Cobalt bis(acetylacetonate)–*tert*-butyl hydroperoxide–triethylsilane: a general reagent combination for the Markovnikov-selective hydrofunctionalization of alkenes by hydrogen atom transfer

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Abstract

We show that cobalt bis(acetylacetonate) [Co(acac)$_2$], *tert*-butyl hydroperoxide (TBHP), and triethylsilane (Et$_3$SiH) constitute an inexpensive, general, and practical reagent combination to initiate a broad range of Markovnikov-selective alkene hydrofunctionalization reactions. These transformations are believed to proceed by cobalt-mediated hydrogen atom transfer (HAT) to the alkene substrate, followed by interception of the resulting alkyl radical intermediate with a SOMOphile. In addition, we report the first reductive couplings of unactivated alkenes and aryldiazonium salts by an HAT pathway. The simplicity and generality of the Co(acac)$_2$–TBHP–Et$_3$SiH reagent combination suggests it as a useful starting point to develop HAT reactions in complex settings.

Introduction

Many powerful methods to effect alkene hydrogenation [1-4] and Markovnikov-selective hydroheterofunctionalization (H–X addition, X = O [5-9], I [3], Br [3], Se [3], S [8-10], Cl [8,11], F [12,13], and N [8,14-17]) by metal-mediated hydrogen atom transfer (HAT) [18-21] are now known. Additionally, methods to achieve carbon–carbon bond formation to alkenes by HAT have been developed (e.g., reductive coupling [22-28], formal hydromethylation [29], cycloisomerization [8,30,31], hydrooxi-

mation [32], hydroheteroarylation [28,33-35], hydroarylation [36-38], and cross-coupling [37]). Many of these transformations have found applications in synthesis [6,39-47]. Although mechanistically-complex [28] the outcome of these reactions can be rationalized as initiating by HAT to the alkene, to form the kinetically- and thermodynamically-favored alkyl radical intermediate, which may be in equilibrium with the corresponding metal alkyl complex. This radical then undergoes addition

to a second reagent (SOMOphile) to form the functionalized product (Scheme 1).

Scheme 1: General mechanism of alkene hydrofunctionalization via HAT.
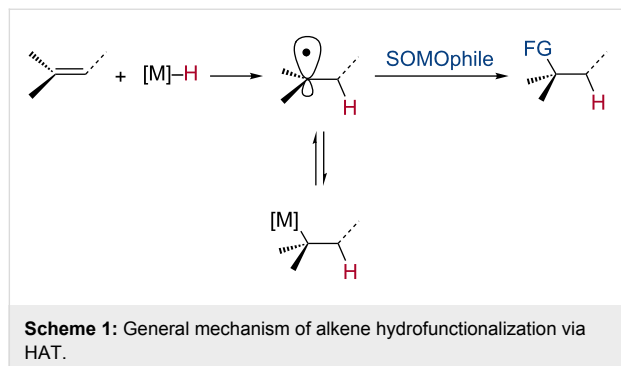
A wide range of manganese, cobalt, or iron-based complexes containing diverse supporting ligands have found use in these reactions. To the best of our knowledge, the iron oxalate–sodium borohydride system, introduced by Boger and co-workers [8], is the only reagent combination shown to accommodate a broad range of SOMOphiles. However, the cobalt–salen complexes that are commonly employed [10,11,13,15,16,30-32,36,37,48] contain many different ligand architectures [21], and often need to be prepared by multistep sequences. Here we report a uniform set of reaction conditions to achieve a broad range of HAT hydrofunctionalization reactions using the simple reagents cobalt acetoacetonate [Co(acac)$_2$], *tert*-butyl hydroperoxide (TBHP), and triethylsilane (Et$_3$SiH). The practicality and generality of this system should motivate its application in synthesis.

