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Metal-Free Amidation Reactions of Terminal Alkynes with Benzenesulfonamide

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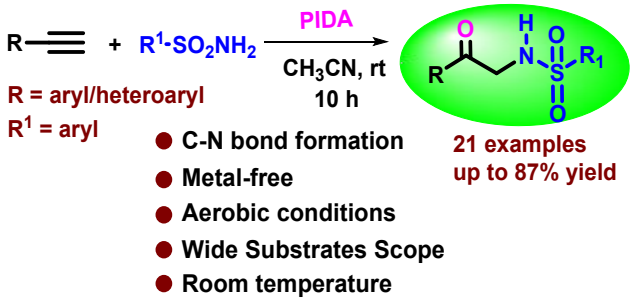


Abstract: A novel and efficient approach has been developed to synthesize α-sulfonylamino ketones through the reaction between terminal alkynes and sulfonamides under ambient air using PIDA (diacetoxy iodobenzene). A library of α-sulfonylamino ketone derivatives having a variety of substituents has been synthesized. A plausible reaction pathway has been predicted. This reaction offers a broad substrate scope, metal-free synthesis, excellent regioselectivity, easily accessible reactants, room temperature reaction conditions under ambient air, and is operationally simple. A gram-scale synthesis demonstrates the potential applications of the

present method. In addition, we have also synthesized α-acetoxy ketones in case of absence of sulfonamide.

Introduction:

α-Amino ketones serve a significant role in organic chemistry as they are found in a large variety of biologically active natural products. Commercial medicines such as mephedrone[1] and bupropion[2] (Figure 1) contain α-amino ketones as well as the proteasome inhibitor epoxomicin.[3] In organic synthesis, this moiety is also very useful for the preparation of 2-amino alcohols[4] and nitrogen-containing heterocycles (Figure 2).[5]

Figure 1: Commercial Medicines Containing α-Amino Ketones

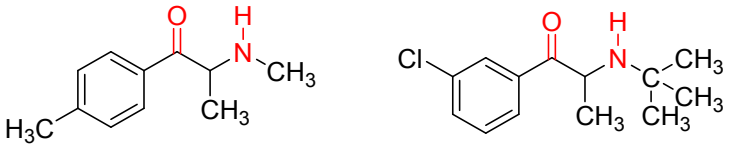
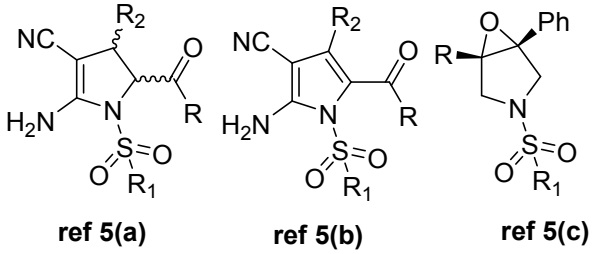
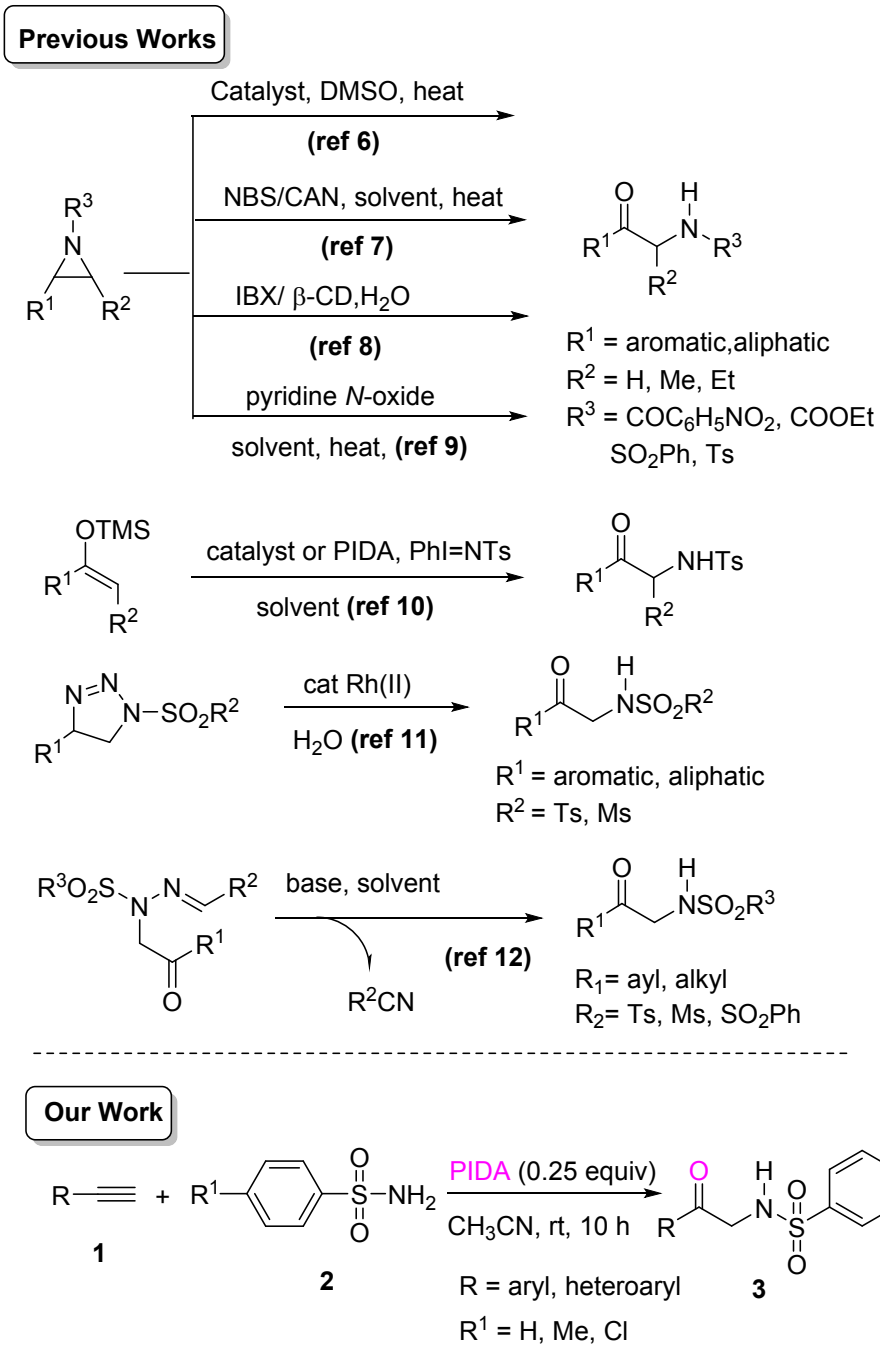


Figure 2: Nitrogen-Containing Heterocycles Synthesized from α-Amino Ketones



Scheme 1: Different Strategies for the Synthesis of α-Sulfonylamino Ketones



Owing to their importance, synthetic organic chemists have attempted various methodologies based on different modifications (Scheme 1). Some of the methodologies are the oxidative ring opening of aziridines by DMSO,[6] NBS combined with CAN,[7] IBX in the presence of β-cyclodextrin,[8] or pyridine *N*-oxide.[9] Another way to synthesize α-amino ketones is through

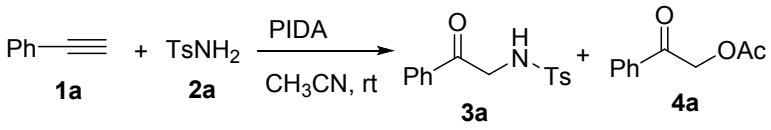
umpolung process using silyl enol ethers, followed by nucleophilic addition of amines.[10] Additionally, a rhodium-catalyzed denitrogenative hydration of *N*-sulfonyl-1,2,3-triazoles was reported by Murakami *et al*.[11] Recently, Zhan *et al*.[12] prepared sulfonylamino ketones via Cs_2CO_3 promoted N-N bond cleavage from hydrazones precursor. As oxidants, hypervalent iodine reagents have recently received much attention due to their low toxicity, mild reactivity, ready availability, high stability, and easy handling.[13] They are useful oxidants in various coupling reactions.[14] Our group is actively engaged in developing various methodologies[15] in organic synthesis involving the chemistry of C-N bond forming/cleavage reactions.[16] Herein, we report a fully different approach from the reported methods using (diacetoxy)iodobenzene (phenyliodine(III) diacetate, (PIDA)[14b] to synthesize α-amino ketones under ambient temperature. We have observed that the reaction of terminal alkynes with benzenesulfonamide affords α-amino ketones (α-sulfonylamino ketones) in good to excellent yields in presence of PIDA as oxidant (Scheme 1).

