Silver-Mediated Methoxylation of Aryl C(*sp*²)-H Bonds Directing by DMEDA

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Received: 24 January 2019; Accepted: 7 February 2019; Published: 12 February 2019

Abstract: The first example of silver-mediated phosphine-promoted methoxylation of aryl C(*sp*²)-H bonds with the commercially available reagent for the preparation of alkyl aryl ethers has been developed. This protocol is characterized by mild reaction conditions, broad substrate scope, and high regioselectivity.

Keywords: Silver-mediated; phosphine-promoted; C–H functionalization; DMEDA; pharmaceutical development

1. Introduction

Alkyl aryl ethers are ubiquitous structural motifs present in both natural and synthetic compounds, particularly in bioactive molecules targeted as pharmaceuticals (Scheme 1) [1,2]. Compared to the traditional method for carbon-oxygen bond coupling [3–6], transition metal catalyzed C–H alkoxylation with alcohols has received much attention in recent decades in terms of atom and step economy [7–10]. However, direct C–H bond alkoxylation has been mostly limited to a palladium- [11–15] or copper-catalyzed system [16–20] which are both more biological toxicity metals.

Scheme 1. Selected pharmaceuticals containing aryl alkyl ether units.

Recently, the first-row transition metals such as iron, cobalt, and nickel for C–H alkoxylation, have attracted more attention owing to low biological toxicity as well as low cost [21–25]. In 2015, Niu and co-workers have first reported cobalt-catalyzed alkoxylation of C(*sp*²)–H bond in aromatic and olefinic carboxamides with Ag₂O as oxidant (Scheme 2a) [21]. Lately, a new cobalt-catalyzed system has reported by same group for C8 alkoxylation of naphthylamine derivatives with both primary and secondary alcohols [22]. In 2018, an efficient Nickel-catalyzed C–H bond alkoxylation of benzamides and olefinic carboxamides with alcohols was also achieved for the first time by Sundararaju’s group (Scheme 2b) [23]. In the same year, our group also reported an iron-catalyzed ethoxylation of aryl C(*sp*²)–H bonds with cobalt co-catalyst (Scheme 2c) [24]. However, all of these reactions were carried out with silver reagents. While silver is also a common transition metal catalyst for C–H functionalization [26–32], silver-mediated alkoxylation of aryl C(*sp*²)–H bonds will be attractive but challenging.

Scheme 2. Direct alkoxylation of C–H bonds using low biotoxicity transition metals.

As a part of our continuous interest towards using the newly developed directing group derived from the drug structure *N,N'*-dimethylethanediamine (DMEDA), we also realized the copper-catalyzed DMEDA-directed methoxylation recently [33]. Considering silver is the heavier congener of copper in the Periodic Table and it also has high catalytic activity for C–H functionalization, we speculated that the DMEDA directing group may facilitate the silver-mediated methoxylation of aryl $C(sp^2)$ –H bonds. We found that this is indeed the case, and we report herein a silver-mediated methoxylation of aryl $C(sp^2)$ –H bonds with methanol to prepare Alkyl aryl ethers for the first time (Scheme 2d).

2. Results

Initially, the synthesis study was carried out with *N*-(2-(dimethylamino)ethyl)benzamide (**1a**) as a model substrate (Table 1). While this transformation is a cross-dehydrogenative coupling (CDC) reaction, high-valent metal is needed for the electrophilic activation of $C(sp^2)$ –H bonds [34–37]. Since high-valent silver is rare in relation to copper under normal conditions, [38] the combination of Ag(I) and $K_2S_2O_8$ which proved to be efficient for a silver-catalyzed or silver-mediated system was used in this system [31,32]. However, no good result was observed after the preliminary screening. Fortunately, the reaction was found to proceed efficiently in the presence of triphenylphosphine as a ligand (Entry 1, 63%). It is obviously that the phosphine ligand was critical for this transformation, when the desired product **3a** was almost unobserved except without the phosphine ligand (Entry 8). In this system, we also found that a large number of phosphine ligands were oxidized to phosphine oxides, while phosphine oxides did not promote this transformation (Entry 3). Subsequently, 1.5 equivalents were screened out as the necessary amount of phosphine ligand (for more details, see Supplementary Materials). The effects of various structures of phosphine ligands for this system was also investigated, and trivalent phosphine ligands were found to promote this transformation efficiently (Scheme 3, Entry 1–7). What's more, by comparing the results of L_2 and L_4 , it was obvious that the steric effect had a great influence on this reaction (Entry 2,4). On the basis of that, a series of silver salts such as $AgNO_3$, Ag_2CO_3 , $AgOAc$, $AgOTf$, Ag_2O , Ag_2SO_4 , $AgOPiv$, and AgF were screened, then $AgOPiv$ was found to be the optimal condition for this reaction (for more details, see SI). Meanwhile, different cosolvents were evaluated, it could be found that polar solvents such as DMSO, DMF and DMA were favorable for promoting the reaction, and DMA was found to be the most suitable cosolvent (Entry 9–12). Various additives were then tested, and the results showed that methoxylated yield increased in the presence of Na_2SO_4 (Entry 13, 72%). While $MgSO_4$ were used as an additive, the yield was improved to 78% (Entry 14, Isolated yield 71%). However, no obvious improvement could be observed when other additives were added to this system (Entry 15–19). This may due to the