Results and Discussion

In 2014, we reported the reduction of alkenyl halides (e.g., **1**, Scheme 2) utilizing Co(acac)$_2$, TBHP, and two reductants, triethylsilane and 1,4-dihydrobenzene (DHB) [2]. Mechanistic studies showed that Et$_3$SiH participates in the formation of a cobalt hydride intermediate that delivers a hydrogen atom to the less-substituted position of the alkene. The resulting alkyl radical is believed to abstract a second hydrogen atom from DHB to generate the reduced product [2]. This mechanism separates the alkyl radical formation and functionalization steps by employing two different reagents. Accordingly, we investigated the application of this system in other HAT reactions. In

these studies, methallyl *p*-methoxybenzoate (**3a**) was used as substrate (Table 1).

Under our standard reduction conditions, alkene **3a** was transformed to isobutyl *p*-methoxybenzoate (**4a**) in 86% yield (entry 1, Table 1). Inspired by the methods of Boger [12] and Hiroya [13], a number of fluorination reagents were examined to achieve hydrofluorination. Although no product was observed using SelectFluor®, diethylaminosulfur trifluoride (DAST), or tosyl fluoride (see Supporting Information File 1, Table S1, entries 2–4), *N*-fluorobenzenesulfonimide (NFSI) provided the desired hydrofluorination product **4b** in 36% yield (Table 1, entry 2). Carreira and co-workers reported the first hydrochlorination reaction via a cobalt-catalyzed HAT process [11]. By utilizing *p*-toluenesulfonyl chloride (TsCl) and *p*-toluenesulfonyl bromide (TsBr) under our conditions, the desired hydrochlorination and hydrobromination products **4c** and **4d** were obtained in 92% and 95% yields, respectively [3] (Table 1, entries 3 and 4). To our knowledge, the formation of **4d** represents the first Markovnikov-selective alkene hydrobromination by an HAT pathway. Attempts to extend this reaction to hydroiodination using related reagents, *p*-toluenesulfonyl iodide, *N*-iodosuccinimide, or molecular iodine failed to provide the expected product (see Supporting Information File 1, Table S1, entries 9–11) [3]. Surprisingly, diiodomethane, possessed the desired reactivity and the hydroiodination product **4e** was isolated in 89% yield (Table 1, entry 5) [3]. Ethyl iodoacetate, iodoacetonitrile, and 1,2-diiodoethane were also effective, but the yields of **4e** and conversion of **3a** were lower (see Supporting Information File 1, Table S1, entries 13–15). Mukaiyama and co-workers' pioneering Markonikov-selective alkene hydration reaction [5,49-54] proceeds using dioxygen as the oxygen atom source. Exposure of the alkene **3a** to similar conditions provided the tertiary alcohol **4f** in 69% yield (Table 1, entry 6). Inspired by Girijavallabhan and co-workers' report [10], we were able to trap the tertiary alkyl radical with *S*-phenyl benzene thiosulfonate (PhSO$_2$SPh, Table 1, entry 7) and *Se*-phenyl 4-methylbenzenesulfonoselenoate (TsSePh, Table 1, entry 8) [3] to afford the corresponding products **4g** and **4h** in 96% and 89% yields, respectively. Carreira and co-workers reported the hydroazidation of alkenes using cobalt–salen complexes as hydrogen atom transfer agents and *para*-toluenesulfonyl azide as an azide source [16,48,55]. After
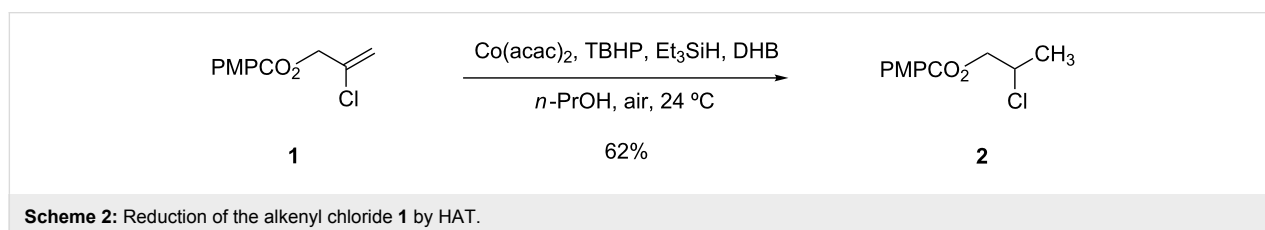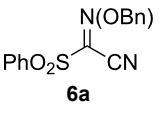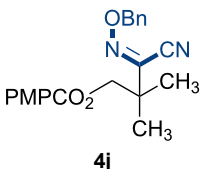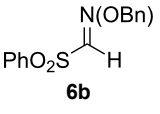

Scheme 2: Reduction of the alkenyl chloride **1** by HAT.

