

## *Supporting Information*

### Photo-Driven Haloazidation Cyclization of 1,5-Enynes Having Cyano Groups with TMSN<sub>3</sub> and NIS/NCS/NBS under Metal-Free Conditions

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## 1. General considerations

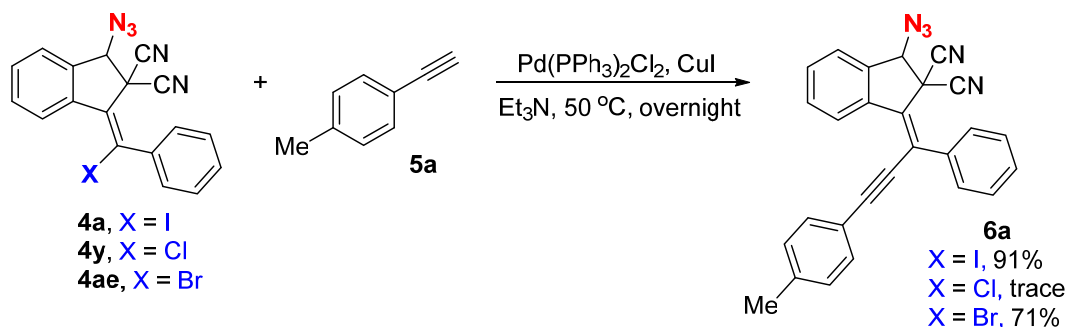
All  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a 600 MHz or 400 MHz Bruker FT-NMR spectrometers (600 MHz, 150 MHz or 400 MHz, 100 MHz, respectively). All chemical shifts are given as  $\delta$  value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The 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 a Waters Micromass GCT instrument. High resolution mass spectroscopy data of the product were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI). The chemicals and solvents were purchased from commercial suppliers either Aldrich (USA), or Shanghai Chemical Company (P. R. China). Products were purified by flash chromatography on 200–300 mesh silica gels,  $\text{SiO}_2$ .

## 2. General procedure for the synthesis of **4**

A 5 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with 2-(2-(phenylethynyl)benzylidene)malononitrile (**1a**, 50.8 mg, 0.20 mmol),  $\text{TMSN}_3$  (**2a**, 46.0 mg, 0.40 mmol), NIS (**3a**, 90.0 mg, 0.40 mmol), and DMF (2.0 mL). The reaction vessel was exposed to LED (380–385 nm, 3.0 W) irradiation at room temperature in air with stirring for 1 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 = 100:1) to give the desired product **4a** (69.4 mg, 82% yield).

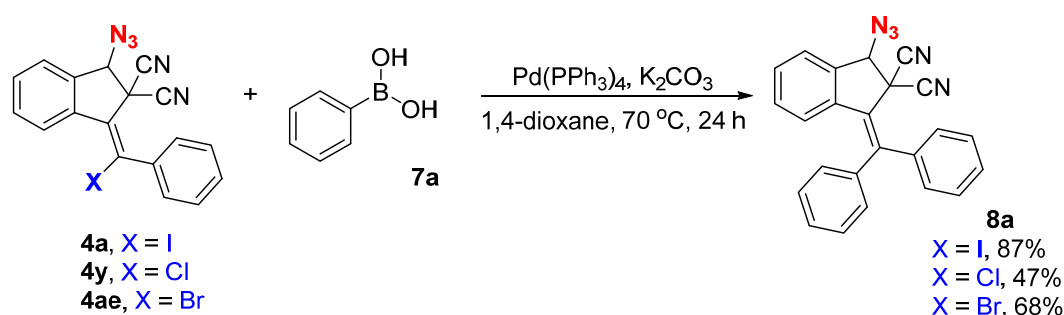
### 3. Further transformations of 4a, 4y and 4ae, and gram-scale synthesis of 4a

#### 3.1 Transformations of 4a, 4y and 4ae via Sonogashira coupling reaction



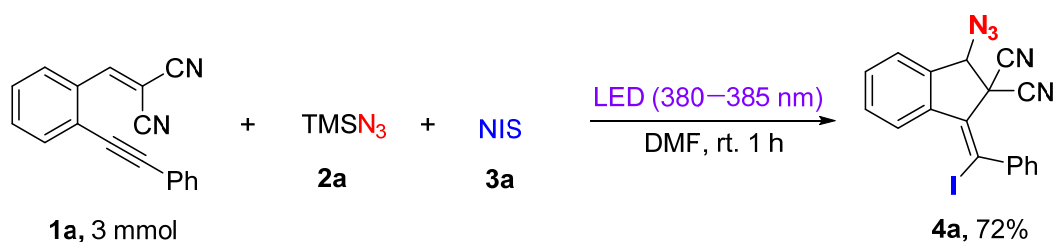
**Representative procedure:** A sealed tube was charged with the obtained product 4a (0.20 mmol, 1.0 equiv), 4-ethynyltoluene (5a, 0.30 mmol, 1.5 equiv.), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (10 mol %), CuI (5 mol %), and Et<sub>3</sub>N (2.0 mL). The reactants were degassed and filled with N<sub>2</sub> for three times. Then the reaction mixture was stirred at 50 °C for 24 h. When the reaction was completed, the solution was concentrated in vacuo and purified by chromatography on silica gel (PE/EA = 100/1) to afford the desired product 6 in 91% yield.

#### 3.2 Transformations of 4a, 4y and 4ae via Suzuki coupling reaction



**Representative procedure:** A sealed tube was charged with the obtained product 4a (0.20 mmol, 1.0 equiv), phenylboronic acid (7a, 0.26 mmol, 1.3 equiv.), Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol %), K<sub>2</sub>CO<sub>3</sub> (0.60 mmol, 3.0 equiv.), and 1,4-dioxane (2.0 mL). The reactants were degassed and filled with N<sub>2</sub> for three times. Then the reaction mixture was stirred at 70 °C for 24 h. When the reaction was completed, the solution was concentrated in vacuo and purified by chromatography on silica gel (PE/EA = 100/1) to afford the desired product 8a in 87% yield.

