有机化学 DOI: 10.6023/cjoc201810004 研究简报
Chinese Journal of Organic Chemistry NOTE

无溶剂的 β-卟啉甲醛与酮的 Aldol 反应

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摘要 发现了一种合成 β-卟啉基-α,β-不饱和酮化合物的简便方法. 在碱催化条件下以 β-卟啉甲醛和酮为底物, 通过 Aldol 反应合成了 β-卟啉基-α,β-不饱和酮化合物, 其反应特点包括无溶剂、条件温和、中等到较高的收率等. 本方法特别适用于在已有报道中反应效果很差的常见的金属化卟啉底物, 反应结果优良.

关键词 金属卟啉; α,β-不饱和酮; Aldol 反应; 无溶剂

Solvent-Free Aldol Reaction of β-Porphyrin Formaldehyde with Ketone

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Abstract A convenient approach for the synthesis of β-substituted α,β-unsaturated carbonyl porphyrin compounds via base-catalyzed aldol reaction was developed. By this method, a series of β-substituted α,β-unsaturated carbonyl porphyrin compounds were constructed using β-porphyrin formaldehyde and ketones with moderate to excellent yields under mild reaction conditions, especially solvent-free, and good functional group tolerance. Furthermore, this process was successfully applied to the reactions of different metal porphyrin which have been reported to have poor reaction effects with good yields.

Keywords metal porphyrin; α,β-unsaturated carbonyl; aldol reaction; solvent-free

1 Introduction

Porphyrins are importantly ubiquitous molecular constructs because of their potential biomedical applications such as photodynamic therapy[1,2] and the ability to incorporate their electronic properties into optical devices.[3] Furthermore, a variety of modes of porphyrinoid-α,β-unsaturated carbonyl connectivity provides sufficiently strong interchromophore electronic interactions to facilitate extensive electronic delocalization.

Tetraarylporphyrins (TPPs) are easily achievable, which could be functionalized at the β-pyrrolic position by relatively few synthetic steps. The use of large or electron-withdrawing substituents and the halogenation of the β-pyrrolic positions over the basic skeleton of TPP have been recognized[4~6] and the use of elaborated porphyrin structures has also been studied. The β-substituted TPP are interesting compounds and have been used in many recent studies, namely, as starting units for the synthesis of elaborated porphyrins or as precursors of photodynamic pharmaceuticals.[7~10] Following our own research in this field,[11] in this paper we present a new method of the aldol reaction of designed β-substituted TPP with α,β-unsaturated carbonyl compound (Scheme 1), which is a more efficient and economical way to get β-substituted α,β-unsaturated carbonyl porphyrin compounds.

Since its discovery by Borodin[12,13] and Wurtz,[14] the aldol addition reaction has become one of the most important transformations in organic synthesis.[15] To the reaction of TPP formaldehyde with excess acetone in chloroform as a previous model,[16] the yield was not high, and the catalyst needed to be prepared in advance. Even more unfortunately, the metalloporphyrin derivatives could not be carried out under this condition. Responsing to the dis-