Table 1: Markovnikov Hydrofunctionalization of **3a**.[a]

Co(acac)$_2$, TBHP
DHB (*x* equiv), Et$_3$SiH (*y* equiv)
SOMOphile (*z* equiv)
—————————————→
solvent, 24 °C
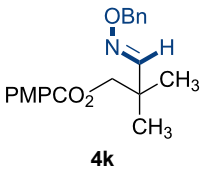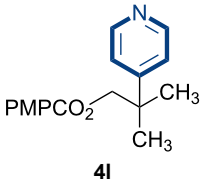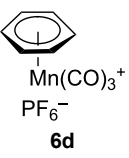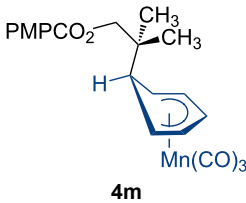
PMPCO$_2$ — (**3a**) → PMPCO$_2$ — FG-CH$_3$/CH$_3$ (**4a–m, 7a**)

entry	x	y	SOMOphile	z	solvent	product	yield[b]
1	5.00	5.00	–	–	*n*-propanol	**4a** (H)	86%
2	2.50	10.0	NFSI	2.50	CH$_2$Cl$_2$	**4b** (F)	36%
3	2.50	10.0	TsCl	2.50	*n*-propanol	**4c** (Cl)	92%
4	3.75	10.0	TsBr	2.50	*n*-propanol	**4d** (Br)	95%
5	3.75	10.0	CH$_2$I$_2$	15.0	CH$_2$Cl$_2$	**4e** (I)	89%
6	10.0	10.0	O$_2$	–	*n*-propanol	**4f** (OH)	69%
7	2.50	10.0	PhSO$_2$SPh	2.50	*n*-propanol	**4g** (S–Ph)	96%
8	2.50	10.0	TsSePh	2.50	*n*-propanol	**4h** (Se–Ph)	89%
9	1.00	10.0	*p*-ABSA	5.00	CH$_3$CN	**4i** (N$_3$)	79%
10	0	6.25	**5a** (H$_3$CO–C$_6$H$_4$–N$_2^+$ BF$_4^-$)	1.50	CH$_2$Cl$_2$	**7a** (N=N–PMP)	92%

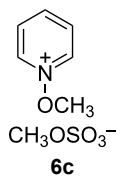**Table 1:** Markovnikov Hydrofunctionalization of **3a**.[a] (continued)

|			SOMOphile		Solvent	Product	Yield
11	3.75	10.0	PhO_2S–C(=N(OBn))–CN **6a**	2.50	*n*-propanol	$PMPCO_2$–CH$_2$–C(CH$_3$)$_2$–C(=N(OBn))CN **4j**	60%
12	3.75	10.0	PhO_2S–CH=N(OBn) **6b**	2.50	*n*-propanol	$PMPCO_2$–CH$_2$–C(CH$_3$)$_2$–CH=N(OBn) **4k**	48%
13	0	5.00	N-methoxypyridinium, $CH_3OSO_3^-$ **6c**	5.00	CH_2Cl_2	$PMPCO_2$–CH$_2$–C(CH$_3$)$_2$–(pyridin-3-yl) **4l**	66% 4.7:1 rr[b]
14	0	5.00	$Mn(CO)_3^+$ PF_6^- **6d**	1.00	CH_3CN	**4m** $PMPCO_2$–CH$_2$–C(CH$_3$)$_2$–cyclohexadienyl–$Mn(CO)_3$	50%

[a]For detailed reaction conditions, see Supporting Information File 1. [b]Isolated yields after purification by flash-column chromatography. [b]rr = ratio of regioisomers.

careful optimization of the azidation reagent (*p*-acetamidobenzenesulfonyl azide (*p*-ABSA)) and additive equivalents (see Supporting Information File 1, Table S1, entries 19–28), the tertiary alkyl azide **4i** was obtained in 79% yield (Table 1, entry 9).

