

Aminations and Arylations by Direct C-O Activations for the Design of 7,8-dihydro-6H-5,8-ethanopyrido[3,2-d]pyrimidines.

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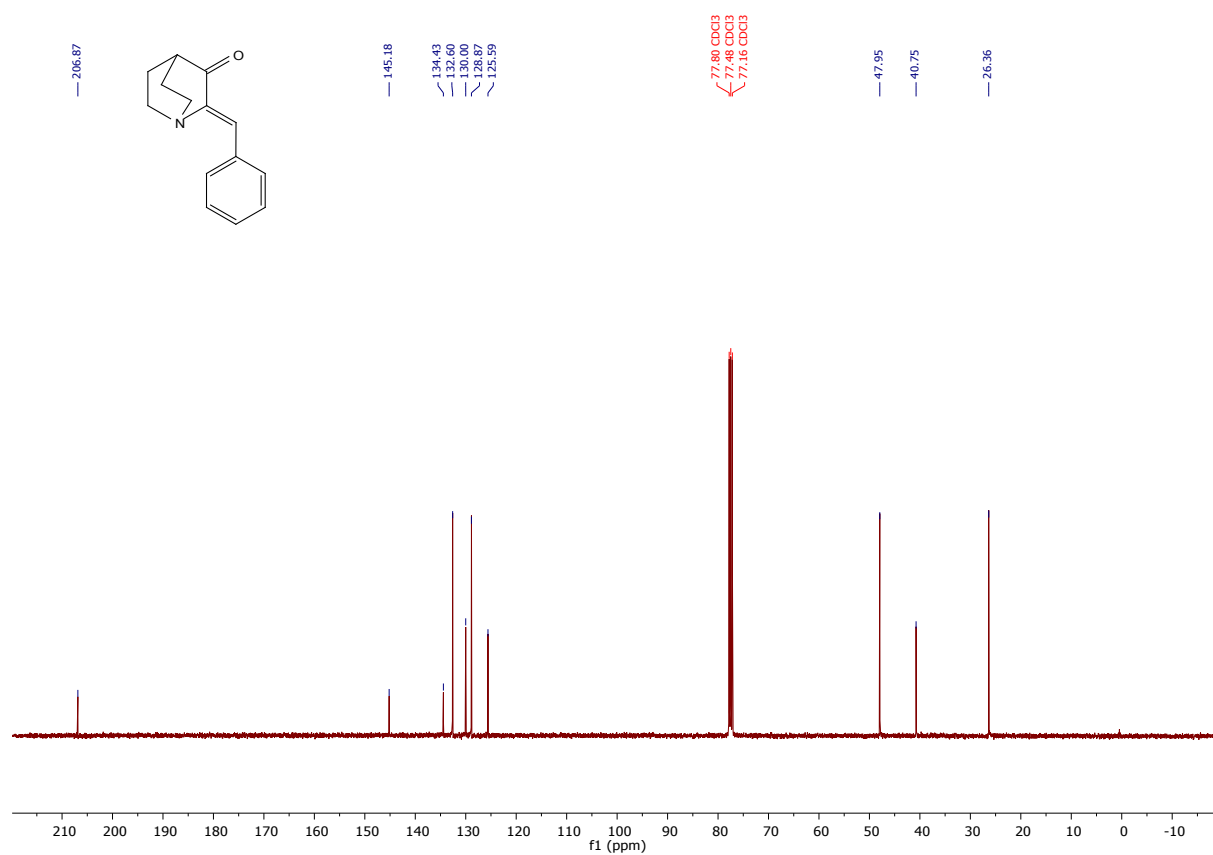
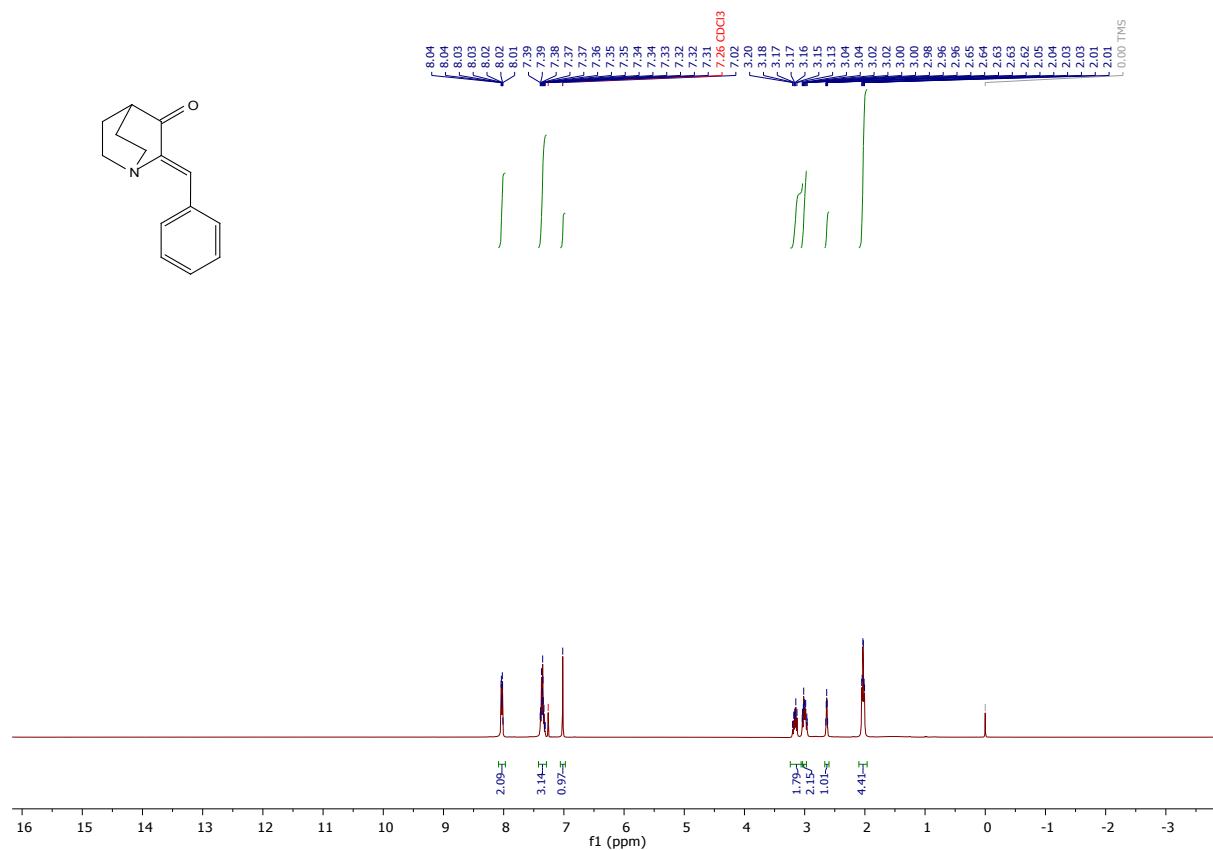
^b ICMCB CNRS-UMR 5026, Université de Bordeaux, Bordeaux, France

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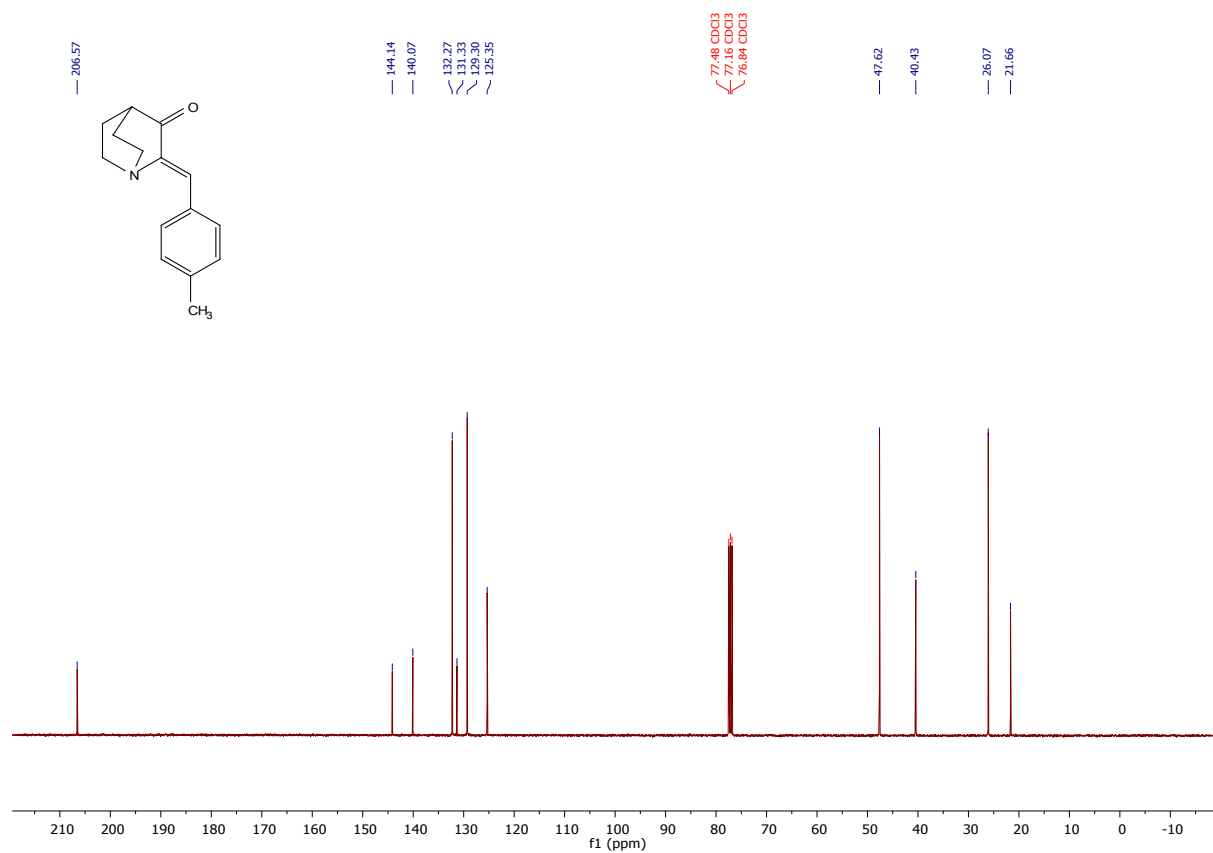
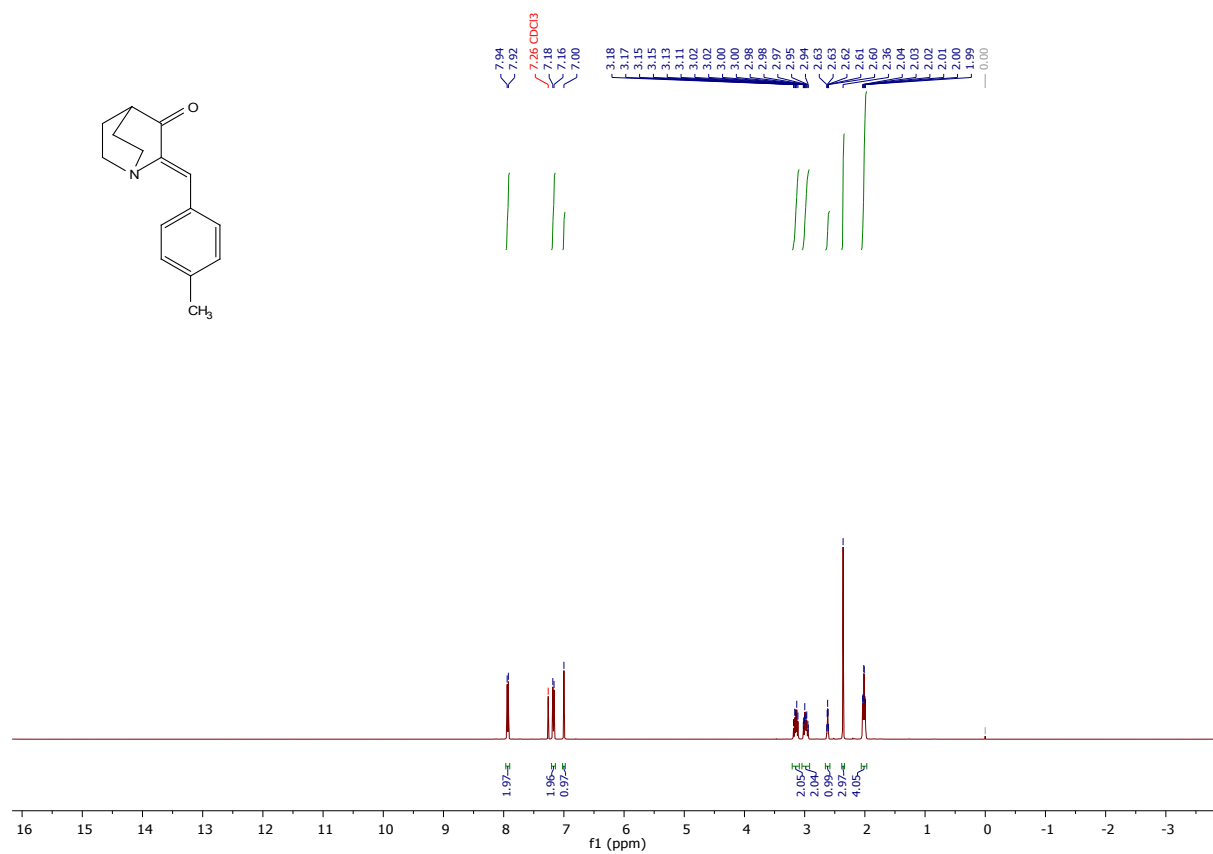
^d Institut de Combustion, Aérothermique, Réactivité, et Environnement (ICARE), 1c, Avenue de la Recherche Scientifique, 45071 CEDEX 2 Orléans, France

The supporting information contains the ¹H NMR and ¹³C NMR copy spectra and crystal data for compound **49**.

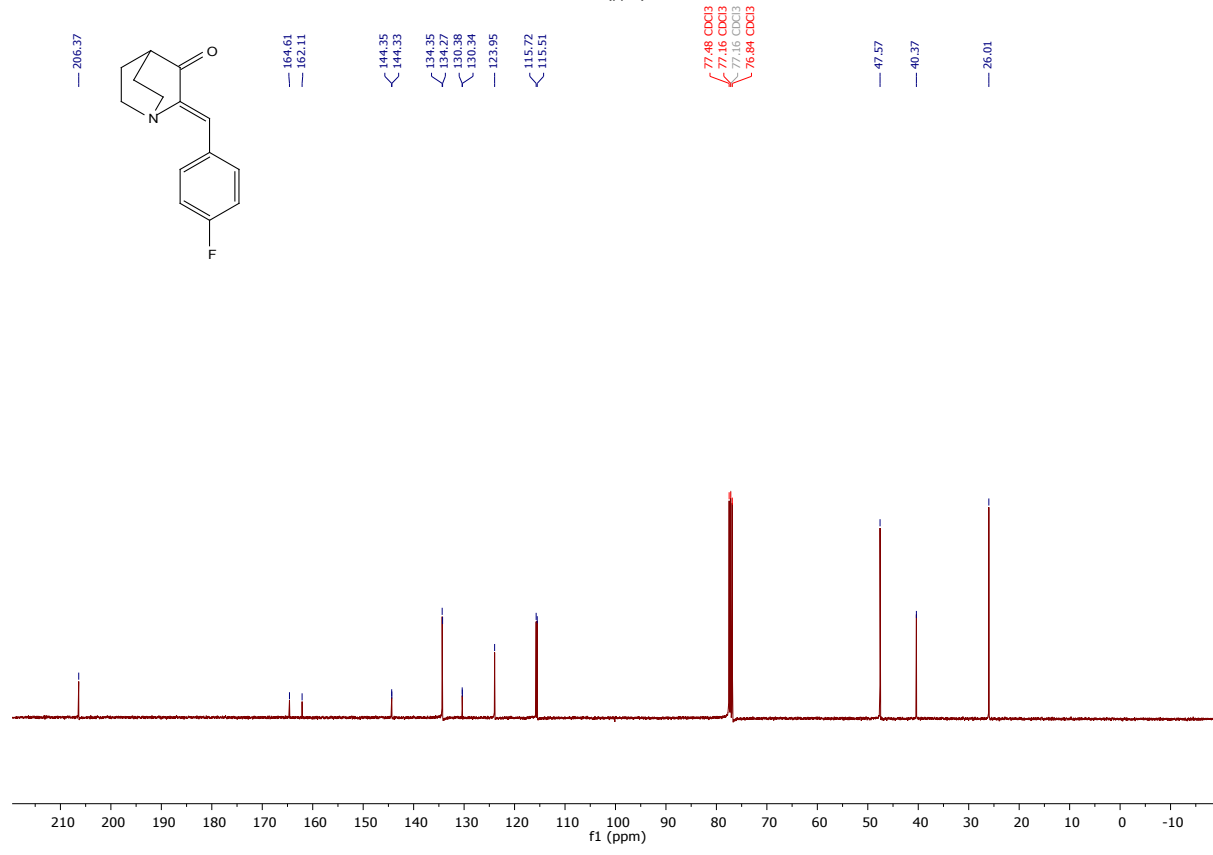
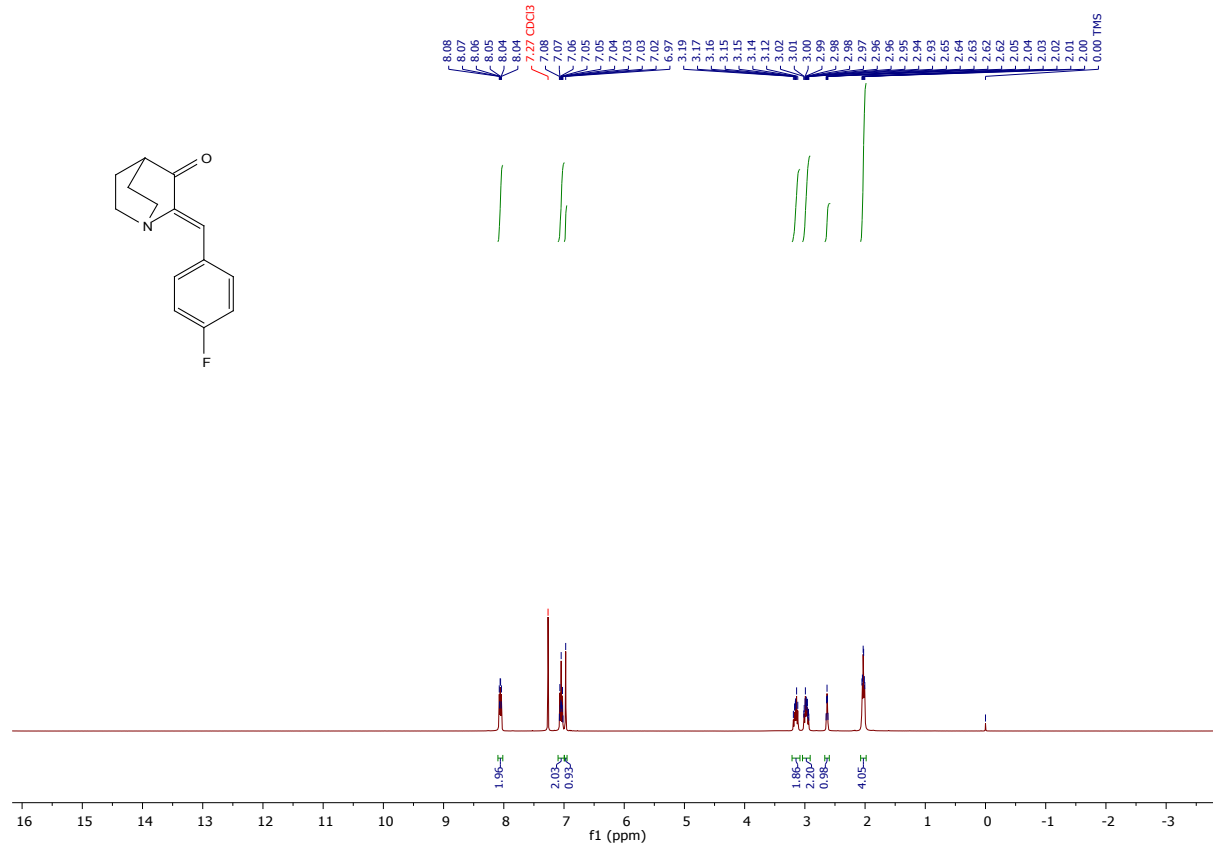
(Z)-2-Benzylidenequinuclidin-3-one (2)



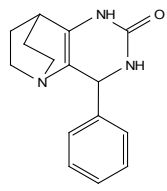
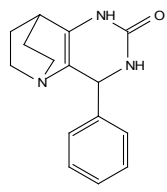
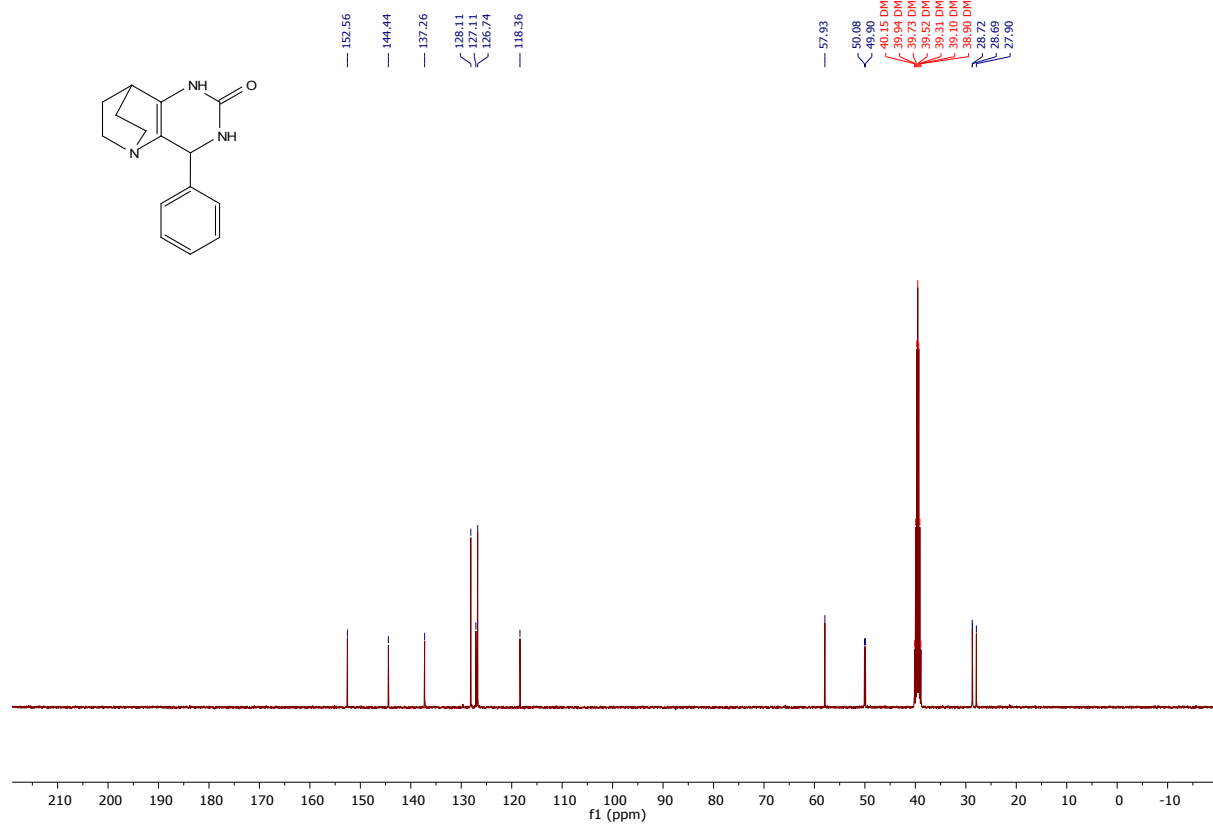
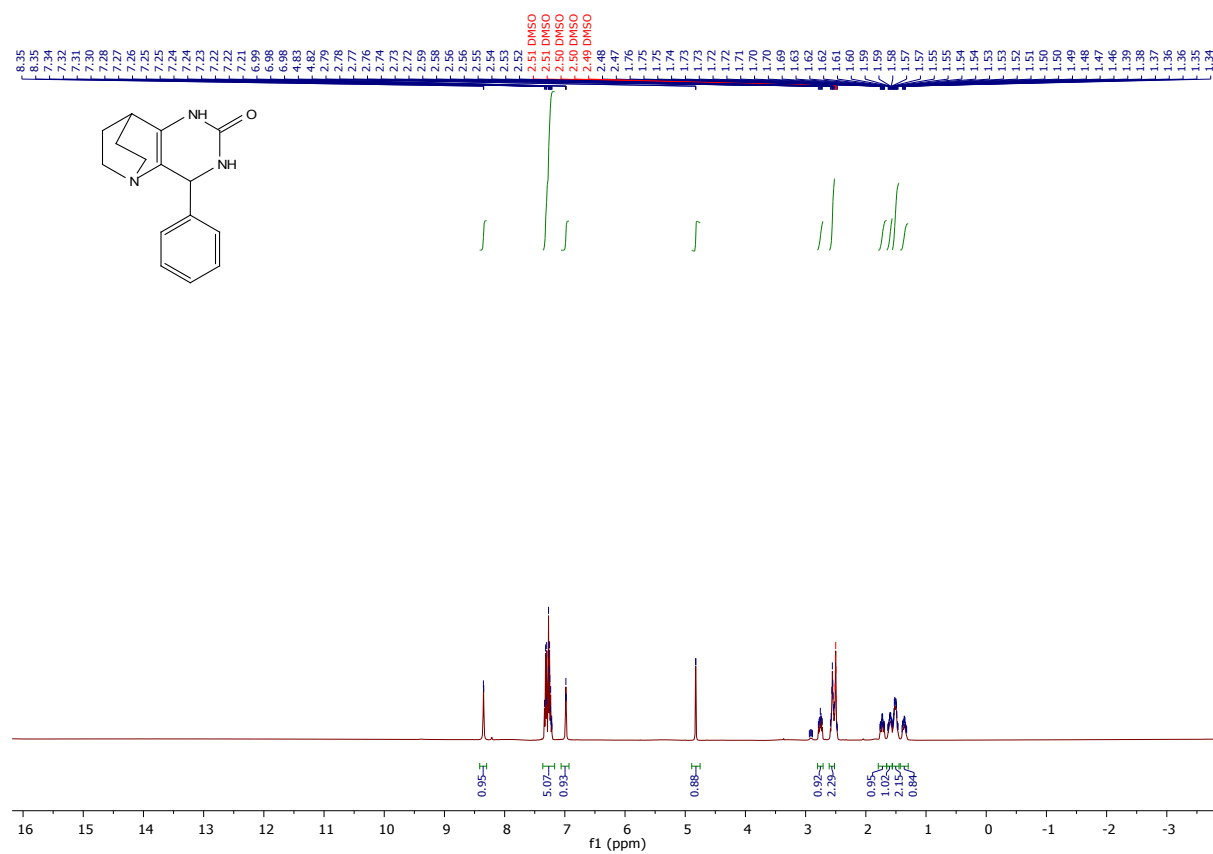
(Z)-2-(4-Methylbenzylidene)quinuclidin-3-one (3)



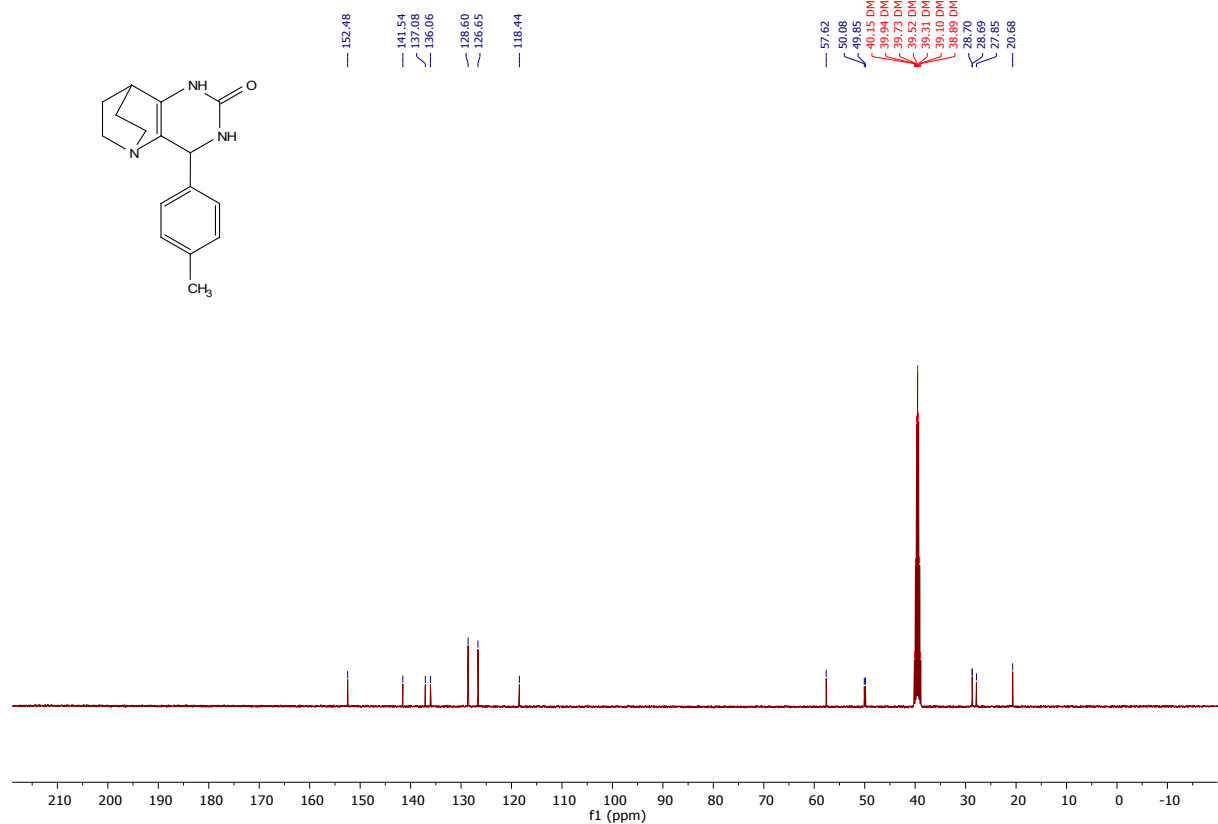
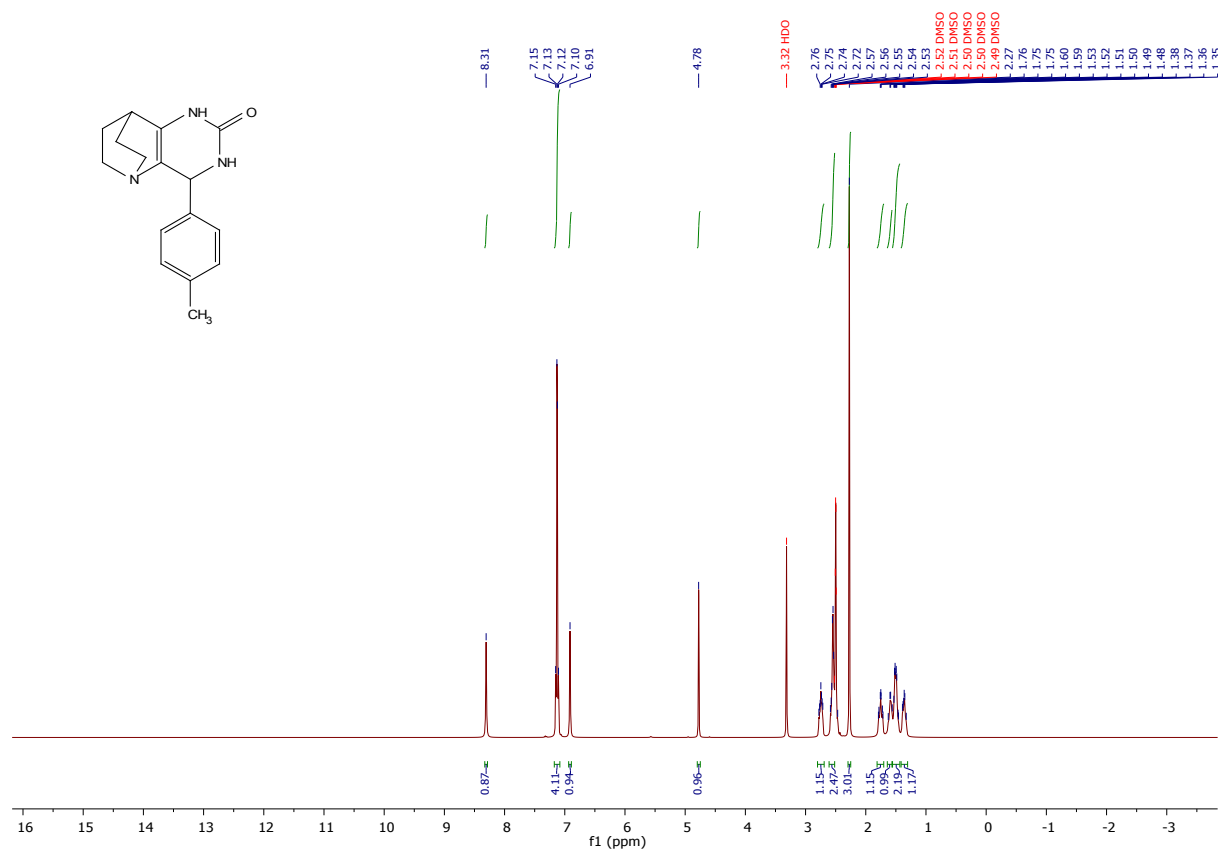
(Z)-2-(4-Fluorobenzylidene)quinuclidin-3-one (4)



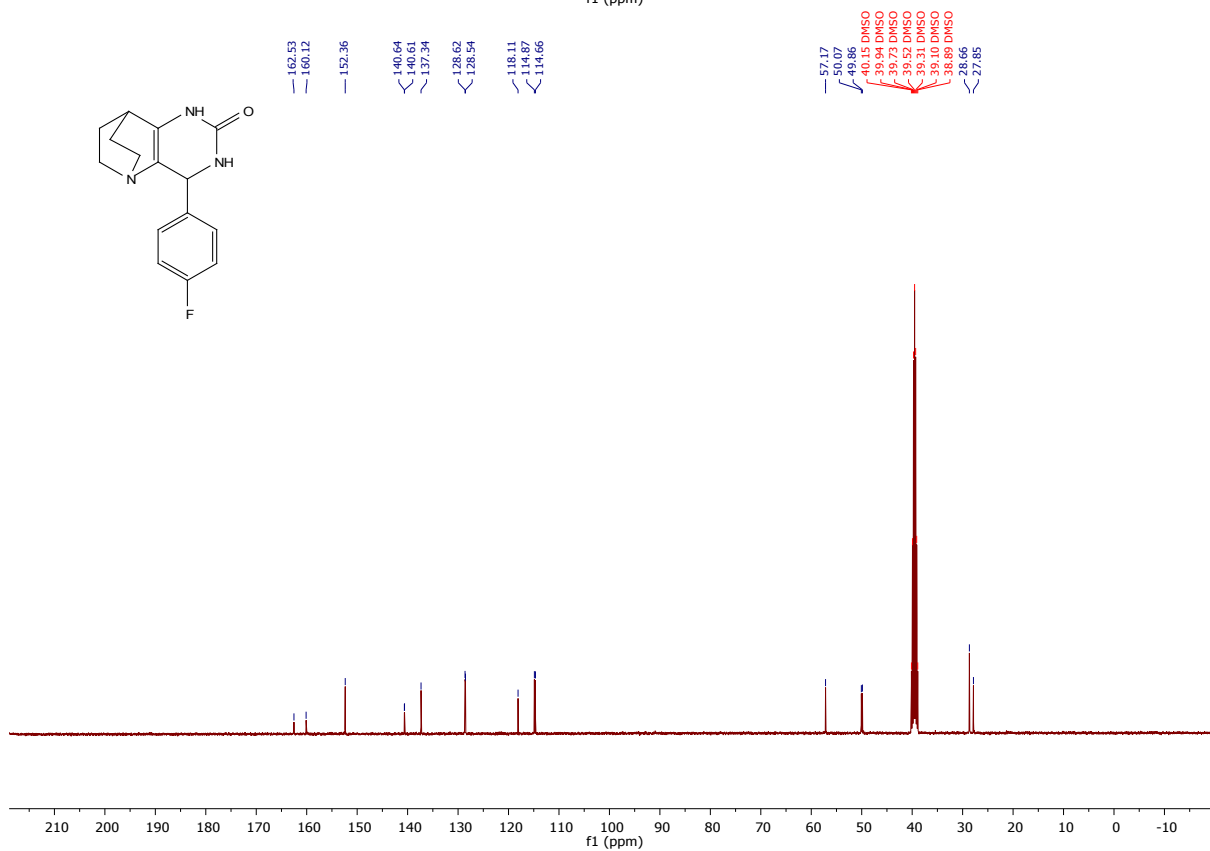
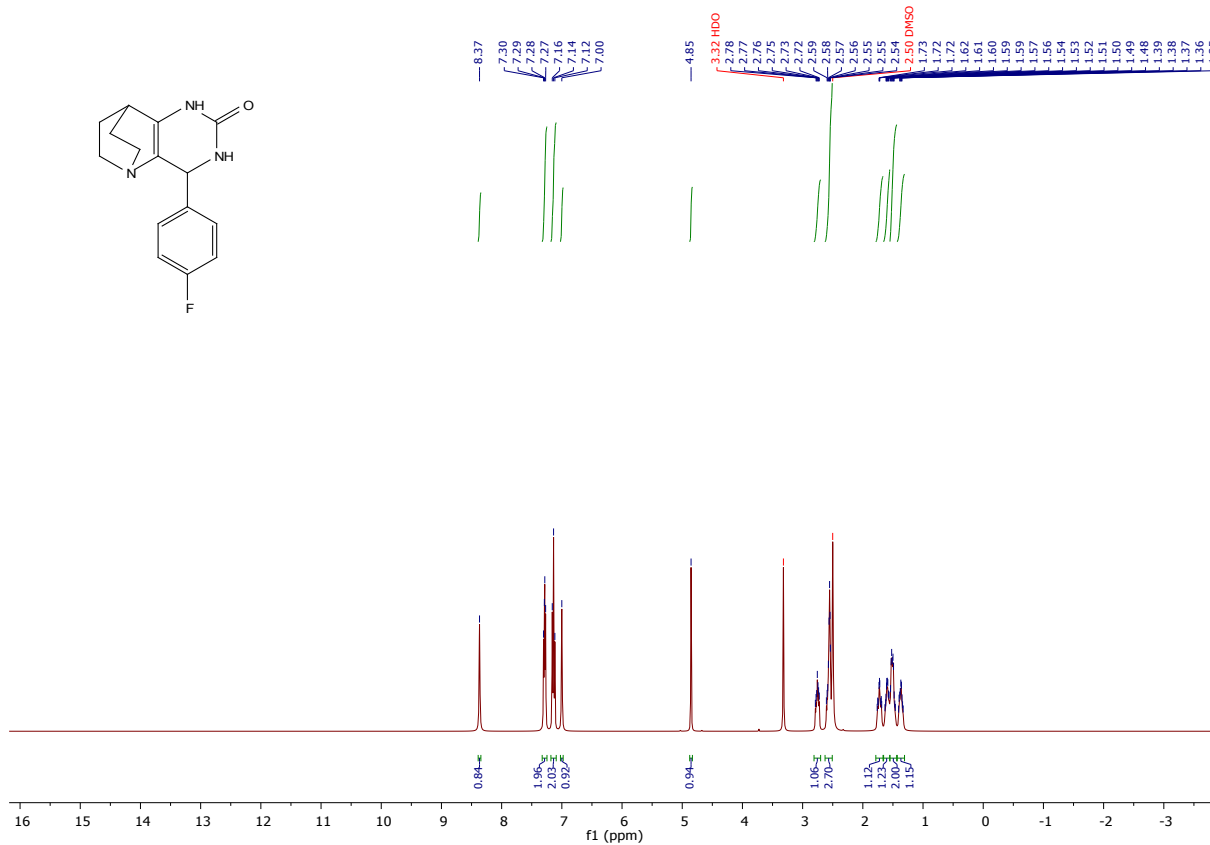
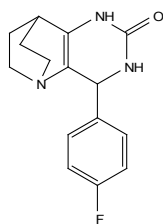
4-Phenyl-3,4,7,8-tetrahydro-1H-5,8-ethanopyrido[3,2-d]pyrimidin-2(6H)-one (5)

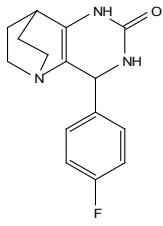


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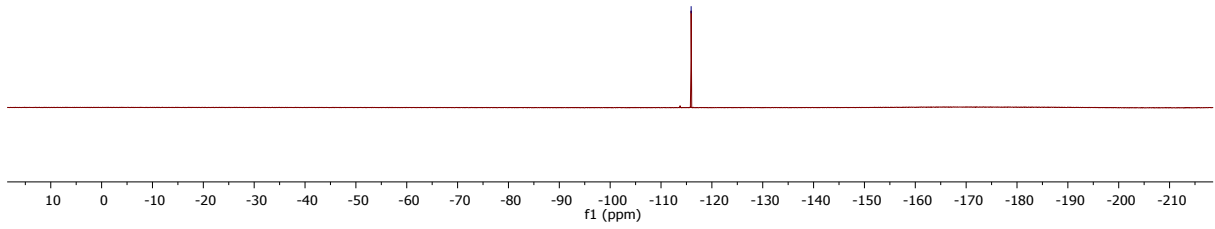


