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Soft-Hard Acid/Base-Controlled, Oxidative, *N*-Selective Arylation of Sulfonanilides *via* a Nitrenium Ion

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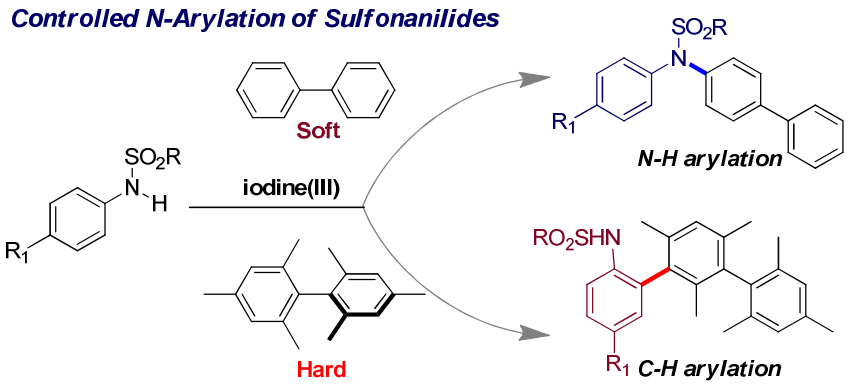
Abstract



In iodine (III)-catalyzed, dehydrogenative arylations of sulfonanilides, the functionalization of C-C bonds is preferred over the functionalization of C-N bonds. Herein, an unprecedented *N*-selective arylation of sulfonanilides using soft-hard acid-base (SHAB) control by a nitrenium ion over a carbenium ion is reported. Treatment of sulfonanilides with iodine (III) led to the formation of nitrenium ions (soft), which preferentially react with biphenyls (soft) over bimesityl (hard) to generate C-N bonds. The iodine (III) was generated *in situ* by using PhI and mCPBA at room temperature.

Introduction

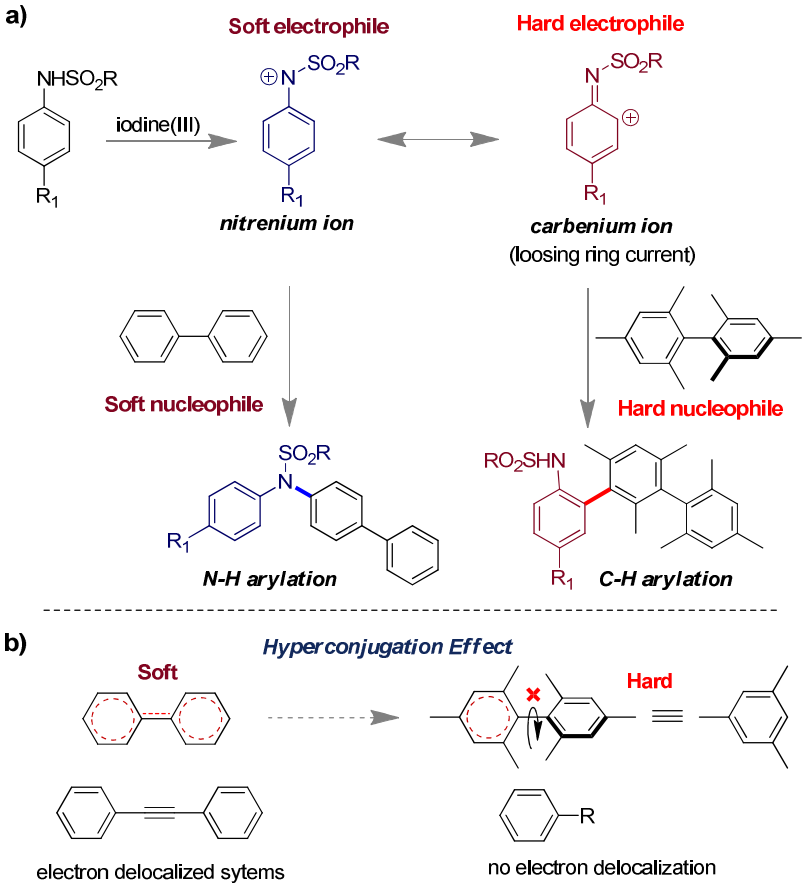
The development of new sustainable methods[1] for C-N bond synthesis is of interests due to the abundance of nitrogenous compounds in many synthetic intermediates, pharmaceutical agents, natural products and biologically active molecules.[2] Dehydrogenative C-N coupling reactions[3] by direct functionalization of C-H and N-H bonds are of great importance due to their advantages of step and atom economy, not requiring prefunctionalization of the starting materials, and so on.[4] Many reports are available on transition metal catalyzed/mediated C-H amination reactions;[5] however, metal-free hypervalent iodine (III) reagents are highly efficient owing to their easy accessibility, low toxicity, high reactivity and safe handling.[6] A limited number of intermolecular C-H amination reactions using hypervalent iodine (III) are known,[7] and most of the reported reactions are based on carbonamide substrates and use catalytic or (super) stoichiometric iodine (III) reagents.[8] The use of either stoichiometric or super-stoichiometric amounts of iodine (III) reagents can be disadvantageous because of the generation of aryl iodide (ArI) by-products. Interestingly, a catalytic amount of ArI with an appropriate oxidant could be used in place of the hypervalent iodine (III) reagents[9] which inspired us to develop conditions for generating iodine (III) *in situ* for the formation of C-N bonds. To the best of our knowledge, there have been no reports on organocatalytic, intermolecular, oxidative *N*-arylations of sulfonanilides.

Results and Discussion

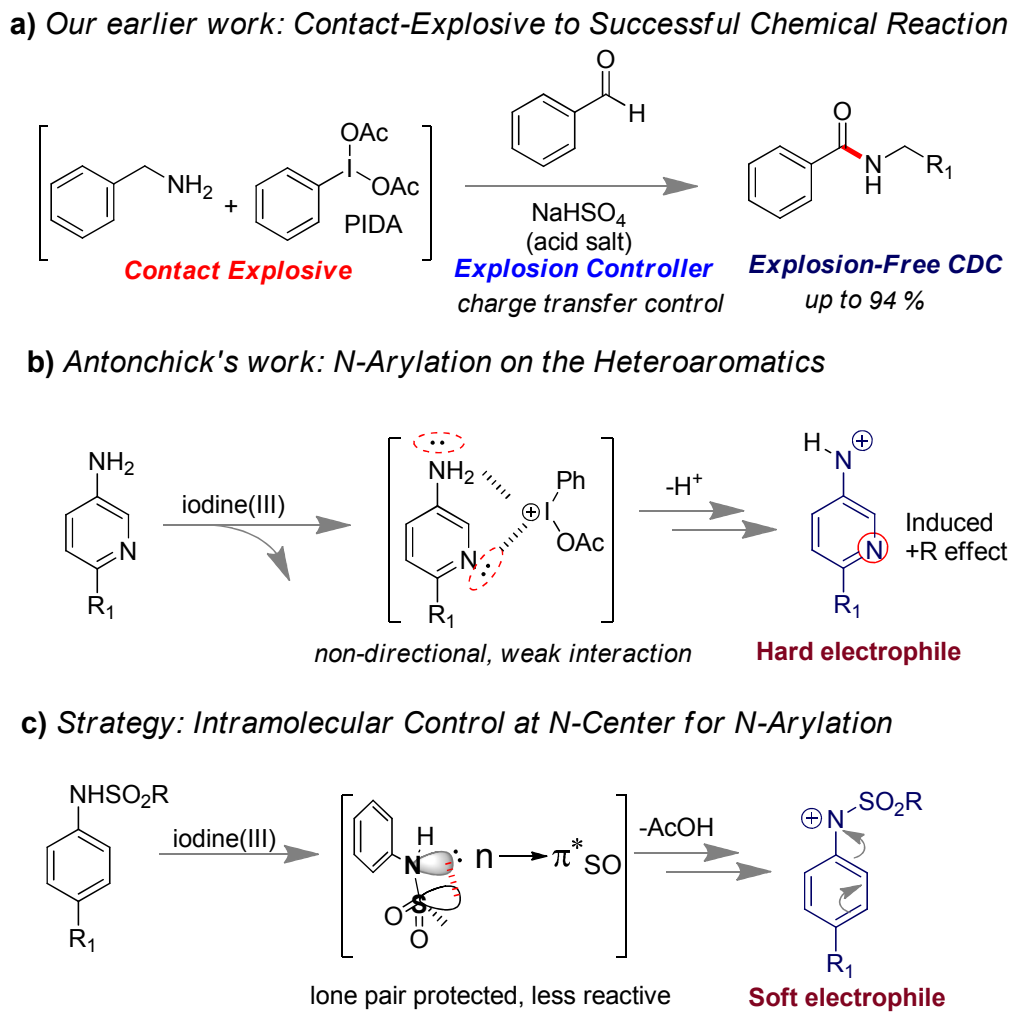
The local environment can control the reactivity of certain chemical systems.[10] Cooperative multiple weak interactions[11] like hydrophobic effects,[12] charge-transfers,[13] halogen bonding,[14] cation-π interactions,[15] and anion-π interactions[16] are often explored in chemical synthesis.[17] As a continuation of our research interest towards controlling the reactivity of non-prefunctionalized aromatic systems[18] by weak interactions,[19] an unprecedented, *N*-selective

