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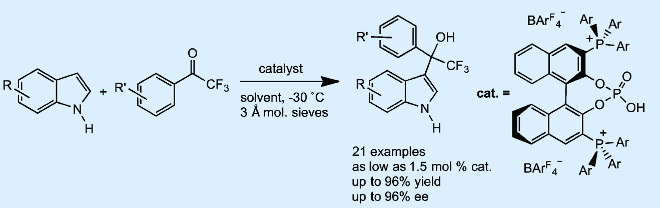
Asymmetric Arylation of 2,2,2-Trifluoroacetophenones Catalyzed by Chiral Electrostatically-Enhanced Phosphoric Acids

Jie Ma and Steven R. Kass*

Department of Chemistry, University of Minnesota, 207 Pleasant Street SE, Minneapolis, Minnesota 55455, United States

Supporting Information

ABSTRACT: A series of highly reactive metal-free chiral phosphoric acids possessing positively charged phosphonium ion substituents are reported and have been applied to Friedel−Crafts alkylations of indoles and 2,2,2-trifluoromethyl aryl ketones. These catalysts are orders-of-magnitude more active and have similar or better enantioselectivities than their noncharged analogues. High tolerance to a range of substrates with electron-withdrawing and electron-donating substituents was also observed.



Indoles are among the most important type of nitrogen-containing heterocyclic scaffolds, as they are widely found in natural products,[1] pharmaceuticals,[2] and synthetic chemicals.[3] Most of these indole-based compounds possess special chemical properties as well as bioactivities, and thus, they have attracted widespread attention.[4] Fluorinated species are another important class of organic materials since the small size and high electronegativity of a fluorine atom lead to compounds with remarkably different properties than their fluorine-free analogues.[5] A combination of fluorine substituents on indole frameworks leading to novel bioactivities and pharmaceutical properties made the synthesis of such compounds inviting targets.[6,7]

A number of strategies have been devised to incorporate fluorine atoms into indole derivatives.[7c,8] Given the electron-rich nature and the enhanced reactivity in electrophilic alkylations (especially at the C-3 position) of this heterocycle,[9] one of the most straightforward methods for synthesizing these derivatives is to carry out a Friedel−Crafts alkylation with an indole and a fluorine-containing electrophile.[10] This type of transformation is also a powerful method for the formation of carbon−carbon bonds that can be applied to construct optically active compounds.[11] In general, these reactions proceed in good yields and high enantioselectivities with suitable catalysts. For the specific case of Friedel−Crafts alkylations of indole derivatives with 2,2,2-trifluoromethyl aryl ketones, inorganic bases,[12] cinchona alkaloids,[13] guanidine,[14] trifluoromethanesulfonic acid,[15] and phosphoric acids[16] were reported to be successful catalysts. Most of these studies, however, focused on either racemic products or bis-coupled adducts. There are only a few reports on asymmetric alkylations, and these required either long reaction times (i.e., up to 96 h)[16] or harsh reaction conditions (i.e., up to 9 kbar pressure)[13] presumably because it is a challenge to trigger the alkylation and terminate it at the monoarylated stage.[15,16] More effective enantioselective catalysts, consequently, are still needed for this transformation.

In general, there is a good correlation between reactivity and the acidity of related organocatalysts.[17] For this reason, electron-withdrawing substituents such as trifluoromethyl or nitro groups are sometimes incorporated into phenyl rings at the 3 and 3′ positions of BINOL-derived phosphoric acids.[18,19]

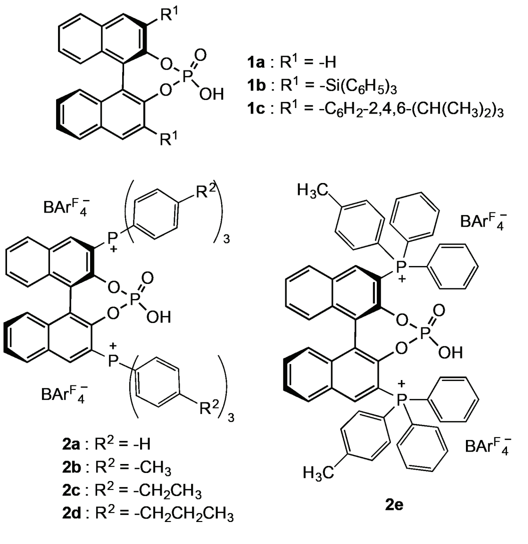


Figure 1. Catalysts used in this work.

