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Direct palladium-catalyzed C-3 alkynylation of indoles

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ABSTRACT

The direct palladium-catalyzed coupling reaction of indoles with alkynyl bromides was described in this paper. In the presence of catalytic amount of $PdCl_2(PPh_3)_2$ and 2.0 equiv. NaOAc, the coupling reaction of indoles with alkynyl bromides proceeded smoothly at 50 °C to give the corresponding 3-alkynylindoles with high regioselectivity in good to excellent yields.

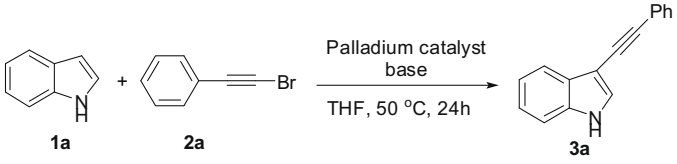
Indole derivatives are one of the most privileged structural motifs frequently found in natural products and pharmaceuticals.[1] Many efficient methods for the synthesis and functionalization of indoles have been developed in recent years;[2] among them the direct functionalization of heterocyclic C–H bonds is one of the most attractive processes. During last two decades, the significant progress in the development of transition metal-catalyzed direct arylation[3] and vinylation[4] of indoles has been achieved. This approach provides direct coupling of indoles with arene derivatives and alkenes. However, direct C–H alkynylation of indoles has not been reported yet. Until recently, Gevorgyan and co-workers developed direct palladium-catalyzed alkynylation reaction of electron-rich heterocycles with alkylnyl halides.[5] This work encouraged us to examine the possibility of preparing 3-alkynylindoles by a similar strategy.

Typically, 3-alkynylindoles were prepared from the Sonogashira reaction of 3-functionalized indoles with alkynes.[6] While these reactions are often synthetically useful, they usually require protection of heteorocyclic nitrogen atom of indoles and prefunctionalization of indoles. The other method included preparation of 2-substituted 3-alkynylinoles via palladium-catalyzed reaction of 1-bromoalkynes with *o*-alkynyltrifluoroacetanilides, which require multiple steps to synthesize.[7] We envisioned a more direct protocol, which allowed us to avoid preactivation of indoles or multistep synthesis of indole fragment, that will serve as an alternative way to supplement these existing methodologies. Herein, we report the direct C-3 alkynylation of indoles with aryl-, cyclohexenyl-substituted 1-bromoalkynes in satisfactory to high yields under mild conditions.

Our initial attempts focused on the coupling of indole (**1a**) with 1-bromophenylacetylene (**2a**),[8,9] various conditions were examined in order to optimize the desired results (Table 1). It was found that $PdCl_2(PPh_3)_2$ and $Pd(PPh_3)_4$ were effective catalysts compared with $Pd(OAc)_2$ and $PdCl_2$. Under the identical conditions, $Pd(OAc)_2$ and $PdCl_2$ completely failed to yield any coupled products (entries 4 and 5). However, when $PdCl_2(PPh_3)_2$ and $Pd(PPh_3)_4$ were applied as the catalysts, the coupling reaction of indole and bromoalkyne led to 3-alkynylindole in 89% and 85% yields respectively (entries 3 and 6). Notably, in the absence of Pd catalyst, using $Cu(OAc)_2$ or CuI as a catalyst, the reaction could not occur (entries 1 and 2).

