# **Supporting Information**

# Photo-Fenton-Like (Trideutero)methylation Reaction of N/O Heterocycles with DMSO(-*d*<sub>6</sub>) Induced by EDA Complex Photocatalysis

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## **Table of Contents**

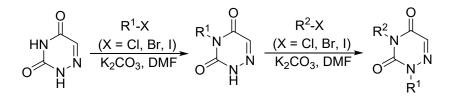
I. General considerations	2
II. Implementation of experiments	3
III. Control experiments	17
IV. Characterization data for the products	23
V. References	57
VI. Copies of <sup>1</sup> H, <sup>13</sup> C and <sup>19</sup> F NMR Spectra	59

#### I. General considerations

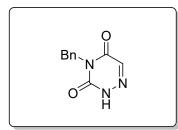
Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Products were purified by column chromatography on 200-300 mesh silica gel, SiO<sub>2</sub>. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a 500 or 400 MHz NMR spectrometer using CDCl<sub>3</sub> as the solvent. The chemical shifts are given in  $\delta$  relative to TMS, and the coupling constants are given in Hertz. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Melting points were measured by a melting point instrument and were uncorrected. The light source for the photocatalytic reaction is manufactured by Photosyn-10 (10 W blue LEDs), broadband source (455-460 nm). A fan was used to maintain the reaction temperature at room temperature (about 25 °C). The reactions were carried out in a sealed tube and the distance from the light source to the irradiation vessel is about 1 cm.

#### **II. Implementation of experiments**

#### **1.** Preparation of 6-azauracils<sup>[1]</sup>



General procedure: Alkyl halides (3.6 mmol, 0.9 equiv.) was added dropwise to a stirring solution of 6-azuracil (4.0 mmol, 1.0 equiv.), K<sub>2</sub>CO<sub>3</sub> (2.0 mmol, 0.5 equiv.) in DMF (40 mL). The reaction mixture was allowed to stir at room temperature for 16 h. Then, the mixture was quenched with saturated Na<sub>2</sub>CO<sub>3</sub> solution and extracted with ethyl acetate for three times. The organic layers were combined, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude products were purified through silica gel column chromatography using petroleum ether/ethyl acetate as eluent to give the corresponding N-4-alkyl-6-azauracils. Alkyl halides (2.0 mmol, 1.0 equiv.) were added dropwise to a stirring solution of N-4-alkyl-6-azauracils (2.0 mmol, 1.0 equiv.), K<sub>2</sub>CO<sub>3</sub> (1.0 mmol, 0.5 equiv.) in DMF (20 mL). The reaction mixture was allowed to stir at room temperature for 16 h. Then, the mixture was quenched with saturated Na<sub>2</sub>CO<sub>3</sub> solution and extracted with ethyl acetate for three times. The organic layers were combined, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude products were purified through silica gel column chromatography using petroleum ether/ethyl acetate as eluent to give the corresponding N-2, N-4dialkyl-6-azauracils (1a-1q, 5a-5c).

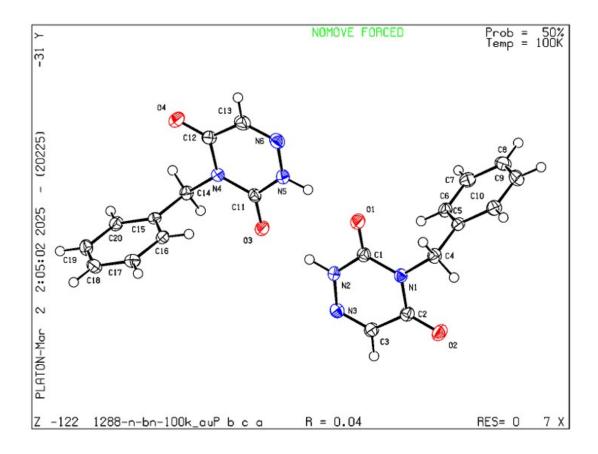


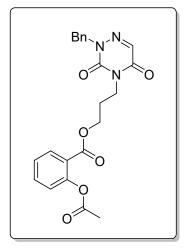
# 4-benzyl-1,2,4-triazine-3,5(2*H*,4*H*)-dione (1aa)<sup>[2]</sup>

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (2:1) as eluent afforded the product as a off whiten solid (0.77 g, 67% yield).

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 10.43 (s, 1H), 7.48 (d, *J* = 5.8 Hz, 2H), 7.43 (s, 1H), 7.32 (dd, *J* = 7.8, 5.6 Hz, 3H), 5.07 (s, 2H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 155.84, 149.74, 135.59, 135.00, 129.35, 128.61, 128.24, 43.33. CCDC 2428737.

	CODO 2429727
Identification code	CCDC 2428737
Empirical formula	$C_{10}H_9N_3O_2$
Formula weight	203.20
Temperature/K	100.02(11)
Crystal system	orthorhombic
Space group	Pbca
a/Å	5.54010(10)
b/Å	21.2296(6)
c/Å	31.9506(7)
α/°	90
β/°	90
γ/°	90
Volume/Å <sup>3</sup>	3757.84(15)
Z	16
$\rho_{calc}g/cm^3$	1.437
μ/mm <sup>-1</sup>	0.104
F(000)	1696.0
Crystal size/mm <sup>3</sup>	0.25  imes 0.12  imes 0.1
Radiation	Mo K $\alpha$ ( $\lambda = 0.71073$ )
2 $\Theta$ range for data collection/°	3.838 to 58.922
Index ranges	$-7 \le h \le 7, -29 \le k \le 25, -42 \le l \le 43$
Reflections collected	42696
Independent reflections	$4638 [R_{int} = 0.0453, R_{sigma} = 0.0290]$
Data/restraints/parameters	4638/0/279
Goodness-of-fit on F <sup>2</sup>	1.036
Final R indexes [I>= $2\sigma$ (I)]	$R_1 = 0.0402, wR_2 = 0.0945$
Final R indexes [all data]	$R_1 = 0.0574, wR_2 = 0.1037$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.24/-0.29





# 3-(2-benzyl-3,5-dioxo-2,5-dihydro-1,2,4-triazin-4(3*H*)-yl)propyl

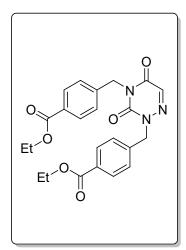
2-

#### acetoxybenzoate (5a)

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (4:1) as eluent afforded the product as a yellow oil (1.13 g, 67% yield).

<sup>1</sup>**H NMR** (500 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 9.6 Hz, 1H), 7.60-7.53 (m, 1H), 7.46

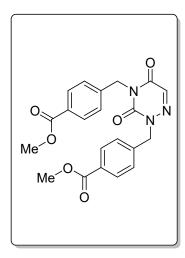
(dd, J = 8.0, 1.6 Hz, 2H), 7.37 (s, 1H), 7.33-7.26 (m, 4H), 7.10 (d, J = 8.1 Hz, 1H), 5.01 (s, 2H), 4.34 (t, J = 6.1 Hz, 2H), 4.13 (t, J = 6.9 Hz, 2H), 2.34 (s, 3H), 2.20 (p, J = 6.6 Hz, 2H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*)  $\delta$  169.59, 164.03, 155.72, 150.63, 148.55, 135.26, 134.36, 133.99, 131.47, 129.34, 128.53, 128.10, 126.00, 123.79, 122.86, 62.26, 49.15, 43.77, 27.21, 20.97. HRMS calcd for C<sub>22</sub>H<sub>21</sub>N<sub>3</sub>O<sub>6</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 446.1323; found 446.1320.



Diethyl 4,4'-((3,5-dioxo-1,2,4-triazine-2,4(3*H*,5*H*)-diyl)bis(methylene))dibenzoate (5b)

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (4:1) as eluent afforded the product as a white solid (1.36 g, 78% yield).

Mp:117-118 °C. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  8.00 (ddd, J = 18.5, 8.2, 3.5 Hz, 4H), 7.49 (dd, J = 8.3, 3.0 Hz, 2H), 7.42 (dd, J = 8.3, 2.9 Hz, 3H), 5.13 (s, 2H), 5.09 (s, 2H), 4.35 (dp, J = 9.0, 3.2 Hz, 4H), 1.37 (tt, J = 7.1, 3.3 Hz, 6H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*)  $\delta$  166.11, 166.05, 155.60, 148.48, 139.89, 134.63, 130.47, 130.24, 130.00, 129.83, 129.05, 128.44, 126.33, 61.05, 60.98, 55.05, 43.62, 14.26. HRMS calcd for C<sub>23</sub>H<sub>23</sub>N<sub>3</sub>O<sub>6</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 438.1660; found 438.1662.



#### Dimethyl

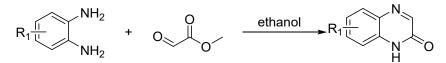
4,4'-((3,5-dioxo-1,2,4-triazine-2,4(3H,5H)-

#### diyl)bis(methylene))dibenzoate (5c)

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (4:1) as eluent afforded the product as a white solid (1.17 g, 72% yield).

Mp:113-114 °C. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  8.01-7.93 (m, 4H), 7.47 (dd, *J* = 8.4, 4.8 Hz, 2H), 7.44-7.39 (m, 3H), 5.09 (d, *J* = 22.1 Hz, 4H), 3.88 (d, *J* = 5.3 Hz, 6H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*)  $\delta$  166.51, 166.43, 155.54, 148.43, 139.99, 139.96, 134.61, 130.02, 129.96, 129.79, 129.00, 128.39, 54.97, 52.11, 52.06, 43.54. HRMS calcd for C<sub>21</sub>H<sub>19</sub>N<sub>3</sub>O<sub>6</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 410.1347; found 410.1352.

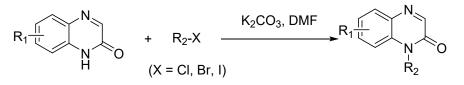
#### **3.** Preparation of quinoxalin-2(1*H*)-one<sup>[3]</sup>



General procedure: Ethyl-2-oxoacetate (22.1 mL, 111.11 mmol) was added to a solution of 1, 2-diaminobenzene (10.0 g, 92.59 mmol) in ethanol (200 mL). The mixture was heated and maintained at 45 °C for 8 h. The resulting precipitate was filtered, thoroughly washed with water and dried under vacuum to afford quinoxalin-2 (1*H*) - ones.

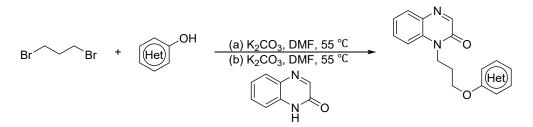
#### 4. Quinoxalin-2(1H)-one derivatives were prepared according to the reported

methods<sup>[2]</sup>

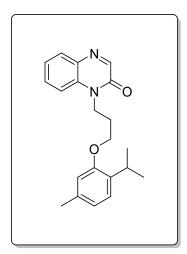


General procedure: To a 100 mL round-bottomed flask with a stir bar was added quinoxalin-2(1*H*)-one (5.0 mmol), DMF (15.0 mL), then was added potassium carbonate (828 mg, 6.0 mmol), followed by the dropwise addition of  $R_2$ -X (8.0 mmol). The reaction mixture was then stirred for 1-12h at room temperature, poured into brine and extracted with EtOAc. The combined extracts were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated. The residue was purified by column chromatography (petroleum ether/EtOAc) to afford the desired quinoxalin-2(1*H*)-ones (**4a-4k**).

**3.** Modification of natural molecules and pharmaceutically relevant compounds are prepared from the following procedure<sup>[2]</sup>



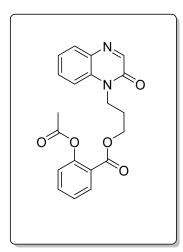
**General procedure:** A mixture of phenol (4.0 mmol) and  $K_2CO_3$  (1.1 g, 8.0 mmol) in DMF (6.4 mL) was stirred at 55 °C, and then 1,3-dibromopropane (8.0 mmol) was added. After stirring overnight, the mixture was added water and extracted with DCM. The organic phase was washed with water (40 mL x 2), then washed with brine (40 mL x 2), dried over Na<sub>2</sub>SO<sub>4</sub>, followed by concentrated and purification on silica gel column chromatography. The resulting compound (1.6 equiv.) was then dissolved anhydrous DMF (10 mL) and quinoxalin-2(1*H*)-one (1.0 equiv.) was added and the mixture stirred for 12 h at 55 °C. After the reaction was complete, reaction mixture was quenched with water and extracted with DCM. Combined organic layers were concentrated in vacuo and the residue obtained was purified by flash chromatography on silica gel to obtain the desired product (**5d-5h**).



1-(3-(2-isopropyl-5-methylphenoxy)propyl)quinoxalin-2(1H)-one (5d) [2b]

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (4:1) as eluent afforded the product as a yellow solid (0.87 g, 65% yield).

<sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.33 (s, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 6.8 Hz, 1H), 7.14 (d, *J* = 7.7 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 1H), 6.66 (s, 1H), 4.50 (t, *J* = 7.9 Hz, 2H), 4.12 (t, *J* = 5.6 Hz, 2H), 3.37 (hept, *J* = 7.0 Hz, 1H), 2.32 (s, 3H), 2.29 (q, *J* = 5.9 Hz, 2H), 1.28 (d, *J* = 6.8 Hz, 6H). **HRMS** calcd for C<sub>21</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 337.1911; found 337.1914.

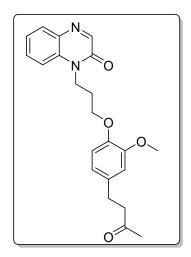


3-(2-oxoquinoxalin-1(2H)-yl)propyl 2-acetoxybenzoate (5e)<sup>[2c]</sup>

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (4:1) as eluent afforded the product as a yellow solid (1.03

g, 70% yield).

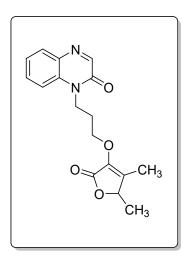
<sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.32 (d, *J* = 7.5 Hz, 1H), 8.01 (t, *J* = 7.5 Hz, 1H), 7.91 (t, *J* = 8.1 Hz, 1H), 7.60 (dq, *J* = 15.5, 7.7 Hz, 2H), 7.38 (dt, *J* = 14.5, 7.5 Hz, 3H), 7.15 (t, *J* = 7.6 Hz, 1H), 4.44 (t, *J* = 7.3 Hz, 4H), 2.36 (d, *J* = 6.8 Hz, 3H), 2.25 (q, *J* = 12.6, 9.7 Hz, 2H). **HRMS** calcd for C<sub>20</sub>H<sub>18</sub>N<sub>2</sub>O<sub>5</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 367.1288; found 367.1292.



#### 1-(3-(2-methoxy-4-(3-oxobutyl)phenoxy)propyl)quinoxalin-2(1*H*)-one (5f)<sup>[2d]</sup>

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (4:1) as eluent afforded the product as a yellow solid (0.97 g, 64% yield).

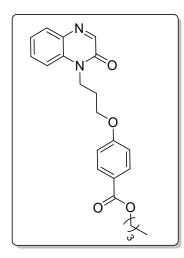
<sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.31 (s, 1H), 7.90 (d, J = 7.9 Hz, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.55 (t, J = 8.0 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 6.81 (d, J = 8.0 Hz, 1H), 6.77 (s, 1H), 6.71 (d, J = 8.2 Hz, 1H), 4.51 (t, J = 7.5 Hz, 2H), 4.12 (t, J = 5.7 Hz, 2H), 3.90 (s, 3H), 2.88 (d, J = 7.5 Hz, 2H), 2.77 (t, J = 7.5 Hz, 2H), 2.30 (d, J = 6.9 Hz, 2H), 2.16 (s, 3H). **HRMS** calcd for C<sub>22</sub>H<sub>24</sub>N<sub>2</sub>O<sub>4</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 381.1809; found 381.1808.



1-(3-((4,5-dimethyl-2-oxo-2,5-dihydrofuran-3-yl)oxy)propyl)quinoxalin-2(1*H*)one (5g)<sup>[2e]</sup>

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (4:1) as eluent afforded the product as a yellow solid (0.89 g, 71% yield).

Mp: 98-100 °C. <sup>1</sup>**H** NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.29 (s, 1H), 7.89 (d, J = 7.7 Hz, 1H), 7.60 (t, J = 7.9 Hz, 1H), 7.48 (d, J = 8.4 Hz, 1H), 7.36 (t, J = 7.4 Hz, 1H), 4.81 (q, J = 6.7 Hz, 1H), 4.44 (t, J = 7.6 Hz, 2H), 4.34 (q, J = 5.7 Hz, 2H), 2.16 (p, J = 6.4 Hz, 2H), 1.94 (s, 3H), 1.42 (d, J = 6.7 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.33, 154.84, 150.03, 141.66, 139.75, 133.55, 132.33, 131.20, 130.69, 123.74, 113.79, 76.86, 68.29, 39.13, 27.73, 16.69, 9.80. **HRMS** calcd for C<sub>17</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 315.1339; found 315.1342.



Butyl 4-(3-(2-oxoquinoxalin-1(2H)-yl)propoxy)benzoate (5h)

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (4:1) as eluent afforded the product as a white solid (1.09 g, 72% yield).

Mp:94-96 °C. <sup>1</sup>**H** NMR (500 MHz, Chloroform-*d*)  $\delta$  8.30-8.22 (m, 1H), 8.01-7.93 (m, 2H), 7.85 (d, J = 7.5 Hz, 1H), 7.47 (dt, J = 35.2, 9.1 Hz, 2H), 7.32 (t, J = 6.6 Hz, 1H), 6.88 (t, J = 6.3 Hz, 2H), 4.46 (d, J = 6.8 Hz, 2H), 4.26 (t, J = 9.2 Hz, 2H), 4.11 (d, J = 12.6 Hz, 2H), 2.30-2.22 (m, 2H), 1.75-1.67 (m, 2H), 1.49-1.40 (m, 2H), 0.95 (t, J = 12.2 Hz, 3H).<sup>13</sup>C NMR (126 MHz, Chloroform-*d*)  $\delta$  166.21, 161.98, 154.79, 149.97, 133.46, 132.30, 131.48, 131.06, 130.65, 123.64, 123.20, 113.86, 113.55, 65.21, 64.47, 39.14, 30.70, 26.94, 19.18, 13.70. **HRMS** calcd for C<sub>22</sub>H<sub>24</sub>N<sub>2</sub>O<sub>4</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 381.1809; found 381.1807.

#### **Biological activity**

(1) **Thymol**<sup>[4]</sup>: Thymol (5-methyl-2-isopropyphenol) is the main active component in oregano and thyme essential oil, and has been confirmed to possess various bioactivities, including antioxidant, antimicrobial, anticarcinogenesis, antiinflammatory, and antispasmodic activities. Furthermore, the antibacterial activity of thymol is better than that of other essential oils components, such as carvacrol, eugenol, cinnamic acid and diacetyl. Thereby, thymol can be applied as a promising

antibacterial agent in food preservation, functional food and medicinal formulations. However, a major limitation for thymol application is its low water solubility, high volatility and strong aromatic odor.

(2) Aspirin<sup>[5]</sup>: Aspirin is the most widely used drug in the world and commonly used for the treatment and prevention of cardiovascular disease, as an analgesic, antipyretic, and for the primary prevention of colorectal cancer.

(3) Zingerone<sup>[6]</sup>: Zingerone (Zing), a bioactive substance of ginger root, has a variety of pharmacological properties such as anticancer, antioxidant, anti-inflammatory, antimicrobial, and antiapoptotic effects. On the other hand, the antioxidant properties of Zing are mediated via increasing the antioxidant capacity and reducing the level of nitric oxide (NO) and lipid peroxidation. The anti-inflammatory effects of Zing have been established in several animal models including sepsis- and cisplatin-induced nephrotoxicity. Zing is a safe substance, and the lethal dose 50% (LD50) for rats is 2580 mg/kg.

(4) Sotolon<sup>[7]</sup>: Sotolon is a furanone derivative lactone (3-hydroxy-4,5-dimethyl-2(5H)-furanone) and is an extremely powerful aroma compound. Sotolon was first isolated from the herb fenugreek in 1975, and it is the major aroma and flavor component of fenugreek seed. It is one of numerous flavor aromatic components of artificial maple syrup, and is also present in molasses, roast tobacco, aged sake, aged rum, and white wine. Sotolon is known as being the main odorant and has also been considered as a potential aging marker of these wine types. The chiral lactone of sotolon is a powerful odorant that depends on its concentration and enantiomeric distribution.

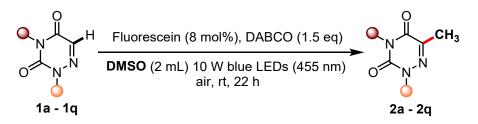
(5) Butylparaben<sup>[8]</sup>: Parabens that methylparaben (MP), ethylparaben (EP), propylparaben (PP), and butylparaben (BP) are the most used, are a class of compounds formed by esterification of parahydroxybenzoic acid with alcohols. They are widely used in shampoos, conditioners, moisturizing creams, tonics, deodorants, perfumes, shaving gels, tanning creams, cosmetics, toothpaste, drinks, syrups, pills, salad sauces, olives, and bakery products. The fact that parabens have low toxicity potential for

humans and show effective antibacterial and antifungal activity has made them the most preferred among the substances used as preservatives in the products. Today, it has been determined that parabens can be found in aquatic environments such as rivers, soils, drinking water, and even indoor dust.

(6) Ethyl benzoate<sup>[9]</sup>: Pure fragrance compounds and essential oils have been largely used in pharmacy, aromatherapy, cosmetics and toiletries, as a condiment in several foods and drinks, and for adding scents to incense and household cleaning products. Ethyl benzoate is one of the aroma components which exists in fruit and leaf of many plants. It also can be artificially synthesized by the condensation of benzoic acid and ethanol. As with many volatile esters, ethyl benzoate has a pleasant odor which could be described similar to wintergreen or mint. It is a component of some artificial fruit flavors and widely used in pharmacy, cosmetic and food industry. Ethyl benzoate is a colorless liquid that is almost insoluble in water.

(7) Methyl benzoate<sup>[10]</sup>: This current study demonstrates that methyl benzoate (MB) is an efficient green pesticide against invasive insect pest D. suzukii, and several other agricultural pests. MB not only effectively prevented D. suzukii from oviposition and inhibited subsequent larvae/pupae development, but also caused complete mortality of adult flies on pre- and post-treated blueberries at a concentration as low as 1%. Moreover, MB possessed ovicidal activity against several different species of eggs, when compared to some commercially available pesticides. On the basis of toxicity data, MB was five times more toxic than the conventional pyrethroid ( $\beta$ -cyfluthrin), 20 times more toxic than sulfur & pyrethrin mixture, and 12 times more toxic than one of the organic commercial products (2-phenethyl propionate, clover oil, rosemary oil, and thyme oil) against H. halys eggs. Neither  $\gamma$ -cyhalothrin nor acetamiprid exhibited ovicidal toxicity against H. halys at tested doses. For M. sexta and P. xylostella, similar toxic results were obtained, but P. xylostella appeared to be more sensitive to MB treatment. To reach 100% egg mortality, only 0.0064 mg/cm<sup>2</sup>

#### 5. General procedure for the synthesis of heteroaromatic-substituted products



Azauracil 1 (0.1 mmol, 1.0 equiv.), Fluorescein (8 mol%.), DABCO (1.5 equiv.), and DMSO (2.0 mL) were added to a 10 mL sealed tube. Then the tube under air and irradiated with 10 W blue LEDs at room temperature for 22 h. After the reaction is complete, the organic phase is filtered with EtOAc, the organic phase is removed with the combined filtrate, and the crude product is extracted with 100 mL saturated NH<sub>4</sub>Cl aqueous solution and (20ml  $\times$  3) EtOAc. The combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. The resulting crude residue was purified via column chromatography on silica gel to afford the desired products **2**.



Figure S1. The instruments of experiments

#### 6. Reusability of Fluorescein for the synthesis of 2a

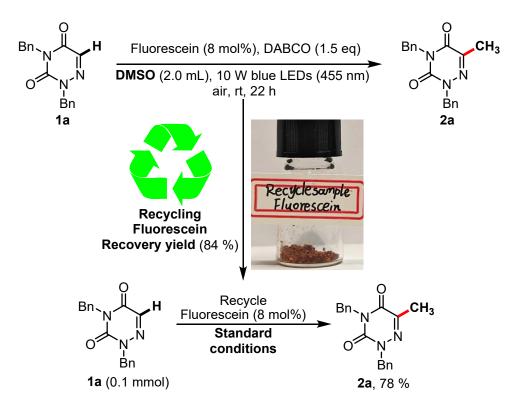
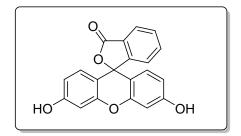


Figure S2. Reusability of Fluorescein for the synthesis of 2a

Repeat the standard conditions experiments six times. Azauracil **1a** (0.1 mmol, 1.0 equiv.), Fluorescein (8 mol%.), DABCO (1.5 equiv.), and DMSO (2.0 mL) were added to a 10 mL sealed tube. Then the tube under air and irradiated with 10 W blue LEDs at room temperature for 22 h. After the reaction is complete, the organic phase is filtered with EtOAc. The crude product was subjected to vacuum distillation under an oil pump to remove the solvent. The resulting crude residue was purified by silica gel column chromatography, and Fluorescein was recovered with a yield of 84%. Under standard conditions, it was re-reacted with **1a** to obtain the target product **2a** with a yield of 78%.



