Supplementary Information

C4-C5 Fused pyrazol-3-amines: When the degree of unsaturation and electronic characteristics of the fused ring controls regioselectivity in Ullmann and Acylation reactions

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Table of contents:

2*H*-**13a**

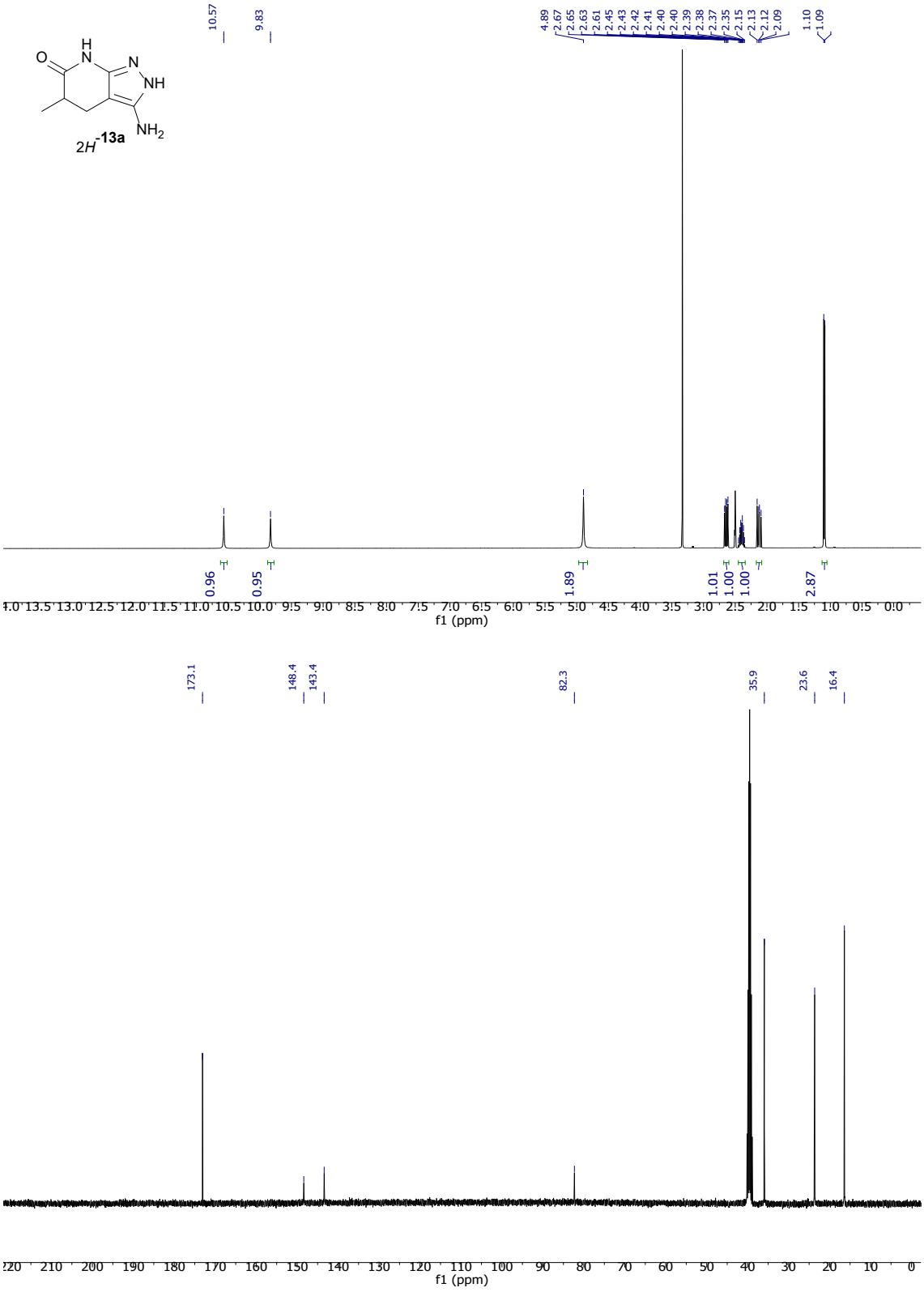

Figure S-1: ^{1}H and ^{13}C-NMR of 3-amino-5-methyl-2,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (2*H*-**13a**)

2*H*-**13b**

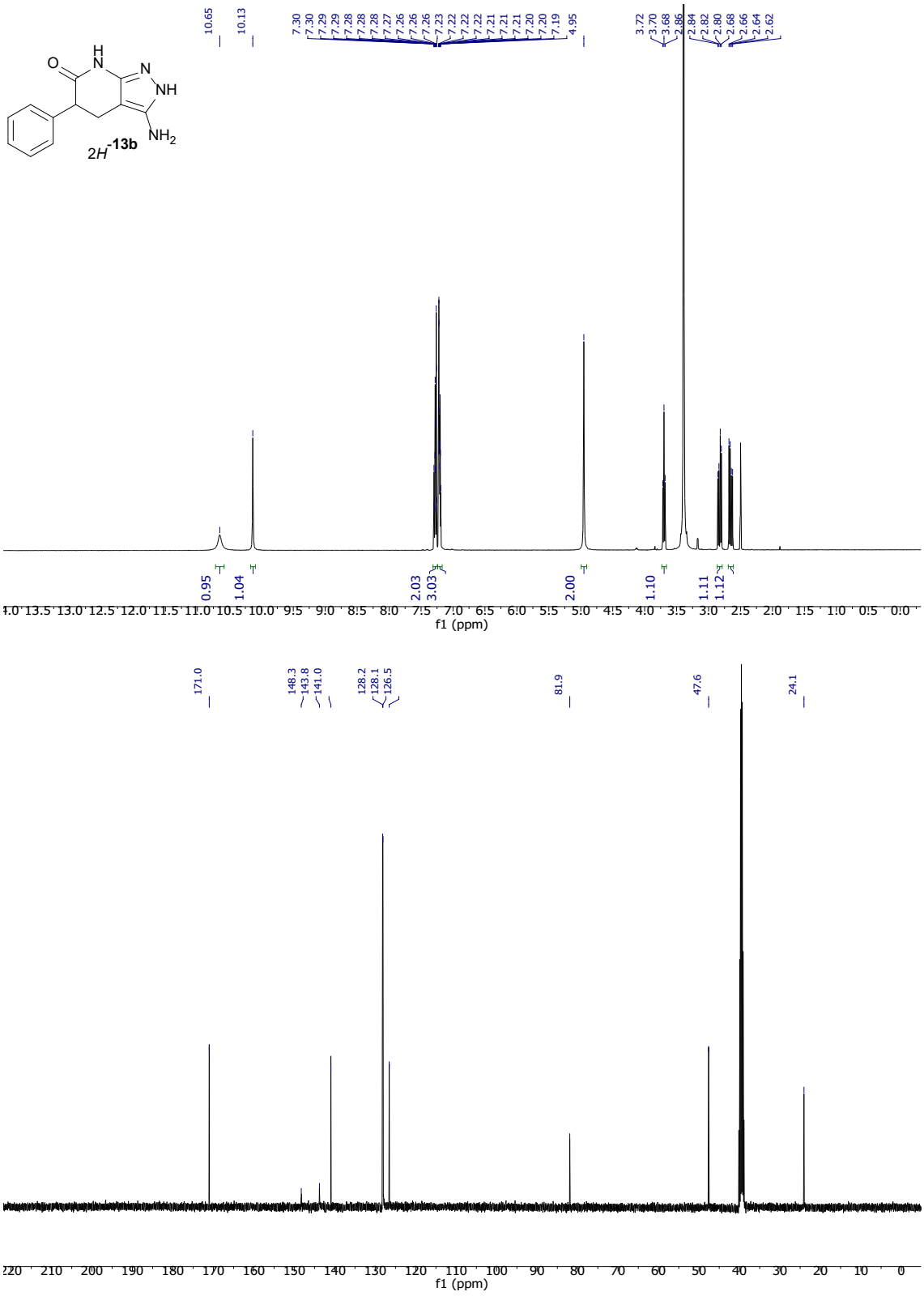

Figure S-2: ^{1}H and ^{13}C-NMR of 3-amino-5-phenyl-2,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (2*H*-**13b**)

2*H*-**13c**

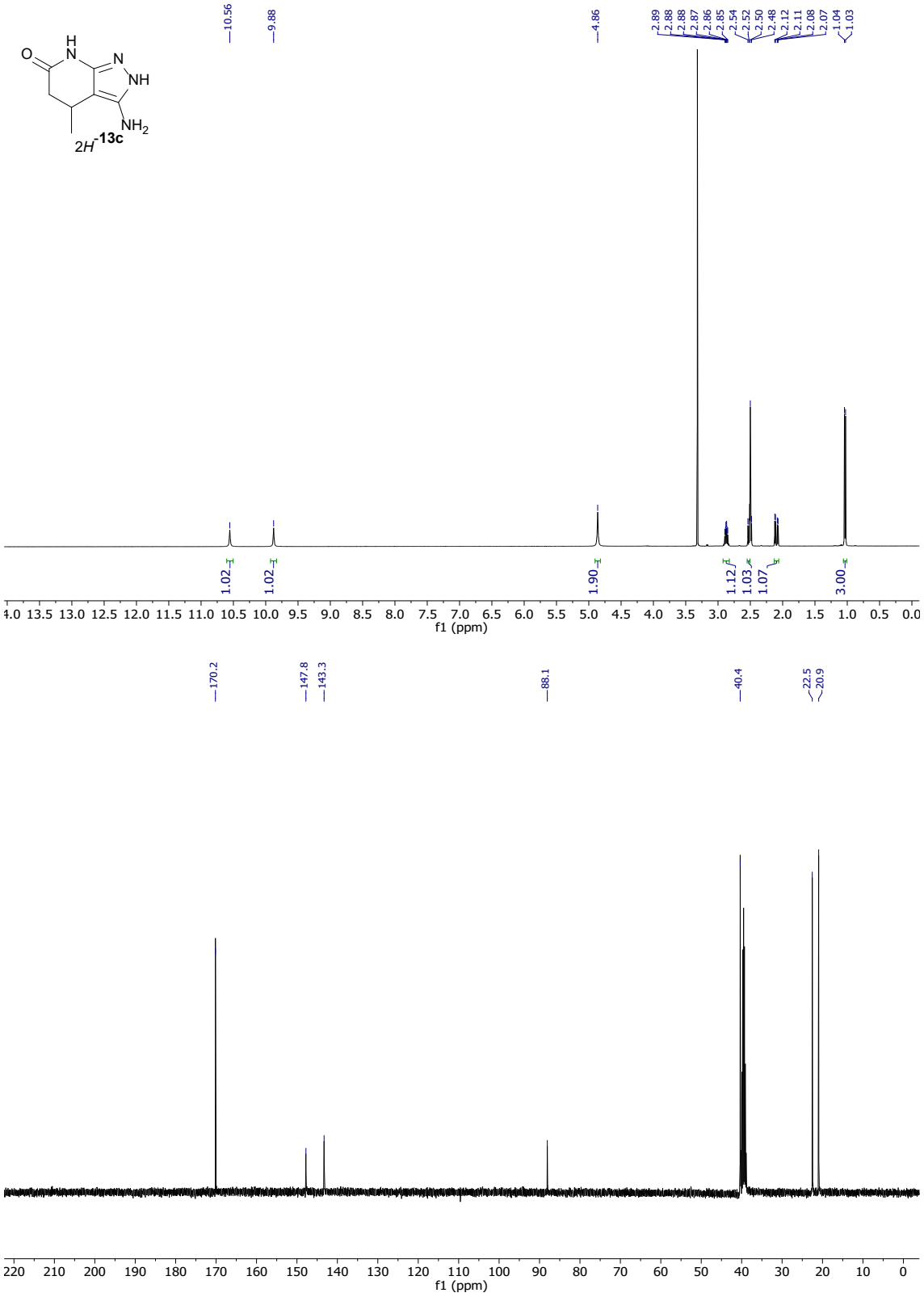

Figure S-3: ^{1}H and ^{13}C-NMR of 3-amino-4-methyl-2,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (2*H*-**13c**)

2Ph-**14a**

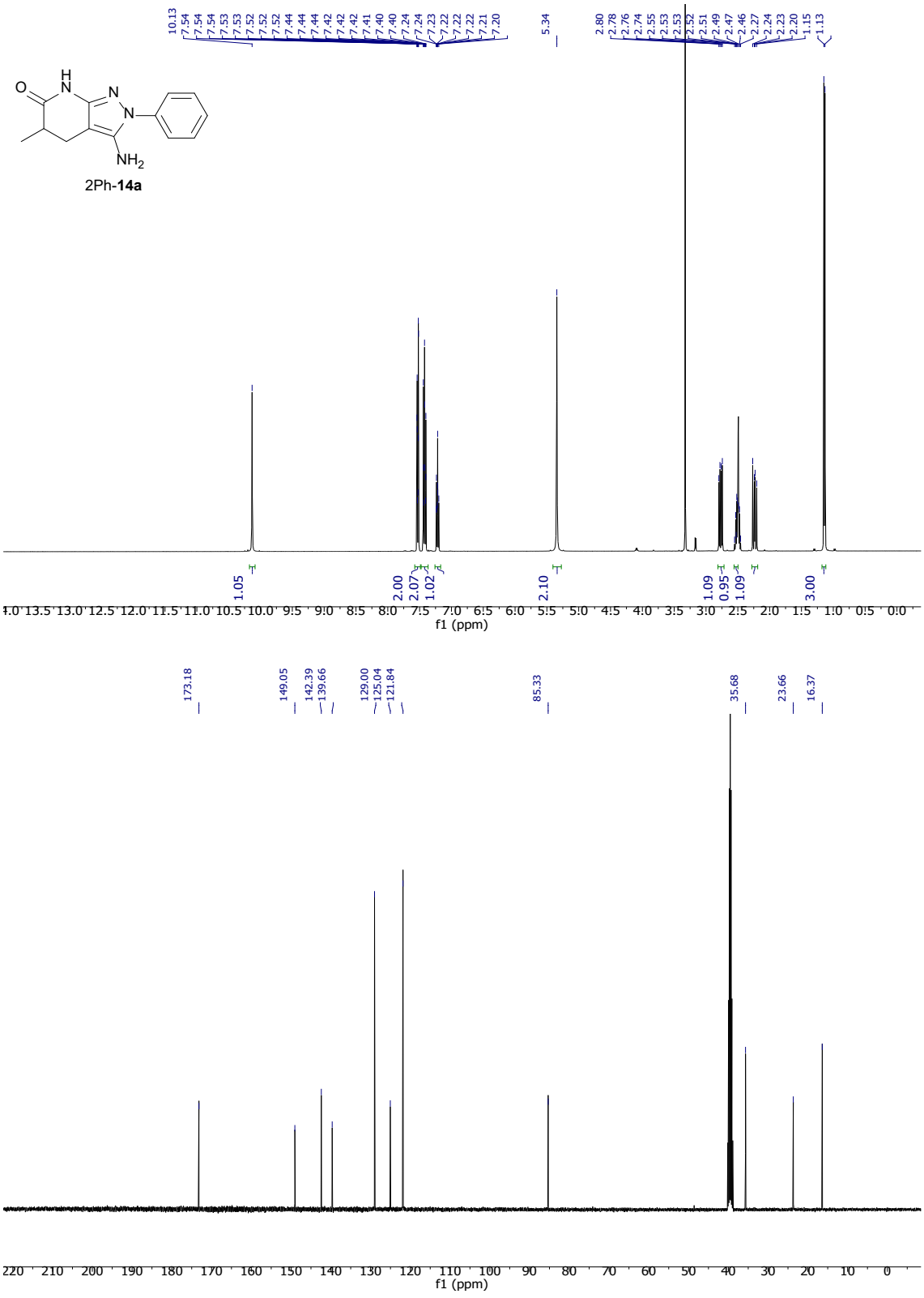

Figure S-4: ^{1}H and ^{13}C-NMR of 3-amino-5-methyl-2-phenyl-2,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (2Ph-**14a**)

