molbank

MDPI

Short Note

6-Nitro-7-tosylquinazolin-4(3*H*)-one

Thi Ngoc Nguyen [1,2], Thi Phuong Thuy Tran [1], Thi Hoang Mai Vu [1], Hoa Binh Nguyen [1], Nguyet Suong Huyen Dao [1], Van Giang Nguyen [1], Dinh Luyen Nguyen [1], Nguyen Trieu Trinh [3] and Van Hai Nguyen [1,*]

[1] Department of Pharmaceutical Industry, Hanoi University of Pharmacy, Hanoi 110403, Vietnam; ngock3a@gmail.com (T.N.N.); phuongthuytran97@gmail.com (T.P.T.T.); vuhoangmai96@gmail.com (T.H.M.V.); hoabinhcvp97@gmail.com (H.B.N.); huyendns@hup.edu.vn (N.S.H.D.); giangnv@hup.edu.vn (V.G.N.); ngdluyen@hotmail.com (D.L.N.)

[2] Department of Pharmaceutical Technology, Thainguyen University of Medicine and Pharmacy, Thainguyen 24117, Vietnam

[3] Faculty of Science, School of Environmental and Life Sciences, University of Newcastle, Newcastle, NSW 2308, Australia; trieu.n.trinh@newcastle.edu.au

* Correspondence: hainv@hup.edu.vn or nguyenvanhaicnd@gmail.com; Tel.: +84-918-971-109

Received: 3 November 2020; Accepted: 19 November 2020; Published: 21 November 2020

Abstract: Sulfones are important building blocks in the construction of biologically active molecules or functional materials. The sulfonyl functional group in sulfones is so versatile that it can act as either a nucleophile, an electrophile, or a radical in different organic reactions. Recently, quinazoline sulfones have been used to build asymmetrical ether derivatives as inhibitors of signaling pathways governed by tyrosine kinases and the epidermal growth factor-receptor. In this paper, we report a facile synthesis of a novel quinazoline sulfone, 6-nitro-7-tosylquinazolin-4(3*H*)-one (**III**), using the modified protocol from 7-chloro-6-nitroquinazolin-4(3*H*)-one (**I**) and sodium *p*-toluenesulfinate (**II**). The structure of the title compound **III** was determined using mass-spectrometry, FT-IR, ^{1}H-NMR, ^{13}C-NMR, DEPT, HSQC (Heteronuclear single quantum coherence), HMBC (Heteronuclear Multiple Bond Correlation Spectroscopy) spectroscopies, and PXRD analysis.

Keywords: 7-chloro-6-nitroquinazolin-4(3*H*)-one; 6-nitro-7-tosylquinazolin-4(3*H*)-one; sulfinate; sulfone

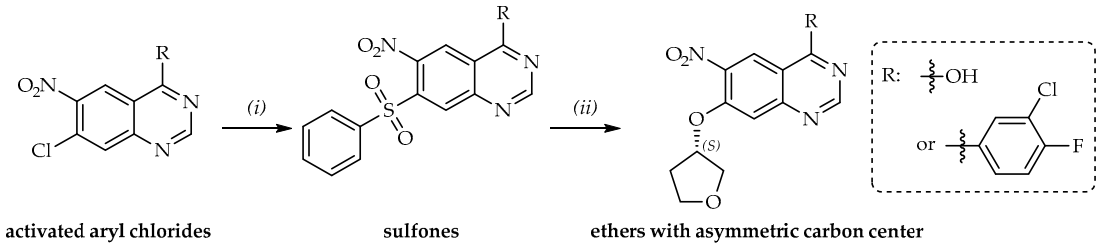
1. Introduction

Sulfones (R-SO_2-R') have been known for over 100 years with widespread applications in organic synthesis, agrochemicals, polymers, and especially pharmaceuticals [1]. Indeed, many important drug substances containing sulfonyl moiety such as amisulpride, bicalutamide, dapsone, diazoxide, eletriptan, laropiprant, rofecoxib, sulbactam, sulfoxone, tazobactam, and tinidazole have been approved for the treatment of various diseases [1–4]. Moreover, sulfones serve as versatile intermediates in many synthetic routes, which can function as nucleophiles, electrophiles, or even radicals in a wide range of synthetic reactions [5,6]. These unique properties of sulfones enable rapid and convenient derivatization of many core structures, including the quinazoline moiety. The latter is widely present in many biologically active compounds exhibiting inhibition against cancer [7,8], HIV [9], bacterial [10], and fungal diseases [11,12].

