Supporting Information:

A Straightforward Entry to Chiral Carbocyclic Nucleoside Analogues via Enantioselective [3+2] Cycloaddition of α-Nucleobase Substituted Acrylates

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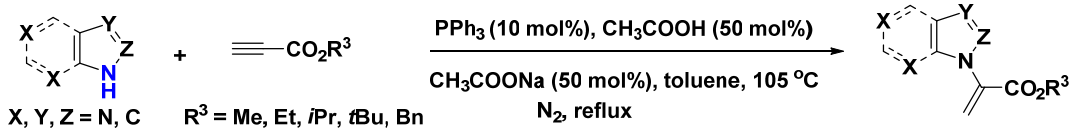
Contents

1. General information

^{1}H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts are recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), coupling constants (Hz), integration. ^{13}C NMR data were collected on commercial instruments (100 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. Enantiomer excesses were determined by chiral HPLC analysis on Chiralcel IA/ASH/ODH/ADH in comparison with the authentic racemates. HRMS was recorded on a commercial apparatus (ESI Source). All the solvents were purified by usual methods before use. Vinyl cyclopropanes **2a**-**2g** were synthesized following reported methods.[1]

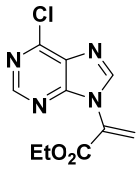
2. General procedure for the synthesis of α-heteroaryl acrylates[2]



To a solution of purine, pyrimidine, isatin, carbazole, benzoimidazole, phthalimide, or imidazole (10.0 mmol), triphenylphosphine (260 mg, 1 mmol), and sodium acetate (420 mg, 5 mmol) in 100 mL of toluene at 105 °C were added sequentially acetic acid (300 mg, 5 mmol) and alkyl propiolate (12 mmol). After the reaction was complete as monitored by TLC, the resulting mixture was partitioned between water and ethyl acetate, and the separated aqueous layer extracted with ethyl acetate. The combined organic layers were washed with brine (100 mL×3), dried over anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (1:5 petroleum ether-EtOAc) to yield α-heteroaryl acrylates.

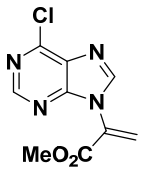
3. The analytical and spectral characterization data for the α-heteroaryl acrylates

Ethyl 2-(6-chloro-9*H*-purin-9-yl) acrylate (1a)



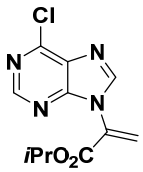
White solid. ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.77 (s, 1H), 8.37 (s, 1H), 6.78 (s, 1H), 6.45 (s, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 161.6, 152.5, 151.9, 151.5, 145.0, 131.4, 130.8, 124.8, 62.8, 14.1. **HRMS**: exact mass calcd for $C_{10}H_9ClN_4O_2Na$ $(M+Na)^+$ requires m/z 275.0306, found m/z 275.0304.

Ethyl 2-(6-chloro-9*H*-purin-9-yl) acrylate (1b)



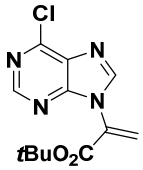
White solid. ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.77 (s, 1H), 8.36 (s, 1H), 6.79 (s, 1H), 6.46 (s, 1H), 3.91 (s, 1H). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 162.1, 152.5, 151.9, 151.6, 144.9, 131.4, 130.6, 125.2, 53.4. **HRMS**: exact mass calcd for $C_9H_7ClN_4O_2Na$ $(M+Na)^+$ requires m/z 261.0150, found m/z 261.0145.

Isopropyl 2-(6-chloro-9*H*-purin-9-yl) acrylate (1c)



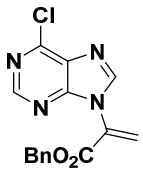
White solid. ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.78 (s, 1H), 8.38 (s, 1H), 6.77 (s, 1H), 6.43 (s, 1H),5.26-5.17 (m, 1H), 1.34 (d, *J* = 6.4 Hz, 6H).^{13}**C NMR** (100 MHz, $CDCl_3$): δ 161.1, 152.5, 151.9, 151.6, 145.1, 131.4, 131.1, 124.5, 71.1, 21.7. **HRMS**: exact mass calcd for $C_{11}H_{12}ClN_4O_2$ $(M+H)^+$ requires m/z 267.0643, found m/z 267.0653.

Tert-butyl 2-(6-chloro-9*H*-purin-9-yl) acrylate (1d)



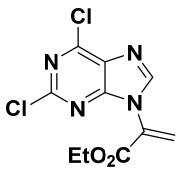
White solid. ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.79 (s, 1H), 8.38 (s, 1H), 6.71 (s, 1H), 6.38 (s, 1H), 1.55 (s, 9H).^{13}**C NMR** (100 MHz, $CDCl_3$): δ 160.5, 152.5, 151.9, 151.5, 145.2, 131.8, 131.4, 124.0, 84.2, 27.9. **HRMS**: exact mass calcd for $C_{12}H_{13}ClN_4O_2Na$ $(M+Na)^+$ requires m/z 303.0619, found m/z 303.0624.

Benzyl 2-(6-chloro-9*H*-purin-9-yl) acrylate (1e)



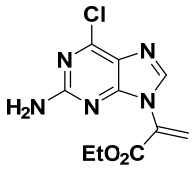
White solid. ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.76 (s, 1H), 8.37 (s, 1H), 7.37 (s, 5H), 6.81 (s, 1H), 6.48 (s, 1H), 5.33 (s, 2H).^{13}**C NMR** (100 MHz, $CDCl_3$): δ 161.5, 152.5, 151.9, 151.6, 144.9, 134.4, 131.4, 130.6, 128.9, 128.8, 128.5, 125.2, 68.4. **HRMS**: exact mass calcd for $C_{15}H_{12}ClN_4O_2$ $(M+H)^+$ requires m/z 315.0643, found m/z 315.0642.

Ethyl 2-(2,6-dichloro-9*H*-purin-9-yl) acrylate (1f)



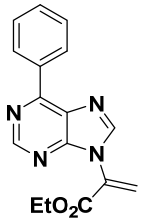
White solid. ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.34 (s, 1H), 6.81 (s, 1H), 6.44(s, 1H), 4.37 (q, J = 7.2 Hz, 2H), 1.36 (t, J = 7.0 Hz, 3H). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 161.4, 153.6, 153.1, 152.3, 145.6, 130.5, 130.3, 125.7, 63.0, 14.1. **HRMS**: exact mass calcd for $C_{10}H_8Cl_2N_4O_2Na$ $(M+Na)^+$ requires m/z 308.9917, found m/z 308.9909.

Ethyl 2-(2-amino-6-chloro-9*H*-purin-9-yl) acrylate (1g)



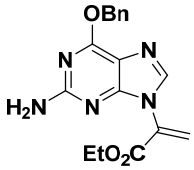
White solid.[1]**H NMR** (400 MHz, $CDCl_3$): δ 7.97 (s, 1H), 6.66 (s, 1H), 6.31 (s, 1H), 5.32 (s, 2H, NH), 4.33 (q, *J* = 7.2 Hz, 2H), 1.33 (t, *J* = 7.0 Hz, 3H). [13]**C NMR** (100 MHz, $CDCl_3$): δ 161.8, 159.4, 153.9, 151.7, 141.9, 131.1, 124.8, 124.2, 62.6, 14.1. **HRMS**: exact mass calcd for $C_{10}H_{10}ClN_5O_2Na$ $(M+Na)^+$ requires m/z 290.0415, found m/z 290.0414.

Ethyl 2-(6-phenyl-9*H*-purin-9-yl) acrylate (1h)



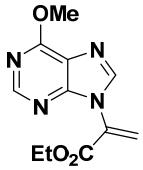
White solid.[1]**H NMR** (400 MHz, $CDCl_3$): δ 9.05 (s, 1H), 8.79-8.77 (m, 2H), 8.36 (s, 1H), 7.60-7.54 (m, 3H), 6.79 (s, 1H), 6.48 (s, 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 1.36 (t, *J* = 7.2 Hz, 3H). [13]**C NMR** (100 MHz, $CDCl_3$): δ 162.0, 155.3, 153.0, 144.1, 135.4, 131.1, 131.1, 130.7, 129.8, 128.7, 124.4, 62.6, 14.1. **HRMS**: exact mass calcd for $C_{16}H_{14}N_4O_2$ $(M+H)^+$ requires m/z 295.1190, found m/z 295.1196.

Ethyl 2-(2-amino-6-(benzyloxy)-9*H*-purin-9-yl) acrylate (1i)



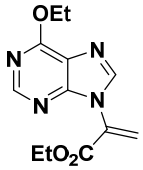
White solid.[1]**H NMR** (400 MHz, $CDCl_3$): δ 7.80 (s, 1H), 7.51 (d, *J* = 7.6 Hz, 2H), 7.38-7.29 (m, 3H), 6.62 (s, 1H), 6.28 (s, 1H), 5.57 (s, 1H), 4.88 (s, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 1.33 (t, *J* = 7.0 Hz, 3H). [13]**C NMR** (100 MHz, $CDCl_3$): δ 162.2, 161.2, 159.5, 139.2, 136.3, 131.6, 128.4, 128.2, 128.0, 123.5, 68.1, 62.3, 14.1. **HRMS**: exact mass calcd for $C_{17}H_{17}N_5O_3$ $(M+H)^+$ requires m/z 340.1404, found m/z 340.1409.

Ethyl 2-(6-methoxy-9*H*-purin-9-yl) acrylate (1j)



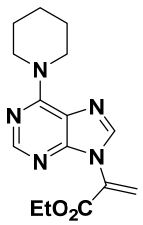
White solid.[1]**H NMR** (400 MHz, $CDCl_3$): δ 8.55 (s, 1H), 8.13 (s, 1H), 6.70 (s, 1H), 6.38 (s, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 4.19 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H). [13]**C NMR** (100 MHz, $CDCl_3$): δ 161.9, 161.3, 152.6, 152.1, 142.0, 131.3, 124.1, 121.3, 62.5, 54.3, 14.0. **HRMS**: exact mass calcd for $C_{11}H_{12}N_4O_3Na$ $(M+Na)^+$ requires m/z 271.0802, found m/z 271.0801.

Ethyl 2-(6-ethoxy-9*H*-purin-9-yl) acrylate (1k)



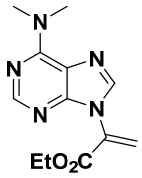
White solid.[1]**H NMR** (400 MHz, $CDCl_3$): δ 8.50 (s, 1H), 8.13 (s, 1H), 6.68 (s, 1H), 6.36 (s, 1H), 4.64 (q, *J* = 7.0 Hz, 2H), 4.31 (q, *J* = 7.0 Hz, 2H), 1.49 (t, *J* = 7.0 Hz, 3H), 1.30 (t, *J* = 7.0 Hz, 3H). [13]**C NMR** (100 MHz, $CDCl_3$): δ 161.9, 161.0, 152.6, 152.1, 141.8, 131.3, 124.0, 121.1, 63.2, 62.5, 14.4, 14.0. **HRMS**: exact mass calcd for $C_{12}H_{14}N_4O_3Na$ $(M+Na)^+$ requires m/z 285.0958, found m/z 285.0960.

Ethyl 2-(6-(piperidin-1-yl)-9*H*-purin-9-yl)acrylate (1l)



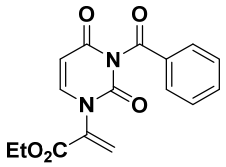
White solid.[1]**H NMR** (400 MHz, $CDCl_3$): δ 8.33 (s, 1H), 7.90 (s, 1H), 6.68 (s, 1H), 6.31 (s, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 4.24 (s, 1H), 1.74-1.67 (m, 7H), 1.33 (t, *J* = 7.2 Hz, 3H). [13]**C NMR** (100 MHz, $CDCl_3$): δ 162.3, 153.9, 153.0, 151.1, 137.8, 131.5, 124.3, 119.3, 62.4, 46.4, 26.1, 24.8, 14.1. **HRMS**: exact mass calcd for $C_{15}H_{19}N_5O_2Na$ $(M+Na)^+$ requires m/z 324.1431, found m/z 324.1422.

Ethyl 2-(6-(dimethylamino)-9*H*-purin-9-yl) acrylate (1m)



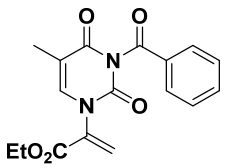
White solid.[1]**H NMR** (400 MHz, $CDCl_3$): δ 8.36 (s, 1H), 7.91 (s, 1H), 6.69 (s, 1H), 6.32 (s, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 3.55 (s, 6H), 1.33 (t, *J* = 7.2 Hz, 3H). [13]**C NMR** (100 MHz, $CDCl_3$): δ 162.3, 155.1, 152.9, 150.9, 138.1, 131.6, 124.2, 119.7, 62.4, 38.4, 14.1. **HRMS**: exact mass calcd for $C_{12}H_{16}N_5O_2$ $(M+H)^+$ requires m/z 262.1299, found m/z 262.1298.

Ethyl 2-(3-benzoyl-2, 4-dioxo-3, 4-dihydropyrimidin-1(2*H*)-yl) acrylate (1n)



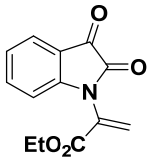
White solid.[1]**H NMR** (400 MHz, $CDCl_3$): δ 7.96 (q, *J* = 7.2 Hz, 2H), 7.67-7.63 (m, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 1H), 6.52 (s, 1H), 5.98 (d, *J* = 1.2 Hz, 1H), 5.86 (d, *J* = 8.0 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 3H) . [13]**C NMR** (100 MHz, $CDCl_3$): δ 168.0, 162.1, 161.6, 148.5, 143.8, 136.7, 135.2, 131.1, 130.4, 129.1, 125.8, 102.5, 62.4, 14.0. **HRMS**: exact mass calcd for $C_{16}H_{14}N_2O_5Na$ $(M+Na)^+$ requires m/z 337.0795, found m/z 337.0796.

Ethyl 2-(3-benzoyl-5-methyl-2, 4-dioxo-3, 4-dihydropyrimidin-1(2*H*)-yl) acrylate (1o)



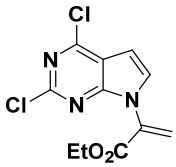
White solid.[1]**H NMR** (400 MHz, $CDCl_3$): δ 7.95 (q, *J* = 7.2 Hz, 2H), 7.67-7.62 (m, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.08 (d, *J* = 1.2 Hz, 1H), 6.51 (d, *J* = 1.2 Hz, 1H), 5.97 (d, *J* = 0.8 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 1.98 (s, 3H), 1.30 (t, *J* = 7.0 Hz, 3H) . [13]**C NMR** (100 MHz, $CDCl_3$): δ 168.2, 163.0, 161.8, 148.6, 139.6, 137.0, 135.1, 131.4, 130.5, 129.1, 125.4, 125.3, 111.1, 62.4, 14.0, 12.4. **HRMS**: exact mass calcd for $C_{17}H_{16}N_2O_5Na$ $(M+Na)^+$ requires m/z 351.0951, found m/z 351.0960.

Ethyl 2-(2, 3-dioxoindolin-1-yl) acrylate (1p)



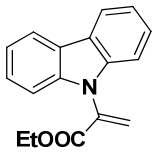
Red solid.[1]**H NMR** (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 7.2 Hz, 1H), 7.60-7.55 (m, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.77 (t, *J* = 7.2 Hz, 2H), 6.09 (s, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 1.28 (t, *J* = 7.0 Hz, 3H). [13]**C NMR** (100 MHz, $CDCl_3$): δ 162.3, 140.9, 136.4, 130.6, 116.7, 106.9, 62.0, 14.1. **HRMS**: exact mass calcd for $C_{13}H_{12}NO_4$ $(M+H)^+$ requires m/z 246.0761, found m/z 246.0756.

Ethyl 2-(2, 4-dichloro-7*H*-pyrrolo[2, 3-*d*]pyrimidin-7-yl) acrylate (1q)



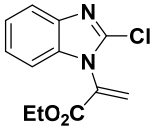
White solid.[1]**H NMR** (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 3.6 Hz, 1H), 6.71-6.69 (m, 2H), 6.22 (d, *J* = 0.8 Hz, 1H), 4.32 (q, *J* = 6.8 Hz, 2H), 1.33 (t, *J* = 7.0 Hz, 3H). [13]**C NMR** (100 MHz, $CDCl_3$): δ 162.2, 153.0, 152.5, 132.9, 130.6, 124.9, 116.8, 100.7, 62.4, 14.1. **HRMS**: exact mass calcd for $C_{11}H_{10}Cl_2N_3O_2$ $(M+H)^+$ requires m/z 286.0145, found m/z 286.0143.

Ethyl 2-(9*H*-carbazol-9-yl) acrylate (1r)



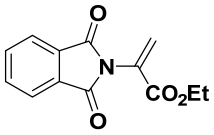
Colorless oil.[1]**H NMR** (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 1.2 Hz, 4H), 6.88 (s, 1H), 6.12 (s, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 1.19 (t, *J* = 7.0 Hz, 3H). [13]**C NMR** (100 MHz, $CDCl_3$): δ 163.6, 140.6, 134.9, 126.2, 125.9, 123.5, 120.3, 120.2, 109.9, 61.8, 14.0. **HRMS**: exact mass calcd for $C_{17}H_{15}NO_2Na$ $(M+Na)^+$ requires m/z 288.0995, found m/z 288.1001.

Ethyl 2-(2-chloro-1*H*-benzo[*d*]imidazol-1-yl) acrylate (1s)



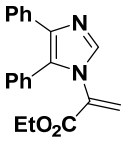
Colorless oil.[1]**H NMR** (400 MHz, $CDCl_3$): δ 7.71-7.68 (m, 1H), 7.31-7.26 (m, 2H), 7.18-7.15 (m, 1H), 6.89 (s, 1H), 6.11 (s, 1H), 4.26 (q, *J* = 6.8 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 3H). [13]**C NMR** (100 MHz, $CDCl_3$): δ 161.7, 141.5, 140.2, 135.8, 132.5, 128.9, 123.8, 123.2, 119.4, 109.7, 62.3, 13.9. **HRMS**: exact mass calcd for $C_{12}H_{12}ClN_2O_2$ $(M+H)^+$ requires m/z 251.0582, found m/z 251.0574.

Ethyl 2-(1, 3-dioxoisoindolin-2-yl) acrylate (1t)



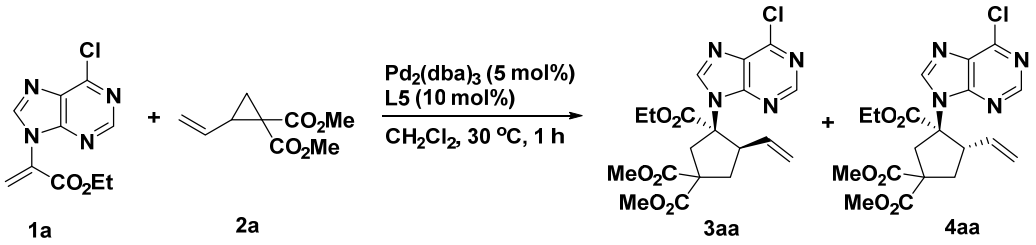
White solid.[1]**H NMR** (400 MHz, $CDCl_3$): δ 7.92 (t, *J* = 2.0 Hz, 2H), 7.79 (t, *J* = 1.4 Hz, 2H), 6.68 (s, 1H), 5.99 (s, 1H), 4.28 (q, *J* = 6.8 Hz, 2H), 1.30 (t, *J* = 7.0 Hz, 3H). [13]**C NMR** (100 MHz, $CDCl_3$): δ 166.4, 162.2, 134.5, 131.8, 129.4, 127.7, 123.9, 62.0, 14.1. **HRMS**: exact mass calcd for $C_{13}H_{11}NO_4Na$ $(M+Na)^+$ requires m/z 268.0580, found m/z 268.0590.

Ethyl 2-(4, 5-diphenyl-1*H*-imidazol-1-yl) acrylate (1u)



Colorless oil.[1]**H NMR** (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 4.8 Hz, 2H), 7.53 (q, *J* = 1.2 Hz, 2H), 7.35 (d, *J* = 1.6 Hz, 3H), 7.28-7.18 (m, 5H), 6.39 (d, *J* = 4.8 Hz, 1H), 5.86 (d, *J* = 4.8 Hz, 1H), 3.99 (q, *J* = 1.6 Hz, 2H), 1.07 (t, *J* = 6.2 Hz, 3H) . [13]**C NMR** (100 MHz, $CDCl_3$): δ 137.5, 134.9, 134.1, 130.3, 128.7, 128.4, 128.1, 127.1, 126.7, 124.4, 62.0, 13.8. **HRMS**: exact mass calcd for $C_{20}H_{18}N_2O_2$ $(M+H)^+$ requires m/z 319.1441, found m/z 319.1450.

4. General procedure for the enantioselective [3+2] cycloaddition



In a test tube, **L5** (10 mol%) and $Pd_2(dba)_3$ (10 mol%) were added, and the tube was filled with N_2 gas. Subsequently, CH_2Cl_2 was added and the mixture was stirred at 30 ^oC for 0.5 h. Sbusequently, α-purine substituted acrylate **1a** (0.05 mmol) and vinyl cyclopropane **2a** (0.075 mmol) were dissolved in CH_2Cl_2 and added to the test tube. The reaction mixture was stirred until α-purine substituted acrylates **1a** was consumed (determined by TLC).

Work up procedure: The mixture was filtered through Celite and the filtrate was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (1:1 petroleum ether-EE) to yield the cycloadducts **3aa** and **4aa**. The ratio (**3aa**/**4aa**) was determined by the ^{1}H-NMR spectroscopic analysis of crude product.

5. The X-ray data for carbocyclic purine nucleoside analogue 3aa

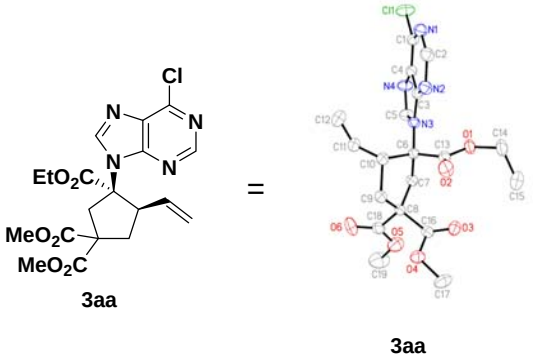
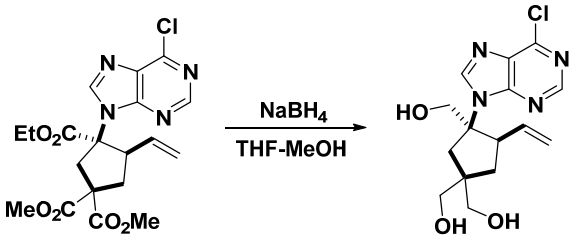


Table 1. Crystal data and structure refinement of **3aa**.

Empirical formula	$C_{19}H_{21}ClN_4O_6$
Temperature	296(2) K
Wavelength	0.71073 Å
Unit cell dimensions	a = 9.960(2) Å b = 8.9114(18) Å c = 12.427(3) Å alpha = 90.00 deg. beta = 105.91 deg. gamma = 90.00 deg.
Volume	1060.7(4) $Å^3$
Z	2
Calculated density	1.368 Mg/m^3
Absorption coefficient	0.223 mm^{-1}
F(000)	456
Crystal size	0.40*0.30*0.25 mm^3

6. Transformation of adduct 3aa

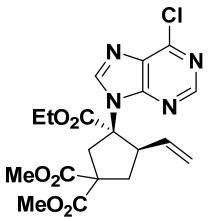


3aa 91% ee **5aa 32% yield, 90% ee**

To a solution of carbocyclic purine nucleoside analogue **3aa** (87.2 mg, 0.2 mmol) in THF/MeOH (1:1) at -10 ºC, $NaBH_4$ (106 mg, 28 mmol) was added. After 1 h, **3aa** was consumed (determined by TLC), water was added to quench the reaction. The aqueous phase was extracted with CH_2Cl_2 and the combined organic phases were dried and concentrated. The residue was purified by silica gel flash chromatography (CH_2Cl_2:MeOH = 15:1) to afford product **5aa** (32%, white solid).

7. The analytical and spectral characterization data for the cycloadducts

(3*R*,4*R*)-3-Ethyl-1,1-dimethyl-3-(6-chloro-9*H*-purin-9-yl)-4-vinylcyclopentane-1,1,3-tricarbo xylate (3aa)

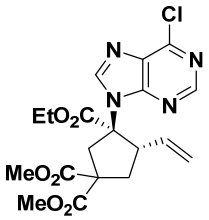


White solid; 66% yield, 91% *ee*.

HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 80/20, flow rate = 0.4 mL/min, colume temperature = 20 ^{o}C, λ = 254 nm, retention time: 24.680 min, 30.983 min.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.68 (s, 1H), 8.34 (s, 1H), 5.63-5.57 (m, 1H), 5.02 (d, *J* = 17.2 Hz, 1H), 4.93 (d, *J* = 10.4 Hz, 1H), 4.23-4.16 (m, 2H), 3.86 (q, *J* = 7.6 Hz, 1H), 3.80 (s, 3H), 3.72 (s, 3H), 3.60 (d, *J* = 14.8 Hz, 1H), 3.40 (d, *J* = 15.2 Hz, 1H), 2.98 (q, *J* = 7.2 Hz, 1H), 2.46 (q, *J* = 5.6 Hz, 1H), 1.13 (t, *J* = 7.2 Hz, 3H). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 171.4, 171.2, 169.2, 152.1, 151.5, 151.2, 144.1, 133.4, 131.4, 119.2, 62.9, 57.2, 53.5, 49.7, 42.2, 37.1, 13.8. **HRMS**: exact mass calcd for $C_{19}H_{21}ClN_4O_6Na$ $(M+Na)^+$ requires m/z 459.1042, found m/z 459.1049.

3-Ethyl-1,1-dimethyl-3-(6-chloro-9*H*-purin-9-yl)-4-vinylcyclopentane-1, 1,3-tricarboxylate (4aa)



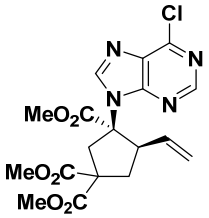
White solid; 33% yield, 90% *ee*.

HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 80/20, flow rate = 0.4 mL/min, colume temperature = 20 ^{o}C, λ = 254 nm, retention time: 23.523 min, 38.401 min.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.69 (s, 1H), 8.36 (s, 1H), 5.82-5.73 (m, 1H), 5.46 (d, *J* = 17.2 Hz, 1H), 5.37 (d, *J* = 10.4 Hz, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 4.01 (d, *J* = 14.8 Hz, 1H), 3.83 (s, 3H), 3.81-3.76 (m, 1H), 3.69 (s, 3H), 2.91 (d, *J* = 15.2 Hz, 1H), 2.77 (t, *J* = 13.2 Hz, 1H), 2.56 (q, *J* =

6.8 Hz, 1H), 1.08 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 172.5, 170.7, 169.0, 152.3, 151.7, 151.2, 142.5, 133.2, 131.6, 120.6, 71.7, 62.7, 57.5, 53.5, 53.2, 50.6, 44.1, 38.1, 13.9. **HRMS**: exact mass calcd for $C_{19}H_{21}ClN_4O_6Na$ $(M+Na)^+$ requires m/z 459.1042, found m/z 459.1034.

Trimethyl-3-(6-chloro-9*H*-purin-9-yl)-4-vinylcyclopentane-1,1,3-tricarboxylate (3ba)

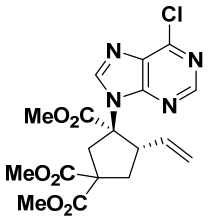


White solid; 50% yield, 88% *ee*.

HPLC CHIRALCEL ASH, *n*-hexane/2-propanol = 80/20, flow rate = 0.6 mL/min, colume temperature = 20 ^oC, λ = 254 nm, retention time: 15.643 min, 24.577 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (s, 1H), 8.35 (s, 1H), 5.64-5.55 (m, 1H), 5.01 (d, *J* = 17.2 Hz, 1H), 4.92 (d, *J* = 10.4 Hz, 1H), 3.87 (q, *J* = 7.6 Hz, 1H), 3.80 (s, 3H), 3.72 (d, *J* = 6.4 Hz, 6H), 3.57 (d, *J* = 15.2 Hz, 1H), 3.40 (d, *J* = 14.8 Hz, 1H), 2.98 (q, *J* = 7.2 Hz, 1H), 2.46 (dd, *J* = 14.4 Hz, 8.4 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 172.5, 169.7, 152.2, 151.8, 151.3, 142.4, 133.1, 120.6, 71.8, 57.6, 53.5, 53.2, 53.2, 50.7, 44.1, 38.1. **HRMS**: exact mass calcd for $C_{18}H_{19}ClN_4O_6Na$ $(M+Na)^+$ requires m/z 445.0885, found m/z 445.0876.

Trimethyl-3-(6-chloro-9*H*-purin-9-yl)-4-vinylcyclopentane-1,1,3-tricarboxylate (4ba)



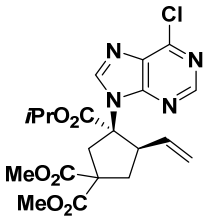
White solid; 49% yield, 77% *ee*.

HPLC CHIRALCEL ASH, *n*-hexane/2-propanol = 80/20, flow rate = 0.6 mL/min, colume temperature = 20 ^oC, λ = 254 nm, retention time: 18.718 min, 24.229 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (s, 1H), 8.38 (s, 1H), 5.80-5.71 (m, 1H), 5.47 (d, *J* = 17.2 Hz, 1H), 5.38 (d, *J* = 10.4 Hz, 1H), 4.00 (d, *J* = 15.2 Hz, 1H), 3.84 (s, 3H), 3.81-3.76 (m, 1H), 3.69 (s,

3H), 3.62 (s, 3H), 2.93 (d, *J* = 15.2 Hz, 1H), 2.77 (t, *J* = 13.2 Hz, 1H), 2.57 (q, *J* = 7.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 172.5, 170.7, 169.7, 152.2, 151.8, 151.3, 142.4, 133.1, 131.7, 120.7, 71.8, 57.6, 53.5, 53.2, 53.2, 50.7, 44.1, 38.1. **HRMS**: exact mass calcd for $C_{18}H_{19}ClN_4O_6Na$ $(M+Na)^+$ requires m/z 445.0885, found m/z 445.0881.

3-Isopropyl-1,1-dimethyl-3-(6-chloro-9*H*-purin-9-yl)-4-vinylcyclopentane-1,1,3-tricarboxylate (3ca)

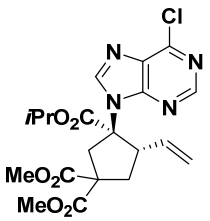


White solid; 71% yield, 86% *ee*.

HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 80/20, flow rate = 0.6 mL/min, colume temperature = 20 ^oC, λ = 254 nm, retention time: 11.916 min, 17.829 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (s, 1H), 8.32 (s, 1H), 5.67-5.58 (m, 1H), 5.11-4.94 (m, 3H), 3.87-3.81 (m, 3H), 3.80 (s, 3H), 3.72 (s, 3H), 3.41 (d, *J* = 15.2 Hz, 1H), 3.38 (d, *J* = 15.2 Hz, 1H), 2.98 (q, *J* = 7.2 Hz, 1H), 2.48 (q, *J* = 5.6 Hz, 1H), 1.16 (d, *J* = 6.4 Hz, 3H), 1.06 (d, *J* = 6.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.4, 171.3, 168.7, 152.2, 151.4, 151.2, 144.2, 133.5, 131.4, 119.1, 72.6, 71.0, 57.3, 53.4, 49.7, 42.1, 37.2, 21.4, 21.3. **HRMS**: exact mass calcd for $C_{20}H_{23}ClN_4O_6Na$ $(M+Na)^+$ requires m/z 473.1198, found m/z 473.1199.

3-Isopropyl-1,1-dimethyl-3-(6-chloro-9*H*-purin-9-yl)-4-vinylcyclopentane-1,1,3-tricarboxylate (4ca)

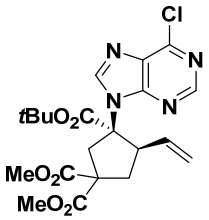


White solid; 28% yield, 76% *ee*.

HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 80/20, flow rate = 0.6 mL/min, colume temperature = 20 ^oC, λ = 254 nm, retention time: 12.659 min, 21.729 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (s, 1H), 8.37 (s, 1H), 5.85-5.76 (m, 1H), 5.47 (d, *J* = 16.8 Hz, 1H), 5.38 (d, *J* = 10.4 Hz, 1H), 5.06-4.99 (m, 1H), 4.01 (d, *J* = 15.2 Hz, 1H), 3.84 (s, 3H), 3.81-3.76 (m, 1H), 3.70 (s, 3H), 2.89 (d, *J* = 15.2 Hz, 1H), 2.78 (t, *J* = 13.2 Hz, 1H), 2.56 (q, *J* = 6.8 Hz, 1H), 1.15 (d, *J* = 6.4 Hz, 3H), 0.97 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 172.6, 170.7, 168.5, 151.7, 142.5, 133.2, 120.6, 71.6, 71.0, 57.5, 53.5, 53.2, 50.6, 44.1, 38.2, 21.6, 21.4. **HRMS**: exact mass calcd for $C_{20}H_{23}ClN_4O_6Na$ $(M+Na)^+$ requires m/z 473.1198, found m/z 473.1197.

3-Tert-butyl-1,1-dimethyl-3-(6-chloro-9*H*-purin-9-yl)-4-vinylcyclopent-ane-1,1,3-tricarboxylate (3da)

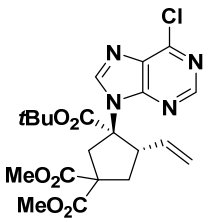


White solid; 66% yield, 69% *ee*.

HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 80/20, flow rate = 0.4 mL/min, colume temperature = 20 ^oC, λ = 254 nm, retention time: 15.374 min, 26.774 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (s, 1H), 8.28 (s, 1H), 5.68-5.60 (m, 1H), 5.03 (d, *J* = 17.2 Hz, 1H), 4.95 (d, *J* = 10.4 Hz, 1H), 3.85-3.81 (m, 1H), 3.80 (s, 3H), 3.70 (s, 3H), 3.61 (d, *J* = 14.8 Hz, 1H), 3.39 (d, *J* = 17.6 Hz, 1H), 2.99 (q, *J* = 6.8 Hz, 1H), 2.47 (q, *J* = 5.6 Hz, 1H), 1.33 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.5, 171.3, 168.1, 152.2, 151.4, 151.1, 144.3, 133.7, 131.3, 119.0, 84.1, 73.1, 57.3, 53.4, 49.7, 42.0, 37.3, 27.6. **HRMS**: exact mass calcd for $C_{21}H_{26}ClN_4O_6(M+H)^+$ requires m/z 465.1535, found m/z 465.1533.

3-Tert-butyl-1,1-dimethyl-3-(6-chloro-9*H*-purin-9-yl)-4-vinylcyclopent-ane-1,1,3-tricarboxylate (4da)

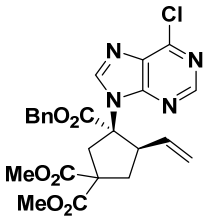


White solid; 33% yield, 73% *ee*.

HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 80/20, flow rate = 0.4 mL/min, colume temperature = 20 ^{o}C, λ = 254 nm, retention time: 15.955 min, 30.072 min.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.70 (s, 1H), 8.35 (s, 1H), 5.90-5.81 (m, 1H), 5.47 (d, *J* = 17.2 Hz, 1H), 5.88 (d, *J* = 10.4 Hz, 1H), 4.99 (d, *J* = 15.2 Hz, 1H), 3.82 (s, 3H), 3.79-3.76 (m, 1H), 3.69 (s, 3H), 2.92 (d, *J* = 15.2 Hz, 1H), 2.78-2.72 (m, 1H), 2.57 (q, *J* = 6.8 Hz, 1H), 1.29 (s, 9H). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 172.6, 170.7, 167.9, 152.4, 151.6, 151.1, 142.7, 133.4, 131.6, 120.4, 84.5, 72.0, 57.6, 53.4, 53.1, 50.6, 44.0, 38.4, 27.7. **HRMS**: exact mass calcd for $C_{21}H_{25}ClN_4O_6Na$ $(M+Na)^+$ requires m/z 487.1355, found m/z 487.1357.

3-Benzyl-1,1-dimethyl-3-(6-chloro-9*H*-purin-9-yl)-4-vinylcyclopentane-1,1,3-tricarboxylate (3ea)

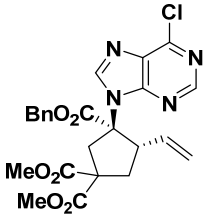


White solid; 64% yield, 70% *ee*.

HPLC CHIRALCEL ASH, *n*-hexane/2-propanol = 70/30, flow rate = 0.6 mL/min, colume temperature = 20 ^{o}C, λ = 254 nm, retention time: 10.989 min, 15.129 min.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.59 (s, 1H), 8.36 (s, 1H), 7.31-7.26 (m, 3H), 7.07 (d, *J* = 7.2 Hz, 2H), 5.66-5.57 (m, 1H), 5.39 (d, *J* = 16.8 Hz, 1H), 5.25 (d, *J* = 10.4 Hz, 1H), 5.06 (d, *J* = 16 Hz, 2H), 4.01 (d, *J* =15.2 Hz, 1H), 3.81-3.77 (m, 1H), 3.75 (s, 3H), 3.68 (s, 3H), 2.92 (d, *J* = 12.4 Hz, 1H), 2.73 (t, *J* = 13 Hz, 1H), 2.53 (q, *J* = 6.8 Hz, 1H). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 172.5, 170.6, 169.0, 152.2, 151.7, 151.2, 142.4, 134.1, 133.0, 131.6, 128.8, 128.6, 128.5, 120.6, 71.8, 68.2, 57.6, 53.4, 53.1, 50.8, 44.0, 38.1. **HRMS**: exact mass calcd for $C_{24}H_{23}ClN_4O_6Na$ $(M+Na)^+$ requires m/z 521.1198, found m/z 521.1195.

3-Benzyl-1,1-dimethyl-3-(6-chloro-9*H*-purin-9-yl)-4-vinylcyclopentane-1,1,3-tricarboxylate (4ea)

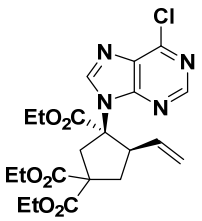


White solid; 35% yield, 72% *ee*.

HPLC CHIRALCEL ASH, *n*-hexane/2-propanol = 80/20, flow rate = 0.6 mL/min, colume temperature = 20 ^{o}C, λ = 254 nm, retention time: 17.932 min, 23.607 min.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.55 (s, 1H), 8.31 (s, 1H), 7.34-7.28 (m, 3H), 7.09 (d, *J* = 6.8 Hz, 2H), 5.62-5.53 (m, 1H), 5.14 (s, 2H), 4.99 (d, *J* = 15.6 Hz, 1H), 4.91 (d, *J* = 10.4 Hz, 1H), 3.88 (q, *J* = 7.6 Hz, 1H), 3.76 (s, 3H), 3.72 (s, 3H), 3.55 (t, *J* = 13.0 Hz, 1H), 3.42 (d, *J* = 15.2 Hz, 1H), 2.97 (q, *J* = 6.8 Hz, 1H), 2.47 (q, *J* = 6.0 Hz, 1H). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 172.5, 170.6, 169.0, 151.7, 142.4, 134.1, 133.0, 131.6, 128.8, 128.6, 128.5, 120.6, 71.8, 68.2, 57.5, 53.4, 53.1, 50.8, 44.0, 38.1. **HRMS**: exact mass calcd for $C_{24}H_{23}ClN_4O_6Na$ $(M+Na)^+$ requires m/z 521.1198, found m/z 521.1196.

Triethyl-3-(6-chloro-9*H*-purin-9-yl)-4-vinylcyclopentane-1,1,3-tricarboxylate (3ab)



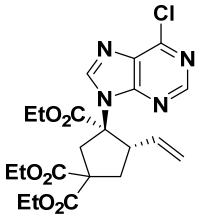
White solid; 62% yield, 90% *ee*.

HPLC CHIRALCEL IA, *n*-hexane/2-propanol = 90/10, flow rate = 0.8 mL/min, colume temperature = 25 ^{o}C, λ = 254 nm, retention time: 18.130 min, 20.995 min.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.69 (s, 1H), 8.39 (s, 1H), 5.68-5.59 (m, 1H), 5.02 (d, *J* = 17.6 Hz, 1H), 4.93 (d, *J* = 10.8 Hz, 1H), 4.29-4.09 (m, 6H), 3.85 (q, *J* = 8.0 Hz, 1H), 3.57 (d, *J* = 15.2 Hz, 1H), 3.37 (d, *J* = 14.8 Hz, 1H), 2.96 (q, *J* = 7.2 Hz, 1H), 2.45 (q, *J* = 5.2 Hz, 1H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.0 Hz, 3H). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 172.1, 170.2, 169.0, 152.3, 151.7, 151.2, 142.6, 133.4, 120.4, 71.9, 62.6, 62.3, 62.0, 57.8, 50.7, 43.9, 38.1,

14.1, 13.9, 13.9. **HRMS**: exact mass calcd for $C_{21}H_{25}ClN_4O_6Na$ $(M+Na)^+$ requires m/z 487.1355, found m/z 487.1362.

Triethyl-3-(6-chloro-9*H*-purin-9-yl)-4-vinylcyclopentane-1,1,3-tricarboxylate (4ab)

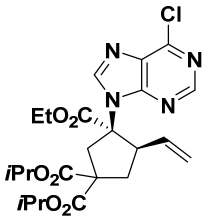


White solid; 27% yield, 89% *ee*.

HPLC CHIRALCEL IA, *n*-hexane/2-propanol = 90/10, flow rate = 0.8 mL/min, colume temperature = 25 ^oC, λ = 254 nm, retention time: 27.139 min, 29.846 min.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.70 (s, 1H), 8.37 (s, 1H), 5.83-5.75 (m, 1H), 5.46 (d, *J* = 17.2 Hz, 1H), 5.37 (d, *J* = 10.0 Hz, 1H), 4.36-4.23 (m, 2H), 4.15-4.10 (m, 4H), 3.96 (d, *J* = 15.2 Hz, 1H), 3.83-3.76 (m, 1H), 2.95 (d, *J* = 14.8 Hz, 1H), 2.79-2.73 (m, H), 2.55 (q, *J* = 6.8 Hz, 1H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H), 1.09 (t, *J* = 7.2 Hz, 3H). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 171.0, 170.8, 169.2, 152.2, 151.5, 144.1, 133.5, 131.4, 119.0, 62.8, 62.4, 62.4, 57.3, 49.7, 42.3, 36.9, 36.9, 14.0, 13.9, 13.8. **HRMS**: exact mass calcd for $C_{21}H_{25}ClN_4O_6Na$ $(M+Na)^+$ requires m/z 487.1355, found m/z 487.1359.

3-Ethyl-1,1-diisopropyl-3-(6-chloro-9*H*-purin-9-yl)-4-vinylcyclopentane-1,1,3-tricarboxylate (3ac)



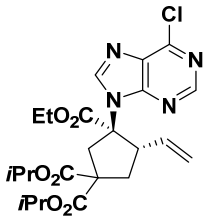
White solid; 70% yield, 91% *ee*.

HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 85/15, flow rate = 0.4 mL/min, colume temperature = 20 ^oC, λ = 254 nm, retention time: 12.602 min, 15.703 min.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.68 (s, 1H), 8.39 (s, 1H), 5.70-5.61 (m, 1H), 5.11-4.93 (m, 4H), 4.23-4.15 (m, 2H), 3.83 (q, *J* = 8.0 Hz, 1H), 3.55 (d, *J* = 15.2 Hz, 1H), 3.32 (d, *J* = 15.2 Hz, 1H),

2.93 (q, *J* = 7.2 Hz, 1H), 2.42 (q, *J* = 5.2 Hz, 1H), 1.27-1.11 (m, 15H). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 170.5, 170.3, 169.2, 156.2, 151.5, 144.1, 133.5, 131.4, 118.9, 83.7, 72.4, 70.1, 70.0, 62.8, 57.4, 49.7, 42.4, 36.8, 29.7, 21.5, 21.5, 21.4, 21.3, 13.8. **HRMS**: exact mass calcd for $C_{23}H_{30}ClN_4O_6$ $(M+H)^+$ requires m/z 493.1848, found m/z 493.1857.

3-Ethyl-1,1-diisopropyl-3-(6-chloro-9*H*-purin-9-yl)-4-vinylcyclopentane-1,1,3-tricarboxylate (4ac)

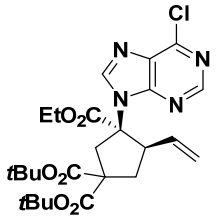


White solid; 19% yield, 74% *ee*.

HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 85/15, flow rate = 0.4 mL/min, colume temperature = 25 ^{o}C, λ = 254 nm, retention time: 13.618 min, 18.725 min.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.70 (s, 1H), 8.36 (s, 1H), 5.84-5.75 (m, 1H), 5.44 (d, *J* = 16.8 Hz, 1H), 5.35 (d, *J* = 10.4 Hz, 1H), 5.16-5.10 (m, 1H), 4.96-4.90 (m, 1H), 4.12 (q, *J* = 6.8 Hz, 2H), 3.88 (d, *J* = 15.2 Hz, 1H), 3.82-3.75 (m, 1H), 2.96 (d, *J* = 15.2 Hz, 1H), 2.72 (t, *J* = 12.8 Hz, 1H), 2.53 (q, *J* = 6.8 Hz, 1H), 1.31-1.27 (m, 6H), 1.19 (d, *J* = 6.4 Hz, 3H), 1.11-1.07 (m, 6H). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 171.6, 169.6, 169.0, 151.7, 151.2, 142.7, 133.5, 131.7, 120.3, 72.1, 70.0, 69.5, 62.6, 57.9, 50.7, 43.7, 38.1, 21.6, 21.5, 21.4, 21.3, 13.9. **HRMS**: exact mass calcd for $C_{23}H_{30}ClN_4O_6$ $(M+H)^+$ requires m/z 493.1848, found m/z 493.1855.

1,1-di-tert-butyl-3-ethyl-3-(6-chloro-9*H*-purin-9-yl)-4-vinylcyclopentane-1,1,3-tricarboxylate (3ad)



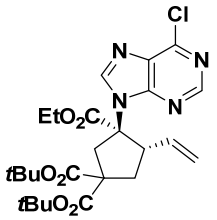
White solid; 41% yield, 90% *ee*.

HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 90/10, flow rate = 0.6 mL/min, colume

temperature = 20 °C, λ = 254 nm, retention time: 7.850 min, 13.807 min.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.68 (s, 1H), 8.40 (s, 1H), 5.71-5.63 (m, 1H), 5.01 (d, *J* = 17.2 Hz, 1H), 4.92 (d, *J* = 10.8 Hz, 1H), 4.24-4.15 (m, 2H), 3.83-3.78 (m, 1H), 3.46 (d, *J* = 15.2 Hz, 1H), 3.23 (d, *J* = 15.2 Hz, 1H), 2.84 (q, *J* = 7.2 Hz, 1H), 2.37 (q, *J* = 4.4 Hz, 1H), 1.47 (s, 9H), 1.37 (s, 9H), 1.12 (q, *J* = 7.0 Hz, 3H). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 170.1, 169.9, 169.2, 151.4, 144.1, 133.7, 131.4, 118.7, 82.6, 82.4, 72.4, 62.7, 58.4, 49.6, 42.5, 36.5, 27.8, 27.6, 13.8. **HRMS**: exact mass calcd for $C_{25}H_{33}ClN_4O_6Na$ $(M+Na)^+$ requires m/z 543.1981, found m/z 543.1979.

1,1-Di-tert-butyl-3-ethyl-3-(6-chloro-9*H*-purin-9-yl)-4-vinylcyclopentane-1,1,3-tricarboxylate (4ad)

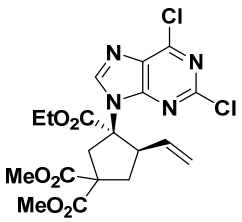


White solid; 57% yield, 45% *ee*.

HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 80/20, flow rate = 0.4 mL/min, colume temperature = 20 °C, λ = 254 nm, retention time: 10.464 min, 13.280 min.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.70 (s, 1H), 8.35 (s, 1H), 5.85-5.76 (m, 1H), 5.42 (d, *J* = 17.2 Hz, 1H), 5.33 (d, *J* = 10.4 Hz, 1H), 4.12 (q, *J* = 6.8 Hz, 2H), 3.81-3.71 (m, 2H), 2.95 (d, *J* = 15.2 Hz, 1H), 2.66 (t, *J* = 12.6 Hz, 1H), 2.49 (q, *J* = 7.2 Hz, 1H), 1.51 (s, 9H), 1.34 (s, 9H), 1.10 (t, *J* = 7.0 Hz, 3H). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 171.3, 169.2, 169.1, 152.3, 151.7, 151.1, 142.7, 133.7, 120.1, 82.5, 81.8, 72.2, 62.5, 59.1, 50.6, 43.5, 38.0, 27.9, 27.6, 14.0. **HRMS**: exact mass calcd for $C_{25}H_{33}ClN_4O_6Na$ $(M+Na)^+$ requires m/z 543.1981, found m/z 543.1987.

3-Ethyl-1,1-dimethyl-3-(2,6-dichloro-9*H*-purin-9-yl)-4-vinylcyclopentane-1,1,3-tricarboxylate (3fa)

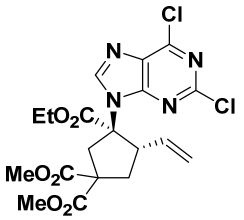


White solid; 69% yield, 71% *ee*.

HPLC CHIRALCEL IA, *n*-hexane/2-propanol = 80/20, flow rate = 0.4 mL/min, colume temperature = 25 ^{o}C, λ = 254 nm, retention time: 21.222 min, 24.781 min.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.32 (s, 1H), 5.68-5.59 (m, 1H), 5.04 (d, *J* = 17.6 Hz, 1H), 4.98 (d, *J* = 10.8 Hz, 1H), 4.28-4.16 (m, 2H), 3.85-3.81 (m, 1H), 3.79 (s, 3H), 3.72 (s, 3H), 3.58 (d, *J* = 15.6 Hz, 1H), 3.36 (d, *J* = 15.6 Hz, 1H), 2.97 (q, *J* = 6.8 Hz, 1H), 2.42 (q, *J* = 5.2 Hz, 1H), 1.18 (t, *J* = 7.2 Hz, 3H). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 171.2, 171.1, 168.8, 153.4, 152.4, 151.9, 144.8, 133.2, 130.5, 119.3, 72.7, 63.1, 57.2, 53.5, 53.5, 49.8, 42.2, 37.0, 13.8 . **HRMS**: exact mass calcd for $C_{19}H_{20}Cl_2N_4O_6Na$ $(M+Na)^+$ requires m/z 493.0652, found m/z 493.0647.

3-Ethyl-1,1-dimethyl-3-(2,6-dichloro-9*H*-purin-9-yl)-4-vinylcyclopentane-1,1,3-tricarboxylat e (4fa)

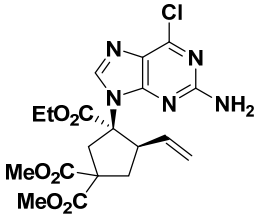


White solid; 30% yield, 69% *ee*.

HPLC CHIRALCEL ADH, *n*-hexane/2-propanol = 80/20, flow rate = 0.6 mL/min, colume temperature =25 ^{o}C, λ = 254 nm, retention time: 16.449 min, 18.982 min.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.36 (s, 1H), 5.80-5.71(m, 1H), 5.47 (d, *J* = 17.2 Hz, 1H), 5.39 (d, *J* = 10.4 Hz, 1H), 4.21-4.11 (m, 2 H), 3.95 (d, *J* = 15.2 Hz, 1H), 3.85 (s, 1H), 3.79-3.74 (m, 1H), 3.71 (s, 3H), 2.93 (d, *J* = 15.2 Hz, 1H), 2.81-2.74 (m, 1H), 2.56 (t, *J* = 6.8 Hz, 1H), 1.13 (t, *J* = 7.2 Hz, 3H). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 172.5, 170.6, 168.7, 153.6, 152.8, 152.0, 143.2, 133.1, 130.8, 120.8, 72.0, 62.9, 57.7, 53.5, 53.2, 50.9, 43.9, 38.3, 29.7, 14.0. **HRMS**: exact mass calcd for $C_{19}H_{20}Cl_2N_4O_6Na$ $(M+Na)^+$ requires m/z 493.0652, found m/z 493.0649.

3-Ethyl-1,1-dimethyl-3-(2-amino-6-chloro-9*H*-purin-9-yl)-4-vinylcyclopentane-1,1,3-tricarboxylate (3ga)

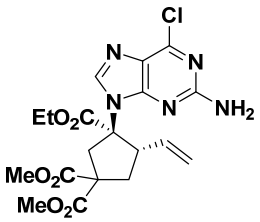


White solid; 48% yield, 81% *ee*.

HPLC CHIRALCEL IA, *n*-hexane/2-propanol = 90/10, flow rate = 0.6 mL/min, colume temperature = 25 ^{o}C, λ = 254 nm, retention time: 60.687 min, 68.897 min.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 7.87 (s, 1H), 5.61-5.52 (m, 1H), 5.17 (s, 2H), 5.05 (d, *J* = 17.2 Hz, 1H), 4.97 (d, *J* = 10.4 Hz, 1H), 4.23-4.15 (m, 2H), 3.77 (s, 3H), 3.72 (s, 3H), 3.52 (d, *J* = 15.2 Hz, 1H), 3.31 (d, *J* = 14.8 Hz, 1H), 2.85 (q, *J* = 7.2 Hz, 1H), 2.57-2.51 (m, 2H), 1.16 (t, *J* = 7.2 Hz, 3H). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 171.5, 171.5, 169.6, 158.5, 154.0, 141.2, 133.6, 118.9, 71.9, 62.6, 57.4, 53.4, 53.3, 49.3, 41.8, 37.2, 13.8. **HRMS**: exact mass calcd for $C_{19}H_{22}ClN_5O_6Na$ $(M+Na)^+$ requires m/z 474.1151, found m/z 474.1149.

3-Ethyl-1,1-dimethyl-3-(2-amino-6-chloro-9*H*-purin-9-yl)-4-vinylcyclopentane-1,1,3-tricarboxylate (4ga)



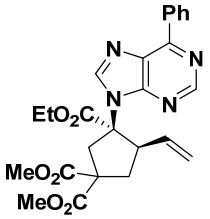
White solid; 32% yield, 72% *ee*.

HPLC CHIRALCEL IA, *n*-hexane/2-propanol = 70/30, flow rate = 0.6 mL/min, colume temperature = 25 ^{o}C, λ = 254 nm, retention time: 17.131 min, 21.379 min.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.01 (s, 1H), 5.80-5.71(m, 1H), 5.42 (d, *J* = 16.8 Hz, 1H), 5.33 (d, *J* = 10.0 Hz, 1H), 5.08 (s, 2H), 4.16-4.07 (m, 2H), 3.95 (d, *J* = 15.2 Hz, 1H), 3.83 (s, 3H), 3.71 (s, 3H), 2.79 (d, *J* = 15.2 Hz, 1H), 2.67 (t, *J* = 13.0 Hz, 1H), 2.59-2.54 (m, 2H), 1.09 (t, *J* = 7.2 Hz, 3H). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 172.6, 171.0, 169.5, 158.6, 154.2, 139.4, 133.4, 128.5, 125.2, 120.2, 71.2, 62.4, 57.6, 52.5, 50.4, 44.0, 38.0, 35.1, 14.0. **HRMS**: exact mass calcd for

$C_{19}H_{22}ClN_5O_6Na$ $(M+Na)^+$ requires m/z 474.1151, found m/z 474.1150.

3-Ethyl-1,1-dimethyl-3-(6-phenyl-9*H*-purin-9-yl)-4-vinylcyclopentane-1,1,3-tricarboxylate (3ha)

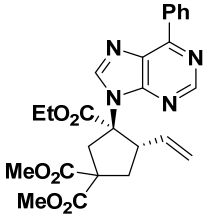


White solid; 36% yield, 91% *ee*.

HPLC CHIRALCEL IA, *n*-hexane/2-propanol = 90/10, flow rate = 0.6 mL/min, colume temperature = 20 ^oC, λ = 254 nm, retention time: 30.916 min, 35.711 min.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.95 (s, 1H), 8.77 (d, *J* = 7.6 Hz, 2H), 8.35 (s, 1H), 7.58-7.52 (m, 3H), 5.71-5.63 (m, 1H), 5.05 (d, *J* = 17.2 Hz, 1H), 4.95 (d, *J* = 10.4 Hz, 1H), 4.26-4.16 (m, 2H), 3.91-3.86 (m, 1H), 3.80 (s, 3H), 3.70 (s, 3H), 3.65 (d, *J* = 15.2 Hz, 1H), 3.43 (d, *J* = 15.2 Hz, 1H), 2.98 (q, *J* = 6.8 Hz, 1H), 2.54 (q, *J* = 5.2 Hz, 1H), 1.13 (t, *J* = 7.2 Hz, 3H). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 171.5, 171.4, 169.7, 154.8, 152.0, 143.1, 133.8, 131.0, 129.7, 128.6, 118.8, 71.9, 70.0, 62.7, 57.3, 53.4, 53.4, 49.7, 42.3, 37.2, 13.9. **HRMS**: exact mass calcd for $C_{25}H_{26}N_4O_6Na$ $(M+Na)^+$ requires m/z 501.1745, found m/z 501.1745.

3-Ethyl-1,1-dimethyl-3-(6-phenyl-9*H*-purin-9-yl)-4-vinylcyclopentane-1,1,3-tricarboxylate (4ha)



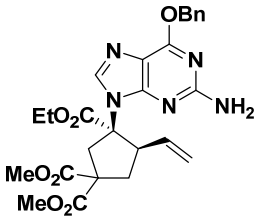
White solid; 57% yield, 80% *ee*.

HPLC CHIRALCEL IA, *n*-hexane/2-propanol = 70/30, flow rate = 0.4 mL/min, colume temperature = 20 ^oC, λ = 254 nm, retention time: 19.065 min, 28.207 min.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.97 (s, 1H), 8.78 (d, *J* = 7.6 Hz, 2H), 8.41 (s, 1H), 7.59-7.53(m, 3H), 5.86-5.77 (m, 1H), 5.48 (d, *J* = 17.2 Hz, 1H), 5.37 (d, *J* = 10.4 Hz, 1H), 4.16-4.08 (m, 3H),

3.88-3.81 (m, 4H), 3.69 (s, 3H), 2.96 (d, *J* = 15.2 Hz, 1H), 2.82-2.76 (m, 1H), 2.61-2.56 (m, 1H), 1.08 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 172.7, 170.9, 169.5, 154.9, 153.0, 152.2, 141.5, 135.6, 133.6, 131.0, 129.7, 128.7, 120.3, 71.3, 62.5, 57.6, 53.4, 53.1, 50.6, 44.2, 38.2, 13.9. **HRMS**: exact mass calcd for $C_{25}H_{27}N_4O_6$ $(M+H)^+$ requires m/z 479.1925, found m/z 479.1925.

3-Ethyl-1,1-dimethyl-3-(2-amino-6-benzyloxy-9*H*-purin-9-yl)-4-vinyl-cyclopentane-1,1,3-tric arboxylate (3ia)

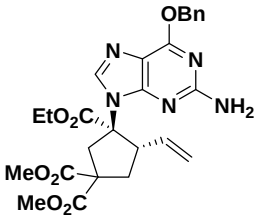


White solid; 46% yield, 76 % *ee*.

HPLC CHIRALCEL ASH, *n*-hexane/2-propanol = 70/30, flow rate = 0.6 mL/min, colume temperature = 20 °C, λ = 254 nm, retention time: 11.894 min, 21.521 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (s, 1H), 7.50 (d, *J* = 7.6 Hz, 2H), 7.37-7.28 (m, 1H), 5.59-5.50 (m, 3H), 5.06 (d, *J* = 17.6 Hz, 1H), 4.95 (d, *J* = 10.4 Hz, 1H), 4.79 (s, 2H), 4.23-4.16 (m, 2H), 3.78-3.73 (m, 7H), 3.55 (d, *J* = 14.8 Hz, 1H), 2.81 (q, *J* = 6.8 Hz, 1H), 2.61 (q, *J* = 4.8 Hz, 1H), 1.17 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.8, 171.6, 170.1, 161.0, 158.6, 154.4, 138.3, 136.4, 134.0, 128.3, 128.3, 127.9, 118.5, 115.4, 71.6, 68.0, 62.4, 57.6, 53.3, 53.2, 49.3, 41.9, 37.4, 13.9. **HRMS**: exact mass calcd for $C_{26}H_{30}N_5O_7$ $(M+H)^+$ requires m/z 524.2140, found m/z 524.2147.

3-Ethyl-1,1-dimethyl-3-(2-amino-6-benzyloxy-9*H*-purin-9-yl)-4-vinyl-cyclopentane-1,1,3-tric arboxylate (4ia)



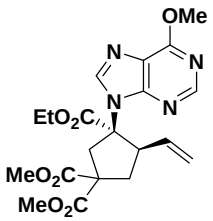
White solid; 24% yield, 68% *ee*.

HPLC CHIRALCEL ASH, *n*-hexane/2-propanol = 70/30, flow rate = 0.6 mL/min, colume

temperature = 20 ^{o}C, λ = 254 nm, retention time: 14.985 min, 25.830 min.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 7.84 (s, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.37-7.30 (m, 1H), 5.83-5.74 (m, 1H), 5.55 (s, 2H), 5.39 (d, *J* = 17.2 Hz, 1H), 5.30 (d, *J* = 10.4 Hz, 1H), 4.79 (s, 2H), 4.14-4.06 (m, 2H), 3.97 (d, *J* = 15.2 Hz, 1H), 3.83 (s, 3H), 3.78-3.72 (m, 1H), 3.68 (s, 3H), 2.76 (d, *J* = 15.2 Hz, 1H), 2.66 (t, *J* = 13.0 Hz, 1H), 2.58-2.53 (m, 1H), 1.08 (t, *J* = 7.0 Hz, 3H). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 172.7, 171.1, 170.0, 161.0, 158.8, 154.7, 136.4, 133.7, 128.4, 128.2, 127.9, 119.7, 100.0, 70.9, 68.0, 62.1, 57.6, 53.3, 53.1, 50.2, 44.2, 37.9, 14.0. **HRMS**: exact mass calcd for $C_{26}H_{30}N_5O_7$ $(M+H)^+$ requires m/z 524.2140, found m/z 524.2146.

3-Ethyl-1,1-dimethyl-3-(6-methoxy-9*H*-purin-9-yl)-4-vinylcyclopentane-1,1,3-tricarboxylate (3ja)

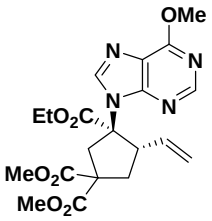


White solid; 50% yield, 68% *ee*.

HPLC CHIRALCEL IA, *n*-hexane/2-propanol = 93/7, flow rate = 0.6 mL/min, colume temperature = 25 ^{o}C, λ = 254 nm, retention time: 60.331 min, 67.486 min.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.47 (s, 1H), 8.10 (s, 1H), 5.63-5.55 (m, 1H), 5.01 (d, *J* = 17.2 Hz, 1H), 4.91 (d, *J* = 10.8 Hz, 1H), 4.23-4.11 (m, 5H), 3.88-3.82 (m, 1H), 3.79 (s, 3H), 3.72 (s, 3H), 3.57 (d, *J* = 14.8 Hz, 1H), 3.37 (d, *J* = 14.8 Hz, 1H), 2.97-2.92 (m, 1H), 2.50 (q, *J* = 5.2 Hz, 1H), 1.11 (t, *J* = 7.0 Hz, 3H). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 171.5, 171.4, 169.8, 161.1, 152.4, 140.9, 133.7, 121.3, 118.7, 71.9, 62.6, 57.3, 54.2, 53.4, 49.5, 42.2, 37.2, 13.8. **HRMS**: exact mass calcd for $C_{20}H_{24}N_4O_7Na$ $(M+Na)^+$ requires m/z 455.1537, found m/z 455.1528.

3-Ethyl-1,1-dimethyl-3-(6-methoxy-9*H*-purin-9-yl)-4-vinylcyclopentane-1,1,3-tricarboxylate (4ja)

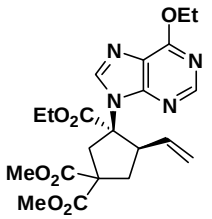


White solid; 49% yield, 77% *ee*.

HPLC CHIRALCEL IA, *n*-hexane/2-propanol = 93/7, flow rate = 0.6 mL/min, colume temperature = 25 ^{o}C, λ = 254 nm, retention time: 52.030 min, 57.844 min.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.48 (s, 1H), 8.16 (s, 1H), 5.82-5.75 (m, 1H), 5.43 (d, *J* = 17.2 Hz, 1H), 5.34 (d, *J* = 10.0 Hz, 1H), 4.17 (s, 3H), 4.13-4.07 (m, 2H), 4.00 (d, *J* = 15.2 Hz, 1H), 3.82 (s, 3H), 3.80-3.75 (m, 1H), 3.67 (s, 3H), 2.89 (d, *J* = 15.2 Hz, 1H), 2.75 (t, *J* = 13.0 Hz, 1H), 2.55 (q, *J* = 6.8 Hz, 1H), 1.06 (t, *J* = 7.0 Hz, 3H). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 172.6, 170.9, 169.5, 161.0, 152.5, 151.8, 139.3, 133.4, 121.5, 120.1, 71.3, 62.3, 57.5, 54.2, 53.3, 53.1, 50.3, 44.2, 38.1, 13.9. **HRMS**: exact mass calcd for $C_{20}H_{24}N_4O_7Na$ $(M+Na)^+$ requires m/z 455.1537, found m/z 455.1530.

3-Ethyl-1,1-dimethyl-3-(6-ethoxy-9*H*-purin-9-yl)-4-vinylcyclopentane-1,1,3-tricarboxylate (3ka)



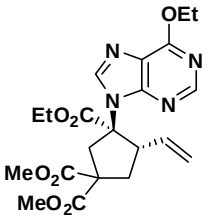
White solid; 39% yield, 71% *ee*.

HPLC CHIRALCEL IA, *n*-hexane/2-propanol = 93/7, flow rate = 0.6 mL/min, colume temperature = 25 ^{o}C, λ = 254 nm, retention time: 43.112 min, 47.126 min.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.44 (s, 1H), 8.08 (s, 1H), 5.62-5.53 (m, 1H), 5.01 (d, *J* = 17.6 Hz, 1H), 4.90 (d, *J* = 10.8 Hz, 1H), 4.64 (q, *J* = 7.2 Hz, 2H), 4.23-4.13 (m, 2H), 3.88-3.79 (m, 1H), 3.79 (s, 3H), 3.72 (s, 3H), 3.57 (d, *J* = 14.8 Hz, 1H), 3.38 (d, *J* = 15.2 Hz, 1H), 2.94 (q, *J* = 6.8 Hz, 1H), 2.51 (q, *J* = 5.6 Hz, 1H), 1.51 (t, *J* = 7.2 Hz, 3H), 1.12 (t, *J* = 7.0 Hz, 3H). ^{13}**C NMR** (100

MHz, $CDCl_3$): δ 171.5, 171.5, 169.8, 160.8, 151.7, 140.7, 133.7, 121.3, 118.7, 95.3, 71.8, 63.1, 62.6, 57.3, 53.4, 49.4, 42.1, 37.2, 14.5, 13.8. **HRMS**: exact mass calcd for $C_{21}H_{26}N_4O_7Na$ $(M+Na)^+$ requires m/z 469.1694, found m/z 469.1695.

3-Ethyl-1,1-dimethyl-3-(6-ethoxy-9*H*-purin-9-yl)-4-vinylcyclopentane-1,1,3-tricarboxylate (4ka)

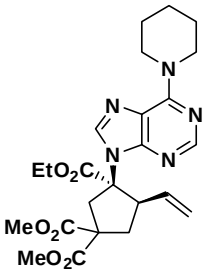


White solid; 38% yield, 53% *ee*.

HPLC CHIRALCEL IA, *n*-hexane/2-propanol = 93/7, flow rate = 0.6 mL/min, colume temperature = 25 ^oC, λ = 254 nm, retention time: 53.803 min, 59.179 min.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.48 (s, 1H), 8.16 (s, 1H), 5.87-5.78 (m, 1H), 5.45 (d, *J* = 17.2 Hz, 1H), 5.36 (d, *J* = 10.4 Hz, 1H), 4.67 (q, *J* = 7.2 Hz, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 4.03 (d, *J* = 15.2 Hz, 1H), 3.85 (s, 3H), 3.83-3.78 (m, 1H), 3.70 (s, 3H), 2.91 (d, *J* = 15.2 Hz, 1H), 2.77 (t, *J* = 13.0 Hz, 1H), 2.58 (q, *J* = 6.8 Hz, 1H), 1.53 (t, *J* = 7.2 Hz, 1H), 1.09 (t, *J* = 7.2 Hz, 3H). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 172.6, 170.9, 169.5, 160.8, 152.6, 151.9, 139.2, 133.5, 121.6, 120.1, 71.4, 63.1, 62.3, 57.6, 53.3, 53.1, 50.3, 44.2, 38.1, 14.5, 13.9. **HRMS**: exact mass calcd for $C_{21}H_{27}N_4O_7$ $(M+H)^+$ requires m/z 469.1694, found m/z 469.1693.

3-Ethyl-1,1-dimethyl-3-[6-(piperidin-1-yl)-9*H*-purin-9-yl]-4-vinylcyclo-pentane-1,1,3-tricarb oxylate (3la)



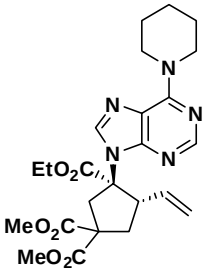
White solid; 50% yield, 77% *ee*.

HPLC CHIRALCEL IA, *n*-hexane/2-propanol = 75/25, flow rate = 0.4 mL/min, colume

temperature = 25 ^{o}C, λ = 254 nm, retention time: 22.406 min, 23.444 min.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.23 (s, 1H), 7.92 (s, 1H), 5.67-5.58 (m, 1H), 5.04 (d, *J* = 17.2 Hz, 1H), 4.93 (d, *J* = 10.4 Hz, 1H), 4.20-4.10 (m, 6H), 3.83-3.79 (m, 1H), 3.77 (s, 3H), 3.69 (s, 3H), 3.50 (d, *J* = 15.2 Hz, 1H), 3.13 (d, *J* = 14.8 Hz, 1H), 2.92 (q, *J* = 6.8 Hz, 1H), 2.51 (q, *J* = 5.6 Hz, 1H), 1.70 (s, 6H), 1.12 (t, *J* = 7.2 Hz, 3H). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 171.5, 170.1, 153.8, 152.0, 151.2, 136.5, 134.0, 119.5, 118.2, 71.3, 62.4, 57.2, 53.3, 53.3, 49.3, 42.3, 37.2, 26.0, 24.8, 13.8. **HRMS**: exact mass calcd for $C_{24}H_{32}N_5O_6$ $(M+H)^+$ requires m/z 486.2347, found m/z 486.2352.

3-Ethyl-1,1-dimethyl-3-[6-(piperidin-1-yl)-9H-purin-9-yl]-4-vinylcyclo-pentane-1,1,3-tricarb oxylate (4la)

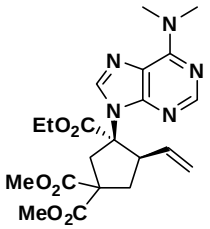


White solid; 49% yield, 56% *ee*.

HPLC CHIRALCEL IA, *n*-hexane/2-propanol = 70/30, flow rate = 0.6 mL/min, colume temperature = 25 ^{o}C, λ = 254 nm, retention time: 12.121 min, 16.718 min.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.26 (s, 1H), 7.99 (s, 1H), 5.83-5.74 (m, 1H), 5.40 (d, *J* = 17.2 Hz, 1H), 5.30 (d, *J* = 10.4 Hz, 1H), 4.22-4.08(m, 6H), 4.00 (d, *J* = 15.2 Hz, 1H), 3.82 (s, 3H), 3.78-3.71 (m, 1H), 3.68 (s, 3H), 2.83 (d, *J* = 15.2 Hz, 1H), 2.73 (t, *J* = 13.0 Hz, 1H), 2.51 (q, *J* = 7.2 Hz, 1H), 1.71-1.69 (m, 6H), 1.08 (t, *J* = 7.0 Hz, 3H). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 172.8, 171.1, 169.8, 153.8, 152.2, 151.4, 135.0, 133.8, 119.7, 70.8, 62.2, 57.5, 53.3, 53.1, 50.1, 44.2, 38.0, 26.1, 24.8, 14.0. **HRMS**: exact mass calcd for $C_{24}H_{32}N_5O_6$ $(M+H)^+$ requires m/z 486.2347, found m/z 486.2354.

3-Ethyl-1,1-dimethyl-3-(6-dimethylamino-9*H*-purin-9-yl)-4-vinylcyclo-pentane-1,1,3-tricarb oxylate (3ma)

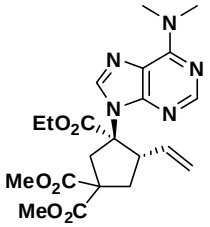


White solid; 58% yield, 69% *ee*.

HPLC CHIRALCEL IA, *n*-hexane/2-propanol = 80/20, flow rate = 0.4 mL/min, colume temperature = 20 ^{o}C, λ = 254 nm, retention time: 23.334 min, 34.212 min.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.26 (s, 1H), 7.92 (s, 1H), 5.67-5.59 (m, 1H), 5.03 (d, *J* = 17.2 Hz, 1H), 4.92 (d, *J* = 10.8 Hz, 1H), 4.22-4.12 (m, 2H), 3.84-3.81 (m, 1H), 3.78 (s, 3H), 3.70 (s, 3H), 3.53-3.50 (m, 6H), 3.32 (d, *J* = 14.8 Hz, 2H), 2.94 (q, *J* = 6.8 Hz, 1H), 2.52 (q, *J* = 5.6 Hz, 1H), 1.11 (t, *J* = 7.0 Hz, 3H). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 171.6, 171.6, 170.1, 154.8, 152.0, 151.0, 136.7, 134.1, 119.9, 118.2, 71.4, 62.4, 57.3, 53.3, 53.3, 49.3, 42.3, 37.2, 13.8. **HRMS**: exact mass calcd for $C_{21}H_{28}N_5O_6$ $(M+H)^+$ requires m/z 446.2034, found m/z 446.2037.

3-Ethyl-1,1-dimethyl-3-(6-dimethylamino-9*H*-purin-9-yl)-4-vinylcyclo-pentane-1,1,3-tricarb oxylate (4ma)



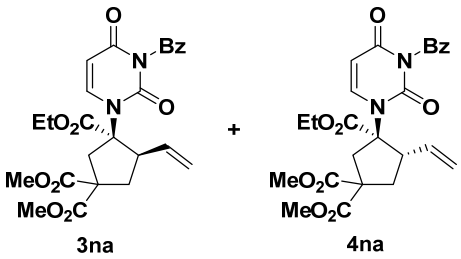
White solid; 38% yield, 46% *ee*.

HPLC CHIRALCEL IA, *n*-hexane/2-propanol = 80/20, flow rate = 0.4 mL/min, colume temperature = 20 ^{o}C, λ = 254 nm, retention time: 23.735 min, 45.933 min.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.28 (s, 1H), 7.99 (s, 1H), 5.83-5.75 (m, 1H), 5.40 (d, *J* = 17.2 Hz, 1H), 5.31 (d, *J* = 10.4 Hz, 1H), 4.14-4.07 (m, 2H), 4.00 (d, *J* = 15.2 Hz, 1H), 3.82 (s, 3H), 3.78-3.72 (m, 1H), 3.68 (s, 3H), 3.53 (s, 6H), 2.85 (d, *J* = 15.6 Hz, 1H), 2.74 (t, *J* = 13.2 Hz, 1H), 2.52 (q, *J* = 6.8 Hz, 1H), 1.08 (t, *J* = 7.0 Hz, 3H). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 172.8, 171.1, 169.8, 154.9, 152.2, 151.2, 135.3, 133.8, 120.2, 119.7, 70.9, 62.2, 57.6, 53.3, 53.1, 50.1, 44.2, 38.0,

14.0. **HRMS**: exact mass calcd for $C_{21}H_{28}N_5O_6$ $(M+H)^+$ requires m/z 446.2034, found m/z 446.2039.

3-Ethyl-1,1-dimethyl-3-(3-benzoyl-2,4-dioxo-3,4-dihydropyrimidin-1(2*H*)-yl)-4-vinylcyclopentane-1,1,3-tricarboxylate (3na+4na)

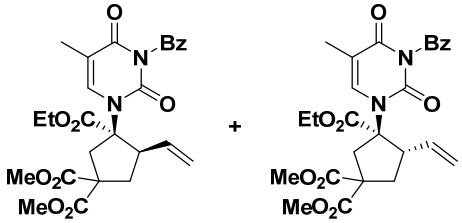


White solid; 97% yield, **3na**/**4na** = 1.5:1, 76% *ee* (**3na**), 86% *ee* (**4na**).

HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 80/20, flow rate = 0.6 mL/min, colume temperature = 25 ^oC, λ = 254 nm, retention time: 45.495 min, 61.632 min, 93.477 min, 111.001 min.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 7.92-7.87 (m, $3H_{3na}$ + $2H_{4na}$), 7.66-7.61 (m, $3H_{3na}$ + $1H_{4na}$), 7.54 (d, *J* = 8.4 Hz, $1H_{4na}$), 7.50-7.44 (m, $3H_{3na}$ + $2H_{4na}$), 5.82-5.77 (m, $1.5H_{3na}$ + $1H_{4na}$), 5.75-5.59 (m, $1.5H_{3na}$ + $1H_{4na}$), 5.39-5.32 (m, $3H_{3na}$), 5.18-5.08 (m, $2H_{4na}$), 4.20-4.07 (m, $3H_{3na}$ + $2H_{4na}$), 3.78-3.74 (m, $9H_{3na}$ + $6H_{4na}$ + $1.5H_{3na}$ + $1H_{4na}$), 3.45-3.38 (m, $1.5H_{3na}$), 3.18-3.08 (m, $2H_{4na}$), 2.99 (d, *J* = 14.0 Hz, $1H_{4na}$), 2.69-2.61 (m, $3H_{3na}$), 2.41-2.36 (m, $1.5H_{3na}$ + $1H_{4na}$), 1.24-1.17 (m, $4.5H_{3na}$ + $3H_{4na}$). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 173.0, 172.0, 170.9, 170.7, 169.7, 169.1, 168.1, 168.0, 161.7, 161.6, 150.5, 149.8, 141.1, 140.0, 135.1, 134.6, 133.0, 131.2, 130.5, 130.4, 129.1, 129.0, 120.2, 118.7, 101.4, 101.3, 73.8, 73.3, 62.5, 62.5, 56.7, 56.4, 53.6, 53.4, 53.3, 52.9, 48.3, 48.2, 44.2, 40.8, 37.8, 13.9, 13.8. **HRMS**: exact mass calcd for $C_{25}H_{26}N_2O_9Na$ $(M+Na)^+$ requires m/z 521.1531, found m/z 521.1535.

3-Ethyl-1,1-dimethyl-3-(3-benzoyl-5-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2*H*)-yl)-4-vinylcyclopentane-1,1,3-tricarboxylate (3oa+4oa)



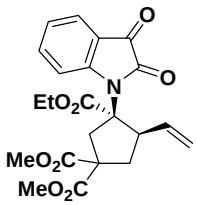
3oa 4oa

White solid; 94% yield, **3oa**/**4oa** = 2:1, 69% *ee* (**3oa**), 68% *ee* (**4oa**).

HPLC CHIRALCEL IA, *n*-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min, colume temperature = 25 ^{o}C, λ = 254 nm, retention time: 12.946 min, 14.685 min, 16.300 min, 51.016 min.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 7.91-7.86 (m, $4H_{3oa}$ + $2H_{4oa}$), 7.65-7.61 (m, $2H_{3oa}$ + $1H_{4oa}$), 7.50-7.44 (m, $4H_{3oa}$ + $2H_{3oa}$ + $2H_{4oa}$), 7.36 (s, $1H_{4oa}$), 5.74-5.63 (m, $2H_{3oa}$ + $1H_{4oa}$), 5.41-5.33 (m, $4H_{3oa}$), 5.15-5.07 (m, $2H_{4oa}$), 4.19-4.07 (m, $4H_{3oa}$ + $2H_{4oa}$), 3.81-3.74 (m, $12H_{3oa}$ + $6H_{4oa}$ + $2H_{3oa}$ + $1H_{4oa}$), 3.47-3.41 (m, $2H_{3oa}$), 3.18-3.08 (m, $2H_{3oa}$), 3.00 (d, *J* = 14.0 Hz, $1H_{4oa}$), 2.69-2.59 (m, $2H_{3oa}$ + $1H_{4oa}$ + $1H_{4oa}$), 2.41-2.35 (m, $2H_{3oa}$ + $1H_{4oa}$), 1.99-1.97 (m, $6H_{3oa}$ + $3H_{4oa}$), 1.23-1.17 (m, $6H_{3oa}$ + $3H_{4oa}$). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 173.2, 172.2, 170.9, 170.8, 170.0, 169.3, 168.4, 162.4, 150.5, 149.8, 137.0, 135.9, 135.0, 134.9, 133.4, 131.4, 130.5, 129.1, 128.9, 120.0, 118.4, 109.8, 73.6, 73.1, 62.5, 62.4, 56.7, 56.4, 53.6, 53.4, 53.3, 52.9, 48.3, 48.2, 44.3, 40.8, 37.9, 37.8, 14.0, 13.9, 12.9, 12.8. **HRMS**: exact mass calcd for $C_{26}H_{28}N_2O_9Na$ $(M+Na)^+$ requires m/z 535.1687, found m/z 535.1687.

3-Ethyl-1,1-dimethyl-3-(2,3-dioxoindolin-1-yl)-4-vinylcyclopentane-1,1,3-tricarboxylate (3pa)

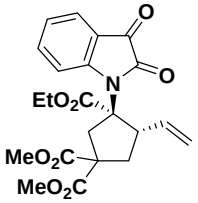


White solid; 50% yield, 92% *ee*.

HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 90/10, flow rate = 0.8 mL/min, colume temperature = 20 ^{o}C, λ = 254 nm, retention time: 22.931 min, 32.641 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (s, 1H), 7.92 (s, 1H), 5.67-5.59 (m, 1H), 5.03 (d, *J* = 17.2 Hz, 1H), 4.92 (d, *J* = 10.8 Hz, 1H), 4.22-4.12 (m, 2H), 3.84-3.81 (m, 1H), 3.78 (s, 3H), 3.70 (s, 3H), 3.53-3.50 (m, 6H), 3.32 (d, *J* = 14.8 Hz, 2H), 2.94 (q, *J* = 6.8 Hz, 1H), 2.52 (q, *J* = 5.6 Hz, 1H), 1.11 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 182.1, 171.9, 171.8, 170.8, 158.6, 151.6, 137.8, 134.9, 125.3, 123.9, 118.6, 117.9, 113.0, 73.0, 62.6, 57.3, 53.3, 49.0, 40.2, 37.8, 30.9, 13.8. **HRMS**: exact mass calcd for $C_{22}H_{23}NO_8Na$ $(M+Na)^+$ requires m/z 452.1316, found m/z 452.1312.

3-Ethyl-1,1-dimethyl-3-(2,3-dioxoindolin-1-yl)-4-vinylcyclo-pentane-1,1,3-tricarboxylate (4pa)

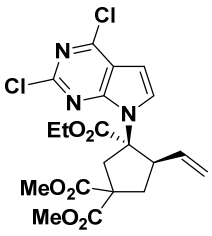


White solid; 25% yield, 71% *ee*.

HPLC CHIRALCEL IA, *n*-hexane/2-propanol = 80/20, flow rate = 0.4 mL/min, colume temperature = 20 ^oC, λ = 254 nm, retention time: 20.850 min, 27.037 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68-7.65 (m, 1H), 7.55- 7.51(m, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.05-5.96 (m, 1H), 5.21-5.13 (m, 2H), 4.80-4.74 (m, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 3.68 (s, 3H), 3.45 (d, *J* = 14.8 Hz, 1H), 2.89 (d, *J* = 14.4 Hz, 1H), 2.61 (d, *J* = 8.8 Hz, 1H), 1.09 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 182.4, 171.9, 171.1, 169.9, 157.2, 151.7, 137.8, 135.1, 125.4, 123.9, 117.9, 117.3, 112.6, 73.7, 62.3, 57.8, 53.3, 53.1, 45.9, 42.0, 36.3, 14.0. **HRMS**: exact mass calcd for $C_{22}H_{23}NO_8Na$ $(M+Na)^+$ requires m/z 452.1316, found m/z 452.1314.

