

Supporting Information for:

**Highly Enantioselective Rh-catalyzed Asymmetric Reductive Dearomatization of
Multi-nitrogen Polycyclic Pyrazolo[1,5-*a*]pyrimidines**

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CONTENTS

1. Experimental Section	S2
2. General Procedure for Synthesis of Substrates 1 , 3 and 5	S2
3. General procedure for asymmetric hydrogenation of compounds 1 , 3 and 5	S8
4. Experimental operation of catalyst loading on substrates 1t and 5j	S10
5. Optimizing Reaction Conditions	S11
6. The Characterization Data for Substrates	S12
7. NMR, SFC and HPLC, optical rotation and HRMS Data of compounds 2 , 4 and 6	S25
8. NMR, SFC and HPLC spectra of compounds	S45
9. X-ray crystallographic analysis of compound 4c	S184
10. DFT calculations	S185

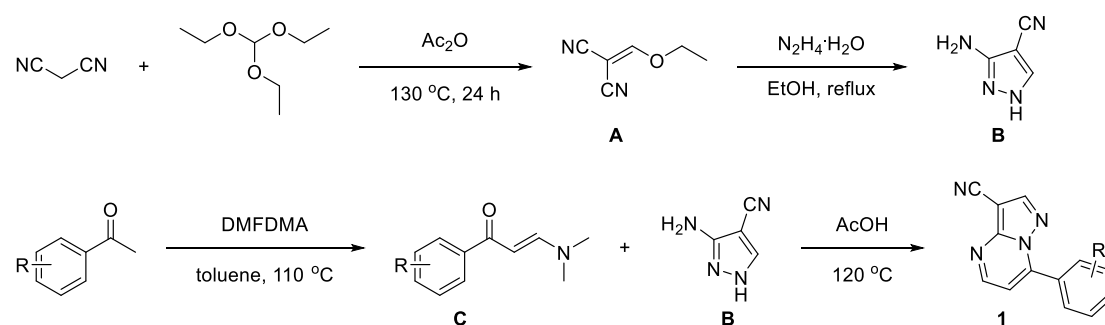
1. Experimental Section

General Information:

All the air or moisture sensitive reactions and manipulations were performed by using standard Schlenk techniques and in a nitrogen-filled glovebox. ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on Bruker AV (400 MHz) spectrometers and JEOL JNM-ECX600P and JNM-ECS600 (400 MHz or 600 MHz) spectrometers. CDCl_3 was the solvent used for the NMR analysis, with TMS as the internal standard. Chemical shifts were reported upfield to TMS (0.00 ppm) for ^1H NMR. Data is represented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, dd = double of doublets, t = triplet, q = quartet, m = multiplet) and coupling constants (J) in Hertz (Hz). Optical rotation was determined using Autopol III Automatic polarimeter (Rudolph research Analytical). GC analysis was conducted on an Agilent 7890A series instrument. HPLC analysis was conducted on Agilent 1260 series instrument. SFC analysis was conducted on Agilent 1260 series instrument. HRMS were recorded on a Waters LCT Premier XE mass spectrometer with APCI or ESI.

2. General Procedure for Synthesis of Substrates 1, 3 and 5.

Method A: **1a-1n** were prepared by the following protocol.^[1]



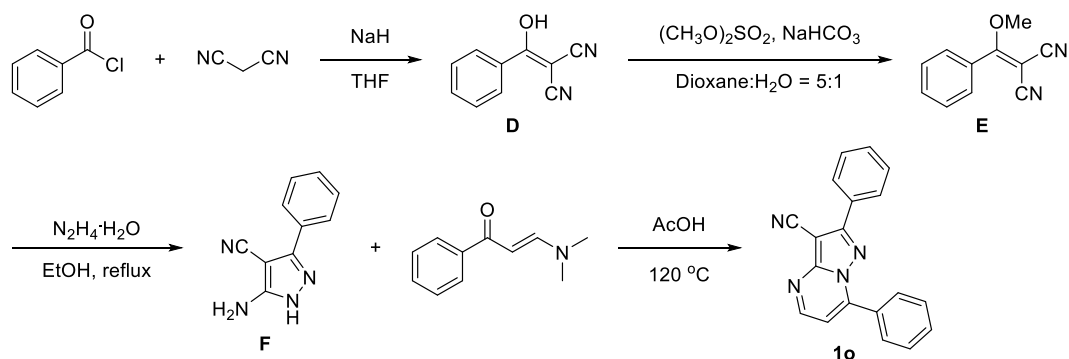
An equimolar amount of malononitrile (20 mmol, 1.0 equiv.) and triethyorthoformate (20 mmol, 1.0 equiv.) were heated at 130 °C in Ac_2O (30 mL) for 24 h to ensure complete conversion. After completion of the reaction, acetic anhydride was evaporated under reduced pressure, and the crude product was purified by column chromatography to obtain product **A** in 85% yield.

To a solution of compound **A** (20 mmol, 1.0 equiv.) in ethanol (20 mL) was added hydrazinium hydroxide solution (30 mmol, 1.5 equiv.). The mixture was stirred at room temperature for 16 h then was concentrated to give the crude product and washed with MeOH (30 mL) to afford product **B** in 80% yield.

To a mixture of aryl ethanone (10 mmol, 1.0 equiv.) in dry toluene (50 mL) was added 1,1-dimethoxy-N,N-dimethylmethanamine (DMF-DMA, 15 mmol, 1.5 equiv.), and the mixture was heated under reflux at 100 °C for 6–12 h. The solvent was evaporated, and the residual viscous liquid was dissolved in ether. The resulting solids were collected by filtration, washed thoroughly with ether, dried, and finally recrystallized from EtOH to afford aryl enaminones **C**.

To a solution of aryl enaminones **C** (10 mmol, 1.0 equiv.) in AcOH (15 mL) was added compound **B** (10 mmol, 1.0 equiv.). The mixture was stirred at 120 °C for 4 h. Then the reaction mixture was concentrated to a residue and partitioned between ethyl acetate (100 mL) and brine (100 mL). Organic layer was separated, washed with brine (2x100 mL), dried over sodium sulfate and concentrated, and the crude product was purified by column chromatography to obtain product **1**.

Method B: **1o** were prepared by the following protocol.^[2]



Sodium hydride (21 mmol, 2.1 equiv.) was suspended in dry THF (10 mL) and the mixture was cooled to 0 °C. Malononitrile (10 mmol, 1.0 equiv.) was dissolved in dry THF (15 mL) and added dropwise to the stirring sodium hydride mixture in THF over 20 min. Benzoyl chloride (11 mmol, 1.1 equiv.) was dissolved in dry THF (15 mL) and added dropwise to the stirring malononitrile mixture over 30 min. The reaction was allowed to warm to room temperature and stirred for an additional 30 min. Then, it was acidified with 1N HCl to pH 2. The mixture was extracted with ethyl acetate (60 mL)

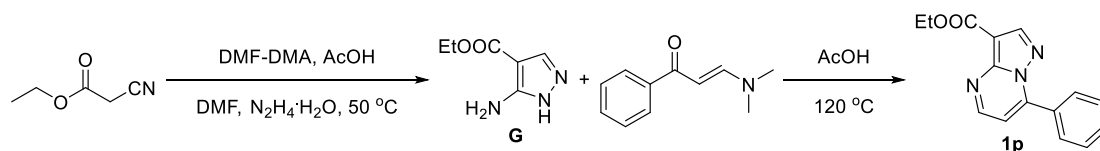
and dried over anhydrous sodium sulfate. The ethyl acetate was evaporated under reduced pressure and the compound was purified by silica gel column chromatography using ethyl acetate as the eluent to afford **D** in 88% yield.

Sodium bicarbonate (80 mmol, 8.0 equiv.) was added over 10 min to a solution of **D** (10 mmol, 1.0 equiv.) in dioxane (40 mL) and water (8 mL). Dimethyl sulfate (50 mmol, 5.0 equiv.) was added to the reaction mixture and the solution was heated to reflux with vigorous stirring for 3 h. The reaction mixture was cooled, diluted with water (40 mL), and extracted with diethyl ether (50 mL). The organic layer was dried with anhydrous sodium sulfate and evaporated under reduced pressure. The residue was purified by silica gel column chromatography using dichloromethane and methanol to afford **E** in 75% yield.

To a solution of compound **E** (10 mmol, 1.0 equiv.) in ethanol (20 mL) was added hydrazinium hydroxide solution (15 mmol, 1.5 equiv.). The mixture was stirred at room temperature for 16 h then was concentrated to give the crude product and washed with MeOH (30 mL) to afford product **F**.

To a solution of aryl enaminones (10 mmol, 1.0 equiv.) in AcOH (15 mL) was added compound **F** (10 mmol, 1.0 equiv.). The mixture was stirred at 120 °C for 4 h. Then the reaction mixture was concentrated to a residue and partitioned between ethyl acetate (100 mL) and brine (100 mL). Organic layer was separated, washed with brine (2x100 mL), dried over sodium sulfate and concentrated, and the crude product was purified by column chromatography to obtain product **1o** in 70% yield.

Method C: **1p** were prepared by the following protocol.^[3]

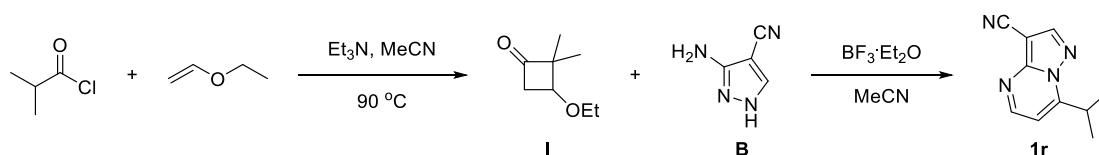


To a solution of ethyl cyanoacetate (10 mmol, 1.0 equiv.) in 10 mL dimethylformamide (DMF) was added glacial acetic acid (4 mmol, 0.4 equiv.) followed by N_2, N -dimethylformamide dimethylacetal (15 mmol, 1.5 equiv.) drop wise at room temperature and stirred for 1 h. To the resultant pale yellow color solution was added hydrazinium hydroxide solution (20 mmol, 2.0 equiv.) drop wise at 0 °C and the

reaction medium was stirred for 2 h at 50 °C. After completion of the reaction, the reaction medium was diluted with water and extracted with 2 × 70 mL of ethyl acetate. The combined organic layer was dried over sodium sulfate, filtered, and concentrated under reduced pressure to obtain the crude product as pale brown liquid. The crude product was further purified by column chromatography over silica gel, eluted with chloroform/methanol to afford the compound **G** as a white solid.

The next synthesis method refers to the synthesis of substrate **1o**.

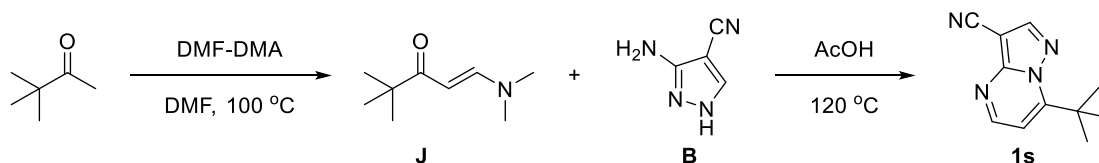
Method D: **1r** were prepared by the following protocol.^[4]



To a flame dried 100 mL three necked round bottom flask equipped with a stir bar was added triethylamine (24 mmol, 1.2 equiv.) and ethyl vinyl ether (40 mmol, 2.0 equiv.) in 20 mL acetonitrile under N₂. Then, a solution of isobutyryl chloride (20 mmol, 1.0 equiv.) in acetonitrile (10 mL) was added dropwise to resulting mixture at reflux. The mixture was stirred at reflux for 2~3 h, resulting in a white precipitate. Upon completion of the reaction, the white precipitate (protonated triethyl amine) was filtered. The filtered was washed with water and brine, dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure and the crude product was purified by flash column chromatograph to give the desired product **I** in 55% yield.

BF₃•Et₂O (1.0 mmol, 1.0 equiv.) was added to a mixture of compound **B** (1.0 mmol, 1.0 equiv.), cyclobutanones **I** (1.5 mmol, 1.5 equiv.), MeCN (5 mL). Then the sealed tube was stirred at 80 °C for 6 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatograph to give the desired product **1s** in 51% yield.

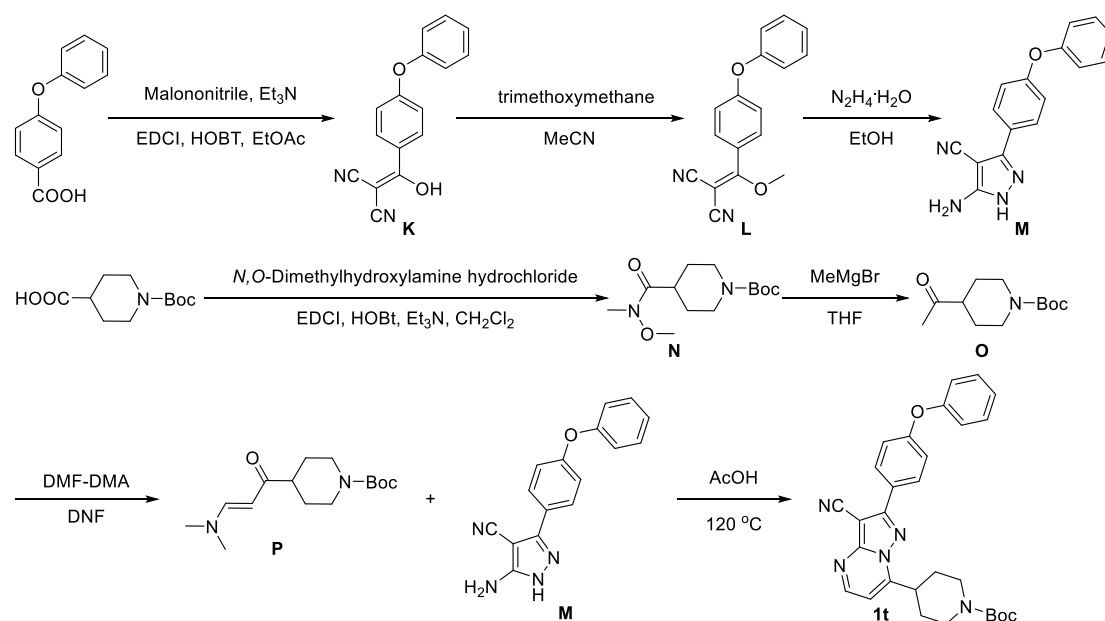
Method E: **1t** were prepared by the following protocol.^[1]



To a mixture of pinacolone (10 mmol, 1.0 equiv.) in dry DMF (50 mL) was added 1,1-dimethoxy-*N,N*-dimethylmethanamine (DMF-DMA, 15 mmol, 1.5 equiv.), and the mixture was heated under reflux at 100 °C for 6–12 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatograph to give the desired product **J** in 79% yield.

The next synthesis method refers to the synthesis of substrate **1o**.

Method F: **1t** were prepared by the following protocol.^[5]



Under nitrogen atmosphere, to a solution of EtOAc (20 mL), HOBT (1-hydroxybenzotriazole, 1.2 equiv.), EDCI (1-ethyl-3-(3-dimethylaminopropyl)carbodiimide, 1.2 equiv.), 4-phenoxybenzoic acid (1.0 equiv.) and malononitrile (1.2 equiv.) was added Et₃N (2.4 equiv.) at 10 °C. The mixture was then stirred at RT until the reaction was completed. The mixture was then centrifuged and the cake was washed with EtOAc. The filtrate was washed with aqueous NaHCO₃ twice and NH₄Cl. The organic phase was washed with 1.5 N H₂SO₄ twice and stirred. Concentrated and the residue was purified by flash column chromatograph to give the desired product **K**.

Under nitrogen atmosphere, a solution of compound **K** (1.0 equiv.) in MeCN was added into trimethoxymethane (1.5 equiv.) at 85 °C. The resultant mixture was stirred until the reaction was completed, the solvent was evaporated under reduced pressure

and the residue was purified by flash column chromatograph to give the desired product **L**.

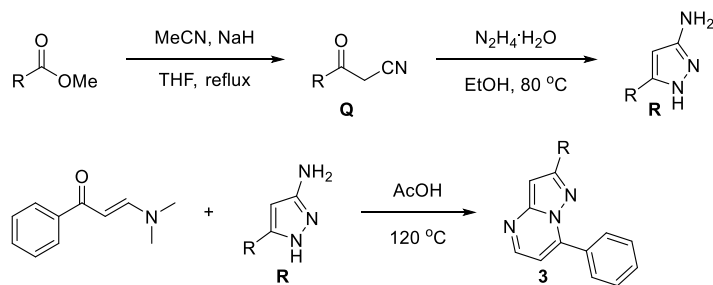
Under nitrogen atmosphere, to a solution of compound **L** (1.0 equiv.) in ethanol hydrazinium hydroxide solution (1.0 equiv.) in ethanol was charged dropwise to the reactor below 15 °C. The solution was heated to RT and stirred until the reaction was completed. Water was added to the reactor. The solution was then cooled to 5 °C, centrifuged and the cake was washed with water. The cake was dried under vacuum. The crude product **M** can be directly used for the next reaction.

To a mixture of DCM, 1-(tert-butoxycarbonyl)piperidine-4-carboxylic acid (1.0 eq.), *N,O*-dimethylhydroxylamine hydrochloride (1.2 equiv.), HOBT (1.2 equiv.) and EDCI (1.2 equiv.), Et₃N (2.6 equiv.) was charged dropwise below 15 °C, the mixture was stirred at RT until the reaction was completed, centrifuged and the cake was washed with DCM twice. The filtrate was washed with 20% aqueous NH₄Cl. The filtrate was concentrated under vacuum to give the crude product **N**, which was used in the next step without further purification.

The residue was dissolved in toluene and THF cooled to 10 °C, charged dropwise MeMgBr (1.4 equiv.) at 10 °C and then stirred at RT until the reaction was completed. The solution was cooled below 10 °C. Saturated aqueous NH₄Cl was charged dropwise below 10 °C. The mixture was centrifuged, separated, filtrated, and the organic phase was washed with aqueous NaCl twice. The organic phase was concentrated to give the crude product, which was used in the next step without further purification.

The next synthesis method refers to the synthesis of substrate **1**.

Method G: **3** were prepared by the following protocol.^[6]

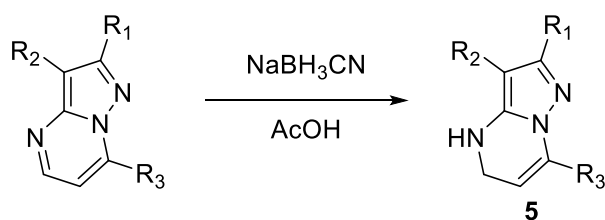


To a solution of acetonitrile (1.28g, 31.2 mmol, 2.0 equiv.) and NaH (1.56 g, 39.0 mmol, 2.5 equiv.) in 25 mL THF at room temperature was added a solution of methyl

formate (2.0 g, 15.6 mmol, 1.0 equiv.) in 15 mL THF dropwise. Then, maintaining the temperature at 80 °C. The reaction was stirred for 5 h before cooling to RT. Consumption of the starting material was monitored by TLC. The reaction mixture was quenched by 1N HCl at 0 °C, the aqueous phase was extracted with further ethyl acetate (3×30 mL), the combined organic phases were dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatograph to give the desired product **Q**.

The next synthesis method refers to the synthesis of substrate **1**.

Method H: **5** were prepared by the following protocol.^[7]



To a suspension of pyrazolo[1,5-a]pyrimidine (10 mmol) in 50 ml of acetic acid was added in portions of sodium cyanoborohydride (22 mmol) at room temperature under N₂. The mixture was stirred at room temperature for 2 h. After removal of the volatile material in vacuo, 400 mL of ethyl acetate was added. The organic phase was neutralized with saturated sodium bicarbonate solution, washed with brine, dried over magnesium sulfate, filtered and concentrated in vacuo. The residue was purified by flash column chromatograph to give the desired product **5**.

3. General procedure for asymmetric hydrogenation of compounds **1**, **3** and **5**

At room temperature, [Rh(COD)Cl]₂ and (*S*)-DTBM-SEGPHOS were mixed in THF at a molar ratio of 1.0:2.2 for 20 minutes in a nitrogen-filled glove box to prepare a stock solution. An aliquot of the catalyst solution (1.0 mL THF, 0.0025 mmol) was transferred by syringe into the vials charged with different substrates **1** (0.125 mmol for each). The vials were then placed into a steel autoclave which hydrogen gas was charged. The reaction mixture was stirred under H₂ (80 atm) at 90 °C for 48 h for the substrates. The hydrogen gas was released slowly and carefully. The solution was

passed through a short column of silica gel to remove the metal complex. The conversion of products were determined by GC or ^1H NMR analysis. The crude products were concentrated and purified by column chromatography and the ee values were determined by HPLC or SFC analysis on a chiral stationary phase.

At room temperature, $[\text{Rh}(\text{COD})\text{Cl}]_2$ and (*S*)-DTBM-SEGPHOS were mixed in THF at a molar ratio of 1.1:2.4 for 20 minutes in a nitrogen-filled glove box to prepare a stock solution. An aliquot of the catalyst solution (1.0 mL THF, 0.00275 mmol) was transferred by syringe into the vials charged with different substrates **3** (0.125 mmol for each). The vials were then placed into a steel autoclave which hydrogen gas was charged. The reaction mixture was stirred under H_2 (80 atm) at 90 °C for 48 h for the substrates. The hydrogen gas was released slowly and carefully. The solution was passed through a short column of silica gel to remove the metal complex. The conversion of products were determined by GC or ^1H NMR analysis. The crude products were concentrated and purified by column chromatography and the ee values were determined by HPLC or SFC analysis on a chiral stationary phase.

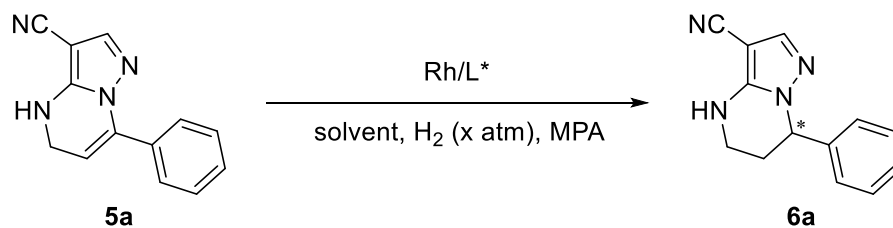
At room temperature, $[\text{Rh}(\text{COD})\text{Cl}]_2$ and (*S,S*)-f-spirophos were mixed in DCM at a molar ratio of 0.5:1.1 for 20 minutes in a nitrogen-filled glove box to prepare a stock solution. An aliquot of the catalyst solution (1.0 mL DCM, 0.00125 mmol) was transferred by syringe into the vials charged with different substrates **5** (0.125 mmol for each) in anhydrous DCM (2.0 ml), then add additives MPA (*N*-methyl-*p*-anisidine, 0.125 mmol). The vials were then placed into a steel autoclave which hydrogen gas was charged. The reaction mixture was stirred under H_2 (80 atm) at room temperature for 24 h for the substrates. The hydrogen gas was released slowly and carefully. The solution was passed through a short column of silica gel to remove the metal complex. The conversion of products were determined by GC or ^1H NMR analysis. The crude products were concentrated and purified by column chromatography and the ee values were determined by HPLC or SFC analysis on a chiral stationary phase.

4. Experimental operation of catalyst loading on substrates **1t** and **5j**

At room temperature, $[\text{Rh}(\text{COD})\text{Cl}]_2$ and (*S*)-DTBM-SEGPHOS were mixed in THF at a molar ratio of 1.0:2.2 for 20 minutes in a nitrogen-filled glove box to prepare a stock solution. An aliquot of the catalyst solution (1.0 mL THF, 0.0025 mmol) was transferred by syringe into the vials charged with substrate **1t** (371.5 mg, 0.75 mmol) in anhydrous THF (4.0 ml). The vials were then placed into a steel autoclave which hydrogen gas was charged. The reaction mixture was stirred under H_2 (80 atm) at 90 °C for 3 days. The hydrogen gas was released slowly and carefully. The solid was washed with DCM, and filtered to give the product **2t** as a white solid (359.5 mg, 96% yield) with 91% ee determined by HPLC with a chiral column.

At room temperature, $[\text{Rh}(\text{COD})\text{Cl}]_2$ and (*S,S*)-f-spirophos were mixed in DCM at a molar ratio of 0.5:1.1 for 20 minutes in a nitrogen-filled glove box to prepare a stock solution. An aliquot of the catalyst solution (1.0 mL DCM, 0.00125 mmol) was transferred by syringe into the vials charged with substrate **5j** (375.0 mg, 1.25 mmol) in anhydrous DCM (4.0 ml), then add additives MPA (*N*-methyl-*p*-anisidine, 17.1 mg, 0.125 mmol). The vials were then placed into a steel autoclave which hydrogen gas was charged. The reaction mixture was stirred under H_2 (80 atm) at 60 °C for 4 days. The hydrogen gas was released slowly and carefully. The solid was washed with DCM, and filtered to give the product **6j** as a white solid (347.5 mg, 92% yield) with 94% ee determined by HPLC with a chiral column.

5. Optimizing Reaction Conditions ^a

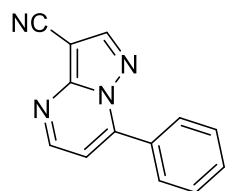


entry	ligand	solvent	H ₂ (atm)	conv ^b (%)	ee ^c (%)
1 ^d	L1	THF	80	40	42
2 ^e	L1	THF	80	97	40
3	L1	THF	80	100	64
4	L4	THF	80	100	68
5	L5	THF	80	96	37
6	L6	THF	80	100	64
7	L7	THF	80	100	73
8	L8	THF	80	100	80
9	L8	DCM	80	100	92
10	L8	MeOH	80	trace	--
11	L8	CHCl ₃	80	trace	--
12	L8	toluene	80	100	82
13	L8	DCM	30	100	92
14^f	L8	DCM	80	100	94

^aUnless otherwise mentioned, all reactions were carried out with a [Rh(COD)Cl]₂/diphosphine (monophosphine)/substrate/MPA = 0.5:1.1:100:100, 80 atm H₂, 60 °C, 24 h. ^bDetermined by GC analysis. ^cDetermined by chiral supercritical fluid chromatography (SFC) using a chiral stationary phase. ^d Rh(cod)BF₄, 80 atm H₂, 60 °C, 24 h. ^e Rh(NBD)BF₄, 80 atm H₂, 60 °C, 24 h. ^f [Rh(COD)Cl]₂, 80 atm H₂, rt, 24 h.

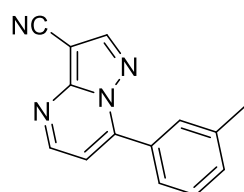
6. The Characterization Data for Substrates

7-phenylpyrazolo[1,5-a]pyrimidine-3-carbonitrile (**1a**)



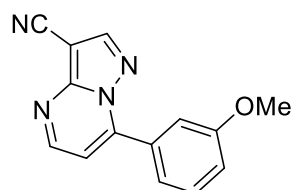
White solid; Yield: 70 %; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.76 (d, $J = 4.39$ Hz, 1H), 8.41 (s, 1H), 8.08 – 7.89 (m, 2H), 7.60 (q, $J = 6.70$ Hz, 3H), 7.16 (d, $J = 4.47$ Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.7, 151.4, 148.5, 147.1, 132.1, 129.5, 129.5, 129.0, 112.8, 109.9, 83.4.^[8]

7-(*m*-tolyl)pyrazolo[1,5-a]pyrimidine-3-carbonitrile (**1b**)



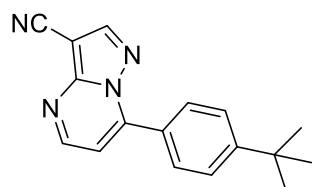
White solid; Yield: 66 %; ^1H NMR (600 MHz, Chloroform-*d*) δ 8.78 (d, $J = 4.19$ Hz, 1H), 8.36 (s, 1H), 7.50 (ddd, $J = 7.69, 5.11, 3.73$ Hz, 1H), 7.40 (d, $J = 7.44$ Hz, 1H), 7.38 – 7.36 (m, 2H), 7.04 (d, $J = 4.25$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 152.6, 150.8, 149.6, 147.4, 137.3, 131.3, 130.9, 129.9, 129.4, 126.4, 112.7, 111.4, 83.5, 19.8.^[8]

7-(3-methoxyphenyl)pyrazolo[1,5-a]pyrimidine-3-carbonitrile (**1c**)



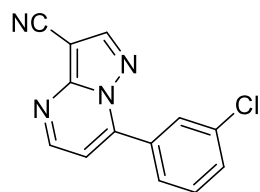
White solid; Yield: 65 %; ^1H NMR (600 MHz, Chloroform-*d*) δ 8.74 (d, $J = 4.41$ Hz, 1H), 8.40 (s, 1H), 7.56 – 7.51 (m, 2H), 7.48 (t, $J = 7.89$ Hz, 1H), 7.16 (d, $J = 4.44$ Hz, 1H), 7.13 (ddd, $J = 8.09, 2.59, 1.13$ Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.8, 152.7, 151.5, 148.4, 147.1, 130.7, 130.2, 121.8, 117.6, 115.3, 112.9, 110.0, 83.4, 55.6.^[9]

7-(4-(*tert*-butyl)phenyl)pyrazolo[1,5-a]pyrimidine-3-carbonitrile (**1d**)



White solid; Yield: 68 %; ^1H NMR (600 MHz, Chloroform-*d*) δ 8.74 (dd, $J = 4.49, 1.12$ Hz, 1H), 8.41 (d, $J = 1.36$ Hz, 1H), 8.02 – 7.91 (m, 2H), 7.65 – 7.54 (m, 2H), 7.15 (d, $J = 3.7$ Hz, 1H), 1.1 (d, $J = 0.98$ Hz, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.9, 152.7, 151.5, 148.6, 147.1, 129.3, 126.6, 126.1, 112.9, 109.6, 83.2, 35.2, 31.1. TOF-HRMS Calcd. for $\text{C}_{17}\text{H}_{17}\text{N}_4$ [$\text{M}+\text{H}^+$]: 277.1448, found 277.1451.

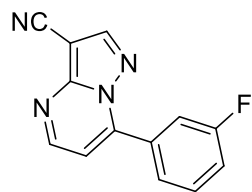
7-(3-chlorophenyl)pyrazolo[1,5-a]pyrimidine-3-carbonitrile (**1e**)



White solid; Yield: 77 %; ^1H NMR (600 MHz, Chloroform-*d*) δ 8.78 (d, $J = 4.35$ Hz, 1H), 8.43 (s, 1H), 8.01 (t, $J = 1.93$ Hz, 1H), 7.90 (dt, $J = 7.60, 1.27$ Hz, 1H), 7.60 (ddd, $J = 8.10, 2.07, 1.10$ Hz, 1H), 7.54 (t, $J = 7.90$ Hz, 1H), 7.16 (d, $J = 4.36$ Hz, 1H). ^{13}C

NMR (151 MHz, Chloroform-*d*) δ 152.7, 151.4, 147.3, 147.0, 135.2, 132.1, 131.2, 130.3, 129.6, 127.7, 112.6, 110.0, 83.9.^[8]

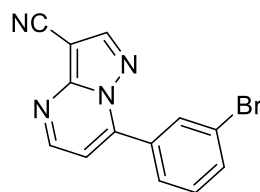
7-(3-fluorophenyl)pyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**1f**)



White solid; Yield: 80 %; ^1H NMR (600 MHz, Chloroform-*d*) δ 8.78 (d, $J = 4.39$ Hz, 1H), 8.43 (s, 1H), 7.83 – 7.75 (m, 2H), 7.58 (td, $J = 8.18, 5.67$ Hz, 1H), 7.33 (tdd, $J = 8.35, 2.55, 1.00$ Hz, 1H), 7.18 (d, $J = 4.38$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ

162.6 (d, $J = 247.6$ Hz), 152.6, 151.4, 147.2, 147.0, 131.3 (d, $J = 8.4$ Hz), 130.8 (d, $J = 7.6$ Hz), 125.3, 119.1 (d, $J = 20.6$ Hz), 116.8 (d, $J = 23.7$ Hz), 112.6, 110.0, 83.8.^[9]

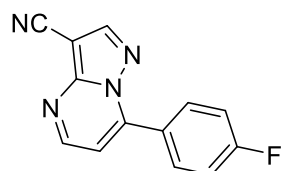
7-(3-bromophenyl)pyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**1g**)



White solid; Yield: 78 %; ^1H NMR (600 MHz, Chloroform-*d*) δ 8.78 (d, $J = 4.39$ Hz, 1H), 8.43 (s, 1H), 8.16 (t, $J = 1.86$ Hz, 1H), 7.95 (ddd, $J = 7.84, 1.80, 1.01$ Hz, 1H), 7.75 (ddd, $J = 8.02, 1.99, 1.02$ Hz, 1H), 7.47 (t, $J = 7.93$ Hz, 1H), 7.15 (d, $J = 4.38$ Hz, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 152.6, 151.4, 147.2, 146.8, 135.0, 132.4, 131.4, 130.5, 128.1, 123.0, 112.6, 110.0, 83.8.^[10]

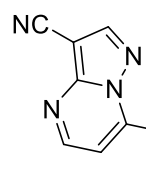
7-(4-fluorophenyl)pyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**1h**)



White solid; Yield: 77 %; ^1H NMR (600 MHz, DMSO-*d*₆) δ 8.86 (t, $J = 5.31$ Hz, 1H), 8.82 (d, $J = 6.24$ Hz, 1H), 8.15 (ddq, $J = 8.70, 5.35, 3.31$ Hz, 2H), 7.55 (t, $J = 5.87$ Hz, 1H), 7.44

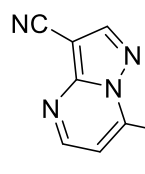
(dtd, $J = 8.84, 6.37, 5.91, 2.92$ Hz, 2H). ^{13}C NMR (151 MHz, DMSO-*d*₆) δ 165.2, 163.5, 154.2, 151.6, 147.7, 147.1, 133.0 (d, $J = 8.8$ Hz), 126.4, 116.3, 116.2, 113.9, 111.1, 81.9.^[10]

7-(4-chlorophenyl)pyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**1i**)



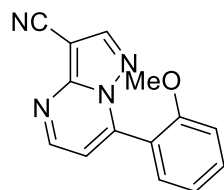
White solid; Yield: 78 %; ¹H NMR (600 MHz, Chloroform-*d*) δ 8.77 (d, *J* = 4.34 Hz, 1H), 8.42 (s, 1H), 7.98 (d, *J* = 8.15 Hz, 2H), 7.58 (d, *J* = 8.15 Hz, 2H), 7.15 (d, *J* = 4.43 Hz, 1H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 152.7, 151.5, 147.3, 147.2, 138.6, 130.9, 129.4, 127.9, 112.7, 109.7, 83.8.^[8]

7-(4-bromophenyl)pyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**1j**)



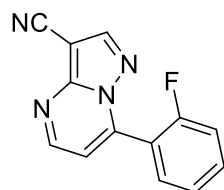
White solid; Yield: 73 %; ¹H NMR (600 MHz, Chloroform-*d*) δ 8.77 (d, *J* = 4.40 Hz, 1H), 8.42 (s, 1H), 7.95 – 7.85 (m, 2H), 7.77 – 7.70 (m, 2H), 7.15 (d, *J* = 4.39 Hz, 1H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 152.7, 151.5, 147.4, 147.2, 132.4, 131.0, 128.4, 127.0, 112.6, 109.7, 83.8.^[8]

7-(2-methoxyphenyl)pyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**1k**)



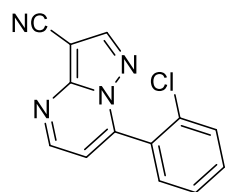
White solid; Yield: 65 %; ¹H NMR (600 MHz, Chloroform-*d*) δ 8.73 (d, *J* = 4.06 Hz, 1H), 8.33 (s, 1H), 7.57 (t, *J* = 7.96 Hz, 1H), 7.52 (d, *J* = 7.48 Hz, 1H), 7.18 – 7.05 (m, 3H), 3.78 (d, *J* = 1.88 Hz, 3H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 157.4, 152.3, 151.0, 147.0, 146.9, 133.1, 130.7, 120.9, 118.9, 113.0, 111.9, 111.8, 83.1, 55.8.

7-(2-fluorophenyl)pyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**1l**)



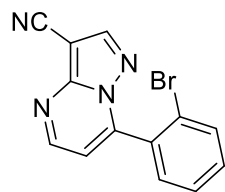
White solid; Yield: 76 %; ¹H NMR (600 MHz, Chloroform-*d*) δ 8.78 (d, *J* = 4.32 Hz, 1H), 8.38 (s, 1H), 7.76 (ddd, *J* = 7.64, 6.89, 1.77 Hz, 1H), 7.61 (dddd, *J* = 8.37, 7.26, 5.24, 1.77 Hz, 1H), 7.37 (td, *J* = 7.62, 1.10 Hz, 1H), 7.30 (ddd, *J* = 9.72, 8.42, 1.09 Hz, 1H), 7.18 (dd, *J* = 4.33, 1.15 Hz, 1H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 160.06 (d, *J* = 254.00 Hz), 152.4, 151.0, 147.1, 143.7, 133.8 (d, *J* = 8.72 Hz), 131.1, 124.7 (d, *J* = 3.65 Hz), 117.8 (d, *J* = 13.67 Hz), 116.7 (d, *J* = 21.11 Hz), 112.6, 111.8 (d, *J* = 3.61 Hz), 83.7.

7-(2-chlorophenyl)pyrazolo[1,5-a]pyrimidine-3-carbonitrile (**1m**)



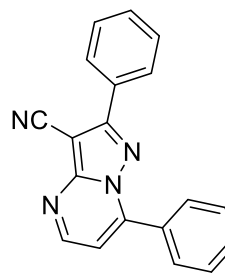
White solid; Yield: 73 %; ^1H NMR (600 MHz, Chloroform-*d*) δ 8.81 (d, $J = 4.29$ Hz, 1H), 8.37 (s, 1H), 7.60 (d, $J = 7.93$ Hz, 1H), 7.56 (t, $J = 7.72$ Hz, 1H), 7.53 (d, $J = 7.52$ Hz, 1H), 7.48 (t, $J = 7.52$ Hz, 1H), 7.12 (d, $J = 4.26$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 152.5, 150.7, 147.3, 146.4, 133.5, 132.5, 131.0, 130.5, 129.2, 127.3, 112.6, 111.8, 83.7.^[8]

7-(2-bromophenyl)pyrazolo[1,5-a]pyrimidine-3-carbonitrile (**1n**)



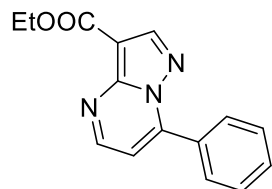
White solid; Yield: 80 %; ^1H NMR (600 MHz, Chloroform-*d*) δ 8.80 (d, $J = 4.22$ Hz, 1H), 8.35 (s, 1H), 7.92 – 7.67 (m, 1H), 7.56 – 7.51 (m, 1H), 7.49 – 7.43 (m, 2H), 7.10 (d, $J = 4.24$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 152.6, 150.7, 147.6, 147.3, 133.6, 132.6, 131.4, 131.1, 128.0, 122.7, 112.6, 111.8, 83.7.

2,7-diphenylpyrazolo[1,5-a]pyrimidine-3-carbonitrile (**1o**)



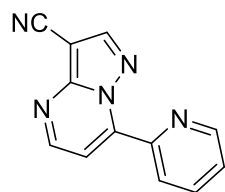
White solid; Yield: 70 %; ^1H NMR (600 MHz, Chloroform-*d*) δ 8.72 (d, $J = 4.44$ Hz, 1H), 8.24 – 8.15 (m, 2H), 8.15 – 8.04 (m, 2H), 7.61 (qd, $J = 8.85, 7.87, 3.71$ Hz, 3H), 7.49 (q, $J = 7.25, 6.69$ Hz, 3H), 7.15 (d, $J = 4.43$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.1, 153.4, 152.3, 147.9, 132.0, 130.6, 130.5, 129.7, 129.1, 128.9, 127.7, 114.1, 110.0, 80.4.^[11]

ethyl 7-phenylpyrazolo[1,5-a]pyrimidine-3-carboxylate (**1p**)



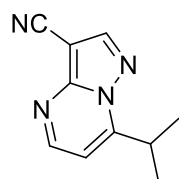
White solid; Yield: 73 %; ^1H NMR (600 MHz, Chloroform-*d*) δ 8.78 (dd, $J = 9.24, 4.39$ Hz, 1H), 8.58 (d, $J = 7.40$ Hz, 1H), 8.06 – 7.92 (m, 2H), 7.62 – 7.51 (m, 3H), 7.05 (dd, $J = 6.20, 4.30$ Hz, 1H), 4.43 (p, $J = 7.35$ Hz, 2H), 1.40 (q, $J = 7.21$ Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 162.6, 152.4, 149.0, 148.0, 147.5, 131.6, 130.3, 129.5, 128.9, 60.5, 14.7.^[12]

7-(pyridin-2-yl)pyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**1q**)



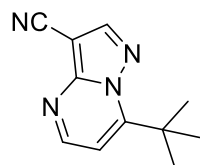
White solid; Yield: 66 %; ^1H NMR (600 MHz, Chloroform-*d*) δ 8.97 (d, $J = 8.17$ Hz, 1H), 8.83 (dd, $J = 6.16, 4.28$ Hz, 2H), 8.47 (s, 1H), 7.97 (d, $J = 4.23$ Hz, 1H), 7.95 (dd, $J = 7.88, 2.15$ Hz, 1H), 7.51 (dd, $J = 7.57, 4.79$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 152.8, 151.7, 150.4, 147.0, 147.0, 145.8, 137.0, 126.5, 126.3, 112.8, 110.6, 83.5.^[13]

7-isopropylpyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**1r**)



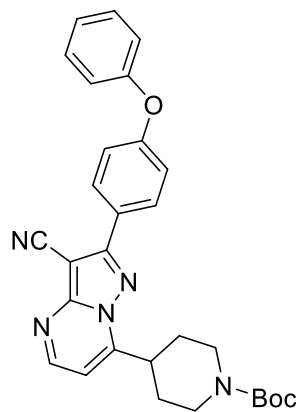
White solid; Yield: 51 %; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.65 (d, $J = 4.31$ Hz, 1H), 8.37 (s, 1H), 6.93 (d, $J = 4.50$ Hz, 1H), 3.87 (p, $J = 6.88$ Hz, 1H), 1.43 (d, $J = 6.91$ Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.3, 152.8, 150.6, 146.8, 113.0, 106.4, 83.0, 28.9, 19.9.^[4]

7-(*tert*-butyl)pyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**1s**)



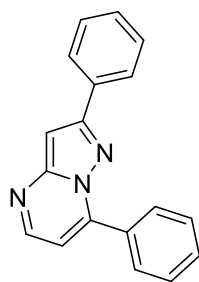
White solid; Yield: 78 %; ^1H NMR (600 MHz, Chloroform-*d*) δ 8.63 (d, $J = 4.71$ Hz, 1H), 8.37 (s, 1H), 6.95 (dd, $J = 4.48, 1.94$ Hz, 1H), 1.60 (d, $J = 2.25$ Hz, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.6, 152.8, 151.8, 145.7, 113.2, 107.1, 82.6, 36.5, 27.0.

tert-butyl 4-(3-cyano-2-(4-phenoxyphenyl)pyrazolo[1,5-*a*]pyrimidin-7-yl)piperidine-1-carboxylate (**1t**)



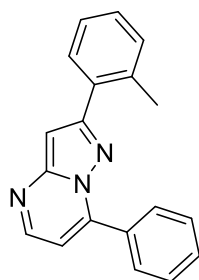
White solid; Yield: 77 %; ^1H NMR (600 MHz, Chloroform-*d*) δ 8.63 – 8.54 (m, 1H), 8.16 – 8.08 (m, 2H), 7.35 (dddd, $J = 8.57, 5.25, 2.61, 1.52$ Hz, 2H), 7.13 (ddt, $J = 8.58, 7.41, 1.11$ Hz, 1H), 7.10 – 7.01 (m, 4H), 6.85 (t, $J = 4.02$ Hz, 1H), 4.32 (s, 2H), 3.76 (td, $J = 12.07, 10.48, 4.43$ Hz, 1H), 2.95 (s, 2H), 2.25 – 2.08 (m, 2H), 1.77 – 1.60 (m, 2H), 1.46 (s, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.7, 156.3, 156.2, 154.7, 153.6, 152.4, 152.3, 130.1, 129.3, 129.3, 125.1, 124.3, 119.8, 118.6, 118.6, 114.2, 107.1, 80.0, 79.8, 43.6, 36.8, 29.1, 28.5.^[5]

2,7-diphenylpyrazolo[1,5-*a*]pyrimidine (**3a**)



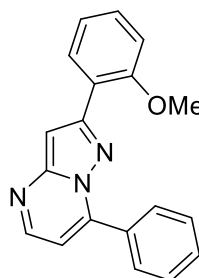
Yellow solid; Yield: 77 %; ^1H NMR (600 MHz, Chloroform-*d*) δ 8.48 (d, $J = 4.29$ Hz, 1H), 8.21 – 8.14 (m, 2H), 8.03 – 7.99 (m, 2H), 7.60 – 7.55 (m, 3H), 7.46 – 7.42 (m, 2H), 7.40 – 7.35 (m, 1H), 7.07 (s, 1H), 6.88 (d, $J = 4.35$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.9, 151.3, 149.0, 146.4, 133.0, 131.2, 129.6, 129.1, 128.8, 128.6, 126.8, 107.2, 93.8.^[12]

7-phenyl-2-(*o*-tolyl)pyrazolo[1,5-*a*]pyrimidine (**3b**)



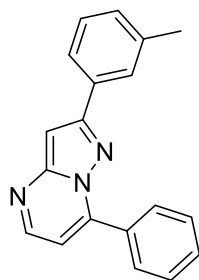
Yellow solid; Yield: 66 %; ^1H NMR (600 MHz, Chloroform-*d*) δ 8.52 (d, $J = 4.59$ Hz, 1H), 8.15 (dd, $J = 6.46, 3.07$ Hz, 2H), 7.71 (d, $J = 6.78$ Hz, 1H), 7.55 (t, $J = 3.51$ Hz, 3H), 7.28 (d, $J = 7.92$ Hz, 3H), 6.95 (s, 1H), 6.91 (d, $J = 4.49$ Hz, 1H), 2.58 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.8, 150.5, 149.0, 146.4, 136.7, 132.9, 131.2, 131.2, 131.1, 130.2, 129.5, 128.6, 126.0, 107.1, 97.0, 21.6. TOF-HRMS Calcd. for $\text{C}_{19}\text{H}_{16}\text{N}_3$ [$\text{M}+\text{H}^+$]: 286.1339, found 286.1332.

2-(2-methoxyphenyl)-7-phenylpyrazolo[1,5-*a*]pyrimidine (**3c**)



Yellow solid; Yield: 70 %; ^1H NMR (600 MHz, Chloroform-*d*) δ 8.48 (d, $J = 4.71$ Hz, 1H), 8.18 (dd, $J = 6.55, 3.06$ Hz, 2H), 8.15 (dd, $J = 7.61, 1.90$ Hz, 1H), 7.56 (q, $J = 3.78$ Hz, 3H), 7.38 (s, 1H), 7.37 – 7.33 (m, 1H), 7.07 – 6.98 (m, 2H), 6.88 (d, $J = 4.68$ Hz, 1H), 3.96 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.8, 152.9, 150.7, 148.5, 146.0, 131.4, 131.0, 130.1, 129.5, 129.4, 128.6, 121.9, 120.9, 111.6, 107.1, 98.3, 55.7.^[14]

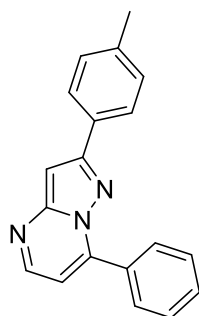
7-phenyl-2-(*m*-tolyl)pyrazolo[1,5-*a*]pyrimidine (**3d**)



Yellow solid; Yield: 75 %; ^1H NMR (600 MHz, Chloroform-*d*) δ 8.48 (d, $J = 4.29$ Hz, 1H), 8.21 – 8.13 (m, 2H), 7.81 (dd, $J = 7.98, 1.57$ Hz, 2H), 7.62 – 7.50 (m, 3H), 7.34 (t, $J = 7.52$ Hz, 1H), 7.22 – 7.16 (m, 1H), 7.06 (s, 1H), 6.87 (dd, $J = 4.33, 1.05$ Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.1, 151.2, 149.0, 146.4, 138.4, 132.9, 131.2, 131.1, 129.9, 129.6, 128.7, 128.7, 127.3, 124.0, 107.2, 93.8, 21.6. TOF-

HRMS Calcd. for C₁₉H₁₆N₃ [M+H⁺]: 286.1339, found 286.1332.

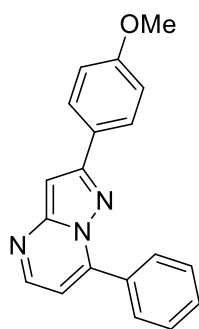
7-phenyl-2-(*p*-tolyl)pyrazolo[1,5-*a*]pyrimidine (**3e**)



Yellow solid; Yield: 68 %; ¹H NMR (600 MHz, Chloroform-*d*) δ 8.48 (d, *J* = 4.30 Hz, 1H), 8.24 – 8.11 (m, 2H), 7.92 – 7.87 (m, 2H), 7.61 – 7.53 (m, 3H), 7.25 (s, 1H), 7.24 (s, 1H), 7.03 (s, 1H), 6.87 (d, *J* = 4.00 Hz, 1H), 2.39 (s, 3H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 156.1, 151.3, 148.9, 146.4, 139.0, 131.2, 131.1, 130.2, 129.6, 129.5, 128.6, 126.6, 107.1, 93.5, 21.5. TOF-HRMS Calcd. for C₁₉H₁₆N₃

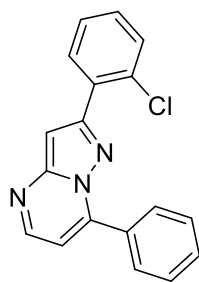
[M+H⁺]: 286.1339, found 286.1332.

2-(4-methoxyphenyl)-7-phenylpyrazolo[1,5-*a*]pyrimidine (**3f**)



Yellow solid; Yield: 62 %; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.46 (dd, *J* = 4.45, 0.61 Hz, 1H), 8.22 – 8.13 (m, 2H), 7.99 – 7.87 (m, 2H), 7.61 – 7.53 (m, 3H), 6.98 (d, *J* = 1.70 Hz, 2H), 6.96 (d, *J* = 2.02 Hz, 1H), 6.86 (dd, *J* = 4.33, 0.68 Hz, 1H), 3.85 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 160.4, 155.9, 151.3, 148.9, 146.3, 131.2, 131.1, 129.6, 128.6, 128.1, 125.7, 114.2, 107.0, 93.0, 55.4.^[14]

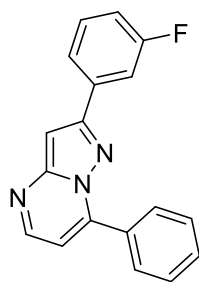
2-(2-chlorophenyl)-7-phenylpyrazolo[1,5-*a*]pyrimidine (**3g**)



Yellow solid; Yield: 71 %; ¹H NMR (600 MHz, Chloroform-*d*) δ 8.52 (d, *J* = 4.33 Hz, 1H), 8.18 – 8.12 (m, 2H), 7.94 – 7.89 (m, 1H), 7.55 (tt, *J* = 4.01, 2.34 Hz, 3H), 7.50 – 7.46 (m, 1H), 7.35 – 7.28 (m, 3H), 6.91 (d, *J* = 4.32 Hz, 1H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 153.7, 150.4, 149.1, 146.4, 133.1, 132.2, 131.5, 131.2, 131.1, 130.6,

129.7, 129.5, 128.7, 127.0, 107.5, 98.3. TOF-HRMS Calcd. for C₁₈H₁₃ClN₃ [M+H⁺]: 306.0793, found 306.0797.

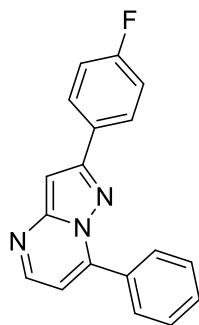
2-(3-fluorophenyl)-7-phenylpyrazolo[1,5-*a*]pyrimidine (**3h**)



Yellow solid; Yield: 66 %; ¹H NMR (600 MHz, Chloroform-*d*) δ 8.49 (d, *J* = 4.20 Hz, 1H), 8.14 (dd, *J* = 6.33, 3.30 Hz, 2H), 7.76 (d, *J* = 7.86 Hz, 1H), 7.74 – 7.69 (m, 1H), 7.60 – 7.55 (m, 3H), 7.44 – 7.36 (m, 1H), 7.09 – 7.05 (m, 1H), 7.04 (s, 1H), 6.90 (d, *J* = 4.42 Hz, 1H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 164.0, 162.4, 154.6, 151.2,

149.2, 146.5, 135.2 (d, $J = 8.5$ Hz), 131.2, 130.9, 130.3 (d, $J = 8.5$ Hz), 129.5, 128.7, 122.4, 115.8 (d, $J = 21.7$ Hz), 113.4 (d, $J = 22.0$ Hz), 107.5, 94.0. TOF-HRMS Calcd. for $C_{18}H_{13}FN_3$ [$M+H^+$]: 290.1088, found 290.1092.

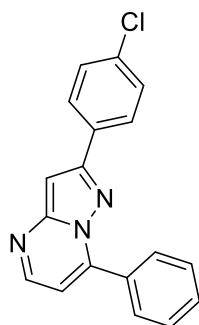
2-(4-fluorophenyl)-7-phenylpyrazolo[1,5-*a*]pyrimidine (**3i**)



Yellow solid; Yield: 63 %; 1H NMR (600 MHz, Chloroform-*d*) δ 8.49 (d, $J = 4.31$ Hz, 1H), 8.19 – 8.11 (m, 2H), 8.01 – 7.95 (m, 2H), 7.63 – 7.55 (m, 3H), 7.16 – 7.09 (m, 2H), 7.00 (s, 1H), 6.89 (d, $J = 4.28$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 164.2, 162.6, 155.0, 151.3, 149.1, 146.4, 131.2, 131.0, 129.5, 129.2, 128.6, 128.5 (d, $J = 8.1$ Hz), 115.7 (d, $J = 21.6$ Hz), 107.3, 93.5. TOF-HRMS Calcd. for

$C_{18}H_{13}FN_3$ [$M+H^+$]: 290.1088, found 290.1092.

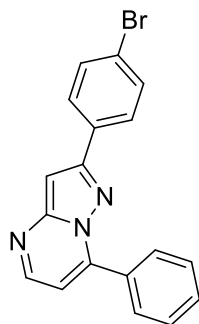
2-(4-chlorophenyl)-7-phenylpyrazolo[1,5-*a*]pyrimidine (**3j**)



Yellow solid; Yield: 71 %; 1H NMR (600 MHz, Chloroform-*d*) δ 8.51 – 8.46 (m, 1H), 8.20 – 8.10 (m, 2H), 7.92 (dd, $J = 8.75, 2.12$ Hz, 2H), 7.62 – 7.55 (m, 3H), 7.40 (dd, $J = 8.69, 2.02$ Hz, 2H), 7.04 – 7.00 (m, 1H), 6.92 – 6.87 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 154.8, 151.3, 149.2, 146.5, 134.9, 131.5, 131.2, 131.0, 129.5, 129.0, 128.7, 128.0, 107.5, 93.7. TOF-HRMS Calcd. for $C_{18}H_{13}ClN_3$ [$M+H^+$]:

306.0793, found 306.0797.

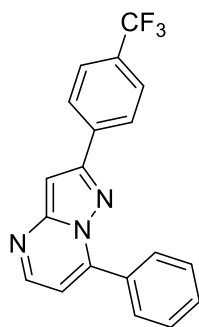
2-(4-bromophenyl)-7-phenylpyrazolo[1,5-*a*]pyrimidine (**3k**)



White solid; Yield: 51 %; 1H NMR (400 MHz, Chloroform-*d*) δ 8.50 (dd, $J = 4.35, 0.69$ Hz, 1H), 8.20 – 8.08 (m, 2H), 7.92 – 7.82 (m, 2H), 7.65 – 7.56 (m, 4H), 7.55 (d, $J = 1.72$ Hz, 1H), 7.03 (d, $J = 0.66$ Hz, 1H), 6.90 (dd, $J = 4.40, 0.68$ Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.8, 151.3, 149.3, 146.5, 132.0, 131.3, 131.0, 129.5, 128.7, 128.2, 123.2, 107.5, 93.8. TOF-HRMS Calcd. for

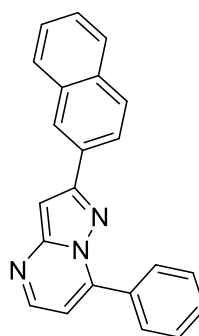
$C_{18}H_{13}BrN_3$ [$M+H^+$]: 350.0287, found 350.0291.

7-phenyl-2-(4-(trifluoromethyl)phenyl)pyrazolo[1,5-*a*]pyrimidine (**3l**)



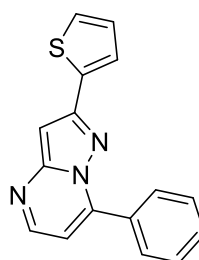
White solid; Yield: 63 %; ^1H NMR (600 MHz, Chloroform-*d*) δ 8.51 (dd, $J = 4.35, 1.56$ Hz, 1H), 8.18 – 8.12 (m, 2H), 8.09 (d, $J = 8.03$ Hz, 2H), 7.68 (d, $J = 8.12$ Hz, 2H), 7.62 – 7.55 (m, 3H), 7.09 (d, $J = 1.07$ Hz, 1H), 6.91 (dd, $J = 4.34, 1.84$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 154.2, 151.3, 149.3, 146.5, 136.4, 131.3, 130.9, 130.7 (d, $J = 32.4$ Hz), 129.5, 129.1, 128.7, 127.0 (d, $J = 86.0$ Hz), 126.9, 125.7 (q, $J = 3.5$ Hz), 124.2 (d, $J = 272.1$ Hz), 107.7, 94.3. TOF-HRMS Calcd. for $\text{C}_{19}\text{H}_{13}\text{F}_3\text{N}_3$ [$\text{M}+\text{H}^+$]: 340.1056, found 340.1058.

2-(naphthalen-2-yl)-7-phenylpyrazolo[1,5-*a*]pyrimidine (**3m**)



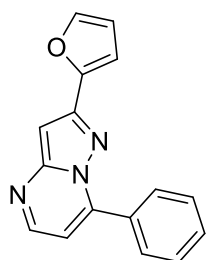
White solid; Yield: 72 %; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.50 (d, $J = 4.34$ Hz, 1H), 8.46 (d, $J = 1.75$ Hz, 1H), 8.25 – 8.18 (m, 2H), 8.15 (dd, $J = 8.53, 1.75$ Hz, 1H), 7.98 – 7.88 (m, 2H), 7.88 – 7.79 (m, 1H), 7.65 – 7.57 (m, 3H), 7.54 – 7.45 (m, 2H), 7.20 (s, 1H), 6.90 (d, $J = 4.33$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.9, 151.4, 149.1, 146.5, 133.8, 133.6, 131.2, 131.2, 130.4, 129.6, 128.7, 128.6, 128.5, 127.9, 126.5, 126.4, 125.9, 124.5, 107.4, 94.1. TOF-HRMS Calcd. for $\text{C}_{22}\text{H}_{16}\text{N}_3$ [$\text{M}+\text{H}^+$]: 322.1339, found 322.1341.

7-phenyl-2-(thiophen-2-yl)pyrazolo[1,5-*a*]pyrimidine (**3n**)



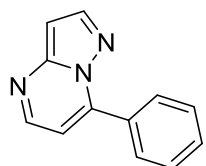
Yellow solid; Yield: 75 %; ^1H NMR (600 MHz, Chloroform-*d*) δ 8.47 (d, $J = 4.32$ Hz, 1H), 8.19 – 8.11 (m, 2H), 7.57 (td, $J = 4.23, 3.76, 2.30$ Hz, 4H), 7.34 (dd, $J = 5.06, 1.13$ Hz, 1H), 7.10 (dd, $J = 5.02, 3.58$ Hz, 1H), 6.94 (s, 1H), 6.88 (d, $J = 4.34$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.3, 151.1, 149.3, 146.3, 136.3, 131.2, 131.0, 129.6, 128.7, 127.9, 126.5, 126.0, 107.3, 93.5. TOF-HRMS Calcd. for $\text{C}_{16}\text{H}_{12}\text{N}_3\text{S}$ [$\text{M}+\text{H}^+$]: 278.0746, found 278.0748.

2-(furan-2-yl)-7-phenylpyrazolo[1,5-a]pyrimidine (**3o**)



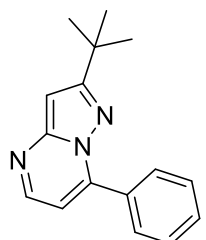
Yellow solid; Yield: 71 %; ^1H NMR (600 MHz, Chloroform-*d*) δ 8.48 (d, $J = 4.82$ Hz, 1H), 8.12 (dd, $J = 6.47, 3.01$ Hz, 2H), 7.56 (t, $J = 3.18$ Hz, 3H), 7.53 (d, $J = 1.81$ Hz, 1H), 6.98 (s, 1H), 6.92 (d, $J = 3.40$ Hz, 1H), 6.88 (d, $J = 2.90$ Hz, 1H), 6.52 – 6.46 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 150.9, 149.3, 148.6, 148.2, 146.5, 143.2, 131.2, 131.0, 129.5, 128.7, 111.7, 108.5, 107.5, 93.5. TOF-HRMS Calcd. for $\text{C}_{16}\text{H}_{12}\text{N}_3\text{O}$ $[\text{M}+\text{H}^+]$: 262.0975, found 262.0980.

7-phenylpyrazolo[1,5-a]pyrimidine (**3p**)



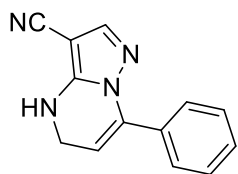
White solid; Yield: 63 %; ^1H NMR (600 MHz, Chloroform-*d*) δ 8.52 (t, $J = 4.63$ Hz, 1H), 8.21 – 8.10 (m, 1H), 8.02 (p, $J = 3.40, 2.87$ Hz, 2H), 7.55 (dt, $J = 7.27, 4.37$ Hz, 3H), 6.88 (t, $J = 4.95$ Hz, 1H), 6.80 – 6.73 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 150.0, 149.1, 146.9, 144.8, 131.2, 131.1, 129.3, 128.8, 107.4, 97.2.^[15]

2-(*tert*-butyl)-7-phenylpyrazolo[1,5-a]pyrimidine (**3q**)



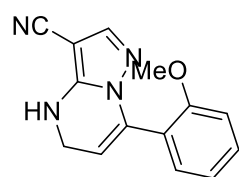
Yellow solid; Yield: 78 %; ^1H NMR (600 MHz, Chloroform-*d*) δ 8.42 (d, $J = 4.44$ Hz, 1H), 8.18 (q, $J = 3.70, 3.10$ Hz, 2H), 7.54 (dd, $J = 5.19, 2.55$ Hz, 3H), 6.83 (dd, $J = 4.62, 1.79$ Hz, 1H), 6.60 (s, 1H), 1.41 (s, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.7, 150.6, 148.4, 146.0, 131.4, 131.0, 129.6, 128.5, 106.3, 93.0, 33.1, 30.6.^[8]

7-phenyl-4,5-dihydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**5a**)



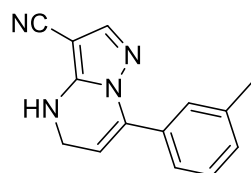
White solid; Yield: 75 %; ^1H NMR (600 MHz, Chloroform-*d*) δ 7.48 (dt, $J = 7.44, 3.56$ Hz, 2H), 7.44 (s, 1H), 7.42 – 7.38 (m, 3H), 5.29 (s, 1H), 5.20 (t, $J = 4.29$ Hz, 1H), 4.27 – 4.20 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 150.0, 140.5, 137.6, 132.2, 129.4, 128.9, 128.3, 114.4, 104.3, 73.1, 40.8.^[16]

7-(2-methoxyphenyl)-4,5-dihydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**5b**)



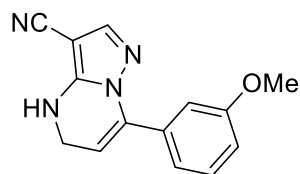
White solid; Yield: 80 %; ^1H NMR (600 MHz, Chloroform-*d*) δ 7.39 (dddd, $J = 8.33, 7.45, 1.82, 0.86$ Hz, 1H), 7.34 (d, $J = 0.89$ Hz, 1H), 7.29 – 7.23 (m, 1H), 6.98 (tt, $J = 7.49, 1.01$ Hz, 1H), 6.94 (dd, $J = 8.33, 1.09$ Hz, 1H), 5.13 (dt, $J = 4.16, 2.49$ Hz, 2H), 4.26 (td, $J = 3.68, 1.76$ Hz, 2H), 3.76 (d, $J = 0.89$ Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.7, 149.4, 140.4, 135.0, 131.2, 131.1, 121.8, 120.6, 114.5, 111.3, 104.8, 72.7, 55.8, 41.1. TOF-HRMS Calcd. for $\text{C}_{14}\text{H}_{13}\text{N}_4\text{O}$ [$\text{M}+\text{H}^+$]: 253.1084, found 253.1077.

7-(*m*-tolyl)-4,5-dihydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**5c**)



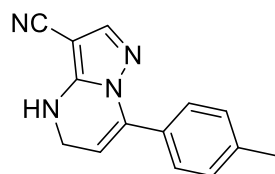
White solid; Yield: 85 %; ^1H NMR (600 MHz, Chloroform-*d*) δ 7.37 (s, 1H), 7.33 (td, $J = 7.44, 1.59$ Hz, 1H), 7.27 (dd, $J = 7.47, 1.61$ Hz, 1H), 7.25 – 7.21 (m, 2H), 5.51 – 5.20 (m, 1H), 5.07 (d, $J = 3.63$ Hz, 1H), 4.37 – 4.17 (m, 2H), 2.19 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 149.5, 141.0, 137.5, 137.2, 132.4, 130.2, 130.0, 129.8, 125.9, 114.4, 104.4, 72.8, 41.0, 19.8. TOF-HRMS Calcd. for $\text{C}_{14}\text{H}_{13}\text{N}_4$ [$\text{M}+\text{H}^+$]: 237.1135, found 237.1140.

7-(3-methoxyphenyl)-4,5-dihydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**5d**)



White solid; Yield: 78 %; ^1H NMR (600 MHz, Chloroform-*d*) δ 7.44 (s, 1H), 7.31 (t, $J = 7.94$ Hz, 1H), 7.09 – 7.04 (m, 1H), 7.02 (t, $J = 2.02$ Hz, 1H), 6.94 (dd, $J = 8.26, 2.61$ Hz, 1H), 5.22 (t, $J = 2.10$ Hz, 1H), 5.16 (s, 1H), 4.24 (dd, $J = 3.93, 1.60$ Hz, 2H), 3.80 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.4, 150.0, 140.6, 137.4, 133.4, 129.4, 121.3, 115.0, 114.7, 114.2, 104.3, 73.2, 55.4, 40.9. TOF-HRMS Calcd. for $\text{C}_{14}\text{H}_{13}\text{N}_4\text{O}$ [$\text{M}+\text{H}^+$]: 253.1084, found 253.1077.

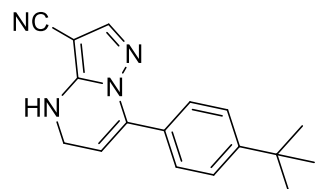
7-(*p*-tolyl)-4,5-dihydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**5e**)



White solid; Yield: 82 %; ^1H NMR (600 MHz, Chloroform-*d*) δ 7.43 (s, 1H), 7.40 – 7.33 (m, 2H), 7.20 (d, $J = 7.86$ Hz, 2H), 5.29 (s, 1H), 5.17 (tt, $J = 3.92, 1.85$ Hz, 1H), 4.22 (tt, $J = 3.94, 2.00$ Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-

d) δ 150.0, 140.5, 139.5, 137.5, 129.3, 129.0, 128.8, 114.4, 103.7, 73.0, 40.8, 21.4.
TOF-HRMS Calcd. for C₁₄H₁₃N₄ [M+H⁺]: 237.1135, found 237.1140.

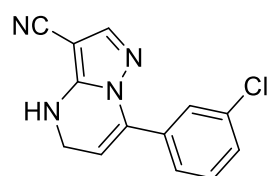
7-(4-(*tert*-butyl)phenyl)-4,5-dihydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**5f**)



White solid; Yield: 75 %; ¹H NMR (600 MHz, Chloroform-*d*) δ 7.45 (s, 1H), 7.42 (s, 4H), 5.19 (td, *J* = 4.01, 1.40 Hz, 1H), 5.15 (s, 1H), 4.24 (dd, *J* = 3.98, 1.25 Hz, 2H), 1.31 (s, 9H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 152.5, 150.0,

140.5, 137.5, 129.2, 128.5, 125.3, 114.3, 103.8, 73.2, 40.9, 34.8, 31.3. TOF-HRMS Calcd. for C₁₇H₁₉N₄ [M+H⁺]: 279.1604, found 279.1606.

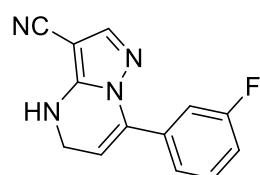
7-(3-chlorophenyl)-4,5-dihydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**5g**)



White solid; Yield: 85 %; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 1.95 Hz, 1H), 7.45 (s, 1H), 7.38 (ddt, *J* = 5.87, 3.74, 1.87 Hz, 2H), 7.35 – 7.30 (m, 1H), 5.25 (td, *J* = 4.05, 1.80 Hz, 1H), 5.10 (s, 1H), 4.28 (dd, *J* = 4.09, 1.64 Hz, 2H). ¹³C NMR

(151 MHz, Chloroform-*d*) δ 149.9, 140.7, 136.4, 134.3, 133.7, 129.6, 129.0, 127.1, 114.1, 105.0, 73.4, 40.9. TOF-HRMS Calcd. for C₁₃H₁₀ClN₄ [M+H⁺]: 257.0589, found 257.0586.

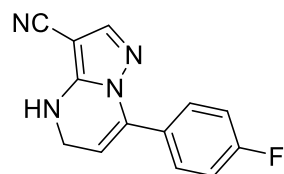
7-(3-fluorophenyl)-4,5-dihydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**5h**)



White solid; Yield: 80 %; ¹H NMR (600 MHz, Chloroform-*d*) δ 7.45 (s, 1H), 7.36 (td, *J* = 8.00, 5.76 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.22 (dt, *J* = 9.69, 2.12 Hz, 1H), 7.10 (td, *J* = 8.42, 2.64 Hz, 1H), 5.26 (td, *J* = 3.98, 1.70 Hz, 1H), 5.08 (s, 1H), 4.28 (dd, *J* = 4.08,

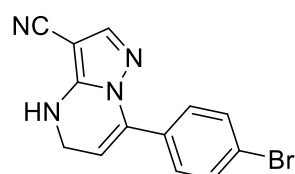
1.54 Hz, 2H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 163.2, 161.6, 149.8, 140.6, 136.5, 134.0 (d, *J* = 8.29 Hz), 129.9 (d, *J* = 8.3 Hz), 124.6 (d, *J* = 3.1 Hz), 116.2 (dd, *J* = 48.2, 22.0 Hz), 114.0, 104.9, 73.4, 40.8. TOF-HRMS Calcd. for C₁₃H₁₀FN₄ [M+H⁺]: 241.0884, found 241.0886.

7-(4-fluorophenyl)-4,5-dihydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**5i**)



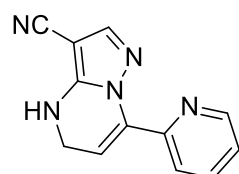
White solid; Yield: 75 %; ¹H NMR (600 MHz, Chloroform-*d*) δ 7.45 (s, 1H), 7.36 (td, *J* = 8.00, 5.76 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.22 (dt, *J* = 9.69, 2.12 Hz, 1H), 7.10 (td, *J* = 8.42, 2.64 Hz, 1H), 5.26 (td, *J* = 3.98, 1.70 Hz, 1H), 5.08 (s, 1H), 4.28 (dd, *J* = 4.08, 1.54 Hz, 2H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 163.2, 161.6, 149.8, 140.6, 136.5, 134.0 (d, *J* = 8.2 Hz), 129.9 (d, *J* = 8.3 Hz), 124.6 (d, *J* = 3.1 Hz), 116.2 (dd, *J* = 48.2, 22.0 Hz), 114.0, 104.9, 73.5, 40.8. TOF-HRMS Calcd. for C₁₃H₁₀FN₄ [M+H⁺]: 241.0884, found 241.0886.

7-(4-bromophenyl)-4,5-dihydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**5j**)



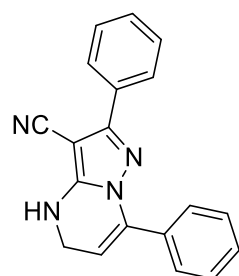
White solid; Yield: 78 %; ¹H NMR (600 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 8.04 Hz, 2H), 7.44 (s, 1H), 7.37 (d, *J* = 8.20 Hz, 2H), 5.23 (s, 1H), 4.99 (s, 1H), 4.27 (d, *J* = 3.43 Hz, 2H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 149.7, 140.6, 136.7, 131.6, 130.9, 130.5, 123.9, 113.9, 104.5, 73.6, 40.9. TOF-HRMS Calcd. for C₁₃H₁₀BrN₄ [M+H⁺]: 301.0083, found 301.0085.

7-(pyridin-2-yl)-4,5-dihydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**5k**)



White solid; Yield: 80 %; ¹H NMR (600 MHz, Chloroform-*d*) δ 8.63 (d, *J* = 4.95 Hz, 1H), 7.79 (d, *J* = 8.02 Hz, 1H), 7.74 (t, *J* = 7.91 Hz, 1H), 7.48 (s, 1H), 7.30 (dd, *J* = 7.49, 4.89 Hz, 1H), 5.79 (t, *J* = 4.11 Hz, 1H), 5.19 (s, 1H), 4.31 (d, *J* = 4.12 Hz, 2H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 150.1, 149.8, 149.6, 140.7, 136.4, 136.4, 124.3, 124.0, 114.1, 107.4, 73.3, 41.0. TOF-HRMS Calcd. for C₁₂H₁₀N₅ [M+H⁺]: 224.0931, found 224.0936.

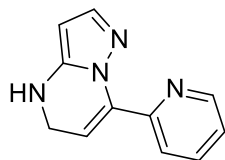
2,7-diphenyl-4,5-dihydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**5l**)



White solid; Yield: 84 %; ¹H NMR (600 MHz, Chloroform-*d*) δ 7.91 – 7.85 (m, 2H), 7.60 – 7.56 (m, 2H), 7.43 – 7.39 (m, 3H), 7.39 – 7.32 (m, 3H), 5.26 (td, *J* = 4.04, 1.77 Hz, 1H), 4.99 (s, 1H), 4.29 (dd, *J* = 4.09, 1.49 Hz, 2H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 151.6, 150.3, 137.6, 132.1, 131.2, 129.3, 129.3, 129.0, 128.7,

128.2, 126.6, 115.3, 104.2, 71.3, 40.8. TOF-HRMS Calcd. for C₁₉H₁₅N₄ [M+H⁺]: 299.1291, found 299.1289.

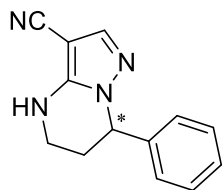
7-phenyl-4,5-dihydropyrazolo[1,5-*a*]pyrimidine (**5m**)



White solid; Yield: 80 %; ¹H NMR (600 MHz, Chloroform-*d*) δ 7.59 – 7.49 (m, 2H), 7.42 – 7.35 (m, 3H), 7.31 (d, *J* = 1.98 Hz, 1H), 5.44 (d, *J* = 2.01 Hz, 1H), 5.26 (t, *J* = 4.16 Hz, 1H), 4.04 (d, *J* = 4.28 Hz, 3H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 145.6, 139.9, 138.6, 133.5, 128.9, 128.2, 104.0, 87.7, 41.0. TOF-HRMS Calcd. for C₁₂H₁₂N₃ [M+H⁺]: 198.1026, found 198.1027.

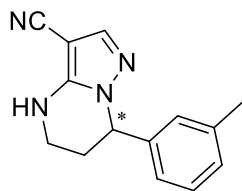
7. NMR, SFC and HPLC, optical rotation and HRMS Data of compounds **2**, **4** and **6**

7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**2a**)



White solid; (PE/EA = 3/1); Yield: 94%; 92% ee; [α]_D²⁵ = -42.0 (*c* = 1.0, CH₂Cl₂); SFC condition: Lux 5u Amylose-1 (250 × 4.60 mm), MeOH:CO₂ = 20:80, 3.0 mL/min, 210 nm; *t*_R = 8.7 min (major), *t*_R = 6.3 min (minor); ¹H NMR (600 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 4.96 Hz, 1H), 7.33 (t, *J* = 7.37 Hz, 2H), 7.28 (dtd, *J* = 7.36, 5.18, 2.69 Hz, 1H), 7.04 – 6.92 (m, 2H), 5.55 (s, 1H), 5.45 (t, *J* = 4.71 Hz, 1H), 3.28 (dq, *J* = 12.08, 4.09 Hz, 1H), 3.18 (dddd, *J* = 12.08, 10.57, 3.28, 1.35 Hz, 1H), 2.57 – 2.33 (m, 1H), 2.17 (dq, *J* = 13.07, 4.15 Hz, 1H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 150.3, 141.0, 140.4, 128.9, 128.1, 128.0, 126.0, 126.0, 115.0, 71.7, 58.5, 35.7, 29.9, 29.8; TOF-HRMS Calcd. for C₁₃H₁₃N₄ [M+H⁺]: 225.1135, found 225.1139.

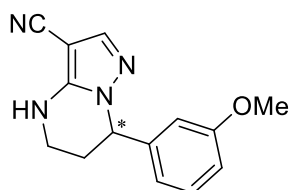
7-(*m*-tolyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**2b**)



White solid; (PE/EA = 3/1); Yield: 92%; 93% ee; [α]_D²⁵ = -40.0 (*c* = 1.0, CH₂Cl₂); SFC condition: Lux 5u Amylose-1 (250 × 4.60 mm), MeOH:CO₂=20:80, 3.0 mL/min, 210 nm; *t*_R = 5.1 min (major), *t*_R = 4.7 min (minor); ¹H NMR (600 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 0.99 Hz, 1H), 7.22 (td, *J* = 7.41, 1.04 Hz, 1H), 7.14 – 7.03 (m, 1H), 6.83

– 6.73 (m, 2H), 5.41 (t, $J = 4.77$ Hz, 1H), 5.05 (s, 1H), 3.34 (dq, $J = 12.12, 4.11$ Hz, 1H), 3.27 (tdd, $J = 11.92, 3.25, 1.36$ Hz, 1H), 2.45 (dddd, $J = 14.24, 9.98, 5.43, 4.15$ Hz, 1H), 2.32 (s, 3H), 2.20 (dq, $J = 13.20, 4.13$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 150.1, 140.9, 140.3, 138.7, 128.9, 128.9, 126.7, 123.1, 114.8, 72.0, 58.6, 36.1, 30.0, 21.6. TOF-HRMS Calcd. for $\text{C}_{14}\text{H}_{15}\text{N}_4$ [$\text{M}+\text{H}^+$]: 239.1291, found 239.1295.

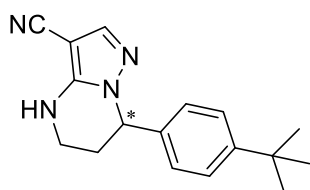
7-(3-methoxyphenyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**2c**)



White solid; (PE/EA = 3/1); Yield: 93%; 92% ee; $[\alpha]_{\text{D}}^{25} = -27.5$ ($c = 1.0, \text{CH}_2\text{Cl}_2$); SFC condition: Lux 5u Amylose-1 (250 \times 4.60 mm), MeOH:CO₂=30:70, 3.0 mL/min, 254 nm; $t_{\text{R}} = 4.6$ min (major), $t_{\text{R}} = 3.4$ min (minor); ^1H NMR (400 MHz, Chloroform-*d*) δ 7.48 (s, 1H), 7.31 – 7.19 (m, 1H), 6.81 (ddd, $J = 8.35, 2.57, 0.97$ Hz, 1H), 6.61 – 6.53 (m, 1H), 6.50 (t, $J = 2.18$ Hz, 1H), 5.42 (t, $J = 4.59$ Hz, 1H), 5.38 (s, 1H), 3.76 (s, 3H), 3.37 – 3.12 (m, 2H), 2.52 – 2.34 (m, 1H), 2.32 – 2.09 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.0, 150.1, 142.0, 140.9, 130.0, 118.2, 114.9, 112.9, 112.3, 71.7, 58.4, 55.3, 35.8, 29.7. TOF-HRMS Calcd. for $\text{C}_{14}\text{H}_{15}\text{N}_4\text{O}$ [$\text{M}+\text{H}^+$]: 255.1240, found 255.1240.

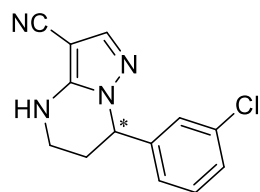
7-(4-(*tert*-butyl)phenyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile

(**2d**)



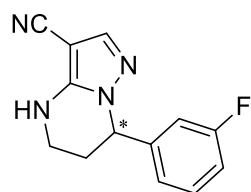
White solid; (PE/EA = 3/1); Yield: 96%; 89% ee; $[\alpha]_{\text{D}}^{25} = -63.0$ ($c = 1.0, \text{CH}_2\text{Cl}_2$); SFC condition: Lux 5u Amylose-1 (250 \times 4.60 mm), MeOH:CO₂ =30:70, 3.0 mL/min, 210 nm; $t_{\text{R}} = 6.1$ min (major), $t_{\text{R}} = 3.0$ min (minor); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.49 (s, 1H), 7.35 (d, $J = 8.38$ Hz, 2H), 6.96 – 6.86 (m, 2H), 5.42 (t, $J = 4.74$ Hz, 1H), 5.16 (s, 1H), 3.41 – 3.07 (m, 2H), 2.44 (dddd, $J = 14.08, 9.87, 5.36, 4.20$ Hz, 1H), 2.31 – 2.08 (m, 1H), 1.28 (s, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.0, 150.1, 140.8, 137.2, 125.8, 125.6, 114.8, 71.9, 58.4, 36.0, 34.6, 31.3, 29.9. TOF-HRMS Calcd. for $\text{C}_{17}\text{H}_{21}\text{N}_4$ [$\text{M}+\text{H}^+$]: 281.1761, found 281.1763.

7-(3-chlorophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**2e**)



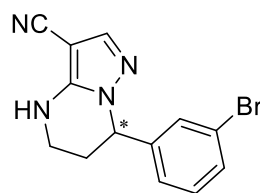
White solid; (PE/EA = 3/1); Yield: 97%; 94% ee; $[\alpha]_{\text{D}}^{25} = -59.8$ (c = 1.0, CH₂Cl₂); SFC condition: Lux 5u Amylose-1 (250 × 4.60 mm), MeOH:CO₂=20:80, 3.0 mL/min, 210 nm; $t_{\text{R}} = 6.3$ min (major), $t_{\text{R}} = 4.3$ min (minor); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.50 (s, 1H), 7.31 – 7.25 (m, 2H), 6.98 (q, *J* = 1.44 Hz, 1H), 6.90 – 6.81 (m, 1H), 5.43 (t, *J* = 4.72 Hz, 1H), 5.35 – 5.18 (m, 1H), 3.42 – 3.30 (m, 1H), 3.22 (dddd, *J* = 12.12, 10.52, 3.25, 1.48 Hz, 1H), 2.47 (dddd, *J* = 14.56, 10.59, 5.46, 4.09 Hz, 1H), 2.30 – 2.07 (m, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 150.1, 142.4, 141.2, 135.0, 130.3, 128.4, 126.3, 124.2, 114.7, 72.0, 58.0, 35.9, 29.7. TOF-HRMS Calcd. for C₁₃H₁₂ClN₄ [M+H⁺]: 259.0745, found 259.0746.

7-(3-fluorophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**2f**)



White solid; (PE/EA = 3/1); Yield: 95%; 92% ee; $[\alpha]_{\text{D}}^{25} = -45.6$ (c = 1.0, CH₂Cl₂); HPLC condition: Lux 5u Amylose-1 (250 × 4.60 mm), ipa:hex =20:80, 3.0 mL/min, 210 nm; $t_{\text{R}} = 14.9$ min (major), $t_{\text{R}} = 9.8$ min (minor); ¹H NMR (600 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 1.36 Hz, 1H), 7.31 (tdd, *J* = 7.54, 5.79, 1.33 Hz, 1H), 7.06 – 6.90 (m, 1H), 6.78 (dd, *J* = 7.79, 1.59 Hz, 1H), 6.68 (dt, *J* = 9.66, 2.10 Hz, 1H), 5.55 – 5.34 (m, 2H), 3.34 (dp, *J* = 11.05, 3.50 Hz, 1H), 3.21 (tt, *J* = 11.54, 3.27 Hz, 1H), 2.60 – 2.37 (m, 1H), 2.19 (dt, *J* = 11.44, 4.13 Hz, 1H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 163.9, 162.3, 150.1, 142.9 (d, *J* = 6.7 Hz), 141.1, 130.6 (d, *J* = 8.3 Hz), 121.6 (d, *J* = 2.9 Hz), 115.1 (d, *J* = 20.9 Hz), 113.2 (d, *J* = 22.5 Hz), 71.9, 58.0, 35.8, 29.7. TOF-HRMS Calcd. for C₁₃H₁₂FN₄ [M+H⁺]: 243.1041, found 243.1043.

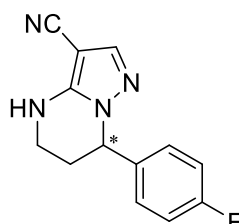
7-(3-bromophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**2g**)



White solid; (PE/EA = 3/1); Yield: 97%; 94% ee; $[\alpha]_{\text{D}}^{25} = -50.5$ (c = 1.0, CH₂Cl₂); SFC condition: Lux 5u Amylose-1 (250 × 4.60 mm), MeOH:CO₂ =20:80, 3.0 mL/min, 210 nm; $t_{\text{R}} = 8.0$ min (major), $t_{\text{R}} = 5.2$ min (minor); ¹H NMR (600 MHz, Chloroform-*d*) δ 7.50 (s, 1H), 7.42 (ddd, *J* = 7.94, 2.01, 1.00 Hz, 1H), 7.21 (t, *J* = 7.87 Hz, 1H), 7.14 (t, *J* = 1.93 Hz, 1H), 6.91 (ddt, *J* = 7.76, 1.75, 0.83 Hz, 1H), 5.41 (dd, *J* = 9.99, 5.12 Hz,

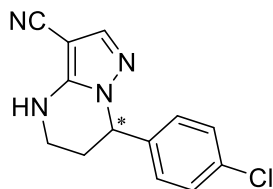
2H), 3.39 – 3.30 (m, 1H), 3.21 (dddd, $J = 12.13, 10.51, 3.24, 1.47$ Hz, 1H), 2.45 (dddd, $J = 14.31, 10.56, 5.47, 4.03$ Hz, 1H), 2.26 – 2.12 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 150.1, 142.6, 141.2, 131.3, 130.5, 129.2, 124.7, 123.1, 114.7, 72.0, 58.0, 35.8, 29.7. TOF-HRMS Calcd. for $\text{C}_{13}\text{H}_{12}\text{BrN}_4$ $[\text{M}+\text{H}^+]$: 303.0240, found 303.0242.

7-(4-fluorophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**2h**)



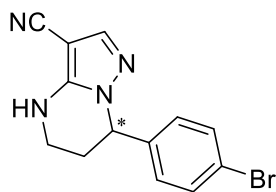
White solid; (PE/EA = 3/1); Yield: 96%; 90% ee; $[\alpha]_{\text{D}}^{25} = -35.4$ ($c = 1.0$, CH_2Cl_2); SFC condition: Lux 5u Amylose-1 (250×4.60 mm), MeOH:CO₂ =30:70, 3.0 mL/min, 210 nm; $t_{\text{R}} = 8.7$ min (major), $t_{\text{R}} = 6.8$ min (minor); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.49 (d, $J = 1.96$ Hz, 1H), 7.04 (td, $J = 8.58, 1.82$ Hz, 2H), 7.00 – 6.92 (m, 2H), 5.43 (t, $J = 4.72$ Hz, 1H), 5.18 (d, $J = 93.21$ Hz, 1H), 3.36 (dtd, $J = 15.07, 7.35, 6.27, 3.55$ Hz, 1H), 3.25 (dddd, $J = 11.58, 9.86, 8.22, 3.13, 1.43$ Hz, 1H), 2.46 (dddd, $J = 15.99, 7.41, 5.84, 2.92$ Hz, 1H), 2.26 – 2.11 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 163.3, 161.6, 150.1, 141.0, 136.0, 127.8, 127.7, 116.0, 115.8, 71.8, 58.0, 36.0, 30.0. TOF-HRMS Calcd. for $\text{C}_{13}\text{H}_{12}\text{FN}_4$ $[\text{M}+\text{H}^+]$: 243.1041, found 243.1043.

7-(4-chlorophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**2i**)



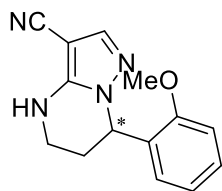
White solid; (PE/EA = 3/1); Yield: 97%; 92% ee; $[\alpha]_{\text{D}}^{25} = -68.8$ ($c = 1.0$, CH_2Cl_2); SFC condition: Lux 5u Amylose-1 (250×4.60 mm), MeOH:CO₂ =30:70, 3.0 mL/min, 210 nm; $t_{\text{R}} = 7.7$ min (major), $t_{\text{R}} = 6.8$ min (minor); ^1H NMR (400 MHz, Chloroform-*d*) δ 7.49 (s, 1H), 7.37 – 7.28 (m, 2H), 7.01 – 6.85 (m, 2H), 5.42 (t, $J = 4.83$ Hz, 1H), 5.36 (s, 1H), 3.35 (ddt, $J = 12.27, 5.08, 3.60$ Hz, 1H), 3.21 (dddd, $J = 12.03, 10.26, 3.31, 1.52$ Hz, 1H), 2.45 (dddd, $J = 14.06, 9.79, 5.43, 4.06$ Hz, 1H), 2.24 – 2.10 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.1, 141.1, 138.8, 134.0, 129.1, 127.5, 114.8, 71.9, 58.0, 35.9, 29.9. TOF-HRMS Calcd. for $\text{C}_{13}\text{H}_{12}\text{ClN}_4$ $[\text{M}+\text{H}^+]$: 259.0745, found 259.0746.

7-(4-bromophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**2j**)



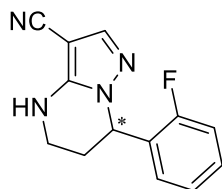
White solid; (PE/EA = 3/1); Yield: 98%; 92% ee; $[\alpha]_{\text{D}}^{25} = -48.7$ ($c = 1.0$, CH_2Cl_2); SFC condition: Lux 5u Amylose-1 (250×4.60 mm), $\text{MeOH}:\text{CO}_2 = 20:80$, 3.0 mL/min, 210 nm; $t_{\text{R}} = 14.5$ min (major), $t_{\text{R}} = 13.6$ min (minor); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.59 – 7.37 (m, 3H), 6.96 – 6.77 (m, 2H), 5.40 (t, $J = 4.87$ Hz, 1H), 5.32 (s, 1H), 3.35 (ddd, $J = 12.33, 5.85, 3.62$ Hz, 1H), 3.22 (dddd, $J = 11.98, 10.26, 3.21, 1.47$ Hz, 1H), 2.53 – 2.39 (m, 1H), 2.16 (dq, $J = 13.66, 4.39$ Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.1, 141.1, 139.3, 132.1, 127.8, 122.1, 114.7, 72.0, 58.1, 35.9, 29.8. TOF-HRMS Calcd. for $\text{C}_{13}\text{H}_{12}\text{BrN}_4$ [$\text{M}+\text{H}^+$]: 303.0240, found 303.0242.

7-(2-methoxyphenyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**2k**)



White solid; (PE/EA = 3/1); Yield: 97%; 92% ee; $[\alpha]_{\text{D}}^{25} = -42.6$ ($c = 1.0$, CH_2Cl_2); SFC condition: Lux 5u Amylose-1 (250×4.60 mm), $\text{MeOH} : \text{CO}_2 = 10:90$, 3.0 mL/min, 210 nm; $t_{\text{R}} = 3.4$ min (major), $t_{\text{R}} = 2.7$ min (minor); ^1H NMR (400 MHz, Chloroform-*d*) δ 7.49 (s, 1H), 7.30 – 7.22 (m, 1H), 6.95 – 6.79 (m, 2H), 6.45 (dd, $J = 7.55, 1.68$ Hz, 1H), 5.80 (dd, $J = 5.49, 3.07$ Hz, 1H), 4.97 (s, 1H), 3.85 (s, 3H), 3.30 (dt, $J = 11.88, 4.11$ Hz, 1H), 3.20 (td, $J = 11.61, 3.28$ Hz, 1H), 2.47 – 2.31 (m, 1H), 2.27 (dq, $J = 13.97, 3.48$ Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.5, 150.4, 140.8, 129.1, 128.3, 126.9, 120.7, 114.8, 110.7, 71.8, 55.4, 54.0, 36.0, 27.2. TOF-HRMS Calcd. for $\text{C}_{14}\text{H}_{15}\text{N}_4\text{O}$ [$\text{M}+\text{H}^+$]: 255.1240, found 255.1240.

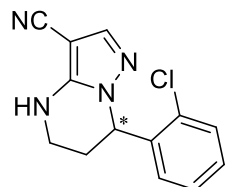
7-(2-fluorophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**2l**)



White solid; (PE:EA = 3/1); Yield: 94%; 94% ee; $[\alpha]_{\text{D}}^{25} = -33.3$ ($c = 1.0$, CH_2Cl_2); HPLC condition: Lux 5u Amylose-1 (250×4.60 mm), ipa:hex=15:85, 1.0 mL/min, 210 nm; $t_{\text{R}} = 11.7$ min (major), $t_{\text{R}} = 9.6$ min (minor); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.49 (s, 1H), 7.27 (dddd, $J = 10.81, 8.34, 5.15, 2.55$ Hz, 1H), 7.13 – 7.01 (m, 2H), 6.62 (td, $J = 7.80, 1.76$ Hz, 1H), 5.74 (t, $J = 4.63$ Hz, 1H), 5.45 (s, 1H), 3.34 (dq, $J = 12.04, 4.01$ Hz, 1H), 3.20 (td, $J = 11.48, 3.32$ Hz, 1H), 2.51 – 2.38 (m, 1H), 2.26 (dt, $J = 14.12, 4.02$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.3 (d, $J = 246.9$ Hz), 150.5, 141.1,

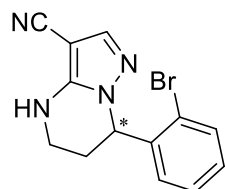
129.8 (d, $J = 8.4$ Hz), 127.8 (d, $J = 3.8$ Hz), 127.5 (d, $J = 12.9$ Hz), 124.5 (d, $J = 3.8$ Hz), 115.8 (d, $J = 20.4$ Hz), 114.8, 71.8, 53.5, 35.9, 28.0; TOF-HRMS Calcd. for $C_{13}H_{12}FN_4$ $[M+H^+]$: 243.1041, found 243.1043.

7-(2-chlorophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**2m**)



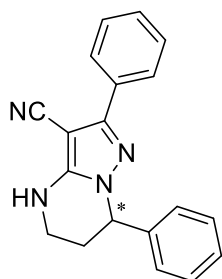
White solid; (PE/EA = 5/1); Yield: 97%; 91% ee; $[\alpha]_D^{25} = -23.5$ (c = 1.0, CH_2Cl_2); HPLC condition: Lux 5u Amylose-1 (250 × 4.60 mm), ipa:hex=20:80, 1.0 mL/min, 210 nm; $t_R = 8.6$ min (major), $t_R = 7.1$ min (minor); 1H NMR (600 MHz, Chloroform-*d*) δ 7.50 (s, 1H), 7.40 – 7.37 (m, 1H), 7.27 – 7.18 (m, 2H), 6.56 (dd, $J = 7.31, 2.06$ Hz, 1H), 5.83 (dd, $J = 5.67, 3.19$ Hz, 1H), 5.46 (s, 1H), 3.32 (dq, $J = 11.91, 3.88$ Hz, 1H), 3.16 (tdd, $J = 11.45, 3.19, 1.24$ Hz, 1H), 2.45 (dddd, $J = 13.97, 11.38, 5.65, 4.11$ Hz, 1H), 2.36 – 2.26 (m, 1H). ^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 150.7, 141.3, 137.5, 131.6, 130.2, 129.4, 127.8, 127.2, 114.9, 71.8, 56.2, 35.6, 27.1. TOF-HRMS Calcd. for $C_{13}H_{12}ClN_4$ $[M+H^+]$: 259.0745, found 259.0746.

7-(2-bromophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**2n**)



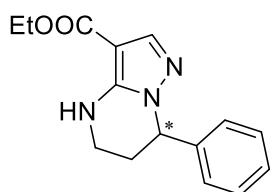
White solid; (PE/EA = 5/1); Yield: 93%; 93% ee; $[\alpha]_D^{25} = -44.4$ (c = 1.0, CH_2Cl_2); HPLC condition: Lux 5u Amylose-1 (250 × 4.60 mm), ipa:hex=15:85, 1.0 mL/min, 210 nm; $t_R = 11.7$ min (major), $t_R = 9.5$ min (minor); 1H NMR (600 MHz, Chloroform-*d*) δ 7.57 (dd, $J = 7.97, 1.24$ Hz, 1H), 7.50 (s, 1H), 7.31 – 7.20 (m, 1H), 7.15 (td, $J = 7.67, 1.69$ Hz, 1H), 6.56 (dd, $J = 7.76, 1.70$ Hz, 1H), 5.78 (dd, $J = 5.66, 3.22$ Hz, 1H), 5.44 (s, 1H), 3.32 (dq, $J = 11.97, 3.94$ Hz, 1H), 3.17 (td, $J = 11.91, 3.19$ Hz, 1H), 2.52 – 2.39 (m, 1H), 2.32 (dd, $J = 13.89, 3.69$ Hz, 1H). ^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 150.7, 141.3, 139.0, 133.6, 129.6, 127.9, 127.8, 121.5, 114.8, 71.8, 58.3, 35.6, 27.3. TOF-HRMS Calcd. for $C_{13}H_{12}BrN_4$ $[M+H^+]$: 303.0240, found 303.0242.

2,7-diphenyl-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**2o**)



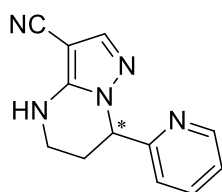
White solid; (PE/EA = 3/1); Yield: 97%; 90% ee; $[\alpha]_{\text{D}}^{25} = 42.0$ ($c = 1.0$, CH_2Cl_2); SFC condition: Lux 5u Amylose-1 (250×4.60 mm), $\text{MeOH}:\text{CO}_2 = 20:80$, 3.0 mL/min, 210 nm; $t_{\text{R}} = 8.6$ min (major), $t_{\text{R}} = 8.0$ min (minor); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.93 – 7.84 (m, 2H), 7.41 – 7.36 (m, 2H), 7.36 – 7.32 (m, 3H), 7.30 – 7.26 (m, 1H), 7.02 (dd, $J = 7.94$, 1.32 Hz, 2H), 5.56 (dd, $J = 5.43$, 3.09 Hz, 1H), 5.17 – 4.99 (m, 1H), 3.35 (dq, $J = 11.79$, 3.89 Hz, 1H), 3.22 (tdd, $J = 11.85$, 3.10, 1.21 Hz, 1H), 2.52 (dddd, $J = 13.75$, 11.68, 5.41, 4.21 Hz, 1H), 2.27 – 2.14 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.5, 151.2, 140.6, 131.5, 129.1, 128.9, 128.7, 128.0, 126.5, 125.9, 115.8, 69.8, 58.3, 35.5, 29.8. TOF-HRMS Calcd. for $\text{C}_{19}\text{H}_{17}\text{N}_4$ $[\text{M}+\text{H}^+]$: 301.1448, found 301.1448.

ethyl-7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carboxylate (**2p**)



White solid; (PE/EA = 3/1); Yield: 96%; 91% ee; $[\alpha]_{\text{D}}^{25} = -65.0$ ($c = 1.0$, CH_2Cl_2); HPLC condition: Lux 5u Amylose-1 (250×4.60 mm), ipa:hex = 20:80, 1.0 mL/min, 210 nm; $t_{\text{R}} = 17.3$ min (major), $t_{\text{R}} = 15.9$ min (minor); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.63 (s, 1H), 7.31 (td, $J = 7.59$, 2.01 Hz, 2H), 7.27 – 7.22 (m, 1H), 7.08 – 6.84 (m, 2H), 5.90 (s, 1H), 5.44 (q, $J = 4.80$, 3.54 Hz, 1H), 4.26 (qt, $J = 7.10$, 1.74 Hz, 2H), 3.33 (dp, $J = 11.70$, 3.91 Hz, 1H), 3.23 (tt, $J = 11.52$, 3.52 Hz, 1H), 2.64 – 2.39 (m, 1H), 2.18 (ddd, $J = 13.78$, 5.84, 2.64 Hz, 1H), 1.33 (td, $J = 7.13$, 1.72 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 164.5, 149.1, 141.1, 139.9, 128.8, 127.8, 126.0, 93.6, 59.5, 58.1, 35.4, 30.0, 14.6. TOF-HRMS Calcd. for $\text{C}_{15}\text{H}_{18}\text{N}_3\text{O}_2$ $[\text{M}+\text{H}^+]$: 272.1394, found 272.1395.

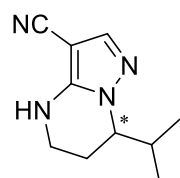
7-(pyridin-2-yl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**2q**)



White solid; (PE/EA = 3/1); Yield: 97%; 95% ee; $[\alpha]_{\text{D}}^{25} = -63.4$ ($c = 1.0$, CH_2Cl_2); HPLC condition: Lux 5u Cellulose-2 (250×4.60 mm), ipa:hex = 30:70, 1.0 mL/min, 210 nm; $t_{\text{R}} = 24.7$ min (major), $t_{\text{R}} = 13.4$ min (minor); ^1H NMR (600 MHz, Chloroform-*d*) δ 8.57 (d, $J = 4.79$ Hz, 1H), 7.65 (tt, $J = 7.76$, 1.65 Hz, 1H), 7.51 (d, $J = 1.34$ Hz, 1H), 7.23 – 7.15

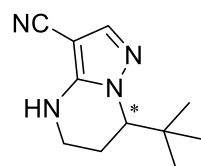
(m, 1H), 6.86 (d, $J = 7.84$ Hz, 1H), 5.51 (t, $J = 4.46$ Hz, 1H), 5.41 (s, 1H), 3.33 (dq, $J = 12.25, 4.07$ Hz, 1H), 3.26 – 3.11 (m, 1H), 2.55 (dt, $J = 11.48, 3.62$ Hz, 1H), 2.43 (ddt, $J = 14.55, 12.51, 4.96$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.0, 150.1, 149.7, 141.1, 137.1, 122.9, 121.2, 114.9, 71.9, 59.4, 36.0, 27.4. TOF-HRMS Calcd. for $\text{C}_{12}\text{H}_{12}\text{N}_5$ [$\text{M}+\text{H}^+$]: 226.1087, found 226.1089.

7-isopropyl-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**2r**)



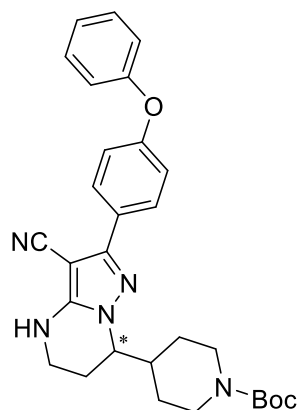
White solid; (PE/EA = 3/1); Yield: 70%; 70% ee; $[\alpha]_{\text{D}}^{25} = +42.3$ ($c = 1.0$, CH_2Cl_2); SFC condition: Lux 5u Amylose-1 (250 \times 4.60 mm), MeOH:CO₂ =20:80, 1.0 mL/min, 210 nm; $t_{\text{R}} = 3.3$ min (major), $t_{\text{R}} = 3.0$ min (minor); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.43 (s, 1H), 5.13 (d, $J = 17.92$ Hz, 1H), 3.96 (q, $J = 6.01$ Hz, 1H), 3.46 – 3.37 (m, 1H), 3.37 – 3.30 (m, 1H), 2.60 – 2.44 (m, 1H), 2.01 (ddd, $J = 22.73, 9.99, 5.17$ Hz, 2H), 1.01 (d, $J = 6.97$ Hz, 3H), 0.82 (d, $J = 6.78$ Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 149.9, 140.0, 115.1, 71.9, 60.1, 37.9, 30.4, 22.1, 19.1, 16.8. TOF-HRMS Calcd. for $\text{C}_{10}\text{H}_{15}\text{N}_4$ [$\text{M}+\text{H}^+$]: 191.1291, found 191.1294.

7-(*tert*-butyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**2s**)



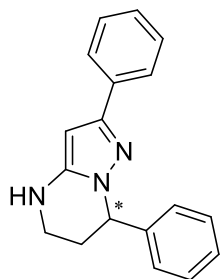
White solid; (PE/EA = 3/1); Yield: 65%; 60% ee; $[\alpha]_{\text{D}}^{25} = +34.5$ ($c = 1.0$, CH_2Cl_2); HPLC condition: Lux 5u Amylose-1 (250 \times 4.60 mm), ipa:hex =20:80, 1.0 mL/min, 210 nm; $t_{\text{R}} = 5.8$ min (major), $t_{\text{R}} = 6.3$ min (minor); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.43 (dd, $J = 2.36, 1.32$ Hz, 1H), 5.03 (s, 1H), 3.97 (ddd, $J = 5.72, 4.02, 1.35$ Hz, 1H), 3.48 – 3.41 (m, 1H), 3.39 (td, $J = 7.82, 6.77, 3.49$ Hz, 1H), 2.23 (dtt, $J = 10.60, 4.55, 2.72$ Hz, 1H), 2.08 – 1.95 (m, 1H), 1.03 (d, $J = 1.39$ Hz, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 150.0, 139.6, 115.2, 71.3, 63.0, 37.8, 36.1, 27.9, 23.5. TOF-HRMS Calcd. for $\text{C}_{11}\text{H}_{17}\text{N}_4$ [$\text{M}+\text{H}^+$]: 205.1448, found 205.1450.

tert-butyl 4-(3-cyano-2-(4-phenoxyphenyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidin-7-yl)piperidine-1-carboxylate (**2t**)



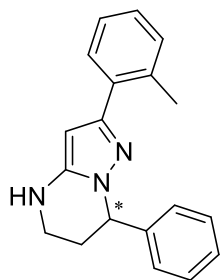
White solid; (PE/EA = 3/1); Yield: 96%; 91% ee; $[\alpha]_{\text{D}}^{25} = +21.6$ ($c = 1.0$, CH_2Cl_2); HPLC condition: Lux 5u Amylose-1 (250×4.60 mm), MeOH:CO₂ = 20:80, 1.0 mL/min, 210 nm; $t_{\text{R}} = 14.8$ min (major), $t_{\text{R}} = 18.4$ min (minor); ¹H NMR (600 MHz, Chloroform-*d*) δ 7.85 (d, $J = 7.96$ Hz, 2H), 7.39 – 7.30 (m, 2H), 7.12 (d, $J = 7.85$ Hz, 1H), 7.03 (d, $J = 8.04$ Hz, 4H), 4.97 (s, 1H), 4.18 (s, 2H), 4.07 (d, $J = 6.82$ Hz, 1H), 3.42 (s, 2H), 2.68 (s, 2H), 2.29 (s, 1H), 2.07 (dd, $J = 26.75, 18.92$ Hz, 2H), 1.69 (d, $J = 13.23$ Hz, 1H), 1.44 (d, $J = 2.88$ Hz, 9H), 1.38 (s, 1H), 1.30 (t, $J = 16.52$ Hz, 2H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 158.1, 156.9, 154.8, 149.9, 129.9, 128.0, 126.7, 123.7, 119.3, 118.9, 115.9, 79.7, 69.8, 68.1, 58.8, 39.3, 28.5, 27.0, 22.9.^[5]

2,7-diphenyl-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine (**4a**)



White solid; (PE/EA = 3/1); Yield: 94%; 92% ee; $[\alpha]_{\text{D}}^{25} = +21.6$ ($c = 1.0$, CH_2Cl_2); SFC condition: Lux 5u Amylose-1 (250×4.60 mm), MeOH:CO₂ = 30:70, 3.0 mL/min, 210 nm; $t_{\text{R}} = 6.7$ min (major), $t_{\text{R}} = 12.2$ min (minor); ¹H NMR (600 MHz, Chloroform-*d*) δ 7.77 – 7.69 (m, 2H), 7.31 (dt, $J = 17.25, 7.62$ Hz, 4H), 7.27 – 7.21 (m, 2H), 7.06 – 6.95 (m, 2H), 5.73 (s, 1H), 5.60 (dd, $J = 5.58, 3.13$ Hz, 1H), 4.21 (s, 1H), 3.15 (dt, $J = 8.61, 2.52$ Hz, 2H), 2.55 (dtd, $J = 13.31, 7.63, 5.54$ Hz, 1H), 2.16 (dq, $J = 13.50, 3.39$ Hz, 1H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 150.9, 147.0, 142.5, 134.1, 128.6, 128.4, 127.5, 127.4, 126.2, 125.7, 83.5, 58.4, 36.0, 31.0.

