**Organic Chemistry**

**π-Extended Polyaromatic Hydrocarbons by Sustainable Alkyne Annulations through Double C–H/N–H Activation**

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**Abstract:** The widespread applications of substituted diketopyrrolopyrroles (DPPs) call for the development of efficient methods for their modular assembly. Herein, we present a π-expansion strategy for polyaromatic hydrocarbons (PAHs) by C–H activation in a sustainable fashion. Thus, twofold C–H/N–H activations were accomplished by versatile ruthenium(II)carboxylate catalysis, providing step-economical access to diversely decorated fluorogenic DPPs that was merged with late-stage palladium-catalyzed C–H arylation on the thus-assembled DPP motif.

Since their first synthesis,[1] diketopyrrolopyrroles (DPPs) have attracted great attention from researchers in various research areas, including optoelectronic material sciences[2] and bioimaging.[3] These inconspicuous small organic DPP molecules exhibit versatile properties ranging from low solubility, chemical resistance, outstanding stabilities and distinct colors, which render them excellent pigments.[4] N-Alkylation leads to DPPs with improved solubilities, the properties of which can be fine-tuned by the incorporation of different aromatic motifs.[3] Due to their strong electron-withdrawing ability and optical properties, DPPs are widely used as small molecules and conjugated semiconducting polymers in organic solar cells (OSC)[2^a–2^c,4], organic field-effect transistors (OFET),[2^d] organic photovoltaic cells (OPVs),[3,8] as well as fluorescent probes,[3,4] photocatalysts,[9] photosensitizers[10] or photothermal therapy agents,[11] promising annihilator molecules,[12] self-assembled dyes,[13] and bioconjugated hybrids.[14]

DPP derivatives with a highly decorated periphery as well as DPP-based polymers are usually obtained through conventional condensation reactions[4b,15] or metal-catalyzed cross-coupling reactions with prefunctionalized substrates.[4a,8b,16] In comparison to the elegant efforts devoted to the modification of the DPP periphery by direct functionalization or direct arylation polymerization (DARp)[17] their de novo assembly leading to π-extended structures continuous to be underdeveloped, with notable recent progress by Zumbusch[18] and Würthner.[11,15] Another possibility is represented by the introduction of an ethylene bridge between the nitrogen and the aromatic moiety, which leads to significantly π-expanded compounds.[20] These DPP derivatives possess sharp absorption and emission peaks, with very high molar absorption coefficients and unique fluorescence quantum yields,[20b] featuring after further modification a two-photon absorption cross-section.[20a] Very recently, π-extended DPP moieties were incorporated into alternating donor–acceptor copolymers resulting in a variety of low band gap copolymers.[21] Despite of these indisputable advances, thus far, these DPPs were obtained by classical N-alkylation with bromoacetaldehyde diethyl acetal, along with electrophilic aromatic substitution. Notably, this approach is hence limited to the introduction of ethylene junctions with only one substituent.

During the past decade, C–H activation has been identified as a transformative platform for various small molecule derivatizations through alkyne annihilations.[22] In sharp contrast, DPP assembly and diversification by C–H functionalization or DARp have thus far largely proven elusive.[17] Within our program on sustainable C–H activation,[23,24] we hence devised a versatile strategy for the modular assembly of DPPs in a single step by twofold C–H/N–H activation (Figure 1). Salient features of our findings include: 1) innovative ruthenium-catalyzed double C–H/N–H annulation of DPPs, 2) a π-expansion-strategy for PAHs, 3) access to valuable dyes with high absorption coeffi-

![Figure 1. Double C–H/N–H activation for modular assembly of diketopyrrolopyrroles PAHs.](image-url)

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cients, and 4) transformative late-stage diversification by C–H arylation on the DPP motif.