arylation of sulfonanilides *via* the regulation of the reactivity of a nitrenium ion[20] over a carbenium ion[21] by soft-hard acid-base (SHAB) control is reported.[22] Nitrenium ions are well-known soft electrophiles[23] whereas carbenium ions can be hard electrophiles because when they are formed from the corresponding nitrenium ion, the aromaticity is broken (Scheme 1a). Additionally, due to electron delocalization, the biphenyls or 1,2-diphenyl acetylenes are expected to act as soft nucleophiles. Analogous to alkyl substituted arenes, the bimesityl can behave like a hard nucleophile because of the restricted rotation between the two aromatic rings (Scheme 1b).[21] Through SHAB control,[24] the competitive reactivity of the nitrenium and carbenium ions is demonstrated herein (Scheme 1) for the oxidative, *N*-selective arylation of sulfonanilides.

Scheme 1. *N*-Arylation vs. *C*-Arylation by SHAB Control



Scheme 2. Reactivity control at the *N*-center. a) Charge transfer control.[13] b) *N*-Arylation of heteroaromatics.[7c] c) Control by the lone pair at *N*-center

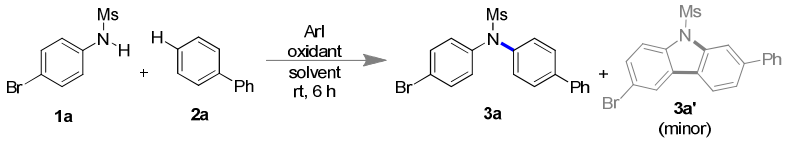


Sulfonanilides are an important class of synthetic scaffolds in organic synthesis. Due to the strong electron-withdrawing effect of the attached sulfonyl group, sulfonanilides have a unique reactivity towards hypervalent iodine (III) reagents[25] over carbonamides.[26] Couplings between sulfonanilides and aromatic substrates were first demonstrated by Canesi and co-workers who documented the formation of a nitrenium ion.[27] In addition, the reactivity of the *N*-center can be controlled either intra- or intermolecularly. We have previously reported a

successful cross dehydrogenative coupling (CDC) reaction using contact explosives, primary amines, and phenyliodine (III) diacetate (PIDA) under maximum contact between the reactants, i.e., solvent-free conditions.[13] The charge transfer basicity of the amine was controlled using an acidic salt, $NaHSO_4$ (Scheme 2a). Antonchick's *N*-arylation of heteroaromatics is shown in Scheme 2b,[7c] and the pyridinium nitrogen center may have reduced the reactivity of PIDA. The absence of an electron-withdrawing group on the amine results in the formation of a highly reactive nitrenium ion that can be considered a hard electrophile. Thus, the reactivity of the nitrenium ion was found to be selective with hard arene nucleophiles. Moreover, due to the $n \rightarrow \pi^*_{SO}$ interaction, the lone-pair of the sulfonanilide nitrogen was protected and led to a softer electrophile for *N*-arylation.[19a] Due to the presence of electron-donating -Me groups and restricted electron mobility between the two aromatic rings, the bimesityl is anticipated to be a relatively harder nucleophile. This hypothesis was successfully proved when the C-arylated product was exclusively isolated from the reaction of sulfonanilide and bimesityl under the standard reaction conditions (*vide infra*).

The reactivity of sulfonanilides in selective *N*-H arylation with arenes under conditions that generate hypervalent iodine (III) *in situ* is shown. The iodine (III) was generated using PhI (30 mol %) and *meta*-chloroperbenzoic acid (*m*CPBA) as the oxidant.[9b, 28] At room temperature, one $C(sp^2)$-H and one $N(sp^3)$-H were functionalized in the intermolecular dehydrogenative C-N bond formation. We have previously demonstrated an intermolecular annulation between sulfonanilides and arenes for the synthesis of carbazoles in which the C-H arylation of the sulfonanilides was established as the intermediate step. C-H Arylation reactions with alkyl- or alkoxy-substituted arenes were found to occur *via* a nitrenium ion.[21]

Table 1. Optimization of the Method[a]



entry	ArI (mol%)	oxidant (1.5 equiv)	solvent	**3a** (%)[b]
1	PhI (30)	mCPBA	HFIP	83
2	PhI (30)	mCPBA	TFE	69
3	4-NO2-C_6H_4-I (30)	mCPBA	HFIP	35
4	4-Me-C6H4-I (30)	mCPBA	HFIP	75
5	PhI (20)	mCPBA	HFIP	77
6	PhI (30)	mCPBA	DCM	27
7	PhI (30)	mCPBA	ACN	66
8	PhI (30)	mCPBA	HFIP/DCM (2:1)	87
9	PhI (30)	DTBP	HFIP	NR
10	PhI (30)	TBHP	HFIP	NR

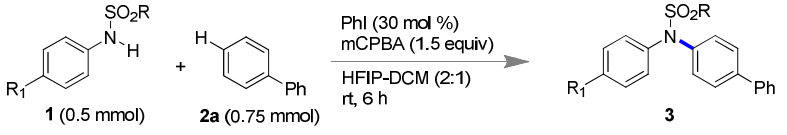
[a]Unless noted otherwise, 1.5 equiv of **2a** was used. [b]Isolated Yields.

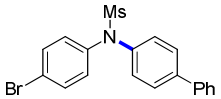
During the optimization of the reaction conditions, *N*-(4-bromophenyl)methanesulfonamide (**1a**) and biphenyl (**2a**) were used as the model substrates. The optimal conditions for the reaction were determined in the presence of 30 mol % of iodobenzene (PhI) and 1.5 equiv of oxidant (*m*CPBA) over 6 h in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP)-dichloromethane (DCM) (2:1) at room temperature. The product (**3a**) was isolated in a satisfactory yield of

87% (Table 1, entry 8). However, the yield was reduced to 83% in pure HFIP (Table 1, entry 1). When using 2,2,2-trifluoroethanol (TFE) as the only solvent, the product formation noticeably dropped to 69% (Table 1, entry 2). Use of other solvents such as dichloromethane (DCM) and acetonitrile (ACN) yielded inferior results (Table 1, entries 6 and 7). Aryl iodides with electron-withdrawing as well as with electron-donating groups also led to inferior results (Table 1, entries 3 and 4). No desired product could be isolated when either di-tert-butyl peroxide (DTBP) or tert-butyl hydroperoxide (TBHP) were used as oxidants (Table 1, entries 9 and 10). Reducing the loading of iodobenzene to 20 mol % led to poorer results (Table 1, entry 5). The use of 1.5 equiv of biphenyl with respect to the sulfonanilide substrate was identified as the optimum stoichiometry for the reaction. Under the optimized conditions, along with the desired diarylamine, a trace amount (6%) of a minor product, carbazole derivative **3a'**, was isolated as well.

