

# Synthesis of new Schiff bases; Investigation of their in situ catalytic activity for Suzuki C—C coupling reactions and antioxidant activities

Özgür Yılmaz 

Department of Chemistry, Faculty of Arts and Sciences, Mersin University, Mersin, Turkey

## Correspondence

Özgür Yılmaz, Department of Chemistry, Faculty of Arts and Sciences, Mersin University, 33343 Mersin, Turkey.  
Email: yilmazozgur@mersin.edu.tr

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## Abstract

New series of Schiff bases have been synthesized from the reaction between cyclohepta-2,4,6-trien-1-ylmethanamine and different aldehydes, and characterized via using  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, FTIR spectroscopy, and GC–MS. After the successful synthesis, the in situ catalytic activity of all Schiff bases have been examined for the Suzuki C—C cross-coupling reactions using phenylboronic acid, aryl bromides, and  $\text{PdCl}_2$  as a catalyst. Before starting these investigations, reaction conditions were optimized using different bases and solvents. At the end of these reactions, the best efficiency was obtained in  $\text{Et}_3\text{N}$  and  $\text{EtOH}$ . In addition to catalytic investigations, antioxidant activities of all synthesized Schiff bases were examined using DPPH and Iron ( $\text{Fe}^{2+}$ ) chelation methods, and  $\text{IC}_{50}$  values were calculated. While many molecules show various amounts of antioxidant activity, especially molecules **8e** and **8g** showed the best activity compared to butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA), which were used as positive controls, in DPPH and Iron chelating methods, respectively.

## KEYWORDS

antioxidant activities, catalytic activity, Schiff base, Suzuki coupling

## 1 | INTRODUCTION

Schiff bases containing imine ( $-\text{C}=\text{N}-$ ) or azomethine ( $-\text{CH}=\text{N}-$ ) groups are one of the most important class functional groups in organic chemistry due to their extensive biological and chemical properties.<sup>1–5</sup> The Schiff bases are also used as intermediates for the synthesis of important drugs, pesticides, and other natural products because of the conversion possibility of  $-\text{C}=\text{N}-$  group to the desirable functional groups through reduction, addition, cyclization, and aziridination reactions.<sup>6–11</sup> Furthermore, antibacterial, anti-fungal, anti-oxidant, anti-tumor, anti-viral, anti-HIV, anti-inflammatory, and anti-proliferative properties of Schiff bases have been reported in the literature.<sup>12–25</sup> Besides the biological importance, the transition metal complexes, which can be obtained from  $\sigma$ -donor and

$\pi$ -acceptor Schiff bases as ligands, have wide catalytic applications in many reactions.<sup>26–30</sup> For example, Yılmaz and coworkers synthesized new palladium and ruthenium complexes of Schiff bases and these complexes showed important catalytic activity for Suzuki, Heck C—C cross-coupling reactions together with catalytic hydrogenation and transfer hydrogenation reactions.<sup>31–33</sup> In addition, Alimirzaei and coworkers examined copper complexes of Schiff-bases for antimicrobial activities against gram-positive and gram-negative bacteria, and obtained relatively good results.<sup>34</sup> On the other hand, there are many reported studies, which showed effective antioxidant properties of Schiff bases in the literature.<sup>35–37</sup>

In this paper, new Schiff base derivatives have been synthesized and all structures have been identified by using NMR, FTIR, and GC–MS techniques. In addition,

in situ catalytic activities for Suzuki cross-coupling reactions and the antioxidant activities via DPPH (2,2-diphenyl-1-picrylhydrazyl) and Ferrous ions ( $\text{Fe}^{2+}$ ) chelating methods have been examined for all synthesized molecules.

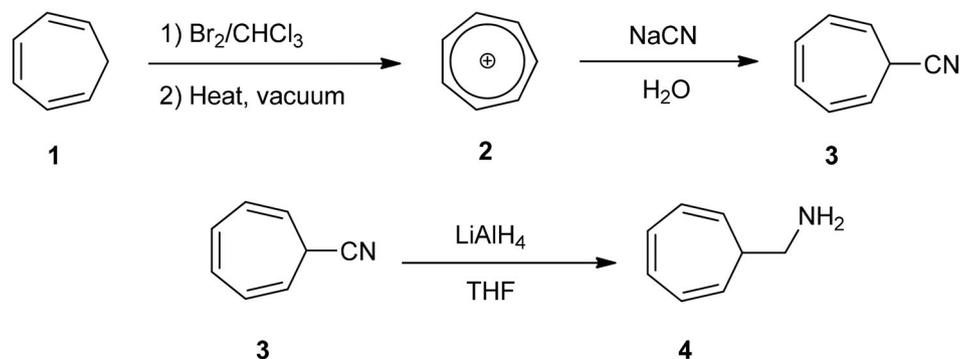
## 2 | RESULTS AND DISCUSSION

First, cyclohepta-2,4,6-trienecarbonitrile (**3**) was synthesized from cycloheptatriene **1** with bromination, elimination, and cyanation reactions, respectively.<sup>38,39</sup> Then, cyclohepta-2,4,6-trien-1-ylmethanamine<sup>40</sup> **4** was obtained in high yield from nitrile **3** with reduction via  $\text{LiAlH}_4$  (Scheme 1).

Upon successful synthesis of amine **4**, a series of reactions have been set up between amine **4** and benzaldehyde **5** for the optimization of reaction conditions (Table 1). The yields of reactions were determined with GC using the internal standard. Results showed that polar protic solvents better than polar aprotic ones.<sup>41</sup> In addition, the temperature increase improved the yield.

After determining the optimal conditions as shown in Table 1/Entry 6, we tested different substrates through the reactions of amine **4** and different aldehydes **7a-h**, and obtained new Schiff base series with high yield **8a-h** (Table 2).

All structures have been identified by using  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , FTIR spectroscopy, and GC-MS methods. When the  $^1\text{H-NMR}$  spectra of synthesized molecules were examined, the signals of the  $-\text{N}=\text{CH}$  protons appear as singlet in the region between  $\delta$  8.85 and 7.77 ppm, which was also confirmed by the literature.<sup>32</sup> While the aromatic protons resonate at  $\delta$  6.84–8.08 ppm,<sup>32</sup> the double bond protons resonate at  $\delta$  5.23–6.73 ppm.<sup>42</sup> The  $-\text{CH}$  and  $-\text{NCH}_2$  protons appear at  $\delta$  2.06–2.27 and  $\delta$  3.57–4.01 ppm, respectively. In addition, the  $-\text{OCH}_3$  protons in the molecule **8d**, resonate at  $\delta$  3.92 ppm.<sup>43</sup> In addition to the  $^1\text{H-NMR}$  results, the  $^{13}\text{C-NMR}$ , FTIR, and GC-MS spectra confirmed the structures of the synthesized molecules. Structures containing  $-\text{OH}$  group in *ortho* position, the  $-\text{OH}$  band was not observed in the FTIR spectra. This is presumably due to the hydrogen bonding between the  $-\text{CH}=\text{N}$  and the  $-\text{OH}$  groups. When the studies in the literature with similar structures are