Next, an examination of selected bases revealed that NaOAc and KOAc were effective to this transformation (entries 6 and 7). However, the use of stronger bases such as Cs_2CO_3, K_2CO_3, and *t*-BuOK did not give the coupled product **3a** (entries 9–11). It

Table 1
Reaction optimization for C-3 alkynylation of indole[a]



Entry	Catalyst	Base	Yield[b] (%)
1	CuI	NaOAc	ND[c]
2	$Cu(OAc)_2$	NaOAc	ND
3	$Pd(PPh_3)_4$	NaOAc	85
4	$Pd(OAc)_2$	NaOAc	ND
5	$PdCl_2$	NaOAc	ND
6	$PdCl_2(PPh_3)_2$	NaOAc	89
7	$PdCl_2(PPh_3)_2$	KOAc	80
8	$PdCl_2(PPh_3)_2$	NEt_3	7
9	$PdCl_2(PPh_3)_2$	Cs_2CO_3	ND
10	$PdCl_2(PPh_3)_2$	K_2CO_3	ND
11	$PdCl_2(PPh_3)_2$	*t*-BuOK	ND
12	$PdCl_2(PPh_3)_2$	DMAP	<5
13	$PdCl_2(PPh_3)_2$	None	<5

[a] Reactions were carried out with indole (0.2 mmol), bromophenylacetylene (0.6 mmol), catalyst (5 mol%), and base (0.4 mmol) in THF (1 mL).
[b] Isolated yield after column chromatography.
[c] No desired product was detected by TLC analysis.

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Table 2
Pd-catalyzed alkynylation of diverse indoles[a]

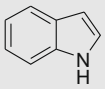
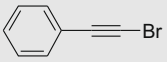
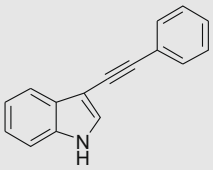
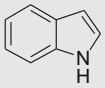
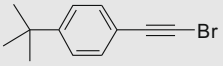
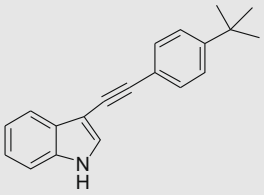
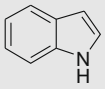
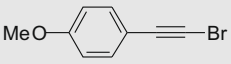
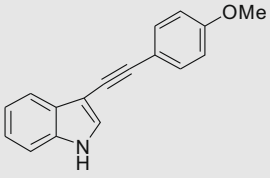
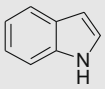
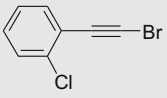
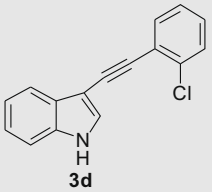
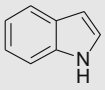
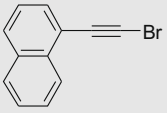
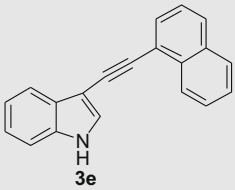
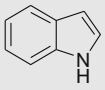
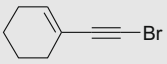
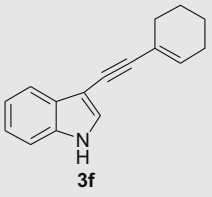
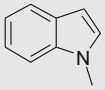
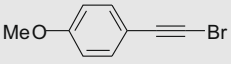
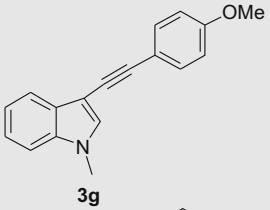
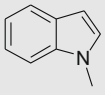
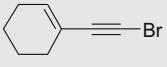
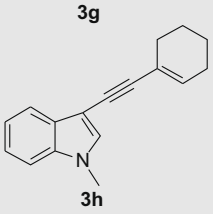
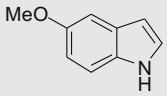
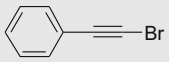
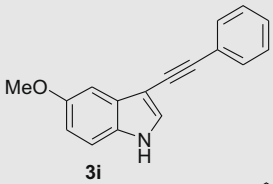
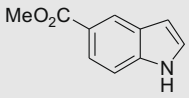
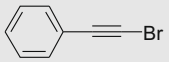
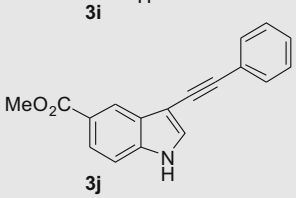
Entry	Heterocycle	Halide	Product	Time (h)	Yield[b] (%)
1			 **3a**	24	89
2			 **3b**	18	92
3			 **3c**	12	90
4			 **3d**	22	53
5			 **3e**	24	95
6			 **3f**	12	65
7			 **3g**	14	88
8			 **3h**	14	72