-(4-Fluorophenyl)-3,4,7,8-tetrahydro-1H-5,8-ethanopyrido[3,2-d]pyrimidin-2(6H)-one (7)

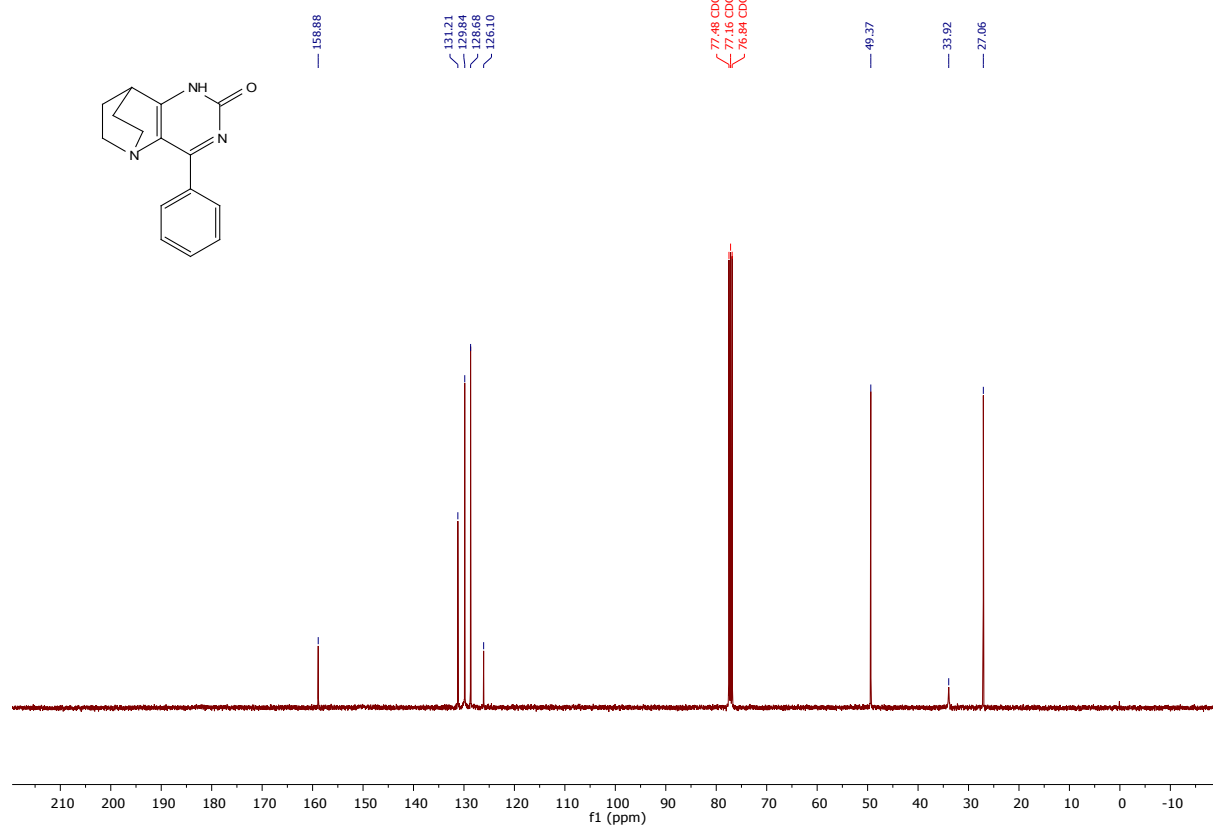
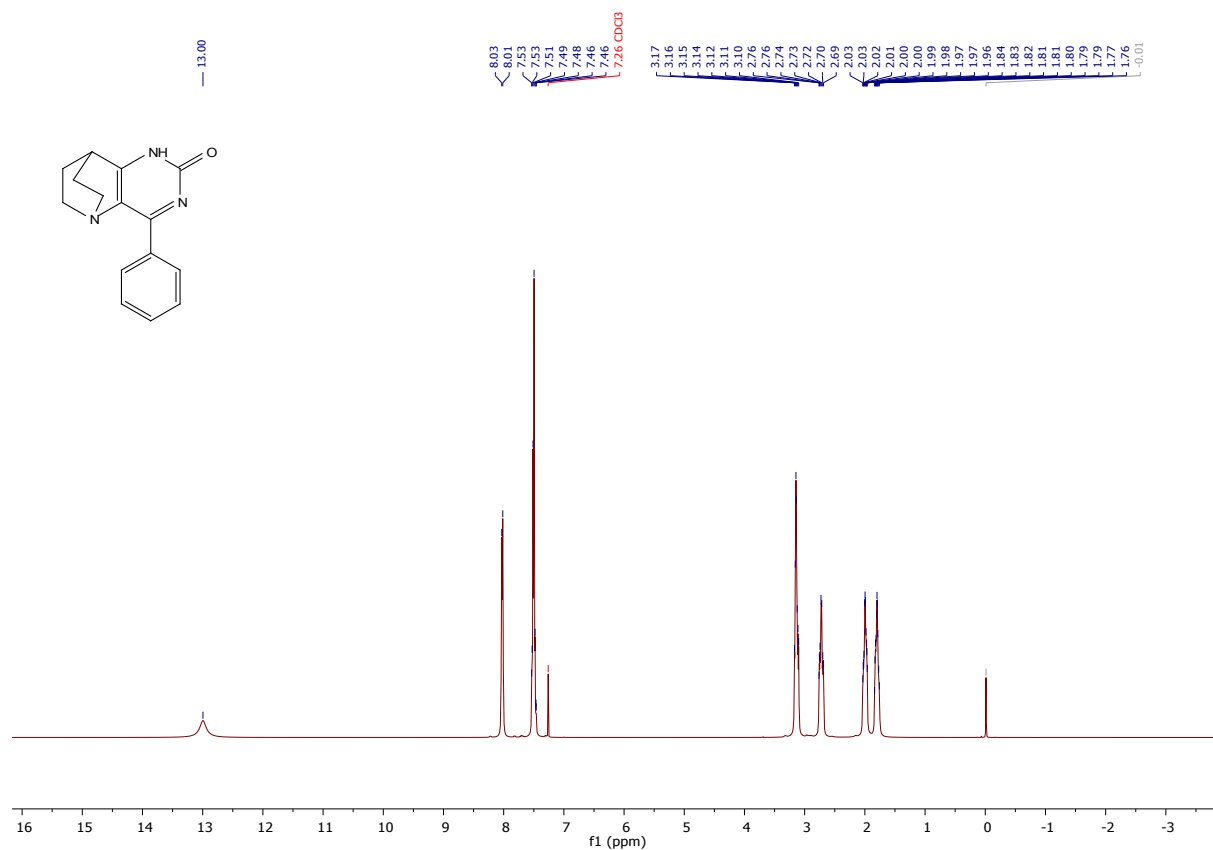




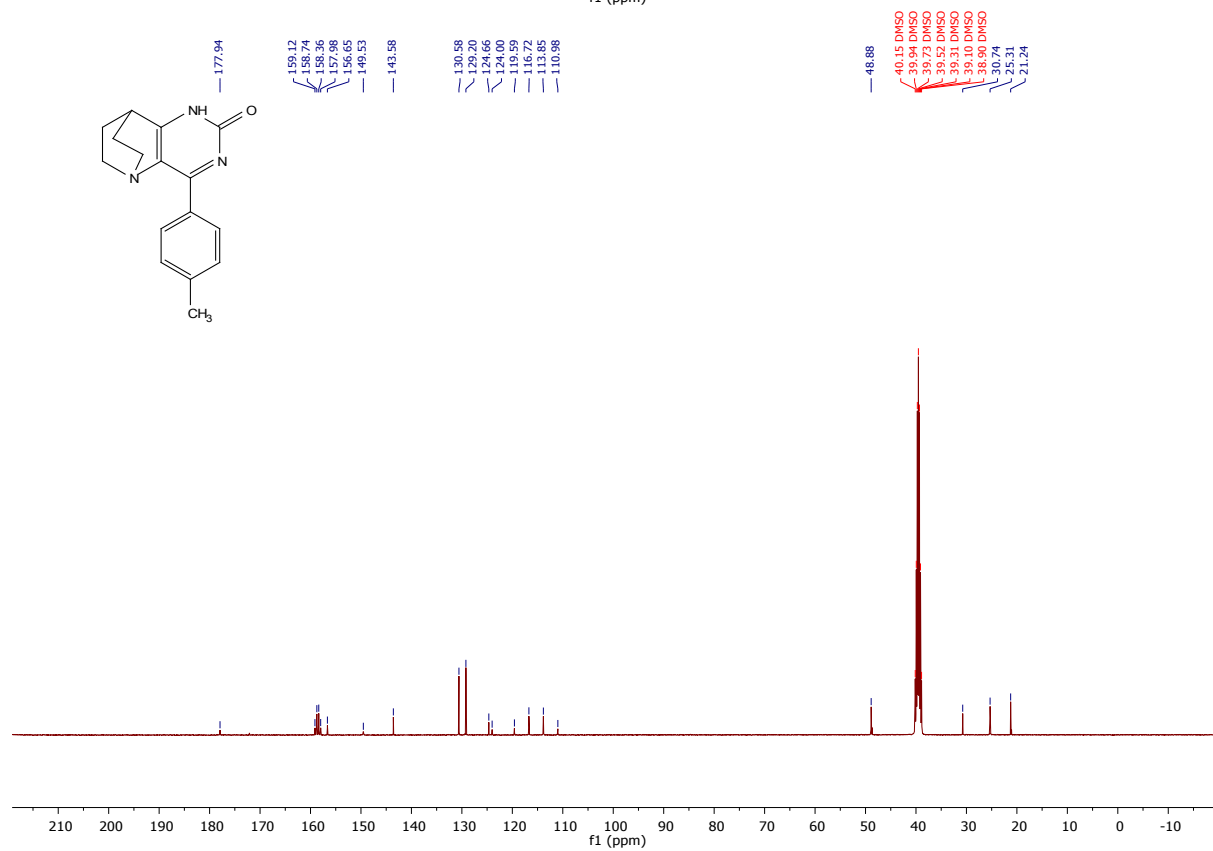
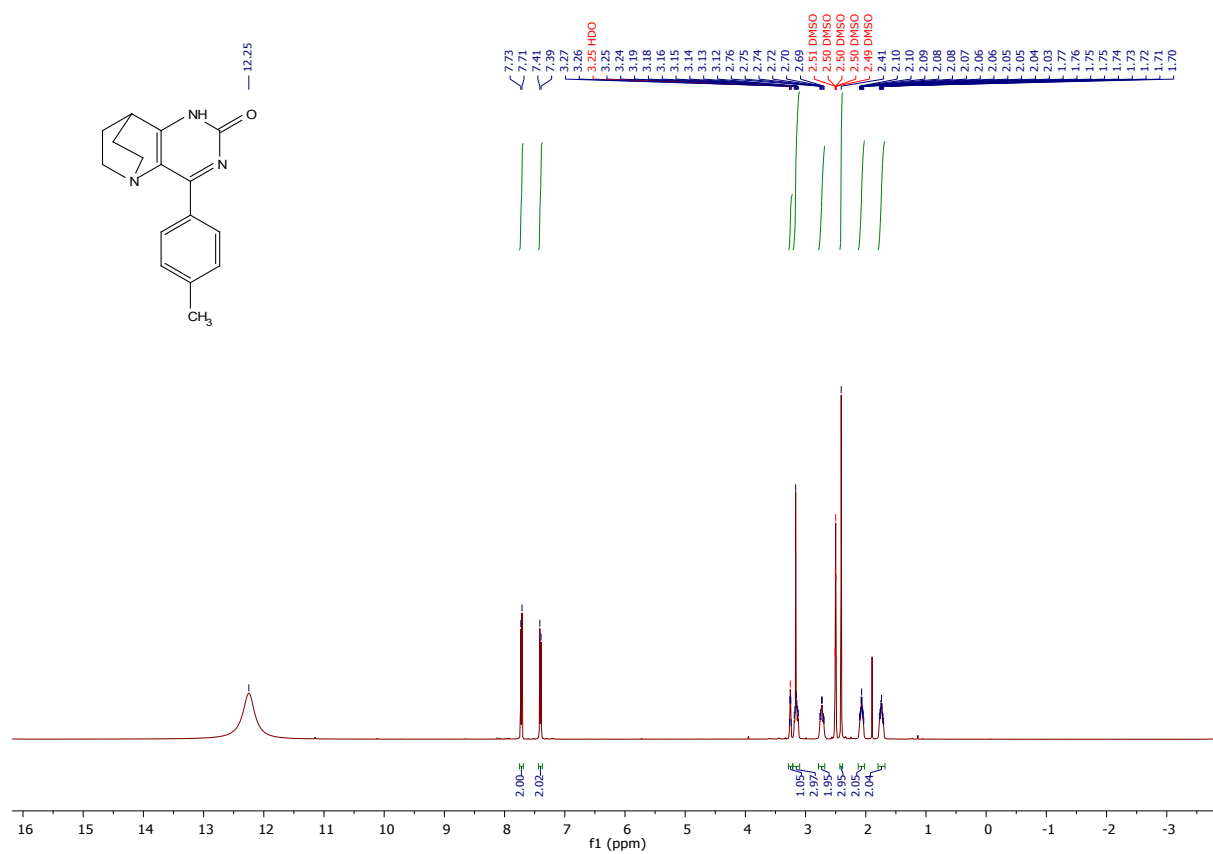
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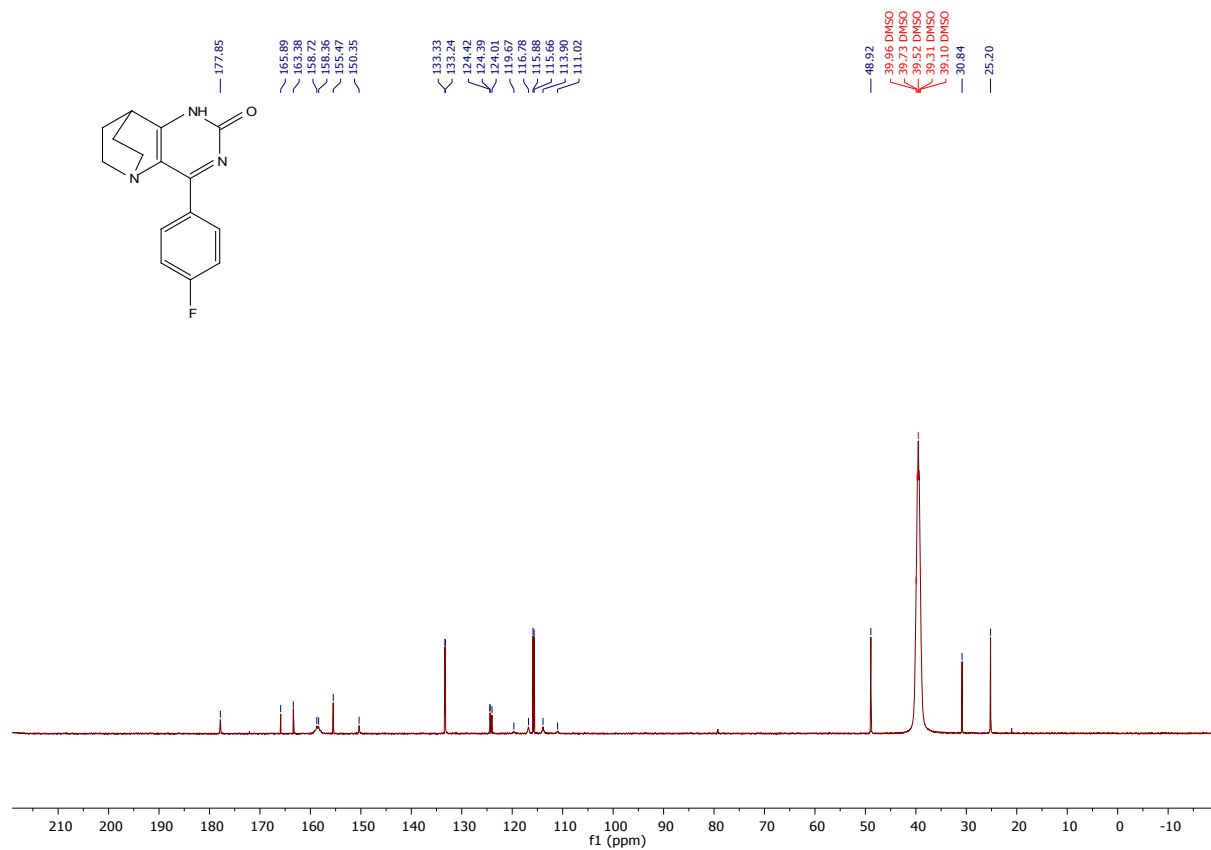
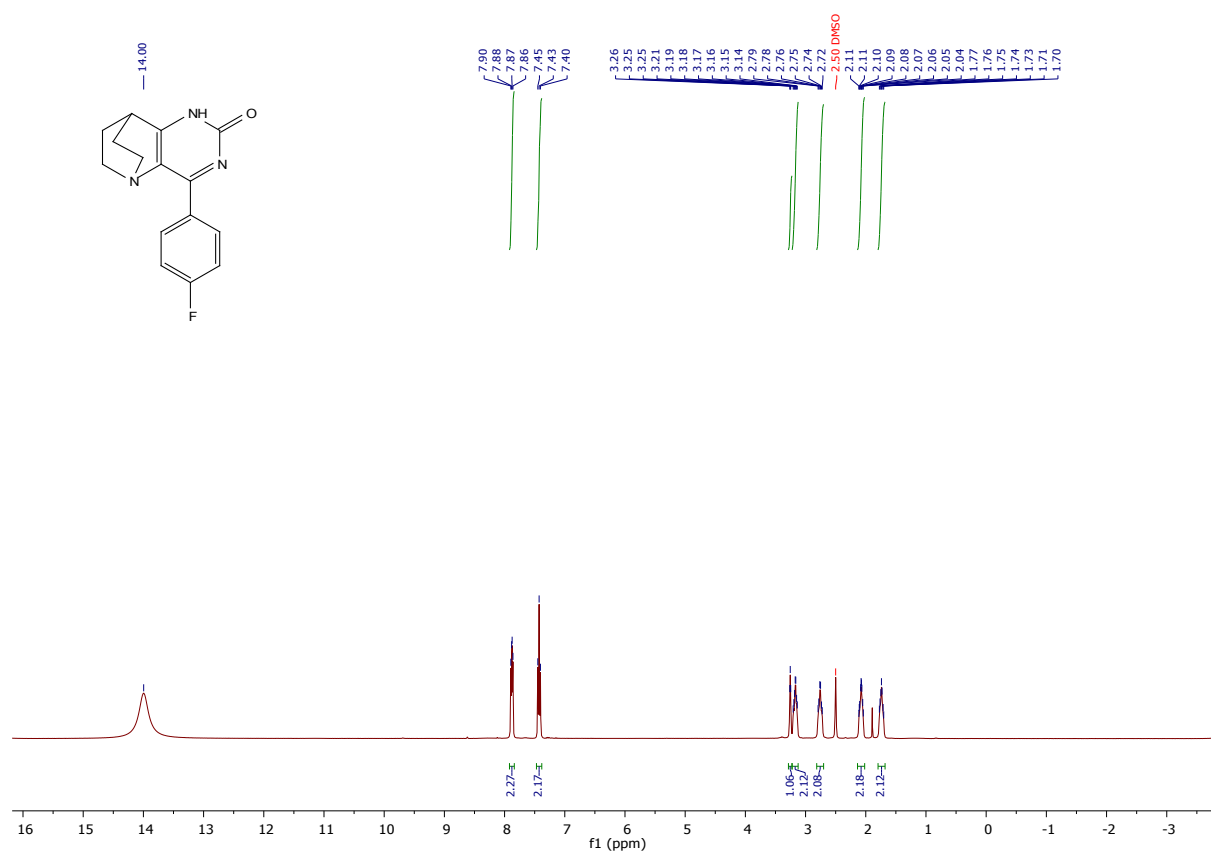
4-Phenyl-7,8-dihydro-1H-5,8-ethanopyrido[3,2-d]pyrimidin-2(6H)-one (8)

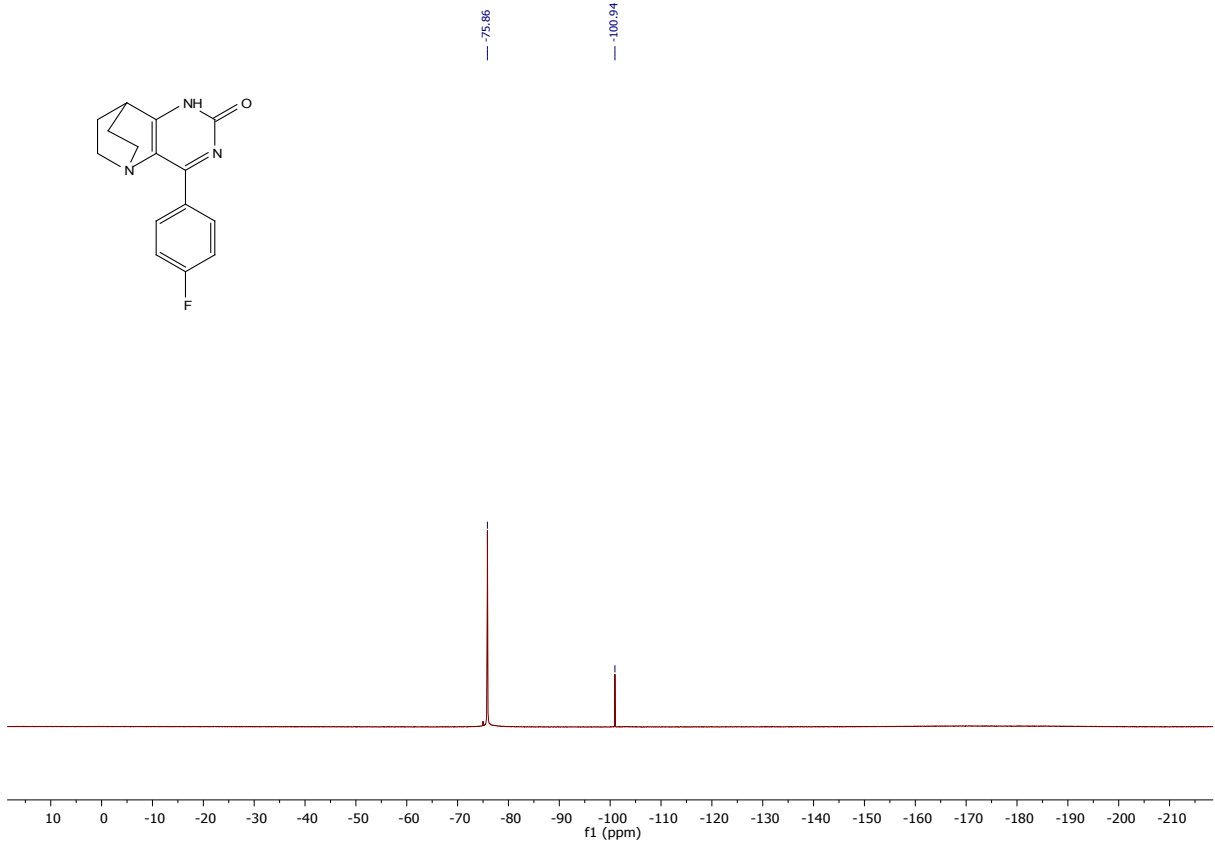
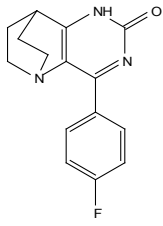


4-(*p*-Tolyl)-7,8-dihydro-1*H*-5,8-ethanopyrido[3,2-*d*]pyrimidin-2(6*H*)-one (9)

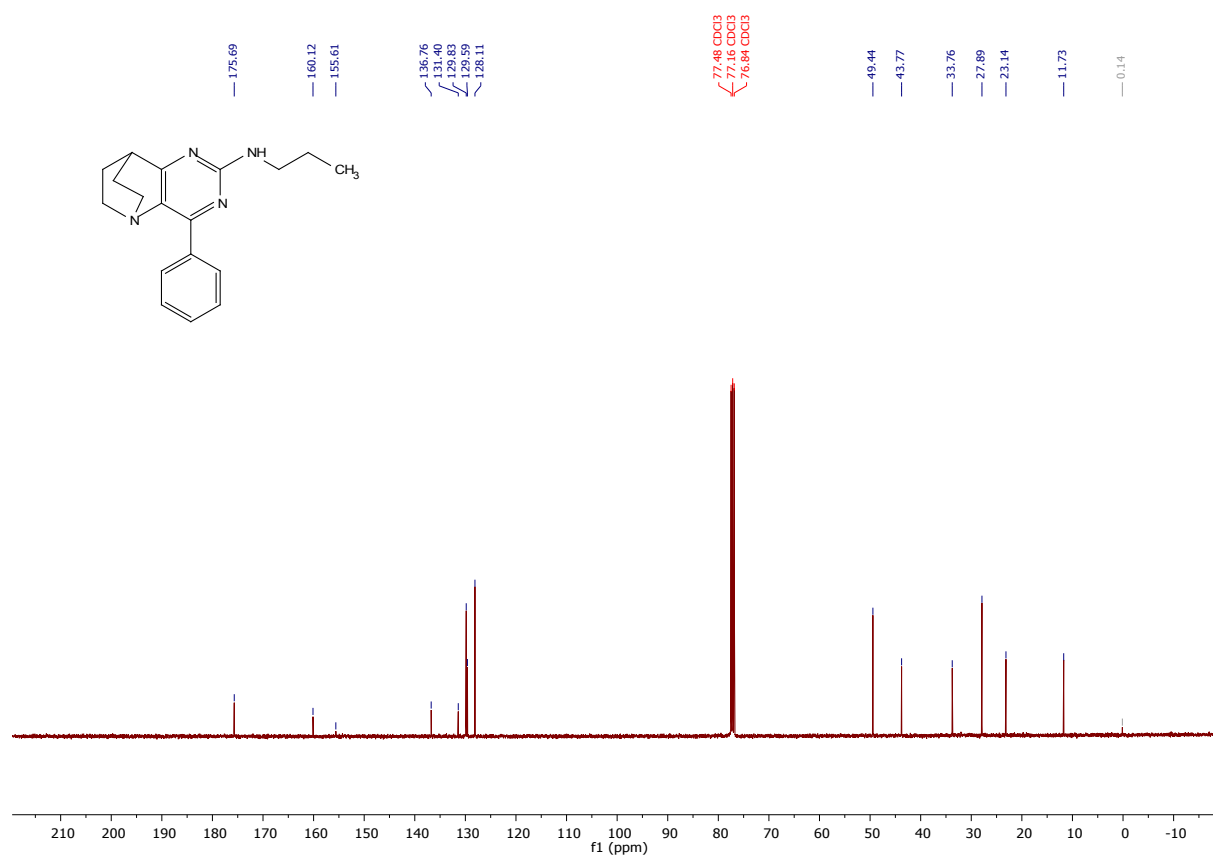
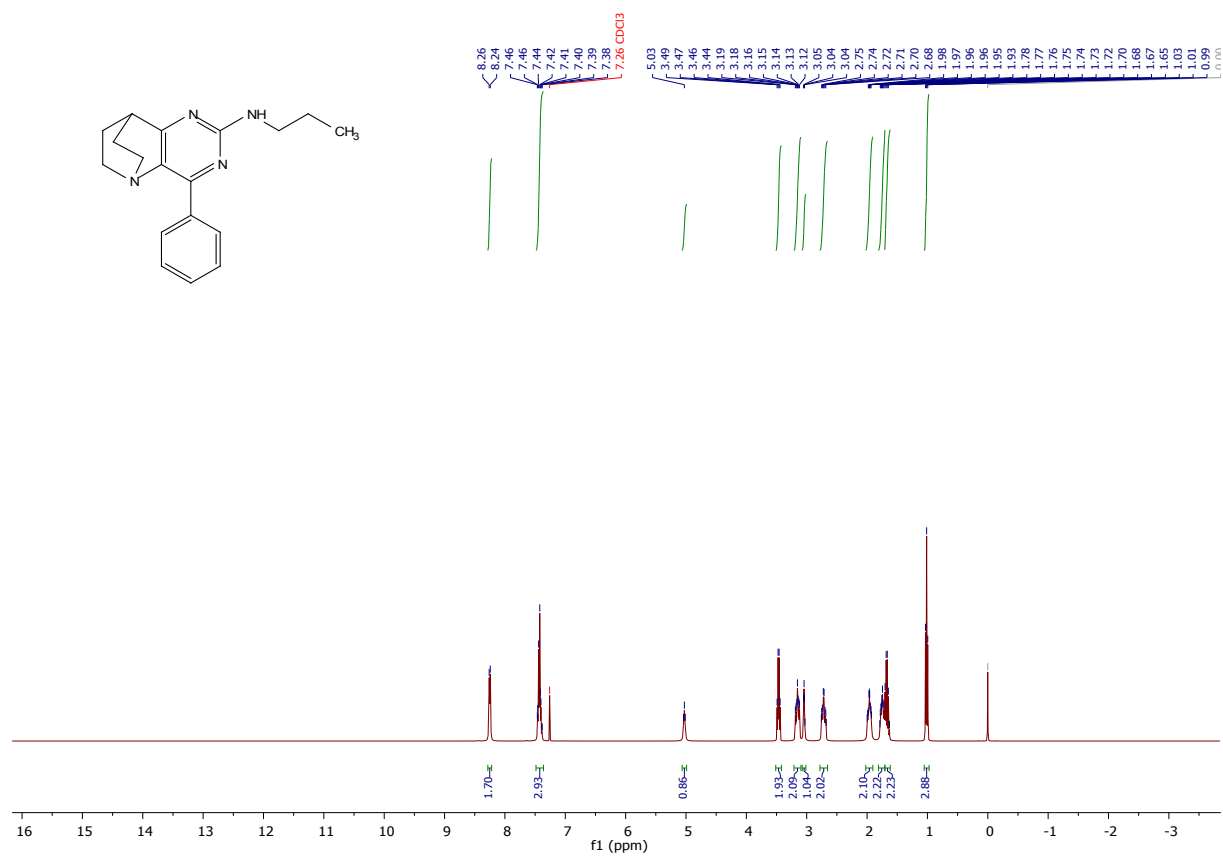


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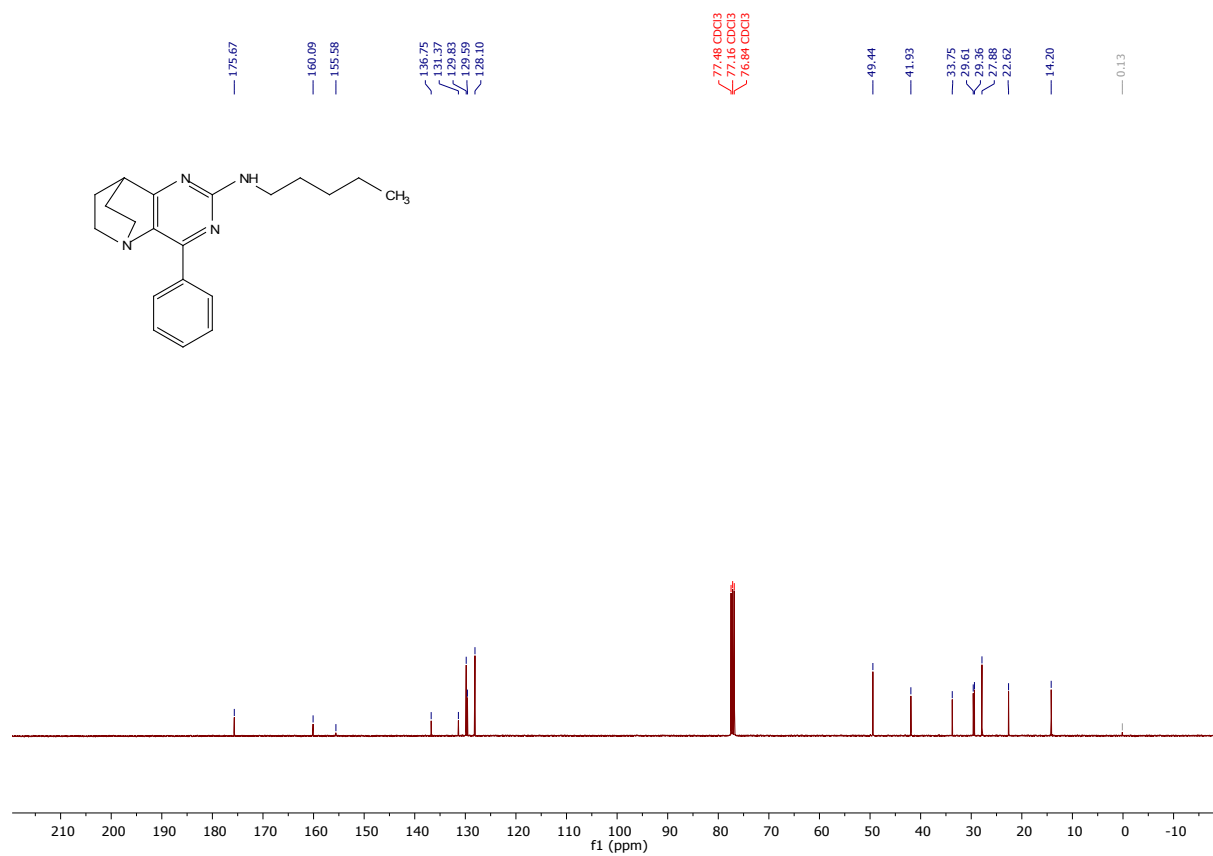
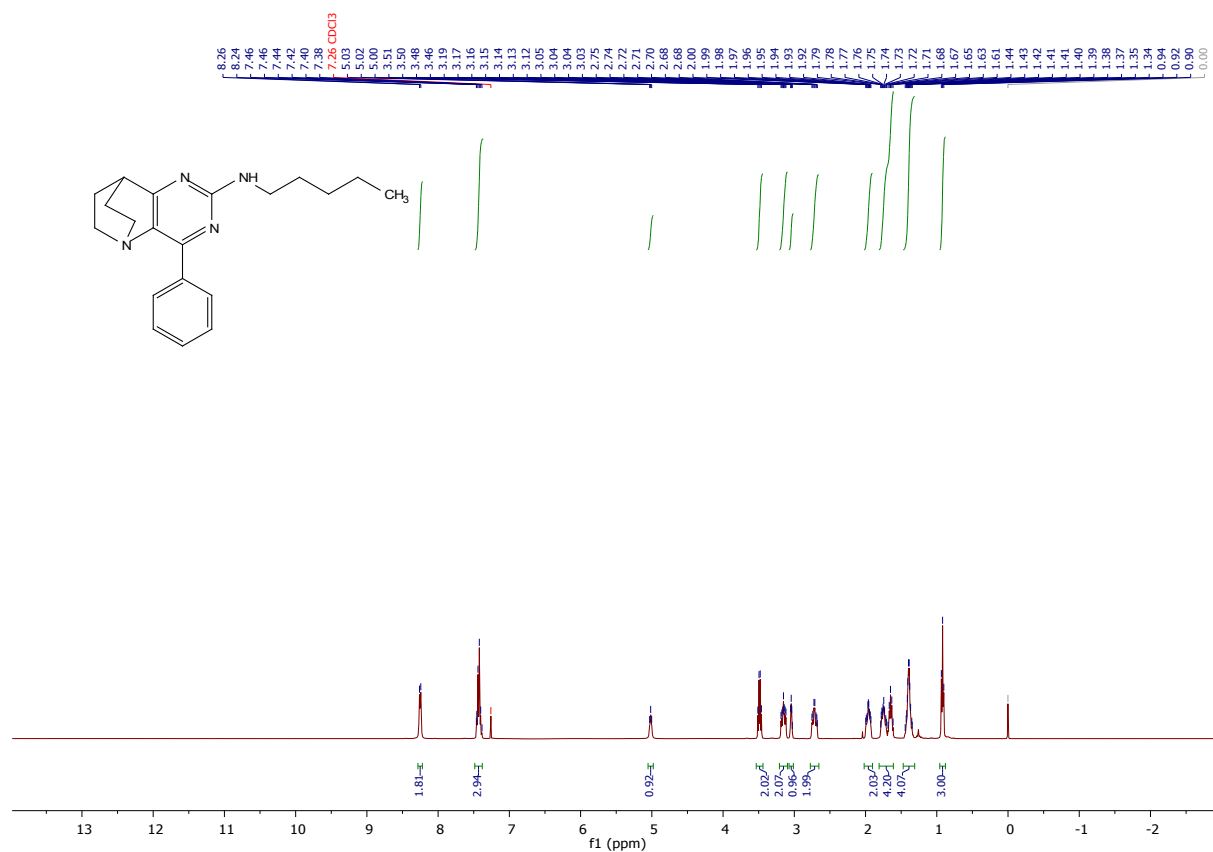




