Organic LETTERS

Letter

pubs.acs.org/OrgLett

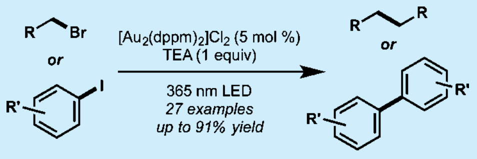
Homocoupling of Iodoarenes and Bromoalkanes Using Photoredox Gold Catalysis: A Light Enabled Au(III) Reductive Elimination

Huy Tran, Terry McCallum, Mathieu Morin, and Louis Barriault*

Centre for Catalysis, Research and Innovation, Department of Chemistry and Biomolecular Sciences, University of Ottawa, Ottawa, Ontario, Canada

Supporting Information

ABSTRACT: The formation of homocoupled alkane byproducts have been identified in the reduction of bromoalkanes via photoredox gold catalysis with dimeric Au(I) complexes. This prompted further investigation into the mechanism of formation of these byproducts and the diversity of C−X bonds amenable to this transformation. Examples were found when considering bromoalkanes while a wide variety of iodoarenes underwent this process in good to excellent yields. The light enabled homocoupling of iodoarenes made possible by photoredox gold catalysis is reported.



Symmetrical biaryl compounds are among potent natural products that present antimitotic activity.[1] These structurally diverse natural products contain linkages that have been the subject of many transition metal oriented synthetic studies.[2] Such molecules are targets for medicinal chemists, total synthesis efforts, and pharmaceutical exploration, Figure 1.[3] When considering haloarenes, the Ullman coupling provides a convenient route to homocoupled arene products, one of the longest standing and practical methods in organic synthesis.[4] This methodology is often subject to stoichiometric transition metals/reagents and additives under harsh conditions. Presently, haloarene homocoupling methodology has seen the development of catalytic transition metals with stoichiometric reductants to achieve such reactivity while such methodology for alkane homocoupling is rare (eq 1).[5] Catalytic methodology involving silyl-functionalized arenes with Au(I) complexes and external oxidants has resulted in homocoupled biaryl products (eq 2).[5g,h] A standing challenge in organic chemistry is the development of arene and haloalkane homocoupling methodology under mild and convenient reaction conditions. Currently, these types of alkane couplings are limited to benzylic functionalized moieties which take advantage of their stability and likeliness to dimerize.[6] In this Letter, the identification and development of the homocoupling of iodoarenes and bromoalkanes using photoredox gold catalysis is described.

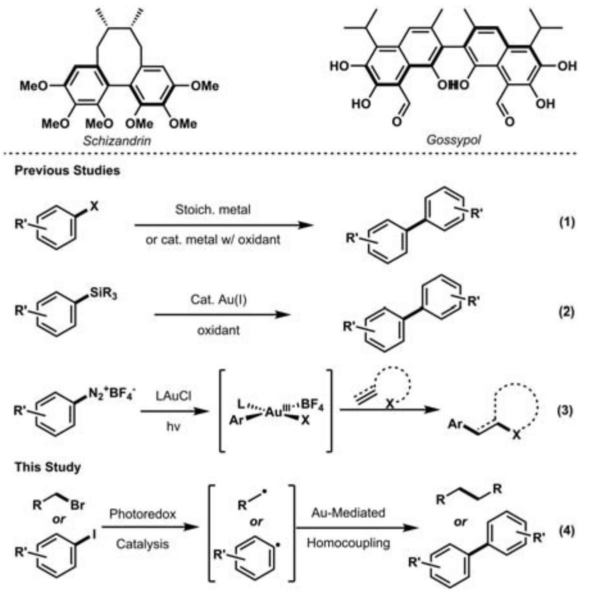


Figure 1. Methods of homocoupling reactions.

