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Annulation of *o*-Quinodimethanes through N-Heterocyclic Carbene Catalysis for the Synthesis of 1-Isochromanones

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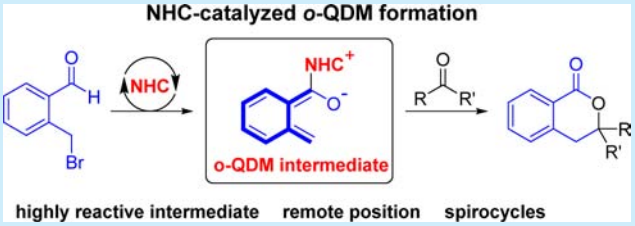
Supporting Information

ABSTRACT: The activation of 2-(bromomethyl)benzaldehydes using N-heterocyclic carbenes represents a novel approach to the generation of *o*-quinodimethane (*o*-QDM) intermediates. Coupling with ketones such as phenylglyoxylates, isatins, or trifluoromethyl ketones via [4 + 2] annulation gives access to functionalized 1-isochromanones.

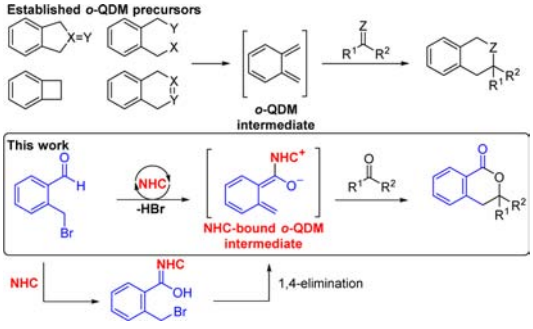


N-Heterocyclic carbenes (NHCs)[1] are established organocatalysts[2] for the activation of aldehydes. Various activation modes have been developed, affording a distinct set of nucleophilic intermediates such as acyl anion equivalents,[3] azolium enolates,[4] homoenolates,[5] or dienolates from aldehydes.[6] Significant efforts have also been made to access these intermediates from different carbonyl precursors and to study their reaction with numerous coupling partners for the synthesis of important structural motifs.[2]

The field of azolium dienolates,[6,7] initially reported by Ye and co-workers in 2011,[6a,b] represents the vinylogous extension of the earlier azolium enolate chemistry. Reported methods to generate azolium dienolates often require the generation of an acylazolium species, which can undergo γ-deprotonation to form an azolium dienolate. These acylazoliums can be accessed starting from substrates on the carboxylic acid oxidation state[6a−d] or by in situ oxidation of the Breslow intermediate derived from aldehydes.[6e−g,7] The ring-opening of cyclobutenones[6h] and the elimination of leaving groups at the 2- or 4-position of enals[6i,l] are also reported methods to generate azolium dienolates.

One particular, highly reactive class of diene, *o*-quinodimethane (*o*-QDM),[8] has not been used as an azolium dienolate before, despite its potential synthetic utility for the synthesis of benzannulated products. *o*-QDMs were first described by Cava and Napier in 1957.[9] Since then, *o*-QDMs have been studied as reactive short-lived species and have evolved into efficient platforms in the synthesis of natural products (e.g., steroids and biologically relevant tetralins), the addition to fullerenes, and the synthesis of polymers and π-extended materials.[8] The most typical reaction for these intermediates is the [4 + 2] Diels−Alder cycloaddition, acting as a highly activated diene. The physicochemical properties of these important species are well studied, and various strategies for *o*-QDM formation have been developed, including 1,4-elimination of leaving groups, electro- or photochemistry, cheleotropic elimination (SO_2, N_2, CO, CO_2), or benzocyclobutene ring-opening from suitable precursors (Scheme 1).[8a] Once formed in situ, the reactivity of *o*-QDMs is dominated by the strong tendency to rearomatize.