Given this versatility, the synthesis of sulfone has attracted a great deal of attention by researchers, and numerous synthetic strategies have been reported [3,5,6,13,14]. The four traditional and still most common approaches for preparing sulfones are the oxidation of the corresponding sulfides or sulfoxides, alkylation of sulfinate salts, Friedel-Crafts-type sulfonylation of arenes, and addition reactions to alkenes or alkynes [1,2]. Among those, the alkylation of sulfinate salts is suitable for a broad range of alkylating agents. This approach affords sulfone products in good to excellent yields via

simple and reproducible reaction conditions [5,15]. The main disadvantage of this reaction, however, is due to the modest availability of sulfinate salts [1,5,16].

Although the rich chemistry of sulfones is widely appreciated and significant advances have been achieved for the preparation of sulfones, opportunities for further exploration still remain. For example, the conversion of diaryl sulfones into asymmetrical ethers has been rarely reported and limited to a couple of references [17,18]. In these reported synthetic routes, the synthesis of asymmetrical ethers was all conducted with sodium benzenesulfinate. The protocol is briefly described as follows: The sodium sulfinates as nucleophiles were reacted with quinazoline halides activated by the electron withdrawing group (-NO_2) in DMF to form sulfones. The resulted sulfones as electrophiles were further reacted with alcohols in a *t*-butoxide base to obtain the desired asymmetrical ethers (Scheme 1). It is important to note that this reaction mechanism retains the chirality of the alcohols, which offers a feasible way to produce pure stereoisomers of interest.

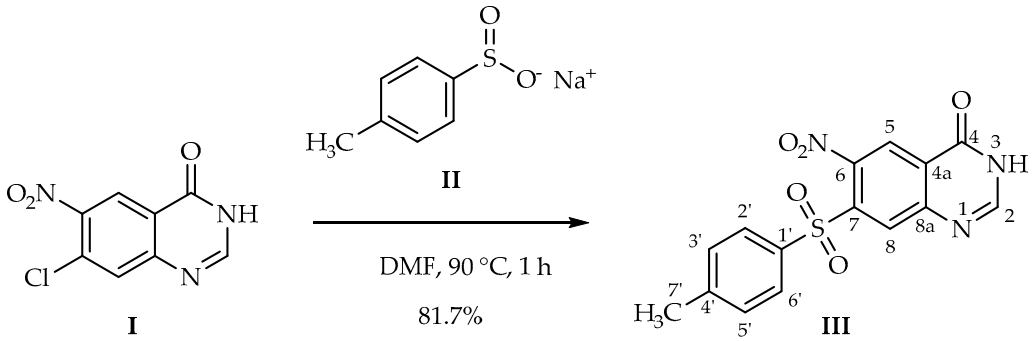


Scheme 1. Strategy for constructing asymmetrical ethers from aryl chlorides and benzenesulfinates. Reagents and conditions [17,18]: (**i**) Sodium benzenesulfinate, DMF, 90 °C, 6 h; (**ii**) (*S*)-tetrahydrofuran-3-ol/*t*-BuOH, DMF, *t*-BuOK/THF.

To further develop the above mentioned strategy, in this paper, we present the synthesis and spectral data of novel sulfone, 6-nitro-7-tosylquinazolin-4(3*H*)-one (**III**), which is an analog of reported compound in [18], 6-nitro-7-(phenylsulfonyl)quinazolin-4(3*H*)-one. Methyl group acting as an electron donor is likely to increase the nucleophilicity of the *p*-toluenesulfinate, which enables a faster coupling reaction with aryl chlorides to form sulfones in comparable high yields.

2. Results and Discussion

The target compound **III** was prepared from 7-chloro-6-nitroquinazolin-4(3*H*)-one (**I**) and sodium *p*-toluenesulfinate (**II**) in 81.7% of yield (Scheme 2). The synthetic procedure was based on [17,18] with some changes.



Scheme 2. Synthesis of 6-nitro-7-tosylquinazolin-4(3*H*)-one (**III**). Reagents and conditions*:* 7-Chloro-6-nitroquinazolin-4(3*H*)-one: Sodium benzenesulfinate (1.3:1), DMF, 90 °C, 6 h.