#### **Recycle Fluorescein**

Purification by column chromatography using MeOH/DCM (1:1) as eluent afforded the product as a red solid (0.013 g, 72% yield).

<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 8.05-7.94 (m, 1H), 7.74 (d, *J* = 37.7 Hz, 2H), 7.28 (s, 1H), 6.67 (d, *J* = 85.1 Hz, 8H).<sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>) δ 168.68, 160.00, 152.13, 135.55, 130.16, 129.25, 126.39, 124.88, 124.32, 102.33.

### **III.** Control experiments

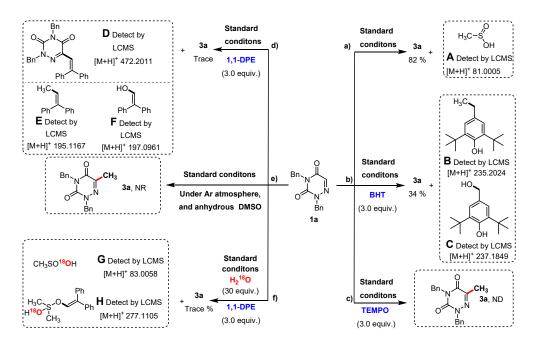
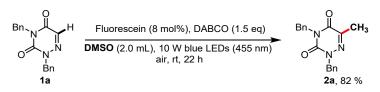


Figure S3. Control experiments

a)



**Reaction conditions:** Azauracil **1a** (0.1 mmol, 1.0 equiv.), Fluorescein (8 mol%.), DABCO (1.5 equiv.), and DMSO (2.0 mL) were added to a 10 mL sealed tube. Then the tube under air and irradiated with 10 W blue LEDs at room temperature for 22 h. After the reaction is complete, the organic phase is filtered with EtOAc, the organic phase is removed with the combined filtrate, and the crude product is extracted with 100 mL saturated NH<sub>4</sub>Cl aqueous solution and (20ml  $\times$  3) EtOAc. The combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. The resulting crude residue was purified via column chromatography on silica gel to afford the desired products **2a**. The reaction was analyzed by LC-MS (ESI positive ionization mode).

LCMS (ESI) calcd for A CH<sub>4</sub>O<sub>2</sub>SH<sup>+</sup> [M+H]<sup>+</sup> : 81.0005, found: 81.0005.

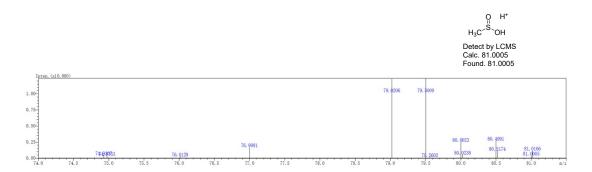


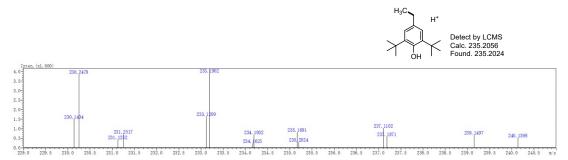
Figure S4. LCMS of methylsulfinic acid (A)

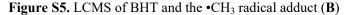
b)



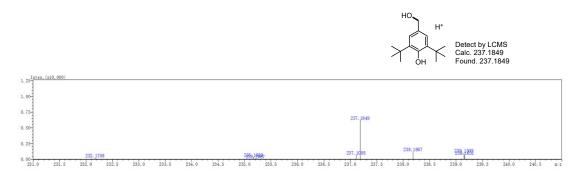
**Reaction conditions:** Azauracil **1a** (0.1 mmol, 1.0 equiv.), Fluorescein (8 mol%.), DABCO (1.5 equiv.), BHT (3.0 equiv.) and DMSO (2.0 mL) were added to a 10 mL sealed tube. Then the tube under air and irradiated with 10 W blue LEDs at room temperature for 22 h. After the reaction is complete, the organic phase is filtered with EtOAc, the organic phase is removed with the combined filtrate, and the crude product is extracted with 100 mL saturated NH<sub>4</sub>Cl aqueous solution and (20ml × 3) EtOAc. The combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. The resulting crude residue was purified via column chromatography on silica gel to afford the desired products **2a**. The reaction was analyzed by LC-MS (ESI positive ionization mode).

LCMS (ESI) calcd for **B**  $C_{16}H_{26}OH^+$  [M+H]<sup>+</sup> : 235.2056, found: 235.2024.





S19



LCMS (ESI) calcd for C  $C_{15}H_{24}O_2H^+$  [M+H]<sup>+</sup> : 237.1849, found: 237.1849.

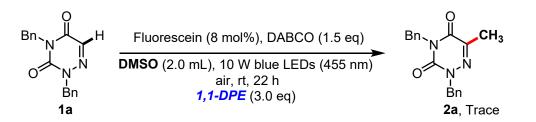
Figure S6. LCMS of BHT and the •OH radical adduct (C)





**Reaction conditions:** Azauracil **1a** (0.1 mmol, 1.0 equiv.), Fluorescein (8 mol%.), DABCO (1.5 equiv.), TEMPO (3.0 equiv.) and DMSO (2.0 mL) were added to a 10 mL sealed tube. Then the tube under air and irradiated with 10 W blue LEDs at room temperature for 22 h. After the reaction is complete, the organic phase is filtered with EtOAc, the organic phase is removed with the combined filtrate, and the crude product is extracted with 100 mL saturated NH<sub>4</sub>Cl aqueous solution and (20ml × 3) EtOAc. The combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. The resulting crude residue was purified via column chromatography on silica gel to afford the desired products **2a**.

d)



Reaction conditions: Azauracil 1a (0.1 mmol, 1.0 equiv.), Fluorescein (8 mol%.),

DABCO (1.5 equiv.), 1,1-DPE (3.0 equiv.) and DMSO (2.0 mL) were added to a 10 mL sealed tube. Then the tube under air and irradiated with 10 W blue LEDs at room temperature for 22 h. After the reaction is complete, the organic phase is filtered with EtOAc, the organic phase is removed with the combined filtrate, and the crude product is extracted with 100 mL saturated NH<sub>4</sub>Cl aqueous solution and (20ml × 3) EtOAc. The combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. The resulting crude residue was purified via column chromatography on silica gel to afford the desired products **2a**. The reaction was analyzed by LCMS (ESI positive ionization mode).

LCMS (ESI) calcd for  $D C_{31}H_{25}N_3O_2H^+$  [M+H]<sup>+</sup>: 472.2020, found: 472.2011.

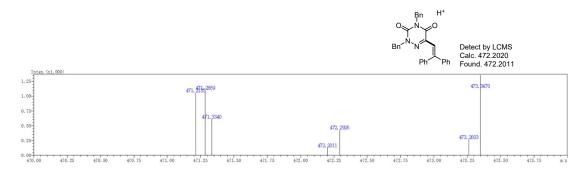


Figure S7. LCMS of 1,1-diphenylethylene and the 1a radical adduct (D)

LCMS (ESI) calcd for  $\mathbf{E} C_{15}H_{14}H^+$  [M+H]<sup>+</sup>: 195.1168, found: 195.1167.

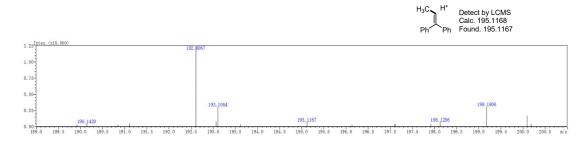


Figure S8. LCMS of 1,1-diphenylethylene and the •CH<sub>3</sub> radical adduct (E)

LCMS (ESI) calcd for **F** C<sub>36</sub>H<sub>31</sub>N<sub>3</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup>: 592.2029, found: 592.2020.

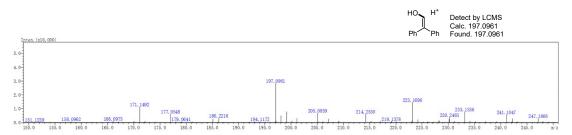
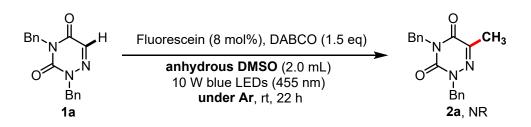


Figure S9. LCMS of 1,1-diphenylethylene and the •OH radical adduct (F)



**Reaction conditions:** Azauracil **1a** (0.1 mmol, 1.0 equiv.), Fluorescein (8 mol%.), DABCO (1.5 equiv.), 1,1-DPE (3.0 equiv.) and DMSO (2.0 mL) were added to a 10 mL sealed tube. Then the tube under air and irradiated with 10 W blue LEDs at room temperature for 22 h. After the reaction is complete, the organic phase is filtered with EtOAc, the organic phase is removed with the combined filtrate, and the crude product is extracted with 100 mL saturated NH<sub>4</sub>Cl aqueous solution and (20ml × 3) EtOAc. The combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. The resulting crude residue was purified via column chromatography on silica gel to afford the desired products **2a**.

f)

e)



LCMS (ESI) calcd for F CH<sub>3</sub>SO<sup>18</sup>OHH<sup>+</sup> [M+H]<sup>+</sup>: 83.0047, found: 83.0058.

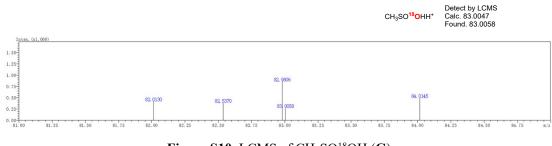


Figure S10. LCMS of CH<sub>3</sub>SO<sup>18</sup>OH (G)

LCMS (ESI) calcd for **F** C<sub>16</sub>H<sub>18</sub>O<sub>18</sub>OSH<sup>+</sup> [M+H]<sup>+</sup>: 277.1143, found: 277.1107.

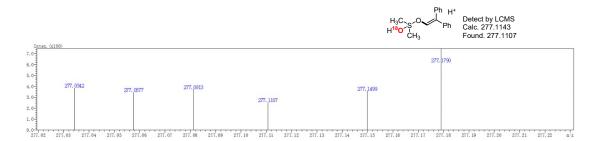


Figure S11. LCMS of 1,1-diphenylethylene and the Int-C radical adduct (H)

#### 3. Light on/off experiments

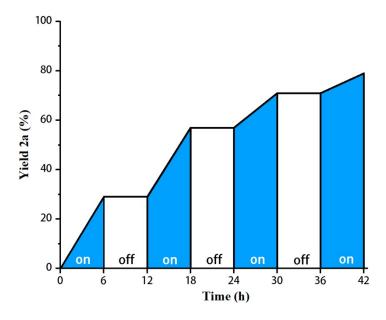
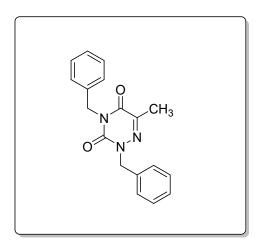


Figure S12. Light on/off experiments

The reaction between **1a** was conducted under the standard conditions on a 0.1 mmol scale. The mixture was subjected to sequential periods of stirring under 10 W blue LEDs followed by stirring in the absence of 10 W blue LEDs, and soon. At each time point, one reaction system was suspended. The yield of **2a** was obtained by column chromatograph.

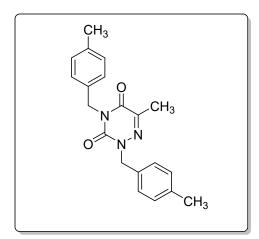
# IV. Characterization data for the products



#### 2,4-dibenzyl-6-methyl-1,2,4-triazine-3,5(2H,4H)-dione (2a).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (10:1) as eluent afforded the product as a white solid (25.2 mg, 82% yield).

Mp: 115-116 °C. <sup>1</sup>**H** NMR(500 MHz, Chloroform-*d*)  $\delta$  7.52 (d, J = 6.8 Hz, 2H), 7.43 (d, J = 7.0 Hz, 2H), 7.40-7.31 (m, 6H), 5.12 (d, J = 4.3 Hz, 4H), 2.27 (s, 3H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*)  $\delta$  156.21, 149.12, 142.84, 135.84, 135.61, 129.37, 128.64, 128.56, 128.50, 128.11, 127.99, 55.10, 44.13, 16.89. **HRMS** calcd for C<sub>18</sub>H<sub>17</sub>N<sub>3</sub>O<sub>2</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 308.1394; found 308.1392.

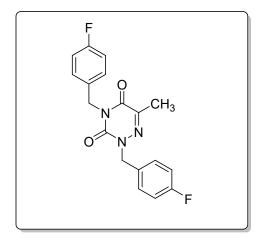


6-methyl-2,4-bis(4-methylbenzyl)-1,2,4-triazine-3,5(2H,4H)-dione (2b).

Following the general procedure and purification by column chromatography using

petroleum ether/ethyl acetate (10:1) as eluent afforded the product as a white solid (25.4 mg, 76% yield).

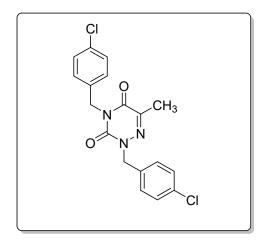
Mp: 132-134 °C. <sup>1</sup>**H** NMR (500 MHz, Chloroform-*d*)  $\delta$  7.40 (d, J = 7.7 Hz, 2H), 7.32 (d, J = 7.6 Hz, 2H), 7.17 (d, J = 7.6 Hz, 2H), 7.14 (d, J = 7.7 Hz, 2H), 5.06 (d, J = 6.1 Hz, 4H), 2.35 (s, 3H), 2.34 (s, 3H), 2.24 (s, 3H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*)  $\delta$  156.22, 149.10, 142.74, 137.87, 137.74, 132.90, 132.71, 129.40, 129.29, 129.14, 128.57, 54.83, 43.84, 21.09, 16.86. **HRMS** calcd for C<sub>20</sub>H<sub>21</sub>N<sub>3</sub>O<sub>2</sub>H<sup>+</sup>[M+H]<sup>+</sup>: 336.1707; found 336.1704.



2,4-bis(4-fluorobenzyl)-6-methyl-1,2,4-triazine-3,5(2*H*,4*H*)-dione (2c).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (3:1) as eluent afforded the product as a yellow solid (25.1 mg, 73% yield).

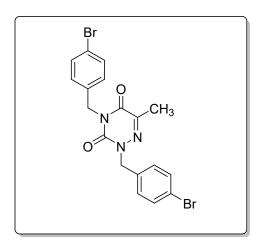
Mp: 113-115 °C. <sup>1</sup>**H** NMR (400 MHz, Chloroform-*d*)  $\delta$  7.47 (ddd, J = 8.6, 5.3, 2.6 Hz, 2H), 7.42-7.36 (m, 2H), 7.06-6.95 (m, 4H), 5.04 (d, J = 2.5 Hz, 4H), 2.23 (s, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  163.87, 163.73, 161.41, 161.28, 156.14, 149.03, 143.03, 131.60, 131.57, 131.49, 131.41, 130.59, 130.51, 115.69, 115.50, 115.48, 115.29, 54.45, 43.44, 16.90. <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -113.68 (d, J = 16.4 Hz). **HRMS** calcd for C<sub>18</sub>H<sub>15</sub>F<sub>2</sub>N<sub>3</sub>O<sub>2</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 344.1205; found 344.1208.



#### 2,4-bis(4-chlorobenzyl)-6-methyl-1,2,4-triazine-3,5(2H,4H)-dione (2d).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (10:1) as eluent afforded the product as an off white solid (25,9 mg, 69% yield).

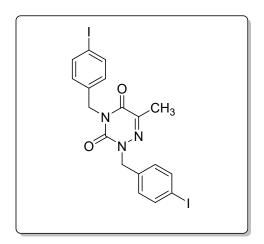
Mp: 124-125 °C. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  7.44 (d, J = 8.0 Hz, 2H), 7.35 (t, J = 6.5 Hz, 4H), 7.30 (d, J = 8.4 Hz, 2H), 5.05 (d, J = 2.5 Hz, 4H), 2.26 (s, 3H). <sup>13</sup>C NMR <sup>13</sup>C NMR (126 MHz, Chloroform-*d*)  $\delta$  156.08, 148.99, 143.10, 134.22, 134.15, 134.06, 133.96, 130.92, 130.06, 128.88, 128.71, 54.48, 43.50, 16.89. **HRMS** calcd for C<sub>18</sub>H<sub>15</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>2</sub>H<sup>+</sup>[M+H]<sup>+</sup>: 376.0614; found 376.0613.



#### 2,4-bis(4-bromobenzyl)-6-methyl-1,2,4-triazine-3,5(2H,4H)-dione (2e).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (3:1) as eluent afforded the product as a white solid (33.9 mg, 73% yield).

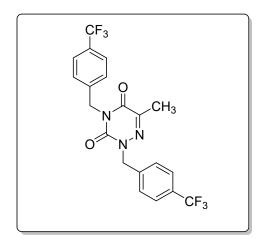
Mp: 142-143 °C. <sup>1</sup>**H** NMR (500 MHz, Chloroform-*d*)  $\delta$  7.49 (d, J = 8.3 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 7.30 (s, 1H), 7.28 (s, 1H), 5.04 (d, J = 2.7 Hz, 4H), 2.25 (s, 3H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*)  $\delta$  156.05, 148.97, 143.10, 134.64, 134.45, 131.84, 131.68, 131.23, 130.37, 122.36, 122.24, 54.53, 43.55, 16.89. HRMS calcd for C<sub>18</sub>H<sub>15</sub>Br<sub>2</sub>N<sub>3</sub>O<sub>2</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 463.9604; found 463.9601.



2,4-bis(4-iodobenzyl)-6-methyl-1,2,4-triazine-3,5(2H,4H)-dione (2f).

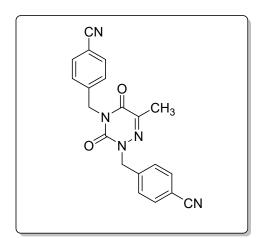
Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (5:1) as eluent afforded the product as a white solid (40.2 mg, 72% yield).

Mp: 160-161 °C. <sup>1</sup>**H** NMR (400 MHz, Chloroform-*d*)  $\delta$  7.69 (dd, J = 14.1, 8.3 Hz, 4H), 7.25 (d, J = 8.3 Hz, 2H), 7.17 (d, J = 8.3 Hz, 2H), 5.04 (d, J = 2.8 Hz, 4H), 2.26 (s, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  156.06, 148.99, 143.12, 137.84, 137.69, 135.30, 135.10, 131.42, 130.57, 94.04, 93.95, 54.65, 43.68, 16.90. **HRMS** calcd for C<sub>18</sub>H<sub>15</sub>I<sub>2</sub>N<sub>3</sub>O<sub>2</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 559.9326; found 559.9323.



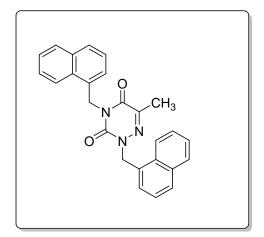
**6-methyl-2,4-bis(4-(trifluoromethyl)benzyl)-1,2,4-triazine-3,5(2H,4H)-dione (2g).** Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate 5:1) as eluent afforded the product as a white solid (30.6 mg, 69% yield).

Mp: 173-175 °C. <sup>1</sup>**H** NMR (400 MHz, Chloroform-*d*)  $\delta$  7.66 (s, 1H), 7.64 (s, 1H), 7.62 (s, 4H), 7.56 (s, 1H), 7.54 (s, 1H), 5.17 (s, 4H), 2.29 (s, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  156.04, 149.05, 143.34, 139.50, 139.27, 130.69, 130.54, 130.37, 130.21, 129.69, 128.90, 128.01, 125.77, 125.73, 125.69, 125.65, 125.61, 125.58, 125.54, 125.50, 125.30, 122.60, 119.89, 54.66, 43.73, 16.89. <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -62.69 (d, *J* = 5.8 Hz). **HRMS** calcd for C<sub>20</sub>H<sub>15</sub>F<sub>6</sub>N<sub>3</sub>O<sub>2</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 444.1141; found 444.1143.



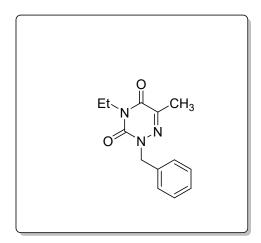
4,4'-((6-methyl-3,5-dioxo-1,2,4-triazine-2,4(3*H*,5*H*)diyl)bis(methylene))dibenzonitrile (2h). Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (6:1) as eluent afforded the product as a white solid (23.6 mg, 66% yield).

Mp:196-197 °C. <sup>1</sup>**H** NMR (500 MHz, Chloroform-*d*)  $\delta$  7.64 (d, *J* = 7.9 Hz, 2H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 5.10 (d, *J* = 3.4 Hz, 4H), 2.25 (s, 3H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*)  $\delta$  155.92, 148.93, 143.52, 140.55, 140.32, 132.56, 132.41, 130.03, 129.23, 118.44, 118.39, 112.26, 112.10, 54.70, 43.79, 16.95. **HRMS** calcd for C<sub>20</sub>H<sub>15</sub>N<sub>5</sub>O<sub>2</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 358.1299; found 358.1301.



**6-methyl-2,4-bis(naphthalen-1-ylmethyl)-1,2,4-triazine-3,5(2H,4H)-dione (2i).** Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (3:1) as eluent afforded the product as an off white oil (23.2 mg, 57% yield).

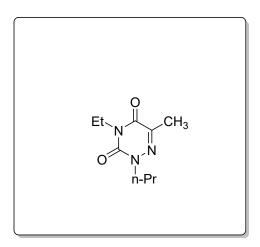
<sup>1</sup>**H NMR** (500 MHz, Chloroform-*d*)  $\delta$  8.30 (d, J = 7.3 Hz, 2H), 7.88 (q, J = 8.9, 8.2 Hz, 3H), 7.81 (d, J = 6.9 Hz, 1H), 7.60-7.51 (m, 5H), 7.48 (t, J = 7.6 Hz, 1H), 7.44-7.39 (m, 2H), 5.61 (d, J = 9.3 Hz, 4H), 2.22 (s, 3H). <sup>13</sup>**C NMR** (126 MHz, Chloroform-*d*)  $\delta$  156.28, 149.26, 142.78, 133.77, 133.71, 131.44, 131.38, 131.22, 130.53, 128.92, 128.71, 128.68, 128.39, 128.05, 126.51, 126.35, 125.88, 125.82, 125.69, 125.21, 125.10, 123.63, 123.38, 52.45, 41.80, 16.95. **HRMS** calcd for C<sub>26</sub>H<sub>21</sub>N<sub>3</sub>O<sub>2</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 408.1707; found 408.1704.



2-benzyl-4-ethyl-6-methyl-1,2,4-triazine-3,5(2H,4H)-dione (2j).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (4:1) as eluent afforded the product as an off white oil (16.7 mg, 68% yield).

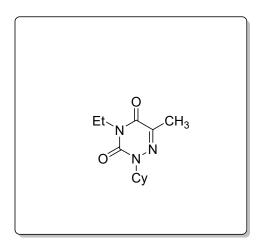
<sup>1</sup>**H NMR** (500 MHz, Chloroform-*d*)  $\delta$  7.43 (d, *J* = 7.3 Hz, 2H), 7.36 (dt, *J* = 11.9, 6.6 Hz, 3H), 5.10 (s, 2H), 4.01 (q, *J* = 7.1 Hz, 2H), 2.26 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>**C NMR** (126 MHz, Chloroform-*d*)  $\delta$  156.18, 148.94, 142.76, 135.98, 128.67, 128.63, 128.13, 55.03, 36.17, 16.90, 12.48. **HRMS** calcd for C<sub>13</sub>H<sub>15</sub>N3O<sub>2</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 246.1237; found 246.1237.



4-ethyl-6-methyl-2-propyl-1,2,4-triazine-3,5(2H,4H)-dione (2k).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (10:1) as eluent afforded the product as a white oil (14.2 mg, 72% yield).

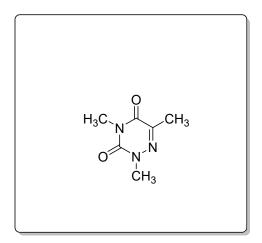
<sup>1</sup>**H NMR** (500 MHz, Chloroform-*d*)  $\delta$  3.99 (q, J = 7.0 Hz, 2H), 3.88 (t, J = 7.4 Hz, 2H), 2.23 (s, 3H), 1.76 (h, J = 7.3 Hz, 2H), 1.23 (t, J = 7.1 Hz, 3H), 0.94 (t, J = 7.4 Hz, 3H). <sup>13</sup>**C NMR** (126 MHz, Chloroform-*d*)  $\delta$  156.24, 148.87, 142.23, 52.97, 36.04, 21.56, 16.81, 12.48, 10.91. **HRMS** calcd for C<sub>9</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 198.1237; found 198.1238.



