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Cobalt(III)-Catalyzed Alkylation of Primary C(sp^3)-H Bonds with Diazo Compounds

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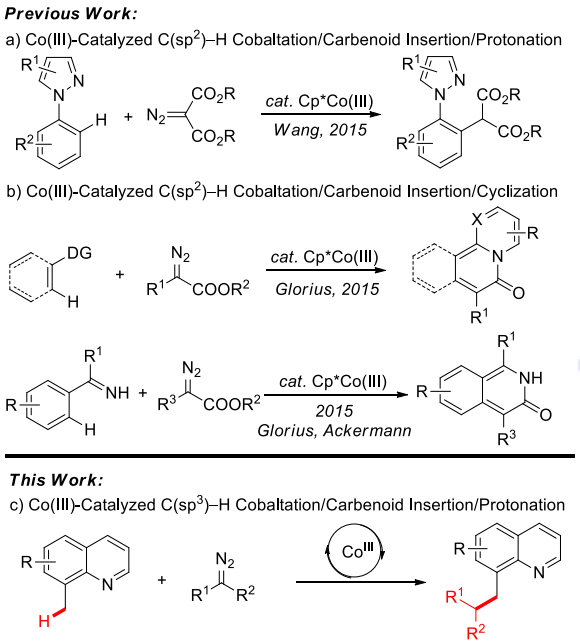
Abstract. Chelation-assisted C(sp^2)–H metalation/carbenoid insertion has been well investigated. However, the analogous carbene functionalization of C(sp^3)–H bonds remains a great challenge. Here we report the first Cobalt(III)-catalyzed alkylation of 8-methylquinolines with diazo compounds through primary C(sp^3)–H cobaltation/carbenoid insertion. The reaction is highly efficient, scalable and tolerates a variety of functional groups. Furthermore, the unique protocol can be applied to the synthesis of azatricyclic antibiotic compounds.

Keywords: cobalt; carbenoid insertion; alkylation; C(sp^3)–H activation; diazo compounds

Over the past decade, metal-carbene insertion into aliphatic C-H bonds has emerged as a powerful strategy to construct C-C bonds.[1] The classic metal-carbene insertion proceeds with a concerted reaction mechanism and exhibits high levels of selectivity controlled by electronic effects, showing an order of activation of tertiary > secondary >> primary C(sp^3)–H. Although significant progress has been achieved on the insertion into tertiary and secondary C(sp^3)–H, the analogous carbene functionalization of primary C(sp^3)–H bonds remains a great challenge.[2]

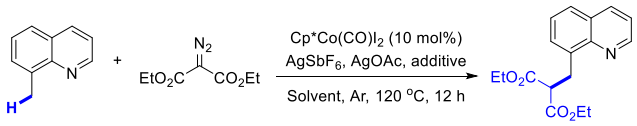
Recently, the pioneering work by Wang, Satoh, and Miura on metal-catalyzed C-H alkylation of 1,3-azoles with N-tosylhydrazones demonstrated that an alternative new reaction pattern was also operative.[3] In contrast to the classic concerted metal-carbene insertion, this novel process is believed to follow a pathway involving C–H metalation, metal-carbene formation, and subsequent migratory insertion.[4] Shortly after, a significant breakthrough was made by Yu and co-workers, who elegantly reported the first example of chelation-assisted insertion of aromatic C(sp^2)–H bonds into α-diazomalonates using a Rh(III) catalyst.[5] Since then, chelation-assisted metal-catalyzed carbene migratory insertion into C(sp^2)-H bonds has been thoroughly studied by Rovis, Li, Glorius, Wang, Ackermann and many others.[6-8] Despite these elegant progress, this novel reaction protocol is limited to the migratory insertion of diazo compounds into aromatic or alkenyl C(sp^2)–H bonds and only one example of Rh(III)-catalyzed carbene insertion into non-acidic primary C(sp^3)-H bonds has been realized by Zhou recently.[9] In this respect, novel designs and the development of a complementary reaction to enable the selective carbene functionalization of primary C(sp^3)–H bonds, which overwhelms the inherent selectivity of classic metal-carbene insertion and C–H metalation/carbene migratory insertion, would be highly desirable, yet challenging.



Scheme 1. Cp*Co(III)-Catalyzed C–H Functionalization with Diazo Compounds.