We initiated our studies by probing various reaction conditions for the envisioned double C–H/N–H activation of diketo-pyrrolopyrrole 1a with alkyne 2a (Table 1, for detailed information, see Tables S1 and S2 in the Supporting Information). 25

| Entry | Catalyst | Additive | Solvent | Yield [%] |
|-------|----------|----------|---------|-----------|
| 1     | [RuCl₂(p-cymene)]₂ | –        | o-xylene | 35        |
| 2     | [RuCl₂(p-cymene)]₂ | KOAc    | o-xylene | 80        |
| 3[a]  | [RuCl₂(p-cymene)]₂ | KOAc    | o-xylene | 92        |
| 4[a]  | [RuCl₂(p-cymene)]₂ | KOAc    | o-xylene | 84        |
| 5     | [RuCl₂(p-cymene)]₂ | KOAc    | DCE     | 70        |
| 6     | [RuCl₂(p-cymene)]₂ | KOAc    | PhMe    | 56        |
| 7     | [RuCl₂(p-cymene)]₂ | KOAc    | tAmOH   | 57        |
| 8     | [RuCl₂(p-cymene)]₂ | KOAc    | DMF     | –         |
| 9     | [RuCl₂(p-cymene)]₂ | KOAc    | GVL     | –         |
| 10    | –         | KOAc    | o-xylene | –         |
| 11[a] | [RuCl₂(p-cymene)]₂ | –        | o-xylene | –         |
| 12[a] | [RuCl₂(p-cymene)]₂ | KOAc    | o-xylene | –         |
| 13[a] | Pd(OAc)₂ | KOAc    | o-xylene | –         |
| 14    | [Cp*RhCl₂]₂ | KOAc    | o-xylene | –         |
| 15    | [RhCp*Cl₂]₂ | KOAc    | o-xylene | 76        |
| 16[a] | [RhCp*Cl₂]₂ | KOAc    | o-xylene | 20        |

[a] Reaction conditions: 1a (0.25 mmol), 2a (1.00 mmol), catalyst (10 mol%), Cu(OAc)₂ · H₂O, additive solvent, 140 °C, 24 h. [b] Isolated yields. [c] 16 h. [d] 100 °C. [e] CuBr₂ as an oxidant. [f] 20 mol %.

Thus, moisture- and air-stable ruthenium(II) complexes emerged as the catalysts of choice, with most effective catalysis accomplished by carboxylate assistance (Table 1, entries 1–4). 26 Given the rather poor solubility of substrate 1a and the aromatic character of PAH 3aa, we next explored various solvents (entries 4–9), with o-xylene being superior. Control experiments confirmed the essential role of carboxylate-assisted ruthenium(II) catalysis (entries 10–11). The particularly challenging character of the twofold C–H/N–H activation was reflected by palladium and iridium catalysts failing short in delivering the desired product 3aa (entries 13 and 14). Likewise [Cp*RhCl₂]-catalysis was significantly less effective than the cost-effective ruthenium(II) manifold (entries 15 and 16).

With the optimized catalyst in hand, we tested its versatility in the double C–H/N–H activation of DPP 1a with a variety of aryl-substituted alkynes 2 (Scheme 1). Thereby, π-extended PAHs were accessed from electron-rich as well as electron-deficient alkynes in an efficient manner, including sensitive tetrabromo DPP 3ag and thiophene-rich 3ah, which should prove instrumental for further modifications and applications of the DPPs 3.

The double ruthenium-catalyzed DPP C–H/N–H activation was not restricted to unsubstituted, parent DPP 1a (Scheme 2). Indeed, the reaction also proceeded efficiently with alkyl-substituted derivative 1b as well as the aryl-modified-DPP 1c, with the isolated yield of annulation product 3ca being caused by the extremely low solubility of substrate 1c.

Next, we evaluated alkyl-substituted alkynes 4 in the twofold ruthenium-catalyzed alkyne annihilation by DPP 1a (Scheme 3). Hence, the desired π-extended PAHs 5aa and 5ab were obtained by efficient oxidative C–H/N–H activations.

The connectivity of the annulated product 3aa was unambiguously established by X-ray crystal diffraction analysis (Figure 2). The dihedral angle between the DPP unit and its adjacent thiophene unit was found with 6.4°, clearly showing the
The importance of the molecular tether to induce planarity, as compared with the unbridged compound.\textsuperscript{[6c]} Further, the individual molecules are arranged in a lamellar packing motif,\textsuperscript{[27]} which appears to be stabilized by dispersive non-covalent C–H–π interaction between the C–H bonds of the aren motif and the thiophene unit (2.82 Å).

