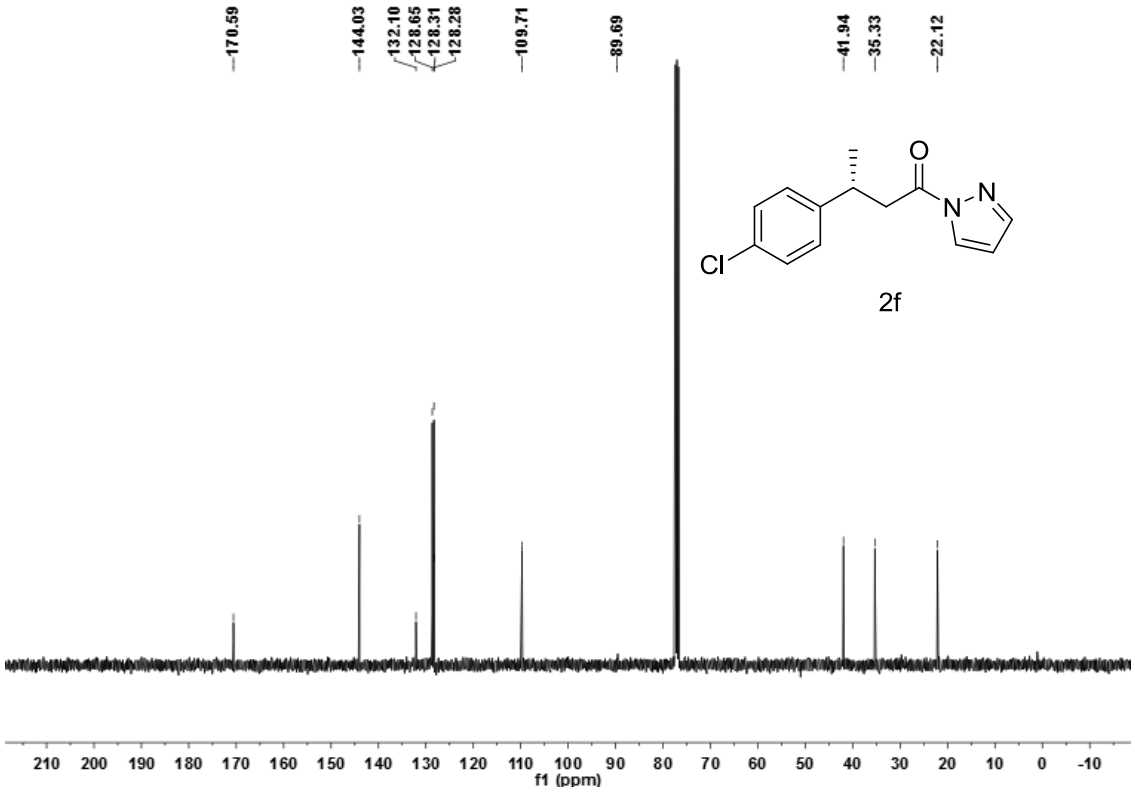

170.93
158.08
143.90
137.72
128.27
127.82
113.87
109.56
55.24
42.32
35.12
22.30
f1 (ppm)

2d

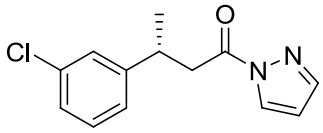

8.22
7.70
7.24
7.22
7.20
6.90
6.88
6.83
6.76
6.75
6.74
6.73
6.42
3.79
3.52
3.51
3.50
3.48
3.47
3.47
3.41
3.39
3.37
3.34
1.37
1.36
O
O
N
N
2e
1.00
1.05
1.06
3.31
1.00
3.27
2.23
1.20
3.40
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


170.84
159.66
147.34
143.94
129.54
128.29
119.25
112.79
111.60
109.61
55.18
41.97
35.89
22.09
O
O
N
N
2e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

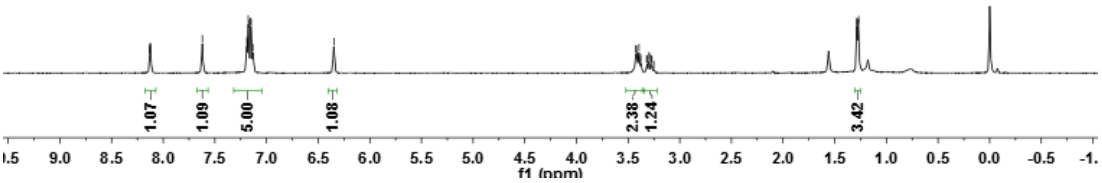

8.21
8.20
7.70
7.27
7.26
7.25
6.43
6.42
3.52
3.51
3.50
3.49
3.49
3.47
3.45
3.40
3.37
3.35
3.33
1.36
1.35
O
N
N
Cl
2f
1.00
1.02
4.81
1.04
2.18
1.17
3.25
f1 (ppm)


170.59
144.03
132.10
128.65
128.31
128.28
109.71
89.69
41.94
35.33
22.12
O
N
N
Cl
2f
f1 (ppm)

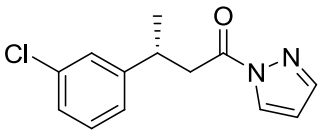

8.13
7.62
7.19
7.18
7.17
7.15
6.35
3.42
3.41
3.40
3.39
3.38
3.32
3.30
3.29
3.27
3.25
1.29
1.27


Cl
O
N
N

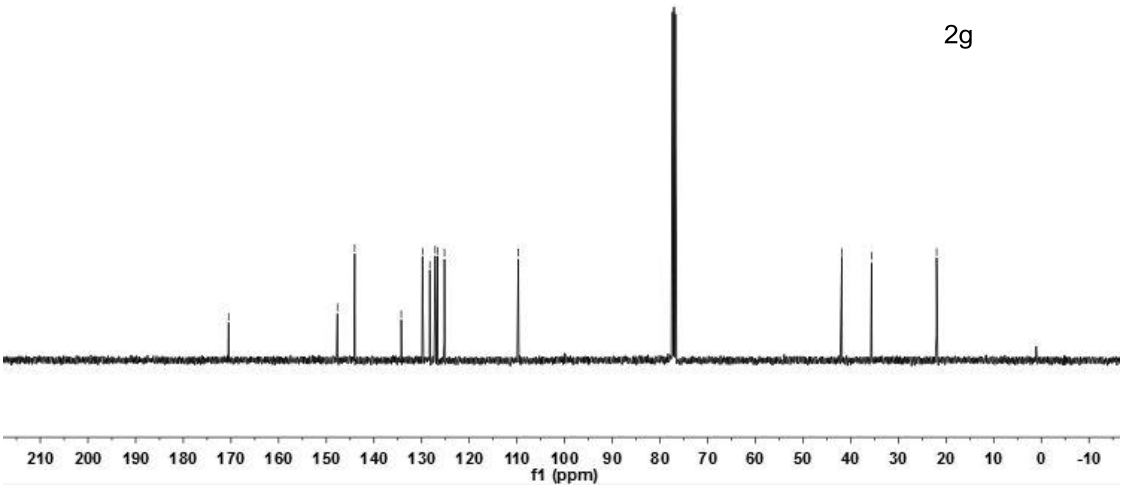
2g

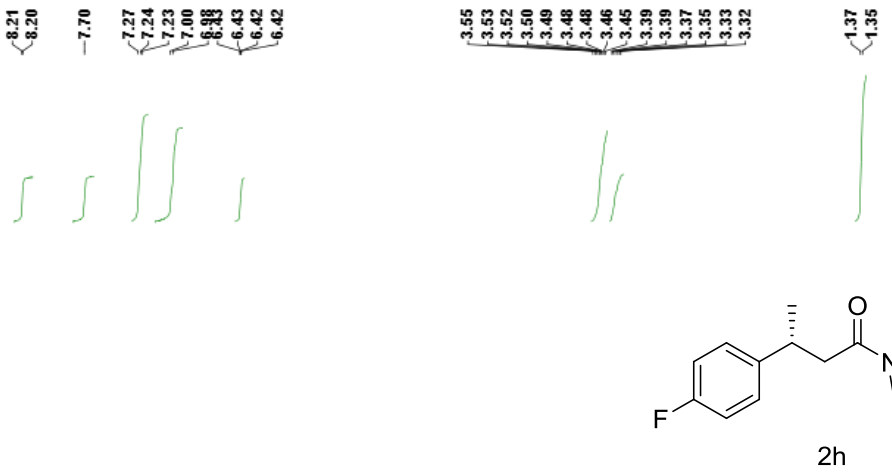

1.07
1.09
5.00
1.08
2.38
1.24
3.42
f1 (ppm)


170.51
147.67
144.04
134.28
129.83
128.29
127.15
126.70
125.20
109.72
41.84
35.61
21.96

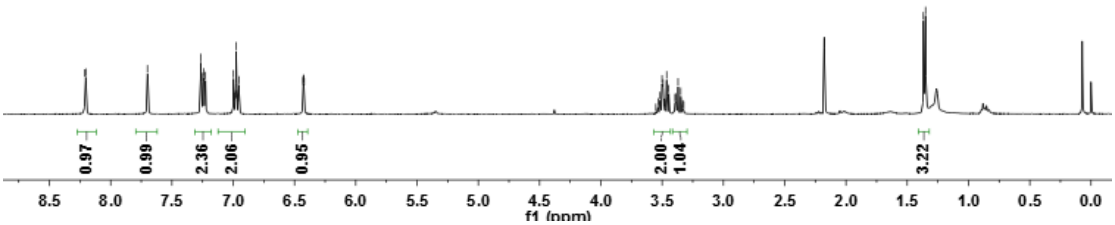

Cl
O
N
N

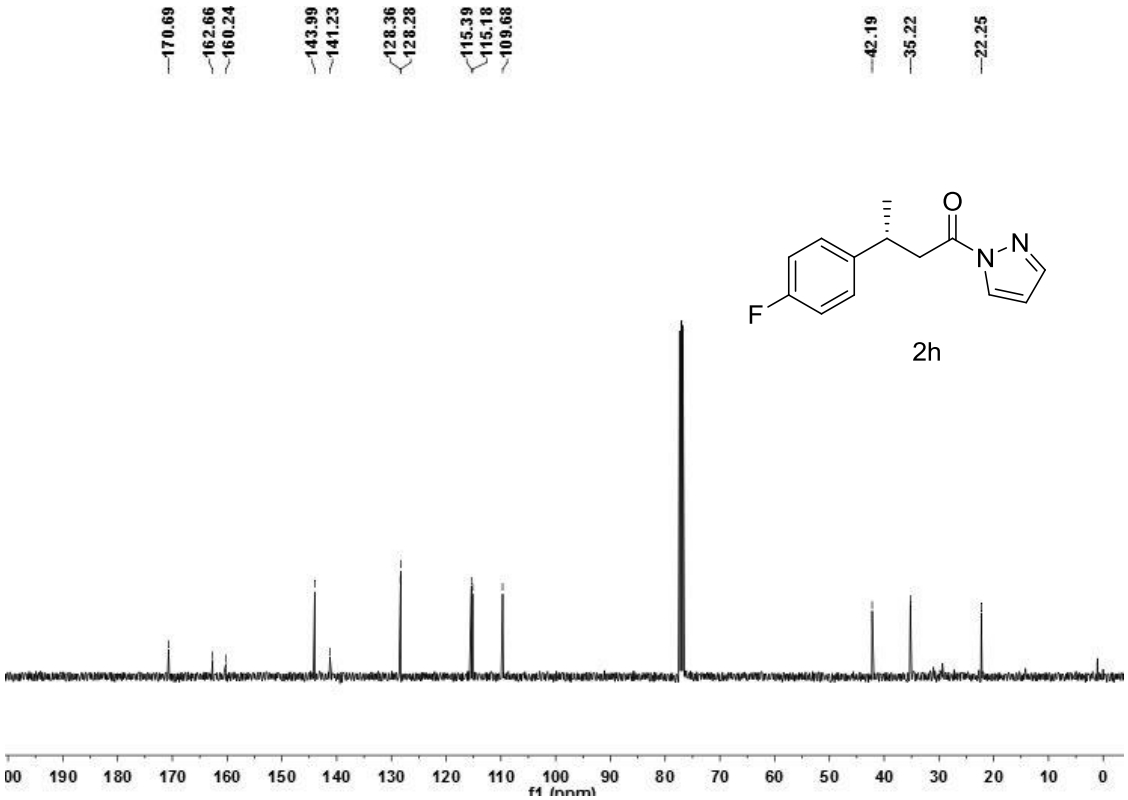
2g


f1 (ppm)

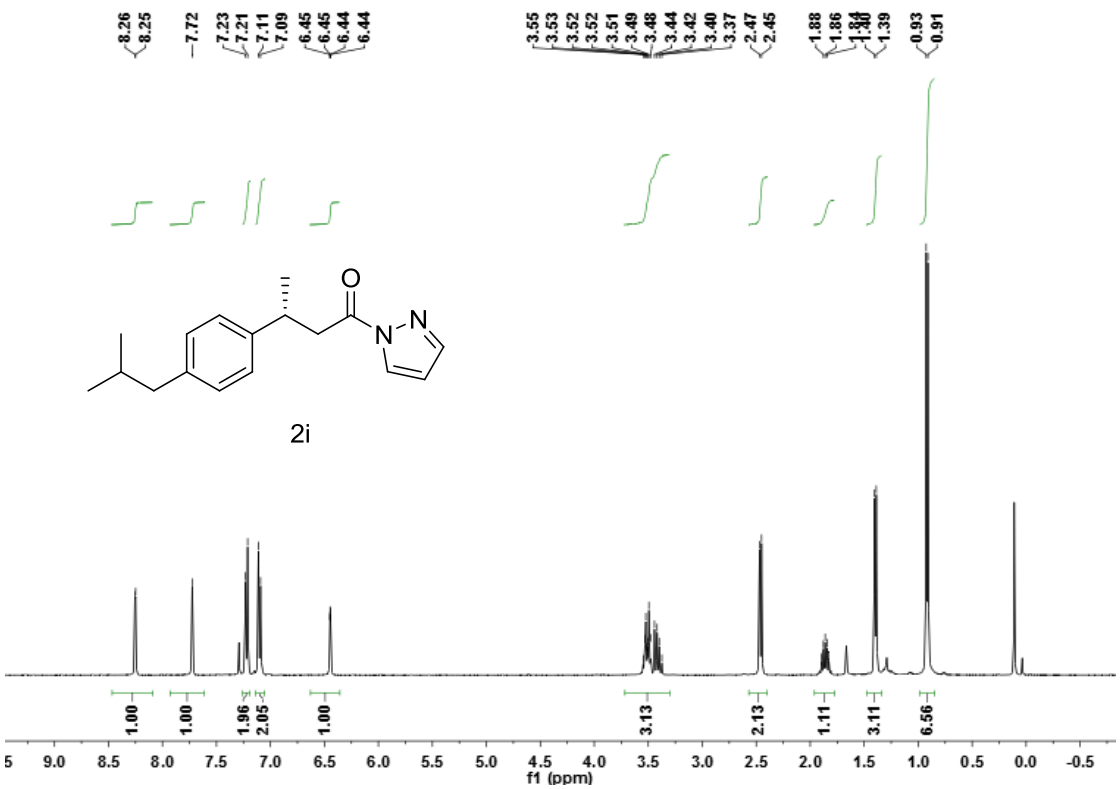

8.21
8.20
7.70
7.27
7.24
7.23
7.00
6.43
6.42
6.42
3.55
3.53
3.52
3.50
3.49
3.48
3.48
3.46
3.45
3.39
3.39
3.37
3.35
3.33
3.32
1.37
1.35
O
N
N
F

2h

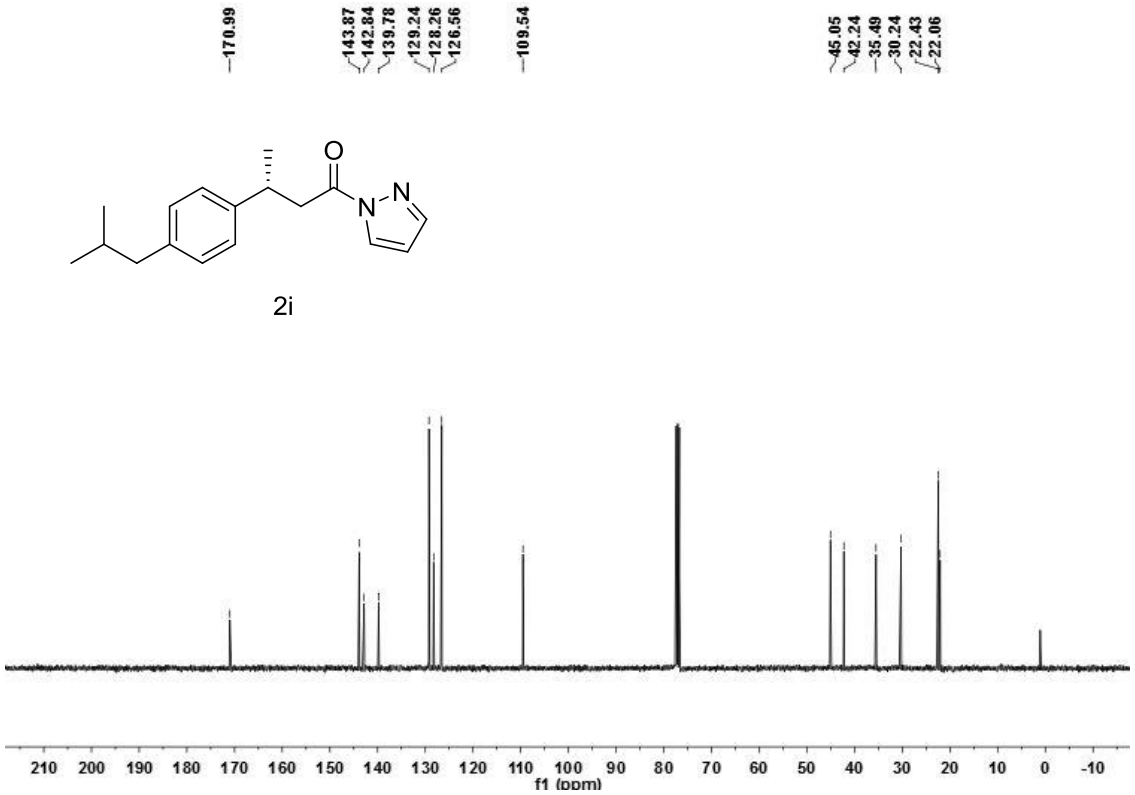

0.97
0.99
2.36
2.06
0.95
2.00
1.04
3.22
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


170.69
162.66
160.24
143.99
141.23
128.36
128.28
115.39
115.18
109.68
42.19
35.22
22.25
O
N
N
F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

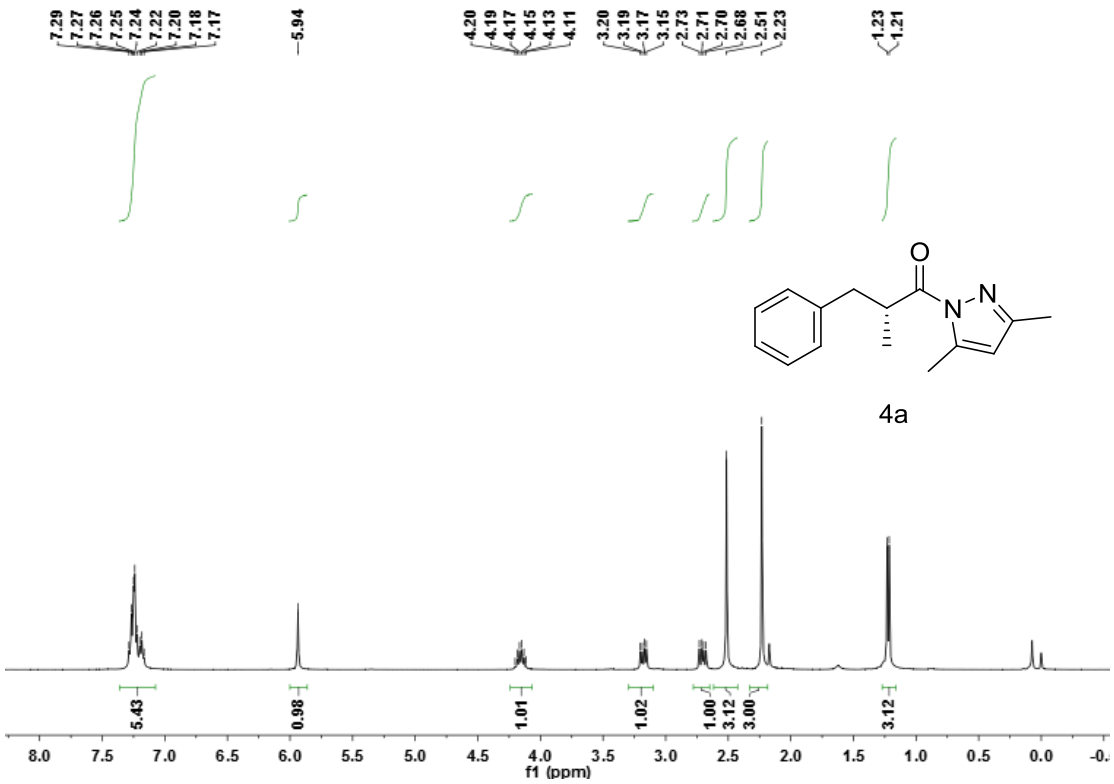
2h


8.26
8.25
7.72
7.23
7.21
7.11
7.09
6.45
6.45
6.44
6.44
3.55
3.53
3.52
3.52
3.51
3.49
3.48
3.44
3.42
3.40
3.37
2.47
2.45
1.88
1.86
1.39
0.93
0.91
O
N
N
1.00
1.00
1.96
2.05
1.00
3.13
2.13
1.11
3.11
6.56
f1 (ppm)

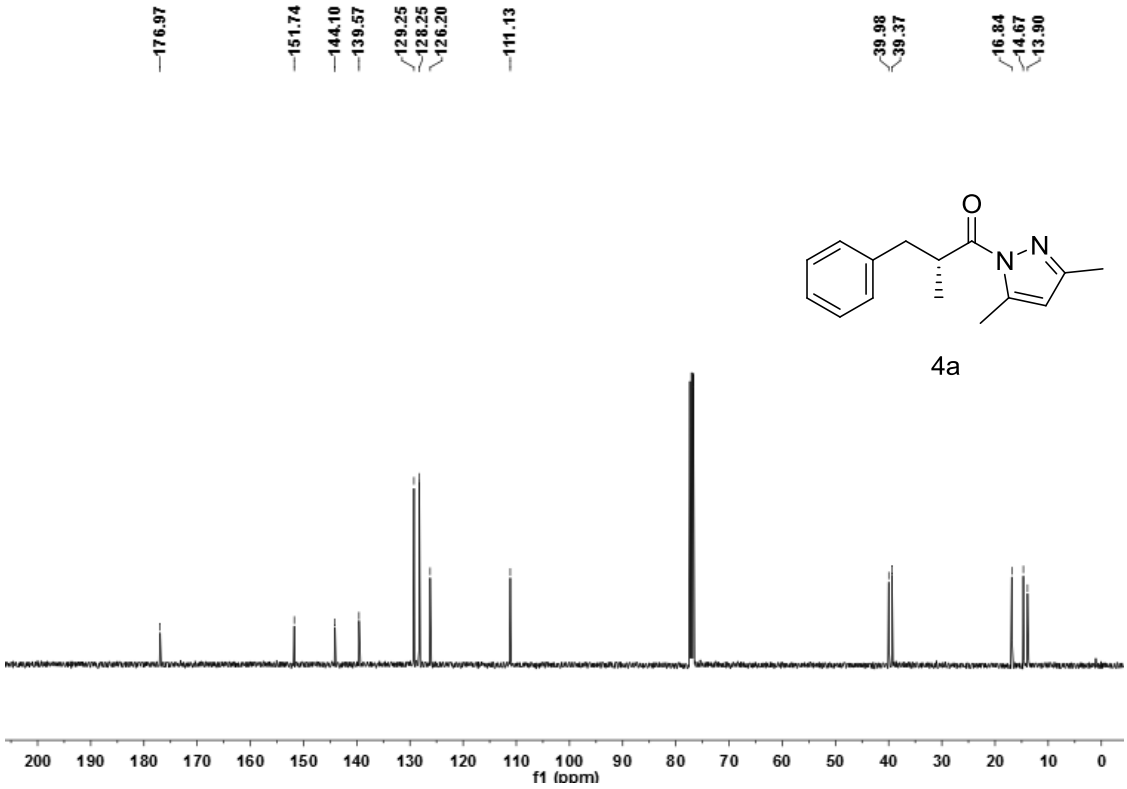
2i


170.99
143.87
142.84
139.78
129.24
128.26
126.56
109.54
45.05
42.24
35.49
30.24
22.43
22.06
O
N
N
f1 (ppm)

