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Understanding the Behavior of *N*-Tosyl and *N*-2-Pyridylsulfonyl Imines in Cu^{II}-Catalyzed Aza-Friedel−Crafts Reactions

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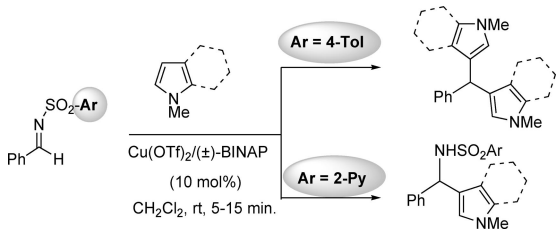
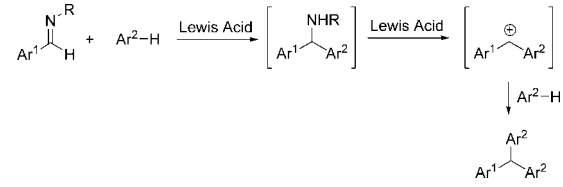


The different behavior of *N*-tosyl imines and *N*-(2-pyridyl)-sulfonyl imines in Cu^{II}-catalyzed AFCR is described. DFT theoretical calculations on the mode of coordination of the copper atom to both types of substrates allow understanding this different reactivity.

The Lewis acid promoted aza-Friedel−Crafts reaction (AFCR) between electron-rich aromatic compounds and imines constitutes a powerful tool for the preparation of benzylic amines and derivatives.[1] This reaction is particularly useful in the case of highly electrophilic imines, such as those derived from glyoxalates,[2] and trifluoroacetaldehyde.[3] In contrast, the AFCR of less activated substrates, such as imines of aromatic aldehydes, is more limited,[4] mainly due to the lower reactivity and/or the formation of side products, especially triarylmethane products.[5] This type of product is the result of a facile further Friedel−Crafts alkylation of the diaryl methyl amine intermediate via a highly stabilized diaryl methyl carbocation (Scheme 1).

SCHEME 1



In recent years, we have reported that heterosubstituted metal-coordinating *N*-sulfonyl imines, such as 2-pyridylsulfonyl imines, represent a very appealing novel type of imines, usually displaying a very different reactivity to that observed with typical phenylsulfonyl or tosyl imines.[6] Within the context of the AFCR, we have found that the Cu^{II}-catalyzed AFCR of *N*-methyl indole with the tosyl imine of benzaldehyde provided the triarylmethane derivative **3**, while the same process using the 2-pyridylsulfonyl imine led selectively to the aza-Friedel−Crafts adduct **2b**.[6b] We describe herein a more detailed comparative study on the different behavior of tosyl and 2-pyridylsulfonyl imines in AFCR and a theoretical study providing some clues to the key role exerted by the 2-pyridyl unit.

The model *N*-sulfonyl imines **1a** and **1b** were readily prepared by condensation of benzaldehyde with *p*-tolyl sulfonamide and 2-pyridylsulfonamide, respectively, catalyzed by Amberlist/4 Å molecular sieves in refluxing toluene[7] (93 and 87% yield, respectively). In Table 1 are shown the results obtained in the reaction of both sulfonyl imines with *N*-methyl indole catalyzed by $Cu(OTf)_2$/(±)-BINAP (10 mol %) at different temperatures and reaction times.

Two main conclusions can be drawn from this study: (a) At room temperature, the AFCR of the tosyl imine **1a** was very fast (≤5 min), giving rise selectively to the triarylmethane **3**, even with only 1 equiv of *N*-methyl indole (entry 4). The intermediate sulfonamide **2a** could be detected and isolated at lower temperatures (entries 1 and 2), although mixtures of **2a** + **3** were always formed. This result shows the easy conversion of **2a** into **3** under the reaction conditions. (b) The 2-pyridylsulfonyl imine **1b** displayed a different reactivity profile: the AFCR was also very fast but completely selective in favor of the product **2b** between −40 °C and room temperature (entries