2Ph-**14b**

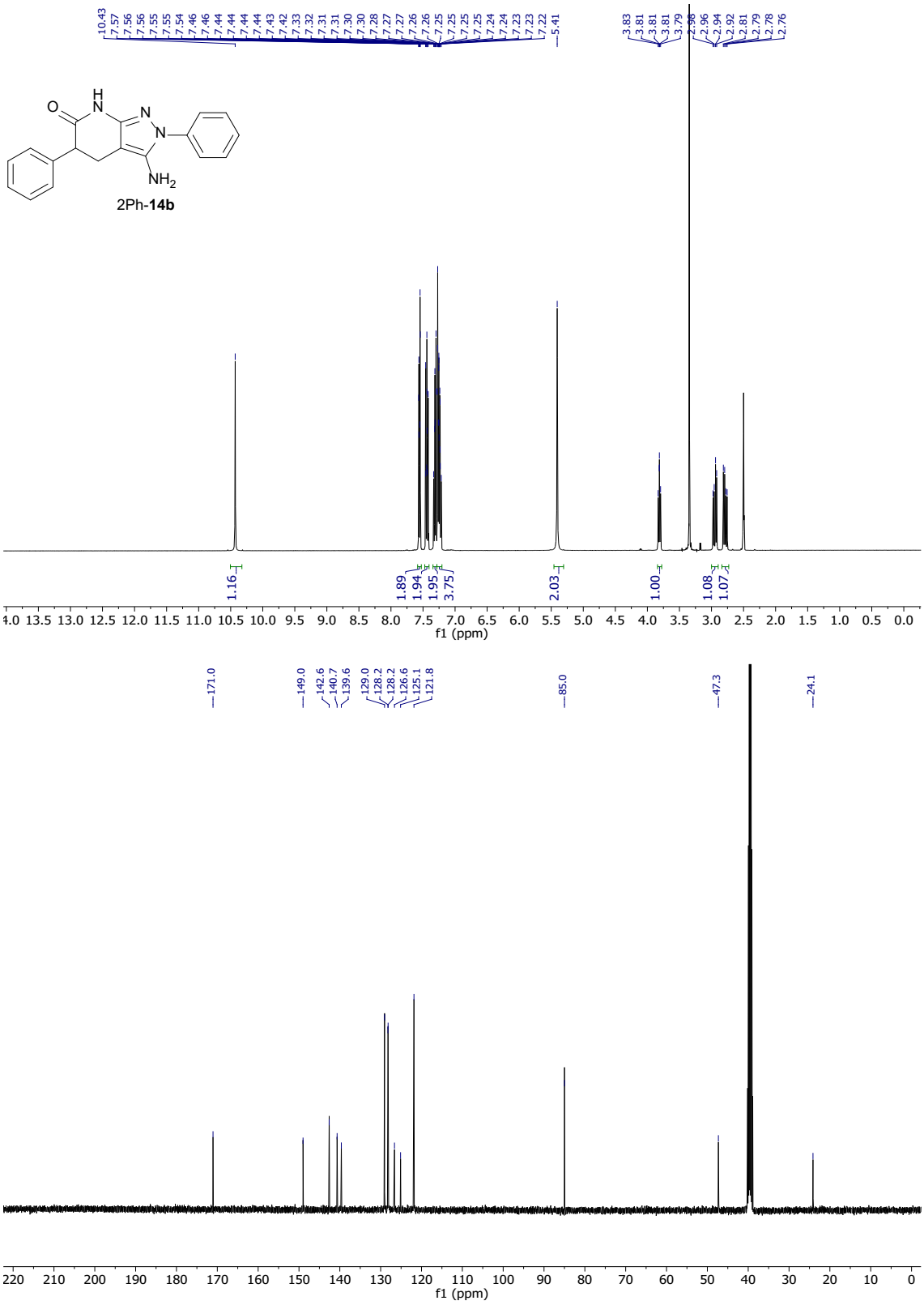

Figure S-5: ^{1}H and ^{13}C-NMR of 3-amino-2,5-diphenyl-2,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (2Ph-**14b**)

2*H*-**15b**

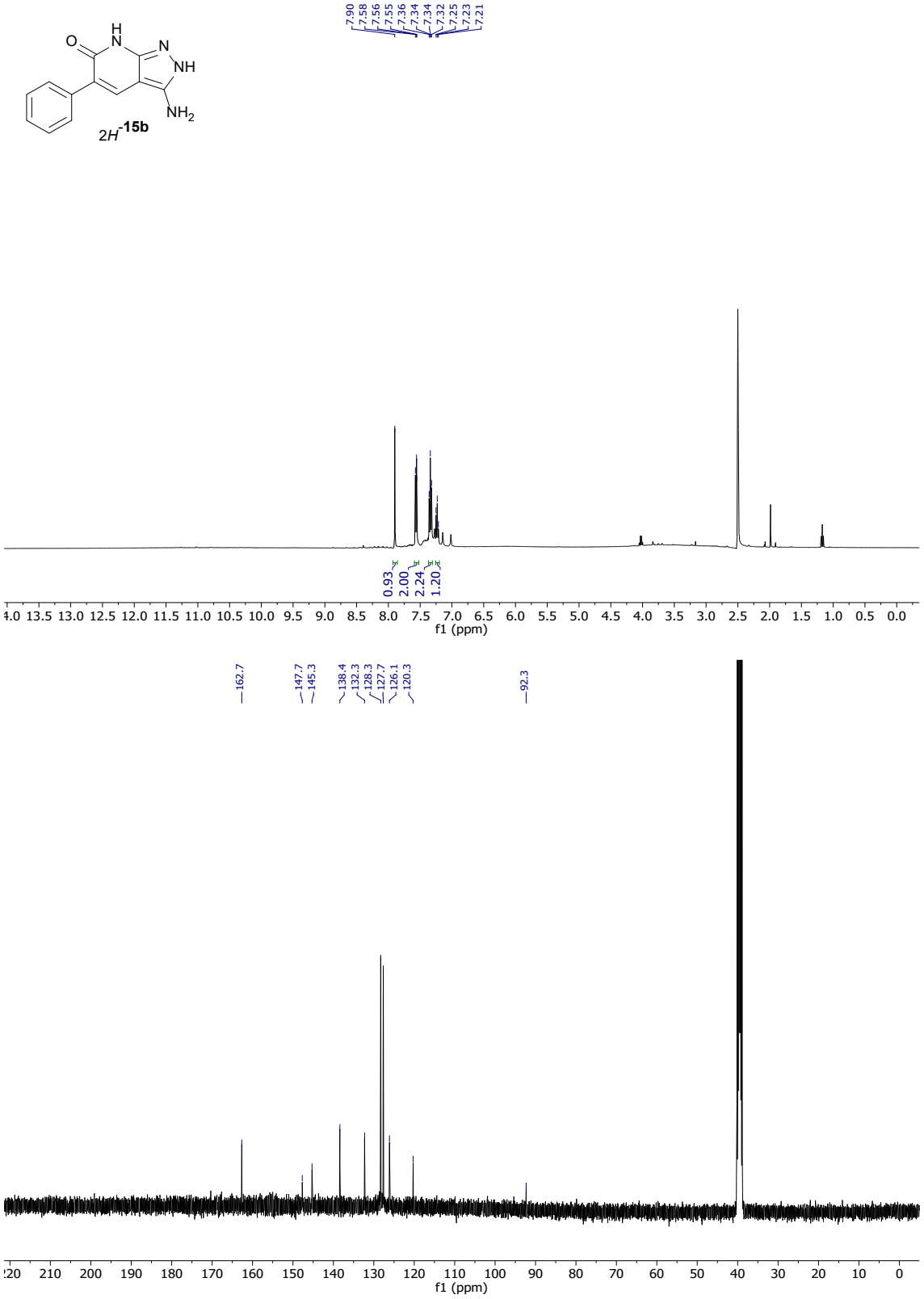

Figure S-6: ^{1}H and ^{13}C-NMR of 3-amino-5-phenyl-2,7-dihydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (2*H*-**15b**)

2Ph-**16b**

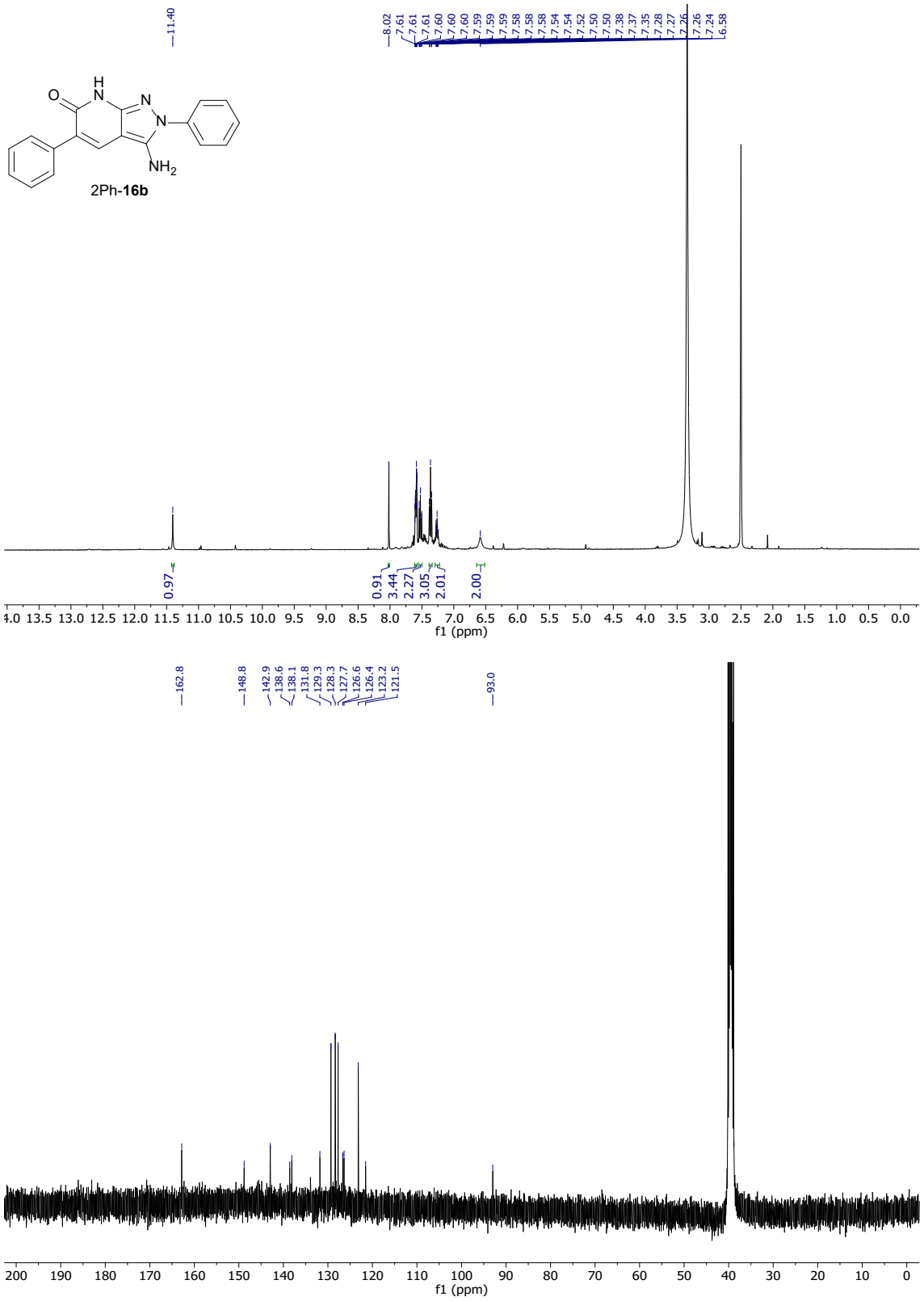

Figure S-7: ^{1}H and ^{13}C-NMR of 3-amino-2,5-diphenyl-2,7-dihydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (2Ph-**16b**)

1Ph-**16b**

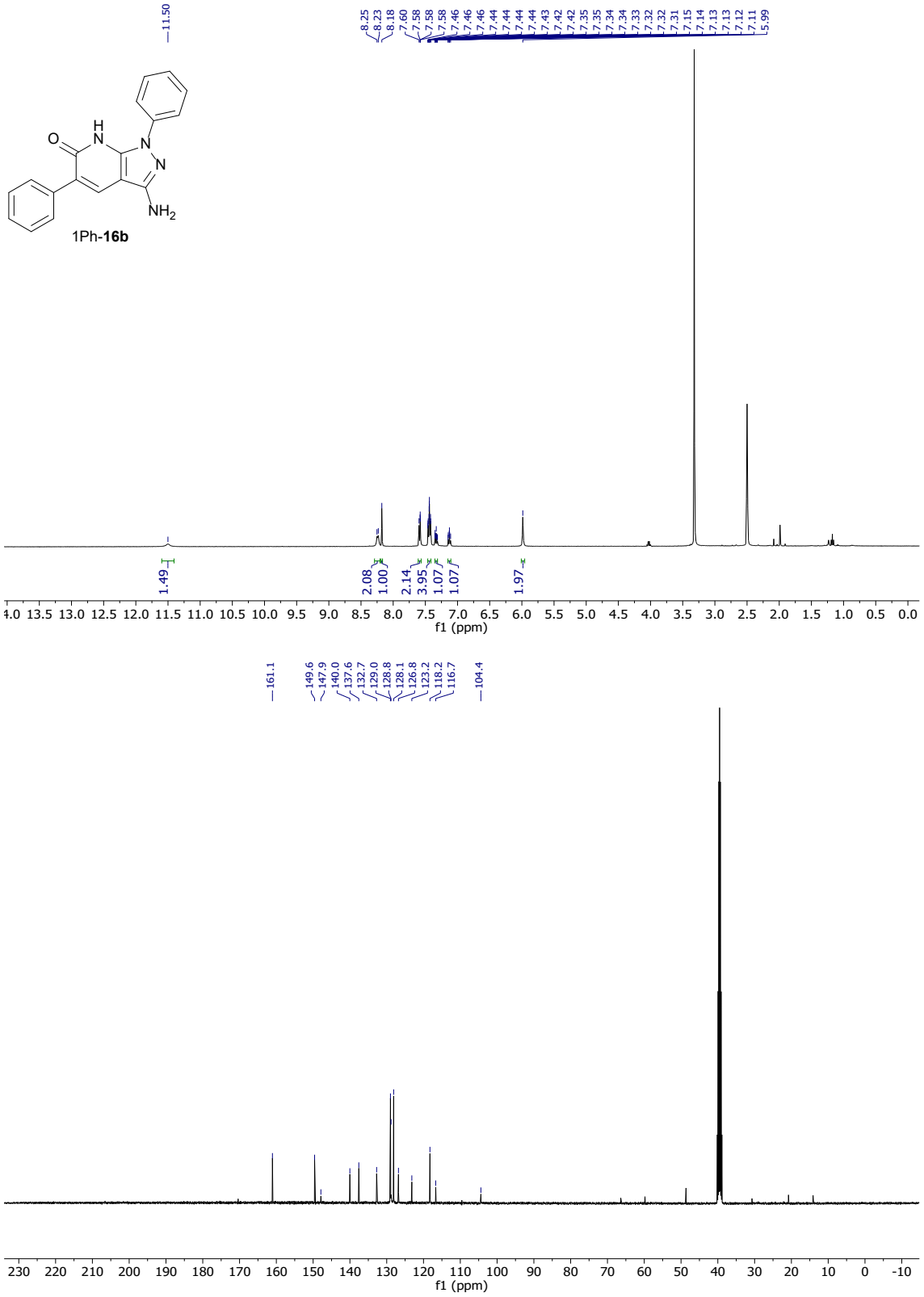

Figure S-8: ^{1}H and ^{13}C-NMR of 3-amino-1,5-diphenyl-1,7-dihydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (1Ph-**16b**)