### 3.3 Gram-scale synthesis of 4a

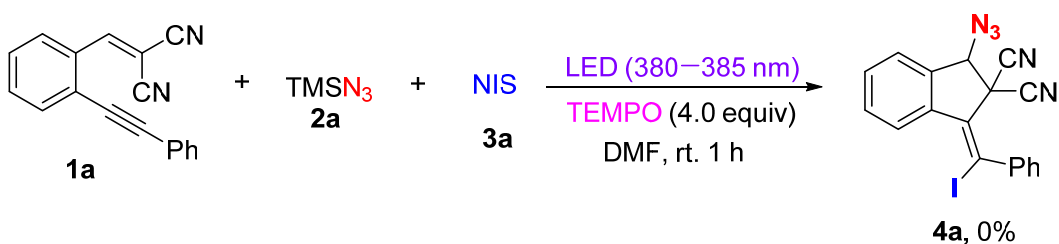


A 100 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with 2-(2-(phenylethynyl)benzylidene)malononitrile (**1a**, 0.765 g, 3.0 mmol), TMSN<sub>3</sub> (**2a**, 7.5 mmol), NIS (**3a**, 7.5 mmol) and DMF (30.0 mL). The reaction vessel was exposed to LED (380–385 nm) irradiation at room temperature in air with stirring for 1 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 = 100:1) to give the desired product **4a** (0.915 g, 72% yield).

## 4. Preliminary mechanistic study

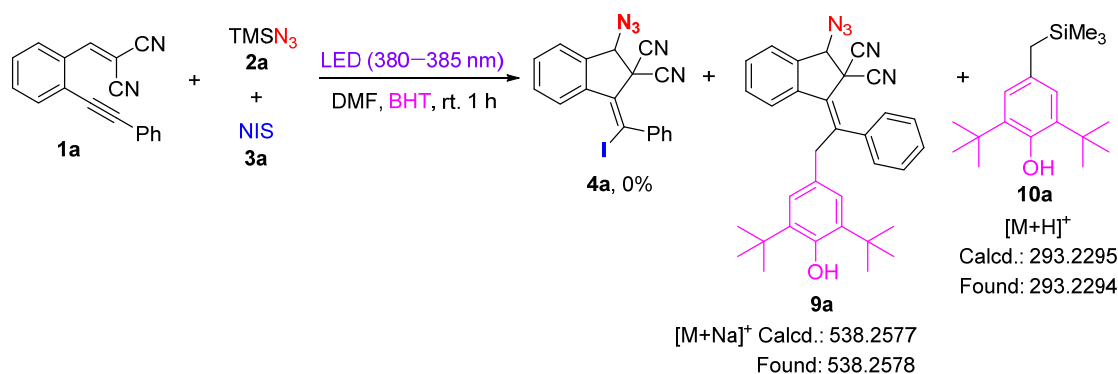
### 4.1 Free radical-trapping experiments

#### 4.1.1 Trapping with TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy)



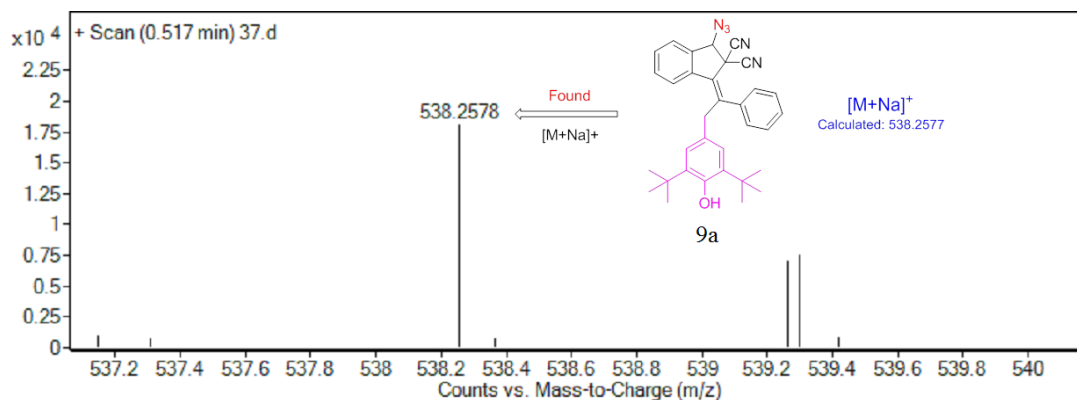
A 5 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with 2-(2-(phenylethynyl)benzylidene)malononitrile (**1a**, 50.8 mg, 0.20 mmol), TMSN<sub>3</sub> (**2a**, 46.0 mg, 0.40 mmol), NIS (**3a**, 90.0 mg, 0.40 mmol), TEMPO (125.0 mg, 0.80 mmol, 4.0 equiv.) and DMF (2.0 mL). The reaction vessel was exposed to LED (380–385 nm, 3.0 W) irradiation at room temperature in air with stirring for 1 h. No **4a** was detected, suggesting that a radical addition mechanism is involved in this transformation.