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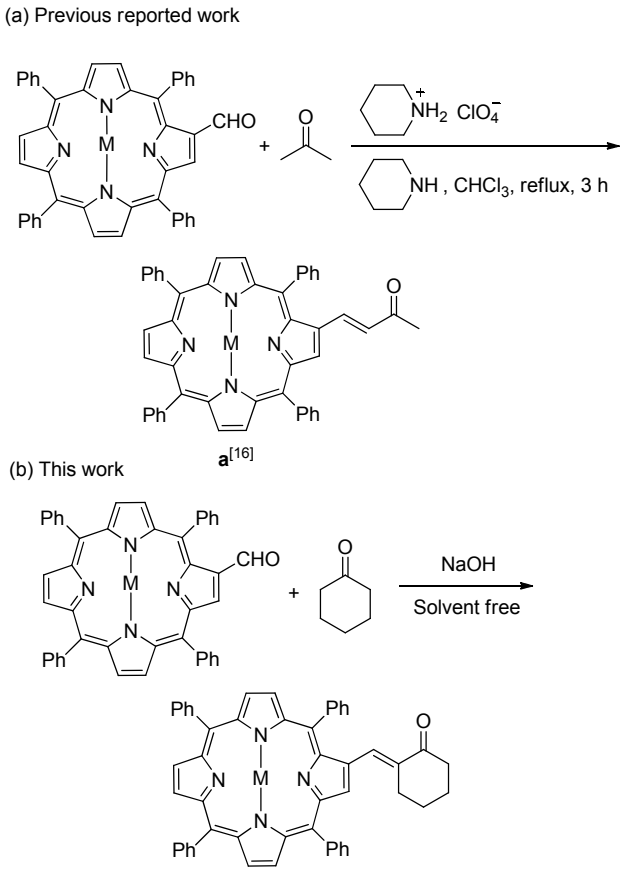
Received October 5, 2018; revised January 18, 2019; published online March 8, 2019.
Project supported by the Science and Technology Planning Project of Henan Province of China (No. 192102310141).
河南省科技攻关(No. 192102310141)资助项目.

advantage above, we decided to change the model reaction.[17] Mixing TPP formaldehyde and α,β-unsaturated carbonyl reagent without solvent (keep the rest of condition), the desired product was obtained in a high yield (Scheme 1). More interesting, the metalloporphyrins formaldehyde (metal-TPP formaldehydes) reacted smoothly with α,β-unsaturated carbonyl compound and the desired product was obtained with good to excellent yields.



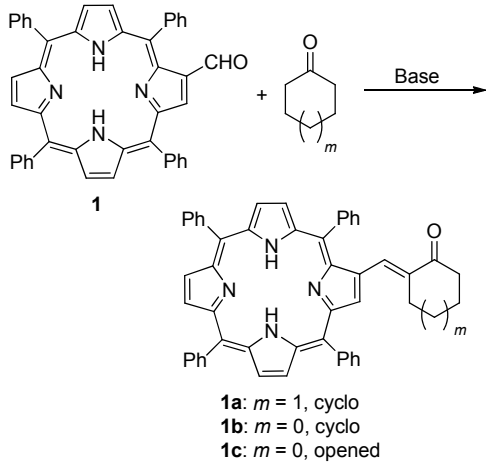
Scheme 1 Synthesis of β-substituted α,β-unsaturated carbonyl TPP

2 Results and discussion

Initially, equimolar cyclohexanone and β-TPP formaldehyde were crushed with NaOH in a mortar at room temperature for 15 min, but no reaction occurred. We suspected that solid aldehydes and ketone could not be mixed thoroughly under this condition. Following a modified procedure, a viscous liquid of NaOH in excessive cyclohexanone and TPP formaldehyde was stirred vigorously for 12 h at room temperature. Thin-layer chromatography (TLC) results showed that only trace product was formed (Table 1, Entry 1). Screening the reaction temperature, the yield will increase along with enhanced temperature. The yield improved to 55% at 75 ℃ for 6 h, and up to 82% at 85 ℃ (Table 1, Entries 3, 4). Further rising temperature will not continuously increase the yield but lead to the increase of by-products (Table 1, Entries 5, 6). So 85 ℃ was the better choice of reaction temperature. For base, NaOH was good for this transformation. Table 1, Entries 6～8 showed that less or more base will lead to reduced yield. 0.5 equiv. of NaOH was suitable for the aldol addition.

Next, different bases such as Na_2CO_3, triethylamine (TEA), sodium ethoxide and KOH were tested. Na_2CO_3 gave a very low yield even up to 110 ℃, and TEA also gave a low yield (Table 1, Entries 9 and 10). As to sodium ethoxide, because of its strong basicity, the reaction resulted in destruction of most of raw materials within 4 h (Table 1, Entry 11). Interestingly, KOH was little better than NaOH in the addition with cyclohexanone, but it's just the opposite in the addition with cyclopentanone and 3-pentanone (Table 1, Entries 13～16). The results showed that the addition of β-TPP formaldehyde with different ketone had slightly difference in their transition state.

