Effect of Heterocycle Content on Metal Binding Isostere Coordination

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SUPPORTING INFORMATION

Experimental

General Materials and Methods. Starting materials were purchased and used from commercially available suppliers (Sigma-Aldrich, Acros Organics, Matrix Scientific, others) without further purification. [($Tp^{Ph,Me}$)ZnOH] ($Tp^{Ph,Me}$= hydrotris(5,3-methylphenylpyrazolyl)borate)) was synthesized as previously reported (*Inorg. Chim. Acta*, **2002**, *337*, 459-462). Column chromatography was performed using a CombiFlash R_f automated system from Teledyne Isco using prepacked silica cartridges. ^{1}H nuclear magnetic resonance (NMR) spectra were collected using a Varian spectrometer running at 400 MHz, a Varian spectrometer running at 500 MHz, or a 300 MHz Bruker AVA. ^{13}C NMR spectra were collected using a Varian spectrometer running at 126 MHz. Mass spectrometry analysis was performed by the University of California San Diego Chemistry and Biochemistry Mass Spectrometry Facility (MMSF).

Single Crystal X-ray Diffraction. Suitable crystals of [($Tp^{Ph,Me}$)Zn(MBI)] complexes were selected and placed on a Bruker APEX-II Ultra diffractometer with a Mo-Kα Microfocus Rotating Anode and an APEX-II CCD area detector or a Bruker Kappa diffractometer equipped with a Bruker X8 APEX II Mo sealed tube and a Bruker APEX-II CCD. The crystals were kept at 100 K during data collection. Using Olex2 (*J. Appl. Crystal.*, **2009**, *42*, 339-341**)**, the structure was solved with the ShelXT (*Acta Crystallogr., Sect. C: Struct. Chem.*, **2015**, *71*, 3-8) structure solution program using direct methods and refined with the XL (*Acta Crystallogr., Sect. A: Found. Adv.*, **2008,** *64*, 112-122) refinement package using least squares minimization. The crystal data file of all complexes was deposited into the Cambridge Crystallographic Data Centre (CCDC, Table S1-S5). Crystallographic data collection and refinement information is listed in Table S1-Table S5. Disordered solvent was treated with the PLATON SQUEEZE function (*Acta Crystallogr., Sect. C: Struct. Chem.*, **2015,** *71*, 9-18) in the [($Tp^{Ph,Me}$)Zn(**3b**)] and [($Tp^{Ph,Me}$)Zn(**5b**)] structures with 39 and 43 electrons squeezed respectively.

Table S1. Crystal data and structure refinement for [(Tp^{Ph,Me})Zn(indazole)] complexes.

Compound	[(Tp^{Ph,Me})Zn(**1**)]	[(Tp^{Ph,Me})Zn(**1a**)]	[(Tp^{Ph,Me})Zn(**1b**)]	[(Tp^{Ph,Me})Zn(**1c**)]	[(Tp^{Ph,Me})Zn(**1d**)]
CCDC code	1999816	1999818	1999817	1999819	1999820
Empirical formula	$C_{42}H_{40}BN_8O_3Zn$	$C_{40}H_{40}BN_9O_3Zn$	$C_{39}H_{38}BN_9O_3Zn$	$C_{38}H_{34}BN_{12}O_{0.5}Zn$	$C_{40.5}H_{39}BN_{10}O_{3.5}Zn$
Formula weight	781.00	770.99	756.96	742.95	797.99
Temperature/K	100.0	100.0	100.0	100.0	100.0
Crystal system	monoclinic	triclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/n$	P-1	P-1	C2/c	$P2_1/c$
a/Å	11.1116(16)	11.652(4)	11.5454(6)	21.265(2)	22.1038(7)
b/Å	22.132(3)	12.368(4)	12.4466(6)	12.2666(12)	18.2437(6)
c/Å	16.382(2)	13.917(4)	13.3968(7)	26.802(3)	20.8443(7)
α/°	90	92.104(6)	87.8610(10)	90	90
β/°	105.947(5)	105.552(4)	72.8450(10)	96.968(2)	110.7280(10)
γ/°	90	103.261(9)	88.9960(10)	90	90
Volume/Å^3	3873.7(9)	1870.4(10)	1838.16(16)	6939.8(12)	7861.5(4)
Z	4	2	2	8	8
ρ_{calc}g/cm^3	1.339	1.369	1.368	1.422	1.348
μ/mm^{-1}	0.684	0.708	0.719	0.758	0.678
F(000)	1628.0	804.0	788.0	3080.0	3320.0
Crystal size/mm^3	0.5 × 0.25 × 0.15	0.08 × 0.08 × 0.08	0.05 × 0.05 × 0.05	0.4 × 0.3 × 0.1	0.2 × 0.02 × 0.01
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.172 to 51.604	3.054 to 52.81	3.184 to 50.73	3.062 to 51.36	2.978 to 51.394
Index ranges	$-13 \le h \le 13$, $-27 \le k \le 26$, $-20 \le l \le 20$	$-14 \le h \le 14$, $-15 \le k \le 15$, $-17 \le l \le 17$	$-13 \le h \le 13$, $-14 \le k \le 14$, $-16 \le l \le 15$	$-25 \le h \le 25$, $-14 \le k \le 14$, $-32 \le l \le 32$	$-26 \le h \le 26$, $-22 \le k \le 15$, $-25 \le l \le 19$
Reflections collected	36424	46382	11609	34629	48279
Independent reflections	7278 [R_{int} = 0.0636, R_{sigma} = 0.0592]	7674 [R_{int} = 0.0515, R_{sigma} = 0.0338]	6726 [R_{int} = 0.0270, R_{sigma} = 0.0452]	6569 [R_{int} = 0.0665, R_{sigma} = 0.0527]	14813 [R_{int} = 0.0602, R_{sigma} = 0.0776]
Data/restraints/parameters	7278/9/501	7674/0/493	6726/0/483	6569/0/480	14813/0/1021
Goodness-of-fit on F^2	1.038	1.046	1.062	1.038	1.090
Final R indexes [I>=2σ (I)]	R_1 = 0.0543, wR_2 = 0.1275	R_1 = 0.0306, wR_2 = 0.0721	R_1 = 0.0335, wR_2 = 0.0711	R_1 = 0.0413, wR_2 = 0.0827	R_1 = 0.0514, wR_2 = 0.1219
Final R indexes [all data]	R_1 = 0.0836, wR_2 = 0.1428	R_1 = 0.0379, wR_2 = 0.0762	R_1 = 0.0455, wR_2 = 0.0749	R_1 = 0.0629, wR_2 = 0.0902	R_1 = 0.0913, wR_2 = 0.1507
Largest diff. peak/hole / e Å^{-3}	0.70/-1.08	0.61/-0.29	0.53/-0.32	0.31/-0.41	0.71/-0.73

Table S2. Crystal data and structure refinement for [(Tp^{Ph,Me})Zn(benzimidazole)] complexes.

Compound	[(Tp^{Ph,Me})Zn(**2**)]	[(Tp^{Ph,Me})Zn(**2a**)]	[(Tp^{Ph,Me})Zn(**2b**)]	[(Tp^{Ph,Me})Zn(**2c**)]	[(Tp^{Ph,Me})Zn(**2d**)]
CCDC code	1999824	1999822	1999840	1999823	1999821
Empirical formula	$C_{53}H_{48}BN_8O_2Zn$	$C_{48}H_{45}BN_9O_2Zn$	$C_{50}H_{46}BN_9O_2Zn$	$C_{91}H_{81}B_2N_{24}Zn_2$	$C_{39}H_{33}BN_{10}O_2Zn$
Formula weight	905.17	856.11	881.14	1663.15	749.93
Temperature/K	100.0	100.0	100.0	100.0	100.0
Crystal system	triclinic	triclinic	triclinic	triclinic	monoclinic
Space group	P-1	P-1	P-1	P-1	$P2_1/c$
a/Å	11.7557(10)	11.951(7)	11.902(2)	14.290(3)	19.2031(17)
b/Å	13.3890(16)	12.222(7)	13.512(3)	16.009(4)	17.4413(16)
c/Å	16.6386(11)	33.40(2)	15.071(2)	20.236(5)	10.8662(10)
α/°	67.385(4)	96.044(11)	65.558(5)	111.296(6)	90
β/°	74.545(2)	90.661(10)	87.822(5)	101.338(4)	103.602(3)
γ/°	89.452(4)	117.154(13)	87.374(8)	94.752(4)	90
Volume/Å^3	2317.3(4)	4307(4)	2203.5(7)	4168.3(16)	3537.3(6)
Z	2	4	2	2	4
ρ_{calc}g/cm^3	1.297	1.320	1.328	1.325	1.408
μ/mm^{-1}	0.581	0.621	0.609	0.638	0.746
F(000)	946.0	1788.0	920.0	1730.0	1552.0
Crystal size/mm^3	0.2 × 0.2 × 0.2	0.1 × 0.1 × 0.03	0.5 × 0.2 × 0.2	0.3 × 0.2 × 0.15	0.25 × 0.25 × 0.07
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.314 to 52.814	2.458 to 48.452	3.416 to 51.494	2.77 to 52.684	4.364 to 52.952
Index ranges	-14 ≤ h ≤ 14, -16 ≤ k ≤ 16, -20 ≤ l ≤ 20	-13 ≤ h ≤ 13, -14 ≤ k ≤ 14, -38 ≤ l ≤ 38	-11 ≤ h ≤ 14, -16 ≤ k ≤ 16, -18 ≤ l ≤ 18	-17 ≤ h ≤ 17, -19 ≤ k ≤ 19, -25 ≤ l ≤ 25	-22 ≤ h ≤ 24, -21 ≤ k ≤ 21, -13 ≤ l ≤ 13
Reflections collected	42525	61119	43680	83446	53135
Independent reflections	9499 [R_{int} = 0.0647, R_{sigma} = 0.0436]	13796 [R_{int} = 0.0983, R_{sigma} = 0.0998]	8391 [R_{int} = 0.0610, R_{sigma} = 0.0563]	16899 [R_{int} = 0.0635, R_{sigma} = 0.0429]	7284 [R_{int} = 0.0621, R_{sigma} = 0.0428]
Data/restraints/parameters	9499/0/589	13796/285/1230	8391/0/572	16899/84/1073	7284/0/481
Goodness-of-fit on F^2	1.055	1.025	1.033	1.040	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0326, wR_2 = 0.0869	R_1 = 0.0568, wR_2 = 0.0986	R_1 = 0.0404, wR_2 = 0.0839	R_1 = 0.0341, wR_2 = 0.0840	R_1 = 0.0421, wR_2 = 0.0958
Final R indexes [all data]	R_1 = 0.0360, wR_2 = 0.0896	R_1 = 0.1049, wR_2 = 0.1126	R_1 = 0.0622, wR_2 = 0.0926	R_1 = 0.0430, wR_2 = 0.0896	R_1 = 0.0622, wR_2 = 0.1038
Largest diff. peak/hole / e Å^{-3}	0.36/-0.28	0.43/-0.44	0.62/-0.52	0.52/-0.40	0.89/-0.42

Table S3. Crystal data and structure refinement for [(Tp^{Ph,Me})Zn(1,2-benzoisothiazole)]

Compound	[(Tp^{Ph,Me})Zn(**3**)]	[(Tp^{Ph,Me})Zn(**3a**)]	[(Tp^{Ph,Me})Zn(**3b**)]	[(Tp^{Ph,Me})Zn(**3c**)]	[(Tp^{Ph,Me})Zn(**3d**)]
CCDC code	1999829	1999827	1999828	1999826	1999825
Empirical formula	$C_{38}H_{32}BN_7O_2SZn$	$C_{45}H_{41}BN_8O_2SZn$	$C_{39}H_{36}BN_8O_3SZn$	$C_{38}H_{32}BN_{11}SZn$	$C_{39}H_{32}BN_9O_2SZn$
Formula weight	726.94	834.10	773.00	750.98	766.97
Temperature/K	100.0	100.0	100.0	100.0	100.0
Crystal system	monoclinic	triclinic	triclinic	triclinic	triclinic
Space group	$P2_1/c$	P-1	P-1	P-1	P-1
a/Å	25.354(4)	11.7747(6)	11.767(3)	11.3854(9)	11.3437(6)
b/Å	12.7294(11)	12.2627(6)	13.044(3)	12.2324(9)	12.4724(6)
c/Å	21.364(3)	16.6658(8)	14.552(4)	12.9278(11)	13.2663(7)
α/°	90	88.998(2)	110.451(4)	95.296(2)	93.307(2)
β/°	99.223(5)	71.4110(10)	94.891(5)	103.872(2)	106.813(2)
γ/°	90	63.5020(10)	107.004(4)	100.760(2)	102.442(2)
Volume/Å^3	6805.8(15)	2019.04(17)	1957.2(9)	1699.4(2)	1740.01(16)
Z	8	2	2	2	2
ρ_{calc}g/cm^3	1.419	1.372	1.312	1.468	1.464
μ/mm^{-1}	0.830	0.710	0.728	0.832	0.817
F(000)	3008.0	868.0	802.0	776.0	792.0
Crystal size/mm^3	0.4 × 0.175 × 0.1	0.1 × 0.04 × 0.04	0.80 × 0.40 × 0.20	0.05 × 0.03 × 0.03	0.12 × 0.06 × 0.06
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.59 to 52.736	2.606 to 52.874	3.054 to 50.844	3.28 to 53.522	3.234 to 52.242
Index ranges	-31 ≤ h ≤ 31, -15 ≤ k ≤ 15, -26 ≤ l ≤ 26	-14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -20 ≤ l ≤ 20	-14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -17 ≤ l ≤ 16	-14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -16 ≤ l ≤ 16	-14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -14 ≤ l ≤ 16
Reflections collected	85431	25629	25768	19604	17297
Independent reflections	13899 [R_{int} = 0.0779, R_{sigma} = 0.0624]	8307 [R_{int} = 0.0309, R_{sigma} = 0.0335]	7169 [R_{int} = 0.0649, R_{sigma} = 0.0718]	7243 [R_{int} = 0.0441, R_{sigma} = 0.0655]	6893 [R_{int} = 0.0329, R_{sigma} = 0.0474]
Data/restraints/parameters	13899/0/907	8307/0/527	7169/0/486	7243/0/472	6893/0/481
Goodness-of-fit on F^2	1.017	1.048	1.027	0.912	1.015
Final R indexes [I>=2σ (I)]	R_1 = 0.0404, wR_2 = 0.0797	R_1 = 0.0313, wR_2 = 0.0704	R_1 = 0.0594, wR_2 = 0.1497	R_1 = 0.0423, wR_2 = 0.0900	R_1 = 0.0337, wR_2 = 0.0700
Final R indexes [all data]	R_1 = 0.0778, wR_2 = 0.0914	R_1 = 0.0409, wR_2 = 0.0742	R_1 = 0.0876, wR_2 = 0.1654	R_1 = 0.0681, wR_2 = 0.1013	R_1 = 0.0474, wR_2 = 0.0749
Largest diff. peak/hole / e Å^{-3}	0.35/-0.47	0.38/-0.27	1.35/-0.95	0.39/-0.53	0.37/-0.31

complexes.