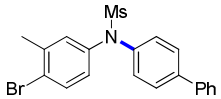
The scope of the *N*-arylation reaction by sulfonanilides is shown in Scheme 3, and the desired diarylamines were isolated in good yields. Halides as well as phenyl groups containing sulfonanilides were well-tolerated (**3a-g, 3o,** and **3r**). Electron-withdrawing anilides containing -COPh, -NO_2, and -CN groups were not completely consumed during the reaction and resulted in lower yields of the corresponding products (**3n** and **3p-q**). Diarylamines from sulfonanilide substrates containing electron-donating groups were also isolated in reasonable yields (**3b, 3h-m,** and **3s-u**). Steric effects were one reasons for the low yields of certain substrates (**3j-k** and **3n**). Furthermore, anilides bearing different sulfonyl groups, such as –SO_2Ph, -Ts, and -Ns, were also found to be efficient in the oxidative C-N coupling protocol (**3r-u**). The structure of compound **3a** was characterized by X-ray crystallographic analysis.

Scheme 3. *N*-Arylation with biphenyls

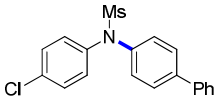




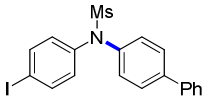
3a, 87%



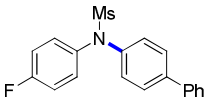
3b, 75%



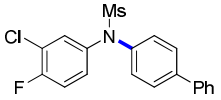
3c, 79%



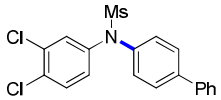
3d, 83%



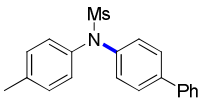
3e, 58%



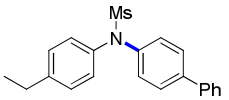
3f, 55%



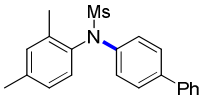
3g, 56%



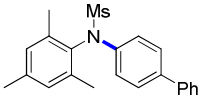
3h, 61%



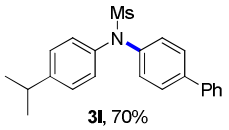
3i, 63%



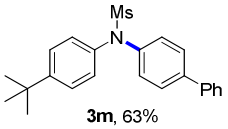
3j, 49%



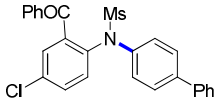
3k, 45%



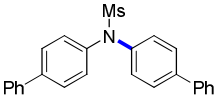
3l, 70%



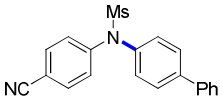
3m, 63%



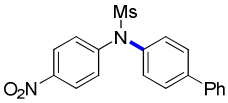
3n, 50%



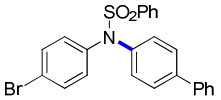
3o, 76%



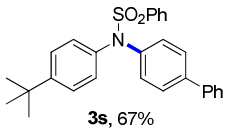
3p, 35%



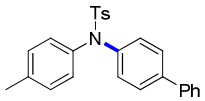
3q, 33%



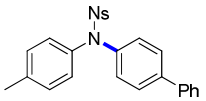
3r, 78%



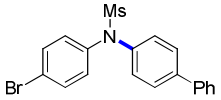
3s, 67%



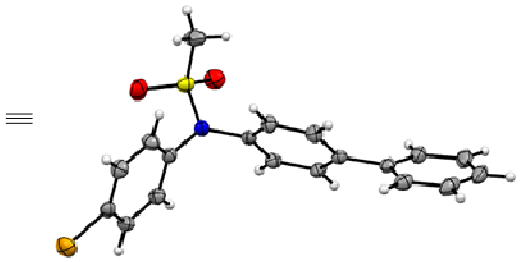
3t, 70%



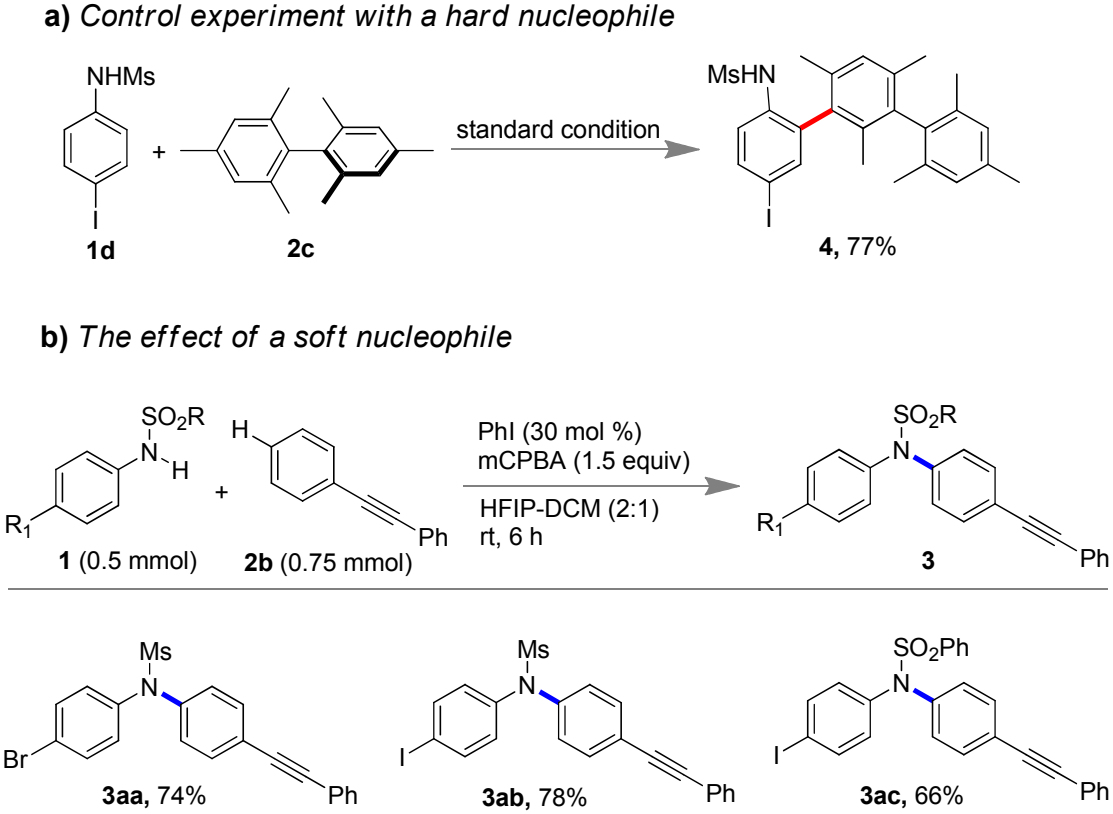
3u, 42%



3a



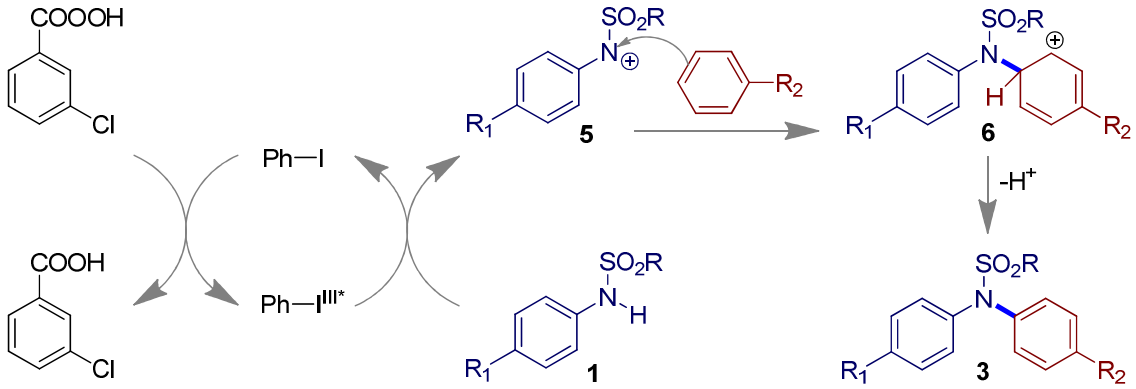
Scheme 4. a) Control experiment. b) 1,2-Diphenylethyne as a nucleophile



The control experiment shown in Scheme 4a proved that the C-arylated product was formed due to the hardness of the bimesityl nucleophile, and **4** was isolated in 77% yield. However, the use of diphenylacetylene (**2b**) as the arene nucleophile (soft) in the arylation reaction led to *N*-arylated diarylamines in good yields (Scheme 4b, **3aa-3ac**).