Table 1 Optimization of reaction conditions[a]



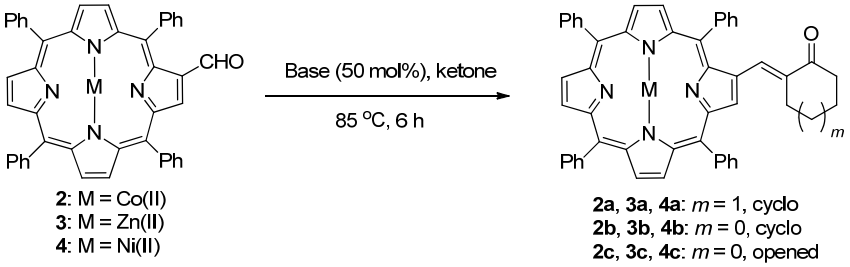
Entry	Base (mol%)	T/℃	Time/h	Yield[b]/%
1	NaOH (50)	r.t.	12	Trace
2	NaOH (50)	50	6	20
3	NaOH (50)	75	6	55
4	NaOH (50)	85	6	75
5	NaOH (50)	90	6	75
6	NaOH (50)	110	6	70
7	NaOH (30)	110	6	63
8	NaOH (70)	110	6	71
9	Na_2CO_3 (50)	110	6	Trace
10	TEA (50)	85	6	10
11	CH_3CH_2ONa (50)	85	4	14
12	KOH (50)	85	6	78
13[c]	KOH (50)	85	6	65
14[c]	NaOH (50)	85	6	69
15[d]	KOH (50)	85	6	79
16[d]	NaOH (50)	85	6	82

[a] The reaction was carried out with **1** (7.788 mmol), ketone was added dropwise until the system is viscous. [b] Isolated yield. [c] Ketone is cyclopentanone. [d] Ketone is 3-pentanone.

To further expand application of this method, a variety of metal-TPP formaldehydes and ketones were investigated, and the results were summarized in Table 2. In general,

the aldol reaction of metalloporphyrin formaldehyde with ketone was good efficient with a medium or high yield up to 87% (Table 2, Entries 9). Same as above, KOH was more suitable for addition with cyclohexanone but NaOH was better for cyclopentanone and 3-pentanone, and more, cyclopentanone showed lower activity than other ketones (Table 2, Entries 2, 5, 8). Among these metalloporphyrins, Zn(II)-TPP-CHO showed the lowest reaction activity (Table 2, Entries 4～6). It was known that Zn(II) has the largest ionic radius and the weakest binding force to the outer electrons, which improve the electron density of the porphyrin ring and reduce addition activity of the TPP formaldehyde. The synthesized *β*-substituted *α*,*β*-unsaturated carbonyl porphyrin compounds were shown in Figure 1.

Table 2 Different ketones react with metalloporphyrins[a]



Entry	M	Ketone	Base	Yield[b]/%
1	Co(II)	Cyclohexanone	KOH	82
2	Co(II)	Cyclopentanone	NaOH	63
3	Co(II)	3-Pentanone	NaOH	82
4	Zn(II)	Cyclohexanone	KOH	76
5	Zn(II)	Cyclopentanone	NaOH	59
6	Zn(II)	3-Pentanone	NaOH	77
7	Ni(II)	Cyclohexanone	KOH	80
8	Ni(II)	Cyclopentanone	NaOH	72
9	Ni(II)	3-Pentanone	NaOH	87

[a] The reaction was carried out with metal-TPP-CHO (7.788 mmol), ketone was added dropwise until the system is viscous. [b] Isolated yield.