Tremendous interest in photoredox catalysis has cultivated a wide variety of methodology development.[7] Owing to the high energy found in excited state complexes, photochemistry has once again established itself as a powerful tool in organic synthesis.[8] Inspired by Nature, excited state transition metal based complexes and organic dyes generated by mild sources of light irradiation (light bulbs and LEDS) are used to trigger single electron transfer (SET) events through an oxidative or reductive quenching mechanism.[9] Access to one-electron mechanisms of important reactions in synthesis has proven to be a valuable alternative to classic protocols in radical chemistry.[10]

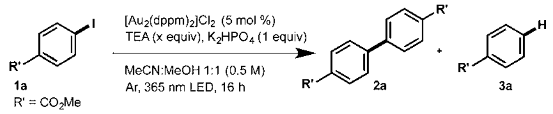
Recently, our group and others have been interested in the development of synthetically useful photoredox catalyzed radical transformations using dimeric Au(I) complexes.[11] During the course of studying mechanisms associated with these complexes, we observed the radical cyclization and subsequent homocoupling of a bromoallylmalonate.[12]

A radical−radical recombination pathway to this peculiar product seemed unlikely and warranted further studies. It has been apparent that many different pathways can be at play in photoredox catalysis using dimeric Au(I) complexes. One may be the rarely accessed Au(I)/Au(III) catalytic cycle. Recently, Au(I)/Au(III) methodology without use of external oxidants has

Received: July 14, 2016
Published: August 15, 2016

DOI: 10.1021/acs.orglett.6b02021
Org. Lett. 2016, 18, 4308−4311

Table 1. Optimization of the Iodoarene Homocoupling[a]



entry	TEA (equiv)	yield (%)		
		1a	2a	3a
1[b]	1	0	75	25
2[b]	2	0	69	11
3	1	0	98 (91)	2
4	–	70	22	8
5[c]	1	22	2	8
6[d]	1	99	0	0

[a] **1a** (0.2 mmol), $[Au_2(dppm)_2]Cl_2$ (5 mol %), TEA (0.2 mmol), K_2HPO_4 (0.2 mmol), MeCN/MeOH (0.5 M), Ar degas, UVA LED irradiation for 16 h at room temperature. Yields determined by ^1H NMR analysis using an internal standard using mesitylene (isolated). [b] In absence of K_2HPO_4. [c] In absence of $[Au_2(dppm)_2]Cl_2$. [d] In absence of UVA LED irradiation.

been developed, but are limited to hazardous aryl diazonium salts that also function as an oxidant (eq 3).[11i,13] This elusive mechanism was probed using readily available iodoarenes and bromoalkanes for the formation of homocoupled products, lending support to a Au(III) reductive elimination process (eq 4).

To begin, extending the previously described methodology to iodoarene **1a** was investigated (Table 1). Preliminary screening using a 1:1 mixture of MeCN/MeOH (0.5 M) in the presence of triethylamine (TEA, 1 equiv) was found to be optimal, yielding product **2a** (75%) and dehalogenated product **3a** (Table 1, entries 1 and 2). To our delight, addition of K_2HPO_4 gave quantitative conversion to the homocoupling product **2a** (Table 1, entry 3). Removal of TEA gave minor conversion to **2a**, and removal of photocatalyst gave mostly degradation (Table 1, entries 4 and 5). No product was formed in the absence of UVA LED irradiation (Table 1, entry 6). It should be noted that the corresponding methyl 4-bromobenzoate had limited success (<20%) under the described optimized conditions.

Having determined the optimal conditions for the homocoupling of iodoarenes, the general applicability of the transformation was investigated (Figure 2). Electron-poor iodoarene **1b** afforded product in 60% yield. Iodoarenes **1c** and **1d** (*m*- and *o*-substituted methyl benzoates) gave **2c** and **2d** in 66% and 14% yields, respectively, showing that steric effects hinder the transformation. Substrates **1e–m** were converted to the corresponding products **2e–m** in 31–63% yields. Surprisingly, *N*-acetyl functionalized **1n** gave exclusively the dehalogenated arene **3n** in 85% yield showing that hydrogen atom transfer (HAT) is a competing process. Relatively electron-neutral alkyl functionalized iodoarenes **1o–q** gave modest conversions of **2o–q** in 34–53% yields while electron-rich **1r** gave **2r** in 29% yield. We were pleased to find phenylalanine and estrone surrogates **1s** and **1t** were compatible to the conditions by giving homocoupled products **3s** and **3t** in 66% and 28% yields, respectively.