In this study, biphenyl and diphenylacetylene were reacted with different sulfonanilides to generate *N*-arylated products. We have already shown that alkyl- or alkoxy-substituted arenes lead to C-arylated products.[21] As a limitation of this methodology, attempts to use diphenylacetylenes with substitutions at the 4- and 4'-positions were unsuccessful. No other substituted biphenyl substrates were tested in the current protocol.

Scheme 5. Plausible mechanism



A plausible mechanism for the intermolecular dehydrogenative C-N coupling reaction is proposed in Scheme 5. A trivalent iodine (III) species (either PhIO or $PhI(OCOPh)_2$) is expected to be formed *in situ* during the reaction of the oxidant (*m*CPBA) and the iodoarene with the concomitant generation of *m*CBA.[28d] Subsequently, the interaction of the sulfonanilide and the iodine (III) species is expected to generate nitrenium ion[20a, 29] intermediate **5**. Depending on the nature of the nucleophiles available in the reaction system, the softer nitrenium ion can be converted to a harder carbenium ion by loss of aromatic ring current *via* resonance. Similarly, because of the extended delocalization of the electrons in the biphenyls or diphenyl acetylenes, they become softer nucleophiles. Therefore, due to the preference of soft for soft, the *N*-arylation was favored over the *C*-arylation. Finally, the nucleophilic attack from arene (**2**) onto the electron deficient *N*-center led to the formation of another carbenium ion intermediate (**6**), which subsequently was transformed into the corresponding diarylamine product (**3**) by the abstraction of one proton by either HO^- or $PhOCO^-$. Substituents on the aryl ring of the sulfonanilides could determine the stability of ionic species **5**; thus, poor yields from anilides bearing stronger electron-withdrawing groups (Scheme 3, **3n** and **3p-q**) were observed. The isolation of trace amounts of carbazoles in

certain cases could be explained by the C-arylation step occurring first (through a carbenium intermediate) followed by C-N bond formation as previously reported.[21]

Conclusions

In summary, we herein report a unique protocol for selective N-H arylation over C-H arylation of sulfonanilides using hypervalent iodine (III). The iodine (III) species was generated *in situ* from PhI and *m*CPBA. Overall, an intermolecular, dehydrogenative C-N bond formation reaction for the construction of diphenylamines from non-prefunctionalized substrates was established under mild, metal-free conditions. We anticipate that this intermolecular N-H arylation method might lead to a powerful approach to the synthesis of diarylamine compounds.[30] The ability to control the reactivity of the N-H arylation reaction using the principles of SHAB can have important applications in supramolecular catalysis.[31]

EXPERIMENTAL SECTION

General Methods. Column chromatographic purifications of the synthesized compounds were performed using silica gel (mesh 230-400) and hexane-ethyl acetate mixtures as eluents unless otherwise specified. NMR spectra were recorded on a 400 MHz instrument at 25 °C. The chemical shift values are reported in parts per million (ppm) with respect to residual chloroform (7.26 ppm for ^{1}H and 77.16 for ^{13}C). Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, brs = broad singlet, and m = multiplet), coupling constant (Hz) and integration. High-resolution mass spectra (HR-MS) were recorded on an ESI-TOF (time of flight) mass spectrometer. Infrared spectral data are reported in wave numbers (cm^{-1}). Melting points of the compounds were determined using a digital melting point apparatus and are uncorrected. FT-IR spectra were recorded after forming a thin layer of the target compound on the surface of a NaCl crystal using

dichloromethane. Thin-layer chromatography (TLC) was performed on Merck Silica Gel F254 plates (0.25 mm). The spots and bands were visualized using 254 nm UV light.

Materials. Iodobenzene (PhI) and *m*-chloroperbenzoic acid (*m*CPBA) were purchased from commercial source and used without further purification. Sulfonanilides were prepared by the reaction of commercially available anilines and sulfonyl chlorides in the presence of pyridine in dichloromethane (DCM) as the solvent.[32]

Representative procedure for the preparation of *N*-([1,1'-biphenyl]-4-yl)-N-(4-bromophenyl)methanesulfonamide (3a). To a stirred solution of N-(4-bromophenyl)methanesulfonamide (**1a**, 250 mg, 1.0 mmol), 1,1'-biphenyl (**2a**, 231 mg, 1.5 mmol) and iodobenzene (33 μL, 0.3 mmol) in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP, $(CF_3)_2CHOH$) – dichloromethane (DCM, CH_2Cl_2) (2:1, 4.5 mL) was added mCPBA (259 mg, 1.5 mmol) in one portion under ambient conditions, and the mixture was allowed to stir for 6 h at room temperature. The progress of the reaction was monitored by TLC using a mixture of hexane and ethyl acetate as the eluent. After completion, the solvent was evaporated and a saturated aqueous solution of $NaHCO_3$ was added. The aqueous phase was extracted with ethyl acetate. The organic phase was dried over anhydrous Na_2SO_4, and the resulting solution was evaporated to dryness. The residue was purified by column chromatography on silica gel to give pure N-([1,1'-biphenyl]-4-yl)-N-(4-bromophenyl)methanesulfonamide (**3a**) as the major product (350 mg white solid, 0.87 mmol, yield 87%).

N-([1,1'-Biphenyl]-4-yl)-N-(4-bromophenyl)methanesulfonamide (3a): R_f = 0.45 (hexane:ethyl acetate 4:1); white solid; yield 87% (350 mg); mp 150-152 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 8 Hz, 2H), 7.57-7.50 (m, 4H), 7.46-7.41 (m, 4H), 7.38 (d, *J* = 8 Hz, 1H), 7.29 (d, *J* = 8 Hz, 2H), 3.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 140.5, 140.0, 139.9, 132.8, 129.0, 128.4, 127.9, 127.9, 127.2, 121.1, 40.2; IR (KBr): $\tilde{\nu}$ = 3024, 2927, 1509, 1337, 1152 cm^{-1}; HR-MS (ESI-TOF): m/z calculated for $C_{19}H_{16}NO_2SBrNa$ $[M + Na]^+$: 423.9977, found: 423.9962.

N-([1,1'-Biphenyl]-4-yl)-N-(4-bromo-3-methylphenyl)methanesulfonamide (3b): R_f = 0.55 (hexane:ethylacetate 4:1); white solid; yield 75% (140 mg); mp 98-99 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.53 (m, 5H), 7.46-7.42 (m, 4H), 7.38-7.36 (m, 1H), 7.29-7.27 (m, 1H), 7.13-7.11 (m,1H), 3.18 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 140.4, 140.2, 140.0, 139.7, 133.4, 130.0, 129.0, 128.4, 127.8, 127.7, 127.2, 126.5, 123.9, 40.2, 23.2; IR (KBr): $\tilde{\nu}$ = 3031, 2927, 1515, 1347, 1156 cm^{-1}; HR-MS (ESI-TOF): m/z calculated for $C_{20}H_{18}NO_2SBrNa$ $[M + Na]^+$: 438.0134, found: 438.0118.

N-([1,1'-Biphenyl]-4-yl)-N-(4-chlorophenyl)methanesulfonamide (3c): R_f = 0.60 (hexane:ethylacetate 4:1); white solid; yield 79% (206 mg); mp 151-153 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61-7.59 (m, 2H), 7.57-7.54 (m, 2H), 7.46-7.42 (m, 4H), 7.38-7.36 (m, 5H), 3.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 140.1, 139.9, 139.9, 133.3, 129.9, 129.8, 129.0, 128.8, 128.4, 127.8, 127.2, 122.3, 40.2; IR (KBr): $\tilde{\nu}$ = 3030, 2926, 1512, 1346, 1156 cm^{-1}; HR-MS (ESI-TOF): m/z calculated for $C_{19}H_{16}NO_2SClNa$ $[M + Na]^+$: 380.0482, found: 380.0491.