In the reported syntheses of sulfones by sulfinates and aryl chlorides, the sulfinate salts have been widely used in excess to promote the completion of the reactions [19–21]. Equimolar mixtures of sodium sulfinates and aryl chlorides have also been used, however, little data on the yield were

available to support any comparison [18]. According to [17] with the ratio of 1.3:1 (sodium sufinates:aryl chlorides), the reaction work-up was fairly simple and the sulfone product was separated by a simple precipitation with water. However, we observed that these conditions generated significant impurities, as indicated by TLC, and needed further proper purification.

In our synthesis, we adjusted the molar ratio of the starting materials and changed the work-up conditions. We found that the 1.2:1 molar ratio of sodium *p*-toluenesulfinate:aryl chloride was enough to facilitate the reaction completion and the reaction time was much quicker when using sodium *p*-toluenesulfinate in place of sodium benzenesulfinate (1 vs. 6 h until completion). Related to the work-up, acetone was first used to precipitate the excess sulfinate salt, which was then filtered out. Other impurities were removed by adding water to the concentrate containing DMF. The reasonably pure sulfone product was obtained without further purification in a good yield (81.7%), which is comparable to those reported in the literature [17].

The structure of compound **III** is different from its reported analog in [18], 6-nitro-7-(phenylsulfonyl)quinazolin-4(3*H*)-one, by a methyl group at position C-4′. This resulted in variations of ^{1}H- and ^{13}C-NMR data signals of hydrogen and carbon at position C-4′. MS data showed a molecular ion peak at *m*/*z* 343.97 ($[M - H]^-$) and 368.0330 ($[M + Na]^+$), which indicated that the chloro-group at C-7 was successfully substituted by the nucleophilic *p*-toluenesulfinate salt. The absorption bands on the infrared spectrum, 1315 and 1145 cm^{-1}, demonstrated the presence of sulfone moiety in compound **III**. This was also supported by the ^{13}C signals at 138.1 (C-7) and 136.4 ppm (C-1′), which indicated there was no *O*-alkylation reaction towards a sulfinate ester [22]. This result is similar to those reported, despite the fact that the exact underlying reason for the selectivity of sulfinate/sulfone formation was not clearly explained [1,23]. All obtained data by DEPT and 2D NMR experiments are in entire agreement with the structure of the title compound **III** (Table 1). The amide-iminol tautomerism of quinazolin-4(3*H*)-one skeleton was again observed as previously reported [18] by ^{1}H-NMR, in which the O-H form generates a proton peak at 12.96 ppm and in the NH form this peak is recorded at 3.35 ppm (overlapped with water, SI). In addition, powder X-ray diffraction (PXRD) data were also collected as an effort to provide a comprehensive spectral data set for the title compound **III** (Table 2).

Table 1. Two-dimensional (2D) NMR (HSQC and HMBC) correlations for the title compound **III.**

	Proton	**H-2**	**H-5**	**H-8**	**H-2′**	**H-3′**	**H-5′**	**H-6′**	**H-7′**	**H-O/H-N**
Carbon	**ppm**	**8.39**	**8.59**	**8.47**	**7.92**	**7.49**	**7.49**	**7.92**	**2.41**	**12.96/3.35 ***
C-2	149.9	x		γ						
C-4	159.1	β	β							
C-4a	126.4			β						
C-5	124.0		x	γ						
C-6	144.1			β						
C-7	138.1		β							
C-8	131.2	γ	γ							
C-8a	151.0	β								
C-1′	136.4					β	β			
C-2′	128.1				x		γ	β	γ	
C-3′	130.1					x	β		β	
C-4′	145.5				β			β	α	
C-5′	130.1					β	x		β	
C-6′	128.1				β	γ		x	γ	
C-7′	21.1					β	β		x	

α: Due to a two-bond coupling ($^{2}J_{CH}$); β: Due to a three-bond coupling ($^{3}J_{CH}$); γ: Due to a four-bond coupling ($^{4}J_{CH}$); x: Coupling by HSQC; *: The tautomeric NH signal is overlapped with a water signal at 3.35 ppm in DMSO-d_6.