More recently, the use of earth-abundant first-row transition metal catalysts, such as cobalt, has received tremendous attention.[10] In particular, since the pioneering work of Kanai and Matsunaga,[11] high-valent Cp*Co(III) (Cp* = pentamethylcyclopentadienyl) has been recognized as a robust and versatile catalyst due to its excellent reactivity.[12] However, so far, only a few examples of Co(III)-catalyzed carbene migratory insertion into C(sp^2)–H bonds have been reported. In 2015, Wang reported Cp*Co(III)-catalyzed alkylation of (hetero)arenes with α-diazomalonates (Scheme 1a).[8a] Glorius realized the first example of Cp*Co(III)-catalyzed C–H coupling with diazo compounds to construct conjugated polycyclic hydrocarbons with tunable emission wavelengths (Scheme 1b).[8b] Later, Glorius and Ackermann reported Co(III)-catalyzed synthesis of isoquinoline derivatives with diazo compounds using imine as directing group, respectively (Scheme 1b).[8c,8d] Inspired by these reports and as a continuation of our interest in Cp*Co(III)-catalyzed C-H functionalization,[13] here we disclose the first Co(III)-catalyzed alkylation of primary C(sp^3)–H bonds with diazo compounds (Scheme 1c). Mechanistically, this protocol proceeds through a quinolyl-directed C(sp^3)–H cobaltation, Co-carbene formation, migratory insertion and subsequent protonation. The reaction is scalable and has been successfully applied to the synthesis of azatricyclic antibiotic compounds.

Table 1. Optimization of the reaction conditions.[a]

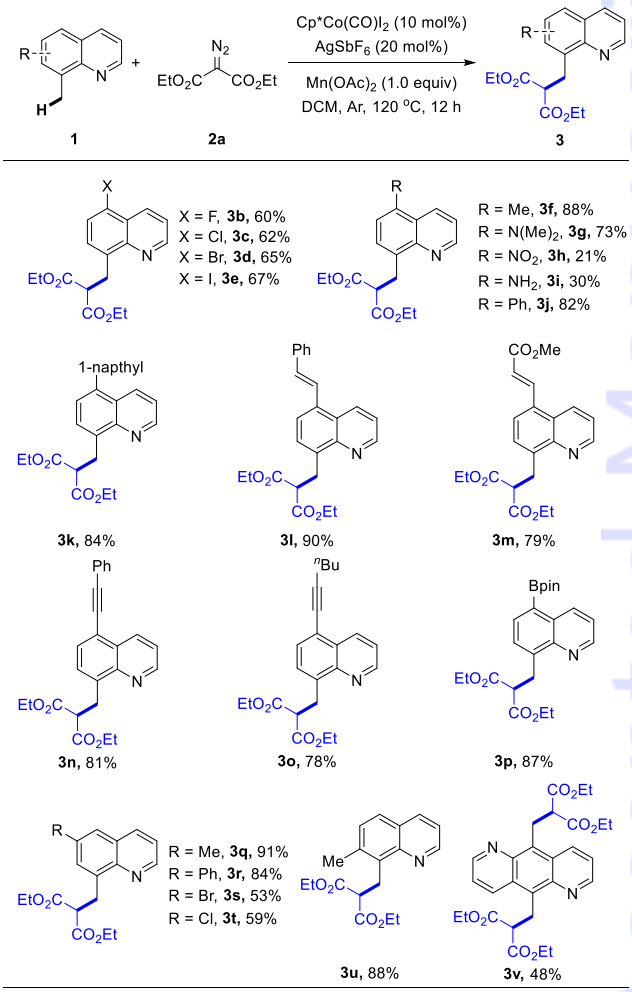


Entry	AgOAc (mol%)	Additive (equiv)	Solvent	Yield (%)[b]
1	20	NaOAc (0.2)	DCE	10
2	20	NaOAc (0.2)	DCM	37
3	20	NaOAc (0.2)	MeCN	0
4	20	NaOAc (0.2)	TFE	0
5	20	$Mn(OAc)_2$ (0.2)	DCM	45
6	20	$Mn(OAc)_2$ (1.0)	DCM	78
7	0	$Mn(OAc)_2$ (1.0)	DCM	89[c]
8[d]	0	$Mn(OAc)_2$ (1.0)	DCM	0

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), $Cp^*Co(CO)I_2$ (10 mol%), $AgSbF_6$ (20 mol%), solvent (1 mL), Ar, 120 °C, 12 h. [b] Yield were determined by ^1H NMR using CH_2Br_2 as internal standard. [c] Isolated yield. [d] No $Cp^*Co(CO)I_2$.