Scheme 1. NHC-Catalyzed Formation of *o*-QDM Intermediates for [4 + 2] Annulation with Activated Ketones



o-QDMs derived from heteroaromatic precursors (*o*-QDM heteroanalogues) are more stable and much easier to form than the corresponding carbocyclic analogues due to their lowered aromaticity compared to benzene. In particular, benzo-fused precursors are more easily converted to the corresponding *o*-QDM.[10]

The in situ oxidation strategy for accessing azolium dienolates[6e−g] was extended by Chi and co-workers for *o*-methyl heteroaryl aldehydes,[7a] giving access to benzo-fused *o*-QDM heteroanalogues, which were reacted with activated ketones. Recently, it was found that this reaction could also be achieved with *o*-QDM formation from *o*-methyl heteroaryl esters and coupling with isatin-derived ketimines.[7b] This methodology for benzofused heteroaryl aldehydes could, unfortunately, not be extended to carbocyclic aromatics such as 2-methylbenzaldehyde, which yielded only 2-methylbenzoic acid derivatives.[7a]

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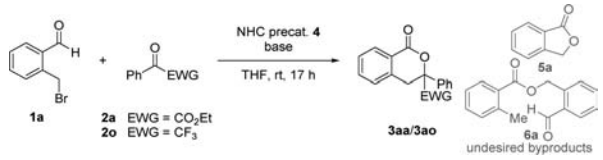
The γ-acidity of the intermediary acylazolium species resulting from 2-methylbenzaldehyde should be dramatically lowered on the basis of the higher resonance stabilization of the benzene ring, which would explain the failure of the reaction under these conditions.[7a]

We hypothesized that the introduction of a leaving group on the aldehyde substrate might directly yield the *o*-QDM intermediate after 1,4-elimination of the leaving group from the corresponding Breslow intermediate, thus circumventing the need for in situ oxidation and formation of a γ-acidic acylazolium species.

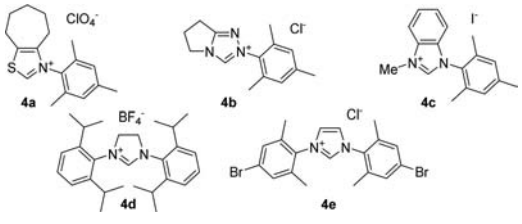
We commenced our study using 2-(bromomethyl)-benzaldehyde **1a** as a model substrate, which was stirred in the presence of the thiazolium-based NHC-precursor **4a**, ethyl phenylglyoxylate **2a** as a ketone coupling partner, and an excess of K_2CO_3 as base in THF. We were pleased to observe the formation of the corresponding product **3aa** in 3% yield. Further optimization (Table 1, entries 1−7) revealed benzimidazolium NHC precursor **4c** as the optimal catalyst and Cs_2CO_3 as the best base, giving **3aa** in 78% yield.

Table 1. Reaction Optimization



entry[a]	2	4	base	1a:2	yield 3 (%)	yield 5 (%)	yield 6 (%)
1	**2a**	**4a**	K_2CO_3	1:1	3	1	3
2	**2a**	**4b**	K_2CO_3	1:1	7	1	3
3	**2a**	**4c**	K_2CO_3	1:1	25	1	3
4	**2a**	**4d**	K_2CO_3	1:1	4	5	3
5	**2a**	**4e**	K_2CO_3	1:1	8	1	1
6	**2a**	**4c**	Cs_2CO_3	1:1	73	6	8
7	**2a**	**4c**	**Cs_2CO_3**	**1.2:1**	**78**	**7**	**12**
8	**2o**	**4c**	Cs_2CO_3	1.2:1	11	3	1
9	**2o**	**4b**	Cs_2CO_3	1.2:1	37	1	4
10	**2o**	**4b**	**Cs_2CO_3**	**1:2**	**57**	**1**	**3**
11		**4b**	Cs_2CO_3		nd	5	14

