Tetrahedron 186 (2025) 134883

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Synthesis of new substituted benzo-sulfonyl-imine derivatives *via* C–C cross-coupling reactions of various aryl halides, isocyanides, and sulfinate salts

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ARTICLE INFO

Keywords:
Ullmann coupling
C-arylation
Aryl halides
Copper-catalyzed
Benzo-sulfonyl-imine
Isocyanides
Sulfinate salt

ABSTRACT

This study presents a rapid and straightforward method for synthesizing a series of novel functionalized benzo-sulfonyl-imine derivatives. The process employs a copper-catalyzed, one-pot, three-component C–C cross-coupling reaction involving various aryl halides, isocyanides, and sulfinate salts. Remarkably, the reaction is carried out in THF at ambient temperature without the requirement for any ligand. Noteworthy features of this protocol include the utilization of readily accessible and simple starting materials, mild copper-catalyzed conditions, elimination of column chromatography for purification, the successful synthesis of fifteen new compounds, and consistently high yields ranging from 72 % to 92 %.

1. Introduction

In the realm of organic chemistry, the construction of C–C bonds constitutes a crucial aspect of synthesizing organic compounds. A variety of C–C bond-forming methodologies, including conjugate addition, nucleophilic addition, and cross-coupling reactions, have been extensively devised and applied within synthetic practices. Nevertheless, the execution of cross-coupling reactions frequently depends on the utilization of organometallic reagents and, occasionally, costly ligands [1–5]. Among the various reactions in organic chemistry, coupling reactions stand out as particularly essential due to their pivotal role in establishing C–C bonds. The Suzuki [6], Negishi [7], and Heck [8] reactions represent three prominent categories of coupling reactions, extensively employed to synthesize a diverse array of complex organic molecules. These reactions hold significant importance across both the chemical and pharmaceutical sectors, where they find numerous practical applications. Extensive studies have been conducted on these reactions employing a broad range of metal catalysts [9]. This reaction has significantly revolutionized the field of chemistry. Notably, it has facilitated the conversion of readily available, low-cost molecules into compounds with substantial practical, industrial, and pharmaceutical significance. Furthermore, the ability to precisely control carbon-carbon bond formation allows for both specificity and selectivity in the synthesis of a wide range of large and structurally diverse molecules, which are critical to pharmaceutical and chemical applications [10]. Research indicates that successfully conducting this reaction often necessitates employing costly and scarce metal catalysts, alongside a range of additives such as oxidants and precious ligands. Additionally, the process frequently involves toxic reagents, extended reaction durations, and conditions of elevated temperature and pressure. Moreover, careful manipulation of directing groups is commonly required to achieve the desired outcome [11]. In contemporary chemistry, the activation of C–X bonds holds great potential for streamlining synthetic pathways by minimizing the number of reaction steps required to obtain complex chemical products. Consequently, the ability to form new C–C bonds *via* cross-coupling reactions has become an indispensable tool for modern synthetic chemists. As highlighted by numerous authoritative texts, the breadth and significance of these reactions are profound and should not be underestimated [12]. Furthermore, the functionalization of aromatic rings at the sp^2 carbon with heteroatoms represents a crucial approach to constructing biologically significant heterocyclic compounds. Concurrently, ongoing research strives to develop C–C cross-coupling reactions that proceed under mild conditions, utilizing readily accessible starting materials and cost-effective catalysts within standard laboratory settings, aiming to facilitate the synthesis of structurally complex molecules.

In our earlier studies, efforts were made to synthesize novel compounds through the Ullmann coupling reaction, involving C–S, C–N, and

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https://doi.org/10.1016/j.tet.2025.134883
Received 8 June 2025; Received in revised form 25 July 2025; Accepted 6 August 2025
Available online 8 August 2025

C–O bond formations, with copper iodide serving as the catalyst [13]. Building upon our prior investigations into the Ullmann coupling, this study introduces a novel reaction for forming C–C bonds. This method employs cost-effective copper iodide catalysts and operates under mild conditions, notably without the need for supplementary oxidants or costly ligands (see Scheme 1).

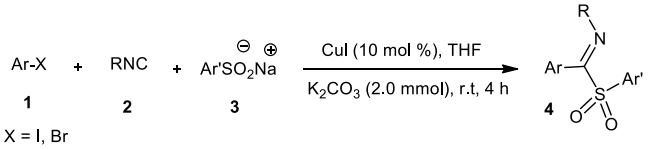
An effective approach for synthesizing novel benzo-sulfonyl-imine derivatives is presented herein, utilizing a copper-catalyzed one-pot *C*-arylation of diverse isocyanides and sulfinate salts. This reaction proceeds under mild conditions at ambient temperature, notably without the need for additional ligands or oxidizing agents. In comparison to traditional techniques [14], this method offers significant benefits, including simplified work-up procedures, milder reaction conditions, higher product purity accompanied by excellent yields, and the use of readily accessible starting materials and catalysts.

