
A fluorogenic C4N4 probe for azide-based labelling

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1. General methods

1-1. Reactions and purifications

Unless otherwise noted, all reactions were carried out in an oven-dried glassware fitted with a 3-way glass stopcock under an argon atmosphere and were stirred with Teflon-coated magnetically stirred bars. All work-up and purification procedures were carried out with reagent-grade solvents under ambient atmosphere. Thin layer chromatography (TLC) was performed on Merck TLC plates (0.25 mm) pre-coated with silica gel 60 F254 and visualized by UV quenching and staining with ninhydrin, $KMnO_4$, anisaldehyde or ceric ammonium molybdate solution. Flash column chromatography was performed on a Teledyne CombiFlash Rf 200 or a Biotage Isolera Spektra One.

1-2. Chracterisations

Infrared (IR) spectra were recorded on a HORIBA FT210 Fourier transform infrared spectrophotometer. NMR spectra were recorded on a JEOL ECS-400, a Bruker AVANCE III HD400 or a Bruker AVANCE III 500. Chemical shifts (δ) are given in ppm relative to residual solvent peaks.[1] Data for ^{1}H NMR are reported as follows: chemical shift (multiplicity, coupling constants where applicable, number of hydrogens). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), dd (doublet of doublet), dt (doublet of triplet), ddd (doublet of doublet of doublet), q (quartet), m (multiplet), br (broad). UV-Visible absorption spectra were recorded using a 0.1 dm cell on a Jasco V-670 spectrophotometer. Fluorecent emission spectra were recorded using a 0.1 dm cell on a Jasco FP-8600 spectrofluorometer, with which absolute fluorecent quatmn yields were also measured with a Jasco ILF-835 unit (100 mm integrating sphere). High-resolution mass spectra (ESI TOF (+)) were measured on a Thermo Fisher Scientific LTQ Orbitrap XL.

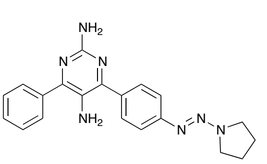
1-3. Solvents and reagents

THF was purified by passing through a solvent purification system (Glass Contour). (1*R*,8*S*,9s)-Bicyclo[6.1.0]non-4-yn-9-ylmethanol was purchased from TCI. All other starting materials were used as supplied by commercial vendors or prepared by the method described in the corresponding reference.

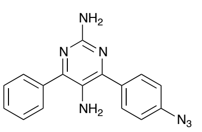
1-4. Computations

All quantum chemical calculations were performed using the Gaussian 16 program.[2] Structural optimizations were conducted with tight optimization parameters, and density functional theory (DFT) calculations employed an ultrafine integration grid (99 radial shells, 590 angular points). Frequency calculations confirmed the identity of geometry minima (no imaginary frequencies).

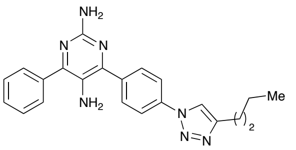
2. Preparation of substrates



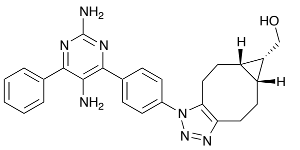
(*E*)-4-Phenyl-6-(4-(pyrrolidin-1-yldiazenyl)phenyl)pyrimidine-2,5-diamine (2): To a suspension of 4-chloro-6-phenylpyrimidine-2,5-diamine (300 mg, 1.36 mmol, 1.0 equiv), boronic ester **1**[3] (429 mg, 1.49 mmol, 1.1 equiv), Na_2CO_3 (721 mg, 6.80 mmol, 5.0 equiv), and $Pd(PPh_3)_4$ (78.5 mg, 0.068 mmol, 5 mol%) in toluene (0.1M) were added EtOH (0.4 M) and H_2O (0.4 M). The solution was stirred under reflux for 14 h, and cooled to RT. After the addition of H_2O, aqueous phase was extracted with EtOAc (3x). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and removed under reduced pressure. The obtained material was purified by silica gel column chromatography (*n*-hexane/EtOAc), and isolated as a yellow solid (510 mg, 99%). **m.p.** 180–182 °C; **IR** (thin film) 3309, 3186, 2970, 2870, 1602, 1552, 1436, 1419, 1315, 1208, 1155, 1049, 1026 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80–7.72 (m, 4H), 7.56–7.43 (m, 5H), 4.70 (s, 2H), 3.82 (s, 2H), 3.52–3.50 (m, 2H), 2.07–2.03 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.9, 154.2, 154.0, 152.4, 137.3, 133.5, 129.4, 129.4, 129.0, 128.7, 128.2, 120.9, 72.0, 24.0; **HRMS** (ESI): *m*/*z* calc'd for $C_{20}H_{22}N_7$ [M + H]$^+$ 360.1931, found 360.1932.



4-(4-Azidophenyl)-6-phenylpyrimidine-2,5-diamine (3): To a solution of **2** (100 mg, 0.278 mmol, 1.0 equiv) in CH_2Cl_2 (280 μL, 1.0 M) were added $BF_3•Et_2O$ (280 μL, 2.22 mmol, 8.0 equiv) and TFA (170 μL, 2.22 mmol, 8.0 equiv) at RT. After it was stirred at RT for 3 h, sat aq $NaHCO_3$ was added. The aqueous phase was extracted with EtOAc (3x). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and removed under reduced pressure. The crude material was purified by flash column chromatography eluting *n*-hexane/EtOAc to afford the title compound as a red amorphous (76.9 mg, 91%). **IR** (thin film) 3326, 3198, 2359, 2113, 1671, 1602, 1281, 1202, 1185, 1132 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85–7.79 (m, 2H), 7.77–7.72 (m, 2H), 7.56–7.42 (m, 3H), 7.19–7.12 (m, 2H), 4.80 (s, 2H), 3.47 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.0, 154.6, 153.0, 141.3, 136.9, 133.7, 130.4, 129.6, 129.1, 128.6, 128.0, 119.5; **HRMS** (ESI): *m*/*z* calc'd for $C_{16}H_{14}N_7$ [M + H]$^+$ 304.1305, found 304.1313.

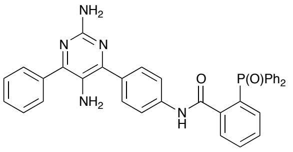


4-(4-(4-Butyl-1*H*-1,2,3-triazol-1-yl)phenyl)-6-phenylpyrimidine-2,5-diamine (4): In a 2 mL vial $[Cu(CH_3CN)_4]PF_6$ (1.3 mg, 0.033 mmol, 10 mol%) and TBTA[4] (2.1 mg, 0.040 mmol, 12 mol%) were dissolved in THF (200 μL) at RT and were allowed to stir for 30 min. To this a solution of azide **3** (10 mg, 0.33 mmol, 1.0 equiv) and 1-hexyne (15 μL, 0.40 mmol, 1.2 equiv) in THF (460 μL) was added at RT. The mixture was stirred at RT for 14 h. All volatiles were removed under reduced pressure to give a crude material, which was purified by flash column chromatography (*n*-hexane/EtOAc) to give **4** (7.4 mg, 59%) as an amorphous solid. **IR** (thin film) 3316, 3196, 2956, 2928, 2857, 1609, 1553, 1518, 1453, 1431, 1377, 1209, 1042 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01–7.95 (m, 2H), 7.90–7.84 (m, 2H), 7.79–7.73 (m, 3H), 7.57–7.43 (m, 3H), 4.75 (s, 2H), 3.51 (s, 2H), 2.82 (t, *J* = 7.7 Hz, 2H), 1.80–1.68 (m, 2H), 1.45 (tq, *J* = 7.3, 7.4 Hz, 2H), 0.97 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.0, 155.0, 152.3, 149.6, 137.8, 137.3, 136.9, 130.3, 129.7, 129.1, 128.6, 128.1, 120.7, 118.8, 31.6, 25.5, 22.5, 14.0; **HRMS** (ESI): *m*/*z* calc'd for $C_{22}H_{24}N_7$ [M + H]$^+$ 386.2088, found 386.2088.

