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Copper-Catalyzed Hydroamination of Terminal Alkynes by Combining N-fluorobenzenesulfonimide and H2O: Synthesis of β-amino Substituted Styrenes

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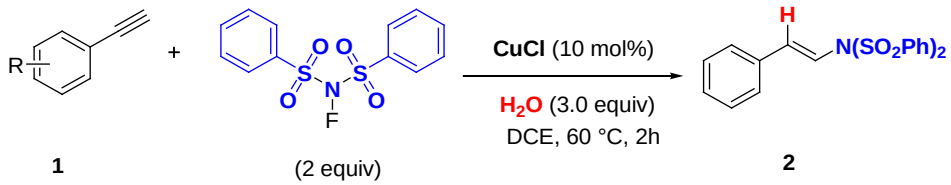
Abstract By using the combining of N-fluorobenzenesulfonimide and H_2O, we have realized the first example of high efficient and easy hydroamination of terminal alkynes. The reaction was catalyzed by copper and the corresponding β-amino substituted styrenes have been afforded in good to excellent yields. The transformation under simple mild conditions feature a broad substrate scope, atom economy, good functional group tolerance and the simple mechanism was proposed. The different products obtained were characterized using ^{1}HNMR, ^{13}CNMR and HRMS.



Graphical Abstract

Keywords: *hydroamination, β-amino substituted styrenes, N-fluorobenzenesulfonimide (NFSI), Copper-Catalyzed*

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1. Introduction

The formation of carbon nitrogen bond using available and inexpensive compounds is essential in organic chemistry and is of great importance in the pharmaceutical and biological fields [1-4].The important of nitrogen-containing compounds is one of the raisons that led the chemists to develop new C−N bond-forming transformations [5,6]. In particular, amination of unsaturated carbon-carbon bonds, such as aminooxygenation [7], aminofluorination [8], carboamination [9], thiocyanation-amination [10], aminocyanation [11], aminoalkylation [12] and hydroamination [13] of alkenes, allenes, and alkynes, has emerged as a powerful tool for C-N bond formation. Among those transformations, the alkyne hydroamination reaction constitutes a powerful synthetic procedure with the potential to gain access to amine products which are widely featured in pharmaceutically active compounds [14-16]. This reaction is much more efficient when catalyzed by a transition metal [17]. In this contexe, Kozlov and all reported in 1936 the first mercury-catalyzed hydroamination, but the toxicity of mercury showed the ineffectiveness of this method [18]. Further, Christina Erken and co-woker reported the hydroaminaion of aromatic alkynes to imines catalyzed by Pd(II)-Anthrophos complexes (Figure 1a) [19]. The complexity of tridentate ligand limits this reaction. To all these problems is added that of origin of the nitrogen source during the formation of C−N bond. In the past several decades, different kinds of nitrogen sources have been used for the constraction of C−N bond [20]. The NFSI can be used as an efficient nitrogen source in the case of

amination. He also used as a strong efficient oxidant in transition-metal-catalyzed transformation to produce high-oxidation state metal complexes [21]. Ainsi, in 2012, our group developed palladium-catalyzed allylic C–H amination of alkenes with *N*-fluorodibenzenesulfonimide. In this reaction, water played an important [22]. Recently, the group of Bi reported silver-catalyzed hydroazidation of Terminal Alkynes by combining a nitrogen source sach as $TMS^{-}N_3$ and H_2O for the Synthesis of Vinyl Azides [23]. These results demonstrated that an appropriate amount of H_2O was essential for the hydroamination of terminal alkynes with TMS-N_3. However, transition-metal-catalyzed hydroamination of alkynes by using a combination of a nitrogen source and H_2O remains an area of study for organic synthesis. In this context, we report Copper-Catalyzed Hydroamination of Terminal Alkynes by Combining N-fluorobenzenesulfonimide as a nitrogen source and H_2O to synthesis of β-amino substituted styrenes (Figure 1b).

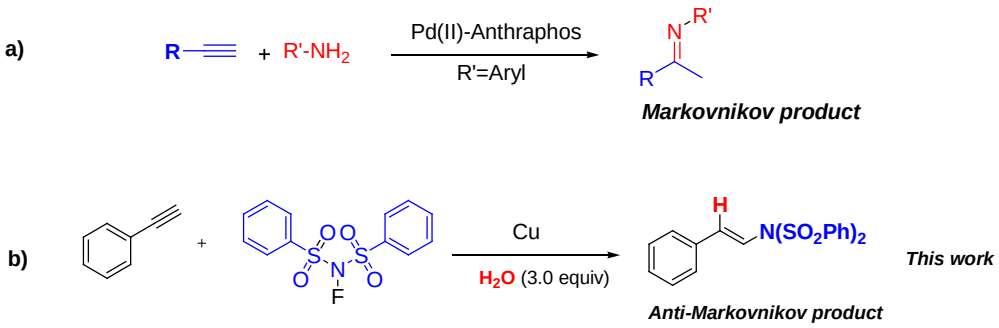


Figure 1. Catalytic Hydroamination of alkynes

2. Experimental Procedures

2.1. Materials

All reactions were carried out under air atmosphere and monitored by Analytical thin-layer chromatography (TLC) with Machery-Nagel 0.20 mm silica gel 60 plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure. ^{1}H NMR spectra were recorded at ambient temperature on a Varian 400 MHz, ^{13}C NMR spectra were recorded at ambient temperature on a Varian 125 MHz and TMS as internal standard. Melting points were obtained with a micro melting point XT4A Beijing Keyi. Chemical shifts for 1H NMR were described in parts per million relative to internal standard TMS (0 ppm for H1) and $CDCl_3$ (77.0 ppm for 13C). High resolution mass spectra were recorded on Bruck microtof. Coupling Constants (J) were then expressed in Hz. The signals have been described according to the following rule: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. All chemicals and solvents were purchased from commercial source and used as received.

2.2. General Procedure for the Synthesis of Compounds

Ethynylbenzene **1a** (25.5 mg, 0.25 mmol), NFSI (157.5 mg, 0.5 mmol), CuCl (2.5 mg, 0.025 mmol) and H_2O (13.5 mg 0.75 mmol) were placed in a round-bottomed flask containing a magnetic stirrer under air atmosphere. 3 mL of dichloromethane (DCM) was dissolved. The mixture was then stirred at 60 ºC for 2 hours and monitored by TLC. After, the aqueous layer was extracted with dichloromethane (5.0 mLx3) and the organic layers were combined, washed with water and dried over anhydrous Na_2SO_4. The organic layer was filtered, concentrated by rotary evaporation and purified by flash colunm chromatography on silicate gel as solid phase and petroleum/ethyl acetate (25:1, v:v) as the eluent to give compound **2a** (84.20 mg, 85 %) as a white solid.

2.3. Characterization Data of Compound 2

(E)-N-(phenylsulfonyl)-N-styrylbenzenesulfonamid (2a)

White solid (84.20 mg, 85%); mp: 171-173 °C; 1H NMR (400 MHz; CDCl3): δ = 6.54 (d, J = 13.6 Hz, 1H, =CH-N), 6.66 (d, J = 13.6 Hz, 1H, Ar-CH=), 7.31 – 7.38 (m, 5H, Ar-H), 7.56 (t, J = 8.0 Hz, 4H,), 7.67 (t, J = 7.6 Hz, 2H), 8.00 (dd, J12= 1.2 Hz, J13= 8.8 Hz, 4H). 13C NMR (125 MHz; CDCl3): δ = 119.4, 127.2, 128.1, 128.8, 129.1, 129.4, 133.7, 134.0, 139.1, 139.4. HRMS (ESI-TOF) calcd for C20H17NNaO4S2, [M+Na]+ 422.0497 Found 422.0512.

(*E*)-*N*-(4-chlorostyryl)-*N*-(phenylsufonyl)benzenesulfonamide (2b)

White solid (63.32 mg, 78%); mp: 153-156 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.51 (d, J = 13.6 Hz, 1H), 6.65 (d, J = 13.6 Hz, 1H), 7.56 – 7.33 (m, 4H), 7.67 (t, J = 8.0 Hz, 4H), 7.69 (t, J = 7.2 Hz, 2H), 7.99 (d, J = 7.6 Hz, 4H). ^{13}C NMR (125 MHz; $CDCl_3$): δ = 120.0, 128.1, 128.4, 129.0, 129.1, 132.2, 134.1, 135.2, 137.4, 139.4. HRMS (ESI-TOF) calcd for $C_{20}H_{16}ClNNaO_4S_2$, $[M+Na]^+$ 456.0107 Found 456.01406.

(*E*)-*N*-(4-fluorostyryl)-*N*-(phenylsufonyl)benzenesulfonamide (2c)

White solid (64.21 mg, 72%); mp: 155-157 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ= 6.45 (d, J = 13.6 Hz, 1H), 6.65 (d, J = 14.0 Hz, 1H), 7.04 (t, J = 8.4 Hz, 2H), 7.32 – 7.35 (m, 2H), 7.57 (t, J = 8.0 Hz, 4H), 7.69 (t, J = 7.2 Hz, 2H), 7.99 (d, J = 7.2 Hz, 4H). ^{13}C NMR (125 MHz; $CDCl_3$): δ = 115.8, 116.0, 119.1, 128.2, 128.9, 129.1, 134.0, 137.9, 139.4, 141.9 HRMS (ESI-TOF) calcd for $C_{20}H_{16}FNNaO_4S_2$, $[M+Na]^+$ 440.0402 Found 440.0407.