To begin, we chose 8-methylquinoline (**1a**) as model substrate,[14] and diethyl diazomalonate **2a** as coupling partner in the presence of 10 mol% of $Cp^*Co(CO)I_2$ as catalyst and catalytic amounts of $AgSbF_6$, AgOAc and NaOAc as additives in 1,2-dichloroethane at 120 °C for 12 h, and the desired product **3a** was afforded in 10% yield (Table 1, entry 1). A survey of different solvents led us to identify that dichloromethane (DCM) was the best reaction medium and the yield was increased to 37% (entries 2–4). $Mn(OAc)_2$ was found to be effective for the transformation, giving **3a** in 45% yield (entry 5). When the amount of $Mn(OAc)_2$ was increased to 1.0 equivalent, the desired product **3a** was obtained in 78% yield (entry 6). To our delight, when AgOAc was removed, the yield was further increased (entry 7, 89%). Finally, control experiment suggested that no desired product was observed when the reaction was conducted in the absence of $Cp^*Co(CO)I_2$.

Table 2. The substrate scope of 8-methylquinoline.[a]

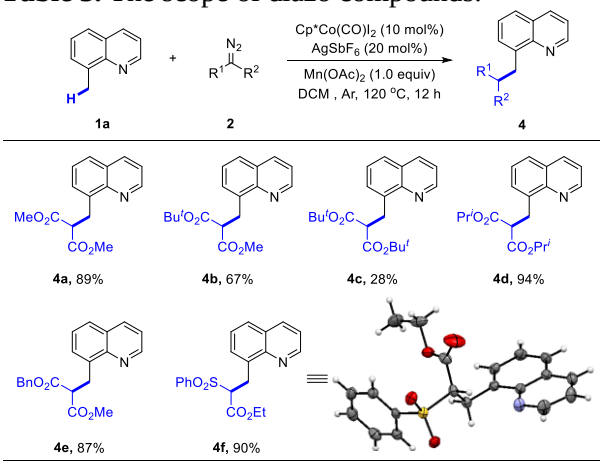


[a] Reaction conditions: **1** (0.1 mmol), **2a** (0.12 mmol), $Cp^*Co(CO)I_2$ (10 mol%), $AgSbF_6$ (20 mol%), $Mn(OAc)_2$ (1.0 equiv), DCM (1 mL) under Ar at 120 °C for 12 h. isolated yield.

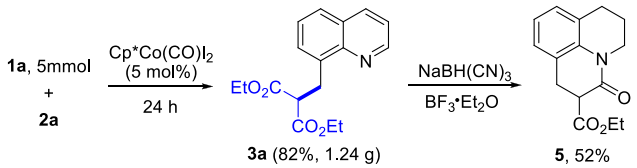
With the optimal reaction conditions in hand, we next investigated the substrate scope of substituted 8-methyl quinolines (Table 2). In general, diverse substituents at the C-5 position were tolerated with the reaction conditions (**3b-3p**). In particular, halides, such as fluoride,

chloride, bromide, and iodide, were all compatible with this protocol, giving the alkylated products in good yields (**3b**-**3e**, 60%-67%). The strong electron-withdrawing nitro group was also feasible, albeit giving the product in a reduced yield (**3h**, 21%). The amine group bearing free hydrogen atom was also tolerated, giving **3i** in 30% yield. Furthermore, the carbene migratory insertion occurred smoothly in the presence of alkenyl and alkynyl substituents on the backbone of the arene (**3l**-**3o**, 79%-90% yield). To our delight, Bpin group at C-5 position of quinoline, was also survived, affording the desired product **3p** in 87% yield; this was a synthetically important result as such substituent could serve as a versatile handle for cross-coupling reaction. Substituents at C-6 or the sterically hindered C-7 position of the quinoline also reacted smoothly with diethyl diazomalonate **2a** (**3q**-**3u**).

Table 3. The scope of diazo compounds.