Results and Discussion:

We started our study by mixing phenylacetylene (**1a**, 0.5 mmol) and 4-methylbenzenesulfonamide (**2a**, 0.5 mmol) using PIDA (1 equiv) as oxidant, at room temperature in acetonitrile solvent. Gratifyingly, benzenesulfonamide (the α-sulfonylamino ketone, **3a**) was obtained in 65% yield along with 12% of α-acetoxyacetophenone (**4a)** after 10 h (Table 1, entry 1). Encouraged by this result, we carried out the reaction in different conditions to optimize the reaction, and the results are summarized in Table 1. At first, we investigated the loading effect of the oxidant (PIDA) and sulfonamide ($TsNH_2$, **2a**) in different ratios. Using 0.5 equiv of PIDA and 1 equiv of $TsNH_2$ (**2a**), the yields of **3a** and **4a** were 74% and <5%

respectively (Table 1, entry 2). When the amount of PIDA was decreased to 0.25 equiv. the desired product (**3a**) was obtained in 80% yield along with trace amount of **4a** (Table 1, entry 3). Again, with increasing the amount of $TsNH_2$ (**2a**) from 1 to 2 equiv. no enhancement of the yield was noticed (Table 1, entry 4). The yield of the reaction did not improve significantly by increasing the reaction time, but upon reducing the reaction time, the yield of **3a** was lowered considerably (Table 1, entries 6). Based on these observations we concluded that using 0.25 equiv. of PIDA and 1 equiv. of the $TsNH_2$ (**2a**) in acetonitrile solvent gave the best result after 10 h (Table 1, entry 3).

Table 1: Optimization of the PIDA Driven Amidation[a]

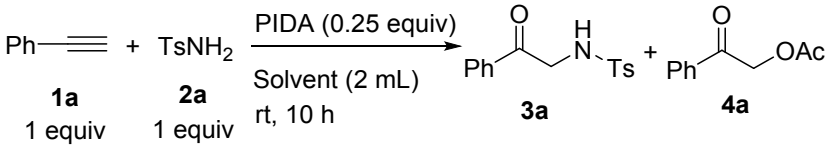


Entry	PIDA (equiv)	$TsNH_2$ (equiv)	time (h)	conversion (%)	yield of **3a** (%)[b]	yield of **4a** (%)[b]
1	1	1	10	77	65	12
2	0.5	1	10	78	74	<5
3	0.25	1	10	82	80	trace
4	0.25	2	10	83	81	trace
5	0.25	1	20	84	81	trace
6	0.25	1	6	48	45	trace

[a]*Reaction conditions:* All reaction are carried out in 0.5 mmol scales, **1a** (0.5 mmol), **2a** (as stated amount) and oxidant (PIDA), at room temperature in MeCN. [b] Isolated yield.

Next, a series of experiments have been carried out to examine the role of solvents which are summarized in Table 2. Considering the green concept, we have tried the reaction in water (Table 2, entry 1) and isolated only **4a** in a 36% yield with a trace amount of **3a**. Whereas in methanol, the desired product (**3a**) was obtained in 25% yield along with 20% of **4a** (Table 2, entry 2). Next, nonpolar aprotic solvent like toluene showed moderate conversion (52%) with 22% of **3a** and 30% of **4a** (Table 2, entry 3), but surprisingly in other aprotic polar solvents like 1,2-DCE and 1,4-dioxane, **3a** was obtained in lower amounts, but the yields were 30-32% for **4a** (Table 2, entries 4 & 5). In the case of acetonitrile, we got the best result (80% yield of **3a**) and trace amount of product **4a** with 82% conversion (Table 2, entry 6). Thus, the optimized reaction condition was achieved using 0.25 equiv of PIDA and 1 equiv of the $TsNH_2$ (**2a**) with respect to phenylacetylene (**1a**) at room temperature in MeCN for 10 h (Table 2, entry 6).

Table 2: Screening of the Solvent Effects of the Amidation Reactions[a]

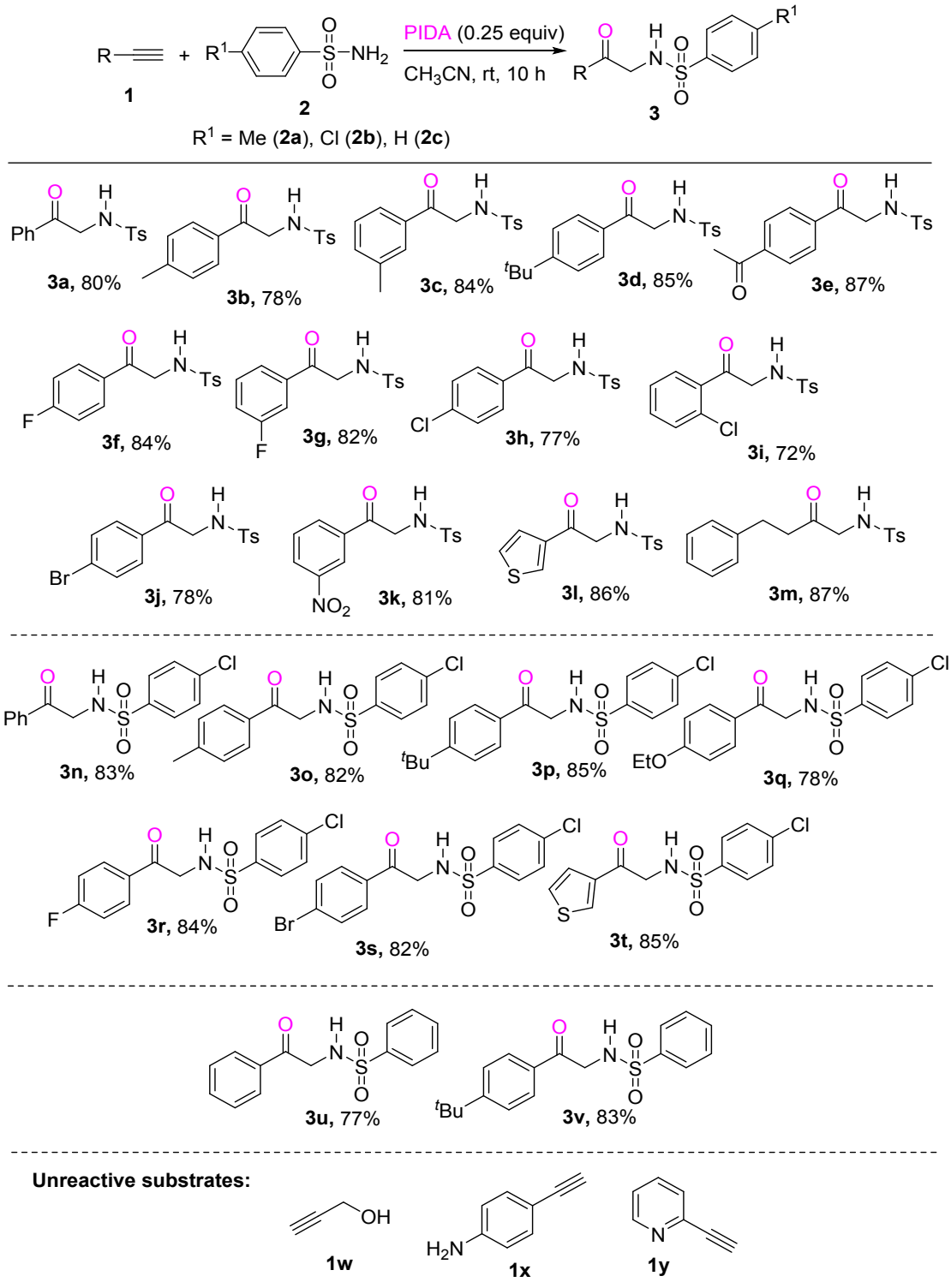


entry	solvent	conversion (%)	yield of **3a** (%)[b]	yield of **4a** (%)[b]
1	H_2O	39	Trace	36
2	MeOH	45	25	20
3	Toluene	52	22	30
4	1,2-DCE	42	10	32
5	1,4-Dioxane	33	Trace	30
6	CH_3CN	82	80	Trace

[a] *Reaction conditions:* All reaction are carried out in 0.5 mmol scale; **1a** (0.5 mmol), **2a** (1 equiv) and oxidant (PIDA, 0.25 equiv), at room temperature in different solvents (2 mL) for 10 h. [b] Isolated yield.

