

## Experimental and computational studies on the absorption properties of novel formazan derivatives

Gülşen TÜRKÖĞLU<sup>1,\*</sup>, M. Emin ÇINAR<sup>2,3</sup>

<sup>1</sup>Department of Chemistry, Faculty of Science, Anadolu University, Eskişehir, Turkey

<sup>2</sup>Department of Chemistry, Faculty of Arts and Sciences, İstanbul Technical University, İstanbul, Turkey

<sup>3</sup>Department Chemie-Biologie, OC1, University Siegen, Siegen, Germany

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**Abstract:** Eight novel 3-(4-(benzyloxy)phenyl)-5-(4-bromophenyl)-1-(4-substituted-phenyl)formazan (**4a–4h**) were synthesized by coupling of substituted phenylhydrazones with diazonium salts of 4-bromoaniline. The substituted phenylhydrazones, which are intermediate products, were obtained from the condensation of substituted phenylhydrazines with 4-(benzyloxy)benzaldehyde. All target compounds were characterized by using FTIR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, LC–MS spectrometry, and elemental analysis. Absorption spectra of these compounds in solvents with different polarities were investigated thoroughly. Time-dependent density functional theory (TD-DFT) studies were conducted to shed light on their electronic structures, Kohn–Sham orbitals, and electronic transitions.

**Key words:** Formazans, UV-visible absorption spectroscopy, substituent effect, solvent effect, density functional theory (DFT)

### 1. Introduction

Although the first synthesis of formazans was accomplished over a century ago, they still attract the interest of chemists, biologists, technologists, and other specialists.<sup>1</sup> The conjugated double bonds in the formazan skeleton (–NH–N=C–N=N–) render colorful compounds. The tetrazolium/formazan couple is known as a proton acceptor or oxidant in a special redox system, which is now broadly applied in different areas of biological science, i.e. medicine, pharmacology, immunology, and botany, particularly in biochemistry and histochemistry.<sup>2</sup>

These compounds have been investigated comprehensively owing to their ready accessibilities, diverse chemical reactivities, and broad spectrum of biological activities.<sup>3</sup> Moreover, they have been found to possess important applications. Their important biological applications, such as antiviral, antimicrobial, antiinflammatory, antifungal, antitubercular, anticancer, antiparkinsonian, antifertility, and anticonvulsant, pave the way for their applications.<sup>4–7</sup>

Catalytic, optical and electrochemical properties of metal and boron formazan complexes were comprehensively investigated for their applications as functional materials.<sup>8–16</sup> In addition, a new formazan derivative was introduced for the modification of pencil graphite electrode to determine the paracetamol in electrochemical sensor applications.<sup>17</sup> As a calculation tool for electronic structural properties, molecular modelling techniques allow a solution for the interpretation of experimental data. Tautomerism, structural and intramolecular hydrogen bonding properties of formazan derivatives were widely investigated by means of DFT.<sup>18–21</sup>

\*Correspondence: gulsent@anadolu.edu.tr

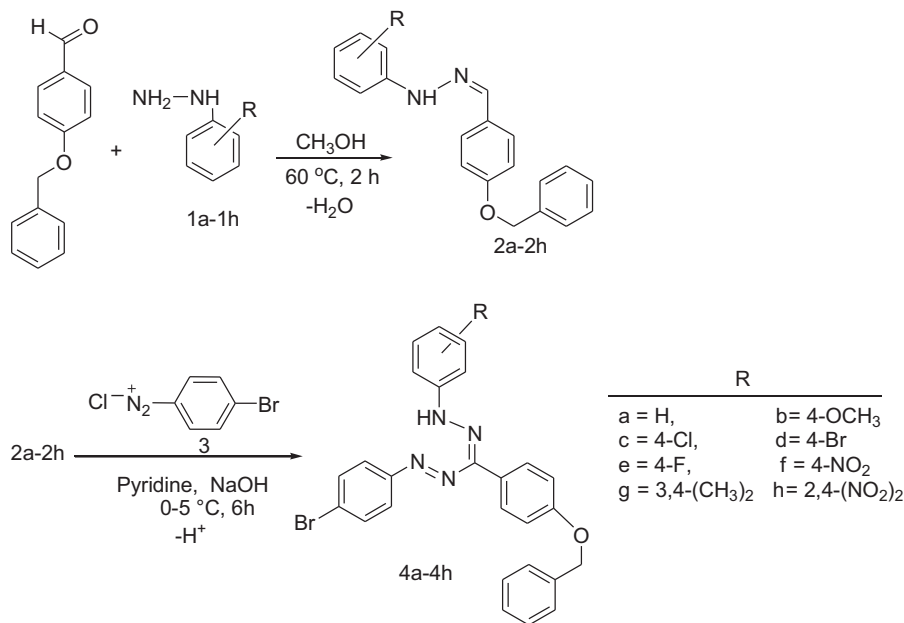
Herein, new 3-(4-(benzyloxy) phenyl)-5-(4-bromophenyl)-1-(4-substituted-phenyl) formazans (**4a–4h**) were synthesized by coupling reactions of substituted phenylhydrazones with appropriate aryl diazonium chlorides in pyridine. Their structures were characterized using elemental analysis, FTIR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and LC–MS spectroscopic methods. The substituent effect on their absorption spectra was explored. The structure and absorption spectra properties of the formazan derivatives were investigated experimentally and computationally.

## 2. Results and discussion

### 2.1. Synthesis

The substituted phenylhydrazones (**2a–2h**) used as the initial substances were obtained in good to excellent yields (72%–97%) via condensation reactions of substituted phenylhydrazines with 4-(benzyloxy) benzaldehyde. In intermediate products, **2a**,<sup>22</sup> **2f**<sup>23</sup> and **2h**<sup>24</sup> are known and **2b**, **2c**, **2e**, and **2g** are commercially available materials. Compound **2d** also is a novel diarylhydrazone. Compounds **2a–2h** were characterized using FTIR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and elemental analysis.

The synthesis of formazan derivatives is a well-known transformation and various protocols have been published.<sup>25,26</sup> In the present study, formazans (**4a–4h**) were synthesized according to the first method reported by Nineham,<sup>27</sup> namely the coupling of substituted phenylhydrazones with 4-bromoaniline diazonium cation (**3**) in basic media at 0 °C as demonstrated in Scheme 1.<sup>28</sup>

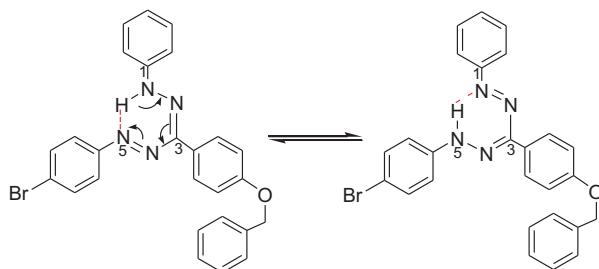


**Scheme 1.** Synthetic route of formazan derivatives.

New formazans **4a–4h**, recrystallized from methanol, were obtained in overall yields of 50%–75%. The optimum basic medium for the coupling step was found to be  $\text{pH} \geq 12$ , while the product was formed as a sticky material that clung to the stirring bar at  $\text{pH} \leq 9$  leaving the reaction incomplete. Moreover, the steric effects of the substituents located at the aryl aldehydes of the starting material significantly affect the coupling reactions. Therefore, *para*-substituted phenyl was chosen to eliminate the steric effects. The analytical and spectral data fully support the structures of all compounds.

## 2.2. Characterization

In the FTIR spectra of formazans **4a–4h**, sharp characteristic C=N tension vibration bands are observed between 1593 and 1610  $\text{cm}^{-1}$ , pointing out the existence of chelate form (Scheme 2).<sup>28–30</sup> The stretching frequencies of the N–H groups were observed as a broad band at 3061–3087  $\text{cm}^{-1}$  for compounds **4a–4g** due to very strong intramolecular hydrogen bonds ( $\text{Ph}^1\text{–NH}\cdots\text{N–Ph}^5$ ) of formazans.<sup>28,31,32</sup> However, the N–H stretching band for compound **4h** appeared at 3276  $\text{cm}^{-1}$  due to nonintramolecular hydrogen bonds. A band recorded at around 1238–1259  $\text{cm}^{-1}$  in all spectra was attributed to the C–O–C stretching vibration. The observation of strong bands at 1456–1498  $\text{cm}^{-1}$  demonstrates the –N=N– group, which is in good agreement with the reported FTIR values.<sup>2,28,33</sup>



**Scheme 2.** Intramolecular hydrogen bonding and tautomerization of the formazan **4a**.

The  $^1\text{H}$  NMR data and the calculated coupling constants for formazans **4a–4h** are given in the experimental section. Due to the existence of intramolecular hydrogen bonds inside the molecule, characteristic NH protons of compounds **4a–4g** are observed as a singlet in the downfield from 14.31 to 15.06 ppm.<sup>6,33,34</sup> However, weakening of the intramolecular hydrogen bonds was detected most probably from the electronic effect of the attached  $\text{NO}_2$  group, pointing out the upfield shift of NH proton (**4h**, 10.78 ppm).<sup>5,7,8,28</sup> The observation of these results confirms the pseudoaromatic  $\text{Ph}^1\text{–NH}\cdots\text{N–Ph}^5$  intramolecular hydrogen bond in the formazan skeleton (Scheme 2). The chemical shifts of the aromatic protons are recorded between 8.25 and 6.31 ppm as expected. While aliphatic  $\text{–OCH}_2\text{–}$  groups' protons are observed as singlets between 4.36 and 5.15 ppm as expected, methoxy group protons for compound **4b** and methyl group protons ( $\text{–CH}_3$ ) for compound **4g** are detected in the upfield at 3.90, 2.36, and 2.33 ppm, respectively.

In the  $^{13}\text{C}$  NMR spectra of formazans **4a–4h**, the obtained peaks belonging to carbon atoms in characteristic N–C=N units are recorded downfield between 164.32 and 158.70 ppm, which are in good alignment with the reported values.<sup>28,30,35</sup> While aliphatic  $\text{–OCH}_2\text{–}$  carbon atoms are observed in the range of 68.79–70.10 ppm as expected, the methoxy group ( $\text{–OCH}_3$ ) for **4b** and methyl groups attached to **4g** appear at 55.66 and 19.82–19.94 ppm, respectively.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra confirm the structures given in Scheme 1.

The mass spectra data of **4a–4h** are given in the experimental section. In the mass spectrum of the compound **4a** ( $\text{C}_{26}\text{H}_{21}\text{BrN}_4\text{O}$ ,  $M = 484.08$  g/mol) the molecular ion peak is observed to be MS,  $\text{ESI}^+$ :  $m/z = 484.1$  (27%,  $M^+$ ), 483.1 (100%,  $M - \text{H}^+$ ) and 485.1 (94%,  $M + \text{H}^+$ ) as anticipated. All synthesized compounds were evaluated in the same manner and the results obtained from the mass spectra prove the validity of the structures given in Scheme 1.

### 2.3. Absorption spectra

The UV-Vis studies of **4a–4h** were performed in solvents with 15 different polarities and the results are listed in Table 1. The UV-Vis spectra of **4a** are given in Figure 1. The visible band in formazans emerges from  $\pi-\pi^*$  transition of the tautomerizing conjugated formazan skeleton ( $-\text{NH}-\text{N}=\text{C}-\text{N}=\text{N}-$ ).<sup>1,28,34,36</sup>

**Table 1.** UV-vis absorption  $\lambda_{\text{max}}$  values of formazans (**4a–4h**) in various solvents.

Comp.	DMSO <sup>a</sup> (log $\epsilon$ ) <sup>b</sup>	DMF (log $\epsilon$ )	EtOH (log $\epsilon$ )	MeOH (log $\epsilon$ )	Acetone (log $\epsilon$ )	Dioxane (log $\epsilon$ )	EtOAc (log $\epsilon$ )	CHCl <sub>3</sub> (log $\epsilon$ )
<b>4a</b>	507 (4.69)	504 (4.70) 303	505 (4.71) 302	503 (4.71) 300	504 (4.94)	513 (4.74) 304	505 (4.64) 302	508 (4.51) 283
<b>4b</b>	502 (4.74) 302	503 (4.62) 304	510 (4.69) 307	493 (4.83) 306	503 (4.99)	518 (4.79) 307	507 (4.85) 305	516 (4.78) 308
<b>4c</b>	519 (4.30)	514 (4.80)	520 (4.38) 349	513 (4.34) 347 310	521 (4.40)	531 (4.59)	527 (4.34) 347 310	527 (4.46) 305
<b>4d</b>	517 (4.46) 351	511 (4.64)	522 (4.46) 346	509 (4.32) 347 309	516 (4.46)	532 (4.54)	522 (4.38) 345 309	531 (4.45) 303
<b>4e</b>	501 (4.65) 300	501 (4.69) 291	507 (4.67) 302	498 (4.72) 301	502 (4.62)	519 (4.62) 304	506 (4.71) 300	501 (4.60) 295
<b>4f</b>	485 (4.76)	475 (4.48) 372	499 (4.55) 364 311	490 (4.45) 362	498 (4.78) 364	514 (4.82) 363 316	501 (4.94) 365 314	501 (4.86) 372 310
<b>4g</b>	504 (4.61) 284	501 (4.67) 301	503 (4.27) 304	499 (4.30) 305	500 (4.97)	512 (4.67) 307	505 (4.71) 304	504 (4.65) 306
<b>4h</b>	402 (4.98)	396 (5.01)	389 (4.30)	390 (4.32)	388 (5.06)	383 (5.03)	383 (4.96)	387 (4.98)
Comp.	THF (log $\epsilon$ )	Butanol (log $\epsilon$ )	Propanol (log $\epsilon$ )	DCM (log $\epsilon$ )	Toluene (log $\epsilon$ )	Cyclohexane (log $\epsilon$ )	<i>n</i> -Hexane (log $\epsilon$ )	
<b>4a</b>	514 (4.74) 304	512 (4.71) 302	511 (4.76) 301	508 (4.64) 300	527 (4.72) 304	523 (4.65) 303	518 (4.40) 275	
<b>4b</b>	516 (4.79) 307	513 (4.83) 307	508 (4.82) 306	510 (4.80) 306	526 (4.86) 307	518 (4.74) 304	520 (4.48) 271	
<b>4c</b>	531 (4.41) 308	531 (4.41) 308	521 (4.26) 310	525 (4.20) 276	537 (4.45) 308	533 (4.34) 304	532 (4.23) 275	
<b>4d</b>	530 (4.45) 312	524 (4.54) 310	531 (4.32) 310	531 (4.51) 304	539 (4.58) 310	540 (4.36) 307	536 (4.49) 306	
<b>4e</b>	516 (4.68) 302	514 (4.61) 302	511 (4.69) 302	514 (4.56) 299	528 (4.71) 302	532 (4.68) 303	524 (4.41) 299	
<b>4f</b>	508 (4.78) 365 316	506 (4.20) 360	500 (4.08) 365	507 (4.88) 364 310	525 (4.72) 366	514 (4.11) 307	508 (3.90) 357 283	
<b>4g</b>	513 (4.80) 307	510 (4.67) 307	510 (4.40) 304	501 (4.78) 306	526 (4.68) 308	523 (4.25) 304	514 (4.70) 304	
<b>4h</b>	386 (4.99)	392 (4.40)	385 (4.12)	387 (4.97)	383 (5.06)	361 (4.20)	375 (4.00)	

<sup>a</sup>Polarity indexes of solvents: Dimethyl sulfoxide (DMSO): 7.2; *N,N*-Dimethylformamide (DMF): 6.4; Ethanol (EtOH): 5.2; Methanol (MeOH): 5.1; Acetone: 5.1; 1,4-dioxane (Dioxane): 4.8; Ethyl acetate (EtOAc): 4.4; Chloroform (CHCl<sub>3</sub>): 4.1; Tetrahydrofuran (THF): 4.0; *n*-Butyl alcohol (Butanol): 3.9; Isopropyl Alcohol (Propanol): 3.9; Dichloromethane (DCM): 3.1; Toluene: 2.4; Cyclohexane: 0.2; *n*-Hexane: 0.1. <sup>b</sup>Molar absorptivity (log $\epsilon$ , 1 M<sup>-1</sup>cm<sup>-1</sup>) for the longest wavelength ( $\pi-\pi^*$ ).

