# **Supporting Information**

# Controllable Chemoselectivity in the Reaction of 2*H*-Indazoles with Alcohols under Visible-Light Irradiation: Synthesis of C3-Alkoxylated 2*H*-Indazoles and *ortho*-Alkoxycarbonylated Azobenzenes

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#### 1. General considerations

Unless otherwise noted, chemicals and materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to the general methods. All <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometer (400/100 MHz,). All chemical shifts are given as  $\delta$ : value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). High resolution mass spectroscopy data of the product were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI). Products were purified by flash chromatography on 200–300 mesh silica gels, SiO<sub>2</sub>.

### 2. Representative procedure for the model reaction

# 2.1 Representative procedure for the model reaction under $N_2$ atmosphere in 0.20 mmol scale



A 10 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with 2-phenyl-2*H*-indazole (**1a**, 38.85 mg, 0.20 mmol), EtOH (**2a**, 3.0 mL), Selectfluor (141.70 mg, 0.40 mmol), Mes-Acr<sup>+</sup>ClO<sub>4</sub><sup>-</sup> (2.47 mg, 3 mol%,) and CH<sub>3</sub>CN (3.0 mL). The reaction vessel was exposed to LED (450–455 nm, 1.5 W) irradiation at room temperature in N<sub>2</sub> atmosphere with stirring for 24 h. After completion of the reaction, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 15:1 to 9:1) to give the desired product **3aa**.

# 2.2 Representative procedure for the model reaction under $N_2$ atmosphere in 5.0 mmol scale



A 10 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with 2-phenyl-2*H*-indazole (**1a**, 971.2 mg, 5.0 mmol), EtOH (**2a**, 25.0 mL), Selectfluor (7085.0 mg, 10.0 mmol), Mes-Acr<sup>+</sup>ClO<sub>4</sub><sup>-</sup> (61.8 mg, 3 mol%,) and CH<sub>3</sub>CN (25.0 mL). The reaction vessel was exposed to LED (450–455 nm) irradiation at room temperature in N<sub>2</sub> atmosphere with stirring for 24 h. After completion of the reaction, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 15:1 to 9:1) to give the desired product **3aa** in 70% yield.

# 2.3 Representative procedure for the model reaction under O<sub>2</sub> atmosphere in 0.10 mmol scale



A 10 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with 2-phenyl-2*H*-indazole (**1a**, 19.42 mg, 0.10 mmol), EtOH (**2a**, 3.0 mL), Mes-Acr<sup>+</sup>ClO<sub>4</sub><sup>-</sup> (1.24 mg, 3 mol%) and CH<sub>3</sub>CN (3.0 mL). The reaction vessel was exposed to LED (450–455 nm, 1.5 W) irradiation at room temperature in O<sub>2</sub> atmosphere with stirring for 24 h. After completion of the reaction, the mixture was concentrated to yield the crude product, which was further purified by flash

chromatography (silica gel, petroleum ether/ethyl acetate = 50:1 to 20:1) to give the desired product **4aa**.

# 2.4 Representative procedure for the model reaction under O<sub>2</sub> atmosphere in 5.0 mmol scale



A 10 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with 2-phenyl-2*H*-indazole (**1a**, 971.2 mg, 5.0 mmol), *i*so-C<sub>3</sub>H<sub>7</sub>OH (**2g**, 25.0 mL), Mes-Acr<sup>+</sup>ClO<sub>4</sub><sup>-</sup> (61.8 mg, 3 mol%) and CH<sub>3</sub>CN (25.0 mL). The reaction vessel was exposed to LED (450–455 nm) irradiation at room temperature in O<sub>2</sub> atmosphere with stirring for 30 h. After completion of the reaction, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 50:1 to 20:1) to give the desired product **4ag** in 66% yield.

# 3. Further optimization of the reaction conditions

N 1a	N	+ EtOH 2a		Mes-Acr <sup>+</sup> ClO <sub>4</sub> <sup>-</sup> (3 mol%) Oxidant (2.0 eq) 450−455 nm, 24 h N <sub>2</sub> , CH <sub>3</sub> CN		→ NNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNNN	
-	entry		02	kidant	yield of	<b>3aa</b> (%) <sup>a</sup>	
-	1		Selectfluor		8	89	
	2		BPO			0	
	3		$K_2S_2O_8$			0	
	4		TBHP			0	
	5		<i>m</i> -CPBA			0	
	6		H	$H_2O_2$		0	
	7		PhI	$(TFA)_2$		0	
	$8^b$		Sele	ectfluor		75	

### 3.1 Optimization of the oxidant on C3-alkoxylation of 2H-indazoles

Reaction conditions: 2-phenyl-2*H*-indazole (**1a**, 0.20 mmol), ethanol (**2a**, 3.0 mL), oxidant (0.40 mmol), CH<sub>3</sub>CN (3.0 mL), N<sub>2</sub> atmosphere, at room temperature under 1.5 W blue LED (450–455 nm) irradiation for 24 h. *a*Isolated yield. *b*For 18 h.

### 3.2 The influence of reaction concentration on the yield of 4aa

N N 1a	N		EtOH 2a	Mes-Acr <sup>+</sup> ClO <sub>4</sub> 450−455 n <mark>O</mark> 2, CH <sub>3</sub>	<u>, (3 mol%)</u> m, 24 h CN	OEt N <sup>EN</sup> 4aa	
entry			1a	(mmol)	Yield	of <b>4aa</b> <sup><i>a</i></sup>	
	1			0.40	<	10%	
	2			0.20	6	51%	
	3			0.10	7	6%	
	4			0.04	4	2%	
	5			0.02	4	0%	
	$6^b$			0.10	7	1%	
	$7^c$			0.10	7	'6%	

Reaction conditions of product **4aa**: 2-phenyl-2*H*-indazole (**1a**, 0.10 mmol), ethanol (**2a**, 3.0 mL), CH<sub>3</sub>CN (3.0 mL), oxygen ball, at room temperature under 1.5 W blue LED (450–455 nm) irradiation for 24 h. *a*Isolated yield. *b* For 18 h. *c* For 36 h.

# 4. Mechanism investigation

#### 4.1 Fluorescence quenching experiment

To further elucidate the possible reaction pathway, the related fluorescence quenching experiments were performed and the results were shown in Figure S1. In a typical experiment, to a 6.0 mL solution of Mes-Acr<sup>+</sup>ClO<sub>4</sub><sup>-</sup> (**PC**, 2.47 mg) in CH<sub>3</sub>CN (3.0 mL) and EtOH (3.0 mL) was added 2-phenyl-2*H*-indazole (**1a**, 38.85 mg, 0.20 mmol,) and Selectfluor (141.70 mg, 0.40 mmol), respectively. It was found that the photocatalyst Mes-Acr<sup>+</sup>ClO<sub>4</sub><sup>-</sup> was obviously quenched by 2-phenyl-2*H*-indazole (**1a**), as shown in Figure S1.



**Figure S1.** Fluorescence quenching of Mes-Acr<sup>+</sup>ClO<sub>4</sub><sup>-</sup> using 2-phenyl-2*H*-indazole (**1a**) or Selectfluor

#### 4.2 Determination of superoxide radicals

In order to determine the active species of oxygen involved in the present reaction, 5,5-dimethyl-pyrroline-*N*-oxide (DMPO) was employed to capture  $O_2^{-}$ . There was no signal when DMPO was added into oxygen-saturated acetonitrile solution of Mes-Acr<sup>+</sup>ClO<sub>4</sub><sup>-</sup> (**PC**) in the absence of light irradiation (Figure S2a). Irradiation of oxygen-saturated acetonitrile solution of DMPO with **PC** in  $O_2$  with LED (450–455 nm) resulted in the formation of a strong characteristic signal of  $O_2^{-}$  adduct with DMPO (Figure S2b). When the reaction time was prolonged, a series of stronger characteristic signal of  $O_2^{-}$  were observed (Figure S2c), indicating the formation of  $O_2^{-}$  in the reaction.