After optimizing the reaction conditions, we explored the substrate scope employing different terminal alkynes to react with 4-methylbenzenesulfonamide, and the results are summarized in Scheme 2. Phenylacetylene afforded the desired product (**3a**) in good yield. The regioselectivity is very important for this reaction, and we found no effect on regioselectivity of the reaction when phenylacetylene was used substituted with electron-donating or electron withdrawing groups in the phenyl moiety. The presence of various electron-donating substituents such as methyl (**3b, 3c**) and *tert*-butyl (**3d**) produced the desired products in good to excellent yields (78-85%). Similarly, a variety of electron withdrawing groups like ketones, halogens (F, Cl, Br) and nitro at different positions of the phenylacetylene substrate (**3e-3k**) also reacted efficiently with good to excellent yields. The heterocyclic moiety, thiophene, afforded the corresponding product with excellent yield (**3l**). It is worthy to mention that an aliphatic alkyne also gave the desired product (**3m**) in excellent yield.

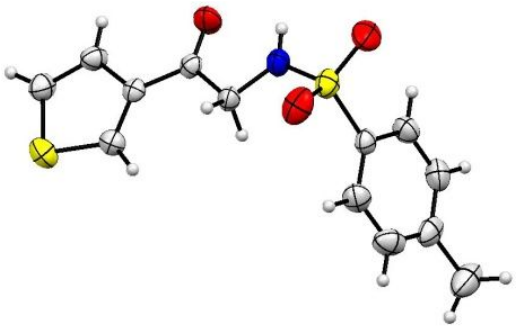
Scheme 2: Substrates Scope of the Amidation Reaction[a]



[a]*Reaction conditions:* All reaction are carried out in 0.5 mmol scale, **1** (0.5 mmol), **2** (0.5 mmol) and PIDA (0.25 equiv), at room temperature in MeCN (2 mL) for 10 h. All are isolated yields.

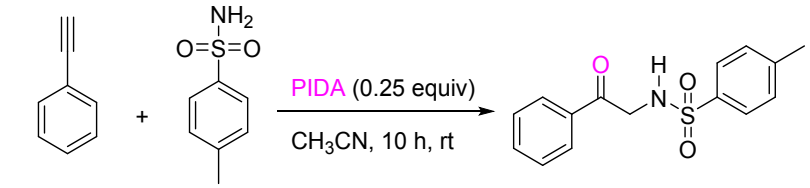
Next, we have explored our present methodology with another sulfonamide to react with terminal alkynes under the same reaction condition. 4-Chlorobenzenesulfonamide (**2b**) reacted with different terminal alkynes. Phenylacetylene, substituted phenylacetylene with electron donating substituents like $–CH_3$, $-C(CH_3)_3$, -OEt, furnished the desired products with good to excellent yields (**3n-3q**).Additionally, phenylacetylene substituted with electron-withdrawing groups like –F, -Br afforded the desired products in good yields (**3r** & **3s**). The thiophene-containing substrate was found to be equally effective to afford the desired product (**3t**) with good yield. Simple benzenesulfonamide (**2c**) also successfully reacted with phenylacetylene and 4-*tert*-butyl phenylacetylene to produce the desired products (**3u** & **3v**) in good yields. However, the present methodology is not applicable for the propargyl alcohol (**1w**), 4-ethynylaniline (**1x**) and 2-ethynylpyridine (**1y**). All these reactions were carried out in an open atmosphere and are not sensitive to air and moisture. The reaction conditions are mild and give no decomposition of the products or polymerization of the starting materials. All of the known synthesized compounds have been characterized by NMR and the new compounds by NMR and mass spectrometry, and the X-ray crystallographic analysis of 4-methyl-*N*-(2-oxo-2-(thiophen-3-yl)ethyl)benzenesulfonamide (**3l**) was performed to confirm the structure of the product as shown in Figure 3.[17]

Figure 3: Crystal Structure (ORTEP) of 4-Methyl-*N*-(2-oxo-2-(thiophen-3-yl)ethyl)benzenesulfonamide (3l)



Furthermore, the potential synthetic applicability of this method was investigated on the gram scale using the model reaction in our laboratory setup. As shown in Scheme 3, the reaction could afford 1.08 g of **3a** in 75% yield without any significant loss of its efficiency, demonstrating the potential applications of the present method for a large scale synthesis of α-sulfonylamino ketone derivatives.

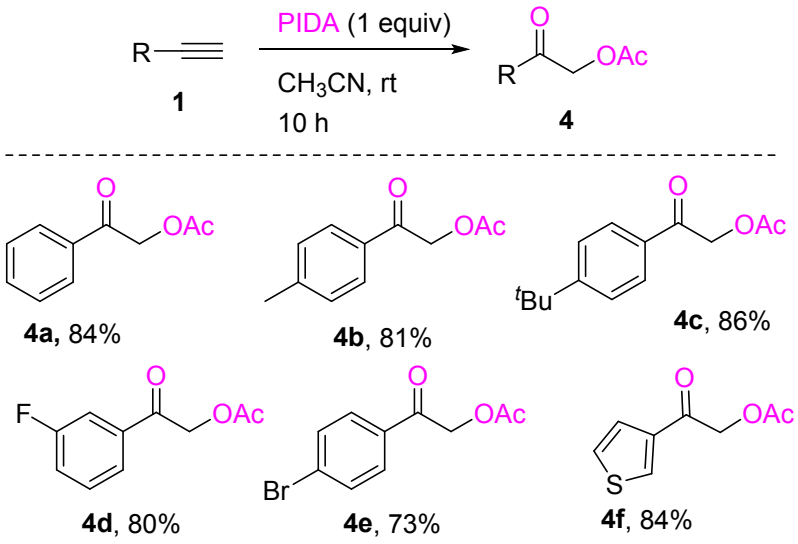
Scheme 3: Gram-Scale Synthesis



Finally, we checked the reaction in absence of sulfonamide, and we isolated exclusively 84% of α-acetoxy ketone (**4a**) when the reaction was performed between phenylacetylene and 1 equiv of PIDA at room temperature.[18] Different α-acetoxy ketone derivatives have been synthesized by varying different phenylacetylenes (Scheme 4). Phenylacetylenes containing electron-donating substituents such as methyl and *tert*-butyl afforded the products in 81% and 86% yields respectively (**4b** and **4c**). Electron-withdrawing groups like -fluoro and -bromo

formed α-acetoxy ketone derivatives in good to excellent yields (**4d** and **4e**). Heterocyclic moiety like 3-ethynylthiophene reacted well to afford corresponding product **4f** in 84% yield.

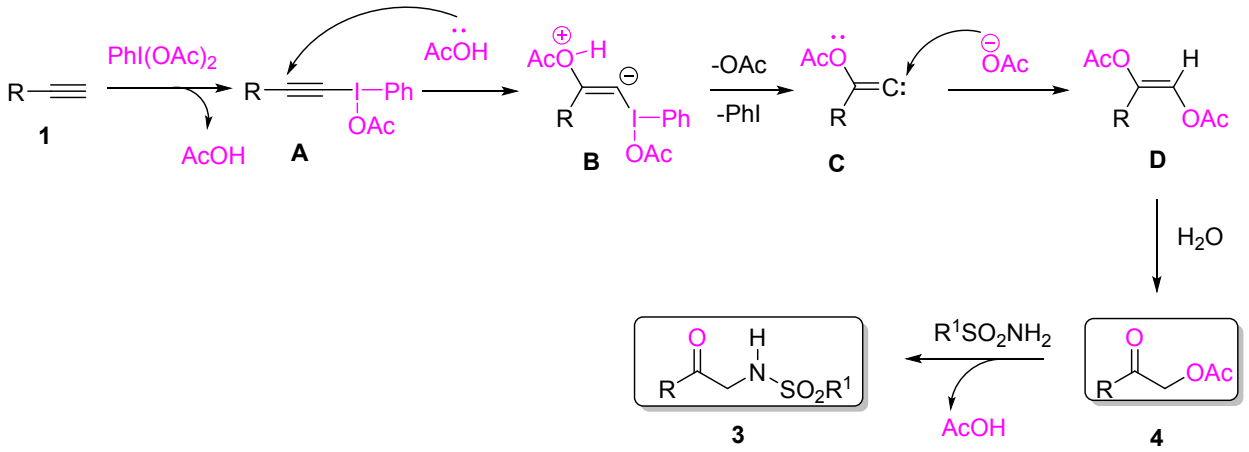
Scheme 4: Substrates Scope of the α-Acetoxy Ketones[a]



[a]*Reaction conditions:* All reactions are carried out in 0.5 mmol scales, **1** (0.5 mmol) and PIDA (1 equiv), at room temperature in MeCN (2 mL) for 10 h. All are isolated yields.