#### 4.1.2 Trapping with BHT (2,6-di-*tert*-butyl-4-methylphenol)

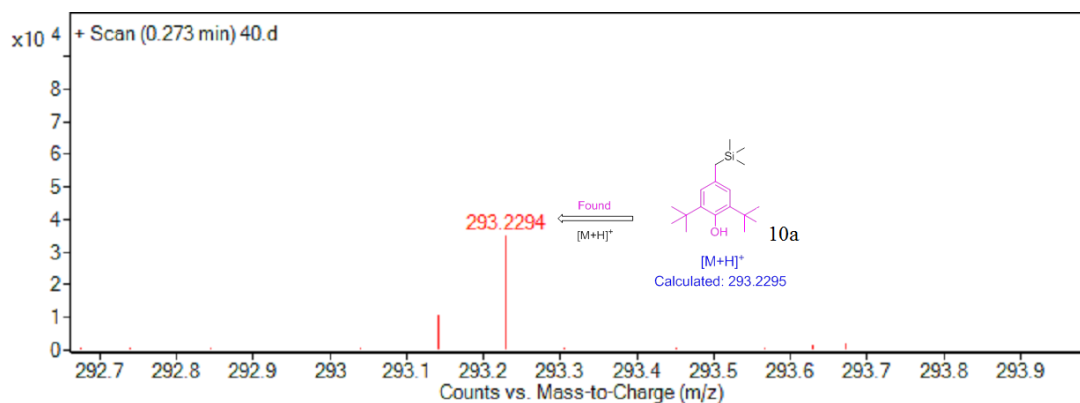


A 5 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with 2-(2-(phenylethynyl)benzylidene)malononitrile (**1a**, 50.8 mg, 0.20 mmol), TMSN<sub>3</sub> (**2a**, 46.0 mg, 0.40 mmol), NIS (**3a**, 90.0 mg, 0.40 mmol), BHT (176.3 mg, 0.80 mmol, 4.0 equiv.) and DMF (2.0 mL). The reaction vessel was exposed to LED (380–385 nm, 3.0 W) irradiation at room temperature in air with stirring for 1 h. No **4a** was detected, and an adduct **9a** was detected by HRMS analysis of reaction mixture (Figure S1), suggesting that a radical addition mechanism is involved in this transformation.

Meanwhile, the formation of another adduct **10a** was also detected by HRMS analysis (Figure S2), implying the formation of TMS<sup>•</sup> radical during the reaction along with the generation of azide radical.



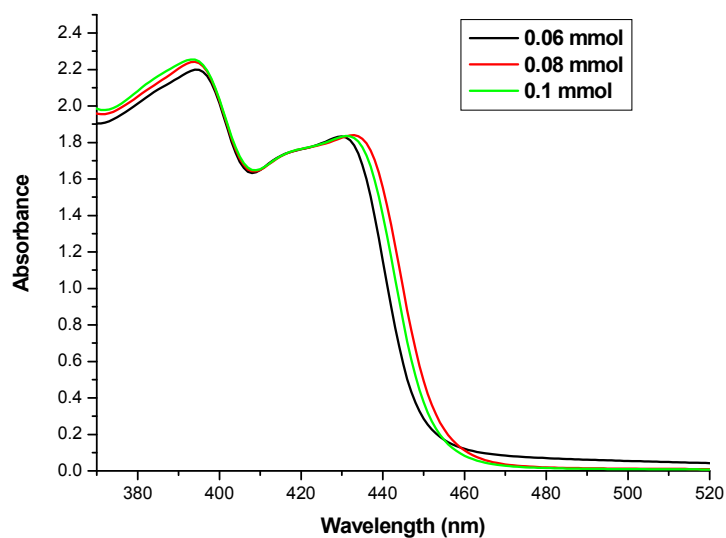
**Figure S1.** Analysis of reaction mixture for the formation of an adduct **9a** by HRMS



**Figure S2.** Analysis of reaction mixture for the formation of an adduct **10a** by HRMS

#### 4.2 The ultraviolet/visible absorption spectra of **1a**

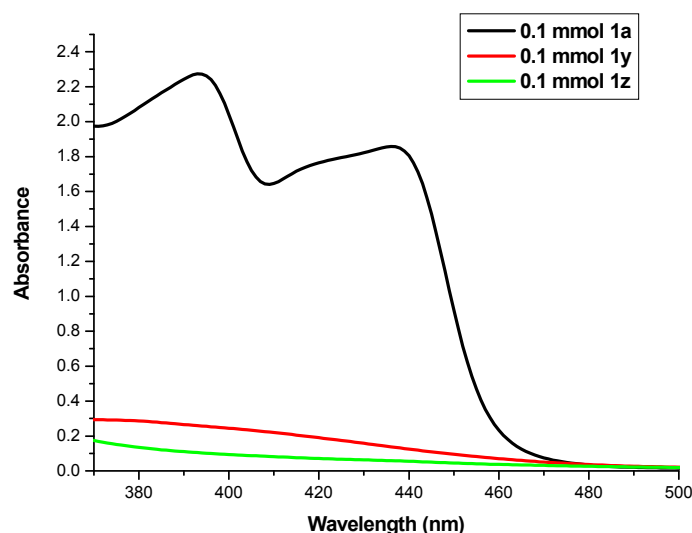
The ultraviolet/visible absorption spectra of 2-(2-(phenylethynyl)benzylidene)-malononitrile (**1a**) in 0.06 mmol/2.0 mL of DMF, 0.08 mmol//2.0 mL of DMF, and 0.1 mmol//2.0 mL of DMF were recorded, respectively on a UV-Visible U-4100 spectrophotometer, shown in Figure S3. From Figure S3, it is obviously to find that the maxium absorption wavelength of **1a** is near 390 nm, and 430 nm, in accord with the wavelength of the LED (380–385 nm) used in the experiment.



**Figure S3.** Absorption spectra of **1a** in DMF

## 4.2 The ultraviolet/visible absorption spectra of **1y** and **1z**, comparing with **1a**

The ultraviolet/visible absorption spectra of 1-(2,2-dibromovinyl)-2-(phenylethynyl)benzene (**1y**) and dimethyl 2-(2-(phenylethynyl)benzylidene)malonate (**1z**), comparing with 2-(2-(phenylethynyl)benzylidene)malononitrile (**1a**) in 0.10 mmol//2.0 mL of DMF were recorded, respectively on a UV-Visible U-4100 spectrophotometer, shown in Figure S4. From Figure S4, UV-visible absorption spectra of substrate **1y** and **1z** indicated that they have little absorption over 370 nm and can't act as photocatalyst.