2-cyclohexyl-4-ethyl-6-methyl-1,2,4-triazine-3,5(2H,4H)-dione (2l).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (4:1) as eluent afforded the product as a white oil (15.6 mg, 66% yield).

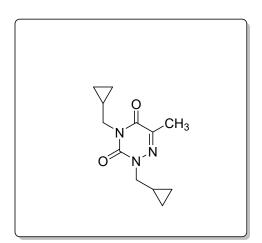
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 4.53-4.46 (m, 1H), 3.98 (q, *J* = 7.1 Hz, 2H), 2.22 (s, 3H), 1.87-1.77 (m, 4H), 1.71-1.63 (m, 3H), 1.39 (d, *J* = 13.2 Hz, 2H), 1.24-1.16 (m, 4H).
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 155.88, 148.70, 141.81, 57.41, 36.12, 30.74, 25.44, 25.14, 16.95, 12.49. HRMS calcd for C<sub>12</sub>H<sub>19</sub>N<sub>3</sub>O<sub>2</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 238.1550; found 238.1549.



#### 2,4,6-trimethyl-1,2,4-triazine-3,5(2*H*,4*H*)-dione (2m).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (10:1) as eluent afforded the product as a white solid (12.4 mg, 80% yield).

Mp: 63-65 °C. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 3.59 (s, 3H), 3.34 (s, 3H), 2.23 (s, 3H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 156.68, 149.36, 141.96, 39.18, 27.05, 16.71. HRMS calcd for C<sub>6</sub>H<sub>9</sub>N<sub>3</sub>O<sub>2</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 156.0768; found 156.0770.

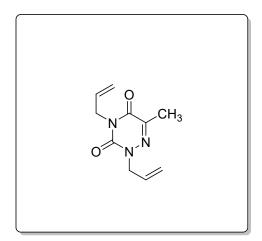


#### 2,4-bis(cyclopropylmethyl)-6-methyl-1,2,4-triazine-3,5(2*H*,4*H*)-dione (2n).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (10:1) as eluent afforded the product as a pink oil (17.4 mg, 74% yield).

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 3.83 (s, 1H), 3.81 (s, 1H), 3.80 (s, 1H), 3.79 (s, 1H), 2.24 (s, 3H), 1.25 (tt, *J* = 12.3, 5.4 Hz, 2H), 0.55-0.51 (m, 2H), 0.47 (dd, *J* = 8.2, S32

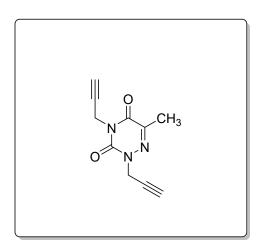
4.0 Hz, 2H), 0.40 (dt, J = 7.0, 4.7 Hz, 4H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*)  $\delta$ 156.70, 149.39, 142.24, 56.17, 45.37, 16.89, 10.02, 9.45, 3.85, 3.47. HRMS calcd for  $C_{12}H_{17}N_3O_2S^+$  [M+H]<sup>+</sup>: 236.1394; found 236.1391.



2,4-diallyl-6-methyl-1,2,4-triazine-3,5(2*H*,4*H*)-dione (20).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (7:1) as eluent afforded the product as a transparent oil (14.1 mg, 68% yield).

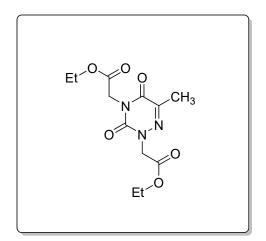
<sup>1</sup>**H** NMR (500 MHz, Chloroform-*d*)  $\delta$  5.98-5.80 (m, 2H), 5.32-5.21 (m, 4H), 4.53 (d, *J* = 6.6 Hz, 4H), 2.24 (s, 3H). <sup>13</sup>**C** NMR (126 MHz, Chloroform-*d*)  $\delta$  156.04, 148.60, 142.77, 131.51, 130.36, 119.16, 118.87, 53.87, 42.87, 16.85. **HRMS** calcd for C<sub>10</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 208.1081; found 208.1078.



6-methyl-2,4-di(prop-2-yn-1-yl)-1,2,4-triazine-3,5(2*H*,4*H*)-dione (2p). S33

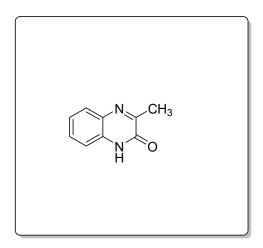
Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (6:1) as eluent afforded the product as a yellow oil (11.0 mg, 54% yield).

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 4.73 (s, 2H), 4.70 (s, 2H), 2.36 (s, 1H), 2.30 (s, 3H), 2.22 (s, 1H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 155.33, 147.71, 143.52, 76.57, 73.37, 71.69, 41.13, 30.04, 16.86. HRMS calcd for C<sub>10</sub>H<sub>9</sub>N<sub>3</sub>O<sub>2</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 204.0768; found 204.0771.



**Diethyl 2,2'-(6-methyl-3,5-dioxo-1,2,4-triazine-2,4(3H,5H)-diyl)diacetate (2q).** Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (4:1) as eluent afforded the product as a yellow oil (23.0 mg, 77% yield).

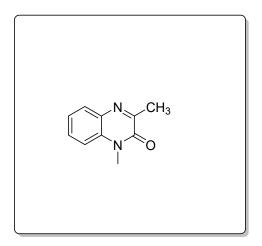
<sup>1</sup>**H NMR** (500 MHz, Chloroform-*d*)  $\delta$  4.64 (d, J = 3.7 Hz, 4H), 4.21 (dq, J = 10.4, 7.1 Hz, 4H), 2.24 (s, 3H), 1.26 (td, J = 7.2, 3.7 Hz, 6H). <sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  167.37, 166.55, 155.71, 148.75, 143.16, 61.87, 61.84, 52.42, 41.37, 16.74, 14.01, 13.98. **HRMS** calcd for C<sub>12</sub>H<sub>17</sub>N<sub>3</sub>O<sub>6</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 300.1190; found 300.1193.



#### 3-methylquinoxalin-2(1*H*)-one (4a) <sup>[11]</sup>

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (2:1) as eluent afforded the product as an off white solid (12.0 mg, 75% yield)

Mp: 195-196 °C. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 11.90 (s, 1H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.52-7.47 (m, 1H), 7.37-7.32 (m, 2H), 2.64 (s, 3H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*) <sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 158.85, 156.65, 132.67, 130.99, 129.72, 128.54, 124.24, 115.57, 20.78.

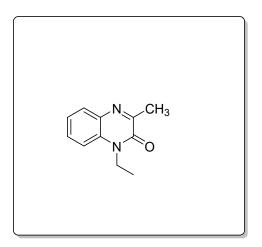


#### 1,3-dimethylquinoxalin-2(1*H*)-one (4b).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (5:1) as eluent afforded the product as an off white solid (13.1 mg, 75% yield).

Mp: 88-89 °C. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  7.80 (d, J = 8.0 Hz, 1H), 7.52 (t, S35

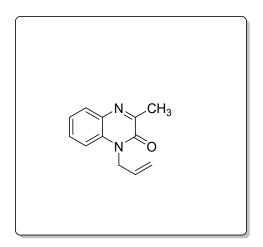
J = 7.9 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 7.29 (d, J = 8.4 Hz, 1H), 3.70 (s, 3H), 2.59 (s, 3H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*)  $\delta$  158.37, 155.19, 133.24, 132.60, 129.57, 129.40, 123.59, 113.58, 29.03, 21.55. HRMS calcd for C<sub>10</sub>H<sub>10</sub>N<sub>2</sub>OH<sup>+</sup> [M+H]<sup>+</sup>: 175.0866; found 175.0867.



#### 1-ethyl-3-methylquinoxalin-2(1*H*)-one (4c).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (2:1) as eluent afforded the product as a white solid (15.1 mg, 80% yield).

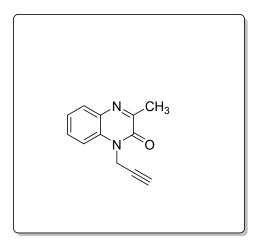
Mp: 78-90 °C. <sup>1</sup>**H** NMR (500 MHz, Chloroform-*d*)  $\delta$  7.82 (d, J = 7.9 Hz, 1H), 7.51 (t, J = 7.8 Hz, 1H), 7.32 (dd, J = 8.5, 5.4 Hz, 2H), 4.31 (q, J = 7.2 Hz, 2H), 2.59 (s, 3H), 1.37 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*)  $\delta$  158.43, 154.67, 132.88, 132.17, 129.65, 129.55, 123.39, 113.43, 37.26, 21.41, 12.36. HRMS calcd for C<sub>11</sub>H<sub>12</sub>N<sub>2</sub>OH<sup>+</sup> [M+H]<sup>+</sup>: 189.1022; found 189.1023.



#### 1-allyl-3-methylquinoxalin-2(1*H*)-one (4d).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (2:1) as eluent afforded the product as a white solid (13.2 mg, 66% yield).

Mp: 57-59 °C. <sup>1</sup>**H** NMR (500 MHz, Chloroform-*d*)  $\delta$  7.82 (d, J = 7.9 Hz, 1H), 7.49 (t, J = 7.8 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 7.28 (d, J = 9.3 Hz, 1H), 5.94 (ddd, J = 22.4, 10.3, 5.1 Hz, 1H), 5.27 (d, J = 10.5 Hz, 1H), 5.17 (d, J = 17.2 Hz, 1H), 4.91 (d, J = 4.7 Hz, 2H), 2.62 (s, 3H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*)  $\delta$  158.45, 154.75, 132.74, 132.47, 130.61, 129.51, 129.48, 123.59, 118.07, 114.17, 44.47, 21.48. HRMS calcd for C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>OH<sup>+</sup> [M+H]<sup>+</sup>: 201.1022; found 201.1022.

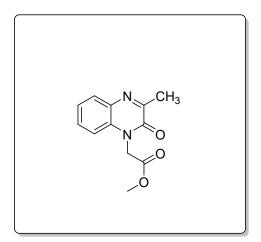


3-methyl-1-(prop-2-yn-1-yl)quinoxalin-2(1H)-one (4e).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (2:1) as eluent afforded the product as a white solid (11.5

mg, 58% yield).

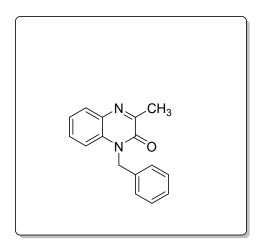
Mp: 153-154 °C. <sup>1</sup>**H** NMR (500 MHz, Chloroform-*d*)  $\delta$  7.82 (d, J = 8.0 Hz, 1H), 7.55 (t, J = 7.8 Hz, 1H), 7.45 (d, J = 8.3 Hz, 1H), 7.38-7.34 (m, 1H), 5.05 (s, 2H), 2.60 (s, 3H), 2.28 (s, 1H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*)  $\delta$  158.28, 154.17, 132.80, 131.72, 129.71, 129.57, 123.99, 114.10, 76.77, 73.17, 31.47, 21.48. **HRMS** calcd for C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>OH<sup>+</sup> [M+H]<sup>+</sup>: 199.0866; found 199.0865.



Methyl 2-(3-methyl-2-oxoquinoxalin-1(2H)-yl)acetate (4f).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (2:1) as eluent afforded the product as a white solid (17.2 mg, 74% yield).

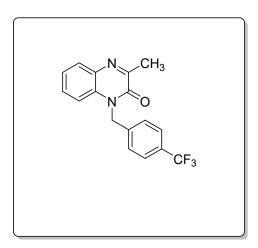
Mp: 129-131 °C. <sup>1</sup>**H** NMR (500 MHz, Chloroform-*d*)  $\delta$  7.82 (d, J = 8.1 Hz, 1H), 7.50-7.45 (m, 1H), 7.33 (t, J = 7.7 Hz, 1H), 7.05 (d, J = 8.4 Hz, 1H), 5.03 (s, 2H), 3.77 (s, 3H), 2.60 (s, 3H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*)  $\delta$  167.59, 158.14, 154.70, 132.69, 132.31, 129.77, 123.92, 112.96, 52.79, 43.34, 21.40. **HRMS** calcd for C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 233.0921; found 233.0921.



#### 1-benzyl-3-methylquinoxalin-2(1*H*)-one (4g).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (5:1) as eluent afforded the product as a white solid (18.8 mg, 75% yield).

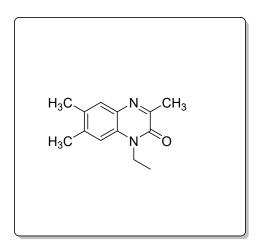
Mp: 90-92 °C. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  7.84 (d, J = 8.0 Hz, 1H), 7.45-7.40 (m, 1H), 7.36-7.32 (m, 3H), 7.31-7.27 (m, 3H), 5.53 (s, 2H), 2.69 (s, 3H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*)  $\delta$  158.52, 155.29, 135.25, 132.90, 132.61, 129.57, 129.54, 128.92, 127.68, 126.86, 123.65, 114.42, 45.91, 21.65. HRMS calcd for C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>OH<sup>+</sup> [M+H]<sup>+</sup>: 251.1179; found 251.1175.



#### 3-methyl-1-(4-(trifluoromethyl)benzyl)quinoxalin-2(1H)-one (4h).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (2:1) as eluent afforded the product as a yellow solid (21.6 mg, 68% yield).

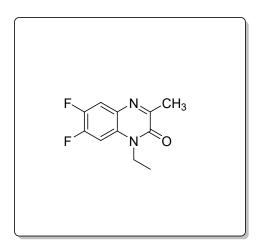
Mp: 138-140 °C. <sup>1</sup>**H** NMR (400 MHz, Chloroform-*d*)  $\delta$  7.84 (d, J = 7.9 Hz, 1H), 7.58 (d, J = 8.1 Hz, 2H), 7.42 (t, J = 7.0 Hz, 1H), 7.37 (d, J = 8.0 Hz, 2H), 7.35-7.29 (m, 1H), 7.17 (d, J = 8.3 Hz, 1H), 5.55 (s, 2H), 2.67 (s, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  158.32, 155.02, 139.27, 132.83, 132.22, 129.68, 129.61, 127.09, 125.86, 125.82, 125.78, 125.74, 123.79, 113.90, 45.34, 21.48. <sup>19</sup>F NMR (471 MHz, Chloroform-*d*)  $\delta$  -62.60. **HRMS** calcd for C<sub>17</sub>H<sub>13</sub>F<sub>3</sub>N<sub>2</sub>OH<sup>+</sup> [M+H]<sup>+</sup>: 319.1053; found 319.1055.



1-ethyl-3,6,7-trimethylquinoxalin-2(1*H*)-one (4i).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (2:1) as eluent afforded the product as a yellow solid (17.1 mg, 79% yield).

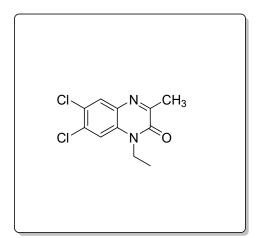
Mp: 132-133 °C. <sup>1</sup>**H** NMR (400 MHz, Chloroform-*d*)  $\delta$  7.55 (s, 1H), 7.06 (s, 1H), 4.28 (q, J = 7.2 Hz, 2H), 2.56 (s, 3H), 2.40 (s, 3H), 2.33 (s, 3H), 1.36 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  157.08, 154.73, 139.13, 132.21, 131.41, 130.12, 129.78, 113.92, 37.07, 21.37, 20.51, 19.14, 12.42. **HRMS** calcd for C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>O H<sup>+</sup> [M+H]<sup>+</sup>: 217.1335; found 217.1335.



#### 1-ehyl-6,7-difluoro-3-methylquinoxalin-2(1H)-one (4j).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (7:1) as eluent afforded the product as a yellow solid (16.4 mg, 73% yield).

Mp: 193-195 °C. <sup>1</sup>**H** NMR (400 MHz, Chloroform-*d*)  $\delta$  7.59 (dd, J = 10.3, 8.2 Hz, 1H), 7.09 (dd, J = 11.5, 7.1 Hz, 1H), 4.22 (q, J = 7.2 Hz, 2H), 2.54 (s, 3H), 1.35 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  159.01, 158.98, 154.20, 152.35, 152.21, 149.85, 149.71, 147.70, 147.56, 145.24, 145.11, 129.27, 129.18, 117.37, 117.35, 117.19, 117.17, 102.08, 101.84, 37.88, 21.34, 12.16. <sup>19</sup>F NMR (471 MHz, Chloroform-*d*)  $\delta$  -132.08, -142.33. **HRMS** calcd for C<sub>11</sub>H<sub>10</sub>F<sub>2</sub>N<sub>2</sub>OH<sup>+</sup> [M+H]<sup>+</sup>: 225.0843; found 225.0836.

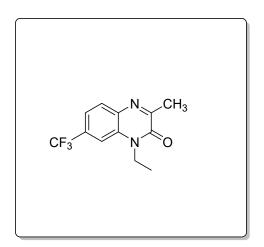


#### 6,7-dichloro-1-ethyl-3-methylquinoxalin-2(1*H*)-one (4k).

Following the general procedure and purification by column chromatography using

petroleum ether/ethyl acetate (4:1) as eluent afforded the product as a yellow solid (19.8 mg, 77% yield).

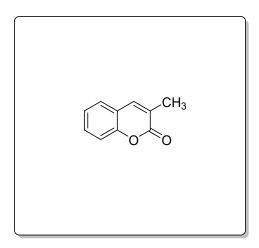
Mp: 210-212 °C. <sup>1</sup>**H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.88 (s, 1H), 7.38 (s, 1H), 4.24 (q, J = 7.2 Hz, 2H), 2.57 (s, 3H), 1.37 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  160.03, 154.10, 133.61, 132.11, 131.59, 130.59, 127.10, 114.85, 37.65, 21.53, 12.28. **HRMS** calcd for C<sub>11</sub>H<sub>10</sub>Cl<sub>2</sub>N<sub>2</sub>OH<sup>+</sup> [M+H]<sup>+</sup>: 257.0243; found 257.0241.



1-ethyl-3-methyl-7-(trifluoromethyl)quinoxalin-2(1*H*)-one (3l).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (5:1) as eluent afforded the product as a yellow solid (20.5 mg, 80% yield).

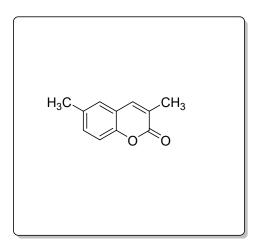
Mp: 138-139 °C. <sup>1</sup>**H** NMR (400 MHz, Chloroform-*d*)  $\delta$  8.09 (d, J = 1.4 Hz, 1H), 7.73 (dd, J = 8.8, 2.1 Hz, 1H), 7.40 (d, J = 8.8 Hz, 1H), 4.33 (q, J = 7.2 Hz, 2H), 2.61 (s, 3H), 1.39 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  160.21, 154.52, 134.55, 132.35, 127.24, 127.24, 125.87, 114.04, 37.58, 21.53, 12.35. <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -62.01. **HRMS** calcd for C<sub>12</sub>H<sub>11</sub>F<sub>3</sub>N<sub>2</sub>OH<sup>+</sup> [M+H]<sup>+</sup>: 257.0896; found 257.0891.



#### 3-methyl-2H-chromen-2-one (4m).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (20:1) as eluent afforded the product as a white solid (9.1 mg, 57% yield).

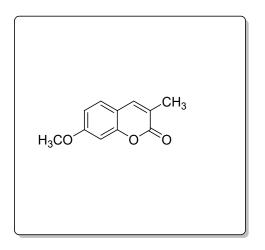
Mp: 125-126 °C. <sup>1</sup>**H** NMR (400 MHz, Chloroform-*d*)  $\delta$  7.55 (s, 1H), 7.52-7.46 (m, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.31-7.27 (m, 1H), 2.25 (s, 3H). <sup>13</sup>**C** NMR (101 MHz, Chloroform-*d*)  $\delta$  162.14, 153.19, 139.15, 130.38, 126.88, 125.77, 124.20, 119.53, 116.37, 17.10. **HRMS** calcd for C<sub>10</sub>H<sub>8</sub>O<sub>2</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 161.0597; found 161.0596.



#### 3,6-dimethyl-2*H*-chromen-2-one (4n).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (10:1) as eluent afforded the product as a white solid (10.6 mg, 61% yield).

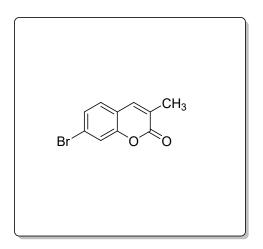
Mp: 131-132 °C. <sup>1</sup>**H** NMR (500 MHz, Chloroform-*d*)  $\delta$  7.46 (s, 1H), 7.25 (d, J = 8.4 Hz, 1H), 7.19 (dd, J = 5.3, 3.2 Hz, 2H), 2.39 (s, 3H), 2.20 (s, 3H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*)  $\delta$  162.41, 151.26, 139.18, 133.83, 131.37, 126.72, 125.54, 119.23, 116.06, 20.72, 17.15. **HRMS** calcd for C<sub>11</sub>H<sub>10</sub>O<sub>2</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 175.0754; found 175.0758.



#### 7-methoxy-3-methyl-2*H*-chromen-2-one (40).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (10:1) as eluent afforded the product as a white solid (11.2 mg, 59% yield).

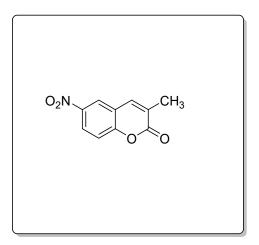
Mp: 156-158 °C. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  7.46 (s, 1H), 7.31 (d, J = 8.4 Hz, 1H), 6.84-6.80 (m, 2H), 3.86 (s, 3H), 2.17 (s, 3H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*)  $\delta$  162.61, 161.70, 154.85, 139.38, 127.78, 122.12, 113.18, 112.36, 100.48, 55.69, 16.97. HRMS calcd for C<sub>11</sub>H<sub>10</sub>O<sub>3</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 191.0703; found 191.0703.



#### 7-bromo-3-methyl-2*H*-chromen-2-one (4p).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (7:1) as eluent afforded the product as a white solid (12.7 mg, 53% yield).

Mp: 165-167 °C. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  7.57 (d, J = 7.7 Hz, 2H), 7.46 (s, 1H), 7.23 (d, J = 10.0 Hz, 1H), 2.25 (s, 3H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*)  $\delta$  161.52, 152.03, 137.81, 133.21, 129.23, 127.24, 121.08, 118.20, 116.80, 17.29. HRMS calcd for C<sub>10</sub>H<sub>7</sub>BrO<sub>2</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 238.9702; found 238.9700.

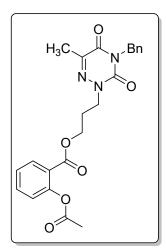


#### 3-methyl-6-nitro-2*H*-chromen-2-one (4q).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (5:1) as eluent afforded the product as a white solid (11.7 mg, 57% yield).

Mp: 221-223 °C. <sup>1</sup>**H NMR** (500 MHz, Chloroform-*d*) δ 8.36 (s, 1H), 8.34 (d, *J* = 11.6 S45

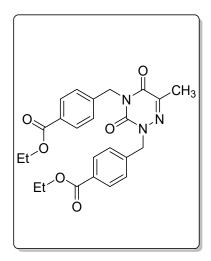
Hz, 1H), 7.60 (s, 1H), 7.44 (d, J = 9.0 Hz, 1H), 2.28 (s, 3H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*)  $\delta$  160.55, 156.67, 143.99, 137.79, 128.54, 125.35, 122.79, 119.56, 117.60, 17.36. HRMS calcd for C<sub>10</sub>H<sub>7</sub>NO<sub>4</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 206.0448; found 206.0438.



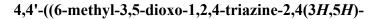
# 3-(4-benzyl-6-methyl-3,5-dioxo-4,5-dihydro-1,2,4-triazin-4(3*H*)-yl)propyl 2acetoxybenzoate (6a).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (5:1) as eluent afforded the product as a yellow oil (33.2 mg, 76% yield).

<sup>1</sup>**H NMR** (500 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 6.2 Hz, 1H), 7.61-7.56 (m, 1H), 7.51 (d, *J* = 1.9 Hz, 2H), 7.33-7.31 (m, 4H), 7.12 (dd, *J* = 8.1, 1.2 Hz, 1H), 5.07 (s, 2H), 4.37 (t, *J* = 6.2 Hz, 2H), 4.15-4.12 (m, 2H), 2.37 (s, 3H), 2.22 (t, *J* = 6.5 Hz, 2H), 2.20 (s, 3H).. <sup>13</sup>**C NMR** δ 169.83, 164.06, 156.07, 150.65, 149.10, 135.81, 133.96, 131.53, 129.42, 128.52, 128.06, 126.01, 123.80, 122.96, 62.68, 48.79, 44.07, 27.18, 20.98, 16.78.



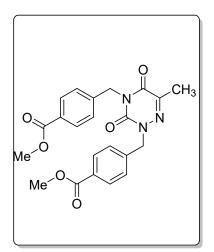
Diethyl



#### diyl)bis(methylene))dibenzoate (6b).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (5:1) as eluent afforded the product as a white solid (30.7 mg, 73% yield).