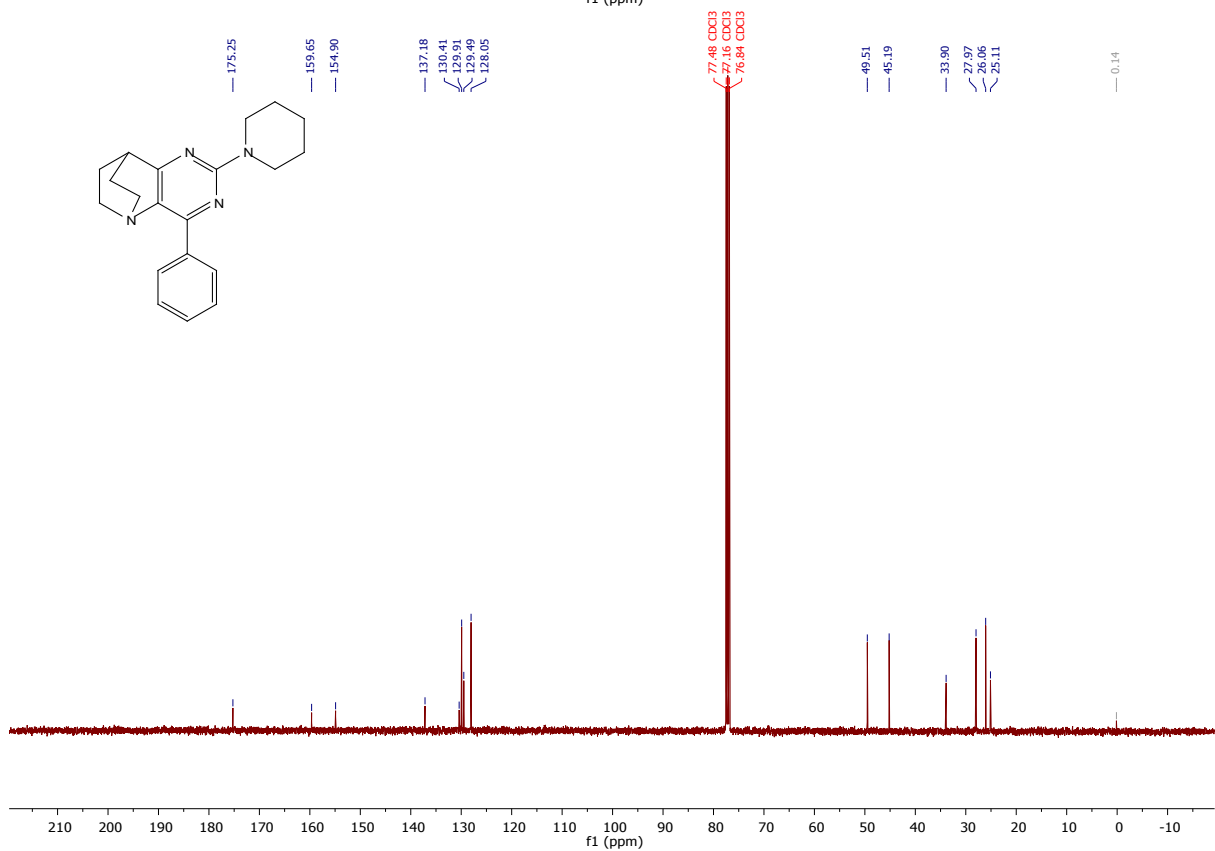
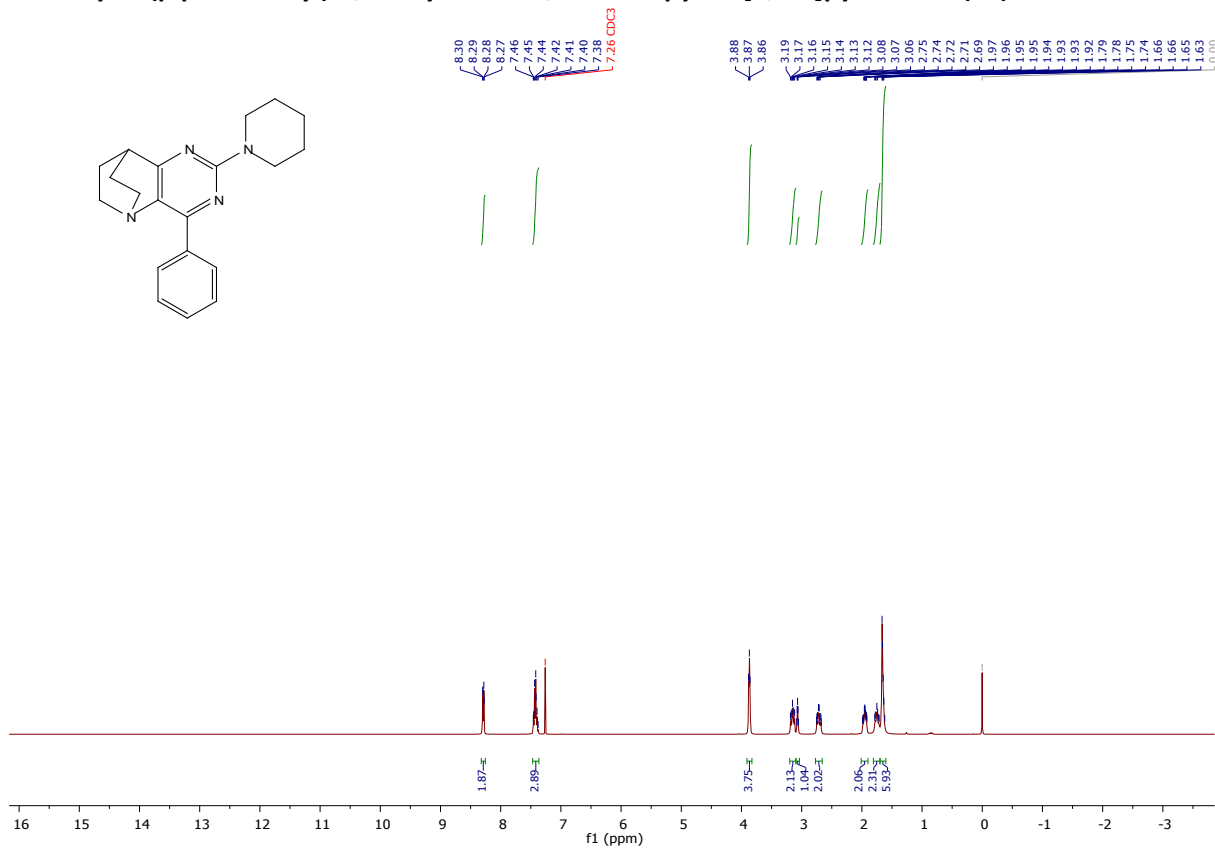
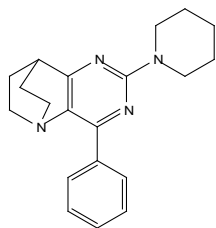
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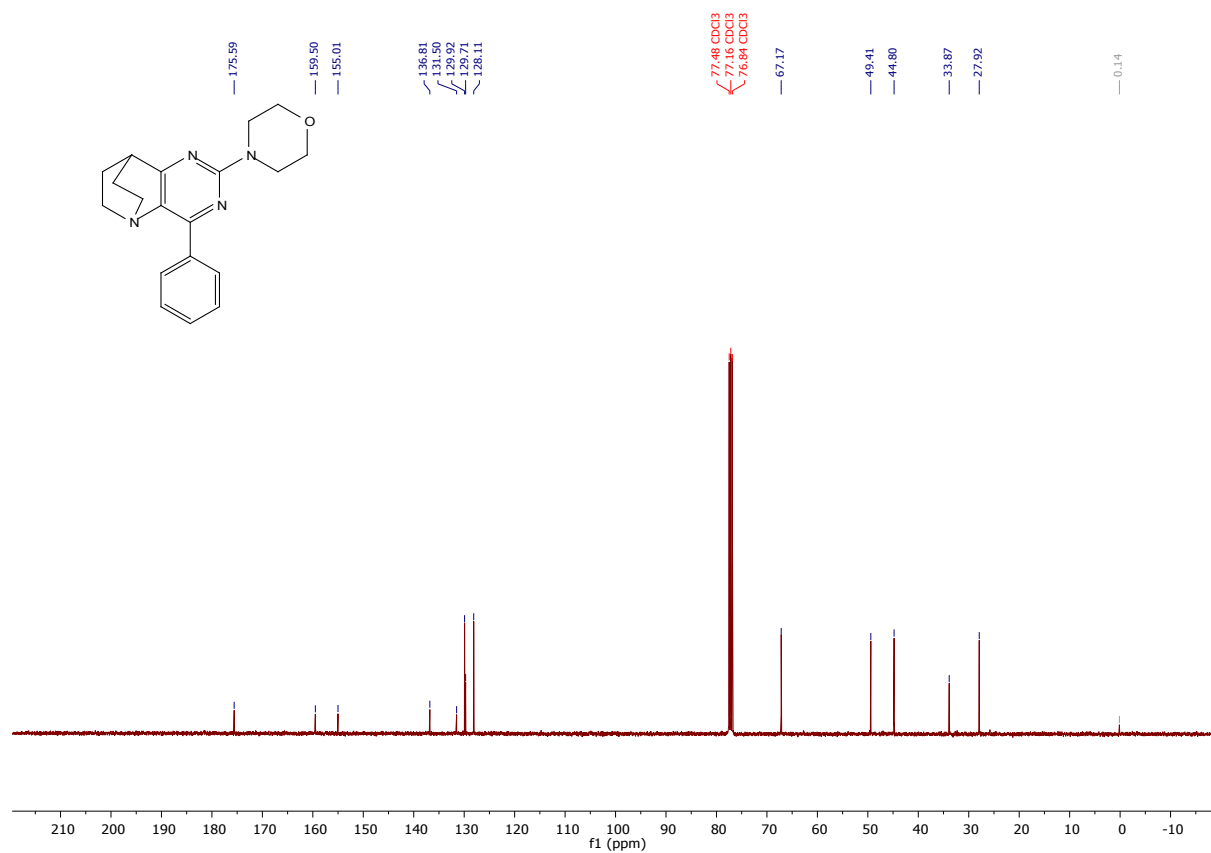
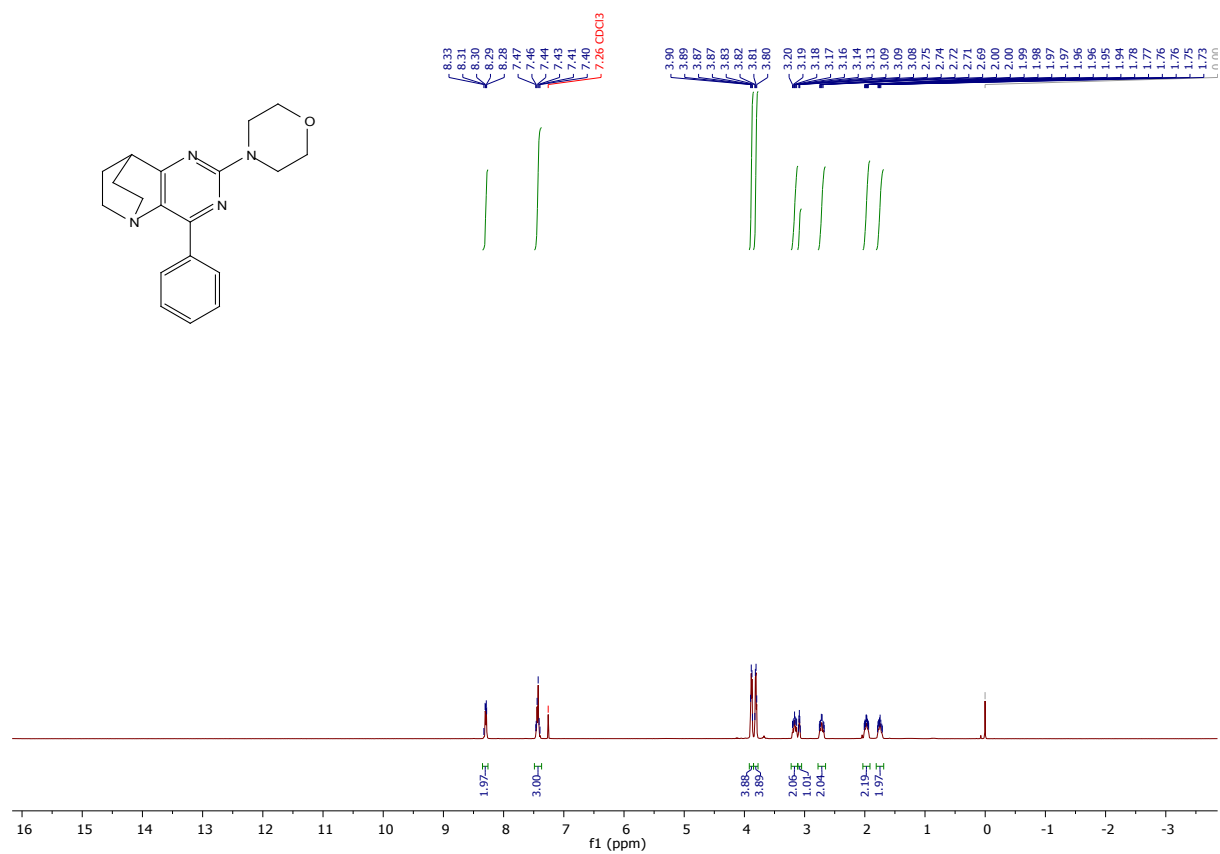
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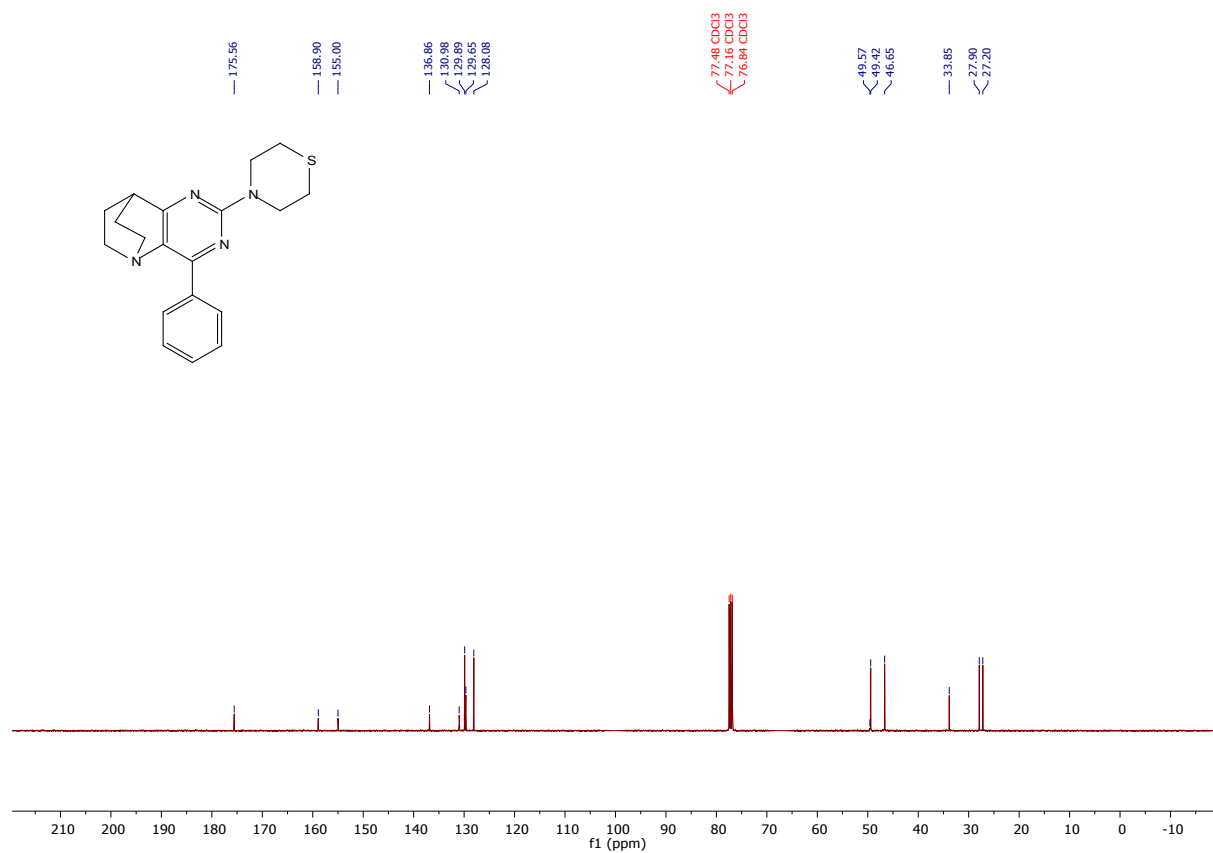
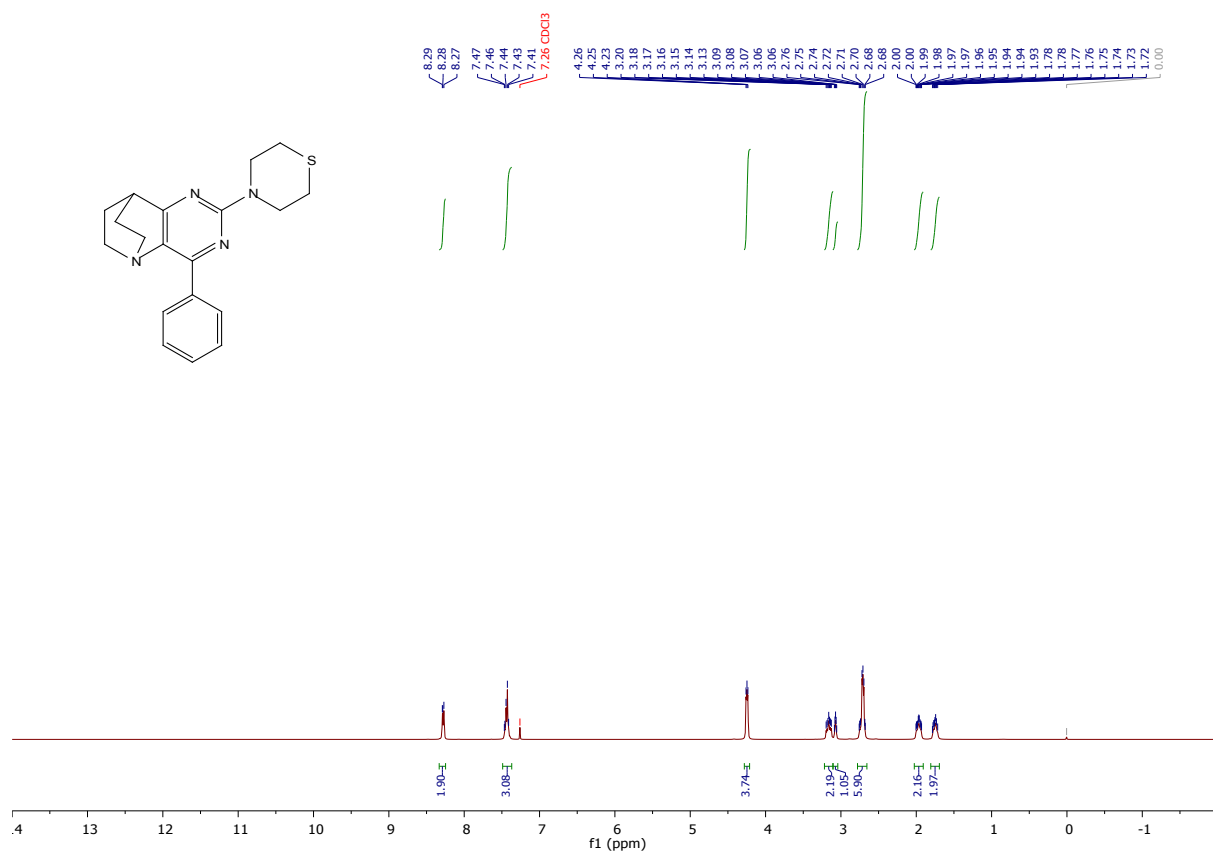
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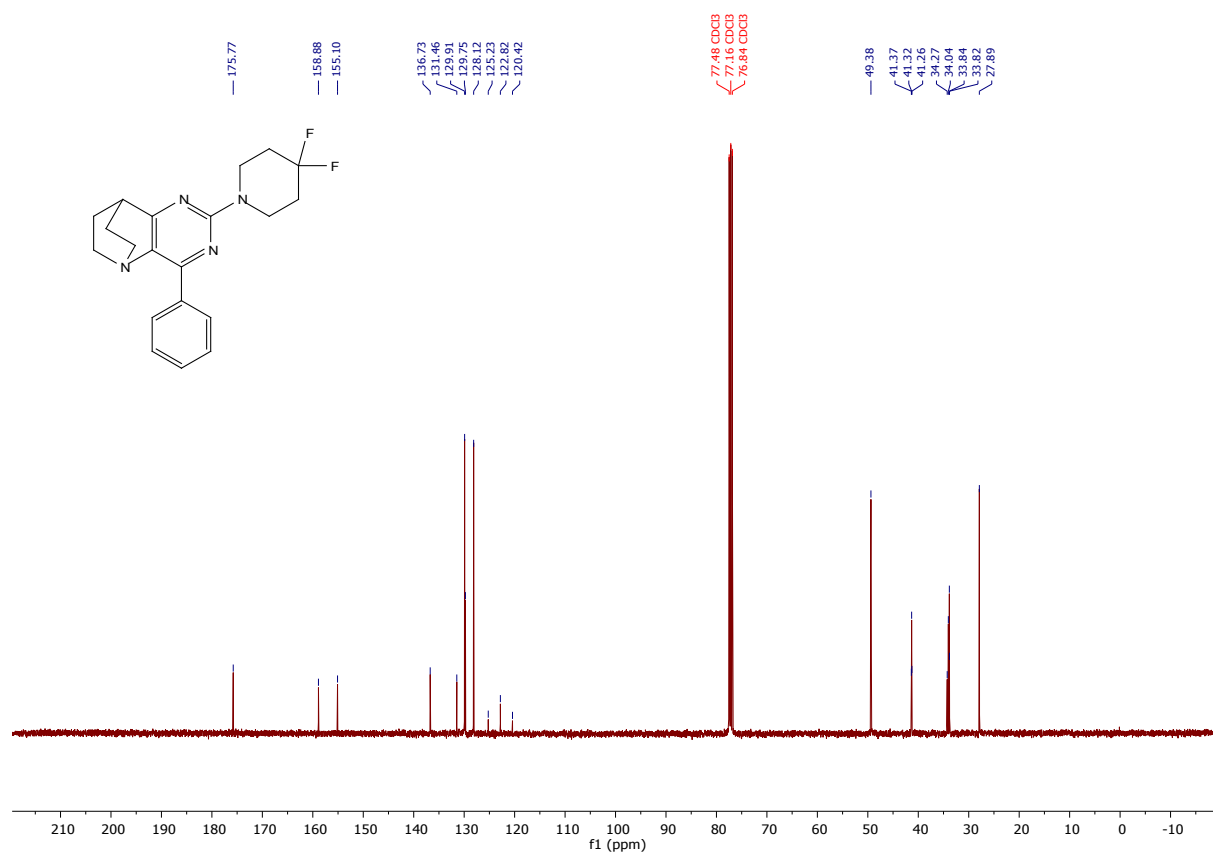
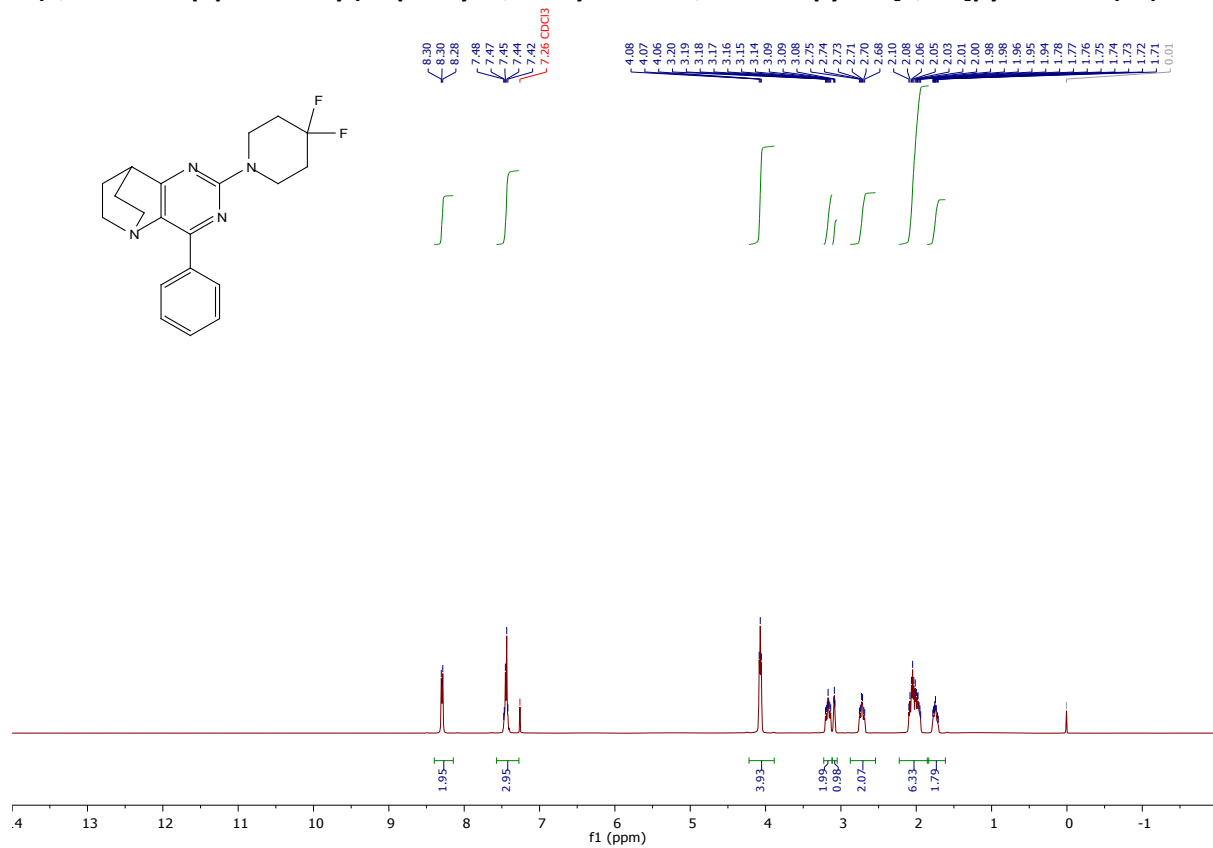
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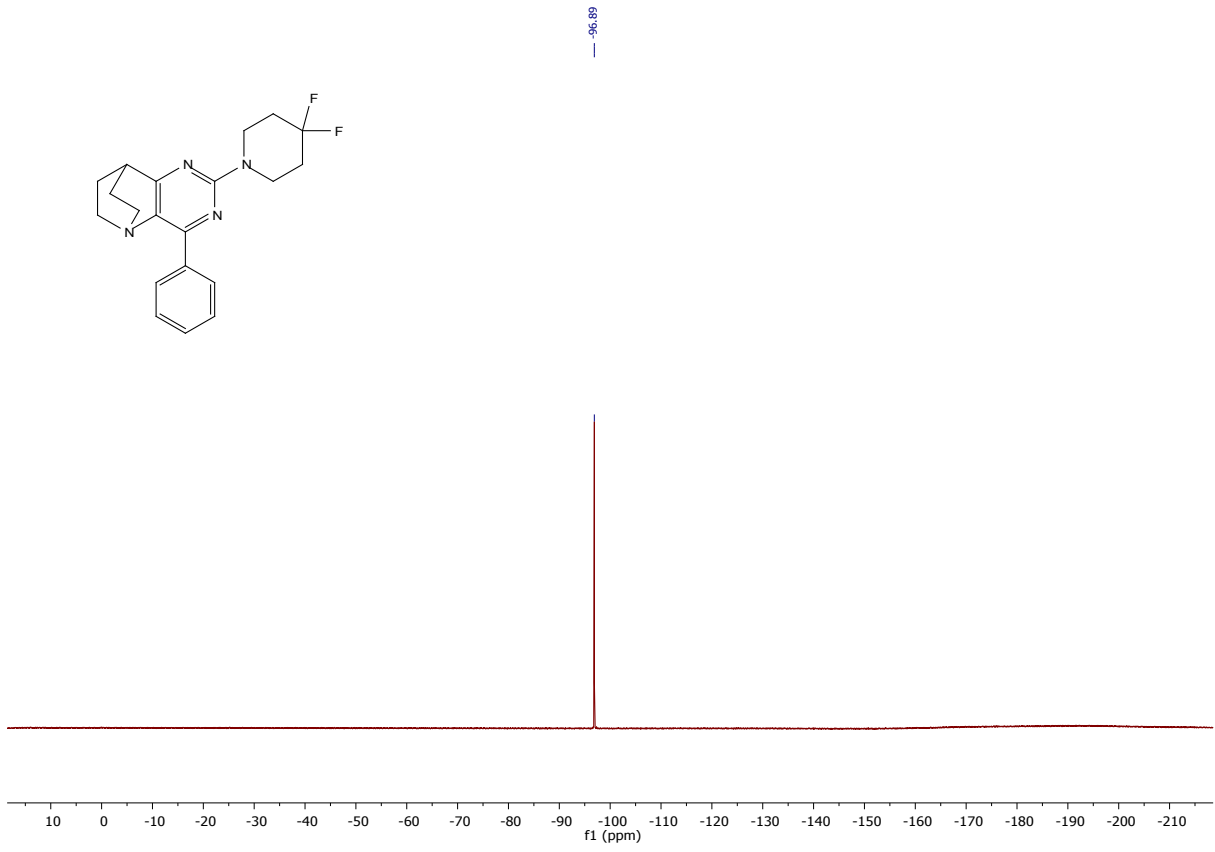
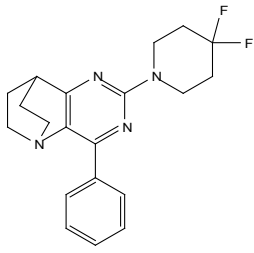


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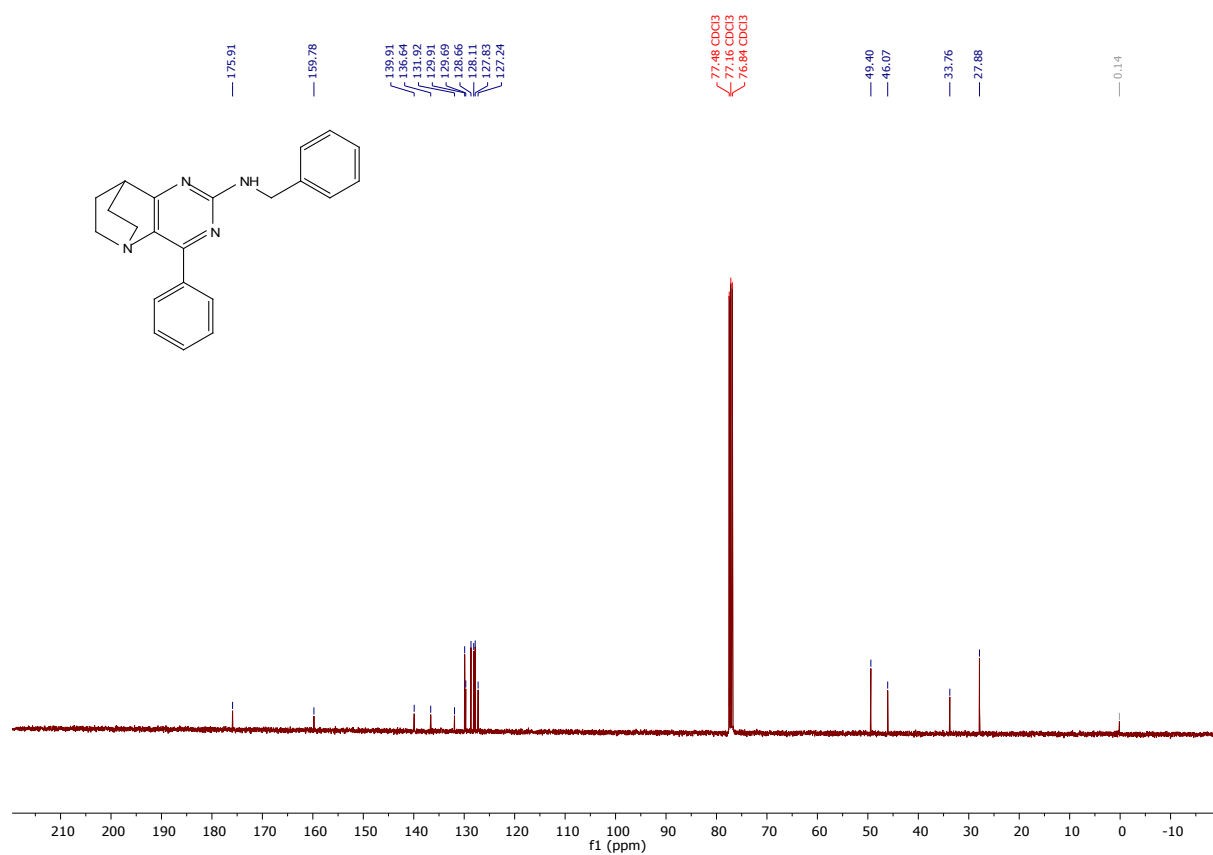
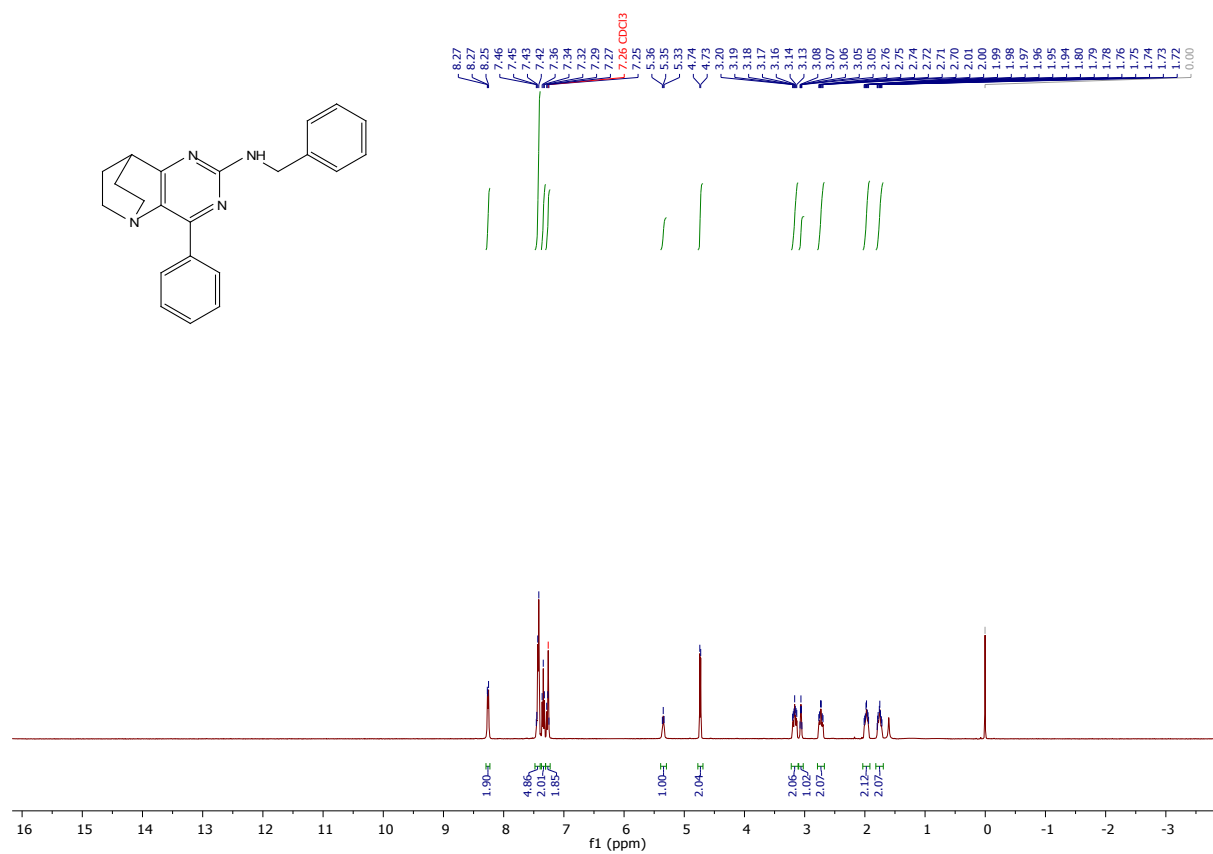


2-(4,4-Difluoropiperidin-1-yl)-4-phenyl-7,8-dihydro-6H-5,8-ethanopyrido[3,2-d]pyrimidine (16)

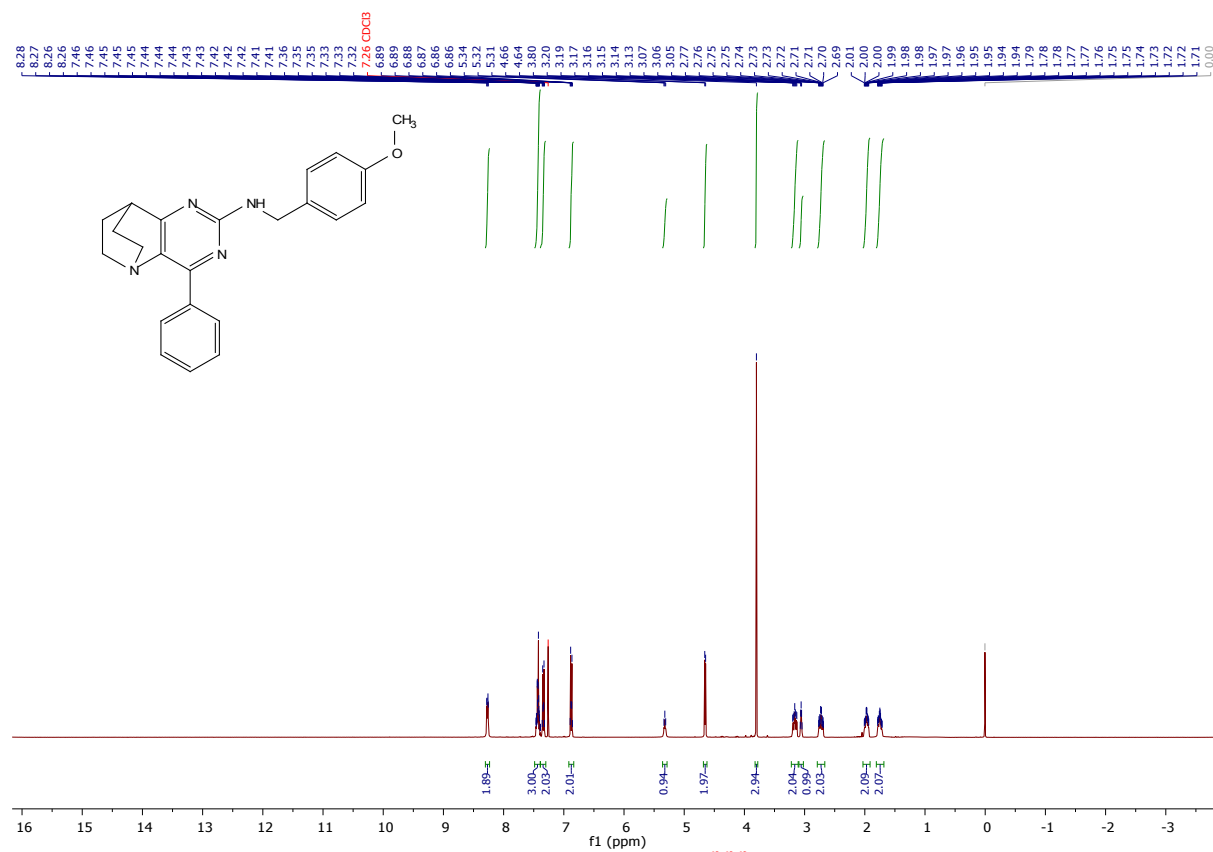


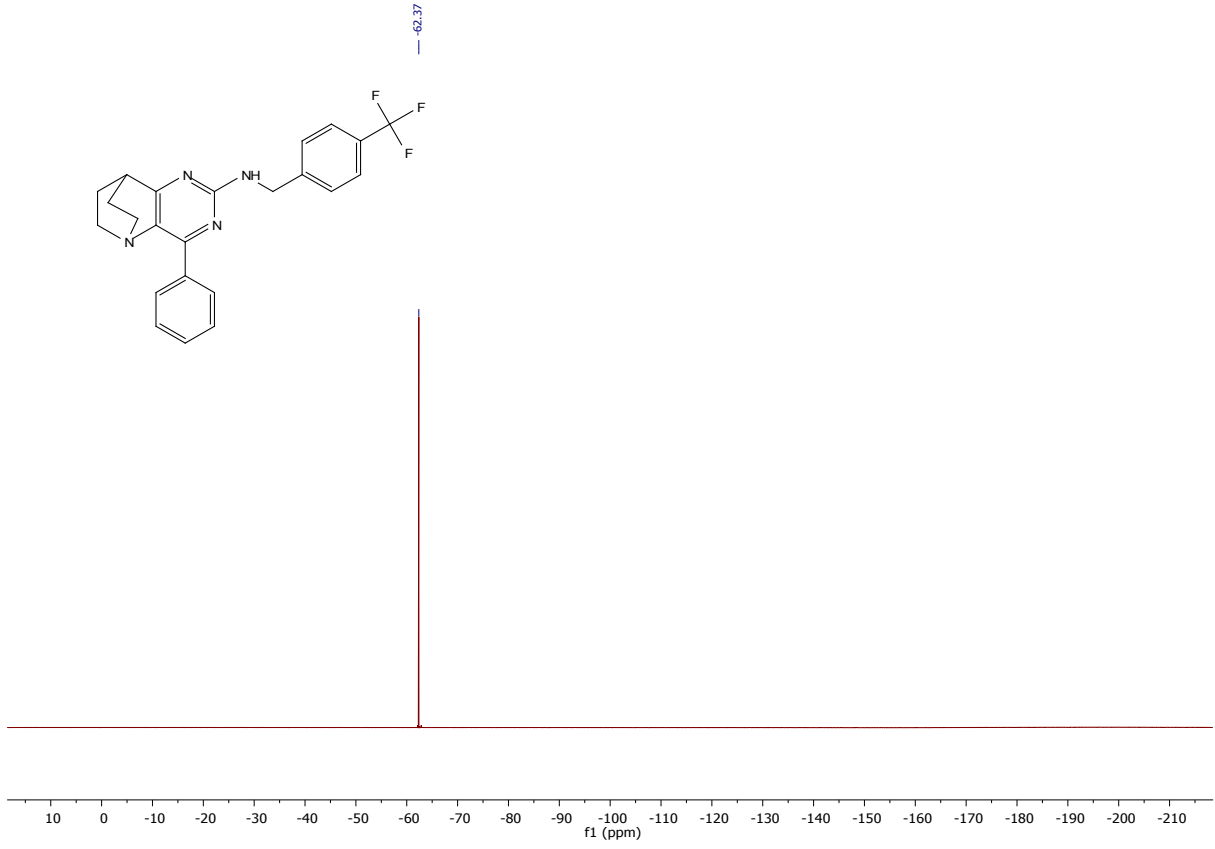
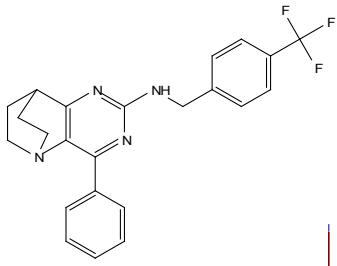


N-Benzyl-4-phenyl-7,8-dihydro-6H-5,8-ethanopyrido[3,2-d]pyrimidin-2-amine (17)