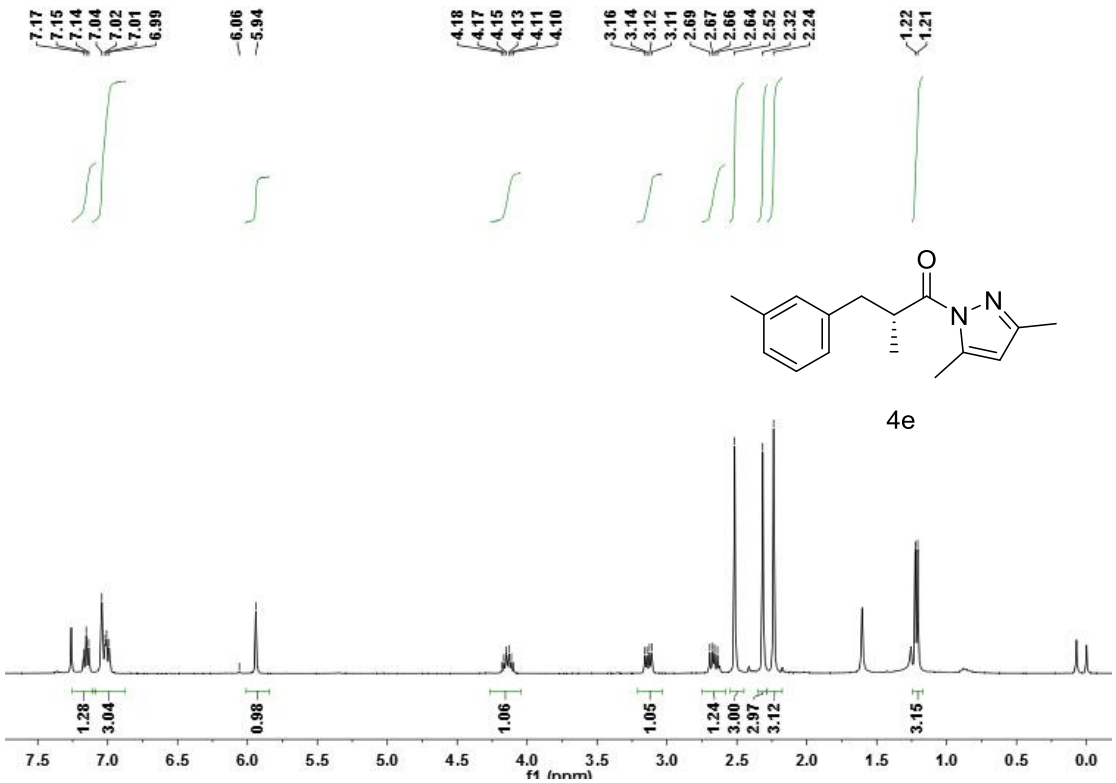
2i

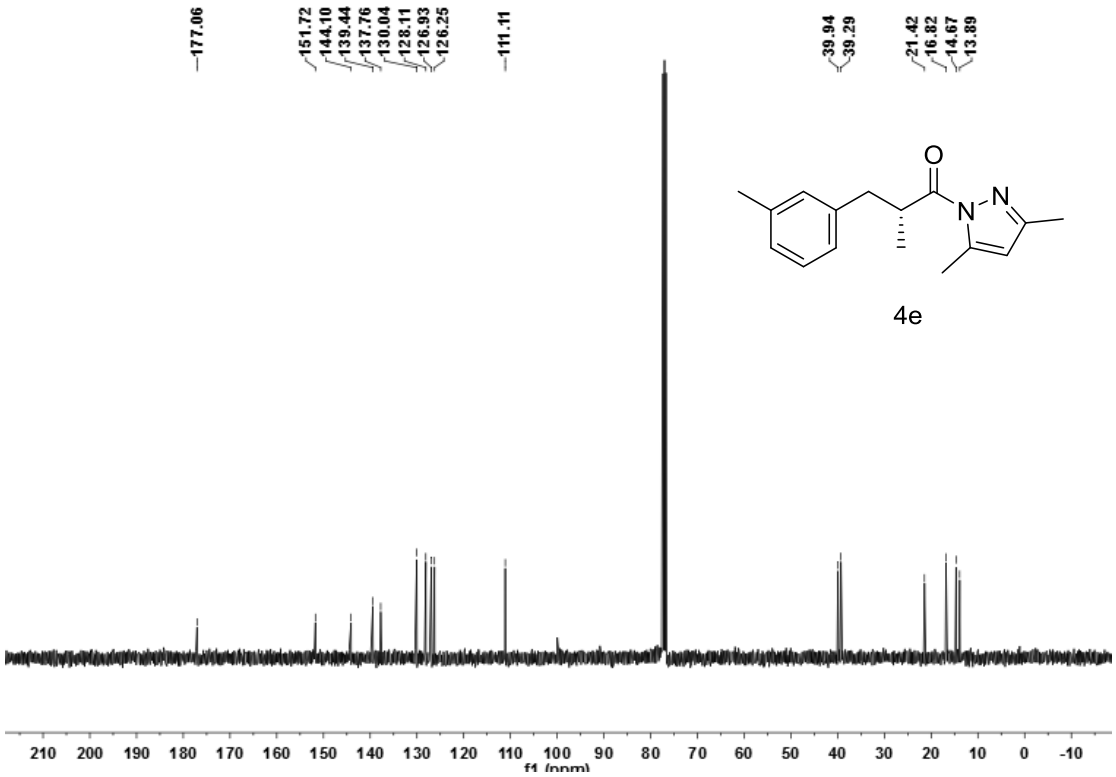

7.29
7.27
7.26
7.25
7.24
7.22
7.20
7.18
7.17
5.94
4.20
4.19
4.17
4.15
4.13
4.11
3.20
3.19
3.17
3.15
2.73
2.71
2.70
2.68
2.51
2.23
1.23
1.21
O
N
N
5.43
0.98
1.01
1.02
1.00
3.12
3.00
3.12
f1 (ppm)

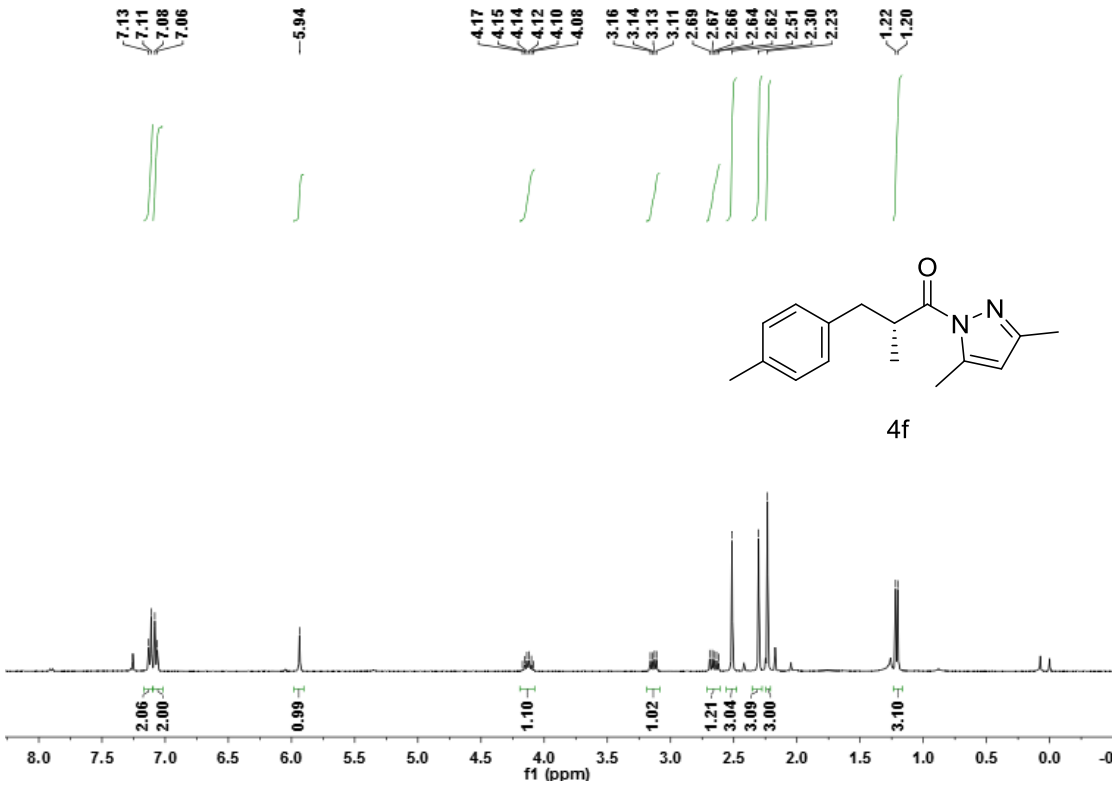
4a


176.97
151.74
144.10
139.57
129.25
128.25
126.20
111.13
39.98
39.37
16.84
14.67
13.90
O
N
N
f1 (ppm)

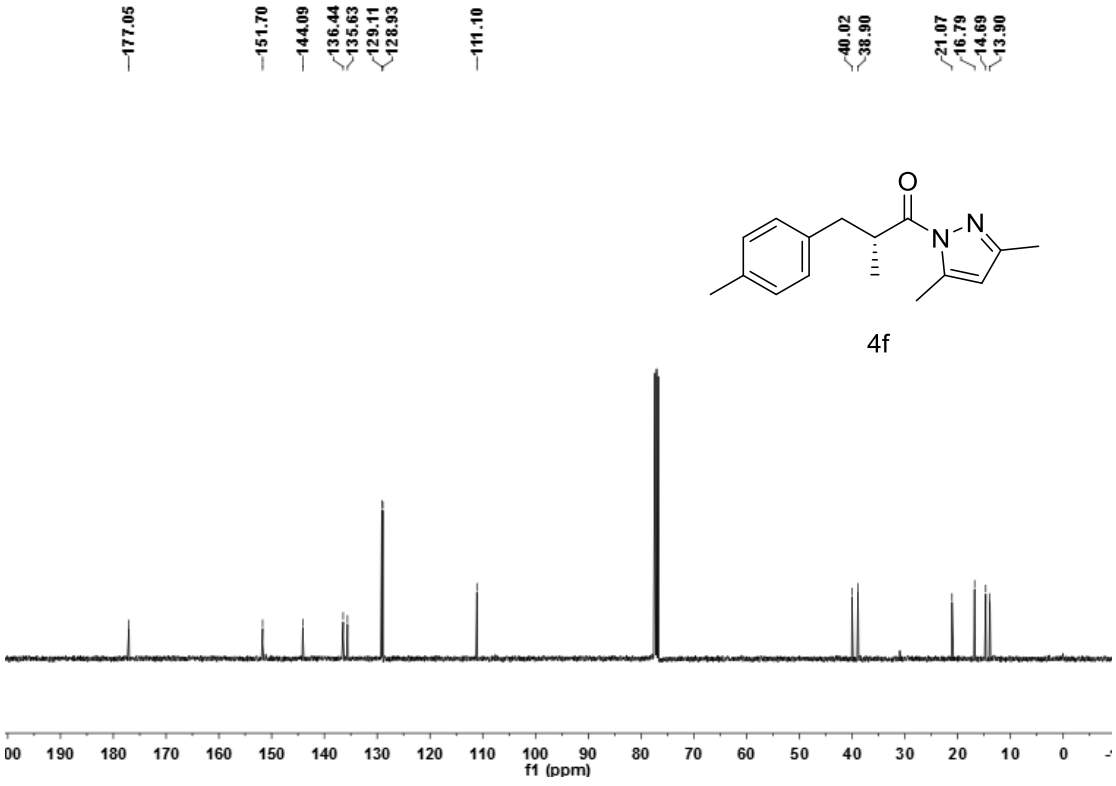
4a


7.17
7.15
7.14
7.04
7.02
7.01
6.99
6.06
5.94
4.18
4.17
4.15
4.13
4.11
4.10
3.16
3.14
3.12
3.11
2.69
2.67
2.66
2.64
2.52
2.32
2.24
1.22
1.21
O
N
N
4e
1.28
3.04
0.98
1.06
1.05
1.24
3.00
2.97
3.12
3.15
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

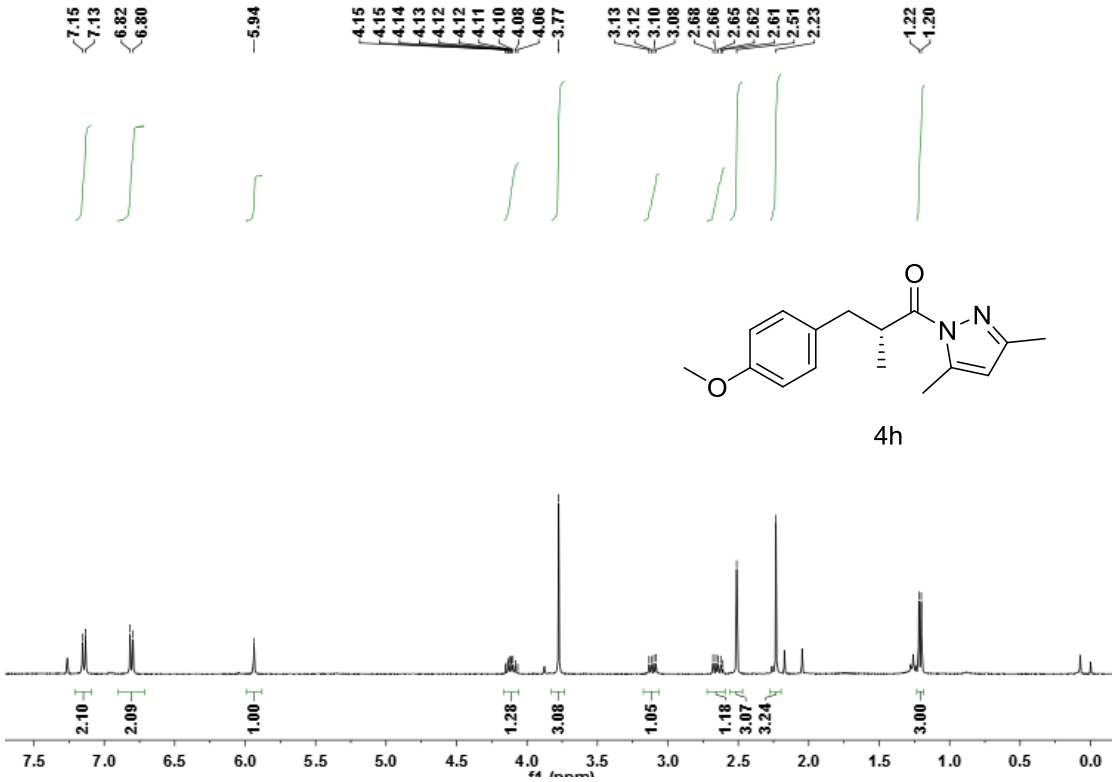

177.06
151.72
144.10
139.44
137.76
130.04
128.11
126.93
126.25
111.11
39.94
39.29
21.42
16.82
14.67
13.89
O
N
N
4e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.13
7.11
7.08
7.06
5.94
4.17
4.15
4.14
4.12
4.10
4.08
3.16
3.14
3.13
3.11
2.69
2.67
2.66
2.64
2.62
2.51
2.30
2.23
1.22
1.20
O
N
N
2.06
2.00
0.99
1.10
1.02
1.21
3.04
3.09
3.00
3.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

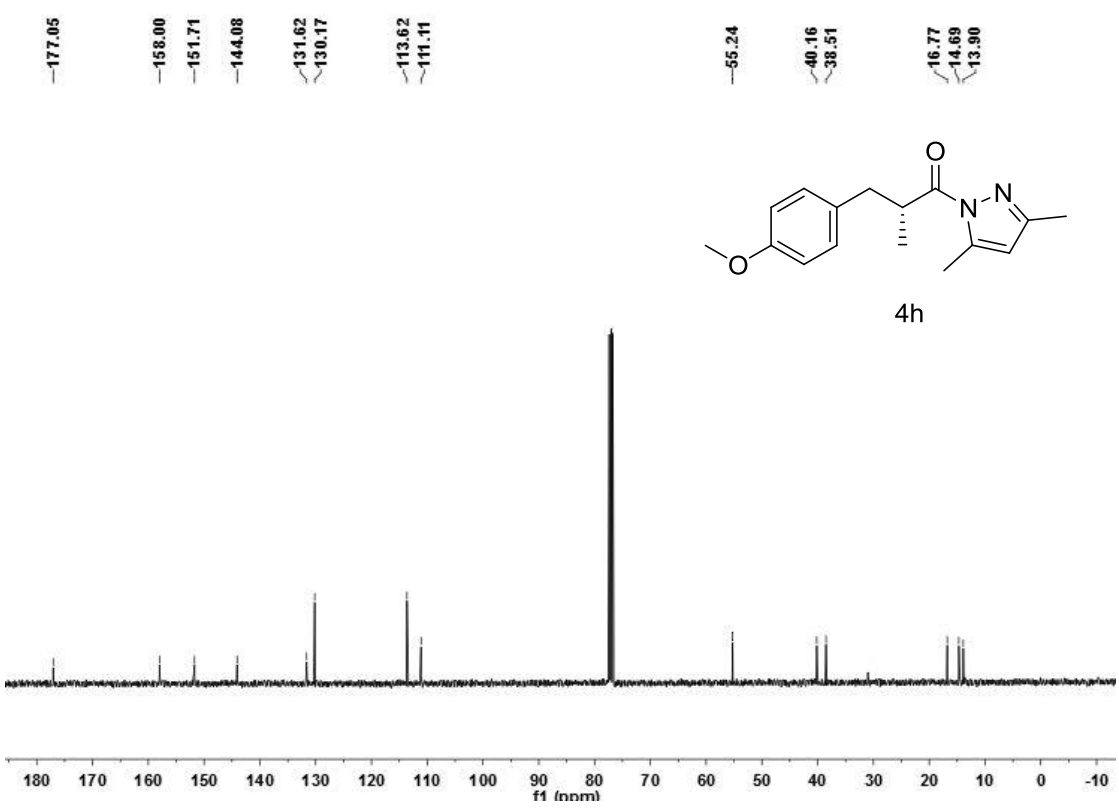
4f


177.05
151.70
144.09
136.44
135.63
129.11
128.93
111.10
40.02
38.90
21.07
16.79
14.69
13.90
O
N
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

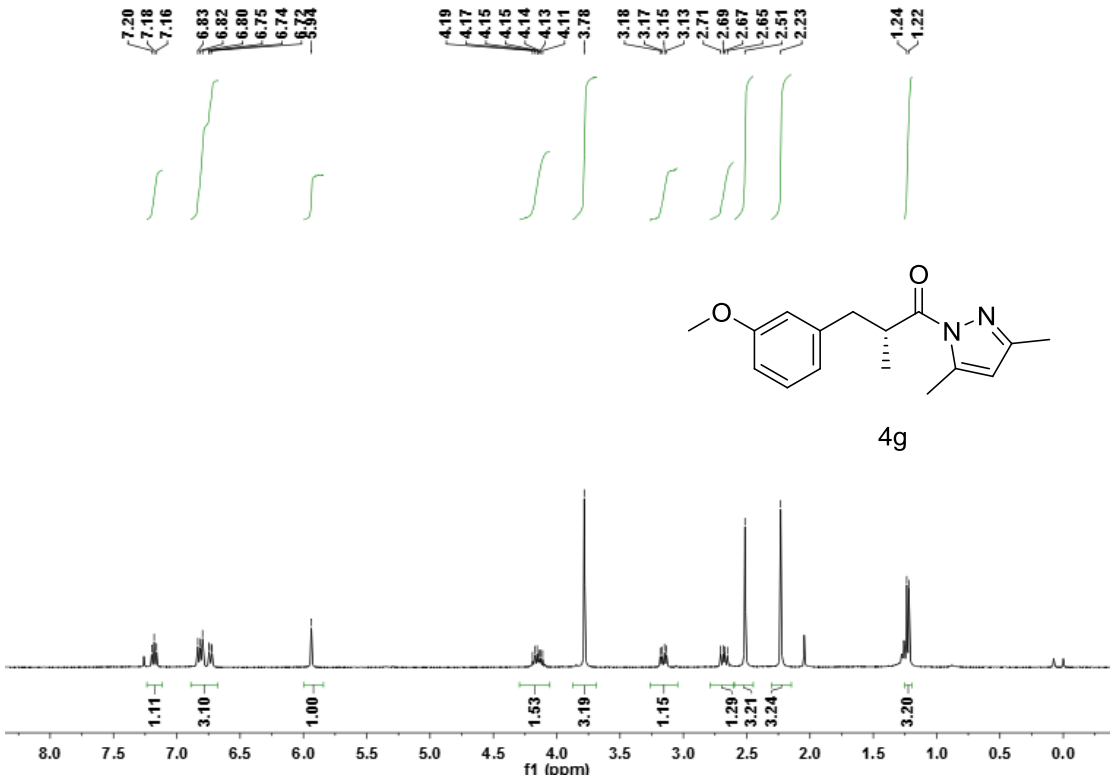
4f


7.15
7.13
6.82
6.80
5.94
4.15
4.15
4.14
4.13
4.12
4.12
4.11
4.10
4.08
4.06
3.77
3.13
3.12
3.10
3.08
2.68
2.66
2.65
2.62
2.61
2.51
2.23
1.22
1.20
O
N
N
O
2.10
2.09
1.00
1.28
3.08
1.05
1.18
3.07
3.24
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

4h


177.05
158.00
151.71
144.08
131.62
130.17
113.62
111.11
55.24
40.16
38.51
16.77
14.69
13.90
O
N
N
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

4h


7.20
7.18
7.16
6.83
6.82
6.80
6.75
6.74
5.94
4.19
4.17
4.15
4.15
4.14
4.13
4.11
3.78
3.18
3.17
3.15
3.13
2.71
2.69
2.67
2.65
2.51
2.23
1.24
1.22
O
O
N
N
1.11
3.10
1.00
1.53
3.19
1.15
1.29
3.21
3.24
3.20
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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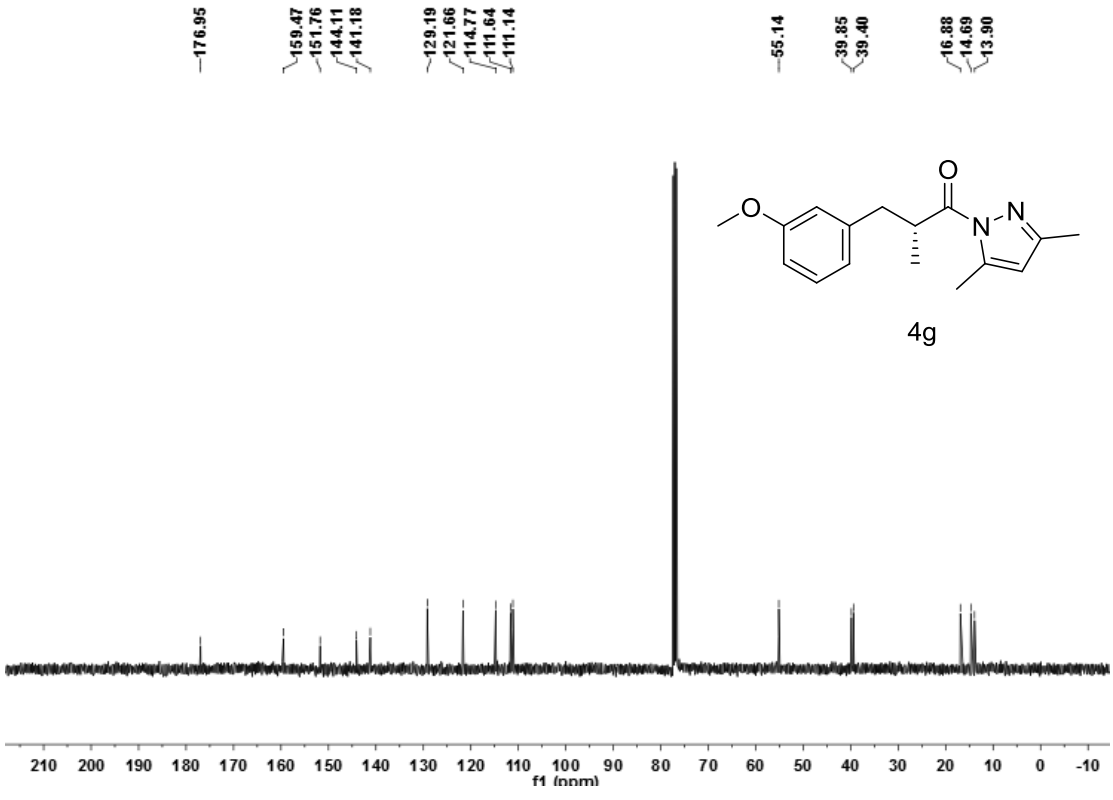
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