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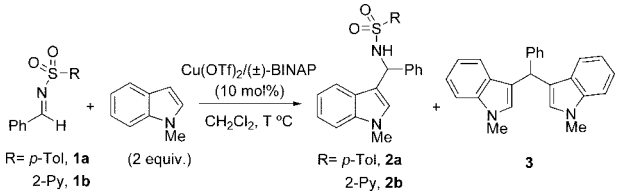
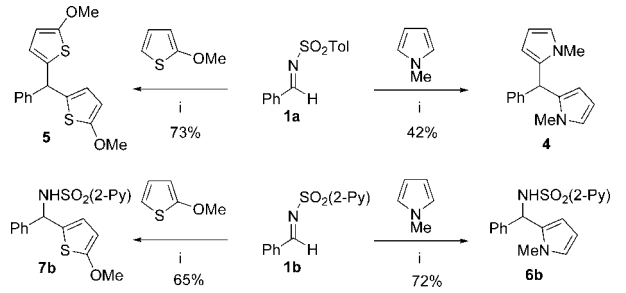
TABLE 1. Cu^{II}-Catalyzed Reaction of *N*-Methyl Indole with *N*-Tosyl and *N*-2-Pyridylsulfonyl Imines of Benzaldehyde



entry[a]	imine	T (°C)	t (min)	yield of **2** (%)[b]	yield of **3** (%)[b]
1	**1a**	−40	120	**2a**, 33	35
2	**1a**	0	35	**2a**, 13	55
3	**1a**	22	5	**2a**, −	72
4[c]	**1a**	22	5	**2a**, −	38
5	**1b**	−40	180	**2b**, 77	
6	**1b**	0	15	**2b**, 81	
7	**1b**	22	5	**2b**, 72	
8[c]	**1b**	22	5	**2b**, 58	
9	**1b**	45	15	**2b**, 39	50
10	**1b**	45	35	**2b**, −	84

[a] Reaction conditions: 2 equiv of *N*-methyl indole and 10 mol % of $Cu(OTf)_2$/(±)-BINAP. [b] In pure product after silica gel chromatography. [c] With 1 equiv of *N*-methyl indole.

SCHEME 2



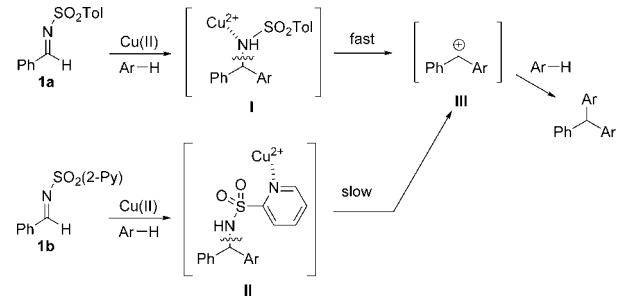
i. $Cu(OTf)_2$/(±)-BINAP (10 mol %), CH_2Cl_2, 22 °C, 5−15 min.

5−8). The formation of the triarylmethane **3** was only observed at higher temperatures (refluxing CH_2Cl_2), being the only product after 35 min of reaction (entry 10). This result clearly indicates that the 2-pyridylsulfonamide **2b** is more reluctant to undergo the second Friedel−Crafts reaction than the parent tosyl analogue **2a**.

This sharp different reactivity between the tosyl imine **1a** and the 2-pyridylsulfonyl imine **1b** was also observed in the AFCR of other electron-rich heteroaromatic compounds, such as *N*-methyl pyrrole and 2-methoxy thiophene (Scheme 2). With both aromatic substrates, the Cu^{II}-catalyzed AFCR with the tosyl imine **1a** at room temperature (5−15 min) provided selectively the corresponding triarylmethane products **4** and **5** (42 and 73% yield, respectively), while under identical reaction conditions, the 2-pyridylsulfonyl imine **1b** led to the intermediate arylated sulfonamides **6b** and **7b** (72 and 65% yield, respectively) without detecting by ^1H NMR the formation of triarylmethane products.