Table S4. Crystal data and structure refinement for [($Tp^{Ph,Me}$)Zn(benzothiazole)] complexes.

Compound	[($Tp^{Ph,Me}$)Zn(**4**)]	[($Tp^{Ph,Me}$)Zn(**4a**)]	[($Tp^{Ph,Me}$)Zn(**4b**)]	[($Tp^{Ph,Me}$)Zn(**4c**)]	[($Tp^{Ph,Me}$)Zn(**4d**)]
CCDC code	1999834	1999830	1999833	1999831	1999832
Empirical formula	$C_{38}H_{32}BN_7O_2SZn$	$C_{45}H_{41}BN_8O_2SZn$	$C_{44}H_{39}BN_8O_2SZn$	$C_{44}H_{38}BN_{11}SZn$	$C_{45}H_{38}BN_9O_2SZn$
Formula weight	726.94	834.10	820.07	829.09	845.08
Temperature/K	100.0	100.0	100.0	100.0	100.0
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/n$
a/Å	11.8071(5)	13.2942(13)	18.2805(12)	11.4626(11)	11.5071(9)
b/Å	20.2004(10)	16.9309(19)	24.6819(16)	24.908(3)	24.8201(16)
c/Å	14.5401(11)	18.117(2)	17.9965(11)	14.0421(15)	14.2983(10)
α/°	90	90	90	90	90
β/°	95.990(2)	90.612(4)	103.0430(10)	92.074(4)	93.957(2)
γ/°	90	90	90	90	90
Volume/$Å^3$	3449.0(3)	4077.5(8)	7910.5(9)	4006.5(7)	4074.0(5)
Z	4	4	8	4	4
$\rho_{calc}g/cm^3$	1.400	1.359	1.377	1.375	1.378
μ/mm^{-1}	0.819	0.703	0.723	0.713	0.705
F(000)	1504.0	1736.0	3408.0	1720.0	1752.0
Crystal size/mm^3	0.4 × 0.4 × 0.4	0.6 × 0.6 × 0.2	0.1 × 0.1 × 0.05	1 × 0.5 × 0.5	0.5 × 0.3 × 0.3
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.464 to 51.348	3.292 to 53.464	4.694 to 54.25	3.332 to 52.824	3.294 to 52.84
Index ranges	$-13 \le h \le 14$, $-22 \le k \le 24$, $-17 \le l \le 17$	$-15 \le h \le 16$, $-21 \le k \le 21$, $-22 \le l \le 22$	$-23 \le h \le 23$, $-31 \le k \le 31$, $-22 \le l \le 23$	$-14 \le h \le 13$, $-31 \le k \le 31$, $-17 \le l \le 16$	$-14 \le h \le 14$, $-31 \le k \le 31$, $-17 \le l \le 17$
Reflections collected	69989	57223	51632	46011	78142
Independent reflections	6548 [R_{int} = 0.0406, R_{sigma} = 0.0169]	8665 [R_{int} = 0.0560, R_{sigma} = 0.0414]	17388 [R_{int} = 0.0483, R_{sigma} = 0.0567]	8205 [R_{int} = 0.0530, R_{sigma} = 0.0455]	8347 [R_{int} = 0.0423, R_{sigma} = 0.0245]
Data/restraints/parameters	6548/30/454	8665/0/527	17388/0/1035	8205/0/526	8347/0/535
Goodness-of-fit on F^2	1.053	1.016	1.025	1.019	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0259, wR_2 = 0.0670	R_1 = 0.0332, wR_2 = 0.0703	R_1 = 0.0386, wR_2 = 0.0903	R_1 = 0.0363, wR_2 = 0.0743	R_1 = 0.0286, wR_2 = 0.0637
Final R indexes [all data]	R_1 = 0.0280, wR_2 = 0.0683	R_1 = 0.0491, wR_2 = 0.0764	R_1 = 0.0583, wR_2 = 0.0987	R_1 = 0.0549, wR_2 = 0.0807	R_1 = 0.0381, wR_2 = 0.0682
Largest diff. peak/hole / e $Å^{-3}$	0.53/-0.41	0.30/-0.35	0.81/-0.54	0.40/-0.33	0.30/-0.33

Table S5. Crystal data and structure refinement for [(Tp^{Ph,Me})Zn(1,2-benzoisoxazole)] complexes.

Compound	[(Tp^{Ph,Me})Zn(**5**)]	[(Tp^{Ph,Me})Zn(**5a**)]	[(Tp^{Ph,Me})Zn(**5b**)]	[(Tp^{Ph,Me})Zn(**5c**)]	[(Tp^{Ph,Me})Zn(**5d**)]
CCDC code	1999839	199836	1999838	1999837	1999835
Empirical formula	$C_{43.5}H_{41}BN_7O_3Zn$	$C_{45}H_{41}BN_8O_3Zn$	$C_{38}H_{35}BN_8O_4Zn$	$C_{38}H_{32}BN_{11}OZn$	$C_{39}H_{32}BN_9O_{2.96}Zn$
Formula weight	786.01	818.04	743.92	734.92	750.91
Temperature/K	100.0	100.0	100.0	100.0	100.0
Crystal system	monoclinic	triclinic	triclinic	triclinic	triclinic
Space group	$P2_1/n$	P-1	P-1	P-1	P-1
a/Å	15.5694(12)	11.7292(11)	11.930(2)	11.4597(7)	11.529(3)
b/Å	14.5978(11)	11.9654(12)	13.078(2)	12.2118(8)	12.532(3)
c/Å	17.7711(14)	16.3974(16)	14.235(3)	12.9190(8)	13.170(3)
α/°	90	100.704(3)	107.583(6)	95.428(2)	92.476(9)
β/°	106.120(2)	96.654(3)	93.055(6)	104.427(2)	108.327(9)
γ/°	90	114.105(3)	106.031(6)	100.399(2)	103.041(8)
Volume/Å^3	3880.2(5)	2016.3(3)	2012.0(6)	1703.57(19)	1746.3(7)
Z	4	2	2	2	2
ρ_{calc}g/cm^3	1.346	1.347	1.228	1.433	1.428
μ/mm^{-1}	0.683	0.661	0.657	0.772	0.757
F(000)	1640.0	852.0	772.0	760.0	776.0
Crystal size/mm^3	0.4 × 0.35 × 0.2	0.4 × 0.35 × 0.35	0.2 × 0.1 × 0.1	0.3 × 0.2 × 0.2	0.2 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.088 to 52.04	4.056 to 52.78	4.138 to 52.292	3.428 to 51.358	3.846 to 52.8
Index ranges	-18 ≤ h ≤ 19, -18 ≤ k ≤ 18, -21 ≤ l ≤ 21	-14 ≤ h ≤ 14, -14 ≤ k ≤ 14, -20 ≤ l ≤ 20	-14 ≤ h ≤ 14, -16 ≤ k ≤ 16, -17 ≤ l ≤ 17	-13 ≤ h ≤ 13, -14 ≤ k ≤ 14, -15 ≤ l ≤ 15	-14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -16 ≤ l ≤ 16
Reflections collected	47206	53797	47161	38782	16915
Independent reflections	7655 [R_{int} = 0.0377, R_{sigma} = 0.0300]	8246 [R_{int} = 0.0295, R_{sigma} = 0.0195]	7991 [R_{int} = 0.0534, R_{sigma} = 0.0423]	6459 [R_{int} = 0.0355, R_{sigma} = 0.0246]	7129 [R_{int} = 0.0428, R_{sigma} = 0.0671]
Data/restraints/parameters	7655/39/531	8246/72/558	7991/0/481	6459/0/472	7129/0/482
Goodness-of-fit on F^2	1.007	0.997	1.037	1.041	1.016
Final R indexes [I>=2σ (I)]	R_1 = 0.0365, wR_2 = 0.0832	R_1 = 0.0279, wR_2 = 0.0701	R_1 = 0.0334, wR_2 = 0.0731	R_1 = 0.0269, wR_2 = 0.0655	R_1 = 0.0410, wR_2 = 0.0784
Final R indexes [all data]	R_1 = 0.0570, wR_2 = 0.0941	R_1 = 0.0334, wR_2 = 0.0734	R_1 = 0.0474, wR_2 = 0.0778	R_1 = 0.0315, wR_2 = 0.0676	R_1 = 0.0607, wR_2 = 0.0859
Largest diff. peak/hole / e Å^{-3}	1.00/-0.71	0.42/-0.33	0.45/-0.36	0.31/-0.26	0.39/-0.34

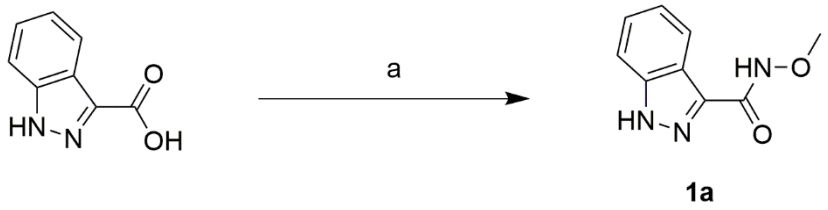
Table S6. MBP/MBI coordinating bond distances and τ_5 parameter values.

MBPs	Zn-Carboxylate Bond (Å)	Zn-Heterocycle Bond (Å)	τ_5 Parameter
1	2.011	2.136	0.34
2	2.007	2.150	0.74
3[a,b]	1.950 (1.930)	2.249 (2.339)	0.62
4	1.967	2.308	0.70
5	1.941	NA	0.72
A Series MBIs	**Zn-C-O Bond(Å)**	**Zn-Heterocycle/N-O Bond (Å)**	**τ_5 Parameter**
1a	1.928	2.227	0.53
2a[a,b]	2.003 (1.951)	2.093 (2.128)	0.35
3a	1.920	2.321	0.81
4a	1.949	2.241	0.66
5a	1.897	2.430	0.77
B Series MBIs	**Zn-C-O Bond(Å)**	**Zn-Heterocycle/N-O Bond (Å)**	**τ_5 Parameter**
1b	2.088	2.000	0.41
2b	2.009	2.123	0.54
3b	2.131	1.953	0.51
4b[a,b]	1.980 (1.979)	2.183 (2.170)	0.59
5b	2.120	1.989	0.59
C Series MBIs	**Zn-Tetrazole Bond(Å)**	**Zn-Heterocycle Bond (Å)**	**τ_5 Parameter**
1c	1.992	2.610	0.56
2c[a]	2.032 (2.027)	2.277 (2.232)	0.53
3c	1.956	3.046	0.66
4c	1.985	2.488	0.65
5c	1.961	3.174	0.62
D Series MBIs	**Zn-Oxadiazolone Bond(Å)**	**Zn-Heterocycle Bond (Å)**	**τ_5 Parameter**
1d[a,b]	1.953 (1.954)	2.654 (2.621)	0.58
2d	2.045	2.230	0.34
3d	1.940	2.988	0.59
4d	1.988	2.425	0.57
5d	1.951	3.187	0.69

[a] Structures with more than one complex in the asymmetric unit have all observed bond distances reported.

[b] The τ_5 parameter values for structures with more than one complex in the asymmetric unit are an average of all τ_5 parameter values of the individual complexes present.

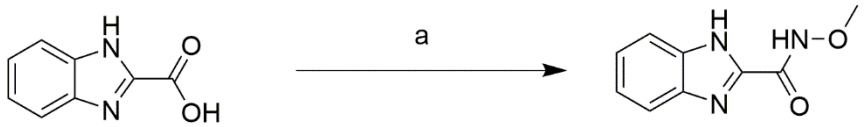
Synthetic Procedures



1a

(a) DMF, CDI, 25 ℃, 1 h, $CH_3ONH_2 \cdot HCl$, 25 ℃, overnight.

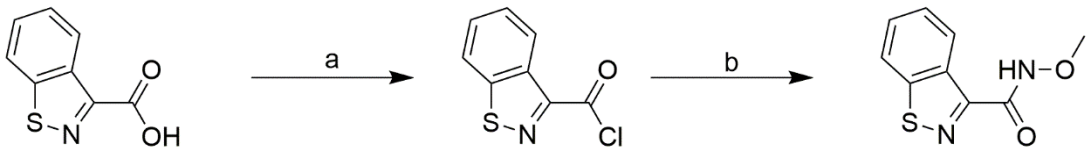
***O*-methyl indazole-3-hydroxamic acid (1a).** In a round bottom flask indazole-3-carboxylic acid (300 mg, 1 equiv, 1.9 mmol) was dissolved in 10 mL of DMF. 1,1'-Carbonyldiimidazole (CDI) (300 mg, 1 equiv, 1.9 mmol) was added to the solution and stirred for 1 h under nitrogen at room temperature. *O*-methylhydroxylamine hydrochloride (309 mg, 2 equiv, 3.7 mmol) was added to the reaction and stirred overnight under nitrogen at room temperature. The reaction was dried down via rotary evaporation to a yellow-brown oil and loaded onto silica. The product was purified via column chromatography using a 0-100% Hexanes:EtOAc gradient. The fractions containing product were dried down via rotary evaporation to obtain a white solid. Yield: 197 mg (56%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 13.63 (s, 1H), 11.76 (s, 1H), 8.13 (d, J = 8.2 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.47 – 7.37 (m, 1H), 7.31 – 7.22 (m, 1H), 3.73 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6): δ 160.4, 140.7, 137.0, 126.5, 121.9, 121.7, 121.3, 110.7. ESI-MS(+) calculated for $[C_9H_{10}N_3O_2]^+$ 192.08, found *m/z* 192.05 $[M+H]^+$.