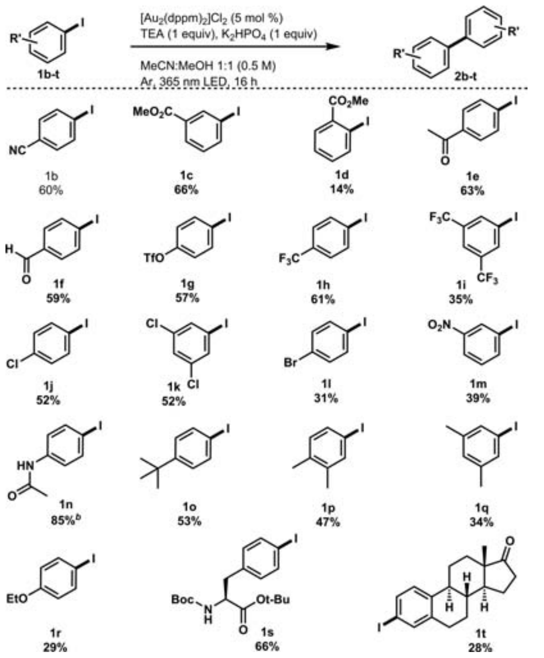
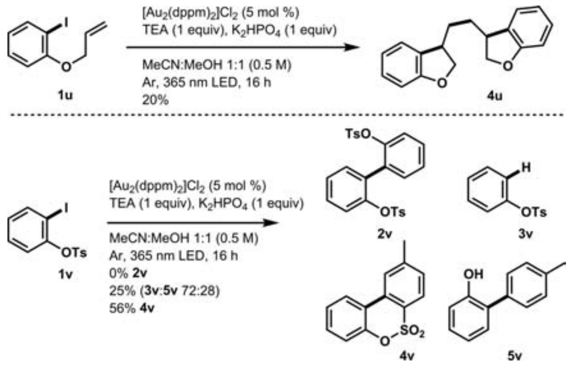


Figure 2. Homocoupling of iodoarenes. Conditions: See Table 1, entry 3. Isolated yields reported. In the case of **1n**, dehalogenated product **3n** was afforded.

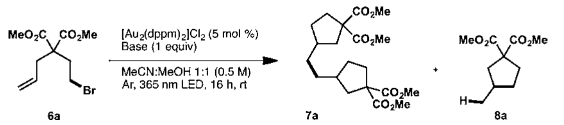
Scheme 1. Possible Mechanistic Insights



To further probe the mechanism of this transformation, substrates **1u** and **1v** were considered to show whether homocoupling or cyclization processes were more favorable under the described conditions (Scheme 1). Allyl functionalized iodoarene **1u** gave the cyclized and homocoupled product **4u** in 20% yield. Interestingly under these conditions, compound **4u** was the only product isolated from the reaction mixture. Iodoarene **1v** gave mostly 1,6-cyclized product **4v** in 56% yield, and homocoupling product **2v** was not observed. Minor products **3v** (reduced) and **5v** (arising from the 1,5-*ipso* substitution and fragmentation of SO_2) were isolated in 25% yield in a 72:28 ratio. These results indicate that free radical intermediates undergo cyclization processes competitively before homocoupling occurs (without consideration of equilibria between free alkyl/aryl radicals and addition to Au centers). Next, the homocoupling of bromoalkanes was revisited by applying the described homocoupling methodology to **6a** (Table 2). It was found that TEA (1 equiv) gave good conversion to homocoupled product **7a** as a mixture of diastereomers in 75% yield (Table 2, entry 1). However, this was accompanied by a significant amount of the reduced product **8a** (24% yield), presumably through a hydrogen atom transfer event (HAT). Deuteration of TEA or the solvents resulted in slightly elevated ratios of **7a**:**8a** (Table 2, entries 2 and 3). The use of deuterated TEA and solvents increased the formation of **7a** (Table 2, entry 4). The addition of cyclohexadiene gave **8a** as the sole product in 95% yield (68% isolated) (Table 2, entry 5). These experiments support the