Similar  $\pi-\pi^*$  transitions were noted in the case of **4a–4g** at  $\lambda_{\text{max}1}$  of 475–540 nm in different polarity solvents, indicating the existence of a chelate form due to the inner-molecular hydrogen transfer over a six-membered ring (Scheme 2).<sup>28,30,37,38</sup> Contrary to the other compounds, **4h** ( $\lambda_{\text{max}1} = 361-402$  nm) shows the

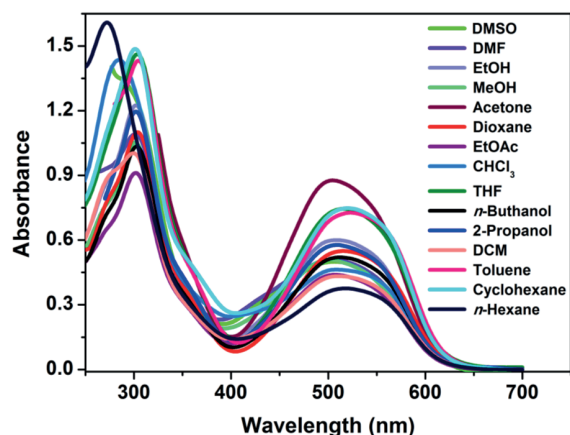
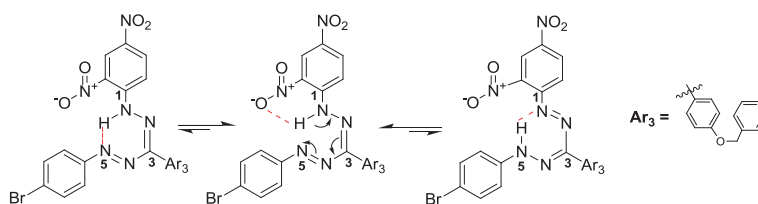
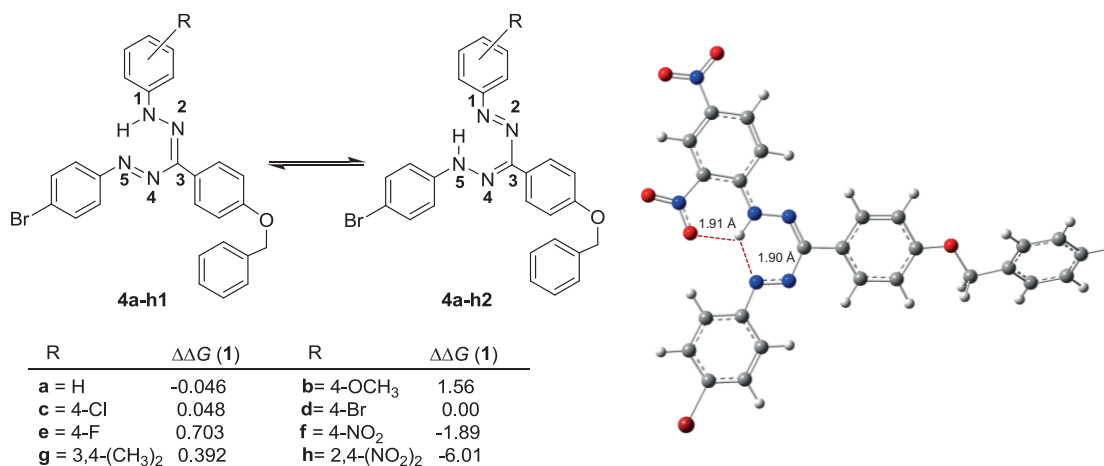


Figure 1. Electronic absorption bands of compound **4a** in various solvents.

blue shift arisen from the hydrogen bond between oxygen of the *ortho*-NO<sub>2</sub> group and Ph<sup>1</sup>-NH equilibrium structure, which hinders the formation of chelation of formazan (Scheme 3).<sup>37,38</sup>



Scheme 3. Hydrogen bond between the *ortho*-NO<sub>2</sub> and N-H and NH...N=N groups in compound **4h**.



Scheme 4. (Left) The relative Gibbs free energies of tautomers at PBE1PBE/6-31G(d) level (relative energies including zpe are given in kcal mol<sup>-1</sup>). (Right) Two intramolecular hydrogen bonds in **4h1** significantly stabilize the tautomer form 1.

The second band  $\lambda_{\max 2}$  between 271 and 372 nm is attributed to the  $\pi$ - $\pi^*$  transitions within the hydrogen bond chelate ring formed by the azo and hydrazo groups in tautomerization (Scheme 2).<sup>37</sup> In accordance to the values in the literature, the observed  $\lambda_{\max 2}$  of 271–307 nm for **4a**, **4b**, **4e**, and **4g** with inner-molecular hydrogen bonds belongs to the  $\pi$ - $\pi^*$  electronic transitions in the formazan skeleton. The band

at 341–372 nm for **4c**, **4d**, and **4f** in some solvents arises from an intramolecular charge transfer from solute–solvent interaction in the form of hydrogen bonding or bulk solvent properties. The observation of these values confirms the intramolecular hydrogen transfer via a pseudoaromatic six-membered ring between Ph<sup>1</sup>–NH with N–Ph<sup>5</sup>.<sup>28</sup>

### 2.3.1. Effect of solvent on the absorption spectra

As depicted in Table 1 and Figure 1, while the polarity of the solvents increases, the absorption peaks of formazans **4a–4g** exhibit a blue shift ( $\lambda_{\max} = 0\text{--}31$  nm). However, they have a slight red shift between 1 and 8 nm in toluene and cyclohexane compared to *n*-hexane, indicating a negative solvatochromism that points out the more stabilized ground state in a solvent cage of already partly oriented solvent molecules with stronger polarity. With increasing polarity of the solvents from *n*-hexane to DMSO, the absorption peaks of the compound **4h** exhibit a red shift ( $\lambda_{\max} = 8\text{--}23$  nm). This can be mainly attributed to the stabilization of  $\pi$  and  $\pi^*$  orbitals through solvation by polar solvents.<sup>32</sup> According to this result, the compound **4h** was demonstrated to have positive solvatochromism with a decrease in  $\pi\text{--}\pi^*$  transition energy concerning the intramolecular charge transfer (ICT) band within the whole molecule.<sup>28,39</sup> While **4d** holds the longest absorption wavelength appearing at 540 nm in cyclohexane, the highest hypsochromic shift having an absorption maximum of 361 nm was observed for **4h**. These results indicate that there is either a hydrogen-bonding interaction between the solute and solvent molecules or intramolecular charge transfer within the whole molecule.

### 2.3.2. Effect of substituent on the absorption spectra

The substituent effects on characteristic absorption bands ( $\lambda_{\max 1}$ ) of formazans **4a–4h** were examined in three solvents (ethanol, THF, and *n*-hexane) (Table 2). The chemical shift values ( $\Delta\lambda_{\max}$ ) were determined according to the difference between the  $\lambda_{\max 1}$  value of unsubstituted parent compound **4a** and  $\lambda_{\max 1}$  values of substituted formazans (**4b–4h**).<sup>28,37,38</sup> The UV-vis spectra of **4a–4h** are given in Figure 2 in ethanol solution.

**Table 2.**  $\lambda_{\max 1}$  values of **4a–4h** and chemical shift ( $\Delta\lambda_{\max}$ ) values in EtOH, THF, and *n*-hexane.

Comp.	Substituent	EtOH		THF		<i>n</i> -Hexane		$E_g^{opt}$ (EtOH) <sup>b</sup> (eV)
		$\lambda_{\max 1}$ (nm)	$\Delta\lambda_{\max}^a$ (nm)	$\lambda_{\max 1}$ (nm)	$\Delta\lambda_{\max}^a$ (nm)	$\lambda_{\max 1}$ (nm)	$\Delta\lambda_{\max}^a$ (nm)	
<b>4a</b>	<i>p</i> -H	505	-	514	-	518	-	1.99
<b>4b</b>	<i>p</i> -OCH <sub>3</sub>	510	-5	516	-2	520	-2	2.00
<b>4c</b>	<i>p</i> -Cl	520	-15	531	-17	532	-14	1.94
<b>4d</b>	<i>p</i> -Br	522	-17	530	-16	536	-18	1.96
<b>4e</b>	<i>p</i> -F	507	-2	516	-2	524	-6	1.97
<b>4f</b>	<i>p</i> -NO <sub>2</sub>	499	6	508	6	508	10	1.97
<b>4g</b>	<i>m, p</i> -(CH <sub>3</sub> ) <sub>2</sub>	503	2	513	1	514	4	1.96
<b>4h</b>	<i>o, p</i> -(NO <sub>2</sub> ) <sub>2</sub>	389	116	386	128	375	143	2.47

<sup>a</sup> $\Delta\lambda_{\max} = \lambda_{\max 1}$  (unsubstituted formazan **4a**) -  $\lambda_{\max 1}$  (substituted formazan (**4b–4h**)). <sup>b</sup>Optical band gap,  $E_g = 1240/\lambda_{onset}$ .

As shown in Table 2, the absorption value ( $\lambda_{\max 1}$ ) of compound **4b** possessing an electron donating –OCH<sub>3</sub> subunit at the *para*-position is recorded  $\Delta\lambda_{\max} = 5$  nm longer wavelength than the parent molecule **4a** in ethanol. In both –Cl and –Br substituted compounds **4c** and **4d**, the  $\Delta\lambda_{\max}$  values showed pronounced bathochromic shifts of 15 nm and 17 nm, respectively. Under these circumstances, the –Cl and –Br atoms, with

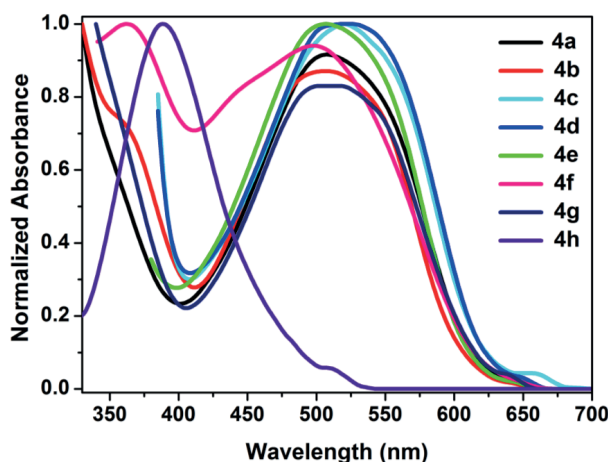


Figure 2. Electronic absorption bands of 4a–4h in ethanol.

inductive electron withdrawing and resonance electron donating effects, ended up with two opposite effects. It can be seen that resonance electron effects are noticeable. The high electronegativity of the fluorine atom attached to the 1-phenyl ring results in slight bathochromic shifts ( $\Delta\lambda_{\max} = 2$  nm for 4e, relative to 4a for the spectra in ethanol and THF). Compound 4f, which includes the *para*-NO<sub>2</sub> group on the 1-phenyl ring with its strong electron withdrawing effect, had a small shift towards shorter wavelength ( $\Delta\lambda_{\max} = 6$  nm) compared to 4a. The  $\lambda_{\max 1}$  value of the compound 4g substituted by the -CH<sub>3</sub> group, which is an inductive electron donating unit at *meta*- and *para*-positions, exhibits a small hypsochromic shift ( $\Delta\lambda_{\max} = 2$  nm). The  $\lambda_{\max 1}$  value of the compound 4h with strong electron attractive -NO<sub>2</sub> groups at *ortho*- and *para*-positions shows a strong hypsochromic shift of  $\Delta\lambda_{\max} = 116$  nm compared to 4a. This phenomenon can be attributed to the formation of a possible hydrogen bond between N-H proton with oxygen of a -NO<sub>2</sub> group attached to the *ortho*-position of the 1-phenyl ring (Scheme 3). Hence, the electron attractive quality of the -NO<sub>2</sub> group decreases, resulting in disappearance of the resonance effect.<sup>28,37,38</sup> Based on these results, electron donating groups and halogens acting with resonance electron effects generally lead to bathochromic shifts, whereas the electron withdrawing units result in hypsochromic shifts.