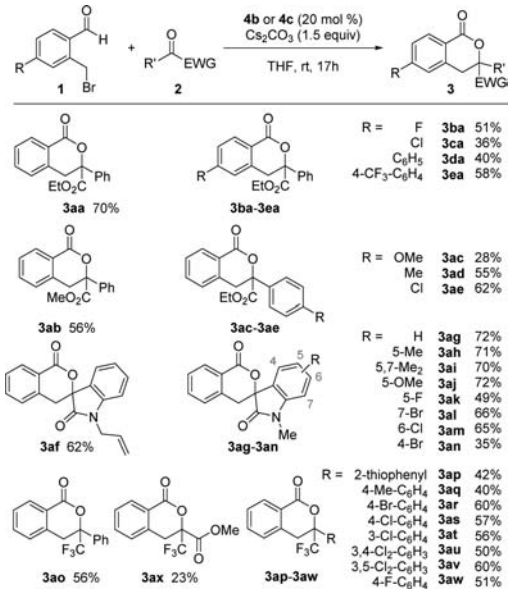
[a]Conditions: **1a**, **2a**/**o**, NHC precatalyst **4** (20 mol %), base (1.5 equiv), THF (0.1 M), rt, 17 h. Yields are determined by ^{1}H NMR spectroscopy from 0.1 mmol scale reactions with CH_2Br_2 as internal standard; nd = not determined.



Trifluoromethyl ketone **2o** was tested as an electrophile with the optimized catalyst **4c**, giving the desired product **3ao** in only 11% NMR yield. We screened various NHC precursors and found that triazolium precatalyst **4b** gave the product in a higher yield of 37%. Using an excess of ketone **2o** was found to provide the desired product **3ao** in 57% NMR yield (Table 1, entries 8−10). Two byproducts were observed to form during the reaction (**5** and **6**), even in the absence of coupling partner **2** (entry 11). Compound **5** is likely formed from intermediate **7**, whereas **6** could result from γ-protonation of the o-QDM, and hydrolysis of the acylazolium to 2-methyl benzoate, which reacts with **1** (vide infra).

We evaluated the substrate scope (Scheme 2) of this reaction initially by varying the benzaldehyde moiety. Various

Scheme 2. Substrate Scope[a]



[a]Conditions A (EWG = COXR): **1a**−**e** (0.6 mmol), **2a**−**n** (0.5 mmol), **4c** (0.1 mmol), Cs_2CO_3 (0.75 mmol), THF (0.1 M), rt, 17 h. Conditions B (EWG = CF_3): **1a** (0.5 mmol), **2o**−**x** (1.0 mmol), **4b** (0.1 mmol), Cs_2CO_3 (0.75 mmol), THF (0.1 M), rt, 17 h. Yields given are isolated yields.

substituents are tolerated on the aromatic ring (Cl-, F-, Ph-, or 4-$CF_3C_6H_4$). Next, we investigated a series of phenyl-glyoxylate esters as electrophilic coupling partner. Changing the ethyl ester of **2a** to methyl resulted in a slight drop in yield to 56% (**3ab**). We noticed that the yield of the products was dependent on the electronic nature of the coupling partner **2c**−**e** with electron-withdrawing groups, providing the annulation product in higher yields.

We next focused our attention on the use of isatin derivatives as ketone coupling partners since the spirocyclic isatin-based products represent an interesting class of spirooxindole derivatives containing 1-isochromanone. 3,3′-Spirooxindoles have shown remarkable biological and pharmaceutical activities, such as antitumor, antimicrobial, and antifungal.[11] The demand for a variety of different 3,3′-spirooxindoles has led to the development of numerous methodologies. These syntheses are generally regarded as challenging due to steric repulsion during spirocycle formation.[11] Compound **3ag** has been synthesized only recently in an acid-catalyzed cyclocondensation reaction.[12]

To our delight, *N*-allyl- and *N*-methylisatin reacted smoothly under these conditions, giving the desired 3,3′-spirooxindole products in 62% (**3af**) and 72% yield (**3ag**). Variations on the isatin core, including both electron-rich and electron-poor substituents, were well tolerated at all possible positions on the aromatic ring (**3ah**−**an**). Slightly lower yields were observed for the 5-fluoro and the sterically more demanding 4-bromo derivative (**3ak** and **3al**).