Based on the literature[18a,c] and our observation in absence of sulfonamide we propose the reaction pathway shown in Scheme 5. Reaction of alkyne **1** with $PhI(OAc)_2$ forms the phenylalkynyl iodanyl acetate intermediate **A** which on Michael-type addition of AcOH provides intermediate **B**. On removal of acetate the intermediate carbene **C** is formed which would then react with an acetoxy nucleophile or acidic acid leading to a diacetoxy alkene intermediate **D**. This one would then evolve to an α-acetoxy ketone **4** by reacting with the residual water, which could then lead to the α–sulfonylamino ketone **3** when sulphonamides are present. When α-acetoxy ketone **4a** was subjected to react with sulphonamide **2a**, it afforded the desired product **3a** which supports our mechanistic path.

Scheme 5: Proposed Mechanism



Conclusion:

To conclude, we have successfully developed an efficient and regioselective methodology for the synthesis of α-sulfonylamino ketones derivatives by the coupling of terminal alkynes with sulfonamides in presence of PIDA at room temperature under ambient air. An array of α-sulfonylamino ketones with broad functionalities have been synthesized in high yields. In addition, we have also observed the formation of α-acetoxy ketones in absence of sulfonamide. We have also proposed a mechanistic pathway for the formation of both of these compounds. The notable advantages of the present methodology are clean reaction, easily accessible reactants, ease of product isolation/purification, and metal-free and environmentally friendly reaction conditions. We believe that the present methodology opens a new door to synthesize important building blocks of α-sulfonylamino ketones.

Experimental Section:

General information: ^{1}H NMR spectra were determined on a 400 MHz spectrometer as solutions in $CDCl_3$. Chemical shifts are expressed in parts per million (δ) and the signals were reported as s (singlet), d (doublet), t (triplet), m (multiplet) and coupling constants *J* were given in Hz. ^{13}C NMR spectra were recorded at 100 MHz in $CDCl_3$ solution. Chemical shifts are expressed in parts per million (δ) and are referenced to $CDCl_3$ (δ = 77.16) as an internal standard. TLC was done on silica gel coated glass slide (Silica gel G for TLC). Silica gel (60-120 mesh) was used for column chromatography. Petroleum ether refers to the fraction boiling in the range of 60-80 °C unless otherwise mentioned. All solvents were dried and distilled before use. Commercially available substrates were freshly distilled before the reaction. All reactions involving moisture sensitive reactants were executed using oven dried glassware. All the starting materials (such as terminal alkynes **1** and benzenesulfonamide **2**) and other reagents were purchased from commercial suppliers.

General procedure for the synthesis of α-amino ketones (3): A mixture of terminal alkyne (**1**, 0.5 mmol) and benzenesulfonamide (**2**, 0.5 mmol) was taken in 2 mL of CH_3CN in a sealed tube. Iodobenzene diacetate (PIDA, 0.25 equiv) was added to the reaction mixture. Next, the reaction mixture was stirred at room temperature for 10 h. After completion of the reaction (monitored by TLC), the reaction mixture was diluted with ethylacetate (10 mL) and water (10 mL). Then organic layer was dried over anhydrous Na_2SO_4. After evaporation of solvent the crude product was collected and purified by column chromatography on silica gel using petroleum ether/ethyl acetate (8% to 10%) as eluent.

Typical procedure for the synthesis of 4-methyl-N-(2-oxo-2-phenylethyl)benzenesulfonamide (3a) on gram scale: A mixture of phenylacetylene (**1a**, 5 mmol) and 4-methylbenzenesulfonamide (**2a**, 5 mmol) was taken in 10 mL of CH_3CN in a 25

mL of round bottom flask. Iodobenzene diacetate (PIDA, 0.25 equiv) was added to the reaction mixture. Next, the reaction mixture was stirred at room temperature for 10 h. After completion of the reaction (monitored by TLC), the reaction mixture was diluted with ethylacetate (25 mL) and water (25 ml). Then organic layer was dried over anhydrous Na_2SO_4. After evaporation of solvent the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (8% to 10%) as eluent to get the analytically pure product as white solid (**3a**, 1.08 g, 75%).

General procedure for the synthesis of α-acetoxy ketone (4): A mixture of terminal alkyne (**1,** 0.5 mmol) and iodobenzene diacetate (PIDA, 0.5 equiv) was taken in 2mL of CH_3CN in a sealed tube. Next, the reaction mixture was stirred at room temperature for 10 h. After completion of the reaction (monitored by TLC), the reaction mixture was diluted with ethylacetate (10 mL) and water (10 mL). Then organic layer was dried over anhydrous Na_2SO_4. After evaporation of solvent the crude product was collected and purified by column chromatography on silica gel using petroleum ether/ethyl acetate (5% to 6%) as eluent.

4-Methyl-N-(2-oxo-2-phenylethyl)benzenesulfonamide (3a):[10c] White solid (115 mg, 80%), mp: 116-118 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86-7.83 (m, 2H), 7.79-7.77 (m, 2H), 7.62-7.59 (m, 1H), 7.48-7.44 (m, 2H), 7.29-7.27 (m, 2H), 5.65 (t, J = 8.0 Hz, 1H), 4.46 (d, J = 4.4 Hz, 2H), 2.39 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 192.7, 143.9, 136.3, 134.5, 134.0, 130.0, 129.1, 128.0, 127.3, 48.8, 21.6.

4-Methyl-N-(2-oxo-2-(p-tolyl)ethyl)benzenesulfonamide (3b):[11,10f] White solid (118 mg, 78%), mp: 120-121 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71-7.66 (m, 4H), 7.22-7.18 (m, 4H), 5.59 (t, J

= 8.4 Hz, 1H), 4.35 (d, *J* = 4.8 Hz, 2H), 2.34 (s, 3H), 2.32 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 192.1, 145.7, 143.9, 136.2, 131.4, 129.9, 129.8, 128.1, 127.3, 48.6, 21.9, 21.6.

4-Methyl-N-(2-oxo-2-(m-tolyl)ethyl)benzenesulfonamide (3c):[10f] White solid (127 mg, 84%), mp: 127-128 °C ; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.79-7.76 (m, 2H), 7.65-7.62 (m, 2H), 7.43-7.40 (m, 1H), 7.36-7.28 (m, 3H), 5.66 (t, *J* = 8.4 Hz, 1H), 4.44 (d, *J* = 4.4 Hz, 2H), 2.39 (s, 6H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 192.8, 143.9, 139.1, 136.2, 135.4, 133.9, 130.0, 129.0, 128.5, 127.3, 125.2, 48.8, 21.6, 21.4.

N-(2-(4-(Tert-butyl)phenyl)-2-oxoethyl)-4-methylbenzenesulfonamide (3d):[6g] White solid (146 mg, 85%), mp: 117-119 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.79-7.76 (m, 4H), 7.48-7.46 (m, 2H), 7.29-7.27 (m, 2H), 5.68 (t, *J* = 8.8 Hz, 1H), 4.43 (d, *J* = 4.4 Hz, 2H), 2.39 (s, 3H), 1.32 (s, 9H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 192.2, 158.6, 143.8, 136.2, 131.3, 129.9, 128.0, 127.3, 126.1, 48.7, 35.4, 31.1, 21.6.

N-(2-(4-Acetylphenyl)-2-oxoethyl)-4-methylbenzenesulfonamide (3e):[7a] White solid (143 mg, 87%), mp: 116-118 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03-8.01 (m, 2H), 7.94-7.92 (m, 2H), 7.79-7.77 (m, 2H), 7.31-7.28 (m, 2H), 5.63 (t, *J* = 8.4 Hz, 1H), 4.49 (d, *J* = 4.4 Hz, 2H), 2.63 (s, 3H), 2.40 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 197.2, 192.4, 144.0, 141.3, 137.0, 136.2, 130.0, 128.9, 128.3, 127.3, 49.2, 27.0, 21.7.

N-(2-(4-Fluorophenyl)-2-oxoethyl)-4-methylbenzenesulfonamide (3f): Colourless oil (128 mg, 84%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.90-7.87 (m, 2H), 7.78-7.76 (m, 2H), 7.29-7.27 (m, 2H), 7.15-7.11 (m, 2H), 5.66 (t, *J* = 8.4 Hz, 1H), 4.43 (d, *J* = 4.4 Hz, 2H), 2.39 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 191.2, 166.5 (d, $^{1}J_{C\text{-}F}$ = 256 Hz), 143.9, 136.2, 130.8 (d, $^{3}J_{C\text{-}F}$ = 10 Hz),

130.4 (d, $^{4}J_{C\text{-}F}$ = 3 Hz), 129.9, 127.3, 116.4 (d, $^{2}J_{C\text{-}F}$ = 23 Hz), 48.7, 21.6. Anal. Calcd. For $C_{15}H_{14}FNO_3S$: C, 58.62; H, 4.59; N, 4.56%; Found: C, 58.68; H, 4.52; N, 4.67%.

