



Cite this: DOI: 10.1039/c5nj02378e

Received (in Montpellier, France)
6th September 2015,
Accepted 10th November 2015

DOI: 10.1039/c5nj02378e

www.rsc.org/njc

Hypervalent-iodine(III) oxidation of hydrazones to diazo compounds and one-pot nickel(II)-catalyzed cyclopropanation†

Haixuan Liu, Yunyang Wei and Chun Cai*

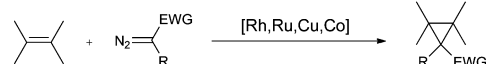
A one-pot process for the catalytic cyclopropanation of various alkenes with unsubstituted hydrazones is described. Iodosobenzene ($\text{PhI}=\text{O}$) was found to be a competent oxidant of hydrazones to diazo compounds. $\text{Ni}(\text{OH})_2$ was chosen as an effective and cheap metal catalyst. The cyclopropane products can be generated efficiently (5 min–4 h) in moderate to good yields (42–91%) under mild (80°C) and neat conditions.

Introduction

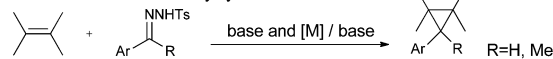
The cyclopropyl moiety is ubiquitous in the structure of naturally occurring compounds.¹ As the smallest strained cycloalkane, cyclopropane arouses chemists' interest in many aspects including the theoretical study of bonding,² potential synthetic transformations³ and its structural importance in drugs and enzyme inhibitors.⁴ Consequently, a variety of synthetic routes to cyclopropanes have been developed.⁵ Among them, transition metal catalytic decomposition of diazo compounds in the presence of alkenes is a classic and common method.⁶ The active metal complexes include rhodium,⁷ ruthenium,⁸ copper,⁹ and cobalt,¹⁰ while only scattered reports concern nickel catalysts.¹¹ And the investigations have been restricted to diazo esters or diazo ketones (Scheme 1a). Diazo compounds are toxic, irritating and sometimes explosive. In order to broaden substrate scopes and to avoid handling of diazo compounds, protocols that combine *in situ* generation of diazo compounds and carbene addition to alkenes are most desirable. Either base elimination of tosylhydrazones or the oxidation of hydrazones is a choice of generating diazo compounds *in situ*. The first strategy has been extensively scanned using aromatic aldehyde tosylhydrazones or substituted acetophenone tosylhydrazones as substrates with a wide range of olefins (Scheme 1b).¹² However, this strategy involves using a strong base or high temperatures and a relatively long reaction time is often needed. The latter strategy faces more challenge since it is hard to tolerate alkenes under an oxidation environment. Conventionally, the oxidizing agents used to oxidize hydrazones to diazo compounds have been

Previous reports:

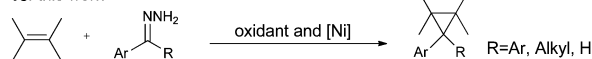
1a: from diazo compounds



1b: base elimination of tosylhydrazones



1c: this work



Scheme 1 Cyclopropanation strategies.

mercuric oxide,¹³ manganese dioxide,¹⁴ silver oxide¹⁵ and lead tetraacetate.¹⁶ Manganese dioxide was chosen to operate cyclopropanation from hydrazones in some reports, but an excess amount of the oxidant was used and the reaction had to be operated in a two-step manner, meaning long reaction times and tedious work-up procedures.¹⁷

On the other hand, the wide application of hypervalent iodine reagents in modern synthesis has been well-documented.¹⁸ Cyclopropanation of alkenes can be achieved by formation of iodonium ylide derived from an active methylene compound and subsequent carbene transfer.¹⁹ However, the strategy of *in situ* generating diazo species mediated by a hypervalent iodine reagent was only applied in one-pot esterification reactions using benzophenone hydrazones or *N*-tert-butyltrimethylsilyl hydrazones with carboxylic acid.²⁰ In these esterification reactions, since both the active intermediate (diazo compound) and the substrate (hydrazone) tended to decomposition, low temperature (-78°C or -10°C) had to be used. We intended to broaden the application of this strategy by exploring new catalytic systems that would be compatible with new reaction types. Also, in order to continue our research on hypervalent iodine reagents²¹ and