As a working hypothesis, we postulated that a different coordination mode of the electrophilic Cu^{II} catalyst to the sulfonamide intermediates formed after the aza-Friedel−Crafts reaction could be at the origin of the interesting opposite selectivity of imines **1a** and **1b** in this transformation (Scheme 3). We envisaged that the coordination of the Cu^{II} catalyst to the sulfonamide nitrogen of the initial AFCR product resulting from tosyl imine **1a** (complex **I**) would enhance the ability of the sulfonamide moiety as a leaving group, facilitating the

SCHEME 3



formation of the highly stabilized carbocation intermediate **III**, required for the final Friedel−Crafts alkylation. In contrast, in the case of the 2-pyridyl analogue, it is reasonable to assume a preferential coordination of the Cu^{II} atom to the pyridyl nitrogen atom (complex **II**), instead of the sulfonamide nitrogen, resulting in a lower leaving group capacity of the sulfonamide moiety which would make more difficult the cleavage of the C−N bond and formation of the carbocation intermediate.

To support this hypothesis, and to have an insight of the coordination mode around the copper atom, the intermediates and transition states involved in the cleavage of the C−N bond were theoretically studied at the DFT (B3LYP)[8] level by using the Gaussian03 program.[9] The standard 6-31G(d)[10] basis set was used for all atoms except Cu, for which LANL2DZ[11] was employed. Harmonic frequencies were calculated at the same level of theory to characterize the stationary points and to determine the zero-point energies (ZPE). Slightly simplified structures of complexes **I** and **II** (with Tol = Ph, Ar = Ph, and 1,2-bis(dimethylphosphino)ethane as ligand for the metal) were used as models.

Optimized geometries of complexes and transition states are depicted in Figure 1. Distances Cu−P and Cu−O are quite similar in all the structures (in the range 2.37−2.42 and 2.04−2.18 Å, respectively). The copper center in complex **I** is assumed to be coordinated with the more electron-rich sulfonamide nitrogen and a sulfonyl oxygen. The conformation around the C−N bond minimizes the steric interaction between one of the phenyl groups and the methyl groups of the phosphorus ligand (closest distance: 2.74 Å). In addition, in this conformation, it is possible a stabilizing π-stacking interaction between the second phenyl group and the phenylsulfonamide group (distance between centroids: 4.57 Å). From this complex, **TSI** was found in which a clear elongation of the C−N bond is observed, but the rest of the molecule shows almost the same conformation as in complex **I**, although the distance between centroids increases (5.23 Å). A quite similar arrangement of the groups is observed in complex **IV**, resulting upon cleavage of the C−N bond. In complex **II**, one of the sulfonyl oxygens and the pyridyl nitrogen are the atoms coordinated with the metal. Complexes in which the sulfonamide nitrogen was involved in the coordination could not be found. However, the coordination of this atom seems to be essential for the cleavage step since **TSII** was the only transition state found in which

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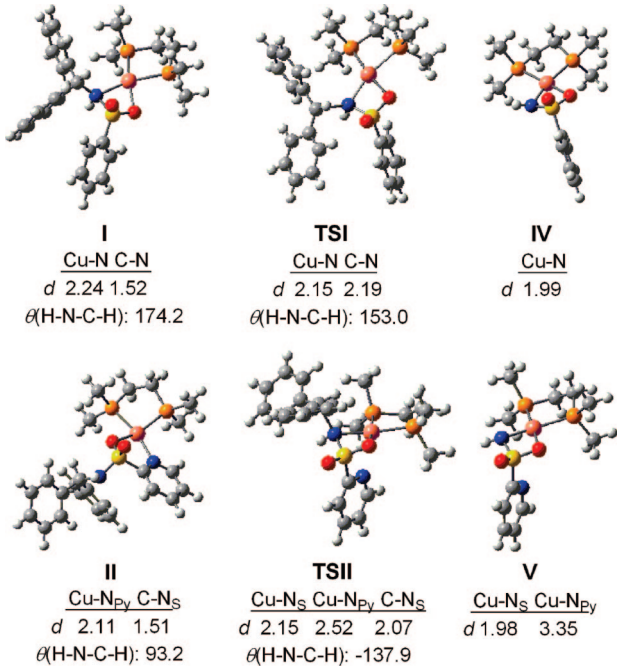

FIGURE 1. Optimized structures of model complexes and transition states most likely involved in the cleavage of the C−N bond of the AFCR products of tosyl imine (**I**, **TSI**, and **IV**) and 2-pyridylsulfonyl imine (**II**, **TSII**, and **V**). Distances (Å) and dihedral angles (°) between selected atoms are also indicated.