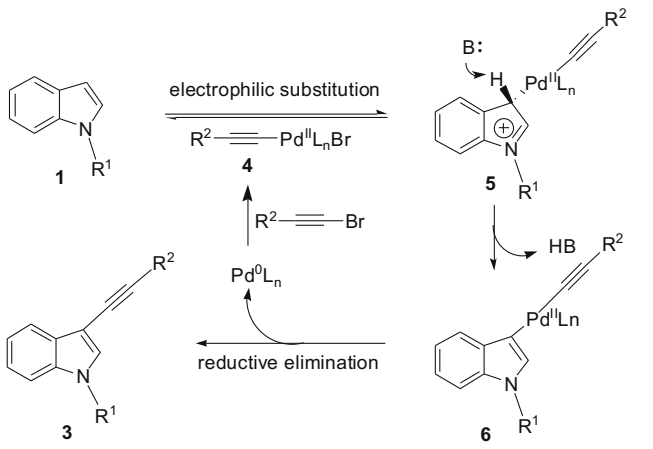
Table 2 (*continued*)

Entry	Heterocycle	Halide	Product	Time (h)	Yield[b] (%)
9			 **3i**	24	77
10			 **3j**	24	75

[a] Reactions were carried out with indole (0.5 mmol), bromoalkyne (1.5 mmol), $PdCl_2(PPh_3)_2$ (10 mol%), and NaOAc (1.0 mmol) in THF (1 mL) at 50 °C.
[b] Isolated yield after column chromatography.

was possible that strong base would remove the proton on nitrogen atom, which altered the electronic distribution of indole aromatic ring system and resulted in no occurrence of the desired reaction.[10] Significantly lower yields were obtained when NEt_3 and DMAP were used as bases (entries 8 and 12).

With optimized conditions in hand, we embarked on an investigation of the reaction scope (Table 2). In the presence of 10 mol% of $PdCl_2(PPh_3)_2$ and 2.0 equiv. of NaOAc in THF, indoles underwent smooth coupling reaction with bromoalkynes to give only C-3 alkynylated products.[11,12] This transformation is not sensitive to air and moisture and could be conveniently carried out on the benchtop using unpurified solvent.[13] Most notably, free indoles showed comparable reactivity to *N*-methyl indoles in this transformation; for example, reaction of indole (**1a**) with 1-bromophenylacetylene (**2a**) provided **3a** in 89% isolated yield; no *N*-alkynylation product was obtained in this reaction (entry 1). It was found that conjugated 1-bromoalkynes, for example, when the substituents of 1-bromoalkynes were aryl or alkenyl groups, the reaction smoothly gave corresponding alkynylindoles in good to excellent yields (entries 1–6).[14] These transformations were also compatible with a diverse variety of functional groups at 1-bromoalkynes, including alkyl, methoxy, and chloro groups (entries 2–4). In addition, *N*-methyl indole proceeded well in this transformation to give corresponding coupled products (entries 7 and 8). When electron-donating or electron-withdrawing substituents, such as methoxy or ester groups, were introduced at 5-position of indole, the reactions occurred in good yields (entries 9 and 10), Surprisingly, the strong electron-withdrawing substitute, nitro group was introduced at the same position, the reaction did not give any coupled product at the same reaction condition, probably the strong electron-withdrawing group significantly lowers the nucleophilicity of the indole.



Scheme 1. Proposed mechanism in the alkynylation of indoles.