School of Chemical Engineering, Nanjing University of Science and Technology,
Xiaolingwei 200, Nanjing 210094, People's Republic of China.
E-mail: c.cai@njust.edu.cn

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5nj02378e

circumvent the existing shortcomings in cyclopropanation, we present here a one-pot cyclopropanation from hydrazones and alkenes, which is highly efficient and can be adapted to general hydrazones (Scheme 1c).

Results and discussion

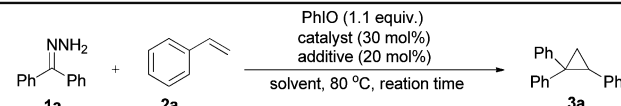
We began our investigations by using benzophenone hydrazone (**1a**) as a model substrate. Upon treating the substrate with hypervalent iodine reagent such as (diacetoxyiodo)benzene (DIB), hydroxy(tosyloxy)iodobenzene (HTIB), [bis(trifluoroacetoxy)iodo]benzene (PIFA), and 2-iodoxybenzoic acid (IBX) in chloroform at room temperature, only decomposition products could be isolated which is consistent with the literature.²² When iodosobenzene was used as an oxidant, the accumulation of diphenyldiazomethane was visible by the outstanding red-violet color spot on the thin layer chromatography (TLC) plate. In order to confirm by GC-MS analysis, methanol was added to the reaction mixture to consume the unstable diazo compound and the corresponding (methoxymethylene) dibenzene could be examined in 35% yield. The parent ketone was found in 40% yield formed by decomposition of the starting hydrazone in solution and reaction with oxygen. The conversion of the starting material is 85% after 10 minutes. With the initial findings, we continued our study by using styrene to trap the *in situ* generated diphenyldiazomethane, the desired cyclopropane product (**3a**) was formed in 35% yield at 80 °C after 20 hours (Table 1, entry 1). Styrene was used in excess to depress side reactions of the starting hydrazone.

In order to accelerate the reaction, various metal catalysts were then scanned at similar reaction conditions, to our delight,

Ni(OAc)₂·4H₂O exhibited catalytic activity and **3a** could be obtained in 46% yield (Table 1, entries 2–5). The attempt to improve product yield using additives like surfactants, ligands and bases only gave inferior results (Table 1, entries 6–10). We then tended to survey Ni(II) salts with different counter ions, the reaction greatly speeded up when using NiF₂·4H₂O or Ni(OH)₂ as a catalyst (Table 1, entries 11–13). As GC-MS analysis showed that byproducts result from the solvent, we ran the reaction under neat conditions and the product yield climbed to 72% (Table 1, entry 14). Careful screening of alkene equivalents showed that 4 equivalents of styrene (with regard to hydrazones) is optimal (Table S1 in the ESI†). The cumbersome nature of running the reaction under argon had little effect on the yield of **3a** (Table 1, entry 15). But in this case, the *in situ* generated diazo compound was decomposed by disproportionation to give the symmetrical azine as the main byproduct. Lowering the reaction temperature to 60 °C led to a drop in reaction performance (Table 1, entry 16). It is worth noting that an acceptable yield (62%) could also be obtained when decreasing the catalyst loading to 10 mol%, only longer reaction time was needed (Table 1, entries 17 and 18).

