ChemComm

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Chem. Commun.*, 2019, **55**, 314

Received 9th October 2018,
Accepted 30th November 2018

DOI: 10.1039/c8cc08064j

rsc.li/chemcomm

Manganese catalyzed α-methylation of ketones with methanol as a C1 source†

Antoine Bruneau-Voisine,[ab] Lenka Pallova,[b] Stéphanie Bastin,[b] Vincent César[b] and Jean-Baptiste Sortais*[bc]

The direct α-methylation of ketones with methanol under hydrogen borrowing conditions using a well-defined manganese PN^{3}P complex as a pre-catalyst was, for the first time, achieved. The reactions typically proceed at 120 °C for 20 h with 3 mol% pre-catalyst loading and in the presence of NaO*t*Bu (50 mol%) as base. The scope of the reaction was extended to the α-methylation of esters.

α-Methylated carbonyl functions are often encountered in biologically active molecules.[1] Characteristically, α-alkylation of ketones is achieved by reaction of the corresponding enolate with an alkyl halide, thus generating stoichiometric amounts of wastes. In the prospect of sustainable chemistry, new strategies to introduce a methyl group under catalytic conditions starting from renewable resources and in an atom economical manner are indeed highly desirable.[2] In this respect, alkylation at the α-position of carbonyl derivatives with alcohols under hydrogen borrowing conditions providing water as the sole by-product constitutes an inviting strategy.[3] Complementarily, methanol, which is produced on an industrial scale from a wide variety of sources including renewable ones,[4,5] represents a very attractive C1 source for an environmentally benign, inexpensive, and abundant alkylating agent.[6]

Yet, although alkylation of ketones with alcohols in the presence of homogeneous catalysts based on precious metals,[3a,b] including Ru,[7] Rh,[8] Ir,[9] and Re,[10] is well established, α-methylation using methanol still remains challenging[11] due to its higher activation barrier for the dehydrogenation step into aldehydes compared to heavier alcohols.[12] In this context, the implementation of an efficient system based on inexpensive and abundant base metals constitutes an additional challenge,[13] with some successes being recently reported by Liu[14] then Morril[15] using cobalt or iron-based catalysts, respectively.

The potential of manganese in (de)-hydrogenation reactions as an alternative to noble metals[16] has been demonstrated with the seminal works of Beller in hydrogenation[17] and Milstein in dehydrogenative coupling of amines with alcohols.[18] Since then, several reactions based on hydrogen borrowing processes involving alcohols have been developed[19] and a few well defined homogeneous manganese-based catalysts (Chart 1) proved their ability to promote complete dehydrogenation of methanol,[20] *N*-formylation,[21] aminomethylation[22] and *N*-methylation reactions,[19a,23] demonstrating that MeOH associated with manganese can be efficiently used as a C1 source *via* a partial oxidation. In line with our interest in manganese organometallic catalysis,[24] we report here, for the first time, the α-methylation of carbonyl compounds using methanol as an alkylating reagent.

The optimisation of the reaction conditions was carried out considering the methylation of propiophenone **a1** with methanol (Scheme 1) as the model reaction (Table 1). Initial assessments were performed in sealed ACE® pressure tubes at 120 °C for 20 h.

In the presence of catalyst **5** (5 mol%) and NaO*t*Bu (20 mol%), the ketone was converted in 93% yield, the major product being the desired isobutyrophenone **b1**, isolated in 55% yield (entry 1). It is worth noting that 1,5-diphenyl-2,4-dimethylpenta-1,5-dione **c1** resulting from the Michael addition of the enolate onto the transient enone **e1** is the sole by-product observed at the end of the reaction, indicating that the hydrogenation step is relatively slow compared to the Michael addition.[25] None of the possible side products (*i.e.* alcohol **d1**, resulting from transfer hydrogenation,[26] enone **e1**, or methyl ether **f1**) were detected by ^{1}H NMR or GC-MS in the crude mixture. Diluting the reaction mixture and increasing the amount of base to 0.5 equivalent finally allowed full conversion and