N-(2-(3-Fluorophenyl)-2-oxoethyl)-4-methylbenzenesulfonamide (3g): White solid (125 mg, 82%), mp: 157-158 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78-7.76 (m, 2H), 7.63-7.61 (m, 1H), 7.55-7.52 (m, 1H), 7.48-7.43 (m, 1H), 7.33-7.28 (m, 3H), 5.63 (t, J = 8.4 Hz, 1H), 4.44 (d, J = 4.4 Hz, 2H), 2.39 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 191.7, 163.0 (d, $^{1}J_{C\text{-}F}$ = 248 Hz), 144.0, 136.1, 135.8 (d, $^{3}J_{C\text{-}F}$ = 7 Hz), 130.9 (d, $^{3}J_{C\text{-}F}$ = 8 Hz), 130.0, 127.3, 123.7 (d, $^{4}J_{C\text{-}F}$ = 3 Hz), 121.6 (d, $^{2}J_{C\text{-}F}$ = 21 Hz), 114.8 (d, $^{2}J_{C\text{-}F}$ = 23 Hz), 49.0, 21.6. Anal. Calcd. For $C_{15}H_{14}FNO_3S$: C, 58.62; H, 4.59; N, 4.56%; Found: C, 58.52; H, 4.51; N, 4.48%.

N-(2-(4-Chlorophenyl)-2-oxoethyl)-4-methylbenzenesulfonamide (3h):[10e] White solid (131 mg, 77%), mp: 166-167 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80-7.76 (m, 4H), 7.45-7.42 (m, 2H), 7.30-7.28 (m, 2H), 5.63 (t, J = 8.0 Hz, 1H), 4.42 (d, J = 4.8 Hz, 2H), 2.39 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 191.6, 144.0, 141.1, 136.2, 132.2, 130.0, 129.5, 129.4, 127.3, 48.8, 21.6.

N-(2-(2-Chlorophenyl)-2-oxoethyl)-4-methylbenzenesulfonamide (3i):[10e] Colourless oil (122 mg, 72%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.77-7.75 (m, 2H), 7.48-7.40 (m, 3H), 7.34-7.28 (m, 3H), 5.56 (t, J = 8.4 Hz, 1H), 4.43 (d, J = 4.0 Hz, 2H), 2.41 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 192.1, 145.7, 143.7, 136.2, 131.4, 129.9, 129.8, 128.1, 127.3, 48.6, 21.9, 21.6.

N-(2-(4-Bromophenyl)-2-oxoethyl)-4-methylbenzenesulfonamide (3j):[10e] White solid (150 mg, 78%), mp: 120-122 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78-7.76 (m, 2H), 7.72-7.69 (m, 2H), 7.63-7.59 (m, 2H), 7.30-7.28 (m, 2H), 5.60 (t, J = 8.4 Hz, 1H), 4.42 (d, J = 4.8 Hz, 2H), 2.40 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 191.8, 144.0, 136.2, 132.6, 132.5, 130.0, 129.9, 129.4, 127.3, 48.7, 21.7.

4-Methyl-N-(2-(3-nitrophenyl)-2-oxoethyl)benzenesulfonamide (**3k**): Yellow solid (135 mg, 81%), mp: 107-108 °C ; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.66-8.65 (m, 1H), 8.47-8.44 (m, 1H), 8.20-8.18 (m, 1H), 7.79 (d, J = 8.4 Hz, 2H), 7.71 (t, J = 8 Hz, 1H), 7.30 (d, J = 8 Hz, 2H), 5.66 (t, J = 4.4 Hz, 1H), 4.53 (d, J = 4.8 Hz, 2H), 2.40 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 191.2, 148.6, 144.2, 136.1, 135.1, 133.5, 130.5, 130.0, 128.6, 127.3, 122.9, 49.2, 21.7. Anal. Calcd. For $C_{15}H_{14}N_2O_5S$: C, 53.89; H, 4.22; N, 8.38%; Found: C, 53.81; H, 4.31; N, 8.46%.***4-Methyl-N-(2-oxo-2-(thiophen-3-yl)ethyl)benzenesulfonamide (3l):***[11] White solid (126 mg, 86%), mp: 130-131 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.07-8.06 (m, 1H), 7.78-7.76 (m, 2H), 7.47-7.45 (m, 1H), 7.35-7.33 (m, 1H), 7.29-7.27 (m, 1H), 5.60 (t, J = 8.4 Hz, 1H), 4.34 (d, J = 4.8 Hz, 2H), 2.39 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 186.9, 143.9, 138.6, 136.1, 133.1, 129.9, 127.3(2C), 126.4, 49.3, 21.6.

4-Methyl-N-(2-oxo-4-phenylbutyl)benzenesulfonamide (3m): White solid (137 mg, 87%), mp: 92-93 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64-7.62 (m, 2H), 7.22-7.15 (m, 4H), 7.12-7.09 (m, 1H), 7.02-7.00 (m, 2H), 5.27 (t, J = 9.2 Hz, 1H), 3.70 (d, J = 4.8 Hz, 2H), 2.76 (t, J = 14.8 Hz, 2H), 2.59 (t, J = 15.2 Hz, 2H), 2.34 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 203.1, 143.9, 140.0, 136.2, 129.9, 128.7, 128.3, 127.3, 126.5, 51.7, 41.7, 29.5, 217. Anal. Calcd. For $C_{17}H_{19}NO_3S$: C, 64.33; H, 6.03; N, 4.41%; Found: C, 64.42; H, 6.11; N, 4.48%.

4-Chloro-N-(2-oxo-2-phenylethyl)benzenesulfonamide (3n):[6g] White solid (128 mg, 83%), mp: 137-138 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86-7.82 (m, 4H), 7.64-7.60 (m, 1H), 7.49-7.45 (m, 4H), 5.73 (t, J = 8.4 Hz, 1H), 4.48 (d, J = 4.4 Hz, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 192.4, 139.6, 137.9, 134.7, 133.8, 129.6, 129.2, 128.7, 128.0, 48.7.

4-Chloro-N-(2-oxo-2-(p-tolyl)ethyl)benzenesulfonamide (3o): Colourless oil (132 mg, 82%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78-7.74 (m, 2H), 7.68-7.66 (m, 2H), 7.41-7.37 (m, 2H), 7.21-7.18 (m, 2H), 5.68 (t, J = 8.8 Hz, 1H), 4.37 (d, J = 4.4 Hz, 2H), 2.34 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 192.0, 145.9, 139.5, 137.9, 131.3, 129.8, 129.6, 128.7, 128.1, 48.6, 21.9. Anal. Calcd. For $C_{15}H_{14}ClNO_3S$: C, 55.64; H, 4.36; N, 4.33%; Found: C, 55.55; H, 4.28; N, 4.27%.

N-(2-(4-(Tert-butyl)phenyl)-2-oxoethyl)-4-chlorobenzenesulfonamide (3p): White solid (155 mg, 85%), mp: 145-146 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.84-7.77 (m, 4H), 7.49-7.44 (m, 4H), 5.77 (t, J = 8.8 Hz, 1H), 4.45 (d, J = 4.8 Hz, 2H), 1.32 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 192.0, 158.8, 139.5, 137.9, 131.2, 129.6, 128.7, 128.0, 126.1, 48.6, 35.4, 31.1. Anal. Calcd. For $C_{18}H_{20}ClNO_3S$: C, 59.09; H, 5.51; N, 3.83%; Found: C, 59.19; H, 5.60; N, 3.92%.

4-Chloro-N-(2-(4-ethoxyphenyl)-2-oxoethyl)benzenesulfonamide (3q): White solid (137 mg, 78%), mp: 153-154 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.84-7.80 (m, 4H), 7.47-7.45 (m, 2H), 6.93-6.90 (m, 2H), 5.74 (t, J = 8.4 Hz, 1H), 4.40 (d, J = 4.4 Hz, 2H), 4.12-4.07 (m, 2H), 1.44 (t, J = 13.6 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 190.6, 164.2, 139.5, 137.9, 130.4, 129.6, 128.7, 126.5, 114.8, 64.1, 48.3, 14.7. Anal. Calcd. For $C_{16}H_{16}ClNO_4S$: C, 54.32; H, 4.56; N, 3.96%; Found: C, 54.41; H, 4.65; N, 3.88%.