DOI: 10.1021/acs.orglett.6b02021
Org. Lett. 2016, 18, 4308–4311

Table 2. Investigation of the Bromoalkane Homocoupling[a]



entry	base	yield (%) 6a	7a	8a
1	TEA	0	75	24
2	d_{15}-TEA	0	72	20
3	TEA[b]	0	66	7
4	d_{15}-TEA[b]	0	89(53)	9[c]
5	TEA[d]	0	0	95(68)
6	TEA[e]	100	0	0
7	–	100	0	0
8	TEA[f]	100	0	0
9	TEA[g]	100	0	0

[a] **6a** (0.2 mmol), $[Au_2(dppm)_2]Cl_2$ (5 mol %), base (1 equiv), 1:1 MeCN:MeOH (0.5 M), Ar degas, UVA LED irradiation for 16 h at room temperature. Yields determined by ^1H NMR analysis using an internal standard of mesitylene (isolated). [b] Deuterated solvents used (CD_3OD and CD_3CN). [c] Produced corresponding deuterated **8a** as byproduct. [d] 1,4-Cyclohexadiene (3 equiv) added. [e] TEMPO (3 equiv) added. [f] In absence of $[Au_2(dppm)_2]Cl_2$. [g] In absence of UVA LED irradiation.

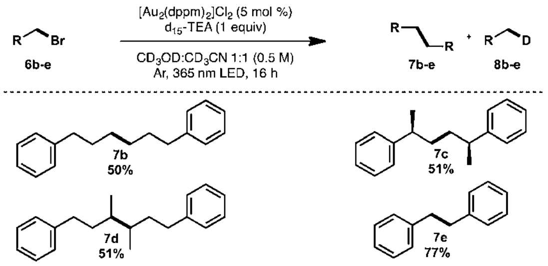


Figure 3. Homocoupling of bromoalkanes. Conditions: See Table 2, entry 4. In the case of **7e**, benzyl chloride used as starting material.

formation of an intermediate free radical that can undergo HAT processes with TEA, the solvents, or intermediates that may form.[14] Using deuterated TEA and solvents, the HAT pathway is attenuated because deuterium is abstracted more slowly by free radicals than hydrogen and allows more time for free radicals to undergo homocoupling processes. The addition of TEMPO resulted in no reaction possibly due to catalyst inhibition rather than the formation of a TEMPO-functionalized product (Table 2, entry 6). Removal of TEA, $[Au_2(dppm)_2]Cl_2$, or UVA LED irradiation resulted in no product formation (Table 2, entries 7–9).

Using the optimized conditions, some bromoalkanes were surveyed (Figure 3). Good yields were found for the homocoupling of a few primary and secondary bromoalkanes (**6b**–**d**, up to 51% yield isolated). As expected, benzyl chloride (**6e**) gave bibenzyl (**7e**) in 77% yield as benzyl radicals are known to undergo radical–radical recombination. Notably, **7c** remained enantiopure when using (*R*)-(1-bromopropan-2-yl)benzene (**6c**) but the corresponding racemic **6c** gave a statistical mixture of diastereomers. This supports products arising from free radicals as intermediates that lead to the statistical mixture of products. Although the bromoalkane homocoupling methodology may not be cost-effective, these results shed light on the possible intermediacy of free radicals in this process.