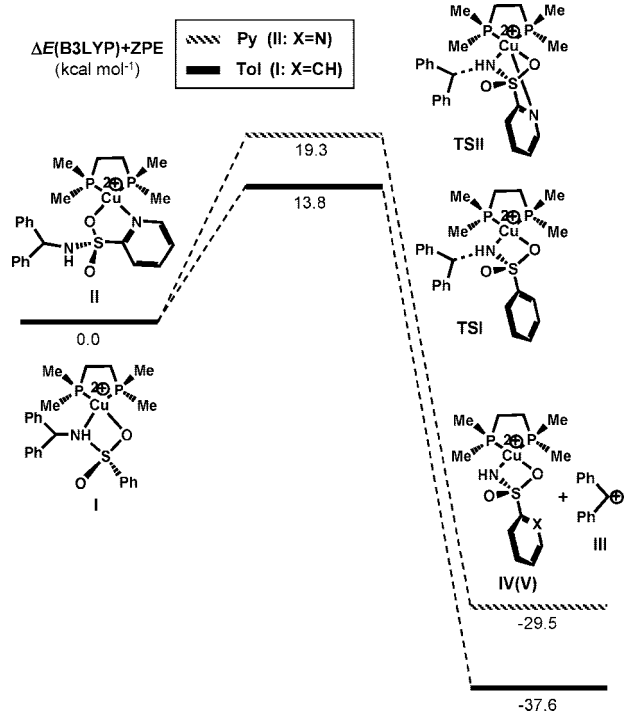

FIGURE 2. Energy profile for the cleavage of the C−N bond during the AFCR from tosyl imine (**I**, **TSI**, and **IV**) and 2-pyridylsulfonyl imine (**II**, **TSII**, and **V**).

the C−N bond is being broken. According to the distances around the metal, in **TSII**, both sulfonamide and pyridyl nitrogen atoms are involved in the coordination. The conformation around the C−N bond in complex **II** locates the diphenylmethyl group far from the phosphorus ligand and allows a π-stacking interaction with the pyridine ring (distance between centroids: 4.74 Å). However, in **TSII**, due to the conformational changes, the diphenylmethyl group is close to the phosphorus ligand (closest distance: 2.58 Å) and any stabilizing π-stacking interaction has been lost. After the cleavage, intermediate **V** (X = N) showing an arrangement of the groups[12] similar to that of **IV** (X = CH) was found.

Regarding the relative stabilities of these intermediates, the energy profile along the reaction coordinate is represented in Figure 2. The reaction for tosyl imine is both kinetically and thermodynamically more favored. The opposite situation is found in the case of the pyridylsulfonyl imine, with an activation barrier 5.5 kcal·mol^{-1} higher than in the case of the tosyl imine. This clearly higher activation barrier for the 2-pyridylsulfonyl substrate nicely explains the selectivity found for the pyridylsulfonyl imine **1b** in AFCR and is in full agreement with the experimental fact that the formation of the triarylmethane product requires a higher temperature from the imine **1b** than from the typical tosyl imine **1a**.

In conclusion, tosyl aryl imines and 2-(pyridyl)sulfonyl aryl imines display a very different behavior in Cu^{II}-catalyzed AFCR with electronically rich heteroaromatic compounds: at room temperature, the former lead to the triarylmethane product through a double Friedel−Crafts process, while the latter afford selectively the diarylmethyl sulfonamide intermediate. DFT theoretical calculations on the second Friedel−Crafts reaction have provided some clues to this different reactive profile, showing that, due to the different mode of coordination of the copper atom to the tosyl and 2-pyridylsulfonyl units, the activation barrier is significantly higher in the second case.

(12) Another complex slightly less stable than **V** (0.3 kcal·mol^{-1}) with only *N*/*N*-coordination was also found (see Supporting Information).

Experimental Section

N-Sulfonyl imines **1a**[13] and **1b**,[6d] as well as the triarylmethanes **3**[14] and **4**[15] were previously described in the literature. See Supporting Information for experimental procedures and characterization data of **1a**, **1b**, **2a**, and **3**.