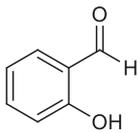
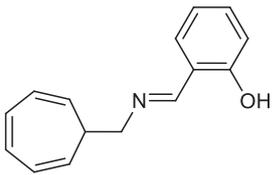
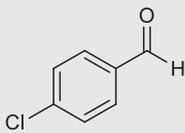
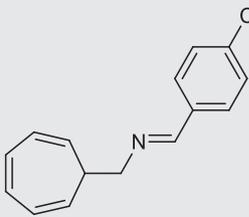
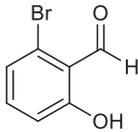
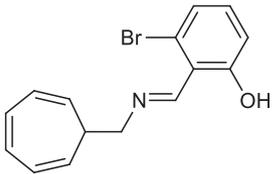
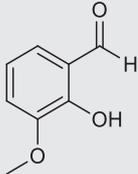
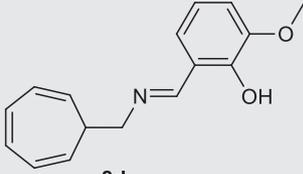
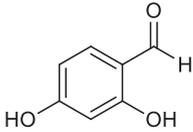
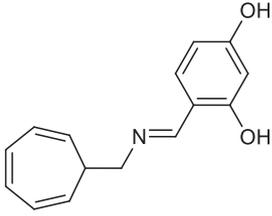
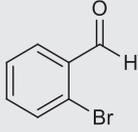
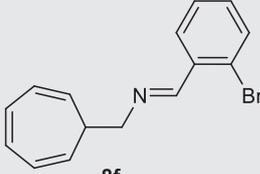
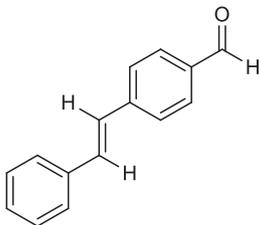
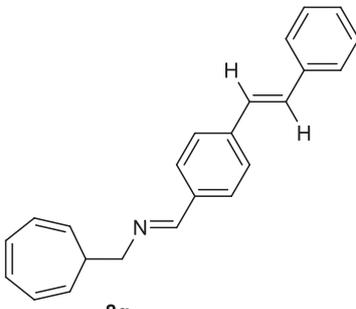


**TABLE 1** Optimizations of condition

Entry	Condition of reaction	Yield % <sup>a</sup>
1	Toluene, 25°C	64
2	Dichloromethane, 25°C	79
3	Methanol, 25°C	83
4	Methanol, AcOH, 25°C	89
5	Methanol, $\text{Na}_2\text{SO}_4$ , 25°C	87
6	Methanol, 40°C	96

<sup>a</sup>Yield was determined by GC using *n*-decane as internal standard.

TABLE 2 Synthesis of new substituted Schiff bases

Entry	Amine	Aldehydes	Product	Isolated yield %
1	4	 7a	 8a	89
2	4	 7b	 8b	92
3	4	 7c	 8c	84
4	4	 7d	 8d	87
5	4	 7e	 8e	82
6	4	 7f	 8f	91
7	4	 7g	 8g	95

(Continues)

TABLE 2 (Continued)

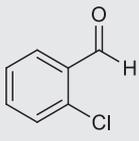
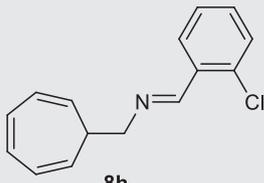
Entry	Amine	Aldehydes	Product	Isolated yield %
8	<b>4</b>	 7h	 8h	92

TABLE 3 Optimizations for Suzuki cross-coupling reaction

Entry	Base	Solvent	<sup>a</sup> Conversion%	<sup>a</sup> Yield%	Selectivity <sup>o</sup> %
1	NaOH	1,4-dioxane	56	48	85.7
2	KOH	1,4-dioxane	56	48	85.7
3	K <sub>2</sub> CO <sub>3</sub>	1,4-dioxane	29	23	79.3
4	Et <sub>3</sub> N	1,4-dioxane	36	31	86.1
5	NaOH	EtOH	76	68	89.5
6	KOH	EtOH	71	63	88.7
7	K <sub>2</sub> CO <sub>3</sub>	EtOH	61	56.5	92.6
8	Et <sub>3</sub> N	EtOH	84	79	94.1
9	NaOH	Toluene	11	2	18.2
10	KOH	Toluene	31	23.5	75.8
11	K <sub>2</sub> CO <sub>3</sub>	Toluene	10	1	10
12	Et <sub>3</sub> N	Toluene	20	15	75
13 <sup>b</sup>	Et <sub>3</sub> N	EtOH	89	83	93.3
<b>14<sup>c</sup></b>	<b>Et<sub>3</sub>N</b>	<b>EtOH</b>	<b>100</b>	<b>97.0</b>	<b>97.0</b>

Note: Reaction conditions: 4-bromoacetophenone (0.5 mmol), phenylboronic acid (0.6 mmol), Schiff base **8e** (1 mol%), PdCl<sub>2</sub> (0.5 mol%), base (0.6 mmol), solvent (2.0 ml), H<sub>2</sub>O (1.0 ml), 2 hr, 80 °C.

<sup>a</sup>The yields was calculated with GC using *n*-decane as internal standard.

<sup>b</sup>100 °C.

<sup>c</sup>4 hr.

analyzed, it is also seen that —OH band is not reported in the FTIR spectrum.<sup>44</sup>

## 2.1 | In situ catalytic activity for Suzuki C—C coupling reactions

After the synthesis of Schiff bases, the in situ catalytic activity in Suzuki C—C coupling reactions of phenylboronic acid **10** and substituted aryl bromides were investigated for all Schiff bases. Series of reactions between phenylboronic acid **10** and 4-bromoacetophenone **9** in the presence of 0.5 mol% molecule **8e** as ligand and 0.2 mol% PdCl<sub>2</sub> as a catalyst has

been tested using different base, solvent, and temperature to optimize the catalytic conditions. For this purpose, KOH, NaOH, K<sub>2</sub>CO<sub>3</sub>, and Et<sub>3</sub>N were chosen as bases to be tested. In addition, EtOH, 1,4-dioxane, and toluene were examined as solvent variables. The best yield was obtained while using Et<sub>3</sub>N as a base in EtOH (Table 3/Entry 8). The other reactions in EtOH with different bases showed better conversion and selectivity compared to the reactions in toluene or 1,4-dioxane. In addition, the worst results for conversion and selectivity have been obtained in toluene especially with K<sub>2</sub>CO<sub>3</sub> (Entry 11). In summary, polar protic solvents improve the catalytic activity better compared to nonpolar solvents. In addition, organic bases appear to be more

effective than inorganic bases when ethanol is used as the solvent. Small but various amounts of biphenyl by-product were obtained from phenylboronic acid in all reactions. In order not to affect the yield calculation of this product originating from phenylboronic acid **10**, 4-bromoacetophenone **9** was used instead of bromobenzene in optimization reactions. After determining the best experimental conditions, reactions were performed at different temperatures and times in order to increase the conversion yield. Looking at the results of these reactions, it was seen that the conversion efficiency increased at 100 °C but did not reach the maximum (Entry 13). 100% conversion was obtained in the reaction, which was continued for 4 hr at 80 °C (Entry 14).