The optical properties of the thus-obtained novel DPP PAHs 3, 5 and 7 were thereafter studied by detailed UV/Vis absorption and fluorescence spectroscopy (Table 2). The unprecedented DPPs exhibited very intense absorption in the UV and visible region, with absorption maxima between maxima between 600–680 nm or maxima between 600–640 nm for the annihilation products 3 and 5, which results in an intense blue to purple color. The absorption maximum in all synthesized derivatives is bathochromically shifted in comparison with the previously synthesized, unsubstituted compounds,\textsuperscript{[20b]} whereas both Stoke shift and absorption coefficient are comparable. Interestingly, the highest absorption coefficients were obtained for the p-tolyl-DPP derivative 3c, while the largest Stokes shift was observed for thiophene-DPP derivative 3a and 7.

To investigate further the electronic structure of the DPPs 3, we performed computational DFT studies for product 3a at the B3LYP-D3(BJ)/6–311+G(d,p) + SMD(ο-Xylene) level of theory (Figure 3).\textsuperscript{[25]} Our calculations showed that the HOMO is delocalized over the DPP core and the ethylene bridge, whereas the LUMO is evenly localized on all condensed rings. Moreover, our TD-DFT calculations, performed at the same level of theory, highlighted an optical gap ($E_{\text{opt}}$) of 2.02 eV. Our computed absorption spectrum is in good qualitative agreement with the experimental data.\textsuperscript{[25]}

Finally, we became attracted by further late-stage functionalization of PAH 3a in terms of the introduction of two aryl motifs\textsuperscript{[17a]} at the alpha positions of the thiophenes (Scheme 4). Thus, the desired assembly of octylphenyl-substituted DPP 7 was realized by palladium-catalyzed twofold C–H arylation. It is noteworthy that the C–H activation-based incorporation of two aromatic moieties drastically shifted both the absorption and the emission maxima into the NIR region, which was mirrored by the green color of PAH 7.

| Compd. | $\lambda_{\text{abs,max}}$ [$\text{nm}$] | $\lambda_{\text{em,max}}$ [$\text{nm}$] | Stokes shift [cm$^{-1}$] | $\varepsilon_{\text{max}}$ [M$^{-1}$ cm$^{-1}$] |
|-------|---------------------------------|---------------------------------|---------------------|---------------------------------|
| 3aa   | 633                            | 645                            | 293                 | 76255                           |
| 3ab   | 635                            | 645                            | 244                 | 52083                           |
| 3ac   | 635                            | 646                            | 268                 | 71946                           |
| 3ad   | 632                            | 641                            | 222                 | 66051                           |
| 3ae   | 631                            | 640                            | 223                 | 47269                           |
| 3af   | 633                            | 644                            | 270                 | 76626                           |
| 3ag   | 633                            | 643                            | 246                 | 76107                           |
| 3ah   | 636                            | 646                            | 243                 | 25878                           |
| 3bd   | 637                            | 644                            | 158                 | 11431                           |
| 3ca   | 604                            | 613                            | 270                 | 92095                           |
| 5aa   | 630                            | 639                            | 223                 | 71598                           |
| 5ab   | 631                            | 642                            | 272                 | 84835                           |
| 7     | 680                            | 604                            | 296                 | 53634                           |

Table 2. Spectroscopic data of DPPs 3, 5, and 7.
Keywords: annihilation · C–H activation · diketopyrrolopyrroles · polyaromatic hydrocarbons · ruthenium

