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# Non-peripherally substituted metallophthalocyanines catalyzed diastereoselective carbonyl-ylide reactions: Synthesis and DFT calculations

Fusun Seyma Gungor<sup>\*</sup>, B. Sebnem Sesalan, Nurcan Senyurt Tuzun, Yilmaz Ozkilic, Olcay Anac

Istanbul Technical University, Faculty of Science and Letters, Department of Chemistry, 34469, Maslak, Istanbul, Turkey

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#### ABSTRACT

Many catalysts are used to control the chemo-selectivity, diastereoselectivity, and enantioselectivity in carbenoid reactions. In this work, the [4 + 1] carbonyl-ylide reaction of dimethyl diazomalonate with  $\alpha$ -ionone and the [3 + 2] carbonyl-ylide reaction of dimethyl diazomalonate with thiophene-2-carbaldehyde were chosen to obtain enriched diastereomeric products with the synthesized metal-lophthalocyanine compounds as catalysts. Four metallophthalocyanines (MPcs) including two neopenthoxy substituted and two novel fenchoxy substituted on non-peripheral positions of phthalocyanine ring were synthesized. Their catalytic activities were also compared with several common catalysts. Our results showed that in both reactions copper-Pc with neopentyl is the most effective catalyst to obtain diastereoselective results with diastereomeric product ratios of 30:70 and 10:90. DFT calculations also performed to explain the effect of the catalyst in diastereoselectivity. The calculations were in good agreement with the experimental results and assisted in understanding the selectivity.

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#### 1. Introduction

Dihydrofurans and dioxolanes are important heterocycles in natural product chemistry and many different synthetic pathways have been reported for their synthesis [1]. While [4 + 1] ring closure of the carbonyl ylide formed by carbene reaction in catalytic conditions is one of the synthetic approaches of dihydrofurans [2-3], [3 + 2] ring closure of the carbonyl ylide is a convenient way of producing of dioxolanes [1i, 2d-e]. Among wide variety of these catalytic reactions, transition metal-catalyzed methods are more popular compared to others since they can be performed under relatively mild conditions. Hence, these catalysts were successfully applied in many reactions such as insertions, additions, ylide formations and rearrangements [2a].

Accordingly, we studied the formal 1,5-electrocyclic reaction of carbonyl ylides derived from  $\alpha$ , $\beta$ -unsaturated ketones, esters, diesters, and enaminones by using Cu(acac)<sub>2</sub>/Rh<sub>2</sub>(OAc)<sub>4</sub> as catalysts [2c, 4a-h]. In these reactions, we obtained dihydrofurans and multi-

functionalized 2,3-dihydrofurans successfully.

We also obtained dioxolanes from  $Cu(acac)_2$  catalyzed [3 + 2] ring closure of the carbonyl ylide derived from thiophene-2-carbaldehyde [2d].

In the last decade, phthalocyanines (Pcs) and metallophthalocyanines (MPcs) have attracted great attention in carbene transfer reactions particularly in cyclopropanation as transition metal-catalysts [5]. Zhou et al. performed one of the first studies in this area [5a] and reported the cyclopropanation reactions of styrene derivatives and ethyl diazoacetate in the presence of modified phthalocyanines. Moreover, the use of metallophthalocyanine as heterogeneous catalyst for the cyclopropanation of olefins with trimethylsilyldiazomethane was reported concomitantly [5b]. In there report, silylcyclopropanes were obtained stereoselectively for the first time. Later, Ventura et al. studied the reactions of olefins and methylphenyldiazoacetate as donor-acceptor carbene source with metallophthalocyanine catalyst [5c]. Moreover, the cyclopropanation of aromatic olefins and carbene insertion into the N-H bonds of aromatic and aliphatic amines in the presences of Ru(IV) binuclear phthalocyanines were investigated [5d].