Table 2. PXRD data for the title compound **III.**

Peak n	2θ (°)	d (Å)	I/Imax (%)	Peak n	2θ (°)	d (Å)	I/Imax (%)
1	9.10	9.7182	2.62	33	27.50	3.2435	32.51
2	10.14	8.7237	15.07	34	28.00	3.1867	4.07
3	13.44	6.5882	12.25	35	28.38	3.1449	2.89
4	14.82	5.9777	32.83	36	28.62	3.1191	3.10
5	14.98	5.9142	21.45	37	28.84	3.0958	2.89
6	15.72	5.6374	2.90	38	29.44	3.0340	5.20
7	16.98	5.2218	3.27	39	29.58	3.0200	4.90
8	17.64	5.0279	18.57	40	29.98	2.9806	15.55
9	18.58	4.7756	2.63	41	30.36	2.9442	24.54
10	18.94	4.6857	17.02	42	30.64	2.9179	12.06
11	19.28	4.6038	2.78	43	31.68	2.8244	6.73
12	19.56	4.5385	3.03	44	32.32	2.7700	3.47
13	20.08	4.4221	5.31	45	33.04	2.7112	5.59
14	20.46	4.3409	7.16	46	33.58	2.6689	3.12
15	20.94	4.2424	12.21	47	34.72	2.5838	6.32
16	21.22	4.1871	4.31	48	35.26	2.5454	16.83
17	21.44	4.1446	5.36	49	35.82	2.5069	4.50
18	21.92	4.0549	32.29	50	36.48	2.4631	12.13
19	22.22	4.0009	7.79	51	37.32	2.4095	4.11
20	22.44	3.9621	6.36	52	37.70	2.3861	3.54
21	22.80	3.9004	56.53	53	38.24	2.3537	3.03
22	23.06	3.8570	15.41	54	38.44	2.3419	4.59
23	23.60	3.7699	11.32	55	38.68	2.3279	3.24
24	23.92	3.7202	20.49	56	39.10	2.3039	3.73
25	24.22	3.6748	100.00	57	39.86	2.2617	8.51
26	24.56	3.6247	7.13	58	40.68	2.2179	5.07
27	25.02	3.5591	4.07	59	44.48	2.0369	7.64
28	25.42	3.5040	5.61	60	45.32	2.0011	4.04
29	25.62	3.4771	4.57	61	45.60	1.9894	3.44
30	25.88	3.4428	4.43	62	46.56	1.9506	3.19
31	26.50	3.3636	21.83	63	48.48	1.8778	3.61
32	27.14	3.2857	5.69				

On the whole, using the amended reaction conditions and work-up procedures, compound **III** has been synthesized for the first time in a good yield, high purity without further purification, and much quicker time of reaction. These results can be useful for extensive research on sulfones, especially aryl and quinazoline sulfones, as well as the synthesis of asymmetrical ethers with a high level of stereoselectivity.

All the mass, FT-IR, ^{1}H-NMR, ^{13}C-NMR, DEPT, HSQC, HMBC, and PXRD spectra are presented in the Supplementary Material File.

3. Materials and Methods

3.1. General Information

7-Chloro-6-nitroquinazolin-4(3*H*)-one (compound **I**, m.p 263.5–265.0 °C, R_f 0.34, dichloromethane/methanol, 20:1) was prepared from the 2-amino-4-chlorobenzoic acid according to [24]. Sodium *p*-toluenesulfinate (compound **II**, 95.0%) was purchased from AK Scientific (Union City, CA, USA). Acetone (99.7%) and methanol (MeOH, 99.8%) were obtained from Samchun (Gyeonggi-do, Korea). Dichloromethane (DCM, 99.5%), *N*,*N*-dimethylformamide (DMF, 99.5%), ethyl acetate (99.5%), *n*-hexane (95.0%) were purchased from Xilong Scientific Co., Ltd. (Shantou, China). The chemicals were used as received without further purification.

The melting point was determined using a SRS EZ-Melt apparatus (Stanford Research Systems, Sunnyvale, CA, USA) and was uncorrected. MS was performed at an LTQ Orbitrap XL™ (Thermo