(*E*)-*N*-(4-bromostyryl)-*N*-(phenylsufonyl)benzenesulfonamide (2d)

White solid (45.11 mg, 67%); mp: 152-154 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6. 52 (d, J = 13.6 Hz, 1H), 6.65 (d, J = 13.6 Hz, 1H), 7.22 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.57 (t, J = 8.4 Hz, 4H), 7.67 (t, J = 7.2 Hz, 2H), 7.99 (d, J = 7.2 Hz, 4H). ^{13}C NMR (125 MHz; $CDCl_3$): δ = 119.4, 127.2, 128.2, 128.8, 129.1, 129.4, 133.7, 134.0, 139.1, 139.5. HRNS (ESI-TOF) calcd for $C_{20}H_{17}BrNO_4S_2$, $[M+H]^+$ 477.9777; Found 477.9288.

(*E*)-*N*-(3-bromostyryl)-*N*-(phenylsufonyl)benzenesulfonamide (2e)

White solid (35.10 mg, 52%); mp: 150-151 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.56 (d, J = 14.0 Hz, 1H), 6.65 (d, J = 14.0 Hz, 1H), 7.22 – 7.27 (m, 2H), 7.46 (d, J = 7.6 Hz, 1H), 7.51 (s, 1H), 7.58 (t, J = 8.0 Hz, 4H), 7.69 (t, J = 7.2 Hz, 2H), 8.00 (dd, J_{12} = 1.6 Hz, J_{13} = 8.0 Hz, 4H).^{13}C NMR (125 MHz; $CDCl_3$): δ =120.8, 122.9, 125.8, 128.1, 129.1, 129.8, 130.3, 132.1, 134.1, 135.8, 136.8, 139.3. HRMS (ESI-TOF) calcd for $C_{20}H_{16}BrNNaO_4S_2$, $[M+Na]^+$ 499.9596 Found 499.9589.

***(E)-N-(4-methoxystyryl)-N*-(phenylsufonyl)benzenesulfonamide (2f)**

White solid (68.78 mg, 83%); mp: 130-132°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.82 (s, 3H), 6.37 (d, J = 13.6 Hz, 1H), 6.60 (d, J = 13.6 Hz, 1H), 6.87 (d, J = 8.8 Hz, 2H), 7.30 (d, J = 8.8 Hz, 2H), 7.56 (t, J = 8.0 Hz, 4H), 7.67 (t, J = 7.2 Hz, 2H), 7.99 (d, J = 7.6 Hz, 4H). ^{13}C NMR (125 MHz; $CDCl_3$): δ = 55.4, 114.2, 117.0, 126.3, 128.2, 128.7, 129.1, 133.9, 139.3, 139.5, 160.5. HRMS (ESI-TOF) calcd for $C_{21}H_{19}NNaO_5S_2$, $[M+Na]^+$ 452.0602 Found 452.0613.

(*E*)-*N*-(2,4-dimethylstyryl)-*N*-(phenylsufonyl)benzenesulfonamide (2g)

White solid (61.97 mg, 74%); mp: 152-154 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ =2.18 (s, 3H), 2.31 (s, 3H), 6.33 (d, J = 13.6 Hz, 1H), 6.84 (d, J = 13.6 Hz, 1H), 6.99 (d, J = 5.6 Hz, 2H), 7.29 (d, J= 8.0 Hz, 1H), 7.53 – 7.57 (m, 4H), 7.64 – 7.69 (m, 2H), 8.00 (d, J = 7.2 Hz, 4H).^{13}C NMR (125 MHz; $CDCl_3$): δ = 19.6, 21.2, 119.3, 126.2, 126.9, 128.1, 129.1, 129.9, 131.3, 133.9, 136.5, 138.0, 139.4, 139.5. HRMS (ESI-TOF) calcd for $C_{22}H_{22}NO_4S_2$, $[M+H]^+$ 428.0985 Found 428.0905.

(*E*)-*N*-(4-methylstyryl)-*N*-(phenylsufonyl)benzenesulfonamide (2h)

White solid (74.43 mg, 82%); mp: 133-135 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.36 (s, 3H), 6.46 (d, J = 13.6 Hz, 1H), 6.64 (d, J = 14.0 Hz, 1H), 7.15 (d, J = 7.6 Hz, 2H), 7.25 (d, J = 7.2 Hz, 2H), 7.56 (t, J = 8.0 Hz, 4H), 7.67 (t, J = 7.2 Hz, 2H), 7.99 (d, J = 8.0 Hz, 4H). ^{13}C NMR (125 MHz; $CDCl_3$): δ = 21.3, 118.3, 127.2, 128.2, 129.0, 129.5, 130.9, 133.9, 139.3, 139.5, 139.6. HRMS (ESI-TOF) calcd for $C_{21}H_{19}NNaO_4S_2$, $[M+Na]^+$ 436.0653 Found 436.0672.

(*E*)-*N*-(2-methylstyryl)-*N*-(phenylsufonyl)benzenesulfonamide (2i)

White solid (72.62 mg, 80%); mp: 131 – 133 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.35 (s, 3H), 6.51 (d, J = 13.6 Hz, 1H), 6.65 (d, J = 14.0 Hz, 1H), 7.15-7.19 (m, 3H), 7.24 (t, J = 6.4 Hz, 1H), 7.57 (t, J = 8.0 Hz, 4H), 7.65 – 7.69 (m, 2H), 8.00 (d, J = 7.2 Hz, 4H). ^{13}C NMR (125 MHz; $CDCl_3$): δ = 21.3, 119.1, 124.4, 127.8, 128.0, 128.1, 128.7, 129.1, 133.6, 133.9, 136.0, 138.5, 139.3. HRMS (ESI-TOF) calcd for $C_{21}H_{19}NNaO_4S_2$, $[M+Na]^+$ 436.0653 Found 436.0609.

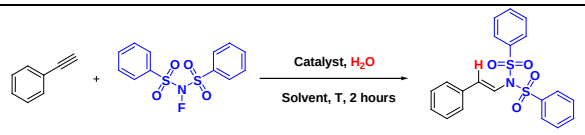
(*E*)-*N*-(4-(ter-butyl)styryl)-*N*-(phenylsufonyl)benzenesulfonamide (2j)

White solid (63.14 mg, 86 mp: 137 – 138 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 (s, 9H), 6.49

(d, J = 13.6 Hz, 1H), 6.66 (d, J = 13.6 Hz, 1H), 7.30 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 7.57 (t, J = 8.0 Hz, 4H), 7.64 – 7.69 (m, 2H), 8.00 (dd, J12 = 1.6 Hz, J13 = 8.0 Hz, 4H). ^{13}C NMR (125 MHz; $CDCl_3$): δ = 31.2, 34.8, 118.5, 125.7, 127.0, 128.1, 129.1, 130.9, 133.9, 139.1, 139.5, 152.8. HRMS (ESI-TOF) calcd for $C_{24}H_{26}NO_4S_2$, $[M+H]^+$ 456.1298 Found 456.1292.

3. Results and Discussion

Table 1. Optimization of reaction Conditions

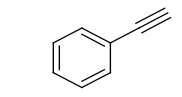
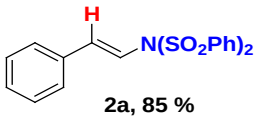
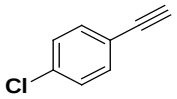
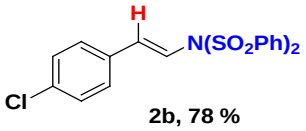
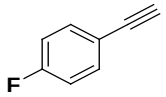
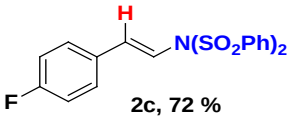
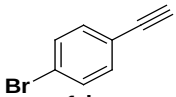
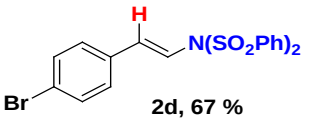
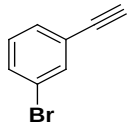
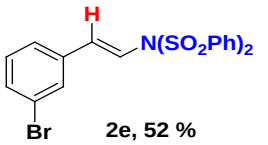
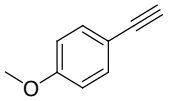
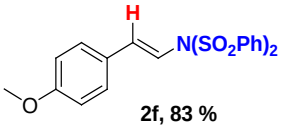
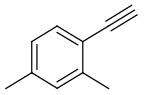
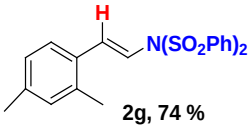
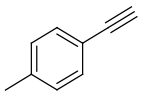
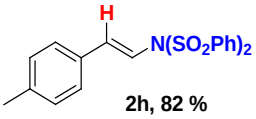
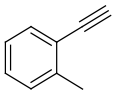
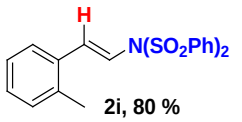
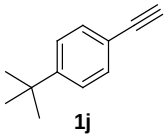
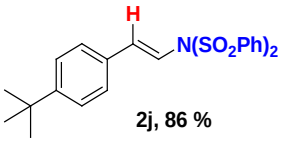