N-([1,1'-Biphenyl]-4-yl)-N-(4-iodophenyl)methanesulfonamide (3d): R_f = 0.55 (hexane:ethylacetate 4:1); white solid; yield 83% (139 mg); (isolated yield 67% when 0.75 equiv of biphenyl was used instead of 1.5 equiv) mp 158-160 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8 Hz, 2H), 7.6-7.55 (m, 4H), 7.47-7.41 (m, 4H), 7.39-7.35 (m, 1H), 7.16 (d, J = 8 Hz, 2H), 3.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 140.7, 139.9, 139.9, 138.8, 129.1, 129.0, 128.4, 128.0, 127.8, 127.2, 92.2, 40.2; IR (KBr): $\tilde{\nu}$ = 3096, 2933, 1513, 1346, 1156 cm^{-1}; HR-MS (ESI-TOF): m/z calculated for $C_{19}H_{16}NO_2SINa$ $[M + Na]^+$: 471.9839, found: 471.9836.

N-([1,1'-Biphenyl]-4-yl)-N-(4-fluorophenyl)methanesulfonamide (3e): R_f = 0.35 (hexane:ethylacetate 9:1); white solid; yield 58% (84 mg); mp 186-188 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.54 (m, 4H), 7.46-7.41 (m, 6H), 7.38-7.34 (m, 1H), 7.12-7.07 (m, 2H), 3.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.85 (d, $^1J_{C,F}$ = 247 Hz), 140.5, 140.4, 140.0, 137.16 (d, $^4J_{C,F}$ = 3 Hz), 130.1 (d, $^3J_{C,F}$ = 9 Hz), 129.0, 128.4, 127.8, 127.4, 127.2, 116.6 (d, $^2J_{C,F}$ = 23 Hz), 40.1; IR (KBr): $\tilde{\nu}$ = 3072, 2927, 1503, 1334, 1144 cm^{-1}; HR-MS (ESI-TOF): m/z calculated for $C_{19}H_{16}NO_2SFNa$ $[M+Na]^+$: 364.0778, found: 364.0790.

N-([1,1'-Biphenyl]-4-yl)-N-(3-chloro-4-fluorophenyl)methanesulfonamide (3f): R_f = 0.40 (hexane:ethylacetate 9:1); white solid; yield 55% (102 mg); mp 145-147 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J = 8 Hz, 2H), 7.56 (d, J = 8 Hz, 2H), 7.50-7.46 (m, 1H), 7.45-7.41 (m, 4H), 7.39-7.31 (m, 2H), 7.17 (t, J = 8 Hz, 1H), 3.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3 (d, $^1J_{C,F}$ = 249 Hz), 140.9, 139.9 (d, $^4J_{C,F}$ = 3 Hz), 137.7 (d, $^3J_{C,F}$ = 4 Hz), 130.1, 129.0, 128.6, 127.9, 127.9, 127.8, 127.8, 127.2, 121.9 (d, $^2J_{C,F}$ = 19 Hz), 117.3 (d, $^2J_{C,F}$ = 22 Hz), 40.3; IR (KBr): $\tilde{\nu}$ = 3097, 2931, 1494, 1348, 1158 cm^{-1}; HR-MS (ESI-TOF): m/z calculated for $C_{19}H_{16}NO_2SClF$ $[M + H]^+$: 376.0569, found: 376.0554.

N-([1,1'-Biphenyl]-4-yl)-N-(3,4-dichlorophenyl)methanesulfonamide (3g): R_f = 0.45 (hexane:ethylacetate 9:1); white solid; yield 56% (116 mg); mp 130-131 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8 Hz, 2H), 7.57 (d, *J* = 8 Hz, 2H), 7.51 (s, 1H), 7.48-7.38 (m, 6H), 7.29-7.26 (m, 1H), 3.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 140.8, 139.8, 139.5, 133.4, 131.3, 131.1, 129.0, 128.7, 128.6, 128.3, 127.9, 127.2, 126.3, 40.3; IR (KBr): $\tilde{\nu}$ = 3031, 2932, 1485, 1349, 1160 cm^{-1}; HR-MS (ESI-TOF): m/z calculated for $C_{19}H_{16}NO_2SCl_2$ $[M + H]^+$: 392.0273, found: 392.0274.

N-([1,1'-Biphenyl]-4-yl)-N-(p-tolyl)methanesulfonamide (3h): R_f = 0.40 (hexane:ethylacetate 9:1); white solid; yield 61% (140 mg); mp 178-180 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.54 (m, 4H), 7.45-7.41 (m, 4H), 7.37-7.32 (m, 3H), 7.21 (d, *J* = 8 Hz, 2H), 3.18 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.8, 140.1, 140.0, 138.6, 137.9, 130.4, 128.9, 128.2, 128.1, 127.7, 127.3, 127.2, 40.1, 21.1; IR (KBr): $\tilde{\nu}$ = 3030, 2925, 1510, 1485, 1339, 1155 cm^{-1}; HR-MS (ESI-TOF): m/z calculated for $C_{20}H_{19}NO_2SNa$ $[M + Na]^+$: 360.1029, found: 360.1058.

N-([1,1'-Biphenyl]-4-yl)-N-(4-ethylphenyl)methanesulfonamide (3i): R_f = 0.35 (hexane:ethylacetate 19:1); white solid; yield 63% (160 mg); mp 98-100 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.54 (m, 4H), 7.46-7.42 (m, 4H), 7.37-7.34 (m, 3H), 7.24 (d, *J* = 8 Hz, 2H), 3.18 (s, 3H), 2.67 (q, *J* = 8 Hz, 2H), 1.25 (t, *J* = 8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 140.8, 140.1, 140.0, 138.7, 129.2, 128.9, 128.2, 128.1, 127.7, 127.4, 127.2, 40.1, 28.5, 15.4; IR (KBr): $\tilde{\nu}$ = 3031, 2931, 1509, 1486, 1346, 1157 cm^{-1}; HR-MS (ESI-TOF): m/z calculated for $C_{21}H_{22}NO_2S$ $[M + H]^+$: 352.1366, found: 352.1361.

N-([1,1'-Biphenyl]-4-yl)-N-(2,4-dimethylphenyl)methanesulfonamide (3j): R_f = 0.40 (hexane:ethylacetate 9:1); white solid; yield 49% (100 mg); mp 94-96 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.53 (m, 4H), 7.45-7.41 (m, 4H), 7.36-7.33 (m, 2H), 7.14-7.11 (m, 2H), 3.20 (s, 3H), 2.36 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.3, 140.1, 139.1, 138.6, 138.6, 136.4, 132.7, 129.5, 128.9, 128.0, 127.9, 127.5, 127.0, 124.6, 40.1, 21.2, 18.6; IR (KBr): $\tilde{\nu}$ = 3030, 2925, 1485, 1345, 1152 cm^{-1}; HR-MS (ESI-TOF): m/z calculated for $C_{21}H_{22}NO_2S$ $[M + H]^+$: 352.1366, found: 352.1370.

N-([1,1'-Biphenyl]-4-yl)-N-mesitylmethanesulfonamide (3k): R_f = 0.40 (hexane:ethylacetate 9:1); semi solid; yield 45% (116 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.51 (m, 4H), 7.43 (t, *J* = 8 Hz, 2H), 7.33 (t, *J* = 8 Hz, 1H), 7.25 (d, *J* = 8 Hz, 2H), 7.00 (s, 2H), 3.32 (s, 3H), 2.33 (s, 3H), 2.28 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.1, 139.0, 138.7, 136.4, 134.5, 130.1, 128.9, 128.1, 127.3, 126.9, 119.2, 40.3, 21.2, 19.1; IR (KBr): $\tilde{\nu}$ = 3031, 2923, 1517, 1485, 1342, 1157 cm^{-1}; HR-MS (ESI-TOF): m/z calculated for $C_{22}H_{23}NSO_2Na$ $[M + Na]^+$: 388.1342, found: 388.1313.