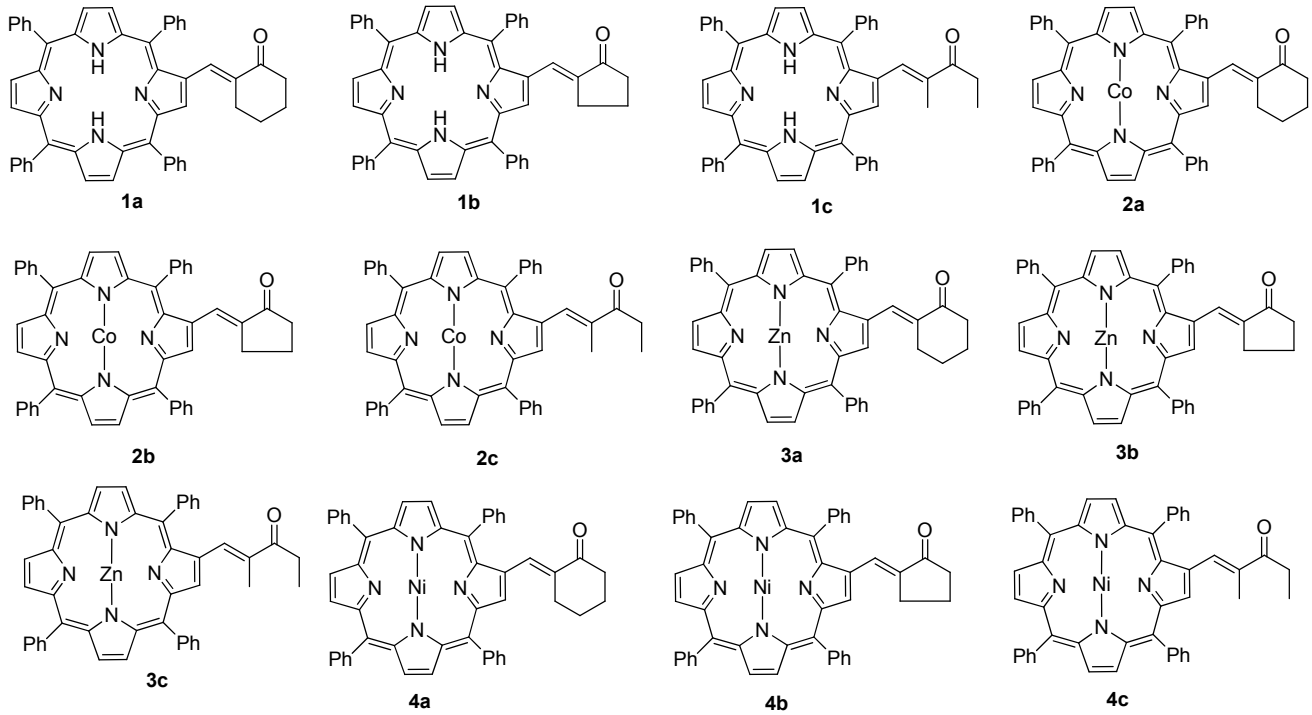


Figure 1 Synthesized *β*-substituted *α*,*β*-unsaturated carbonyl porphyrin compounds

3 Conclusions

A solvent-free procedure to carry on the aldol addition of TPP formaldehyde including metal-TPP formaldehydes with ketones was successfully developed. A series of *β*-substituted *α*,*β*-unsaturated carbonyl porphyrin compounds were obtained with moderate to excellent yields under mild reaction conditions. This method is concise and efficient for the synthesis of porphyrin derivatives.

4 Experimental section

4.1 Instruments and reagents

NMR spectra were recorded on a Bruker AVIII-400 spectrometer at 400 MHz for ^{1}H NMR. All new products were further characterized by high resolution mass spectrometry (HRMS) with an APEX IV Fourier Transform Ion Cyclotron Resonance Mass Spectrometer equipped with an ESI source. All absorption spectra were measured on a Hewlett-Packard 8453 UV/vis spectrophotometer. Melting points were uncorrected. Column chromatography (CC) was performed on a silica gel (300 mesh) column. Thin layer Chromatography (TLC) was performed using glass plates coated with silica gel GF254. All reactions were run in 15 mL sealed tubes. Solvents were used as received. Other reagents were commercially available and used without further purification.