#### 2.4. Computation

The electronic and structural properties of compounds were explored further by conducting density functional theory (DFT) calculations. Geometry optimizations of both tautomers of formazans were achieved without any symmetry constraints by means of the Gaussian 09 package program. PBE1PBE<sup>40</sup> method with 6-31G(d) basis set was applied because of its good performance in exploring structures and properties of formazans.<sup>20,41,42</sup> Analysis of the harmonic vibrational frequencies using analytical second derivatives was performed to confirm the minima. Orbital composition analysis with Mulliken partition was carried out using the Multiwfn program (a multifunctional wavefunction analyzer).<sup>43</sup> TD-DFT calculations with incorporation of solvent effect using a polarizable continuum model (PCM)<sup>44</sup> were carried out using coulomb-attenuating method density functional theory (CAM-TD-B3LYP)<sup>45</sup> with 6-311+G(d,p) basis set to ascertain the lowest singlet-singlet vertical excitations due to the fact that CAM-B3LYP/6-311+G(d,p) provided good results that are close to experimentally recorded excitation energies.<sup>21</sup> Dimethyl sulfoxide, which possesses the highest dielectric constant ( $\epsilon = 46.83$ ) among the solvents used in UV-vis measurements, was chosen for TD-DFT calculations. Absorption bands were

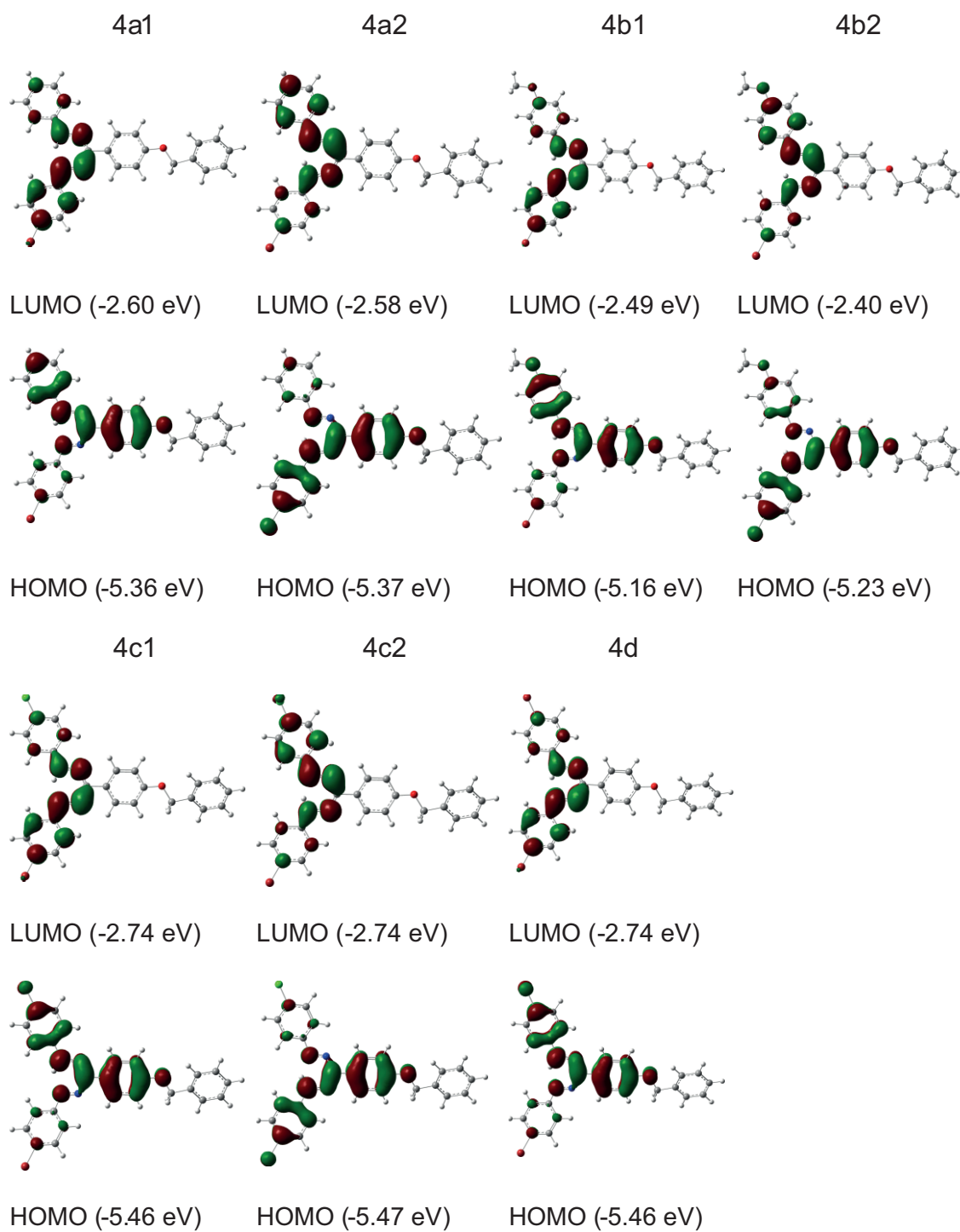
gathered for singlets with  $NStates$  of 50. Visualization of MOs with an isosurface value of 0.03 au was done using GaussView 5.0 and absorption spectra with oscillator strengths were pictured with GaussSum 3.0.<sup>46</sup>

Relative Gibbs free energies of tautomers calculated at PBE1PBE/6-31G(d) level are given in Scheme 4 (left), which pointed out almost degenerate ( $\Delta\Delta G < 1.0$  kcal mol<sup>-1</sup>) tautomers except for **4b**, **4f**, and **4h**. While tautomer 2 is more stable by 1.56 kcal mol<sup>-1</sup> in the case of **4b**, holding MeO substituent at the *para*-position of the phenyl unit located on N1, **4f** and **4h** possessing one and two NO<sub>2</sub> subunits, respectively, were predicted to have adapted to tautomer form 1 with relative energies of 1.89 kcal mol<sup>-1</sup> for **4f** and 6.01 kcal mol<sup>-1</sup> for **4h**. The reason for the strong shift of the equilibrium towards the tautomer 1 in **4h** is the intramolecular hydrogen bonding formed between N1-H and oxygen of *ortho*-NO<sub>2</sub> unit in a six membered ring (Scheme 4, right). The DFT calculations illustrated that all molecules are almost planar except for phenyl groups of benzyloxy substituents, which deviate from planarity by ca. 30°, and *para*-substituted phenyl unit located on C3 having a dihedral of 8–12° with core unit. N-H and N···H distances were estimated to be 1.02–1.03 Å and 1.80–1.82 Å in both tautomers, respectively, indicating hydrogen in a six-membered heterocyclic system. However, N···H distance in **4h1** was predicted to be larger (1.90 Å) owing to the hydrogen bonding formed with oxygen of the *ortho*-NO<sub>2</sub> group in a six membered ring (Scheme 4, right).

Frontier molecular orbitals (FMOs) were surfaced to analyze the intramolecular charge transfer (ICT) properties of formazans (Figure 3). HOMOs of the molecules are spreading over the core unit (–NH–N=C–N=N–) and phenyl subgroups located on N1 and C3 in tautomer 1, whereas HOMOs of tautomer 2 were found to localize on the core unit and phenyl subgroups located on N5 and C3. On the other hand, the localized LUMOs were obtained on the core unit of the molecules spreading a little over the phenyl substituent attached on N5. LUMOs of tautomer 2 were observed on a core unit with a contribution of the phenyl group on N1. FMOs noticeably indicated an efficient ICT from phenyl groups on N1 and C3 to the phenyl unit on N5 over a core unit in tautomer 1, and from phenyl groups on C3 and N5 to the phenyl unit on N1 via a core unit in tautomer 2. Orbital composition analysis provided the highest HOMO and LUMO orbital compositions of 14.3%–15.4% for N1 and 19.9%–20.3% for N4 of **4a–4h** in tautomer 1, while those were predicted as 14.8%–16.3% for N5 and 20.2%–21.6% for N1 in tautomer 2, respectively. However, NO<sub>2</sub> containing **4f** and **4h** had HOMO orbital compositions of 14.4% and 13.0% for N1 and LUMO compositions of 20.0% and 19.4% for N5 of **4f** and **4h** in tautomer 1, while those were predicted as 12.9% and 10.3% for N5 in HOMO and 17.8% and 16.3% for N2 in LUMO in tautomer 2, respectively. The estimated HOMO energy levels were found to be in the range of –5.16 to –5.47 eV, whereas those of **4f** and **4h** possessing one and two NO<sub>2</sub> units, respectively, were predicted as –5.70 to –6.06 eV owing to the strong electron withdrawing groups, which diminish the HOMO energy levels. A similar phenomenon was observed with LUMO energy levels. While LUMOs have energies between –2.40 and –2.74 eV, those of **4f** and **4h** with NO<sub>2</sub> units were calculated to be –3.08 to –3.59 eV depending on the number of NO<sub>2</sub> units attached on the phenyl group on N1.

The predicted UV-Vis absorption spectra of the less energy tautomers and their vertical excitation energies are listed in Figure S17 (see Supplementary Information) and Table 3, respectively. The calculated absorption properties are in good alignment with the experimentally recorded data except for **4h1**, having a predicted absorption band at 486 nm red shifted by 84 nm compared to the experimental value. The reason might be TD-DFT calculations performed on a gas phase optimized **4h1** with two NO<sub>2</sub> units, which can significantly interact with surrounding solvent and consequently distort the planarity of molecule and hence conjugation is decreased. The  $\lambda_{max}$  values emerge from HOMO to LUMO excitations, indicating the low energy transitions taking place from HOMO→LUMO.





**Figure 3.** HOMO and LUMO representations of both tautomers of **4a–4d** at PBE1PBE/6-31G(d) level (isosurface value: 0.3 a.u.).

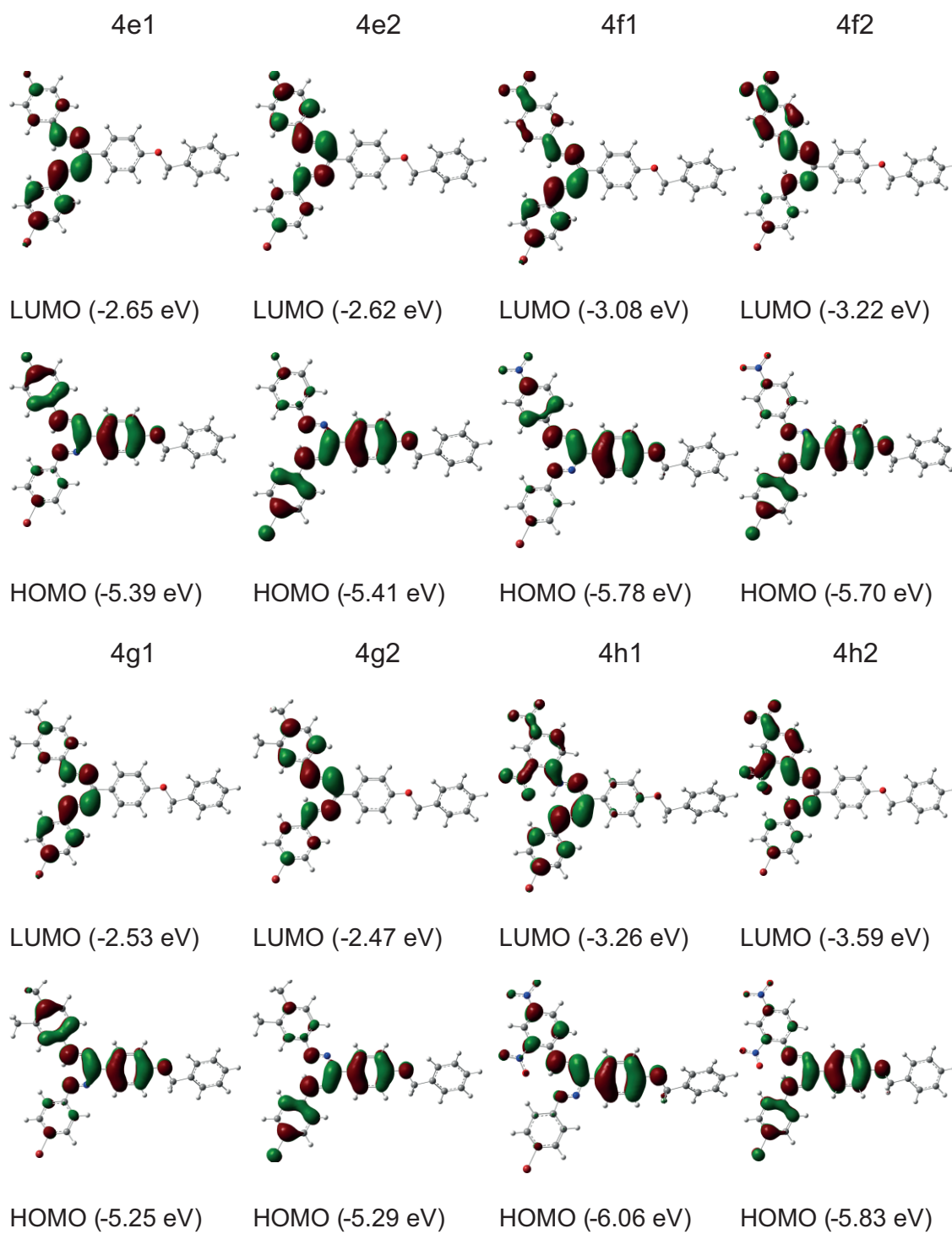


Figure 3. Continued.

**Table 3.** Excited state electronic transitions at (PCM:DMSO)-CAM-TD-B3LYP/6-311+G(d,p)//PBE1PBE/6-31G(d) level.

	$\lambda_{abs}$ (nm)	E (eV)	$F^a$	Major contribution <sup>b</sup> (%)	Exp. (nm)
<b>4a1</b>	491	2.52	0.572	H → L (96%)	507
	316	3.92	0.521	H-1 → L (83%)	–
<b>4b2</b>	482	2.57	0.660	H → L (96%)	502
	325	3.81	0.652	H-1 → L (89%)	302
<b>4c2</b>	492	2.52	0.619	H → L (96%)	519
	317	3.90	0.516	H-1 → L (76%), H-4 → L (15%)	–
<b>4d</b>	493	2.51	0.639	H → L (96%)	517
	319	3.88	0.529	H-1 → L (79%)	351
<b>4e2</b>	484	2.56	0.590	H → L (97%)	501
	313	3.96	0.468	H-1 → L (74%), H-4 → L (18%)	300
<b>4f</b>	497	2.50	0.746	H → L (93%)	485
	333	3.72	0.388	H → L+1 (70%), H-1 → L (18%)	–
	328	3.78	0.683	H-1 → L (62%), H → L+1 (14%)	–
<b>4g2</b>	482	2.57	0.627	H → L (96%)	504
	320	3.88	0.505	H-1 → L (55%), H → L+1 (36%)	–
	286	4.33	0.508	H → L+1 (35%), H-2 → L (26%)	284
<b>4h1</b>	486	2.55	0.662	H → L (91%)	402
	342	3.63	0.783	H-1 → L (80%)	–

<sup>a</sup>Oscillator strength. <sup>b</sup>H: HOMO, L: LUMO.