4g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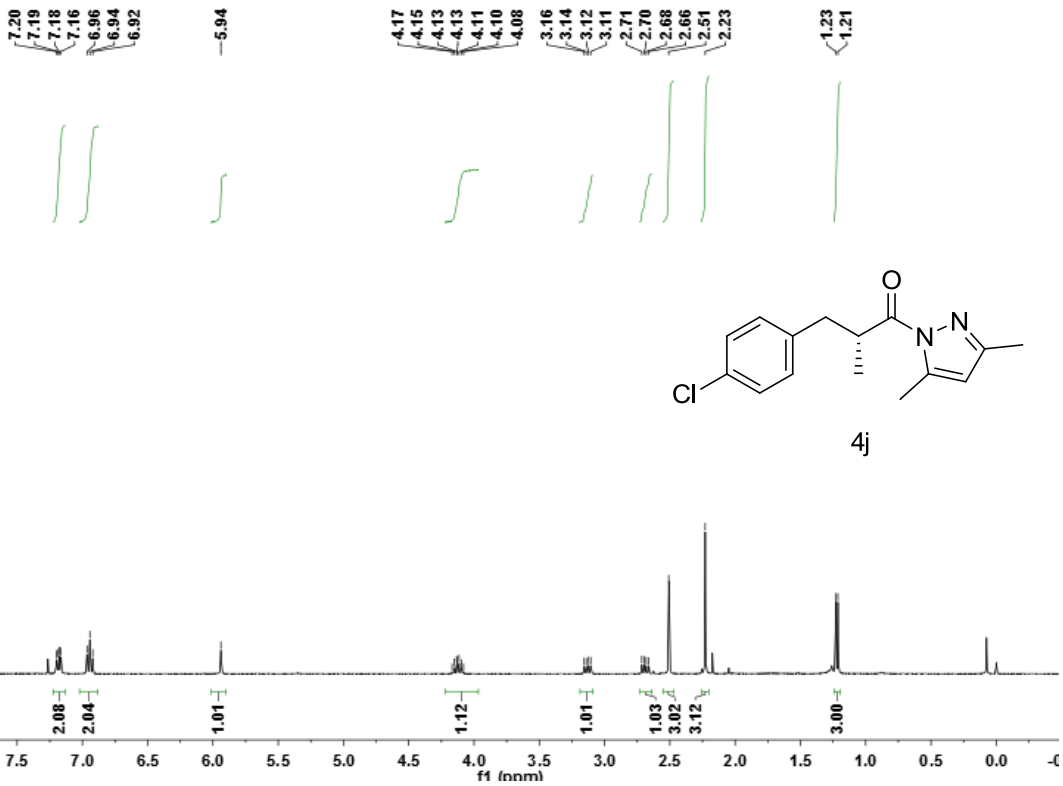
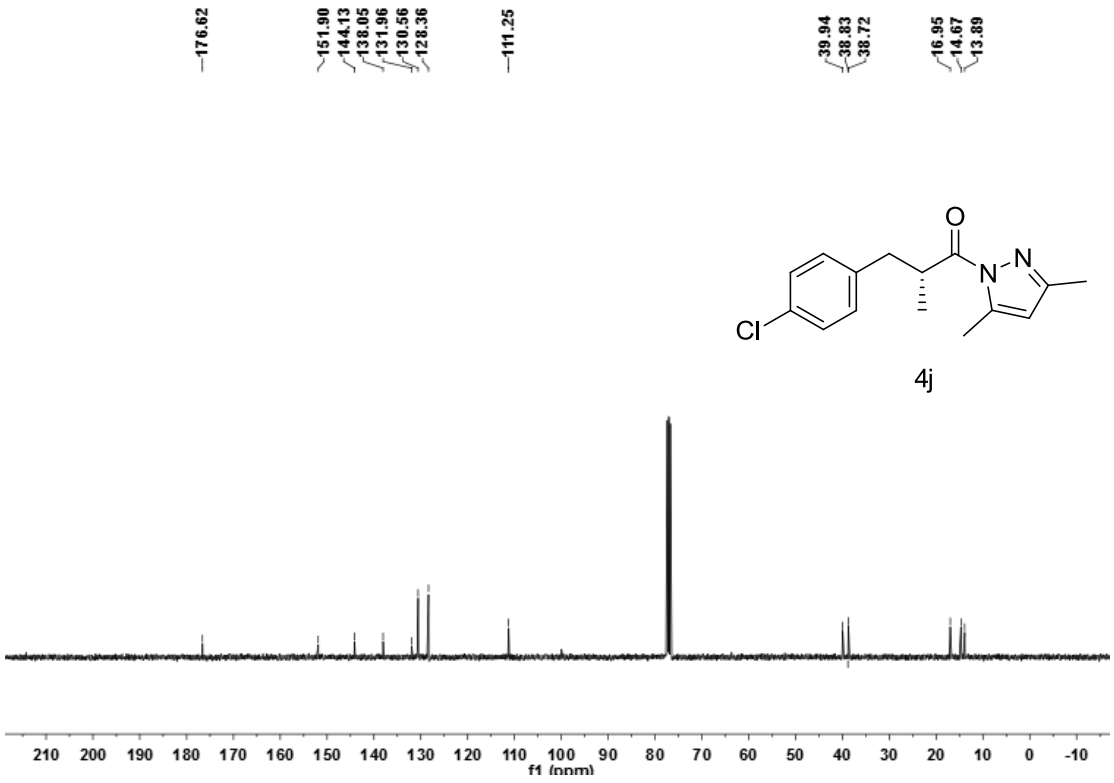
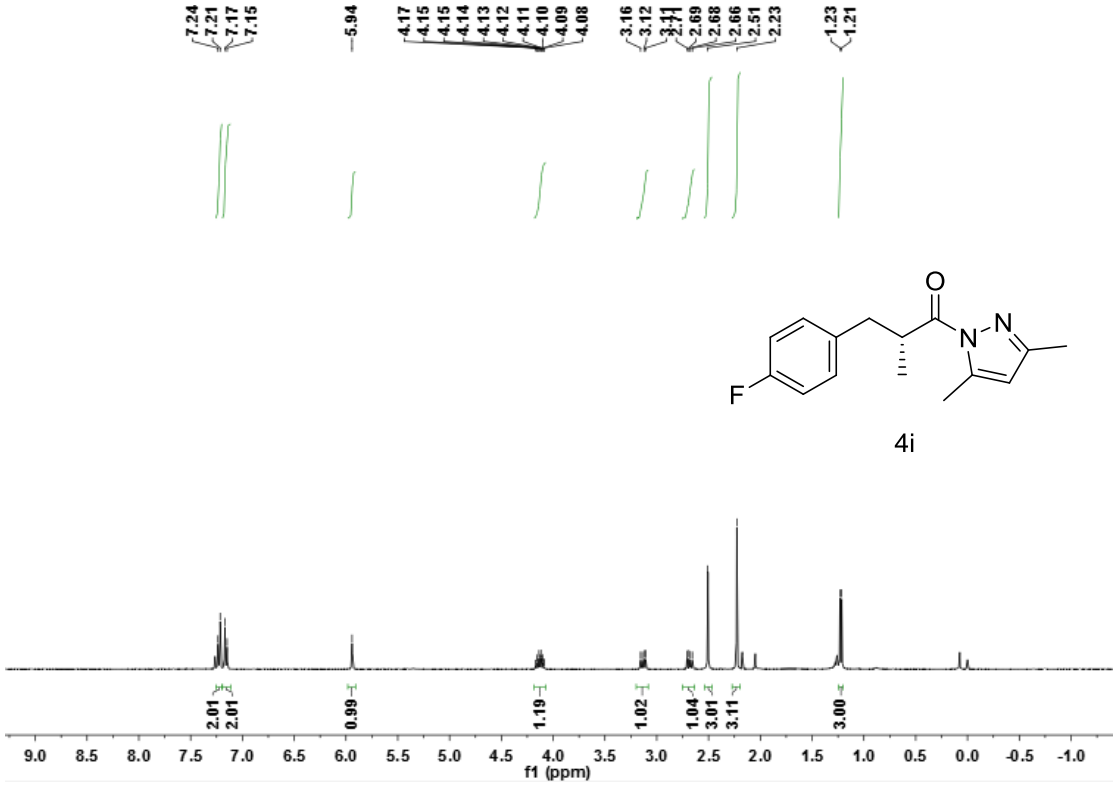
159.47
151.76
144.11
141.18
129.19
121.66
114.77
111.64
111.14
55.14
39.85
39.40
16.88
14.69
13.90
O
O
N
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

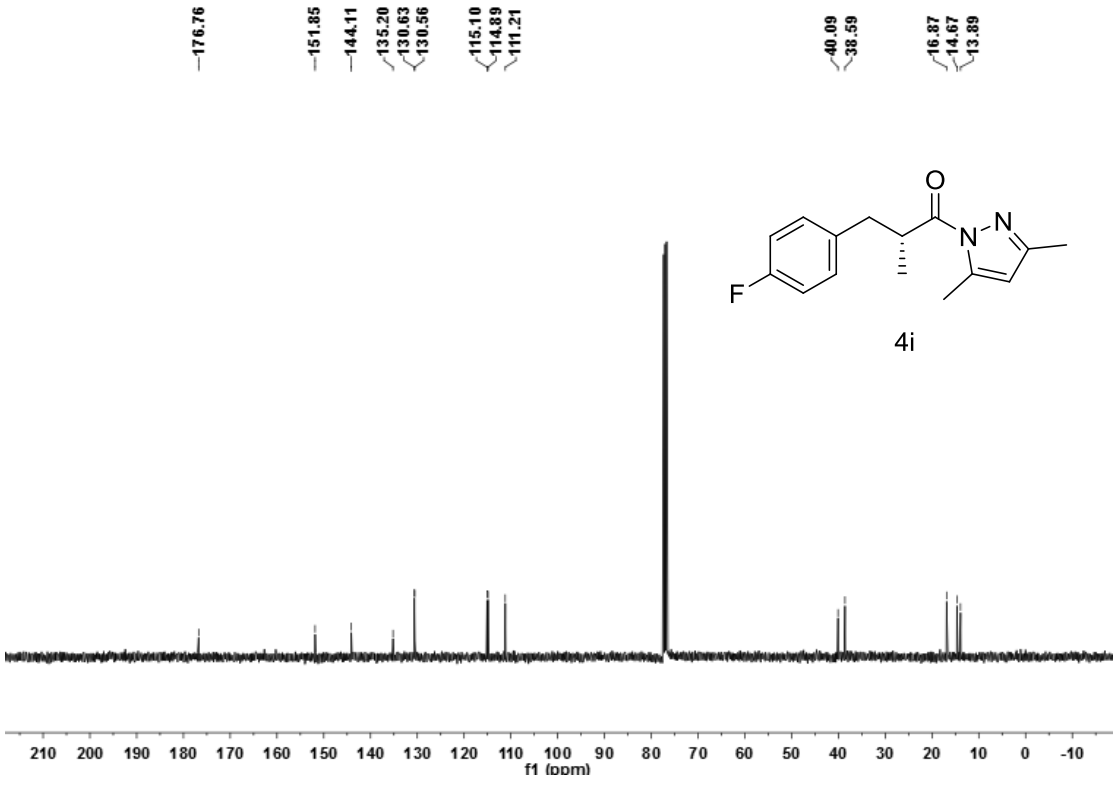
4g


7.20
7.19
7.18
7.16
6.96
6.94
6.92
5.94
4.17
4.15
4.13
4.13
4.11
4.10
4.08
3.16
3.14
3.12
3.11
2.71
2.70
2.68
2.66
2.51
2.23
1.23
1.21
O
N
N
Cl
4j
2.08
2.04
1.01
1.12
1.01
1.03
3.02
3.12
3.00
0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

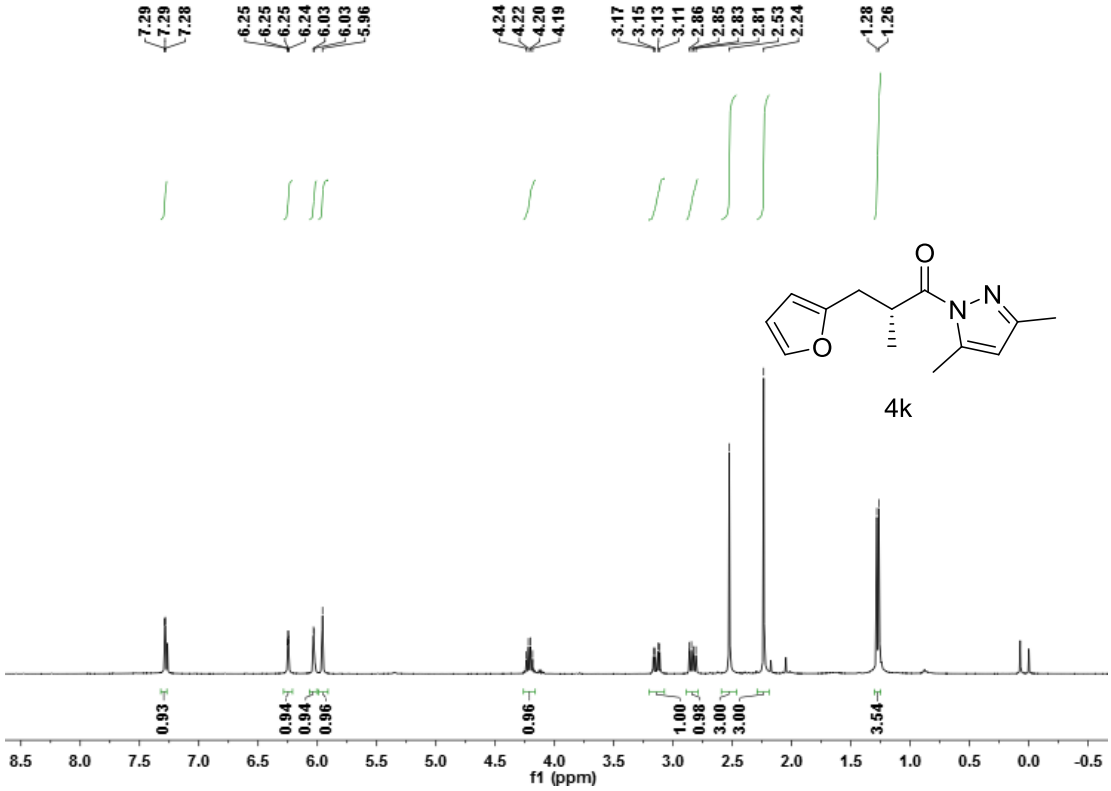

176.62
151.90
144.13
138.05
131.96
130.56
128.36
111.25
39.94
38.83
38.72
16.95
14.67
13.89
O
N
N
Cl
4j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

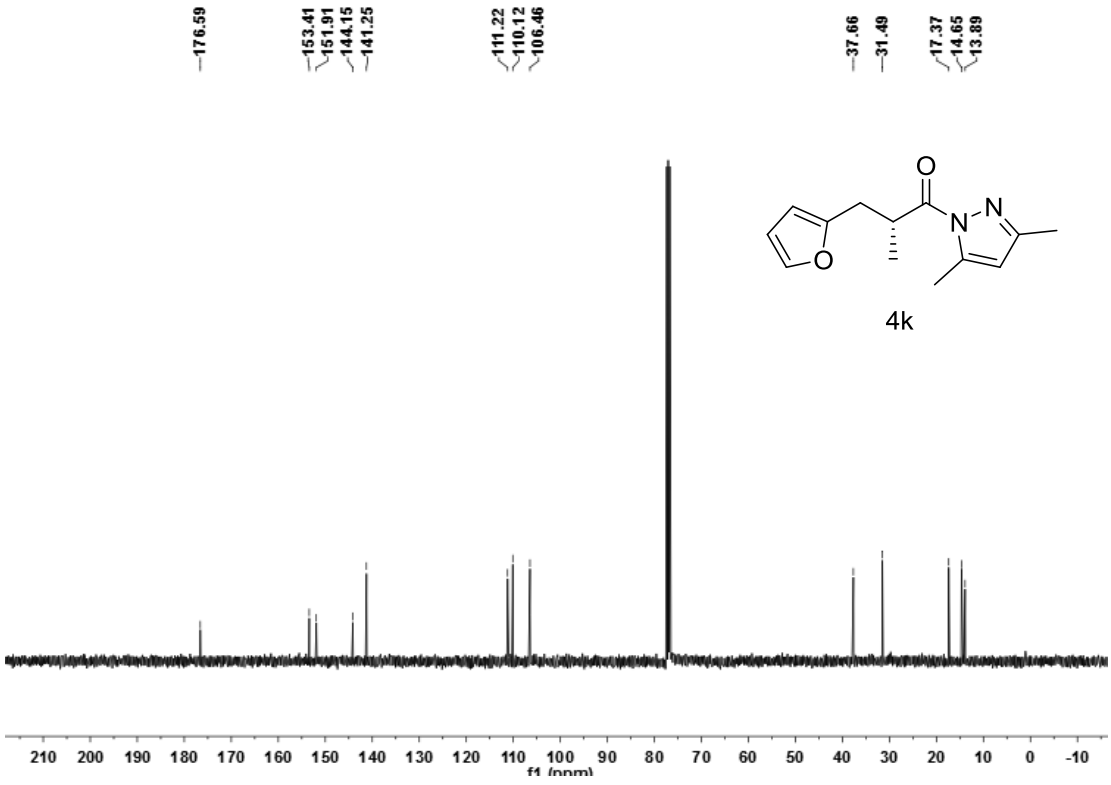

7.24
7.21
7.17
7.15
5.94
4.17
4.15
4.15
4.14
4.13
4.12
4.11
4.10
4.09
4.08
3.16
3.12
2.69
2.68
2.66
2.51
2.23
1.23
1.21
O
N
N
F
2.01
2.01
0.99
1.19
1.02
1.04
3.01
3.11
3.00
f1 (ppm)

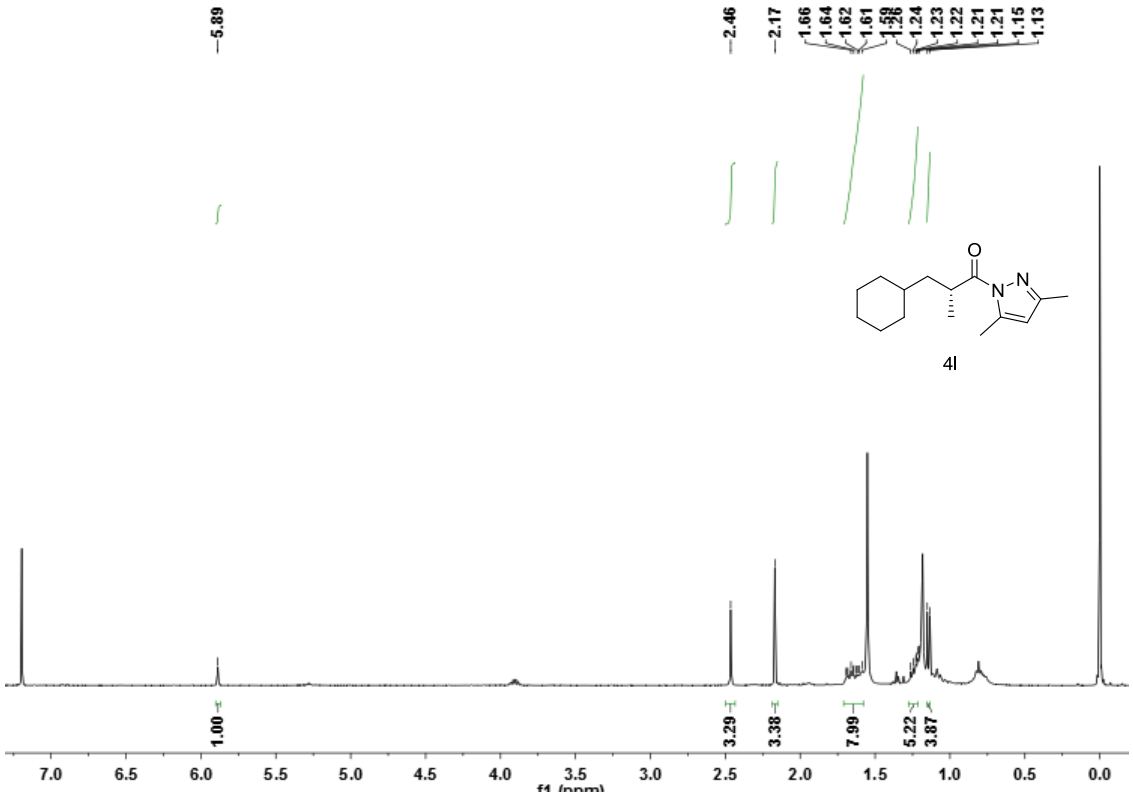
4i

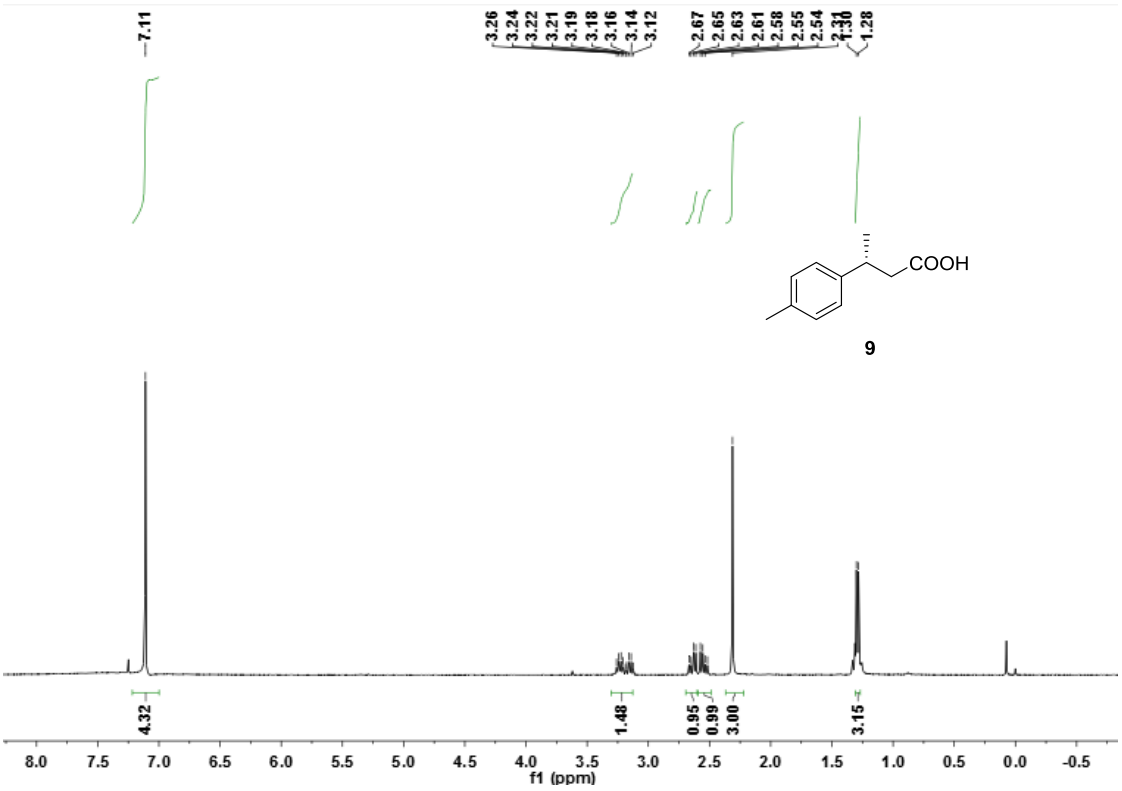

176.76
151.85
144.11
135.20
130.63
130.56
115.10
114.89
111.21
40.09
38.59
16.87
14.67
13.89
O
N
N
F
f1 (ppm)

4i

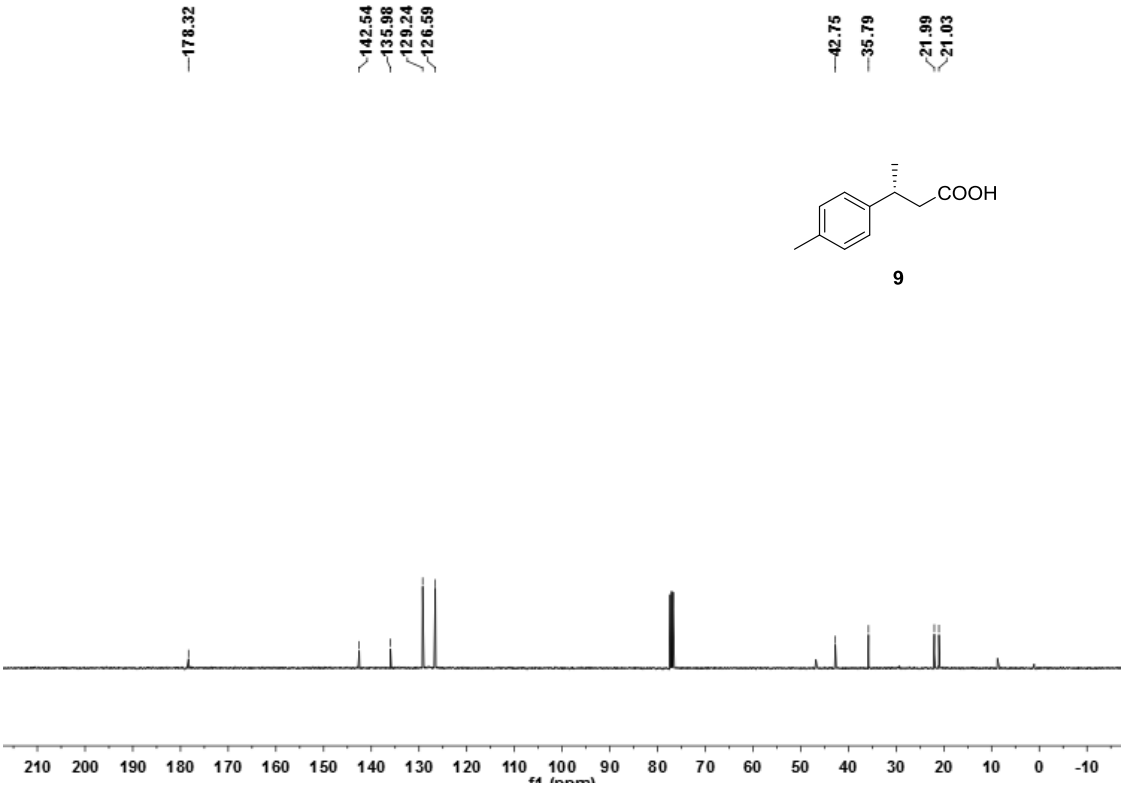

7.29
7.29
7.28
6.25
6.25
6.25
6.24
6.03
6.03
5.96
4.24
4.22
4.20
4.19
3.17
3.15
3.13
3.11
2.86
2.85
2.83
2.81
2.53
2.24
1.28
1.26
O
N
N
O
4k
0.93
0.94
0.94
0.96
0.96
1.00
0.98
3.00
3.00
3.54
f1 (ppm)


176.59
153.41
151.91
144.15
141.25
111.22
110.12
106.46
37.66
31.49
17.37
14.65
13.89
O
N
N
O
4k
f1 (ppm)