3-Ethyl-1,1-dimethyl-3-(2,4-dichloro-1*H*-pyrrolo[2,3-*d*]pyrimidin-1-yl)-4-vinylcyclopentane-1,1,3-tricarboxylate (3qa)

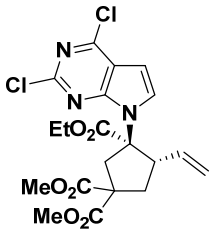


White solid; 69% yield, 80% *ee*.

HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 80/20, flow rate = 0.6 mL/min, colume temperature = 20 ^{o}C, λ = 254 nm, retention time: 10.654 min, 13.257 min.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 4.0 Hz, 1H), 6.56 (d, *J* = 3.6 Hz, 1H), 5.61-5.53 (m, 1H), 4.95 (d, *J* = 17.2 Hz, 1H), 4.84 (d, *J* = 10.4 Hz, 1H), 4.24-4.15 (m, 2H), 3.87 (q, *J* = 7.6 Hz, 1H), 3.79 (s, 3H), 3.73 (s, 3H), 3.46 (d, *J* = 15.2 Hz, 1H), 3.31 (d, *J* = 15.2 Hz, 1H), 2.96 (q, *J* = 6.8 Hz, 1H), 2.46 (q, *J* = 6.0 Hz, 1H), 1.16 (t, *J* = 7.0 Hz, 3H). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 171.7, 171.4, 170.0, 152.6, 134.0, 128.8,118.1, 116.5, 99.8, 72.5, 62.6, 57.2, 53.4, 53.4, 49.5, 42.6, 37.4, 13.9. **HRMS**: exact mass calcd for $C_{20}H_{22}Cl_2N_3O_6$ $(M+H)^+$ requires m/z 470.0880, found m/z 470.0880.

3-Ethyl-1,1-dimethyl-3-(2,4-dichloro-1*H*-pyrrolo[2,3-*d*]pyrimidin-1-yl)-4-vinylcyclopentane-1,1,3-tricarboxylate (4qa)

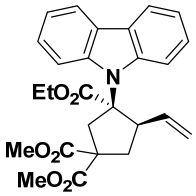


White solid; 30% yield, 70% *ee*.

HPLC CHIRALCEL ASH, *n*-hexane/2-propanol = 85/15, flow rate = 0.6 mL/min, colume temperature = 20 ^{o}C, λ = 254 nm, retention time: 11.886 min, 13.871 min.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 4.0 Hz, 1H), 6.59 (d, *J* = 3.6 Hz, 1H), 5.82-5.74 (m, 1H), 5.41 (d, *J* = 17.2 Hz, 1H), 5.32 (d, *J* = 10.4 Hz, 1H), 4.17-4.07 (m, 2H), 4.00 (d, *J* = 14.8 Hz, 1H), 3.84 (s, 3H), 3.75-3.69 (m, 4H), 2.83-2.70 (m, 2H), 2.53 (q, *J* = 6.8 Hz, 1H), 1.10 (t, *J* = 7.2 Hz, 3H). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 172.8, 170.9, 169.7, 152.7, 133.7, 127.2, 119.7, 116.8, 99.8, 71.9, 62.3, 57.6, 53.3, 53.1, 50.2, 44.6, 37.9, 14.0. **HRMS**: exact mass calcd for $C_{20}H_{22}Cl_2N_3O_6$ $(M+H)^+$ requires m/z 470.0880, found m/z 470.0879.

3-Ethyl-1,1-dimethyl-3-(9*H*-carbazol-9-yl)-4-vinylcyclopentane-1,1,3-tricarboxylate (3ra)

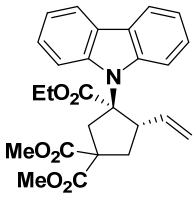


White solid; 22% yield, 75% *ee*.

HPLC CHIRALCEL IA, *n*-hexane/2-propanol = 95/5, flow rate = 0.4 mL/min, colume temperature = 20 ^{o}C, λ = 254 nm, retention time: 20.857 min, 23.215 min.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 7.6 Hz, 2H), 7.45-7.36 (m, 4H), 7.24-7.22 (m, 2H), 6.42-6.35 (m, 1H), 6.32-5.27 (m, 2H), 4.69-4.68 (m, 1H), 4.09-4.01 (m, 3H), 3.85 (s, 3H), 3.56 (s, 3H), 2.85- 2.80(m, 1H), 2.70-2.62 (m, 2H), 0.95 (t, *J* = 7.0 Hz, 3H). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 172.5, 172.0, 171.4, 140.3, 135.1, 125.9, 124.3, 120.0, 119.5, 117.7, 112.0, 75.3, 61.8, 57.0, 53.1, 53.1, 46.7, 44.7, 36.0, 13.9. **HRMS**: exact mass calcd for $C_{26}H_{27}NO_6Na$ $(M+Na)^+$ requires m/z 472.1731, found m/z 472.1734.

3-Ethyl-1,1-dimethyl-3-(9*H*-carbazol-9-yl)-4-vinylcyclopentane-1,1,3-tricarboxylate (4ra)

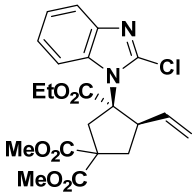


White solid; 8% yield, 87% *ee*.

HPLC CHIRALCEL IA, *n*-hexane/2-propanol = 95/5, flow rate = 0.4 mL/min, colume temperature = 20 ^{o}C, λ = 254 nm, retention time: 19.174 min, 21.113 min.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.0 Hz, 2H), 7.44-7.36 (m, 4H), 7.24-7.22 (m, 2H), 6.42-6.34 (m, 1H), 5.31-5.27 (m, 2H), 4.70-4.67 (m, 1H), 4.09-4.01 (m, 3H), 3.85 (s, 3H), 3.56 (s, 3H), 2.84-2.79 (m, 1H), 2.70-2.62 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 172.5, 172.0, 171.4, 140.3, 135.1, 125.9, 124.3, 120.0, 119.5, 117.7, 112.0, 75.2, 61.8, 57.0, 53.1, 53.1, 46.7, 44.7, 36.0, 13.9. **HRMS**: exact mass calcd for $C_{26}H_{27}NO_6Na$ $(M+Na)^+$ requires m/z 472.1731, found m/z 472.1731.

3-Ethyl-1,1-dimethyl-3-(2-chloro-1*H*-benzo[*d*]imidazol-1-yl)-4-vinylcyclopentane-1,1,3-tricar boxylate (3sa)

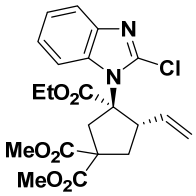


White solid; 32% yield, 83% *ee*.

HPLC CHIRALCEL ASH, *n*-hexane/2-propanol = 80/20, flow rate = 0.6 mL/min, colume temperature = 20 ^{o}C, λ = 254 nm, retention time: 8.716 min, 16.235 min.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 7.67-7.58 (m, 2H), 7.28-7.23 (m, 2H), 5.49-5.40 (m, 1H), 5.12 (s, 1H), 4.84 (d, *J* = 10.4 Hz, 1H), 4.19-4.09 (m, 3H), 3.81-3.77 (m, 8H), 3.19 (s, 1H), 2.52 (d, *J* = 14.4 Hz, 1H), 1.13 (t, *J* = 6.2 Hz, 3H). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 172.0, 171.1, 141.8, 134.5, 123.4, 122.7, 119.9, 118.7, 112.4, 74.7, 62.7, 57.2, 53.6, 53.3, 41.4, 41.1, 41.4, 13.8. **HRMS**: exact mass calcd for $C_{21}H_{23}ClN_2O_6Na$ $(M+Na)^+$ requires m/z 457.1137, found m/z 457.1138.

3-Ethyl-1,1-dimethyl-3-(2-chloro-1*H*-benzo[*d*]imidazol-1-yl)-4-vinylcyclopentane-1,1,3-tricar boxylate (4sa)

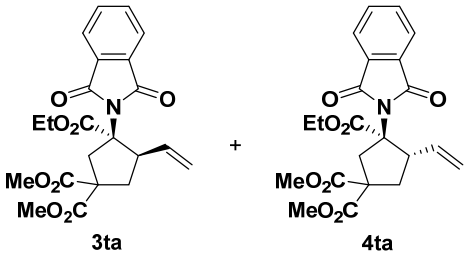


White solid; 63% yield, 78% *ee*.

HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 80/20, flow rate = 0.6 mL/min, colume temperature = 20 ^{o}C, λ = 254 nm, retention time: 13.519 min, 15.608 min.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 7.72-7.70 (m, 1H), 7.51-7.49 (m, 1H), 7.30-7.24 (m, 2H), 6.23-6.15 (m, 1H), 5.29-5.24 (m, 2H), 4.56-4.50 (m, 1H), 4.16-4.08 (m, 2H), 3.98 (d, *J* = 14.8 Hz, 1H), 3.83 (s, 3H), 3.67 (s, 3H), 2.73-2.63 (m, 3H), 1.13 (t, *J* = 7.0 Hz, 3H). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 172.5, 170.8, 170.0, 142.1, 141.3, 134.7, 133.7, 123.7, 122.6, 120.1, 118.3, 112.5, 75.2, 62.4, 56.9, 53.4, 53.1, 46.1, 45.5, 35.5, 13.9. **HRMS**: exact mass calcd for $C_{21}H_{23}ClN_2O_6Na$ $(M+Na)^+$ requires m/z 457.1137, found m/z 457.1137.

3-Ethyl-1,1-dimethyl-3-(1,3-dioxoisoindolin-2-yl)-4-vinylcyclopentane-1,1,3-tricarboxylate (3ta+4ta)

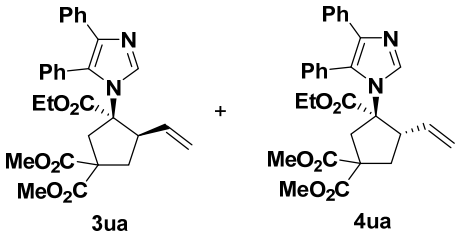


White solid; 99% yield, **3ta**/**4ta** = 2:1, 62% *ee* (**3ta**), 58% *ee* (**4ta**) .

HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 80/20, flow rate = 0.4 mL/min, colume temperature = 20 ^{o}C, λ = 254 nm, retention time: 17.952 min, 19.671 min, 22.010 min, 38.727 min.

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 7.78-7.66 (m, $8H_{3ta}$ + $4H_{4ta}$), 5.99-5.91 (m, $2H_{3ta}$), 5.81-5.72 (m, $1H_{4ta}$), 5.15-5.06 (m, $4H_{3ta}$), 4.97 (d, *J* = 17.2 Hz, $1H_{4ta}$), 4.87 (d, *J* = 10.4 Hz, $1H_{4ta}$), 4.56-4.49 (m, $2H_{4ta}$), 4.23-4.11 (m, $2H_{3ta}$), 4.07 (q, *J* = 6.8 Hz, $4H_{3ta}$), 3.77 (s, $3H_{4ta}$), 3.73-3.68 (m, $3H_{4ta}$ + $6H_{3ta}$ + $1H_{4ta}$ + $1H_{4ta}$), 3.65 (s, $6H_{3ta}$), 3.53 (d, *J* = 14.8 Hz, $3H_{3ta}$), 3.15 (d, *J* = 15.6 Hz, $1H_{4ta}$), 2.80 (d, *J* = 14.8 Hz, $2H_{3ta}$), 2.65-2.51 (m, $2H_{3ta}$ + $1H_{4ta}$ + $1H_{4ta}$), 2.46-2.41 (m, $2H_{3ta}$), 1.18 (t, *J* = 7.2 Hz, $3H_{4ta}$), 1.12 (t, *J* = 7.2 Hz, $6H_{3ta}$). ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 172.4, 172.0, 171.8, 171.1, 170.4, 169.6, 168.3, 168.2, 135.2, 135.0, 134.1, 131.4, 131.1, 123.1, 123.1, 117.1, 116.7, 71.5, 70.5, 61.8, 61.7, 57.7, 57.2, 53.0, 52.9, 52.8, 48.9, 44.5, 43.7, 39.9, 37.1, 36.0, 13.9, 13.8. **HRMS**: exact mass calcd for $C_{22}H_{23}NO_8Na$ $(M+Na)^+$ requires m/z 452.1316, found m/z 452.1315.

3-Ethyl-1,1-dimethyl-3-(4,5-diphenyl-1*H*-imidazol-1-yl)-4-vinylcyclopentane-1,1,3-tricarboxylate (3ua+4ua)



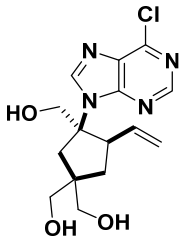
White solid; 98% yield, **3ua**/**4ua** = 1.6:1, 52% *ee* (**3ua**), 58% *ee* (**4ua**).

HPLC CHIRALCEL IA, *n*-hexane/2-propanol = 70/30, flow rate = 0.4 mL/min, colume temperature = 20 ^{o}C, λ = 254 nm, retention time: 26.270 min, 28.672 min, 30.383 min, 35.644

min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (s, $1H_{4ua}$), 7.79 (s, $1.6H_{3ua}$), 7.46-7.34 (m, $8H_{3ua}$ + $5H_{4ua}$), 7.29-7.26 (m, $3.2H_{3ua}$ + $2H_{4ua}$), 7.16-7.09 (m, $4.8H_{3ua}$ + $3H_{4ua}$), 5.88-5.79 (m, $1H_{4ua}$), 5.76-5.67 (m, $1.6H_{3ua}$), 5.39-5.30 (m, $2H_{4ua}$), 5.21-5.15 (m, $3.2H_{3ua}$), 4.12-3.93 (m, $3.2H_{3ua}$ + $2H_{4ua}$), 3.78-3.73 (m, $1H_{4ua}$), 3.71 (s, $4.8H_{3ua}$ + $3H_{4ua}$), 3.67 (s, $4.8H_{3ua}$ + $3H_{4ua}$), 3.24 (s, $1.6H_{3ua}$), 3.10 (s, $1.6H_{3ua}$ + $1H_{4ua}$), 2.89 (q, J = 6.8 Hz, $1.6H_{3ua}$), 2.80 (d, J = 14.8 Hz, $1H_{4ua}$), 2.58-2.54 (m, $3.2H_{3ua}$), 2.43 (d, J = 1.2 Hz, $2H_{4ua}$), 1.21-1.14 (m, $3H_{3ua}$ + $4.8H_{4ua}$). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 172.6, 171.4, 171.3, 170.8, 170.4, 169.9, 139.3, 135.9, 135.0, 134.6, 134.3, 134.2, 134.0, 132.4, 132.3, 130.5, 129.4, 129.3, 128.8, 128.6, 128.2, 128.0, 127.9, 126.4, 126.4, 126.3, 119.4, 118.4, 72.0, 71.8, 62.4, 62.1, 57.2, 56.5, 53.4, 53.1, 52.8, 51.2, 48.5, 45.1, 42.0, 37.4, 37.3, 13.9, 13.6. **HRMS**: exact mass calcd for $C_{29}H_{30}N_2O_6Na$ $(M+Na)^+$ requires m/z 525.1996, found m/z 525.1991.

((*3R,4R*)-3-(6-Chloro-9*H*-purin-9-yl)-4-vinylcyclopentane-1,1,3-triyl)trimethanol (5aa)



White solid; 32% yield, 90% *ee*.

HPLC CHIRALCEL ASH, *n*-hexane/2-propanol = 80/20, flow rate = 0.40 mL/min, colume temperature = 25 ^oC, λ = 254 nm, retention time: 14.021 min, 16.107 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (s, 1H), 8.62 (s, 1H), 5.63-5.54 (m, 1H), 5.09 (t, J = 5.8 Hz, 1H), 4.91 (d, J = 16.8 Hz, 1H), 4.77 (t, J = 5.2 Hz, 1H), 4.73 (t, J = 5.2 Hz, 1H), 4.69 (d, J = 10.4 Hz, 1H), 4.21 (q, J = 6.0 Hz, 1H), 3.73 (q, J = 6.0 Hz, 1H), 3.50-3.38 (m, 3H), 3.32-3.28 (m, 2H), 2.38 (s, 2H), 1.84 (q, J = 6.4 Hz, 1H), 1.72 (q, J = 8.4 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 152.2, 150.4, 148.9, 147.6, 137.6, 131.2, 116.3, 73.5, 65.7, 65.2, 64.0, 48.4, 46.8, 36.9, 35.1. **HRMS**: exact mass calcd for $C_{15}H_{19}ClN_4O_3Na$ $(M+Na)^+$ requires m/z 361.1038, found m/z 361.1041.

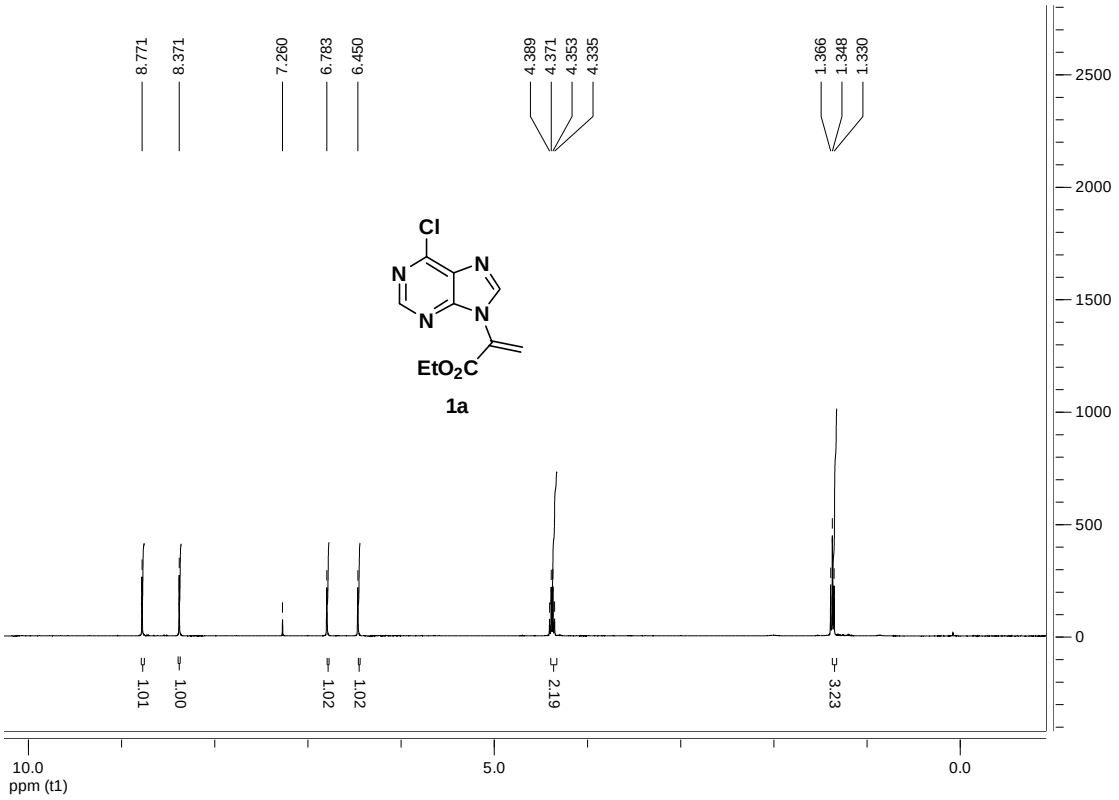
8. References

[1] A. T. Parsons, M. J. Campbell and J. S. Johnson, *Org. Lett.*, 2008, **10**, 2541

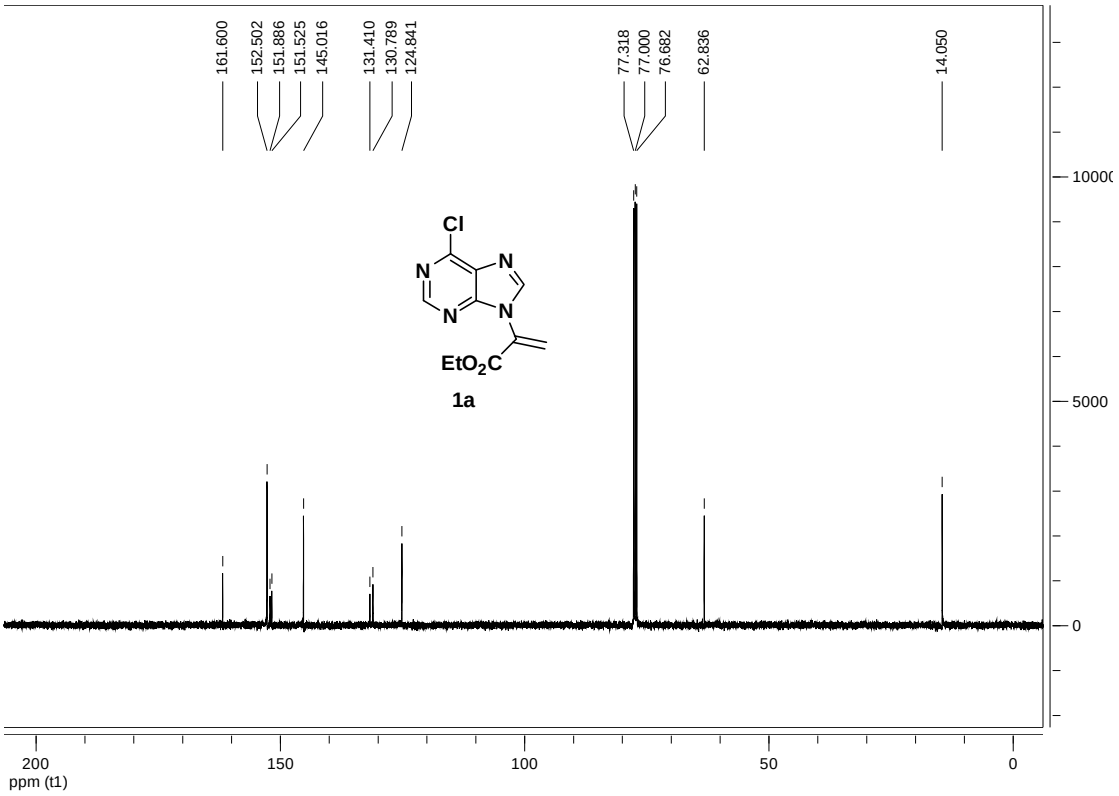
[2] B. M. Trost and G. R. Dake, *J. Am. Chem. Soc.*, 1997, **119**, 7595.

9. Copies of NMR spectra for the α-heteroaryl acrylates and cycloadducts

^{1}H-NMR for 1a



^{13}C-NMR for 1a



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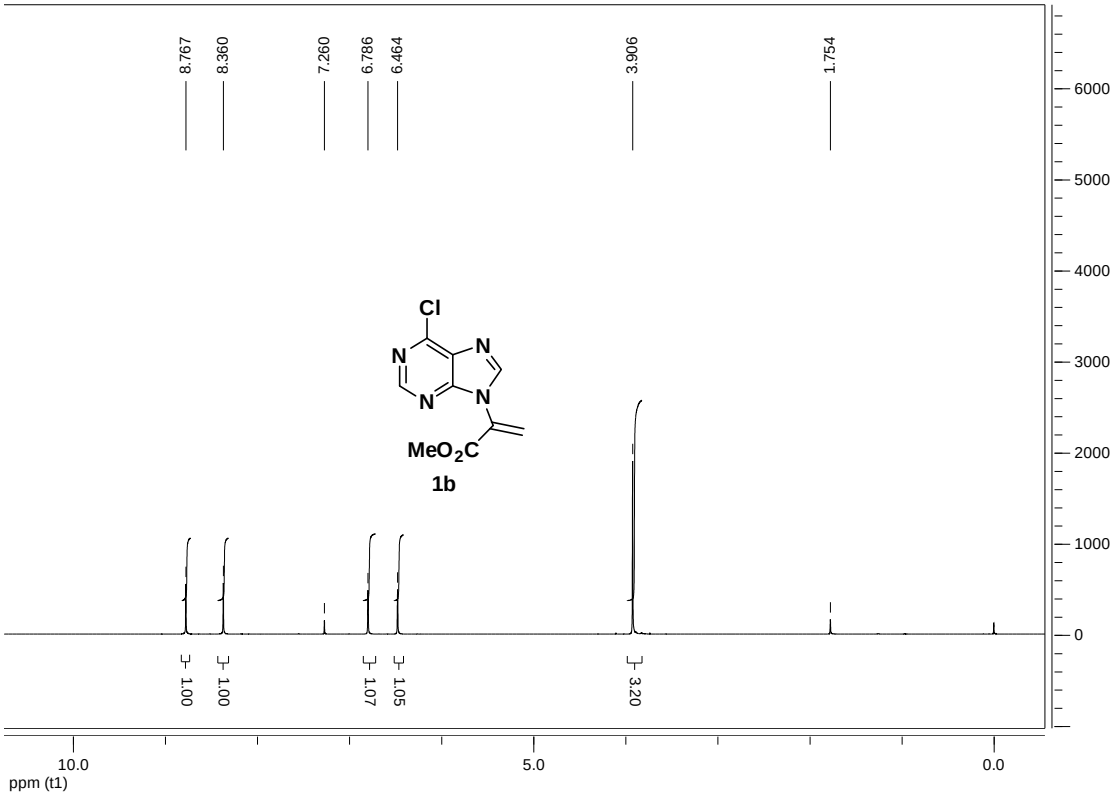

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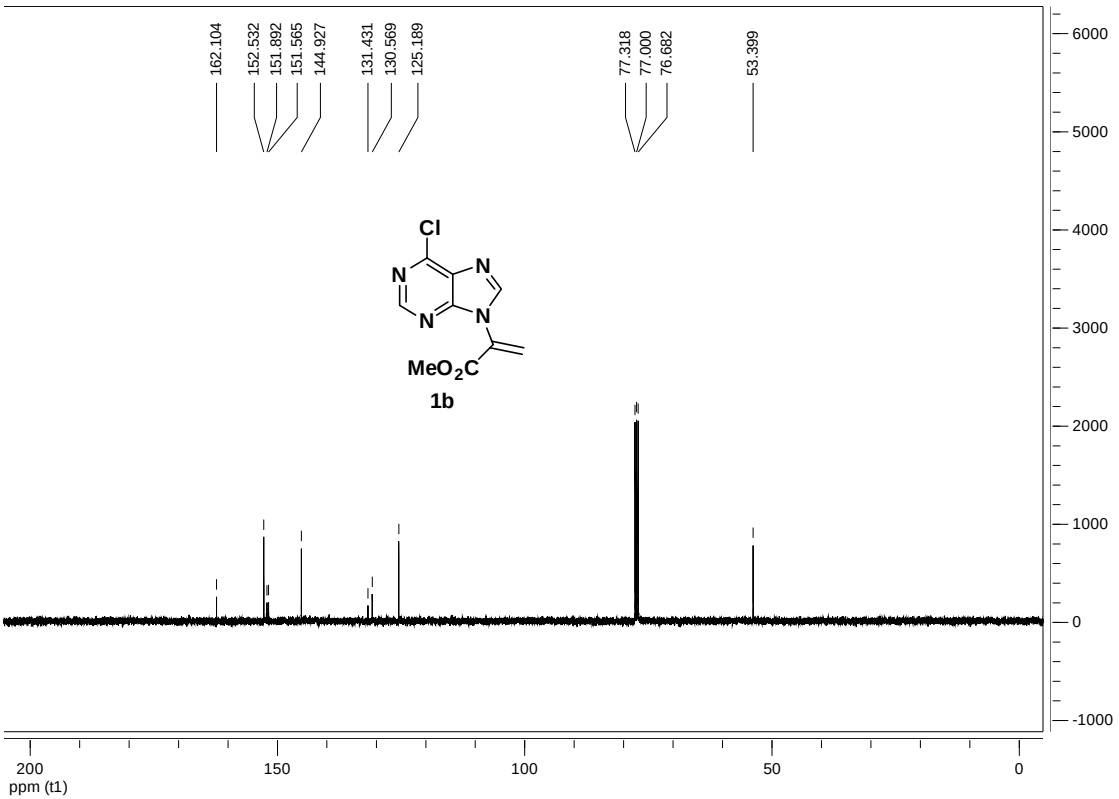

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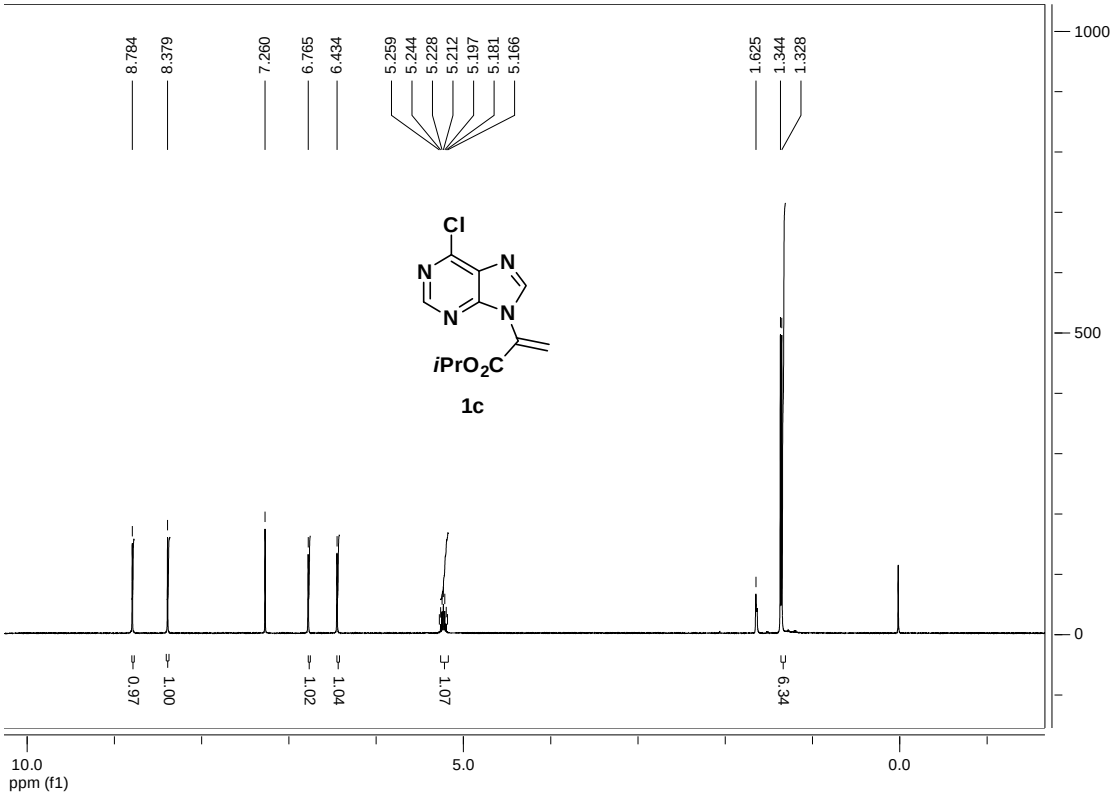

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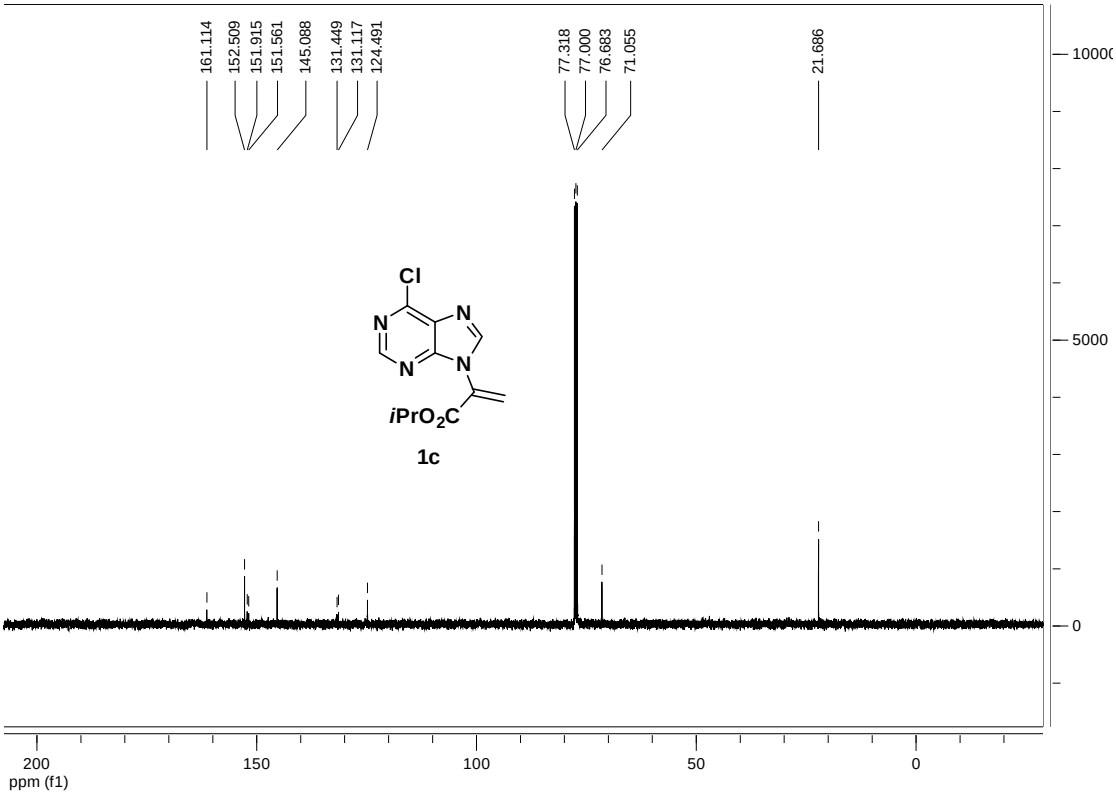

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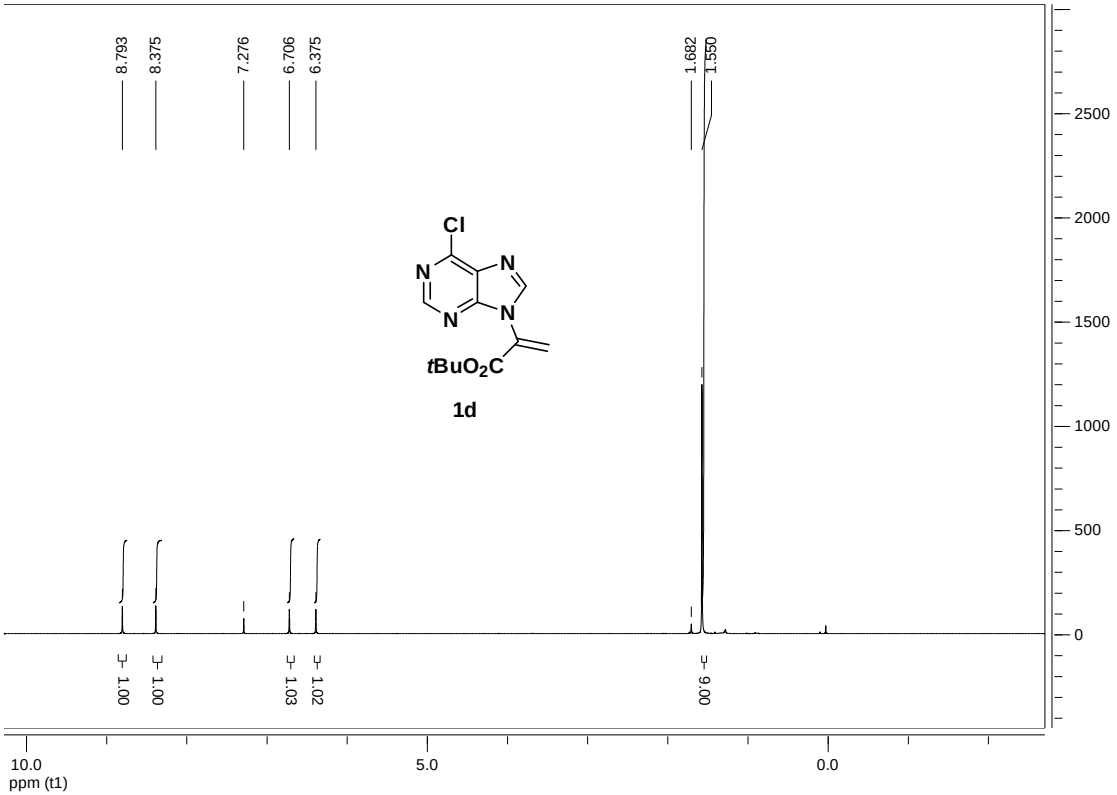

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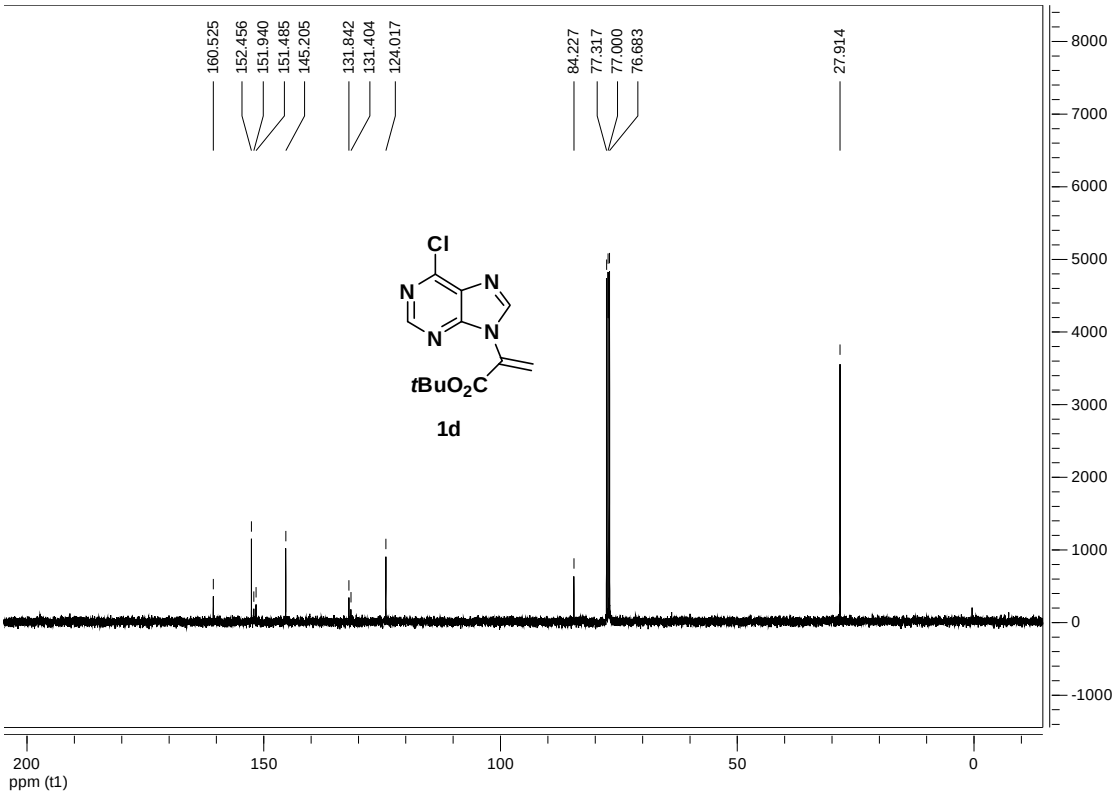

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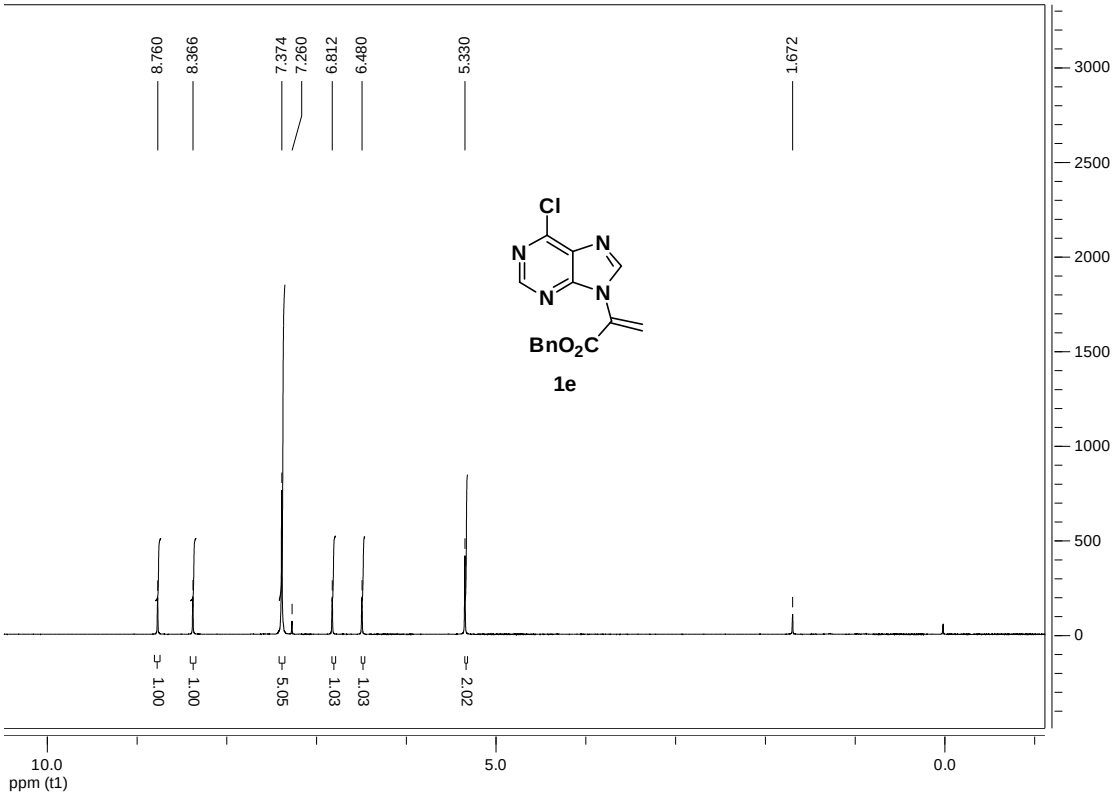

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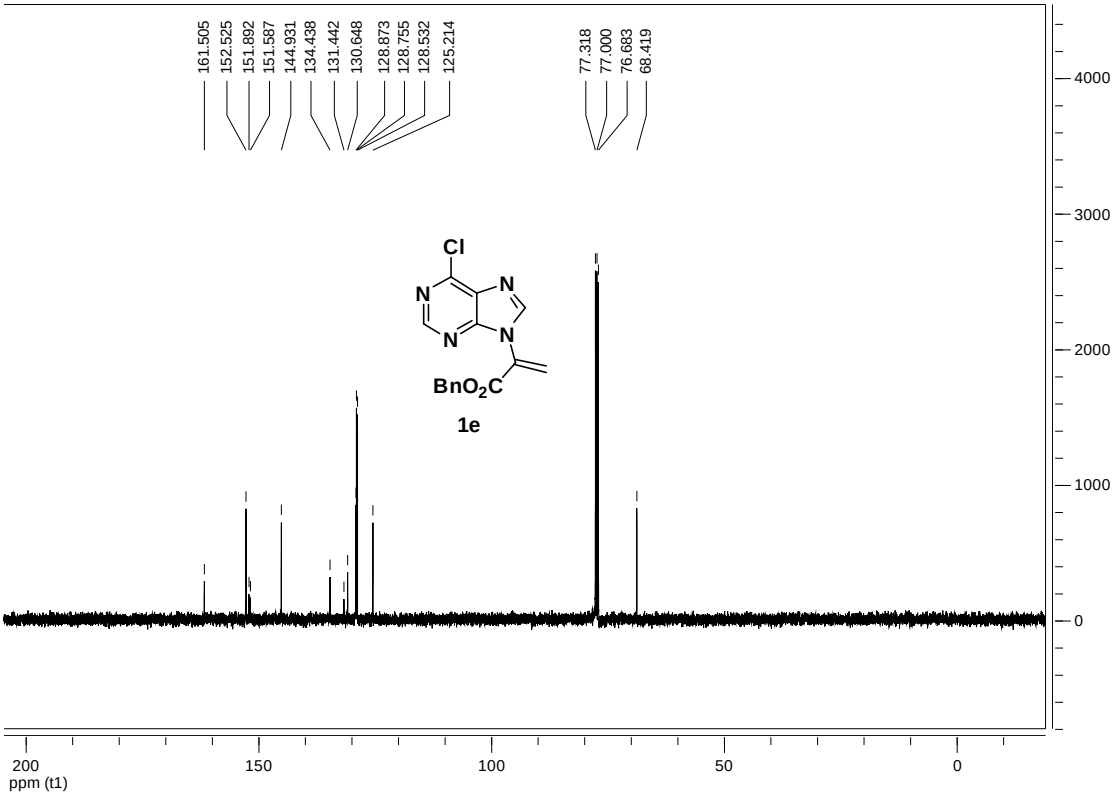

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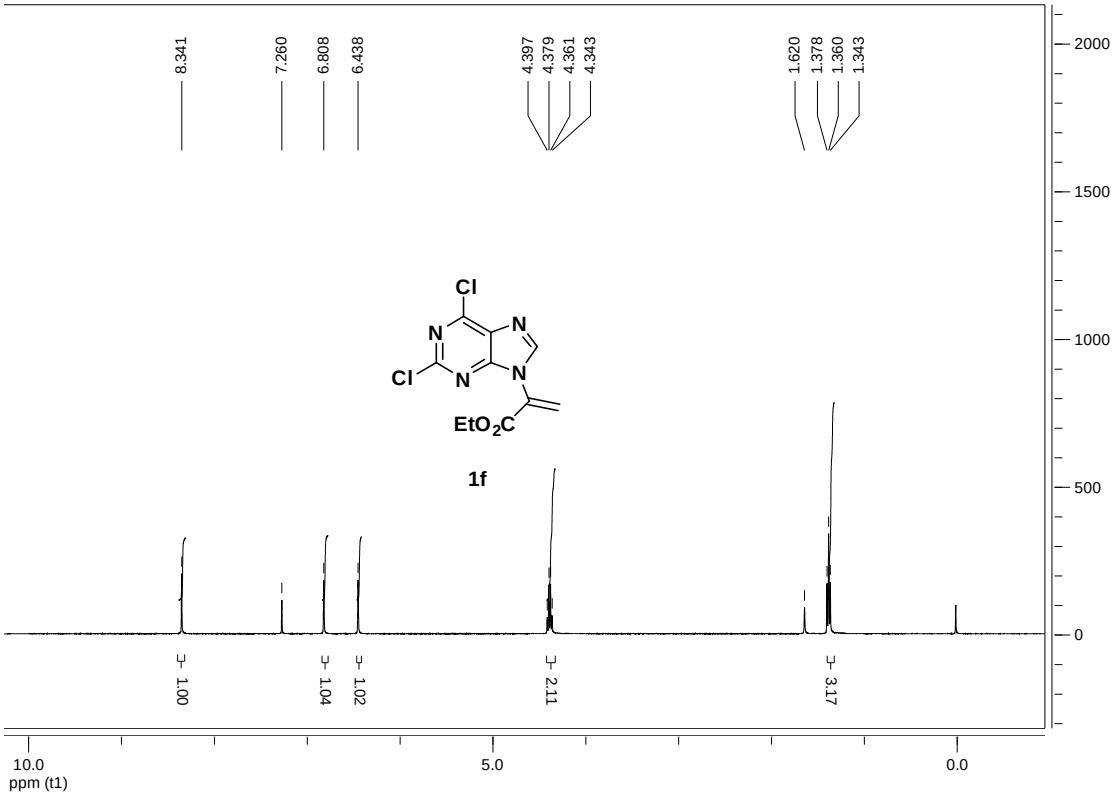

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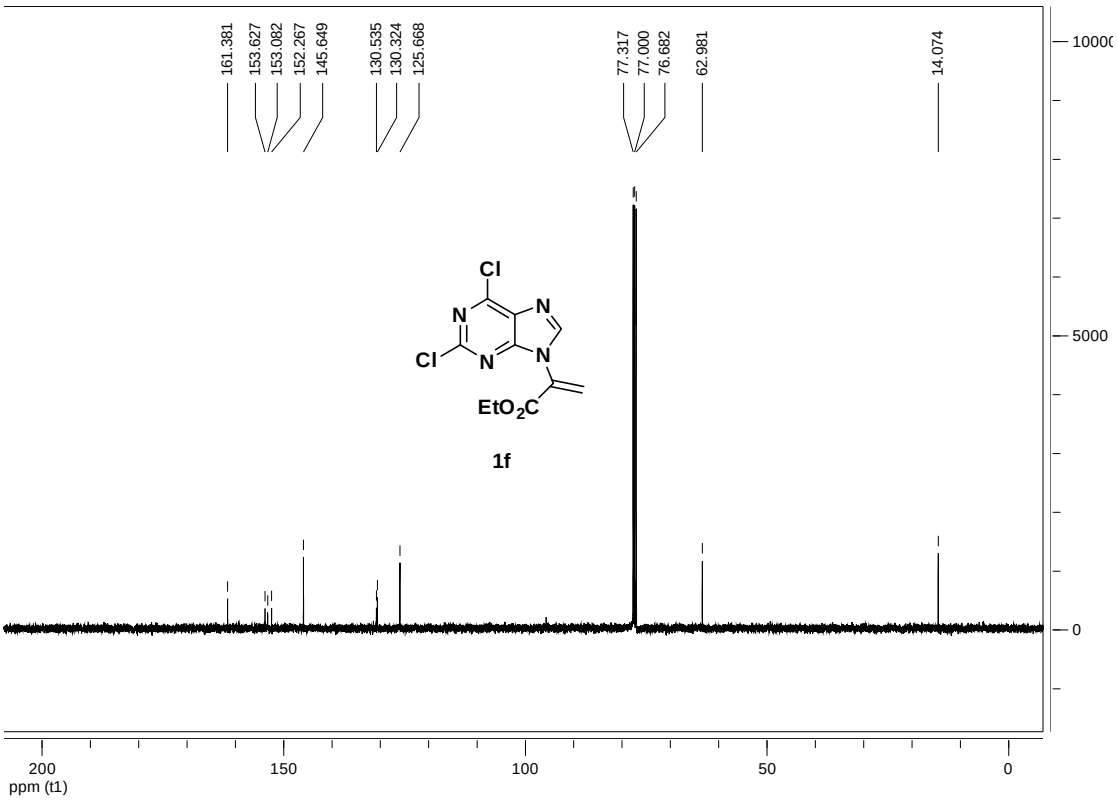
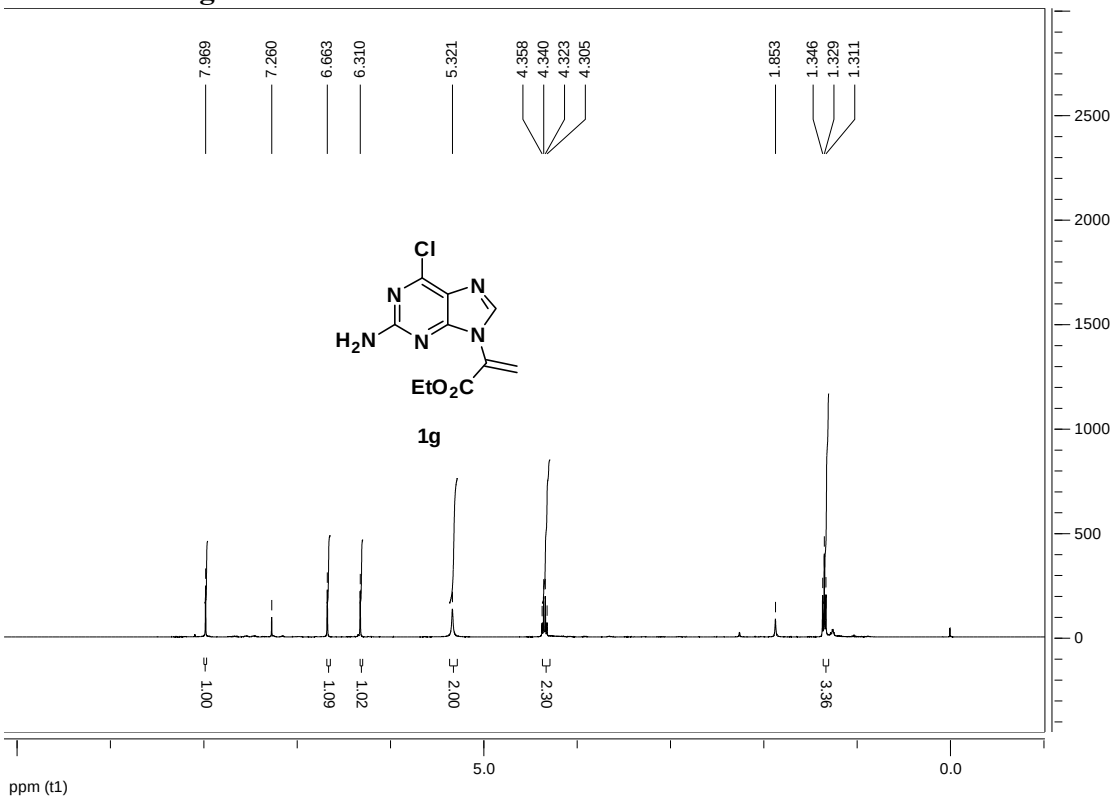


^{1}H-NMR for 1g



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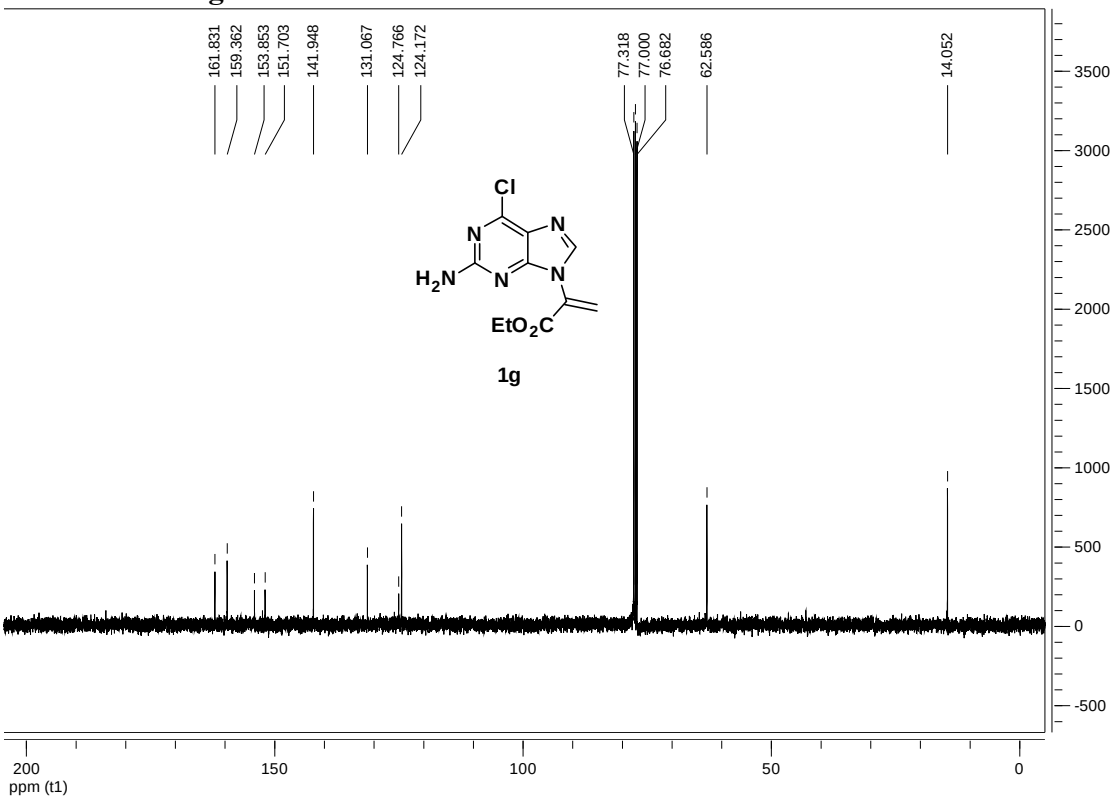

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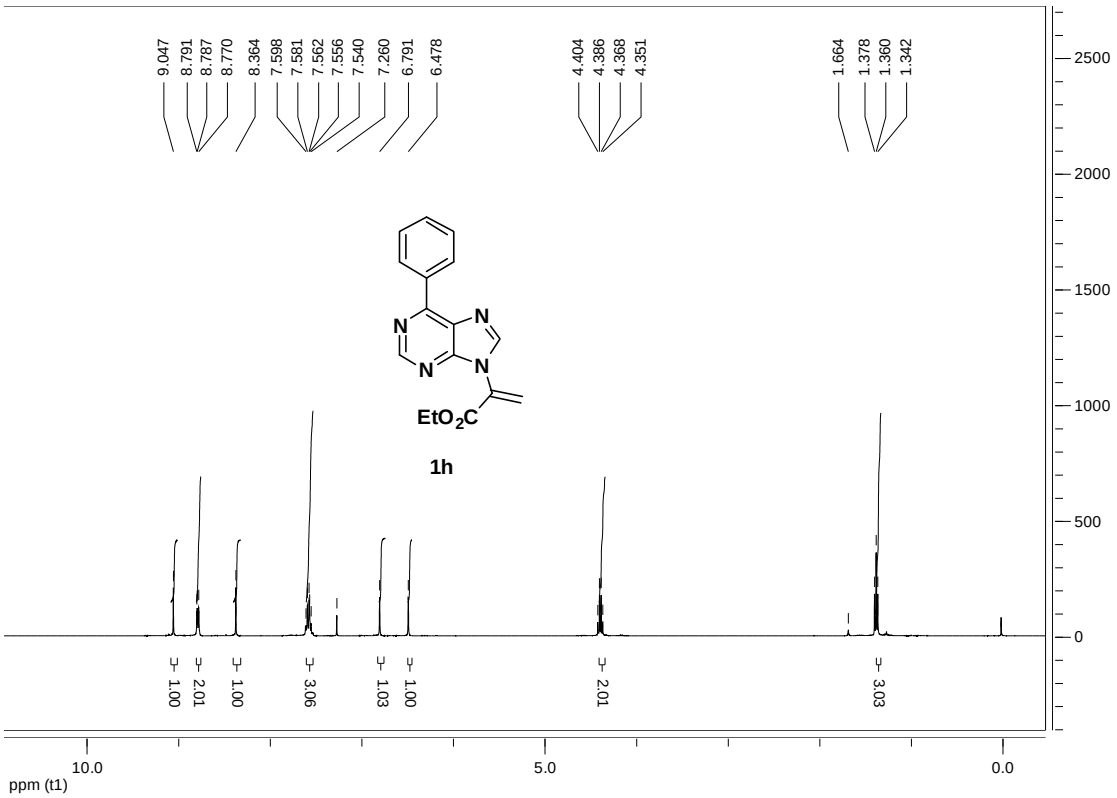

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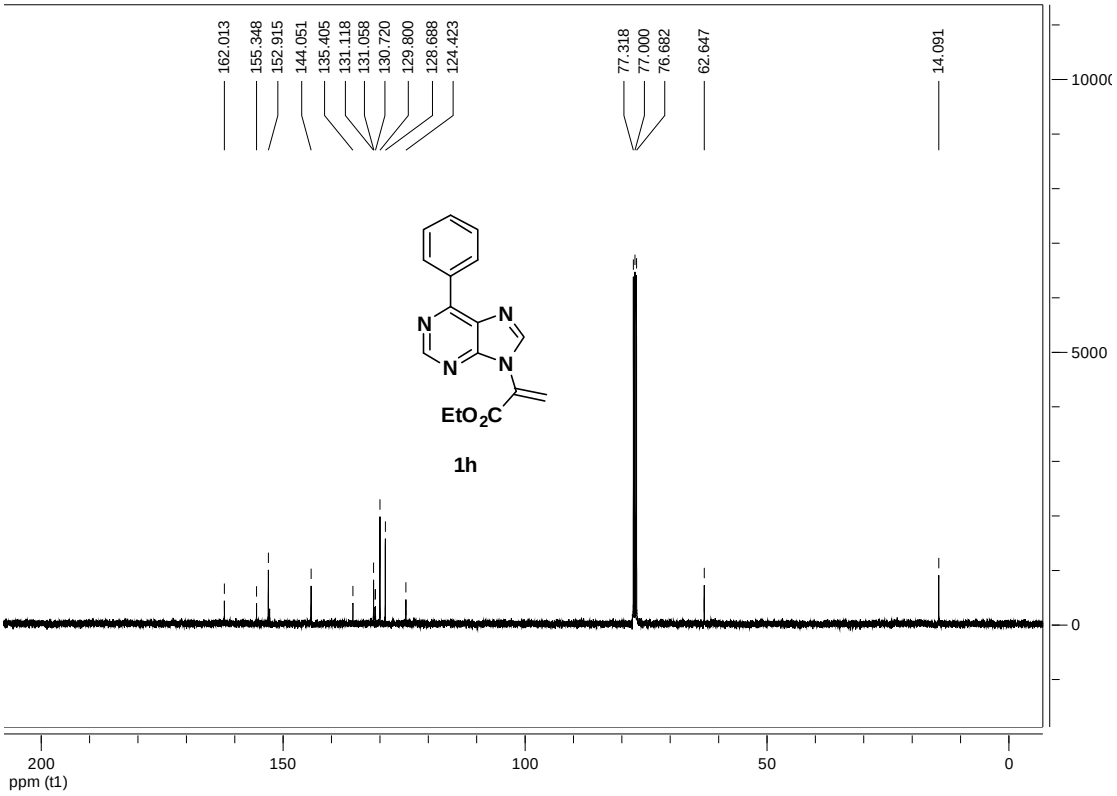

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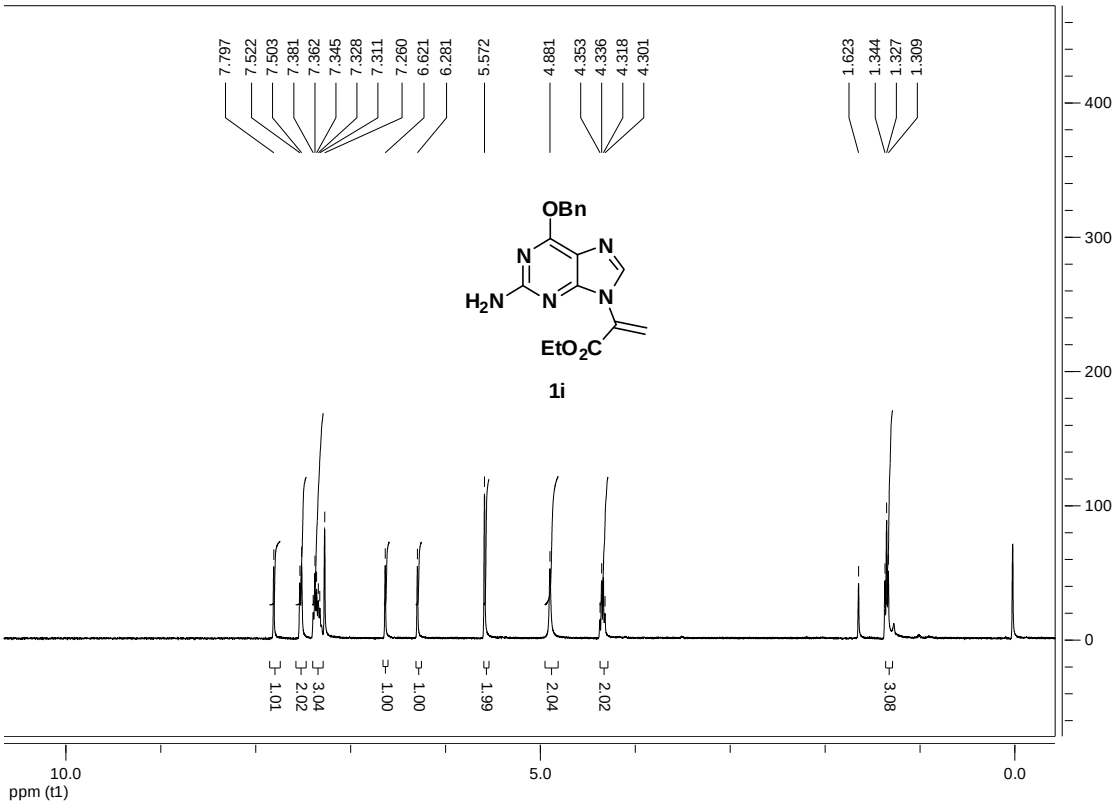

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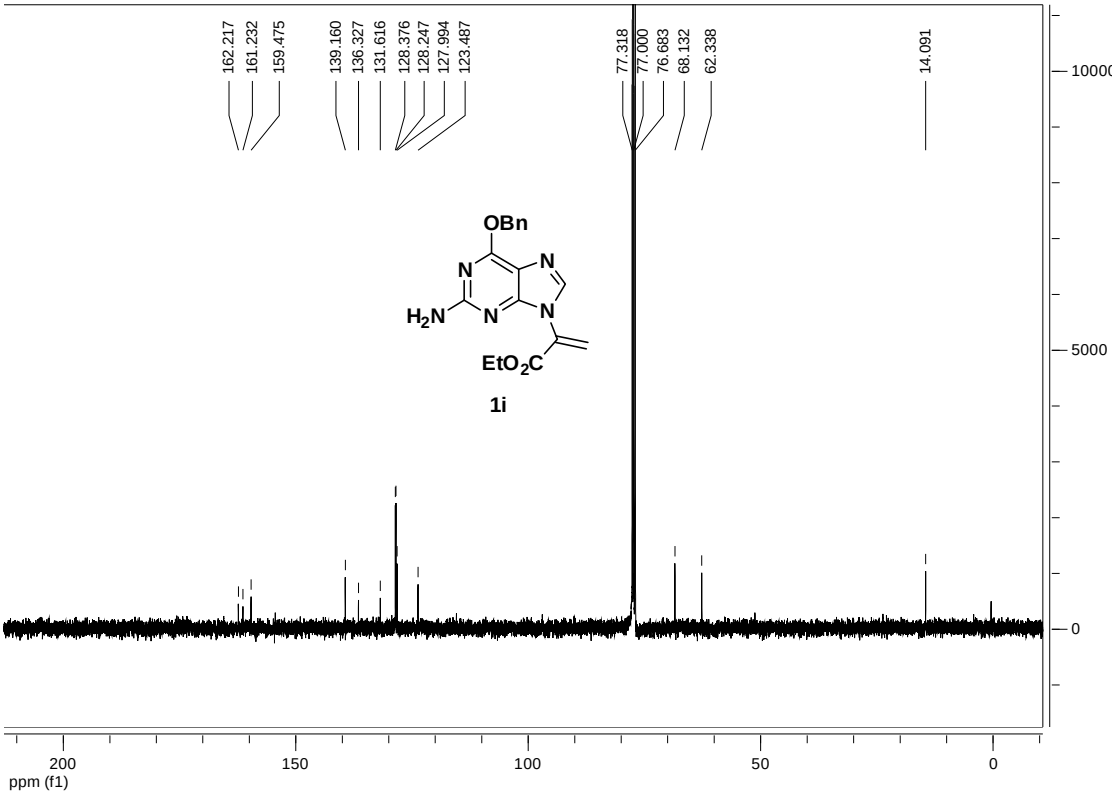

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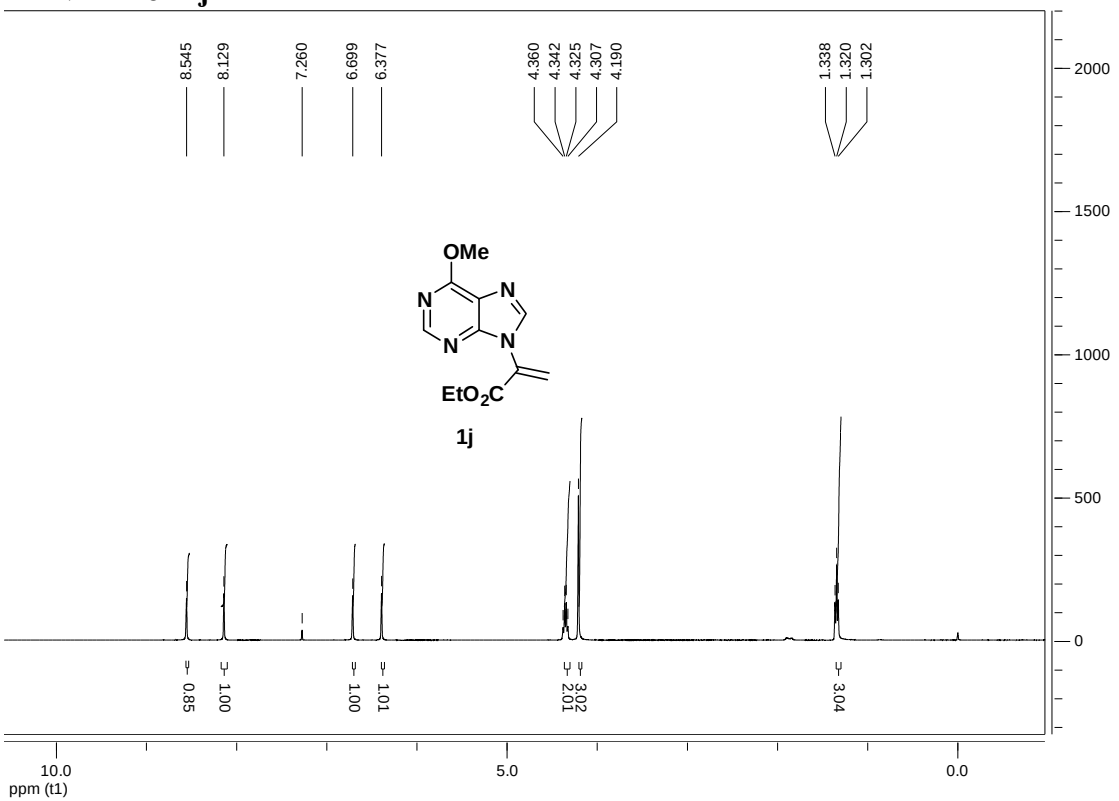

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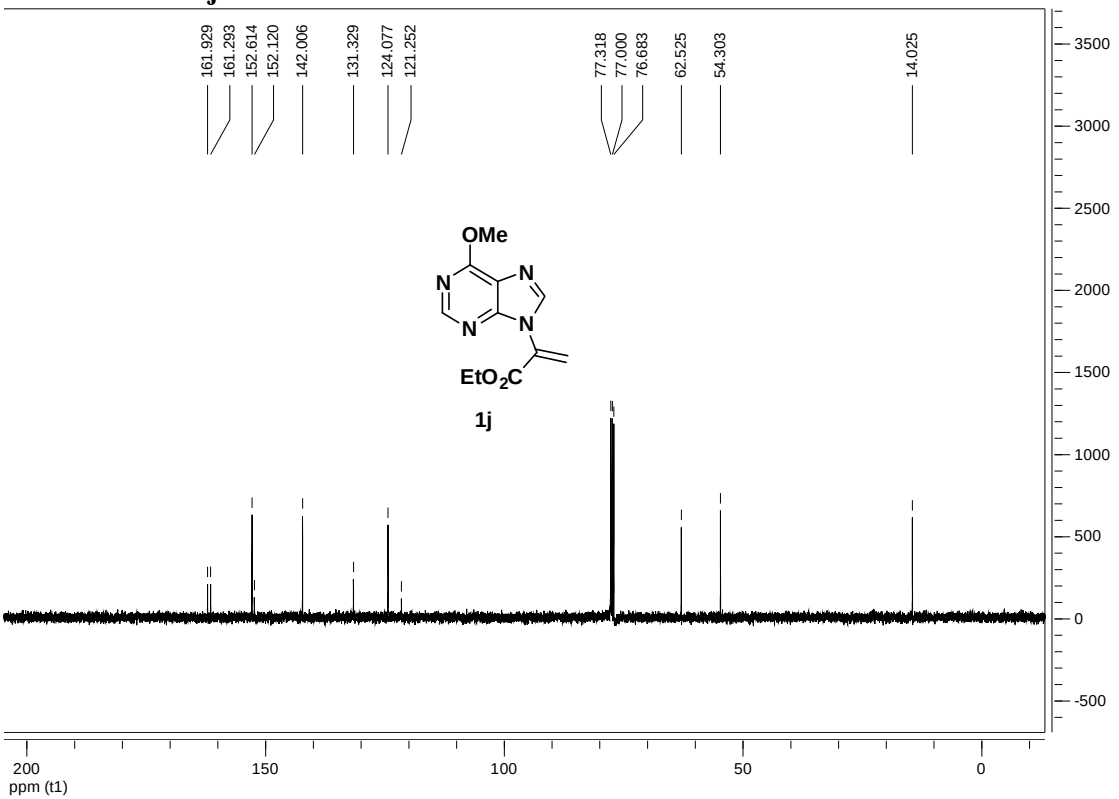

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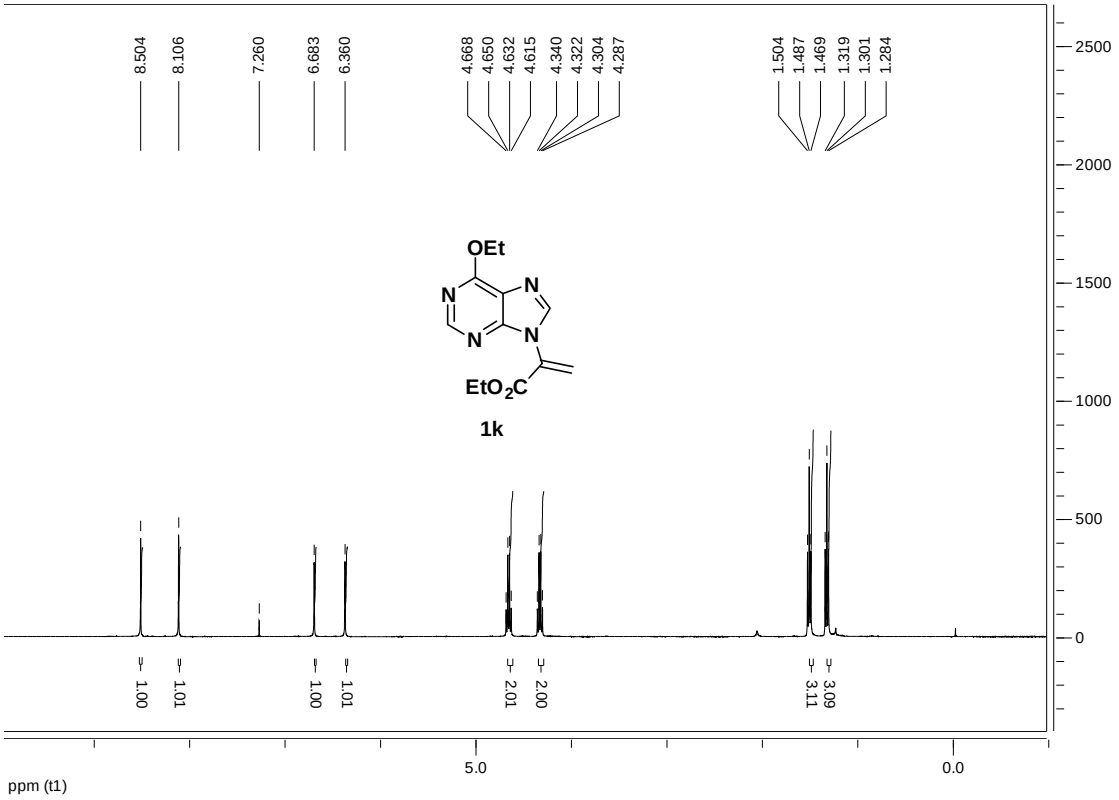

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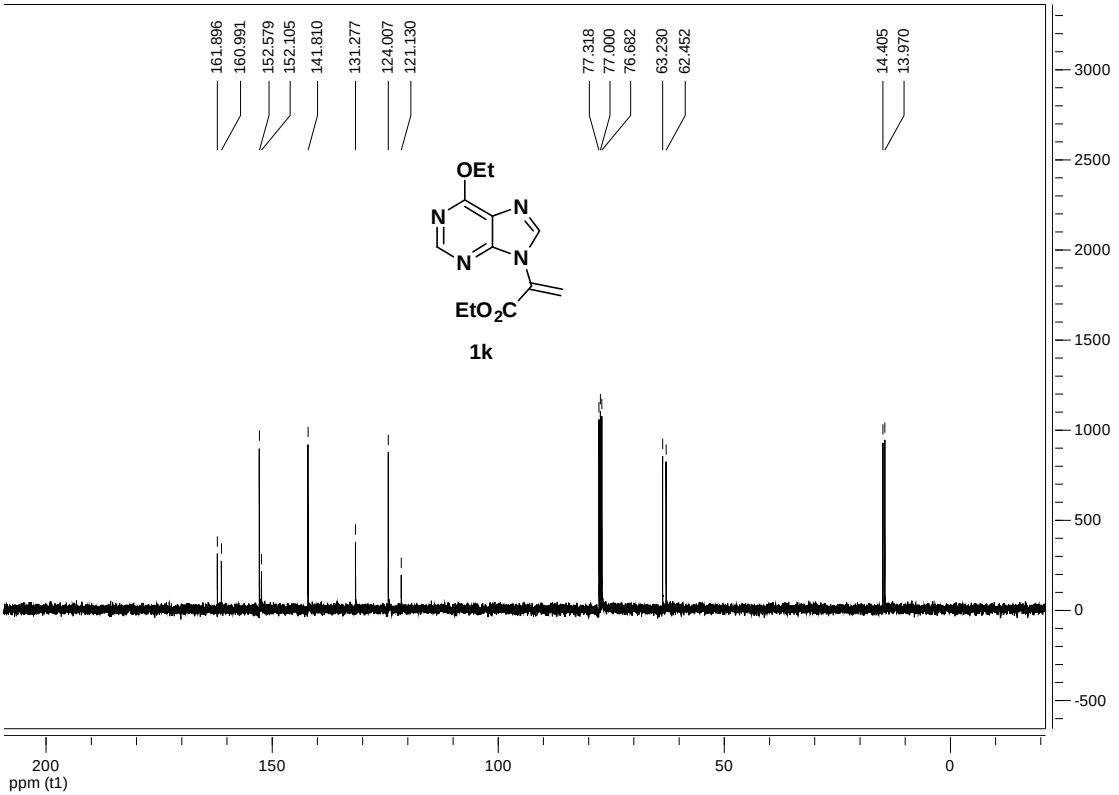

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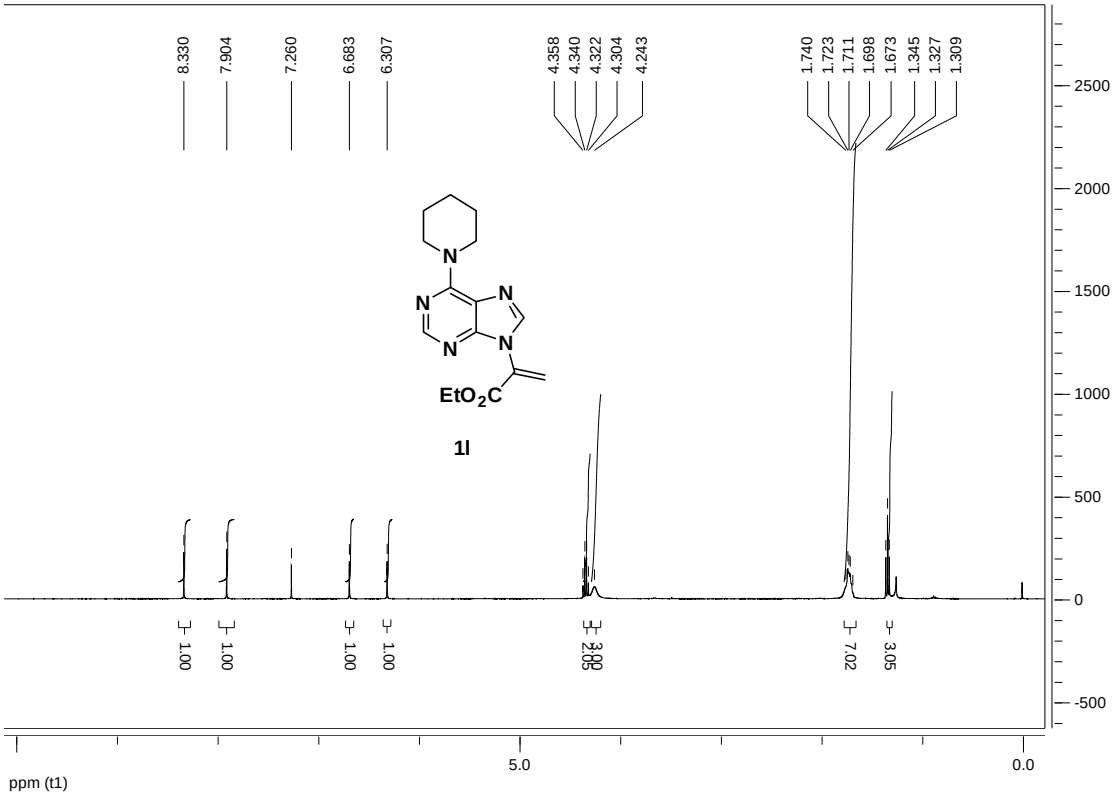

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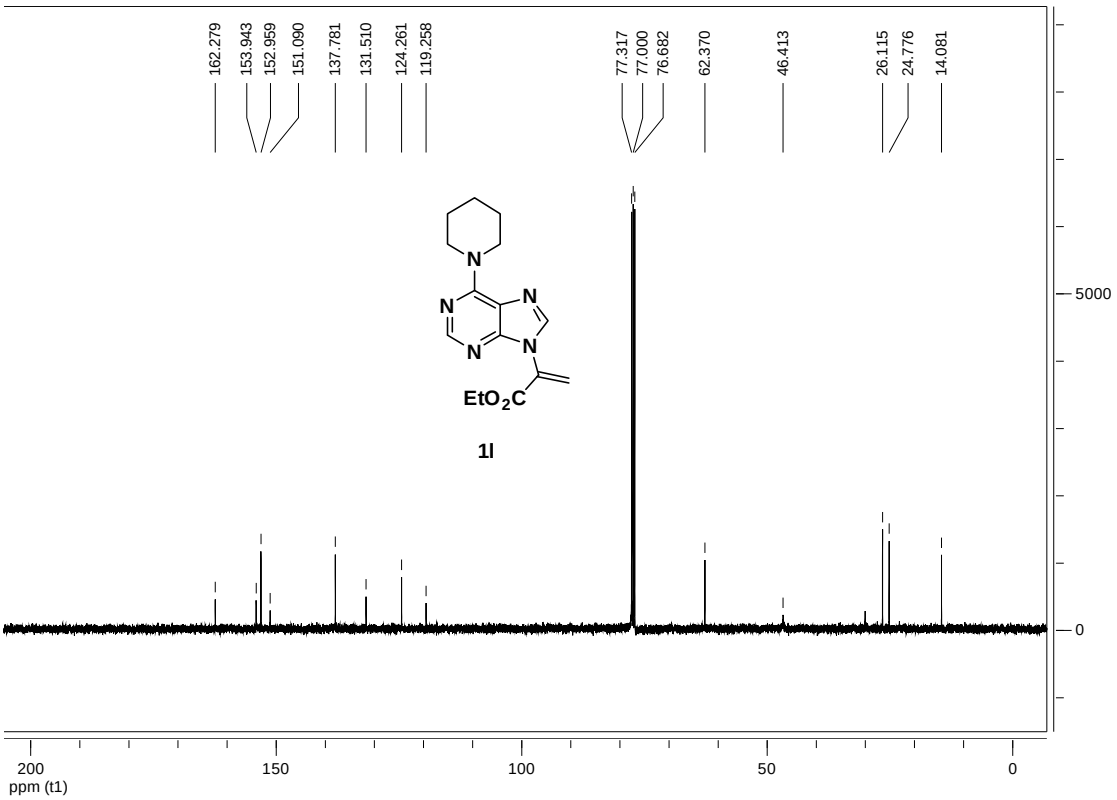