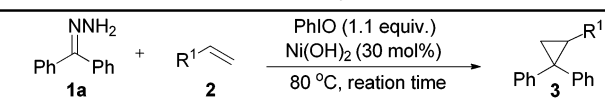
With the optimized conditions in hand (Table 1, entry 14), the scope of this protocol was examined for the reaction of benzophenone hydrazone (**1a**) with a series of substituted alkenes (Table 2). The reactions proceeded smoothly to afford the target cyclopropanes in moderate to good yields. For 4-substituted styrenes in which the substituent is a halogen and an alkyl group (**2b**, **2c**, **2f–2h**), the protocol was applicable without significant differences in product yields (**3b**, **3c**, **3f–3h**). When 2-bromostyrene was used as a substrate, the yield of the product was a bit reduced compared with 3- and 4-bromostyrene which shows an influence of

Table 1 Optimization of the reaction conditions^a

					
Entry	Catalyst	Additive	Solvent	Time	Yield ^b (%)
1	—	—	CHCl ₃	20 h	35
2	CuBr ₂	—	CHCl ₃	20 h	—
3	VOSO ₄ ·xH ₂ O	—	CHCl ₃	20 h	—
4	BiCl ₃	—	CHCl ₃	20 h	—
5	Ni(OAc) ₂ ·4H ₂ O	—	CHCl ₃	20 h	46
6	Ni(OAc) ₂ ·4H ₂ O	TBAC	CHCl ₃	20 h	26
7	Ni(OAc) ₂ ·4H ₂ O	SDS	CHCl ₃	20 h	32
8	Ni(OAc) ₂ ·4H ₂ O	Ph ₃ P	CHCl ₃	20 h	28
9	Ni(OAc) ₂ ·4H ₂ O	TMEDA	CHCl ₃	20 h	22
10	Ni(OAc) ₂ ·4H ₂ O	K ₂ CO ₃	CHCl ₃	20 h	35
11	Ni(acac) ₃	—	CHCl ₃	20 h	40
12	NiF ₂ ·4H ₂ O	—	CHCl ₃	4 h	55
13	Ni(OH) ₂	—	CHCl ₃	1 h	58
14	Ni(OH) ₂	—	—	40 min	72
15 ^c	Ni(OH) ₂	—	—	1 h	73
16 ^d	Ni(OH) ₂	—	—	20 h	25
17 ^e	Ni(OH) ₂	—	—	1 h	67
18 ^f	Ni(OH) ₂	—	—	2 h	62

^a Conditions: **1a** (0.5 mmol), **2a** (4.0 equiv.), catalyst (30 mol%), additive (20 mol%) in solvent (2 mL) at 80 °C. TBAC = tetrabutylammonium chloride, SDS = sodium dodecyl sulfate, TMEDA = tetramethylethylenediamine. ^b Isolated yield. ^c Under argon. ^d Reaction was performed at 60 °C. ^e Ni(OH)₂ (20 mol%) was used. ^f Ni(OH)₂ (10 mol%) was used.