1a NFSI (2 equiv) 2a

Entry	Catalyst	Solvent	H_2O	T (°)	Yield (%)
1	-	DCM	-	60	0
2	$Cu(OAc)_2$	DCM	-	60	0
3	$Cu(OAc)_2$	DCM	1equiv	60	□1
4	$CuSO_4$	DCM	1 equiv	60	15
5	$CuCl_2$	DCM	1 equiv	60	18
6	CuBr	DCM	1 equiv	60	54
7	CuCl	DCM	1 equiv	60	58
8	CuCl	DCM	2 equiv	60	60
9	CuCl	DCM	3 equiv	60	85
10	CuCl	DMF	3 equiv	60	23
11	CuCl	THF	3 equiv	60	29
12	CuCl	DCE	3 equiv	60	79
13	CuCl	Toluene	3 equiv	60	trace
14	CuCl	DMSO	3 equiv	60	trace
15	CuCl	dioxane	3 equiv	60	0
16	CuCl	DCM	3 equiv	80	60
17	CuCl	DCM	3 equiv	100	52
18	CuCl	DCM	3 equiv	rt	0
19	CuCl	DCM	3 equiv	0	0

Reaction Conditions: 1a (0.25 mmol), NFSI (0.5 mmol), catalyst (10 mol%), solvent (3 mL), under air for 2 hours.

Table 2. Scope of Copper-calalyzed Hydroamination of Terminal Alkynes

Substrat 1	Product 2
 1a	 2a, 85 %
 1b	 2b, 78 %
 1c	 2c, 72 %
 1d	 2d, 67 %
 1e	 2e, 52 %
 1f	 2f, 83 %
 1g	 2g, 74 %
 1h	 2h, 82 %
 1i	 2i, 80 %
 1j	 2j, 86 %

In the absence of metal and water (Table 1, entry 1), no product was obtained. The use of copper Cu(OAc)2 as a catalyst in the absence of water (Table 1, entry 2) had no effect on the reaction. The combination of copper Cu(OAc)2 and an equivalent of water in the presence of dichloromethane at 60˚C (Table 1, entry 3) made it possible to obtain for the first time the desired product 2a in 21% yield. Different kind of copper such as CuSO4, CuCl2, CuBr and CuCl were used during this reaction (Table 1, entries 4-7), in the presence of DCM and an equivalent of water; the desired product 2a was obtained in 58% yield by using CuCl as catalyst. When we increased water, from 2 equivalents to 3 equivalents, under the same conditions (Table 1, entry 7), the desired product 2a was obtained in 60 % and 85 % yields, respectively. Several types of solvents were also used during this series such as: DMF, THF, DCE, Toluène, DMSO and Dioxane (Table 1, entries 10-15); only the DCE clearly gave product 2a in 79 % yield (Table 1, entry 12). Temperature also played a fairly important role in this reaction. When the reaction temperature was increased from 80˚C to 100˚C, we found a drop in the yield of product 2a from 60 % to 50 % respectively (Table 1, entries 16-17). With a decrease in temperature, no products were obtained.

Base on the optimization of this reaction in (Table 1, entry 9), the scope of copper-catalyzed Hydroamination of Terminal Alkynes was examined in a series of ethynylbenzene and the results are summarized in Table 2. The monohalogenated derivatives in the para position of the benzene ring such as 1b, 1c, and 1d were satisfactory during this reaction, giving the products 2b, 2c and 2d in yields of 78 %, 72 % and 67 % yields, respectively. When bromine is used in meta position (1e), we obtained product 2e with a slightly lower yield than products 2b, 2c and 2d. This reduction in yield can be explained by the delocalization of the benzene nucleus caused by the halogens in the para or meta position. The compounds 1f, 1g, 1h, 1i and 1j carrying electron donating groups such as methoxy, methyl and tertiobethyl (tBu) were also satisfactory during this transformation, giving the products 2(f-j) in 80 %, 74 %, 82 %, 80 % and 86% yields, respectively.

4. Proposed Mechanism

We proposed a plausible reaction radical mechanism for this transformation, in which the Cu(I) species reacted with NFSI to form the species Cu(III) A which can be in equilibrium with a radical species Cu(II) B. The radical addition reaction between the radical species Cu(II) B with a terminal alkyne 1leads to species Cu(II) D avec the radical intermediate C [24-28]. Afterwards, la combinaison entre species C and D in the presence of water leads to the desired product 2 and also the complex E which subsequently undergoes decomposition to give hypofluorous acid and generated the catalyst Cu(I).