1Bz-**17c**

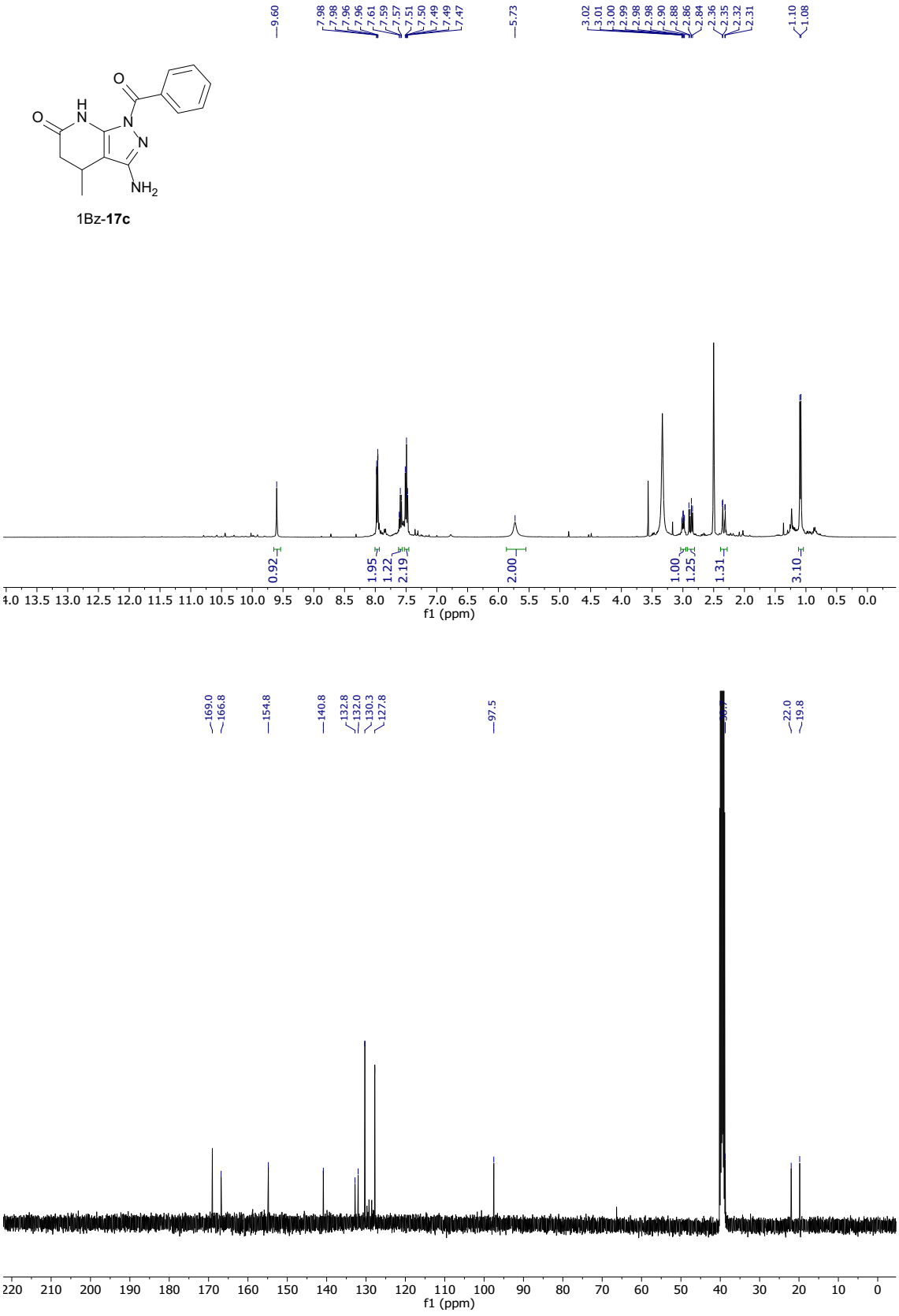

Figure S-9: ^{1}H and ^{13}C-NMR of 3-amino-1-benzoyl-4-methyl-1,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (1Bz-**17c**)

2Bz-**17c**

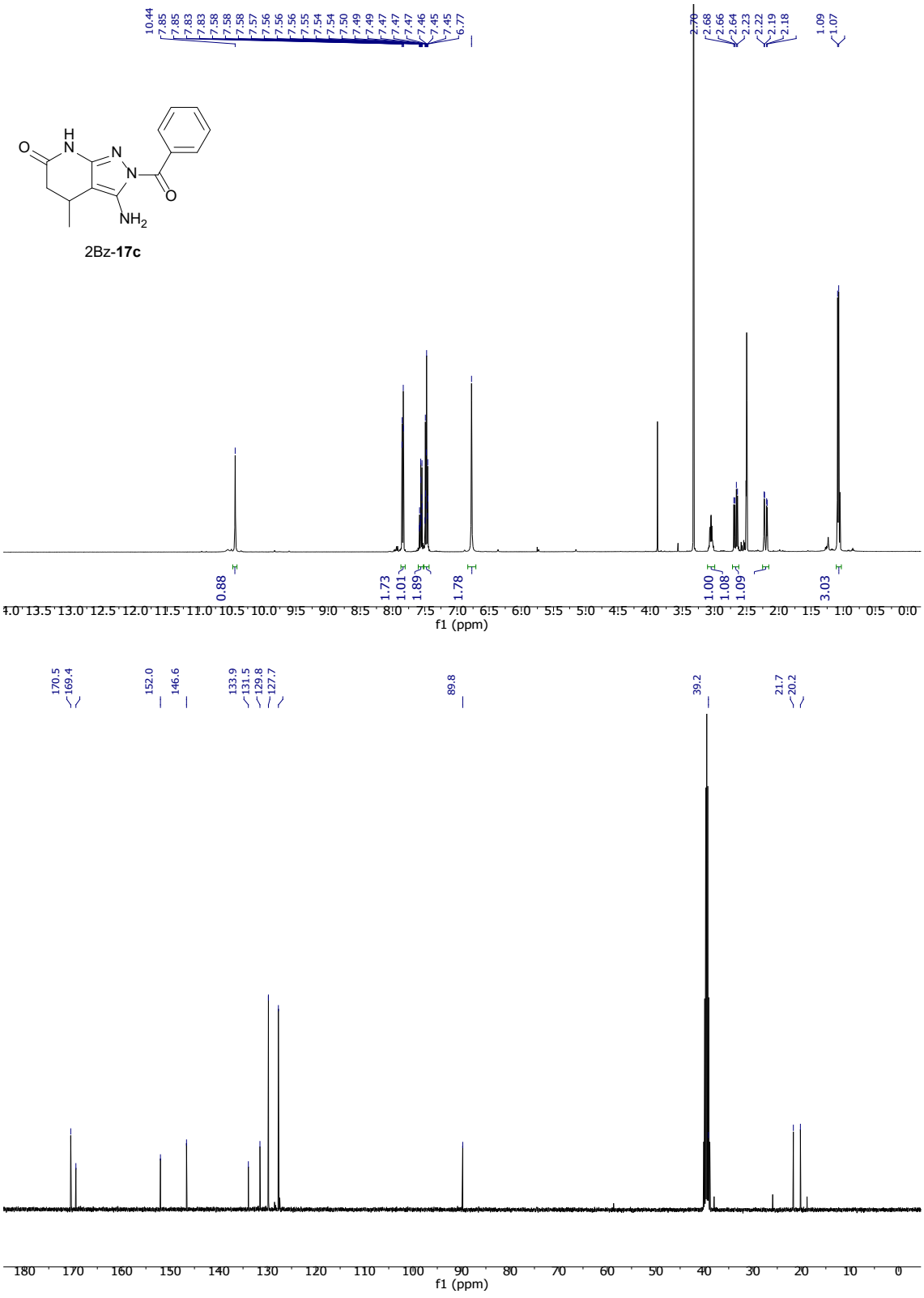

Figure S-10: ^{1}H and ^{13}C-NMR of 3-amino-2-benzoyl-4-methyl-2,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (2Bz-**17c**)

^{13}C-2Bz-**17c**

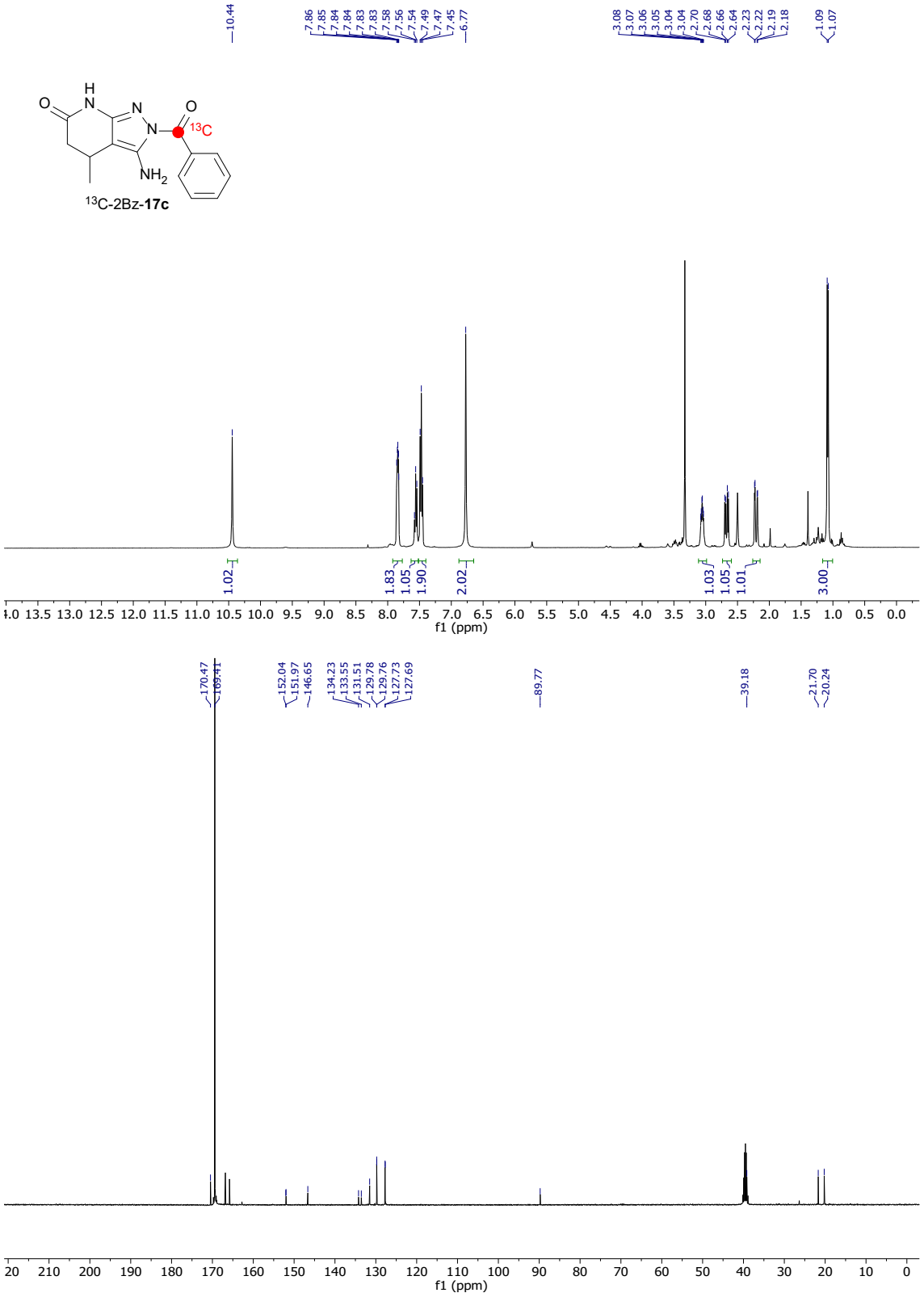

Figure S-11: ^{1}H and ^{13}C-NMR of ^{13}C labelled 3-amino-2-benzoyl-4-methyl-2,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (^{13}C-2Bz-**17c**)

1*H*-**20**

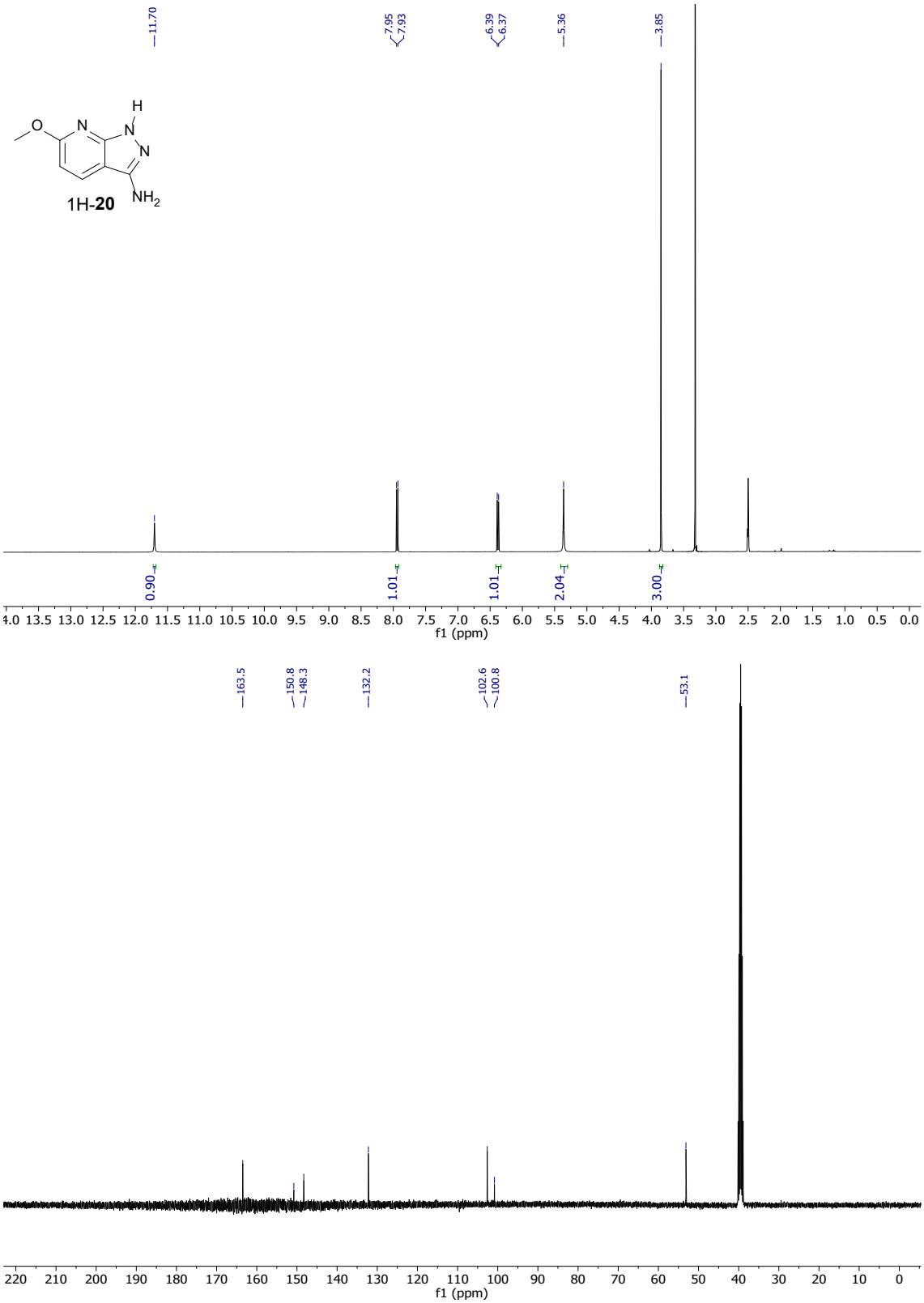

Figure S-12: ^{1}H and ^{13}C-NMR of 6-methoxy-1*H*-pyrazolo[3,4-*b*]pyridin-3-amine (1*H*-**20**)

2Bz-**21b**

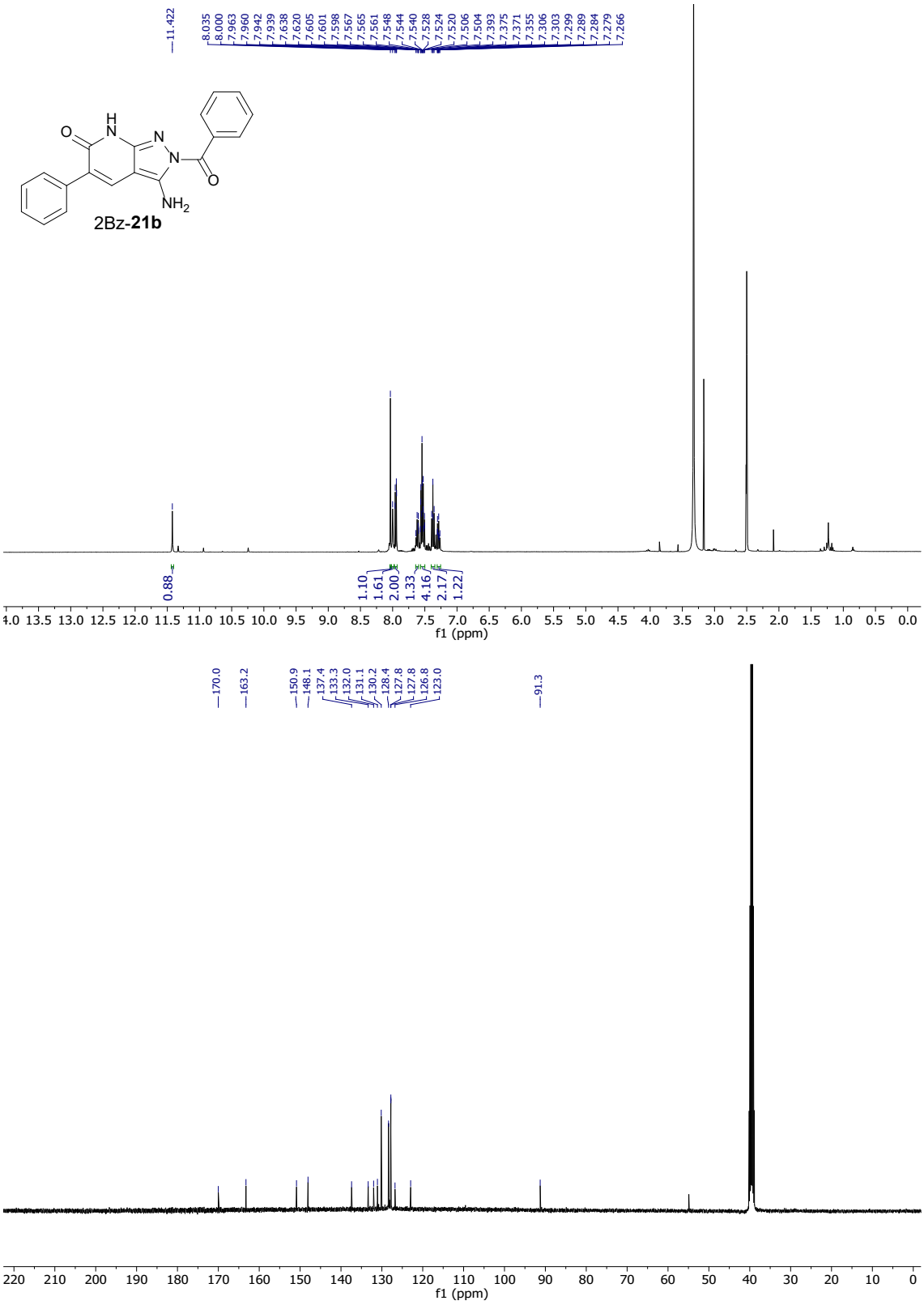

Figure S-13: ^{1}H and ^{13}C-NMR of 3-amino-2-benzoyl-5-phenyl-2,7-dihydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (2Bz-**21b**)