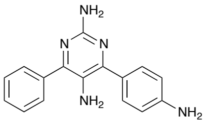


((5a*R*,6*S*,6a*S*)-1-(4-(2,5-Diamino-6-phenylpyrimidin-4-yl)phenyl)-1,4,5,5a,6,6a,7,8-octahydrocyclopropa[5,6]cycloocta[1,2-*d*][1,2,3]triazol-6-yl)methanol (5): To a solution of azide **3** (10 mg, 0.33 mmol, 1.0 equiv) in THF (330 μL, 0.1 M) was added (1*R*,8*S*,9s)-bicyclo[6.1.0]non-4-yn-9-ylmethanol (5.0 mg, 0.33 mmol, 1.0 equiv) at RT. After the solution was stirred for 8 h at RT, the solvent was removed under reduced pressure. The crude material was purified by flash column chromatography (*n*-hexane/EtOAc) to give **5** (9.1 mg, 61%) as a yellow solid. **m.p.** 237–240 °C; **IR** (thin film) 3316, 3204, 2923, 2862, 2080, 1907, 1607, 1552, 1454, 1435, 1378, 1208, 1025 cm^{-1}; **^{1}H NMR** (400 MHz, THF-*d*$_8$) δ 7.36–7.25 (m, 2H), 7.12–7.02 (m, 2H), 6.80–6.72 (m, 2H), 6.72–6.65 (m, 2H), 6.65–6.57 (m, 1H), 4.58 (s, 2H), 3.19 (s, 2H), 2.92–2.83 (m, 2H), 2.52 (t, *J* = 3.5 Hz, 1H), 2.38 (ddd, *J* = 3.4, 7.9, 15.5 Hz, 1H), 2.25 (ddd, *J* = 3.1, 6.9, 16.1 Hz, 1H), 2.11 (ddd, *J* = 3.4, 9.3, 15.5 Hz, 1H), 1.95 (ddd, *J* = 3.1, 10.2, 16.1 Hz, 1H), 1.53–1.33 (m, 2H), 0.93–0.78 (m, 2H), 0.39–0.28 (m, 1H), 0.28–0.14 (m, 2H); **^{13}C NMR** (100 MHz, THF-*d*$_8$) δ 158.9, 155.2, 152.9, 145.7, 140.2, 139.3, 138.4, 134.9, 130.8, 129.8, 129.6, 129.2, 129.0, 126.4, 67.1, 59.3, 27.1, 24.8, 24.0, 23.6, 22.7, 21.0, 20.6; **HRMS** (ESI): *m*/*z* calc'd for $C_{26}H_{28}ON_7$ [M + H]$^+$ 454.2350, found 454.2348.

N-(4-(2,5-Diamino-6-phenylpyrimidin-4-yl)phenyl)-2-(diphenylphosphoryl)benzamide (6): To a solution of azide **3** (8.8 mg, 0.029 mmol, 1.0 equiv) in 19:1 CH_3CN/H_2O (145 µL, 0.2 M) was added methyl 2-(diphenylphosphino)benzoate (10.2 mg, 0.032 mmol, 1.1 equiv) at RT. After the solution was stirred for 20 h at RT, the solvent was removed under reduced pressure. The crude material was purified by flash column chromatography (*n*-hexane/EtOAc) to give **6** (6.8 mg, 40%) as a yellow solid. **m.p.** 284–287 °C (decomp.); **IR** (thin film) 3305, 3178, 3055, 2926, 1671, 1600, 1531, 1436, 1379, 1322, 1208, 1181, 1118 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.92 (s, 1H), 8.12 (ddd, J = 1.3, 4.0, 7.7 Hz, 1H), 7.76–7.72 (m, 2H), 7.71–7.59 (m, 9H), 7.57–7.49 (m, 3H), 7.48–7.41 (m, 7H), 7.12 (ddd, J = 1.3, 7.7, 14.5 Hz, 1H), 4.74 (s, 2H), 3.49 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.7 (d, *J* = 4.0 Hz), 156.9, 153.9 (d, *J* = 42.4 Hz), 141.3, 141.2, 139.1, 137.2, 133.4 (d, *J* = 11.8 Hz), 133.1 (d, *J* = 2.5 Hz), 132.7 (d, *J* = 2.9 Hz), 132.6, 131.8 (d, *J* = 10.0 Hz), 131.0, 130.5 (d, *J* = 12.0 Hz), 130.2, 130.0, 129.4, 129.1 (d, *J* = 13.4 Hz), 129.0, 128.9, 128.6, 128.1, 12f0.5; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 36.0; **HRMS** (ESI): *m/z* calc'd for $C_{35}H_{29}O_2N_5P$ $[M + H]^+$ 582.2053, found 582.2054.



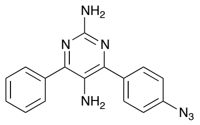
4-(4-Aminophenyl)-6-phenylpyrimidine-2,5-diamine (7): To a solution of azide **3** (12.1 mg, 39.9 µmol, 1.0 equiv) in 1:1 THF/EtOH (527 µL, 0.075 M) was added 10% Pd/C (5.3 mg). The suspension was stirred under a hydrogen atmosphere for 2 h. After Ar was flushed into the flask, the mixture was filtered through a pad of Celite, washed with THF, and removed under reduced pressure. The crude material was purified by flash column chromatography ($CHCl_3$/MeOH) to give **7** (6.4 mg, 58%) as an orange solid. **m.p.** 209–211 °C; **IR** (thin film) 3320, 3200, 1608, 1550, 1517, 1449, 1380, 1293, 1208, 1178 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79–7.72 (m, 2H), 7.68–7.61 (m, 2H), 7.54–7.46 (m, 2H), 7.46–7.39 (m, 1H), 6.83–6.71 (m, 2H), 4.69 (s, 2H), 3.88 (s, 2H), 3.49 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.9, 154.5, 153.6, 147.7, 137.4, 130.1, 129.3, 129.0, 128.7, 127.9, 127.0, 115.0; **HRMS** (ESI): *m/z* calc'd for $C_{16}H_{16}N_5$ $[M + H]^+$ 278.1400, found 278.1399.



3. Absorption/emission spectra

3-1. Spectra in EtOH

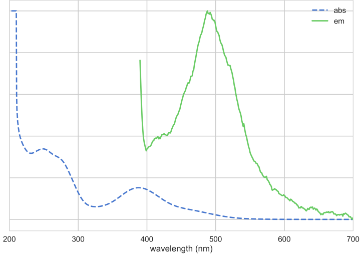
All spectra were recorded in EtOH using 0.2 mM solution for absorption, and 0.02 mM for emission with excitation at 375 nm.

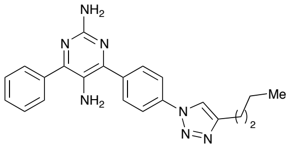


3

λ$_{abs}$: 388 (nm)

λ$_{em}$: 488 (nm)

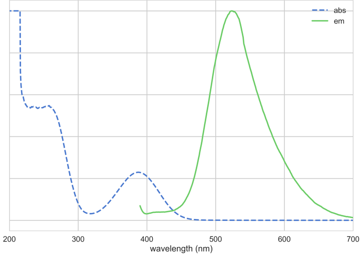


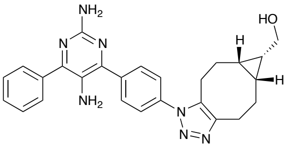


4

λ$_{abs}$: 388 (nm)

λ$_{em}$: 523 (nm)

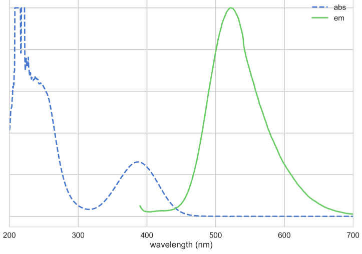


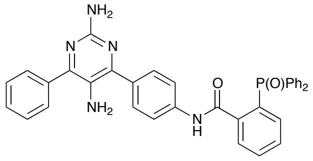


5

λ$_{abs}$: 387 (nm)

λ$_{em}$: 521 (nm)

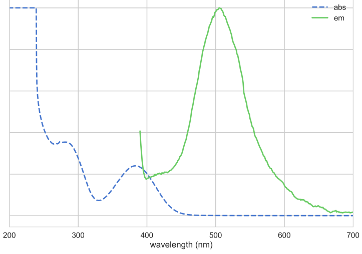


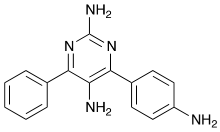


6

λ$_{abs}$: 384 (nm)

λ$_{em}$: 505 (nm)

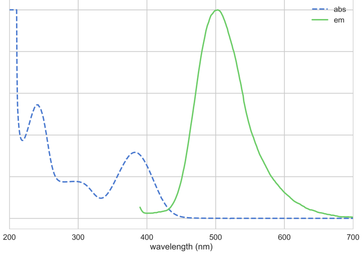


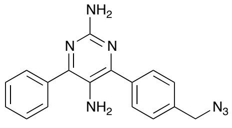


7

λ$_{abs}$: 383 (nm)

λ$_{em}$: 503 (nm)

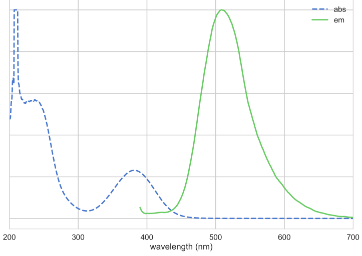




S1

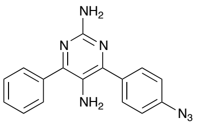
λ$_{abs}$: 382 (nm)

λ$_{em}$: 508 (nm)



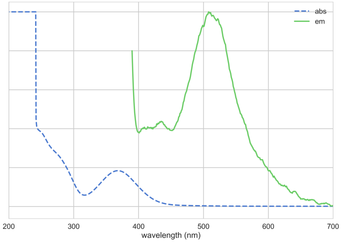
3-2. Spectra in aqueous buffer

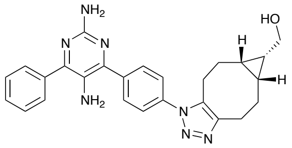
For prospective applications, absorption and emission spectra of azide **3** and triazole **5** were recorded in pH 7.4 buffer containing 20% DMSO.