high binding energy of $\text{Ag}(3d_{5/2})$ states for AgSO_4 , a Ag(II) compound [39]. The effect of the amount of AgOPiv was also investigated, decreasing the amount of AgOPiv to 3.0 equivalent reduced the yield of **1a** to 55% (Entry 20). Furthermore, the reaction was found to be sensitive to air and moisture, switching the atmosphere from argon to air led to no reaction at all (Entry 21). Finally, different temperatures were also evaluated, and 55°C was found to be the optimum temperature (for more details, see SI).

Table 1. Optimization of the reaction conditions ^a.

Entry	Ligand	Additive	Cosolvent	Yield [%] ^b
1	L ₁	-	DMA	63
2	L ₂	-	DMA	54
3	L ₃	-	DMA	Trace
4	L ₄	-	DMA	17
5	L ₅	-	DMA	51
6	L ₆	-	DMA	9
7	L ₇	-	DMA	36
8	-	-	DMA	n.r
9	L ₁	-	DMSO	51
10	L ₁	-	DMF	56
11	L ₁	-	Toluene	4
12	L ₁	-	EA	30
13	L ₁	Na_2SO_4	DMA	72
14	L ₁	MgSO_4	DMA	78(71 ^c)
15	L ₁	Na_2CO_3	DMA	30
16	L ₁	K_2CO_3	DMA	n.r
17	L ₁	Li_2CO_3	DMA	20
18	L ₁	Li_3PO_4	DMA	38
19	L ₁	NaOAc	DMA	50
20 ^d	L ₁	MgSO_4	DMA	55
21 ^e	L ₁	MgSO_4	DMA	n.r

^a Reaction condition: **1a** (0.1 mmol), Ligand (1.5 equiv.), AgOPiv (4.0 equiv.), $\text{K}_2\text{S}_2\text{O}_8$ (4.0 equiv.), Additive (2.0 equiv.), in $\text{MeOH}/\text{cosolvent}$ (1/1) 1 mL, 55°C for 3 h, under Ar atmosphere. ^b ^1H NMR yield using CH_2Br_2 as the internal standard. ^c Isolated yield. ^d AgOPiv (3.0 equiv.). ^e Under air atmosphere.

Scheme 3. The structure of phosphine ligands.

Using the optimal reaction conditions, the reaction scope with respect to aromatic substrates is presented in Table 2. In general, the demonstrated transformation was found to be compatible with a variety of benzamide derivatives bearing either electron-withdrawing or electron-donating groups, providing the corresponding methoxylated products with moderate to good yields (**2b–2s**). For example, fluoro (**2c,2o**), chloro (**2d,2n,2s**), bromo (**2b,2p**), nitro (**2e**), and cyano (**2h**) groups are well tolerated, which are convenient handles for further functionality. Due to the reactive activity of the iodine functional group, the reaction of **1g** only gave the methoxylated product in 14% yield

accompanied by the compounds **1a** (yield 23%) and **2a** (yield 31%). The reaction protocol was sensitive to steric hindrance, methoxylation with *ortho*-substituted substrates gave no encouraging results. But gratifyingly, the methoxylation of *meta*-substituted substrates showed high regioselectivity, which proceeded exclusively at the less hindered C–H bonds irrespective of the electronic properties of the substrates (**2l–2r**). Disubstituted substrate such as 3,5-dichloro-N-(2-(dimethylamino)ethyl) benzamide were also tolerated well under the optimized conditions (**2s**). Finally, other alcohols such as ethanol, propanol, isopropanol, butanol, and 2-butyl alcohol were also screened; however, encouraging results were not obtained.