1Ph-**22**

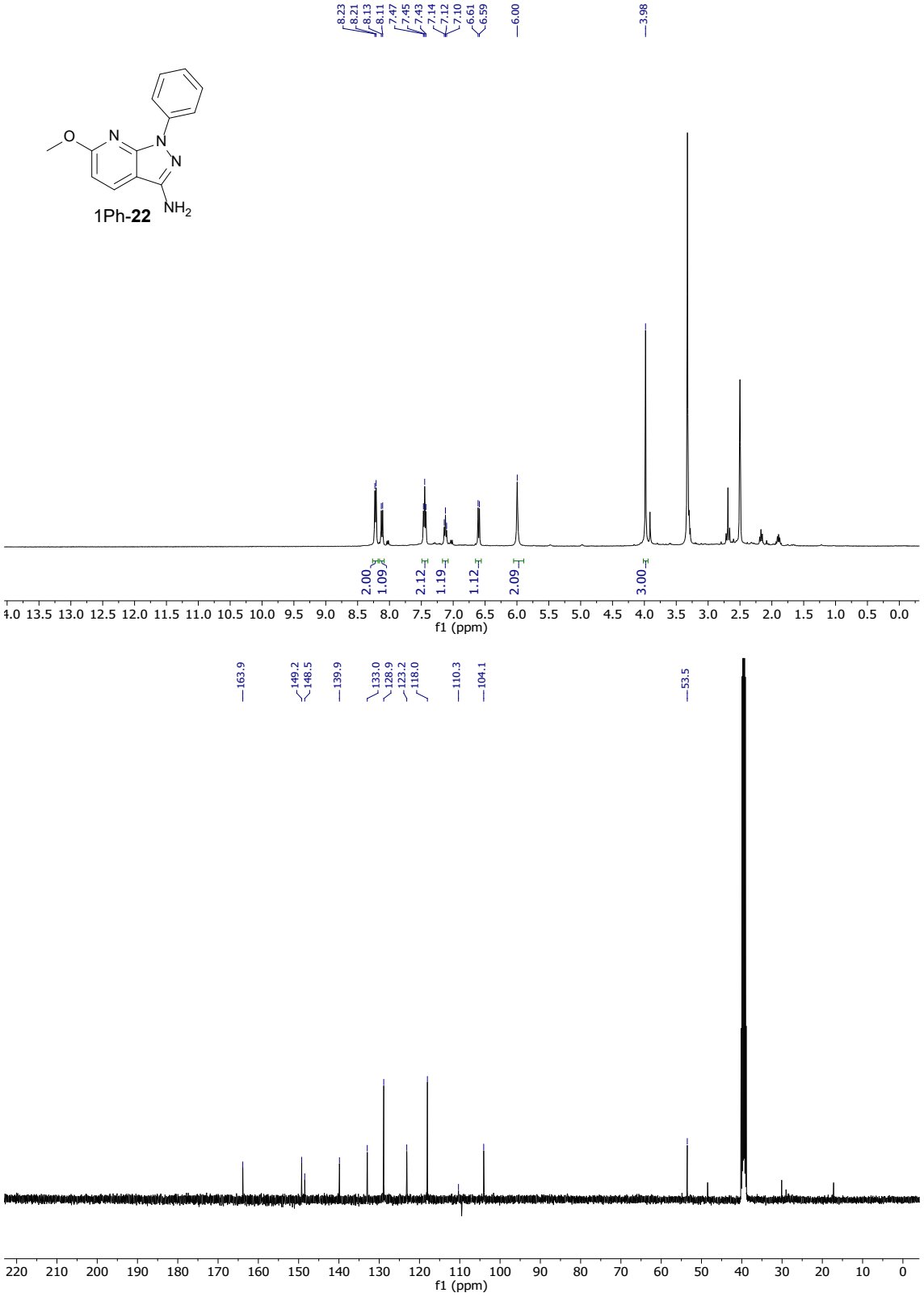

Figure S-14: ^{1}H and ^{13}C-NMR of 6-methoxy-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridin-3-amine (1Ph-**22**)

23

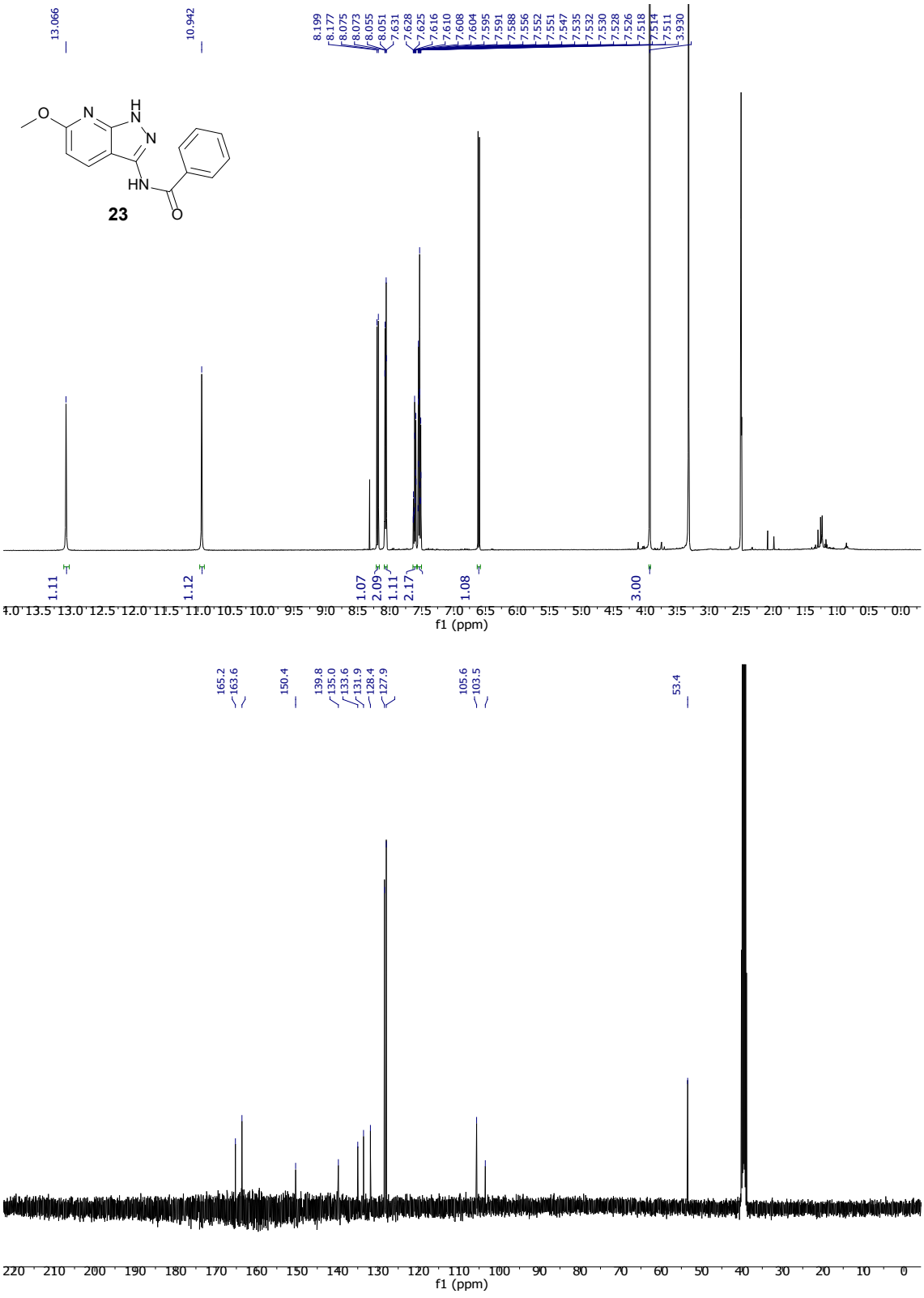

Figure S-15: ^{1}H and ^{13}C-NMR of N-(6-methoxy-1*H*-pyrazolo[3,4-*b*]pyridin-3-yl)benzamide (**23**)

1Ph-**24**

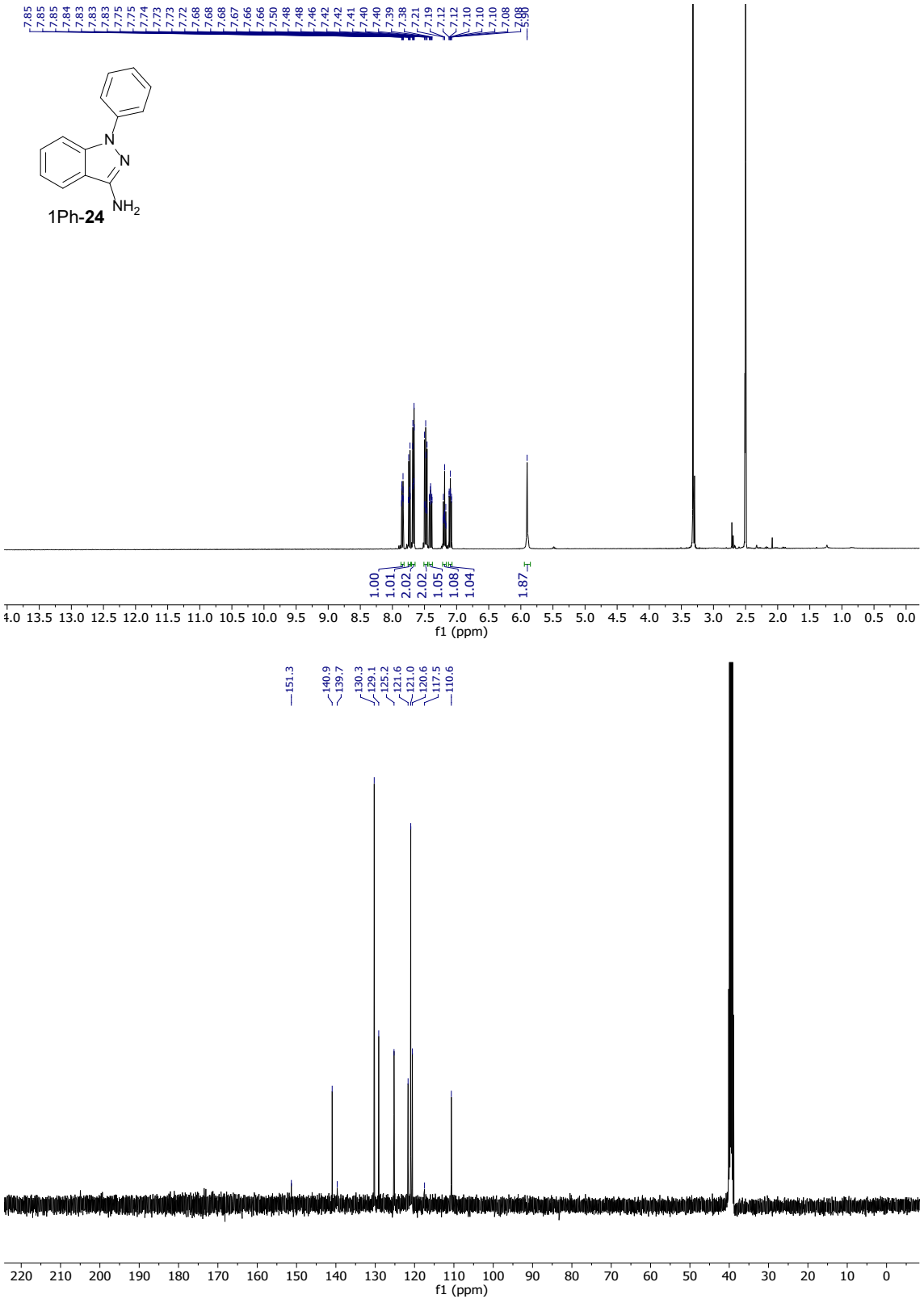

Figure S-16: ^{1}H and ^{13}C-NMR of 1-phenyl-1*H*-indazol-3-amine (1Ph-**24**)

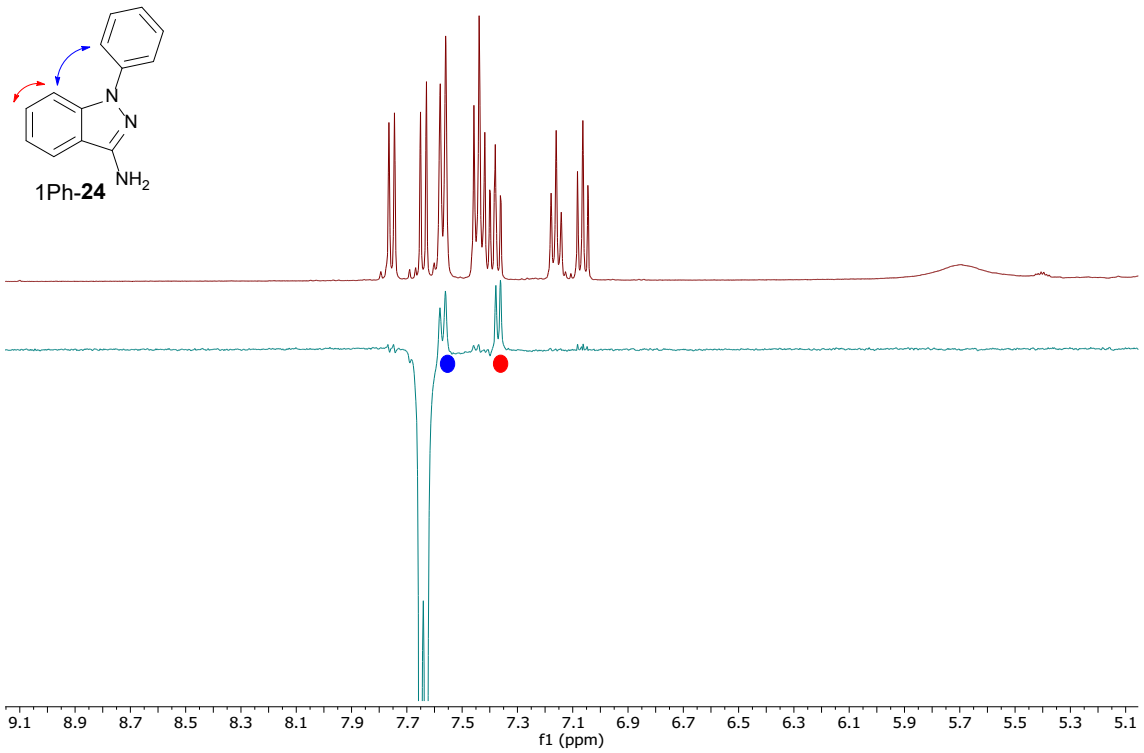

Figure S-17: ^{1}H and 1D NOESY (irradiation of C7-H) of 1-phenyl-1*H*-indazol-3-amine (1Ph-**24**)