Although some metallophthalocyanine catalyzed cyclopropanations were reported previously, [4 + 1] and [3 + 2]-ring







<sup>\*</sup> Corresponding author. E-mail address: gungorfus@itu.edu.tr (F.S. Gungor).

closures of the carbonyl ylide to obtain dihydrofurans and dioxolanes have never been reported. In continuation to our works [2c-d, 4], we studied the activity of MPc as a catalyst in [4 + 1] and [3 + 2] cycloaddition reactions via carbonyl-ylide intermediate by selected two models of carbenoid reactions. For this purpose, copper- and nickel-Pcs, substituted with non-peripherally fenchoxy as novel MPcs and neopentoxy MPcs were synthesized according to a modified procedure reported in the literature. In addition, DFT calculations were performed to explain the structural effects that led to diastereoselectivity in the model reactions.

#### 2. Results and discussion

In this study,  $\alpha$ -ionone (1) and dimethyl diazomalonate (2) were reacted to obtain one diastereomeric product excessively in the presence of a series of catalysts, which include MPcs (7–10) (Scheme 1).

First of all, MPc complexes (**7**–**10**) were synthesized by the cyclotetramerization of 3-fenchoxy-phthalonitrile (**5**) and 3-neopentoxy-phthalonitrile (**6**) in the presence of metal salts  $(Cu(acac)_2 \text{ or } Ni(OAc)_2)$  in *n*-pentanol (Scheme 2). Catalyst **7** and **8** were obtained for the first time in this study. However, **1**(4), **8**(11), 15(18), 22(25)-tetrakis(3-neopentoxy) phthalo-cyaninato nick-el(II)/copper (II) (**9**/**10**) were synthesized by Chen et al. in 2012 [**6**].

Having synthesized the MPc catalyts, our reported  $Cu(acac)_2$  catalyzed carbonyl-ylide reaction of  $\alpha$ -ionone and dimethyl diazomalonate [2c] was also re-studied in the presence of several common catalysts, including the MPcs that have not been used previously in this reaction. To understand the product distribution (chemo-selectivity) and also diastereoselectivity in the reaction, various parameters (rate of reactants, reaction time etc.) were examined (Table 1).

Dihydrofuran (**3**) and furofuran (**4**) derivatives were formed in a ratio of 77:33 with a diastereoselectivity of **3a:3b** = 42:58, respectively, from our previous reaction of  $\alpha$ -ionone and dimethyl diazomalonate in the presence of Cu(acac)<sub>2</sub> under the conditions of entry 1, Table 1 [2c]. For this catalyst, we re-designed the procedure so that the formation of furofuran compound (**4**) was prevented by controlled dropping of the diazo compound slowly (entry 2, Table 1). Thus, increasing the amount of  $\alpha$ -ionone was not sufficient alone in order to give any significant difference for preventing the formation of furofuran (**4**) (entries 1 and 2, Table 1).

According to the literature, in the presence of excess diazo compound, Tang et al. have used CuCl:AgSbF<sub>6</sub> with chiral additives to increase diastereoselectivity [3b]. However, in our results (entries 5 and 6) with similar conditions to that study, no significant diastereoselectivity improvement was observed. Then, to



3a: 3S, 1'R and 3R, 1'S 3b: 3S, 1'S and 3R, 1'R

 $\label{eq:Reaction condition: 1 (1.5 equiv., 0.904 mmol) and catalyst (0.007 equiv., 0.0042 mmol) in 10 mL of benzene and 2 (1 equiv., 0.602 mmol) in 1 mL of benzene, reflux under N_2.$ 

**Scheme 1.** Chemoselective/diastereoselective reaction of  $\alpha$ -ionone and dimethyl diazomalonate [2c].



Scheme 2. Synthesis of MPcs (7–10).

understand the catalytic effect of MPcs, Ni and Cu-Pc complexes were used as catalysts in the same carbene transformation reaction. When Ni-Pc was used as catalyst (entries 7, 8, 10 and 11), it was slightly more efficient than the standard catalysts used (entries 1–6). Among the trials, entry 12 with **10** had the most satisfying catalytic activity with a ratio of 30:70 diastereomeric excess. However, in the case of the catalyst **8**, substituted with fenchoxy group, the consumption of the diazo reagent was limited possibly due to the bulky side group effect on MPc.