Table 2 Reaction of benzophenone hydrazone (**1a**) with alkenes^a

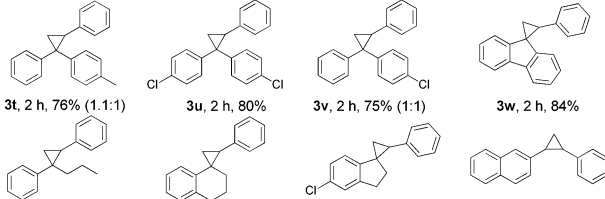
				
Alkene 2	Product 3	Yield (%)	Time	Notes
Ph-CH=CH ₂ (2a)	Ph-CH ₂ -CH ₂ -Ph (3a)	72%	40 min	
Ph-CH=CH-Cl (2b)	Ph-CH ₂ -CH ₂ -Ph (3b)	73%	40 min	
Ph-CH=CH-Br (2c)	Ph-CH ₂ -CH ₂ -Ph (3c)	74%	40 min	
Ph-CH=CH-Br (2d)	Ph-CH ₂ -CH ₂ -Ph (3d)	67%	50 min	
Ph-CH=CH-OMe (2e)	Ph-CH ₂ -CH ₂ -Ph (3e)	71%	20 min	
Ph-CH=CH-F (2f)	Ph-CH ₂ -CH ₂ -Ph (3f)	74%	40 min	
Ph-CH=CH-OMe (2g)	Ph-CH ₂ -CH ₂ -Ph (3g)	73%	40 min	
Ph-CH=CH-OMe (2h)	Ph-CH ₂ -CH ₂ -Ph (3h)	70%	20 min	
Ph-CH=CH-OMe (2i)	Ph-CH ₂ -CH ₂ -Ph (3i)	63%	2 h	
Ph-CH=CH-OMe (2j)	Ph-CH ₂ -CH ₂ -Ph (3j)	68%	40 min	
Ph-CH=CH-OMe (2k)	Ph-CH ₂ -CH ₂ -Ph (3k)	72%	1 h	
Ph-CH=CH-OMe (2l)	Ph-CH ₂ -CH ₂ -Ph (3l)	42%	1 h	
Ph-CH=CH-OMe (2m)	Ph-CH ₂ -CH ₂ -Ph (3m)	46%	4 h	
Ph-CH=CH-OMe (2n)	Ph-CH ₂ -CH ₂ -Ph (3n)	81%	10 min	
Ph-CH=CH-OMe (2o)	Ph-CH ₂ -CH ₂ -Ph (3o)	67%	4 h	
Ph-CH=CH-OMe (2p)	Ph-CH ₂ -CH ₂ -Ph (3p)	51%	40 min	
Ph-CH=CH-OMe (2q)	Ph-CH ₂ -CH ₂ -Ph (3q)	80%	5 min	
Ph-CH=CH-OMe (2r)	Ph-CH ₂ -CH ₂ -Ph (3r)	79%	5 min	
Ph-CH=CH-OMe (2s)	Ph-CH ₂ -CH ₂ -Ph (3s)	91%	1 h	

^a Conditions: **1a** (0.5 mmol), **2** (4.0 equiv.), Ni(OH)₂ (30 mol%), PhIO (1.1 equiv.), at 80 °C. For solid alkenes, chloroform (0.2 mL) was used as solvent. The isolated yields of the products were shown.

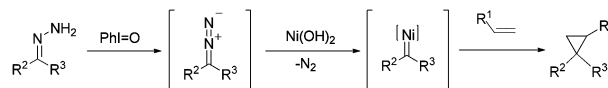
steric effects (**3c–3e**). The presence of a moderate electron-donating group ($-\text{OAc}$) or a strong electron-donating group ($-\text{OMe}$) on the benzene ring of styrene gave the products (**3j**, **3i**) in slightly lower yields. When we employed 4-nitrostyrene as the substrate, the corresponding product (**3n**) was achieved in 81% yield, suggesting that styrene with a strong electron-withdrawing group is favored in this transformation. But unexpectedly, the trifluoromethyl-substituted product (**3l**) was only isolated in 32% yield, which may be attributed to the high volatility of 4-(trifluoromethyl)styrene. The protocol was also applicable to α -methylstyrene and 2-vinylnaphthalene, affording the desired products (**3m**, **3k**) in 46% and 72% yields, respectively. Aliphatic alkenes were also examined. To our delight, allyl chloride and allyl bromide could react and afford the desired cyclopropanes in moderate yields (**3o**, **3p**). Halogen containing products were highly meaningful since the halogen enables further functional group manipulations to more complex structures. Meanwhile, this kind of product can't be synthesized from tosylhydrazones, because, under basic conditions, the known *N*-alkylation of tosylhydrazones with an alkyl halide will be a dominant side reaction.²³ Alkyl acrylates such as methyl acrylate and ethyl acrylate can react with benzophenone hydrazone efficiently and generated the corresponding cyclopropanes in 80% and 79% yields, respectively (**3q**, **3r**). Unfortunately, acyclic internal alkenes show no reactivity under the reaction conditions, only the decomposed products of benzophenone hydrazone (azine and ketone) were detected by GC-MS (for example 1-chloro-2-butene, (*E*)-stilbene *etc.* was tested). A cyclic internal alkene such as norbornene was used, but the 1,3-dipolar cycloaddition product was isolated in 89% yield.²⁴ The product does not exclude molecular nitrogen when it came into contact with $\text{Ni}(\text{OH})_2$ or is heated at 120 °C. When cyclohexene was used, C–H insertion out competes cyclopropanation and the C–H insertion product was formed in 47% yield.²⁴ The special reactivity toward the allylic C–H insertion product may contribute to both steric and electronic effects.²⁵ For conjugated alkenes, (*E*)-1-phenyl-1,3-butadiene could also smoothly undergo the reaction and the desired product was obtained in 91% yield (**3s**).