[1] D. G. Farnum, G. Mehta, G. G. I. Moore, F. P. Siegel, Tetrahedron Lett. 1974, 15, 2549 – 2552.
[2] a) C. Zhao, Y. Guo, Y. Zhang, N. Yan, S. You, W. Li, J. Mater. Chem. A 2019, 7, 10174 – 10199; b) Y. Patil, R. Misra, Chem. Asian J. 2018, 13, 220 – 229; c) W. Li, K. H. Hendriks, M. M. Wiken, R. A. J. Janssen, Acc. Chem. Res. 2016, 49, 78 – 85; d) M. J. Robb, S.-Y. Xu, F. G. Brunet, C. J. Hawker, J. Polym. Sci. Part A 2013, 51, 1263 – 1271; e) Y. Wu, W. Zhu, Chem. Soc. Rev. 2013, 42, 2039 – 2058; f) Y. Li, P. Sonar, L. Murphy, W. Hong, Energy Environ. Sci. 2013, 6, 1684 – 1710; b) T. Tieke, A. Rabin drath, K. Zhang, Y. Zhu, Belstein J. Org. Chem. 2010, 6, 830 – 845.
[3] M. Kaur, D. H. Choi, Chem. Soc. Rev. 2015, 44, 58 – 77.
[4] a) M. Csutat, B. Dittmar, H. Makowska, T. Marszalek, S. Kus hida, U. H. F. Bunz, J. Freudenberg, D. Jänsch, K. Müllen, Chem. Eur. J. 2019, 25, 2723 – 2728; b) M. Grzybowski, D. T. Gryko, Adv. Opt. Mater. 2015, 3, 280 – 320; c) O. Wallquist, R. Lenz, in High Performance Pigments (Eds.: E. B. Faulkner, R. J. Schwartz), 2009; d) Z. Hao, A. Iqbal, Chem. Soc. Rev. 1997, 26, 203 – 213.
[5] a) X. Zhang, R. Jin, Front. Chem. 2019, 7, 122; b) Z. Liu, G. Zhang, D. Zhang, Acc. Chem. Res. 2018, 51, 1422 – 1432; c) S. D. Dimitroff, J. R. Dur rant, Chem. Mater. 2014, 26, 616 – 630; d) M. A. Naik, S. Patil, J. Polym. Sci. Part A 2013, 51, 4241 – 4260; e) D. Gendron, M. Leclerc, Energy Environ. Sci. 2011, 4, 1225 – 1237.
[6] a) M. Gängler, D. Bialas, L. Huang, M. Stolte, F. Wüthner, Adv. Mater. 2016, 28, 3615 – 3645; b) S. Holliday, J. E. Donaghey, I. McCulloch, Chem. Mater. 2014, 26, 647 – 663; c) C. B. Nielsen, M. Turbiez, I. McCulloch, Adv. Mater. 2013, 25, 1859 – 1880.
[7] Y. Lin, Y. Li, X. Zhan, Chem. Soc. Rev. 2012, 41, 4245 – 4272.
[8] a) J. W. Jiang, L. Liu, W. Xu, Z. Yang, Y. Xue, X. Wang, T. Yi, C. Wang, J. Hua, Anal. Chem. 2019, 91, 5786 – 5793; b) S. Grieseck, M. Evripidis, C. Wang, H. Ogasawara, S. Lorenzen, L. Gerstner, T. Zang, J. Nitsch, Y. Sato, R. Bertermann, M. Taki, C. Lambert, S. Yamaguchi, T. B. Marder, Chem. Sci. 2019, 10, 5405 – 5422.