2a

(a) DMF, CDI, 25 ℃ 1 h, $CH_3ONH_2 \cdot HCl$, 25 ℃, overnight.

***O*-methyl benzimidazole-2-hydroxamic acid (2a).** In a round bottom flask benzimidazole-2-carboxylic acid (300 mg, 1 equiv, 1.9 mmol) was dissolved in 10 mL of DMF. 1,1'-Carbonyldiimidazole (CDI) (300 mg, 1 equiv, 1.9 mmol) was added to the solution and stirred for 1 h under nitrogen at room temperature. *O*-methylhydroxylamine hydrochloride (310 mg, 2 equiv, 3.7 mmol) was added to the reaction mixture and stirred overnight under nitrogen at room temperature. The reaction mixture was then dried down via rotary evaporation giving a brown oil that was purified via column chromatography using a 0-60 % Hexanes:EtOAc gradient. The fractions containing product were dried down via rotary evaporation to obtain a tan solid. Yield: 160 mg (45%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 13.38 (s, 1H), 12.39 (s, 1H), 7.63 (d, J = 45.7 Hz, 2H), 7.31 (s, 2H), 3.74 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d6): δ 167.9, 161.9, 157.9, 140.8, 132.5, 132.2, 129.2, 128.2, 68.7. ESI-MS(+) calculated for $[C_9H_{10}N_3O_2]^+$ 192.08, found *m/z* 192.07 $[M+H]^+$.

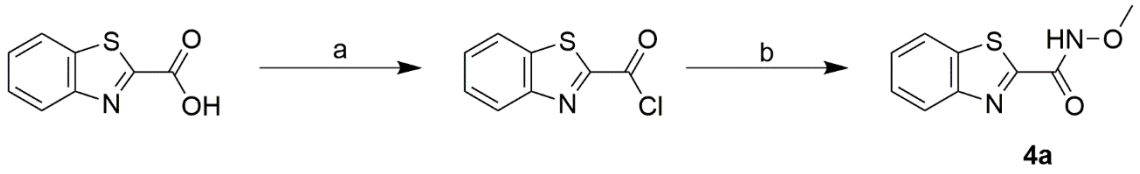


3a

(a) CH_2Cl_2, $(COCl)_2$, DMF (cat.), 25 °C, 3 h; (b) CH_2Cl_2, CH_3ONH_2·HCl, TEA, 25 °C, overnight.

***O*-methyl 1,2-benzisothiazole-3-hydroxamic acid (3a).** To a solution of 1,2-benzisothiazole-3-carboxylic acid (300 mg, 1 equiv, 1.7 mmol) in 25 mL of CH_2Cl_2, oxalyl chloride (637 mg, 0.440 mL, 3 equiv, 5.0 mmol) was slowly added along with 5 drops of DMF. The solution was stirred for 3 h at room temperature under nitrogen. The reaction mixture was then evaporated to provide the crude acid chloride which was moved forward to the next step. The dried solids were dissolved

in 25 mL of CH_2Cl_2 and *O*-methylhydroxylamine hydrochloride (168 mg, 1.2 equiv, 2.0 mmol) and triethylamine (678 mg, 0.933 mL, 4 equiv, 6.7 mmol) were added. The mixture was stirred overnight at room temperature under nitrogen. The reaction mixture was washed with a saturated brine solution and the organic layer was dried over $MgSO_4$. The organic layer was then dried down via rotary evaporation and loaded onto silica. The product was purified via column chromatography using a 0-40% Hexanes:EtOAc gradient. The fractions containing product were dried down via rotary evaporation. The product was recrystallized in isopropyl alcohol and obtained as a white solid. Yield: 83 mg (24%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 12.20 (s, 1H), 8.67 (d, J = 8.1 Hz, 1H), 8.34 – 8.30 (m, 1H), 7.73 – 7.58 (m, 2H), 3.77 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d6): δ 158.3, 155.1, 152.6, 133.8, 128.4, 126.1, 125.4, 120.8, 63.4. ESI-MS(+) calculated for $[C_9H_9N_2O_2S]^+$ 209.04, found *m/z* 208.98 $[M+H]^+$.

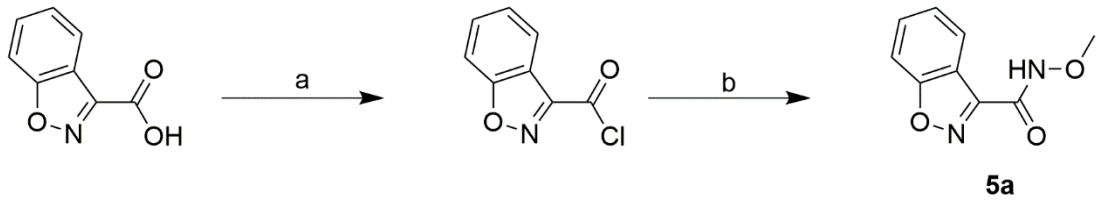


4a

(a) CH_2Cl_2, $(COCl)_2$, DMF (cat.), 25 °C, 3 h; (b) CH_2Cl_2, CH_3ONH_2·HCl, TEA, 25 °C, 2 h.

***O*-methyl benzothiazole-2-hydroxamic acid (4a).** To a solution of benzothiazole-2-carboxylic acid (500 mg, 1 equiv, 2.79 mmol) in 50 mL of CH_2Cl_2, oxalyl chloride (1.06 g, 0.733 mL, 3 equiv, 8.37 mmol) was slowly added along with 5 drops of DMF. The reaction as stirred for 3 h at room temperature under nitrogen. The reaction mixture was then dried down to a solid via rotary evaporation to provide the crude acid chloride which was moved forward onto the next step. To a solution of the crude acid chloride dissolved in 50 mL of CH_2Cl_2, *O*-methylhydroxylamine hydrochloride (280 mg, 1.2 equiv, 3.4 mmol) and triethylamine (678 mg, 0.93 mL, 2.4 equiv, 6.7 mmol) were added. The reaction was stirred at room temperature for 2 h. The reaction solution

was then washed with a saturated brine solution, dried over $MgSO_4$, and dried down to a brown solid and loaded onto silica. The product was purified via column chromatography using a gradient of 0-60% Hexanes:EtOAc. The fractions containing product were dried down via rotary evaporation to obtain a tan solid. Yield: 326 mg (56%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 12.61 (s, 1H), 8.28 – 8.22 (m, 1H), 8.17 – 8.10 (m, 1H), 7.69 – 7.55 (m, 2H), 3.76 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d6): δ 162.8, 156.7, 152.7, 135.7, 127.3, 127.0, 124.0, 123.1, 63.5. ESI-MS(+) calculated for $[C_9H_9N_2O_2S]^+$ 209.04, found *m/z* 208.98 $[M+H]^+$.

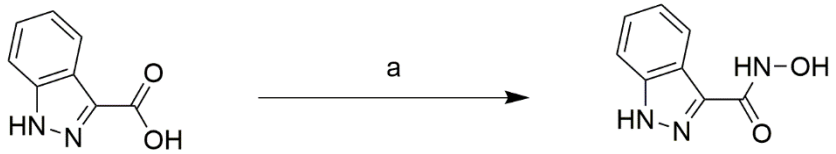


5a

(a) CH_2Cl_2, $SOCl_2$, DMF (cat.), 25 °C, 3-4 h; (b) CH_2Cl_2, CH_3ONH_2·HCl, TEA, 25 °C, 2 h.

***O*-methyl 1,2-benzisothiazole-3-hydroxamic acid (5a).** In a round bottom flask 1,2-benzisoxazole-3-carboxylic acid (300 mg, 1 equiv, 1.84 mmol) was dissolved in CH_2Cl_2 (10 mL). Thionyl chloride (3.3 g, 2.0 mL, 15 equiv, 28 mmol) was added slowly along with a few drops of DMF. The reaction mixture was then stirred at room temperature under a nitrogen atmosphere for 3 to 4 hr. The reaction mixture was dried down to a tan residue and redissolved in CH_2Cl_2 (10 mL). *O*-methylhydroxylamine hydrochloride (307 mg, 2 equiv, 3.68 mmol) and triethylamine (744 mg, 1.0 mL, 4 equiv, 7.36 mmol) were added and the reaction was stirred at room temperature overnight under a nitrogen atmosphere. The reaction mixture was dried down via rotary evaporation and loaded onto silica. The product was isolated via column chromatography using a 0-20% Hexanes:EtOAc gradient. Fractions containing product were dried down via rotary evaporation to obtain a white solid. The product was recrystallized in Hexanes:EtOAc resulting

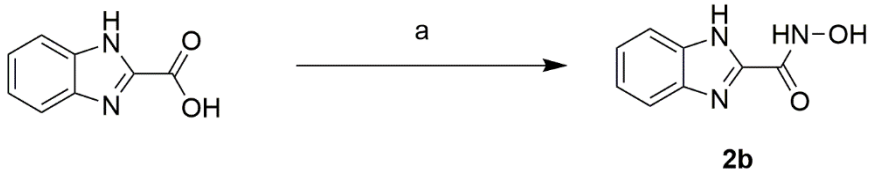
in clear block crystals which were collected via filtration. Yield: 80 mg (23%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.46 (s, 1H), 8.08 (dd, J = 8.0, 0.9 Hz, 1H), 7.88 (d, J = 8.5 Hz, 1H), 7.77 – 7.72 (m, 1H), 7.54 – 7.49 (m, 1H), 3.78 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d6): δ 162.9, 155.8, 150.8, 131.2, 125.3, 123.0, 119.4, 110.1, 63.6. ESI-MS(+) calculated for $[C_9H_9N_2O_3]^+$ 193.06, found *m/z* 193.22 $[M+H]^+$.



1b

(a) DMF, CDI, 25 ℃, 1 h, $NH_2OH{\cdot}HCl$, 25 ℃, overnight.

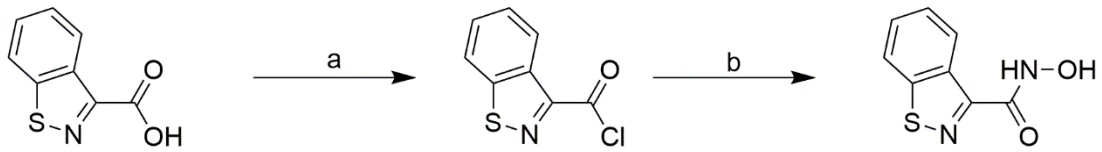
Indazole-3-hydroxamic acid (1b). To a solution of indazole-3-carboxylic acid (500 mg, 1 equiv, 3.1 mmol) dissolved in 10 mL of DMF, CDI (500 mg, 1 equiv, 3.1 mmol) was added and the solution was stirred for 1 h under nitrogen at room temperature. Hydroxylamine hydrochloride (429 mg, 2 equiv, 6.2 mmol) was added to the reaction and the mixture was stirred overnight under nitrogen at room temperature. The reaction mixture was dried via rotary evaporation and loaded onto silica. The product was purified via column chromatography using a 0-100% Hexanes:EtOAc gradient. The fractions containing product were dried down via rotary evaporation and the product was isolated by dissolving the solid in a minimal amount of MeOH and titrating with chloroform resulting in the product precipitating out as a white solid which was collected via vacuum filtration and dried. Yield: 110 mg (20%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 13.52 (s, 1H), 11.14 (s, 1H), 9.00 (s, 1H), 8.12 (d, J = 8.1 Hz, 1H), 7.61 (d, J = 8.4 Hz, 1H), 7.42 (t, J = 7.9 Hz, 1H), 7.24 (t, J = 7.5 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d6): δ 160.4, 140.7, 137.0, 126.5, 121.9, 121.7, 121.3, 110.7. ESI-MS(+) calculated for $[C_8H_8N_3O_2]^+$ 178.06, found *m/z* 178.07 $[M+H]^+$.



2b

(a) DMF, CDI, 25 ℃, 1 h, $NH_2OH{\cdot}HCl$, 25 ℃, overnight.

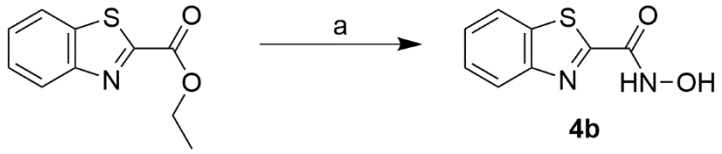
Benzimidazole-2-hydroxamic acid (2b). To a solution of benzimidazole-2-carboxylic acid (500 mg, 1 equiv, 3.1 mmol) dissolved in 10 mL of DMF, CDI (500 mg, 1 equiv, 3.08 mmol) was added to the solution and stirred for 1 h under nitrogen at room temperature. Hydroxylamine hydrochloride (429 mg, 2.0 equiv, 6.17 mmol) was added to the reaction mixture and stirred overnight under nitrogen at room temperature. The reaction solution was dried down to a brown residue and loaded onto silica. The product was purified via column chromatography using a 0-100% Hexanes:EtOAc gradient. The fractions containing product were dried down via rotary evaporation to obtain a solid that was dissolved in a minimal amount of MeOH and titrated with CH_2Cl_2 resulting in a white precipitate that was collected via filtration. Yield: 204 mg (37%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 13.25 (s, 1H), 11.78 (s, 1H), 9.33 (s, 1H), 7.62 (d, J = 44.4 Hz, 2H), 7.29 (d, J = 4.9 Hz, 2H). ^{13}C NMR (126 MHz, DMSO-d6): δ 156.9, 145.0, 143.0, 134.5, 124.4, 122.9, 120.2, 112.8. ESI-MS(+) calculated for $[C_8H_{10}N_3O_2]^+$ 178.06, found m/z 178.11 $[M+H]^+$.