Figure S2. Electron spin resonance (ESR) spectra of  $O_2^{-}$  adduct with DMPO (a) A solution of DMPO (0.20 mol/L) with Mes-Acr<sup>+</sup>ClO<sub>4</sub><sup>-</sup> (PC) in oxygen - saturated acetonitrile without light irradiation.

(b) A solution of DMPO (0.20 mol/L) with Mes-Acr<sup>+</sup>ClO<sub>4</sub><sup>-</sup> (PC) in oxygen - saturated acetonitrile under LED (450–455 nm, 1.5 W) irradiation for 30 s.

(c) A solution of DMPO (0.20 mol/L) with Mes-Acr<sup>+</sup>ClO<sub>4</sub><sup>-</sup> (PC) in oxygen - saturated acetonitrile under LED (450–455 nm, 1.5 W) irradiation for 60 s.

# 4.3 Determination of the generated intermediates/products in the reaction



A 10 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with 2-phenyl-2*H*-indazole (**1a**, 38.85 mg, 0.20 mmol), EtOH (**2a**, 3.0 mL), Selectfluor (141.70 mg, 0.40 mmol), Mes-Acr<sup>+</sup>ClO<sub>4</sub><sup>-</sup> (2.47 mg, 3 mol%) and CH<sub>3</sub>CN (3.0 mL). The reaction vessel was exposed to LED (450–455 nm, 1.5 W) irradiation at room temperature in N<sub>2</sub> atmosphere with stirring for 24 h. After completion of the reaction, cation **5** and anion **6** were detected by HRMS analysis (Figure S3).



Figure S3. HRMS analysis of cation 5 and anion 6

#### 4.4 Free-radical trapping experiment

#### 4.4.1 Free- -radical trapping experiment (I)



A 10 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with 2-phenyl-2*H*-indazole (**1a**, 38.85 mg, 0.20 mmol), EtOH (**2a**, 3.0 mL), Selectfluor (141.70 mg, 0.40 mmol), Mes-Acr<sup>+</sup>ClO<sub>4</sub><sup>-</sup> (2.47 mg, 3 mol%), BHT (132.21 mg, 0.60 mmol) and CH<sub>3</sub>CN (3.0 mL). The reaction vessel was exposed to LED (450–455 nm, 1.5 W) irradiation at room temperature in N<sub>2</sub> atmosphere with stirring for 24 h. The alkoxylation of 2*H*-indazole was almost prohibited, providing the desired product **3aa** in less than 5% yield, along with the formation an adduct product **7**, which was detected by HRMS analysis (Figure S4).



Figure S4. HRMS analysis of adduct product 7

#### 4.4.2 Free-radical trapping experiment (II)



A 10 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with 2-phenyl-2*H*-indazole (**1a**, 19.42 mg, 0.10 mmol), EtOH (**2a**, 3.0 mL), Mes-Acr<sup>+</sup>ClO<sub>4</sub><sup>-</sup> (1.24 mg, 3 mol%), BHT (66.11 mg, 0.30 mmol) and CH<sub>3</sub>CN (3.0 mL). The reaction vessel was exposed to LED (450–455 nm, 1.5 W) irradiation at room temperature in O<sub>2</sub> atmosphere with stirring for 24 h. After completion of the reaction, only received less than 10% of **4aa** and a radical coupling product **8** was detected by HRMS analysis (Figure S5).



Figure S5. HRMS analysis of radical coupling product 8

### 4.5 Isotope-labelling experiments

#### 4.5.1 Isotope-labelling experiment (I)



A 10 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with 2-phenyl-2*H*-indazole (**1a**, 19.42 mg, 0.10 mmol), EtOH (**2a**, 3.0 mL), Mes-Acr<sup>+</sup>ClO<sub>4</sub><sup>-</sup> (1.24 mg, 3 mol%) and CH<sub>3</sub>CN (3.0 mL). The reaction vessel was exposed to LED (450–455 nm, 1.5 W) irradiation at room temperature in <sup>18</sup>O<sub>2</sub> atmosphere with stirring for 24 h. After completion of the reaction, the product **4aa** (<sup>18</sup>O-**4aa** +<sup>16</sup>O-**4aa**) was isolated in 73% yield, and the HRMS analysis of **4aa** indicated the oxygen in the carbonyl of the product **4aa** was from O<sub>2</sub> in major (Figure S6).



Figure S6. HRMS analysis of the 4aa

#### 4.5.2 Isotope-labelling experiment (II)



A 10 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with 2-phenyl-2*H*-indazole (**1a**, 19.42 mg, 0.10 mmol), EtOH (**2a**, 3.0 mL), Mes-Acr<sup>+</sup>ClO<sub>4</sub><sup>-</sup> (1.24 mg, 3 mol%), H<sub>2</sub><sup>18</sup>O (0.50 mL) and CH<sub>3</sub>CN (3.0 mL). The reaction vessel was exposed to LED (450–455 nm, 1.5 W) irradiation at room temperature in O<sub>2</sub> atmosphere with stirring for 24 h. After completion of the reaction, the product **4aa** (<sup>18</sup>O-**4aa** + <sup>16</sup>O-**4aa**) was isolated in 66% yield and the HRMS analysis of **4aa** indicated the oxygen in the carbonyl of the product **4aa** is from H<sub>2</sub>O in minor (Figure S7).



Figure S7. HRMS analysis of the 4aa

#### 5. Further transformations of 3ra and 4ma

#### 5.1 The transformation of 3ra to 9 via Sonogashira coupling reaction:



A sealed tube was charged with the obtained product **3ra** (0.20 mmol, 1.0 equiv), phenylacetylene (0.24 mmol, 1.2 equiv.), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (10 mol %), CuI (5 mol %), and Et<sub>3</sub>N (3.0 mL). The reactants were degassed and filled with  $N_2$  for three times. Then the reaction mixture was stirred at 50 °C for 12 h. When the reaction was completed, the solution was concentrated in vacuo and purified by chromatography on silica gel (PE/EA = 50/1) to afford the desired product **9** in 92% yield.

#### 5.2 The transformation of 4ma to 10 via Suzuki coupling reaction:



A sealed tube was charged with the obtained product **4ma** (0.20 mmol, 1.0 equiv), 4-methylphenylboronic acid (0.30 mmol, 1.5 equiv.), Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol %),  $K_2CO_3$  (0.40 mmol, 2.0 equiv.), and DME (3.0 mL). The reactants were degassed and filled with  $N_2$  for three times. Then the reaction mixture was stirred at 50 °C for 12 h. When the reaction was completed, the solution was concentrated in vacuo and purified by chromatography on silica gel (PE/EA = 50/1) to afford the desired product **10** in 89% yield.

#### 6. Characterization data for all products



**3-Ethoxy-2-phenyl-2***H***-indazole (3aa):** Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.86–7.83 (m, 2H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.40–7.36 (m, 1H), 7.24–7.22 (m, 1H), 6.96–6.92 (m, 1H), 4.53 (q, *J* = 7.2 Hz, 2H), 1.43 (d, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 147.8, 146.0, 138.7, 128.9, 127.7, 127.0, 123.9, 120.3, 119.7, 117.9, 108.4, 69.9, 15.4. HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for [C<sub>15</sub>H<sub>15</sub>N<sub>2</sub>O]<sup>+</sup>: 239.1179, Found: 239.1181.