25

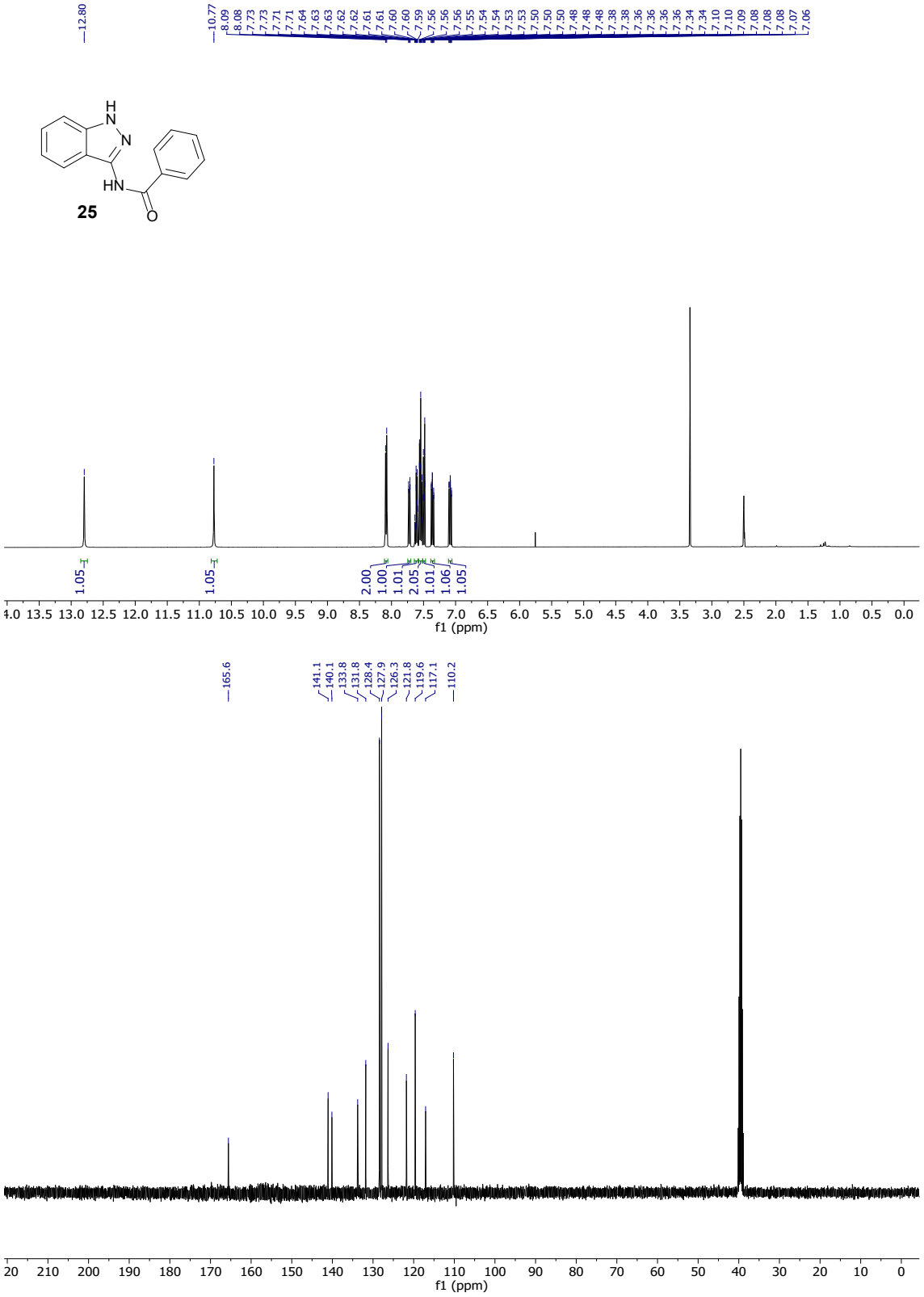

Figure S-18: ^{1}H and ^{13}C-NMR of N-(1*H*-indazol-3-yl)benzamide (**25**)

X-Ray crystallography data

Compound 1Ph-**16b**

A single monocrystal was obtained from a solution of 2 mg of the crystalline compound 1Ph-**16b** in 1 mL of methanol introduced in a tube closed in a flask containing an antisolvent (water). After two weeks, methanol was partially evaporated and a monoclinic orange prism-like specimen of 1Ph-**16b** was obtained.

Crystal Structure Report

A orange prism-like specimen of $C_{18}H_{14}N_4O$, approximate dimensions 0.066 mm x 0.130 mm x 0.292 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a D8 Venture system equipped with a multilayer monochromator and a Mo microfocus (λ = 0.71073 Å).

The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 24789 reflections to a maximum θ angle of 27.61° (0.77 Å resolution), of which 3348 were independent (average redundancy 7.404, completeness = 99.1%, R_{int} = 4.76%, R_{sig} = 2.60%) and 2631 (78.58%) were greater than $2\sigma(F^2)$. The final cell constants of a = 27.7141(13) Å, b = 6.4562(3) Å, c = 20.6251(10) Å, β = 128.1800(10)°, volume = 2900.9(2) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6825 and 0.7456.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group C 1 2/c 1, with Z = 8 for the formula unit, $C_{18}H_{14}N_4O$. The final anisotropic full-matrix least-squares refinement on F^2 with 216 variables converged at R1 = 4.91%, for the observed data and wR2 = 14.76% for all data. The goodness-of-fit was 1.063. The largest peak in the final difference electron density synthesis was 0.404 $e^-/Å^3$ and the largest hole was -0.270 $e^-/Å^3$ with an RMS deviation of 0.055 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.384 g/cm^3 and F(000), 1264 e^-.

Table S1. Crystal data and structure refinement for 1Ph-**16b**.

Identification code	mo_023WB46_0m_a	
Empirical formula	C18 H14 N4 O	
Formula weight	302.33	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 27.7141(13) Å	α= 90°.
	b = 6.4562(3) Å	β= 128.1800(10)°.
	c = 20.6251(10) Å	γ = 90°.
Volume	2900.9(2) Å^3	
Z	8	
Density (calculated)	1.384 Mg/m^3	
Absorption coefficient	0.090 mm^{-1}	
F(000)	1264	
Crystal size	0.292 x 0.130 x 0.066 mm^3	
Theta range for data collection	2.947 to 27.605°.	
Index ranges	-35<=h<=36, -8<=k<=8, -26<=l<=26	
Reflections collected	24789	
Independent reflections	3348 [R(int) = 0.0476]	
Completeness to theta = 25.242°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6825	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3348 / 0 / 216	
Goodness-of-fit on F^2	1.063	
Final R indices [I>2sigma(I)]	R1 = 0.0491, wR2 = 0.1358	
R indices (all data)	R1 = 0.0646, wR2 = 0.1476	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.404 and -0.270 e.Å^{-3}	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 1Ph-**16b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	2935(1)	8892(2)	5851(1)	33(1)
N(1)	3278(1)	7044(2)	5280(1)	25(1)
N(2)	3731(1)	5226(2)	4732(1)	22(1)
N(3)	4254(1)	5497(2)	4779(1)	23(1)
N(4)	5079(1)	7858(2)	5439(1)	29(1)
C(1)	4231(1)	13272(3)	6897(1)	35(1)
C(2)	4335(1)	14701(3)	7481(1)	46(1)
C(3)	4232(1)	14154(4)	8032(1)	47(1)
C(4)	4020(1)	12202(4)	8010(1)	42(1)
C(5)	3909(1)	10769(3)	7430(1)	34(1)
C(6)	4018(1)	11292(3)	6871(1)	28(1)
C(7)	3926(1)	9752(3)	6270(1)	25(1)
C(8)	4337(1)	9490(3)	6114(1)	24(1)
C(9)	4230(1)	7949(2)	5552(1)	21(1)
C(10)	3713(1)	6710(2)	5179(1)	21(1)
C(11)	3357(1)	8563(3)	5809(1)	26(1)
C(12)	4544(1)	7127(2)	5262(1)	21(1)
C(13)	3331(1)	3532(2)	4277(1)	22(1)
C(14)	2986(1)	2663(3)	4486(1)	27(1)
C(15)	2592(1)	1031(3)	4026(1)	31(1)
C(16)	2558(1)	211(3)	3379(1)	33(1)
C(17)	2918(1)	1050(3)	3187(1)	34(1)
C(18)	3300(1)	2720(3)	3626(1)	28(1)

Table S3. Bond lengths [Å] and angles [°] for 1Ph-**16b**.

O(1)-C(11)	1.243(2)	C(2)-C(3)	1.379(3)	C(9)-C(10)	1.386(2)
N(1)-C(10)	1.361(2)	C(2)-H(2)	0.95	C(9)-C(12)	1.427(2)
N(1)-C(11)	1.380(2)	C(3)-C(4)	1.380(3)	C(13)-C(14)	1.390(2)
N(1)-H(1N)	0.88	C(3)-H(3)	0.95	C(13)-C(18)	1.394(2)
N(2)-C(10)	1.352(2)	C(4)-C(5)	1.388(3)	C(14)-C(15)	1.386(2)
N(2)-N(3)	1.4013(18)	C(4)-H(4)	0.95	C(14)-H(14)	0.95
N(2)-C(13)	1.421(2)	C(5)-C(6)	1.404(3)	C(15)-C(16)	1.384(3)
N(3)-C(12)	1.325(2)	C(5)-H(5)	0.95	C(15)-H(15)	0.95
N(4)-C(12)	1.375(2)	C(6)-C(7)	1.483(2)	C(16)-C(17)	1.389(3)
N(4)-H(4NA)	0.90(2)	C(7)-C(8)	1.370(2)	C(16)-H(16)	0.95
N(4)-H(4NB)	0.91(3)	C(7)-C(11)	1.459(2)	C(17)-C(18)	1.385(2)
C(1)-C(6)	1.394(3)	C(8)-C(9)	1.414(2)	C(17)-H(17)	0.95
C(1)-C(2)	1.397(3)	C(8)-H(8)	0.95	C(18)-H(18)	0.95
C(1)-H(1)	0.95				

C(10)-N(1)-C(11)	120.77(13)	C(4)-C(5)-C(6)	120.2(2)	N(3)-C(12)-N(4)	121.62(14)
C(10)-N(1)-H(1N)	119.6	C(4)-C(5)-H(5)	119.9	N(3)-C(12)-C(9)	111.61(14)
C(11)-N(1)-H(1N)	119.6	C(6)-C(5)-H(5)	119.9	N(4)-C(12)-C(9)	126.77(15)
C(10)-N(2)-N(3)	109.69(12)	C(1)-C(6)-C(5)	119.24(17)	C(14)-C(13)-C(18)	120.23(15)
C(10)-N(2)-C(13)	130.78(13)	C(1)-C(6)-C(7)	119.90(17)	C(14)-C(13)-N(2)	120.77(14)
N(3)-N(2)-C(13)	119.51(12)	C(5)-C(6)-C(7)	120.85(17)	C(18)-C(13)-N(2)	118.99(15)
C(12)-N(3)-N(2)	105.69(12)	C(8)-C(7)-C(11)	120.20(15)	C(15)-C(14)-C(13)	119.69(15)
C(12)-N(4)-H(4NA)	116.2(14)	C(8)-C(7)-C(6)	122.59(15)	C(15)-C(14)-H(14)	120.2
C(12)-N(4)-H(4NB)	121.1(19)	C(11)-C(7)-C(6)	117.14(14)	C(13)-C(14)-H(14)	120.2
H(4NA)-N(4)-H(4NB)	122(2)	C(7)-C(8)-C(9)	119.72(15)	C(16)-C(15)-C(14)	120.49(16)
C(6)-C(1)-C(2)	119.8(2)	C(7)-C(8)-H(8)	120.1	C(16)-C(15)-H(15)	119.8
C(6)-C(1)-H(1)	120.1	C(9)-C(8)-H(8)	120.1	C(14)-C(15)-H(15)	119.8
C(2)-C(1)-H(1)	120.1	C(10)-C(9)-C(8)	118.81(14)	C(15)-C(16)-C(17)	119.49(16)
C(3)-C(2)-C(1)	120.1(2)	C(10)-C(9)-C(12)	103.91(14)	C(15)-C(16)-H(16)	120.3
C(3)-C(2)-H(2)	119.9	C(8)-C(9)-C(12)	137.13(15)	C(17)-C(16)-H(16)	120.3
C(1)-C(2)-H(2)	119.9	N(2)-C(10)-N(1)	128.78(14)	C(18)-C(17)-C(16)	120.75(17)
C(2)-C(3)-C(4)	120.62(18)	N(2)-C(10)-C(9)	109.05(14)	C(18)-C(17)-H(17)	119.6
C(2)-C(3)-H(3)	119.7	N(1)-C(10)-C(9)	122.17(14)	C(16)-C(17)-H(17)	119.6
C(4)-C(3)-H(3)	119.7	O(1)-C(11)-N(1)	118.75(15)	C(17)-C(18)-C(13)	119.30(16)
C(3)-C(4)-C(5)	119.9(2)	O(1)-C(11)-C(7)	123.35(15)	C(17)-C(18)-H(18)	120.4
C(3)-C(4)-H(4)	120	N(1)-C(11)-C(7)	117.86(14)	C(13)-C(18)-H(18)	120.4
C(5)-C(4)-H(4)	120				

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 1Ph-**16b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	22(1)	46(1)	38(1)	-20(1)	22(1)	-9(1)
N(1)	17(1)	32(1)	29(1)	-12(1)	16(1)	-7(1)
N(2)	18(1)	26(1)	27(1)	-5(1)	17(1)	-2(1)
N(3)	19(1)	26(1)	29(1)	-2(1)	18(1)	-1(1)
N(4)	24(1)	28(1)	46(1)	-7(1)	27(1)	-4(1)
C(1)	23(1)	37(1)	39(1)	-12(1)	17(1)	-3(1)
C(2)	29(1)	41(1)	59(1)	-24(1)	23(1)	-7(1)
C(3)	26(1)	59(1)	47(1)	-31(1)	18(1)	-2(1)
C(4)	26(1)	64(1)	30(1)	-15(1)	15(1)	4(1)
C(5)	25(1)	44(1)	30(1)	-9(1)	16(1)	-1(1)
C(6)	15(1)	35(1)	28(1)	-13(1)	10(1)	-2(1)
C(7)	18(1)	28(1)	25(1)	-7(1)	12(1)	-2(1)
C(8)	15(1)	28(1)	26(1)	-5(1)	11(1)	-2(1)
C(9)	16(1)	25(1)	25(1)	-2(1)	14(1)	-1(1)
C(10)	18(1)	25(1)	23(1)	-4(1)	14(1)	-1(1)
C(11)	20(1)	33(1)	28(1)	-9(1)	16(1)	-4(1)
C(12)	19(1)	22(1)	24(1)	1(1)	14(1)	2(1)
C(13)	18(1)	24(1)	23(1)	-3(1)	12(1)	-1(1)
C(14)	28(1)	30(1)	29(1)	-6(1)	21(1)	-4(1)
C(15)	31(1)	30(1)	38(1)	-4(1)	25(1)	-6(1)
C(16)	32(1)	31(1)	34(1)	-10(1)	20(1)	-10(1)
C(17)	35(1)	40(1)	31(1)	-12(1)	22(1)	-7(1)
C(18)	28(1)	35(1)	29(1)	-5(1)	22(1)	-4(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 1Ph-**16b**.

	x	y	z	U(eq)
H(1N)	2943	6283	5005	30
H(4NA)	5254(10)	7050(40)	5282(13)	36(6)
H(4NB)	5215(14)	9170(50)	5636(18)	69(8)
H(1)	4304	13648	6520	42
H(2)	4478	16053	7498	55
H(3)	4307	15131	8429	56
H(4)	3950	11839	8392	50
H(5)	3758	9431	7412	41
H(8)	4692	10341	6384	28
H(14)	3019	3185	4943	32
H(15)	2344	471	4155	37
H(16)	2291	-917	3068	40
H(17)	2902	471	2751	41
H(18)	3538	3306	3484	34

Compound 2Bz-**17c**

A single monocrystal was obtained from a solution of 2 mg of compound 2Bz-**17c** in 1 mL of methanol introduced in a tube closed in a flask containing an antisolvent (water). After four weeks, methanol was partially evaporated and a monoclinic colorless prism-like specimen of 2Bz-**17c** was obtained.

Crystal Structure Report

A colorless prism-like specimen of $C_{14}H_{16}N_4O_3$, approximate dimensions 0.122 mm x 0.175 mm x 0.395 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a D8 Venture system equipped with a multilayer monochromator and a Mo microfocus (λ = 0.71073 Å).