In previous studies from our laboratory, positively charged ion centers were found to enhance the catalytic reactivities of phenols,[20] thioureas,[21] and phosphoric acids[22] by orders of magnitude. This approach was also used to obtain good to excellent enantioselectivities for the alkylation of indoles with *trans-β*-nitrostyrene derivatives using chiral thioureas.[23] As a result, we decided to develop a series of BINOL-based phosphoric acid catalysts possessing 3,3′-phosphonium ion substituents (Figure 1) that were prepared using reported synthetic methods.[24] These large groups provide needed steric bulk and two acidity-enhancing positively charged ion centers. Their performance in the

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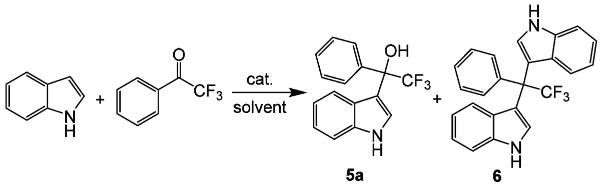
Friedel−Crafts reactions of indole derivatives with 2,2,2-trifluoromethyl aryl ketones are reported herein.

This investigation was initiated by examining the reaction of indole (**3a**) with 2,2,2-trifluoroacetophenone (**4a**) using the tri(*p*-tolyl)phosphonium ion containing phosphoric acid at the 3,3′-positions of the (*R*)-BINOL backbone (i.e., **2b**) along with the noncoordinating tetrakis(3,5-bis(trifluoromethyl)phenyl)-borate ($BAr^F{}_4{}^-$) counterion; more common and interacting anions lead to less active catalysts.[20−22] At room temperature in CH_2Cl_2 with a 5 mol % catalyst loading, both the desired and undesired mono- and bis-coupled products (**5a** and **6**, respectively) were formed, respectively (eq 1). This led to a loss of yield for the former species, as previously has been reported with other strong acid catalysts,[12,15] and the enantioselectivity was also poor (Table 1, entry 1). To our delight, when the reaction temperature was reduced to 0 °C, the formation of the bis-coupled byproduct was nearly eliminated and a dramatic increase in the ee from 17% to 85% was observed (entry 2). A further decrease to −30 °C only led to a 1% increase in the ee at the expense of a much longer reaction time (entry 3), and this result was surpassed by adding 3 Å molecular sieves (MS) at 0 °C (i.e., 87% ee, entry 4). Other MS (4 Å, 5 Å, and 13X) decreased both the yield and the enantioselectivity (entries 5−7). Attempts to improve this transformation with inorganic salts (Na_2SO_4, NaCl, $MgSO_4$, and $CaCl_2$) as drying agents also led to poorer results (entries 8−11). An increase in the catalyst loading to 10 mol % did not improve the enantioselectivity further (entry 12) so the other phosphonium ion containing species were screened with 5 mol % catalyst at 0 °C in the presence of 3 Å MS. The triphenylphosphonium containing derivative **2a** gave a much lower yield (30%) and selectivity (77% ee) (entry 13), while the tri(*p*-ethylphenyl) and tri(*p*-propylphenyl)phosphonium derivatives **2c** and **2d** gave similar results to **2b** (entries 14−15). Interestingly, the diphenyl(*p*-tolyl)phosphonium ion tagged catalyst **2e**, which is sterically similar to **2a** and electronically in between **2a** and **2b**, afforded the product with a reduced yield and ee relative to **2b** of 68% and 84%, respectively. These results suggest that the large difference between **2a** and **2b** is due to electronic effects brought about by replacing a hydrogen atom with a methyl group on each of the phenyl rings attached to the phosphorus atom. A lower temperature experiment at −30 °C was also performed with 3 Å MS, and a 3% increase in ee to 90% was observed (entry 17). A further drop in the temperature to −50 °C was impractical due to reduced catalyst solubility.



5a **6**

(1)

Table 1. Optimization Conditions for the Reaction of Indole with 2,2,2-Trifluoroacetophenone[a]

entry	cat.	*t* (°C)	additive	time (h)	yield of **5a** (%)[b]	ee (%)[c]
1	**2b**	20		5	48	17
2	**2b**	0		22	90	85
3	**2b**	−30		96	87	86
4[d]	**2b**	0	3 Å MS	22	92	87
5[d]	**2b**	0	4 Å MS	22	87	66
6[d]	**2b**	0	5 Å MS	21	79	80
7[d]	**2b**	0	13X MS	21	58	85
8[e]	**2b**	0	Na_2SO_4	20	81	83
9[e]	**2b**	0	NaCl	20	86	80
10[e]	**2b**	0	$MgSO_4$	20	83	80
11[e]	**2b**	0	$CaCl_2$	20	81	80
12[d,f]	**2b**	0	3 Å MS	20	87	87
13[d]	**2a**	0	3 Å MS	22	30[g]	77
14[d]	**2c**	0	3 Å MS	22	91	86
15[d]	**2d**	0	3 Å MS	22	86	86
16[d]	**2e**	0	3 Å MS	22	68[g]	84
17[d]	**2b**	−30	3 Å MS	40	85	90