We started investigating the scope of trifluoromethyl ketones and found that electron-poor derivatives (**3ar**−**aw**) again

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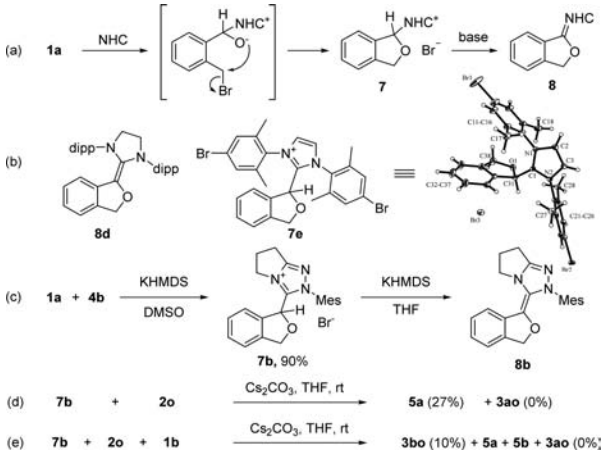
performed slightly better than their electron-rich counterparts (**3ap** and **3aq**). Employing methyl ester substituted trifluoroketone, which has an even higher electrophilicity, under these conditions provided product **3ax** in only 23% yield, which was structurally confirmed by single-crystal X-ray diffraction analysis.[13]

Inspired by Berkessel's reports on in isolating Breslow intermediates, as well as azolium−enolates and NHC−homoenolates,[14] we attempted to isolate the *o*-QDM intermediate using catalytically inactive NHC SIPr (derived from **4d**) but found full conversion to cyclic Breslow intermediate **8d**, which is formed via deprotonation of **7**. However, related derivative **7e** (derived from **4e**) could be formed and structurally confirmed by single-crystal X-ray diffraction analysis (Scheme 3a,b).

Scheme 3. Intramolecular *O*-Alkylation Leads to Stable Off-Cycle Substrate−NHC Adduct 7 and Cyclic Breslow Intermediate Analogue 8[a]



[a](a) Formation of **7** and **8** from **1a** and NHC; (b) structure of **8d** and molecular structure of **7e**; (c) isolation of **7b** and deprotonation to **8b**; (d) **7b** is not reactive toward annulation with **2o**; (e) **7b** serves as NHC precursor.

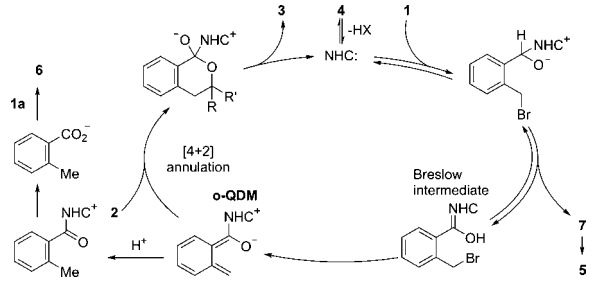
Finally, attempts to isolate these adducts using the catalytically active NHC **4b** were successful, with **7b** isolated in 90% yield from DMSO. The acidic C−H bond undergoes deuterium exchange in the presence of D_2O. One equivalent of base in THF led to the formation of **8b** (Scheme 3c).

To investigate whether **7b** or **8b** is catalytically active, we subjected **7b** to the developed [4 + 2] annulation conditions in the absence of **4b** and **1a**. The desired product **3ao** was not formed. Instead, phthalide **5a** was found as an oxidation product after workup (Scheme 3d). In a crossover experiment (Scheme 3e), adding fluorine-substituted aldehyde **1b**, it could be shown that the observed adduct **7b** is still catalytically active (formation of **3bo**), but it represents an off-cycle intermediate (no formation of **3ao**), which only forms **5a** (as well as fluoro-substituted **5b**) rather than the *o*-QDM intermediate.

Regarding the catalytic cycle (Scheme 4), we hypothesize the formation of the Breslow intermediate from **1** and **4**, which leads to the elimination of HBr. Once formed, the *o*-QDM reacts with the ketone via [4 + 2] annulation, followed by elimination and regeneration of the NHC.