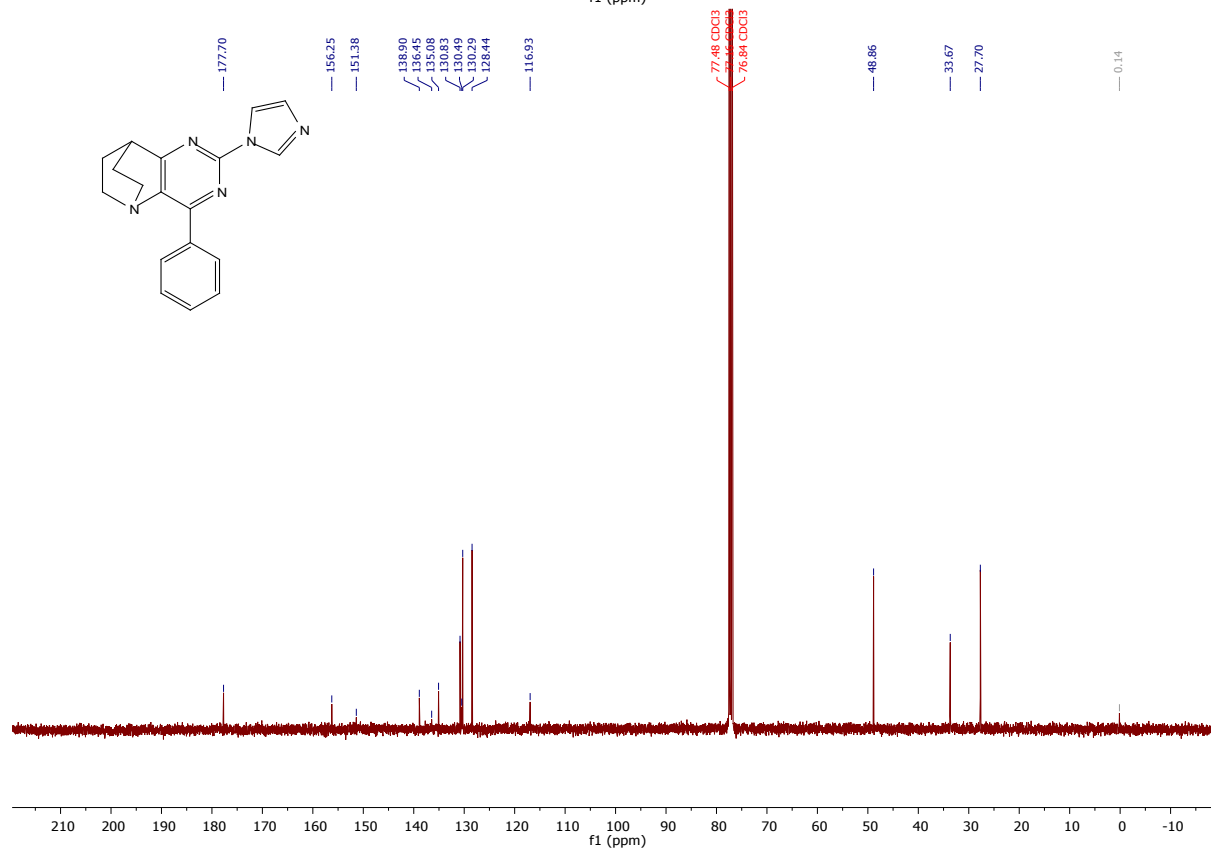
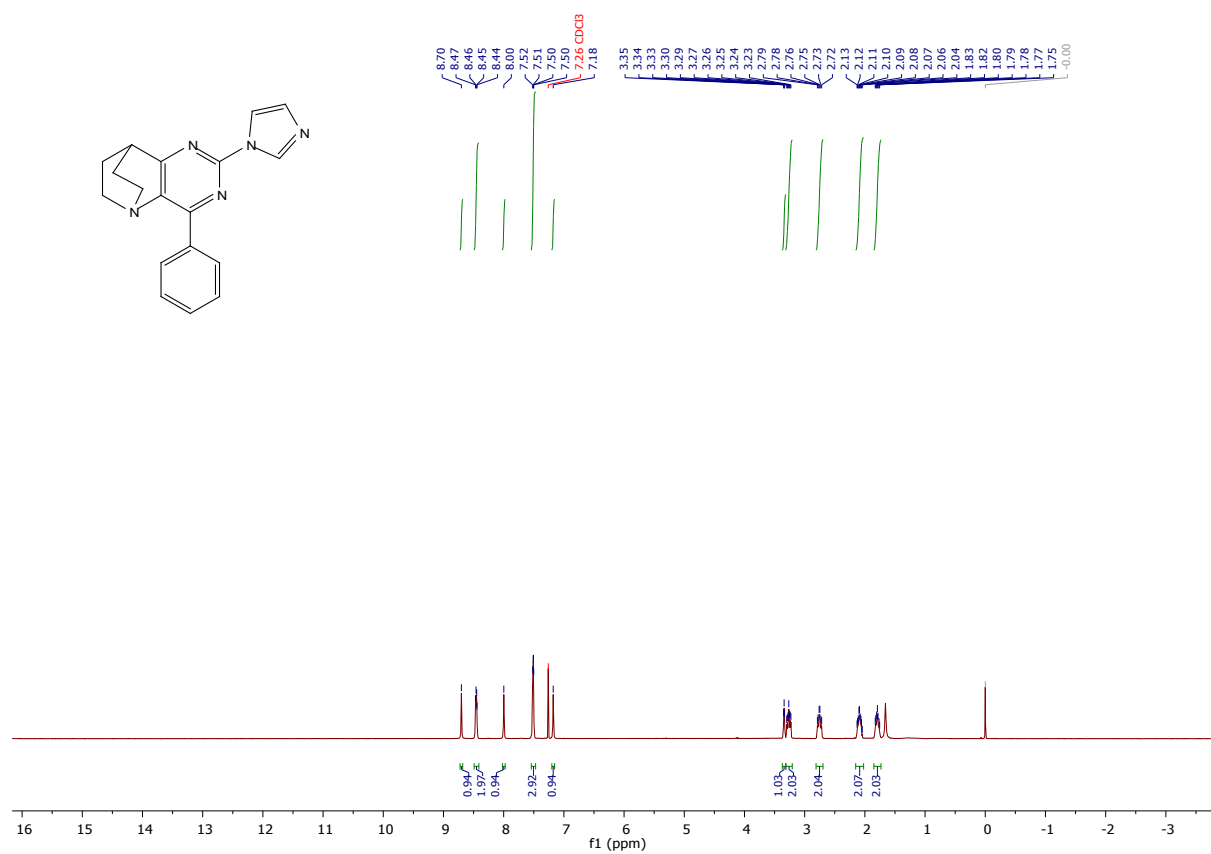


N-(4-Methoxybenzyl)-4-phenyl-7,8-dihydro-6H-5,8-ethanopyrido[3,2-d]pyrimidin-2-amine (18)

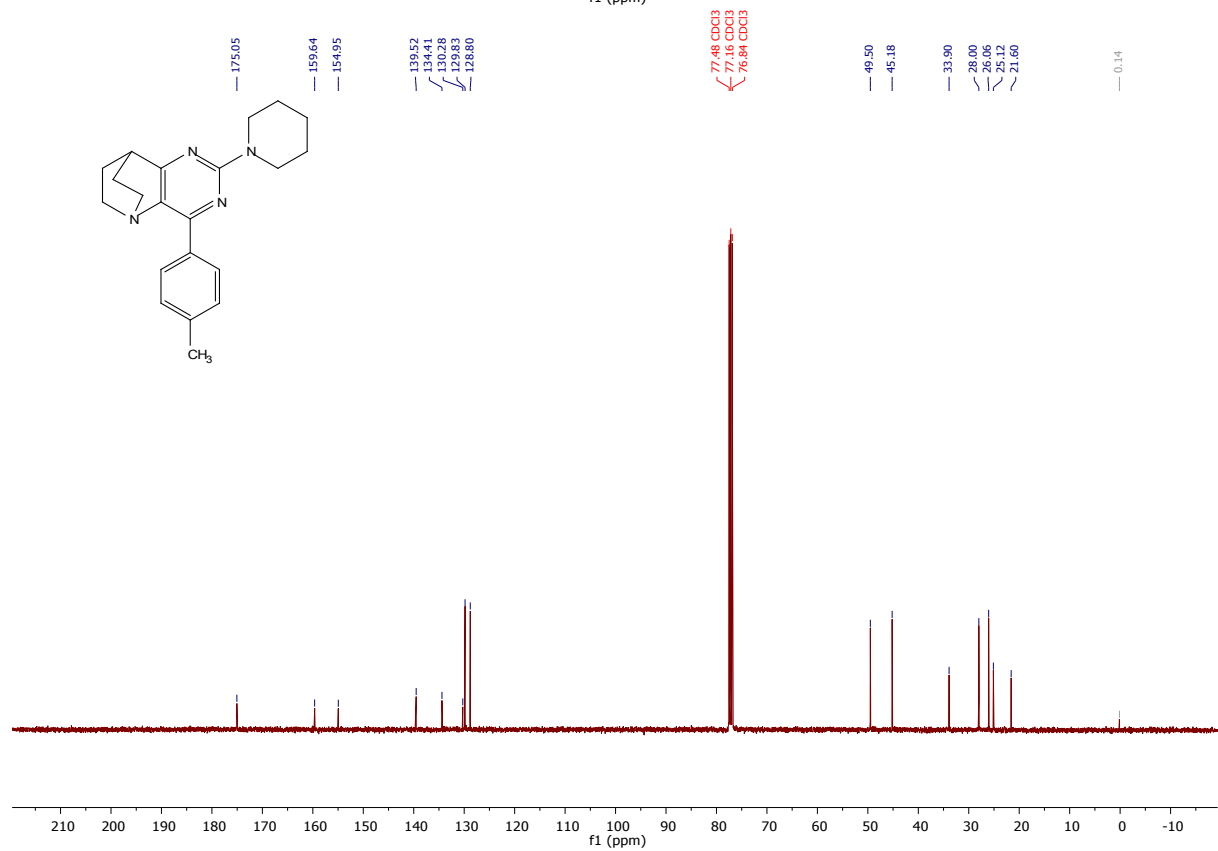
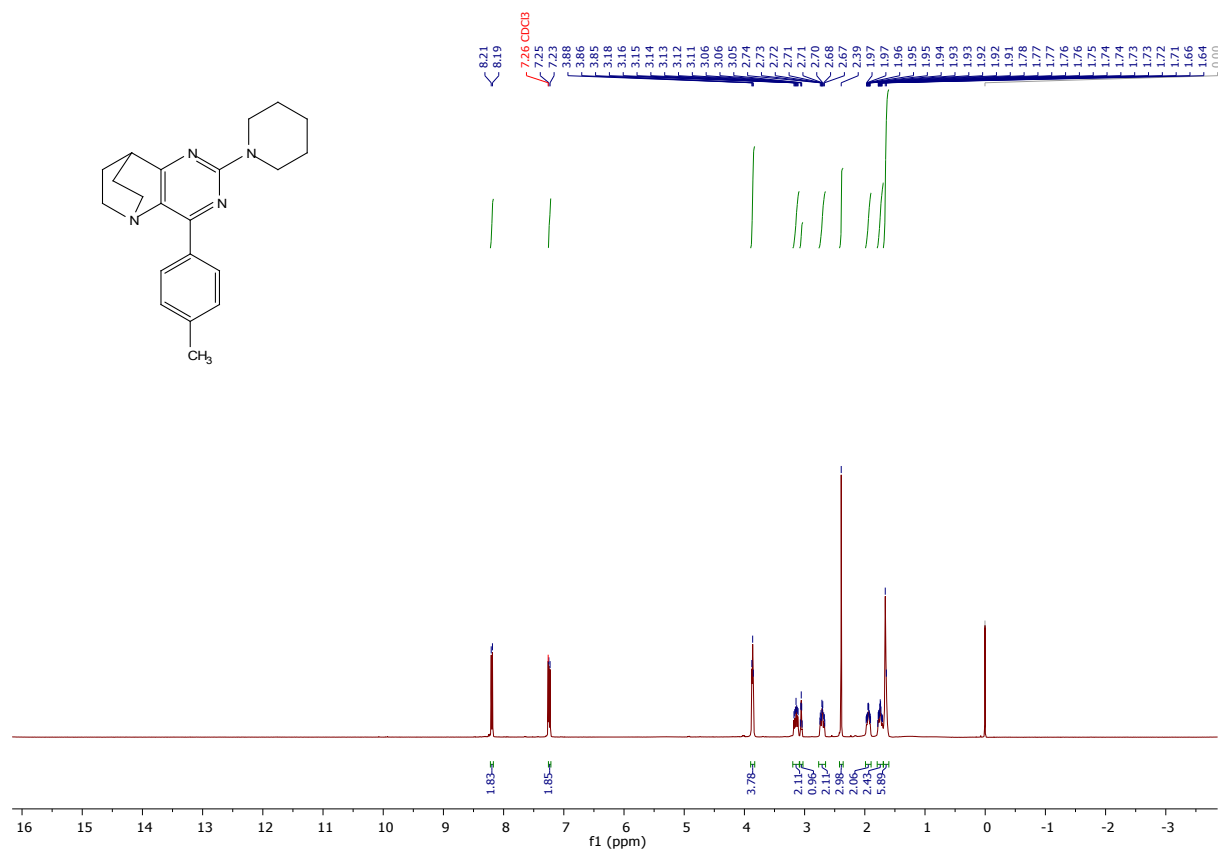




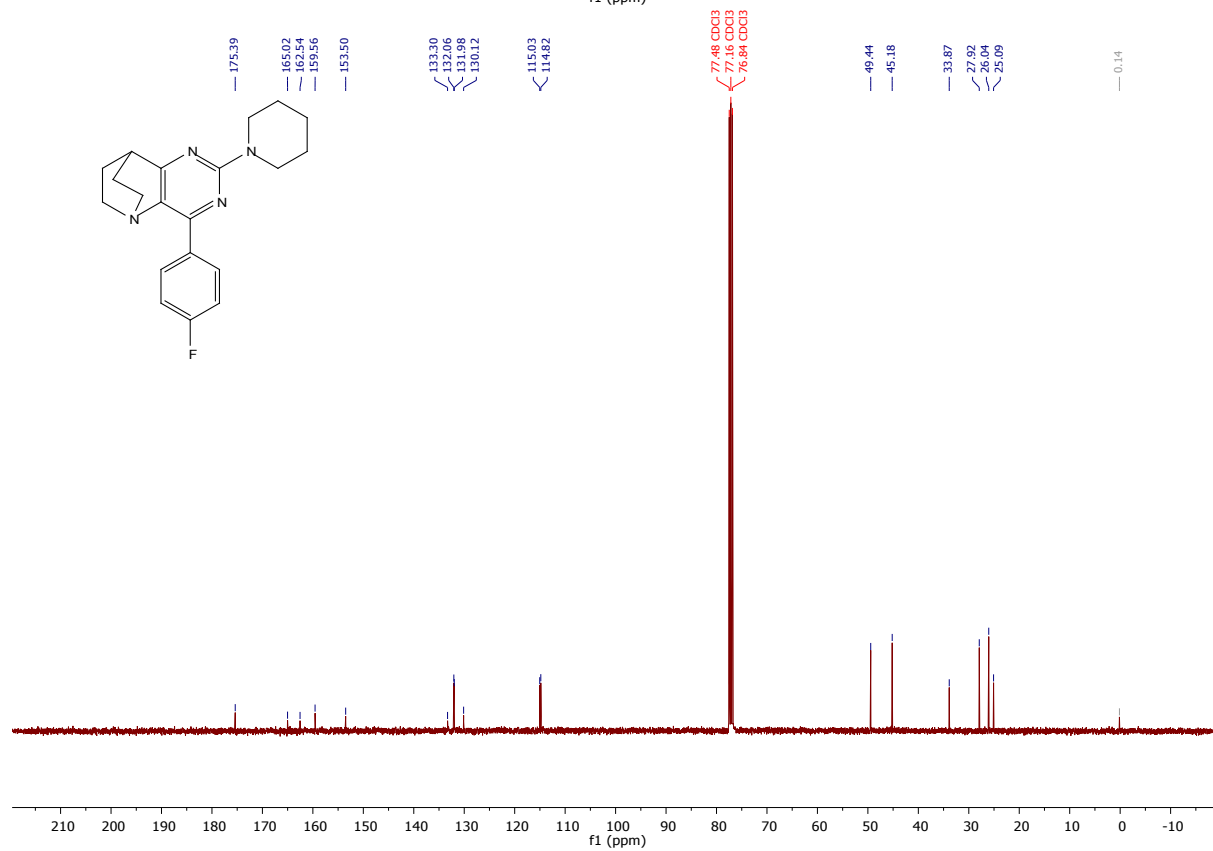
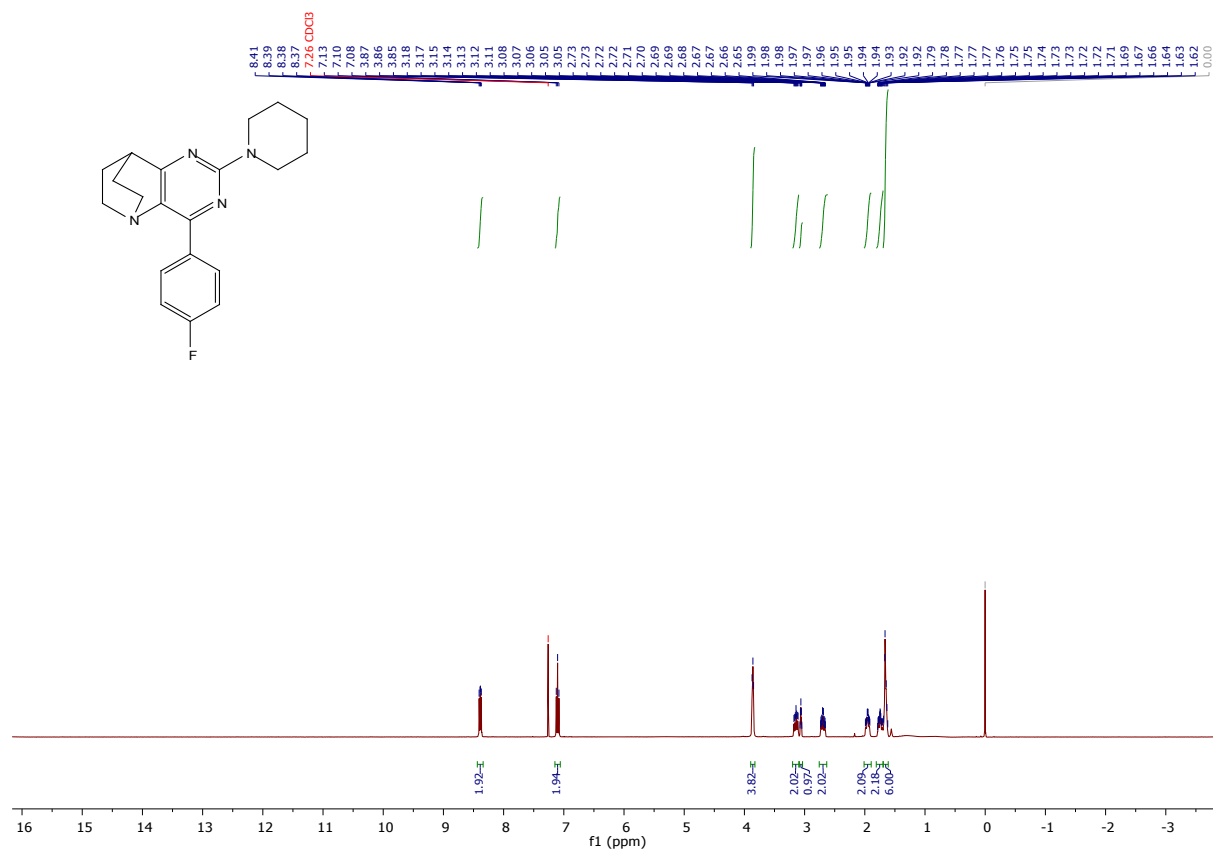
2-(1*H*-Imidazol-1-yl)-4-phenyl-7,8-dihydro-6*H*-5,8-ethanopyrido[3,2-*d*]pyrimidine (20)

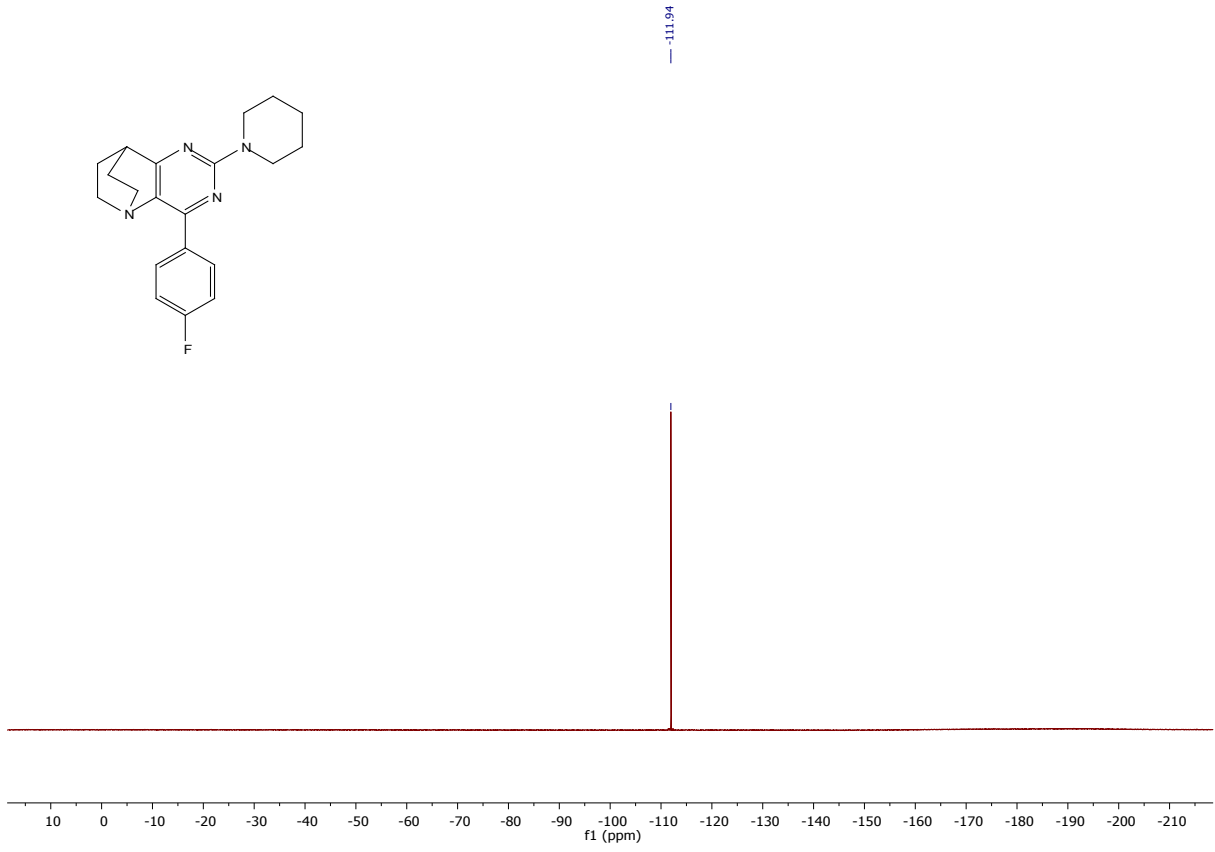
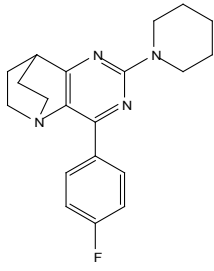


2-(Piperidin-1-yl)-4-(*p*-tolyl)-7,8-dihydro-6H-5,8-ethanopyrido[3,2-*d*]pyrimidine (23)

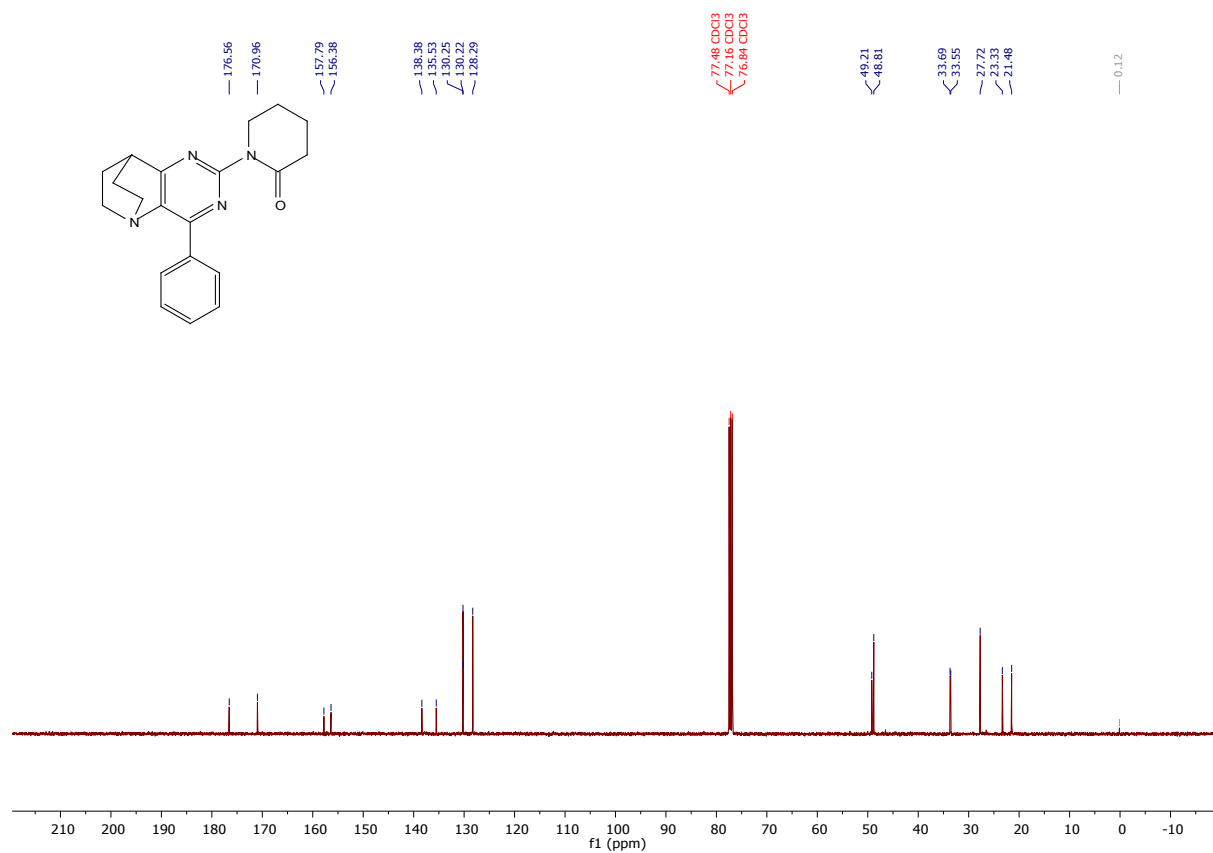
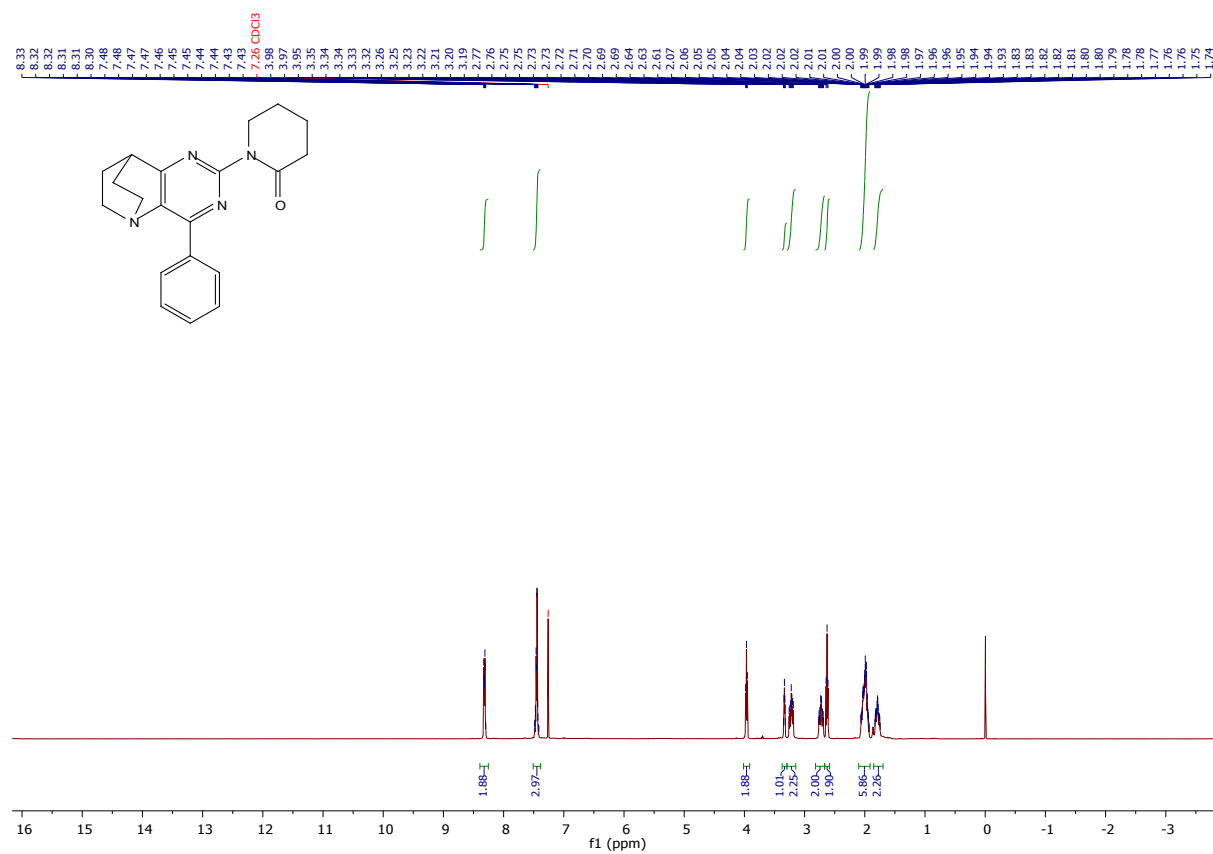


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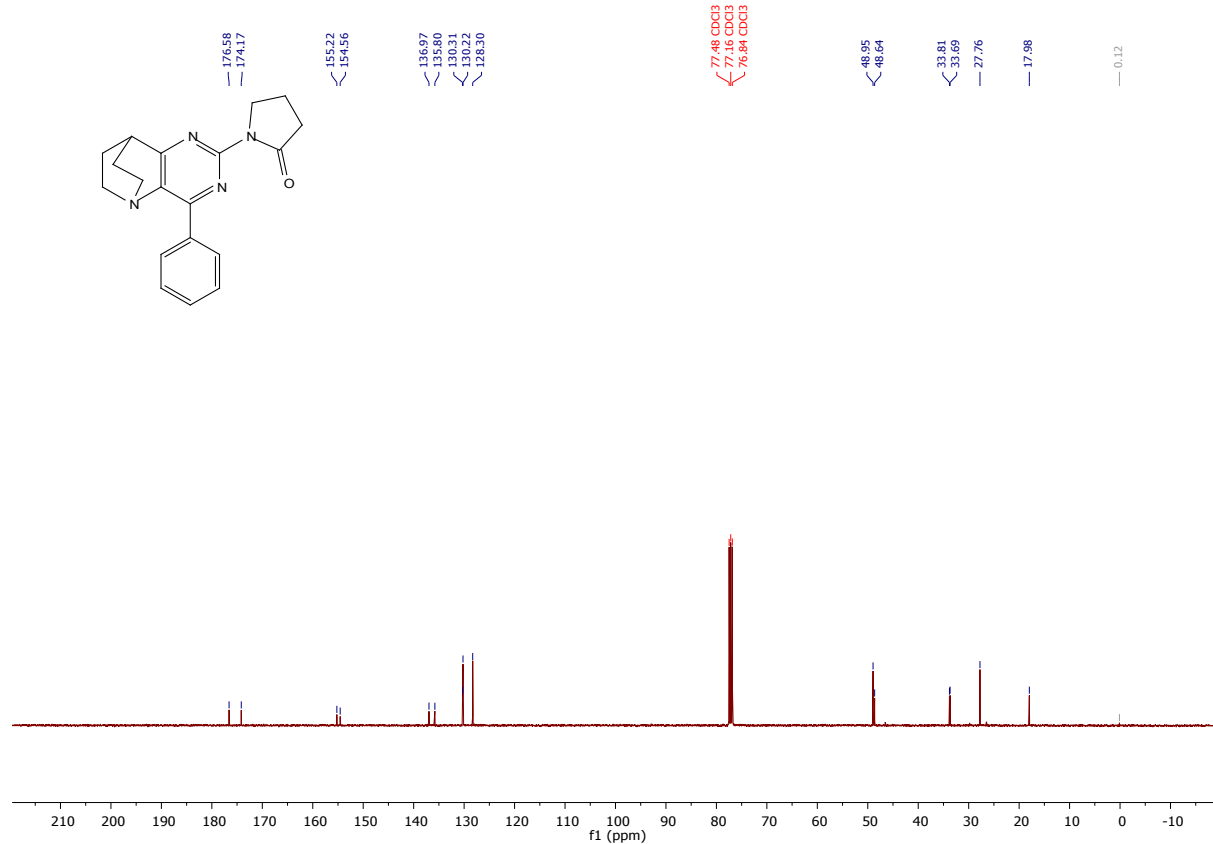
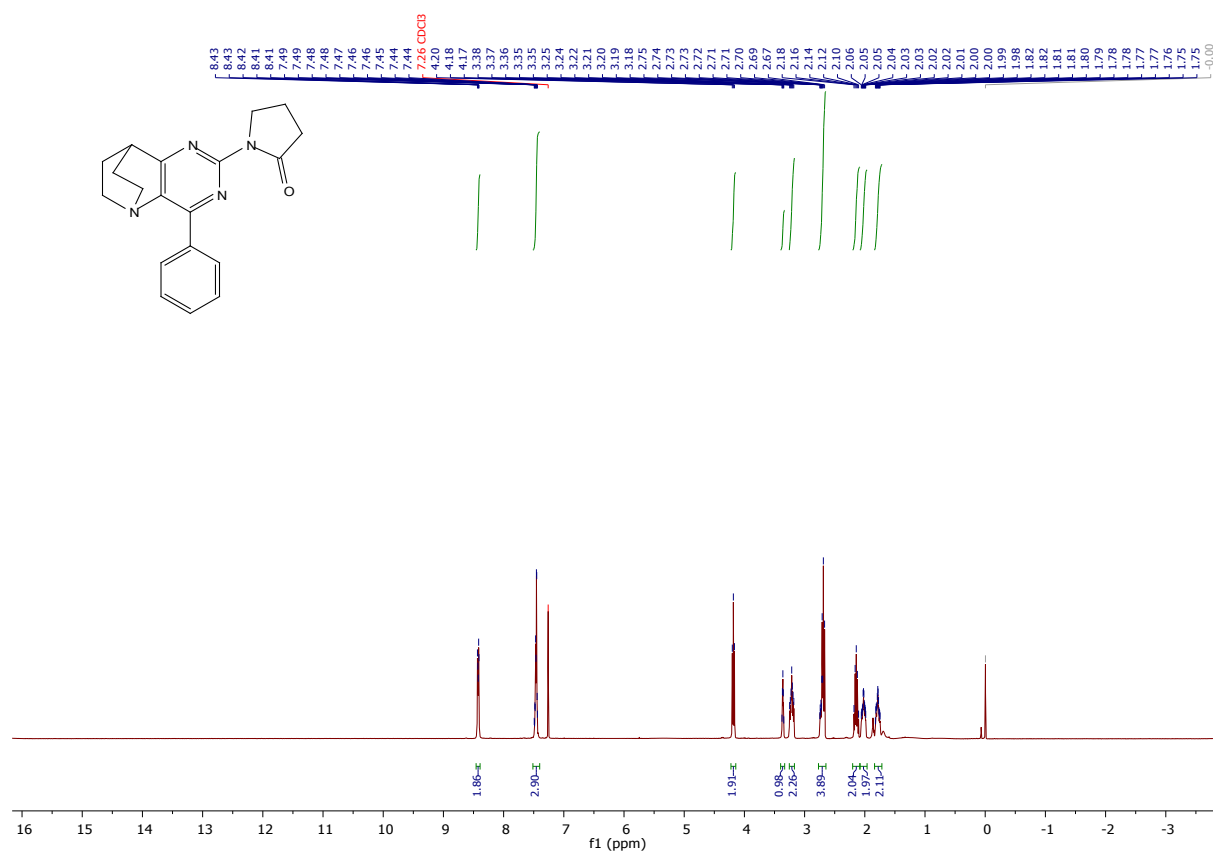