[9] X. Zhang, R. Sun, S. Sun, F. Ren, X. Chen, L. Wu, R. Xing, ACS Omega 2019, 4, 6068 – 6076.
[10] X. Yang, Q. Yu, N. Yang, L. Xue, J. Shao, B. Li, J. Shao, X. Dong, J. Mater. Chem. B 2019, 7, 2454 – 2462.
[11] Y. Yu, J. Chen, L. Tong, P. Su, Y. Liu, B. Gu, B. Bao, L. Wang, J. Controlled Release 2019, 293, 94 – 103.
[12] a) A. P. Bun, L. M. Campos, D. N. Congreve, J. Am. Chem. Soc. 2019, 141, 3777 – 3781.
[13] B. Soberats, M. Hecht, F. Wüthner, Angew. Chem. Int. Ed. 2017, 56, 10771 – 10774; Angew. Chem. 2017, 129, 10911 – 10914.
[14] E. Heyer, P. Lory, J. Lepinec, M. Moreau, A. Murcie, D. Guerguiev, A. Roda, R. Zießel, Angew. Chem. Int. Ed. 2015, 54, 2995 – 2999; Angew. Chem. 2015, 127, 3038 – 3042.
[15] S. Ghosh, R. Raveendran, A. Saeki, S. Seki, M. Namboothiri, A. Ajayag osh, ACS Appl. Mater. Interfaces 2019, 11, 1088 – 1095.
[16] B. Carsten, F. He, H. J. Son, T. Lu, Y. Yu, Chem. Rev. 2011, 111, 1493 – 1528.
[17] a) L. Ni, H. Wang, H. Dong, Y. Dang, Q. Zhao, X. Zhang, W. Hu, Nat. Chem. 2019, 11, 271 – 277; b) D. Feng, G. Barton, C. N. Scott, Org. Lett. 2019, 21, 1973 – 1978; c) S.-Y. Liu, D.-G. Wang, A.-G. Zhong, H.-R. Wen, Org. Chem. Front. 2018, 5, 653 – 661; d) M. Wakiokam, F. Ozawa, Asian J. Org. Chem. 2018, 7, 1206 – 1216; e) J. Yu, F. Liu, J. Yu, S. Zhang, C. Caba nos, Y. Gao, W. Huang, J. Mater. Chem. C 2017, 5, 29 – 40.
[18] a) T. Marks, E. Daltroz zo, A. Zumbach, Chem. Eur. J. 2014, 20, 6494 – 6504; b) G. M. Fischer, M. Isomäki-Klordned, I. Göttler-Schnetmann, E. Daltroz zo, A. Z umbach, Chem. Eur. J. 2009, 15, 4857 – 4864; c) G. M. Fischer, A. P. Ehlers, A. Zumbach, E. Daltroz zo, Angew. Chem. Int. Ed. 2007, 46, 3750 – 3753; Angew. Chem. 2007, 119, 3824 – 3827.
[19] a) M. Hecht, B. Sobetas, J. Zhu, Y. Stepanenko, S. Agarwal, A. Greiner, F. Wüthner, Nanoscale Horiz. 2019, 4, 169 – 174; b) T. He, P. Leow anawat, C. Burschka, V. Stepanenko, M. Stolte, F. Wüthner, Adv. Mater. 2018, 30, 1804032; c) W. Yue, S.-L. Suraru, D. Bialas, M. Müller, F. Wüthner, Angew. Chem. Int. Ed. 2014, 53, 6159 – 6162; Angew. Chem. 2014, 126, 6273 – 6276.