Mp: 145-146 °C. <sup>1</sup>**H** NMR (500 MHz, Chloroform-*d*)  $\delta$  8.00 (dd, J = 17.5, 8.3 Hz, 4H), 7.51 (d, J = 8.3 Hz, 2H), 7.44 (d, J = 8.2 Hz, 2H), 5.12 (s, 4H), 4.36 (qd, J = 7.2, 5.1 Hz, 4H), 2.25 (s, 3H), 1.38 (td, J = 7.1, 4.1 Hz, 6H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*)  $\delta$  166.07, 166.04, 155.98, 148.94, 143.10, 140.40, 140.15, 130.22, 130.07, 129.87, 129.73, 129.02, 128.27, 60.94, 60.89, 54.69, 43.78, 16.87, 14.20. HRMS calcd for C<sub>24</sub>H<sub>25</sub>N<sub>3</sub>O<sub>6</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 452.1816; found 452.1810.



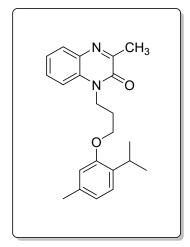
Dimethyl

4,4'-((6-methyl-3,5-dioxo-1,2,4-triazine-2,4(3H,5H)-

#### diyl)bis(methylene))dibenzoate (6c).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (4:1) as eluent afforded the product as a white solid (28.8 mg, 68% yield).

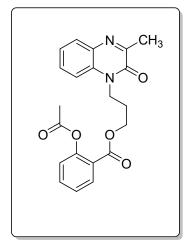
Mp: 148-149 °C. <sup>1</sup>**H** NMR (500 MHz, Chloroform-*d*)  $\delta$  8.00 (dd, J = 17.7, 8.1 Hz, 4H), 7.48 (dd, J = 34.0, 8.2 Hz, 4H), 5.13 (d, J = 1.9 Hz, 4H), 3.91 (d, J = 5.5 Hz, 6H), 2.26 (s, 3H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*)  $\delta$  166.59, 166.56, 156.02, 148.97, 143.16, 140.53, 140.28, 129.94, 129.89, 129.80, 129.74, 129.08, 128.33, 54.73, 52.12, 52.08, 43.80, 16.90. **HRMS** calcd for C<sub>22</sub>H<sub>21</sub>N<sub>3</sub>O<sub>6</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 424.1503; found 424.1505.



**1-(3-(2-isopropyl-5-methylphenoxy)propyl)-3-methylquinoxalin-2(1***H***)-one (6d). Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (4:1) as eluent afforded the product as a yellow oil (18.9 mg, 55% yield).** 

<sup>1</sup>**H NMR** (500 MHz, Chloroform-*d*) δ 7.84 (d, J = 8.0 Hz, 1H), 7.49 (d, J = 4.1 Hz, 2H), 7.34 (dt, J = 8.2, 4.2 Hz, 1H), 7.14 (d, J = 7.6 Hz, 1H), 6.78 (d, J = 7.7 Hz, 1H), 6.66 (s, 1H), 4.53-4.47 (m, 2H), 4.13 (t, J = 5.6 Hz, 2H), 3.38 (p, J = 7.0 Hz, 1H), 2.62 (s, 3H), 2.32 (s, 3H), 2.28 (dt, J = 11.4, 5.8 Hz, 2H), 1.29 (s, 3H), 1.27 (s, 3H). <sup>13</sup>**C NMR** (126 MHz, Chloroform-*d*) δ 158.33, 155.52, 154.99, 136.53, 133.67, 132.82, 132.43, 129.65, 129.63, 125.87, 123.59, 121.47, 113.60, 112.07, 65.09, 39.92, 27.28, 26.73, 22.85, 21.48, 21.33. **HRMS** calcd for C<sub>22</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 351.2067; found

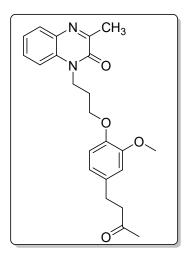
351.2070.



## 3-(3-methyl-2-oxoquinoxalin-1(2*H*)-yl)propyl 2-acetoxybenzoate (6e).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (4:1) as eluent afforded the product as a yellow oil (23.2 mg, 61% yield).

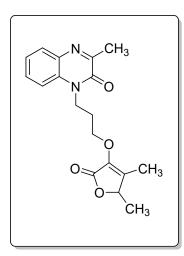
<sup>1</sup>**H NMR** (500 MHz, Chloroform-*d*)  $\delta$  7.98 (d, J = 9.6 Hz, 1H), 7.80 (d, J = 6.8 Hz, 1H), 7.58 (t, J = 8.6 Hz, 1H), 7.48 (t, J = 7.8 Hz, 1H), 7.33 (t, J = 7.4 Hz, 3H), 7.12 (d, J = 8.1 Hz, 1H), 4.41 (q, J = 6.5 Hz, 4H), 2.57 (s, 3H), 2.33 (s, 3H), 2.22 (dt, J = 12.5, 6.5 Hz, 2H). <sup>13</sup>**C NMR** (126 MHz, Chloroform-*d*)  $\delta$  169.69, 164.15, 158.26, 154.89, 150.69, 134.05, 132.80, 132.18, 131.44, 129.72, 129.63, 126.05, 123.79, 123.61, 122.95, 113.29, 62.62, 39.48, 26.51, 21.42, 21.01. **HRMS** calcd for C<sub>21</sub>H<sub>20</sub>N<sub>2</sub>O<sub>5</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 381.1445; found 381.1441.



1-(3-(2-methoxy-4-(3-oxobutyl)phenoxy)propyl)-3-methylquinoxalin-2(1*H*)-one (6f).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (4:1) as eluent afforded the product as a white solid (24,8 mg, 63% yield).

Mp: 115-116 °C. <sup>1</sup>**H** NMR (400 MHz, Chloroform-*d*)  $\delta$  7.79 (d, J = 7.9 Hz, 1H), 7.57 (d, J = 8.4 Hz, 1H), 7.47-7.41 (m, 1H), 7.32-7.27 (m, 1H), 6.80-6.73 (m, 2H), 6.68 (d, J = 8.1 Hz, 1H), 4.51-4.46 (m, 2H), 4.10 (t, J = 5.8 Hz, 2H), 3.87 (s, 3H), 2.84 (t, J = 7.7 Hz, 2H), 2.75 (d, J = 7.2 Hz, 2H), 2.57 (s, 3H), 2.30-2.22 (m, 2H), 2.13 (s, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  207.93, 158.16, 155.06, 149.53, 146.38, 134.46, 132.90, 132.50, 129.59, 129.47, 123.43, 120.17, 113.98, 113.89, 112.22, 66.57, 55.86, 45.32, 39.64, 30.08, 29.38, 27.30, 21.41. HRMS calcd for C<sub>23</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 395.1965; found 395.1957.

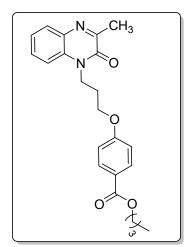


## 1-(3-((4,5-dimethyl-2-oxo-2,5-dihydrofuran-3-yl)oxy)propyl)-3-

#### methylquinoxalin-2(1*H*)-one (6g).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (4:1) as eluent afforded the product as a yellow solid (23.9 mg, 73% yield).

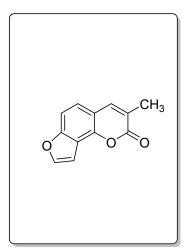
Mp: 93-94 °C. <sup>1</sup>**H** NMR (500 MHz, Chloroform-*d*)  $\delta$  7.77 (d, J = 8.1 Hz, 1H), 7.49 (t, J = 7.8 Hz, 1H), 7.39 (d, J = 8.5 Hz, 1H), 7.29 (t, J = 7.5 Hz, 1H), 4.78 (q, J = 6.6 Hz, 1H), 4.43-4.38 (m, 2H), 4.31 (td, J = 5.8, 3.2 Hz, 2H), 2.55 (s, 3H), 2.15-2.09 (m, 2H), 1.92 (s, 3H), 1.39 (d, J = 6.7 Hz, 3H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*)  $\delta$  168.27, 158.10, 154.83, 141.51, 139.64, 132.75, 132.22, 129.62, 129.54, 123.48, 113.50, 76.77, 68.27, 39.31, 27.61, 21.38, 18.43, 9.75. HRMS calcd for C<sub>18</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 329.1496; found 329.1488.



#### Butyl 4-(3-(3-methyl-2-oxoquinoxalin-1(2H)-yl)propoxy)benzoate (6h).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (4:1) as eluent afforded the product as a yellow solid (30.3 mg, 77% yield).

Mp: 84-86 °C. <sup>1</sup>**H** NMR (500 MHz, Chloroform-*d*)  $\delta$  7.99 (d, J = 8.8 Hz, 2H), 7.81 (d, J = 8.1 Hz, 1H), 7.46 (t, J = 7.7 Hz, 1H), 7.40 (d, J = 9.9 Hz, 1H), 7.31 (t, J = 8.2 Hz, 1H), 6.90 (d, J = 8.9 Hz, 2H), 4.48 (t, J = 7.3 Hz, 2H), 4.28 (t, J = 6.6 Hz, 2H), 4.14 (t, J = 5.7 Hz, 2H), 2.57 (s, 3H), 2.28 (dt, J = 12.9, 6.1 Hz, 2H), 1.73 (dt, J = 14.4, 6.7 Hz, 2H), 1.46 (h, J = 7.4 Hz, 2H), 0.97 (t, J = 7.4 Hz, 3H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*)  $\delta$  166.36, 162.08, 158.23, 155.00, 132.82, 132.35, 131.55, 129.67, 123.60, 123.22, 113.92, 113.41, 65.37, 64.57, 39.54, 30.76, 26.98, 21.45, 19.24, 13.75. HRMS calcd for C<sub>23</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 395.1965; found 395.1956.

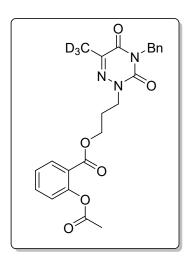


#### 3-methyl-2*H*-furo[2,3-*h*]chromen-2-one (6i).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (4:1) as eluent afforded the product as a white solid (11.2 mg, 56% yield).

Mp: 141-143 °C. <sup>1</sup>**H** NMR (500 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 2.2 Hz, 1H), 7.66 (d, *J* = 1.4 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.35 (d, *J* = 8.5 Hz, 1H), 7.16 (s, 1H), 2.27 (s, 3H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 162.33, 156.55, 147.31, 145.66, 140.39,

123.16, 123.00, 116.60, 114.13, 108.60, 103.99, 17.17. **HRMS** calcd for C<sub>12</sub>H<sub>8</sub>O<sub>3</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 201.0546; found 201.0542.

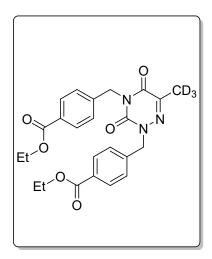


3-(4-benzyl-6-(methyl-*d*<sub>3</sub>)-3,5-dioxo-4,5-dihydro-1,2,4-triazin-2(3*H*)-yl)propyl 2acetoxybenzoate (7a).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (4:1) as eluent afforded the product as a yellow oil (28.1 mg, 64% yield).

<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 6.1 Hz, 1H), 7.61-7.56 (m, 1H), 7.50 (d, *J* = 6.4 Hz, 2H), 7.36-7.29 (m, 4H), 7.12 (d, *J* = 6.9 Hz, 1H), 5.07 (d, *J* = 5.3 Hz, 2H), 4.37 (t, *J* = 6.1 Hz, 2H), 4.13 (t, *J* = 6.9 Hz, 2H), 2.37 (s, 3H), 2.22 (p, *J* = 6.6 Hz, 2H).
<sup>13</sup>C NMR (126 MHz, Chloroform-*d*) <sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 169.61, 164.08, 156.16, 150.67, 149.08, 135.58, 133.97, 131.54, 129.44, 128.54, 128.04, 126.02, 123.82, 122.97, 62.47, 48.90, 44.04, 27.30, 20.99.

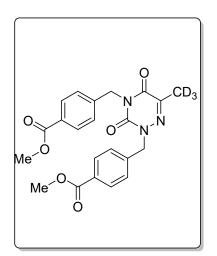
**HRMS** calcd for  $C_{23}H_{20}D_3N_3O_6H^+$  [M+H]<sup>+</sup>: 441.1848; found 441.1842.



Diethyl  $4,4'-((6-(methyl-d_3)-3,5-dioxo-1,2,4-triazine-2,4(3H,5H)-diyl)bis(methylene))dibenzoate (7b).$ 

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (4:1) as eluent afforded the product as a white solid (33.1 mg, 73% yield).

Mp: 139-140 °C. <sup>1</sup>**H** NMR (500 MHz, Chloroform-*d*)  $\delta$  8.00 (dd, J = 17.9, 8.2 Hz, 4H), 7.50 (d, J = 8.2 Hz, 2H), 7.43 (d, J = 8.2 Hz, 2H), 5.12 (s, 4H), 4.36 (qd, J = 7.1, 5.2 Hz, 4H), 1.38 (td, J = 7.1, 4.3 Hz, 6H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*)  $\delta$  166.18, 166.16, 156.09, 149.02, 143.12, 140.44, 140.20, 130.33, 130.18, 129.96, 129.83, 129.11, 128.37, 61.04, 60.99, 54.79, 43.87, 14.28. **HRMS** calcd for C<sub>24</sub>H<sub>22</sub>D<sub>3</sub>N<sub>3</sub>O<sub>6</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 455.2004; found 455.2007.

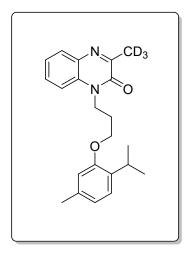


#### Dimethyl 4,4'-((6-(methyl-*d*<sub>3</sub>)-3,5-dioxo-1,2,4-triazine-2,4(3*H*,5*H*)-

#### diyl)bis(methylene))dibenzoate (7c).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (4:1) as eluent afforded the product as a white solid (30.0 mg, 68% yield).

Mp: 143-144 °C. <sup>1</sup>**H** NMR (500 MHz, Chloroform-*d*)  $\delta$  7.99 (dd, J = 17.8, 8.0 Hz, 4H), 7.50 (d, J = 8.1 Hz, 2H), 7.43 (d, J = 8.1 Hz, 2H), 5.11 (s, 4H), 3.90 (d, J = 5.5 Hz, 6H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*)  $\delta$  166.64, 166.62, 156.08, 149.01, 143.13, 140.55, 140.31, 129.99, 129.95, 129.86, 129.80, 129.13, 128.38, 54.79, 52.17, 52.13, 43.84. HRMS calcd for C<sub>22</sub>H<sub>18</sub>D<sub>3</sub>N<sub>3</sub>O<sub>6</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 427.1691; found 427.1694.

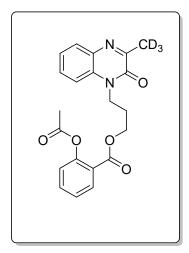


# 1-(3-(2-isopropyl-5-methylphenoxy)propyl)-3-(methyl-*d*<sub>3</sub>)quinoxalin-2(1*H*)-one (7d).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (4:1) as eluent afforded the product as a white oil (21.5 mg, 61% yield).

<sup>1</sup>**H NMR** (500 MHz, Chloroform-*d*)  $\delta$  7.84 (d, J = 7.9 Hz, 1H), 7.50 (d, J = 4.1 Hz, 2H), 7.37-7.31 (m, 1H), 7.14 (d, J = 7.7 Hz, 1H), 6.79 (d, J = 6.3 Hz, 1H), 6.67 (s, 1H), 4.55-4.47 (m, 2H), 4.13 (t, J = 5.5 Hz, 2H), 3.39 (hept, J = 6.9 Hz, 1H), 2.33 (s, 3H), 2.28 (dt, J = 11.5, 5.5 Hz, 2H), 1.30 (s, 3H), 1.28 (s, 3H). <sup>13</sup>C **NMR** (126 MHz, Chloroform-*d*)  $\delta$  158.25, 155.48, 154.97, 136.48, 133.62, 132.86, 132.38, 129.64,

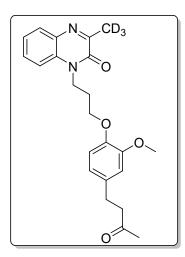
129.59, 125.83, 123.54, 121.43, 113.56, 112.03, 65.06, 39.86, 27.26, 26.70, 22.82, 21.31. **HRMS** calcd for C<sub>22</sub>H<sub>23</sub>D<sub>3</sub>N<sub>2</sub>O<sub>2</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 354.2255; found 354.2249.



#### 3-(3-(methyl-*d*<sub>3</sub>)-2-oxoquinoxalin-1(2*H*)-yl)propyl 2-acetoxybenzoate (7e).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (4:1) as eluent afforded the product as a yellow oil (22.6 mg, 59% yield).

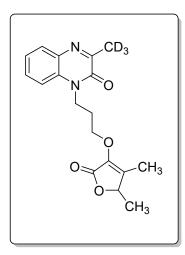
<sup>1</sup>**H NMR** (500 MHz, Chloroform-*d*)  $\delta$  7.98 (d, J = 7.8 Hz, 1H), 7.75 (d, J = 9.6 Hz, 1H), 7.58 (t, J = 6.9 Hz, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.33 (d, J = 6.9 Hz, 3H), 7.12 (d, J = 7.0 Hz, 1H), 4.41 (q, J = 7.3, 6.6 Hz, 4H), 2.33 (s, 3H), 2.22 (dt, J = 12.6, 6.4 Hz, 2H).<sup>13</sup>**C NMR** (126 MHz, Chloroform-*d*) $\delta$  169.83, 164.14, 158.21, 154.91, 150.69, 134.03, 132.87, 132.14, 131.44, 129.86, 129.59, 126.04, 123.79, 123.58, 119.22, 113.11, 62.85, 62.61, 39.38, 26.53, 21.00. **HRMS** calcd for C<sub>21</sub>H<sub>17</sub>D<sub>3</sub>N<sub>2</sub>O<sub>5</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 384.1633; found 384.1631.



1-(3-(2-methoxy-4-(3-oxobutyl)phenoxy)propyl)-3-(methyl-*d*<sub>3</sub>)quinoxalin-2(1*H*)one (7f).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (4:1) as eluent afforded the product as a white solid (25.4 mg, 64% yield).

Mp: 123-124 °C. <sup>1</sup>**H** NMR (400 MHz, Chloroform-*d*)  $\delta$  7.78 (d, J = 6.4 Hz, 1H), 7.56 (d, J = 7.2 Hz, 1H), 7.46-7.40 (m, 1H), 7.29 (t, J = 7.0 Hz, 1H), 6.77 (d, J = 8.1 Hz, 1H), 6.73 (s, 1H), 6.67 (d, J = 10.2 Hz, 1H), 4.51-4.43 (m, 2H), 4.09 (t, J = 5.8 Hz, 2H), 3.86 (s, 3H), 2.88-2.69 (m, 4H), 2.29-2.21 (m, 2H), 2.12 (s, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  207.90, 158.08, 155.03, 149.49, 132.46, 129.56, 129.43, 120.14, 113.94, 113.85, 112.19, 66.53, 55.82, 45.28, 39.60, 30.05, 29.34, 27.26. HRMS calcd for C<sub>23</sub>H<sub>23</sub>D<sub>3</sub>N<sub>2</sub>O<sub>4</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 398.2154; found 398.2151.

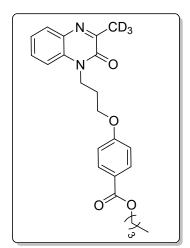


1-(3-((4,5-dimethyl-2-oxo-2,5-dihydrofuran-3-yl)oxy)propyl)-3-(methyl-

### d<sub>3</sub>)quinoxalin-2(1H)-one (7g).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (4:1) as eluent afforded the product as a yellow solid (23.5 mg, 71% yield).

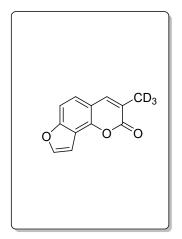
Mp: 95-96 °C. <sup>1</sup>**H** NMR (500 MHz, Chloroform-*d*)  $\delta$  7.76 (d, J = 8.0 Hz, 1H), 7.49 (t, J = 7.8 Hz, 1H), 7.39 (d, J = 8.5 Hz, 1H), 7.29 (t, J = 7.0 Hz, 1H), 4.78 (q, J = 6.7 Hz, 1H), 4.44-4.38 (m, 2H), 4.31 (tq, J = 7.5, 4.1 Hz, 2H), 2.15-2.09 (m, 2H), 1.91 (s, 3H), 1.39 (d, J = 6.7 Hz, 3H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*)  $\delta$  168.26, 158.05, 154.83, 141.51, 139.63, 132.74, 132.21, 129.62, 129.53, 123.47, 113.49, 76.77, 68.26, 39.29, 27.60, 18.42, 9.74. HRMS calcd for C<sub>18</sub>H<sub>17</sub>D<sub>3</sub>N<sub>2</sub>O<sub>4</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 332.1684; found 332.1684.



Butyl 4-(3-(3-(methyl-*d*<sub>3</sub>)-2-oxoquinoxalin-1(2*H*)-yl)propoxy)benzoate (7h). S58

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (4:1) as eluent afforded the product as a yellow solid (29.8 mg, 75% yield).

Mp: 90-92 °C. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  7.98 (d, J = 8.8 Hz, 2H), 7.80 (d, J = 6.4 Hz, 1H), 7.45 (t, J = 7.8 Hz, 1H), 7.40 (d, J = 8.5 Hz, 1H), 7.33-7.28 (m, 1H), 6.89 (d, J = 8.9 Hz, 2H), 4.50-4.44 (m, 2H), 4.28 (t, J = 6.6 Hz, 2H), 4.13 (t, J = 5.7 Hz, 2H), 2.31-2.25 (m, 2H), 1.77-1.69 (m, 2H), 1.46 (h, J = 7.4 Hz, 2H), 0.96 (t, J = 7.4 Hz, 3H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*)  $\delta$  166.32, 162.06, 158.17, 154.98, 132.78, 132.33, 131.53, 129.65, 129.64, 123.56, 123.20, 113.90, 113.39, 65.35, 64.53, 39.50, 30.73, 26.96, 19.22, 13.73. HRMS calcd for C<sub>23</sub>H<sub>23</sub>D<sub>3</sub>N<sub>2</sub>OH<sup>+</sup> [M+H]<sup>+</sup>: 398.2154; found 398.2145



#### **3-(methyl-***d*<sub>3</sub>**)-2***H***-furo**[**2**,**3**-*h*]**chromen-2-one** (7**i**).

Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (4:1) as eluent afforded the product as a white solid (10.8 mg, 53% yield).

Mp: 140-142 °C. <sup>1</sup>**H** NMR (500 MHz, Chloroform-*d*)  $\delta$  7.71 (d, J = 2.3 Hz, 1H), 7.66 (s, 1H), 7.44 (d, J = 7.6 Hz, 1H), 7.35 (d, J = 8.5 Hz, 1H), 7.15 (d, J = 3.1 Hz, 1H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*)  $\delta$  162.35, 156.55, 147.33, 145.65, 140.44, 123.00, 120.37, 116.60, 114.13, 108.60, 103.99, 29.70. HRMS calcd for C<sub>12</sub>H<sub>5</sub>D<sub>3</sub>O<sub>3</sub>H<sup>+</sup> [M+H]<sup>+</sup>: 204.0735; found 204.0726.