The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 30489 reflections to a maximum θ angle of 34.35° (0.63 Å resolution), of which 5780 were independent (average redundancy 5.275, completeness = 99.7%, R_{int} = 6.44%, R_{sig} = 5.13%) and 4178 (72.28%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.0257(7) Å, b = 13.4533(8) Å, c = 10.8045(7) Å, β = 108.456(2)°, volume = 1382.34(16) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). Data were corrected for absorption effects using the Multi-Scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.5755 and 0.7468.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with Z = 4 for the formula unit, $C_{14}H_{16}N_4O_3$. The final anisotropic full-matrix least-squares refinement on F^2 with 199 variables converged at R1 = 5.32%, for the observed data and wR2 = 16.15% for all data. The goodness-of-fit was 1.034. The largest peak in the final difference electron density synthesis was 0.528 $e^-/Å^3$ and the largest hole was -0.537 $e^-/Å^3$ with an RMS deviation of 0.071 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.385 g/cm^3 and F(000), 608 e^-.

Table S6. Crystal data and structure refinement for 2Bz-**17c**.

Identification code	028XB107_0m_a	
Empirical formula	C14 H16 N4 O3	
Formula weight	288.31	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 10.0257(7) Å	α= 90°.
	b = 13.4533(8) Å	β= 108.456(2)°.
	c = 10.8045(7) Å	γ = 90°.
Volume	1382.34(16) $Å^3$	
Z	4	
Density (calculated)	1.385 Mg/m^3	
Absorption coefficient	0.100 mm^{-1}	
F(000)	608	
Crystal size	0.395 x 0.175 x 0.122 mm^3	
Theta range for data collection	2.498 to 34.350°.	
Index ranges	-15<=h<=15, -21<=k<=20, -13<=l<=17	
Reflections collected	30489	
Independent reflections	5780 [R(int) = 0.0644]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7468 and 0.5755	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5780 / 0 / 199	
Goodness-of-fit on F^2	1.034	
Final R indices [I>2sigma(I)]	R1 = 0.0532, wR2 = 0.1301	
R indices (all data)	R1 = 0.0862, wR2 = 0.1615	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.528 and -0.537 $e.Å^{-3}$	

Table S7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 2Bz-**17c**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	5580(1)	4409(1)	3831(1)	26(1)
O(2)	228(1)	1048(1)	5901(1)	26(1)
N(1)	3971(1)	3820(1)	4703(1)	19(1)
N(2)	2130(1)	3160(1)	5414(1)	17(1)
N(3)	1898(1)	572(1)	4473(1)	22(1)
N(4)	1560(1)	2195(1)	5323(1)	16(1)
C(1)	4794(1)	3725(1)	3922(1)	19(1)
C(2)	4668(1)	2783(1)	3131(1)	20(1)
C(3)	4364(1)	1839(1)	3800(1)	20(1)
C(4)	3211(1)	2098(1)	4349(1)	17(1)
C(5)	3096(1)	3051(1)	4826(1)	16(1)
C(6)	2215(1)	1542(1)	4678(1)	17(1)
C(7)	512(1)	1927(1)	5856(1)	18(1)
C(8)	-243(1)	2702(1)	6363(1)	18(1)
C(9)	-784(1)	2385(1)	7343(1)	21(1)
C(10)	-1564(1)	3035(1)	7840(1)	24(1)
C(11)	-1820(2)	3999(1)	7358(2)	27(1)
C(12)	-1315(2)	4308(1)	6362(2)	26(1)
C(13)	-531(1)	3662(1)	5856(1)	21(1)
C(14)	5680(2)	1483(1)	4878(2)	29(1)
O(1W)	7860(1)	4921(1)	3009(1)	26(1)

Table S8. Bond lengths [Å] and angles [°] for 2Bz-**17c**.

O(1)-C(1)	1.2357(15)	C(2)-C(3)	1.5394(18)	C(10)-C(11)	1.392(2)
O(2)-C(7)	1.2206(15)	C(2)-H(2A)	0.9900	C(10)-H(10)	0.9500
N(1)-C(1)	1.3606(16)	C(2)-H(2AB)	0.9900	C(11)-C(12)	1.389(2)
N(1)-C(5)	1.3895(15)	C(3)-C(4)	1.4982(17)	C(11)-H(11)	0.9500
N(1)-H(1)	0.8800	C(3)-C(14)	1.534(2)	C(12)-C(13)	1.3943(19)
N(2)-C(5)	1.3241(15)	C(3)-H(3)	1.0000	C(12)-H(12)	0.9500
N(2)-N(4)	1.4096(14)	C(4)-C(6)	1.3809(16)	C(13)-H(13)	0.9500
N(3)-C(6)	1.3456(16)	C(4)-C(5)	1.4002(16)	C(14)-H(14A)	0.9800
N(3)-H(3A)	0.8800	C(7)-C(8)	1.4897(17)	C(14)-H(14B)	0.9800
N(3)-H(3B)	0.8800	C(8)-C(13)	1.3977(18)	C(14)-H(14C)	0.9800
N(4)-C(7)	1.3960(15)	C(8)-C(9)	1.4005(18)	O(1W)-H(1WA)	0.98(3)
N(4)-C(6)	1.4057(15)	C(9)-C(10)	1.3896(19)	O(1W)-H(1WB)	0.94(3)
C(1)-C(2)	1.5108(18)	C(9)-H(9)	0.9500		

C(1)-N(1)-C(5)	120.97(10)	C(14)-C(3)-C(2)	111.34(11)	C(8)-C(9)-H(9)	120.00
C(1)-N(1)-H(1)	119.50	C(4)-C(3)-H(3)	109.30	C(9)-C(10)-C(11)	120.12(13)
C(5)-N(1)-H(1)	119.50	C(14)-C(3)-H(3)	109.30	C(9)-C(10)-H(10)	119.90
C(5)-N(2)-N(4)	101.92(9)	C(2)-C(3)-H(3)	109.30	C(11)-C(10)-H(10)	119.90
C(6)-N(3)-H(3A)	120.00	C(6)-C(4)-C(5)	104.54(10)	C(12)-C(11)-C(10)	119.95(13)
C(6)-N(3)-H(3B)	120.00	C(6)-C(4)-C(3)	133.43(11)	C(12)-C(11)-H(11)	120.00
H(3A)-N(3)-H(3B)	120.00	C(5)-C(4)-C(3)	121.48(10)	C(10)-C(11)-H(11)	120.00
C(7)-N(4)-C(6)	125.04(10)	N(2)-C(5)-N(1)	122.94(11)	C(11)-C(12)-C(13)	120.44(13)
C(7)-N(4)-N(2)	123.35(10)	N(2)-C(5)-C(4)	115.81(10)	C(11)-C(12)-H(12)	119.80
C(6)-N(4)-N(2)	111.56(9)	N(1)-C(5)-C(4)	121.24(10)	C(13)-C(12)-H(12)	119.80
O(1)-C(1)-N(1)	120.42(12)	N(3)-C(6)-C(4)	129.44(11)	C(12)-C(13)-C(8)	119.66(12)
O(1)-C(1)-C(2)	121.39(11)	N(3)-C(6)-N(4)	124.39(11)	C(12)-C(13)-H(13)	120.20
N(1)-C(1)-C(2)	118.14(10)	C(4)-C(6)-N(4)	106.17(10)	C(8)-C(13)-H(13)	120.20
C(1)-C(2)-C(3)	114.77(11)	O(2)-C(7)-N(4)	118.77(11)	C(3)-C(14)-H(14A)	109.50
C(1)-C(2)-H(2A)	108.60	O(2)-C(7)-C(8)	120.73(11)	C(3)-C(14)-H(14B)	109.50
C(3)-C(2)-H(2A)	108.60	N(4)-C(7)-C(8)	120.50(10)	H(14A)-C(14)-H(14B)	109.50
C(1)-C(2)-H(2AB)	108.60	C(13)-C(8)-C(9)	119.72(12)	C(3)-C(14)-H(14C)	109.50
C(3)-C(2)-H(2AB)	108.60	C(13)-C(8)-C(7)	124.66(11)	H(14A)-C(14)-H(14C)	109.50
H(2A)-C(2)-H(2AB)	107.60	C(9)-C(8)-C(7)	115.38(11)	H(14B)-C(14)-H(14C)	109.50
C(4)-C(3)-C(14)	111.02(11)	C(10)-C(9)-C(8)	120.07(13)	H(1WA)-O(1W)-H(1WB)	101(2)
C(4)-C(3)-C(2)	106.68(10)	C(10)-C(9)-H(9)	120.00		

Symmetry transformations used to generate equivalent atoms:

Table S9. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 2Bz-**17c**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	28(1)	22(1)	36(1)	-7(1)	21(1)	-10(1)
O(2)	33(1)	17(1)	37(1)	0(1)	22(1)	-4(1)
N(1)	19(1)	16(1)	27(1)	-4(1)	14(1)	-4(1)
N(2)	17(1)	13(1)	24(1)	-1(1)	11(1)	-2(1)
N(3)	25(1)	15(1)	32(1)	-4(1)	17(1)	-4(1)
N(4)	16(1)	13(1)	22(1)	-1(1)	10(1)	-1(1)
C(1)	18(1)	18(1)	23(1)	-2(1)	11(1)	-3(1)
C(2)	21(1)	19(1)	23(1)	-4(1)	12(1)	-3(1)
C(3)	20(1)	17(1)	26(1)	-3(1)	13(1)	-1(1)
C(4)	16(1)	15(1)	23(1)	-2(1)	10(1)	-1(1)
C(5)	14(1)	15(1)	21(1)	0(1)	9(1)	-2(1)
C(6)	17(1)	14(1)	22(1)	0(1)	9(1)	0(1)
C(7)	17(1)	17(1)	22(1)	1(1)	10(1)	-1(1)
C(8)	16(1)	19(1)	21(1)	-1(1)	9(1)	-1(1)
C(9)	18(1)	26(1)	23(1)	1(1)	10(1)	-1(1)
C(10)	20(1)	34(1)	23(1)	-2(1)	12(1)	-1(1)
C(11)	21(1)	32(1)	30(1)	-5(1)	12(1)	3(1)
C(12)	23(1)	23(1)	33(1)	0(1)	13(1)	4(1)
C(13)	18(1)	20(1)	26(1)	1(1)	11(1)	1(1)
C(14)	23(1)	29(1)	38(1)	6(1)	15(1)	7(1)
O(1W)	29(1)	24(1)	32(1)	1(1)	19(1)	-1(1)

Table S10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 2Bz-**17c**.

	x	y	z	U(eq)
H(1)	3993	4377	5136	23
H(3A)	2358	199	4075	27
H(3B)	1231	309	4737	27
H(2A)	5555	2684	2927	24
H(2AB)	3905	2872	2293	24
H(3)	4032	1301	3135	23
H(9)	-618	1725	7668	26
H(10)	-1924	2820	8510	29
H(11)	-2339	4447	7710	32
H(12)	-1505	4963	6025	31
H(13)	-195	3874	5170	25
H(14A)	6384	1257	4485	43
H(14B)	5429	932	5354	43
H(14C)	6067	2031	5481	43
H(1WA)	7060(30)	4630(20)	3220(30)	71(9)
H(1WB)	7970(30)	5520(20)	3470(30)	62(8)

Computational study

Setting the study (Ph-14b, Ph-15b, Ph-16b)

Cartesian coordinates of 1Ph-**14b**

	Coordinates (Å)		
Element	x	y	z
C	6.1291	-0.5361	0.1317
C	5.5860	-0.3388	-1.1349
C	4.2068	-0.1999	-1.2882
C	3.3524	-0.2541	-0.1843
C	3.9093	-0.4570	1.0834
C	5.2851	-0.5970	1.2406
H	7.2005	-0.6473	0.2553
H	6.2319	-0.2955	-2.0048
H	3.7910	-0.0505	-2.2799
H	3.2646	-0.5261	1.9524
H	5.6992	-0.7613	2.2292
C	1.8650	-0.0410	-0.3653
C	1.0216	-1.2178	0.1741
C	1.3948	1.3399	0.1788
C	-0.0941	1.4337	0.0606
H	1.7275	1.4547	1.2188
C	-0.8661	0.2982	0.0705
O	1.4706	-2.3015	0.4816
N	-0.3478	-0.9823	0.2171
H	-0.9198	-1.7430	0.5601
C	-1.0423	2.4844	-0.0568
N	-2.2879	2.0306	-0.1071
N	-2.1751	0.6532	-0.0601
N	-0.7709	3.8421	-0.1874
H	-1.5971	4.4193	-0.1020
H	-0.0140	4.1805	0.3899
H	1.8980	2.1219	-0.3965
H	1.6479	-0.0352	-1.4416
C	-3.3358	-0.1566	-0.0631
C	-3.3293	-1.4082	-0.6885
C	-4.5030	0.3156	0.5456
C	-4.4784	-2.1965	-0.6683
H	-2.4492	-1.7494	-1.2192
C	-5.6480	-0.4736	0.5412
H	-4.4959	1.2960	1.0023
C	-5.6404	-1.7355	-0.0543
H	-4.4667	-3.1648	-1.1554
H	-6.5508	-0.1020	1.0127
H	-6.5345	-2.3478	-0.0487

Total Energy: -990.0445102 Hartree

No imaginary frequencies

Cartesian coordinates of 2Ph-**14b**

	Coordinates (Å)		
Element	x	y	z
C	-6.3298	0.8687	-0.3405
C	-5.7448	1.2170	0.8739
C	-4.4171	0.8767	1.1320
C	-3.6554	0.1876	0.1854
C	-4.2553	-0.1606	-1.0298
C	-5.5801	0.1762	-1.2915
H	-7.3629	1.1277	-0.5434
H	-6.3202	1.7490	1.6235
H	-3.9713	1.1454	2.0847
H	-3.6914	-0.7173	-1.7704
H	-6.0310	-0.1094	-2.2354
C	-2.1989	-0.1236	0.4591
C	-1.8866	-1.6370	0.3561
C	-1.2457	0.7741	-0.3823

H	-1.9933	0.1071	1.5127
C	0.1651	0.3270	-0.1699
H	-1.5321	0.7065	-1.4399
H	-1.4047	1.8142	-0.0827
C	0.4593	-1.0162	0.1332
O	-2.7395	-2.5001	0.4145
N	-0.5469	-1.9631	0.2787
H	-0.3098	-2.9450	0.3336
C	1.4090	0.9241	-0.2460
N	2.3420	-0.0491	0.0259
N	1.7441	-1.2791	0.2495
N	1.7409	2.2469	-0.5104
H	2.6413	2.3824	-0.9522
H	1.0118	2.7463	-1.0003
C	3.7555	0.0447	0.0207
C	4.5080	-1.0118	-0.5039
C	4.4008	1.1645	0.5564
C	5.8962	-0.9345	-0.5049
H	3.9934	-1.8814	-0.8898
C	5.7928	1.2367	0.5318
H	3.8225	1.9559	1.0161
C	6.5458	0.1919	0.0018
H	6.4739	-1.7576	-0.9101
H	6.2868	2.1063	0.9502
H	7.6280	0.2486	-0.0071

Total Energy: -990.04712913 Hartree
No imaginary frequencies

Cartesian coordinates of 1Ph-**15b**

	Coordinates (Å)		
Element	x	y	z
C	4.6249	0.8357	-0.0766
C	4.1826	-0.3180	-0.7225
C	2.8406	-0.6841	-0.6779
C	1.9056	0.1069	0.0080
C	2.3675	1.2577	0.6662
C	3.7106	1.6219	0.6215
H	5.6724	1.1136	-0.1088
H	4.8870	-0.9405	-1.2632
H	2.5136	-1.5892	-1.1706
H	1.6717	1.8604	1.2397
H	4.0439	2.5118	1.1442
C	0.4604	-0.2279	0.0259
C	0.0586	-1.6377	0.1865
C	-0.4942	0.7528	-0.0992
C	-1.8771	0.4485	-0.0517
H	-0.1742	1.7768	-0.2599
C	-2.2577	-0.8817	0.1019
O	0.8061	-2.5987	0.2941
N	-1.3380	-1.8738	0.2218
H	-1.5958	-2.8456	0.3339
C	-3.1241	1.1493	-0.1574
N	-4.1548	0.3288	-0.0685
N	-3.6018	-0.9350	0.0727
N	-3.2970	2.5036	-0.3966
H	-4.2537	2.8105	-0.2817
H	-2.6426	3.1102	0.0767
H	-4.2160	-1.7237	0.1826