To broaden the scope of C–N coupling process via HAT, we investigated other nitrogen-containing SOMOphiles in the HAT reaction. Employing 4-methoxyphenyldiazonium tetrafluoroborate (**5a**) in our HAT conditions, the alkyl aryl azo product **7a** was obtained in 92% yield (Table 1, entry 10). Due to the importance of azo compounds in synthetic organic chemistry, industrial dyes, and medicinal chemistry [56,57], we investigated the scope of this transformation (Scheme 3). By varying the alkene substitution pattern, we determined that the coupling of tertiary radicals is more efficient than secondary radicals. For example, methallyl *p*-methoxybenzoate (**3a**) and prenyl *p*-methoxybenzoate (**3c**, not shown) afforded the azo compounds **7a** and **7c** in 92% and 91% yields, respectively. By comparison the yield of the azo product using allyl *p*-methoxybenzoate (**3b**, now shown) as substrate was somewhat lower (77%). Diazonium salts bearing substituents with different

steric and electronic properties were examined. These experiments revealed that this coupling is compatible with a broad range of functional groups and aryl substitution patterns (**7d–j**, 52–97%). The naphthylazo derivative **7k** was obtained in 69% yield using 1-naphthyldiazonium tetrafluoroborate. However, aryldiazonium salts bearing nitro substituents were not compatible with this HAT coupling. For example, the use of *p*-nitrobenzendiazonium tetrafluoroborate failed to provide the expected coupling product **7l**. This may be due to alternative reaction pathways involving reduction of the nitro substituent [17].