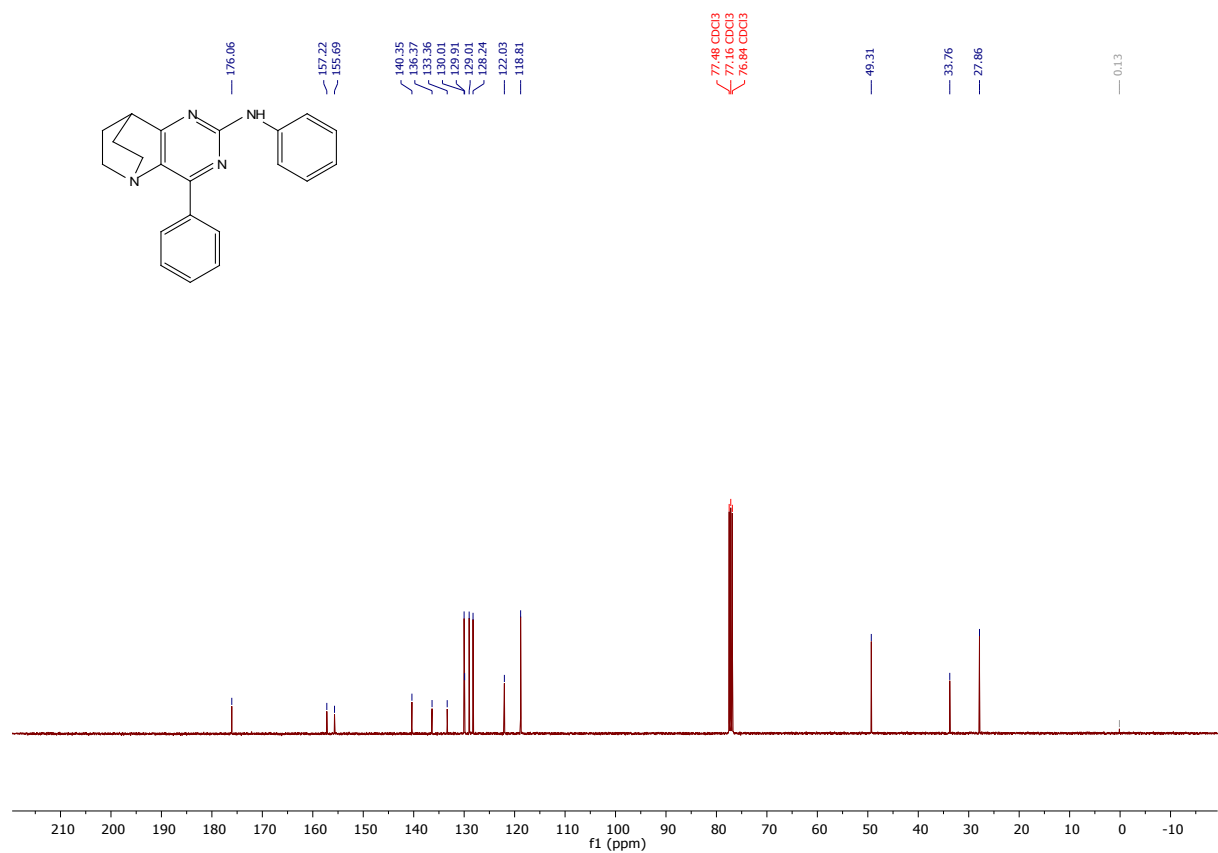
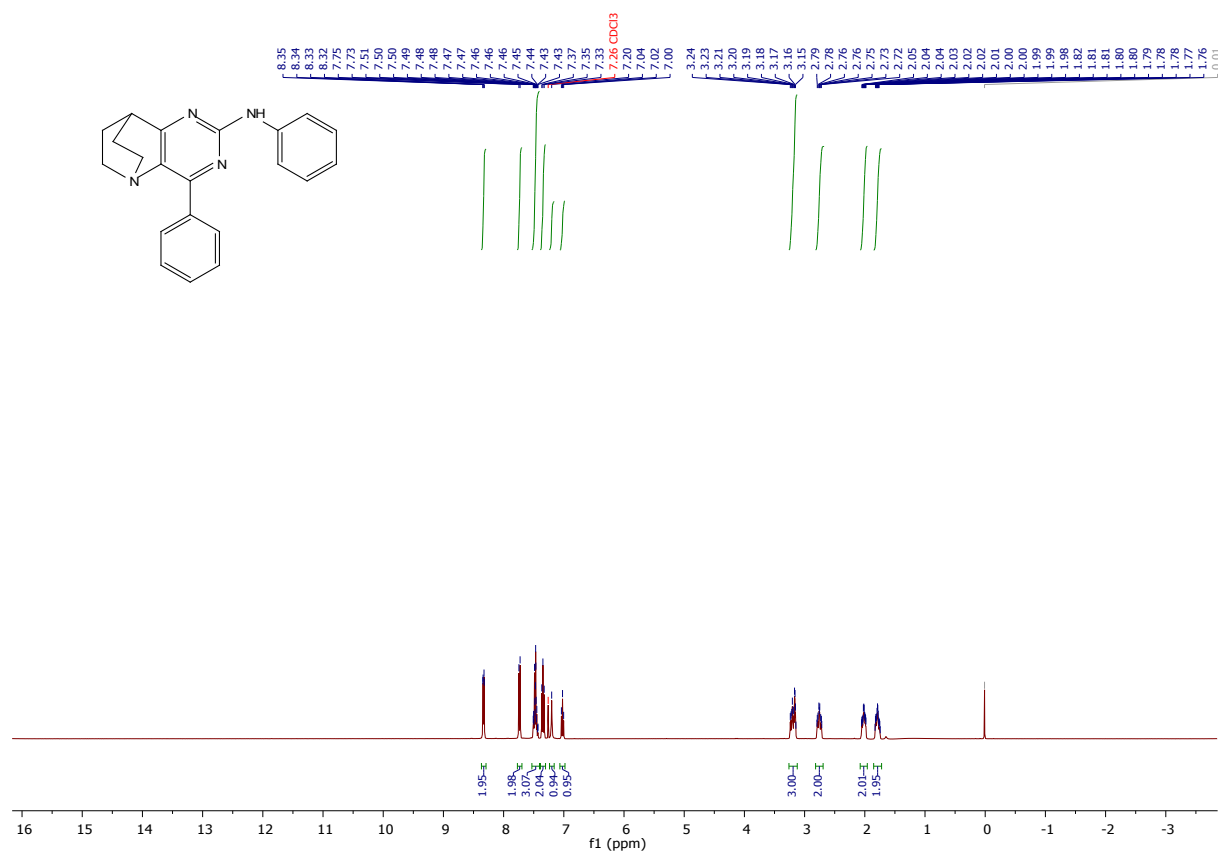
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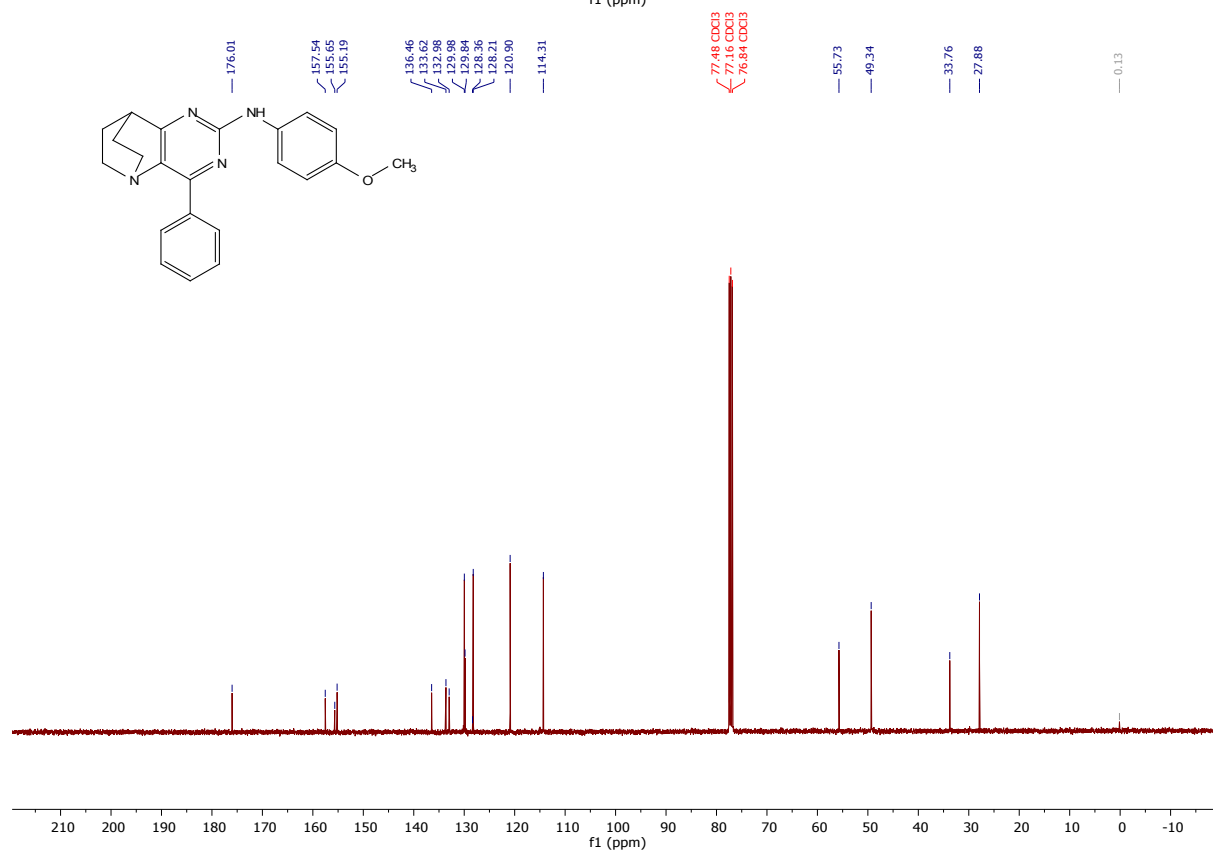
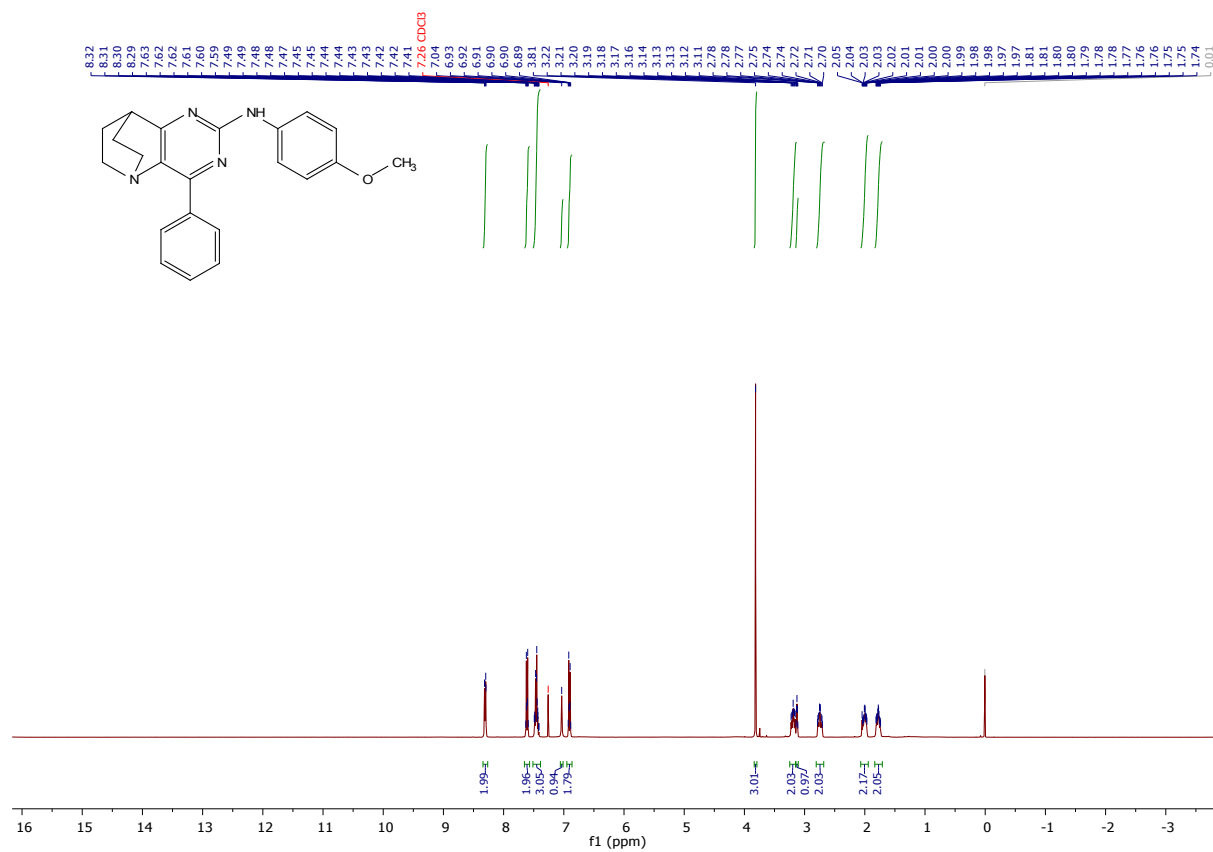
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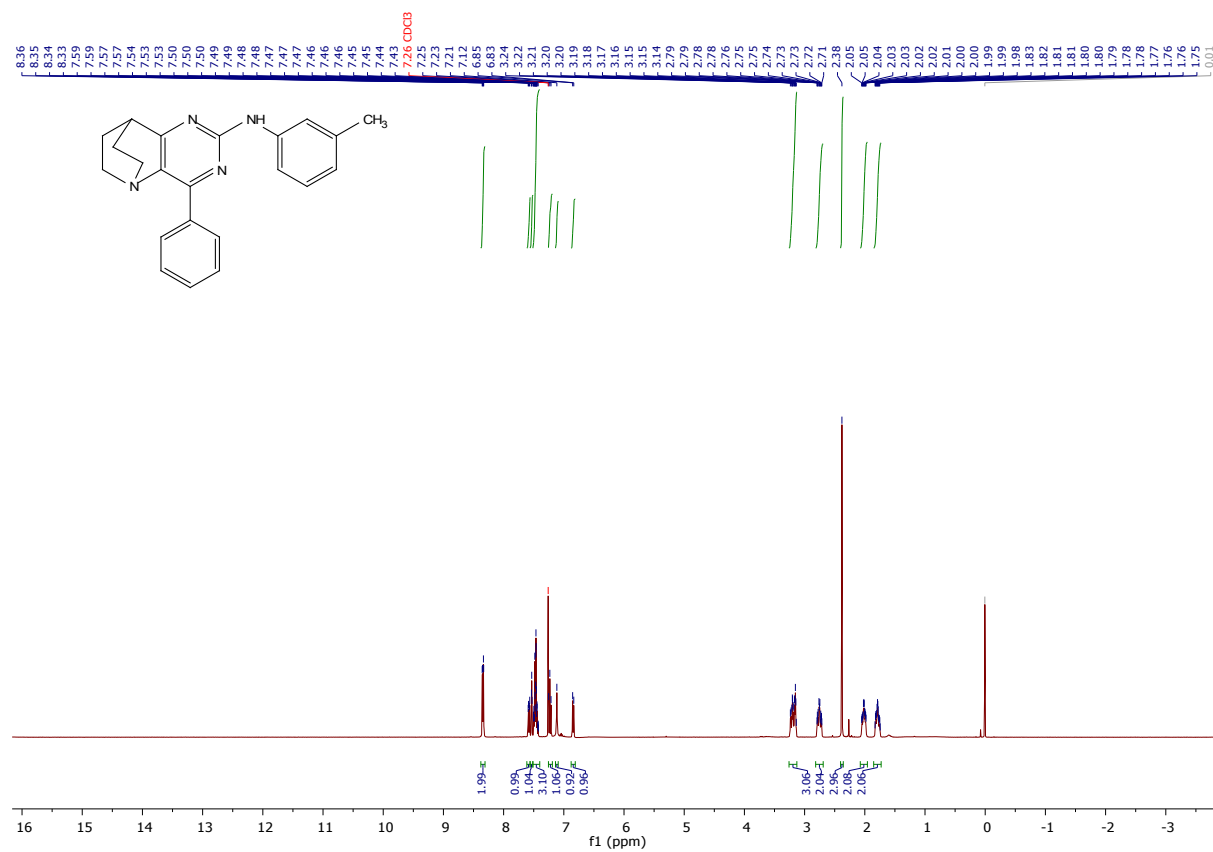
N,4-Diphenyl-7,8-dihydro-6H-5,8-ethanopyrido[3,2-d]pyrimidin-2-amine (24)



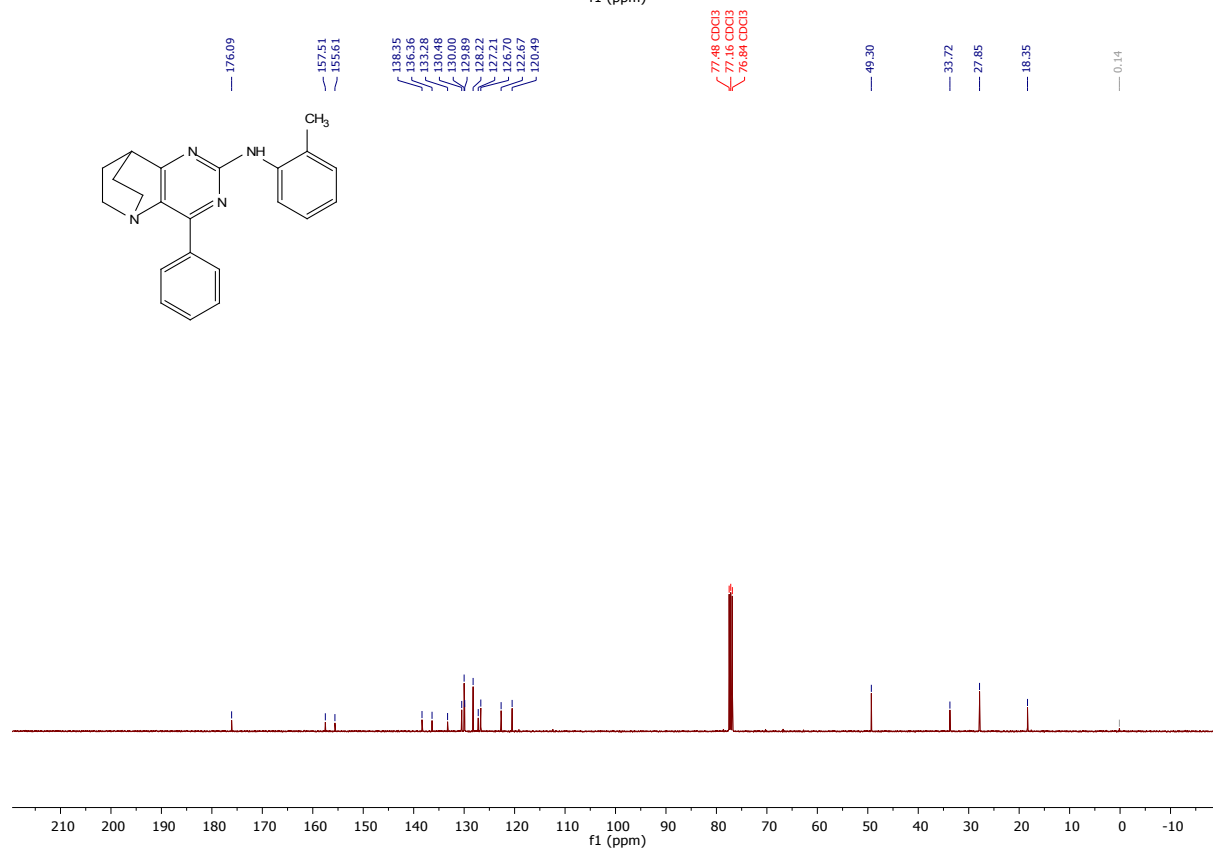
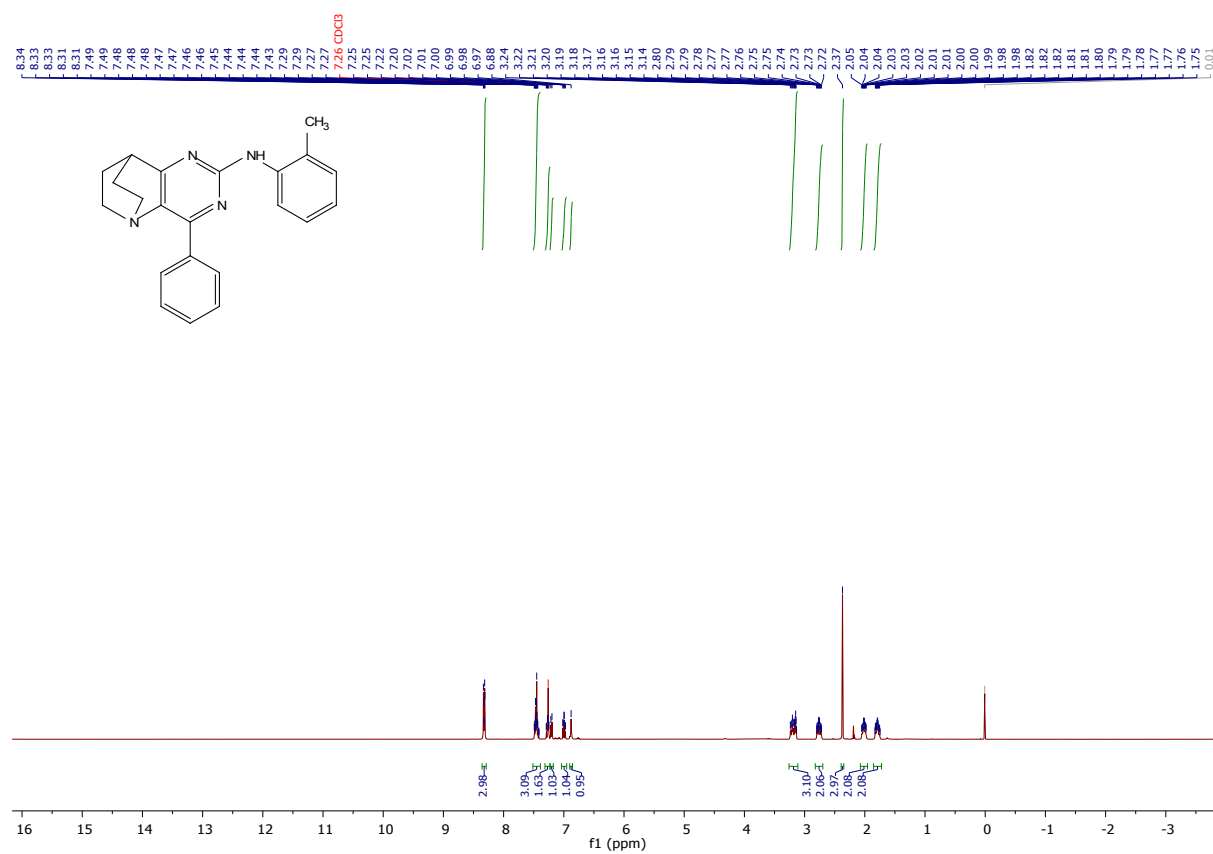
N-(4-Methoxyphenyl)-4-phenyl-7,8-dihydro-6H-5,8-ethanopyrido[3,2-d]pyrimidin-2-amine (25)



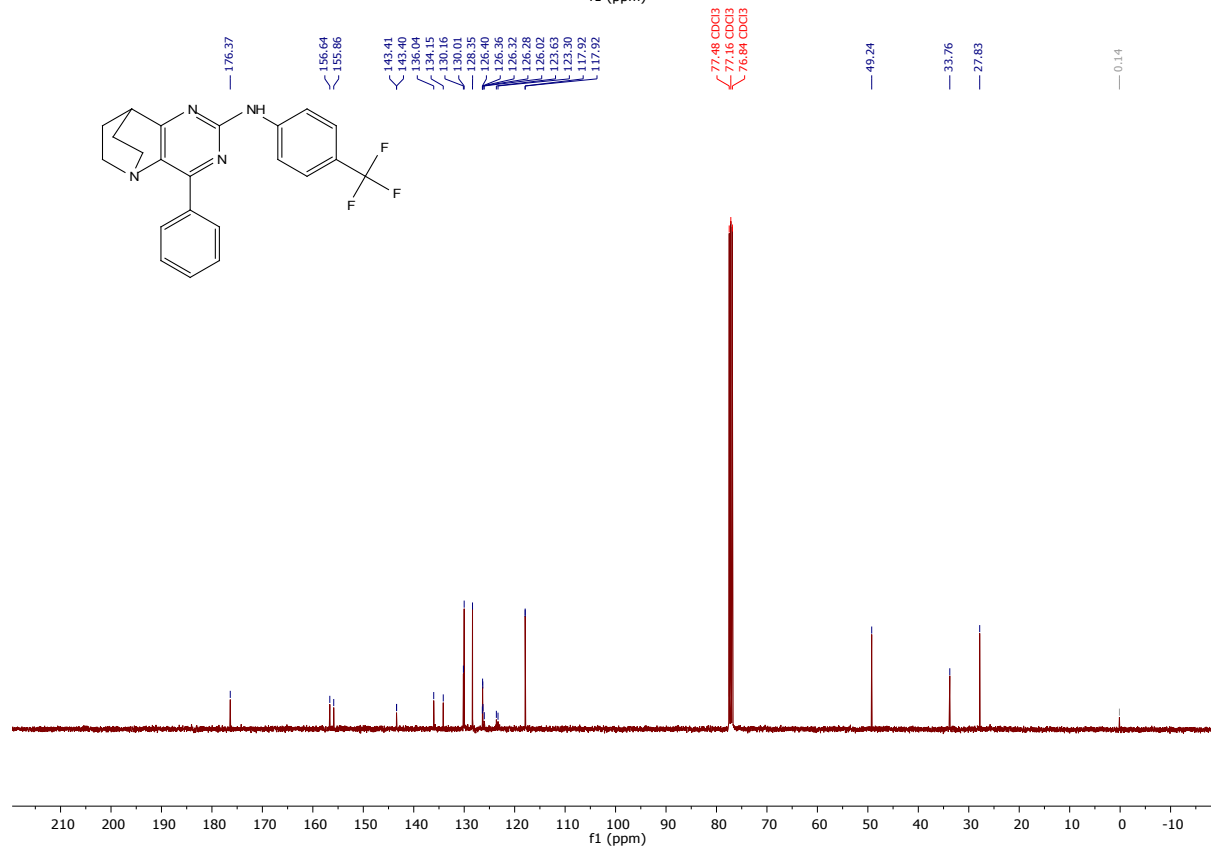
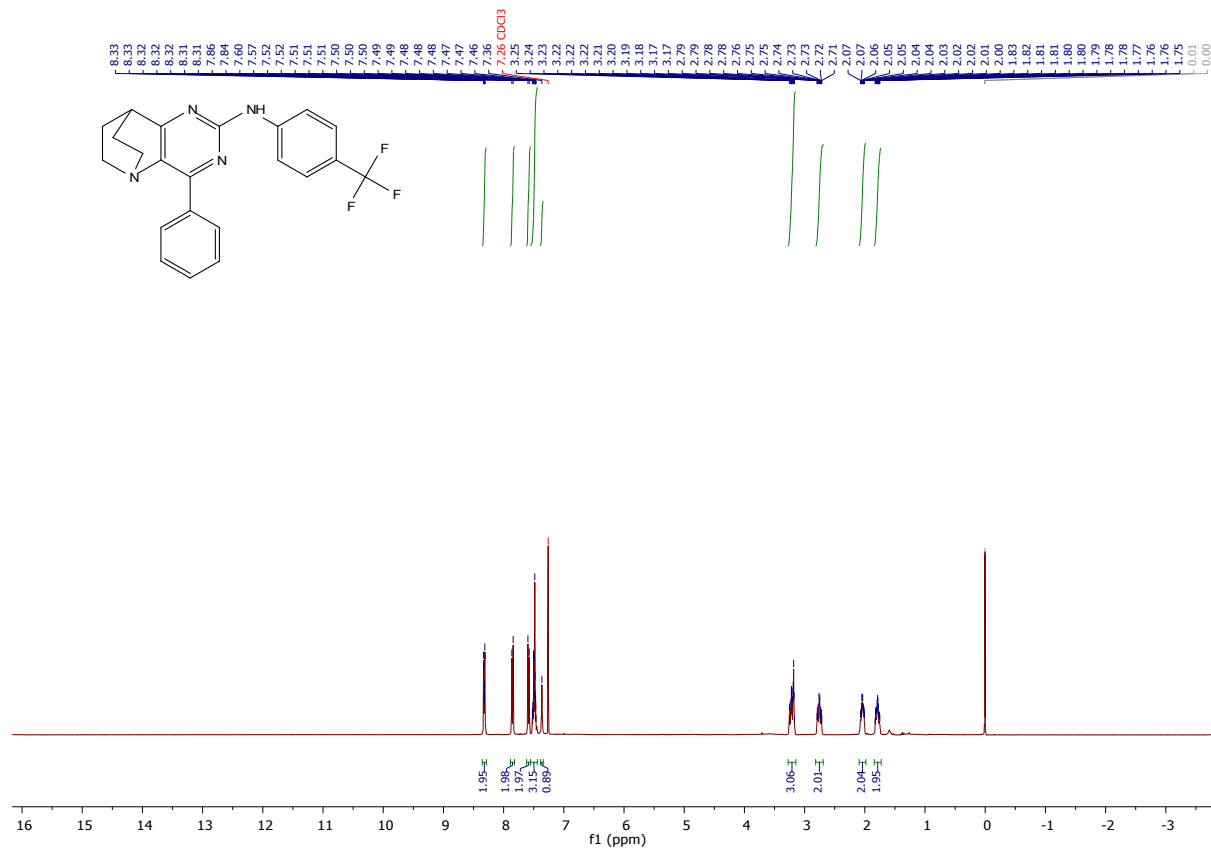
4-Phenyl-N-(*m*-tolyl)-7,8-dihydro-6H-5,8-ethanopyrido[3,2-*d*]pyrimidin-2-amine (27)

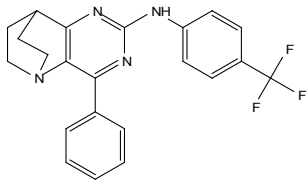


4-Phenyl-N-(*o*-tolyl)-7,8-dihydro-6H-5,8-ethanopyrido[3,2-*d*]pyrimidin-2-amine (28)

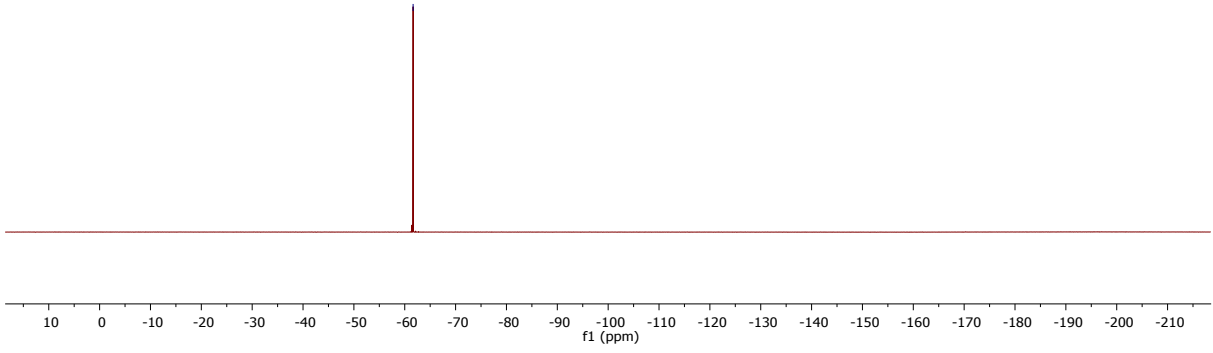


4-Phenyl-N-(4-(trifluoromethyl)phenyl)-7,8-dihydro-6H-5,8-ethanopyrido[3,2-d]pyrimidin-2-amine (29)

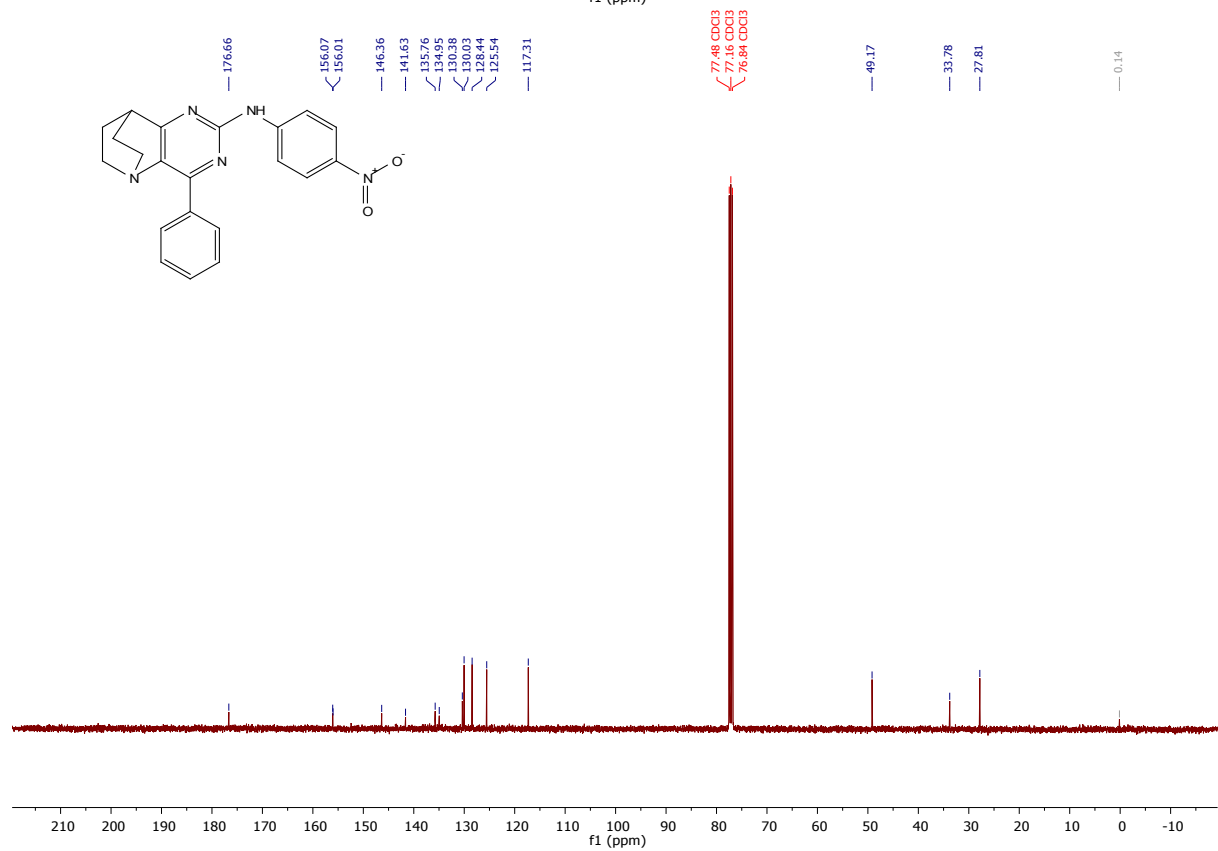
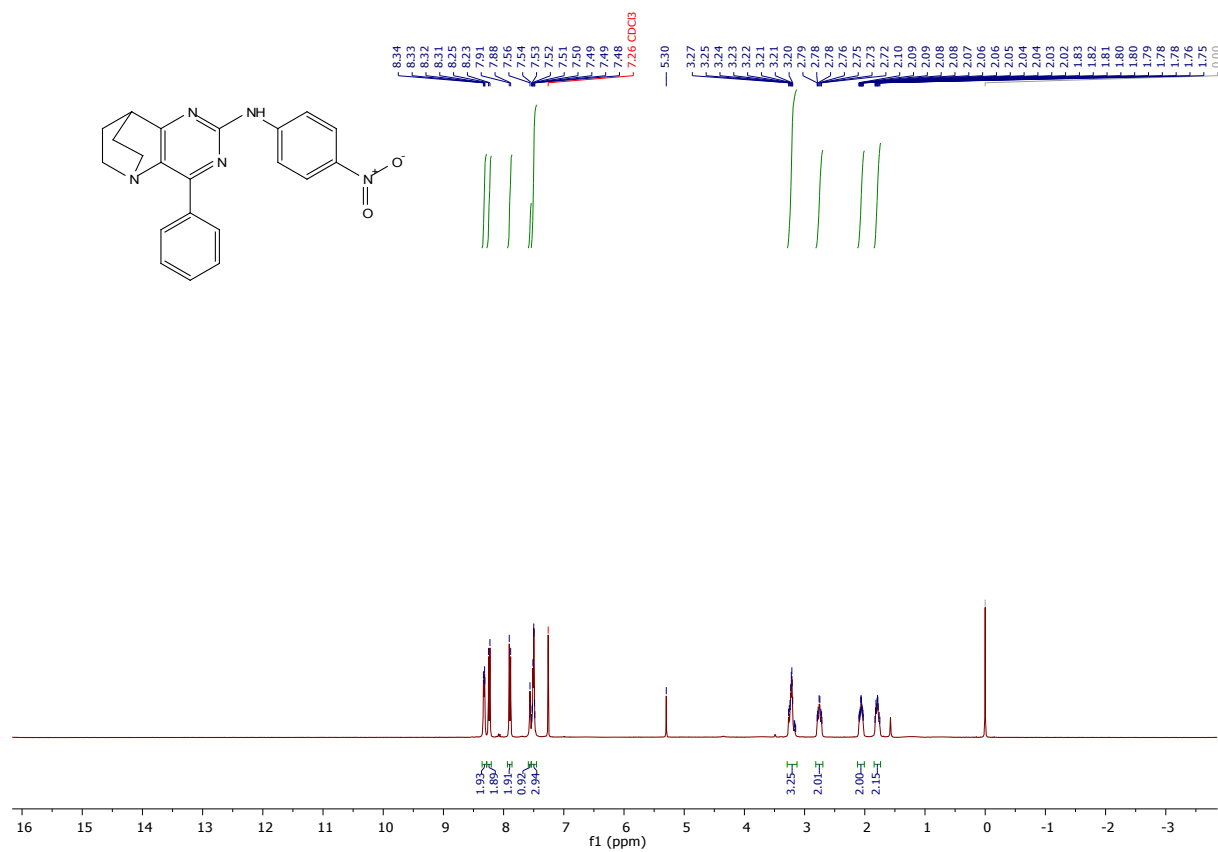




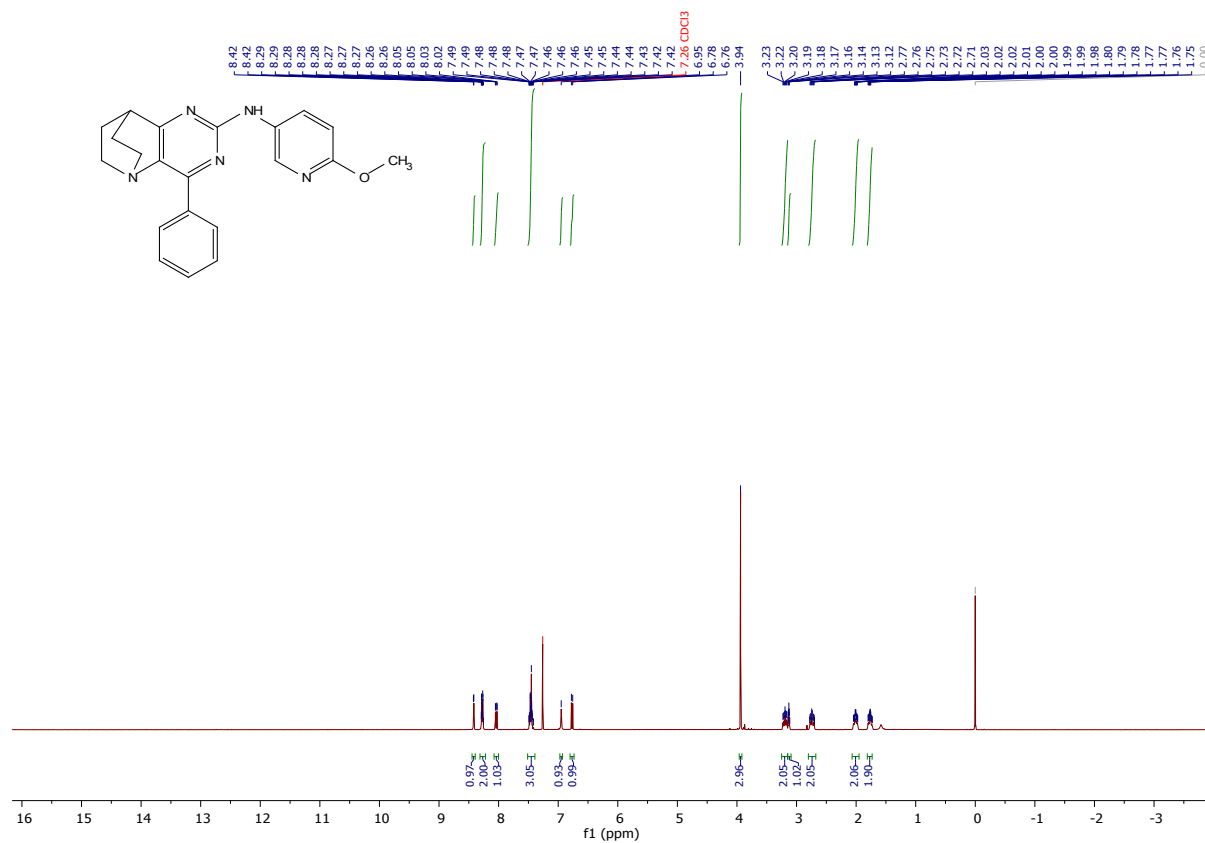
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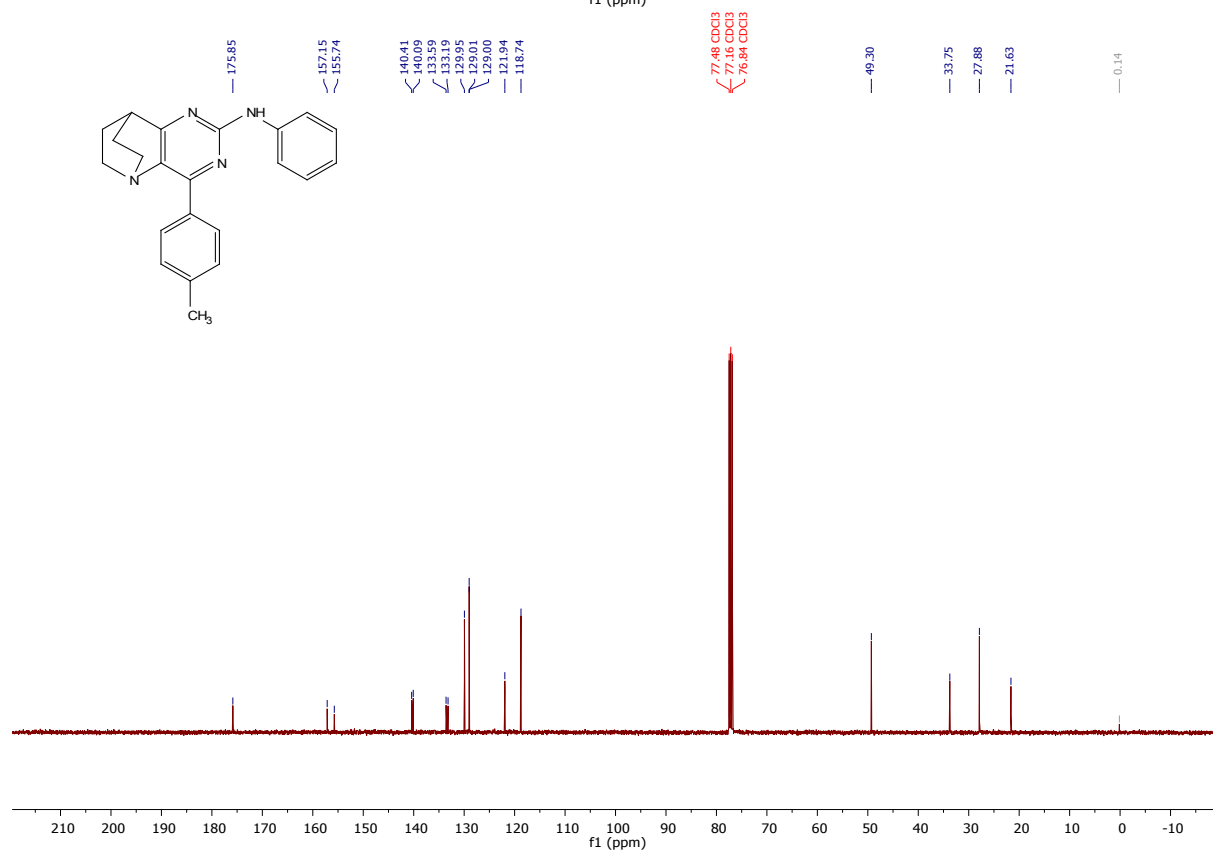
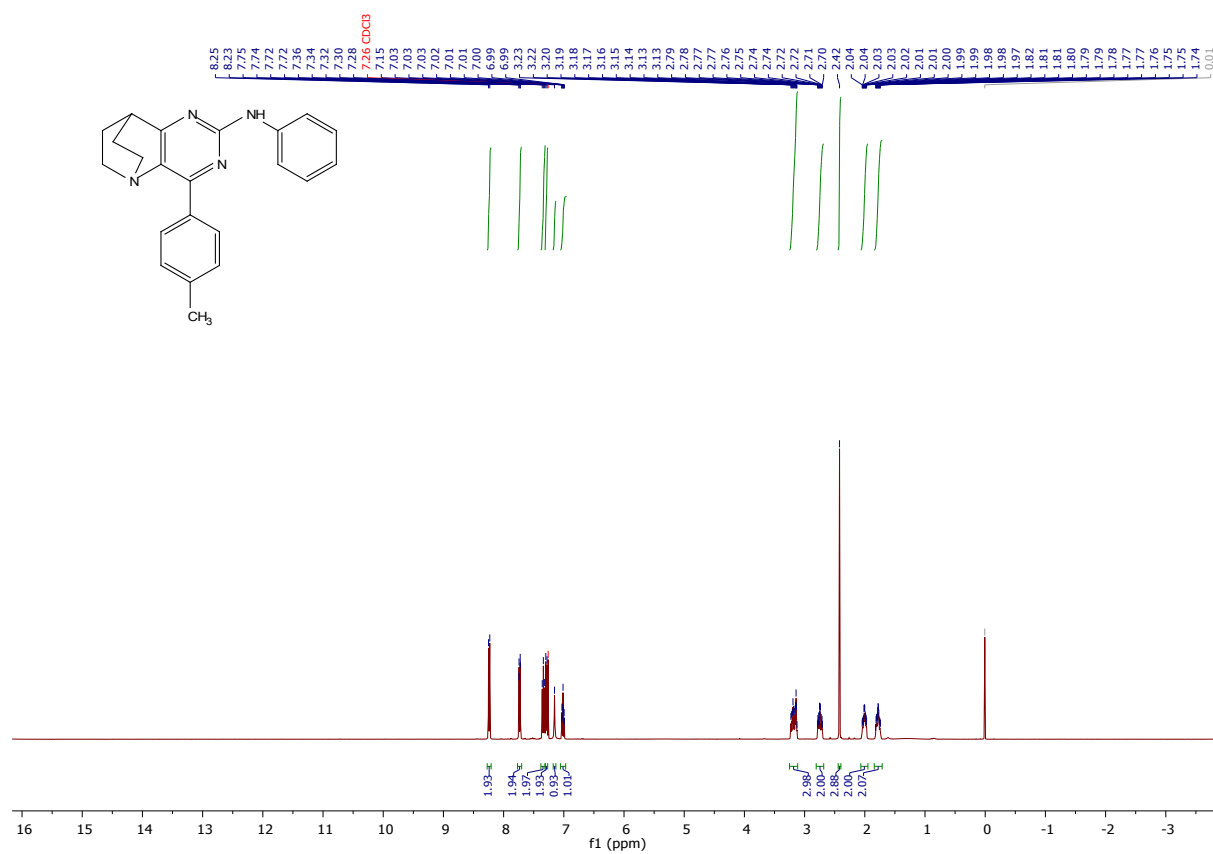
***N*-(4-Nitrophenyl)-4-phenyl-7,8-dihydro-6*H*-5,8-ethanopyrido[3,2-*d*]pyrimidin-2-amine (31)**