Total Energy: -757.7351217 Hartree
No imaginary frequencies

Cartesian coordinates of 2Ph-**15b**

	Coordinates (Å)		
Element	x	y	z
C	-4.6222	0.8410	0.0630
C	-4.1801	-0.3017	0.7287

C	-2.8381	-0.6684	0.6916
C	-1.9027	0.1120	-0.0060
C	-2.3642	1.2514	-0.6841
C	-3.7076	1.6158	-0.6475
H	-5.6700	1.1185	0.0890
H	-4.8852	-0.9154	1.2784
H	-2.5105	-1.5654	1.1983
H	-1.6675	1.8428	-1.2684
H	-4.0412	2.4958	-1.1865
C	-0.4575	-0.2207	-0.0143
C	-0.0501	-1.6434	-0.1784
C	0.4893	0.7574	0.1162
C	1.8747	0.4404	0.0764
H	0.1669	1.7825	0.2702
C	2.2794	-0.9100	-0.1006
O	-0.8265	-2.5824	-0.2817
N	1.3261	-1.8867	-0.2233
H	1.5989	-2.8534	-0.3454
C	3.0826	1.1376	0.1640
N	4.0571	0.2085	0.0296
H	5.0494	0.3456	0.1309
N	3.5865	-1.0805	-0.1344
N	3.3559	2.4729	0.4097
H	4.1259	2.8665	-0.1149
H	2.5447	3.0732	0.3769

Total Energy: -757.73480128 Hartree
No imaginary frequencies

Cartesian coordinates of 1Ph-**16b**

	Coordinates (Å)		
Element	x	y	z
C	6.1951	-0.4748	0.1012
C	5.4144	-1.4264	-0.5538
C	4.0275	-1.3128	-0.5727
C	3.3892	-0.2325	0.0566
C	4.1867	0.7096	0.7253
C	5.5740	0.5937	0.7446
H	7.2749	-0.5708	0.1186
H	5.8871	-2.2660	-1.0514
H	3.4335	-2.0659	-1.0716
H	3.7145	1.5278	1.2581
H	6.1676	1.3305	1.2745
C	1.9174	-0.0573	0.0035
C	1.0529	-1.2425	0.1553
C	1.3567	1.1854	-0.1687
C	-0.0478	1.3636	-0.1959
C	-0.8662	0.2455	-0.0770
O	1.4252	-2.3940	0.3265
N	-0.3399	-0.9945	0.0995
H	-0.9224	-1.8081	0.2483
C	-0.9739	2.4500	-0.3179
N	-2.2248	2.0340	-0.2712
N	-2.1594	0.6454	-0.1505
N	-0.6654	3.7809	-0.5377
H	-1.4551	4.4033	-0.4325
H	0.1607	4.1188	-0.0657
C	-3.3463	-0.1168	-0.0310
C	-3.4363	-1.3814	-0.6212
C	-4.4347	0.4111	0.6693
C	-4.6020	-2.1306	-0.4732
H	-2.6238	-1.7613	-1.2291
C	-5.5989	-0.3393	0.7925
H	-4.3549	1.4012	1.0974
C	-5.6854	-1.6151	0.2339
H	-4.6666	-3.1100	-0.9330
H	-6.4418	0.0729	1.3354
H	-6.5933	-2.1970	0.3402
H	2.0097	2.0407	-0.3063

Total Energy: -988.84197063 Hartree
No imaginary frequencies

Cartesian coordinates of 2Ph-**16b**

	Coordinates (Å)		
Element	x	y	z
C	6.3314	-1.0694	-0.0598
C	5.9623	0.0236	0.7234
C	4.6453	0.4733	0.7369
C	3.6611	-0.1726	-0.0281
C	4.0502	-1.2620	-0.8239
C	5.3686	-1.7094	-0.8375
H	7.3602	-1.4114	-0.0723
H	6.7054	0.5334	1.3267
H	4.3755	1.3311	1.3368
H	3.3172	-1.7467	-1.4597
H	5.6455	-2.5480	-1.4671
C	2.2392	0.2459	0.0106
C	1.9178	1.6982	0.0111
C	1.2332	-0.6817	0.0400
C	-0.1288	-0.2790	0.0454
H	1.4920	-1.7351	0.0821
C	-0.4520	1.1014	0.0238
O	2.7466	2.5973	0.0055
N	0.5570	2.0268	0.0109
H	0.3434	3.0159	0.0078
C	-1.3747	-0.9101	0.0643
N	-2.3129	0.0807	0.0746
N	-1.7442	1.3533	0.0306
N	-1.6778	-2.2570	0.0971
H	-2.5746	-2.5160	-0.2929
H	-0.9313	-2.8528	-0.2310
C	-3.7264	-0.0421	0.0370
C	-4.4629	0.8177	-0.7833
C	-4.3797	-0.9921	0.8282
C	-5.8487	0.7088	-0.8221
H	-3.9406	1.5645	-1.3661
C	-5.7682	-1.1006	0.7674
H	-3.8129	-1.6164	1.5075
C	-6.5065	-0.2548	-0.0567
H	-6.4172	1.3782	-1.4576
H	-6.2715	-1.8360	1.3846
H	-7.5864	-0.3372	-0.0946

Total Energy: -988.8413182 Hartree
No imaginary frequencies

Relative stability of the pyrazol-3-amine tautomers

	Total electronic energy	Gibbs free energy	Zero point corrected total energy
1H-**6**	-281.643091	-281.583698	-281.555611
2H-**6**	-281.638998	-281.579976	-281.551492
1H-**7**	-437.738581	-437.591043	-437.558045
2H-**7**	-437.734133	-437.587013	-437.553839
1H-**8**	-435.322004	-435.220243	-435.188153
2H-**8**	-435.309481	-435.207186	-435.17515
1H-**9**	-451.367828	-451.277139	-451.245336
2H-**9**	-451.350161	-451.259565	-451.227599
1H-**13**	-527.835002	-527.719197	-527.685031
2H-**13**	-527.838391	-527.722291	-527.688177
1H-**15**	-526.62565	-526.532302	-526.498882
2H-**15**	-526.625087	-526.531551	-526.498124
1H-**20**	-565.937776	-565.817969	-565.782856
2H-**20**	-565.92274	-565.803343	-565.767998

Energy calculations performed at B3LYP/6-311++G(d,p) level of theory. DFT calculations where conducted with ultrafine integration grid.

Cartesian coordinates of *1H*-**6**

	Coordinates (Å)		
Element	x	y	z
C	-0.676	0.0222	-0.0068
N	-2.0694	0.0004	-0.0863
H	-2.4567	-0.9132	0.1171
H	-2.5281	0.7264	0.4484
C	0.1717	1.1644	-0.0074
H	-0.1128	2.2058	-0.0323
C	1.4521	0.6434	0.0049
N	1.3231	-0.7055	0.006
H	2.4189	1.1262	0.0065
N	0.0236	-1.1125	0.0089
H	2.0504	-1.4017	0.016

No imaginary frequencies

Cartesian coordinates of *2H*-**6**

	Coordinates (Å)		
Element	x	y	z
C	0.9049	0.7946	0.3722
H	1.7783	1.3522	0.6768
C	-0.4367	1.2409	0.3048
H	-0.8309	2.2125	0.5544
C	-1.1474	0.1371	-0.1327
N	-0.2358	-0.8579	-0.2940
N	-2.4940	-0.0586	-0.4582
H	-3.0399	0.7871	-0.3680
H	-2.9380	-0.8114	0.0545
N	1.0317	-0.4761	0.0177
H	-0.3962	-1.7765	-0.6745

No imaginary frequencies

Cartesian coordinates of *1H*-**7**

	Coordinates (Å)		
Element	x	y	z
C	1.6902	-0.2426	0.0158
N	2.6417	-1.2675	-0.0221
H	3.5829	-0.9207	0.1231
H	2.4394	-2.0413	0.5990
C	0.2743	-0.3893	0.0199
C	-0.2067	0.9071	-0.0211
N	0.8766	1.7249	-0.0557
N	2.0581	1.0372	-0.0244
H	0.9026	2.7308	-0.0938
C	-1.6502	1.3065	-0.0534
H	-1.8448	2.1532	0.6175
H	-1.9284	1.6383	-1.0645
C	-2.5140	0.0916	0.3522
H	-3.5647	0.2954	0.1169
H	-2.4525	-0.0451	1.4403
C	-2.0545	-1.2022	-0.3460
H	-2.1013	-1.0566	-1.4340
H	-2.7448	-2.0194	-0.1068
C	-0.6150	-1.5993	0.0488
H	-0.2415	-2.3748	-0.6326
H	-0.6256	-2.0524	1.0527

No imaginary frequencies

Cartesian coordinates of *2H*-**7**

	Coordinates (Å)		
Element	x	y	z
C	0.1966	-0.9494	-0.0227
C	-0.2715	0.3912	0.0244
C	-1.6535	0.2725	0.0242
N	-1.9228	-1.0618	-0.0227
N	-2.6873	1.2167	0.1192
H	-2.3369	2.1537	0.2761
H	-3.3211	1.2179	-0.6740
N	-0.7976	-1.8335	-0.0557
H	-2.8249	-1.5037	0.0599
C	0.6289	1.5941	0.0688
H	0.2608	2.3959	-0.5870
H	0.6591	2.0176	1.0846
C	2.0612	1.1927	-0.3459
H	2.7546	2.0087	-0.1113
H	2.0962	1.0493	-1.4349
C	2.5149	-0.1067	0.3455
H	2.4491	0.0251	1.4346
H	3.5679	-0.3062	0.1158
C	1.6530	-1.3137	-0.0784
H	1.8536	-2.1831	0.5577
H	1.9176	-1.6103	-1.1033

No imaginary frequencies

Cartesian coordinates of *1H*-**8**

	Coordinates (Å)		
Element	x	y	z
C	1.5907	-0.2558	-0.0012
N	2.5479	-1.2647	-0.0755
H	3.4882	-0.9227	0.0842
H	2.3455	-2.0758	0.4957
C	0.1623	-0.4227	-0.0033
C	-0.3443	0.9024	0.0034
N	0.7455	1.7225	-0.0093
N	1.9279	1.0215	0.0057
H	0.7798	2.7277	0.0136

C	-1.7255	1.1652	0.0112
H	-2.1115	2.1800	0.0182
C	-2.5788	0.0699	0.0084
H	-3.6522	0.2360	0.0147
C	-2.0890	-1.2586	-0.0069
H	-2.7939	-2.0841	-0.0174
C	-0.7241	-1.5140	-0.0146
H	-0.3532	-2.5348	-0.0382

No imaginary frequencies

Cartesian coordinates of *2H*-**8**

	Coordinates (Å)		
Element	x	y	z
C	0.3408	-0.9213	0.0000
C	-0.1580	0.4270	0.0000
C	-1.5540	0.2796	0.0000
N	-1.7677	-1.0607	-0.0001
N	-2.6544	1.1625	0.0000
H	-2.6844	1.7532	-0.8259
H	-2.6847	1.7530	0.8260
N	-0.6639	-1.8269	0.0000
H	-2.6811	-1.4953	0.0000
C	0.7401	1.5256	0.0000
H	0.3729	2.5484	0.0001
C	2.0917	1.2572	0.0000
H	2.8039	2.0772	0.0000
C	2.5855	-0.0850	0.0000
H	3.6601	-0.2439	0.0000
C	1.7380	-1.1708	0.0000
H	2.1110	-2.1901	0.0000

No imaginary frequencies

Cartesian coordinates of *1H*-**9**

	Coordinates (Å)		
Element	x	y	z
C	-1.5821	0.2520	0.0004
N	-2.5691	1.2299	-0.0779
H	-3.5008	0.8550	0.0582
H	-2.4054	2.0419	0.5041
C	-0.1595	0.4547	0.0004
C	0.3794	-0.8603	0.0057
N	-0.6816	-1.7085	-0.0058
N	-1.8801	-1.0362	0.0052
H	-0.6712	-2.7156	-0.0004
N	1.6768	-1.1907	0.0114
C	2.5065	-0.1458	0.0068
H	3.5677	-0.3849	0.0124
C	2.0992	1.2079	-0.0083
H	2.8529	1.9880	-0.0200
C	0.7442	1.5241	-0.0132
H	0.4100	2.5577	-0.0346

No imaginary frequencies

Cartesian coordinates of *2H*-**9**

	Coordinates (Å)		
Element	x	y	z
C	0.3745	-0.8944	0.0001
C	-0.1495	0.4474	0.0002
C	-1.5422	0.2802	0.0000
N	-1.7264	-1.0641	0.0000
N	-2.6597	1.1392	0.0001
H	-2.7119	1.7248	-0.8280

H	-2.7103	1.7266	0.8269
N	-0.6126	-1.8154	-0.0001
H	-2.6319	-1.5157	-0.0002
C	0.7598	1.5299	0.0000
H	0.4208	2.5627	0.0000
C	2.0997	1.2104	-0.0001
H	2.8594	1.9854	-0.0003
C	2.5095	-0.1605	0.0000
H	3.5748	-0.3864	-0.0001
N	1.6971	-1.1991	0.0000

No imaginary frequencies

Cartesian coordinates of *1H*-**13**

	Coordinates (Å)		
Element	x	y	z
C	1.9957	0.1755	-0.0103
N	3.0151	1.1265	0.0447
H	3.9357	0.7078	-0.0197
H	2.9116	1.8896	-0.6124
C	0.5983	0.4261	-0.0954
C	0.0385	-0.8325	-0.0393
N	1.0366	-1.7372	0.0774
N	2.2695	-1.1260	0.0848
H	0.9843	-2.7357	0.1959
N	-1.3300	-1.0865	-0.0712
H	-1.7039	-1.9912	-0.3293
C	-2.2459	-0.0463	0.0179
O	-3.4403	-0.2476	-0.1460
C	-1.6612	1.3153	0.3964
H	-1.5737	1.3093	1.4919
H	-2.4119	2.0632	0.1340
C	-0.2771	1.6387	-0.2164
H	0.1529	2.4996	0.3075
H	-0.3994	1.9402	-1.2674

No imaginary frequencies

Cartesian coordinates of *2H*-**13**

	Coordinates (Å)		
Element	x	y	z
C	0.0459	-0.8706	-0.0453
C	0.5975	0.4310	-0.1001
C	1.9619	0.2073	-0.0105
N	2.1295	-1.1420	0.0973
N	3.0585	1.0696	-0.0774
H	2.7920	2.0404	-0.1810
H	3.7237	0.9656	0.6813
N	0.9428	-1.8359	0.0751
H	2.9943	-1.6547	0.0331
C	-0.2843	1.6339	-0.2475
H	0.1346	2.5195	0.2464
H	-0.4092	1.8983	-1.3077
C	-1.6671	1.3147	0.3662
H	-2.4187	2.0523	0.0783
H	-1.5910	1.3387	1.4621
C	-2.2453	-0.0620	0.0218
O	-3.4491	-0.2632	-0.0803
N	-1.3300	-1.0858	-0.1010
H	-1.6911	-2.0223	-0.2360

No imaginary frequencies

Cartesian coordinates of *1H*-**15**

	Coordinates (Å)		
Element	x	y	z
C	-1.9784	0.2032	0.0009
N	-2.9937	1.1461	-0.0715
H	-3.9134	0.7533	0.0887

H	-2.8387	1.9865	0.4697
C	-0.5668	0.4581	0.0031
C	0.0011	-0.8192	0.0053
N	-1.0035	-1.7169	-0.0101
N	-2.2442	-1.0950	0.0033
H	-0.9656	-2.7230	0.0027
N	1.3497	-1.0150	0.0077
H	1.7677	-1.9376	0.0116
C	2.2688	0.0655	0.0029
O	3.4742	-0.1773	0.0100
C	1.6600	1.3916	-0.0133
H	2.3557	2.2217	-0.0292
C	0.3053	1.5826	-0.0145
H	-0.0983	2.5916	-0.0364

No imaginary frequencies

Cartesian coordinates of *2H*-**15**

	Coordinates (Å)		
Element	x	y	z
C	0.0074	-0.8540	-0.0073
C	0.5595	0.4608	-0.0119
C	1.9406	0.2382	-0.0043
N	2.1016	-1.1068	0.0078
N	3.0134	1.1144	-0.0732
H	2.7587	2.0872	0.0331
H	3.8107	0.8781	0.5052
N	0.9146	-1.8172	0.0054
H	2.9650	-1.6195	-0.0797
C	-0.3173	1.5884	-0.0007
H	0.0758	2.6027	0.0005
C	-1.6631	1.3809	0.0048
H	-2.3710	2.2009	0.0126
C	-2.2627	0.0374	0.0030
O	-3.4743	-0.1783	0.0067
N	-1.3556	-1.0291	-0.0012
H	-1.7507	-1.9619	0.0009