3

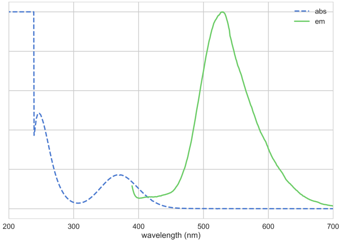
λ_{abs}: 368 (nm)
λ_{em}: 508 (nm)





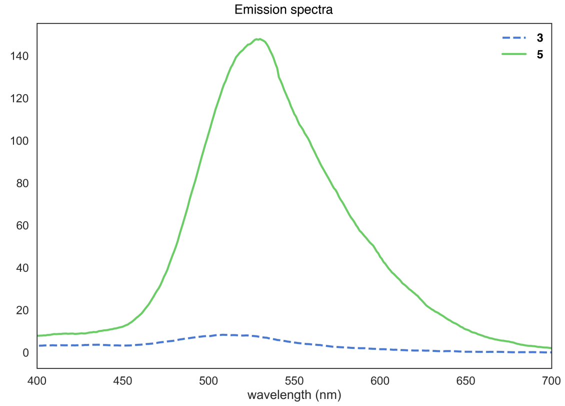
5

λ_{abs}: 370 (nm)
λ_{em}: 530 (nm)



Photophysical properties are summarized below. An enhancement in fluorescence intensity was also observed in the aqueous buffer.

C4N4	ε (M^{-1} cm^{-1})	λ_{abs} (nm)	λ_{em} (nm)	Stokes Shift	Φ_F	brightness 10^2 (ε x Φ)	x-fold brightness
3	0.3 x 10^4	368	508	140	0.01	0.257	1.0
5	0.6 x 10^4	370	530	160	0.14	5.83	23



4. Computational investigations

4-1. Computational details

The ground state geometries were optimized at the B3LYP/6-31+G(d) level of theory. Vertical transition energies were analyzed by TD/CAM-B3LYP/6-311++G(2d,p) level on the above optimized structure either in the gas phase or EtOH using the polarizable continuum model (IEFPCM) without explicit solvent molecules.

4-2. Sumarry of TD–DFT calculations

Table S1. Summary of TD–DFT calculation of **3** in the gas phase

State	Excitation energy (eV)	Transition wavelength (nm)	Oscillator strength	Main transition orbital(s)			Contribution
S_1	3.5595	348.32	0.3826	HOMO	→	LUMO	0.90
S_2	3.9081	317.25	0.0003	HOMO–1	→	LUMO+1	0.61
				HOMO	→	LUMO+1	0.14
S_3	4.3484	285.13	0.0088	HOMO–4	→	LUMO	0.35
				HOMO–2	→	LUMO	0.23
				HOMO–3	→	LUMO	0.12

Table S2. Summary of TD–DFT calculation of **3** in EtOH

State	Excitation energy (eV)	Transition wavelength (nm)	Oscillator strength	Main transition orbital(s)			Contribution
S_1	3.3972	364.96	0.5976	HOMO	→	LUMO	0.92
S_2	3.9020	317.74	0.0005	HOMO–1	→	LUMO+1	0.62
				HOMO	→	LUMO+1	0.15
S_3	4.3608	284.32	0.1631	HOMO–1	→	LUMO	0.36
				HOMO	→	LUMO+2	0.30

Table S3. Summary of TD–DFT calculation of **8** in the gas phase

State	Excitation energy (eV)	Transition wavelength (nm)	Oscillator strength	Main transition orbital(s)			Contribution
S_1	3.5461	349.64	0.3725	HOMO	→	LUMO	0.90
S_2	4.3410	285.61	0.0057	HOMO–4	→	LUMO	0.42
				HOMO–2	→	LUMO	0.17
				HOMO–3	→	LUMO	0.09
S_3	4.5696	271.33	0.0267	HOMO	→	LUMO+1	0.76

Table S4. Summary of TD–DFT calculation of **8** in EtOH

State	Excitation energy (eV)	Transition wavelength (nm)	Oscillator strength	Main transition orbital(s)			Contribution
S_1	3.3846	366.32	0.5368	HOMO	→	LUMO	0.90
S_2	4.3920	282.29	0.0248	HOMO–4	→	LUMO	0.25
				HOMO–1	→	LUMO	0.17
				HOMO	→	LUMO+1	0.13
S_3	4.4778	276.89	0.0350	HOMO	→	LUMO+1	0.58
				HOMO–4	→	LUMO	0.11

Table S5. Summary of TD–DFT calculation of **S1** in the gas phase

State	Excitation energy (eV)	Transition wavelength (nm)	Oscillator strength	Main transition orbital(s)			Contribution
S_1	3.5813	346.20	0.2890	HOMO	→	LUMO	0.95
S_2	4.2424	292.25	0.0000	HOMO–6	→	LUMO+1	0.17
				HOMO–6	→	LUMO	0.15
				HOMO–2	→	LUMO+2	0.08
S_3	4.3501	285.01	0.0040	HOMO–5	→	LUMO	0.23
				HOMO–2	→	LUMO	0.21
				HOMO–4	→	LUMO	0.19
				HOMO–1	→	LUMO	0.19

Table S6. Summary of TD–DFT calculation of **S1** in EtOH

State	Excitation energy (eV)	Transition wavelength (nm)	Oscillator strength	Main transition orbital(s)			Contribution
S_1	3.4321	361.25	0.4489	HOMO	→	LUMO	0.95
S_2	4.2103	294.48	0.0001	HOMO–6	→	LUMO+1	0.31
				HOMO–6	→	LUMO+2	0.18
				HOMO–2	→	LUMO+1	0.09
				HOMO–3	→	LUMO+1	0.08
S_3	4.4273	280.05	0.0086	HOMO–5	→	LUMO	0.51
				HOMO–1	→	LUMO	0.15
				HOMO–2	→	LUMO	0.13
				HOMO–4	→	LUMO	0.07

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6. Optimized coordinates

Optimized structure of **3** at the ground state
B3LYP/6-31+G(d)
Charge = 0 Multiplicity = 1

C	-1.16261	2.46035	-0.33032
N	-2.2963	1.75615	-0.23409
C	-2.19103	0.43191	-0.04847
C	-0.92944	-0.20093	0.06367
C	0.20092	0.62808	-0.13252
N	0.07409	1.95215	-0.31556
N	-0.8063	-1.57785	0.34217
H	0.04953	-1.81098	0.83666
H	-1.60798	-1.95781	0.83604
N	-1.28043	3.83519	-0.42598
H	-0.47649	4.30976	-0.81578
H	-2.17804	4.16717	-0.75404
C	-3.481	-0.30654	0.06438
C	-3.68574	-1.5519	-0.55578
C	-4.54789	0.27933	0.76849
C	-4.9229	-2.19538	-0.46669
H	-2.88529	-2.0066	-1.13235
C	-5.77747	-0.37113	0.86793
H	-4.39968	1.25122	1.22867
C	-5.96991	-1.61181	0.25098
H	-5.06835	-3.15067	-0.96484
H	-6.58854	0.09231	1.42408
H	-6.92994	-2.1164	0.32482
C	1.59846	0.1163	-0.11917
C	1.96343	-1.10693	-0.71167
C	2.61423	0.90519	0.45
C	3.2901	-1.53008	-0.72771
H	1.20815	-1.72342	-1.18918
C	3.94102	0.48589	0.45232
H	2.34937	1.86187	0.88839
C	4.28479	-0.73951	-0.13934
H	3.56993	-2.46722	-1.19928
H	4.70344	1.11196	0.90912
N	5.60611	-1.25431	-0.19192
N	6.52079	-0.58784	0.30893
N	7.45404	-0.08323	0.72948

Optimized structure of **8** at the ground state
B3LYP/6-31+G(d)
Charge = 0 Multiplicity = 1

C	-2.39288	2.5123	-0.31296
N	-3.44862	1.69333	-0.23747
C	-3.21073	0.38728	-0.04961
C	-1.89189	-0.11193	0.08713
C	-0.85168	0.83127	-0.08617
N	-1.11071	2.13551	-0.27252
N	-1.6329	-1.46873	0.36513
H	-0.76612	-1.6191	0.8722
H	-2.40041	-1.93421	0.83937
N	-2.65207	3.86723	-0.41335
H	-1.89521	4.42354	-0.78901
H	-3.57321	4.10338	-0.75874
C	-4.41874	-0.48149	0.03811
C	-4.48197	-1.73856	-0.58898
C	-5.55267	-0.01252	0.72474
C	-5.64702	-2.50726	-0.52367
H	-3.62871	-2.10527	-1.15232
C	-6.70946	-0.78766	0.8008
H	-5.51423	0.96731	1.19032
C	-6.76118	-2.03872	0.177
H	-5.68372	-3.47026	-1.02675
H	-7.57374	-0.41364	1.34393
H	-7.66465	-2.64066	0.23257
C	0.59194	0.46845	-0.04219
C	1.09502	-0.70671	-0.62903
C	1.50437	1.35304	0.55822
C	2.45916	-0.99179	-0.62018
H	0.41945	-1.39335	-1.12953
C	2.8657	1.06558	0.59702
H	1.13112	2.26953	1.00304
C	3.34603	-0.10623	0.00017
H	2.84267	-1.8893	-1.09192
H	3.54577	1.74279	1.10475
N	4.73479	-0.40444	0.02296
C	5.80125	0.44469	0.09914
C	6.90952	-0.37348	0.0866
H	5.69305	1.51788	0.12197
N	5.16936	-1.69153	-0.03224
N	6.47003	-1.66914	0.00609
C	8.36491	-0.03174	0.13707
H	8.88627	-0.41339	-0.74821
H	8.51333	1.05182	0.18206
H	8.84117	-0.47972	1.01689