2. Results and discussion

To identify the most effective catalytic conditions, a comprehensive screening of different catalysts, bases, and solvents was conducted, employing aryl halides, sulfinate salts, and isocyanides as representative model substrates. As presented in Table 1, a series of copper salts CuI, CuBr, and CuCl (each at 10 mol%) were evaluated, among which CuI emerged as the most efficient catalyst. Additionally, THF was identified as the optimal solvent for the reaction after thorough screening. Various bases, including Cs_2CO_3, KOH, K_2CO_3, and NaOH, were also examined, with K_2CO_3 delivering the superior outcome. Consequently, the reaction was carried out in THF utilizing 10 mol% CuI as the catalyst, 2.0 mmol K_2CO_3 as the base, 1.5 mmol isocyanides, and equimolar amounts (1.0 mmol) of assorted aryl halides and sulfinate salts. For further investigation, the reaction was carried out in the presence of copper (II) salts, including $Cu(OAc)_2$ and $CuSO_4$. Evidence shows that no products were observed under these conditions. This study confirms the role of copper (I) for the reaction progress (Table 1, Entries 13–16). Furthermore, to gain deeper insight into the catalytic function of copper salts, the reaction was conducted both in the presence of elemental copper and in the absence of any catalyst under identical conditions. The results indicate that the desired product was not produced (refer to Table 1, Entries 17–20). Additionally, when the catalyst loading was decreased to 5 mol % of CuI, an extension in the reaction time to 6 h was observed.

Applying the optimized conditions outlined previously, employing CuI as the catalyst and K_2CO_3 as the base, various C–C coupling reactions were carried out using sulfonate salts and isocyanides bearing different electron-withdrawing or electron-donating substituents on their aromatic rings, as well as aryl compounds with a range of substituents. These transformations were achieved under straightforward conditions at room temperature, utilizing an inexpensive copper catalyst without the need for additional ligands. As highlighted in Table 2, the reaction involving bromobenzene exhibited lower efficiency compared to that with iodobenzene (see Table 2, Entries **4k-o**).

Compounds with iodine (I) as the halide consistently show higher yields ranging from 80 % to 92 %. Compounds with bromine (Br) generally exhibit lower yields between 72 % and 78 %. For example, **4a** (I) gives 84 % while **4k** (Br) gives 77 %. This suggests that iodides undergo the catalytic reaction more efficiently than bromides, possibly due to the better leaving group ability of iodine, enhancing the oxidative addition step. Electron-donating groups (e.g., 4-Me-C_6H_4, 3-Me-C_6H_4, 4-OMe-C_6H_4) tend to give good to excellent yields. **4g** has the highest yield of 92 %. **4h** and **4i** with methyl and methoxy groups yield 85 % and 82 %, respectively. Electron-withdrawing groups (e.g., 4-Cl-C_6H_4, 4-NO_2-C_6H_4, 4-Br-C_6H_4) also lead to satisfactory yields, generally in the range of 80–87 %. **4c** achieves 87 % **4d** at 85 %. Substitution at different positions (*ortho, meta, para*) does impact the yield but not drastically, indicating some tolerance in steric effects. For instance, **4j** yields 80 %, close to **4a′s** 84 %. When both Ar and Ar' possess electron-withdrawing

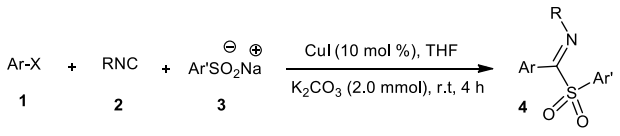


Scheme 1. Synthesis of various benzo-sulfonyl-imines by Cu-catalyzed Ullmann coupling, C–C bond formation reaction.

Table 1
The reaction conditions were optimized for the synthesis of product **4a** using 1.5 mmol of isocyanides, 1.0 mmol of iodobenzene, and 1.0 mmol of sulfinate salt, with 10 mol% of copper salt serving as the catalyst, alongside 2.0 mmol of various bases, all conducted at ambient temperature ([a] Reaction time of 4 h;[b] 5 mol% catalyst, reaction time was 6 h).

Entry	Catalyst	Base	Solvent	Yield (%)[a]
1[b]	**CuI**	**K_2CO_3**	**THF**	**84**
2	CuI	Cs_2CO_3	MeCN	72
3	CuI	NaOH	DMF	45
4	CuI	KOH	Dioxane	56
5	CuCl	K_2CO_3	THF	70
6	CuCl	Cs_2CO_3	MeCN	59
7	CuCl	NaOH	DMF	27
8	CuCl	KOH	Dioxane	37
9	CuBr	K_2CO_3	THF	75
10	CuBr	Cs_2CO_3	MeCN	64
11	CuBr	NaOH	DMF	39
12	CuBr	KOH	Dioxane	48
13	$Cu(OAc)_2$	K_2CO_3	THF	–
14	$Cu(OAc)_2$	Cs_2CO_3	MeCN	–
15	$CuSO_4$	K_2CO_3	THF	–
16	$CuSO_4$	Cs_2CO_3	MeCN	–
17	Cu	K_2CO_3	THF	–
18	Cu	Cs_2CO_3	MeCN	–
19	–	K_2CO_3	THF	–
20	–	Cs_2CO_3	MeCN	–

Table 2
The synthesis of diverse benzo-sulfonyl-imine derivatives was achieved through a copper-catalyzed C–C coupling reaction involving aryl halides, sulfonate salts, and isocyanides.