No imaginary frequencies

Cartesian coordinates of *1H*-**20**

	Coordinates (Å)		
Element	x	y	z
C	-2.3990	-0.0016	0.0020
N	-3.5603	0.7631	-0.0716
H	-4.3980	0.2106	0.0709
H	-3.5569	1.5898	0.5128
C	-1.0463	0.4764	0.0013
C	-0.2613	-0.7010	0.0027
N	-1.1288	-1.7426	-0.0089
N	-2.4420	-1.3241	0.0045
H	-0.9187	-2.7274	-0.0071
N	1.0813	-0.7677	0.0044
C	1.6861	0.4108	-0.0005
O	3.0371	0.4651	0.0040
C	3.7525	-0.7770	0.0093
H	4.8067	-0.4986	0.0121
H	3.5137	-1.3668	-0.8802
H	3.5080	-1.3628	0.9000
C	1.0217	1.6721	-0.0135
H	1.6207	2.5745	-0.0274
C	-0.3598	1.7045	-0.0142
H	-0.8871	2.6540	-0.0344

No imaginary frequencies

Cartesian coordinates of *2H*-**20**

	Coordinates (Å)		
Element	x	y	z

C	0.2671	-0.7483	-0.0063
C	1.0352	0.4699	-0.0127
C	2.3676	0.0419	-0.0091
N	2.3057	-1.3106	-0.0108
N	3.5916	0.7165	-0.0577
H	3.4893	1.7040	-0.2548
H	4.1795	0.5832	0.7591
N	1.0462	-1.8368	0.0071
H	3.0923	-1.9414	-0.0611
C	0.3440	1.7081	0.0008
H	0.8687	2.6602	0.0065
C	-1.0254	1.6665	0.0080
H	-1.6338	2.5629	0.0194
C	-1.6869	0.3856	0.0033
O	-3.0390	0.4603	0.0049
C	-3.7617	-0.7789	0.0026
H	-4.8145	-0.4950	0.0054
H	-3.5178	-1.3708	0.8891
H	-3.5212	-1.3655	-0.8883
N	-1.0963	-0.7817	-0.0008

No imaginary frequencies

Kinetic vs thermodynamic control in acylation of 2H-13d

Reactants (*2H*-**13d**)

	Coordinates (Å)		
Element	x	y	z
N	-0.74007	1.42675	-1.28103
C	-1.88078	0.74162	-1.64687
O	-2.99171	1.19604	-1.45245
C	-1.64550	-0.58490	-2.38106
C	-0.41529	-1.39856	-1.92758
H	-1.53061	-0.31524	-3.44753
H	-2.57861	-1.15865	-2.29486
H	-0.64472	-1.90957	-0.97245
C	0.74571	-0.46388	-1.76812
H	-0.21306	-2.19858	-2.66093
C	0.53859	0.89646	-1.43208
N	1.65532	1.58587	-1.28463
H	-0.85978	2.35170	-0.87905
C	2.13326	-0.57563	-1.81382
N	2.62767	0.65746	-1.51620
N	2.95679	-1.67339	-2.02069
H	2.47173	-2.47822	-2.40385
H	3.80768	-1.48208	-2.54327
H	3.59604	0.94796	-1.43195
Cl	4.64261	3.27338	-0.91809
C	0.29610	6.19135	-0.67738
C	1.43907	5.44707	1.32805
C	0.39911	6.15797	0.71896
C	2.37647	4.76763	0.54867
C	3.21675	4.10229	-1.76377
C	1.23006	5.51536	-1.46097
C	2.27655	4.79796	-0.85061
O	3.17828	4.07518	-2.94783
H	1.16354	5.52761	-2.55089
H	-0.51604	6.74535	-1.15539
H	1.51833	5.41803	2.41806
H	3.18309	4.20427	1.01732
H	-0.33466	6.68699	1.33331

Total Energy: -1331.55470634 Hartree
No imaginary frequencies

Transition state (**19d**)

	Coordinates (Å)		
Element	x	y	z
N	-0.4557	1.7056	-1.3021
C	-1.6376	1.0436	-1.6196
O	-2.7164	1.5615	-1.4343
C	-1.4684	-0.3277	-2.2816
C	-0.2648	-1.1651	-1.8017
H	-1.3619	-0.1204	-3.3626
H	-2.4215	-0.8578	-2.1499
H	-0.4953	-1.6217	-0.8206
C	0.93283	-0.2683	-1.7026
H	-0.1000	-2.0031	-2.4998
C	0.7775	1.0992	-1.4277
N	1.9582	1.7145	-1.2988
H	-0.5322	2.6579	-0.9532
C	2.3247	-0.4493	-1.7662
N	2.8939	0.7513	-1.5259
N	3.0597	-1.5943	-1.9390
H	2.5588	-2.3873	-2.3213
H	3.9991	-1.4925	-2.3081

H	3.8649	1.0921	-1.4984
Cl	4.4463	3.2052	-1.2416
C	0.3696	6.2914	-0.6601
C	1.1970	5.0806	1.2687
C	0.4588	6.1418	0.7262
C	1.8427	4.1721	0.4304
C	2.3822	3.3707	-1.9363
C	1.0115	5.3804	-1.5054
C	1.7475	4.3168	-0.9617
O	2.3025	3.3979	-3.1231
H	0.9515	5.4805	-2.5915
H	-0.2009	7.1198	-1.0887
H	1.2759	4.9680	2.3536
H	2.4443	3.3584	0.8377
H	-0.0433	6.8533	1.3873

Total Energy: -1331.26357064 Hartree
1 imaginary frequency (-202.38 cm^{-1})

Products (1Bz-**17d**)

	Coordinates (Å)		
Element	x	y	z
N	-0.44636	1.80781	-1.32747
C	-1.61761	1.05112	-1.33230
O	-2.66535	1.52766	-0.95519
C	-1.48690	-0.36073	-1.90602
C	-0.15459	-1.07754	-1.60526
H	-1.60198	-0.24740	-3.00008
H	-2.35739	-0.92677	-1.54806
H	-0.15678	-1.46058	-0.56732
C	0.97243	-0.10890	-1.81117
H	-0.06110	-1.96146	-2.25754
C	0.77950	1.24309	-1.62848
N	1.96918	1.89132	-1.86768
H	-0.51977	2.75980	-0.97998
C	2.35421	-0.21715	-2.15940
N	2.94119	0.97506	-2.21430
N	3.06801	-1.37142	-2.34722
H	2.55051	-2.20458	-2.59558
H	3.96752	-1.27395	-2.80475
H	4.22786	1.36069	-1.06158
Cl	4.84056	1.75221	0.06029
C	0.46271	6.37692	-0.75300
C	0.78494	4.84589	1.10201
C	0.31283	6.06520	0.60421
C	1.38854	3.92416	0.24190
C	2.24942	3.30946	-2.05099
C	1.08066	5.46929	-1.61367
C	1.52487	4.22881	-1.12472
O	3.03723	3.67085	-2.88304
H	1.22700	5.70714	-2.66969
H	0.10293	7.33435	-1.13771
H	0.69246	4.61511	2.16631
H	1.79922	2.98883	0.62986
H	-0.16404	6.78132	1.27867

Total Energy: -1331.55743967 Hartree
No imaginary frequencies

Reactants (*1H*-**13d**)

	Coordinates (Å)		
Element	x	y	z
N	-2.21191	-2.01384	-0.17162
C	-2.95990	-2.90614	-0.93077
O	-3.85144	-3.56142	-0.43309
C	-2.61998	-2.93397	-2.42427
C	-1.12730	-2.76188	-2.78054
H	-3.19473	-2.10196	-2.87229

H	-3.04241	-3.86658	-2.82262
H	-0.59040	-3.71562	-2.60896
C	-0.55658	-1.65585	-1.94270
H	-1.03159	-2.54451	-3.85730
C	-1.11258	-1.35805	-0.71062
N	-0.41925	-0.33291	-0.17191
H	-2.45201	-1.94716	0.81284
C	0.51287	-0.72098	-2.06050
N	0.59795	0.06596	-0.98943
N	1.36133	-0.55218	-3.15030
H	1.67302	-1.42132	-3.57358
H	2.14891	0.05491	-2.93846
H	-0.56899	0.17250	0.69463
C	2.59015	3.35196	-1.72746
C	3.87958	3.34962	-2.25687
C	4.94078	2.81841	-1.51293
C	4.70764	2.28928	-0.23927
C	3.41799	2.28637	0.29507
C	2.35242	2.81788	-0.44667
H	1.75060	3.75909	-2.29384
H	4.05995	3.76384	-3.25186
H	5.95243	2.81805	-1.92814
H	5.53498	1.87450	0.34161
H	3.22914	1.86904	1.28371
C	0.94862	2.86449	0.03297
Cl	0.69224	2.18681	1.73901
O	0.01506	3.32904	-0.52909

Total Energy: -1331.55044116 Hartree
No imaginary frequencies

Transition state (**18d**)

	Coordinates (Å)		
Element	x	y	z
N	-2.1110	-1.9493	-0.0196
C	-2.7609	-2.9168	-0.7876
O	-3.5905	-3.6474	-0.2953
C	-2.4065	-2.9175	-2.2767
C	-0.9445	-2.5675	-2.6282
H	-3.0797	-2.1709	-2.7374
H	-2.7044	-3.8996	-2.6678
H	-0.2970	-3.4471	-2.4484
C	-0.5117	-1.4012	-1.7895
H	-0.8742	-2.3448	-3.7057
C	-1.1012	-1.1715	-0.5487
N	-0.5142	-0.1132	0.0259
H	-2.3984	-1.8695	0.9514
C	0.4665	-0.3836	-1.9035
N	0.4718	0.3672	-0.7829
N	1.2855	-0.1091	-2.9661
H	1.4860	-0.8730	-3.5988
H	2.0626	0.5211	-2.7994
H	-0.6583	0.4206	0.8933
C	2.6267	3.3254	-1.8138
C	3.9902	3.5182	-2.0618
C	4.9401	2.7531	-1.3807
C	4.5252	1.7948	-0.4455
C	3.1673	1.6012	-0.1920
C	2.2121	2.3642	-0.8798
H	1.8697	3.9143	-2.3356
H	4.3092	4.2710	-2.7880
H	6.0060	2.9048	-1.5726
H	5.2672	1.2022	0.0958
H	2.8297	0.8776	0.5515
C	0.7317	2.2069	-0.6897
Cl	0.4623	2.2398	1.4486
O	-0.1310	2.7770	-1.2756

Total Energy: -1331.26189775 Hartree
1 imaginary frequency (-199.33 cm^{-1})

Products (2Bz-**17d**)

	Coordinates (Å)		
Element	x	y	z
N	-2.32574	-1.54293	-0.21513
C	-2.77881	-2.71460	-0.80763
O	-3.63713	-3.39436	-0.28846
C	-2.18427	-3.02816	-2.18455
C	-0.70810	-2.62983	-2.38832
H	-2.81384	-2.47935	-2.90840
H	-2.35283	-4.09906	-2.36090
H	-0.05344	-3.37177	-1.89263
C	-0.49078	-1.26461	-1.80752
H	-0.46370	-2.66915	-3.46319
C	-1.30066	-0.78512	-0.74849
N	-0.95444	0.41039	-0.31250
H	-2.78213	-1.25052	0.64490
C	0.44372	-0.25770	-1.99677
N	0.14980	0.74138	-1.07682
N	1.41325	-0.14684	-2.96233
H	1.62005	-1.00665	-3.45686
H	2.23591	0.40294	-2.73900
H	-0.34387	0.62271	1.35272
C	2.58874	3.41608	-1.86058
C	3.96040	3.63228	-1.99609
C	4.87138	2.72667	-1.43777
C	4.40987	1.60550	-0.73916
C	3.03694	1.37309	-0.61587
C	2.12126	2.27346	-1.19007
H	1.86522	4.12439	-2.27003
H	4.32325	4.51445	-2.52978
H	5.94597	2.90299	-1.53750
H	5.12066	0.91632	-0.27631
H	2.66509	0.52587	-0.03395
C	0.65017	2.10715	-0.98990
Cl	0.49005	0.60954	2.39354
O	-0.09539	3.01278	-0.72990

Total Energy: -1331.55898825 Hartree
No imaginary frequencies

Copper complexes that lead to 1Ph-16 and 2Ph-16

We have assessed the relative stability of Copper complexes that lean to 1Ph-**16** and 2Ph-**16** following the reaction mechanism described by Andrada et al. (Catalyst 2017,7,388 doi:10.3390/catal7120388), given the similarity between the compounds described therein and Ph-**16** systems. Energy optimization and frequency calculations were conducted at B3LYP/def2TZVP level of theory.

1Ph-**16**-Cu complex

	Coordinates (Å)		
Element	x	y	z
Cu	0.8120	0.3639	0.3262
N	2.1787	1.8216	0.1043
H	2.8388	1.6406	0.8572
N	1.1923	0.6698	-2.4765
H	1.7666	-0.1676	-2.4146
C	2.9260	1.8764	-1.1805
H	1.7241	2.7109	0.2919
H	3.5786	1.0041	-1.1944
H	3.5513	2.7731	-1.1995
C	2.0279	1.8746	-2.4075
H	2.6870	1.9857	-3.2774
H	0.7109	0.6358	-3.3703
H	1.3707	2.7486	-2.3979
I	2.7878	-1.4470	0.3661
C	-0.5681	1.6997	0.7546
C	-0.8824	1.8520	2.0944
C	-1.0748	2.5521	-0.2135
C	-1.6920	2.9215	2.4787
H	-0.5405	1.1356	2.8312
C	-1.8969	3.6089	0.1814
H	-0.8589	2.4055	-1.2640
C	-2.1973	3.7977	1.5251
H	-1.9390	3.0516	3.5253
H	-2.3052	4.2743	-0.5695
H	-2.8374	4.6170	1.8268
N	-0.6171	-0.8406	0.5072
C	-1.6424	-0.9737	-0.3594
N	-1.0123	-1.2981	1.7420
C	-2.7109	-1.6138	0.2591
N	-1.6734	-0.6101	-1.6627
C	-2.2405	-1.7770	1.6001
C	-3.8571	-1.8992	-0.5207
H	-0.8801	-0.1257	-2.0669
C	-2.7811	-0.8528	-2.4898
N	-2.9207	-2.3286	2.6632
C	-3.8877	-1.5362	-1.8352
H	-4.7144	-2.3985	-0.0829
O	-2.7520	-0.4862	-3.6588
H	-3.5230	-3.1061	2.4421
H	-2.3363	-2.5030	3.4677
H	-4.7466	-1.7347	-2.4595

Total Energy: -2886.83255484 Hartree

No imaginary frequencies

2Ph-**16**-Cu complex

	Coordinates (Å)		
Element	x	y	z
Cu	-0.8327	0.0564	0.7207
N	-2.4293	0.8563	1.6735
H	-3.0372	1.1490	0.9115

N	-1.1915	-1.5829	2.0013
H	-1.6531	-2.2627	1.4025
C	-3.1012	-0.1772	2.5042
H	-2.1694	1.6768	2.2122
H	-3.7589	-0.7329	1.8362
H	-3.7076	0.2795	3.2890
C	-2.0565	-1.1150	3.0944
H	-2.5502	-1.9323	3.6281
H	-0.3036	-1.9574	2.3182
H	-1.4287	-0.5840	3.8133
I	-2.8745	-1.0727	-1.2283
C	-0.2242	1.7973	0.0981
C	-0.8805	2.3889	-0.9664
C	0.7374	2.4553	0.8415
C	-0.5773	3.7177	-1.2691
H	-1.6075	1.8406	-1.5524
C	1.0241	3.7851	0.5286
H	1.2854	1.9438	1.6239
C	0.3662	4.4137	-0.5222
H	-1.0828	4.1988	-2.0975
H	1.7769	4.3152	1.0992
H	0.5995	5.4417	-0.7686
N	1.7773	-0.5896	1.1359
C	2.9295	-0.6656	0.4887
N	0.8235	-0.5853	0.1315
C	2.7856	-0.6814	-0.9213
N	4.1658	-0.7828	1.0498
C	1.4006	-0.5864	-1.1070
C	3.9393	-0.8091	-1.7352
H	4.2758	-0.7819	2.0538
C	5.3443	-0.9022	0.2971
N	0.6695	-0.5099	-2.2482
C	5.1619	-0.9105	-1.1523
H	3.8554	-0.8217	-2.8164
O	6.4204	-0.9882	0.8690
H	1.0980	-0.8608	-3.0881
H	-0.3292	-0.6883	-2.1697
H	6.0684	-1.0034	-1.7319

Total Energy: -2886.84359455 Hartree

No imaginary frequencies