Scientific, Waltham, MA, USA) system in an electrospray ionization (ESI) mode. The FT-IR spectrum was recorded by a Shimadzu spectrometer (Kyoto, Japan). Nuclear magnetic resonance (^{1}H, ^{13}C, DEPT, HSQC, and HMBC) experiments were measured on a Bruker Ascend spectrometer (Billerica, MA, USA) at 500 MHz for proton and 125 MHz for carbon-13 using DMSO-d_6 as the solvent and tetramethylsilane (TMS) as an internal standard. Powder X-ray diffraction (PXRD) was performed on a D8-Advance Bruker AXS diffractometer (Karlsruhe, Germany) with CuKα radiation (λ = 1.541874 Å) at room temperature, 40 mA and 40 kV (Göbel mirror; θ–2θ scan; 2θ= 2–60 °; step size = 0.020 °; scan speed = 0.6 s/step). The PXRD data were analyzed by Match! version 3.11.1.183 64-bit (Crystal Impact, Bonn, Germany, author: Dr. Holger Putz, serial number: 7.3.9.2015001.0001). The reaction mixtures were monitored, and the purity of the compounds was checked by thin-layer chromatography (TLC) on silica gel 60 F_{254} plates (Merck, Darmstadt, Germany).

3.2. Synthetic Procedure

6-Nitro-7-tosylquinazolin-4(3*H*)-one (**III**)

The synthetic procedure for compound **III** was based on [17,18] with some modifications.

7-Chloro-6-nitroquinazolin-4(3*H*)-one (compound **I**, 2.0 g, 8.87 mmol, 1 eq) and sodium *p*-toluenesulfinate (compound **II**, 1.90 g, 10.66 mmol, 1.2 eq) were suspended at 20 °C in DMF (20 mL), then heated to 90 °C and kept for 1 h at this temperature. After completion of the reaction as indicated by TLC, the reaction mixture was cooled, diluted with acetone (60 mL), and the precipitate was filtered to remove the residual sulfinate salt. The filtrate was distilled by a rotary vacuum to recover acetone. The concentrate was then diluted with water (80 mL) and the precipitate was collected by vacuum filtration, washed three times with water (5 mL each time). The resulting solid was dried at 60 °C for 3 h to obtain 6-nitro-7-tosylquinazolin-4(3*H*)-one (**III**) as a yellow solid (2.50 g, 81.7%). M.p 280.5–282.0 °C. TLC R_f 0.23 (*n*-hexane/ethyl acetate, 1:3). LR-MS (ESI$^-$, MeOH/DCM), *m/z*: Calculated for $C_{15}H_{11}N_3O_5S$ $[M - H]^-$ 344.03, found 343.97. HR-MS (ESI$^+$, MeOH), *m/z*: Calculated for $[M + Na]^+$: 368.0317, found: 368.0330. FT-IR (KBr), ν_{max} (cm^{-1}): 3180 (N-H); 3078, 3020 (C-H); 1685 (C=O); 1598 (C=N); 1527, 1490 (C=C); 1350 (NO_2); 1315, 1145 (SO_2). ^{1}H-NMR (DMSO-d_6), δ (ppm): 8.59 (s, 1 H, H-5); 8.47 (s, 1 H, H-8); 8.39 (s, 1 H, H-2); 7.92 (d, J = 8.50 Hz, 2 H, H-2′, H-6′); 7.49 (d, J = 8.00 Hz, 2 H, H-3′, H-5′); 2.41 (s, 1 H, H-7′). ^{13}C-NMR (DMSO-d_6), δ (ppm): 159.1 (C-4); 151.0 (C-8a); 149.9 (C-2); 145.5 (C-4′); 144.1 (C-6); 138.1 (C-7); 136.4 (C-1′); 131.2 (C-8); 130.1 (C-3′, C-5′); 128.1 (C-2′, C-6′); 126.4 (C-4a); 124.0 (C-5); 21.1 (C-7′).

4. Conclusions

A new sulfone, 6-nitro-7-tosylquinazolin-4(3*H*)-one, was synthesized from 7-chloro-6-nitroquinazolin-4(3*H*)-one and sodium *p*-toluenesulfinate. The use of *p*-toluenesulfinate in place of benzenesulfinate demonstrated a significantly quicker reaction and a cleaner product in a comparably high yield (81.7%). The target compound has been fully characterized by the melting point, mass-spectrometry, FT-IR, ^{1}H-NMR, ^{13}C-NMR, DEPT, HSQC, HMBC spectroscopies, and PXRD analysis.