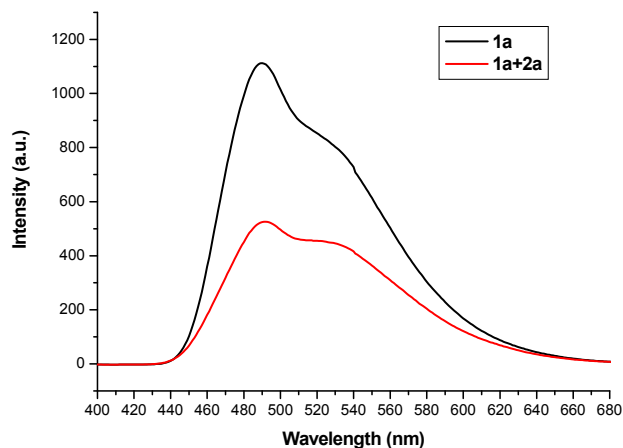


**Figure S4.** Absorption spectra of **1a**, **1y** and **1z** in DMF

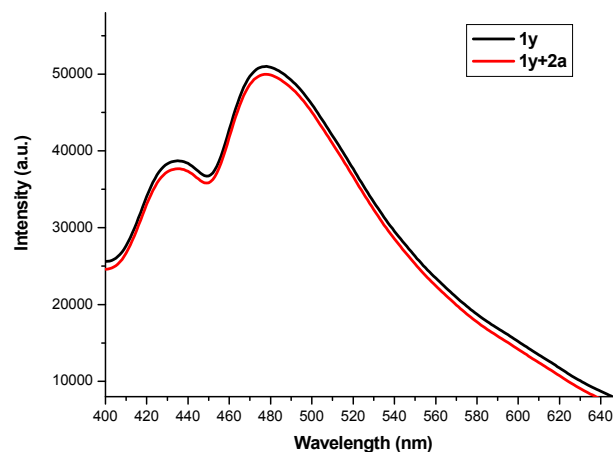
## 4.4 Fluorescence quenching experiments of **1a**, **1y** and **1z** by the addition of **2a**

To further elucidate the possible reaction pathway, fluorescence quenching experiment was also performed. The fluorescence emission intensity was recorded on a RF-5301PC fluorescence spectrophotometer and the excitation wavelength was fixed at 380 nm, shown in Figures S5–S7. From Figure S5, it indicated that the fluorescence of 2-(2-(phenylethynyl)benzylidene)malononitrile (**1a**, 50.8 mg, 0.20

mmol in 2.0 mL of DMF) can be obviously quenched by the addition of TMSN<sub>3</sub> (**2a**, 46.0 mg, 0.20 mmol in 2.0 mL of DMF). However, 1-(2,2-dibromovinyl)-2-(phenylethynyl)benzene (**1y**) and dimethyl 2-(2-(phenylethynyl)benzylidene)malonate (**1z**) could not be quenched by TMSN<sub>3</sub> (**2a**) under the present reaction conditions (Figure S6 and Figure S7).



**Figure S5.** Quenching experiment of **1a** by the addition of TMSN<sub>3</sub> (**2a**)



**Figure S6.** Quenching experiment of **1y** by the addition of TMSN<sub>3</sub> (**2a**)



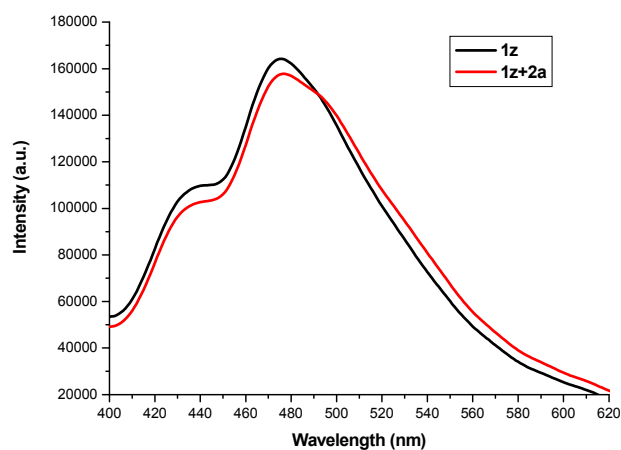
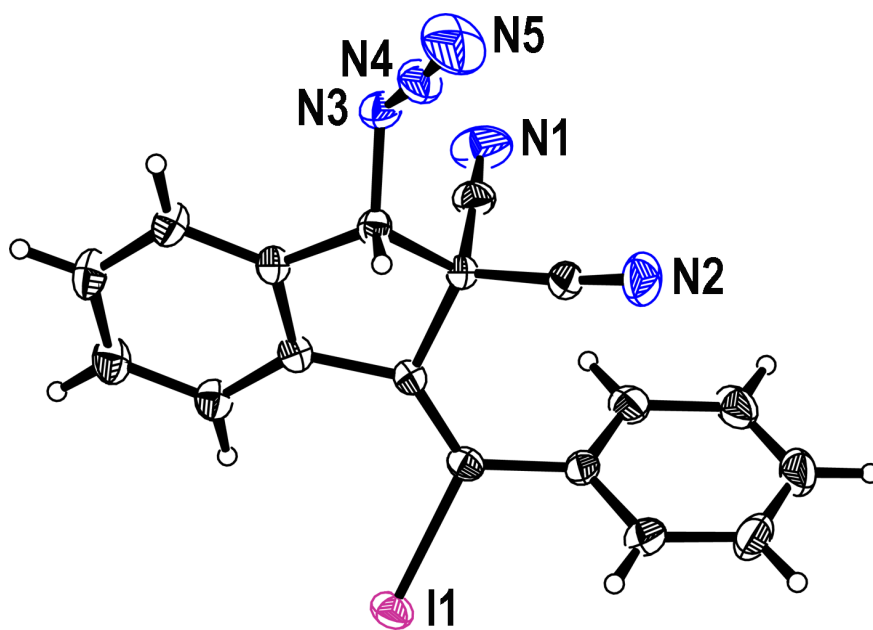