5.89
2.46
2.17
1.66
1.64
1.62
1.61
1.24
1.23
1.22
1.21
1.21
1.15
1.13
O
N
N
4l
1.00
3.29
3.38
7.99
5.22
3.87
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


7.11
3.26
3.24
3.22
3.21
3.19
3.18
3.16
3.14
3.12
2.67
2.65
2.63
2.61
2.58
2.55
2.54
1.30
1.28
COOH
4.32
1.48
0.95
0.99
3.00
3.15
f1 (ppm)

9

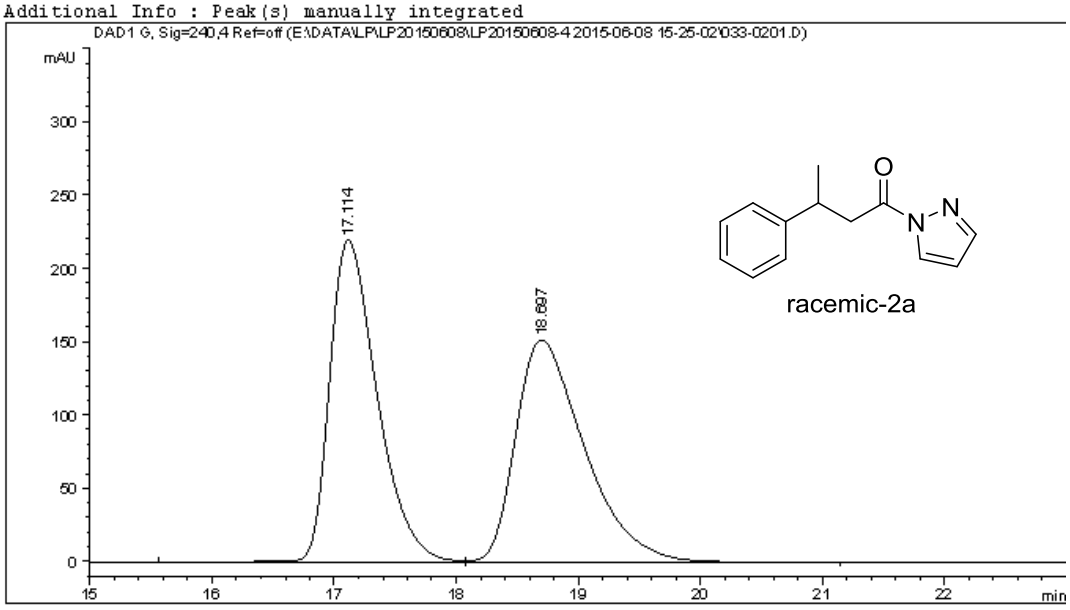

178.32
142.54
135.98
129.24
126.59
42.75
35.79
21.99
21.03
COOH
f1 (ppm)

9

VI. HPLC spectra

Data File E:\DATA\LP\LP20150608\LP20150608-4 2015-06-08 15-25-02\033-0201.D
Sample Name: LP-1-H XIAOXUAN

```
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   2
    Acq. Instrument : 1260HPLC-DAD                   Location : Vial 33
    Injection Date  : 6/8/2015 3:38:06 PM                 Inj :   1
                                                  Inj Volume : 10.000 µl
    Acq. Method     : E:\DATA\LP\LP20150608\LP20150608-4 2015-06-08 15-25-02\DAD-0J(1-6)-95-5-
                      1ML-10U-ALL  30MIN.M
    Last changed    : 6/8/2015 3:25:02 PM by SYSTEM
    Analysis Method : E:\DATA\LP\LP20150608\LP20150608-4 2015-06-08 15-25-02\DAD-0J(1-6)-95-5-
                      1ML-10U-ALL  30MIN.M (Sequence Method)
    Last changed    : 4/23/2016 4:58:48 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```

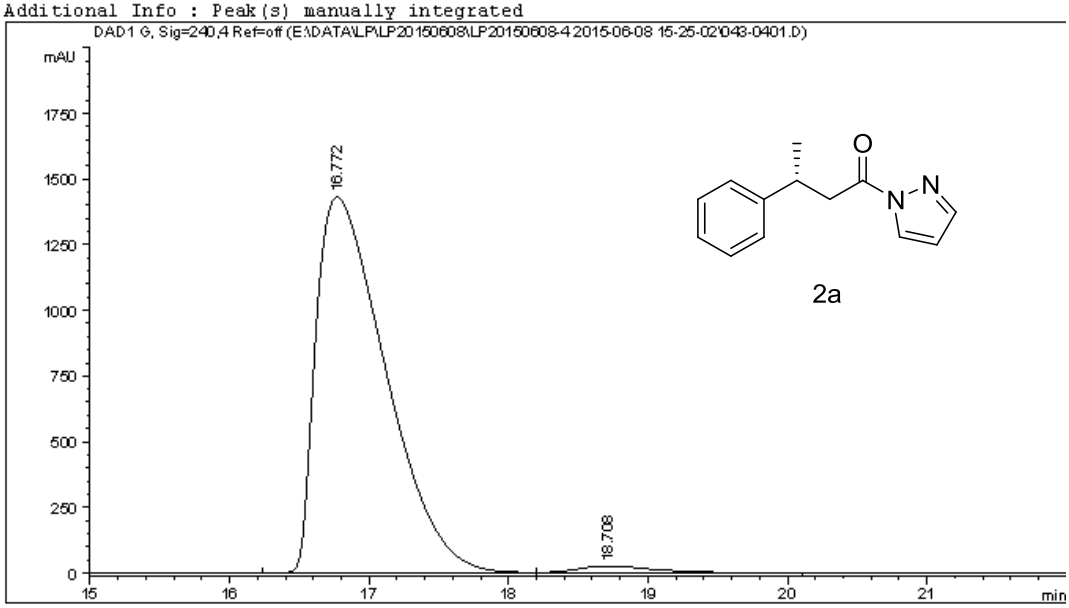


racemic-2a

```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 G, Sig=240,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]       [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  17.114 BV    0.4141 5904.73633  219.32953  50.0284
       2  18.697 VB    0.5885 5898.03955  151.41437  49.9716

    Totals :                  1.18028e4   370.74390


    ======================================================================
                              *** End of Report ***
```

Data File E:\DATA\LP\LP20150608\LP20150608-4 2015-06-08 15-25-02\043-0401.D
Sample Name: LP-1-H 5-1

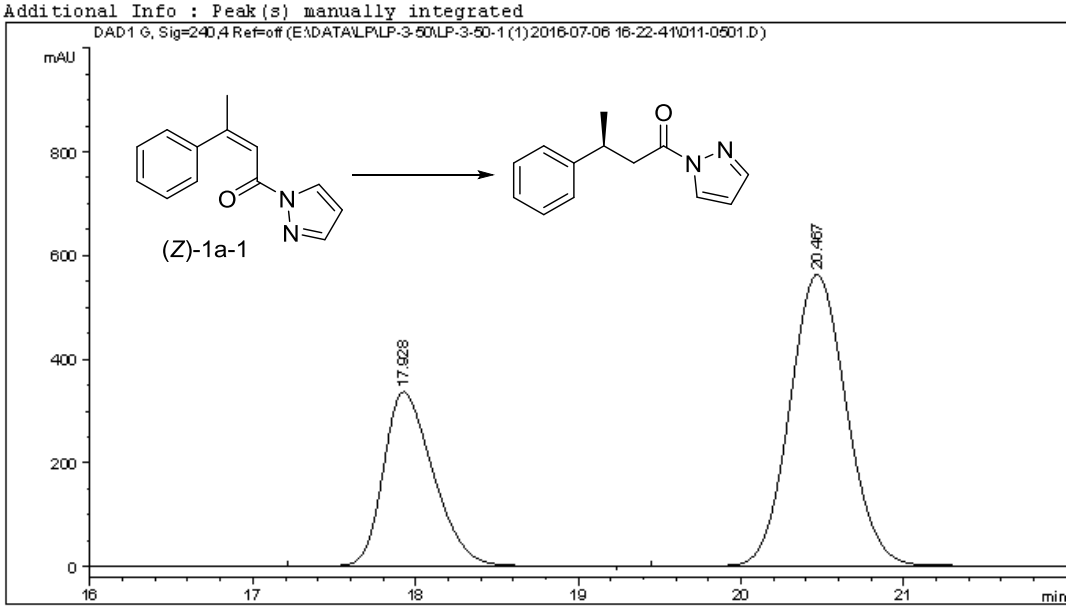
```
    ====================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   4
    Acq. Instrument : 1260HPLC-DAD                   Location : Vial 43
    Injection Date  : 6/8/2015 4:40:05 PM                 Inj :   1
                                                   Inj Volume : 10.000 µl
    Acq. Method     : E:\DATA\LP\LP20150608\LP20150608-4 2015-06-08 15-25-02\DAD-0J(1-6)-95-5-
                      1ML-10U-ALL  30MIN.M
    Last changed    : 6/8/2015 3:25:02 PM by SYSTEM
    Analysis Method : E:\DATA\LP\LP20150608\LP20150608-4 2015-06-08 15-25-02\DAD-0J(1-6)-95-5-
                      1ML-10U-ALL  30MIN.M (Sequence Method)
    Last changed    : 4/23/2016 5:03:48 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ====================================================================
                            Area Percent Report
    ====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 G, Sig=240,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  16.772 BV    0.5462 4.95520e4  1430.23523  98.0728
       2  18.708 VB    0.5835  973.71332   25.04695   1.9272

    Totals :                  5.05257e4  1455.28218


    ====================================================================
                            *** End of Report ***
```

Data File E:\DATA\LP\LP-3-50\LP-3-50-1 (1) 2016-07-06 16-22-41\011-0501.D
Sample Name: LP-3-50-2

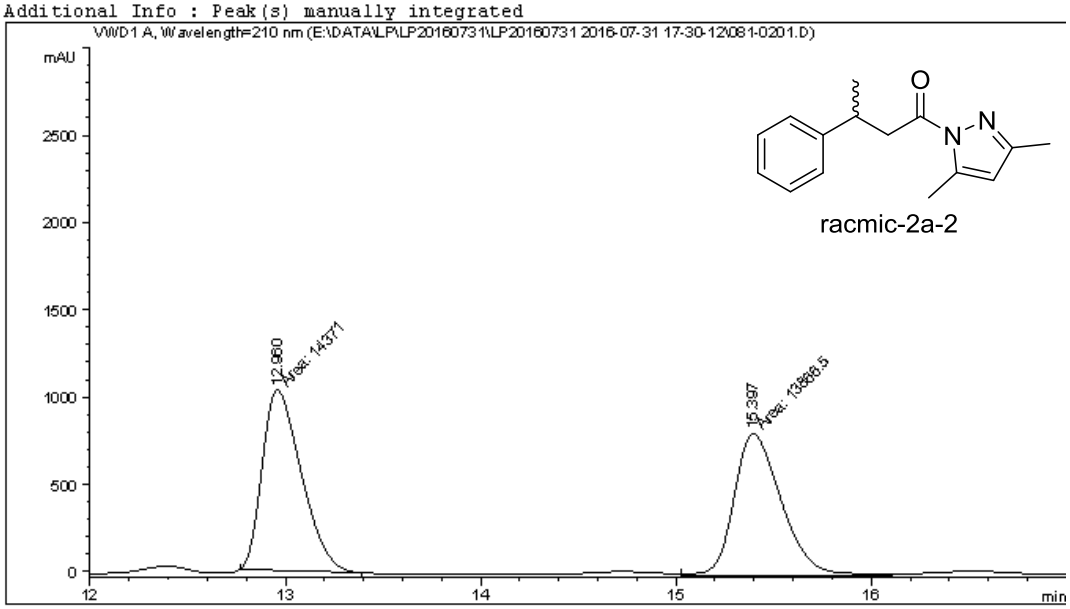
```
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   5
    Acq. Instrument : 1260HPLC-DAD                   Location : Vial 11
    Injection Date  : 7/6/2016 6:01:59 PM                 Inj :   1
                                                  Inj Volume : 10.000 µl
    Acq. Method     : E:\DATA\LP\LP-3-50\LP-3-50-1 (1) 2016-07-06 16-22-41\DAD-0J(1-6)-95-5-
                      1ML-10U-ALL  30MIN.M
    Last changed    : 7/6/2016 5:49:47 PM by SYSTEM
    Analysis Method : E:\DATA\LP\LP-3-50\LP-3-50-1 (1) 2016-07-06 16-22-41\DAD-0J(1-6)-95-5-
                      1ML-10U-ALL  30MIN.M (Sequence Method)
    Last changed    : 8/23/2016 4:25:07 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 G, Sig=240,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  17.928 BB    0.3279 7128.77686  335.52017  34.4243
       2  20.467 BB    0.3758 1.35798e4   562.30396  65.5757

    Totals :                  2.07086e4   897.82413


    ======================================================================
                              *** End of Report ***
```

Data File E:\DATA\LP\LP20160731\LP20160731 2016-07-31 17-30-12\081-0201.D
Sample Name: LP

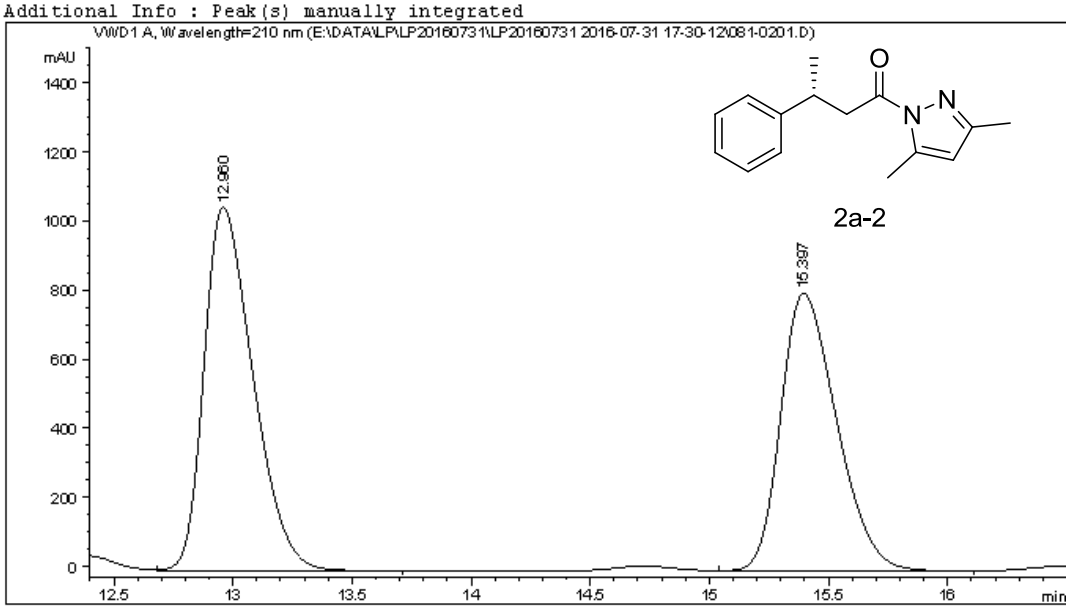
```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   2
    Acq. Instrument : 1260HPLC-VWD                     Location : Vial 81
    Injection Date  : 7/31/2016 5:34:43 PM                  Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LP\LP20160731\LP20160731 2016-07-31 17-30-12\VWD-0J(1-6)-95-5-0.
                      6ML-5UL-210-60MIN.M
    Last changed    : 7/31/2016 5:30:12 PM by SYSTEM
    Analysis Method : E:\DATA\LP\LP20160731\LP20160731 2016-07-31 17-30-12\VWD-0J(1-6)-95-5-0.
                      6ML-5UL-210-60MIN.M (Sequence Method)
    Last changed    : 8/23/2016 4:10:38 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                               Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=210 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  12.960 MM    0.2322 1.43710e4  1031.45593  50.8932
       2  15.397 MM    0.2837 1.38665e4   814.60529  49.1068

    Totals :                  2.82375e4  1846.06122


    ======================================================================
                               *** End of Report ***
```

Data File E:\DATA\LP\LP20160731\LP20160731 2016-07-31 17-30-12\081-0201.D
Sample Name: LP

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   2
    Acq. Instrument : 1260HPLC-VWD                     Location : Vial 81
    Injection Date  : 7/31/2016 5:34:43 PM                  Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LP\LP20160731\LP20160731 2016-07-31 17-30-12\VWD-0J(1-6)-95-5-0.
                      6ML-5UL-210-60MIN.M
    Last changed    : 7/31/2016 5:30:12 PM by SYSTEM
    Analysis Method : E:\DATA\LP\LP20160731\LP20160731 2016-07-31 17-30-12\VWD-0J(1-6)-95-5-0.
                      6ML-5UL-210-60MIN.M (Sequence Method)
    Last changed    : 8/23/2016 4:05:32 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```

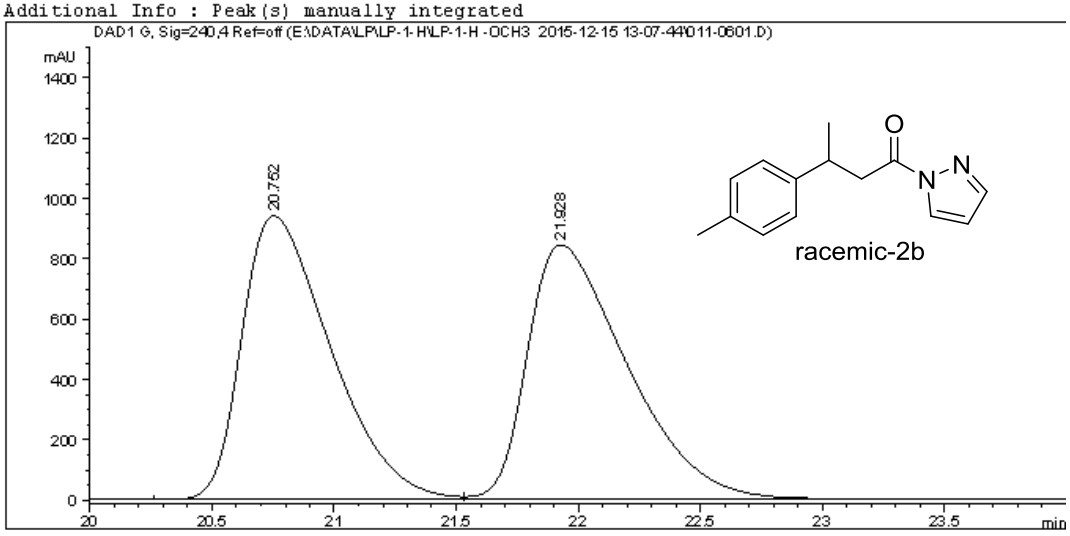


2a-2

```
    ======================================================================
                               Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=210 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  12.960 VB    0.2206 1.49993e4  1050.40625  53.3239
       2  15.397 VV    0.2527 1.31294e4   803.13306  46.6761

    Totals :                  2.81287e4  1853.53931


    ======================================================================
                               *** End of Report ***
```

Data File E:\DATA\LP\LP-1-H\LP-1-H -OCH3 2015-12-15 13-07-44\011-0601.D
Sample Name: LP-1-H CH3 RAC

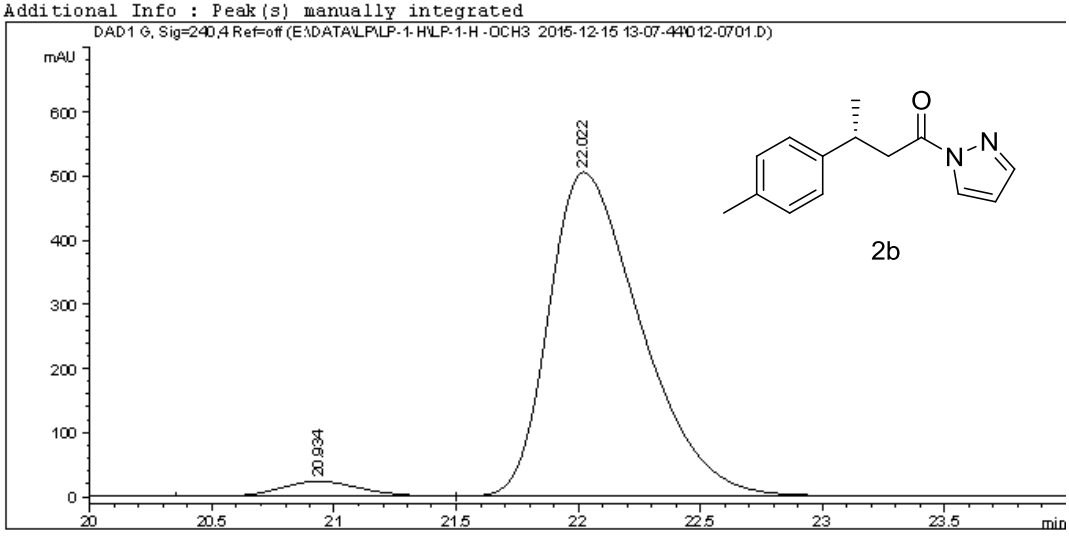
```
    ====================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   6
    Acq. Instrument : 1260HPLC-DAD                   Location : Vial 11
    Injection Date  : 12/15/2015 4:44:08 PM              Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LP\LP-1-H\LP-1-H -OCH3  2015-12-15 13-07-44\DAD-0J(1-6)-90-0.6ML
                      -ALLNM-60MIN2015-3.M
    Last changed    : 12/15/2015 2:04:30 PM by SYSTEM
    Analysis Method : E:\DATA\LP\LP-1-H\LP-1-H -OCH3  2015-12-15 13-07-44\DAD-0J(1-6)-90-0.6ML
                      -ALLNM-60MIN2015-3.M (Sequence Method)
    Last changed    : 12/22/2015 11:25:38 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ====================================================================
                            Area Percent Report
    ====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 G, Sig=240,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  20.752 VV    0.3871 2.38091e4   941.29773  49.6589
       2  21.928 VB    0.4353 2.41362e4   844.87860  50.3411

    Totals :                  4.79453e4  1786.17633


    ====================================================================
                            *** End of Report ***
```

Data File E:\DATA\LP\LP-1-H\LP-1-H -OCH3 2015-12-15 13-07-44\012-0701.D
Sample Name: LP-1-H -CH3

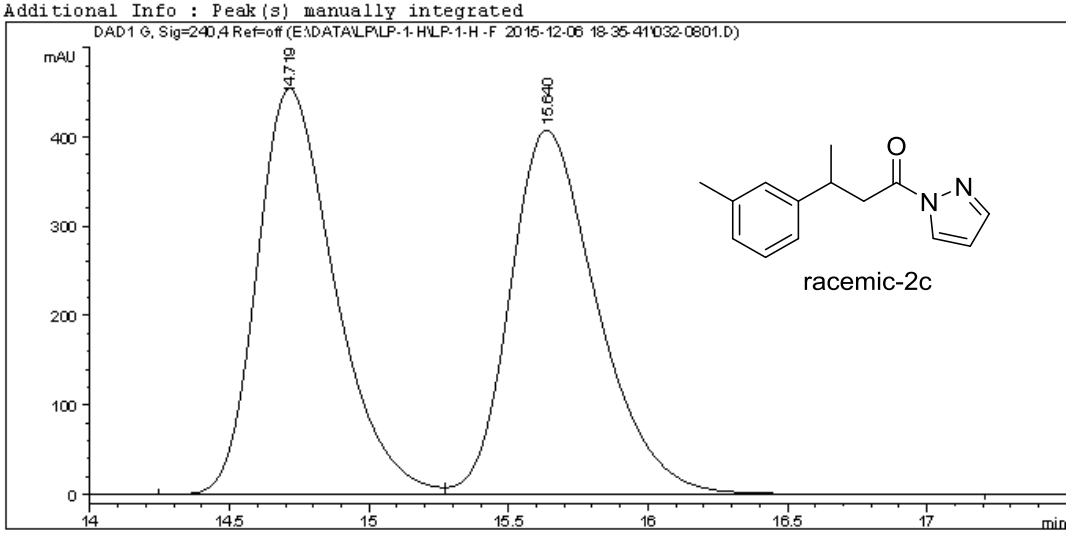
```
    ====================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   7
    Acq. Instrument : 1260HPLC-DAD                   Location : Vial 12
    Injection Date  : 12/15/2015 5:35:06 PM               Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LP\LP-1-H\LP-1-H -OCH3  2015-12-15 13-07-44\DAD-0J(1-6)-90-0.6ML
                      -ALLNM-60MIN2015-3.M
    Last changed    : 12/15/2015 2:04:30 PM by SYSTEM
    Analysis Method : E:\DATA\LP\LP-1-H\LP-1-H -OCH3  2015-12-15 13-07-44\DAD-0J(1-6)-90-0.6ML
                      -ALLNM-60MIN2015-3.M (Sequence Method)
    Last changed    : 12/22/2015 11:27:09 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ====================================================================
                           Area Percent Report
    ====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 G, Sig=240,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  20.934 BV    0.3561  548.13611   23.67835   3.9545
       2  22.022 VB    0.4034 1.33128e4   505.21228  96.0455