## V. References

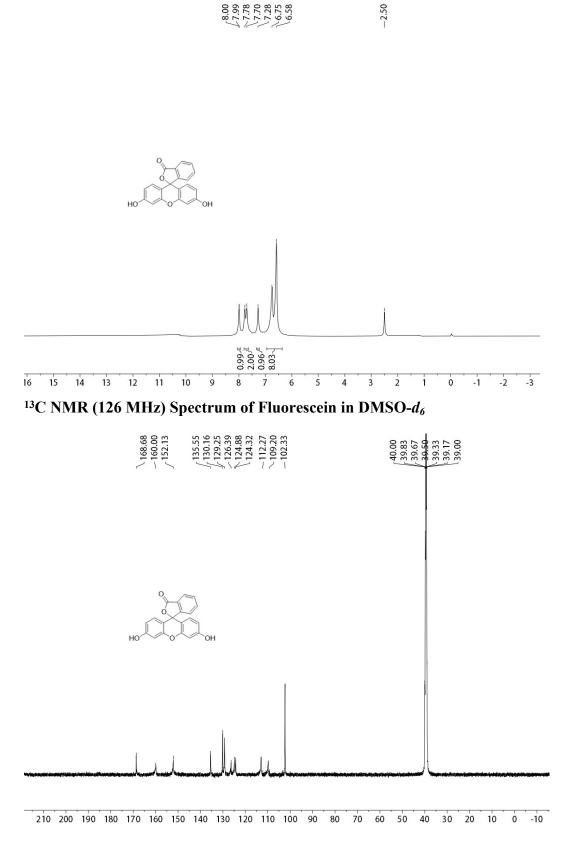
- (a)K. Sun, A. Shi, Y. Liu, X. Chen, P. Xiang, X. Wang, L. Qu, B. Yu, A general electron donor-acceptor complex for photoactivation of arenes via thianthrenation. Chemical Science 13(19) 2022 5659-5666. (b) J. Zhu, Y. Guo, Y. Zhang, W. Li, P Zhang, J. Xu, Visible-light-induced direct perfluoroalkylation/heteroarylation of [1.1. 1] propellane to diverse bicyclo [1.1. 1] pentanes (BCPs) under metal and photocatalyst-free conditions. Green Chemistry. 25(3) (2023) 986-992.
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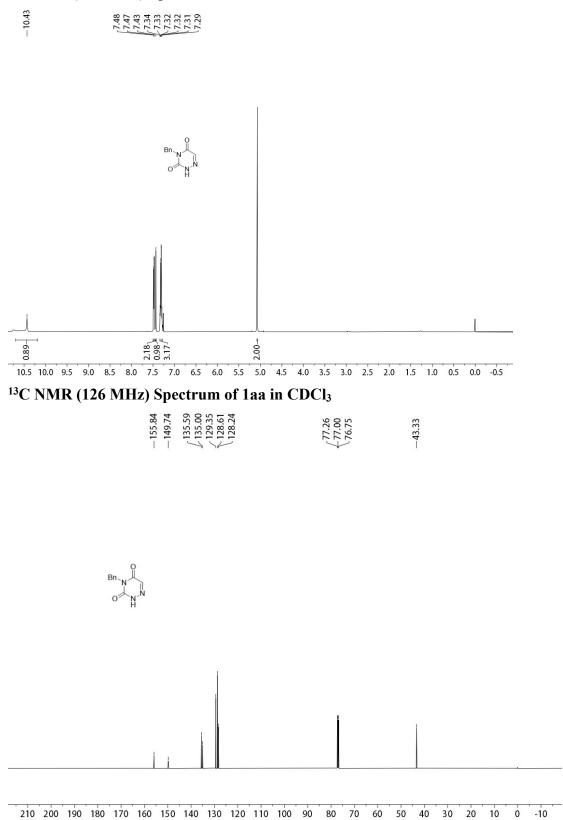
- (a) S. Mehrzadi, H. Khalili, I. Fatemi, A. Malayeri, A. Siahpoosh, M. Goudarzi, Zingerone mitigates carrageenan-induced inflammation through antioxidant and anti-inflammatory activities. Inflammation. 44 (2021) 186-193. (b) J. Choi, S. Kim, Mi. Jeong, M. Oh, Pharmacotherapeutic potential of ginger and its compounds in age-related neurological disorders. Pharmacology & therapeutics. 182 (2018) 56-69. (c) M. Mahomoodally, M. Aumeeruddy, K. Rengasamy, S. Roshan, S. Hammad, J. Pandohee, X. H, G. Zengin, Ginger and its active compounds in cancer therapy: From folk uses to nano-therapeutic applications. Seminars in cancer biology. 69 (2021) 140-149.
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## VI. Copies of <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR Spectra

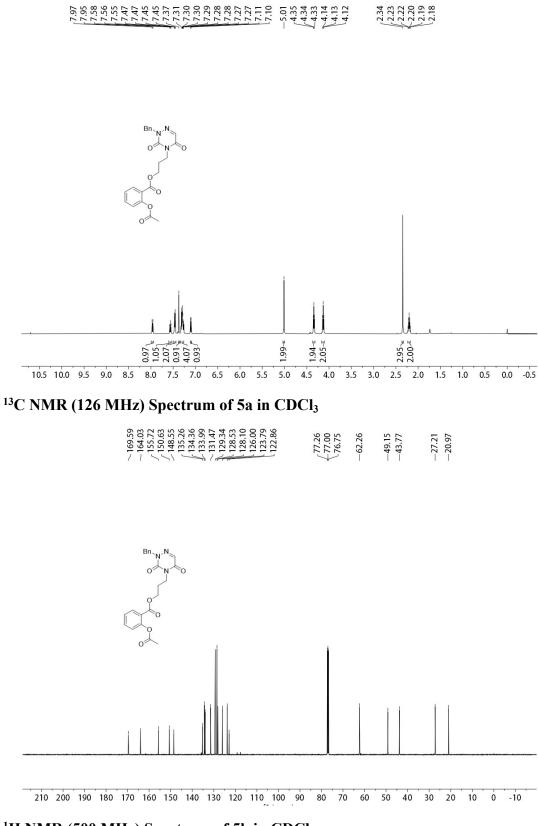




<sup>1</sup>H NMR (500 MHz) Spectrum of 1aa in CDCl<sub>3</sub>



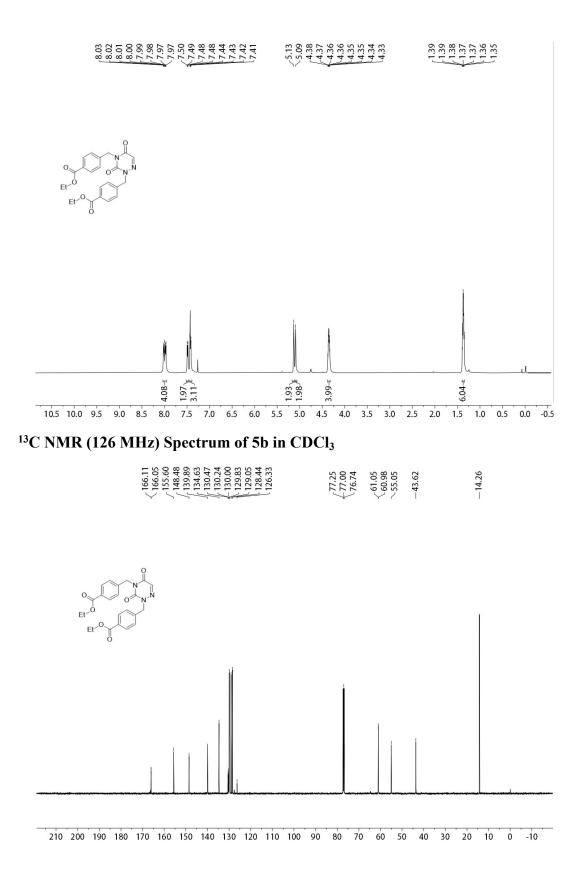
S63

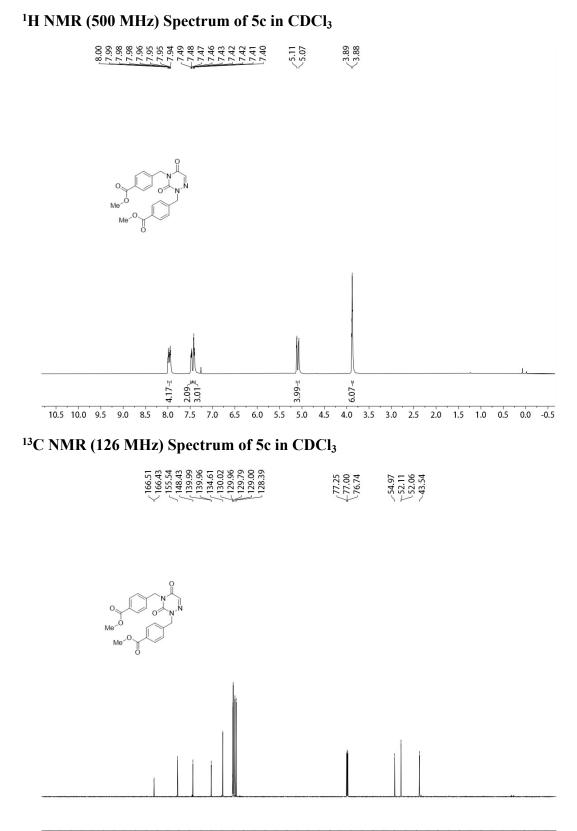




<sup>1</sup>H NMR (500 MHz) Spectrum of 5a in CDCl<sub>3</sub>

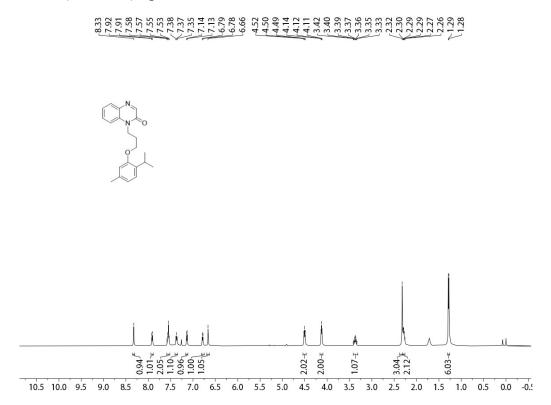
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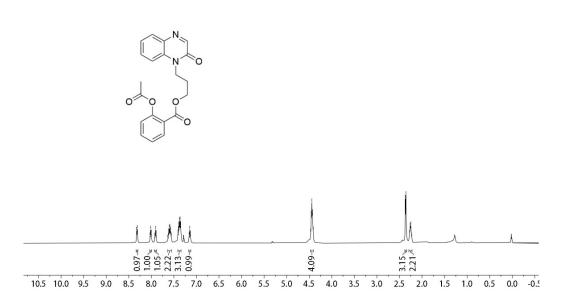


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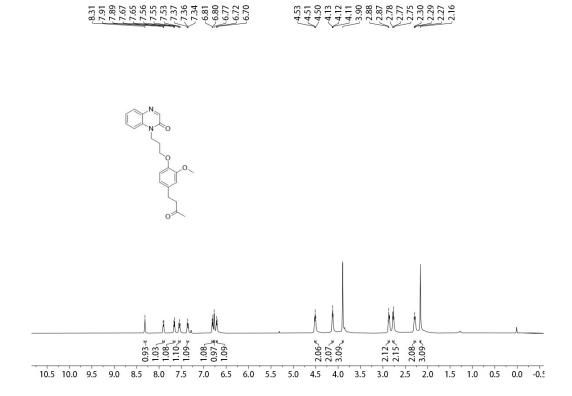
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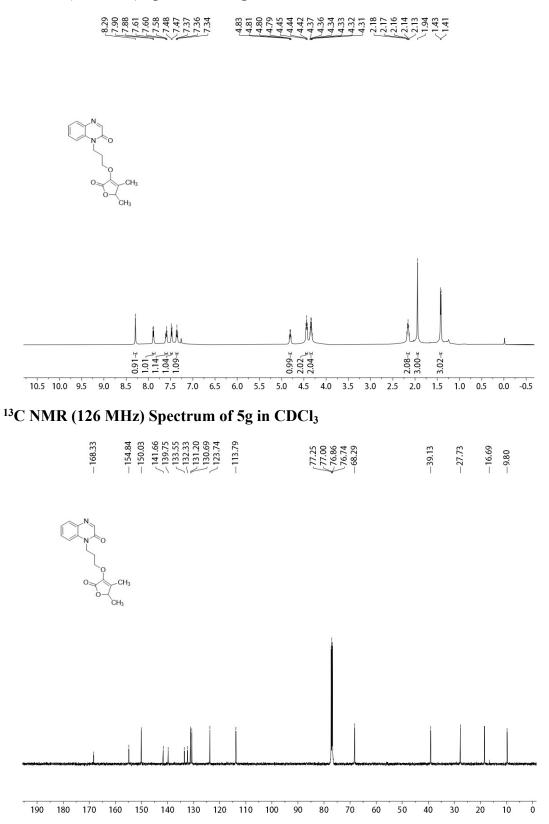


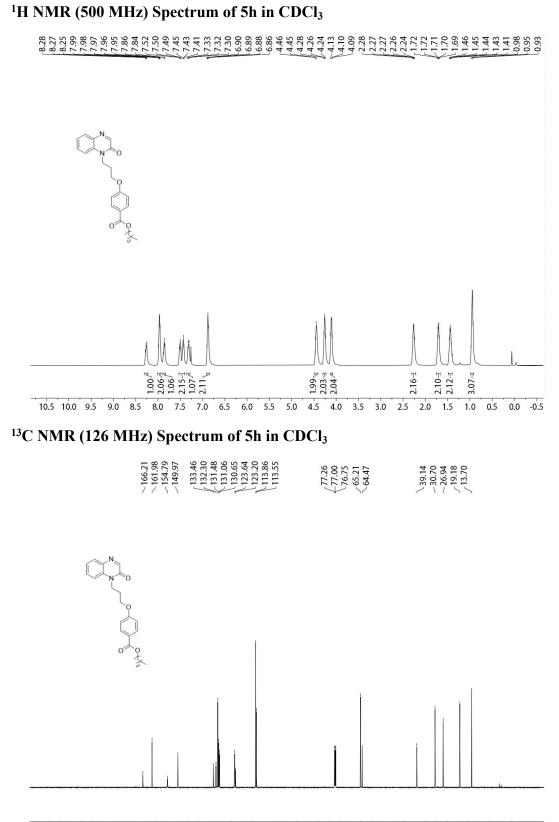
# <sup>1</sup>H NMR (500 MHz) Spectrum of 5e in CDCl<sub>3</sub>



## <sup>1</sup>H NMR (500 MHz) Spectrum of 5f in CDCl<sub>3</sub>

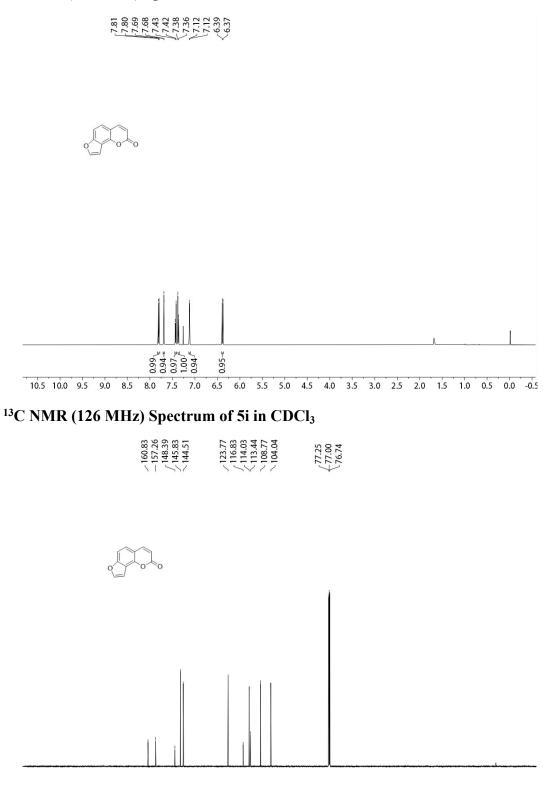






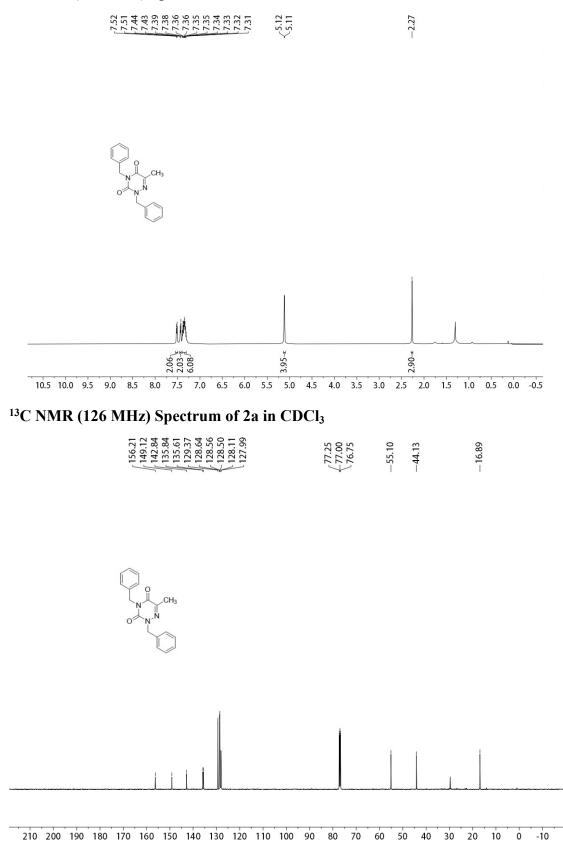
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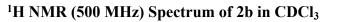
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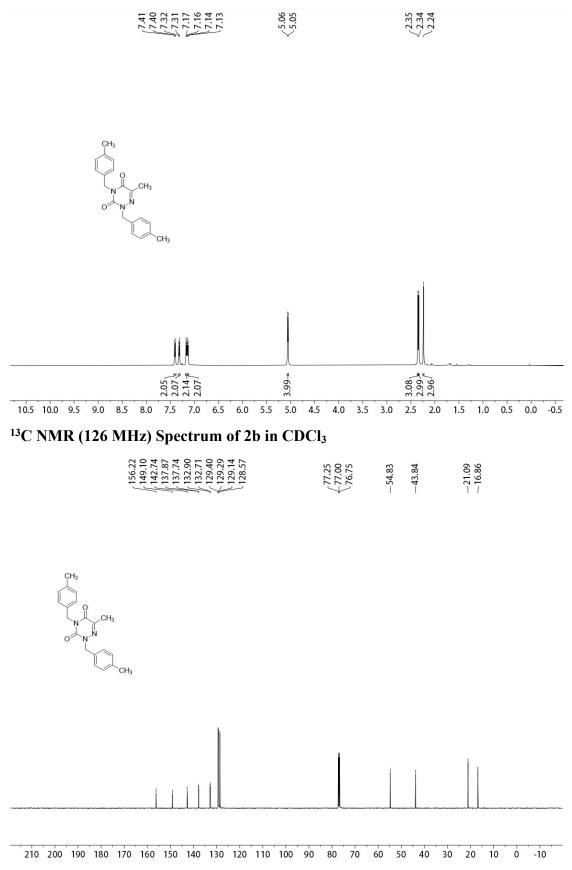


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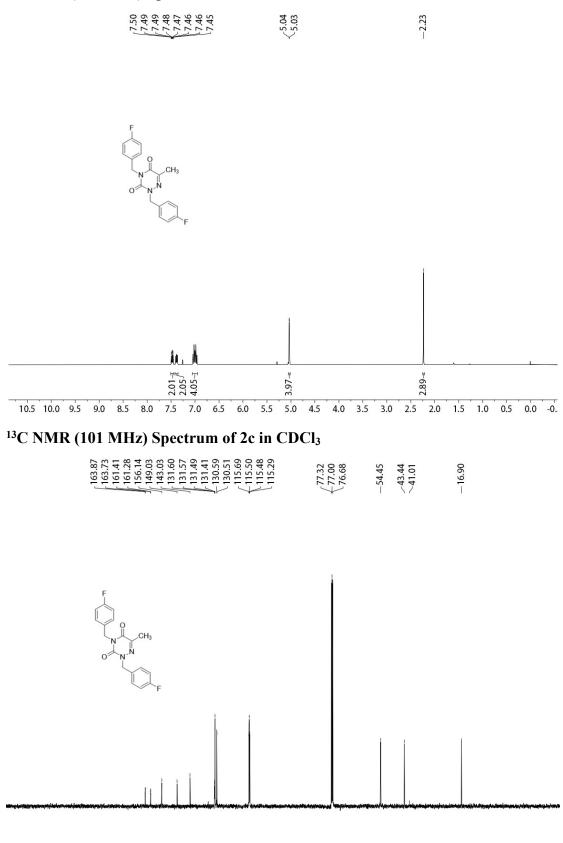
### <sup>1</sup>H NMR (500 MHz) Spectrum of 2a in CDCl<sub>3</sub>







### <sup>1</sup>H NMR (400 MHz) Spectrum of 2c in CDCl<sub>3</sub>

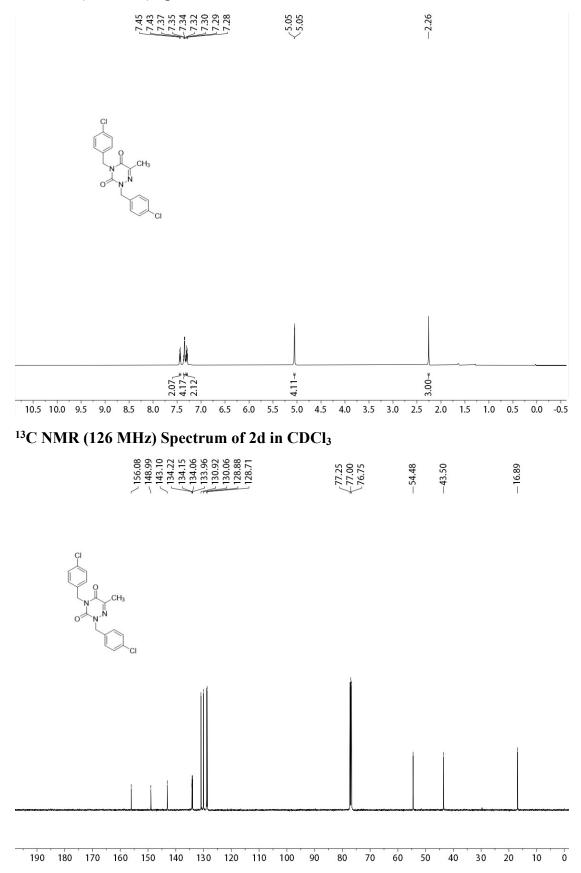


## <sup>19</sup>F NMR (376 MHz) Spectrum of 2c in CDCl<sub>3</sub>

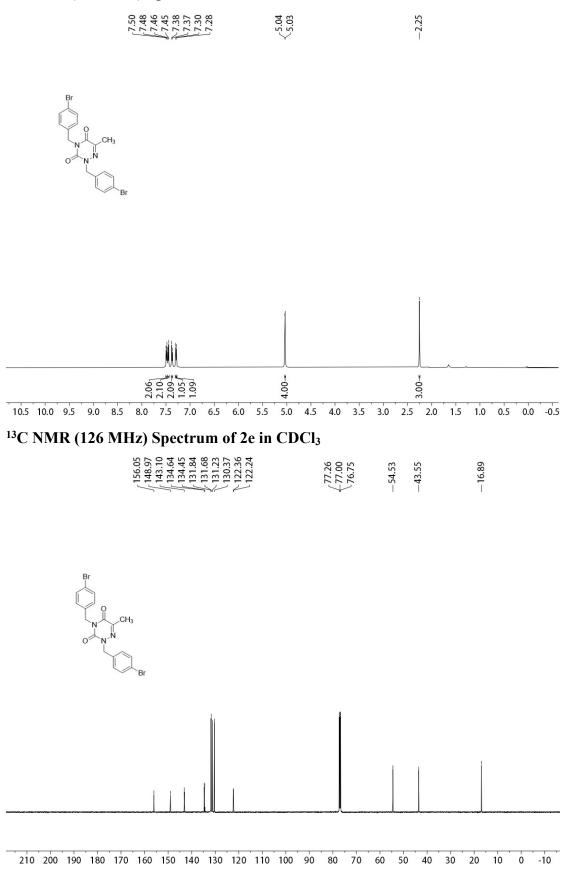
 $<^{-113.66}_{-113.71}$ 

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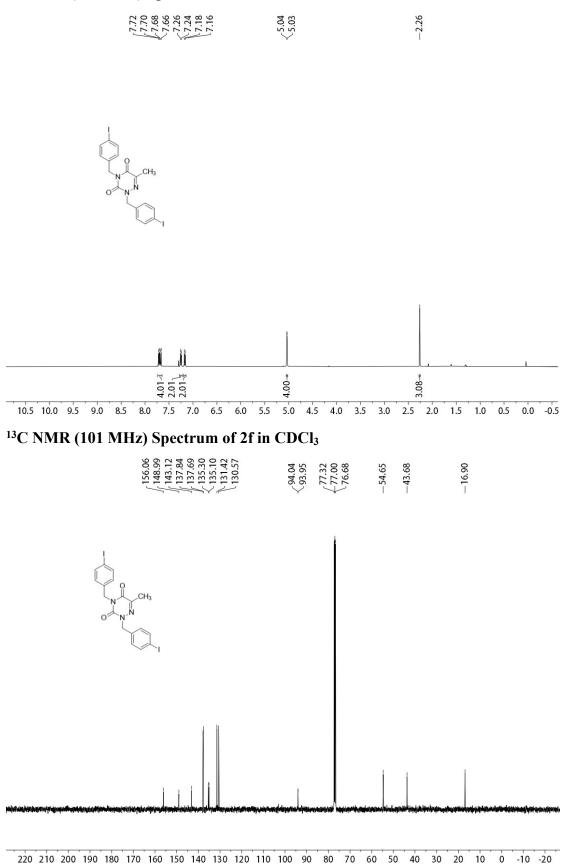
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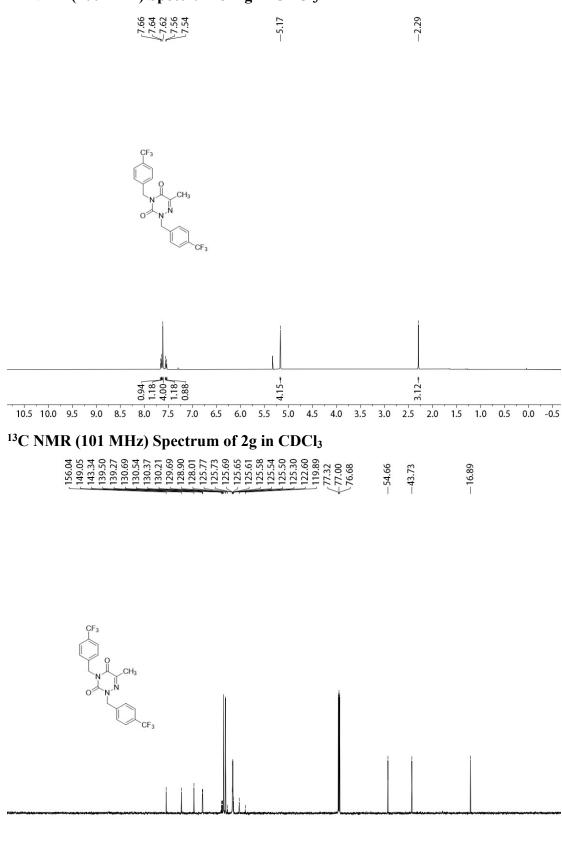
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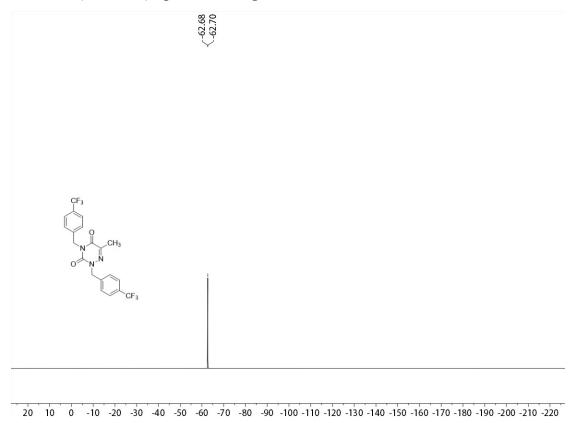
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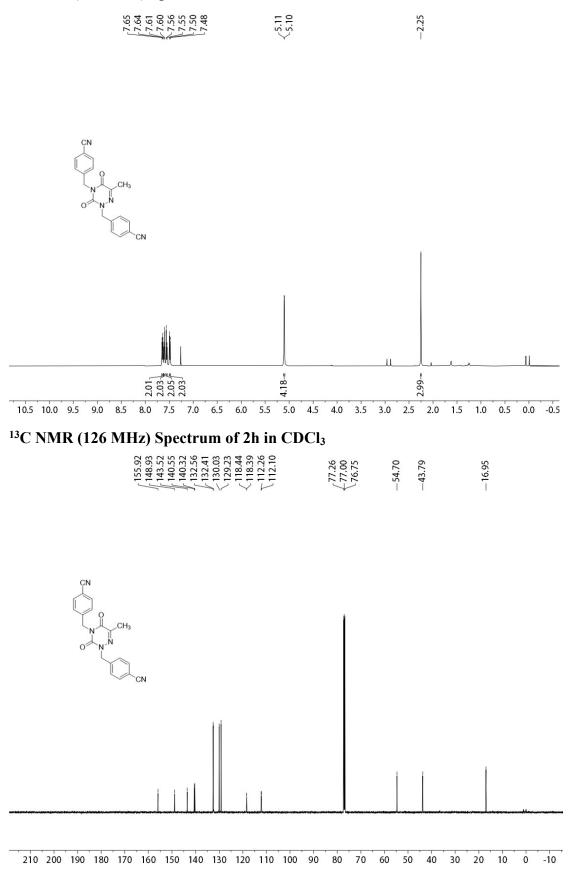
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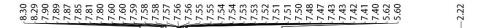