N-([1,1'-Biphenyl]-4-yl)-N-(4-isopropylphenyl)methanesulfonamide (3l): R_f = 0.45 (hexane:ethylacetate 9:1); white solid; yield 70% (60 mg); mp 114-116 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.53 (m, 4H), 7.46-7.41 (m, 4H), 7.37-7.33 (m, 3H), 7.26-7.24 (m, 1H), 3.18 (s, 3H), 2.91 (sept, *J* = 8 Hz, 1H), 1.24 (d, *J* = 4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.6, 140.8, 140.2, 140.1, 138.7, 128.9, 128.2, 128.0, 127.8, 127.7, 127.6, 127.2, 40.1, 33.8, 24.0; IR (KBr): $\tilde{\nu}$ = 3031, 2960, 1508, 1486, 1347, 1157 cm^{-1}; HR-MS (ESI-TOF): m/z calculated for $C_{22}H_{23}NO_2SNa$ $[M + Na]^+$: 388.1342, found: 388.1339.

N-([1,1'-Biphenyl]-4-yl)-N-(4-(tert-butyl)phenyl)methanesulfonamide (3m): R_f = 0.45 (hexane:ethylacetate 9:1); white solid; yield 63% (105 mg); mp 142-144 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.54 (m, 4H), 7.46-7.39 (m, 6H), 7.37-7.33 (m, 3H), 3.19 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.8, 140.7, 140.2, 138.5, 128.9, 128.2, 127.7, 127.5, 127.2, 126.7, 40.1, 34.7, 31.4; IR (KBr): $\tilde{\nu}$ = 3031, 2962, 1486, 1347, 1158 cm^{-1}; HR-MS (ESI-TOF): m/z calculated for $C_{23}H_{26}NO_2S$ $[M + H]^+$: 380.1679, found: 380.1665.

N-([1,1'-Biphenyl]-4-yl)-N-(2-benzoyl-4-chlorophenyl)methanesulfonamide (3n): R_f = 0.30 (hexane:ethylacetate 9:1); semi-solid; yield 50% (88 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8 Hz, 2H), 7.61 (d, *J* = 8 Hz, 1H), 7.55-7.50 (m, 1H), 7.46-7.38 (m, 11H), 7.36-7.33 (m, 2H), 3.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.8, 140.2, 140.1, 140.1, 140.0, 137.9, 136.1, 133.8, 133.3, 132.8, 131.5, 130.6, 129.6, 128.9, 128.5, 128.1, 127.7, 127.7, 127.2, 40.64; IR (KBr): $\tilde{\nu}$ = 3031, 2925, 1668, 1516, 1485, 1349, 1157cm^{-1}; HR-MS (ESI-TOF): m/z calculated for $C_{26}H_{20}NO_3SClNa$ $[M + Na]^+$: 484.0745, found: 484.0736.

N,N-di([1,1'-Biphenyl]-4-yl)methanesulfonamide (3o): R_f = 0.45 (hexane:ethylacetate 9:1); white solid; yield 76% (122 mg); mp 170-172 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ7.63-7.56 (m, 8H), 7.51-7.43 (m, 8H), 7.39-7.35 (m, 2H), 3.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.5, 140.4, 140.1, 129.0, 128.4, 127.9, 127.8, 127.2, 40.25; IR (KBr): $\tilde{\nu}$ = 3031, 2933, 1513, 1486, 1342, 1148cm^{-1}; HR-MS (ESI-TOF): m/z calculated for $C_{25}H_{21}NO_2SNa$ $[M + Na]^+$: 422.1185, found: 422.1207.

N-([1,1'-Biphenyl]-4-yl)-N-(4-cyanophenyl)methanesulfonamide (3p): R_f = 0.35 (hexane:ethylacetate 4:1); white solid; yield 35% (44 mg); mp 180-182 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68-7.65 (m, 2H), 7.64-7.61 (m, 2H), 7.59-7.57 (m, 2H), 7.48-7.37 (m, 7H),

3.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.8, 141.9, 139.6, 138.6, 133.4, 129.4, 129.1, 128.8, 128.1, 127.2, 124.6, 118.3, 109.1, 40.32; IR (KBr): $\tilde{\nu}$ = 3031, 2932, 2229, 1601, 1502, 1485, 1350, 1158 cm^{-1}; HR-MS (ESI-TOF): m/z calculated for $C_{20}H_{16}N_2O_2S$ $[M + H]^+$: 349.1005, found: 349.1020.

N-([1,1'-Biphenyl]-4-yl)-N-(4-nitrophenyl)methanesulfonamide (3q): R_f = 0.40 (hexane:ethylacetate 4:1); white solid; yield 33% (31 mg); mp 194-196 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, *J* = 8 Hz, 2H), 7.69 (d, *J* = 12 Hz, 2H), 7.59 (d, *J* = 8 Hz, 2H), 7.49-7.38 (m, 7H), 3.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 144.6, 142.2, 139.6, 138.5, 129.6, 129.1, 129.0, 128.2, 127.3, 125.0, 123.8, 40.3; IR (KBr): $\tilde{\nu}$ = 3031, 2933, 1590, 1515, 1486, 1344, 1112 cm^{-1}; HR-MS (ESI-TOF): m/z calculated for $C_{19}H_{17}N_2O_4S$ $[M + H]^+$: 369.0904, found: 369.0894.

N-([1,1'-Biphenyl]-4-yl)-N-(4-bromophenyl)benzenesulfonamide (3r): R_f = 0.50 (hexane:ethylacetate 9:1); white solid; yield 78% (116 mg); mp 168-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8 Hz, 2H), 7.62 (t, *J* = 8 Hz, 1H), 7.56-7.49 (m, 6H), 7.47-7.42 (m, 4H), 7.38-7.34 (m, 1H), 7.30 (d, *J* = 8 Hz, 2H), 7.18 (d, *J* = 8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.8, 140.6, 140.3, 140.2, 140.0, 133.2, 132.6, 129.8, 129.2, 129.0, 128.6, 128.2, 127.8, 127.8, 127.2, 121.5; IR (KBr): $\tilde{\nu}$ = 3031, 2924, 1513, 1485, 1355, 1164 cm^{-1}; HR-MS (ESI-TOF): m/z calculated for $C_{24}H_{19}NO_2SBr$ $[M + H]^+$: 464.0314, found: 464.0300.

N-([1,1'-Biphenyl]-4-yl)-N-(4-(tert-butyl)phenyl)benzenesulfonamide (3s): R_f = 0.45 (hexane:ethylacetate 9:1); white solid; yield 67% (96 mg); mp 154-156 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ7.76 (d, *J* = 8 Hz, 2H), 7.61 (t, *J* = 8 Hz, 1H), 7.55-7.48 (m, 6H), 7.43 (t, *J* = 8 Hz, 2H), 7.36-7.32 (m, 5H), 7.21 (d, *J* = 8 Hz, 2H), 1.30 (s, 9H); ^{13}C NMR (100 MHz,

$CDCl_3$): δ 150.8, 140.8, 140.8, 140.4, 140.2, 138.7, 132.8, 129.0, 128.9, 128.6, 128.0, 128.0, 127.9, 127.7, 127.2, 126.4, 34.7, 31.4; IR (KBr): $\tilde{\nu}$ = 3031, 2903, 1510, 1486, 1355, 1166 cm^{-1}; HR-MS (ESI-TOF): m/z calculated for $C_{28}H_{27}NSO_2Na$ $[M + Na]^+$: 464.1655, found: 464.1650.

N-([1,1'-Biphenyl]-4-yl)-4-methyl-N-(p-tolyl)benzenesulfonamide (3t): R_f = 0.55 (hexane:ethylacetate 9:1); white solid; yield 70% (165 mg); mp 148-150 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8 Hz, 2H), 7.54-7.50 (m, 4H), 7.42 (t, *J* = 8 Hz, 2H), 7.36-7.32 (m, 3H), 7.28 (d, *J* = 8 Hz, 2H), 7.19-7.12 (m,4H), 2.44 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 141.1, 140.2, 140.1, 138.9, 137.8, 137.8, 130.1, 129.6, 128.9, 128.6, 128.2, 128.0, 127.9, 127.6, 127.2, 21.7, 21.2; IR (KBr): $\tilde{\nu}$ = 3047, 2923, 1511, 1485, 1351, 1158 cm^{-1}; HR-MS (ESI-TOF): m/z calculated for $C_{26}H_{24}NO_2S$ $[M + H]^+$: 414.1522, found: 414.1510.