Figure S7. Quenching experiment of **1z** by the addition of  $\text{TMSN}_3$  (**2a**)

## 5. X-Ray single crystal diffraction analysis of **4a** (CCDC: 1960896)



## checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found.    CIF dictionary    Interpreting this report

### Datablock: a

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Bond precision:    C-C = 0.0061 Å                      Wavelength=0.71073

Cell:              a=8.547(3)              b=10.078(4)              c=10.245(4)  
                    alpha=92.009(7)      beta=106.090(6)      gamma=100.898(6)  
Temperature:    293 K

	Calculated	Reported
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Space group	P -1	P-1
Hall group	-P 1	?
Moiety formula	C18 H10 I N5	?
Sum formula	C18 H10 I N5	C18 H10 I N5
Mr	423.21	423.21
Dx, g cm <sup>-3</sup>	1.695	1.695
Z	2	2
Mu (mm <sup>-1</sup> )	1.940	1.940
F000	412.0	412.0
F000'	411.17	
h,k,lmax	10,11,12	10,11,12
Nref	2920	2867
Tmin,Tmax	0.575,0.653	0.603,0.675
Tmin'	0.564	

Correction method= # Reported T Limits: Tmin=0.603 Tmax=0.675  
AbsCorr = MULTI-SCAN

Data completeness= 0.982                      Theta(max)= 24.990

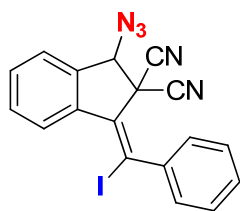
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S = 1.080                                      Npar= 217

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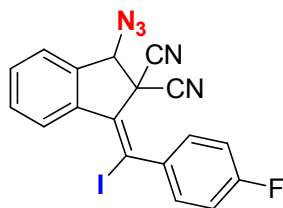
The following ALERTS were generated. Each ALERT has the format  
**test-name\_ALERT\_alert-type\_alert-level.**  
Click on the hyperlinks for more details of the test.

## 6. Characterization data for the products



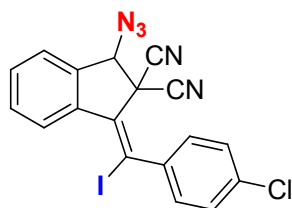
### **(E)-1-Azido-3-(iodo(phenyl)methylene)-1H-indene-2,2(3H)-dicyanitrile (4a):**

Yellow solid; m. p. 128.2–130.1 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.43 (d,  $J = 7.5$  Hz, 1H), 7.47 (d,  $J = 5.6$  Hz, 2H), 7.41 (t,  $J = 6.7$  Hz, 1H), 7.36 (t,  $J = 7.7$  Hz, 4H), 7.32 (d,  $J = 6.7$  Hz, 1H), 5.15 (s, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 138.6, 137.5, 135.0, 131.0, 130.6, 130.2, 129.6, 129.0, 128.4, 126.8, 124.9, 124.7, 112.4, 111.0, 70.4, 47.2. HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd. for  $\text{C}_{18}\text{H}_{10}\text{IN}_5\text{Na}^+$ : 445.9873, Found: 445.9873.

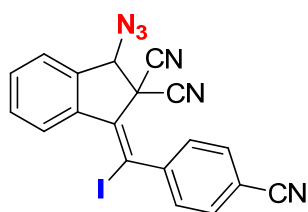


### **(E)-1-Azido-3-((4-fluorophenyl)iodomethylene)-1H-indene-2,2(3H)-dicyanitrile**

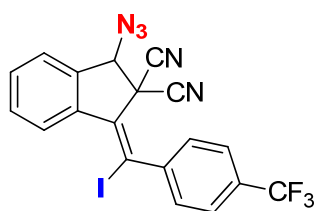
**(4b):** Yellow solid; m. p. 131.3–133.7 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.71 (d,  $J = 7.7$  Hz, 1H), 7.62–7.57 (m, 2H), 7.54 (d,  $J = 7.9$  Hz, 2H), 7.50 (d,  $J = 7.4$  Hz, 1H), 7.18 (t,  $J = 8.5$  Hz, 2H), 5.27 (s, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 162.4 (d,  $J = 251.1$  Hz), 139.3 (d,  $J = 3.7$  Hz), 138.4, 135.9, 134.0, 131.7, 130.0, 126.6, 125.2, 116.5 (d,  $J = 22.0$  Hz), 102.6, 111.3, 98.2, 70.5, 47.5. HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd. for  $\text{C}_{18}\text{H}_9\text{FIN}_5\text{Na}^+$ : 463.9779, Found: 463.9781.



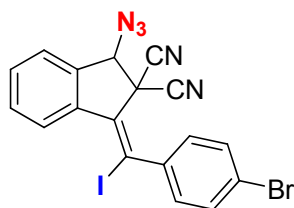
**(E)-1-Azido-3-((4-chlorophenyl)iodomethylene)-1H-indene-2,2(3H)-dicyanonitrile (4c):** Yellow solid; m. p. 134.3–135.6 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 8.57 (d, *J* = 7.7 Hz, 1H), 7.66 (d, *J* = 8.6 Hz, 2H), 7.61–7.56 (m, 2H), 7.52–7.50 (m, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 5.33 (s, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 137.8, 137.7, 135.1, 132.6, 131.5, 130.7, 130.4, 130.2, 127.2, 125.4, 125.2, 123.5, 112.6, 111.1, 70.8, 47.4. HRMS (ESI) ([M+Na]<sup>+</sup>) Calcd. for C<sub>18</sub>H<sub>9</sub>ClIN<sub>5</sub>Na<sup>+</sup>: 479.9483, Found: 479.9483.