[a] Experiments performed with 0.140 mmol of indole, 0.168 mmol of 2,2,2-trifluoroacetophenone, 0.007 mmol of catalyst in 0.25 mL of CH_2Cl_2. [b] Isolated yield. [c] Determined by chiral HPLC. [d] 5 mg of MS were used. [e] 1.0 equiv of salt was used. [f] 0.014 mmol catalyst was employed. [g] Starting material was present.

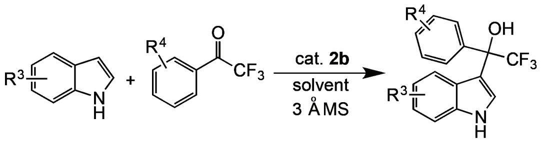
Reaction media were examined next with catalyst **2b**, and the results are summarized in Table 2. Solvents were found to have a large influence on the reactivity and enantioselectivity. For example, $CHCl_3$ (entry 2) led to both a lower yield and enantioselectivity than CH_2Cl_2 (entry 1). Chlorobenzene (entry 3) and 1,2-dichloroethane (DCE, entry 4) gave similar results (91% and 89% yields along with 62% and 63% ee), neither of which is as good as CH_2Cl_2. Several mixtures using CH_2Cl_2 and aromatic solvents (i.e., benzene, toluene, *m*-xylene) or CCl_4 were also tested (entries 5−8). None of these screenings led to better results than when CH_2Cl_2 was used.

Table 2. Screening of Reaction Solvents[a]

entry	solvent	time (h)	yield of **5a** (%)[b]	ee (%)[c]
1	CH_2Cl_2	22	92	87
2	$CHCl_3$	22	37	67
3	C_6H_5Cl	22	91	62
4	DCE	22	89	63
5	1:1 CH_2Cl_2/C_6H_6	20	86	84
6	1:1 $CH_2Cl_2/C_6H_5CH_3$	20	81	83
7	1:1 CH_2Cl_2/1,3-$(CH_3)_2C_6H_4$	20	88	83
8	1:1 CH_2Cl_2/CCl_4	20	89	85

[a] Experiments performed with 0.140 mmol of indole, 0.168 mmol of 2,2,2-trifluoroacetophenone, 0.007 mmol of catalyst **2b**, and 5 mg of 3 Å MS in 0.25 mL of solvent at 0 °C. [b] Isolated yield. [c] Determined by chiral HPLC.

The scope of this transformation was examined at 0 °C using 5 mol % **2b**, CH_2Cl_2 as the solvent, and 3 Å MS as a drying agent (eq 2). As summarized in Table 3, a wide variety of substituents including electron-withdrawing and electron-donating groups on either reactant were tolerated. With a few exceptions, excellent yields (82−94%) and good enantioselectivities (79−91% ee) were obtained at 0 °C (entry 1−19). Halide substituents at the 5-positon of indole did not affect the selectivity (85−87% ee) (entries 1−2) relative to the parent compound (i.e., R^3, $R^4 = H$), whereas electron-donating groups at the 5- and 6-positions led to reduced enantioselectivities of 79% and 48% ee (entries 3−4). Interestingly, while 6-methylindole (**3e**) gave the worst product enantiomeric purity (48% ee), its isomer 7-methylindole (**3h**) provided the highest enantioselectivity (91% ee, entry 7). This difference should be quite helpful in developing computational models for the mechanism of this reaction. Other substituents at the 7-position of indole (Cl, Br, Et) had no impact on the enantiomeric excess (entries 5−6 and 8), but 7-bromoindole (**3g**) slowed the reaction leading to approximately half the yield over the same time period. Introduction of electron-withdrawing



(2)

3a: R^3 = H-
3b: R^3 = 5-F-
3c: R^3 = 5-Br-
3d: R^3 = 5-MeO-
3e: R^3 = 6-Me-
3f : R^3 = 7-Cl-
3g: R^3 = 7-Br-
3h: R^3 = 7-Me-
3i : R^3 = 7-Et-