Additional carbon–carbon bond formation strategies were also examined using the Co(acac)$_2$ HAT system. Sulfonyl oximes **6a** and **6b** [32] afforded the carbon–carbon coupled products **4j** and **4k** in 60% and 48% yields, respectively (Table 1, entries 11 and 12, respectively). Recently, our laboratory reported a formal intermolecular hydroheteroarylation using *N*-methoxy heteroarenium salts by Co(acac)$_2$-mediated HAT [33,34]. In the original reports, 36 discrete unactivated alkenes were coupled with 38 different heteroarenium salts under mild conditions [33,34]. A representative example comprises the coupling of methallyl *p*-methoxybenzoate (**3a**) with *N*-methoxypyridinium
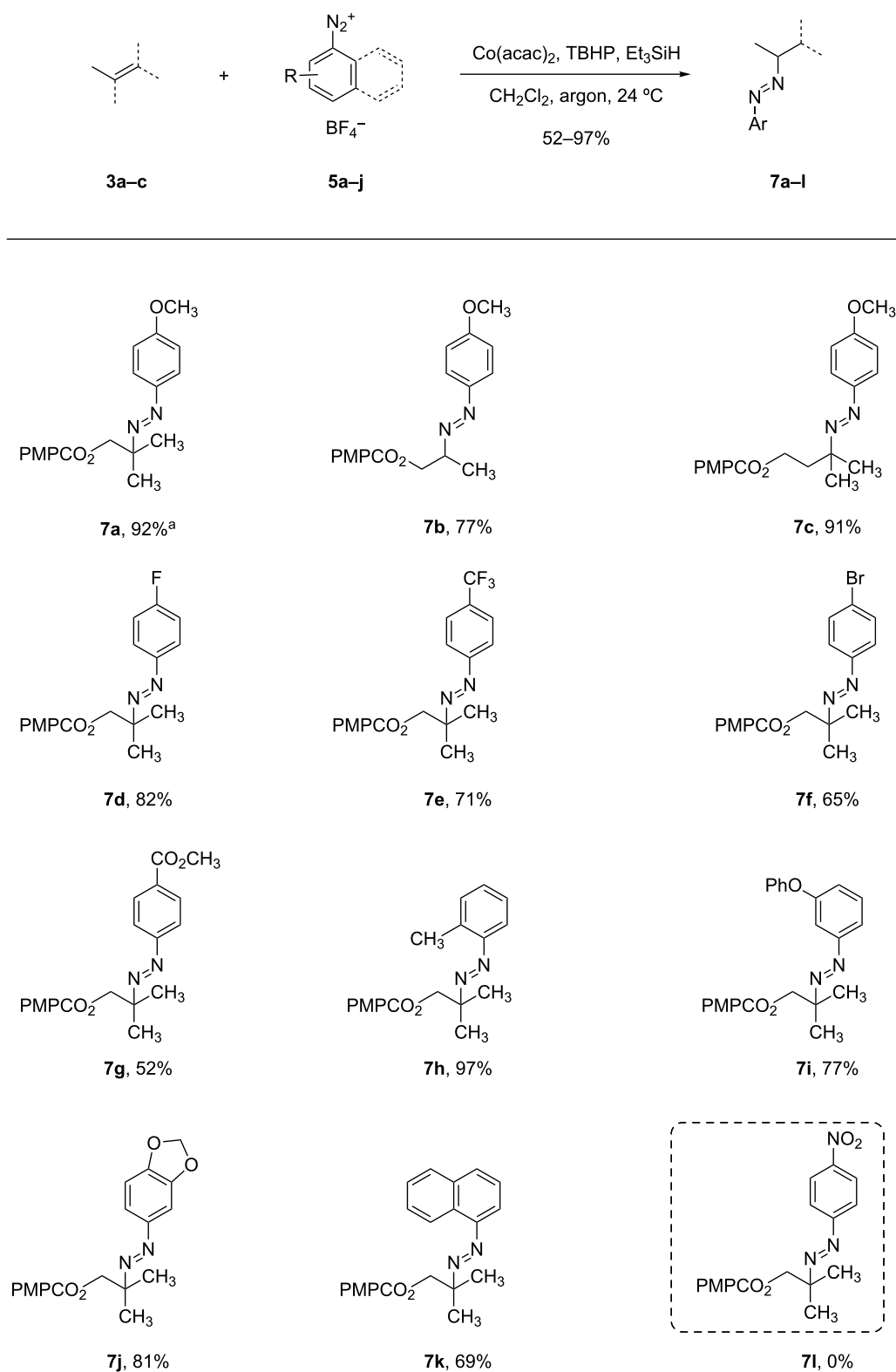
Scheme 3: Substrate scope of alkyl-aryl azo compound synthesis via HAT. Conditions: alkene (0.250 mmol), diazonium salt (1.50 equiv), Co(acac)$_2$ (1.00 equiv), TBHP (1.00 equiv), Et$_3$SiH (6.25 equiv), CH$_2$Cl$_2$ (0.2 M), argon, 15–120 min. All yields are isolated yields after flash-column chromatography. [a]Reaction conducted on 1.00 mmol scale.

methyl sulfate (**6c**) to form the hydropyridylation product **4l** in 66% yield and as a 4.7:1 ratio of regioisomers (Table 1, entry 13). We also demonstrated that the alkyl radical generated from the HAT process can be trapped by (η^6-benzene)manganese tricarbonyl hexafluorophosphate (**6d**) to provide the reductive coupling product **4m** in 50% yield (Table 1, entry 14).

Conclusion

In summary, we have demonstrated that under a consistent set of conditions, the Co(acac)$_2$–TBHP–Et$_3$SiH system effects a diverse array of Markovnikov-selective hydrofunctionalization reactions of unactivated alkenes (H–X addition, X = H, F, Cl, Br, I, O, S, Se, N, and C). We have also reported the first reductive coupling reactions of alkenes and aryldiazonium salts under HAT conditions. These transformations proceed in high regioselectivity and efficiency. Further efforts will focus on expanding the alkene scope and exploring the site-selectivity in polyene substrates.