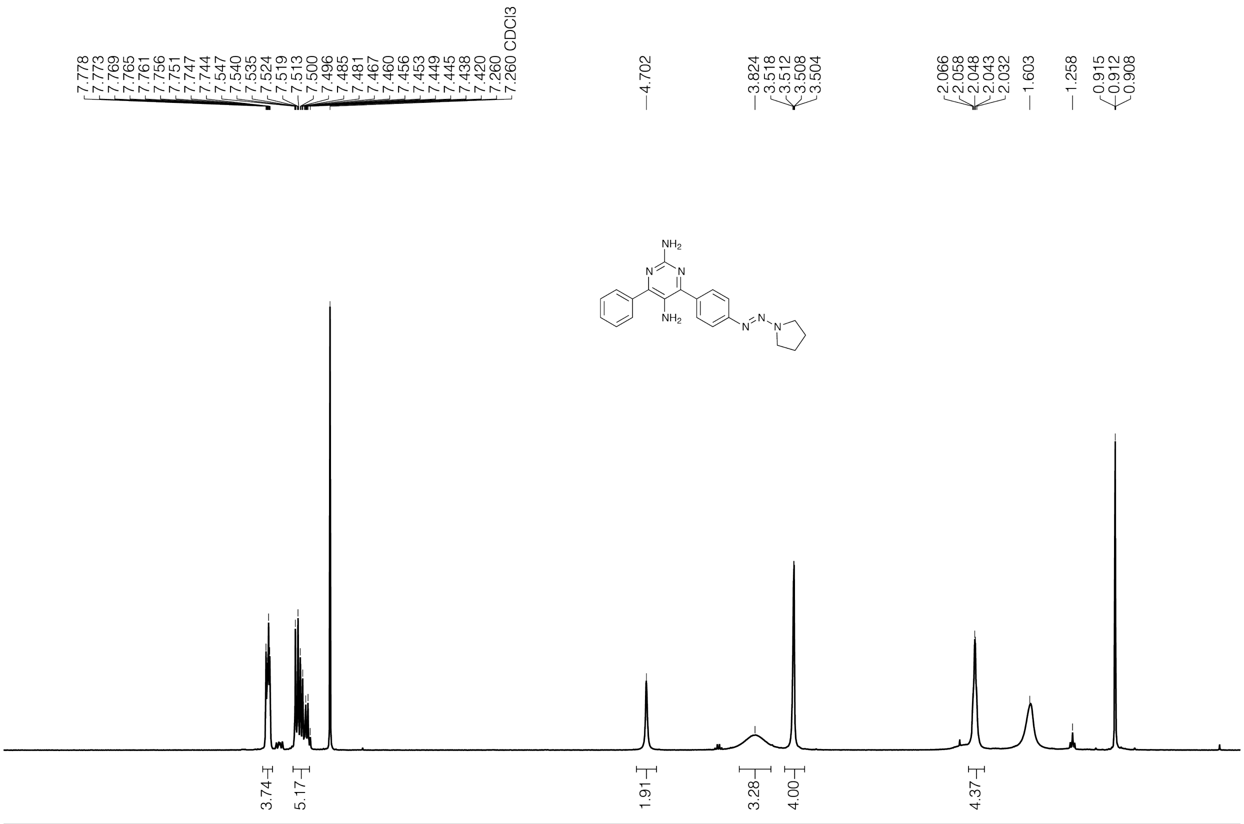
Optimized structure of **S1** at the ground state
B3LYP/6-31+G(d)
Charge = 0 Multiplicity = 1

C	-1.75539	2.58771	0.01528
N	-2.76138	1.70563	0.03696
C	-2.44762	0.40247	-0.00327
C	-1.1001	-0.03225	-0.04525
C	-0.12329	0.98695	-0.13801
N	-0.45729	2.28614	-0.09581
N	-0.75464	-1.39801	-0.01061
H	0.16264	-1.57155	0.38877
H	-1.45121	-1.97586	0.44947
N	-2.08531	3.9242	0.14859
H	-1.38663	4.57558	-0.18448
H	-3.04085	4.15689	-0.08855
C	-3.60258	-0.53911	0.03498
C	-3.65705	-1.6887	-0.77307
C	-4.69868	-0.24654	0.86582
C	-4.77589	-2.52529	-0.74398
H	-2.8351	-1.91587	-1.44581
C	-5.80813	-1.09061	0.9039
H	-4.6689	0.65229	1.47369
C	-5.85113	-2.23404	0.09914
H	-4.80759	-3.40194	-1.38613
H	-6.64258	-0.8541	1.55939
H	-6.71801	-2.88942	0.12578
C	1.33576	0.70566	-0.25321
C	1.84075	-0.31259	-1.07767
C	2.25053	1.51984	0.44042
C	3.21834	-0.51397	-1.19641
H	1.15924	-0.93514	-1.64954
C	3.62097	1.30671	0.32921
H	1.86871	2.32573	1.05896
C	4.12545	0.28554	-0.49146
H	3.587	-1.29744	-1.85552
H	4.31082	1.93826	0.8848
N	6.18919	-0.64269	0.60733
N	5.76062	-1.78026	0.82731
N	5.44135	-2.83335	1.13588
C	5.61435	0.04129	-0.59041
H	5.85216	-0.54029	-1.49075
H	6.16467	0.98277	-0.6438

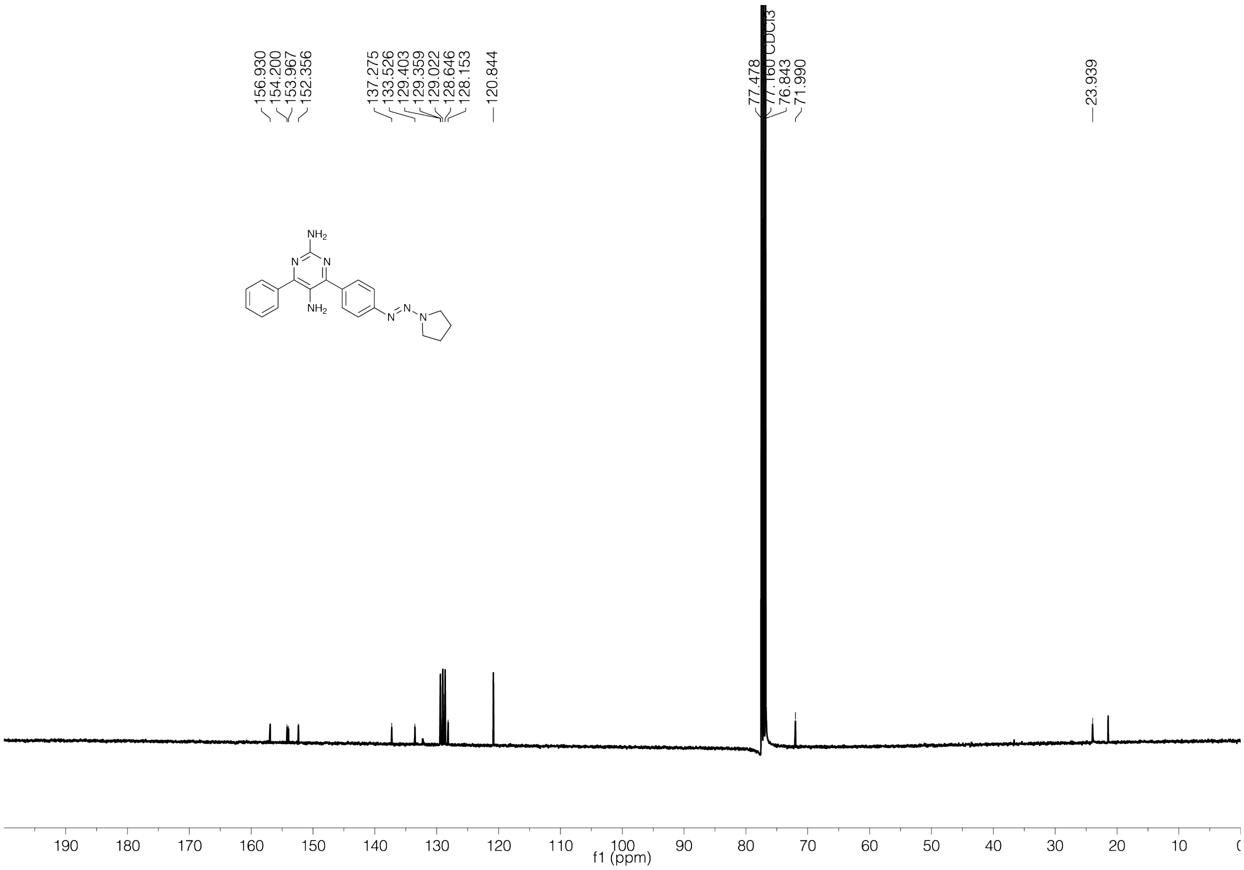
7. Spectra

(*E*)-4-Phenyl-6-(4-(pyrrolidin-1-yldiazenyl)phenyl)pyrimidine-2,5-diamine (2):