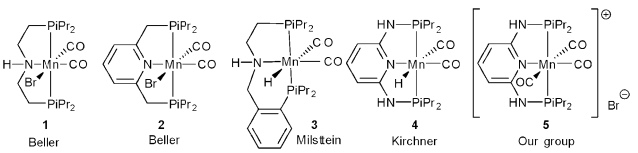
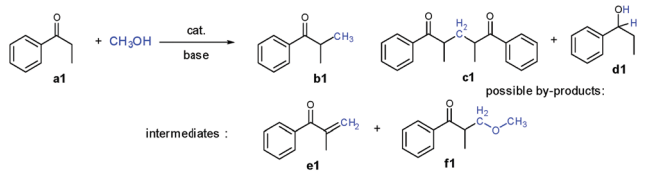


Chart 1 Manganese catalysts promoting reactions with methanol.

[a] *Univ Rennes, CNRS, ISCR – UMR 6226, F-35000 Rennes, France*
[b] *LCC-CNRS, Université de Toulouse, CNRS, UPS, Toulouse, France. E-mail: jean-baptiste.sortais@lcc-toulouse.fr*
[c] *Institut Universitaire de France, 1 rue Descartes, F-75231 Paris Cedex 05, France*

† Electronic supplementary information (ESI) available: Experimental procedures and characterization of the products. See DOI: 10.1039/c8cc08064j



Scheme 1 Methylation of propiophenone **a1** with MeOH.

Table 1 Optimization of the parameters of the α-methylation of **a1** catalysed by **5**

Entry	*t*BuONa (mol%)	CH_3OH (mL)	Toluene (mL)	Conv. (%)	Yield[c] **b1**	Yield[c] **c1**
1[a]	20	1	1	93	55 (55)	39 (14)
2[a]	50	2	4	98	90	10
3	50	2	4	99	87 (64)	13
4[b]	50	6	12	50	44	6
5	50	6	0	99	84	16
6[d]	50	2	4	29	11	18
7[d]	100	0.5	0.5	99	33	66 (63)
8[e]	100	2	4	<5	<5	<5

Reaction conditions: in a glovebox, an Ace® pressure tube was charged with propiophenone **a1** (0.5 mmol, 66 μL), MeOH, toluene, Mn complex **5** (3 mol%, 8.4 mg), and base, in that order. The closed pressure tube was then heated at 120 °C for 20 h.[a] 5 mol% of Mn complex **5** (14 mg). [b] Propiophenone **a1** (1.5 mmol, 198 μL) and Mn complex **5** (1.5 mol%, 16 mg). [c] NMR yield determined by ^{1}H NMR spectroscopy and compared with GC/MS of the crude mixture. Isolated yields in parentheses. [d] 100 °C. [e] No Mn catalyst.

good selectivity toward the desired methylated ketone **b1** (90% NMR yield, entry 2).

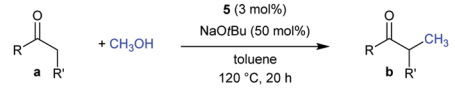
The catalyst loading could be decreased to 3 mol% while maintaining high conversion and good selectivity (entry 3), but further lowering to 1.5 mol% had a detrimental effect on conversion (entry 4). This model reaction could be carried out in pure MeOH with comparable results (entry 5), but during the reaction scope development, it appeared that toluene greatly improved the solubility of most substrates (*vide infra*, Table 2). Lowering the temperature to 100 °C resulted in a drastic decrease of the conversion rate to 29% (entry 6). Different alternative bases such as *t*BuOK, KHMDS, and K_3PO_4 have been evaluated, leading to similar conversions and selectivities (Table S1, ESI†).

Finally, reasoning that 1,5-diketones are valuable products as starting materials for the synthesis of pyridines[27] or cyclic alkenes,[28] the formation of **c1** was tentatively optimized. Carrying out the reaction at higher concentration in the presence of catalyst **5** (3 mol%) and a stoichiometric amount of base at 100 °C afforded the 1,5-diphenyl-2,4-dimethyl-penta-1,5-dione **c1** in 66% yield (Table 1, entry 7).[29] A blank test omitting the manganese catalyst (Table 1, entry 8) led to no conversion.