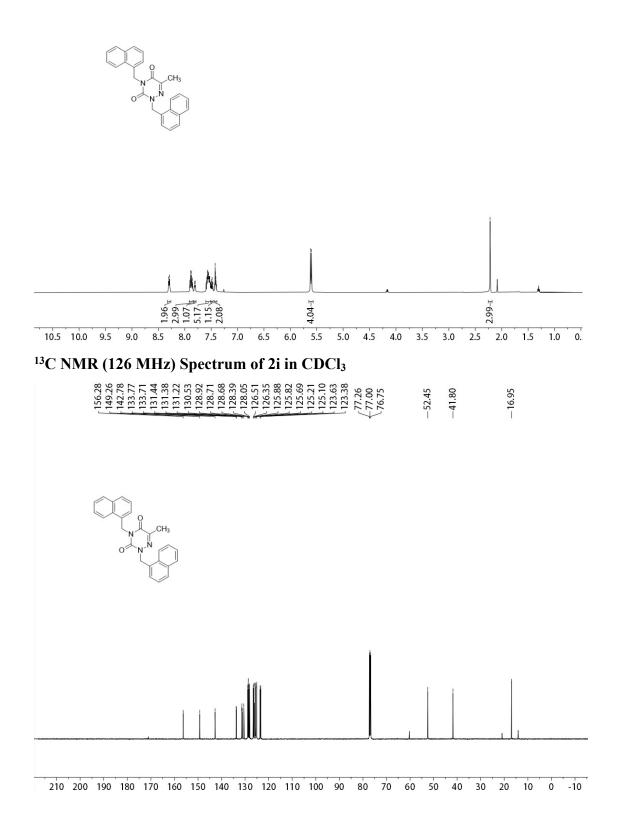
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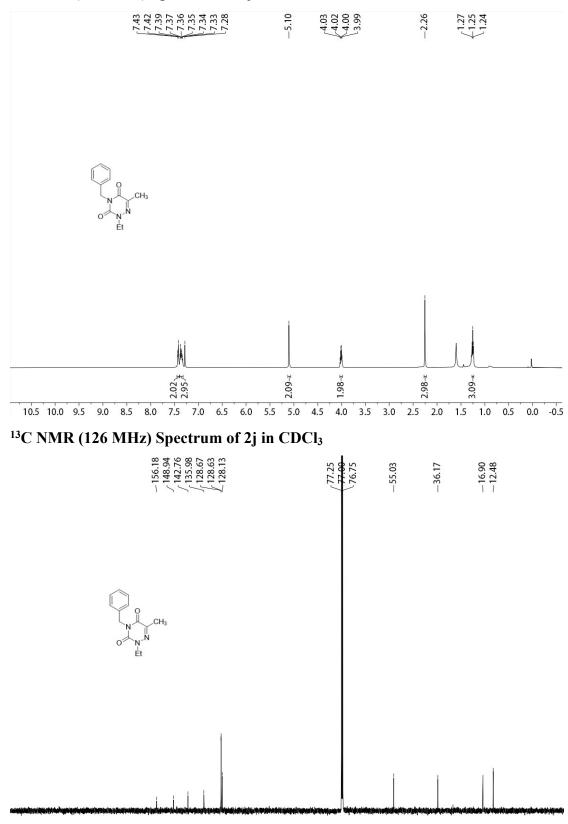


### <sup>1</sup>H NMR (500 MHz) Spectrum of 2h in CDCl<sub>3</sub>





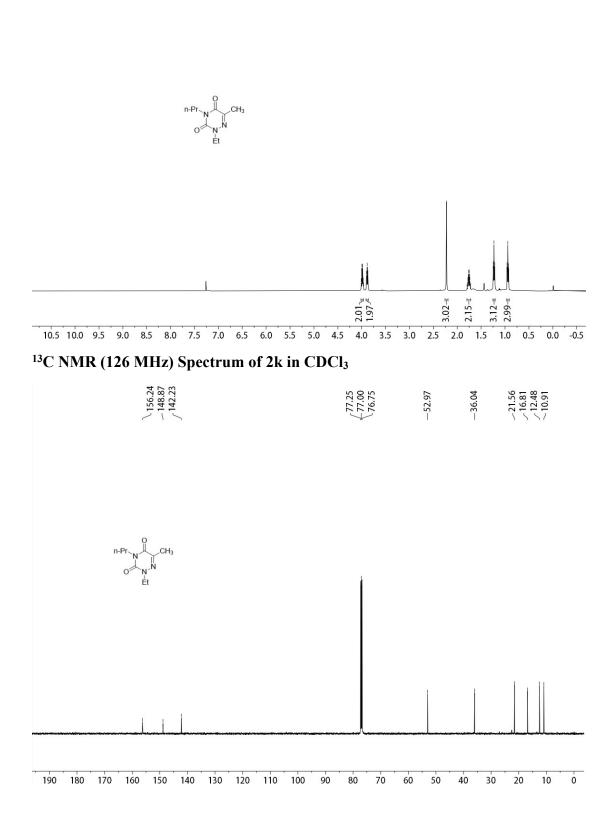


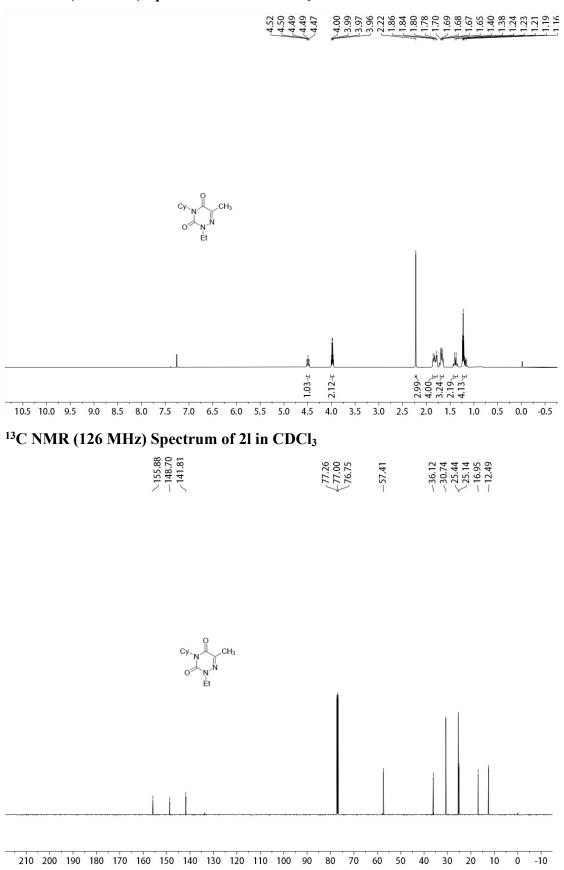


### <sup>1</sup>H NMR (500 MHz) Spectrum of 2j in CDCl<sub>3</sub>

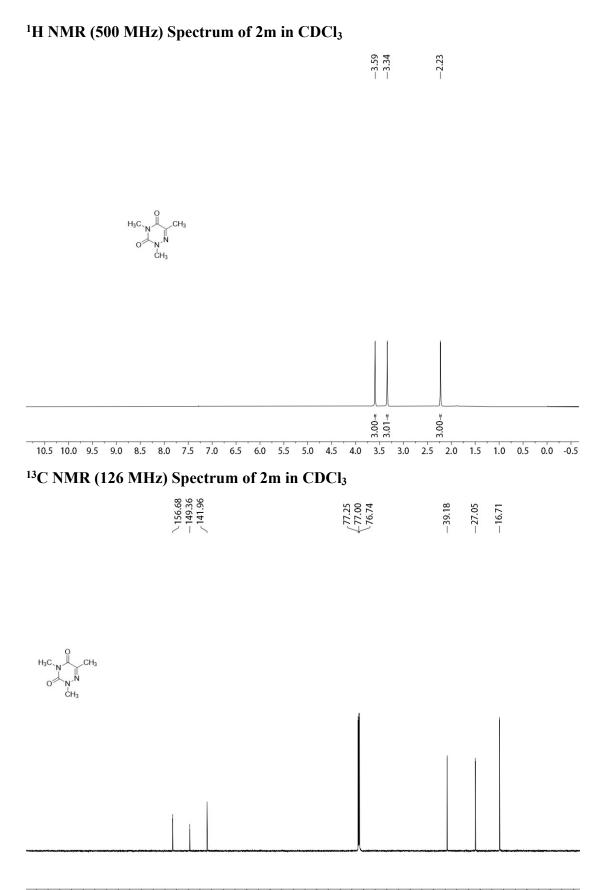
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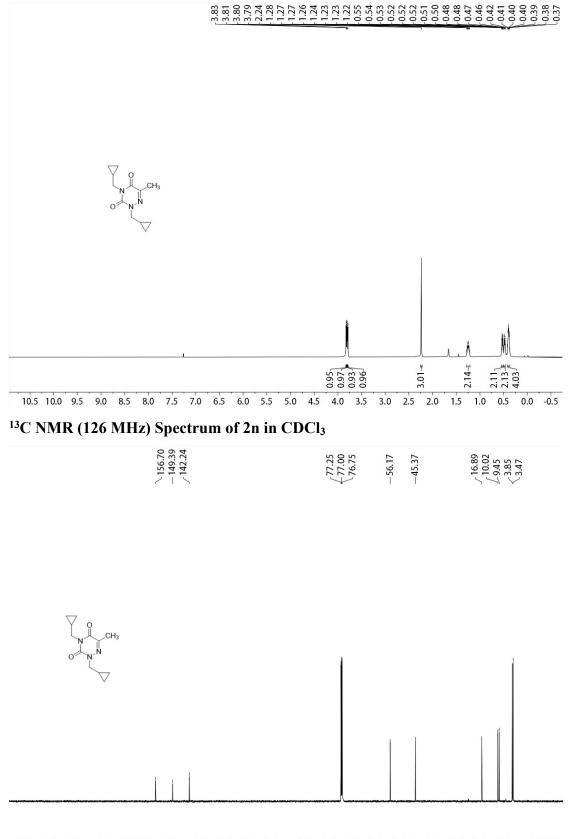
### 4.01 4.00 3.3.97 3.





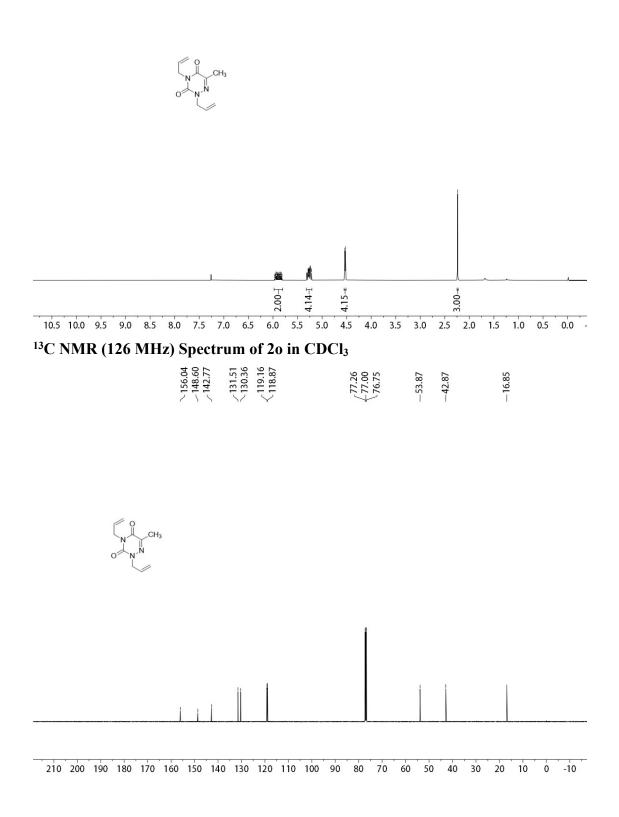
<sup>1</sup>H NMR (500 MHz) Spectrum of 2l in CDCl<sub>3</sub>