3b

(a) CH_2Cl_2, $(COCl)_2$, DMF (cat.), 25 ℃, 3 h; (b) CH_2Cl_2, $NH_2OH{\cdot}HCl$, TEA, 25 ℃, overnight.

1,2-Benzisothiazole-3-hydroxamic acid (3b). To a solution of 1,2-benzisothiazole-3-carboxylic acid (300 mg, 1 equiv, 1.7 mmol) in 25 mL of CH_2Cl_2, oxalyl chloride (637 mg, 0.440 mL, 3 equiv, 5.0 mmol) was slowly added along with 5 drops of DMF. The solution was stirred for 3 h at room temperature under nitrogen. The reaction mixture was then dried down to a solid via rotary evaporation to provide the crude acid chloride which was moved forward onto the next step. The dried solid was dissolved in 25 mL of CH_2Cl_2 and hydroxylamine hydrochloride (140 mg, 1.2 equiv, 2.0 mmol) and triethylamine (678 mg, 0.933 mL, 4 equiv, 6.7 mmol) were added. The mixture was stirred overnight at room temperature under nitrogen. The reaction mixture was washed with a saturated brine solution and the organic layer was dried over $MgSO_4$. The organic layer was then dried down via rotary evaporation and loaded onto silica. The product was purified via column chromatography using a 0-60% Hexanes:EtOAc gradient. The fractions containing product were dried down via rotary evaporation to obtain a solid. The product was then recrystallized using isopropyl alcohol yielding an off-white solid. Yield: 117 mg (36%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 11.57 (s, 1H), 9.34 (s, 1H), 8.63 (d, J = 8.0 Hz, 1H), 8.30 (d, J = 8.2 Hz, 1H), 7.71 – 7.52 (m, 2H). ^{13}C NMR (126 MHz, DMSO-d6): δ 158.8, 155.9, 152.5, 133.9, 128.3, 126.0, 125.4, 120.7. ESI-MS(+) calculated for $[C_8H_7N_2O_2S]^+$ 195.02, found *m/z* 195.02 $[M+H]^+$.

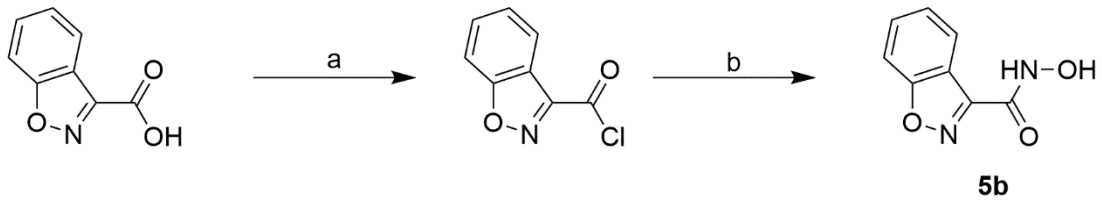


4b

(a) MeOH, KOH, NH_3OH ·HCl, 60 ℃, 24 h, KOH, NH_2OH·HCl 60 ℃, overnight.

Benzothiazole-2-hydroxamic acid (4b). To a solution of hydroxylamine hydrochloride (335 mg, 1 equiv, 4.8 mmol) in MeOH (50 mL), ethyl benzothiazole-2-carboxylate (1.00 g, 1 equiv, 4.8 mmol) and potassium hydroxide (271 mg, 1 equiv, 4.83 mmol) were added. The reaction mixture

was stirred for 24 h at 60 ℃. By TLC the starting material was not consumed, so more KOH (948 mg, 3.5 equiv, 16.9 mmol) and hydroxylamine hydrochloride (336 mg, 1 equiv, 4.83 mmol) were added and the reaction was stirred while being heated to 60 ℃ overnight. The reaction was dried down via rotary evaporation and the residue was dissolved in water and acidified with HCl to pH ~7. The aqueous layer was extracted with EtOAc and then dried over $MgSO_4$. The material was loaded onto silica and purified via column chromatography using a CH_2Cl_2:MeOH gradient of 0-10%. The fractions containing product were dried down via rotary evaporation to obtain an off-white solid. Yield: 190 mg (20%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 12.02 (s, 1H), 9.52 (s, 1H), 8.27 – 8.19 (m, 1H), 8.15 – 8.08 (m, 1H), 7.67 – 7.53 (m, 2H). ^{13}C NMR (126 MHz, DMSO-d6): δ 163.5, 156.9, 152.9, 135.6, 127.1, 126.8, 123.9, 123.0. ESI-MS(+) calculated for $[C_8H_7N_2O_2S]^+$ 195.02, found *m/z* 195.11 $[M+H]^+$.

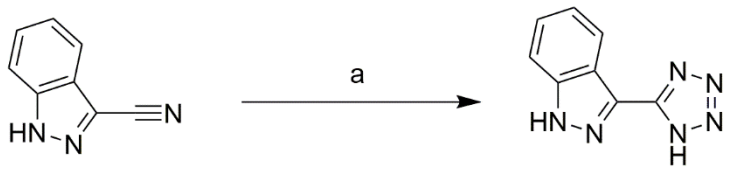


5b

(a) CH_2Cl_2, $SOCl_2$, DMF (cat.), 25 ℃, 3-4 h; (b) CH_2Cl_2, $NH_2OH{\cdot}HCl$, TEA, 25 ℃, overnight.

1,2-Benzisoxazole-3-hydroxamic acid (5b). In a round bottom flask benzisoxazole-3-carboxylic acid (300 mg, 1 equiv, 1.84 mmol) was dissolved in CH_2Cl_2 (10 mL). Thionyl chloride (3.3 g, 2.0 mL, 15 equiv, 28 mmol) was added slowly along with a few drops of DMF, the reaction mixture was stirred at room temperature under a nitrogen atmosphere for 3 to 4 hr. The reaction mixture was dried down to a tan residue and redissolved in CH_2Cl_2 (10 mL). Hydroxylamine hydrochloride (256 mg, 2 equiv, 3.68 mmol) and triethylamine (744 mg, 1.0 mL, 4 equiv, 7.36 mmol) were added and the reaction was stirred at room temperature overnight under a nitrogen atmosphere. The

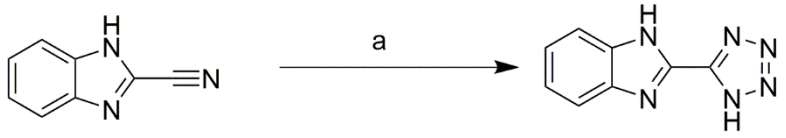
reaction mixture was dried down via rotary evaporation and loaded onto silica. The product was isolated via column chromatography using a 0-30% Hexanes:EtOAc gradient. Fractions containing product were dried down via rotary evaporation to obtain an off-white solid. Yield: 100 mg (31%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.84 (s, 1H), 9.61 (s, 1H), 8.04 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 8.5 Hz, 1H), 7.74 (m, 1H), 7.50 (t, J = 7.5 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d6): δ 163.2, 156.5, 151.8, 131.6, 125.5, 123.4, 120.0, 110.5. ESI-MS(+) calculated for $[C_8H_7N_2O_3]^+$ 179.05, found *m/z* 179.10 $[M+H]^+$.



1c

(a) DMF, NaN_3, NH_4Cl, 110 °C, overnight.

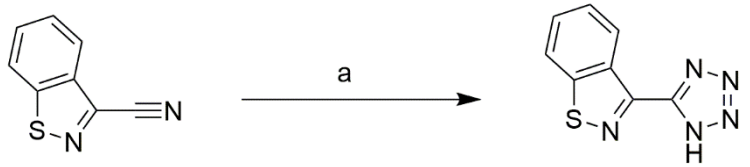
Indazole-3-tetrazole (1c). To a solution of indazole-3-carbonitrile (400 mg, 1 equiv, 2.8 mmol) dissolved in 10 mL of DMF, sodium azide (236 mg, 1.3 equiv, 3.6 mmol) and ammonium chloride (194 mg, 1.3 equiv, 3.6 mmol) were added. The solution was stirred at 110 °C overnight under nitrogen. The mixture was concentrated down via rotary evaporation almost to dryness. Water was added to the residue and the solution was then acidified, resulting in the product precipitating as an off-white solid that was collected via filtration. Yield: 400 mg (77%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 13.97 (s, 1H), 8.29 (d, J = 8.3 Hz, 1H), 7.72 (d, J = 8.5 Hz, 1H), 7.57 – 7.48 (m, 1H), 7.40 – 7.31 (m, J = 7.9, 6.9, 0.9 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d6): δ 150.8, 141.5, 130.9, 127.7, 123.0, 121.2, 121.0, 111.4. ESI-MS(+) calculated for $[C_8H_7N_6]^+$ 187.07, found m/z 187.08$[M+H]^+$.



2c

(a) DMF, NaN_3, NH_4Cl, 110 °C, overnight.

Benzimidazole-2-tetrazole (2c). To a solution of benzimidazole-2-carbonitrile (200 mg, 1 equiv, 1.4 mmol) dissolved in 10 mL of DMF, sodium azide (118 mg, 1.3 equiv, 1.8 mmol) and ammonium chloride (97 mg, 1.3 equiv, 1.8 mmol) were added. The solution was stirred at 110 °C overnight under nitrogen. The mixture was concentrated down via rotary evaporation almost to dryness, then water was added (20 mL) and a few drops of 1 M NaOH to dissolve residual solids. The solution was then acidified, resulting in the product precipitating as an off-white solid that was collected via filtration. Yield: 230 mg (88%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.72 (dd, J = 6.1, 3.2 Hz, 2H), 7.43 (dd, J = 6.1, 3.2 Hz, 2H). ^{13}C NMR (126 MHz, DMSO-d6): δ 149.2, 140.4, 135.6, 124.6, 115.1. ESI-MS(+) calculated for $[C_8H_7N_6]^+$ 187.07, found m/z 187.11$[M+H]^+$.

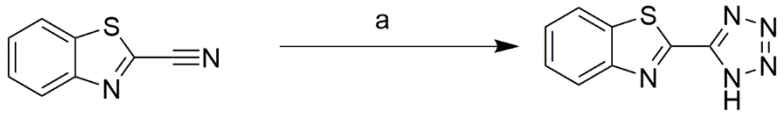


3c

(a) DMF, NaN_3, NH_4Cl, 110 °C, overnight.

1,2-Benzisothiazole-3-tetrazole (3c). To a 50 mL round bottom flask 1,2-benzisothiazole-3-carbonitrile (200 mg, 1 equiv, 1.25 mmol), sodium azide (106 mg, 1.3 equiv, 1.62 mmol), ammonia hydrochloride (86.8 mg, 1.3 equiv, 1.62 mmol), and DMF (10 mL) were added. The solution was

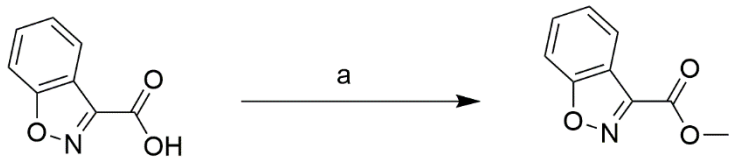
heated to 110 ºC overnight, under nitrogen while being stirred. The mixture was then concentrated down via rotary evaporation to almost dryness, then water was added (20 mL) and a few drops of 1 M NaOH to dissolve any solids. The solution was then acidified, resulting in the product precipitating as an off-white powder that was collected by filtration. Yield: 250 mg (99%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.97 (d, J = 7.8 Hz, 1H), 8.40 (d, J = 7.7 Hz, 1H), 7.83 – 7.66 (m, 2H). ^{13}C NMR (126 MHz, DMSO-d6): δ 153.1, 151.3, 148.6, 132.9, 128.9, 126.7, 125.1, 121.1. ESI-MS(+) calculated for $[C_8H_6N_5S]^+$ 204.03, found m/z 204.17$[M+H]^+$.



4c

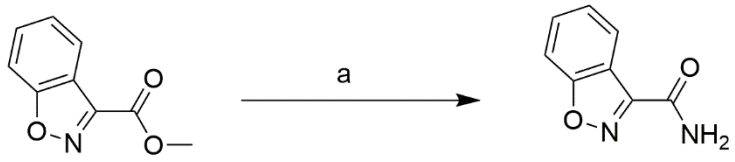
(a) DMF, NaN_3, NH_4Cl, 110 ℃, overnight.

Benzothiazole-2-tetrazole (4c). To a solution of benzothiazole-2-carbonitrile (200 mg, 1 equiv, 1.3 mmol) dissolved in 10 mL of DMF, sodium azide (106 mg, 1.3 equiv, 1.6 mmol) and ammonium chloride (87 mg, 1.3 equiv, 1.6 mmol) were added. The solution was stirred at 110 ℃ overnight under nitrogen. The mixture was concentrated down via rotary evaporation almost to dryness, then water was added (20 mL) and a few drops of 1 M NaOH to dissolve residual solids. The solution was then acidified, resulting in the product precipitating as an off-white solid that was collected via filtration. Yield: 246 mg (97%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.35 – 8.27 (m, 1H), 8.25 – 8.18 (m, 1H), 7.72 – 7.58 (m, 2H). ^{13}C NMR (126 MHz, DMSO-d6): δ 152.8, 152.0, 146.7, 134.8, 127.4, 127.1, 123.7, 123.1. ESI-MS(+) calculated for $[C_8H_6N_5S]^+$ 204.03, found *m/z* 204.02 $[M+H]^+$.



(a) MeOH, H_2SO_4, NH_4Cl, reflux, overnight.