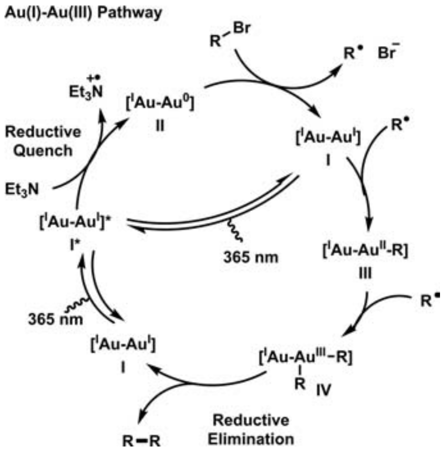


Figure 4. Proposed mechanism of homocoupling reactions.

Given the relatively low concentration of radical intermediates present, it is difficult to consider a radical–radical coupling mechanism as the major pathway to homocoupled products. Furthermore, the cyclization products observed in Scheme 1, the complete reduction of **6a** to **8a** in the presence of cyclohexadiene (Table 2, entry 5), and the statistical mixture of products obtained by racemic **6c** indicate that free radicals may be intermediates in this process (possibly in equilibrium with addition upon a Au center). In the presence of triethylamine, it is likely that a reductive quenching pathway of the excited state dimeric Au(I) complex **I*** is dominating (2.7×10^7 M^{-1} s^{-1} for *N*,*N*-diisopropylethylamine (similar to triethylamine) vs 2.9×10^6 M^{-1} s^{-1} for bromobutane), leading to intermediate **II** (Figure 4).[12] One can assume that this dimeric gold intermediate is a powerful reducing agent, capable of activating bromoalkanes and iodoarenes (~ −1.9 to −2.5 V vs SCE),[15] leading to carbon centered radicals and regeneration of the photocatalyst **I**. This pathway likely takes place until a high enough concentration of carbon centered radicals is formed, where addition upon Au(I) is favorable, intermediate **III**. The resulting intermediate **III** is prone to accept another radical to reach a more stable Au(III) intermediate **IV**, which can then reductively eliminate homocoupled arenes and alkanes along with catalyst regeneration.[13i,l] An oxidative quenching pathway of the excited state dimeric Au(I) complex with iodoarenes or bromoalkanes seems unlikely but cannot be ruled out. Complex **I*** could form an exciplex with C–X bonds, leading to productive pathways, but the lack of reactivity in the absence of TEA does not support such a mechanism. In summary, the light enabled homocoupling of iodoarenes and bromoalkanes was disclosed. These findings show promise that Au(I) complexes have potential in future studies considering alkyl and aryl homocoupling processes, possibly through an unusual Au(I)/Au(III) mediated coupling pathway. The current study found broad applicability in scope of iodoarene homocoupling and reasonable applicability when considering bromoalkanes. A dimeric Au(I) photocatalyst was required in the homocoupling of these substrates. Studies in the application of this methodology to cross-coupling processes and also to the synthesis of natural products are currently underway and will be reported in due course.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02021.

Experimental procedures and analytical data including ^{1}H and ^{13}C NMR spectra for all new compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: lbarriau@uottawa.ca.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Natural Sciences and Engineering Research Council (for Accelerator, Discovery and CREATE grants to L.B.) and the University of Ottawa (for a University Research Chair to L.B.) for support of this research. Acknowledgement is also made to the donors of the American Chemical Society Petroleum Research Fund for support of this research. T.M. thanks NSERC for a Ph.D. scholarship Alexander Graham Bell CGS-D. M.M. thanks OGS for funding of a Ph.D. scholarship.

■ REFERENCES

(1) Baudoin, O.; Gueritte, F. *Stud. Nat. Prod. Chem.* **2003**, *29*, 355.