Supplementary Materials: The following are available online. Spectral data of the title compound **III** are available online. Figure S1: MS spectrum of compound 6-nitro-7-tosylquinazolin-4(3*H*)-one (**III**); Figure S2: HR-MS spectrum of 6-nitro-7-tosylquinazolin-4(3*H*)-one (**III**); Figure S3: FT-IR spectrum of compound 6-nitro-7-tosylquinazolin-4(3*H*)-one (**III**); Figure S4: ^{1}H-NMR spectrum of 6-nitro-7-tosylquinazolin-4(3*H*)-one (**III**); Figure S5: ^{13}C-NMR spectrum of 6-nitro-7-tosylquinazolin-4(3*H*)-one (**III**); Figure S6: DEPT spectrum of compound 6-nitro-7-tosylquinazolin-4(3*H*)-one (**III**); Figure S7: 2D-HSQC spectrum of 6-nitro-7-tosylquinazolin-4(3*H*)-one (**III**); Figure S8: 2D-HMBC spectrum of 6-nitro-7-tosylquinazolin-4(3*H*)-one (**III**); Figure S9: PXRD spectrum of 6-nitro-7-tosylquinazolin-4(3*H*)-one (**III**).

Author Contributions: T.N.N., T.P.T.T., T.H.M.V., and H.B.N. synthesized the compounds; N.S.H.D., V.G.N., and D.L.N. designed the experiments; V.H.N. analyzed spectroscopic data and wrote the manuscript; V.H.N. and N.T.T. edited the manuscript. All authors discussed the results, read, and approved the final version of the manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: The authors would like to thank Hanoi University of Pharmacy and Thainguyen University of Medicine and Pharmacy for the financial support and research facilities.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Liu, N.-W.; Liang, S.; Manolikakes, G. Recent advances in the synthesis of sulfones. *Synthesis* **2016**, *48*, 1939–1973. [CrossRef]
2. Feng, M.; Tang, B.; Liang, S.H.; Jiang, X. Sulfur containing scaffolds in drugs: Synthesis and application in medicinal chemistry. *Curr. Top. Med. Chem.* **2016**, *16*, 1200–1216. [CrossRef]
3. Matavos-Aramyan, S.; Soukhakian, S.; Jazebizadeh, M.H. Selected methods for the synthesis of sulfoxides and sulfones with emphasis on oxidative protocols. *Phosphorus Sulfur Silicon Relat. Elem.* **2020**, *195*, 181–193. [CrossRef]
4. The DrugBank Database. Available online: https://www.drugbank.ca (accessed on 18 May 2020).
5. Richards-Taylor, C.S.; Blakemore, D.C.; Willis, M.C. One-pot three-component sulfone synthesis exploiting palladium-catalysed aryl halide aminosulfonylation. *Chem. Sci.* **2014**, *5*, 222–228. [CrossRef]
6. Trost, B.M.; Kalnmals, C.A. Sulfones as chemical chameleons: Versatile synthetic equivalents of small-molecule synthons. *Chem. Eur. J.* **2019**, *25*, 11193–11213. [CrossRef] [PubMed]
7. Noser, A.A.; El-Naggar, M.; Donia, T.; Abdelmonsef, A.H. Synthesis, in silico and in vitro assessment of new quinazolinones as anticancer agents via potential AKT inhibition. *Molecules* **2020**, *25*, 4780. [CrossRef] [PubMed]
8. El-Azab, A.S.; Abdel-Aziz, A.A.; AlSaif, N.A.; Alkahtani, H.M.; Alanazi, M.M.; Obaidullah, A.J.; Eskandrani, R.O.; Alharbi, A. Antitumor activity, multitarget mechanisms, and molecular docking studies of quinazoline derivatives based on a benzenesulfonamide scaffold: Cell cycle analysis. *Bioorg. Chem.* **2020**, *104*, 104345. [CrossRef] [PubMed]
9. Sancineto, L.; Iraci, N.; Massari, S.; Attanasio, V.; Corazza, G.; Barreca, M.L.; Sabatini, S.; Manfroni, G.; Avanzi, N.R.; Cecchetti, V.; et al. Computer–aided design, synthesis and validation of 2–phenylquinazolinone fragments as CDK9 inhibitors with anti–HIV–1 Tat–mediated transcription activity. *ChemMedChem* **2013**, *8*, 1941–1953. [CrossRef] [PubMed]
10. Yang, G.; Cheng, C.; Xu, G.B.; Tang, L.; Chua, K.L.; Yang, Y.Y. Synthesis and antibiofilm evaluation of 3-hydroxy-2,3-dihydroquinazolin-4(1*H*)-one derivatives against opportunistic pathogen *Acinetobacter Baumannii*. *Bioorg. Med. Chem.* **2020**, *28*, 115606. [CrossRef]
11. Liu, G.; Liu, C.P.; Ji, C.N.; Sun, L. Synthesis and antifungal activities of *N*-3-substituted quinazolin-4-one catalyzed by 3-methylimidazole ionic liquids. *Asian J. Chem.* **2013**, *25*, 9853–9856. [CrossRef]
12. Noureldin, N.A.; Kothayer, H.; Lashine, E.M.; Baraka, M.M.; Huang, Y.; Li, B.; Ji, Q. Design, synthesis and biological evaluation of novel quinazoline-2,4-diones conjugated with different amino acids as potential chitin synthase inhibitors. *Eur. J. Med. Chem.* **2018**, *152*, 560–569. [CrossRef] [PubMed]
13. Aziz, J.; Messaoudi, S.; Alami, M.; Hamze, A. Sulfinate derivatives: Dual and versatile partners in organic synthesis. *Org. Biomol. Chem.* **2014**, *12*, 9743–9759. [CrossRef] [PubMed]
14. Kaiser, D.; Klose, I.; Oost, R.; Neuhaus, J.; Maulide, N. Bond-forming and -breaking reactions at sulfur(IV): Sulfoxides, sulfonium salts, sulfur ylides, and sulfinate salts. *Chem. Rev.* **2019**, *119*, 8701–8780. [CrossRef] [PubMed]
15. Tranquilino, A.; Andrade, S.R.C.P.; da Silva, A.P.M.; Menezes, P.H.; Oliveira, R.A. Non-expensive, open-flask and selective catalytic systems for the synthesis of sulfinate esters and thiosulfonates. *Tetrahedron Lett.* **2017**, *58*, 1265–1268. [CrossRef]
16. Li, Y.; Fan, Y. Recent advances in C–S bond construction to synthesize sulfone. *Synth. Commun.* **2019**, *49*, 3227–3264. [CrossRef]
17. Schroeder, J.; Dziewas, G.; Fachinger, T.; Jaeger, B.; Reichel, C.; Renner, S. Process for Preparing Aminocrotonylamino-Substituted Quinazoline Derivatives. U.S. Patent US8188274B2, 29 May 2012.
18. Slobbe, P.; Poot, A.J.; Van Dongen, A.A.M.S.; Niessen, H.; Windhorst, A.D. Radiolabeled Quinazoline Derivatives. U.S. Patent US20150368230A1, 24 December 2015.