4-Chloro-N-(2-(4-fluorophenyl)-2-oxoethyl)benzenesulfonamide (3r): White solid (137 mg, 84%), mp: 124-126 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91-7.87 (m, 2H), 7.84-7.82 (m, 2H), 7.48-7.46 (m, 2H), 7.17-7.13 (m, 2H), 5.74 (t, J = 8.4 Hz, 1H), 4.45 (d, J = 4.4 Hz, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 190.9, 166.7 (d, $^1J_{C\text{-}F}$ = 256 Hz), 139.6, 137.9, 130.8 (d, $^3J_{C\text{-}F}$ = 9

Hz), 130.2 (d, $^4J_{C\text{-}F}$ = 2 Hz), 129.7, 128.7, 116.5 (d, $^2J_{C\text{-}F}$ = 22 Hz), 48.6. Anal. Calcd. For $C_{14}H_{11}ClFNO_3S$: C, 51.30; H, 3.38; N, 4.27%; Found: C, 51.23; H, 3.30; N, 4.18%.

N-(2-(4-Bromophenyl)-2-oxoethyl)-4-chlorobenzenesulfonamide (3s): White solid (159 mg, 82%), mp: 138-139 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.84-7.82 (m, 2H), 7.72-7.70 (m, 2H), 7.63-7.61 (m, 2H), 7.48-7.45 (m, 2H), 5.71 (t, J = 8.4 Hz, 1H), 4.44 (d, J = 4.4 Hz, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 191.6, 139.7, 137.9, 132.6, 132.5, 130.1, 129.7, 129.4, 128.7, 48.7. Anal. Calcd. For $C_{14}H_{11}BrClNO_3S$: C, 43.27; H, 2.85; N, 3.60%; Found: C, 43.38; H, 2.95; N, 3.67%.

4-Chloro-N-(2-oxo-2-(thiophen-3-yl)ethyl)benzenesulfonamide (3t): White solid (133 mg, 85%), mp: 119-120 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.09-8.08 (m, 1H), 7.84-7.81 (m, 2H), 7.47-7.44 (m, 3H), 7.36-7.34 (m, 1H), 5.74 (t, J = 8.8 Hz, 1H), 4.37 (d, J = 4.4 Hz, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 186.8, 139.6, 138.5, 137.9, 133.2, 129.6, 128.7, 127.4, 126.4, 49.3. Anal. Calcd. For $C_{12}H_{10}ClNO_3S_2$: C, 45.64; H, 3.19; N, 4.44%; Found: C, 45.72; H, 3.28; N, 4.51%.

N-(2-Oxo-2-phenylethyl)benzenesulfonamide (3u):[12] White solid (105 mg, 77%), mp: 40-41 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91-7.89 (m, 2H), 7.86-7.83 (m, 2H), 7.63-7.45 (m, 6H), 5.69 (t, J = 8.4 Hz, 1H), 4.48 (d, J = 4.4 Hz, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 192.6, 139.3, 134.6, 133.9, 133.1, 129.4, 129.1, 128.0, 127.3, 48.8.

N-(2-(4-(Tert-butyl)phenyl)-2-oxoethyl)benzenesulfonamide (3v): Yellow oil (137 mg, 83%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91-7.88 (m, 2H), 7.79-7.77 (m, 2H), 7.55-7.46 (m, 5H), 5.71 (t, J = 8.4 Hz, 1H), 4.45 (d, J = 4.4 Hz, 2H), 1.32 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ

192.1, 158.7, 139.3, 133.0, 131.3, 129.3, 128.0, 127.2, 126.1, 48.7, 35.4, 31.1. Anal. Calcd. For $C_{18}H_{21}NO_3S$: C, 65.23; H, 6.39; N, 4.23%; Found: C, 65.33; H, 6.30; N, 4.28%.

2-Oxo-2-phenylethyl acetate (4a):[18f] White Solid (75 mg, 84%), mp: 42-43 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91-7.88 (m, 2H), 7.61-7.57 (m, 1H), 7.49-7.45 (m, 2H), 5.32 (s, 2H), 2.21 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 192.3, 170.5, 134.3, 134.0, 129.0, 127.9, 66.2, 20.7.

2-Oxo-2-(p-tolyl)ethyl acetate (4b):[18f] White Solid (78 mg, 81%), mp: 84-85 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80-7.78 (m, 2H), 7.27-7.25 (m, 2H), 5.30 (s, 2H), 2.40 (s, 3H), 2.20 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 191.8, 170.5, 144.9, 131.8, 129.6, 127.9, 66.0, 21.8, 20.6.

2-(4-(Tert-butyl)phenyl)-2-oxoethyl acetate (4c):[18b] White Solid (100 mg, 86%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86-7.84 (m, 2H), 7.50-7.48 (m, 2H), 5.32 (s, 2H), 2.22 (s, 3H), 1.33 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 191.9, 170.6, 157.9, 131.7, 127.8, 125.9, 66.1, 35.3, 31.1, 20.7.

2-(3-Fluorophenyl)-2-oxoethyl acetate (4d): Yellowish oil (81 mg, 80%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65-7.63 (m, 1H), 7.57-7.53 (m, 1H), 7.45-7.40 (m, 1H), 7.28-7.25 (m, 1H), 5.26 (s, 2H), 2.16 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 191.2, 170.3, 162.8 (d, $^1J_{C\text{-}F}$ = 248 Hz), 136.1 (d, $^3J_{C\text{-}F}$ = 6 Hz), 130.6 (d, $^3J_{C\text{-}F}$ = 8 Hz), 123.5 (d, $^4J_{C\text{-}F}$ = 3 Hz), 120.9 (d, $^2J_{C\text{-}F}$ = 22 Hz), 114.5 (d, $^2J_{C\text{-}F}$ = 22 Hz), 66.0, 20.4. Anal. Calcd. For $C_{10}H_9FO_3$: C, 61.23; H, 4.62%; Found: C, 61.29; H, 4.72%.

2-(4-Bromophenyl)-2-oxoethyl acetate (4e):[18f] White Solid (94 mg, 73%), mp: 82-83 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78-7.76 (m, 2H), 7.64-7.62 (m, 2H), 5.28 (s, 2H), 2.22 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 191.5, 170.5, 133.1, 132.4, 130.0, 129.4, 65.9, 20.6.

2-Oxo-2-(thiophen-3-yl)ethyl acetate (4f):[18c] Yellow Solid (77 mg, 84%), mp: 75-76 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.10-8.09 (m, 1H), 7.53-7.51 (m, 1H), 7.36-7.34 (m, 1H), 5.19 (s, 2H), 2.20 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 186.8, 170.5, 138.7, 132.3, 126.9, 126.5, 66.3, 20.6.

Supporting information: Scanned copies of ^{1}H and ^{13}C NMR spectra of the synthesized compounds, CIF file for compound **3l** are available as supporting information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

References

(1) Foley, K. F.; Cozzi, N. V. Novel Aminopropiophenones as Potential Antidepressants. *Drug Dev. Res.* **2003**, *60* (4), 252–260.

(2) Perrine, D. M.; Ross, J. T.; Nervi, S. J.; Zimmerman, R. H. A Short, One-Pot Synthesis of Bupropion (Zyban, Wellbutrin). *J. Chem. Educ.* **2000**, *77* (11), 1479.

(3) (a) Hanada, M.; Sugawara, K.; Kaneta, K.; Toda, S.; Nishiyama, Y.; Tomita, K.; Yamamoto, H.; Konishi, M.; Oki, T. Epoxomicin, a New Antitumor Agent of Microbial Origin. *J. Antibiot. (Tokyo).* **1992**, *45* (11), 1746–1752. (b) Meng, L.; Mohan, R.; Kwok, B. H. B.; Elofsson, M.; Sin, N.; Crews, C. M. Epoxomicin, a Potent and Selective Proteasome Inhibitor, Exhibits in Vivo Antiinflammatory Activity. *Proc. Natl. Acad. Sci.* **1999**, *96* (18), 10403–10408.

(4) (a) Kitamura, M.; Ohkuma, T.; Inoue, S.; Sayo, N.; Kumobayashi, H.; Akutagawa, S.; Ohta, T.; Takaya, H.; Noyori, R. Homogeneous Asymmetric Hydrogenation of Functionalized Ketones. *J. Am. Chem. Soc.* **1988**, *110* (2), 629–631. (b) Takahashi, H.; Sakuraba, S.; Takeda, H.; Achiwa, K. Asymmetric Reactions Catalyzed by Chiral Metal Complexes. 41. Highly Efficient Asymmetric Hydrogenation of Amino Ketone Derivatives Leading to Practical Syntheses of (S)-Propranolol and Related Compounds. *J. Am. Chem. Soc.* **1990**, *112* (15), 5876–5878. (c) Cho, B. T.; Chun, Y. S.

Enantioselective Synthesis of Optically Active β-Aminoalcohols via Asymmetric Reduction. *Tetrahedron: Asymmetry* **1992**, *3* (3), 341–342. (d) Pace, R. D.; Kabalka, G. W. Allylboration of. Alpha.-Amino Ketones. *J. Org. Chem.* **1995**, *60* (15), 4838–4844.