After optimizing the reaction conditions for the Suzuki cross-coupling reaction, the catalytic activity of all synthesized Schiff bases was investigated by reactions between various aryl bromides and phenylboronic acid **10**. As is known

in the literature, besides the steric effect, substituted groups in aryl bromide significantly affect their reaction yields. For example, electron-donating groups and steric barriers reduce reaction efficiency, while electron-withdrawing groups increase reaction efficiency. In order to demonstrate these effects, a sterically hindered aryl bromide molecule was selected as well as aryl bromides substituted with electron-donating or electron-withdrawing groups. 100% conversions were observed with all Schiff bases in the reactions with 4-bromoacetophenone **9** (Table 4/Entry 1) and 2-bromobenzaldehyde **12a** (Entry 2), which are selected as aryl bromide structures containing electron-withdrawing substituted groups, and obtained 1-([1,1'-biphenyl]-4-yl) ethanone (**11**) and [1,1'-biphenyl]-2-carbaldehyde (**13a**) with high yields (up to 93%), respectively. Other aryl bromide structures selected to study the effect position of electron-withdrawing groups are *para*- **12b** and *ortho*-trifluoromethyl

**TABLE 4** In situ catalytic activities of synthesized Schiff bases for the Suzuki C—C coupling reactions between phenylboronic acid and different aryl bromides

Entry	ArBr	Product <sup>a</sup>	Conversion <sup>b</sup> , (yield) <sup>b</sup> , [selectivity] %								
			<b>6</b>	<b>8a</b>	<b>8b</b>	<b>8c</b>	<b>8d</b>	<b>8e</b>	<b>8f</b>	<b>8g</b>	<b>8h</b>
1			100	100	100	100	96.4	100	100	100	100
			(96.7)	(97.4)	(96.5)	(97.2)	(94.2)	(97.0)	(93.2)	(97.6)	(96.3)
			[96.7]	[97.4]	[96.5]	[97.2]	[97.7]	[97.0]	[93.2]	[97.6]	[96.3]
			N.R. <sup>c</sup>	N.R. <sup>c</sup>	N.R. <sup>c</sup>	N.R. <sup>c</sup>	N.R. <sup>c</sup>	N.R. <sup>c</sup>	N.R. <sup>c</sup>	N.R. <sup>c</sup>	N.R. <sup>c</sup>
			N.R. <sup>d</sup>	N.R. <sup>d</sup>	N.R. <sup>d</sup>	N.R. <sup>d</sup>	N.R. <sup>d</sup>	N.R. <sup>d</sup>	N.R. <sup>d</sup>	N.R. <sup>d</sup>	
2			100	100	100	100	100	100	100	100	100
			(98.3)	(98.4)	(96.8)	(97.9)	(97.5)	(97.4)	(97.7)	(98.3)	(97.6)
			[98.3]	[98.4]	[96.8]	[97.9]	[97.5]	[97.4]	[97.7]	[98.3]	[97.6]
3			94.1	92.6	86.9	97.3	93.3	95.1	94.8	97.4	85.5
			(89.3)	(89.2)	(81.8)	(93.5)	(89.9)	(93.0)	(89.3)	(93.9)	(82.9)
			[97.6]	[94.9]	[94.1]	[96.1]	[96.4]	[97.8]	[94.2]	[96.4]	[97.0]
4			90.3	84.1	82.6	96.1	97.3	87.6	83.5	96.8	78.2
			(87.1)	(80.1)	(78.3)	(93.3)	(91.8)	(84.9)	(78.9)	(95.2)	(75.7)
			[96.5]	[95.2]	[94.8]	[97.1]	[94.3]	[96.9]	[94.5]	[98.4]	[96.8]
5			21.6	18.9	16.9	17.4	7.9	7.1	54.6	32.1	17.9
			(2.8)	(2.7)	(1.8)	(1.9)	(1.1)	(1.2)	(4.3)	(1.7)	(2.4)
			[13.0]	[10.7]	[10.9]	[10.9]	[13.9]	[16.9]	[7.9]	[5.3]	[13.4]
6			80.0	74.8	70.2	84.1	84.4	77.5	73.1	87.0	70.7
			(74.5)	(68.5)	(66.0)	(78.5)	(79.9)	(70.7)	(67.2)	(82.1)	(64.4)
			[93.1]	[91.6]	[94.0]	[93.3]	[94.7]	[91.2]	[91.9]	[94.4]	[91.1]
7			62.6	63.9	52.6	69.3	78.3	68.6	69.0	78.8	42.3
			(57.1)	(60.1)	(46.3)	(63.6)	(73.3)	(63.4)	(62.9)	(74.6)	(36.4)
			[91.2]	[94.1]	[88.0]	[91.8]	[93.6]	[92.4]	[91.2]	[94.7]	[86.1]

Note: Reaction conditions: aryl bromide (0.5 mmol), phenylboronic acid (0.6 mmol), Schiff base (1 mol%), PdCl<sub>2</sub> (0.5 mol%), NEt<sub>3</sub> (0.6 mmol), EtOH (2.0 ml), H<sub>2</sub>O (1.0 ml), 4 hr, 80 °C. N.R., no reaction.

<sup>a</sup>All biaryl products determined with NMR.

<sup>b</sup>The yields were calculated with GC using *n*-decane as internal standard.

<sup>c</sup>In addition to the reaction conditions, 1 mmol Hg was added and calculated the conversion after 1 hr.

<sup>d</sup>Conversion after 4 hr for Hg reactions.

bromobenzene **12c** (Entry 3 and Entry 4). The obtained results showed that the substituent attached in the *ortho* position reduces the yield of the product slightly due to the steric barrier. In reactions with sterically hindered aryl bromide **12d**, the best conversion was achieved with ligand **8f**, but exceptionally low selectivity was observed in all ligands (Entry 5). In addition, the poorest results are obtained for activated substrates 4-bromoanisole **12e** and 4-bromotoluene **12f** when Schiff bases **8b** and **8h** are used but, good conversions are obtained with ligand **8g** (Entry 6 and Entry 7). While it can be seen that all Schiff bases show moderate and good catalytic activity, it can be said that the best catalytic activity in general is achieved with **8g** and the worst catalytic activity with **8h** Schiff base. Considering the results obtained in all Suzuki C—C coupling reactions with synthesized Schiff bases, it is seen that Schiff bases substituted with halogen groups that are deactivating show less catalytic activity than Schiff bases substituted with activating —OH groups.