19. Baskin, J.M.; Wang, Z. An efficient copper catalyst for the formation of sulfones from sulfinic acid salts and aryl iodides. *Org. Lett.* **2002**, *4*, 4423–4425. [CrossRef] [PubMed]
20. Chen, L.; Liang, J.; Chen, Z.; Chen, J.; Yan, M.; Zhang, X. A convenient synthesis of sulfones via light promoted coupling of sodium sulfinates and aryl halides. *Adv. Synth. Catal.* **2019**, *361*, 956–960. [CrossRef]
21. Nguyen, V.D.; Nguyen, V.T.; Haug, G.C.; Dang, H.T.; Arman, H.D.; Ermler, W.C.; Larionov, O.V. Rapid and chemodivergent synthesis of *N*–heterocyclic sulfones and sulfides: Mechanistic and computational details of the persulfate-initiated catalysis. *ACS Catal.* **2019**, *9*, 4015–4024. [CrossRef]
22. Pretsch, E.; Bühlmann, P.; Badertscher, M. *Structure Determination of Organic Compounds*, 4th ed.; Springer: Berlin/Heidelberg, Germany, 2009.
23. Pogaku, N.; Krishna, P.R.; Prapurna, Y.L. Substrate- and temperature-controlled divergence in reactions of alcohols with TosMIC catalyzed by $BF_3 \cdot Et_2O$: Facile access to sulfinates and sulfones. *Synth. Commun.* **2017**, *47*, 1239–1249. [CrossRef]
24. Nguyen, T.N.; Tran, T.H.; Dao, N.S.H.; Nguyen, V.G.; Nguyen, D.L.; Trinh, N.T.; Nguyen, V.H. Synthesis and spectral characterization of 4,7-dichloro-6-nitroquinazoline. *Molbank* **2020**, *2020*, M1134. [CrossRef]