4.2 General procedure for the Aldol reaction

TPP formaldehyde (7.788 mmol) and excess cyclohexanone were added to a 35 mL sealed tube under stirring until the mixture is viscous. Then NaOH (3.894 mmol) was added and the mixture was stirred at 85 ℃ for 6 h under seal. The progress of the reactions was monitored by TLC. The mixture was cooled and washed with a saturated sodium bicarbonate solution, then extracted with dichloromethane (DCM). The solvent was removed under vacuum. The residue was purified via column chromatography in silica gel eluted with cyclohexane/CH_2Cl_2 (V∶V=1∶2.5) to afford the corresponding purified products.

(5,10,15,20-Tetraphenylporphyrin-2-yl)-3-buten-2-one (**a**)[16]: purple solid, 70% yield. m.p. 202～204 ℃ (dec.); UV-Vis (CH_2Cl_2) λ_{max}: 444, 526, 566, 603, 661 nm; ^{1}H NMR (400 MHz, $CDCl_3$) δ: −2.45 (s, 2H, inner NH), 2.16 (s, 3H, CH_3), 6.90 (d, J=16 Hz, 1H, TPP-CH=), 7.43 (d, J=16 Hz, 1H,=CHCO), 7.65～7.96 (m, 12H, *m*- and *p*-ArH), 8.20～8.43 (m, 8H, *o*-ArH), 8.82～9.12 (m, 7H, *β*-pyrrole-H); IR (KBr) ν: 3430, 1668, 1627, 1520, 1452 cm^{-1}; HRMS calcd for $C_{48}H_{35}N_4O$ $[M+H]^+$ 683.2416, found 683.2431.

(5,10,15,20-Tetraphenylporphyrin-2-yl)-2-methylenecyclohexanone (**1a**): purple solid, 82% yield. m.p. 205～206 ℃ (dec.); UV-Vis (CH_2Cl_2) λ_{max}: 432, 521, 568, 615, 653 nm; ^{1}H NMR (400 MHz, $CDCl_3$) δ: −2.69 (s, 2H, inner NH), 1.74～1.80 (m, 2H, C**H**$_2$CH$_2$C=CH), 1.90～1.96 (m, 2H, C**H**$_2$CH$_2$C=O), 2.48 (t, J=6 Hz, 2H, C**H**$_2$C=CH), 2.86 (t, J=6 Hz, 2H, CH$_2$C=O), 7.37 (s, 1H, TPPCH=), 7.65～7.76 (*m*, 12H, *m*- and *p*-ArH), 8.03～8.22 (m, 8H, *o*-ArH), 8.59～8.86 (m, 7H, *β*-pyrrole-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.9, 24.3, 26.9, 40.6, 120.0, 120.2, 120.2, 120.5, 126.7, 126.7, 126.8, 127.1, 127.8, 128.5, 131.8, 133.9, 134.6, 134.6, 134.7, 141.7, 141.9, 142.1, 142.2, 201.4; IR (KBr) ν: 3458,1675, 1638, 1525,1453 cm^{-1}; HRMS calcd for $C_{51}H_{39}N_4O$ $[M+H]^+$ 723.3124, found 723.3120.