4a: R^4 = H-
4b: R^4 = 4-F-
4c: R^4 = 4-Cl-
4d: R^4 = 4-Br-
4e: R^4 = 4-Me-
4f : R^4 = 4-CF_3-
4g: R^4 = 3-Cl-
4h: R^4 = 3,5-F_2-
4i : R^4 = 3,5-Cl-F-
4j : R^4 = 3,5-Cl_2-
4k: R^4 = 2,3,4,5,6-F_5-
4l : $PhCOCF_2Cl$

5a: R^3 = H-, R^4 = H-
5b: R^3 = 5-F-, R^4 = H-
5c: R^3 = 5-Br-, R^4 = H-
5d: R^3 = 5-MeO-, R^4 = H-
5e: R^3 = 6-Me-, R^4 = H-
5f : R^3 = 7-Cl-, R^4 = H-
5g: R^3 = 7-Br-, R^4 = H-
5h: R_3 = 7-Me-, R^4 = H-
5i: R^3 = 7-Et-, R^4 = H-
5j: R^3 = H-, R^4 = 4-F-
5k: R^3 = H-, R^4 = 4-Cl-
5l: R^3 = H-, R^4 = 4-Br-
5m: R^3 = H-, R^4 = 4-Me-
5n: R^3 = H-, R^4 = 4-CF_3-
5o: R^3 = H-, R^4 = 3-Cl-
5p: R^3 = H-, R^4 = 3,5-F_2-
5q: R^3 = H-, R^4 = 3,5-Cl-F-
5r : R^3 = H-, R^4 = 3,5-Cl_2-
5s: R^3 = H-, R^4 = 2,3,4,5,6-F_5-
5t : 3-(CPh(OH)(CF_2Cl))indole

Table 3. Reaction Scope[a]

entry	substrate	adduct	time (h)	yield (%)[b]	ee (%)[c]
1	**3b** + **4a**	**5b**	26	85	85
2	**3c** + **4a**	**5c**	26	82	87
3	**3d** + **4a**	**5d**	20	84	79
4	**3e** + **4a**	**5e**	20	83	48
5	**3f** + **4a**	**5f**	28	87	87
6	**3g** + **4a**	**5g**	28	41	88
7	**3h** + **4a**	**5h**	14	92	91
8	**3i** + **4a**	**5i**	20	85	88
9	**3a** + **4b**	**5j**	20	92	90
10	**3a** + **4c**	**5k**	20	88	89
11	**3a** + **4d**	**5l**	20	94	89
12	**3a** + **4e**	**5m**	28	86	85
13	**3a** + **4f**	**5n**	20	90	88
14	**3a** + **4g**	**5o**	20	89	85
15	**3a** + **4h**	**5p**	20	91	86
16	**3a** + **4i**	**5q**	20	85	86
17	**3a** + **4j**	**5r**	20	88	88
18	**3a** + **4k**	**5s**	24	28	64
19	**3a** + **4l**	**5t**	28	36	84
20[d]	**3h** + **4a**	**5h**	18	96	95
21[d]	**3a** + **4b**	**5j**	42	91	93
22[d,e]	**3h** + **4a**	**5h**	65	93	96
23[f]	**3h** + **4a**	**5h**	70	96	96

[a] Experiments performed with 0.140 mmol of indole, 0.168 mmol of 2,2,2-trifluoroacetophenone, 5 mol % of **2b** and 5 mg of 3 Å MS in 0.25 mL of CH_2Cl_2 at 0 °C. [b] Isolated yield. [c] Determined by chiral HPLC. [d] Reaction run at −30 °C with 10 mg of 3 Å MS. [e] 1.5 mol % catalyst. [f] Larger scale reaction with 0.840 mmol of 7-methylindole, 1.008 mmol of 2,2,2-trifluoroacetophenone, 1.5 mol % of **2b** and 30 mg of 3 Å MS in 1.50 mL of CH_2Cl_2 at −30 °C; 247.5 mg of product was produced.

groups (F, Cl, Br, and CF_3) to the para position of 2,2,2-trifluoroacetophenone gave slight improvements of 1−3% in the ee (entries 9−11 and 13), whereas an electron-donating methyl group at the same location lowered the enantioselectivity by an equivalent amount (entry 12). Halogen substituents at one or both of the meta positions in 2,2,2-trifluoroacetophenone had little, if any, impact on the reaction outcome (entries 14−17). Perfluoroacetophenone (**4k**) was found to give both a low yield (28%) and ee (64%, entry 18), while 2-chloro-2,2-difluoroacetophenone (**4l**) also gave a low yield (36%) but without much difference in the enantioselectivity (i.e., an 84% ee was observed, entry 19). For the two reactions that gave ≥90% ee at 0 °C (entries 7 and 9), a decrease in temperature to −30 °C resulted in improved selectivities of 95% and 93% ee (entries 20−21). The former transformation was further examined with a decreased catalyst loading of 1.5 mol %, and the enantioselectivity was preserved with a measured ee of 96% (entry 22). A larger scale reaction was also performed with six times more material and reactant weights in excess of 100 mg along with a catalyst loading of 1.5 mol %. This led to similar results to the small-scale transformation and afforded a 96% yield and a 96% ee (entry 23).