Entry	X	R	Ar	Ar'	Compound	Yield of 4 (%)
1	I	Ph	Ph	Ph	**4a**	84
2	I	Ph	4-Me-C_6H_4	*p*-Tol	**4b**	80
3	I	Ph	4-Cl-C_6H_4	Ph	**4c**	87
4	I	4-Cl-C_6H_4	4-NO_2-C_6H_4	*p*-Tol	**4d**	85
5	I	4-Cl-C_6H_4	4-Br-C_6H_4	*p*-Tol	**4e**	83
6	I	4-Br-C_6H_4	4-Me-C_6H_4	Ph	**4f**	81
7	I	4-Me-C_6H_4	4-Br-C_6H_4	Ph	**4g**	92
8	I	4-Me-C_6H_4	3-Me-C_6H_4	*p*-Tol	**4h**	85
9	I	4-Me-C_6H_4	4-OMe-C_6H_4	*p*-Tol	**4i**	82
10	I	2-Br-C_6H_4	Ph	Ph	**4j**	80
11	Br	2-Br-C_6H_4	4-Br-C_6H_4	Ph	**4k**	77
12	Br	4-NO_2-C_6H_4	3-Me-C_6H_4	Ph	**4l**	72
13	Br	4-NO_2-C_6H_4	4-NO_2-C_6H_4	*p*-Tol	**4m**	75
14	Br	Isopropyl	4-Br-C_6H_4	*p*-Tol	**4n**	78
15	Br	Isopropyl	4-Me-C_6H_4	Ph	**4o**	76

groups (e.g., nitro), yields remain satisfactory but tend slightly downward in bromides. **4m** shows 75 %, which is lower relative to most iodides. Isopropyl substitution (**4n**, **4o** with Br) yields are still moderate (76–78 %), suggesting alkyl substitution is tolerated but with lower efficiency than aryl groups. The lowest yield is 72 % (**4l**) involving bromide, 4-NO_2-C_6H_4, and 3-Me-C_6H_4, indicating that this particular combination could be challenging, likely due to the interplay of an electron-withdrawing nitro group on the bromide substrate and sterically hindered *meta* substituent. Despite lower yields with bromides overall, the yields mostly stay above 70 %, reflecting reasonable efficiency but clearly emphasizing iodine as the preferable halide. Both electron-donating and electron-withdrawing substituents are compatible; however, electron-donating groups combined with iodide are slightly more favorable. *Ortho*-substitution (e.g., 2-Br-C_6H_4) slightly reduces yield but does not prevent product formation, showing decent steric tolerance.

The structural elucidation of compounds **4a–o** was confirmed through analysis of ^{1}H NMR, ^{13}C NMR, IR, and mass spectra. Specifically, the ^{1}H NMR spectrum of compound **4a** revealed distinctive multiple patterns corresponding to the phenyl protons. In line with the expected structure, the ^{13}C NMR spectrum of **4a** displayed thirteen signals. Spectral data for the remaining compounds closely resembled that of **4a**, differing primarily in the substituent regions, which produced characteristic signals at their respective chemical shifts. Additionally, the mass spectrum of **4a** featured a molecular ion peak at $m/z = 321$, consistent with its molecular weight.

In Scheme 2, a proposed mechanism for the synthesis of compound **4a** is outlined. Initially, compound **1** undergoes oxidative addition with CuI in the presence of K_2CO_3 as the base, resulting in the formation of intermediate **5**. Subsequently, the isocyanide **2** functions as an active nucleophile, attacking from the carbon center and displacing one iodine atom in intermediate **5** to generate complex **6**. The reductive elimination of complex **6** then produces the C-arylated compound **7**, releasing the copper catalyst [15]. Finally, nucleophilic attack by sulfinate salt **3** on compound **7** leads to the formation of the desired final product.

3. Conclusion

In summary, the CuI-catalyzed one-pot multicomponent reaction combining diverse isocyanides, aryl halides, and sulfonate salts offers a novel approach for forming aryl–carbon bonds, enabling the synthesis of benzo-sulfonyl imines with moderate to good yields. This transformation proceeds smoothly in THF at room temperature over 4 h. The method's key advantages include the use of readily accessible starting materials, mild reaction conditions, and a straightforward purification process that delivers high yields. Together, these features establish this protocol as an efficient and practical strategy for producing a broad range of sulfonyl imine derivatives.