To understand the catalytic mechanism, mercury test was performed. Hg (0) reacts with Pd (0) to form amalgamate. Thus, the catalytic activity of Pd (0) in the reaction medium is quenched.<sup>45</sup> If there is no conversion in reactions after this poisoning test, it is understood that there is heterogeneous catalysis.<sup>46–48</sup> The observation of palladium black in catalytic activity reactions strengthened the idea that the catalytic cycle is heterogeneous. For this purpose, the reactions between phenylboronic acid **10** and 4-bromoacetophenone **12a** were repeated with all Schiff bases and 1 mmol mercury was added to the reaction medium (Entry 1). When the results were examined by GC, it was seen that there was no conversion in all reactions. Thus, it was understood that Schiff bases catalyze Suzuki coupling reactions with heterogeneous catalyst by stabilizing Pd (0) formed in the reaction medium.

## 2.2 | Antioxidant activities

Antioxidant molecules are so important because they can be kept under control by the unstable free radicals, which are produced always in the human body.<sup>49,50</sup> Thus, they can hinder some common diseases such as cancer and cardiovascular so the synthesis of antioxidant molecules and examine their antioxidant properties are important topic in the literature.<sup>51–53</sup> In this work, the antioxidant activities of synthesized molecules were examined as used DPPH free radical scavenging activity and ferrous ions (Fe<sup>2+</sup>) chelating activity, which is known methods in the literature.<sup>54–56</sup> In the beginning, the highest concentration (800 µg/ml) of all synthesized molecules were prepared for specify of active compounds in methods (DPPH or Iron chelating) using for investigation of antioxidant capacity (Table 5). Molecules

**TABLE 5** The inhibition ratio of synthesized molecules at the concentration of 800 µg/ml

Compound	DPPH inhibition ratio (%)	Metal chelating ratio (%)
6	<b>74.5</b>	<b>86.1</b>
8a	<b>83.7</b>	31.1
8b	57.9	<b>93.6</b>
8c	<b>89.9</b>	35.4
8d	<b>81.3</b>	32.4
8e	<b>97.1</b>	38.7
8f	56.3	<b>95.6</b>
8g	<b>68.1</b>	<b>98.2</b>
8h	<b>67.1</b>	<b>93.3</b>

with high antioxidant activity at this concentration are shown in bold type in Table 5 and lower concentrations of these molecules were prepared to calculate IC<sub>50</sub> values by relevant methods.

In particular, when looking at the preliminary measurements of molecule **6**, which does not contain a substituted group obtained with benzaldehyde, it can be said that aromatic Schiff bases have various antioxidant properties. In addition, according to these results, it is seen that the antioxidant properties of aromatic Schiff bases are significantly affected compared to the substituted group in the aromatic ring. After obtaining these results, it is aimed to calculate the IC<sub>50</sub> values of the molecules that are active in each method. For this purpose, various concentrations of molecules and positive controls BHT and BHA were prepared.

## 2.3 | DPPH scavenging activity

DPPH method is one of the most used for antioxidant measurement of molecules by UV. The ability of a molecule to be active in this method depends on its ability to deliver protons. If the molecule transfers protons to the DPPH radical, the solution of purple-colored DPPH in ethanol turns into yellow-colored DPPH-H. Thus, DPPH, which absorbs at 517 nm, decreases the absorbance and the antioxidant activity of the molecule is calculated according to this decrease.<sup>50,56,57</sup>

According to preliminary studies, all aromatic Schiff bases show various amounts of DPPH scavenging activity. The 74.5% activity of molecule **6** without any substituted group in the first studies in Table 5 shows that aromatic Schiff bases have DPPH scavenging activity. Since the DPPH method is dependent on the transfer of the H atom, molecules **8a**, **8c**, **8d**, and **8e**, which

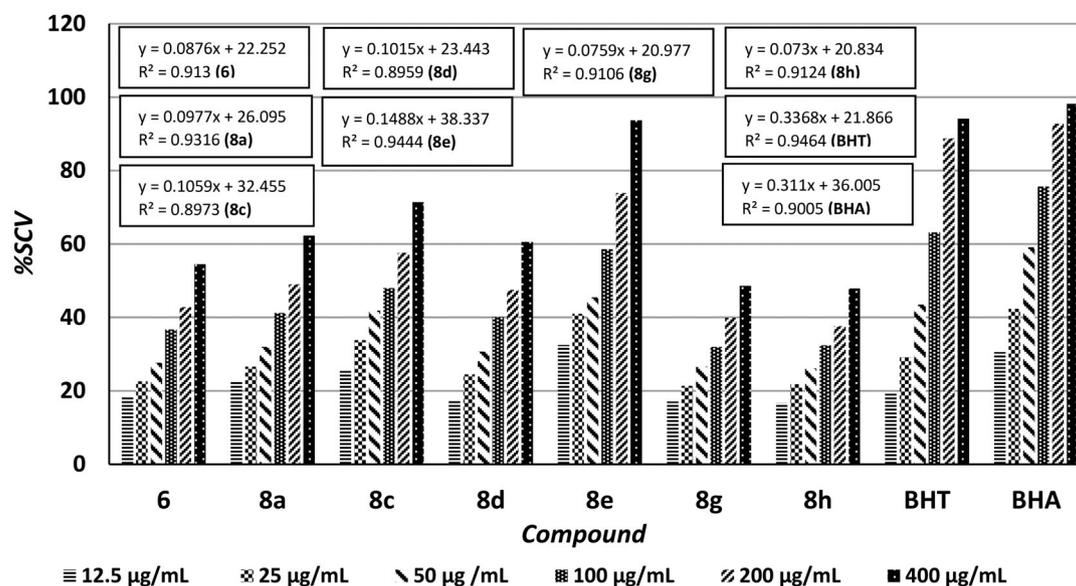


FIGURE 1 DPPH scavenging activities of each molecule for each concentration

TABLE 6  $IC_{50}$  values of synthesized molecules for DPPH scavenging activity

Compound	6	8a	8c	8d	8e	8g	8h	BHT	BHA
$IC_{50}$ values (µg/ml)	316.7	244.7	165.7	261.6	78.4	382.4	399.5	83.5	45

contain the —OH groups in the phenyl ring showed higher activity as expected. In addition, it can be seen that deactivating groups such as -Br, -Cl slightly decrease DPPH activity. Based on these results,  $IC_{50}$  values of **6**, **8a**, **8c**, **8d**, **8e**, **8g**, and **8h** molecules were calculated. According to the results obtained, the DPPH scavenging activities of the molecules change in the order of BHA > **8e** > BHT > **8c** > **8a** > **8d** > **6** > **8g** > **8h** (Figure 1; Table 6).