(5,10,15,20-Tetraphenylporphyrin-2-yl)-2-methylenecyclopentanone (**1b**): purple solid, 85% yield. m.p. 205～206 ℃ (dec.); UV-Vis (CH_2Cl_2) λ_{max}: 428, 520, 567, 612, 650 nm; ^{1}H NMR (400 MHz, $CDCl_3$) δ: −2.61 (s, 2H, inner NH), 1.99～2.07 (m, 2H, CH$_2$C**H**$_2$CH$_2$), 2.38 (t, J=8 Hz, 2H, CH$_2$C=), 3.00 (t, J=8 Hz, 2H, CH$_2$CO), 7.24 (s, 1H, TPPCH=), 7.70～7.83 (m, 12H, *m*- and *p*-ArH), 8.08 ～ 8.23 (m, 8H, *o*-ArH), 8.79 ～ 8.86 (m, 7H, *β*-pyrrole-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.5, 29.5, 38.2, 120.2, 120.2, 120.4, 120.5, 126.7, 126.7, 126.8, 127.2, 127.8, 127.9, 128.9, 134.0, 134.5, 134.6, 134.6, 136.3, 141.4, 142.1, 142.4, 206.8; IR (KBr) ν: 3455,1676, 1638, 1520, 1446 cm^{-1}; HRMS calcd for $C_{50}H_{37}N_4O$ $[M+H]^+$ 709.2967, found 709.2963.

(5,10,15,20-Tetraphenylporphyrin-2-yl)-2-methylene-3-pentanone (**1c**): purple solid, 87% yield. m.p. 204～206 ℃ (dec.); UV-Vis (CH_2Cl_2) λ_{max}: 431, 520, 569, 610, 653 nm; ^{1}H NMR (400 MHz, $CDCl_3$) δ: −2.67 (s, 2H, inner NH), 1.08 (t, J=8 Hz, 3H, CH$_2$C**H**$_3$), 2.11 (s, 3H, CH$_3$), 2.38 (q, J=8 Hz, 2H, C**H**$_2$CH$_3$), 7.57 (s, 1H, TPPCH=), 7.65～7.78 (m, 12H, *m*- and *p*-ArH), 8.07～8.21 (m, 8H, *o*-ArH), 8.68～8.87 (m, 7H, *β*-pyrrole-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 8.6, 13.2, 29.9, 119.9, 120.1, 120.3, 120.6, 126.7, 126.8, 127.2, 127.8, 127.9, 128.4, 134.1, 134.5, 134.6, 135.3, 136.2, 141.8, 142.1, 142.2, 142.2, 203.0; IR (KBr) ν: 3448, 1677, 1630, 1527, 1450 cm^{-1}; HRMS calcd for $C_{50}H_{39}N_4O$ $[M+H]^+$ 711.3124, found 711.3119.

Co(II)-(5,10,15,20-Tetraphenylporphyrin-2-yl)-2-methylenecyclohexanone (**2a**): purple solid, 83% yield. m.p. 205～206 ℃ (dec.); UV-Vis (CH_2Cl_2) λ_{max}: 418, 535, 585 nm; IR (KBr) ν: 3434, 3335, 3144, 2957, 2922, 2851, 1740, 1661, 1615, 1455, 1400, 1350, 1215, 1073, 1039, 1005, 796, 751, 701 cm^{-1}; HRMS calcd for $C_{51}H_{36}N_4OCo$ $[M+H]^+$ 779.2221, found 779.2217.

Co(II)-(5,10,15,20-Tetraphenylporphyrin-2-yl)-2-methylene-cyclopentanone (**2b**): purple solid, 63% yield. m.p. 205～206 ℃ (dec.); UV-Vis (CH_2Cl_2) λ_{max}: 437, 535, 583 nm; IR (KBr) ν: 2954, 2871, 2362, 2334, 1705, 1638, 1452, 1251, 1222, 1166, 1070 cm^{-1}; HRMS calcd for $C_{50}H_{34}N_4OCo$ $[M+H]^+$ 765.2065, found 765.2096.