### 3. Conclusion

In this work, the formazans **4a–4h** were prepared in a two-step synthesis in good yields (50%–75%). The structures of the formazans were characterized by spectroscopic methods. Intramolecular hydrogen bonding and the effect of *para* substituents were elaborated by performing DFT calculations. Spectroscopic and computational investigations indicated the existence of a hydrogen bond between Ph<sup>1</sup>–NH and N–Ph<sup>5</sup>, which is in good agreement with the literature. Their optical investigations were performed in different polarity solvents. The UV-vis measurements indicated that  $\lambda_{max}$  values depend on the solvent polarities. All compounds, excluding **4h**, which shows a bathochromic shift, have a slight hypsochromic shift with increase in the polarity of solvents. However, unlike **4h**, compounds **4a–4g** showed negative solvatochromism in polar solvents. The examination of the substituent effects in various solvents pointed out a bathochromic shift for electron donating and halogen groups and a hypsochromic shift for electron withdrawing units. The TD-DFT method with incorporation of solvent (DMSO) was applied to calculate the electronic excitations of formazans, which pointed out the low energy transitions taking place from HOMO → LUMO. These structural isomers might be promising candidates as ligands for the coordination chemistry in the field of functional materials.

## 4. Experimental

### 4.1. Materials and methods

4-Bromoaniline, substituted phenylhydrazines, 4-(benzyloxy) benzaldehyde, NaOH, and high grade organic solvents for UV-Vis and fluorescence measurements were purchased from Sigma-Aldrich and used without any further purification. Thin layer chromatography plates (DC-Alufolien Kieselgel 60 F<sub>254</sub>) were obtained from Merck (Darmstadt, Germany). Isolation of compounds was performed by using column chromatography over Sigma silica gel 60 (63–200  $\mu$ m).

Microanalyses were carried out using a Leco CHNS-932 elemental analyzer. The melting points were measured on a Gallenkamp apparatus using a capillary tube.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker DPX FT-NMR (500 MHz) spectrometer ( $\text{SiMe}_4$  as internal standard) and chemical shifts ( $\delta$ ) are given in ppm. The spectrometer was equipped with a 5-mm PABBO BB-inverse gradient probe. The concentration of the solute compounds was 5 mg in 1.0 mL of  $\text{DMSO}-d_6$  and 10 mg in 1.0 mL of  $\text{CDCl}_3$ . The FTIR spectra were recorded as KBr pellets using a Bruker IFS 66 v/S FTIR Spectrophotometer in a 4000–400  $\text{cm}^{-1}$  range at room temperature. The electronic spectra of the formazans in different solvents were measured using a Shimadzu UV-3150 UV-VIS-NIR spectrophotometer. LC-MS studies of the formazans were carried out with an Agilent 1100 Series LC/MSD Trap VL&SL using atmospheric pressure chemical ionization and electrospray with positive and negative ion detection.

## 4.2. Synthesis of substituted phenylhydrazones (2a–2h)

The substituted phenylhydrazones were synthesized by condensation of 4-(benzyloxy) benzaldehyde with substituted phenylhydrazine compounds.<sup>28</sup>

### 4.2.1. General procedure for synthesis of (*E*)-1-(4-(benzyloxy)benzylidene)-2-phenylhydrazine (2a)

To a solution of 2.15 g of 4-(benzyloxy)benzaldehyde (10.2 mmol) in 25 mL of methanol was added a solution of 1.11 g of phenylhydrazine (920  $\mu\text{L}$ , 10.2 mmol) in 25 mL of methanol dropwise at 60 °C. The reaction mixture was stirred for 2 h and cooled down to room temperature over 30 min. The yellow precipitate was filtered off and dried in an oven at 60 °C. The crude product was recrystallized from methanol. The compound **2a** was obtained as bright cream color needles in 97% yield (5.82 g);  $R_f$ : 0.69 (*n*-hexane/ethylacetate, 5:1). mp: 144–145 °C. FTIR (KBr):  $\nu_{\text{max}}$  3315, 1313 (N–H str., C–N str.), 3033, 1506 (aromatic ring, C–H str., C=C str.), 1597 (HC=N str. in Schiff base), 1290, 1259 (C–O–C)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.60 (s, 1H); 7.57 (d,  $J = 8.50$  Hz, 2H); 7.46 (s, 1H); 7.38 (t,  $J = 7.00$  Hz, 2H); 7.32 (d,  $J = 8.00$  Hz, 2H); 7.20 (d,  $J = 8.50$  Hz, 2H); 7.02 (d,  $J = 8.00$  Hz, 2H); 6.90–6.95 (m, 4H); 5.10 (s, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.98; 132.95; 136.36; 129.52; 128.47; 127.36; 116.78; 114.16; 70.12. Anal. Calcd. for  $\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}$  (302.14): C, 79.44; H, 6.00; N, 9.26. Found: C, 79.20; H, 6.21; N, 9.39.

The other compounds (**2b–2h**) were prepared in a similar manner.

### 4.2.2. (*E*)-1-(4-(Benzyloxy)benzylidene)-2-(4-methoxyphenyl)hydrazine (2b)

Light yellow solid (crystallized from methanol). Yield: 3.11 g (74%); mp: 156–158 °C.  $R_f$ : 0.59 (*n*-hexane/ethylacetate, 5:1). FTIR (KBr):  $\nu_{\text{max}}$  3300, 1315 (N–H str., C–N str.), 3035, 1525, 1508 (aromatic ring, C–H str., C=C str.), 1604 (HC=N str. in Schiff base), 1244, (C–O–C)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.60 (s, 1H); 7.50 (d,  $J = 7.50$  Hz, 2H); 7.44 (s, 1H); 7.40 (d,  $J = 8.00$  Hz, 2H); 7.35 (t,  $J = 7.50$  Hz, 2H); 7.30 (d,  $J = 8.00$  Hz, 2H); 7.20 (d,  $J = 7.50$  Hz, 1H); 6.96–7.02 (m, 4H); 5.13 (s, 2H); 3.82 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.20; 138.00; 132.00; 128.61; 128.05; 127.66; 127.66; 115.15; 114.29; 70.06; 55.45. Anal. Calcd. for  $\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_2$  (332.15): C, 75.88; H, 6.06; N, 8.43. Found: C, 75.65; H, 6.10; N, 8.20.

**4.2.3. (E)-1-(4-(Benzyloxy)benzylidene)-2-(4-chlorophenyl)hydrazine (2c)**

Light white needles (crystallized from methanol). Yield: 2.45 g (73%); mp: 154–155 °C.  $R_f$ : 0.56 (*n*-hexane/ethylacetate, 5:1). FTIR (KBr):  $\nu_{max}$  3315, 1307 (N–H str., C–N str.), 3033, 1498 (aromatic ring, C–H str., C=C str.), 1597 (HC=N str. in Schiff base), 1288, 1244 (C–O–C)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.64 (s, 1H); 7.58 (d,  $J = 8.00$  Hz, 2H); 7.48 (s, 1H); 7.44 (d,  $J = 7.50$  Hz, 2H); 7.39 (t,  $J = 7.50$  Hz, 2H); 7.34 (d,  $J = 7.00$  Hz, 1H); 7.21 (d,  $J = 9.00$  Hz, 2H); 6.96–7.03 (m, 4H); 5.09 (s, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.20; 137.91; 129.12; 128.60; 128.04; 127.64; 127.46; 115.07; 113.73; 70.06. Anal. Calcd. for  $\text{C}_{20}\text{H}_{17}\text{ClN}_2\text{O}$  (336.10): C, 71.32; H, 5.09; N, 8.32. Found: C, 71.12; H, 4.95; N, 8.60.

**4.2.4. (E)-1-(4-(Benzyloxy)benzylidene)-2-(4-bromophenyl)hydrazine (2d)**

White solid (crystallized from methanol). Yield: 3.68 g (81%); mp: 171–172 °C.  $R_f$ : 0.63 (*n*-hexane/ethylacetate, 5:1). FTIR (KBr):  $\nu_{max}$  3313, 1307 (N–H str., C–N str.), 3034, 1498 (aromatic ring, C–H str., C=C str.), 1602 (HC=N str. in Schiff base), 1288, 1244 (C–O–C)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.64 (s, 1H); 7.58 (d,  $J = 8.50$  Hz, 2H); 7.48 (s, 1H); 7.44 (d,  $J = 7.50$  Hz, 2H); 7.39 (t,  $J = 7.50$  Hz, 2H); 7.34 (d,  $J = 8.50$  Hz, 2H); 7.23 (t,  $J = 7.50$  Hz, 1H); 6.95–7.01 (m, 4H); 5.09 (s, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.20; 138.00; 132.00; 128.61; 128.05; 127.66; 127.46; 115.08; 114.19; 70.06. Anal. Calcd. for  $\text{C}_{20}\text{H}_{17}\text{BrN}_2\text{O}$  (380.05): C, 63.00; H, 4.49; N, 7.35. Found: C, 62.98; H, 4.32; N, 7.16.

**4.2.5. (E)-1-(4-(Benzyloxy)benzylidene)-2-(4-fluorophenyl)hydrazine (2e)**

White-off solid (from methanol). Yield: 2.40 g (75%); mp: 148–149 °C.  $R_f$ : 0.62 (*n*-hexane/ethylacetate, 5:1). FTIR (KBr):  $\nu_{max}$  3319, 1313 (N–H str., C–N str.), 3036, 1525, 1508 (aromatic ring, C–H str., C=C str.), 1607 (HC=N str. in Schiff base), 1257, 1211 (C–O–C)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.60 (s, 1H); 7.56 (d,  $J = 8.50$  Hz, 2H); 7.47 (s, 1H); 7.43 (d,  $J = 7.00$  Hz, 2H); 7.36 (t,  $J = 7.00$  Hz, 2H); 7.30 (d,  $J = 8.50$  Hz, 2H); 7.24 (d,  $J = 8.50$  Hz, 1H); 6.94–6.99 (m, 4H); 5.11 (s, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.20; 136.00; 130.00; 128.54; 128.30; 127.16; 126.76; 116.08; 113.18; 70.09. Anal. Calcd. for  $\text{C}_{20}\text{H}_{17}\text{FN}_2\text{O}$  (320.13): C, 74.98; H, 5.35; N, 8.74. Found: C, 74.70; H, 5.12; N, 8.58.

**(E)-1-(4-(Benzyloxy)benzylidene)-2-(4-nitrophenyl)hydrazine (2f)**

Light red needles (from methanol). Yield: 2.32 g (83%); mp: 182–184 °C.  $R_f$ : 0.38 (*n*-hexane/ethylacetate, 5:1). FTIR (KBr):  $\nu_{max}$  3263, 1379 (N–H str., C–N str.), 3045, 1510 (aromatic ring, C–H str., C=C str.), 1616 (HC=N str. in Schiff base), 1274, 1245 (C–O–C), 1469, 1292 (–NO<sub>2</sub>, N=O str.)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.80 (s, 1H); 7.70 (d,  $J = 8.50$  Hz, 2H); 7.62 (s, 1H); 7.54 (d,  $J = 7.00$  Hz, 2H); 7.42 (t,  $J = 7.00$  Hz, 2H); 7.34 (d,  $J = 8.50$  Hz, 2H); 7.22 (d,  $J = 8.50$  Hz, 1H); 6.93–6.99 (m, 4H); 5.14 (s, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.20; 148.00; 136.00; 132.54; 128.87; 128.16; 126.76; 115.08; 114.18; 70.08. Anal. Calcd. for  $\text{C}_{20}\text{H}_{17}\text{N}_3\text{O}_3$  (347.13): C, 69.15; H, 4.93; N, 12.10. Found: C, 69.35; H, 4.84; N, 12.33.

**4.2.6. (E)-1-(4-(Benzyloxy)benzylidene)-2-(3,4-dimethylphenyl)hydrazine (2g)**

Light yellow solid (from methanol). Yield: 2.37 g (72%); mp: 136–138 °C.  $R_f$ : 0.72 (*n*-hexane/ethylacetate, 5:1). FTIR (KBr):  $\nu_{max}$  3328, 1315 (N–H str., C–N str.), 3035, 1504 (aromatic ring, C–H str., C=C str.), 1612 (HC=N str. in Schiff base), 1296, 1240 (C–O–C)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.60 (s, 1H);

7.54 (d,  $J = 8.50$  Hz, 2H); 7.46 (s, 1H); 7.32 (d,  $J = 7.50$  Hz, 2H); 7.20 (d,  $J = 7.50$  Hz, 2H); 7.02 (d,  $J = 8.50$  Hz, 2H); 6.81–6.86 (m, 4H); 5.04 (s, 2H); 2.28 (s, 3H); 2.23 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.73; 138.60; 134.71; 130.26; 129.20; 128.21; 127.44; 114.65; 112.16; 70.40; 20.29; 19.09. Anal. Calcd. for  $\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}$  (330.42): C, 79.97; H, 6.71; N, 8.48. Found: C, 79.74; H, 6.52; N, 8.62.

#### 4.2.7. (*E*)-1-(4-(Benzyloxy)benzylidene)-2-(2,4-dinitrophenyl)hydrazine (2h)

Light brown powder (from methanol). Yield: 3.77 g (96%); mp: 233–235 °C.  $R_f$ : 0.75 (*n*-hexane/ethylacetate, 5:1). FTIR (KBr):  $\nu_{\text{max}}$  3277, 1328 (N–H str., C–N str.), 3089, 1587 (aromatic ring, C=C str., C–H str.), 1614 (HC=N str. in Schiff base), 1259 (C–O–C), 1452, 1280 (–NO<sub>2</sub>, N=O str.)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.00 (s, 1H); 8.14 (d,  $J = 8.60$  Hz, 1H); 7.68 (d,  $J = 8.60$  Hz, 2H); 7.52 (d,  $J = 7.00$  Hz, 2H); 7.48 (d,  $J = 7.00$  Hz, 2H); 7.36 (d,  $J = 7.00$  Hz, 2H); 6.95–7.01 (m, 4H); 5.17 (s, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  161.52; 152.32; 146.33; 139.50; 129.47; 129.10; 128.29; 127.10; 117.18; 115.04; 70.56. Anal. Calcd. for  $\text{C}_{20}\text{H}_{16}\text{N}_4\text{O}_5$  (392.11): C, 61.22; H, 4.11; N, 14.28. Found: C, 61.40; H, 3.95; N, 14.34.