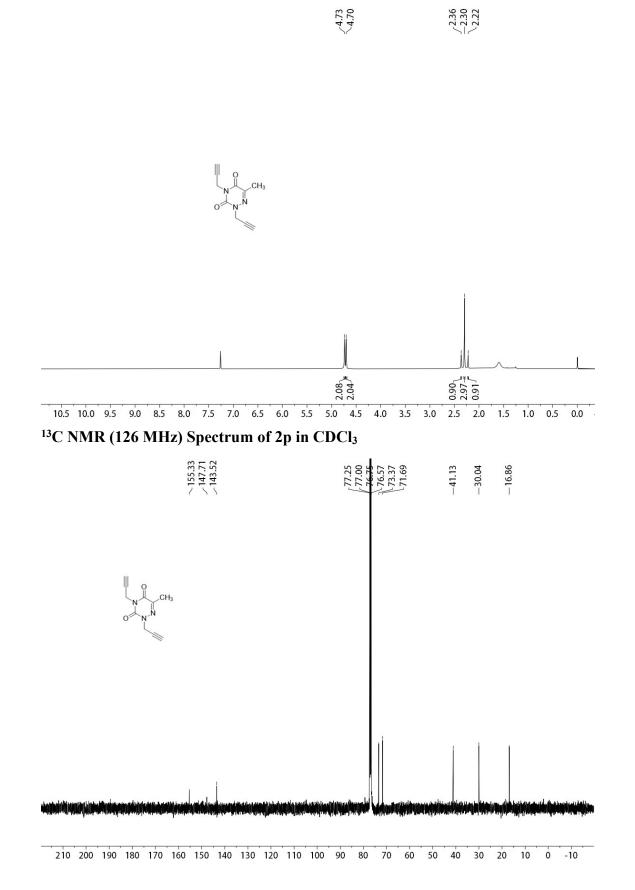


### <sup>1</sup>H NMR (500 MHz) Spectrum of 2n in CDCl<sub>3</sub>

### <sup>1</sup>H NMR (500 MHz) Spectrum of 20 in CDCl<sub>3</sub>

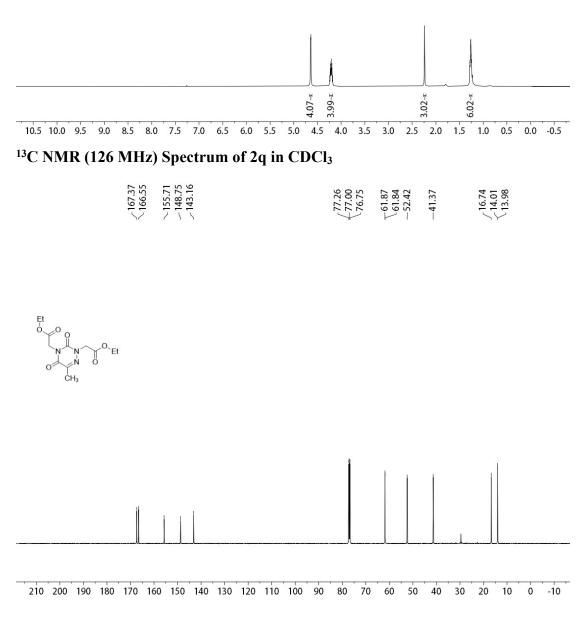


### <sup>1</sup>H NMR (500 MHz) Spectrum of 2p in CDCl<sub>3</sub>

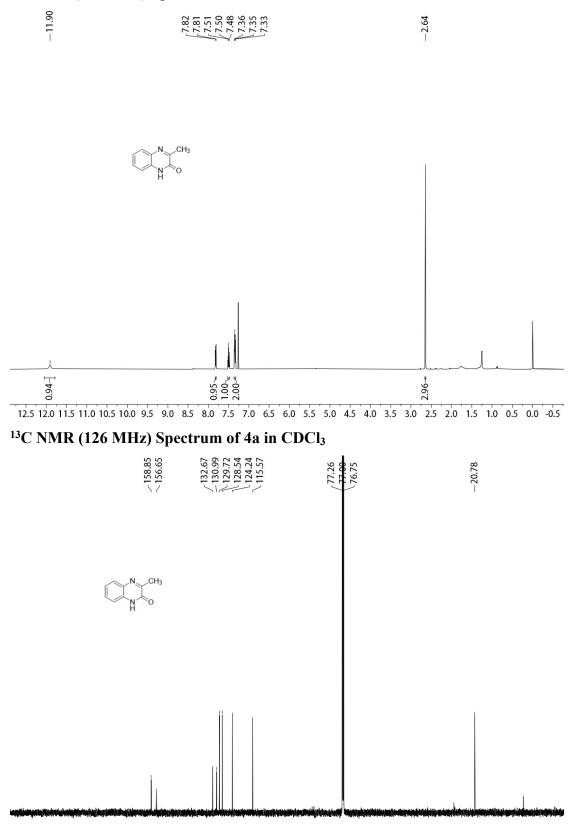


<sup>1</sup>H NMR (500 MHz) Spectrum of 2q in CDCl<sub>3</sub>

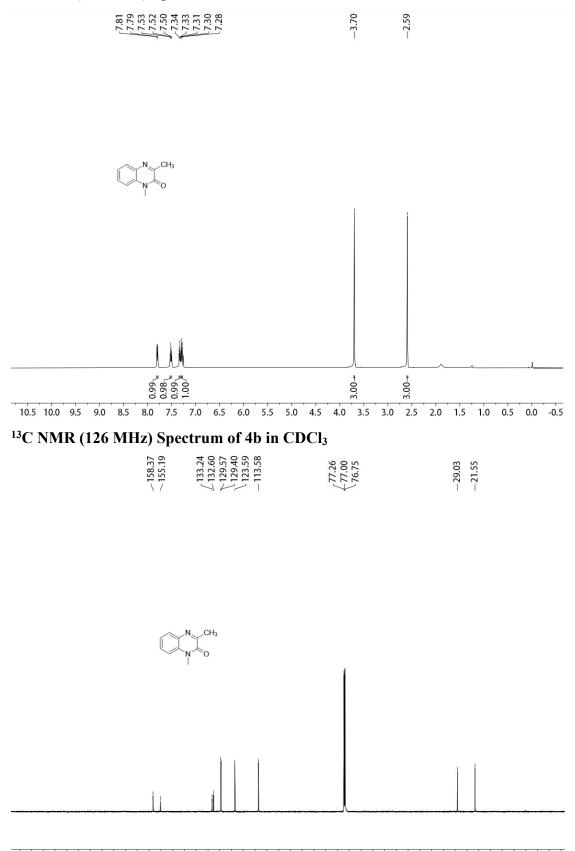




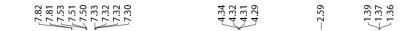


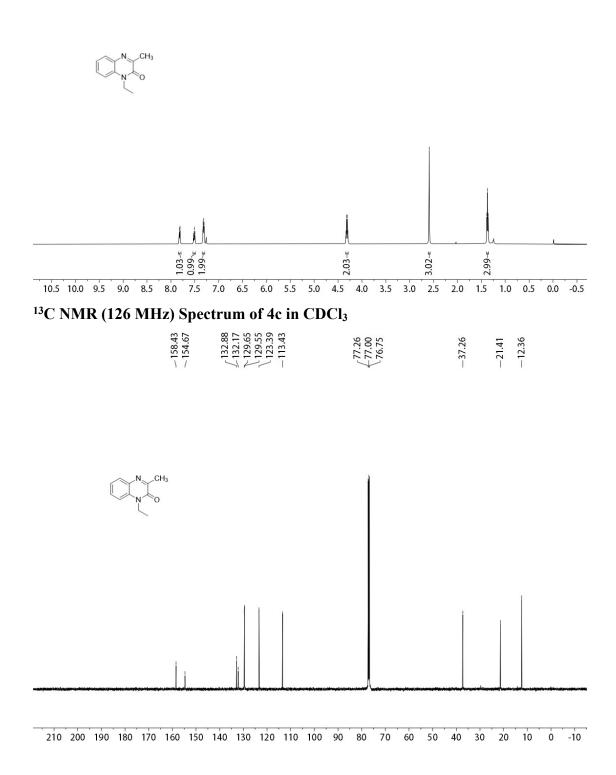




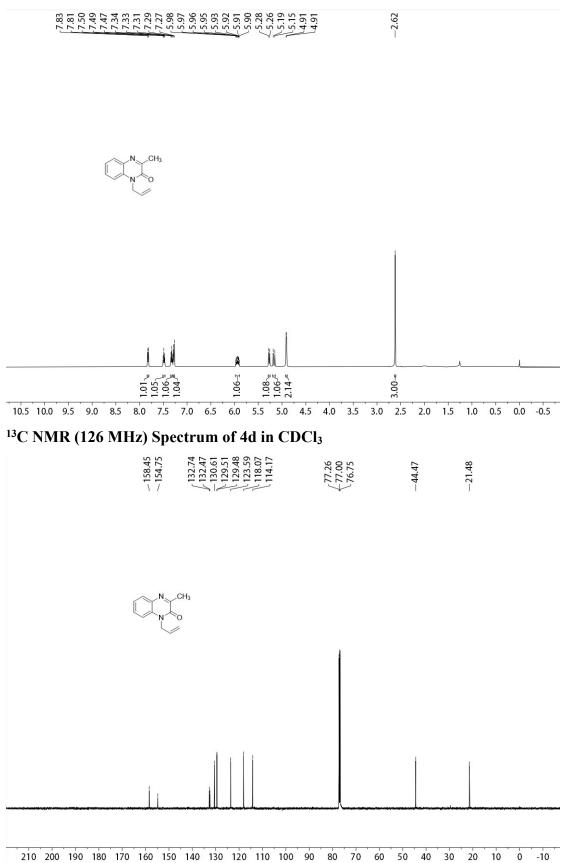


### <sup>1</sup>H NMR (500 MHz) Spectrum of 4c in CDCl<sub>3</sub>

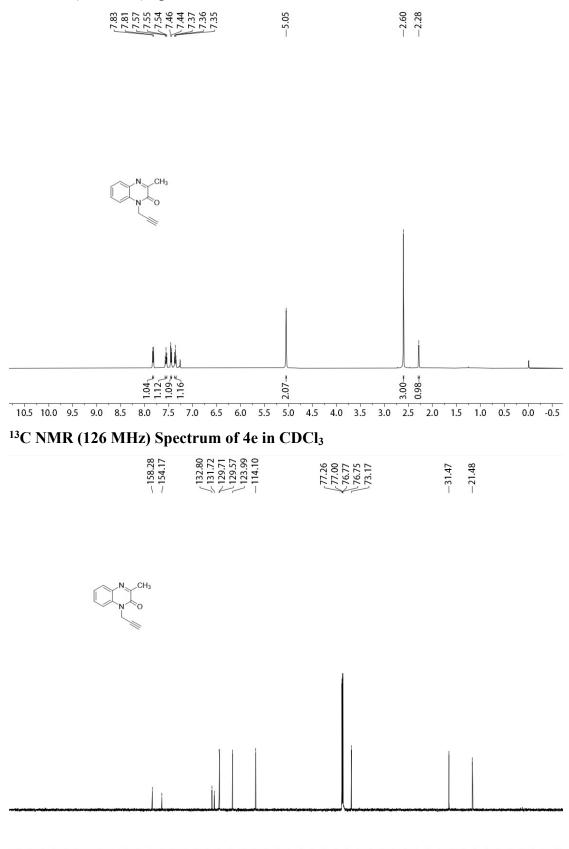


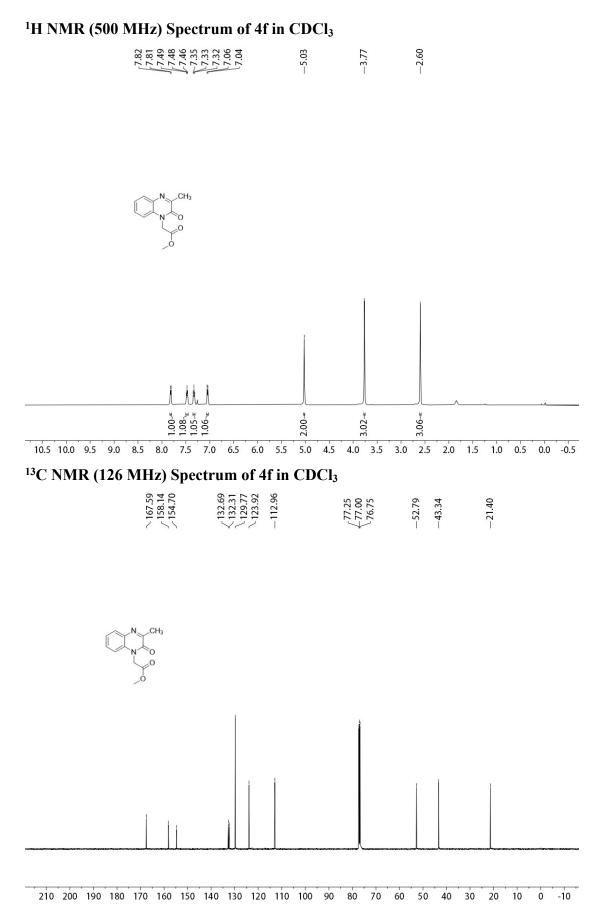




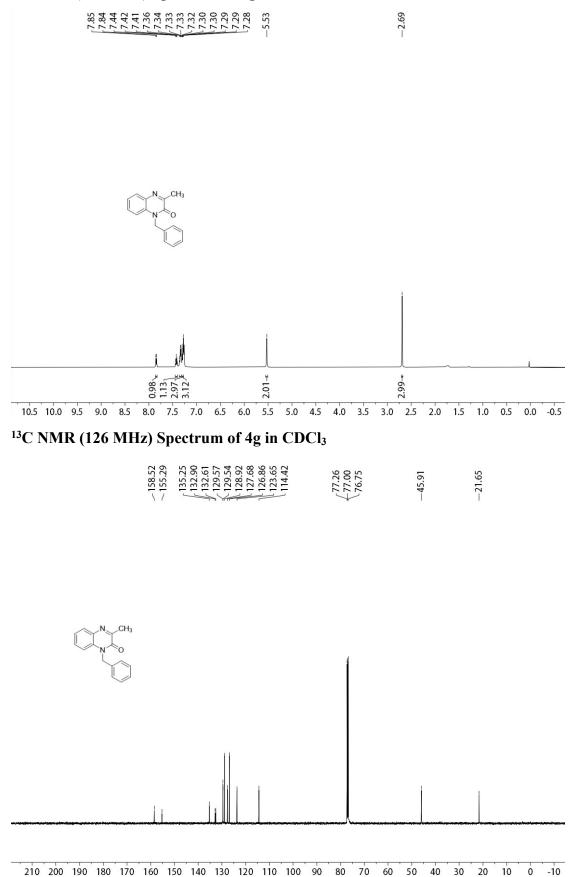


### <sup>1</sup>H NMR (500 MHz) Spectrum of 4e in CDCl<sub>3</sub>

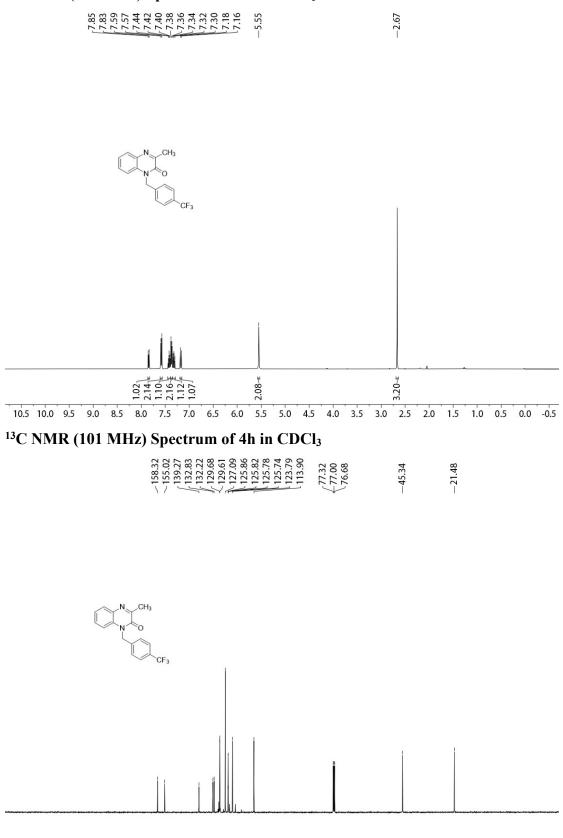










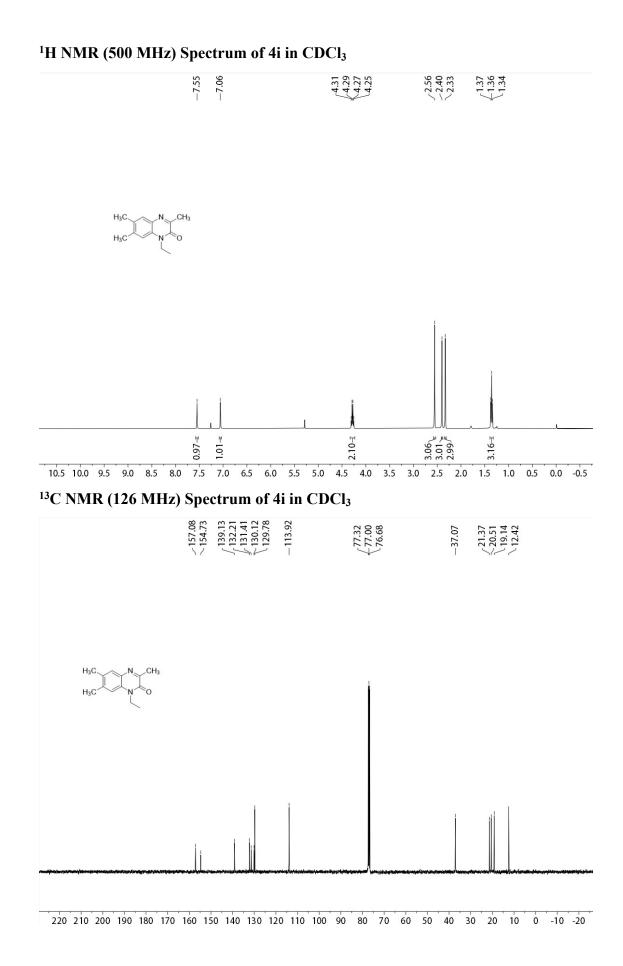


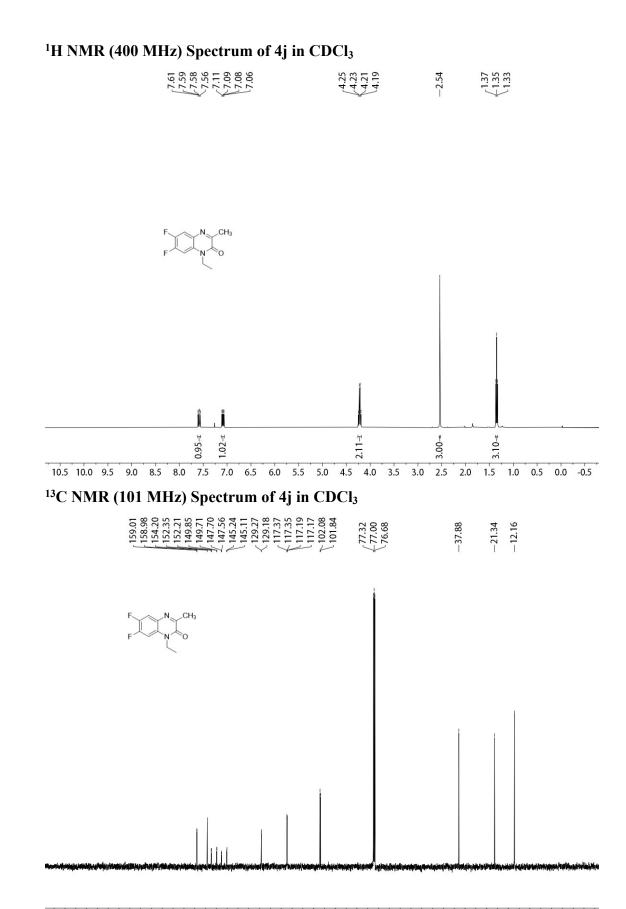
## <sup>19</sup>F NMR (471 MHz) Spectrum of 4h in CDCl<sub>3</sub>





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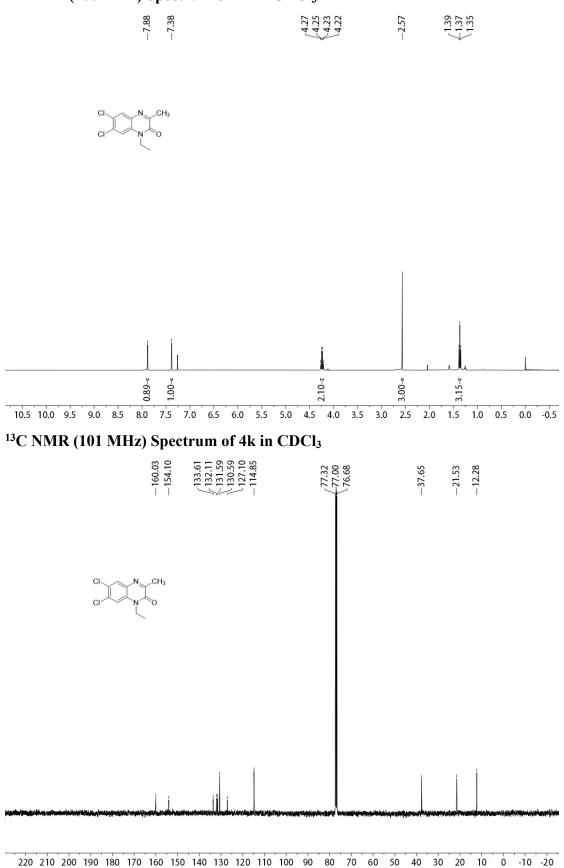
# <sup>19</sup>F NMR (471 MHz) Spectrum of 4j in CDCl<sub>3</sub>

---132.08 ---142.33



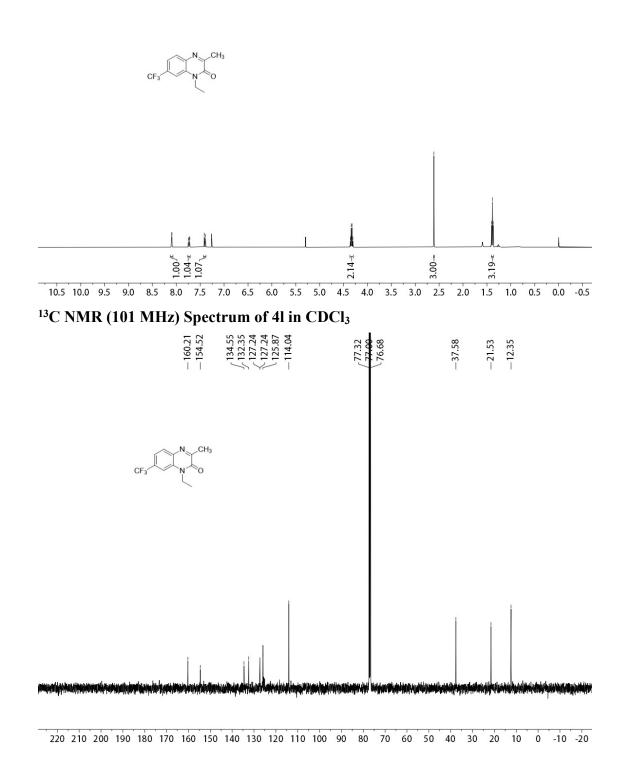
0 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210





### <sup>1</sup>H NMR (400 MHz) Spectrum of 4l in CDCl<sub>3</sub>





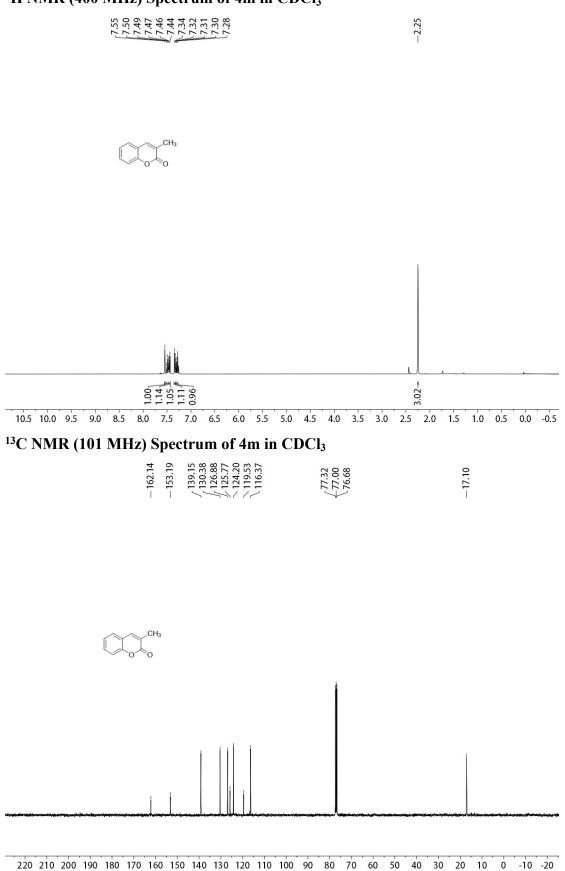
## <sup>19</sup>F NMR (376 MHz) Spectrum of 4l in CDCl<sub>3</sub>

---62.01

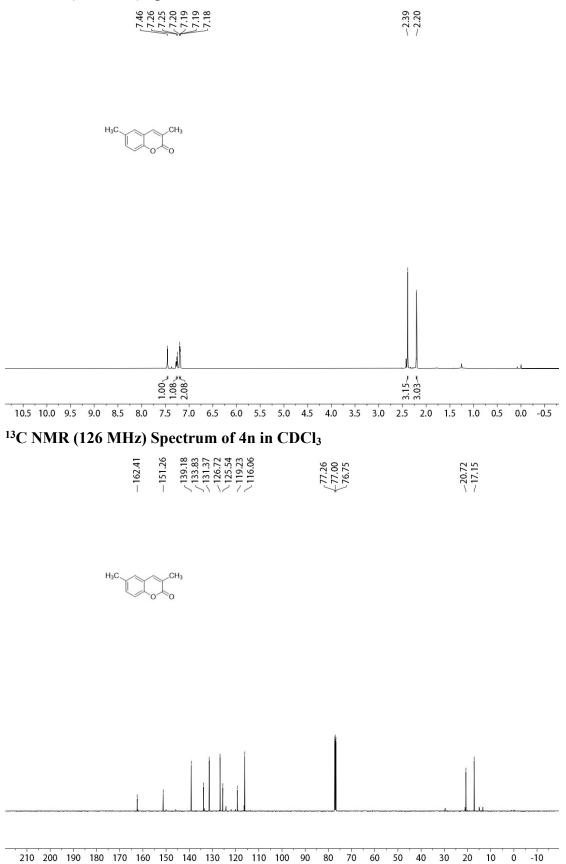
CF3 0

20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220

#### <sup>1</sup>H NMR (400 MHz) Spectrum of 4m in CDCl<sub>3</sub>



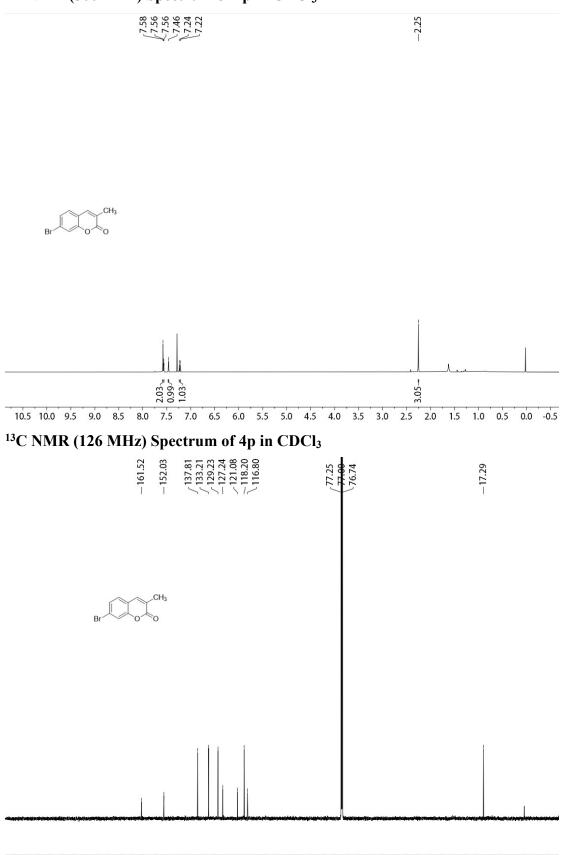
#### <sup>1</sup>H NMR (500 MHz) Spectrum of 4n in CDCl<sub>3</sub>



## <sup>1</sup>H NMR (500 MHz) Spectrum of 40 in CDCl<sub>3</sub> -3.86 -2.17 7.32 7.32 6.83 6.83 6.83 CH3 H<sub>3</sub>CO<sup>2</sup> ~86.0 2.02 -3.01--3.05--10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 <sup>13</sup>C NMR (126 MHz) Spectrum of 40 in CDCl<sub>3</sub> ~127.78 \_122.12 ∫113.18 ∫112.36 162.61 161.70 154.85 77.26 77.00 76.75 -55.69 -16.97 H<sub>3</sub>CO<sup>2</sup>

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

<sup>1</sup>H NMR (500 MHz) Spectrum of 4p in CDCl<sub>3</sub>

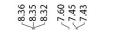


50 40 30

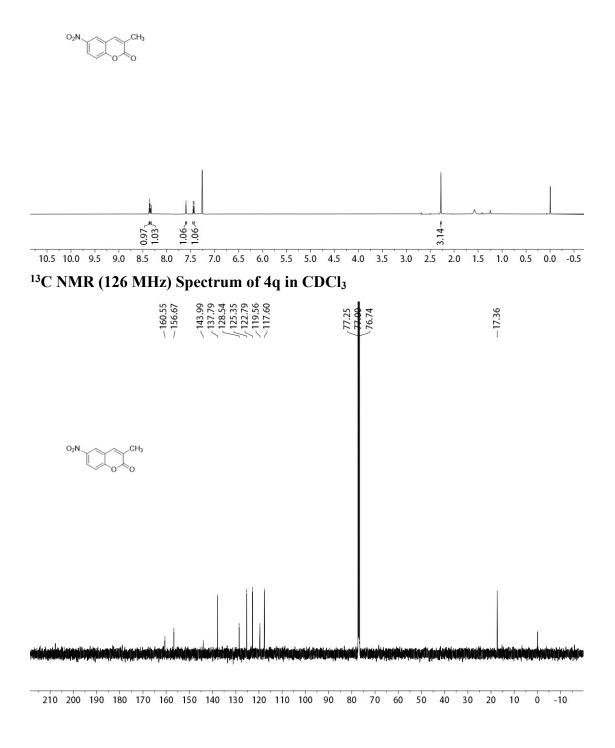
20 10 0 -10

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60

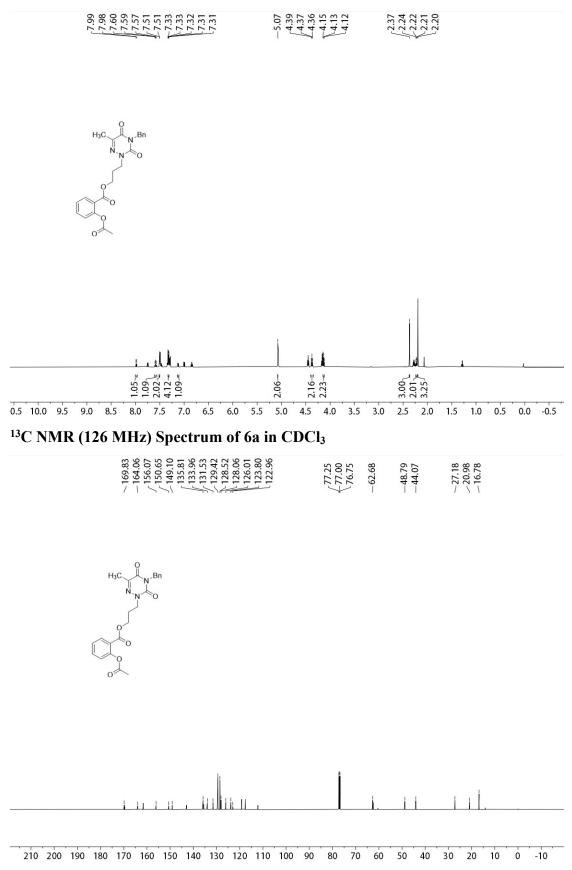




-2.28

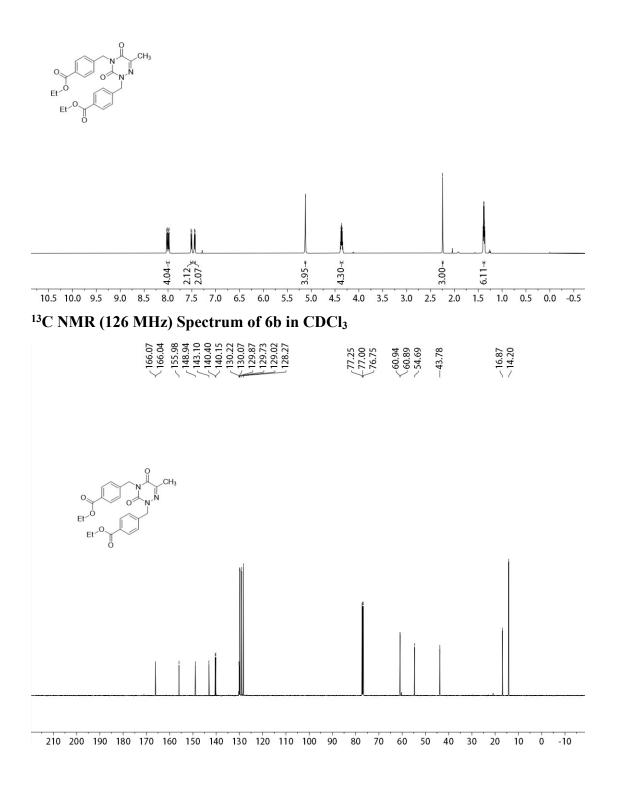


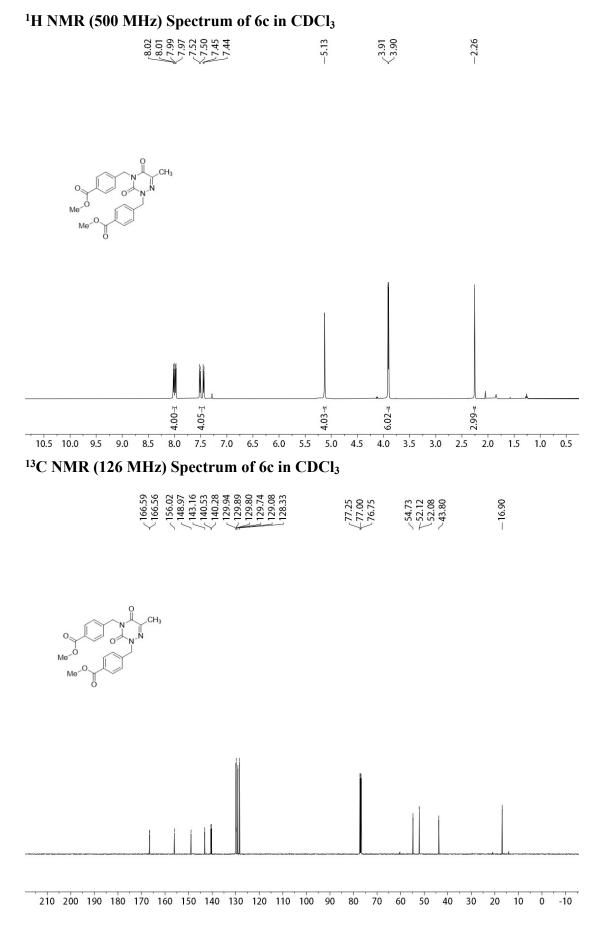




#### <sup>1</sup>H NMR (500 MHz) Spectrum of 6b in CDCl<sub>3</sub>

43 45 45 43 43 43 43 43 43 43 43 43 43 43 43 43	335 335 345 35 35 35 35 35 35 35 35 35 35 35 35 35	25 25 39 33 33 36 36
00000000	04444444	$\alpha$ $       -$