^{1}H NMR (400MHz, $CDCl_3$)

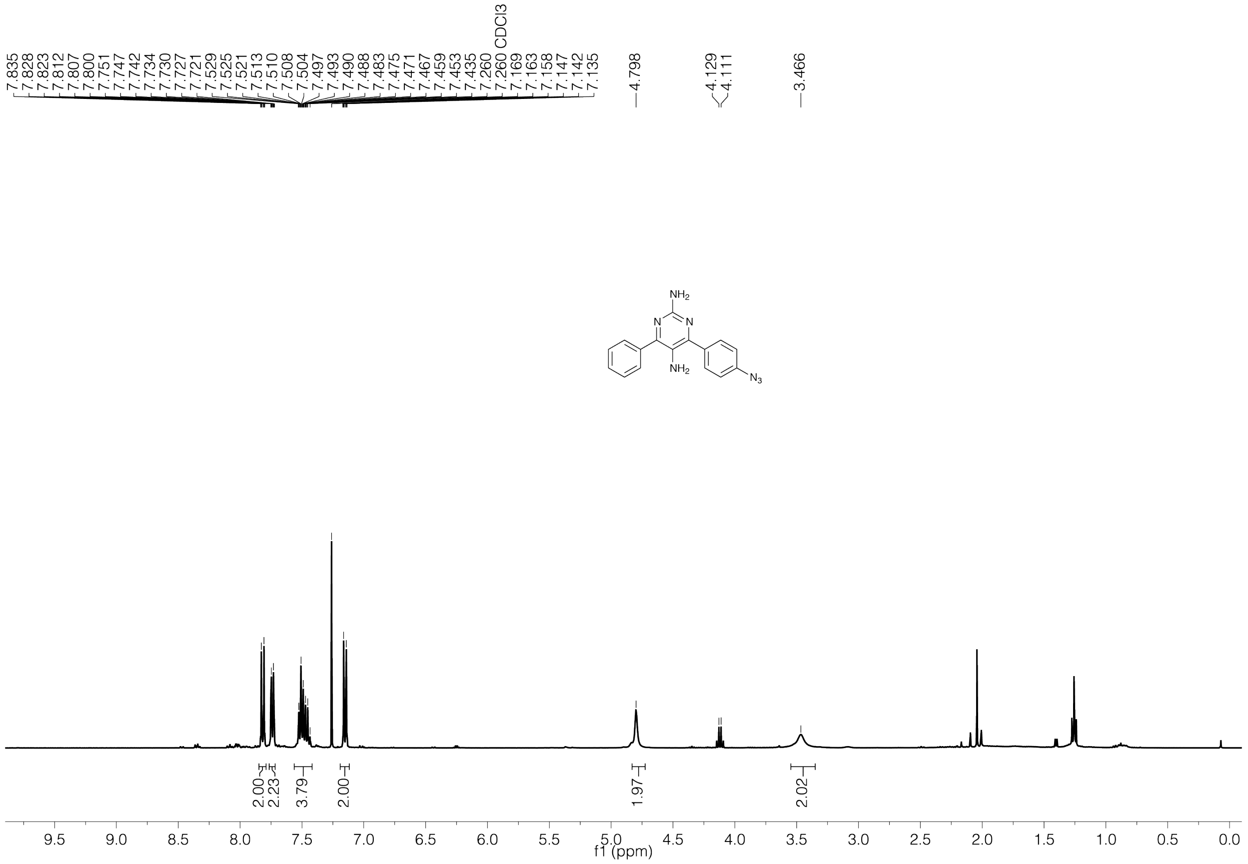


^{13}C NMR (100MHz, $CDCl_3$)

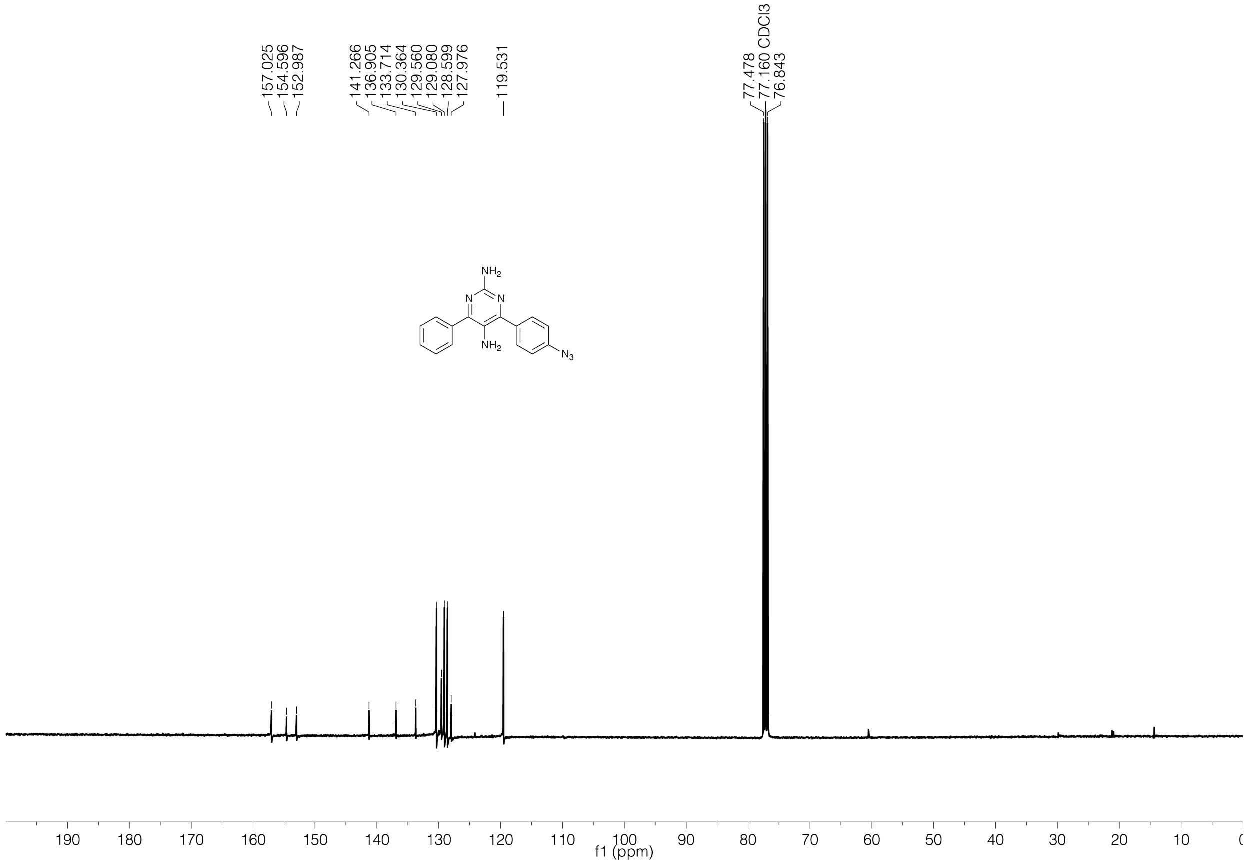


4-(4-Azidophenyl)-6-phenylpyrimidine-2,5-diamine (3):

^{1}H NMR (400MHz, $CDCl_3$)