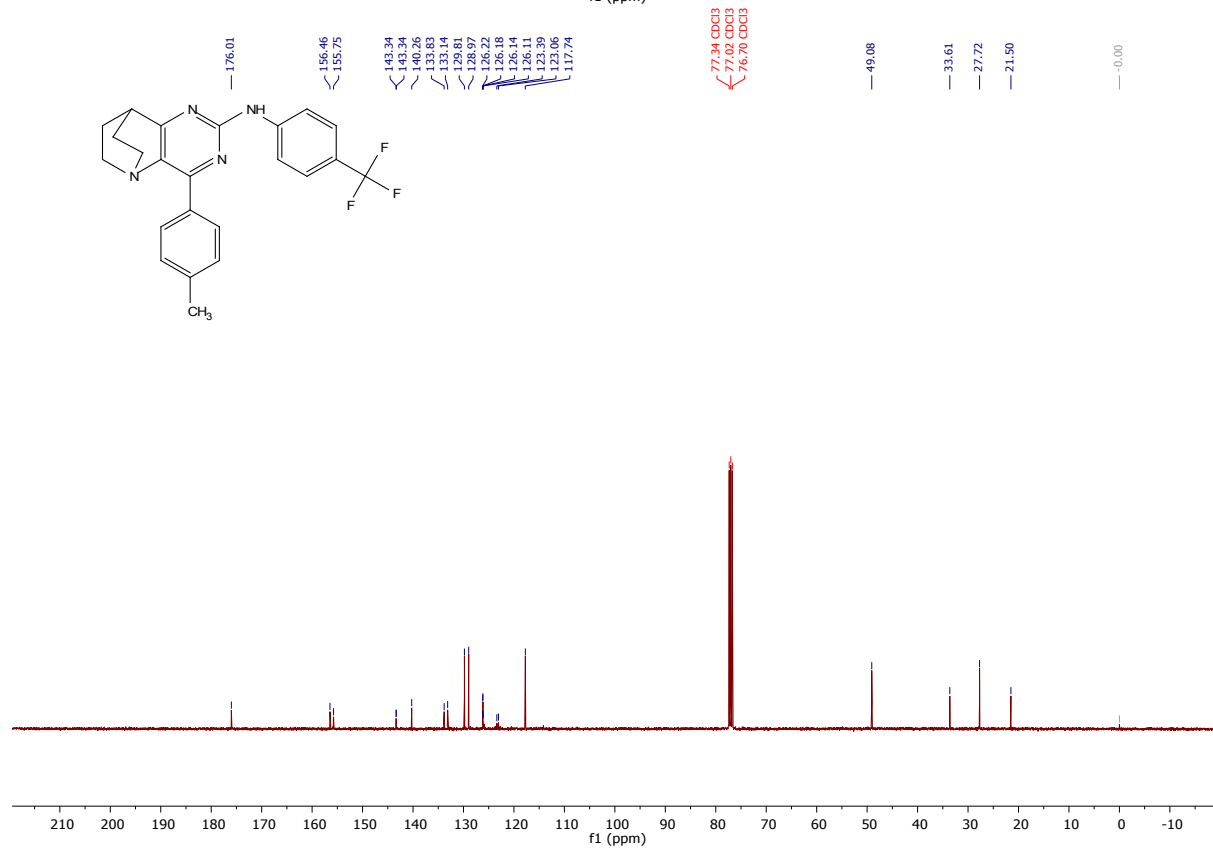
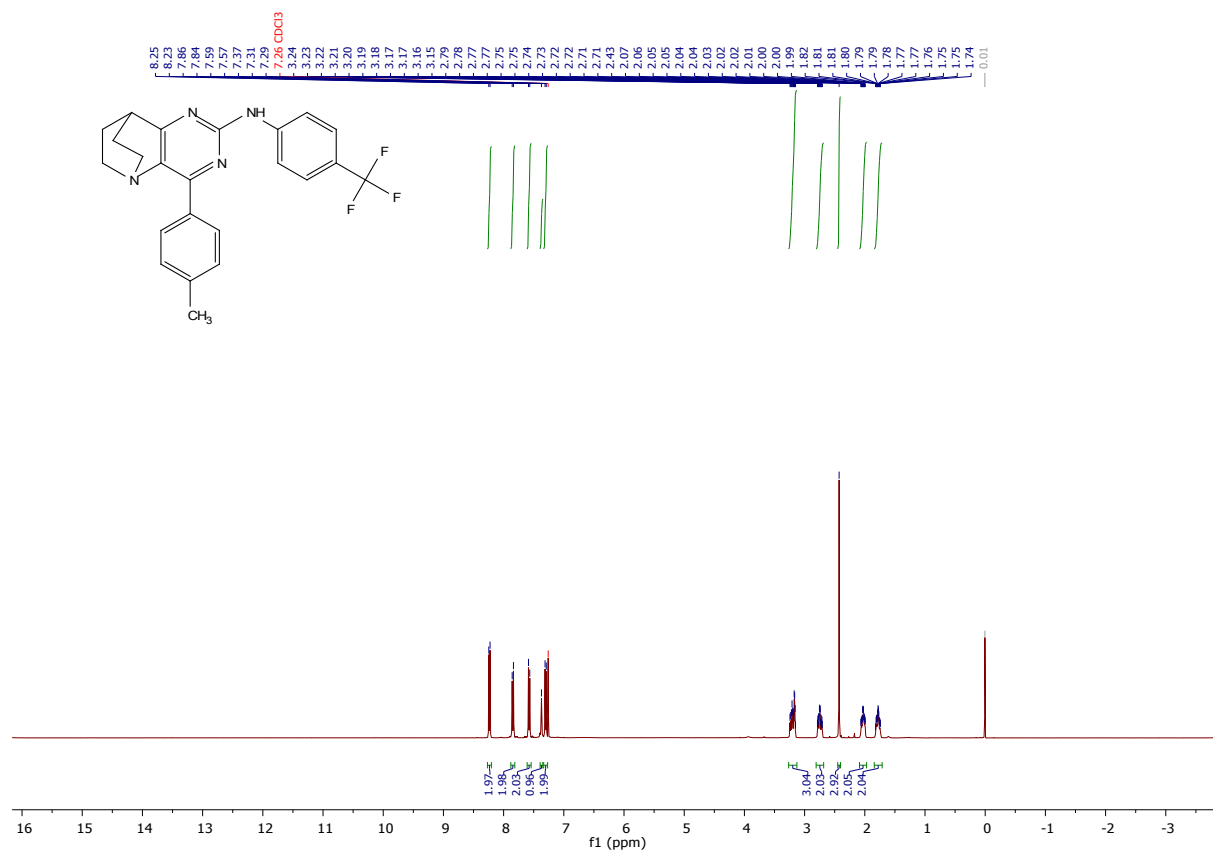
***N*-(6-Methoxypyridin-3-yl)-4-phenyl-7,8-dihydro-6*H*-5,8-ethanopyrido[3,2-*d*]pyrimidin-2-amine (33)**

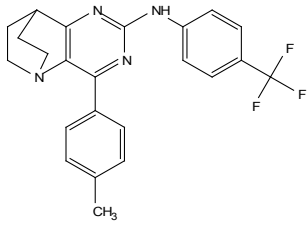


N-Phenyl-4-(p-tolyl)-7,8-dihydro-6H-5,8-ethanopyrido[3,2-d]pyrimidin-2-amine (34)

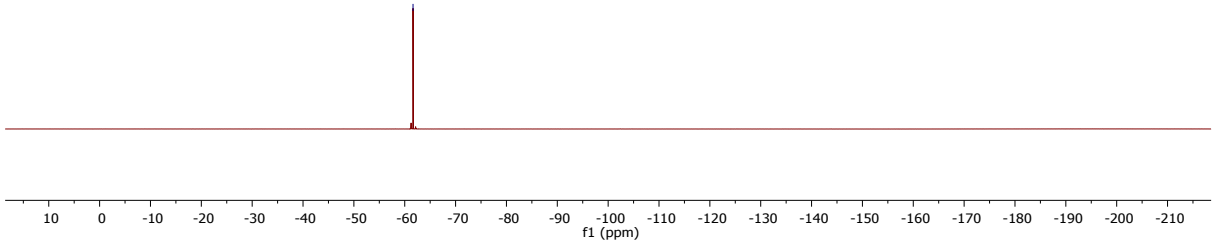


-(*p*-Tolyl)-*N*-(4-(trifluoromethyl)phenyl)-7,8-dihydro-6*H*-5,8-ethanopyrido[3,2-*d*]pyrimidin-2-amine (35)

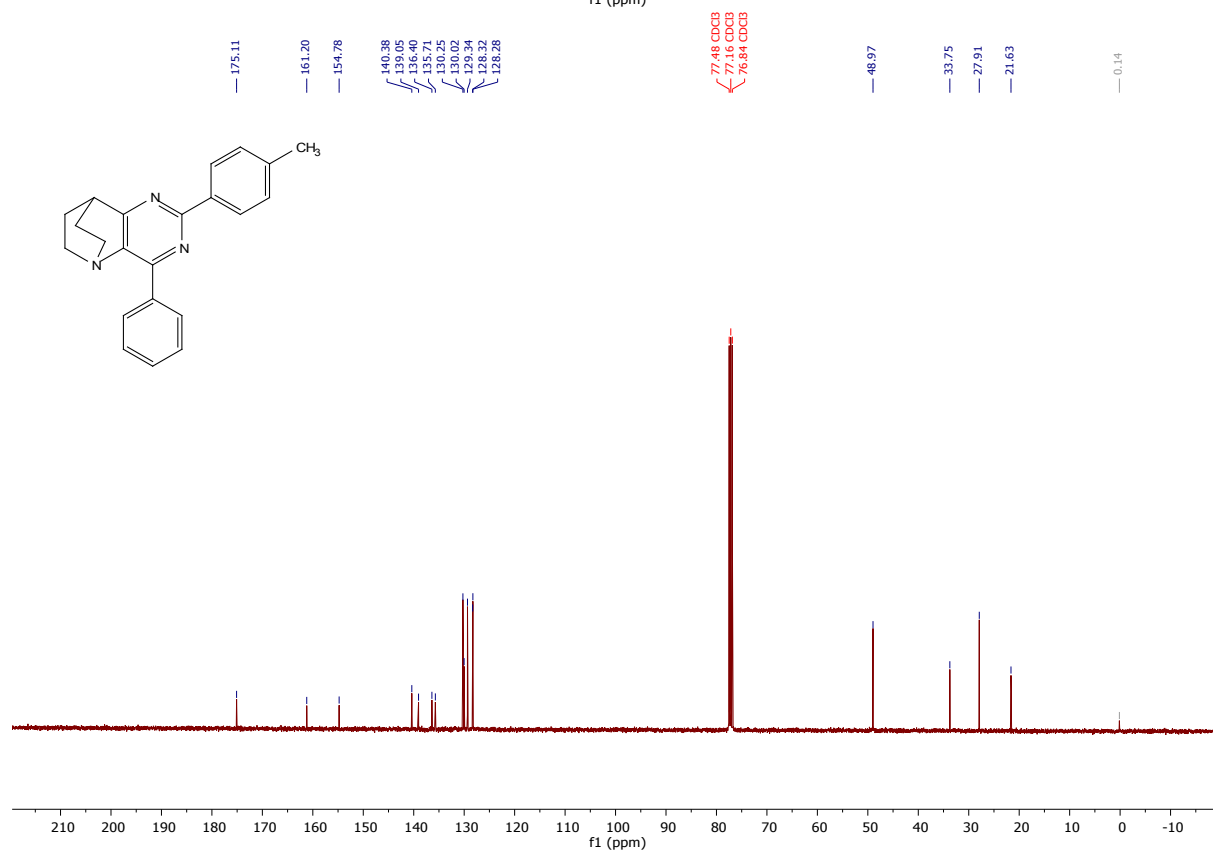
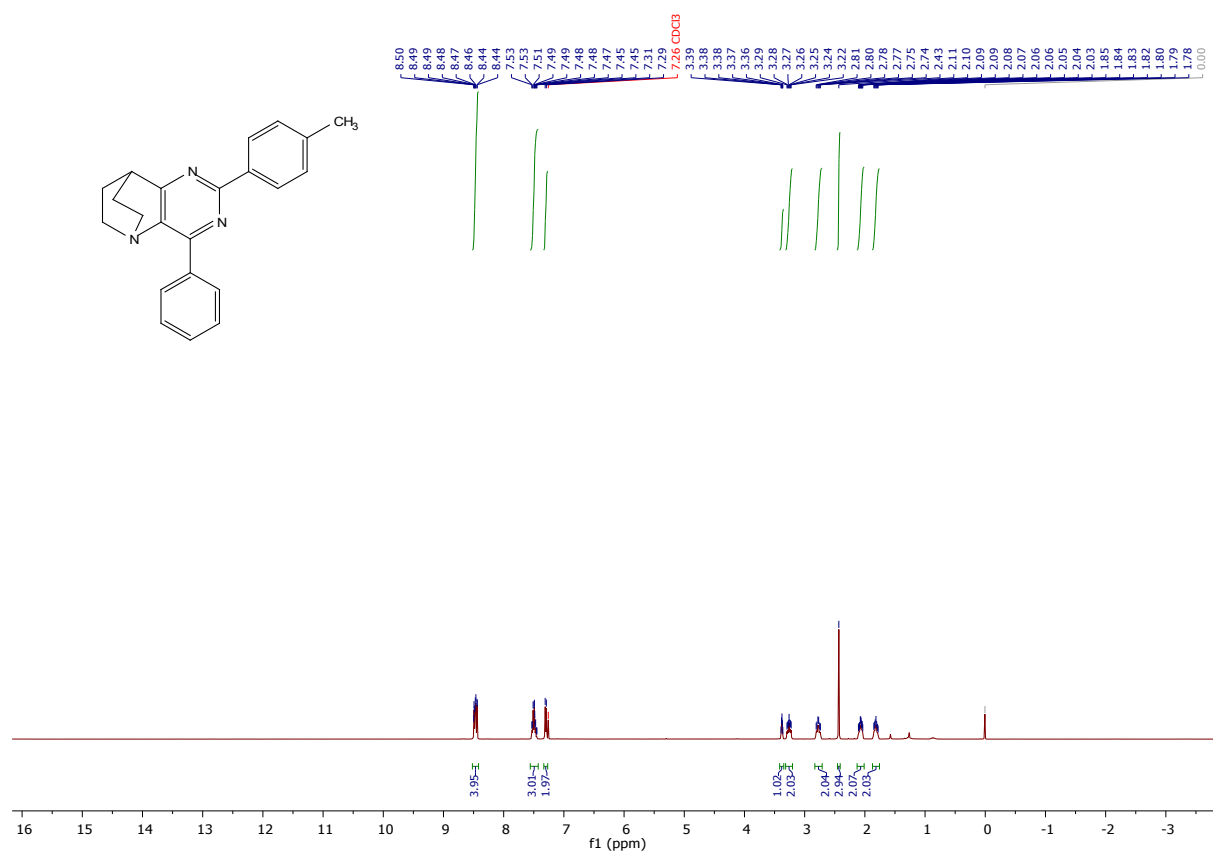




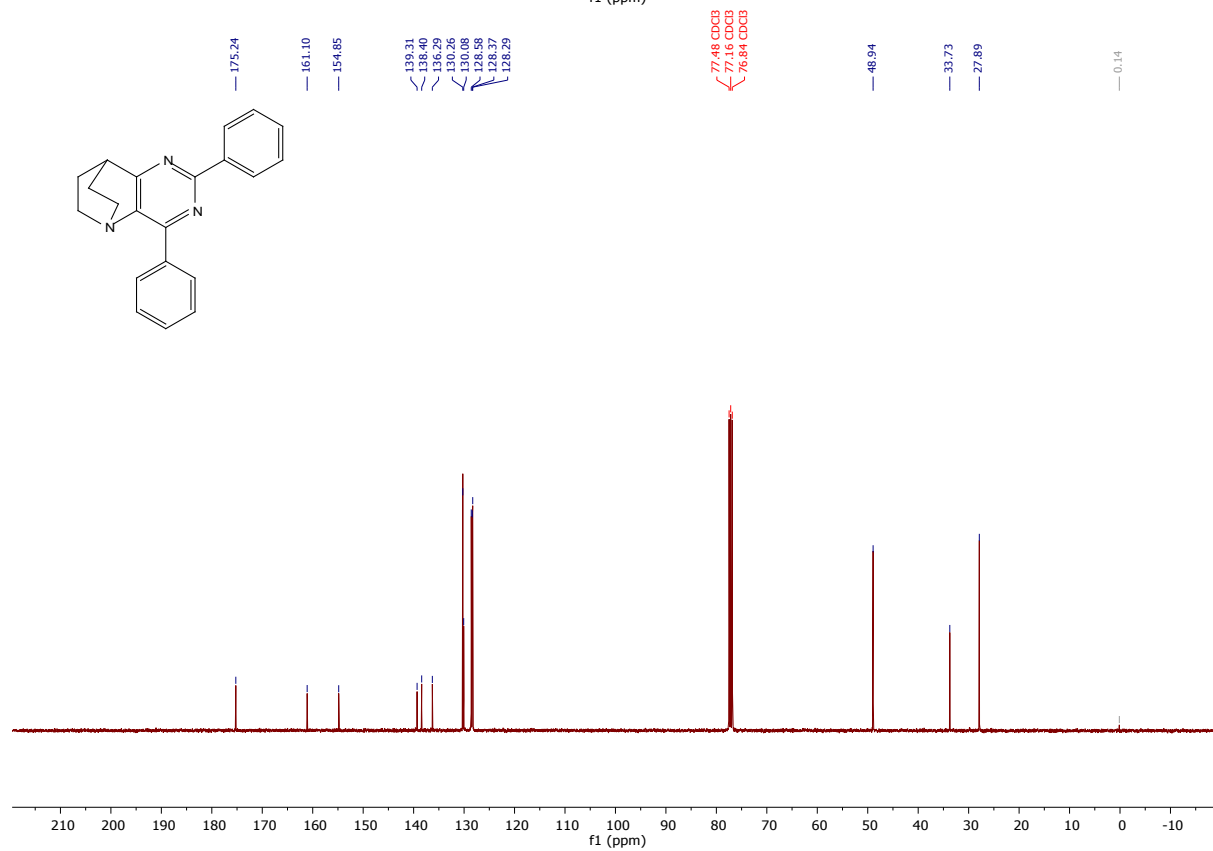
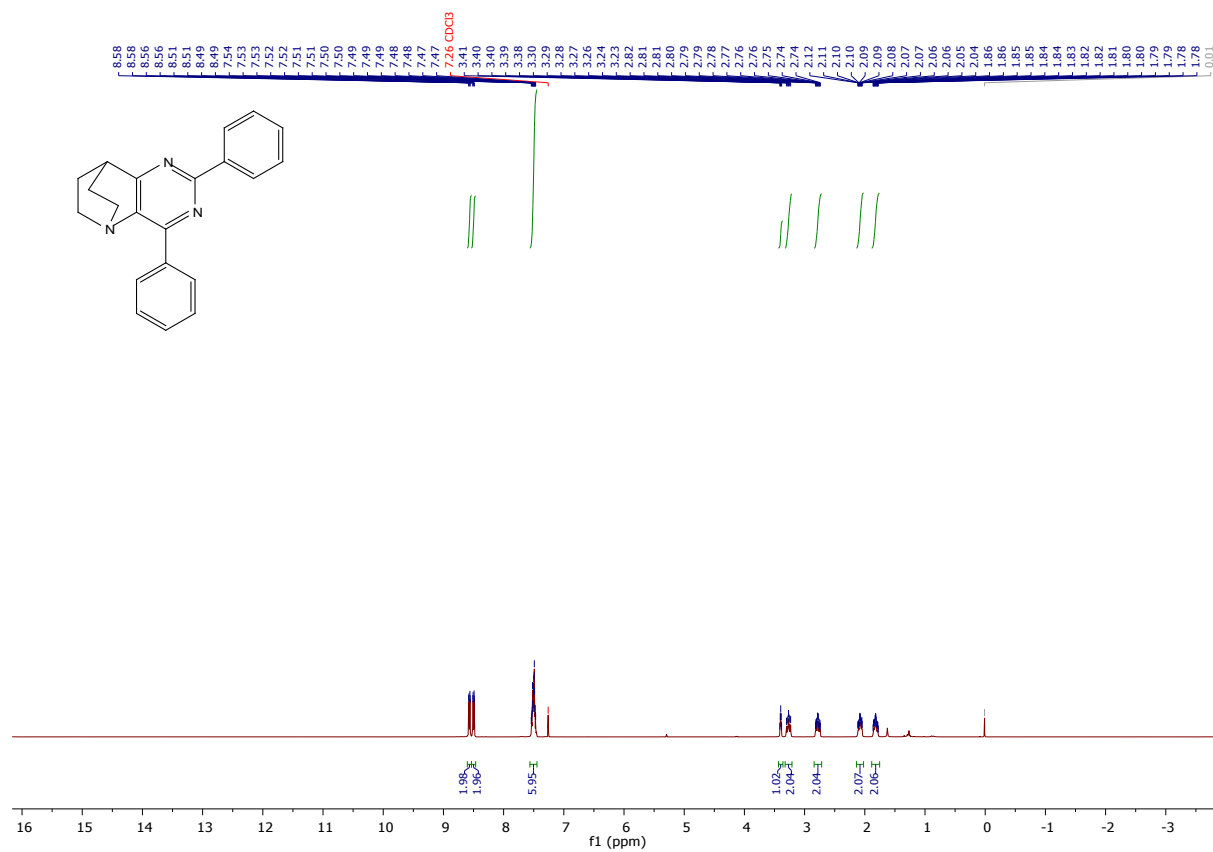
-61.63



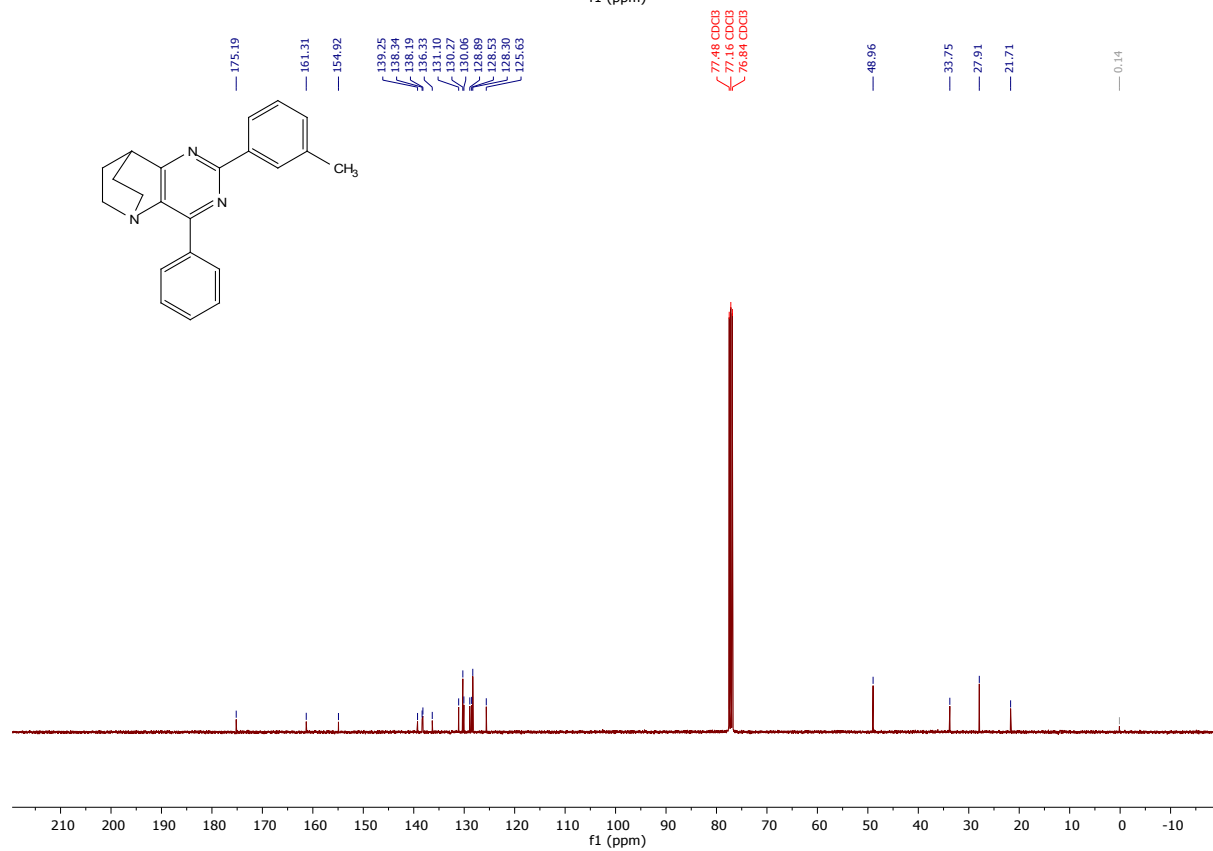
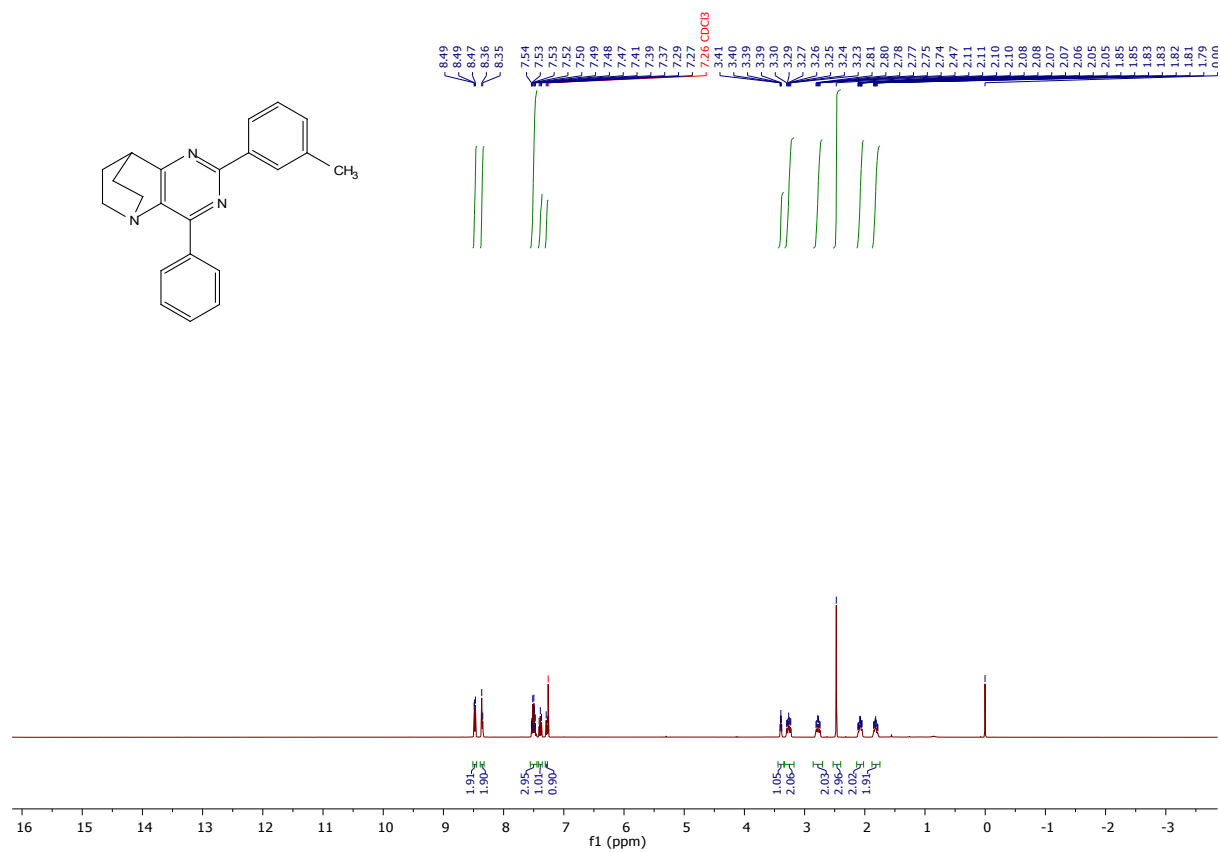
4-Phenyl-2-(*p*-tolyl)-7,8-dihydro-6H-5,8-ethanopyrido[3,2-*d*]pyrimidine (38)



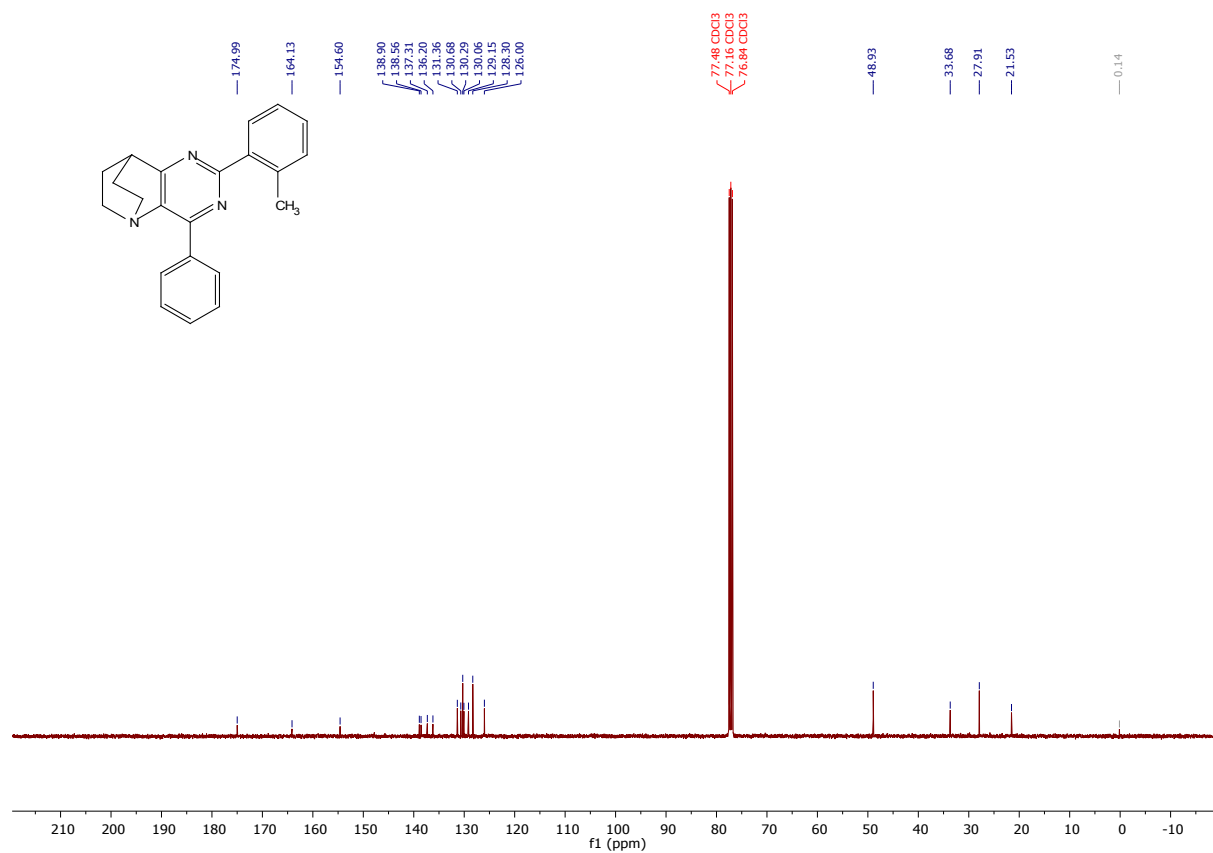
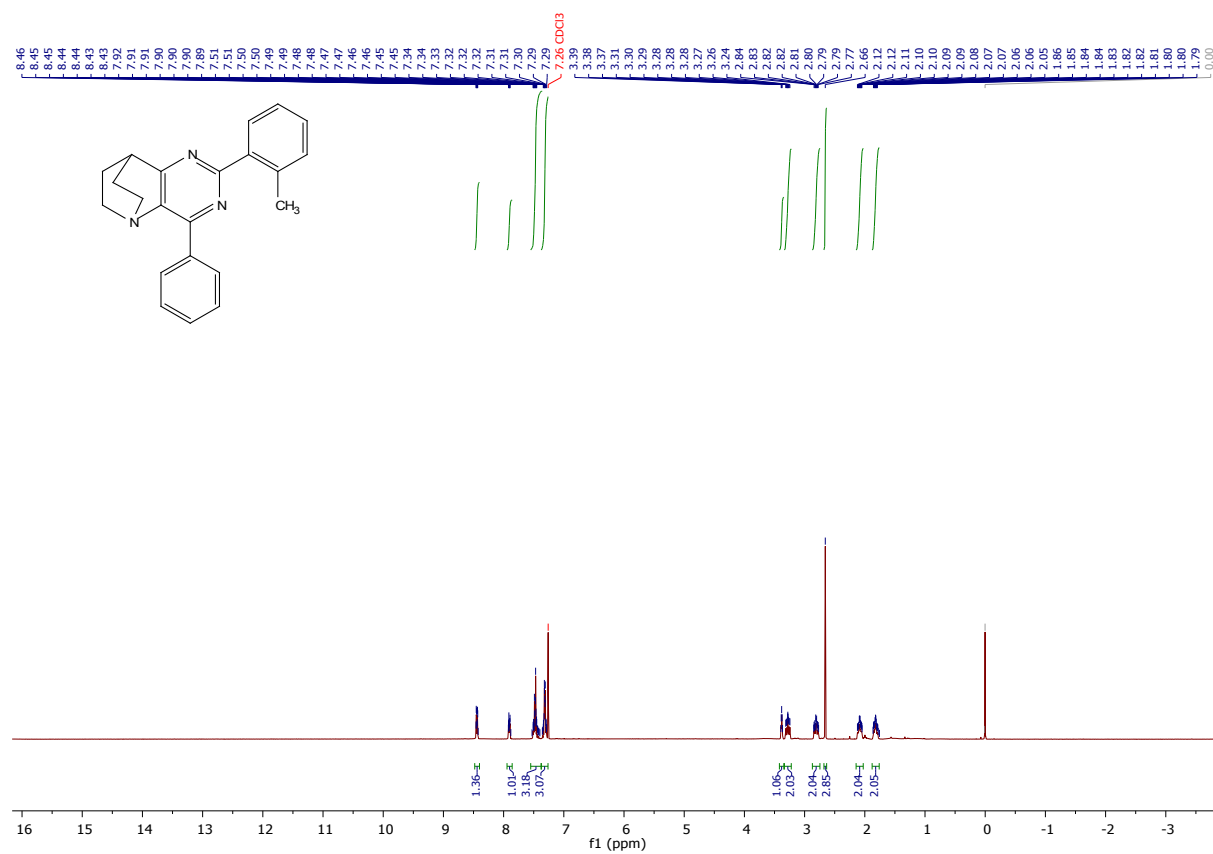
2,4-Diphenyl-7,8-dihydro-6H-5,8-ethanopyrido[3,2-d]pyrimidine (39)



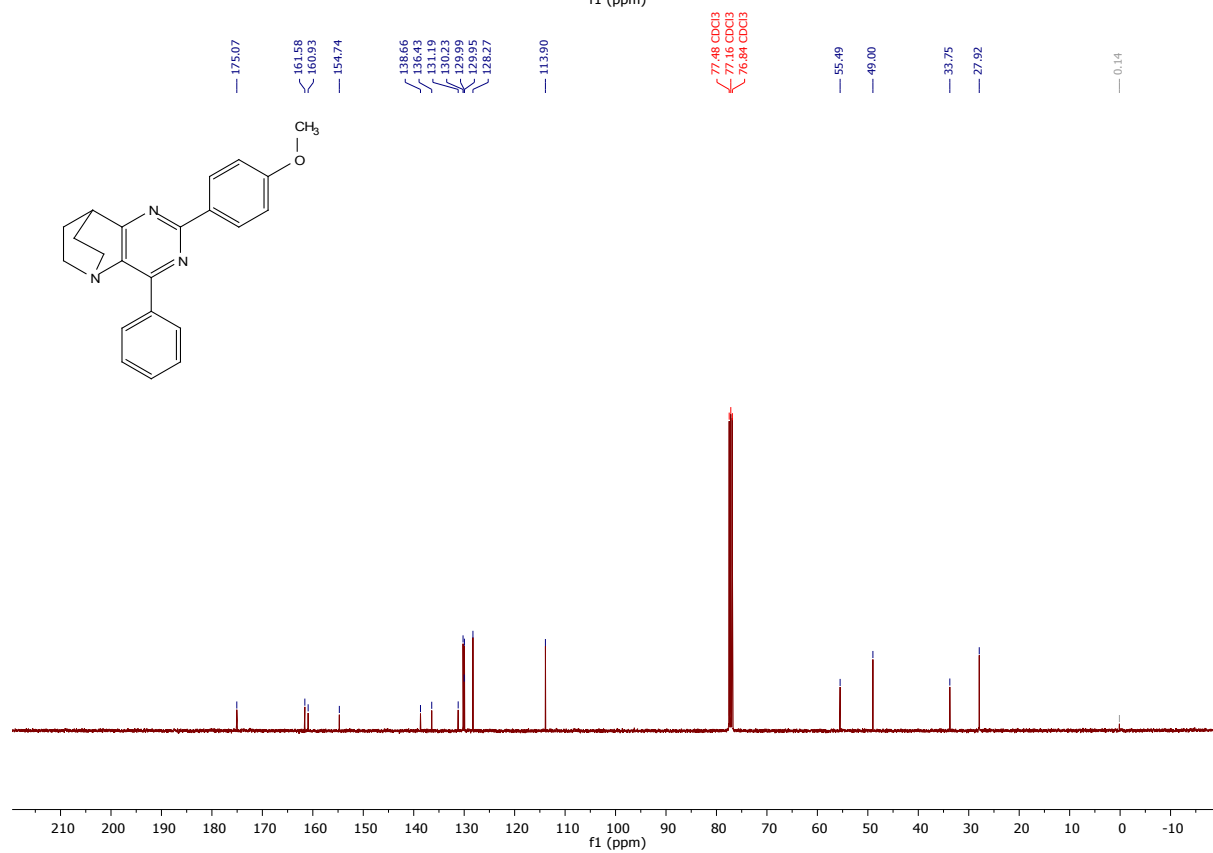
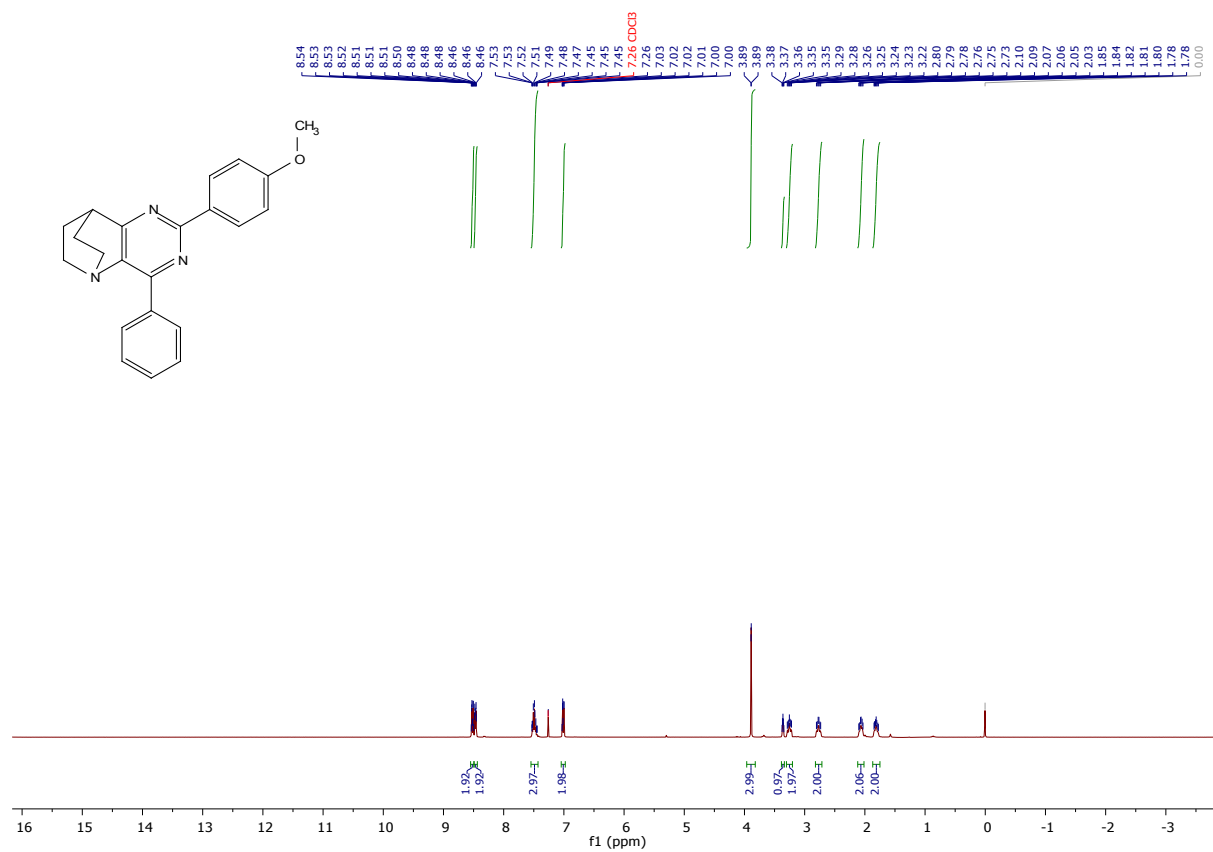
4-Phenyl-2-(*m*-tolyl)-7,8-dihydro-6*H*-5,8-ethanopyrido[3,2-*d*]pyrimidine (40)