4. Experimental section

4.1. Chemicals and apparatus

Melting points (m.p.) were determined using the *Electrothermal-9100* apparatus. ^{1}H and ^{13}C NMR Spectra using TMS as internal standard and $CDCl_3$ as applied solvent at 500.1 and 125.7 MHz, respectively *Bruker DRX-500 Avance* instrument was used to obtain. IR Infrared Spectra were acquired on a PerkinElmer 1420 ratio recording spectrometer. Mass spectra were obtained on a *Finnigan-MAT-8430EI-MS* mass spectrometer at 70 eV; in *m/z* (rel. %). All chemicals and reagents were obtained commercially from Aldrich or Merck and used without further purification.

4.2. Experimental procedure

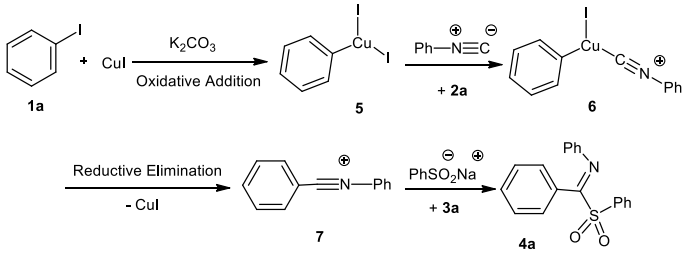
4.2.1. General procedure for preparation of compounds *4a*

A mixture of iodobenzene **1a** (1.0 mmol) and isocyanide **2a** (1.5 mmol), CuI (0.10 mmol), K_2CO_3 (2.0 mmol), and sodium sulfinate salt **3a** (1.0 mmol) in THF (2 mL) was stirred at r.t. for 4 h. The progress of the reaction was monitored by TLC in *n*-hexane-ethyl acetate (1:5) solvent. After the reaction was completed, to remove the copper iodide catalyst from the reaction medium, CH_2Cl_2 (2 mL) and aqueous NH_4Cl solution (3 mL) were added to the reaction mixture and stirred for 10 min. Then the layers were separated. The aqueous layer was extracted with CH_2Cl_2, and the combined organic fractions (Na_2SO_4) were dried and concentrated under reduced pressure. The resulting solid was washed with acetone.

*4.2.1.1. N-(Phenyl(phenylsulfonyl)methylene) aniline **(4a)**.* White powder; yield: 0.27 g (84 %); mp: 167–169 °C. IR (KBr) (ν_{max}, cm^{-1}): 1634, 1516, 1355, 1169, 1009. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta_H = 7.30–7.35$ (m, 6 H, Ph), 7.49–7.51 (m, 5 H, Ph), 7.60 (t, $^3J = 7.7$, 2 H, Ar), 7.98 (d, $^3J = 7.6$, 2 H, Ar). ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta_C = 128.5$ (2 CH), 129.3 (2 CH), 129.5 (CH), 129.8 (2 CH), 132.6 (2 CH), 133.8 (2 CH), 134.7 (2 CH), 135.8 (CH), 136.7 (CH), 140.1 (C), 144.1 (C), 152.6 (C), 165.5 (C). MS: *m/z* (%) = 321 (M^+, 12), 244 (89), 180 (73), 141 (100), 77 (47). Anal. Calc. for $C_{19}H_{15}NO_2S$ (321.39): C, 71.00; H, 4.70; N, 4.36 %. Found: C, 71.05; H, 4.73; N, 4.32 %.

*4.2.1.2. N-(p-Tolyl(tosyl)methylene) aniline **(4b)**.* Cream powder; yield: 0.28 g (80 %); mp: 182–184 °C. IR (KBr) (ν_{max}, cm^{-1}): 1622, 1580, 1352, 1160, 1009. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta_H = 2.23$ (s, 3 H, Me), 2.83 (s, 3 H, Me), 7.29–7.34 (m, 7 H, Ph), 7.39 (d, $^3J = 7.8$, 2 H, Ar), 7.48 (t, $^3J = 7.7$, 2 H, Ar), 7.91 (d, $^3J = 7.7$, 2 H, Ar). ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta_C = 28.3$ (Me), 32.5 (Me), 126.3 (2 CH), 126.7 (2 CH), 127.6 (CH), 128.7 (2 CH), 129.5 (2 CH), 131.4 (2 CH), 132.3 (2 CH), 134.5 (C), 135.3 (C), 142.5 (C), 147.3 (C), 152.3 (C), 165.3 (C). MS: *m/z* (%) = 349 (M^+, 14), 272 (40), 194 (42), 155 (100), 91 (70), 77 (41). Anal. Calc. for $C_{21}H_{19}NO_2S$ (349.45): C, 72.18; H, 5.48; N, 4.01 %. Found: C, 72.14; H, 5.42; N, 4.06 %.