Table 2. Substrate scope of aromatic compounds ^a.

<div style="text-align: center;"> </div>			
Entry	1	2	Yield ^b
1			65
2			58
3			62
4			35
5			62
6			14
7			61
8			63
9			72

Table 2. Cont.

10			55
11			68
12			67
13			60
14			54
15			40
16			64
17			64
18			55

^a Reaction condition: 1 (0.1 mmol), L₁ (1.5 equiv.), AgOPiv (4.0 equiv.), K₂S₂O₈ (4.0 equiv.), MgSO₄ (2.0 equiv.), in MeOH / DMA (1/1) 1 mL at 55 °C under Ar atmosphere. ^b Isolated yield.

3. Discussion

A plausible mechanism is proposed in Scheme 4 on the basis of the above observations and preliminary mechanistic studies. [38–41] It is known that in the presence of peroxydisulfate, the silver(I) salt is oxidized to a silver(II) species [40,41]. Complexation of benzamide 1a and phosphine ligand (L) to the silver(II) species (intermediate A), followed by C–H activation, affords the intermediate B. The intermediate B undergoes reductive elimination to give intermediate C, which was followed by protonation to generate the desired product 2a. While silver also existed as an oxidant in the stage of C–H activation, the stoichiometric silver reagent was indispensable.

Scheme 4. Plausible mechanism for C–H ethoxylation catalyzed by iron.

4. Materials and Methods

4.1. Materials

Methanol, MeCN, THF, Toluene, EA, DMSO, DMF, DMA, 1,4-dioxane was dried by distillation over CaH_2 and distilled under reduced pressure, then stored in dry argon atmosphere. All reagents were purchased from commercial suppliers and used without purification unless otherwise stated. Column chromatography was performed with silica gel (300–400 mesh) produced by Qingdao Marine Chemical Factory, Qingdao (China). NMR spectra were recorded on Bruker AVANCE III 500MHz instrument (Bruker, Hamburg, Germany) with TMS as internal standard. Coupling constants were reported in Hertz (Hz). HRMS analysis of determination of conversion was performed on the instrument of Waters Q-TOF.

4.2. General Procedure for Silver-Mediated Methoxylation

Under argon atmosphere, AgOPiv (0.40 mmol), $\text{K}_2\text{S}_2\text{O}_8$ (0.40 mmol), L_1 (0.15 mmol), **1a** (0.10 mmol), MgSO_4 (0.20 mmol), and MeOH/DMA (1/1, 1 mL) were introduced into a 15 mL seal tube. The mixture was fiercely stirred at 55 °C for 3 h. After cooling in an ice bath, the mixture was diluted in the mixed solvent of dichloromethane (30 mL) and edetate tetrasodium saturated aqueous solution (30 mL). After separated, the aqueous phase was extracted thrice with dichloromethane (30 mL). The organic layers were combined and evaporated under vacuum and the crude product was purified by column chromatograph using silica gel with n-hexane/ethyl acetate (v/v 1:2) to n-hexane/ethyl acetate/triethylamine (v/v/v 1:2:0.03) as eluent to afford **2a**. Isolated yield: 15.8 mg (71%).

5. Conclusions

We presented the first example of silver-mediated phosphine-promoted methoxylation of aryl $\text{C}(\text{sp}^2)\text{--H}$ bonds with the commercially available reagent for the preparation of alkyl aryl ethers. This protocol is characterized by mild reaction conditions, broad substrate scope, and high regioselectivity. In addition, without the use of more biological toxicity metals such as copper and palladium, this system will be more suitable for the synthesis of related active drug molecules. Further exploration of this strategy to the synthesis of related active drug molecules is currently in progress.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/9/2/171/s1>.

Author Contributions: Conceptualization, C.D; methodology, J.Z.; formal analysis, L.X.; and Writing—Original Draft preparation, G.Z.

Funding: This research was funded by the National Natural Science Foundation of China (no. 20702051), the Natural Science Foundation of Zhejiang Province (LY13B020017).