(5) (a) Magedov, I.V.; Luchetti, G.; Evdokimov, N. M.; Manpadi, M.; Steelant, W. F. A.; Van slambrouck, S. ; Tongwa, P.; Antipin, M. Yu.; Kornienko, A.; Novel three-component synthesis and antiproliferative properties of diversely functionalized pyrrolines. *Bioorg. & Med. Chem. Lett*. **2008**, (*18)*, 1392–1396 (b) Frolova, L. V; Evdokimov, N. M.; Hayden, K.; Malik, I.; Rogelj, S.; Kornienko, A.; Magedov, I. V. One-Pot Multicomponent Synthesis of Diversely Substituted 2-Aminopyrroles. A Short General Synthesis of Rigidins A, B, C, and D. *Org. Lett.* **2011**, *13* (5), 1118–1121 and references therein. (c) Matlock, J. V.; Fritz, S. V.; Harrison, S. A.; Coe, D. M.; McGarrigle, E. M.; Aggarwal, V. K. Synthesis of α-Substituted Vinylsulfonium Salts and Their Application as Annulation Reagents in the Formation of Epoxide and Cyclopropane-Fused Heterocycles. *J. Org. Chem.* **2014**, (79), 10226−10239 (d) Adam, I.; Orain, D.; Meier, P. Concise Synthesis of 1H-Pyrazin-2-Ones and 2-Aminopyrazines. *Synlett* **2004**, (11), 2031–2033. (e) Langer, P.; Bodtke, A. Sequential Cyclizations of 2-Isothiocyanatobenzonitrile and 2-Isocyanatobenzonitrile with α-Aminoketones. *Tetrahedron Lett.* **2003**, *44* (32), 5965–5967. (f) Frantz, D. E.; Morency, L.; Soheili, A.; Murry, J. A.; Grabowski, E. J. J.; Tillyer, R. D. Synthesis of Substituted Imidazoles via Organocatalysis. *Org. Lett.* **2004**, *6* (5), 843–846. (g) Unthank, M. G.; Hussain, N.; Aggarwal, V. K. The Use of Vinyl Sulfonium Salts in the Stereocontrolled Asymmetric Synthesis of Epoxide-and Aziridine-Fused Heterocycles: Application to the Synthesis of (−)-Balanol. *Angew. Chem.* **2006**, *118* (42), 7224–7227.

(6) (a) Heine, H. W.; Newton, T. Aziridines Xiv. Reaction of 1-Aroylaziridines with Dimethyl Sulfoxide. *Tetrahedron Lett.* **1967**, *8* (20), 1859–1860. (b) Fujita, S.; Hiyama, T.; Nozaki, H. Steric Course in Oxidative Ring Opening of Aziridine-1-Carboxylates with Dimethyl Sulphoxide. *Tetrahedron Lett.* **1969**, *10* (21), 1677–1678. (c) Fujita, S.; Hiyama, T.; Nozaki, H. Oxidative Ring-Opening of Aziridine-1-Carboxylates with Sulphoxides. *Tetrahedron* **1970**, *26* (18), 4347–4352. (d) Guthikonda, K.; Wehn, P. M.; Caliando, B. J.; Du Bois, J. Rh-Catalyzed Alkene Oxidation: A Highly Efficient and Selective Process for Preparing N-Alkoxysulfonyl Aziridines. *Tetrahedron* **2006**, *62* (49), 11331–11342. (e) Trost, B. M.; Dong, G. New Class of Nucleophiles for Palladium-Catalyzed Asymmetric Allylic Alkylation. Total Synthesis of Agelastatin A. *J. Am. Chem. Soc.* **2006**, *128* (18), 6054–6055. (f) Ghorai, M. K.; Kumar, A.; Das, K. Lewis Acid-Mediated Unprecedented Ring-Opening Rearrangement of 2-Aryl-N-Tosylazetidines to Enantiopure (*E*)-Allylamines. *Org. Lett.* **2007**, *9* (26), 5441–5444. (g) Zhang, X.; Li, S.-S.; Wang, L.; Xu, L.; Xiao, J.; Liu, Z.-J. 2-Methylquinoline Promoted Oxidative Ring-Opening of N-Sulfonyl Aziridines with DMSO: Facile Synthesis of α-Amino Aryl Ketones. *Tetrahedron* **2016**, *72* (49), 8073–8077.

(7) (a) Reddy, M. S.; Narender, M.; Rao, K. R. A Mild and Efficient Synthesis of α-Tosylamino Ketones from Aryl Aziridines in the Presence of β-Cyclodextrin and NBS in Water. *Tetrahedron Lett.* **2005**, *46* (8), 1299–1301.(b) Surendra, K.; Krishnaveni, N. S.; Rao, K. R. A Mild and Efficient Procedure for the Oxidation of Epoxides and Aziridines Using Cerium (IV) Ammonium Nitrate and NBS. *Tetrahedron Lett.* **2005**, *46* (23), 4111–4113.

(8) Surendra, K.; Krishnaveni, N. S.; Reddy, M. A.; Nageswar, Y. V. D.; Rao, K. R. Highly

Selective Oxidative Cleavage of β-Cyclodextrin− Epoxide/Aziridine Complexes with IBX in Water. *J. Org. Chem.* **2003**, *68* (23), 9119–9121.

(9) Luo, Z.-B.; Wu, J.-Y.; Hou, X.-L.; Dai, L.-X. Facile Preparation of α-Amino Ketones from Oxidative Ring-Opening of Aziridines by Pyridine N-Oxide. *Org. Biomol. Chem.* **2007**, *5* (21), 3428–3430.

(10) (a) Liang, J.-L.; Yu, X.-Q.; Che, C.-M. Amidation of Silyl Enol Ethers and Cholesteryl Acetates with Chiral Ruthenium (II) Schiff-Base Catalysts: Catalytic and Enantioselective Studies. *Chem. Commun.* **2002**, No. 2, 124–125. (b) Evans, D. A.; Faul, M. M.; Bilodeau, M. T. Copper-Catalyzed Aziridination of Olefins by (N-(p-Toluenesulfonyl) Imino) Phenyliodinane. *J. Org. Chem.* **1991**, *56* (24), 6744–6746. (c) Mizar, P.; Wirth, T. Flexible Stereoselective Functionalizations of Ketones through Umpolung with Hypervalent Iodine Reagents. *Angew. Chemie Int. Ed.* **2014**, *53* (23), 5993–5997. (d) Nakanishi, M.; Salit, A.; Bolm, C. Iron-Catalyzed Aziridination Reactions. *Adv. Synth. Catal.* **2008**, *350* (11-12), 1835–1840. (e) Yoshimura, A.; Nemykin, V. N.; Zhdankin, V. V. O-Alkoxyphenyliminoiodanes: Highly Efficient Reagents for the Catalytic Aziridination of Alkenes and the Metal-Free Amination of Organic Substrates. *Chem. Eur. J.* **2011**, *17* (38), 10538–10541.(f) Lim, B.-W.; Ahn, K.-H. The Reaction of [N-(p-Toluenesulfonyl) Imino]-Phenyliodinane with Enol Silanes. *Synth. Commun.* **1996**, *26* (18), 3407–3412.

(11) Miura, T.; Biyajima, T.; Fujii, T.; Murakami, M. Synthesis of α-Amino Ketones from Terminal Alkynes via Rhodium-Catalyzed Denitrogenative Hydration of N-Sulfonyl-1, 2, 3-Triazoles. *J. Am. Chem. Soc.* **2011**, *134* (1), 194–196.

(12) Tang, H.; Zhou, Y.; Zhu, Y.; Sun, H.; Lin, M.; Zhan, Z. Base-Catalyzed N-N

Bond Cleavage of Hydrazones: Synthesis of A-Amino Ketones. *Chem. Asian J.* **2014**, *9* (5), 1278–1281.