    Totals :                  1.38609e4   528.89063


    ====================================================================
                           *** End of Report ***
```

Data File E:\DATA\LP\LP-1-H\LP-1-H -F 2015-12-06 18-35-41\032-0801.D
Sample Name: LP-1-H 3-CH3 RAC

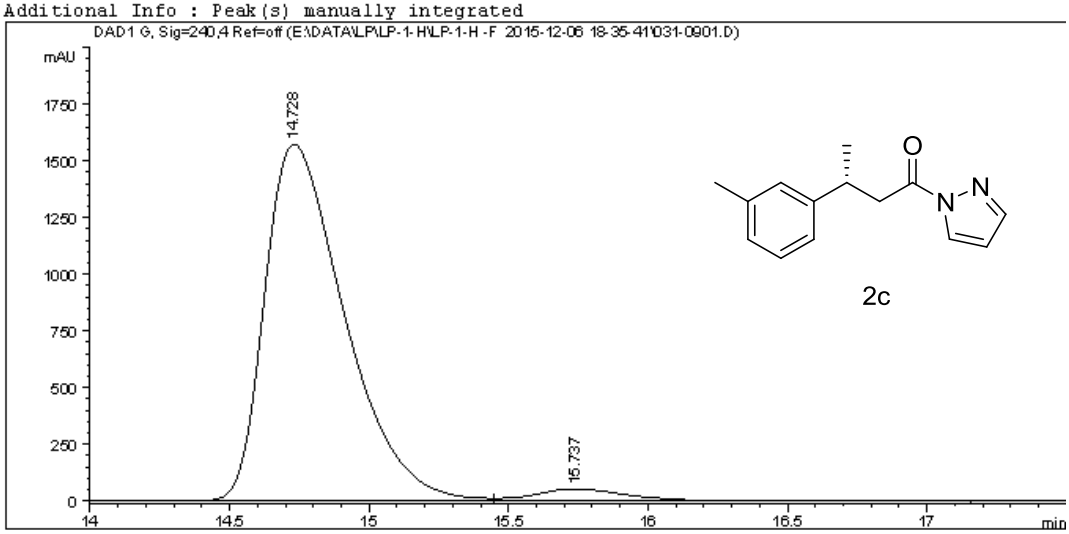
```
    ====================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   8
    Acq. Instrument : 1260HPLC-DAD                   Location : Vial 32
    Injection Date  : 12/6/2015 8:25:25 PM               Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LP\LP-1-H\LP-1-H -F  2015-12-06 18-35-41\DAD-0J(1-6)-90-0.6ML-
                      ALLNM-60MIN2015-3.M
    Last changed    : 12/6/2015 8:23:10 PM by SYSTEM
    Analysis Method : E:\DATA\LP\LP-1-H\LP-1-H -F  2015-12-06 18-35-41\DAD-0J(1-6)-90-0.6ML-
                      ALLNM-60MIN2015-3.M (Sequence Method)
    Last changed    : 12/6/2015 8:51:08 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ====================================================================
                            Area Percent Report
    ====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 G, Sig=240,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  14.719 BV    0.2955 8786.37305  454.61768  49.6933
       2  15.640 VB    0.3322 8894.83984  408.25012  50.3067

    Totals :                  1.76812e4   862.86780


    ====================================================================
                            *** End of Report ***
```

Data File E:\DATA\LP\LP-1-H\LP-1-H -F 2015-12-06 18-35-41\031-0901.D
Sample Name: LP-1-H 3-CH3

```
    ====================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   9
    Acq. Instrument : 1260HPLC-DAD                   Location : Vial 31
    Injection Date  : 12/6/2015 8:46:20 PM               Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LP\LP-1-H\LP-1-H -F  2015-12-06 18-35-41\DAD-0J(1-6)-90-0.6ML-
                      ALLNM-60MIN2015-3.M
    Last changed    : 12/6/2015 8:23:10 PM by SYSTEM
    Analysis Method : E:\DATA\LP\LP-1-H\LP-1-H -F  2015-12-06 18-35-41\DAD-0J(1-6)-90-0.6ML-
                      ALLNM-60MIN2015-3.M (Sequence Method)
    Last changed    : 12/6/2015 9:14:39 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```

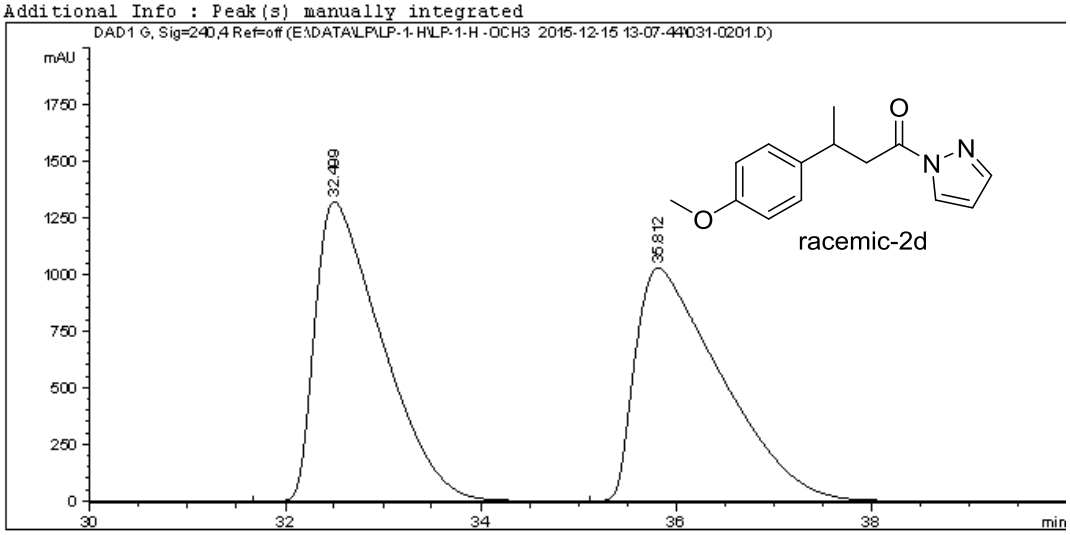


2c

```
    ====================================================================
                            Area Percent Report
    ====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 G, Sig=240,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  14.728 BV    0.3062 3.13390e4  1574.60608  96.2315
       2  15.737 VB    0.3462 1227.26953   52.98319   3.7685

    Totals :                  3.25663e4  1627.58927


    ====================================================================
                            *** End of Report ***
```

Data File E:\DATA\LP\LP-1-H\LP-1-H -OCH3 2015-12-15 13-07-44\031-0201.D
Sample Name: LP-1-H -OCH3 RAC

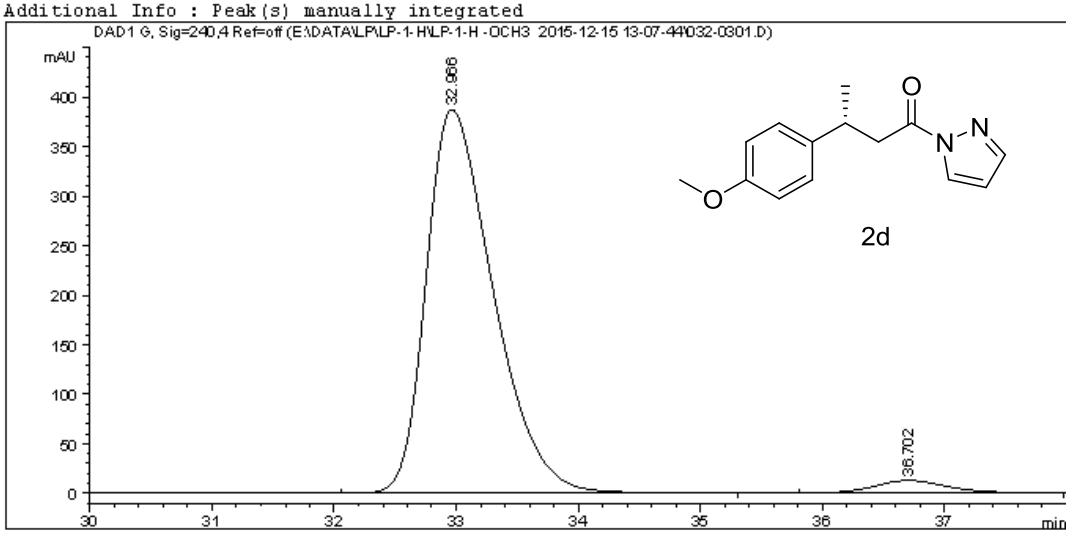
```
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   2
    Acq. Instrument : 1260HPLC-DAD                   Location : Vial 31
    Injection Date  : 12/15/2015 1:20:20 PM              Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LP\LP-1-H\LP-1-H -OCH3  2015-12-15 13-07-44\DAD-0J(1-6)-90-0.6ML
                      -ALLNM-60MIN2015-3.M
    Last changed    : 12/15/2015 2:04:30 PM by SYSTEM
                      (modified after loading)
    Analysis Method : E:\DATA\LP\LP-1-H\LP-1-H -OCH3  2015-12-15 13-07-44\DAD-0J(1-6)-90-0.6ML
                      -ALLNM-60MIN2015-3.M (Sequence Method)
    Last changed    : 12/22/2015 11:16:03 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                               Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 G, Sig=240,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  32.499 BB    0.7170 6.29396e4  1323.15295  49.8897
       2  35.812 BB    0.8963 6.32178e4  1029.64429  50.1103

    Totals :                  1.26157e5  2352.79724

    ======================================================================
                               *** End of Report ***
```

Data File E:\DATA\LP\LP-1-H\LP-1-H -OCH3 2015-12-15 13-07-44\032-0301.D
Sample Name: LP-1-H -OCH3

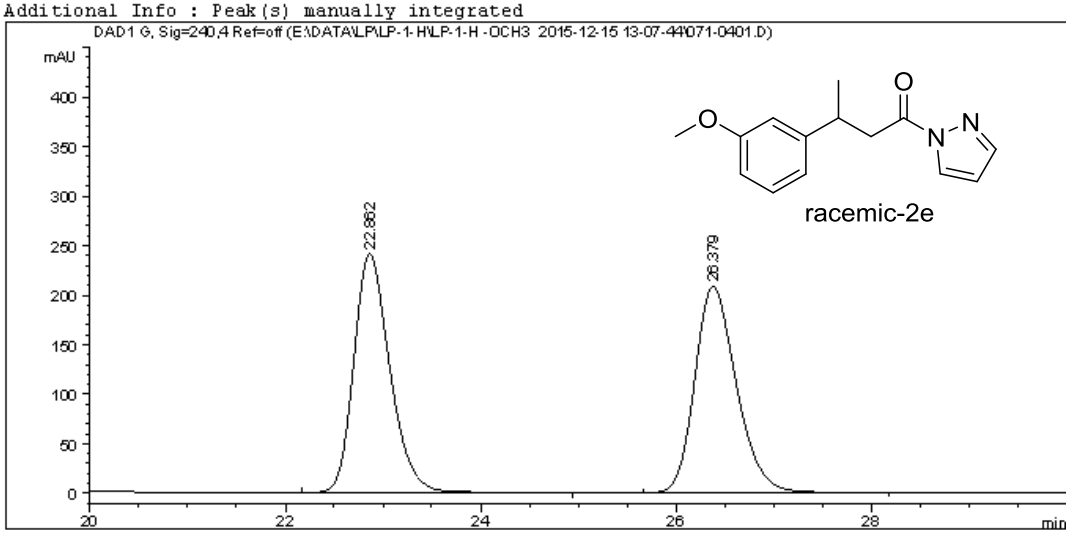
```
    ====================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   3
    Acq. Instrument : 1260HPLC-DAD                   Location : Vial 32
    Injection Date  : 12/15/2015 2:11:17 PM               Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LP\LP-1-H\LP-1-H -OCH3  2015-12-15 13-07-44\DAD-0J(1-6)-90-0.6ML
                      -ALLNM-60MIN2015-3.M
    Last changed    : 12/15/2015 2:04:30 PM by SYSTEM
    Analysis Method : E:\DATA\LP\LP-1-H\LP-1-H -OCH3  2015-12-15 13-07-44\DAD-0J(1-6)-90-0.6ML
                      -ALLNM-60MIN2015-3.M (Sequence Method)
    Last changed    : 12/22/2015 11:19:36 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ====================================================================
                            Area Percent Report
    ====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 G, Sig=240,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  32.966 BB    0.5822 1.47415e4   387.18433  96.6631
       2  36.702 BB    0.5934  508.88422   12.43564   3.3369

    Totals :                  1.52504e4   399.61997

    ====================================================================
                            *** End of Report ***
```

Data File E:\DATA\LP\LP-1-H\LP-1-H -OCH3 2015-12-15 13-07-44\071-0401.D
Sample Name: LP-1-H -3-OCH3 RAC

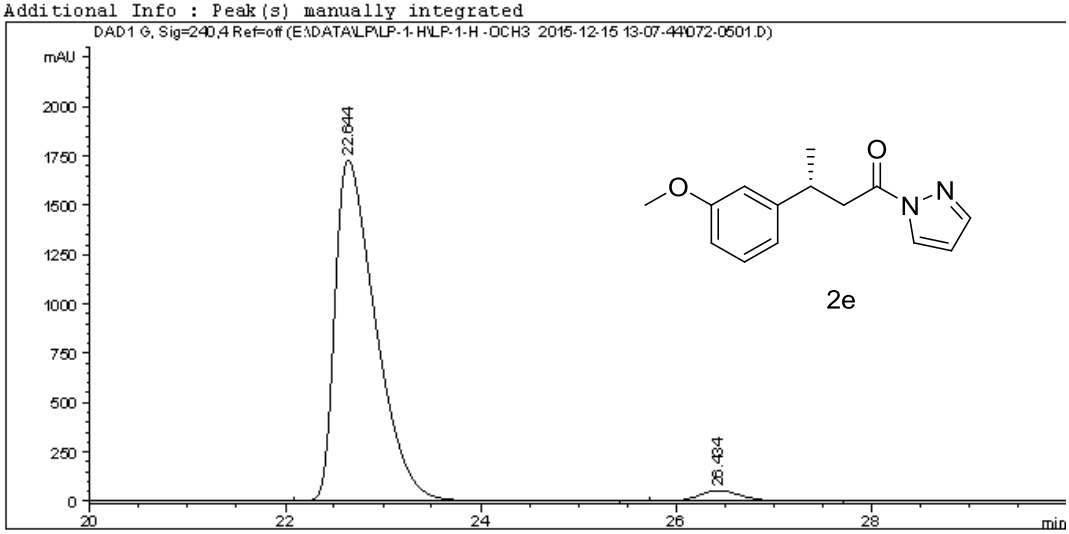
```
    ====================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   4
    Acq. Instrument : 1260HPLC-DAD                   Location : Vial 71
    Injection Date  : 12/15/2015 3:02:14 PM              Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LP\LP-1-H\LP-1-H -OCH3  2015-12-15 13-07-44\DAD-0J(1-6)-90-0.6ML
                      -ALLNM-60MIN2015-3.M
    Last changed    : 12/15/2015 2:04:30 PM by SYSTEM
    Analysis Method : E:\DATA\LP\LP-1-H\LP-1-H -OCH3  2015-12-15 13-07-44\DAD-0J(1-6)-90-0.6ML
                      -ALLNM-60MIN2015-3.M (Sequence Method)
    Last changed    : 12/22/2015 11:21:28 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ====================================================================
                            Area Percent Report
    ====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 G, Sig=240,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  22.862 BB    0.3922 6149.76563  240.59865  49.9949
       2  26.379 BB    0.4547 6151.02441  208.18143  50.0051

    Totals :                  1.23008e4   448.78008


    ====================================================================
                            *** End of Report ***
```

Data File E:\DATA\LP\LP-1-H\LP-1-H -OCH3 2015-12-15 13-07-44\072-0501.D
Sample Name: LP-1-H 3-OCH3

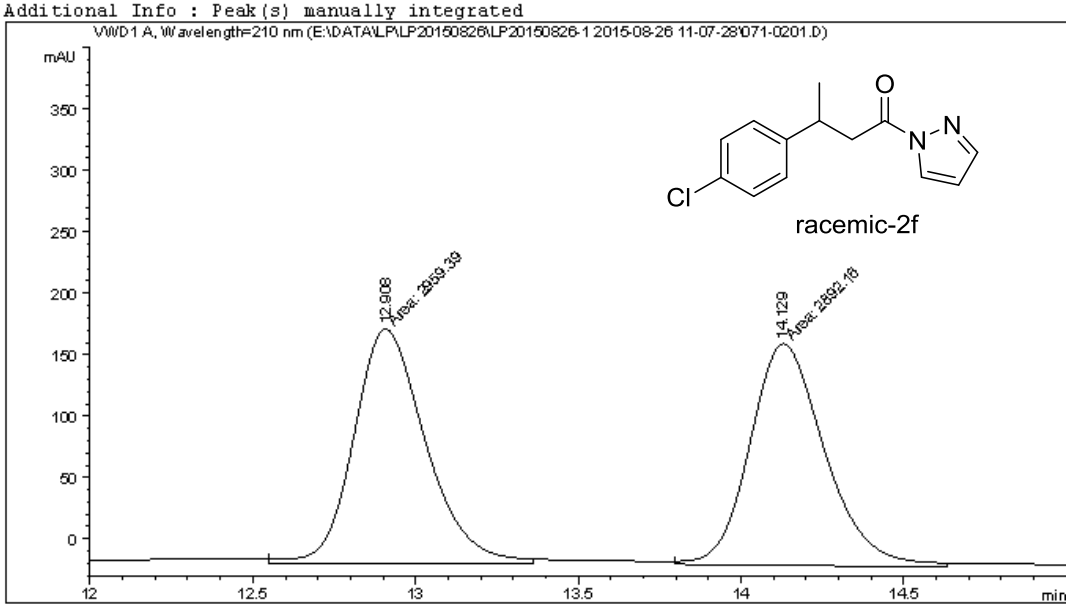
```
    ====================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   5
    Acq. Instrument : 1260HPLC-DAD                   Location : Vial 72
    Injection Date  : 12/15/2015 3:53:09 PM               Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LP\LP-1-H\LP-1-H -OCH3  2015-12-15 13-07-44\DAD-0J(1-6)-90-0.6ML
                      -ALLNM-60MIN2015-3.M
    Last changed    : 12/15/2015 2:04:30 PM by SYSTEM
    Analysis Method : E:\DATA\LP\LP-1-H\LP-1-H -OCH3  2015-12-15 13-07-44\DAD-0J(1-6)-90-0.6ML
                      -ALLNM-60MIN2015-3.M (Sequence Method)
    Last changed    : 12/22/2015 11:23:32 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ====================================================================
                            Area Percent Report
    ====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 G, Sig=240,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  22.644 BB    0.4377 4.98479e4  1732.20117  96.9325
       2  26.434 BB    0.4502 1577.49573   53.78045   3.0675

    Totals :                  5.14254e4  1785.98162


    ====================================================================
                            *** End of Report ***
```

Data File E:\DATA\LP\LP20150826\LP20150826-1 2015-08-26 11-07-28\071-0201.D
Sample Name: LP-1-H 4-CL RAC

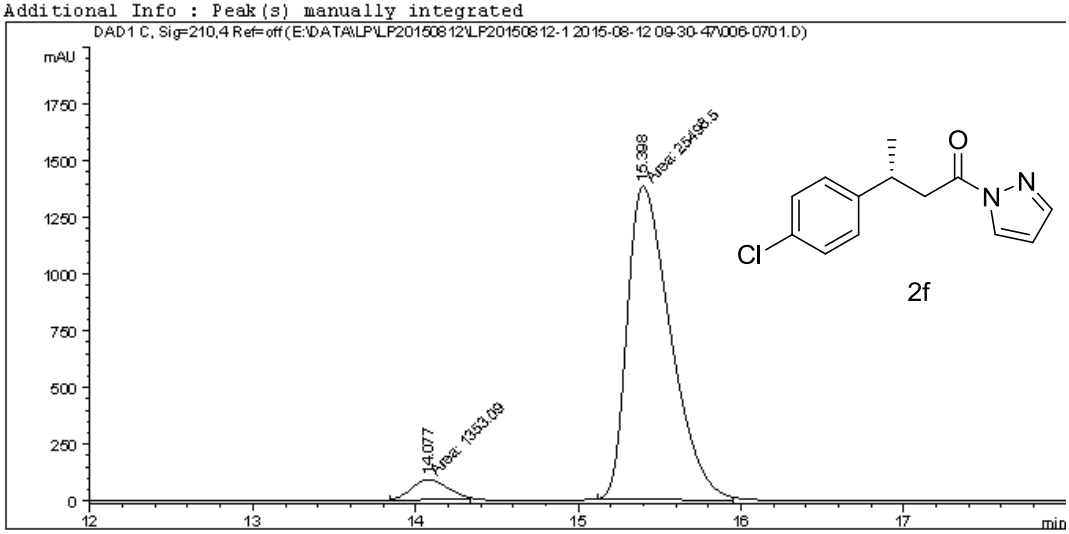
```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   2
    Acq. Instrument : 1260HPLC-VWD                     Location : Vial 71
    Injection Date  : 8/26/2015 11:20:06 AM                 Inj :   1
                                                    Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LP\LP20150826\LP20150826-1 2015-08-26 11-07-28\VWD-0J(1-2)-90-10
                      -0.6ML-210NM-60MIN.M
    Last changed    : 8/26/2015 11:07:29 AM by SYSTEM
    Analysis Method : E:\DATA\LP\LP20150826\LP20150826-1 2015-08-26 11-07-28\VWD-0J(1-2)-90-10
                      -0.6ML-210NM-60MIN.M (Sequence Method)
    Last changed    : 4/26/2016 10:57:46 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=210 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  12.908 MM    0.2579 2959.39258  191.28188  50.5745
       2  14.129 MM    0.2675 2892.16089  180.20035  49.4255

    Totals :                  5851.55347  371.48222


    ======================================================================
                              *** End of Report ***
```

Data File E:\DATA\LP\LP20150812\LP20150812-1 2015-08-12 09-30-47\006-0701.D
Sample Name: LP-1-H -Cl

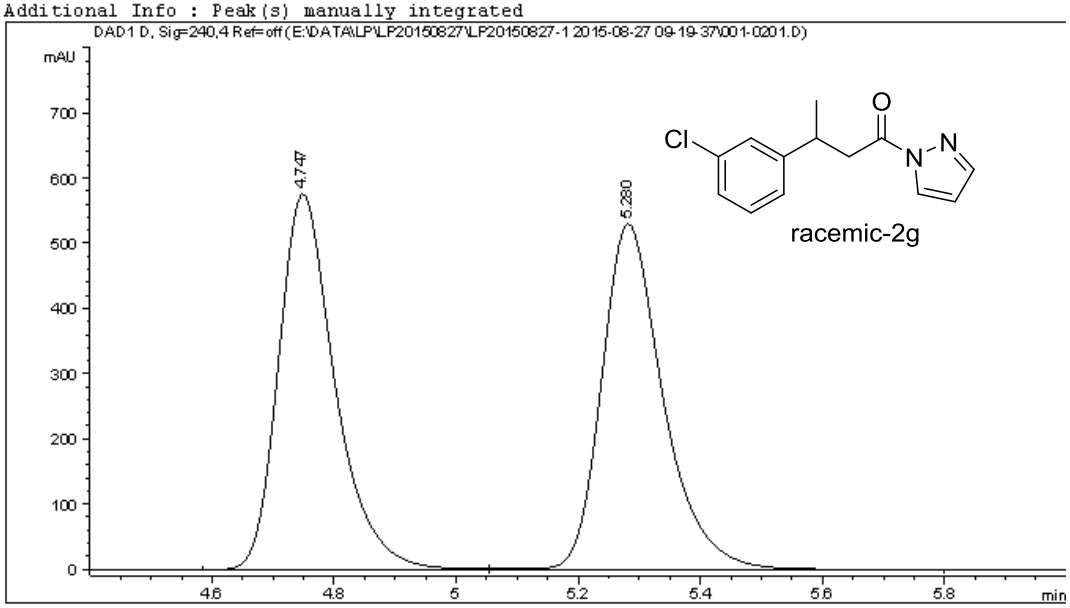
```
    ====================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   7
    Acq. Instrument : 1260HPLC-DAD                   Location : Vial 6
    Injection Date  : 8/12/2015 1:20:23 PM               Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LP\LP20150812\LP20150812-1 2015-08-12 09-30-47\DAD-0J(1-6)-90-0.
                      6ML-ALLNM-30MIN2015-3.M
    Last changed    : 8/12/2015 11:43:25 AM by SYSTEM
    Analysis Method : E:\DATA\LP\LP20150812\LP20150812-1 2015-08-12 09-30-47\DAD-0J(1-6)-90-0.
                      6ML-ALLNM-30MIN2015-3.M (Sequence Method)
    Last changed    : 4/26/2016 10:42:46 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ====================================================================
                            Area Percent Report
    ====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  14.077 MM    0.2523 1353.08643   89.37776   5.0391
       2  15.398 MM    0.3080 2.54985e4  1379.89917  94.9609

    Totals :                  2.68516e4  1469.27693


    ====================================================================
                            *** End of Report ***
```

Data File E:\DATA\LP\LP20150827\LP20150827-1 2015-08-27 09-19-37\001-0201.D
Sample Name: LP-1-H 3-CL RAC