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

References

1. Maligres, P.E.; Li, J.; Krska, S.W.; Schreier, J.D.; Raheem, I.T. C–O cross-coupling of activated aryl and heteroaryl halides with aliphatic alcohols. *Angew. Chem. Int. Ed.* **2012**, *51*, 9071–9074. [[CrossRef](#)] [[PubMed](#)]
2. Anand, M.; Sunoj, R.B. Role of Explicit Solvents in Palladium(II)-Catalyzed Alkoxylation of Arenes: An Interesting Paradigm for Preferred Outer-Sphere Reductive Elimination over Inner-Sphere Pathway. *Organometallics* **2012**, *31*, 6466–6481. [[CrossRef](#)]
3. Qiao, J.X.; Lam, P.Y.S. Copper-Promoted Carbon-Heteroatom Bond Cross-Coupling with Boronic Acids and Derivative. *Synthesis* **2011**, *6*, 829–856. [[CrossRef](#)]
4. Monnier, F.; Taillefer, M. Catalytic C–C, C–N, and C–O Ullmann-Type Coupling Reactions. *Angew. Chem. Int. Ed.* **2009**, *48*, 6954–6971. [[CrossRef](#)] [[PubMed](#)]
5. Hartwig, J.F. Carbon–Heteroatom Bond Formation Catalysed by Organometallic Complexes. *Nature* **2008**, *455*, 314–322. [[CrossRef](#)] [[PubMed](#)]
6. Ley, S.V.; Thomas, A.W. Modern Synthetic Methods for Copper-Mediated C(aryl)–O, C(aryl)–N, and C(aryl)–S Bond Formation. *Angew. Chem. Int. Ed.* **2003**, *42*, 5400–5449. [[CrossRef](#)] [[PubMed](#)]
7. Hu, Y.; Zhou, B.; Wang, C. Inert C–H Bond Transformations Enabled by Organometallic Manganese Catalysis. *Acc. Chem. Res.* **2018**, *51*, 816–827. [[CrossRef](#)] [[PubMed](#)]
8. Wei, D.; Zhu, X.; Niu, J.-L.; Song, M.-P. High-Valent-Cobalt-Catalyzed C–H Functionalization Based on Concerted Metalation-Deprotonation and Single-Electron-Transfer Mechanisms. *ChemCatChem* **2016**, *8*, 1242–1263. [[CrossRef](#)]
9. Su, B.; Cao, Z.-C.; Shi, Z.-J. Exploration of Earth-Abundant Transition Metals (Fe, Co, and Ni) as Catalysts in Unreactive Chemical Bond Activations. *Acc. Chem. Res.* **2015**, *48*, 886–896. [[CrossRef](#)]
10. Liu, C.; Liu, D.; Lei, A. Recent Advances of Transition-Metal Catalyzed Radical Oxidative Cross-Couplings. *Acc. Chem. Res.* **2014**, *47*, 3459–3470. [[CrossRef](#)]
11. Qiu, F.-C.; Xie, Q.; Guan, B.-T. Palladium-Catalyzed *ortho*-Alkoxylation of Tertiary Benzamides: H₂SO₄ as an Effective Additive. *Asian J. Org. Chem.* **2018**, *7*, 107–110. [[CrossRef](#)]
12. Li, S.; Zhu, W.; Gao, F.; Li, C.; Wang, J.; Liu, H. Palladium-Catalyzed *Ortho*-Alkoxylation of N-Benzoyl *alpha*-Amino Acid Derivatives at Room Temperature. *J. Org. Chem.* **2017**, *82*, 126–134. [[CrossRef](#)] [[PubMed](#)]
13. Shan, G.; Yang, X.; Zong, Y.; Rao, Y. An Efficient Palladium-Catalyzed C–H Alkoxylation of Unactivated Methylene and Methyl Groups with Cyclic Hypervalent Iodine (I³⁺) Oxidants. *Angew. Chem. Int. Ed.* **2013**, *52*, 13606–13610. [[CrossRef](#)] [[PubMed](#)]
14. Zhang, S.-Y.; He, G.; Zhao, Y.; Wright, K.; Nack, W.A.; Chen, G. Efficient Alkyl Ether Synthesis via Palladium-Catalyzed, Picolinamide-Directed Alkoxylation of Unactivated C(sp³)–H and C(sp²)–H Bonds at Remote Positions. *J. Am. Chem. Soc.* **2012**, *134*, 7313–7316. [[CrossRef](#)] [[PubMed](#)]
15. Anand, M.; Sunoj, R.B. Palladium(II)-Catalyzed Direct Alkoxylation of Arenes: Evidence for Solvent-Assisted Concerted Metalation Deprotonation. *Org. Lett.* **2011**, *13*, 4802–4805. [[CrossRef](#)] [[PubMed](#)]
16. Tran, C.B.; Duong, X.N.T.; Lu, H.D.; Cao, T.T.V.; Thanh, T. Auxiliary-Directed Etherification of sp² C–H Bonds Under Heterogeneous Metal–Organic Framework Catalysis: Synthesis of Ethenamide. *RSC Adv.* **2018**, *8*, 2829–2836. [[CrossRef](#)]
17. Salvador, T.K.; Arnett, C.H.; Kundu, S.; Sapiezynski, N.G.; Bertke, J.A.; Boroujeni, M.R.; Warren, T.H. Copper Catalyzed sp³ C–H Etherification with Acyl Protected Phenols. *J. Am. Chem. Soc.* **2016**, *138*, 16580–16583. [[CrossRef](#)] [[PubMed](#)]
18. Yu, M.; Wang, Z.; Hu, J.; Li, S.; Du, H. Copper-Catalyzed Intramolecular Alkoxylation of Purine Nucleosides: One-Step Synthesis of 5′-O,8-Cyclopurine Nucleosides. *J. Org. Chem.* **2015**, *80*, 9446–9453. [[CrossRef](#)]
19. Yin, X.-S.; Li, Y.-C.; Yuan, J.; Gu, W.-J.; Shi, B.-F. Copper(II)-Catalyzed Methoxylation of Unactivated (hetero)Aryl C–H Bonds Using a Removable Bidentate Auxiliary. *Org. Chem. Front.* **2015**, *2*, 119–123. [[CrossRef](#)]
20. Bhadra, S.; Dzik, W.I.; Goossen, L.J. Synthesis of Aryl Ethers from Benzoates through Carboxylate-Directed C–H-Activating Alkoxylation with Concomitant Protodecarboxylation. *Angew. Chem. Int. Ed.* **2013**, *52*, 2959–2962. [[CrossRef](#)] [[PubMed](#)]