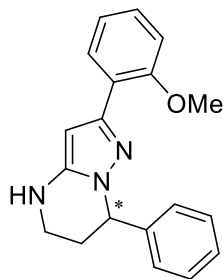
7-phenyl-2-(*o*-tolyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine (**4b**)



White solid; (PE/EA = 3/1); Yield: 95%; 91% ee; $[\alpha]_{\text{D}}^{25} = +135.5$ ($c = 2.0$, CH_2Cl_2); SFC condition: Lux 5u Amylose-1 (250×4.60 mm), MeOH:CO₂ = 20:80, 3.0 mL/min, 210 nm; $t_{\text{R}} = 3.5$ min (major), $t_{\text{R}} = 6.7$ min (minor); ¹H NMR (600 MHz, Chloroform-*d*) δ 7.53 – 7.46 (m, 1H), 7.31 (t, $J = 7.54$ Hz, 2H), 7.26 – 7.21 (m, 1H), 7.20 – 7.13 (m, 3H), 7.01 (d, $J = 7.65$ Hz, 2H), 5.63 – 5.49 (m, 2H), 4.14 (s, 1H), 3.23 – 3.10 (m,

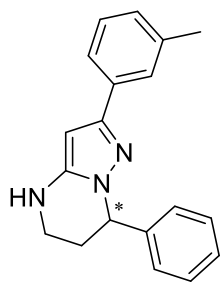
2H), 2.58 (ddt, $J = 11.23, 9.18, 5.66$ Hz, 1H), 2.43 (s, 3H), 2.18 (dq, $J = 13.57, 3.70$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.4, 146.3, 142.7, 136.2, 134.2, 130.6, 129.4, 128.5, 127.5, 127.3, 126.2, 125.6, 86.9, 58.4, 36.3, 31.2, 21.2. TOF-HRMS Calcd. for $\text{C}_{19}\text{H}_{20}\text{N}_3$ [$\text{M}+\text{H}^+$]: 290.1652, found 290.1651.

2-(2-methoxyphenyl)-7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine (**4c**)



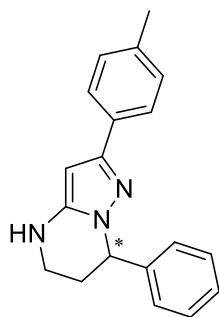
White solid; (PE/EA = 3/1); Yield: 96%; 90% ee; $[\alpha]_{\text{D}}^{25} = +25.0$ ($c = 1.0$, CH_2Cl_2); SFC condition: Lux 5u Amylose-1 (250 \times 4.60 mm), MeOH:CO₂ = 20:80, 3.0 mL/min, 210 nm; $t_{\text{R}} = 11.8$ min (major), $t_{\text{R}} = 13.9$ min (minor); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.84 (dd, $J = 7.64, 1.80$ Hz, 1H), 7.29 (dd, $J = 8.29, 7.00$ Hz, 2H), 7.24 – 7.19 (m, 2H), 7.01 (dd, $J = 7.88, 1.41$ Hz, 2H), 6.94 – 6.88 (m, 2H), 6.01 (s, 1H), 5.61 (dd, $J = 5.60, 3.26$ Hz, 1H), 4.11 (q, $J = 5.01, 2.84$ Hz, 1H), 3.88 (s, 3H), 3.17 (dd, $J = 8.95, 3.18$ Hz, 2H), 2.61 – 2.49 (m, 1H), 2.17 (dq, $J = 13.54, 3.41$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.9, 147.8, 146.2, 142.7, 128.9, 128.6, 128.5, 127.3, 126.2, 123.1, 120.8, 111.3, 87.8, 58.4, 55.6, 36.2, 31.2. TOF-HRMS Calcd. for $\text{C}_{19}\text{H}_{20}\text{N}_3\text{O}$ [$\text{M}+\text{H}^+$]: 306.1601, found 306.1602.

7-phenyl-2-(*m*-tolyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine (**4d**)



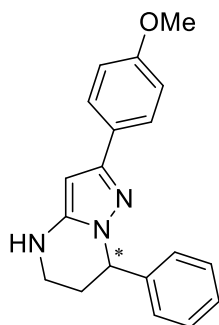
White solid; (PE/EA = 3/1); Yield: 95%; 90% ee; $[\alpha]_{\text{D}}^{25} = +140.2$ ($c = 2.0$, CH_2Cl_2); SFC condition: Lux 5u Amylose-1 (250 \times 4.60 mm), MeOH:CO₂ = 30:70, 3.0 mL/min, 210 nm; $t_{\text{R}} = 6.4$ min (major), $t_{\text{R}} = 27.9$ min (minor); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.58 (tt, $J = 1.74, 0.77$ Hz, 1H), 7.50 (ddd, $J = 7.79, 2.10, 1.07$ Hz, 1H), 7.29 (dd, $J = 8.20, 6.93$ Hz, 2H), 7.22 (td, $J = 7.52, 1.99$ Hz, 2H), 7.06 (ddd, $J = 7.48, 1.87, 0.94$ Hz, 1H), 7.01 – 6.96 (m, 2H), 5.73 (s, 1H), 5.61 (dd, $J = 5.57, 3.03$ Hz, 1H), 4.16 (s, 1H), 3.22 – 3.10 (m, 2H), 2.56 (dtd, $J = 13.32, 7.79, 5.47$ Hz, 1H), 2.33 (s, 3H), 2.17 (dd, $J = 13.47, 3.34$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.1, 146.9, 142.5, 138.0, 134.0, 128.6, 128.3, 128.3, 127.3, 126.3, 126.1, 122.9, 83.6, 58.4, 36.0, 31.0, 21.5. TOF-HRMS Calcd. for $\text{C}_{19}\text{H}_{20}\text{N}_3$ [$\text{M}+\text{H}^+$]: 290.1652, found 290.1651.

7-phenyl-2-(*p*-tolyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine (**4e**)



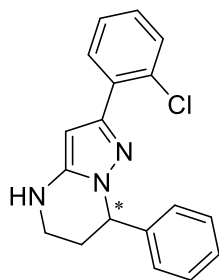
White solid; (PE/EA = 3/1); Yield: 94%; 93% ee; $[\alpha]_{\text{D}}^{25} = +129.6$ ($c = 2.0$, CH_2Cl_2); HPLC condition: Lux 5u Amylose-1 (250 × 4.60 mm), ipa:hex = 20:80, 1.0 mL/min, 210 nm; $t_{\text{R}} = 10.8$ min (major), $t_{\text{R}} = 13.1$ min (minor); $^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.61 (d, $J = 8.16$ Hz, 2H), 7.31 – 7.27 (m, 2H), 7.24 – 7.19 (m, 1H), 7.17 – 7.09 (m, 2H), 7.04 – 6.94 (m, 2H), 5.71 (s, 1H), 5.59 (dd, $J = 5.57$, 3.11 Hz, 1H), 4.13 (s, 1H), 3.17 (dd, $J = 8.07$, 3.18 Hz, 2H), 2.61 – 2.50 (m, 1H), 2.32 (s, 3H), 2.17 (dq, $J = 13.51$, 3.35 Hz, 1H). $^{13}\text{C NMR}$ (151 MHz, Chloroform-*d*) δ 151.0, 146.9, 142.5, 137.2, 131.3, 129.1, 128.5, 127.3, 126.2, 125.6, 83.4, 58.3, 36.1, 31.0, 21.3. TOF-HRMS Calcd. for $\text{C}_{19}\text{H}_{20}\text{N}_3$ $[\text{M}+\text{H}^+]$: 290.1652, found 290.1651.

2-(4-methoxyphenyl)-7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine (**4f**)



White solid; (PE/EA = 3/1); Yield: 96%; 91% ee; $[\alpha]_{\text{D}}^{25} = +38.4$ ($c = 1.0$, CH_2Cl_2); HPLC condition: Lux 5u Amylose-1 (250 × 4.60 mm), ipa:hex = 30:70, 1.0 mL/min, 254 nm; $t_{\text{R}} = 9.9$ min (major), $t_{\text{R}} = 12.9$ min (minor); $^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.70 – 7.61 (m, 2H), 7.29 (dd, $J = 8.36$, 6.94 Hz, 2H), 7.24 – 7.20 (m, 1H), 7.00 (dd, $J = 7.23$, 1.68 Hz, 2H), 6.88 – 6.81 (m, 2H), 5.67 (s, 1H), 5.58 (dd, $J = 5.56$, 3.12 Hz, 1H), 4.14 (s, 1H), 3.79 (s, 3H), 3.25 – 3.04 (m, 2H), 2.55 (dtd, $J = 13.30$, 7.71, 5.45 Hz, 1H), 2.16 (dq, $J = 13.52$, 3.43 Hz, 1H). $^{13}\text{C NMR}$ (151 MHz, Chloroform-*d*) δ 159.3, 150.8, 146.9, 142.6, 128.6, 127.3, 127.0, 126.9, 126.2, 113.8, 83.1, 58.3, 55.4, 36.1, 31.0. TOF-HRMS Calcd. for $\text{C}_{19}\text{H}_{20}\text{N}_3\text{O}$ $[\text{M}+\text{H}^+]$: 306.1601, found 306.1602.

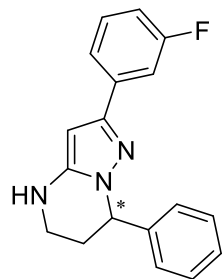
2-(2-chlorophenyl)-7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine (**4g**)



White solid; (PE/EA = 3/1); Yield: 91%; 91% ee; $[\alpha]_{\text{D}}^{25} = +56.4$ ($c = 1.0$, CH_2Cl_2); SFC condition: Lux 5u Amylose-1 (250 × 4.60 mm), MeOH:CO₂ = 20:80, 3.0 mL/min, 210 nm; $t_{\text{R}} = 8.4$ min (major), $t_{\text{R}} = 16.1$ min (minor); $^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.78 – 7.66 (m, 1H), 7.38 (dd, $J = 7.64$, 1.62 Hz, 1H), 7.31 (dd, $J = 8.33$, 7.02 Hz, 2H), 7.25 – 7.15 (m, 3H), 7.05 – 6.97 (m, 2H), 5.96 (s, 1H), 5.59 (dd, $J = 5.56$,

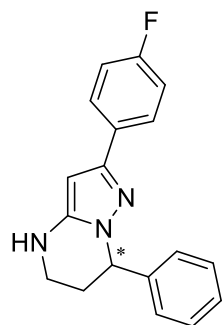
3.41 Hz, 1H), 4.27 – 4.08 (m, 1H), 3.25 – 3.09 (m, 2H), 2.65 – 2.49 (m, 1H), 2.18 (dq, $J = 13.59, 3.54$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 148.7, 146.2, 142.5, 133.2, 132.3, 130.8, 130.2, 128.6, 128.6, 127.4, 126.7, 126.2, 87.7, 58.5, 36.2, 31.1. TOF-HRMS Calcd. for $\text{C}_{18}\text{H}_{17}\text{ClN}_3$ [$\text{M}+\text{H}^+$]: 310.1106, found 310.1102.

2-(3-fluorophenyl)-7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine (**4h**)



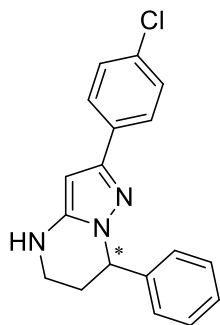
White solid; (PE/EA = 3/1); Yield: 94%; 93% ee; $[\alpha]_{\text{D}}^{25} = +67.3$ ($c = 1.0$, CH_2Cl_2); HPLC condition: Lux 5u Amylose-1 (250×4.60 mm), ipa:hex = 20:80, 1.0 mL/min, 210 nm; $t_{\text{R}} = 8.5$ min (major), $t_{\text{R}} = 10.1$ min (minor); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.49 (dd, $J = 7.78, 1.52$ Hz, 1H), 7.42 (dt, $J = 10.45, 1.99$ Hz, 1H), 7.30 (t, $J = 7.59$ Hz, 2H), 7.28 – 7.21 (m, 2H), 7.00 (d, $J = 7.63$ Hz, 2H), 6.92 (td, $J = 8.45, 2.61$ Hz, 1H), 5.70 (d, $J = 3.70$ Hz, 1H), 5.58 (dt, $J = 5.12, 2.35$ Hz, 1H), 4.24 (d, $J = 8.68$ Hz, 1H), 3.25 – 3.06 (m, 2H), 2.55 (dtt, $J = 16.26, 7.55, 5.14$ Hz, 1H), 2.17 (dp, $J = 13.94, 3.57$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 163.1 (d, $J = 244.3$ Hz), 149.8, 147.1, 142.3, 136.4, 129.8 (d, $J = 8.3$ Hz), 128.6, 127.4, 126.1, 121.2 (d, $J = 2.8$ Hz), 114.2 (d, $J = 21.1$ Hz), 112.4 (d, $J = 22.4$ Hz), 83.6, 58.5, 36.0, 30.9. TOF-HRMS Calcd. for $\text{C}_{18}\text{H}_{17}\text{FN}_3$ [$\text{M}+\text{H}^+$]: 294.1401, found 294.1406.

2-(4-fluorophenyl)-7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine (**4i**)



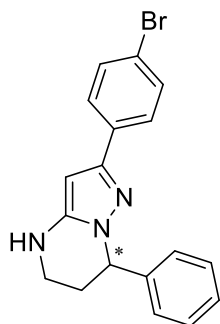
White solid; (PE/EA = 3/1); Yield: 94%; 92% ee; $[\alpha]_{\text{D}}^{25} = +40.4$ ($c = 1.0$, CH_2Cl_2); SFC condition: Lux 5u Cellulose-2 (250×4.60 mm), MeOH: $\text{CO}_2 = 20:80$, 3.0 mL/min, 210 nm; $t_{\text{R}} = 16.2$ min (major), $t_{\text{R}} = 8.1$ min (minor); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.74 – 7.58 (m, 2H), 7.35 – 7.27 (m, 2H), 7.25 – 7.21 (m, 1H), 7.06 – 6.93 (m, 4H), 5.68 (s, 1H), 5.58 (dd, $J = 5.56, 3.18$ Hz, 1H), 4.17 (s, 1H), 3.25 – 3.01 (m, 2H), 2.60 – 2.46 (m, 1H), 2.17 (dq, $J = 13.51, 3.36$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 163.3, 161.7, 150.0, 147.0, 142.3, 130.3, 128.6, 127.4, 127.3, 127.2, 126.1, 115.2 (d, $J = 21.6$ Hz), 83.3, 58.4, 36.0, 30.9. TOF-HRMS Calcd. for $\text{C}_{18}\text{H}_{17}\text{FN}_3$ [$\text{M}+\text{H}^+$]: 294.1401, found 294.1406.

2-(4-chlorophenyl)-7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine (**4j**)



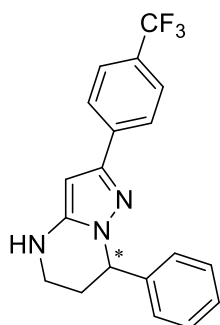
White solid; (PE/EA = 3/1); Yield: 90%; 91% ee; $[\alpha]_{\text{D}}^{25} = +91.4$ ($c = 2.0$, CH_2Cl_2); HPLC condition: Lux 5u Amylose-1 (250 × 4.60 mm), ipa:hex =20:80, 1.0 mL/min, 210 nm; $t_{\text{R}} = 12.2$ min (major), $t_{\text{R}} = 13.2$ min (minor); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.69 – 7.60 (m, 2H), 7.33 – 7.26 (m, 4H), 7.25 – 7.21 (m, 1H), 7.00 (dd, $J = 7.18$, 1.72 Hz, 2H), 5.69 (s, 1H), 5.58 (dd, $J = 5.51$, 3.21 Hz, 1H), 4.19 (s, 1H), 3.25 – 2.99 (m, 2H), 2.64 – 2.46 (m, 1H), 2.17 (dq, $J = 13.50$, 3.38 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 163.3, 161.7, 150.0, 147.0, 142.3, 130.3, 128.6, 127.4, 127.3, 127.2, 126.1, 115.2 (d, $J = 21.6$ Hz), 83.3, 58.4, 36.0, 30.9. TOF-HRMS Calcd. for $\text{C}_{18}\text{H}_{17}\text{ClN}_3$ [$\text{M}+\text{H}^+$]: 310.1106, found 310.1102.

2-(4-bromophenyl)-7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine (**4k**)



White solid; (PE/EA = 3/1); Yield: 90%; 94% ee; $[\alpha]_{\text{D}}^{25} = +43.5$ ($c = 1.0$, CH_2Cl_2); HPLC condition: Lux 5u Amylose-1 (250 × 4.60 mm), ipa:hex =30:70, 1.0 mL/min, 254 nm; $t_{\text{R}} = 13.8$ min (major), $t_{\text{R}} = 16.0$ min (minor); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.62 – 7.54 (m, 2H), 7.47 – 7.40 (m, 2H), 7.30 (t, $J = 7.60$ Hz, 2H), 7.26 – 7.20 (m, 1H), 7.04 – 6.95 (m, 2H), 5.68 (s, 1H), 5.57 (dd, $J = 5.56$, 3.23 Hz, 1H), 4.22 (s, 1H), 3.15 (dt, $J = 7.19$, 2.59 Hz, 2H), 2.53 (dtd, $J = 13.35$, 7.66, 5.43 Hz, 1H), 2.16 (dq, $J = 13.57$, 3.46 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 149.8, 147.1, 142.3, 133.1, 131.5, 128.6, 127.5, 127.3, 126.1, 121.3, 83.4, 58.5, 36.0, 30.9. TOF-HRMS Calcd. for $\text{C}_{18}\text{H}_{17}\text{BrN}_3$ [$\text{M}+\text{H}^+$]: 354.0600, found 354.0595.

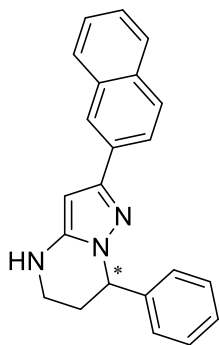
7-phenyl-2-(4-(trifluoromethyl)phenyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine (**4l**)



White solid; (PE/EA = 3/1); Yield: 96%; 91% ee; $[\alpha]_{\text{D}}^{25} = +160.9$ ($c = 2.0$, CH_2Cl_2); SFC condition: Lux 5u Amylose-1 (250 × 4.60 mm), $\text{CO}_2:\text{MeOH} = 20:80$, 3.0 mL/min, 210 nm; $t_{\text{R}} = 5.3$ min (major), $t_{\text{R}} = 6.8$ min (minor); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.81 (d, $J = 8.15$ Hz, 2H), 7.56 (d, $J = 8.20$ Hz, 2H), 7.31 (dd, $J = 8.21$, 7.02 Hz, 2H), 7.27 – 7.21 (m, 1H), 7.00 (dd, $J = 7.27$, 1.84 Hz, 2H), 5.76

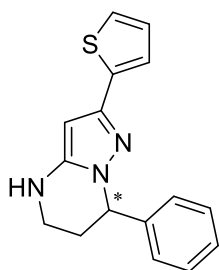
(s, 1H), 5.60 (dd, $J = 5.53, 3.24$ Hz, 1H), 4.25 (s, 1H), 3.28 – 3.08 (m, 2H), 2.63 – 2.47 (m, 1H), 2.18 (dq, $J = 13.56, 3.47$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 149.4, 147.2, 142.2, 137.5, 129.2 (d, $J = 32.3$ Hz), 128.6, 127.5, 126.0, 125.7, 125.4 (d, $J = 4.3$ Hz), 123.5, 83.7, 58.5, 36.0, 30.9. TOF-HRMS Calcd. for $\text{C}_{19}\text{H}_{17}\text{F}_3\text{N}_3$ [$\text{M}+\text{H}^+$]: 344.1369, found 344.1367.

2-(naphthalen-2-yl)-7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine (**4m**)



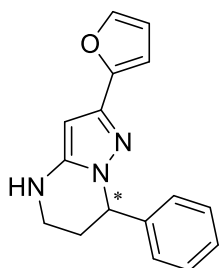
White solid; (PE/EA = 3/1); Yield: 94%; 94% ee; $[\alpha]_{\text{D}}^{25} = +129.6$ (c = 2.0, CH_2Cl_2); HPLC condition: Lux 5u Amylose-1 (250 \times 4.60 mm), ipa:hex = 30:70, 1.0 mL/min, 254 nm; $t_{\text{R}} = 8.6$ min (major), $t_{\text{R}} = 21.0$ min (minor); ^1H NMR (400 MHz, Chloroform-*d*) δ 8.17 (d, $J = 1.63$ Hz, 1H), 7.89 (dd, $J = 8.54, 1.74$ Hz, 1H), 7.80 (ddd, $J = 12.75, 8.77, 3.08$ Hz, 3H), 7.48 – 7.36 (m, 2H), 7.31 (dd, $J = 8.23, 6.56$ Hz, 2H), 7.27 – 7.19 (m, 1H), 7.04 (dd, $J = 7.46, 1.67$ Hz, 2H), 5.86 (s, 1H), 5.64 (dd, $J = 5.53, 3.12$ Hz, 1H), 4.21 (s, 1H), 3.17 (ddd, $J = 5.86, 3.90, 2.35$ Hz, 2H), 2.68 – 2.43 (m, 1H), 2.18 (dq, $J = 13.57, 3.50$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 150.9, 147.1, 142.5, 133.7, 133.1, 131.5, 128.6, 128.2, 128.0, 127.7, 127.4, 126.2, 126.0, 125.6, 124.3, 124.0, 83.7, 58.5, 36.0, 31.0. TOF-HRMS Calcd. for $\text{C}_{22}\text{H}_{20}\text{N}_3$ [$\text{M}+\text{H}^+$]: 326.1652, found 326.1654.

7-phenyl-2-(thiophen-2-yl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine (**4n**)



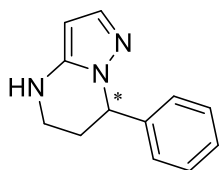
White solid; (PE/EA = 3/1); Yield: 96%; 94% ee; $[\alpha]_{\text{D}}^{25} = +56.4$ (c = 2.0, CH_2Cl_2); HPLC condition: Lux 5u Amylose-1 (250 \times 4.60 mm), ipa:hex = 15:85, 1.0 mL/min, 210 nm; $t_{\text{R}} = 16.6$ min (major), $t_{\text{R}} = 20.3$ min (minor); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.29 (t, $J = 7.60$ Hz, 2H), 7.26 – 7.24 (m, 1H), 7.22 (t, $J = 7.33$ Hz, 1H), 7.06 – 6.92 (m, 3H), 5.63 (s, 1H), 5.57 (dd, $J = 5.53, 2.95$ Hz, 1H), 4.24 (s, 1H), 3.12 (dt, $J = 8.62, 2.33$ Hz, 2H), 2.61 – 2.38 (m, 1H), 2.14 (dq, $J = 13.54, 3.29$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 146.9, 146.2, 142.3, 137.7, 128.6, 127.4, 127.3, 126.1, 124.1, 123.4, 83.6, 58.3, 35.8, 30.8. TOF-HRMS Calcd. for $\text{C}_{16}\text{H}_{16}\text{N}_3\text{S}$ [$\text{M}+\text{H}^+$]: 282.1059, found 282.1057.

2-(furan-2-yl)-7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine (**4o**)



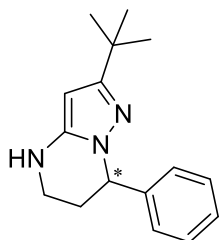
White solid; (PE/EA = 3/1); Yield: 96%; 95% ee; $[\alpha]_{\text{D}}^{25} = +52.7$ ($c = 1.0$, CH_2Cl_2); HPLC condition: Lux 5u Amylose-1 (250 × 4.60 mm), ipa:hex = 30:70, 1.0 mL/min, 210 nm; $t_{\text{R}} = 9.8$ min (major), $t_{\text{R}} = 11.1$ min (minor); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.37 (s, 1H), 7.29 (t, $J = 7.56$ Hz, 2H), 7.21 (t, $J = 7.34$ Hz, 1H), 6.98 (d, $J = 7.69$ Hz, 2H), 6.57 (d, $J = 3.37$ Hz, 1H), 6.42 – 6.36 (m, 1H), 5.66 (s, 1H), 5.58 (dd, $J = 5.70$, 2.98 Hz, 1H), 4.16 (s, 1H), 3.17 (dd, $J = 8.34$, 3.26 Hz, 2H), 2.54 (dtd, $J = 13.62$, 7.96, 5.54 Hz, 1H), 2.16 (dq, $J = 13.63$, 3.32 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 149.6, 146.6, 143.5, 142.3, 141.5, 128.6, 127.4, 126.1, 111.2, 105.5, 83.3, 58.4, 35.9, 30.8. TOF-HRMS Calcd. for $\text{C}_{16}\text{H}_{16}\text{N}_3\text{O}$ $[\text{M}+\text{H}^+]$: 266.1288, found 266.1293.

7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine (**4p**)



White solid; (PE/EA = 3/1); Yield: 90%; 90% ee; $[\alpha]_{\text{D}}^{25} = +20.1$ ($c = 1.0$, CH_2Cl_2); HPLC condition: Lux 5u Amylose-1 (250 × 4.60 mm), ipa:hex = 30:70, 1.0 mL/min, 210 nm; $t_{\text{R}} = 8.3$ min (major), $t_{\text{R}} = 6.1$ min (minor); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.34 – 7.28 (m, 3H), 7.25 – 7.22 (m, 1H), 7.02 – 6.95 (m, 2H), 5.47 (t, $J = 4.97$ Hz, 1H), 5.40 (d, $J = 1.96$ Hz, 1H), 4.14 (s, 1H), 3.19 (dp, $J = 7.15$, 2.41 Hz, 2H), 2.55 – 2.44 (m, 1H), 2.22 – 2.09 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 146.1, 142.4, 139.6, 128.7, 127.5, 126.2, 86.2, 58.7, 36.8, 31.4.

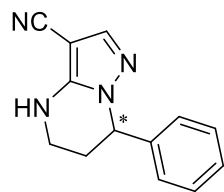
2-(*tert*-butyl)-7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine (**4q**)



White solid; (PE/EA = 3/1); Yield: 95%; 95% ee; $[\alpha]_{\text{D}}^{25} = +70.9$ ($c = 1.0$, CH_2Cl_2); HPLC condition: Lux 5u Amylose-1 (250 × 4.60 mm), ipa:hex = 10:90, 1.0 mL/min, 210 nm; $t_{\text{R}} = 8.0$ min (major), $t_{\text{R}} = 8.9$ min (minor); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.27 (t, $J = 8.56$ Hz, 2H), 7.22 – 7.17 (m, 1H), 6.87 (d, $J = 7.58$ Hz, 2H), 5.52 (d, $J = 5.58$ Hz, 1H), 5.28 (d, $J = 2.86$ Hz, 1H), 4.01 (s, 1H), 3.08 (d, $J = 7.42$ Hz, 2H), 2.53 (dt, $J = 10.64$, 5.63 Hz, 1H), 2.11 (d, $J = 13.47$ Hz, 1H), 1.24 (s, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 161.8, 146.0, 143.0, 128.3, 127.1, 126.1, 82.8, 57.8, 36.0, 32.2, 31.1,

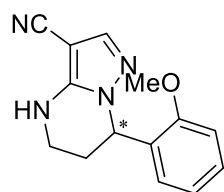
30.6.

7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**6a**)



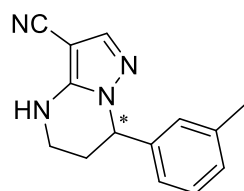
White solid; (PE/EA = 3/1); Yield: 95%; 94% ee; $[\alpha]_{\text{D}}^{25} = -42.0$ ($c = 1.0$, CH_2Cl_2); SFC condition: Lux 5u Amylose-1 (250×4.60 mm), MeOH:CO₂ = 20:80, 3.0 mL/min, 210 nm; $t_{\text{R}} = 8.7$ min (major), $t_{\text{R}} = 6.3$ min (minor); ¹H NMR (600 MHz, Chloroform-*d*) δ 7.49 (d, $J = 4.96$ Hz, 1H), 7.33 (t, $J = 7.37$ Hz, 2H), 7.28 (dtd, $J = 7.36, 5.18, 2.69$ Hz, 1H), 7.04 – 6.92 (m, 2H), 5.55 (s, 1H), 5.45 (t, $J = 4.71$ Hz, 1H), 3.28 (dq, $J = 12.08, 4.09$ Hz, 1H), 3.18 (dddd, $J = 12.08, 10.57, 3.28, 1.35$ Hz, 1H), 2.57 – 2.33 (m, 1H), 2.17 (dq, $J = 13.07, 4.15$ Hz, 1H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 150.3, 141.0, 140.4, 128.9, 128.1, 128.0, 126.0, 126.0, 115.0, 71.7, 58.5, 35.7, 29.9, 29.8.

7-(2-methoxyphenyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**6b**)



White solid; (PE/EA = 3/1); Yield: 95%; 92% ee; $[\alpha]_{\text{D}}^{25} = -42.6$ ($c = 1.0$, CH_2Cl_2); HPLC condition: Lux 5u Amylose-1 (250×4.60 mm), ipa:hex = 30:70, 1.0 mL/min, 210 nm; $t_{\text{R}} = 6.9$ min (major), $t_{\text{R}} = 5.3$ min (minor); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.49 (s, 1H), 7.30 – 7.22 (m, 1H), 6.95 – 6.79 (m, 2H), 6.45 (dd, $J = 7.55, 1.68$ Hz, 1H), 5.80 (dd, $J = 5.49, 3.07$ Hz, 1H), 4.97 (s, 1H), 3.85 (s, 3H), 3.30 (dt, $J = 11.88, 4.11$ Hz, 1H), 3.20 (td, $J = 11.61, 3.28$ Hz, 1H), 2.47 – 2.31 (m, 1H), 2.27 (dq, $J = 13.97, 3.48$ Hz, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 155.5, 150.4, 140.8, 129.1, 128.3, 126.9, 120.7, 114.8, 110.7, 71.8, 55.4, 54.0, 36.0, 27.2.

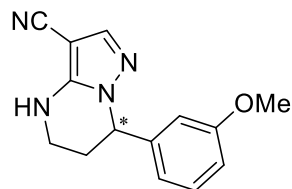
7-(*m*-tolyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**6c**)



White solid; (PE/EA = 3/1); Yield: 94%; 93% ee; $[\alpha]_{\text{D}}^{25} = -40.0$ ($c = 1.0$, CH_2Cl_2); SFC condition: Lux 5u Amylose-1 (250×4.60 mm), MeOH:CO₂=20:80, 3.0 mL/min, 210 nm; $t_{\text{R}} = 5.1$ min (major), $t_{\text{R}} = 4.7$ min (minor); ¹H NMR (600 MHz, Chloroform-*d*) δ 7.49 (d, $J = 0.99$ Hz, 1H), 7.22 (td, $J = 7.41, 1.04$ Hz, 1H), 7.14 – 7.03 (m, 1H), 6.83 – 6.73 (m, 2H), 5.41 (t, $J = 4.77$ Hz, 1H), 5.05 (s, 1H), 3.34 (dq, $J = 12.12, 4.11$ Hz, 1H), 3.27 (tdd, $J = 11.92, 3.25, 1.36$ Hz, 1H), 2.45 (dddd, $J = 14.24, 9.98, 5.43, 4.15$ Hz, 1H), 2.32 (s, 3H), 2.20 (dq, $J = 13.20, 4.13$ Hz, 1H). ¹³C NMR (151 MHz,

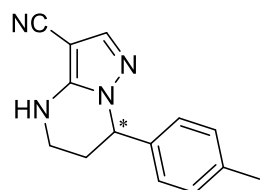
Chloroform-*d*) δ 150.1, 140.9, 140.3, 138.7, 128.9, 128.9, 126.7, 123.1, 114.8, 72.0, 58.6, 36.1, 30.0, 21.6.

7-(3-methoxyphenyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**6d**)



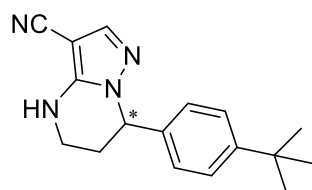
White solid; (PE/EA = 3/1); Yield: 96%; 92% ee; $[\alpha]_{\text{D}}^{25} = -27.5$ ($c = 1.0$, CH_2Cl_2); HPLC condition: Lux 5u Amylose-1 (250×4.60 mm), ipa:hex = 20:80, 1.0 mL/min, 254 nm; $t_{\text{R}} = 21.7$ min (major), $t_{\text{R}} = 13.3$ min (minor); ^1H NMR (400 MHz, Chloroform-*d*) δ 7.48 (s, 1H), 7.31 – 7.19 (m, 1H), 6.81 (ddd, $J = 8.35, 2.57, 0.97$ Hz, 1H), 6.61 – 6.53 (m, 1H), 6.50 (t, $J = 2.18$ Hz, 1H), 5.42 (t, $J = 4.59$ Hz, 1H), 5.38 (s, 1H), 3.76 (s, 3H), 3.37 – 3.12 (m, 2H), 2.52 – 2.34 (m, 1H), 2.32 – 2.09 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.0, 150.1, 142.0, 140.9, 130.0, 118.2, 114.9, 112.9, 112.3, 71.7, 58.4, 55.3, 35.8, 29.7.

7-(*p*-tolyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**6e**)



White solid; (PE/EA = 3/1); Yield: 94%; 95% ee; $[\alpha]_{\text{D}}^{25} = -81.9$ ($c = 1.0$, CH_2Cl_2); SFC condition: Lux 5u Amylose-1 (250×4.60 mm), MeOH:CO₂ = 20:80, 3.0 mL/min, 210 nm; $t_{\text{R}} = 10.0$ min (major), $t_{\text{R}} = 8.0$ min (minor); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.48 (d, $J = 1.61$ Hz, 1H), 7.19 – 7.10 (m, 2H), 6.88 (d, $J = 7.80$ Hz, 2H), 5.46 – 5.15 (m, 2H), 3.36 – 3.28 (m, 1H), 3.28 – 3.19 (m, 1H), 2.43 (ddd, $J = 14.35, 9.54, 5.08$ Hz, 1H), 2.31 (s, 3H), 2.17 (ddd, $J = 12.16, 8.58, 4.27$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 150.2, 150.2, 140.9, 137.9, 137.9, 137.4, 137.4, 129.6, 126.0, 115.1, 71.7, 58.5, 36.1, 36.0, 30.0, 21.1. TOF-HRMS Calcd. for $\text{C}_{14}\text{H}_{15}\text{N}_4$ [$\text{M}+\text{H}^+$]: 239.1291, found 239.1295.

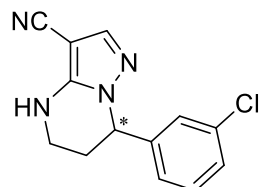
7-(4-(*tert*-butyl)phenyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**6f**)



White solid; (PE/EA = 3/1); Yield: 94%; 94% ee; $[\alpha]_{\text{D}}^{25} = -63.0$ ($c = 1.0$, CH_2Cl_2); SFC condition: Lux 5u Amylose-1 (250×4.60 mm), MeOH:CO₂ = 30:70, 3.0 mL/min, 210 nm; $t_{\text{R}} = 5.9$ min (major), $t_{\text{R}} = 2.9$ min (minor); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.49 (s, 1H), 7.35 (d, $J = 8.38$ Hz, 2H), 6.96 – 6.86 (m, 2H),

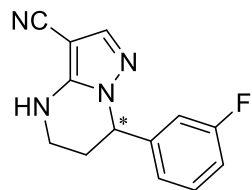
5.42 (t, $J = 4.74$ Hz, 1H), 5.16 (s, 1H), 3.41 – 3.07 (m, 2H), 2.44 (dddd, $J = 14.08, 9.87, 5.36, 4.20$ Hz, 1H), 2.31 – 2.08 (m, 1H), 1.28 (s, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.0, 150.1, 140.8, 137.2, 125.8, 125.6, 114.8, 71.9, 58.4, 36.0, 34.6, 31.3, 29.9.

7-(3-chlorophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**6g**)



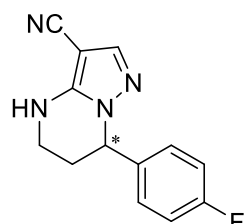
White solid; (PE/EA = 3/1); Yield: 97%; 97% ee; $[\alpha]_{\text{D}}^{25} = -59.8$ ($c = 1.0, \text{CH}_2\text{Cl}_2$); SFC condition: Lux 5u Amylose-1 (250 \times 4.60 mm), MeOH:CO₂ = 20:80, 3.0 mL/min, 210 nm; $t_{\text{R}} = 10.4$ min (major), $t_{\text{R}} = 7.1$ min (minor); ^1H NMR (400 MHz, Chloroform-*d*) δ 7.50 (s, 1H), 7.31 – 7.25 (m, 2H), 6.98 (q, $J = 1.44$ Hz, 1H), 6.90 – 6.81 (m, 1H), 5.43 (t, $J = 4.72$ Hz, 1H), 5.35 – 5.18 (m, 1H), 3.42 – 3.30 (m, 1H), 3.22 (dddd, $J = 12.12, 10.52, 3.25, 1.48$ Hz, 1H), 2.47 (dddd, $J = 14.56, 10.59, 5.46, 4.09$ Hz, 1H), 2.30 – 2.07 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.1, 142.4, 141.2, 135.0, 130.3, 128.4, 126.3, 124.2, 114.7, 72.0, 58.0, 35.9, 29.7.

7-(3-fluorophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**6h**)



White solid; (PE/EA = 3/1); Yield: 96%; 96% ee; $[\alpha]_{\text{D}}^{25} = -45.6$ ($c = 1.0, \text{CH}_2\text{Cl}_2$); SFC condition: Lux 5u Amylose-1 (250 \times 4.60 mm), MeOH:CO₂ = 20:80, 3.0 mL/min, 210 nm; $t_{\text{R}} = 6.8$ min (major), $t_{\text{R}} = 5.5$ min (minor); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.50 (d, $J = 1.36$ Hz, 1H), 7.31 (tdd, $J = 7.54, 5.79, 1.33$ Hz, 1H), 7.06 – 6.90 (m, 1H), 6.78 (dd, $J = 7.79, 1.59$ Hz, 1H), 6.68 (dt, $J = 9.66, 2.10$ Hz, 1H), 5.55 – 5.34 (m, 2H), 3.34 (dp, $J = 11.05, 3.50$ Hz, 1H), 3.21 (tt, $J = 11.54, 3.27$ Hz, 1H), 2.60 – 2.37 (m, 1H), 2.19 (dt, $J = 11.44, 4.13$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 163.9, 162.3, 150.1, 142.9 (d, $J = 6.7$ Hz), 141.1, 130.6 (d, $J = 8.3$ Hz), 121.6 (d, $J = 2.9$ Hz), 115.1 (d, $J = 20.9$ Hz), 113.2 (d, $J = 22.5$ Hz), 71.9, 58.0, 35.8, 29.7.

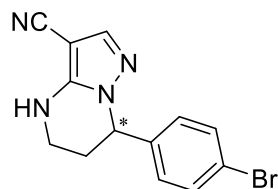
7-(4-fluorophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**6i**)



White solid; (PE/EA = 3/1); Yield: 97%; 97% ee; $[\alpha]_{\text{D}}^{25} = -35.4$ ($c = 1.0, \text{CH}_2\text{Cl}_2$); SFC condition: Lux 5u Amylose-1 (250 \times 4.60 mm), MeOH:CO₂ = 30:70, 3.0 mL/min, 210 nm; $t_{\text{R}} = 6.4$ min (major), $t_{\text{R}} = 5.2$ min (minor); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.49 (d, $J = 1.96$ Hz, 1H), 7.04 (td, $J = 8.58, 1.82$ Hz, 2H), 7.00 – 6.92 (m, 2H),

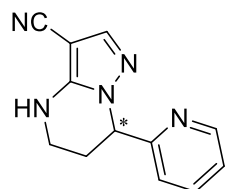
5.43 (t, $J = 4.72$ Hz, 1H), 5.18 (d, $J = 93.21$ Hz, 1H), 3.36 (dtd, $J = 15.07, 7.35, 6.27, 3.55$ Hz, 1H), 3.25 (dddd, $J = 11.58, 9.86, 8.22, 3.13, 1.43$ Hz, 1H), 2.46 (dddd, $J = 15.99, 7.41, 5.84, 2.92$ Hz, 1H), 2.26 – 2.11 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 163.3, 161.6, 150.1, 141.0, 136.0, 127.8, 127.7, 116.0, 115.8, 71.8, 58.0, 36.0, 30.0.

7-(4-bromophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**6j**)



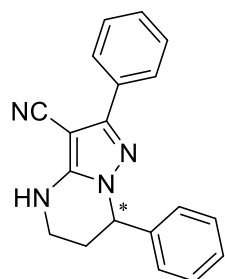
White solid; (PE/EA = 3/1); Yield: 95%; 98% ee; $[\alpha]_{\text{D}}^{25} = -48.7$ ($c = 1.0, \text{CH}_2\text{Cl}_2$); SFC condition: Lux 5u Amylose-1 (250 \times 4.60 mm), MeOH:CO₂ =20:80, 3.0 mL/min, 210 nm; $t_{\text{R}} = 15.3$ min (major), $t_{\text{R}} = 14.4$ min (minor); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.59 – 7.37 (m, 3H), 6.96 – 6.77 (m, 2H), 5.40 (t, $J = 4.87$ Hz, 1H), 5.32 (s, 1H), 3.35 (ddd, $J = 12.33, 5.85, 3.62$ Hz, 1H), 3.22 (dddd, $J = 11.98, 10.26, 3.21, 1.47$ Hz, 1H), 2.53 – 2.39 (m, 1H), 2.16 (dq, $J = 13.66, 4.39$ Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.1, 141.1, 139.3, 132.1, 127.8, 122.1, 114.7, 72.0, 58.1, 35.9, 29.8.

7-(pyridin-2-yl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**6k**)



White solid; (PE/EA = 3/1); Yield: 91%; 92% ee; $[\alpha]_{\text{D}}^{25} = -63.4$ ($c = 1.0, \text{CH}_2\text{Cl}_2$); SFC condition: Lux 5u Amylose-1 (250 \times 4.60 mm), MeOH:CO₂ =20:80, 3.0 mL/min, 210 nm; $t_{\text{R}} = 8.6$ min (major), $t_{\text{R}} = 13.4$ min (minor); ^1H NMR (600 MHz, Chloroform-*d*) δ 8.57 (d, $J = 4.79$ Hz, 1H), 7.65 (tt, $J = 7.76, 1.65$ Hz, 1H), 7.51 (d, $J = 1.34$ Hz, 1H), 7.23 – 7.15 (m, 1H), 6.86 (d, $J = 7.84$ Hz, 1H), 5.51 (t, $J = 4.46$ Hz, 1H), 5.41 (s, 1H), 3.33 (dq, $J = 12.25, 4.07$ Hz, 1H), 3.26 – 3.11 (m, 1H), 2.55 (dt, $J = 11.48, 3.62$ Hz, 1H), 2.43 (ddt, $J = 14.55, 12.51, 4.96$ Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.0, 150.1, 149.7, 141.1, 137.1, 122.9, 121.2, 114.9, 71.9, 59.4, 36.0, 27.4.

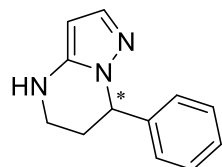
2,7-diphenyl-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**6l**)



White solid; (PE/EA = 3/1); Yield: 96%; 97% ee; $[\alpha]_{\text{D}}^{25} = 42.0$ ($c = 1.0, \text{CH}_2\text{Cl}_2$); SFC condition: Lux 5u Amylose-1 (250 \times 4.60 mm), MeOH:CO₂ =20:80, 3.0 mL/min, 210 nm; $t_{\text{R}} = 11.9$ min (major), $t_{\text{R}} = 11.0$ min (minor); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.93 – 7.84 (m, 2H), 7.41 – 7.36 (m, 2H), 7.36 – 7.32 (m, 3H), 7.30 – 7.26

(m, 1H), 7.02 (dd, $J = 7.94, 1.32$ Hz, 2H), 5.56 (dd, $J = 5.43, 3.09$ Hz, 1H), 5.17 – 4.99 (m, 1H), 3.35 (dq, $J = 11.79, 3.89$ Hz, 1H), 3.22 (tdd, $J = 11.85, 3.10, 1.21$ Hz, 1H), 2.52 (dddd, $J = 13.75, 11.68, 5.41, 4.21$ Hz, 1H), 2.27 – 2.14 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.5, 151.2, 140.6, 131.5, 129.1, 128.9, 128.7, 128.0, 126.5, 125.9, 115.8, 69.8, 58.3, 35.5, 29.8.

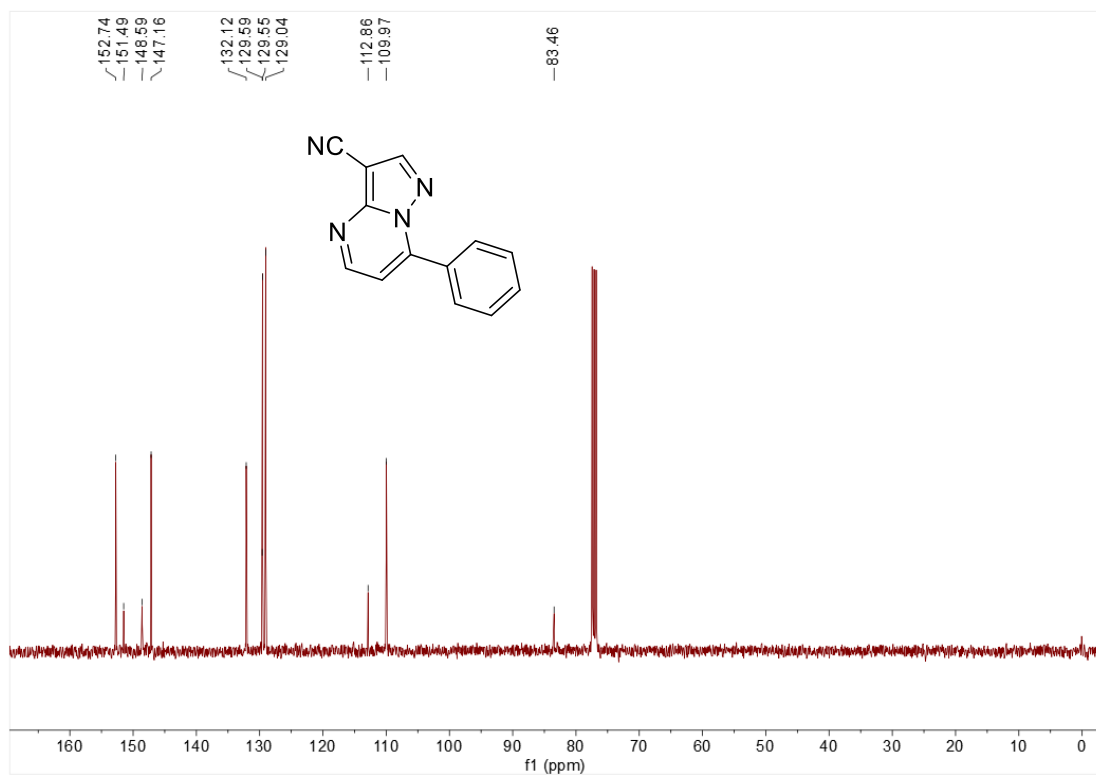
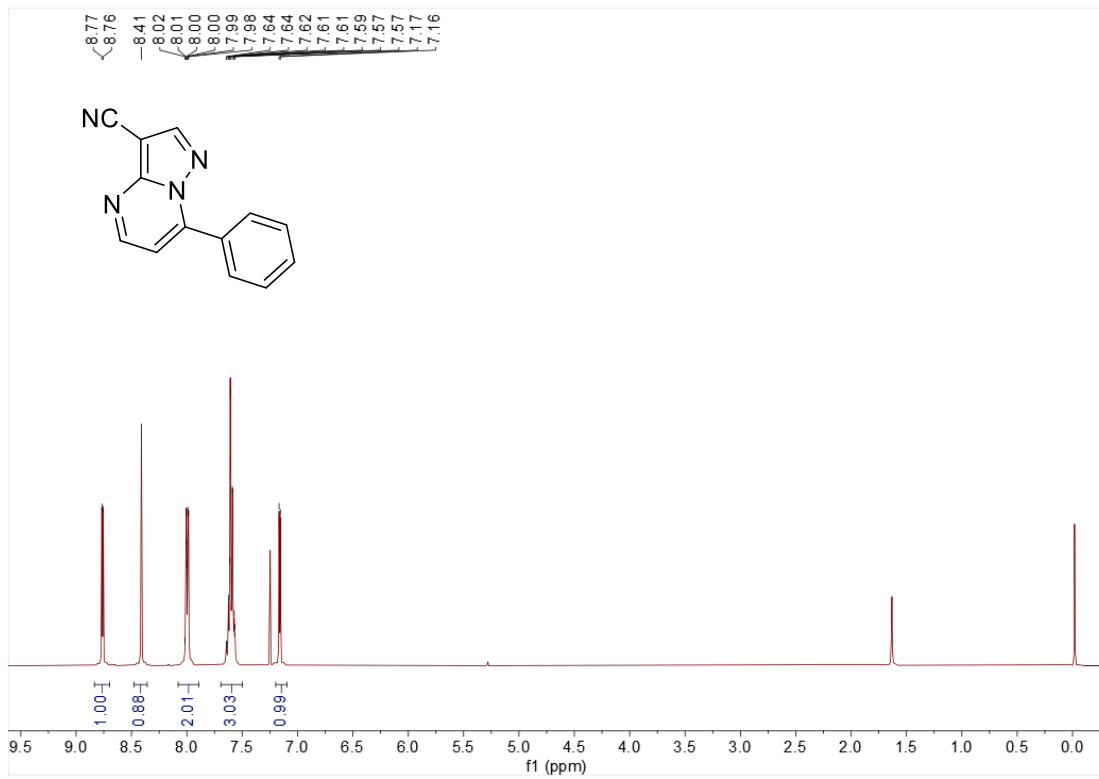
7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine (**6m**)



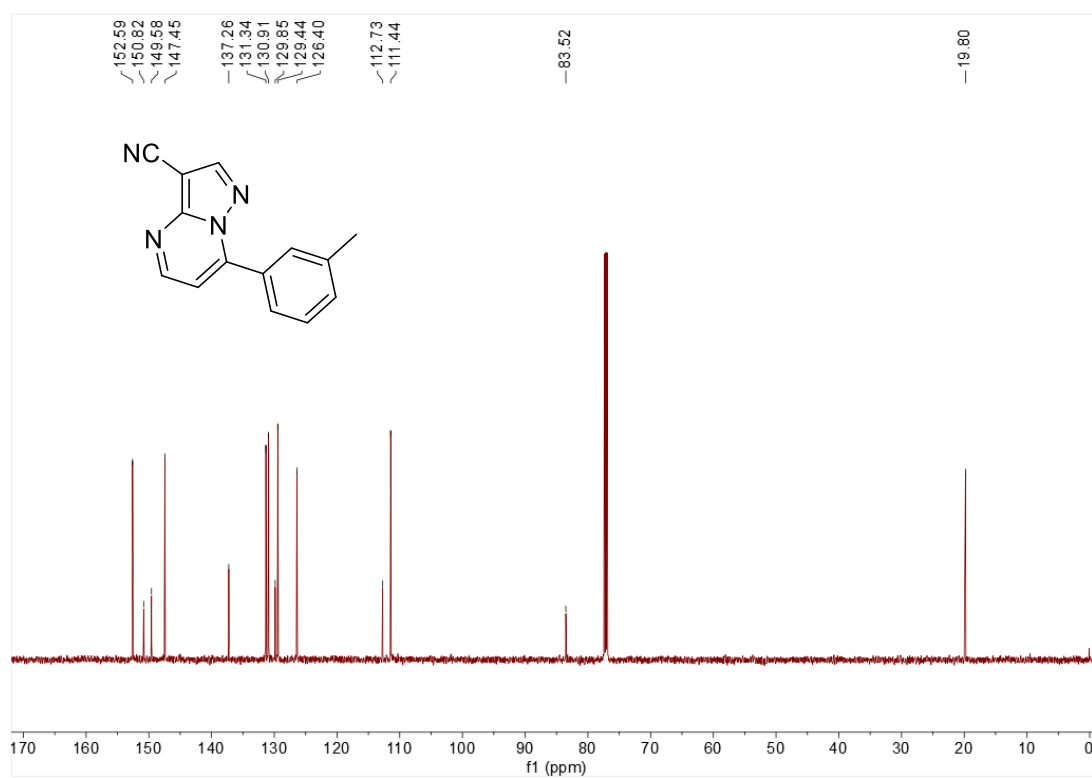
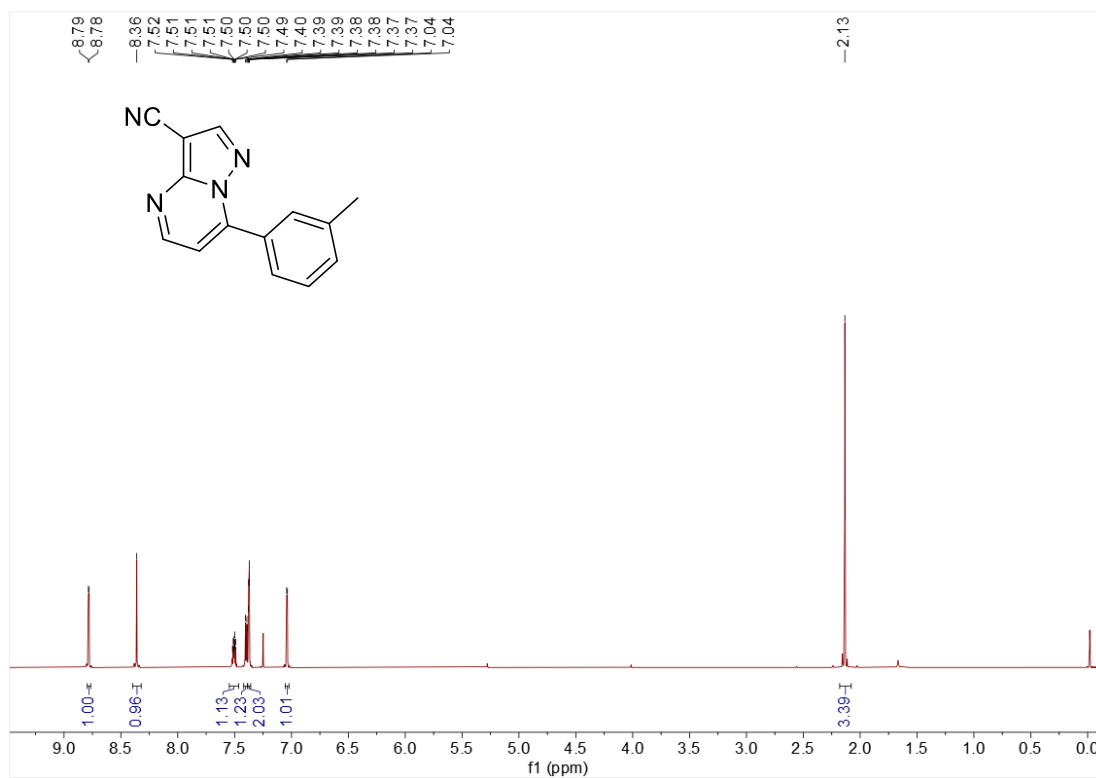
White solid; (PE/EA = 3/1); Yield: 63%; 94% ee; $[\alpha]_{\text{D}}^{25} = +20.1$ ($c = 1.0, \text{CH}_2\text{Cl}_2$); HPLC condition: Lux 5u Amylose-1 (250 \times 4.60 mm), ipa:hex = 30:70, 1.0 mL/min, 210 nm; $t_{\text{R}} = 8.3$ min (major), $t_{\text{R}} = 6.1$ min (minor); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.34 – 7.28 (m, 3H), 7.25 – 7.22 (m, 1H), 7.02 – 6.95 (m, 2H), 5.47 (t, $J = 4.97$ Hz, 1H), 5.40 (d, $J = 1.96$ Hz, 1H), 4.14 (s, 1H), 3.19 (dp, $J = 7.15, 2.41$ Hz, 2H), 2.55 – 2.44 (m, 1H), 2.22 – 2.09 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 146.1, 142.4, 139.6, 128.7, 127.5, 126.2, 86.2, 58.7, 36.8, 31.4.

8. NMR, SFC and HPLC spectra of compounds

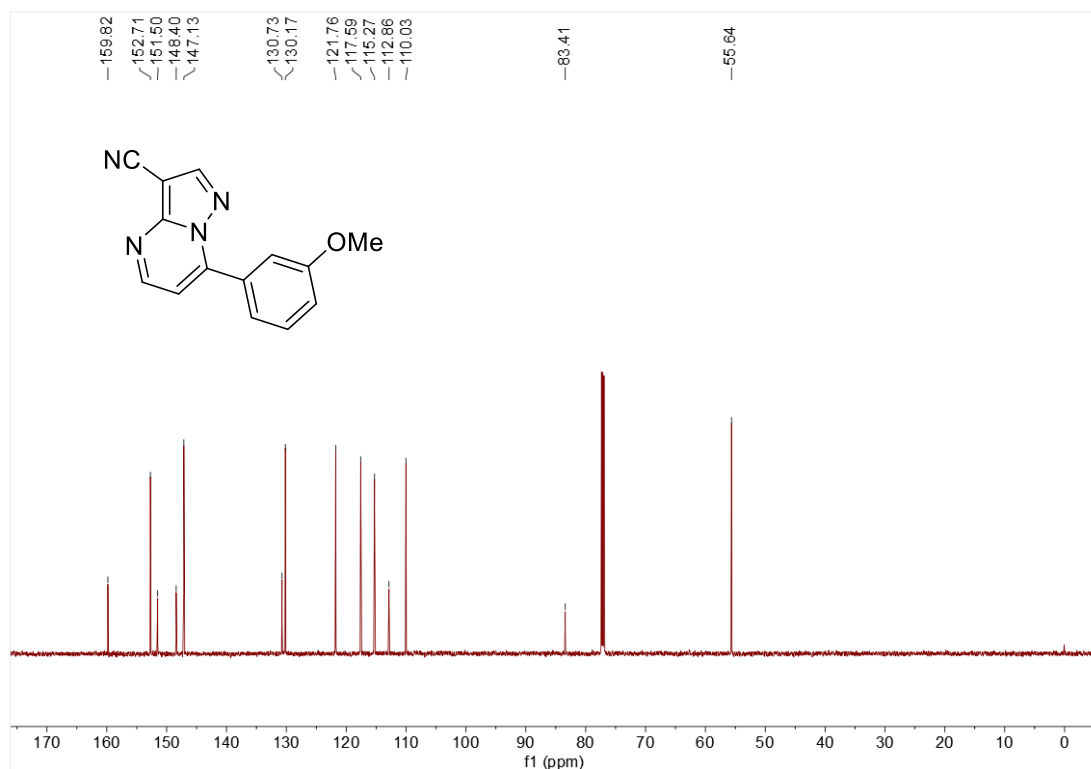
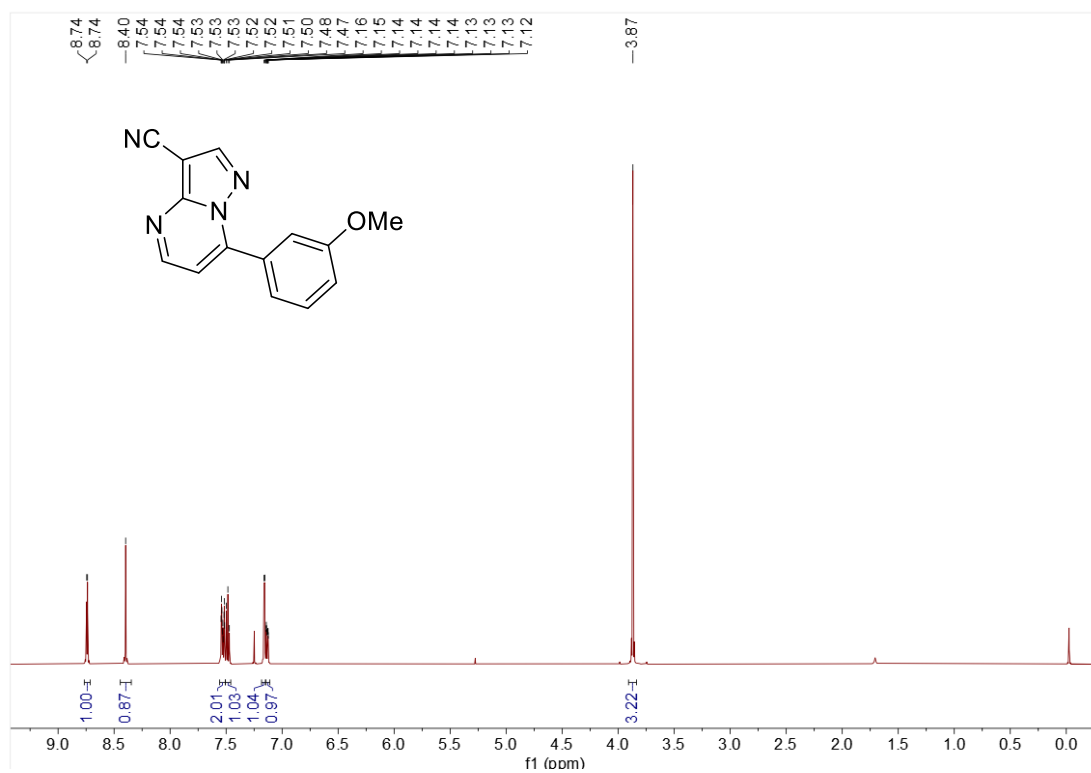
7-phenylpyrazolo[1,5-a]pyrimidine-3-carbonitrile (**1a**)



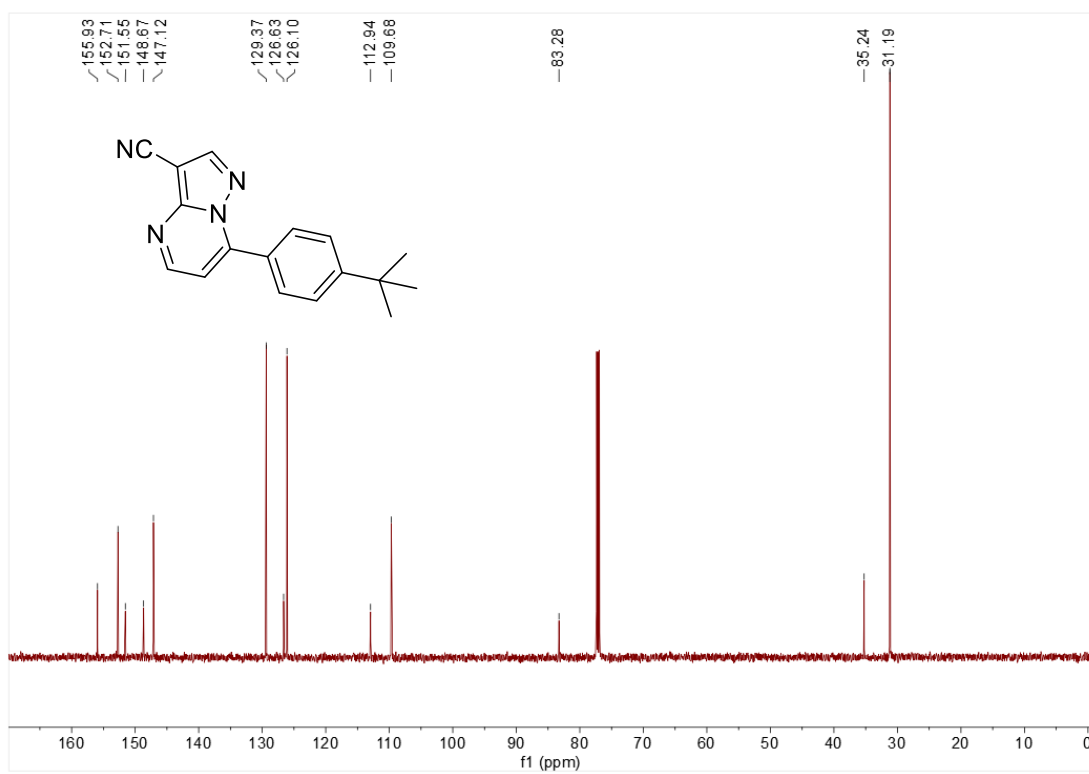
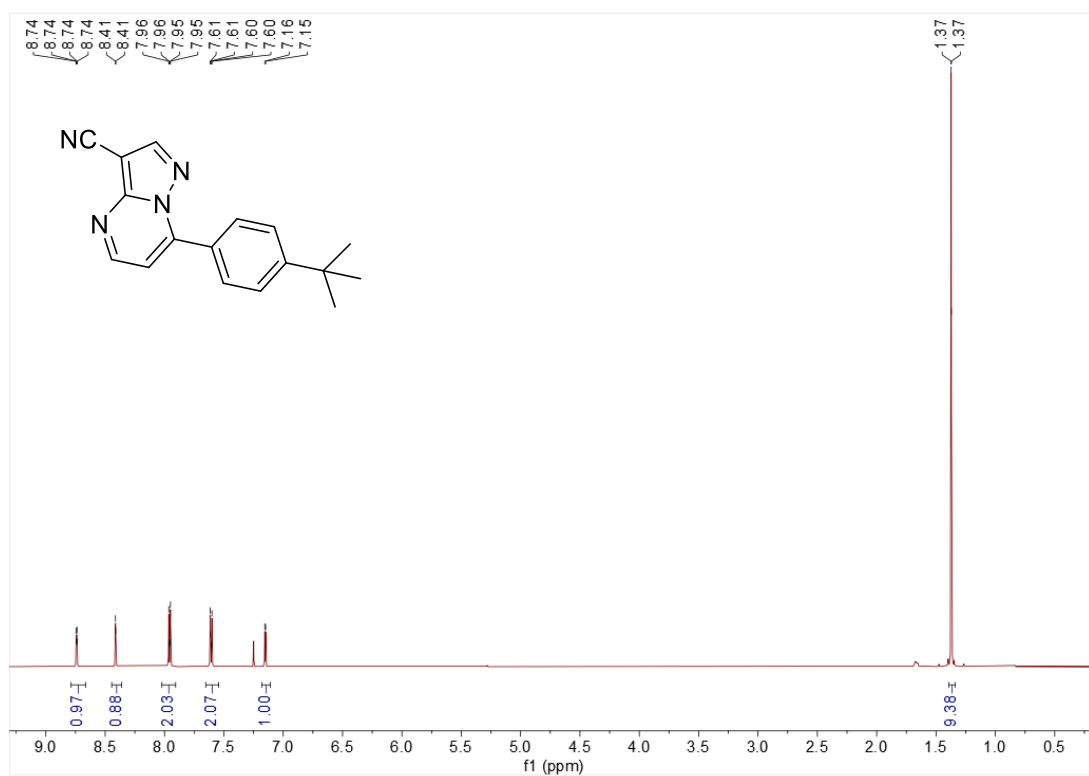
7-(*m*-tolyl)pyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**1b**)



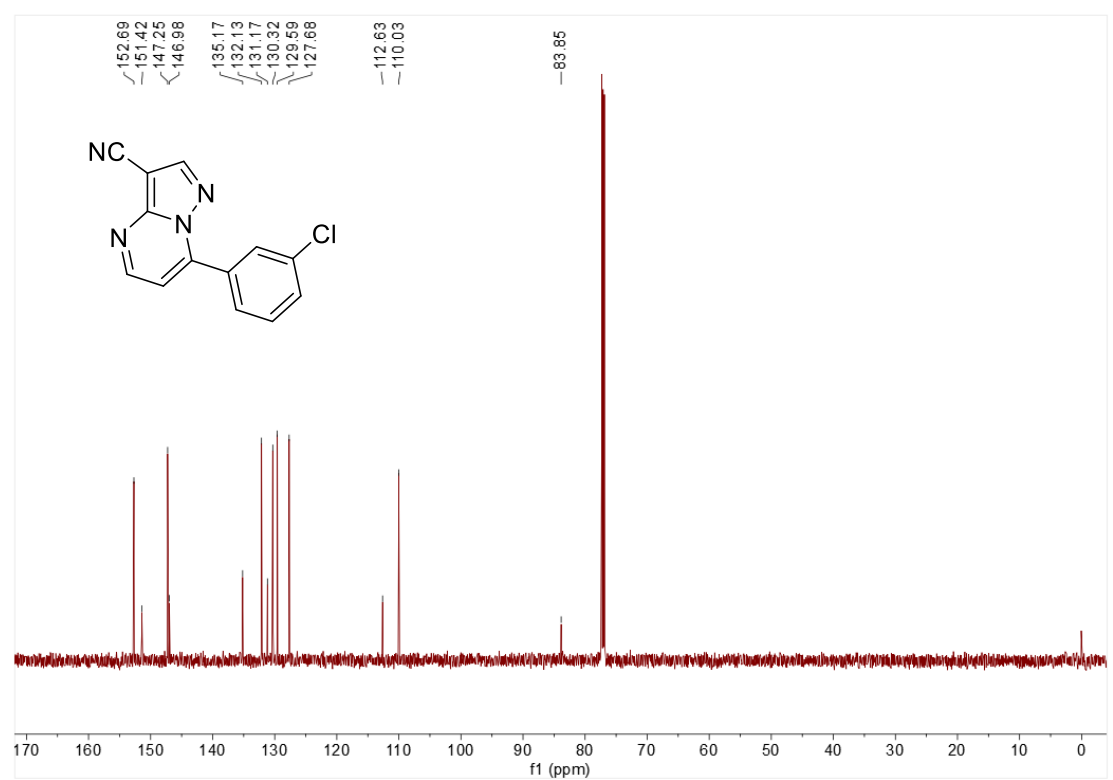
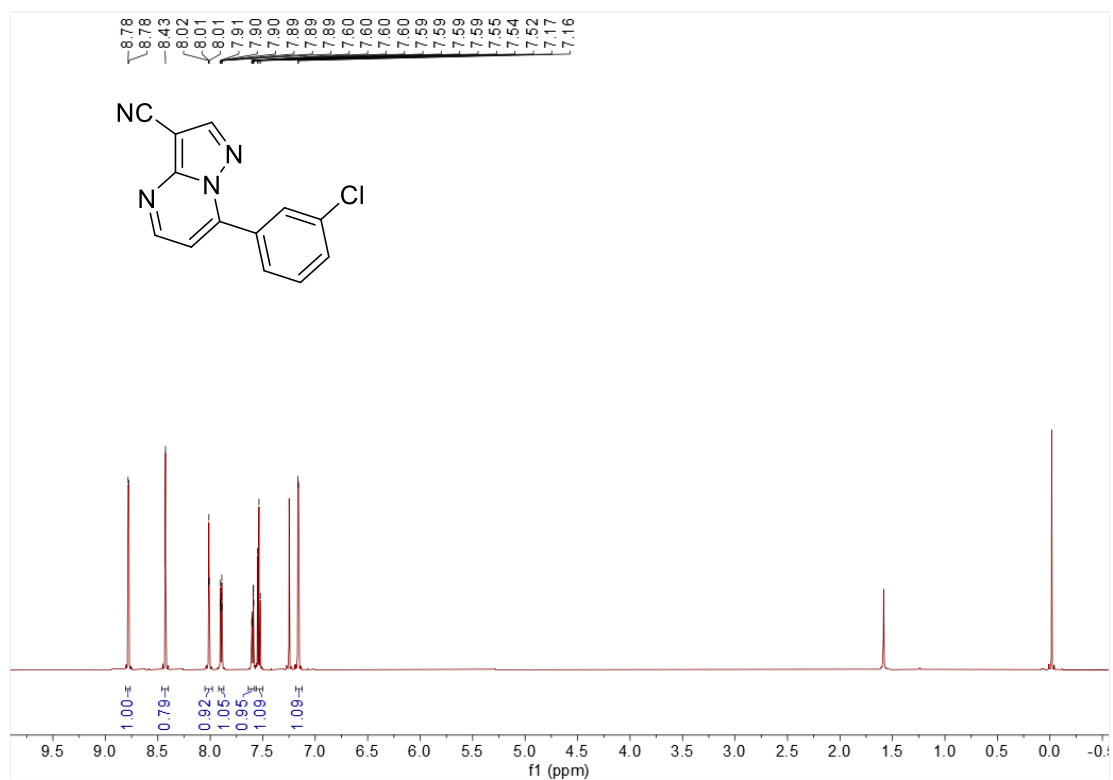
7-(3-methoxyphenyl)pyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**1c**)



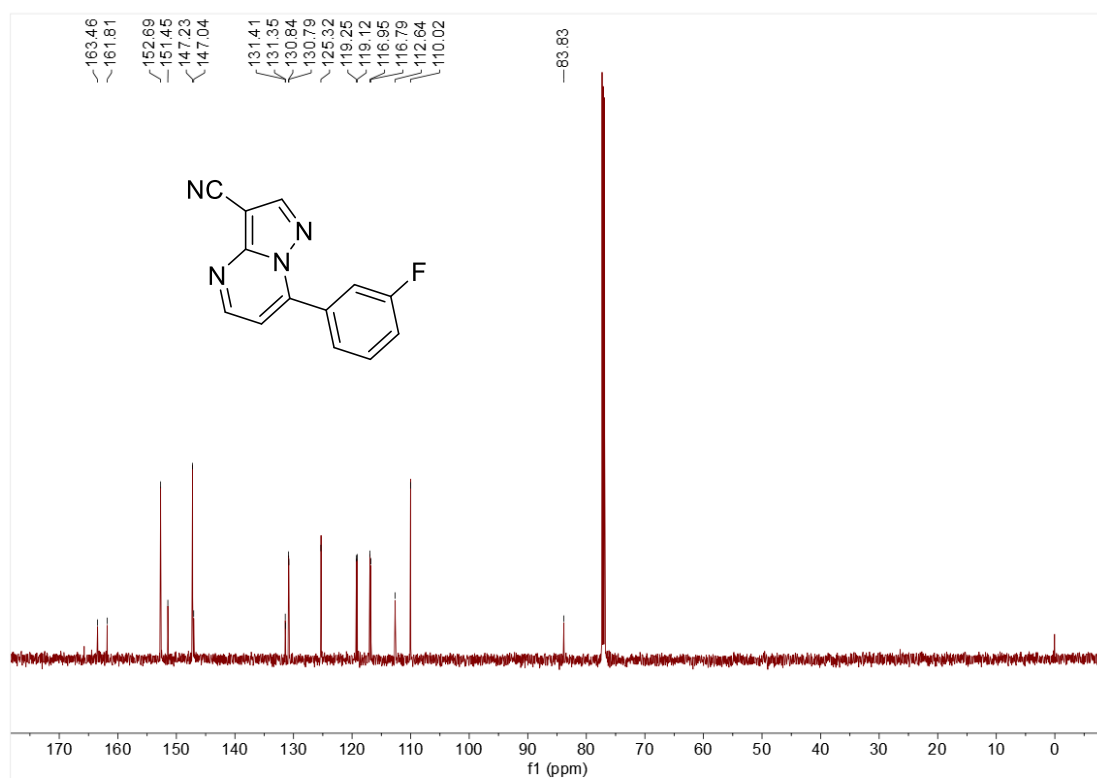
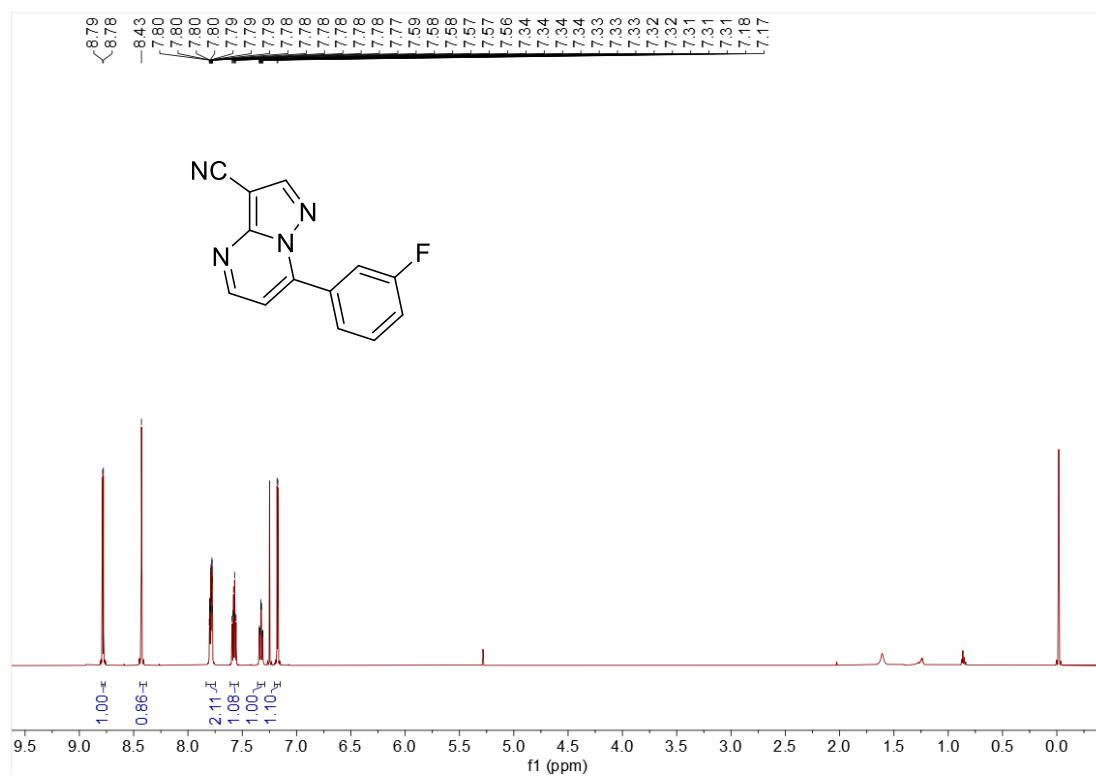
7-(4-(tert-butyl)phenyl)pyrazolo[1,5-a]pyrimidine-3-carbonitrile (**1d**)



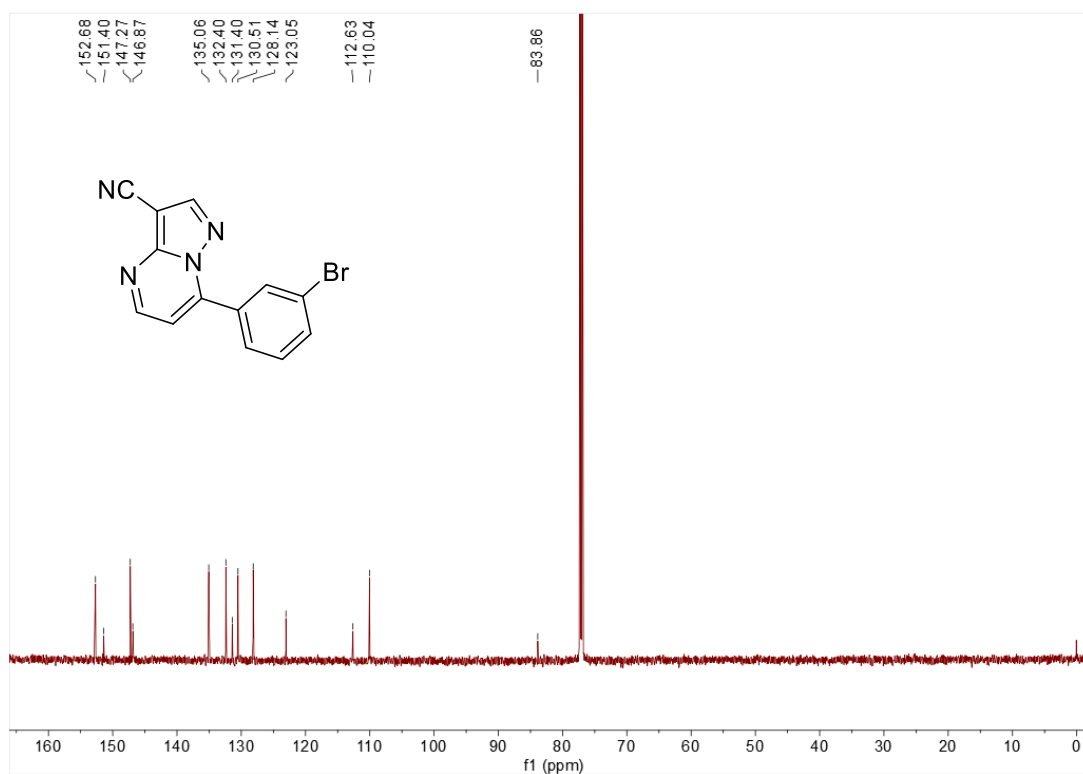
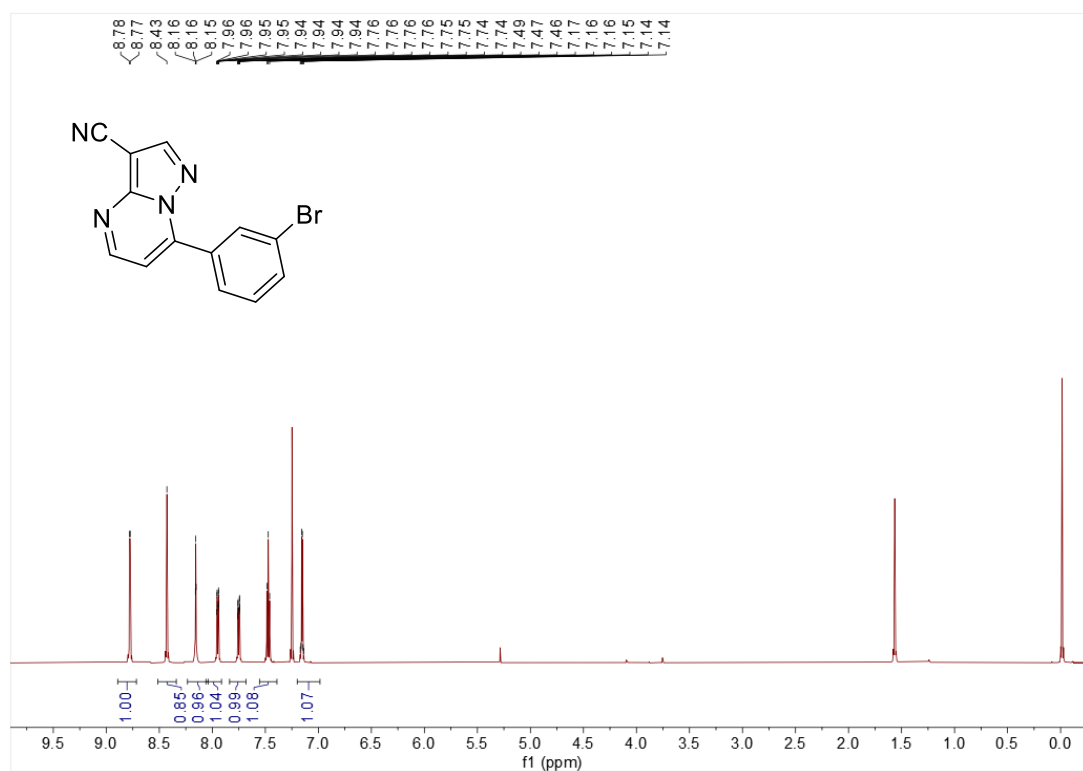
7-(3-chlorophenyl)pyrazolo[1,5-a]pyrimidine-3-carbonitrile (**1e**)



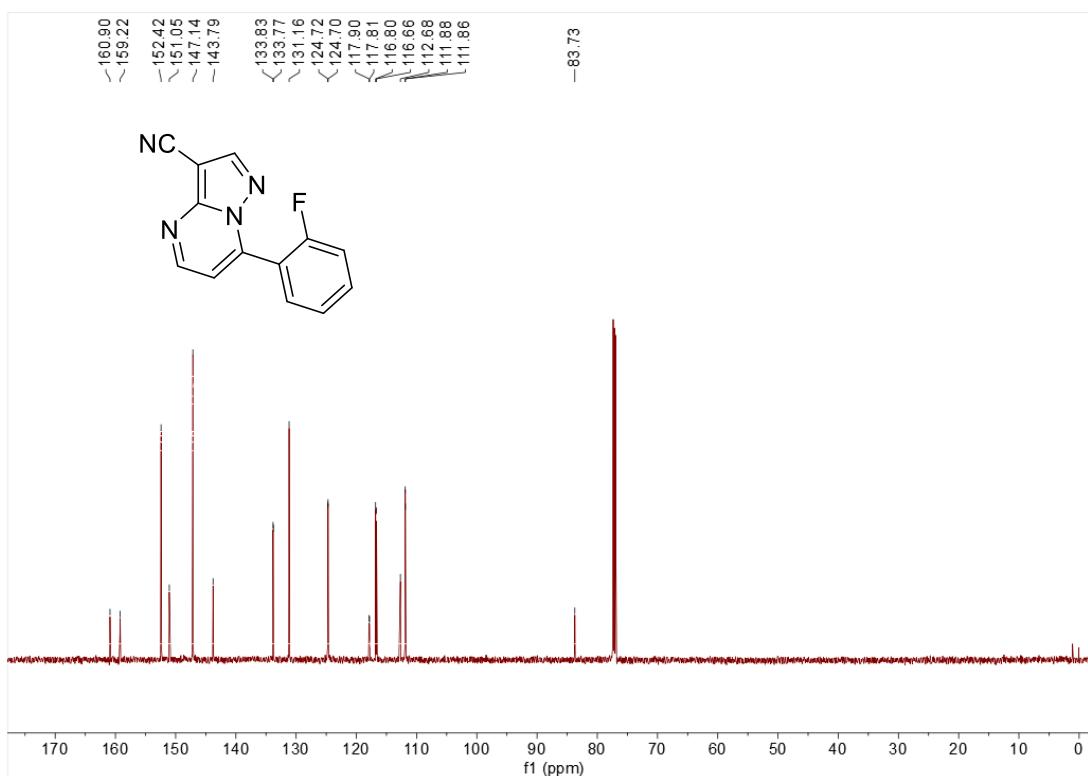
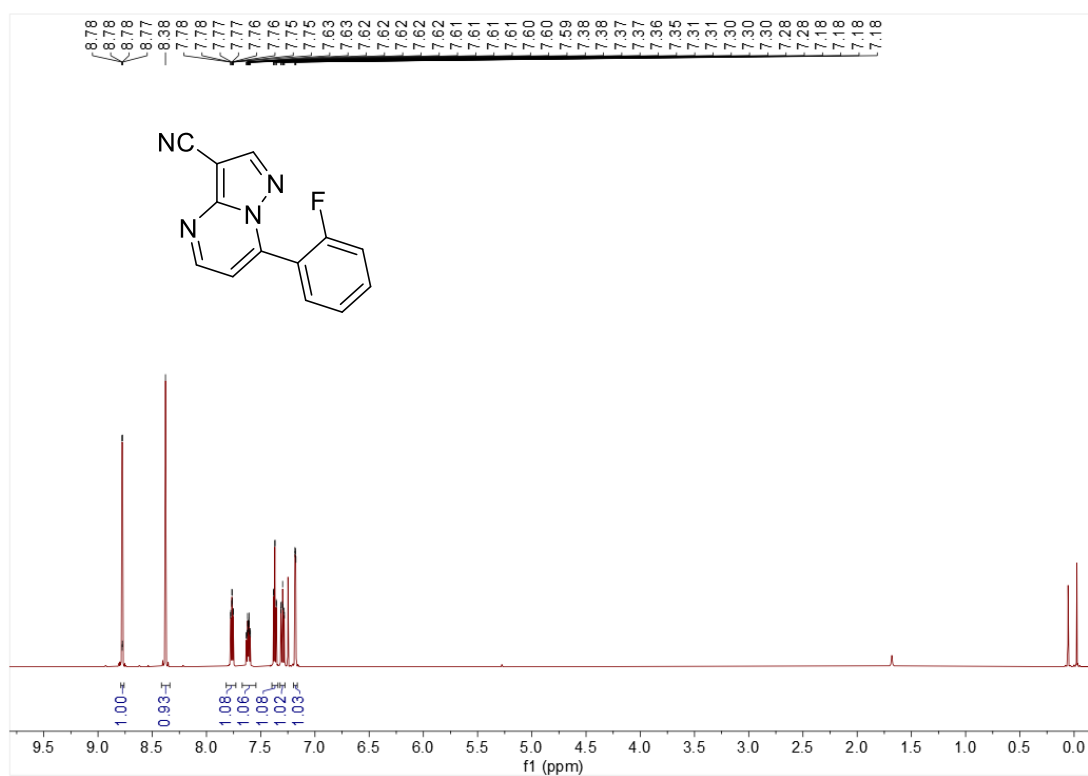
7-(3-fluorophenyl)pyrazolo[1,5-a]pyrimidine-3-carbonitrile (**1f**)



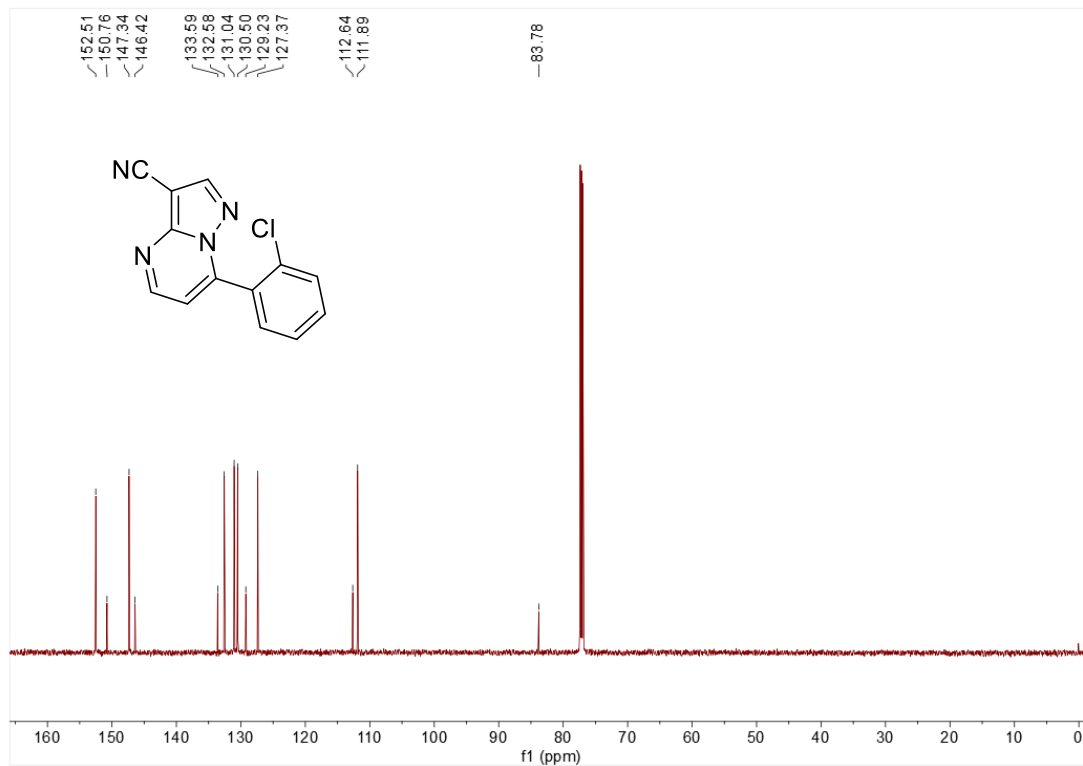
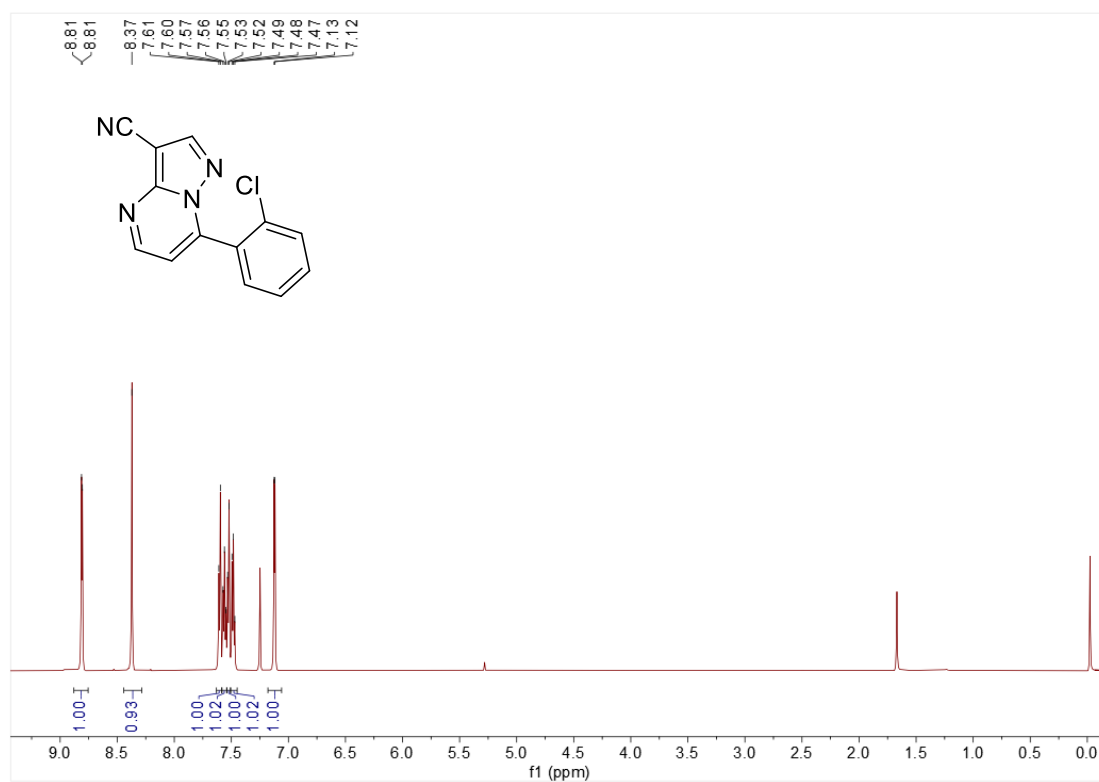
7-(3-bromophenyl)pyrazolo[1,5-a]pyrimidine-3-carbonitrile (**1g**)



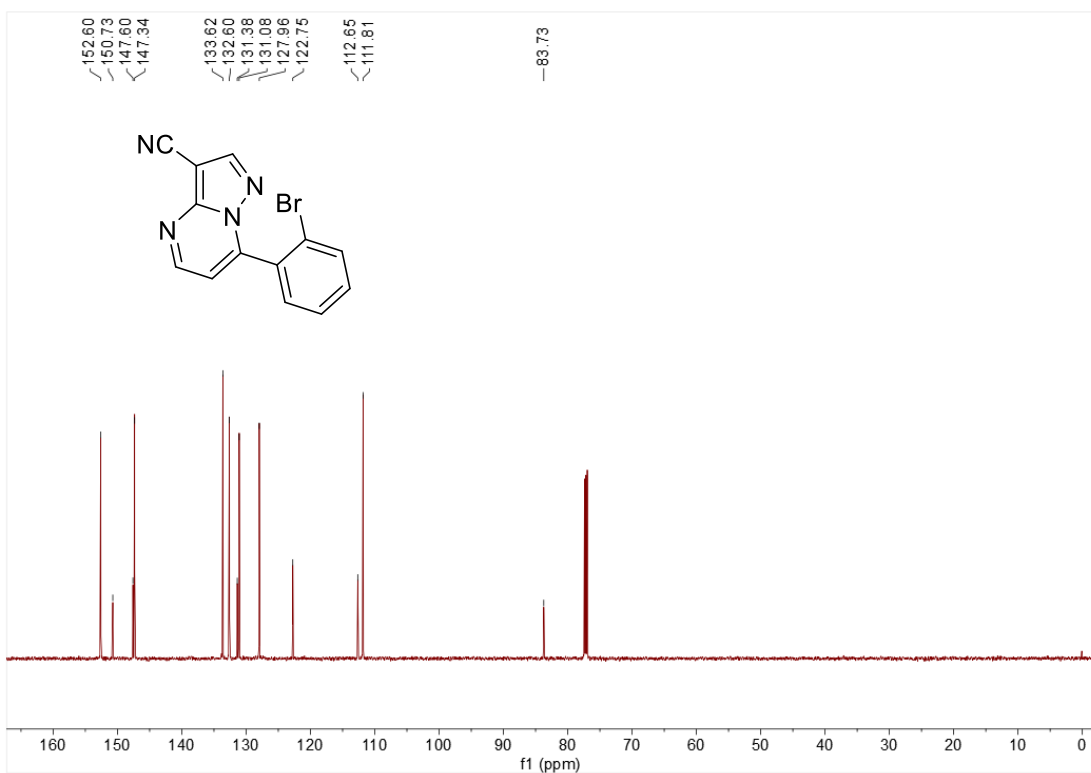
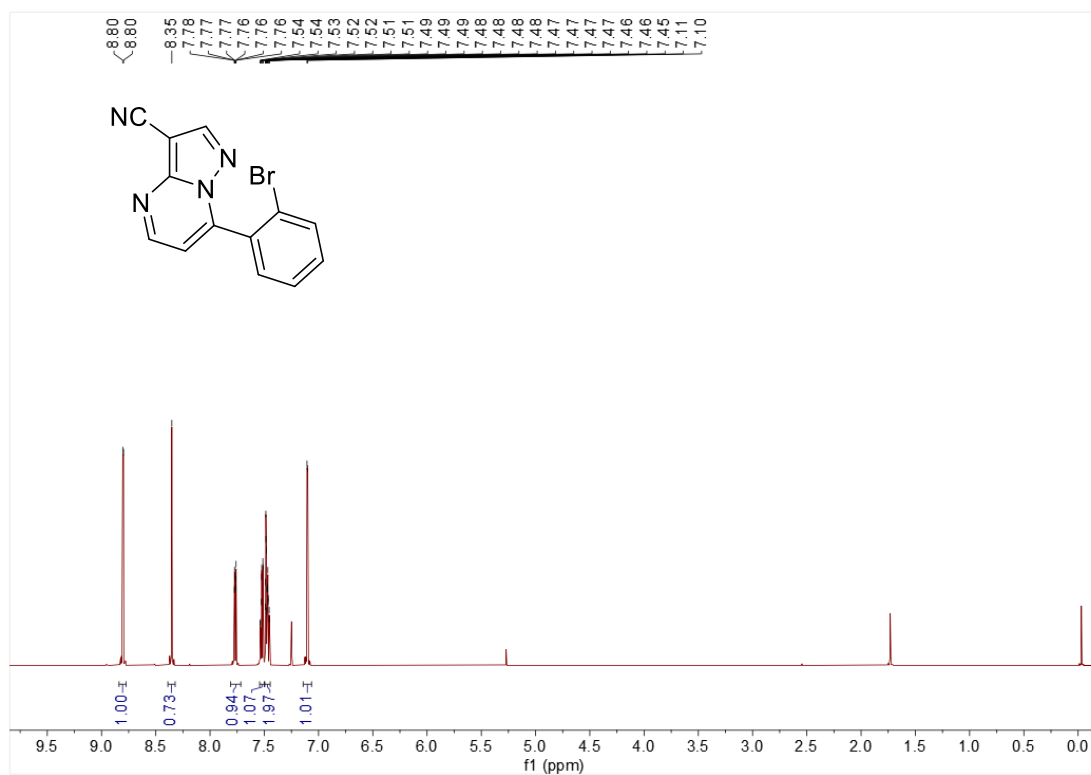
7-(2-fluorophenyl)pyrazolo[1,5-a]pyrimidine-3-carbonitrile (**1h**)



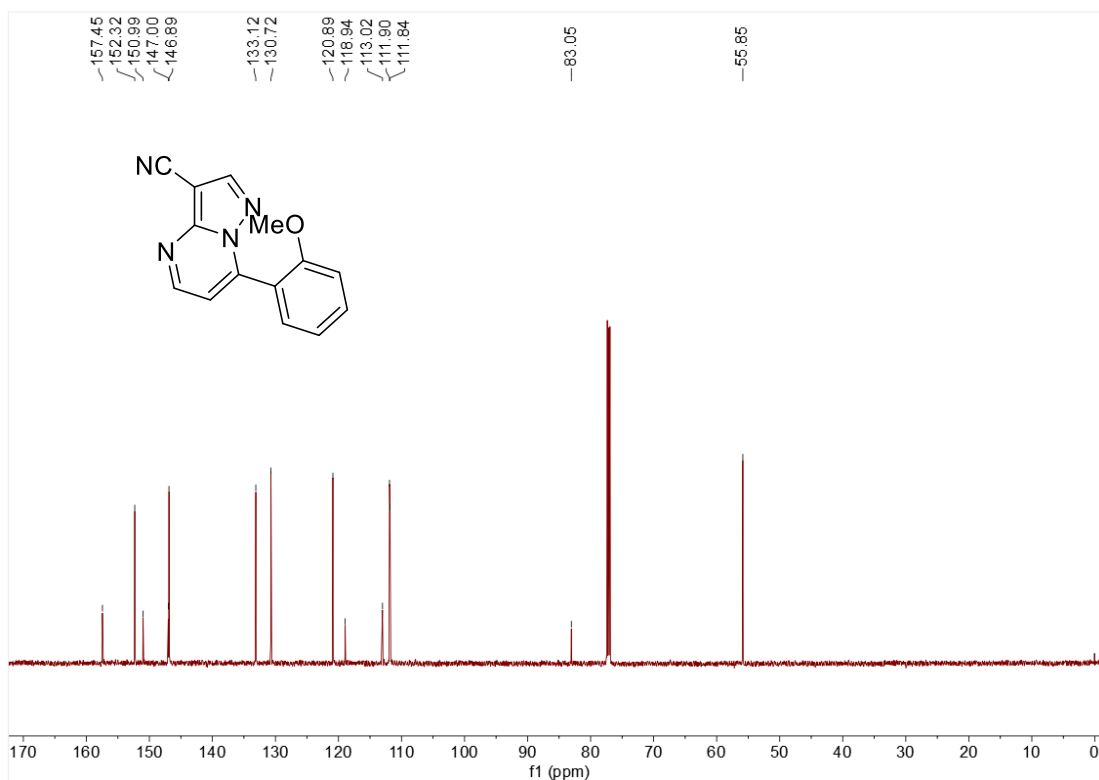
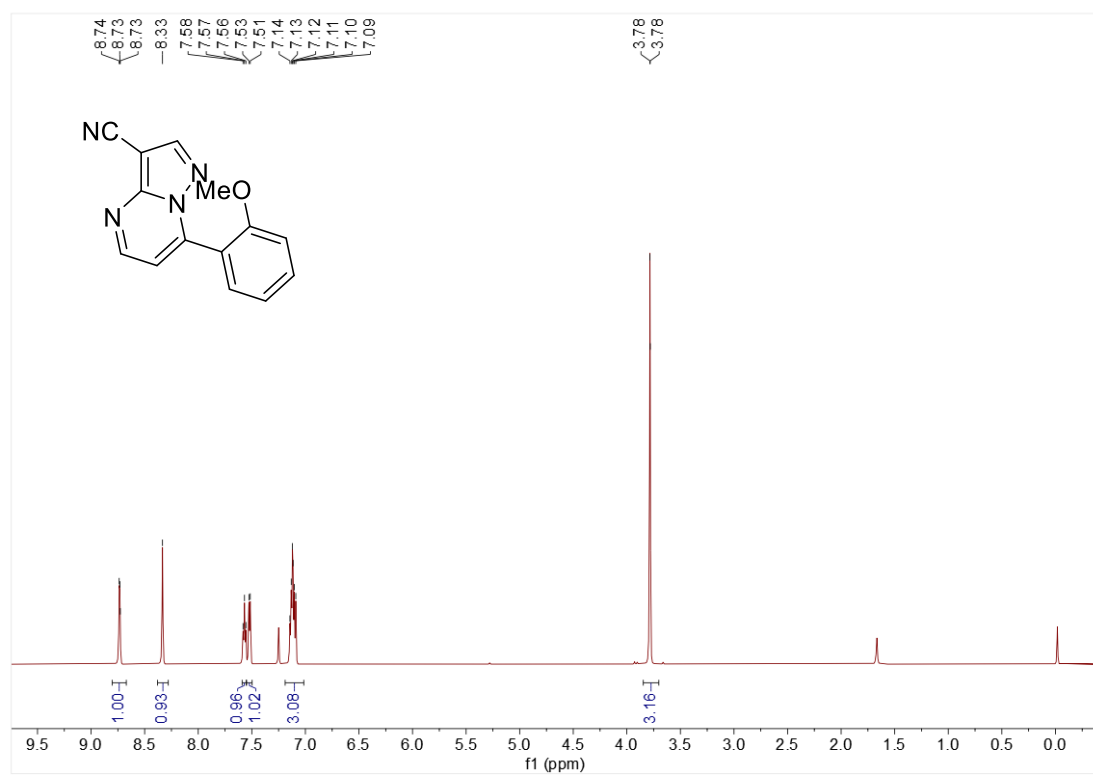
7-(2-chlorophenyl)pyrazolo[1,5-a]pyrimidine-3-carbonitrile (**1i**)