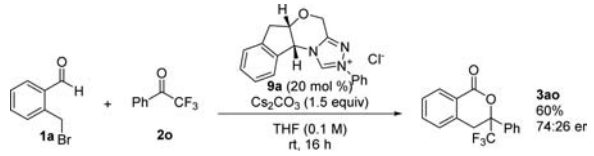
For an enantioselective reaction, an initial screen of chiral NHC precursors, especially those that have been successfully

Scheme 4. Proposed Catalytic Cycle



employed in NHC−dienolates,[6,7] revealed **9a** as the best catalyst, leading to 74:26 er (Scheme 5). Sterically more demanding NHCs led to shutdown of the reactivity, presumably due to the preferred formation of **7**.

Scheme 5. Enantioselective Catalysis[a]



[a]Yields are determined by ^{1}H NMR spectroscopy from 0.1 mmol scale reactions with CH_2Br_2 as internal standard. The er was determined via HPLC using a chiral stationary phase.

There is little known about enantioselective methods involving *o*-QDM intermediates for [4 + 2] annulations, which have been attributed to the high reactivity compared to classical dienes, although it has been found that organocatalysis can offer an appropriate solution.[7,15] Further catalyst development for higher enantioinduction with these useful intermediates will be a challenge for future research.

In conclusion, we have found a novel strategy to generate *o*-QDM intermediates via NHC organocatalysis, making use of an 1,4-elimination reaction. Subsequent [4 + 2] annulation with ketones led to interesting 1-isochromanones, including new 3,3′-spirooxindoles. Chiral NHCs led to enantiomerically enriched product and stoichiometric transformations with NHCs reveal an alternative reaction path of the NHC with the substrate, thus explaining the formation of phthalide as a byproduct from catalysis and allowing formation of stable cyclic Breslow intermediate analogues.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02335.

X-ray data for compounds **3ax** and **7e** (CIF)
Experimental procedures and spectroscopic data (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Hopkinson, M. N.; Richter, C.; Schedler, M.; Glorius, F. *Nature* **2014**, *510*, 485.

(2) For reviews on NHC organocatalysis, see: (a) Zeitler, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 7506. (b) Marion, N.; Díez-González, S.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 2988. (c) Enders, D.; Niemeier, O.; Henseler, A. *Chem. Rev.* **2007**, *107*, 5606. (d) Rovis, T. *Chem. Lett.* **2008**, *37*, 2. (e) Phillips, E. M.; Chan, A.; Scheidt, K. A. *Aldrichimica Acta* **2009**, *42*, 55. (f) Moore, J. L.; Rovis, T. *Top. Curr. Chem.* **2010**, *291*, 77. (g) Vora, H. U.; Rovis, T. *Aldrichimica Acta* **2011**, *44*, 3. (h) Hirano, K.; Piel, I.; Glorius, F. *Chem. Lett.* **2011**, *40*, 786. (i) Chiang, P.-C.; Bode, J. W. *TCI Mail* **2011**, *149*, 2. (j) Nair, V.; Menon, R. S.; Biju, A. T.; Sinu, C. R.; Paul, R. R.; Jose, A.; Sreekumar, V. *Chem. Soc. Rev.* **2011**, *40*, 5336. (k) Biju, A. T.; Kuhl, N.; Glorius, F. *Acc. Chem. Res.* **2011**, *44*, 1182. (l) Cohen, D. T.; Scheidt, K. A. *Chem. Sci.* **2012**, *3*, 53. (m) Grossmann, A.; Enders, D. *Angew. Chem., Int. Ed.* **2012**, *51*, 314. (n) Bugaut, X.; Glorius, F. *Chem. Soc. Rev.* **2012**, *41*, 3511. (o) Izquierdo, J.; Hutson, G. E.; Cohen, D. T.; Scheidt, K. A. *Angew. Chem., Int. Ed.* **2012**, *51*, 11686. (p) Mahatthananchai, J.; Bode, J. W. *Chem. Sci.* **2012**, *3*, 192. (q) Vora, H. U.; Wheeler, P.; Rovis, T. *Adv. Synth. Catal.* **2012**, *354*, 1617. (r) Fèvre, M.; Pinaud, J.; Gnanou, Y.; Vignolle, J.; Taton, D. *Chem. Soc. Rev.* **2013**, *42*, 2142. (s) Ryan, S. J.; Candish, L.; Lupton, D. W. *Chem. Soc. Rev.* **2013**, *42*, 4906. (t) Mahatthananchai, J.; Bode, J. W. *Acc. Chem. Res.* **2014**, *47*, 696. (u) Flanigan, D. M.; Romanov-Michailidis, F.; White, N. A.; Rovis, T. *Chem. Rev.* **2015**, *115*, 9307. (v) Menon, R. S.; Biju, A. T.; Nair, V. *Chem. Soc. Rev.* **2015**, *44*, 5040. (w) Yetra, S. R.; Patra, A.; Biju, A. T. *Synthesis* **2015**, *47*, 1357 and references cited therein.