General Procedure for the Aza-Friedel−Crafts Reaction of *N*-2-Pyridylsulfonyl imine 1b. A solution of $Cu(OTf)_2$ (3.6 mg, 0.01 mmol) and (±)-BINAP (6.8 mg, 0.011 mmol) in CH_2Cl_2 (0.5 mL) was stirred at rt for 20 min before a solution of imine **1b** (24.6 mg, 0.1 mmol) in CH_2Cl_2 (0.5 mL) was added. The mixture was stirred at rt for 5 min, and the electron-rich arene (0.12 mmol) was added. Upon completion (TLC monitoring), the reaction was quenched with saturated aq NH_4Cl, the organic phase was extracted with CH_2Cl_2 (3 × 20 mL), and the combined organic phase was dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography (*n*-hexanes−EtOAc 2:1).

(1-Methyl-1*H*-indol-3-yl)(phenyl)-*N*-[(2-pyridyl)sulfonyl]methanamine (2b): Yield 72%, yellow solid; mp 202−204 °C; ^{1}H NMR (300 MHz, $CDCL_3$) δ 8.24 (ddd, J = 4.6, J = 1.6, and J = 0.8 Hz, 1H), 7.65 (m, 1H), 7.58−7.42 (m, 2H), 7.31−7.10 (m, 8H), 7.05 (m, 1H), 6.61 (s, 1H), 6.51 (s, 1H), 6.24 (d, J = 7.0 Hz, 1H), 6.03 (d, J = 7.0 Hz, 1H), 3.59 (s, 3H); ^{13}C NMR (75 MHz, $CDCL_3$) δ 157.7, 149.5, 140.0, 137.2, 137.1, 127.5, 128.2, 127.3, 126.0, 125.8, 122.1, 122.0, 119.6, 119.5, 114.4, 109.2, 55.5, 32.6; MS-FAB$^+$ *m*/*z*

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337.1 (M^+, 53), 235.1 [$M^+ - SO_2$(2-Py), 100]; HRMS-FAB$^+$ calcd for $C_{21}H_{19}O_2N_3S$ (M^+) 377.1198, found 377.1193.

(1-Methyl-1*H*-pyrrol-2-yl)(phenyl)-*N*-[(2-pyridyl)sulfonyl]methanamine (6b): Yield 72%, white solid; mp 165−167 °C; ^{1}H NMR (300 MHz, $CDCL_3$) δ 8.35 (ddd, $J = 4.6$, $J = 1.6$, and $J = 0.8$ Hz, 1H), 7.60 (m, 2H), 7.25 (m, 1H), 7.15−7.05 (m, 5H), 6.57 (m, 1H), 6.12 (d, $J = 9.1$ Hz, 1H), 5.89 (dd, $J = 3.6$ and $J = 2.8$ Hz, 1H), 5.82 (d, $J = 9.1$ Hz, 1H), 5.58 (m, 1H), 3.69 (s, 3H); ^{13}C NMR (75 MHz, $CDCL_3$) δ 157.4, 149.7, 138.2, 137.4, 130.2, 128.1, 127.4, 127.3, 126.1, 123.6, 122.0, 110.0, 106.7, 55.2, 34.3; MS-FAB$^+$ *m*/*z* 328.1 (M^+, 21), 170.1 ($M^+ - SO_2$(2-Py), 100); HRMS-FAB$^+$ calcd for $C_{17}H_{18}N_3O_2S$ (M^+) 328.1122, found 328.1120.

(5-Methoxythiophen-2-yl)(phenyl)-*N*-[(2-pyridyl)sulfonyl]methanamine (7b): Yield 65%, white solid; mp 153−155 °C; ^{1}H NMR (300 MHz, $CDCL_3$) δ 8.43 (ddd, $J = 4.6$, $J = 1.6$, and $J = 0.8$ Hz, 1H), 7.70−7.59 (m, 2H), 7.26 (ddd, $J = 7.3$, $J = 4.7$, and $J = 1.4$ Hz, 1H), 7.14−7.08 (m, 5H), 6.20 (dd, $J = 3.9$ and $J = 1.1$ Hz, 1H), 5.84 (d, $J = 8.1$ Hz, 1H), 5.80 (d, $J = 3.9$ Hz, 1H), 5.71 (dd, $J = 8.1$ and $J = 1.1$ Hz, 1H), 3.71 (s, 3H); ^{13}C NMR (75 MHz, $CDCL_3$) δ 166.8, 157.6, 149.8, 139.3, 137.5, 129.9, 128.4, 127.9, 127.2, 126.3, 124.2, 122.0, 103.0, 60.2, 58.3; MS-FAB$^+$ *m*/*z* 361.1 (M^+, 11); HRMS-FAB$^+$ calcd for $C_{17}H_{18}N_2O_3S_2$ (M^+) 361.0666, found 361.0661.