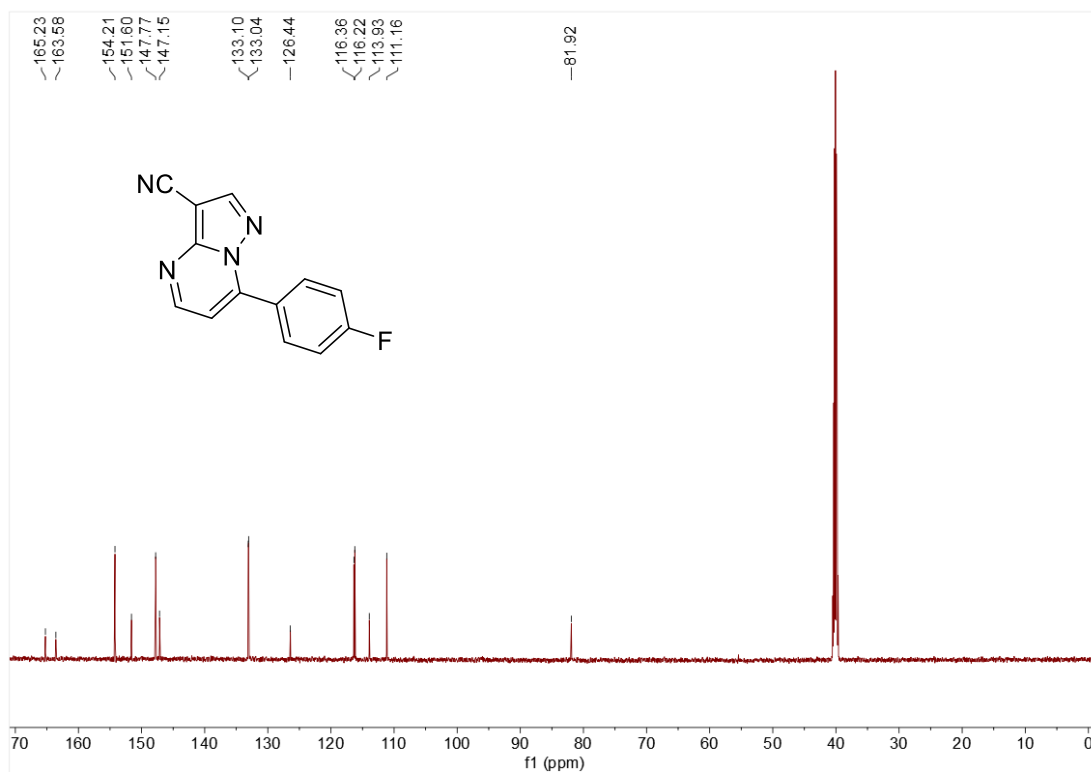
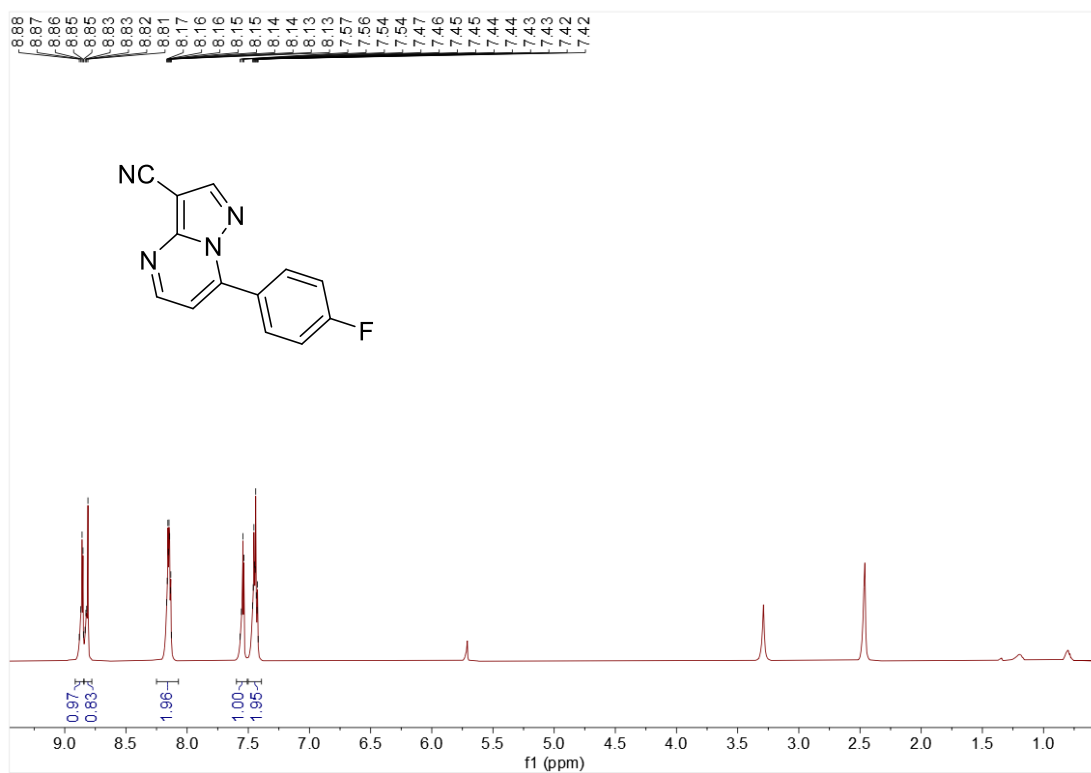
7-(2-bromophenyl)pyrazolo[1,5-a]pyrimidine-3-carbonitrile (**1j**)



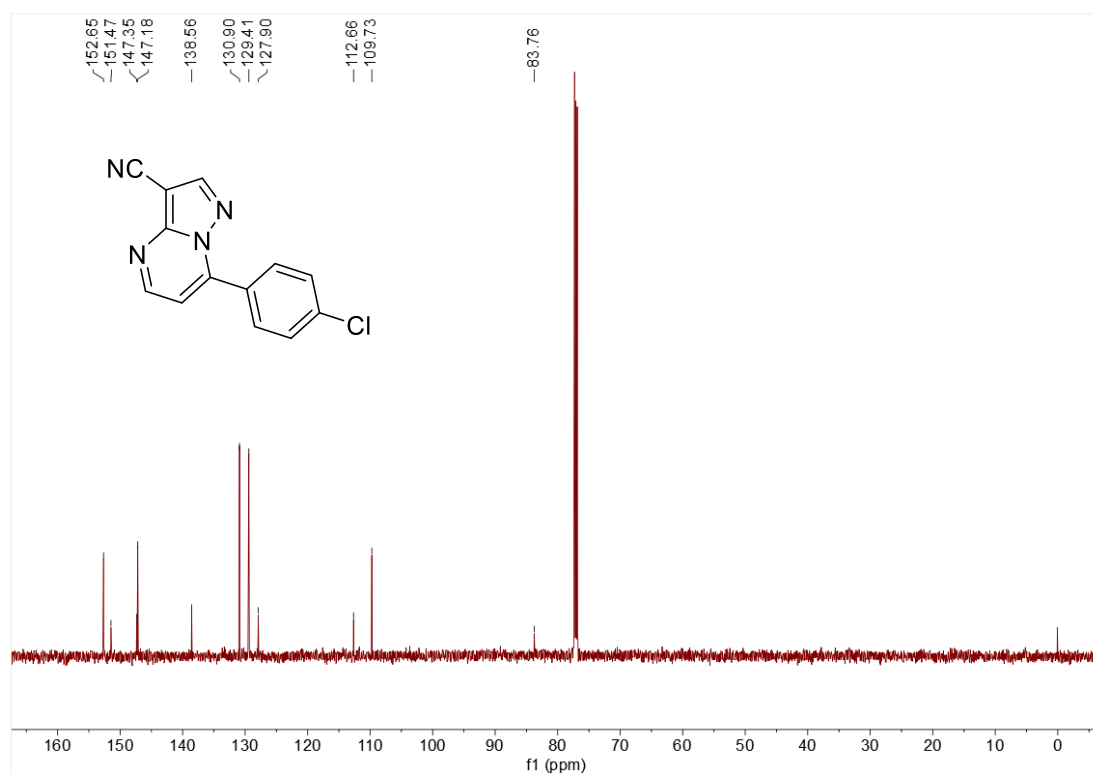
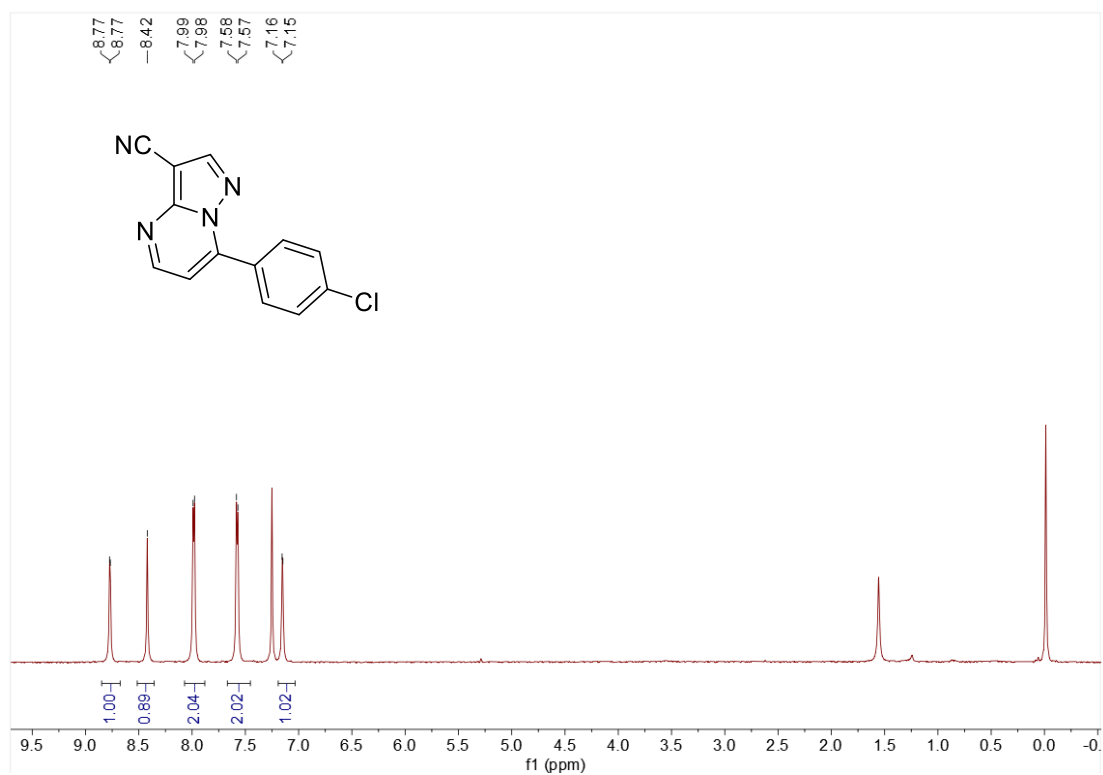
7-(2-methoxyphenyl)pyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**1k**)



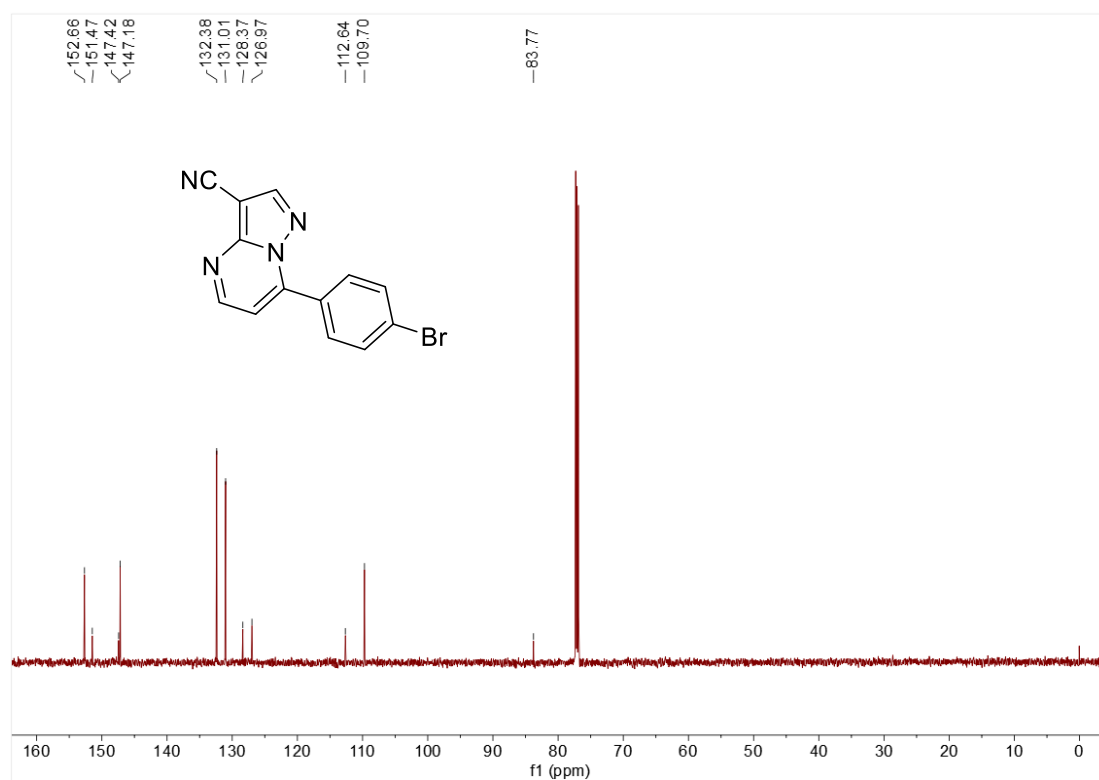
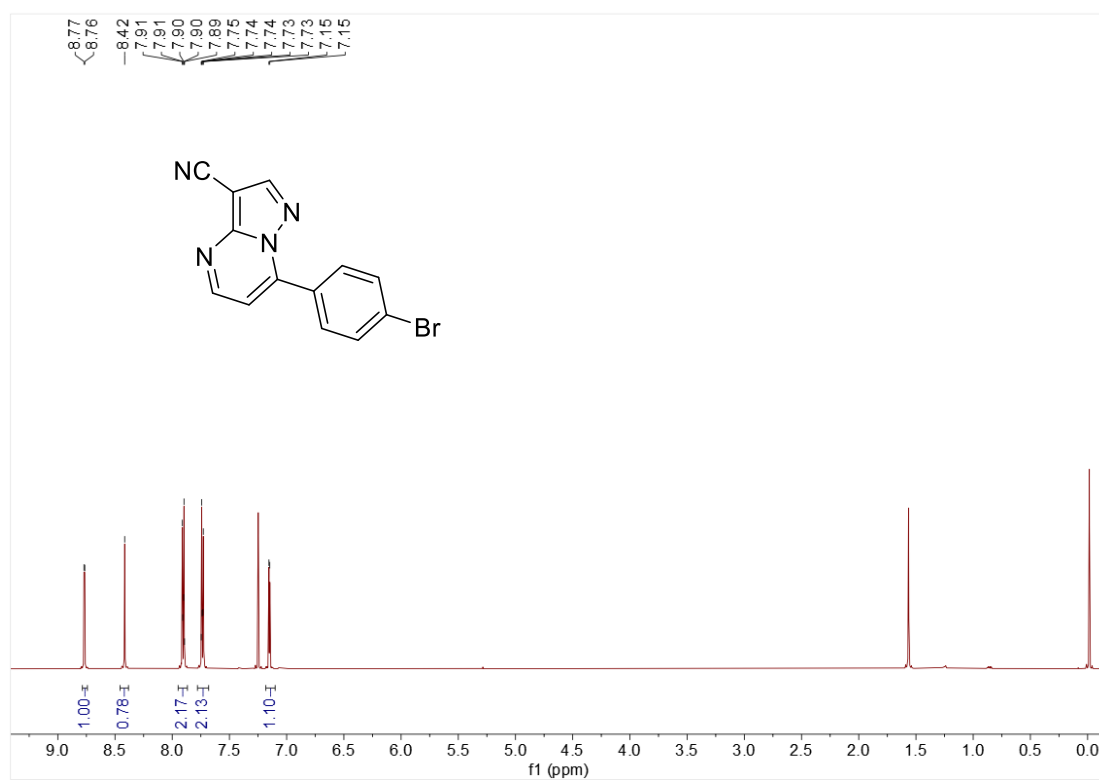
7-(4-fluorophenyl)pyrazolo[1,5-a]pyrimidine-3-carbonitrile (**II**)



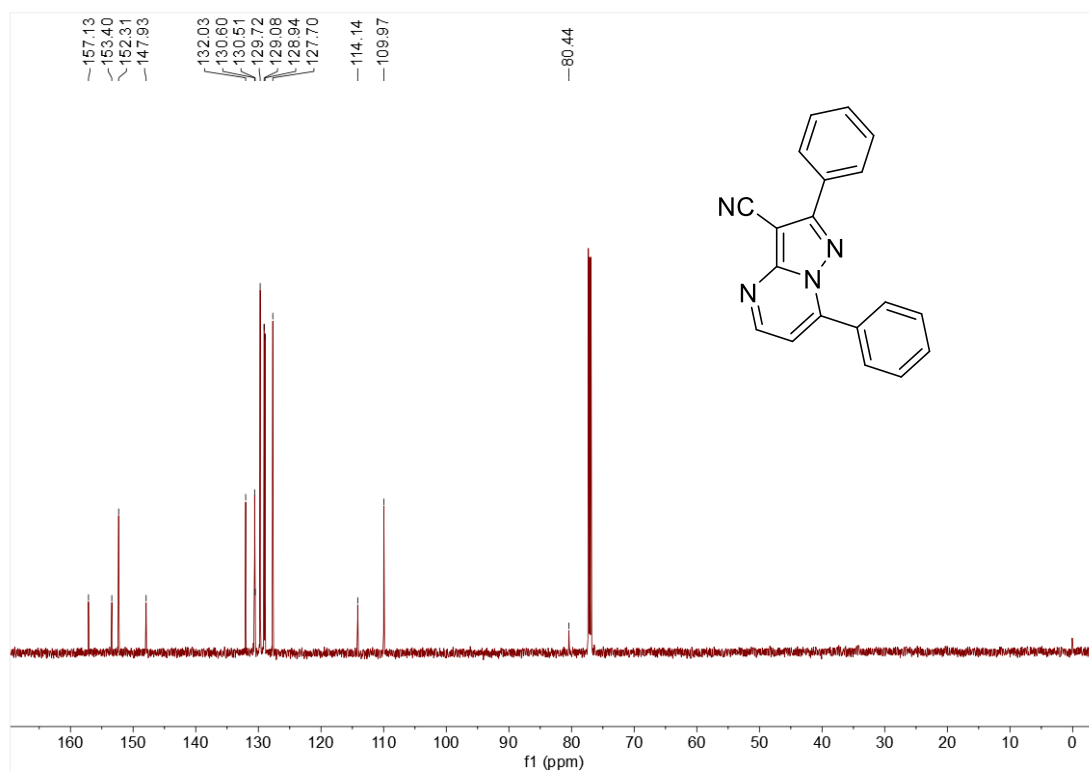
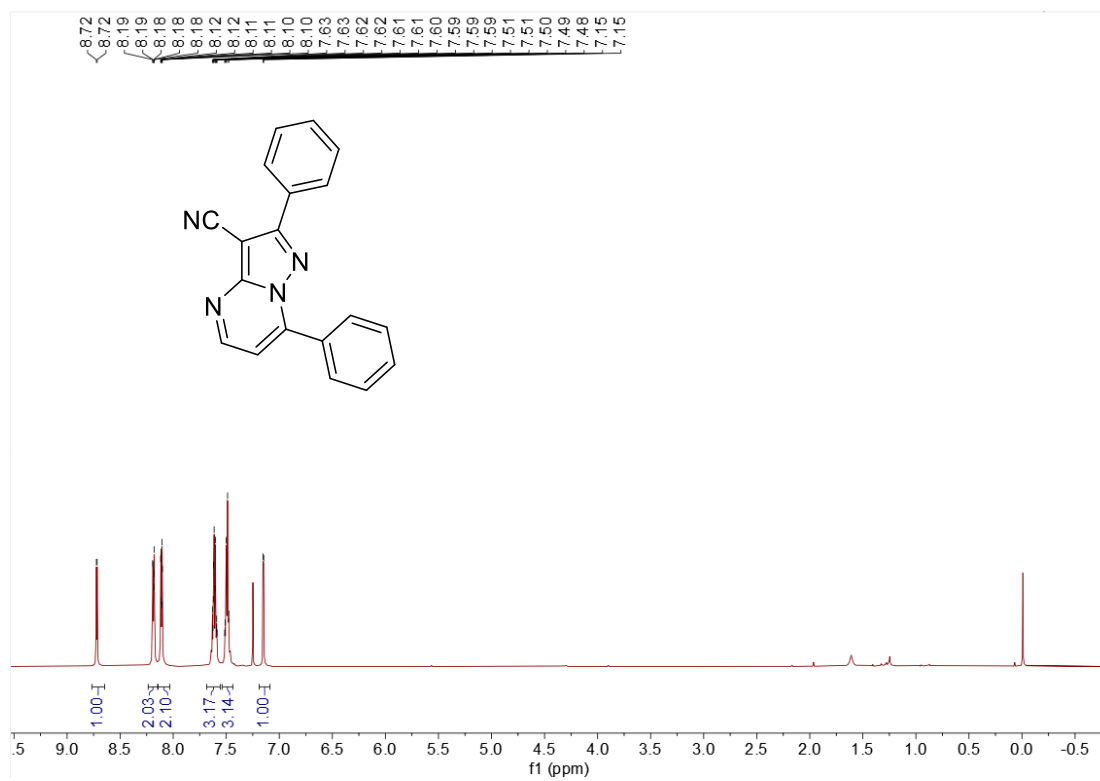
7-(4-chlorophenyl)pyrazolo[1,5-a]pyrimidine-3-carbonitrile (**1m**)



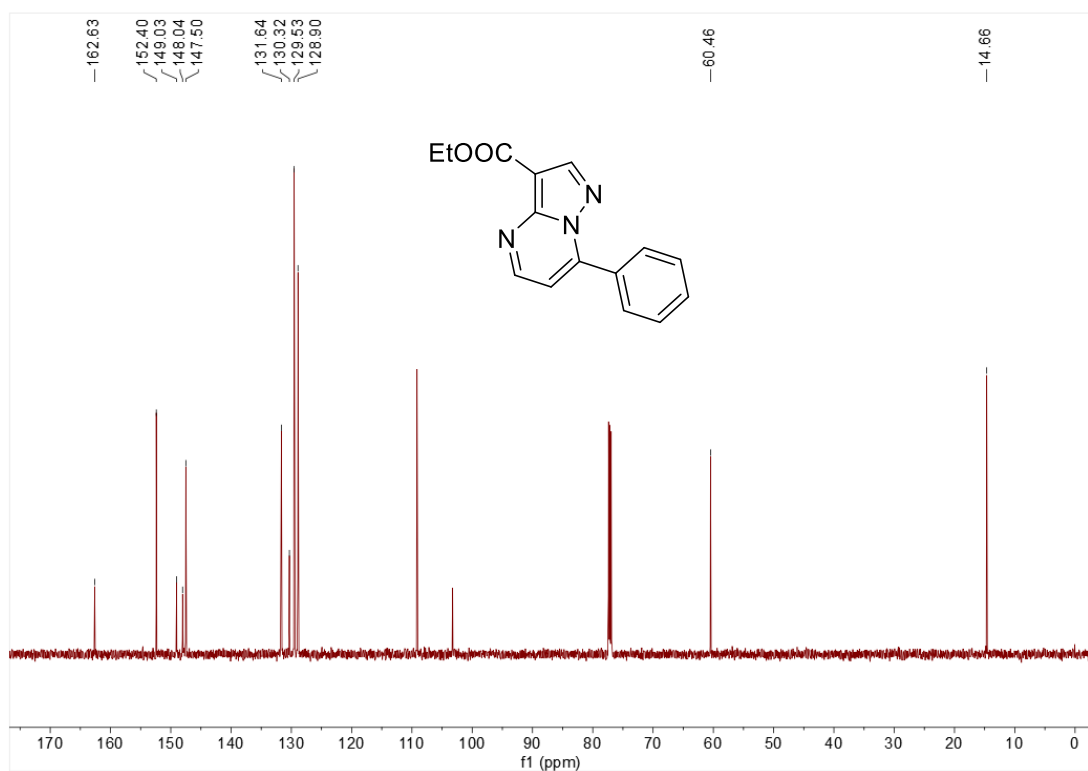
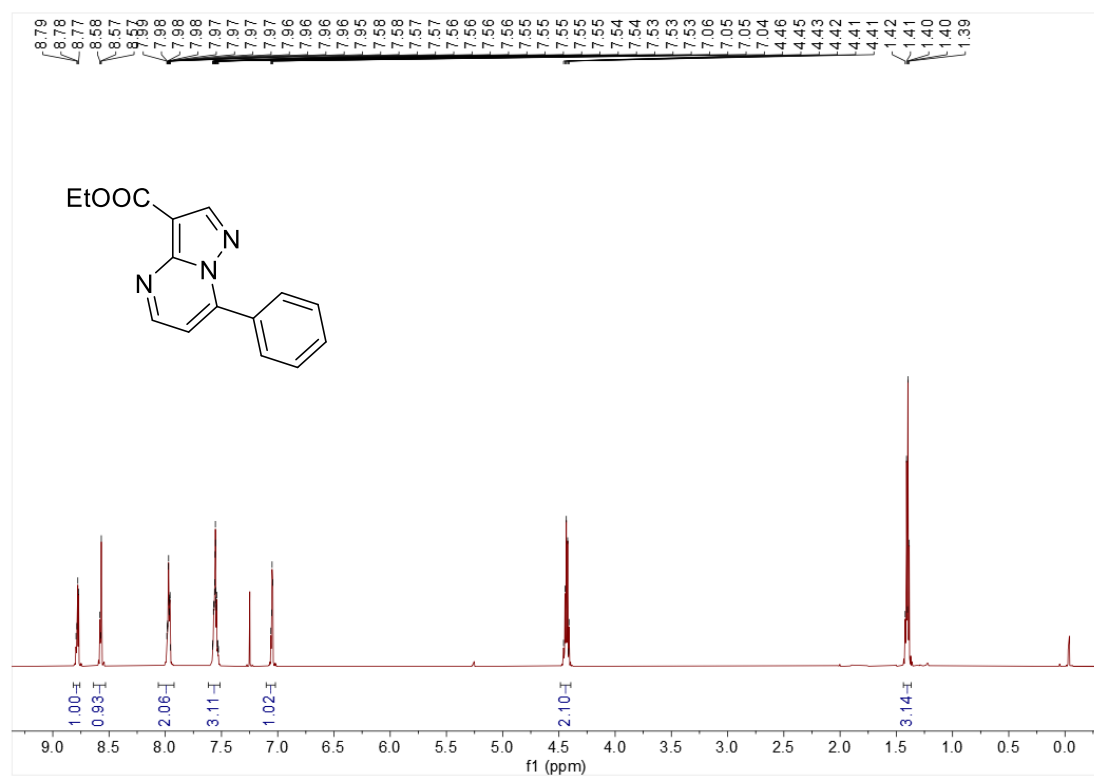
7-(4-bromophenyl)pyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**1n**)



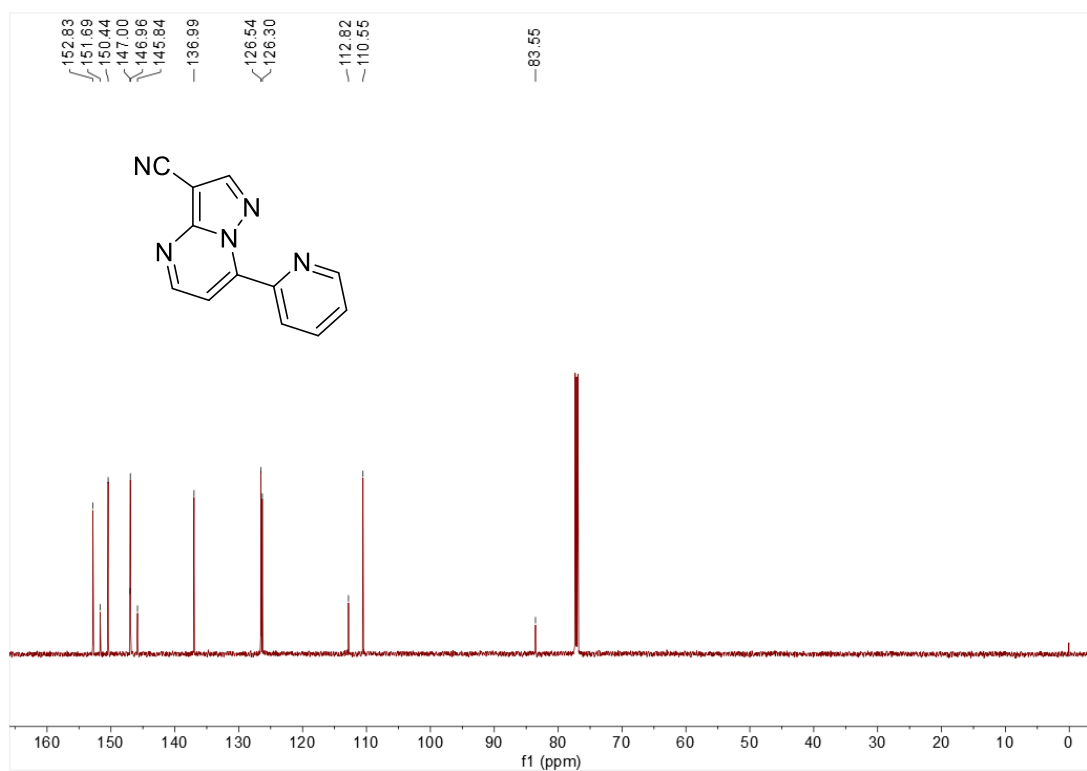
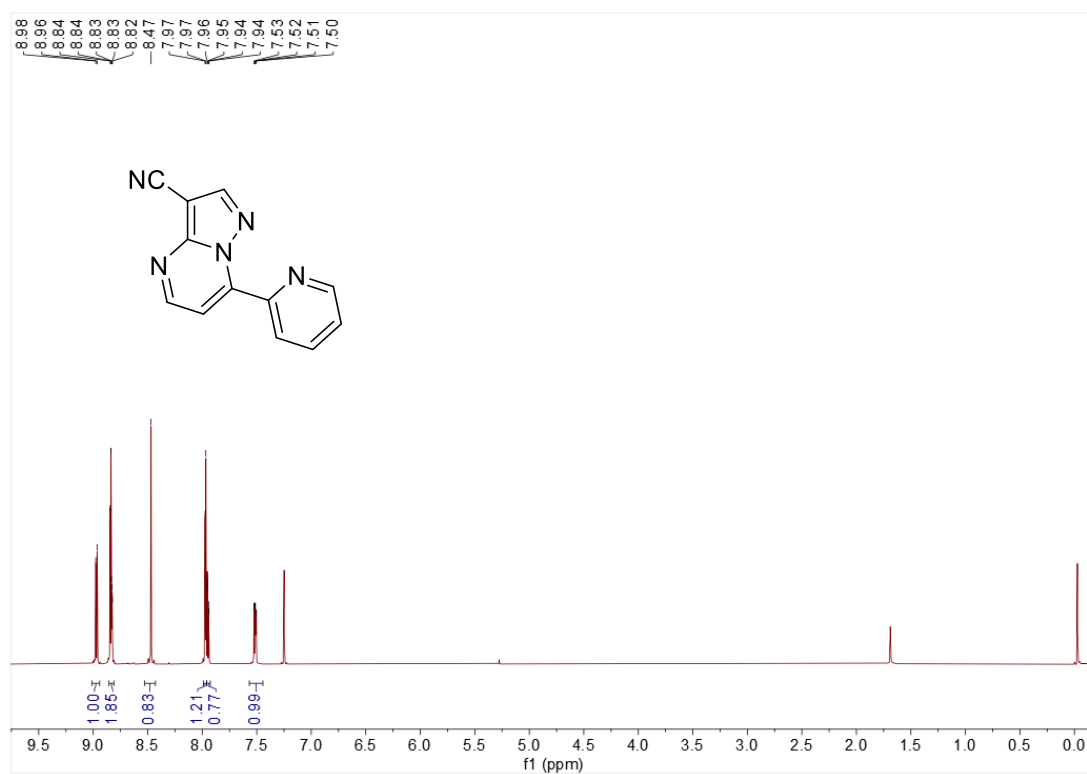
2,7-diphenylpyrazolo[1,5-a]pyrimidine-3-carbonitrile (**10**)



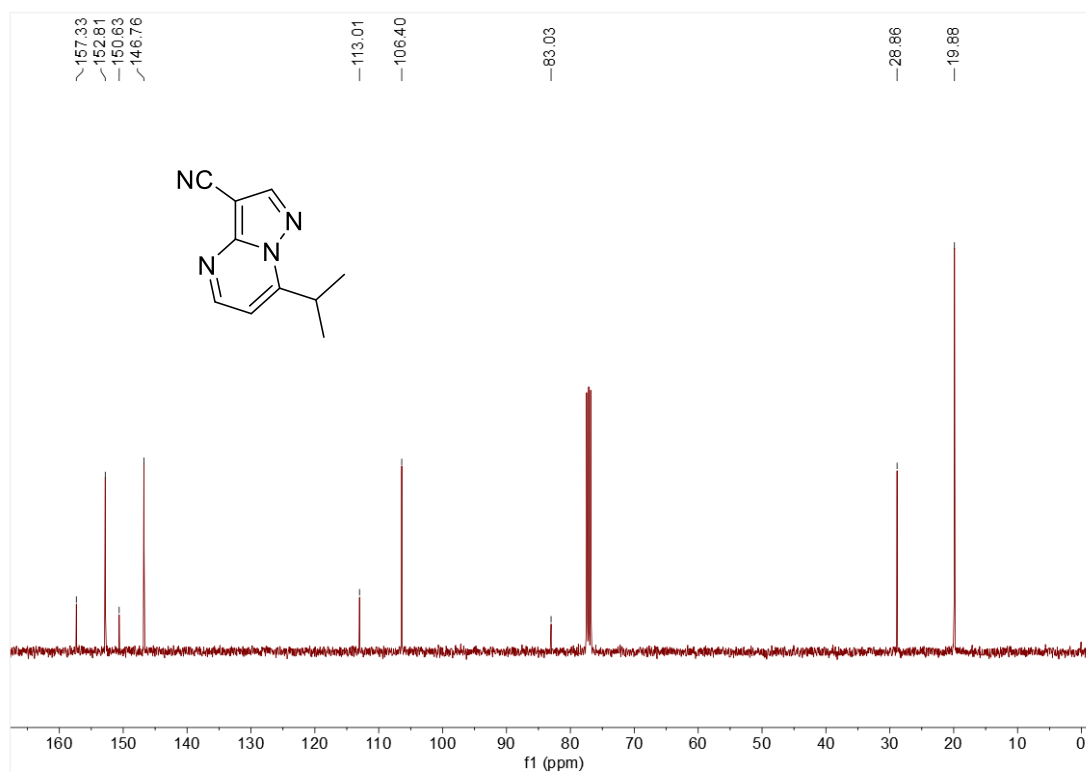
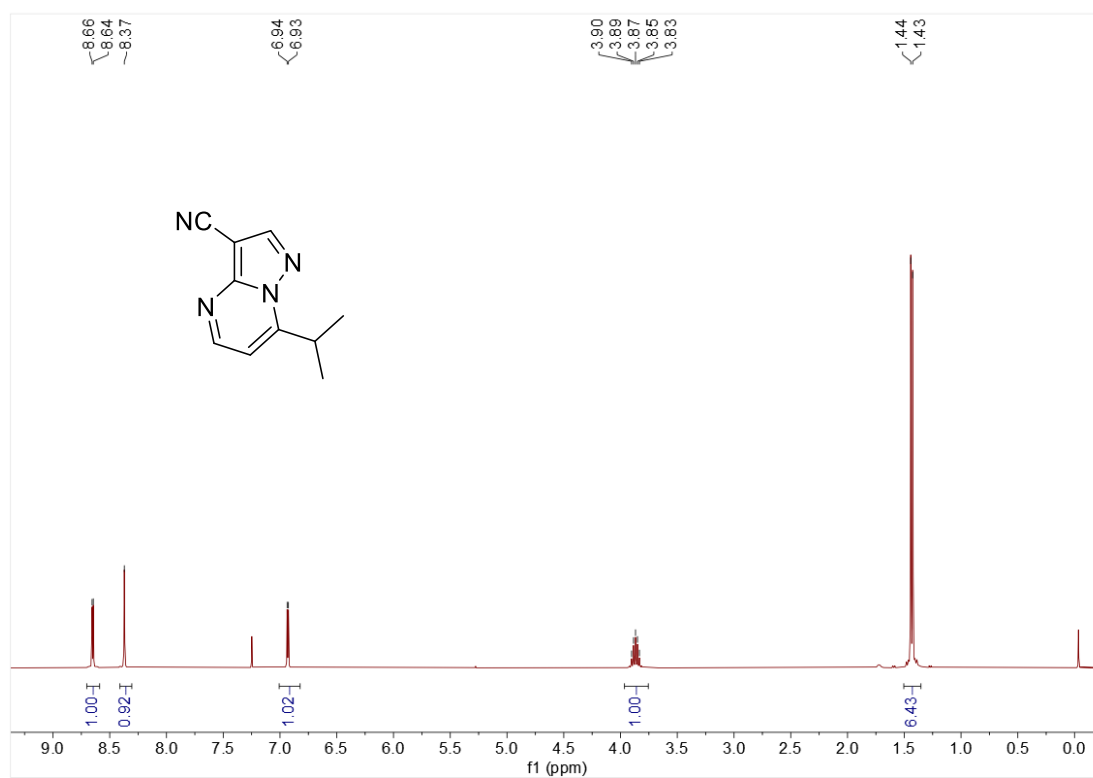
ethyl 7-phenylpyrazolo[1,5-a]pyrimidine-3-carboxylate (**1p**)



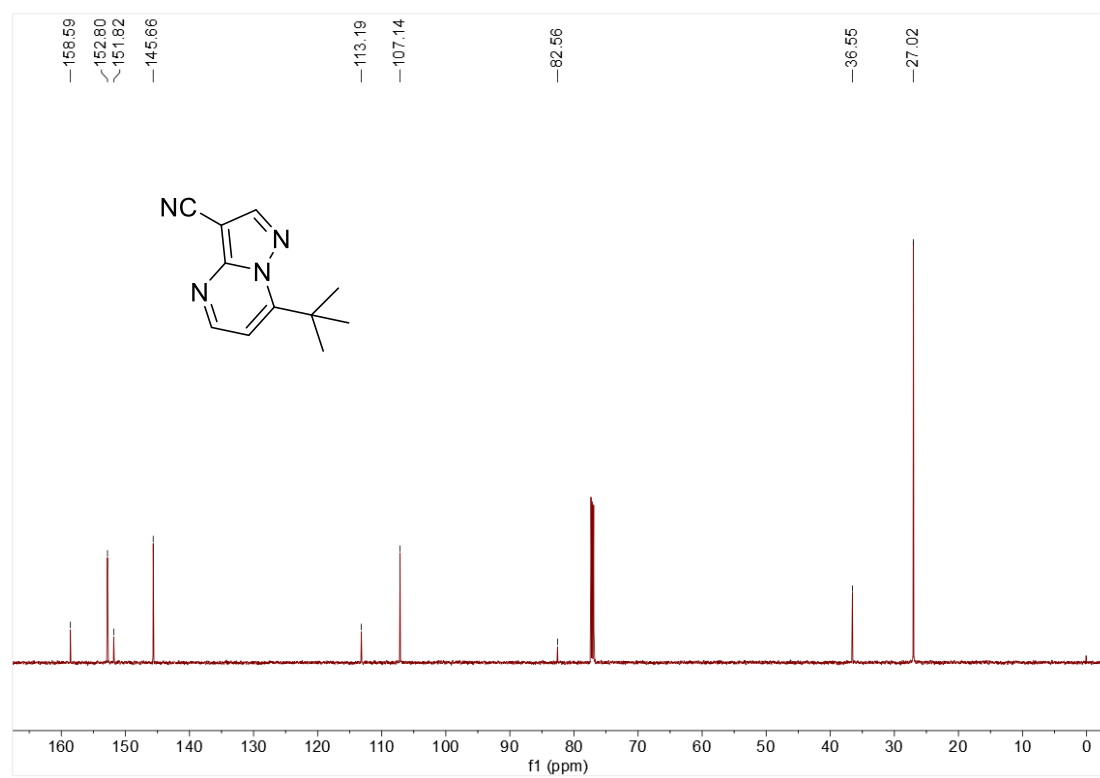
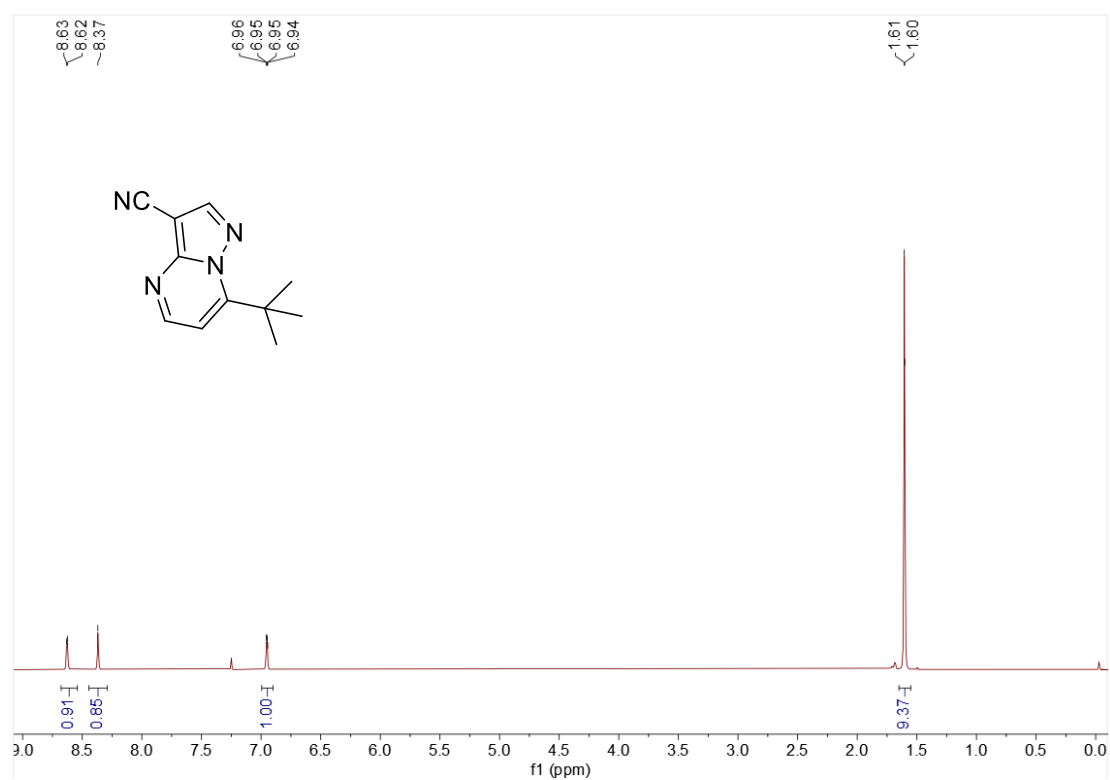
7-(pyridin-2-yl)pyrazolo[1,5-a]pyrimidine-3-carbonitrile (**1q**)



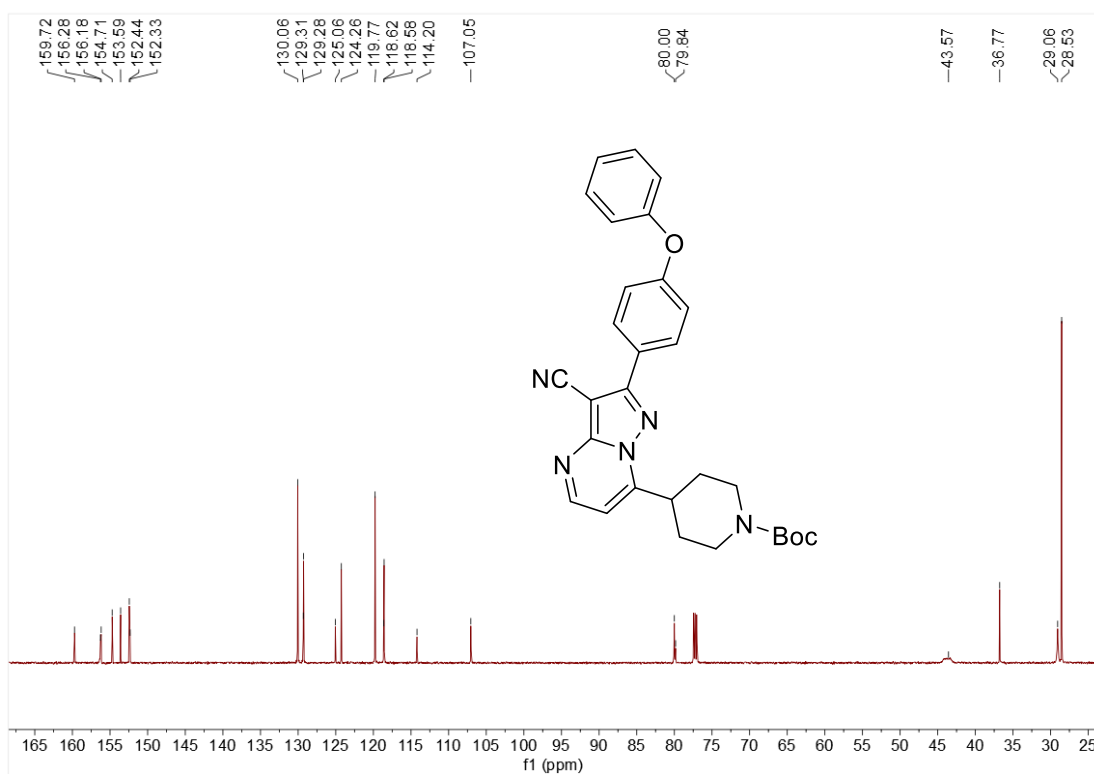
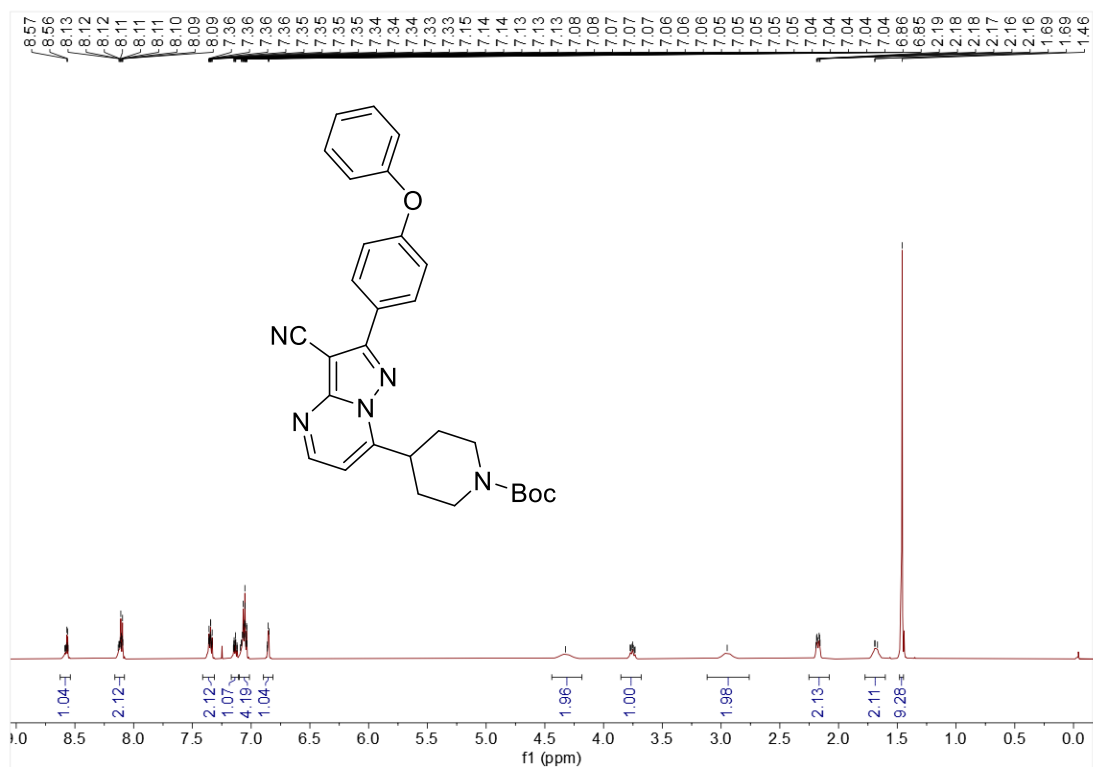
7-isopropylpyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**1r**)



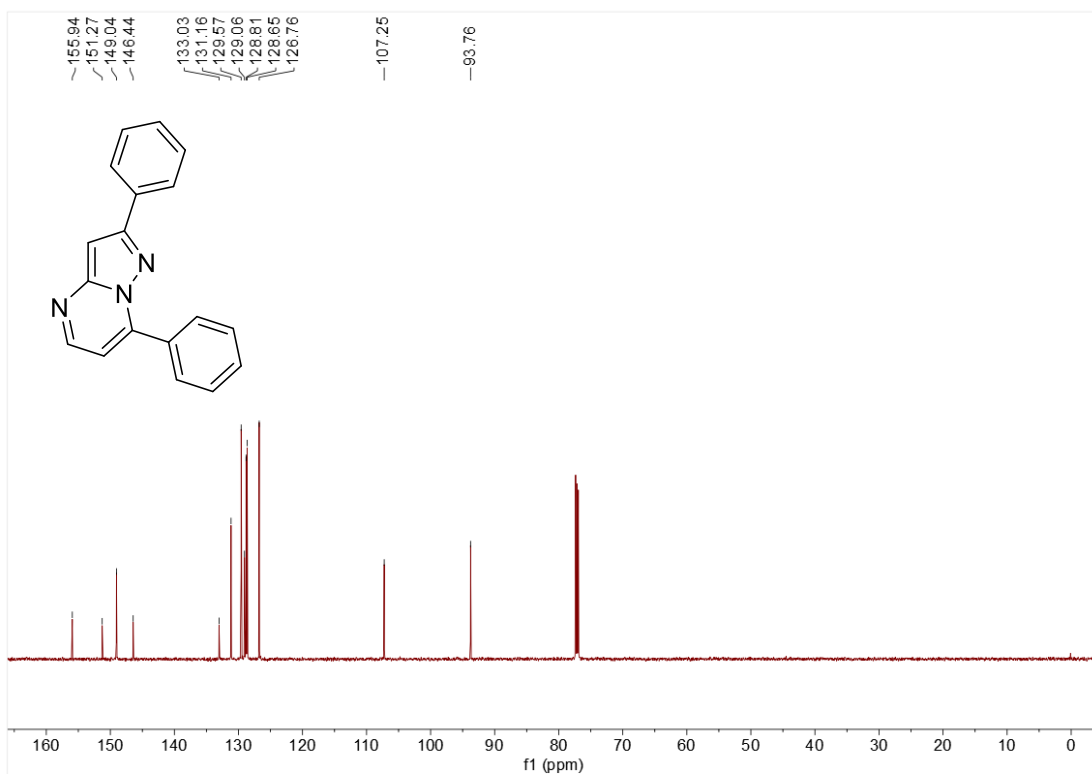
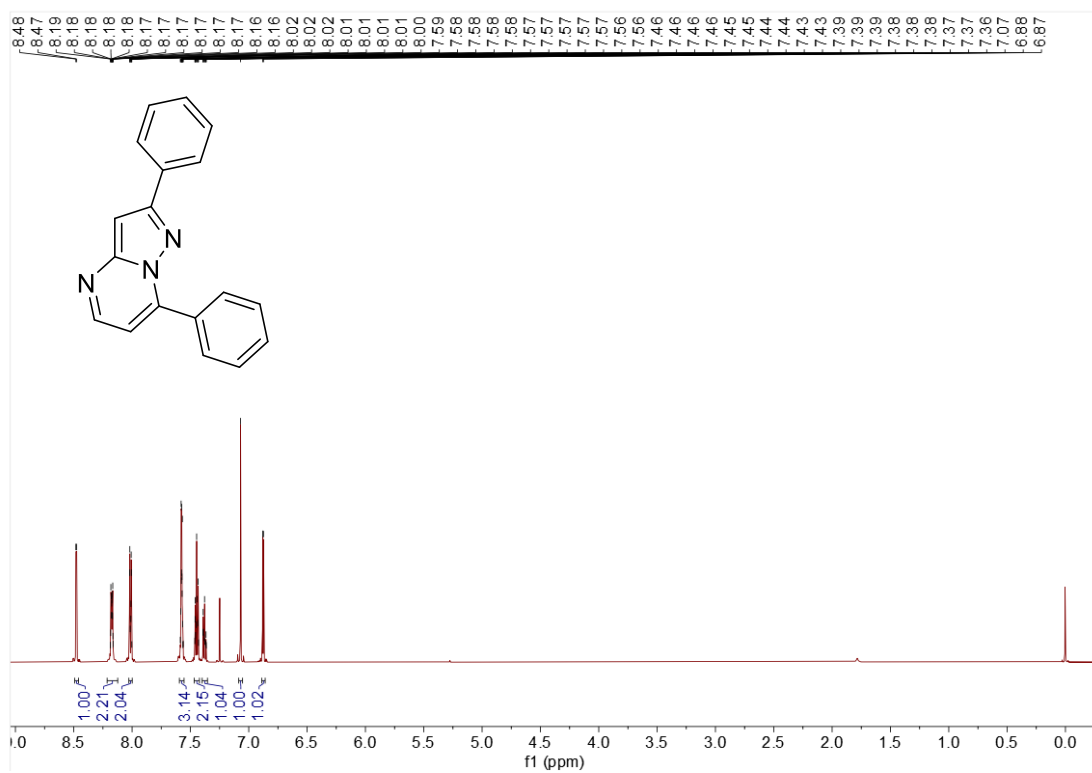
7-(*tert*-butyl)pyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**1s**)



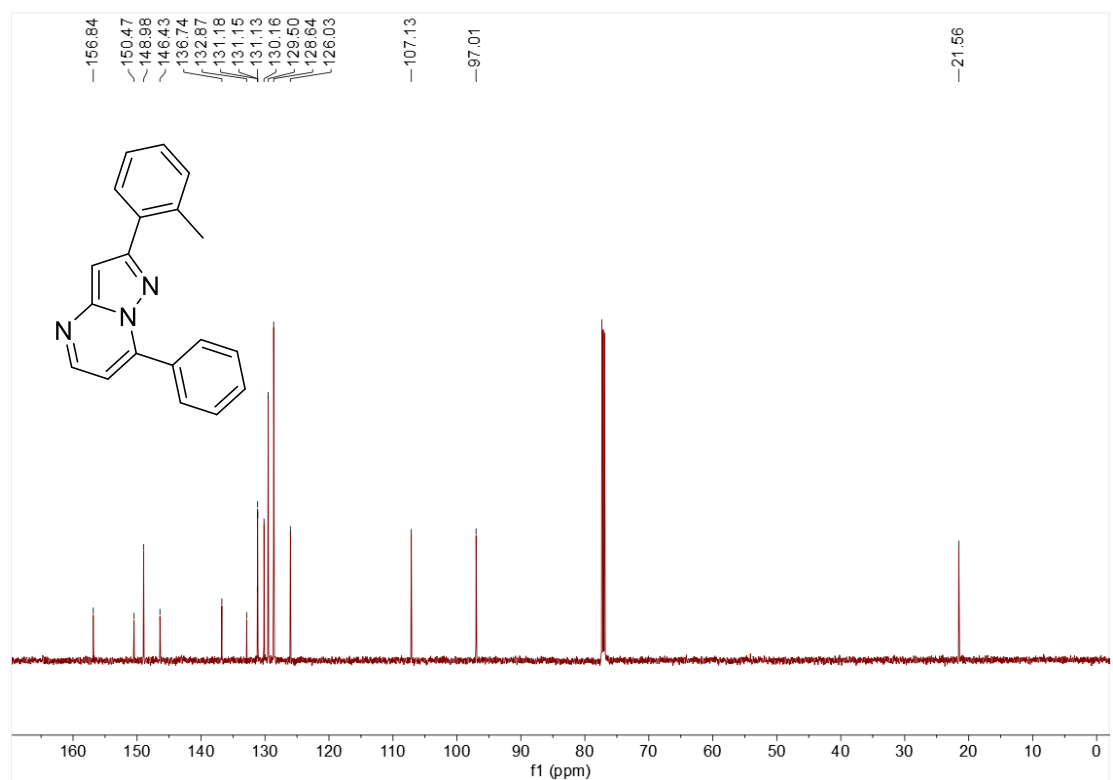
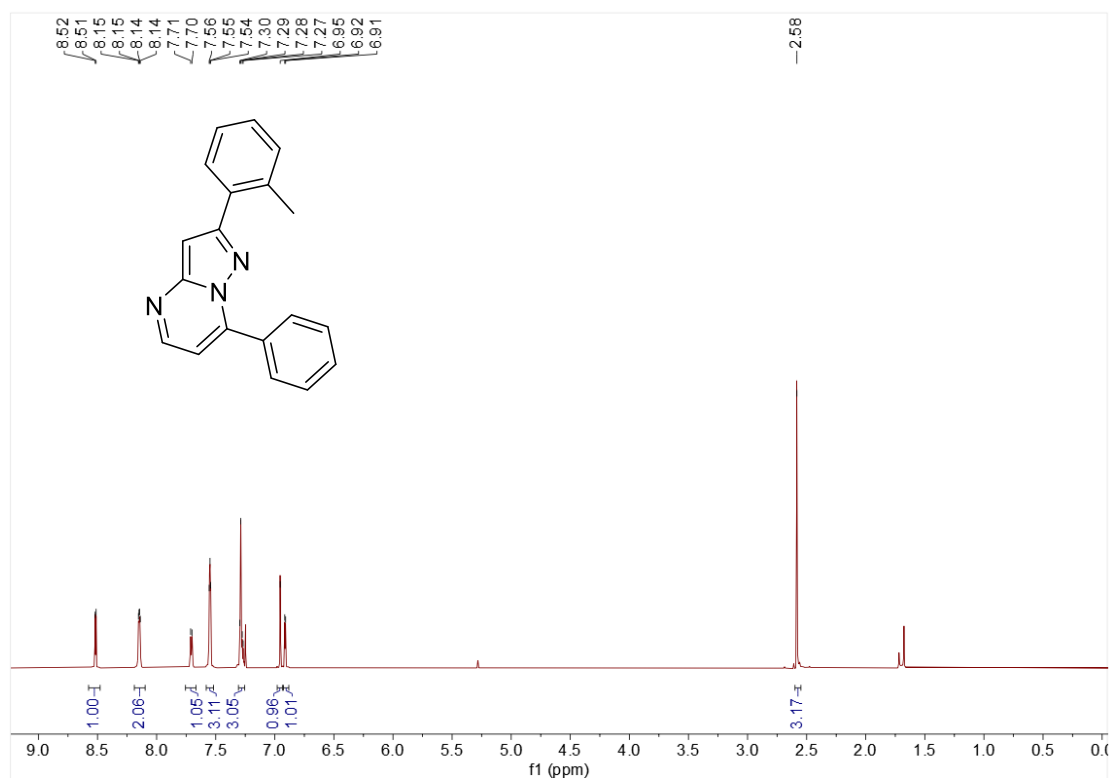
tert-butyl 4-(3-cyano-2-(4-phenoxyphenyl)pyrazolo[1,5-a]pyrimidin-7-yl)piperidine-1-carboxylate (**1t**)



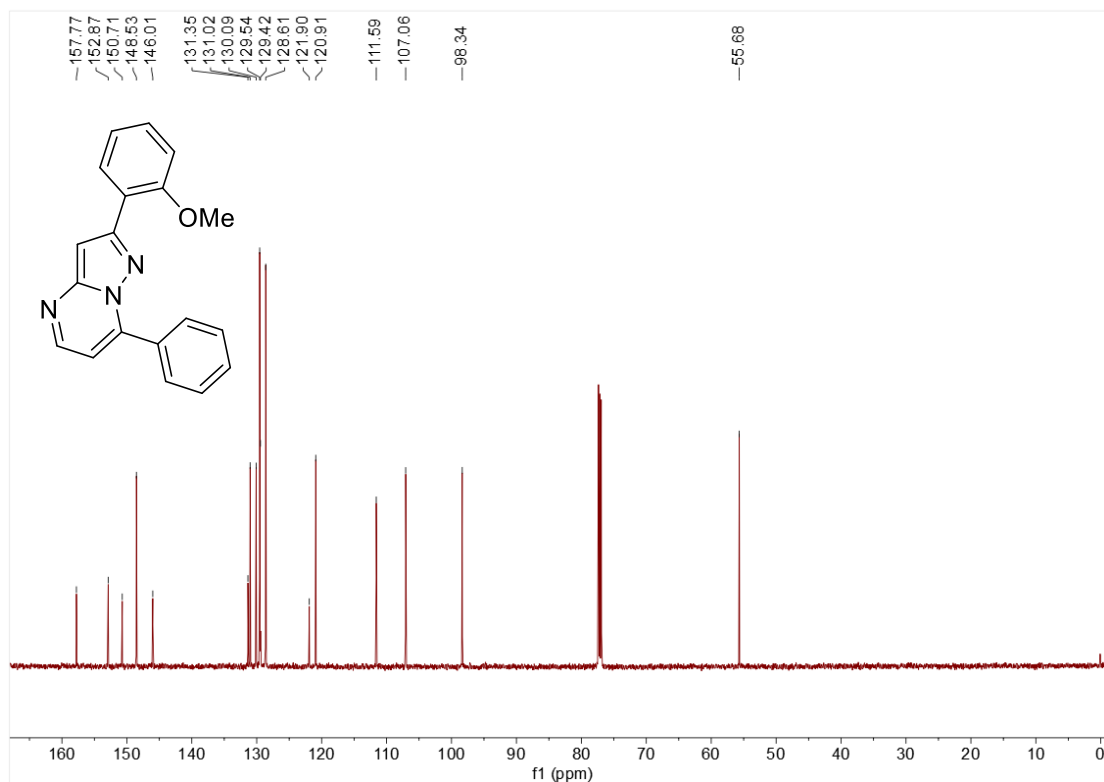
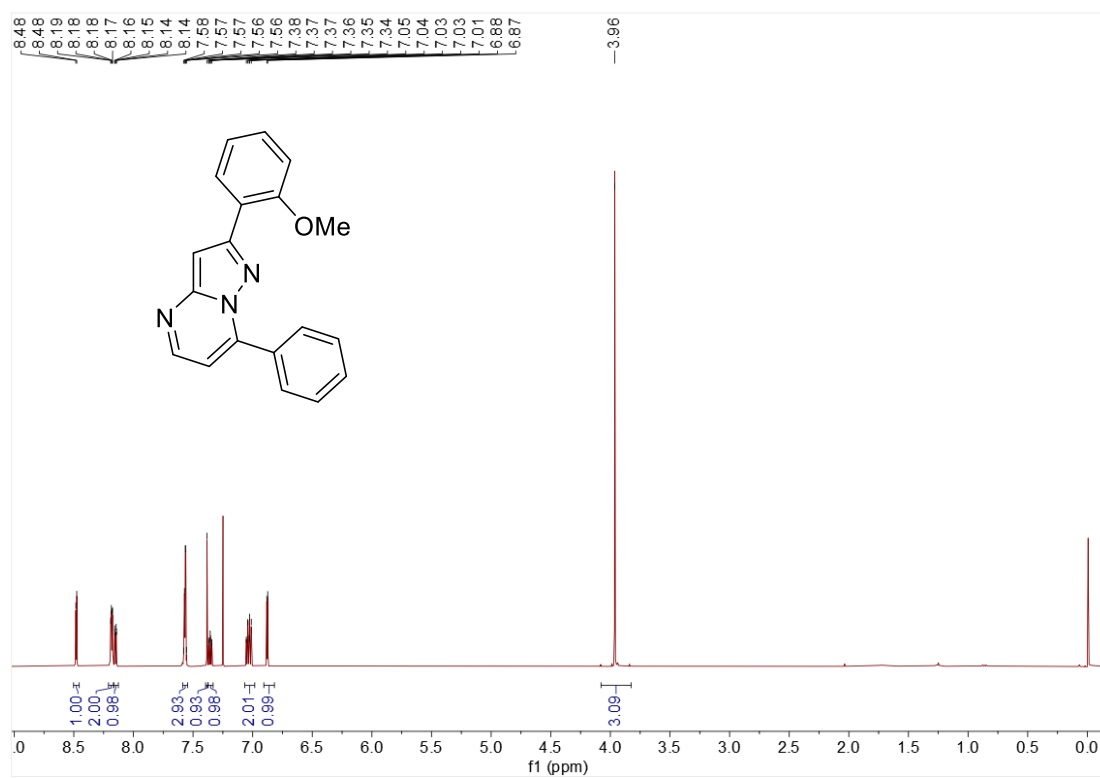
2,7-diphenylpyrazolo[1,5-a]pyrimidine (**3a**)



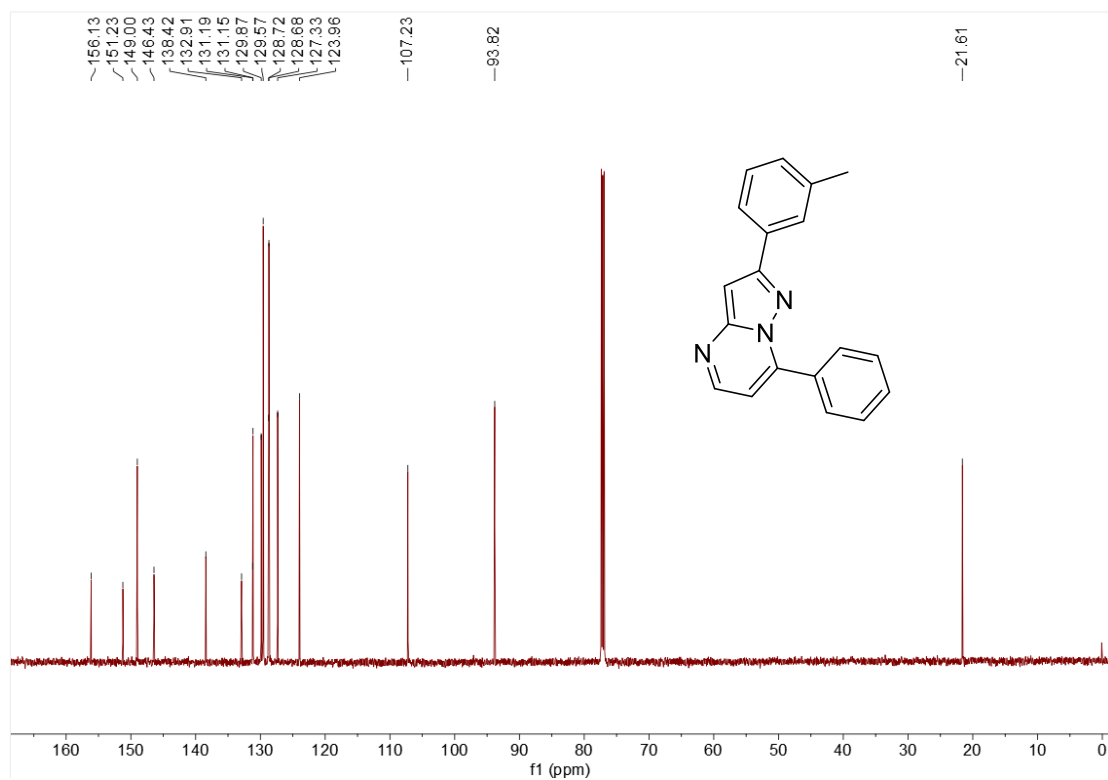
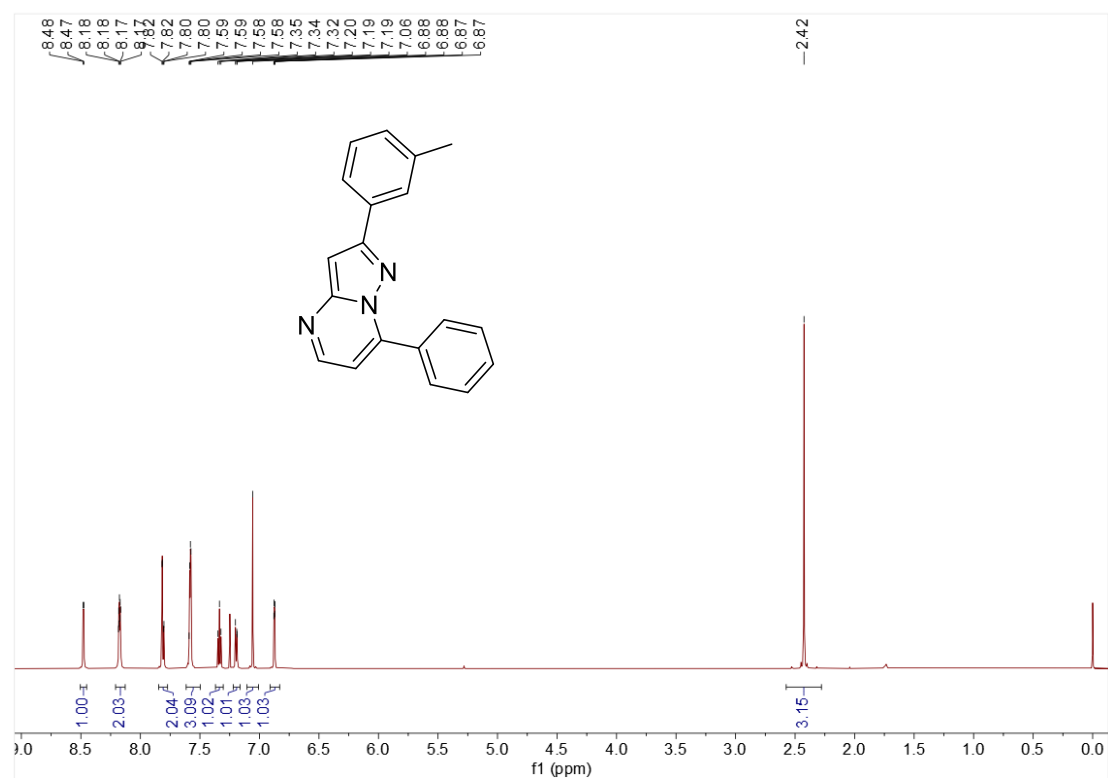
7-phenyl-2-(*o*-tolyl)pyrazolo[1,5-*a*]pyrimidine (**3b**)



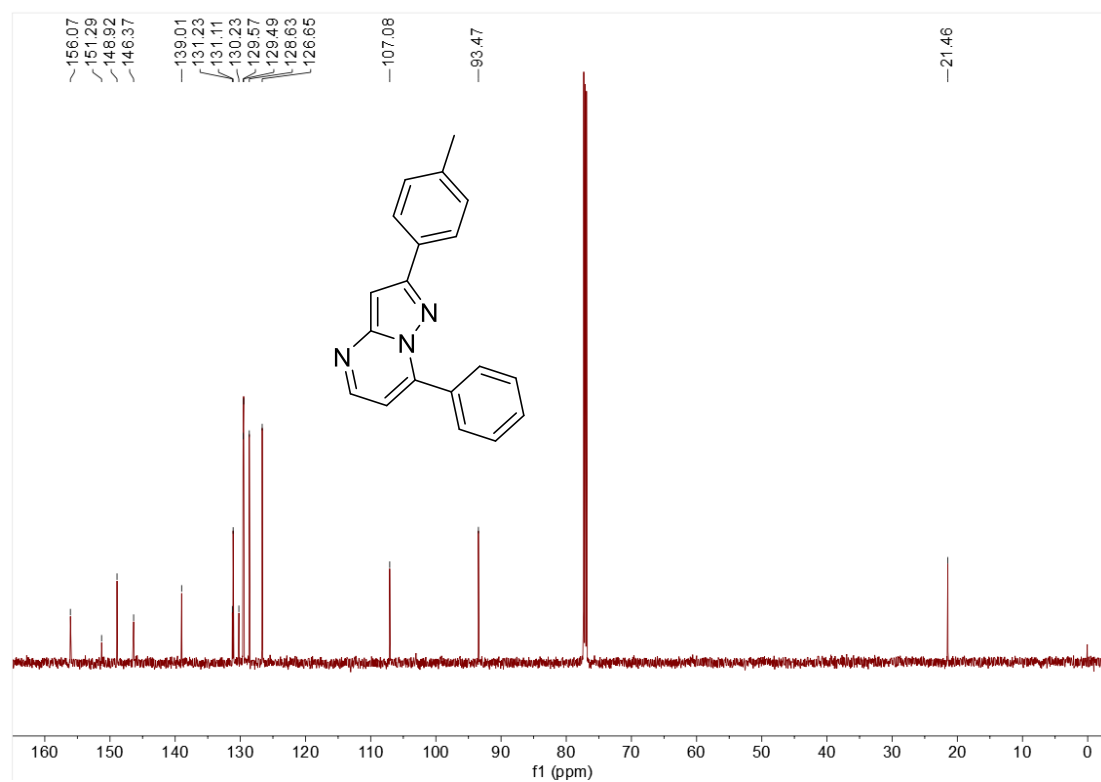
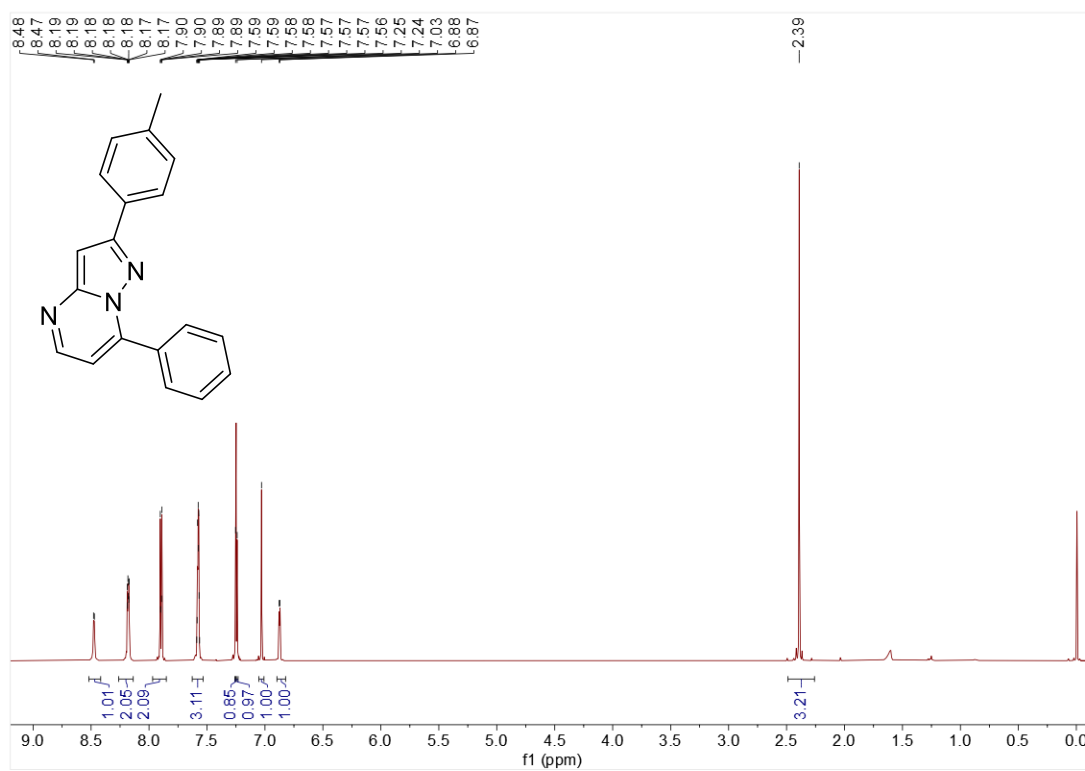
2-(2-methoxyphenyl)-7-phenylpyrazolo[1,5-a]pyrimidine (**3c**)



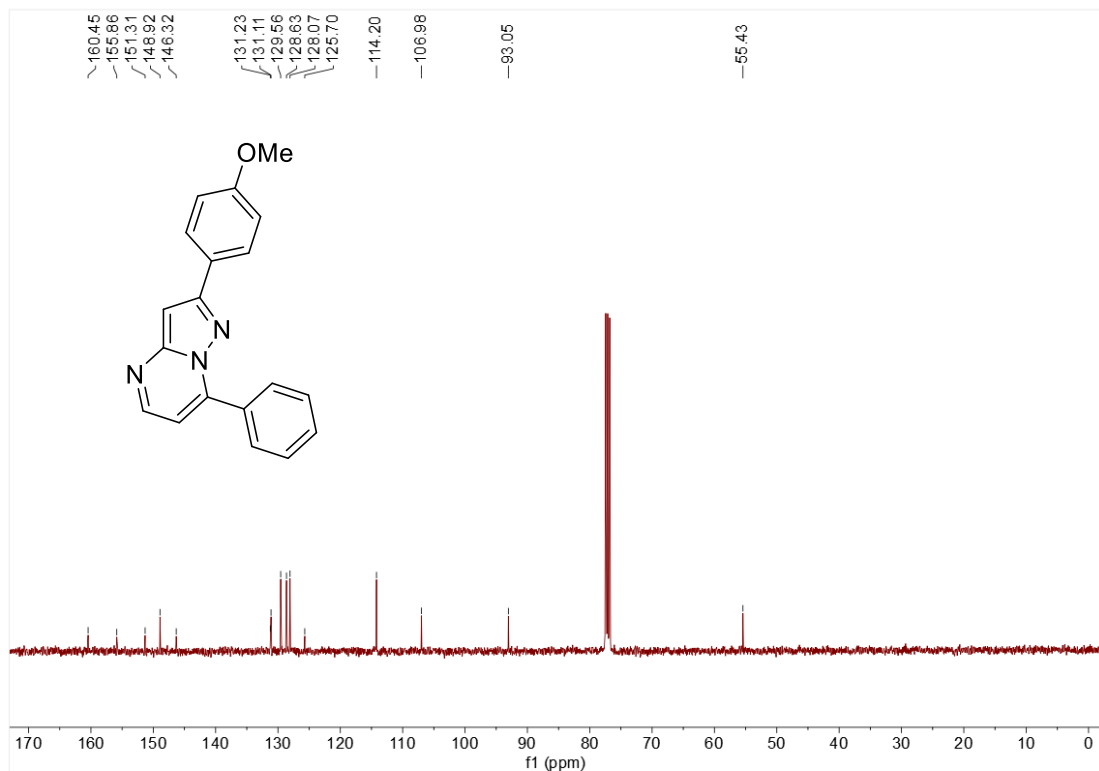
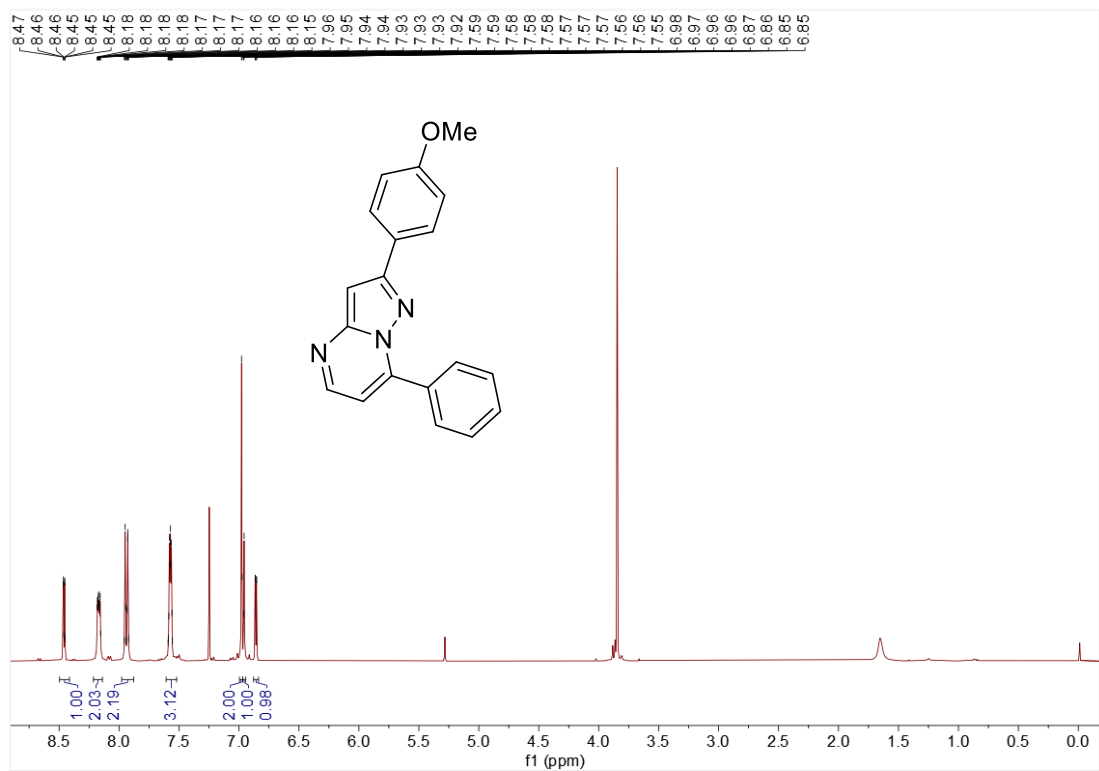
7-phenyl-2-(*m*-tolyl)pyrazolo[1,5-*a*]pyrimidine (**3d**)



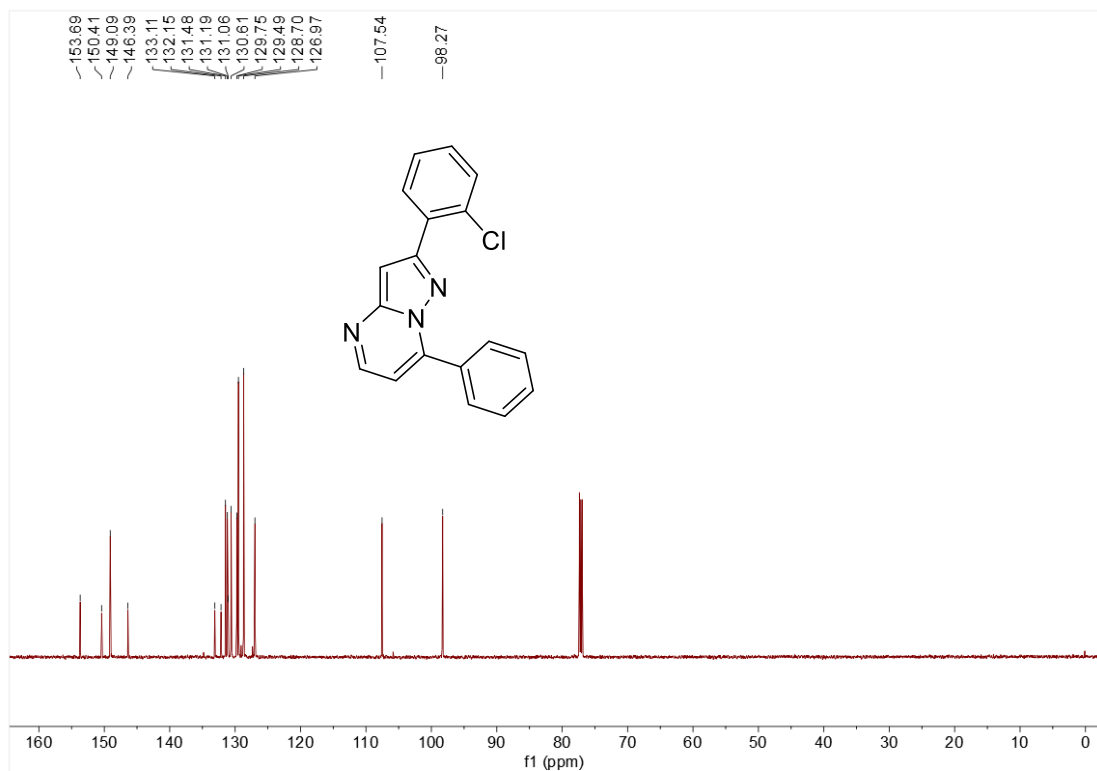
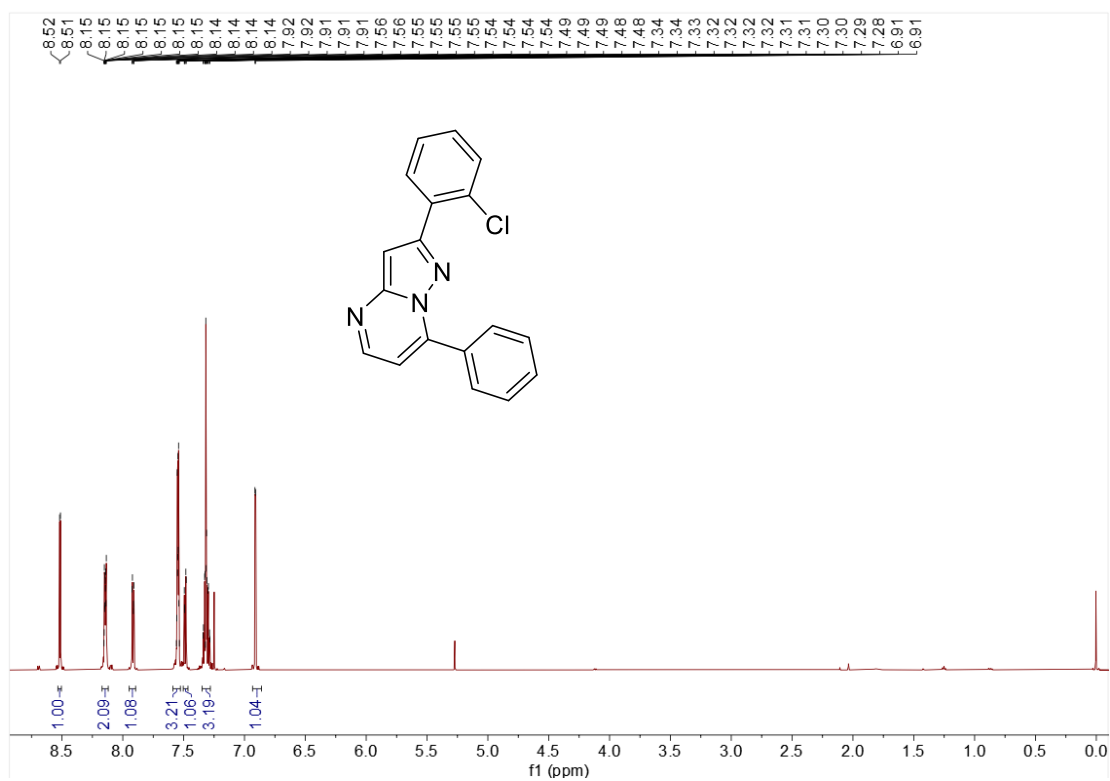
7-phenyl-2-(*p*-tolyl)pyrazolo[1,5-*a*]pyrimidine (**3e**)



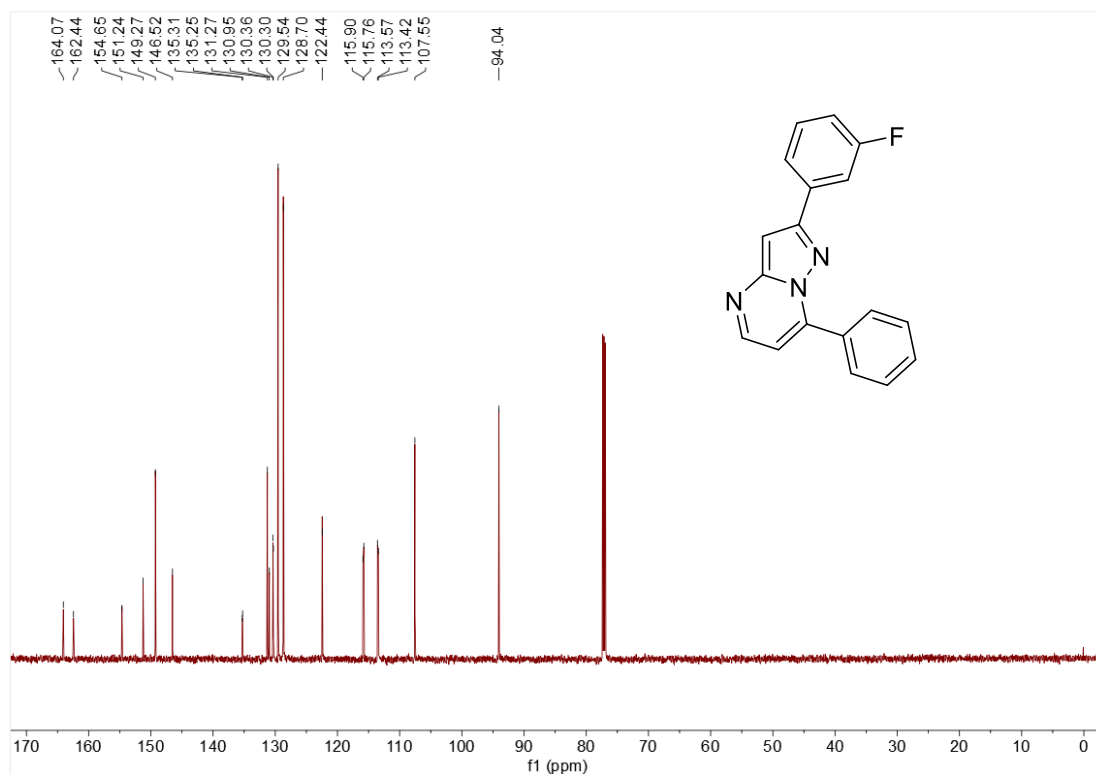
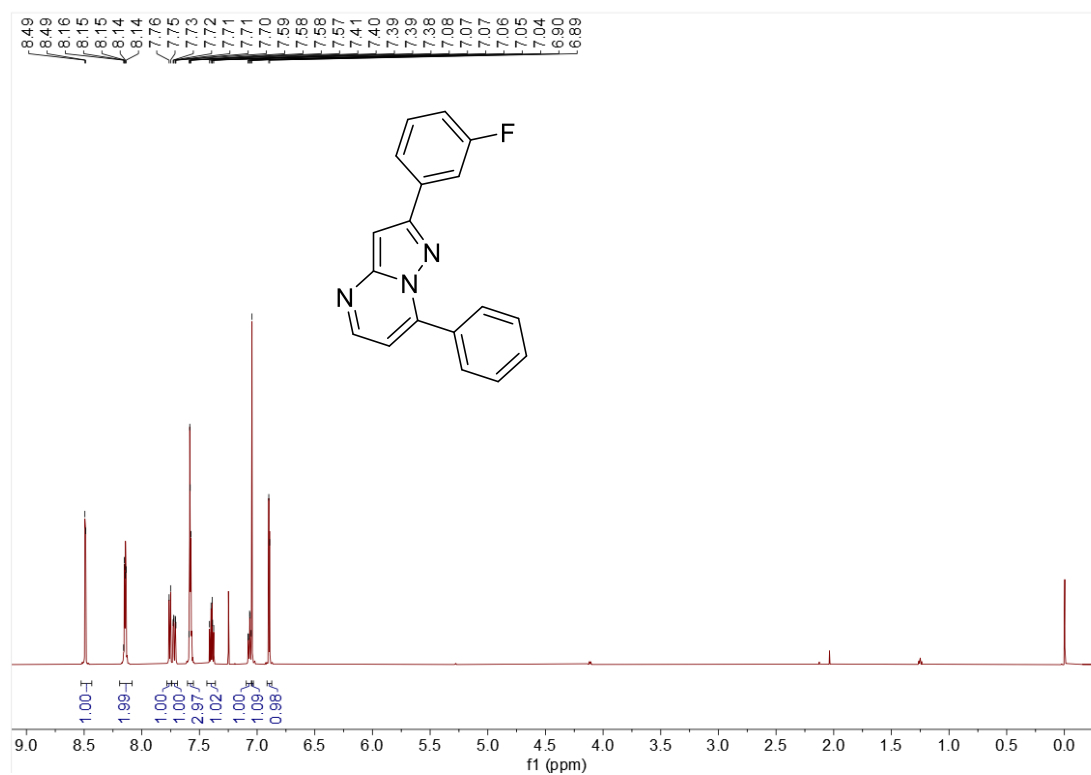
2-(4-methoxyphenyl)-7-phenylpyrazolo[1,5-a]pyrimidine (**3f**)



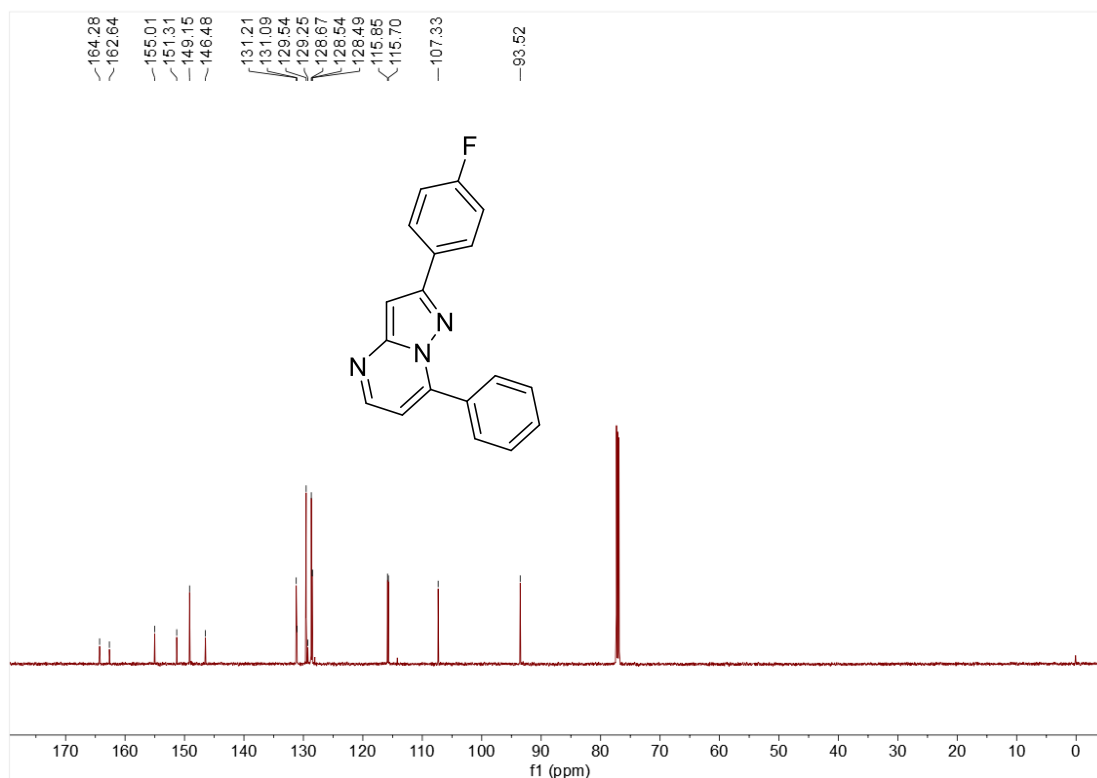
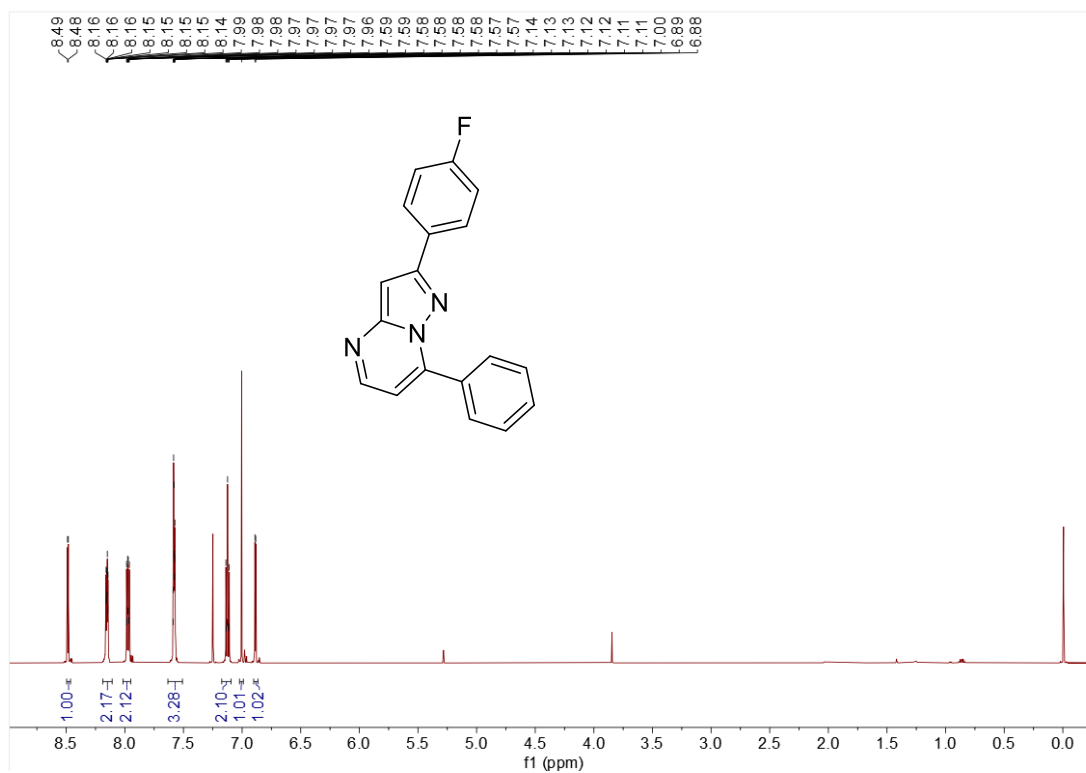
2-(2-chlorophenyl)-7-phenylpyrazolo[1,5-a]pyrimidine (**3g**)



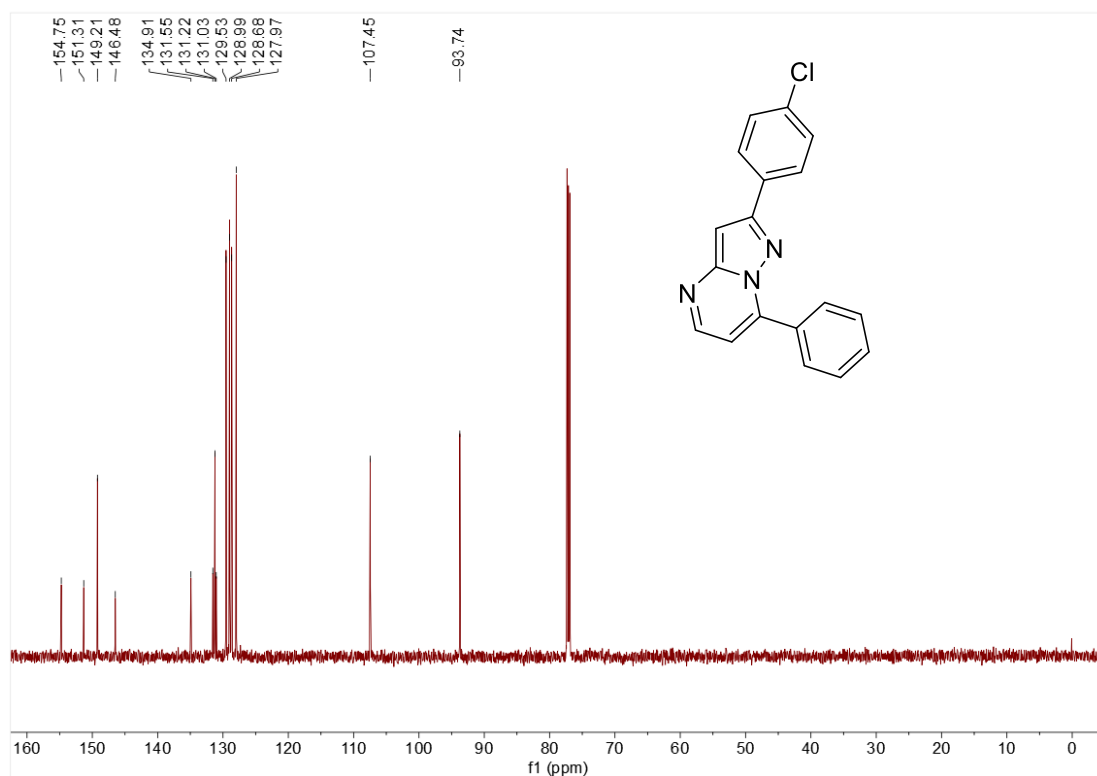
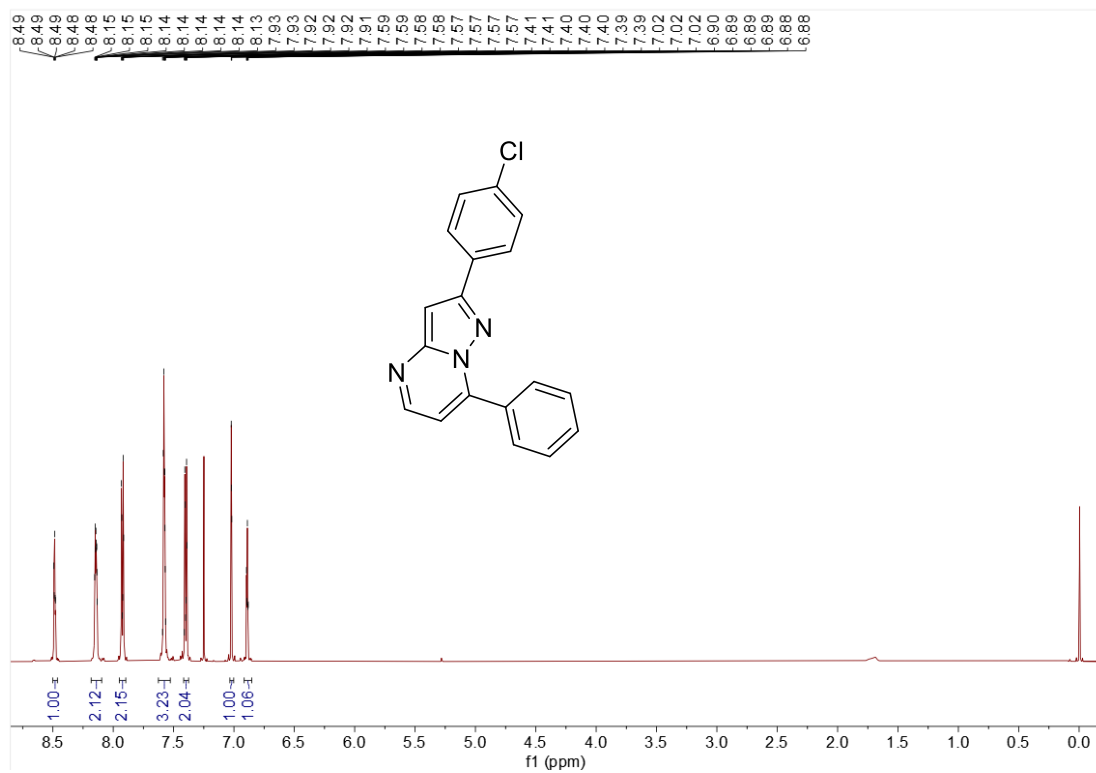
2-(3-fluorophenyl)-7-phenylpyrazolo[1,5-a]pyrimidine (**3h**)



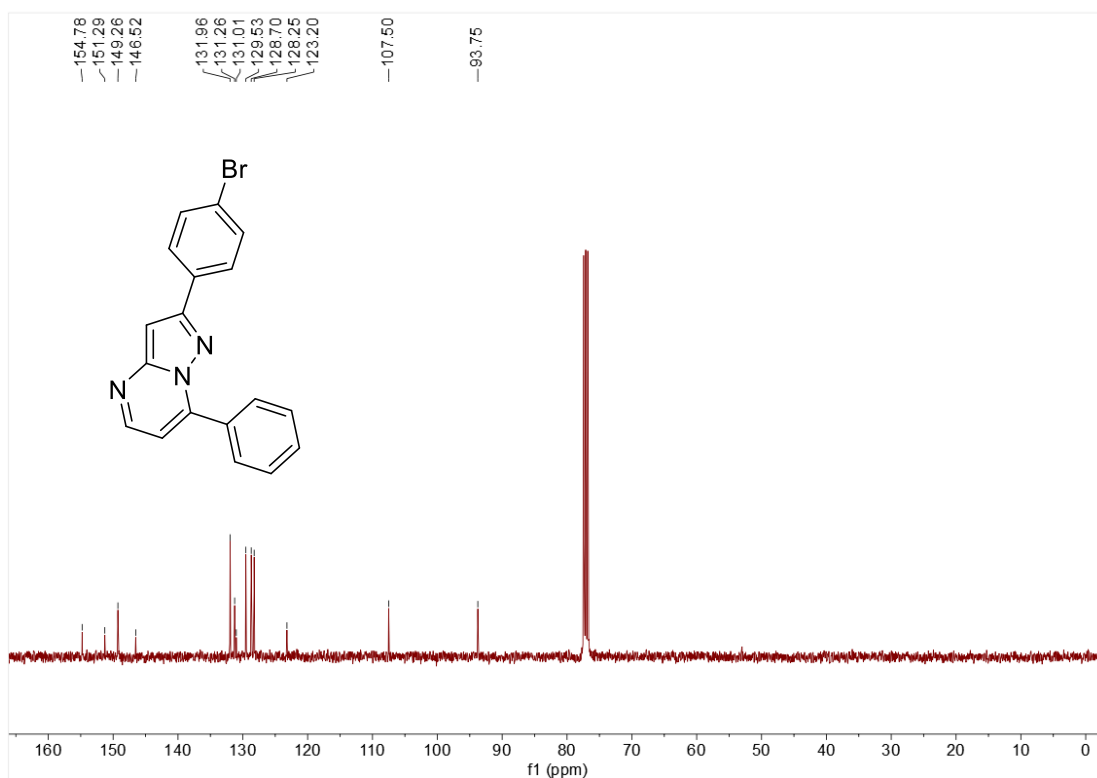
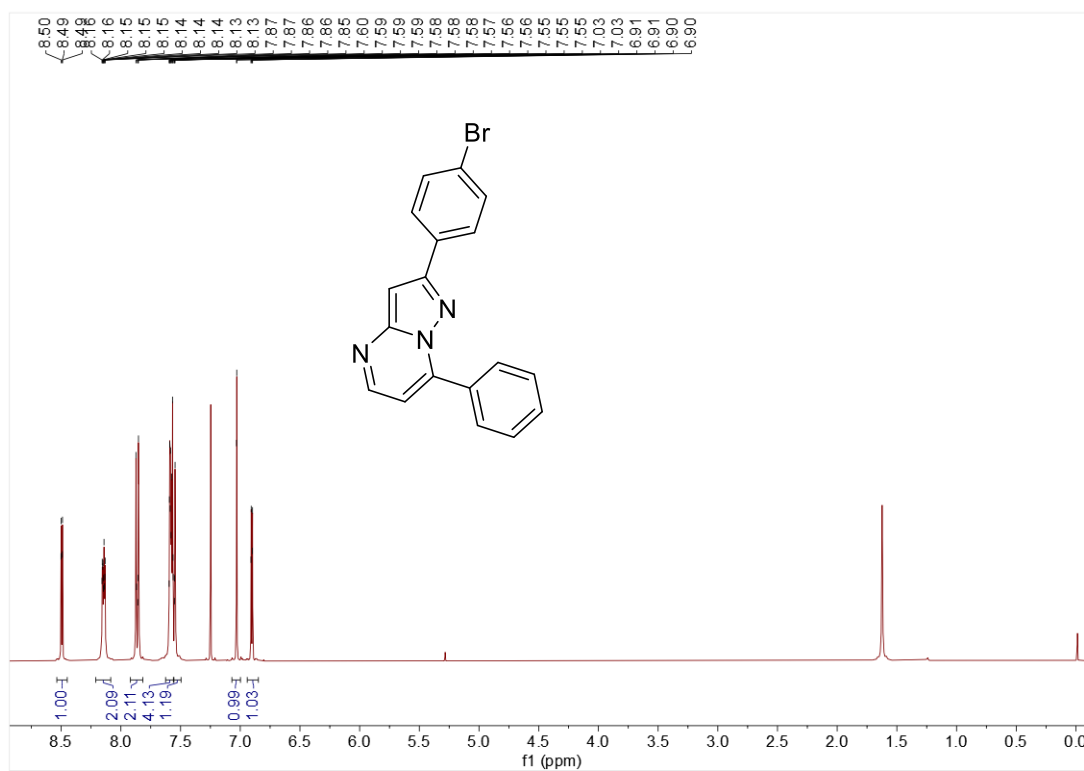
2-(4-fluorophenyl)-7-phenylpyrazolo[1,5-a]pyrimidine (**3i**)