### 4.3. General synthesis of formazans 4a–4h

A 4-bromoaniline diazonium salt (**3**) solution was obtained first. To a solution of substituted arylamine in 10 mL of  $\text{HCl}_{(\text{aq})}$  (50%, v/v) was dropped a solution of  $\text{NaNO}_2$  in 5 mL of water at 0–5 °C over 1 h. The reaction mixture was allowed to stir for another 1 h. Completion of diazotization was checked using starch iodide paper. The diazonium salt of substituted arylamine solution was added dropwise at 0–5 °C to a solution of **2a–2h** in pyridine (20 mL) and 20% NaOH (10 mL). The coupling reaction mixture was allowed to stir for another 3 h and then poured into 250 mL of ice-cold water. After stirring for 45–60 min, the product was collected by filtration, washed with water, and dried. The crude product was crystallized out of methanol.

#### 4.3.1. (2*Z*,4*E*)-3-(4-(Benzyloxy)phenyl)-5-(4-bromophenyl)-1-phenylformazan (4a)

Compound **4a** was obtained from **2a** (1.50 g, 4.96 mmol) and diazonium salt **3** (840 mg, 4.96 mmol) as dark red powder. Yield: 1.20 g, 50%;  $R_f$ : 0.67 (*n*-hexane/ethylacetate, 5:1); mp: 142–143 °C. FTIR (KBr):  $\nu_{\text{max}}$  3062, 1379 (N–H w., C–N str.), 1512, 3028 (aromatic ring, C=C str., C–H str.), 1596 (C=N str. in Schiff base), 1498 (N=N of formazans), 1238–1170 (C–O–C)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  15.13 (s, 1H); 8.03 (d,  $J = 9.00$  Hz, 2H); 7.69 (d,  $J = 7.50$  Hz, 2H); 7.54 (d,  $J = 9.00$  Hz, 2H); 7.50 (d,  $J = 9.00$  Hz, 2H); 7.46 (dd,  $J = 8.00, 5.00$  Hz, 4H); 7.41 (t,  $J = 7.50$  Hz, 2H); 7.35 (d,  $J = 7.50$  Hz, 1H); 7.33 (t,  $J = 7.50$  Hz, 1H); 7.05 (d,  $J = 9.00$  Hz, 2H); 5.14 (s, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.77; 148.21; 146.53; 141.36; 136.97; 132.42; 130.11; 129.41; 128.70; 128.59; 127.96; 127.47; 127.29; 119.94; 119.67; 119.13; 114.79; 70.06. ESI-MS:  $m/z$  485.0 ((M+H)<sup>+</sup>, 94%); 484.1 ((M)<sup>+</sup>, 27%); 483.1 ((M-H)<sup>+</sup>, 100%). Anal. Calcd. for  $\text{C}_{26}\text{H}_{21}\text{BrN}_4\text{O}$ : C, 64.34; H, 4.36; N, 11.54. Found: C, 64.10; H, 4.42; N, 11.45.

#### 4.3.2. (2*Z*,4*E*)-3-(4-(Benzyloxy)phenyl)-5-(4-bromophenyl)-1-(4-methoxyphenyl)formazan (4b)

Compound **4b** was obtained from **2b** (1.20 g, 3.61 mmol) and diazonium salt **3** (610 mg, 3.61 mmol) as a claret red solid. Yield: 1.40 g, 75%;  $R_f$ : 0.50; mp: 153–155 °C. FTIR (KBr):  $\nu_{\text{max}}$  3064, 1352 (N–H w., C–N str.), 1510, 3004 (aromatic ring, C=C str., C–H str.), 1598 (C=N str. in Schiff base), 1490 (N=N of formazans), 1243–1172 (C–O–C)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.77 (s, 1H); 8.02 (d,  $J = 9.00$  Hz, 2H); 7.85

(d,  $J = 9.00$  Hz, 2H); 7.47 (d,  $J = 7.50$  Hz, 2H); 7.44 (d,  $J = 9.00$  Hz, 2H); 7.40 (t,  $J = 7.50$  Hz, 2H); 7.34 (t,  $J = 7.25$  Hz, 1H); 7.27 (d,  $J = 9.00$  Hz, 2H); 7.03 (d,  $J = 8.00, 2.50$  Hz, 4H); 5.13 (s, 2H); 3.90 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  162.15; 158.72; 146.18; 143.29; 141.25; 136.99; 132.25; 130.19; 128.58; 127.95; 127.47; 127.44; 123.71; 116.64; 115.55; 114.72; 114.63; 70.05; 55.66. ESI-MS:  $m/z$  515.1 ((M+H) $^+$ , 100%); 514.1 ((M) $^+$ , 27%); 513.1 ((M-H) $^+$ , 99%). Anal. Calcd. for  $\text{C}_{27}\text{H}_{23}\text{BrN}_4\text{O}_2$ : C, 62.92; H, 4.50; N, 10.87. Found: C, 62.74; H, 4.62; N, 10.66.

#### 4.3.3. (2Z,4E)-3-(4-(Benzyloxy)phenyl)-5-(4-bromophenyl)-1-(4-chlorophenyl)formazan (4c)

Compound **4c** was obtained from **2c** (1.21 g, 3.59 mmol) and diazonium salt **3** (610 mg, 3.59 mmol) as a dark purple solid. Yield: 1.10 g, 58%;  $R_f$ : 0.75; mp: 148–150 °C. FTIR (KBr):  $\nu_{\text{max}}$  3063, 1382 (N–H w., C–N str.), 1596, 3033 (aromatic ring, C=C str., C–H str.), 1602 (C=N str. in Schiff base), 1467 (N=N of formazans), 1244–1171 (C–O–C)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  15.04 (s, 1H); 8.01 (d,  $J = 9.00$  Hz, 2H); 7.62 (d,  $J = 7.75$  Hz, 2H); 7.56 (dd,  $J = 9.00, 4.00$  Hz, 2H); 7.38–7.45 (m, 4H); 7.20 (d,  $J = 9.00$  Hz, 2H); 7.05 (d,  $J = 9.00$  Hz, 1H); 7.01 (d,  $J = 8.50$  Hz, 2H); 6.98 (d,  $J = 9.00$  Hz, 2H); 5.14 (s, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.32; 158.87; 146.79; 143.54; 137.88; 136.71; 132.49; 129.58; 129.10; 128.60; 128.04; 127.62; 127.46; 127.34; 120.18; 119.79; 115.06; 114.83; 113.71; 70.05. ESI-MS:  $m/z$  519.0 ((M+H) $^+$ , 100%); 518.0 ((M) $^+$ , 28%); 517.0 ((M-H) $^+$ , 100%). Anal. Calcd. for  $\text{C}_{26}\text{H}_{20}\text{BrClN}_4\text{O}$ : C, 60.07; H, 3.88; N, 10.78. Found: C, 60.38; H, 3.92; N, 10.59.

#### 4.3.4. (2Z,4E)-3-(4-(Benzyloxy)phenyl)-1,5-bis(4-bromophenyl)formazan (4d)

Compound **4d** was obtained from **2d** (1.43 g, 3.75 mmol) and diazonium salt **3** (640 mg, 3.75 mmol) as a violet solid. Yield: 1.41 g, 67%;  $R_f$ : 0.79; mp: 157–159 °C. FTIR (KBr):  $\nu_{\text{max}}$  3087, 1380 (N–H w., C–N str.), 1593, 3033 (aromatic ring, C=C str., C–H str.), 1605 (C=N str. in Schiff base), 1498 (N=N of formazans), 1247–1172 (C–O–C)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  15.02 (s, 1H); 8.00 (d,  $J = 9.00$  Hz, 2H); 7.56 (dd,  $J = 9.00, 7.00$  Hz, 4H); 7.51 (d,  $J = 9.00$  Hz, 2H); 7.47 (d,  $J = 7.50$  Hz, 1H); 7.43 (dd,  $J = 7.00, 5.25$  Hz, 2H); 7.40 (t,  $J = 7.50$  Hz, 2H); 7.33 (d,  $J = 9.00$  Hz, 2H); 7.04 (d,  $J = 10.00$  Hz, 1H); 6.97 (dd,  $J = 9.00, 5.25$  Hz, 2H); 5.13 (s, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.33; 158.88; 146.77; 137.96; 132.50; 131.96; 128.60; 128.03; 127.99; 127.64; 127.46; 127.53; 120.81; 120.13; 115.06; 114.83; 114.17; 70.05. ESI-MS:  $m/z$  565.0 ((M+H) $^+$ , 47%); 564.0 ((M) $^+$ , 28%); 563.0 ((M-H) $^+$ , 100%). Anal. Calcd. for  $\text{C}_{26}\text{H}_{20}\text{Br}_2\text{N}_4\text{O}$ : C, 55.34; H, 3.57; N, 9.93. Found: C, 55.51; H, 3.84; N, 10.04.

#### 4.3.5. (2Z,4E)-3-(4-(Benzyloxy)phenyl)-5-(4-bromophenyl)-1-(4-fluorophenyl)formazan (4e)

Compound **4e** was obtained from **2e** (1.33 g, 4.15 mmol) and diazonium salt **3** (710 mg, 2.65 mmol) as a dark purple solid. Yield: 1.00 g, 74%;  $R_f$ : 0.52; mp: 168–170 °C. FTIR (KBr):  $\nu_{\text{max}}$  3061, 1352 (N–H w., C–N str.), 1589, 3034 (aromatic ring, C=C str., C–H str.), 1603 (C=N str. in Schiff base), 1492 (N=N of formazans), 1244–1172 (C–O–C)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.96 (s, 1H); 8.00 (d,  $J = 9.00$  Hz, 2H); 7.78 (dd,  $J = 9.00, 5.00$  Hz, 2H); 7.48 (dd,  $J = 8.00, 2.87$  Hz, 4H); 7.41 (d,  $J = 7.50$  Hz, 2H); 7.38 (dd,  $J = 7.00, 2.87$  Hz, 2H); 7.34 (t,  $J = 7.50$  Hz, 1H); 7.18 (t,  $J = 8.50$  Hz, 2H); 7.04 (d,  $J = 9.00$  Hz, 2H); 5.13 (s, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.32; 162.32; 158.82; 146.76; 146.74; 144.50; 141.31; 136.94; 132.39; 129.93; 128.59; 128.98; 127.47; 127.32; 122.38; 122.31; 118.14; 117.96; 116.50; 116.32; 114.79;

70.06. ESI-MS:  $m/z$  503.0 ((M+H)<sup>+</sup>, 88%); 502.1 ((M)<sup>+</sup>, 27%); 501.1 ((M-H)<sup>+</sup>, 100%). Anal. Calcd. for C<sub>26</sub>H<sub>20</sub>BrFN<sub>4</sub>O: C, 62.04; H, 4.00; N, 11.13. Found: C, 62.16; H, 4.28; N, 11.32.

#### 4.3.6. (2Z,4E)-3-(4-(Benzyloxy)phenyl)-5-(4-bromophenyl)-1-(4-nitrophenyl)formazan (4f)

Compound **4f** was obtained from **2f** (1.22 g, 3.51 mmol) and diazonium salt **3** (600 mg, 3.51 mmol) as a darkish solid. Yield: 1.10 g, 59%;  $R_f$ : 0.58; mp: 209 °C. FTIR (KBr):  $\nu_{\max}$  3083, 1321 (N-H w, C-N str.), 1502, 3031 (aromatic ring, C=C str., C-H str.), 1593 (C=N str. in Schiff base), 1477 (N=N of formazans), 1245–1171 (C-O-C) cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  14.31 (s, 1H); 8.25 (d,  $J$  = 8.50 Hz, 2H); 8.01 (d,  $J$  = 8.50 Hz, 2H); 7.80 (d,  $J$  = 8.50 Hz, 2H); 7.70 (d,  $J$  = 8.50 Hz, 2H); 7.41–7.46 (m, 6H); 7.35 (d,  $J$  = 7.00 Hz, 1H); 7.07 (d,  $J$  = 8.50 Hz, 2H); 5.15 (s, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  159.49; 150.88; 148.92; 143.23; 142.75; 136.74; 132.85; 128.64; 128.17; 128.07; 127.47; 126.80; 125.86; 123.81; 114.93; 114.39; 70.10. ESI-MS:  $m/z$  529.0 ((M)<sup>+</sup>, 40%); 528.0 ((M-H)<sup>+</sup>, 100%). Anal. Calcd. for C<sub>26</sub>H<sub>20</sub>BrN<sub>5</sub>O<sub>3</sub>: C, 58.88; H, 3.80; N, 13.20. Found: C, 58.77; H, 3.68; N, 13.31.

#### 4.3.7. (2Z,4E)-3-(4-(Benzyloxy)phenyl)-5-(4-bromophenyl)-1-(3,4-dimethylphenyl)formazan (4g)

Compound **4g** was obtained from **2g** (1.00 g, 3.02 mmol) and diazonium salt **3** (510 mg, 3.02 mmol) as a dark purple solid. Yield: 0.90 g, 58%;  $R_f$ : 0.71; mp: 177–179 °C. FTIR (KBr):  $\nu_{\max}$  3062, 1386 (N-H w., C-N str.), 1587, 3033 (aromatic ring, C=C str., C-H str.), 1604 (C=N str. in Schiff base), 1490 (N=N of formazans), 1244–1190 (C-O-C) cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  15.06 (s, 1H); 8.03 (dd,  $J$  = 7.00, 2.00 Hz, 2H); 7.56 (s, 1H); 7.53 (dd,  $J$  = 8.00, 2.00 Hz, 1H); 7.48 (t,  $J$  = 7.25 Hz, 3H); 7.41 (d,  $J$  = 7.50 Hz, 2H); 7.38 (d,  $J$  = 9.00 Hz, 2H); 7.34 (t,  $J$  = 7.50 Hz, 1H); 7.24 (d,  $J$  = 8.50 Hz, 1H); 7.04 (dd,  $J$  = 7.00, 2.00 Hz, 2H); 5.14 (s, 2H); 2.36 (s, 3H); 2.33 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  158.70; 148.49; 144.80; 141.24; 139.00; 137.82; 137.01; 132.30; 130.55; 130.27; 128.58; 127.94; 127.47; 127.33; 121.59; 118.32; 118.04; 117.48; 114.75; 70.05; 19.82; 19.94. ESI-MS:  $m/z$  513.1 ((M+H)<sup>+</sup>, 100%); 512.1 ((M)<sup>+</sup>, 27%); 511.1 ((M-H)<sup>+</sup>, 95%). Anal. Calcd. for C<sub>28</sub>H<sub>25</sub>BrN<sub>4</sub>O: C, 65.50; H, 4.91; N, 10.91. Found: C, 65.37; H, 4.77; N, 10.79.