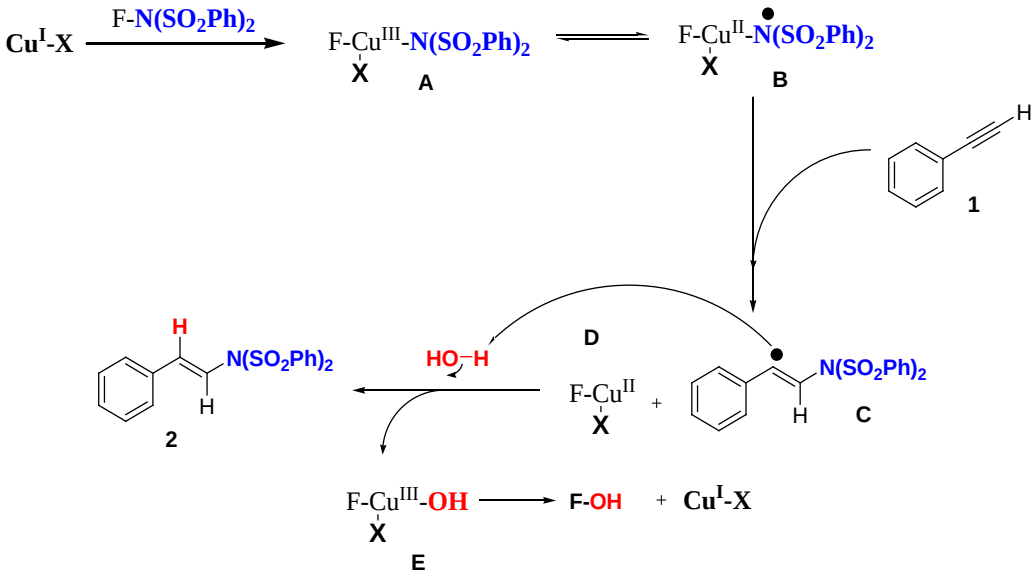


Figure 2. Proposed Mechanism for the synthesis of compounds 2

1H and 13C Spectra of New Compounds

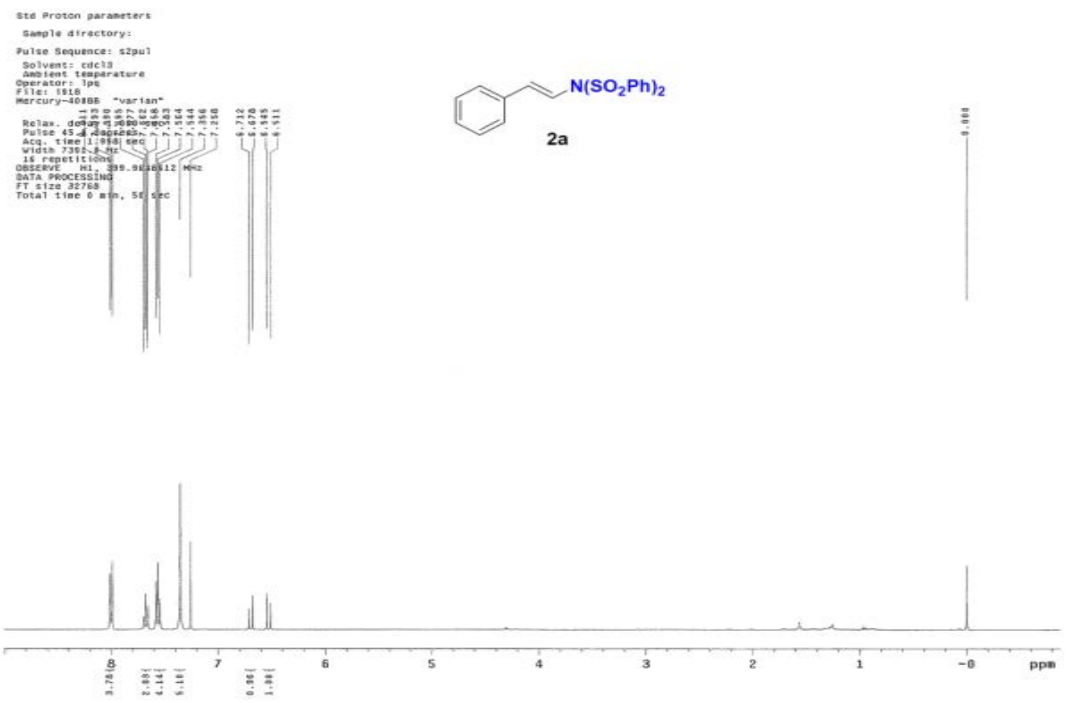
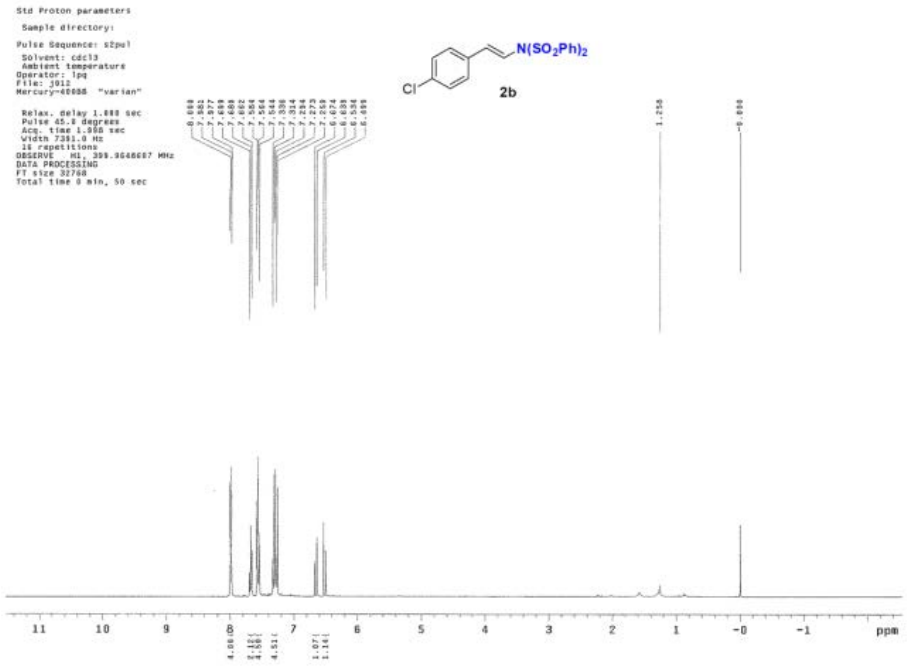