With the optimized conditions in hand, a series of ketones were methylated with methanol (Table 2). Propiophenone **a1** and acetophenone **a2** led to the same product, namely, isobutyrophenone **b1**, in 87% and 67% NMR yield, respectively.

It is worth noting that in the case of acetophenone **a2**, which is less sterically hindered than **a1**, more 1,5-diketone was formed;

Table 2 Scope of the α-methylation of ketones with methanol in the presence of **5** as a precatalyst. Typical reaction conditions: in a glovebox, an Ace® pressure tube was charged with ketone (0.5 mmol), MeOH (2 mL), toluene (4 mL), **5** (3 mol%, 8.4 mg) and NaO*t*Bu (50 mol%, 24.0 mg), in that order. The closed pressure tube was then heated at 120 °C for 20 h. Yields were determined by ^{1}H NMR analysis of the crude mixture and confirmed by GC-MS analysis



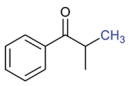
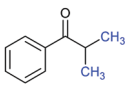
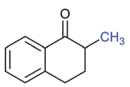
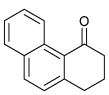
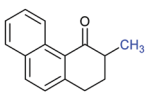
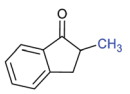
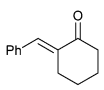
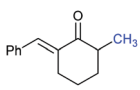
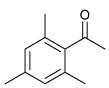
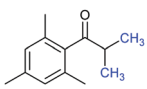
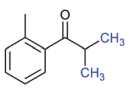
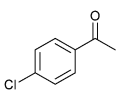
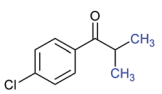
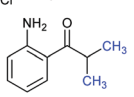
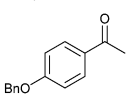
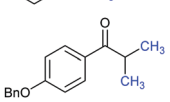
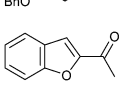
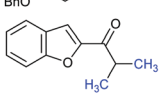
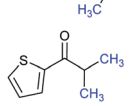
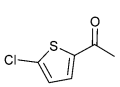
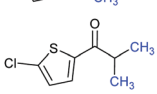
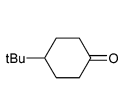
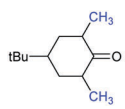
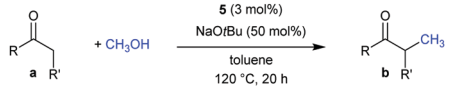
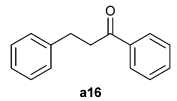
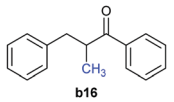
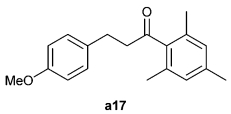
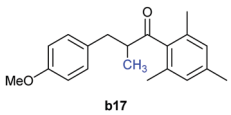
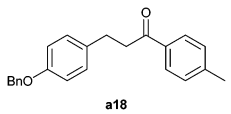
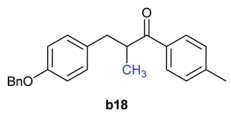
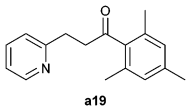
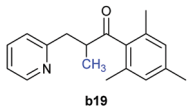
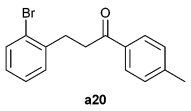
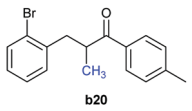
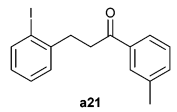
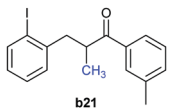
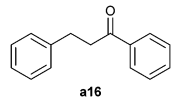
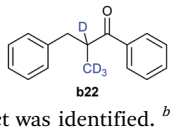
Entry	Substrate		Product		NMR yield (%) (isolated yield)
1		**a1**		**b1**	87 (64)
2		**a2**		**b1**	67 (43)
3		**a3**		**b3**	82 (38)
4		**a4**		**b4**	85 (79)
5		**a5**		**b5**	95 (46)
6		**a6**		**b6**	73 (51)
7		**a7**		**b7**	92 (66)
8		**a8**		**b8**	80 (71)
9		**a9**		**b9**	65 (56)
10		**a10**		**b10**	45 (40)
11		**a11**		**b11**	80 (78)
12		**a12**		**b12**	n.d. (46)
13		**a13**		**b13**	87 (41)
14		**a14**		**b14**	n.d. (34)
15		**a15**		**b15**	30 (23)