#### 4.3.8. (2Z,4E)-3-(4-(Benzyloxy)phenyl)-5-(4-bromophenyl)-1-(2,4-dinitrophenyl)formazan (4h)

Compound **4h** was obtained from **2h** (1.71 g, 4.36 mmol) and diazonium salt **3** (740 mg, 4.36 mmol) as a light claret solid. Yield: 1.3 g, 52%;  $R_f$ : 0.63; mp: 214–216 °C. FTIR (KBr):  $\nu_{\max}$  3276, 1328 (N-H w., C-N str.), 1589, 3032 (aromatic ring, C=C str., C-H str.), 1610 (C=N str. in Schiff base), 1456 (N=N of formazans), 1259–1172 (C-O-C) cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  10.78 (s, 1H); 8.04 (d,  $J$  = 2.50 Hz, 1H); 7.81 (s, 1H); 7.52 (dd,  $J$  = 9.50, 2.00 Hz, 1H); 7.25 (d,  $J$  = 9.50 Hz, 2H); 6.93 (d,  $J$  = 9.00 Hz, 2H); 6.65 (d,  $J$  = 7.50 Hz, 3H); 6.59 (t,  $J$  = 7.50 Hz, 2H); 6.52 (t,  $J$  = 7.50 Hz, 1H); 6.31 (d,  $J$  = 9.00 Hz, 2H); 4.36 (s, 2H). <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  159.06; 153.03; 148.23; 145.95; 139.57; 135.53; 133.81; 128.67; 128.06; 127.42; 126.93; 125.49; 124.82; 123.52; 122.09; 115.75; 115.64; 114.38; 114.10; 99.14; 68.79. ESI-MS:  $m/z$  574.0 ((M)<sup>-</sup>, 35%); 573.0 ((M-H)<sup>-</sup>, 100%). Anal. Calcd. for C<sub>26</sub>H<sub>19</sub>BrN<sub>6</sub>O<sub>5</sub>: C, 54.27; H, 3.33; N, 14.61. Found: C, 54.32; H, 3.40; N, 14.52.



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## Supplementary Information

NMR spectra, computed absorption spectra, and Cartesian coordinates.

### NMR spectra of target compounds

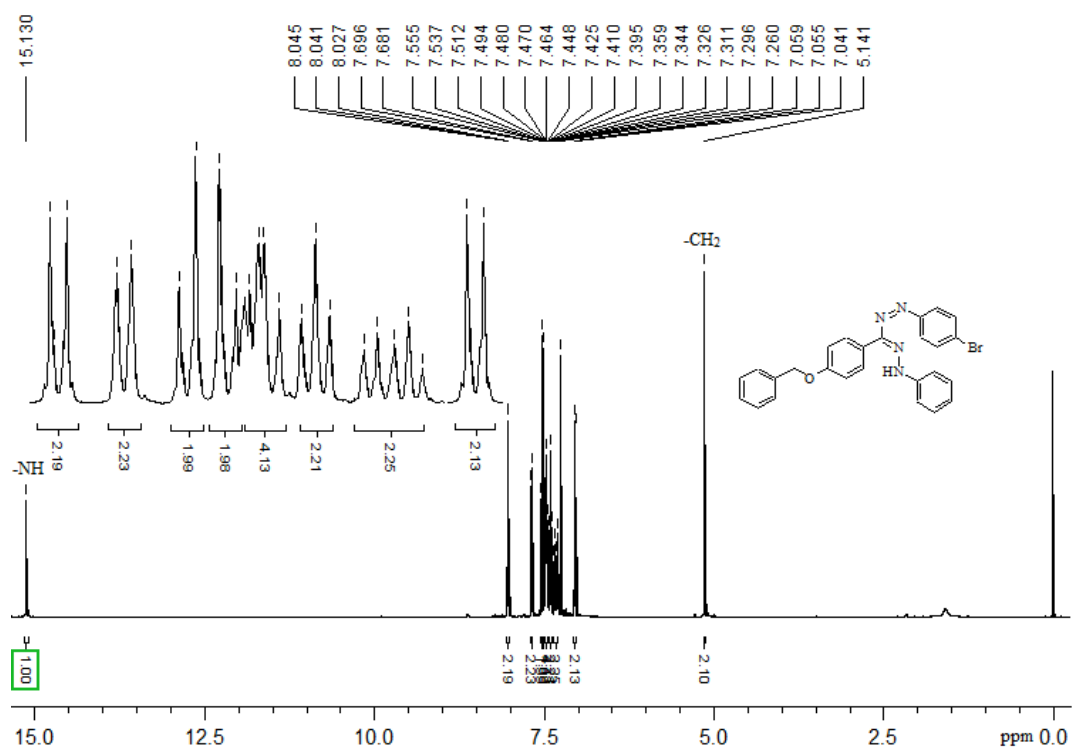


Figure S1.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound 4a.

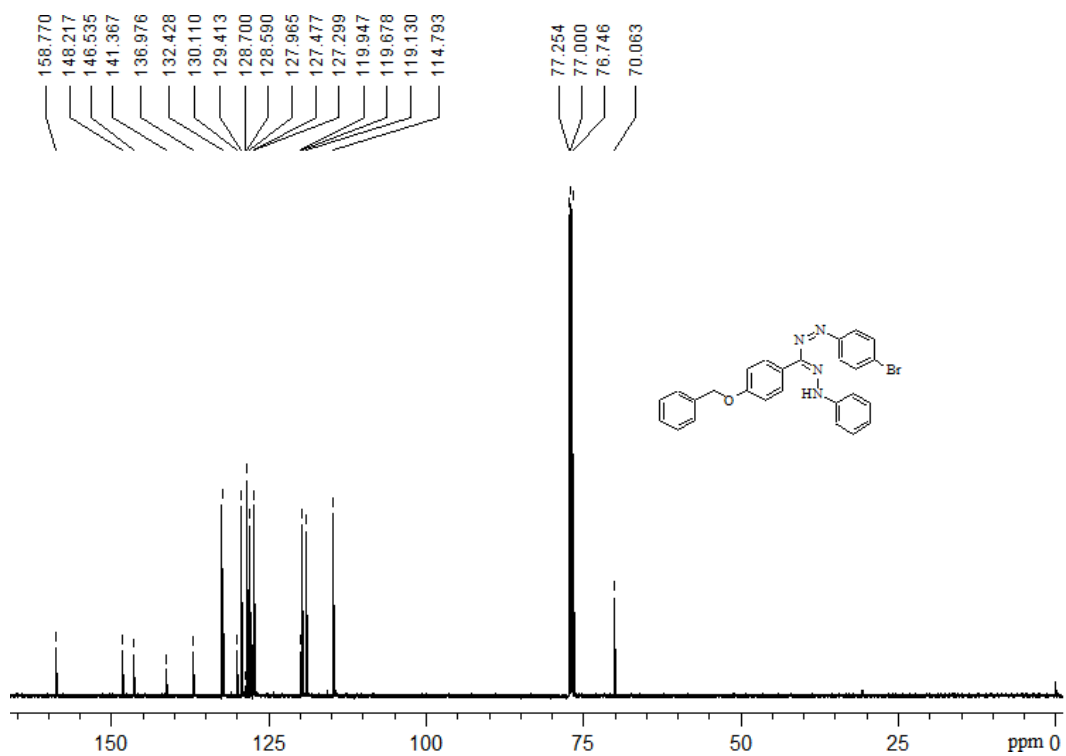


Figure S2.  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) spectrum of compound 4a.

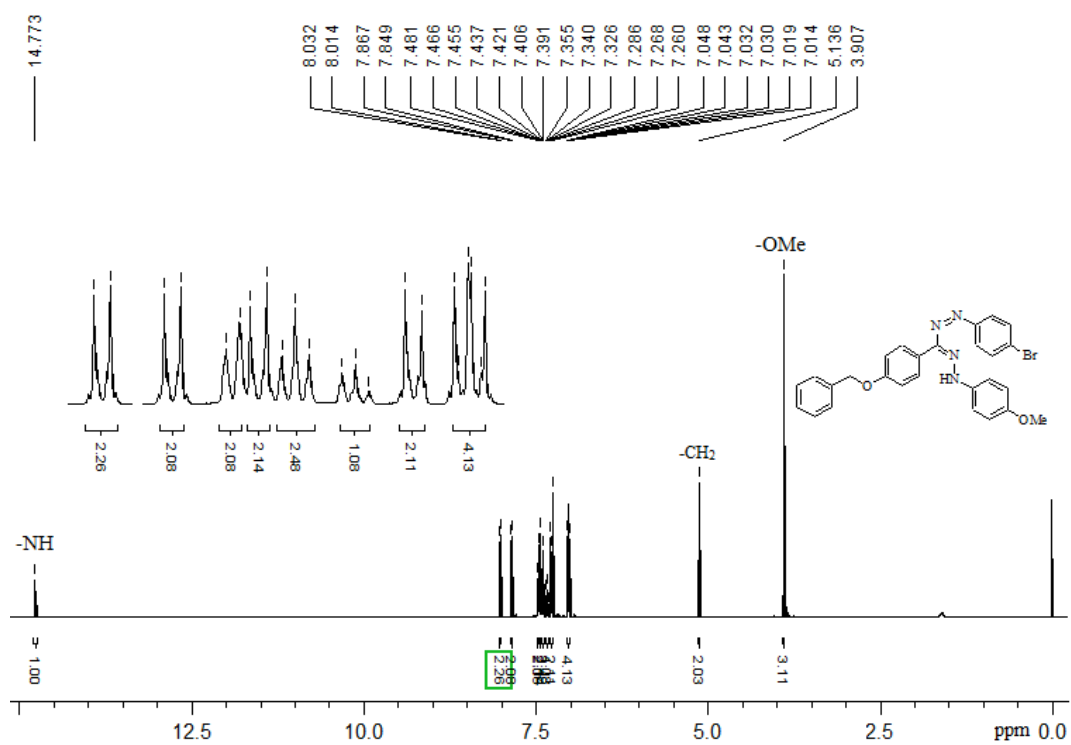


Figure S3.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound 4b.

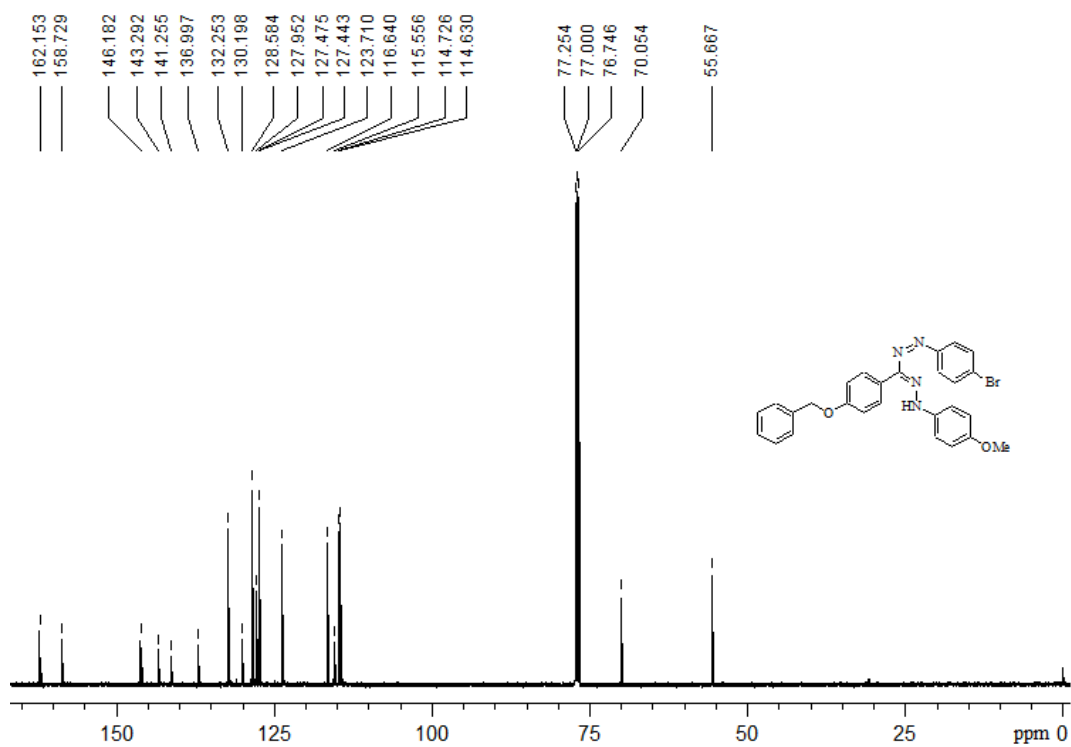


Figure S4.  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) spectrum of compound 4b.

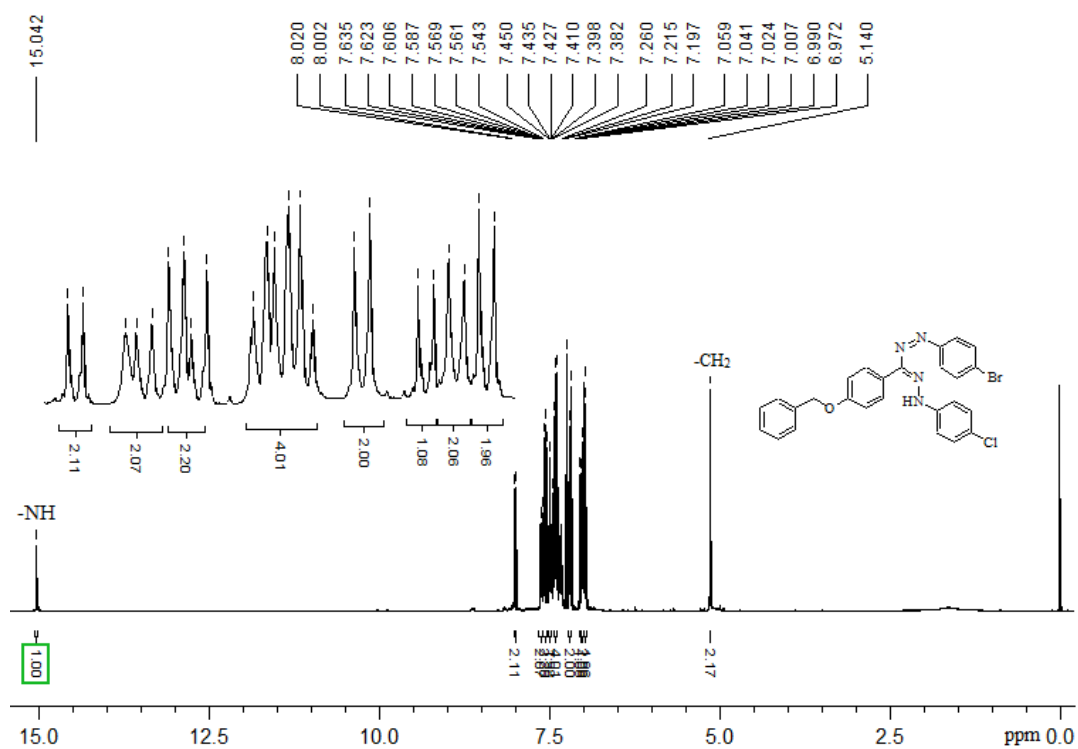


Figure S5. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 4c.