Co(II)-(5,10,15,20-Tetraphenylporphyrin-2-yl)-2-methylene-3-pentanone (**2c**): purple solid, 85% yield. m.p. 204～206 ℃ (dec.); UV-Vis (CH_2Cl_2) λ_{max}: 417, 534, 569 nm; IR (KBr) ν: 3384, 2948, 2836, 2370, 1638, 1592, 1473, 1402, 1111, 1025 cm^{-1}; HRMS calcd for $C_{50}H_{36}N_4OCo$ $[M+H]^+$ 767.2221, found 767.2218.

Zn(II)-(5,10,15,20-Tetraphenylporphyrin-2-yl)-2-methylenecyclohexanone (**3a**): purple solid, 75% yield. m.p. 205～206 ℃ (dec.); UV-Vis (CH_2Cl_2) λ_{max}: 441, 567, 654

nm; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.74～1.80 (m, 2H, C**H**$_2$CH$_2$C＝CH), 1.90～1.96 (m, 2H, C**H**$_2$CH$_2$C＝O), 2.48 (t, J＝6 Hz, 2H, C**H**$_2$C＝CH), 2.86 (t, J＝6 Hz, 2H, CH$_2$C＝O), 7.37 (s, 1H, TPPCH＝), 7.65～7.76 (m, 12H, *m*- and *p*-ArH), 8.03～8.23 (m, 8H, *o*-ArH), 8.69～8.74 (m, 7H, *β*-pyrroleH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.9, 24.4, 26.9, 40.6, 120.0, 120.3, 120.2, 120.5, 126.7, 126.6, 126.8, 127.1, 127.8, 128.5, 131.8, 133.9, 134.7, 134.6, 134.7, 141.7, 141.9, 142.0, 142.2, 201.4; HRMS calcd for $C_{51}H_{37}N_4OZn$ $[M+H]^+$ 785.2259, found 785.2253.

Zn(II)-(5,10,15,20-Tetraphenylporphyrin-2-yl)-2-methyl-Ene-cyclopentanone (**3b**): purple solid, 80% yield. m.p. 205～206 ℃ (dec.); UV-Vis (CH_2Cl_2) λ_{max}: 437, 565, 649 nm; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.92～2.02 (m, 2H, CH$_2$C**H**$_2$CH$_2$), 2.32 (t, J＝8 Hz, 2H, CH$_2$C＝), 2.99 (t, J＝8 Hz, 2H, CH$_2$CO), 7.16 (s, 1H, TPPCH＝), 7.67～7.71 (m, 12H, *m*- and *p*-ArH), 8.00～8.16 (m, 8H, *o*-ArH), 8.60～8.80 (m, 7H, *β*-pyrroleH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.5, 29.5, 38.2, 120.3, 120.2, 120.4, 120.5, 126.7, 126.8, 126.8, 127.2, 127.8, 127.8, 128.9, 134.0, 134.5, 134.5, 134.6, 136.3, 141.3, 142.1, 142.4, 206.8; HRMS calcd for $C_{50}H_{35}N_4OZn$ $[M+H]^+$ 771.2102, found 771.2009.

Zn(II)-(5,10,15,20-Tetraphenylporphyrin-2-yl)-2-methyl-ene-3-pentanon*e* (**3c**): purple solid, 67% yield. m.p. 204～206 ℃ (dec.); UV-Vis (CH_2Cl_2) λ_{max}: 440, 568, 653 nm; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.02 (t, J＝8 Hz, 3H, CH$_2$C**H**$_3$), 2.06 (s, 3H, CH$_3$), 2.33 (q, J＝8 Hz, 2H, C**H**$_2$CH$_3$), 7.50 (s, 1H, TPPCH＝), 7.67～7.71 (m, 12H, *m*- and *p*-ArH), 8.00～8.12 (m, 8H, *o*-ArH), 8.70～8.78 (m, 7H, *β*-pyrrole-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 8.5, 13.2, 29.9, 119.9, 120.1, 120.3, 120.7, 126.7, 126.8, 127.3, 127.8, 127.9, 128.3, 134.1, 134.5, 134.7, 135.3, 136.2, 141.8, 142.2, 142.2, 142.1, 203.0; HRMS calcd for $C_{50}H_{37}N_4OZn$ $[M+H]^+$ 773.2295, found 773.2293.