**3-Methoxy-2-phenyl-2***H***-indazole (3ab):** Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.82–7.80 (m, 2H), 7.73–7.71 (m, 1H), 7.59–7.56 (m, 1H), 7.52–7.48 (m, 2H), 7.41–7.37 (m, 1H), 7.25–7.21 (m, 1H), 6.96–6.92 (m, 1H), 4.28 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 147.9, 146.7, 138.6, 128.9, 127.8, 126.9, 124.0, 120.2, 119.7, 117.9, 107.7, 60.7. HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for [C<sub>14</sub>H<sub>13</sub>N<sub>2</sub>O]<sup>+</sup>: 225.1022, Found: 225.1027.



**2-Phenyl-3-**(*n*-propoxy)-2*H*-indazole (3ac): Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.85–7.83 (m, 2H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 8.8 Hz, 1H), 7.50–7.45 (m, 2H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.24–7.20 (m, 1H), 6.94–6.90 (m, 1H), 4.41 (t, *J* = 6.8 Hz, 2H), 1.84–1.76 (m, 2H), 0.99 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 147.9, 146.2, 138.7, 128.8, 127.6, 126.8, 123.9, 120.1, 119.7, 117.8, 108.2,

75.6, 23.0, 10.2. HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for [C<sub>16</sub>H<sub>17</sub>N<sub>2</sub>O]<sup>+</sup>: 253.1335, Found: 253.1340.



**3-(***n***-Butoxy)-2-phenyl-2***H***-indazole (3ad):** Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.84–7.82 (m, 2H), 7.66–7.64 (m, 1H), 7.59–7.57 (m, 1H), 7.51–7.46 (m, 2H), 7.39–7.35 (m, 1H), 7.24–7.20 (m, 1H), 6.95–6.91 (m, 1H), 4.46 (t, *J* = 6.8 Hz, 2H), 1.80–1.73 (m, 2H), 1.49–1.40 (m, 2H), 0.92 (t, *J* = 7.6 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 147.9, 146.2, 138.7, 128.8, 127.6, 126.8, 123.9, 120.1, 119.8, 117.9, 108.2, 73.9, 31.6, 18.9, 13.6. HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for [C<sub>17</sub>H<sub>19</sub>N<sub>2</sub>O]<sup>+</sup>: 267.1492, Found: 267.1497.



**3**-(*n*-Pentyloxy)-2-phenyl-2*H*-indazole (3ae): Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.85–7.82 (m, 2H), 7.67–7.64 (m, 1H), 7.58 (d, *J* = 8.8 Hz, 1H), 7.52–7.47 (m, 2H), 7.40–7.36 (m, 1H), 7.25–7.21 (m, 1H), 6.96–6.92 (m, 1H), 4.46 (t, *J* = 6.4 Hz, 2H), 1.82–1.75 (m, 2H), 1.41–1.29 (m, 4H), 0.88 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 147.9, 146.3, 138.7, 128.8, 127.6, 126.9, 124.0, 120.1, 119.8, 117.9, 108.3, 74.2, 29.3, 27.8, 22.2, 13.9. HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for [C<sub>18</sub>H<sub>21</sub>N<sub>2</sub>O]<sup>+</sup>: 281.1684, Found: 281.1652.



**3-(***n***-Hexyloxy)-2-phenyl-2***H***-indazole (3af):** Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.85–7.82 (m, 2H), 7.67–7.65 (m, 1H), 7.59–7.57 (m, 1H), 7.51–7.47 (m, 2H), 7.41–7.36 (m, 1H), 7.25–7.21 (m, 1H), 6.96–6.92 (m, 1H), 4.47 (t, *J* = 6.8 Hz, 2H), 1.82–1.75 (m, 2H), 1.45–1.37 (m, 2H), 1.29–1.26 (m, 4H), 0.87 (t, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 147.9, 146.3, 138.7, 128.9, 127.7, 126.9, 124.0, 120.1, 119.8, 117.9, 108.3, 74.2, 31.3, 29.6, 25.4, 22.5, 13.9. HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for [C<sub>19</sub>H<sub>23</sub>N<sub>2</sub>O]<sup>+</sup>: 295.1805, Found: 295.1815.



**3**-(*iso*-Propoxy)-2-phenyl-2*H*-indazole (3ag): Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.87–7.86 (m, 1H), 7.84 (s, 1H), 7.59 (d, *J* = 9.6 Hz, 2H), 7.52–7.48 (m, 2H), 7.40–7.37 (m, 1H), 7.26–7.22 (m, 1H), 6.98–6.94 (m, 1H), 4.80–4.74 (m, 1H), 1.34 (d, *J* = 6.4 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 147.9, 145.2, 138.9, 128.9, 127.7, 126.9, 124.1, 120.4, 119.6, 117.9, 109.4, 77.8, 22.6. HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for [C<sub>16</sub>H<sub>17</sub>N<sub>2</sub>O]<sup>+</sup>: 253.1335, Found: 253.1342.



**3**-(*iso*-Butoxy)-2-phenyl-2*H*-indazole (3ah): Yellow solid; m.p. = 44.9–45.8 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.85–7.83 (m, 2H), 7.66 (d, J = 8.8 Hz, 1H), 7.59–7.57 (m, 1H), 7.51–7.47 (m, 2H), 7.38 (t, J = 7.6 Hz, 1H), 7.25–7.21 (m, 1H), 6.95–6.91 (m, 1H), 4.25 (d, J = 6.0 Hz, 2H), 2.15–2.05 (m, 1H), 1.00 (d, J = 6.8 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 147.9, 146.3, 138.7, 128.8, 127.6, 126.9, 124.0, 120.1, 119.8, 117.9, 108.1, 80.2, 28.8, 18.9. HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for [C<sub>17</sub>H<sub>19</sub>N<sub>2</sub>O]<sup>+</sup>: 267.1492, Found: 267.1497.



**3-**(*sec*-Butoxy)-2-phenyl-2*H*-indazole (3ai): Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.86–7.83 (m, 2H), 7.61–7.58 (m, 2H), 7.51–7.47 (m, 2H), 7.41–7.36 (m, 1H), 7.26–7.22 (m, 1H), 6.98–6.94 (m, 1H), 4.67–4.60 (m, 1H), 1.83–1.60 (m, 2H), 1.27 (d, *J* = 6.4 Hz, 3H), 0.96 (t, *J* = 7.6 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 147.9, 145.4, 138.9, 128.8, 127.7, 126.8, 124.2, 120.3, 119.7, 118.0, 109.1, 82.5, 29.4, 19.7, 9.5. HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for [C<sub>17</sub>H<sub>19</sub>N<sub>2</sub>O]<sup>+</sup>: 267.1492, Found: 267.1497.



**3-(Cyclopentyloxy)-2-phenyl-2***H***-indazole (3aj):** Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.84–7.81 (m, 2H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.58 (d, *J* = 8.8 Hz, 1H), 7.51–7.47 (m, 2H), 7.40–7.36 (m, 1H), 7.24–7.22 (m, 1H), 6.97–6.93 (m, 1H), 5.22–5.18 (m, 1H), 1.97–1.92 (m, 2H), 1.82–1.76 (m, 2H), 1.72–1.67 (m, 2H), 1.65–1.58 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 148.0, 145.4, 138.9, 128.8, 127.6, 126.9, 124.1, 120.2, 119.9, 117.9, 108.8, 86.6, 33.2, 23.3. HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for [C<sub>18</sub>H<sub>19</sub>N<sub>2</sub>O]<sup>+</sup>: 279.1492, Found: 279.1501.