Supporting Information

Supporting Information File 1
Detailed experimental procedures and characterization data for all new compounds.
[https://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-14-201-S1.pdf]

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References

1. Iwasaki, K.; Wan, K. K.; Oppedisano, A.; Crossley, S. W. M.; Shenvi, R. A. *J. Am. Chem. Soc.* **2014,** *136,* 1300–1303. doi:10.1021/ja412342g
2. King, S. M.; Ma, X.; Herzon, S. B. *J. Am. Chem. Soc.* **2014,** *136,* 6884–6887. doi:10.1021/ja502885c
3. Ma, X.; Herzon, S. B. *Chem. Sci.* **2015,** *6,* 6250–6255. doi:10.1039/C5SC02476E
4. Obradors, C.; Martinez, R. M.; Shenvi, R. A. *J. Am. Chem. Soc.* **2016,** *138,* 4962–4971. doi:10.1021/jacs.6b02032
5. Isayama, S.; Mukaiyama, T. *Chem. Lett.* **1989,** *18,* 573–576. doi:10.1246/cl.1989.573
6. Ishikawa, H.; Colby, D. A.; Boger, D. L. *J. Am. Chem. Soc.* **2008,** *130,* 420–421. doi:10.1021/ja078192m
7. Ishikawa, H.; Colby, D. A.; Seto, S.; Va, P.; Tam, A.; Kakei, H.; Rayl, T. J.; Hwang, I.; Boger, D. L. *J. Am. Chem. Soc.* **2009,** *131,* 4904–4916. doi:10.1021/ja809842b
8. Leggans, E. K.; Barker, T. J.; Duncan, K. K.; Boger, D. L. *Org. Lett.* **2012,** *14,* 1428–1431. doi:10.1021/ol300173v
9. Ma, X.; Herzon, S. B. *J. Org. Chem.* **2016,** *81,* 8673–8695. doi:10.1021/acs.joc.6b01709
10. Girijavallabhan, V.; Alvarez, C.; Njoroge, F. G. *J. Org. Chem.* **2011,** *76,* 6442–6446. doi:10.1021/jo201016z
11. Gaspar, B.; Carreira, E. M. *Angew. Chem., Int. Ed.* **2008,** *47,* 5758–5760. doi:10.1002/anie.200801760
12. Barker, T. J.; Boger, D. L. *J. Am. Chem. Soc.* **2012,** *134,* 13588–13591. doi:10.1021/ja3063716
13. Shigehisa, H.; Nishi, E.; Fujisawa, M.; Hiroya, K. *Org. Lett.* **2013,** *15,* 5158–5161. doi:10.1021/ol402696h
14. Kato, K.; Mukaiyama, T. *Chem. Lett.* **1992,** *21,* 1137–1140. doi:10.1246/cl.1992.1137
15. Waser, J.; Carreira, E. M. *J. Am. Chem. Soc.* **2004,** *126,* 5676–5677. doi:10.1021/ja048698u
16. Waser, J.; Nambu, H.; Carreira, E. M. *J. Am. Chem. Soc.* **2005,** *127,* 8294–8295. doi:10.1021/ja052164r