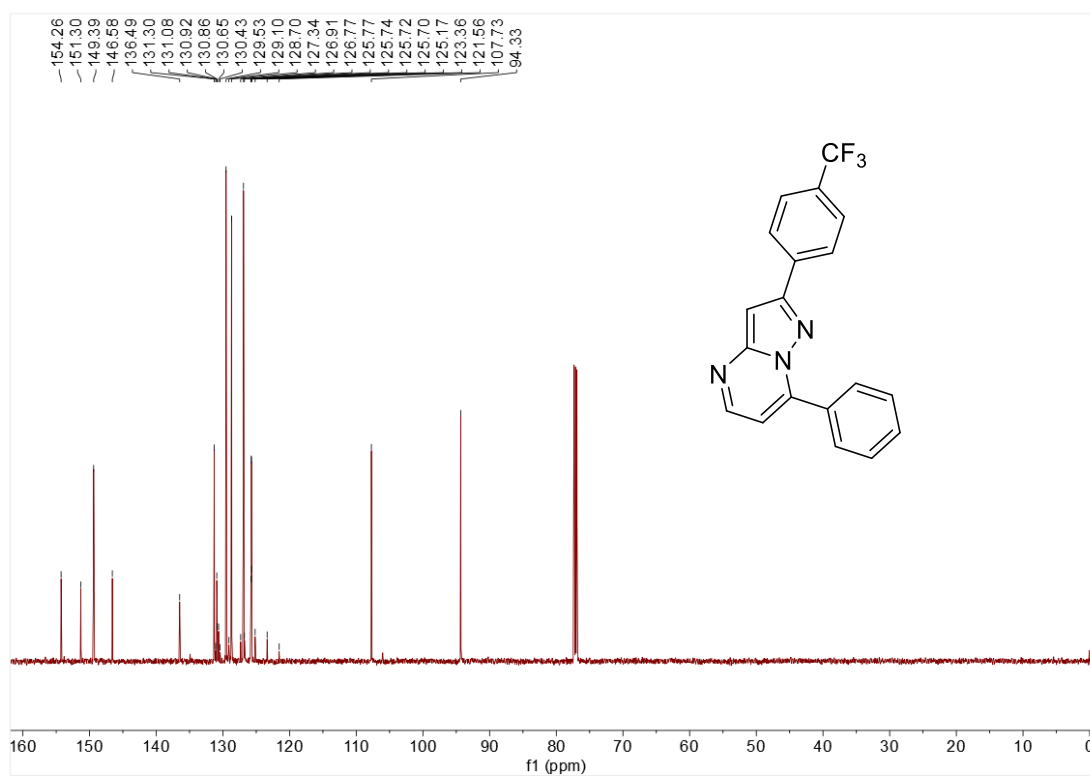
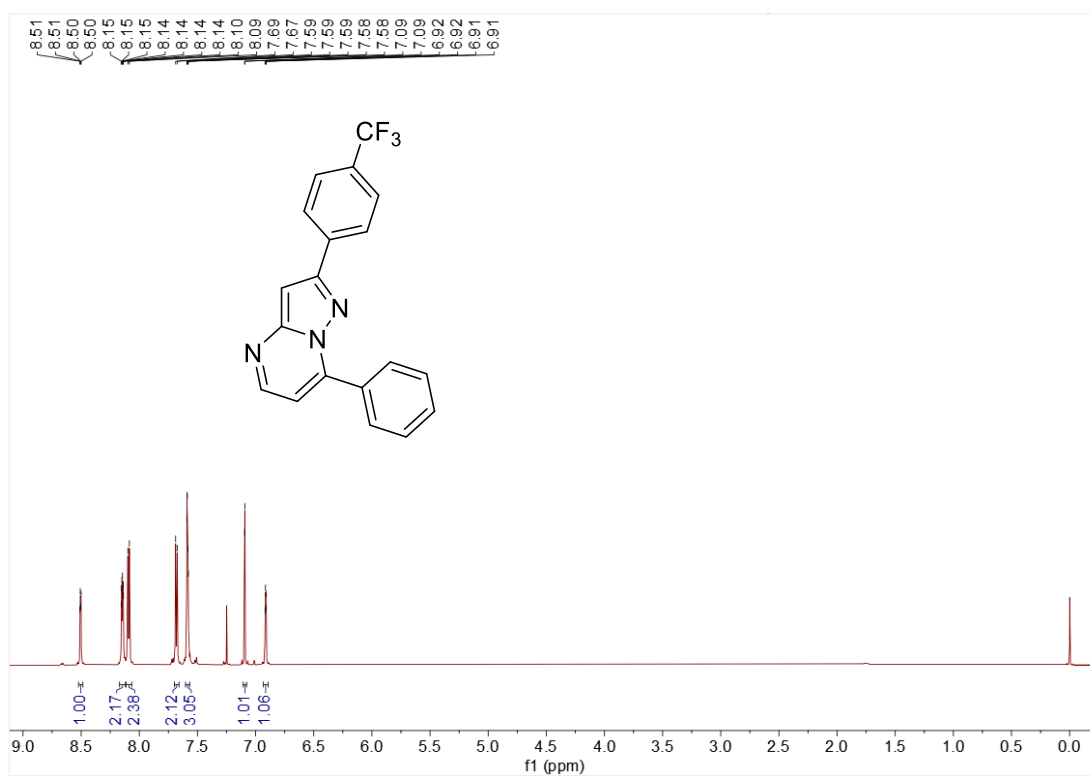
2-(4-chlorophenyl)-7-phenylpyrazolo[1,5-a]pyrimidine (**3j**)



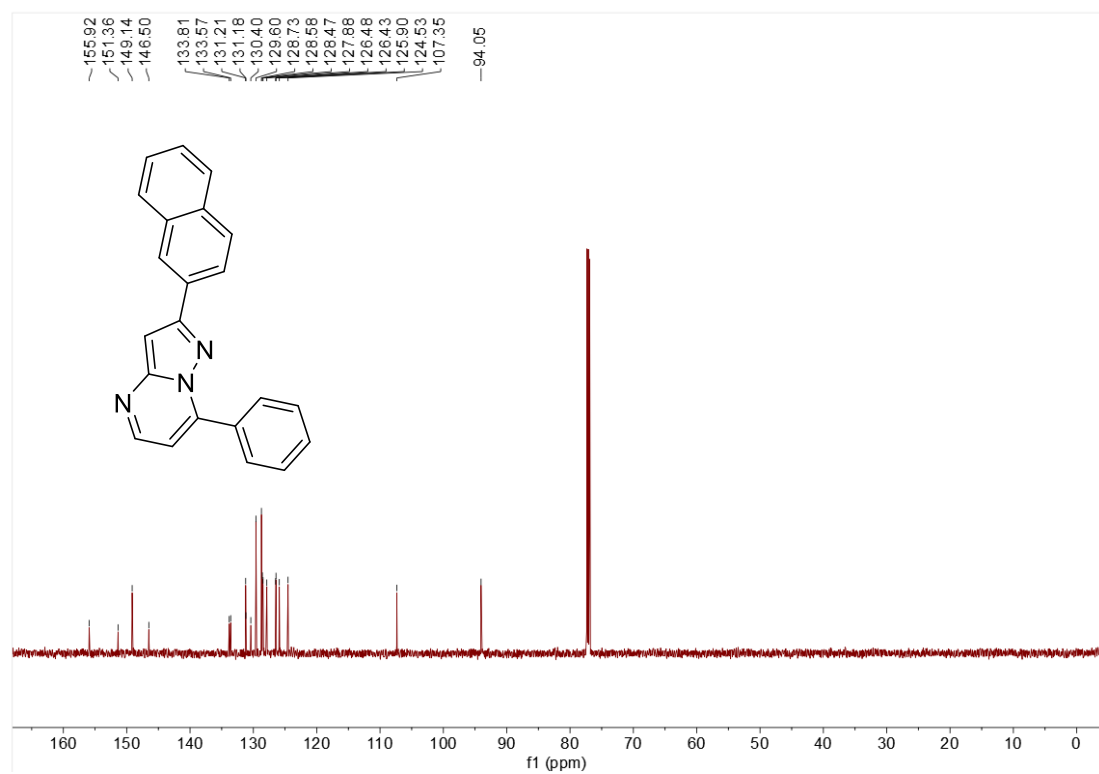
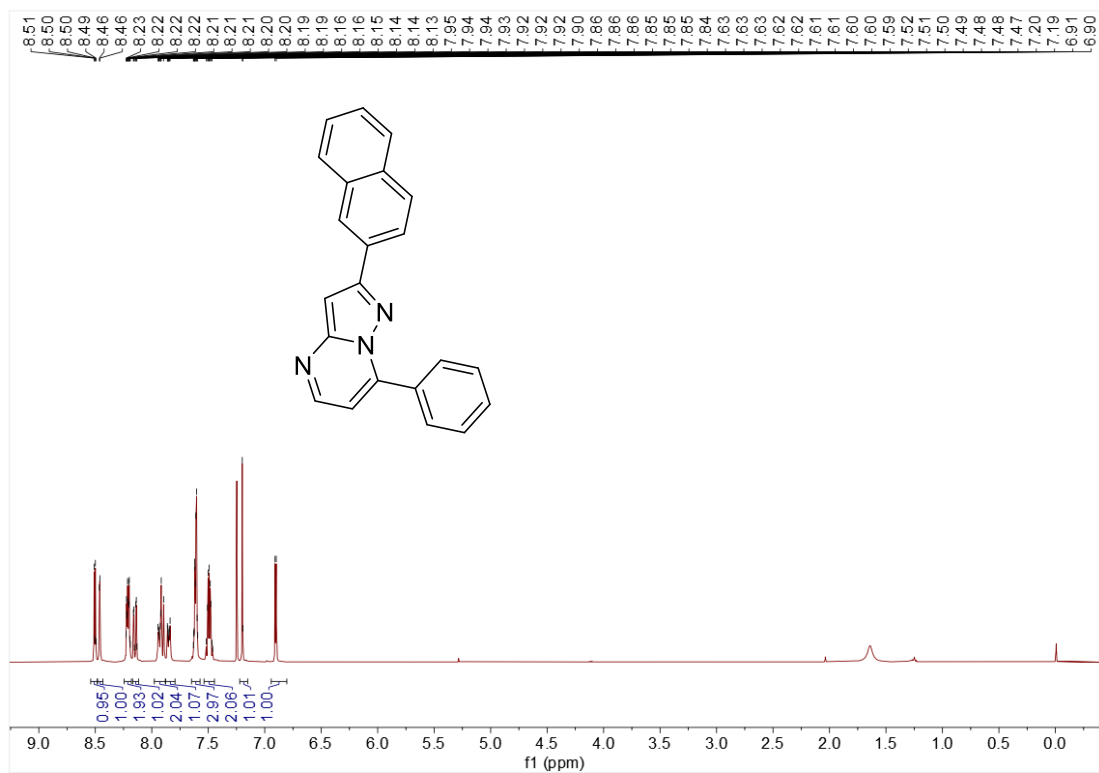
2-(4-bromophenyl)-7-phenylpyrazolo[1,5-a]pyrimidine (**3k**)



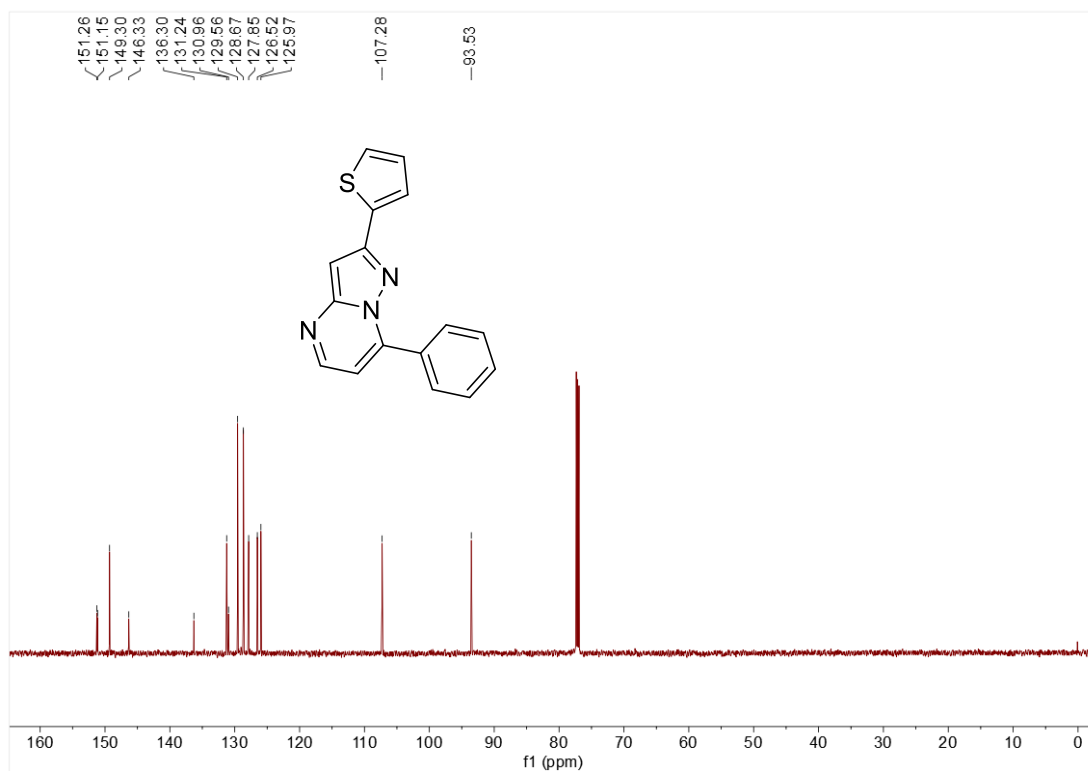
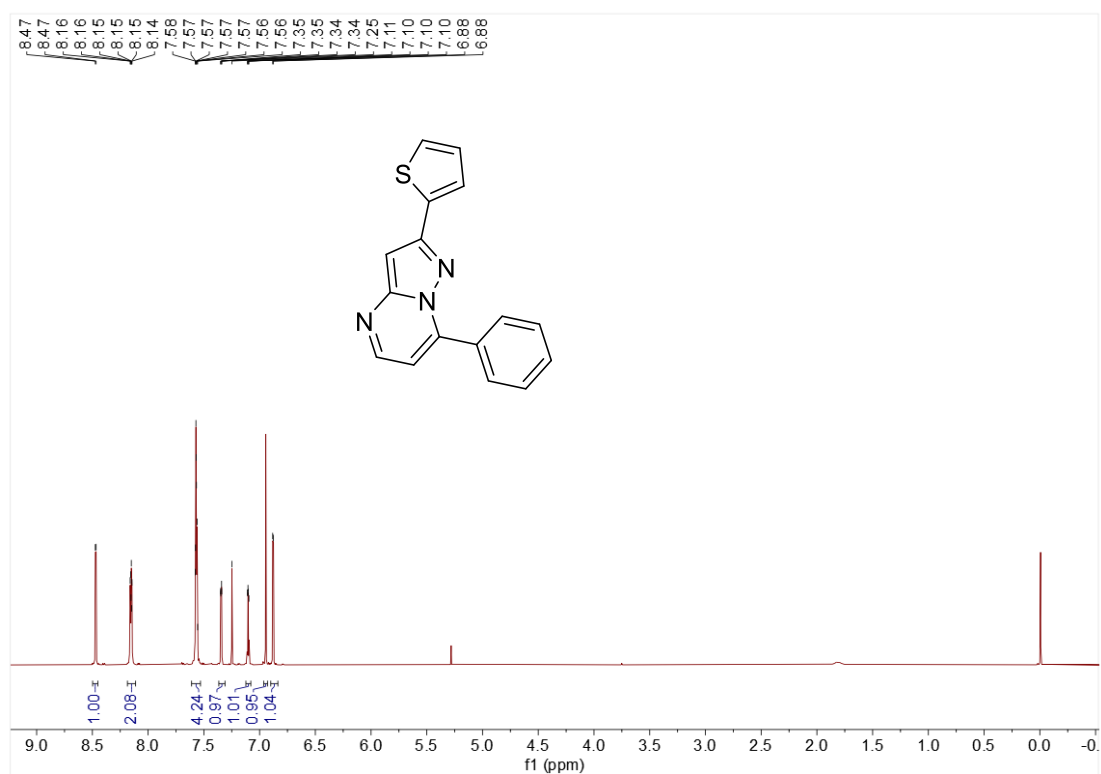
7-phenyl-2-(4-(trifluoromethyl)phenyl)pyrazolo[1,5-a]pyrimidine (**31**)



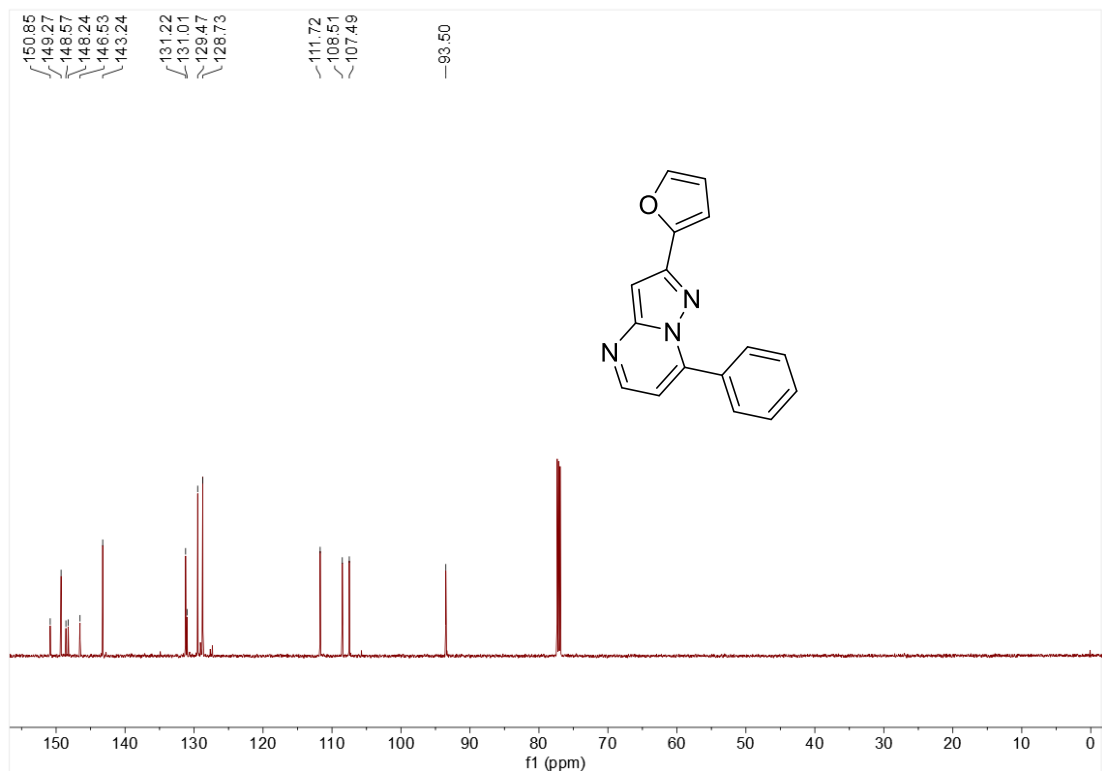
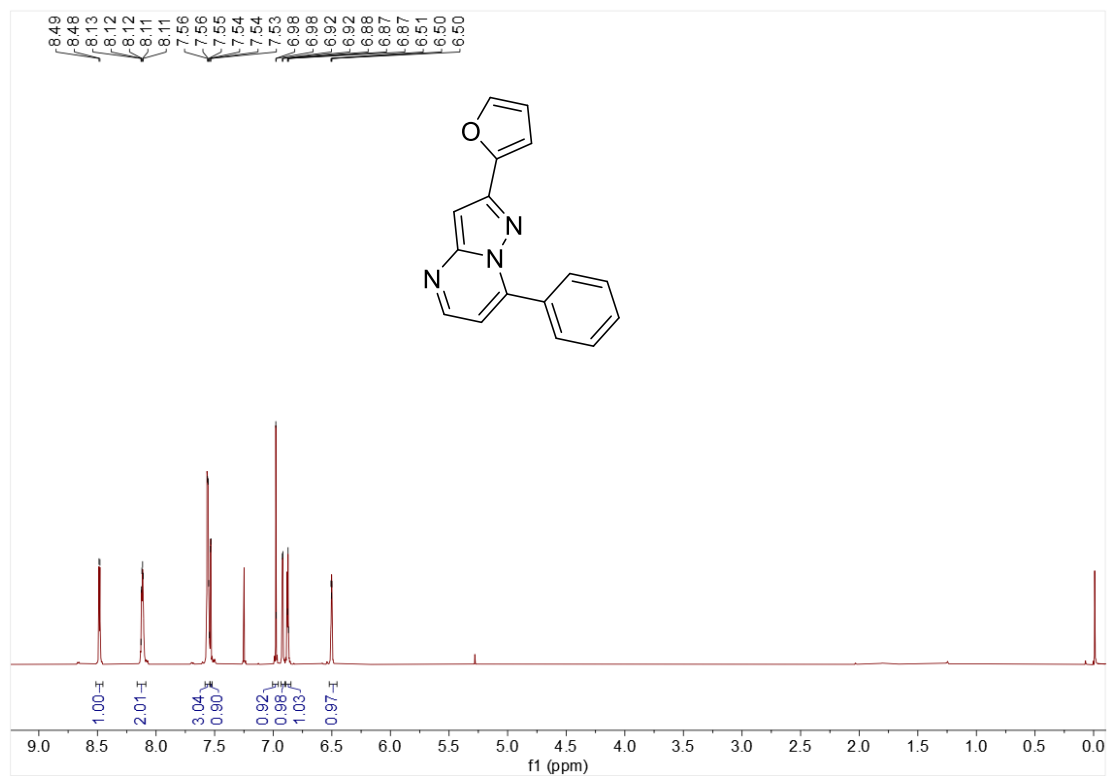
2-(naphthalen-2-yl)-7-phenylpyrazolo[1,5-a]pyrimidine (**3m**)



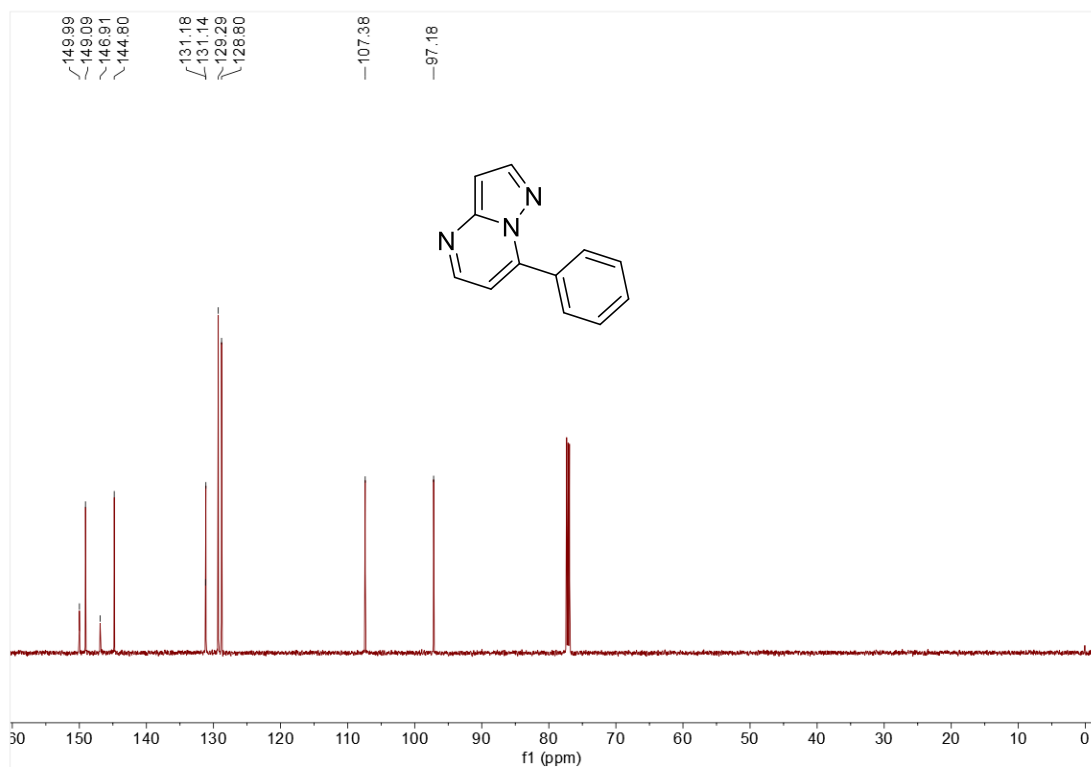
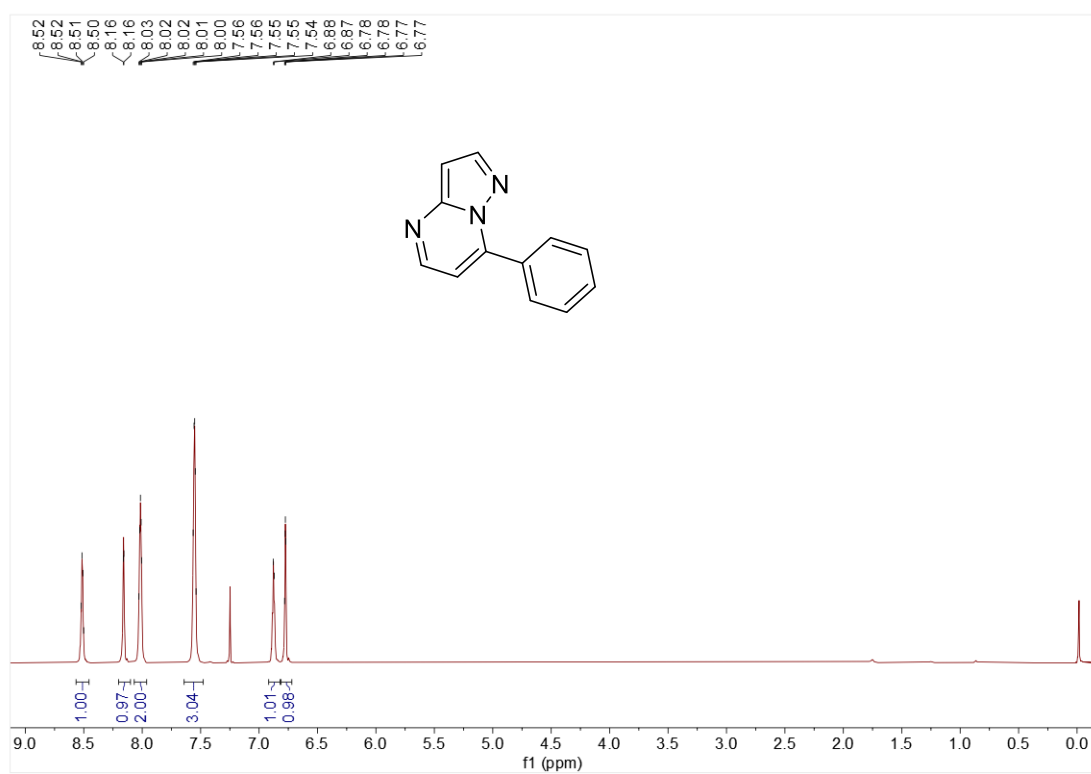
7-phenyl-2-(thiophen-2-yl)pyrazolo[1,5-a]pyrimidine (**3n**)



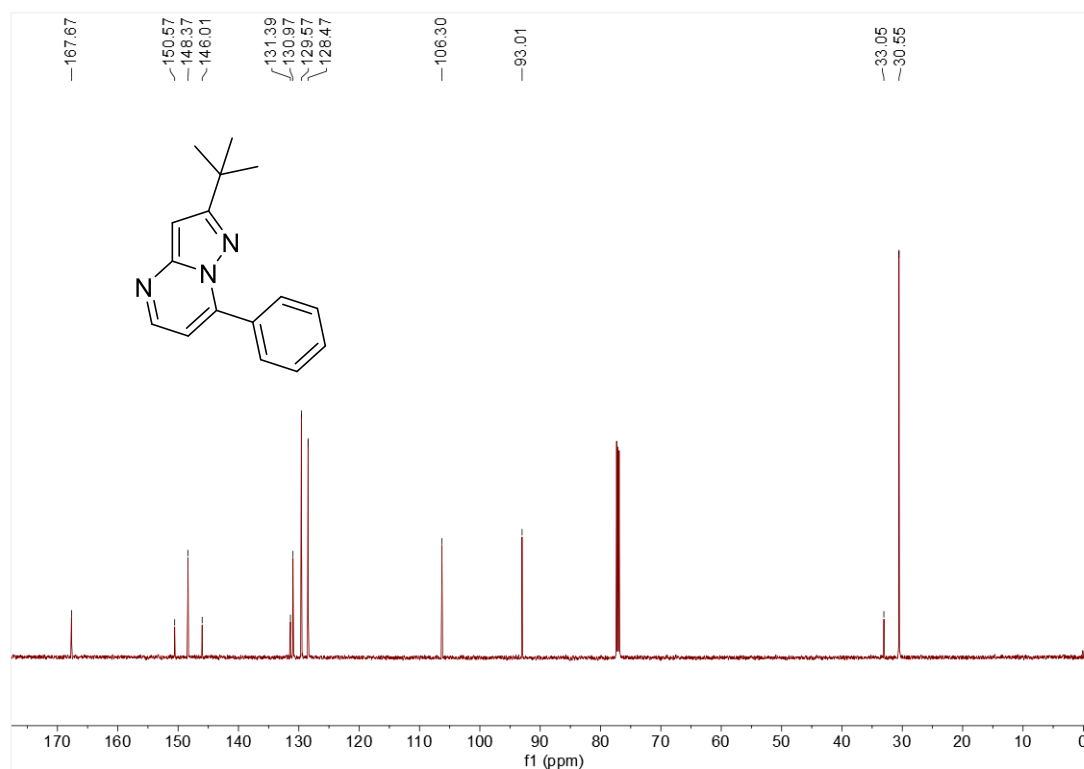
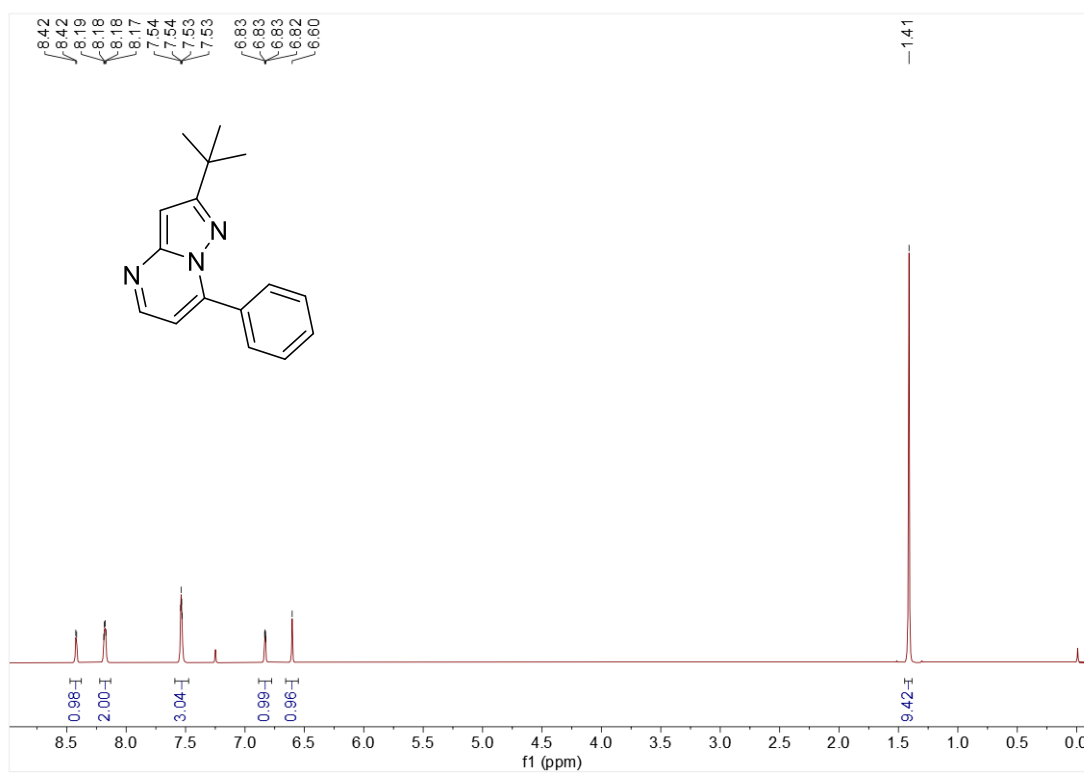
2-(furan-2-yl)-7-phenylpyrazolo[1,5-a]pyrimidine (**30**)



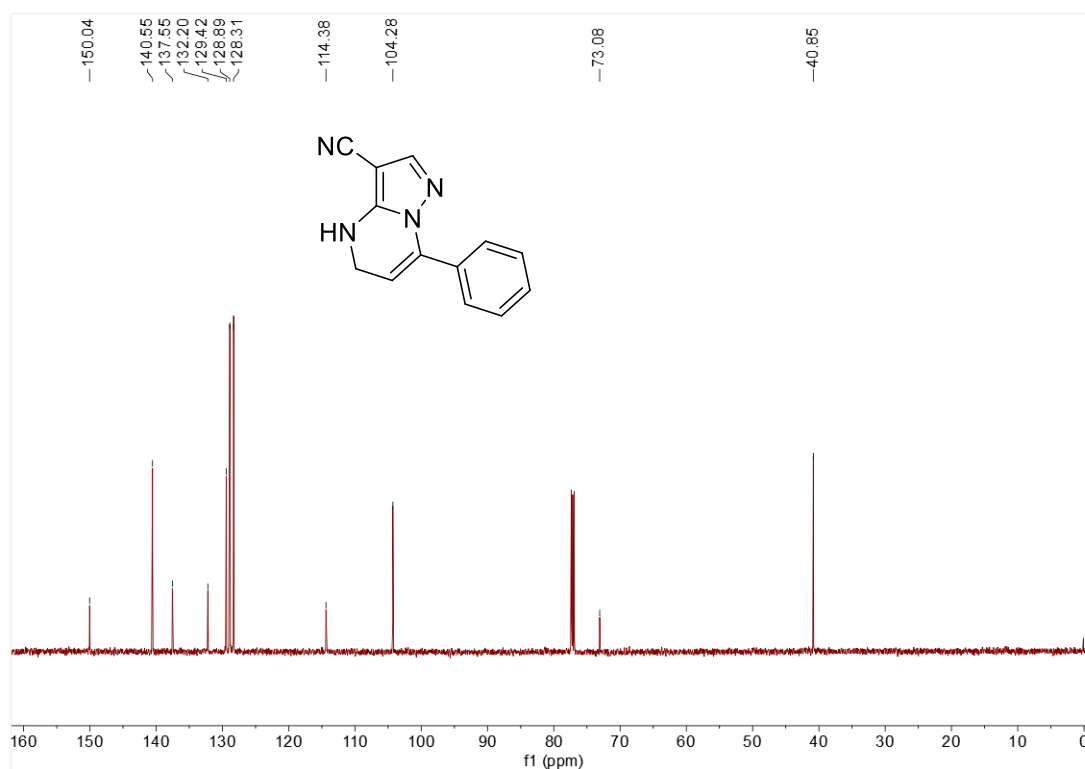
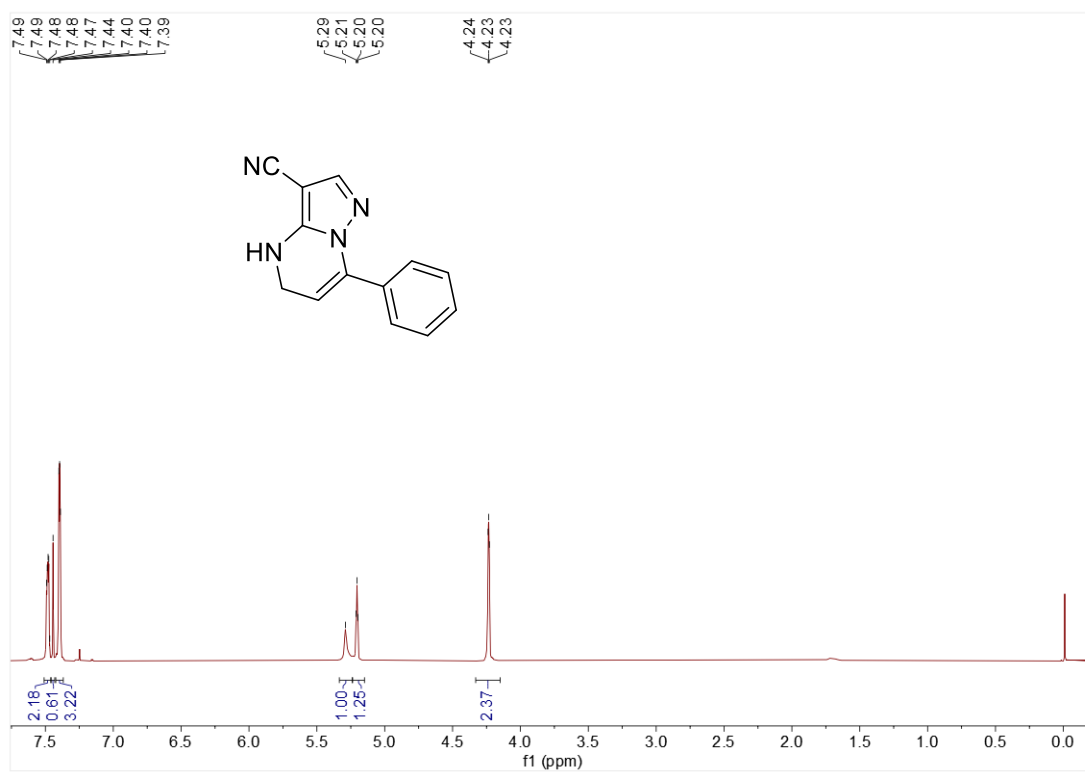
7-phenylpyrazolo[1,5-a]pyrimidine (**3p**)



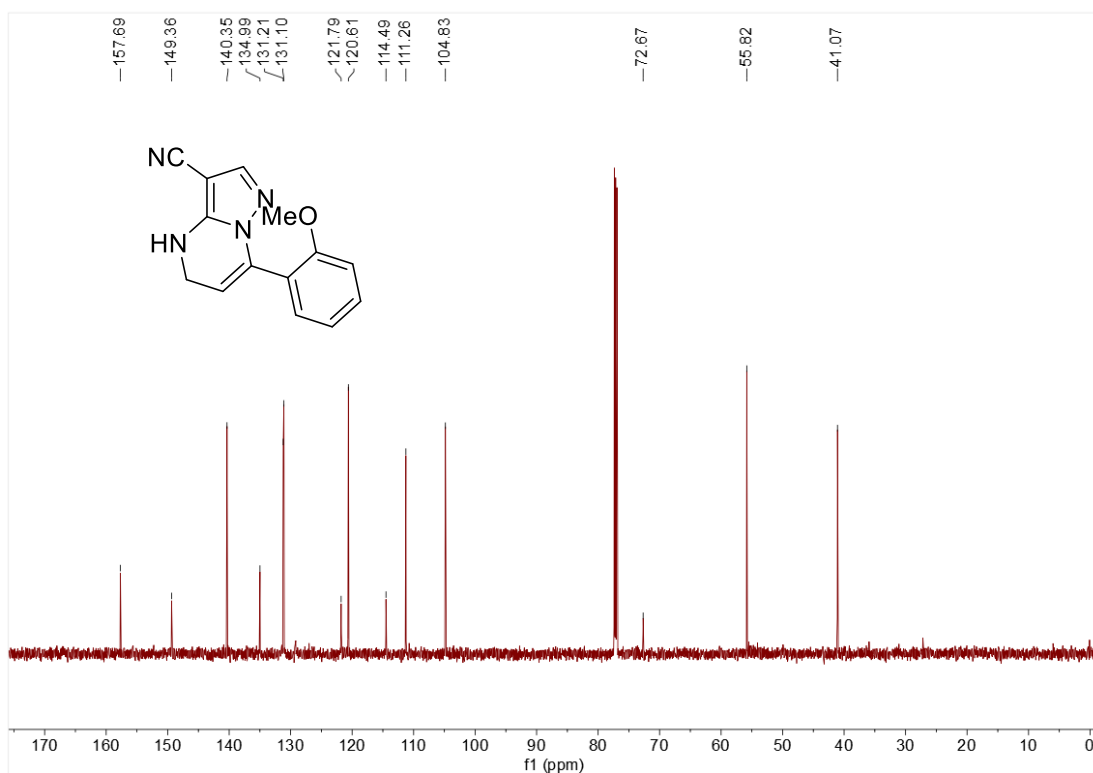
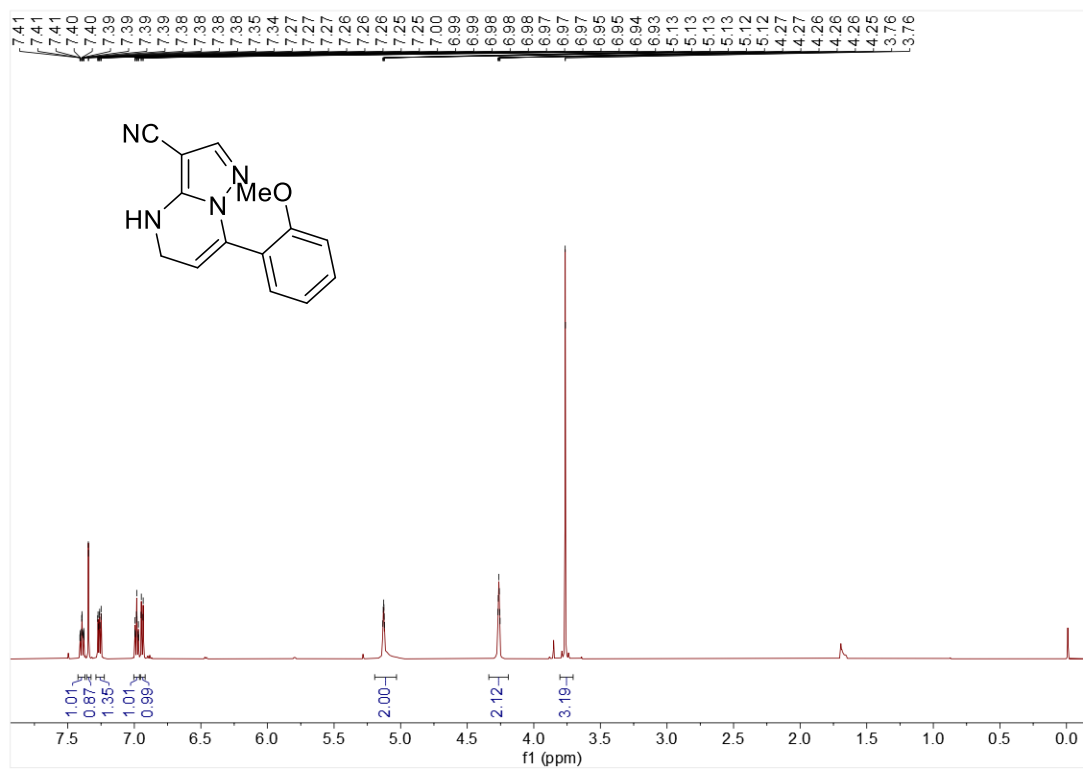
2-(*tert*-butyl)-7-phenylpyrazolo[1,5-*a*]pyrimidine (**3q**)



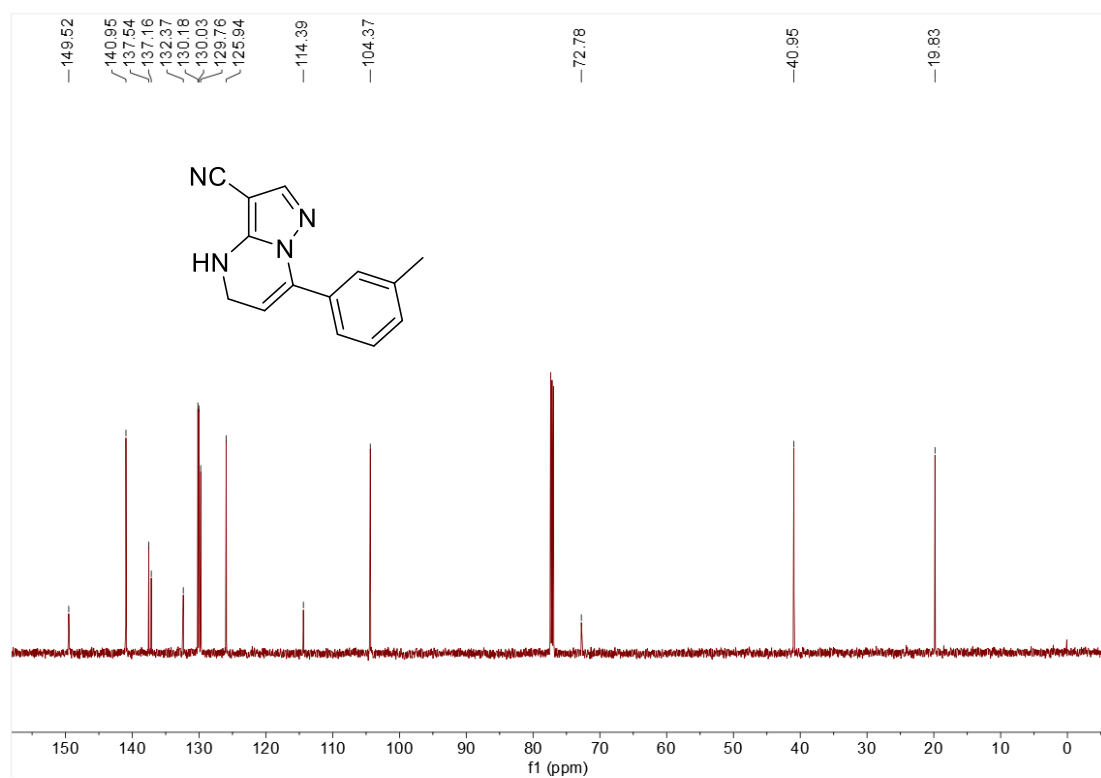
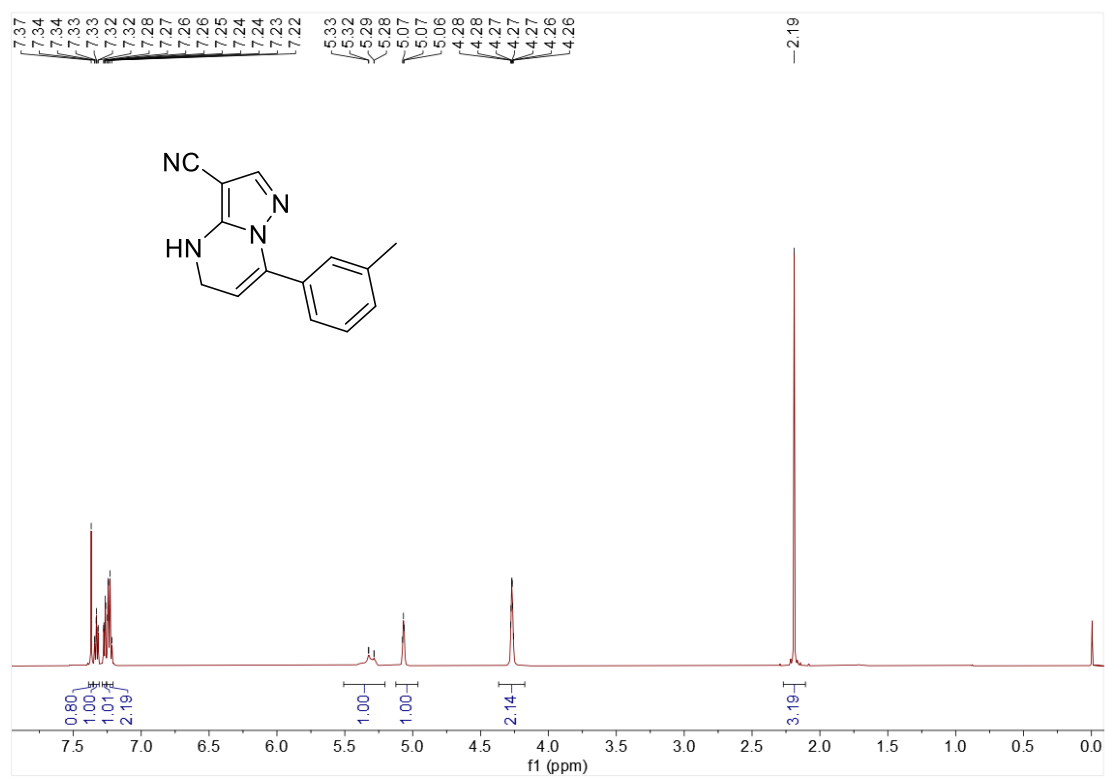
7-phenyl-4,5-dihydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**5a**)



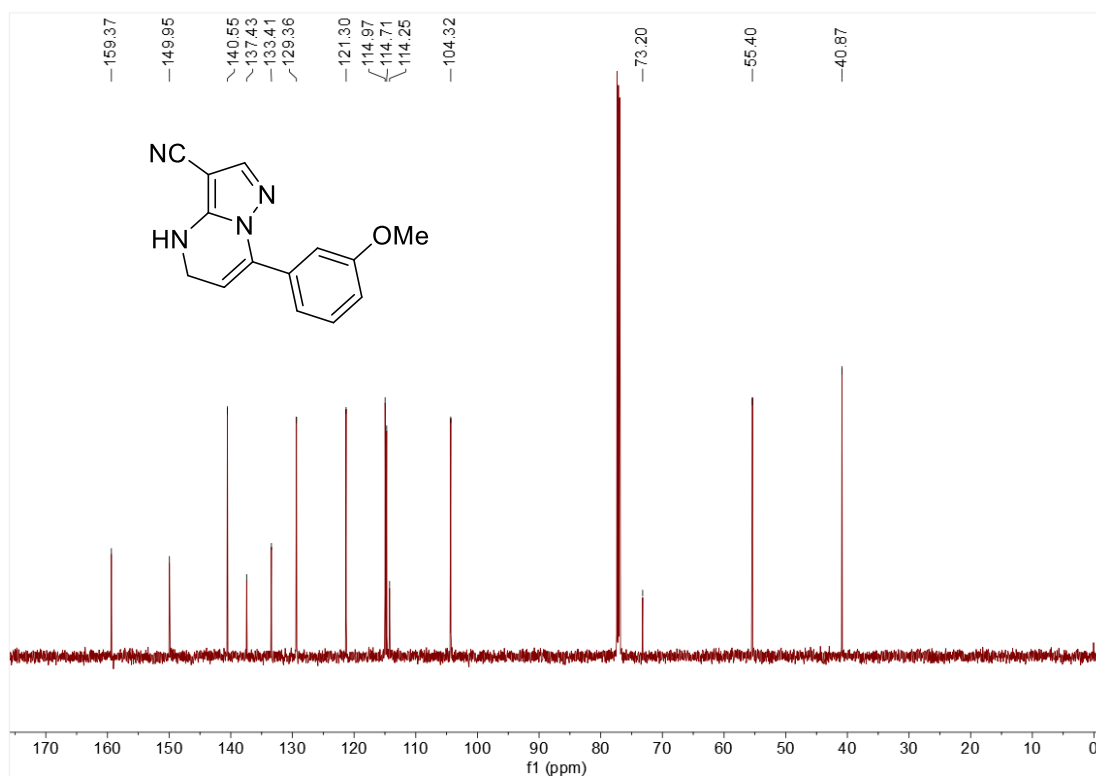
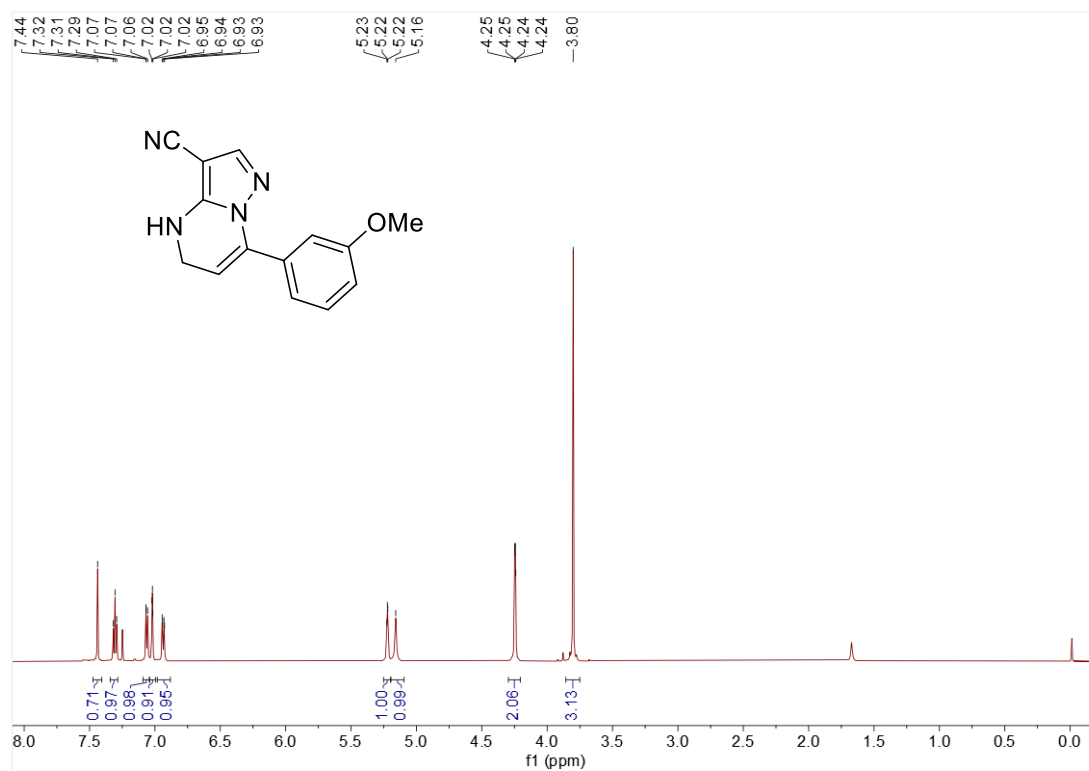
7-(2-methoxyphenyl)-4,5-dihydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**5b**)



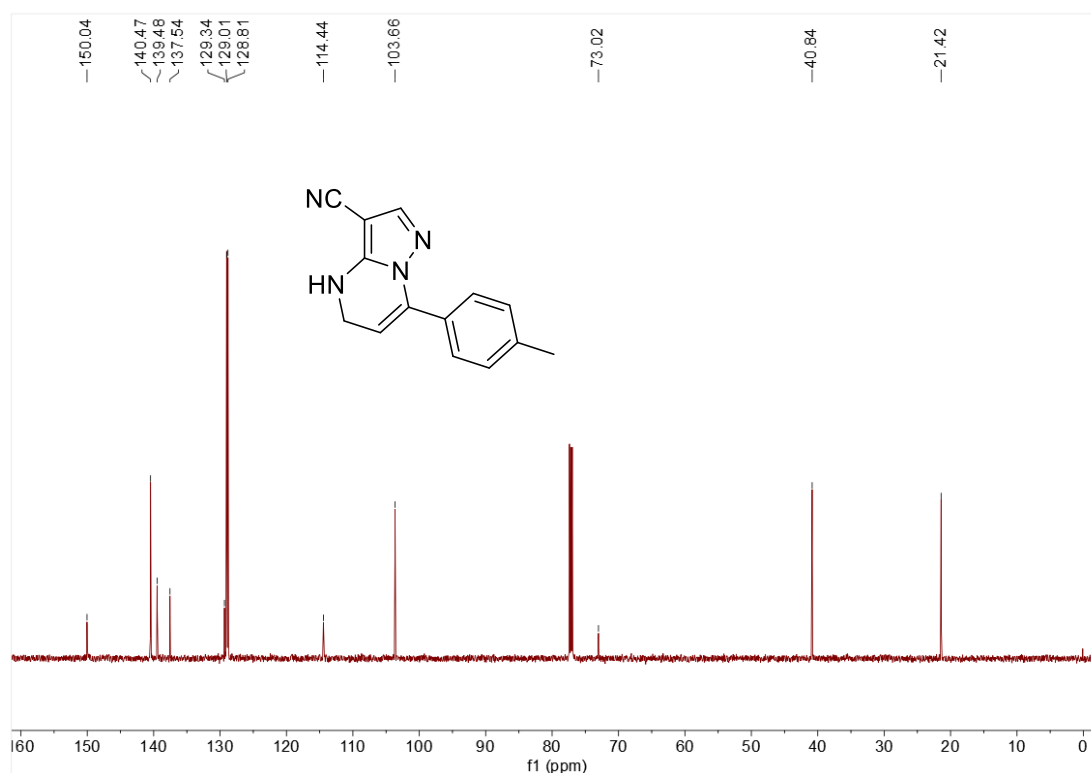
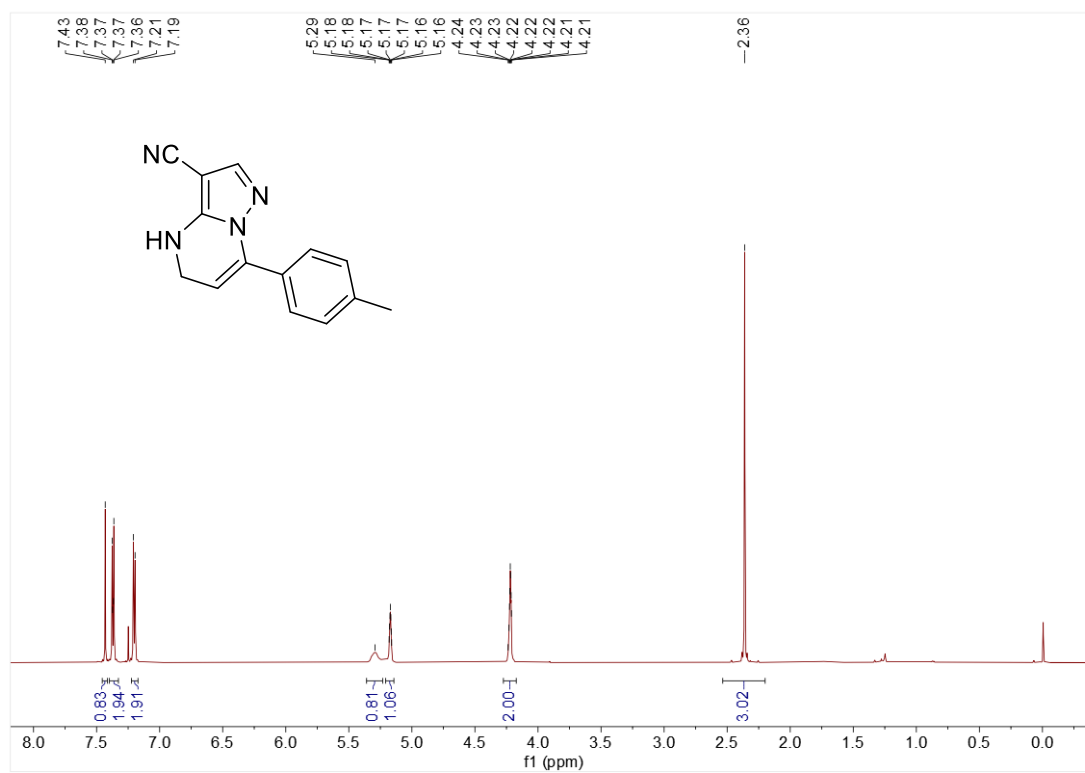
7-(*m*-tolyl)-4,5-dihydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**5c**)



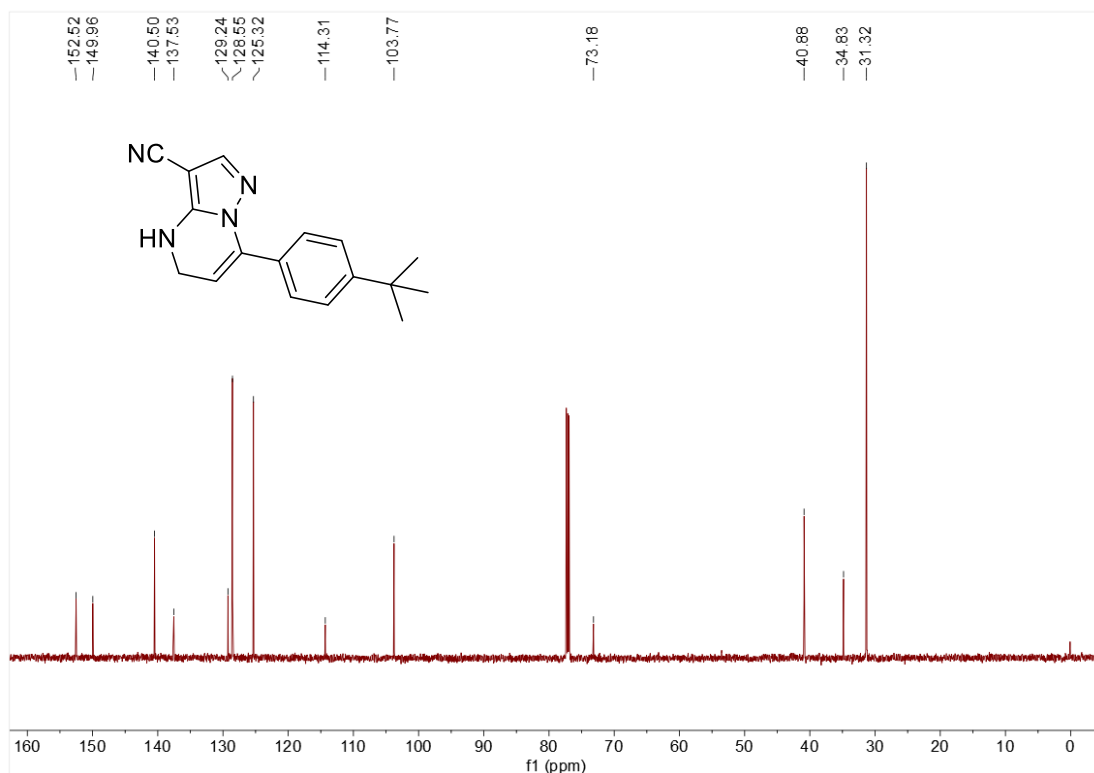
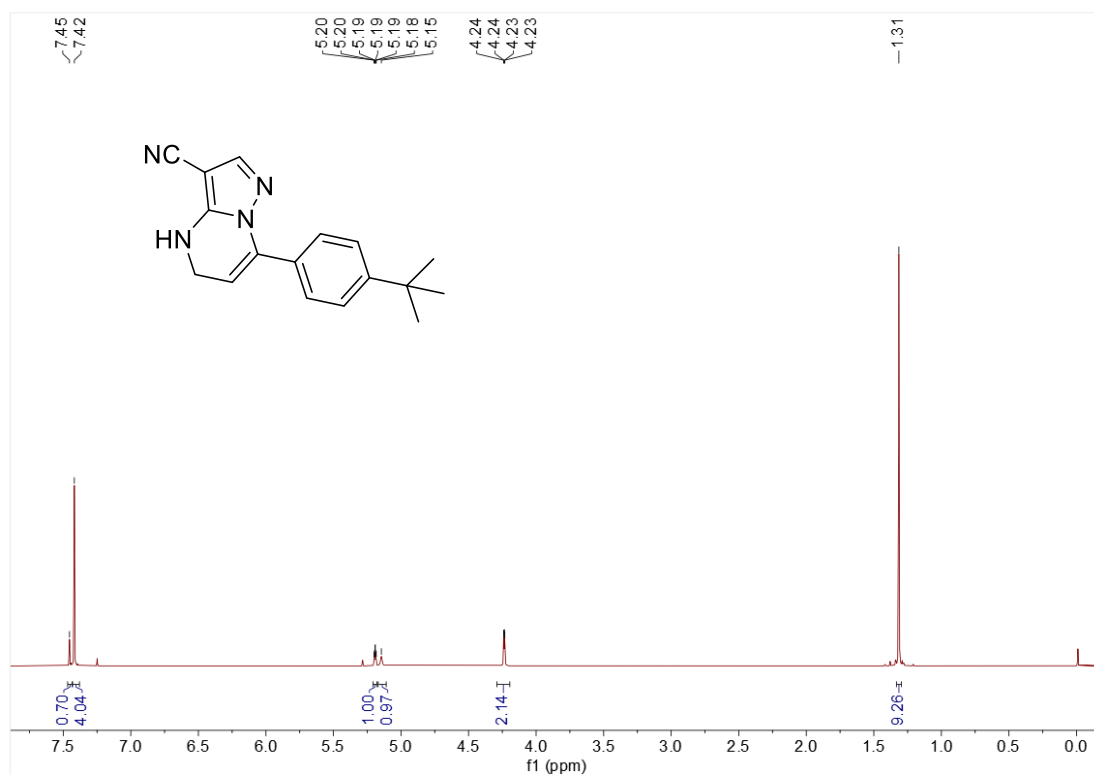
7-(3-methoxyphenyl)-4,5-dihydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**5d**)



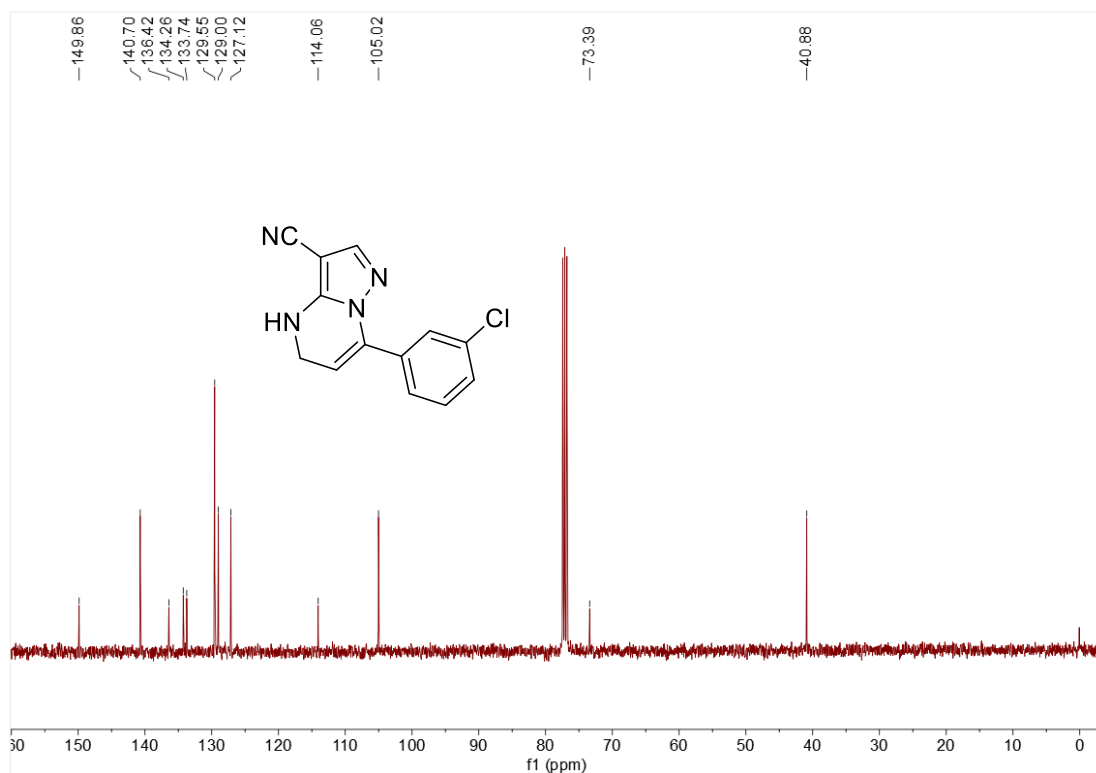
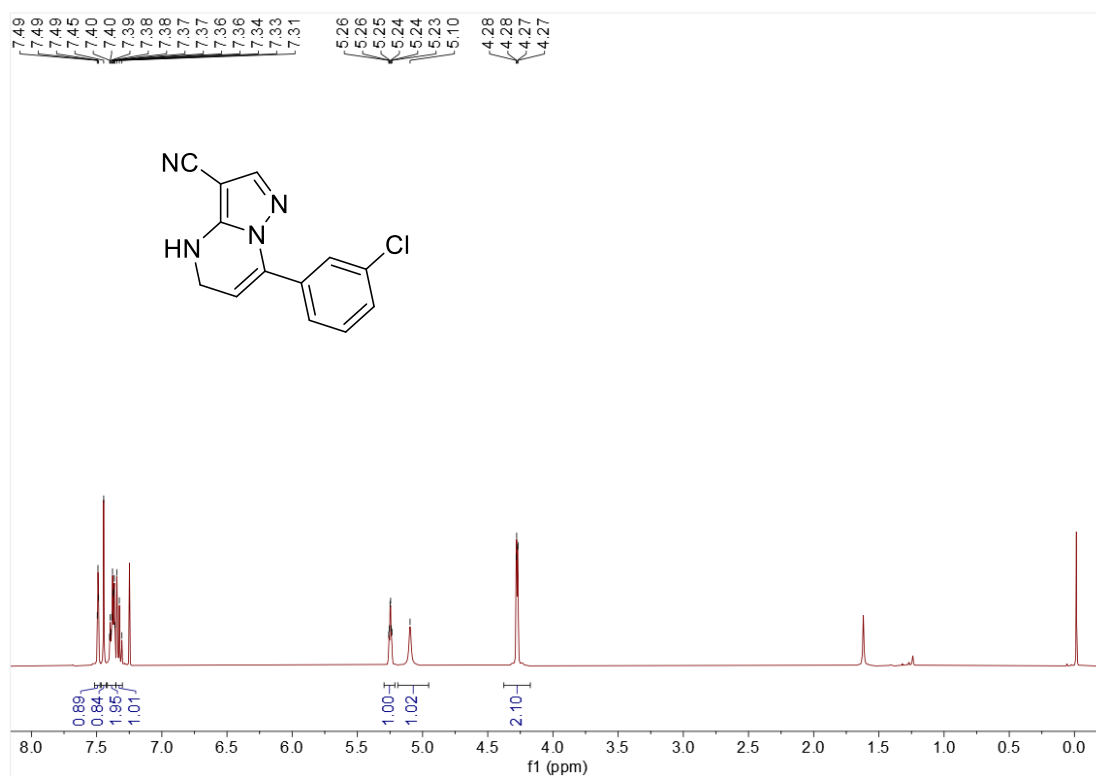
7-(*p*-tolyl)-4,5-dihydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**5e**)



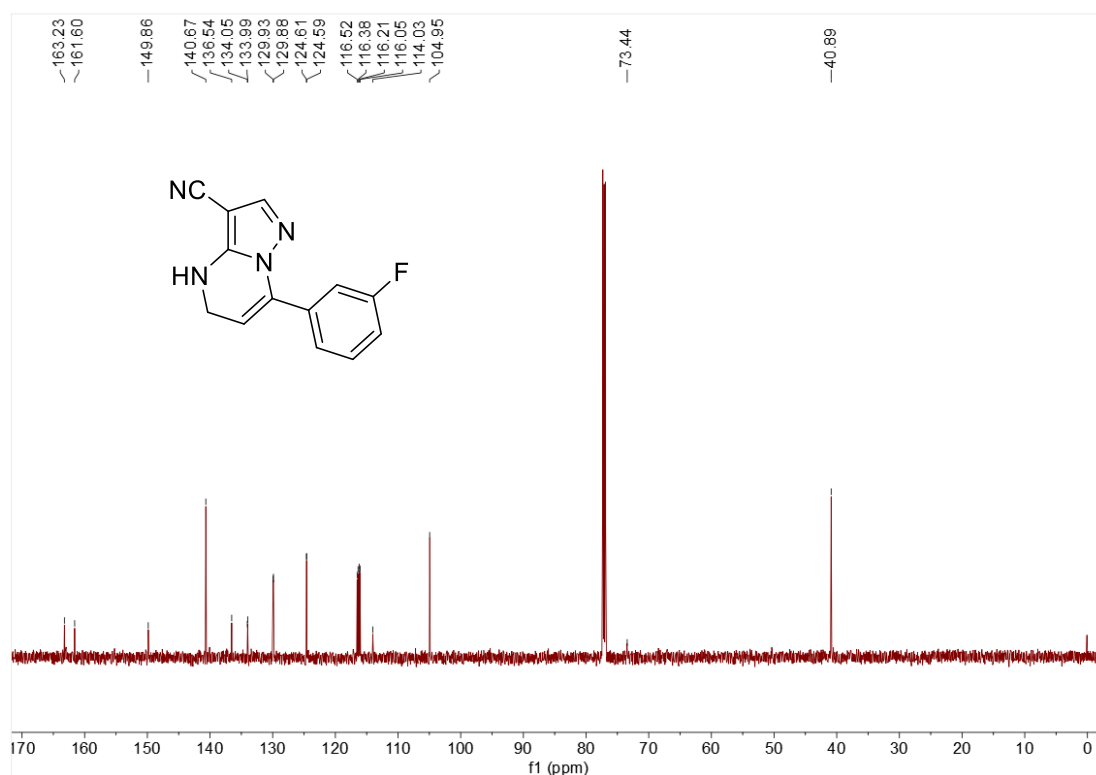
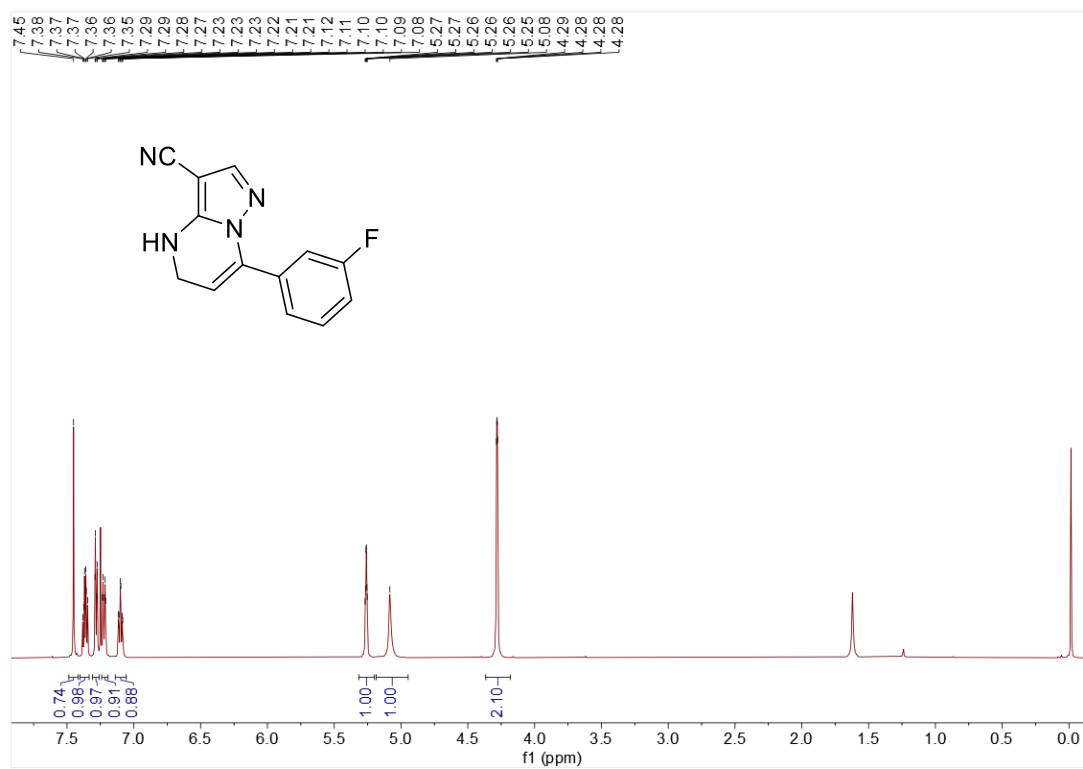
7-(4-(*tert*-butyl)phenyl)-4,5-dihydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**5f**)



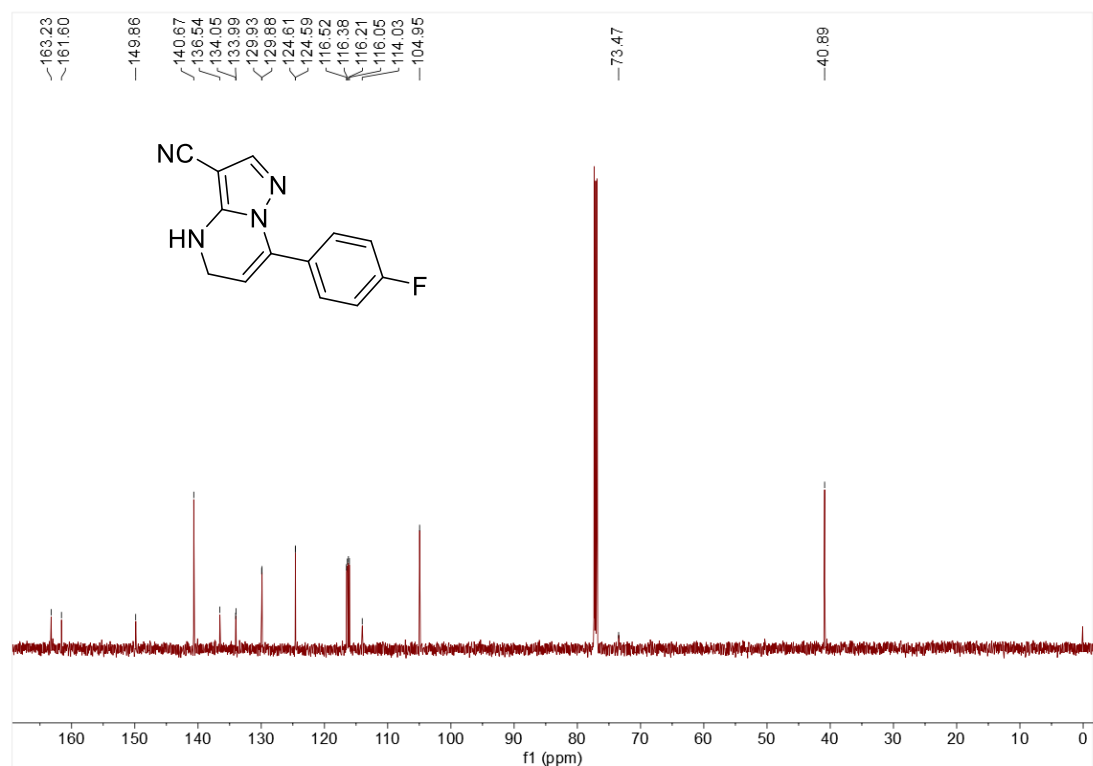
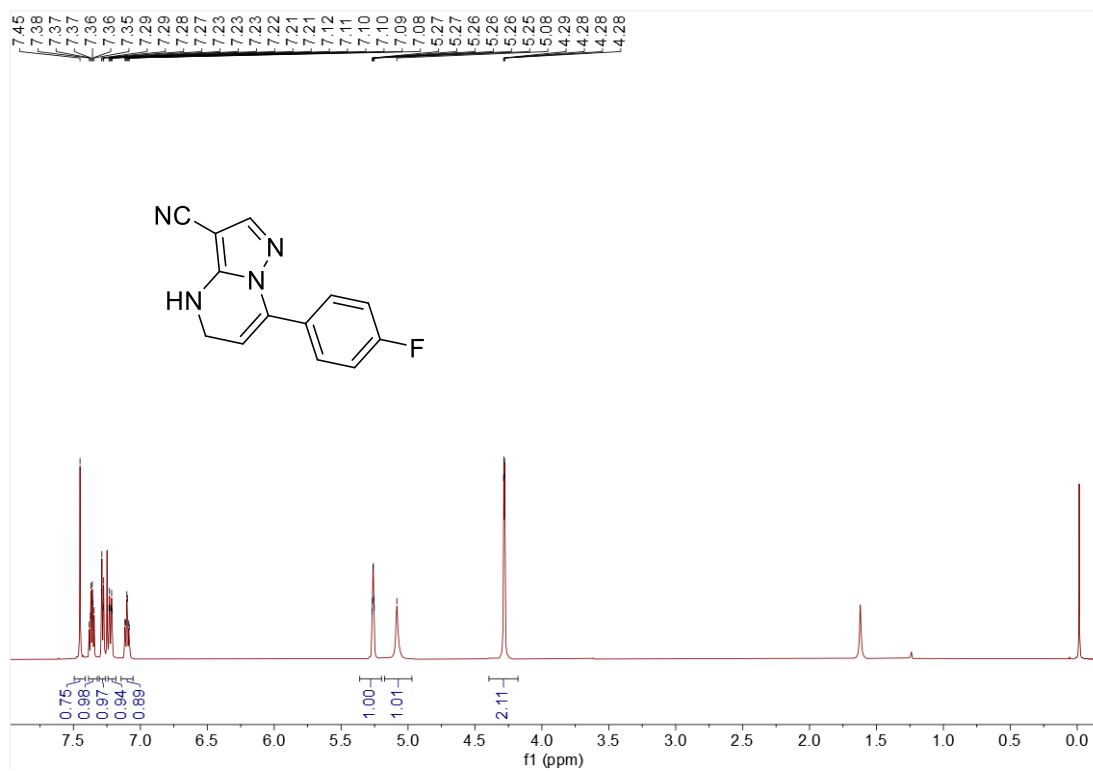
7-(3-chlorophenyl)-4,5-dihydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**5g**)



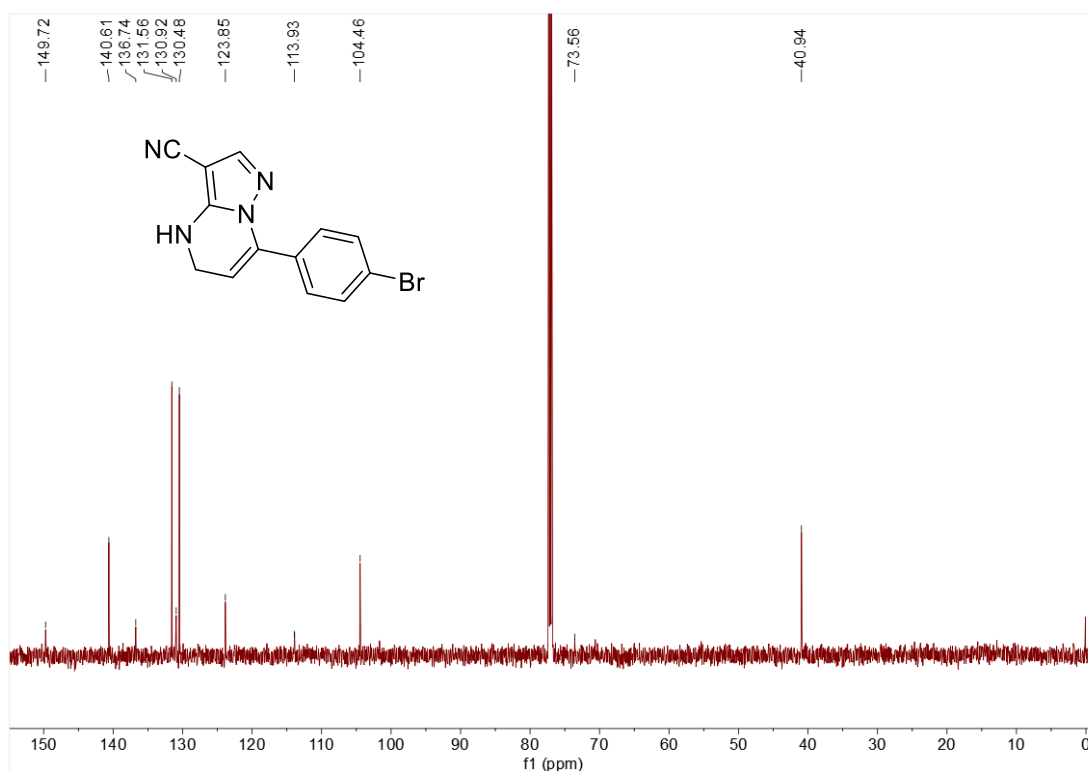
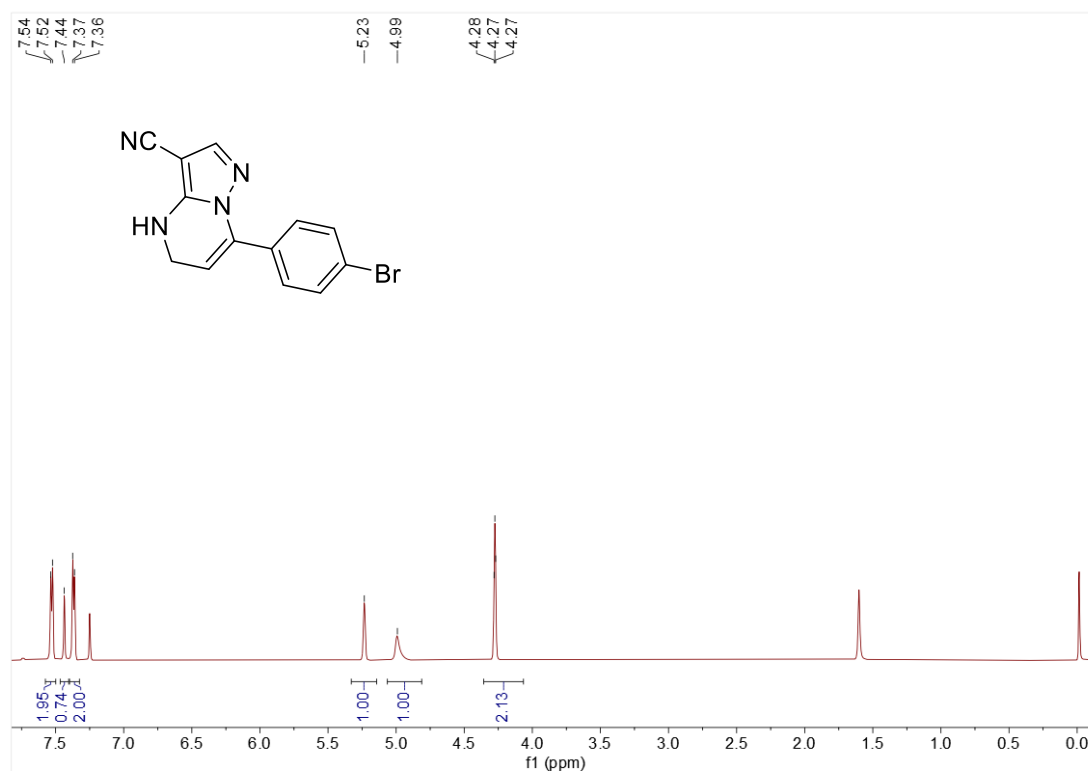
7-(3-fluorophenyl)-4,5-dihydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**5h**)



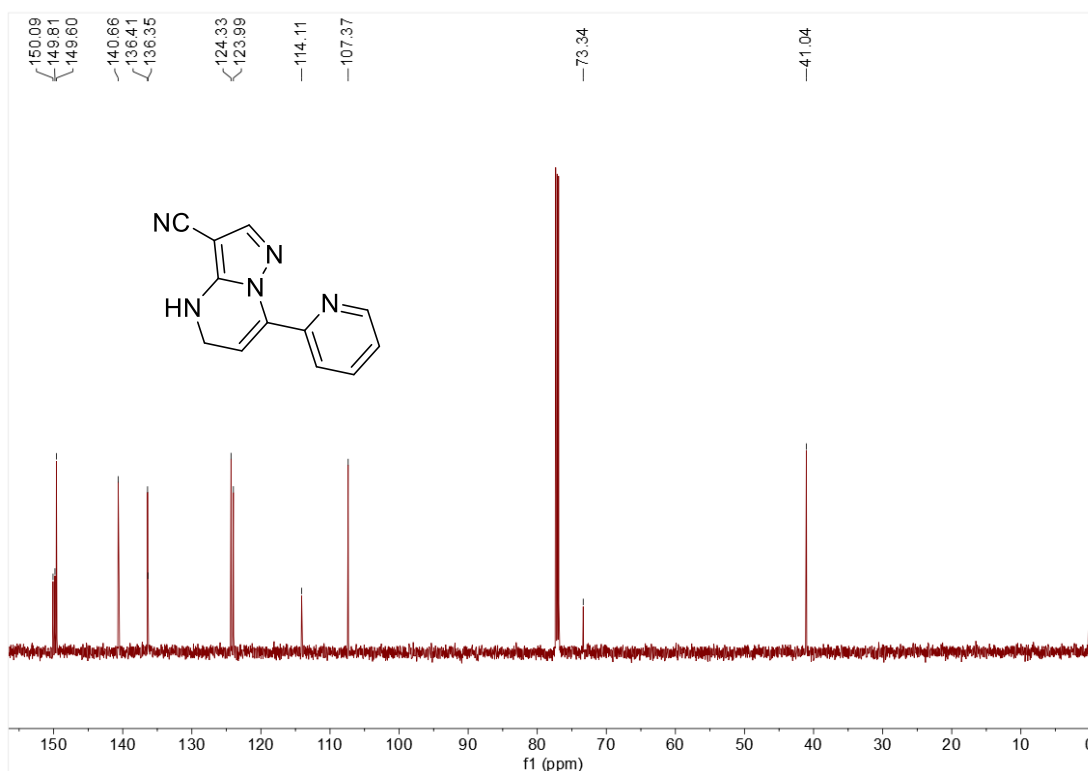
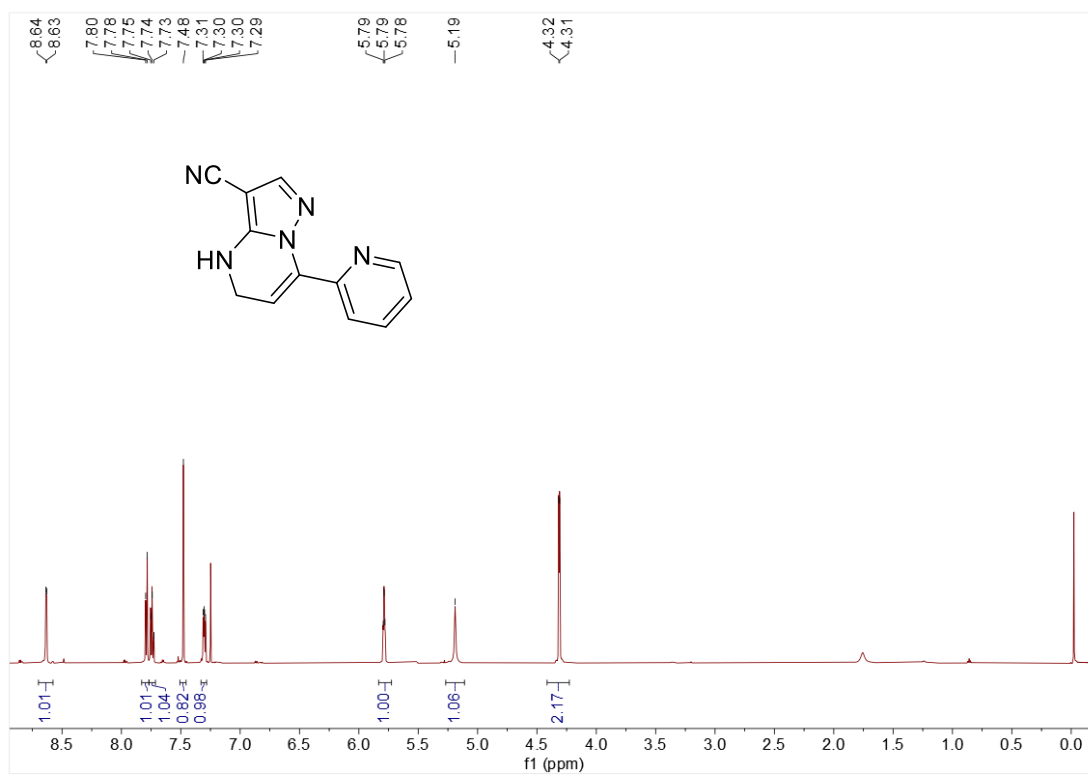
7-(4-fluorophenyl)-4,5-dihydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**5i**)



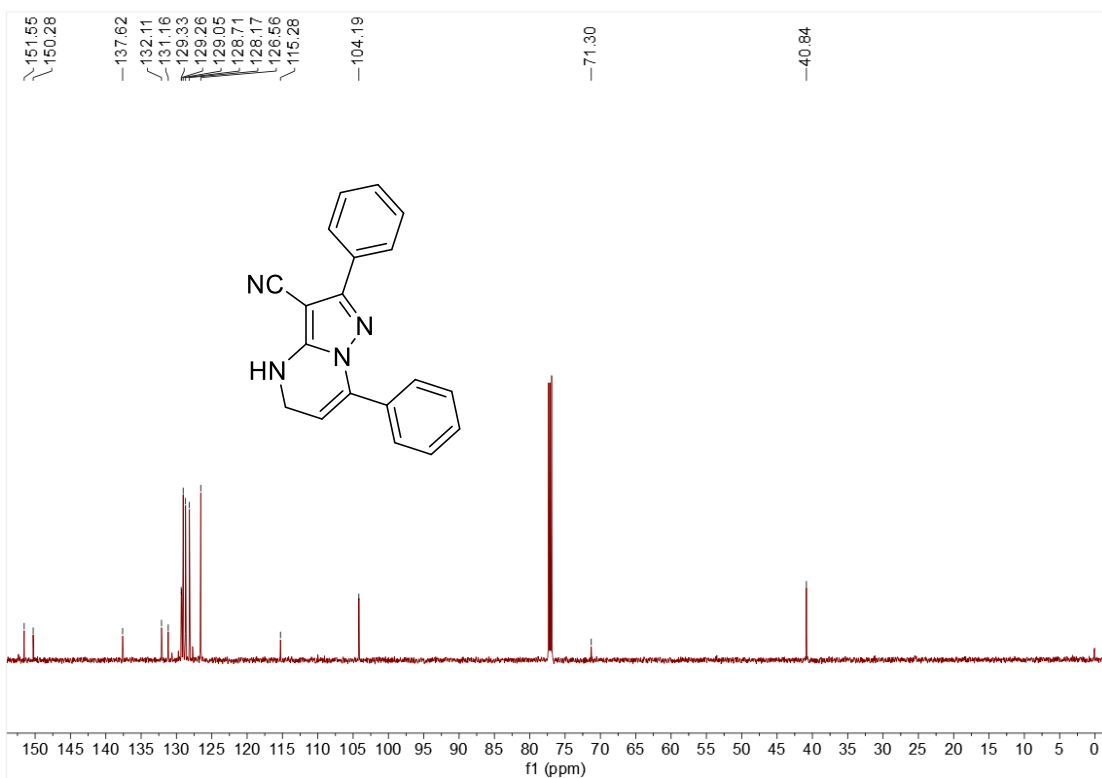
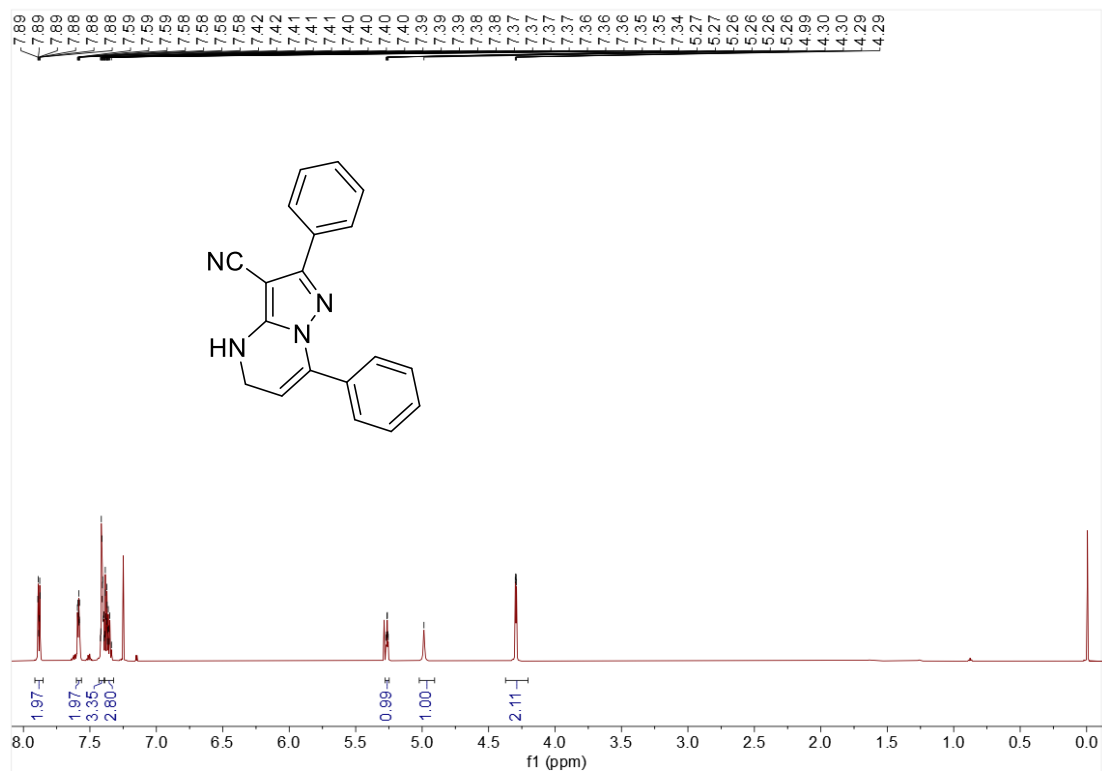
7-(4-bromophenyl)-4,5-dihydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**5j**)



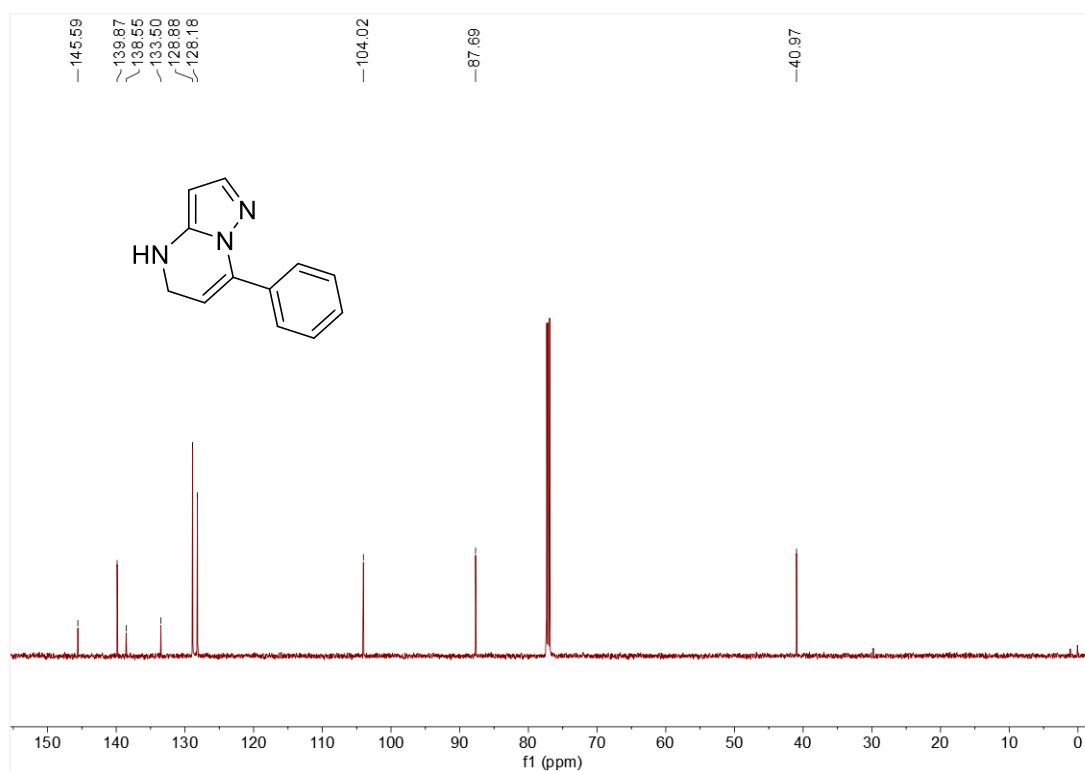
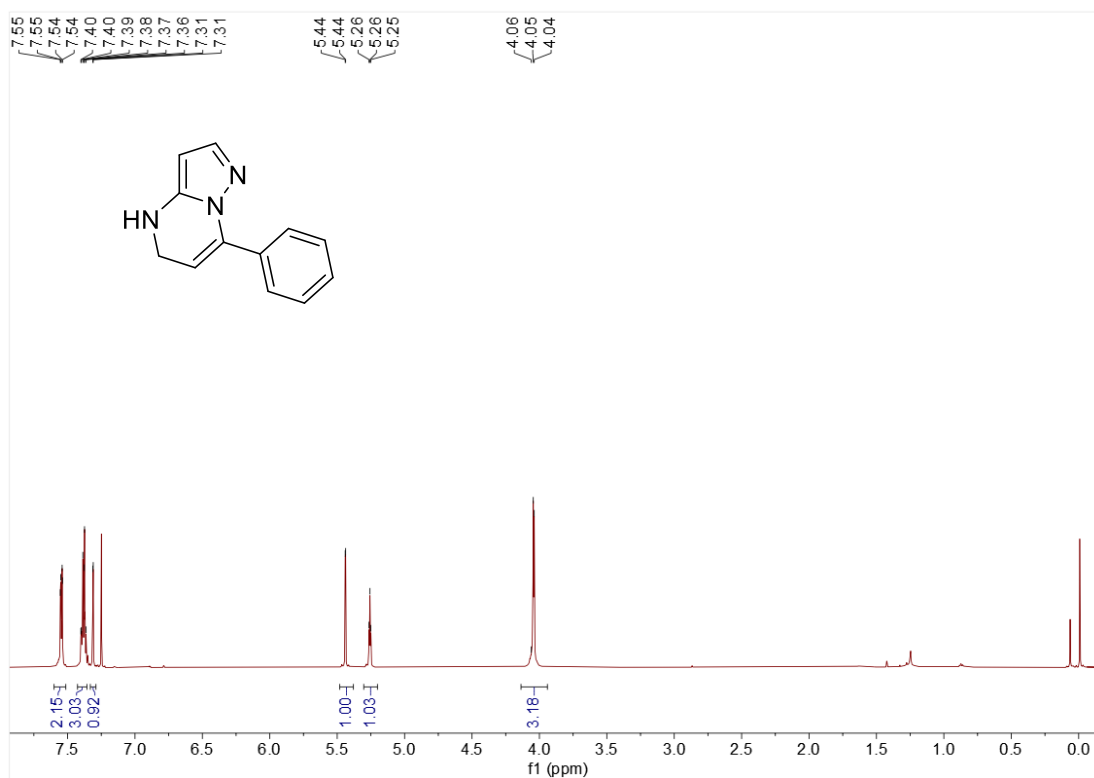
7-(pyridin-2-yl)-4,5-dihydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**5k**)



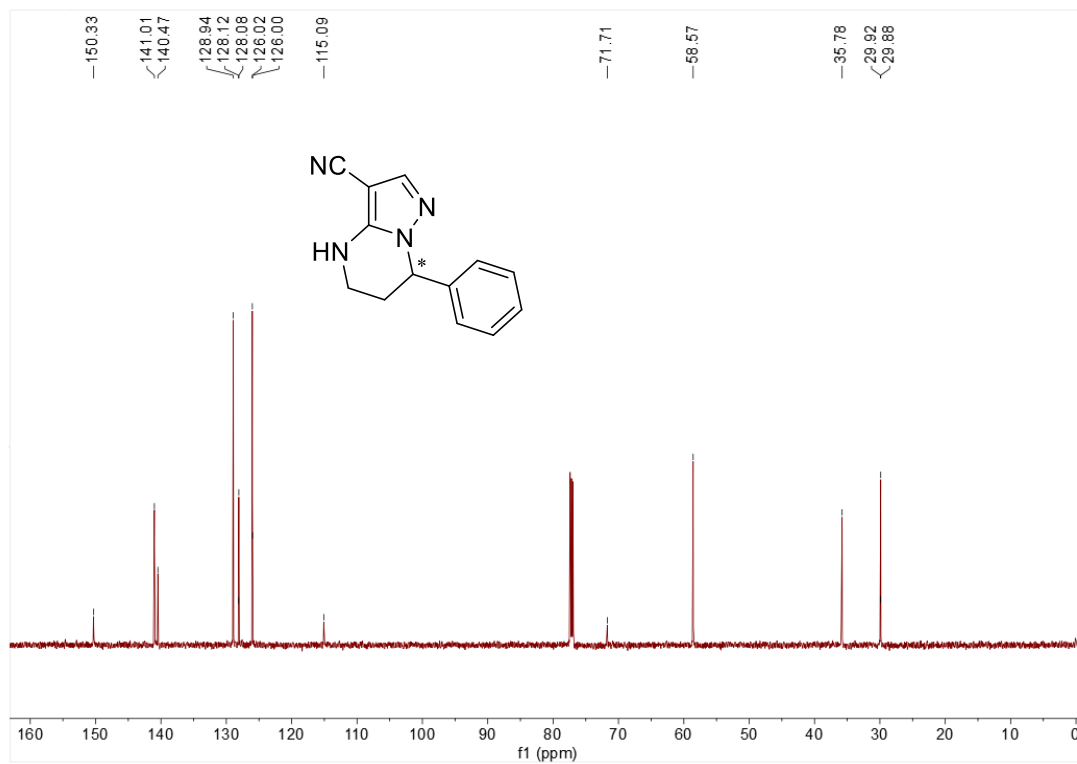
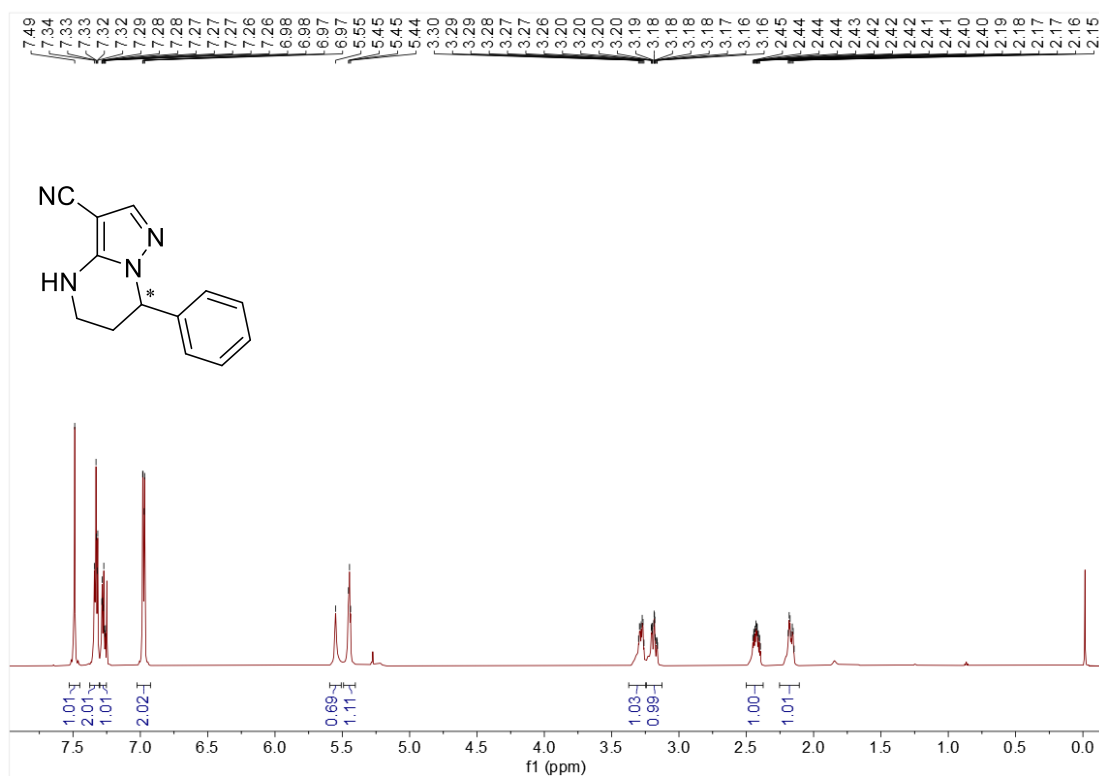
2,7-diphenyl-4,5-dihydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**5I**)