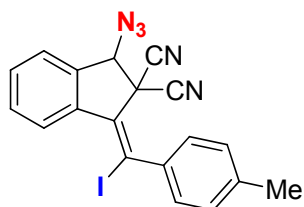
**(E)-1-Azido-3-((4-cyanophenyl)iodomethylene)-1H-indene-2,2(3H)-dicyanonitrile (4d):** Yellow solid; m. p. 135.6–137.3 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 8.66 (dd, *J*<sub>1</sub> = 2.0 Hz, *J*<sub>2</sub> = 6.2 Hz, 1H), 7.71 (d, *J* = 8.6 Hz, 2H), 7.58–7.56 (m, 4H), 7.46 (t, *J* = 6.1 Hz, 1H), 5.24 (s, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 147.0, 138.6, 135.5, 135.0, 133.0, 132.0, 130.2, 126.4, 125.3, 117.9, 114.0, 112.4, 111.0, 95.9, 70.5, 47.3. HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for C<sub>19</sub>H<sub>10</sub>IN<sub>6</sub><sup>+</sup>: 449.0006, Found: 449.0004.



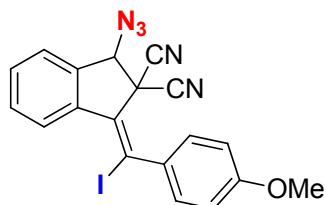
**(E)-1-Azido-3-(iodo(4-(trifluoromethyl)phenyl)methylene)-1H-indene-2,2(3H)-dicyanonitrile (4e):** Yellow solid; m. p. 127.6–129.7 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 8.73 (dd, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 7.3 Hz, 2H), 7.61 (t, *J* = 7.9 Hz, 2H), 7.50 (d, *J* = 7.2 Hz, 1H), 5.29 (s, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 146.3, 138.5, 135.6, 134.6, 132.0, 131.9 (q, *J* = 32.6 Hz), 130.1, 128.7, 126.6, 126.2 (q, *J* = 3.6 Hz), 125.3, 123.5 (q, *J* = 270.9 Hz), 112.4, 111.1, 96.8, 70.5, 47.3. HRMS (ESI) ([M+Na]<sup>+</sup>) Calcd. for C<sub>19</sub>H<sub>9</sub>F<sub>3</sub>IN<sub>5</sub>Na<sup>+</sup>: 513.9747, Found: 513.9747.



**(E)-1-Azido-3-((4-bromophenyl)iodomethylene)-1H-indene-2,2(3H)-dicyanitrile (4f):** Yellow solid; m. p. 136.8–139.5 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.71 (d,  $J = 7.5$  Hz, 1H), 7.64–7.58 (m, 3H), 7.51 (d,  $J = 7.3$  Hz, 1H), 7.44–7.39 (m, 3H), 5.29 (s, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 141.9, 138.4, 135.9, 134.0, 132.6, 131.8, 130.9, 130.1, 126.6, 125.3, 124.8, 112.6, 111.2, 97.9, 70.6, 47.5. HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd. for  $\text{C}_{18}\text{H}_9\text{BrIN}_5\text{Na}^+$ : 523.8978, Found: 523.8978.

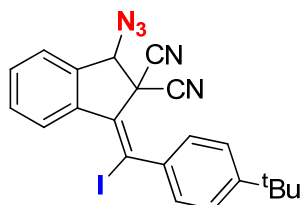


**(E)-1-Azido-3-(iodo(p-tolyl)methylene)-1H-indene-2,2(3H)-dicyanitrile (4g):** Yellow solid; m. p. 130.3–131.9 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.69 (d,  $J = 7.2$  Hz, 1H), 7.60–7.53 (m, 2H), 7.48–7.43 (m, 3H), 7.29 (d,  $J = 8.0$  Hz, 2H), 5.25 (s, 1H), 2.41 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 140.8, 140.4, 138.2, 136.2, 133.0, 131.4, 139.9, 128.1, 126.6, 125.1, 112.6, 111.3, 100.3, 70.6, 47.7, 21.5. HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd. for  $\text{C}_{19}\text{H}_{12}\text{IN}_5\text{Na}^+$ : 460.0030, Found: 460.0030.

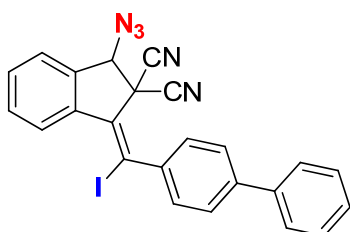


**(E)-1-Azido-3-(iodo(4-methoxyphenyl)methylene)-1H-indene-2,2(3H)-dicyanitrile (4h):** Yellow solid; m. p. 135.3–137.7 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.68 (d,  $J = 7.8$  Hz, 1H), 7.57 (t,  $J = 7.3$  Hz, 1H), 7.53 (t,  $J = 7.4$  Hz, 1H), 7.49 (d,  $J = 8.9$  Hz, 2H), 7.46 (d,  $J = 7.5$  Hz, 1H), 6.98 (d,  $J = 8.8$  Hz, 2H), 5.25 (s, 1H), 3.84 (s, 3H);  $^{13}\text{C}$

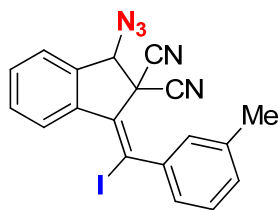
NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$ : 160.9, 138.1, 136.2, 135.6, 132.8, 131.2, 129.9, 126.5, 125.1, 114.5, 112.7, 111.4, 100.3, 70.5, 55.3, 47.8. HRMS (ESI) ([M+Na]<sup>+</sup>) Calcd. for C<sub>19</sub>H<sub>12</sub>IN<sub>3</sub>NaO<sup>+</sup>: 475.9979, Found: 475.9979.