*4.2.1.3. N-((4-Chlorophenyl) (phenylsulfonyl)methylene) aniline **(4c)**.* White powder; yield: 0.31 g (87 %); mp: 191–193 °C. IR (KBr) (ν_{max}, cm^{-1}): 1633, 1539, 1384, 1164, 1025. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta_H = 7.16$ (d, $^3J = 7.8$, 2 H, Ar), 7.23 (t, $^3J = 7.8$, 1 H, Ar), 7.27–7.31 (m, 4 H, Ph), 7.44 (d, $^3J = 7.9$, 2 H, Ar), 7.56 (t, $^3J = 7.7$, 2 H, Ar), 7.70 (t, $^3J = 7.7$, 1 H, Ar), 7.99 (d, $^3J = 7.9$, 2 H, Ar). ^{13}C NMR (125.7 MHz, $CDCl_3$):



Scheme 2. Possible formation mechanism of compounds **4a**.

δ_C = 126.3 (2 CH), 126.6 (2 CH), 127.2 (2 CH), 127.7 (2 CH), 128.2 (CH), 128.7 (2 CH), 129.6 (2 CH), 130.2 (C), 131.6 (CH), 132.5 (C), 135.8 (C), 144.7 (C), 166.1 (C). MS: *m/z* (%) = 355 (M^+, 1), 278 (18), 244 (71), 214 (26), 141 (100), 111 (30), 77 (59). Anal. Calc. for $C_{19}H_{14}ClNO_2S$ (355.84): C, 64.13; H, 3.97; N, 3.94 %. Found: C, 64.15; H, 3.93; N, 3.90 %.

4.2.1.4. 4-Chloro-N-((4-nitrophenyl) (tosyl)methylene) aniline ***(4d)***. Yellow powder; yield: 0.35 g (85 %); mp: 204–206 °C. IR (KBr) (ν_{max}, cm^{-1}): 1655, 1580, 1543, 1359, 1300, 1164, 1009. ^1H NMR (500 MHz, $CDCl_3$): δ_H = 2.45 (s, 3 H, Me), 7.19 (d, ^3J = 7.8, 2 H, Ar), 7.27–7.33 (m, 4 H, Ph), 7.38 (d, ^3J = 7.9, 2 H, Ar), 7.47 (d, ^3J = 7.9, 2 H, Ar), 7.88 (d, ^3J = 7.8, 2 H, Ar). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 30.0 (Me), 126.5 (2 CH), 126.7 (C), 127.5 (2 CH), 127.8 (2 CH), 128.8 (C), 129.5 (2 CH), 129.9 (2 CH), 130.0 (2 CH), 132.5 (C), 142.9 (C), 148.5 (C), 152.8 (C), 164.8 (C). MS: *m/z* (%) = 414 (M^+, 2), 322 (29), 303 (18), 292 (43), 122 (43), 111 (100), 91 (40). Anal. Calc. for $C_{20}H_{15}ClN_2O_4S$ (414.86): C, 57.90; H, 3.64; N, 6.75 %. Found: C, 57.93; H, 3.61; N, 6.78 %.

4.2.1.5. N-((4-Bromophenyl) (tosyl)methylene)-4-chloroaniline ***(4e)***. Cream powder; yield: 0.37 g (83 %); mp: 219–221 °C. IR (KBr) (ν_{max}, cm^{-1}): 1656, 1534, 1352, 1169, 1003. ^1H NMR (500 MHz, $CDCl_3$): δ_H = 2.81 (s, 3 H, Me), 7.31–7.36 (m, 4 H, Ph), 7.50 (d, ^3J = 7.7, 2 H, Ar), 7.59 (d, ^3J = 7.9, 2 H, Ar), 7.78 (d, ^3J = 7.7, 2 H, Ar), 7.98 (d, ^3J = 7.9, 2 H, Ar). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 31.3 (Me), 126.8 (2 CH), 126.9 (2 CH), 127.2 (2 CH), 127.8 (C), 128.2 (C), 129.9 (2 CH), 130.2 (2 CH), 131.2 (2 CH), 132.9 (C), 135.3 (C), 144.7 (C), 153.0 (C), 165.9 (C). MS: *m/z* (%) = 448 (M^+, 1), 355 (17), 335 (54), 292 (50), 154 (33), 111 (100), 91 (42). Anal. Calc. for $C_{20}H_{15}BrClNO_2S$ (448.76): C, 53.53; H, 3.37; N, 3.12 %. Found: C, 53.50; H, 3.34; N, 3.18 %.