Figure 3. [1]HNMR spectrum of compound 2a

Figure 4. ^{13}C NMR spectrum of compound 2a



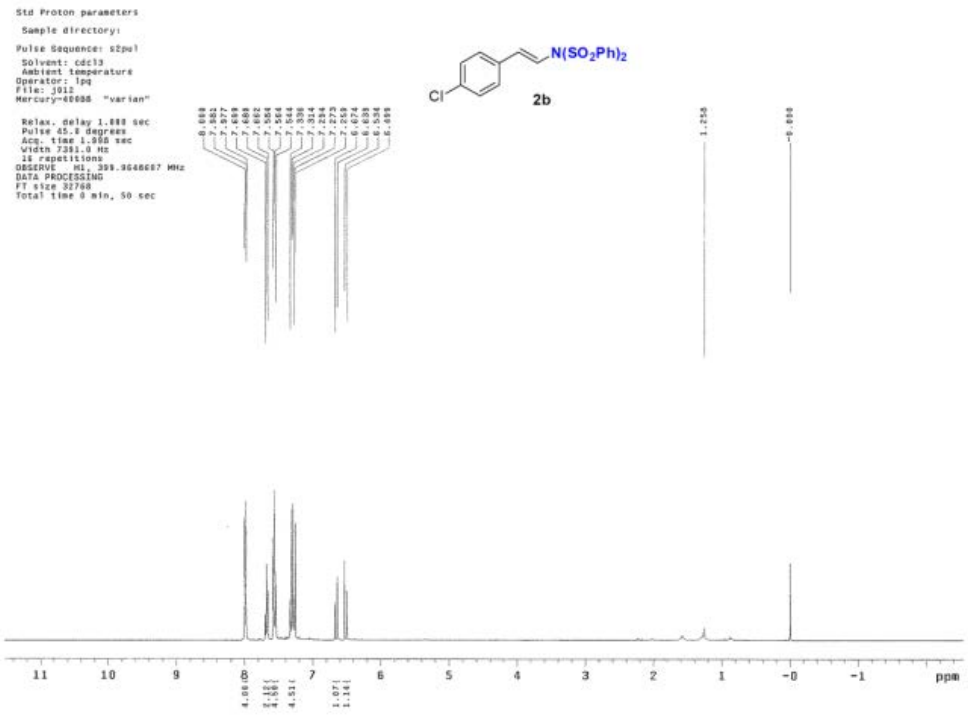


Figure 5. [1]HNMR spectrum of compound 2b

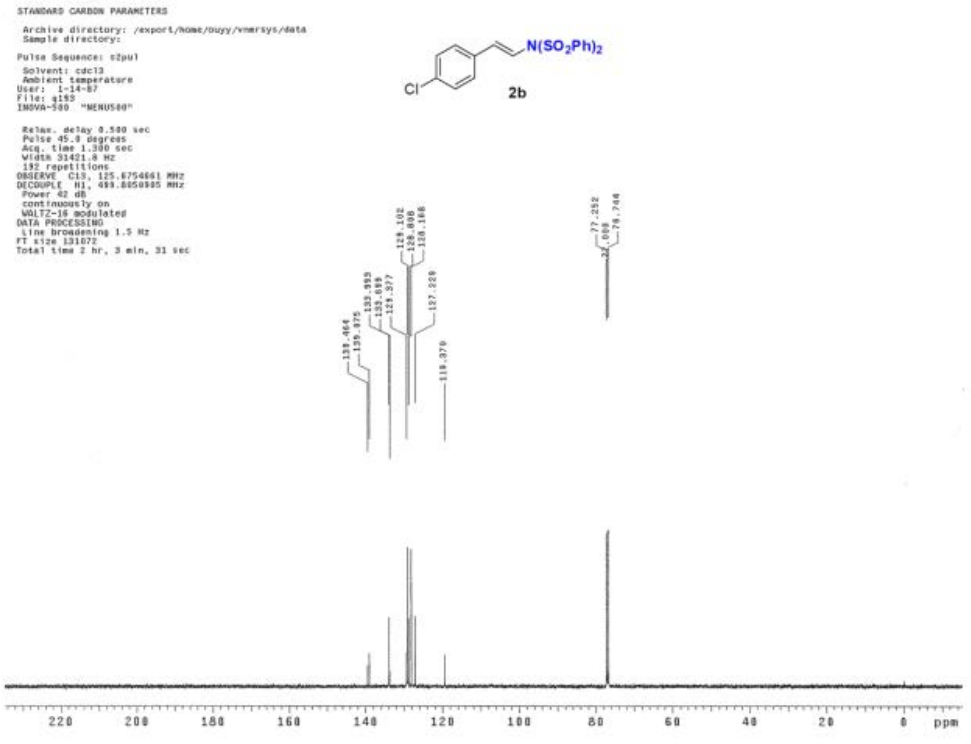


Figure 6. [13]CNMR spectrum of compound 2b

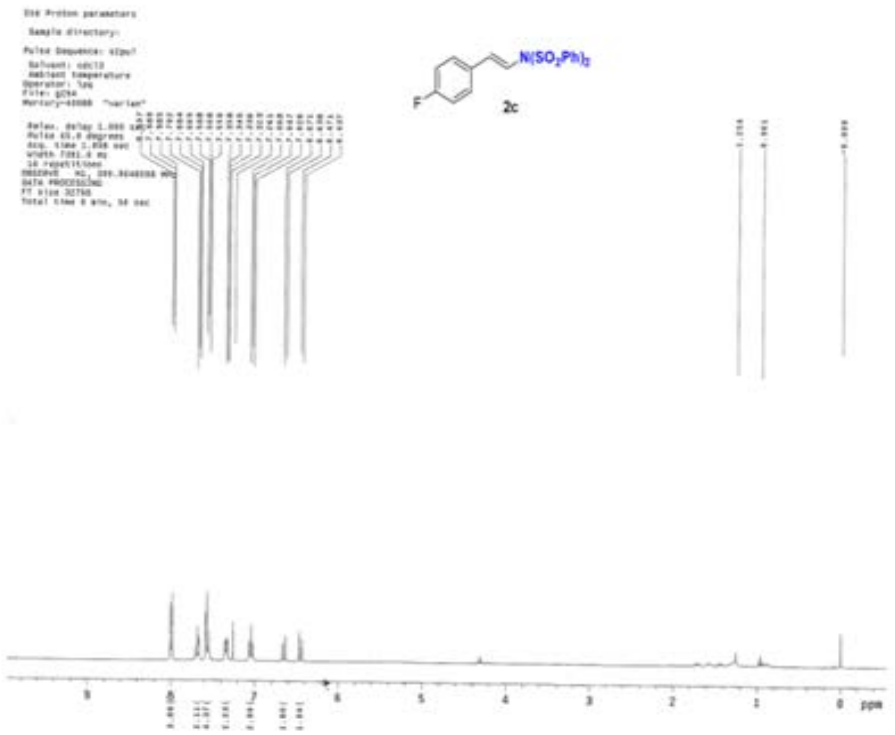


Figure 7. [1]HNMR spectrum of compound 2c

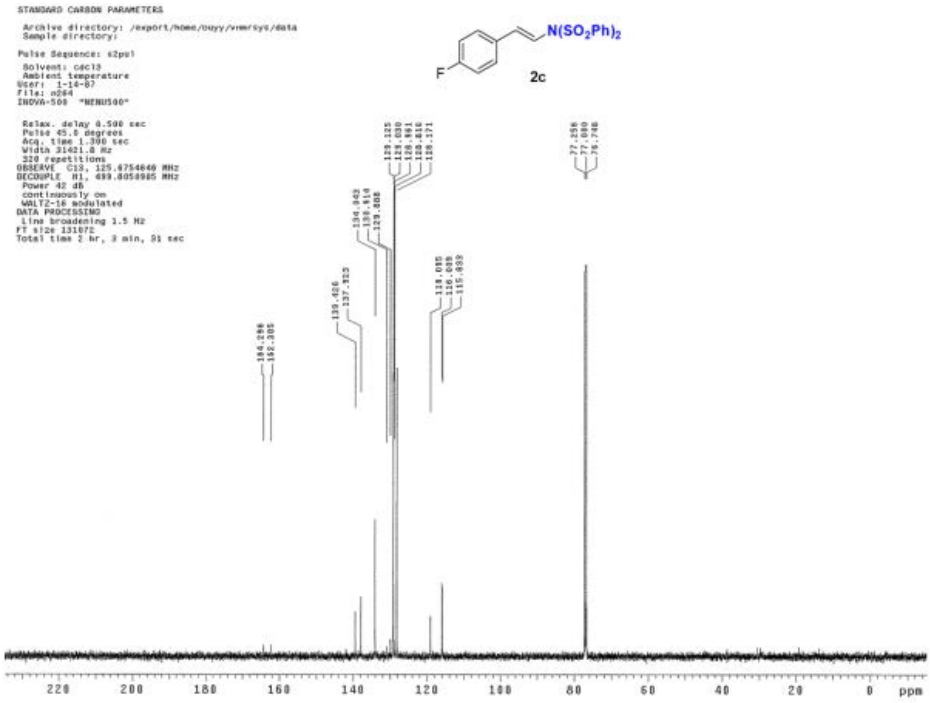


Figure 8. [13]CNMR spectrum of compound 2c

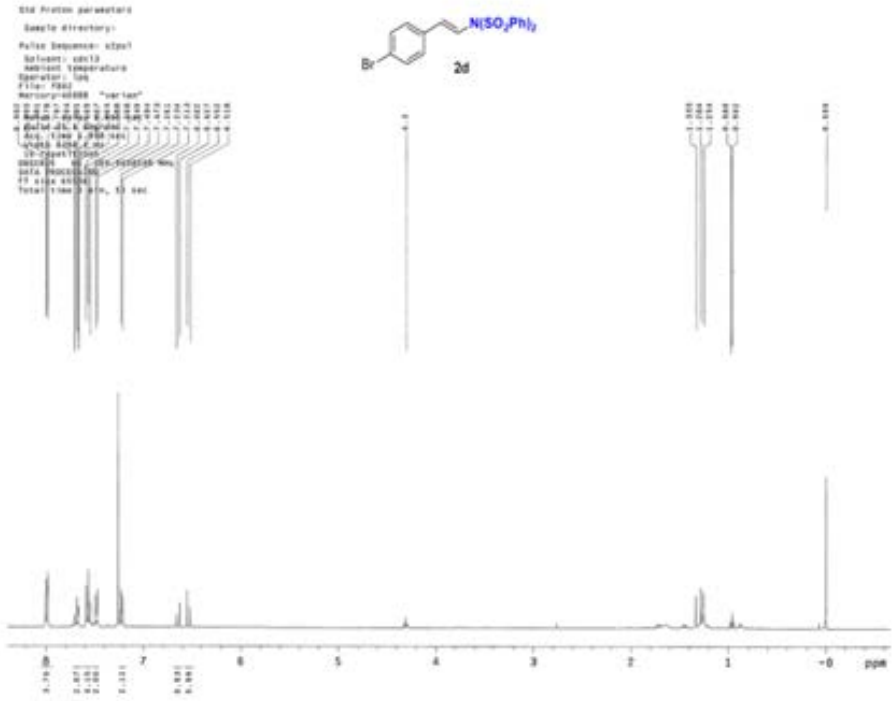


Figure 9. [1]HNMR spectrum of compound 2d

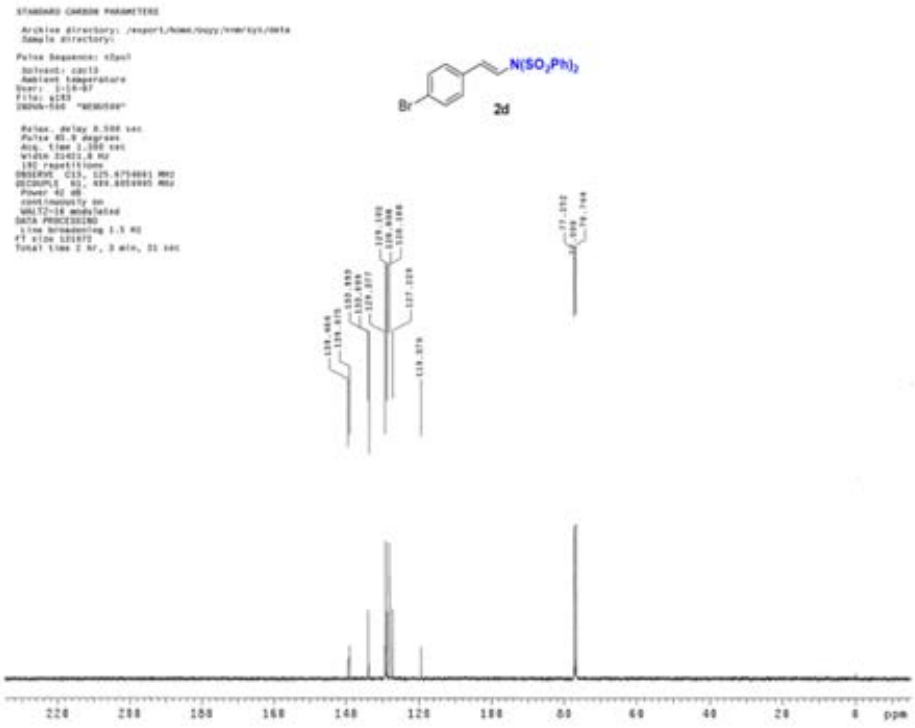


Figure 10. [13]CNMR spectrum of compound 2d