**3-(Cyclohexyloxy)-2-phenyl-2***H***-indazole (3ak):** Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.86 (d, *J* = 7.6 Hz, 2H), 7.59 (d, *J* = 9.2 Hz, 2H), 7.50 (t, *J* = 8.0 Hz, 2H),

7.39 (t, J = 7.2 Hz, 1H), 7.24–7.22 (m, 1H), 6.98–6.94 (m, 1H), 4.58–4.52 (m, 1H), 1.95–1.91 (m, 2H), 1.71–1.68 (m, 2H), 1.61–1.56 (m, 2H), 1.52–1.25 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 147.9, 145.2, 138.9, 128.8, 127.6, 126.9, 124.1, 120.3, 119.7, 117.9, 109.1, 82.6, 32.2, 25.2, 23.3. HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for [C<sub>19</sub>H<sub>21</sub>N<sub>2</sub>O]<sup>+</sup>: 293.1684, Found: 293.1653.



**3-Ethoxy-2-**(*p*-tolyl)-2*H*-indazole (3ba): Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.70 (d, *J* = 8.4 Hz, 2H), 7.65–762 (m, 1H), 7.59–7.56 (m, 1H), 7.29–7.27 (m, 2H), 7.24–7.20 (m, 1H), 6.95–6.91 (m, 1H), 4.50 (q, *J* = 7.2 Hz, 2H), 2.41 (s, 3H), 1.41 (t, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 147.7, 145.8, 137.6, 136.2, 129.4, 126.8, 123.7, 120.1, 119.6, 117.8, 108.4, 69.8, 21.1, 15.4. HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for [C<sub>16</sub>H<sub>17</sub>N<sub>2</sub>O]<sup>+</sup>: 253.1335, Found: 253.1340.



**3-Ethoxy-2-(4-methoxyphenyl)-2***H***-indazole (3ca):** Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.74–7.72 (m, 2H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.58 (d, *J* = 9.2 Hz, 1H), 7.24–7.22 (m, 1H), 7.01 (d, *J* = 9.2 Hz, 2H), 6.97–6.93 (m, 1H), 4.51 (q, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 1.42 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 159.0, 147.5, 145.8, 131.7, 126.8, 125.4, 120.2, 119.6, 117.7, 114.1, 108.4, 69.8, 55.5, 15.4. HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for [C<sub>16</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub>]<sup>+</sup>: 269.1285, Found: 269.1290.



**3-Ethoxy-2-(4-fluorophenyl)-2***H***-indazole (3da):** Yellow solid; m.p. 71.2–71.9 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.83–7.80 (m, 2H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.56 (d, *J* 

= 9.2 Hz, 1H), 7.25–7.15 (m, 3H), 6.96–6.92 (m, 1H), 4.54 (q, J = 7.2 Hz, 2H), 1.43 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 161.7 (d, J = 246.2 Hz), 147.8, 145.9, 134.8 (d, J = 3.1 Hz) 127.1, 125.7 (d, J = 8.6 Hz), 120.3, 119.7, 117.8, 115.8 (d, J = 22.7 Hz), 108.1, 69.8, 15.4. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$ : –113.83. HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for [C<sub>15</sub>H<sub>14</sub>FN<sub>2</sub>O]<sup>+</sup>: 257.1085, Found: 257.1089.



**2-(4-Chlorophenyl)-3-ethoxy-2***H***-indazole (3ea):** Yellow solid; m.p. 67.1–68.2 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.84–7.80 (m, 2H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.56 (d, *J* = 9.2 Hz, 1H), 7.48– 7.44 (m, 2H), 7.25–7.21 (m, 1H), 6.95–6.91 (m, 1H), 4.56 (q, *J* = 7.2 Hz, 2H), 1.44 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 148.0, 146.1, 137.2, 133.3, 129.0, 127.2, 124.9, 120.4, 119.7, 117.8, 108.2, 69.9, 15.4. HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for [C<sub>15</sub>H<sub>14</sub>ClN<sub>2</sub>O]<sup>+</sup>: 273.0789, Found: 273.0793.



**2-(4-Bromophenyl)-3-ethoxy-2***H***-indazole (3fa):** Yellow solid; m.p. 62.2–64.1 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.78–7.76 (m, 2H), 7.64–7.60 (m, 3H), 7.56 (d, J = 8.8 Hz, 1H), 7.24–7.21 (m, 1H), 6.96–6.92 (m, 1H), 4.56 (q, J = 7.2 Hz, 2H), 1.44 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 148.0, 146.1, 137.7, 132.0, 127.3, 125.2, 121.3, 120.5, 119.7, 117.8, 108.2, 69.9, 15.4. HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for [C<sub>15</sub>H<sub>14</sub>BrN<sub>2</sub>O]<sup>+</sup>: 317.0284, Found: 317.0287.



**3-Ethoxy-2-(4-(trifluoromethyl)phenyl)-2***H***-indazole (3ga):** Yellow solid; m.p. 74.7–75.9 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.07–8.04 (m, 2H), 7.75 (d, *J* = 8.4 Hz,

2H), 7.66–7.63 (m, 1H), 7.57–7.55 (m, 1H), 7.26–7.22 (m, 1H), 6.96–6.92 (m, 1H), 4.61 (q, J = 7.2 Hz, 2H), 1.47 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 148.4, 146.5, 141.6, 129.4, 129.1, 127.5, 126.1 (q, J = 3.9 Hz), 123.6, 120.7, 119.9, 118.0, 108.2, 70.0, 15.4. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$ : –62.40. HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for [C<sub>16</sub>H<sub>14</sub>F<sub>3</sub>N<sub>2</sub>O]<sup>+</sup>: 307.1053, Found: 307.1059.



Ethyl 4-(3-ethoxy-2*H*-indazol-2-yl)benzoate (3ha): Yellow solid; m.p. 97.6–99.4 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.20–8.16 (m, 2H), 8.03–7.99 (m, 2H), 7.66–7.63 (m, 1H), 7.58–7.55 (m, 1H), 7.26–7.22 (m, 1H), 6.96–6.92 (m, 1H), 4.59 (q, *J* = 6.8 Hz, 2H), 4.41 (q, *J* = 6.8 Hz, 2H), 1.47 (t, *J* = 7.2 Hz, 3H), 1.42 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 165.9, 148.4, 146.5, 142.4, 130.4, 129.2, 127.4, 123.1, 120.6, 119.8, 118.0, 108.4, 70.1, 61.2, 15.4, 14.3. HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for [C<sub>18</sub>H<sub>19</sub>N<sub>2</sub>O<sub>3</sub>]<sup>+</sup>: 311.1390, Found: 311.1395.



**3-Ethoxy-2-(***m***-tolyl)-2***H***-indazole (3ia): Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.68–7.61 (m, 3H), 7.60–7.57 (m, 1H), 7.36 (t,** *J* **= 8.0 Hz, 1H), 7.25–7.18 (m, 2H), 6.95–6.91 (m, 1H), 4.51 (q,** *J* **= 6.8 Hz, 2H), 2.43 (s, 3H), 1.42 (t,** *J* **= 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 147.7, 146.0, 139.0, 138.5, 128.6, 128.5, 126.9, 124.6, 120.9, 120.2, 119.7, 117.8, 108.4, 69.8, 21.3, 15.3. HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for [C<sub>16</sub>H<sub>17</sub>N<sub>2</sub>O]<sup>+</sup>: 253.1335, Found: 253.1337.** 



**2-(3-Chlorophenyl)-3-ethoxy-2***H***-indazole (3ja):** Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.94 (t, J = 2.0 Hz, 1H), 7.81–7.78 (m, 1H), 7.65–7.62 (m, 1H), 7.56 (d, J = 8.8 Hz, 1H), 7.41 (t, J = 8.0 Hz, 1H), 7.36–7.33 (m, 1H), 7.25–7.21 (m, 1H), 6.96–6.91 (m, 1H), 4.57 (q, J = 6.8 Hz, 2H), 1.46 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 148.0, 146.2, 139.7, 134.6, 129.9, 127.6, 127.3, 123.8, 121.6, 120.5, 119.8, 117.9, 108.2, 70.0, 15.4. HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for [C<sub>15</sub>H<sub>14</sub>ClN<sub>2</sub>O]<sup>+</sup>: 273.0789, Found: 273.0794.