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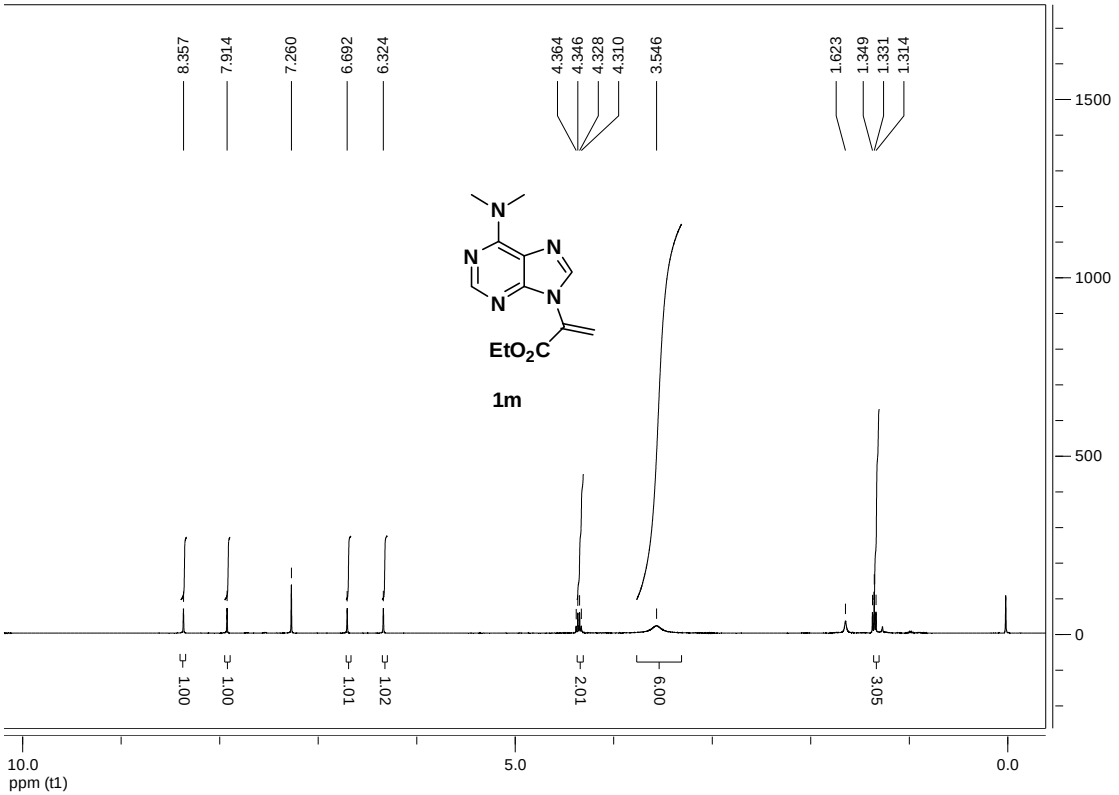

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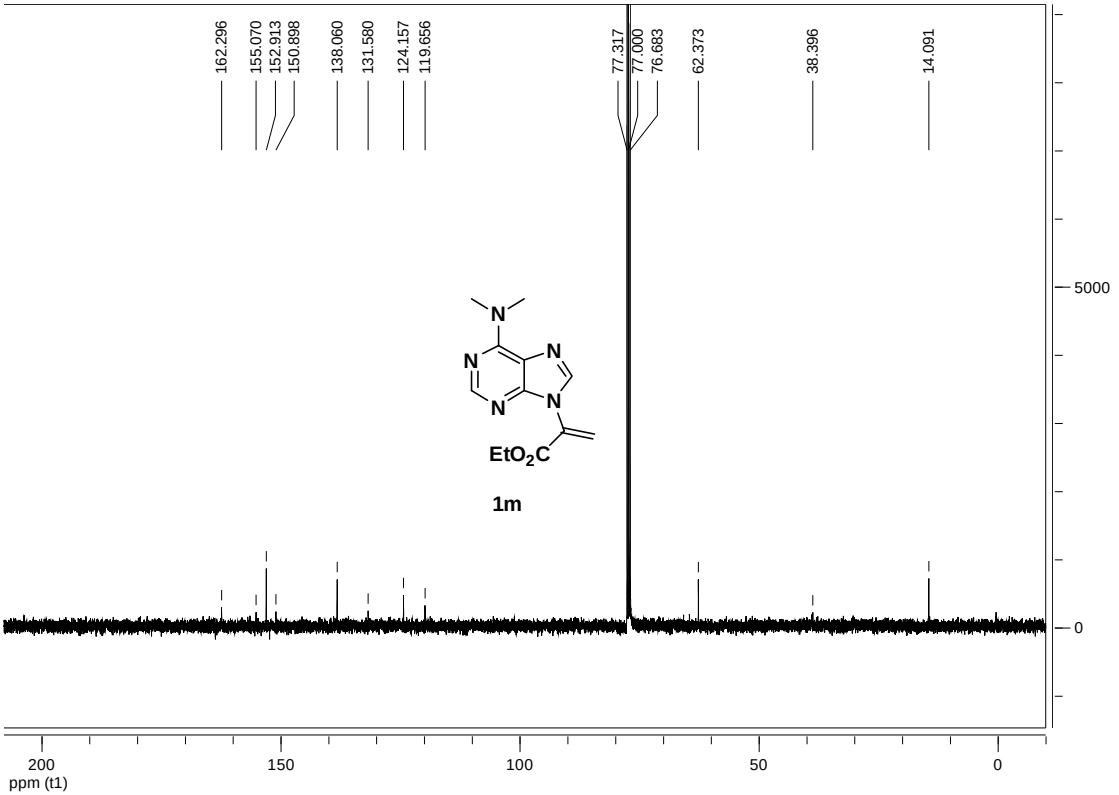

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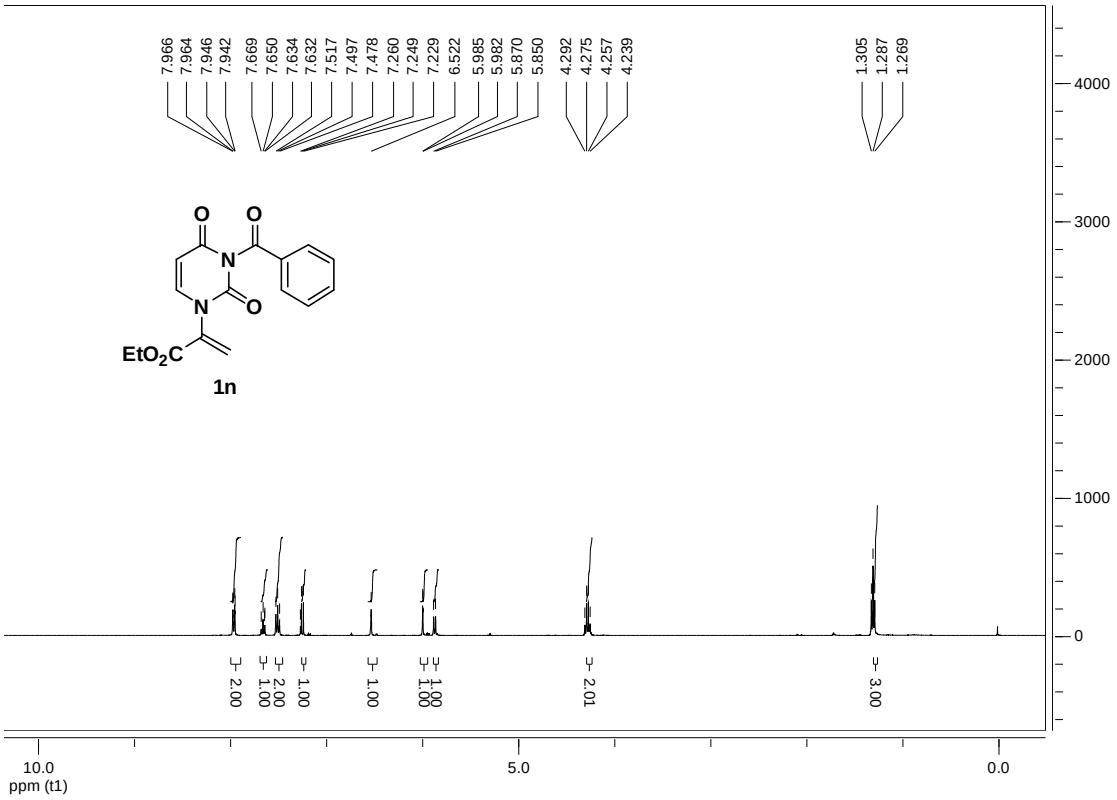

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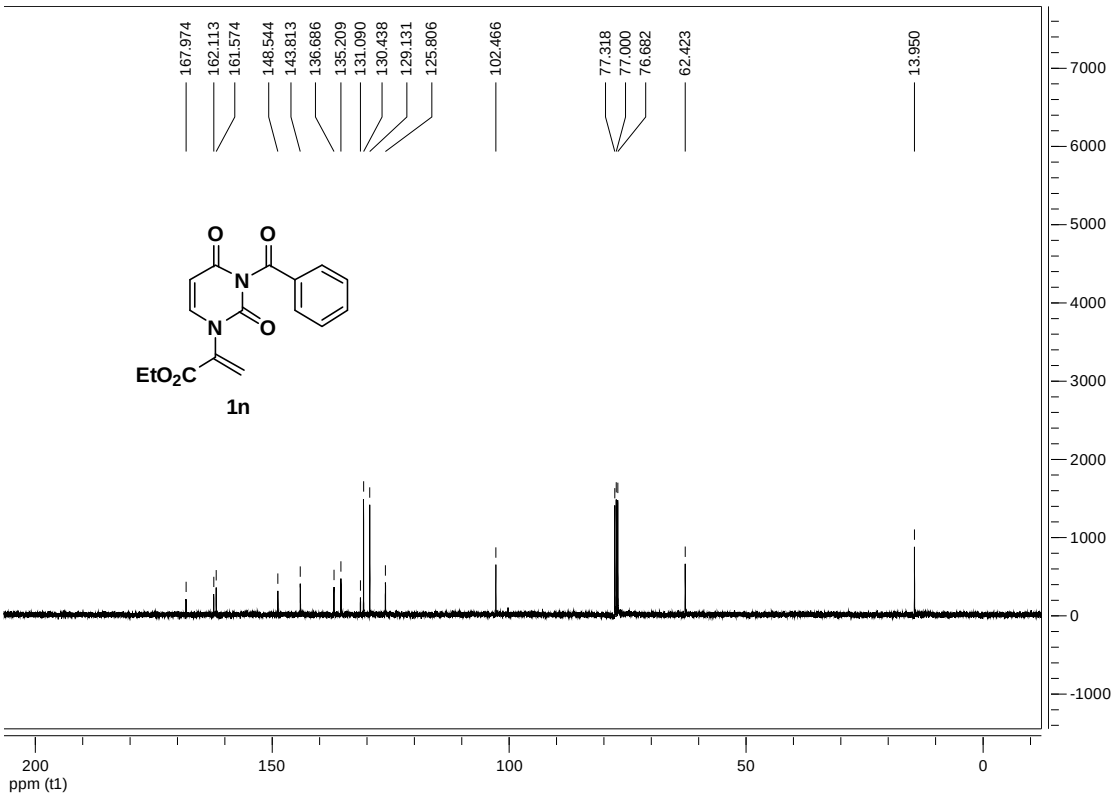

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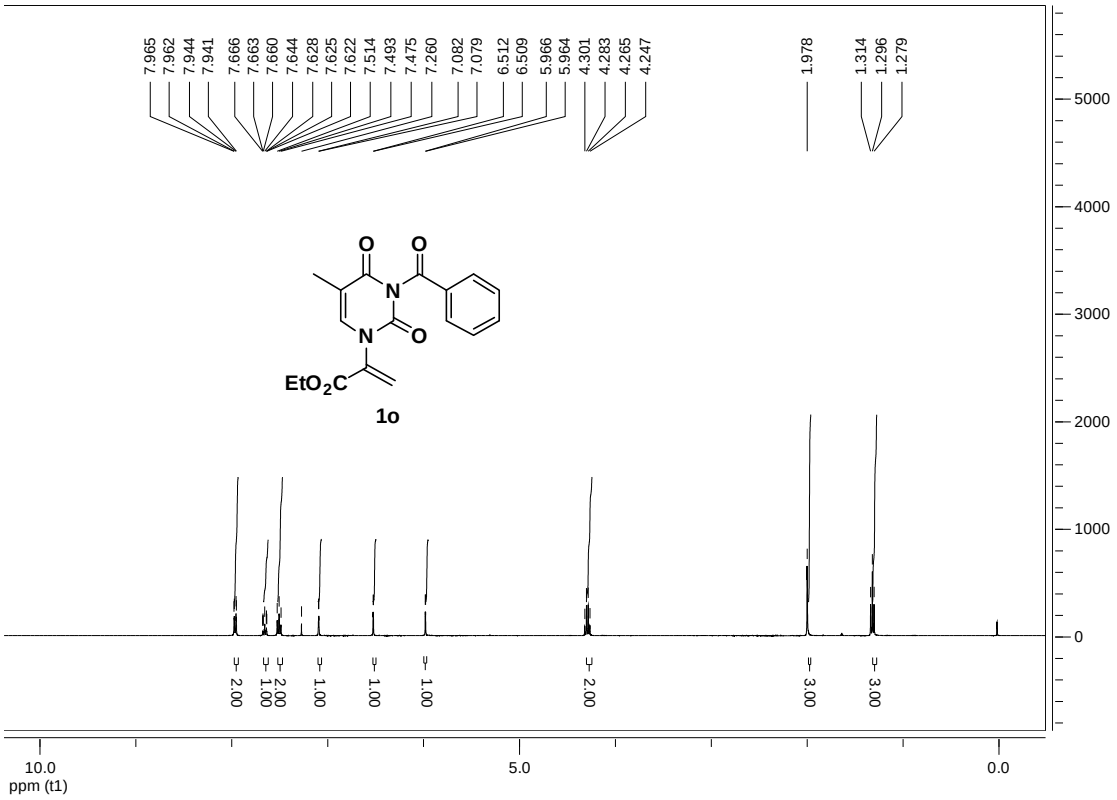

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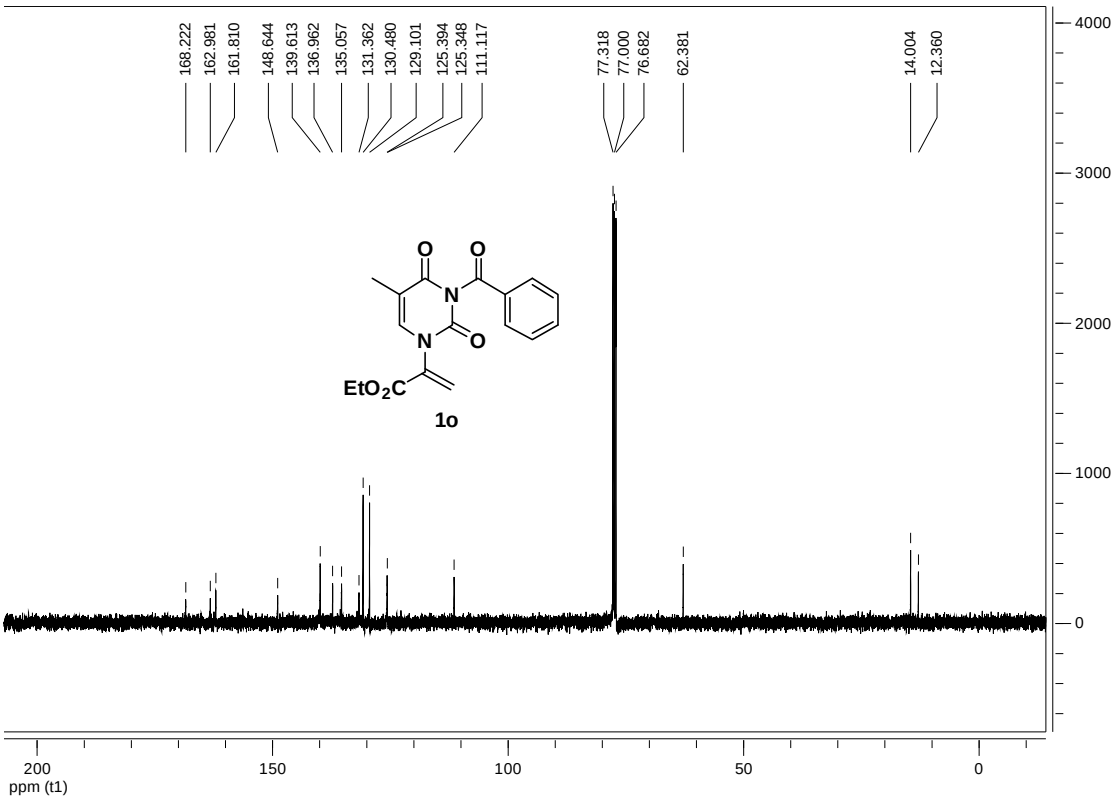

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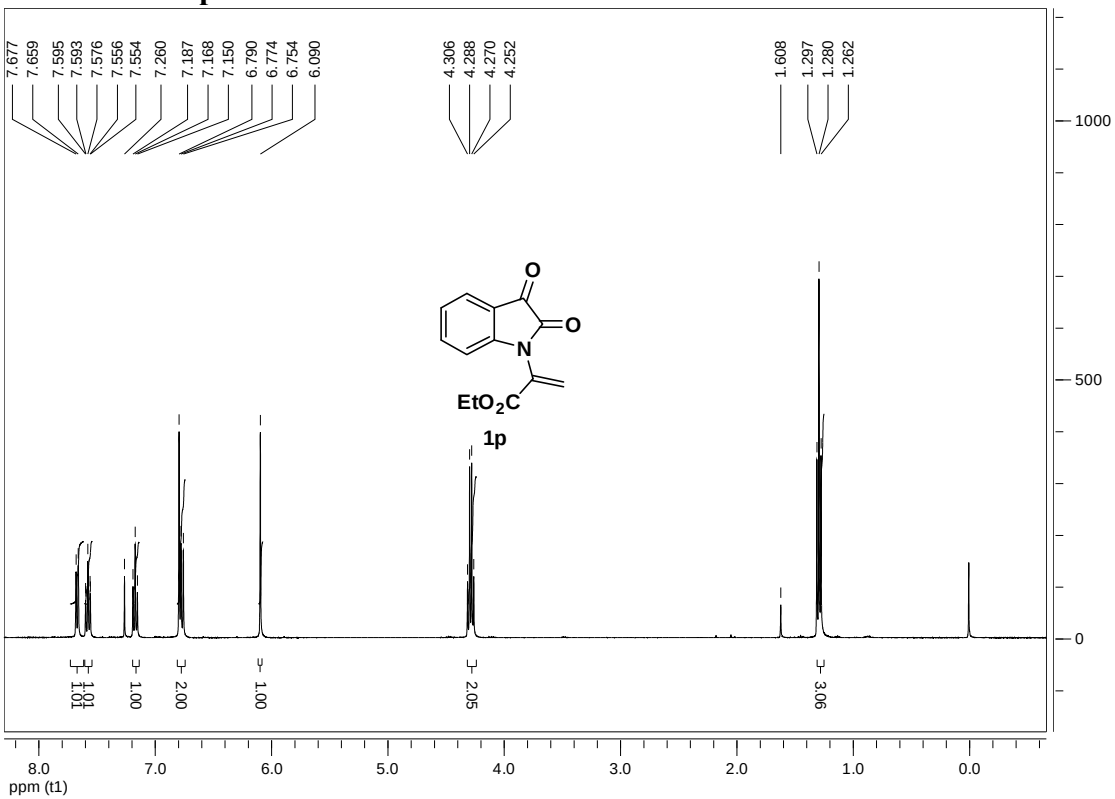

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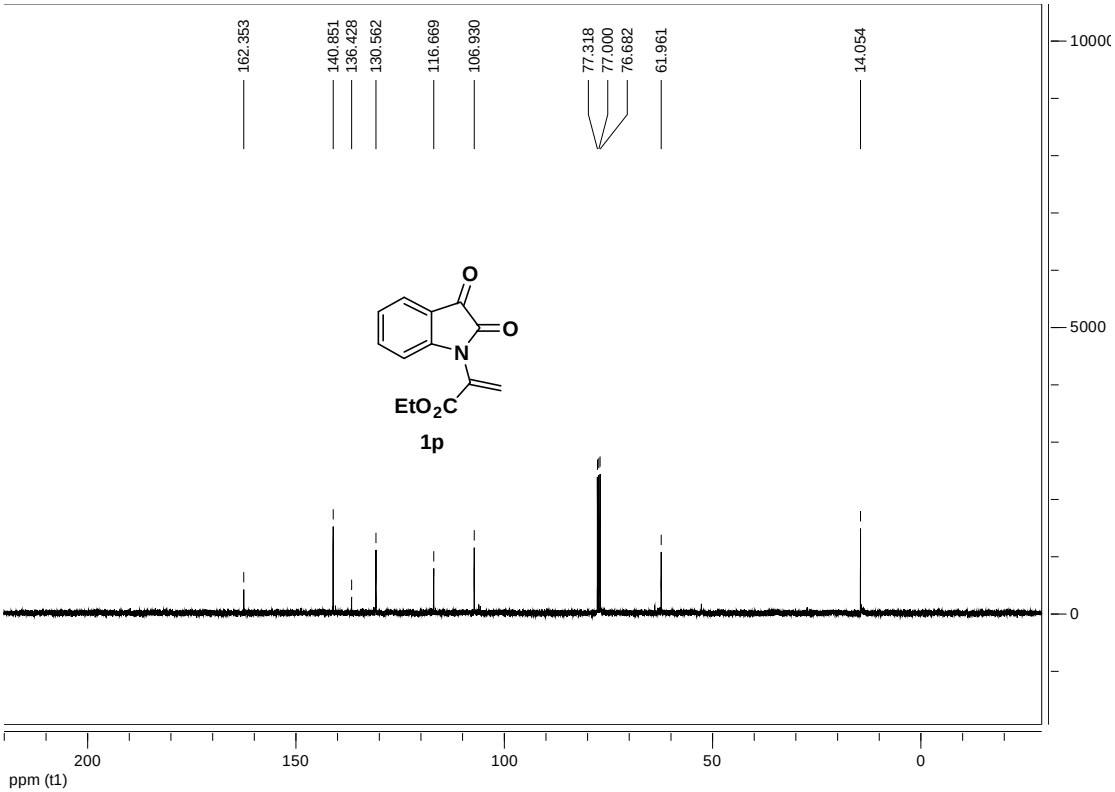

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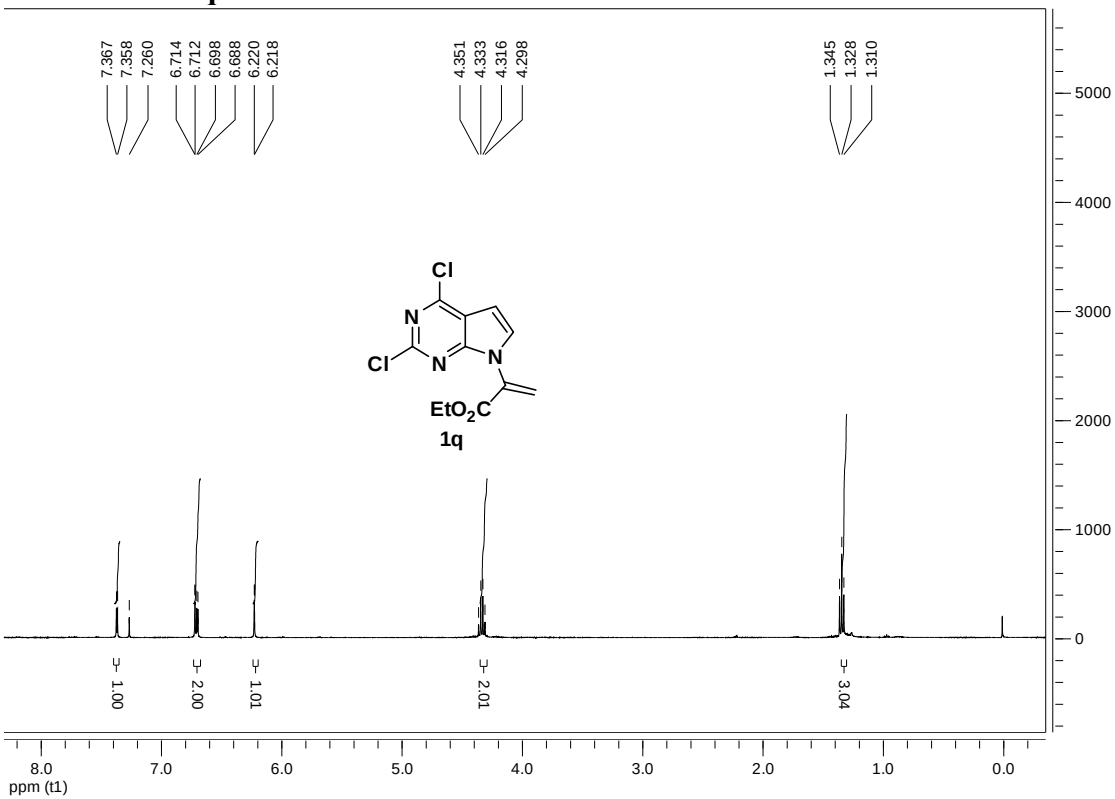

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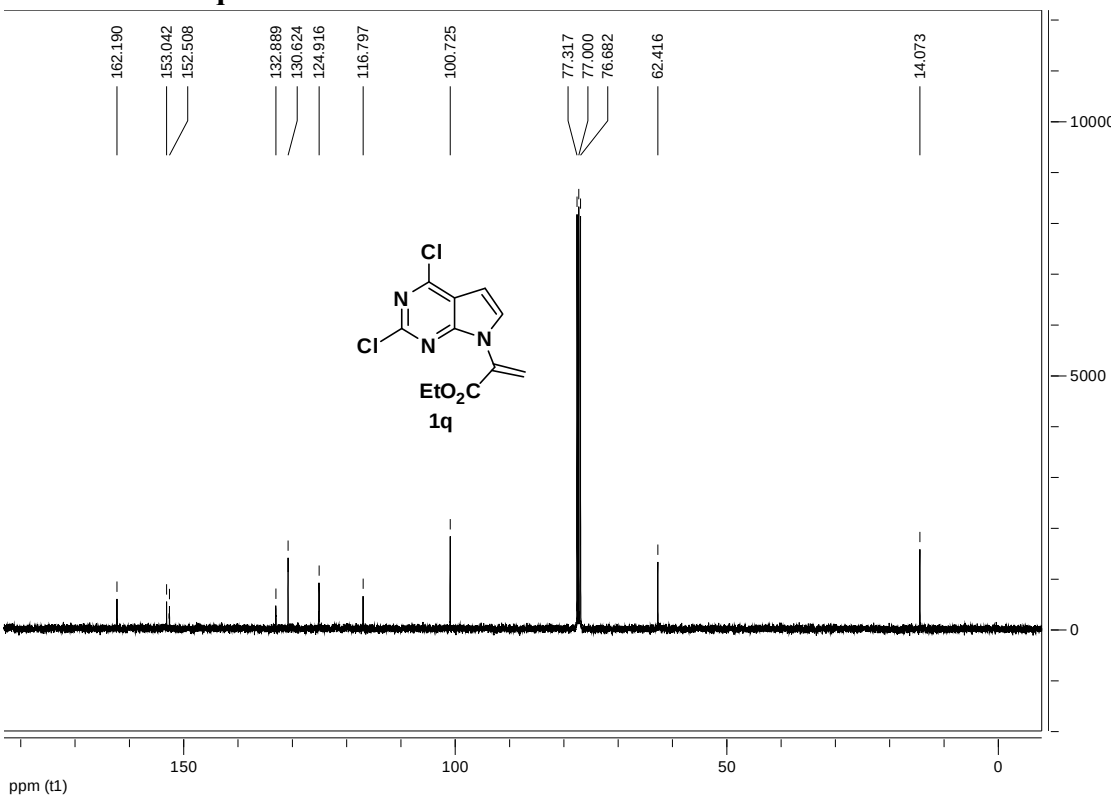

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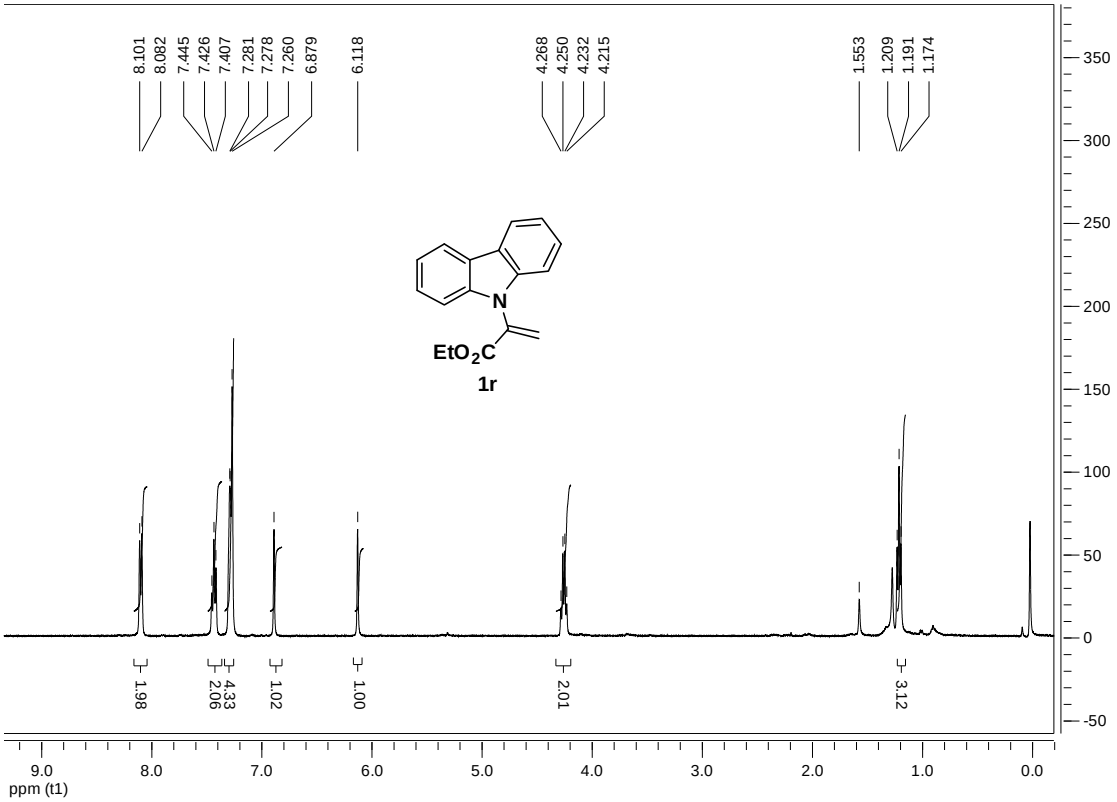

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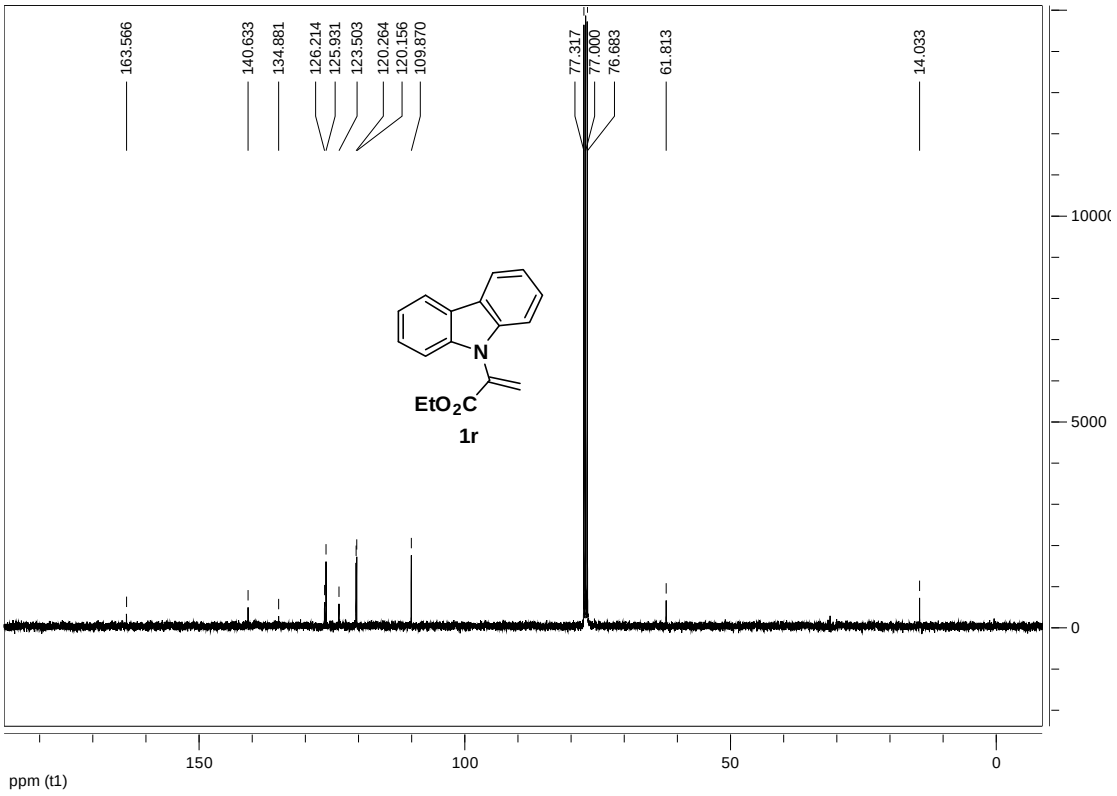

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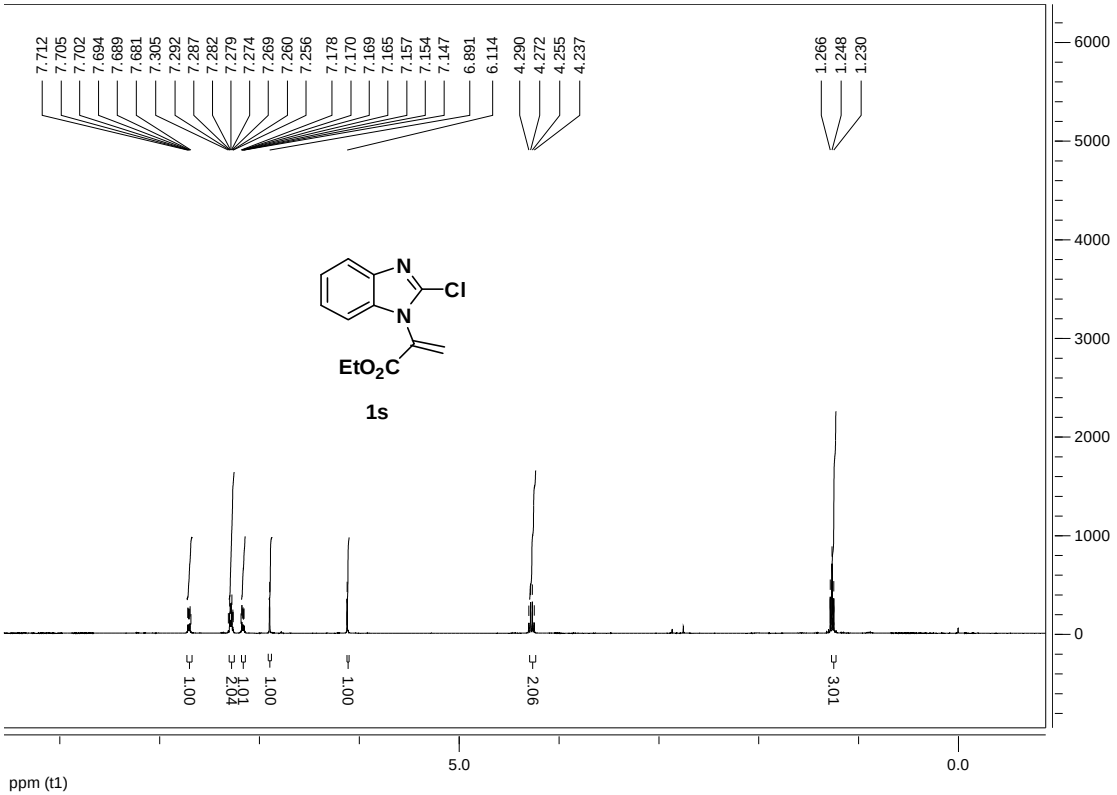

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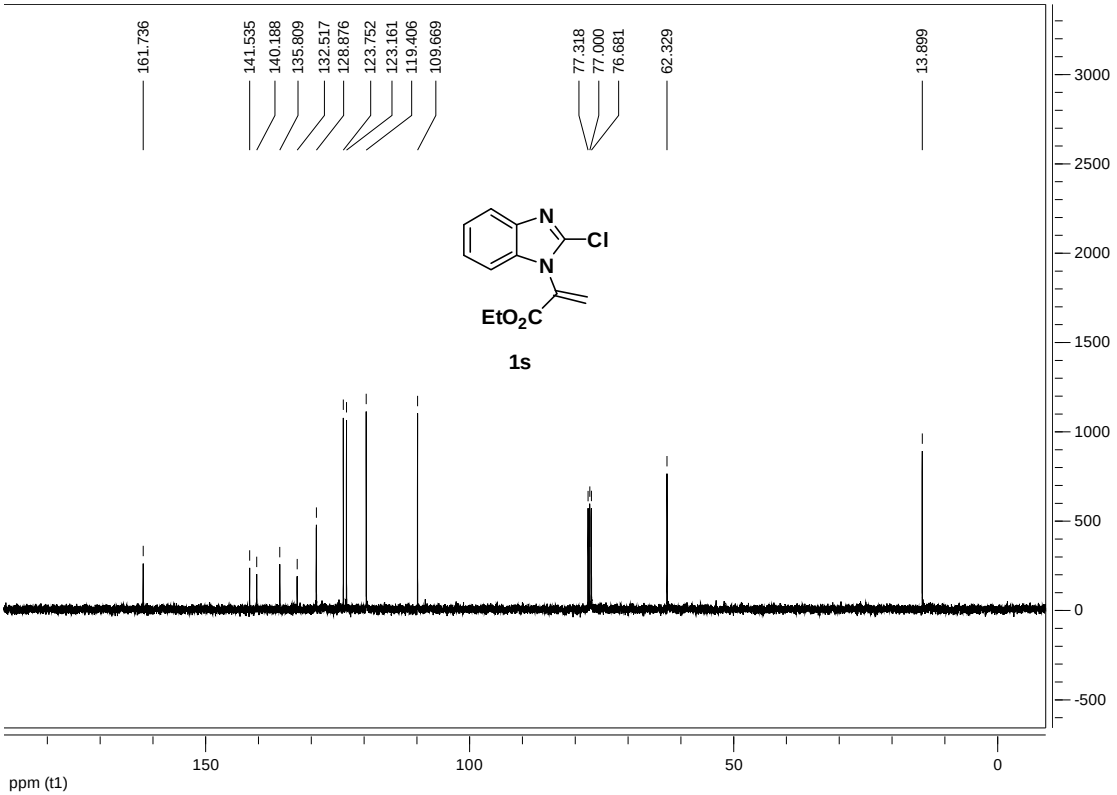

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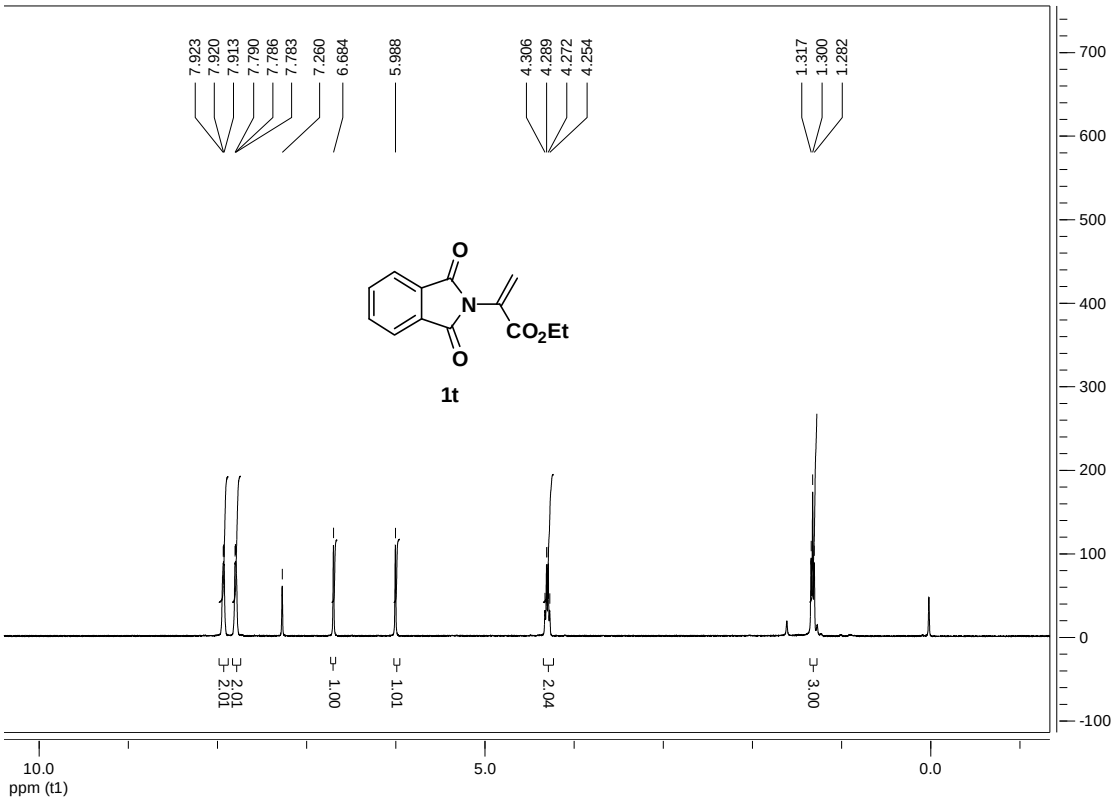

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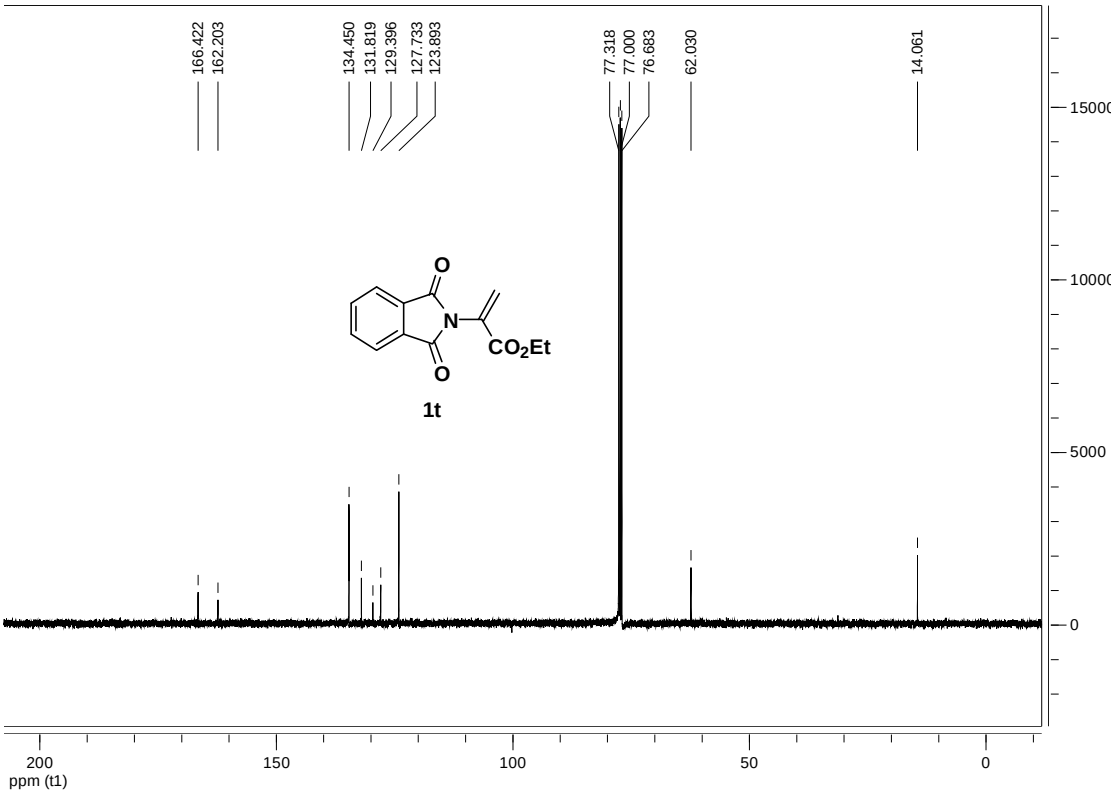

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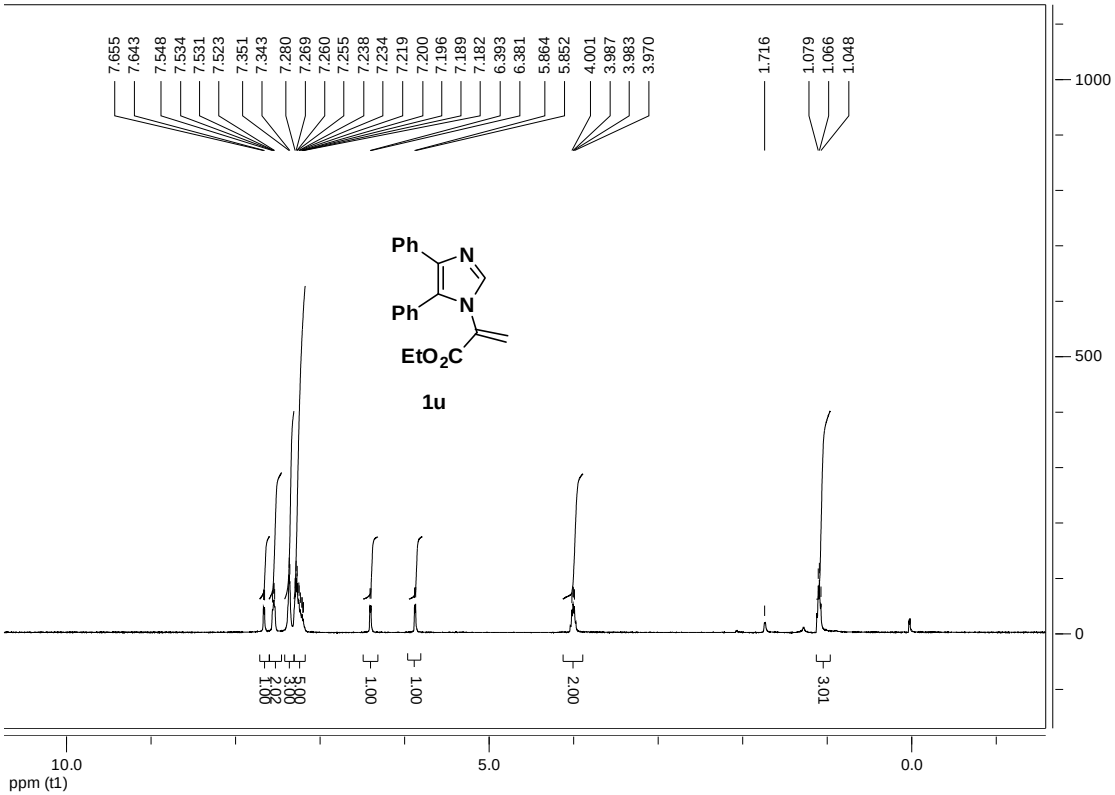

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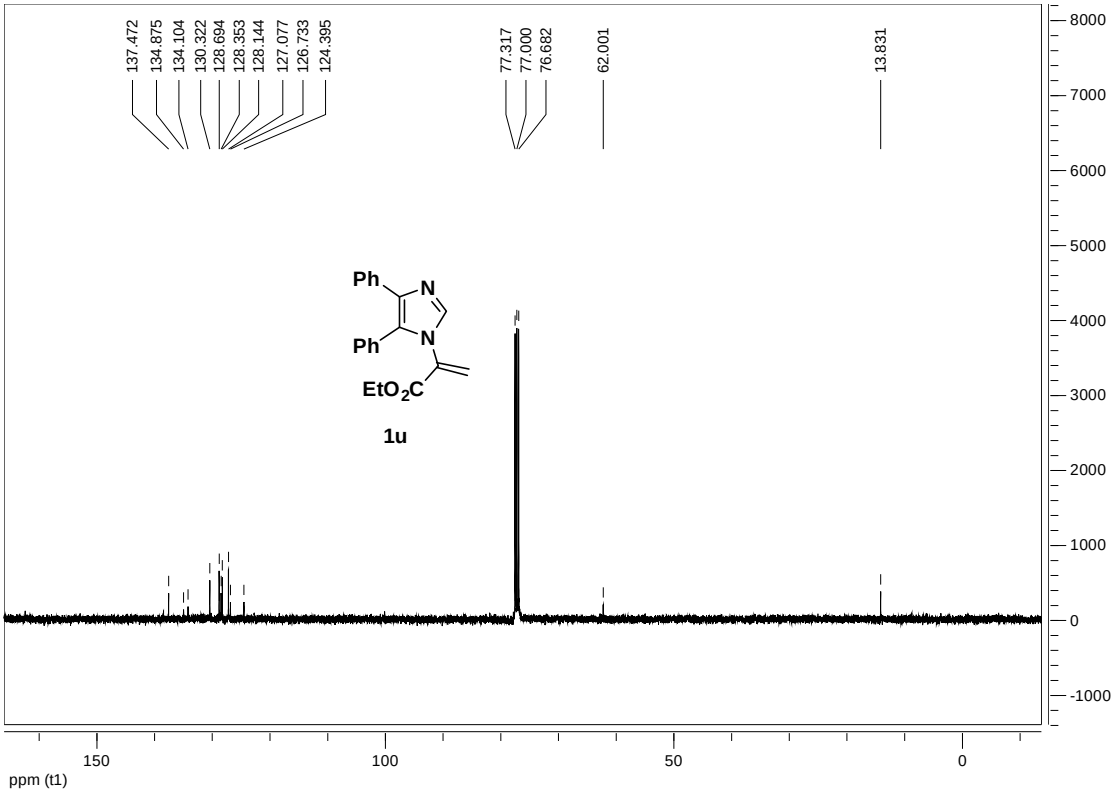

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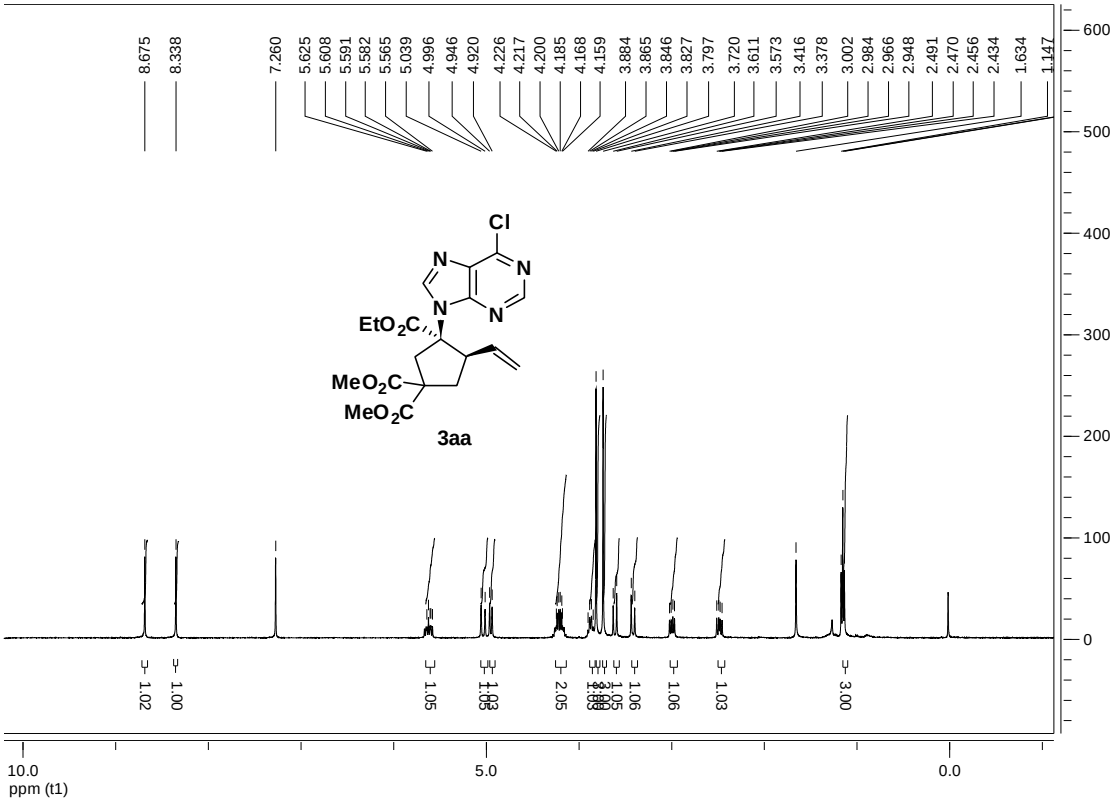

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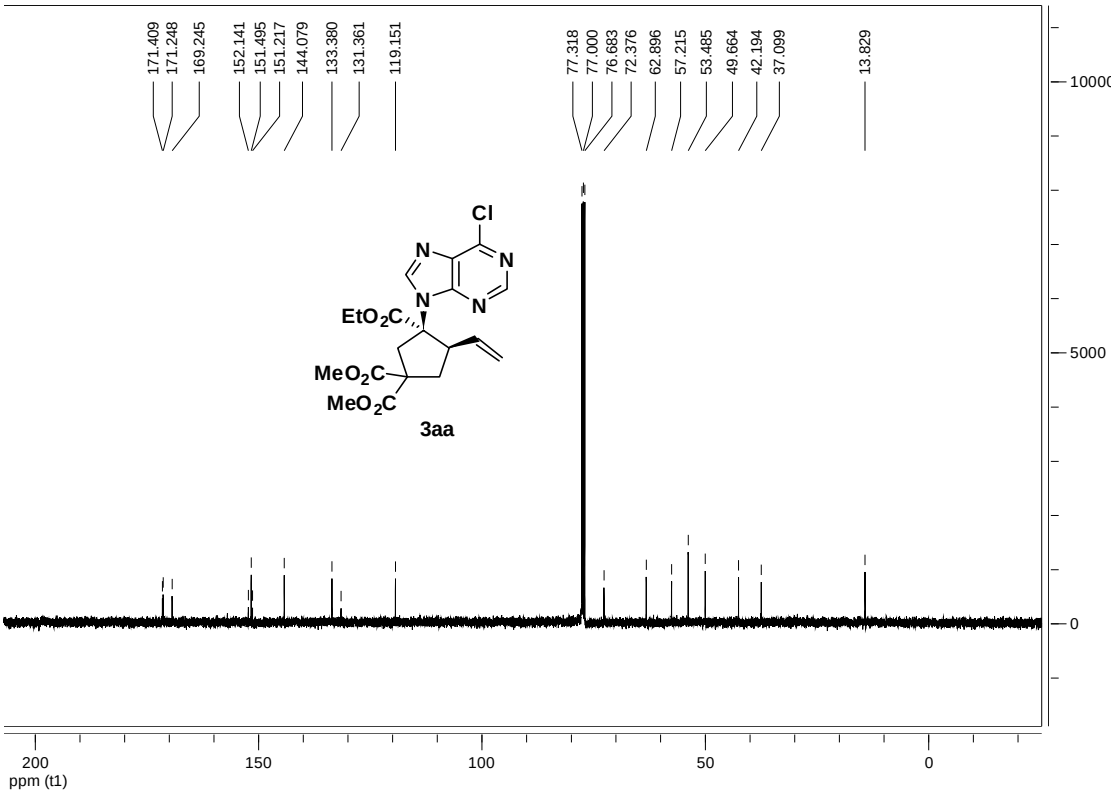

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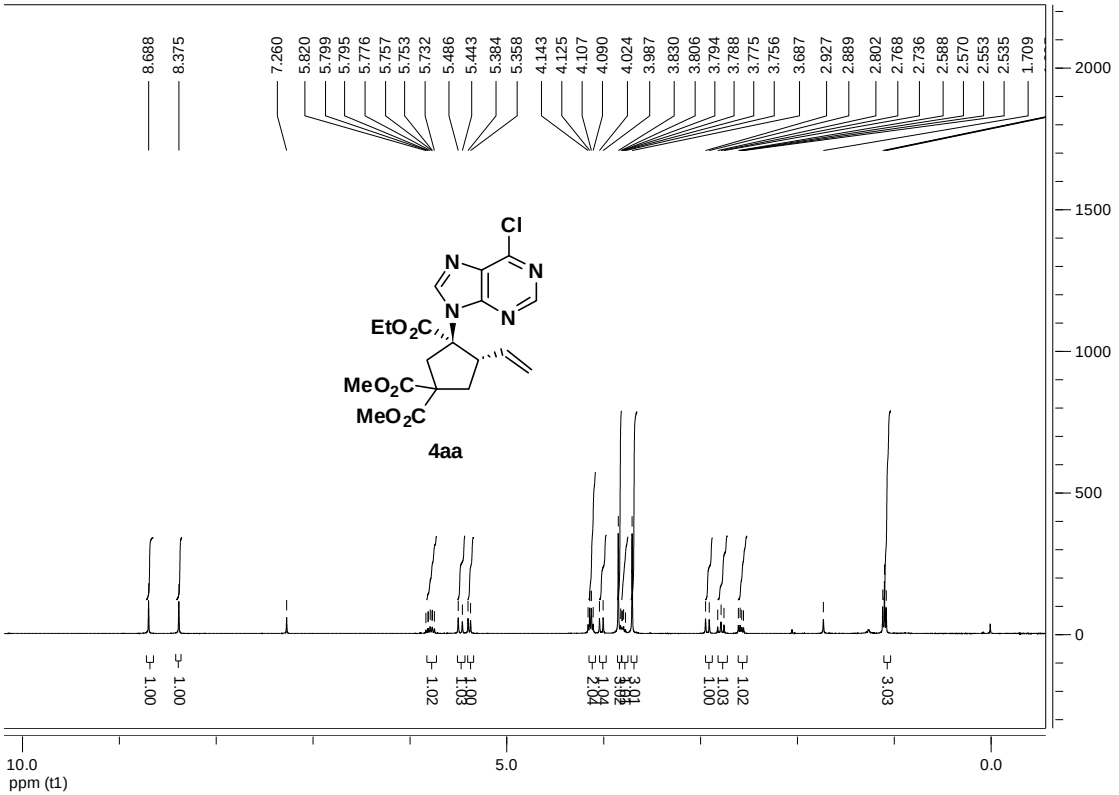

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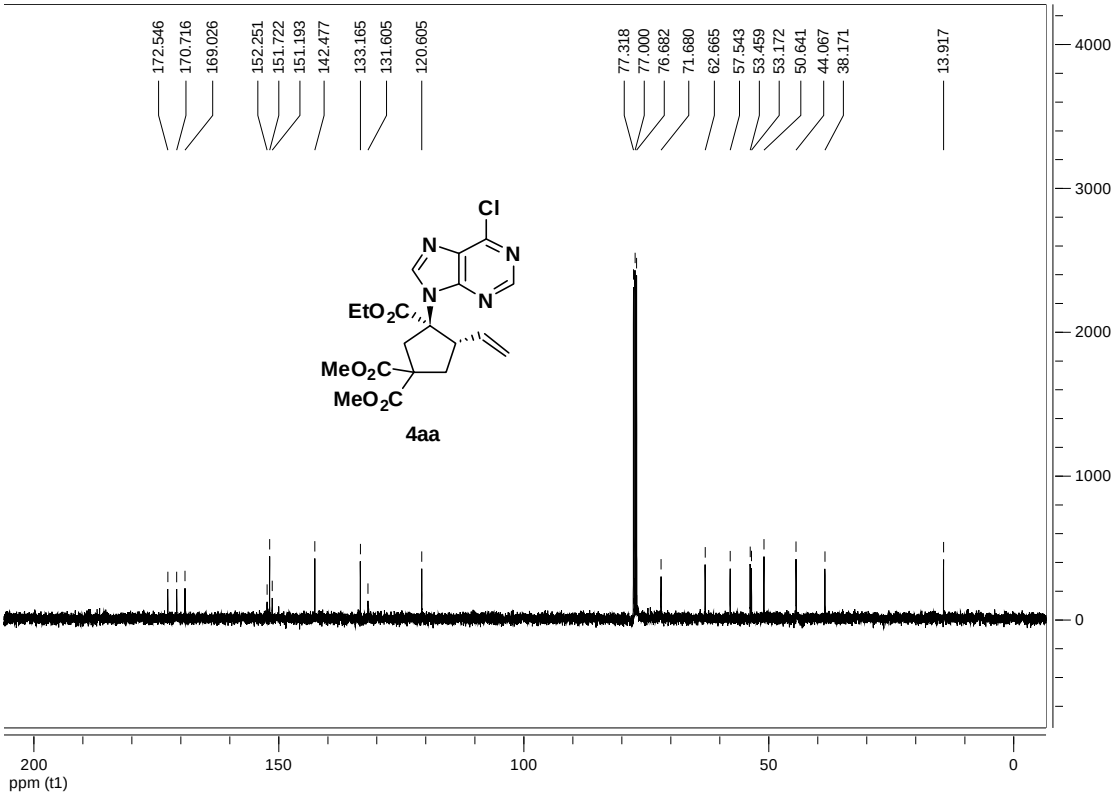

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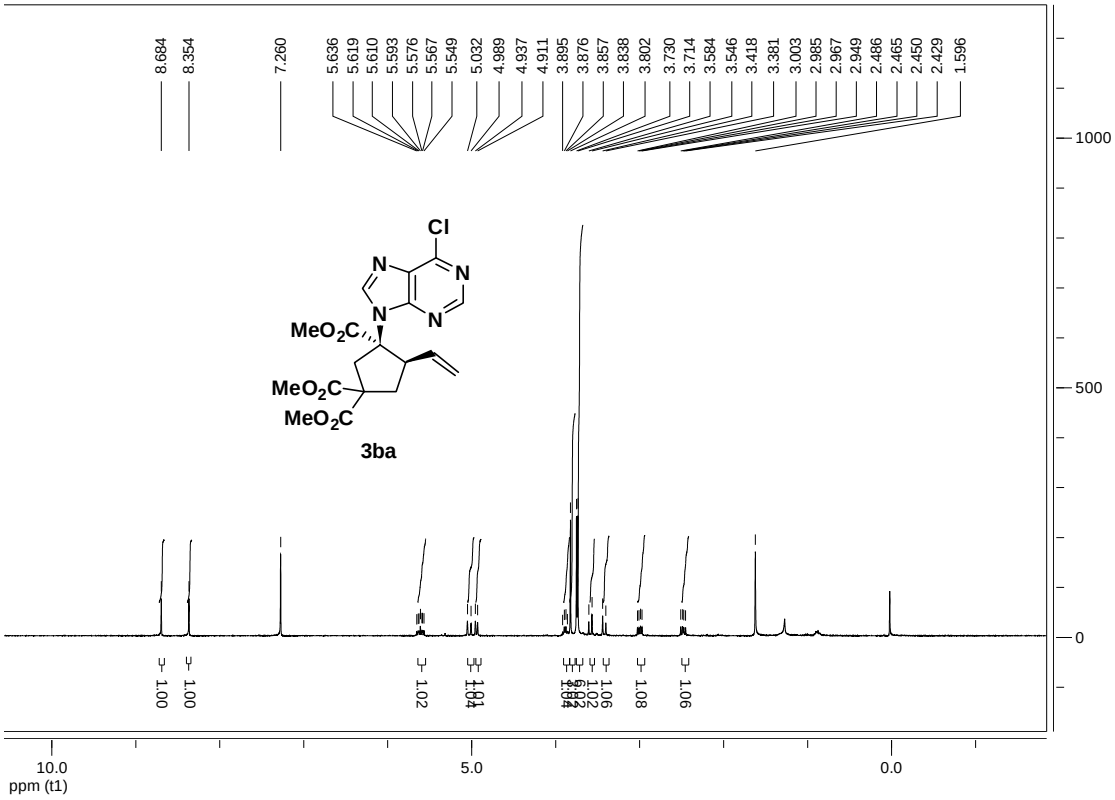

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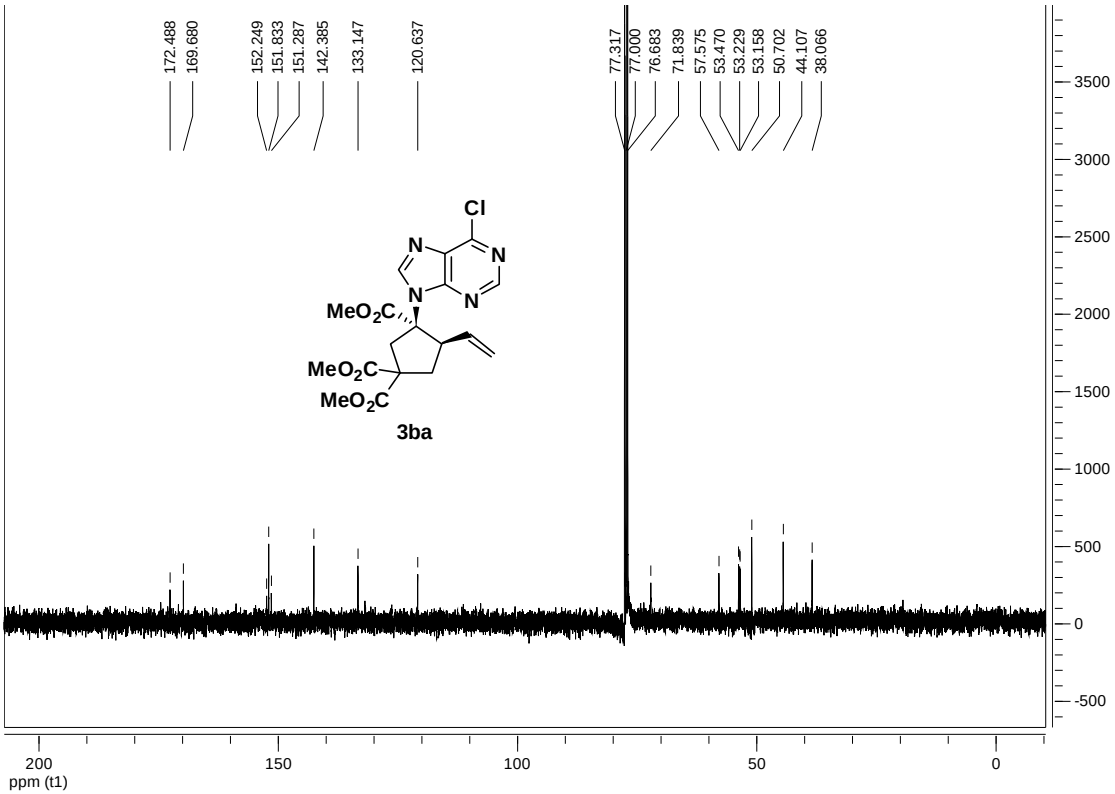

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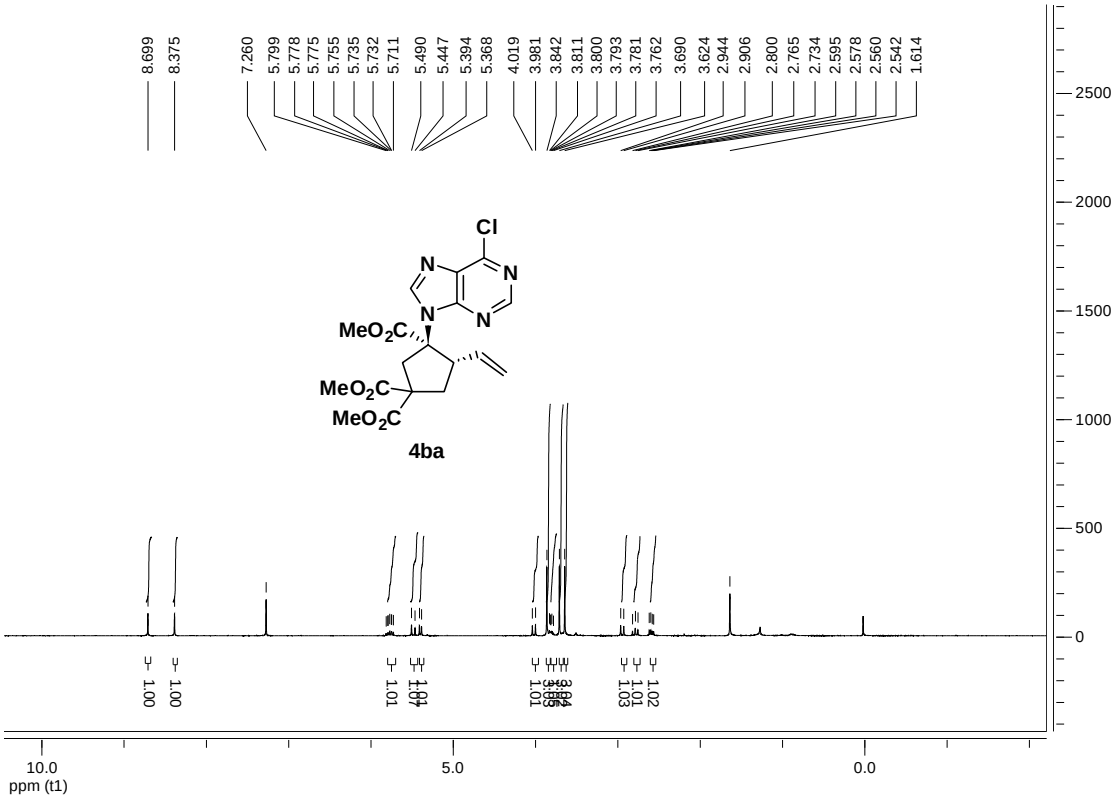

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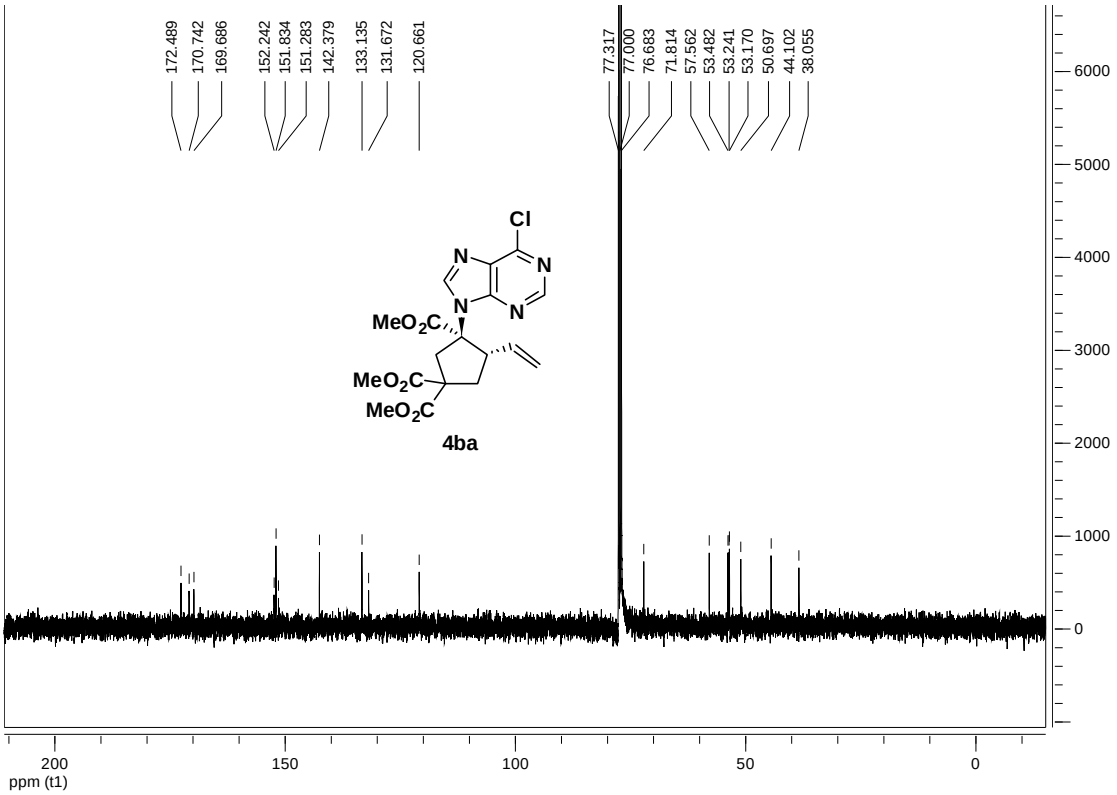

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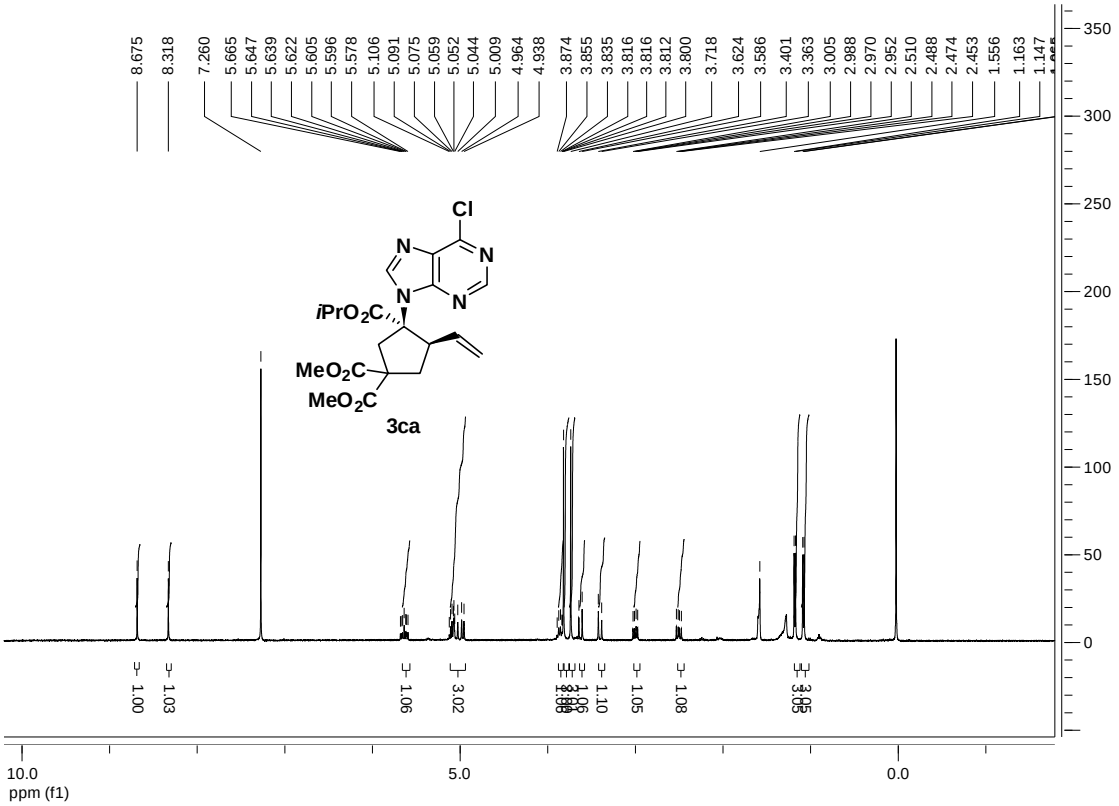

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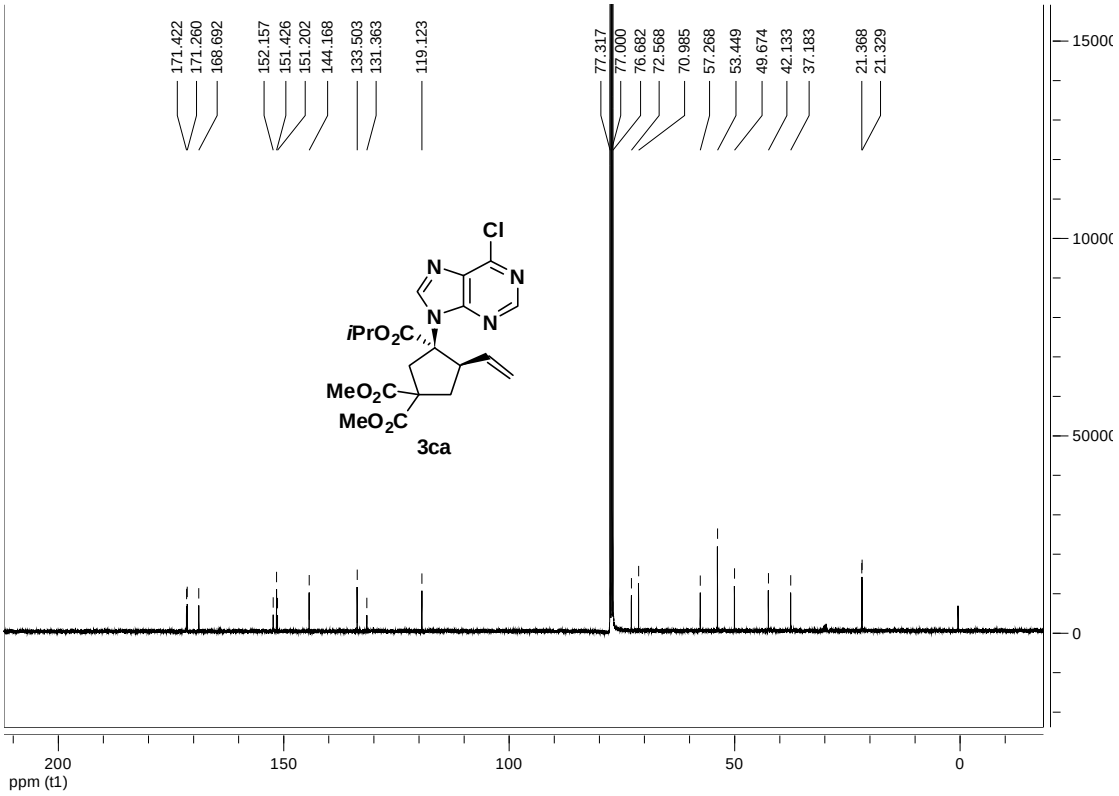

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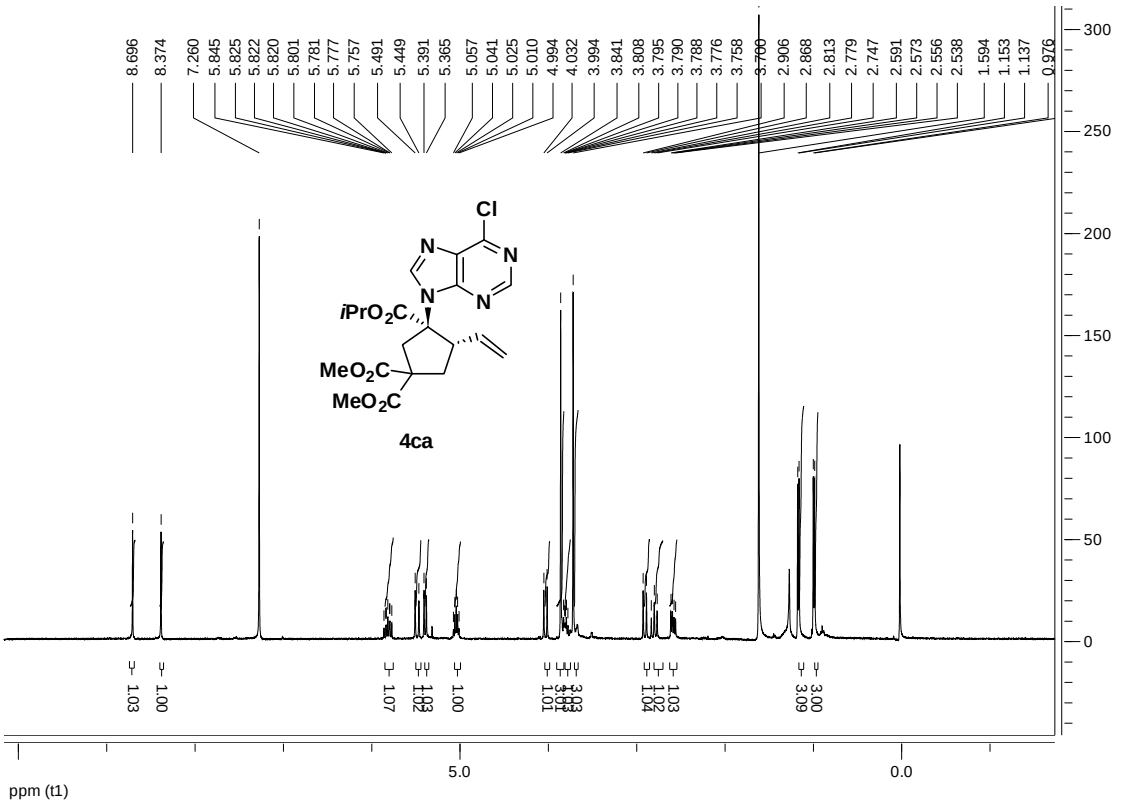

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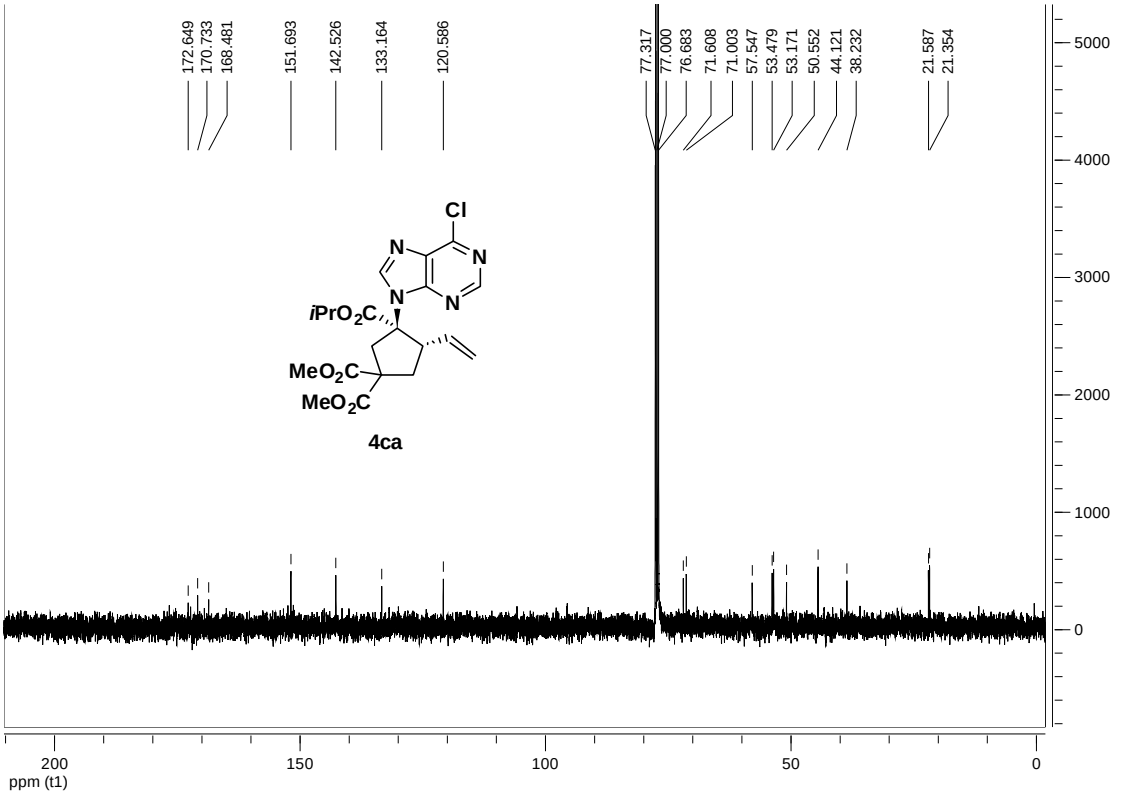
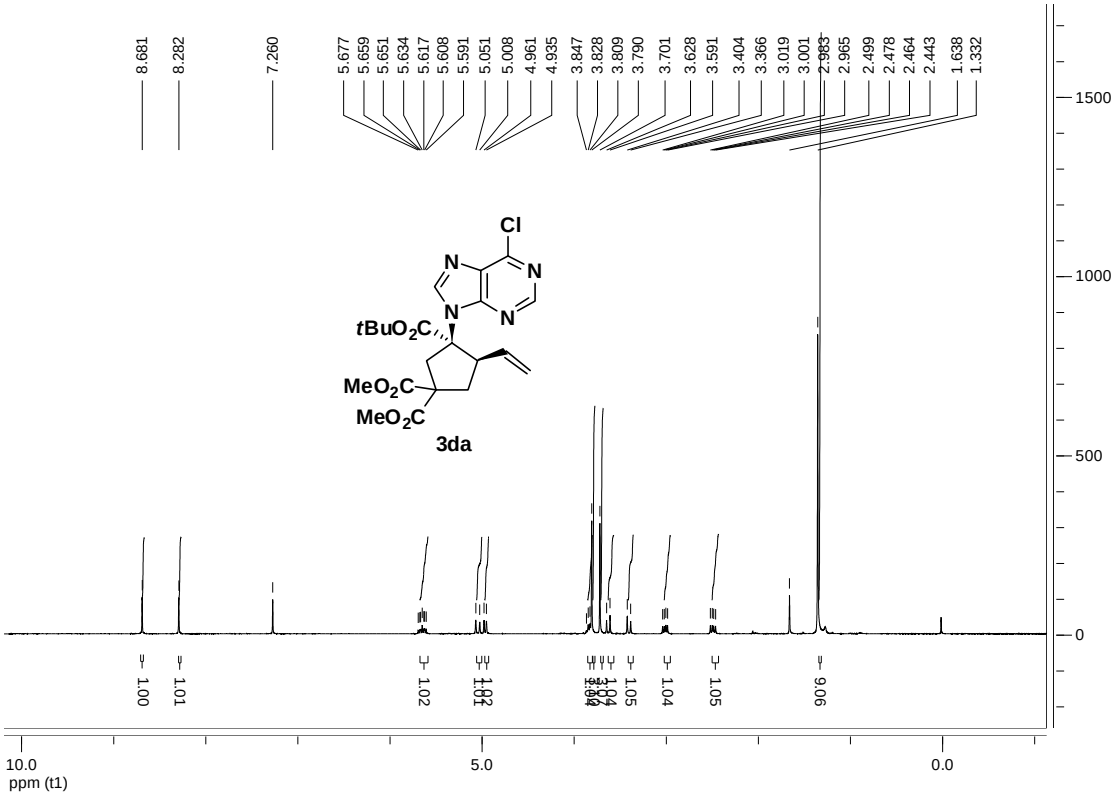
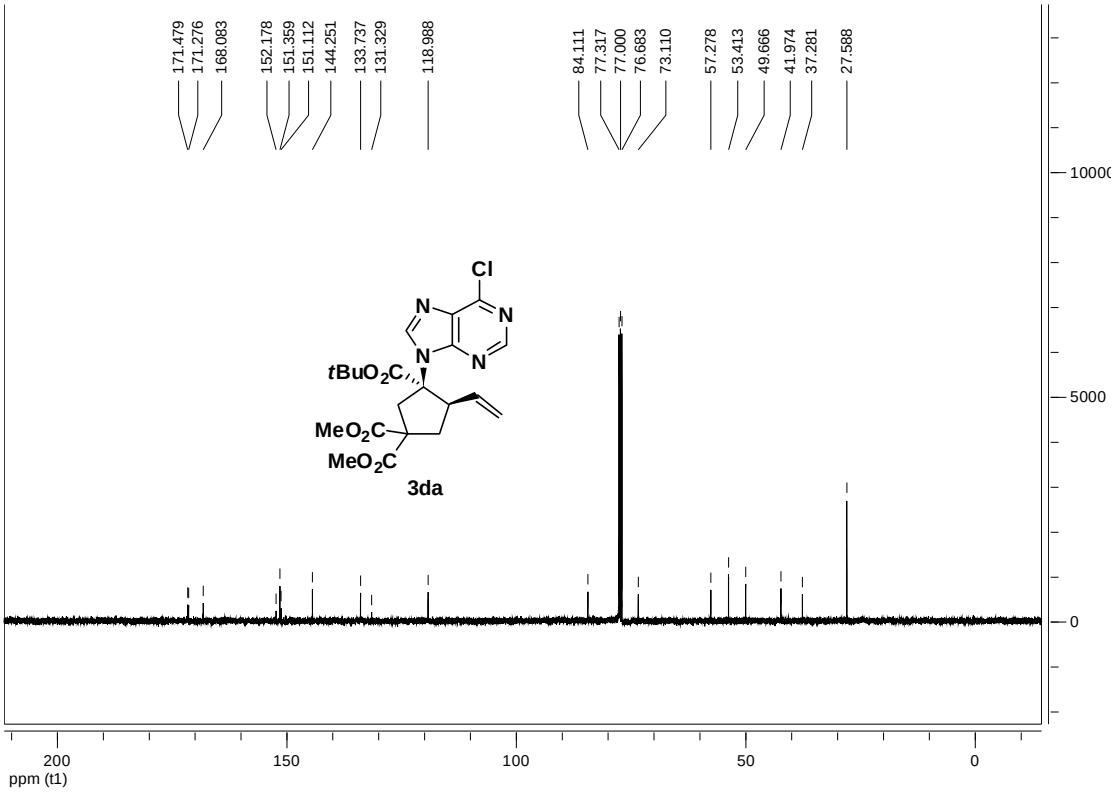