4.2.1.6. 4-Bromo-N-((phenylsulfonyl)(p-tolyl)methylene) aniline ***(4f)***. Cream powder; yield: 0.33 g (81 %); mp: 208–210 °C. IR (KBr) (ν_{max}, cm^{-1}): 1677, 1580, 1355, 1162, 1045. ^1H NMR (500 MHz, $CDCl_3$): δ_H = 2.47 (s, 3 H, Me), 7.17–7.21 (m, 5 H, Ph), 7.23 (t, ^3J = 7.8, 2 H, Ar), 7.31 (d, ^3J = 7.9, 2 H, Ar), 7.36 (d, ^3J = 7.8, 2 H, Ar), 7.86 (d, ^3J = 7.9, 2 H, Ar). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 30.8 (Me), 126.1 (2 CH), 126.7 (2 CH), 127.4 (2 CH), 127.8 (CH), 128.9 (2 CH), 129.5 (2 CH), 130.0 (2 CH), 130.7 (C), 142.0 (C), 142.2 (C), 147.5 (C), 150.5 (C), 164.1 (C). MS: *m/z* (%) = 414 (M^+, 1), 335 (27), 321 (19), 258 (24), 154 (100), 91 (37), 77 (49). Anal. Calc. for $C_{20}H_{16}BrNO_2S$ (414.32): C, 57.98; H, 3.89; N, 3.38 %. Found: C, 57.92; H, 3.84; N, 3.35 %.

4.2.1.7. N-((4-Bromophenyl) (phenylsulfonyl)methylene)-4-methylaniline ***(4g)***. White powder; yield: 0.39 g (92 %); mp: 215–217 °C. IR (KBr) (ν_{max}, cm^{-1}): 1666, 1589, 1350, 1162, 1004. ^1H NMR (500 MHz, $CDCl_3$): δ_H = 2.15 (s, 3 H, Me), 7.20 (d, ^3J = 7.6, 2 H, Ar), 7.25 (t, ^3J = 7.6, 1 H, Ar), 7.29–7.34 (m, 6 H, Ph), 7.47 (d, ^3J = 8.0, 2 H, Ar), 7.86 (d, ^3J = 8.0, 2 H, Ar). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 32.8 (Me), 125.5 (2 CH), 126.1 (2 CH), 127.8 (2 CH), 128.7 (2 CH), 128.9 (2 CH), 129.1 (CH), 129.2 (C), 130.0 (2 CH), 131.6 (C), 132.5 (C), 141.5 (C), 144.5 (C), 165.6 (C). MS: *m/z* (%) = 414 (M^+, 1), 335 (34), 321 (29), 258 (50), 154 (43), 91 (84), 77 (100). Anal. Calc. for $C_{20}H_{16}BrNO_2S$ (414.32): C, 57.98; H, 3.89; N, 3.38 %. Found: C, 57.93; H, 3.84; N, 3.35 %.

4.2.1.8. 4-methyl-N-(m-tolyl(tosyl)methylene) aniline ***(4h)***. Cream powder; yield: 0.31 g (85 %); mp: 179–181 °C. IR (KBr) (ν_{max}, cm^{-1}): 1678, 1553, 1359, 1128, 1069. ^1H NMR (500 MHz, $CDCl_3$): δ_H = 2.01 (s, 3 H, Me), 2.24 (s, 3 H, Me), 2.95 (s, 3 H, Me), 7.19 (d, ^3J = 7.8, 2 H, Ar), 7.26 (d, ^3J = 7.6, 2 H, Ar), 7.32 (d, ^3J = 7.8, 2 H, Ar), 7.39–7.45 (m, 3 H, Ph), 7.59 (t, ^3J = 7.7, 1 H, Ar), 7.72 (d, ^3J = 7.7, 1 H, Ar), 8.00 (d, ^3J = 7.7, 1 H, Ar). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 24.0 (Me), 30.0 (Me), 34.3 (Me), 125.0 (CH), 126.5 (2 CH), 127.1 (C), 127.7 (2 CH), 128.1 (C), 130.0 (2 CH), 130.1 (2 CH), 131.8 (CH), 132.0 (C), 132.0 (CH), 135.7 (CH), 140.0 (C), 144.6 (C), 152.0 (C), 164.0 (C). MS: *m/z* (%) = 363 (M^+, 16), 272 (26), 208 (80), 155 (100), 91 (75). Anal. Calc. for $C_{22}H_{21}NO_2S$ (363.47): C, 72.70; H, 5.82; N, 3.85 %. Found: C, 72.74; H, 5.80; N, 3.87 %.

4.2.1.9. N-((4-Methoxyphenyl) (tosyl)methylene)-4-methylaniline ***(4i)***. Yellow powder; yield: 0.31 g (82 %); mp: 165–167 °C. IR (KBr) (ν_{max}, cm^{-1}): 1635, 1523, 1359, 1162, 1009. ^1H NMR (500 MHz, $CDCl_3$): δ_H = 2.44 (s, 3 H, Me), 2.82 (s, 3 H, Me), 3.82 (s, 3 H, OMe), 7.29–7.34 (m, 4 H, Ph), 7.38 (d, ^3J = 7.7, 2 H, Ar), 7.40 (d, ^3J = 7.5, 2 H, Ar), 7.48 (d, ^3J = 7.7, 2 H, Ar), 7.91 (d, ^3J = 7.5, 2 H, Ar). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 30.7 (Me), 32.8 (Me), 57.5 (OMe), 126.6 (2 CH), 127.5 (2 CH), 128.8 (2 CH), 129.1 (C), 129.3 (2 CH), 130.7 (2 CH), 131.0 (2 CH), 132.5 (C), 136.6 (C), 137.6 (C), 142.7 (C), 147.8 (C), 167.7 (C). MS: *m/z* (%) = 379 (M^+, 17), 288 (41), 272 (39), 224 (45), 155 (40), 107 (100), 91 (82). Anal. Calc. for $C_{22}H_{21}NO_3S$ (379.47): C, 69.63; H, 5.58; N, 3.69 %. Found: C, 69.60H, 5.53; N, 3.66 %.