21. Zhang, L.-B.; Hao, X.-Q.; Zhang, S.-K.; Liu, Z.-J.; Zheng, X.-X.; Gong, J.-F.; Niu, J.-L.; Song, M.-P. Cobalt-Catalyzed C(sp²)-H Alkoxylation of Aromatic and Olefinic Carboxamides. *Angew. Chem. Int. Ed.* **2015**, *54*, 272–275. [[CrossRef](#)] [[PubMed](#)]
22. Han, J.-N.; Du, C.; Zhu, X.; Wang, Z.-L.; Zhu, Y.; Chu, Z.-Y.; Niu, J.-L.; Song, M.-P. Cobalt-Catalyzed *peri*-Selective Alkoxylation of 1-Naphthylamine Derivatives. *Beilstein J. Org. Chem.* **2018**, *14*, 2090–2097. [[CrossRef](#)] [[PubMed](#)]
23. Rajesh, N.; Sundararaju, B. Nickel-catalyzed C–H bond Alkoxylation of Amides with Alcohols. *Asian J. Org. Chem.* **2018**, *7*, 1368–1371. [[CrossRef](#)]
24. Zhang, G.; Zhu, J.; Ding, C. Pharmaceutical-Oriented Iron-Catalyzed Ethoxylation of Aryl C(sp²)-H Bonds with Cobalt Co-Catalyst. *Chemistryselect* **2018**, *3*, 9803–9806. [[CrossRef](#)]
25. Liu, S.-K.; Cui, X.-F.; Liu, X.-X.; Ma, H.-J.; Wei, D.-D.; Luo, X.-L.; Huang, G.-S. Cobalt(II)-Catalyzed Cross-Dehydrogenative Coupling Reaction of Benzamides with Alcohols to Build C–O Bond. *Chemistryselect* **2018**, *3*, 3989–3992. [[CrossRef](#)]
26. Zhu, S.-Q.; Xu, X.-H.; Qing, F.-L. Silver-Mediated Oxidative C–H Difluoromethylation of Phenanthridines and 1,10-Phenanthrolines. *Chem. Commun.* **2017**, *53*, 11484–11487. [[CrossRef](#)] [[PubMed](#)]
27. Ouyang, X.-H.; Song, R.-J.; Hu, M.; Yang, Y.; Li, J.-H. Silver-Mediated Intermolecular 1,2-Alkylarylation of Styrenes with Carbonyl Alkyl Bromides and Indoles. *Angew. Chem. Int. Ed.* **2016**, *55*, 3187–3191. [[CrossRef](#)] [[PubMed](#)]
28. Liu, J.; Liu, Z.; Liao, P.; Zhang, L.; Tu, T.; Bi, X. Silver-Catalyzed Cross-Coupling of Isocyanides and Active Methylene Compounds by a Radical Process. *Angew. Chem. Int. Ed.* **2015**, *54*, 10618–10622. [[CrossRef](#)] [[PubMed](#)]
29. Yang, M.; Su, B.; Wang, Y.; Chen, K.; Jiang, X.; Zhang, Y.-F.; Zhang, X.-S.; Chen, G.; Cheng, Y.; Cao, Z.; et al. Silver-Catalysed Direct Amination of Unactivated C–H Bonds of Functionalized Molecules. *Nature Commun.* **2014**, *5*, 4707. [[CrossRef](#)] [[PubMed](#)]
30. Xu, P.; Guo, S.; Wang, L.; Tang, P. Silver-Catalyzed Oxidative Activation of Benzylic C–H Bonds for the Synthesis of Difluoromethylated Arenes. *Angew. Chem. Int. Ed.* **2014**, *53*, 5955–5958. [[CrossRef](#)] [[PubMed](#)]