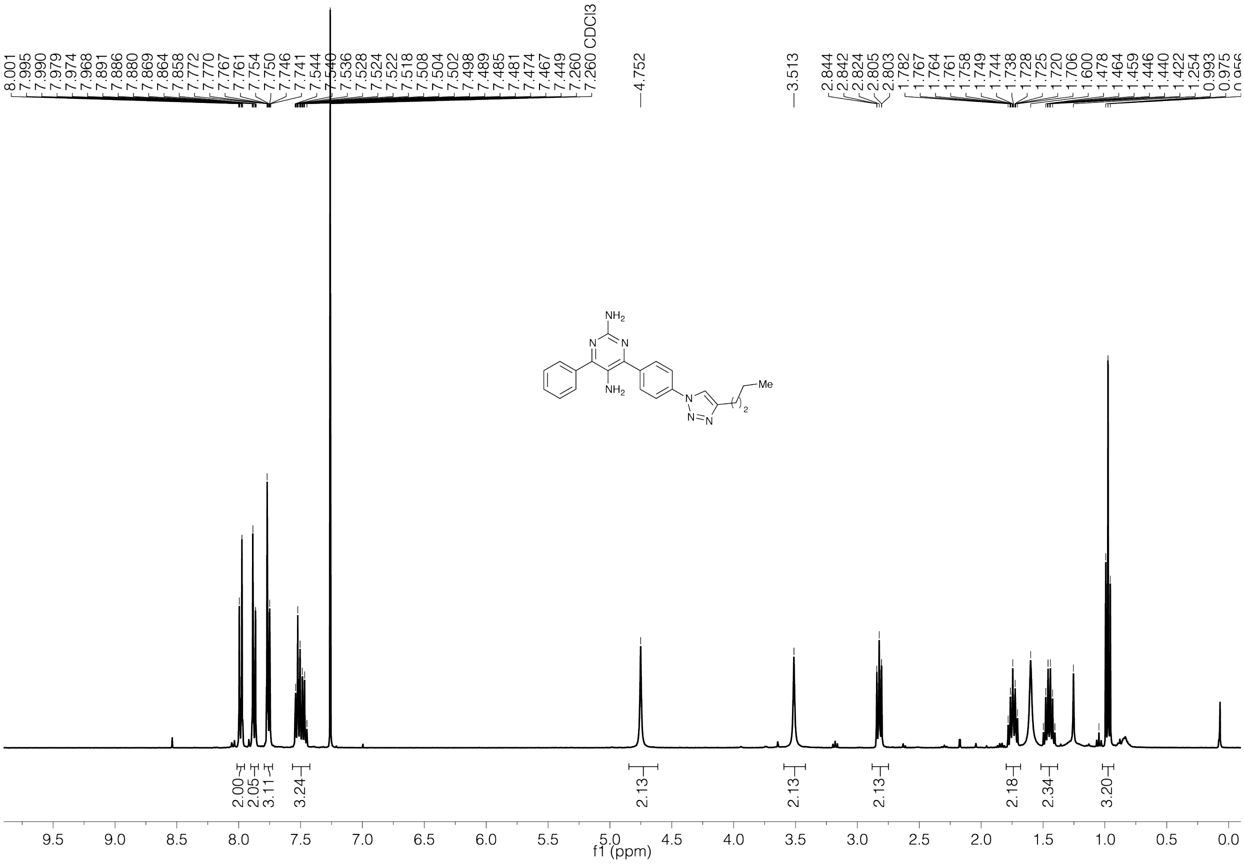


^{13}C NMR (100MHz, $CDCl_3$)

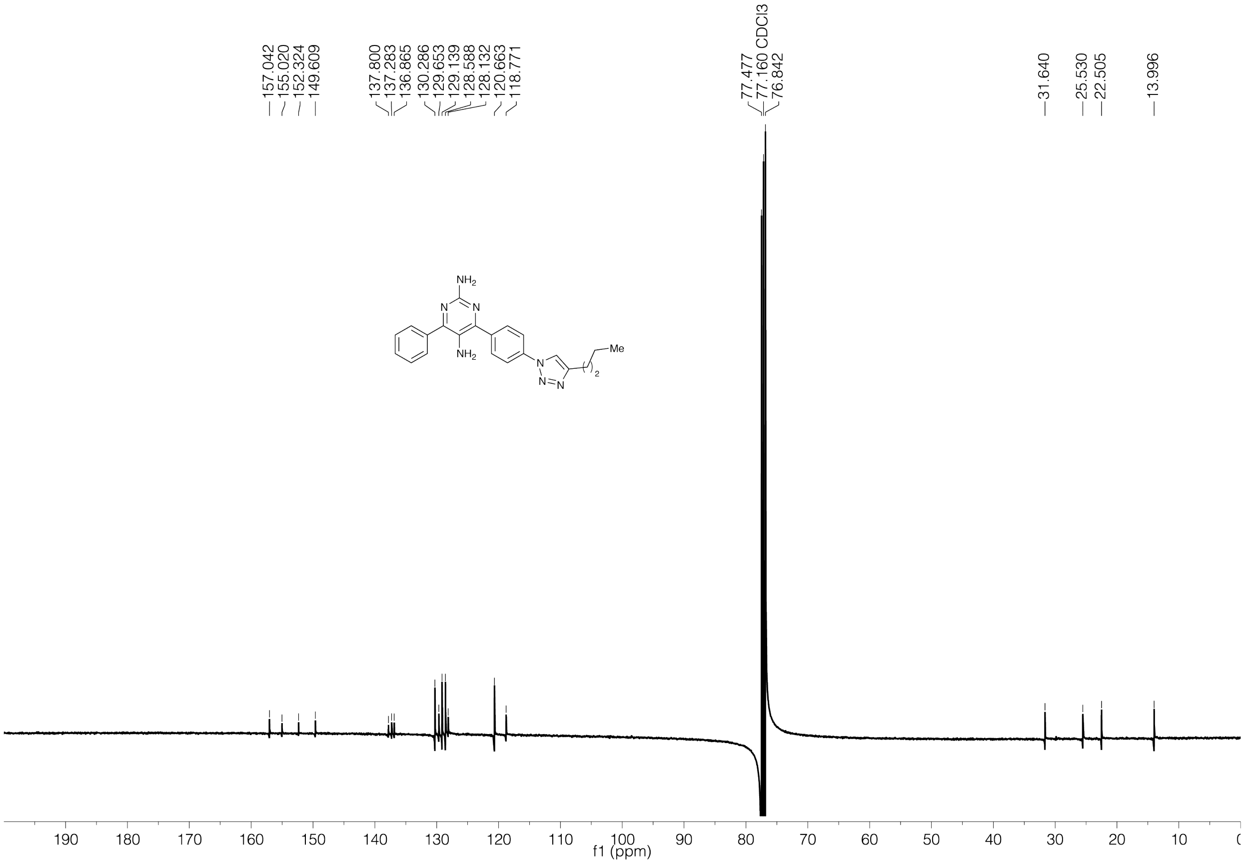


4-(4-(4-Butyl-1*H*-1,2,3-triazol-1-yl)phenyl)-6-phenylpyrimidine-2,5-diamine (4):

^{1}**H NMR** (400MHz, $CDCl_3$)

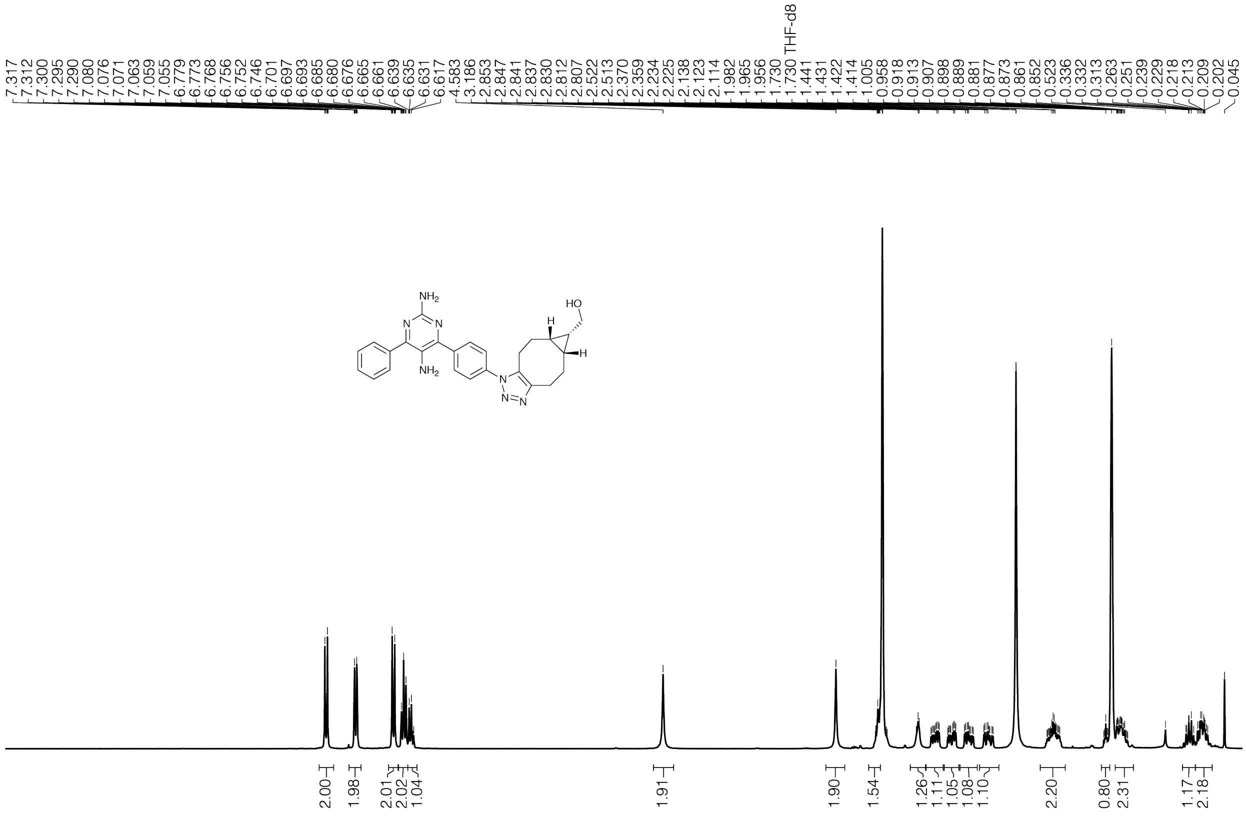


^{13}**C NMR** (100MHz, $CDCl_3$)