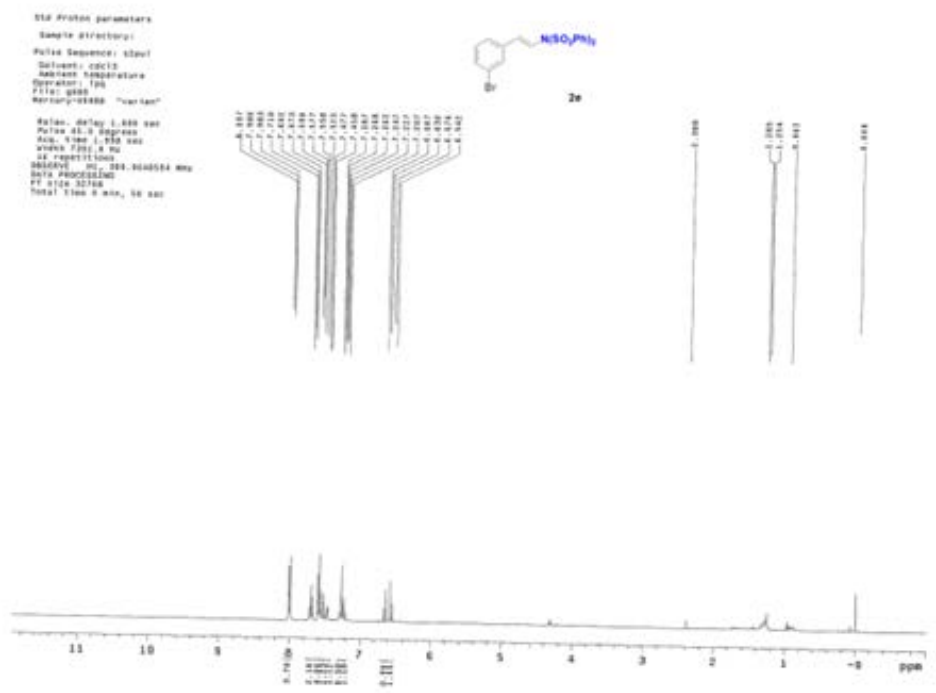


Figure 11. [1]HNMR spectrum of compound 2e

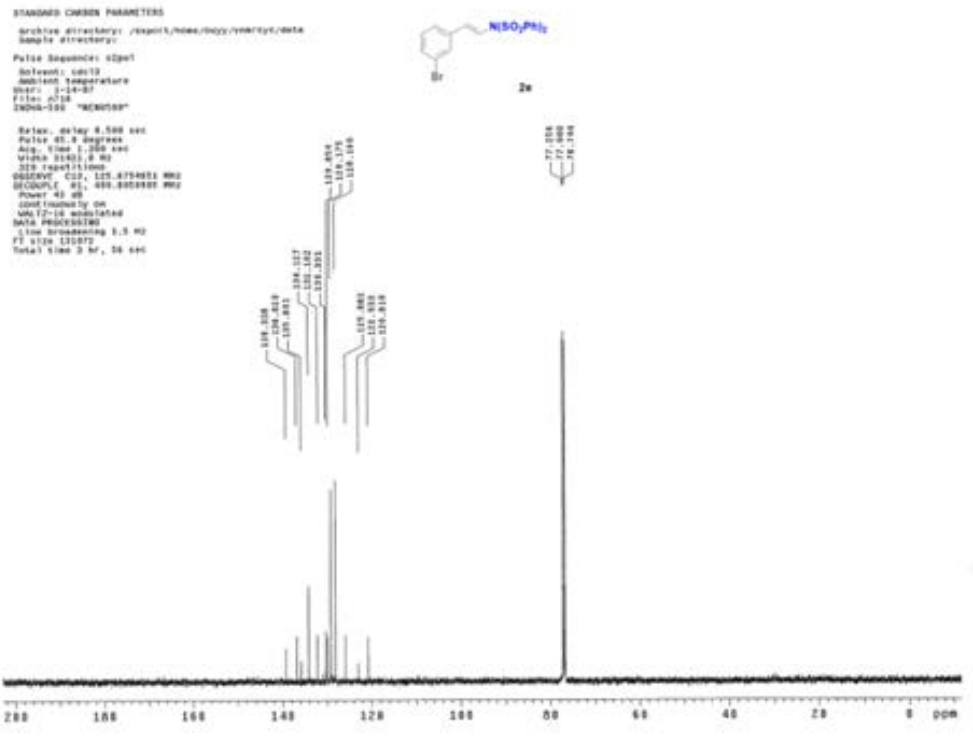


Figure 12. [13]CNMR spectrum of compound 2e

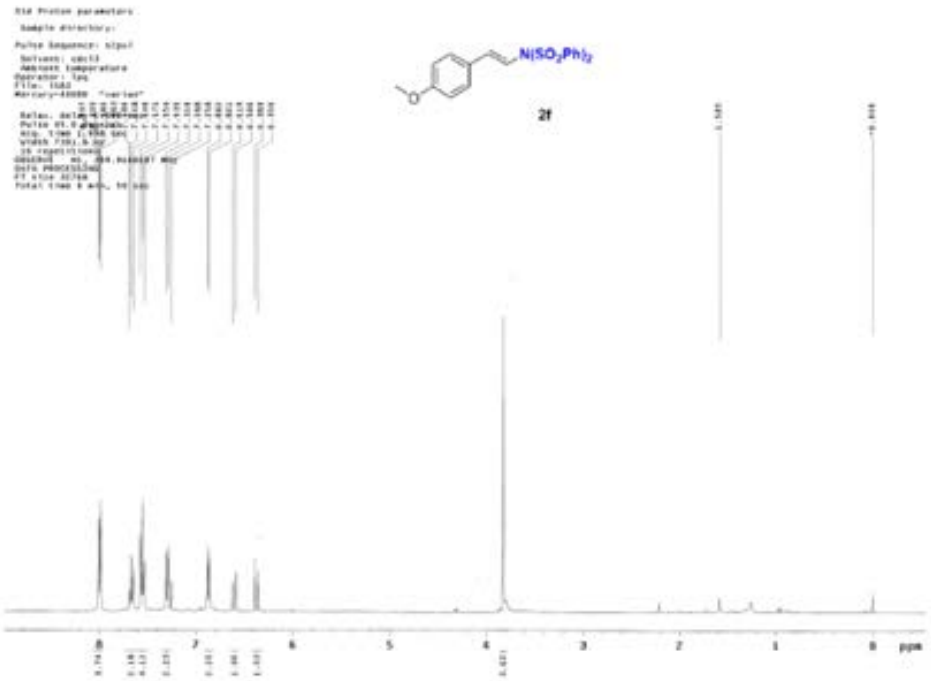


Figure 13. [1]HNMR spectrum of compound 2f

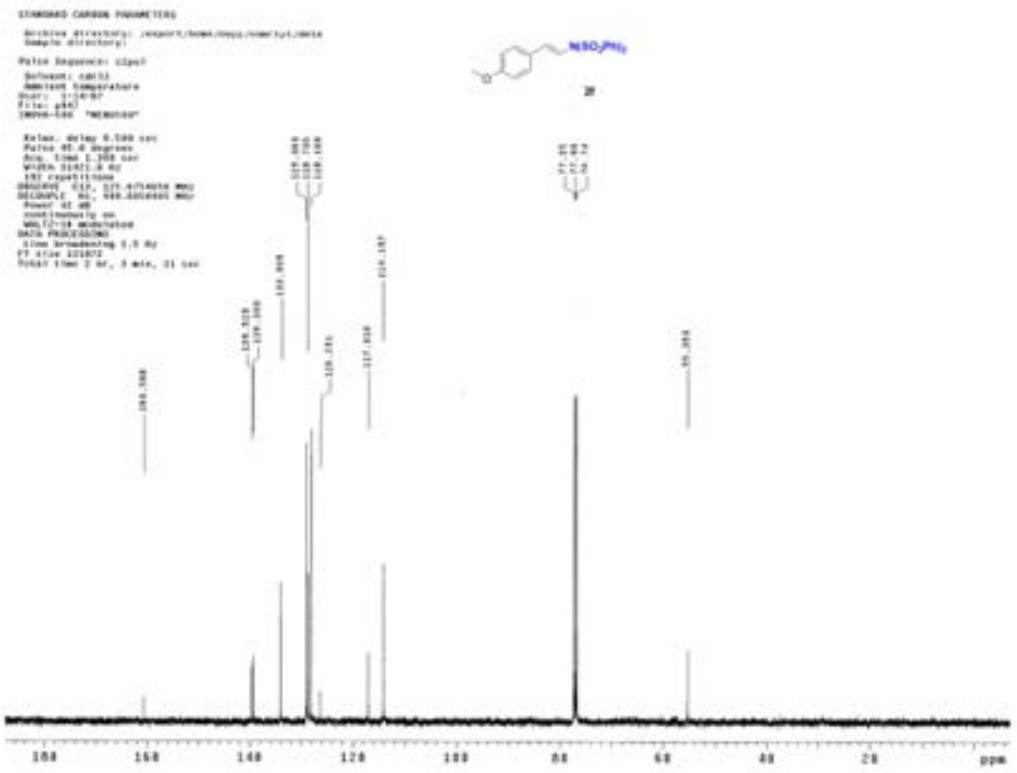


Figure 14. [13]CNMR spectrum of compound 2f

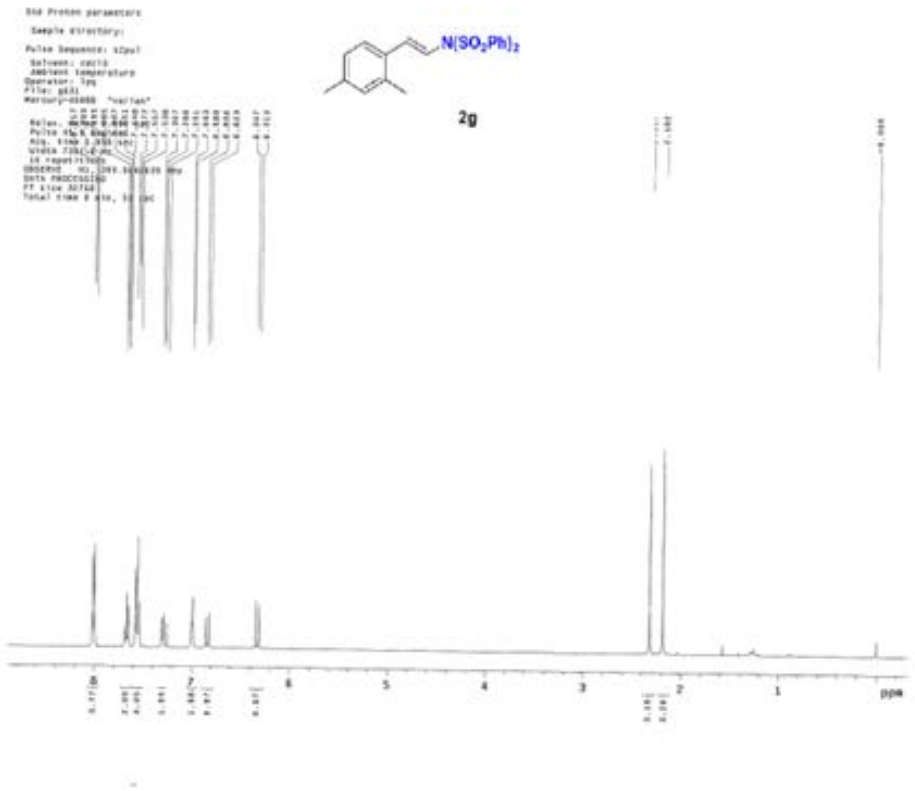


Figure 15. [1]HNMR spectrum of compound 2g

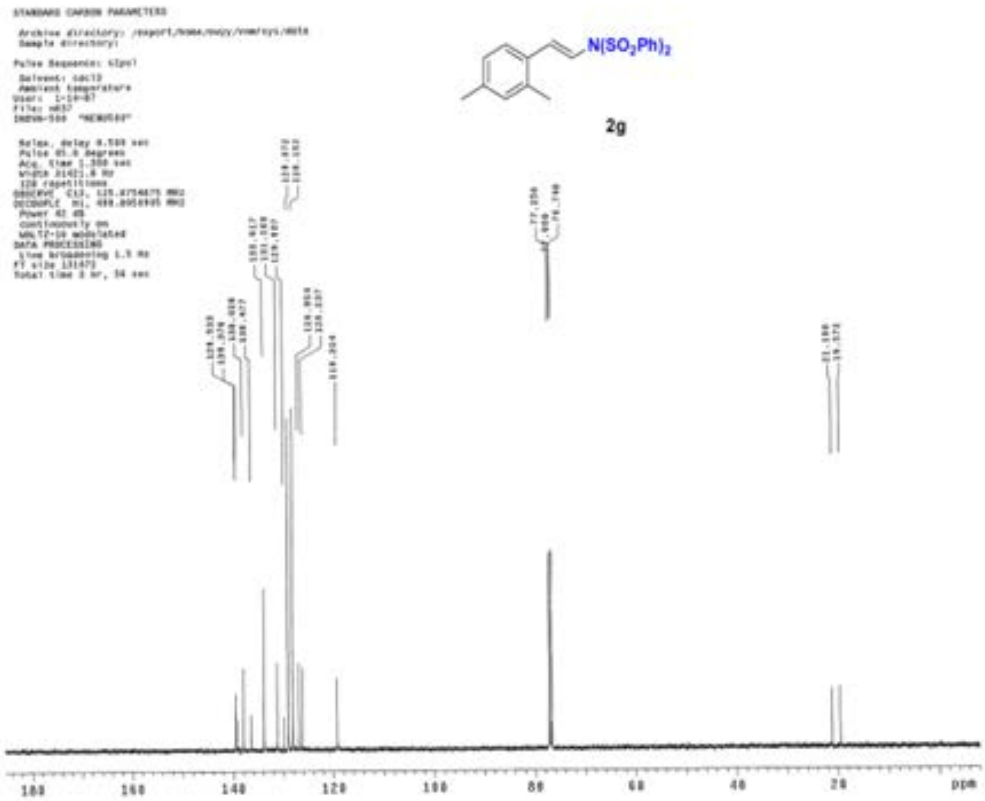


Figure 16. [13]CNMR spectrum of compound 2g

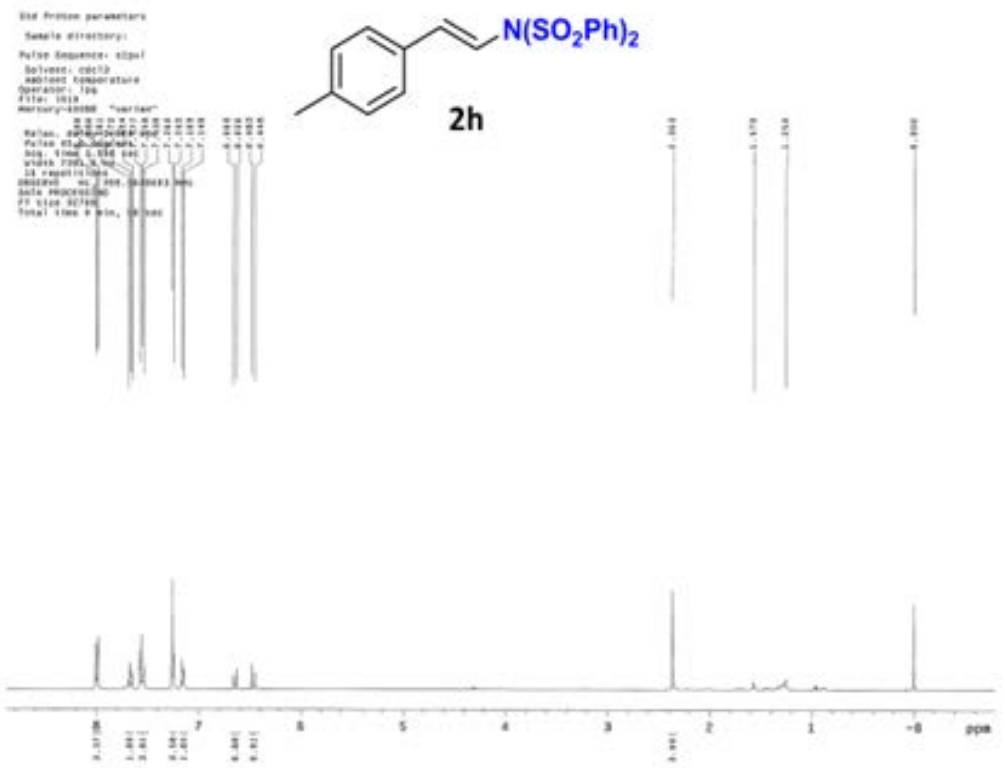


Figure 17. [1]HNMR spectrum of compound 2h

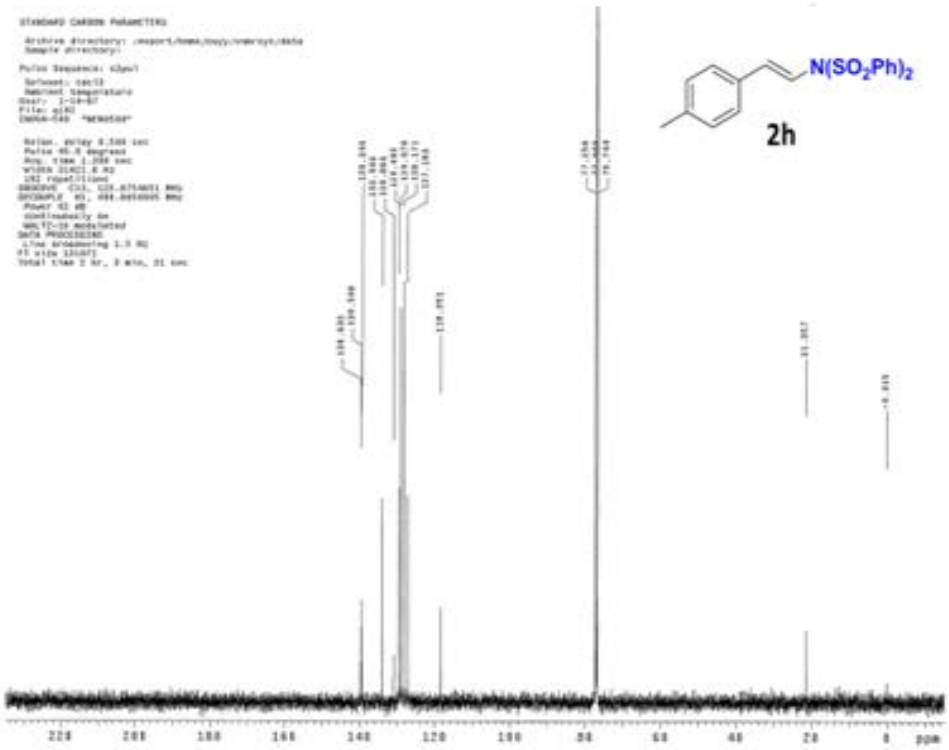