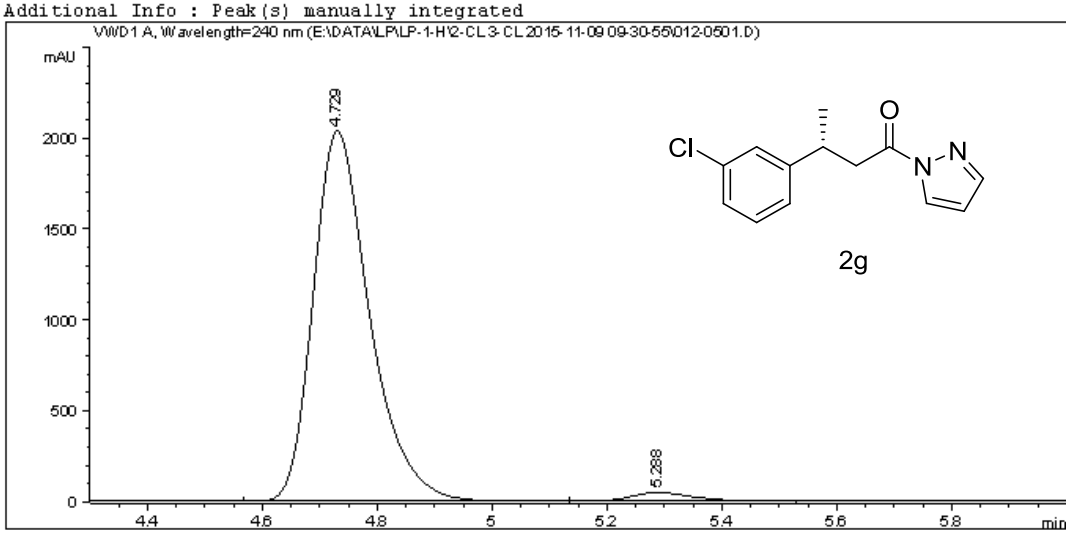
```
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   2
    Acq. Instrument : 1260HPLC-DAD                   Location : Vial 1
    Injection Date  : 8/27/2015 9:34:46 AM               Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LP\LP20150827\LP20150827-1 2015-08-27 09-19-37\DAD-AD(1-2)-90-10
                      -1.0ML-210-254-30MIN.M
    Last changed    : 8/27/2015 9:19:37 AM by SYSTEM
    Analysis Method : E:\DATA\LP\LP20150827\LP20150827-1 2015-08-27 09-19-37\DAD-AD(1-2)-90-10
                      -1.0ML-210-254-30MIN.M (Sequence Method)
    Last changed    : 12/6/2015 7:56:37 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 D, Sig=240,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   4.747 BV    0.0967 3696.48535  577.36884  49.9205
       2   5.280 VB    0.1055 3708.26611  531.09973  50.0795

    Totals :                   7404.75146 1108.46857


    ======================================================================
                              *** End of Report ***
```

Data File E:\DATA\LP\LP-1-H\2-CL 3-CL 2015-11-09 09-30-55\012-0501.D
Sample Name: LP-1-H 3-Cl

```
    ====================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   5
    Acq. Instrument : 1260HPLC-VWD                   Location : Vial 12
    Injection Date  : 11/9/2015 11:55:55 AM              Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LP\LP-1-H\2-CL 3-CL 2015-11-09 09-30-55\VWD-AD(1-2)-90-10-1ML-
                      240NM-60MIN.M
    Last changed    : 11/9/2015 9:30:55 AM by SYSTEM
    Analysis Method : E:\DATA\LP\LP-1-H\2-CL 3-CL 2015-11-09 09-30-55\VWD-AD(1-2)-90-10-1ML-
                      240NM-60MIN.M (Sequence Method)
    Last changed    : 12/6/2015 8:00:19 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```

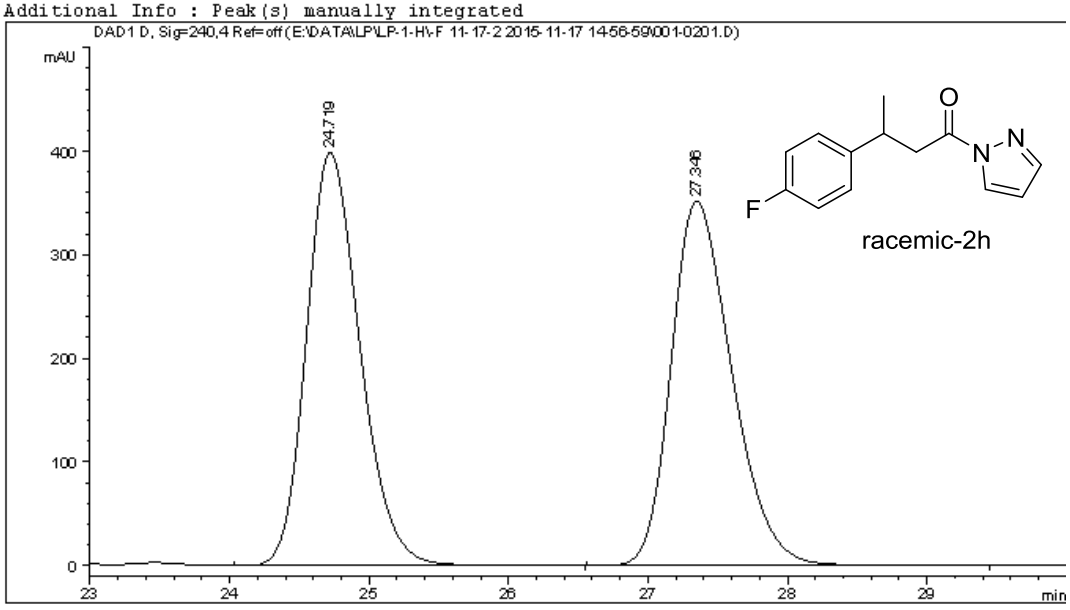


2g

```
    ====================================================================
                           Area Percent Report
    ====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=240 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   4.729 BV    0.1035 1.38982e4  2039.50220  97.4617
       2   5.288 VV    0.1132  361.95911   48.44436   2.5383

    Totals :                  1.42601e4  2087.94656


    ====================================================================
                           *** End of Report ***
```

Data File E:\DATA\LP\LP-1-H\-F 11-17-2 2015-11-17 14-56-59\001-0201.D
Sample Name: LP-1-H -F RAC

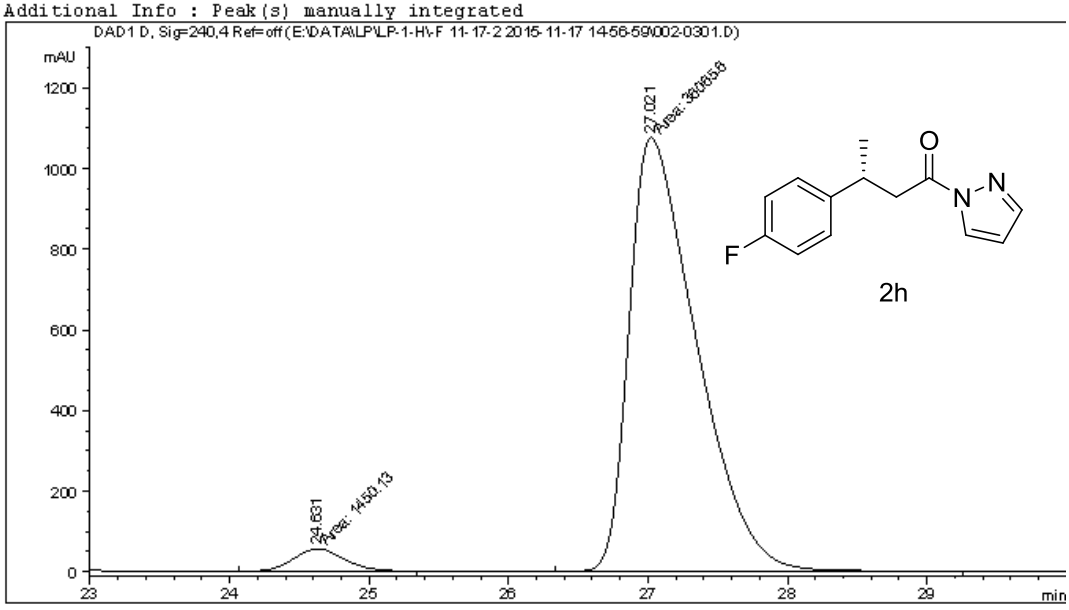
```
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   2
    Acq. Instrument : 1260HPLC-DAD                   Location : Vial 1
    Injection Date  : 11/17/2015 3:09:06 PM              Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LP\LP-1-H\-F 11-17-2 2015-11-17 14-56-59\DAD-0J(1-6)-98-2-0.6ML-
                      210-254-60MIN.M
    Last changed    : 11/17/2015 2:57:00 PM by SYSTEM
    Analysis Method : E:\DATA\LP\LP-1-H\-F 11-17-2 2015-11-17 14-56-59\DAD-0J(1-6)-98-2-0.6ML-
                      210-254-60MIN.M (Sequence Method)
    Last changed    : 12/6/2015 4:46:42 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 D, Sig=240,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  24.719 BB    0.4111 1.06488e4   399.34598  49.9749
       2  27.346 BB    0.4653 1.06595e4   352.01514  50.0251

    Totals :                  2.13084e4   751.36111


    ======================================================================
                              *** End of Report ***
```

Data File E:\DATA\LP\LP-1-H\-F 11-17-2 2015-11-17 14-56-59\002-0301.D
Sample Name: LP-1-H -F

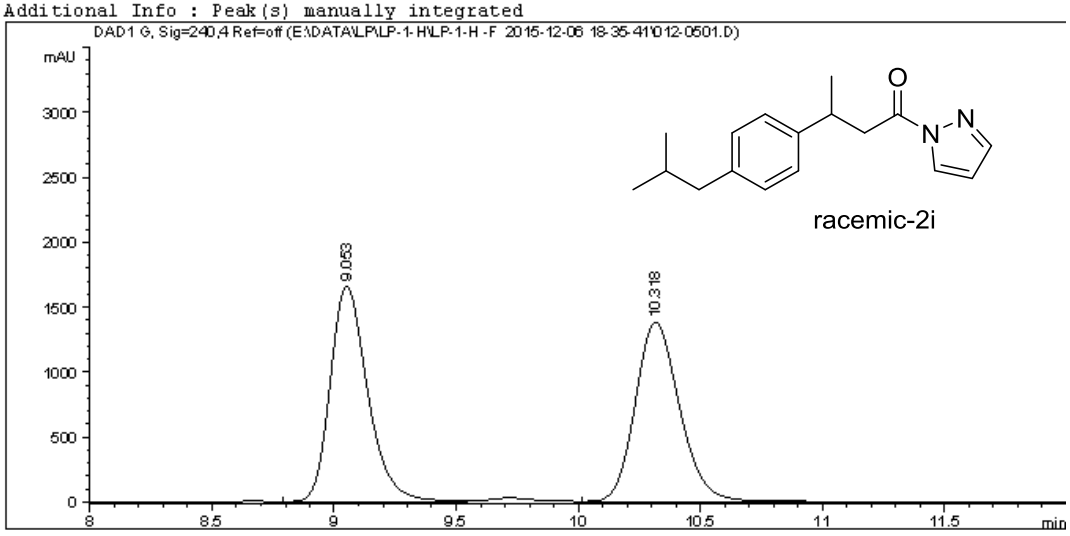
```
    ====================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   3
    Acq. Instrument : 1260HPLC-DAD                   Location : Vial 2
    Injection Date  : 11/17/2015 4:10:11 PM             Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LP\LP-1-H\-F 11-17-2 2015-11-17 14-56-59\DAD-0J(1-6)-98-2-0.6ML-
                      210-254-60MIN.M
    Last changed    : 11/17/2015 2:57:00 PM by SYSTEM
    Analysis Method : E:\DATA\LP\LP-1-H\-F 11-17-2 2015-11-17 14-56-59\DAD-0J(1-6)-98-2-0.6ML-
                      210-254-60MIN.M (Sequence Method)
    Last changed    : 12/6/2015 5:09:50 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ====================================================================
                            Area Percent Report
    ====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 D, Sig=240,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]        %
    ----|-------|----|-------|----------|----------|--------|
       1  24.631 MM    0.4329 1450.13452   55.82598   3.8654
       2  27.021 MM    0.5586 3.60656e4  1076.16211  96.1346

    Totals :                  3.75157e4  1131.98809


    ====================================================================
                            *** End of Report ***
```

Data File E:\DATA\LP\LP-1-H\LP-1-H -F 2015-12-06 18-35-41\012-0501.D
Sample Name: LP-1-H -iPr RAC

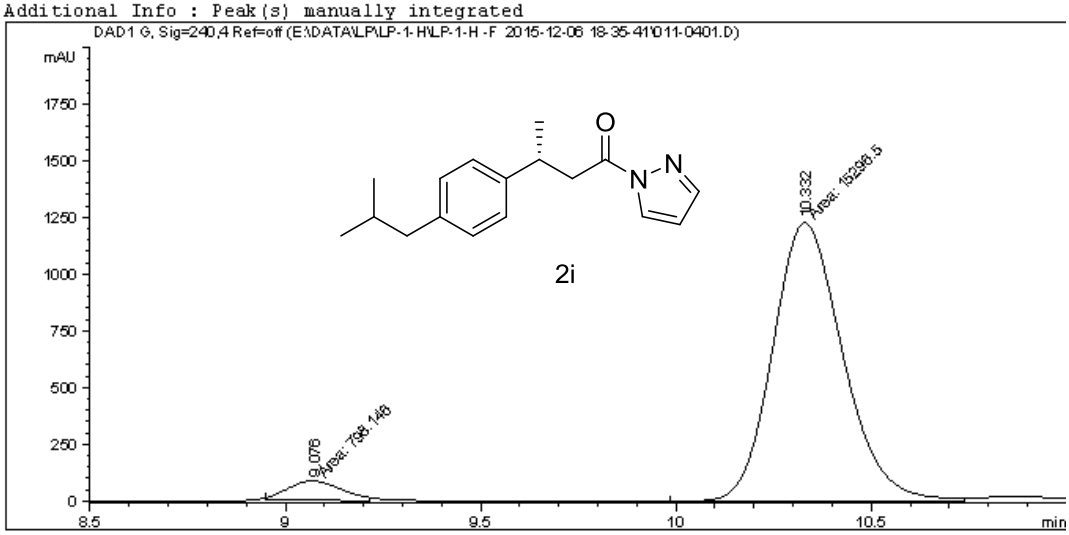
```
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   5
    Acq. Instrument : 1260HPLC-DAD                   Location : Vial 12
    Injection Date  : 12/6/2015 7:37:25 PM               Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LP\LP-1-H\LP-1-H -F  2015-12-06 18-35-41\DAD-0J(1-6)-95-0.6ML-
                      ALLNM-60MIN2015-3.M
    Last changed    : 12/6/2015 7:34:52 PM by SYSTEM
    Analysis Method : E:\DATA\LP\LP-1-H\LP-1-H -F  2015-12-06 18-35-41\DAD-0J(1-6)-95-0.6ML-
                      ALLNM-60MIN2015-3.M (Sequence Method)
    Last changed    : 12/6/2015 8:03:25 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 G, Sig=240,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   9.053 VV    0.1644 1.77368e4  1663.09924  50.3450
       2  10.318 VB    0.1956 1.74937e4  1382.44446  49.6550

    Totals :                  3.52306e4  3045.54370

    ======================================================================
                              *** End of Report ***
```

Data File E:\DATA\LP\LP-1-H\LP-1-H -F 2015-12-06 18-35-41\011-0401.D
Sample Name: lp-1-h -ipr

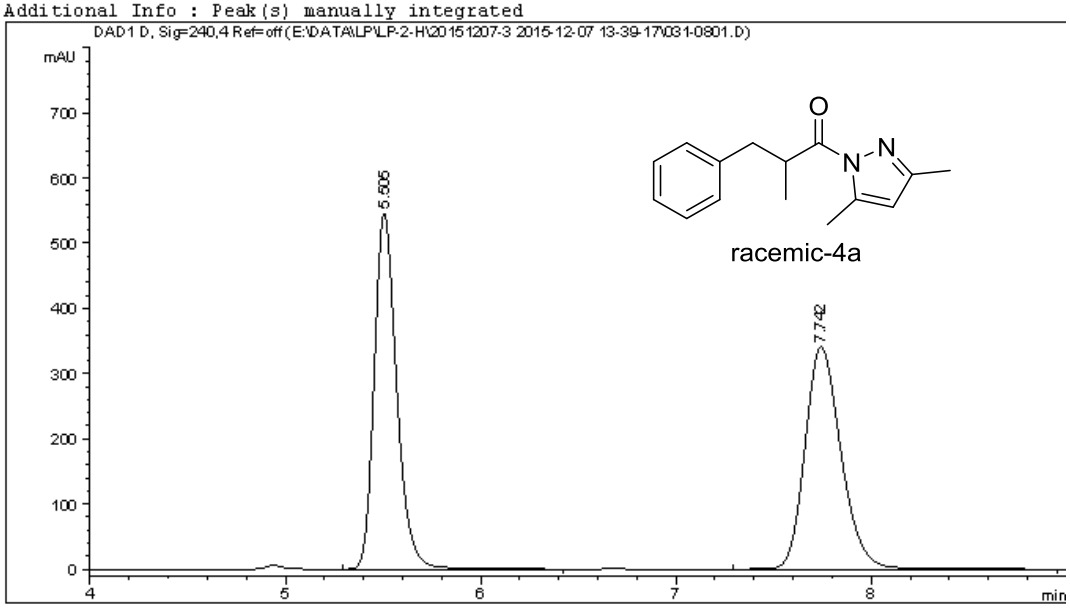
```
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   4
    Acq. Instrument : 1260HPLC-DAD                   Location : Vial 11
    Injection Date  : 12/6/2015 7:21:30 PM               Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LP\LP-1-H\LP-1-H -F  2015-12-06 18-35-41\DAD-0J(1-6)-95-0.6ML-
                      ALLNM-60MIN2015-3.M
    Last changed    : 12/6/2015 7:34:52 PM by SYSTEM
                      (modified after loading)
    Analysis Method : E:\DATA\LP\LP-1-H\LP-1-H -F  2015-12-06 18-35-41\DAD-0J(1-6)-95-0.6ML-
                      ALLNM-60MIN2015-3.M (Sequence Method)
    Last changed    : 6/14/2016 9:26:40 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 G, Sig=240,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]       [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   9.076 MM    0.1588  798.14618   83.74681   4.9591
       2  10.332 MF    0.2077 1.52965e4  1227.36108  95.0409

    Totals :                  1.60946e4  1311.10789

    ======================================================================
                              *** End of Report ***
```

Data File E:\DATA\LP\LP-2-H\20151207-3 2015-12-07 13-39-17\031-0801.D
Sample Name: LP-2-H ADD 2-CH3 RAC

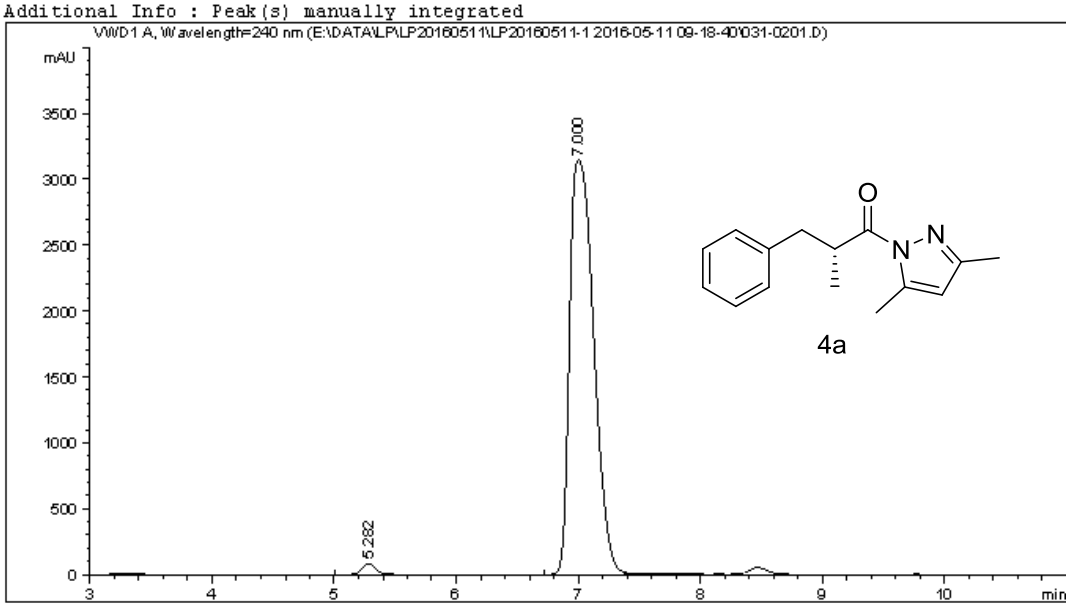
```
    ==================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   8
    Acq. Instrument : 1260HPLC-DAD                   Location : Vial 31
    Injection Date  : 12/7/2015 5:28:07 PM               Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LP\LP-2-H\20151207-3 2015-12-07 13-39-17\DAD-0J(1-6)-98-2-1.0ML-
                      210-254-60MIN.M
    Last changed    : 12/7/2015 1:39:18 PM by SYSTEM
    Analysis Method : E:\DATA\LP\LP-2-H\20151207-3 2015-12-07 13-39-17\DAD-0J(1-6)-98-2-1.0ML-
                      210-254-60MIN.M (Sequence Method)
    Last changed    : 5/16/2016 9:23:09 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                            Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 D, Sig=240,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]       [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   5.505 BB    0.1229 4351.47852  546.41278  49.8943
       2   7.742 BB    0.1976 4369.91992  340.75269  50.1057

    Totals :                   8721.39844  887.16547


    ==================================================================
                            *** End of Report ***
```

Data File E:\DATA\LP\LP20160511\LP20160511-1 2016-05-11 09-18-40\031-0201.D
Sample Name: LP-2-H sample

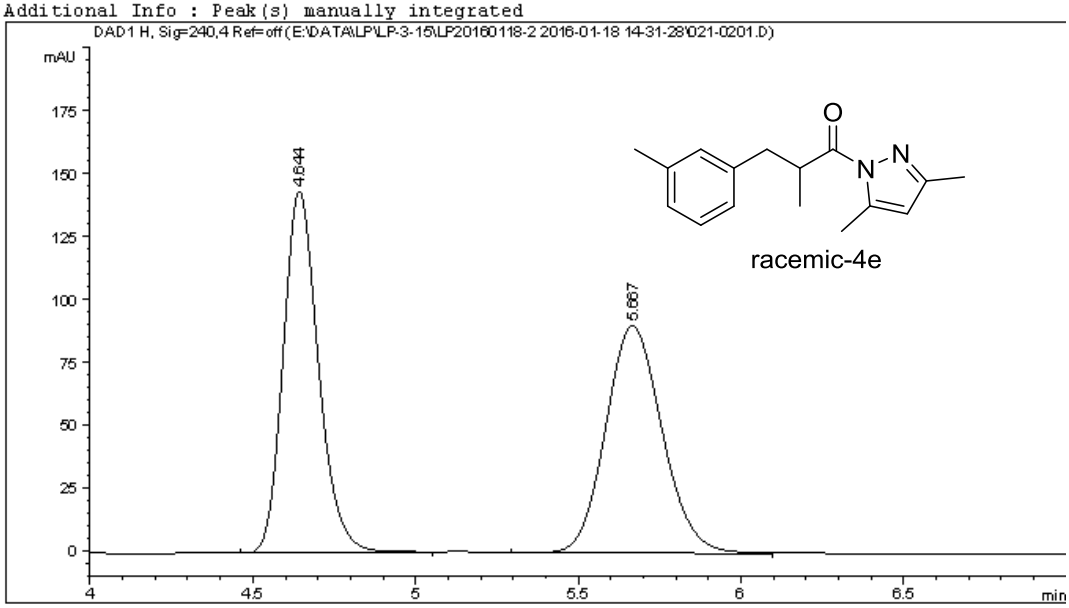
```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   2
    Acq. Instrument : 1260HPLC-VWD                     Location : Vial 31
    Injection Date  : 5/11/2016 9:32:03 AM                 Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LP\LP20160511\LP20160511-1 2016-05-11 09-18-40\VWD-0J(1-6)-98-2-
                      1ML-5U-240ALL 30MIN.M
    Last changed    : 5/11/2016 9:42:26 AM by SYSTEM
                      (modified after loading)
    Analysis Method : E:\DATA\LP\LP20160511\LP20160511-1 2016-05-11 09-18-40\VWD-0J(1-6)-98-2-
                      1ML-5U-240ALL 30MIN.M (Sequence Method)
    Last changed    : 5/16/2016 9:40:11 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=240 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   5.282 BB    0.1147  622.92249   83.83946   1.4178
       2   7.000 BB    0.2176 4.33120e4  3145.68481  98.5822

    Totals :                  4.39349e4  3229.52428


    ======================================================================
```

Data File E:\DATA\LP\LP-3-15\LP20160118-2 2016-01-18 14-31-28\021-0201.D
Sample Name: 3-CH3

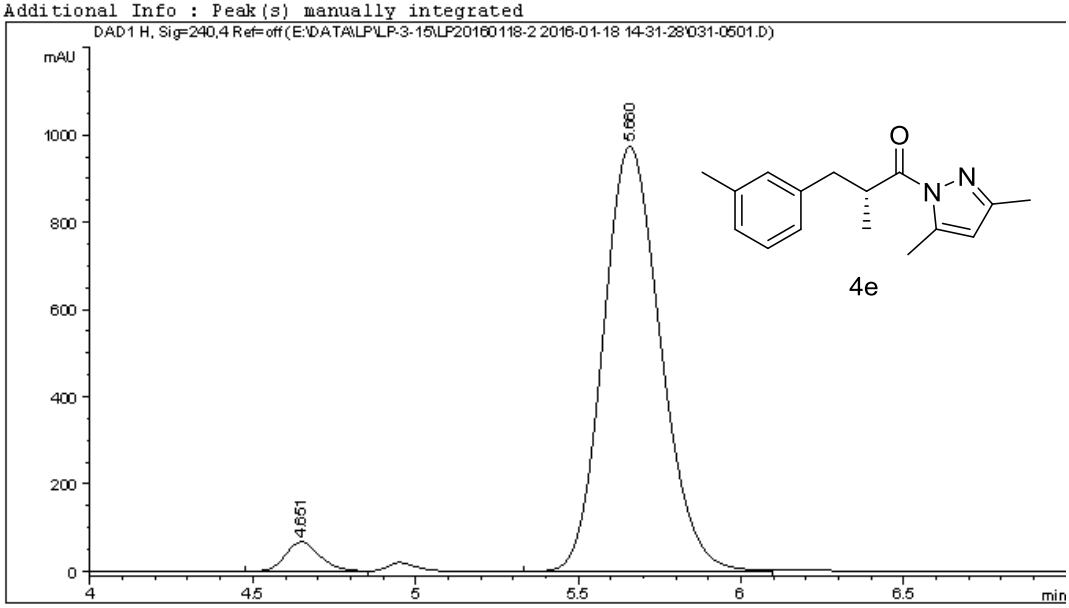
```
    ====================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   2
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 21
    Injection Date  : 1/18/2016 2:44:02 PM                 Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LP\LP-3-15\LP20160118-2 2016-01-18 14-31-28\DAD-0J(1-2)-98-2-1-
                      ALLUM-30MIN.M
    Last changed    : 1/18/2016 2:31:28 PM by SYSTEM
    Analysis Method : E:\DATA\LP\LP-3-15\LP20160118-2 2016-01-18 14-31-28\DAD-0J(1-2)-98-2-1-
                      ALLUM-30MIN.M (Sequence Method)
    Last changed    : 1/25/2016 3:12:06 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ====================================================================
                            Area Percent Report
    ====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 H, Sig=240,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]        %
    ----|-------|----|-------|----------|----------|--------|
       1   4.644 BB    0.1159 1084.44165  144.01190  49.8970
       2   5.667 BV    0.1865 1088.91895   90.42944  50.1030