Ni(II)-(5,10,15,20-Tetraphenylporphyrin-2-yl)-2-methyl-enecyclohexanone **(4a)**: purple solid, 70% yield. m.p. 205～206 ℃ (dec.); UV-Vis (CH_2Cl_2) λ_{max}: 430, 546, 594 nm; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.74～1.80 (m, 2H, C**H**$_2$CH$_2$C＝CH), 1.90～1.96 (m, 2H, C**H**$_2$CH$_2$C＝O), 2.48 (t, J＝6 Hz, 2H, C**H**$_2$C＝CH), 2.86 (t, J＝6 Hz, 2H, CH$_2$C＝O), 7.36 (s, 1H, TPPCH＝), 7.65～7.76 (m, 12H, *m*- and *p*-ArH), 8.03～8.22 (m, 8H, *o*-ArH), 8.59～8.76 (m, 7H, *β*-pyrroleH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.8, 24.3, 26.9, 40.5, 120.0, 120.2, 120.2, 120.5, 126.8, 126.7, 126.8, 127.1, 127.9, 128.5, 131.7, 133.9, 134.6, 134.6, 134.8, 141.7, 141.9, 142.2, 142.2, 201.4; HRMS calcd for $C_{51}H_{37}N_4ONi$ $[M+H]^+$ 779.2321, found 779.2316.

Ni(II)-(5,10,15,20-Tetraphenylporphyrin-2-yl)-2-methyl-ene-cyclopentanone (**4b**): purple solid, 75% yield. m.p. 205～206 ℃ (dec.); UV-Vis (CH_2Cl_2) λ_{max}: 425, 549, 588 nm; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.93～2.09 (m, 2H, CH$_2$-C**H**$_2$-CH$_2$), 2.31 (t, J＝8 Hz, 2H, -CH$_2$-C＝), 2.93 (t, J＝8 Hz, 2H, -CH$_2$-CO), 7.14 (s, 1H, TPP-CH＝), 7.64～7.67 (m, 12H, *m*- and *p*-ArH), 7.97～8.13 (m, 8H, *o*-ArH), 8.57～8.77 (m, 7H, *β*-pyrroleH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.5, 29.5, 38.3, 120.2, 120.2, 120.3, 120.5, 126.7, 126.7, 126.9, 127.2, 127.8, 127.9, 128.9, 134.1, 134.5, 134.6, 134.7, 136.3, 141.4, 142.1, 142.5, 206.8; HRMS calcd for $C_{50}H_{35}N_4ONi$ $[M+H]^+$ 765.2164, found 765.2160.

Ni(II)-(5,10,15,20-Tetraphenylporphyrin-2-yl)-2-methyl-ene-3-pentanone **(4c)**: purple solid, 67% yield. m.p. 204～206 ℃ (dec.); UV-Vis (CH_2Cl_2) λ_{max}: 428, 547, 593 nm; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.02 (t, J＝8 Hz, 3H, CH$_2$C**H**$_3$), 2.04 (s, 3H, CH$_3$), 2.33 (q, J＝8 Hz, 2H, C**H**$_2$CH$_3$), 7.47 (s, 1H, TPPCH＝), 7.55～7.67 (m, 12H, *m*- and *p*-ArH), 8.00～8.11 (m, 8H, *o*-ArH), 8.69～8.75 (m, 7H, *β*-pyrroleH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 8.6, 13.2, 29.8, 119.9, 120.1, 120.2, 120.6, 126.7, 126.8, 127.3, 127.7, 127.9, 128.4, 134.1, 134.4, 134.6, 135.3, 136.3, 141.8, 142.1, 142.1, 142.2, 203.1; HRMS calcd for $C_{50}H_{37}N_4ONi$ $[M+H]^+$ 767.2321, found 767.2308.

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