4.2.1.10. 2-Bromo-N-(phenyl(phenylsulfonyl)methylene) aniline ***(4j)***. White powder; yield: 0.32 g (80 %); mp: 178–180 °C. IR (KBr) (ν_{max}, cm^{-1}): 1645, 1579, 1351, 1163, 1012. ^1H NMR (500 MHz, $CDCl_3$): δ_H = 7.29–7.35 (m, 5 H, Ph), 7.39 (d, ^3J = 7.7, 2 H, Ar), 7.48 (d, ^3J = 7.8, 2 H, Ar), 7.61 (t, ^3J = 7.7, 2 H, Ar), 7.74 (t, ^3J = 7.9, 1 H, Ar), 7.90 (d, ^3J = 7.9, 1 H, Ar), 8.04 (d, ^3J = 7.9, 1 H, Ar). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 127.6 (2 CH), 127.7 (CH), 128.7 (2 CH), 129.3 (CH), 130.1 (2 CH), 130.7 (2 CH), 131.0 (2 CH), 132.5 (2 CH), 135.6 (C), 141.6 (C), 143.6 (C), 146.6 (C), 168.6 (C). MS: *m/z* (%) = 400 (M^+, 2), 321 (49), 244 (40), 154 (92), 141 (100), 77 (44). Anal. Calc. for $C_{19}H_{14}BrNO_2S$ (400.29): C, 57.01; H, 3.53; N, 3.50 %. Found: C, 57.05; H, 3.50; N, 3.55 %.

4.2.1.11. 2-Bromo-N-((4-bromophenyl) (phenylsulfonyl)methylene) aniline ***(4k)***. Cream powder; yield: 0.37 g (77 %); mp: 230–232 °C. IR (KBr) (ν_{max}, cm^{-1}): 1654, 1580, 1353, 1169, 1005. ^1H NMR (500 MHz, $CDCl_3$): δ_H = 7.30–7.36 (m, 4 H, Ph), 7.40 (d, ^3J = 7.8, 2 H, Ar), 7.48 (d, ^3J = 7.8, 2 H, Ar), 7.62 (t, ^3J = 7.7, 1 H, Ar), 7.75 (t, ^3J = 7.9, 2 H, Ar), 7.91 (d, ^3J = 8.0, 1 H, Ar), 8.03 (d, ^3J = 8.0, 1 H, Ar). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 126.8 (2 CH), 127.8 (C), 128.8 (2 CH), 129.7 (CH), 130.1 (2 CH), 130.7 (CH), 130.9 (CH), 131.0 (2 CH), 131.2 (CH), 132.7 (C), 136.7 (CH), 142.2 (C), 144.5 (C), 147.3 (C), 168.6 (C). MS: *m/z* (%) = 479 (M^+, 1), 399 (44), 321 (29), 298 (35), 154 (62), 141 (100), 77 (47). Anal. Calc. for $C_{19}H_{13}Br_2NO_2S$ (479.19): C, 47.62; H, 2.73; N, 2.92 %. Found: C, 47.65; H, 2.70; N, 2.97 %.

4.2.1.12. 4-nitro-N-((phenylsulfonyl)(m-tolyl)methylene) aniline ***(4l)***. Yellow powder; yield: 0.27 g (72 %); mp: 202–204 °C. IR (KBr) (ν_{max}, cm^{-1}): 1654, 1579, 1549, 1349, 1315, 1154, 1020. ^1H NMR (500 MHz, $CDCl_3$): δ_H = 2.52 (s, 3 H, Me), 7.29–7.36 (m, 5 H, Ph), 7.48 (d, ^3J = 7.7, 2 H, Ar), 7.50 (t, ^3J = 7.8, 1 H, Ar), 7.61 (d, ^3J = 8.0, 2 H, Ar), 7.74 (d, ^3J = 7.8, 1 H, Ar), 8.04 (d, ^3J = 8.0, 2 H, Ar). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 32.2 (Me), 125.1 (2 CH), 127.4 (2 CH), 128.8 (2 CH), 129.3 (CH), 130.2 (2 CH), 131.1 (CH), 131.9 (CH), 132.3 (C), 132.8 (C), 133.5 (CH), 135.7 (C), 142.3 (C), 144.2 (C), 150.2 (C), 167.1 (C). MS: *m/z* (%) = 380 (M^+, 14), 303 (70), 289 (23), 258 (30), 141 (34), 122 (47), 91 (100), 77 (80). Anal. Calc. for $C_{20}H_{16}N_2O_4S$ (380.42): C, 63.14; H, 4.24; N, 7.36 %. Found: C, 63.11; H, 4.20; N, 7.32 %.