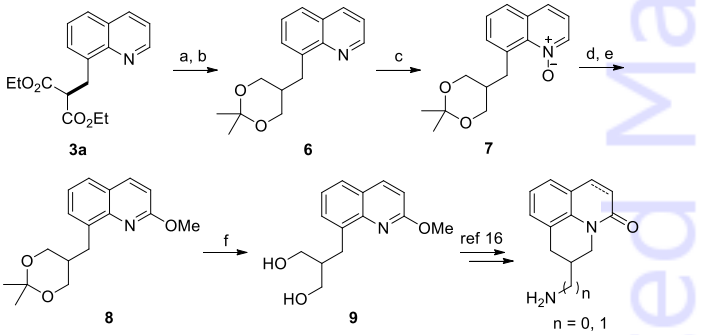
Next, we explored the reactivity of various carbene precursors with 8-methylquinoline **1a** (Table 3). Both the symmetrical and unsymmetrical diazomalonates (**4a**–**4e**) were compatible with the reaction. However, the coupling of **1a** with di-tert-butyl diazomalonate **2c** only gave the alkylated product **4c** in 28% yield. When ethyl 2-diazo-2-(phenylsulfonyl)acetate **2f** was used as carbene precursor, the alkylation product was obtained in excellent yield (**4f**, 90%). It's structure was unambiguously confirmed by X-crystallography.[15] Unfortunately, other α-diazocarbonyl compounds obtained from β-keto ester, β-diketo, α-aryl ester compounds failed to produce any desired product.



Scheme 2. Gram-scale synthesis and derivatization of **3a**.

To demonstrate the synthetic utility of this protocol, a scale-up reaction (5 mmol) has been conducted at a reduced catalyst loading (5 mol% $Cp^*Co(CO)I_2$), and the alkylated product **3a** was obtained in 82% yield (Scheme 2, 1.24 g). **3a** could be transformed to ethyl 3-oxo-1,2,3,5,6,7-hexahydropyrido[3,2,1-ij]quinoline-2-carboxylate **5** in 52% yield in the presence of $NaBH(CN)_3/BF_3{\cdot}Et_2O$.

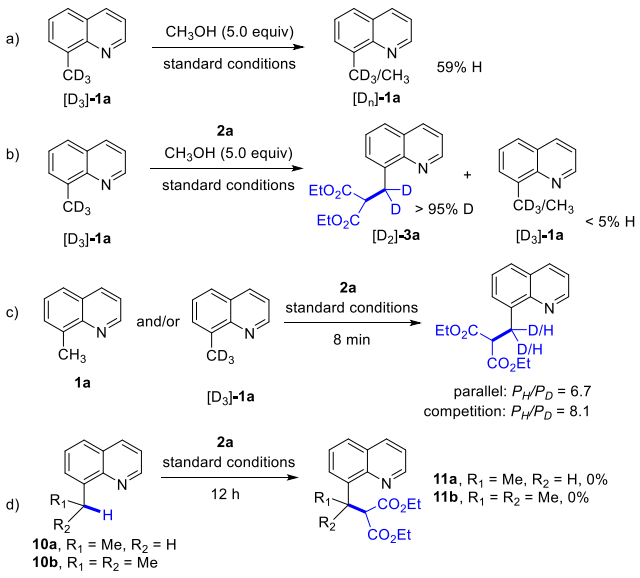
Moreover, the synthetic potential of this protocol was demonstrated by the elaboration of alkylated product **3a** to the important intermediate of azatricyclic antibiotic compounds (Scheme 3).[16] Reducing of **3a** with $LiAlH_4$, followed by protection of the corresponding diol with 2,2-dimethoxypropane, could give compound **6**, which could be oxidized to the N-oxide **7** in 64% yield with m-CPBA. After introduction of methoxyl group at the C-2 position and subsequent removal of the isoproylidene group, diol **9** was affored. The diol **9** could be further elaborated to azatricyclic antibiotic compounds.



Scheme 3. Synthesis the intermediate of azatricyclic antibiotic compounds. Reagents and conditions: a) $LiAlH_4$, THF, 6 h, 61%; b) 2,2-dimethoxypropane, TsOH, acetone, rt, 3 h, 93%; c) m-CPBA, $CHCl_3$, rt, overnight, 64%; d) benzoyl chloride, NaOH (aq), CH_2Cl_2, 0 °C, 1 h; e) MeI, DMF, K_2CO_3, 100 °C, 10 h, 47% for two steps; f) TFA/H_2O (1:1), rt, overnight, 85%.