^{1}H-NMR for 3da



^{13}C-NMR for 3da



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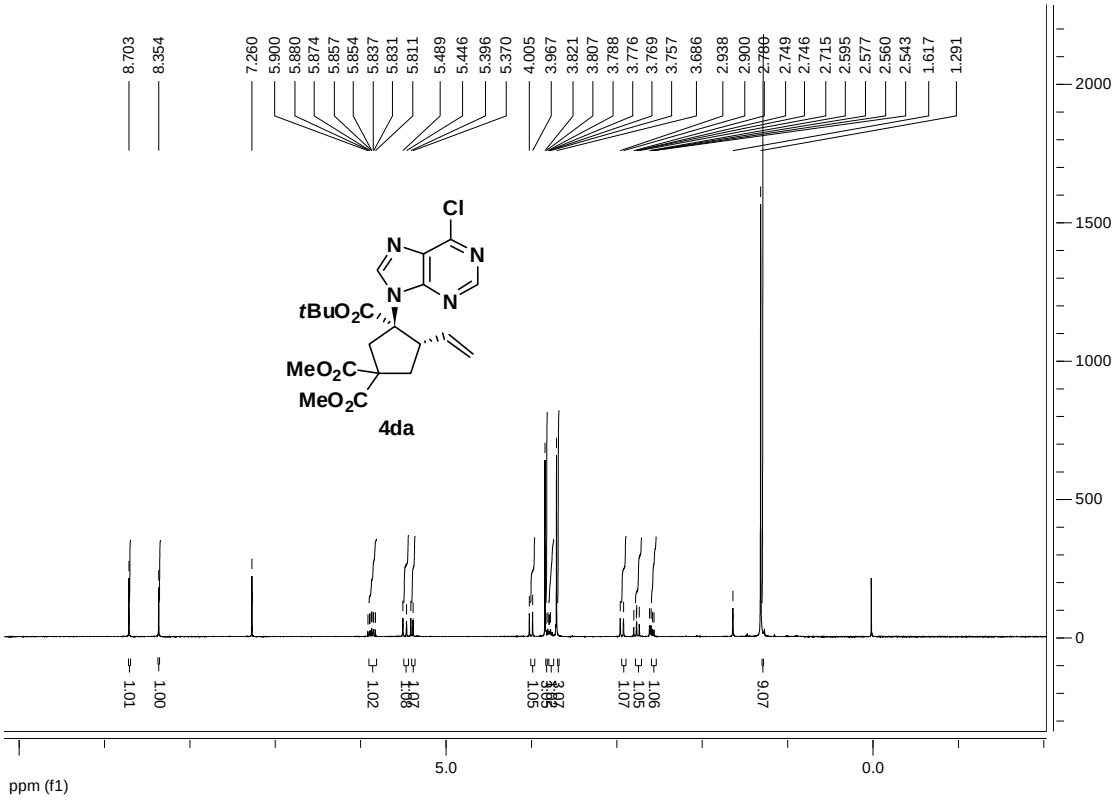
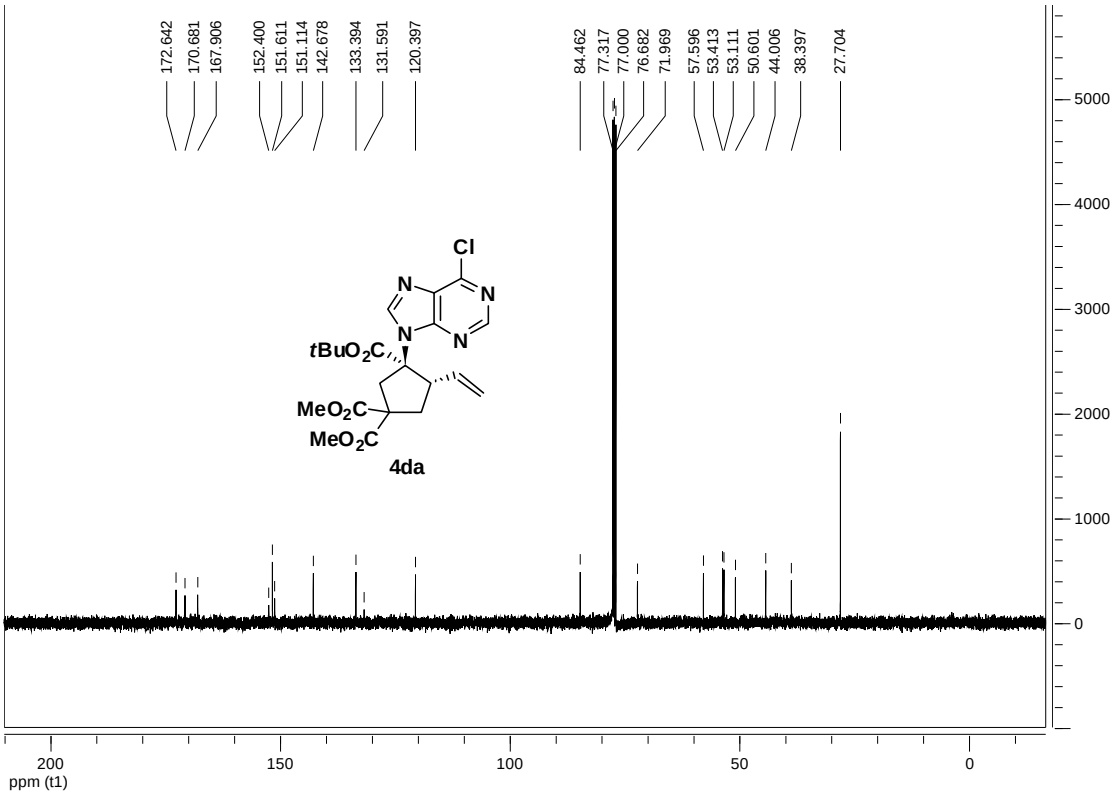
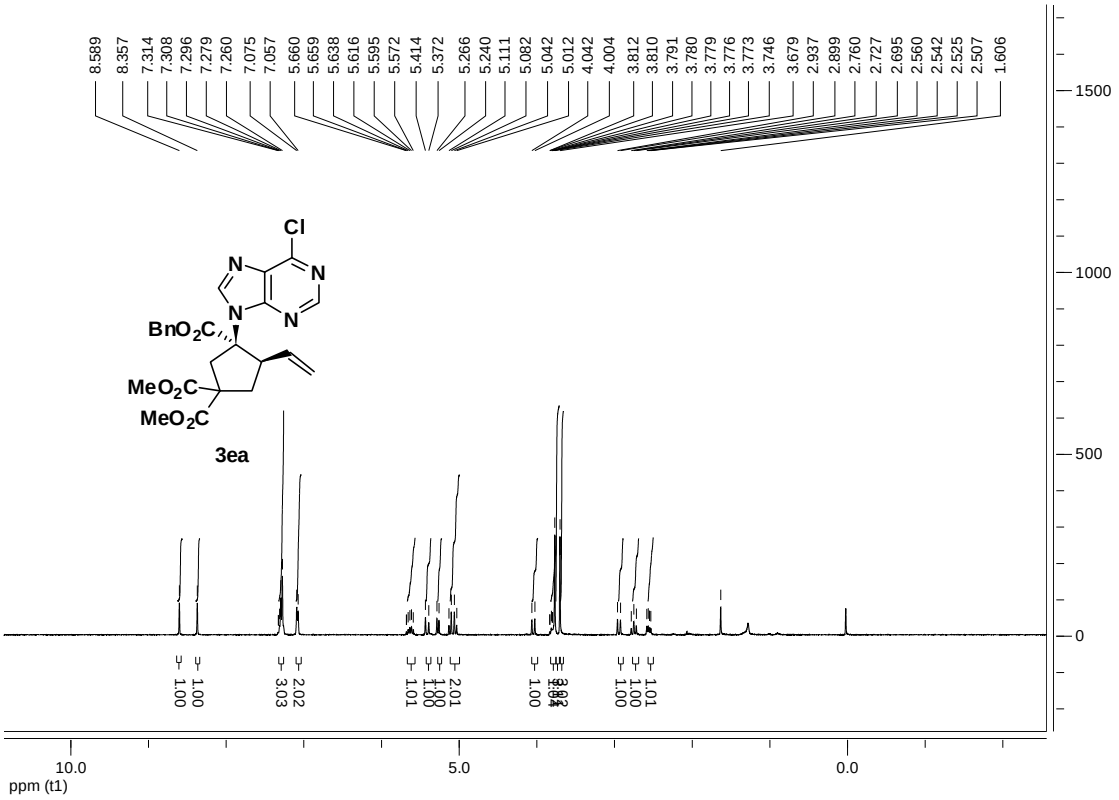


^{13}C-NMR for 4da



^{1}H-NMR for 3ea



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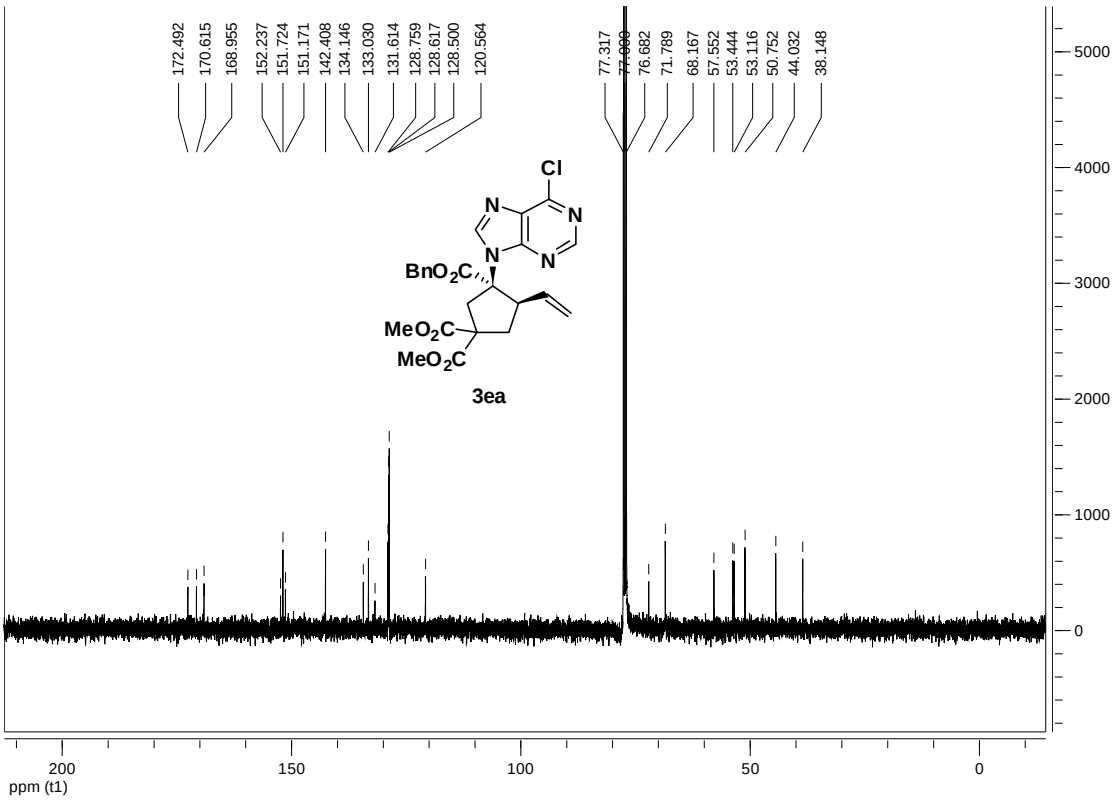

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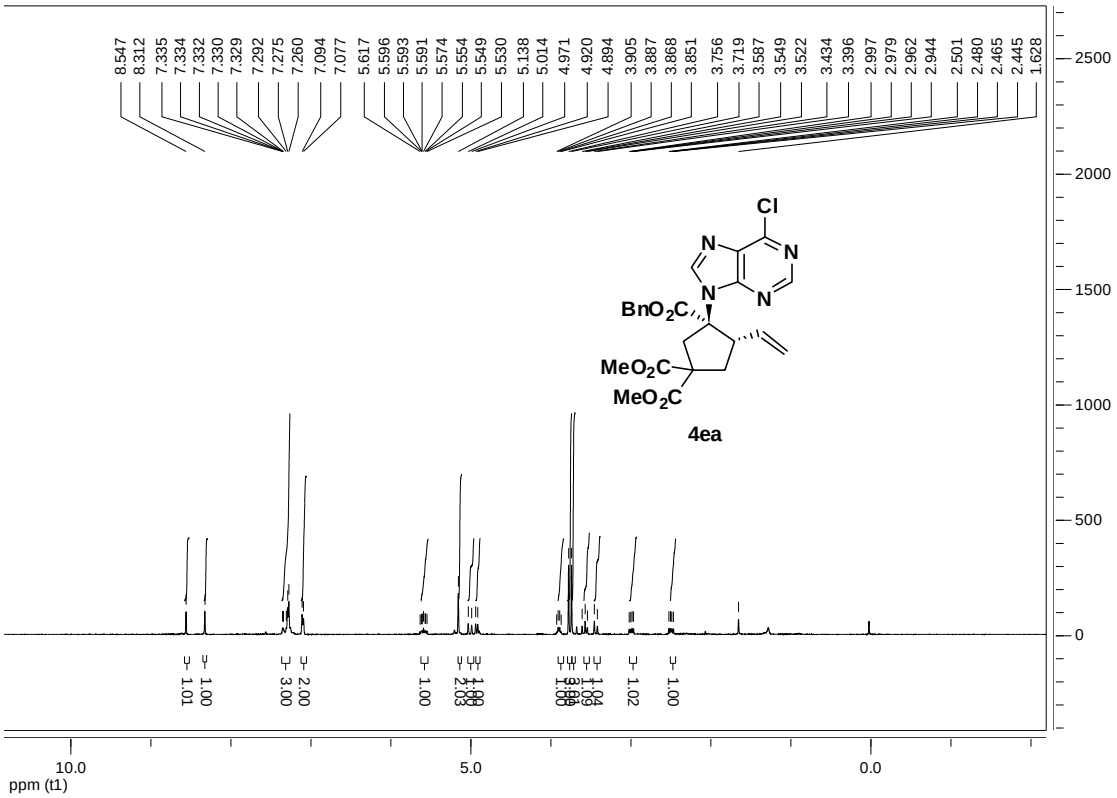

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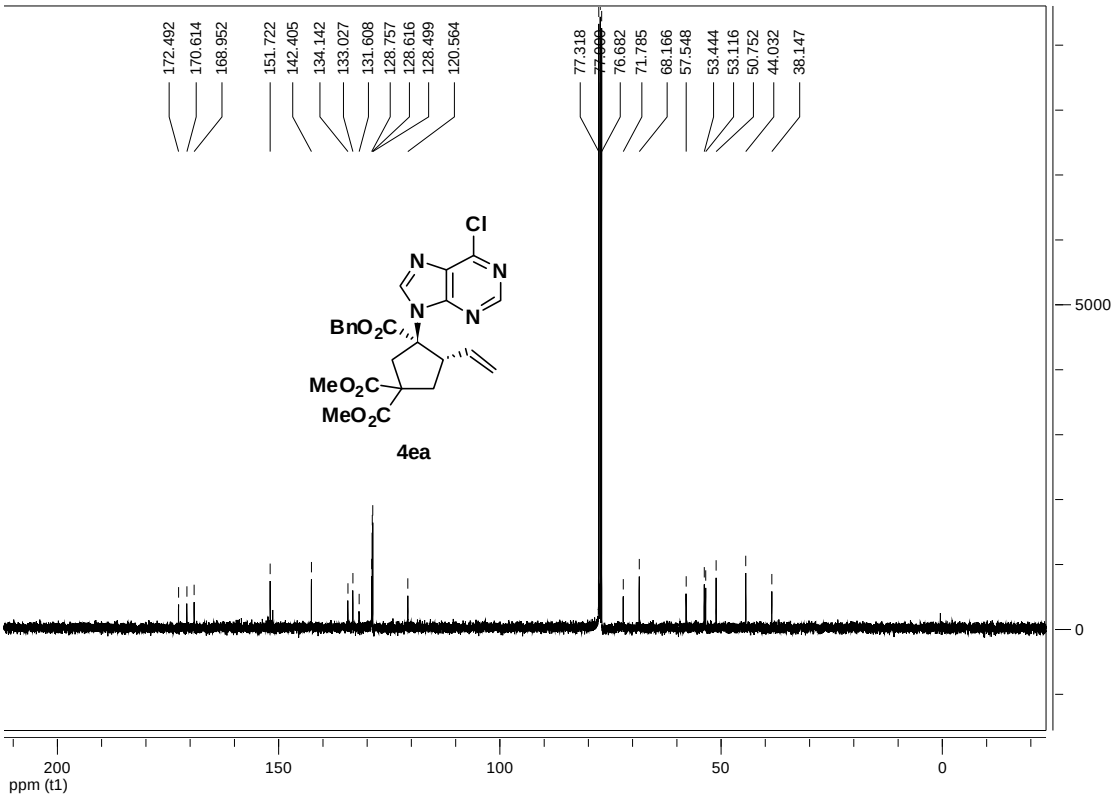
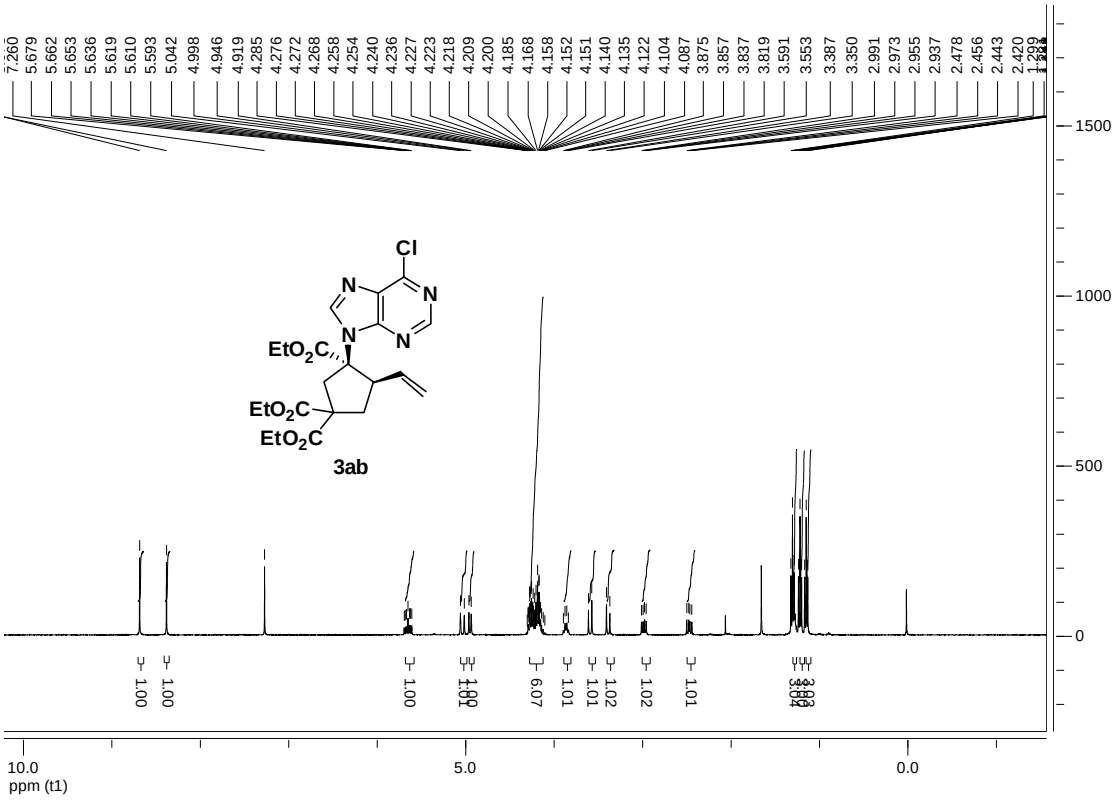
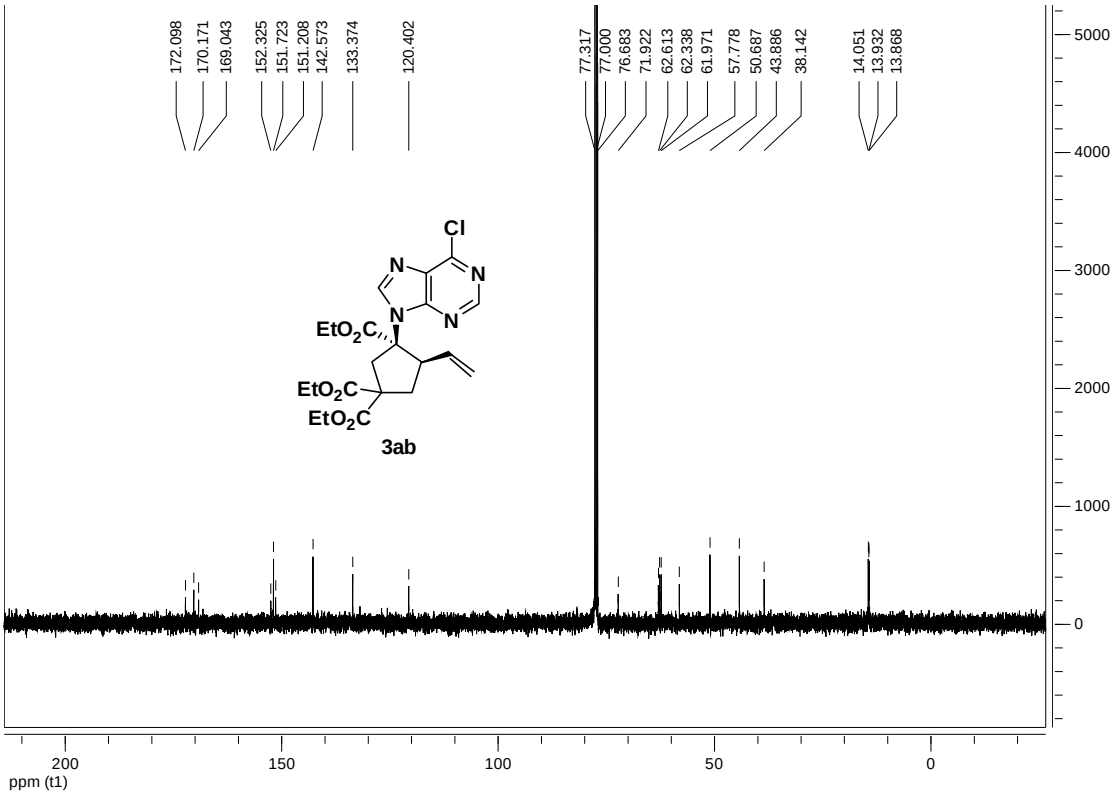


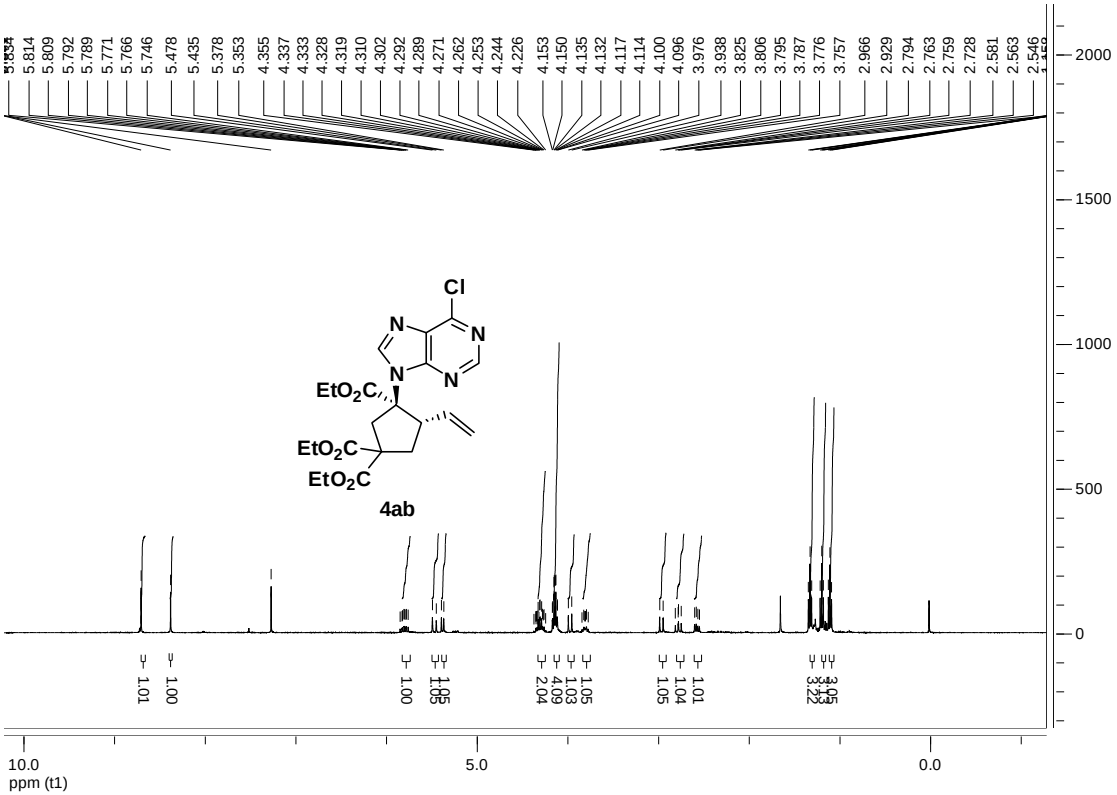
^{1}H-NMR for 3ab



^{13}C-NMR for 3ab



^{1}H-NMR for 4ab



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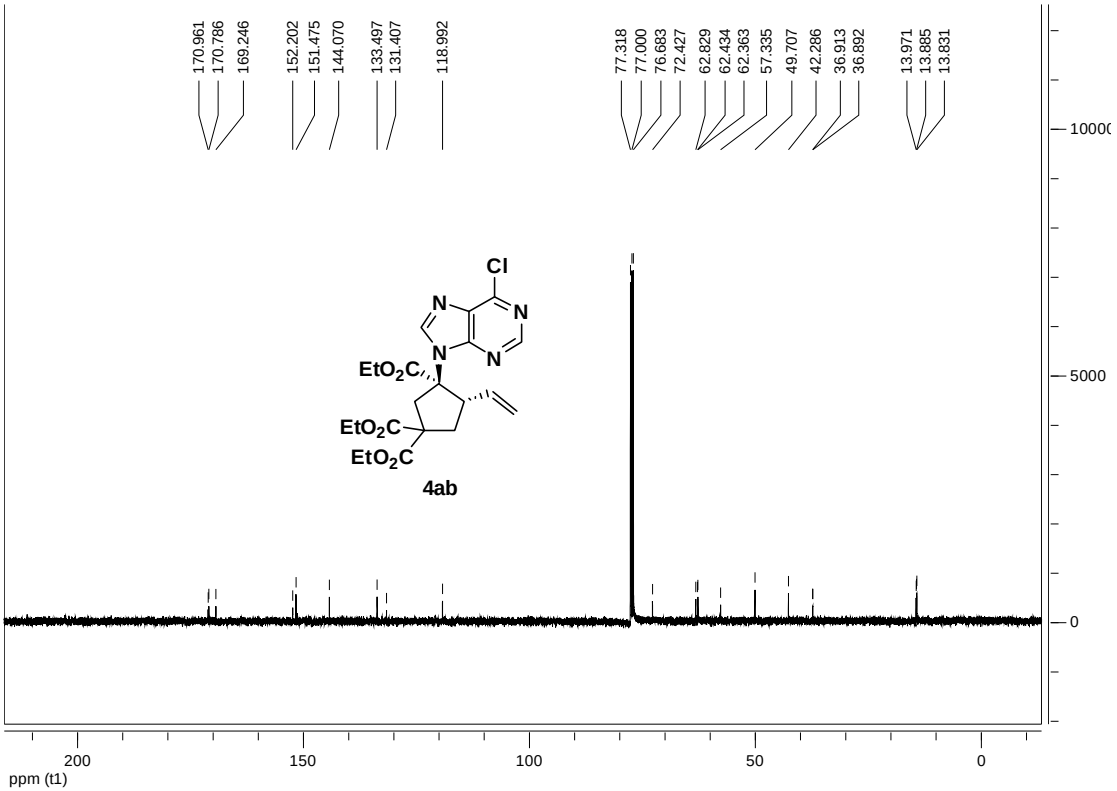
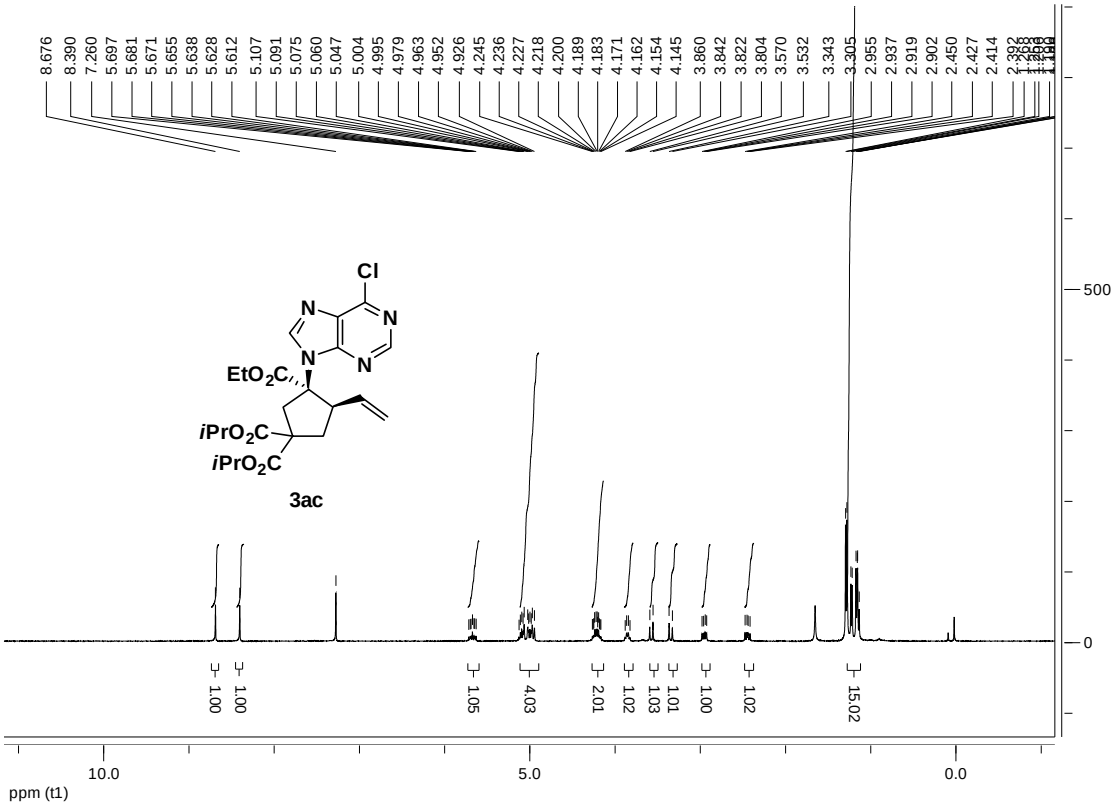
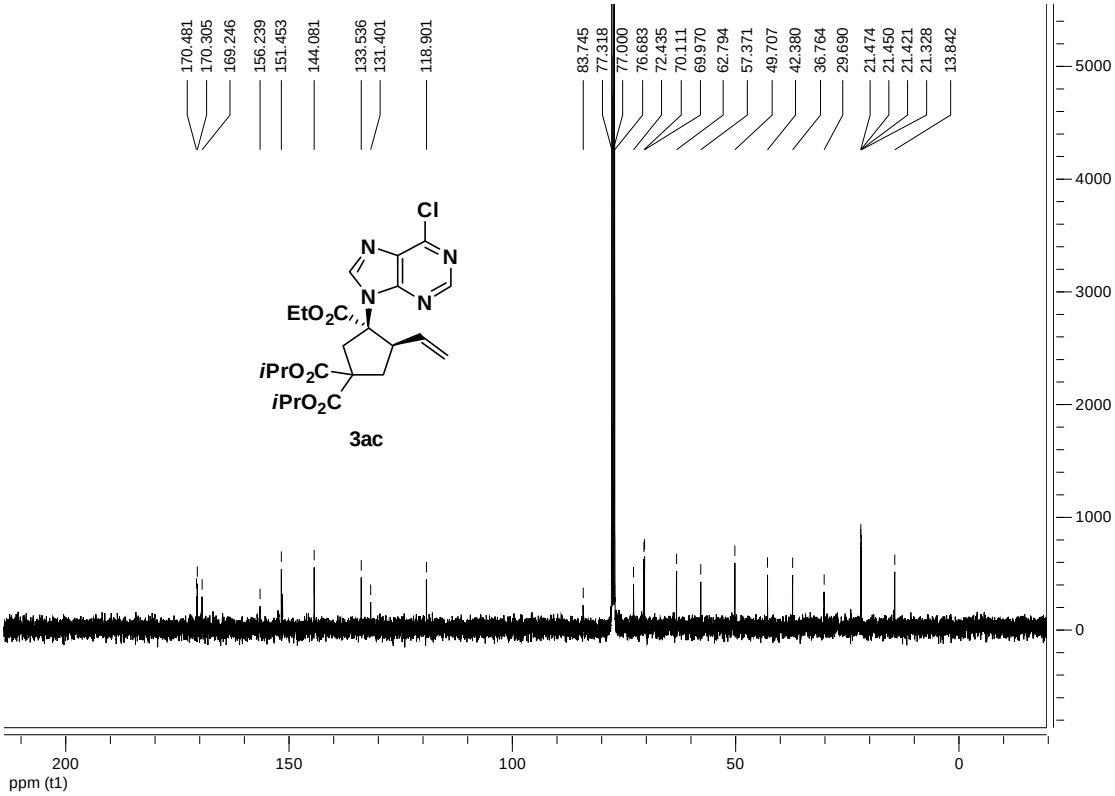


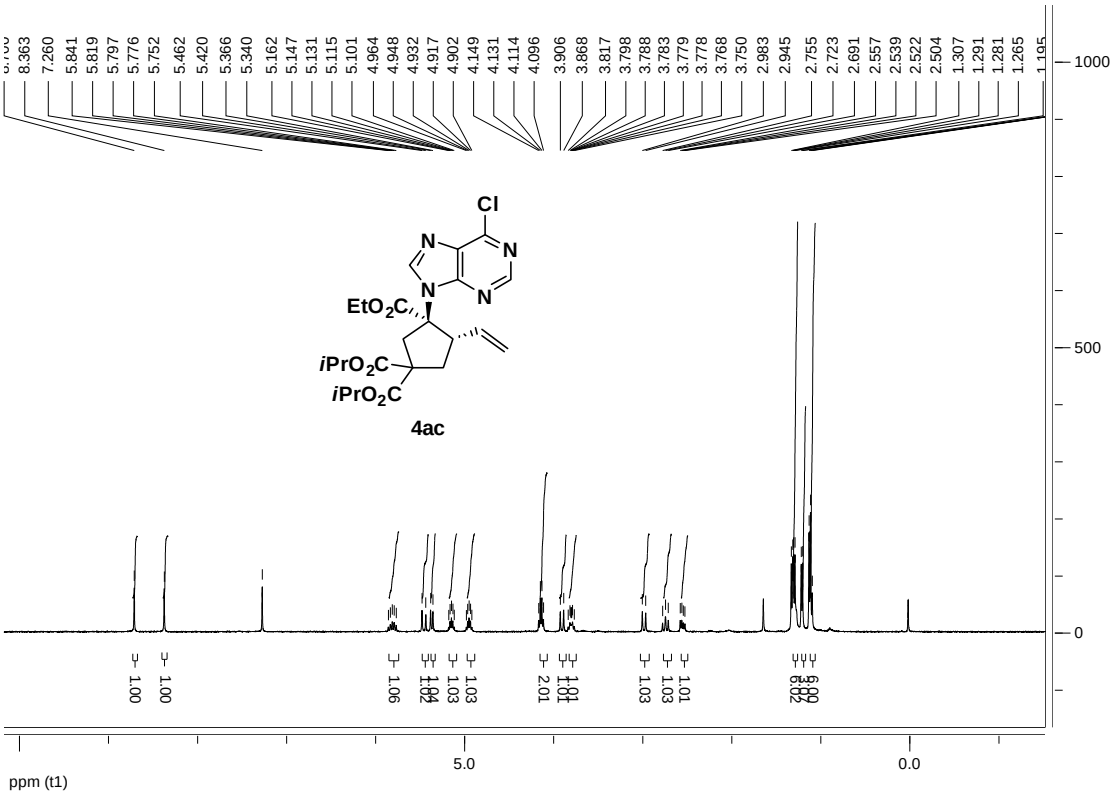
^{1}H-NMR for 3ac



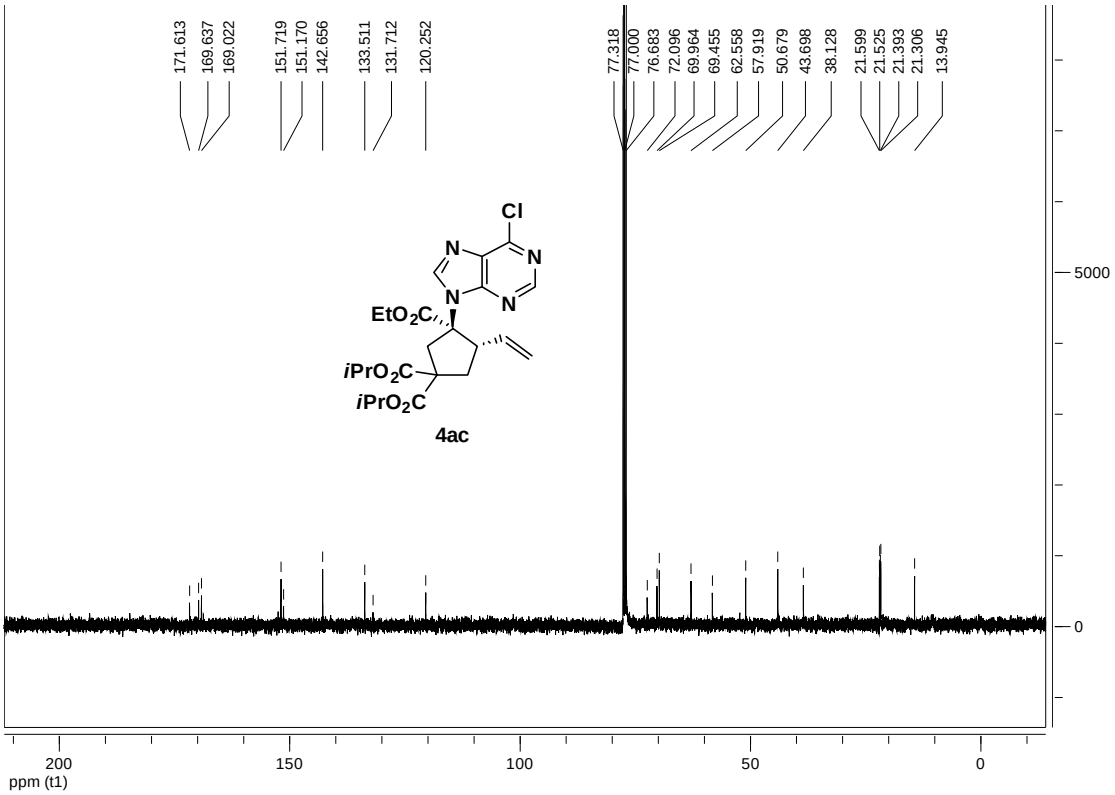
^{13}C-NMR for 3ac



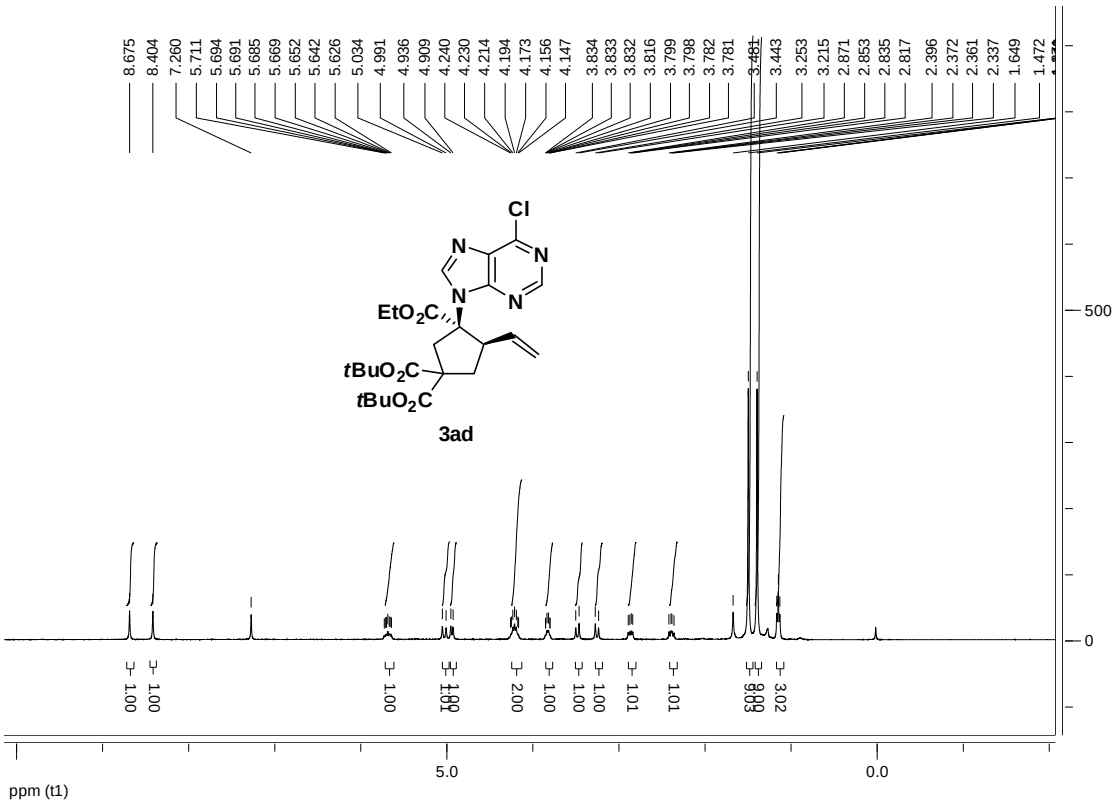
^{1}H-NMR for 4ac



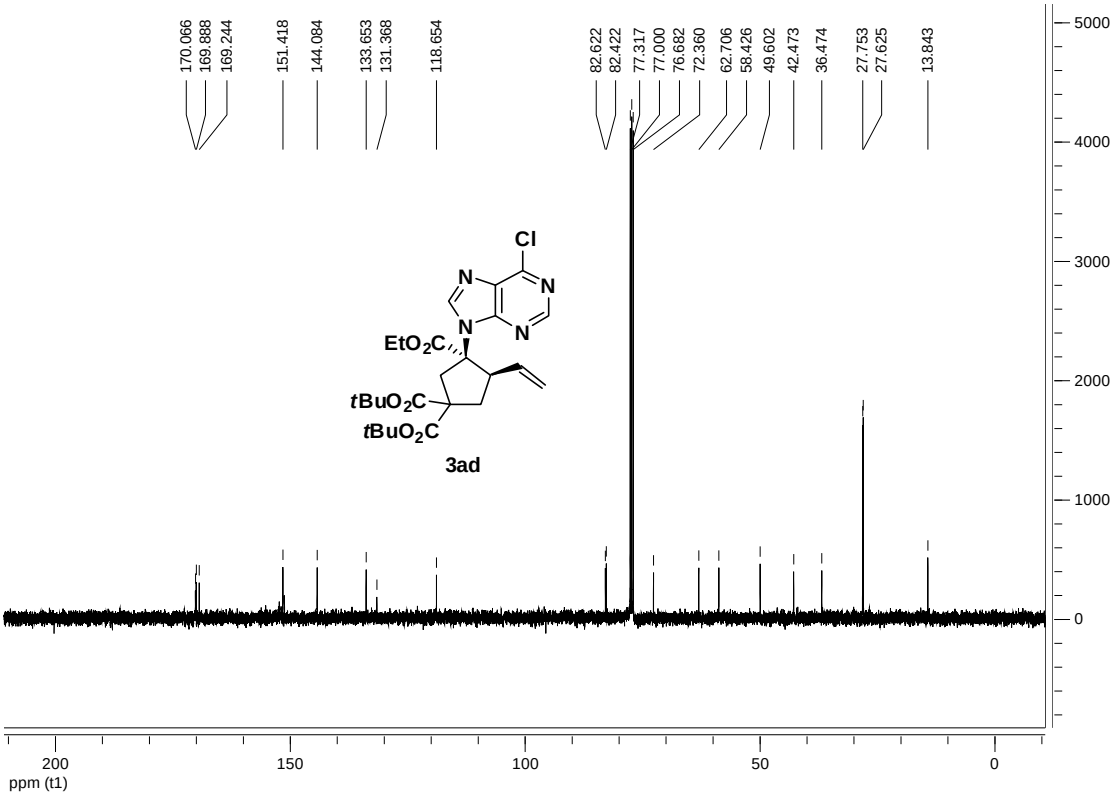
^{13}C-NMR for 4ac



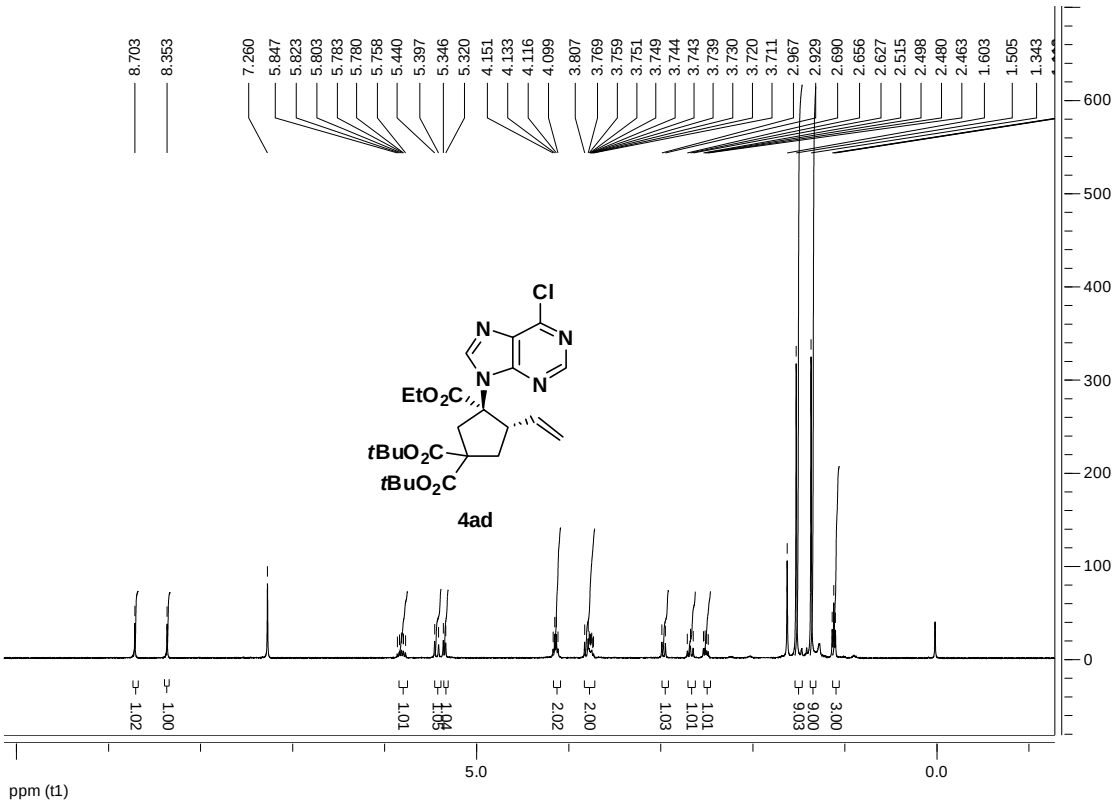
^{1}H-NMR for 3ad



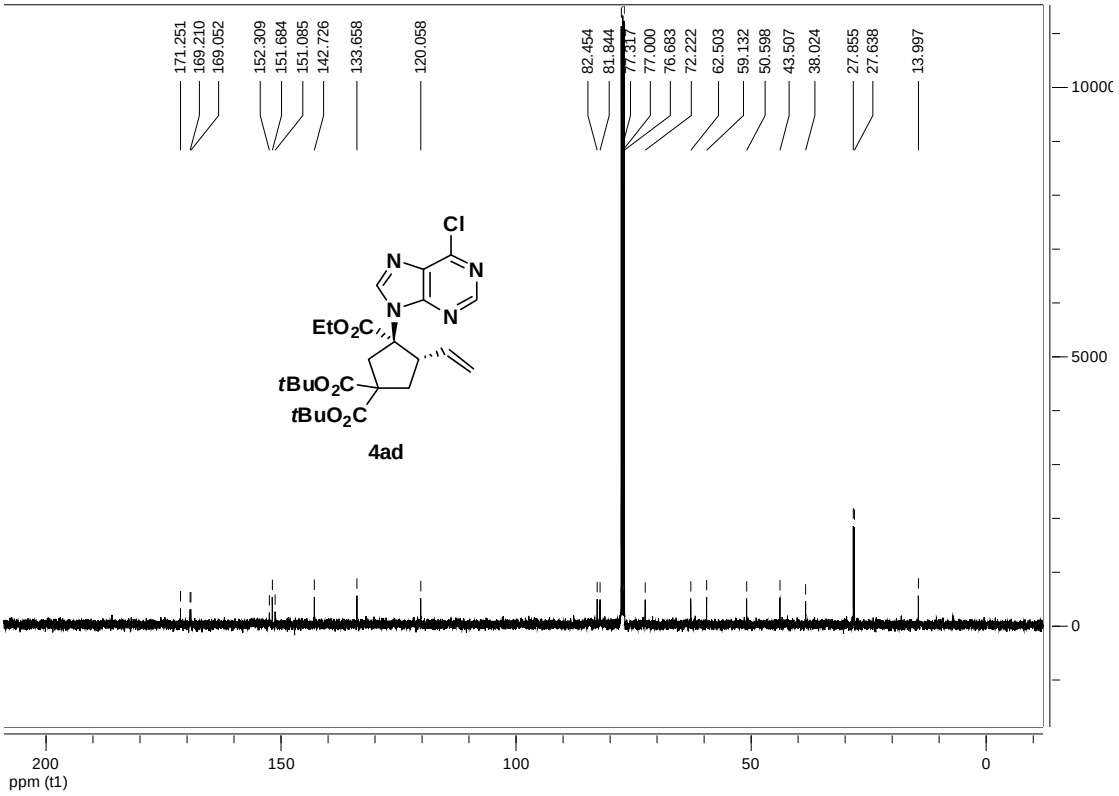
^{13}C-NMR for 3ad



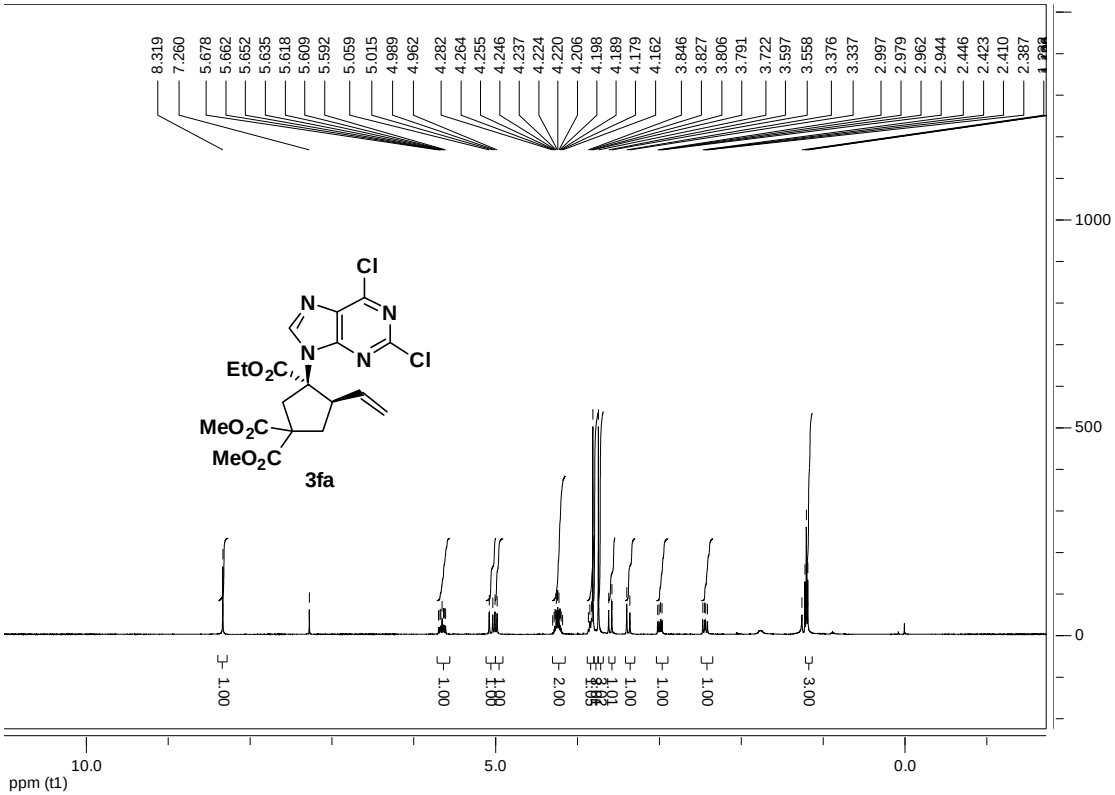
^{1}H-NMR for 4ad



^{13}C-NMR for 4ad



^{1}H-NMR for 3fa



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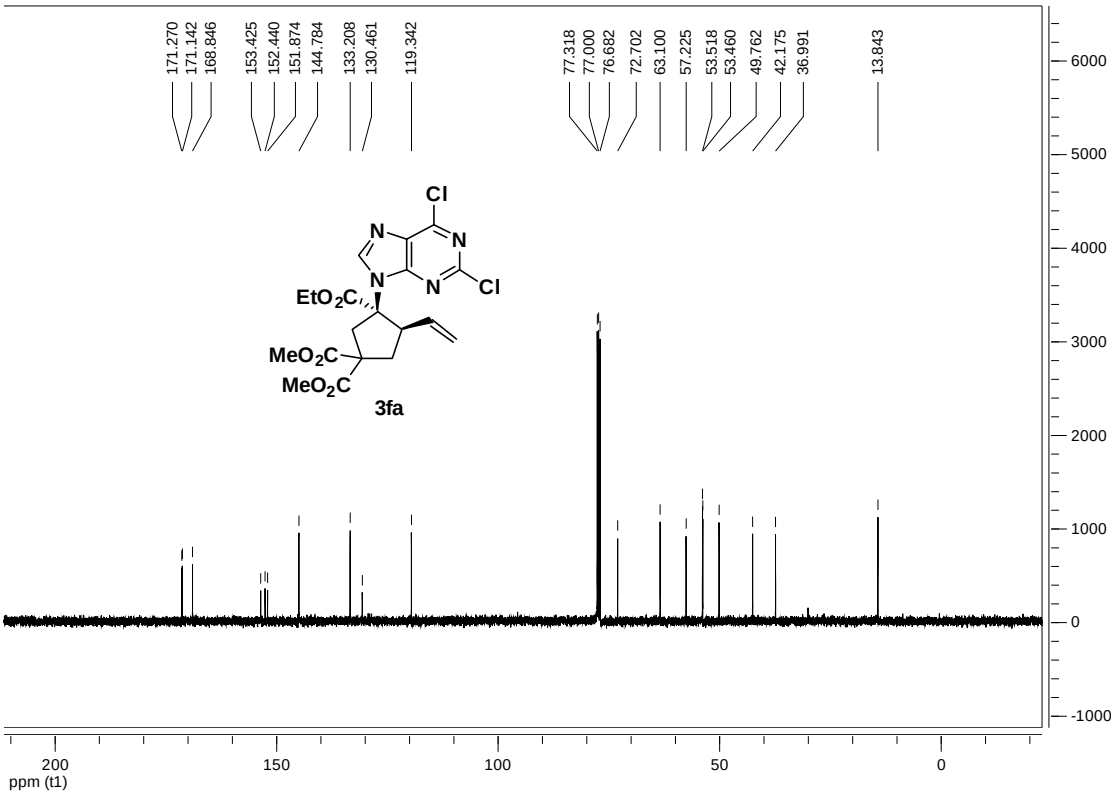

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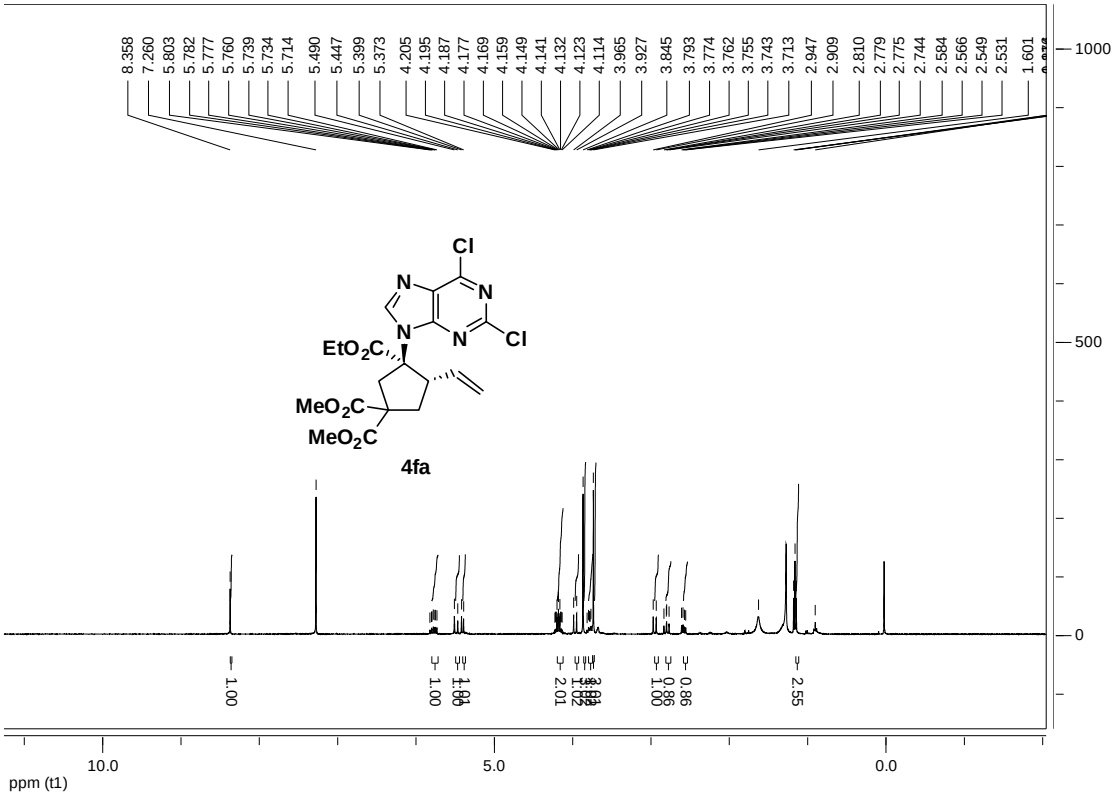

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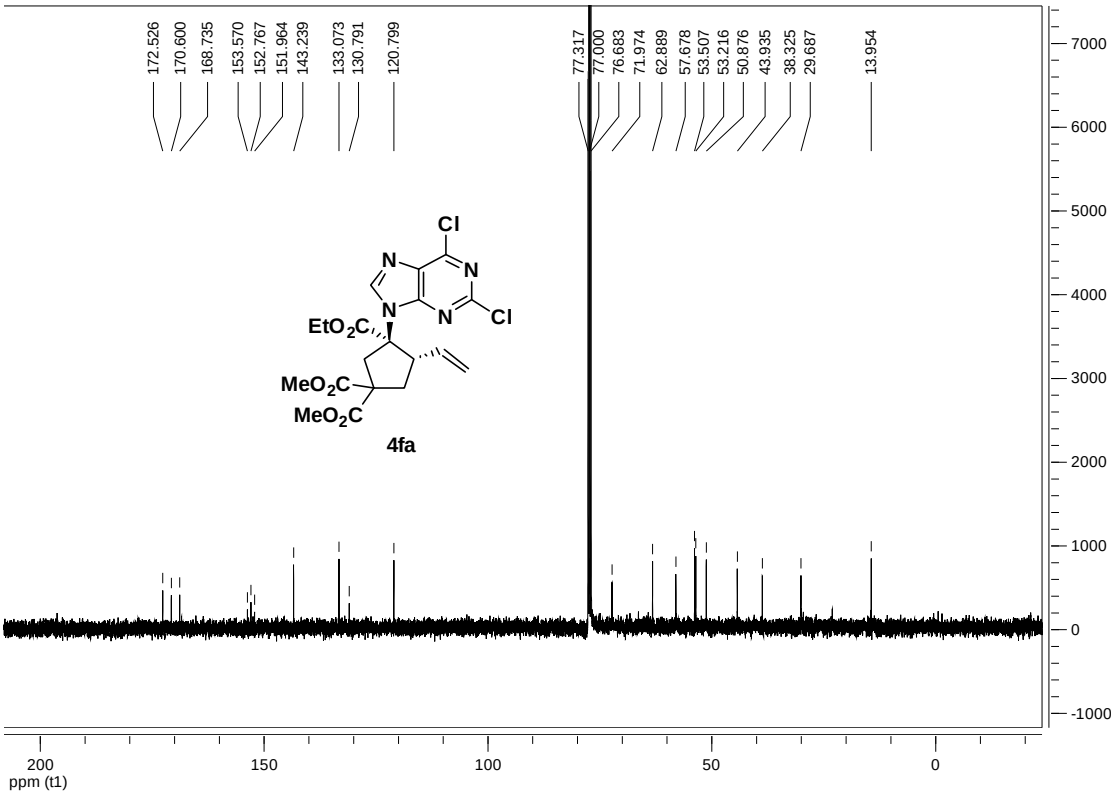
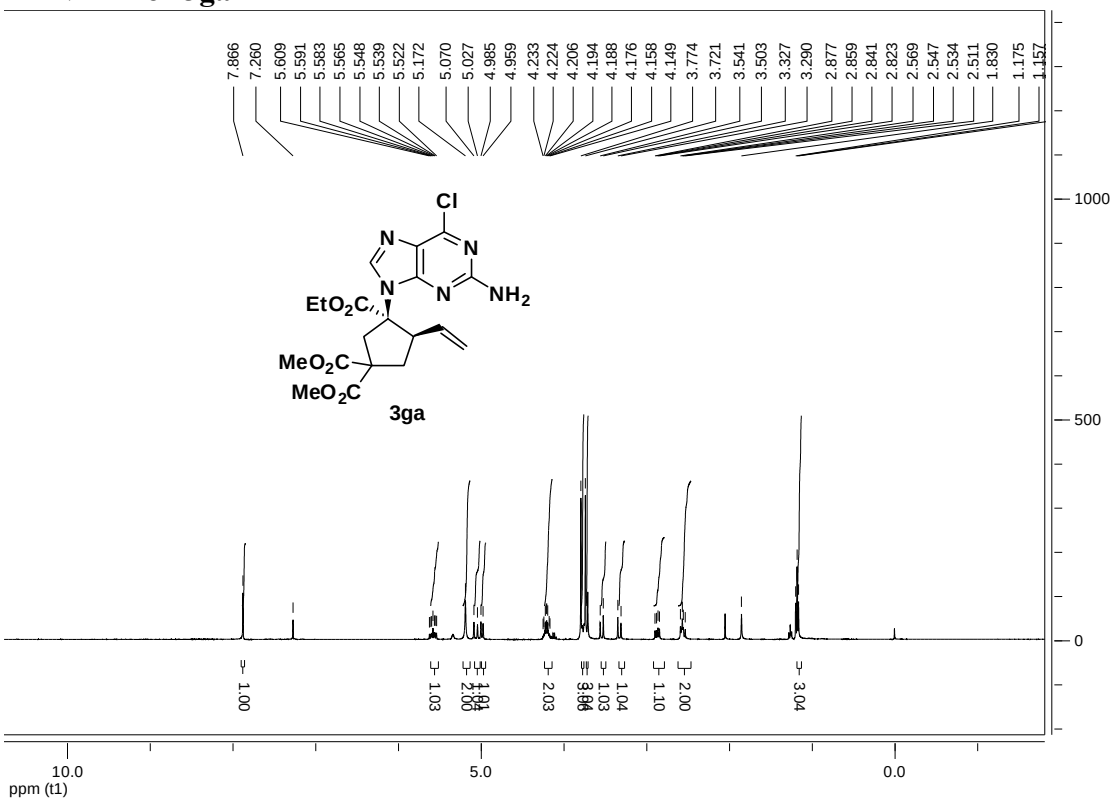
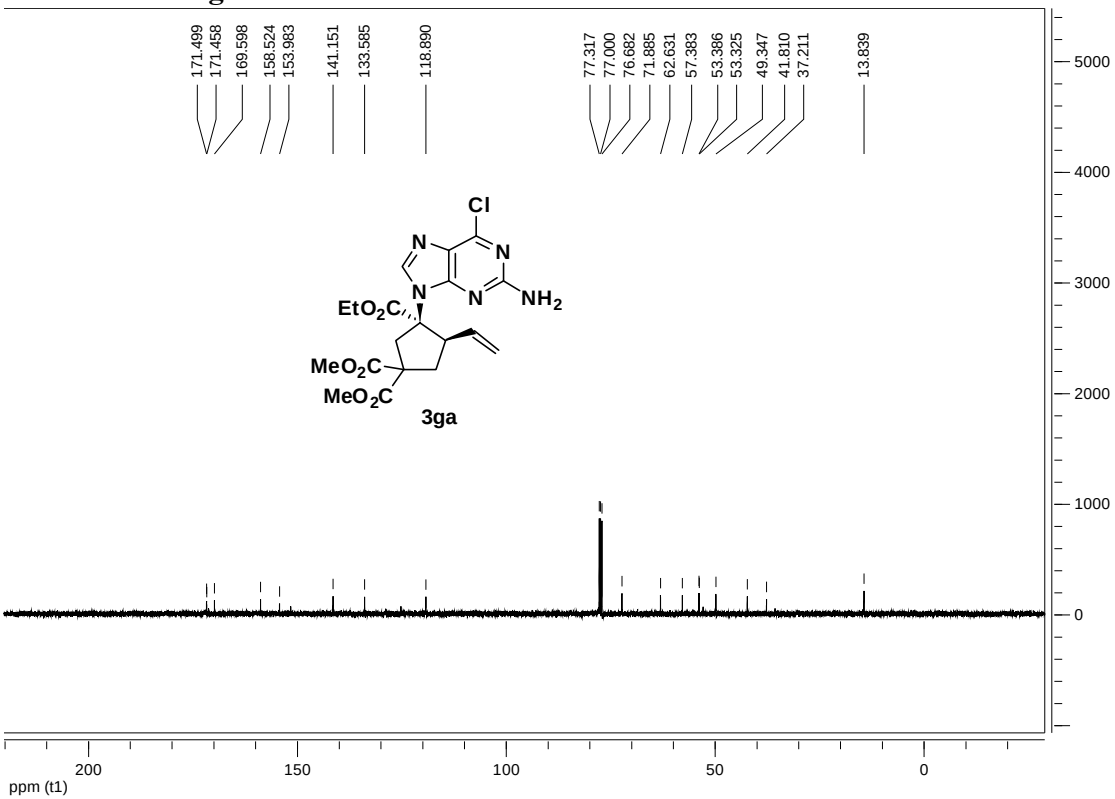