Importantly, these coupling reactions typically provided the 3-alkynylindoles with high selectivity (>20:1). When C-3 was blocked (for example, in 3-methylindole), no C-2 substituted product was observed (Eq. 1). However, when C-2 was blocked (for example, in 2-methylindole), C-3 alkynylated indole **3k** was obtained in moderate yield,[15] probably due to steric effect (Eq. 2). According to our findings, we proposed a possible mechanism in the C-3 alkynylation of indoles (Scheme 1), which is very similar to the previous postulated for the palladium-catalyzed arylation of indoles.[3b] Direct palladium-catalyzed C–H alkynylation of indole operates via an electrophilic palladation pathway. Oxidative addition of alkynyl bromide with palladium catalyst forms alkynylpalladium intermediate **4**, which attacks the most electron-rich C-3 position of indole **1** to furnish iminium intermediate **5**. Deprotonation of **5** with a base gives the palladium intermediate **6**, which undergoes reductive elimination to provide 3-alkynylindoles **3** and regenerate the palladium catalyst.

In conclusion, we have developed a new palladium-catalyzed method for the direct 3-alkynylation of indoles. These reactions represent a practical approach to synthesize 3-alkynylindoles with mild conditions, high regioselectivity and no need to protect indole nitrogen atom. Ongoing work to expand the substrate scope and apply this reaction to the synthesis of complex molecules is underway.