In order to gain some insights into the mechanism of this reaction, a series of experiments have been performed. First, the reversibility of the C-H activation step was studied. A significant H/D exchange was observed when [D_3]-**1a** was subjected to the standard conditions in the absence of carbene precursor **2a** (Scheme 4a). However, essentially no H/D exchange was detected in the recovered starting material **1a** in the presence of **2a** (Scheme 4b). These results suggested that the carbene formation/migratory insertion process was significantly faster than the back reaction of

the C–H activation step. Second, the kinetic isotope effect was investigated in parallel and competition experiments (Scheme 4c). A P_H/P_D value of 6.7 (parallel experiment) and 8.1 (competition experiment) were observed. These rather large values of P_H/P_D indicate that cleavage of the C-H bond is likely involved in the rate-determining step.[17] Finally, we investigate whether the reaction mechanism could proceed in a classic concerted metal-carbene insertion or quinolyl-assisted primary C(sp^3)-H activation/carbenoid insertion. As shown in Scheme 4d, when 8-ethylquinoline (**10a**) and 8-isopropylquinoline (**10b**) were subjected to the standard reaction conditions respectively, no alkylated product was observed. The reaction tendency is in accordance with the quinolyl-assisted primary C(sp^3)-H activation/carbenoid insertion pathway.



Scheme 4. Mechanistic studies.

Based on the preliminary experimental results and literature precedents,[4-8] we proposed a plausible mechanism in Figure 1. The active catalyst Cp*Co^{III} **I** is generated by the ligand abstraction with $AgSbF_6$. Cobaltacycle **II** was formed by a rating-determining C-H bond cleavage process. Cobaltacycle **II** may further react with the diazo compound to form the metal–carbene intermediate **III** by dediazonization. Subsequently, cobalt-carbene migratory insertion affords intermediate **IV**, followed by protonation with the HOAc to afford the alkylated product and regenerates the active catalyst species **I**.

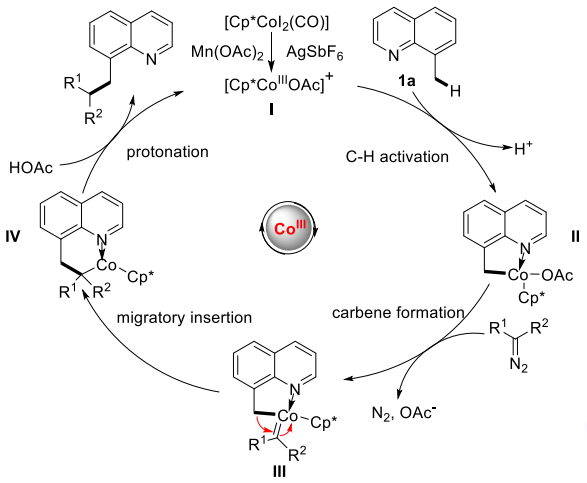


Figure 1. Plausible catalytic cycle.

In summary, we have developed for the first time an efficient Cp*Co(III)-catalyzed coupling 8-methylquinoline with diazo compounds via C(sp^3)−H bond activation process. The protocol tolerates a variety of functional group and can be scaled up easily. A plausible reaction mechanism has been proposed, moreover the alkylated products can be derived to synthesize important intermediate of azatricyclic antibiotic compounds. Further studies aimed at applying this catalytic system to other more challenging C(sp^3)−H bond are underway in our laboratory.

Experimental Section

General Procedure for the Alkylation of 8-Methylquinolines with Diazo Compounds. To a 50 mL Schlenk tube was added 8-aminoquinoline **1** (0.1 mmol), diazo compound **2** (0.12 mmol), $Mn(OAc)_2$ (17.3 mg, 0.1 mmol), Cp*$Co(CO)I_2$ (4.8 mg, 0.01 mmol), then $AgSbF_6$ (6.9 mg, 0.02 mmol) and DCM (1 mL). The vial was evacuated and filled with Ar (1 atm) and then stirred at 120 °C for 12 h. After cooling to room temperature, the mixture was diluted with ethyl acetate, filtrated through ceilt. After concentration, the resulting residue was purified by preparative TLC using hexane/EtOAc as the eluent to afford the product.