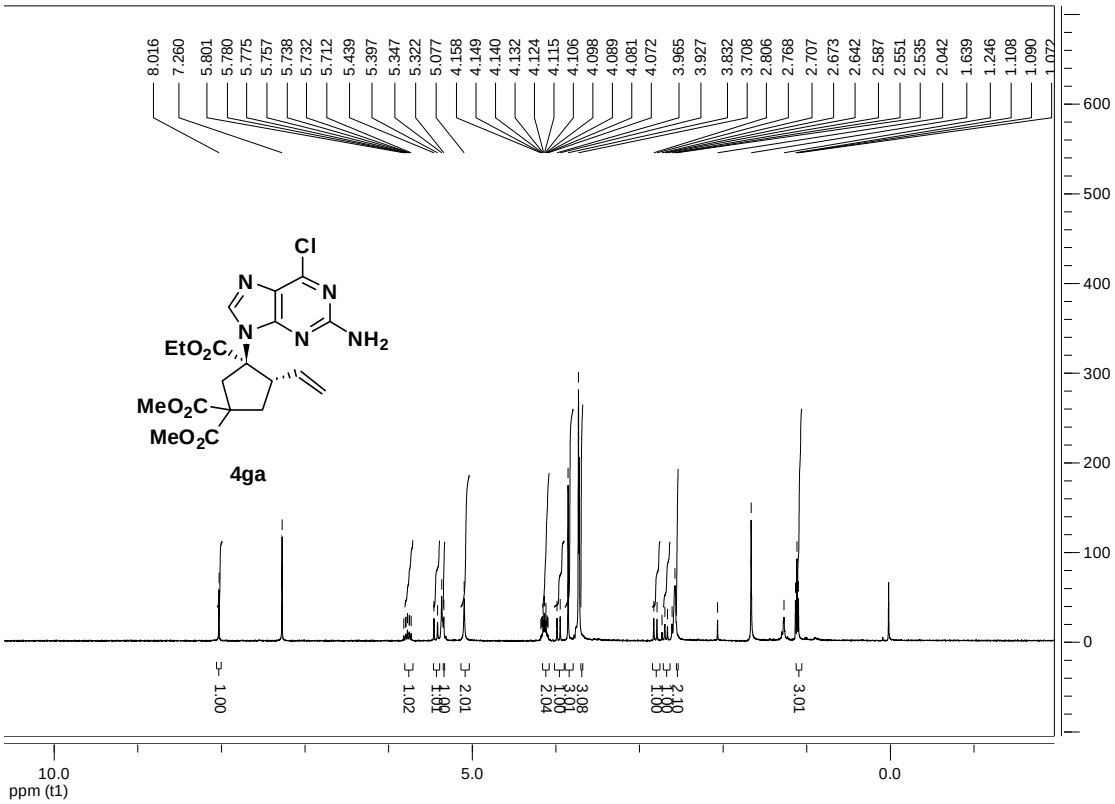
^{1}H-NMR for 3ga



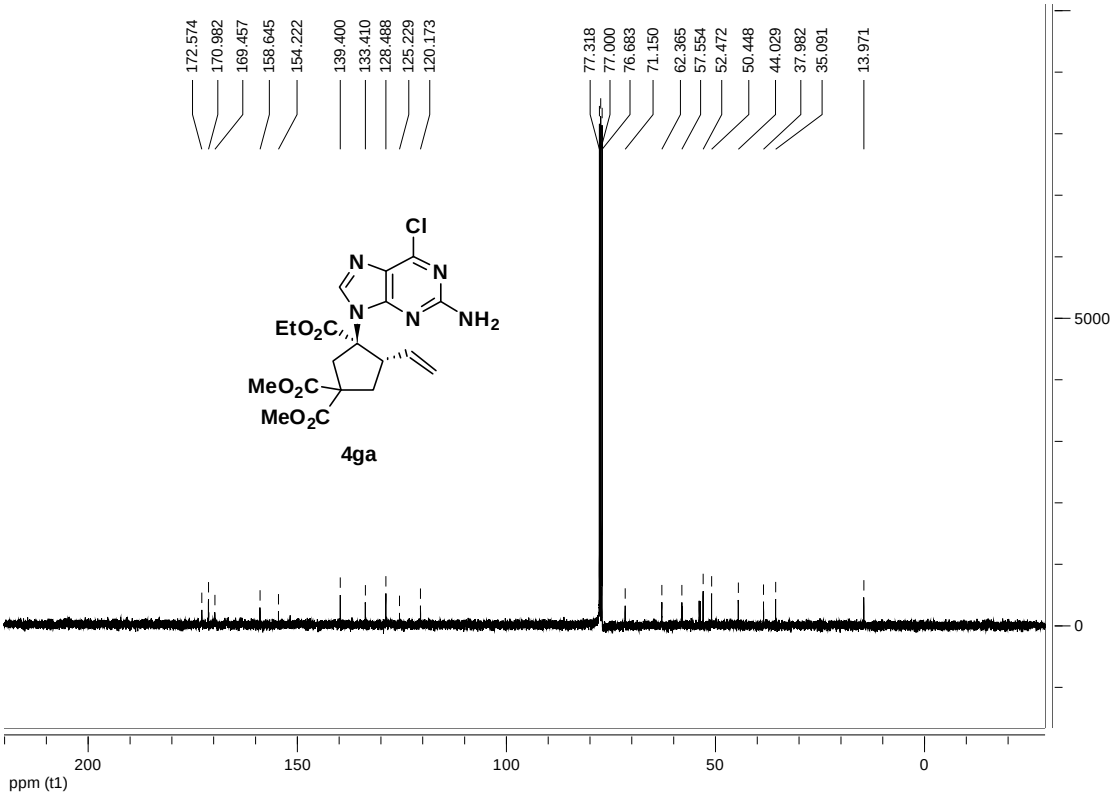
^{13}C-NMR for 3ga



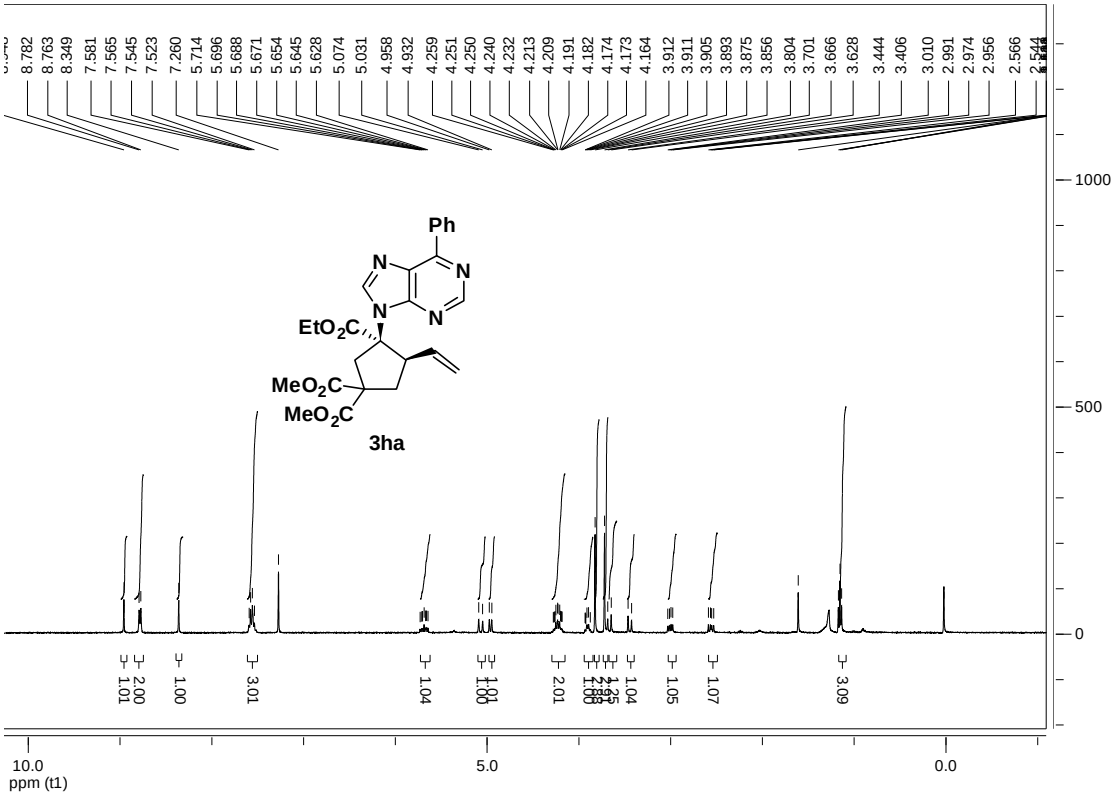
^{1}H-NMR for 4ga



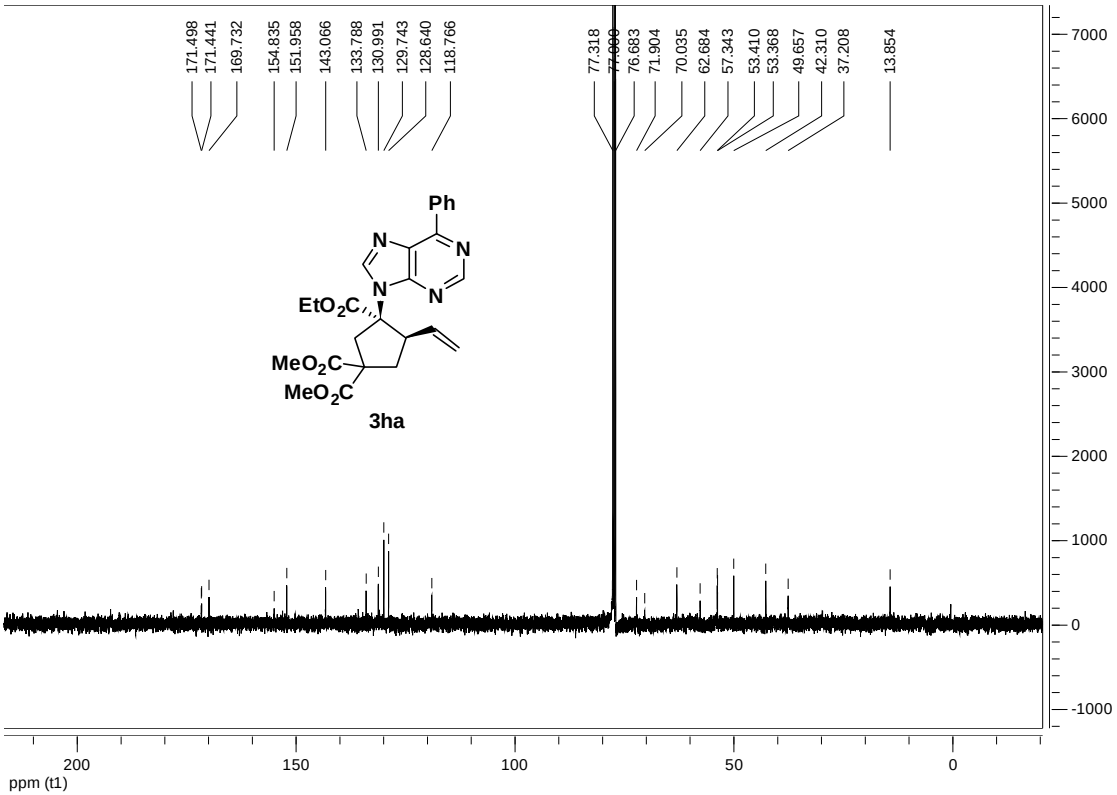
^{13}C-NMR for 4ga



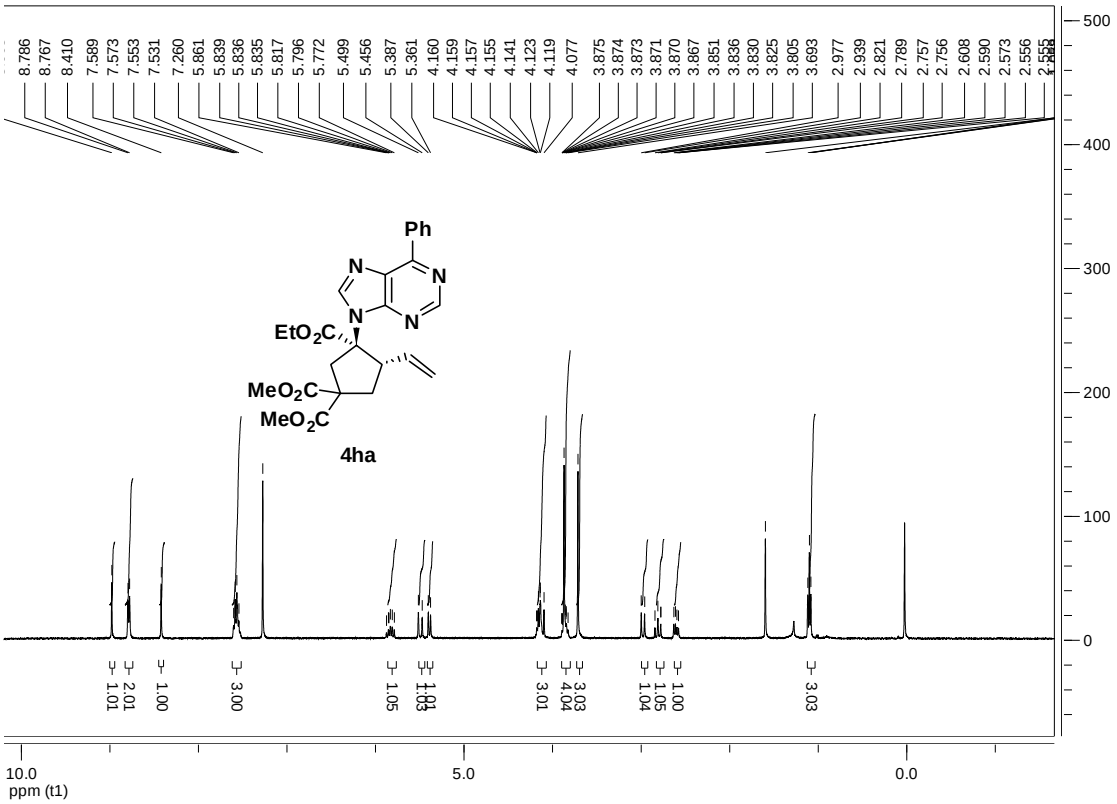
^{1}H-NMR for 3ha



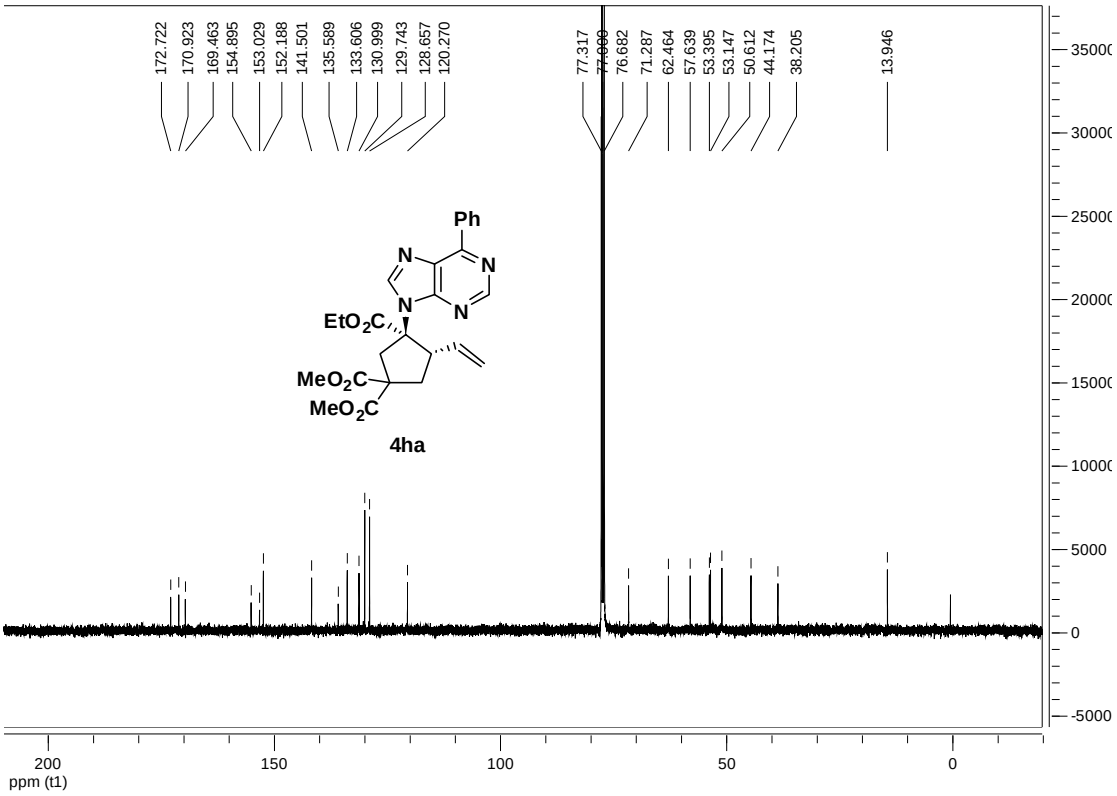
^{13}C-NMR for 3ha



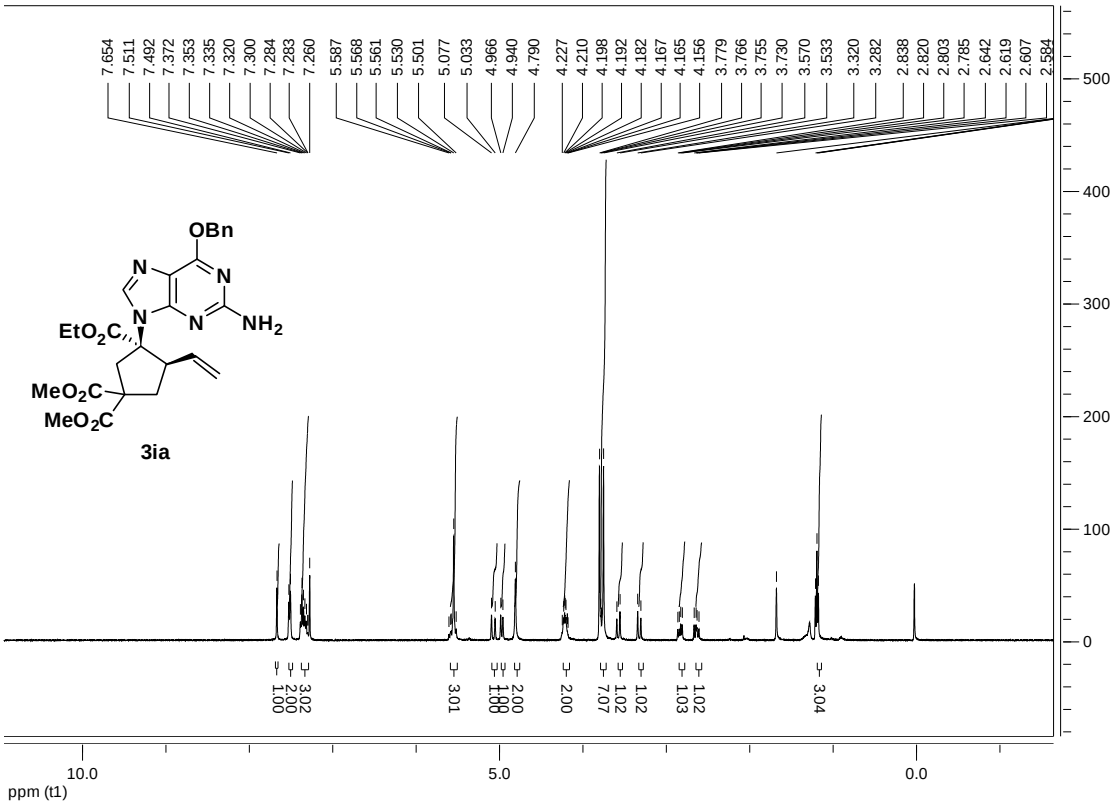
^{1}H-NMR for 4ha



^{13}C-NMR for 4ha



^{1}H-NMR for 3ia



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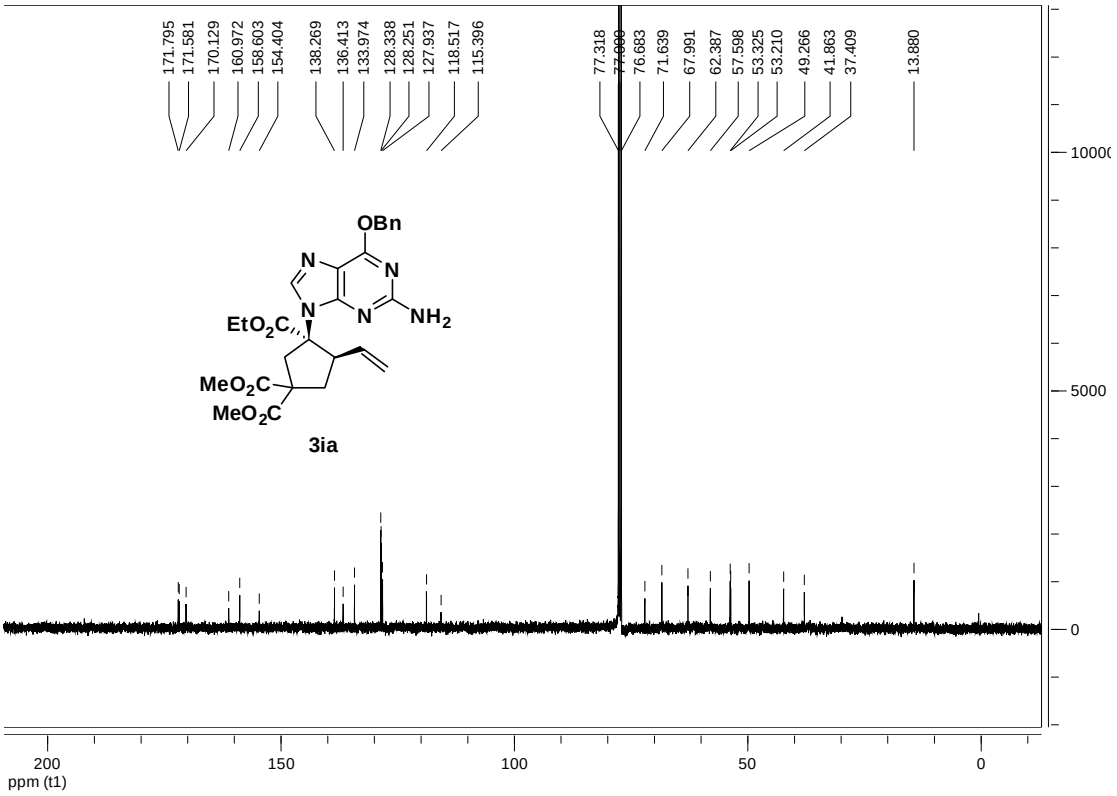
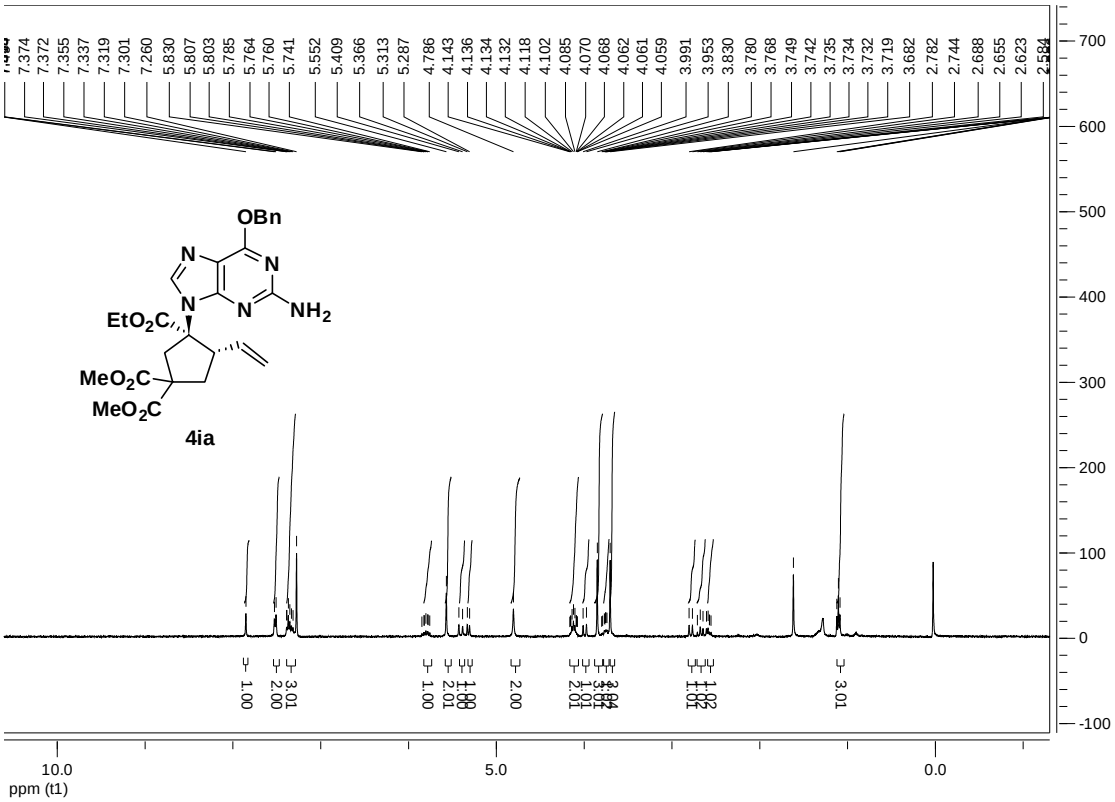
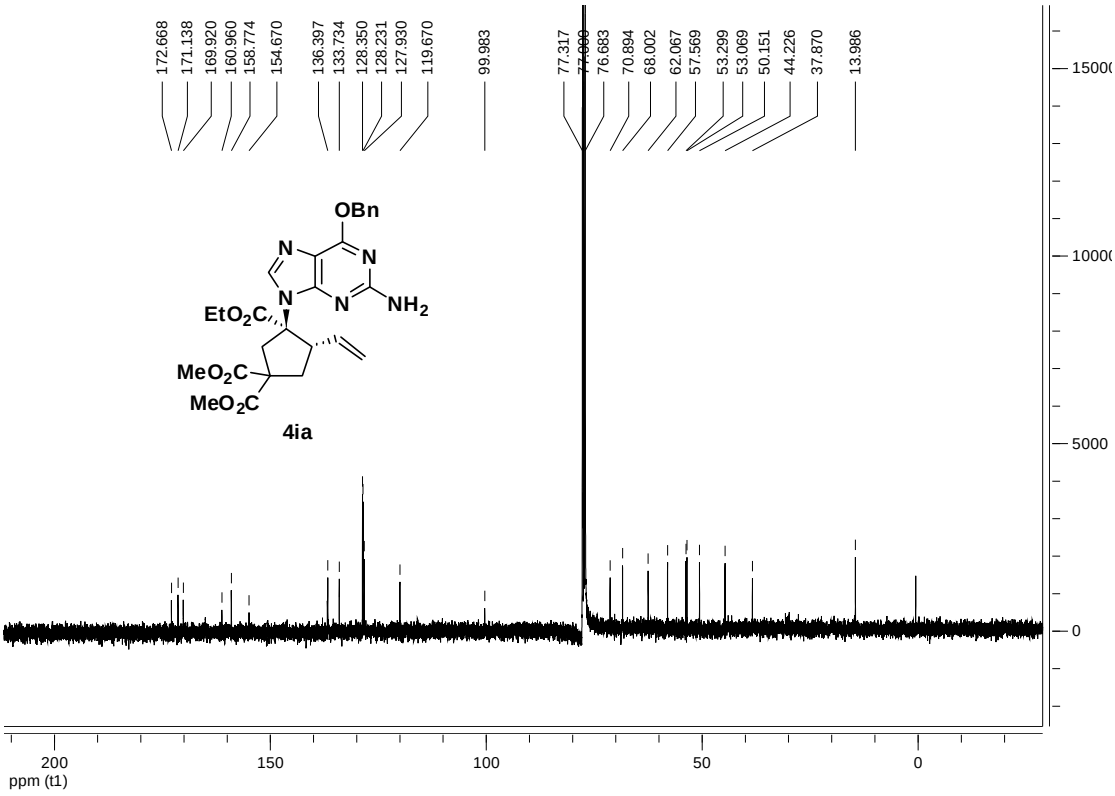


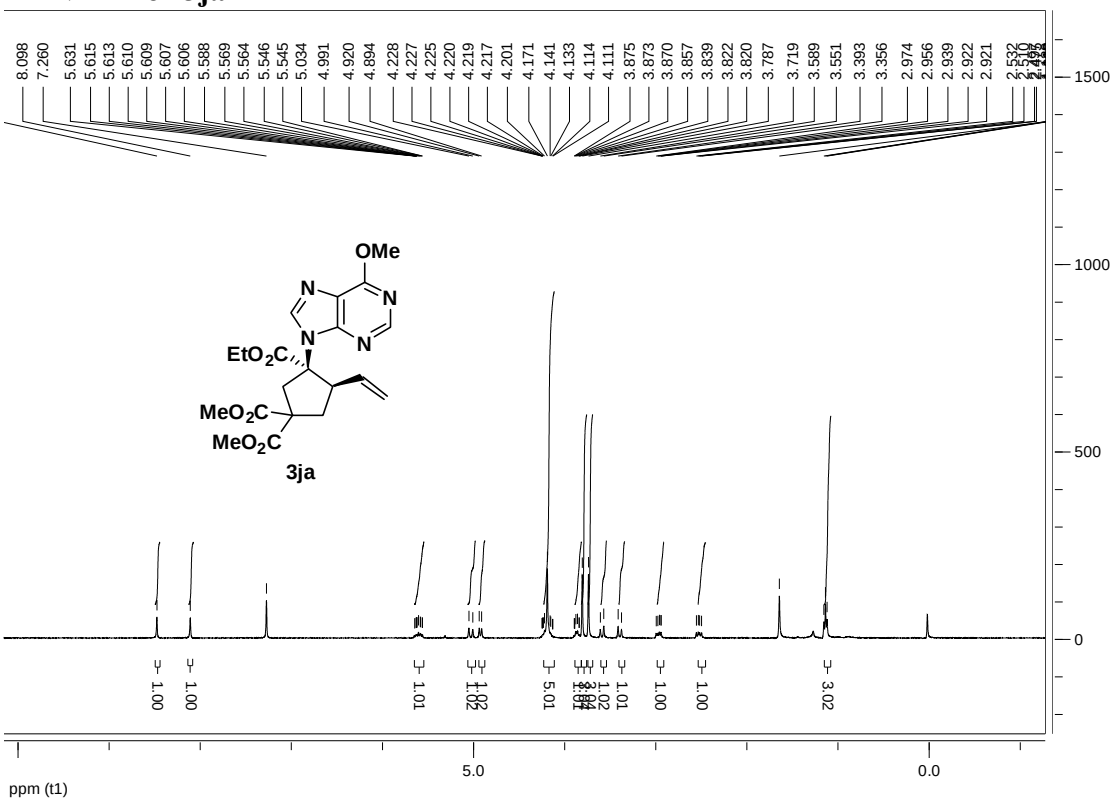
^{1}H-NMR for 4ia



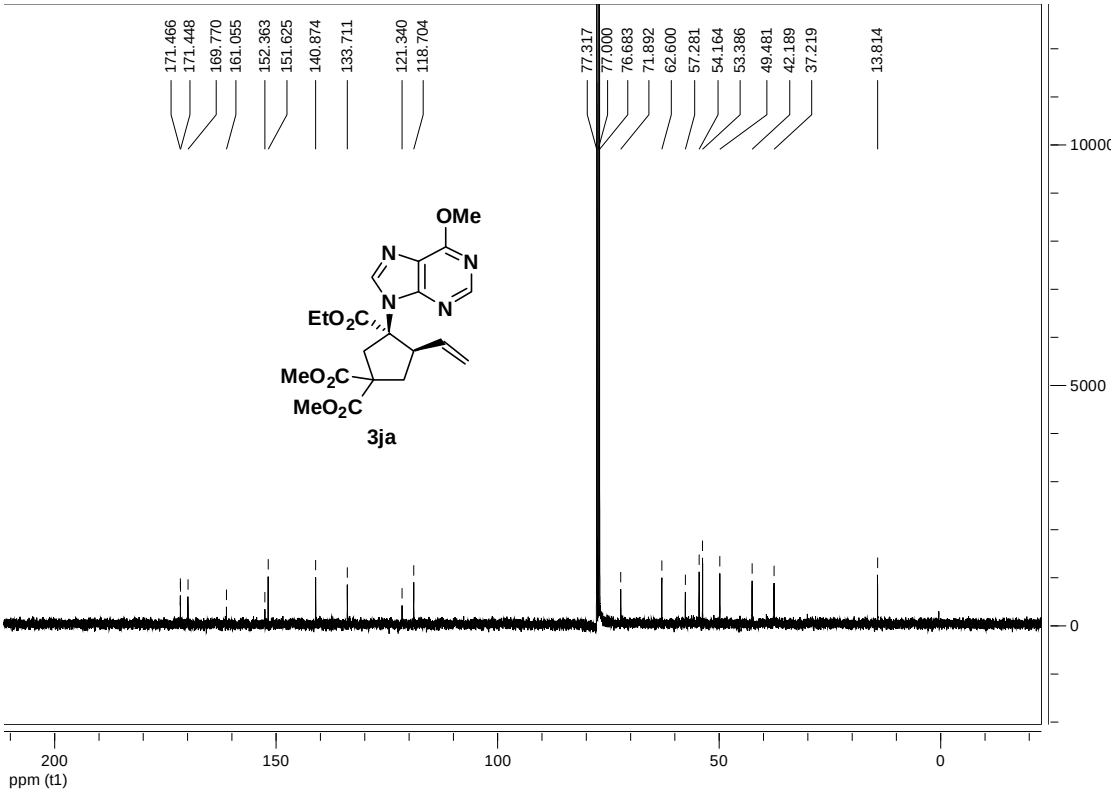
^{13}C-NMR for 4ia



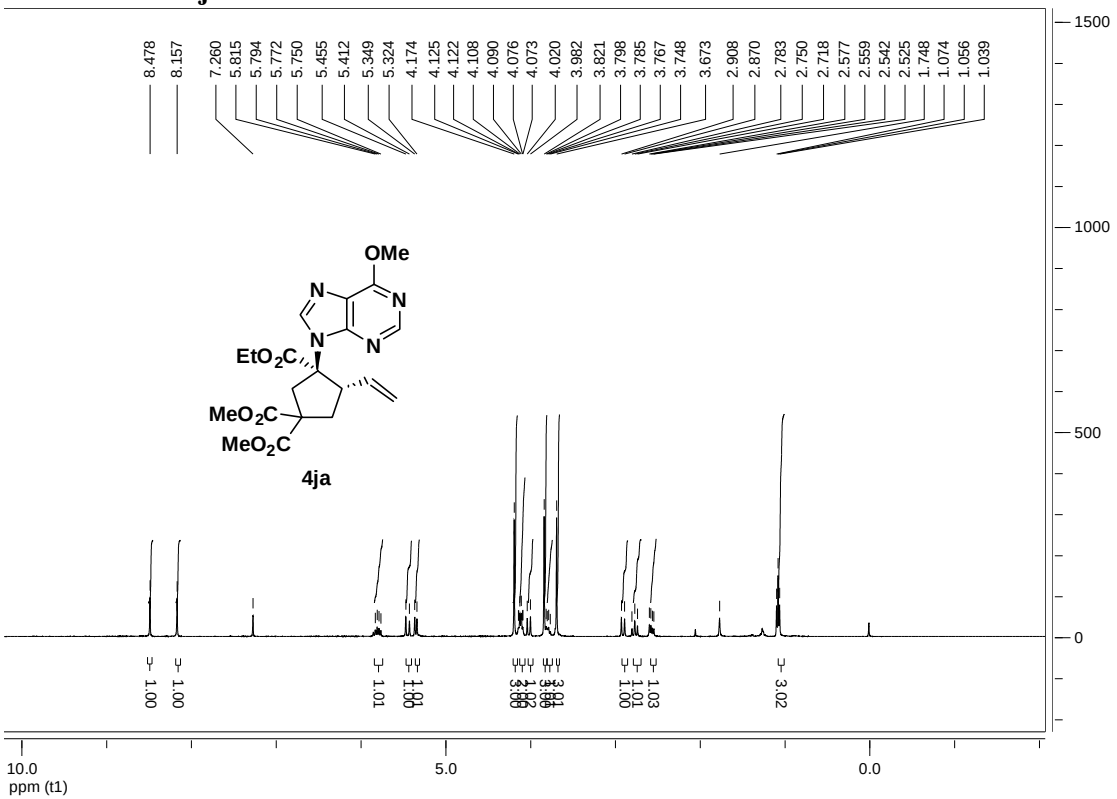
^{1}H-NMR for 3ja



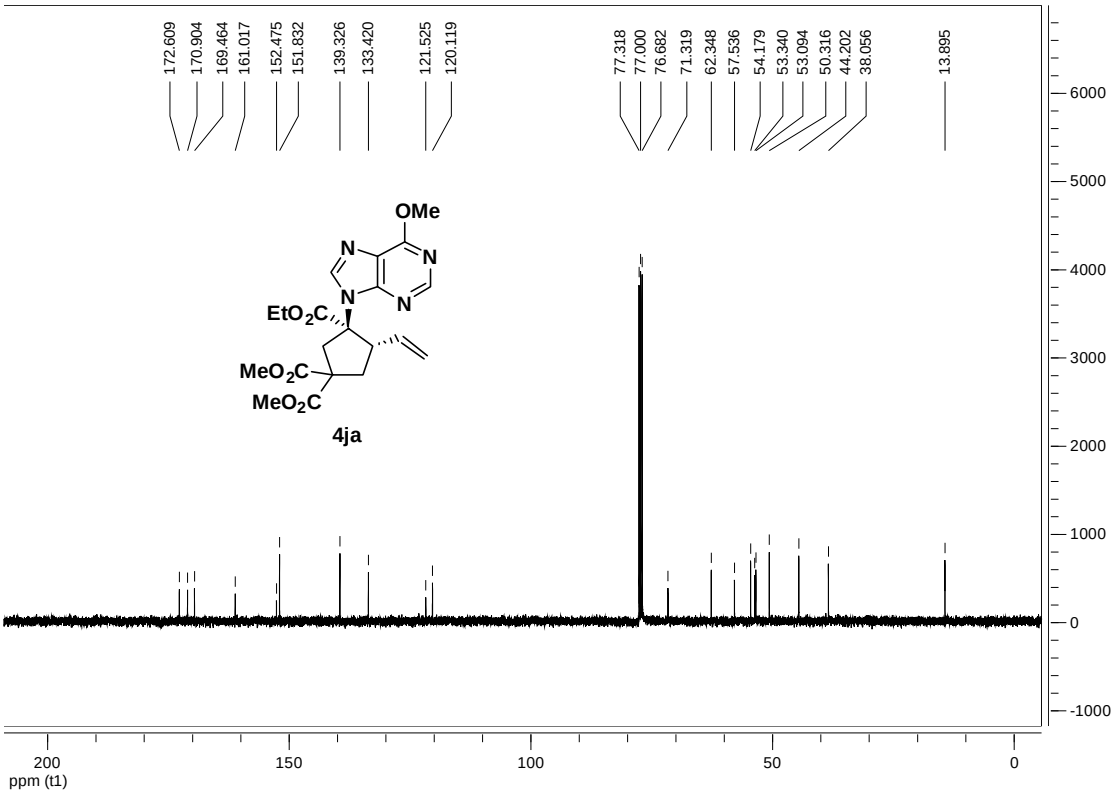
^{13}C-NMR for 3ja



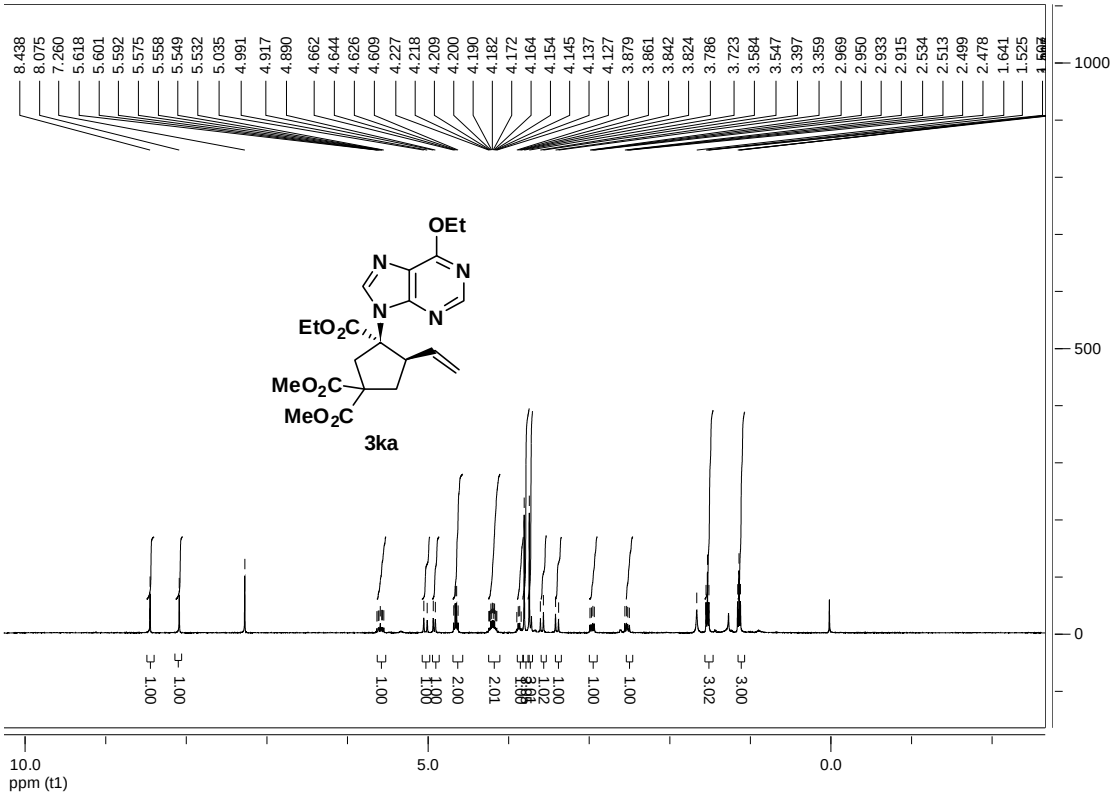
^{1}H-NMR for 4ja



^{13}C-NMR for 4ja



^{1}H-NMR for 3ka



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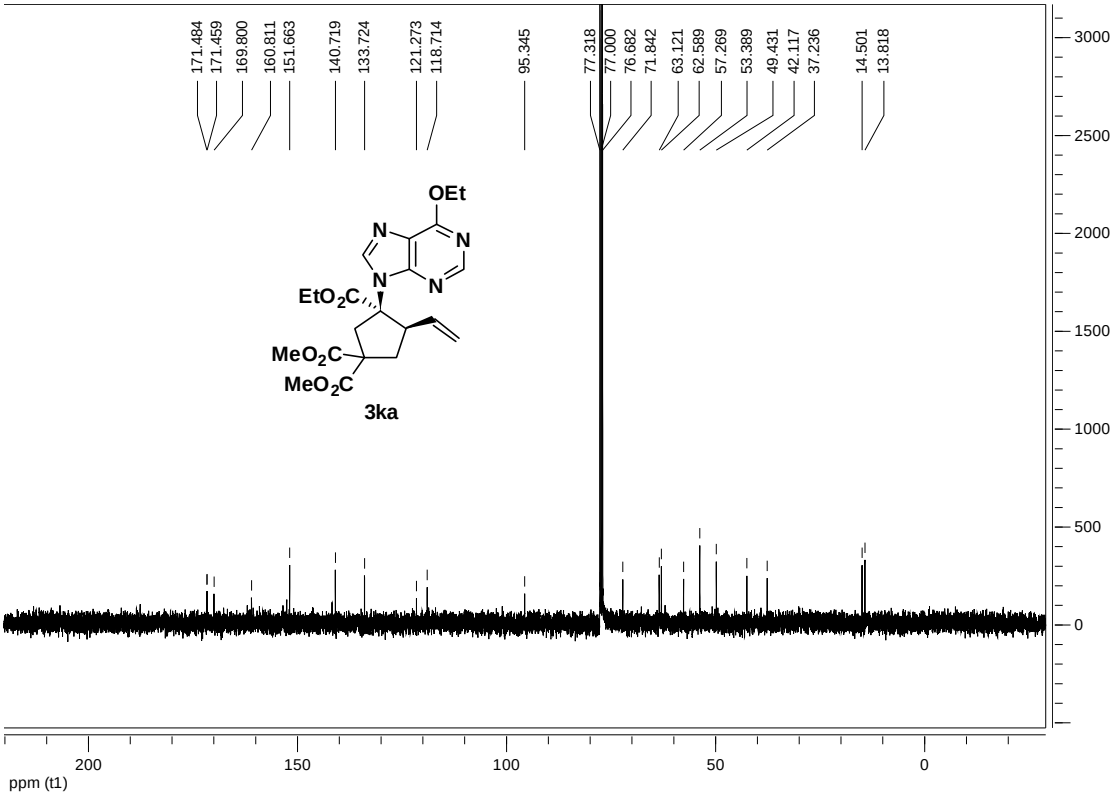

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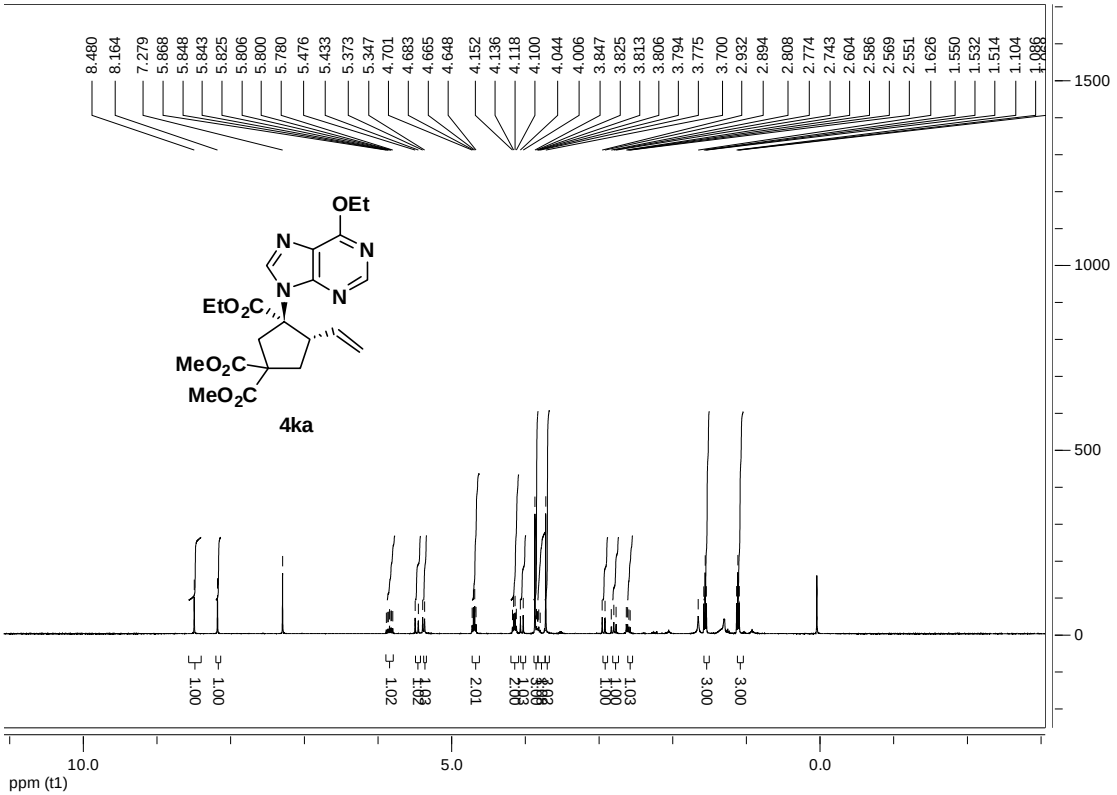

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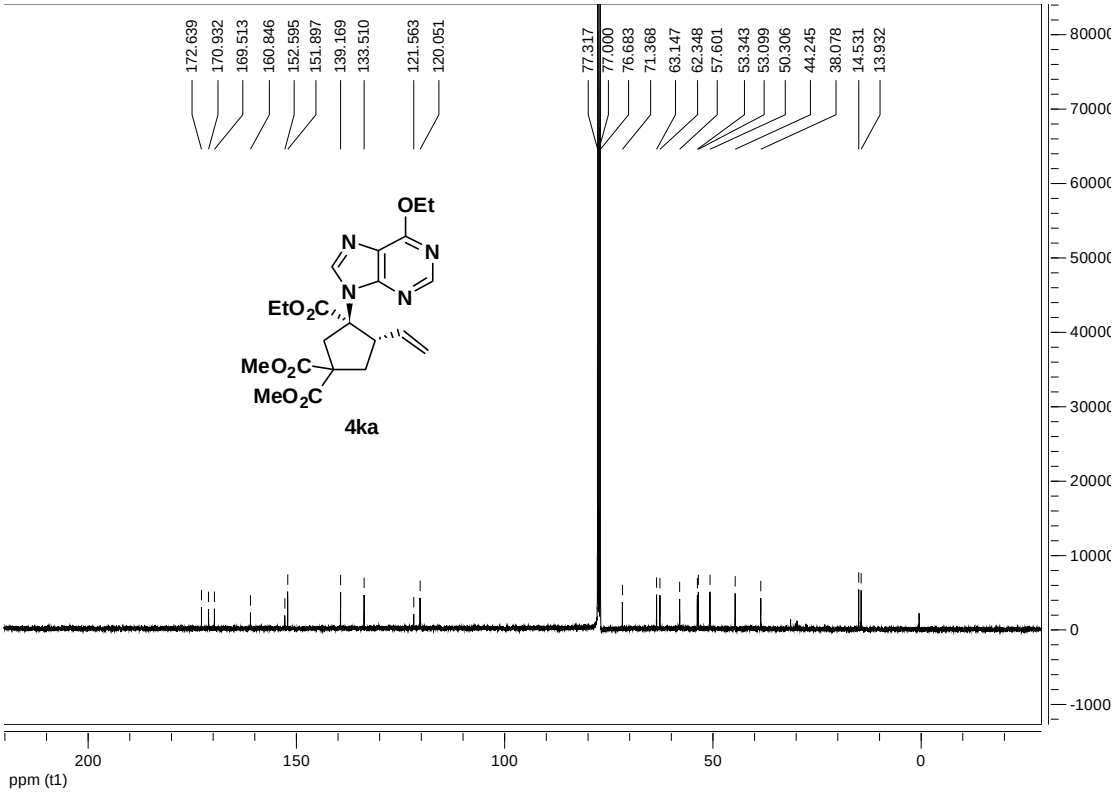

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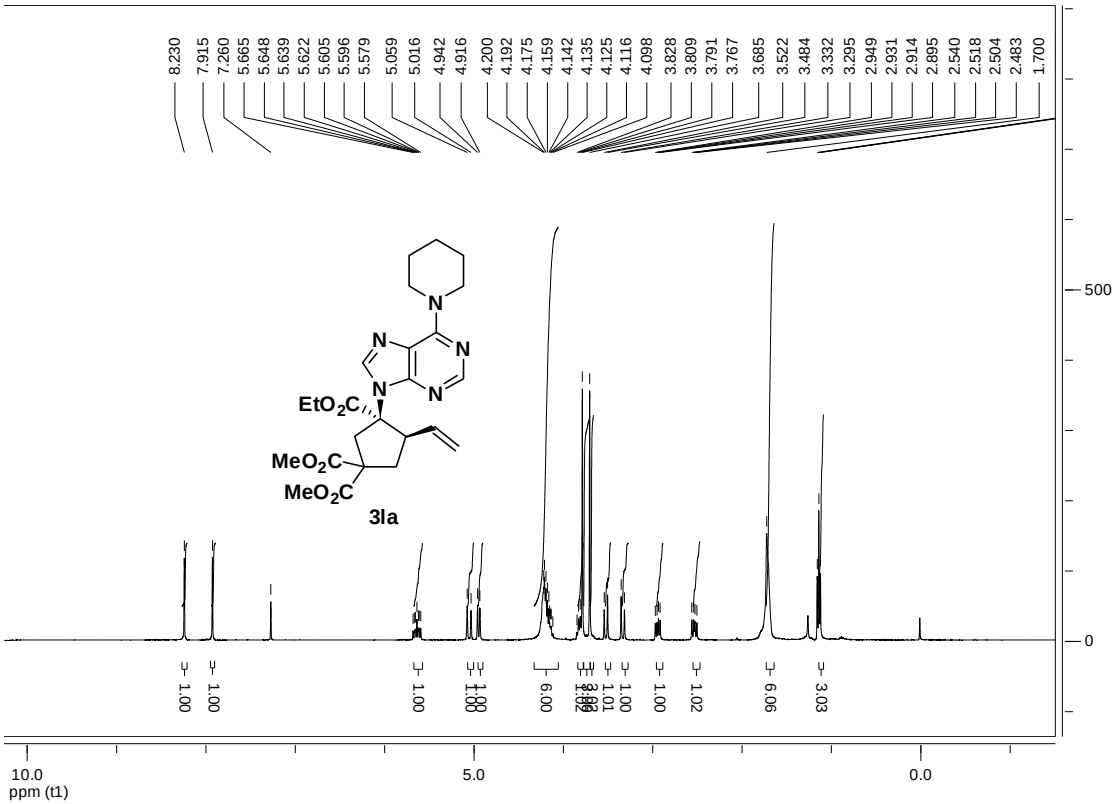

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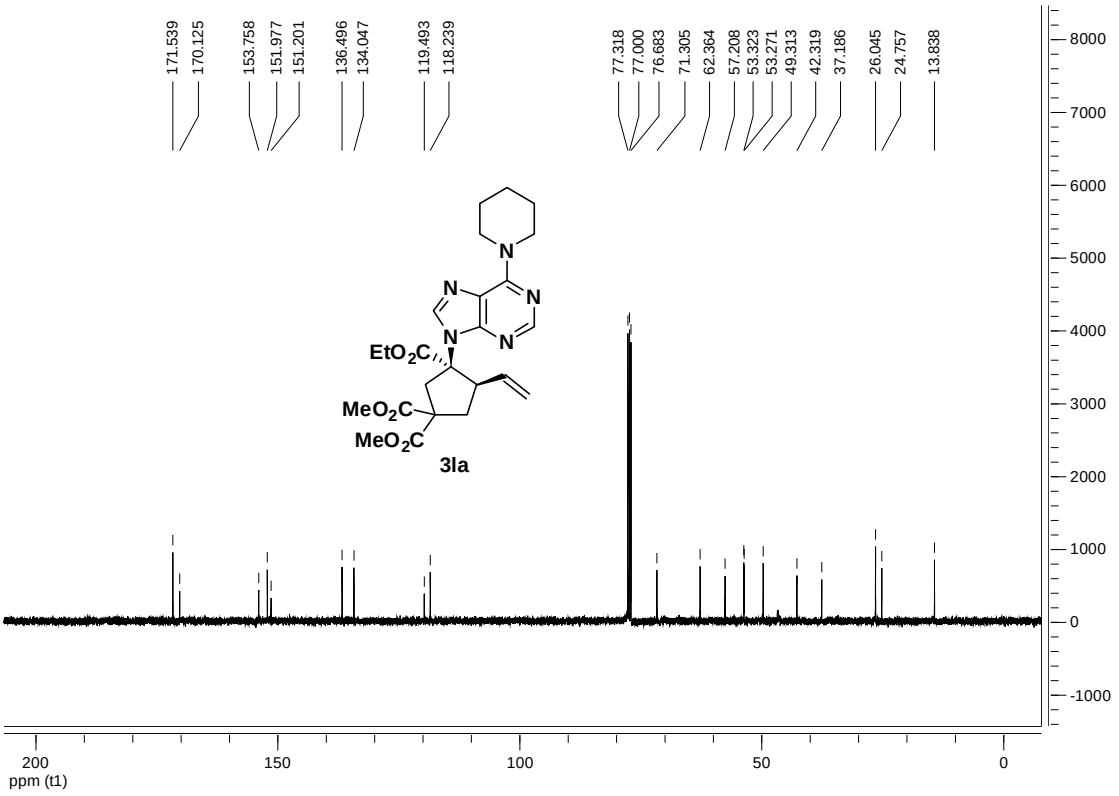
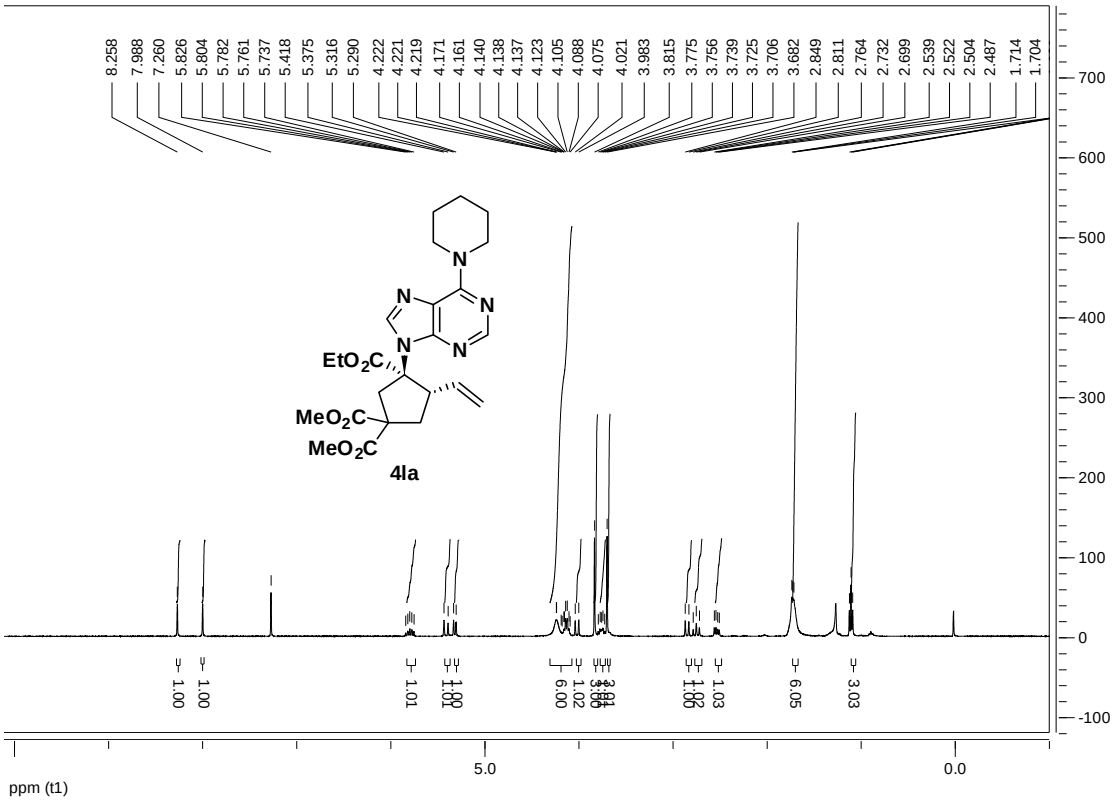


^{1}H-NMR for 4la



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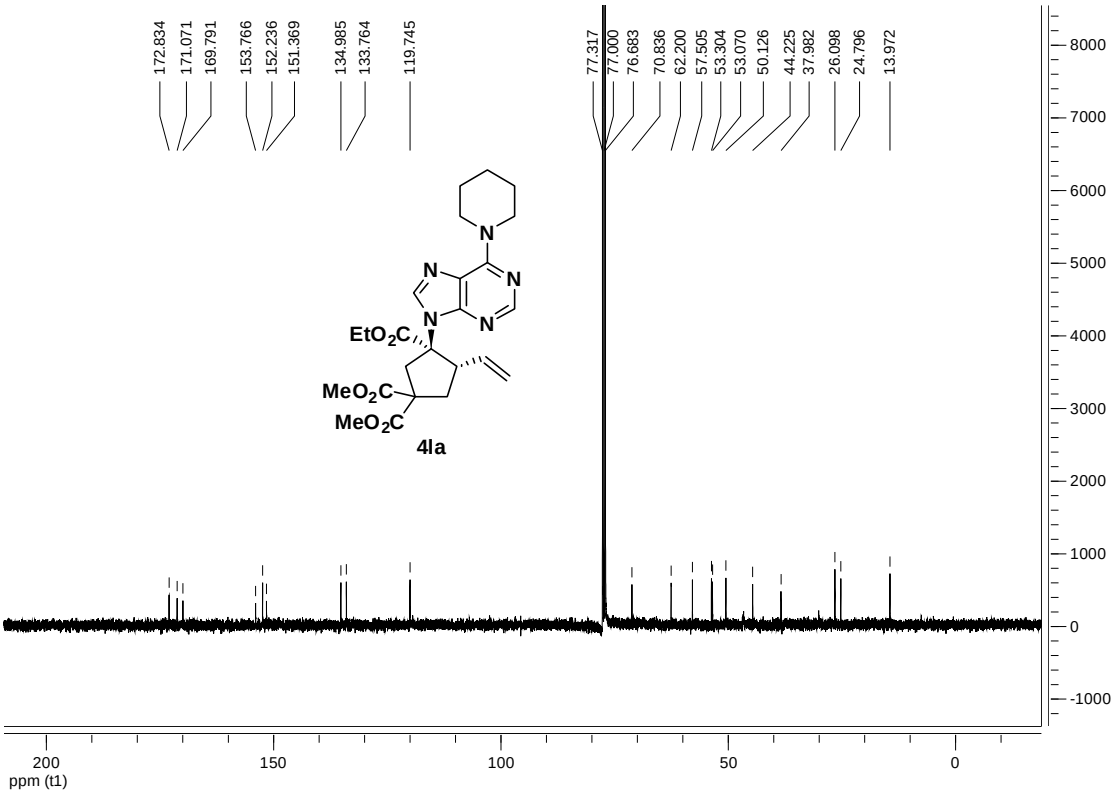
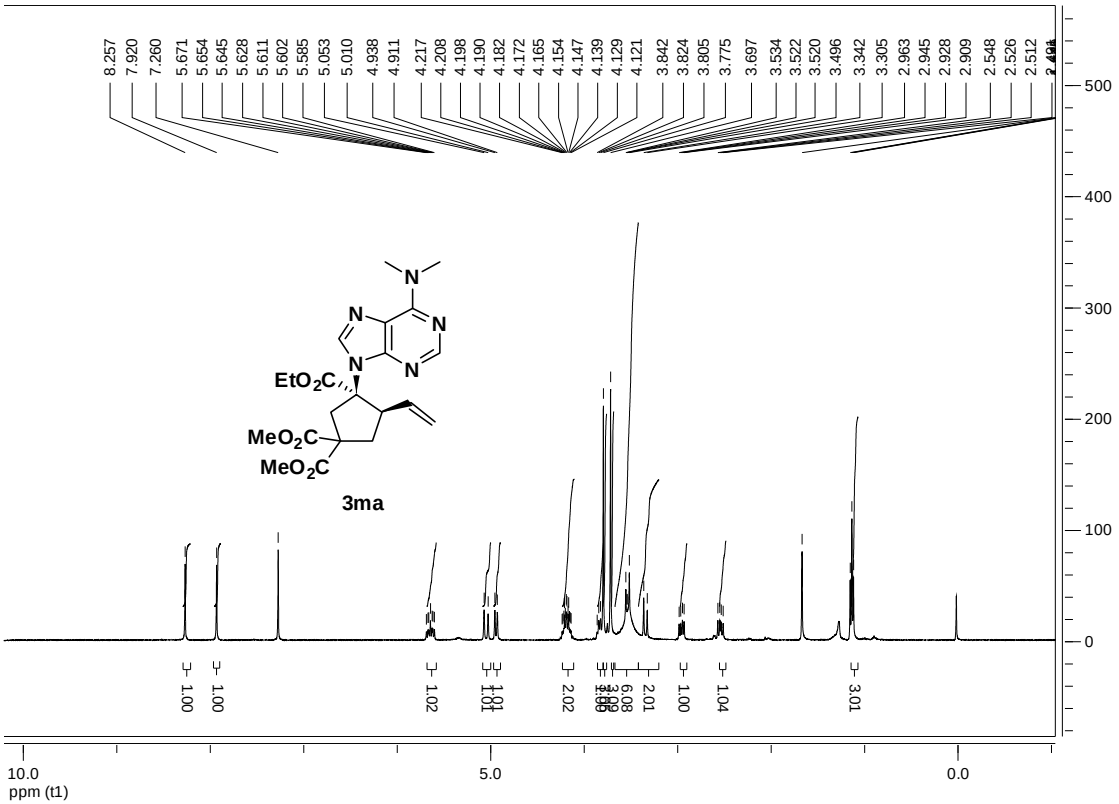


^{1}H-NMR for 3ma



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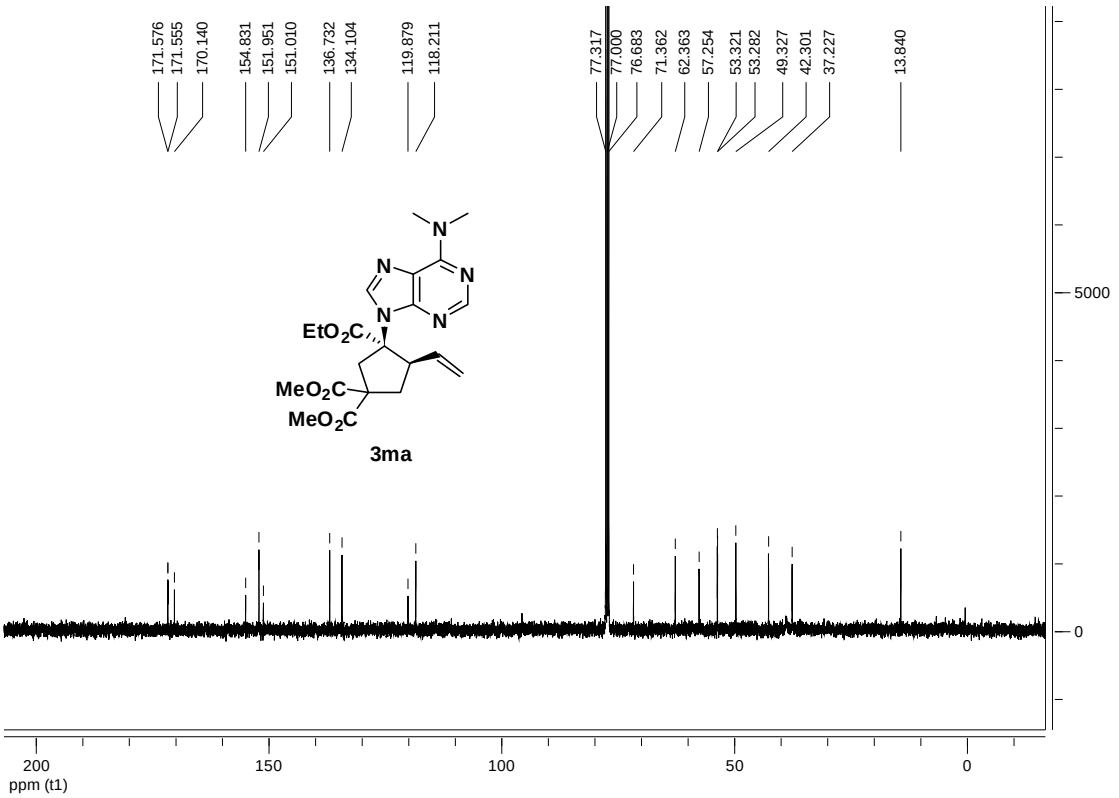
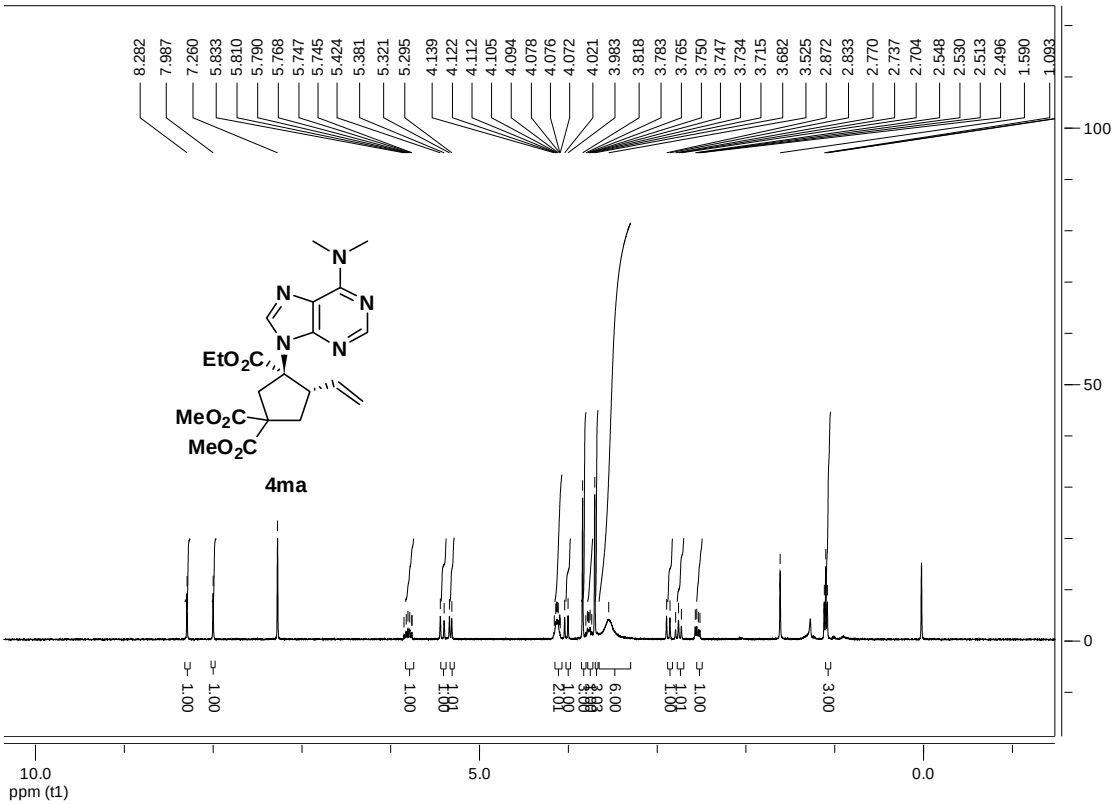
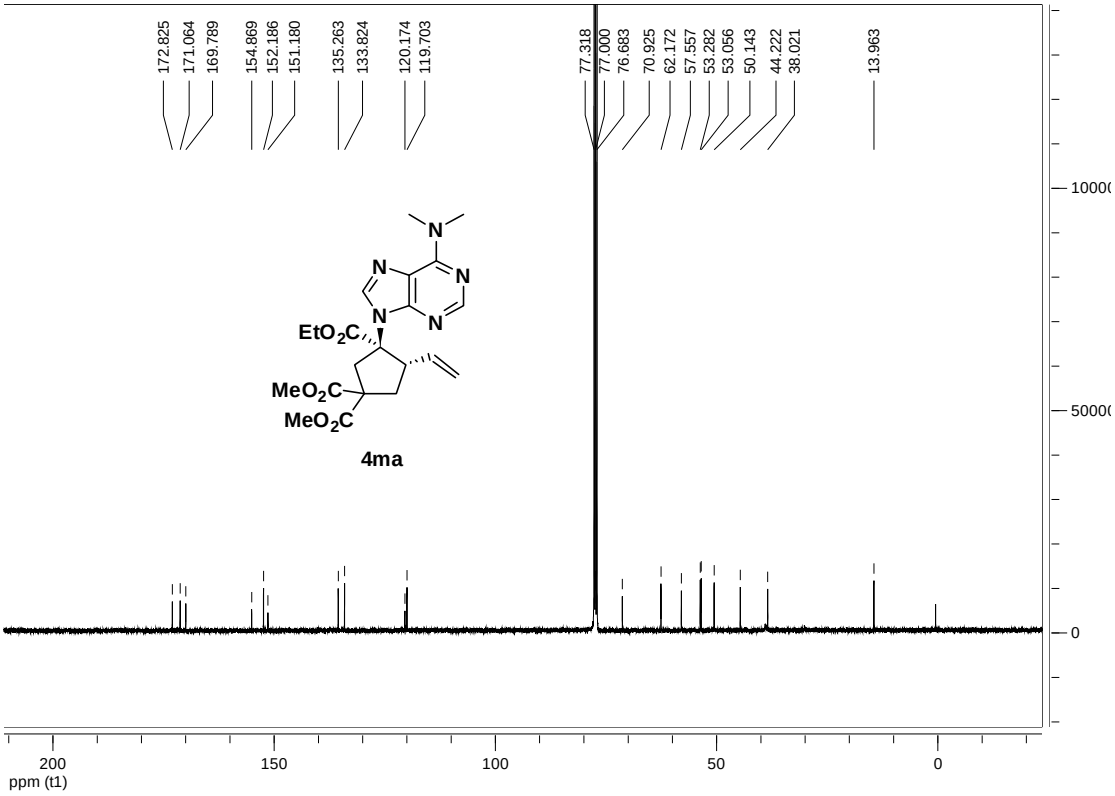