(3) (a) Stetter, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 639. (b) Kerr, M. S.; Read de Alaniz, J.; Rovis, T. *J. Am. Chem. Soc.* **2002**, *124*, 10298. (c) Enders, D.; Niemeier, O.; Balensiefer, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 1463. (d) Janssen-Müller, D.; Schedler, M.; Fleige, M.; Daniliuc, C. G.; Glorius, F. *Angew. Chem., Int. Ed.* **2015**, *54*, 12492.

(4) (a) Chow, K. Y.-K.; Bode, J. W. *J. Am. Chem. Soc.* **2004**, *126*, 8126. (b) Reynolds, N. T.; Read de Alaniz, J.; Rovis, T. *J. Am. Chem. Soc.* **2004**, *126*, 9518. (c) Reynolds, N. T.; Rovis, T. *J. Am. Chem. Soc.* **2005**, *127*, 16406. (d) Vora, H. U.; Rovis, T. *J. Am. Chem. Soc.* **2010**, *132*, 2860.

(5) (a) Sohn, S. S.; Rosen, E. L.; Bode, J. W. *J. Am. Chem. Soc.* **2004**, *126*, 14370. (b) Burstein, C.; Glorius, F. *Angew. Chem., Int. Ed.* **2004**, *43*, 6205.

(6) For NHC-catalyzed reactions with nonaromatic azolium dienolates, see: (a) Shen, L.-T.; Shao, P.-L.; Ye, S. *Adv. Synth. Catal.* **2011**, *353*, 1943. (b) Wang, T.; Ye, S. *Scientia Sinica Chim.* **2011**, *41*, 1306. (c) Xu, J.; Jin, Z.; Chi, Y. R. *Org. Lett.* **2013**, *15*, 5028. (d) Jia, W.-Q.; Zhang, H.-M.; Zhang, C.-L.; Gao, Z.-H.; Ye, S. *Org. Chem. Front.* **2016**, *3*, 77. (e) Mo, J.; Chen, X.; Chi, Y. R. *J. Am. Chem. Soc.* **2012**, *134*, 8810. (f) Liu, R.; Yu, C.; Xiao, Z.; Li, T.; Wang, X.; Xie, Y.; Yao, C. *Org. Biomol. Chem.* **2014**, *12*, 1885. (g) Wang, M.; Huang, Z.; Xu, J.; Chi, Y. R. *J. Am. Chem. Soc.* **2014**, *136*, 1214. (h) Li, B.-S.; Wang, Y.; Jin, Z.; Zheng, P.; Ganguly, R.; Chi, Y. R. *Nat. Commun.* **2015**, *6*, 6207. (i) Yao, C.; Xiao, Z.; Liu, R.; Li, T.; Jiao, W.; Yu, C. *Chem. - Eur. J.* **2013**, *19*, 456. (j) Xiao, Z.; Yu, C.; Li, T.; Wang, X.-S.; Yao, C. *Org. Lett.* **2014**, *16*, 3632. (k) Chen, X.-Y.; Xia, F.; Cheng, J.-T.; Ye, S. *Angew. Chem., Int. Ed.* **2013**, *52*, 10644. (l) Cheng, J.-T.; Chen, X.-Y.; Gao, Z. H.; Ye, S. *Eur. J. Org. Chem.* **2015**, *2015*, 1047.

(7) (a) Chen, X.; Yang, S.; Song, B.-A.; Chi, Y. R. *Angew. Chem., Int. Ed.* **2013**, *52*, 11134. (b) Xu, J.; Yuan, S.; Miao, M. *Org. Lett.* **2016**, *18*, 3822.