Acknowledgements

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References

[1] For recent reviews, see: a) H. M. L. Davies, D. Morton, *Chem. Soc. Rev.* **2011**, *40*, 1857; b) M. P. Doyle, R. Duffy, M. Ratnikov, L. Zhou, *Chem. Rev.* **2010**, *110*, 704; b) H. M. L. Davies, J. R. Manning, *Nature* **2008**, *451*, 417.

[2] For examples on steric-effect controlled site-selectivity using sterically more demanding rhodium catalysts, see: a) C. M. Qin, H. M. Davies, *J. Am. Chem. Soc.* **2014**, *136*, 9792; b) D. M. Guptill, H. M. L. Davies, *J. Am. Chem. Soc.* **2014**, *136*, 17718.

[3] a) X. Zhao, G. Wu, Y. Zhang, J. Wang, *J. Am. Chem. Soc.* **2011**, *133*, 3296; b) T. Yao, K. Hirano, T. Satoh, M. Miura, *Angew. Chem. Int. Ed.* **2012**, *51*, 775.

[4] For reviews, see: a) Q. Xiao, Y. Zhang, J. Wang, *Acc. Chem. Res.* **2013**, *46*, 236; b) Z. Liu, J. Wang, *J. Org. Chem.* **2013**, *78*, 10024; c) Y. Xia, Y. Zhang, J. Wang, *ACS Catal.* **2013**, *3*, 2586; d) F. Hu, Y. Xia, C. Ma, Y. Zhang, J. Wang, *Chem. Commun.* **2015**, *51*, 7986; e) M. Peña-López, M. Beller, *Angew. Chem. Int. Ed.* **2017**, *56*, 46.

[5] W.-W. Chan, S.-F. Lo, Z. Zhou, W.-Y. Yu, *J. Am. Chem. Soc.* **2012**, *134*, 13565.

[6] For selected representative examples catalyzed by Rh(III), see: a) T. K. Hyster, K. E. Ruhl, T. Rovis, *J. Am. Chem. Soc.* **2013**, *135*, 5364; b) Z. Shi, D. C. Koester, M. Boultadakis- Arapinis, F. Glorius, *J. Am. Chem. Soc.* **2013**, *135*, 12204; c) X.-Z. Yu, S.-J. Yu, J. Xiao, B.-S. Wan, X.-W. Li, *J. Org. Chem.* **2013**, *78*, 5444; d) S. Cui, Y. Zhang, D. Wang, Q. Wu, *Chem. Sci.* **2013**, *4*, 3912; e) F.-D. Hu, Y. Xia, F. Ye, Z.-X. Liu, C. Ma, Y. Zhang, J.-B. Wang, *Angew. Chem., Int. Ed.* **2014**, *53*, 1364; f) J. Jeong, P. Patel, H. Hwang, S. Chang, *Org. Lett.* **2014**, *16*, 4598; g) S. G. Dawande, V. Kanchupalli, J. Kalepu, H. Chennamsetti, B. S. Lad, S. Katukojvala, *Angew. Chem., Int. Ed.* **2014**, *53*, 4076; h) Y. Liang, K. Yu, B. Li, S. Xu, H. Song, B. Wang, *Chem. Commun.* **2014**, *50*, 6130; i) Y. Zhang, J. Zheng, S. Cui, *J. Org. Chem.* **2014**, *79*, 6490; j) H.-W. Lam, K.-Y. Man, W.-W. Chan, Z.-Y. Zhou, W.-Y. Yu, *Org. Biomol. Chem.* **2014**, *12*, 4112; k) W. Ai, X. Yang, Y. Wu, X. Wang, Y. Li, Y. Yang, B. Zhu, *Chem. Eur. J.* **2014**, *20*, 17653; l) L.-L. Shi, K. Yu, B.-Q. Wang, *Chem. Commun.* **2015**, *51*, 17277; m) B. Zhou, Z. Chen, Y. Yang, W. Ai, H. Tang, Y. Wu, W. Zhu, Y. Li, *Angew. Chem. Int. Ed.* **2015**, *54*, 12121; n) Y. Yang, X. Wang, Y. Li, B. Zhou, *Angew. Chem. Int. Ed.* **2015**, *54*, 15400; o) S. Sharma, S. H. Han, S. Han, W. Ji, J. Oh, S.-Y. Lee, J. S. Oh, Y. H. Jung, I. S. Kim, *Org. Lett.* **2015**, *17*, 2852; p) S.-J. Yu, S. Liu, Y. Lan, B.-S. Wan, X.-W. Li, *J. Am. Chem. Soc.* **2015**, *137*, 1623; q) J. Zhou, J. Shi, X. Liu, J. Jia, H. Song, H. E. Xu, W. Yi, *Chem. Commun.* **2015**, *51*, 5868; r) R. B. Dateer, S. Chang, *Org. Lett.* **2016**, *18*, 68; s) D. Das, A. Biswas, U. Karmakar, S. Chand, R. Samanta, *J. Org. Chem.* **2016**, *81*, 842; t) Z. Qi, S. Yu, X. Li, *Org. Lett.* **2016**, *18*, 700; u) J.-Q. Wu, Z. Yang, S.-S. Zhang, C.-Y. Jiang, Q.-J. Li, Z.-S. Huang, H.-G. Wang, *ACS Catal.* **2015**, *5*, 6453.