N-([1,1'-Biphenyl]-4-yl)-N-(4-bromophenyl)-4-nitrobenzenesulfonamide (3u): R_f = 0.50 (hexane:ethylacetate 10:1); white solid; yield 42% (54 mg); mp 138-140 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, *J* = 8 Hz, 2H), 7.91 (d, *J* = 8 Hz, 2H), 7.57-7.53 (m, 4H), 7.50-7.44 (m, 5H), 7.28 (d, *J* = 8 Hz, 2H), 7.17 (d, *J* = 8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4, 145.8, 141.5, 139.9, 139.7, 139.5, 132.9, 129.8, 129.1, 128.6, 128.5, 128.1, 127.2, 127.1, 124.5, 122.3; IR (KBr): $\tilde{\nu}$ = 3031, 2923, 1528, 1484, 1348, 1164cm^{-1}; HR-MS (ESI-TOF): m/z = calculated for $C_{24}H_{17}BrN_2O_4SNa$ $[M + Na]^+$: 530.9984, found: 530.9969.

N-(4-Bromophenyl)-N-(4-(phenylethynyl)phenyl)methanesulfonamide (3aa): R_f = 0.50 (hexane:ethylacetate 9:1); white solid; yield 74% (76 mg); mp 197-198 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8 Hz, 1H), 7.73-7.72 (m, 1H), 7.53-7.50 (m, 1H), 7.38-7.27 (m,

8H), 7.19-7.17 (m, 2H), 2.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.9, 135.6, 132.0, 131.9, 131.8, 130.3, 129.9, 129.2, 128.6, 128.4, 127.9, 127.5, 123.8, 123.0, 118.1, 117.1, 41.0; IR (KBr): $\tilde{\nu}$ = 3011, 2925, 2853, 1443, 1377, 1174 cm^{-1}; HR-MS (ESI-TOF): m/z calculated for $C_{21}H_{17}NO_2SBr$ $[M + H]^+$: 426.0158, found: 426.0126.

N-(4-Iodophenyl)-N-(4-(phenylethynyl)phenyl)methanesulfonamide (3ab): R_f = 0.50 (hexane:ethylacetate 9:1); white solid; yield 78% (124 mg); mp 202-203 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8 Hz, 1H), 7.92-7.91 (m, 1H), 7.70-7.68 (m, 1H), 7.37-7.28 (m, 8H), 7.19-7.16 (m, 2H), 2.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.5, 136.3, 134.0, 132.5, 131.9, 131.8, 130.2, 129.9, 129.2, 128.6, 127.9, 127.5, 123.6, 117.5, 88.8, 41.0; IR (KBr): $\tilde{\nu}$ = 3031, 2923, 2852, 1442, 1373, 1173cm^{-1}; HR-MS (ESI-TOF): m/z calculated for $C_{21}H_{16}O_2SNINa$ $[M + Na]^+$: 495.9839, found: 495.9837.

N-(4-(tert-Butyl)phenyl)-N-(4-(phenylethynyl)phenyl)benzenesulfonamide (3ac): R_f = 0.45 (hexane:ethylacetate 9:1); white solid; yield 66% (106 mg); mp 157-158 °C; ^{1}HNMR (400 MHz, $CDCl_3$): δ8.33 (d, *J* = 8 Hz, 1H), 7.51-7.45 (m, 5H), 7.32-7.28 (m, 5H), 7.24-7.19 (m, 5H), 7.11-7.09 (m, 2H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 138.5, 136.9, 135.4, 133.5, 132.9, 132.2, 131.0, 130.1, 130.0, 128.8, 128.5, 128.3, 127.4, 127.1, 127.0, 125.1, 123.4, 116.1, 115.8, 34.8, 31.7; IR (KBr): $\tilde{\nu}$ = 3062, 2962, 1604, 1585, 1460, 1381, 1183 cm^{-1}; HR-MS (ESI-TOF): m/z calculated for $C_{30}H_{28}NO_2S$ $[M + H]^+$: 466.1835, found: 466.1813.

6-Bromo-9-(methylsulfonyl)-2-phenyl-carbazole (3a'): R_f = 0.55 (hexane:ethylacetate 19:1); white solid; yield 6% (6 mg); mp 216-217 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (s, 1H), 8.15 (s, 1H), 8.06 (d, *J* = 8 Hz, 1H), 8.02 (d, *J* = 8 Hz, 1H), 7.71-7.68 (m, 3H), 7.62-7.59

(m, 1H), 7.51-7.48 (m, 1H), 7.42-7.39 (m, 1H), 3.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 140.8, 139.4, 137.6, 130.4, 129.1, 128.0, 127.9, 127.7, 124.2, 124.0, 123.3, 120.8, 117.8, 116.3, 113.3, 39.09. HR-MS (ESI-TOF): m/z calculated for $C_{18}H_{11}BrN$ $[M - SO_2Me]^+$ 320.0075, found 320.0085.[33]

***N*-(5-Iodo-2',2'',4',4'',6',6''-hexamethyl-[1,1':3',1''-terphenyl]-2-yl)methanesulfonamide (4)**: R_f = 0.45 (hexane:ethylacetate 9:1); white solid; yield 77% (69 mg); mp 199-200 °C;^{1}H NMR (700 MHz, $CDCl_3$): δ 7.68 (d, 1H, *J* = 14 Hz), 7.49 (s, 1H), 7.45 (d, 1H, *J* = 7 Hz), 7.11 (s, 1H), 6.95 (s, 1H), 6.00 (s, 1H{NH}), 2.96 (s, 3H), 2.33 (s, 3H), 2.01 (s, 3H), 1.91 (s, 3H), 1.89 (s, 3H), 1.87 (s, 3H), 1.56 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 137.7, 137.3, 136.7, 136.5, 135.3, 135.2, 135.1, 134.9, 134.4, 133.0, 131.6, 130.4, 128.7, 128.6, 119.1, 87.9, 40.0, 21.2, 20.3, 20.1, 20.0, 19.9, 17.5; IR (KBr): $\tilde{\nu}$ = 3042, 2913, 1529, 1585, 1483, 1335 cm^{-1}; HR-MS (ESI-TOF): m/z calculated for $C_{25}H_{29}INO_2S$ (M+H) 534.0958, found: 534.0932.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information file contains NMR spectra and crystallographic information.

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Notes

The authors declare no competing financial interest.

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REFERENCES

1. Li, C.-J., *Chem* **2016,** *1*, 423.

2. (a) Bariwal, J.; Van der Eycken, E., *Chem. Soc. Rev.* **2013,** *42*, 9283; (b) Hartwig, J. F., *Acc. Chem. Res.* **2008,** *41*, 1534.

3. (a) Girard, S. A.; Knauber, T.; Li, C.-J., CHAPTER 1 The Evolution of the Concept of Cross-Dehydrogenative-Coupling Reactions. In *From C-H to C-C Bonds: Cross-Dehydrogenative-Coupling*, The Royal Society of Chemistry: 2015; pp 1; (b) Narayan, R.; Manna, S.; Antonchick, A. P., *Synlett* **2015,** *26*, 1785.

4. (a) Girard, S. A.; Knauber, T.; Li, C.-J., *Angew. Chem. Int. Ed.* **2014,** *53*, 74; (b) Li, C.-J., *Acc. Chem. Res.* **2009,** *42*, 335; (c) Li, X.; Pan, J.; Song, S.; Jiao, N., *Chem. Sci.* **2016,** *7*, 5384; (d) Louillat, M.-L.; Patureau, F. W., *Chem. Soc. Rev.* **2014,** *43*, 901.

5. (a) Kim, H.; Chang, S., *ACS Catal.* **2016,** *6*, 2341; (b) Jiao, J.; Murakami, K.; Itami, K., *ACS Catal.* **2016,** *6*, 610; (c) Kantak, A. A.; Marchetti, L.; DeBoef, B., *Chem. Commun.* **2015,** *51*, 3574; (d) Park, Y.; Kim, Y.; Chang, S., *Chem. Rev.* **2017,** *117*, 9247.