In order to increase the substrate scope with respect to diastereoselective reaction effect of catalyst **10**, we performed the Cu(acac)<sub>2</sub>-catalyzed carbonyl-ylide ring closure reaction of thiophene-2-carbaldehyde (**11**) and dimethyl diazomalonate in recent study [2d] (Scheme 3). While this reported study with Cu(acac)<sub>2</sub> had yielded diastereomeric dioxolanes **12** with a non-selective way the new attempt with catalyst **10** gave diastereoselective dioxolanes mixture with a ratio of 10:90 diastereomeric excess.

In order to understand the benefits of the catalyst system and the experimentally observed product distribution between diastereomers **3a** (3S, 1'R and 3R, 1'S) and **3b** (3R, 1'R and 3S, 1'S), DFT calculations were carried out for the cyclization step of the reaction involving **10**. Although the calculations presented herein only include the 3S, 1'R vs. 3R, 1'R cases, these results can be extended to the remaining mirror-image products, 3R, 1'S vs. 3S, 1'S for both **3a** and **3b** due to the racemic nature of the reactant.

To find the most populated conformational state of the copper complexed Pc system, an extended conformational analysis was conducted. As can be seen from Fig. 1, there are mainly four possible conformers relative to the Cu-Pc plane: all of the four neopentyl substituents oriented on one side of the plane of Pc (**10a**); one leaning above the Pc plane and the others leaning below (**10b**); two adjacent substituents leaning up and the others down (**10c**); two substituents on one of the diagonal axis of the Pc plane directed above and the others below the Pc plane (**10d**).

Clearly, **10d** is the most stable conformer by approximately 3 kcal/mol relative to the other conformers and therefore, the reaction must preferentially take place on its two distinct surfaces.

As a start, a Cu-carbene complex is modelled. Today, it is wellknown that these reactions start with the diazo-decomposition leading to metal-carbene complexes and this is the rate

#### Table 1

Product ratios of reactions of  $\alpha$ -ionone (1) and dimethyl diazomalonate (2)<sup>a</sup>.

Entry	Catalyst (equiv) <sup>b</sup>	Reaction time (hour)	Ratio 1:2 <sup>c</sup>	3:4 <sup>d</sup>	3a:3b (d.r.) <sup>e</sup>
1	Cu(acac) <sub>2</sub> (0.007)	3	1.5:1	77:33	42:58 [2c]
2	Cu(acac) <sub>2</sub> (0.007)	24	1:1	100:0	42:58 [2c]
3	CuCl (0.007)	8	1.5:1	100:0	45:55
4	$Rh_2(OAc)_4 (0.007)$	9	1.5:1	100:0	46:54
5	CuCl:AgSbF <sub>6</sub> (0.025:0.029)	8	1:1.5	100:0	38:62
	Chiral add:2,2'-isopropylydene-bis[(4S)-4-phenyl-2-oxazoline (0.032)				
6	CuCl:AgSbF <sub>6</sub> (0.025:0.029)	8	1:1.5	100:0	40:60
	Chiral add:2,2'-bipyridine (0.032)				
7	<b>7</b> (0.007)	48	1.5:1	100:0	37:63
8	<b>7</b> (0.007)	52	1:1	100:0	35:65
9	<b>8</b> (0.007)	100	1.5:1	100:0	40:60 <sup>f</sup>
10	<b>9</b> (0.007)	32	1.5:1	100:0	40:60
11	<b>9</b> (0.007)	27	2:1	100:0	38:62
12	<b>10</b> (0.007)	9	1.5:1	100:0	30:70

<sup>a</sup> Reaction conditions: Substrate (1.5 equiv.) and catalyst (0.007 equiv.) in 10 mL of benzene, and dimethyl diazomalonate (1 equiv.) in 1 mL of benzene, reflux under N<sub>2</sub> (details in given supporting information).

<sup>b</sup> Diazo compound was used as 1 equivalent.

<sup>c</sup> mmol ratio of **1** and **2**.

<sup>d</sup> Determined by <sup>1</sup>H NMR spectroscopy.

<sup>e</sup> d.r. is diastereomeric ratio of **3** was determined <sup>1</sup>H NMR spectroscopy.

<sup>f</sup> Diazo compound did not consume completely.



<sup>a</sup> **11** (1.5 equiv., 0.9 mmol) and **2** (1 equiv., 0.6 mmol) were reacted in 10 mL benzene in the presence of catalyst (0.007 equiv., 0.0042 mmol)

<sup>b</sup> Diastereomer ratio was determined by <sup>1</sup>H NMR analysis.