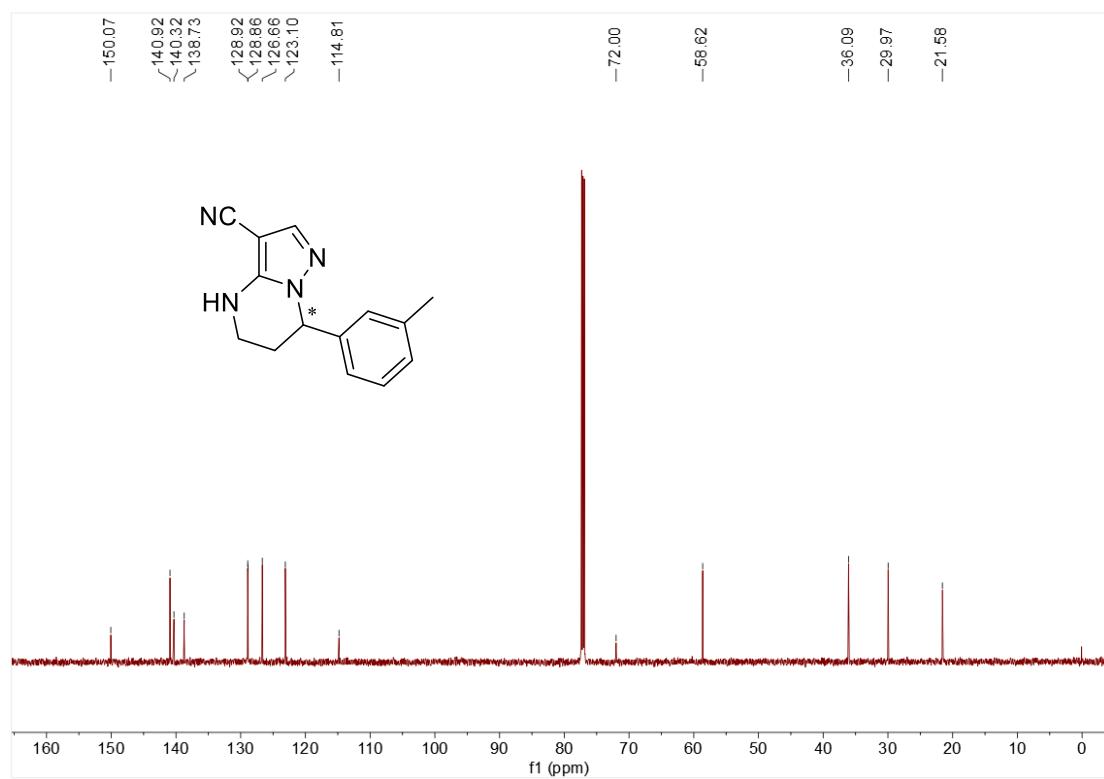
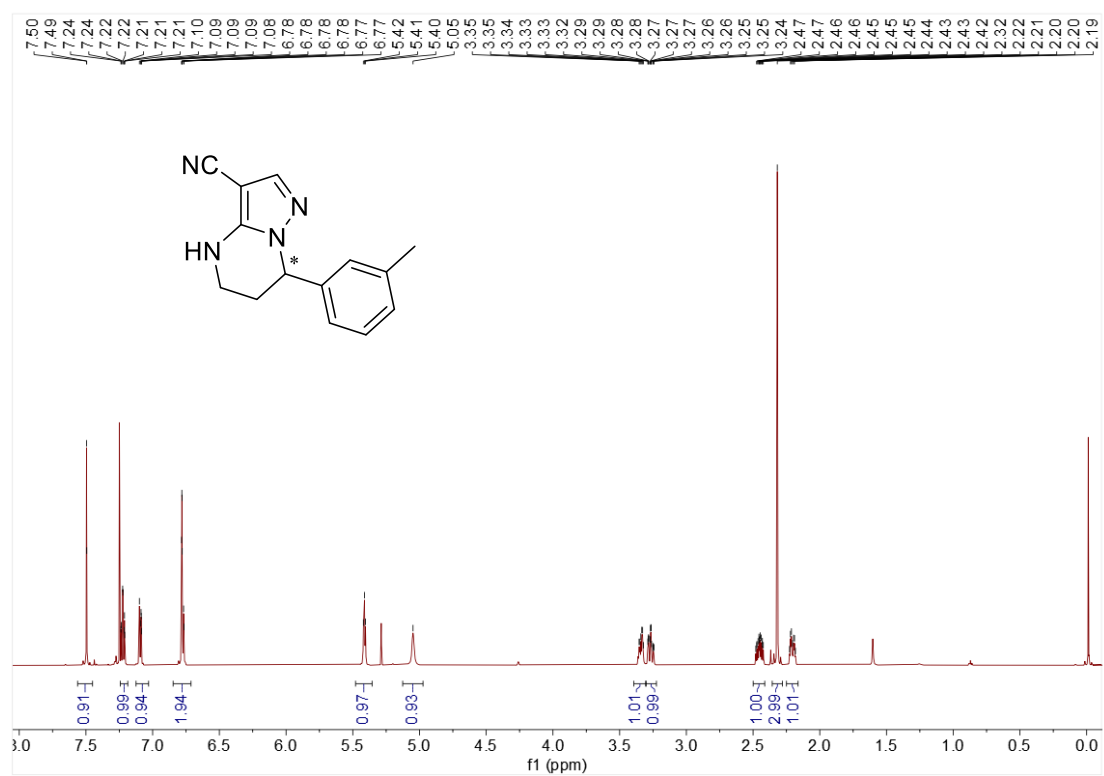
7-phenyl-4,5-dihydropyrazolo[1,5-*a*]pyrimidine (**5m**)



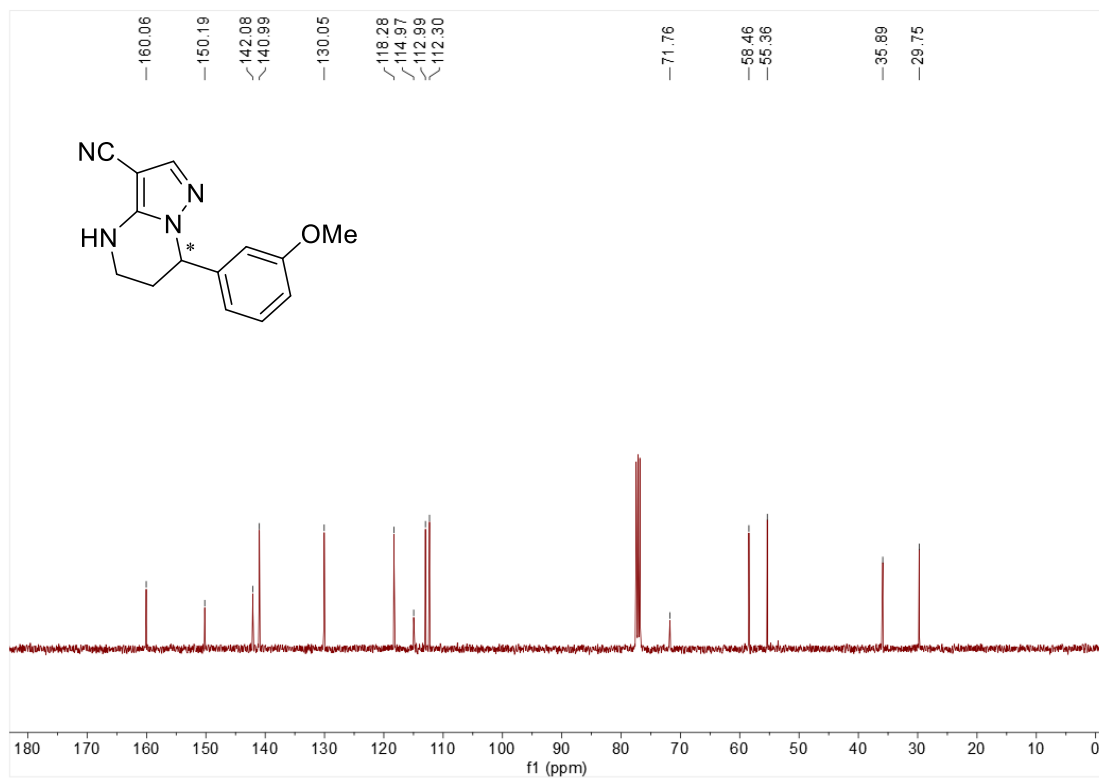
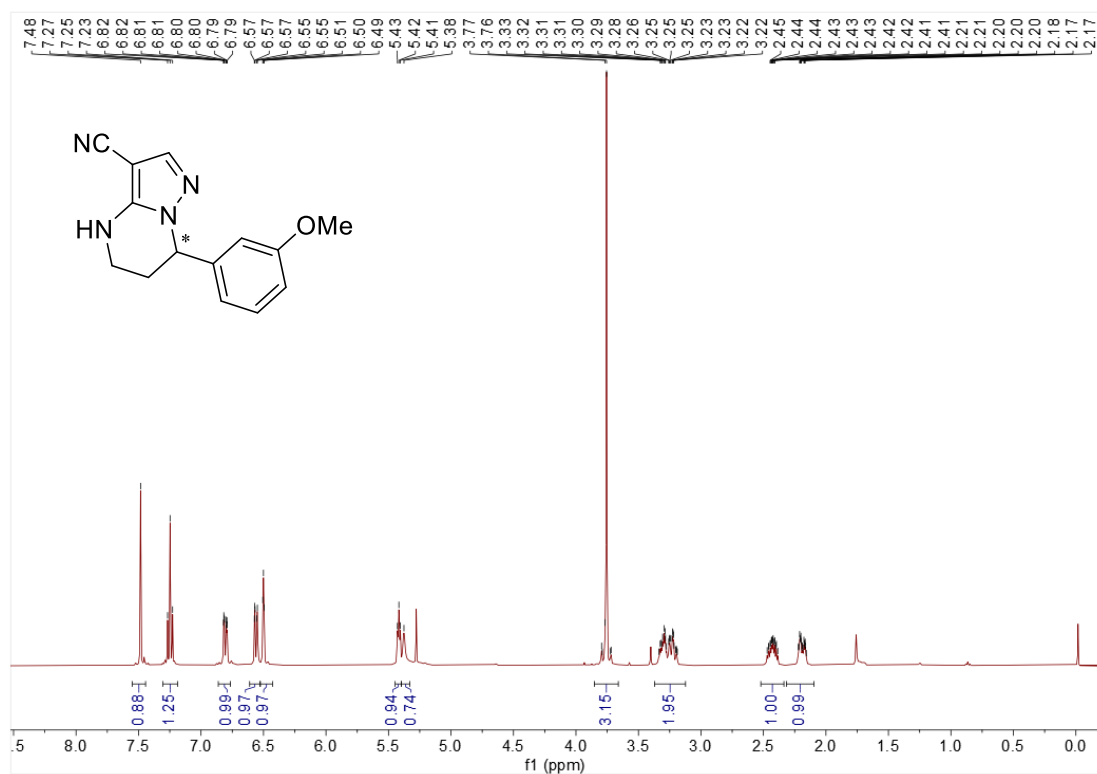
7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**2a**)



7-(*m*-tolyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**2b**)

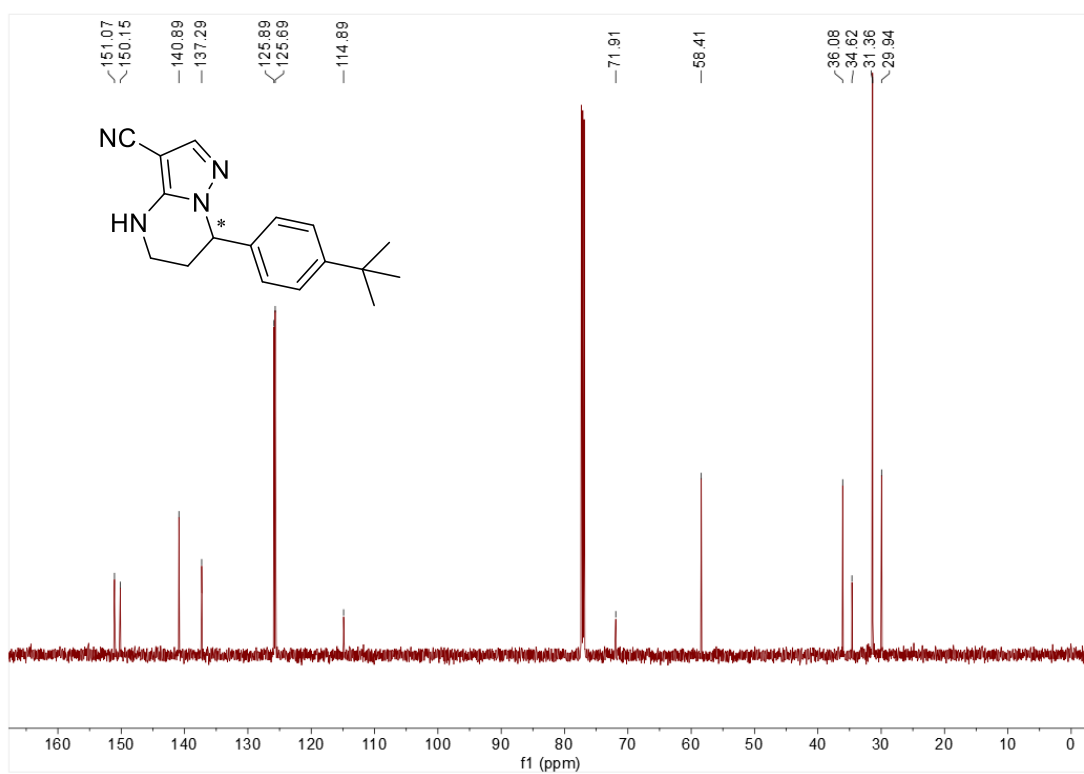
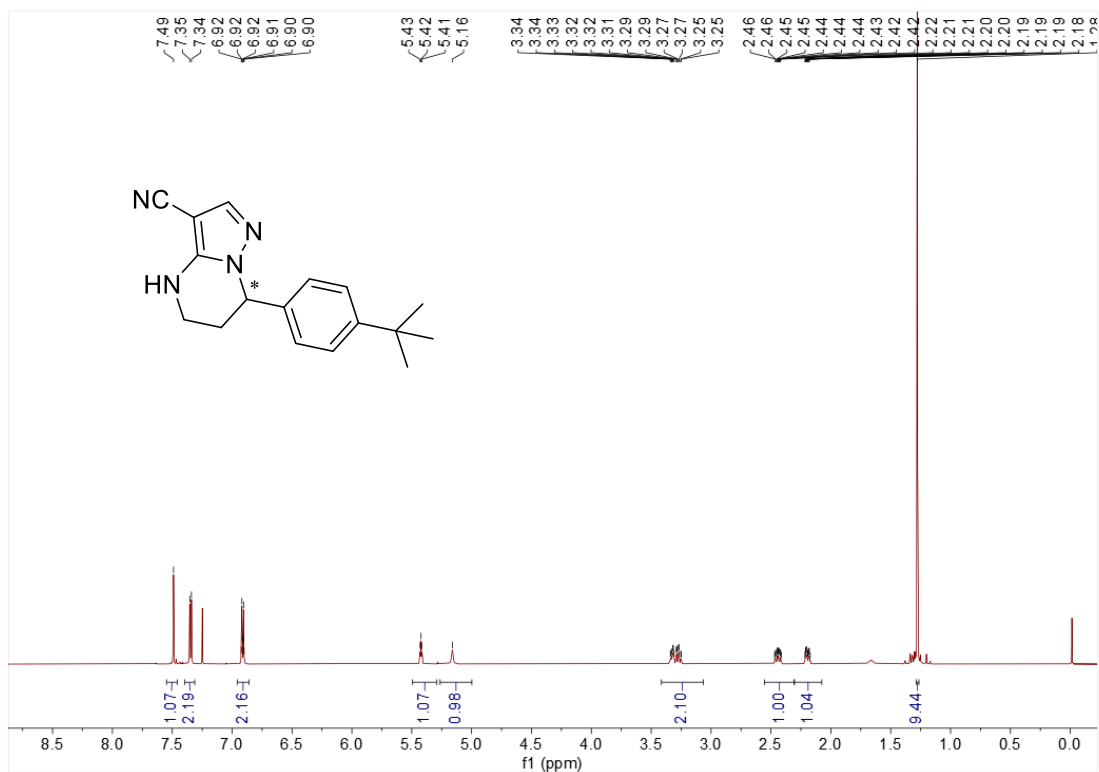


7-(3-methoxyphenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**2c**)

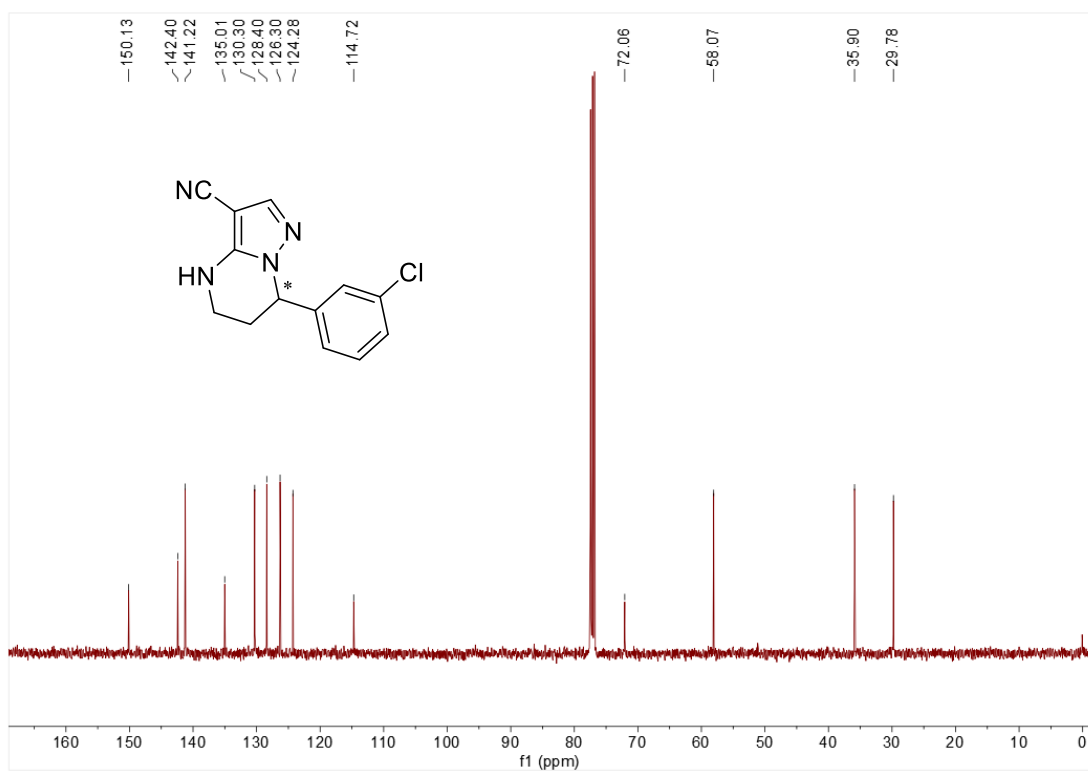
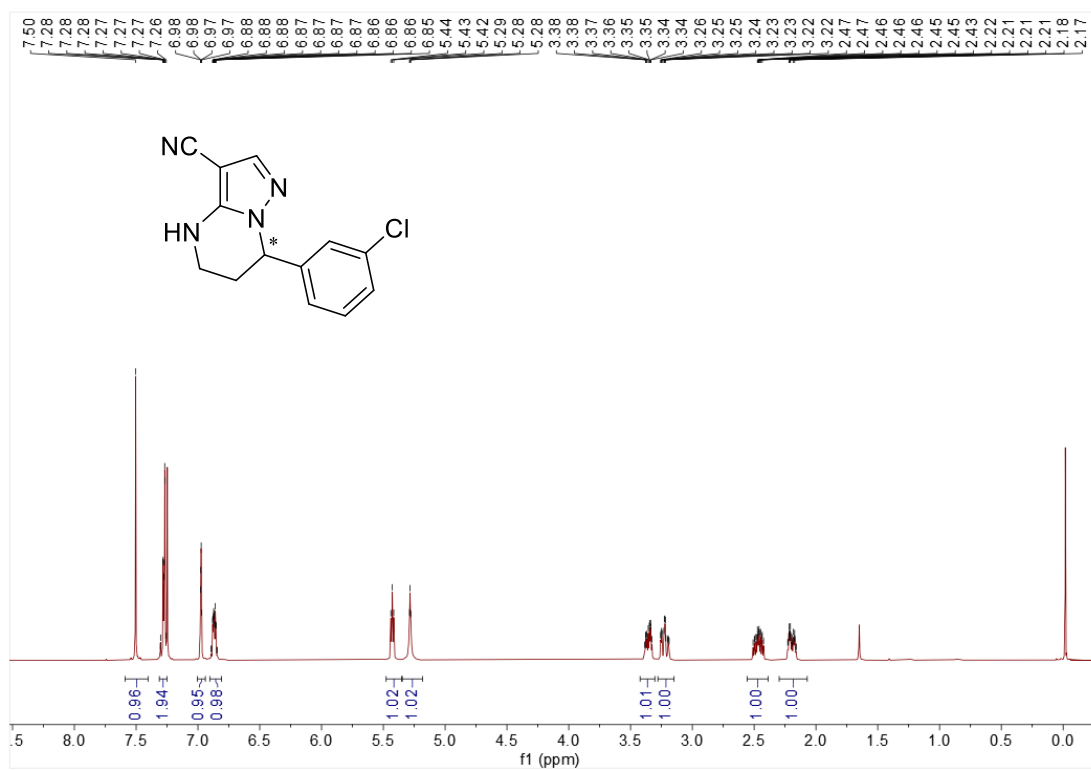


7-(4-(*tert*-butyl)phenyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile

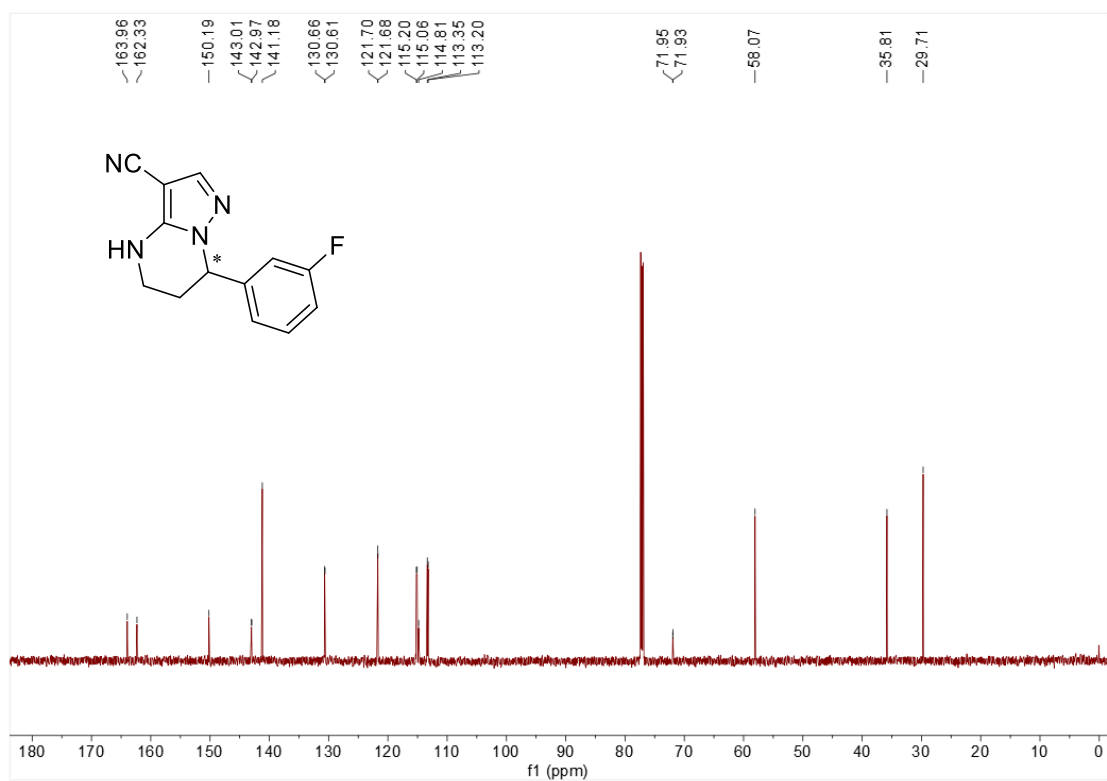
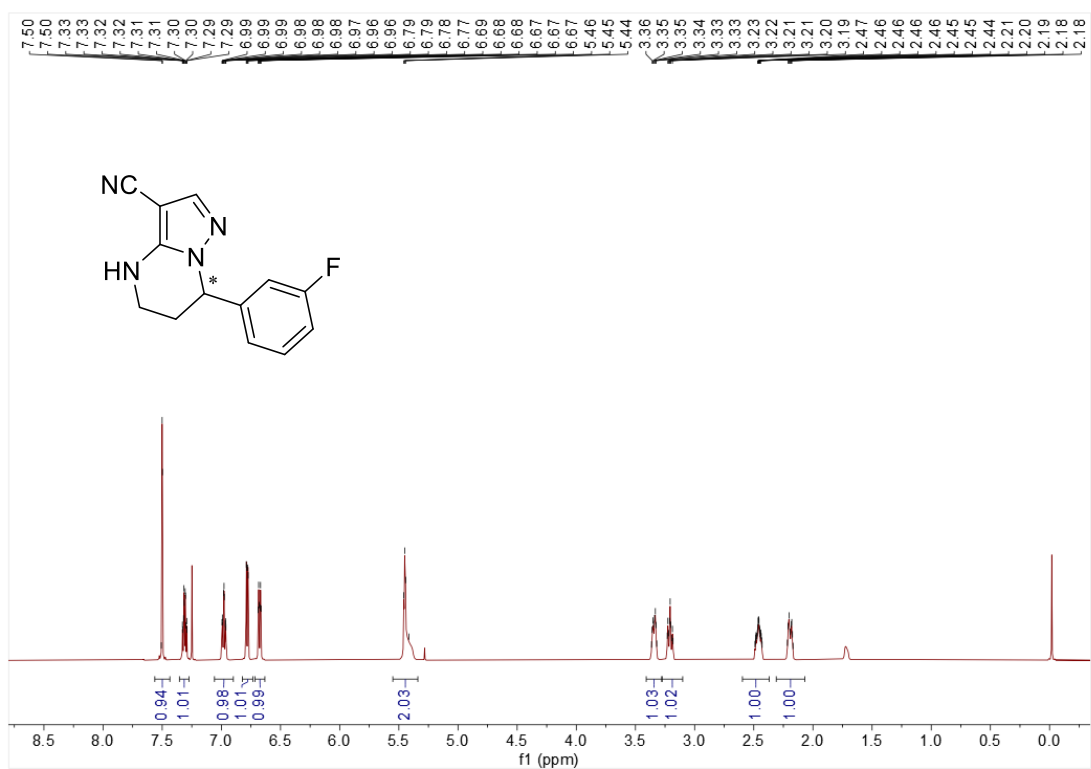
(2d)



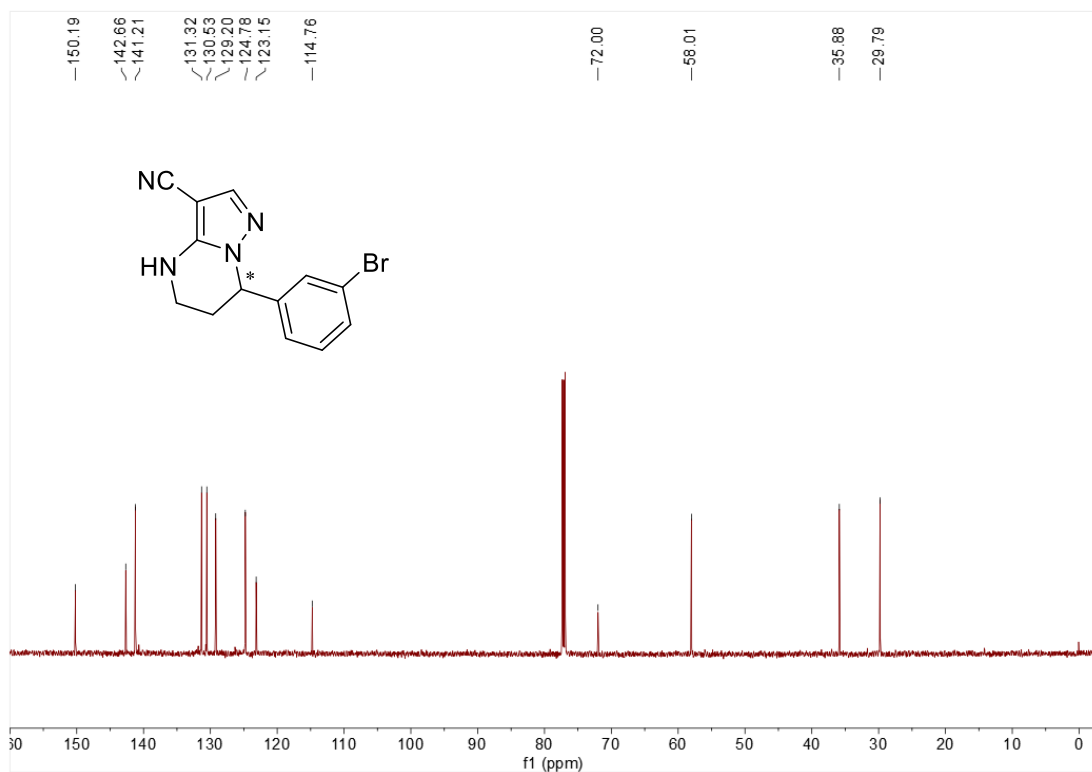
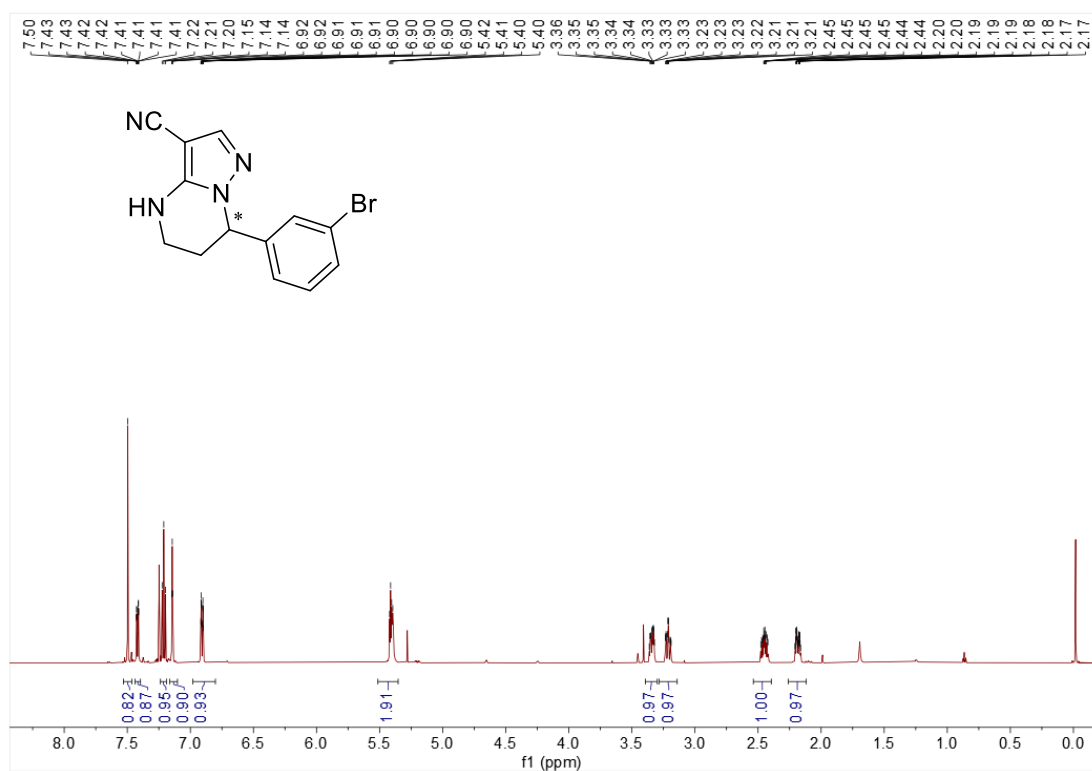
7-(3-chlorophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**2e**)



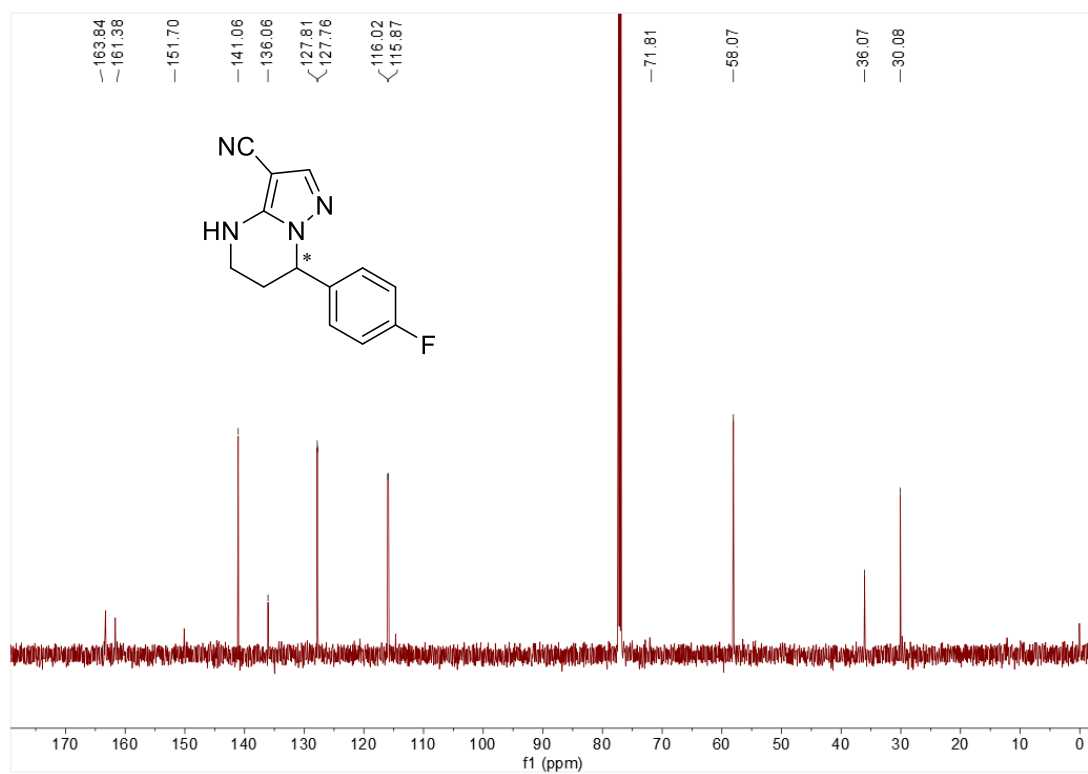
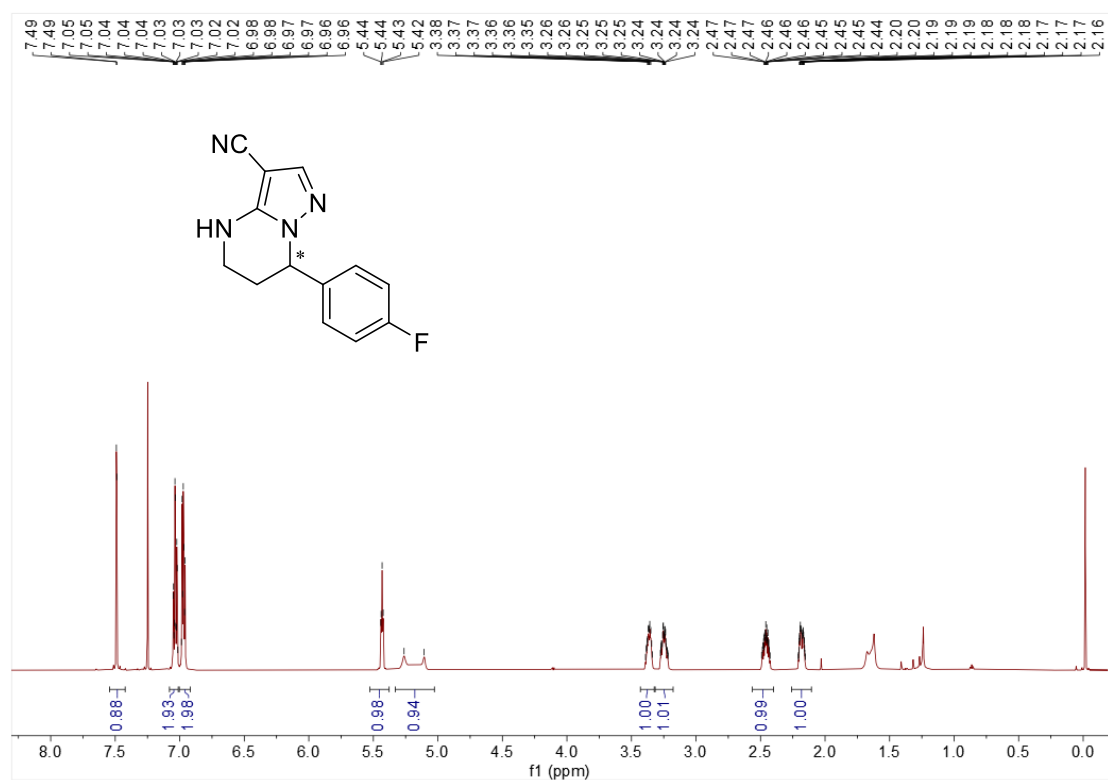
7-(3-fluorophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**2f**)



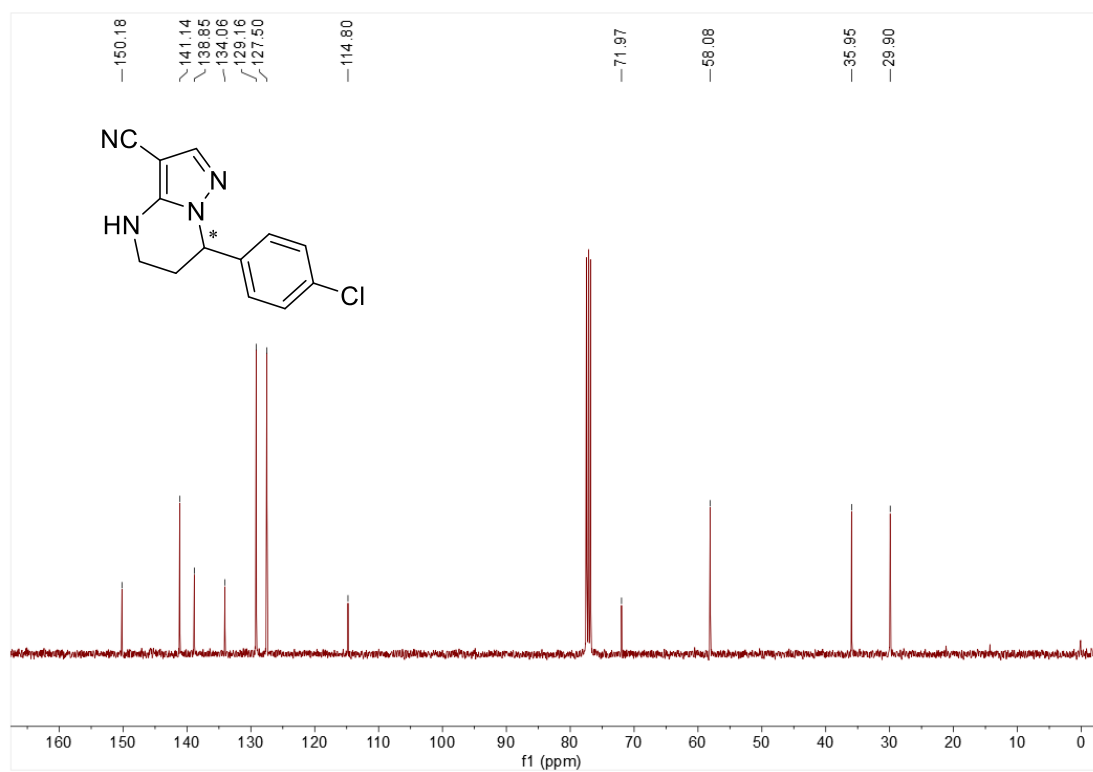
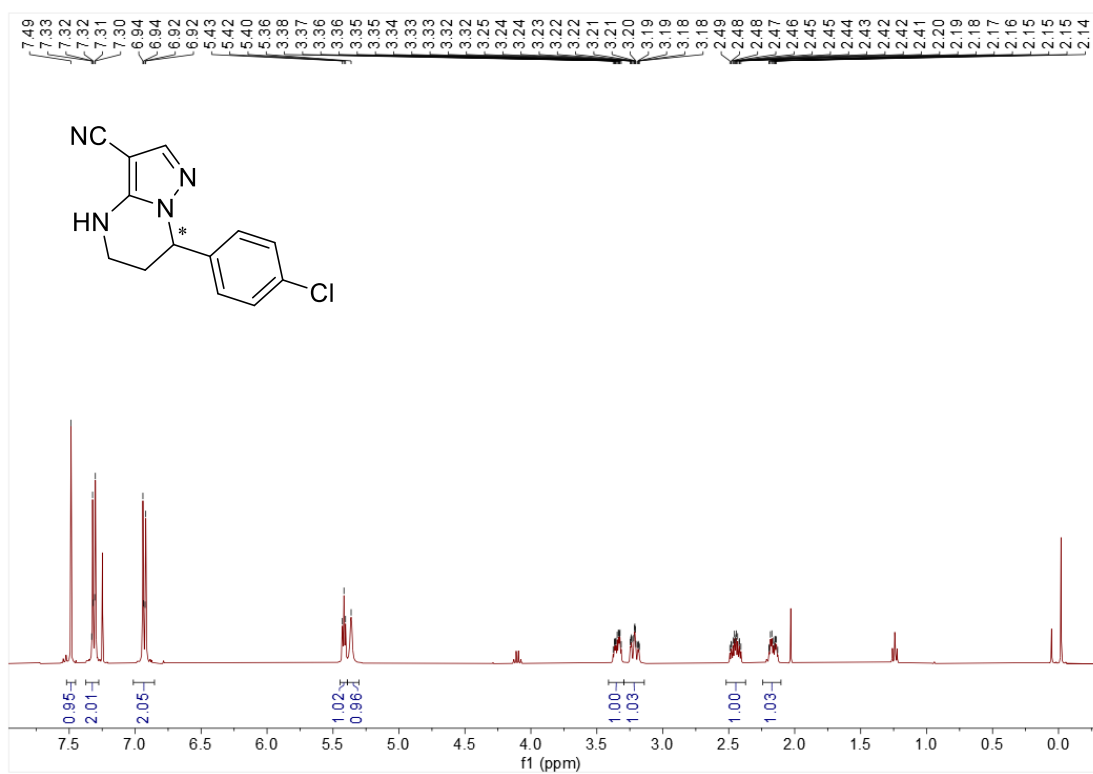
7-(3-bromophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**2g**)



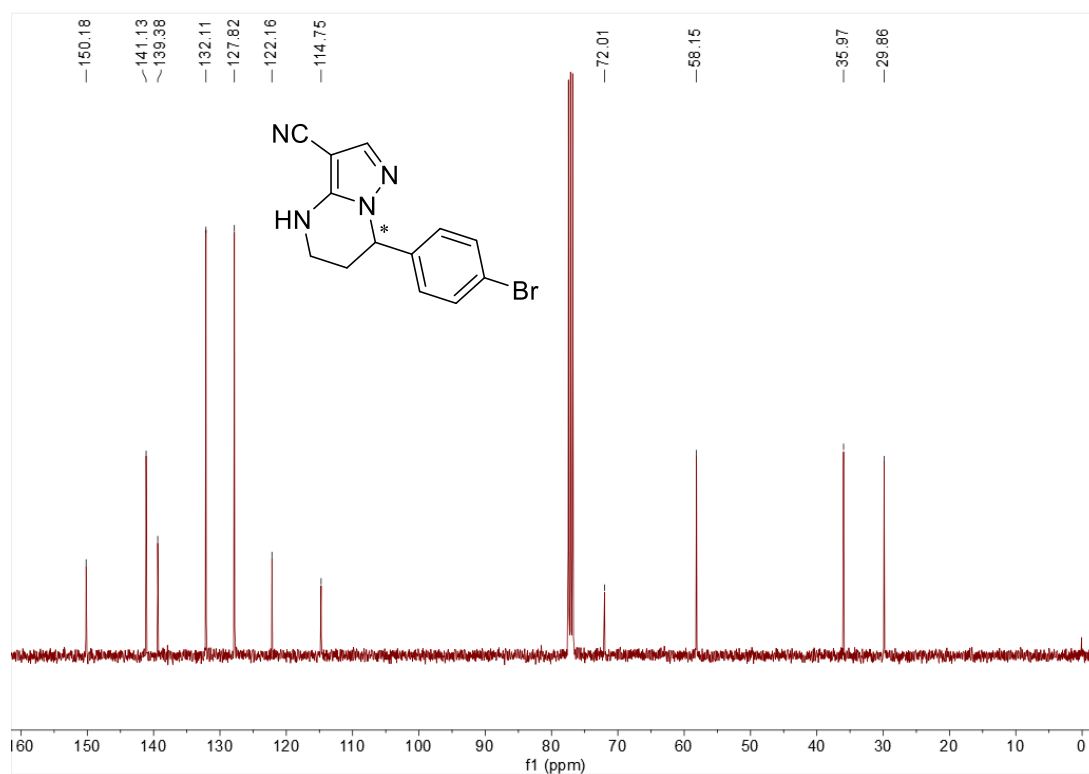
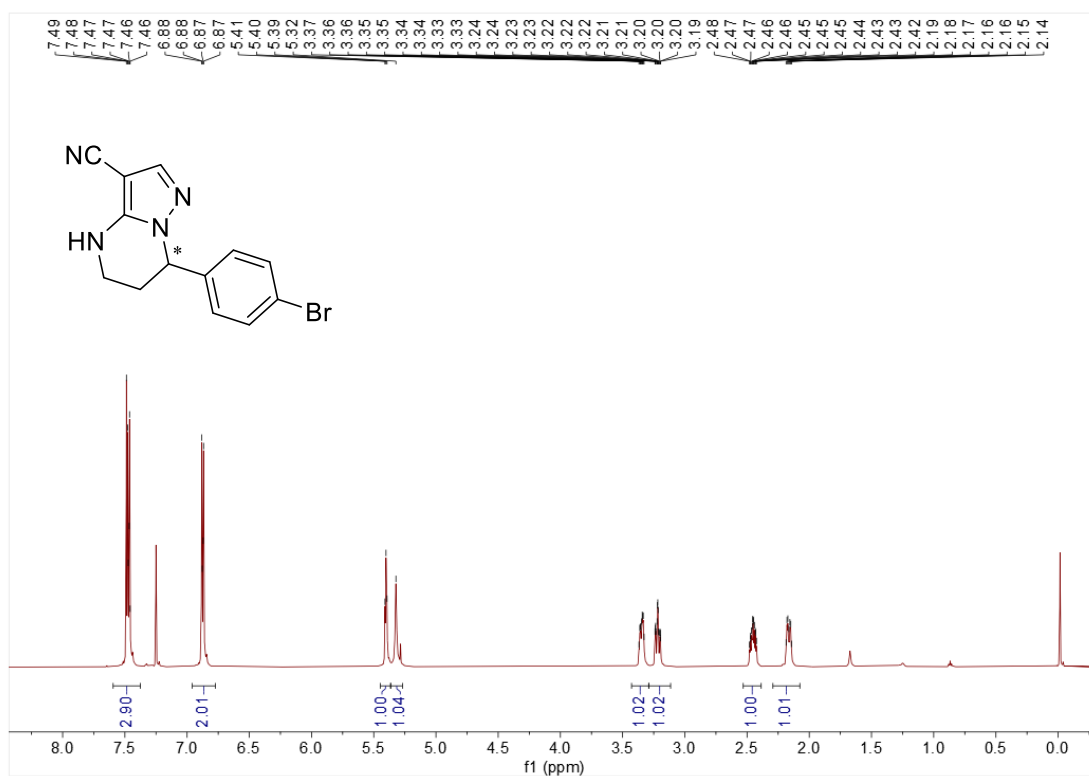
7-(4-fluorophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**2h**)



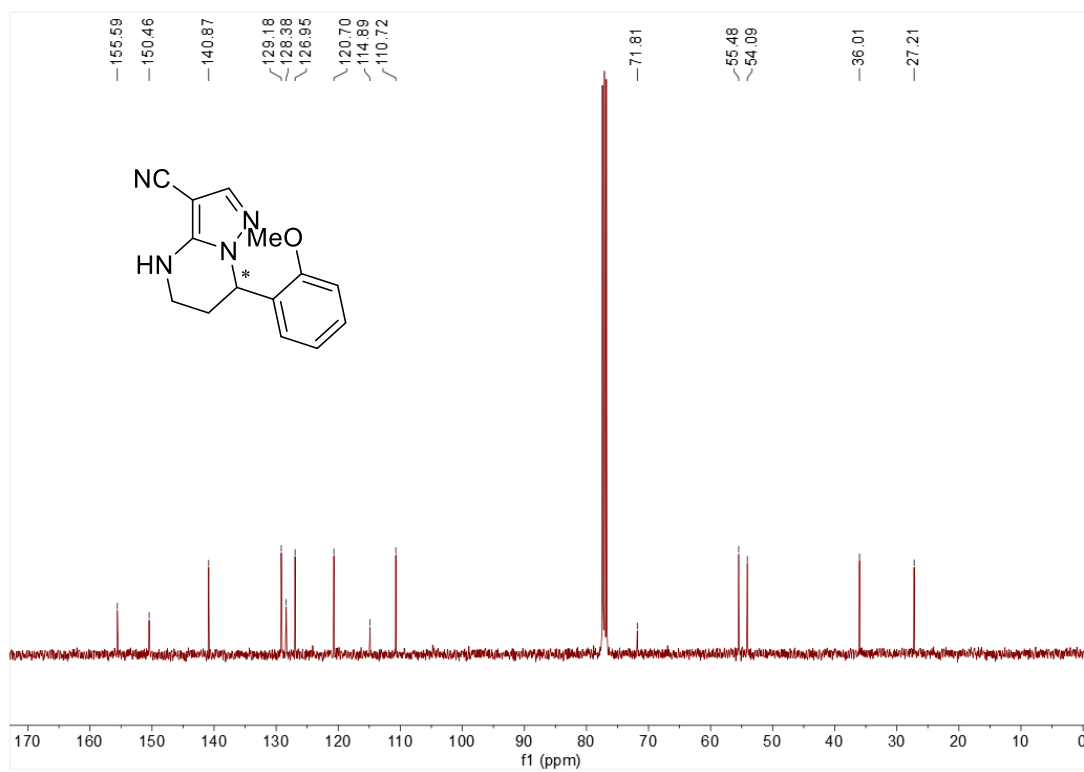
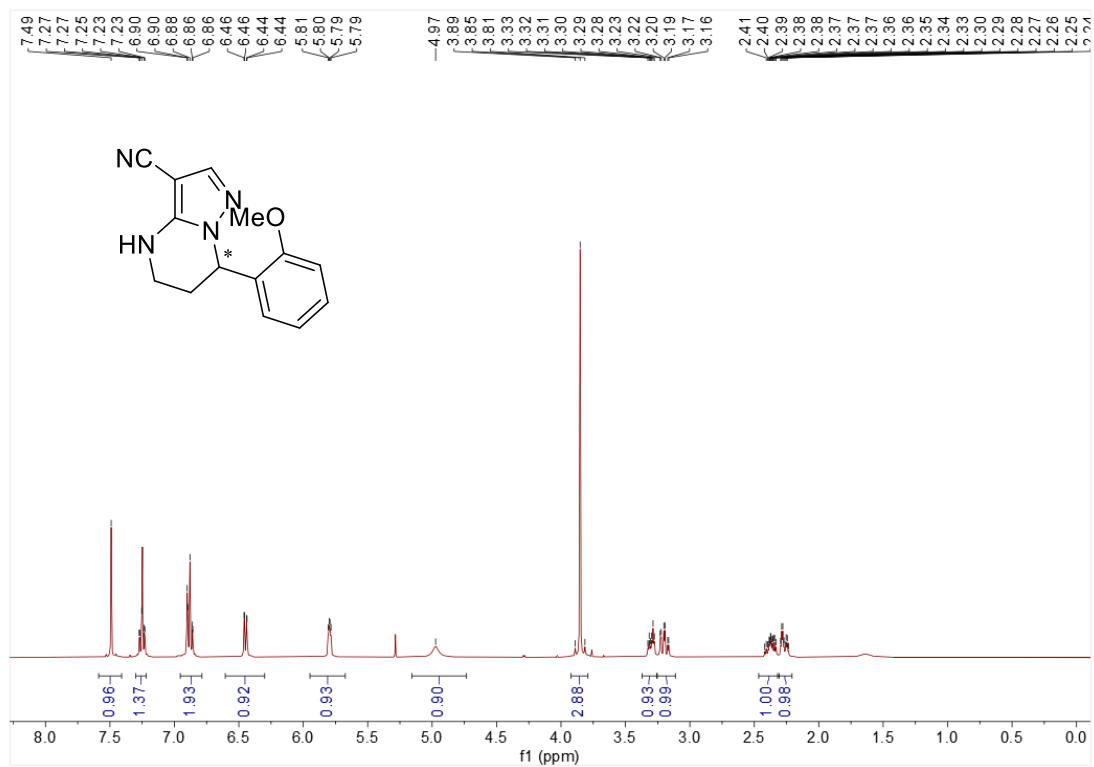
7-(4-chlorophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**2i**)



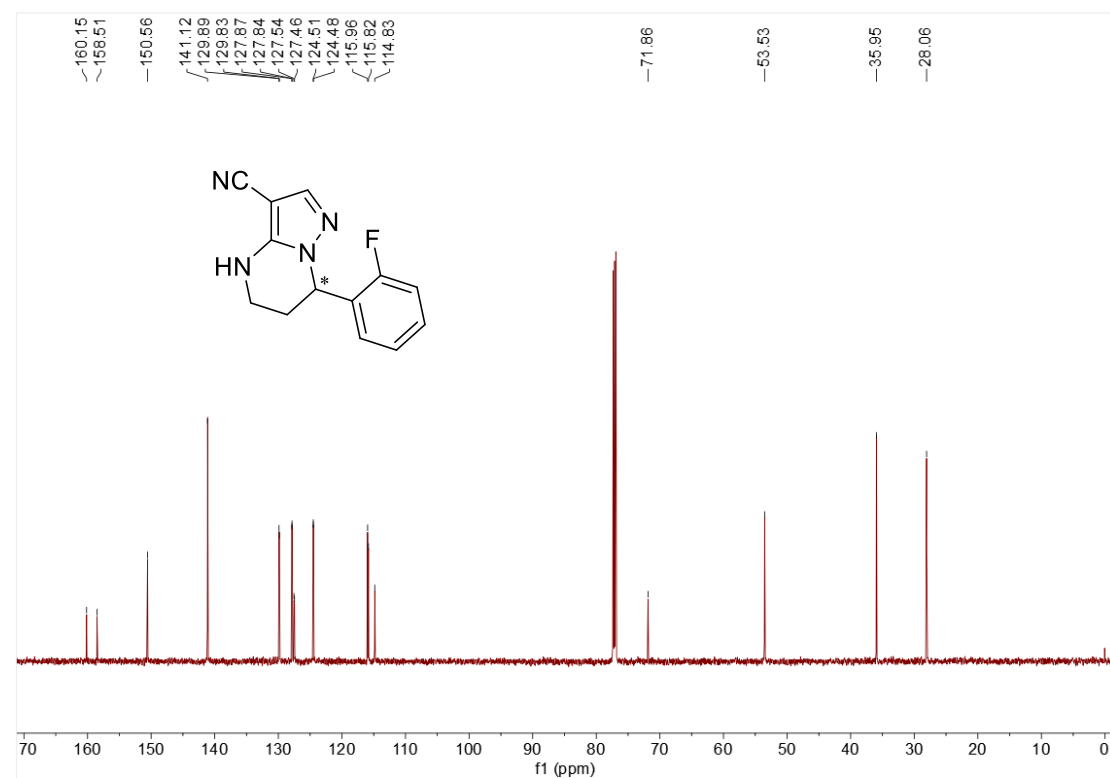
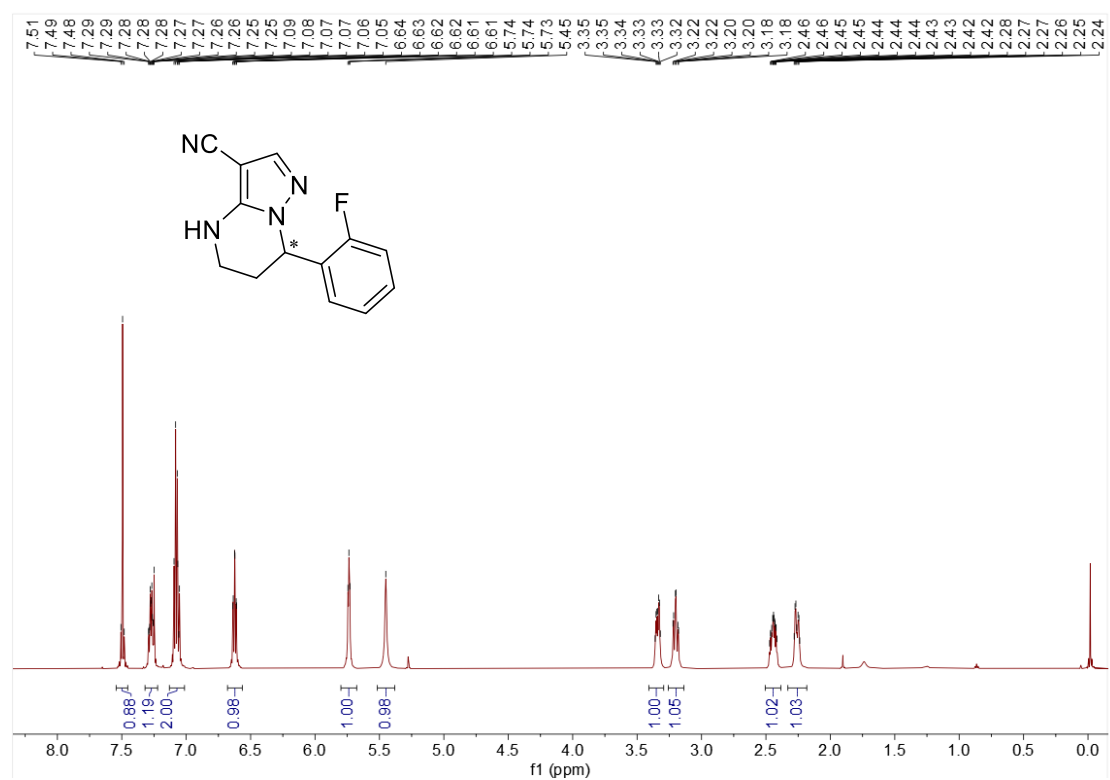
7-(4-bromophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**2j**)



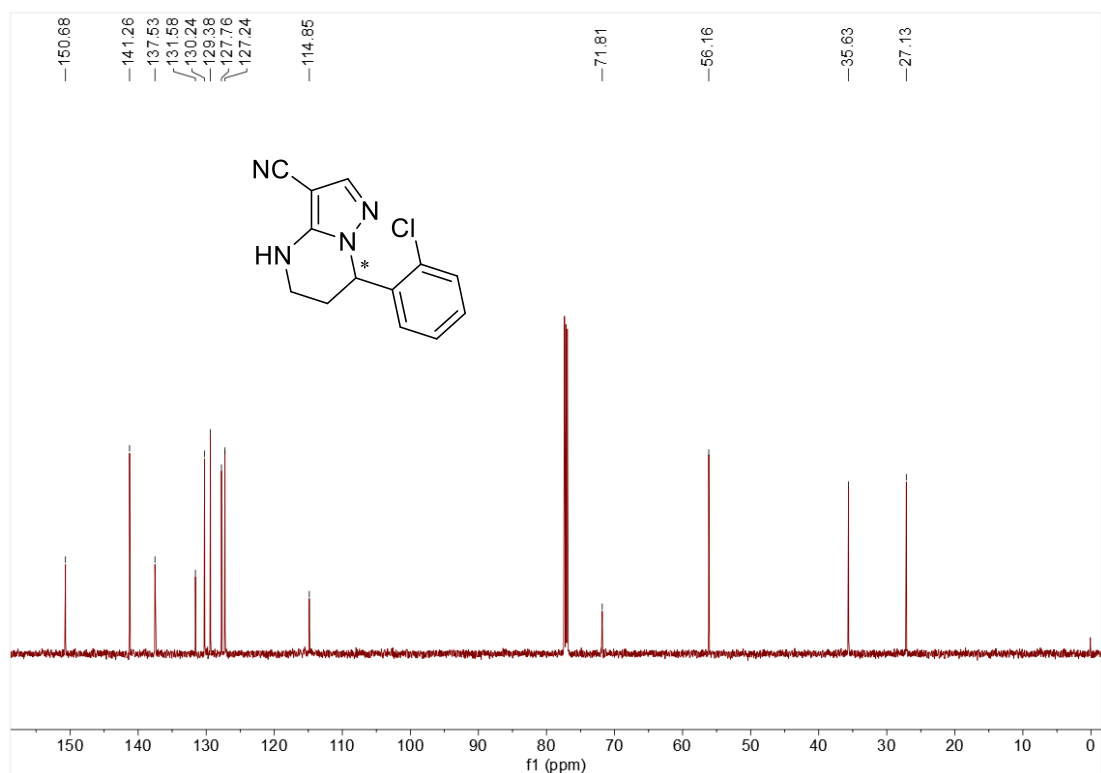
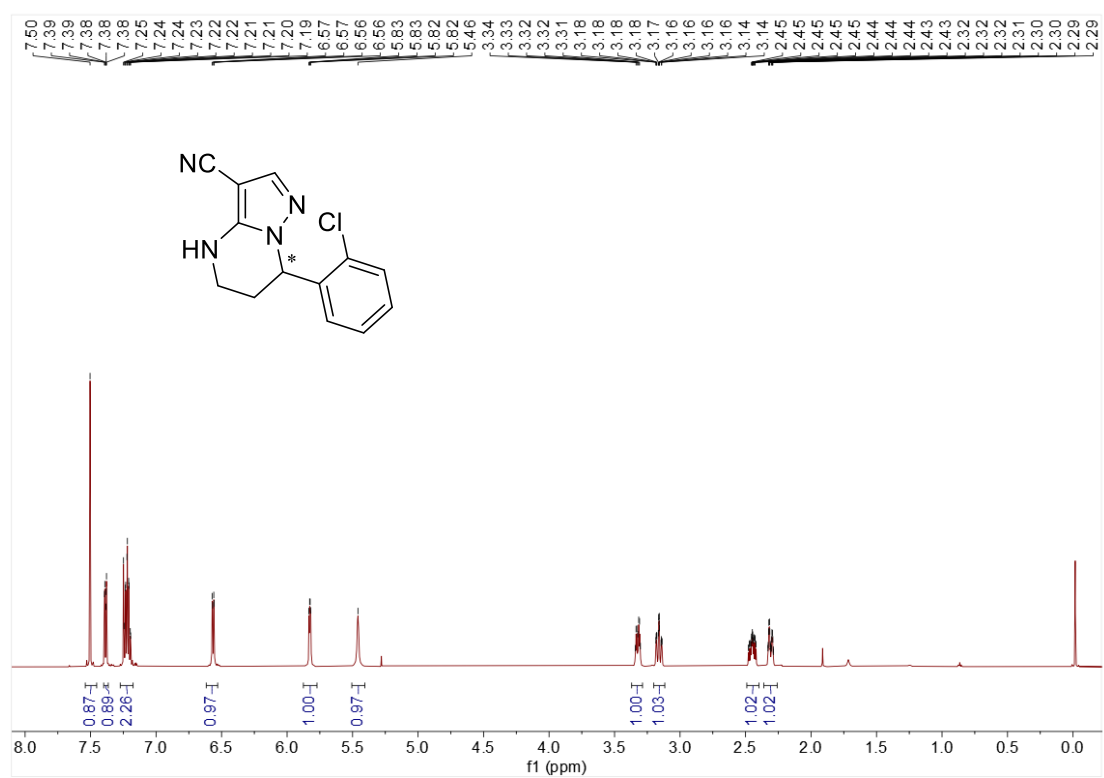
7-(2-methoxyphenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**2k**)



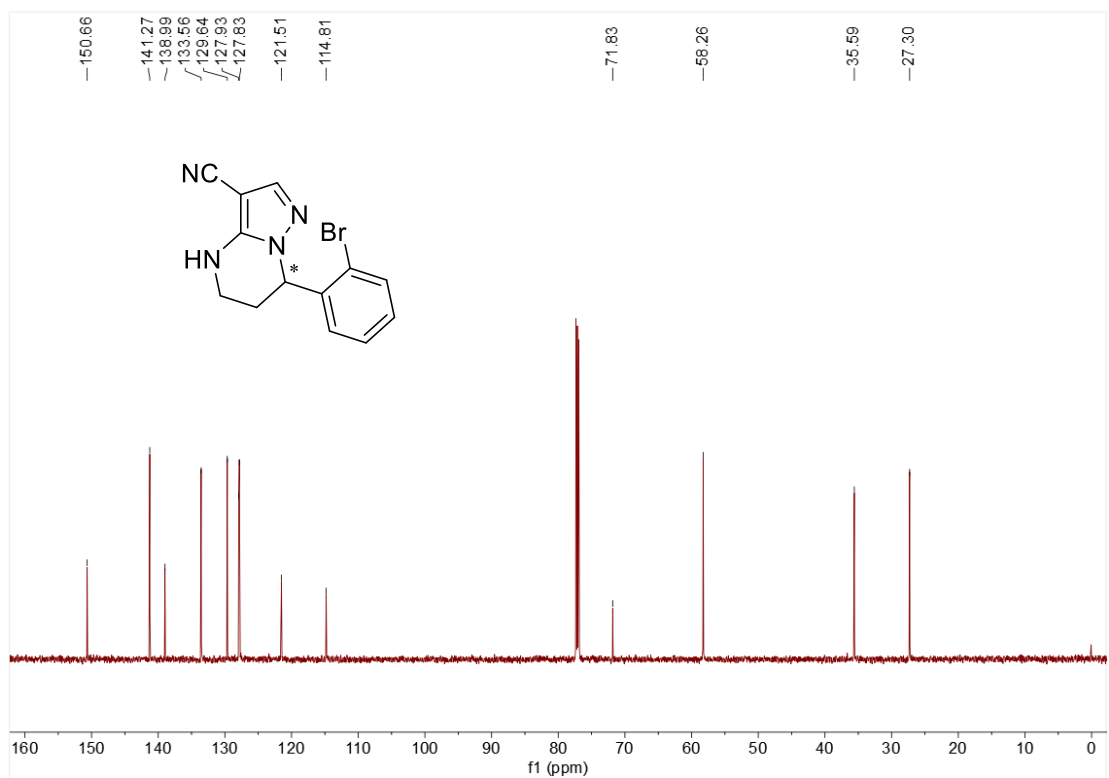
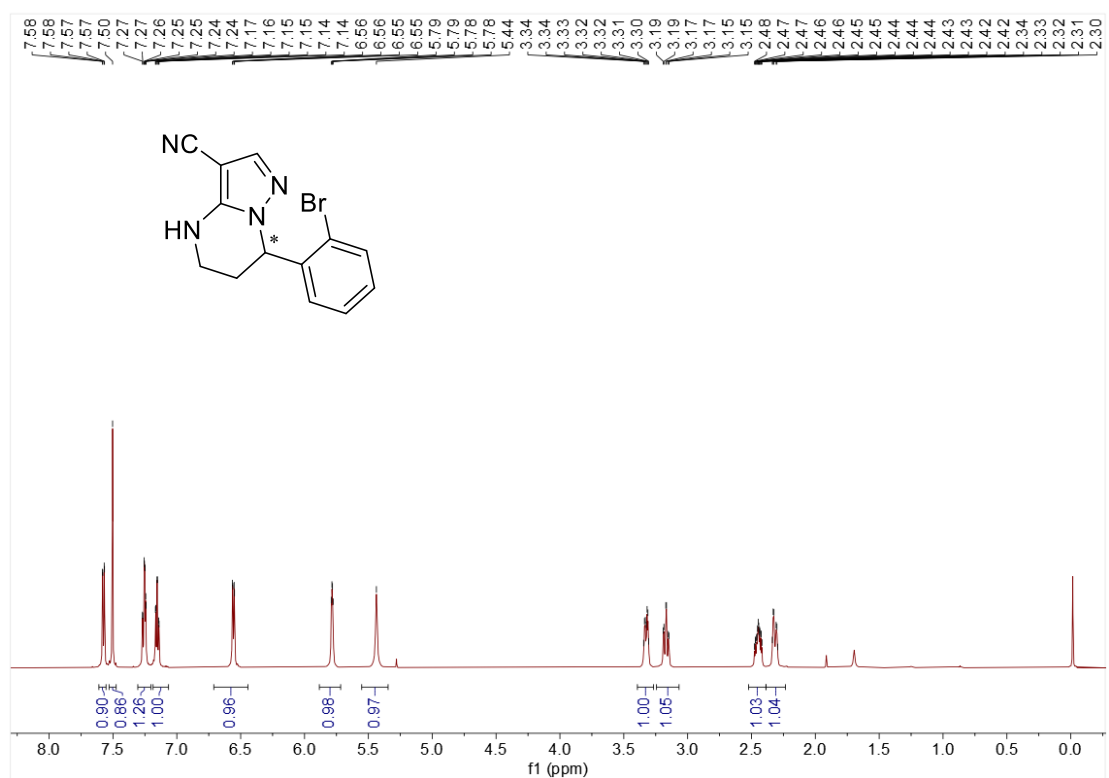
7-(2-fluorophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**21**)



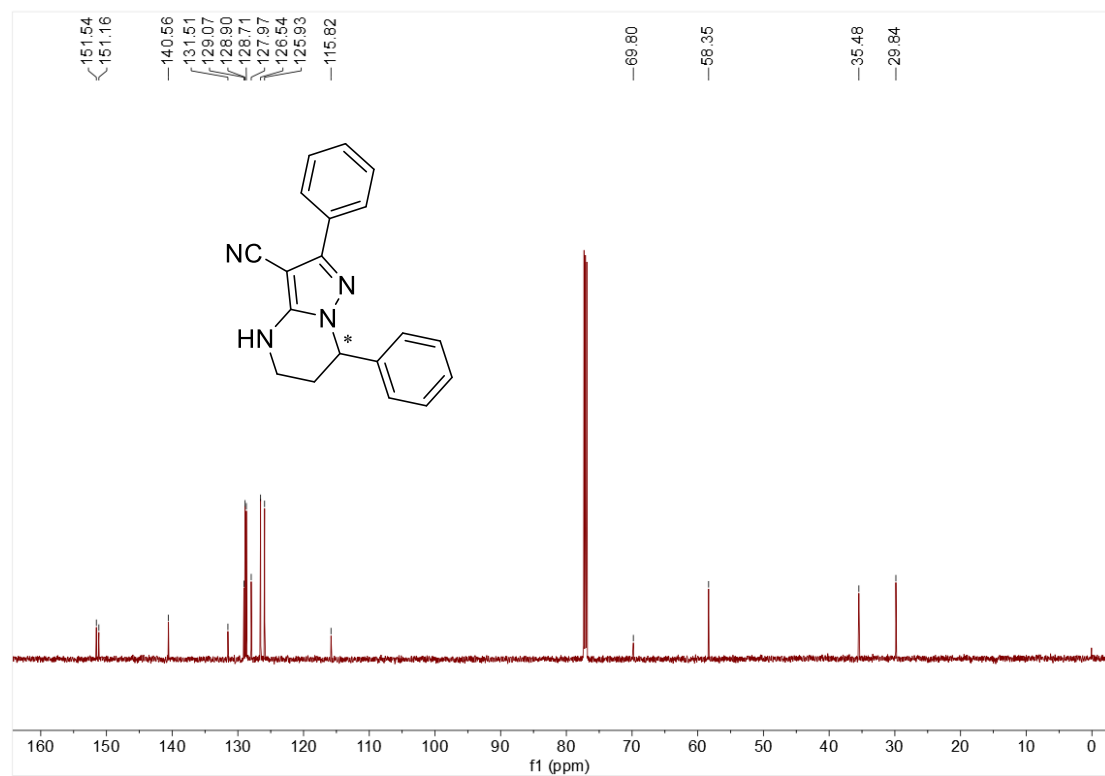
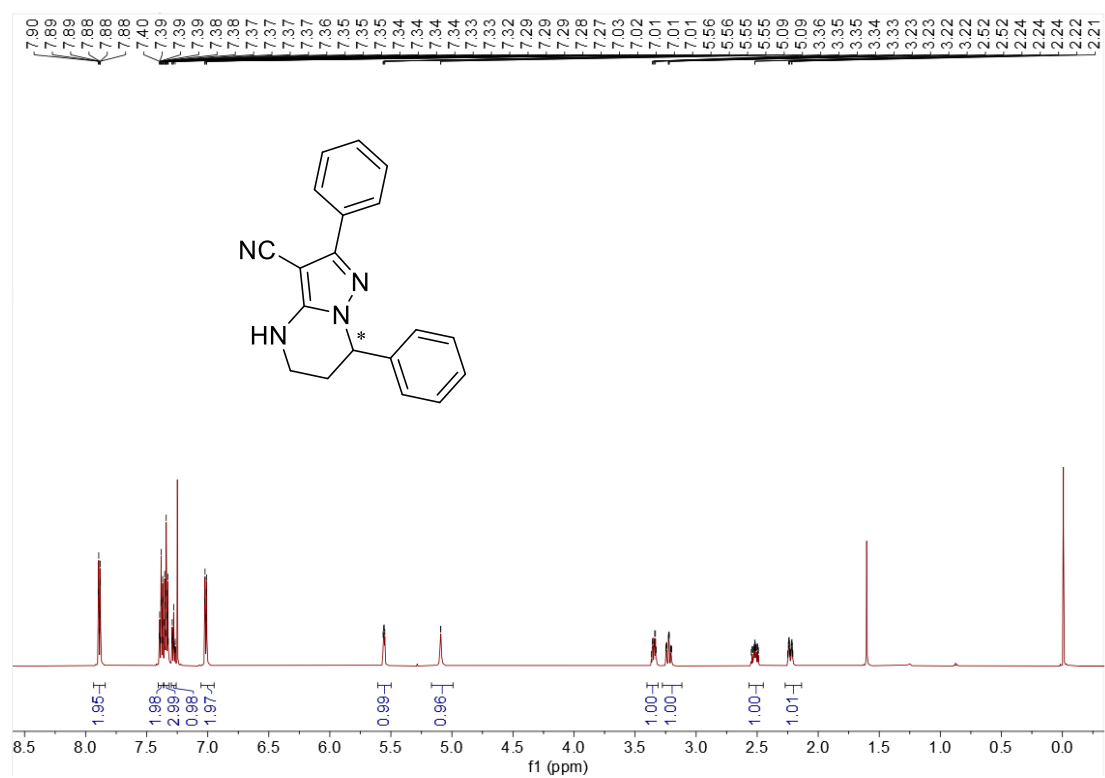
7-(2-chlorophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**2m**)



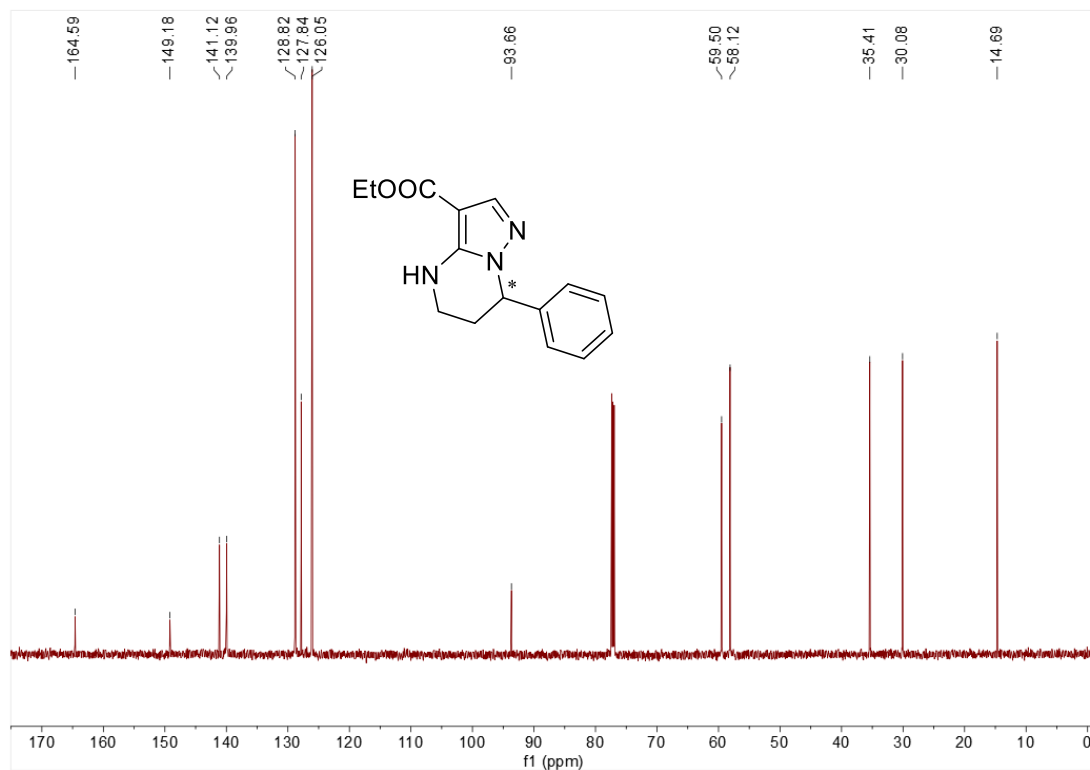
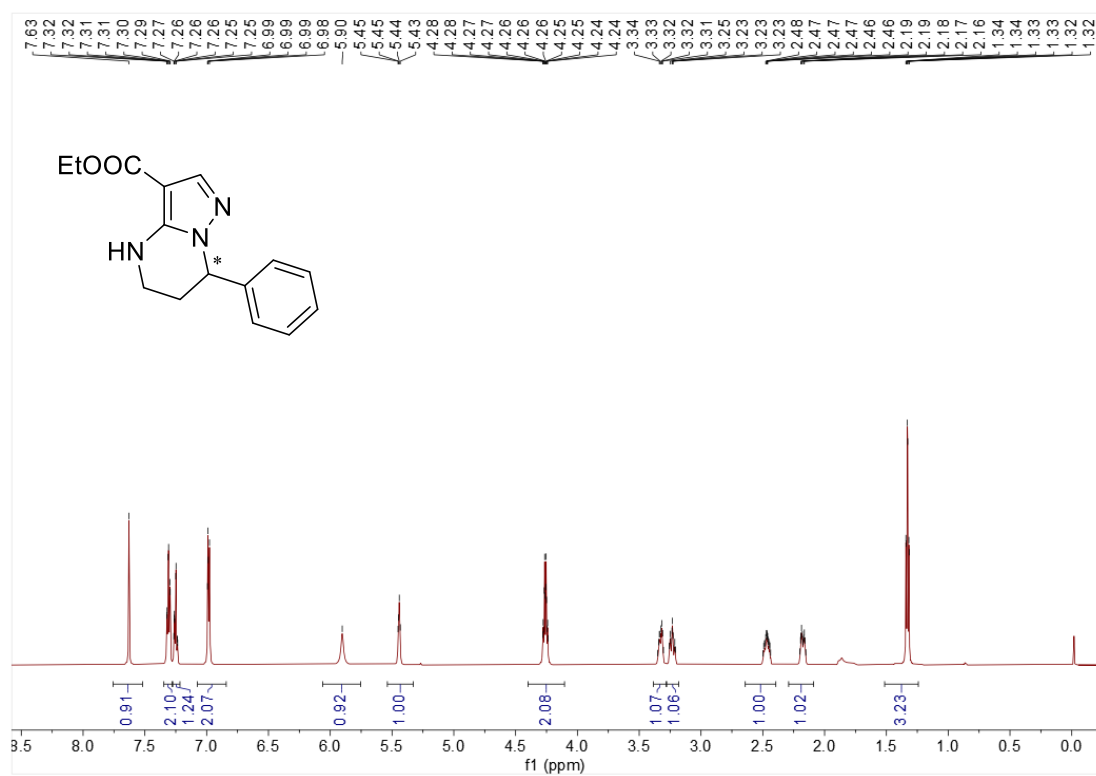
7-(2-bromophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**2n**)



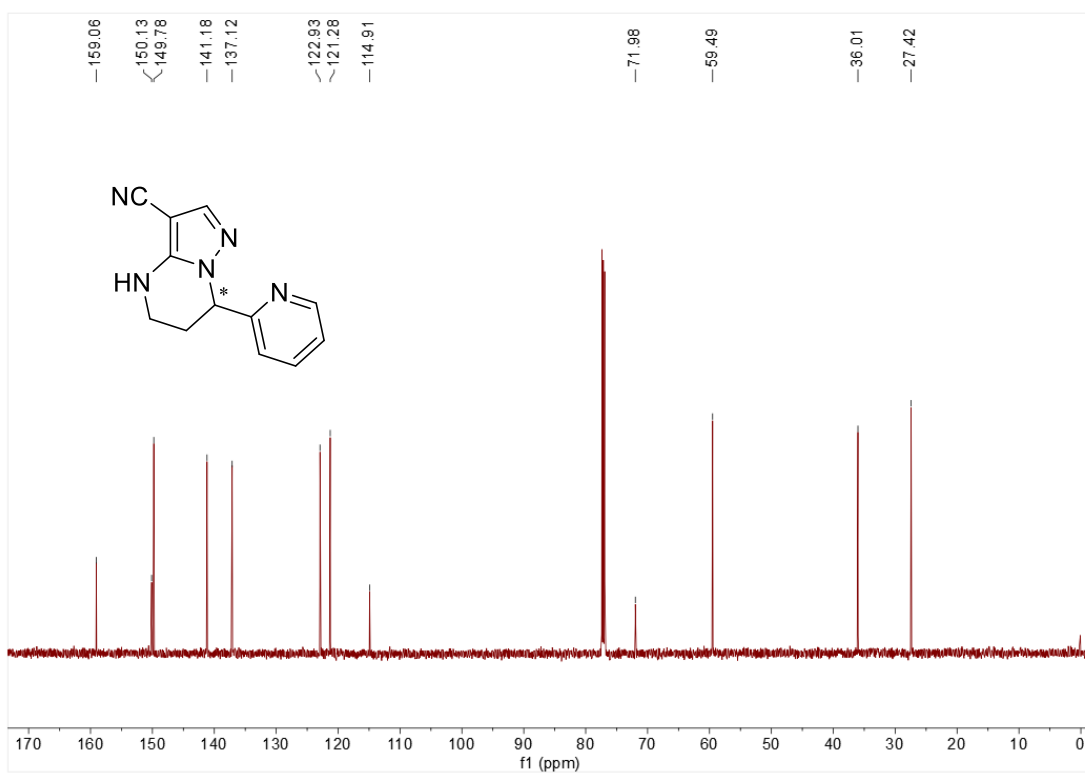
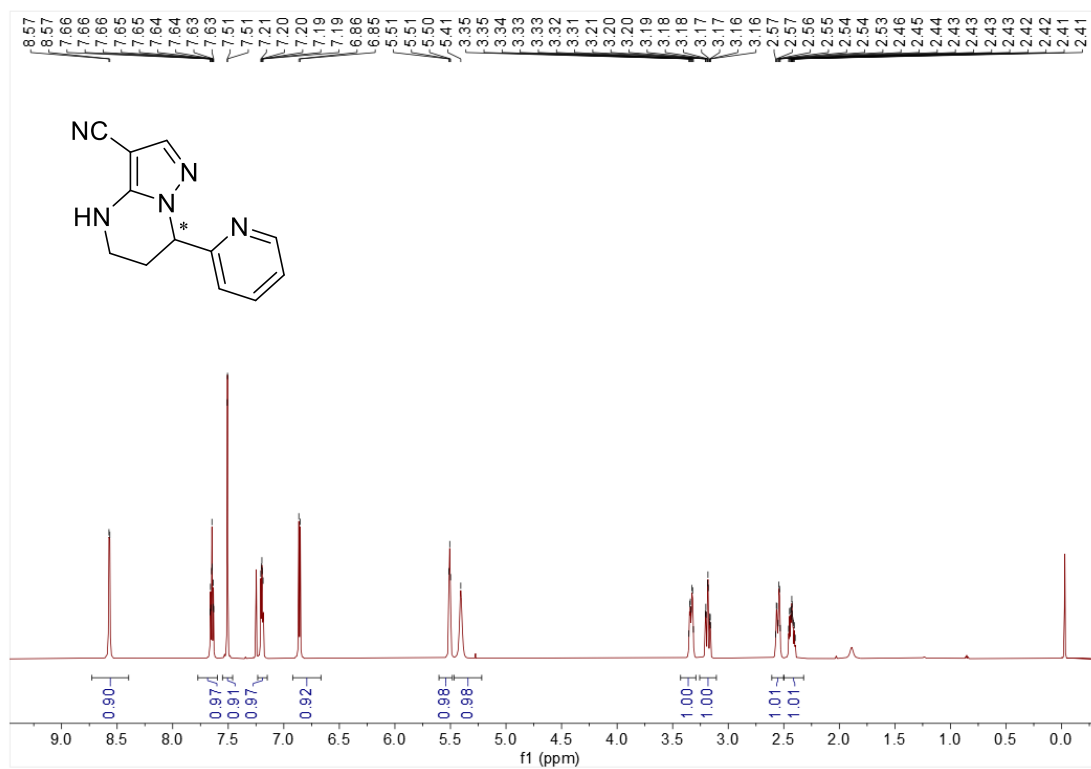
2,7-diphenyl-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**2o**)



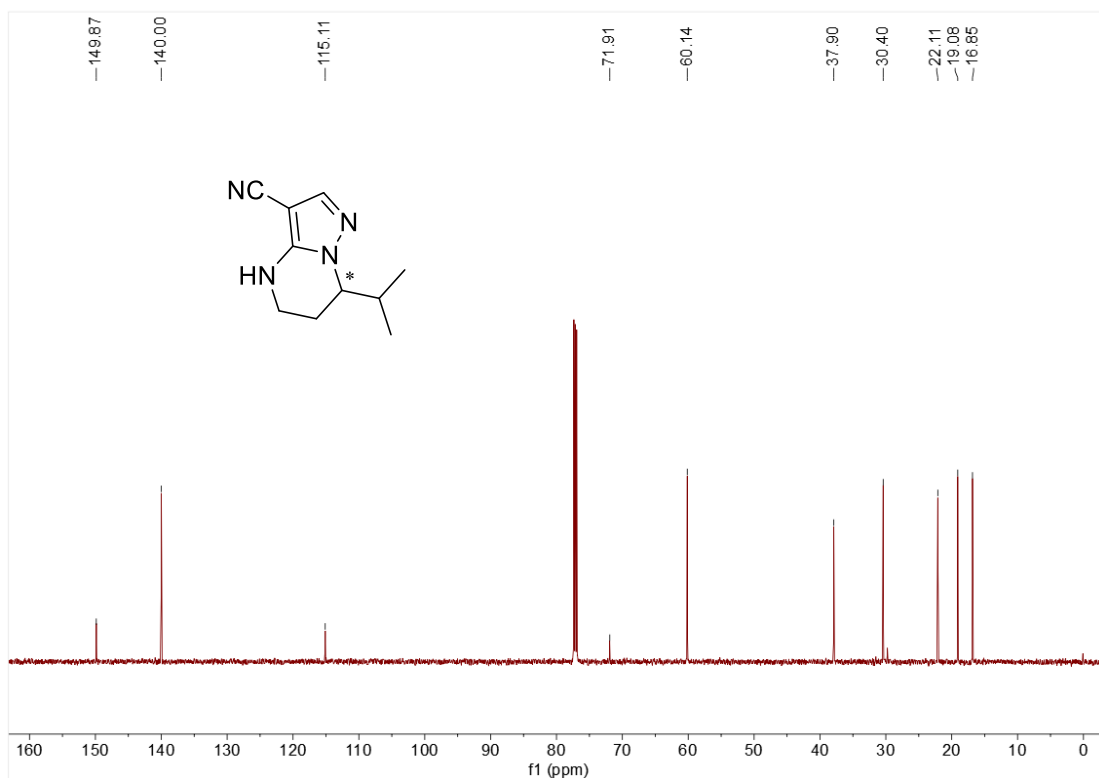
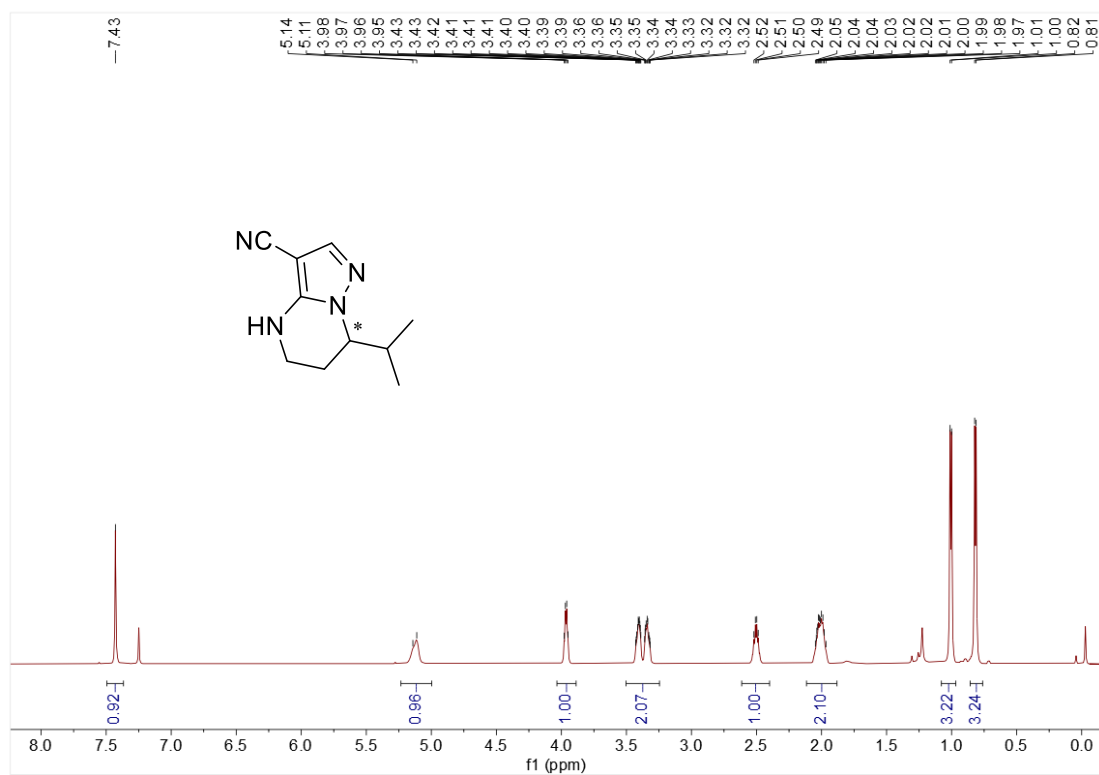
ethyl 7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carboxylate (**2p**)



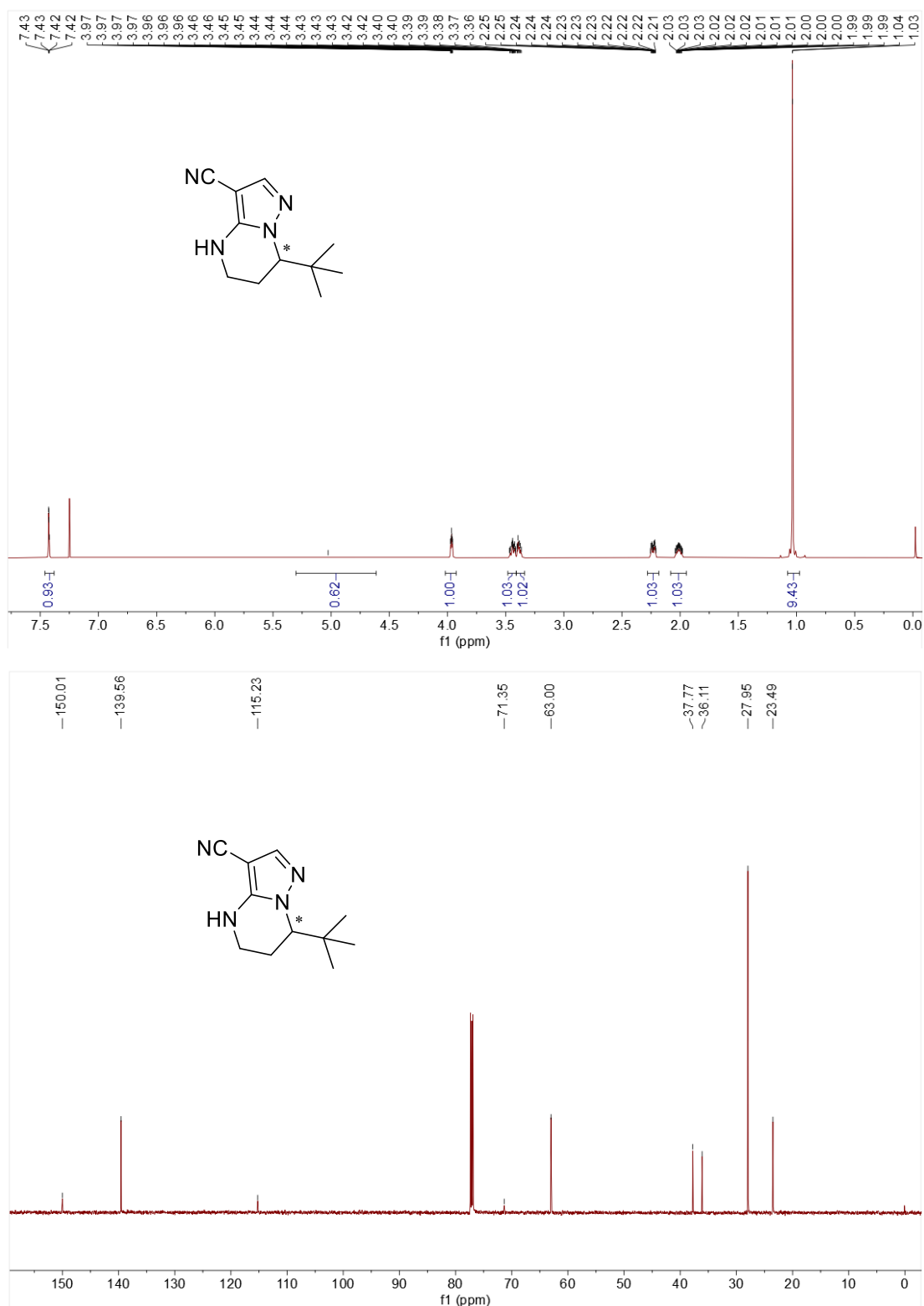
7-(pyridin-2-yl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**2q**)



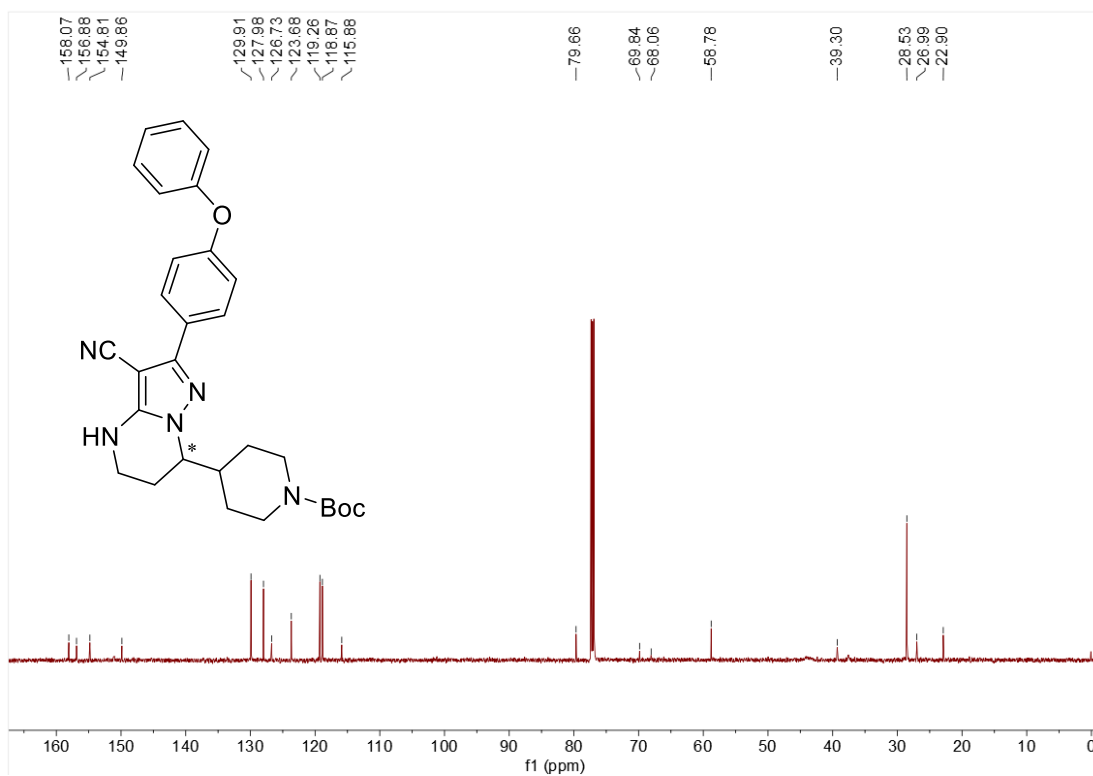
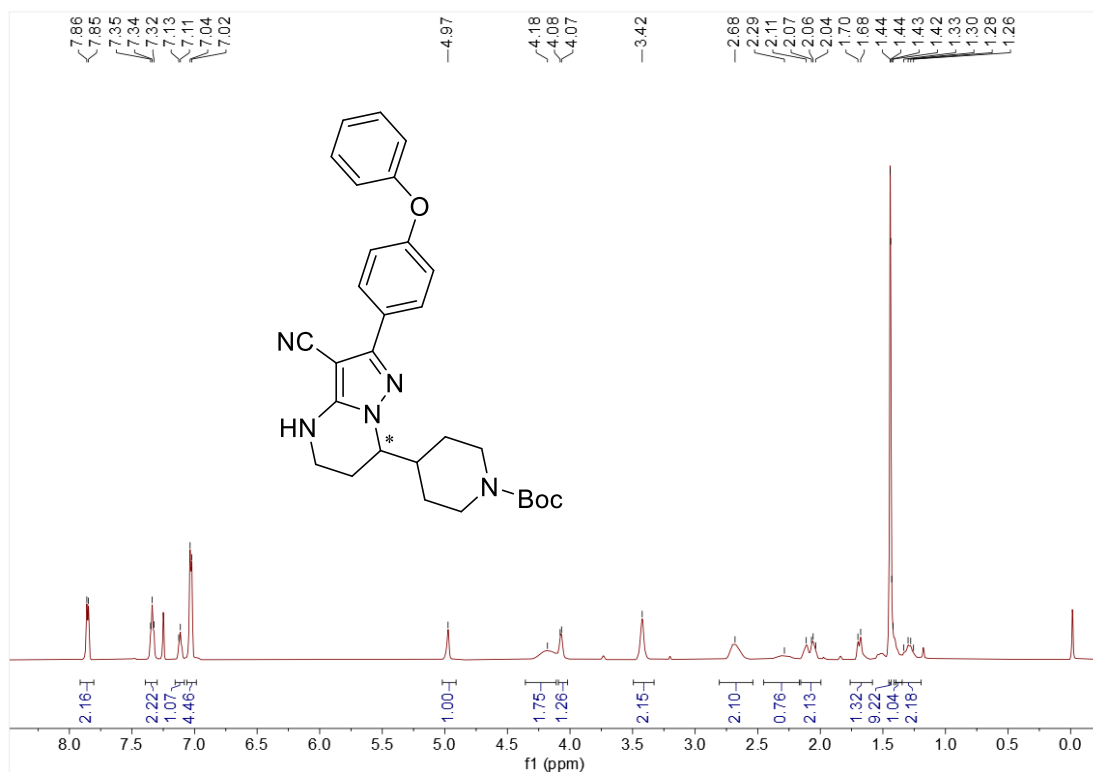
7-isopropyl-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**2r**)



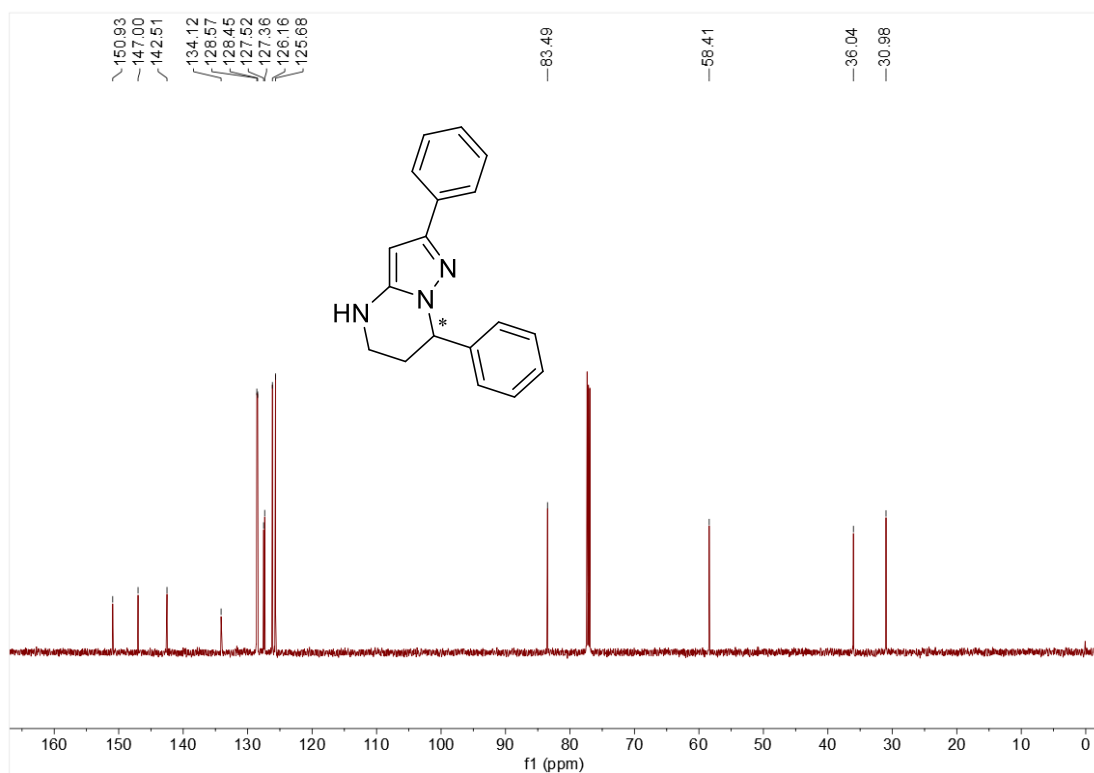
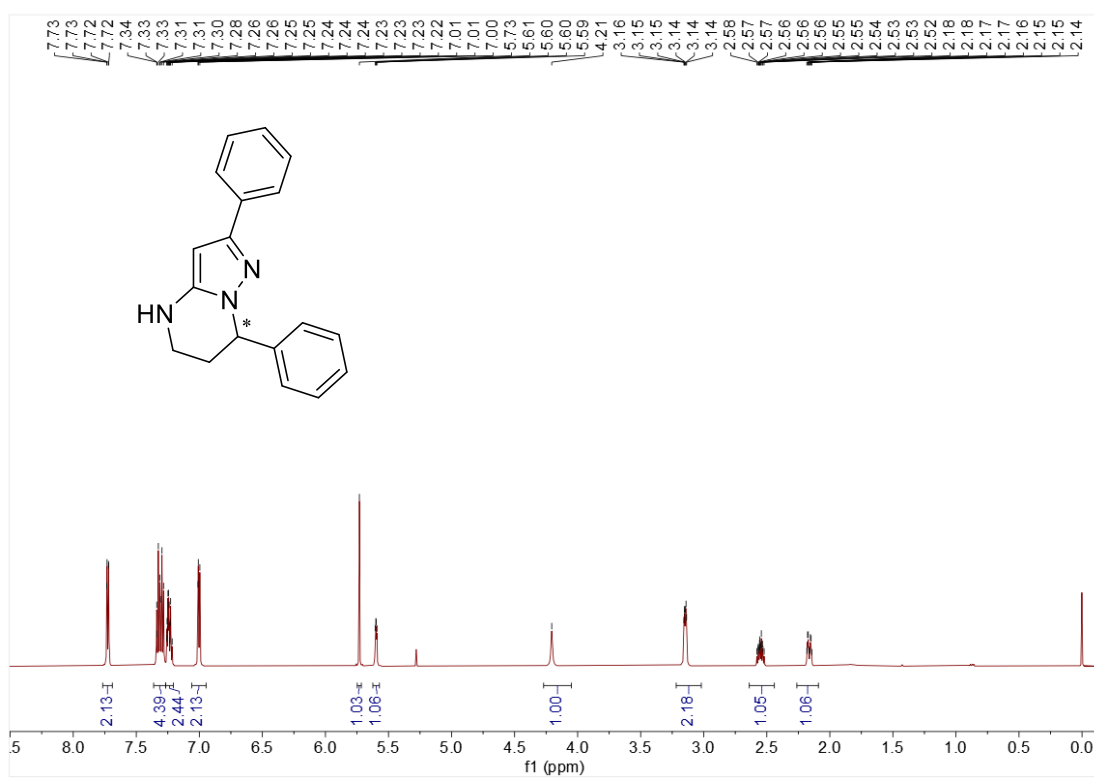
7-(*tert*-butyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**2s**)



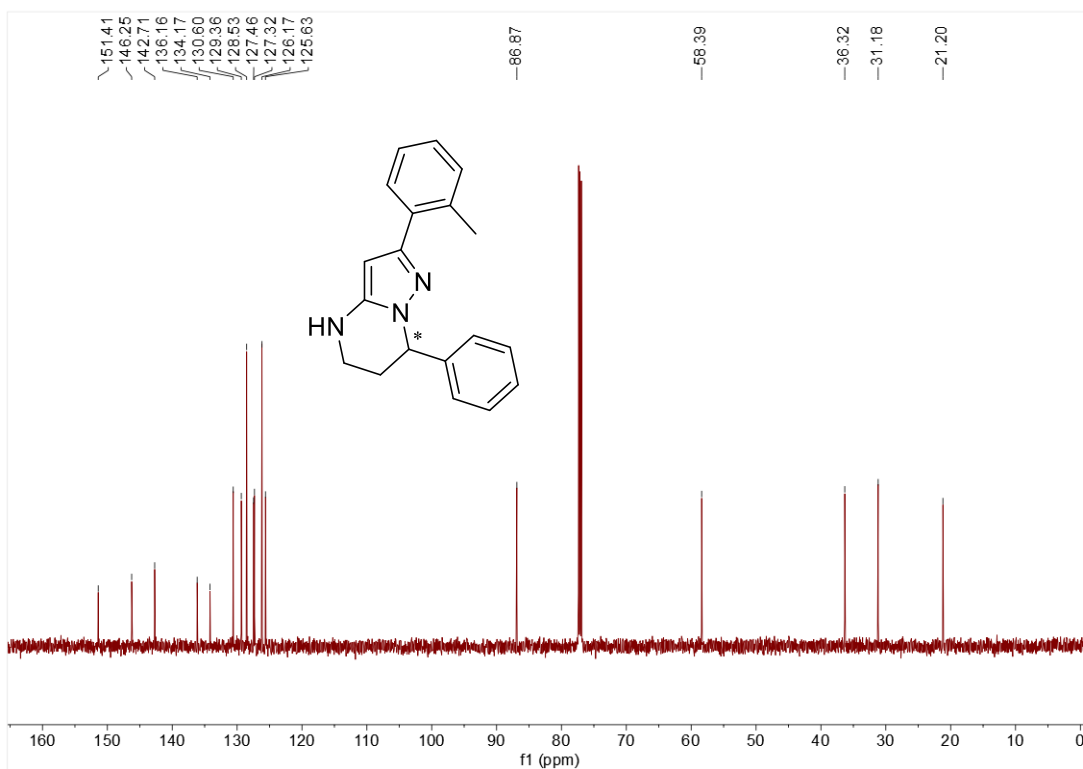
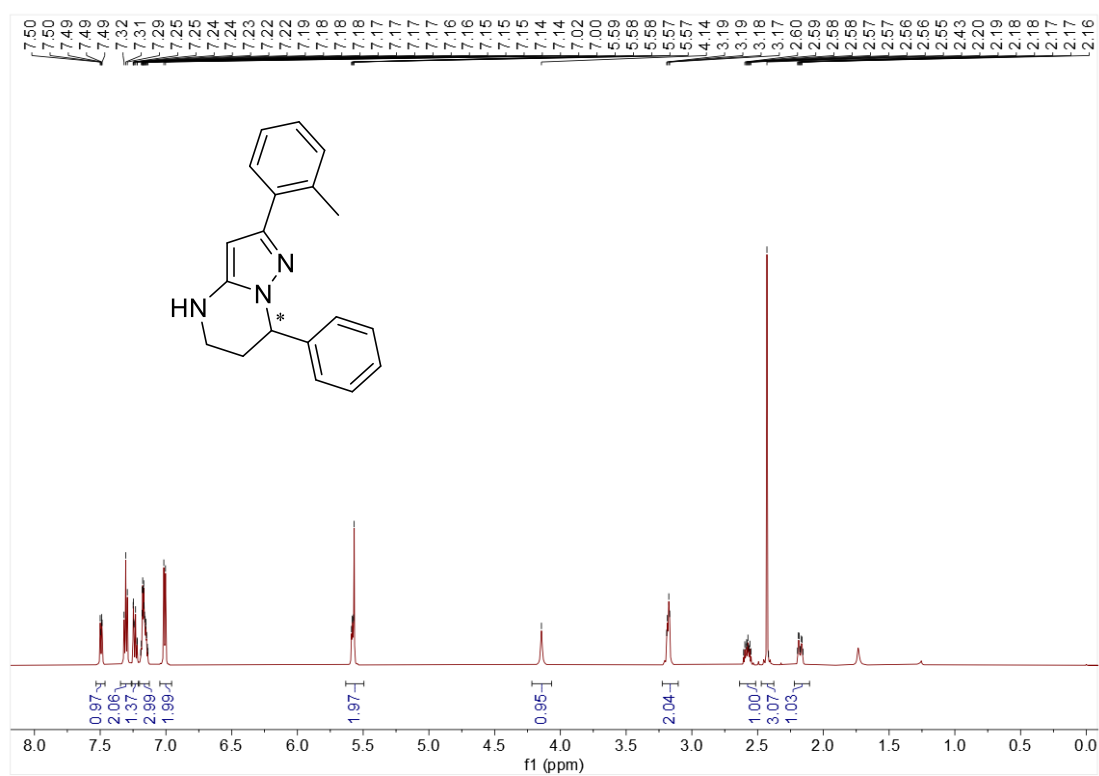
tert-butyl 4-(3-cyano-2-(4-phenoxyphenyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidin-7-yl)piperidine-1-carboxylate (**2t**)