Then, the generality of this protocol concerning the hydrazone part was investigated (Table 3). Diaryl ketone hydrazones with chlorine or a methyl substituent and 9-fluorenone hydrazone all furnished the corresponding cyclopropanes (**3t–3w**) in satisfactory yields. Furthermore, aryl-alkyl ketone hydrazones exhibited high reactivity and completed the reactions in 5 min with good product yields (**3x–3z**). Notably, the thermally sensitive aldehyde hydrazone substrate (**3aa**) could undergo this transformation efficiently, and generated the desired product in 88% yield. Products **3t**, **3v**, and **3x–3aa** were isolated as mixtures of diastereoisomers and the *trans/cis* ratios were calculated according to NMR spectra. Compared to the diaryl diazo compound, the aryl-alkyl diazo compound and the aryl diazo compound are even more unstable and difficult to handle for the lack of one stabilized benzene ring and the electron-donating effect of the alkyl- or the H-group.²⁶ We believe that the efficiency applicable to **3x–3aa** makes this protocol more practically useful and a better choice in this field. Next, when cyclohexanone hydrazone was used, again, only the 1,3-dipolar cycloaddition product was obtained in 43% yield.²⁴

Table 3 Scanning of hydrazones^a

$\text{R}^2\text{C}=\text{N}=\text{NH}_2$ (1) + $\text{PhCH}=\text{CH}_2$ (2a)		$\xrightarrow[\text{80 } ^\circ\text{C, reaction time}]{\text{PhIO (1.1 equiv.)}, \text{Ni}(\text{OH})_2 \text{ (30 mol\%)}}$	$\text{R}^2\text{C}(\text{R}^3)\text{CH}_2\text{Ph}$ (3)
			
3t , 2 h, 76% (1.1:1)		3u , 2 h, 80%	3v , 2 h, 75% (1:1)
3x , 5 min, 86% (1.1:1)		3y , 5 min, 76% (2:1)	3z , 5 min, 70% (1.5:1)
		3aa , 5 min, 88% (2.8:1)	

^a Conditions: **1a** (0.5 mmol), **2** (4.0 equiv.), $\text{Ni}(\text{OH})_2$ (30 mol%), PhIO (1.1 equiv.), at 80 °C. For solid alkenes, chloroform (0.2 mL) was used as solvent. The isolated yields of the products were shown. For **3t**, **3v**, and **3x–3aa**, the *trans/cis* ratios of diastereoisomer were shown in brackets.



Scheme 2 Proposed mechanisms.

Based on the knowledge of transition metal-catalyzed cyclopropanation and the above experiments we explored, we proposed a reaction pathway for this one-pot nickel(II)-catalyzed cyclopropanation of alkenes with hydrazones (Scheme 2). Iodosobenzene functions as the oxidizing agent and *in situ* oxidize hydrazones to diazo compounds. The interaction of diazo compounds with the nickel salt generates metal-carbene intermediates and subsequent carbene addition leads to the desired product.