Acknowledgments

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2. Cacchi, S.; Fabrizi, G. *Chem. Rev.* **2005**, *105*, 2873.
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9. The reaction of 1-iodophenylacetylene with indole (**1a**) under various conditions did not give alkynylated indole, only homocoupled product 1,3-diyne was observed.
10. Zhang, Z.; Hu, Z.; Yu, Z.; Lei, P.; Chi, H.; Wang, Y.; He, R. *Tetrahedron Lett.* **2007**, *48*, 2175.
11. *General Procedure*: To a mixture of indole (0.5 mmol), $PdCl_2(PPh_3)_2$ (0.05 mmol, 10 mol %), and NaOAc (1.0 mmol, 2 equiv.) in THF (1.0 mL), bromoalkyne (1.5 mmol, 3.0 equiv.) was added. The resulting mixture was stirred under 50 °C until completion (as monitored by TLC). The solvent was removed under reduced pressure and the residue was purified by flash column chromatography using petroleum/EtOAc as eluent to afford pure products (**3a–j**).
Compound **3a**: (89%); IR (KBr) ν 3390, 2214, 1635, 1457, 1237, 747, 689 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.21 (br s, 1H, NH), 7.84 (d, J = 6.3 Hz, 1H), 7.57 (d, J = 7.8 Hz, 2H), 7.43 (d, J = 2.4 Hz, 1H), 7.38–7.30 (m, 4H), 7.26–7.20 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.4, 131.5 (2C), 128.6, 128.5 (2C), 128.0, 127.7, 124.3, 123.3, 120.9, 120.2, 111.5, 98.9, 91.3, 83.1.
Compound **3b**: (92%); IR (KBr) ν 3413, 3059, 2961, 2208, 1618, 1500, 1458, 1416, 1362, 1331, 1260, 834, 744 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.20 (br s, 1H, NH), 7.82 (d, J = 6.9 Hz, 1H), 7.50 (d, J = 8.1 Hz, 2H), 7.42 (d, J = 2.7 Hz, 1H), 7.38–7.34 (m, 3H), 7.25–7.18 (m, 2H), 1.30 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.0, 135.4, 131.2 (2C), 128.7, 127.8, 125.4 (2C), 123.2, 121.3, 120.8, 120.2, 111.5, 99.2, 91.3, 82.3, 34.9, 31.4(3C); HRMS (EI) calcd for $C_{20}H_{19}N$ (M^+) 273.1517, found 273.1517.
Compound **3c**: (90%); IR (KBr) ν 3383, 2216, 1605, 1503, 1423, 1247, 836, 817 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.15 (s, 1H, NH), 7.82 (d, J = 6.6 Hz, 1H), 7.50 (d, J = 8.7 Hz, 2H), 7.39 (d, J = 2.7 Hz, 1H), 7.33 (d, J = 6.6 Hz, 1H), 7.26–7.21 (m, 2H), 6.88 (d, J = 8.7 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.3, 135.4, 132.9 (2C), 128.6, 127.6, 123.2, 120.8, 120.2, 116.5, 114.1 (2C), 111.5, 99.2, 91.0, 81.5, 55.4; HRMS (EI) calcd for $C_{17}H_{13}NO$ (M^+) 247.0997, found 247.0993.
Compound **3d**: (53%); IR (KBr) ν 3402, 2207, 1624, 1536, 1465, 1415, 1235, 1097, 747 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.18 (s, 1H, NH), 7.90–7.87 (m, 1H), 7.58–7.55 (m, 1H), 7.44–7.39 (m, 2H), 7.32–7.29 (m, 1H), 7.25–7.19 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.2 (2C), 133.7, 130.2, 129.4 (2C), 129.2, 127.4, 125.0, 124.2, 121.9, 121.1, 112.4, 99.4, 89.7, 89.1; HRMS (EI) calcd for $C_{16}H_{10}NCl$ (M^+) 251.0502, found 251.0498.
Compound **3e**: (95%); IR (KBr) ν 3424, 2201, 1634, 1538, 1506, 1456, 1419, 1236, 803, 772, 746 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.54 (d, J = 8.4 Hz, 1H), 8.15 (s, 1H, NH), 7.93–7.90 (m, 1H), 7.86–7.76 (m, 3H), 7.59 (d, J = 7.8 Hz, 1H), 7.53–7.41 (m, 3H), 7.38–7.32 (m, 1H), 7.27–7.22 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.4, 133.4, 133.3, 130.0, 128.6, 128.4, 128.2, 128.1, 126.8, 126.5, 126.4, 125.5, 123.4, 122.0, 121.0, 120.2, 111.6, 99.1, 89.4, 88.2; HRMS (EI) calcd for $C_{20}H_{13}N$ (M^+) 267.1048, found 267.1041.