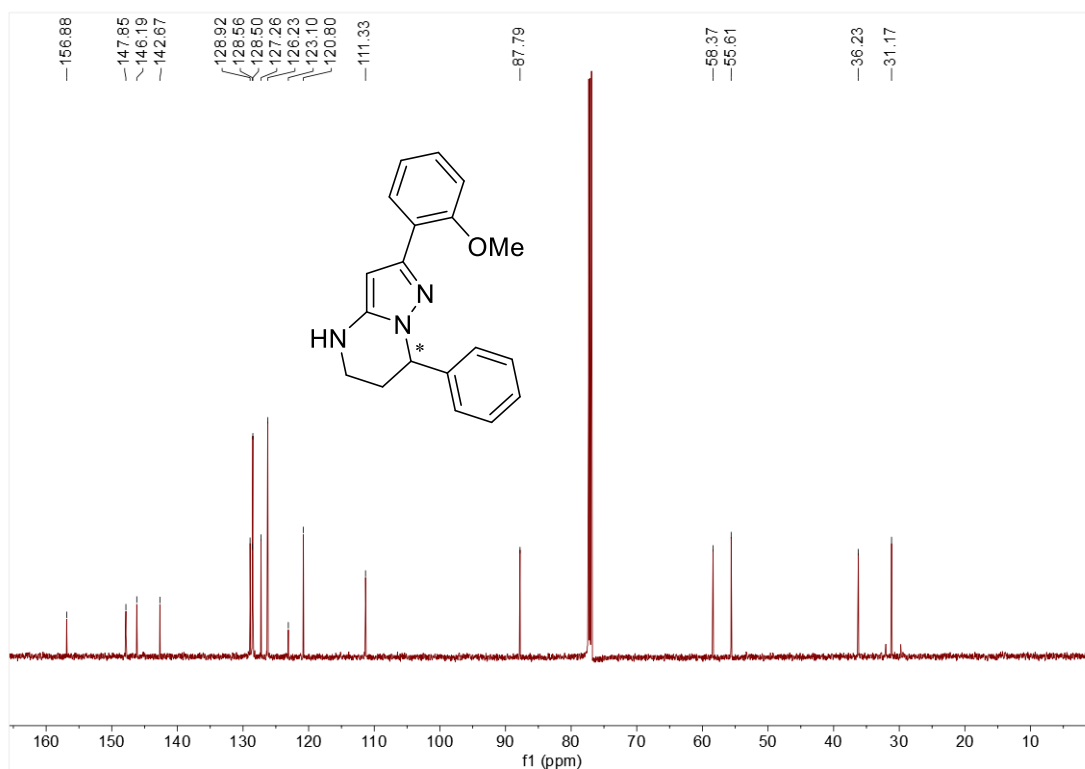
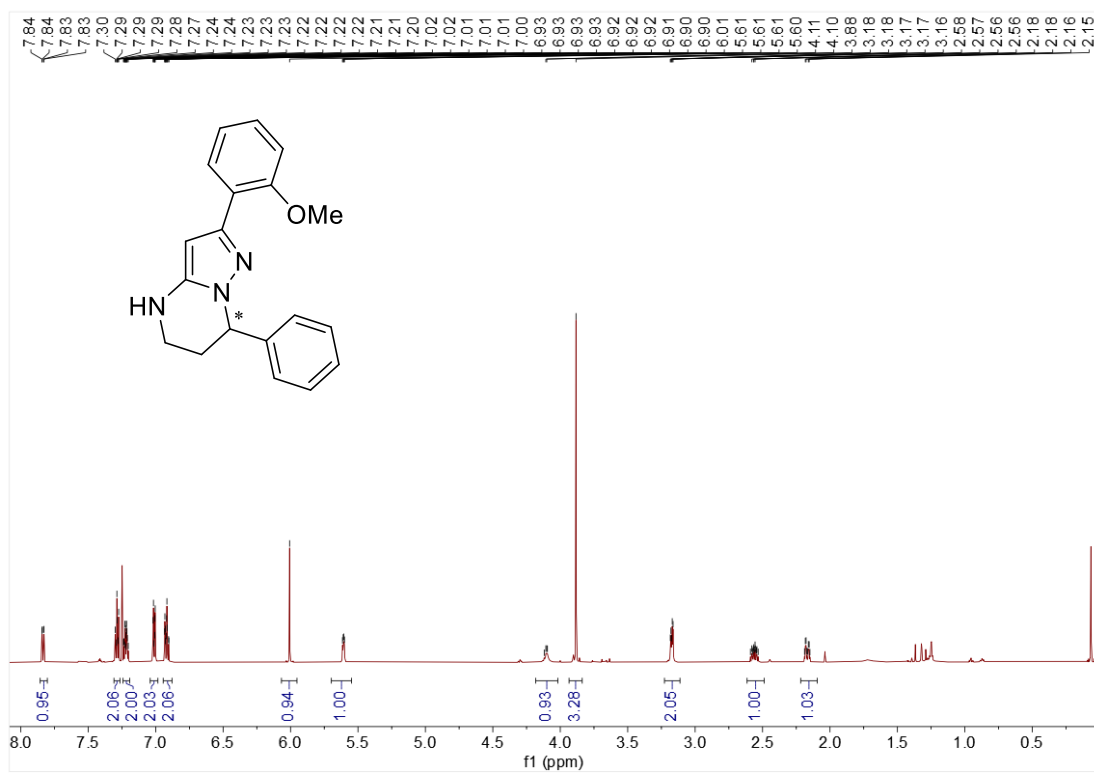
2,7-diphenyl-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine (**4a**)



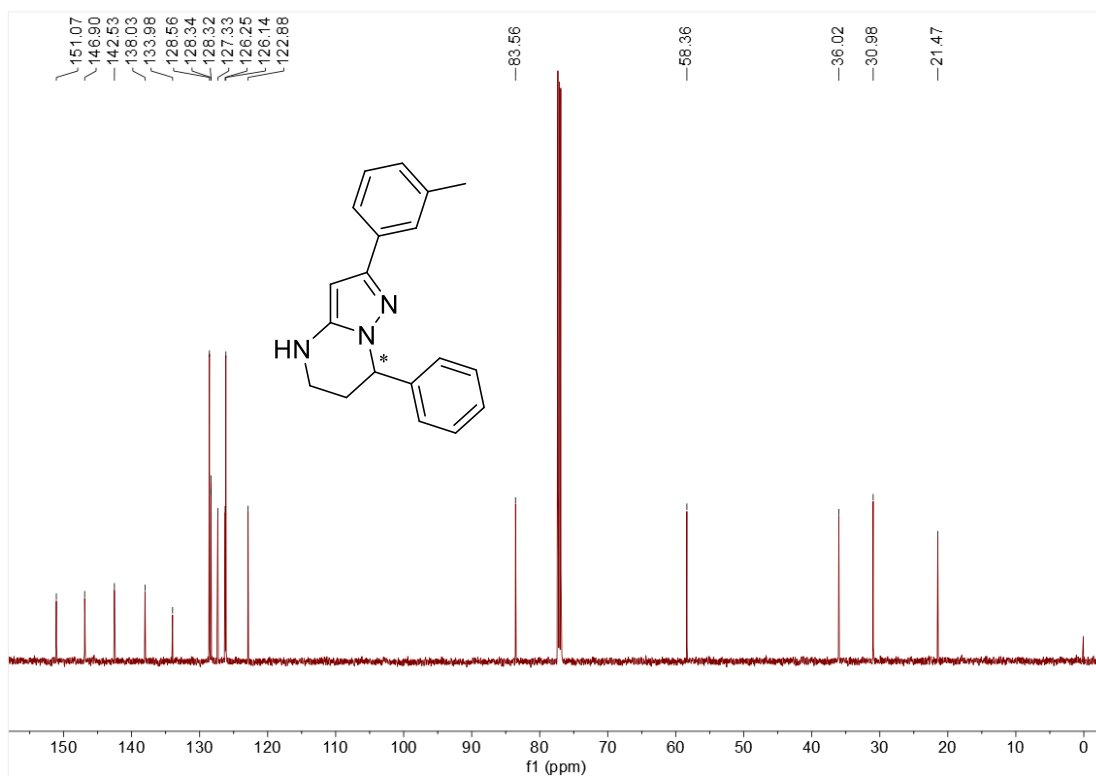
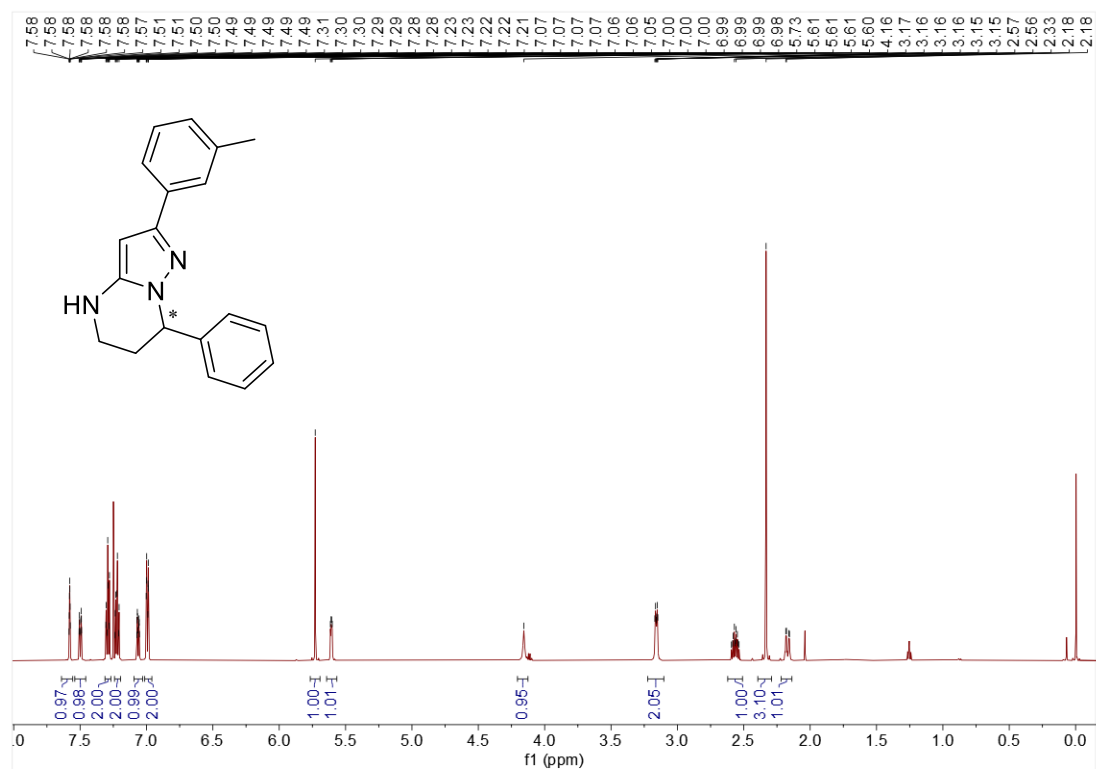
7-phenyl-2-(*o*-tolyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine (**4b**)



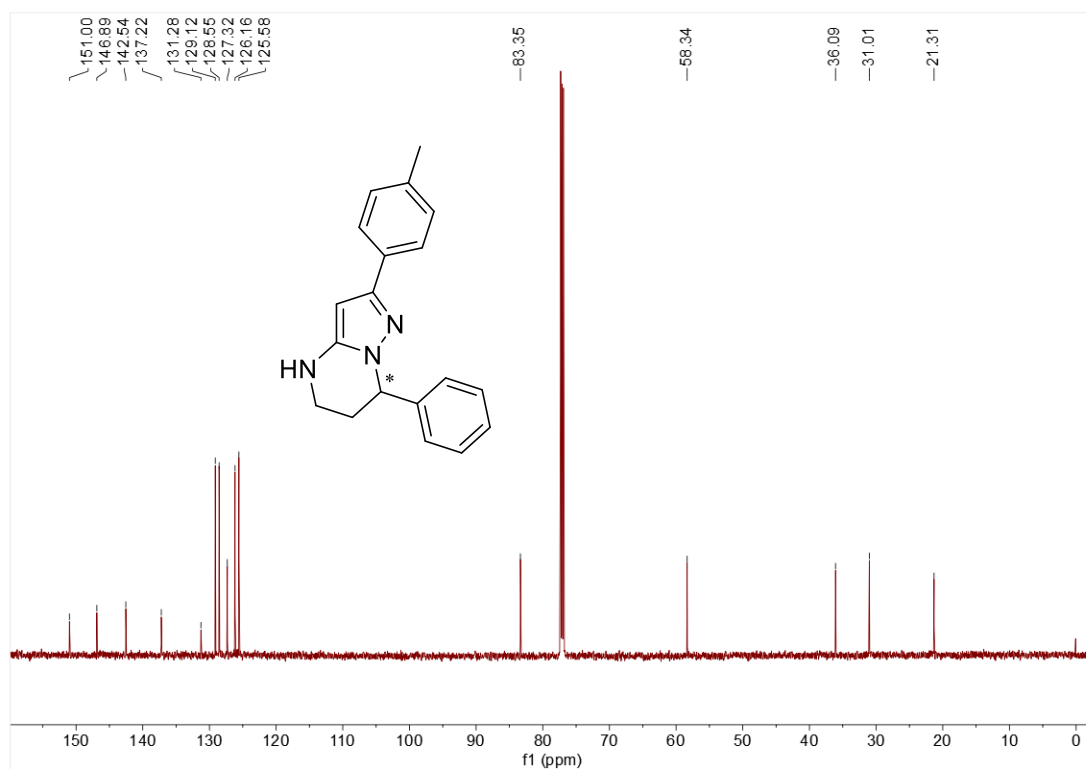
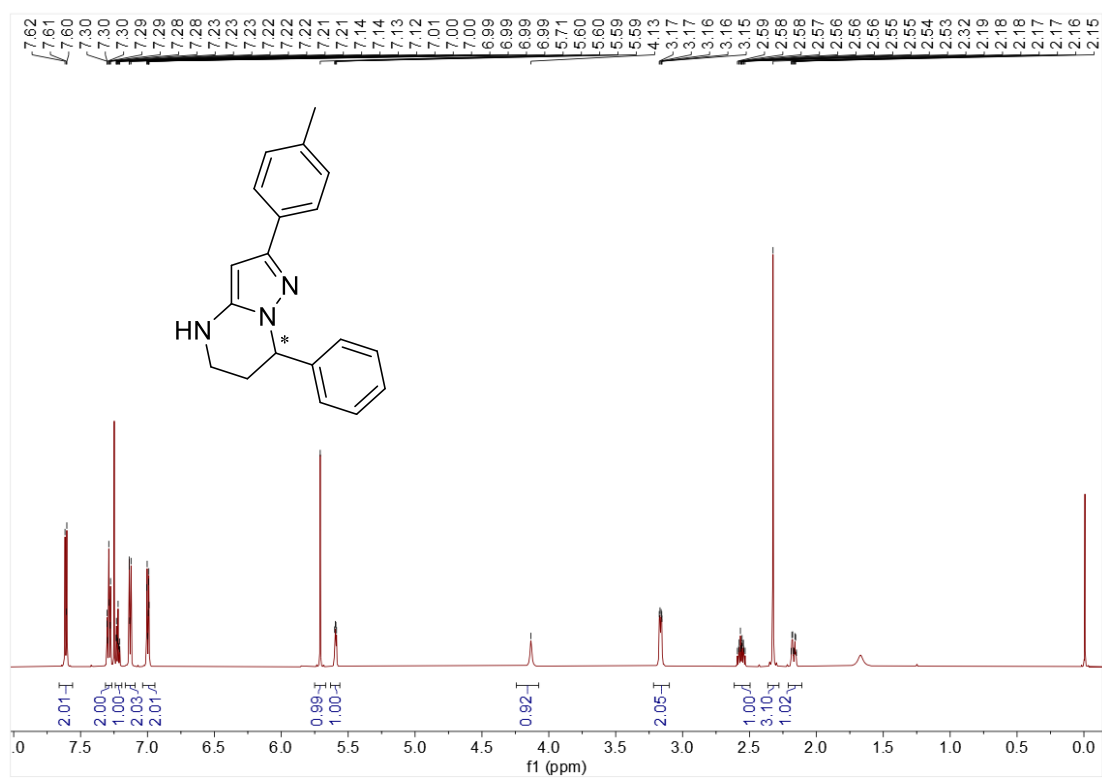
2-(2-methoxyphenyl)-7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine (**4c**)



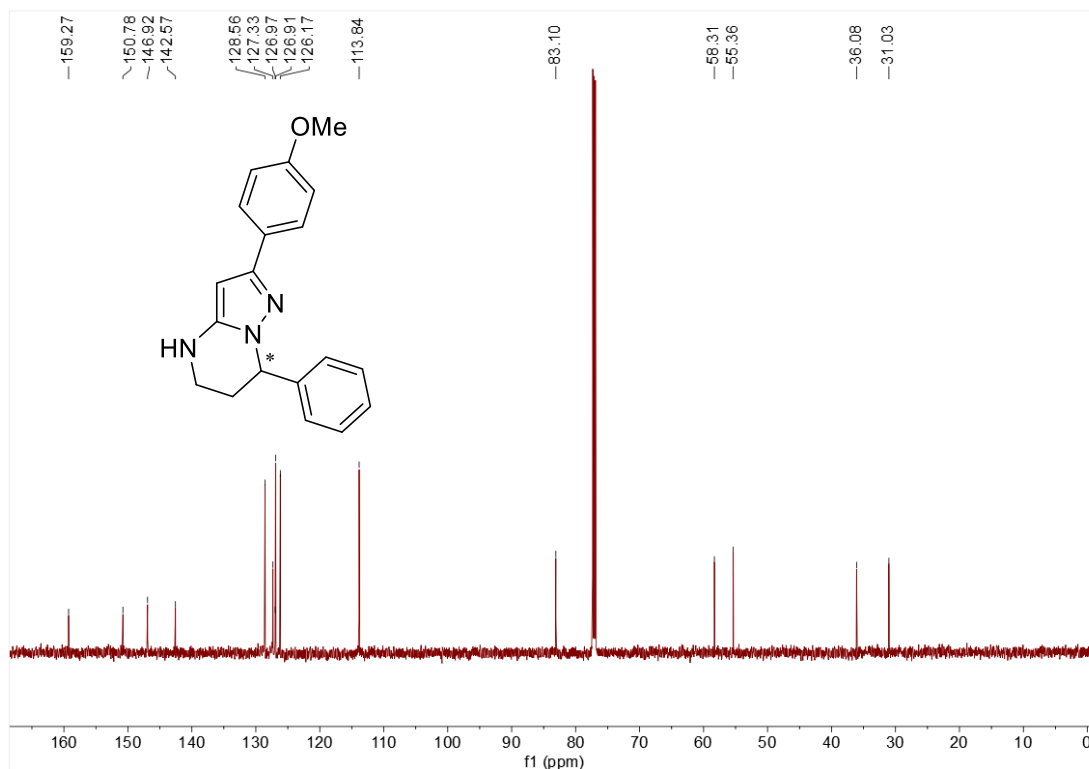
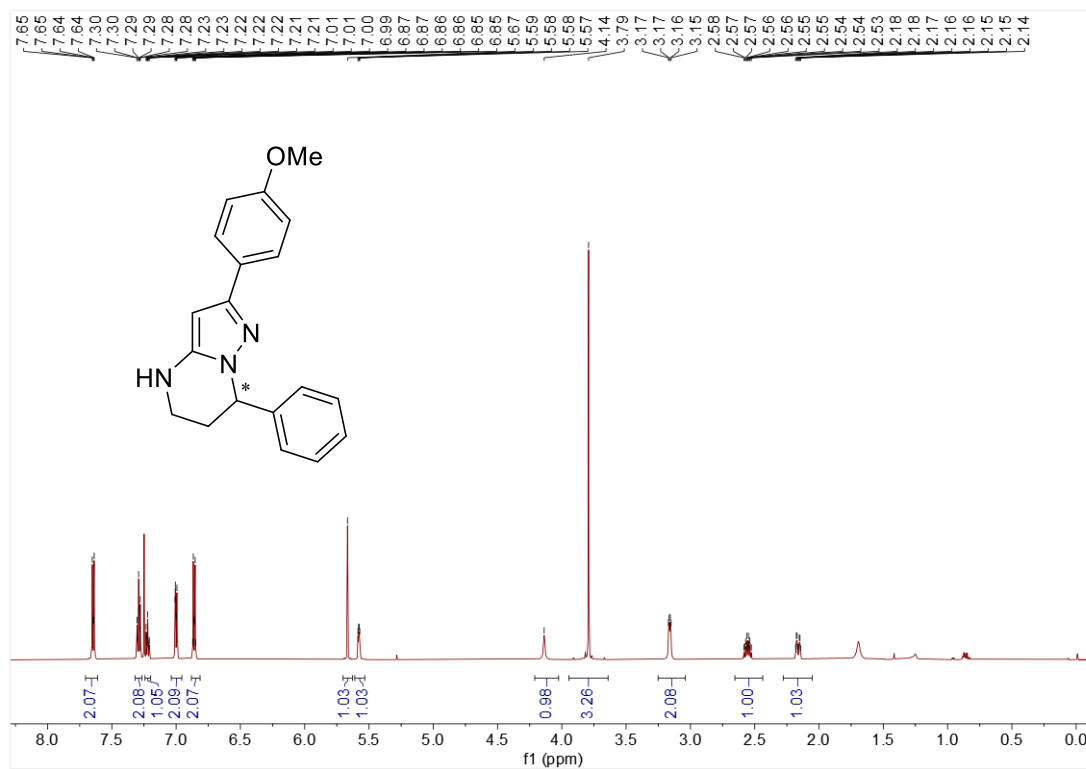
7-phenyl-2-(*m*-tolyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine (**4d**)



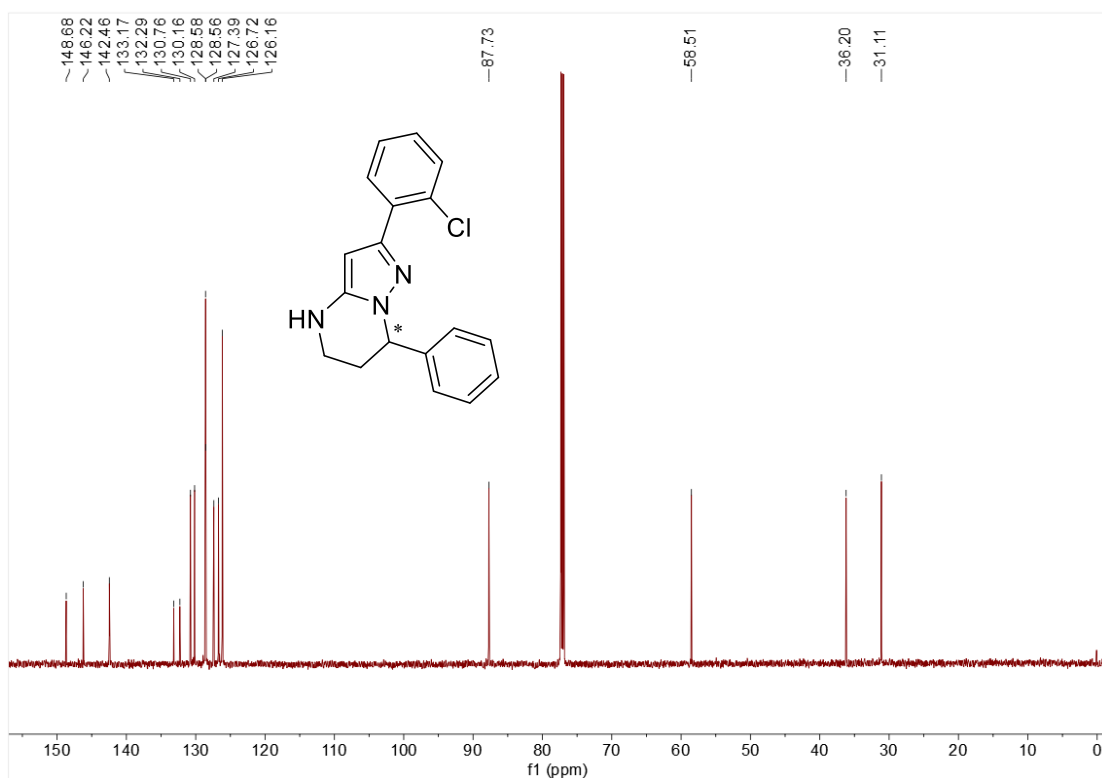
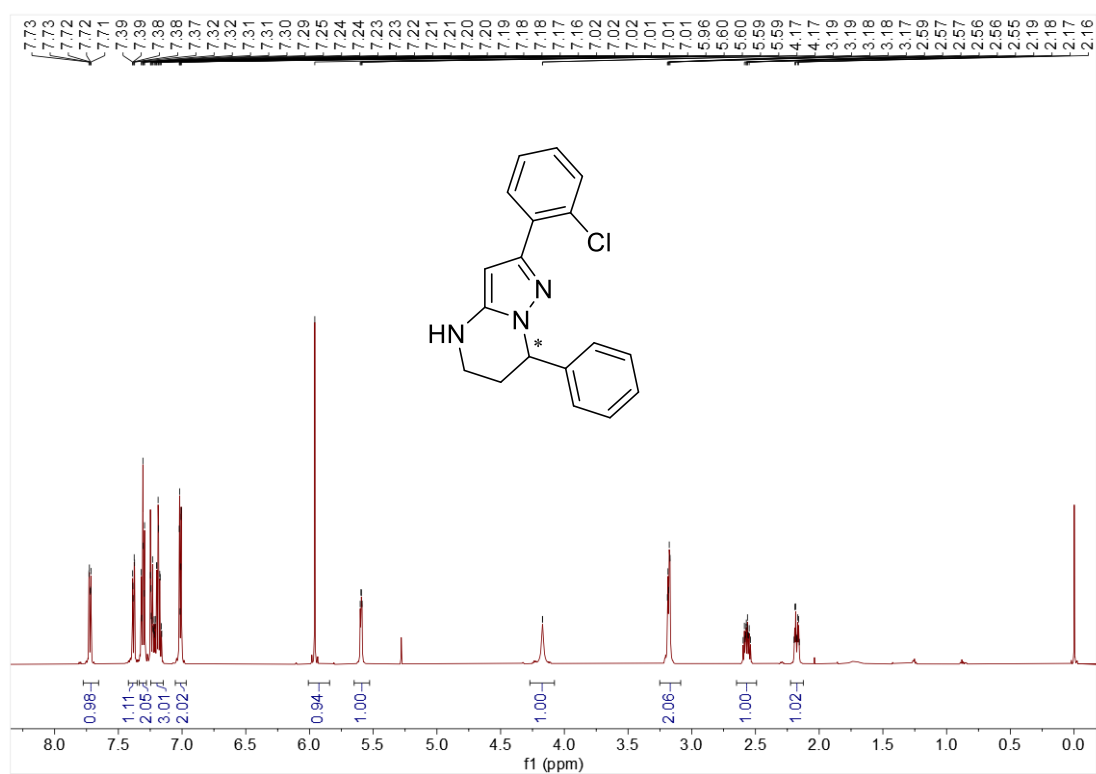
7-phenyl-2-(*p*-tolyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine (**4e**)



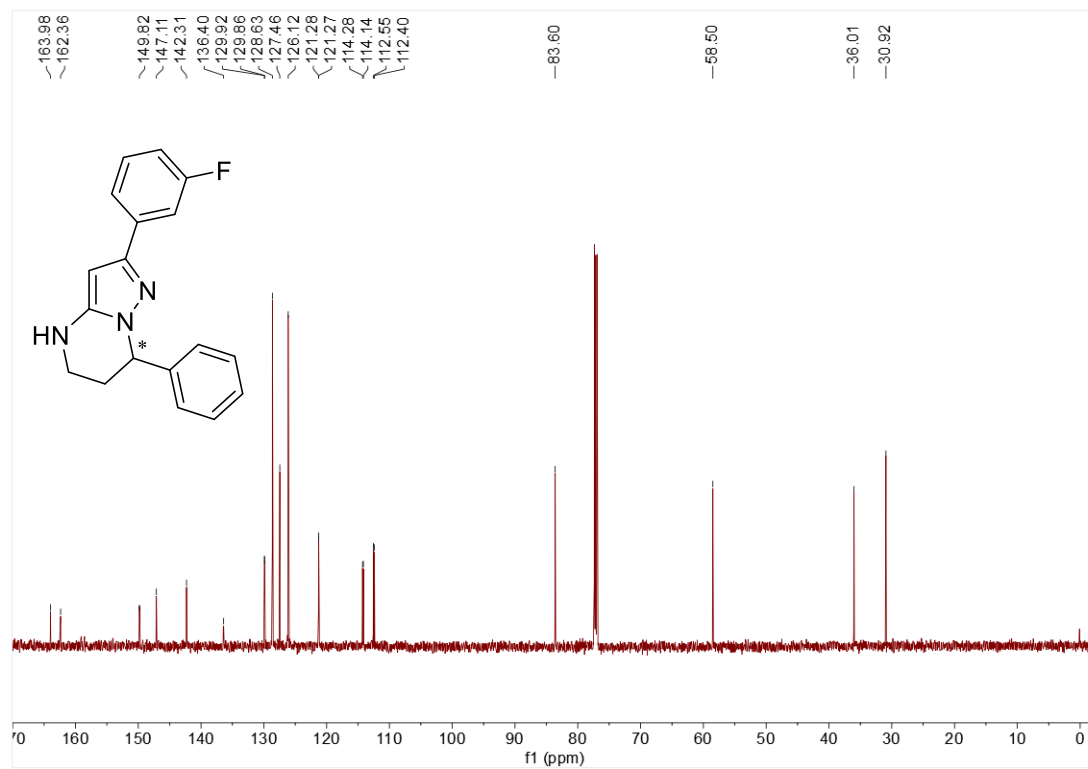
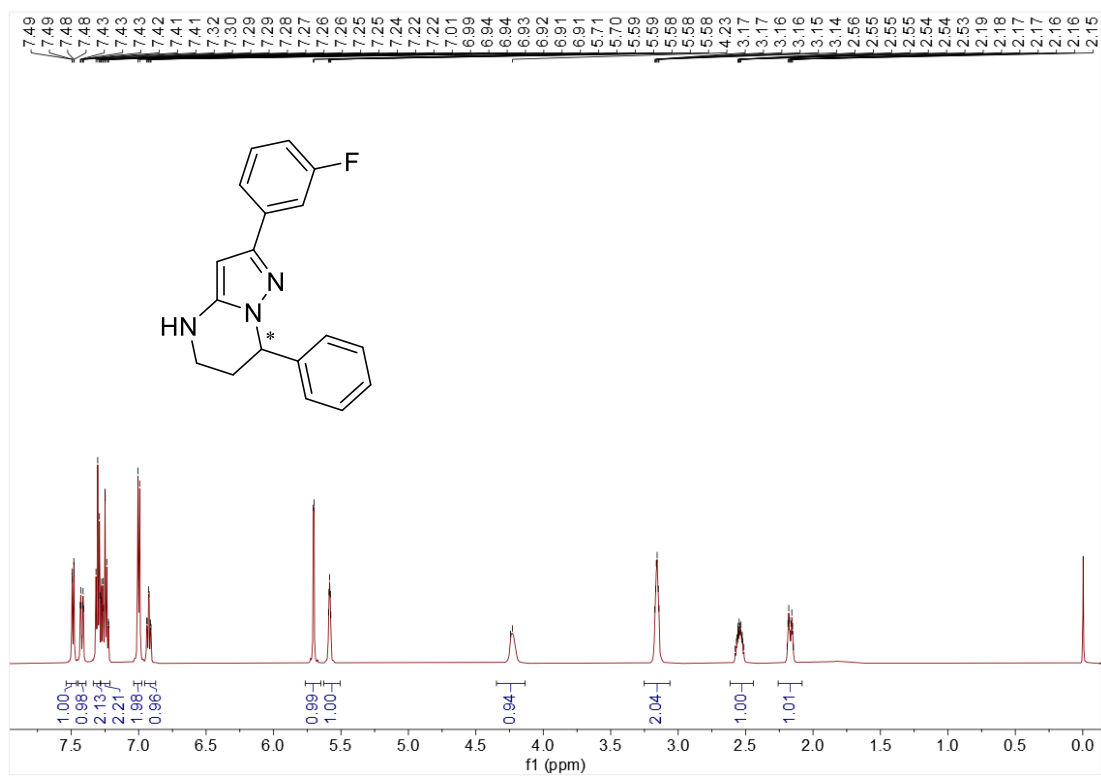
2-(4-methoxyphenyl)-7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine (**4f**)



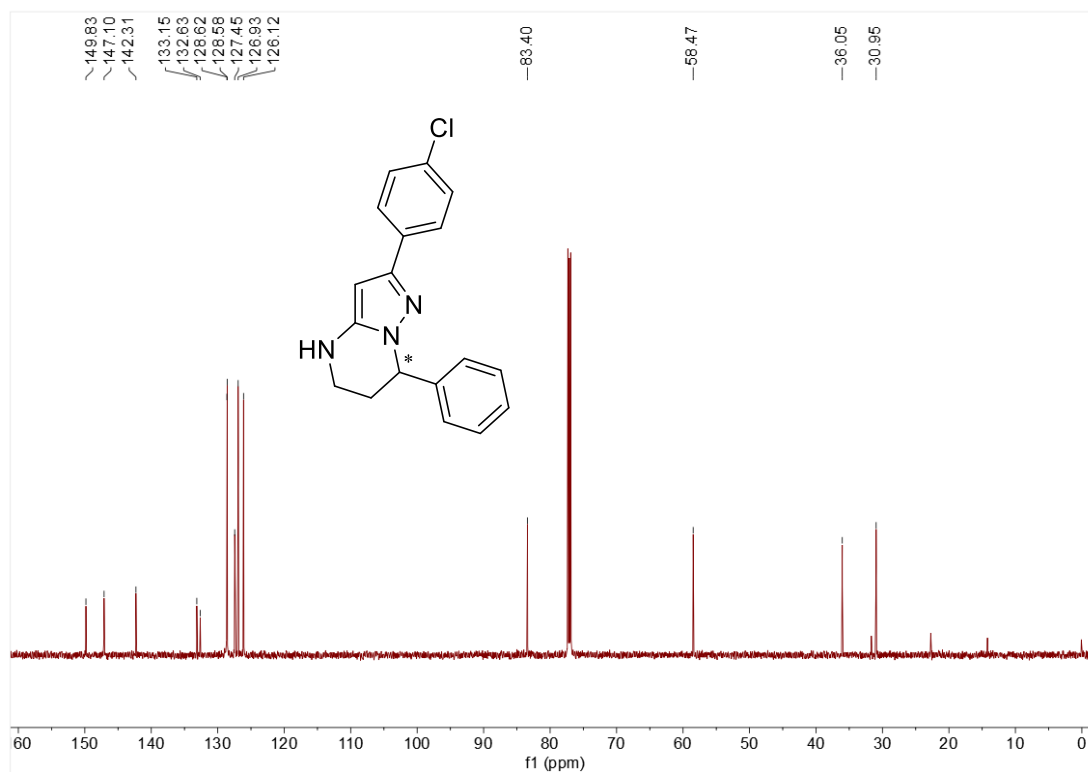
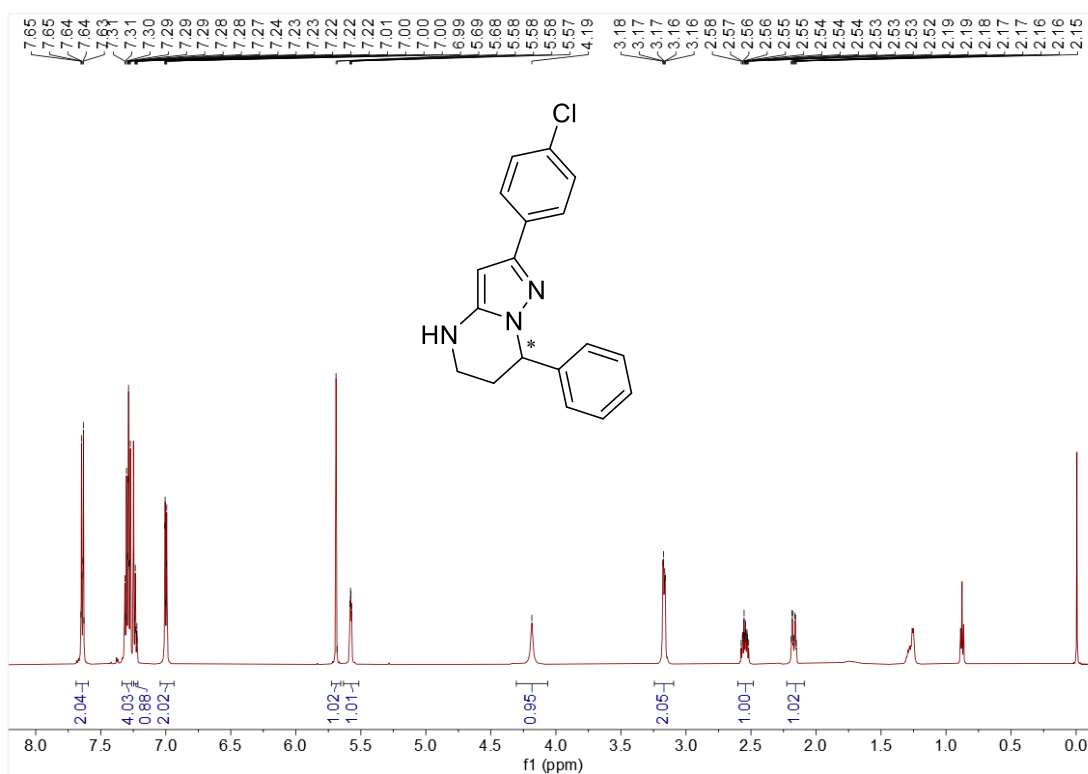
2-(2-chlorophenyl)-7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine (**4g**)



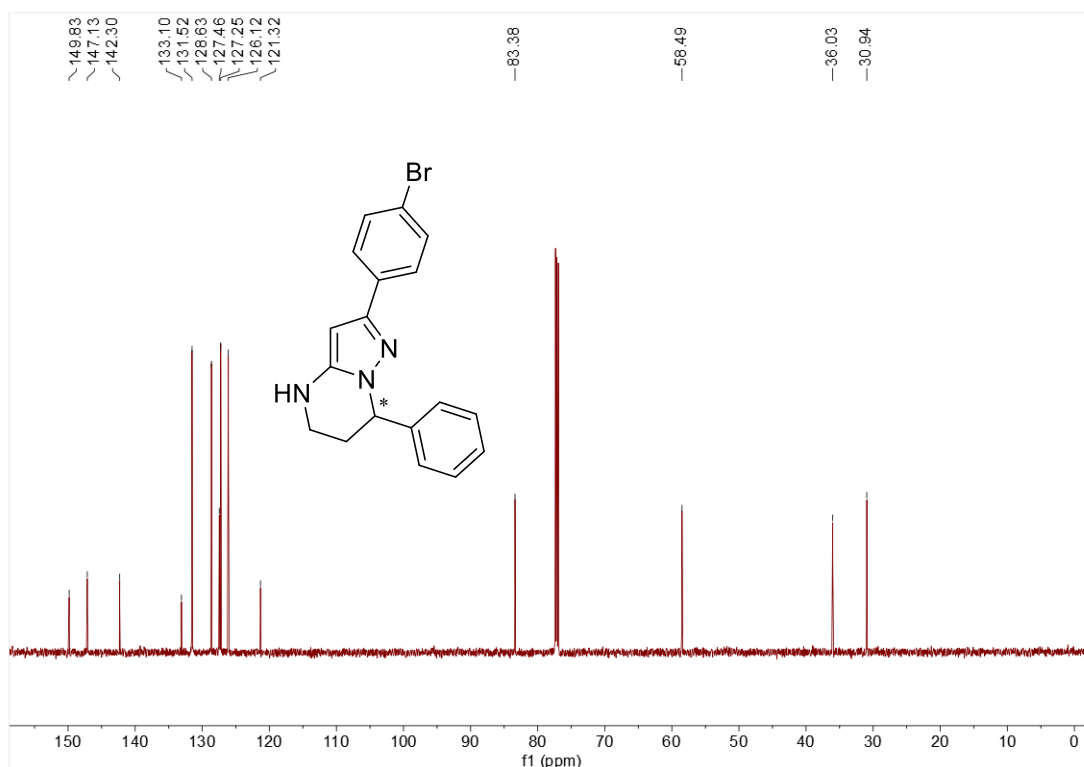
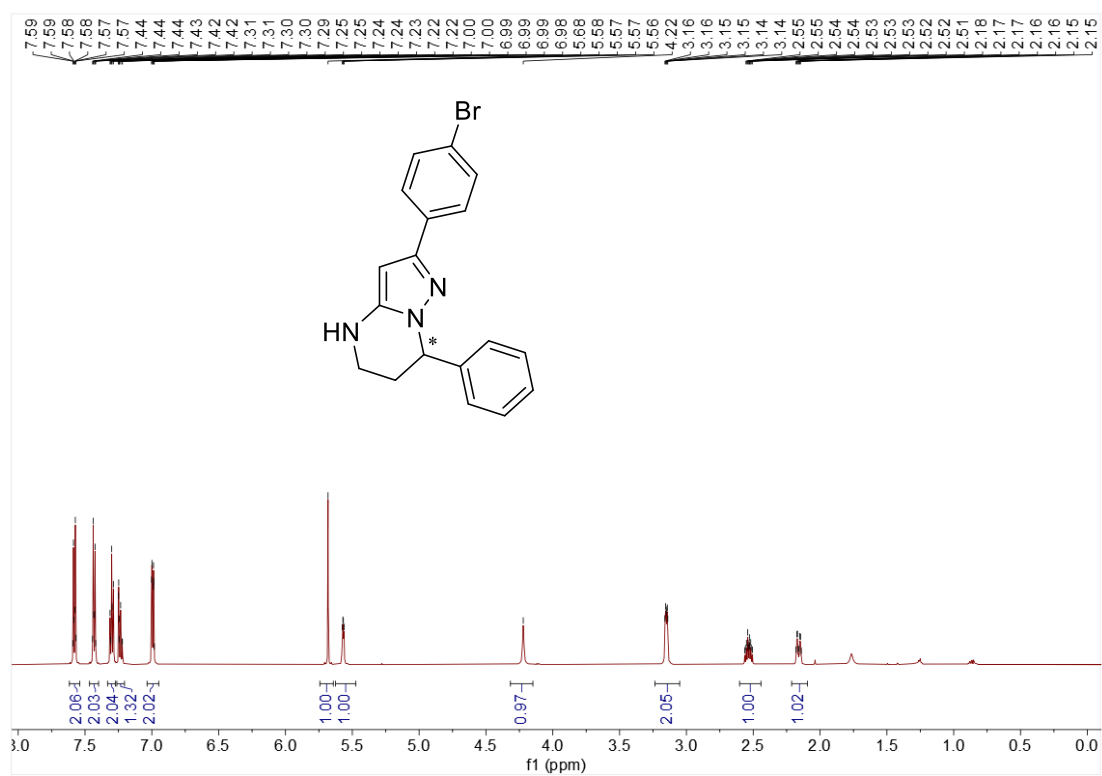
2-(3-fluorophenyl)-7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine (**4h**)



2-(4-chlorophenyl)-7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine (**4j**)

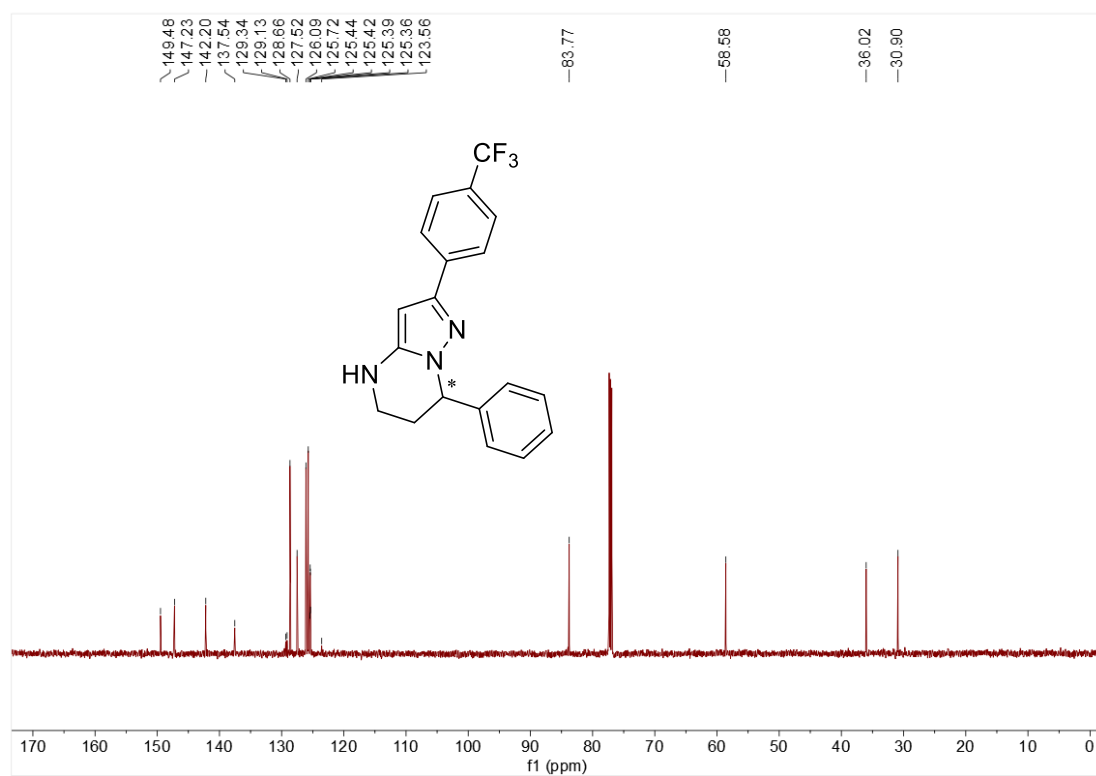
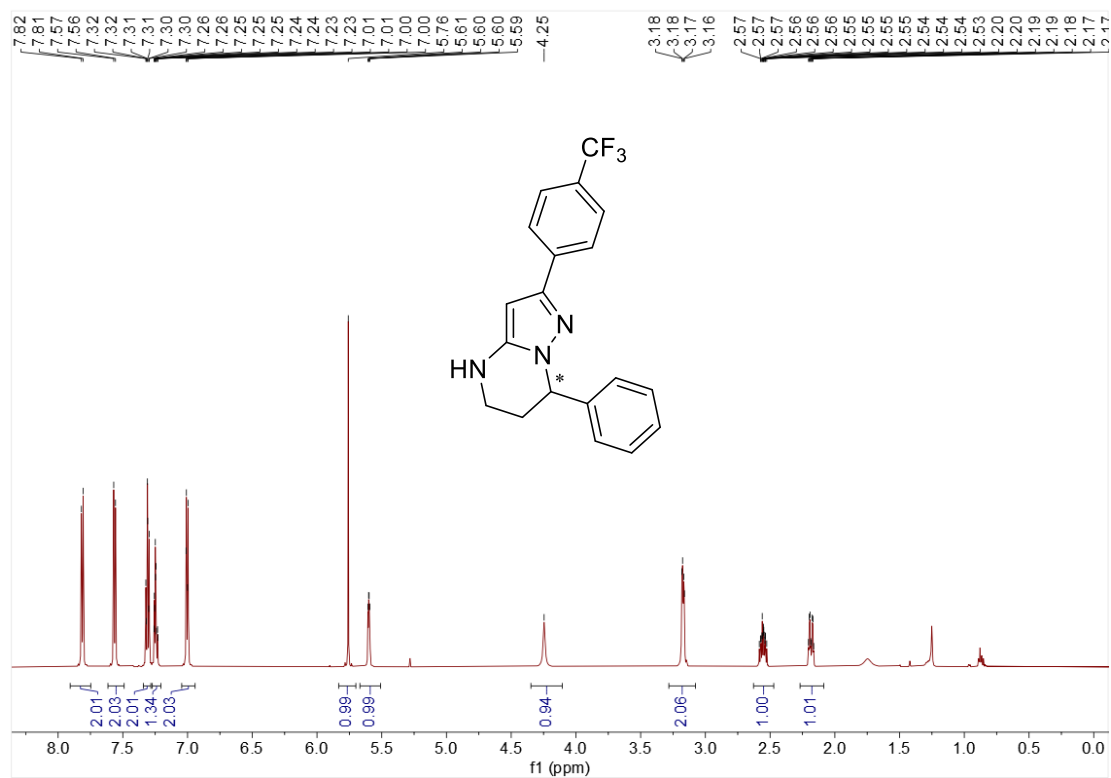


2-(4-bromophenyl)-7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine (**4k**)

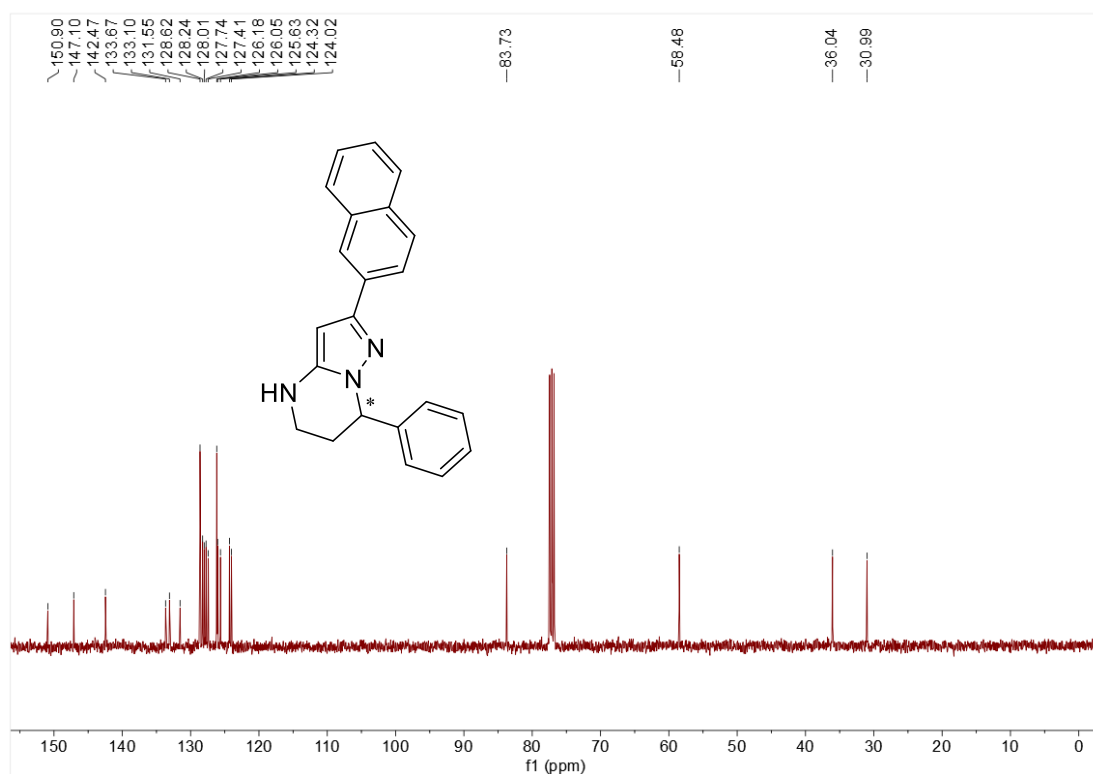
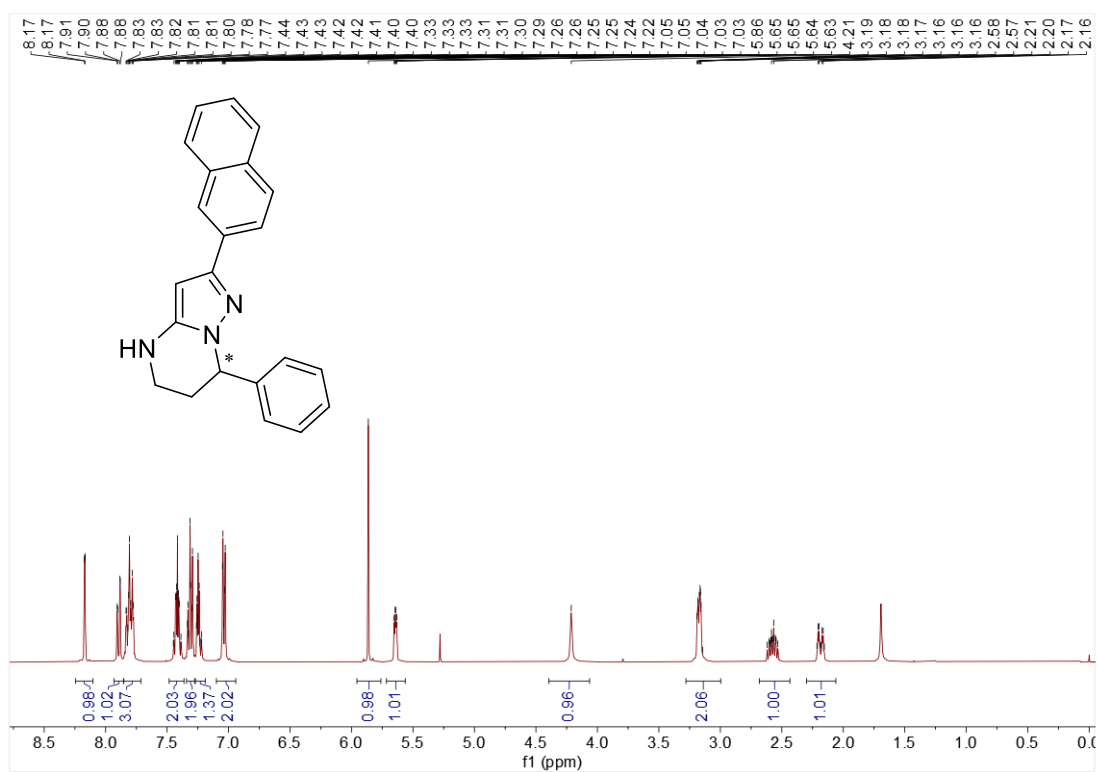


7-phenyl-2-(4-(trifluoromethyl)phenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine

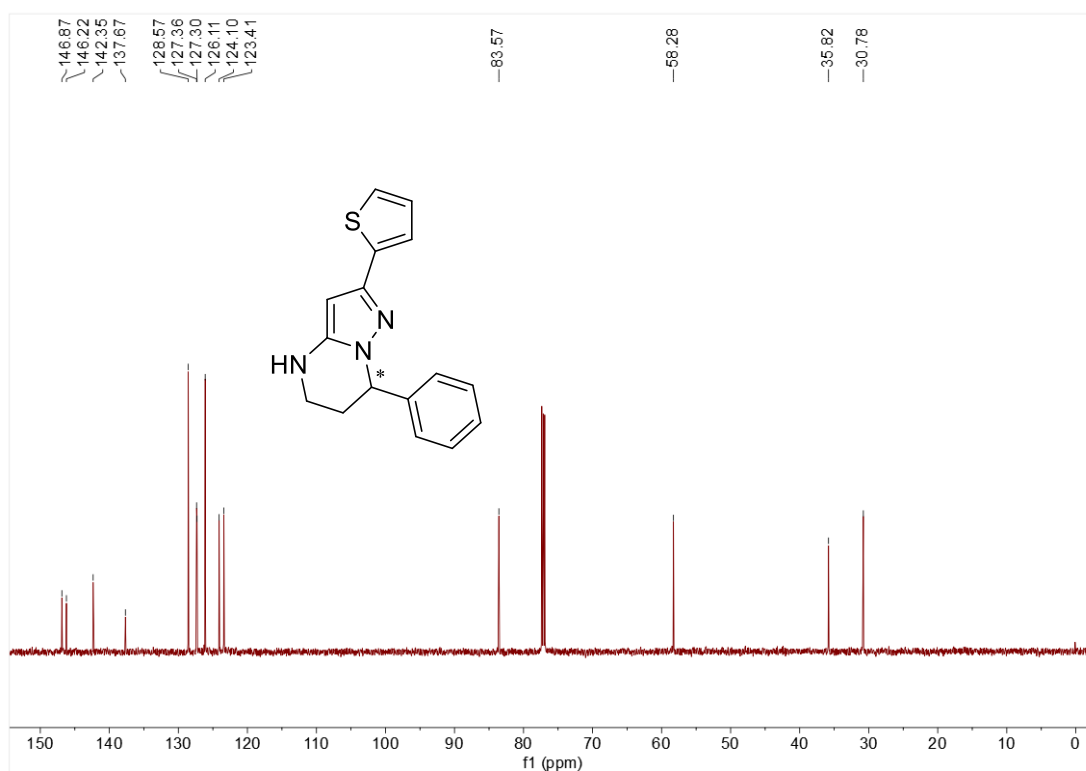
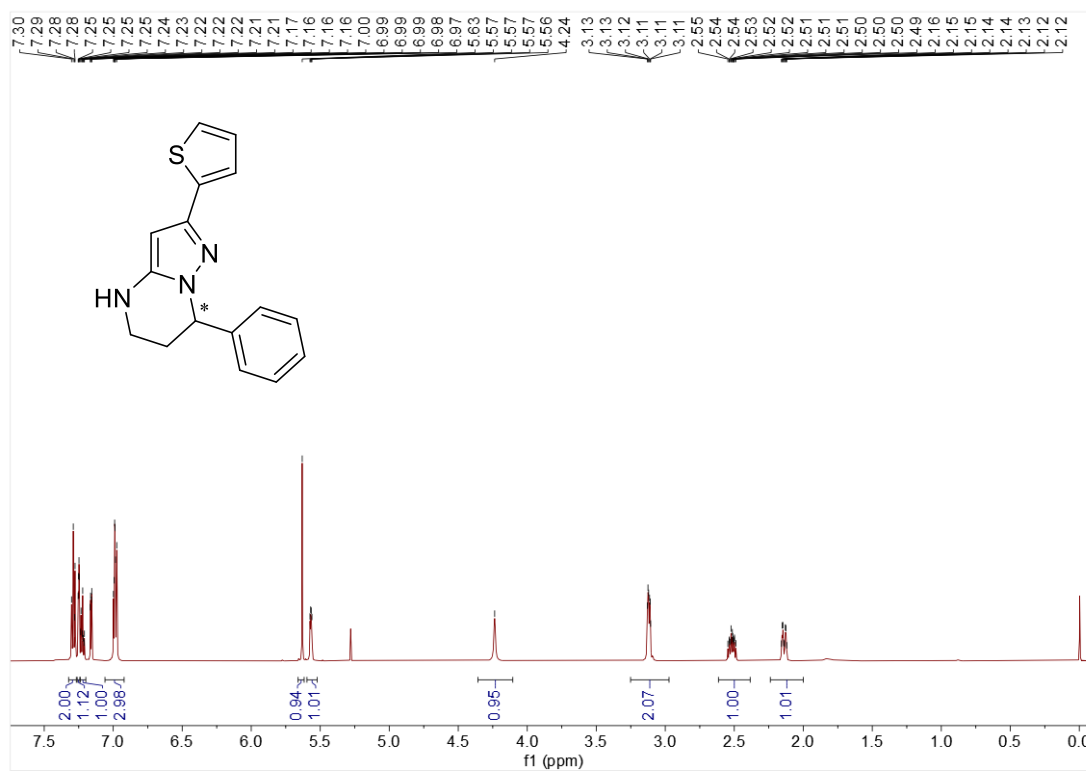
(41)



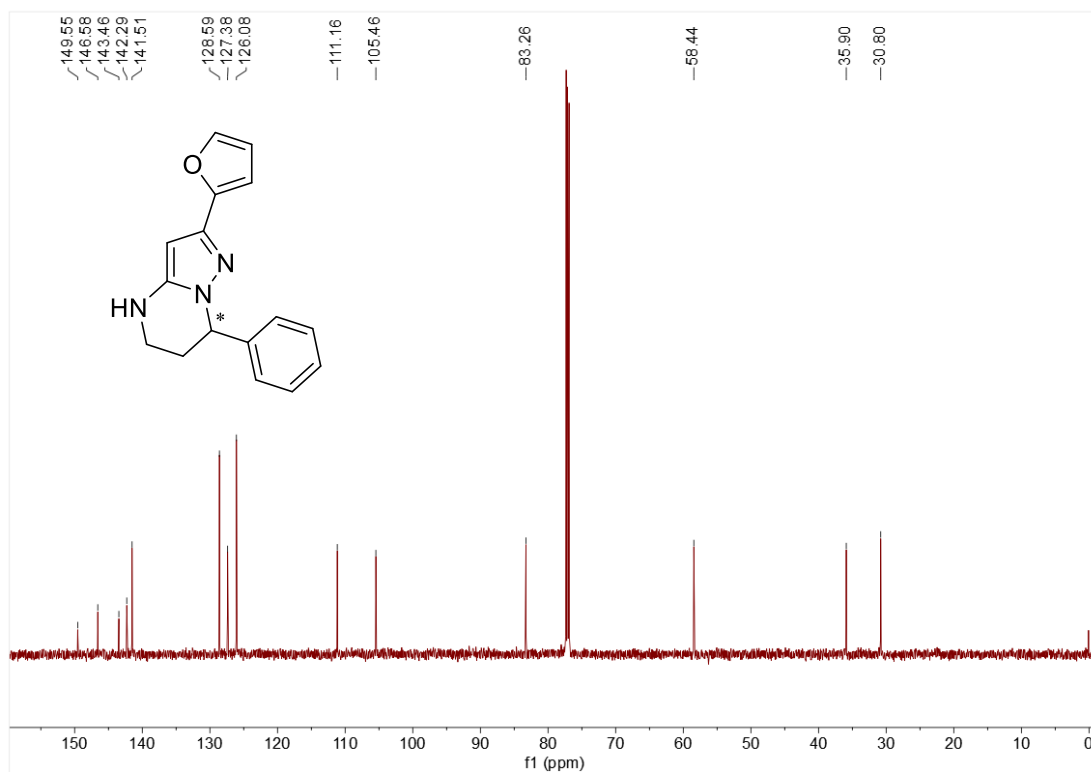
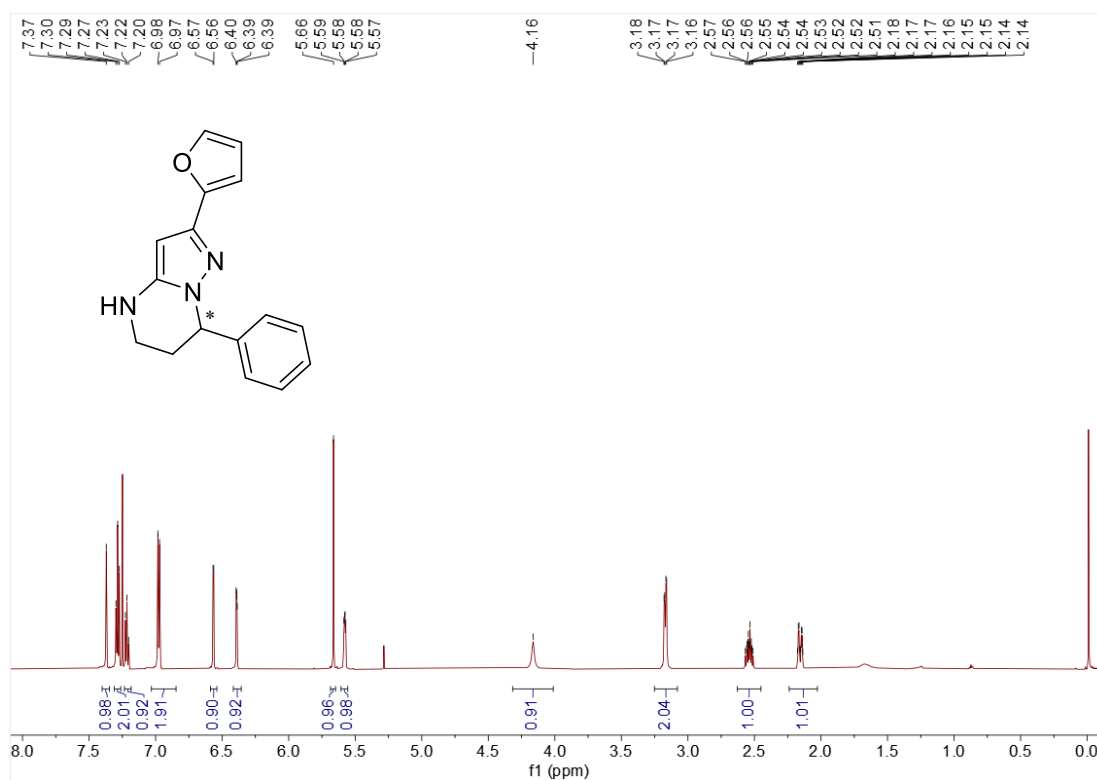
2-(naphthalen-2-yl)-7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine (**4m**)



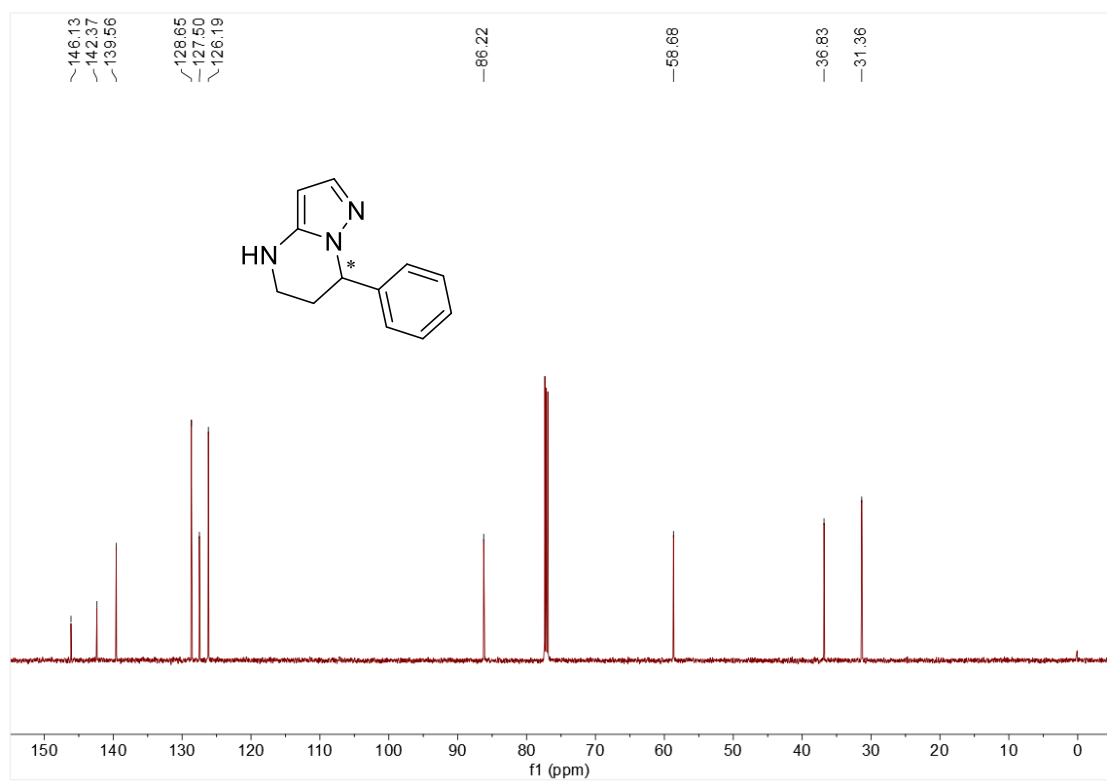
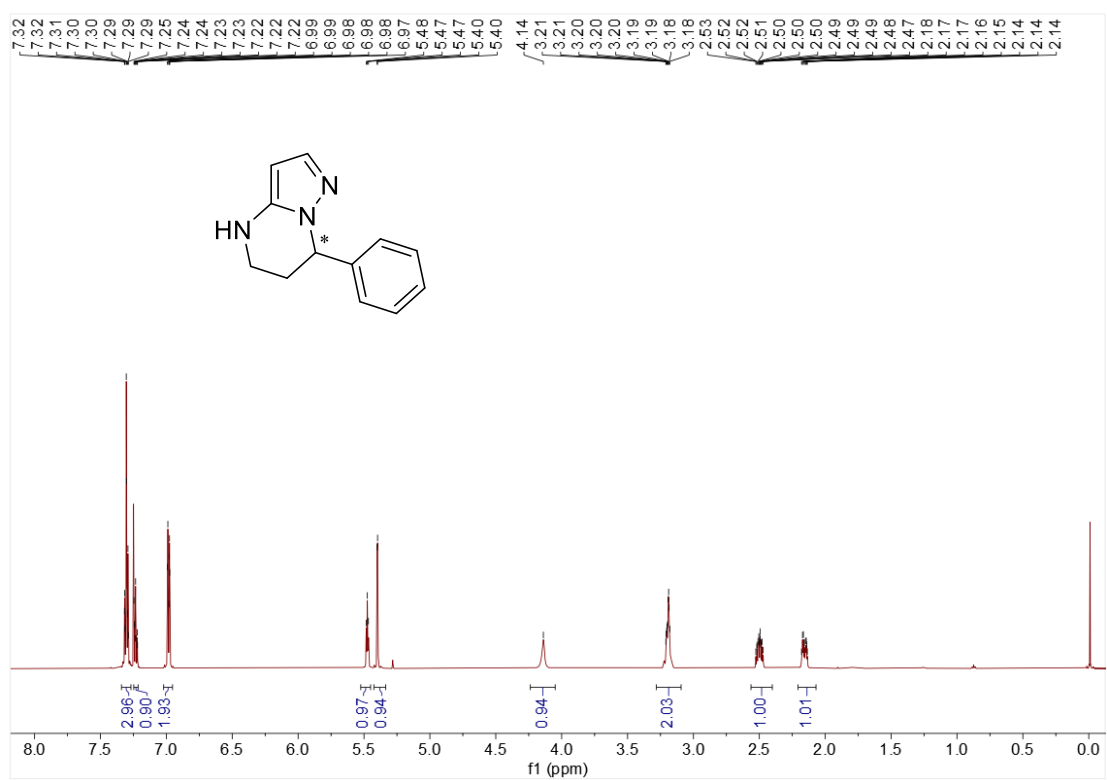
7-phenyl-2-(thiophen-2-yl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine (**4n**)



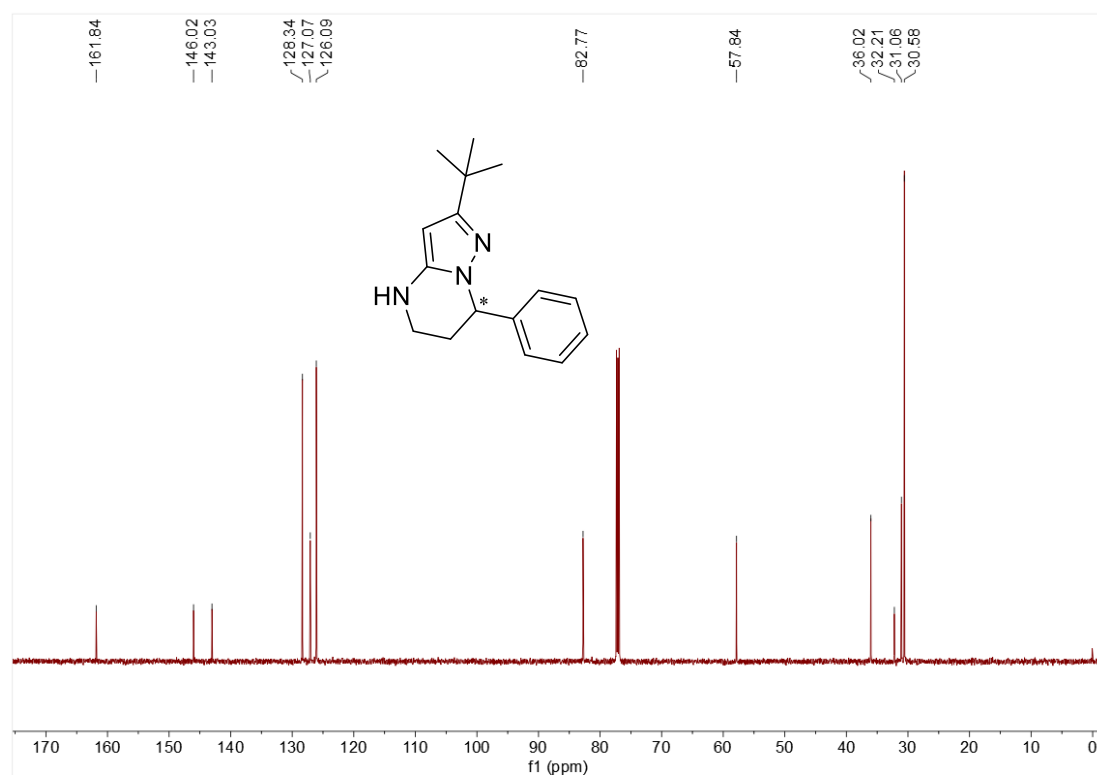
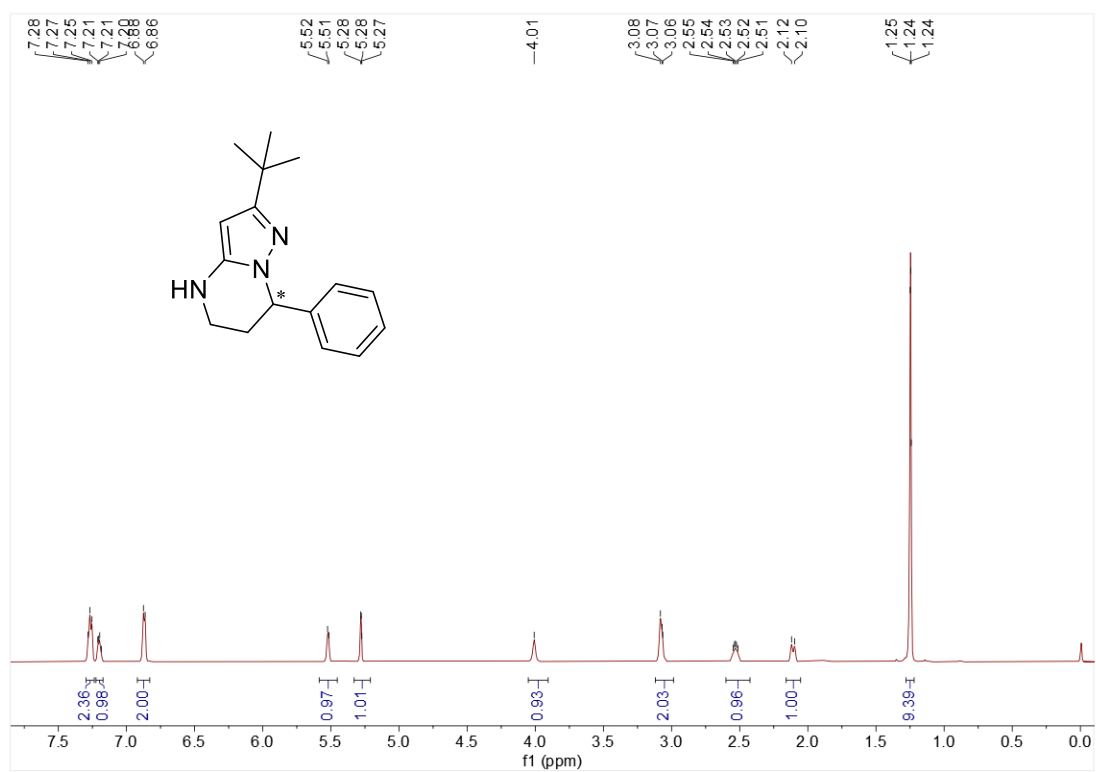
2-(furan-2-yl)-7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine (**4o**)



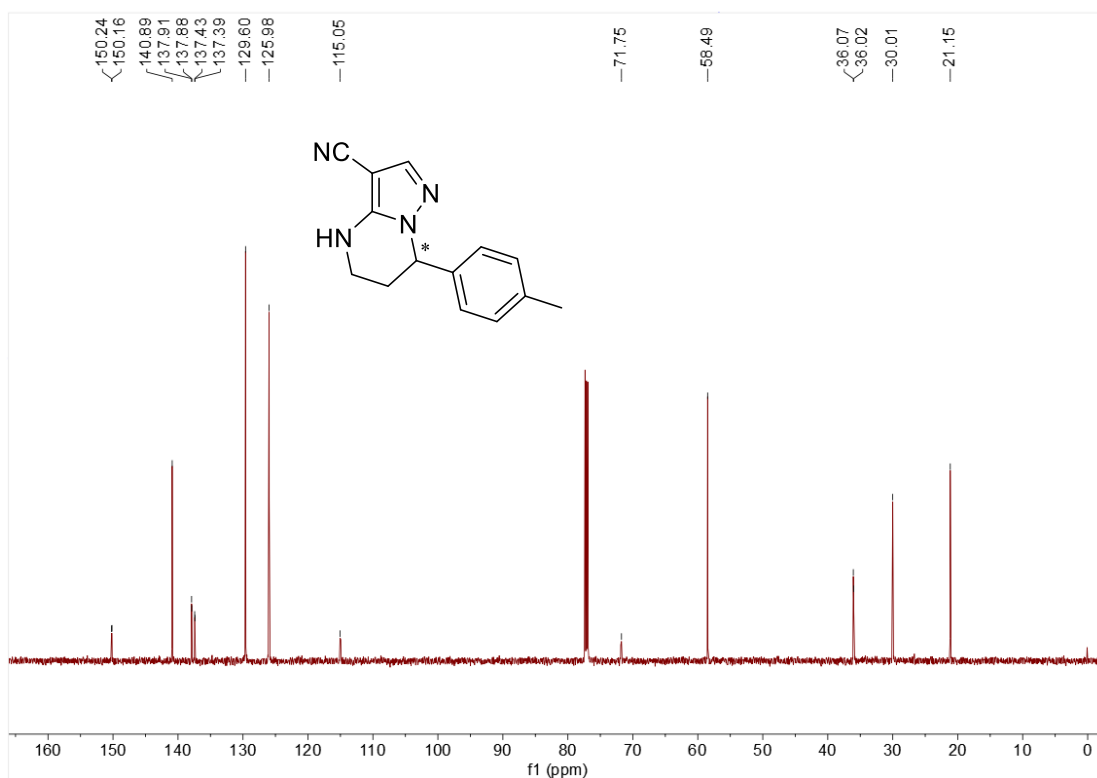
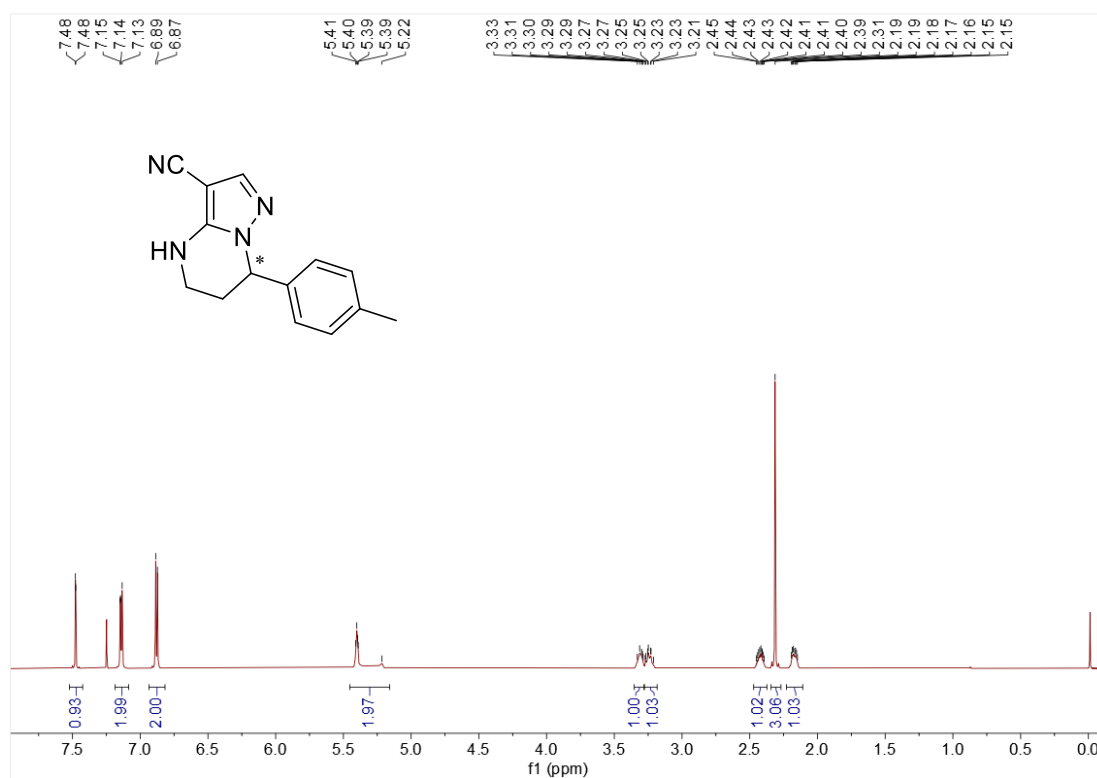
7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine (**4p**)



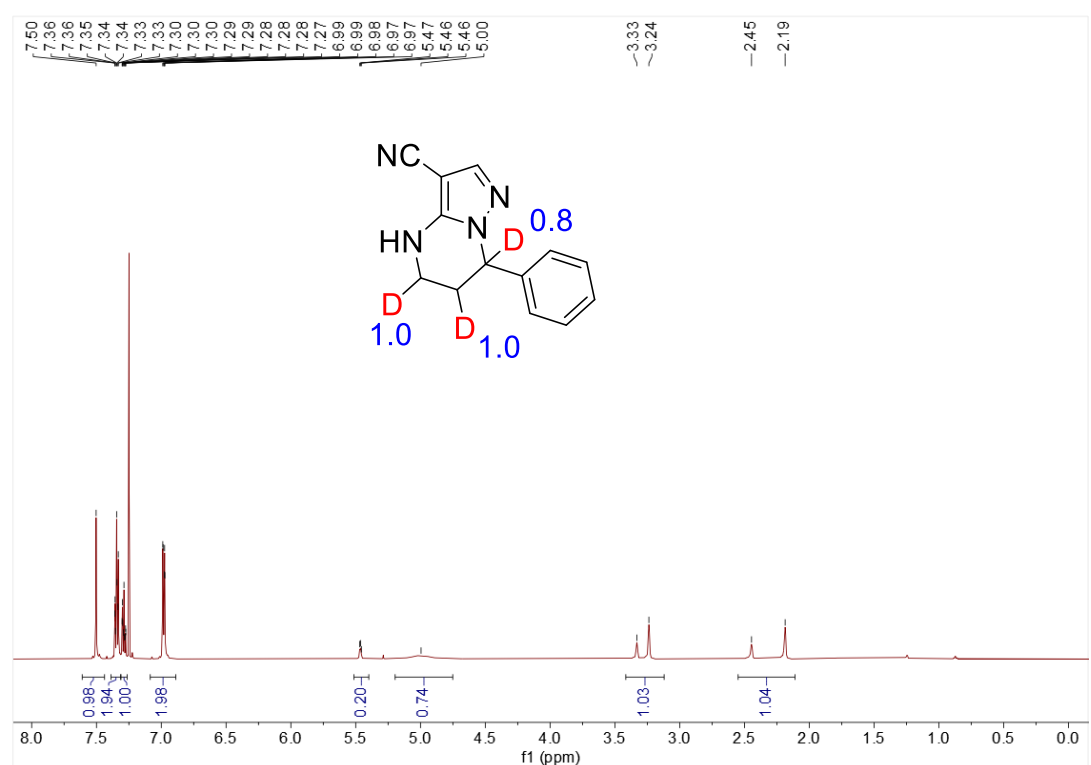
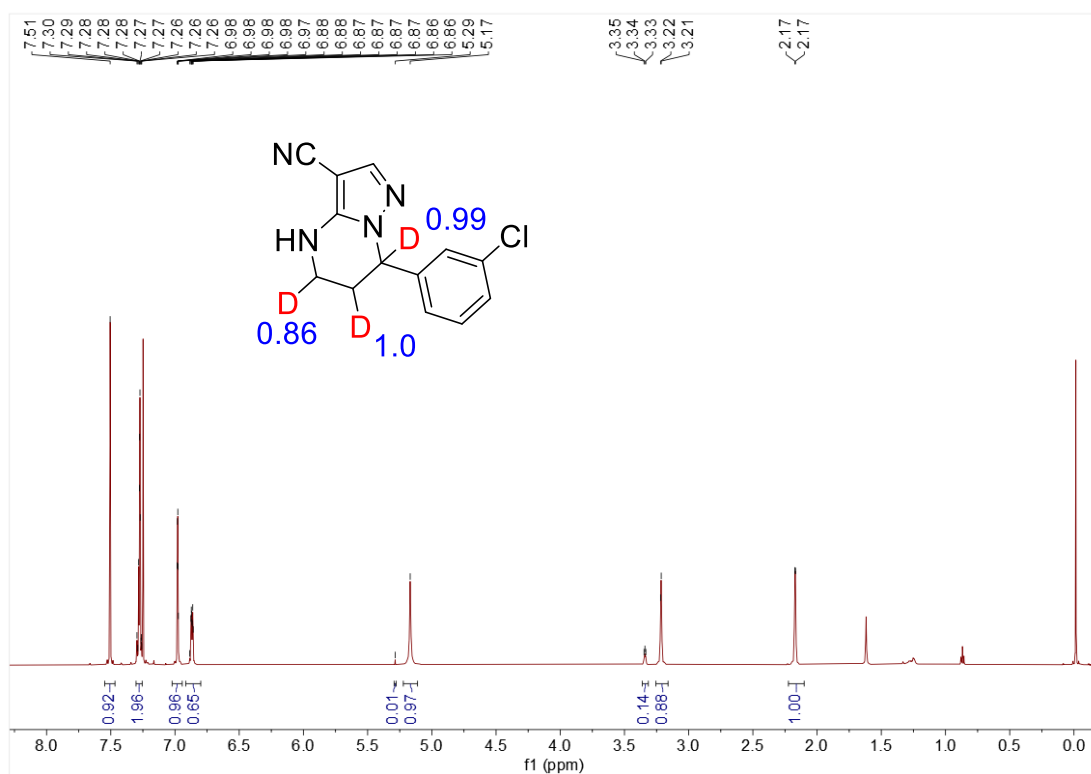
2-(*tert*-butyl)-7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine (**4q**)



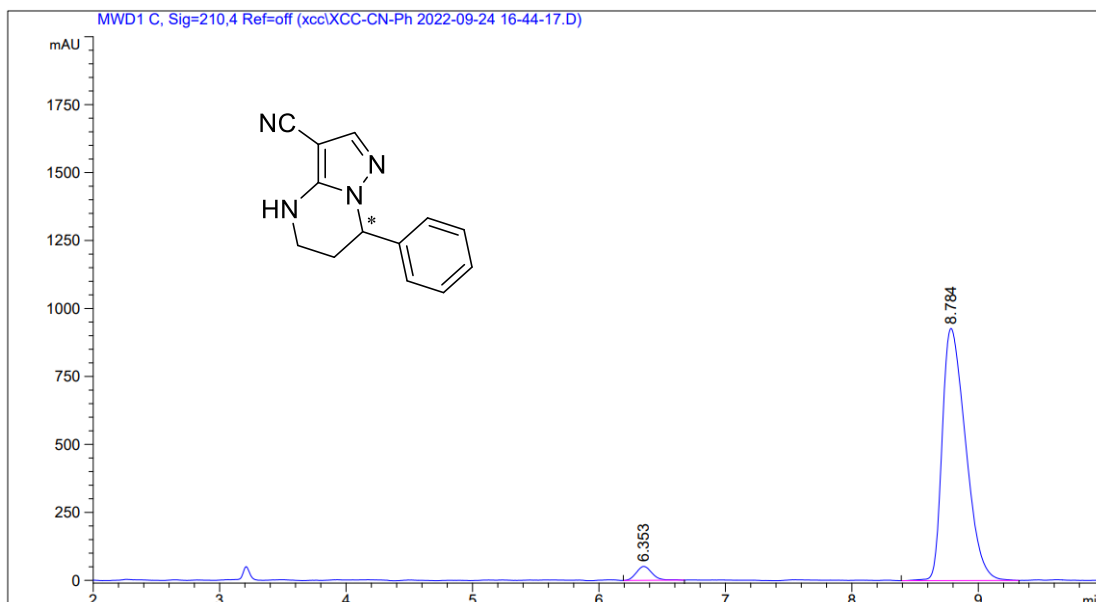
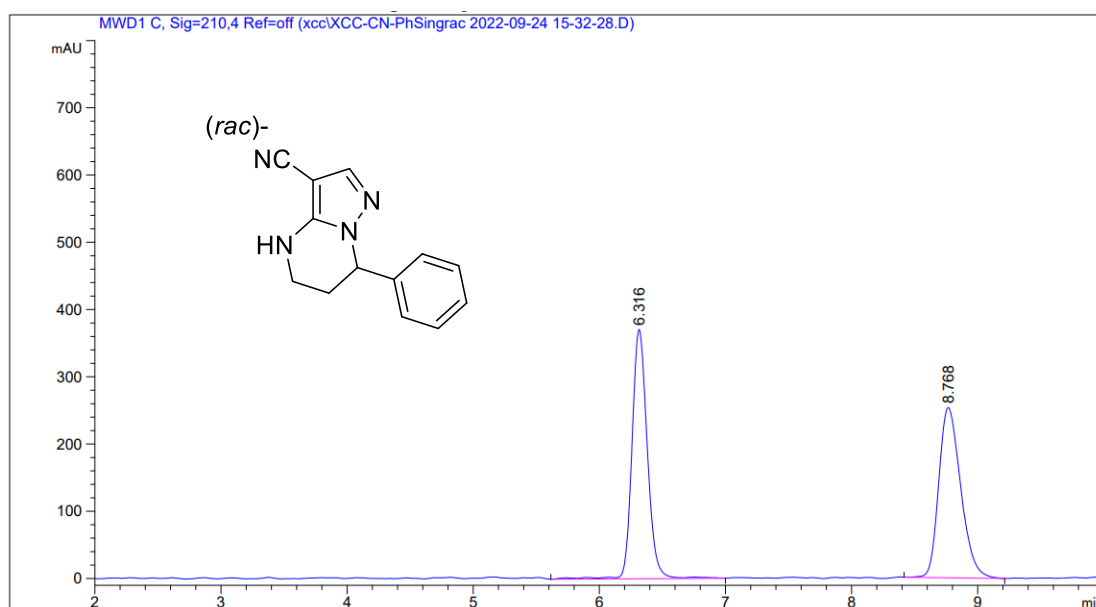
7-(*p*-tolyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**6e**)



The ^1H NMR of deuterium labeling experiments.



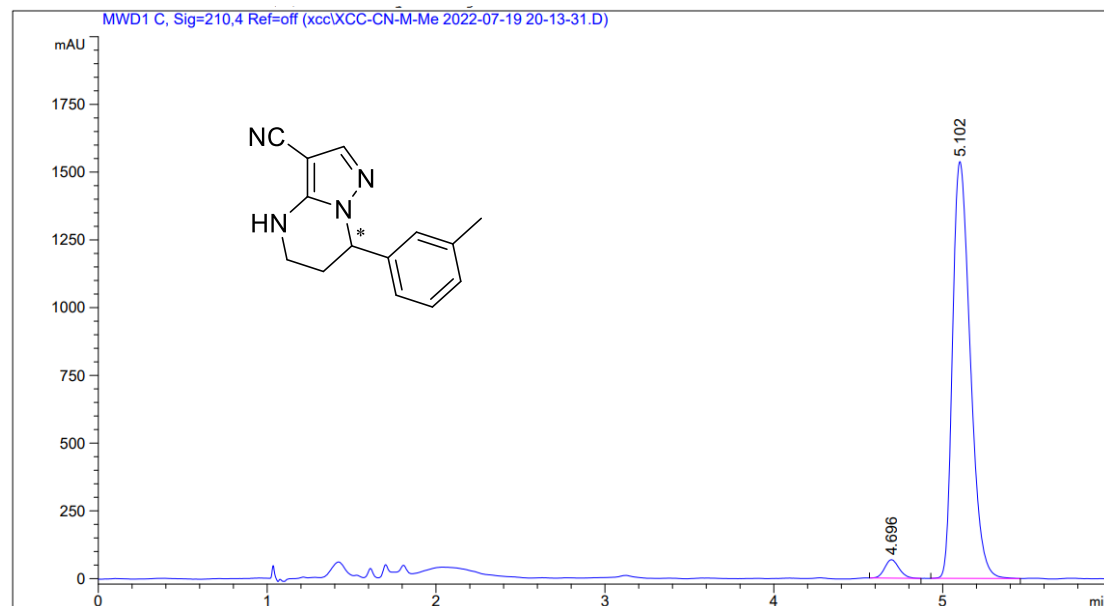
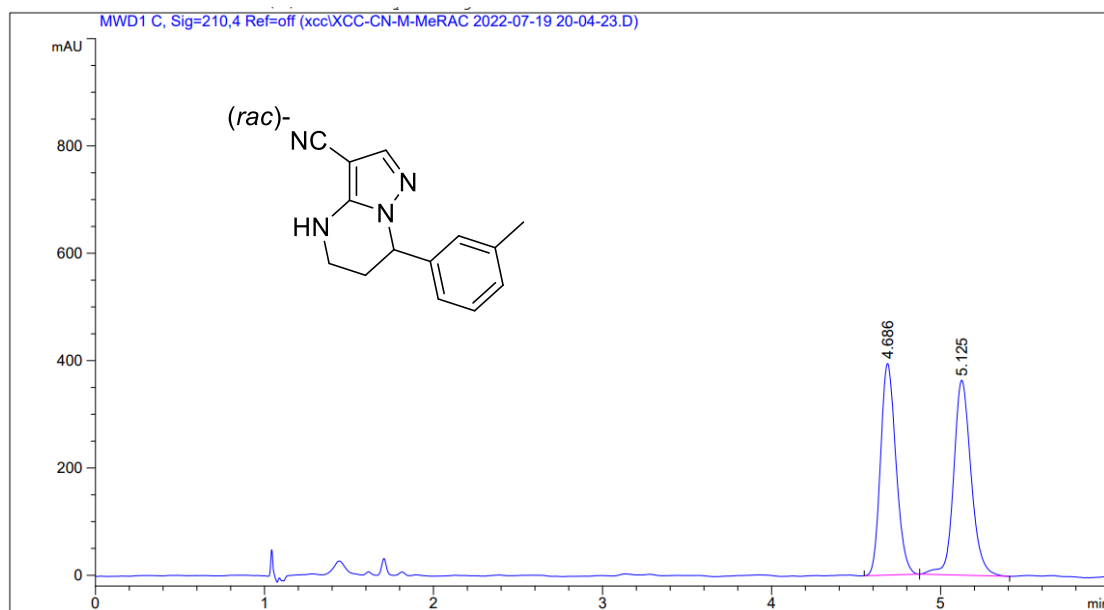
7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**2a**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.353	BB	0.1328	442.56970	51.22913	3.5822
2	8.784	BB	0.2058	1.19121e4	927.51611	96.4178

Totals : 1.23546e4 978.74524

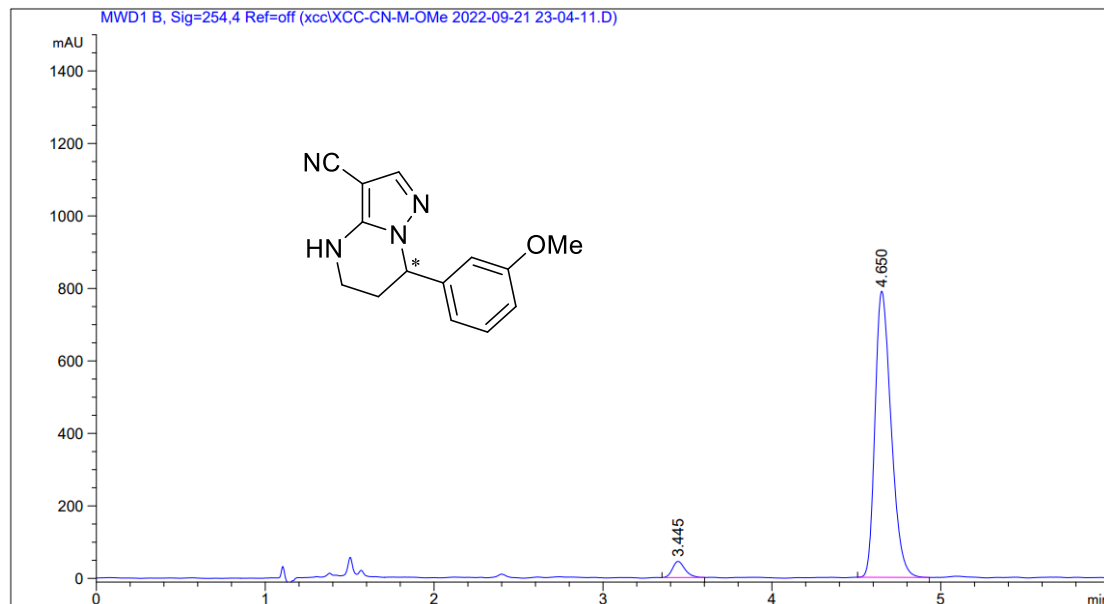
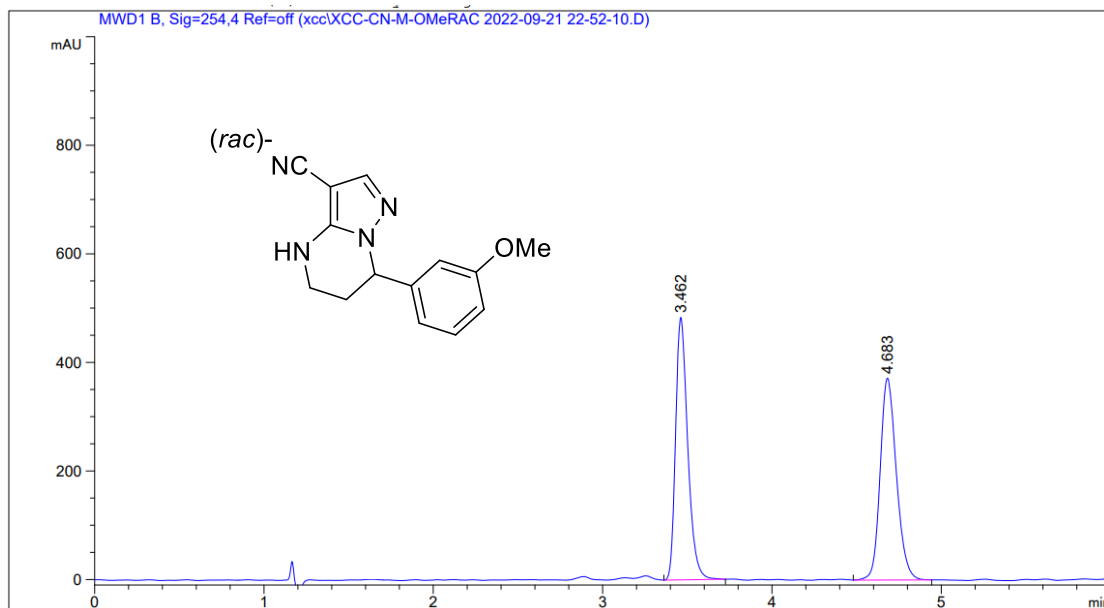
7-(*m*-tolyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**2b**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.696	BB	0.0906	402.78244	68.01381	3.4822
2	5.102	BB	0.1132	1.11642e4	1538.27539	96.5178

Totals : 1.15670e4 1606.28920

7-(3-methoxyphenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**2c**)

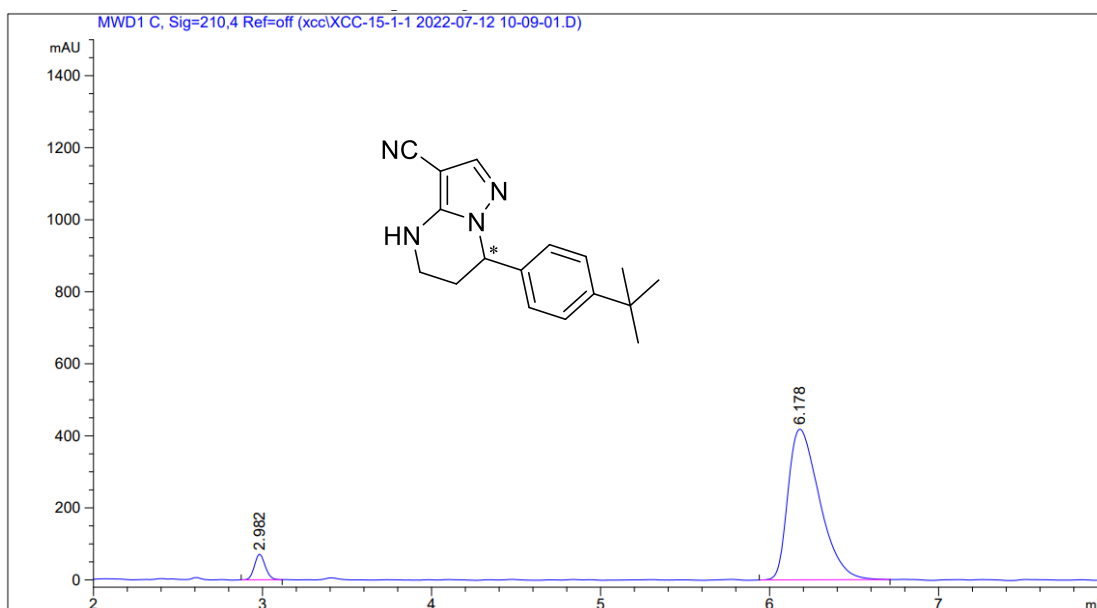
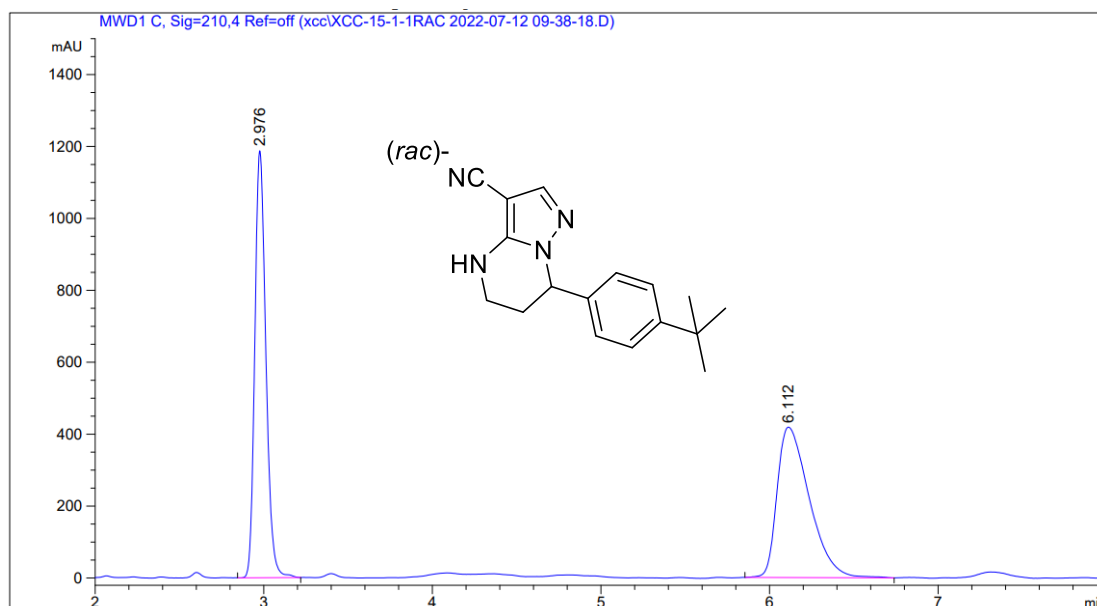


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.445	BB	0.0793	227.38565	44.35575	4.1746
2	4.650	BB	0.1027	5219.56396	789.19562	95.8254

Totals : 5446.94962 833.55137

7-(4-(*tert*-butyl)phenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile

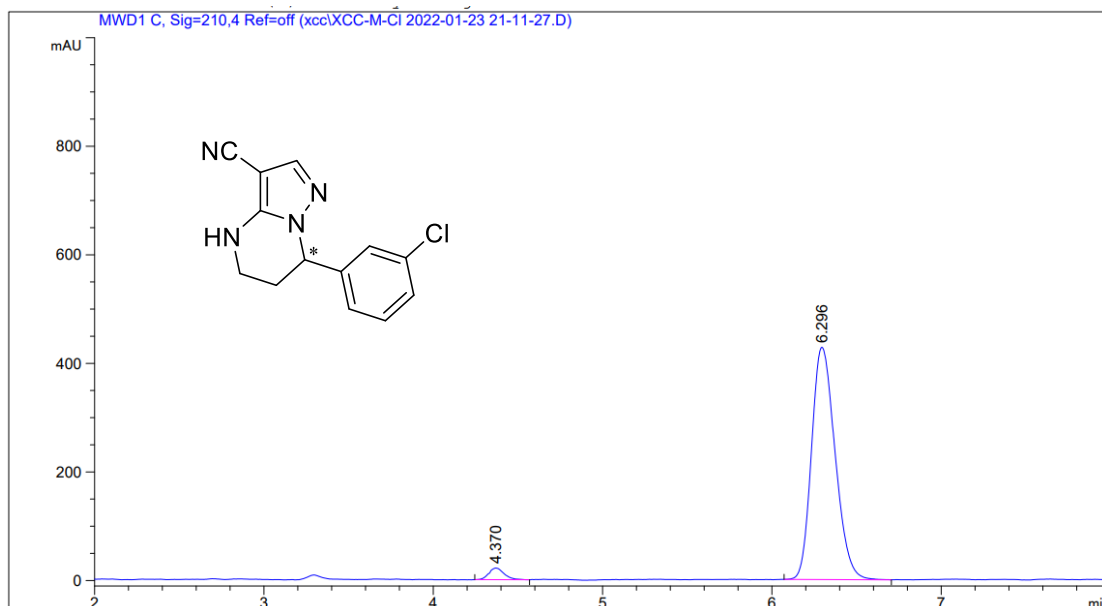
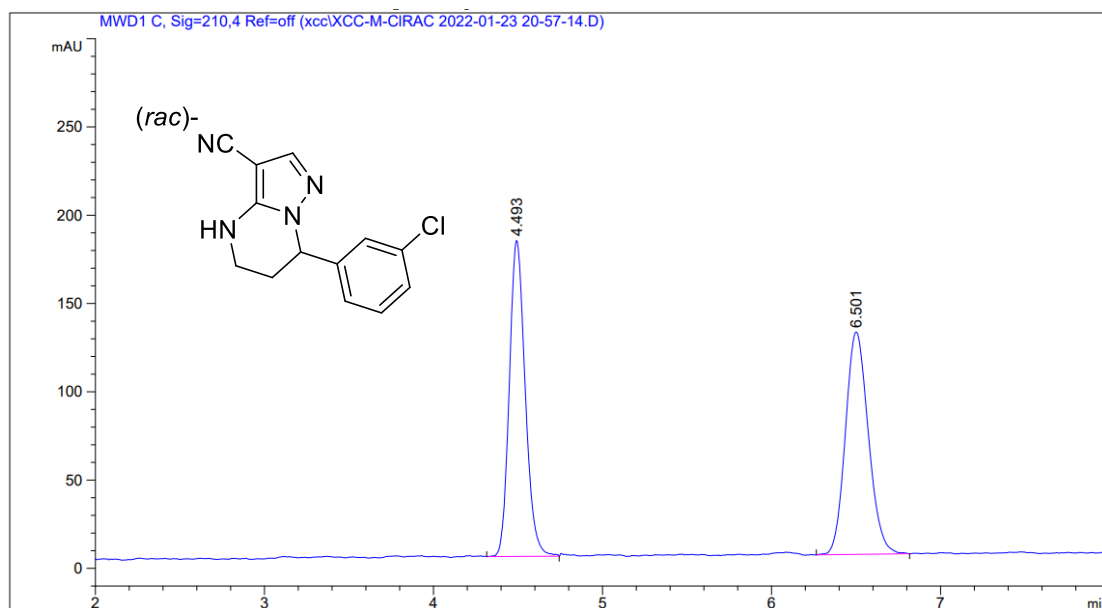
(2d)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.982	BB	0.0684	314.35291	70.66316	5.4629
2	6.178	BB	0.1928	5440.00049	418.16071	94.5371