(8) (a) Segura, J. L.; Martin, N. *Chem. Rev.* **1999**, *99*, 3199. (b) Martín, N.; Seoane, C.; Hanack, M. *Org. Prep. Proced. Int.* **1991**, *23*, 237. (c) Charlton, J. L.; Alauddin, M. M. *Tetrahedron* **1987**, *43*, 2873. (d) Yoshida, H.; Ohshita, J.; Kunai, A. *Bull. Chem. Soc. Jpn.* **2010**, *83*, 199.

(9) Cava, M. P.; Napier, D. R. *J. Am. Chem. Soc.* **1957**, *79*, 1701.

(10) For *o*-QDM hetero analogues, see: (a) Collier, S. J.; Storr, R. C. *Prog. Heterocycl. Chem.* **1998**, *10*, 25. (b) Joule, J. A.; Mills, K. *Heterocyclic Chemistry*, 5th ed.; John Wiley & Sons: Chichester, U.K., 2010.

(11) For 3,3′-spirooxindoles, see: (a) da Silva, J. F. M.; Garden, S. J.; Pinto, A. C. *J. Braz. Chem. Soc.* **2001**, *12*, 273. (b) Xia, M.; Ma, R.-Z. *J. Heterocyclic Chem.* **2014**, *51*, 539. (c) Dalpozzo, R.; Bartoli, G.; Bencivenni, G. *Chem. Soc. Rev.* **2012**, *41*, 7247. (d) Marti, C.; Carreira, E. M. *Eur. J. Org. Chem.* **2003**, *2003*, 2209. (e) Galliford, C. V.; Scheidt, K. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 8748. (f) Singh, G. S.; Desta, Z. Y. *Chem. Rev.* **2012**, *112*, 6104. (g) Trost, B. M.; Brennan, M. K. *Synthesis* **2009**, *2009*, 3003.

(12) Zhou, F.; Ding, M.; Zhou, J. *Org. Biomol. Chem.* **2012**, *10*, 3178.

(13) See the Supporting Information for more details.

(14) For isolation of *O*-methyl Breslow intermediates, see: (a) Maji, B.; Mayr, H. *Angew. Chem., Int. Ed.* **2012**, *51*, 10408. For pioneering work on the isolation of Breslow intermediates, see: (b) Berkessel, A.; Elfert, S.; Yatham, V. R.; Neudörfl, J.-M.; Schlörer, N. E.; Teles, J. H. *Angew. Chem., Int. Ed.* **2012**, *51*, 12370. (c) Berkessel, A.; Yatham, V. R.; Elfert, S.; Neudörfl, J.-M. *Angew. Chem., Int. Ed.* **2013**, *52*, 11158.

(15) For enantioselective reaction with *o*-QDMs and chiral auxiliaries or chiral complexation agent, see: (a) Grosch, B.; Orlebar, C. N.; Herdtweck, E.; Massa, W.; Bach, T. *Angew. Chem., Int. Ed.* **2003**, *42*, 3693. (b) Grosch, B.; Orlebar, C. N.; Herdtweck, E.; Kaneda, M.; Wada, T.; Inoue, Y.; Bach, T. *Chem. - Eur. J.* **2004**, *10*, 2179. (c) Takinami, T.; Ukaji, Y.; Inomata, K. *Tetrahedron: Asymmetry* **2006**, *17*, 1554. For catalytic enantioselective methods involving *o*-QDMs, see: (d) Liu, Y.; Nappi, M.; Arceo, E.; Vera, S.; Melchiorre, P. *J. Am. Chem. Soc.* **2011**, *133*, 15212. (e) Xiao, Y.-C.; Zhou, Q.-Q.; Dong, L.; Liu, T.-Y.; Chen, Y.-C. *Org. Lett.* **2012**, *14*, 5940. (f) Shirakawa, H.; Sano, H. *Tetrahedron Lett.* **2014**, *55*, 4095. (g) Dell'Amico, L.; Vega-Peñaloza, A.; Cuadros, S.; Melchiorre, P. *Angew. Chem., Int. Ed.* **2016**, *55*, 3313.

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