**3-Ethoxy-2-**(*o*-tolyl)-2*H*-indazole (3ka): Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.69–7.67 (m, 1H), 7.60–7.57 (m, 1H), 7.40–7.30 (m, 4H), 7.28–7.23 (m, 1H), 6.99–6.96 (m, 1H), 4.47 (q, *J* = 7.2 Hz, 2H), 2.14 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 147.9, 146.6, 137.3, 135.4, 130.7, 129.3, 127.5, 126.6, 126.3, 120.1, 119.7, 117.9, 107.2, 69.5, 17.5, 15.3. HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for [C<sub>16</sub>H<sub>17</sub>N<sub>2</sub>O]<sup>+</sup>: 253.1335, Found: 253.1340.



**2-(3-Chloro-4-methylphenyl)-3-ethoxy-2***H***-indazole (3la):** Yellow solid; m.p. 57.9–59.3 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.91 (d, *J* = 2.4 Hz, 1H), 7.70–7.67 (m, 1H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.57 (d, *J* = 8.8 Hz, 1H), 7.35–7.33 (m, 1H), 7.24–7.22 (m, 1H), 6.96–6.92 (m, 1H), 4.57 (q, *J* = 6.8 Hz, 2H), 2.43 (s, 3H), 1.46 (t, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 147.9, 146.1, 137.3, 135.5, 134.5, 131.0, 127.2, 124.2, 121.8, 120.4, 119.7, 117.8, 108.3, 70.0, 19.7, 15.4. HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for [C<sub>16</sub>H<sub>16</sub>ClN<sub>2</sub>O]<sup>+</sup>: 287.0946, Found: 287.0951.



**3-Ethoxy-2-(naphthalen-1-yl)-2***H***-indazole (3ma):** Yellow solid; m.p. 75.1–75.9 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.01–7.99 (m, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.66– 7.59 (m, 3H), 7.55–7.51 (m, 1H), 7.49–7.43 (m, 2H), 7.33–7.29 (m, 1H), 7.05–7.01 (m, 1H), 4.44 (q, *J* = 6.8 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 148.1, 147.6, 134.5, 134.0, 129.8, 129.8, 128.0, 127.3, 127.0, 126.6, 125.3, 124.9, 123.2, 120.4, 119.7, 118.0, 107.4, 69.8, 15.3. HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for [C<sub>19</sub>H<sub>17</sub>N<sub>2</sub>O]<sup>+</sup>: 289.1335, Found: 289.1341.



**3-Ethoxy-5-fluoro-2-phenyl-***2H***-indazole (3na):** Yellow solid; m.p. 41.2–43.9 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.83–7.81 (m, 2H), 7.57–7.54 (m, 1H), 7.51–7.47 (m, 2H), 7.41–7.36 (m, 1H), 7.23–7.20 (m, 1H), 7.07–7.02 (m, 1H), 4.41 (q, *J* = 6.8 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 157.2 (d, *J* = 237.6 Hz), 146.2 (d, *J* = 8.4 Hz), 145.3, 138.6, 128.9, 127.8, 123.8, 120.0 (d, *J* = 9.5 Hz), 118.6 (d, *J* = 28.9 Hz), 107.2 (d, *J* = 11.1 Hz), 101.9 (d, *J* = 25.1 Hz), 70.0, 15.3. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$ : –121.56. HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for [C<sub>15</sub>H<sub>14</sub>FN<sub>2</sub>O]<sup>+</sup>: 257.1085, Found: 257.1089.



**5-Chloro-3-ethoxy-2-phenyl-2***H***-indazole (3oa):** Yellow solid; m.p. 52.9–53.9 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.83–7.80 (m, 2H), 7.623–7.616 (m, 1H), 7.53–7.47 (m, 3H), 7.41–7.36 (m, 1H), 7.17–7.14 (m, 1H), 4.46 (q, *J* = 7.2 Hz, 2H), 1.41 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 146.0, 145.6, 138.4, 129.0, 128.3, 128.0, 125.7, 123.8, 119.5, 118.3, 114.2, 108.6, 70.1, 15.3. HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for [C<sub>15</sub>H<sub>14</sub>ClN<sub>2</sub>O]<sup>+</sup>: 273.0789, Found: 273.0795.



**5-Bromo-3-ethoxy-2-phenyl-2***H***-indazole (3pa):** Yellow solid; m.p. 45.9–47.2 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.83–7.80 (m, 3H), 7.51–7.45 (m, 3H), 7.41–7.37 (m, 1H), 7.28–7.25 (m, 1H), 4.48 (q, *J* = 7.2 Hz, 2H), 1.42 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 146.1, 145.3, 138.4, 130.4, 129.0, 127.9, 123.8, 121.7, 119.7, 113.3, 109.5, 70.1, 15.3. HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for [C<sub>15</sub>H<sub>14</sub>BrN<sub>2</sub>O]<sup>+</sup>: 317.0284, Found: 317.0288.



**3-Ethoxy-6-methyl-2-phenyl-2***H***-indazole (3qa):** Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.84–7.82 (m, 2H), 7.54 (d, J = 8.8 Hz, 1H), 7.48 (t, J = 8.0 Hz, 2H), 7.38–7.32 (m, 2H), 6.79–6.77 (m, 1H), 4.53 (q, J = 6.8 Hz, 2H), 2.41 (s, 3H), 1.43 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 148.5, 145.9, 138.8, 136.8, 128.8, 127.4, 123.8, 123.2, 119.3, 116.1, 106.6, 69.7, 22.2, 15.4. HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for [C<sub>16</sub>H<sub>17</sub>N<sub>2</sub>O]<sup>+</sup>: 253.1335, Found: 253.1340.



**6-Bromo-3-ethoxy-2-phenyl-2***H***-indazole (3ra):** Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.82–7.75 (m, 3H), 7.51–7.47 (m, 3H), 7.41–7.36 (m, 1H), 6.99–6.97 (m, 1H), 4.50 (q, *J* = 6.8 Hz, 2H), 1.42 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 148.3, 146.3, 138.3, 128.9, 127.8, 123.8, 123.8, 121.2, 120.1, 106.8, 69.9, 15.3. HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for [C<sub>15</sub>H<sub>14</sub>BrN<sub>2</sub>O]<sup>+</sup>: 317.0284, Found: 317.0286.



**Ethyl (***E***)-2-(phenyldiazenyl)benzoate (4aa):** Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.94–7.91 (m, 2H), 7.85–7.82 (m, 1H), 7.61–7.56 (m, 2H), 7.54–7.46 (m, 4H), 4.37 (q, *J* = 7.2 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 167.5, 152.5, 152.0, 131.8, 131.4, 129.7, 129.7, 129.1, 129.0, 123.2, 118.6, 61.4, 14.3. HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for [C<sub>15</sub>H<sub>15</sub>N<sub>2</sub>O<sub>2</sub>]<sup>+</sup>: 255.1128, Found: 255.1134.



**Methyl (***E***)-2-(phenyldiazenyl)benzoate (4ab):** Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.93–7.89 (m, 2H), 7.84–7.81 (m, 1H), 7.63–7.56 (m, 2H), 7.53–7.46 (m, 4H), 3.90 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 167.8, 152.6, 151.9, 131.9, 131.4, 129.7, 129.1, 128.5, 123.1, 118.7, 52.4. HRMS (ESI) ([M+Na]<sup>+</sup>) Calcd. for [C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>Na]<sup>+</sup>: 263.0791, Found: 263.0795.