Scheme 3. The reactions of thiophene-2-carbaldehyde and dimethyl diazomalonate.



Fig. 1. Possible conformers of 10. The energies are presented relative to 10d.

determining step as we have shown in our earlier reports with DFT calculations [4e, 7]. The planar structure of the Pc ring does not allow a convential Cu=C interaction as seen with other geometrically free ligands. Thus, the C(carbene)-Cu distance of 2.47 Å in **10d**-



Fig. 2. The three-dimensional geometry of 10d-carbene.

**carbene** structure (Fig. 2) is much longer than the  $Cu(acac)_2$  analogue from our earlier report (1.771 Å) [4e]. However, the donor-acceptor energies between **10d** and carbene carbon, exhibited by the NBO analysis show strong interactions in between, mostly from the carbene carbon to Cu. (See supporting information for details).

Once  $\alpha$ -ionone is added, a carbonyl-ylide intermediate is known to occur (Scheme 4). The carbene carbon of this ylide can attack the present olefinic carbon atom via two modes, yielding a tetrahedral carbon with different stereocenters. Additionally, the cyclization step can take place on both sides of the Pc ring. As can be seen in Fig. 1, energetically, these two faces must cause a variation during the cyclization reaction since they are stereochemically different due to the alignment of the neopentyl substituents (See supplementary material in Fig. S1). Thus, we have considered the alignments of the  $\alpha$ -ionone on the up and down faces of the Pc planes and the reactions were modelled on both faces of **10d** (Schemes 5 and 6) for formation of both S,R and R,R products.

With the substrate  $\alpha$ -ionone, pre-reactant complexes will form (**10d-up** and **10d-down** in Schemes 5 and 6, respectively). Since the pre-reactant complex **10d-up** is the most stable structure, all the energies of Schemes 5 and 6 are reported relative to this structure. Once the  $\alpha$ -ionone interacts with the Cu-carbene and forms a ylide, the distance between the carbene carbon and copper center extended to 3.10 Å in both up and down structures. This result implies that the binding of the substrate carbonyl oxygen to the carbene carbon weakens its interaction with the copper center appreciably so that the new ylide fragment obtained above/below the Cu-Pc plane binds to the catalyst system via the van der Waals interaction originating from both carbene carbon-copper center



Scheme 4. Formation of 3a and 3b.

and the stacking interactions. In the proceeding sections of the cyclization reactions, these interactions are continuously weakened due the destruction of the carbene character of the carbon atoms as the carbon-copper center distances extend to 3.40 Å, 3.21 Å, 3.38 Å, 3.25 Å in the **TS-up-SR**, **TS-up-RR**, **TS-down-SR** and **TS-down-RR** transition state structures, respectively. Eventually, these interactions vanish as these distances further extend to 4.32 Å, 3.91 Å, 4.13 Å and 4.26 Å in the product structures, namely, **SR-up**, **RR-up**, **SR-down** and **RR-down**, respectively.

The effect of copper was reported to initiate the diazo decomposition and formation of metal carbenoid. At the same time, copper facilitated the cyclization by bringing the reacting sites to geometrically available position. The geometries of the transition state structures show that the presence of the neopentyl groups in this system can make a directional effect by holding them in a proper 3-dimensional geometry in space. This suggest that the non/ peripheral substituents can be varied so that the desired interactions can be built between the substrate and the substituents to dominate only one mode of cyclization.

#### 3. Conclusion

In this study, a series of MPc complexes substituted nonperipherally with fenchoxy and neopentoxy moieties were employed as catalysts in a designed and known metal-carbenoid reaction. The Pc's with fenchoxy group have been synthesized for the first time. These metal complexes were used in the reaction of  $\alpha$ -ionone (1) and dimethyl diazomalonate (2), along with a series of common catalysts. Among these catalysts, 1(4), 8(11), 15(18), 22(25)-tetrakis(3-neopentoxy) phthalocyaninato copper (II) (10) gave better yields with enriched diastereomeric excess, leading to formation of one diastereomer (3b). In the reaction of  $\alpha$  thiophene-2-carbaldehyde (11) and dimethyl diazomalonate (2) with catalyst 10 also resulted enriched diastereomeric excess similarly.