Compound **3f**: (65%); IR (KBr) ν 3408, 3058, 2858, 2196, 1617, 1534, 1455, 1417, 1245, 743 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.13 (s, 1H, NH), 7.73 (d, J = 7.2 Hz, 1H), 7.34–7.32 (m, 2H), 7.24–7.14 (m, 2H), 6.21–6.18 (m, 1H), 2.28 (d, J = 1.8 Hz, 2H), 2.16–2.14 (m, 2H), 1.73–1.55 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.3, 133.8, 128.6, 127.4, 123.1, 121.4, 120.6, 120.1, 111.4, 99.4, 93.0, 80.0, 29.8, 25.9, 22.6, 21.8; HRMS (EI) calcd for $C_{16}H_{15}N$ (M^+) 221.1204, found 221.1208.
Compound **3g**: (88%); IR (KBr) ν 2928, 2204, 1605, 1564, 1504, 1463, 1382, 1288, 1247, 1176, 1116, 1032, 831, 743 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, J = 7.8 Hz, 1H), 7.41 (d, J = 8.7 Hz, 2H), 7.24–7.10 (m, 4H), 6.79 (d, J = 8.7 Hz, 2H), 3.73 (s, 3H), 3.67 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 136.4, 132.8 (2C), 132.0, 129.3, 122.7, 120.3 (2C), 116.6, 114.1 (2C), 109.6, 97.4, 90.8, 81.6, 55.4, 33.1; HRMS (EI) calcd for $C_{18}H_{15}NO$ (M^+) 261.1154, found 261.1146.
Compound **3h**: (72%); IR (KBr) ν 3053, 2928, 2197, 1723, 1613, 1536, 1469, 1380, 1337, 1251, 1161, 1052, 918, 802, 742, 510, 426 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, J = 7.5 Hz, 1H), 7.31–7.15 (m, 4H), 6.18 (br s, 1H), 3.76 (s, 3 H), 2.28 (m, 2 H), 2.16–2.15 (m, 2 H), 1.70–1.57 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.4, 133.4, 131.8, 129.4, 122.7, 121.5, 120.3, 120.2, 109.5, 99.4, 93.0, 80.2, 33.1, 29.8, 25.9, 22.7, 21.8; HRMS (EI) calcd for $C_{17}H_{17}N$ (M^+) 235.1361, found 235.1360.
Compound **3i**: (77%); IR (KBr) ν 3415, 2936, 2210, 1485, 1212, 1050, 756, 690 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.14 (s, 1H, NH), 7.59–7.55 (m, 2H), 7.41 (d, J = 2.7 Hz, 1H), 7.35–7.21 (m, 5H), 6.90 (dd, J = 6.6, 2.4 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.9, 131.3 (2C), 130.3, 129.0, 128.6, 128.3 (2C), 127.6, 124.1, 113.5, 112.2, 101.5, 98.2, 91.2, 83.2, 55.8; HRMS (EI) calcd for $C_{17}H_{13}NO$ (M^+) 247.0997, found 247.0993.
Compound **3j**: (75%); IR (KBr) ν 3435, 2948, 2215, 1692, 1620, 1432, 1273, 1194, 1114, 986, 746, 689 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.57 (s, 1H, NH), 7.94 (d, J = 8.7 Hz, 1H), 7.57 (d, J = 7.8 Hz, 2 H), 7.49 (d, J = 2.4 Hz, 1H), 7.38–7.30 (m, 3H), 7.28–7.24 (m, 2H), 3.95 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.3, 138.0, 131.5 (2C), 129.8, 129.4, 128.8, 128.5 (2C), 128.2, 128.0, 124.5, 123.0, 111.5, 100.3, 91.9, 82.2, 52.1; HRMS (EI) calcd for $C_{18}H_{13}NO_2$ (M^+) 275.0946, found 275.0946.
12. The structure of 3-phenylethynylindole (**3a**) was established by 2D NOESY experiment, which showed cross peak between proton on C-2 at δ 7.43 (d, J = 2.4 Hz, 1H) and proton on indole nitrogen at δ 8.21 (br s, 1H, NH); additionally, 2-phenylethynylindole is a known compound, which showed proton on C-3 at δ 6.84 (d, J = 2.4 Hz, 1H). See: Nagamochi, M.; Fang, Y.-Q.; Lautens, M. *Org. Lett.* **2007**, *9*, 2955.
13. When the reaction of indole (**1a**) with 1-bromophenylacetylene (**2a**) was carried out in unpurified THF in the presence of 5% $PdCl_2(PPh_3)_2$ and 2 equiv. NaOAc, 88% yield of **3a** was obtained.
14. When the substitute of bromoalkyne **2** is alkyl group (e.g., in 1-bromo-1-octyne), no alkynylated indole was produced, only homocoupled product 1,3-diyne was observed.
15. Compound **3k**: (55%); IR (KBr) ν 3400, 3057, 2920, 2204, 1597, 1555, 1488, 1457, 1260, 749, 692 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.91 (br s, 1H, NH), 7.72–7.69 (m, 1H), 7.57–7.53 (m, 2H), 7.36–7.27 (m, 3H), 7.20–7.13 (m, 3H), 2.48 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.6, 134.9, 131.4 (2C), 129.3, 128.4 (2C), 127.5, 124.6, 122.3, 120.7, 119.4, 110.7, 96.5, 93.0, 83.4, 12.9; HRMS (EI) calcd for $C_{17}H_{13}N$ (M^+) 231.1048, found 231.1049.