## 2.4 | Ferrous ions ( $Fe^{2+}$ ) chelating activity

Besides the radical scavenging effects of molecules, it is important in terms of antioxidant properties that they can form chelates with metals. Because these molecules prevent the metal catalyzed oxidation by keeping the metals in the body like iron, which is more active than other metals.<sup>54–56</sup> In order to examine the antioxidant activities of molecules in this respect, Ferrous ions ( $Fe^{2+}$ ) method is commonly used based on the reduction of  $Fe^{2+}$ -Ferrozine complex, which gives absorbance in 562 nm.<sup>54–56</sup> Considering that Schiff bases are used as ligand in obtaining metal complexes, this study was conducted since it was expected that the iron ions chelating activities of the synthesized molecules would be high.

According to preliminary study (Table 5), unlike the DPPH results, while the —Br, —Cl, or —C=C— substitution increase the Ferrous ions chelating activity, the —OH group decrease the activity dramatically. Actually, according to the literature, the structures, which containing OH, —O—, —C=O, —C=N, —COOH groups have high potential for show iron chelating activity.<sup>56</sup> However, unlike BHT and BHA, which contain —OH and show high efficiency, molecules **8a**, **8c**, **8d**, and **8e**, which containing —OH group in ortho position showed low iron chelating activity. This may have been caused by the hydrogen bond between the —OH group and the adjacent —C=N group. Looking at the FTIR spectra of these molecules, the absence of the —OH band proves this interaction.

For this reason, the  $IC_{50}$  values were only calculated for compound **6**, **8b**, **8f**, **8g**, and **8h**, which showed good activity in this method (Figure 2). In addition, BHT and BHA used as positive controls. The  $IC_{50}$  values for ferrous ions ( $Fe^{2+}$ ) chelating activity increase in order of **8g** > BHT > **8f** > BHA > **8b** > **8h** > **6** (Table 7).

## 3 | EXPERIMENTAL

All reagents were purchased from Sigma-Aldrich or Merck. The  $^1H$ ,  $^{13}C$  NMR spectra, the antioxidant activities, and FT-IR spectra were examined with Bruker

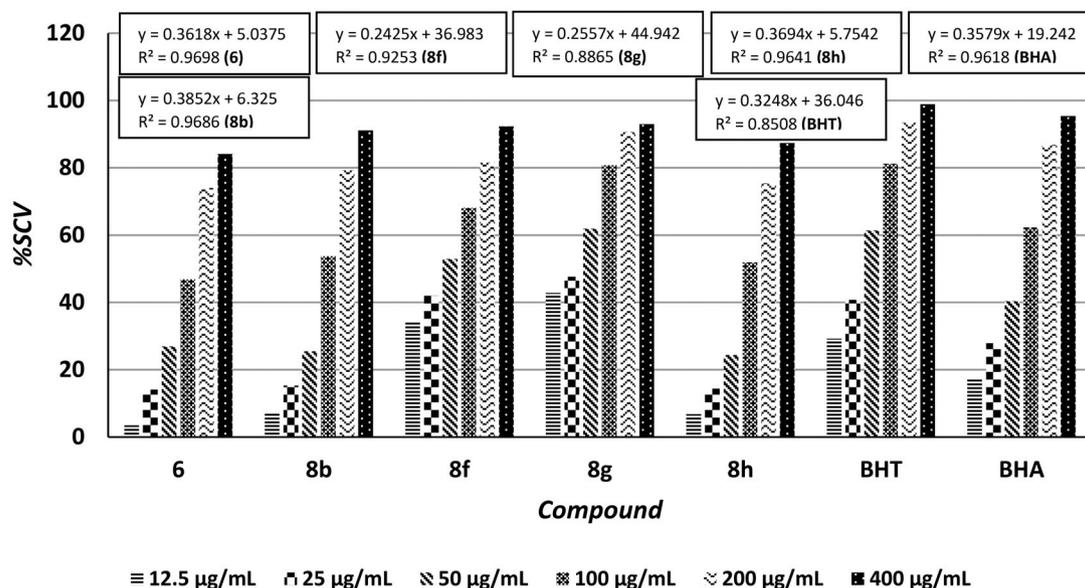


FIGURE 2 Ferrous ions chelating activities of each molecule for each concentration

Compound	6	8b	8f	8g	8h	BHT	BHA
IC <sub>50</sub> values (µg/ml)	214.3	113.4	53.7	19.78	119.8	42.96	85.94

TABLE 7 IC<sub>50</sub> values of synthesized molecules for ferrous ions chelating activity

Ultrasield Plus Biospin Avance III 400 MHz NaNoBay FT-NMR, Chebios Optimum-One UV-Vis spectrophotometer and Perkin Elmer Spectrum-100, respectively.

### 3.1 | Synthesis of cyclohepta-2,4,6-trien-1-ylmethanamine (4) (C<sub>8</sub>H<sub>11</sub>N)

In the beginning the nitrile **3** was synthesized according to the literature.<sup>38,39</sup> Then, 10 g (85.3 mmol) of nitrile **3** was dissolved in 100 mL ether and added dropwise at 0°C to slurry of 6.48 g (170.7 mmol) LiAlH<sub>4</sub> in 150 mL of ether.<sup>42</sup> The mixture was stirred 2 hr. After the starting compound finished according to TLC analysis, 30 mL of water and 10 mL of 20% NaOH solution were added slowly in the reaction mixture and stirred for 10 more minutes. Then, the residue filtered, and ether phase was separated. The water phase was washed three times with 25 mL of ether. All ether phases were combined and dried over Na<sub>2</sub>SO<sub>4</sub>. The ether phase was evaporated and the product **4** was obtained in 95% yield (81.0 mmol, 9.82 g).<sup>40,58</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.66–6.64 (m, 2H, —C=CH), 6.24 (dddd, *J* = 8.9, 3.8, 2.6, 1.3 Hz, 2H, —C=CH), 5.25 (dd, *J* = 9.0, 5.6 Hz, 2H, —C=CH), 3.00 (d, *J* = 7.4 Hz, 2H, —NCH<sub>2</sub>), 1.86–1.78 (m, 1H, —CH); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 130.9, 125.7, 124.4, 44.4, 42.7 ppm; IR (KBr):  $\bar{\nu}$  = 3,351, 3,294, 3,009, 2,919, 2,849, 1,566, 1,453, 742, 696 cm<sup>-1</sup>; GC-MS: 121.0 (M<sup>+</sup>), 91.0

(M<sup>+</sup>, —CH<sub>2</sub>NH<sub>2</sub>), 65.0, 30.1; **Elemental analysis: Anal. Cal. for C<sub>8</sub>H<sub>11</sub>N**; C, 79.29%; H, 9.15%; N, 11.56%. **Found:** C, 79.02%; H, 9.08%; N, 11.41%.