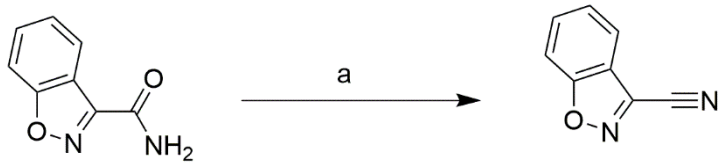
Methyl 1,2-benzisoxazole-3-carboxylate. In a round bottom flask 1,2-benzisoxazole-3-carboxylic acid (500 mg, 1 equiv, 3.07 mmol) was dissolved in MeOH (100 mL) and sulfuric acid (15.0 mg, 0.008 mL, 0.05 equiv, 0.15 mmol) was added. The reaction mixture was heated to reflux while being stirred overnight under nitrogen. The reaction mixture was dried down to a white solid via rotary evaporation and then dissolved in EtOAc and water. The organic layer was separated, and the aqueous layer was washed with EtOAc. All the organic layers were combined and washed with water, then brine, and then dried with anhydrous $MgSO_4$ and filtered. The filtrate was dried down via rotary evaporation to obtain the product as an off-white solid. Yield: 480 mg (88%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.12 – 8.08 (m, 1H), 7.94 – 7.90 (m, H), 7.79 – 7.74 (m, 1H), 7.58 – 7.53 (m, 1H), 4.01 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d6): δ 164.1, 160.3, 150.7, 131.7, 126.1, 123.4, 119.5, 110.8, 53.6. ESI-MS(+) calculated for $[C_9H_8NO_3]^+$ 178.05, found *m/z* 178.09 $[M+H]^+$.



(a) NH_3, MeOH, 25 °C, overnight.

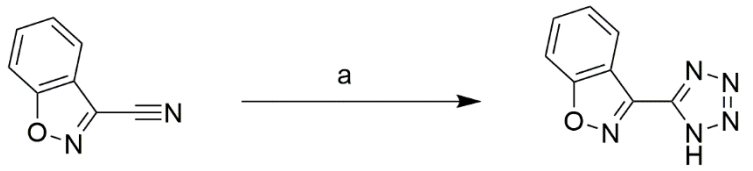
1,2-Benzisoxazole-3-carboxamide. In a round bottom flask methyl 1,2-benzisoxazole-3-carboxylate (100 mg, 1 equiv, 0.56 mmol) was dissolved in a 7 M ammonia (12 g, 15 mL, 200 equiv, 0.1 mol) solution in MeOH. The mixture was stirred overnight in a capped vessel at room

temperature. The reaction mixture was then dried down via rotary evaporation to obtain the product as a white solid in quantitative yield. Yield: 92 mg (100%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.43 (s, 1H), 8.12 – 8.08 (m, 1H), 8.07 (s, 1H), 7.87 – 7.83 (m, 1H), 7.74 – 7.70 (m, 1H), 7.51 – 7.47 (m, 1H). ^{13}C NMR (126 MHz, DMSO-d6): δ 163.6, 160.9, 152.7, 131.3, 125.5, 123.8, 120.0, 110.4. ESI-MS(+) calculated for $[C_8H_7N_2O_2]^+$ 163.05, found *m/z* 163.11 $[M+H]^+$.



(a) $POCl_3$, ACN, 65 ℃, overnight.

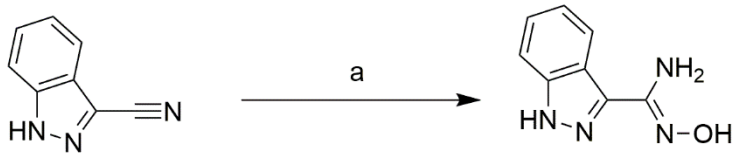
1,2-Benzisoxazole-3-carbonitrile. In a round bottom flask 1,2-benzisoxazole-3-carboxamide (100 mg, 1 equiv, 0.56 mmol) was dissolved in ACN (5 mL) and phosphoryl trichloride (3.3 g, 2.0 mL, 35 equiv, 21 mmol) was added slowly. The reaction was then stirred under an argon atmosphere at while being heated to 65 ºC overnight. The reaction mixture was then dried down via rotary evaporation to a residue. The residue was then dissolved in EtOAc and extracted with saturated sodium bicarbonate. The organic layer was collected, and the aqueous layer was extracted again with EtOAc. All organic layers were combined and washed with water, then brine, and then dried with $MgSO_4$. The organic layers were dried down to yield the product as a white-yellow solid. Yield: 72 mg (81%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.11 – 8.08 (m, 1H), 8.06 – 8.04 (m, 1H), 7.89 – 7.85 (m, 1H), 7.65 – 7.61 (m, 1H). ^{13}C NMR (126 MHz, DMSO-d6): δ 163.7, 136.3, 133.0, 126.9, 121.9, 120.3, 111.2, 110.3. Compound was not detected by MS but moved forward anyway.



5c

(a) DMF, NaN_3, NH_4Cl, 110 °C, overnight.

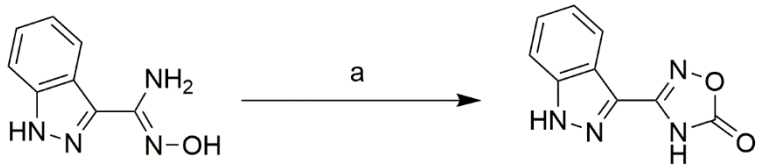
1,2-Benzisoxazole-3-tetrazole (5c). To a 50 mL round bottom flask 1,2-benzisoxazole-3-carbonitrile (65 mg, 1 equiv, 0.45 mmol), sodium azide (38 mg, 1.3 equiv, 0.59 mmol), ammonia hydrochloride (31 mg, 1.3 equiv, 0.59 mmol), and DMF (6 mL) were added. The solution was heated to 110 ºC overnight, under nitrogen while being stirred. The mixture was then concentrated down via rotary evaporation to almost dryness, then water was added (20 mL) and a few drops of 1 M NaOH to dissolve any solids. The solution was then acidified, resulting in the product precipitating as an off-white powder that was collected by filtration. Yield: 26 mg (31%). ^{1}H NMR (500 MHz, DMSO-*d*$_6$): δ 8.36 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.5 Hz, 1H), 7.81 (t, J = 7.7 Hz, 1H), 7.59 (t, J = 7.5 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d6): δ 163.7, 149.2, 147.0, 132.1, 125.9, 123.5, 119.4, 110.7. ESI-MS(+) calculated for $[C_8H_4N_5O]^+$ 186.04, found *m/z* 186.15 $[M-H]^-$.



(a) EtOH, K_2CO_3, $CH_3ONH_3 \cdot HCl$, 80 °C, overnight.

***N*'-hydroxy indazole-3-amidine.** To a solution of indazole-3-carbonitrile (300 mg, 1 equiv, 2.1 mmol) dissolved in 15 mL of EtOH, potassium carbonate (319 mg, 1.1 equiv, 2.3 mmol) and

hydroxylamine hydrochloride (291 mg, 2 equiv, 4.2 mmol) were added. The mixture was stirred and heated to reflux overnight under nitrogen. The resulting mixture was filtered and washed with MeOH. The filtrate was collected and dried down to a solid via rotary evaporation. The solid was dissolved in basic water and extracted with CH_2Cl_2 twice. The aqueous layer was acidified to weakly acidic (pH ~6) and extracted with EtOAc twice. The organic layers were combined, dried using $MgSO_4$, and dried down via rotary evaporation to yield the product as a tan solid. Yield: 320 mg (87%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 13.20 (s, 1H), 9.77 (s, 1H), 8.10 (d, J = 8.2 Hz, 1H), 7.54 (d, J = 8.4 Hz, 1H), 7.41 – 7.27 (m, 1H), 7.21 – 7.05 (m, 1H), 5.67 (s, 2H). ^{13}C NMR (126 MHz, DMSO-d6): δ 148.0, 141.2, 137.6, 126.4, 122.5, 121.0, 119.6, 110.3. ESI-MS(+) calculated for $[C_8H_9N_4O]^+$ 177.08, found *m/z* 177.15 $[M+H]^+$.

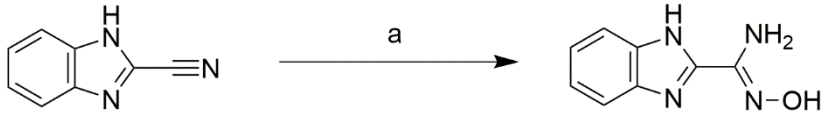


1d

(a) Pyridine, ethyl chloroformate, 115 ℃, 8 h.

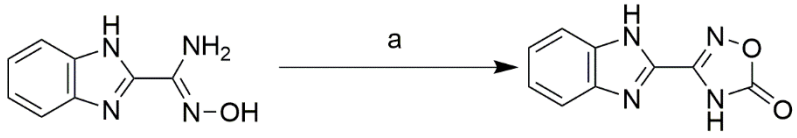
Indazole-3-oxadiazolone (1d). To a solution of *N'*-hydroxy indazole-3-amidine (150 mg, 1 equiv, 0.9 mmol) dissolved in 5 mL of pyridine, ethyl chloroformate (92 mg, 0.082 mL, 1 equiv, 0.9 mmol) was added. The reaction mixture was stirred and heated to reflux for 8 h. The reaction mixture was dried down to a brown oil via rotary evaporation. The product was recrystallized from a water:isopropanol mixture, yielding the product as an off-white solid. Yield: 87 mg (51%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 14.06 (s, 1H), 13.17 (s, 1H), 8.01 (d, J = 8.2 Hz, 1H), 7.72 (d, J = 8.5 Hz, 1H), 7.56 – 7.48 (m, 1H), 7.39 – 7.30 (m, 1H). ^{13}C NMR (126 MHz, DMSO-d6): δ

159.5, 154.1, 141.1, 129.4, 127.5, 122.9, 120.6, 119.8, 111.2. ESI-MS(-) calculated for $[C_9H_5N_4O_2]^-$ 201.04, found m/z 201.12 $[M-H]^-$.



(a) EtOH, K_2CO_3, $CH_3ONH_3 \cdot HCl$, 80 ℃, overnight.

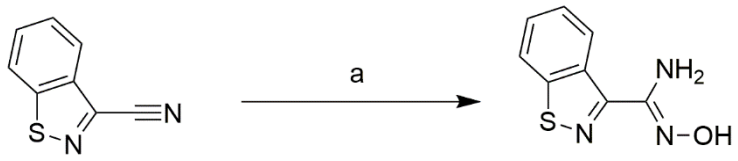
***N'*-hydroxy benzimidazole-2-amidine.** In a round bottom flask benzimidazole-2-carbonitrile (500 mg, 1 equiv, 3.49 mmol) was dissolved in 50 mL of EtOH. Hydroxylamine hydrochloride (485 mg, 2 equiv, 6.99 mmol) and potassium carbonate (483 mg, 1 equiv, 3.49 mmol) were added to the solution and stirred while the mixture was heated to reflux (90 ºC) overnight. The reaction mixture was dried down via rotary evaporation and then the resulting solid was dissolved in water and EtOAc. The aqueous layer was adjusted to neutral pH and the organic layer was dried with $MgSO_4$. The organic layer was dried down via rotary evaporation and loaded onto silica. The product was purified via column chromatography using a 0-70% Hexanes:EtOAc gradient. The fractions containing product were dried down via rotary evaporation and the product was then recrystallized from EtOAc, yielding a white solid that was collected via filtration. Yield: 350 mg (57%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 12.54 (s, 1H), 10.05 (s, 1H), 7.64 (d, J = 7.5 Hz, 1H), 7.46 (d, J = 7.3 Hz, 1H), 7.27 – 7.14 (m, 2H), 5.89 (s, 2H). ^{13}C NMR (126 MHz, DMSO-d6): δ 146.2, 145.0, 134.9, 122.8, 123.4, 122.1, 119.3, 112.2. ESI-MS(+) calculated for $[C_8H_9N_4O]^+$ 177.08, found m/z 177.18 $[M+H]^+$.



2d

(a) Pyridine, ethyl chloroformate, 115 ℃, 8 h.

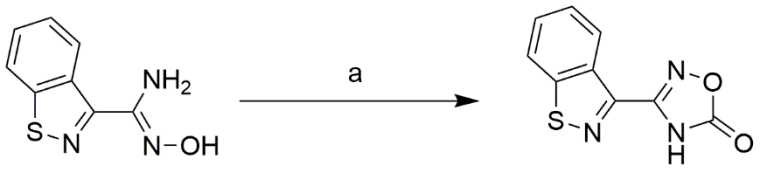
Benzimidazole-2-oxadiazolone (2d). To a solution of *N'*-hydroxy benzimidazole-2-amidine (200 mg, 1 equiv, 1.14 mmol) dissolved in anhydrous pyridine (25 mL), ethyl chloroformate (148 mg, 0.131 mL, 1.2 equiv, 1.36 mmol) was added. The reaction was then heated to reflux and stirred overnight. The reaction mixture was dried down via rotary evaporation to a residue. The residue was dissolved in 1 M KOH and then the solution was acidified using HCl, resulting in a brown precipitate forming that was collected via filtration. Yield: 70 mg (31%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 13.60 (s, 1H), 7.68 (s, 2H), 7.37 – 7.33 (m, 2H). ESI-MS(+) calculated for $[C_9H_7N_4O_2]^+$ 203.06, found m/z 203.19 $[M+H]^+$.



(a) EtOH, K_2CO_3, CH_3ONH_3·HCl, 80 ℃, overnight.

***N'*-hydroxy 1,2-benzisothiazole-3-amidine.** In a round bottom flask 1,2-benzisothiazole-3-carbonitrile (500 mg, 1 equiv, 3.12 mmol) was dissolved in 50 mL of EtOH. Hydroxylamine hydrochloride (434 mg, 2 equiv, 6.24 mmol) and potassium carbonate (431 mg, 1 equiv, 3.12 mmol) were added to the solution and stirred while the mixture was heated to reflux (90 ºC) overnight. The reaction mixture was dried down via rotary evaporation and then the resulting solid was dissolved in water and EtOAc. The aqueous layer was adjusted to neutral pH and the organic layer was dried with $MgSO_4$. The organic layer was dried down and the product was obtained as a white solid. Yield: 450 mg (75%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.27 (s, 1H), 8.80 (d, J = 8.2 Hz, 1H), 8.22 (d, J = 8.2 Hz, 1H), 7.64 – 7.58 (m, 1H), 5.96 (s, 2H). ^{13}C NMR (126 MHz,

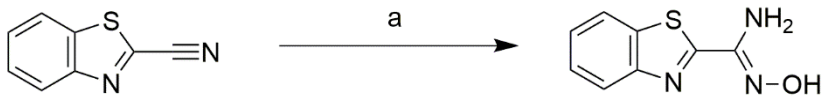
DMSO-d6): δ 155.9, 152.9, 149.4, 132.7, 128.4, 127.2, 126.0, 120.9. ESI-MS(+) calculated for $[C_8H_8N_3OS]^+$ 194.04, found m/z 194.13 $[M+H]^+$.