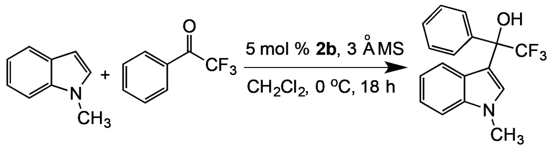
To compare the reactivity and enantioselectivity of our charged BINOL phosphoric acid derivative **2b** with noncharged analogues, three different structures (**1a**−**1c**) were used. These species included the unsubstituted BINOL phosphoric acid (**1a**), a sterically similar structure with triphenylsilyl substituents at the 3- and 3′-positions (**1b**), and 3,3′-bis(2,4,6-triisopropylphenyl)-BINOL phosphoric acid (**1c**). The last of these derivatives is known as TRIP and is one of the most successful phosphoric acid catalysts that has been reported.[25] 7-Methylindole (**3h**) and 2,2,2-trifluoroacetophenone (**4a**) in CH_2Cl_2 at −30 °C with a 1.5 mol % catalyst loading were used as the test reaction, and the results after 65 h are given in Table 4. The least sterically hindered parent structure with hydrogen atoms at the 3 and 3′-positions (**1a**) was ineffective. Only a 1% yield was obtained, and this material was essentially racemic (i.e., 1% ee, entry 1). The catalyst **1b** with two triphenylsilyl substituents only gave a yield of 9%, but this product was formed in 93% ee (entry 2). TRIP is more reactive, but only resulted in a 43% yield. The observed ee of 97%, however, is quite impressive (entry 3). Our charged phosphonium ion tagged phosphoric acid catalyst **2b** proved to be superior in that an excellent yield of 93% was obtained along with a 96% ee (entry 4). Assuming second-order kinetics for these processes,[26] one can estimate that **2b** is more reactive than **1a**−**1c** by factors of 690, 70, and 10, respectively, but still is as selective as the best of these noncharged species.

Table 4. Catalyst Comparisons[a]

entry	catalyst	yield (%)[b]	ee (%)[c]
1	**1a**	1	1
2	**1b**	9	93
3	**1c**	43	97
4	**2b**	93	96

[a] Experiments performed with 0.140 mmol of 7-methylindole, 0.168 mmol of 2,2,2-trifluoroacetophenone, 1.5 mol % of the desired catalyst, and 10 mg of 3 Å MS in 0.25 mL of CH_2Cl_2 at −30 °C. [b] Isolated yield after 65 h. [c] Determined by chiral HPLC.

To investigate the role of hydrogen bonding between the phosphoryl oxygen and indole substrate, a reaction lacking this interaction was performed with 1-methylindole and 2,2,2-trifluoroacetophenone at 0 °C (eq 3). The yield after 18 h was 71%, and the product was formed with a 24% ee. These results show that the selectivity is significantly lower and that the yield is



5u

(3)

worse than when indole is used (92% yield and 87% ee in 22 h). These findings indicate that indole reacts 2.6 times faster than *N*-methylindole even though the latter compound is a better nucleophile. This suggests that the P=O···H−N hydrogen bond is important both in terms of the reaction rate and the enantioselectivity as previously reported.[27]

In summary, we demonstrated a successful application of chiral electrostatically enhanced phosphoric acids to a Friedel−Crafts alkylation to generate fluorinated indole derivatives. A wide scope of substrates is tolerated, giving the corresponding products in good yields and enantioselectivities. A larger synthetic scale reaction affording 250 mg of product was carried out with little, if any, change in the performance of the reaction. Our charged catalyst **2b** was also found to outperform noncharged analogues in terms of reaction rates by orders of magnitude, yet still gave as good or better enantioselectivities.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b00900.

Experiment procedures, NMR spectra, and HPLC traces (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: kass@umn.edu.

ORCID

Steven R. Kass: 0000-0001-7007-9322

Notes

The authors declare no competing financial interest.

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