General Procedure for the Synthesis of Triarylmethanes from *N*-Tosyl Imine 1a. A solution of $Cu(OTf)_2$ (3.6 mg, 0.01 mmol) and (±)-BINAP (6.8 mg, 0.011 mmol) in CH_2Cl_2 (0.5 mL) was stirred at room temperature for 20 min before a solution of sulfonyl imine **1a** (25.9 mg, 0.1 mmol) in CH_2Cl_2 (0.5 mL) was added. The mixture was stirred at room temperature for 5 min, and then the electron-rich arene (0.12 mmol) was added. Upon completion (TLC monitoring), the reaction was quenched with saturated aq NH_4Cl, the organic phase was extracted with CH_2Cl_2 (3 × 20 mL), and the combined organic phase was dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography (*n*-hexanes−EtOAc 4:1).

Bis(1-methyl-1*H*-pyrrol-2-yl)(phenyl)methane (4):.[15] Yield 42%, white solid; mp 81−82 °C (lit[15b] 85−86 °C); ^{1}H NMR (300 MHz, $CDCL_3$) δ 7.26−7.15 (m, 3H), 7.08−7.02 (m, 2H), 6.51 (dd, $J =$ 2.2 and $J = 2.0$ Hz, 2H), 5.94 (dd, $J = 3.5$ and $J = 2.8$ Hz, 2H), 5.41 (ddd, $J = 3.3$, $J = 1.9$, and $J = 0.9$ Hz, 2H), 5.19 (s, 1H), 3.31 (s, 6H); ^{13}C NMR (75 MHz, $CDCL_3$) δ 141.3, 133.5, 128.8, 128.6, 128.4, 128.2, 126.6, 122.0, 108.9, 106.4, 42.0, 33.9; MS-ESI$^+$ *m*/*z* 251.1 ($(M + H)^+$, 100), 301.0 ($M^+ - CH_3$, 22); HRMS-ESI$^+$ calcd for $C_{17}H_{18}N_2$ [$(M + H)^+$] 251.1548, found 251.1543.

Bis(5-methoxythiophen-2-yl)(phenyl)methane (5): Yield 73%, yellow oil; ^{1}H NMR (300 MHz, $CDCL_3$) δ 7.25−7.15 (m, 5H), 6.32 (dd, $J = 3.8$ and $J = 1.1$ Hz, 2H), 5.92 (d, $J = 3.8$ Hz, 2H), 5.40 (s, 1H), 3.75 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.7, 143.2, 133.3, 128.4, 128.3, 127.1, 123.2, 102.8, 60.1, 48.1; MS-ESI$^+$ *m*/*z* 317.1 ($(M + H)^+$, 100); HRMS-ESI$^+$ calcd for $C_{17}H_{16}O_2S_2$ [$(M + H)^+$] 317.0670, found 317.0665.

Acknowledgment. Financial support of this work by the Ministerio de Educación y Ciencia (MEC, project CTQ2006-01121) and Consejería de Educación de la Comunidad de Madrid, Universidad Autónoma de Madrid (UAM/CAM CCG07-UAM/PPQ-1799) is gratefully acknowledged. J.E. thanks the MEC for a predoctoral fellowship. A generous allocation of computer time at the Centro de Computación Científica de la UAM is also acknowledged.

Supporting Information Available: Copies of NMR spectra. Experimental procedures and characterization data for **1a**, **1b**, **2a**, and **3**. Full citation for ref 9, Cartesian coordinates for all optimized structures and their electronic energies and ZPVEs. This material is available free of charge via the Internet at http://pubs.acs.org.

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