Herein, we present the first successful attempts that utilize MPc as a catalyst in [4 + 1] and 3 + 2] cycloaddition reactions. DFT calculations were performed to explain the benefits of the catalyst system and the structural effects that led to diastereoselectivity in this [4 + 1] reaction. With the calculations, the experimentally observed product distribution was reproduced and explained by the steric effects caused by the pendant group during the

cyclization step. According to the computations conducted in this study, the catalyst provides a van der Waals surface to the prereaction structure of the cyclization step. Additionally, the bulky neopentyl groups have directed the positioning of the  $\alpha$ -ionone and the dimethyl diazomalonate groups, which played a directional role in the diastereoselectivity.

These results show that the MPcs incorporate the synergistic effect of the electrophilicity of Cu and the high electron donating ability of Pc ring, which has a potential to design catalysts for stereoselective synthesis. This study has shown that further efforts on MPcs with suitable peripheral/non-peripheral substituents can lead to new catalysts for stereoselective carbenoid reactions in future studies.

#### 4. Experimental section

#### 4.1. Materials and methods

All solvents and reactants are commercially available. Dimethyl diazomalonate (2) (dmdm) was prepared according to literature [8]. All reactions of diazo compounds and substrates were carried out under nitrogen atmosphere. A rotary evaporator equipped with a water condenser and attached to a vacuum system was used to concentrate in vacuo. UV-visible spectra were measured with a Shimadzu UV-1601 double beam spectrometer. <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectra were recorded on Agilent VNMRS 500/125 MHz, respectively. Chemical shifts ( $\delta$ ) are reported in ppm with respect to the internal standard tetramethylsilane (TMS). Splitting patterns were described as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad signal). GC-MS analyses were performed on a Thermo Finnigan trace dsq instrument equipped with a flame ionization detector. 5% Phenyl polysilphenylene-siloxane capillary column (TR-5MS) was used with helium as the carrier gas. Temperature program is as follows: Start 100 °C then 5 min isothermal, ramp 20°/min; final 290 °C and then 10 min isothermal. Retention times  $(t_R)$  are reported in min. ESI-MS analysis were performed on Bruker Micro TOF-ESI/MS. Melting points were recorded on Buchi Melting Points B-540 apparatus.



Reaction Coordinate

**Scheme 5.** The cyclization modelled for the approach of the substrates from the upper side of **10d**. Energies are not to scale.  $R = CH_2C(CH_3)_3$ ,  $E = CO_2CH_3$ . 3D version of this scheme is given in Fig. S2 in supporting information.

#### 4.2. General procedure 1 for synthesis of ligands (5–6)

3-Nitrophthalonitrile (7 mmol) and alcohol (5 mmol) were dissolved in 15 mL dry DMSO under nitrogen atmosphere. Then dry  $K_2CO_3$  (4 g, 23 mmol) was added to reaction flask during 2 h in

equal portions. Reaction was monitored by TLC. After completion of reaction, the reaction mixture was poured onto water and extracted with dichloromethane (2  $\times$  50 mL), and diethyl ether (1  $\times$  50 mL), respectively. Organic phases were collected and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure and the crude



Scheme 6. The cyclization reaction modelled for the approach of the substrates below the Pc plane of **10d.** Energies are not to scale. R = CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>, E = CO<sub>2</sub>CH<sub>3</sub>. 3D version of this scheme is given in Fig. S3 in supporting information.

product was purified by column chromatography.