6. (a) Murarka, S.; Antonchick, A. P., Oxidative Heterocycle Formation Using Hypervalent Iodine(III) Reagents. In *Hypervalent Iodine Chemistry*, Wirth, T., Ed. Springer International: Cham, Switzerland: 2016; pp 75; (b) Yoshimura, A.; Zhdankin, V. V., *Chem. Rev.* **2016,** *116*, 3328; (c) Sun, C.-L.; Shi, Z.-J., *Chem. Rev.* **2014,** *114*, 9219; (d) Muñiz, K.,

Top. Curr. Chem. **2016,** *373*, 105; (e) Dohi, T.; Kita, Y.; Kita, Y., *Top. Curr. Chem.* **2016,** *373*, 1.

7. (a) Souto, J. A.; Becker, P.; Iglesias, Á.; Muñiz, K., *J. Am. Chem. Soc.* **2012,** *134*, 15505; (b) Mondal, S.; Samanta, S.; Jana, S.; Hajra, A., *J. Org. Chem.* **2017,** *82*, 4504; (c) Manna, S.; Serebrennikova, P. O.; Utepova, I. A.; Antonchick, A. P.; Chupakhin, O. N., *Org. Lett.* **2015,** *17*, 4588.

8. (a) Lucchetti, N.; Scalone, M.; Fantasia, S.; Muñiz, K., *Adv. Synth. Catal.* **2016,** *358*, 2093; (b) Itoh, N.; Sakamoto, T.; Miyazawa, E.; Kikugawa, Y., *J. Org. Chem.* **2002,** *67*, 7424; (c) Samanta, R.; Lategahn, J.; Antonchick, A. P., *Chem. Commun.* **2012,** *48*, 3194; (d) Samanta, R.; Bauer, J. O.; Strohmann, C.; Antonchick, A. P., *Org. Lett.* **2012,** *14*, 5518; (e) Kantak, A. A.; Potavathri, S.; Barham, R. A.; Romano, K. M.; DeBoef, B., *J. Am. Chem. Soc.* **2011,** *133*, 19960; (f) Kim, H. J.; Kim, J.; Cho, S. H.; Chang, S., *J. Am. Chem. Soc.* **2011,** *133*, 16382.

9. (a) Ochiai, M.; Takeuchi, Y.; Katayama, T.; Sueda, T.; Miyamoto, K., *J. Am. Chem. Soc.* **2005,** *127*, 12244; (b) Dohi, T.; Maruyama, A.; Yoshimura, M.; Morimoto, K.; Tohma, H.; Kita, Y., *Angew. Chem. Int. Ed.* **2005,** *44*, 6193; (c) Dohi, T.; Kita, Y., *Chem. Commun.* **2009,** *0*, 2073.

10. (a) Zarra, S.; Wood, D. M.; Roberts, D. A.; Nitschke, J. R., *Chem. Soc. Rev.* **2015,** *44*, 419; (b) Rissanen, K., *Chem. Soc. Rev.* **2017,** *46*, 2638.

11. (a) Mahadevi, A. S.; Sastry, G. N., *Chem. Rev.* **2016,** *116*, 2775; (b) Guha, S.; Kazi, I.; Nandy, A.; Sekar, G., *Eur. J. Org. Chem.* **2017,** 5497.

12. (a) Li, C.-J., *Chem. Rev.* **2005,** *105*, 3095; (b) Percastegui, E. G.; Mosquera, J.; Nitschke, J. R., *Angew. Chem., Int. Ed.* **2017,** *56*, 9136.

13. Achar, T. K.; Mal, P., *Adv. Synth. Catal.* **2015,** *357*, 3977.

14. Bulfield, D.; Huber, S. M., *Chem. - Eur. J.* **2016,** *22*, 14434.

15. (a) Dougherty, D. A., *Acc. Chem. Res.* **2013,** *46*, 885; (b) Kennedy, C. R.; Lin, S.; Jacobsen, E. N., *Angew. Chem. Int. Ed.* **2016,** *55*, 12596; (c) Achar, T. K.; Maiti, S.; Mal, P., *Org. Biomol. Chem.* **2016,** *14*, 4654.

16. Giese, M.; Albrecht, M.; Rissanen, K., *Chem. Rev.* **2015,** *115*, 8867.

17. (a) Wheeler, S. E.; Seguin, T. J.; Guan, Y.; Doney, A. C., *Acc. Chem. Res.* **2016,** *49*, 1061; (b) Breugst, M.; von der Heiden, D.; Schmauck, J., *Synthesis* **2017,** *49*, 3224.

18. Bose, A.; Mal, P., *J. Org. Chem.* **2015,** *80*, 11219.

19. (a) Bose, A.; Mal, P., *Chem. Commun.* **2017,** *53*, 11368; (b) Achar, T. K.; Sahoo, P. K.; Mal, P., *ChemistrySelect* **2017,** *2*, 1944.

20. (a) Gassman, P. G., *Acc. Chem. Res.* **1970,** *3*, 26; (b) Borodkin, G. I.; Shubin, V. G., *Russ. Chem. Rev.* **2008,** *77*, 395.

21. (a) Maiti, S.; Mal, P., *Org. Lett.* **2017,** *19*, 2454; (b) Maiti, S.; Achar, T. K.; Mal, P., *Org. Lett.* **2017,** *19*, 2006.

22. (a) Mayr, H.; Ofial, A. R., *Angew. Chem. Int. Ed.* **2006,** *45*, 1844; (b) Mayr, H.; Breugst, M.; Ofial, A. R., *Angew. Chem. Int. Ed.* **2011,** *50*, 6470.

23. Parham, J. C.; Templeton, M. A., *J. Org. Chem.* **1982,** *47*, 652.

24. Woodward, S., *Tetrahedron* **2002,** *58*, 1017.

25. Ito, M.; Kubo, H.; Itani, I.; Morimoto, K.; Dohi, T.; Kita, Y., *J. Am. Chem. Soc.* **2013,** *135*, 14078.

26. Antonchick, A. P.; Samanta, R.; Kulikov, K.; Lategahn, J., *Angew. Chem. Int. Ed.* **2011,** *50*, 8605.

27. (a) Jean, A.; Cantat, J.; Bérard, D.; Bouchu, D.; Canesi, S., *Org. Lett.* **2007,** *9*, 2553; (b) Jacquemot, G.; Menard, M.-A.; L'Homme, C.; Canesi, S., *Chem. Sci.* **2013,** *4*, 1287; (c) Deruer, E.; Canesi, S., *Org. Biomol. Chem.* **2017,** *15*, 3736.

28. (a) Dohi, T.; Maruyama, A.; Minamitsuji, Y.; Takenaga, N.; Kita, Y., *Chem. Commun.* **2007,** 1224; (b) Miyamoto, K.; Sakai, Y.; Goda, S.; Ochiai, M., *Chem. Commun.* **2012,** *48*, 982; (c) Ngatimin, M.; Frey, R.; Andrews, C.; Lupton, D. W.; Hutt, O. E., *Chem. Commun.* **2011,** *47*, 11778; (d) Ochiai, M.; Miyamoto, K., *Eur. J. Org. Chem.* **2008,** 4229.

29. Kikugawa, Y.; Nagashima, A.; Sakamoto, T.; Miyazawa, E.; Shiiya, M., *J. Org. Chem.* **2003,** *68*, 6739.

30. Xie, Y.; Liu, S.; Liu, Y.; Wen, Y.; Deng, G.-J., *Org. Lett.* **2012,** *14*, 1692.

31. (a) Rix, D.; Lacour, J., *Angew. Chem., Int. Ed.* **2010,** *49*, 1918; (b) Raynal, M.; Ballester, P.; Vidal-Ferran, A.; van Leeuwen, P. W. N. M., *Chem. Soc. Rev.* **2014,** *43*, 1660; (c) Meeuwissen, J.; Reek, J. N. H., *Nat. Chem.* **2010,** *2*, 615.

32. Kloeckner, U.; Nachtsheim, B. J., *Chem. Commun.* **2014,** *50*, 10485.

33. The ESI-MS data of the compound **3a´** is found to be after the elimination of methane sulfonyl (mesyl) group.