### 3.2 | General method for the synthesis of substituted Schiff bases

*Synthetic method carried out by the following procedure:* 0.5 g (4.1 mmol) amine **4** was dissolved with MeOH (8 mL) and then aldehyde (4.0 mmol) was added. The resulting solution was stirred at room temperature until starting material was consumed by TLC analysis. The solvent was evaporated, and the products were purified by chromatographic techniques.

#### **N-benzylidene-1-(cyclohepta-2,4,6-trien-1-yl)methanamine (6) (C<sub>15</sub>H<sub>15</sub>N).**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.42 (s, 1H, —N=CH), 7.79 (dd, *J* = 6.6, 3.1 Hz, 2H, Ph-H), 7.45 (dd, *J* = 5.1, 1.8 Hz, 3H, Ph-H), 6.69 (dd, *J* = 2.8, 1.2 Hz, 2H, —C=CH), 6.26 (dddd, *J* = 8.9, 3.8, 2.6, 1.3 Hz, 2H, —C=CH), 5.38 (dd, *J* = 9.0, 5.6 Hz, 2H, —C=CH), 3.97 (dd, *J* = 6.8, 1.3 Hz, 2H, —NCH<sub>2</sub>), 2.25–2.17 (m, 1H, —CH); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 161.9 (C=N), 136.2 (ArC), 130.9 (C=C), 130.6 (ArC), 128.5 (ArC), 128.2 (ArC), 125.2 (C=C), 124.7 (C=C), 63.4 (NCH<sub>2</sub>), 40.0 (CH) ppm; IR (KBr):  $\bar{\nu}$  = 3,012, 2,833, 1,643, 1,448, 1,309, 1,024, 688 cm<sup>-1</sup>; GC-MS: 210.1 (M<sup>+</sup>), 118.0 (M<sup>+</sup>,

—CH<sub>2</sub>Ph), 91.0, 77.0, 65.0, 51.0; **Elemental analysis:** **Anal. Cal. for C<sub>15</sub>H<sub>15</sub>N;** C, 86.08%; H, 7.22%; N, 6.69%. **Found:** C, 85.89%; H, 7.18%; N, 6.59%.

**2-(((cyclohepta-2,4,6-trien-1-ylmethyl)imino)methyl)phenol (8a)** (C<sub>15</sub>H<sub>15</sub>NO).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.45 (s, 1H, —N=CH), 7.36–7.31 (m, 2H, Ph-H), 6.99 (d, *J* = 7.4 Hz, 1H, Ph-H), 6.93–6.90 (m, 1H, Ph-H), 6.73–6.67 (m, 2H, —C=CH), 6.28 (dddd, *J* = 8.9, 3.8, 2.6, 1.2 Hz, 2H, —C=CH), 5.35 (dd, *J* = 9.0, 5.7 Hz, 2H, —C=CH), 3.91 (dd, *J* = 7.0, 1.1 Hz, 2H, —NCH<sub>2</sub>), 2.27–2.12 (m, 1H, —CH) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.7 (ArC), 161.2 (C=N), 132.3 (ArC), 131.3 (ArC), 131.0 (C=C), 125.8 (C=C), 123.8 (C=C), 118.8 (ArC), 118.6 (ArC), 117.1 (ArC), 61.2 (NCH<sub>2</sub>), 39.9 (CH) ppm; **IR (KBr):**  $\bar{\nu}$  = 3,011, 2,846, 1,629, 1,579, 1,494, 1,276, 1,150, 753, 731, 702, 647 cm<sup>-1</sup>; **GC-MS:** 225.1 (M<sup>+</sup>), 207.9 (M<sup>+</sup>, —OH), 134.0, 104.0, 91.0, 77.0, 65.0, 51.0, 39.0, 32.0; **Elemental analysis:** **Anal. Cal. for C<sub>15</sub>H<sub>15</sub>NO;** C, 79.97%; H, 6.71%; N, 6.22%. **Found:** C, 79.68%; H, 6.69%; N, 6.14%.

**N-(4-chlorobenzylidene)-1-(cyclohepta-2,4,6-trien-1-yl)methanamine (8b)** (C<sub>15</sub>H<sub>14</sub>ClN).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.36 (s, 1H, —N=CH), 7.72 (d, *J* = 8.5 Hz, 2H, Ph-H), 7.41 (d, *J* = 8.5 Hz, 2H, Ph-H), 6.70–6.67 (m, 2H, —C=CH), 6.28 (dddd, *J* = 8.9, 3.7, 2.6, 1.1 Hz, 2H, —C=CH), 5.36 (dd, *J* = 9.1, 5.6 Hz, 2H, —C=CH), 3.95 (dd, *J* = 6.8, 1.3 Hz, 2H, —NCH<sub>2</sub>), 2.23–2.15 (m, 1H, —CH) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 160.5 (C=N), 136.6 (ArC), 134.7 (ArC), 130.9 (C=C), 129.4 (ArC), 128.8 (ArC), 125.2 (C=C), 124.5 (C=C), 63.3 (NCH<sub>2</sub>), 39.9 (CH) ppm; **IR (KBr):**  $\bar{\nu}$  = 3,011, 2,840, 1,643, 1,593, 1,487, 1,085, 1,012, 819, 700, 504 cm<sup>-1</sup>; **GC-MS:** 243.0 (M<sup>+</sup>), 208.1 (M<sup>+</sup>, —Cl), 178.0, 151.9, 124.9, 104.0, 91.0, 77.0, 65.0, 51.0, 32.0; **Elemental analysis:** **Anal. Cal. for C<sub>15</sub>H<sub>14</sub>ClN;** C, 73.92%; H, 5.79%; N, 5.75%. **Found:** C, 73.84%; H, 5.74%; N, 5.71%.

**3-bromo-2-(((cyclohepta-2,4,6-trien-1-ylmethyl)imino)methyl)phenol (8c)** (C<sub>15</sub>H<sub>14</sub>BrNO).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.34 (s, 1H, —N=CH), 7.40 (dd, *J* = 7.3, 2.3 Hz, 2H, Ph-H), 6.90–6.85 (m, 1H, Ph-H), 6.69 (dd, *J* = 3.5, 2.9 Hz, 2H, —C=CH), 6.28 (dddd, *J* = 9.0, 3.7, 2.6, 1.2 Hz, 2H, —C=CH), 5.32 (dd, *J* = 9.0, 5.7 Hz, 2H, —C=CH), 3.89 (dd, *J* = 7.0, 1.1 Hz, 2H, —NCH<sub>2</sub>), 2.25–2.18 (m, 1H, —CH) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 164.4 (ArC), 160.3 (C=N), 134.9 (ArC), 133.4 (ArC), 131.0 (C=C), 125.9 (C=C), 123.5 (C=C), 120.1 (ArC), 119.1 (ArC), 109.9 (ArC), 61.0 (NCH<sub>2</sub>), 39.8 (CH) ppm; **IR (KBr):**  $\bar{\nu}$  = 3,012, 2,842, 1,631, 1,474, 1,274, 1,178, 816, 730, 695, 623 cm<sup>-1</sup>; **GC-MS:** 304.9 (M<sup>+</sup>), 287.9 (M<sup>+</sup>, —OH), 211.9, 184.9, 104.0, 91.0, 77.0, 51.0, 39.0, 32.0; **Elemental analysis:** **Anal. Cal. for C<sub>15</sub>H<sub>14</sub>BrNO;** C, 59.23%; H, 4.63%; N, 4.60%. **Found:** C, 59.11%; H, 4.61%; N, 4.55%.