#### 4.2.1. 3-Fenchoxy-phthalonitrile (5)

According to general procedure 1, 3-nitrophthalonitrile (1.20 g, 7 mmol) and (+)-fenchol (0.77 g, 5 mmol) were dissolved in 15 mL dry DMSO under nitrogen atmosphere. After work-up, crude product was purified by silica column chromatography (30% ethyl acetate/hexane) to give compound **5** was obtained as a white solid, m.p.: 110–113 °C;  $t_{\rm R} = 13.2$ ; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.59 (dd, <sup>3</sup> $J_{\rm H,H} = 8.6/7.7$ , 1H), 7.31 (dd, <sup>3</sup> $J_{\rm H,H} = 7.7$ , <sup>5</sup> $J_{\rm H,H} = 0.7$ , 1H), 7.22 (d, <sup>3</sup> $J_{\rm H,H} = 8.6$ , 1H), 4.04 (d, <sup>4</sup> $J_{\rm H,H} = 1.5$ , 1H), 2.18–2.12 (m, 1H), 1.84 (m, 1H), 1.63 (dd, <sup>2</sup> $J_{\rm H,H} = 10.7$ , <sup>3</sup> $J_{\rm H,H} = 1.3$ , 1H), 1.21 (s, 3H), 1.20 (m, 1H),

1.14 (s, 3H), 0.88 (s, 3H);  $^{13}$ C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  162.5, 134.2, 124.6, 117.8, 117.1, 115.4, 113.1, 105.3, 92.5, 49.8, 48.9, 41.3, 40.3, 30.5, 26.3, 25.6, 20.5, 19.8;

#### 4.2.2. 3-Neopentoxy-phthalonitrile (6)

According to general procedure 1, 3-nitrophthalonitrile (1.20 g, 7 mmol) and neopentanol (0.44 g, 5 mmol) were dissolved in 15 mL dry DMSO under nitrogen atmosphere. After work-up, crude product was purified by silica column chromatography (20% ethyl acetate:petroleum ether) to give compound **6** as a grey solid, m.p.: 120–121.5 °C;  $t_R = 11.95$ ; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.62 (t, <sup>3</sup> $J_{H,H} = 8.2$ , 1H), 7.34 (d, <sup>3</sup> $J_{H,H} = 7.7$ , 1H), 7.22 (d, <sup>3</sup> $J_{H,H} = 8.7$ , 1H), 3.76 (s, 2H), 1.11 (s, 9H).

#### 4.3. General procedure 2 for synthesis of MPc (7–10)

A mixture of ligand (0.35 mmol, 4 equiv.) and metal salt (0.0875 mmol, 1 equiv.) in 1 mL *n*-pentanol in Schlenk tube was heated at 80 °C under nitrogen atmosphere. 1–2 drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were added to the reaction mixture and heated at 140–145 °C for 24 h. After cooling down to room temperature, methanol was added to the reaction mixture, and then the mixture was filtered. The precipitate was purified by chromatography.

## 4.3.1. 1(4), 8(11), 15(18), 22(25)-tetrakis(3-fenchoxy) phthalocyaninato nickel (II) (7)

According to general procedure 2, 0.1 g (0.35 mmol) 3-fenchoxyphthalonitrile (**5**) and 0.015 g (0.0875 mmol) Ni(OAc)<sub>2</sub> was reacted in 1 mL *n*-pentanol at 140–145 °C for 24 h in the presence of 1–2 drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). After work-up, precipitate was dissolved in dichloromethane and purified by *p*-TLC (silica plate, 10% methanol:dichloromethane and purified by *p*-TLC (silica plate, 10% methanol:dichloromethane). Compound **7** was obtained as blue-green solid (13 mg, 10.5%); UV–Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$ nm (log  $\varepsilon$ ) = 318.5 (4.33), 631 (3.24), 703.5 (3.97); FTIR [ $\nu_{max}$ ]: 2992, 2866, 1589, 1489, 1325 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.17 (d, <sup>3</sup>*J*<sub>H,H</sub> = 7.8, 1H), 7.98 (t, <sup>3</sup>*J*<sub>H,H</sub> = 7.7, 1H), 7.59 (d, <sup>3</sup>*J*<sub>H,H</sub> = 7.8, 1H), 4.68 (s, 1H), 2.30–2.24 (m, 1H), 1.99 (bs, 1H), 1.92–1.81 (m, 3H), 1.29–1.21 (m, 6H), 0.88–0.80 (m, 5H); FAB-MS (*m*/*z*, %): 1178 (M<sup>+</sup>, 100), 1194 (17), 1211 (11).