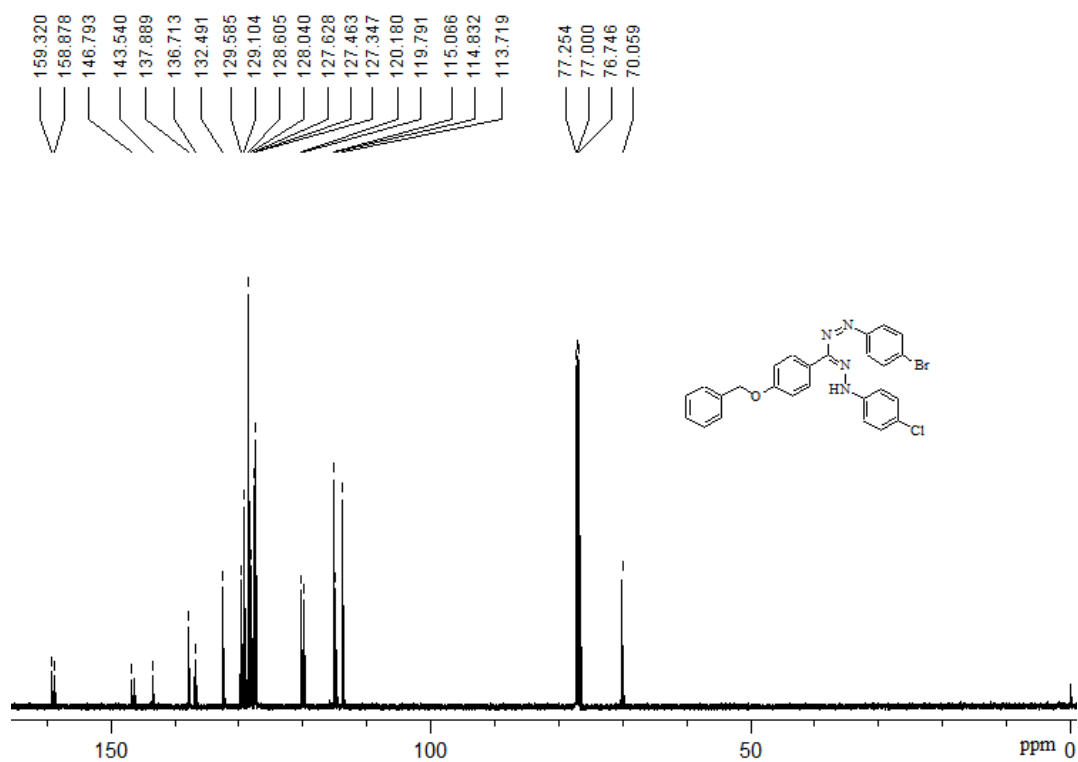


Figure S6. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) spectrum of compound 4c.

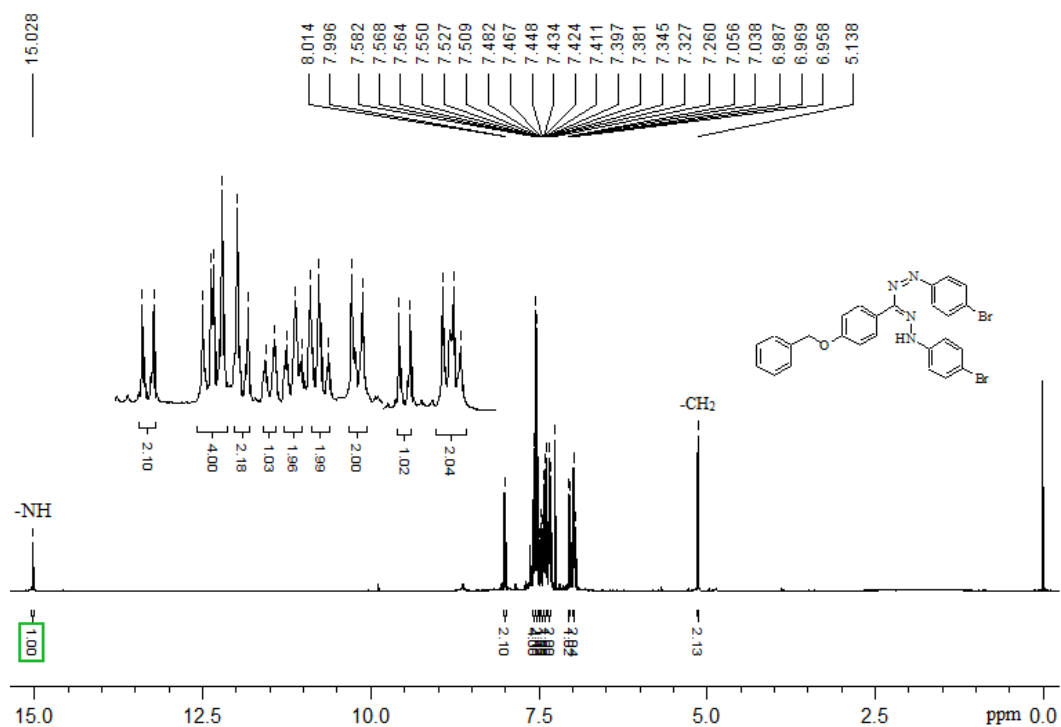


Figure S7.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound 4d.

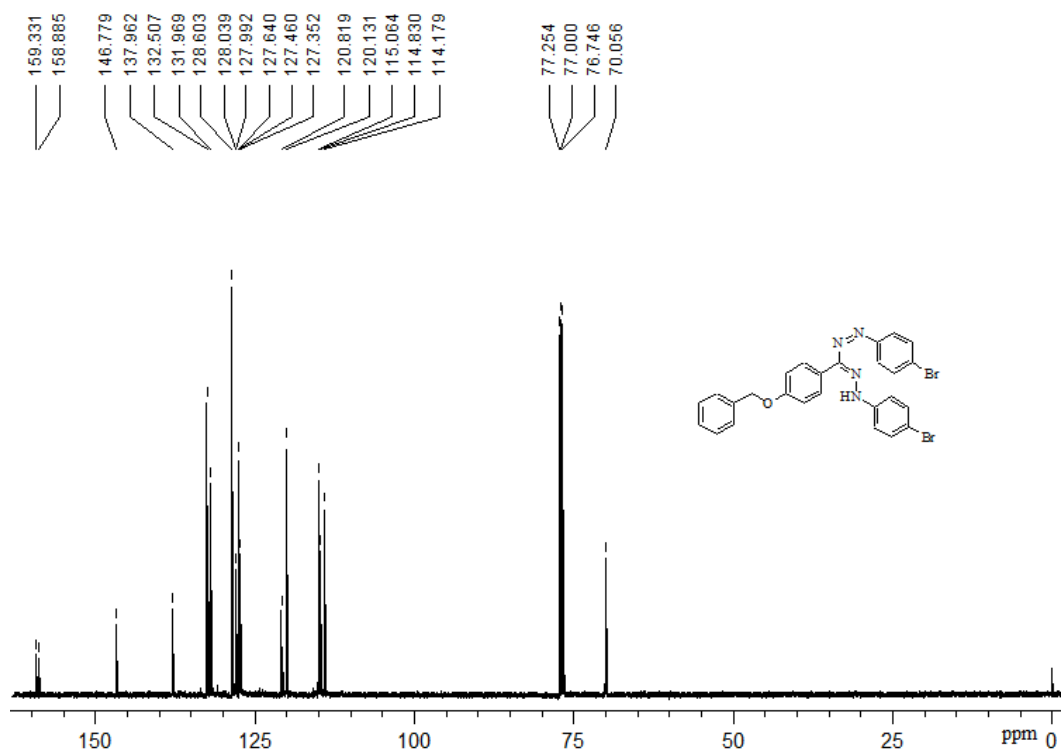


Figure S8.  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) spectrum of compound 4d.

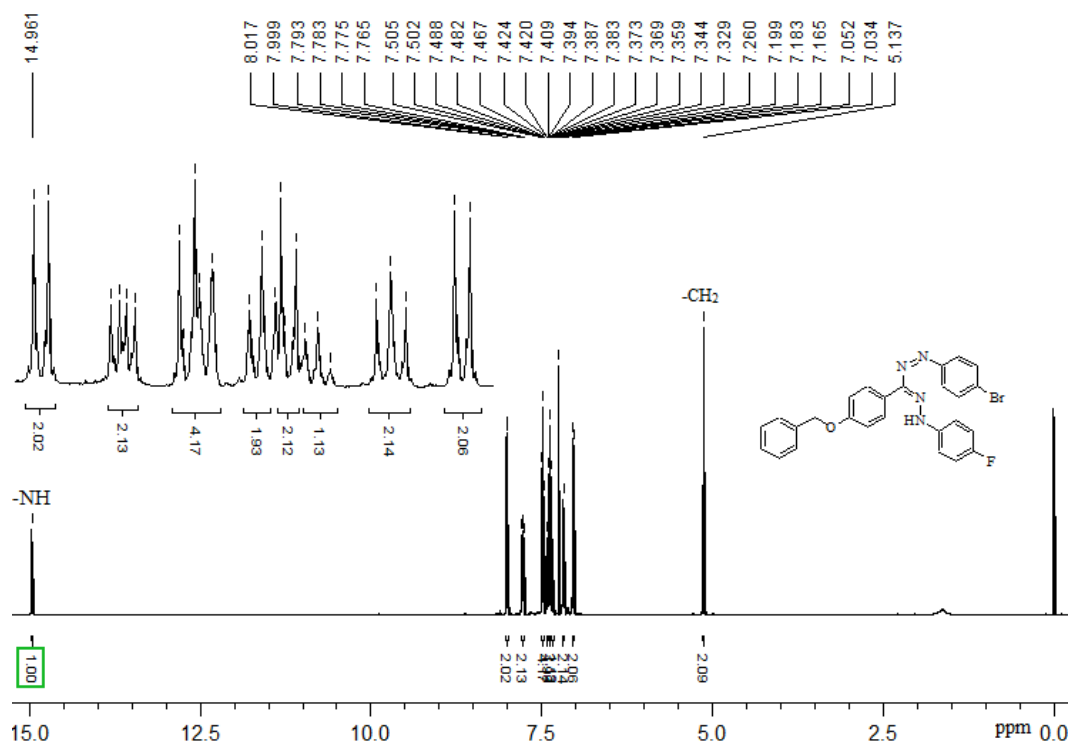


Figure S9.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound **4e**.

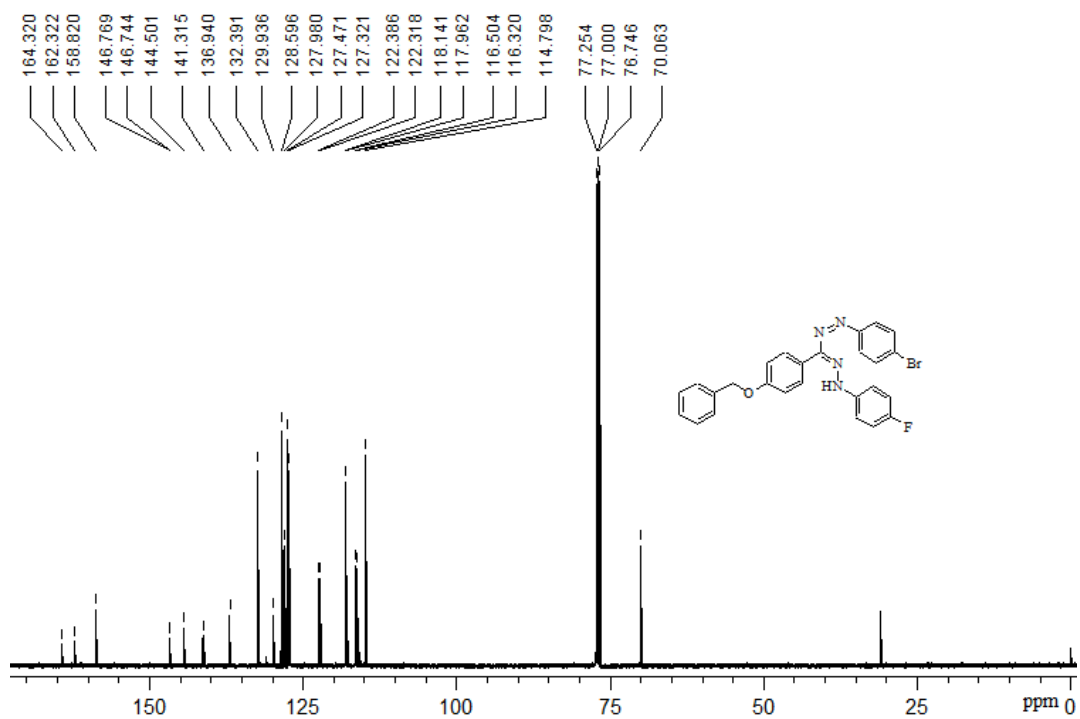


Figure S10.  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) spectrum of compound **4e**.