*n*-Propyl (*E*)-2-(phenyldiazenyl)benzoate (4ac): Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.93–7.91 (m, 2H), 7.85–7.82 (m, 1H), 7.60–7.55 (m, 2H), 7.54–7.46 (m, 4H), 4.28 (t, *J* = 6.8 Hz, 2H), 1.74–1.65 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 167.6, 152.5, 152.0, 131.8, 131.4, 129.7, 129.7, 129.0, 129.0, 123.2, 118.6, 67.0, 22.0, 10.4. HRMS (ESI) ([M+Na]<sup>+</sup>) Calcd. for [C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>Na]<sup>+</sup>: 291.1104, Found: 291.1109.



*n*-Butyl (*E*)-2-(phenyldiazenyl)benzoate (4ad): Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.93–7.90 (m, 2H), 7.85–7.82 (m, 1H), 7.58–7.56 (m, 2H), 7.53–7.46 (m, 4H), 4.32 (t, *J* = 6.8 Hz, 2H), 1.68–1.61 (m, 2H), 1.39–1.28 (m, 2H), 0.85 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 167.6, 152.5, 152.0, 131.8, 131.4, 129.7, 129.6, 129.0, 123.2, 118.5, 65.3, 30.7, 19.1, 13.6. HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for [C<sub>17</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub>]<sup>+</sup>: 283.1441, Found: 283.1446.



*n*-Pentyl (*E*)-2-(phenyldiazenyl)benzoate (4ae): Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.93–7.91 (m, 2H), 7.84–7.82 (m, 1H), 7.58–7.56 (m, 2H), 7.52–7.45 (m, 4H), 4.30 (t, *J* = 6.8 Hz, 2H), 1.69–1.62 (m, 2H), 1.31–1.22 (m, 4H), 0.81 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 167.6, 152.5, 152.0, 131.8, 131.4, 129.7, 129.6, 129.0, 123.2, 118.6, 65.6, 28.4, 28.1, 22.2, 13.8. HRMS (ESI) ([M+Na]<sup>+</sup>) Calcd. for [C<sub>18</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>Na]<sup>+</sup>: 319.1417, Found: 319.1418.



*n*-Hexyl (*E*)-2-(phenyldiazenyl)benzoate (4af): Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.93–7.90 (m, 2H), 7.84–7.82 (m, 1H), 7.58–7.57 (m, 2H), 7.53–7.46 (m, 4H), 4.30 (t, *J* = 6.8 Hz, 2H), 1.68–1.61 (m, 2H), 1.34–1.27 (m, 2H), 1.22–1.19 (m, 4H), 0.83 (t, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl3) δ: 167.6, 152.5, 152.0, 131.8, 131.4, 129.7, 129.6, 129.0, 129.0, 123.2, 118.6, 65.6, 31.4, 28.7, 25.6, 22.4,

13.9. HRMS (ESI) ( $[M+Na]^+$ ) Calcd. for  $[C_{19}H_{22}N_2O_2Na]^+$ : 333.1573, Found: 333.1578.



*iso*-Propyl (*E*)-2-(phenyldiazenyl)benzoate (4ag): Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.94–7.91 (m, 2H), 7.82–7.80 (m, 1H), 7.59–7.56 (m, 2H), 7.54–7.45 (m, 4H), 5.31–5.22 (m, 1H), 1.30 (d, *J* = 6.4 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 167.1, 152.5, 151.9, 131.6, 131.4, 129.6, 129.6, 129.0, 123.2, 118.4, 69.0, 21.9. HRMS (ESI) ([M+Na]<sup>+</sup>) Calcd. for [C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>Na]<sup>+</sup>: 291.1104, Found: 291.1107.



*iso*-Butyl (*E*)-2-(phenyldiazenyl)benzoate (4ah): Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.93–7.90 (m, 2H), 7.85–7.83 (m, 1H), 7.58–7.57 (m, 2H), 7.53–7.46 (m, 4H), 4.10 (d, J = 6.4 Hz, 2H), 2.02 – 1.92 (m, 1H), 0.90 (d, J = 6.8 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 167.5, 152.5, 152.0, 131.8, 131.4, 129.7, 129.6, 129.1, 129.0, 123.2, 118.5, 71.6, 27.7, 19.1. HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for [C<sub>17</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub>]<sup>+</sup>: 283.1441, Found: 283.1447.



*sec*-Butyl (*E*)-2-(phenyldiazenyl)benzoate (4ai): Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.93–7.90 (m, 2H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.60–7.55 (m, 2H), 7.54–7.46 (m, 4H), 5.16–5.08 (m, 1H), 1.72–1.53 (m, 2H), 1.29 (d, *J* = 6.4 Hz, 3H), 0.90 (t, *J* =

7.6 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 167.2, 152.5, 151.9, 131.6, 131.4, 129.8, 129.6, 129.5, 129.0, 123.2, 118.3, 73.6, 28.9, 19.5, 9.7. HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for [C<sub>17</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub>]<sup>+</sup>: 283.1441, Found: 283.1445.



**Cyclopentyl** (*E*)-2-(phenyldiazenyl)benzoate (4aj): Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.93–7.91 (m, 2H), 7.82–7.80 (m, 1H), 7.57–7.45 (m, 6H), 5.44–5.40 (m, 1H), 1.94–1.86 (m, 2H), 1.79–1.74 (m, 2H), 1.63–1.50 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 167.4, 152.5, 152.0, 131.7, 131.4, 129.7, 129.6, 129.0, 123.2, 118.4, 95.7, 78.3, 32.7, 23.7. HRMS (ESI) ([M+Na]<sup>+</sup>) Calcd. for [C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>Na]<sup>+</sup>: 317.1260, Found: 317.1265.



**Cyclohexyl** (*E*)-2-(phenyldiazenyl)benzoate (4ak): Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.93–7.91 (m, 2H), 7.84–7.82 (m, 1H), 7.57–7.46 (m, 6H), 5.07–5.01 (m, 1H), 1.94–1.90 (m, 2H), 1.71–1.67 (m, 2H), 1.53–1.18 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 166.9, 152.5, 152.0, 131.7, 131.3, 129.7, 129.7, 129.6, 129.0, 123.2, 118.3, 73.9, 31.6, 25.3, 23.6. HRMS (ESI) ([M+Na]<sup>+</sup>) Calcd. for [C<sub>19</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>Na]<sup>+</sup>: 331.1417, Found: 331.1420.



**Ethyl (E)-2-(p-tolyldiazenyl)benzoate (4ba):** Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.84–7.82 (m, 3H), 7.60–7.53 (m, 2H), 7.49–7.45 (m, 1H), 7.31 (d, J = 8.0

Hz, 2H), 4.37 (q, J = 7.2 Hz, 2H), 2.44 (s, 3H), 1.30 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 167.7, 152.0, 150.6, 142.1, 131.8, 129.7, 129.7, 129.4, 128.8, 123.2, 118.8, 61.4, 21.5, 14.3. HRMS (ESI) ([M+Na]<sup>+</sup>) Calcd. for [C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>Na]<sup>+</sup>: 291.1104, Found: 291.1107.



Ethyl (*E*)-2-((4-methoxyphenyl)diazenyl)benzoate (4ca): Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.93–7.90 (m, 2H), 7.82–7.79 (m, 1H), 7.60–7.54 (m, 2H), 7.47–7.43 (m, 1H), 7.03–6.99 (m, 2H), 4.36 (q, *J* = 7.2 Hz, 2H), 3.89 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 167.8, 162.4, 152.1, 147.0, 131.7, 129.6, 129.1, 128.7, 125.1, 118.8, 114.2, 61.3, 55.6, 14.3. HRMS (ESI) ([M+Na]<sup>+</sup>) Calcd. for [C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>Na]<sup>+</sup>: 307.1053, Found: 307.1058.