3d

(a) Pyridine, ethyl chloroformate, 115 °C, overnight.

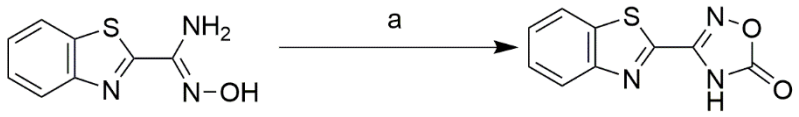
1,2-benzisothiazole-3-oxadiazolone (3d). To a solution of *N′*-hydroxy 1,2-benzisothiazole-3-amidine (230 mg, 1 equiv, 1.19 mmol) dissolved in anhydrous pyridine (25 mL), ethyl chloroformate (155 mg, 0.137 mL, 1.2 equiv, 1.43 mmol) was added. The reaction was then heated to reflux and stirred overnight. The reaction mixture was dried down via rotary evaporation to a residue. The residue was dissolved in 1 M KOH and then the solution was acidified using HCl, resulting in a brown precipitate forming that was collected via filtration. Yield: 212 mg (81%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 13.50 (s, 1H), 8.59 (d, J = 8.2 Hz, 1H), 8.39 (d, J = 8.3 Hz, 1H), 7.77 – 7.71 (m, 1H), 7.69 – 7.64 (m, 1H). ^{13}C NMR (126 MHz, DMSO-d6): δ 159.1, 154.5, 153.0, 147.2, 132.0, 128.9, 126.8, 124.6, 121.3. ESI-MS(+) calculated for $[C_9H_6N_3O_2S]^+$ 220.02, found m/z 220.11 $[M+H]^+$.



(a) EtOH, K_2CO_3, CH_3ONH_3·HCl, 80 °C, overnight.

***N′*-hydroxy benzothiazole-2-amidine.** In a round bottom flask benzothiazole-2-carbonitrile (500 mg, 1 equiv, 3.12 mmol) was dissolved in 50 mL of EtOH. Hydroxylamine hydrochloride (434

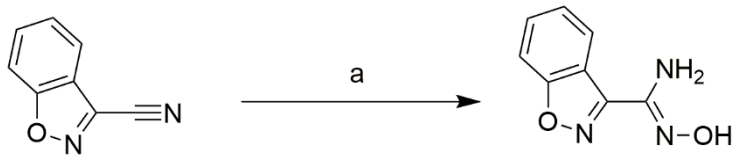
mg, 2 equiv, 6.24 mmol) and potassium carbonate (431 mg, 1 equiv, 3.12 mmol) were added to the solution and stirred while the mixture was heated to reflux (90 ºC) overnight. The reaction mixture was dried down via rotary evaporation and then the resulting solid was dissolved in water and EtOAc. The aqueous layer was adjusted to neutral pH and the organic layer was dried with $MgSO_4$. The organic layer was dried down via rotary evaporation and the product was obtained as a white solid. Yield: 580 mg (96%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.48 (s, 1H), 8.08 (d, J = 7.8 Hz, 1H), 8.00 (d, J = 8.1 Hz, 1H), 7.49 (dt, J = 15.0, 6.9 Hz, 2H), 6.11 (s, 2H). ^{13}C NMR (126 MHz, DMSO-d6): δ 162.3, 152.3, 147.3, 134.2, 126.4, 126.1, 122.9, 122.3. ESI-MS(+) calculated for $[C_8H_8N_3OS]^+$ 194.04, found m/z 194.32 $[M+H]^+$.



4d

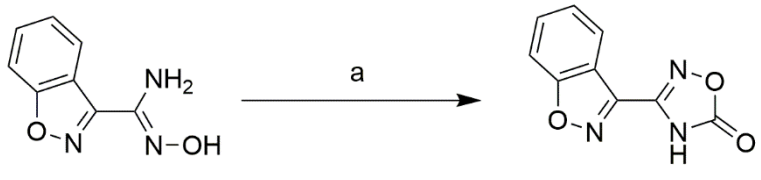
(a) Pyridine, ethyl chloroformate, 115 ºC, 8 h.

Benzothiazole-2-oxadiazolone (4d). To a solution of *N*′-hydroxy benzothiazole-2-amidine (200 mg, 1 equiv, 1.04 mmol) dissolved in anhydrous pyridine (25 mL), ethyl chloroformate (225 mg, 0.199 mL, 2.0 equiv, 2.07 mmol) was added. The reaction was then heated to reflux and stirred overnight. The reaction mixture was dried down via rotary evaporation to a residue. The residue was dissolved in 1 M KOH and then the solution was acidified using HCl, resulting in a brown precipitate forming that was collected via filtration. Yield: 215 mg (95%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 13.88 (s, 1H), 8.32 – 8.28 (m, 1H), 8.21 – 8.18 (m, 1H), 7.70 – 7.62 (m, 2H). ^{13}C NMR (126 MHz, DMSO-d6): δ 159.4, 154.5, 152.1, 151.6, 134.4, 127.8, 127.6, 123.9, 123.2. ESI-MS(+) calculated for $[C_9H_6N_3O_2S]^+$ 220.02, found m/z 220.19 $[M+H]^+$.



(a) EtOH, K_2CO_3, $CH_3ONH_3 \cdot HCl$, 80 ℃, overnight.

***N'*-hydroxy 1,2-benzisoxazole-3-amidine.** In a round bottom flask 1,2-benzisothiazole-3-carbonitrile (200 mg, 1 equiv, 1.25 mmol) was dissolved in 50 mL of EtOH. Hydroxylamine hydrochloride (174 mg, 2 equiv, 2.50 mmol) and potassium carbonate (173 mg, 1 equiv, 1.25 mmol) were added to the solution and stirred while the mixture was heated to reflux (90 ºC) overnight. The reaction mixture was dried down via rotary evaporation and then the resulting solid was dissolved in water and EtOAc. The organic layer was collected and the aqueous layer was washed with EtOAc then all the organic layers were collected and dried with $MgSO_4$. The combined organic layers were dried down via rotary evaporation and the product was loaded onto silica and purified via column chromatography utilizing a 0-40% Hexanes:EtOAc gradient. Fractions containing the product were dried down via rotary evaporation and the product was obtained as a white solid. Yield: 151 mg (63%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.55 (s, 1H), 8.12 – 8.08 (m, 1H), 7.79 (d, J = 8.5 Hz, 1H), 7.67 (t, J = 7.8 Hz, 1H), 7.43 (t, J = 7.5 Hz, 1H), 6.08 (s, 2H).z. ^{13}C NMR (126 MHz, DMSO-d6): δ 163.2, 151.8, 145.3, 131.0, 125.0, 124.8, 119.1, 110.3. ESI-MS(+) calculated for $[C_8H_8N_3O_2]^+$ 178.06, found m/z 178.20 $[M+H]^+$.



5d

(a) Pyridine, ethyl chloroformate, 115 ℃, overnight.

1,2-benzisoxazole-3-oxadiazolone (5d). To a solution of *N*′-hydroxy 1,2-benzisoxazole-3-amidine (125 mg, 1 equiv, 0.65 mmol) dissolved in anhydrous pyridine (25 mL), ethyl chloroformate (140 mg, 0.124 mL, 2.0 equiv, 1.29 mmol) was added. The reaction was then heated to reflux and stirred overnight. The reaction mixture was dried down via rotary evaporation to a residue. The residue was dissolved in 1 M KOH and then the solution was extracted with EtOAc. The aqueous layer was then acidified using HCl, resulting in a white precipitate forming that was collected via filtration. Yield: 40 mg (28%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.12 – 8.07 (m, 1H), 8.00 – 7.94 (m, 1H), 7.85 – 7.79 (m, 1H), 7.61 – 7.56 (m, 1H). ^{13}C NMR (126 MHz, DMSO-d6): δ 163.4, 159.34, 151.2, 145.4, 132.0, 126.0, 122.8, 117.7, 110.5. ESI-MS(-) calculated for $[C_9H_4N_3O_3]^-$ 202.03, found m/z 202.22 $[M-H]^-$.

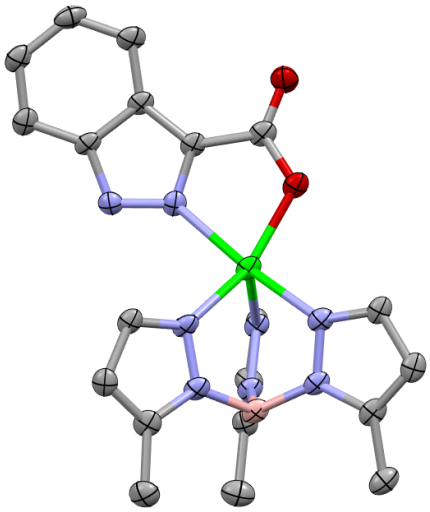


Figure S1. Structure of [(Tp^{Ph,Me})Zn(**1**)] rendered as an ORTEP with atoms at 50% thermal probability ellipsoids. Hydrogen atoms and Tp^{Ph,Me} phenyl groups have been removed for clarity. The asymmetric unit consists of the complex, a molecule of MeOH (not shown), and half a molecule of benzene (not shown). Color scheme: carbon = gray, oxygen = red, nitrogen = blue, boron = pink, and zinc = green.

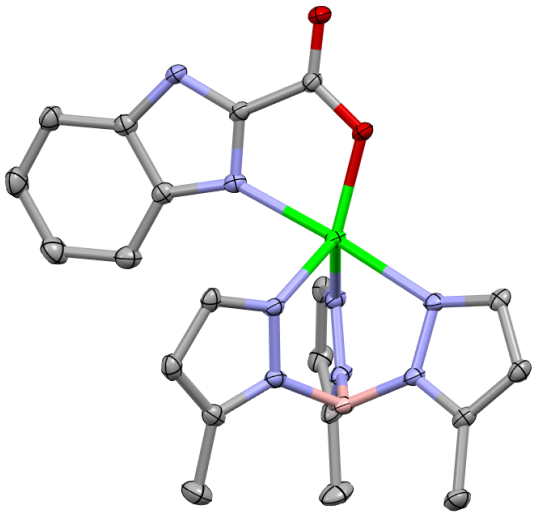


Figure S2. Structure of [(Tp^{Ph,Me})Zn(**2**)] rendered as an ORTEP with atoms at 50% thermal probability ellipsoids. Hydrogen atoms and Tp^{Ph,Me} phenyl groups have been removed for clarity. The asymmetric unit consists of the complex and two and a half molecules of benzene (not shown). Color scheme: carbon = gray, oxygen = red, nitrogen = blue, boron = pink, and zinc = green.

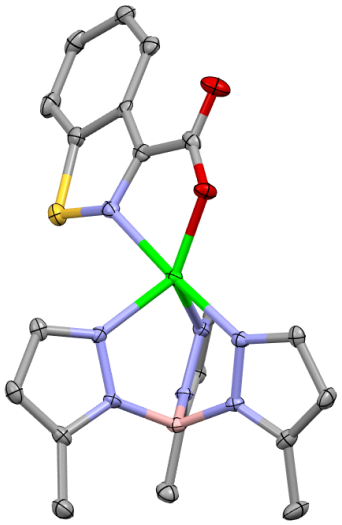


Figure S3. Structure of [(Tp^{Ph,Me})Zn(**3**)] rendered as an ORTEP with atoms at 50% thermal probability ellipsoids. Hydrogen atoms and Tp^{Ph,Me} phenyl groups have been removed for clarity. The asymmetric unit consists of two complexes (one not shown). Color scheme: carbon = gray, sulfur = yellow, oxygen = red, nitrogen = blue, boron = pink, and zinc = green.

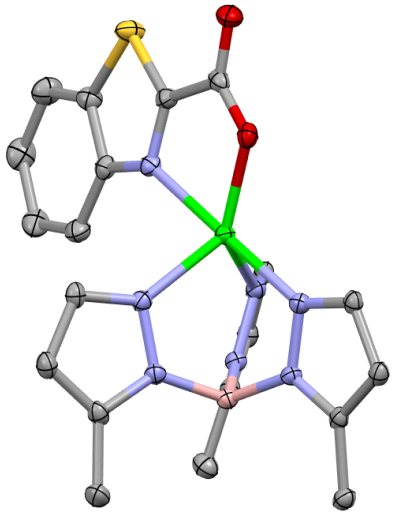


Figure S4. Structure of [(Tp^{Ph,Me})Zn(**4**)] rendered as an ORTEP with atoms at 50% thermal probability ellipsoids. Hydrogen atoms and Tp^{Ph,Me} phenyl groups have been removed for clarity. The asymmetric unit consists only of the complex. Color scheme: carbon = gray, sulfur = yellow, oxygen = red, nitrogen = blue, boron = pink, and zinc = green.

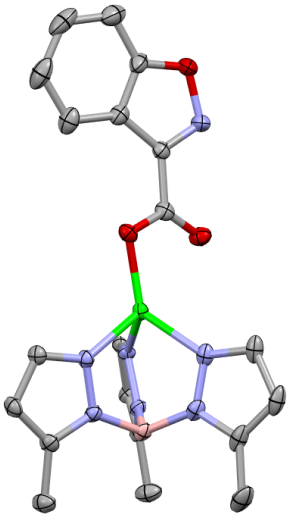


Figure S5. Structure of [(Tp^{Ph,Me})Zn(**5**)] rendered as an ORTEP with atoms at 50% thermal probability ellipsoids. Hydrogen atoms and Tp^{Ph,Me} phenyl groups have been removed for clarity. The asymmetric unit consists of the complex and mixed occupancy solvent (benzene/pentane) molecule (not shown). Color scheme: carbon = gray, oxygen = red, nitrogen = blue, boron = pink, and zinc = green.