17. Gui, J.; Pan, C.-M.; Jin, Y.; Qin, T.; Lo, J. C.; Lee, B. J.; Spergel, S. H.; Mertzman, M. E.; Pitts, W. J.; La Cruz, T. E.; Schmidt, M. A.; Darvatkar, N.; Natarajan, S. R.; Baran, P. S. *Science* **2015,** *348,* 886–891. doi:10.1126/science.aab0245
18. Eisenberg, D. C.; Norton, J. R. *Isr. J. Chem.* **1991,** *31,* 55–66. doi:10.1002/ijch.199100006
19. Gansäuer, A.; Shi, L.; Otte, M.; Huth, I.; Rosales, A.; Sancho-Sanz, I.; Padial, N. M.; Oltra, J. E. *Hydrogen Atom Donors: Recent Developments.* In *Radicals in Synthesis III;* Heinrich, M.; Gansäuer, A., Eds.; Topics in Current Chemistry; Springer: Berlin Heidelberg, 2012. doi:10.1007/128_2011_124
20. Hoffmann, R. W. *Chem. Soc. Rev.* **2016,** *45,* 577–583. doi:10.1039/C5CS00423C
21. Crossley, S. W. M.; Obradors, C.; Martinez, R. M.; Shenvi, R. A. *Chem. Rev.* **2016,** *116,* 8912–9000. doi:10.1021/acs.chemrev.6b00334
22. Choi, J.; Tang, L.; Norton, J. R. *J. Am. Chem. Soc.* **2007,** *129,* 234–240. doi:10.1021/ja066325i
23. Choi, J.; Pulling, M. E.; Smith, D. M.; Norton, J. R. *J. Am. Chem. Soc.* **2008,** *130,* 4250–4252. doi:10.1021/ja710455c
24. Li, G.; Han, A.; Pulling, M. E.; Estes, D. P.; Norton, J. R. *J. Am. Chem. Soc.* **2012,** *134,* 14662–14665. doi:10.1021/ja306037w
25. Lo, J. C.; Yabe, Y.; Baran, P. S. *J. Am. Chem. Soc.* **2014,** *136,* 1304–1307. doi:10.1021/ja4117632
26. Lo, J. C.; Gui, J.; Yabe, Y.; Pan, C.-M.; Baran, P. S. *Nature* **2014,** *516,* 343–348. doi:10.1038/nature14006
27. Kuo, J. L.; Hartung, J.; Han, A.; Norton, J. R. *J. Am. Chem. Soc.* **2015,** *137,* 1036–1039. doi:10.1021/ja511883b
28. Lo, J. C.; Kim, D.; Pan, C.-M.; Edwards, J. T.; Yabe, Y.; Gui, J.; Qin, T.; Gutiérrez, S.; Giacoboni, J.; Smith, M. W.; Holland, P. L.; Baran, P. S. *J. Am. Chem. Soc.* **2017,** *139,* 2484–2503. doi:10.1021/jacs.6b13155
29. Dao, H. T.; Li, C.; Michaudel, Q.; Maxwell, B. D.; Baran, P. S. *J. Am. Chem. Soc.* **2015,** *137,* 8046–8049. doi:10.1021/jacs.5b05144
30. Crossley, S. W. M.; Barabé, F.; Shenvi, R. A. *J. Am. Chem. Soc.* **2014,** *136,* 16788–16791. doi:10.1021/ja5105602
31. Gaspar, B.; Carreira, E. M. *Angew. Chem., Int. Ed.* **2007,** *46,* 4519–4522. doi:10.1002/anie.200700575
32. Gaspar, B.; Carreira, E. M. *J. Am. Chem. Soc.* **2009,** *131,* 13214–13215. doi:10.1021/ja904856k

