

SUPPORTING INFORMATION

(5 pages)

Reactivity of Ortho-Palladated Benzamides Toward CO, Isocyanides, and Alkynes. Synthesis of Functionalized Isoindolin-1-ones and 4,5-Disubstituted Benzo[*c*]azepine-1,3-diones

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Synthesis of 2-iodo-*N*-methylbenzamide. To a solution of 2-iodobenzoic acid (5 g, 20.16 mmol) in dry CH₂Cl₂ (80 mL) was added SOCl₂ (10 mL, 137.85 mmol) and the mixture was stirred at 50 °C for 6 h under an N₂ atmosphere. The solvent was evaporated under reduced pressure to give an oil. Aqueous MeNH₂ (40%, 100 mL) was then added dropwise while keeping the solution at 0 °C in an ice-bath. The resulting suspension was stirred at 0 °C for 1 h and then concentrated to ca. 50 mL. The colorless precipitate was collected by filtration, washed with H₂O (5 × 5 mL) and vacuum-dried at 50 °C for 16 h. Yield: 4.64 g, 88%. HRMS (ESI+, m/z): exact mass calcd for C₈H₉INO [M+H]⁺ requires 261.9723, found 261.9729, error = 2.33 ppm. Mp: 153 °C (lit 145-147 °C¹). The ¹H NMR data are in agreement with those reported in the literature.¹

Synthesis of 2-iodo-*N,N*-dimethylbenzamide. To a solution of 2-iodobenzoic acid (5.00 g, 20.16 mmol) in dry CH₂Cl₂ (80 mL) was added SOCl₂ (10 mL, 137.85 mmol) and the mixture was stirred at 50 °C for 6 h under an N₂ atmosphere. The solvent was evaporated under reduced pressure to give an oil. Aqueous Me₂NH (40%, 40 mL) was then added dropwise while keeping the solution at 0 °C in an ice-bath. The mixture was stirred at 0 °C for 30 min, treated with a saturated solution of K₂CO₃ in H₂O (100 mL), and extracted with CH₂Cl₂ (3 × 50 mL). The combined organic extracts were dried over anhydrous MgSO₄ and filtered. The solvent was then evaporated under reduced pressure and the residue was vacuum-dried at 60 °C for 16 h to give the product as a viscous oil. Yield: 5.30 g, 96%. HRMS (ESI+, m/z): exact mass calcd for C₉H₁₁INO [M+H]⁺ requires 275.988, found 275.9891, error = 3.96 ppm. The ¹H NMR data are in agreement with those reported in the literature.²

¹ Kundu, N. G.; Khan, M. W. *Tetrahedron* **2000**, *56*, 4777–4792.

² Schröder, N.; Wencel-Delord, J.; Glorius, F. *J. Am. Chem. Soc.* **2012**, *134*, 8298–8301.

¹H NMR (400.9 MHz, CDCl₃) of the mixture of 3-[carboxy(methoxycarbonyl)methyl]-2-methyl-3-phenylisoindolin-1-one (15a) and (tmedaH)TfO. δ 9.60 (br, 2 H), 8.09 (d, ³J_{HH} = 7.6 Hz, 1 H), 7.73 (m, 2 H), 7.56 (m, 2 H), 7.47 (m, 2 H), 7.39 (td, ⁴J_{HH} = 1.2 Hz, ³J_{HH} = 7.2 Hz, 1 H), 7.33-7.23 (m, 6 H), 7.13 (m, 2 H), 7.00 (m, 2 H), 4.82 (s, 1 H), 4.72 (s, 1 H), 3.69 (s, 3 H), 3.59 (s, 3 H), 3.17 (s, 6 H, CH₂, tmedaH⁺), 2.87 (s, 3 H), 2.59 (s, 3 H, 12 H, Me, tmedaH⁺).