Totals : 5754.35339 488.82387

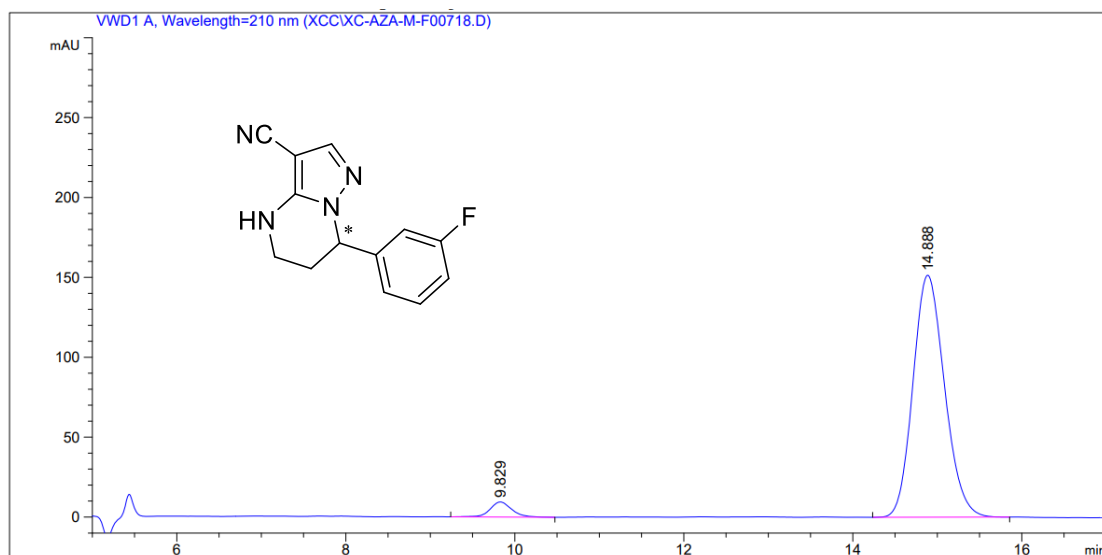
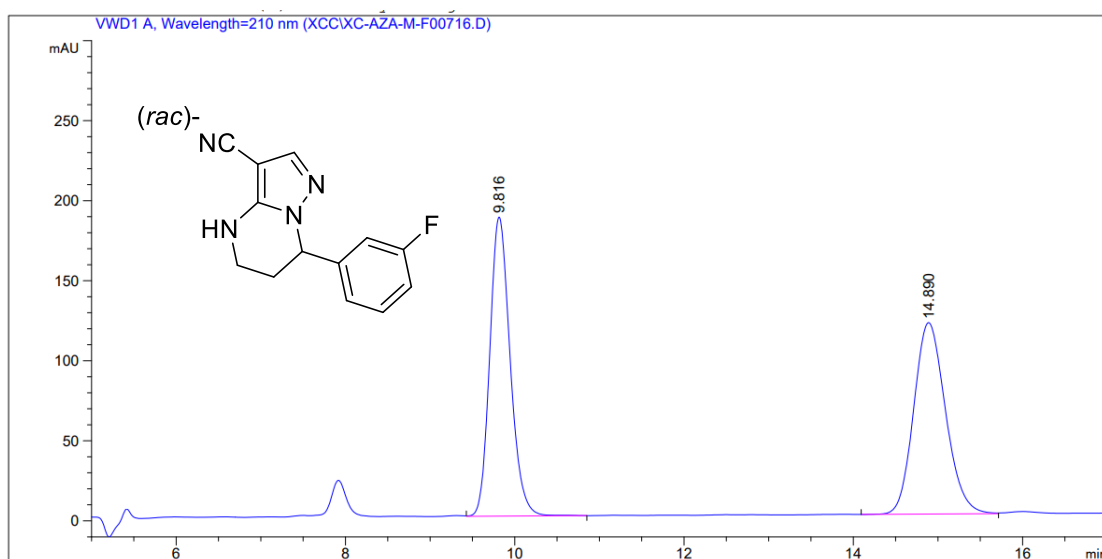
7-(3-chlorophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**2e**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.370	BB	0.0927	134.71066	21.47473	3.1522
2	6.296	BB	0.1478	4138.79443	428.12140	96.8478

Totals : 4273.50510 449.59613

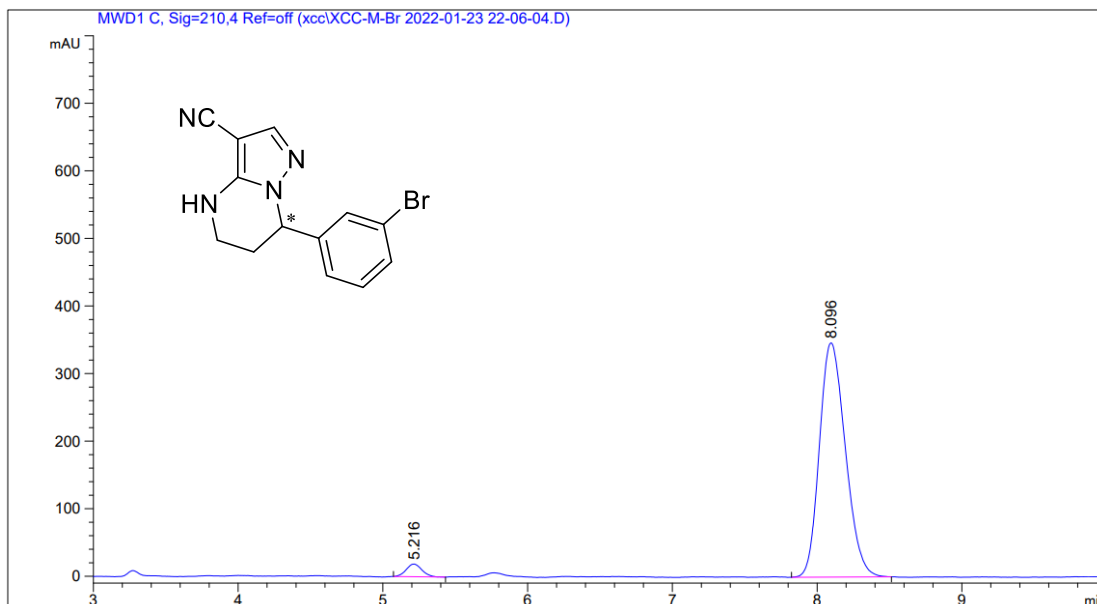
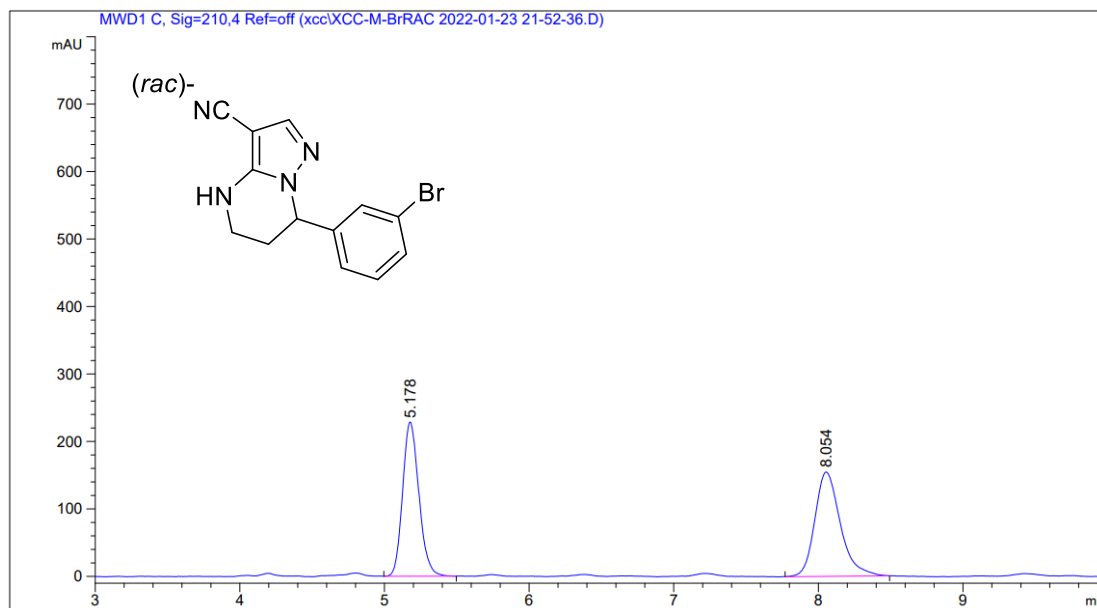
7-(3-fluorophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**2f**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.829	BB	0.2708	168.09373	9.43937	4.1057
2	14.888	BB	0.4024	3926.06006	151.44839	95.8943

Totals : 4094.15379 160.88776

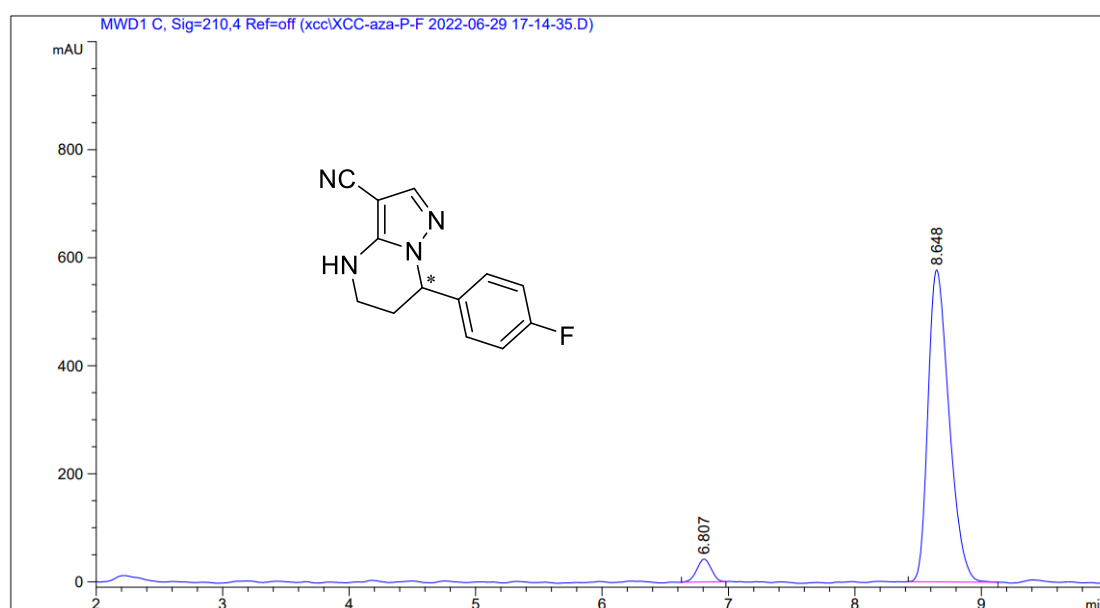
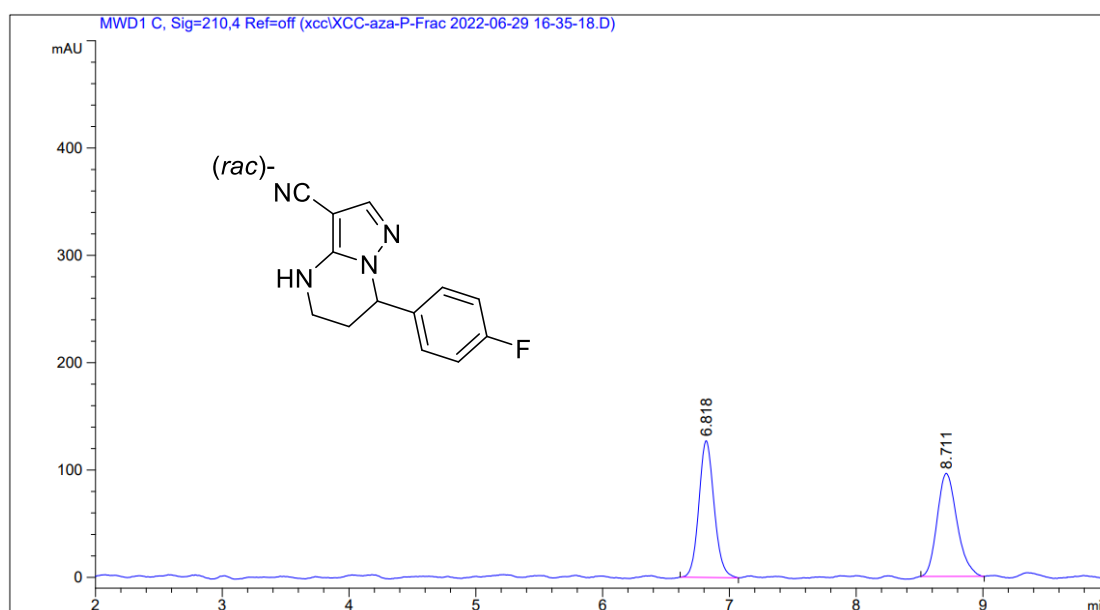
7-(3-bromophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**2g**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.216	BB	0.0929	140.72729	18.66773	3.1534
2	8.096	BB	0.1945	4321.95557	346.53735	96.8466

Totals : 4462.68286 365.20508

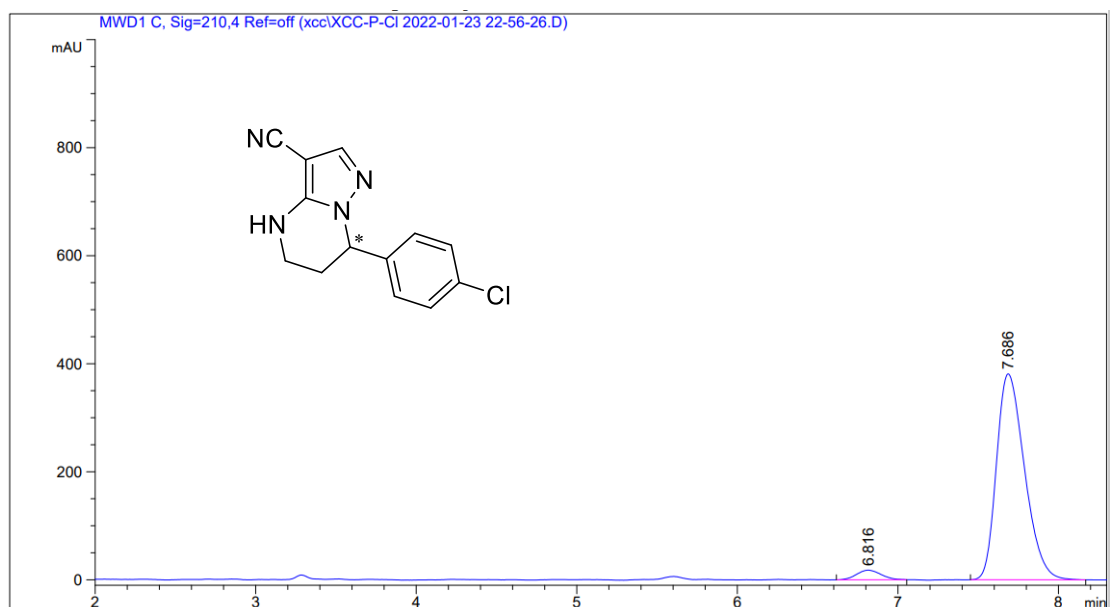
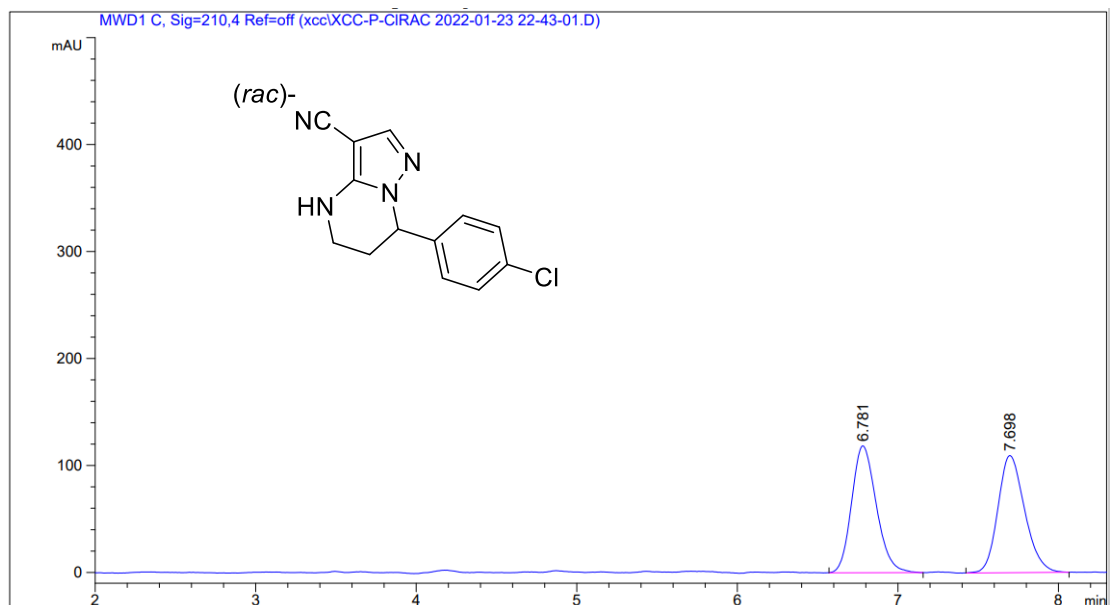
7-(4-fluorophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**2h**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.807	BB	0.1056	334.99820	42.22084	4.7697
2	8.648	BB	0.1761	6688.40771	577.55975	95.2303

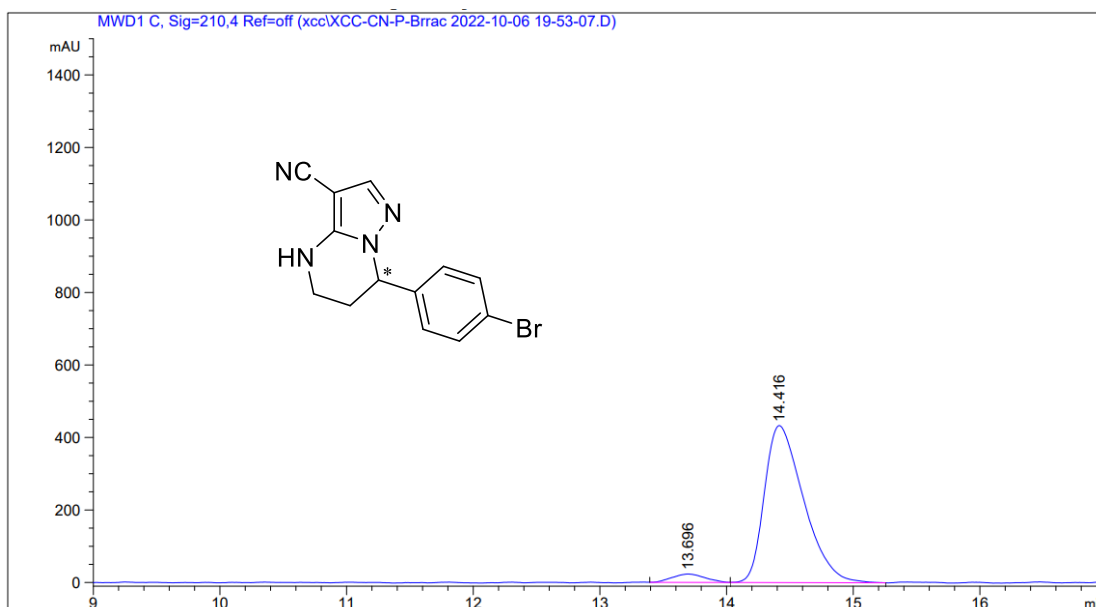
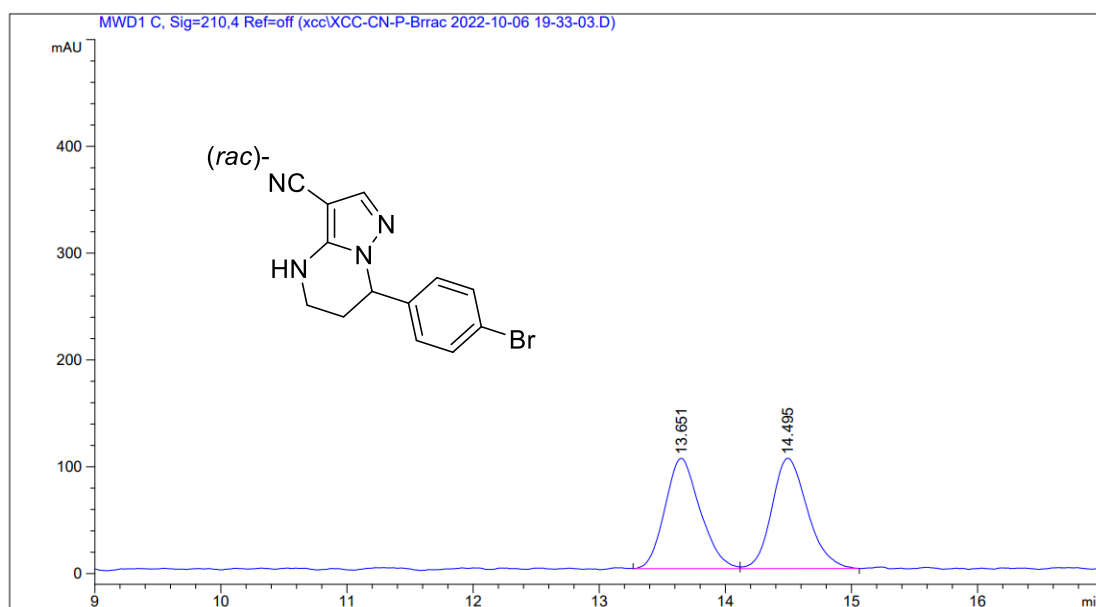
Totals : 7023.40591 619.78059

7-(4-chlorophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**2i**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.816	BB	0.1262	187.15504	17.79132	3.8932
2	7.686	BB	0.1864	4620.02002	381.19168	96.1068
Totals :				4807.17506	398.98300	

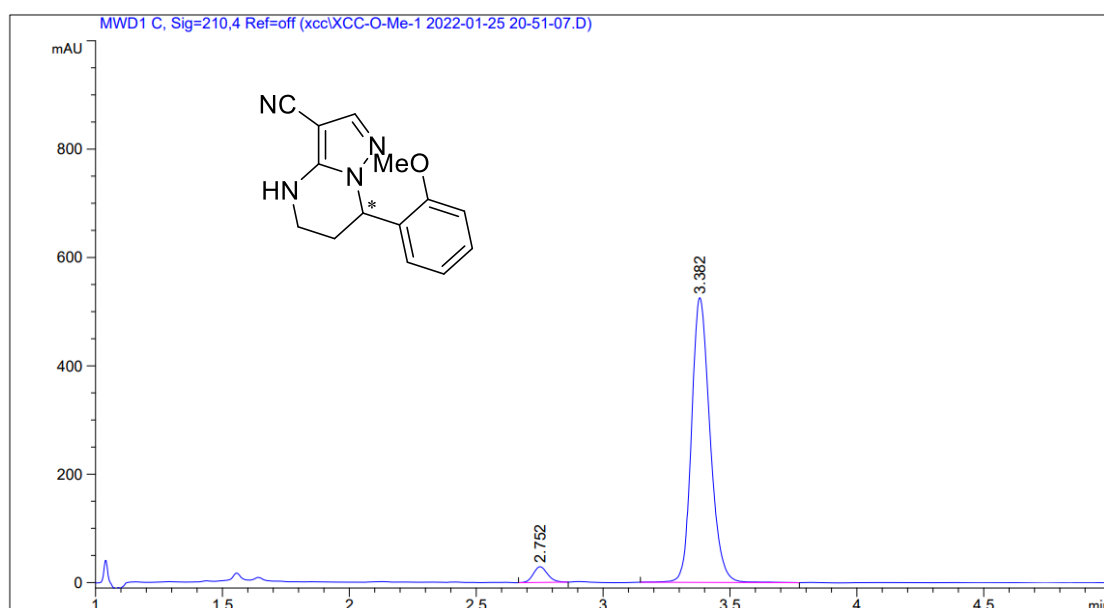
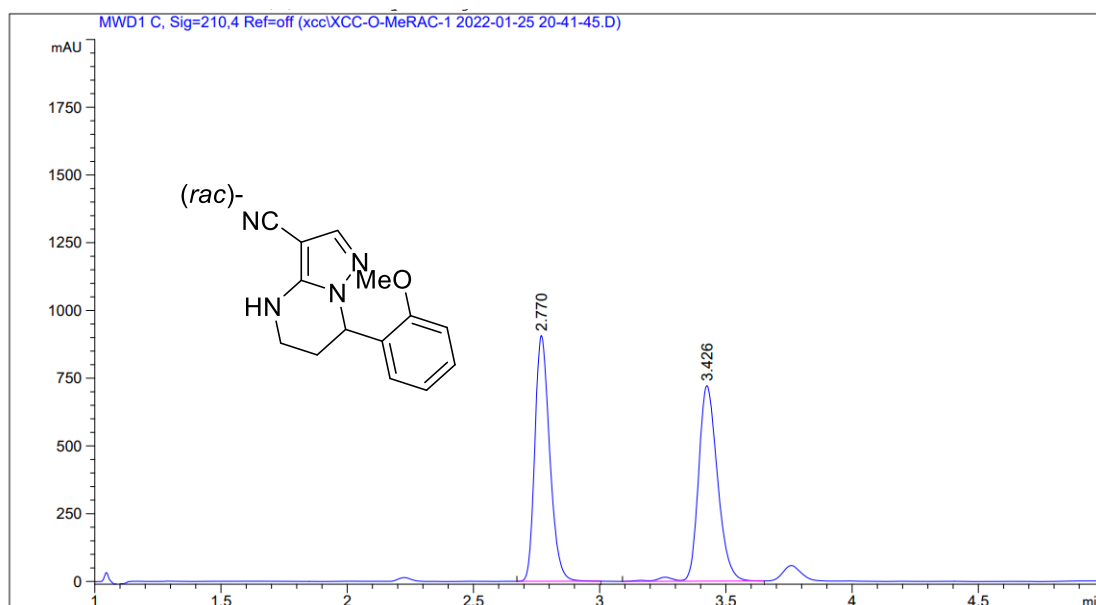
7-(4-bromophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**2j**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.696	VB R	0.2118	409.96548	23.07668	4.2216
2	14.416	VV R	0.2876	9301.07910	433.00989	95.7784

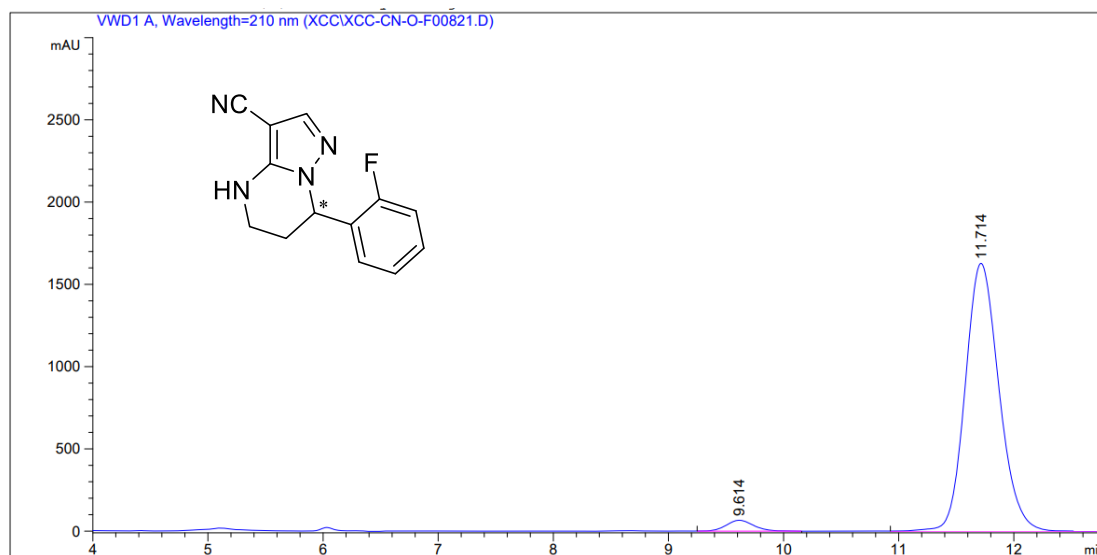
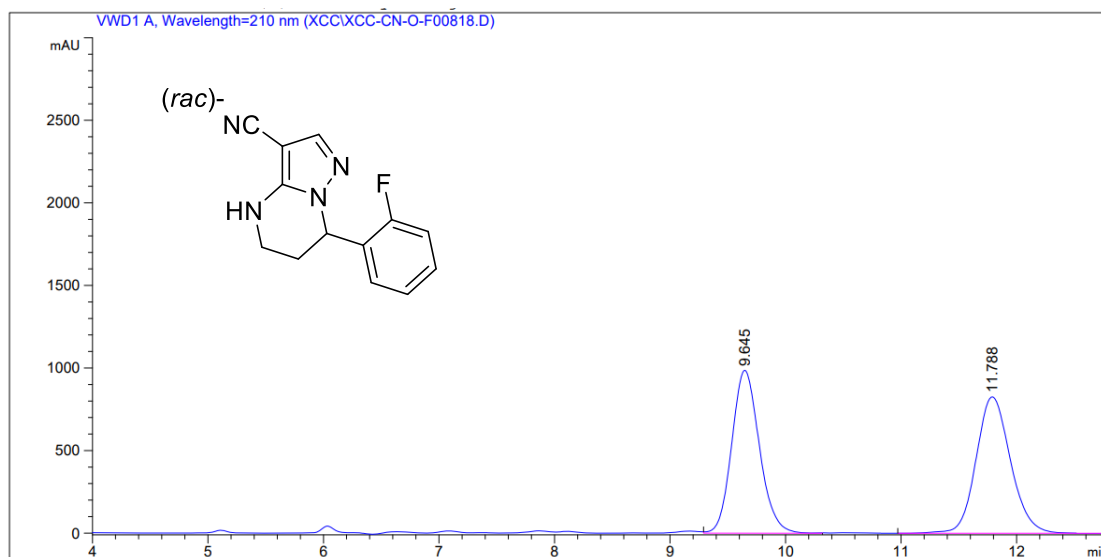
Totals : 9711.04459 456.08657

7-(2-methoxyphenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**2k**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.752	BB	0.0616	112.95475	28.91854	4.0706
2	3.382	BB	0.0772	2661.90649	524.46478	95.9294
Totals :				2774.86124	553.38332	

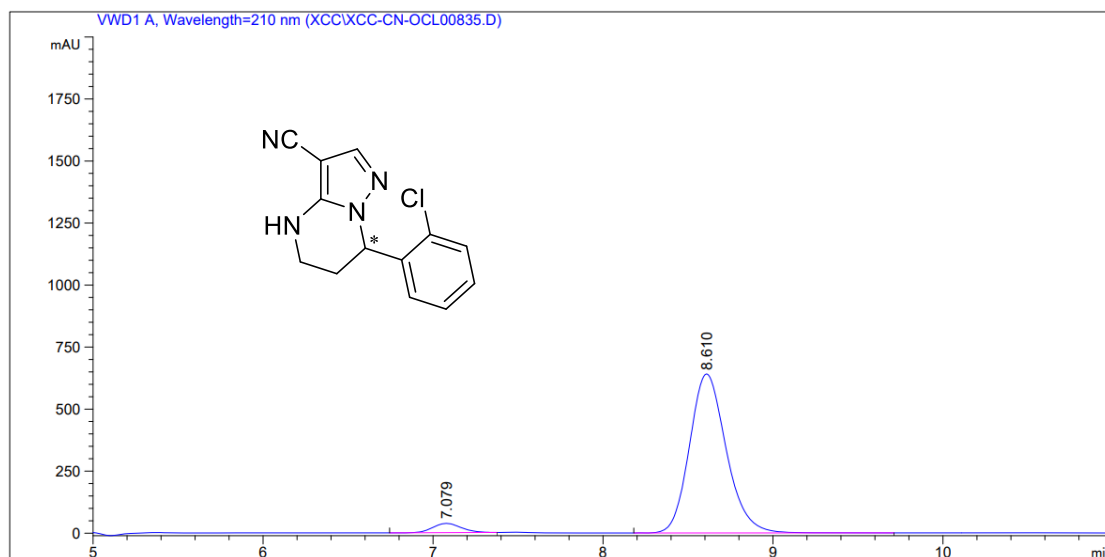
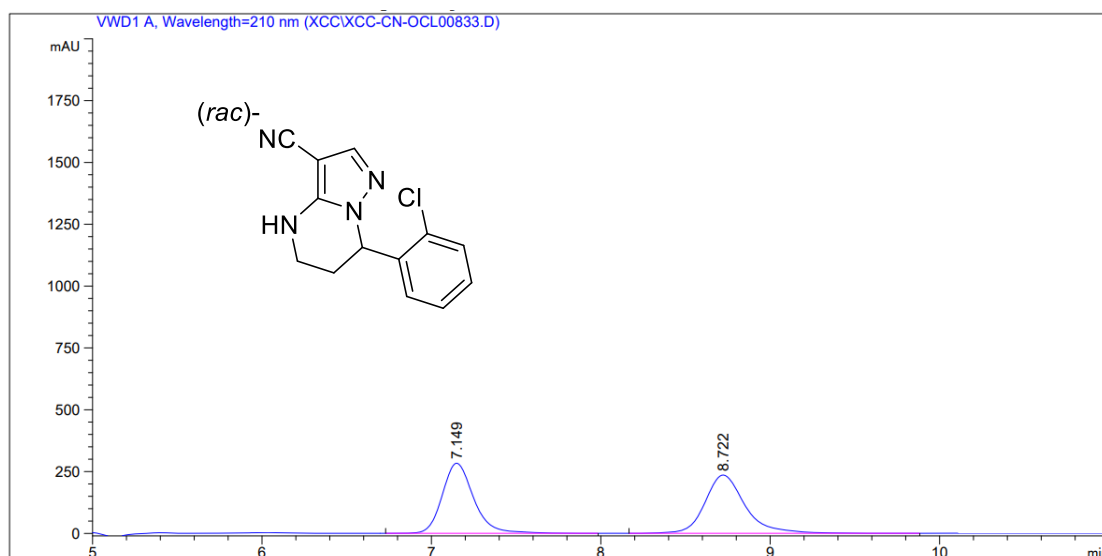
7-(2-fluorophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**21**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.614	VB	0.2521	1083.78918	66.17799	3.1684
2	11.714	VB	0.3143	3.31221e4	1628.28284	96.8316

Totals : 3.42059e4 1694.46082

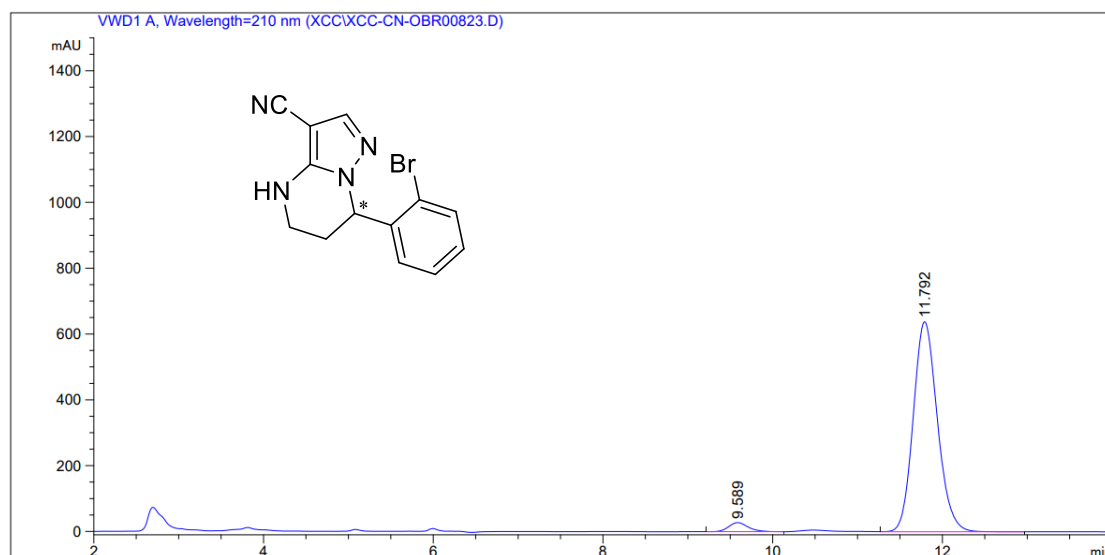
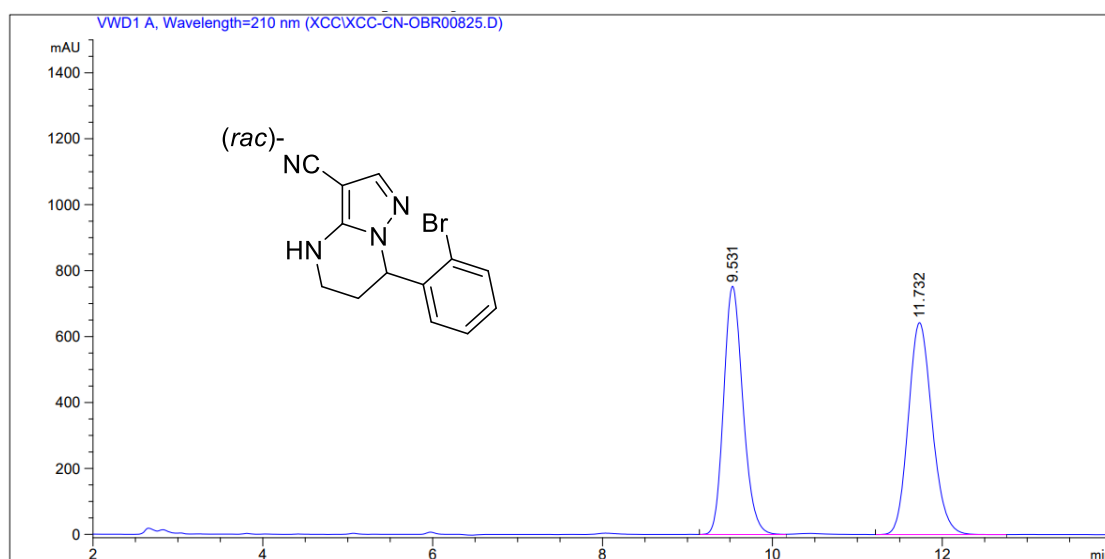
7-(2-chlorophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**2m**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.079	BB	0.1808	435.70203	37.41910	4.3333
2	8.610	BB	0.2311	9618.93164	640.76038	95.6667

Totals : 1.00546e4 678.17947

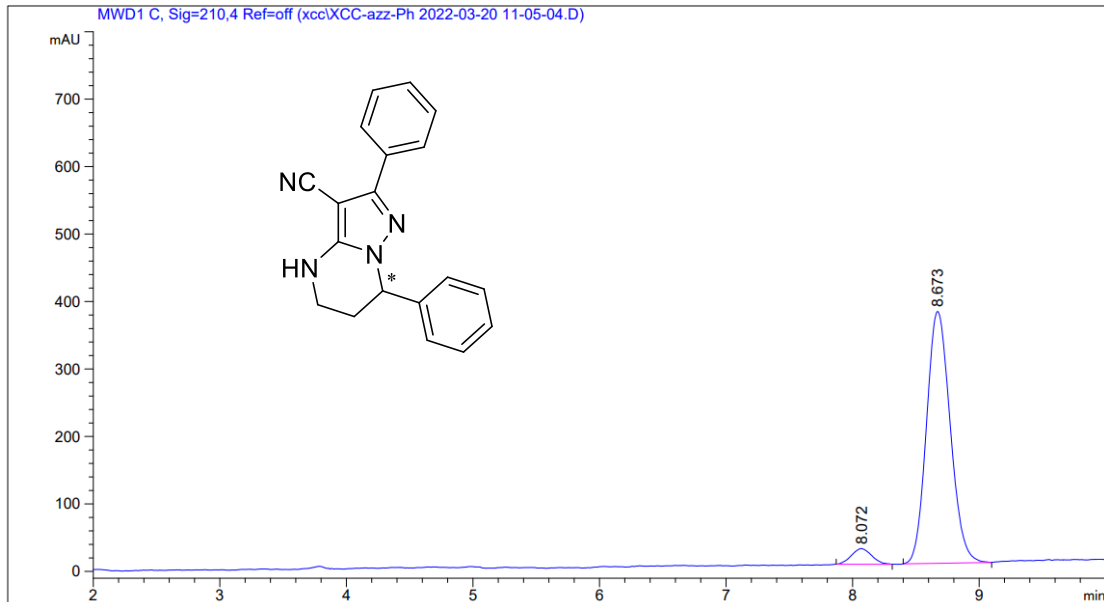
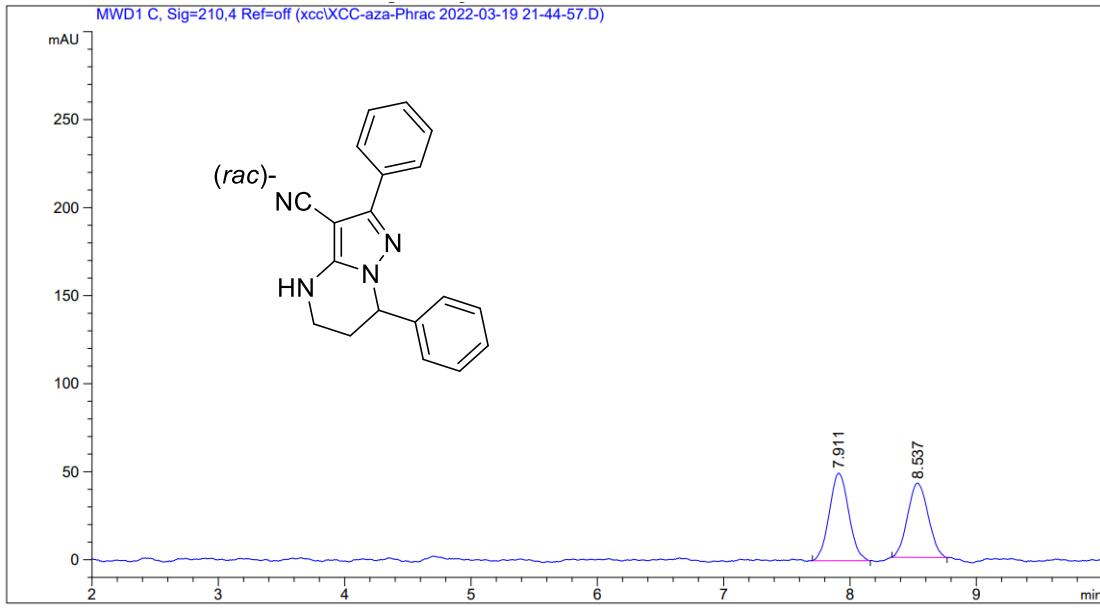
7-(2-bromophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**2n**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.589	BB	0.2436	437.16492	27.47937	3.3571
2	11.792	VB	0.3052	1.25851e4	637.95734	96.6429

Totals : 1.30223e4 665.43671

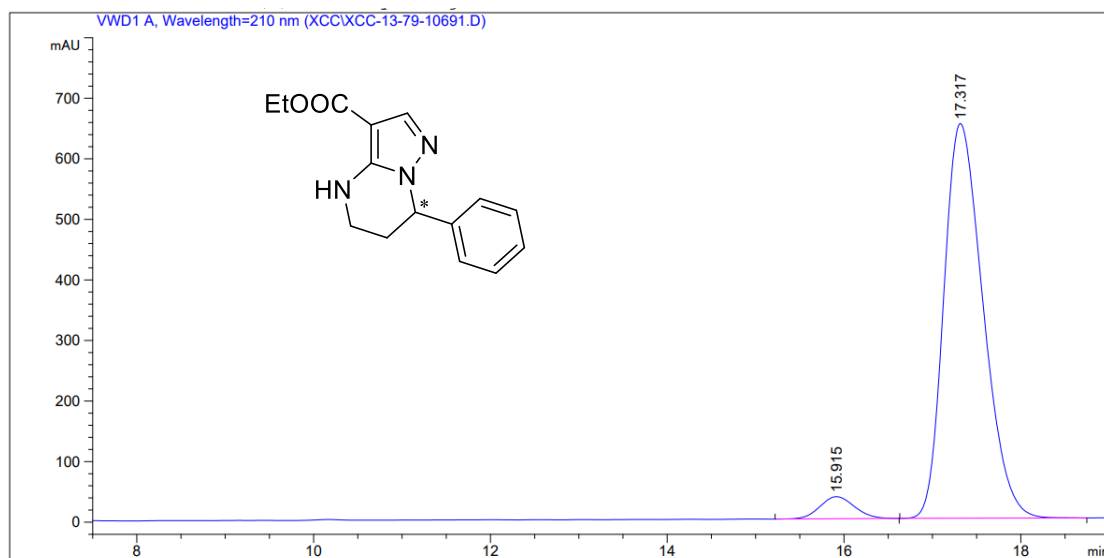
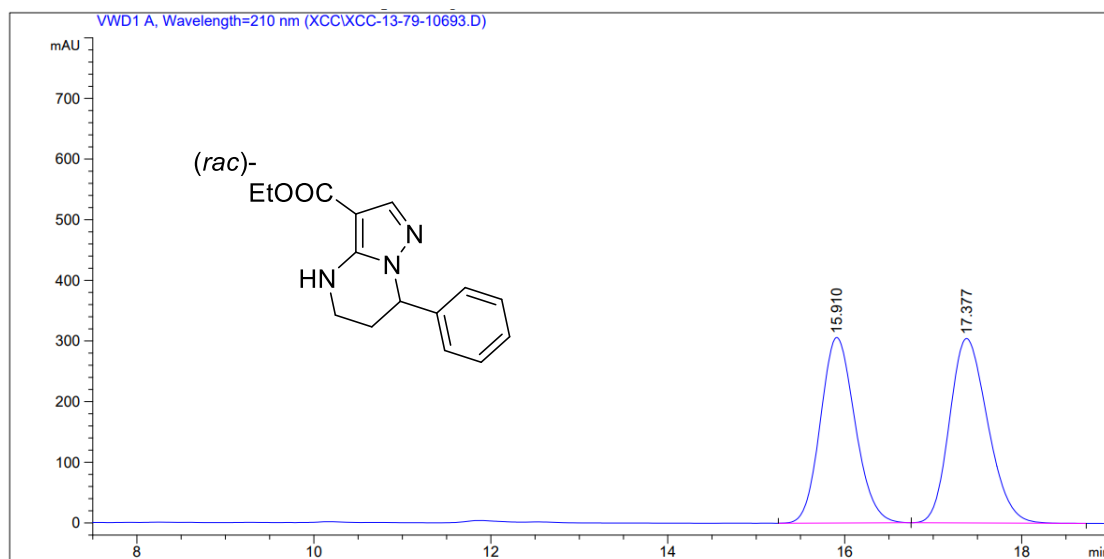
2,7-diphenyl-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**2o**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.072	BB	0.1367	256.75662	23.17806	5.0190
2	8.673	BB	0.1893	4858.91211	373.38199	94.9810

Totals : 5115.66873 396.56005

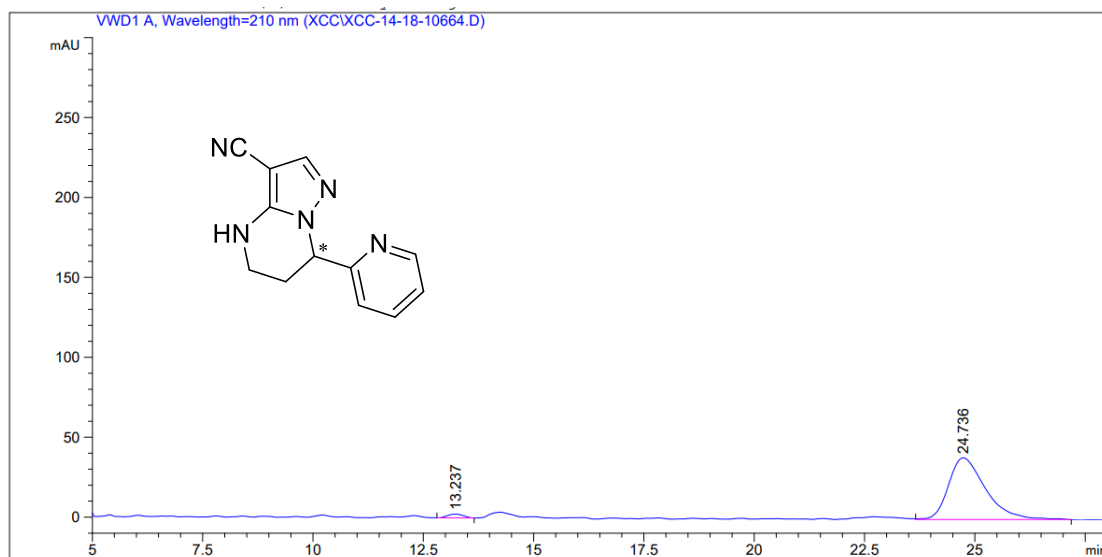
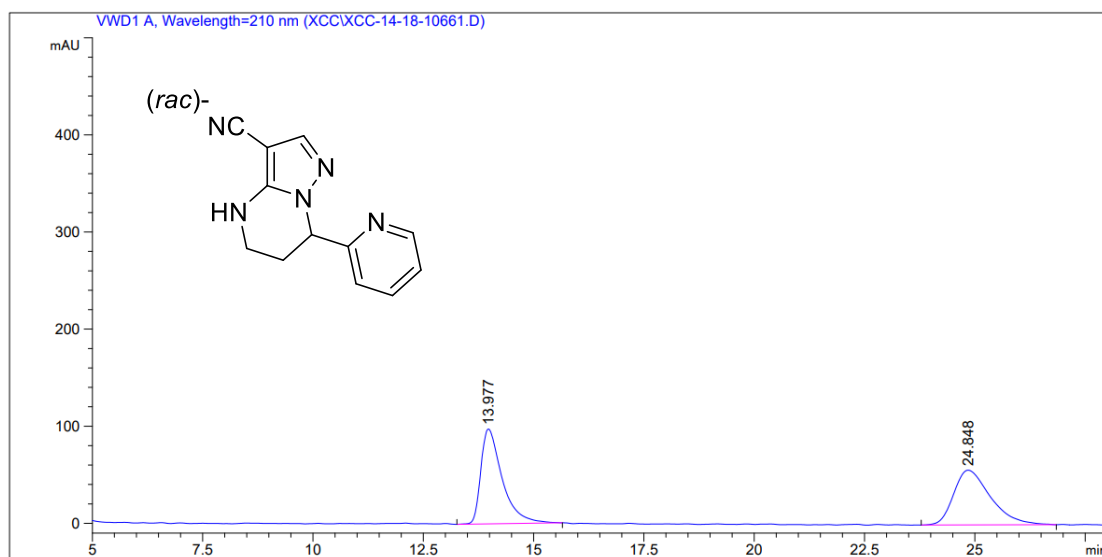
ethyl-7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carboxylate (**2p**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.915	BB	0.4224	988.37842	36.43888	4.6980
2	17.317	BB	0.4789	2.00501e4	651.74005	95.3020

Totals : 2.10385e4 688.17893

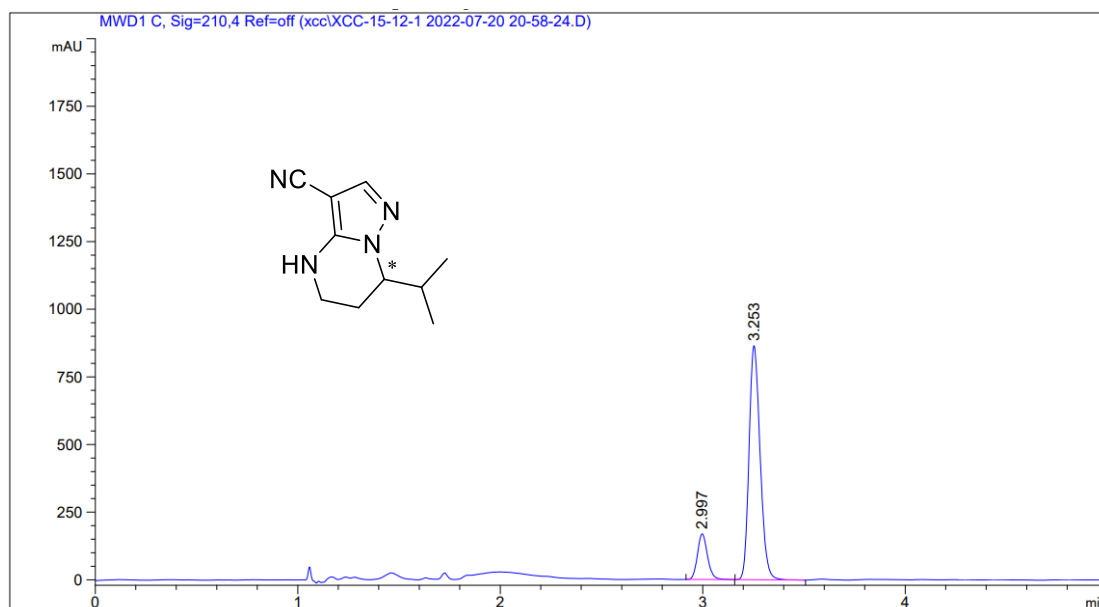
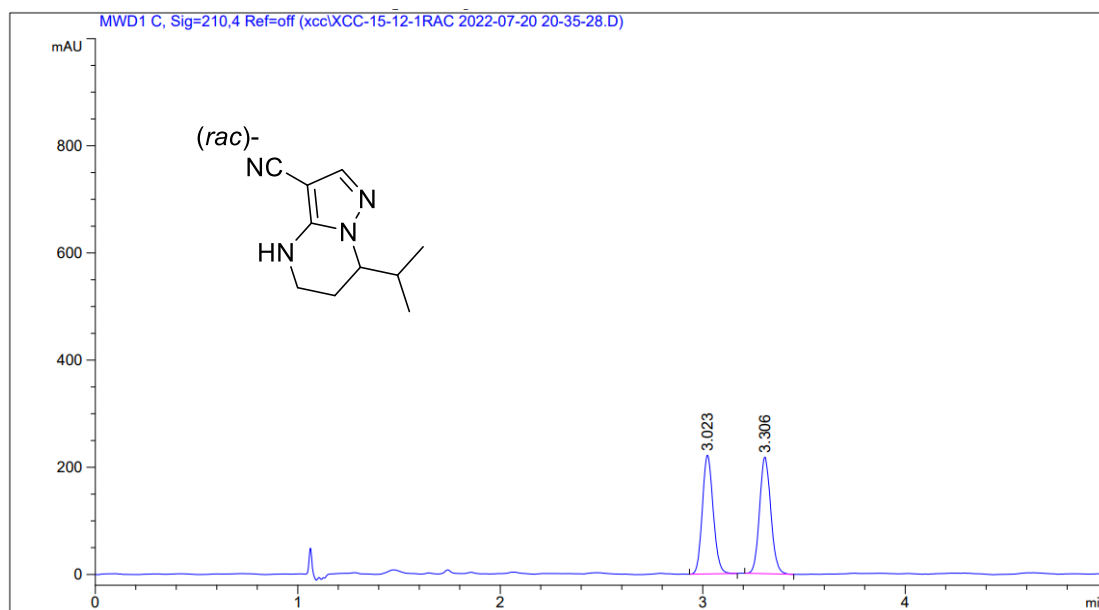
7-(pyridin-2-yl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**2q**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.237	BB	0.3993	58.56708	2.37851	2.5396
2	24.736	VB	0.8959	2247.62793	38.56899	97.4604

Totals : 2306.19501 40.94750

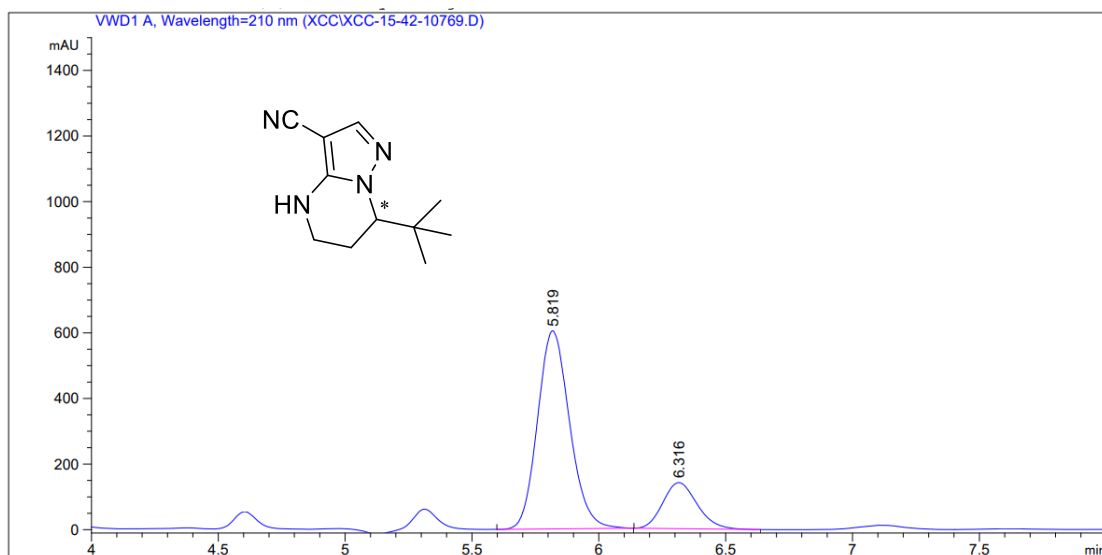
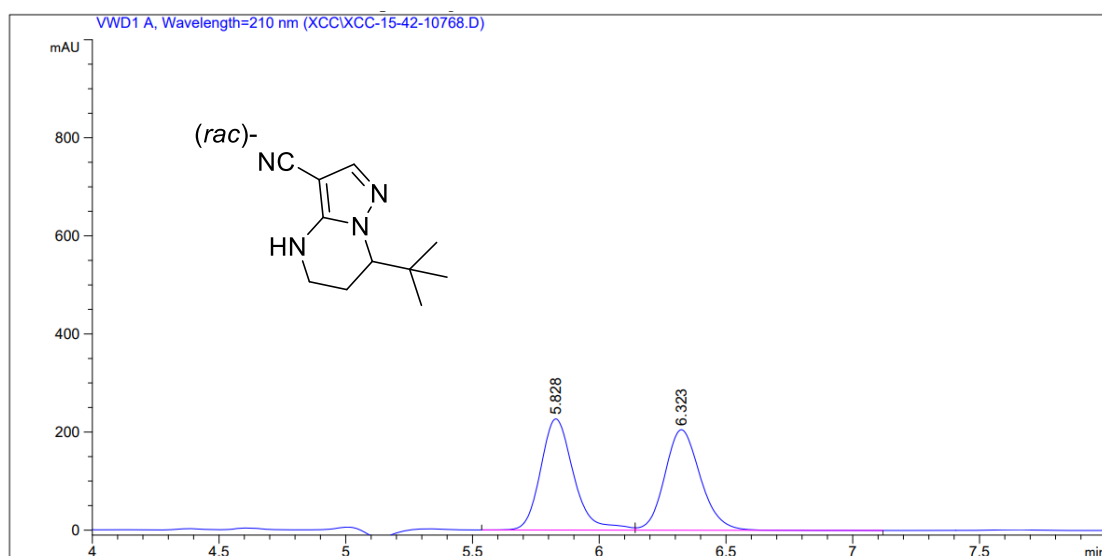
7-isopropyl-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**2r**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.997	BB	0.0531	578.97577	168.64436	14.9544
2	3.253	BB	0.0594	3292.63257	864.89130	85.0456

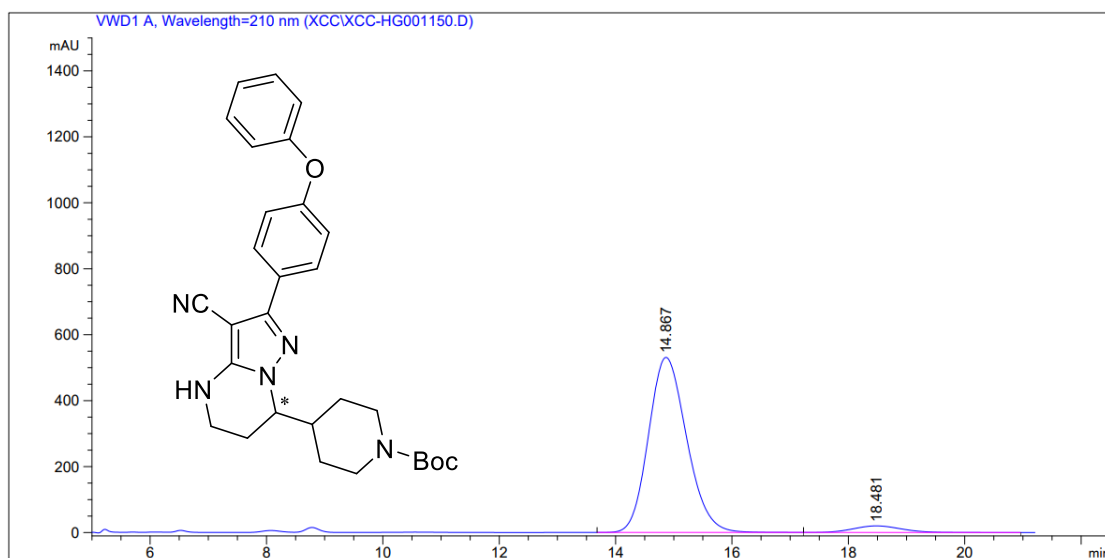
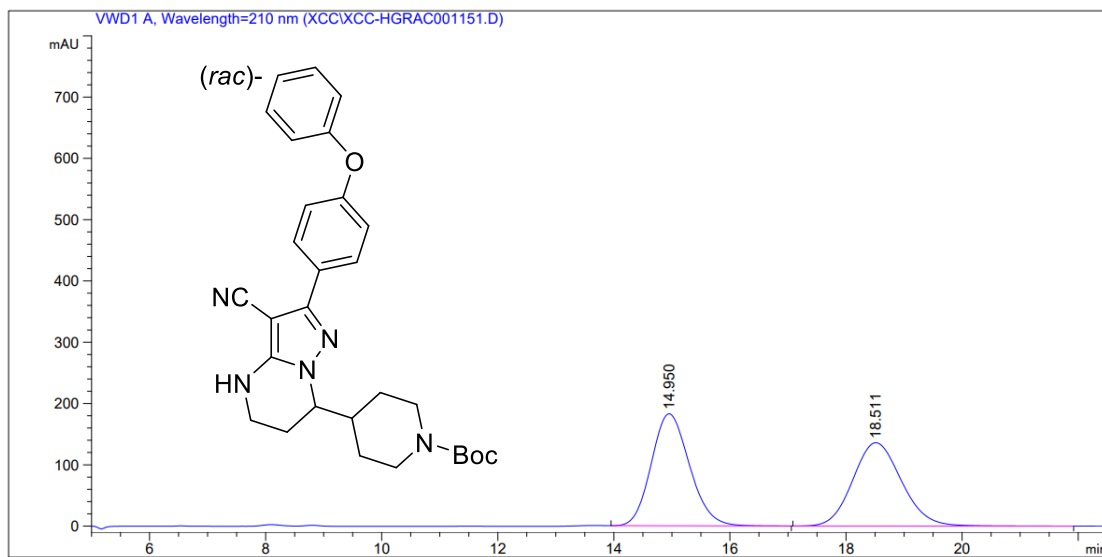
Totals : 3871.60834 1033.53566

7-(*tert*-butyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**2s**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.819	BB	0.1366	5313.63574	604.05463	80.0620
2	6.316	BB	0.1458	1323.26538	140.60860	19.9380
Totals :				6636.90112	744.66322	

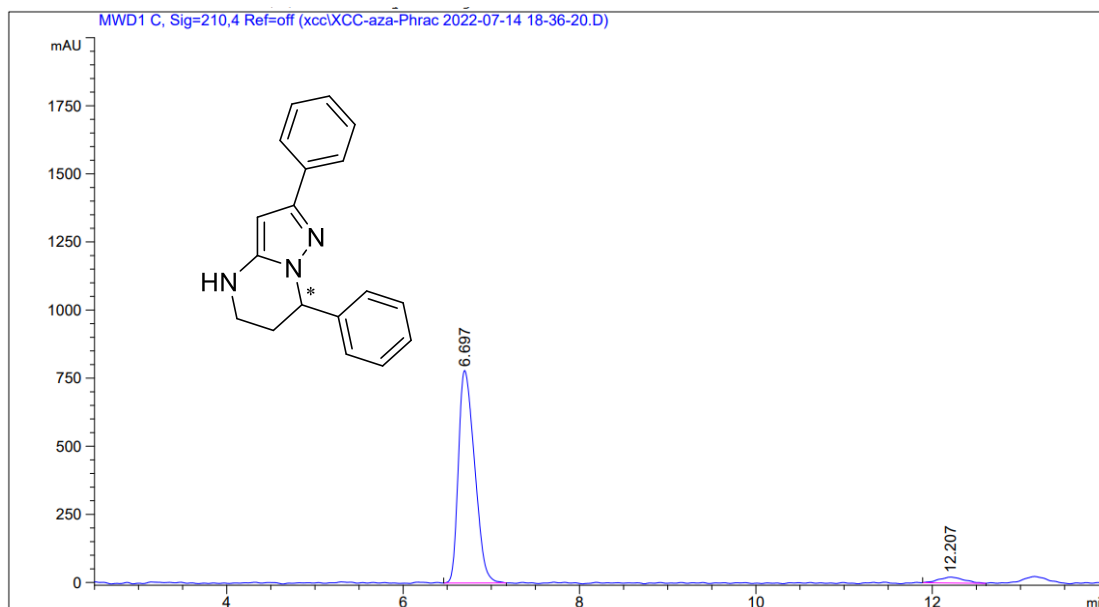
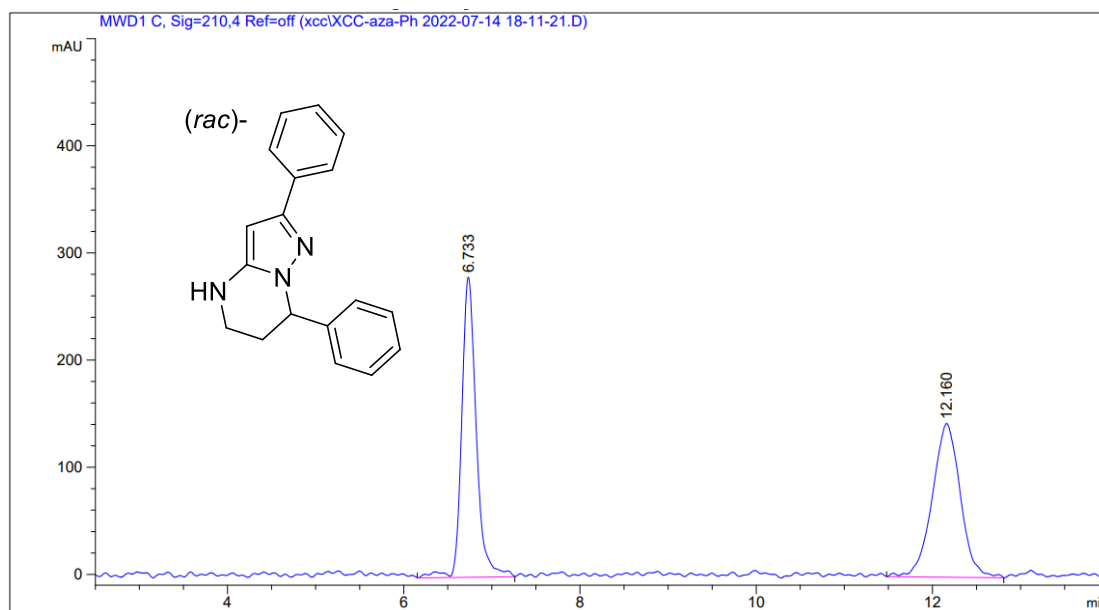
tert-butyl 4-(3-cyano-2-(4-phenoxyphenyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidin-7-yl)piperidine-1-carboxylate (**2t**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.867	BB	0.7102	2.42103e4	530.74377	95.4280
2	18.481	BB	0.8975	1159.91797	19.97307	4.5720

Totals : 2.53703e4 550.71685

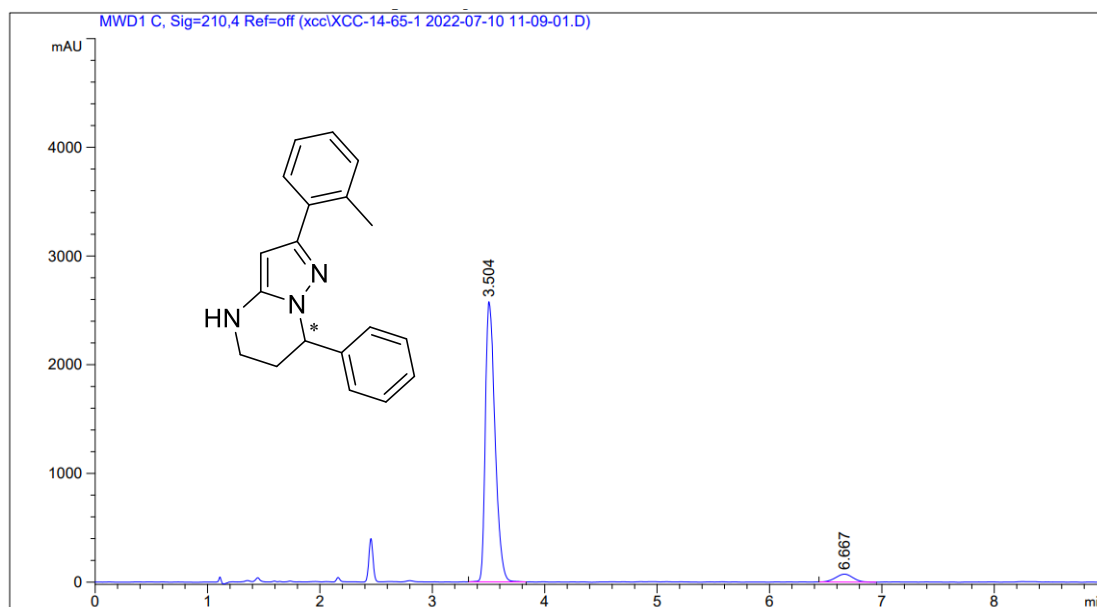
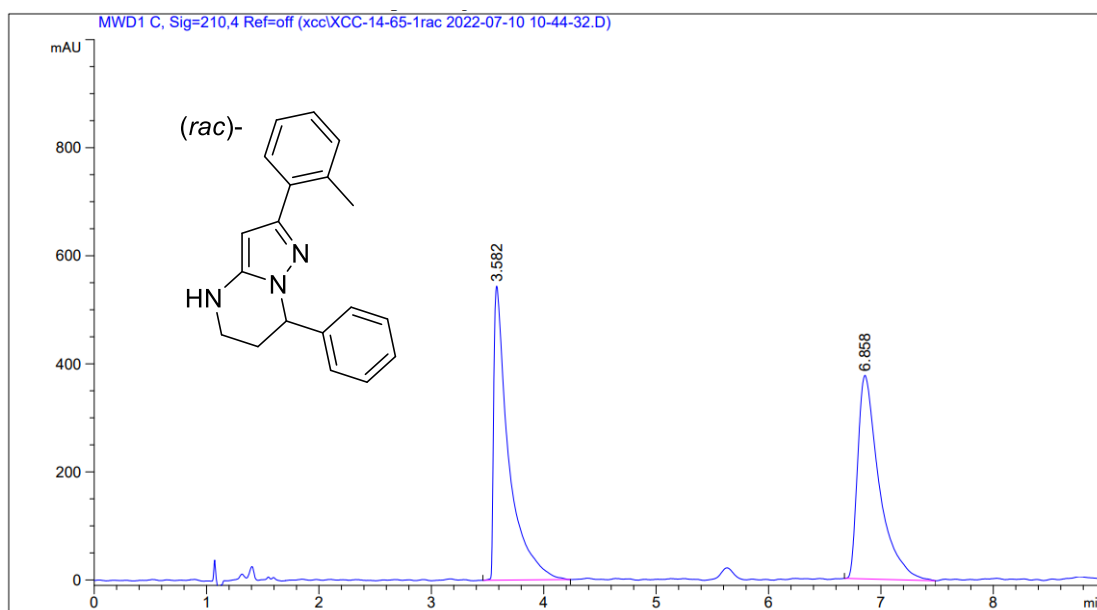
2,7-diphenyl-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine (**4a**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.697	BB	0.1917	9942.35449	780.21906	95.8940
2	12.207	BB	0.2329	425.70871	21.64690	4.1060

Totals : 1.03681e4 801.86596

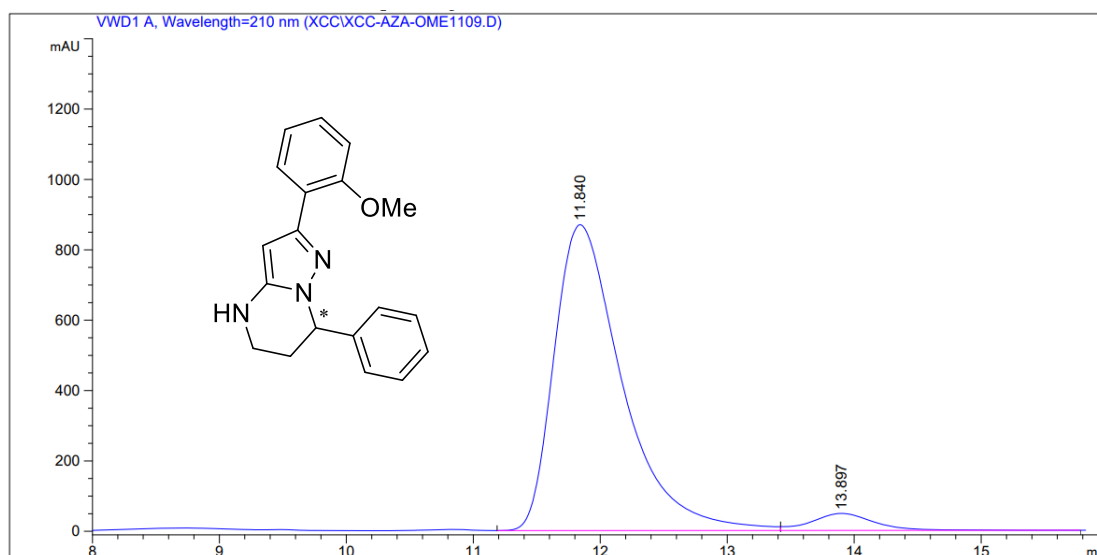
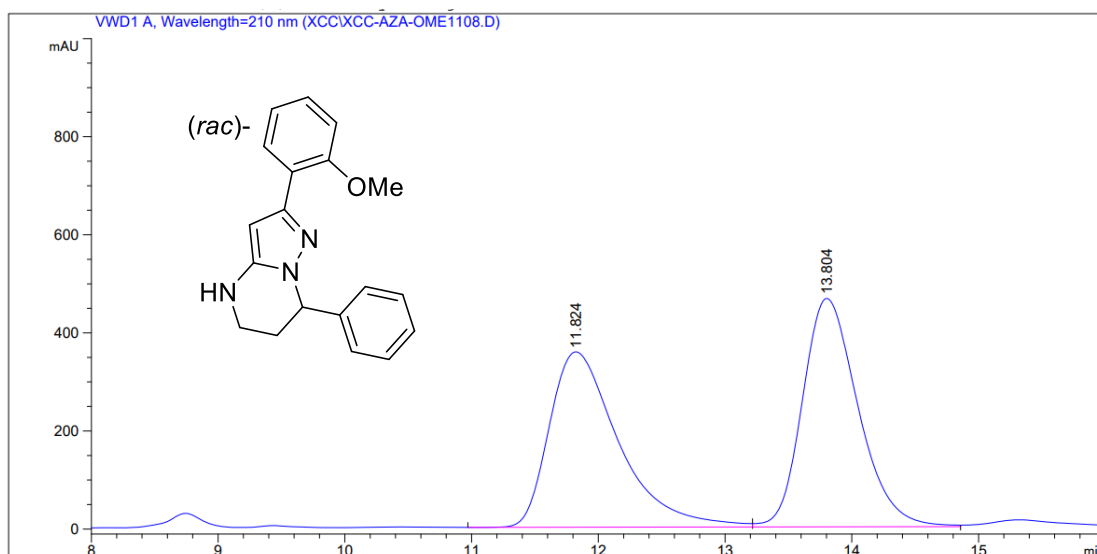
7-phenyl-2-(*o*-tolyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine (**4b**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.504	BB	0.0884	1.54357e4	2577.53296	95.2120
2	6.667	BB	0.1560	776.21973	72.44343	4.7880

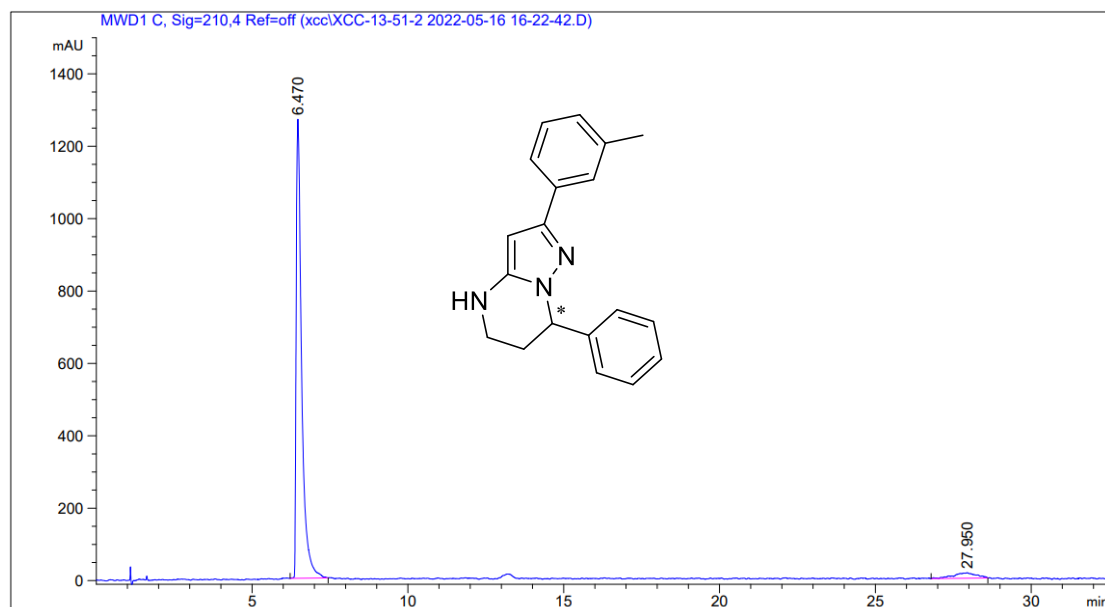
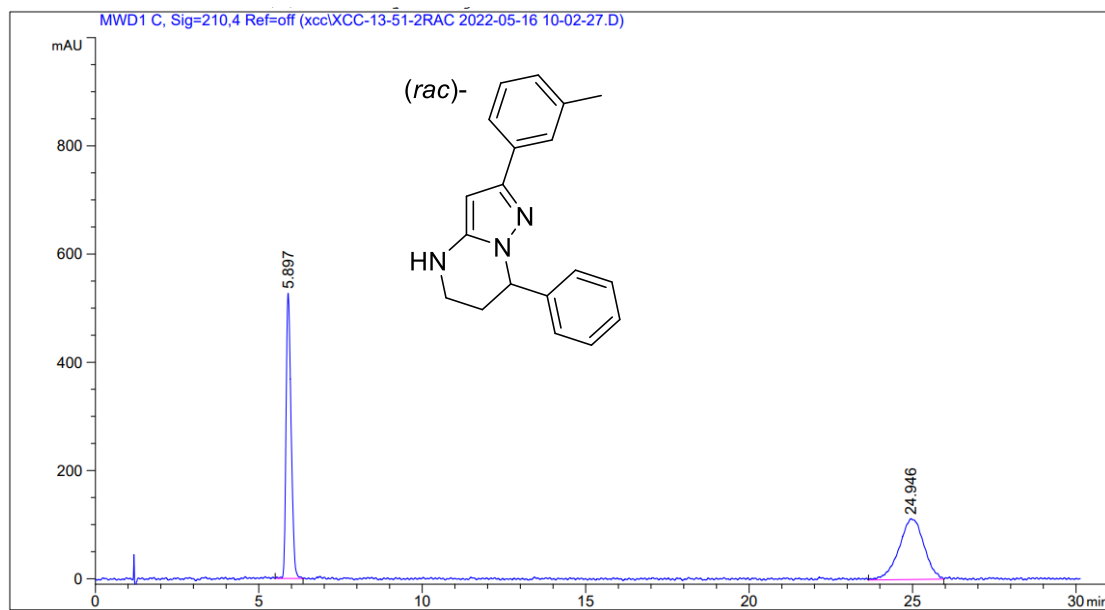
Totals : 1.62119e4 2649.97639

7-(2-methoxyphenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**4c**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.840	VV	0.5664	3.23675e4	869.33826	95.1623
2	13.897	VB	0.5107	1645.44849	48.26830	4.8377
Totals :				3.40130e4	917.60656	

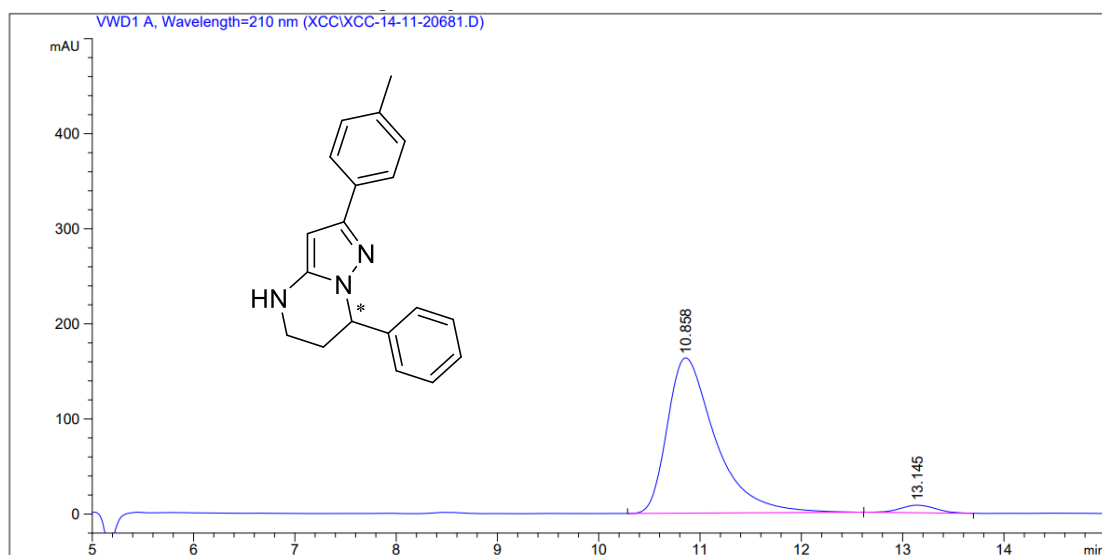
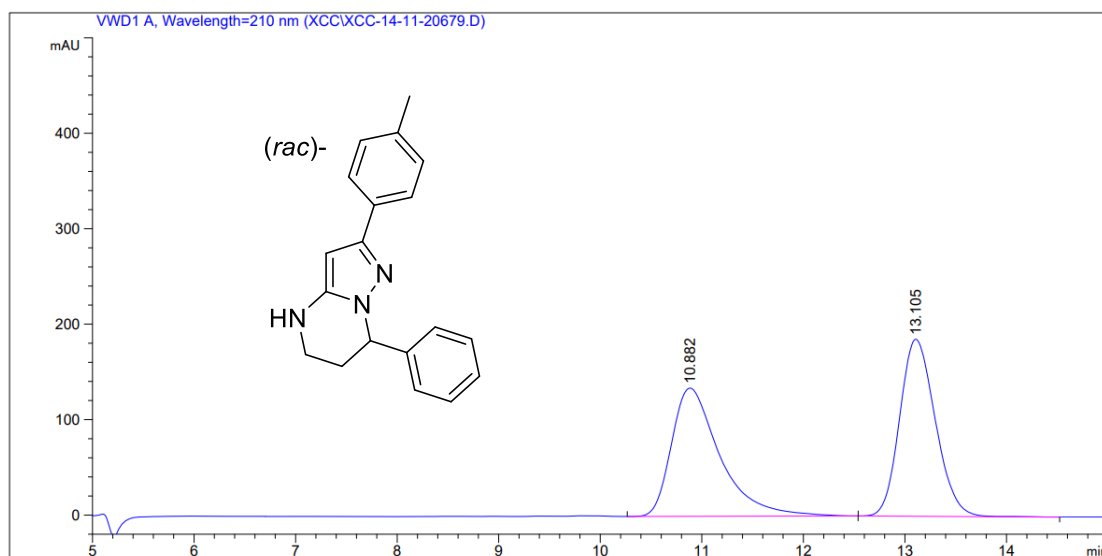
7-phenyl-2-(*m*-tolyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine (**4d**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.470	BB	0.1806	1.53949e4	1268.03137	95.1872
2	27.950	BB	0.6168	778.38605	15.16570	4.8128

Totals : 1.61733e4 1283.19707

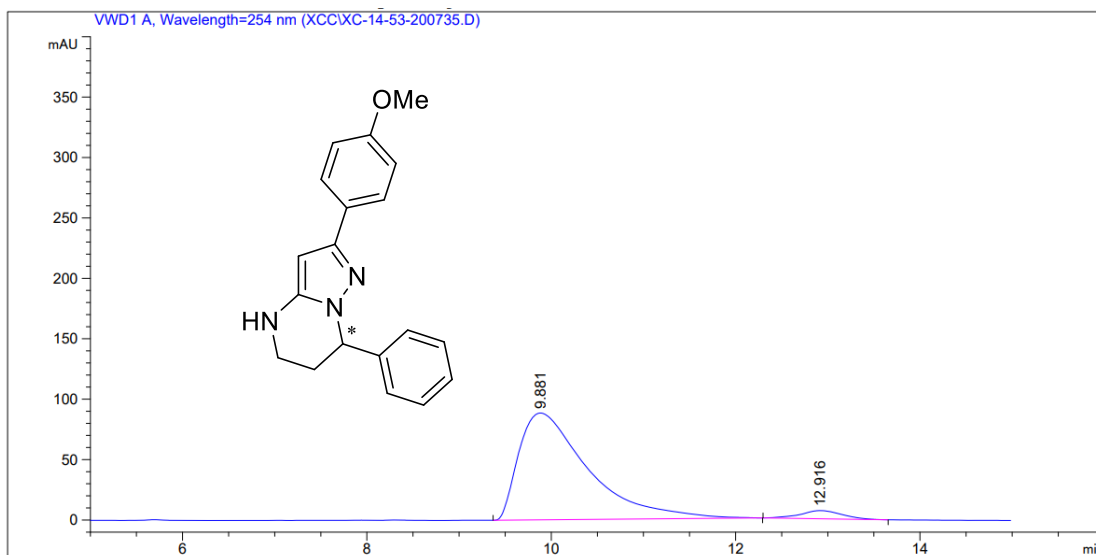
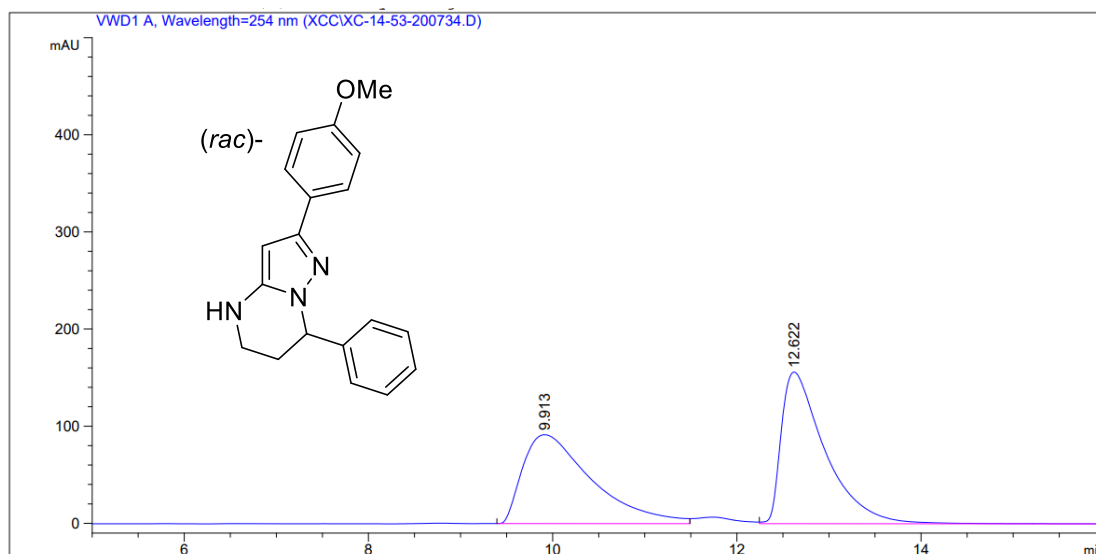
7-phenyl-2-(*p*-tolyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine (**4e**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.858	BB	0.4944	5384.78857	163.42589	96.5632
2	13.145	BB	0.3704	191.64958	8.03140	3.4368

Totals : 5576.43816 171.45729

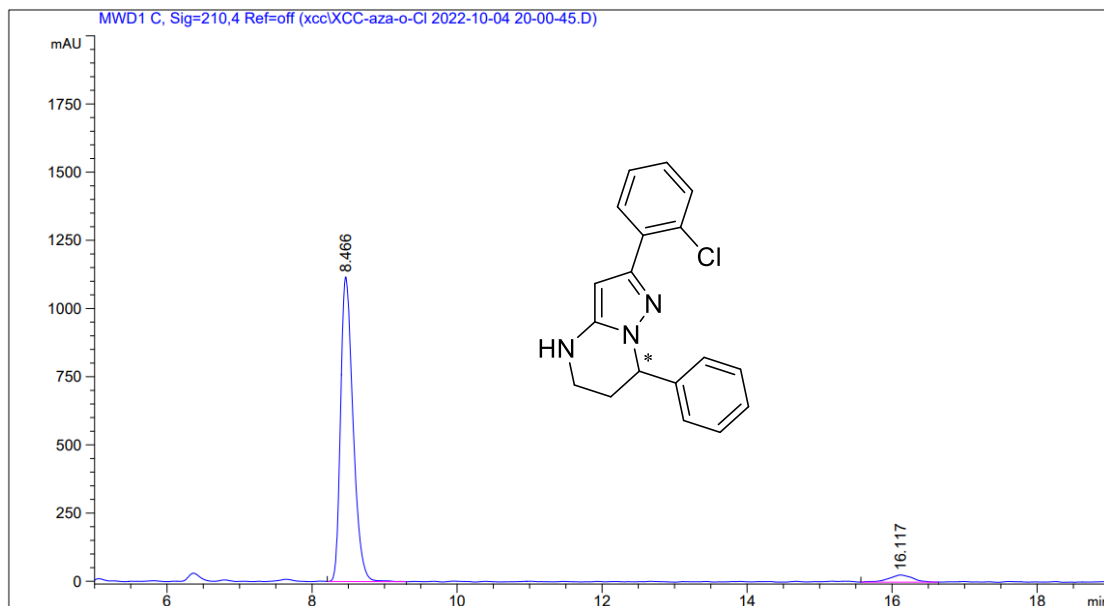
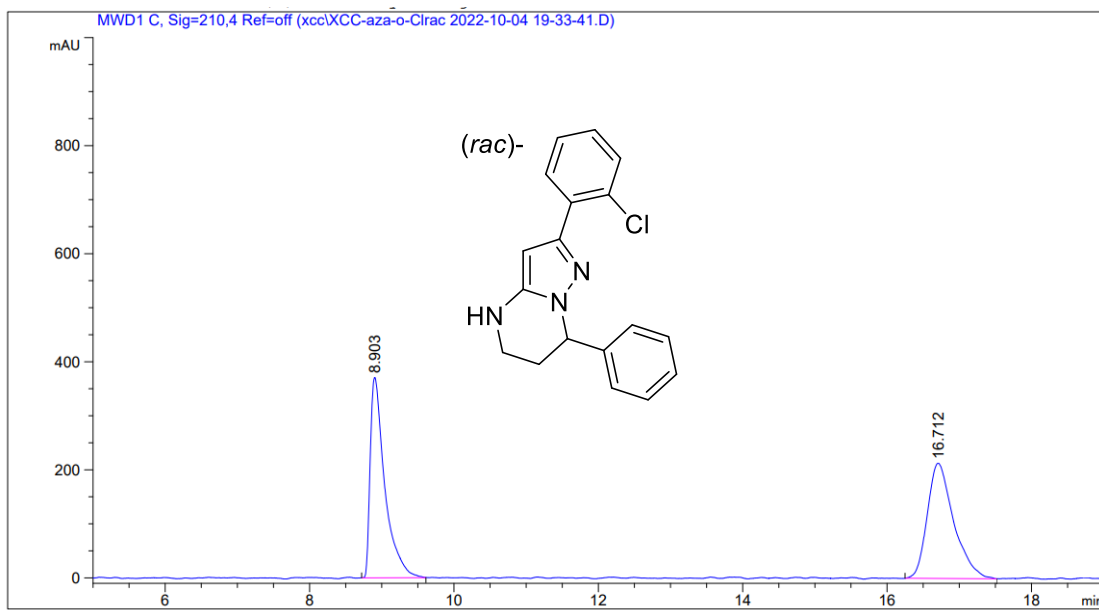
2-(4-methoxyphenyl)-7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine (**4f**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.881	BB	0.7852	4616.51123	88.41042	95.5986
2	12.916	BBA	0.4757	212.54488	6.78152	4.4014

Totals : 4829.05611 95.19194

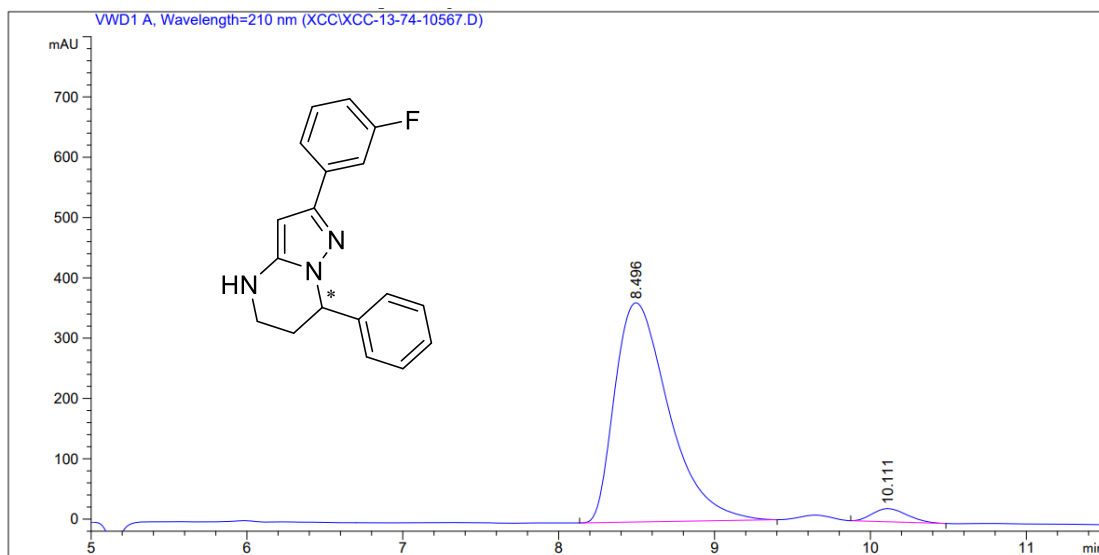
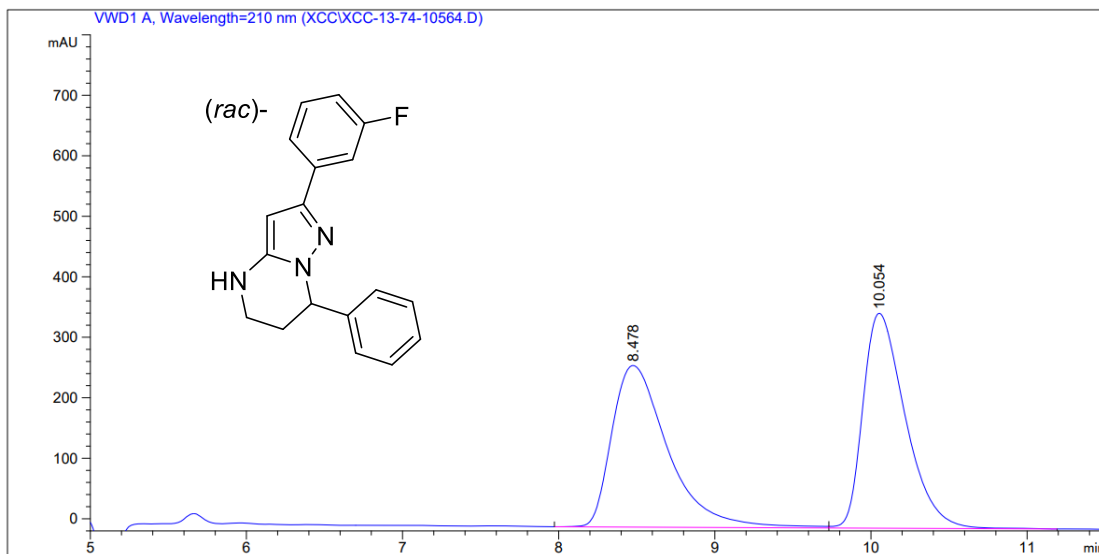
2-(2-chlorophenyl)-7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine (**4g**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.466	BB	0.1855	1.33608e4	1117.37659	95.6663
2	16.117	BB	0.3113	605.25043	26.21869	4.3337

Totals : 1.39661e4 1143.59528

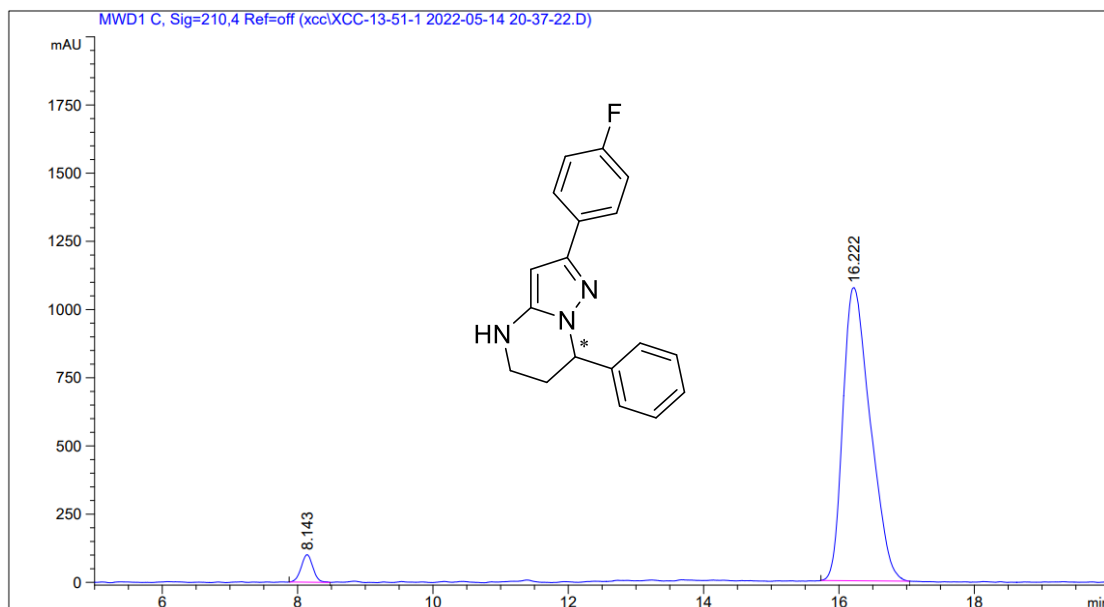
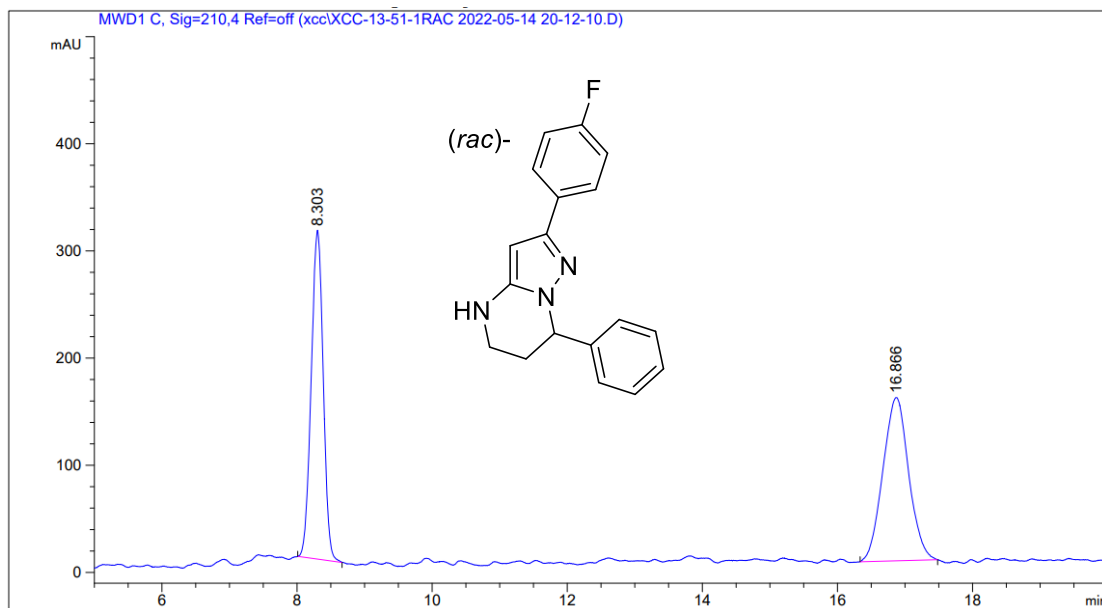
2-(3-fluorophenyl)-7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine (**4h**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.496	BB	0.3744	8738.81836	363.55539	96.2781
2	10.111	BB	0.2446	337.82162	21.82385	3.7219

Totals : 9076.63998 385.37924

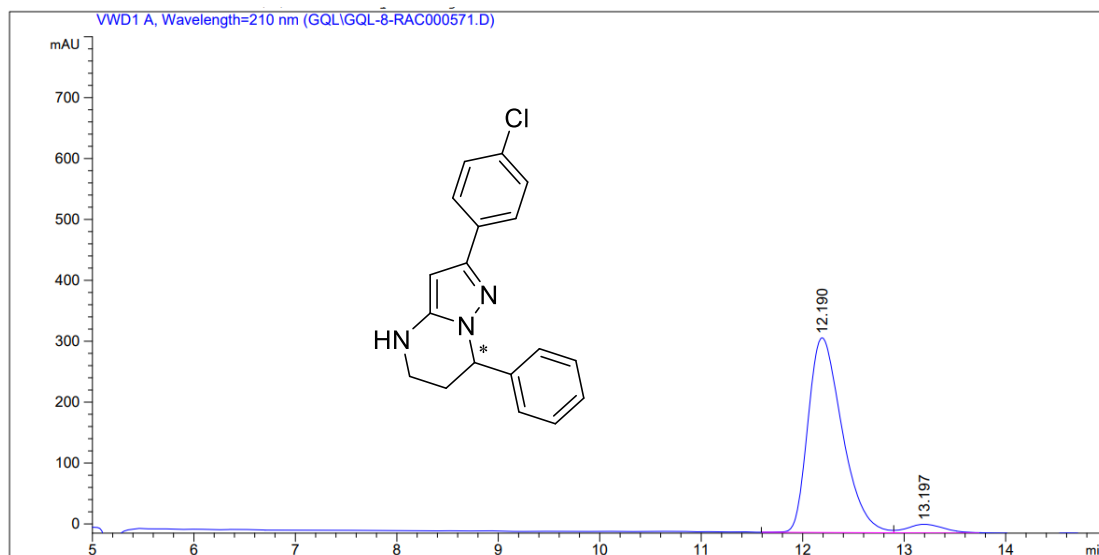
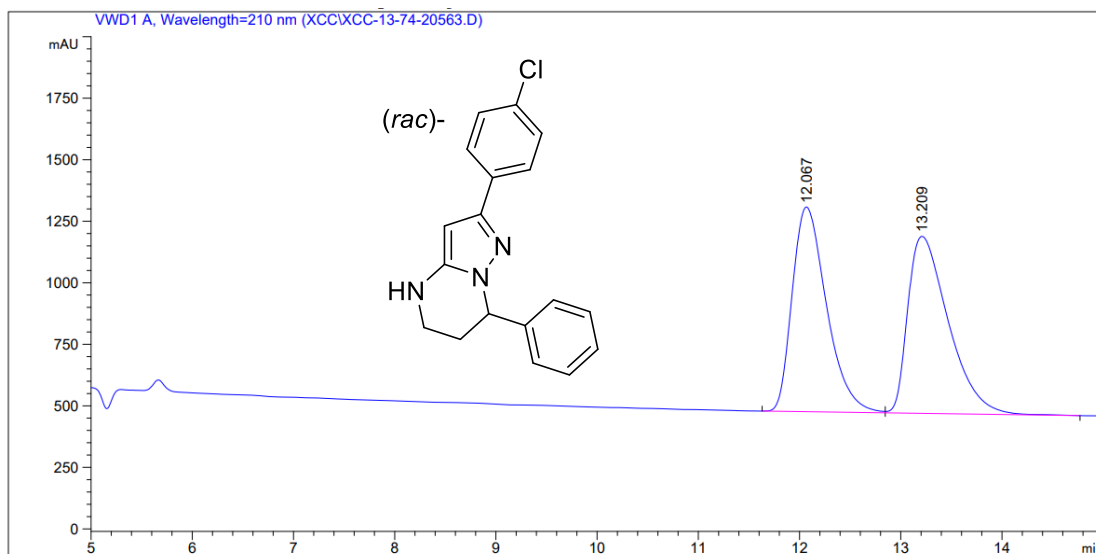
2-(4-fluorophenyl)-7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine (**4i**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.143	BB	0.1543	1221.59644	100.85883	3.8958
2	16.222	BB	0.3321	3.01353e4	1074.79321	96.1042