**2-(((cyclohepta-2,4,6-trien-1-ylmethyl)imino)methyl)-6-methoxyphenol (8d)** (C<sub>16</sub>H<sub>17</sub>NO<sub>2</sub>).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.42 (s, *J* = 1.1 Hz, 1H, —N=CH), 6.96–6.90 (m, 2H, Ph-H), 6.84 (d, *J* = 7.8 Hz, 1H, Ph-H), 6.69–6.65 (m, 2H, —C=CH), 6.25 (dddd, *J* = 9.0, 3.8, 2.6, 1.2 Hz, 2H, —C=CH), 5.34 (dd, *J* = 9.0, 5.7 Hz, 2H, —C=CH), 3.92 (s, 3H, —OCH<sub>3</sub>), 3.89 (dd, *J* = 7.1, 1.1 Hz, 2H, —NCH<sub>2</sub>), 2.23–2.16 (m, 1H, —CH) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.6 (C=N), 152.0 (ArC), 148.5 (ArC), 130.9 (C=C), 125.7 (C=C), 123.7 (C=C), 122.9 (ArC), 118.5 (ArC), 117.8 (ArC), 114.1 (ArC), 60.5 (NCH<sub>2</sub>), 56.1 (OCH<sub>3</sub>), 39.9 (CH) ppm; **IR (KBr):**  $\bar{\nu}$  = 3,011, 2,835, 1,629, 1,461, 1,249, 1,078, 907, 725, 645 cm<sup>-1</sup>; **GC-MS:** 255.1 (M<sup>+</sup>), 207.0 (M<sup>+</sup>, —OH, —OCH<sub>3</sub>), 168.9, 105.0, 91.0, 77.0, 66.9, 54.9, 43.9, 32.0; **Elemental analysis:** **Anal. Cal. for C<sub>16</sub>H<sub>17</sub>NO<sub>2</sub>;** C, 75.27%; H, 6.71%; N, 5.49%. **Found:** C, 75.19%; H, 6.67%; N, 5.48%.

**4-(((cyclohepta-2,4,6-trien-1-ylmethyl)imino)methyl)benzene-1,3-diol (8e)** (C<sub>15</sub>H<sub>15</sub>NO<sub>2</sub>).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.77 (s, 1H, —N=CH), 6.90 (d, *J* = 8.8 Hz, 1H, Ph-H), 6.62–6.59 (m, 2H, —C=CH), 6.34 (s, 1H, Ph-H), 6.26–6.20 (m, 3H, —C=CH and Ph-H), 5.23 (dd, *J* = 9.2, 6.2 Hz, 2H, —C=CH), 3.57 (d, *J* = 7.2 Hz, 2H, —NCH<sub>2</sub>), 2.32–2.23 (m, 1H, —CH) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 164.1 (ArC), 164.0 (ArC), 162.9 (C=N), 131.0 (ArC), 131.0 (C=C), 126.9 (ArC), 126.1 (C=C), 123.1 (C=C), 110.9 (ArC), 107.9 (ArC), 104.3 (ArC), 50.6 (NCH<sub>2</sub>), 39.7 (CH) ppm; **IR (KBr):**  $\bar{\nu}$  = 3,314, 3,011, 2,922, 1,632, 1,600, 1,537, 1,446, 1,221, 904, 790, 700 cm<sup>-1</sup>; **GC-MS:** 224.1 (M<sup>+</sup>, —OH), 207 (M<sup>+</sup>, -2OH), 132.0, 118.0, 104.0, 91.0, 77.0, 65.0, 39.0, 32.0; **Elemental analysis:** **Anal. Cal. for C<sub>15</sub>H<sub>15</sub>NO<sub>2</sub>;** C, 74.67%; H, 6.27%; N, 5.81%. **Found:** C, 74.61%; H, 6.24%; N, 5.73%.

**N-(2-bromobenzylidene)-1-(cyclohepta-2,4,6-trien-1-yl)methanamine (8f)** (C<sub>15</sub>H<sub>14</sub>BrN).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.77 (s, 1H, —N=CH), 8.05 (dd, *J* = 7.7, 1.9 Hz, 1H, Ph-H), 7.60 (dd, *J* = 7.9, 1.1 Hz, 1H, Ph-H), 7.38–7.33 (m, 1H, Ph-H), 7.29 (ddd, *J* = 9.7, 6.9, 1.9 Hz, 1H, Ph-H), 6.69 (dd, *J* = 3.5, 2.8 Hz, 2H, —C=CH), 6.27 (dddd, *J* = 8.9, 3.8, 2.6, 1.3 Hz, 2H, —C=CH), 5.38 (dd, *J* = 9.0, 5.6 Hz, 2H, —C=CH), 4.01 (dd, *J* = 6.8, 1.4 Hz, 2H, —NCH<sub>2</sub>), 2.25–2.18 (m, 1H, —CH) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 161.0 (C=N), 134.6 (ArC), 132.9 (ArC), 131.7 (ArC), 130.9 (C=C), 129.0 (ArC), 127.6 (ArC), 125.3 (ArC), 125.0 (C=C), 124.5 (C=C), 63.3 (NCH<sub>2</sub>), 39.9 (CH) ppm; **IR (KBr):**  $\bar{\nu}$  = 3,011, 2,886, 1,633, 1,435, 1,269, 1,020, 752, 702, 591 cm<sup>-1</sup>; **GC-MS:** 287.9 (M<sup>+</sup>), 206.0 (M<sup>+</sup>, -Br), 168.9, 104.0, 91.0, 77.0, 65.0, 51.0, 39.0, 32.0; **Elemental analysis:** **Anal. Cal. for C<sub>15</sub>H<sub>14</sub>BrN;** C, 62.52%; H, 4.90%; N, 4.86%. **Found:** C, 62.44%; H, 4.88%; N, 4.82%.