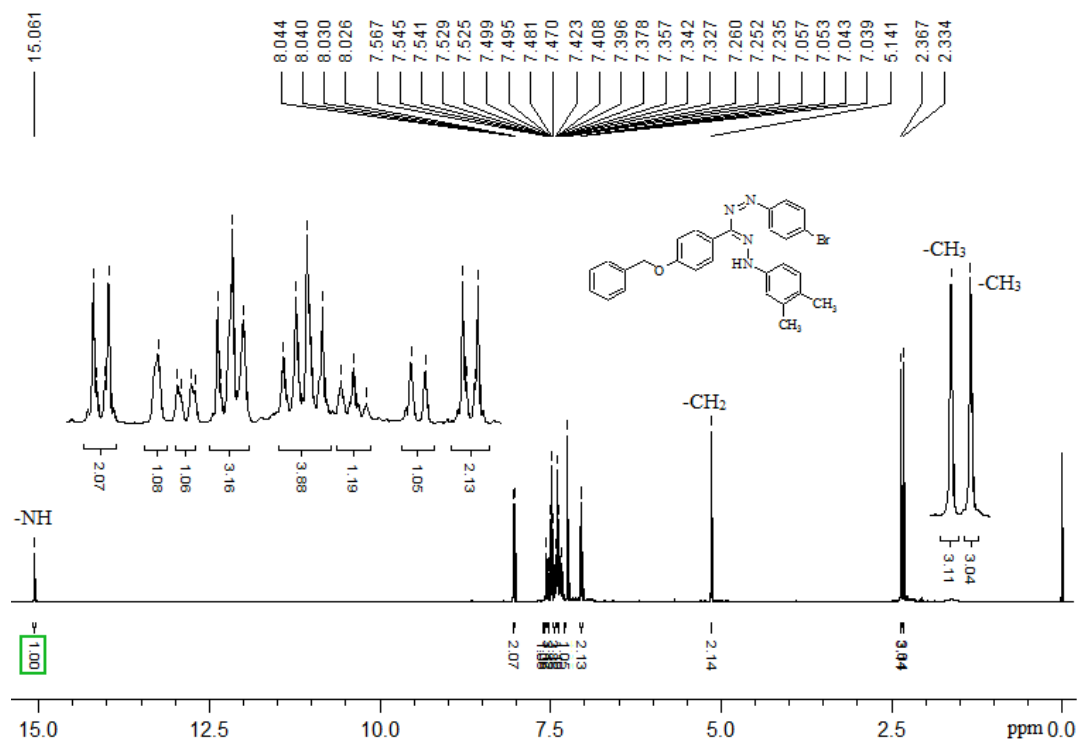


Figure S13. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 4g.

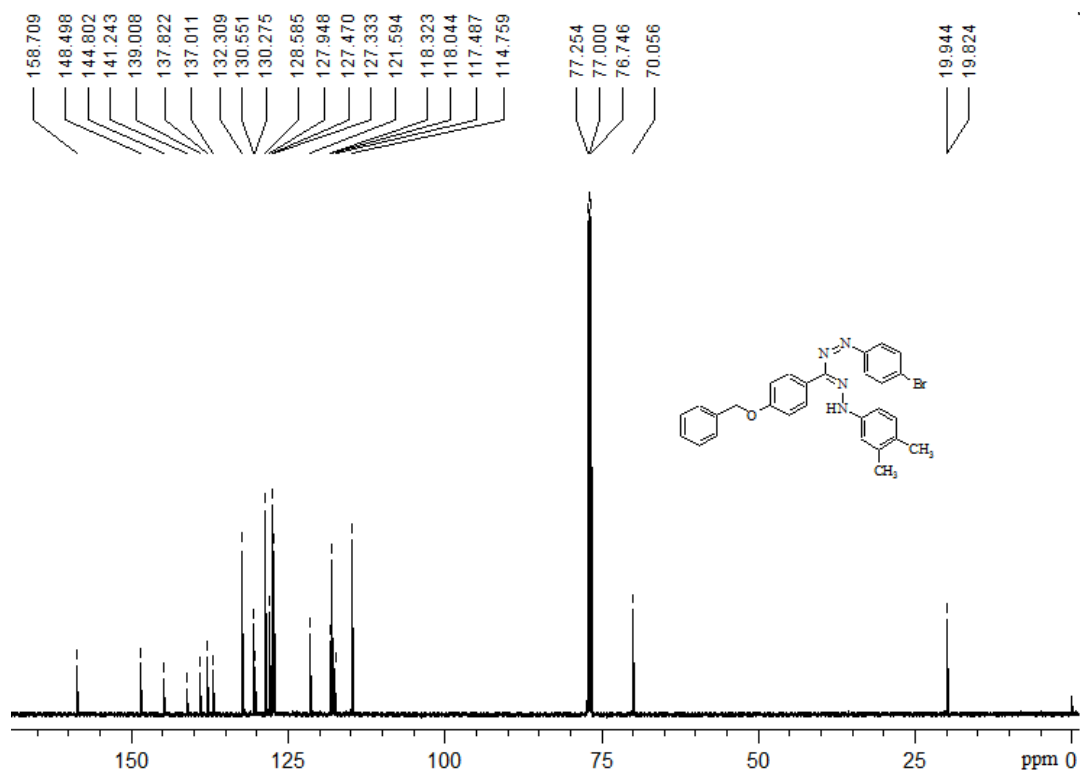


Figure S14. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) spectrum of compound 4g.

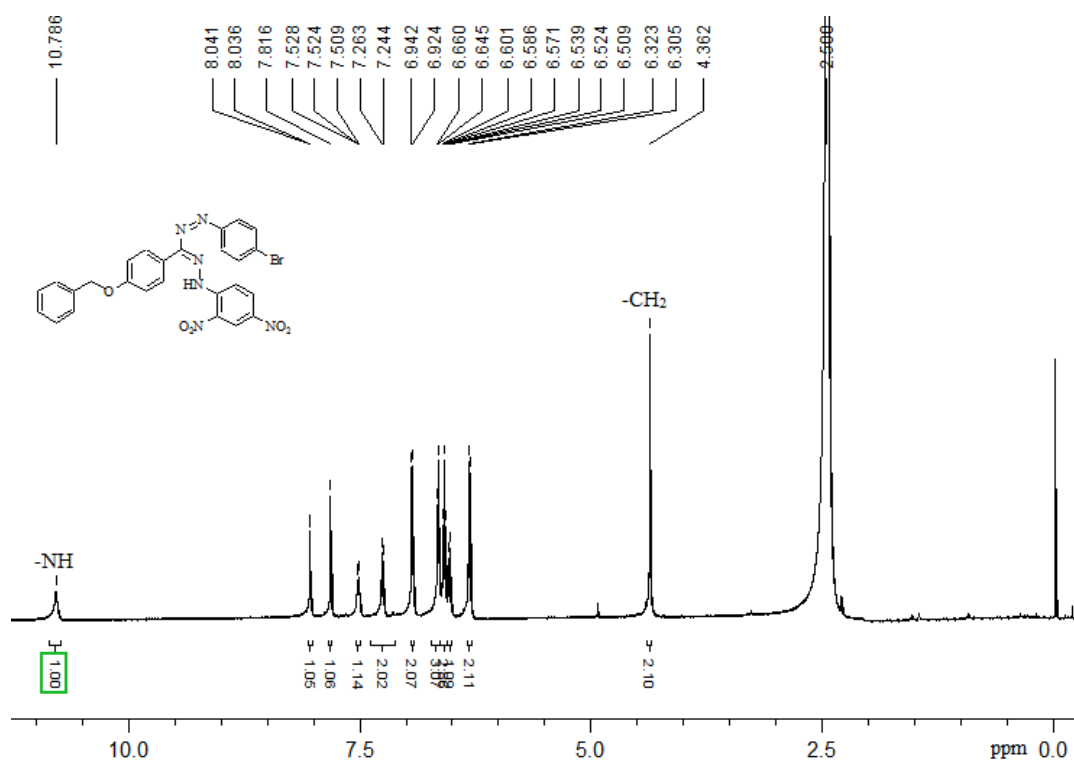


Figure S15.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ ) spectrum of compound 4h.

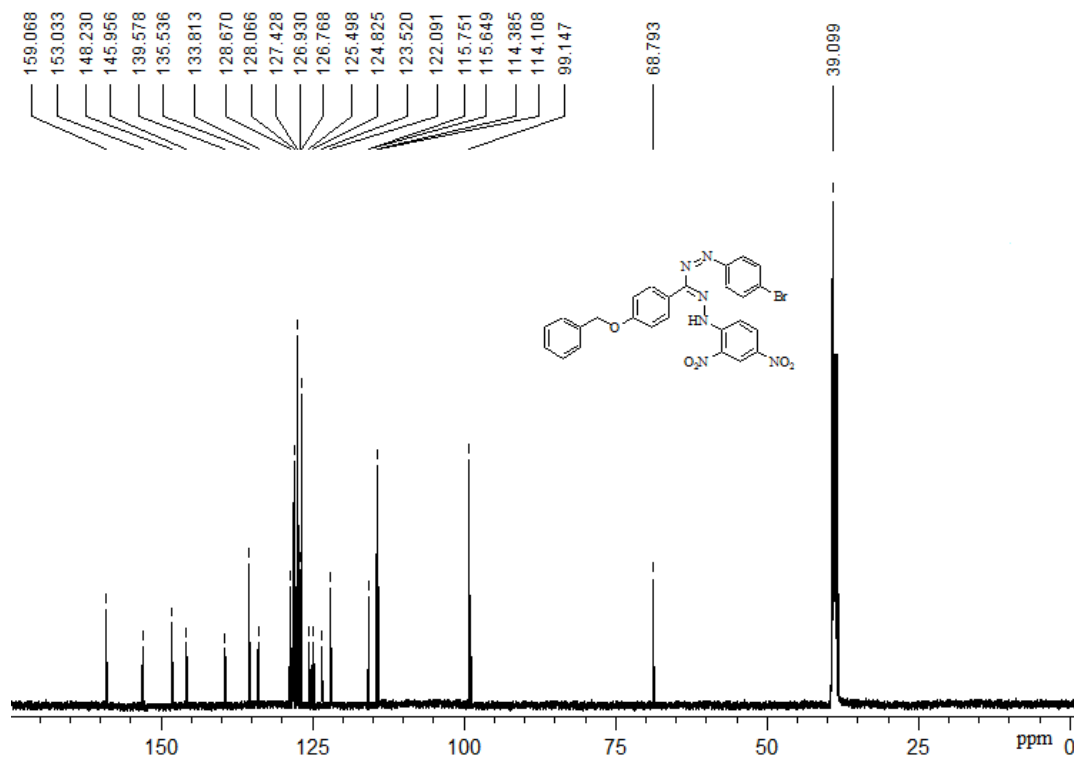
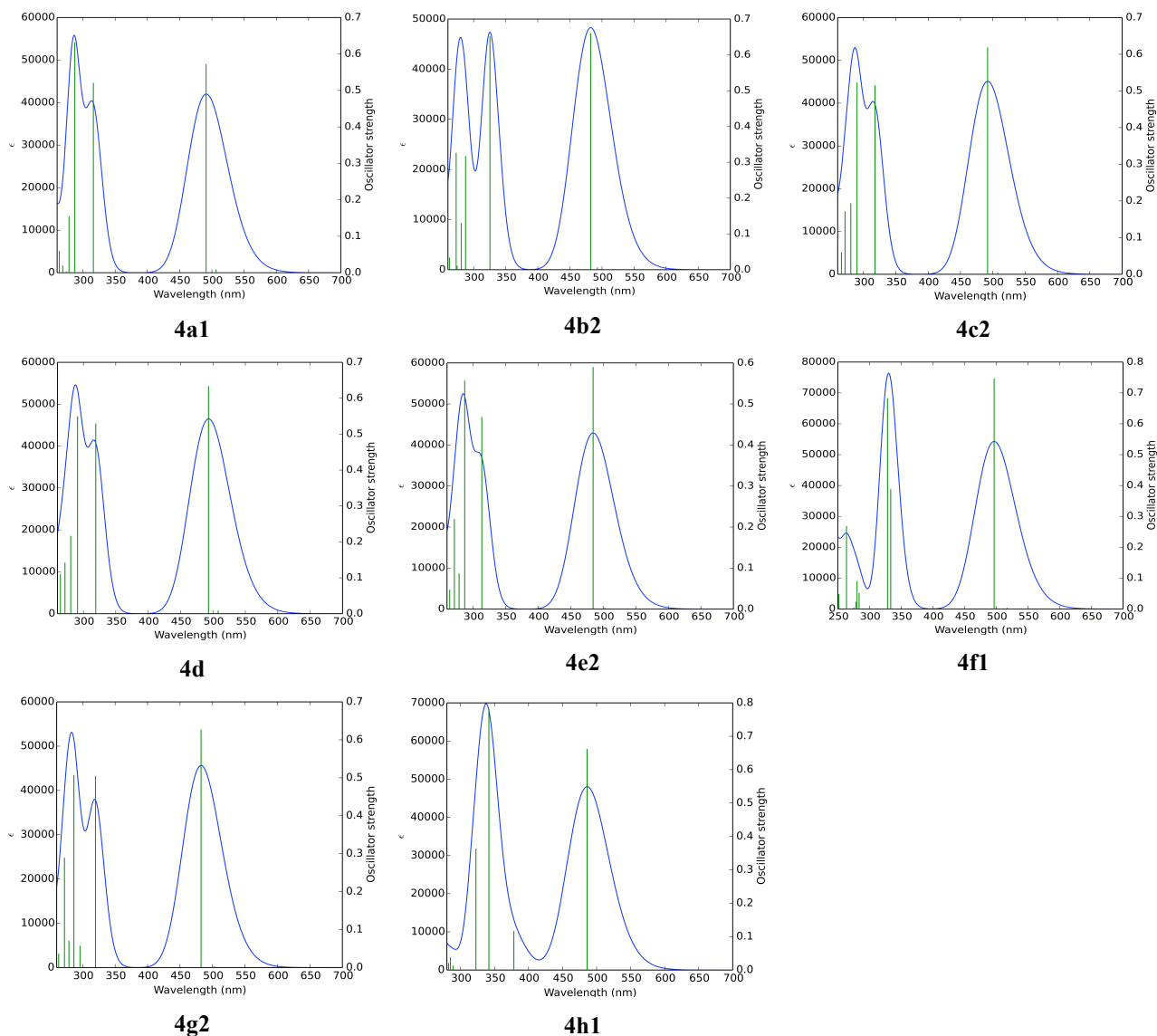


Figure S16.  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO-}d_6$ ) spectrum of compound 4h.

## Computation

### Absorption Spectra



**Figure S17.** Absorption spectra predicted at (PCM:DMSO)-CAM-TD-B3LYP/6-311+G(d,p)//PBE1PBE/6-31G(d) level.

## Cartesian Coordinates

### 4a1

C 1.7642540 -3.3146930 0.1465240  
 C 0.4801720 -3.8305430 -0.0649570  
 C -0.5826530 -2.9509070 -0.2695320  
 C -0.3554690 -1.5767230 -0.2571990  
 C 0.9192030 -1.0476840 -0.0458950  
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 C 4.2951780 3.8770440 0.0802060  
 C 6.4108800 2.0736660 0.0649210  
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**4c1**

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**4c2**

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**4d**

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H -1.5831660 -5.3524430 0.5569760  
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C -0.7121550 -10.0291340 0.2028480  
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Br 8.4394270 4.0537440 0.1361440

**4e1**

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C 0.9190810 -1.0468900 -0.0420240  
C 1.9746460 -1.9482080 0.1694210  
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H -1.1848570 -0.9011560 -0.4340060  
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H 0.0659570 5.0025160 -0.3028240  
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**4e2**

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**4g1**

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#### 4g2

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#### 4h1

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#### 4h2

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