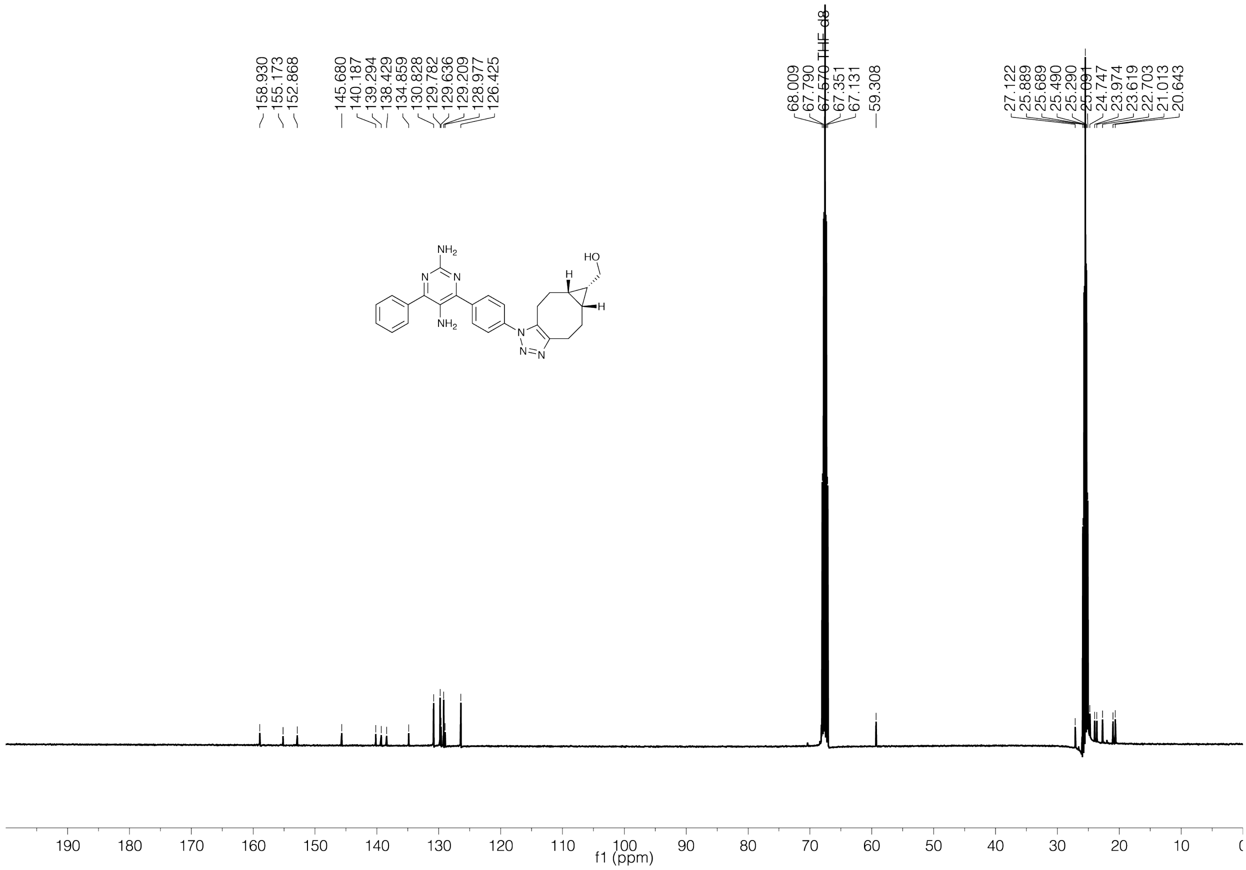


((5a*R*,6*S*,6a*S*)-1-(4-(2,5-Diamino-6-phenylpyrimidin-4-yl)phenyl)-1,4,5,5a,6,6a,7,8-octahydrocyclopropa[5,6]cycloocta[1,2-*d*][1,2,3]triazol-6-yl)methanol (5):

^{1}H NMR (400MHz, THF-*d*$_8$)

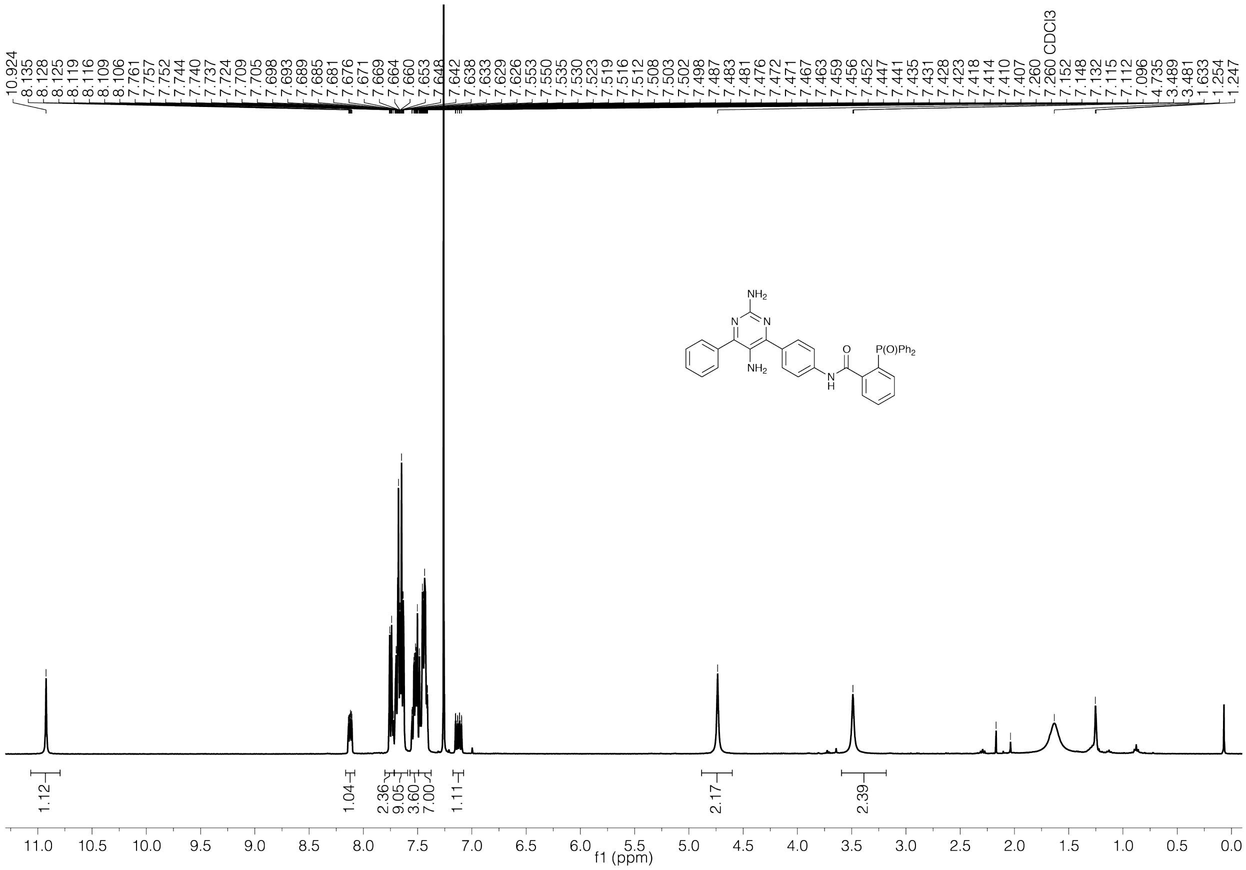


^{13}C NMR (100MHz, THF-*d*$_8$)