Conclusions

In summary, a new approach to cyclopropane compounds has been introduced in this paper. The one-pot and easy operation procedure utilizes iodosobenzene as an oxidant to generate non-stabilized diazo compounds *in situ* from unsubstituted hydrazones. There's no need to isolate the diazo compound or to run the reaction stepwise. With the aid of a nickel catalyst, the diazo compound decomposes readily and reacts with the alkene at 80 °C to furnish the cyclopropane efficiently (5 min–4 h) and in moderate to good yields (42–91%). The mild protocol is generally applicable to aryl alkenes with different electronic effect substituents ($-\text{OMe}$, $-\text{NO}_2$, $-\text{t-Bu}$, $-\text{F}$, *etc.*), aliphatic alkenes with halogen functional groups, alkyl acrylates and hydrazones derived from diaryl ketones, aryl-alkyl ketones and aldehydes. If lower catalyst loading was used, an acceptable yield could also be obtained and for all reactions the termination can be clearly indicated by the vanishing of the special color of diazo compounds. We concentrated on the synthesis of 1,1-diaryl cyclopropanes because of its lack of systematic investigation and a good supplement to the existing methods. The enantioselective version of this protocol through adding chiral ligands or chiral auxiliaries of the substrate, and further exploration of

this reliable way of generating diazo intermediates is now in progress in our laboratory.

Experimental

A screwed tube was charged with the corresponding hydrazone (0.5 mmol), Ni(OH)₂ (30 mol%, 0.014 g) and alkene (4 equiv.). For solid alkenes, chloroform (0.2 mL) was used as the solvent. A magnetic stirrer with an oil bath was used and pre-heated to 80 °C. The screwed tube was then put to the oil bath and at the same time iodosobenzene (1.1 equiv., 0.121 g) was added. The reaction was stirred at 80 °C until total disappearance of the red-violet color which indicated the completion of the reaction. The reaction mixture was purified by column chromatography using petroleum ether or petroleum ether/ethyl acetate as an eluent.

Acknowledgements

We thank the Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD). We also thank Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences for testing HRMS.