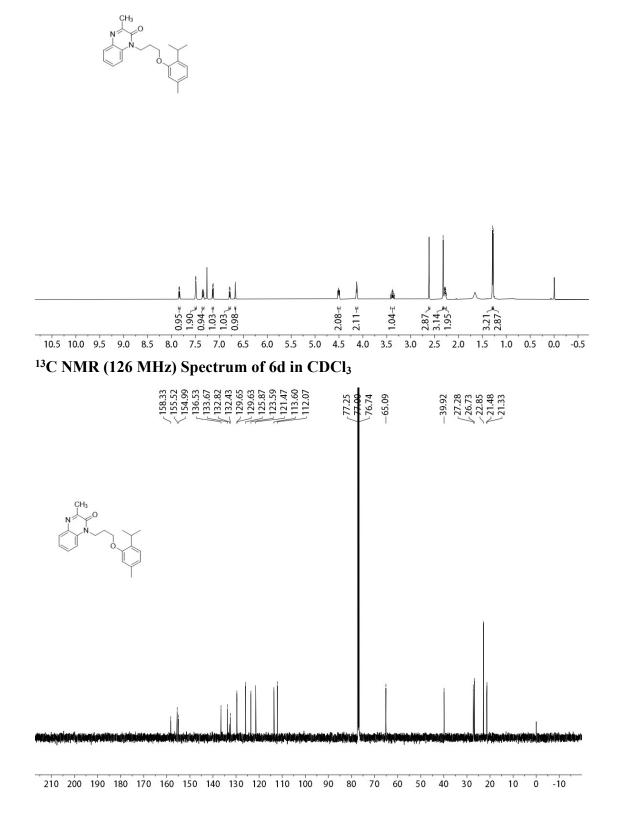




<sup>1</sup>H NMR (500 MHz) Spectrum of 6d in CDCl<sub>3</sub>

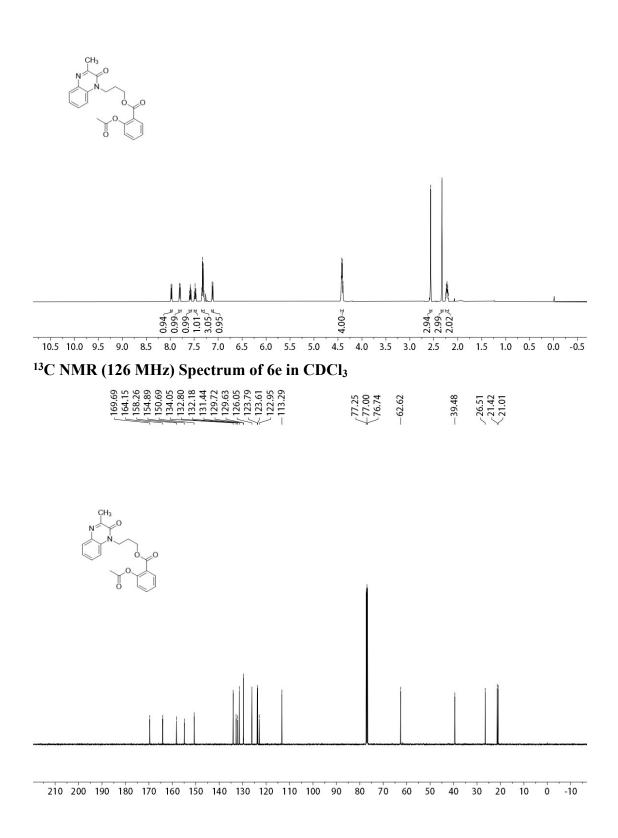
7.35 7.35 7.35 7.35 7.35 7.35 7.35 7.33 6.7 6.79 6.66 6.79

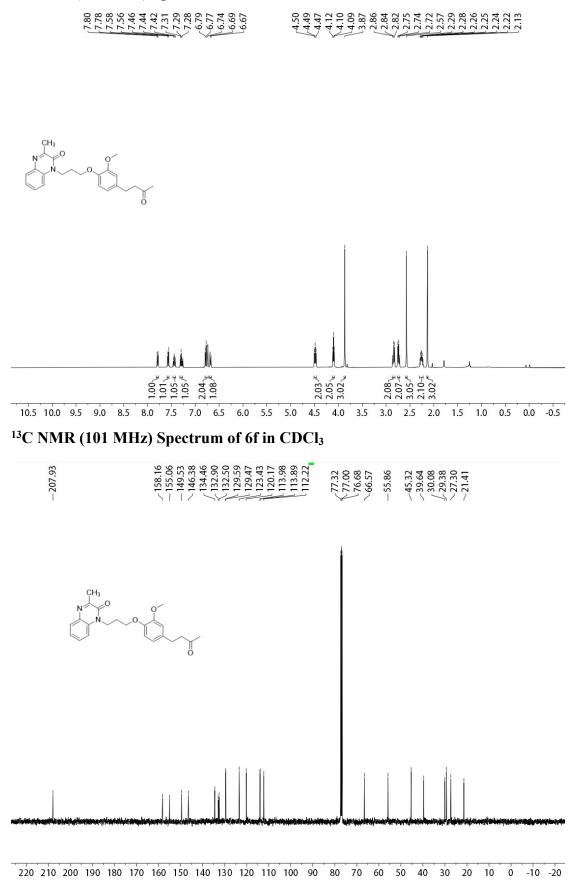
 $\begin{array}{c} 3.42\\ 3.32\\ 3.33\\$ 



#### <sup>1</sup>H NMR (500 MHz) Spectrum of 6e in CDCl<sub>3</sub>

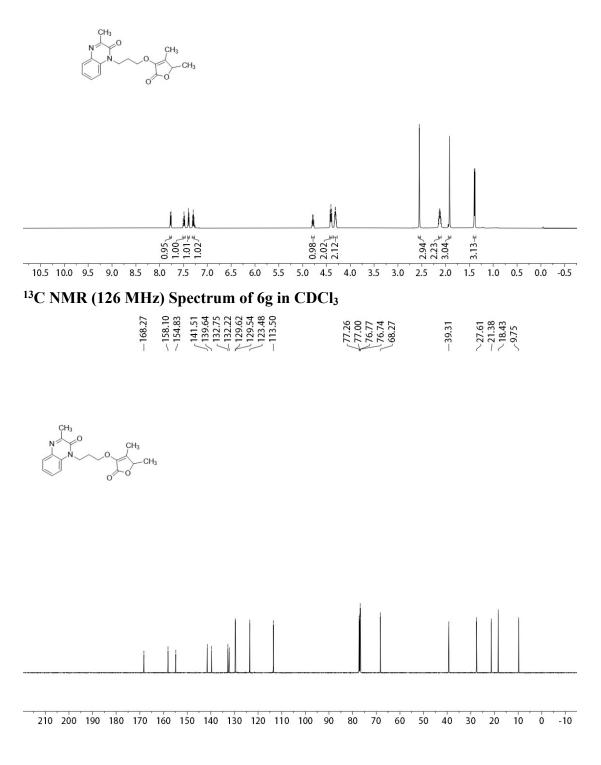
7.97 7.97 7.97 7.77 7.77 7.7.75 7.7.75 7.7.77 7.7.77 7.7.73 7.7.73 7.7.73 7.7.73 7.7.33 7.7.33 7.7.33 7.7.33 7.7.33 7.7.33 7.7.33 7.7.33 7.7.33 7.7.33 7.7.33 7.7.33 7.7.33 7.7.33 7.7.33 7.7.33 7.7.33 7.7.347 7.7.347 7.7.347 7.7.347 7.7.347 7.7.347 7.7.3347 7.7.347 7.7	4.43 4.42 4.41 4.39	2.25 2.25 2.24 2.22 2.20 2.20 2.20
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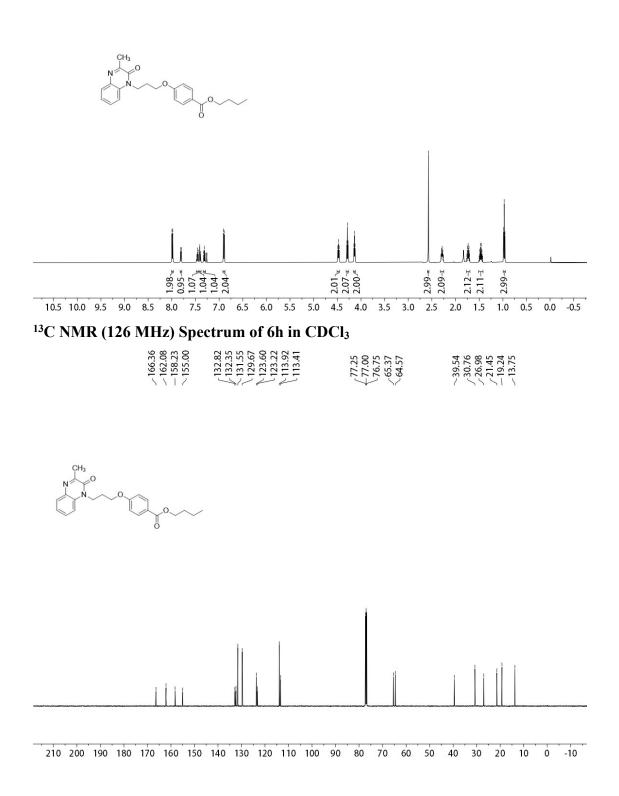
#### <sup>1</sup>H NMR (500 MHz) Spectrum of 6g in CDCl<sub>3</sub>

### 

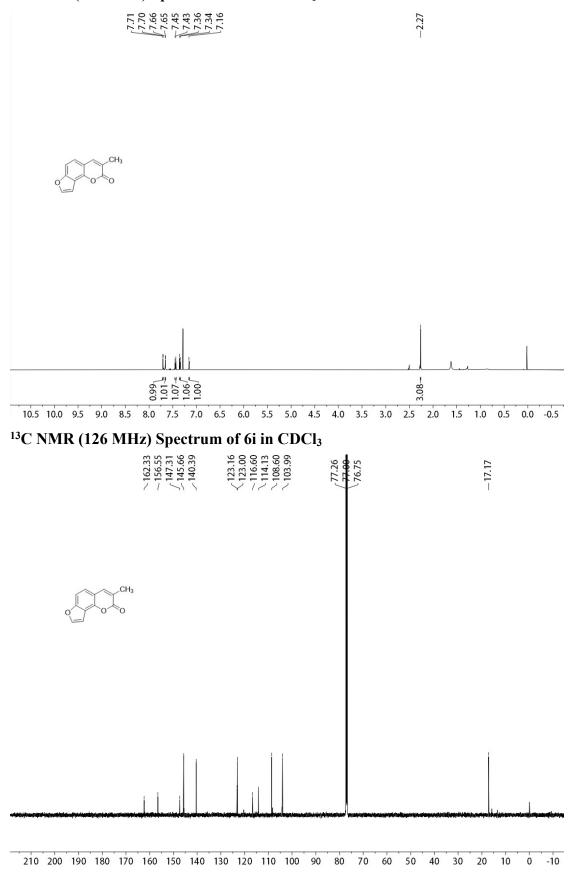


#### <sup>1</sup>H NMR (500 MHz) Spectrum of 6h in CDCl<sub>3</sub>

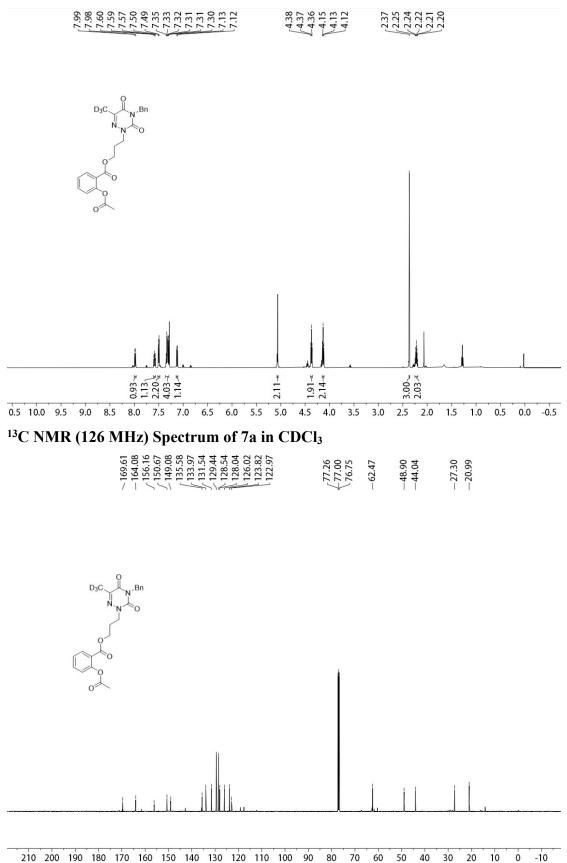




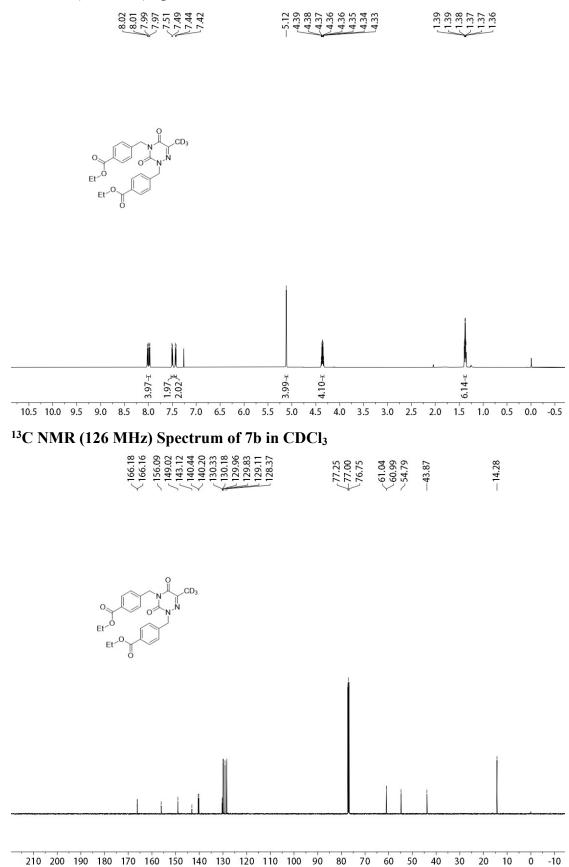
#### <sup>1</sup>H NMR (500 MHz) Spectrum of 6i in CDCl<sub>3</sub>





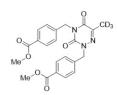


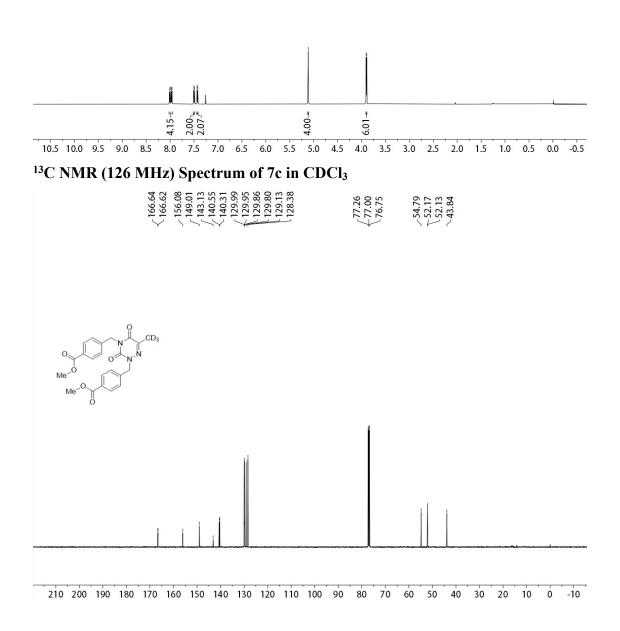
#### <sup>1</sup>H NMR (500 MHz) Spectrum of 7b in CDCl<sub>3</sub>



#### <sup>1</sup>H NMR (500 MHz) Spectrum of 7c in CDCl<sub>3</sub>



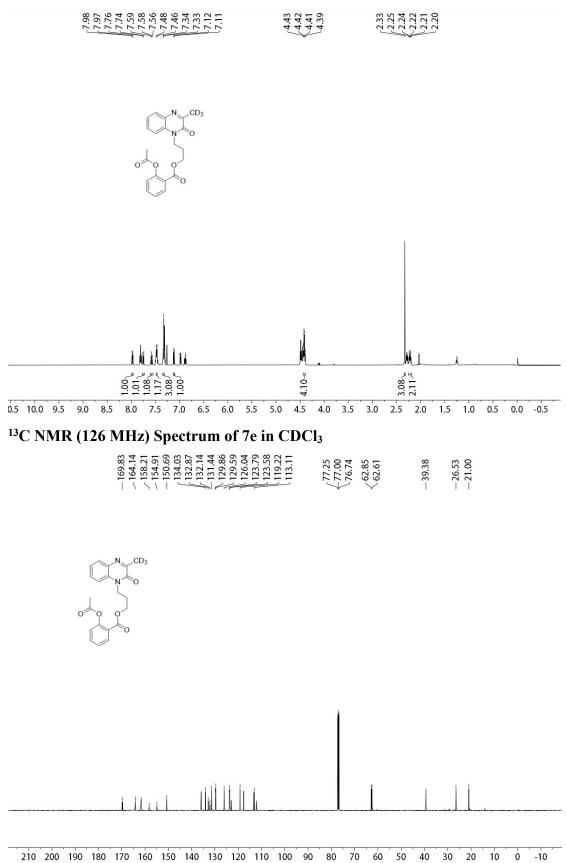


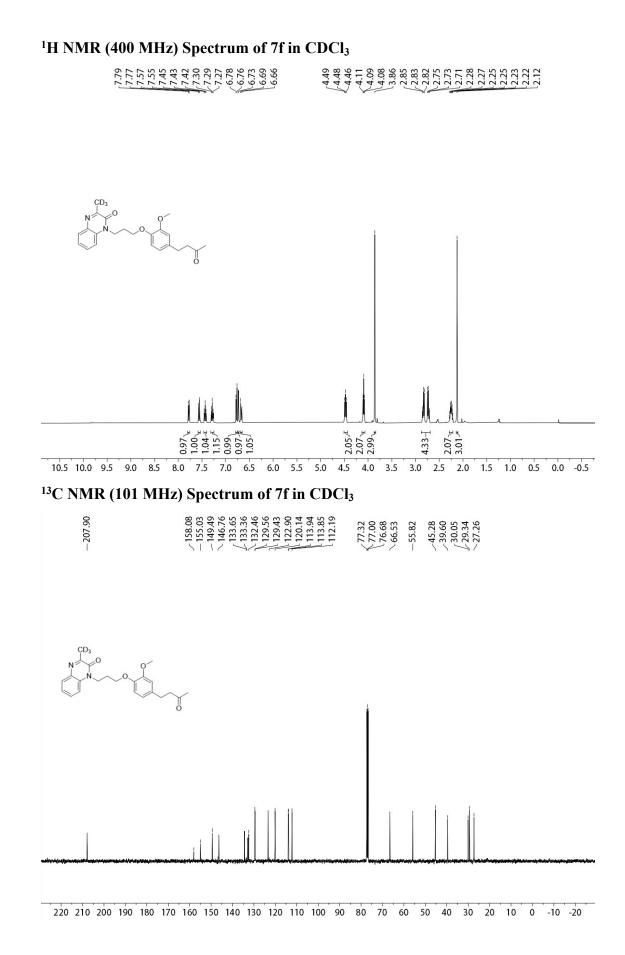


# <sup>1</sup>H NMR (500 MHz) Spectrum of 7d in CDCl<sub>3</sub> 7.85 7.83 7.83 7.15 7.15 7.15 7.15 7.13 6.73 6.67 8 .95*⊥* 1.98<sub>-</sub>T 3.06 € 1.85 € 2.91 3.10 0.98⊣ -66.0 .92 0.95 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 <sup>13</sup>C NMR (126 MHz) Spectrum of 7d in CDCl<sub>3</sub> 7158.25 7155.48 7154.48 7136.48 7132.86 7132.86 7132.86 7132.86 7132.85 7132.85 7132.85 7132.85 7132.85 7132.85 7132.85 7132.56 7172.56 7175.56 7175.5 77.25 777.00 76.74 -65.06 -39.8627.2626.7022.8221.31

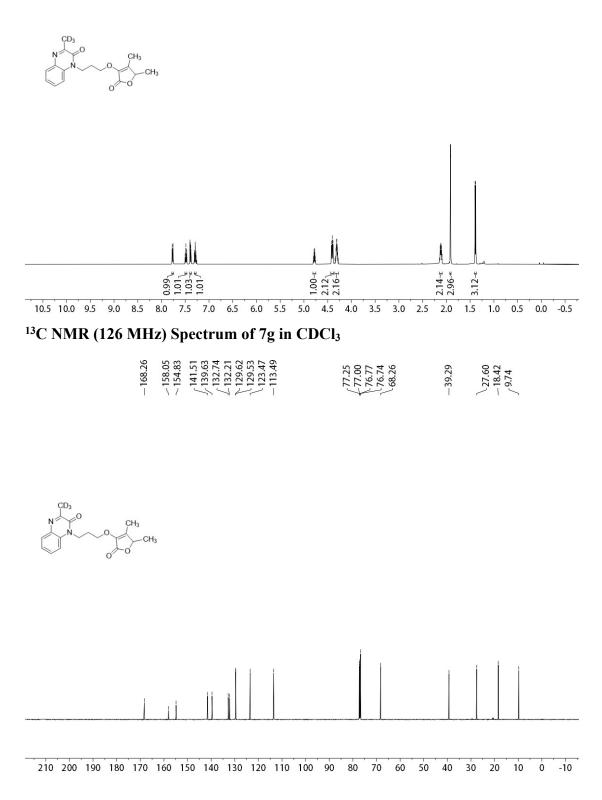
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10



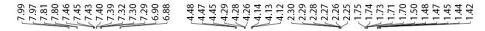


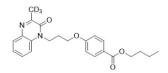


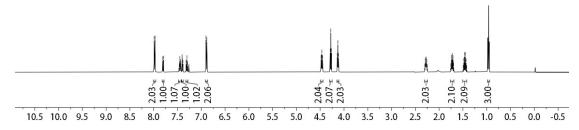
#### <sup>1</sup>H NMR (500 MHz) Spectrum of 7g in CDCl<sub>3</sub>



#### <sup>1</sup>H NMR (500 MHz) Spectrum of 7h in CDCl<sub>3</sub>

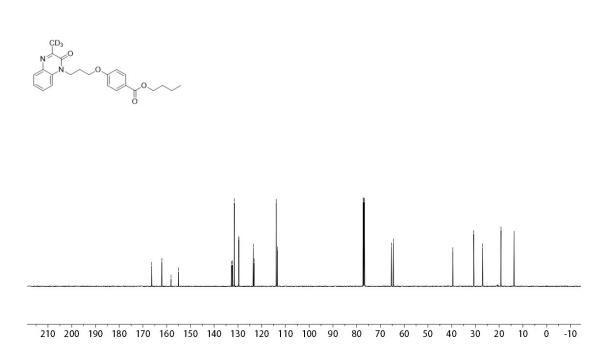






#### <sup>13</sup>C NMR (126 MHz) Spectrum of 7h in CDCl<sub>3</sub>

58 58 54	132.78 132.33 131.53 131.53 129.64 123.56 113.30 113.30 113.39	$\overbrace{77.06}^{77.26} \overbrace{76.75}^{76.75} \overbrace{64.53}^{64.53}$	\ 39.50 30.73 26.96 19.22 13.73
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#### <sup>1</sup>H NMR (500 MHz) Spectrum of 7i in CDCl<sub>3</sub>