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Conflict of interest

The authors declare no conflict of interest.

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Figure 3. Energies of shapes of frontier orbitals (HOMO and LUMO) of 3aa calculated at the B3LYP-D3(BJ)/6–311+G(d,p)+SMD(o-Xylene) level of theory.

Scheme 4. Late-stage PAH diversification by double C–H alylations. Cy = cyclohexyl; DMA = dimethylacetamide; PiOH = pivalic acid.

In summary, we have devised an enabling strategy for the assembly of π-extended DPPs. Thus, ruthenium(II)-catalyzed double C–H/N–H activation allowed for the synthesis of novel, diversely-decorated DPP derivatives in a step-economical manner. The novel DPPs were fully characterized, including spectroscopy, XRD and DFT computation. The twofold alkyne annulation was furthermore merged with C–H alylations of the thus obtained π-extended PAHs to furnish DPPs with absorption and emission maxima shifted into the NIR region. Our findings should prove invaluable for applications to optoelectronics, material sciences and live cell imaging.28

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[20] a) M. Grzybowski, V. Hugues, M. Blanchard-Desce, D. T. Gryko, Chem. Eur. J. 2014, 20, 12493–12501; b) M. Grzybowski, E. Glodowski-Mrowka, T. Stoklosa, D. T. Gryko, Org. Lett. 2012, 14, 2670–2673.
[21] F. Trilling, O. Sachnik, U. Scherf, Polym. Chem. 2019, 10, 627–632.
[22] For select review, see: a) H. Ito, Y. Segawa, K. Murakami, K. Itami, J. Am. Chem. Soc. 2019, 141, 3–10; b) P. Gandeepan, T. Müller, D. Zell, G. Cera, S. Warratz, L. Ackermann, Chem. Rev. 2019, 119, 2192–2452; c) X. Liu, Y. Huang, X. Meng, J. Li, D. Wang, Y. Chen, D. Tang, B. Chen, Synlett 2019, 30, 207; d) Y. Xiang, C. Wang, Q. Ding, Y. Peng, Adv. Synth. Catal. 2019, 361, 919–944; e) Y. Koga, T. Kaneda, Y. Saito, K. Murakami, K. Itami, Science 2018, 359, 435–439; f) S. Prakash, R. Kuppusamy, C. H. Cheng, ChemCatChem 2018, 10, 683–705; g) S. J. Hein, D. Lehnher, H. Arslan, F. J. Uribe-Romo, W. R. Dichtel, Acc. Chem. Res. 2017, 50, 2776–2788; h) W. Yang, W. A. Chalifoux, Synlett 2017, 28, 625–632; i) R. Manikandan, M. Jeganmohan, Chem. Commun. 2017, 53, 8931–8947; j) M. Guillot, J. J. Mascareñas, Angew. Chem. Int. Ed. 2016, 55, 11000–11019; k) Angew. Chem. 2016, 128, 11164–11184; l) Y. Segawa, T. Maekawa, K. Itami, Angew. Chem. Int. Ed. 2015, 54, 66–81; Angew. Chem. 2015, 127, 68–83; m) L. Ackermann, Acc. Chem. Res. 2014, 47, 281–295; n) T. Jin, J. Zhao, N. Asao, Y. Yamamoto, Chem. Eur. J. 2014, 20, 3554–3576; o) B. Li, P. H. Dixneuf, Chem. Soc. Rev. 2013, 42, 5744–5767; p) P. B. Arockiam, C. Bruneau, P. H. Dixneuf, Chem. Rev. 2012, 112, 5879–5918; q) L. Ackermann, R. Vicente, A. R. Kapdi, Angew. Chem. Int. Ed. 2009, 48, 9792–9826; Angew. Chem. 2009, 121, 9976–1001; q) for select examples of simple C=H/N=H transformations, see: a) Obata, A. Sasagawa, K. Yamazaki, Y. Ano, N. Chatani, Chem. Sci. 2019, 10, 3242–3248; r) T. Wexman, R. Soppeltt, F. F. Tirani, K. Severin, Adv. Synth. Catal. 2019, 361, 1383–1388; s) M. Shankar, K. Ghosh, K. Mukherjee, R. K. Ritt, A. K. Sahoo, Org. Lett. 2016, 18, 6416–6419; t) X. Zhang, W. Si, M. Bao, N. Asao, Y. Yamamoto, T. Jin, Org. Lett. 2014, 16, 4830–4833; u) B. Li, H. Feng, N. Wang, J. Ma, H. Song, S. Xu, B. Wang, Chem. Eur. J. 2012, 18, 12873–12879; v) T. K. Hyster, T. Rovis, J. Am. Chem. Soc. 2010, 132, 10565–10569; w) K. Morimoto, K. Hirano, T. Satoh, M. Miura, Org. Lett. 2010, 12, 2068–2071; x) G. Song, D. Chen, C.-L. Pan, R. H. Crabtree, X. Li, J. Org. Chem. 2010, 75, 7487–7490; y) N. Umeda, H. Tsurugi, T. Satoh, M. Miura, Angew. Chem. Int. Ed. 2008, 47, 4019–4022; Angew. Chem. 2008, 120, 4083–4086, and cited references therein.
[23] a) L. Ackermann, Pure Appl. Chem. 2010, 82, 1403–1413; b) L. Ackermann, Synlett 2007, 0507–0526.
[24] Selected examples: a) Y. Qiu, C. Tian, L. Massignan, T. Rogge, L. Ackermann, Angew. Chem. Int. Ed. 2018, 57, 5818–5822; Angew. Chem. 2018, 130, 5920–5924; b) D. Mei, J. Koeller, L. Ackermann, Chem. Commun. 2018, 54, 12879–12882; c) D. Mei, S.-K. Zhang, L. Ackermann, Synlett 2017, 28, 1715–1718; d) L. Ackermann, L. Wang, A. V. Lygin, Chem. Sci. 2012, 3, 177–180; e) L. Ackermann, A. V. Lygin, Org. Lett. 2012, 14, 764–767; f) L. Ackermann, A. V. Lygin, N. Hofmann, Org. Lett. 2011, 13, 3278–3281; g) L. Ackermann, A. V. Lygin, N. Hofmann, Angew. Chem. Int. Ed. 2011, 50, 6379–6382; Angew. Chem. 2011, 123, 6503–6506, and cited references.
[25] For detailed information, see the Supporting Information.
[26] L. Ackermann, Chem. Rev. 2011, 111, 1315–1345.
[27] C. Wang, H. Dong, L. Jiang, W. Hu, Chem. Soc. Rev. 2018, 47, 422–500.
[28] Recent reviews: a) C. Zhao, L. Mendive-Tapia, M. Vendrell, Arch. Biochem. Biophys. 2019, 661, 187–195; b) G. G. Dias, A. King, F. de Moliner, M. Vendrell, E. N. da Silva Júnior, Chem. Soc. Rev. 2018, 47, 12–27.

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