31. Yang, H.; Wang, F.; Jiang, X.; Zhou, Y.; Xu, X.; Tang, P. Silver-Promoted Oxidative Benzylic C–H Trifluoromethoxylation. *Angew. Chem. Int. Ed.* **2018**, *57*, 13266–13270. [[CrossRef](#)]
32. Zhu, Y.; Huang, K.; Pan, J.; Qiu, X.; Luo, X.; Qin, Q.; Wei, J.; Wen, X.; Zhang, L.; Jiao, N. Silver-Catalyzed Remote Csp³-H Functionalization of Aliphatic Alcohols. *Nature Commun.* **2018**, *9*, 2625. [[CrossRef](#)] [[PubMed](#)]
33. Zhang, G.; Zhu, J.; Tong, C.; Ding, C. Pharmaceutical-Oriented Methoxylation of Aryl C(sp²)-H Bonds using Copper Catalysts. *Synlett* **2018**, *29*, 1451–1454.
34. Girard, S.A.; Knauber, T.; Li, C.-J. The Cross-Dehydrogenative Coupling of Csp³-H Bonds: A Versatile Strategy for C–C Bond Formations. *Angew. Chem. Int. Ed.* **2014**, *53*, 74–100. [[CrossRef](#)] [[PubMed](#)]
35. Yeung, C.S.; Dong, V.M. Catalytic Dehydrogenative Cross-Coupling: Forming Carbon–Carbon Bonds by Oxidizing Two Carbon–Hydrogen Bonds. *Chem. Rev.* **2011**, *111*, 1215–1292. [[CrossRef](#)] [[PubMed](#)]
36. Li, C.-J. Cross-Dehydrogenative Coupling (CDC): Exploring C–C Bond Formations beyond Functional Group Transformations. *Acc. Chem. Res.* **2009**, *42*, 335–344. [[CrossRef](#)] [[PubMed](#)]
37. Ackermann, L.; Vicente, R.; Kapdi, A.R. Transition-Metal-Catalyzed Direct Arylation of (Hetero)Arenes by C–H Bond Cleavage. *Angew. Chem. Int. Ed.* **2009**, *48*, 9792–9826. [[CrossRef](#)] [[PubMed](#)]
38. Grochala, W.; Mazej, Z. Chemistry of Silver(II): A Cornucopia of Peculiarities. *Philos. T. Roy. Soc. A* **2015**, *373*, 12. [[CrossRef](#)] [[PubMed](#)]
39. Grzelak, A.; Jaron, T.; Mazej, Z.; Michalowski, T.; Szarek, P.; Grochala, W. Anomalous Chemical Shifts In X-ray Photoelectron Spectra of Sulfur-Containing Compounds of Silver (I) and (II). *J. Electron Spectrosc. Relat. Phenom.* **2015**, *202*, 38–45. [[CrossRef](#)]
40. Seo, S.; Taylor, J.B.; Greaney, M.F. Protodecarboxylation of Benzoic Acids under Radical Conditions. *Chem. Commun.* **2012**, *48*, 8270–8272. [[CrossRef](#)]
41. Anderson, J.M.; Kochi, J.K. Silver(I)-Catalyzed Oxidative Decarboxylation of Acids by Peroxydisulfate. Role of Silver(II). *J. Am. Chem. Soc.* **1970**, *92*, 1651–1659. [[CrossRef](#)]