4.2.1.13. 4-nitro-N-((4-nitrophenyl) (tosyl)methylene) aniline ***(4m)***. Yellow powder; yield: 0.32 g (75 %); mp: 229–231 °C. IR (KBr) (ν_{max}, cm^{-1}): 1636, 1589, 1550, 1378, 1352, 1161, 1003. ^1H NMR (500 MHz, $CDCl_3$): δ_H = 2.16 (s, 3 H, Me), 7.31–7.36 (m, 4 H, Ph), 7.51 (d, ^3J = 7.9, 2 H, Ar), 7.59 (d, ^3J = 7.9, 2 H, Ar), 7.71 (d, ^3J = 8.1, 2 H, Ar), 8.05 (d, ^3J = 8.1, 2 H, Ar). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 31.5 (Me), 127.0 (2 CH), 127.9 (2 CH), 128.0 (2 CH), 129.3 (2 CH), 130.2 (C), 131.3 (2 CH), 132.6 (2 CH), 136.1 (C), 139.9 (C), 140.0 (C), 144.0 (C), 150.5 (C), 164.0 (C). MS: *m/z* (%) = 425 (M^+, 13), 334 (89), 303 (32), 270 (43),

155 (100), 122 (50), 91 (43). Anal. Calc. for $C_{20}H_{15}N_3O_6S$ (425.41): C, 56.47; H, 3.55; N, 9.88 %. Found: C, 56.42; H, 3.51; N, 9.85 %.

4.2.1.14. N-((4-Bromophenyl) (tosyl)methylene) propan-2-amine ***(4n)***. White powder; yield: 0.30 g (78 %); mp: 188–190 °C. IR (KBr) (ν_{max}, cm^{-1}): 1656, 1579, 1315, 1160, 1011. ^1H NMR (500 MHz, $CDCl_3$): δ_H = 1.37 (d, ^3J = 5.9, 6 H, 2 CH_3), 2.58 (s, 3 H, Me), 3.15–3.17 (m, 1 H, CH), 7.39 (d, ^3J = 7.8, 2 H, Ar), 7.48 (d, ^3J = 8.0, 2 H, Ar), 7.83 (d, ^3J = 7.8, 2 H, Ar), 7.91 (d, ^3J = 8.0, 2 H, Ar). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 22.1 (2 Me), 27.2 (Me), 42.1 (CH), 128.7 (2 CH), 129.6 (2 CH), 130.8 (2 CH), 132.6 (2 CH), 135.9 (C), 142.1 (C), 146.7 (C), 147.7 (C), 167.3 (C). MS: *m/z* (%) = 380 (M^+, 1), 335 (42), 287 (89), 224 (57), 155 (100), 91 (67), 43 (44). Anal. Calc. for $C_{17}H_{18}BrNO_2S$ (380.30): C, 53.69; H, 4.77; N, 3.68 %. Found: C, 53.63; H, 4.70; N, 3.64 %.

4.2.1.15. N-((Phenylsulfonyl)(p-tolyl) methylene) propan-2-amine ***(4o)***. Cream powder; yield: 0.23 g (76 %); mp: 176–178 °C. IR (KBr) (ν_{max}, cm^{-1}): 1666, 1589, 1351, 1134, 1014. ^1H NMR (500 MHz, $CDCl_3$): δ_H = 1.41 (d, ^3J = 5.7, 6 H, 2 CH_3), 2.15 (s, 3 H, Me), 3.11–3.16 (m, 1 H, CH), 7.40 (d, ^3J = 7.6, 2 H, Ar), 7.61 (t, ^3J = 7.6, 1 H, Ar), 7.75 (t, ^3J = 7.6, 2 H, Ar), 7.92 (d, ^3J = 7.7, 2 H, Ar), 8.04 (d, ^3J = 7.7, 2 H, Ar). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 23.0 (2 Me), 30.0 (Me), 42.8 (CH), 127.5 (2 CH), 127.6 (2 CH), 128.9 (CH), 130.7 (2 CH), 132.5 (2 CH), 142.5 (C), 147.2 (C), 150.5 (C), 167.5 (C). MS: *m/z* (%) = 301 (M^+, 16), 258 (26), 224 (29), 210 (55), 91 (100), 77 (37), 43 (40). Anal. Calc. for $C_{17}H_{19}NO_2S$ (301.40): C, 67.74; H, 6.35; N, 4.65 %. Found: C, 67.72; H, 6.37; N, 4.61 %.

CRediT authorship contribution statement

Manijeh Nematpour: Writing – review & editing, Supervision, Software, Resources, Project administration, Methodology, Investigation, Formal analysis, Data curation. **Yavar Ahmadi:** Writing – original draft.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by Farhangian University.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2025.134883.

Data availability

Data will be made available on request.

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