[7] For representative examples catalyzed by Ir(III), see: a) Y. Xia, Z. Liu, S. Feng, Y. Zhang, J. Wang, *J. Org. Chem.* **2015**, *80*, 223; b) G.-D. Tang, C.-L. Pan, X. Li, *Org. Chem. Front.* **2016**, *3*, 87; c) Y. Li, F. Wang, S. Yu, X. Li, *Adv. Synth. Catal.* **2016**, *358*, 880; d) R. S. Phatake, P. Patel, C. V. Ramana, *Org. Lett.* **2016**, *18*, 292, d) S.-S. Zhang, C.-Y. Jiang, J.-Q. Wu, X.-G. Liu, Q.-J. Li, Z.-S. Huang, D. Li, H.-G. Wang, *Chem. Commun.* **2015**, 51, 10240.

[8] For examples catalyzed by Co(III), see: a) X.-G. Liu, S.-S. Zhang, J.-Q. Wu, Q. Li, H. Wang, *Tetrahedron Lett.* **2015**, *56*, 4093; b) D. Zhao, J. H. Kim, L. Stegemann, C. A. Strassert, F. Glorius, *Angew. Chem. Int. Ed.* **2015**, *54*, 4508; c) J. Li, M.-Y. Tang, L. Zang, X.-L. Zhang, Z. Zhang, L. Ackermann, *Org. Lett.* **2016**, *18*, 2742; d) J. H. Kim, S. Greβies, F. Glorius, *Angew. Chem. Int. Ed.* **2016**, *55*, 5577.

[9] W. Hou, Y.-X. Yang, Y.-X. Wang, H.-J. Fang, Y.-C. Li, B. Zhou, *Chem. Commun.* **2016**, *52*, 9672.

[10] For recent reviews, see: a) S. I. Kozhushkov, H. K. Potukuchi, L. Ackermann, *Catal. Sci. Technol.* **2013**, *3*, 562; b) K. Gao, N. Yoshikai, *Acc. Chem. Res.* **2014**, *47*, 1208; c) L. Ackermann, *J. Org. Chem.* **2014**, *79*, 8948; d) N. Yoshikai, *ChemCatChem* **2015**, *7*, 732; e) M. Moselage, J. Li, L. Ackermann, *ACS Catal.* **2016**, *6*, 498; f) D. Wei, X. Zhu, J.-L. Niu, M.-P. Song, *ChemCatChem*. **2016**, *8*, 1242.

[11] a) T. Yoshino, H. Ikemoto, S. Matsunaga, M. Kanai, *Angew. Chem. Int. Ed.* **2013**, *52*, 2207; b) T. Yoshino, H. Ikemoto, S. Matsunaga, M. Kanai, *Chem. Eur. J.* **2013**, *19*, 9142.