Notes and references

- (a) R. Faust, *Angew. Chem., Int. Ed.*, 2001, **40**, 2251; (b) Y. Fujimoto, F. Irreverre, J. M. Karle, I. L. Karle and B. Witkop, *J. Am. Chem. Soc.*, 1971, **93**, 3471; (c) W. A. Donaldson, *Tetrahedron*, 2001, **57**, 8589.
- A. De Meijere, *Angew. Chem., Int. Ed.*, 1979, **18**, 809.
- (a) A. Maercker, K. S. Oeffner and U. Girreser, *Tetrahedron*, 2004, **60**, 8245; (b) J. P. Dinnocenzo, H. Zuillhof, D. R. Lieberman, T. R. Simpson and M. W. McKechney, *J. Am. Chem. Soc.*, 1997, **119**, 994.
- C. J. Suckling, *Angew. Chem., Int. Ed.*, 1988, **27**, 537.
- (a) G. Brunner, S. Elmer and F. Schröder, *Eur. J. Org. Chem.*, 2011, 4623; (b) M. G. Apenova, O. O. Semivrazhskaya, E. V. Borkovskaya, N. M. Belov, I. N. Loffe, V. Y. Markov, S. I. Troyanov, N. S. Lukonina, L. N. Sidorov and A. A. Goryunkov, *Chem. – Asian J.*, 2015, **10**, 1370.
- (a) J. R. Denton and H. M. L. Davies, *Org. Lett.*, 2009, **11**, 787; (b) M. Verdecchia, C. Tubaro and A. Biffis, *Tetrahedron Lett.*, 2011, **52**, 1136; (c) T. M. Gregg, M. K. Farrugia and J. R. Frost, *Org. Lett.*, 2009, **11**, 4434; (d) Z. H. Zhang and J. B. Wang, *Tetrahedron*, 2008, **64**, 6577. For some reviews, see: (e) H. Lebel, J. Marcoux, C. Molonaro and A. B. Charette, *Chem. Rev.*, 2003, **103**, 977; (f) G. Maas, *Chem. Soc. Rev.*, 2004, **33**, 183; (g) T. Ye and M. A. Mckerverve, *Chem. Rev.*, 1994, **94**, 1091; (h) M. P. Doyle and D. C. Forbes, *Chem. Rev.*, 1998, **98**, 911.
- (a) M. P. Doyle and R. J. Pieters, *J. Am. Chem. Soc.*, 1991, **113**, 1424; (b) H. M. L. Davies and S. A. Panaro, *Tetrahedron*, 2000, **56**, 4871; (c) T. Nishimura, Y. Maeda and T. Hayashi, *Angew. Chem., Int. Ed.*, 2010, **49**, 7324; (d) K. P. Kornecki, J. F. Briones, V. Boyarskikh, F. Fullilove, J. Autschbach, K. E. Schrote, K. M. Lancaster, H. M. L. Davies and J. F. Berry, *Science*, 2013, **342**, 351; (e) P. Muller, G. Bernardinelli, Y. F. Allenbach, M. Ferri and H. D. Flack, *Org. Lett.*, 2004, **6**, 1725; (f) Y. Su, M. Bai, J. B. Qiao, X. J. Li, R. Li, Y. Q. Tu and P. Gu, *Tetrahedron Lett.*, 2015, **56**, 1805.
- (a) H. Nishiyama, Y. Itoh, H. Matsumoto, S. B. Park and K. Itoh, *J. Am. Chem. Soc.*, 1994, **116**, 2223; (b) C. M. Che, J. S. Huang, F. W. Lee, Y. Li, T. S. Lai, H. L. Kwong, P. F. Teng, W. S. Lee, W. C. Lo, S. M. Peng and Z. Y. Zhou, *J. Am. Chem. Soc.*, 2001, **123**, 4119; (c) B. G. Kim and M. L. Snapper, *J. Am. Chem. Soc.*, 2006, **128**, 52; (d) J. A. Miller, W. Jin and S. T. Nguyen, *Angew. Chem., Int. Ed.*, 2002, **114**, 3077; (e) S. Priya, M. S. Balakrishna, S. M. Mobin and R. McDonald, *J. Organomet. Chem.*, 2003, **688**, 227.
- (a) R. E. Lowenthal, A. Abiko and S. Masamune, *Tetrahedron Lett.*, 1990, **31**, 6005; (b) W. Zhang, F. Xie, S. Matsuo, Y. Imahori, T. Kida, Y. Nakatsuji and I. Ikeda, *Tetrahedron: Asymmetry*, 2006, **17**, 767; (c) X. Dai and T. H. Warren, *J. Am. Chem. Soc.*, 2004, **126**, 10085.
- (a) S. F. Zhu, J. A. Perman and X. P. Zhang, *Angew. Chem., Int. Ed.*, 2008, **47**, 8460; (b) S. F. Zhu, J. V. Ruppel, H. J. Lu, L. Wojtas and X. P. Zhang, *J. Am. Chem. Soc.*, 2008, **130**, 5042; (c) L. Y. Huang, Y. Chen, G. Y. Gao and X. P. Zhang, *J. Org. Chem.*, 2003, **68**, 8179; (d) M. Otte, P. F. Kuijpers, O. Troeppner, I. Ivanović-Burmazović, J. N. H. Reek and B. D. Bruin, *Chem. – Eur. J.*, 2014, **20**, 4880; (e) S. Fantauzzi, E. Gallo, E. Rose, N. Raoul, A. Caselli, S. Issa, F. Ragaini and S. Cenini, *Organometallics*, 2008, **27**, 6143; (f) S. L. Marquard, M. W. Bezpalko, B. M. Foxman and C. M. Thomas, *J. Am. Chem. Soc.*, 2013, **135**, 6018.
- (a) J. J. Eisch, A. A. Aradi, M. A. Lucarelli and Y. Qian, *Tetrahedron*, 1998, **54**, 1169; (b) A. Nakamura, T. Yoshida, M. Cowie and S. Otsuka, *J. Am. Chem. Soc.*, 1977, **99**, 2108; (c) M. Ishikawa, A. Naka, S. Okazaki and H. Sakamoto, *Organometallics*, 1993, **12**, 87; (d) D. J. Mindiola and G. L. Hillhouse, *J. Am. Chem. Soc.*, 2002, **124**, 9976; (e) R. Waterman and G. L. Hillhouse, *J. Am. Chem. Soc.*, 2003, **125**, 13350; (f) B. Gabor, C. Kruger, B. Marczinke, R. Mynott and G. iEke, *Angew. Chem., Int. Ed.*, 1991, **30**, 1666; (g) B. Gabor, C. Kruger, B. Marczinke, R. Mynott and G. WiEke, *Angew. Chem., Int. Ed.*, 2015, **54**, 10670.
- (a) V. K. Aggarwal, J. de Vicente and R. V. Bonnert, *Org. Lett.*, 2004, **3**, 2785; (b) H. Jiang and H. Chen, *Chem. – Eur. J.*, 2012, **18**, 11884; (c) J. Barluenga, N. Quiñones, M. Tomás-Gamasa and M. P. Cabal, *Eur. J. Org. Chem.*, 2012, 2312.
- L. I. Smith and K. L. Howard, *Org. Synth.*, 1944, **24**, 53.
- S. Kumar and R. W. Murray, *J. Am. Chem. Soc.*, 1984, **106**, 1040.
- W. Schroeder and L. Katz, *J. Org. Chem.*, 1954, **19**, 718.
- T. L. Holton and H. Shechter, *J. Org. Chem.*, 1995, **60**, 4725.
- (a) J. R. Denton, D. Sukumaran and H. M. L. Davies, *Org. Lett.*, 2007, **9**, 2625; (b) N. M. Roda, D. N. Tran, C. Battilocchio, R. Labes, R. J. Ingham, J. M. Hawkins and S. V. Ley, *Org. Biomol. Chem.*, 2015, **13**, 2550.
- (a) V. V. Zhdankin, *ARKIVOC*, 2009, **1**; (b) P. J. Stang, *Chem. Rev.*, 1996, **96**, 1123; (c) G. Qian, B. Liu, Q. Tan, S. Zhang and B. Xu, *Eur. J. Org. Chem.*, 2014, 4837.