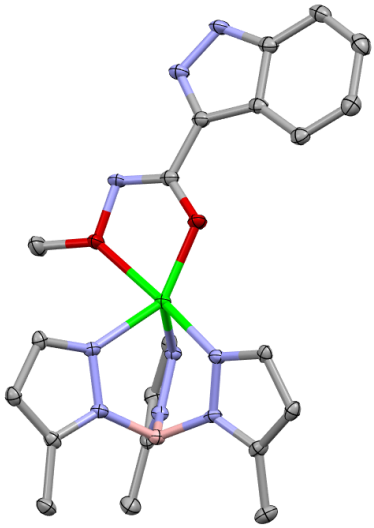


Figure S6. Structure of [(Tp^{Ph,Me})Zn(**1a**)] rendered as an ORTEP with atoms at 50% thermal probability ellipsoids. Hydrogen atoms and Tp^{Ph,Me} phenyl groups have been removed for clarity. The asymmetric unit consists of the complex and a molecule of MeOH (not shown). Color scheme: carbon = gray, oxygen = red, nitrogen = blue, boron = pink, and zinc = green.

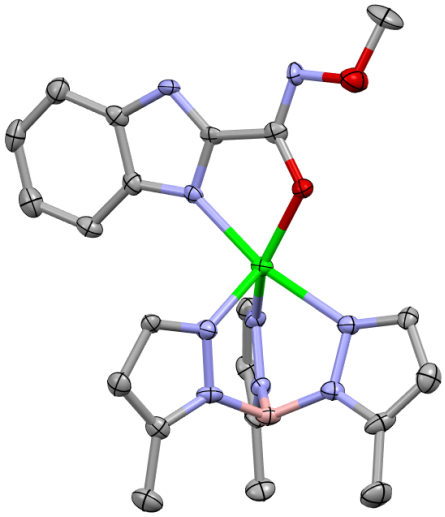


Figure S7. Structure of [(Tp^{Ph,Me})Zn(**2a**)] rendered as an ORTEP with atoms at 50% thermal probability ellipsoids. Hydrogen atoms and Tp^{Ph,Me} phenyl groups have been removed for clarity. The asymmetric unit consists of two complexes (one not shown) and three molecules of benzene (not shown). Color scheme: carbon = gray, oxygen = red, nitrogen = blue, boron = pink, and zinc = green.

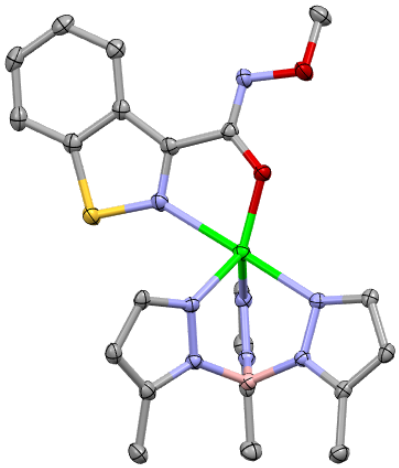


Figure S8. Structure of [(Tp^{Ph,Me})Zn(**3a**)] rendered as an ORTEP with atoms at 50% thermal probability ellipsoids. Hydrogen atoms and Tp^{Ph,Me} phenyl groups have been removed for clarity. The asymmetric unit consists of the complex and a molecule of benzene (not shown). Color scheme: carbon = gray, sulfur = yellow, oxygen = red, nitrogen = blue, boron = pink, and zinc = green.

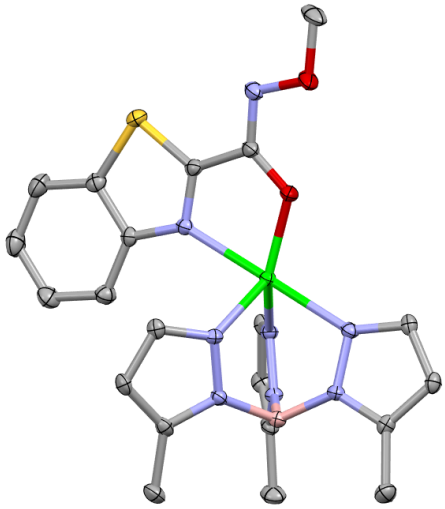


Figure S9. Structure of [(Tp^{Ph,Me})Zn(**4a**)] rendered as an ORTEP with atoms at 50% thermal probability ellipsoids. Hydrogen atoms and Tp^{Ph,Me} phenyl groups have been removed for clarity. The asymmetric unit consists of the complex and a molecule of benzene (not shown). Color scheme: carbon = gray, sulfur = yellow, oxygen = red, nitrogen = blue, boron = pink, and zinc = green.

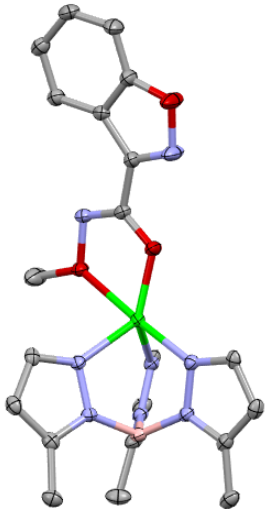


Figure S10. Structure of [(Tp^{Ph,Me})Zn(**5a**)] rendered as an ORTEP with atoms at 50% thermal probability ellipsoids. Hydrogen atoms and Tp^{Ph,Me} phenyl groups have been removed for clarity. The asymmetric unit consists of the complex and a molecule of benzene (not shown). Color scheme: carbon = gray, oxygen = red, nitrogen = blue, boron = pink, and zinc = green.

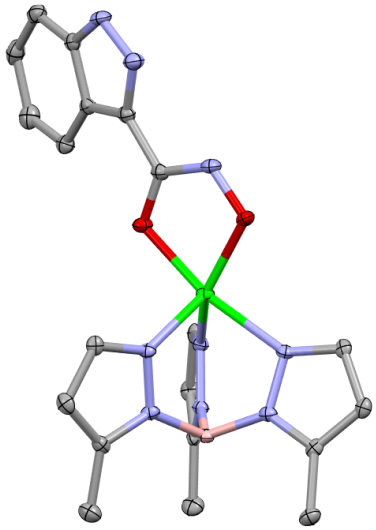


Figure S11. Structure of [(Tp^{Ph,Me})Zn(**1b**)] rendered as an ORTEP with atoms at 50% thermal probability ellipsoids. Hydrogen atoms and Tp^{Ph,Me} phenyl groups have been removed for clarity. The asymmetric unit consists of the complex and a molecule of MeOH (not shown). Color scheme: carbon = gray, oxygen = red, nitrogen = blue, boron = pink, and zinc = green.

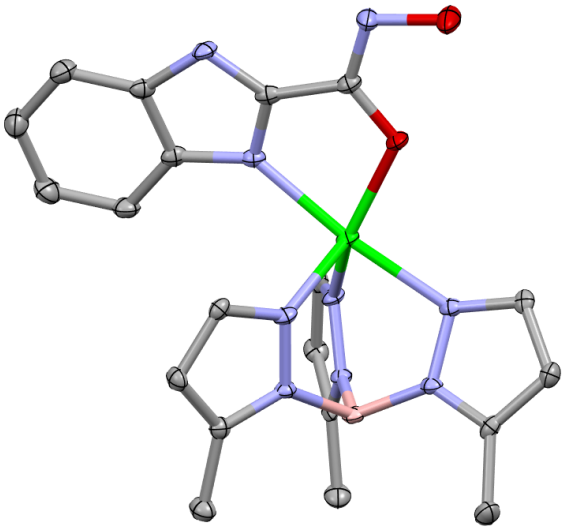


Figure S12. Structure of [(Tp^{Ph,Me})Zn(**2b**)] rendered as an ORTEP with atoms at 50% thermal probability ellipsoids. Hydrogen atoms and Tp^{Ph,Me} phenyl groups have been removed for clarity. The asymmetric unit consists of the complex and two molecules of benzene (not shown). Color scheme: carbon = gray, oxygen = red, nitrogen = blue, boron = pink, and zinc = green.

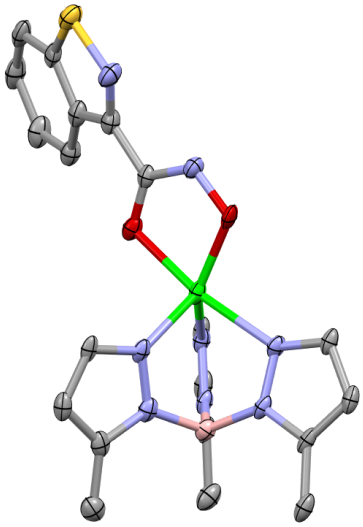


Figure S13. Structure of [(Tp^{Ph,Me})Zn(**3b**)] rendered as an ORTEP with atoms at 50% thermal probability ellipsoids. Hydrogen atoms and Tp^{Ph,Me} phenyl groups have been removed for clarity. The asymmetric unit consists of the complexes and a molecule of methanol (not shown). Color scheme: carbon = gray, sulfur = yellow, oxygen = red, nitrogen = blue, boron = pink, and zinc = green.

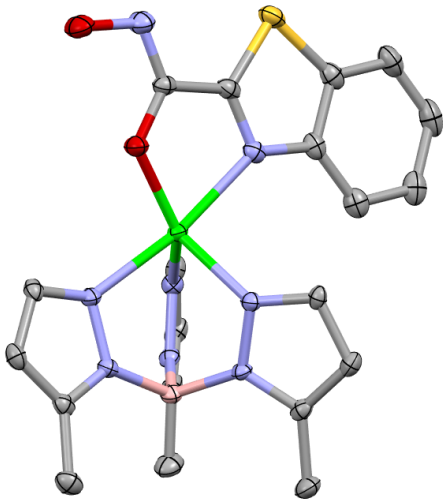


Figure S14. Structure of [(Tp^{Ph,Me})Zn(**4b**)] rendered as an ORTEP with atoms at 50% thermal probability ellipsoids. Hydrogen atoms and Tp^{Ph,Me} phenyl groups have been removed for clarity. The asymmetric unit consists of two complexes (one not shown) and two molecules of benzene (not shown). Color scheme: carbon = gray, sulfur = yellow, oxygen = red, nitrogen = blue, boron = pink, and zinc = green.

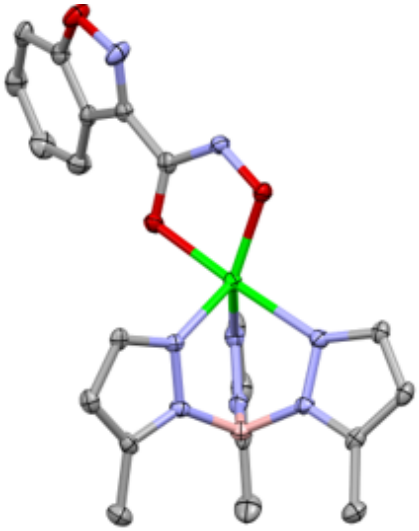


Figure S15. Structure of [(Tp^{Ph,Me})Zn(**5b**)] rendered as an ORTEP with atoms at 50% thermal probability ellipsoids. Hydrogen atoms and Tp^{Ph,Me} phenyl groups have been removed for clarity. The asymmetric unit consists of the complex and a molecule of water (not shown). Color scheme: carbon = gray, oxygen = red, nitrogen = blue, boron = pink, and zinc = green.

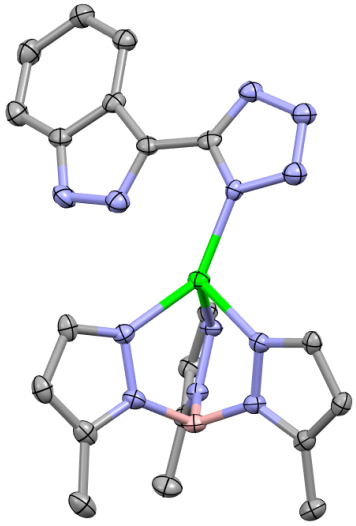


Figure S16. Structure of [(Tp^{Ph,Me})Zn(**1c**)] rendered as an ORTEP with atoms at 50% thermal probability ellipsoids. Hydrogen atoms and Tp^{Ph,Me} phenyl groups have been removed for clarity. The asymmetric unit consists of the complex and a molecule of water (not shown). Color scheme: carbon = gray, nitrogen = blue, boron = pink, and zinc = green.

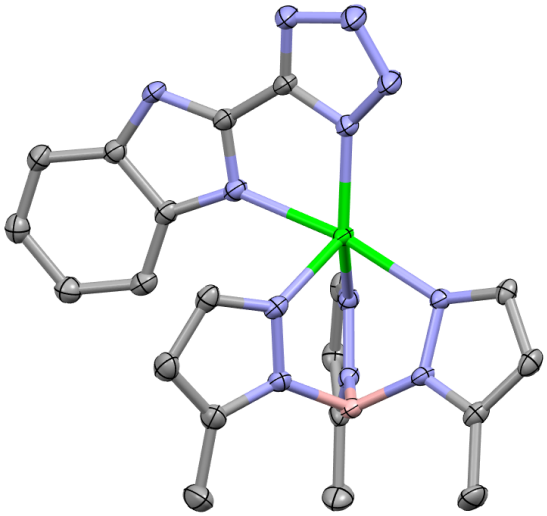


Figure S17. Structure of [(Tp^{Ph,Me})Zn(**2c**)] rendered as an ORTEP with atoms at 50% thermal probability ellipsoids. Hydrogen atoms and Tp^{Ph,Me} phenyl groups have been removed for clarity. The asymmetric unit consists of two complexes (one not shown) and two and a half molecules of benzene (not shown). Color scheme: carbon = gray, nitrogen = blue, boron = pink, and zinc = green.

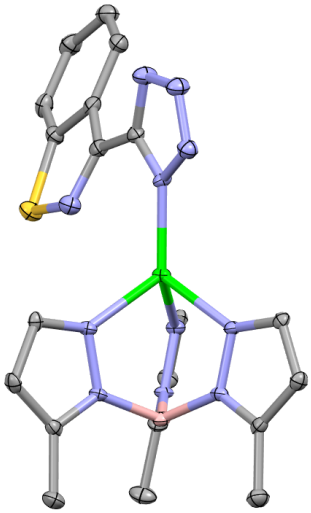


Figure S18. Structure of [(Tp^{Ph,Me})Zn(**3c**)] rendered as an ORTEP with atoms at 50% thermal probability ellipsoids. Hydrogen atoms and Tp^{Ph,Me} phenyl groups have been removed for clarity. The asymmetric unit consists only of the complex. Color scheme: carbon = gray, sulfur = yellow, nitrogen = blue, boron = pink, and zinc = green.