Table 2 (*continued*)



Entry	Substrate	Product	NMR yield (%) (isolated yield)
16	 a16	 b16	95 (80)
17	 a17	 b17	99 (93)
18	 a18	 b18	93 (86)
19	 a19	 b19	60 (51)
20	 a20	 b20	82 (82)
21	 a21	 b21	67 (42[a])
22	 a16	 b22	84 (82[b])

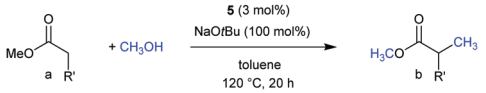
[a] 10% of the deiodination product was identified. [b] CD_3OD instead of MeOH.

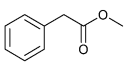
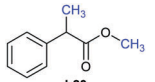
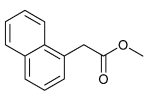
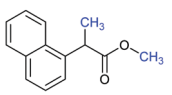
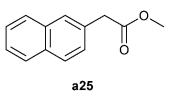
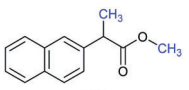
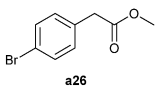
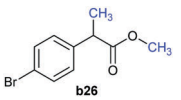
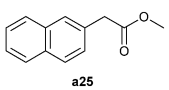
cyclic ketones including α-tetralone **a3**, 2,3-dihydrophenanthren-4(1*H*)-one **a4**, 1-indanone **a5**, and 2-benzylidenecyclohexanone **a6** were methylated in moderate to good yields (82%, 85%, 95%, and 73%, respectively). Steric hindrance actually disfavored the formation of the undesired 1,5-diketones, allowing the double methylation of 2′,4′,6′-trimethylacetophenone **a7** and 2′-methylacetophenone **a8** in high yields (92%, and 80%, respectively). This protocol is also tolerant toward chlorinated substrate **a9** to afford the corresponding 4-chloroisobutyrophenone **b9** (65%), this being in line with the functional group tolerance observed for the hydrogenation of ketones.[30] In the case of 2′-aminoacetophenone **a10**, the methylation occurred at the α-position of the carbonyl function, with the isobutyrophenone derivative being obtained as the major product. This result contrasts with the *N*-methylation of 4′-aminoacetophenone using the same catalyst under similar reaction conditions where the methylation occurred at the nitrogen.[23b] It is likely that intramolecular hydrogen bonds N–H···O favor the formation of the enolate and direct the selectivity. Besides, we have previously noticed that *ortho*-substituted anilines were more difficult to methylate.[23b] 2-Acetylbenzofuran **a12** and thiophene derivatives **a13** and **a14** were α-methylated under these conditions (entries 12–14). 4-*tert*-Butylcyclohexanone **a15** was dimethylated in moderate yield (30%) due to the formation of the corresponding undesired 1,5-diketone. The methylation of propiophenone **a1** also proceeded well in the presence of competing substrates such as fluoro- and trifluoromethyl-benzene, 1-octene or 4-nitrotoluene (Table S2, ESI†).

Dihydrochalcone **a16**, in which the transient enolate and enone are stabilized by the phenyl ring, was methylated in very high yield (95%). A series of dihydrochalcone derivatives **a17–a21** were subsequently methylated. The presence of a pyridinyl moiety in **a19** had a detrimental impact on the yield of the reaction (60%). Interestingly, the catalytic system tolerated brominated substrate **a20**, but dehalogenation (about 10%) was observed with the iodo derivative **a21**. Finally, deuterated methanol CD_3OD was successfully employed as an alkylating agent, allowing the introduction of the deuterated CD_3 fragment in **b22** (82% isolated yield).

The scope of the reaction was finally extended to the catalytic α-methylation of esters (Table 3),[31] which has barely been achieved, even using noble metal precatalysts.[11d] Under the same reaction conditions as above yet in the presence of one equivalent of base, several aryl acetic esters **a23–a26** were methylated with methanol in moderate to good yields (Table 3), including the brominated substrate (**a26**) and deuterated product (**b27**). It is worth noting that isolation of the methylated esters as pure products was difficult, thus leading to low yields.