**(E)-1-Azido-3-((4-(*tert*-butyl)phenyl)iodomethylene)-1*H*-indene-2,2(3*H*)-dicyanitrile (4i)**: Yellow solid; m. p. 151.6–153.3 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.63 (d,  $J$  = 7.7 Hz, 1H), 7.53–7.47 (m, 3H), 7.44–7.40 (m, 4H), 5.19 (s, 1H), 1.29 (s, 9H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$ : 154.1, 140.3, 138.3, 136.2, 133.1, 131.4, 129.9, 126.6, 126.2, 125.1, 112.6, 111.4, 100.4, 70.7, 47.9, 34.9, 31.1. HRMS (ESI) ([M+Na]<sup>+</sup>) Calcd. for C<sub>22</sub>H<sub>18</sub>IN<sub>3</sub>Na<sup>+</sup>: 502.0499, Found: 502.0498.

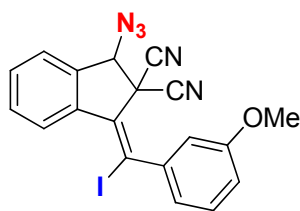


**(E)-1-([1,1'-Biphenyl]-4-yl)iodomethylene)-3-azido-1*H*-indene-2,2(3*H*)-dicyanitrile (4j)**: Yellow solid; m. p. 147.3–148.9 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.59 (d,  $J$  = 7.8 Hz, 1H), 7.76 (d,  $J$  = 8.6 Hz, 2H), 7.66 (t,  $J$  = 8.7 Hz, 4H), 7.58 (t,  $J$  = 7.2 Hz, 1H), 7.54 (td,  $J_1$  = 1.1 Hz,  $J_2$  = 7.5 Hz, 1H), 7.49 (d,  $J$  = 7.5 Hz, 1H), 7.46 (t,  $J$  = 7.5 Hz, 2H), 7.38 (td,  $J_1$  = 1.0 Hz,  $J_2$  = 7.4 Hz, 1H), 5.33 (s, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$ : 143.7, 139.8, 137.8, 137.7, 135.5, 131.4, 130.7, 130.0, 129.3, 129.0, 128.1, 128.0, 127.3, 125.2, 125.0, 112.8, 111.4, 71.1, 47.8. HRMS (ESI) ([M+Na]<sup>+</sup>) Calcd. for C<sub>24</sub>H<sub>14</sub>IN<sub>3</sub>Na<sup>+</sup>: 522.0186, Found: 522.0186.



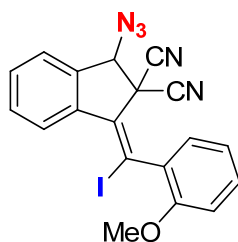
**(E)-1-Azido-3-(iodo(m-tolyl)methylene)-1H-indene-2,2(3H)-dicyanitrile (4k):**

Yellow solid; m. p. 130.5–132.7 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.63 (d,  $J = 7.8$  Hz, 1H), 7.52 (t,  $J = 7.0$  Hz, 1H), 7.48 (td,  $J_1 = 1.0$  Hz,  $J_2 = 7.5$  Hz, 1H), 7.41 (d,  $J = 7.5$  Hz, 1H), 7.32–7.28 (m, 3H), 7.18 (d,  $J = 7.3$  Hz, 1H), 5.16 (s, 1H), 2.33 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 143.0, 139.2, 138.2, 136.1, 133.1, 131.4, 131.2, 130.5, 129.9, 129.1, 126.6, 125.1, 112.6, 111.3, 100.2, 70.5, 47.7, 21.3. HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd. for  $\text{C}_{19}\text{H}_{12}\text{IN}_5\text{Na}^+$ : 460.0030, Found: 460.0031.



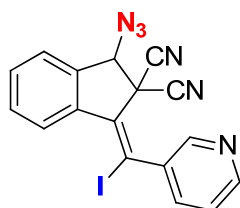
**(E)-1-Azido-3-(iodo(3-methoxyphenyl)methylene)-1H-indene-2,2(3H)-dicyanitrile (4l):**

Yellow solid; m. p. 134.3–135.7 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.72 (d,  $J = 7.7$  Hz, 1H), 7.61 (t,  $J = 7.5$  Hz, 1H), 7.58 (t,  $J = 6.7$  Hz, 1H), 7.50 (d,  $J = 7.4$  Hz, 1H), 7.41 (t,  $J = 8.0$  Hz, 1H), 7.15 (s, 1H), 7.07 (s, 1H), 7.00 (dd,  $J_1 = 2.2$  Hz,  $J_2 = 8.3$  Hz, 1H), 5.27 (s, 1H), 3.86 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 159.9, 144.1, 138.4, 136.1, 133.3, 131.6, 130.7, 130.4, 130.0, 126.7, 125.2, 116.9, 112.6, 112.2, 99.6, 70.6, 55.5, 47.8. HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd. for  $\text{C}_{19}\text{H}_{12}\text{IN}_5\text{NaO}^+$ : 475.9979, Found: 475.9980.