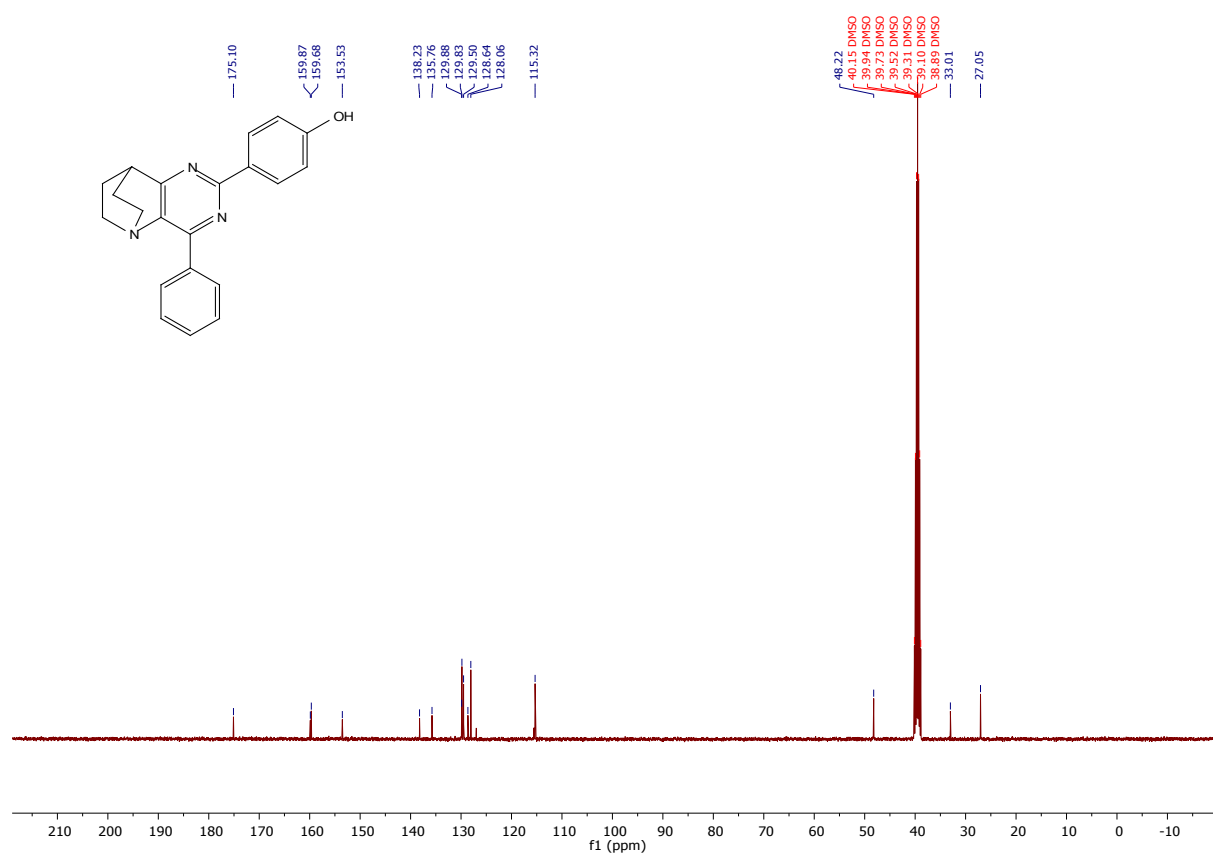
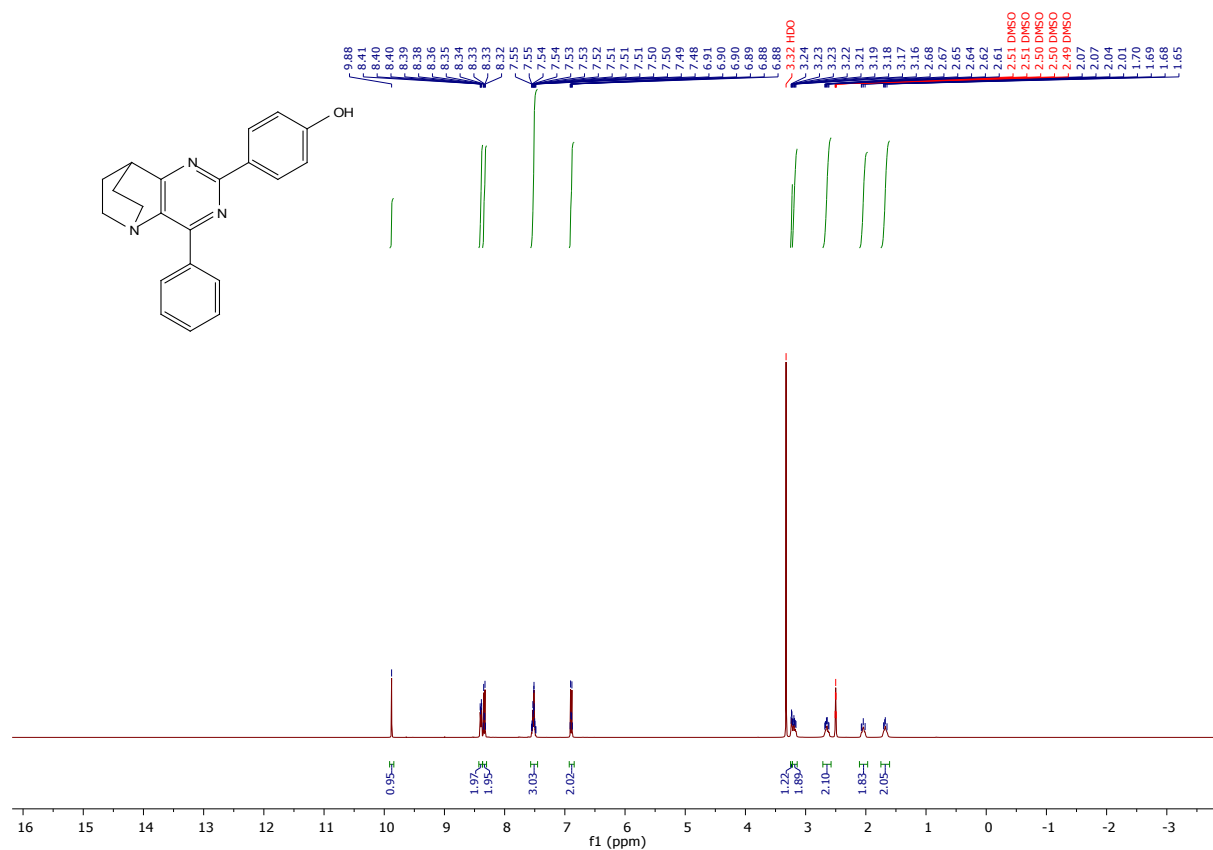
4-Phenyl-2-(*o*-tolyl)-7,8-dihydro-6H-5,8-ethanopyrido[3,2-d]pyrimidine (41)



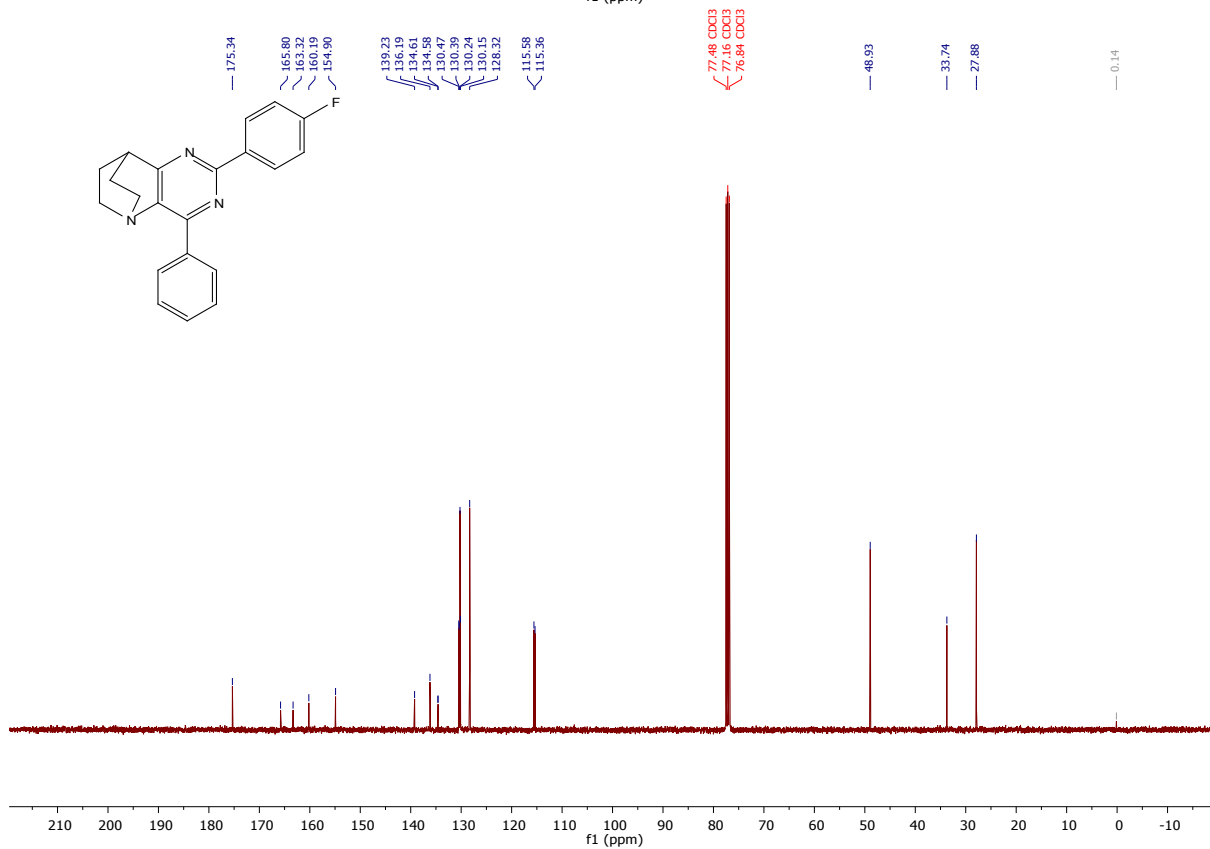
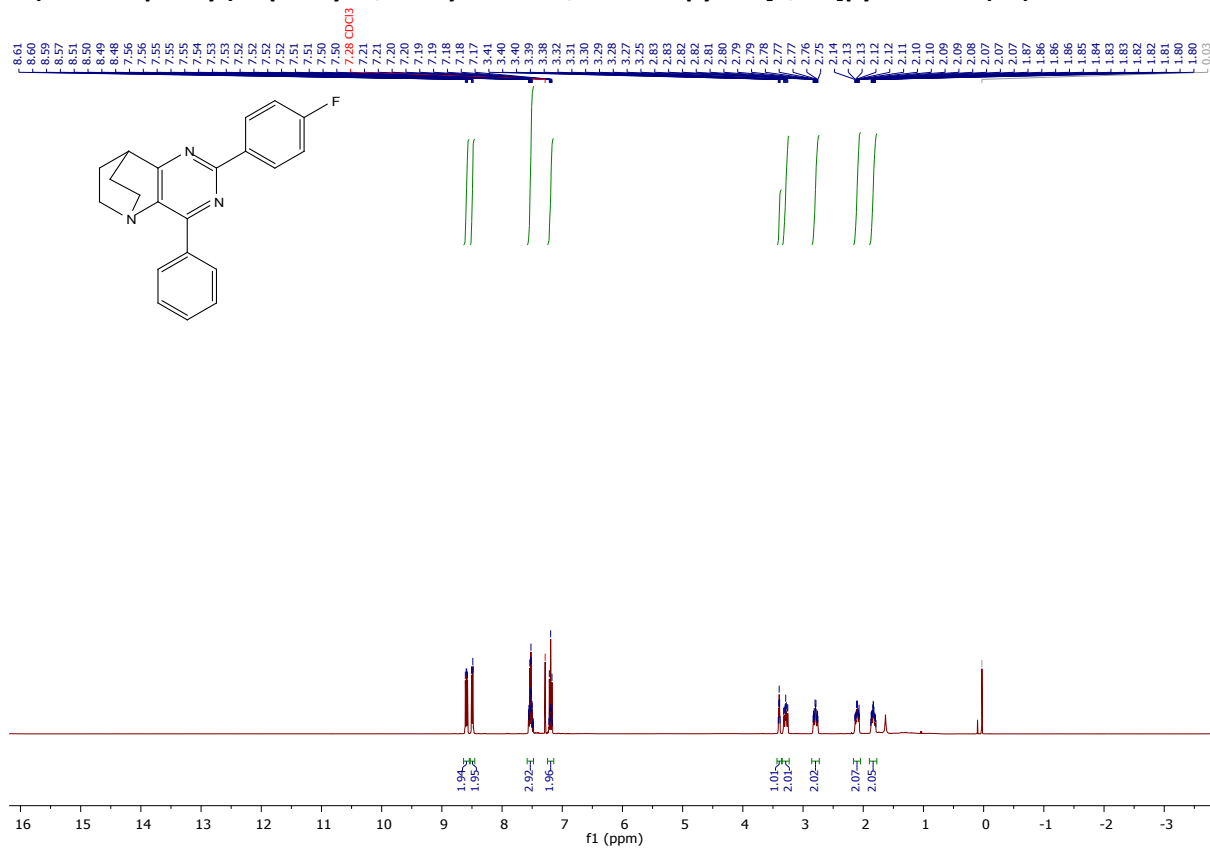
2-(4-Methoxyphenyl)-4-phenyl-7,8-dihydro-6H-5,8-ethanopyrido[3,2-d]pyrimidine (42)

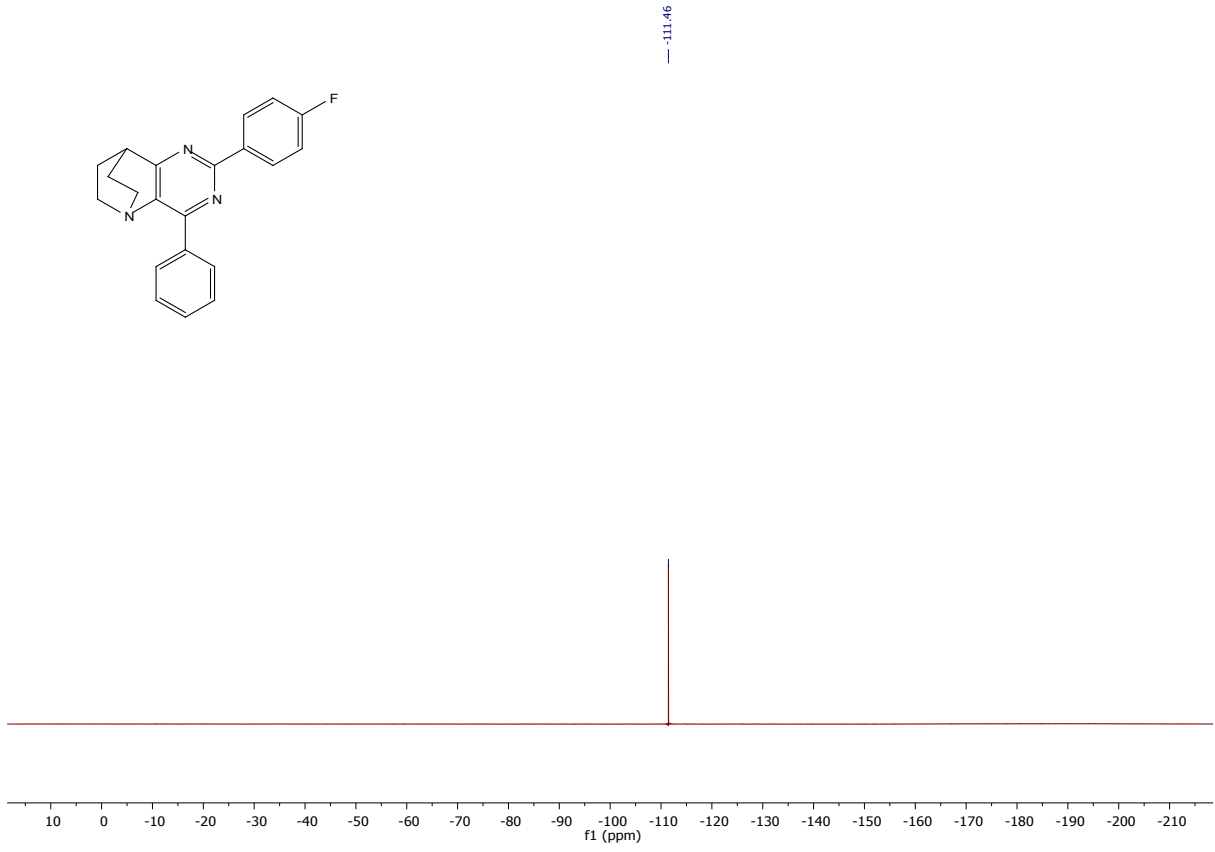
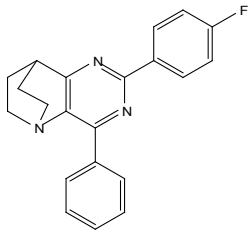


4-(4-Phenyl-7,8-dihydro-6H-5,8-ethanopyrido[3,2-d]pyrimidin-2-yl)phenol (43)

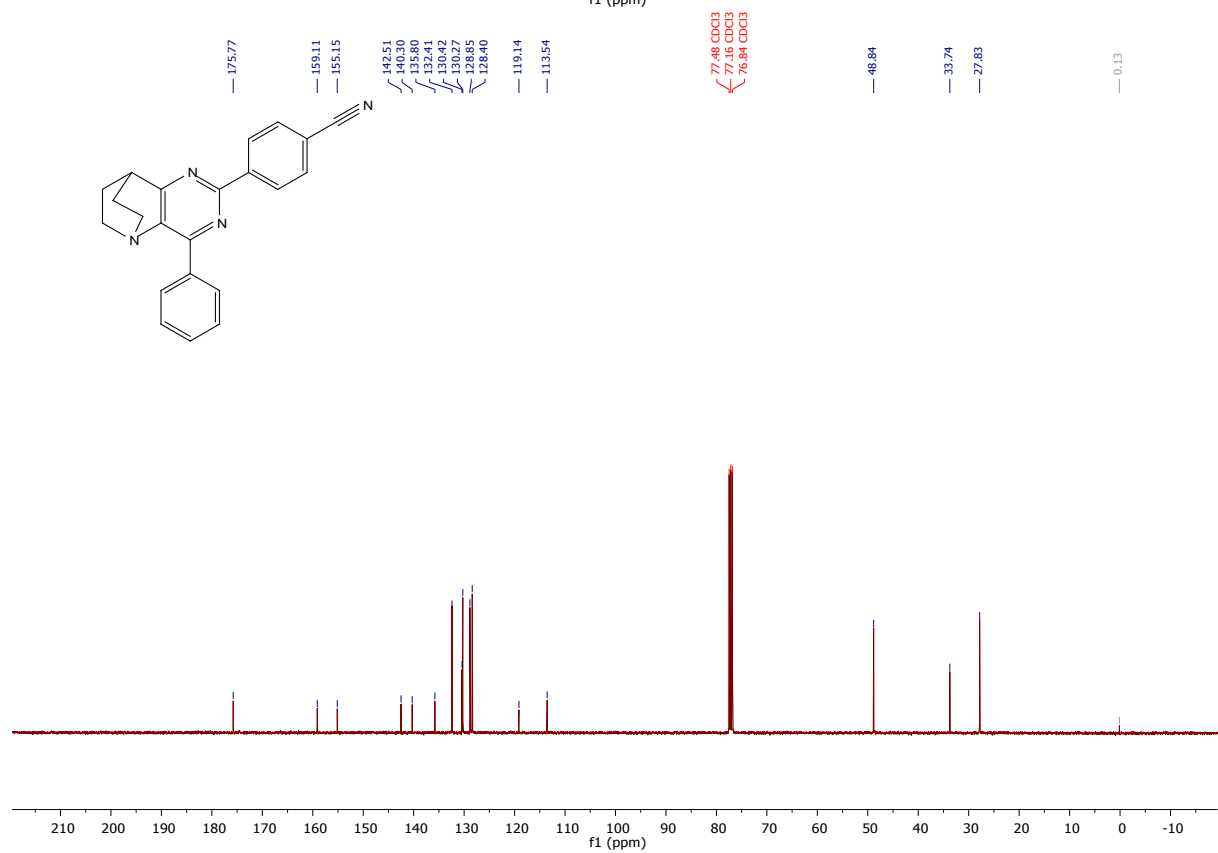
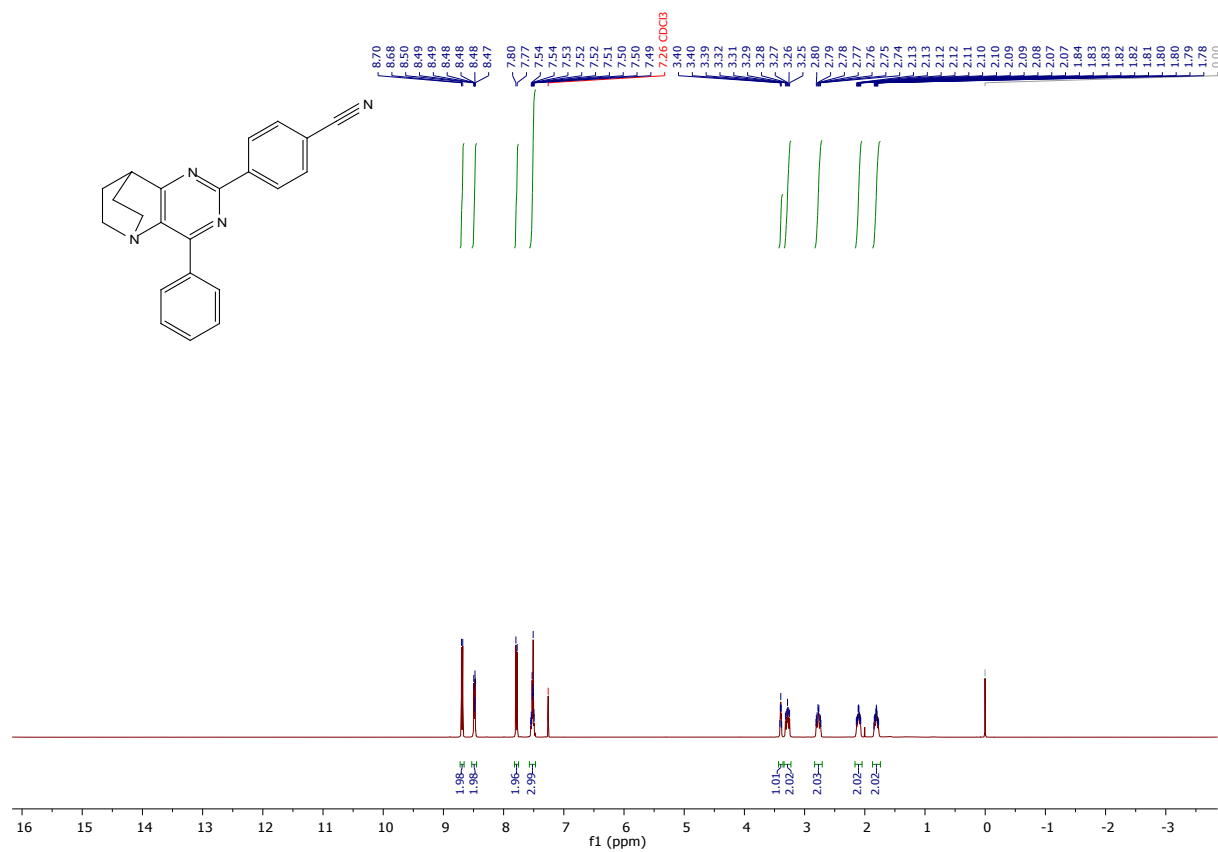


2-(4-Fluorophenyl)-4-phenyl-7,8-dihydro-6H-5,8-ethanopyrido[3,2-d]pyrimidine (46)

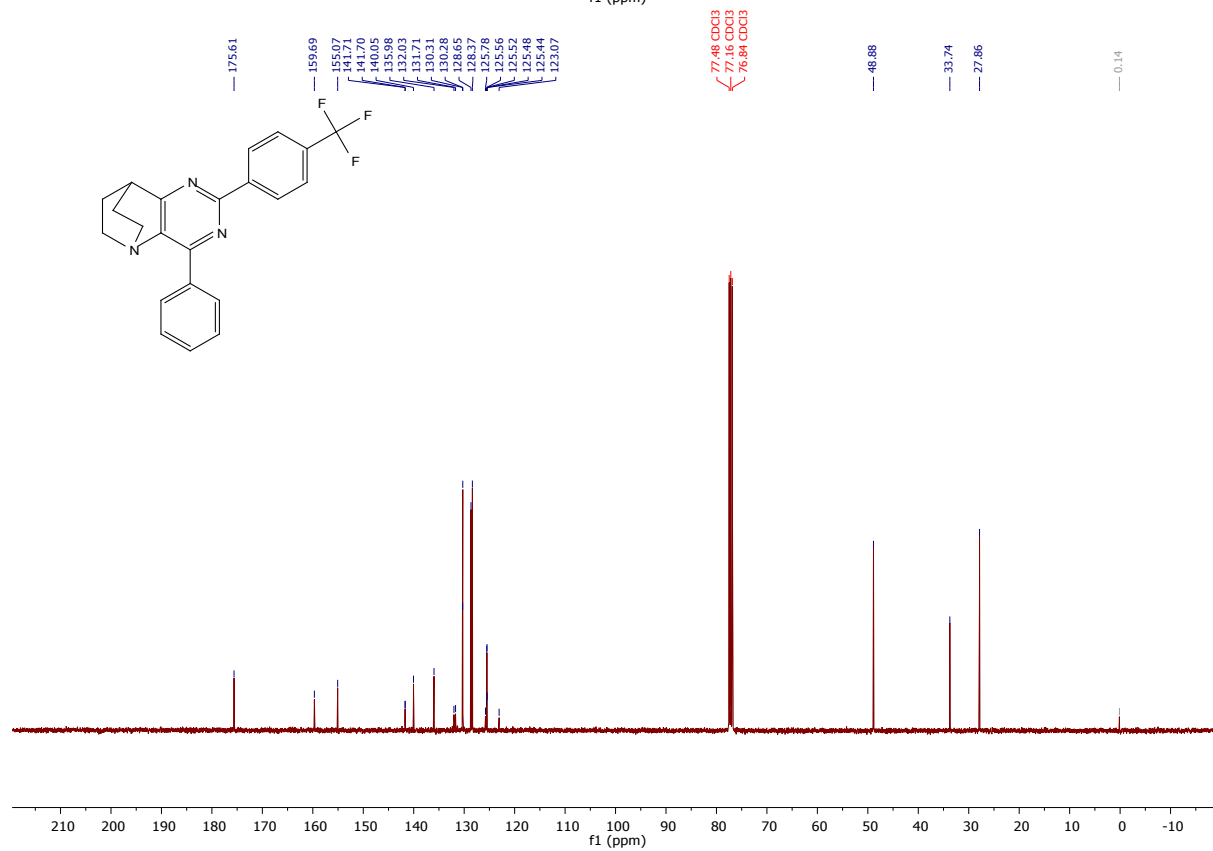
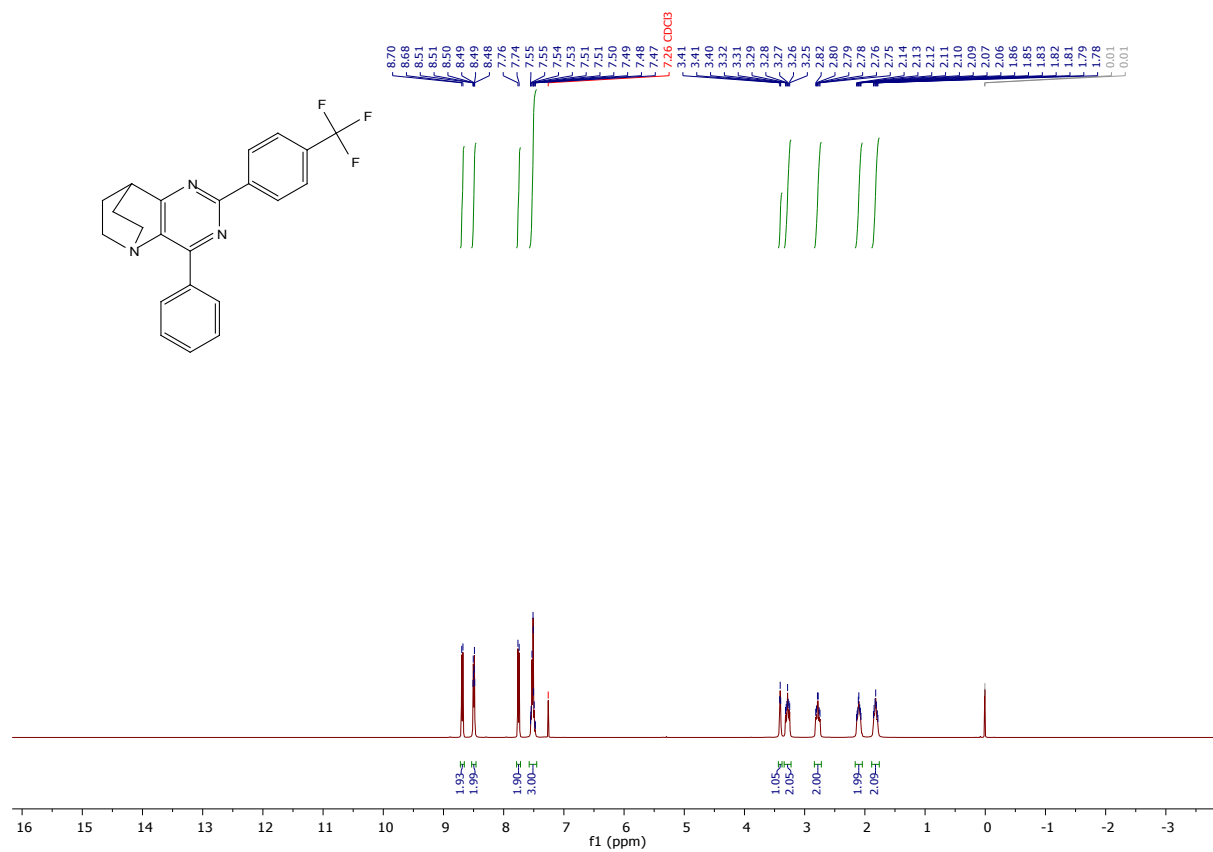


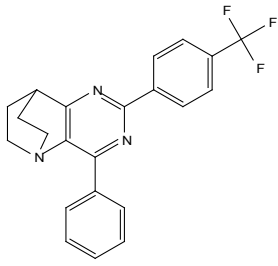


4-(4-Phenyl-7,8-dihydro-6H-5,8-ethanopyrido[3,2-d]pyrimidin-2-yl)benzonitrile (47)

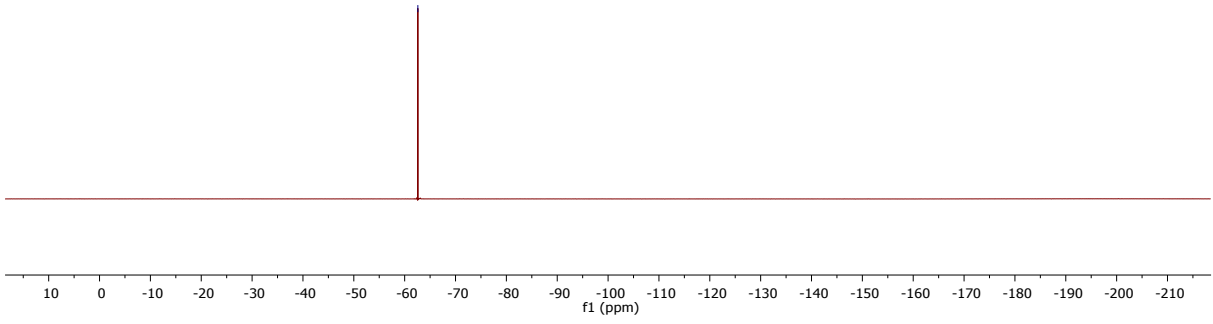


4-Phenyl-2-(4-(trifluoromethyl)phenyl)-7,8-dihydro-6H-5,8-ethanopyrido[3,2-d]pyrimidine (48)

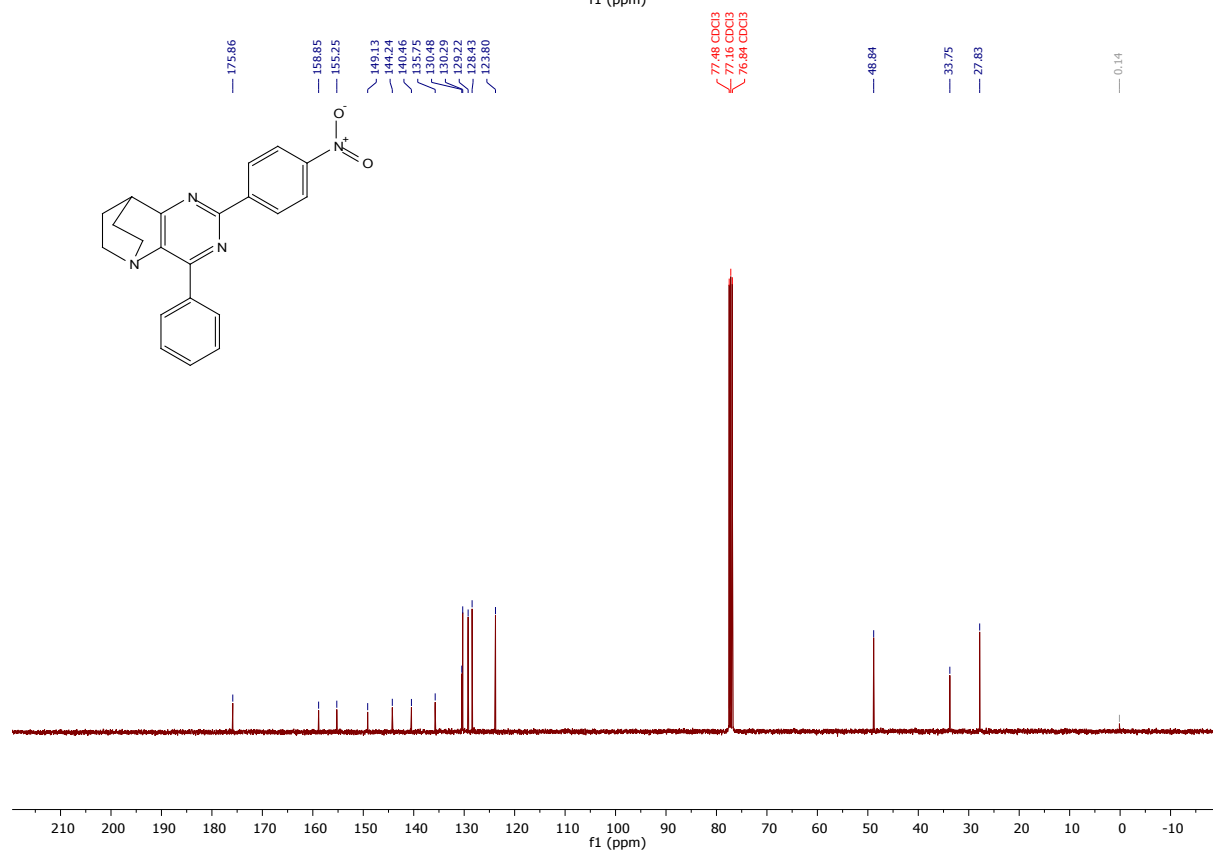
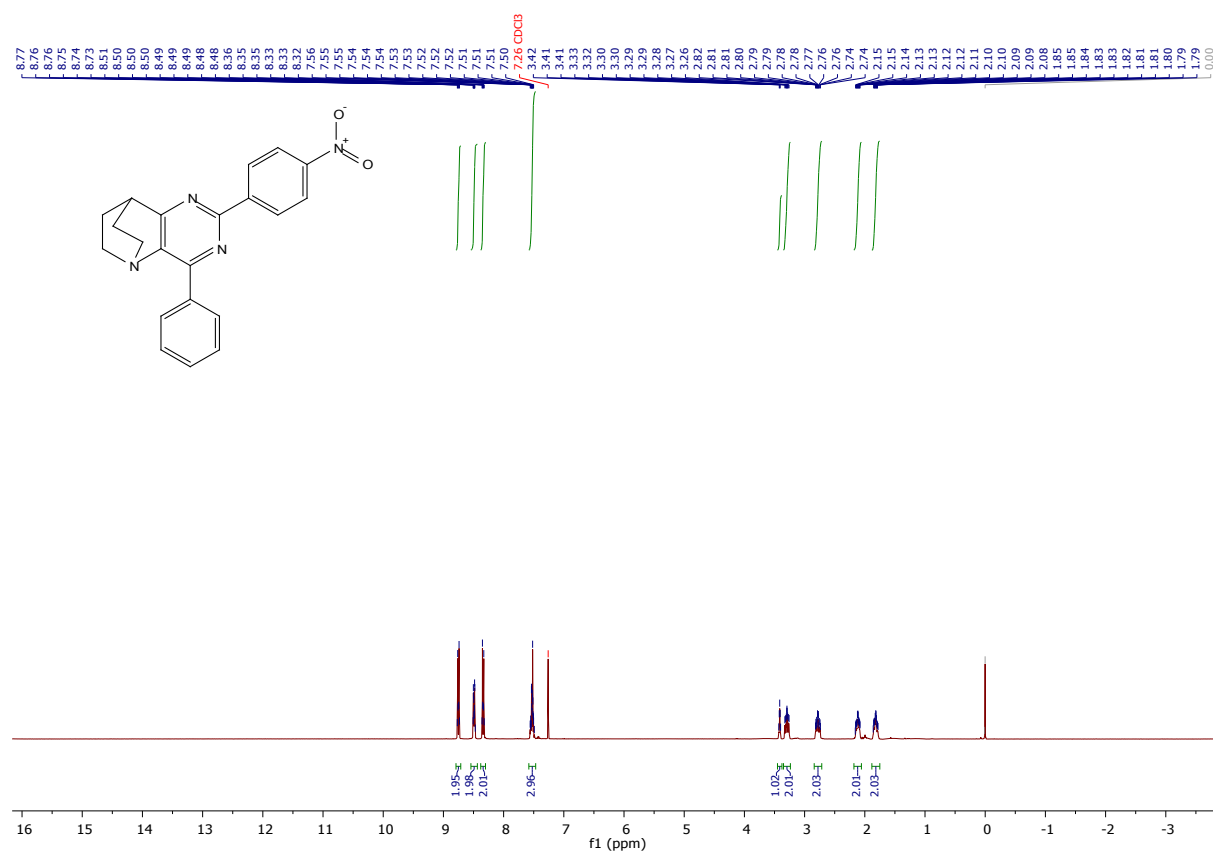