Table 3 Scope of the α-methylation of esters with methanol in the presence of **5** as a precatalyst. Conditions: in a glovebox, an Ace® pressure tube was charged with ester (0.5 mmol), MeOH (2 mL), toluene (4 mL), **5** (3 mol%, 8.4 mg) and NaO*t*Bu (100 mol%, 48.1 mg), in that order. The closed pressure tube was then heated at 120 °C for 20 h. Yields were determined by ^{1}H NMR analysis of the crude mixture and confirmed by GC/MS analysis



Entry	Substrate	Product	NMR yield (%) (isolated yield)
1	 a23	 b23	95
2	 a24	 b24	95 (31)
3	 a25	 b25	50 (37[a])
4	 a26	 b26	68 (35)
5	 a25	 b27	n.d. (20[b])

[a] 50 mol% of *t*BuOK (24 mg) was used. [b] CD_3OD instead of MeOH, 48 h.

In conclusion, the manganese-catalyzed α-alkylation of ketones using methanol as a green alkylating reagent was, for the first time, achieved in the presence of a manganese catalyst based on a 2,6-diaminopyridine scaffold. The defined protocol could be successfully extended to the even more challenging ester derivatives, demonstrating further the great potential of manganese catalysis in the field of (de)-hydrogenation reactions.

We thank Noël Lugan for discussions, and the Centre National de la Recherche Scientifique (CNRS), the Université Paul Sabatier, the Institut Universitaire de France (IUF) and the Agence Nationale de la Recherche (ANR Agency, grant JCJC ANR-15-CE07-0001).

Conflicts of interest

There are no conflicts to declare.