Ethyl (*E*)-2-((4-chlorophenyl)diazenyl)benzoate (4da): Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.88–7.83 (m, 3H), 7.60–7.59 (m, 2H), 7.53–7.48 (m, 3H), 4.38 (q, *J* = 7.2 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 167.4, 151.7, 150.9, 137.4, 131.9, 130.0, 129.8, 129.4, 129.2, 124.4, 118.4, 61.5, 14.4. HRMS (ESI) ([M+Na]<sup>+</sup>) Calcd. for [C<sub>15</sub>H<sub>13</sub>ClN<sub>2</sub>O<sub>2</sub>Na]<sup>+</sup>: 311.0558, Found: 311.0562.



Ethyl (*E*)-2-((4-(trifluoromethyl)phenyl)diazenyl)benzoate (4ea): Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.00 (d, *J* = 8.0 Hz, 2H), 7.88–7.85 (m, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.62–7.58 (m, 2H), 7.56–7.51 (m, 1H), 4.39 (q, *J* = 7.2 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 167.2, 154.3, 151.6, 132.6 (q, *J* = 32.2 Hz), 131.9, 130.5, 129.9, 129.5, 126.3 (q, *J* = 3.8 Hz), 123.8 (q, *J* = 270.7 Hz), 123.3, 118.3, 61.5, 14.3. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$ : –62.60. HRMS (ESI) ([M+Na]<sup>+</sup>) Calcd. for [C<sub>16</sub>H<sub>13</sub>F<sub>3</sub>N<sub>2</sub>O<sub>2</sub>Na]<sup>+</sup>: 345.0821, Found: 345.0828.



Ethyl (*E*)-2-((4-(ethoxycarbonyl)phenyl)diazenyl)benzoate (4fa): Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.22–8.19 (m, 2H), 7.97–7.94 (m, 2H), 7.86–7.84 (m, 1H), 7.64–7.58 (m, 2H), 7.54–7.50 (m, 1H), 4.45–4.36 (m, 4H), 1.43 (t, *J* = 7.2 Hz, 3H), 1.32 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 167.3, 165.9, 154.9, 151.7, 132.5, 131.9, 130.6, 130.3, 129.8, 129.5, 122.9, 118.4, 61.5, 61.3, 14.3, 14.3. HRMS (ESI) ([M+Na]<sup>+</sup>) Calcd. for [C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>Na]<sup>+</sup>: 349.1159, Found: 349.1164.



Ethyl (*E*)-2-(*m*-tolyldiazenyl)benzoate (4ga): Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.83 (d, *J* = 7.6 Hz, 1H), 7.73 (t, *J* = 2.4 Hz, 2H), 7.58 (d, *J* = 3.6 Hz, 2H), 7.51–7.45 (m, 1H), 7.43–7.39 (m, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 2.45 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 167.6, 152.6, 152.0, 139.0, 132.2, 131.8, 129.7, 129.6, 128.9, 128.8, 123.4, 120.7, 118.7, 61.4, 21.3, 14.3. HRMS (ESI) ([M+Na]<sup>+</sup>) Calcd. for [C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>Na]<sup>+</sup>: 291.1104, Found: 291.1109.



Ethyl (*E*)-2-((3-chlorophenyl)diazenyl)benzoate (4ha): Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.89–7.88 (m, 1H), 7.86–7.82 (m, 2H), 7.60–7.58 (m, 2H), 7.53–7.49 (m, 1H), 7.47–7.46 (m, 2H), 4.39 (q, *J* = 7.2 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 167.3, 153.3, 151.5, 135.2, 131.9, 131.1, 130.2, 130.2, 129.8, 129.4, 122.6, 122.1, 118.4, 61.5, 14.3. HRMS (ESI) ([M+Na]<sup>+</sup>) Calcd. for [C<sub>15</sub>H<sub>13</sub>ClN<sub>2</sub>O<sub>2</sub>Na]<sup>+</sup>: 311.0558, Found: 311.0563.



Ethyl (*E*)-5-fluoro-2-(phenyldiazenyl)benzoate (4ia): Yellow solid; m.p. 65.2–66.1 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.91–7.88 (m, 2H), 7.70–7.67 (m, 1H), 7.53–7.47 (m, 4H), 7.28–7.23 (m, 1H), 4.39 (q, *J* = 7.2 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 166.3 (d, *J* = 2.3 Hz), 163.0 (d, *J* = 250.5 Hz), 152.3, 147.9 (d, *J* = 3.0 Hz), 131.6 (d, *J* = 7.5 Hz), 131.5, 129.1, 123.1, 120.6 (d, *J* = 8.3 Hz), 118.7 (d, *J* = 22.4 Hz), 116.4 (d, *J* = 24.5 Hz), 61.7, 14.2. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$ : –109.91. HRMS (ESI) ([M+Na]<sup>+</sup>) Calcd. for [C<sub>15</sub>H<sub>13</sub>FN<sub>2</sub>O<sub>2</sub>Na]<sup>+</sup>: 295.0853, Found: 295.0858.



**Ethyl (E)-5-chloro-2-(phenyldiazenyl)benzoate (4ja):** Yellow solid; m.p. 61.2–61.9 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.92–7.89 (m, 2H), 7.80 (d, *J* = 2.0 Hz, 1H), 7.62–7.60 (m, 1H), 7.55–7.50 (m, 4H), 4.39 (q, *J* = 7.2 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 166.3, 152.4, 150.0, 135.8, 131.8, 131.7, 130.8,

129.6, 129.1, 123.3, 120.0, 61.8, 14.3. HRMS (ESI) ( $[M+Na]^+$ ) Calcd. for  $[C_{15}H_{13}CIN_2O_2Na]^+$ : 311.0558, Found: 311.0565.



Ethyl (*E*)-5-bromo-2-(phenyldiazenyl)benzoate (4ka): Yellow solid; m.p. 71.5–73.4 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.95 (d, J = 2.4 Hz, 1H), 7.92–7.89 (m, 2H), 7.70–7.68 (m, 1H), 7.52–7.50 (m, 4H), 4.38 (q, J = 7.2 Hz, 2H), 1.32 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 166.1, 152.4, 150.4, 134.8, 132.5, 131.7, 130.9, 129.1, 123.8, 123.3, 120.1, 61.8, 14.3. HRMS (ESI) ([M+Na]<sup>+</sup>) Calcd. for [C<sub>15</sub>H<sub>13</sub>BrN<sub>2</sub>O<sub>2</sub>Na]<sup>+</sup>: 355.0053, Found: 355.0059.



Ethyl (*E*)-4-methyl-2-(phenyldiazenyl)benzoate (4la): Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.93–7.91 (m, 2H), 7.78 (d, J = 8.0 Hz, 1H), 7.54–7.48 (m, 3H), 7.33–7.28 (m, 2H), 4.35 (q, J = 7.2 Hz, 2H), 2.45 (s, 3H), 1.30 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 167.3, 152.6, 152.5, 142.8, 131.3, 130.2, 130.1, 129.1, 125.8, 123.2, 118.7, 61.2, 21.5, 14.3. HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for [C<sub>16</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub>]<sup>+</sup>: 269.1285, Found: 269.1290.