(2) (a) Kozlowski, M. C.; Morgan, B. J.; Linton, E. C. *Chem. Soc. Rev.* **2009**, *38*, 3193. (b) Bringmann, G.; Gulder, T.; Gulder, T. A. M.; Breuning, M. *Chem. Rev.* **2011**, *111*, 563.

(3) Schizandrin: (a) Ghera, E.; Ben-David, Y. *J. Chem. Soc., Chem. Commun.* **1978**, 480. (b) Warshawsky, A. M.; Meyers, A. I. *J. Am. Chem. Soc.* **1990**, *112*, 8090. (c) Tanaka, M.; Mukaiyama, C.; Mitsuhashi, H.; Wakamatsu, T. *Tetrahedron Lett.* **1992**, *33*, 4165. Gossypol: (d) Edwards, J. D., Jr. *J. Am. Chem. Soc.* **1958**, *80*, 3798. (e) Venuti, M. C. *J. Org. Chem.* **1981**, *46*, 3124. (f) Meyers, A. I.; Willemsen, J. J. *Chem. Commun.* **1997**, 1573. (+)-Chaetocin and epidithiodiketopiperazines: (g) Overman, L. E.; Sato, T. *Org. Lett.* **2007**, *9*, 5267. (h) Kim, J.; Ashenhurst, J. A.; Movassaghi, M. *Science* **2009**, *324*, 238. (i) Iwasa, E.; Hamashima, Y.; Fujishiro, S.; Higuchi, E.; Ito, A.; Yoshida, M.; Sodeoka, M. *J. Am. Chem. Soc.* **2010**, *132*, 4078. (j) Kim, J.; Movassaghi, M. *J. Am. Chem. Soc.* **2010**, *132*, 14376.

(4) Ullmann, F.; Bielecki, J. *Ber. Dtsch. Chem. Ges.* **1901**, *34*, 2174.

(5) For a comprehensive review: (a) Hassan, J.; Sevignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359. For selected examples: (b) Moncomble, A.; Le Floch, P.; Gosmini, C. *Chem. - Eur. J.* **2009**, *15*, 4770. (c) Maddaluno, J.; Durandetti, M. *Synlett* **2015**, *26*, 2385. (d) Buter, J.; Heijnen, D.; Vila, C.; Hornillos, V.; Otten, E.; Giannerini, M.; Minnaard, A. J.; Feringa, B. L. *Angew. Chem., Int. Ed.* **2016**, *55*, 3620. Alkyl radical recombination approaches diffusion control but suffers from low steady state concentration from competing reaction pathways. (e) Terry, J. O.; Futrell, J. H. *Can. J. Chem.* **1967**, *45*, 2327. (f) Hiatt, R.; Benson, S. W. *J. Am. Chem. Soc.* **1972**, *94*, 6886. For Au-mediated homocouplings: (g) Ball, L. T.; Green, M.; Lloyd-Jones, G. C.; Russell, C. A. *Org. Lett.* **2010**, *12*, 4724. (h) Ball, L. T.; Lloyd-Jones, G. C.; Russell, C. A. *Chem. - Eur. J.* **2012**, *18*, 2931.

(6) (a) Hironaka, K.; Fukuzumi, S.; Tanaka, T. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1705. (b) Kern, J.-M.; Sauvage, J.-P. *J. Chem. Soc., Chem. Commun.* **1987**, 546. (c) Focsaneanu, K.-S.; Scaiano, J. C. *Helv. Chim. Acta* **2006**, *89*, 2473. For a recent example using Au nanoparticles: (d) Lanterna, A. E.; Elhage, A.; Scaiano, J. C. *Catal. Sci. Technol.* **2015**, *5*, 4336.