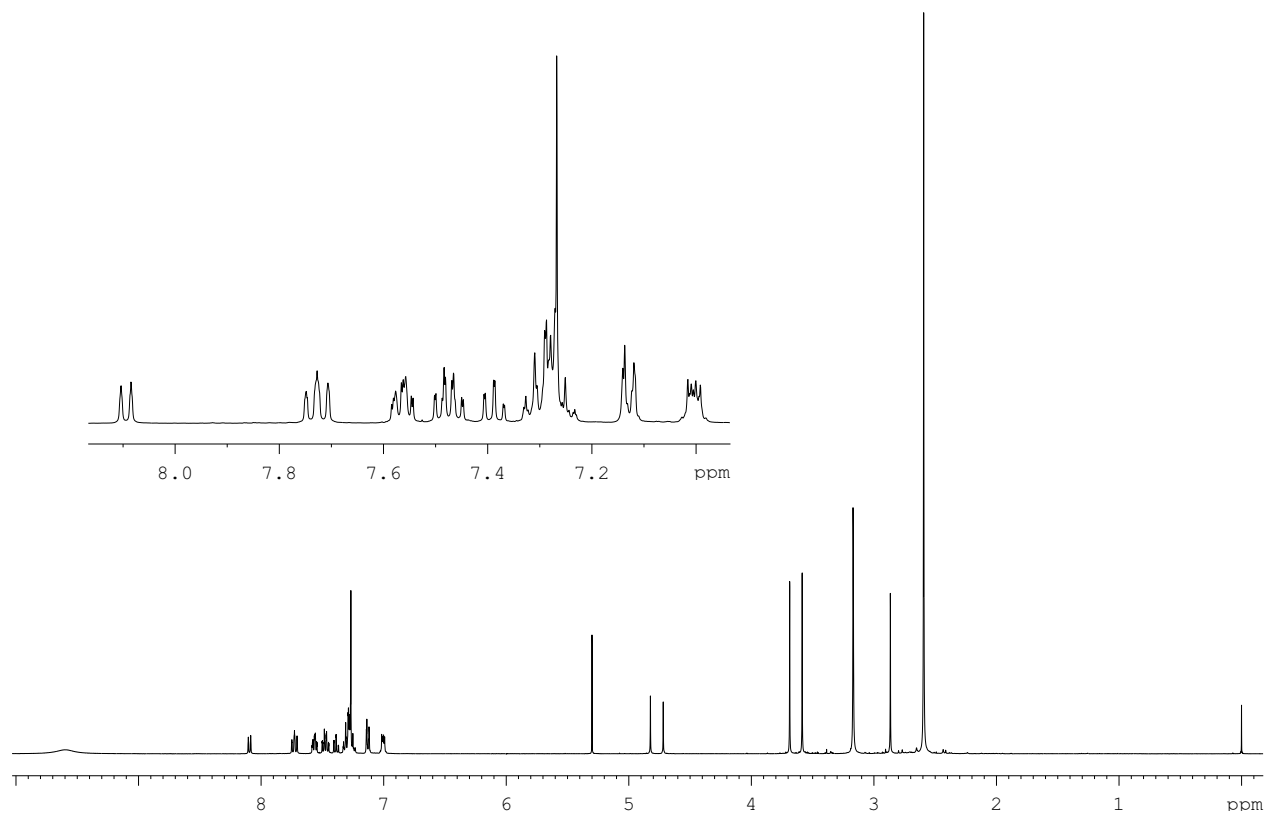


Figure S1. ¹H NMR spectrum (400.9 MHz, CDCl₃) of the mixture of **15a** and (tmedaH)TfO.

Table S1. Crystallographic Data for **2a**, **3a**, **7a**, and **11b**.

	2a	3a ·1.17H ₂ O	7a	11b
formula	C ₁₄ H ₂₂ F ₃ N ₃ O ₄ PdS	C ₁₃ H _{21.34} N ₃ O _{1.17} Pd	C ₂₃ H ₃₀ F ₃ N ₃ O ₄ PdS	C ₂₅ H ₃₂ F ₃ N ₃ O ₆ PdS
fw	491.81	344.84	607.96	666.00
<i>T</i> (K)	100	100	100	100
λ (Å)	1.54148	0.71073	0.71073	0.71073
cryst syst	trigonal	monoclinic	orthorhombic	orthorhombic
space	<i>P</i> ₃ ₂ ₁	<i>C</i> 2/ <i>c</i>	<i>Pbcn</i>	<i>Pbca</i>
<i>a</i> (Å)	11.60504(8)	17.7877(7)	28.1406(8)	17.8564(4)
<i>b</i> (Å)	11.60504(8)	12.4571(3)	9.4389(3)	16.0031(4)
<i>c</i> (Å)	24.7296(2)	15.6840(6)	19.7762(6)	19.9027(4)
α (deg)	90	90	90	90
β (deg)	90	124.139(6)	90	90
γ (deg)	120	90	90	90
<i>V</i> (Å ³)	2884.31(4)	2876.42(17)	5252.9(3)	5687.3(2)
<i>Z</i>	6	8	8	8
ρ_{calcd} (Mg)	1.699	1.593	1.538	1.556
μ (mm ⁻¹)	9.3	1.3	0.8	0.8
<i>R</i> 1 ^{<i>a</i>}	0.0144	0.0223	0.0306	0.0290
<i>wR</i> 2 ^{<i>b</i>}	0.0374	0.0531	0.0673	0.0656

^{*a*} $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ for reflections with $I > 2\sigma(I)$. ^{*b*} $wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_o^2)/3$ and *a* and *b* are constants set by the program.

Table S2. Crystallographic Data for **14b**, **15b**, **18** and **19**.

	14b	15b	18 ·CH ₂ Cl ₂	19
formula	C ₁₈ H ₁₅ NO ₂	C ₂₀ H ₁₉ NO ₅	C ₂₁ H ₃₁ Cl ₂ N ₃ O ₅ Pd	C ₁₄ H ₁₃ NO ₅
fw	277.31	353.36	582.79	275.25
<i>T</i> (K)	100	100	100	100
λ (Å)	1.54148	0.71073	0.71073	1.54148
cryst syst	triclinic	triclinic	orthorhombic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>Pca</i> 2 ₁	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	8.8386(10)	8.5887(2)	18.1799(2)	10.2315(6)
<i>b</i> (Å)	9.2130(10)	13.2148(4)	8.36643(10)	6.8252(4)
<i>c</i> (Å)	10.0650(10)	15.8792(4)	15.7760(2)	18.2358(11)
α (deg)	115.140(10)	99.440(2)	90	90
β (deg)	105.462(10)	96.959(2)	90	104.125(6)
γ (deg)	98.329(10)	96.003(2)	90	90
<i>V</i> (Å ³)	683.09(13)	1750.45(8)	2399.54(5)	1234.93(13)
<i>Z</i>	2	4	4	4
ρ_{calcd} (Mg m ⁻³)	1.348	1.341	1.613	1.480
μ (mm ⁻¹)	0.7	0.1	1.0	1.0
R1 ^a	0.0318	0.0443	0.0167	0.0320
wR2 ^b	0.0812	0.1085	0.0404	0.0903

^a $R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ for reflections with $I > 2\sigma(I)$. ^b $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_o^2)/3$ and *a* and *b* are constants set by the program.