**1-(cyclohepta-2,4,6-trien-1-yl)-N-(4-([E]-styryl)benzylidene)methanamine (8 g)** (C<sub>23</sub>H<sub>21</sub>N).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.26 (s, 1H, —N=CH), 7.65 (d, *J* = 8.3 Hz, 2H, Ph-H), 7.49–7.40 (m, 4H, Ph-H), 7.27 (t, *J* = 7.5 Hz, 2H, Ph-H), 7.21–7.15 (m, 1H, Ph-H), 7.05 (d, *J* = 9.8 Hz, 2H, Ph-CH=CH-), 6.60–6.55 (m, 2H, —C=CH), 6.17 (dddd, *J* = 8.9, 3.8, 2.6, 1.3 Hz, 2H, —C=CH), 5.25 (dd, *J* = 9.0, 5.6 Hz, 2H, —C=CH), 3.84 (dd, *J* = 6.8, 1.0 Hz, 2H, —NCH<sub>2</sub>), 2.13–2.06 (m, 1H, —CH) ppm; **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 161.6 (C=N), 139.7 (ArC), 137.0 (ArC), 135.3 (ArC), 130.9 (C=C), 130.0 (ArC), 128.7 (ArC), 128.6 (ArC), 128.0 (ArC), 127.9 (C=C), 126.7 (ArC), 125.2 (C=C), 124.7 (C=C), 63.5 (NCH<sub>2</sub>), 40.0 (CH) ppm; **IR (KBr):**  $\bar{\nu}$  = 3,014, 2,835, 1,639, 1,602, 1,447, 960, 906, 815, 727, 687, 537 cm<sup>-1</sup>; **GC-MS:** 208.0 (M<sup>+</sup>, —C=C-Ph), 179.0, 165.0, 152.0, 89.0, 76.0, 51.0, 39.0, 32.0; **Elemental analysis:** **Anal. Cal. for C<sub>23</sub>H<sub>21</sub>N;** C, 88.71%; H, 6.80%; N, 4.50%. **Found:** C, 88.60%; H, 6.77%; N, 4.49%.

***N*-(2-chlorobenzylidene)-1-(cyclohepta-2,4,6-trien-1-yl)methanamine (8 h)** (C<sub>15</sub>H<sub>14</sub>ClN).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.85 (s, 1H, —N=CH), 8.08 (d, *J* = 7.5 Hz, 1H, Ph-H), 7.44–7.28 (m, 3H, Ph-H), 6.76–6.64 (m, 2H, —C=CH), 6.27 (d, *J* = 9.1 Hz, 2H, —C=CH), 5.38 (dd, *J* = 9.1, 5.6 Hz, 2H, —C=CH), 4.01 (d, *J* = 6.2 Hz, 2H, —NCH<sub>2</sub>), 2.25–2.17 (m, 1H, —CH) ppm; **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 158.7 (C=N), 135.1 (ArC), 133.2 (ArC), 131.5 (ArC), 130.9 (C=C), 129.7 (ArC), 128.5 (ArC), 126.9 (ArC), 125.2 (C=C), 124.5 (C=C), 63.5 (NCH<sub>2</sub>), 39.9 (CH) ppm; **IR (KBr):**  $\bar{\nu}$  = 3,012, 2,888, 1,634, 1,591, 1,436, 1,270, 1,051, 753, 701 cm<sup>-1</sup>; **GC-MS:** 208.0 (M<sup>+</sup>, —Cl), 180.9, 167.0, 153.0, 144.0, 104.0, 91.0, 77.0, 65.0, 51.0, 39.0, 32.0; **Elemental analysis:** **Anal. Cal. for C<sub>15</sub>H<sub>14</sub>ClN;** C, 73.92%; H, 5.79%; N, 5.75%. **Found:** C, 73.79%; H, 5.74%; N, 5.71%.

**General method for the synthesis of Suzuki C—C coupling products.**

**Synthetic method carried out by the following procedure :** Aryl bromide (0.5 mmol), phenylboronic acid (0.6 mmol), base (0.6 mmol), EtOH-H<sub>2</sub>O (2:1 ml), Schiff base (0.8 mol%), and PdCl<sub>2</sub> (0.4 mol%) were added to a sealed tube and stirred for 4 hours at 80°C. After the reaction time was completed, the mixture was washed with CHCl<sub>3</sub> and dried with Na<sub>2</sub>SO<sub>4</sub>. After filtering rapidly through SiO<sub>2</sub>, internal standard was added, and GC-MS was taken. The biphenyl product was characterized by <sup>1</sup>H NMR and GC, and agreement with the literature data.<sup>59–63</sup>

### 3.3 | DPPH free radical scavenging activity

Free radical scavenging activity was measured using the DPPH. In order to examine the activity tests, the

concentrations (6,75–400 µg/ml) of all synthesized compounds and reference test materials (Butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA)) were prepared in EtOH. Then 1 ml of DPPH solution was added into different test tubes and 1 ml of solutions in different concentrations was added for each sample. After incubation for half an hour in the dark, UV measurements at 517 nm were taken. According to the decrease in absorbance value, antioxidant activity was calculated using the formula below (Equation 1).<sup>53,57</sup>

$$\% \text{DPPH Scavenging} = (A_0 - A_s / A_0) \times 100 \quad (1)$$

where *A*<sub>0</sub> is the absorbance of the control; *A*<sub>s</sub> is the absorbance of the sample at 517 nm.

### 3.4 | Ferrous ions (Fe<sup>2+</sup>) chelating activity

Concentrations prepared in the DPPH method were also used for this method. 1 ml of each solution prepared for each synthesized molecule was taken and added to 0.4 ml FeCl<sub>2</sub> solution of 2 mM previously taken into the test tubes. 0.2 ml of 5 mM ferrozine solution was added to these mixtures and the resulting solutions were left to incubate in the dark for 10 min. After the incubation was completed, the activity was calculated using the Equation (2) according to the decrease in absorbance value by taking UV measurements at 562 nm.<sup>64</sup>

$$\% \text{Ferrous ions (Fe}^{2+} \text{) chelating activity} = (A_0 - A_s / A_0) \times 100 \quad (2)$$

*A*<sub>0</sub> is the absorbance of the control; *A*<sub>s</sub> is the absorbance of the sample at 562 nm

## 4 | CONCLUSIONS

Several new Schiff bases were synthesized, and their structures were illuminated by various spectroscopic methods. The catalytic activity of all synthesized Schiff bases in Suzuki coupling reactions using phenyl boronic acid and various aryl bromides were investigated. All Schiff bases showed good to excellent catalytic activity according to aryl bromide used in the reactions. In addition to their catalytic activities, the antioxidant properties of all Schiff bases were examined by DPPH and iron chelation methods. IC<sub>50</sub> values of Schiff bases, which give good results compared to BHT and BHA used as positive control, were calculated.

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## ORCID

Özgür Yılmaz  <https://orcid.org/0000-0001-9278-1091>

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