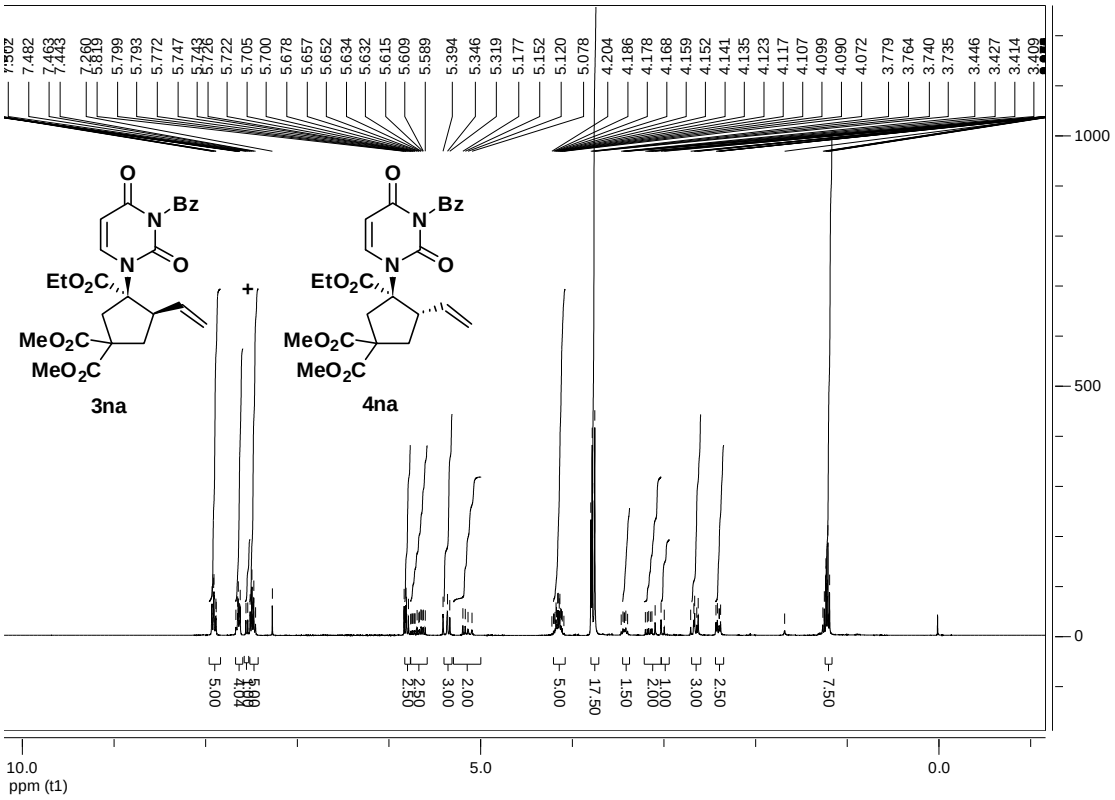
^{1}H-NMR for 4ma



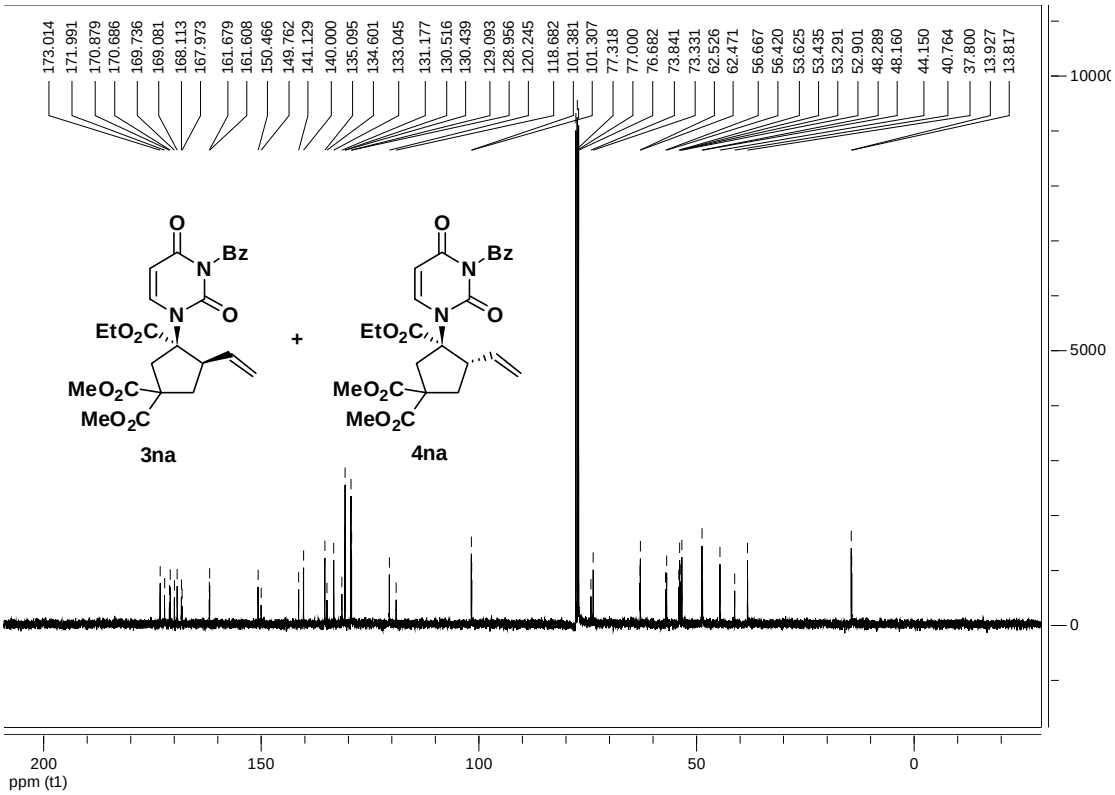
^{13}C-NMR for 4ma



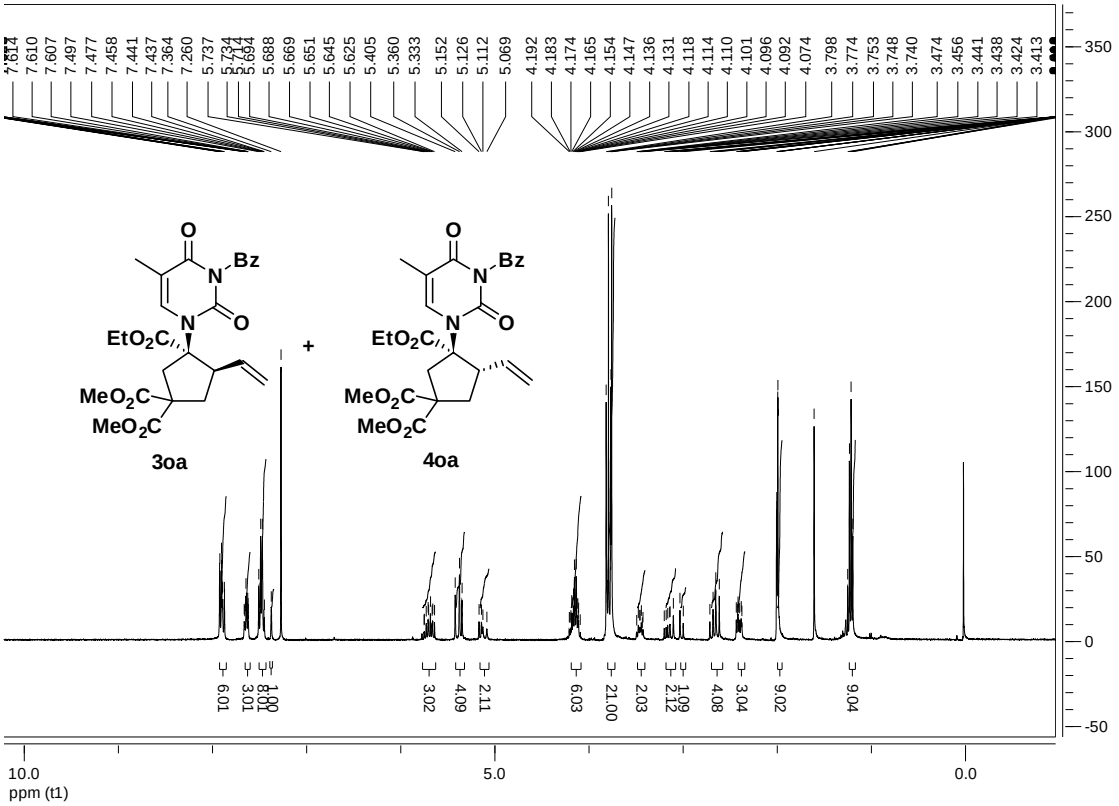
^{1}H-NMR for 3na+4na



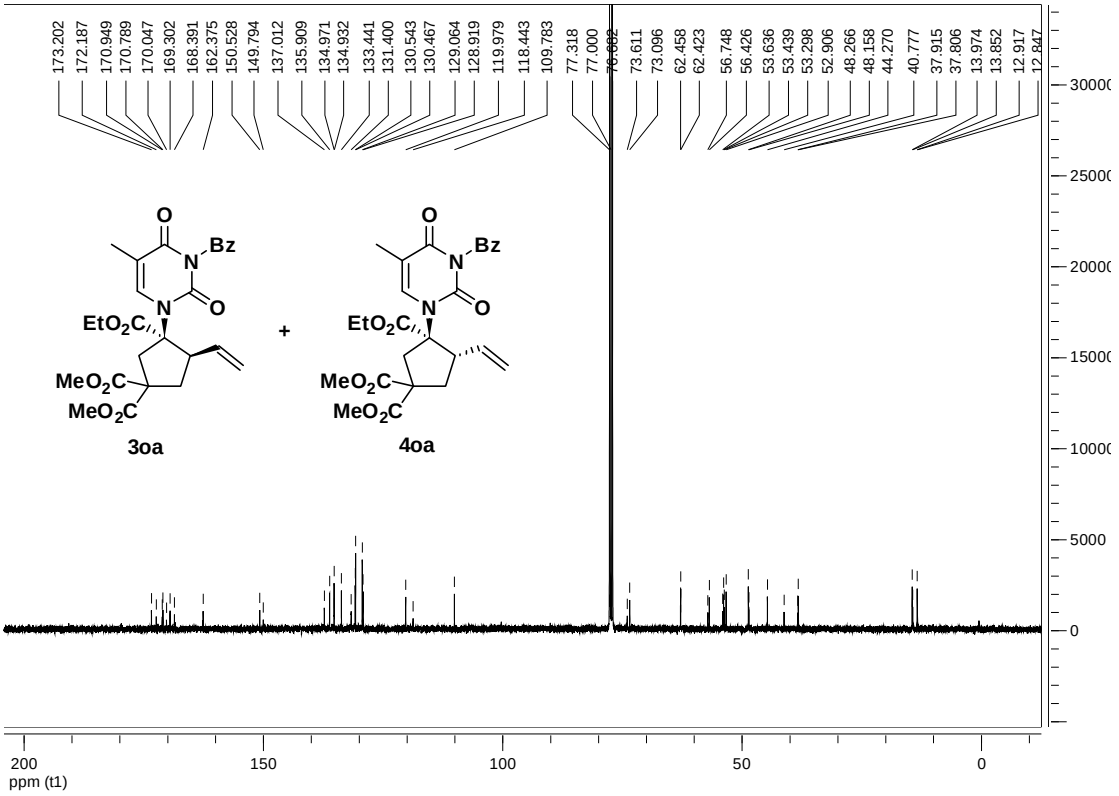
^{13}C-NMR for 3na+4na



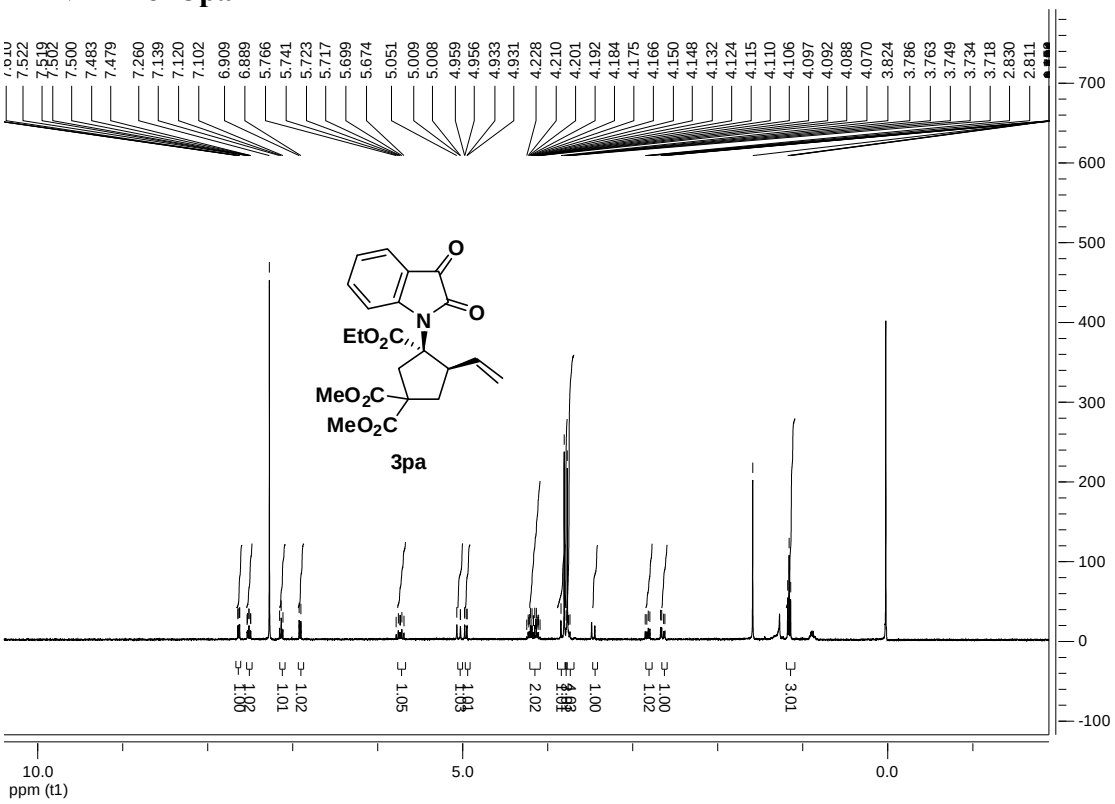
^{1}H-NMR for 3oa+4oa



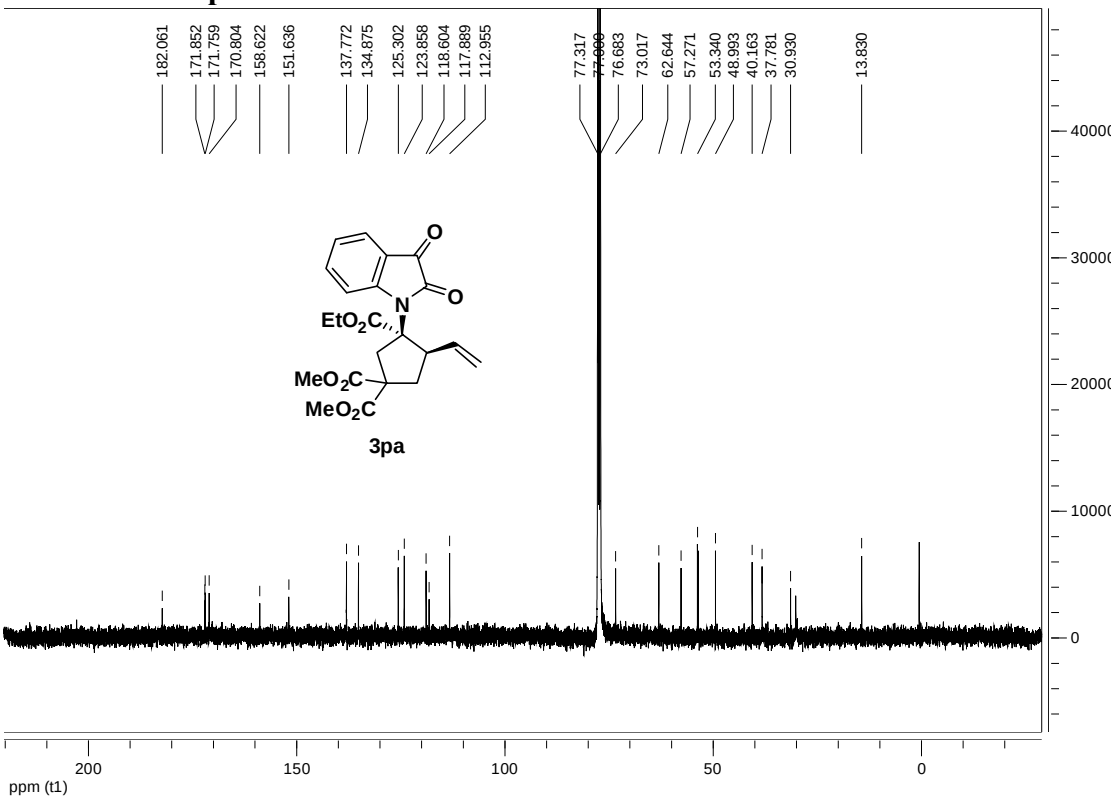
^{13}C-NMR for 3oa+4oa



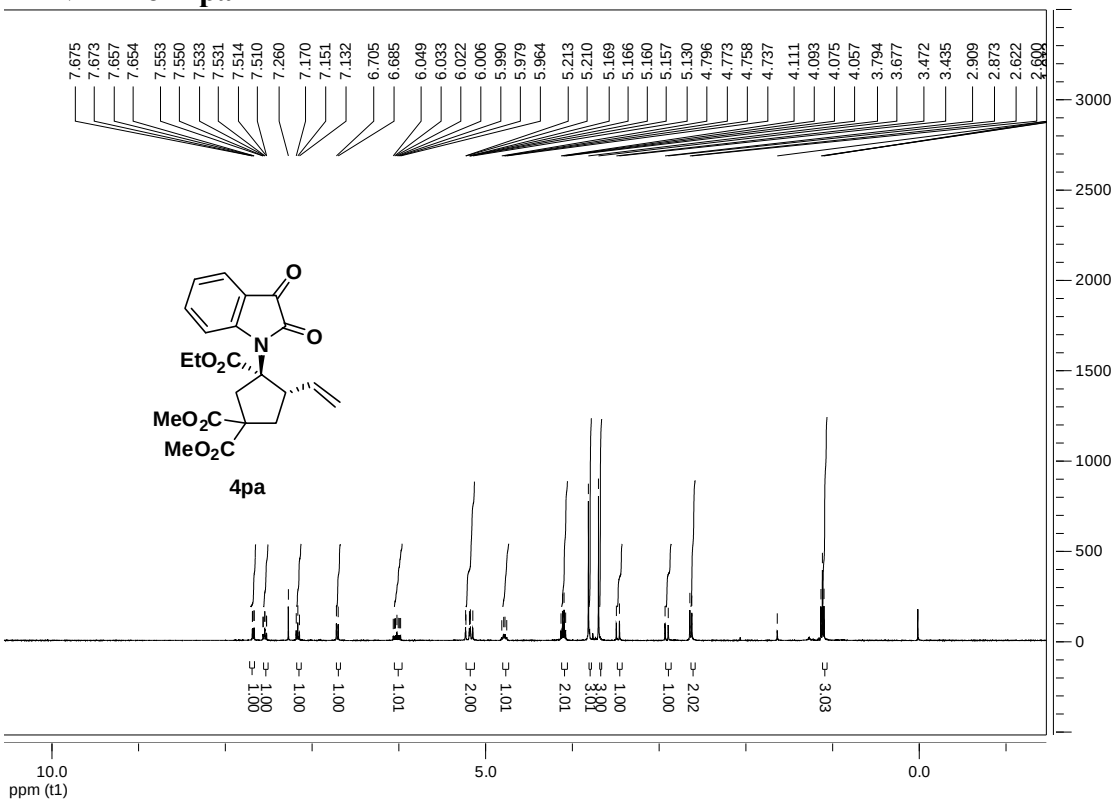
^{1}H-NMR for 3pa



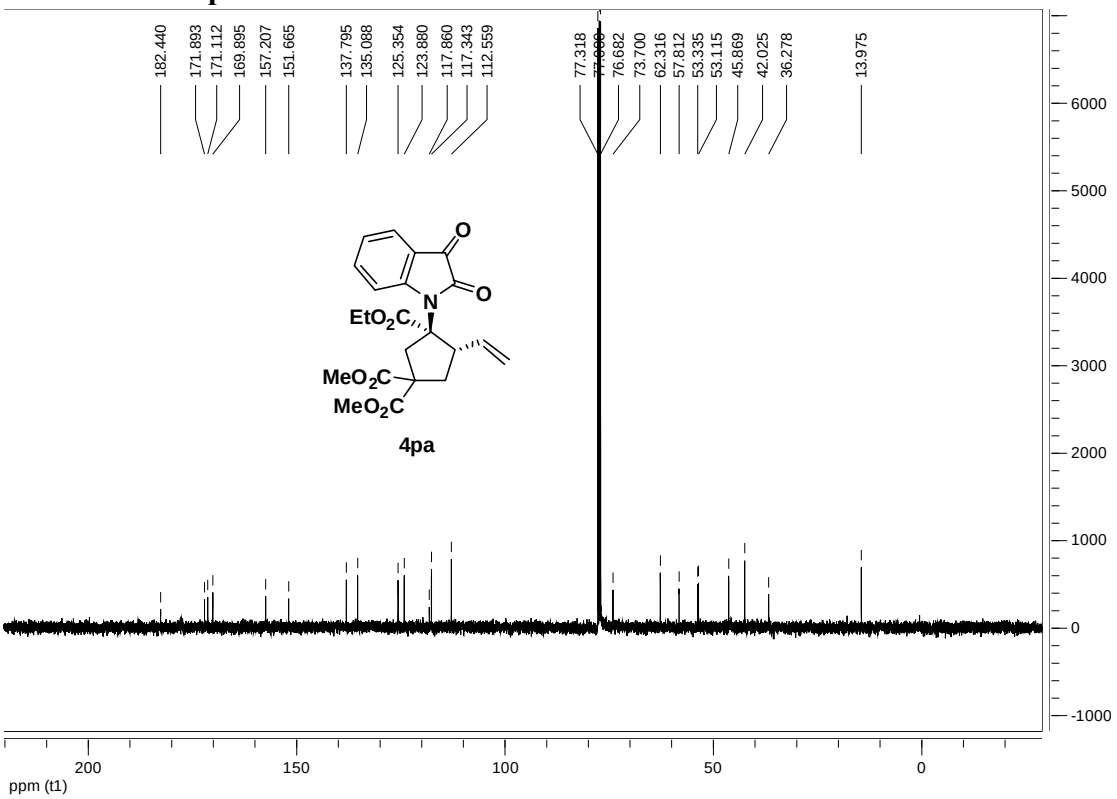
^{13}C-NMR for 3pa



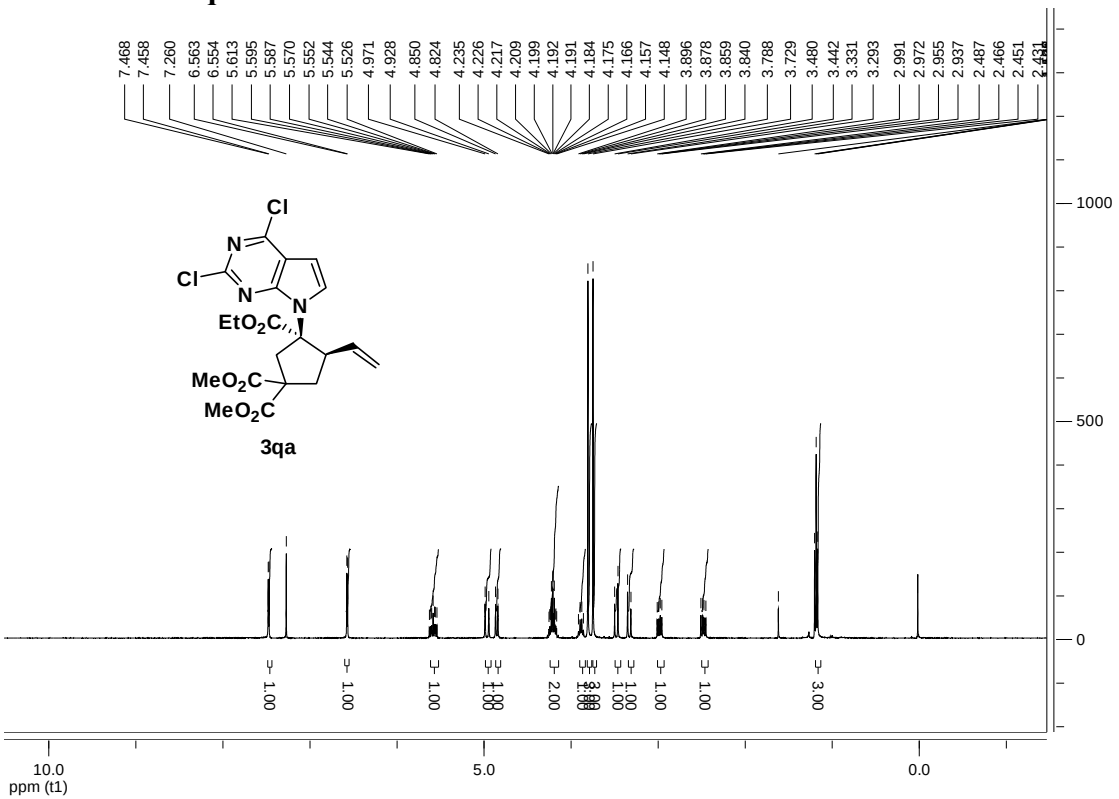
^{1}H-NMR for 4pa



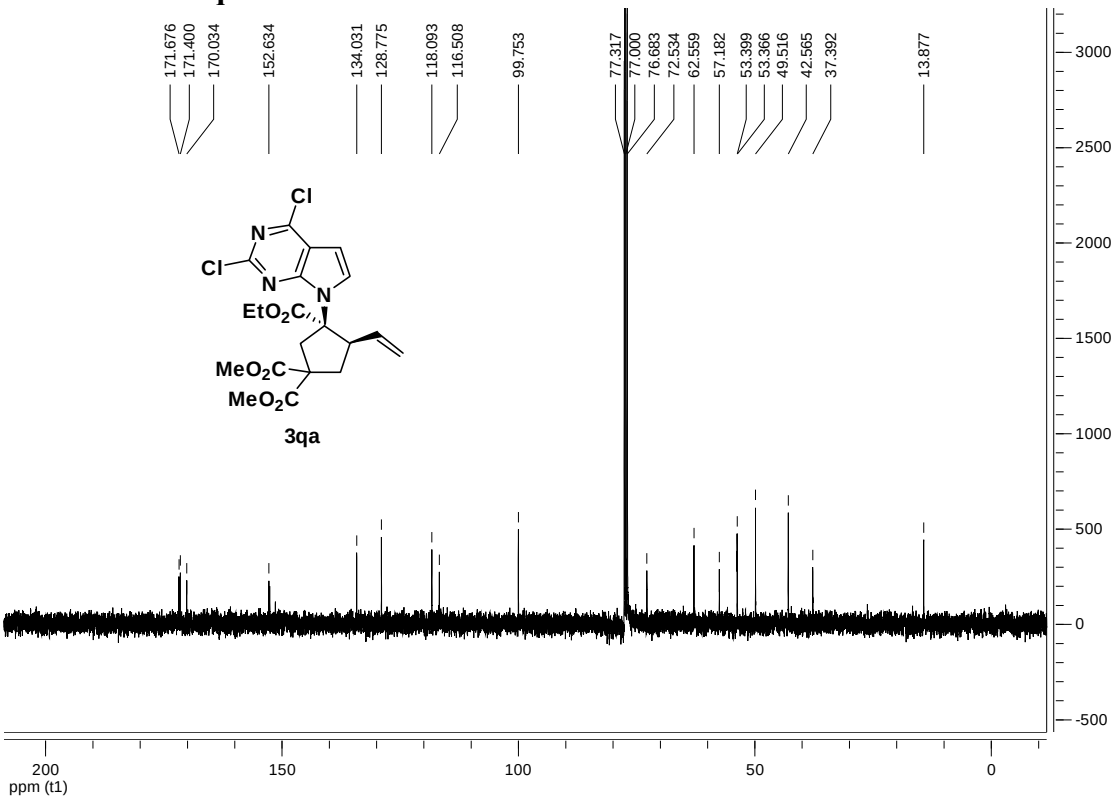
^{13}C-NMR for 4pa



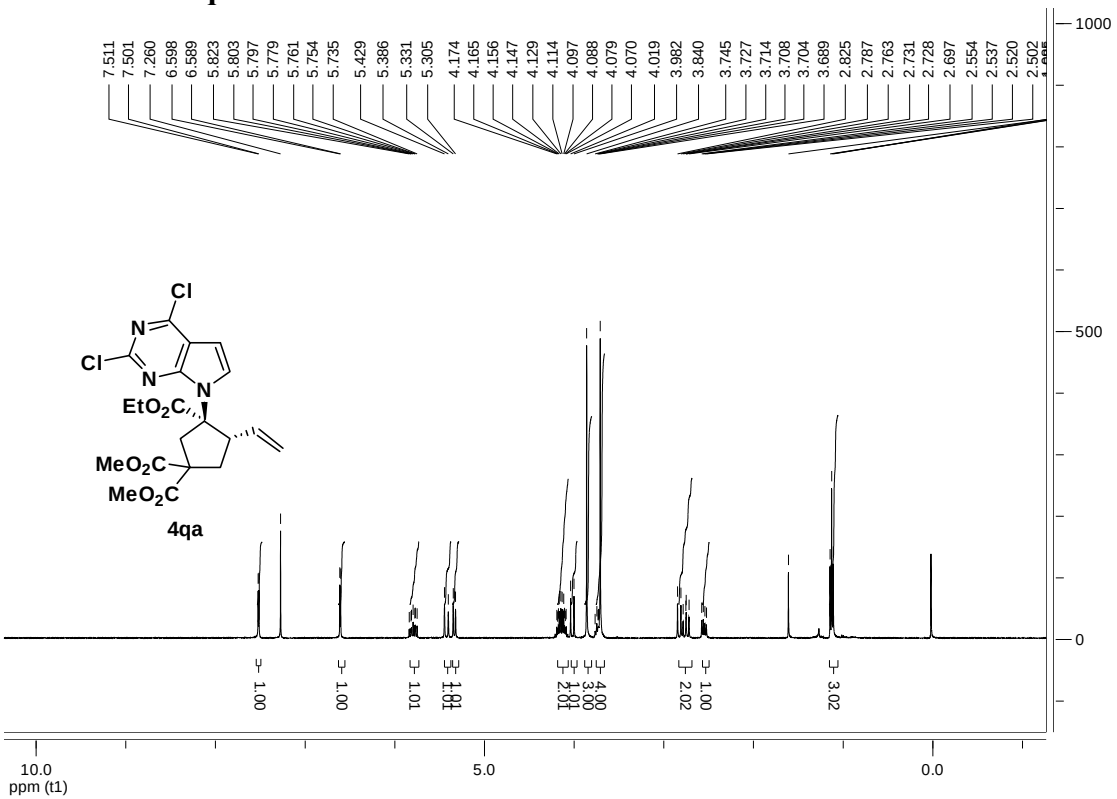
^{1}H-NMR for 3qa



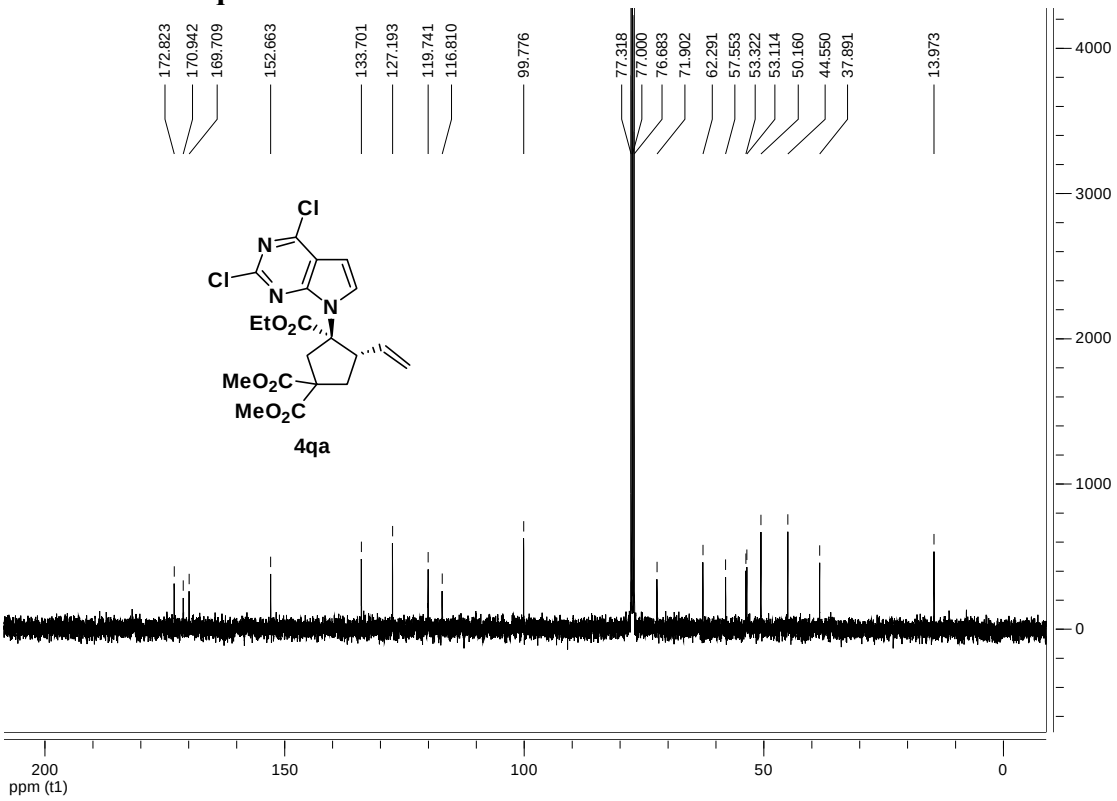
^{13}C-NMR for 3qa



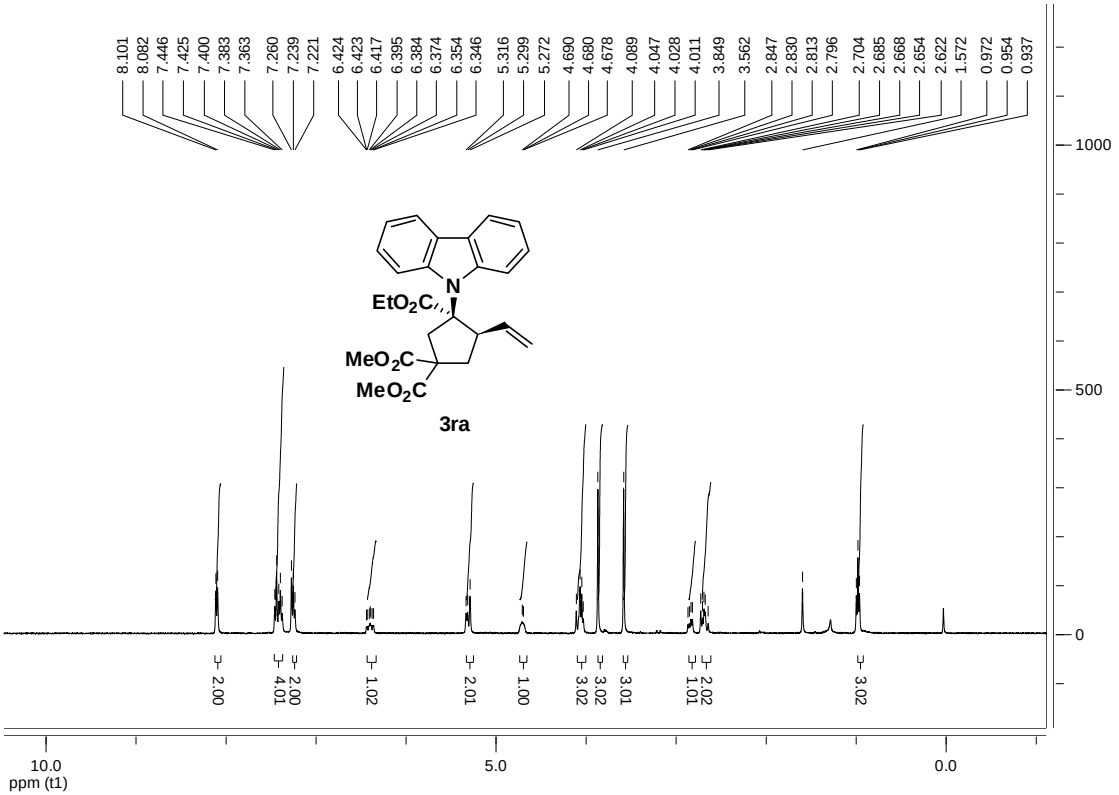
^{1}H-NMR for 4qa



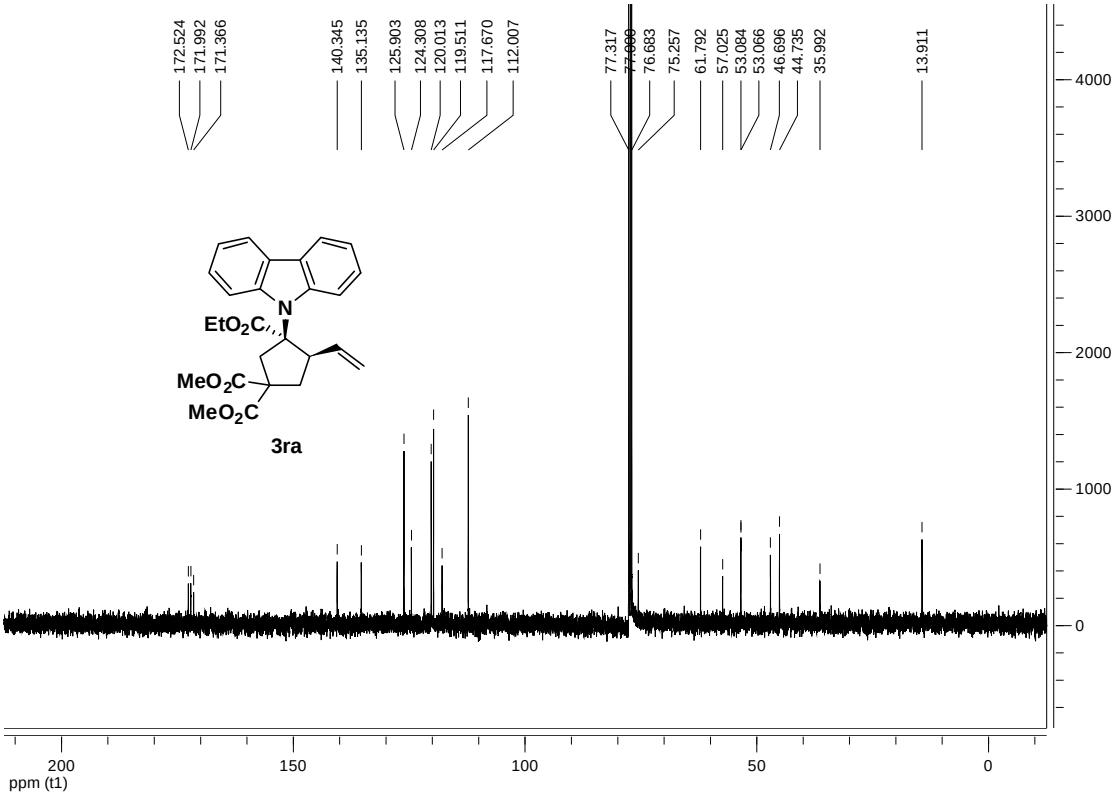
^{13}C-NMR for 4qa



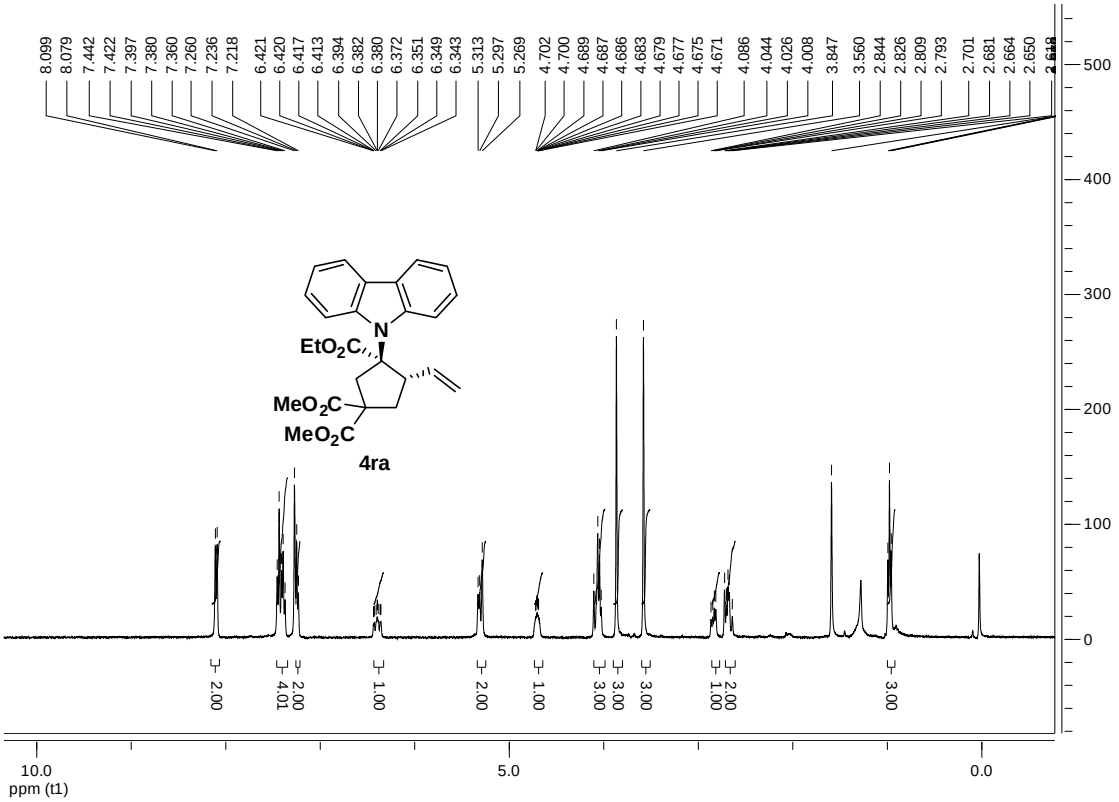
^{1}H-NMR for 3ra



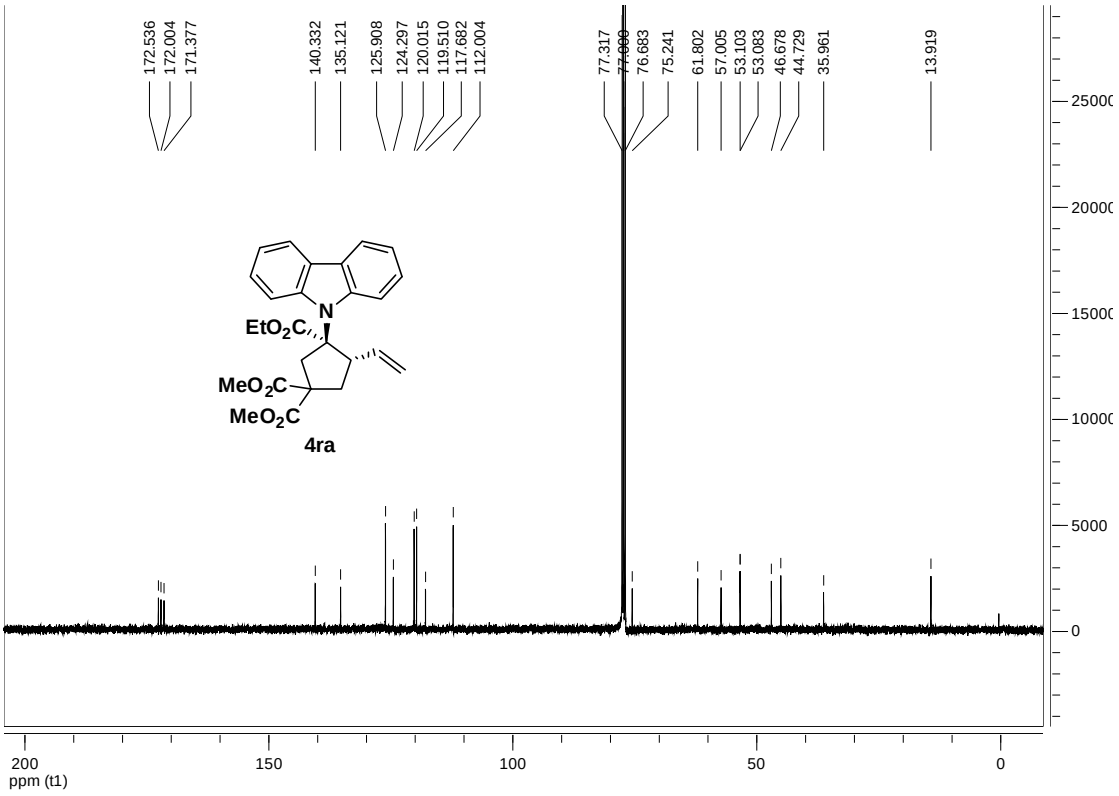
^{13}C-NMR for 3ra



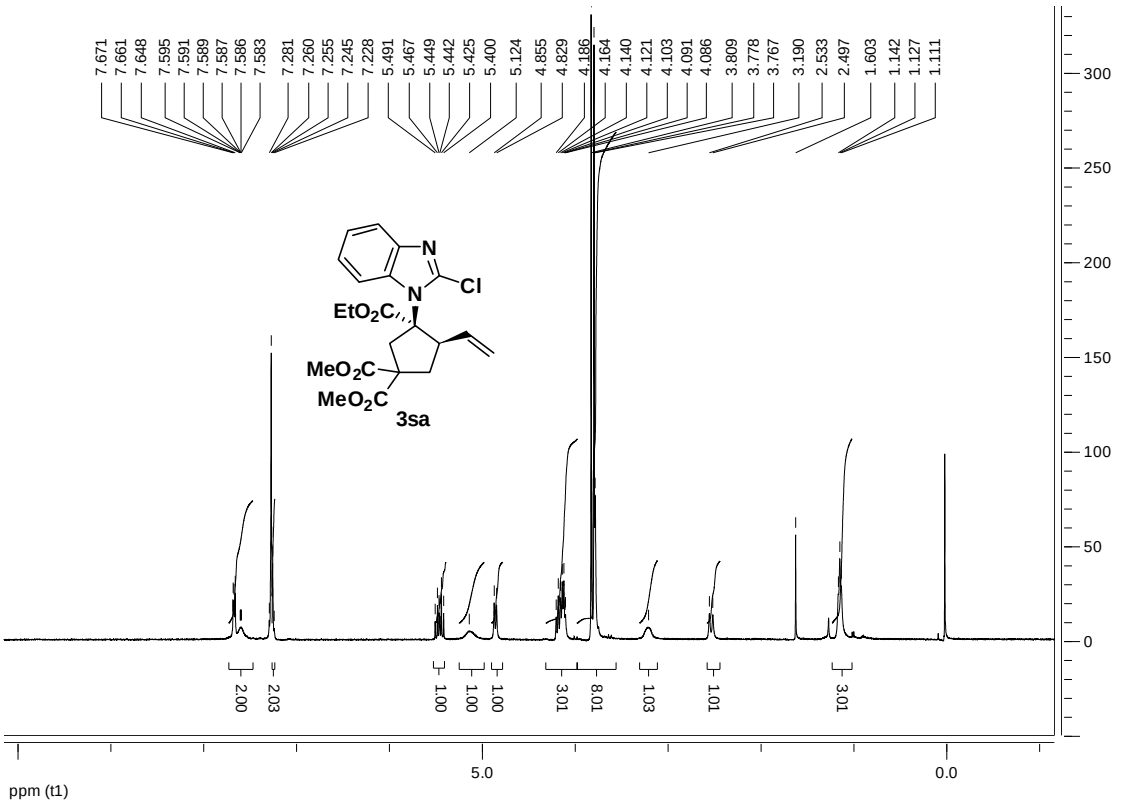
^{1}H-NMR for 4ra



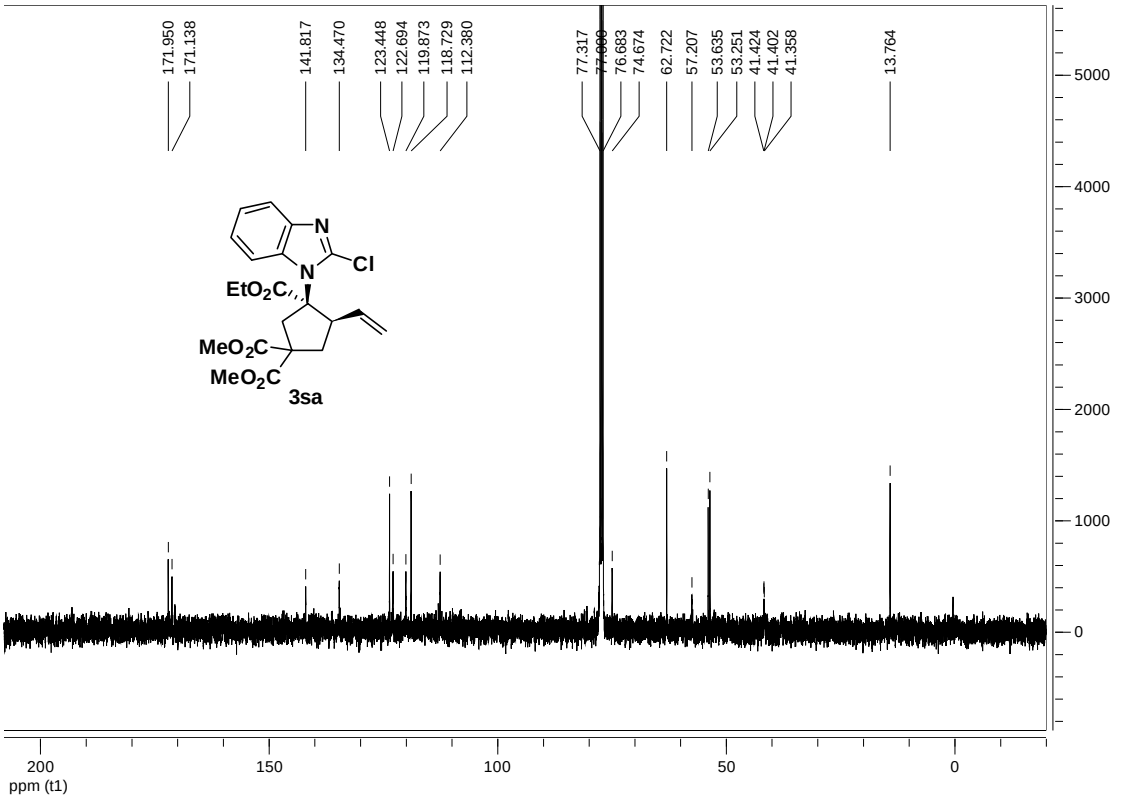
^{13}C-NMR for 4ra



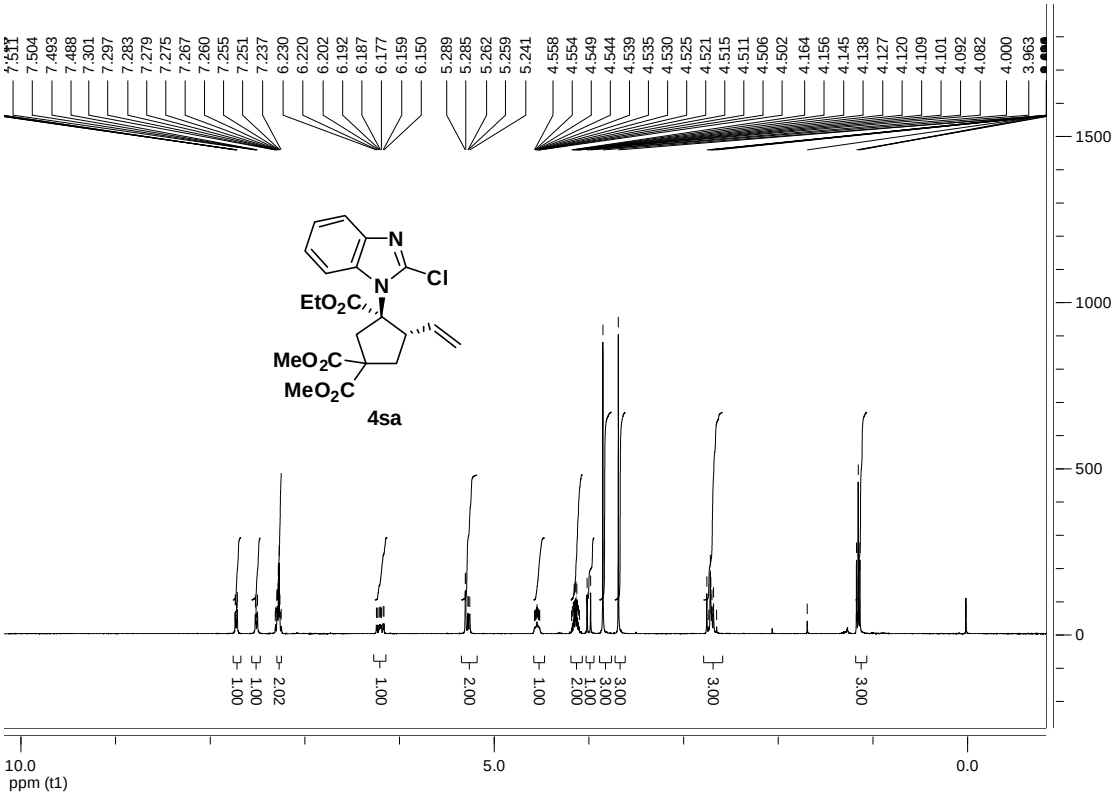
^{1}H-NMR for 3sa



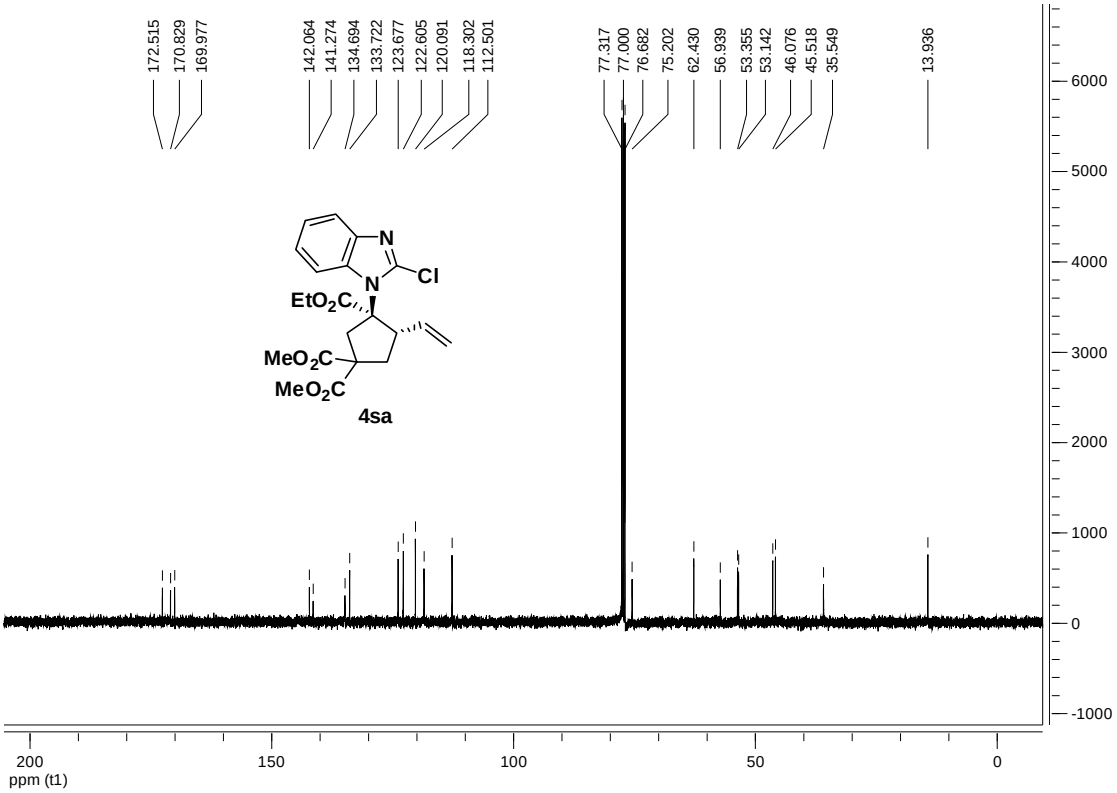
^{13}C-NMR for 3sa



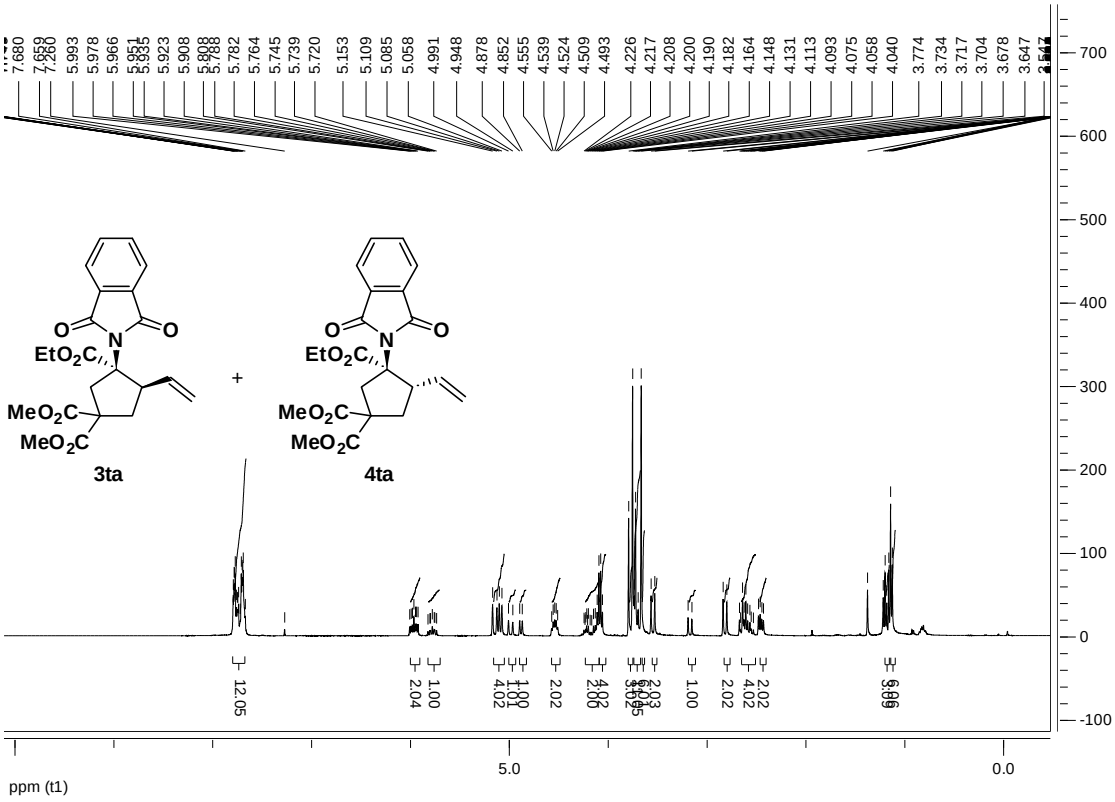
^{1}H-NMR for 4sa



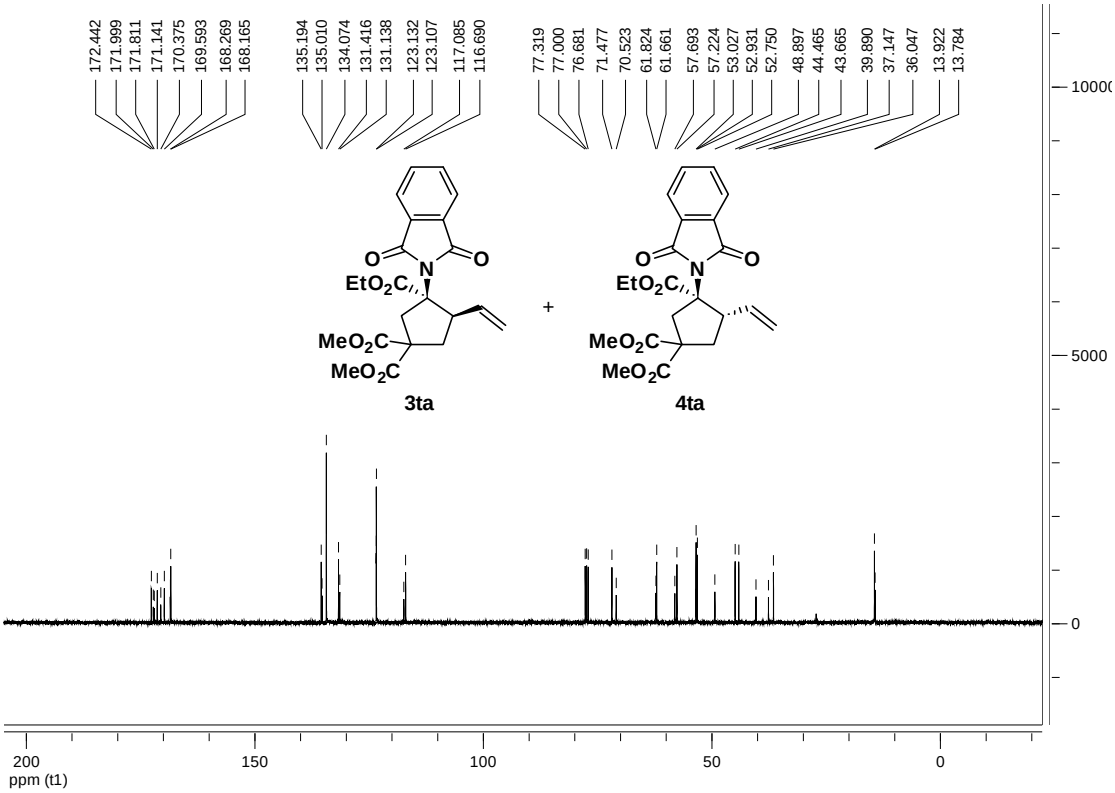
^{13}C-NMR for 4sa



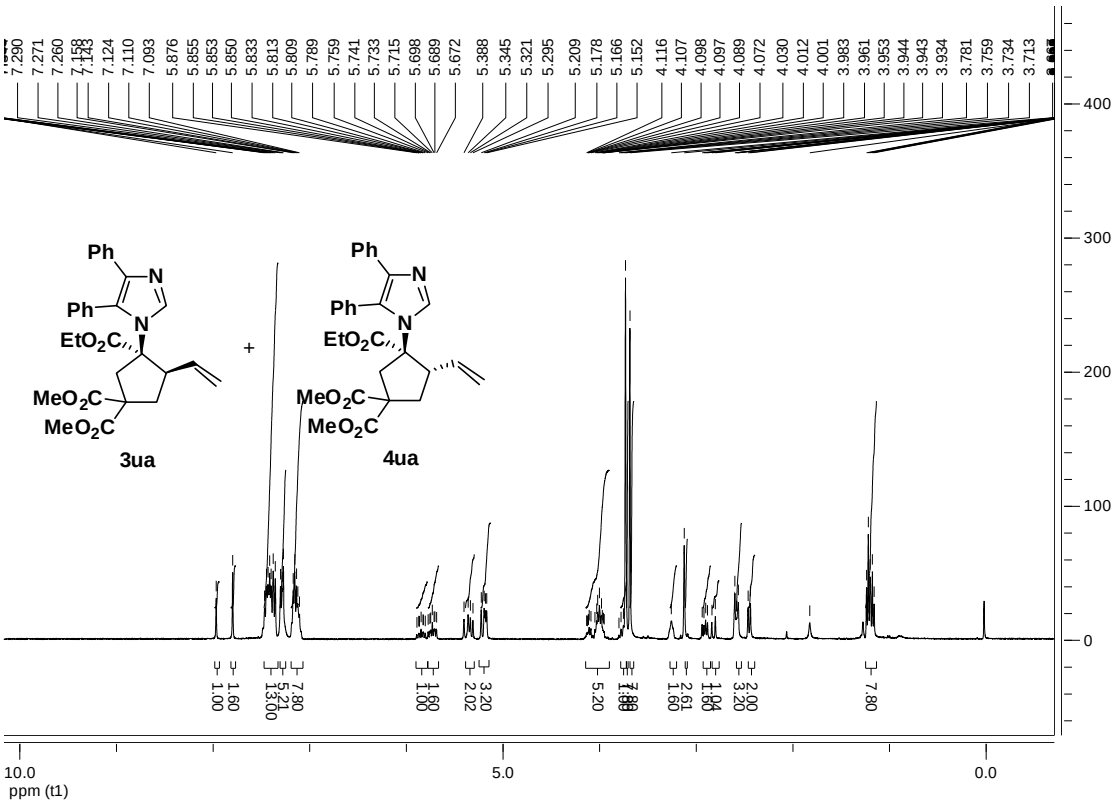
^{1}H-NMR for 3ta+4ta



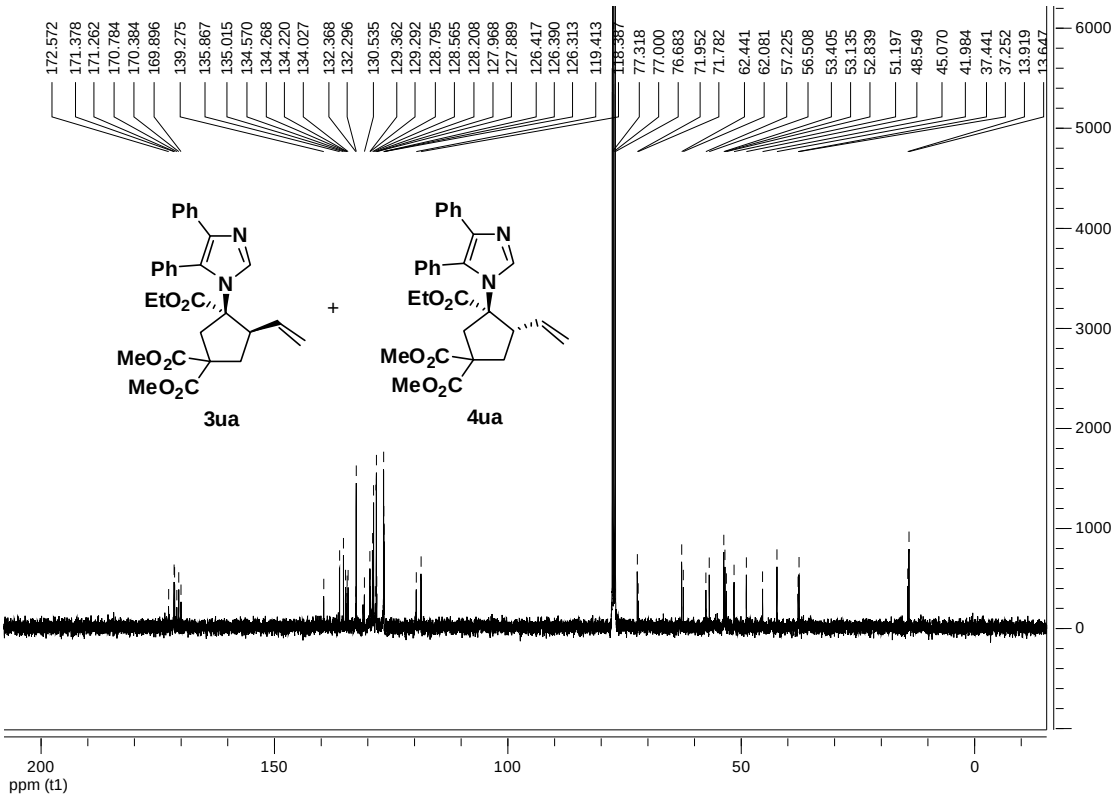
^{13}C-NMR for 3ta+4ta



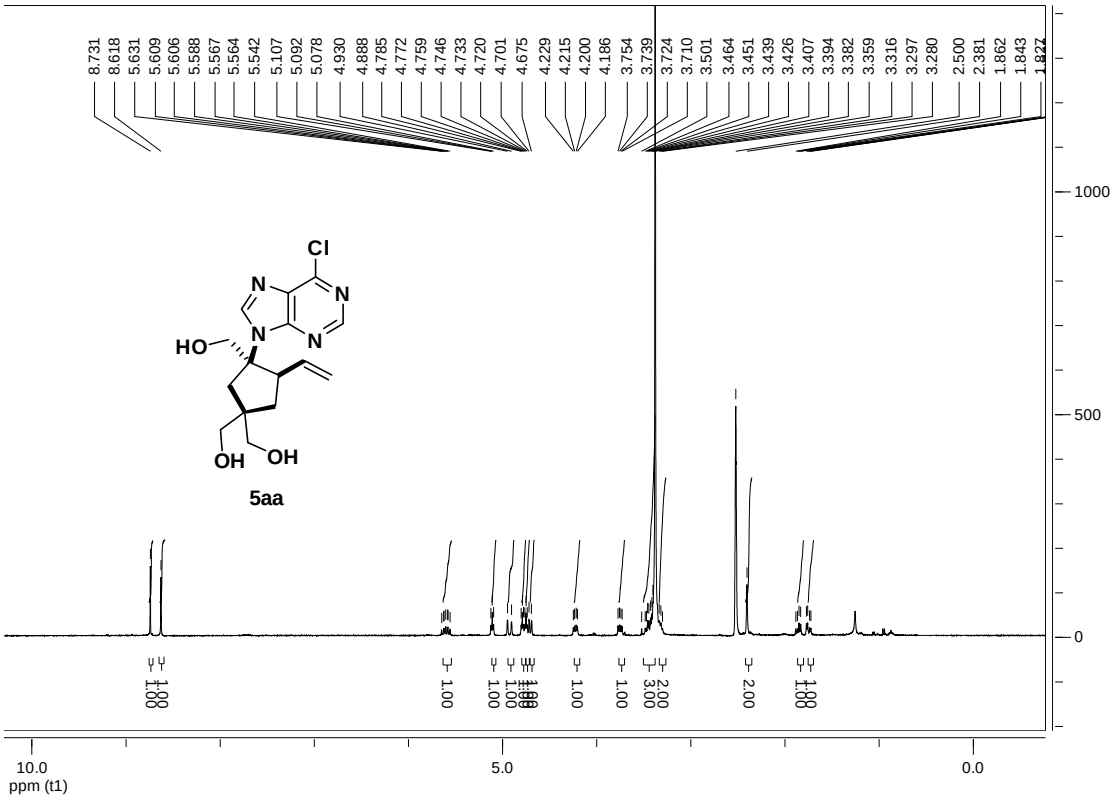
^{1}H-NMR for 3ua+4ua



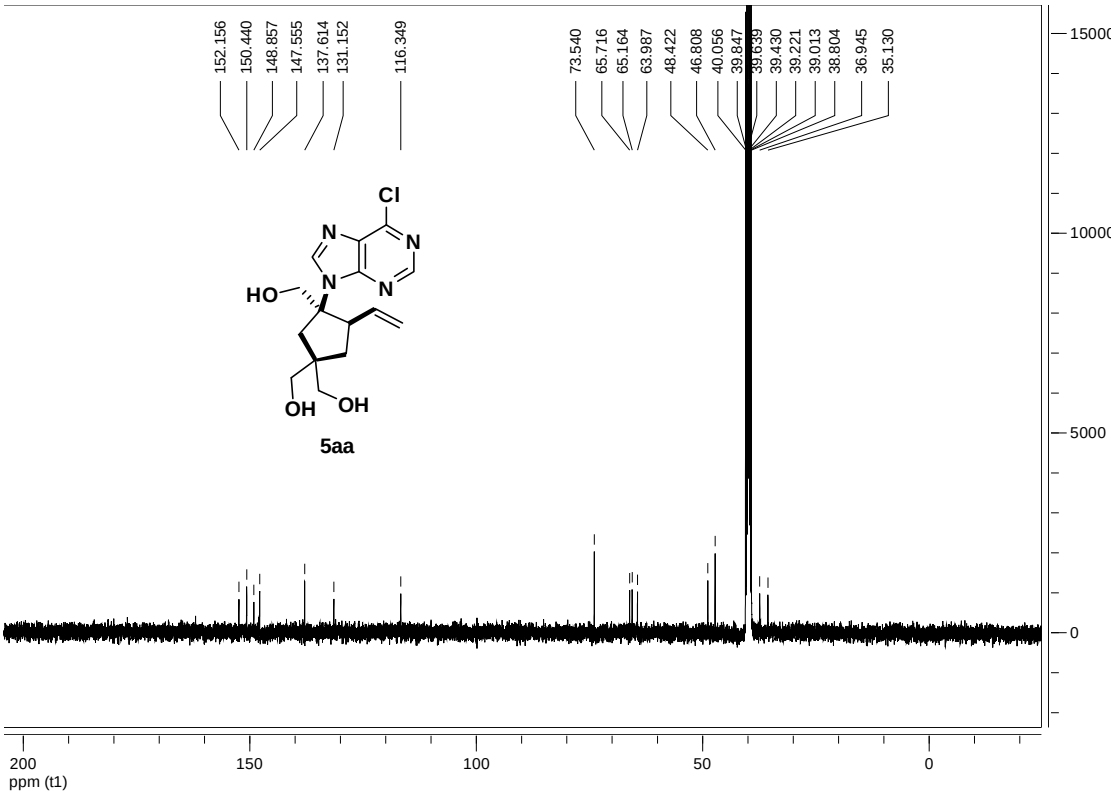
^{13}C-NMR for 3ua+4ua



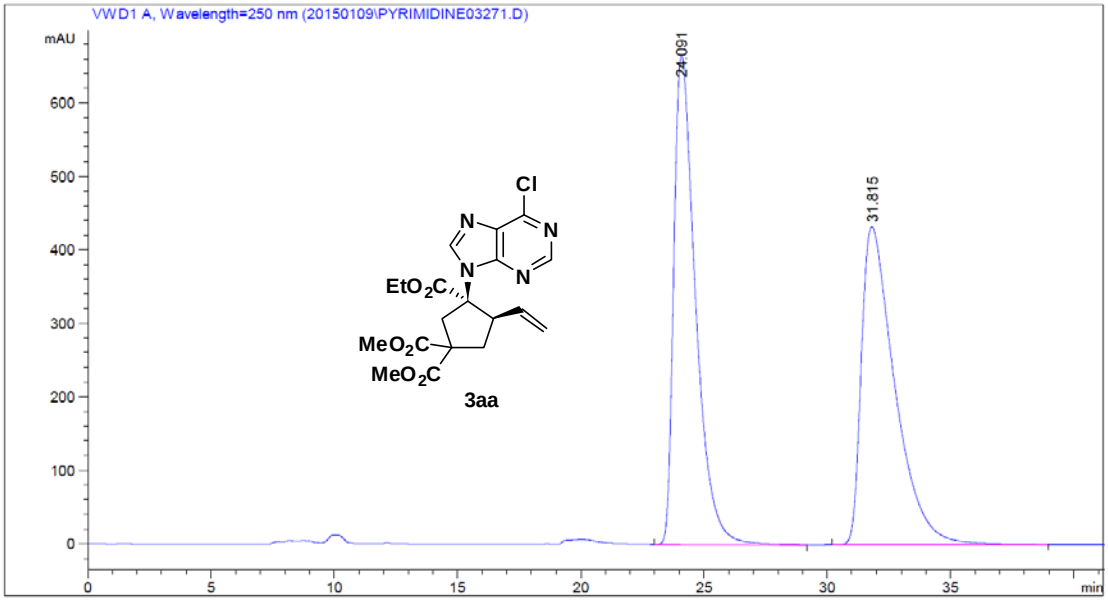
^{1}H-NMR for 5aa



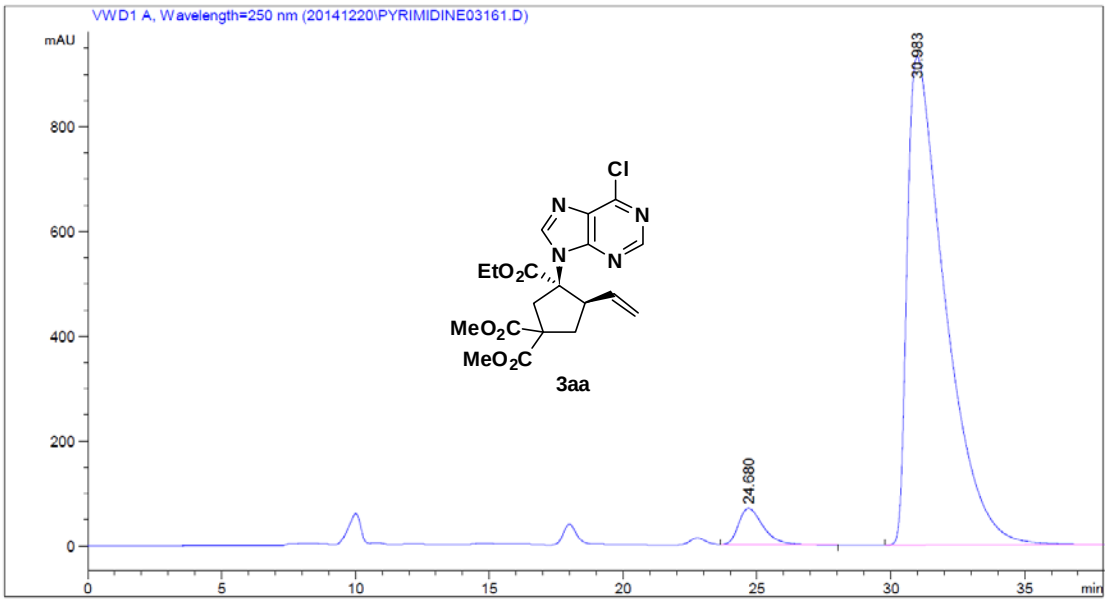
^{13}C-NMR for 5aa



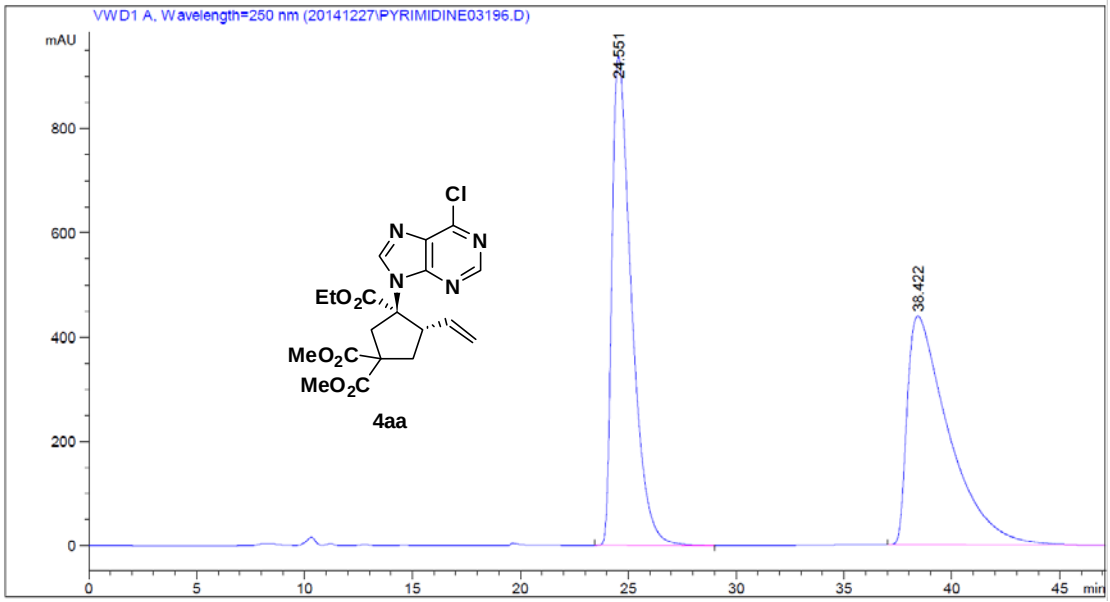
10. Copies of HPLC spectra for racemic and chiral compounds



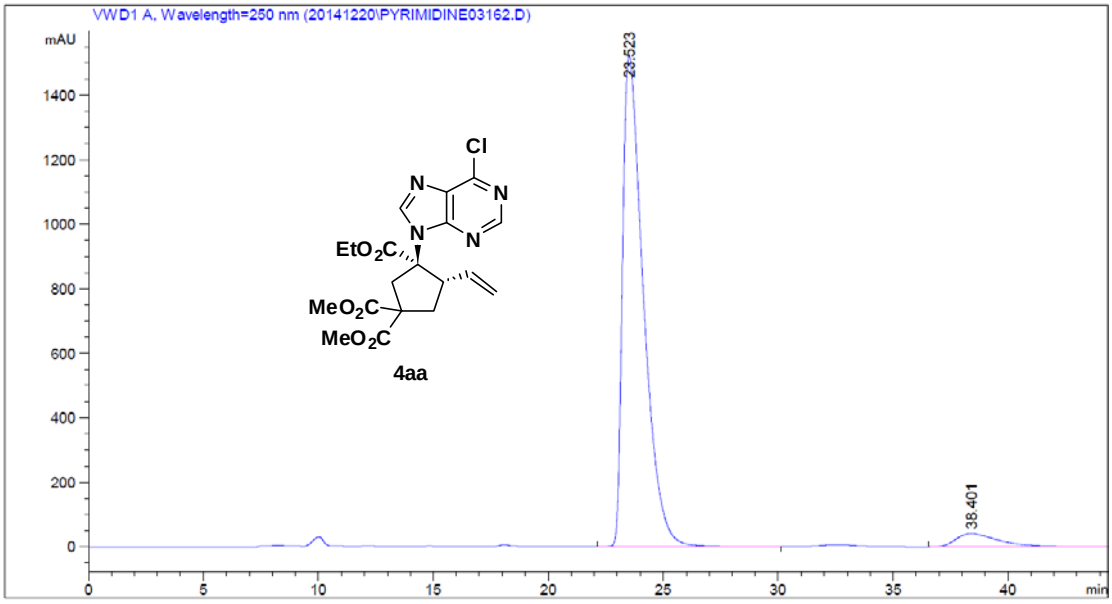
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.091	BB	0.9088	4.07308e4	665.79797	50.0516
2	31.815	BB	1.3739	4.06468e4	432.76617	49.9484



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.680	VB	0.9638	4509.07471	70.16232	4.6944
2	30.983	BBA	1.4278	9.15429e4	932.47876	95.3056

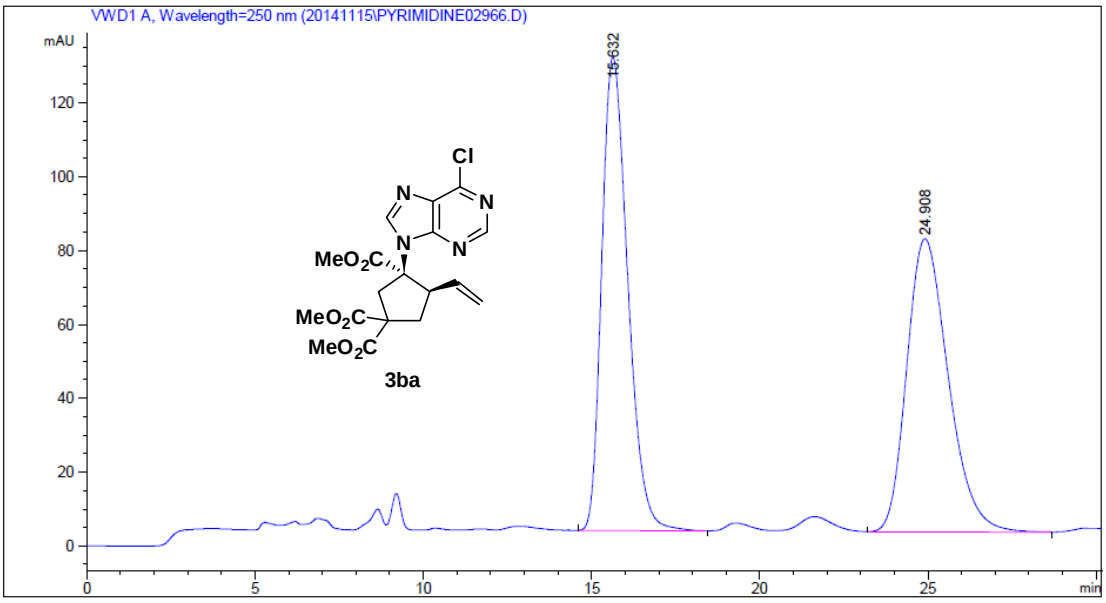


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.551	BB	0.9391	5.89973e4	938.01630	50.0130
2	38.422	BBA	1.9009	5.89666e4	439.29965	49.9870

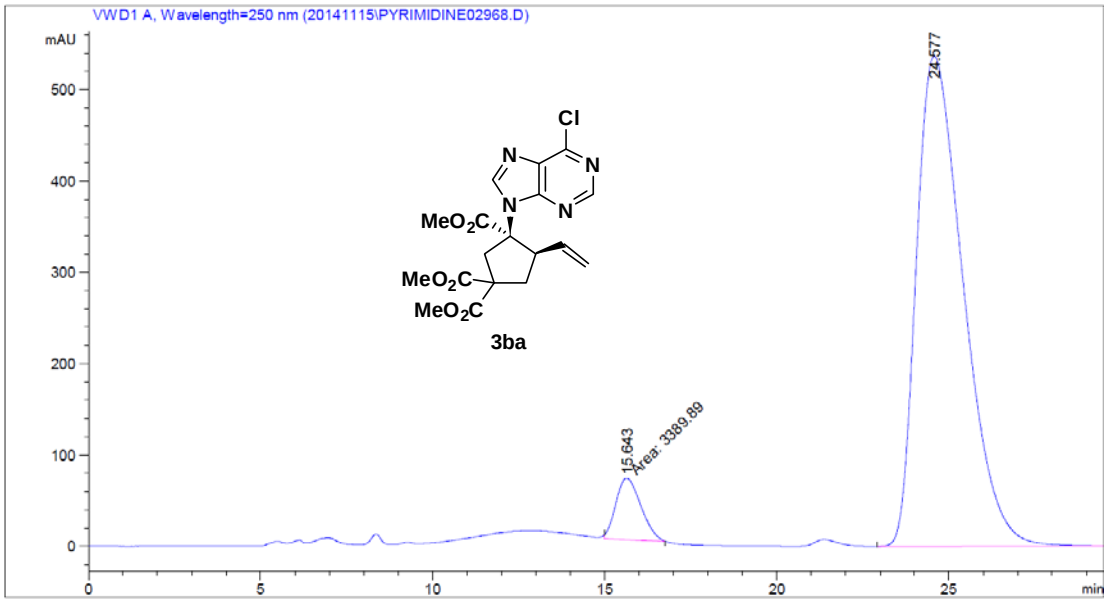


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.523	BB	0.9312	9.58123e4	1521.58008	94.8348
2	38.401	BBA	1.8073	5218.46777	41.38996	5.1652

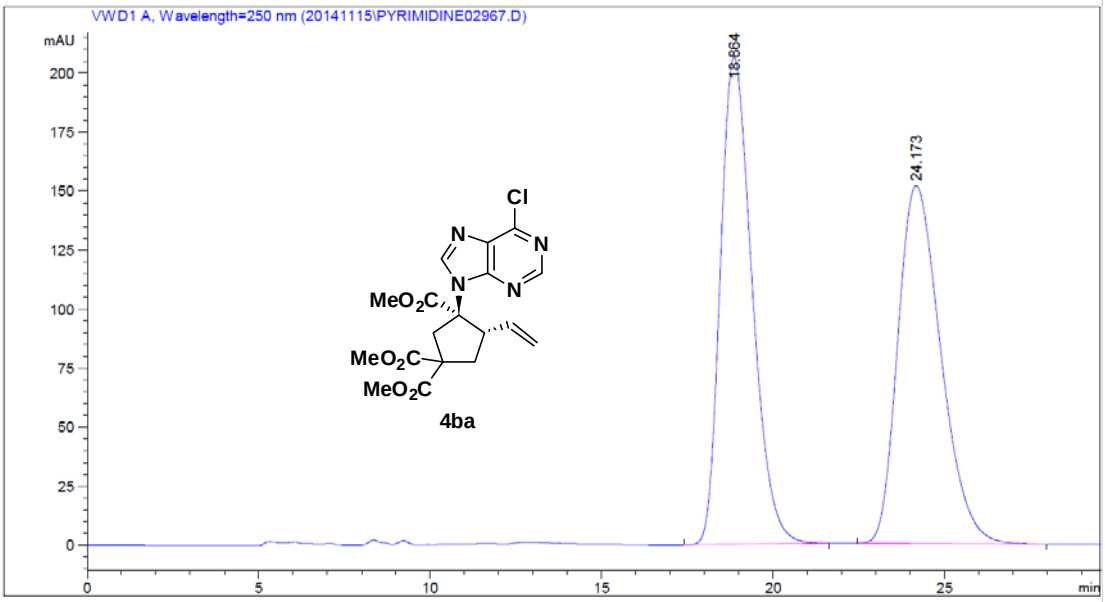
附图



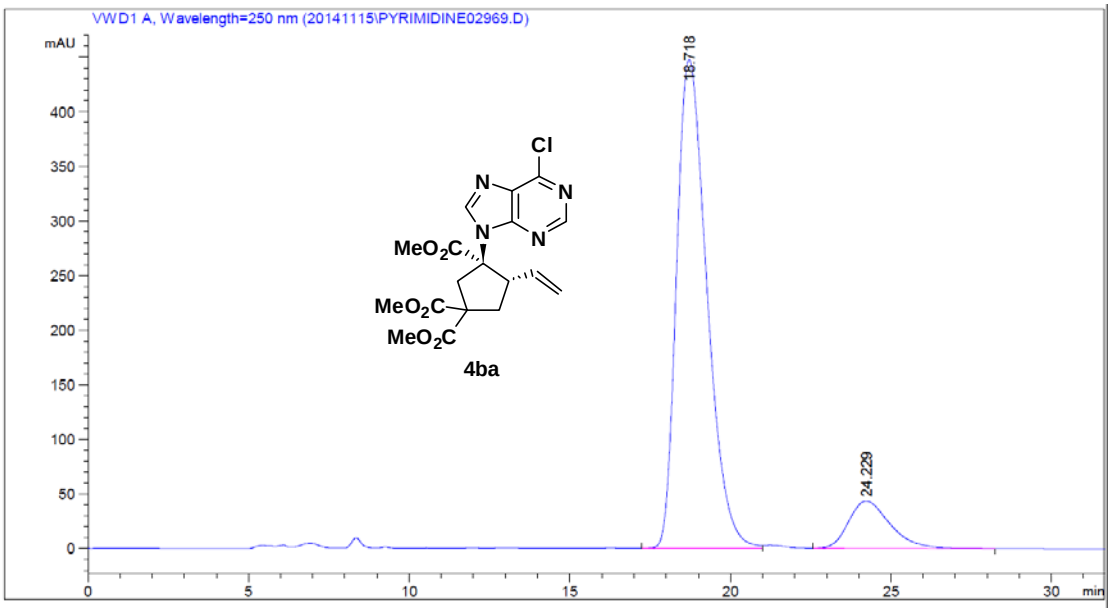
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.632	BB	0.8337	6871.03320	128.16833	50.2278
2	24.908	BB	1.3155	6808.72070	79.35571	49.7722



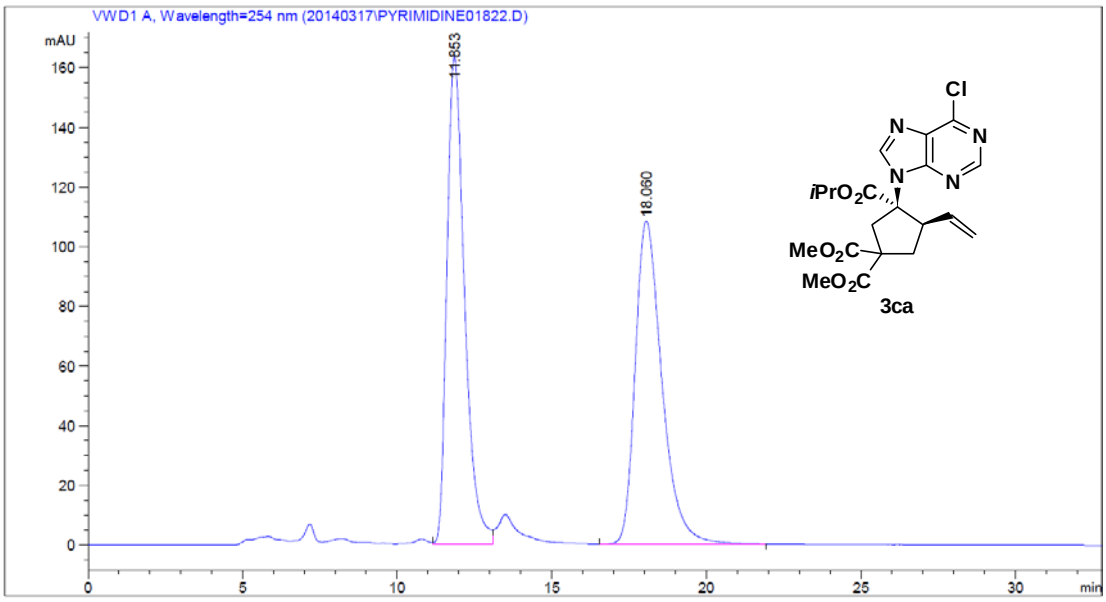
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.643	MM	0.8400	3389.88647	67.26059	6.2541
2	24.577	BBA	1.4482	5.08131e4	536.67584	93.7459



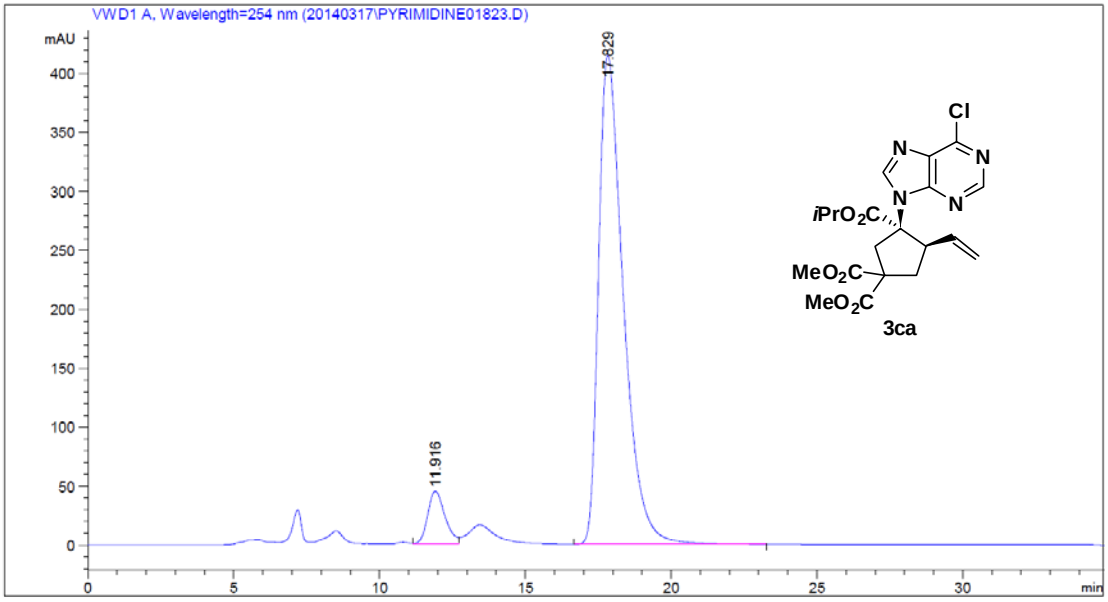
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.864	BB	1.0054	1.32579e4	206.47656	50.1368
2	24.173	BB	1.3433	1.31856e4	151.66927	49.8632



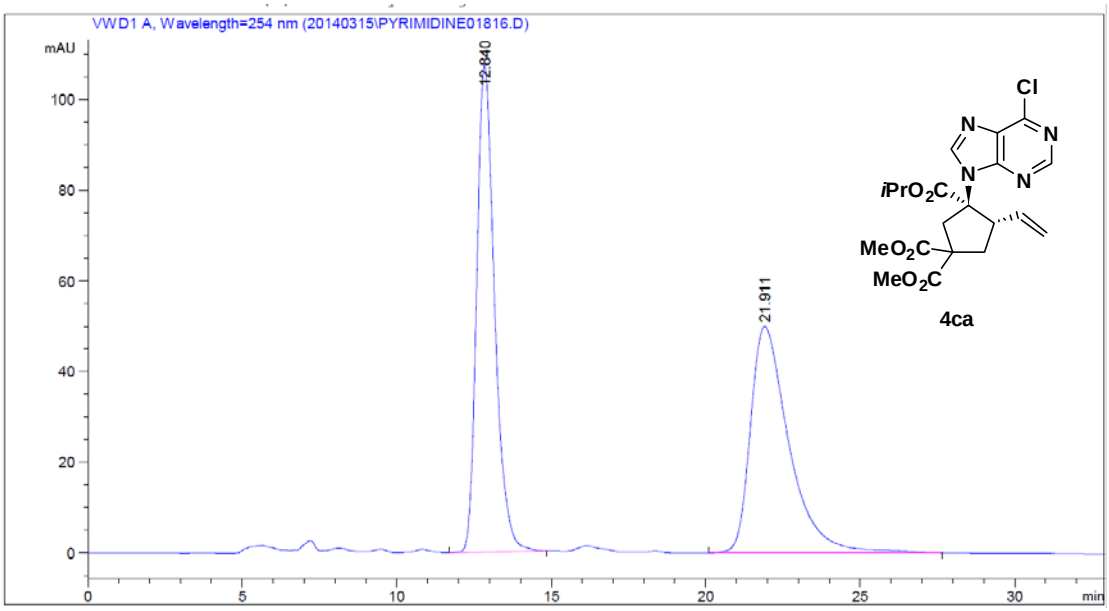
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.718	BV	1.0214	2.93405e4	447.38724	88.3031
2	24.229	BB	1.3575	3886.54590	43.41147	11.6969



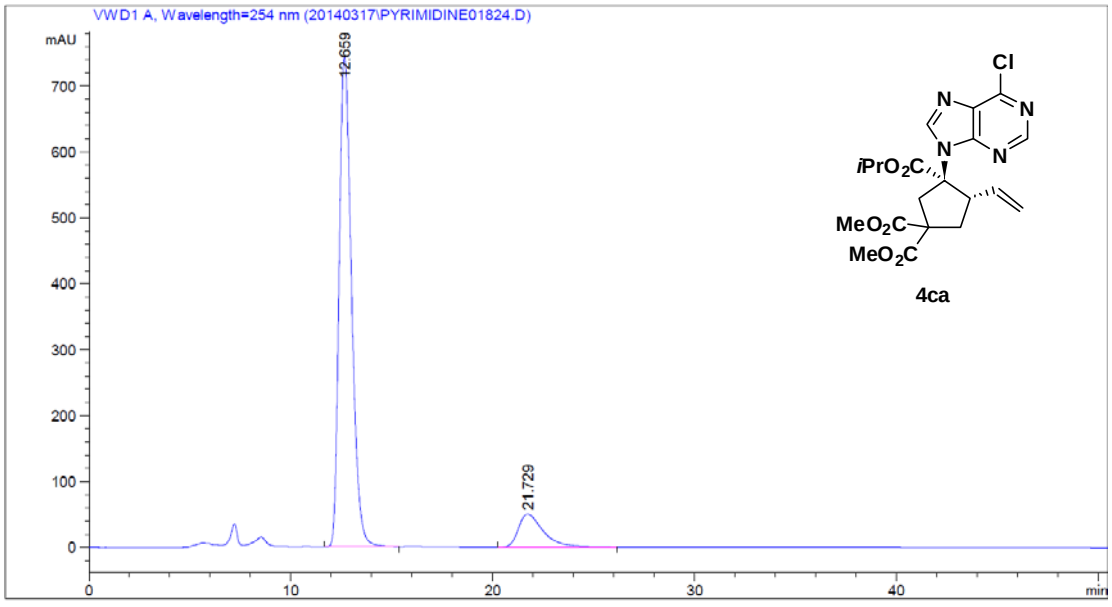
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.853	VV	0.6097	6471.43115	163.20473	49.9180
2	18.060	BB	0.9079	6492.68018	108.26465	50.0820



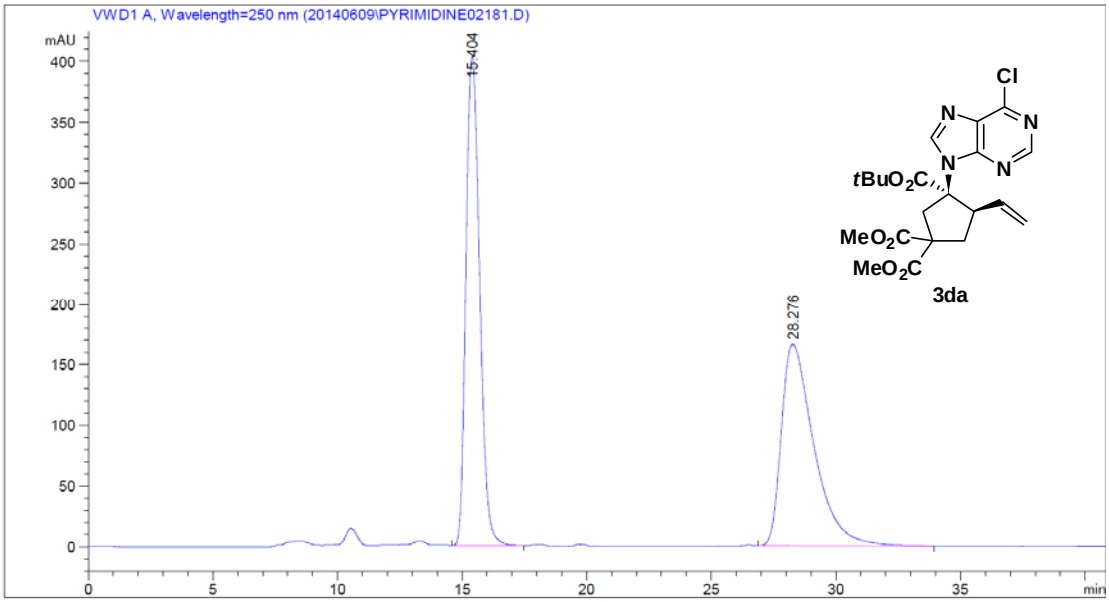
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.916	VV	0.6303	1859.51501	45.02452	7.0425
2	17.829	BB	0.8967	2.45448e4	415.02490	92.9575



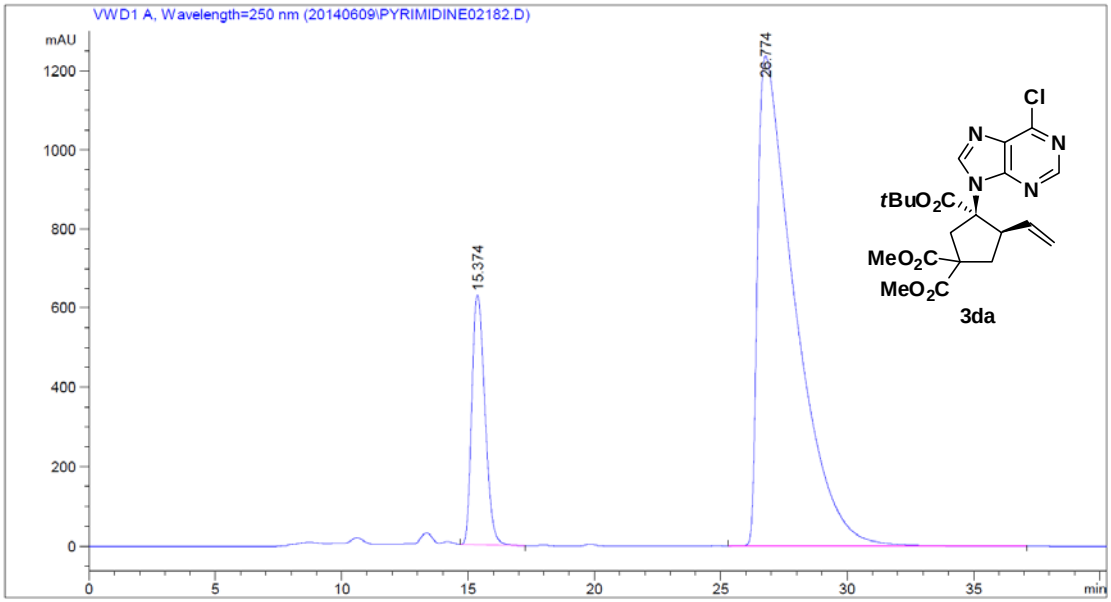
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.840	BB	0.6218	4320.90479	107.50692	49.9299
2	21.911	BB	1.2920	4333.04102	49.93214	50.0701



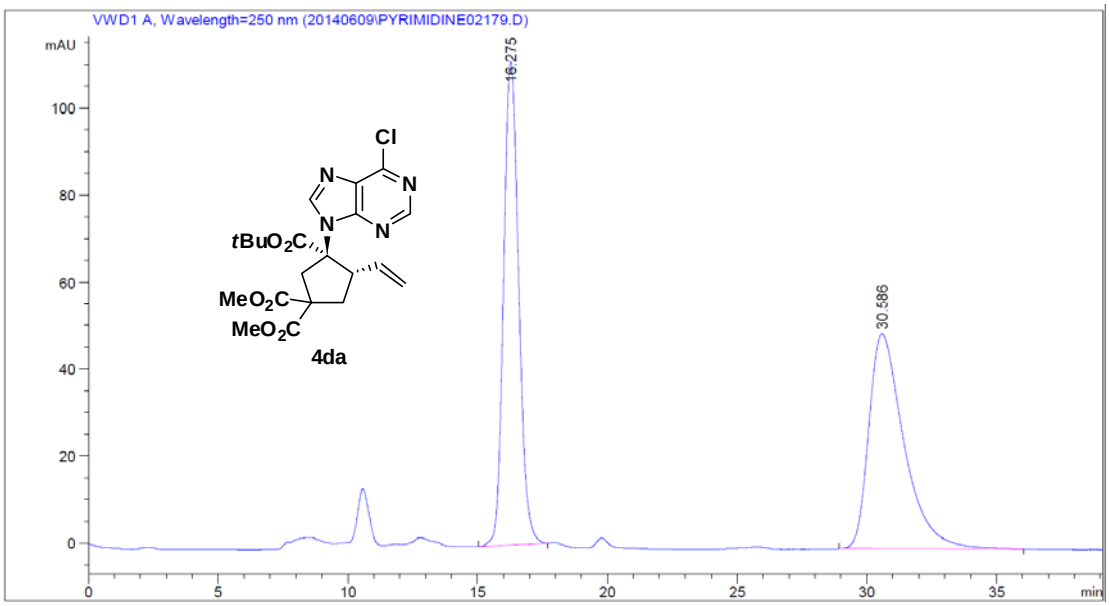
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.659	BB	0.6596	3.16678e4	744.04474	88.0454
2	21.729	BB	1.2761	4299.77441	49.97068	11.9546



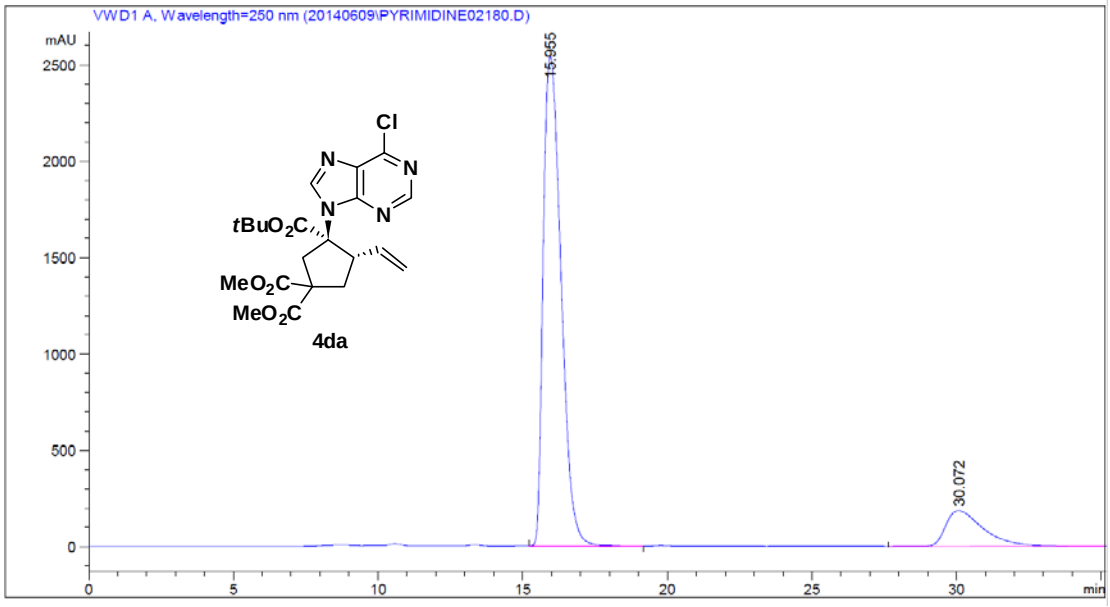
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.404	BB	0.6083	1.54335e4	403.05850	50.6381
2	28.276	BB	1.3405	1.50446e4	166.11404	49.3619