33. Ma, X.; Herzon, S. B. *J. Am. Chem. Soc.* **2016,** *138,* 8718–8721. doi:10.1021/jacs.6b05271
34. Ma, X.; Dang, H.; Rose, J. A.; Rablen, P.; Herzon, S. B. *J. Am. Chem. Soc.* **2017,** *139,* 5998–6007. doi:10.1021/jacs.7b02388
35. Bordi, S.; Starr, J. T. *Org. Lett.* **2017,** *19,* 2290–2293. doi:10.1021/acs.orglett.7b00833
36. Crossley, S. W. M.; Martinez, R. M.; Guevara-Zuluaga, S.; Shenvi, R. A. *Org. Lett.* **2016,** *18,* 2620–2623. doi:10.1021/acs.orglett.6b01047
37. Green, S. A.; Matos, J. L. M.; Yagi, A.; Shenvi, R. A. *J. Am. Chem. Soc.* **2016,** *138,* 12779–12782. doi:10.1021/jacs.6b08507
38. Green, S. A.; Vásquez-Céspedes, S.; Shenvi, R. A. *J. Am. Chem. Soc.* **2018**. doi:10.1021/jacs.8b05868
39. Shenvi, R. A.; Guerrero, C. A.; Shi, J.; Li, C.-C.; Baran, P. S. *J. Am. Chem. Soc.* **2008,** *130,* 7241–7243. doi:10.1021/ja8023466
40. Schindler, C. S.; Stephenson, C. R. J.; Carreira, E. M. *Angew. Chem., Int. Ed.* **2008,** *47,* 8852–8855. doi:10.1002/anie.200803655
41. Jeker, O. F.; Carreira, E. M. *Angew. Chem., Int. Ed.* **2012,** *51,* 3474–3477. doi:10.1002/anie.201109175
42. Barker, T. J.; Duncan, K. K.; Otrubova, K.; Boger, D. L. *ACS Med. Chem. Lett.* **2013,** *4,* 985–988. doi:10.1021/ml400281w
43. Leggans, E. K.; Duncan, K. K.; Barker, T. J.; Schleicher, K. D.; Boger, D. L. *J. Med. Chem.* **2013,** *56,* 628–639. doi:10.1021/jm3015684
44. Shigehisa, H.; Suwa, Y.; Furiya, N.; Nakaya, Y.; Fukushima, M.; Ichihashi, Y.; Hiroya, K. *Angew. Chem., Int. Ed.* **2013,** *52,* 3646–3649. doi:10.1002/anie.201210099
45. George, D. T.; Kuenstner, E. J.; Pronin, S. V. *J. Am. Chem. Soc.* **2015,** *137,* 15410–15413. doi:10.1021/jacs.5b11129
46. Ruider, S. A.; Sandmeier, T.; Carreira, E. M. *Angew. Chem., Int. Ed.* **2015,** *54,* 2378–2382. doi:10.1002/anie.201410419
47. Allemann, O.; Brutsch, M.; Lukesh, J. C.; Brody, D. M.; Boger, D. L. *J. Am. Chem. Soc.* **2016,** *138,* 8376–8379. doi:10.1021/jacs.6b04330
48. Waser, J.; Gaspar, B.; Nambu, H.; Carreira, E. M. *J. Am. Chem. Soc.* **2006,** *128,* 11693–11712. doi:10.1021/ja062355+
49. Mukaiyama, T.; Isayama, S.; Inoki, S.; Kato, K.; Yamada, T.; Takai, T. *Chem. Lett.* **1989,** *18,* 449–452. doi:10.1246/cl.1989.449
50. Inoki, S.; Kato, K.; Takai, T.; Isayama, S.; Yamada, T.; Mukaiyama, T. *Chem. Lett.* **1989,** *18,* 515–518. doi:10.1246/cl.1989.515
51. Isayama, S.; Mukaiyama, T. *Chem. Lett.* **1989,** *18,* 569–572. doi:10.1246/cl.1989.569
52. Isayama, S.; Mukaiyama, T. *Chem. Lett.* **1989,** *18,* 1071–1074. doi:10.1246/cl.1989.1071
53. Kato, K.; Yamada, T.; Takai, T.; Inoki, S.; Isayama, S. *Bull. Chem. Soc. Jpn.* **1990,** *63,* 179–186. doi:10.1246/bcsj.63.179
54. Isayama, S. *Bull. Chem. Soc. Jpn.* **1990,** *63,* 1305–1310. doi:10.1246/bcsj.63.1305
55. Gaspar, B.; Waser, J.; Carreira, E. M. *Synthesis* **2007,** 3839–3845. doi:10.1055/s-2007-1000817
56. Hunger, K.; Mischke, P.; Rieper, W.; Zhang, S. Azo Dyes. *Ullmann's Encyclopedia of Industrial Chemistr;* Wiley-VCH Verlag GmbH & Co. KGaA, 2000. doi:10.1002/14356007.o03_o07.pub2
57. Acton, Q. A. *Azo Compounds—Advances in Research and Application: 2013 Edition: ScholarlyBrief;* ScholarlyEditions: Atlanta, GA, 2013.