Ethyl (*E*)-4-bromo-2-(phenyldiazenyl)benzoate (4ma): Yellow solid; m.p. 64.4–66.3 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.93–7.91 (m, 2H), 7.74–7.72 (m, 2H), 7.61–7.58 (m, 1H), 7.53–7.49 (m, 3H), 4.37 (q, J = 7.2 Hz, 2H), 1.31 (t, J = 7.2 Hz,

3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 166.4, 152.6, 152.3, 132.3, 131.8, 131.3, 129.1, 127.9, 126.3, 123.3, 121.1, 61.6, 14.3. HRMS (ESI) ([M+Na]<sup>+</sup>) Calcd. for [C<sub>15</sub>H<sub>13</sub>BrN<sub>2</sub>O<sub>2</sub>Na]<sup>+</sup>: 355.0053, Found: 355.0058.



Ethyl (*E*)-5-fluoro-2-((4-methoxyphenyl)diazenyl)benzoate (4na): Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.89 (d, *J* = 8.8 Hz, 2H), 7.69–7.66 (m, 1H), 7.49– 7.46 (m, 1H), 7.27–7.22 (m, 1H), 7.00 (d, *J* = 9.2 Hz, 2H), 4.39 (q, *J* = 7.2 Hz, 2H), 3.88 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 166.6 (d, *J* = 2.4 Hz), 162.7 (d, *J* = 249.6 Hz), 162.4, 148.0 (d, *J* = 3.3 Hz), 146.8, 131.1 (d, *J* = 7.8 Hz), 125.1, 120.7 (d, *J* = 8.4 Hz), 118.6 (d, *J* = 22.4 Hz), 116.3 (d, *J* = 24.4 Hz), 114.2, 61.7, 55.6, 14.3. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$ : –110.93. HRMS (ESI) ([M+Na]<sup>+</sup>) Calcd. for [C<sub>16</sub>H<sub>15</sub>FN<sub>2</sub>O<sub>3</sub>Na]<sup>+</sup>: 325.0959, Found: 325.0958.



Ethyl (*E*)-4-bromo-2-(*p*-tolyldiazenyl)benzoate (4oa): Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.83 (d, *J* = 8.4 Hz, 2H), 7.74–7.71 (m, 2H), 7.60–7.58 (m, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.37 (q, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 166.6, 152.7, 150.5, 142.7, 132.1, 131.2, 129.8, 127.8, 126.3, 123.4, 121.2, 61.6, 21.6, 14.3. HRMS (ESI) ([M+Na]<sup>+</sup>) Calcd. for [C<sub>16</sub>H<sub>15</sub>BrN<sub>2</sub>O<sub>2</sub>Na]<sup>+</sup>: 369.0209, Found: 369.0209.



Ethyl (*E*)-2-((4-bromophenyl)diazenyl)-4-methylbenzoate (4pa): Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.81–7.78 (m, 3H), 7.67–7.64 (m, 2H), 7.33–7.30 (m, 2H), 4.35 (q, *J* = 7.2 Hz, 2H), 2.46 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 167.1, 152.2, 151.3, 142.9, 132.4, 130.6, 130.1, 126.0, 125.8, 124.6, 118.4, 61.3, 21.5, 14.4. HRMS (ESI) ([M+Na]<sup>+</sup>) Calcd. for [C<sub>16</sub>H<sub>15</sub>BrN<sub>2</sub>O<sub>2</sub>Na]<sup>+</sup>: 369.0209, Found: 369.0213.



Ethyl (*E*)-5-chloro-2-((3-chloro-4-methylphenyl)diazenyl)benzoate (4qa): Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.88–7.87 (m, 1H), 7.79 (d, *J* = 2.0 Hz, 1H), 7.74-7.71 (m, 1H), 7.59–7.57 (m, 1H), 7.53–7.51 (m, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 4.40 (q, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 166.2, 151.4, 149.5, 139.9, 136.0, 135.2, 131.8, 131.3, 131.0, 129.7, 122.7, 122.5, 119.7, 61.8, 20.2, 14.3. HRMS (ESI) ([M+Na]<sup>+</sup>) Calcd. for [C<sub>16</sub>H<sub>14</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>Na]<sup>+</sup>: 359.0325, Found: 359.0329.



**3-Ethoxy-2-phenyl-6-(phenylethynyl)-2***H***-indazole (9):** Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.85–7.83 (m, 2H), 7.79 (s, 1H), 7.63–7.61 (m, 1H), 7.58–7.56 (m, 2H), 7.52–7.48 (m, 2H), 7.42–7.34 (m, 4H), 7.06–7.04 (m, 1H), 4.54 (q, *J* = 7.2 Hz, 2H), 1.44 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 147.4, 146.2, 138.6,

131.6, 129.0, 128.3, 128.2, 127.8, 123.9, 123.3, 123.2, 121.6, 121.5, 119.8, 107.6, 90.2, 89.6, 69.9, 15.4. HRMS (ESI) ([M+Na]<sup>+</sup>) Calcd. for [C<sub>18</sub>H<sub>23</sub>N<sub>2</sub>ONa]<sup>+</sup>: 361.1311, Found: 361.1315.



Ethyl (*E*)-4'-methyl-3-(phenyldiazenyl)-[1,1'-biphenyl]-4-carboxylate (10): Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.96–7.91 (m, 3H), 7.76–7.75 (m, 1H), 7.70–7.68 (m, 1H), 7.62–7.49 (m, 5H), 7.28–7.27 (m, 2H), 4.38 (q, *J* = 7.2 Hz, 2H), 2.40 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 167.2, 152.8, 152.6, 145.0, 138.3, 136.6, 131.4, 130.5, 129.6, 129.1, 127.7, 127.1, 126.8, 123.2, 116.8, 61.3, 21.1, 14.3. HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for [C<sub>22</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub>]<sup>+</sup>: 345.1598, Found: 345.1602.



# 7. <sup>1</sup>H and <sup>13</sup>C NMR spectra of the products

100 90 f1 (ppm) 180 170 160 


































---113.831







0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 fl (ppm)






















































































## 8. HRMS analysis for the products















































































180 200

220 240 260 280 300 320 340 360 380 400 420 440


























1: TOF MS ES+

sml-3 w/20210119-3 60 (0.577) AM2 (Ar,20000.0,0.00,0.00); Cm (60-5x2.000) 100- 325.0958





## 9. X-Ray crystal structure of 4ia (CCDC: 2063557)



## checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 1

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No syntax errors found. CIF dictionary Interpreting this report

## **Datablock: 1**

Bond precision:	Sond precision: C-C = 0.0044 A Wavelength=0.710		gth=0.71073	
Cell:	a=4.5093(13)	b=10.415(3)	c=15.589(4)	
_	alpha=70.4900	beta=87.920(4)	gamma=83.761(5)	
Temperature:	296 K			
	Calculated	Reporte	ed	
Volume	686.0(3)	686.0(	3)	
Space group	P -1	P -1	P -1	
Hall group	-P 1	-P 1	-P 1	
Moiety formula	C15 H13 F N2 O2	?		
Sum formula	C15 H13 F N2 O2	C15 H1:	3 F N2 O2	
Mr	272.27	272.27		
Dx,g cm-3	1.318	1.318		
Z	2	2		
Mu (mm-1)	0.098	0.098		
F000	284.0	284.0		
F000'	284.15			
h,k,lmax	5,12,18	5,12,10	3	
Nref	2420	2396		
Tmin,Tmax	0.972,0.979			
Tmin'	0.972			
Correction method= Not given				
Data completeness= 0.990		Theta(max) = 24.992		
R(reflections) = 0.0534(1677) WF		wR2(reflection	wR2(reflections) = 0.1228( 2396)	
S = 0.691 Npar= 182				

The following ALERTS were generated. Each ALERT has the format test-name\_ALERT\_alert-type\_alert-level. Click on the hyperlinks for more details of the test.