- 19 (a) S. Lin, M. Li, Z. Dong, F. Liang and J. Zhang, *Org. Biomol. Chem.*, 2014, **12**, 1341; (b) H. T. Bonge and T. Hansen, *Synlett*, 2007, 55; (c) B. Moreau, D. Albrico, V. N. G. Lindsay and A. B. Charette, *Tetrahedron*, 2012, **68**, 3487.
- 20 (a) M. E. Furrow and A. G. Myers, *J. Am. Chem. Soc.*, 2004, **126**, 12222; (b) L. Lapatsanis, G. Miliadis and S. Paraskewas, *Synthesis*, 1985, 513.
- 21 H. Liu and Y. Wei, *Tetrahedron Lett.*, 2013, **54**, 4645.
- 22 K. C. Nicolaou, C. J. Mathison and T. Montagnon, *J. Am. Chem. Soc.*, 2004, **126**, 5192.
- 23 (a) S. Cacchi, F. La Torre and D. Misiti, *Synthesis*, 1977, 301; (b) Y. Kong, W. Zhang, M. Tang and H. Wang, *Tetrahedron*, 2013, **69**, 7487.
- 24 For the structure and spectroscopic data of the products, see the ESI†.
- 25 (a) Y. Li, J. S. Huang, Z. Y. Zhou, C. M. Che and X. Z. You, *J. Am. Chem. Soc.*, 2002, **124**, 13185; (b) P. Müller and S. Tohill, *Tetrahedron*, 2000, **56**, 1725.
- 26 (a) M. Regitz and G. Mess, *Diazo compounds: Properties and Synthesis*, Academic press, New York, 1986, p. 71; (b) G. L. Closs and R. A. Moss, *J. Am. Chem. Soc.*, 1964, **86**, 4042.