(13) (a) Stang, P. J.; Zhdankin, V. V. Organic Polyvalent Iodine Compounds. *Chem. Rev.* **1996**, *96* (3), 1123–1178. (b) Kita, Y.; Takada, T.; Tohma, H. Hypervalent Iodine Reagents in Organic Synthesis: Nucleophilic Substitution of p-Substituted Phenol Ethers. *Pure Appl. Chem.* **1996**, *68* (3), 627–630. (c) Varvoglis, A. *Hypervalent Iodine in Organic Synthesis*; Academic Press, 1996. (d) Kitamura, T.; Fujiwara, Y. Recent Progress in the Use of Hypervalent Iodine Reagents in Organic Synthesis. A Review. *Org. Prep. Proced. Int.* **1997**, *29* (4), 409–458. (e) Akiba, K. *Chemistry of Hypervalent Compounds*; John Wiley & Sons, 1999. (f) Zhdankin, V. V; Stang, P. J. Recent Developments in the Chemistry of Polyvalent Iodine Compounds. *Chem. Rev.* **2002**, *102* (7), 2523–2584. (g) Wirth, T. Oxidations and Rearrangements. In *Hypervalent Iodine Chemistry*; Springer, 2003; pp 185–208. (h) Wirth, T. Hypervalent Iodine Chemistry in Synthesis: Scope and New Directions. *Angew. Chemie Int. Ed.* **2005**, *44* (24), 3656–3665. (i) Ochiai, M. Stoichiometric and Catalytic Oxidations with Hypervalent Organo-λ3-iodanes. *Chem. Rec.* **2007**, *7* (1), 12–23.

(14) (a) Yoshimura, A.; Zhdankin, V. V. Advances in Synthetic Applications of Hypervalent Iodine Compounds. *Chem. Rev.* **2016**, *116* (5), 3328–3435. (b) Merritt, E. A.; Olofsson, B. Diaryliodonium Salts: A Journey from Obscurity to Fame. *Angew. Chemie Int. Ed.* **2009**, *48* (48), 9052–9070. (c) Liu, D.; Lei, A. Iodine-Catalyzed Oxidative Coupling Reactions Utilizing C-H and X-H as Nucleophiles. *Chem. Asian J.* **2015**, *10* (4), 806–823. (d) Kalbandhe, A. H.; Kavale, A. C.; Karade, N. N. Ring-Opening Reaction of Imidazo[1,2-*a*]Pyridines Using (Diacetoxyiodo) Benzene and NaN3: The

Synthesis of A-Iminonitriles. *European J. Org. Chem.* **2017**, *2017* (10), 1318–1322. (e) Manna, S.; Matcha, K.; Antonchick, A. P. Metal-Free Annulation of Arenes with 2-Aminopyridine Derivatives: The Methyl Group as a Traceless Non-Chelating Directing Group. *Angew. Chemie Int. Ed.* **2014**, *53* (31), 8163–8166. (f) Maiti, S.; Bose, A.; Mal, P. Oxidative N-Arylation for Carbazole Synthesis by CC Bond Activation. *J. Org. Chem.* **2018**, *83* (15), 8127–8138. (g) Manna, S.; Serebrennikova, P. O.; Utepova, I. A.; Antonchick, A. P.; Chupakhin, O. N. Hypervalent Iodine (III) in Direct Oxidative Amination of Arenes with Heteroaromatic Amines. *Org. Lett.* **2015**, *17* (18), 4588–4591. (h) Kantak, A. A.; Potavathri, S.; Barham, R. A.; Romano, K. M.; DeBoef, B. Metal-Free Intermolecular Oxidative C–N Bond Formation via Tandem C–H and N–H Bond Functionalization. *J. Am. Chem. Soc.* **2011**, *133* (49), 19960–19965.

(15) (a) Mahato, S.; Santra, S.; Chatterjee, R.; Zyryanov, G. V; Hajra, A.; Majee, A. Brønsted Acidic Ionic Liquid-Catalyzed Tandem Reaction: An Efficient Approach towards Regioselective Synthesis of Pyrano [3, 2-c] Coumarins under Solvent-Free Conditions Bearing Lower E-Factors. *Green Chem.* **2017**, *19* (14), 3282–3295. (b) Ojha, N. K.; Zyryanov, G. V; Majee, A.; Charushin, V. N.; Chupakhin, O. N.; Santra, S. Copper Nanoparticles as Inexpensive and Efficient Catalyst: A Valuable Contribution in Organic Synthesis. *Coord. Chem. Rev.* **2017**, *353*, 1–57. (c) Sarkar, A.; Santra, S.; Kundu, S. K.; Hajra, A.; Zyryanov, G. V; Chupakhin, O. N.; Charushin, V. N.; Majee, A. A Decade Update on Solvent and Catalyst-Free Neat Organic Reactions: A Step Forward towards Sustainability. *Green Chem.* **2016**, *18* (16), 4475–4525. (d) Santra, S.; Kopchuk, D. S.; Kovalev, I. S.; Zyryanov, G. V; Majee, A.; Charushin, V. N.; Chupakhin, O. N. Solvent-Free Synthesis of Pillar [6] Arenes. *Green Chem.* **2016**, *18* (2), 423–426.

(16) (a) Kopchuk, D. S.; Chepchugov, N. V; Kovalev, I. S.; Santra, S.; Rahman, M.; Giri, K.; Zyryanov, G. V; Majee, A.; Charushin, V. N.; Chupakhin, O. N. Solvent-Free Synthesis of 5-(Aryl/Alkyl) Amino-1, 2, 4-Triazines and α-Arylamino-2, 2′-Bipyridines with Greener Prospects. *RSC Adv.* **2017**, *7* (16), 9610–9619. (b) Ghosal, N. C.; Santra, S.; Das, S.; Hajra, A.; Zyryanov, G. V; Majee, A. Organocatalysis by an Aprotic Imidazolium Zwitterion: Regioselective Ring-Opening of Aziridines and Applicable to Gram Scale Synthesis. *Green Chem.* **2016**, *18* (2), 565–574. (c) Ghosal, N. C.; Santra, S.; Zyryanov, G. V; Hajra, A.; Majee, A. Conversion of Aziridines to Oxazolidines through Geminal Difunctionalization of Vinyl Arenes or by Tandem Ring-Opening/Closing Reaction of Aziridine Itself. *Tetrahedron Lett.* **2016**, *57* (31), 3551–3555. (d) Kovalev, I. S.; Taniya, O. S.; Slovesnova, N. V; Kim, G. A.; Santra, S.; Zyryanov, G. V; Kopchuk, D. S.; Majee, A.; Charushin, V. N.; Chupakhin, O. N. Fluorescent Detection of 2,4-DNT and 2,4,6-TNT in Aqueous Media by Using Simple Water-Soluble Pyrene Derivatives. *Chem. Asian J.* **2016**, *11* (5), 775–781.

(17) CCDC 1873498 contains the supplementary crystallographic data for compound**3l**.

(18) (a) Mo, D.-L.; Dai, L.-X.; Hou, X.-L. The Reaction of Terminal Alkynes with PhI(OAc)2: A Convenient Procedure for the Preparation of α-Acyloxy Ketones. *Tetrahedron Lett.* **2009**, *50* (40), 5578–5581. (b) Deng, G.; Luo, J. Silver(I)-Catalyzed Reaction of Terminal Alkynes with (Diacetoxyiodo)Benzene: A Convenient, Efficient and Clean Preparation of α-Acetoxy Ketones. *Tetrahedron* **2013**, *69* (29), 5937–5944. (c) Srinivas, B. T. V; Rawat, V. S.; Sreedhar, B. Iron-Catalyzed Dioxygenation of Alkenes and Terminal Alkynes by Using (Diacetoxyiodo)Benzene as Oxidant. *Adv. Synth. Catal.*

2015, *357* (16-17), 3587–3596. (d) Srinivas, B. T. V; Supriya, P.; Rohithrao, V.; Naidu, N. V. S.; Sreedhar, B. Magnetic CuFe2O4 and Fe3O4 Nanoparticles Catalyzed Diacetoxylation of Alkenes and 1,2-Oxyacetoxylation of Terminal Alkynes Using PhI(OAc)2 as Oxidant. *ChemistrySelect* **2017**, *2* (8), 2600–2604. (e) Wu, C.; Liang, Z.; Yan, D.; He, W.; Xiang, J. Straightforward and Highly Efficient Synthesis of α-Acetoxy Ketones through Gold-Catalyzed Intermolecular Oxidation of Terminal Alkynes. *Synthesis (Stuttg)*. **2013**, *45* (18), 2605–2611. (f) Sheng, J.; Li, X.; Tang, M.; Gao, B.; Huang, G. An Efficient Method for the α-Acetoxylation of Ketones. *Synthesis (Stuttg)*. **2007**, *2007* (08), 1165–1168. (g) Reed, K. L.; Gupton, J. T.; McFarlane, K. L. The Mercury (II) Catalyzed, One-Pot Oxidation of Terminal Alkynes by Sodium Perborate in Acetic Acid. *Synth. Commun.* **1989**, *19* (13–14), 2595–2602. (h) Abedi, Y.; Biffis, A.; Gava, R.; Tubaro, C.; Chelucci, G.; Stoccoro, S. Cu–iminopyridine Complexes as Catalysts for Carbene and Nitrene Transfer Reactions. *Appl. Organomet. Chem.* **2014**, *28* (7), 512–516.