    Totals :                   2173.36060  234.44134


    ====================================================================
                            *** End of Report ***
```

Data File E:\DATA\LP\LP-3-15\LP20160118-2 2016-01-18 14-31-28\031-0501.D
Sample Name: 3-ch3

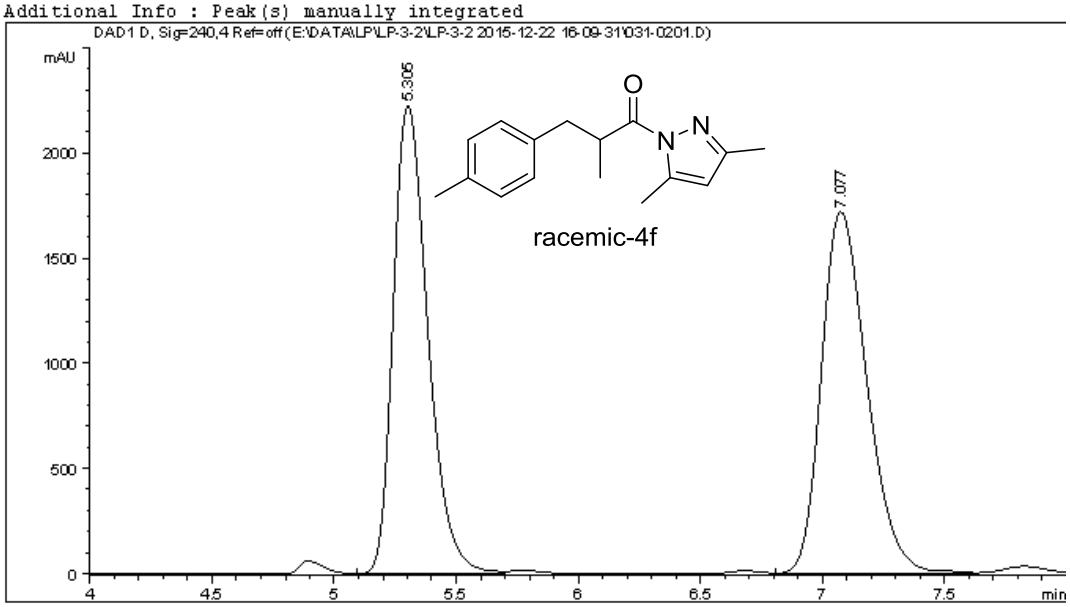
```
    ==================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   5
    Acq. Instrument : 1260HPLC-DAD                   Location : Vial 31
    Injection Date  : 1/18/2016 4:10:45 PM               Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LP\LP-3-15\LP20160118-2 2016-01-18 14-31-28\DAD-0J(1-2)-98-2-1-
                      ALLUM-30MIN.M
    Last changed    : 1/18/2016 4:09:51 PM by SYSTEM
    Analysis Method : E:\DATA\LP\LP-3-15\LP20160118-2 2016-01-18 14-31-28\DAD-0J(1-2)-98-2-1-
                      ALLUM-30MIN.M (Sequence Method)
    Last changed    : 1/25/2016 7:54:44 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                          Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 H, Sig=240,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   4.651 VV    0.1149  503.57791   67.63942   4.0564
       2   5.660 BV    0.1886 1.19109e4   974.44037  95.9436

    Totals :                   1.24145e4  1042.07979


    ==================================================================
                          *** End of Report ***
```

Data File E:\DATA\LP\LP-3-2\LP-3-2 2015-12-22 16-09-31\031-0201.D
Sample Name: -CH3 RAC

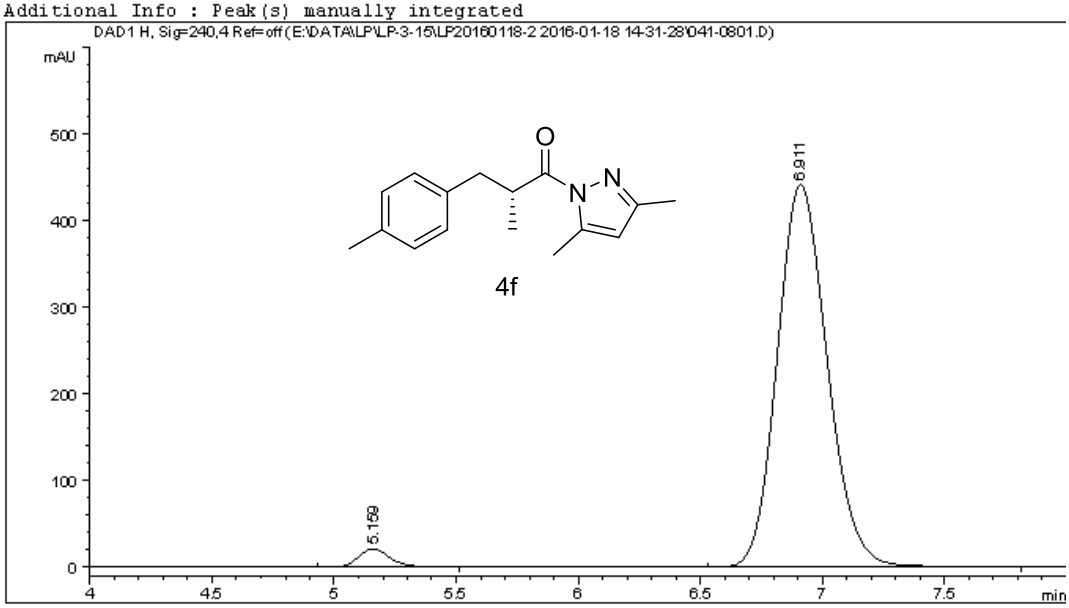
```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   2
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 31
    Injection Date  : 12/22/2015 4:22:08 PM                 Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LP\LP-3-2\LP-3-2 2015-12-22 16-09-31\DAD-0J(1-6)-98-2-1.0ML-210-
                      254-30MIN.M
    Last changed    : 12/22/2015 4:42:56 PM by SYSTEM
                      (modified after loading)
    Analysis Method : E:\DATA\LP\LP-3-2\LP-3-2 2015-12-22 16-09-31\DAD-0J(1-6)-98-2-1.0ML-210-
                      254-30MIN.M (Sequence Method)
    Last changed    : 1/25/2016 8:01:35 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 D, Sig=240,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   5.305 BV    0.1528 2.18940e4  2224.44580  49.4421
       2   7.077 VV    0.2018 2.23880e4  1721.14331  50.5579

    Totals :                   4.42820e4  3945.58911

    ======================================================================
```

Data File E:\DATA\LP\LP-3-15\LP20160118-2 2016-01-18 14-31-28\041-0801.D
Sample Name: -CH3(2)

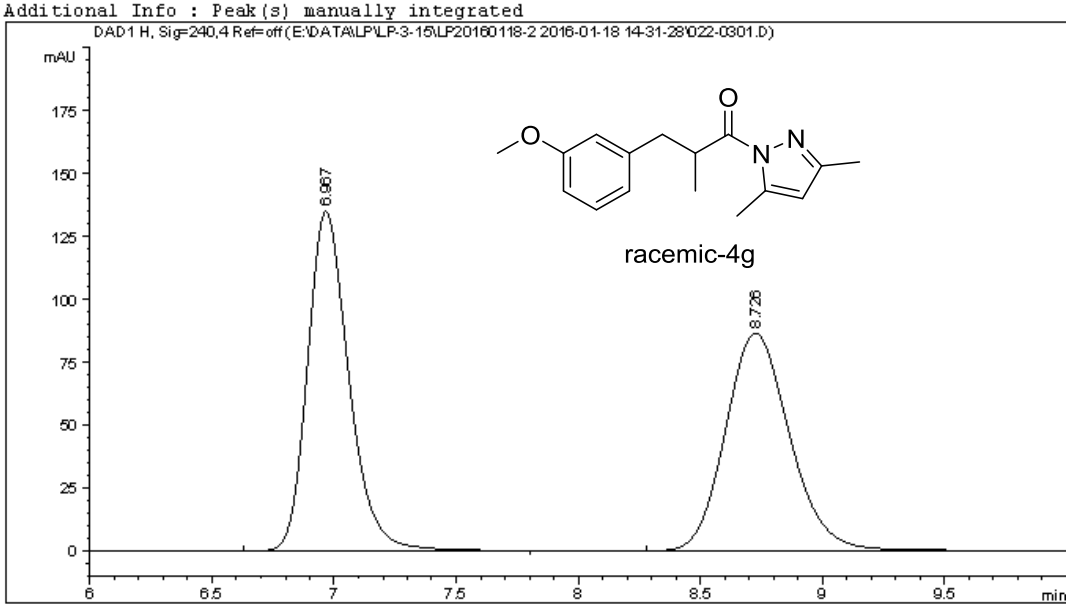
```
    ==================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   8
    Acq. Instrument : 1260HPLC-DAD                   Location : Vial 41
    Injection Date  : 1/18/2016 4:58:27 PM               Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LP\LP-3-15\LP20160118-2 2016-01-18 14-31-28\DAD-0J(1-2)-98-2-1-
                      ALLUM-30MIN.M
    Last changed    : 1/18/2016 4:09:51 PM by SYSTEM
    Analysis Method : E:\DATA\LP\LP-3-15\LP20160118-2 2016-01-18 14-31-28\DAD-0J(1-2)-98-2-1-
                      ALLUM-30MIN.M (Sequence Method)
    Last changed    : 1/25/2016 8:16:05 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                            Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 H, Sig=240,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   5.159 BB    0.1362  187.58426   20.99443   2.8964
       2   6.911 BB    0.2221 6288.79346  441.78464  97.1036

    Totals :                   6476.37772  462.77907


    ==================================================================
                            *** End of Report ***
```

Data File E:\DATA\LP\LP-3-15\LP20160118-2 2016-01-18 14-31-28\022-0301.D
Sample Name: 3-OCH3

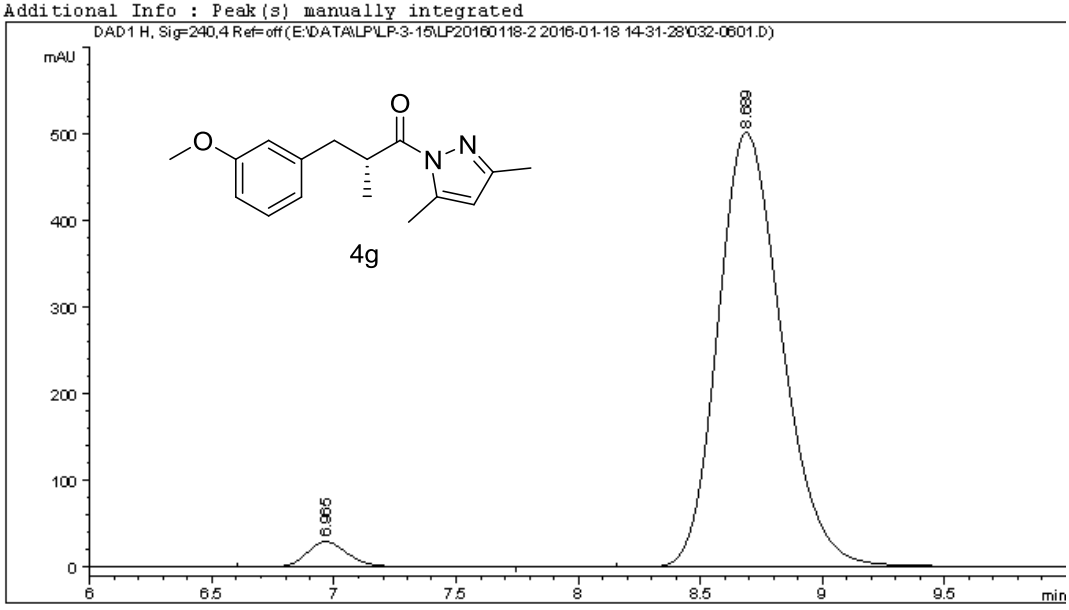
```
    ==================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   3
    Acq. Instrument : 1260HPLC-DAD                   Location : Vial 22
    Injection Date  : 1/18/2016 3:14:55 PM               Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LP\LP-3-15\LP20160118-2 2016-01-18 14-31-28\DAD-OJ(1-2)-98-2-1-
                      ALLUM-30MIN.M
    Last changed    : 1/18/2016 2:31:28 PM by SYSTEM
    Analysis Method : E:\DATA\LP\LP-3-15\LP20160118-2 2016-01-18 14-31-28\DAD-OJ(1-2)-98-2-1-
                      ALLUM-30MIN.M (Sequence Method)
    Last changed    : 1/25/2016 7:49:26 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                          Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 H, Sig=240,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   6.967 BB    0.1790 1586.65857  135.13722  50.0449
       2   8.726 BB    0.2815 1583.81018   86.55563  49.9551

    Totals :                   3170.46875  221.69286


    ==================================================================
                          *** End of Report ***
```

Data File E:\DATA\LP\LP-3-15\LP20160118-2 2016-01-18 14-31-28\032-0601.D
Sample Name: 3-och3

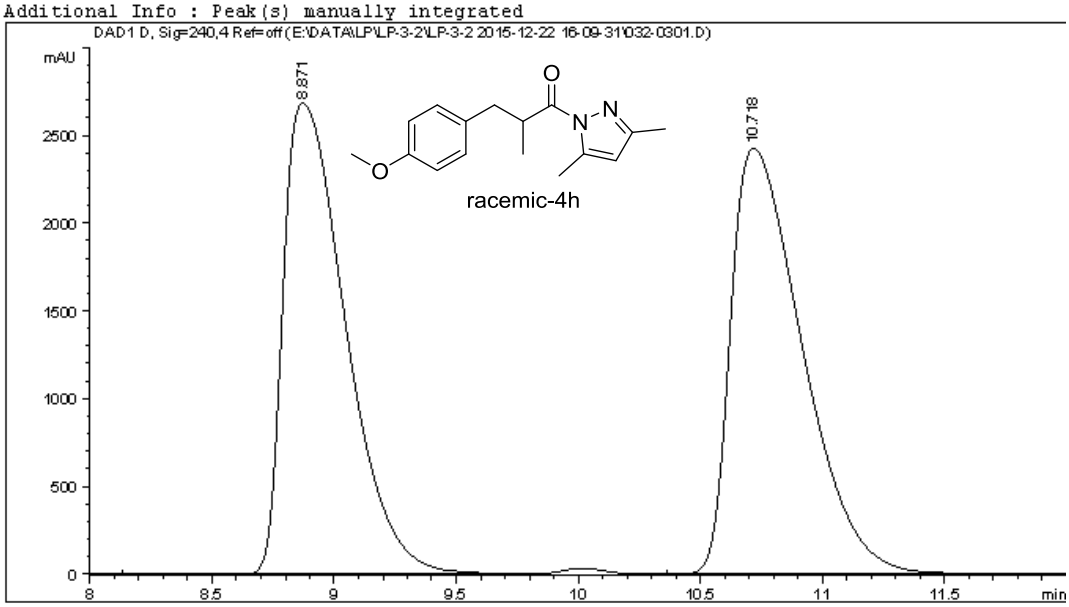
```
    ====================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   6
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 32
    Injection Date  : 1/18/2016 4:26:40 PM                 Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LP\LP-3-15\LP20160118-2 2016-01-18 14-31-28\DAD-0J(1-2)-98-2-1-
                      ALLUM-30MIN.M
    Last changed    : 1/18/2016 4:09:51 PM by SYSTEM
    Analysis Method : E:\DATA\LP\LP-3-15\LP20160118-2 2016-01-18 14-31-28\DAD-0J(1-2)-98-2-1-
                      ALLUM-30MIN.M (Sequence Method)
    Last changed    : 1/25/2016 7:56:18 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ====================================================================
                            Area Percent Report
    ====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 H, Sig=240,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]        %
    ----|-------|----|-------|----------|----------|--------|
       1   6.965 BB    0.1833  352.72330   29.53148   3.7100
       2   8.689 BB    0.2808 9154.66211  501.85910  96.2900

    Totals :                   9507.38541  531.39058


    ====================================================================
                            *** End of Report ***
```

Data File E:\DATA\LP\LP-3-2\LP-3-2 2015-12-22 16-09-31\032-0301.D
Sample Name: -OCH3 RAC

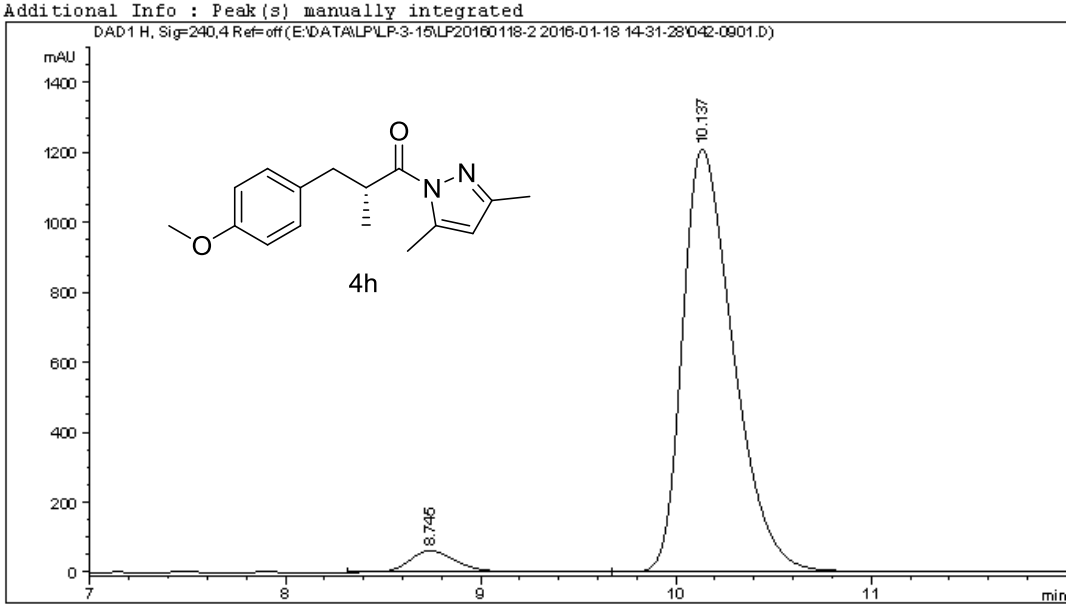
```
    ====================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   3
    Acq. Instrument : 1260HPLC-DAD                   Location : Vial 32
    Injection Date  : 12/22/2015 4:43:53 PM              Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LP\LP-3-2\LP-3-2 2015-12-22 16-09-31\DAD-0J(1-6)-98-2-1.0ML-210-
                      254-30MIN.M
    Last changed    : 12/22/2015 4:43:10 PM by SYSTEM
                      (modified after loading)
    Analysis Method : E:\DATA\LP\LP-3-2\LP-3-2 2015-12-22 16-09-31\DAD-0J(1-6)-98-2-1.0ML-210-
                      254-30MIN.M (Sequence Method)
    Last changed    : 1/25/2016 8:02:48 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ====================================================================
                            Area Percent Report
    ====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 D, Sig=240,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   8.871 BV    0.2750 4.75866e4  2682.58374  49.1126
       2  10.718 BB    0.3151 4.93063e4  2425.97192  50.8874

    Totals :                  9.68929e4  5108.55566


    ====================================================================
```

Data File E:\DATA\LP\LP-3-15\LP20160118-2 2016-01-18 14-31-28\042-0901.D
Sample Name: -OCH3(2)

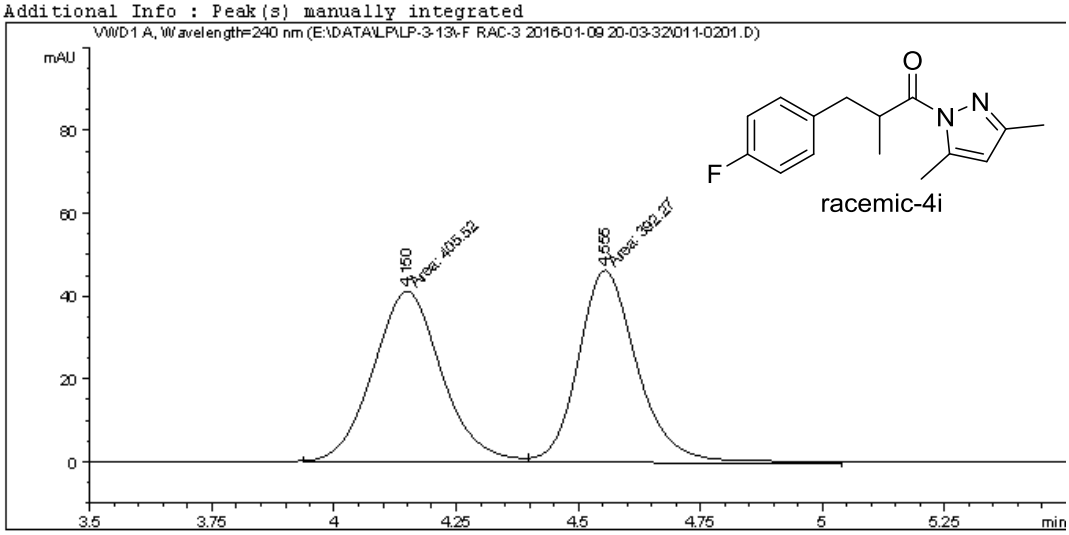
```
    ==================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   9
    Acq. Instrument : 1260HPLC-DAD                   Location : Vial 42
    Injection Date  : 1/18/2016 5:14:21 PM               Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LP\LP-3-15\LP20160118-2 2016-01-18 14-31-28\DAD-0J(1-2)-98-2-1-
                      ALLUM-30MIN.M
    Last changed    : 1/18/2016 4:09:51 PM by SYSTEM
    Analysis Method : E:\DATA\LP\LP-3-15\LP20160118-2 2016-01-18 14-31-28\DAD-0J(1-2)-98-2-1-
                      ALLUM-30MIN.M (Sequence Method)
    Last changed    : 1/25/2016 8:17:28 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                            Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 H, Sig=240,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   8.745 BB    0.2542 1022.45892   61.41182   4.4457
       2  10.137 BB    0.2780 2.19764e4  1209.36194  95.5543

    Totals :                  2.29989e4  1270.77375


    ==================================================================
                            *** End of Report ***
```

Data File E:\DATA\LP\LP-3-13\-F RAC-3 2016-01-09 20-03-32\011-0201.D
Sample Name: -F RAC

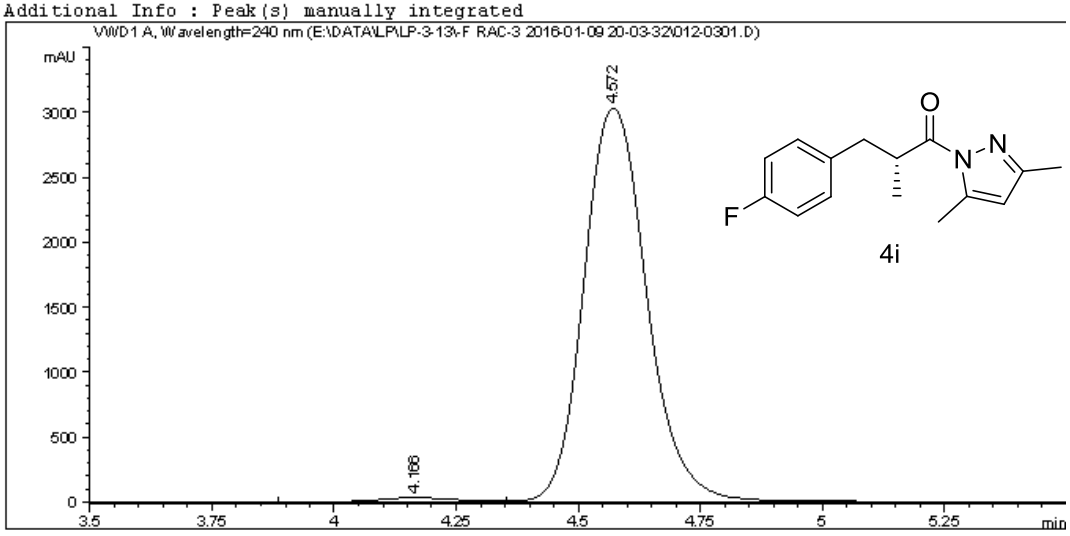
```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   2
    Acq. Instrument : 1260HPLC-VWD                     Location : Vial 11
    Injection Date  : 1/9/2016 8:16:02 PM                   Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LP\LP-3-13\-F RAC-3 2016-01-09 20-03-32\VWD-AD(1-2)-99-1-1ML-
                      240NM-60MIN.M
    Last changed    : 1/9/2016 8:27:16 PM by SYSTEM
                      (modified after loading)
    Analysis Method : E:\DATA\LP\LP-3-13\-F RAC-3 2016-01-09 20-03-32\VWD-AD(1-2)-99-1-1ML-
                      240NM-60MIN.M (Sequence Method)
    Last changed    : 5/25/2016 4:18:53 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=240 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   4.150 MF    0.1639  405.51953   41.23326  50.8304
       2   4.555 FM    0.1407  392.27005   46.45706  49.1696