Notes and references

1 E. J. Barreiro, A. E. Kümmerle and C. A. M. Fraga, *Chem. Rev.*, 2011, **111**, 5215–5246.
2 (*a*) C. S. Yeung and V. M. Dong, *Chem. Rev.*, 2011, **111**, 1215–1292; (*b*) P. T. Anastas and J. C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, 2000.
3 (*a*) Y. Obora, *ACS Catal.*, 2014, **4**, 3972–3981; (*b*) M. H. S. A. Hamid, P. A. Slatford and J. M. J. Williams, *Adv. Synth. Catal.*, 2007, **349**, 1555–1575; (*c*) G. Guillena, D. J. Ramón and M. Yus, *Chem. Rev.*, 2010, **110**, 1611–1641; (*d*) A. Corma, J. Navas and M. J. Sabater, *Chem. Rev.*, 2018, **118**, 1410–1459.
4 (*a*) G. A. Olah, *Angew. Chem., Int. Ed.*, 2013, **52**, 104–107; (*b*) G. A. Olah, *Angew. Chem., Int. Ed.*, 2005, **44**, 2636–2639.
5 http://www.methanol.org, retrieved June 29th 2018.
6 (*a*) C. Chauvier and T. Cantat, *ACS Catal.*, 2017, **7**, 2107–2115; (*b*) K. Natte, H. Neumann, M. Beller and R. V. Jagadeesh, *Angew. Chem., Int. Ed.*, 2017, **56**, 6384–6394.
7 (*a*) C. S. Cho, B. T. Kim, T.-J. Kim and S. C. Shim, *J. Org. Chem.*, 2001, **66**, 9020–9022; (*b*) A. R. Sahoo, G. Lalitha, V. Murugesh, C. Bruneau, G. V. M. Sharma, S. Suresh and M. Achard, *J. Org. Chem.*, 2017, **82**, 10727–10731.
8 R. Grigg, T. R. B. Mitchell, S. Sutthivaiyakit and N. Tongpenyai, *J. Chem. Soc., Chem. Commun.*, 1981, 611–612.
9 K. Taguchi, H. Nakagawa, T. Hirabayashi, S. Sakaguchi and Y. Ishii, *J. Am. Chem. Soc.*, 2004, **126**, 72–73.
10 P. Piehl, M. Pena-Lopez, A. Frey, H. Neumann and M. Beller, *Chem. Commun.*, 2017, **53**, 3265–3268.
11 (*a*) L. K. M. Chan, D. L. Poole, D. Shen, M. P. Healy and T. J. Donohoe, *Angew. Chem., Int. Ed.*, 2014, **53**, 761–765; (*b*) S. Ogawa and Y. Obora, *Chem. Commun.*, 2014, **50**, 2491–2493; (*c*) X. Quan, S. Kerdphon and P. G. Andersson, *Chem. – Eur. J.*, 2015, **21**, 3576–3579; (*d*) T. T. Dang and A. M. Seayad, *Adv. Synth. Catal.*, 2016, **358**, 3373–3380; (*e*) S. M. A. H. Siddiki, A. S. Touchy, M. A. R. Jamil, T. Toyao and K.-i. Shimizu, *ACS Catal.*, 2018, **8**, 3091–3103; (*f*) R. L. Wingad, E. J. E. Bergström, M. Everett, K. J. Pellow and D. F. Wass, *Chem. Commun.*, 2016, **52**, 5202–5204; (*g*) K. Chakrabarti, M. Maji, D. Panja, B. Paul, S. Shee, G. K. Das and S. Kundu, *Org. Lett.*, 2017, **19**, 4750–4753.
12 (*a*) W.-H. Lin and H.-F. Chang, *Catal. Today*, 2004, **97**, 181–188; (*b*) M. Qian, M. A. Liauw and G. Emig, *Appl. Catal., A*, 2003, **238**, 211–222.
13 R. M. Bullock, *Science*, 2013, **342**, 1054–1055.
14 Z. Liu, Z. Yang, X. Yu, H. Zhang, B. Yu, Y. Zhao and Z. Liu, *Org. Lett.*, 2017, **19**, 5228–5231.
15 K. Polidano, B. D. W. Allen, J. M. J. Williams and L. C. Morrill, *ACS Catal.*, 2018, **8**, 6440–6445.
16 (*a*) D. A. Valyaev, G. Lavigne and N. Lugan, *Coord. Chem. Rev.*, 2016, **308**, 191–235; (*b*) F. Kallmeier and R. Kempe, *Angew. Chem., Int. Ed.*, 2018, **57**, 46–60.
17 S. Elangovan, C. Topf, S. Fischer, H. Jiao, A. Spannenberg, W. Baumann, R. Ludwig, K. Junge and M. Beller, *J. Am. Chem. Soc.*, 2016, **138**, 8809–8814.
18 A. Mukherjee, A. Nerush, G. Leitus, L. J. W. Shimon, Y. Ben David, N. A. Espinosa Jalapa and D. Milstein, *J. Am. Chem. Soc.*, 2016, **138**, 4298–4301.