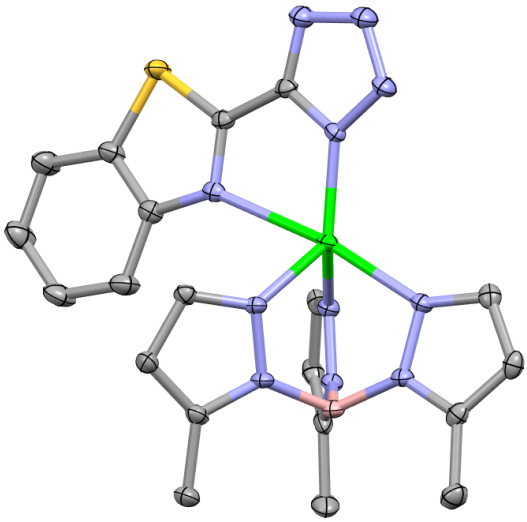


Figure S19. Structure of [(Tp^{Ph,Me})Zn(**4c**)] rendered as an ORTEP with atoms at 50% thermal probability ellipsoids. Hydrogen atoms and Tp^{Ph,Me} phenyl groups have been removed for clarity. The asymmetric unit consists of the complex and a molecule of benzene (not shown). Color scheme: carbon = gray, sulfur = yellow, nitrogen = blue, boron = pink, and zinc = green.

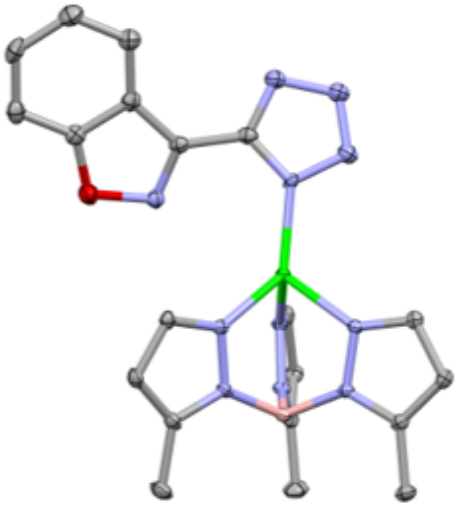


Figure S20. Structure of [(Tp^{Ph,Me})Zn(**5c**)] rendered as an ORTEP with atoms at 50% thermal probability ellipsoids. Hydrogen atoms and Tp^{Ph,Me} phenyl groups have been removed for clarity. The asymmetric unit consists of just the complex. Color scheme: carbon = gray, oxygen = red, nitrogen = blue, boron = pink, and zinc = green.

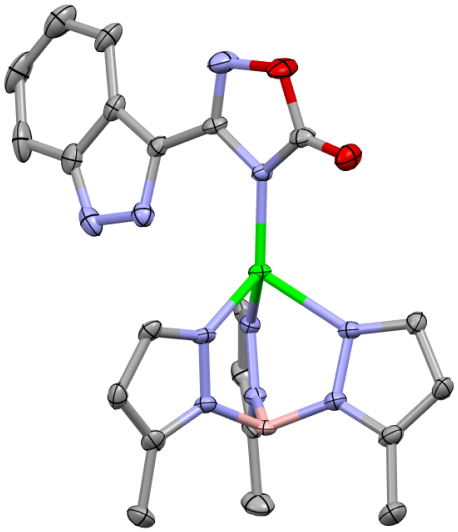


Figure S21. Structure of [(Tp^{Ph,Me})Zn(**1d**)] rendered as an ORTEP with atoms at 50% thermal probability ellipsoids. Hydrogen atoms and Tp^{Ph,Me} phenyl groups have been removed for clarity. The asymmetric unit consists of two complexes (one not shown) and three molecules of MeOH (not shown). Color scheme: carbon = gray, oxygen = red, nitrogen = blue, boron = pink, and zinc = green.

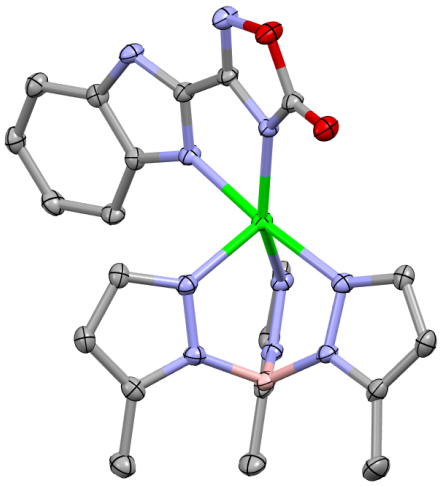


Figure S22. Structure of [(Tp^{Ph,Me})Zn(**2d**)] rendered as an ORTEP with atoms at 50% thermal probability ellipsoids. Hydrogen atoms and Tp^{Ph,Me} phenyl groups have been removed for clarity. The asymmetric unit consists only of the complex. Color scheme: carbon = gray, oxygen = red, nitrogen = blue, boron = pink, and zinc = green.

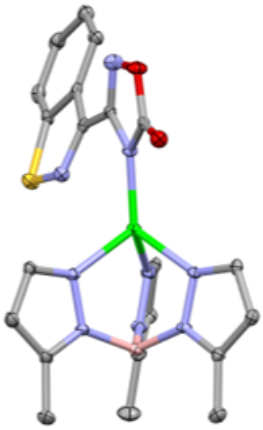


Figure S23. Structure of [(Tp^{Ph,Me})Zn(**3d**)] rendered as an ORTEP with atoms at 50% thermal probability ellipsoids. Hydrogen atoms and Tp^{Ph,Me} phenyl groups have been removed for clarity. The asymmetric unit consists of just the complex. Color scheme: carbon = gray, oxygen = red, sulfur = yellow, nitrogen = blue, boron = pink, and zinc = green.

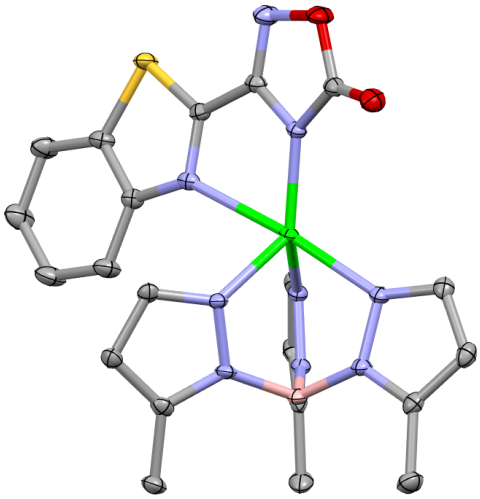


Figure S24. Structure of [(Tp^{Ph,Me})Zn(**4d**)] rendered as an ORTEP with atoms at 50% thermal probability ellipsoids. Hydrogen atoms and Tp^{Ph,Me} phenyl groups have been removed for clarity. The asymmetric unit consists of the complex and a molecule of benzene (not shown). Color scheme: carbon = gray, oxygen = red, sulfur = yellow, nitrogen = blue, boron = pink, and zinc = green.

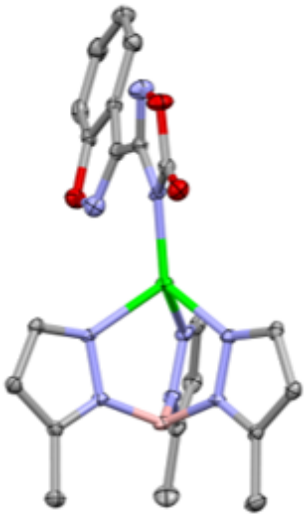


Figure S25. Structure of [(Tp^{Ph,Me})Zn(**5d**)] rendered as an ORTEP with atoms at 50% thermal probability ellipsoids. Hydrogen atoms and Tp^{Ph,Me} phenyl groups have been removed for clarity. The asymmetric unit consists of just the complex. Color scheme: carbon = gray, oxygen = red, nitrogen = blue, boron = pink, and zinc = green.

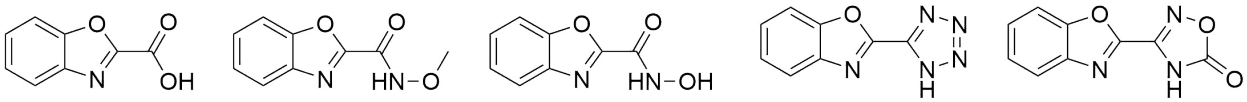


Figure S26. Chemical structures of the benzoxazole derivatives examined using DFT.

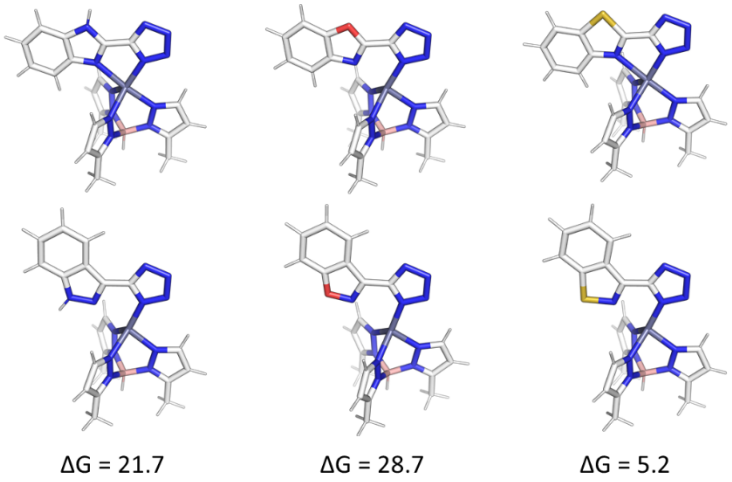


Figure S27. ωB97x-D/def2-TZVPP optimized geometries of: isomeric Tp^{Me}Zn(**2c**) and Tp^{Me}Zn(**1c**) (*top and bottom left*, respectively), isomeric Tp^{Me}Zn(benzoxazole-2-tetrazole) and Tp^{Me}Zn(**5c**) (*top and bottom middle*, respectively), and isomeric Tp^{Me}Zn(**4c**) and Tp^{Me}Zn(**5c**) (*top and bottom right*, respectively). Energies (in kcal mol^{-1}) are electronic energies determined at the ωB97x-D/def2-TZVPP level of theory.

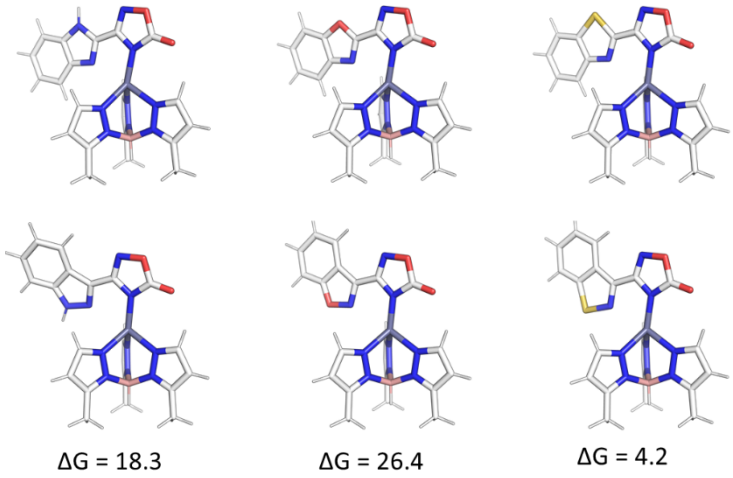


Figure S28. ωB97x-D/def2-TZVPP optimized geometries of: isomeric Tp^{Me}Zn (**2d**) and Tp^{Me}Zn (**1d**) (*top and bottom left*, respectively), isomeric Tp^{Me}Zn (benzoxazole-2-oxadiazolone) and Tp^{Me}Zn (**5d**) (*top and bottom middle*, respectively), as well as isomeric Tp^{Me}Zn (**4d**) and Tp^{Me}Zn (**5d**). (*top and bottom right*, respectively). Energies (in kcal mol^{-1}) are electronic energies determined at the ωB97x-D/def2-TZVPP level of theory.

$TpZn(L_1) + L_2 \longrightarrow TpZn(L_2) + L_1$

L_1 = **1, 3, 5**
L_2 = **2**, **4**, benzoxazole-2-carboxylate

	1,2 isomer	1,3 isomer	1,2 complex	1,3 complex		ΔE (kcal/mol)
N,N	-567.889306	-567.929678	-3167.001006	-3167.069459		-17.6
N,O	-587.738441	-587.778722	-3186.856971	-3186.902011		-3.0
N,S	-910.749756	-910.763224	-3509.872263	-3509.887730		-1.3

$TpZn(L_3) + L_4 \longrightarrow TpZn(L_4) + L_3$

L_3 = **1c**, **3c**, **5c**
L_4 = **2c**, **4c**, benzoxazole-2-tetrazole

	1,2 isomer	1,3 isomer	1,2 complex	1,3 complex		ΔE (kcal/mol)
N,N	-636.153482	-636.190283	-3235.498377	-3235.541196		-3.8
N,O	-655.994509	-656.034429	-3255.33432	-3255.377050		-1.8
N,S	-979.002337	-979.016231	-3578.349116	-3578.357224		3.6

$TpZn(L_5) + L_6 \longrightarrow TpZn(L_6) + L_5$

L_5 = **1d**, **3d**, **5d**
L_6 = **2d**, **4d**, benzoxazole-2-oxadiazolone

	1,2 isomer	1,3 isomer	1,2 complex	1,3 complex		ΔE (kcal/mol)
N,N	-715.204366	-715.240913	-3314.533695	-3314.594179		-15.0
N,O	-735.043253	-735.080720	-3334.389077	-3334.430644		-2.6
N,S	-1058.051542	-1058.064085	-3657.403599	-3657.416018		0.1

Figure S29. Analysis of ligand effects using the isodesmic equations reported above. All energies are reported in atomic units unless otherwise noted. Additional details regarding our computational protocol are provided in the methods section of the main text.