Figure 18. [13]CNMR spectrum of compound 2h

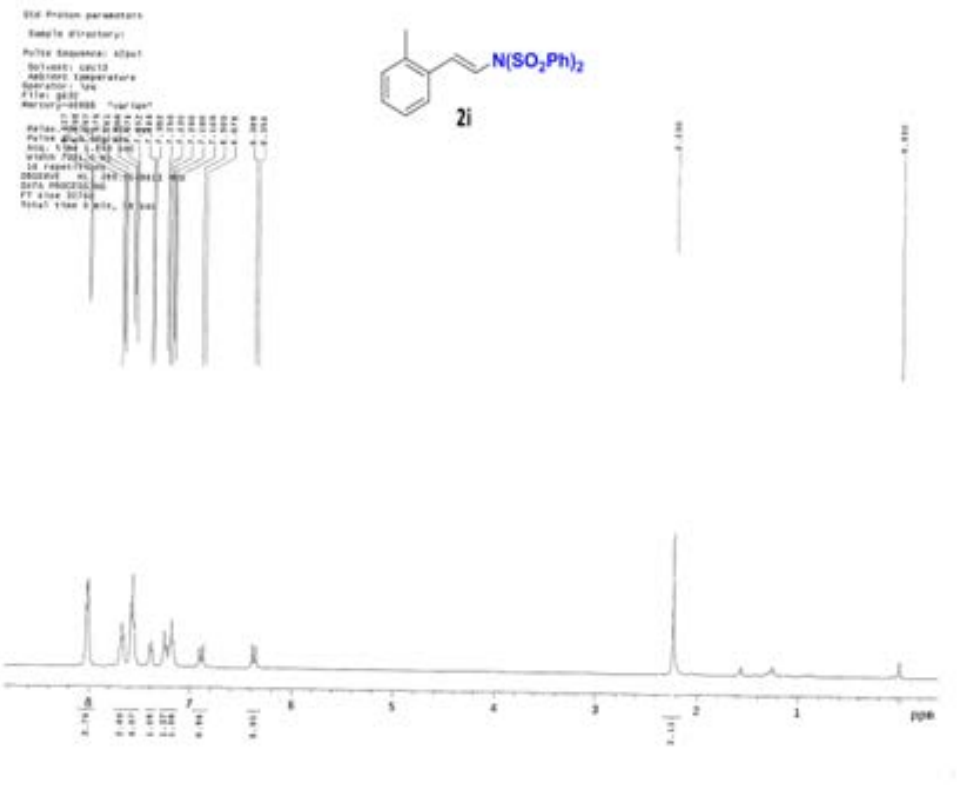


Figure 19. [1]HNMR spectrum of compound 2i

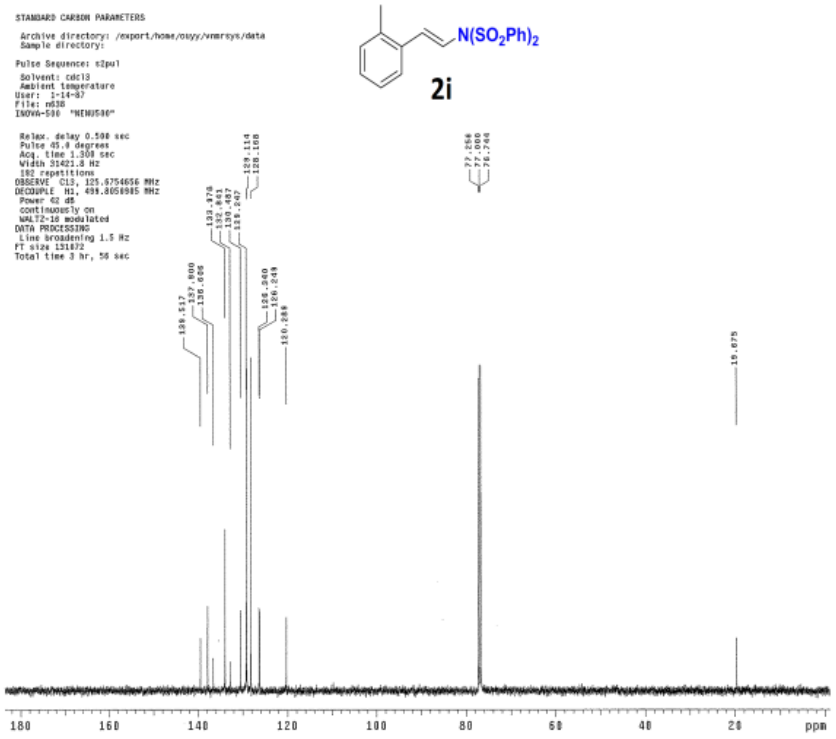


Figure 20. [13]CNMR spectrum of compound 2i

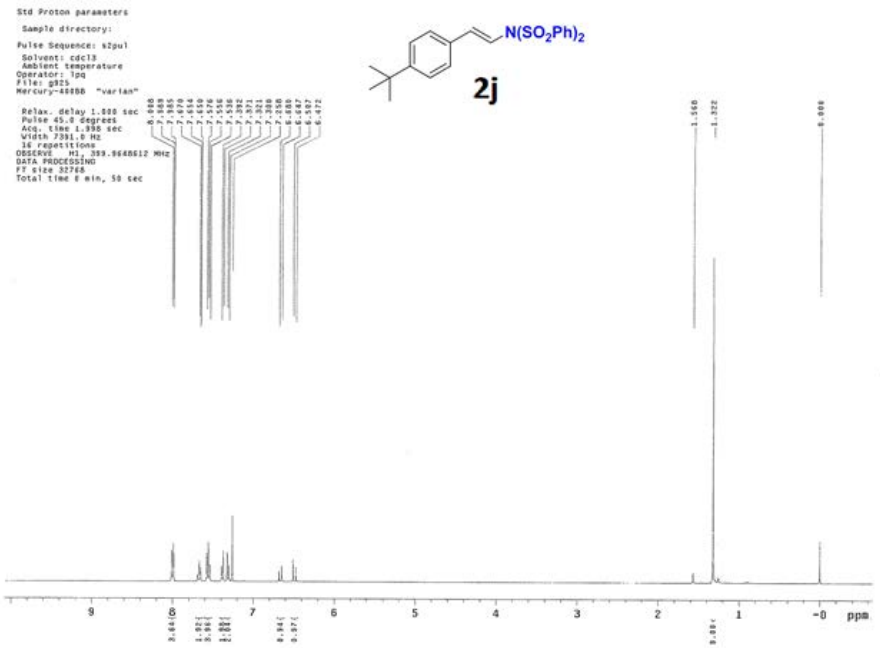


Figure 21. [1]HNMR spectrum of compound 2j

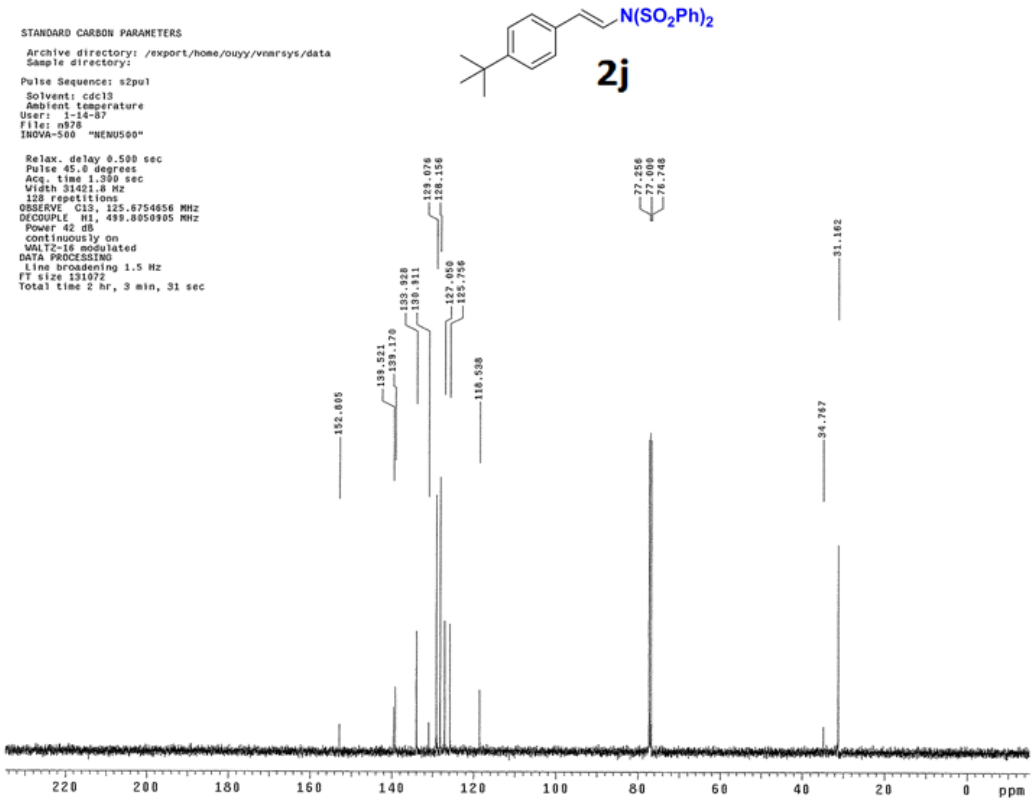


Figure 22. [13]CNMR spectrum of compound 2j

5. Conclusion

In conclusion, we have established a highly efficient protocol for the synthesis of β-amino substituted styrenes 2 via a terminal alkynes with *N*-fluorobenzenesulfonimide (NFSI) as a nitrogen source and also an oxidant in the presence of copper as a catalyst, which would be useful in organic synthesis and medicinal chemistry. In this transformation, water played a very important role in the fixation of a hydrogen atom at the level of the triple bond of a terminal alkyne in the anti-markovnikov position. This novel strategy provides a mild and efficient method

for to realize a C-N bond. The reaction shows high efficiency and selectivity, as well as a broad substrate scope. Further, mechanistic studies and applications of this transformation are underway in our laboratory.

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