[12] a) A. Lerchen, T. Knecht, C. G. Daniliuc, F. Glorius, *Angew. Chem. Int. Ed.* **2016**, *55*, 15166; b) H. Wang, M. M. Lorion, L. Ackermann, *Angew. Chem. Int. Ed.* **2016**, *55*, 10386; c) D. Zell, Q. Bu, M. Feldt, L. Ackermann, *Angew. Chem. Int. Ed.* **2016**, *55*, 7408; d) R. Mei, J. Loup, L. Ackermann, *ACS Catal.* **2016**, *6*, 793; e) A. Lerchen, S. Vasquez-Céspedes, F. Glorius, *Angew. Chem. Int. Ed.* **2016**, *55*, 3208; f) D.-G. Yu, T. Gensch, F. de Azambuja, S. Vásquez-Céspedes, F. Glorius, *J. Am. Chem. Soc.* **2014**, *136*, 17722; g) J. Li, L. Ackermann, *Angew. Chem. Int. Ed.* **2015**, *54*, 8551; h) J. Li, L. Ackermann, *Angew. Chem. Int. Ed.* **2015**, *54*, 3635; i) J. R. Hummel, J. A. Ellman, *J. Am. Chem. Soc.* **2015**, *137*, 490; j) J. R. Hummel, J. A. Ellman, *Org. Lett.* **2015**, *17*, 2400; k) B. Sun, T. Yoshino, S. Matsunaga, M. Kanai, *Adv. Synth. Catal.* **2014**, *356*, 1491; l) H. Ikemoto, T. Yoshino, K. Sakata, S. Matsunaga, M. Kanai, *J. Am. Chem. Soc.* **2014**, *136*, 5424; m) B. Sun, T. Yoshino, M. Kanai, S. Matsunaga, *Angew. Chem. Int. Ed.* **2015**, *54*, 4508; n) J. Park, S. Chang, *Angew. Chem. Int. Ed.* **2015**, *54*, 12711; o) P. Patel, S. Chang, *ACS Catal.* **2015**, *5*, 853; p) M. Sen, D. Kalsi, B. Sundararaju, *Chem. Eur. J.* **2015**, *21*, 15529; q) S. Prakash, K. Muralirajan, C.-H. Cheng, *Angew. Chem. Int. Ed.* **2016**, *55*, 1844; r) K. Muralirajan, R. Kuppusamy, S. Prakash, C.-H. Cheng, *Adv. Synth. Catal.* **2016**, *358*, 774; s) X. Wu, K. Yang, Y. Zhao, H. Sun, G. Li, H. Ge, *Nat. Commun.* **2015**, *6*, 6462; t) Q.-Q. Yan, Z.-K. Chen, Z.-X. Liu, Y.-H. Zhang, *Org. Chem. Front.* **2016**, *3*, 678; u) L. B. Zhang, X.-Q. Hao, S.-K. Zhang, Z.-J. Liu, X.-X. Zheng, J.-F. Gong, J.-L. Niu, M.-P. Song, *Angew. Chem. Int. Ed.* **2015**, *54*, 272; v) L. Kong, S. Yu, X. Zhou, X. Li, *Org. Lett.* **2016**, *18*, 588; w) F. Wang, H. Wang, Q. Wang, S. Yu, X. Li, *Org. Lett.* **2016**, 18, 1306; x) Y. Liang, N. Jiao,

Angew. Chem. Int. Ed. **2016**, *55*, 4035; y) X.-G. Liu, S.-S. Zhang, C.-Y. Jiang, J.-Q. Wu, Q. Li, H. Wang, *Org. Lett.* **2015**, *17*, 5404.

[13] a) Z.-Z. Zhang, B. Liu, C.-Y. Wang, B.-F. Shi, *Org. Lett.* **2015**, *17*, 4094; b) Z.-Z. Zhang, B. Liu, J.-W. Xu, S.-Y. Yan, B.-F. Shi, *Org. Lett*. **2016**, *18*, 1776.

[14] a) M. Sen, B. Emayavaramban, N. Barsu, J. R. Premkumar, B.Sundararaju, *ACS Catal*. **2016**, *6*, 2792; b) N. Barsu, M. A. Rahman, M. Sen, B. Sundararaju, *Chem. Eur. J.* **2016**, *22*, 9135.

[15] CCDC 1518676 (**4f**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[16] H. Christian, R. Georg, S. Jean-Philippe, Z. A. Cornelia, US2010/331318 A1, **2010**.

[17] E. M. Simmons, J. F. Hartwig, *Angew. Chem. Int. Ed.* **2012**, *51*, 3066.

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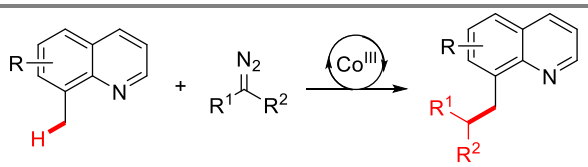
Co(III)-Catalyzed Alkylation of Primary C(sp^3)-H Bonds with Diazo Compounds



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