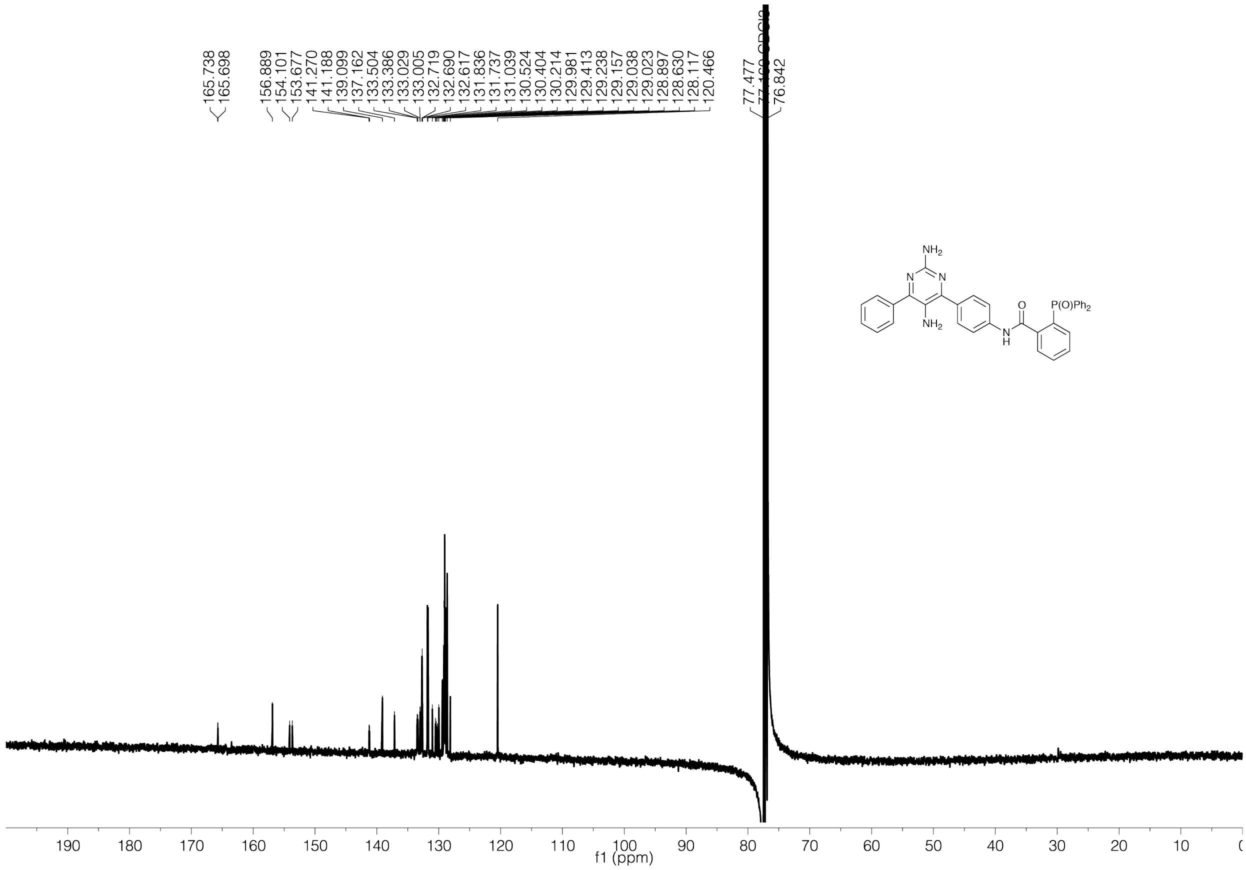


N-(4-(2,5-Diamino-6-phenylpyrimidin-4-yl)phenyl)-2-(diphenylphosphoryl)benzamide (6):

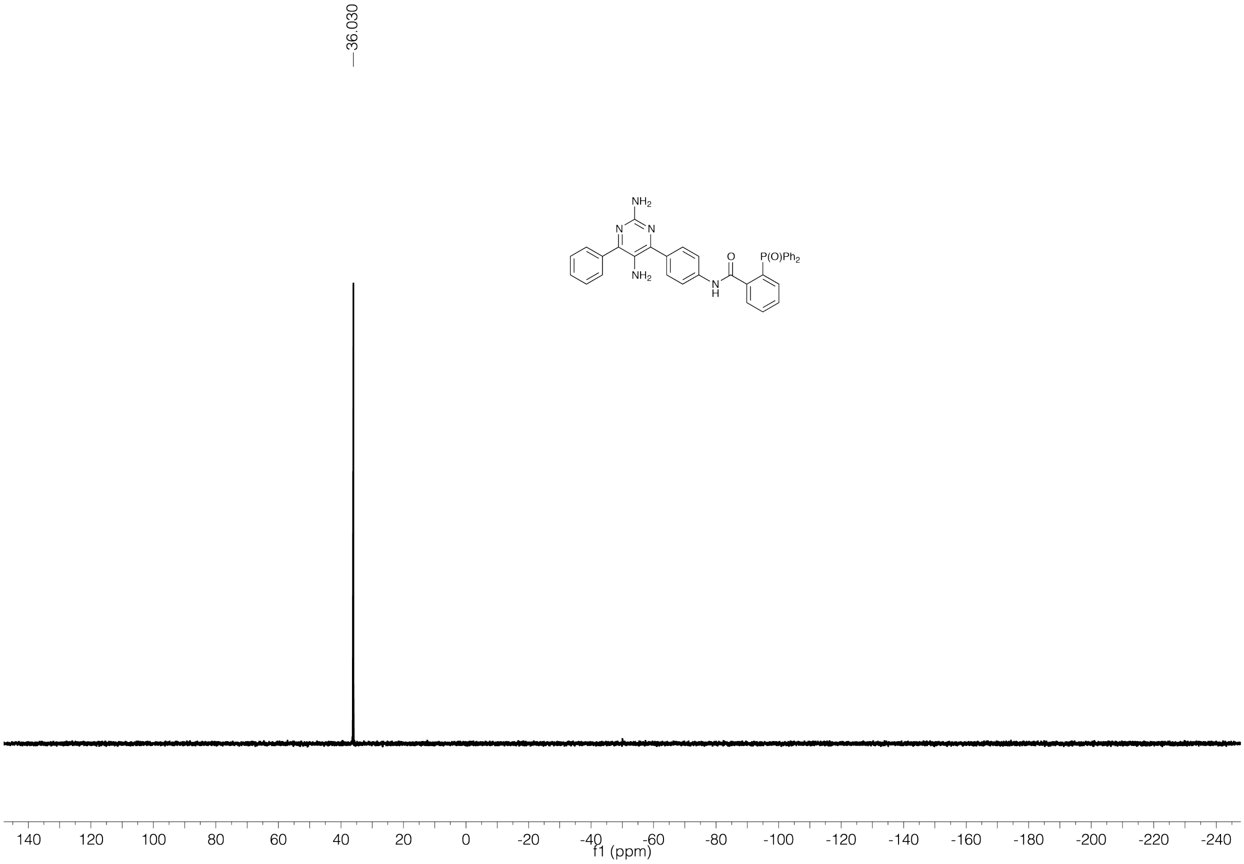
¹H NMR (400MHz, $CDCl_3$)



¹³C NMR (100MHz, $CDCl_3$)

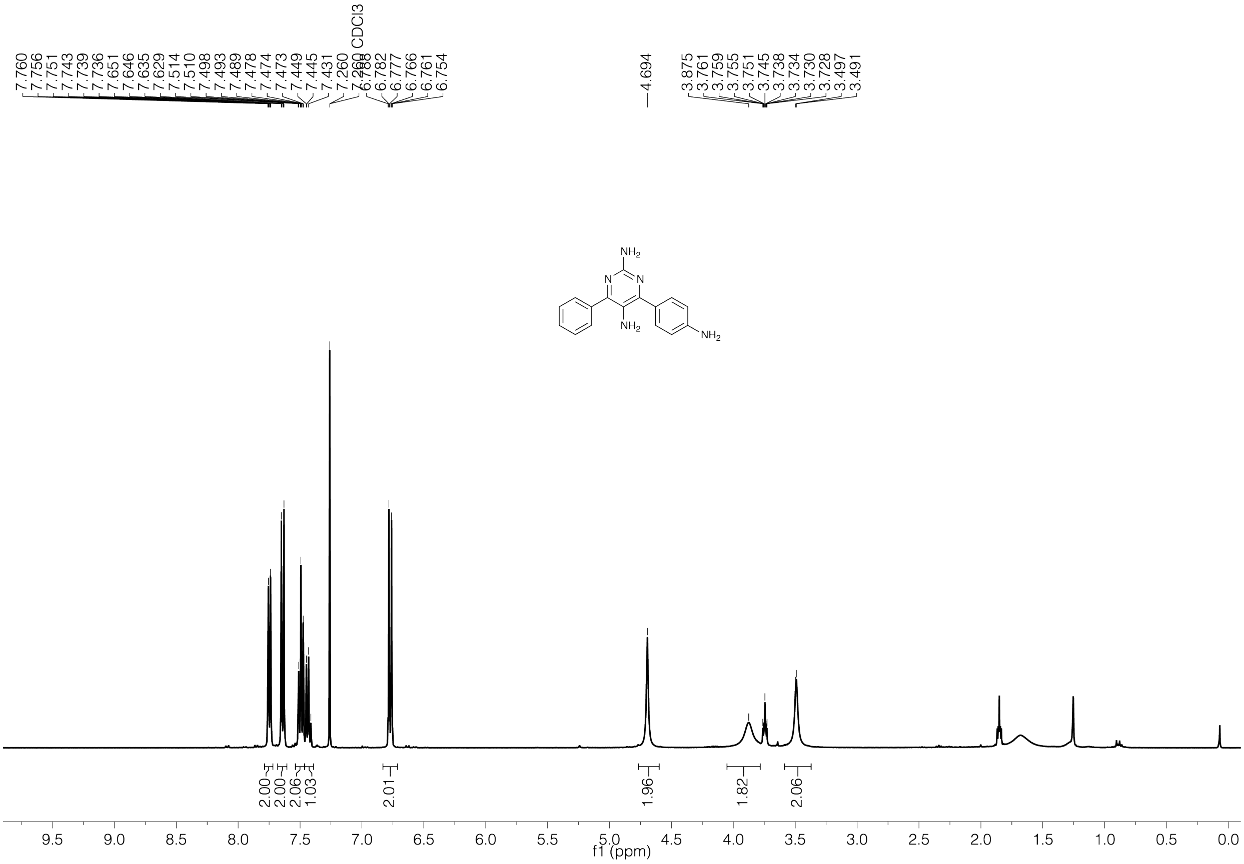


^{31}P NMR (162 MHz, $CDCl_3$)



4-(4-Aminophenyl)-6-phenylpyrimidine-2,5-diamine (7):

^{1}H NMR (400MHz, CDCl$_3$)



^{13}C NMR (100MHz, CDCl$_3$)