19 (*a*) S. Elangovan, J. Neumann, J.-B. Sortais, K. Junge, C. Darcel and M. Beller, *Nat. Commun.*, 2016, **7**, 12641; (*b*) N. Deibl and R. Kempe, *Angew. Chem., Int. Ed.*, 2017, **56**, 1663–1666; (*c*) F. Kallmeier, B. Dudziec, T. Irrgang and R. Kempe, *Angew. Chem., Int. Ed.*, 2017, **56**, 7261–7265; (*d*) M. Mastalir, M. Glatz, N. Gorgas, B. Stöger, E. Pittenauer, G. Allmaier, L. F. Veiros and K. Kirchner, *Chem. – Eur. J.*, 2016, **22**, 12316–12320; (*e*) M. Mastalir, M. Glatz, E. Pittenauer, G. Allmaier and K. Kirchner, *J. Am. Chem. Soc.*, 2016, **138**, 15543–15546; (*f*) M. Peña-López, P. Piehl, S. Elangovan, H. Neumann and M. Beller, *Angew. Chem., Int. Ed.*, 2016, **55**, 14967–14971; (*g*) N. V. Kulkarni, W. W. Brennessel and W. D. Jones, *ACS Catal.*, 2018, **8**, 997–1002; (*h*) U. K. Das, Y. Ben-David, Y. Diskin-Posner and D. Milstein, *Angew. Chem., Int. Ed.*, 2018, **57**, 2179–2182; (*i*) M. K. Barman, S. Waiba and B. Maji, *Angew. Chem., Int. Ed.*, 2018, **57**, 9126–9130; (*j*) D. H. Nguyen, X. Trivelli, F. Capet, J.-F. Paul, F. Dumeignil and R. M. Gauvin, *ACS Catal.*, 2017, **7**, 2022–2032.
20 M. Andérez-Fernández, L. K. Vogt, S. Fischer, W. Zhou, H. Jiao, M. Garbe, S. Elangovan, K. Junge, H. Junge, R. Ludwig and M. Beller, *Angew. Chem., Int. Ed.*, 2017, **56**, 559–562.
21 S. Chakraborty, U. Gellrich, Y. Diskin-Posner, G. Leitus, L. Avram and D. Milstein, *Angew. Chem., Int. Ed.*, 2017, **56**, 4229–4233.
22 M. Mastalir, E. Pittenauer, G. Allmaier and K. Kirchner, *J. Am. Chem. Soc.*, 2017, **139**, 8812–8815.
23 (*a*) J. Neumann, S. Elangovan, A. Spannenberg, K. Junge and M. Beller, *Chem. – Eur. J.*, 2017, **23**, 5410–5413; (*b*) A. Bruneau-Voisine, D. Wang, V. Dorcet, T. Roisnel, C. Darcel and J.-B. Sortais, *J. Catal.*, 2017, **347**, 57–62.
24 (*a*) D. Wei, A. Bruneau-Voisine, D. A. Valyaev, N. Lugan and J.-B. Sortais, *Chem. Commun.*, 2018, **54**, 4302–4305; (*b*) D. Wei, A. Bruneau-Voisine, T. Chauvin, V. Dorcet, T. Roisnel, D. A. Valyaev, N. Lugan and J.-B. Sortais, *Adv. Synth. Catal.*, 2018, **360**, 676–681; (*c*) H. Li, D. Wei, A. Bruneau-Voisine, M. Ducamp, M. Henrion, T. Roisnel, V. Dorcet, C. Darcel, J.-F. Carpentier, J.-F. Soulé and J.-B. Sortais, *Organometallics*, 2018, **37**, 1271–1279; (*d*) D. Wang, A. Bruneau-Voisine and J.-B. Sortais, *Catal. Commun.*, 2018, **105**, 31–36; (*e*) A. Bruneau-Voisine, D. Wang, V. Dorcet, T. Roisnel, C. Darcel and J.-B. Sortais, *Org. Lett.*, 2017, **19**, 3656–3659; (*f*) J. Zheng, S. Chevance, C. Darcel and J.-B. Sortais, *Chem. Commun.*, 2013, **49**, 10010–10012; (*g*) J. Zheng, S. Elangovan, D. A. Valyaev, R. Brousses, V. César, J.-B. Sortais, C. Darcel, N. Lugan and G. Lavigne, *Adv. Synth. Catal.*, 2014, **356**, 1093–1097; (*h*) D. A. Valyaev, D. Wei, S. Elangovan, M. Cavailles, V. Dorcet, J.-B. Sortais, C. Darcel and N. Lugan, *Organometallics*, 2016, **35**, 4090–4098.
25 For the proposed mechanism, see the ESI†.
26 In contrast, using *n*-butanol or benzyl alcohol instead of methanol led to 1-phenylpropan-1-ol as the main product.
27 T. W. Bell and S. D. Rothenberger, *Tetrahedron Lett.*, 1987, **28**, 4817–4820.
28 A. Fürstner and B. Bogdanović, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2442–2469.
29 Under the same conditions, 2,2′-methyleneditetralone **c3** was obtained starting from α-tetralone in 38% isolated yield, see the ESI†.
30 A. Bruneau-Voisine, D. Wang, T. Roisnel, C. Darcel and J.-B. Sortais, *Catal. Commun.*, 2017, **92**, 1–4.
31 In the case of amides: for acetanilide, only *N*-methylaniline (*ca.* 25%) resulting from trans-esterification/methylation was detected. In contrast, the lactam 2-oxindole **a28** was methylated in good isolated yield (**b28**, 71%). See the ESI†.