(7) (a) Fagnoni, M.; Dondi, D.; Ravelli, D.; Albini, A. *Chem. Rev.* **2007**, *107*, 2725. (b) Narayanam, J. M. R.; Stephenson, C. R. J. *Chem. Soc. Rev.* **2011**, *40*, 102. (c) Shi, L.; Xia, W. *Chem. Soc. Rev.* **2012**, *41*, 7687. (d) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. *Chem. Rev.* **2013**, *113*, 5322. (e) Schultz, D. M.; Yoon, T. P. *Science* **2014**, *343*, 985. (f) Nicewicz, D. A.; Nguyen, T. M. *ACS Catal.* **2014**, *4*, 355. (g) Studer, A.; Curran, D. P. *Angew. Chem., Int. Ed.* **2016**, *55*, 58. (h) Pitre, S. P.; McTiernan, C. D.; Scaiano, J. C. *Acc. Chem. Res.* **2016**, *49*, 1320. (i) Pitre, S. P.; McTiernan, C. D.; Scaiano, J. C. *ACS Omega* **2016**, *1*, 66.

(8) (a) Albini, A.; Fagnoni, M. *Green Chem.* **2004**, *6*, 1. (b) Stephenson, C. R. J.; Studer, A.; Curran, D. P. *Beilstein J. Org. Chem.* **2013**, *9*, 2778. (c) Griesbeck, A. G. *Beilstein J. Org. Chem.* **2014**, *10*, 1097. (d) Yoon, T. P.; Stephenson, C. R. J. *Adv. Synth. Catal.* **2014**, *356*, 2739. (e) Shenvi, R. A. *Synlett* **2016**, *27*, 678.

(9) (a) Ciamician, G. *Science* **1912**, *36*, 385. (b) Gray, H. B.; Maverick, A. W. *Science* **1981**, *214*, 1201. (c) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85. (d) Balzani, V.; Credi, A.; Venturi, M. *ChemSusChem* **2008**, *1*, 26.

(10) (a) Curran, D. P. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Semmelhack, M. F., Eds.; Pergamon: Oxford, 1991; Vol. 4, p 715. (b) Chatgilialoglu, C. *Acc. Chem. Res.* **1992**, *25*, 188. (c) Chatgilialoglu, C. *Chem. Rev.* **1995**, *95*, 1229. (d) Baguley, P. A.; Walton, J. C. *Angew. Chem., Int. Ed.* **1998**, *37*, 3072. (e) *Radicals in Organic Synthesis*; Renaud, P., Sibi, M. P., Eds; Wiley-VCH: Weinheim, 2001. (f) Ollivier, C.; Renaud, P. *Chem. Rev.* **2001**, *101*, 3415. (g) Studer, A.; Amrein, S. *Synthesis* **2002**, *2002*, 835. (h) *Topics in Current Chemistry, Radicals in Synthesis I and II*; Gansuer, A., Ed.; Springer: Berlin, 2006; Vol. 263. (i) Quiclet-Sire, B.; Zard, S. Z. *Int. J. Pure Appl. Chem.* **2011**, *83*, 519. (j) *Encyclopedia of Radicals in Chemistry, Biology and Materials*; Chatgilialoglu, C., Studer, A., Eds.; Wiley: Chichester, 2012; Vols. *1 and 2*. (k) Studer, A.; Curran, D. P. *Nat. Chem.* **2014**, *6*, 765.