## 4.3.2. 1(4), 8(11), 15(18), 22(25)-tetrakis(3-fenchoxy) phthalocyaninato copper (II) (**8**)

According to general procedure 2, 0.1 g (0.35 mmol) 3-fenchoxyphthalonitrile (**5**) was treated with 0.022 g (0.085 mmol) Cu(acac)<sub>2</sub> in 1 mL *n*-pentanol in the presence of 1–2 drops of 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU). After work-up, precipitate was dissolved in dichloromethane and purified by silica column chromatography (10% dichloromethane:methanol). Compound **8** was as dark greenish blue solid (33 mg, 26.8%); UV–Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$ , nm (log  $\varepsilon$ ) = 320 (3.87), 640.5 (3.65), 713 (4.34); FTIR [ $\nu_{max}/cm^{-1}$ ]: 2965, 2935, 2700, 1589, 1487, 1261, 1243 cm<sup>-1</sup>; FAB-MS (*m*/*z*, %): 1181 (M<sup>+</sup> – 2, 100), 1200 (11), 1216 (11).

## 4.3.3. 1(4), 8(11), 15(18), 22(25)-tetrakis(3-neopentoxy) phthalocyaninato nickel (II) (**9**)

According to general procedure 2, 0.1 g (0.46 mmol) 3neopentoxy phthalonitrile (**6**) was reacted with 0.02 g (0.115 mmol) Ni(OAc)<sub>2</sub> in 1 mL *n*-pentanol in the presence of 1–2 drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). After work-up, precipitate was washed with methanol, hexane, and diethyl ether respectively. The product dried in vacuo. Compound **9** was obtained as mazerine blue solid (15 mg, 4%); UV–Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$ , nm (log  $\varepsilon$ ) = 629 (3.15), 698 (3.74); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.18 (d, <sup>3</sup>J<sub>H,H</sub> = 7.8, 1H), 8.04 (d, <sup>3</sup>J<sub>H,H</sub> = 7.8, 1H), 7.55 (d, <sup>3</sup>J<sub>H,H</sub> = 7.6, 1H), 3.53–3.38 (m, 2H), 1.26 (bs, 3H), 0.90–0.80 (m, 6H); FAB-MS (*m*/*z*, %): 915 (M<sup>+</sup>, 100), 916 (M<sup>+1</sup>, 60), 917 (M<sup>+2</sup>, 7).

## 4.3.4. 1(4), 8(11), 15(18), 22(25)-tetrakis(3-neopentoxy) phthalocyaninato copper (II) (10) [2]

According to general procedure 2, 0.1 g (0.46 mmol) 3neopentoxy phthalonitrile (**6**) and 0.03 g (0.115 mmol) Cu(acac)<sub>2</sub> were reacted in 1 mL *n*-pentanol, in the presence of 1–2 drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). After work-up, precipitate was washed with methanol, hexane and diethyl ether respectively. The product dried in vacuo. Compound **10** was obtained as blue solid (13 mg, 4%); UV–Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  nm (log  $\varepsilon$ ) = 317 (3.42), 347 (3.36), 635 (3.34), 707 (4.05).

#### 4.4. General procedure for metal-carbenoid reactions

The reaction of substrate (**1** and **11**) and dimethyl diazomalonate (**2**) was performed according to our previous work [2c, 2d]. Experimental details were given in supplementary material.

#### 4.5. Computational details

Gaussian 16, Revision A.03 software [9] was utilized for the DFT calculations. Due to large number of electrons in the computational system, geometry optimizations and frequency calculations in the unrestricted doublet multiplicity state were carried out with LANL2DZ [10] effective core potential for copper and 6-31G(d) basis set for the rest of the atoms, using M06-L functional [11], which has been successful with Cu catalyst in our earlier report [12]. Then, to refine the energies, single point calculations were carried out with the 6-311 + G(2d, 2p) basis set for the atoms other than copper and with PCM solvation scheme [13] to represent the solvent benzene in a continuum model. Every transition state reported in this study has one imaginary frequency belonging to the reaction coordinate. Intermediate states belonging to the located transition states were obtained utilizing intrinsic reaction coordinate [14] (IRC) calculations. The reported energies are electronic energies from single point calculations (high level). In the figures, hydrogens are omitted for clarity while reported distances are in the units of Å.

#### **Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2020.131892.

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