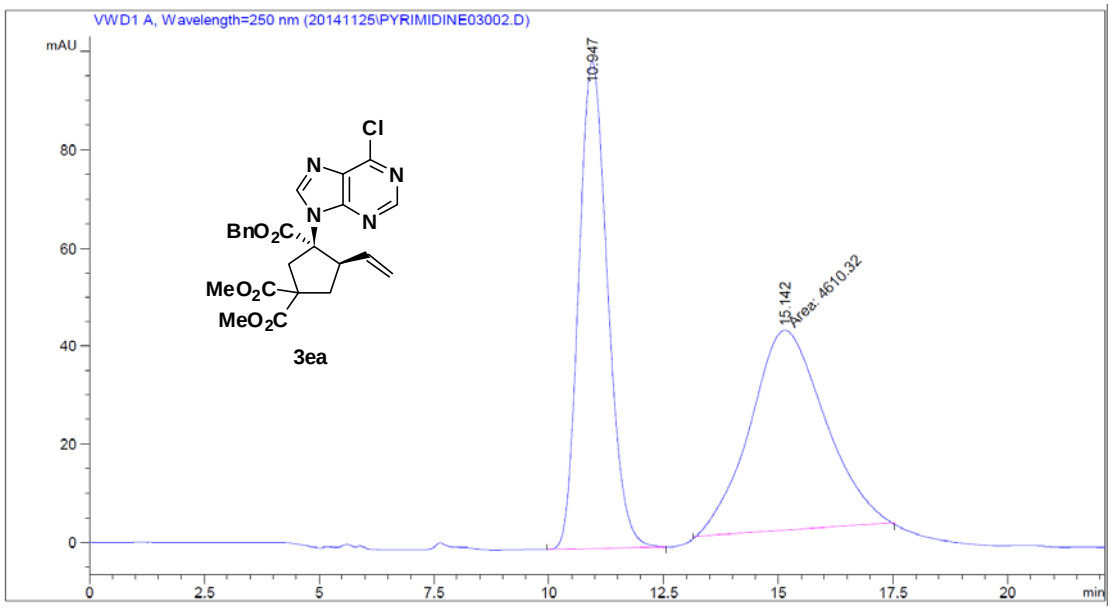
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.374	VB	0.5640	2.27110e4	631.09937	15.2977
2	26.774	BB	1.4043	1.25749e5	1235.57471	84.7023



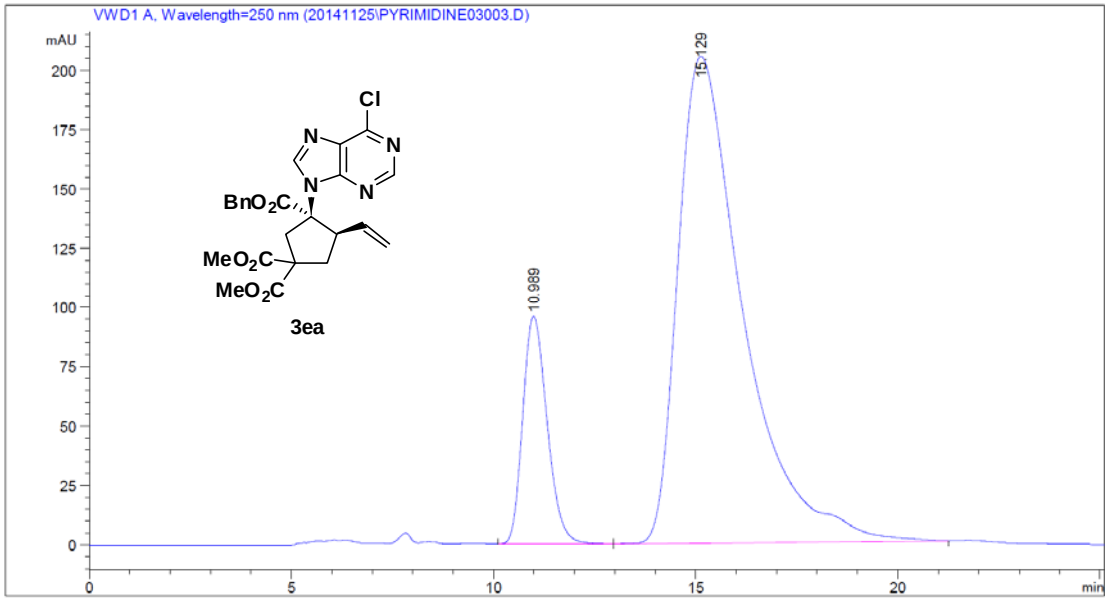
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.275	BB	0.6214	4491.74023	111.15520	49.2052
2	30.586	BB	1.3393	4636.84375	49.28643	50.7948



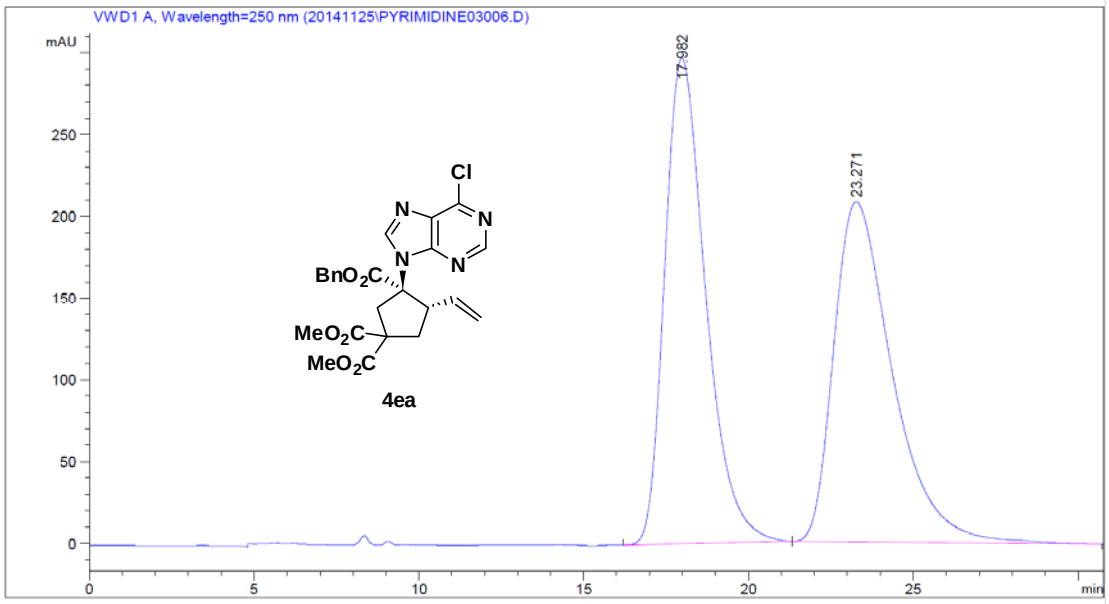
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.955	VB	0.6842	1.08839e5	2543.14746	86.4642
2	30.072	BBA	1.3226	1.70384e4	186.93054	13.5358



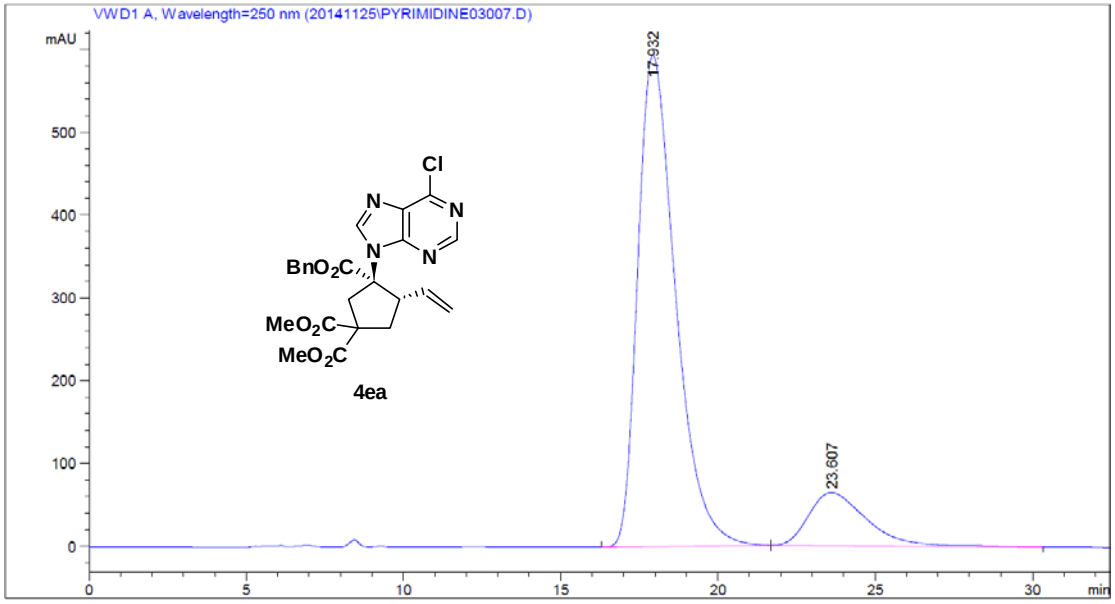
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.947	BB	0.6704	4325.55566	99.19466	48.4066
2	15.142	MM	1.8880	4610.32373	40.69844	51.5934



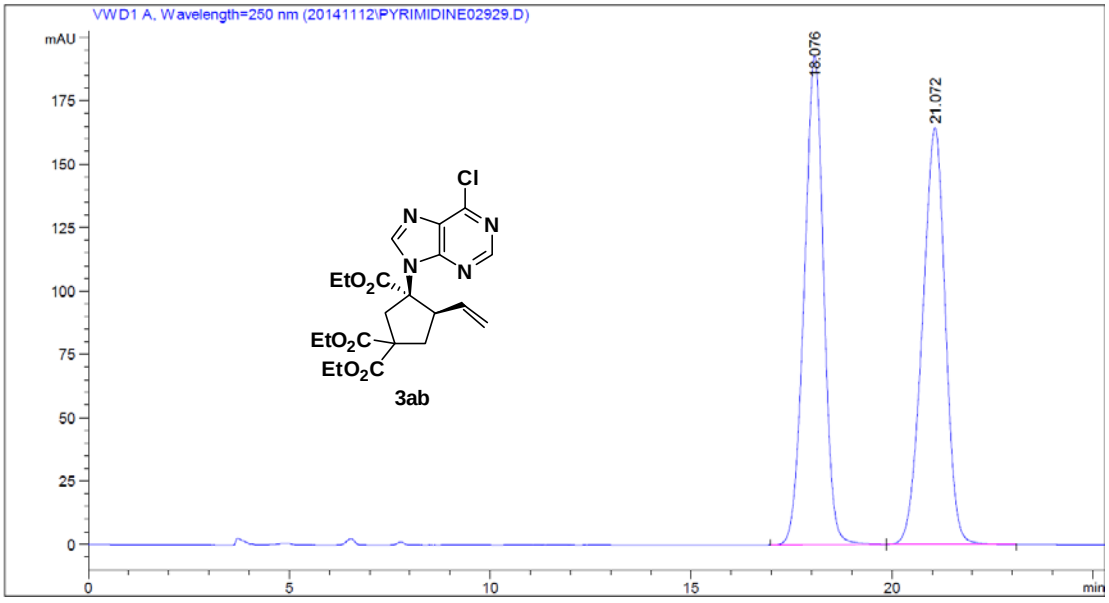
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.989	BB	0.6457	4007.11670	95.70467	14.8528
2	15.129	BB	1.6312	2.29717e4	205.12367	85.1472



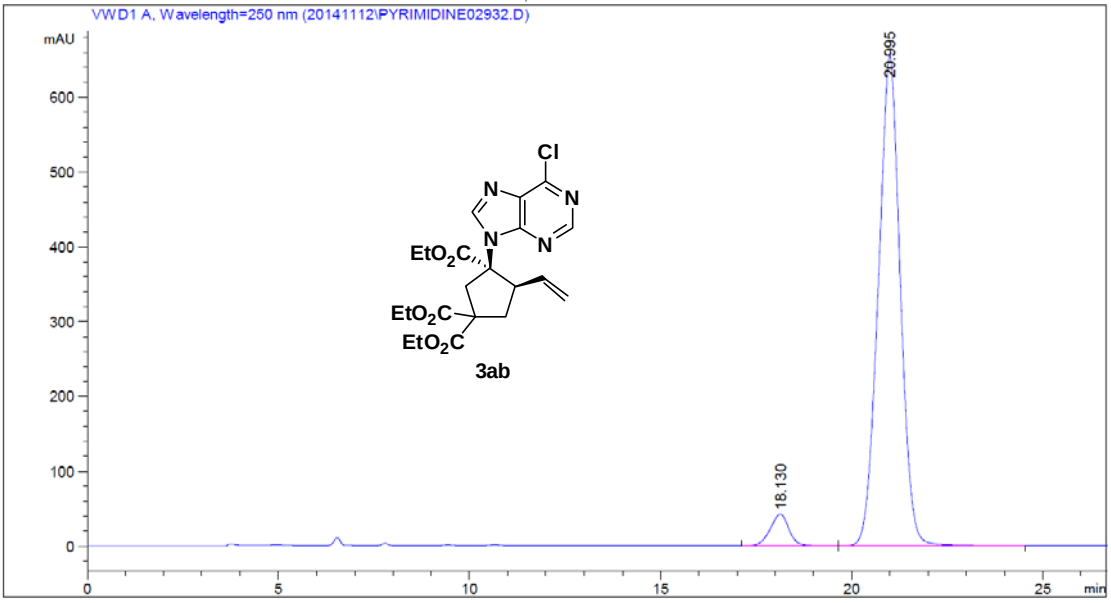
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.982	BB	1.3172	2.56252e4	296.85184	49.9797
2	23.271	BBA	1.7882	2.56461e4	208.16629	50.0203



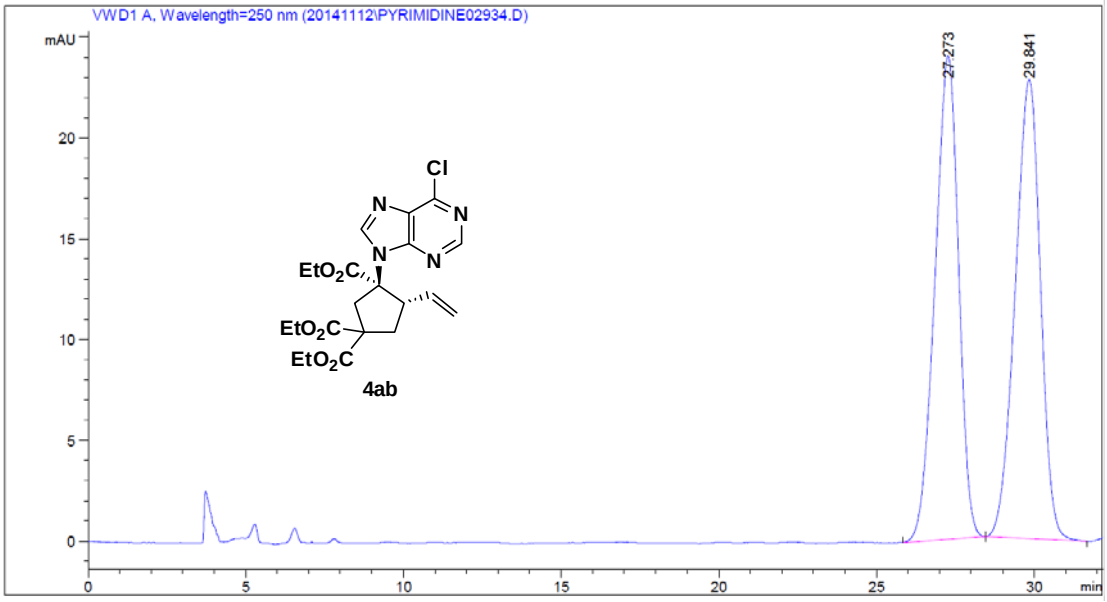
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.932	BB	1.2646	4.94698e4	592.90533	85.8843
2	23.607	BB	1.8318	8130.74658	63.93077	14.1157



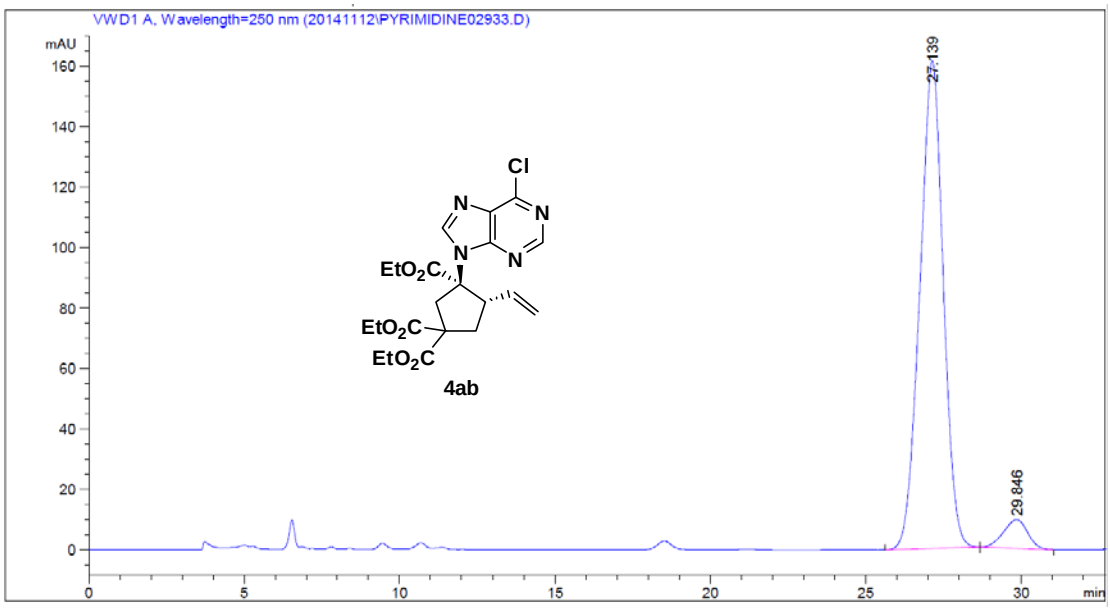
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.076	BB	0.5108	6476.70605	193.03288	49.8534
2	21.072	BB	0.6094	6514.79541	164.40807	50.1466



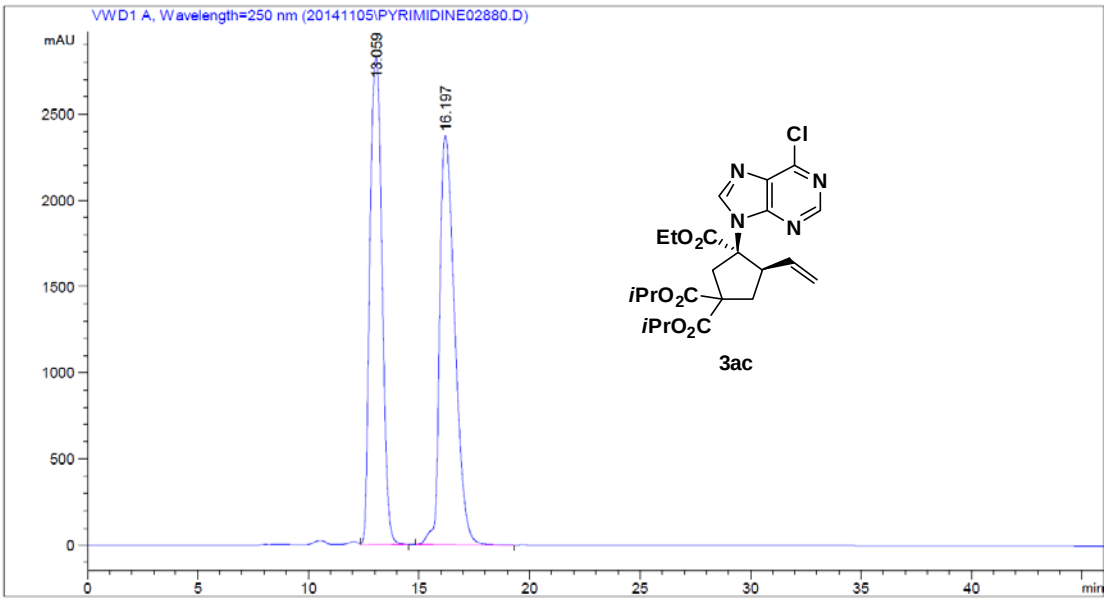
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.130	BB	0.5200	1443.07983	42.33468	5.2399
2	20.995	BB	0.5911	2.60970e4	655.51215	94.7601



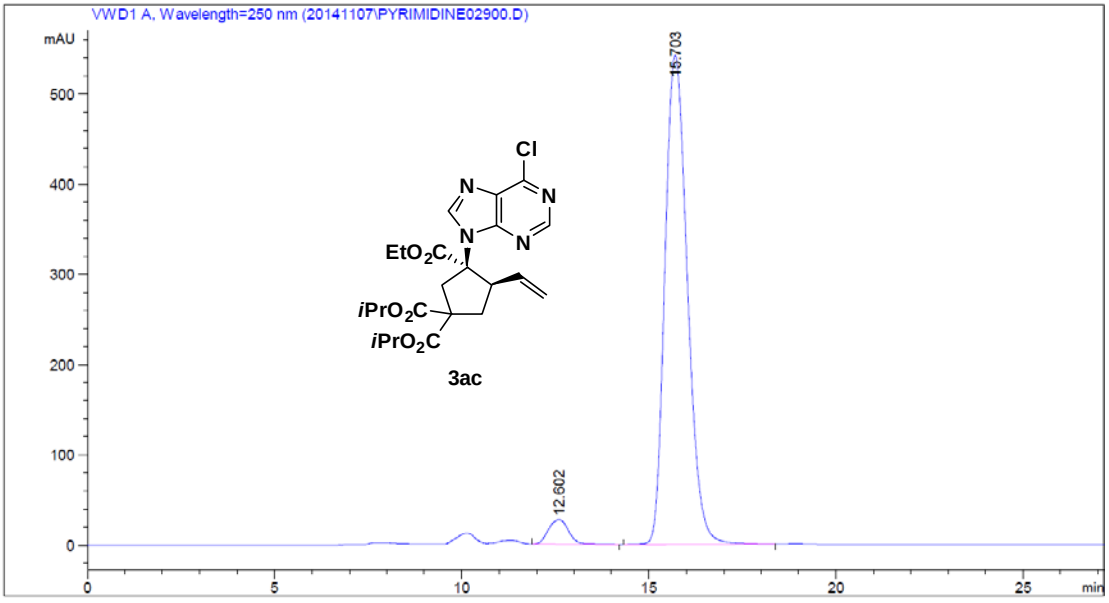
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.273	BB	0.7962	1247.13232	23.97345	49.5696
2	29.841	BB	0.8435	1268.79114	22.77703	50.4304



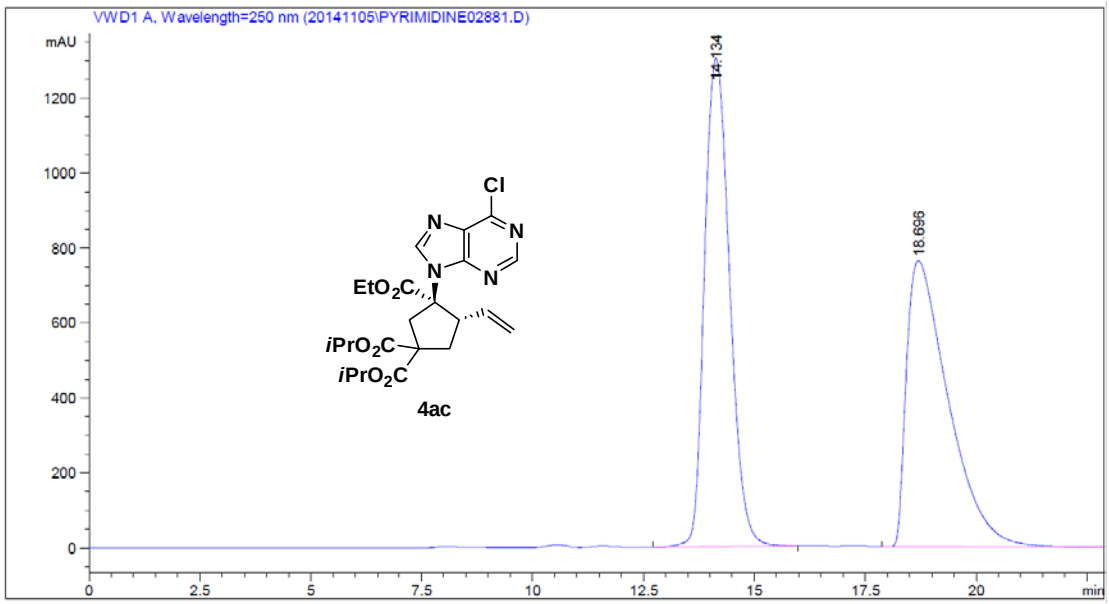
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.139	BB	0.7796	8452.59668	161.47734	94.2596
2	29.846	BB	0.8088	514.76215	9.53753	5.7404



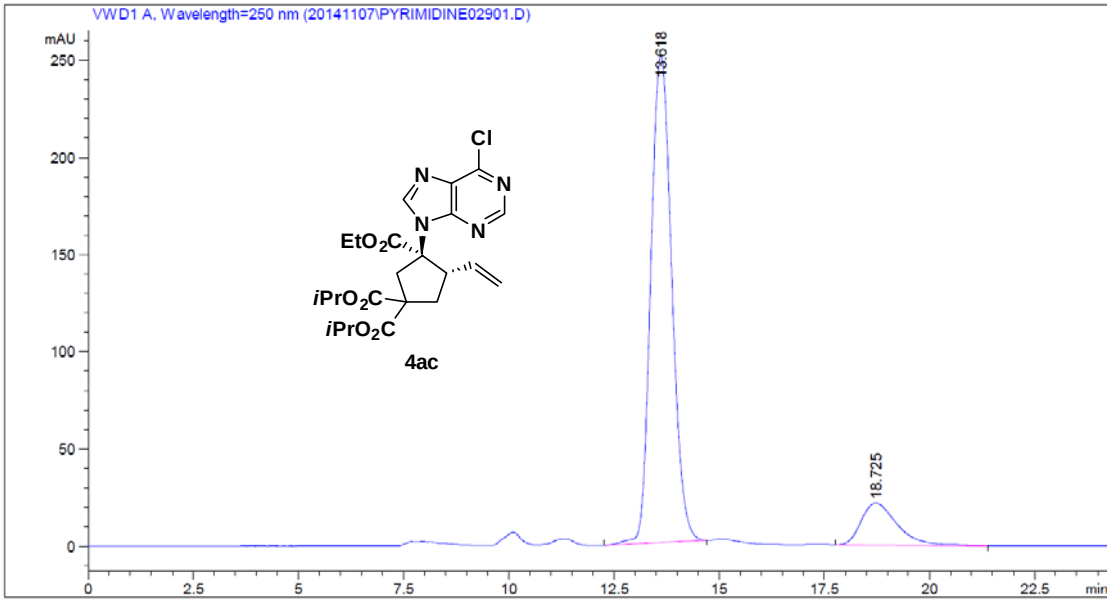
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.059	VB	0.6215	1.07258e5	2828.18799	48.7800
2	16.197	BB	0.7422	1.12623e5	2370.17896	51.2200



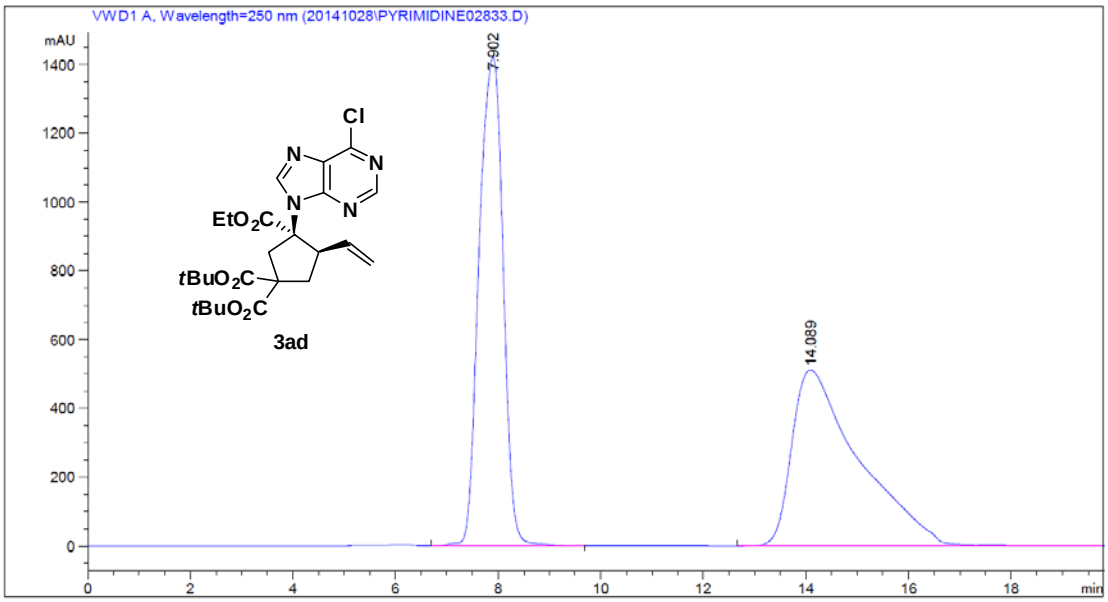
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.602	BB	0.6049	1016.15186	27.19337	4.3094
2	15.703	BB	0.6602	2.25635e4	542.27911	95.6906



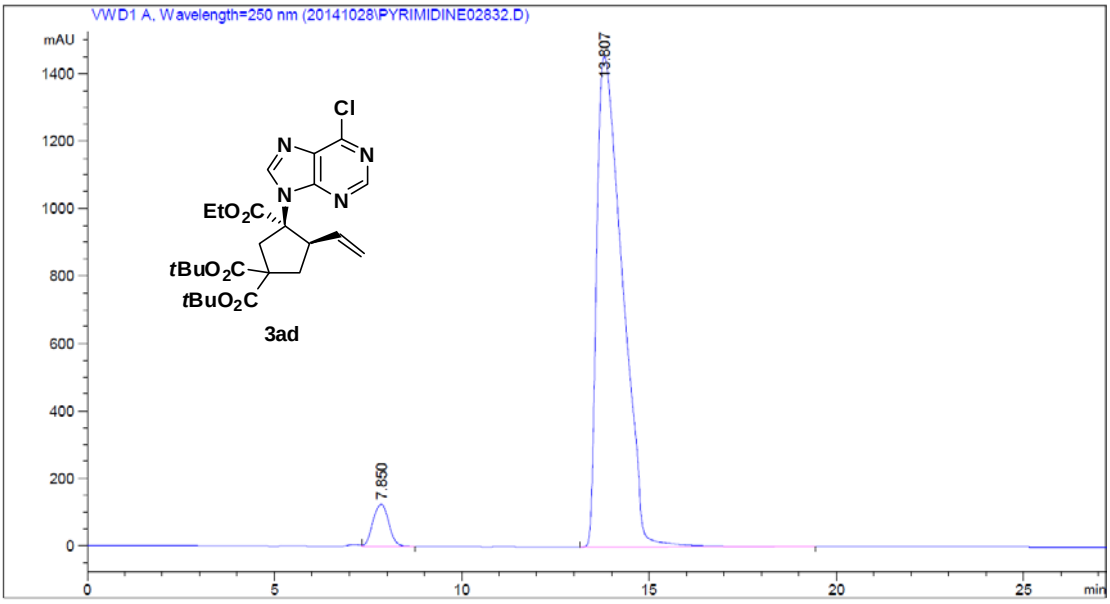
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.134	BB	0.6238	5.13154e4	1303.60779	50.6420
2	18.696	BBA	0.9792	5.00145e4	764.06042	49.3580



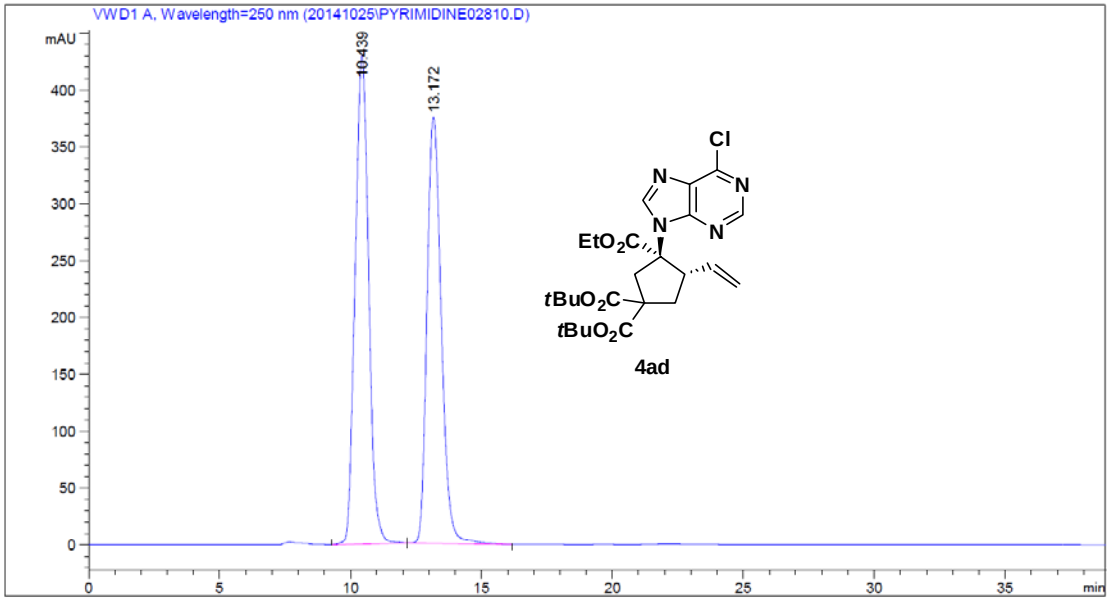
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.618	BB	0.5418	8670.31250	250.69495	87.1130
2	18.725	BB	0.9026	1282.63428	21.64187	12.8870



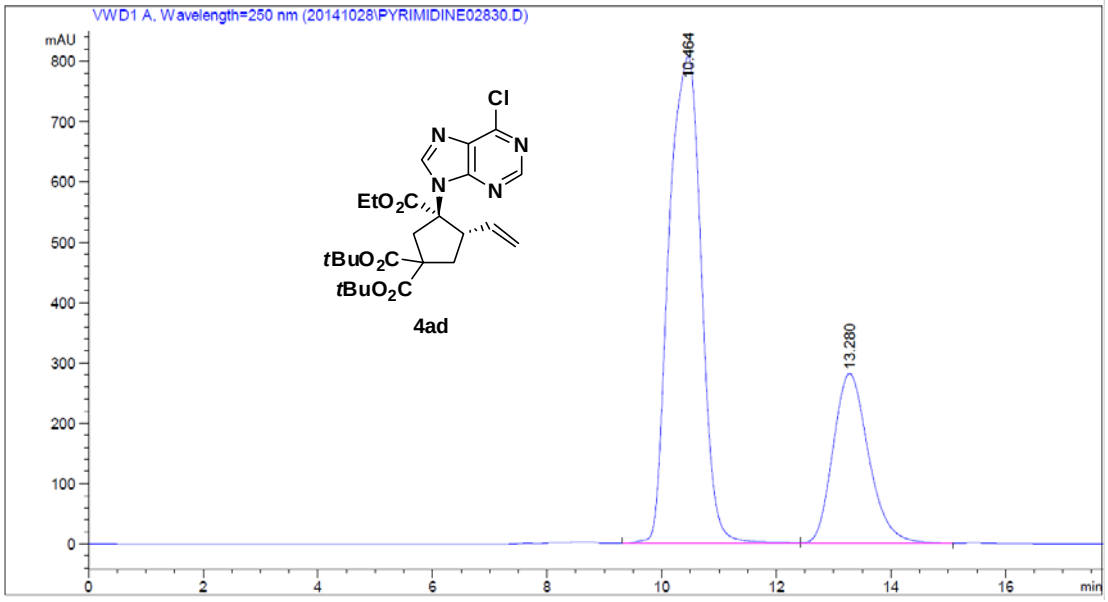
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.902	BB	0.5326	4.60939e4	1421.67676	49.8384
2	14.089	BBA	1.2816	4.63929e4	511.20132	50.1616



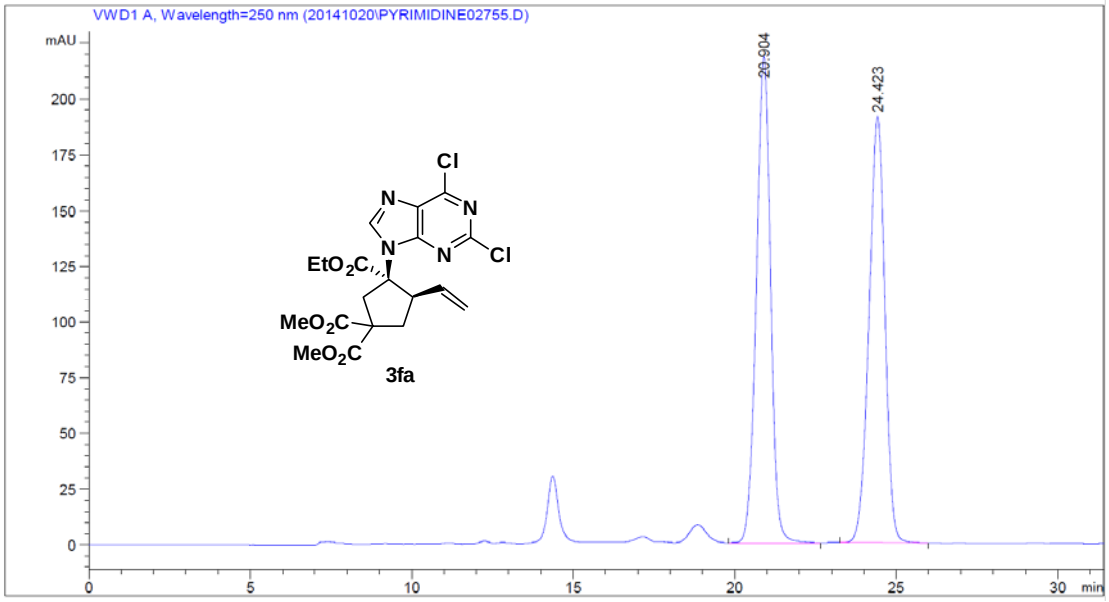
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.850	VB	0.4809	3694.26758	125.27534	5.0764
2	13.807	BB	0.7106	6.90786e4	1456.55249	94.9236



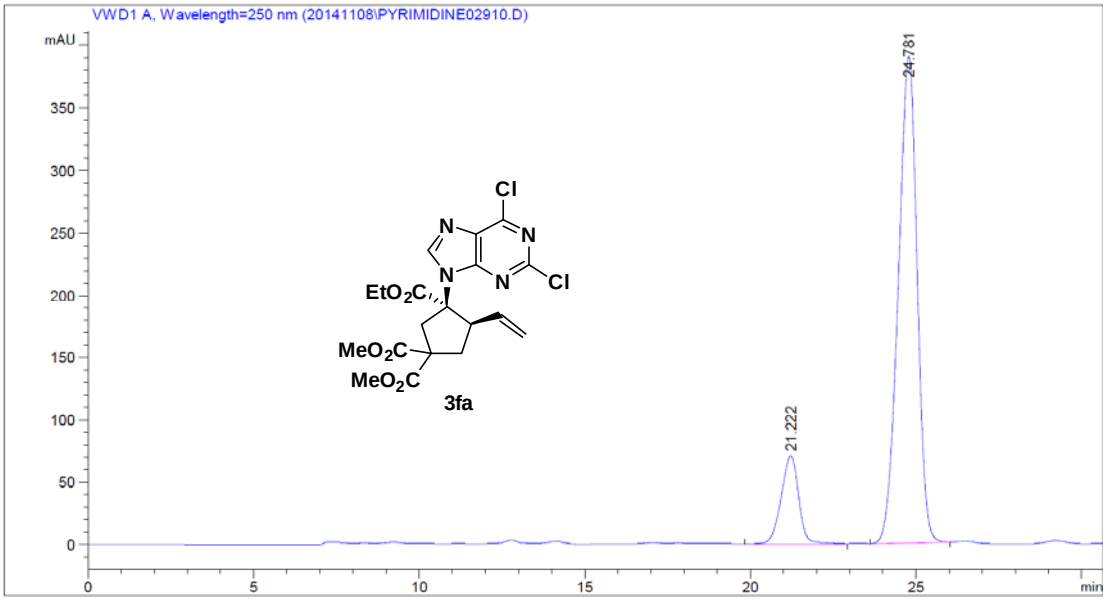
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.439	BB	0.5563	1.53879e4	429.51047	52.0821
2	13.172	BB	0.5877	1.41576e4	374.81131	47.9179



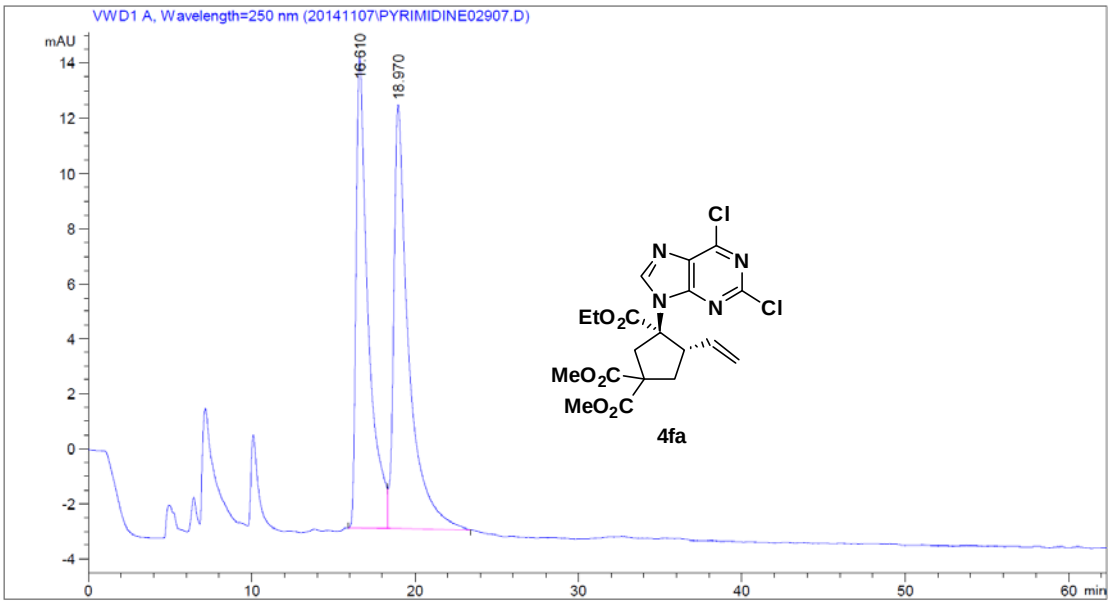
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.464	BV	0.6396	3.14372e4	806.62860	72.3200
2	13.280	VB	0.6661	1.20324e4	280.70132	27.6800



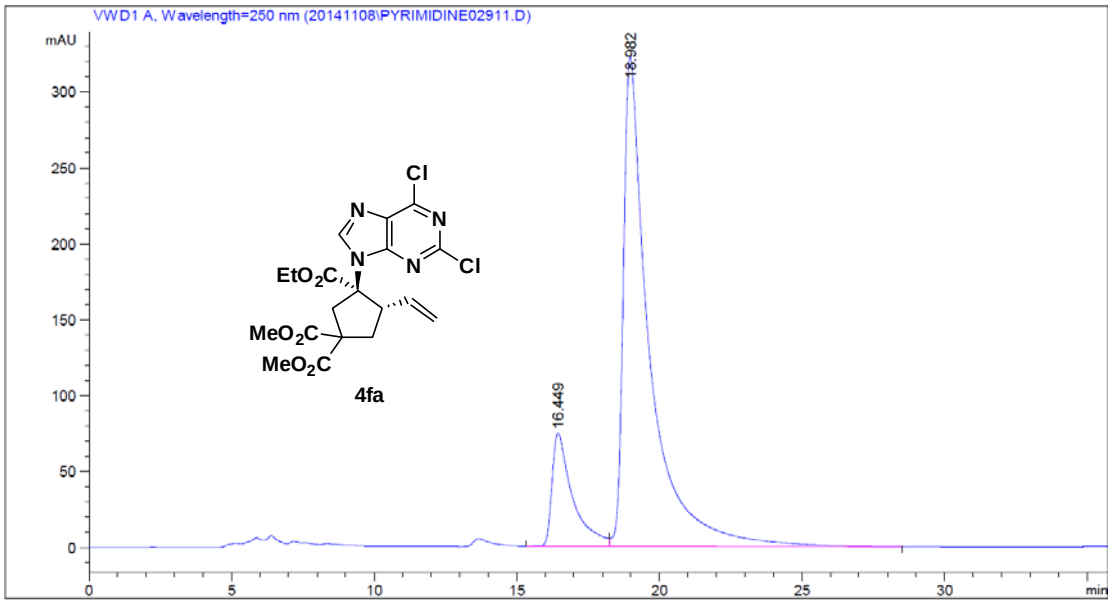
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.904	BB	0.4699	6686.82715	218.05472	50.5770
2	24.423	BB	0.5195	6534.26563	191.21613	49.4230



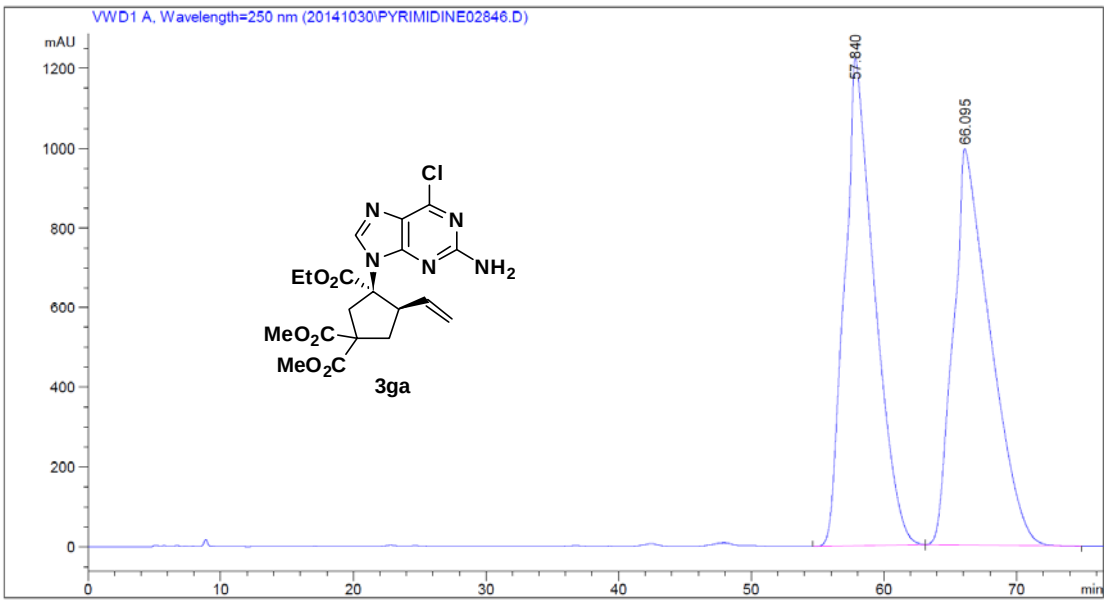
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.222	BB	0.5592	2583.94116	70.88277	14.3725
2	24.781	BB	0.6131	1.53945e4	390.27124	85.6275



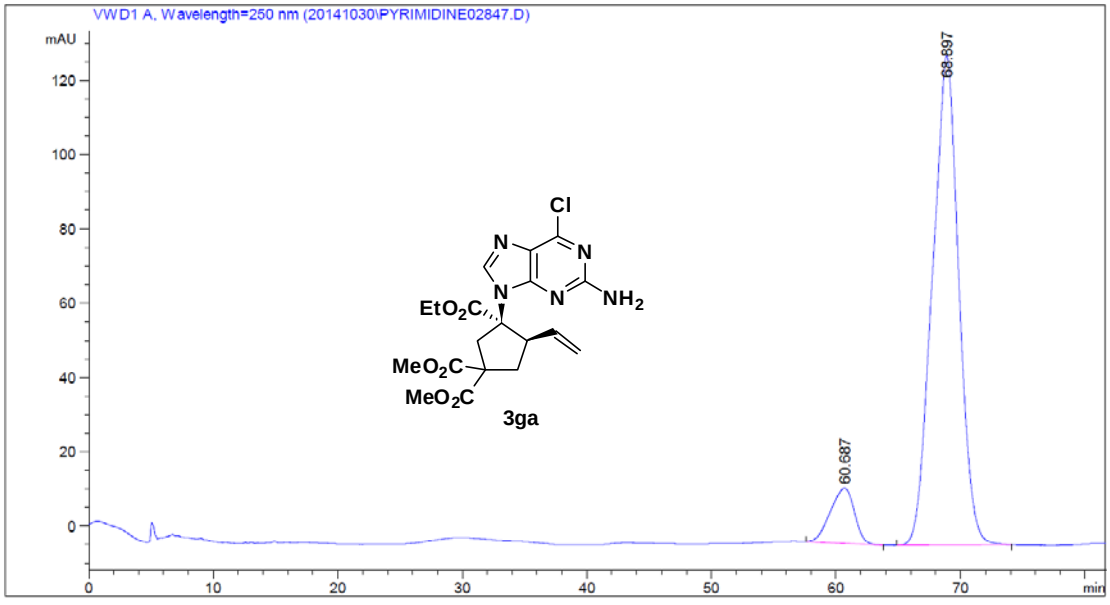
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.610	BV	0.7330	885.68542	17.08245	47.5016
2	18.970	VB	0.8829	978.85120	15.39814	52.4984



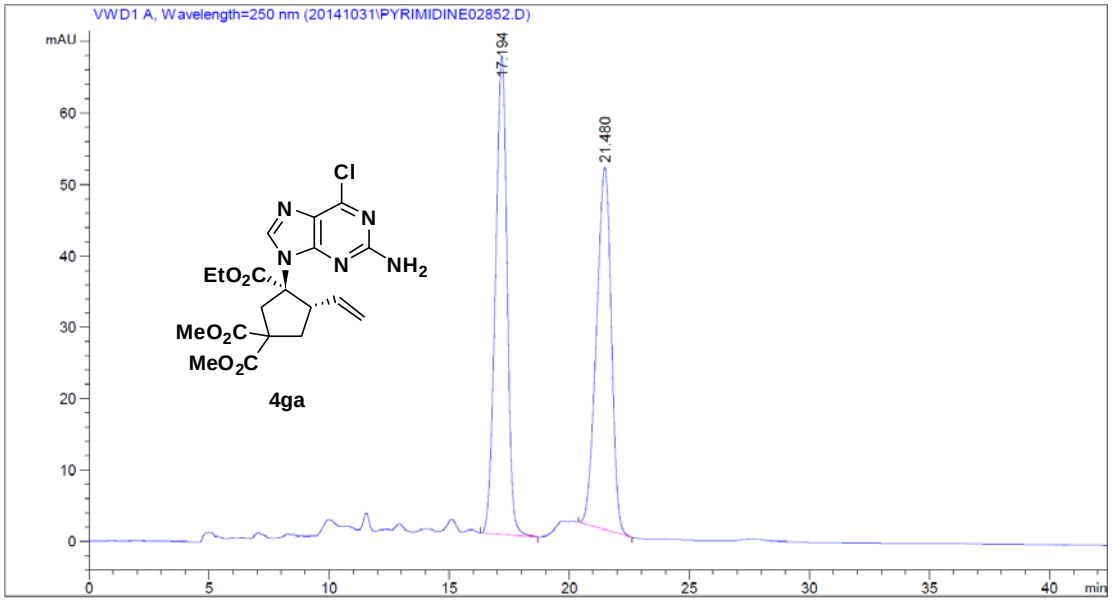
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.449	BV	0.7086	3737.05396	74.74033	15.2702
2	18.982	VB	0.8897	2.07358e4	322.58212	84.7298



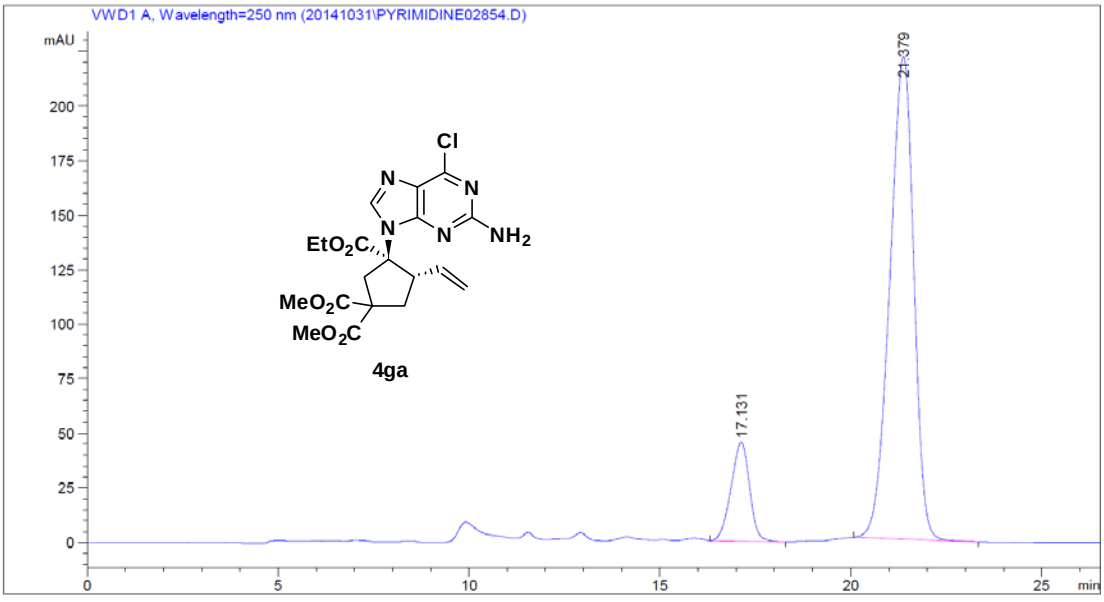
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	57.840	BB	2.1139	1.92426e5	1222.87378	49.9761
2	66.095	BB	2.4889	1.92610e5	994.15344	50.0239



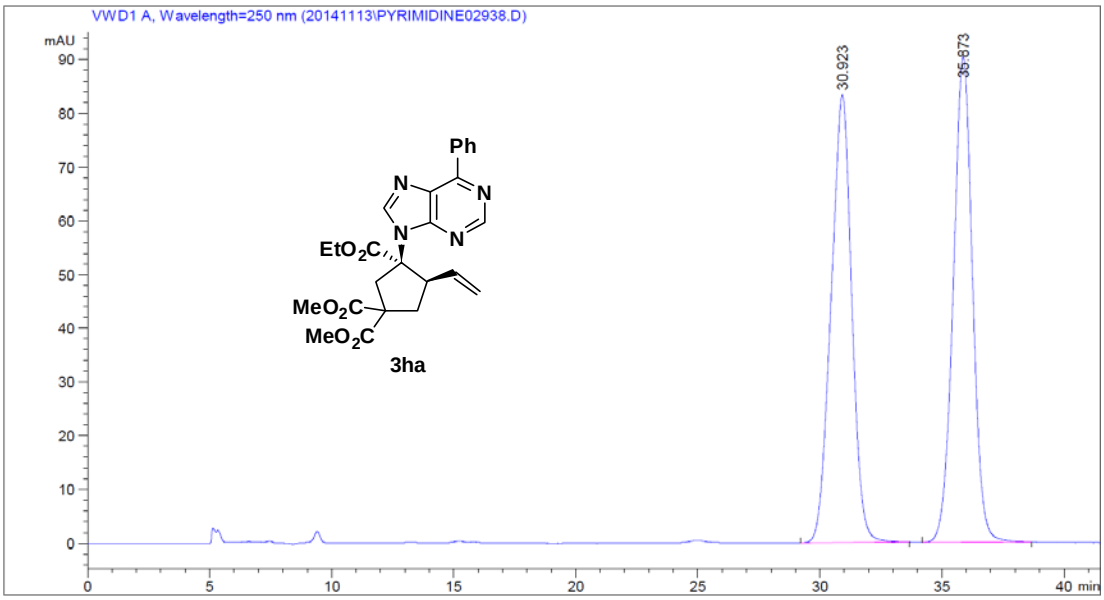
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	60.687	BB	1.6064	1985.28064	14.91910	9.2952
2	68.897	BB	2.0348	1.93727e4	131.82967	90.7048



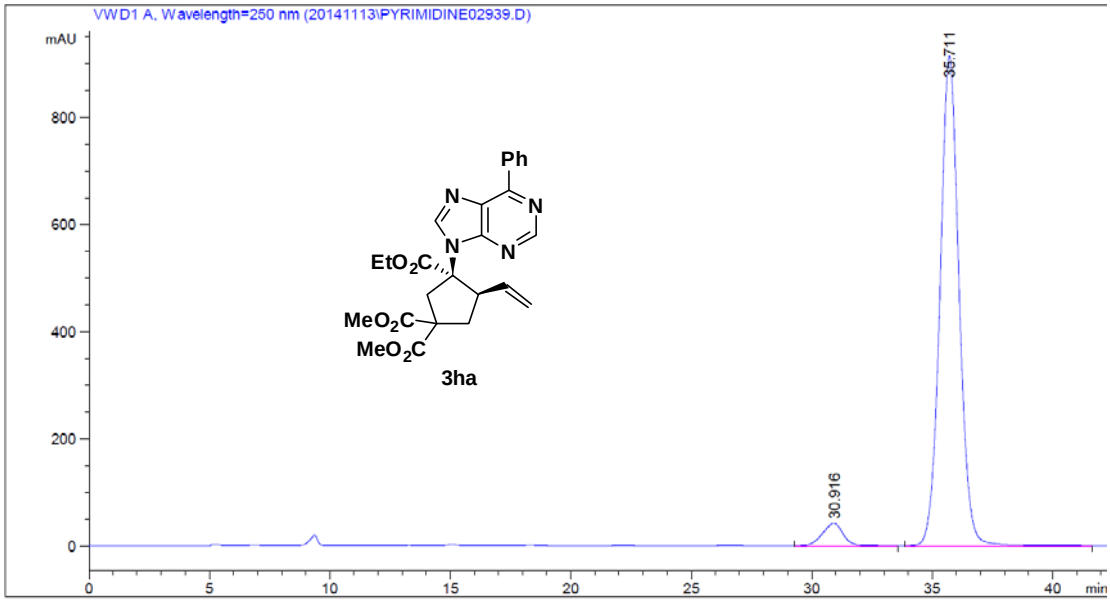
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.194	BB	0.5210	2256.92041	67.02615	50.7914
2	21.480	BB	0.6636	2186.58862	50.82133	49.2086



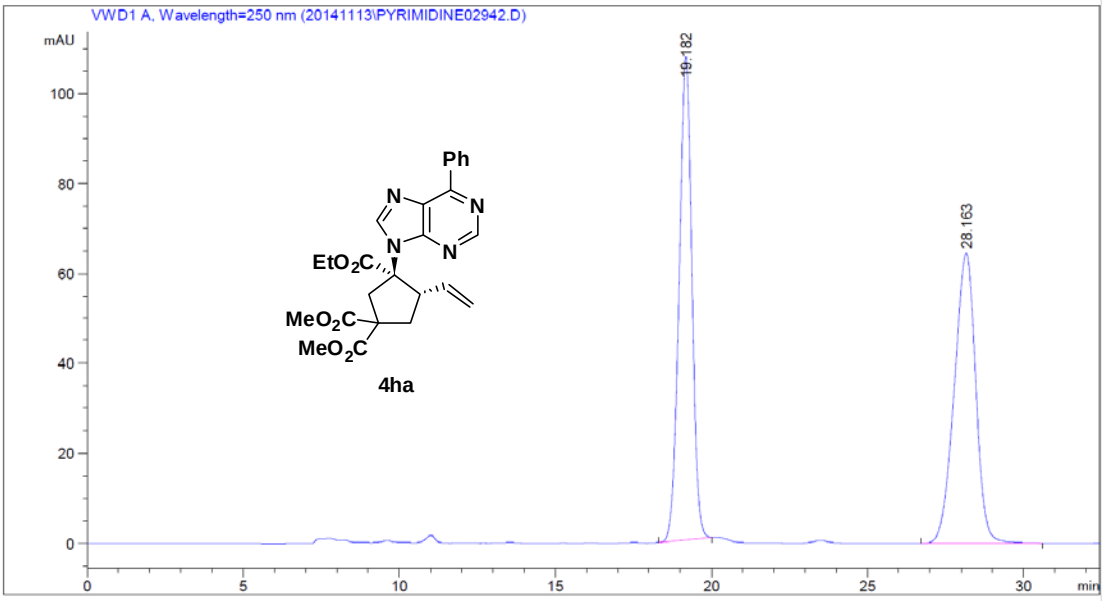
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.131	VB	0.5227	1532.83984	45.32785	13.7276
2	21.379	BB	0.6671	9633.28320	221.07919	86.2724



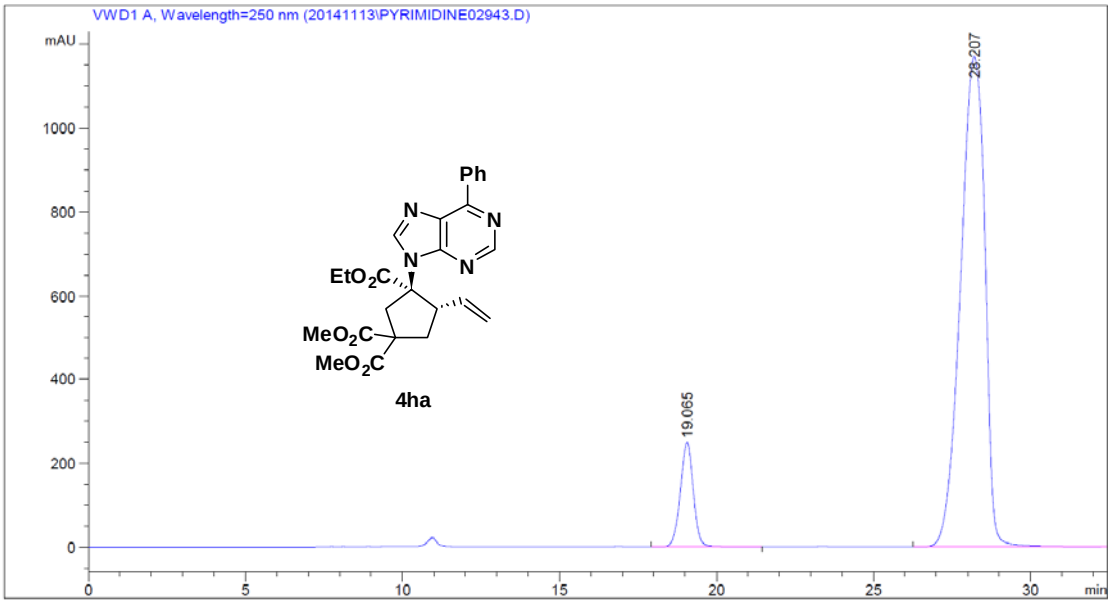
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.923	BB	0.8500	4910.12842	83.39417	49.7714
2	35.873	BB	0.8325	4955.23535	90.28885	50.2286



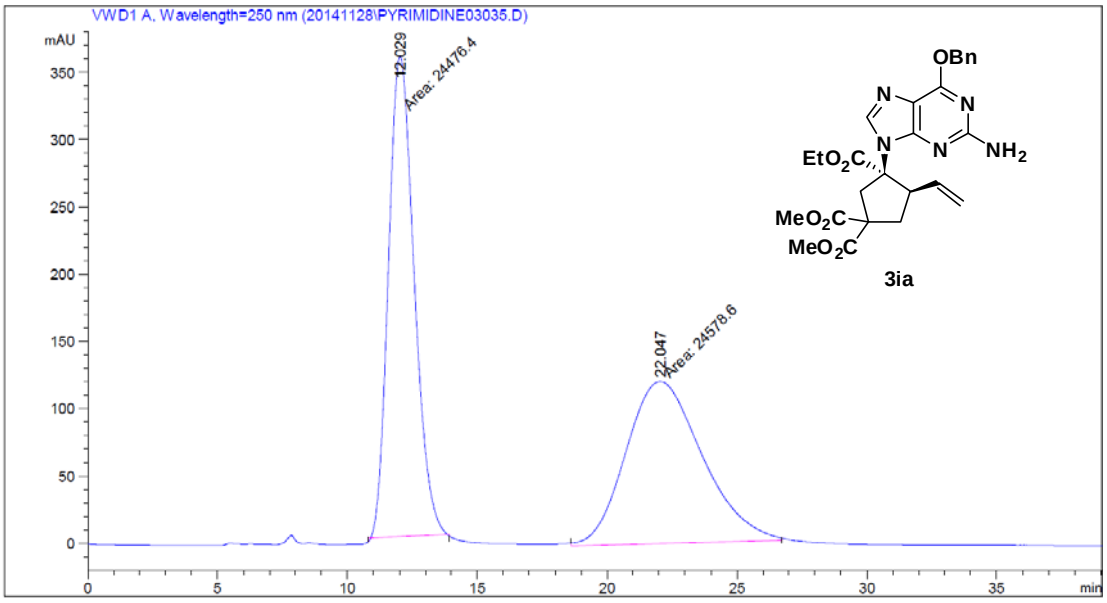
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.916	BB	0.8811	2503.75220	42.30922	4.7584
2	35.711	BB	0.8295	5.01141e4	915.30432	95.2416



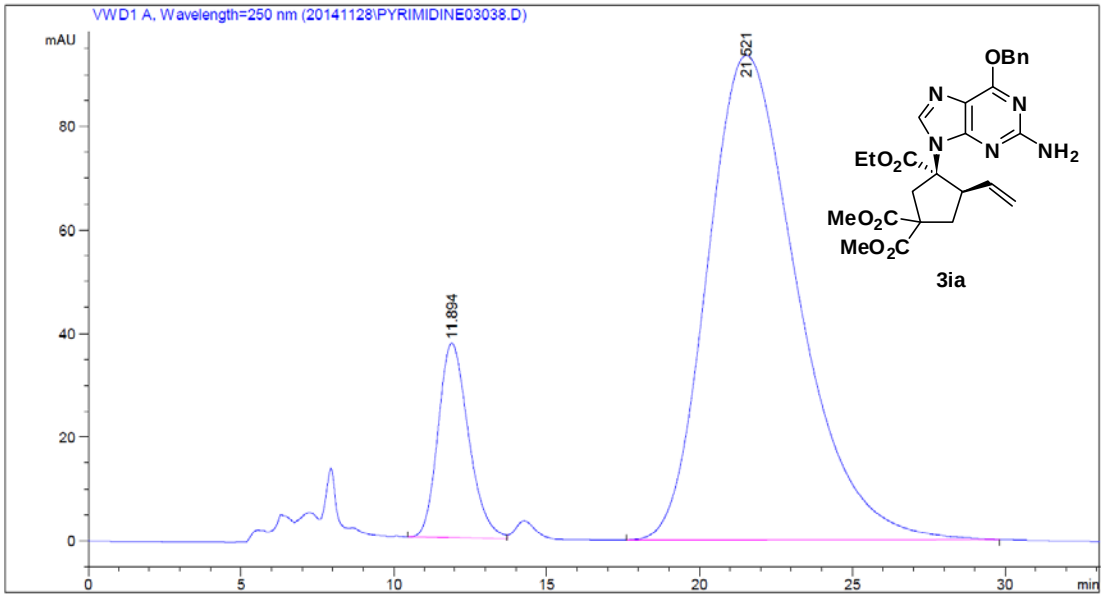
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.182	BB	0.4368	3060.08032	107.53363	49.7802
2	28.163	BB	0.7338	3087.09717	64.58956	50.2198



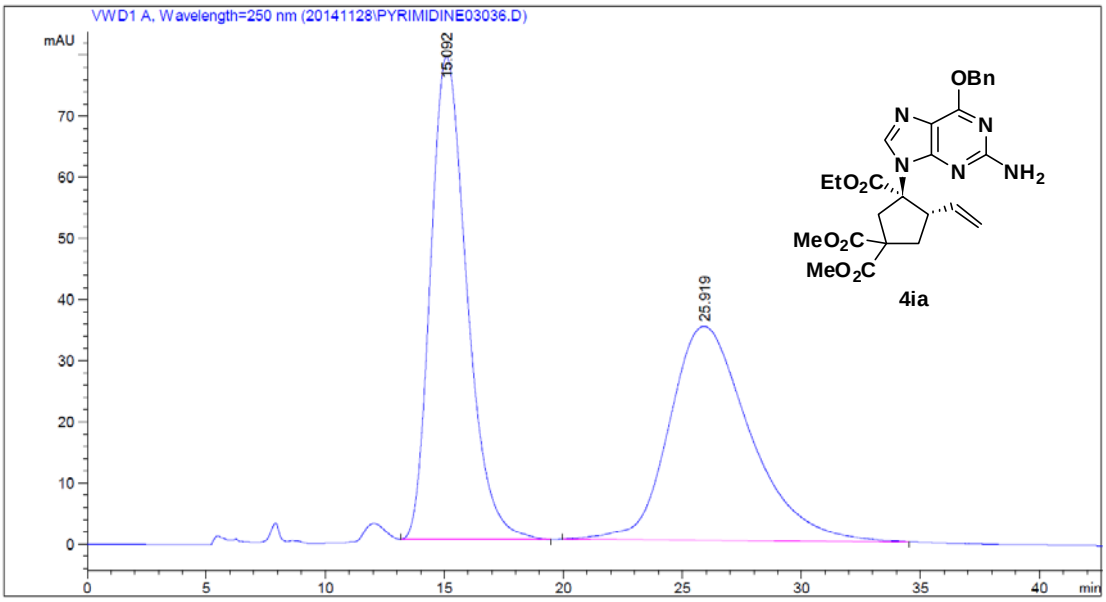
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.065	BB	0.4411	7220.18604	249.41505	10.2541
2	28.207	BBA	0.8633	6.31923e4	1169.57813	89.7459



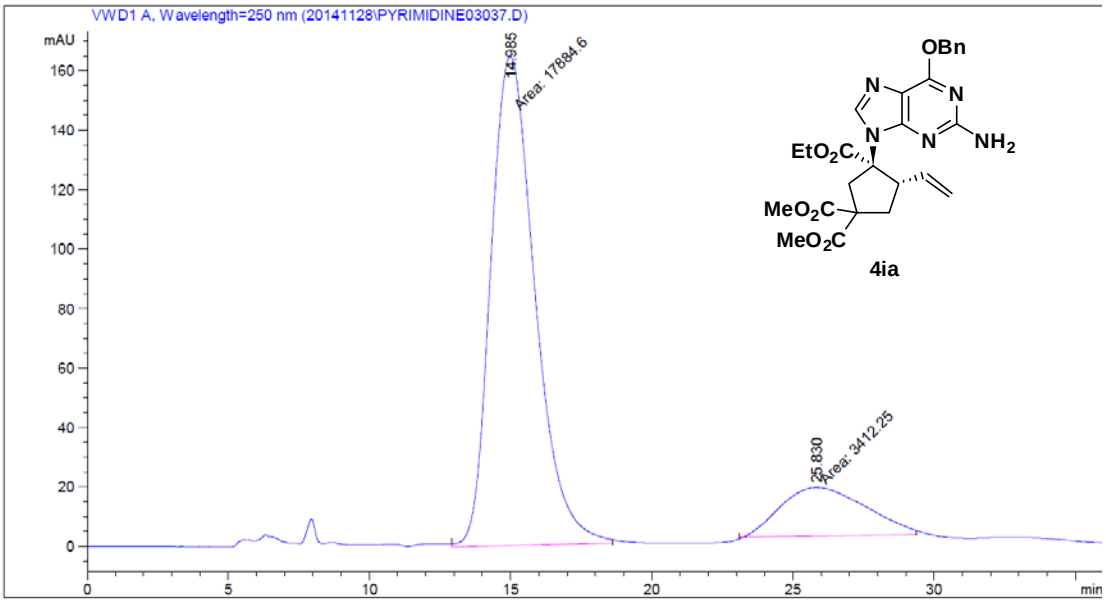
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.029	MM	1.1436	2.44764e4	356.72733	49.8959
2	22.047	MM	3.4040	2.45786e4	120.34171	50.1041



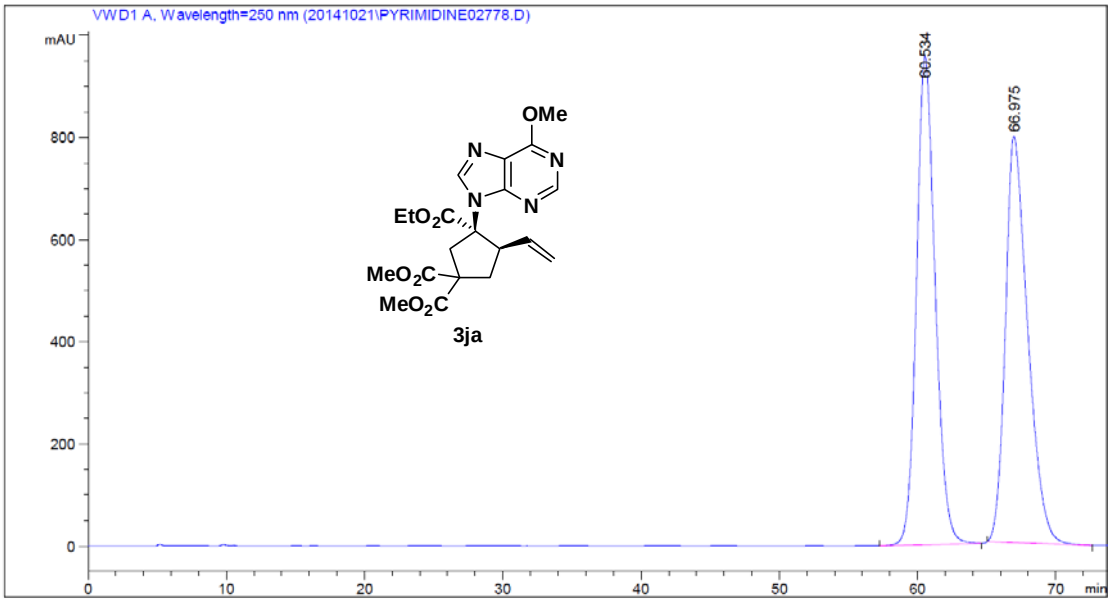
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.894	BV	1.0584	2600.66333	37.55042	11.9386
2	21.521	BB	2.7317	1.91830e4	93.54465	88.0614



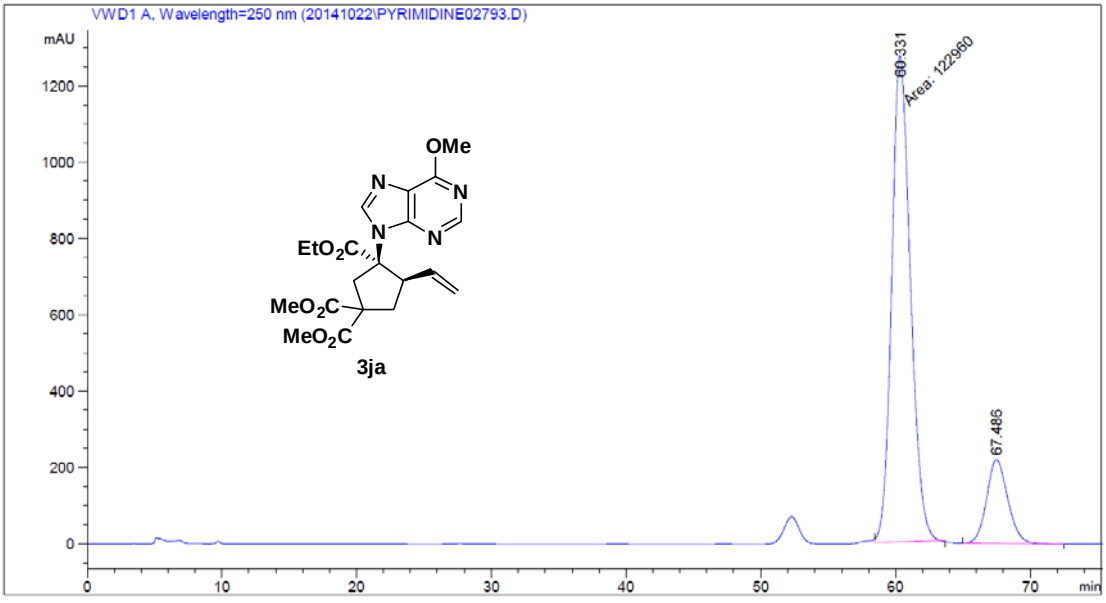
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.092	BB	1.6055	8387.47949	79.00355	50.4593
2	25.919	BB	2.7930	8234.80078	35.05616	49.5407



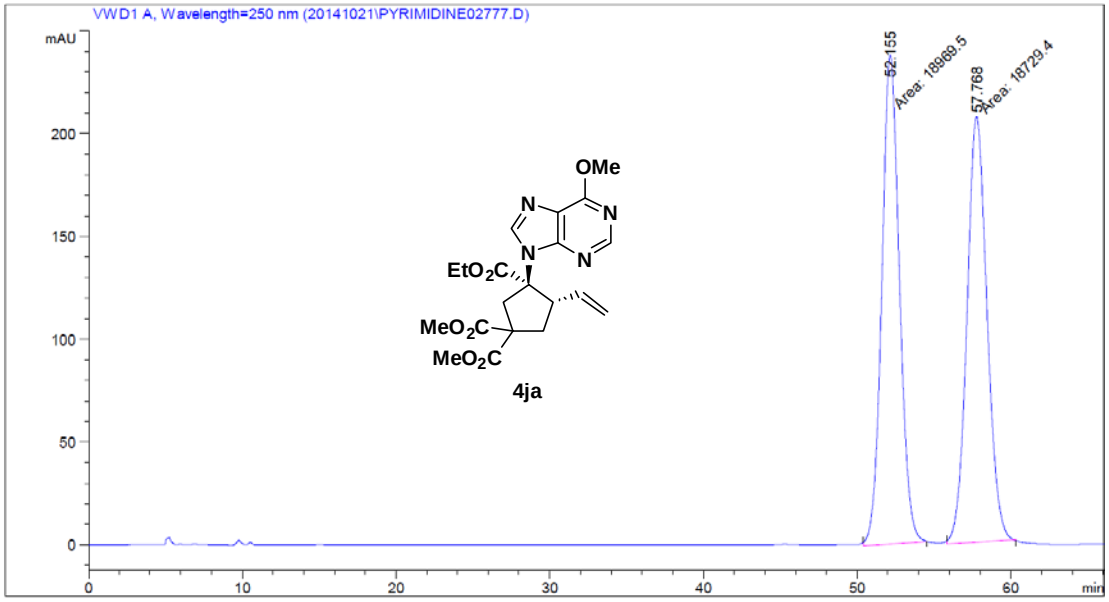
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.985	MM	1.8116	1.78846e4	164.53629	83.9777
2	25.830	MM	3.4916	3412.24683	16.28800	16.0223



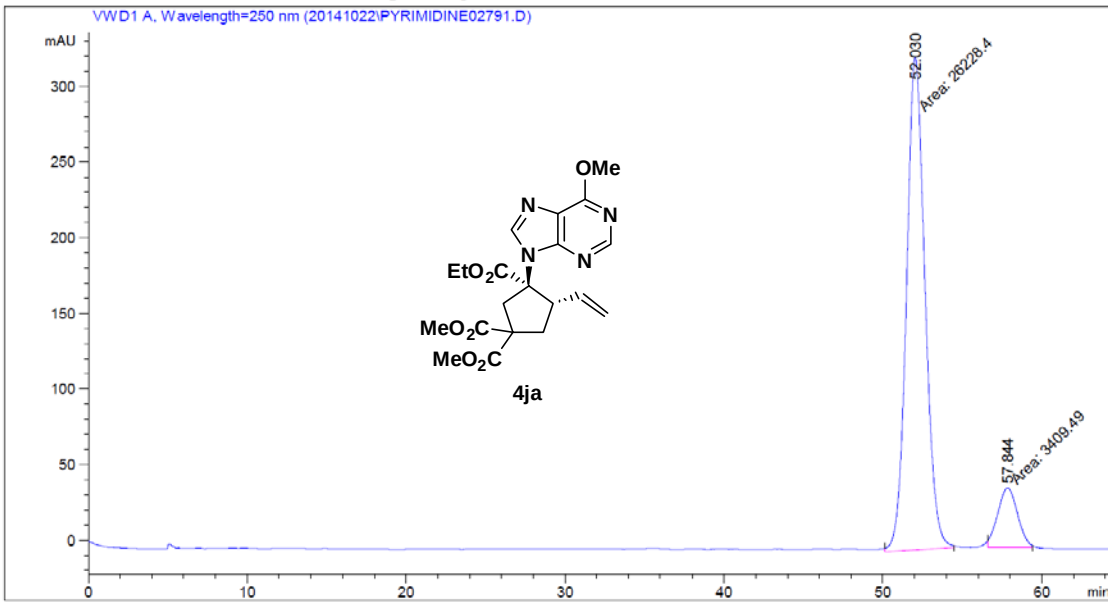
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	60.534	BB	1.3679	8.99628e4	956.67401	50.1999
2	66.975	BBA	1.5702	8.92463e4	795.95868	49.8001



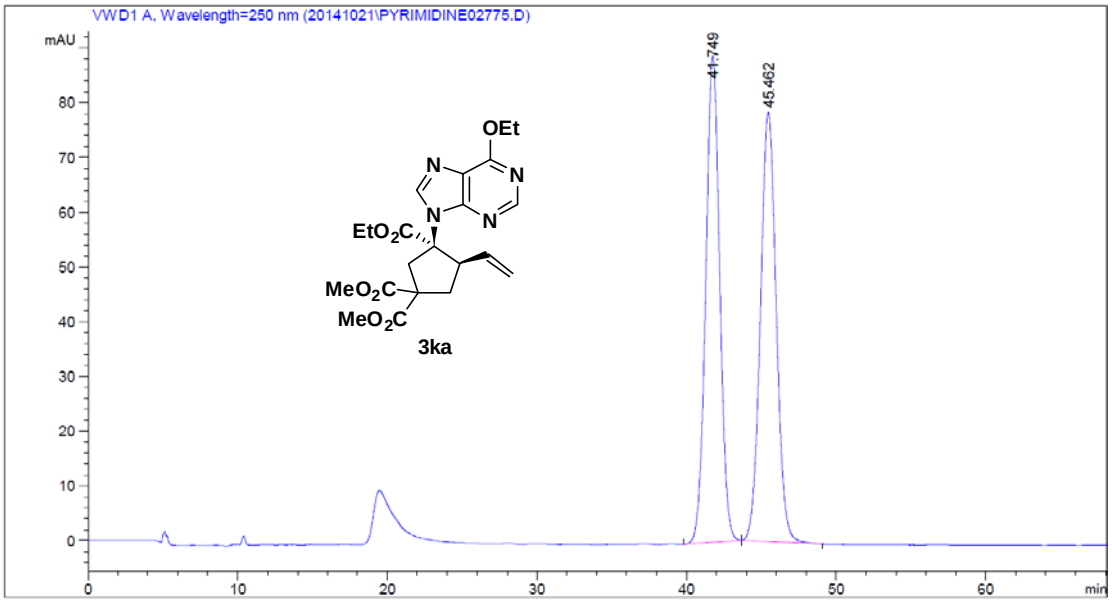
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	60.331	MM	1.6074	1.22960e5	1274.90112	83.7791
2	67.486	BB	1.6075	2.38069e4	219.50912	16.2209