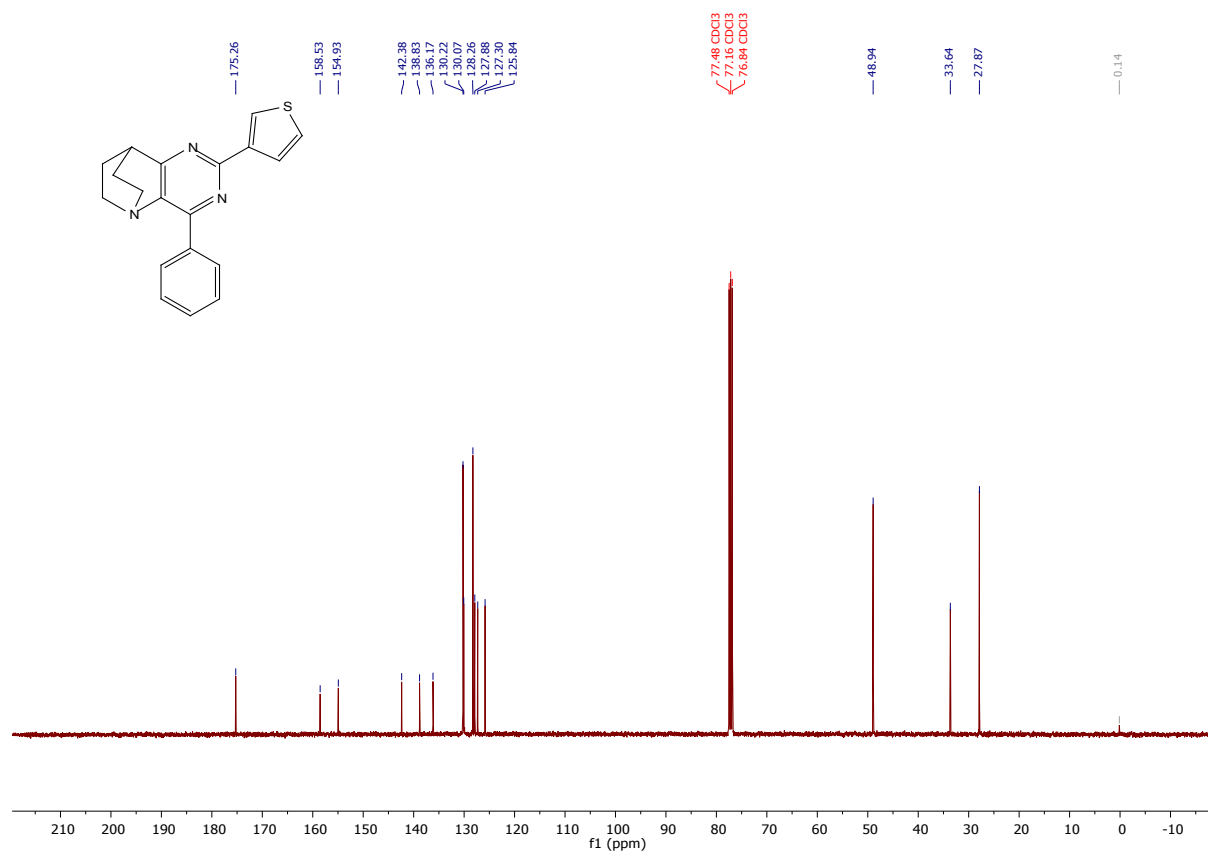
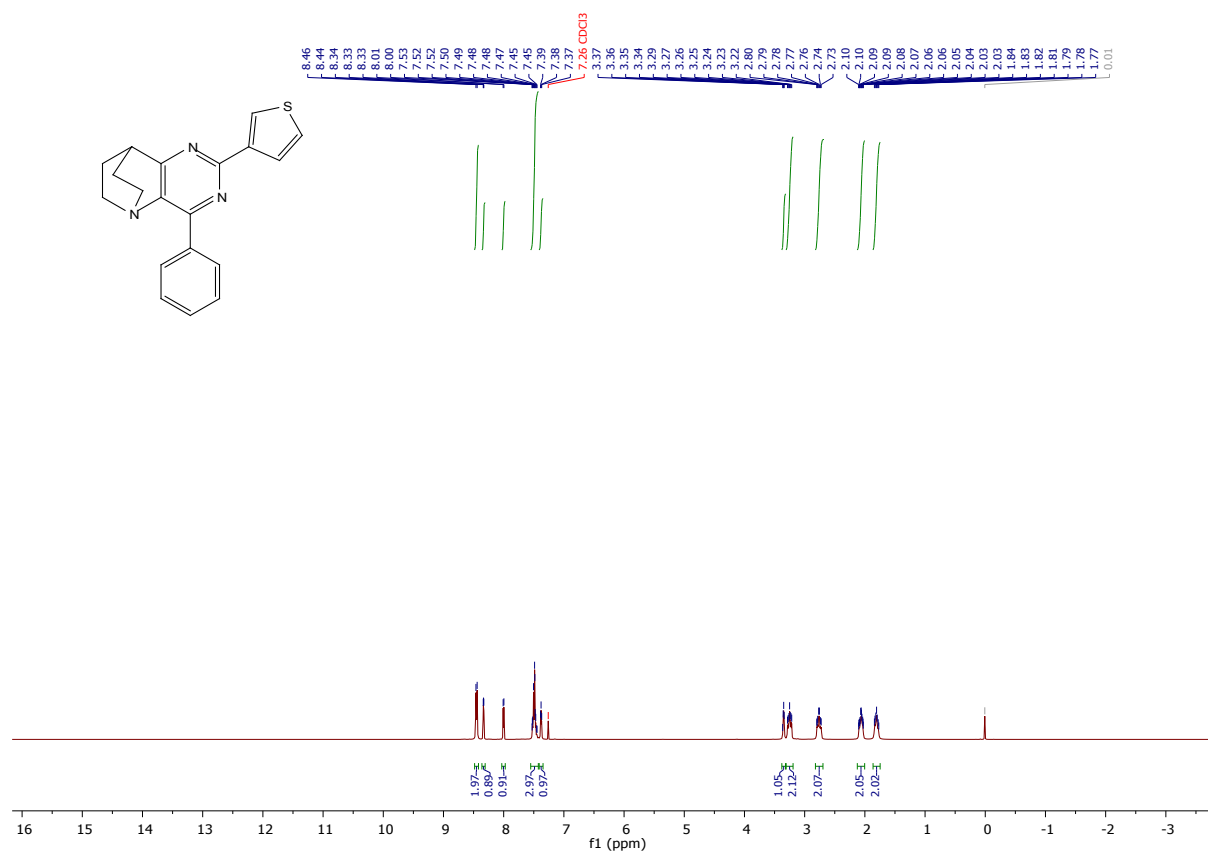
65.79



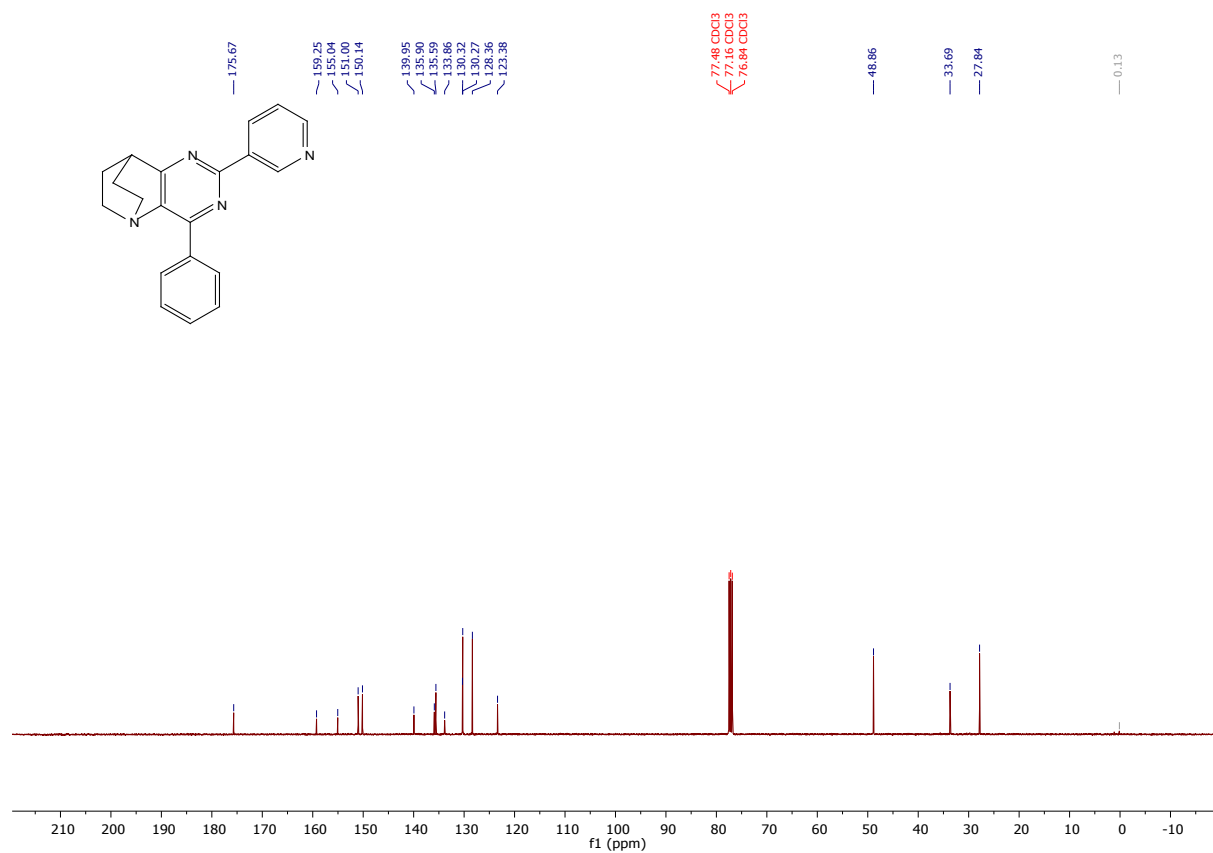
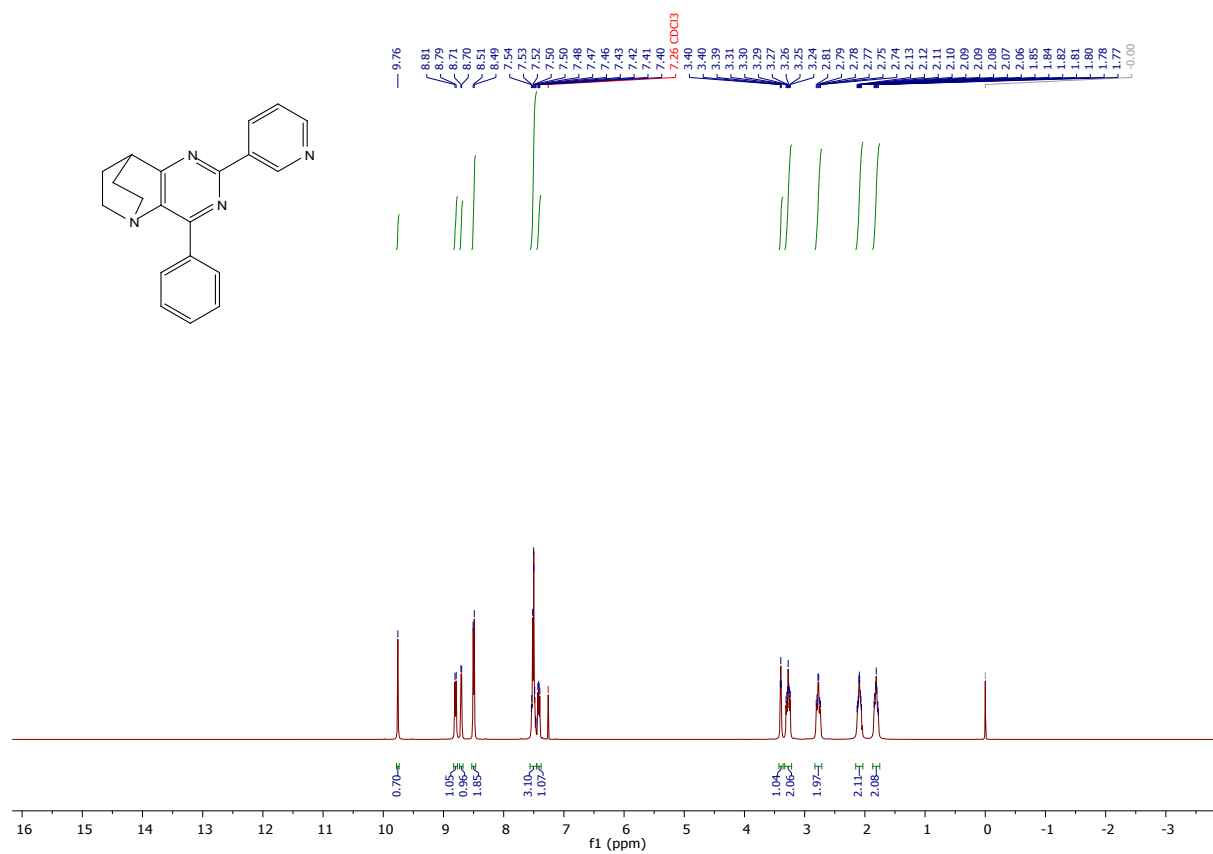
2-(4-Nitrophenyl)-4-phenyl-7,8-dihydro-6H-5,8-ethanopyrido[3,2-d]pyrimidine (49)



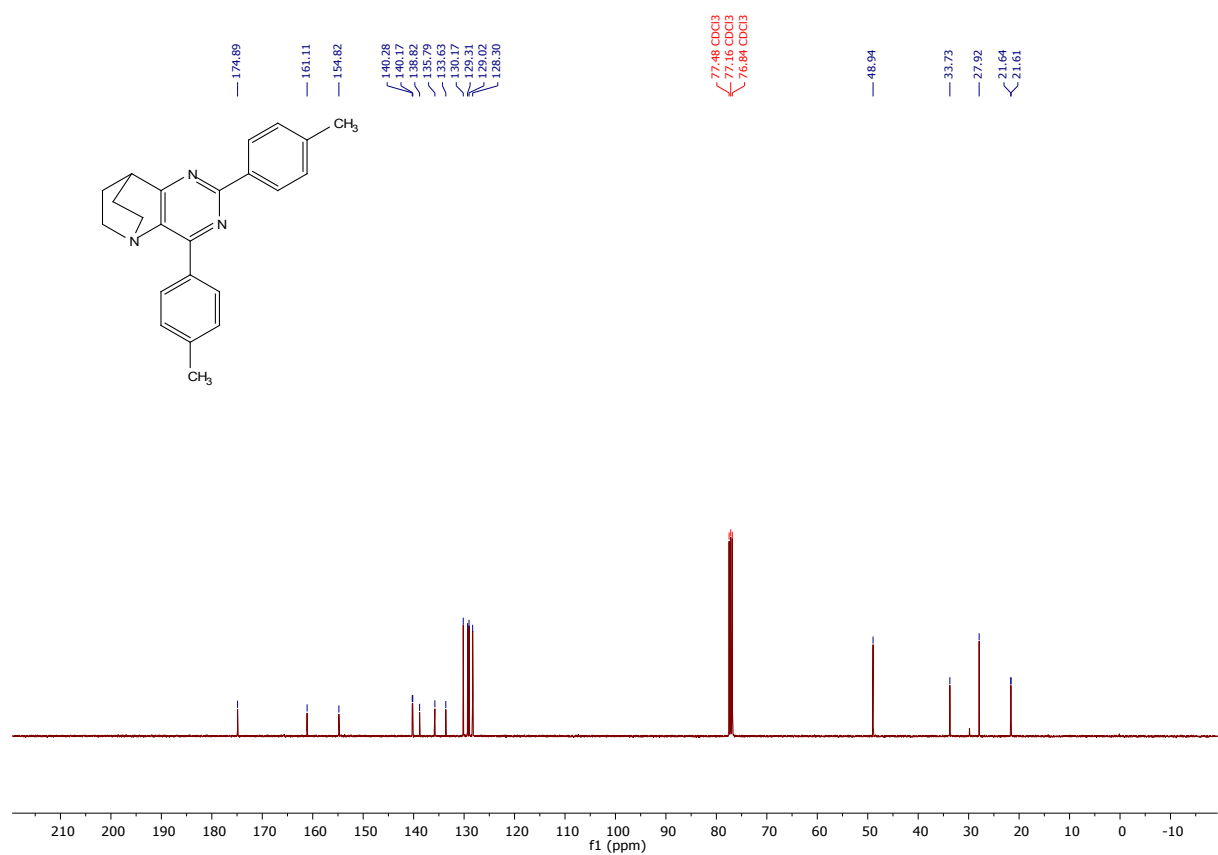
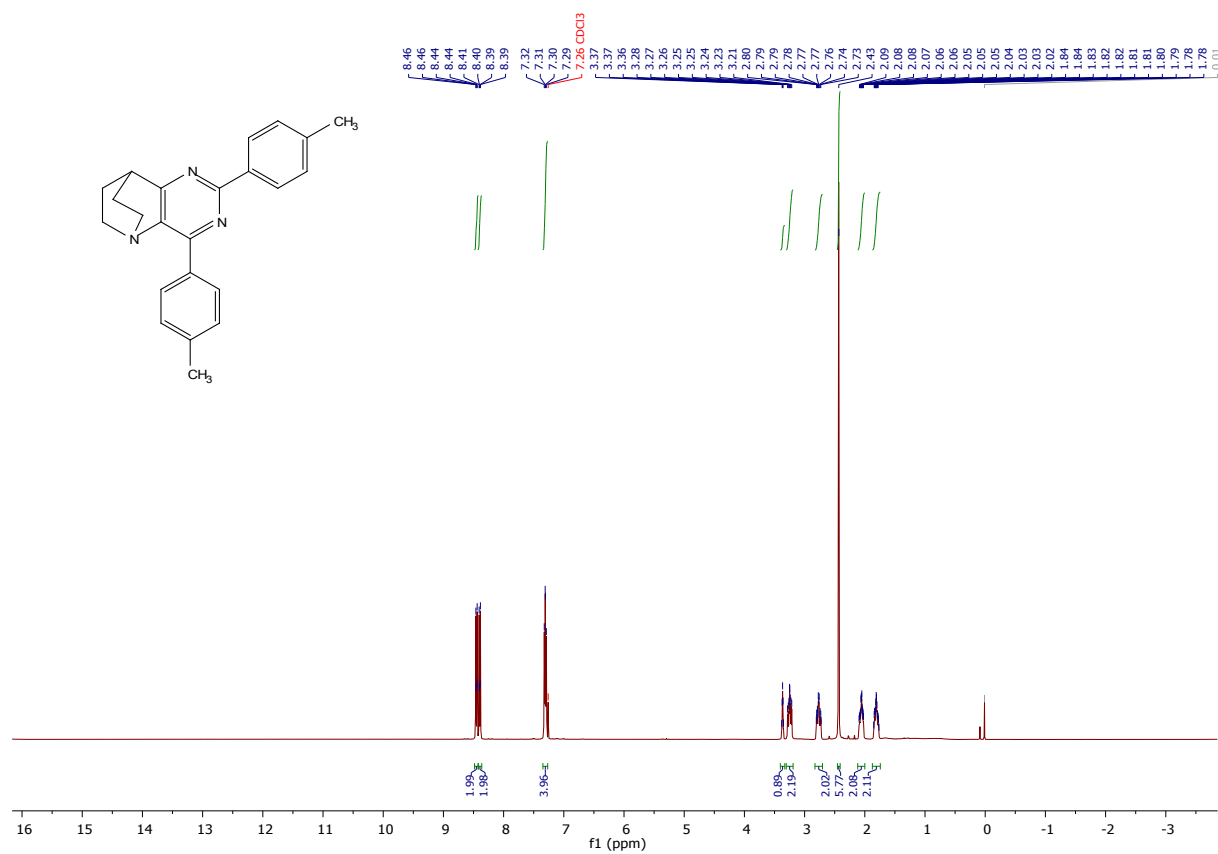
4-Phenyl-2-(thiophen-3-yl)-7,8-dihydro-6H-5,8-ethanopyrido[3,2-d]pyrimidine (50)



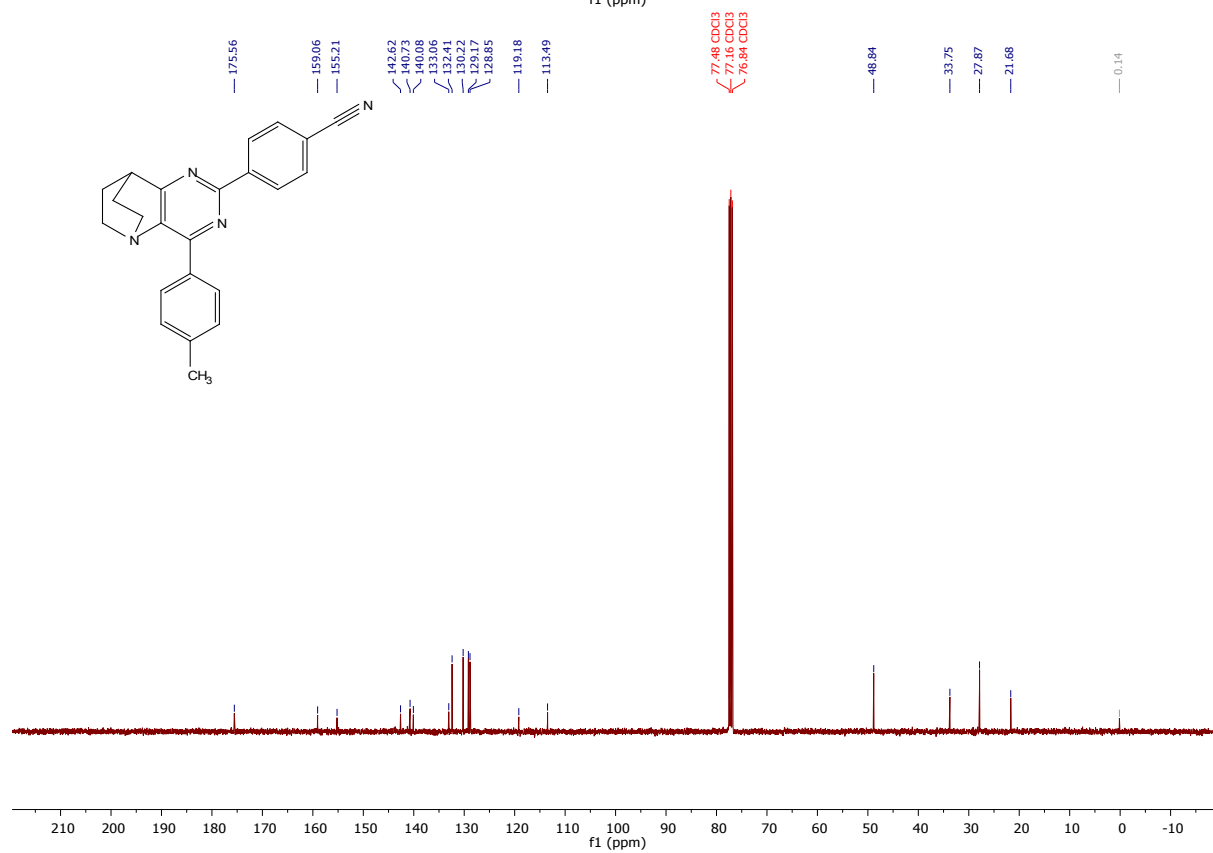
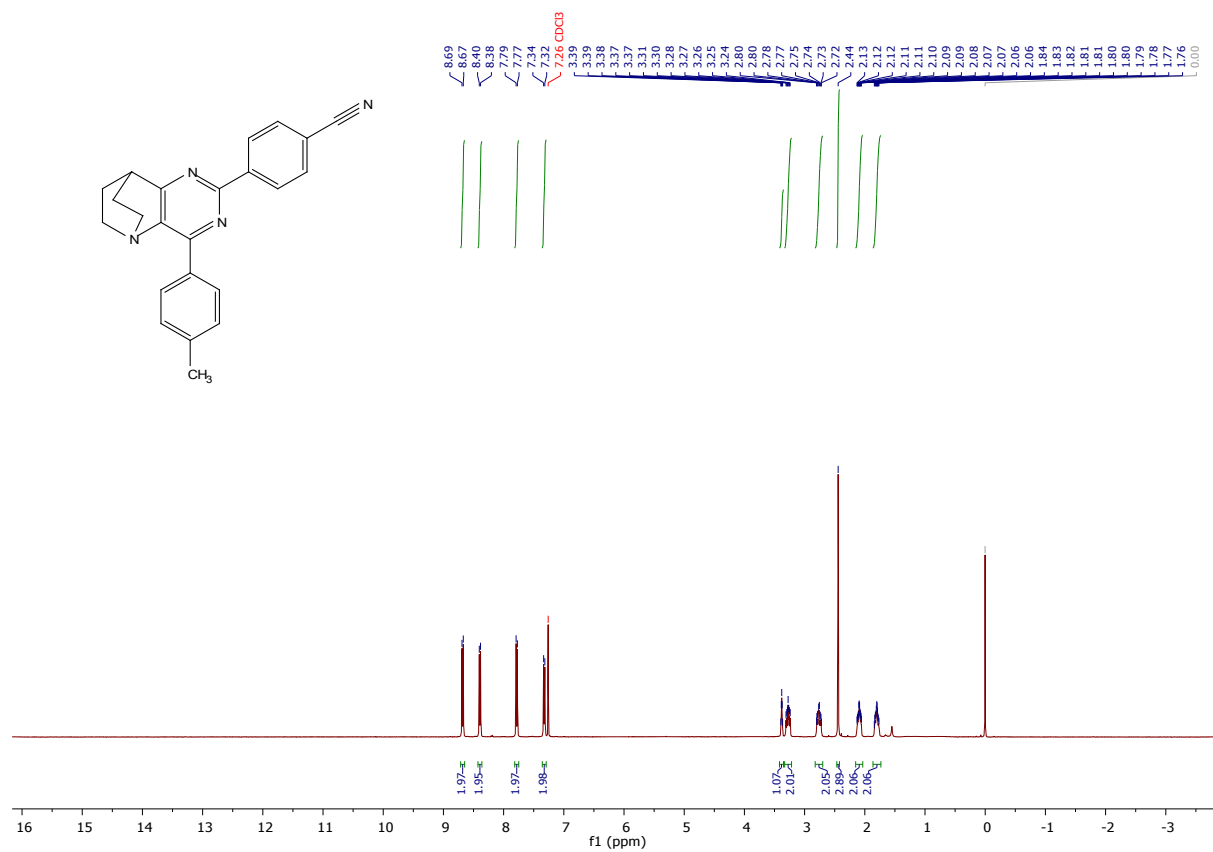
4-Phenyl-2-(pyridin-3-yl)-7,8-dihydro-6H-5,8-ethanopyrido[3,2-d]pyrimidine (51)

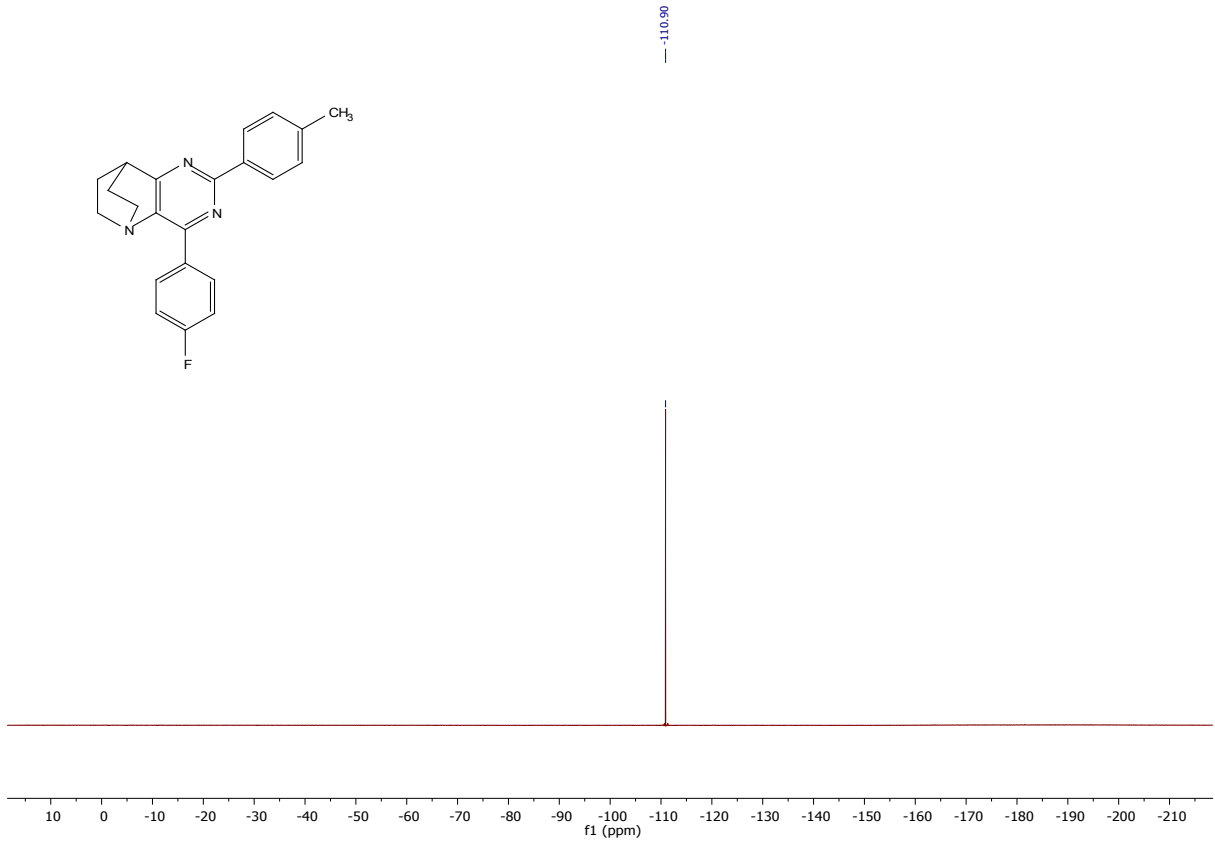
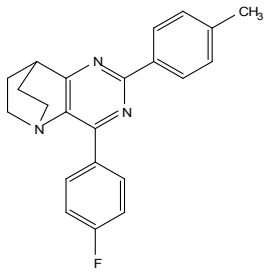


2,4-Di-*p*-tolyl-7,8-dihydro-6*H*-5,8-ethanopyrido[3,2-*d*]pyrimidine (52)

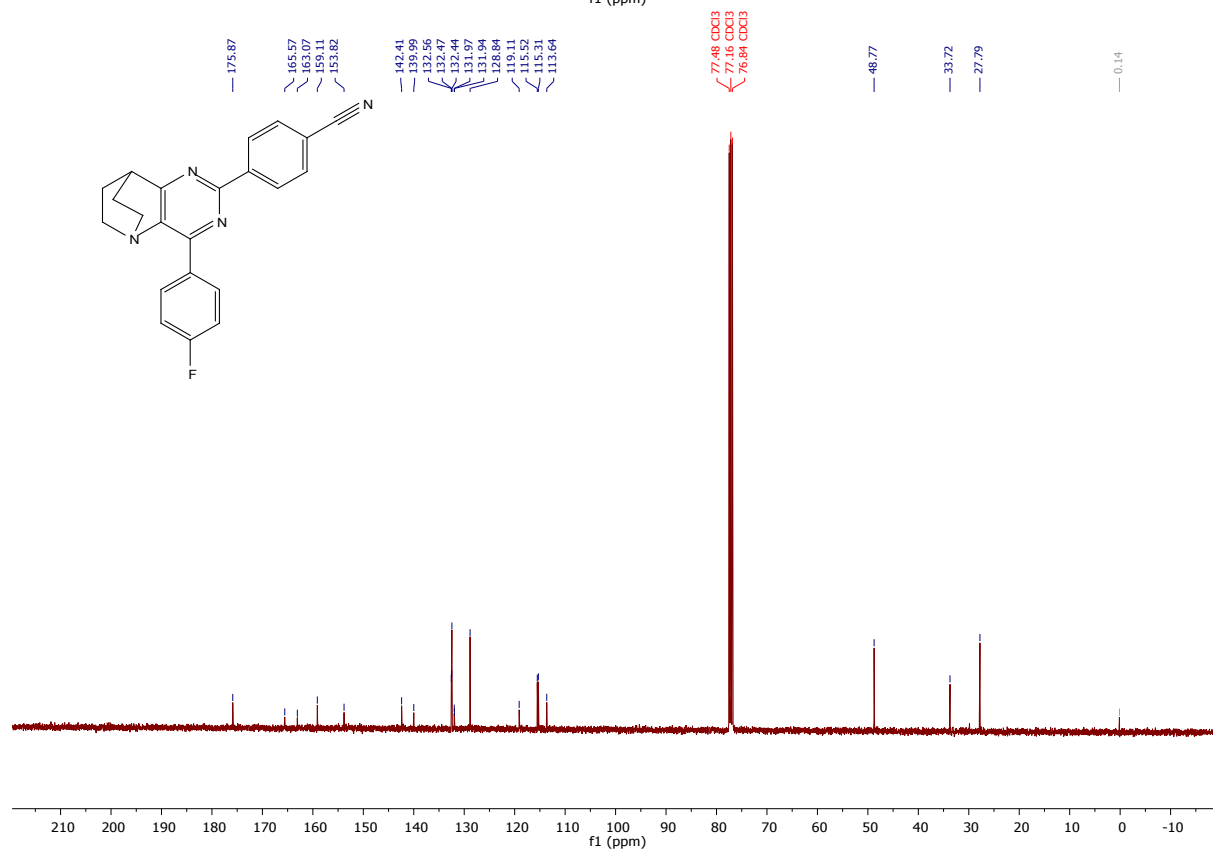
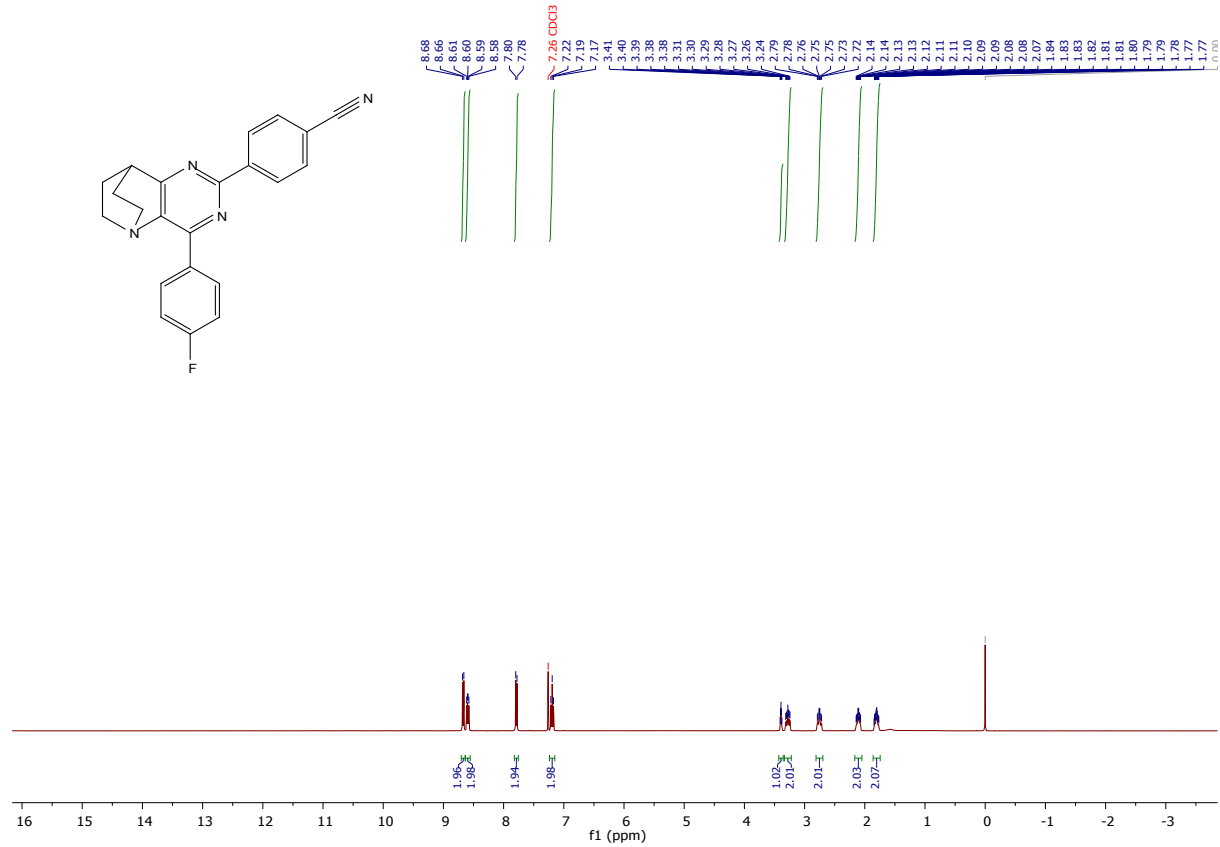


4-(4-(*p*-Tolyl)-7,8-dihydro-6*H*-5,8-ethanopyrido[3,2-*d*]pyrimidin-2-yl)benzonitrile (53)





4-(4-(4-Fluorophenyl)-7,8-dihydro-6H-5,8-ethanopyrido[3,2-d]pyrimidin-2-yl)benzotrile (55)



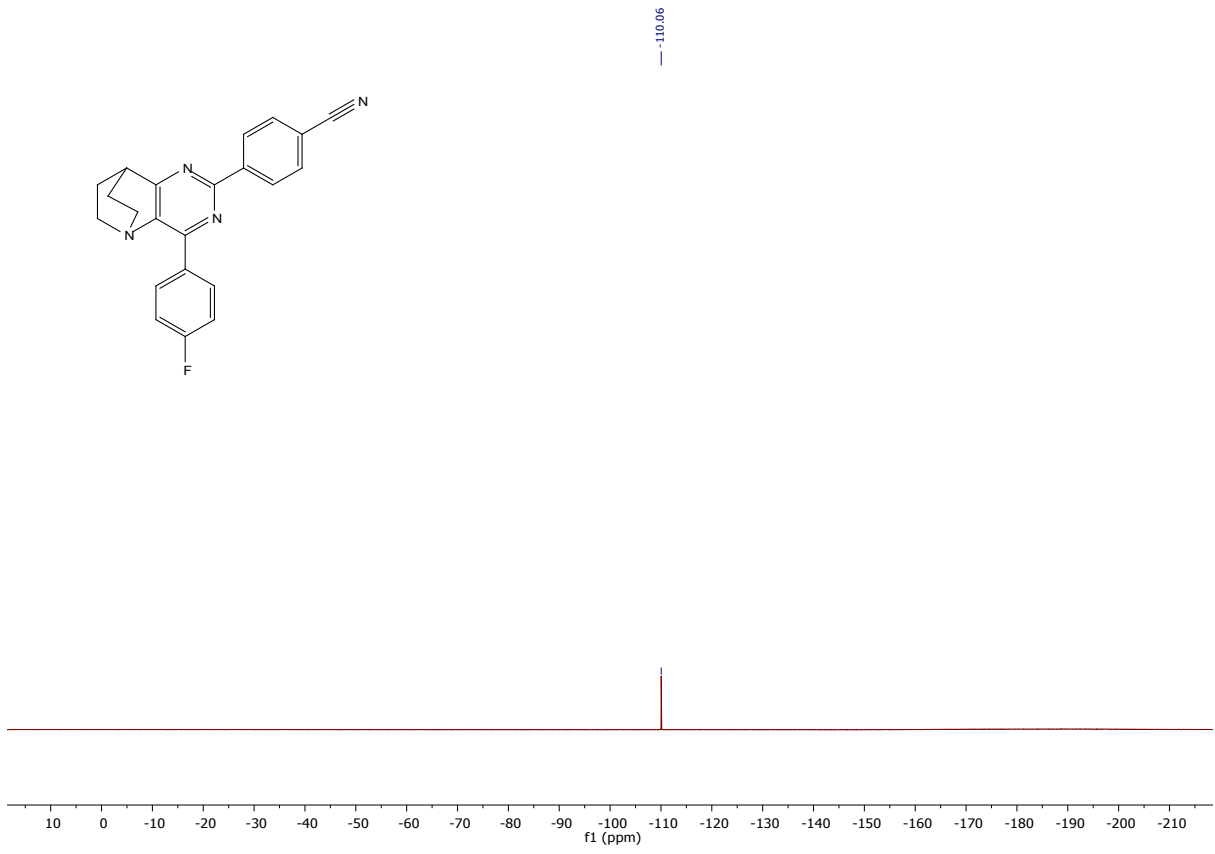
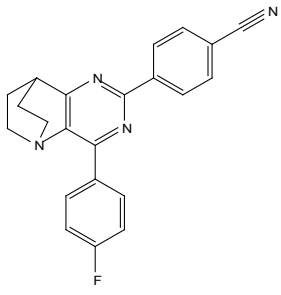


Table S1. Crystal data and structure refinement for compound **49**.

Identification code	MZL_E_501_0m
Empirical formula	C ₂₂ H ₁₈ F ₃ N ₃
Formula weight	381.39
Temperature/K	299.59
Crystal system	monoclinic
Space group	P2 ₁
a/Å	15.3849(12)
b/Å	5.8934(4)
c/Å	22.187(2)
α/°	90
β/°	110.051(4)
γ/°	90
Volume/Å ³	1889.8(3)
Z	4
ρ _{calc} /cm ³	1.341
μ/mm ⁻¹	0.101
F(000)	792.0
Crystal size/mm ³	0.4 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	2.818 to 50.484
Index ranges	-18 ≤ h ≤ 18, -7 ≤ k ≤ 7, -26 ≤ l ≤ 26
Reflections collected	16348
Independent reflections	6319 [R _{int} = 0.0321, R _{sigma} = 0.0430]
Data/restraints/parameters	6319/1/525
Goodness-of-fit on F ²	1.042
Final R indexes [I>=2σ (I)]	R ₁ = 0.0543, wR ₂ = 0.1350
Final R indexes [all data]	R ₁ = 0.0820, wR ₂ = 0.1503

Largest diff. peak/hole / e Å⁻³

0.24/-0.28

Flack parameter

-0.1(3)

CCDC number

2074887