Totals : 3.13569e4 1175.65205

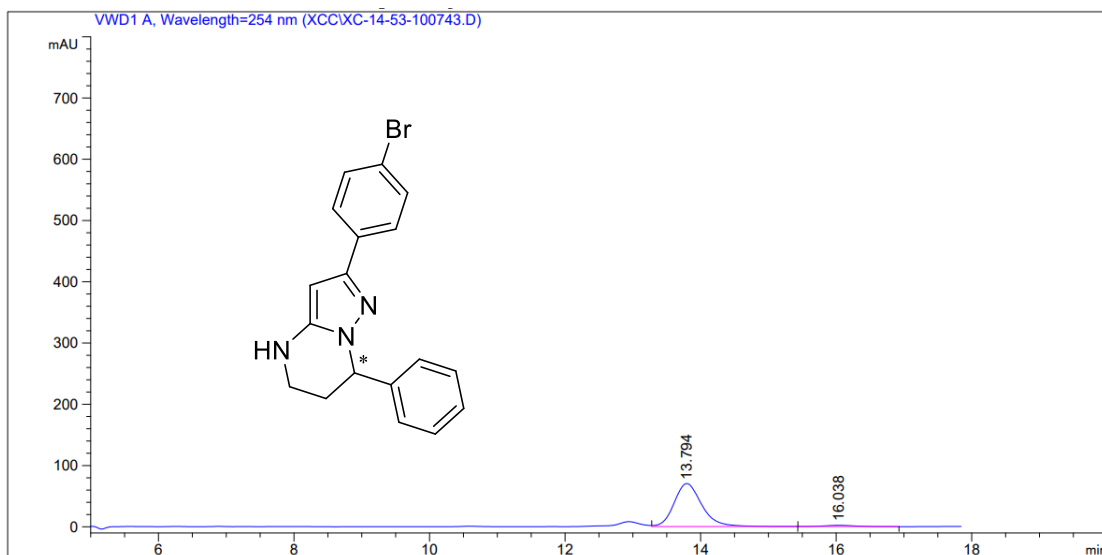
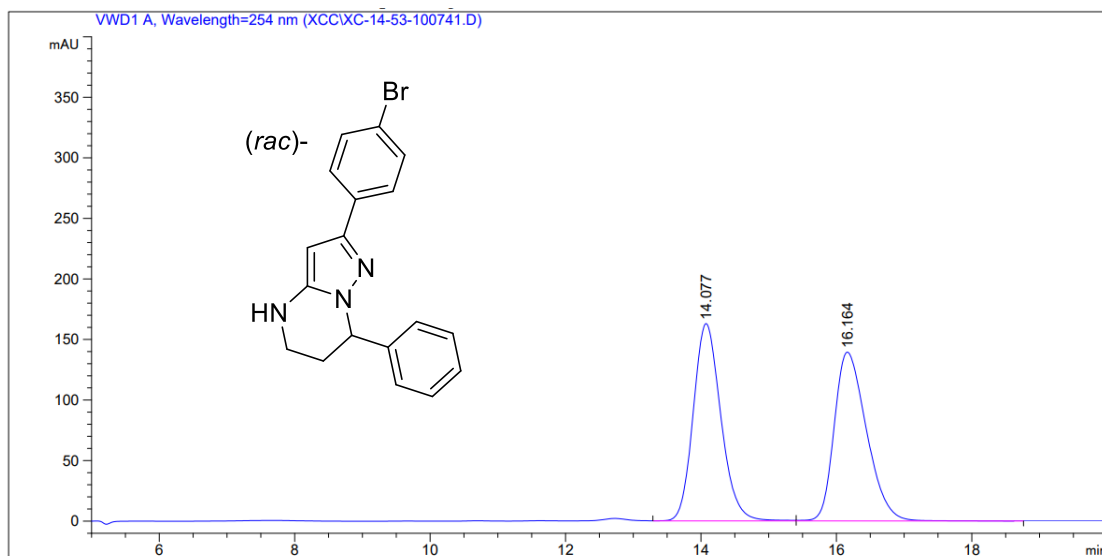
2-(4-chlorophenyl)-7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine (**4j**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.190	BV	0.3599	7448.48877	319.55609	95.3664
2	13.197	VB	0.3854	361.90259	14.19566	4.6336

Totals : 7810.39136 333.75175

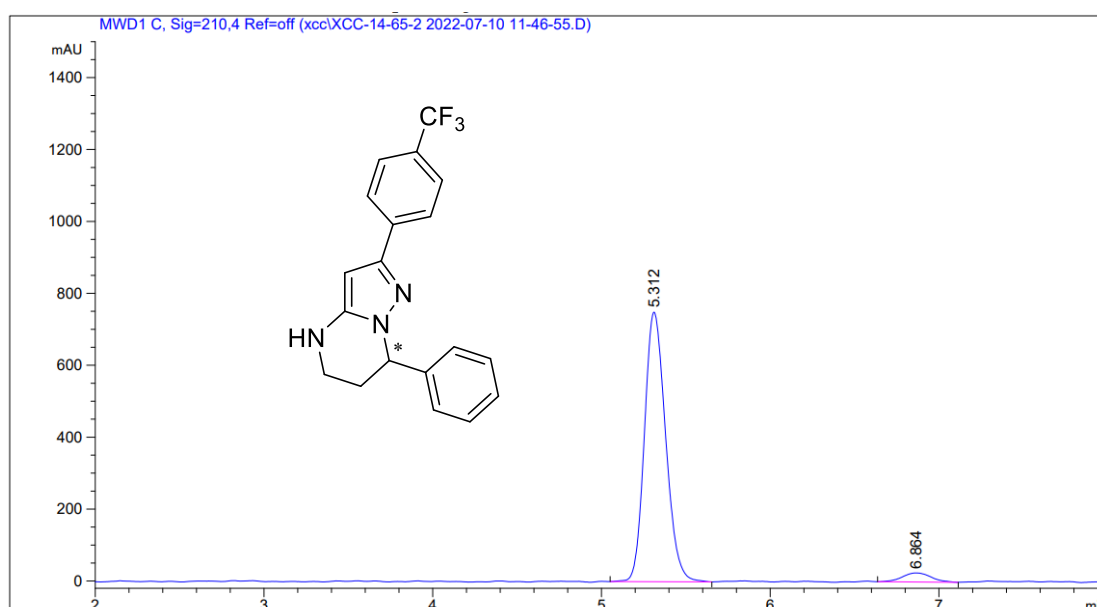
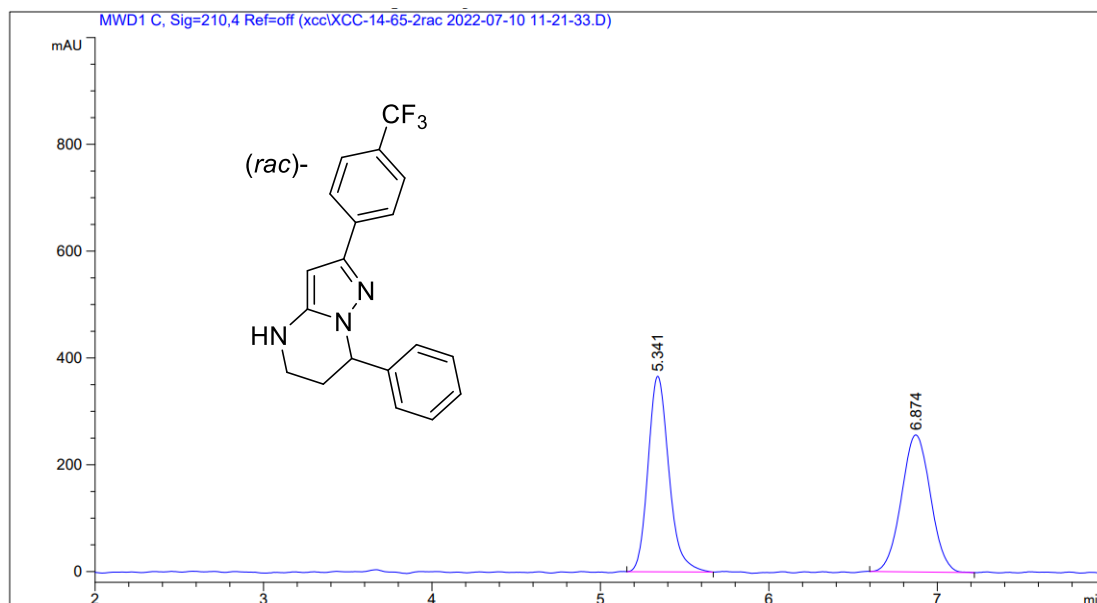
2-(4-bromophenyl)-7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine (**4k**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.794	VB	0.4349	1990.88904	70.20167	97.0279
2	16.038	BB	0.4697	60.98322	2.01162	2.9721
Totals :				2051.87226	72.21328	

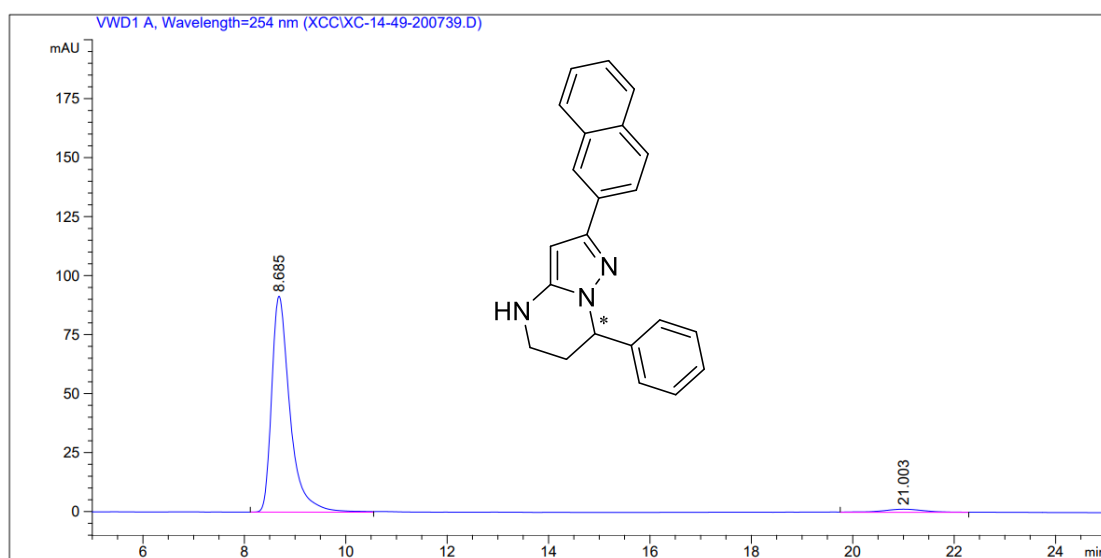
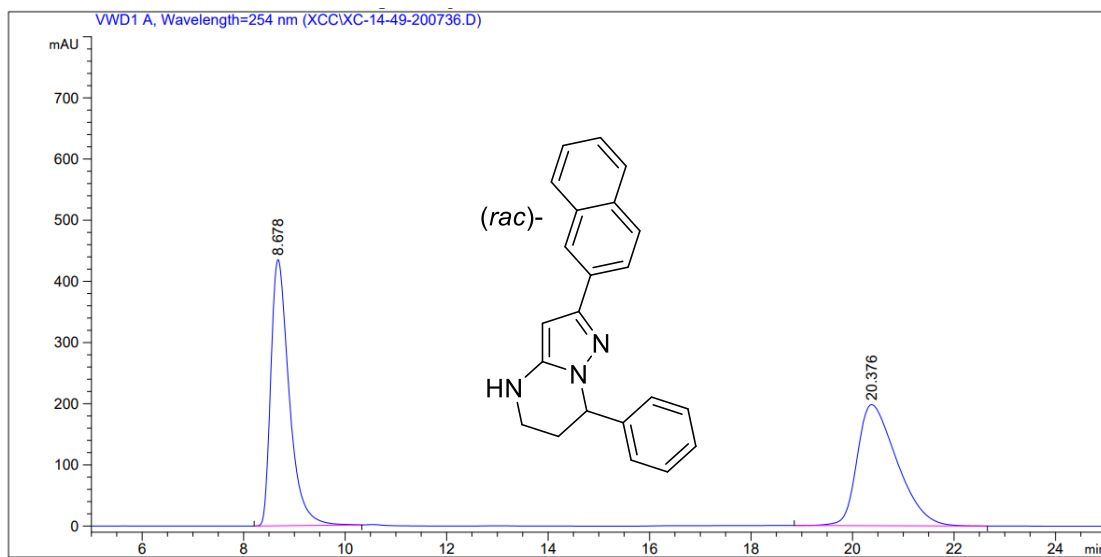
7-phenyl-2-(4-(trifluoromethyl)phenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine

(4I)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.312	BB	0.1352	6536.08594	749.73846	95.6197
2	6.864	BB	0.1485	299.41840	25.21825	4.3803
Totals :				6835.50433	774.95671	

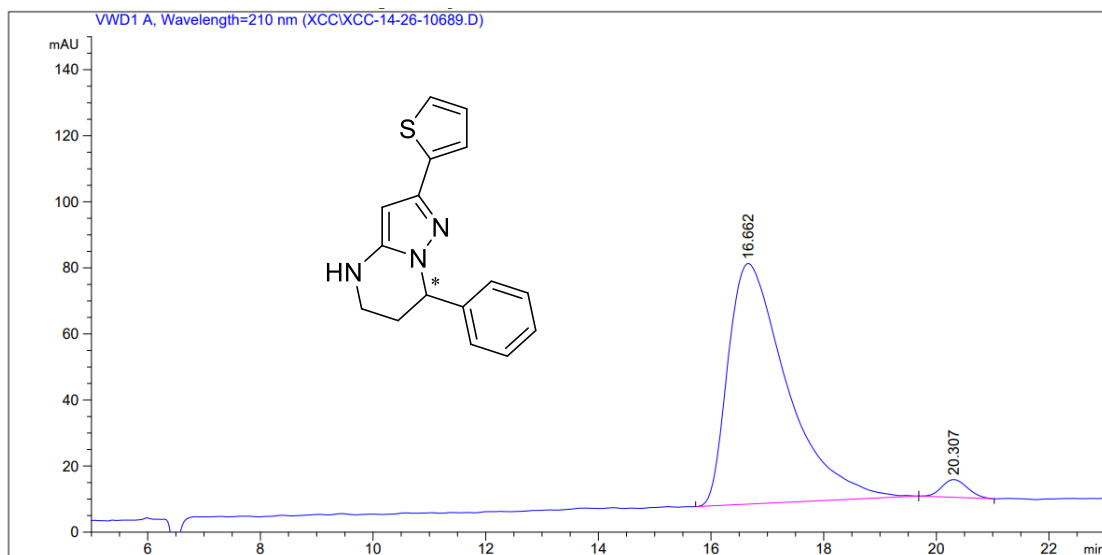
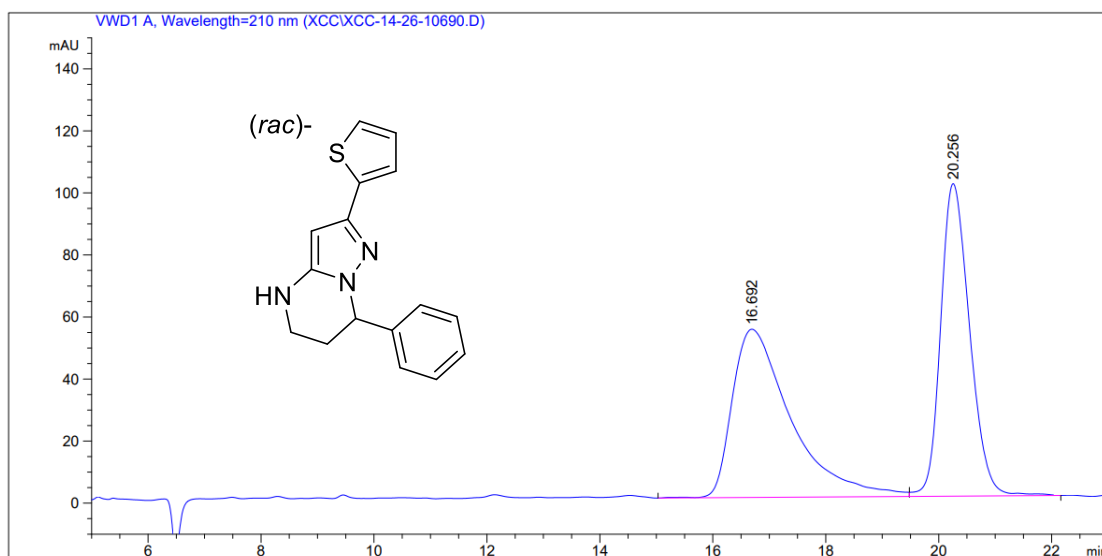
2-(naphthalen-2-yl)-7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine (**4m**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.685	BV	0.3781	2291.18457	91.51552	96.7304
2	21.003	VV	0.8588	77.44549	1.31556	3.2696

Totals : 2368.63006 92.83108

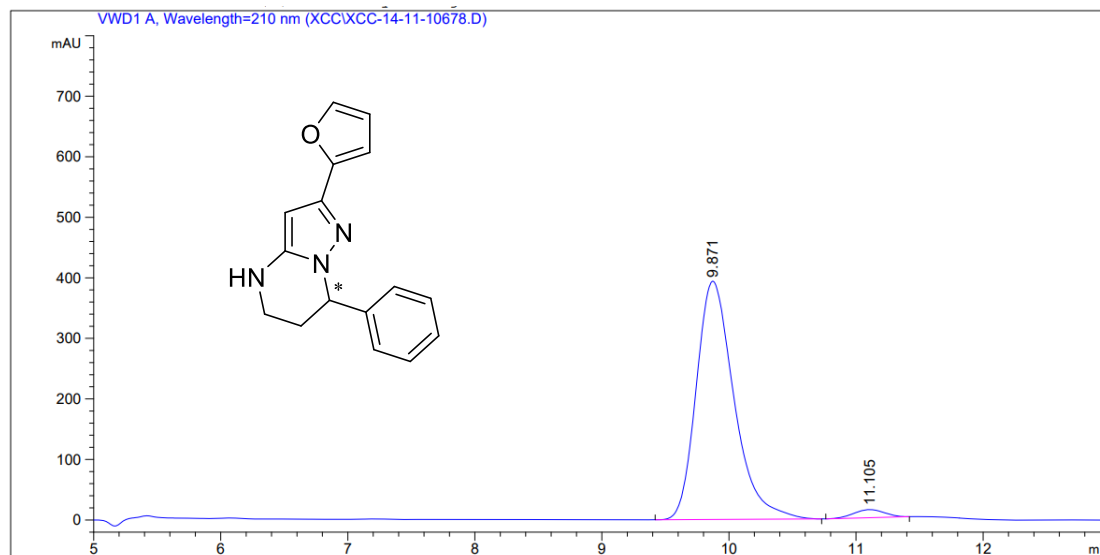
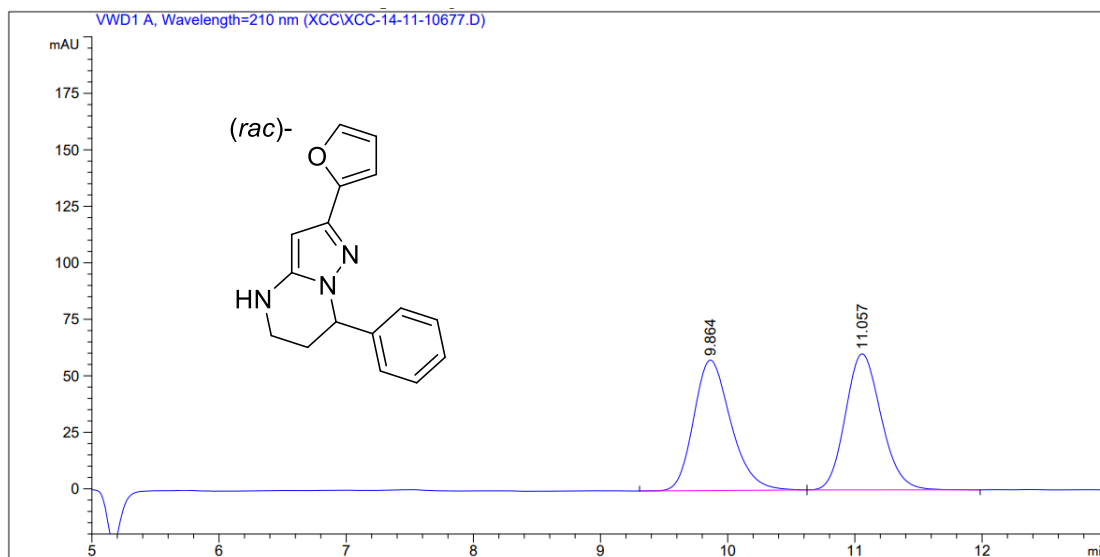
7-phenyl-2-(thiophen-2-yl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine (**4n**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.662	BB	1.0983	5296.42334	72.83888	96.8850
2	20.307	BB	0.4946	170.28668	5.36098	3.1150

Totals : 5466.71002 78.19987

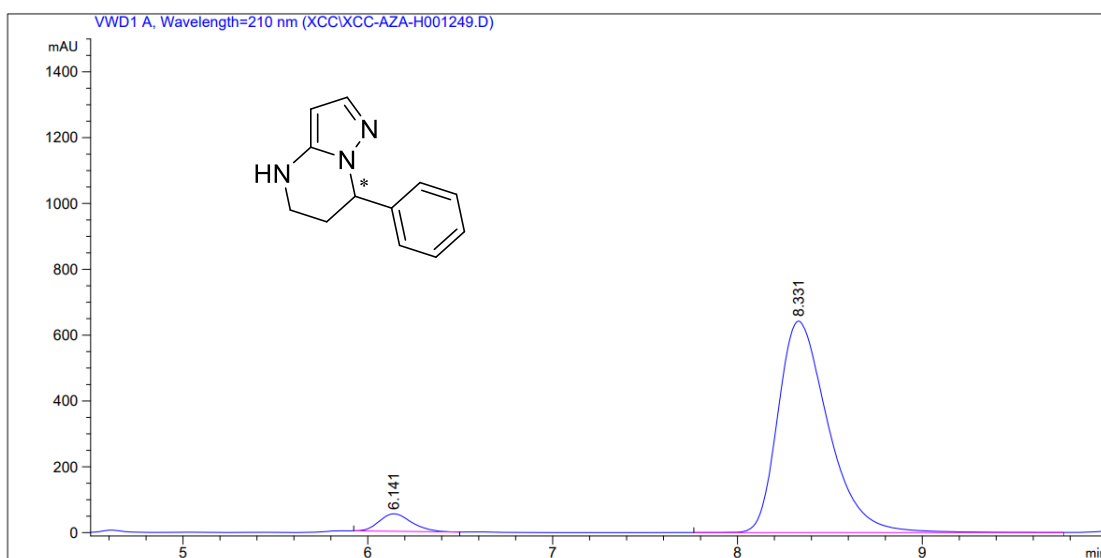
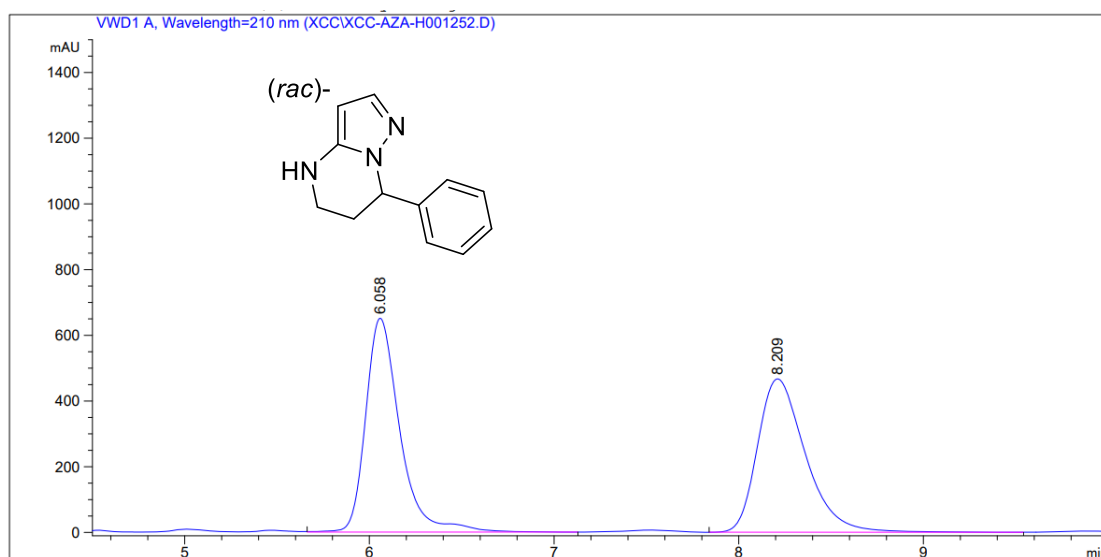
2-(furan-2-yl)-7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine (**4o**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.871	BB	0.3170	8128.21533	393.55322	97.2984
2	11.105	BB	0.2673	225.69115	13.41588	2.7016

Totals : 8353.90648 406.96911

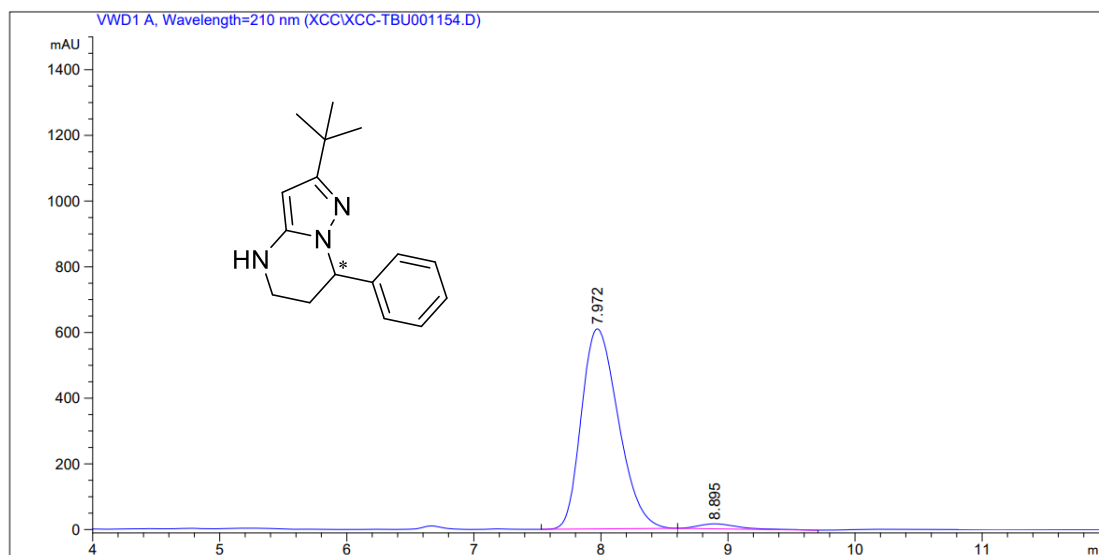
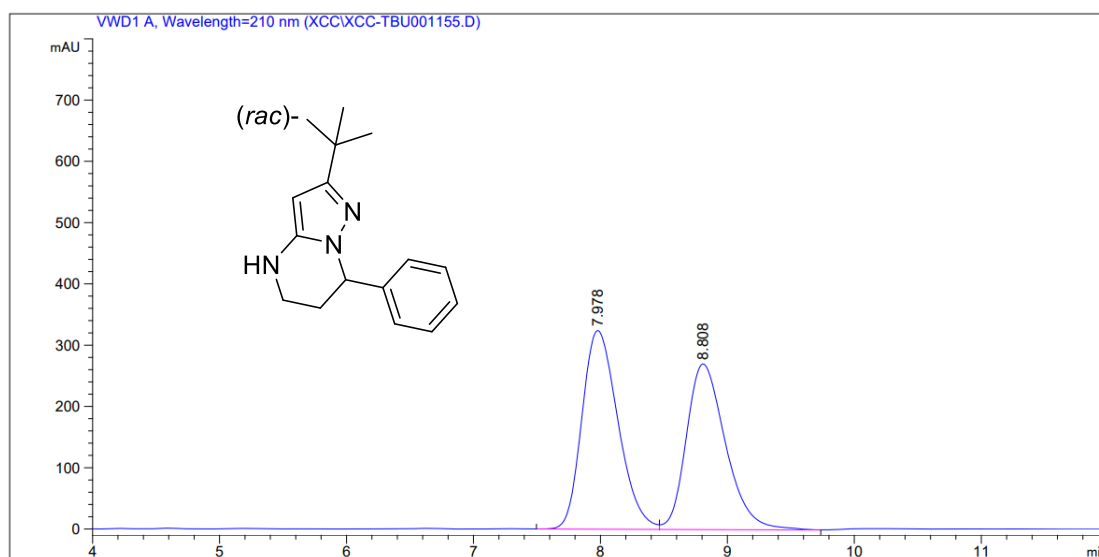
7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine (**4p**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.141	BB	0.1886	645.44043	53.18734	5.0677
2	8.331	BB	0.2886	1.20908e4	642.23553	94.9323

Totals : 1.27363e4 695.42288

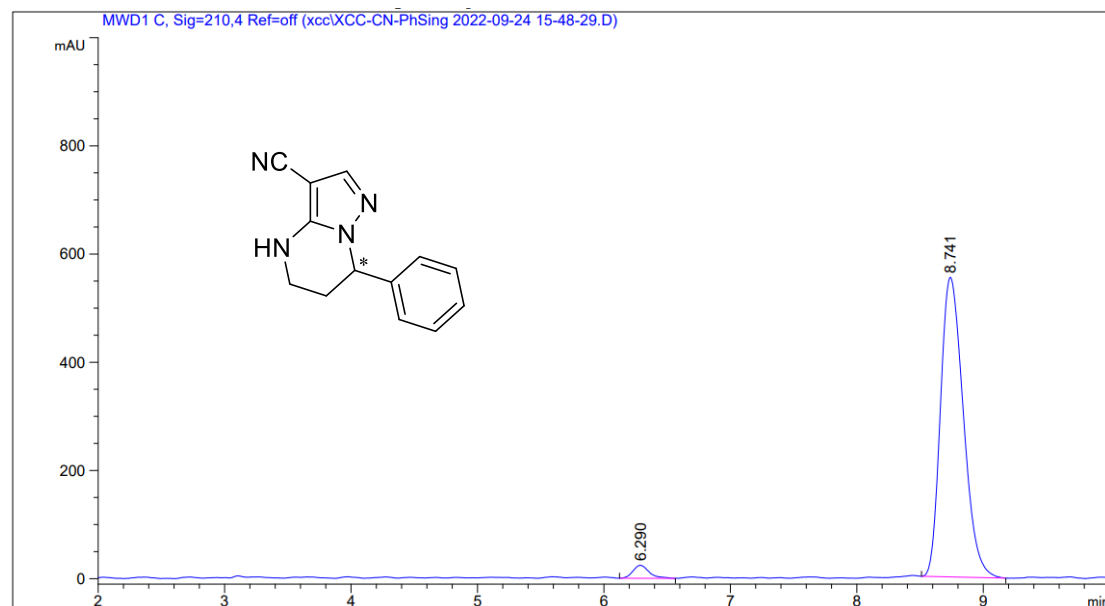
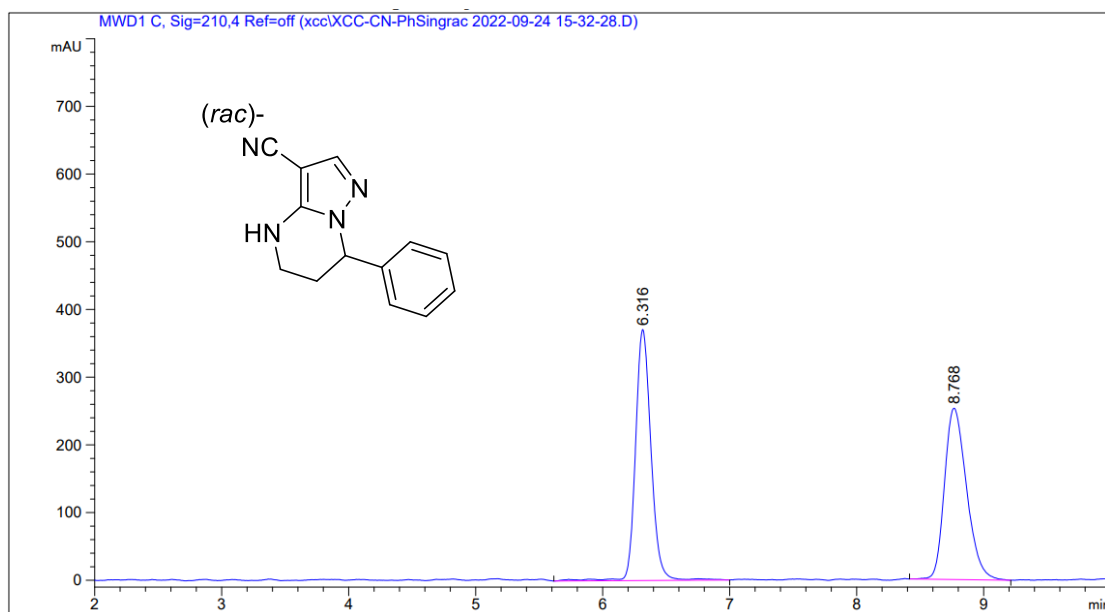
2-(*tert*-butyl)-7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine (**4q**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.972	BB	0.3180	1.23123e4	608.76038	97.3918
2	8.895	BB	0.3363	329.73004	15.06691	2.6082

Totals : 1.26421e4 623.82729

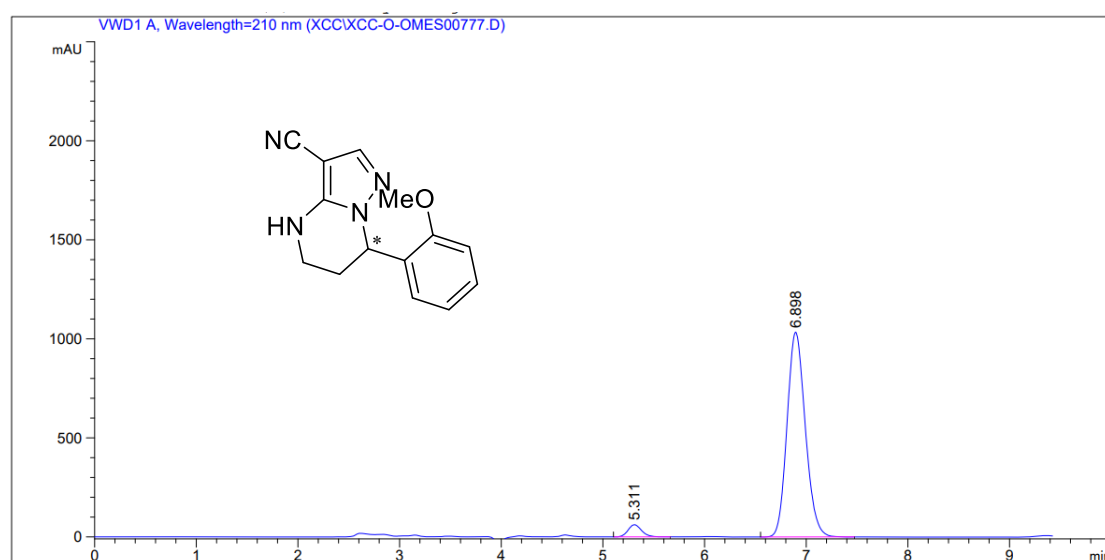
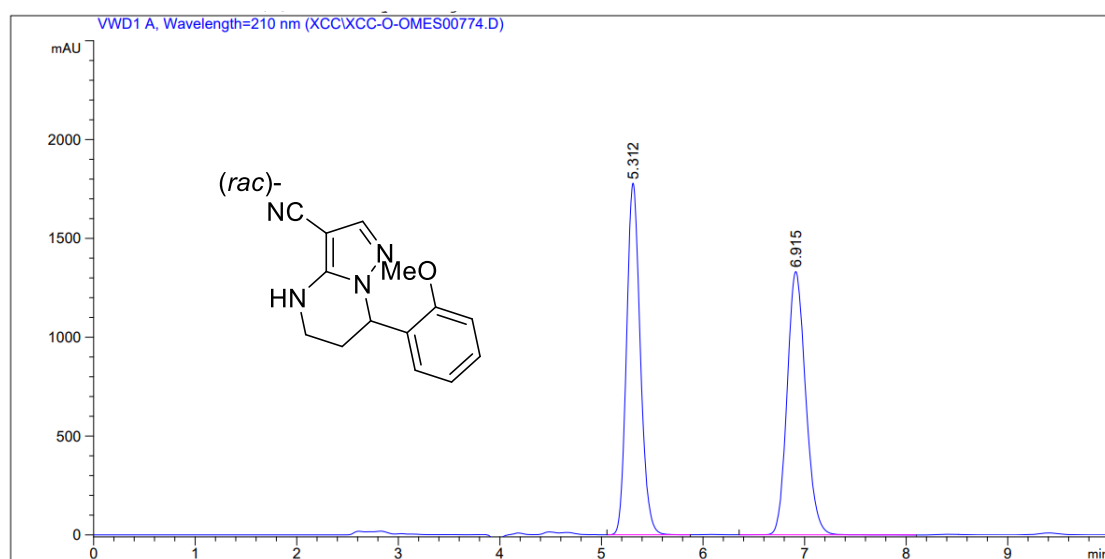
7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**6a**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.290	BB	0.1110	213.65065	23.97683	2.9838
2	8.741	BB	0.1934	6946.65283	553.67578	97.0162

Totals : 7160.30348 577.65261

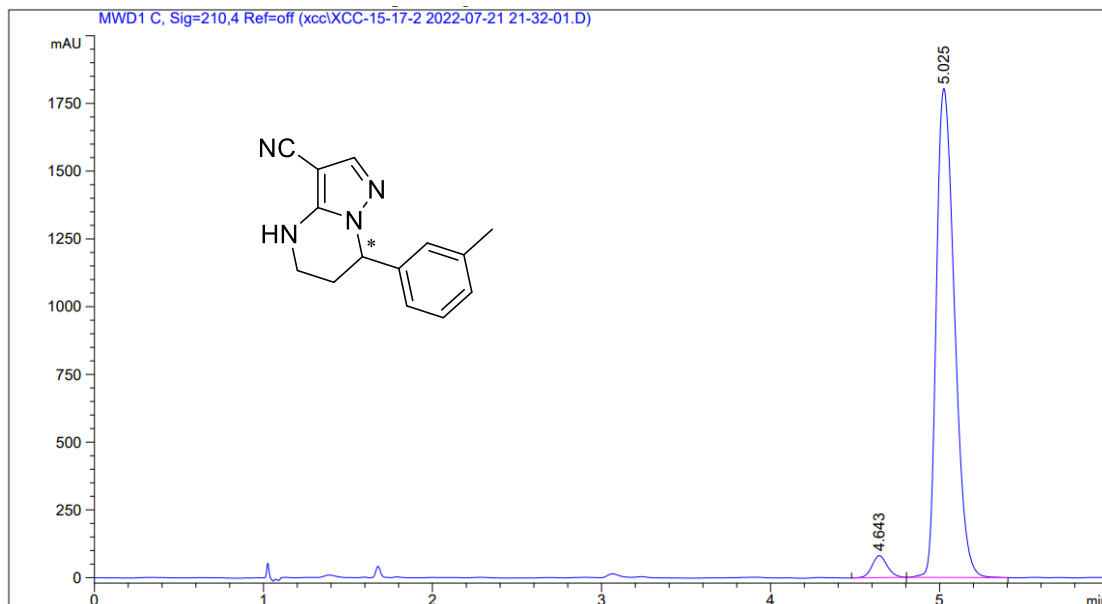
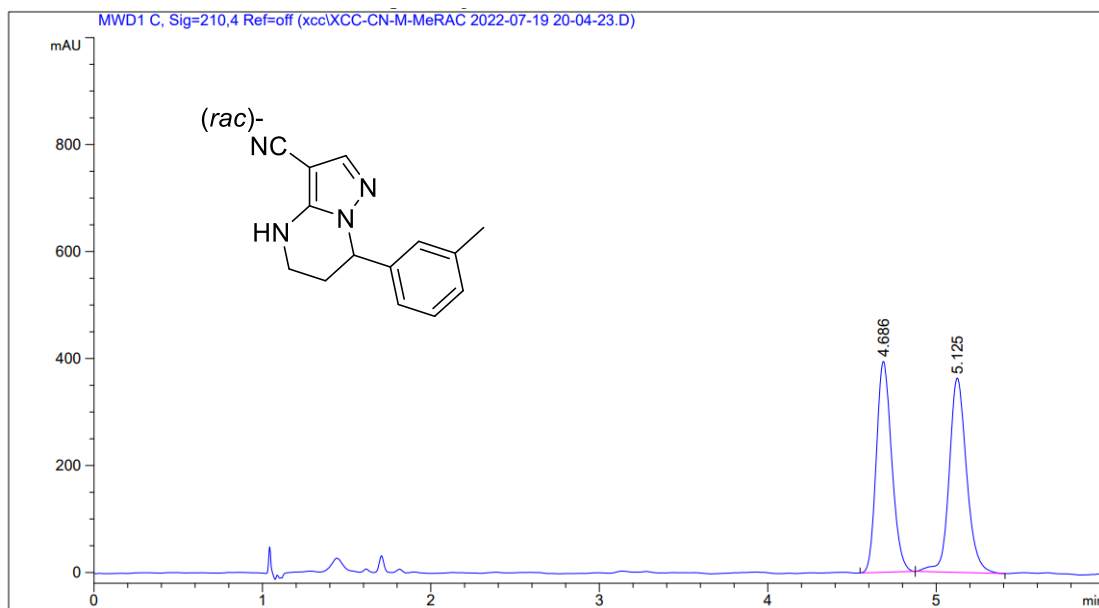
7-(2-methoxyphenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**6b**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.311	BB	0.1414	567.88715	61.67021	4.2105
2	6.898	BB	0.1938	1.29195e4	1033.45605	95.7895

Totals : 1.34874e4 1095.12626

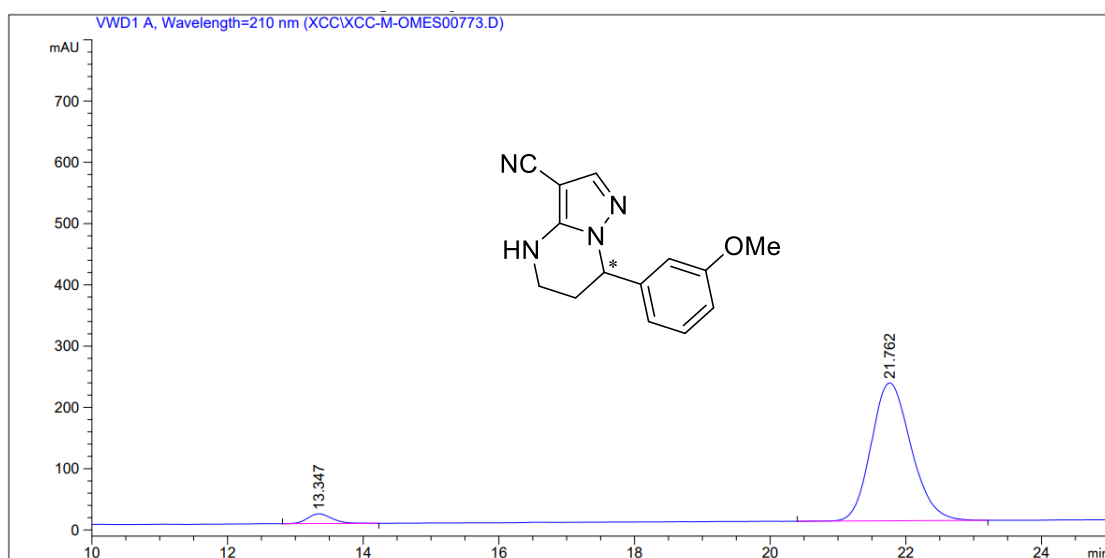
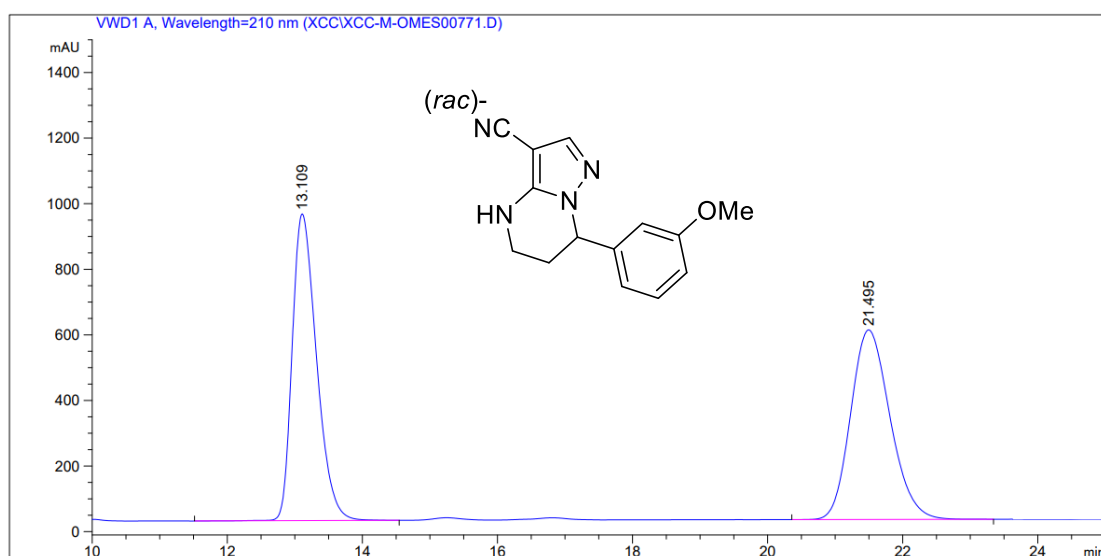
7-(*m*-tolyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**6c**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.643	BB	0.0951	509.20541	81.24929	3.6508
2	5.025	BB	0.1189	1.34385e4	1804.07251	96.3492

Totals : 1.39477e4 1885.32180

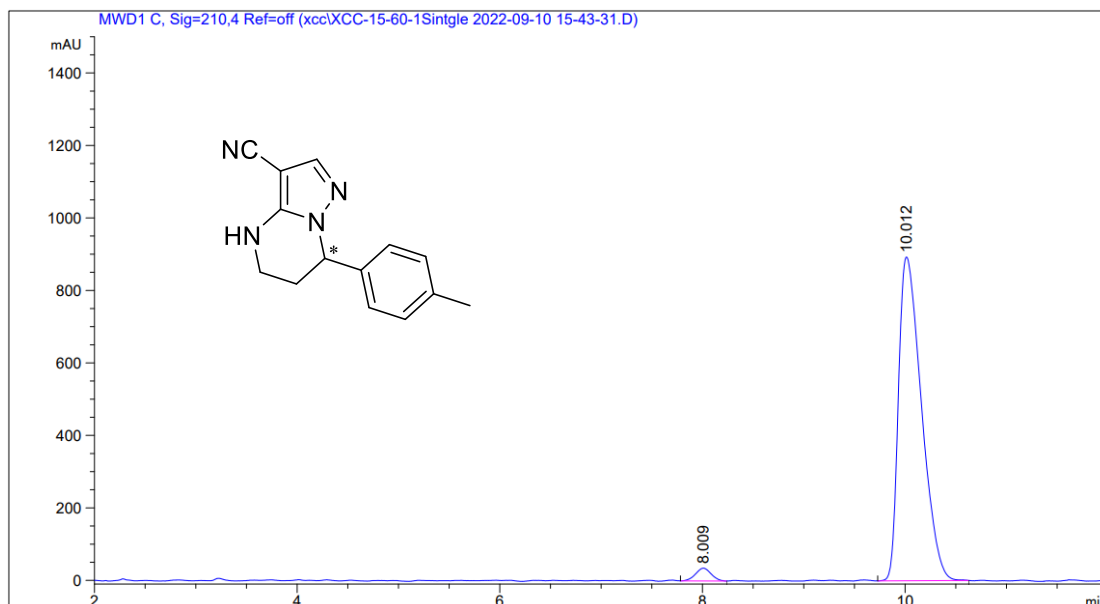
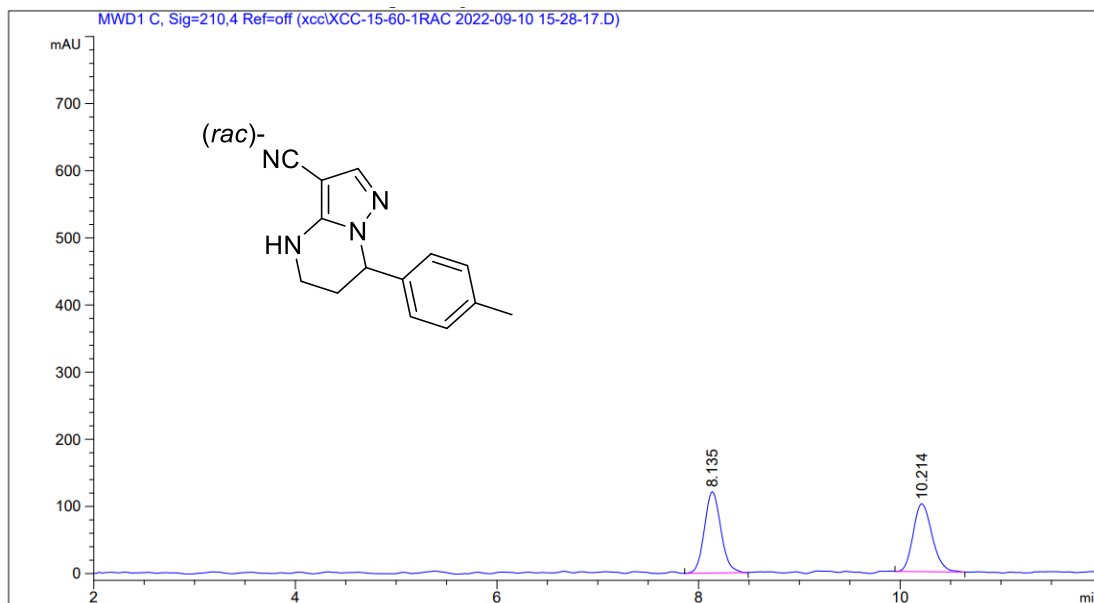
7-(3-methoxyphenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**6d**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.347	BB	0.3828	396.57285	15.90961	4.1336
2	21.762	BB	0.6328	9197.22949	225.05836	95.8664

Totals : 9593.80234 240.96798

7-(*p*-tolyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**6e**)

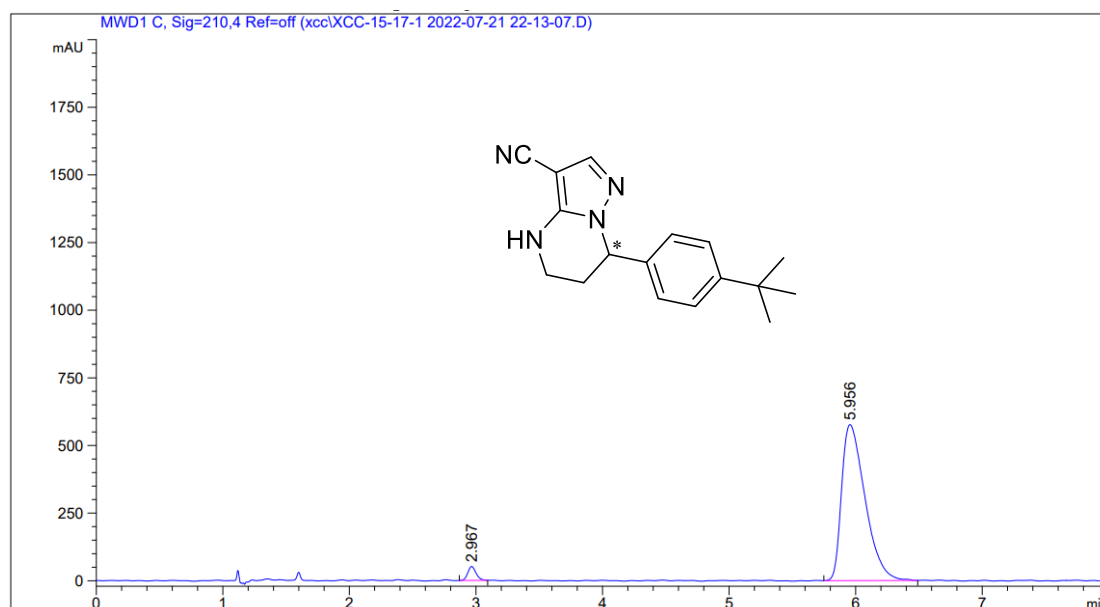
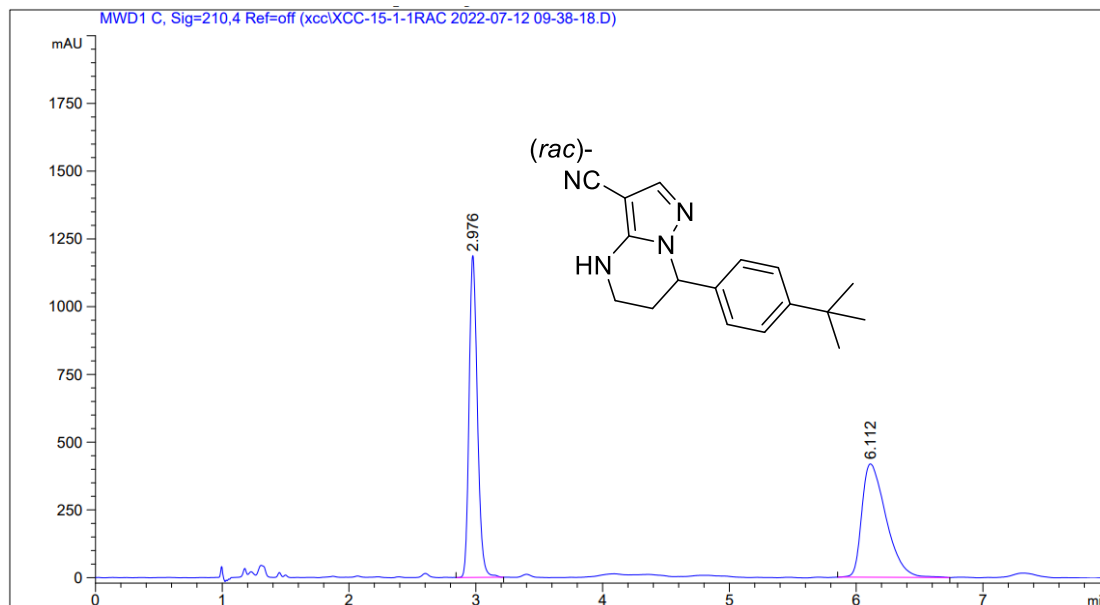


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.009	VB R	0.1358	377.72217	35.46671	2.6266
2	10.012	BV R	0.2209	1.40030e4	892.98193	97.3734

Totals : 1.43807e4 928.44865

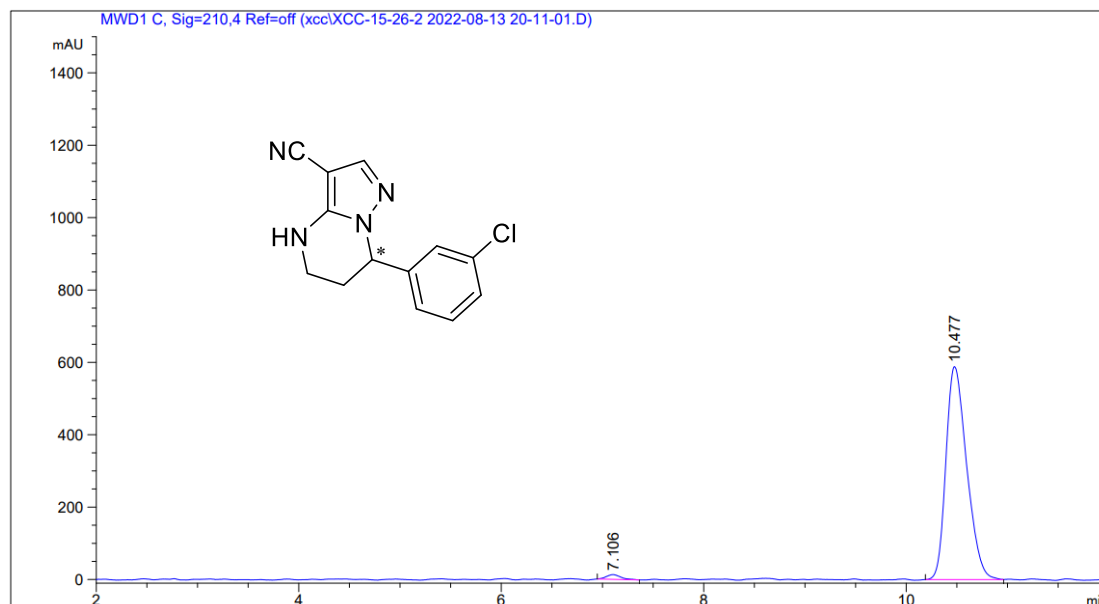
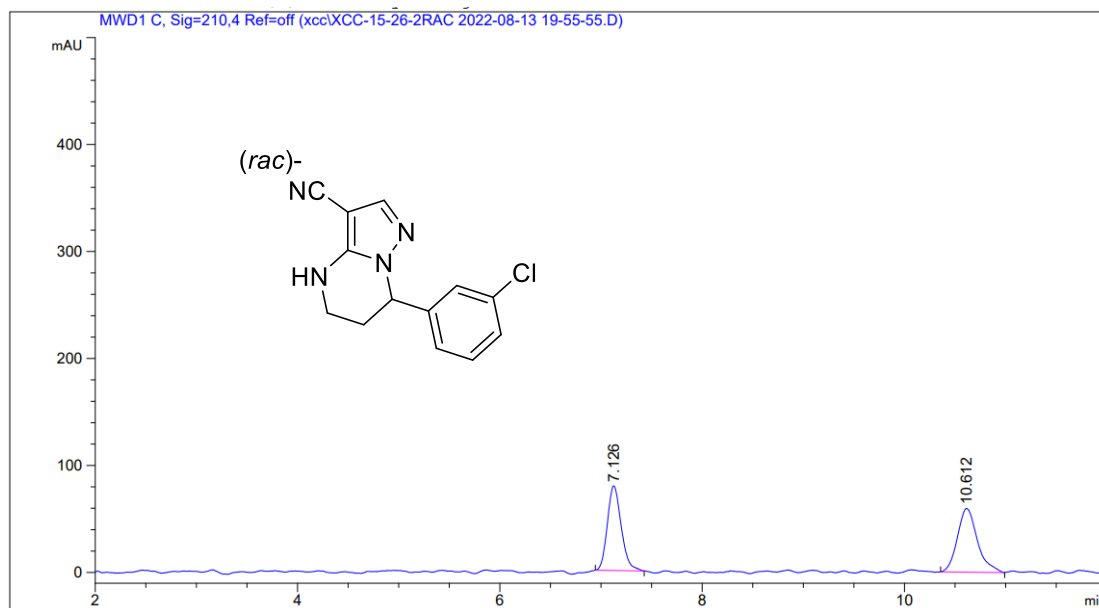
7-(4-(*tert*-butyl)phenyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile

(6f)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.967	BB	0.0701	232.44370	51.53968	3.0361
2	5.956	BB	0.1917	7423.67529	576.49438	96.9639
Totals :				7656.11899	628.03406	

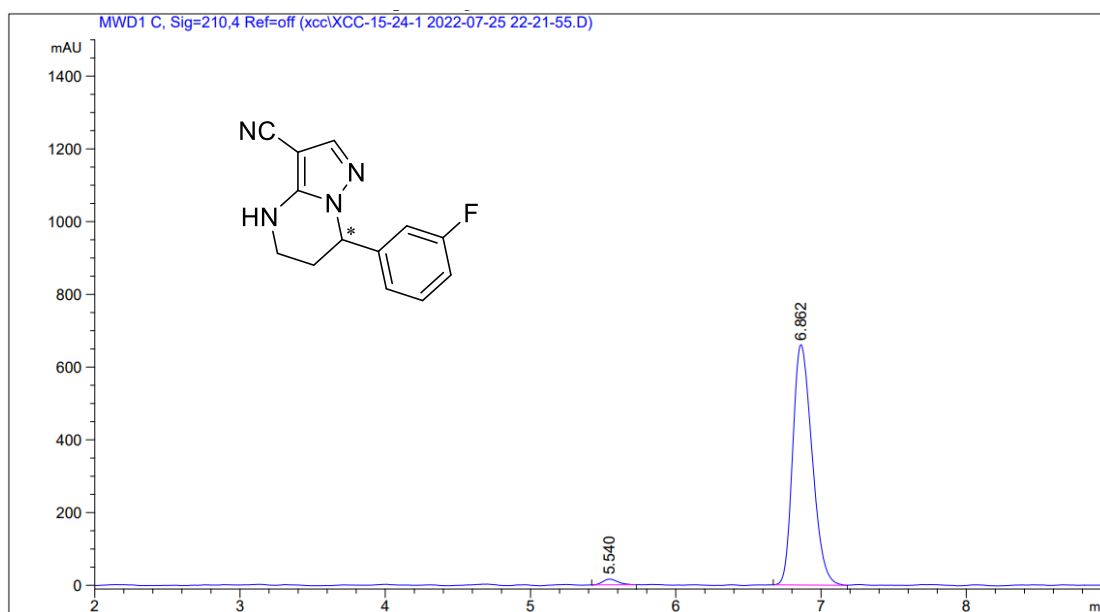
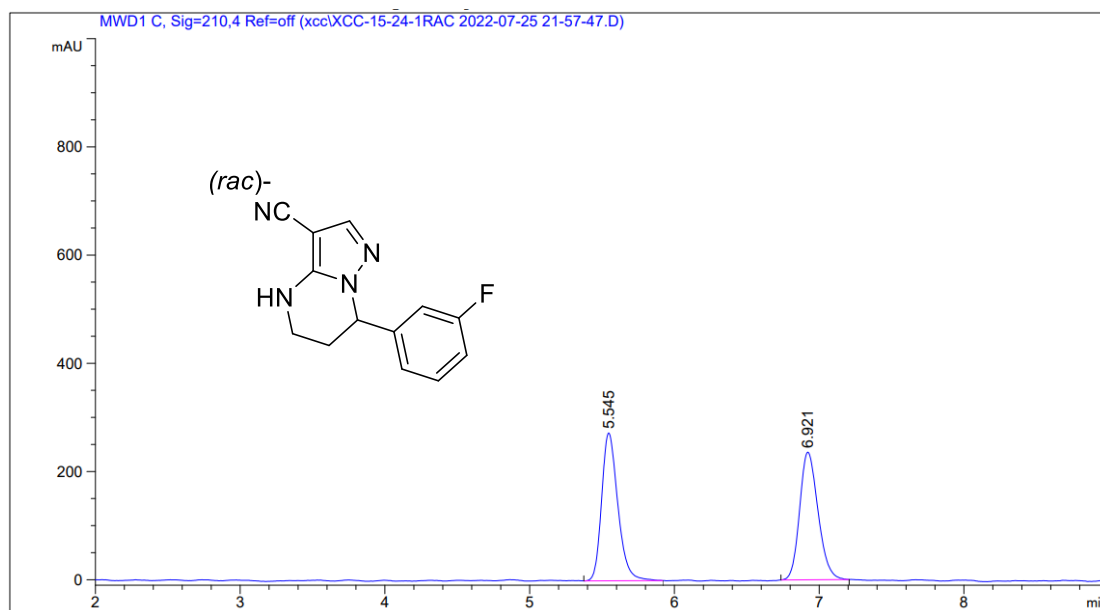
7-(3-chlorophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**6g**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.106	BB	0.1211	129.20503	13.09125	1.5178
2	10.477	BB	0.1977	8383.29883	588.40875	98.4822

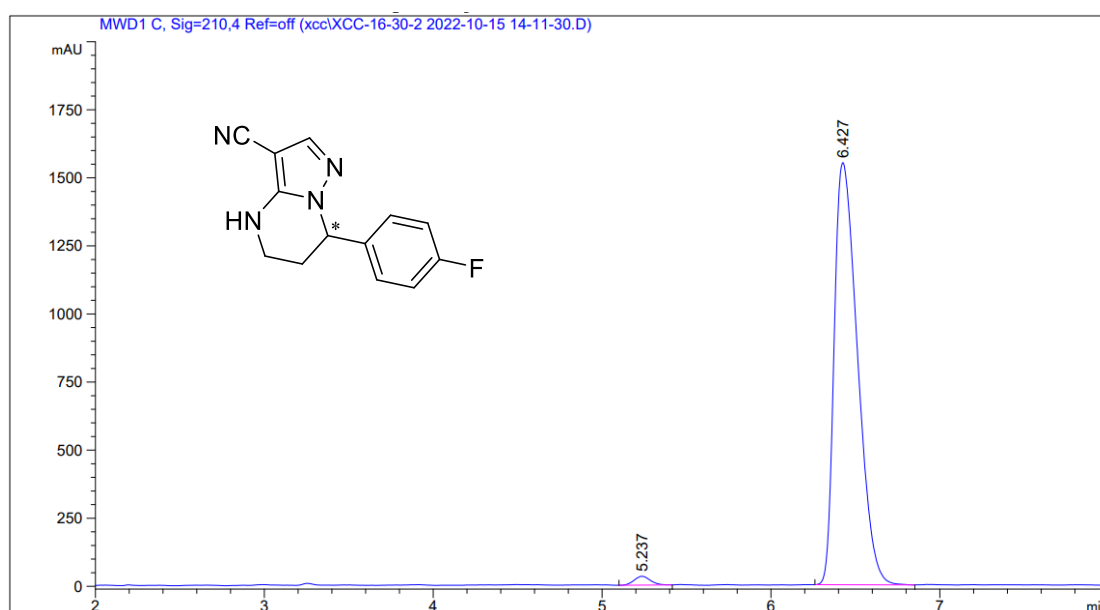
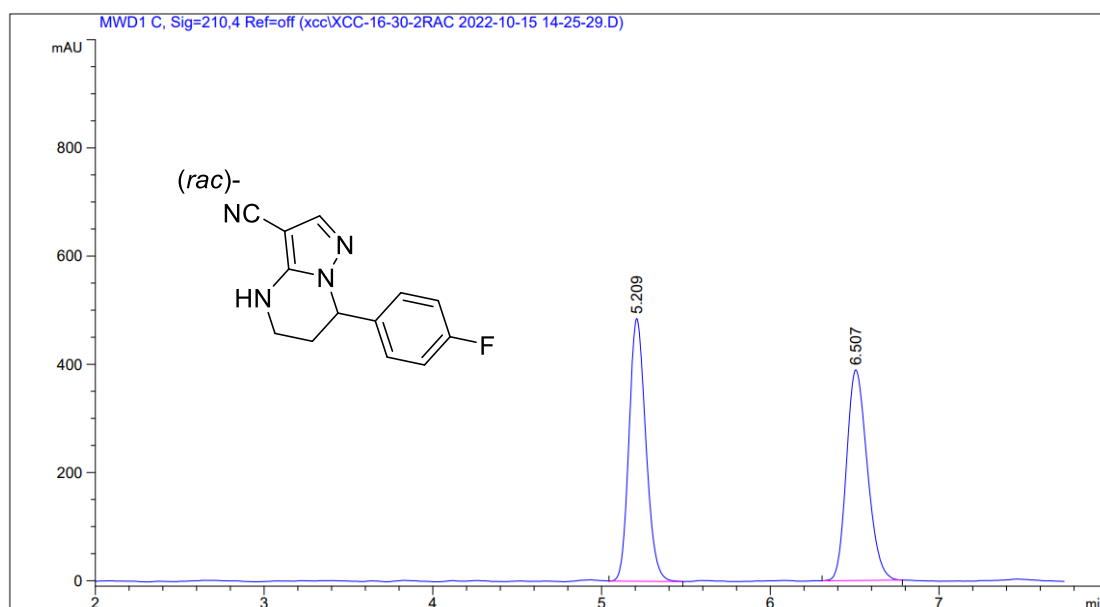
Totals : 8512.50386 601.50001

7-(3-fluorophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**6h**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.540	BB	0.0963	114.30991	15.72785	1.8342
2	6.862	BB	0.1446	6117.87354	660.44977	98.1658
Totals :				6232.18344	676.17761	

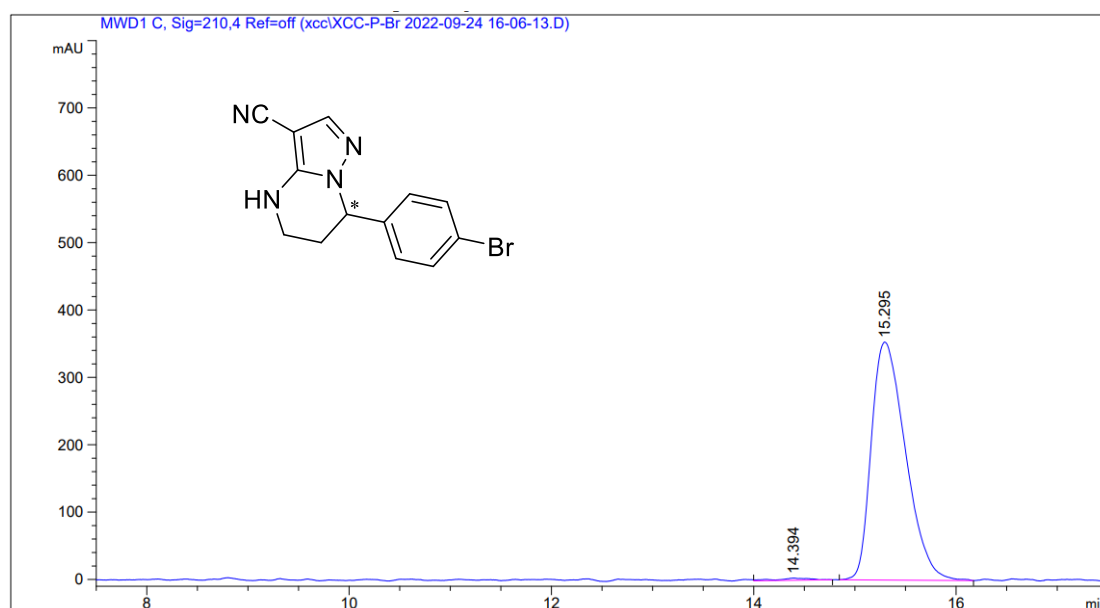
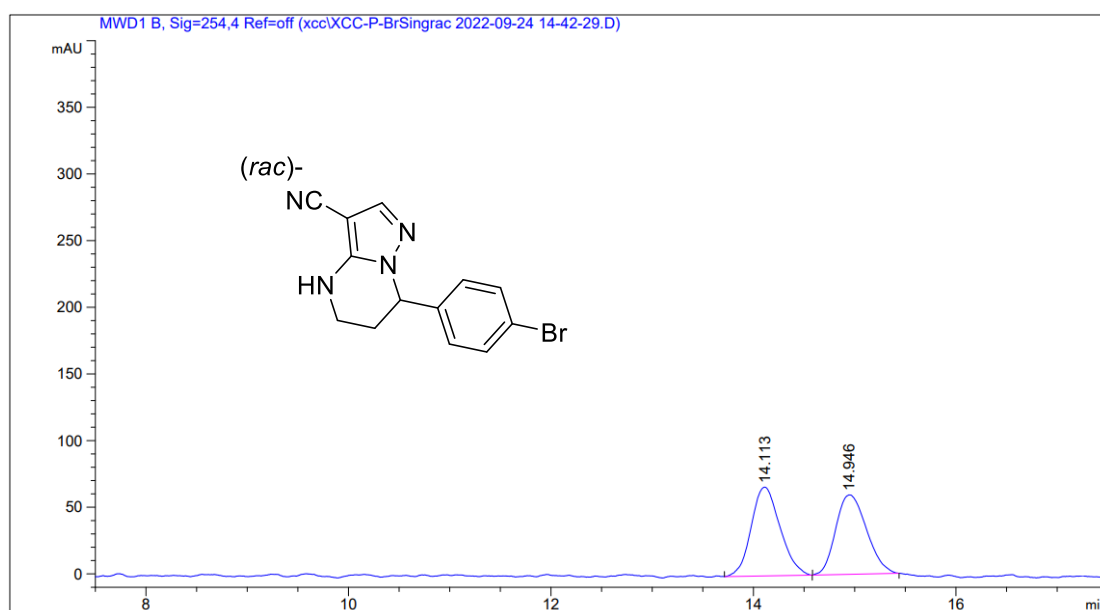
7-(4-fluorophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**6i**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.237	BB	0.0997	214.50722	32.40227	1.4319
2	6.427	BB	0.1332	1.47662e4	1549.90491	98.5681

Totals : 1.49807e4 1582.30717

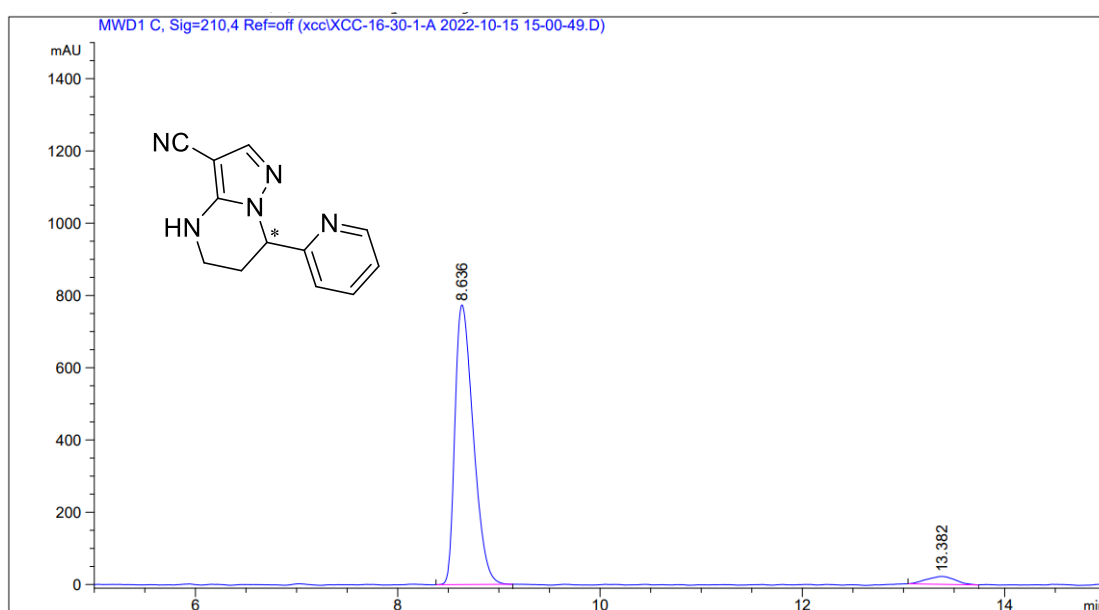
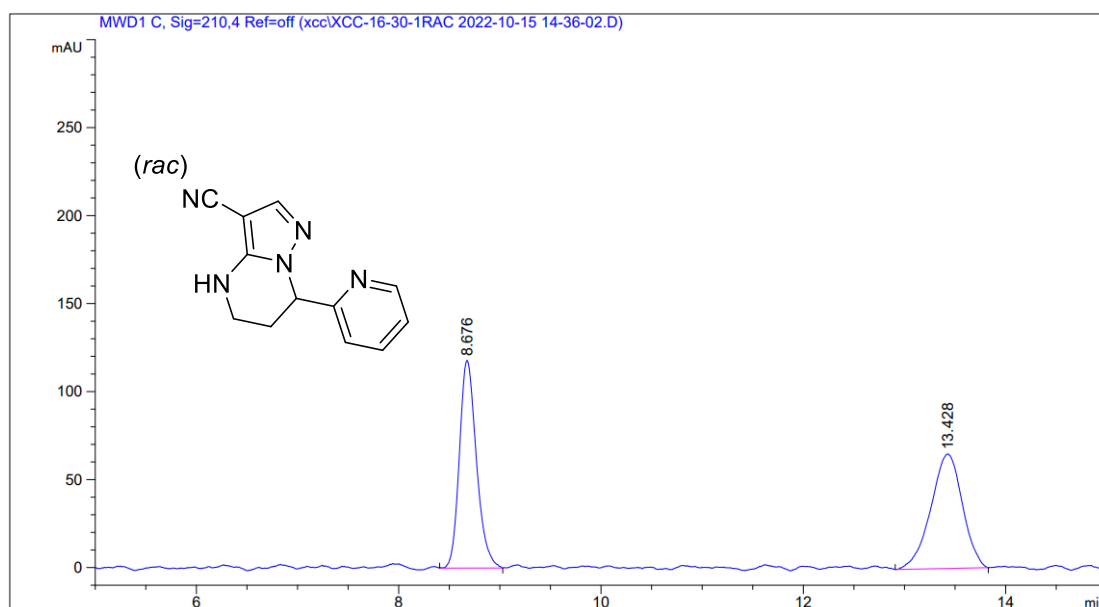
7-(4-bromophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**6j**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.394	VB	0.2733	73.67776	3.28997	0.8806
2	15.295	BB	0.3498	8293.36621	353.32397	99.1194

Totals : 8367.04398 356.61395

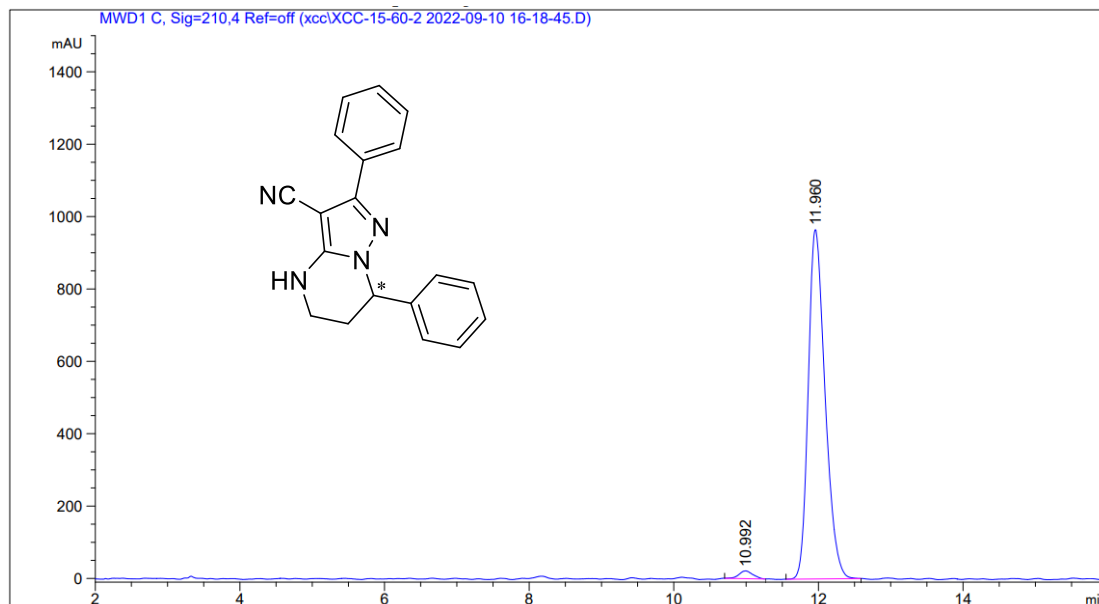
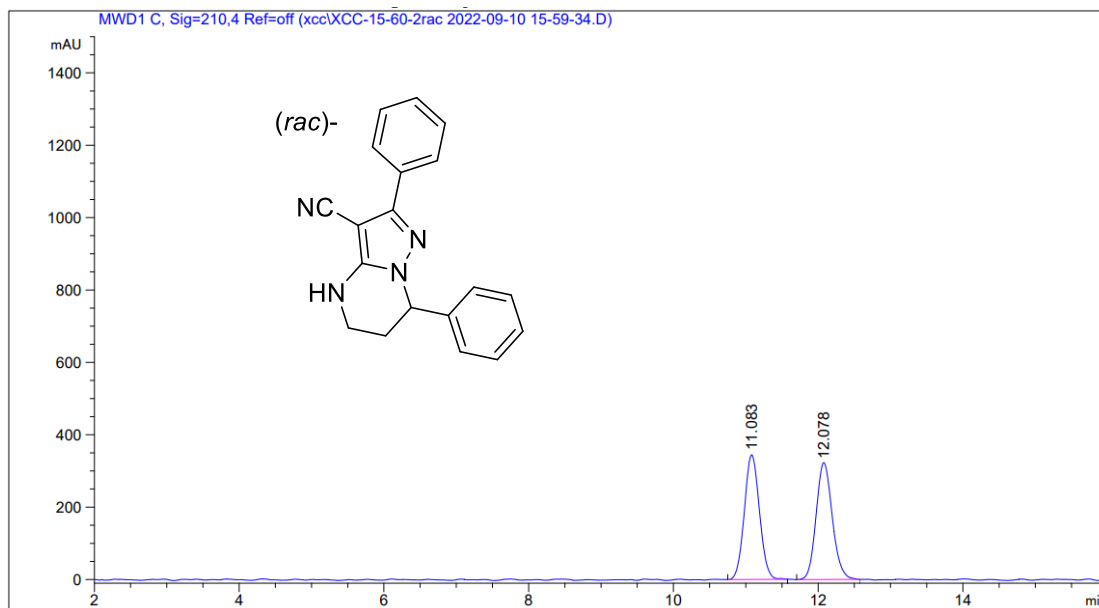
7-(pyridin-2-yl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**6k**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.636	BB	0.1837	9765.12598	773.96906	95.7790
2	13.382	BB	0.2307	430.34714	22.04581	4.2210

Totals : 1.01955e4 796.01487

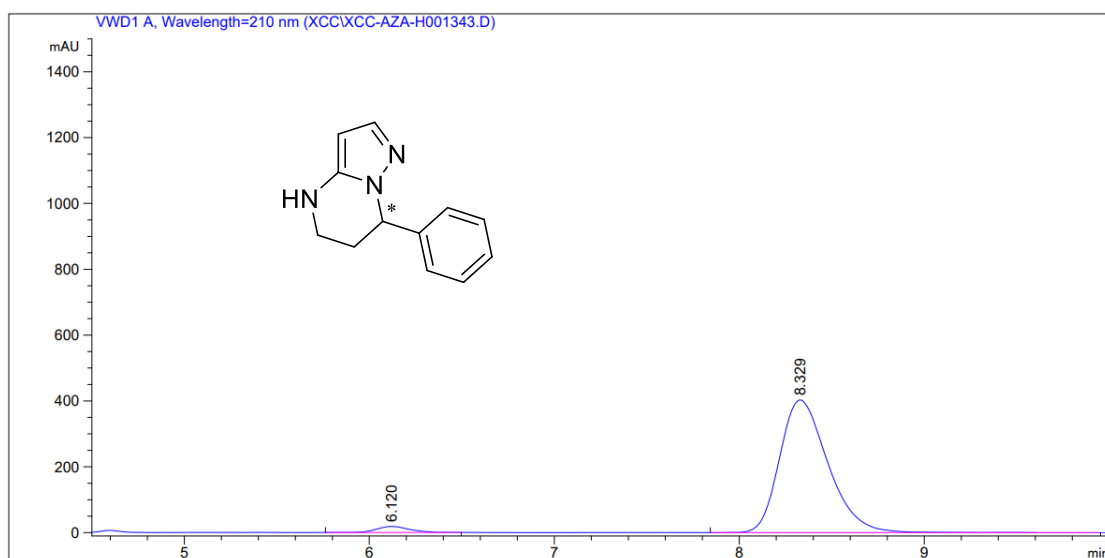
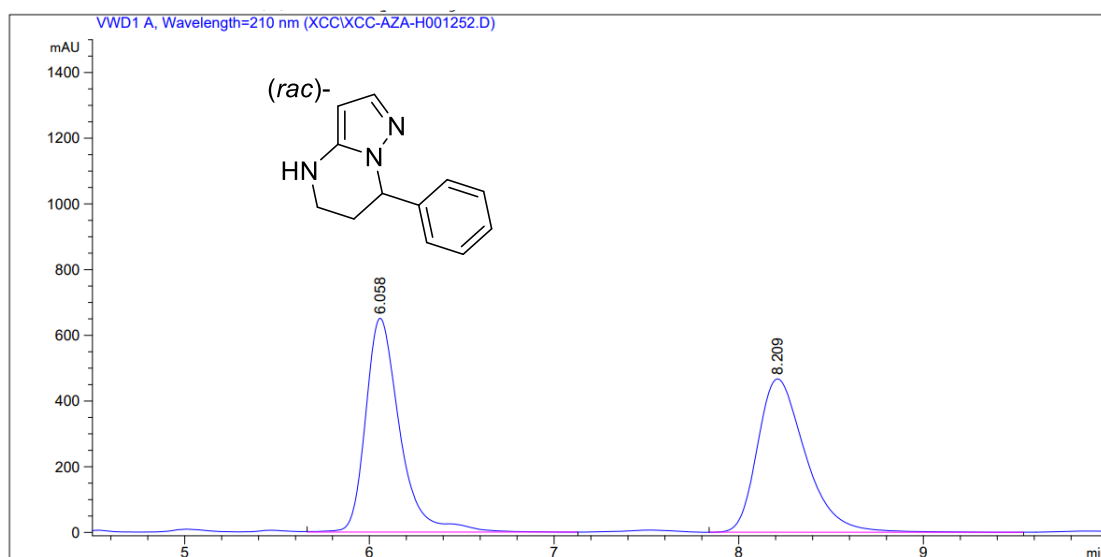
2,7-diphenyl-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine-3-carbonitrile (**6l**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.992	VB R	0.1617	283.91626	21.40568	1.7897
2	11.960	VV R	0.2199	1.55799e4	965.02570	98.2103

Totals : 1.58639e4 986.43137

7-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-a]pyrimidine (**6m**)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.120	BB	0.1873	225.23874	18.46704	2.9917
2	8.329	BB	0.2794	7303.46729	402.98465	97.0083

Totals : 7528.70602 421.45169

9. X-ray crystallographic analysis of compound 4c.

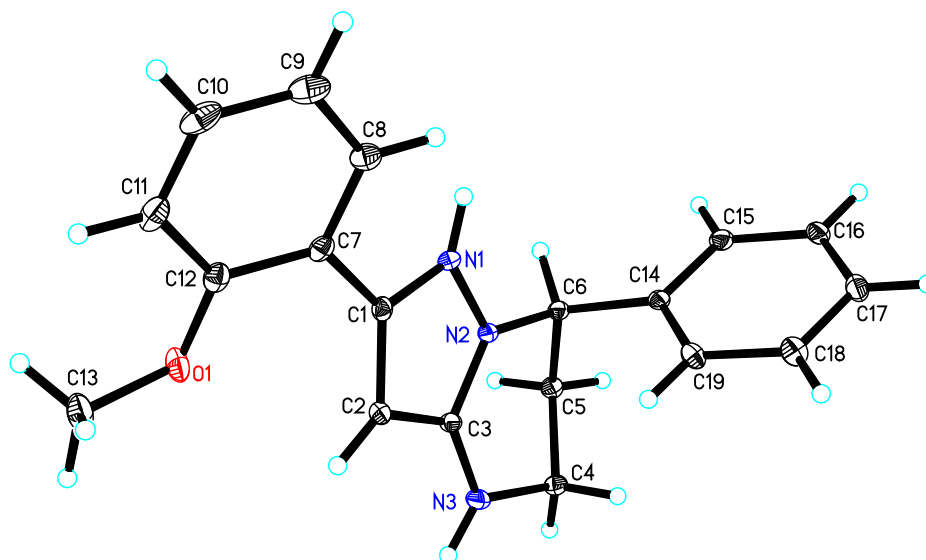


Table S1. Crystal Data and Experimental Parameters for Compound 4c

Compound	4c
Formula	C ₁₉ H ₂₀ N ₃ O
Fw	306.38
crystal system	Orthorhombic
space group	P2(1)2(1)2(1)
<i>a</i> (Å)	6.3426(10)
<i>b</i> (Å)	12.1336(2)
<i>c</i> (Å)	20.3228(2)
α (deg)	90
β (deg)	90
γ (deg)	90
<i>V</i> (Å ³)	1564.01(4)
<i>Z</i>	4
<i>D</i> _{calc} (g/cm ³)	1.301
μ (Mo/K α) _{calc} (cm ⁻¹)	0.651
size (mm)	0.15 x 0.15 x 0.15
<i>F</i> (000)	652

Theta range for data collection (deg)	4.244 to 75.988
no. of reflns, collected	8762
no of obsd reflns	3124
no of variables	209
abscorr (T_{\max} , T_{\min})	1.00, 0.58
R	0.034
R_w	0.089
R_{all}	0.035
Absolute structure parameter	-0.06(11)
Gof	1.08
CCDC	2243486

10. DFT calculations.

All calculations were carried out using Gaussian 09 program package.¹⁷ The B3LYP¹⁸ functional of density functional theory (DFT) was employed combined with mixed basis set where effective core potential SDD and its corresponding basis set¹⁹ was used to treat Rh atom, and all-electron basis set 6-31G*²⁰ used for other non-metal atoms including H, C, N, O, P, and Cl. In order to more accurately simulate the experimental conditions, all stationary points were fully optimized in THF solvent using the polarizable continuum model (PCM).²¹ Vibrational frequency analysis was followed to confirm each stationary point a minimum (no imaginary frequency) or a transition state (only imaginary frequency) and to abstract zero-point energy corrections and corresponding thermochemistry values. The vector of the imaginary mode of each transition state indicated that it connected the two expected adjacent minima on the reaction profile as evidenced by the geometry-optimized structures on either side of the transition state. Solutional entropy was corrected with Fang's THERMO program²² at the temperature of 363.15 K.

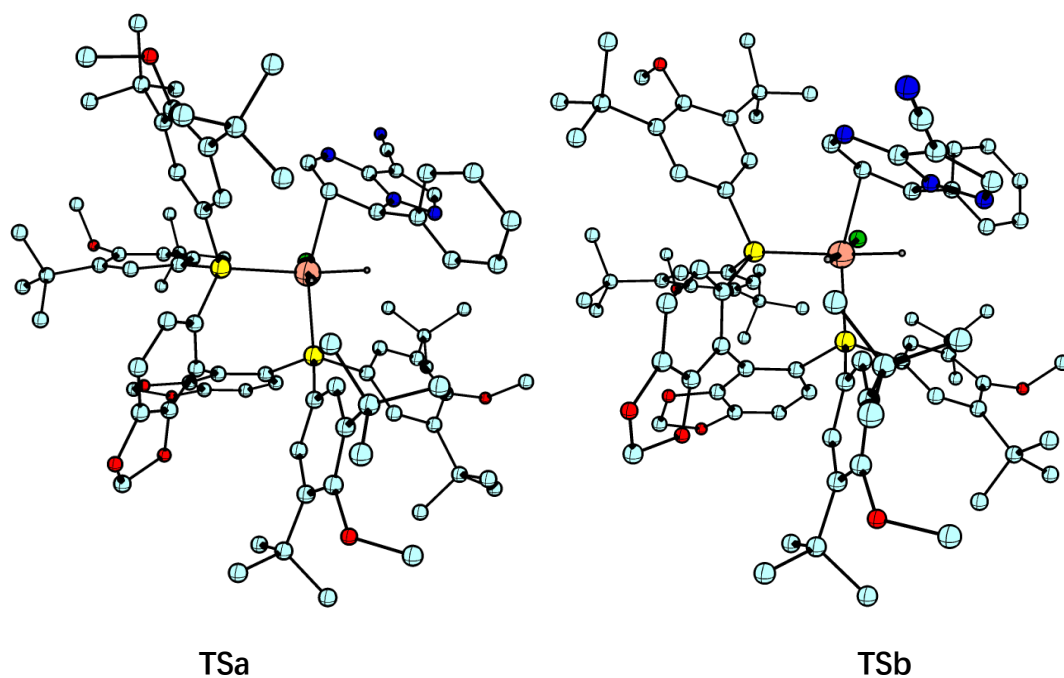


Figure S1. Optimized schematic structures of TSa and TSb

Table S2 The electronic energies (ZPE included), Gibbs free energies, enthalpies (in au), and entropies (in $\text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), and corresponding relative values (in kcal/mol in the parathesis) for Cpdb + 1a, obtained at the B3LYP-PCM(solvent=furan)/SDDU6-31G* level.

	E	G^a	H	S^a
Cpdb	-4964.84660	-4965.02721	-4964.74582	562.1
1a	-718.98124	-719.01985	-718.96806	99.4
THF	-229.94864	-229.96807	-229.94398	44.7
Cpdb+1a-THF	-5453.87920 (0.0)	-5454.07899	-5453.76990	616.8
TSa	-5453.85736 (13.70)	-5454.04982 (18.30)	-5453.74859 (13.37)	603.1
TSb	-5453.84947 (18.66)	-5454.04618 (20.59)	-5453.74003 (18.74)	611.7

^aThe values were corrected at 363.15 K.

Table S3 The optimized Cartesian Coordinates (in Å) and structures (the hydrogen atoms except for the H atom directly involved in the reaction omitted for clarity) of stationary points for Cpdb + 1a, obtained with B3LYP-PCM(solvent=furan)/SDDU6-31G* method.

Species	Cartesian Coordinates			structures	
Cpdb	6	-0.685383	-2.330216	1.626601	
	6	-0.122860	-1.091541	1.351442	
	6	0.992851	-1.108262	0.456029	
	6	1.410979	-2.313751	-0.119330	
	6	0.788326	-3.547038	0.148882	
	6	-0.255975	-3.522198	1.045267	
	1	2.268194	-2.316481	-0.780644	
	1	1.132885	-4.468778	-0.306936	
	6	-0.638255	0.089879	2.116783	
	6	-1.355022	1.223327	1.603556	
	6	-0.489091	0.060035	3.496941	
	6	-1.846503	2.198919	2.481038	
	6	-0.973126	1.049983	4.351858	
	6	-1.670335	2.136498	3.873374	
	1	-2.385917	3.047557	2.080466	
	1	-2.062923	2.903665	4.531106	
	8	-1.732590	-2.599703	2.477921	
	8	-1.026412	-4.563781	1.504104	
	8	-0.669448	0.739378	5.648409	
	8	0.119202	-0.919166	4.241894	
	6	-1.725616	-4.024354	2.633297	
	6	0.163157	-0.430268	5.588129	
	1	1.192864	-0.156343	5.845169	
	1	-0.230992	-1.191056	6.265450	
	1	-2.750039	-4.394787	2.639646	
	1	-1.190327	-4.286768	3.555666	
	15	1.906211	0.482046	0.164518	
	15	-1.545354	1.538876	-0.207779	
	6	3.353883	0.037568	-0.902572	
	6	4.652645	0.375174	-0.522808	
	6	3.162175	-0.496616	-2.187448	
	6	5.773812	0.121665	-1.333172	
	1	4.805038	0.862547	0.431203	
	6	4.233547	-0.848943	-3.014470	
	1	2.149603	-0.653133	-2.534987	
	6	5.545210	-0.616260	-2.514930	
	6	2.699846	0.703633	1.826529	
	6	2.623069	1.913936	2.523401	
	6	3.345336	-0.380140	2.427140	
	6	3.260257	2.087270	3.762339	
1	2.062508	2.726357	2.078230		
6	3.988663	-0.287856	3.669322		

1	3.341263	-1.332687	1.911019
6	4.027351	1.000197	4.261188
6	-2.808521	2.893058	-0.367302
6	-4.149530	2.592781	-0.607896
6	-2.436842	4.241875	-0.239643
6	-5.124577	3.584142	-0.815371
1	-4.455972	1.557347	-0.651441
6	-3.355402	5.278966	-0.440081
1	-1.406592	4.472920	0.001373
6	-4.669377	4.919637	-0.848468
6	-2.450104	0.080802	-0.885135
6	-2.324805	-0.270250	-2.226259
6	-3.378581	-0.613924	-0.093931
6	-3.124858	-1.255530	-2.830399
1	-1.575779	0.236589	-2.820338
6	-4.248683	-1.566131	-0.637878
1	-3.435238	-0.385068	0.961914
6	-4.157869	-1.806353	-2.037918
1	-0.462869	2.894929	-2.134215
6	-2.760174	-1.654679	-4.289349
6	-3.139973	-0.511517	-5.261189
1	-4.220001	-0.328574	-5.273532
1	-2.832125	-0.766539	-6.282639
1	-2.647031	0.427554	-4.985785
6	-3.380446	-2.979191	-4.793756
1	-4.453278	-2.919825	-4.975860
1	-3.199004	-3.802110	-4.095805
1	-2.904847	-3.236735	-5.747531
6	-1.223579	-1.870006	-4.365987
1	-0.903422	-2.651088	-3.667027
1	-0.651536	-0.965588	-4.145478
1	-0.950074	-2.187417	-5.378590
6	-5.195779	-2.381007	0.283870
6	-5.072055	-1.939586	1.759121
1	-5.395862	-0.901697	1.903401
1	-4.052959	-2.039585	2.141563
1	-5.723271	-2.571896	2.372934
6	-4.793503	-3.874864	0.196750
1	-4.924283	-4.259968	-0.817384
1	-5.416638	-4.472410	0.874061
1	-3.745129	-4.016180	0.482569
6	-6.691306	-2.238890	-0.089924
1	-7.303705	-2.703256	0.692424
1	-6.930957	-2.733937	-1.030305

1	-6.988233	-1.185834	-0.158149
6	4.546728	-1.607167	4.279632
6	3.059222	3.397529	4.570363
6	4.366758	4.214543	4.704453
1	4.828782	4.386599	3.725065
1	5.094082	3.724269	5.352558
1	4.142937	5.194875	5.142828
6	2.018633	4.318802	3.897937
1	1.049885	3.822668	3.776174
1	2.339029	4.671363	2.912888
1	1.864764	5.199092	4.532681
6	2.515627	3.061469	5.982331
1	1.547776	2.550053	5.916107
1	2.362879	3.988188	6.550049
1	3.207639	2.428371	6.540815
6	5.836440	-2.036368	3.540227
1	6.196562	-2.996223	3.931317
1	6.641739	-1.304169	3.661783
1	5.655735	-2.157150	2.466303
6	4.823317	-1.553475	5.800218
1	5.675227	-0.928915	6.066796
1	5.040312	-2.570106	6.149192
1	3.952007	-1.188404	6.353863
6	3.490834	-2.732154	4.089089
1	3.319806	-2.985909	3.039342
1	2.526763	-2.448253	4.524178
1	3.837648	-3.644334	4.588034
6	3.978904	-1.391807	-4.445418
6	4.487108	-2.842636	-4.623979
1	4.087914	-3.502590	-3.844329
1	5.575467	-2.899428	-4.605755
1	4.152327	-3.232620	-5.593208
6	2.474187	-1.401264	-4.788558
1	2.027786	-0.404218	-4.710521
1	1.905321	-2.085285	-4.148805
1	2.347759	-1.738922	-5.823085
6	4.676257	-0.469337	-5.476494
1	4.487465	-0.837631	-6.492818
1	5.755914	-0.437698	-5.317665
1	4.284201	0.551946	-5.408273
6	7.127964	0.726682	-0.864078
6	6.890755	2.223012	-0.515162
1	6.189347	2.363652	0.311942
1	6.502097	2.767741	-1.382925

1	7.839593	2.685447	-0.219300
6	8.257877	0.724892	-1.919578
1	7.929470	1.164853	-2.865723
1	8.657103	-0.268095	-2.127949
1	9.086029	1.332294	-1.535110
6	7.627821	0.001146	0.407574
1	7.833706	-1.057838	0.215303
1	6.891978	0.055269	1.217133
1	8.556468	0.462651	0.765678
8	6.611873	-1.108855	-3.249677
8	-5.100478	-2.643804	-2.606577
8	-5.514813	5.934940	-1.262810
8	4.801799	1.226967	5.388138
6	6.194979	1.413801	5.118451
1	6.671489	0.487152	4.782781
1	6.650785	1.729751	6.059883
1	6.352099	2.187451	4.359089
6	-5.635493	6.040900	-2.686220
1	-6.262972	6.914674	-2.876865
1	-6.109603	5.153880	-3.119327
1	-4.656572	6.182839	-3.156570
6	-2.960692	6.751369	-0.151244
6	-1.558039	6.843028	0.484671
1	-0.766372	6.501493	-0.188615
1	-1.486738	6.256485	1.407077
1	-1.352881	7.889271	0.739395
6	-3.959152	7.356464	0.868192
1	-4.980231	7.358401	0.482178
1	-3.674171	8.391266	1.095647
1	-3.942987	6.791491	1.808105
6	-2.935378	7.624180	-1.428834
1	-2.504396	8.604714	-1.191866
1	-3.934324	7.794314	-1.832272
1	-2.313521	7.167257	-2.207642
6	-6.597739	3.103092	-0.946830
6	-6.899458	2.133932	0.229229
1	-6.767359	2.637585	1.193773
1	-6.264375	1.243896	0.224610
1	-7.939412	1.793039	0.165536
6	-7.672692	4.210273	-0.848413
1	-7.696808	4.871947	-1.714321
1	-7.539079	4.825476	0.046216
1	-8.655370	3.727740	-0.781506
6	-6.787444	2.337875	-2.278366

	1	-7.812318	1.953045	-2.350829	
	1	-6.101952	1.486734	-2.354786	
	1	-6.610755	2.985341	-3.144482	
	6	-6.132774	-1.963635	-3.331141	
	1	-6.820130	-2.736134	-3.683289	
	1	-5.732149	-1.417261	-4.190133	
	1	-6.671543	-1.261696	-2.685988	
	6	7.198563	-2.293497	-2.700510	
	1	7.987540	-2.595365	-3.393392	
	1	6.460358	-3.098717	-2.614592	
	1	7.635278	-2.110300	-1.713539	
	1	0.184937	0.893384	-2.099753	
	45	0.443504	2.082641	-1.127331	
	17	1.095907	4.199084	0.176051	
	6	3.930446	3.901448	-3.491851	
	6	3.131464	3.357472	-4.557863	
	6	2.112124	2.679951	-3.968964	
	8	2.225808	2.765186	-2.602236	
	6	3.341473	3.517674	-2.329808	
	1	4.824088	4.502447	-3.586622	
	1	3.297412	3.464836	-5.620819	
	1	1.266143	2.118942	-4.329765	
	1	3.530520	3.694101	-1.284617	
1a	7	2.935248	4.580871	13.079918	
	7	3.490553	4.644028	11.836380	
	7	4.741609	3.273907	10.295617	
	6	3.239806	3.364292	13.522430	
	6	3.986441	2.607301	12.593487	
	6	4.142815	3.456650	11.481604	
	6	4.675799	4.293835	9.454135	
	1	5.159966	4.160592	8.489674	
	6	4.034990	5.517277	9.746686	
	1	4.049131	6.322638	9.023702	
	6	3.421094	5.713142	10.971592	
	6	2.738623	6.965904	11.348821	
	6	2.010409	7.658083	10.363925	
	1	1.903634	7.230095	9.371977	
	6	1.397466	8.873485	10.661297	
	1	0.827312	9.389447	9.894470	
	6	1.511873	9.419945	11.941874	
	1	1.035366	10.368077	12.174135	
	6	2.237161	8.741204	12.924704	
	1	2.332192	9.163621	13.920736	
	6	2.842474	7.519114	12.637982	

	1	3.398094	6.996738	13.406290	
	6	4.471690	1.287884	12.724298	
	7	4.868477	0.198380	12.841897	
	1	2.910100	3.055856	14.505645	
THF	6	-1.030696	0.000213	-3.672337	
	6	-1.030696	-1.029312	-2.669649	
	6	-1.030696	-0.387897	-1.468672	
	8	-1.030696	0.965795	-1.651076	
	6	-1.030696	1.183832	-2.999470	
	1	-1.030696	-0.129948	-4.745781	
	1	-1.030696	-2.098945	-2.828101	
	1	-1.030696	-0.722431	-0.442289	
	1	-1.030696	2.218693	-3.306785	
TSa	6	-0.755767	-2.198962	1.701679	
	6	-0.219899	-0.960352	1.377674	
	6	0.819136	-0.983051	0.393229	
	6	1.184980	-2.189136	-0.215401	
	6	0.588070	-3.421868	0.107987	
	6	-0.373607	-3.393888	1.092574	
	1	1.988110	-2.196611	-0.941010	
	1	0.892769	-4.344522	-0.373360	
	6	-0.708291	0.225406	2.153171	
	6	-1.463448	1.335436	1.644806	
	6	-0.522007	0.216074	3.529066	
	6	-1.963502	2.305756	2.520419	
	6	-1.008869	1.206346	4.382458	
	6	-1.751136	2.264555	3.908979	
	1	-2.532984	3.135554	2.122083	
	1	-2.148482	3.028407	4.567819	
	8	-1.736171	-2.464548	2.629187	
	8	-1.101641	-4.432866	1.616788	
	8	-0.664643	0.920511	5.675723	
	8	0.125360	-0.739062	4.271705	
	6	-1.713891	-3.887297	2.793980	
	6	0.192313	-0.229695	5.609676	
	1	1.222238	0.069953	5.835180	
	1	-0.165947	-0.990056	6.307269	
	1	-2.733519	-4.260166	2.881368	
	1	-1.107332	-4.143126	3.672810	
	15	1.762722	0.579721	0.066064	
	15	-1.646127	1.618662	-0.171914	
	6	3.200604	0.098737	-1.009712	
	6	4.503825	0.395466	-0.608868	
	6	3.012419	-0.418313	-2.303136	

6	5.630359	0.121563	-1.406019
1	4.657148	0.866240	0.352647
6	4.087456	-0.782660	-3.122205
1	2.000955	-0.545974	-2.668429
6	5.398544	-0.593534	-2.600963
6	2.593454	0.778755	1.716018
6	2.671803	1.994601	2.402399
6	3.158686	-0.360429	2.297310
6	3.375293	2.105974	3.612933
1	2.169624	2.855483	1.981542
6	3.862090	-0.328959	3.508864
1	3.044231	-1.310148	1.790701
6	4.047162	0.949779	4.093060
6	-2.960943	2.920356	-0.380779
6	-4.256834	2.576003	-0.768104
6	-2.675064	4.277197	-0.149844
6	-5.257646	3.533236	-1.013581
1	-4.508580	1.532306	-0.890911
6	-3.622511	5.281420	-0.376892
1	-1.686508	4.543394	0.199925
6	-4.873461	4.888141	-0.926508
6	-2.509586	0.112709	-0.809020
6	-2.348040	-0.304700	-2.127793
6	-3.437784	-0.563162	-0.001127
6	-3.115882	-1.339437	-2.694571
1	-1.596536	0.186585	-2.733033
6	-4.271810	-1.566100	-0.507959
1	-3.522284	-0.278004	1.039102
6	-4.149962	-1.874072	-1.891985
1	-0.421660	3.204949	-2.084745
6	-2.727217	-1.815020	-4.123958
6	-3.183587	-0.776246	-5.176202
1	-4.272666	-0.662523	-5.195468
1	-2.862652	-1.088733	-6.177604
1	-2.748180	0.208992	-4.978082
6	-3.258189	-3.214295	-4.517998
1	-4.332827	-3.243054	-4.694736
1	-3.019658	-3.962878	-3.755974
1	-2.767410	-3.516253	-5.450767
6	-1.181048	-1.930162	-4.202998
1	-0.798468	-2.616620	-3.438913
1	-0.673657	-0.970398	-4.082160
1	-0.895381	-2.321962	-5.185553
6	-5.213549	-2.359548	0.438001

6	-5.107158	-1.857742	1.895059
1	-5.448133	-0.820414	1.996675
1	-4.088546	-1.926057	2.286615
1	-5.751856	-2.475859	2.529830
6	-4.790738	-3.850293	0.415807
1	-4.913628	-4.281270	-0.580458
1	-5.408321	-4.425407	1.117133
1	-3.741730	-3.966849	0.709517
6	-6.707651	-2.255300	0.046687
1	-7.319546	-2.702034	0.839658
1	-6.931051	-2.787203	-0.877440
1	-7.021323	-1.210814	-0.061778
6	4.328437	-1.693534	4.097138
6	3.334594	3.431015	4.420916
6	4.726701	4.094849	4.549320
1	5.201048	4.212029	3.567698
1	5.397080	3.529340	5.197015
1	4.614951	5.095675	4.984251
6	2.405240	4.467988	3.756366
1	1.385768	4.089924	3.632295
1	2.765394	4.783179	2.772057
1	2.357368	5.358470	4.393472
6	2.763004	3.151594	5.834528
1	1.744078	2.750764	5.769772
1	2.715819	4.086448	6.407201
1	3.382698	2.442643	6.387377
6	5.581243	-2.202494	3.344538
1	5.875835	-3.188684	3.724608
1	6.436675	-1.530057	3.464633
1	5.383021	-2.300753	2.271257
6	4.613672	-1.673584	5.617289
1	5.505592	-1.109903	5.887228
1	4.761764	-2.705480	5.957081
1	3.770370	-1.255321	6.177094
6	3.201778	-2.746168	3.900306
1	3.018362	-2.986936	2.849297
1	2.257405	-2.402644	4.334101
1	3.490754	-3.680284	4.395268
6	3.844093	-1.287764	-4.568854
6	4.337833	-2.739989	-4.776998
1	3.923637	-3.412959	-4.016734
1	5.424967	-2.809958	-4.751215
1	4.006654	-3.102643	-5.757747
6	2.345285	-1.272132	-4.932941

1	1.904227	-0.272639	-4.849352
1	1.761315	-1.960711	-4.312897
1	2.230099	-1.592149	-5.974264
6	4.568435	-0.348395	-5.565718
1	4.399734	-0.694860	-6.592844
1	5.644671	-0.323821	-5.384183
1	4.179373	0.674282	-5.489670
6	6.996581	0.671977	-0.903210
6	6.809347	2.166451	-0.518667
1	6.081804	2.318958	0.283021
1	6.488863	2.755902	-1.385666
1	7.764753	2.575993	-0.171428
6	8.140781	0.658646	-1.943324
1	7.838703	1.128025	-2.884181
1	8.514819	-0.340588	-2.167072
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