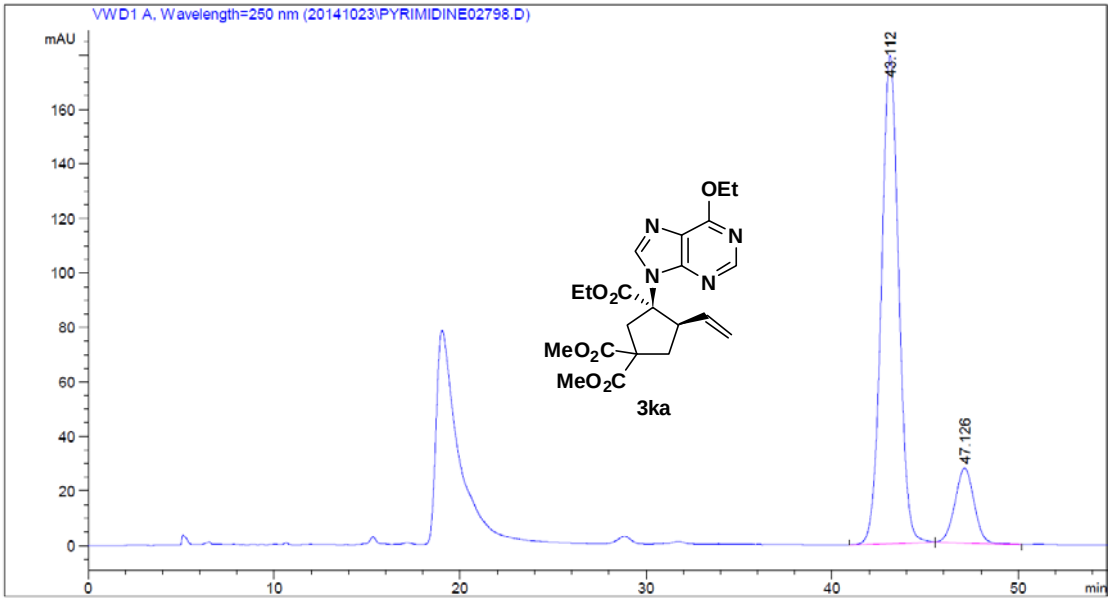
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	52.155	MM	1.3295	1.89695e4	237.80397	50.3185
2	57.768	MM	1.5094	1.87294e4	206.81013	49.6815



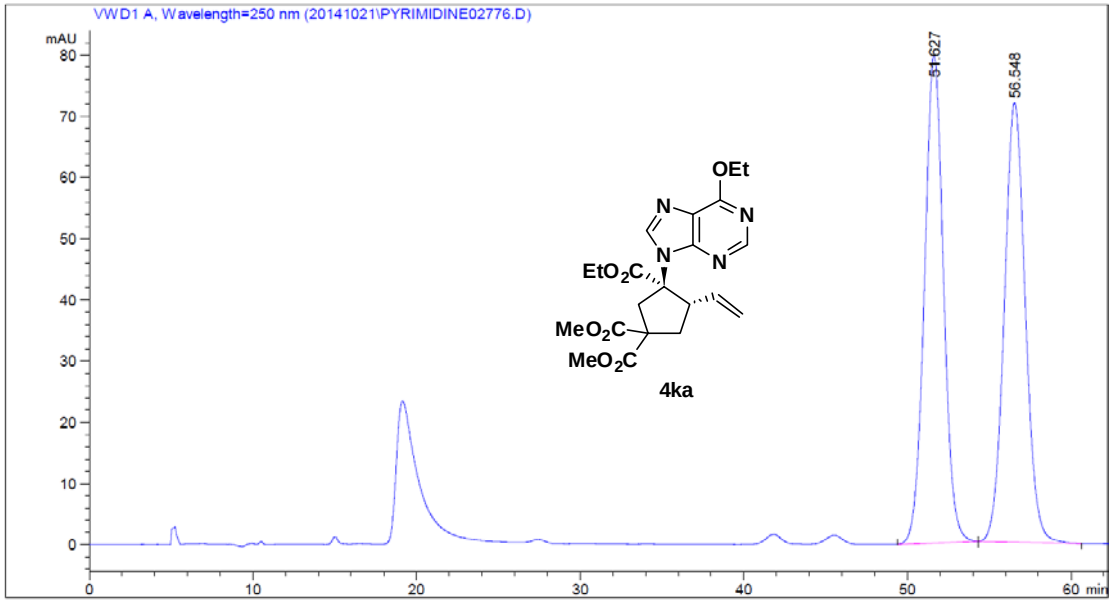
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	52.030	MM	1.3427	2.62284e4	325.56058	88.4962
2	57.844	MM	1.4448	3409.48511	39.33187	11.5038



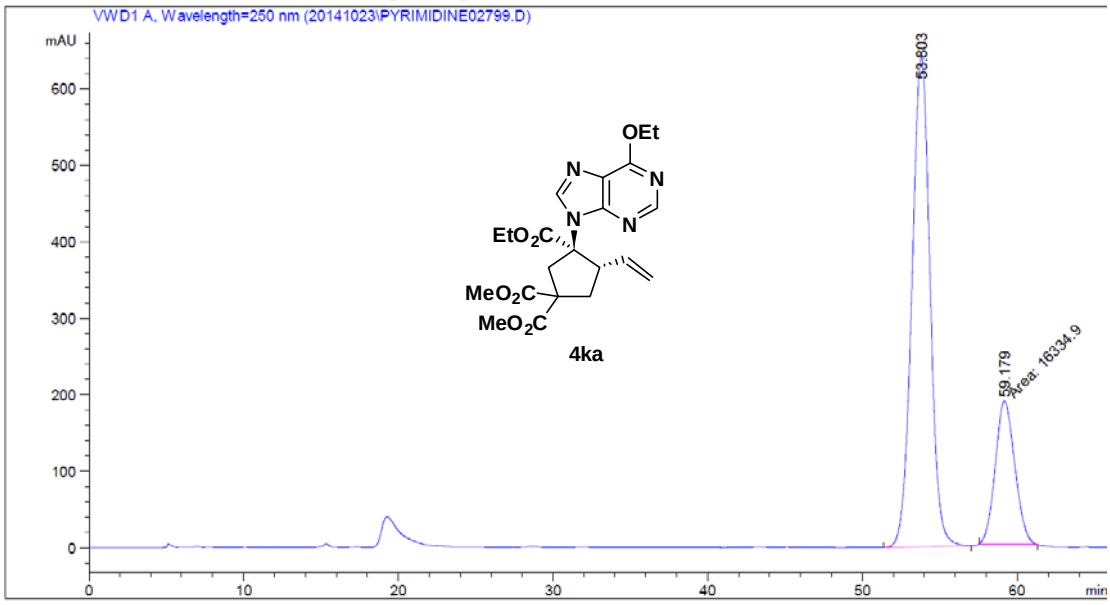
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	41.749	BB	0.9923	5756.54785	88.78997	50.0136
2	45.462	BB	1.1104	5753.41797	78.44952	49.9864



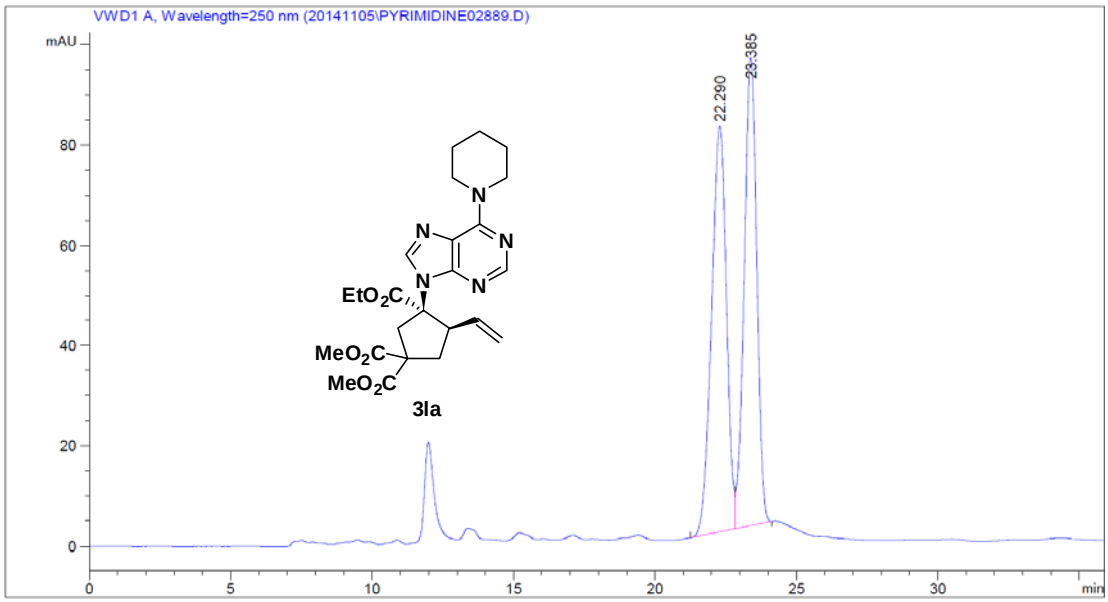
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	43.112	BB	1.0005	1.16072e4	179.14270	85.5981
2	47.126	BB	1.0851	1952.90247	27.44070	14.4019



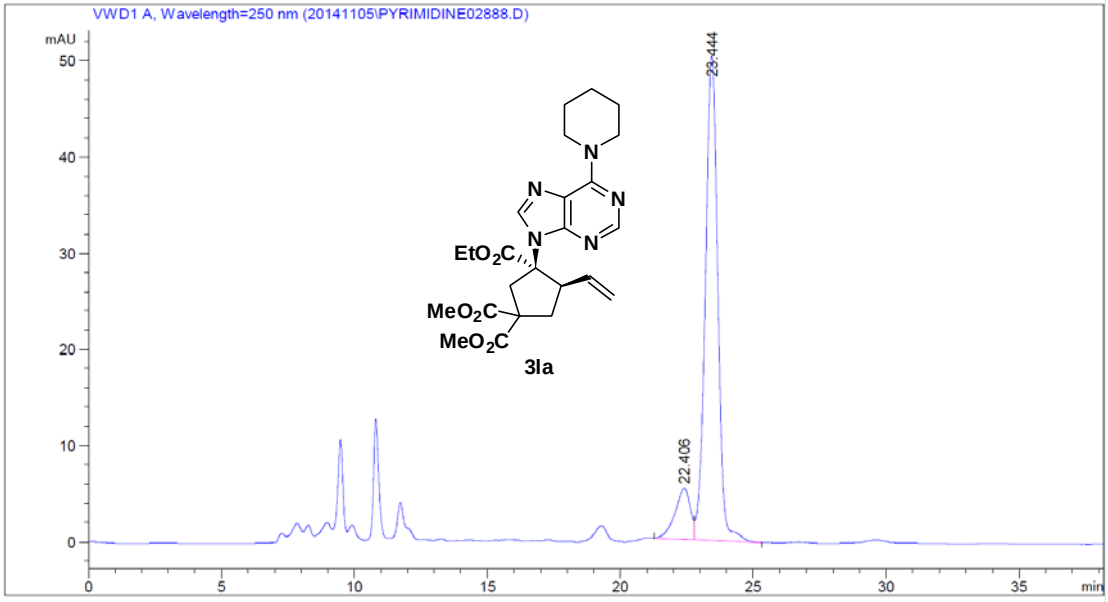
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	51.627	BB	1.2266	6450.12549	79.70204	50.1678
2	56.548	BB	1.3371	6406.97266	71.86560	49.8322



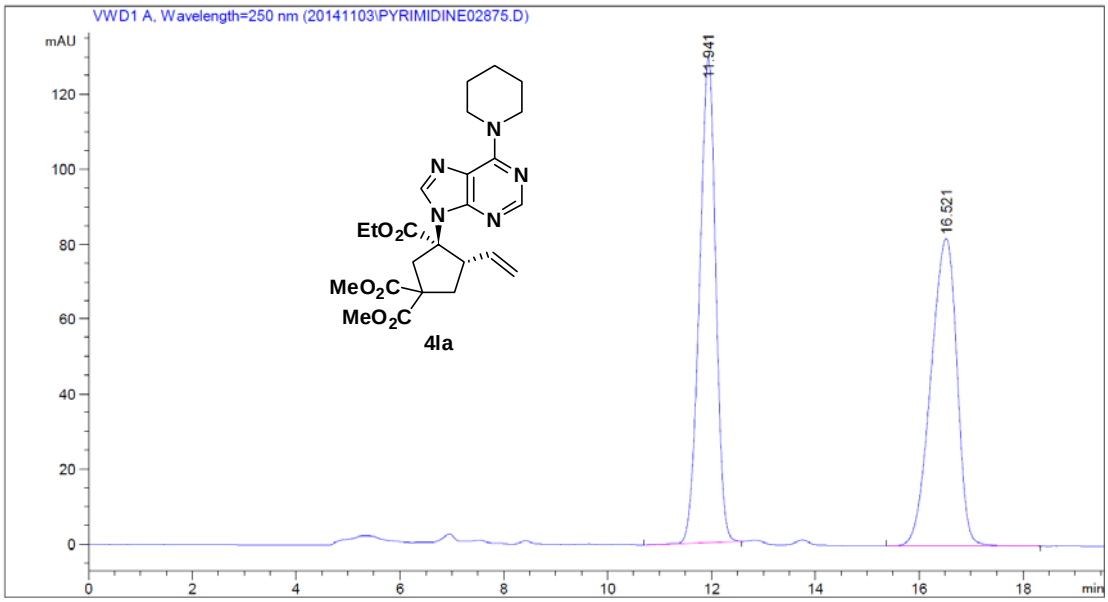
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	53.803	BB	1.2332	5.21924e4	640.47211	76.1629
2	59.179	MM	1.4566	1.63349e4	186.91147	23.8371



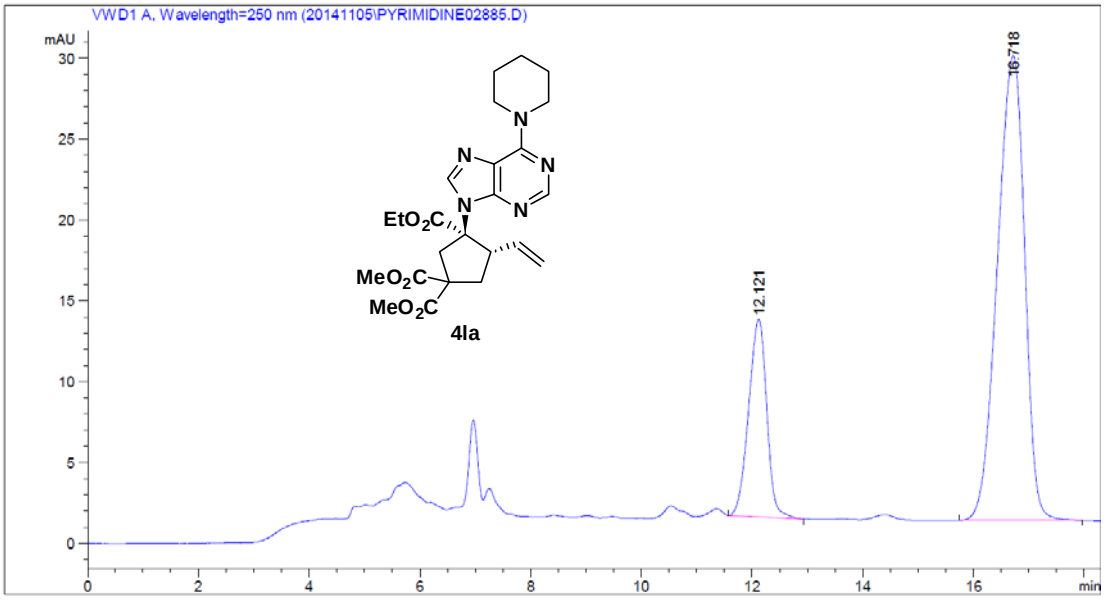
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.290	BV	0.5529	2956.80664	80.93110	50.6630
2	23.385	VB	0.4808	2879.42310	93.32737	49.3370



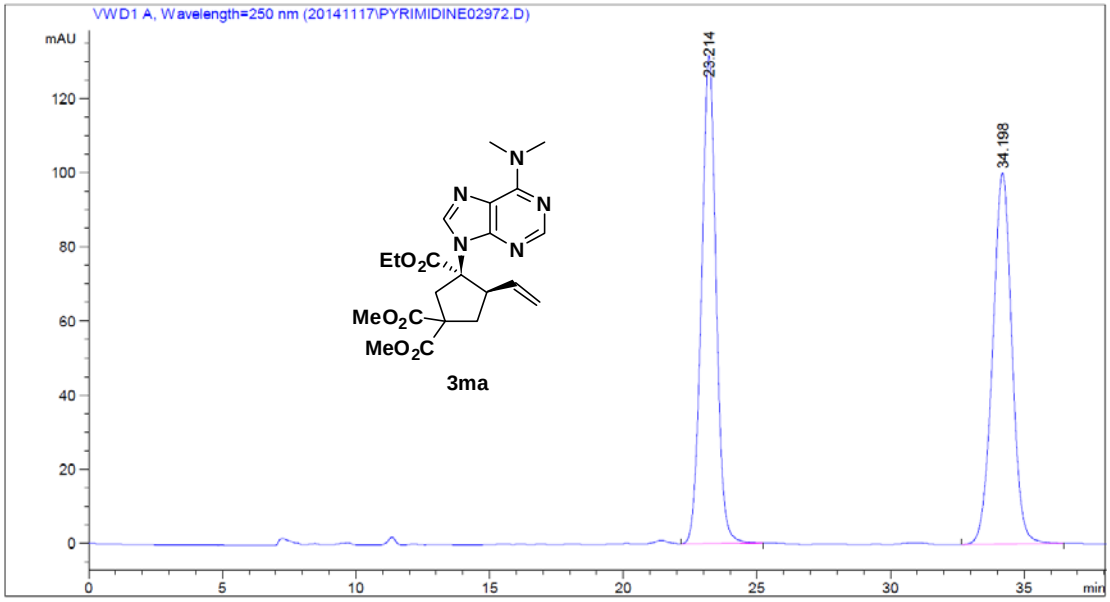
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.406	BV	0.5865	211.37563	5.29566	11.4412
2	23.444	VB	0.4983	1636.11438	50.38309	88.5588



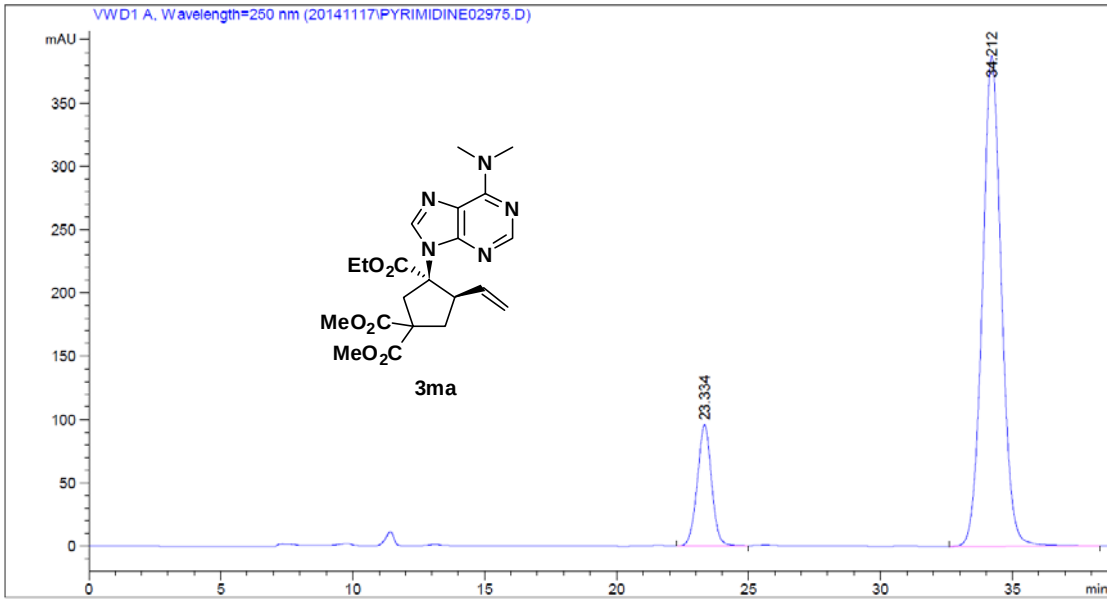
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.941	BB	0.3360	2822.85767	129.42659	49.6432
2	16.521	BB	0.5586	2863.43115	82.04362	50.3568



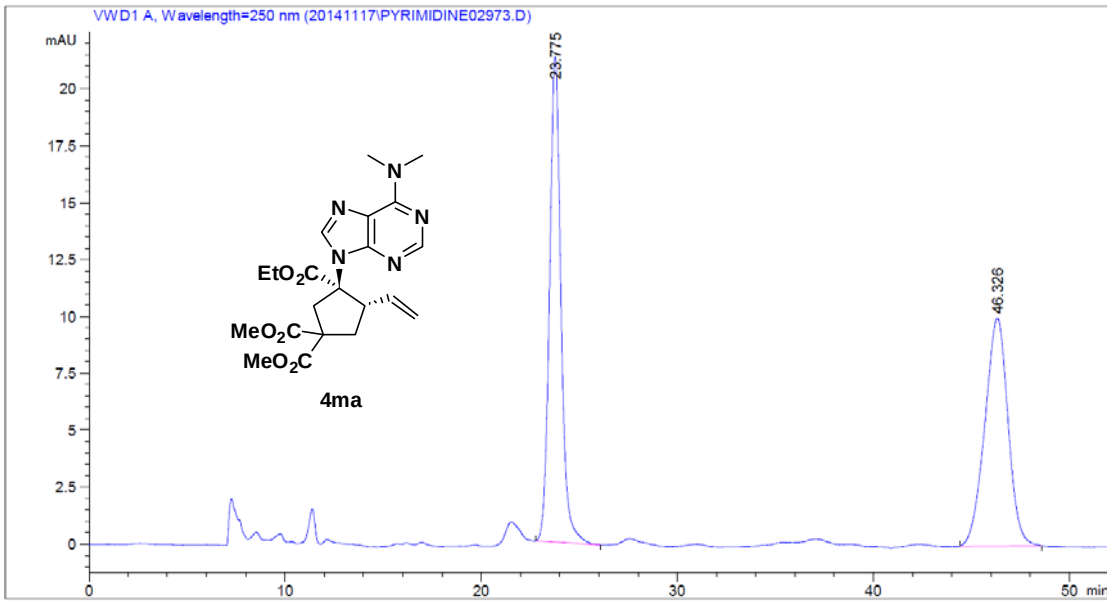
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.121	BB	0.3574	278.14072	12.21427	22.0573
2	16.718	BB	0.5415	982.85370	28.75180	77.9427



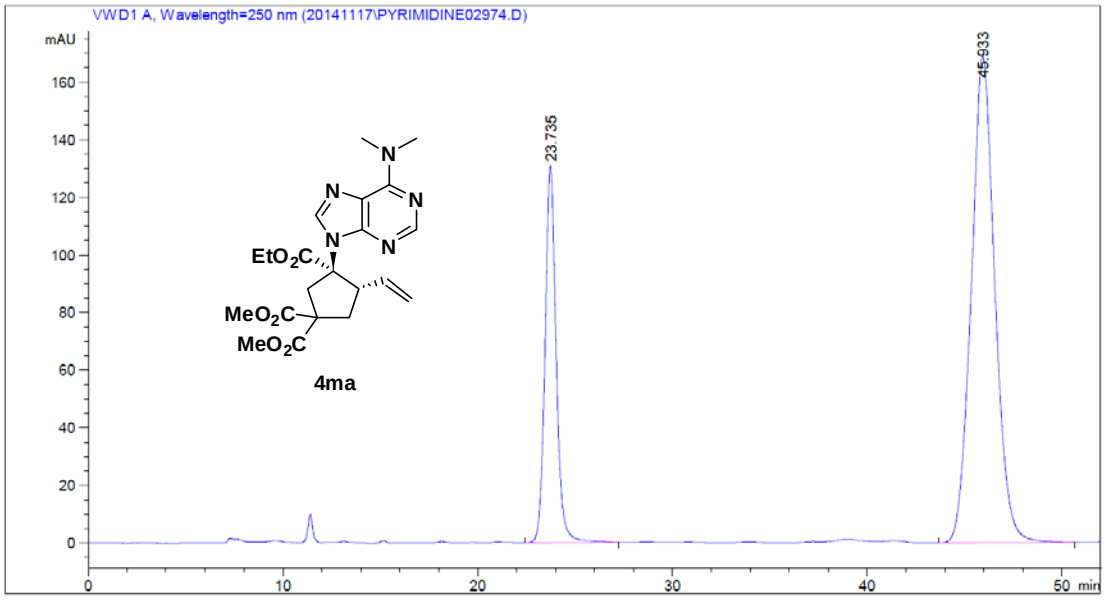
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.214	BB	0.5766	5015.42480	131.75063	50.0234
2	34.198	BB	0.7690	5010.74219	100.08888	49.9766



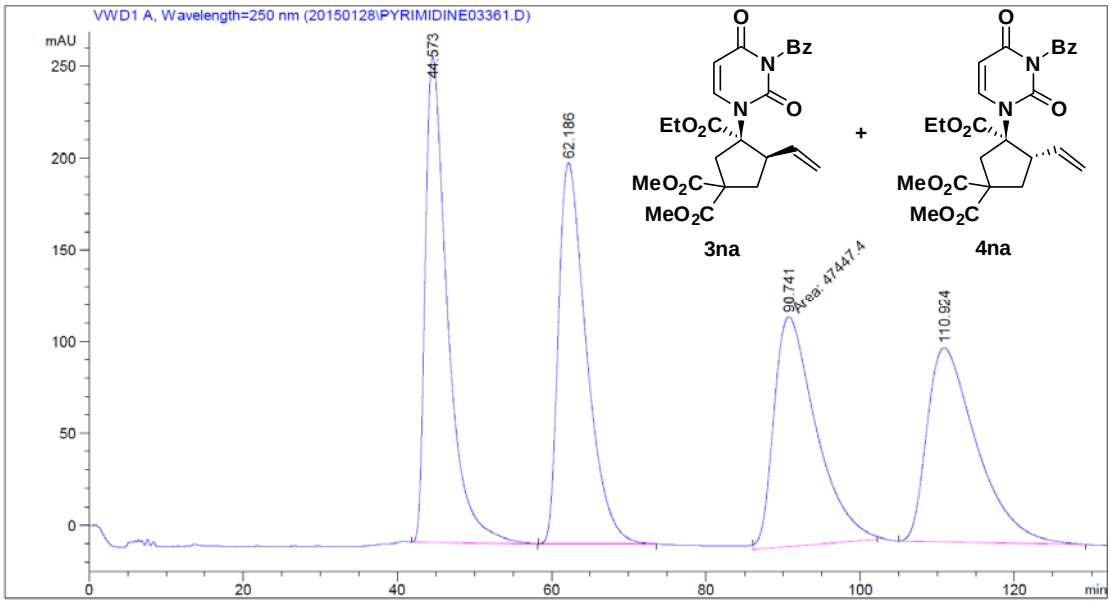
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.334	BB	0.5672	3604.75879	95.78169	15.6201
2	34.212	BB	0.7562	1.94730e4	387.77127	84.3799



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.775	BB	0.6099	858.92584	21.31340	51.0540
2	46.326	BB	1.0490	823.46173	10.02041	48.9460

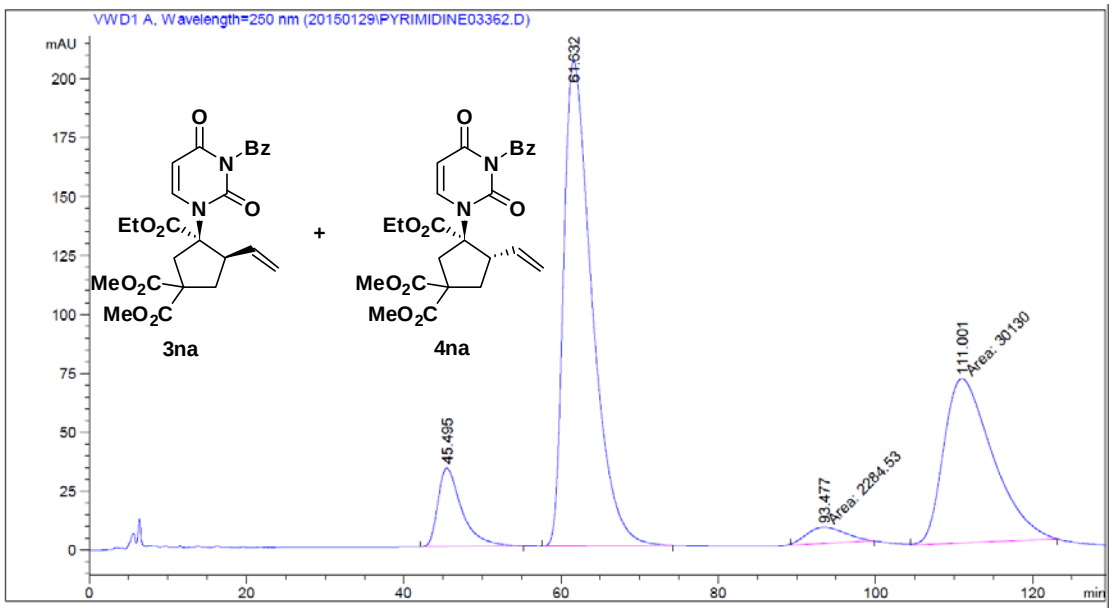


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.735	BB	0.5983	5191.40186	130.84914	26.7818
2	45.933	BB	1.2143	1.41926e4	168.97255	73.2182



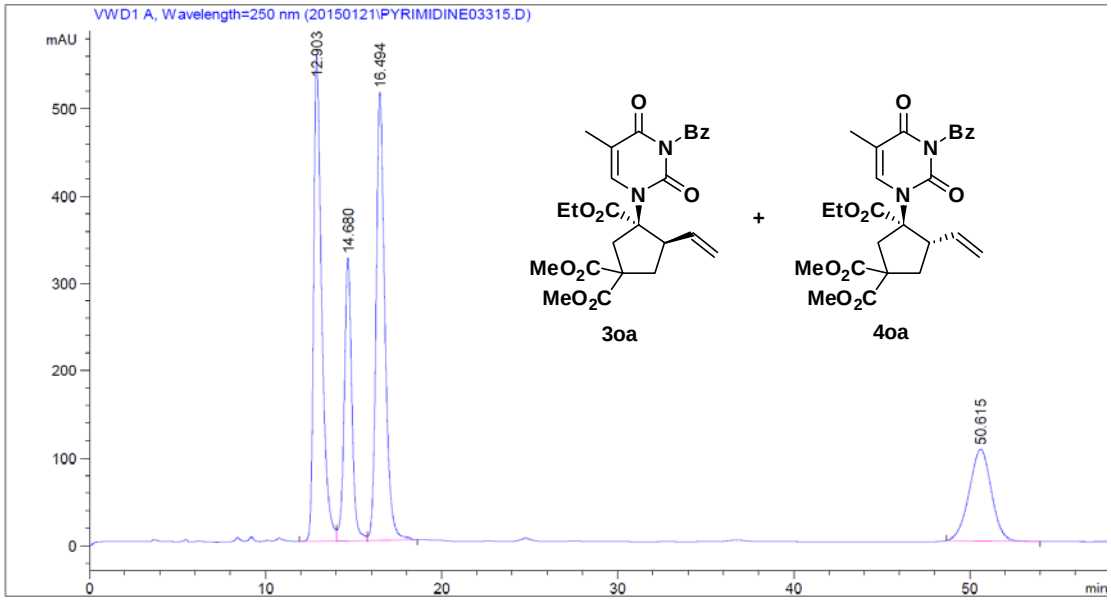
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.573	BB	2.7689	5.31399e4	264.51447	26.5854
2	62.186	BB	3.5239	5.22112e4	207.80190	26.1208
3	90.741	MM	6.3282	4.74474e4	124.96268	23.7375

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
4	110.924	BB	5.2286	4.70852e4	105.44368	23.5563

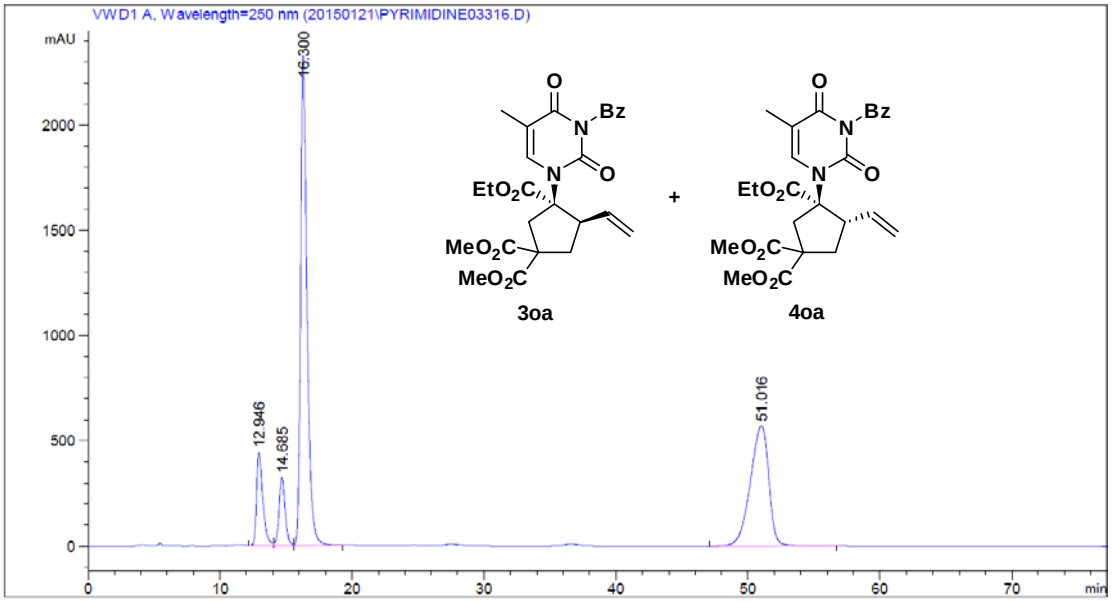


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	45.495	BB	2.5851	7020.23145	33.29535	7.7200
2	61.632	BB	3.5721	5.15007e4	205.88675	56.6343
3	93.477	MM	3.9664	2284.53296	6.73378	2.5123

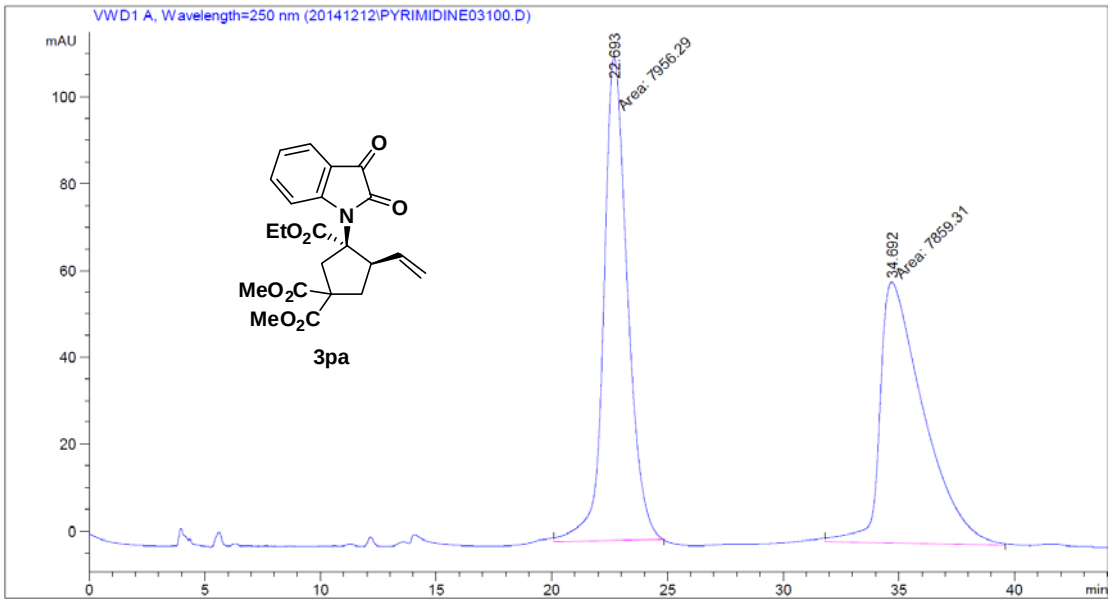
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
4	111.001	MM	7.2211	3.01300e4	69.54163	33.1334



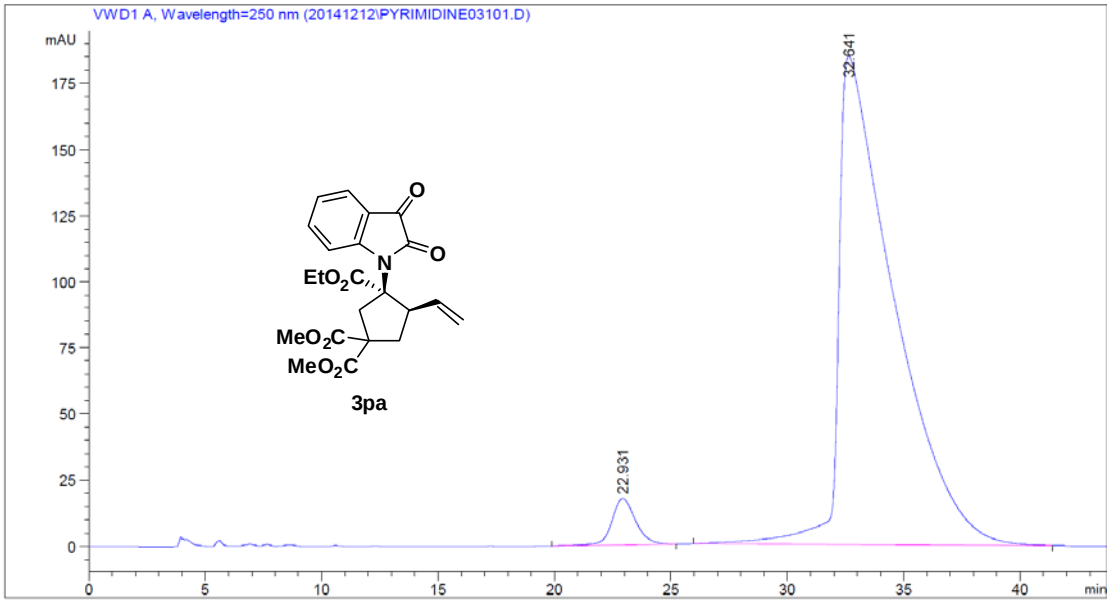
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.903	BV	0.4720	1.76339e4	555.93262	32.6341
2	14.680	VV	0.4525	9657.04004	324.08856	17.8717
3	16.494	VB	0.5113	1.75970e4	512.44000	32.5658
4	50.615	BB	1.2910	9147.32227	104.31042	16.9284



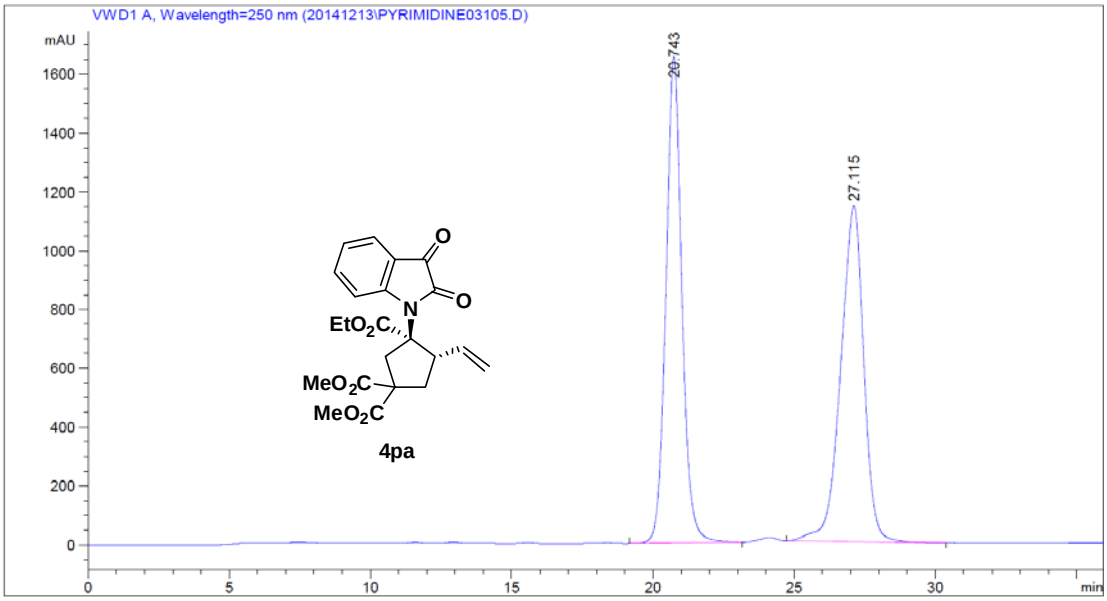
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.946	BV	0.4932	1.46142e4	444.01828	9.2104
2	14.685	VV	0.4869	1.03762e4	325.55728	6.5394
3	16.300	VB	0.4972	7.83179e4	2328.60767	49.3584
4	51.016	BB	1.5184	5.53635e4	571.03864	34.8918



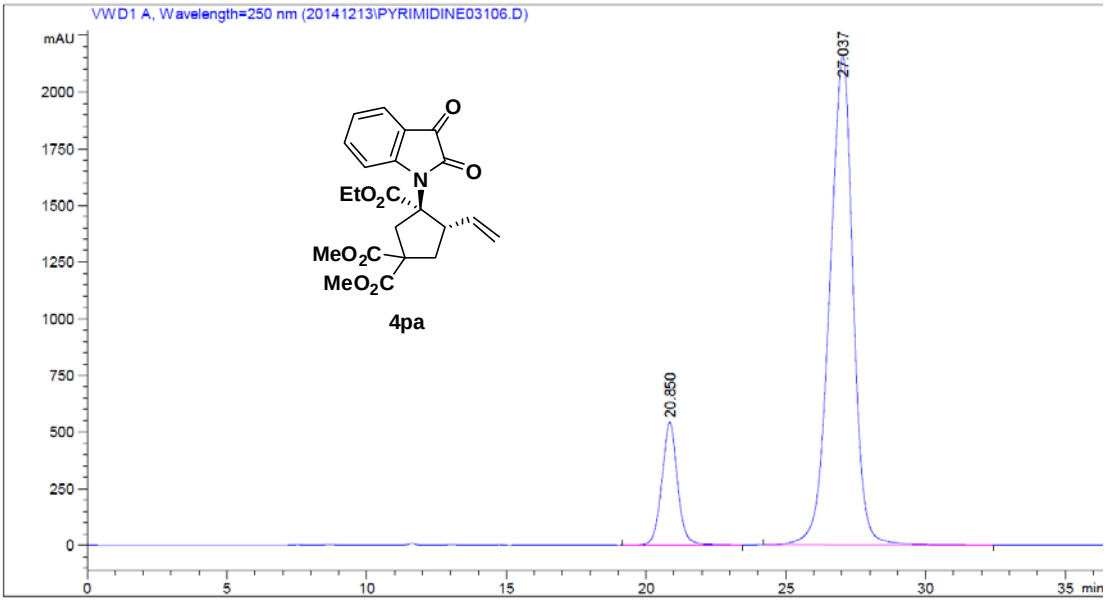
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.693	MM	1.1925	7956.29004	111.20143	50.3066
2	34.692	MM	2.1807	7859.30713	60.06773	49.6934



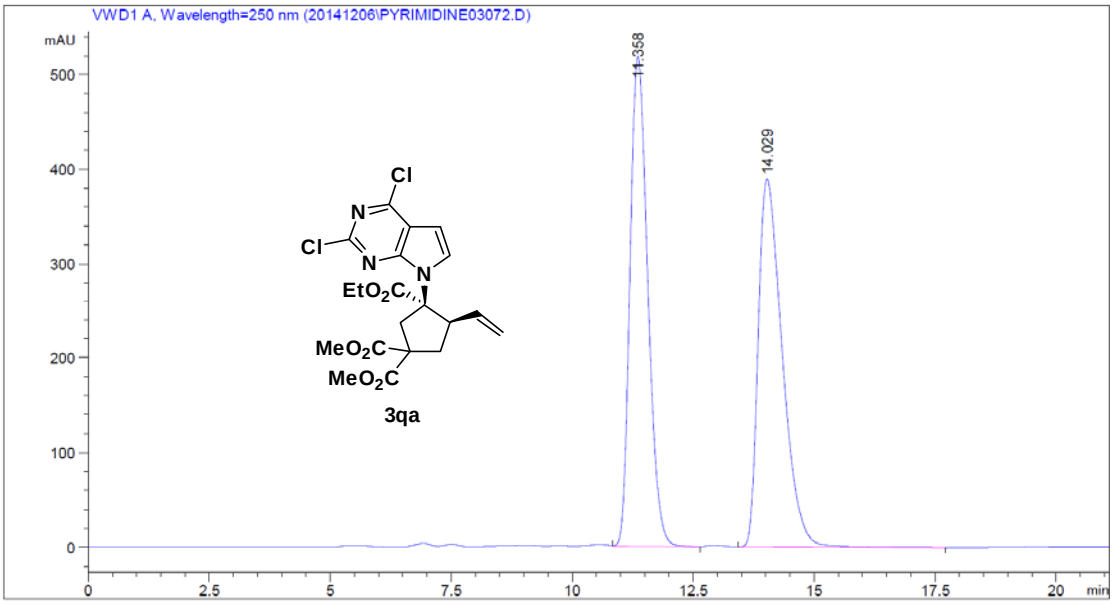
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.931	BB	1.0495	1242.99219	17.50908	3.9017
2	32.641	BB	2.1948	3.06151e4	184.53171	96.0983



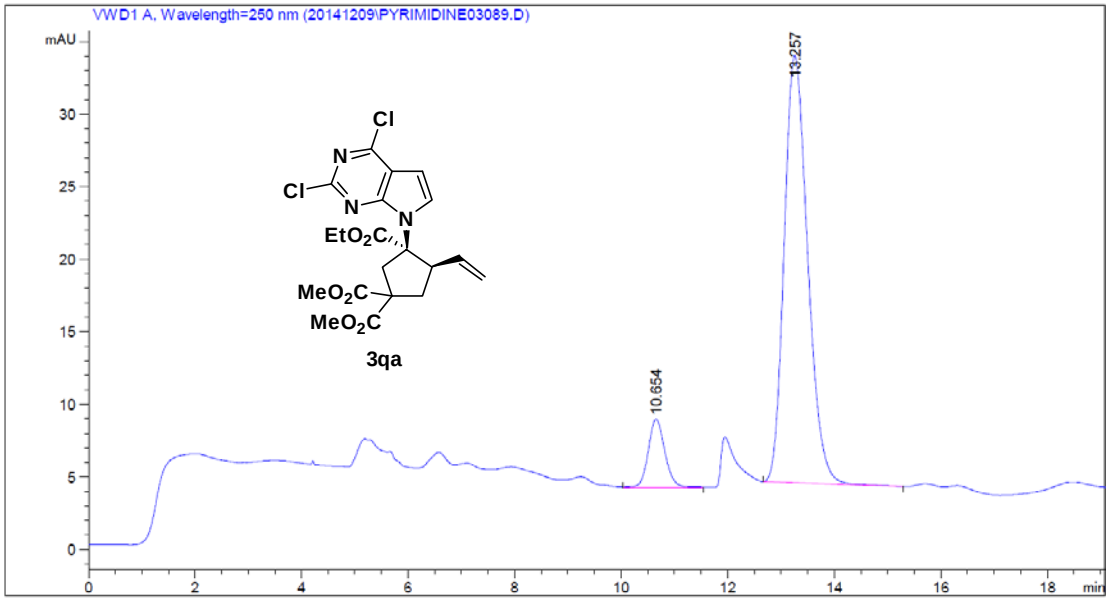
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.743	BB	0.5928	6.48049e4	1653.08398	49.8856
2	27.115	BB	0.8509	6.51022e4	1142.96973	50.1144



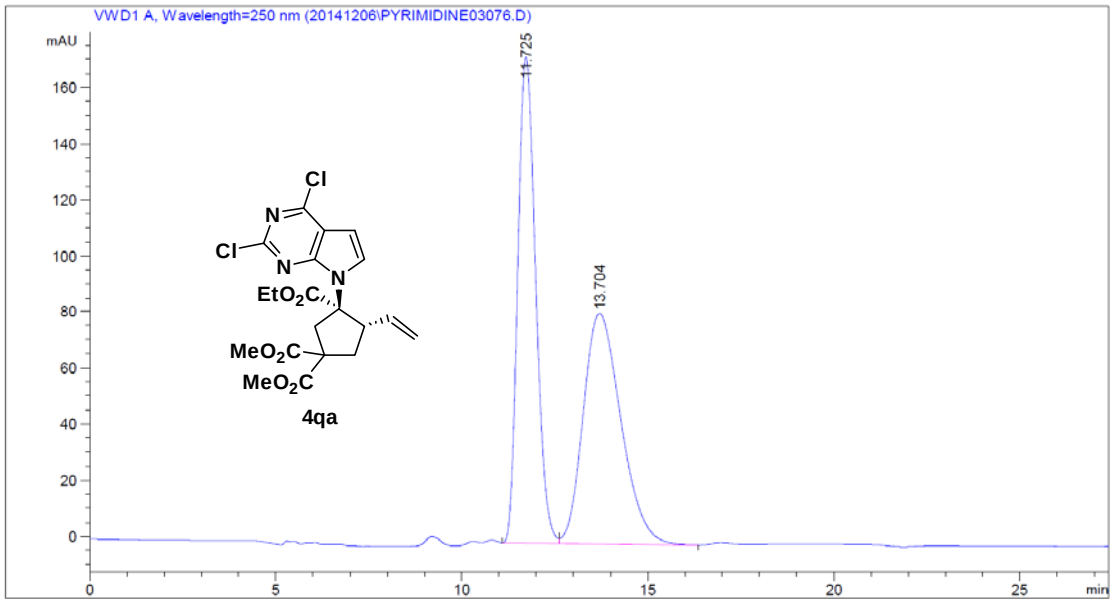
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.850	BB	0.5902	2.13374e4	543.90198	14.5071
2	27.037	BB	0.8872	1.25745e5	2160.67236	85.4929



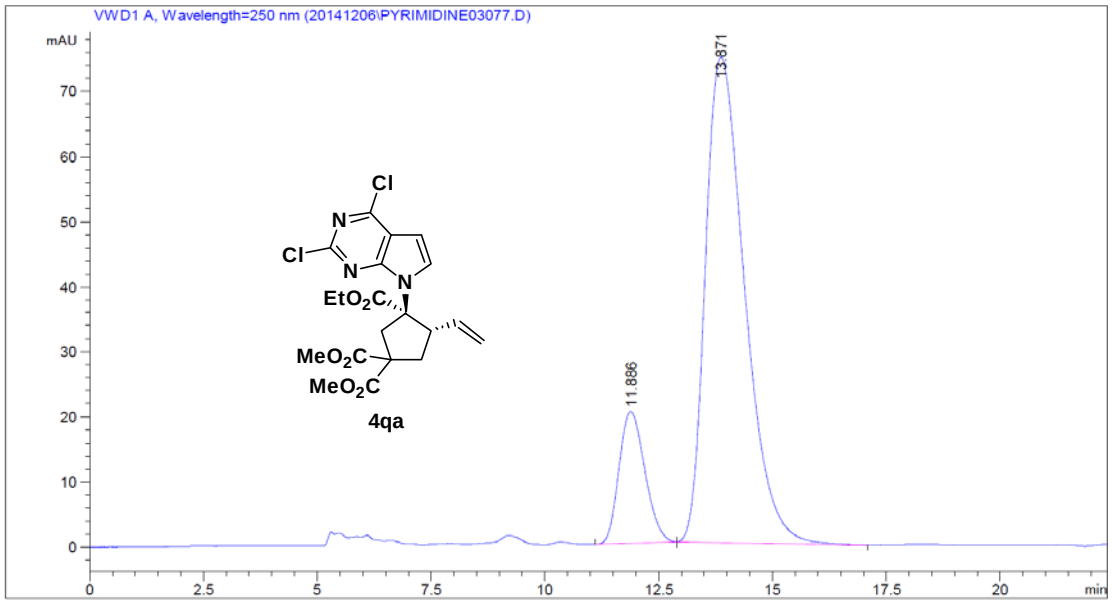
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.358	VB	0.3973	1.31893e4	518.35974	49.5321
2	14.029	BB	0.5292	1.34385e4	389.51166	50.4679



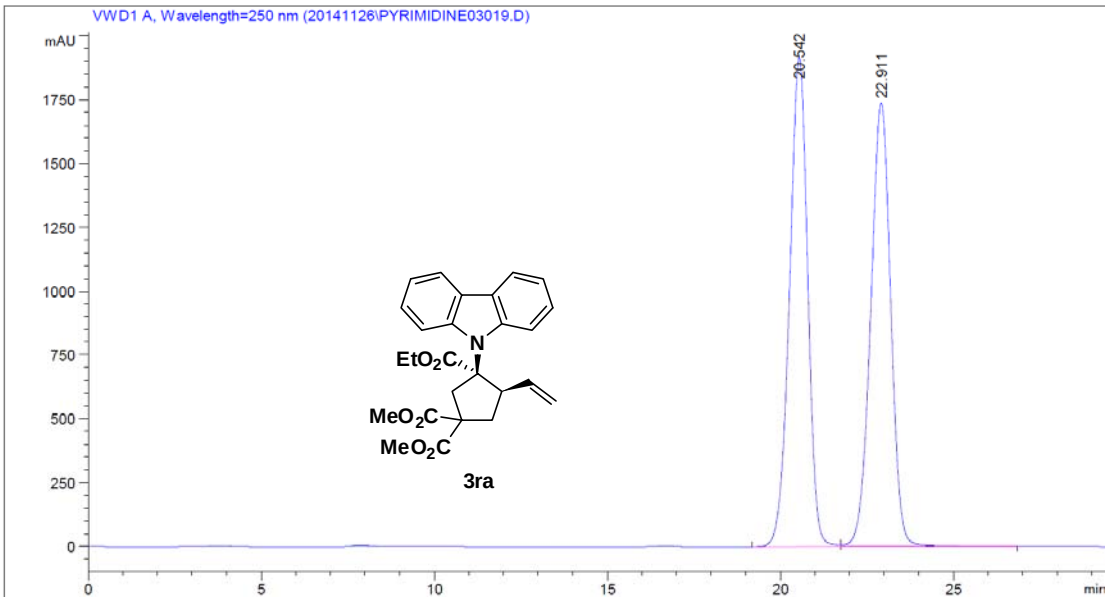
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.654	BB	0.3298	99.90943	4.66761	9.9888
2	13.257	BB	0.4735	900.30609	29.42331	90.0112



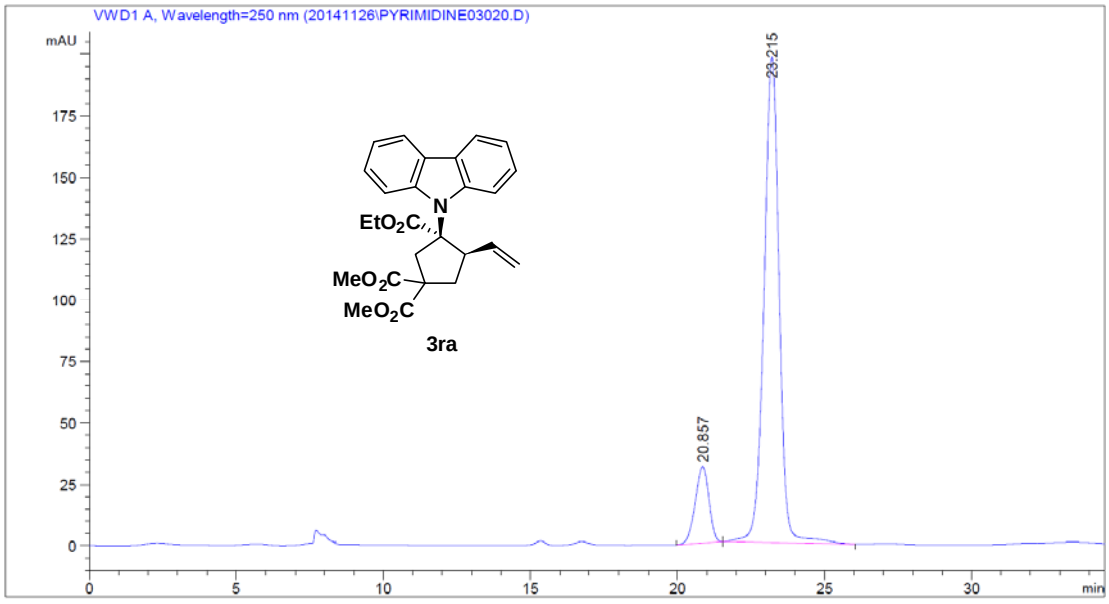
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.725	BV	0.5247	5780.08008	173.24382	50.0558
2	13.704	VB	1.0907	5767.19971	81.92511	49.9442



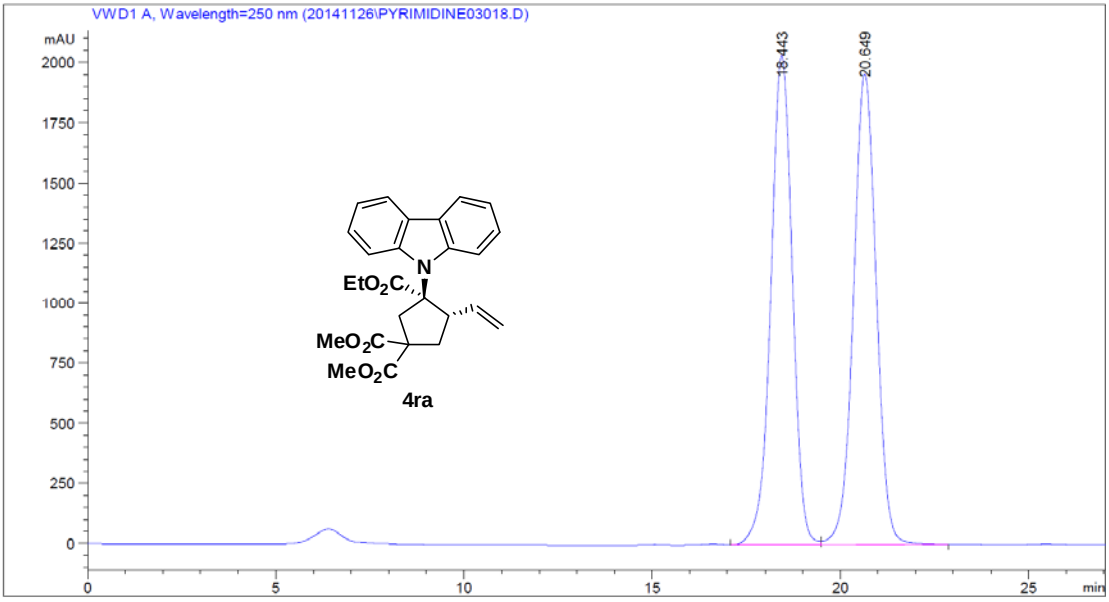
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.886	BB	0.6175	797.99817	20.23023	15.1687
2	13.871	BB	0.9225	4462.82910	74.56639	84.8313



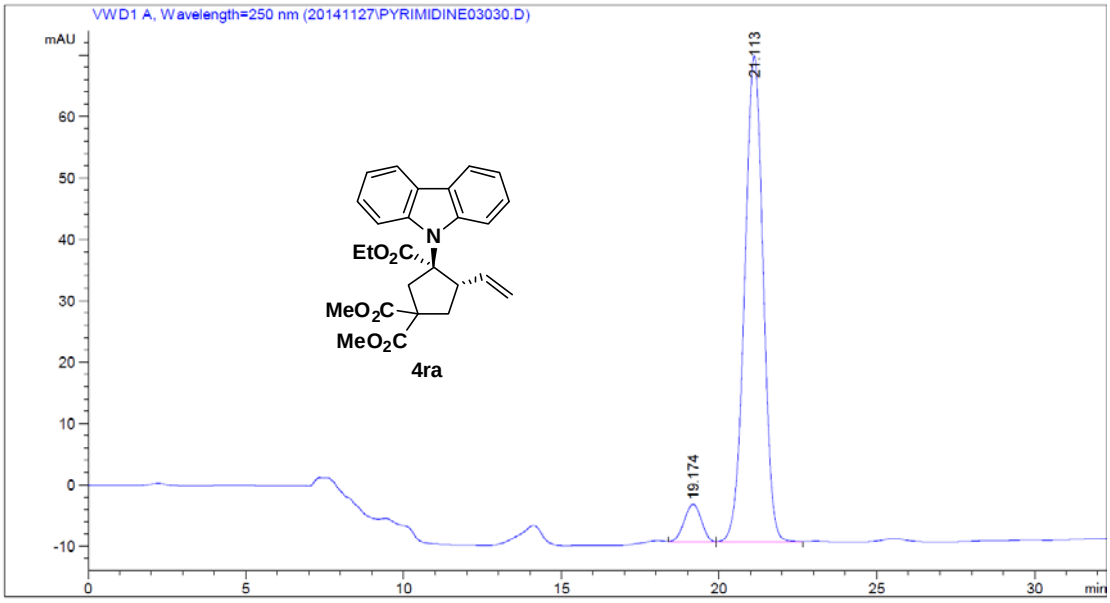
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.542	BV	0.5590	7.00351e4	1915.72168	50.0655
2	22.911	VB	0.6132	6.98519e4	1737.49402	49.9345



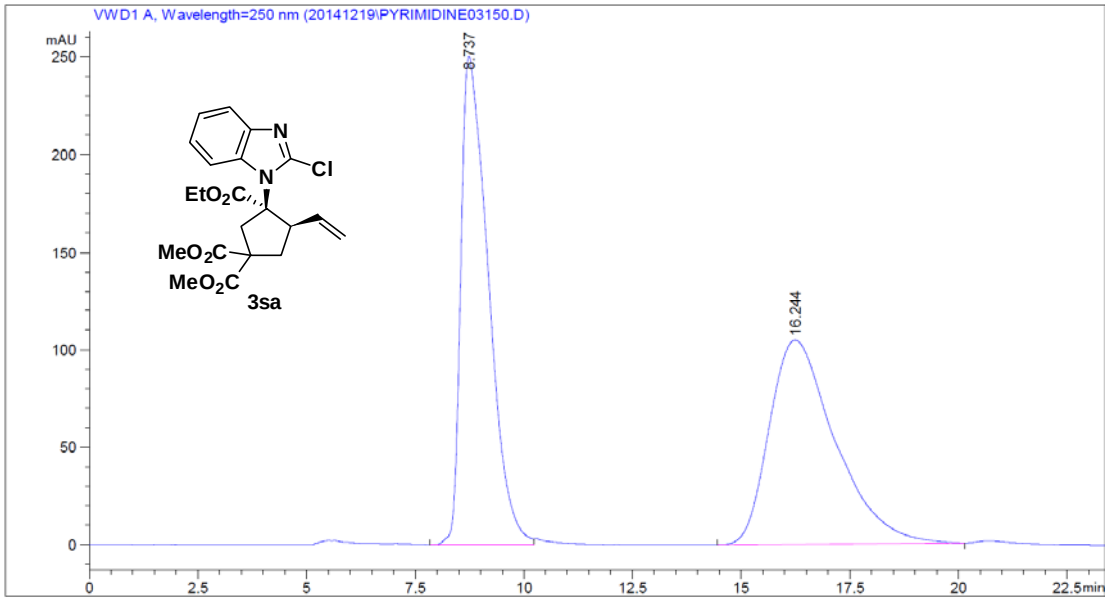
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.857	BB	0.5077	1006.03986	31.03748	12.4119
2	23.215	BB	0.5460	7099.42871	197.53603	87.5881



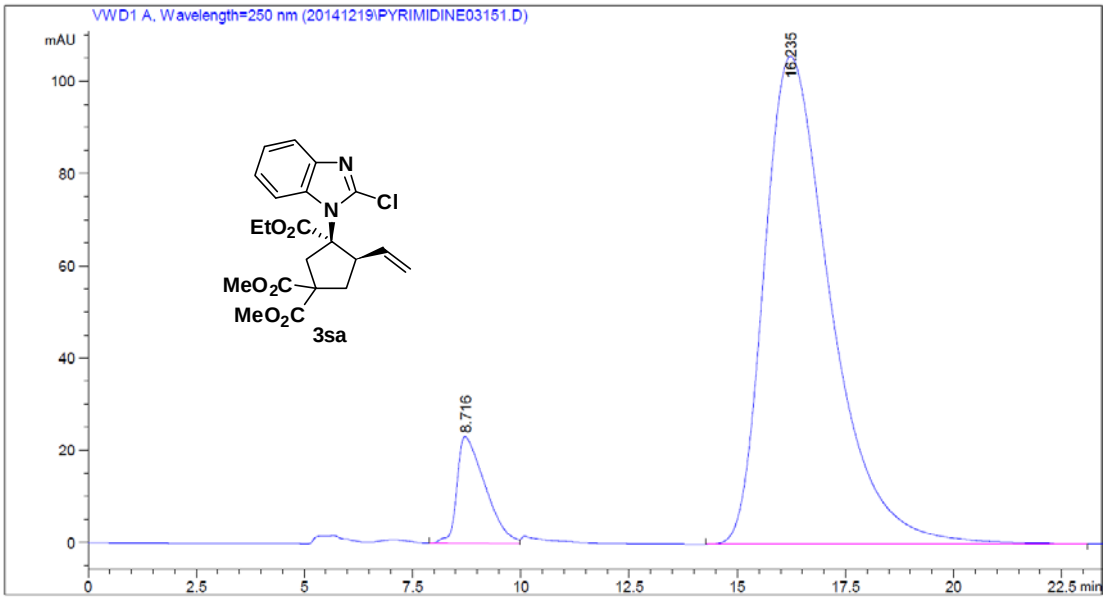
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.443	VV	0.6140	8.08859e4	2033.46643	49.5717
2	20.649	VB	0.6536	8.22835e4	1956.86938	50.4283



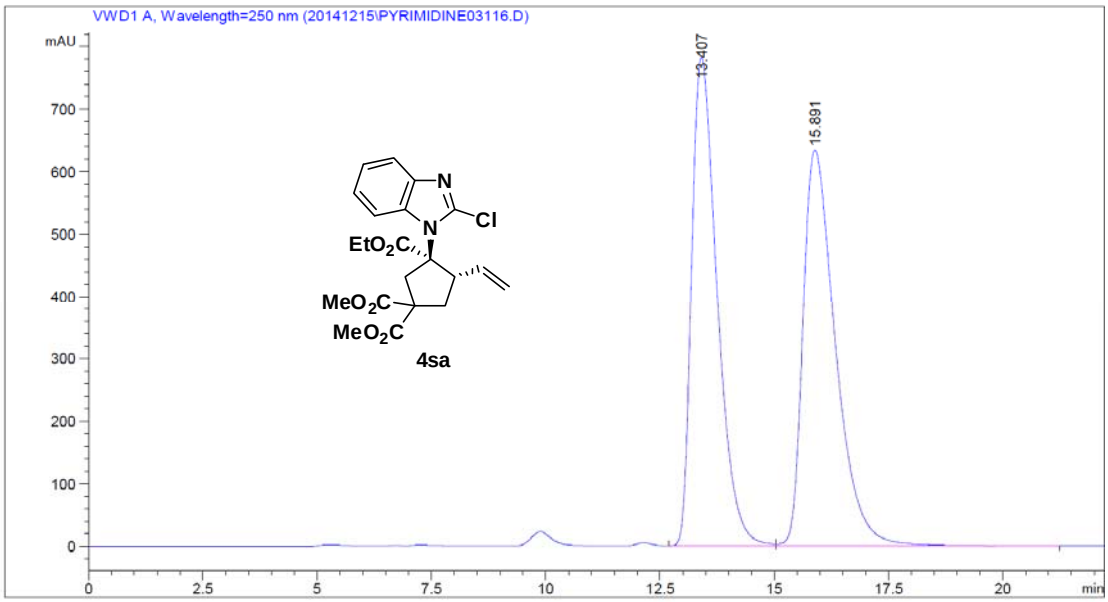
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.174	BB	0.5802	230.38408	6.14295	6.6709
2	21.113	BB	0.6248	3223.20435	79.19800	93.3291



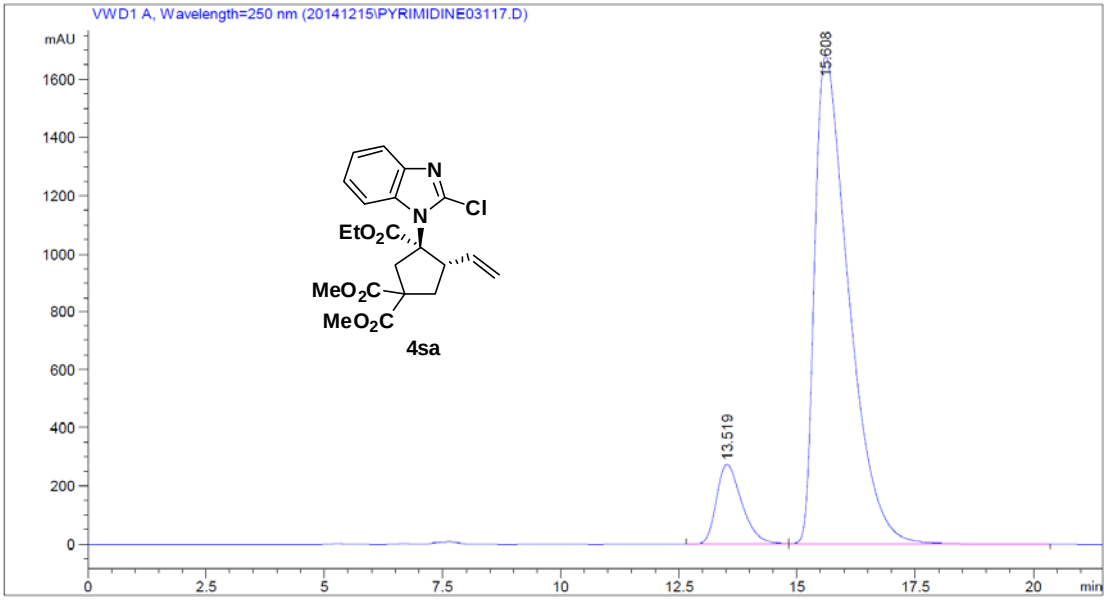
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.737	BV	0.7047	1.09977e4	250.33685	49.9688
2	16.244	BB	1.5604	1.10114e4	104.58104	50.0312



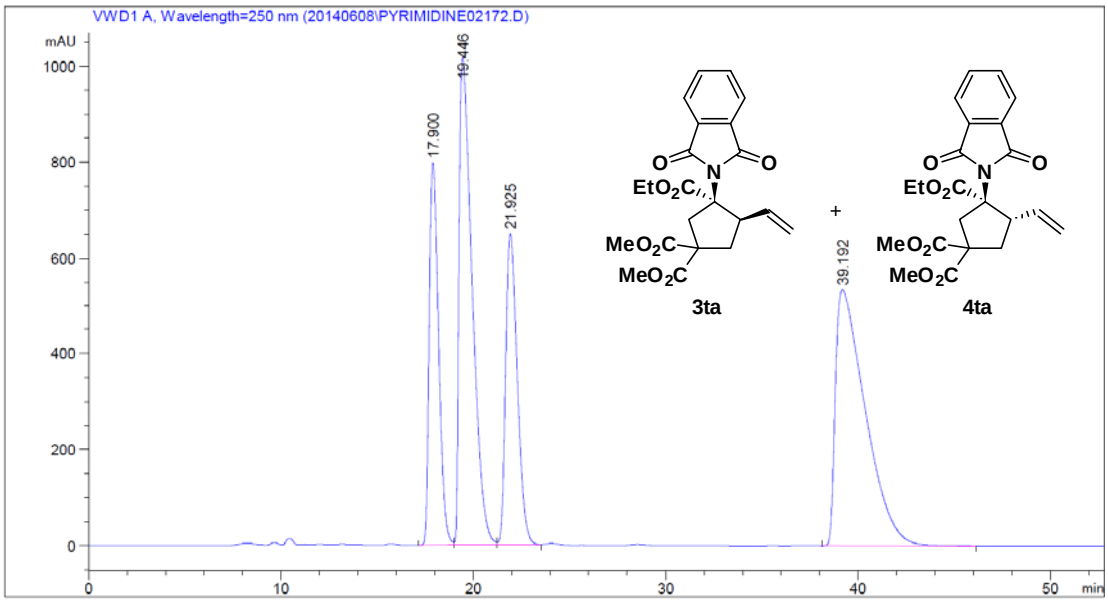
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.716	BV	0.6684	1041.09851	23.10493	8.4362
2	16.235	BB	1.6054	1.12998e4	105.69853	91.5638



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.407	VV	0.5982	3.03433e4	782.23840	49.2102
2	15.891	VB	0.7525	3.13173e4	633.97339	50.7898

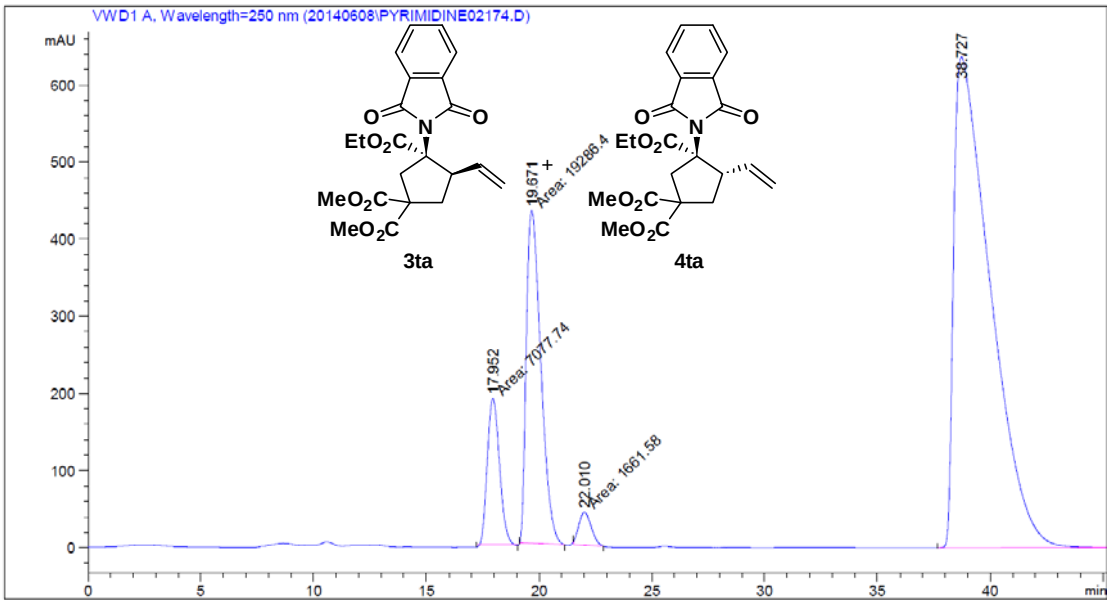


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.519	BV	0.5726	1.02008e4	273.14572	10.7930
2	15.608	VB	0.7581	8.43124e4	1681.79578	89.2070



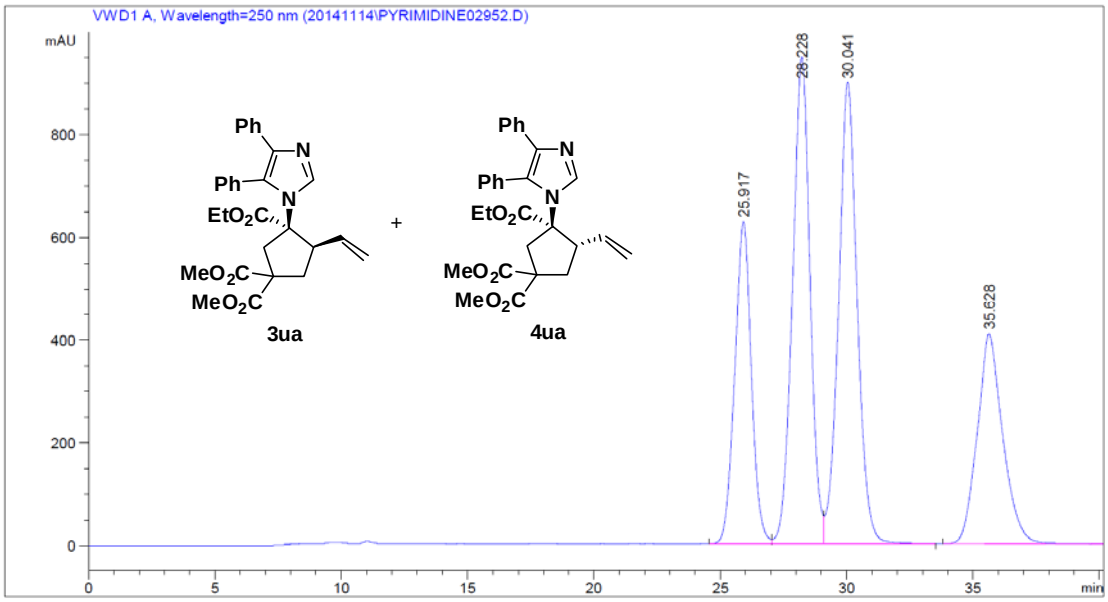
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.900	BV	0.5360	2.70120e4	798.28741	16.9070
2	19.446	VV	0.7055	4.80206e4	1016.47522	30.0563
3	21.925	VB	0.6551	2.72412e4	649.83197	17.0504

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
4	39.192	BB	1.4936	5.74948e4	535.78473	35.9863



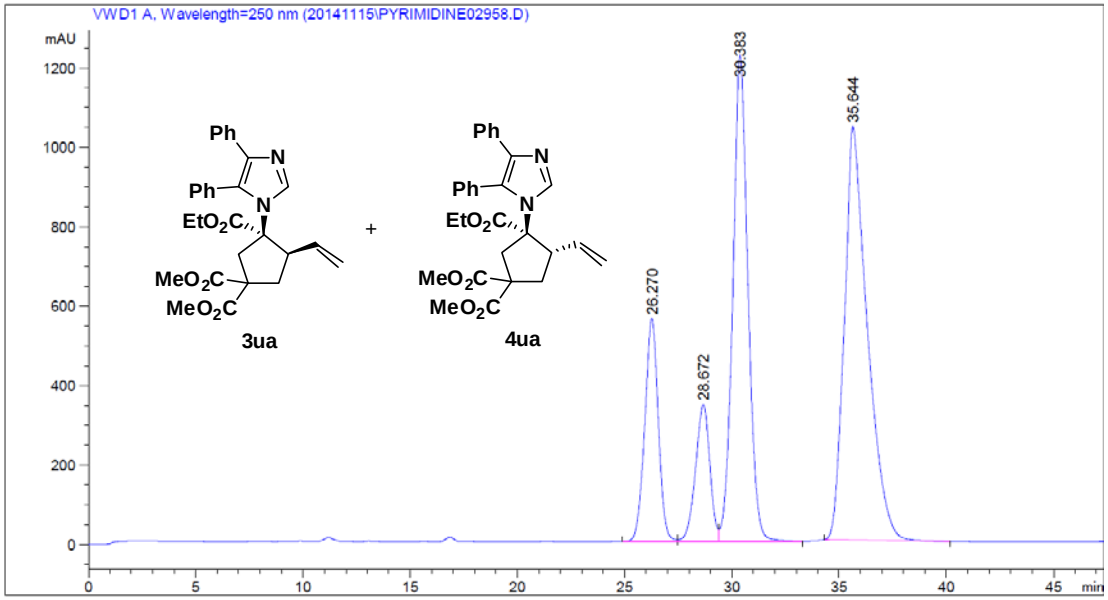
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.952	MM	0.6234	7077.73926	189.22290	7.1000
2	19.671	MM	0.7459	1.92864e4	430.95389	19.3470
3	22.010	MM	0.6457	1661.57642	42.88876	1.6668

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
4	38.727	BBA	1.5518	7.16606e4	636.72180	71.8861



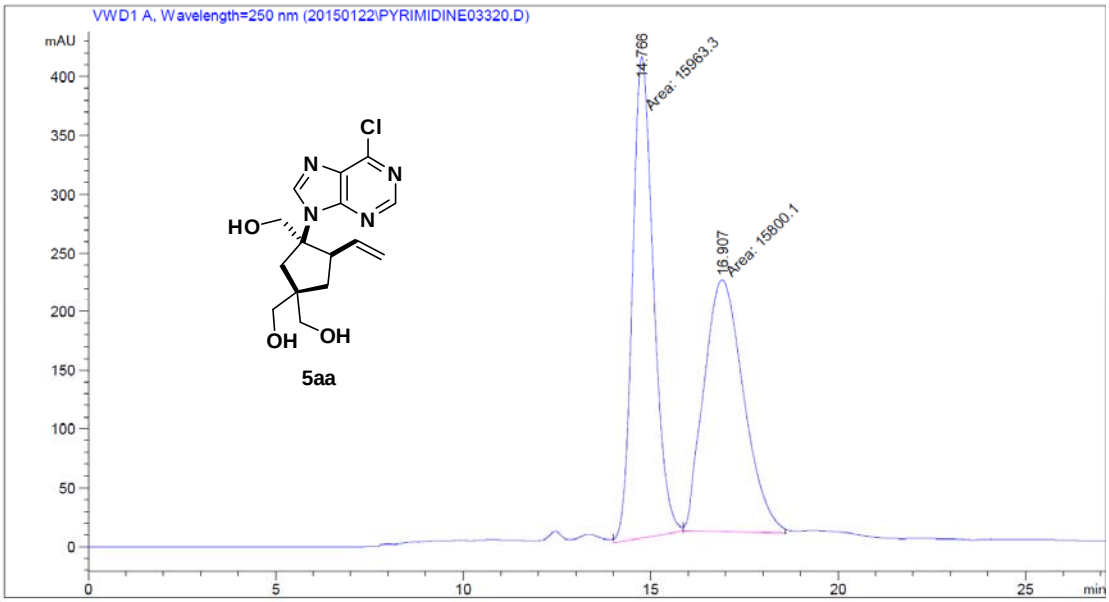
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.917	BV	0.6824	2.86271e4	627.30438	19.2466
2	28.228	VV	0.7301	4.55296e4	946.46558	30.6105
3	30.041	VB	0.7588	4.59885e4	898.37567	30.9190

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
4	35.628	BBA	0.9902	2.85932e4	408.32840	19.2238

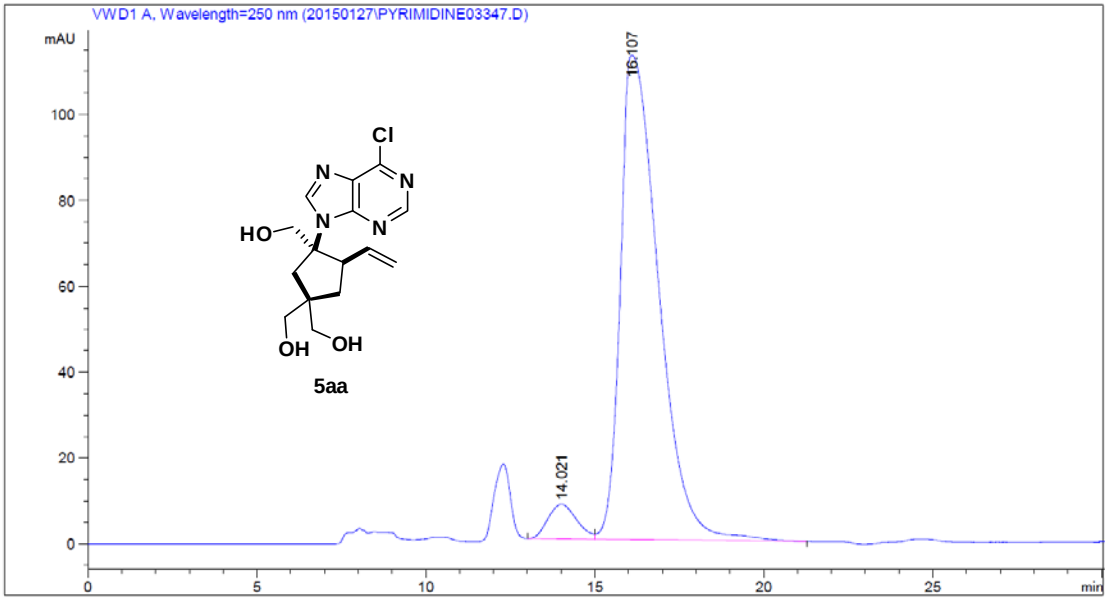


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.270	BV	0.6545	2.45573e4	561.33618	13.8120
2	28.672	VV	0.7017	1.60096e4	344.90875	9.0045
3	30.383	VB	0.7244	5.98124e4	1223.99988	33.6410

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
4	35.644	BB	1.0172	7.74169e4	1041.43054	43.5425



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.766	MM	0.6500	1.59633e4	409.34464	50.2569
2	16.907	MM	1.2248	1.58001e4	215.00868	49.7431



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.021	BV	0.8318	480.71237	8.13803	5.1264
2	16.107	VB	1.1910	8896.40527	112.79997	94.8736