(11) (a) Che, C.-M.; Kwong, H.-L.; Yam, V. W.-W.; Cho, K.-C. *J. Chem. Soc., Chem. Commun.* **1989**, 885. (b) Che, C.-M.; Kwong, H.-L.; Poon, C.-K.; Yam, V. W.-W. *J. Chem. Soc., Dalton Trans.* **1990**, 3215. (c) Kwong, H.-L.; Yam, V. W.-W.; Li, D. D.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **1992**, 3325. (d) Revol, G.; McCallum, T.; Morin, M.; Gagosz, F.; Barriault, L. *Angew. Chem., Int. Ed.* **2013**, *52*, 13342. (e) McCallum, T.; Slavko, E.; Morin, M.; Barriault, L. *Eur. J. Org. Chem.* **2015**, *2015*, 81. (f) Kaldas, S.; Cannillo, A.; McCallum, T.; Barriault, L. *Org. Lett.* **2015**, *17*, 2864. (g) Xie, J.; Shi, S.; Zhang, T.; Mehrkens, N.; Rudolph, M.; Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2015**, *54*, 6046. (h) Nzulu, F.; Telitel, S.; Stoffelbach, F.; Graff, B.; Marlet-Savary, F.; Lalevée, J.; Fensterbank, L.; Goddard, J.-P.; Ollivier, C. *Polym. Chem.* **2015**, *6*, 4605. (i) Xie, J.; Zhang, T.; Chen, F.; Mehrkens, N.; Rominger, F.; Rudolph, M.; Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2016**, *55*, 2934. (j) Cannillo, A.; Schwantje, T. R.; Bégin, M.; Barabé, F.; Barriault, L. *Org. Lett.* **2016**, *18*, 2592. (k) McCallum, T.; Barriault, L. *Chem. Sci.* **2016**, *7*, 4754.

(12) McTiernan, C. D.; Morin, M.; McCallum, T.; Scaiano, J. C.; Barriault, L. *Catal. Sci. Technol.* **2016**, *6*, 201.

(13) (a) Sahoo, B.; Hopkinson, M. N.; Glorius, F. *J. Am. Chem. Soc.* **2013**, *135*, 5505. (b) Shu, X.; Zhang, M.; He, Y.; Frei, H.; Toste, F. D. *J. Am. Chem. Soc.* **2014**, *136*, 5844. (c) Hopkinson, M. N.; Sahoo, B.; Glorius, F. *Adv. Synth. Catal.* **2014**, *356*, 2794. (d) Cai, R.; Lu, M.; Aguilera, E. Y.; Xi, Y.; Akhmedov, N. G.; Petersen, J. L.; Chen, H.; Shi, X. *Angew. Chem., Int. Ed.* **2015**, *54*, 8772. (e) Patil, D. V.; Yun, H.; Shin, S. *Adv. Synth. Catal.* **2015**, *357*, 2622. (f) He, Y.; Wu, H.; Toste, F. D. *Chem. Sci.* **2015**, *6*, 1194. (g) Kim, S.; Rojas-Martin, J.; Toste, F. D. *Chem. Sci.* **2016**, *7*, 85. (h) Tlahuext-Aca, A.; Hopkinson, M. N.; Sahoo, B.; Glorius, F. *Chem. Sci.* **2016**, *7*, 89. (i) Zhang, Q.; Zhang, Z.-Q.; Fu, Y.; Yu, H.-Z. *ACS Catal.* **2016**, *6*, 798. (j) Tlahuext-Aca, A.; Hopkinson, M. N.; Garza-Sanchez, R. A.; Glorius, F. *Chem. - Eur. J.* **2016**, *22*, 5909. (k) Huang, L.; Rudolph, M.; Rominger, F.; Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2016**, *55*, 4808. (l) Huang, L.; Rominger, F.; Rudolph, M.; Hashmi, A. S. K. *Chem. Commun.* **2016**, *52*, 6435.

(14) For α-amino radicals: (a) Cossy, J.; Ranaivosata, J.-L.; Bellosta, V. *Tetrahedron Lett.* **1994**, *35*, 8161. (b) Jonsson, M.; Wayner, D. D. M.; Lusztyk, J. *J. Phys. Chem.* **1996**, *100*, 17539. (c) Ismaili, H.; Pitre, S. P.; Scaiano, J. C. *Catal. Sci. Technol.* **2013**, *3*, 935.

(15) (a) Fry, A. J.; Krieger, R. L. *J. Org. Chem.* **1976**, *41*, 54. (b) Rondinini, S.; Mussini, P. R.; Muttini, P.; Sello, G. *Electrochim. Acta* **2001**, *46*, 3245. (c) Roth, H. G.; Romero, N. A.; Nicewicz, D. A. *Synlett* **2016**, *27*, 714.