    Totals :                    797.78958   87.69032

    ======================================================================
                              *** End of Report ***
```

Data File E:\DATA\LP\LP-3-13\-F RAC-3 2016-01-09 20-03-32\012-0301.D
Sample Name: -F

```
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   3
    Acq. Instrument : 1260HPLC-VWD                   Location : Vial 12
    Injection Date  : 1/9/2016 8:28:00 PM                 Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LP\LP-3-13\-F RAC-3 2016-01-09 20-03-32\VWD-AD(1-2)-99-1-1ML-
                      240NM-60MIN.M
    Last changed    : 1/9/2016 8:27:16 PM by SYSTEM
    Analysis Method : E:\DATA\LP\LP-3-13\-F RAC-3 2016-01-09 20-03-32\VWD-AD(1-2)-99-1-1ML-
                      240NM-60MIN.M (Sequence Method)
    Last changed    : 1/25/2016 8:20:00 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```

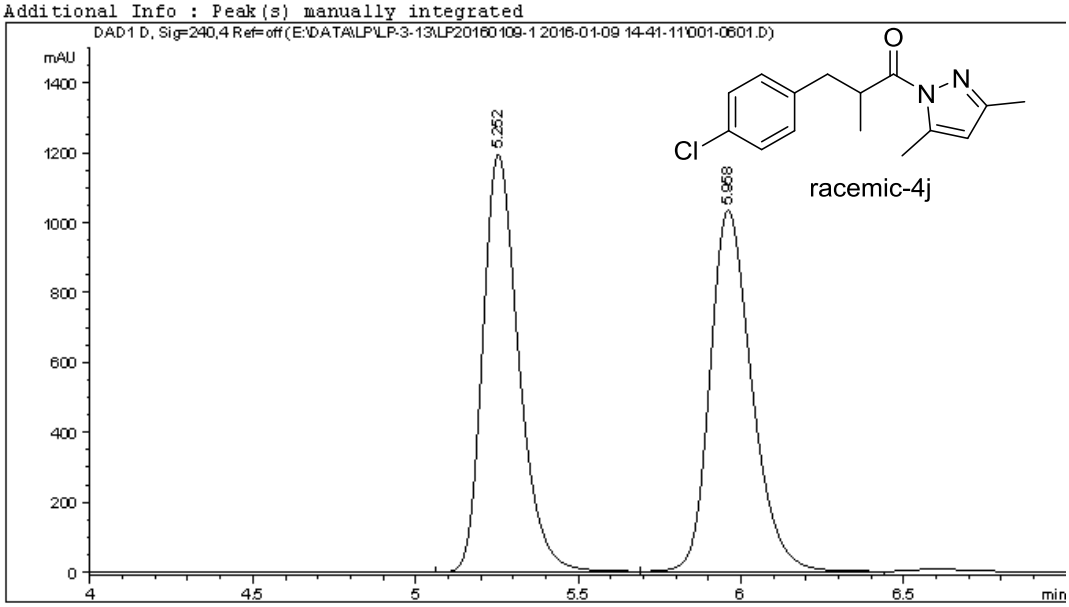


4i

```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=240 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   4.166 BV    0.1657  348.73050   31.61261   1.2627
       2   4.572 VB    0.1389 2.72691e4  3031.86963  98.7373

    Totals :                   2.76178e4  3063.48224

    ======================================================================
                              *** End of Report ***
```

Data File E:\DATA\LP\LP-3-13\LP20160109-1 2016-01-09 14-41-11\001-0601.D
Sample Name: -Cl 1 RAC

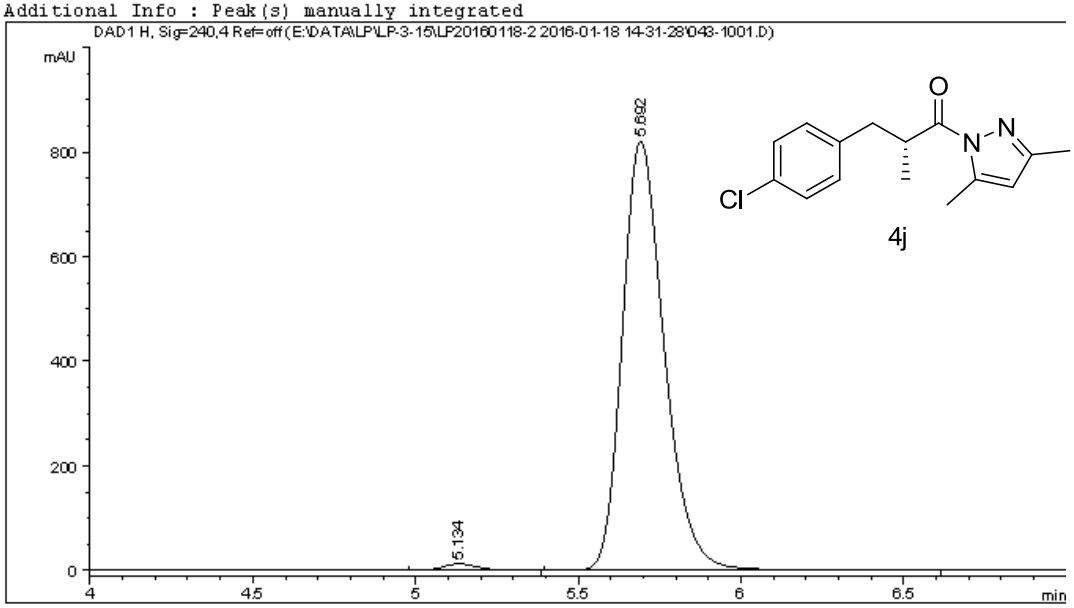
```
    ====================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   6
    Acq. Instrument : 1260HPLC-DAD                   Location : Vial 1
    Injection Date  : 1/9/2016 3:50:33 PM                 Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LP\LP-3-13\LP20160109-1 2016-01-09 14-41-11\DAD-0J(1-6)-98-2-1.
                      0ML-210-254-30MIN.M
    Last changed    : 1/9/2016 3:57:22 PM by SYSTEM
                      (modified after loading)
    Analysis Method : E:\DATA\LP\LP-3-13\LP20160109-1 2016-01-09 14-41-11\DAD-0J(1-6)-98-2-1.
                      0ML-210-254-30MIN.M (Sequence Method)
    Last changed    : 1/25/2016 8:06:04 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ====================================================================
                            Area Percent Report
    ====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 D, Sig=240,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   5.252 BB    0.1172 9141.96094 1196.20447  49.7308
       2   5.958 BV    0.1362 9240.93652 1034.62537  50.2692

    Totals :                  1.83829e4  2230.82983


    ====================================================================
```

Data File E:\DATA\LP\LP-3-15\LP20160118-2 2016-01-18 14-31-28\043-1001.D
Sample Name: -Cl(2)

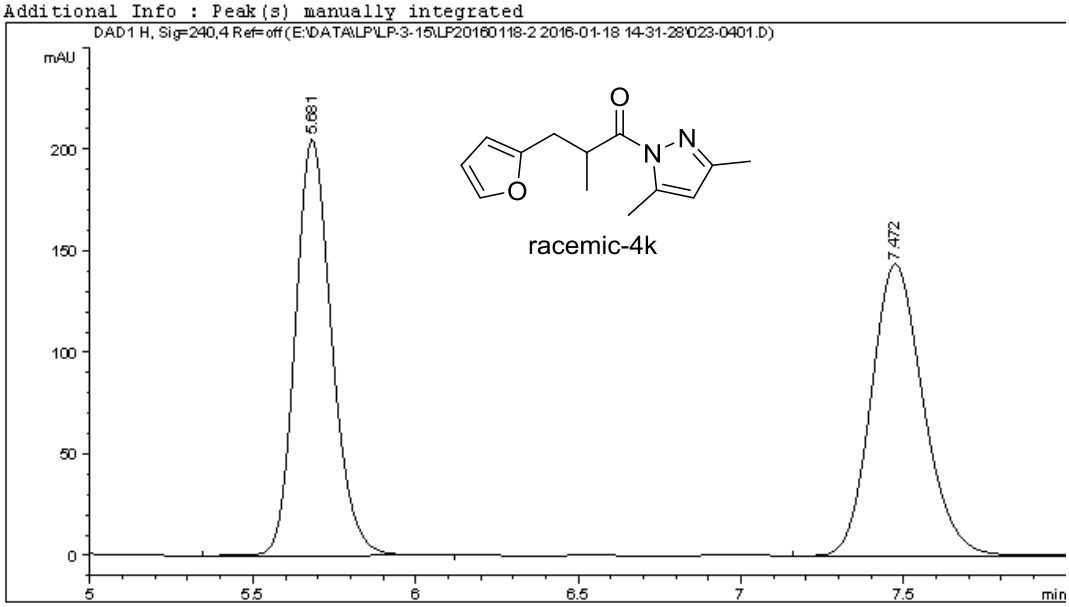
```
    ==================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :  10
    Acq. Instrument : 1260HPLC-DAD                   Location : Vial 43
    Injection Date  : 1/18/2016 5:30:16 PM                Inj :   1
                                                  Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LP\LP-3-15\LP20160118-2 2016-01-18 14-31-28\DAD-0J(1-2)-98-2-1-
                      ALLUM-30MIN.M
    Last changed    : 1/18/2016 4:09:51 PM by SYSTEM
    Analysis Method : E:\DATA\LP\LP-3-15\LP20160118-2 2016-01-18 14-31-28\DAD-0J(1-2)-98-2-1-
                      ALLUM-30MIN.M (Sequence Method)
    Last changed    : 1/25/2016 8:14:35 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ==================================================================
                            Area Percent Report
    ==================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 H, Sig=240,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]       [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   5.134 BB    0.1191   95.60490   12.51784   1.2826
       2   5.692 BB    0.1364 7358.16504  821.98718  98.7174

    Totals :                   7453.76994  834.50502


    ==================================================================
                            *** End of Report ***
```

Data File E:\DATA\LP\LP-3-15\LP20160118-2 2016-01-18 14-31-28\023-0401.D
Sample Name: Fruyl

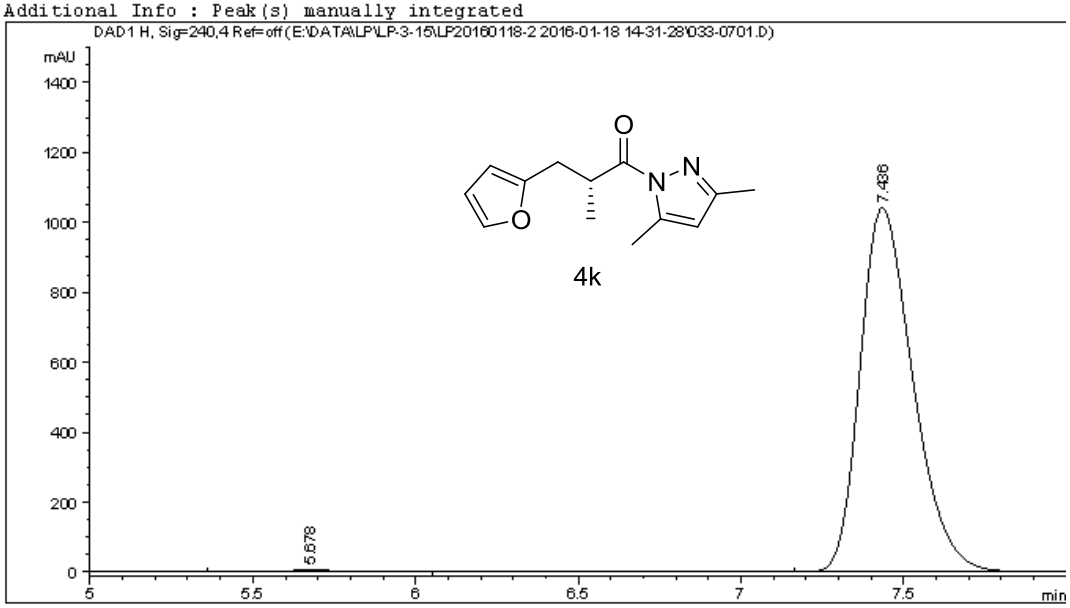
```
    ====================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   4
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 23
    Injection Date  : 1/18/2016 3:45:49 PM                 Inj :   1
                                                     Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LP\LP-3-15\LP20160118-2 2016-01-18 14-31-28\DAD-0J(1-2)-98-2-1-
                      ALLUM-30MIN.M
    Last changed    : 1/18/2016 4:09:51 PM by SYSTEM
                      (modified after loading)
    Analysis Method : E:\DATA\LP\LP-3-15\LP20160118-2 2016-01-18 14-31-28\DAD-0J(1-2)-98-2-1-
                      ALLUM-30MIN.M (Sequence Method)
    Last changed    : 1/25/2016 7:50:39 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ====================================================================
                            Area Percent Report
    ====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 H, Sig=240,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   5.681 BB    0.1187 1594.19800  204.98987  50.0613
       2   7.472 BB    0.1711 1590.29651  143.67979  49.9387

    Totals :                   3184.49451  348.66966


    ====================================================================
```

Data File E:\DATA\LP\LP-3-15\LP20160118-2 2016-01-18 14-31-28\033-0701.D
Sample Name: fruyl

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   7
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 33
    Injection Date  : 1/18/2016 4:42:34 PM                  Inj :   1
                                                    Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LP\LP-3-15\LP20160118-2 2016-01-18 14-31-28\DAD-0J(1-2)-98-2-1-
                      ALLUM-30MIN.M
    Last changed    : 1/18/2016 4:09:51 PM by SYSTEM
    Analysis Method : E:\DATA\LP\LP-3-15\LP20160118-2 2016-01-18 14-31-28\DAD-0J(1-2)-98-2-1-
                      ALLUM-30MIN.M (Sequence Method)
    Last changed    : 1/25/2016 7:57:37 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```



4k

```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 H, Sig=240,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]       [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   5.678 BB    0.1286   73.65875    8.53807   0.6214
       2   7.436 BB    0.1758 1.17796e4  1042.33997  99.3786

    Totals :                   1.18532e4  1050.87804


    ======================================================================
                              *** End of Report ***
```

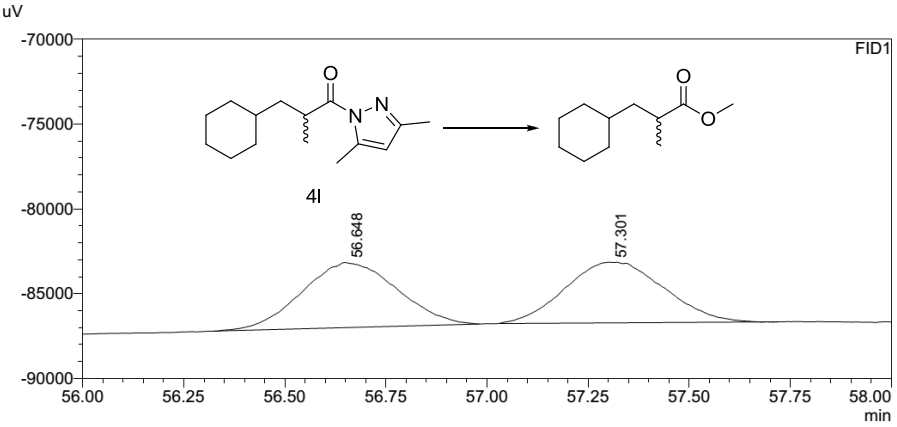
SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: LP-C-hex rac		
Sample ID	:		
Data Filename	: lp-c-hex rac.gcd		
Method Filename	: bdex120-250-80~150-260-150min.gcm		
Batch Filename	: zrt-7-8-1.gcb		
Vial #	: 21	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 2016-7-28 10:29:47	Acquired by	: System Administrator
Date Processed	: 2016-8-23 17:09:56	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

FID1

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	56.648	62679	3835	50.814		M	
2	57.301	60671	3573	49.186		M	
Total		123350	7408				

D:\DATA FILE\LP\data\lp-c-hex rac.gcd

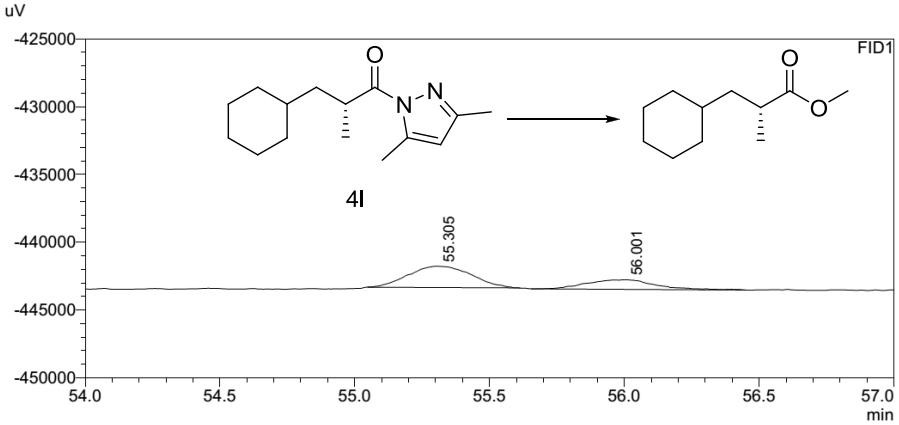
SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: lp20160730-guanghuo		
Sample ID	:		
Data Filename	: lp-c-hex guanghuo.gcd		
Method Filename	: bdex120-250-80~150-260-150min.gcm		
Batch Filename	: zrt-7-8-1.gcb		
Vial #	: 21	Sample Type	: Unknown
Injection Volume	: 1 uL		
Date Acquired	: 2016-7-30 21:01:31	Acquired by	: System Administrator
Date Processed	: 2016-7-30 22:02:59	Processed by	: System Administrator

<Chromatogram>



4l

<Peak Table>

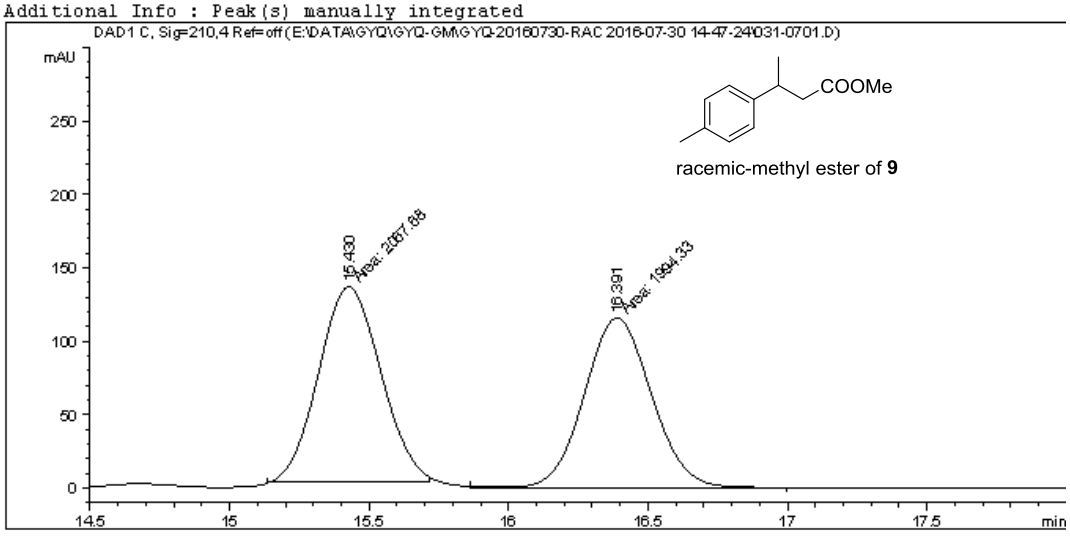
FID1

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	55.305	25528	1571	66.890		M	
2	56.001	12636	705	33.110		M	
Total		38164	2276				

D:\DATA FILE\LP\data\lp-c-hex guanghuo.gcd

Data File E:\DATA\GYQ\GYQ-GM\GYQ-20160730-RAC 2016-07-30 14-47-24\031-0701.D
Sample Name: rac

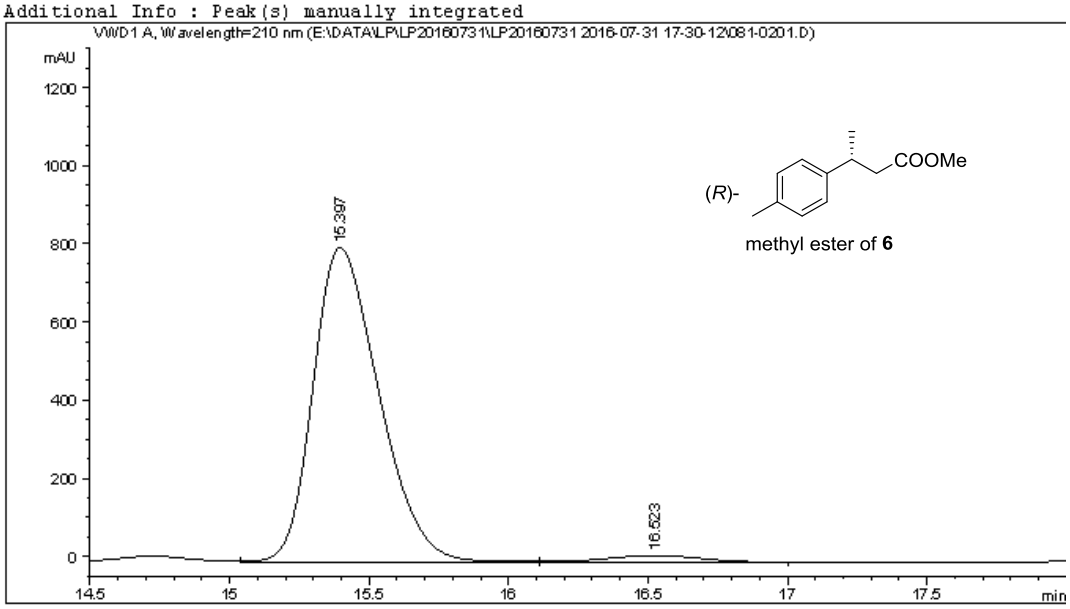
```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   7
    Acq. Instrument : 1260HPLC-DAD                     Location : Vial 31
    Injection Date  : 7/30/2016 6:39:22 PM                  Inj :   1
                                                    Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\GYQ\GYQ-GM\GYQ-20160730-RAC 2016-07-30 14-47-24\DAD-0J(1-6)-95-0
                      .6ML-ALLNM-60MIN2015-3.M
    Last changed    : 7/30/2016 7:04:26 PM by SYSTEM
                      (modified after loading)
    Analysis Method : E:\DATA\GYQ\GYQ-GM\GYQ-20160730-RAC 2016-07-30 14-47-24\DAD-0J(1-6)-95-0
                      .6ML-ALLNM-60MIN2015-3.M (Sequence Method)
    Last changed    : 7/31/2016 9:45:53 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  15.430 MM    0.2585 2067.68335  133.32091  50.9029
       2  16.391 MM    0.2857 1994.32837  116.35642  49.0971

    Totals :                  4062.01172  249.67733


    ======================================================================
                              *** End of Report ***
```

Data File E:\DATA\LP\LP20160731\LP20160731 2016-07-31 17-30-12\081-0201.D
Sample Name: LP

```
    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   2
    Acq. Instrument : 1260HPLC-VWD                     Location : Vial 81
    Injection Date  : 7/31/2016 5:34:43 PM                  Inj :   1
                                                    Inj Volume : 5.000 µl
    Acq. Method     : E:\DATA\LP\LP20160731\LP20160731 2016-07-31 17-30-12\VWD-0J(1-6)-95-5-0.
                      6ML-5UL-210-60MIN.M
    Last changed    : 7/31/2016 5:30:12 PM by SYSTEM
    Analysis Method : E:\DATA\LP\LP20160731\LP20160731 2016-07-31 17-30-12\VWD-0J(1-6)-95-5-0.
                      6ML-5UL-210-60MIN.M (Sequence Method)
    Last changed    : 7/31/2016 9:48:57 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=210 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  15.397 VV    0.2527 1.31294e4   803.13306  97.3857
       2  16.523 VB    0.3359  352.45477   16.45183   2.6143

    Totals :                  1.34819e4   819.58489


    ======================================================================
                               *** End of Report ***

1260HPLC-VWD 7/31/2016 9:49:03 PM SYSTEM                    Page 1 of 1
```

VII. Reference

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2. M. Abe, K. Nishikawa, H. Fukuda, K. Nakanishi, Y. Tazawa, T. Taniguchi, S.-Y. Park, S. Hiradate, Y. Fujii, K. Okuda, M. Shindo, *Phytochemistry*, 2012, **84**, 56-67.

3. K. Dong, Y. Li, Z. Wang, K. Ding, *Org. Chem. Front*, 2014, **1**, 155-160.

4. S. Li, S.-F. Zhu, C.-M. Zhang, S. Song, Q.-L. Zhou, *J. Am. Chem. Soc*, 2008, **130**, 8584-8585.

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