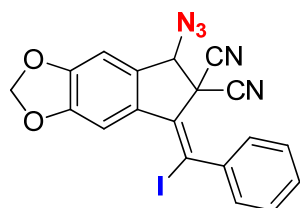
**(E)-1-Azido-3-(iodo(2-methoxyphenyl)methylene)-1H-indene-2,2(3H)-dicyanitrile (4m):**

**rile (4m):** Yellow solid; m. p. 132.3–133.6 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 8.67 (d, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 6.9 Hz, 1H), 7.52 (td, *J*<sub>1</sub> = 1.0 Hz, *J*<sub>2</sub> = 7.5 Hz, 1H), 7.49 (d, *J* = 9.0 Hz, 2H), 7.46 (d, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 5.24 (s, 1H), 3.83 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 160.9, 138.1, 136.2, 135.5, 132.8, 131.2, 130.5, 129.8, 126.5, 125.0, 114.7, 114.5, 112.7, 111.4, 100.3, 70.5, 55.3, 47.7. HRMS (ESI) ([M+Na]<sup>+</sup>) Calcd. for C<sub>19</sub>H<sub>12</sub>IN<sub>5</sub>NaO<sup>+</sup>: 475.9979, Found: 475.9980.



**(E)-1-Azido-3-(iodo(pyridin-3-yl)methylene)-1H-indene-2,2(3H)-dicarbonitrile**

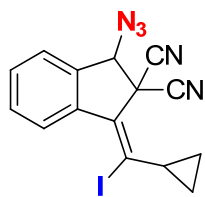
**(4n):** Yellow solid; m. p. 129.3–130.6 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 8.69 (d, *J* = 3.8 Hz, 1H), 8.63 (s, 1H), 7.76 (s, 1H), 7.47 (d, *J* = 7.0 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.27 (d, *J* = 8.1 Hz, 1H), 5.61 (s, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 150.7, 148.0, 139.4, 138.3, 138.2, 135.7, 134.8, 131.2, 130.9, 125.8, 125.1, 124.1, 112.8, 110.0, 98.2, 70.9. HRMS (ESI) ([M+Na]<sup>+</sup>) Calcd. for C<sub>17</sub>H<sub>9</sub>IN<sub>6</sub>Na<sup>+</sup>: 446.9826, Found: 446.9826.



**(E)-5-Azido-7-(iodo(phenyl)methylene)-5H-indeno[5,6-d][1,3]dioxole-6,6(7H)-dicarbonitrile (4o):**

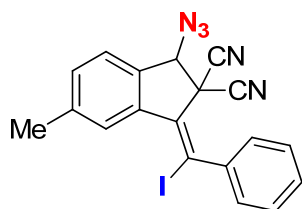
Yellow solid; m. p. 129.8–130.7 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 8.02 (s, 1H), 7.58 (d, *J* = 6.5 Hz, 2H), 7.54–7.50 (m, 3H), 6.90 (s, 1H), 6.14 (s, 2H), 5.18 (s, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 150.5, 149.9, 139.0, 132.8, 130.8, 129.8, 129.3, 128.8, 122.2, 112.7, 111.1, 106.7, 104.9, 102.8, 70.4, 47.8. HRMS (ESI) ([M+Na]<sup>+</sup>) Calcd. for C<sub>19</sub>H<sub>10</sub>IN<sub>5</sub>NaO<sub>2</sub><sup>+</sup>: 489.9771, Found: 489.9770.





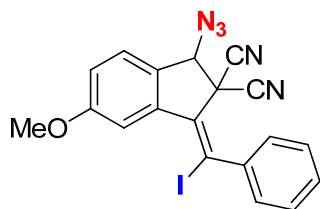
**(E)-1-Azido-3-(cyclopropyliodomethylene)-1H-indene-2,2(3H)-dicyanitrile (4p):**

Yellow solid; m. p. 123.4–125.3 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.68 (d,  $J = 8.5$  Hz, 1H), 7.50 (t,  $J = 4.0$  Hz, 2H), 7.46 (d,  $J = 6.2$  Hz, 1H), 5.40 (s, 1H), 1.99–1.95 (m, 1H), 1.29–1.27 (m, 1H), 1.26–1.23 (m, 1H), 1.20–1.16 (m, 1H), 1.13–1.09 (m, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 137.6, 136.5, 132.5, 130.7, 129.8, 126.1, 125.1, 113.4, 112.5, 111.2, 70.5, 46.7, 24.4, 14.5, 13.6. HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd. for  $\text{C}_{15}\text{H}_{10}\text{IN}_5\text{Na}^+$ : 409.9873, Found: 409.9873.



**(E)-1-Azido-3-(iodo(phenyl)methylene)-5-methyl-1H-indene-2,2(3H)-dicyanitrile (4q):**

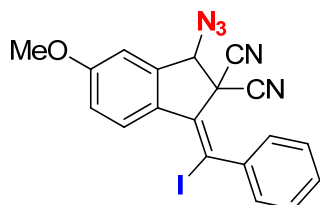
Yellow solid; m. p. 131.2–133.1 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.53 (s, 1H), 7.54 (s, 1H), 7.50–7.43 (m, 4H), 7.38 (s, 2H), 5.19 (s, 1H), 2.50 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 143.2, 140.4, 136.2, 135.6, 133.5, 132.5, 130.4, 129.2, 127.0, 124.9, 112.7, 112.3, 99.3, 70.4, 47.8, 21.9. HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd. for  $\text{C}_{19}\text{H}_{12}\text{IN}_5\text{Na}^+$ : 460.0030, Found: 460.0030.



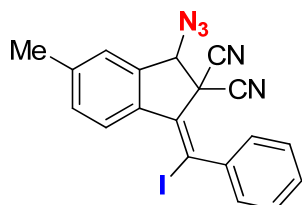
**(E)-1-Azido-3-(iodo(phenyl)methylene)-5-methoxy-1H-indene-2,2(3H)-dicyanitrile (4r):**

Yellow solid; m. p. 133.7–135.1 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.16 (d,  $J = 2.2$  Hz, 1H), 7.46 (s, 2H), 7.41 (t,  $J = 7.2$  Hz, 2H), 7.37 (d,  $J = 7.3$  Hz, 1H), 7.31 (d,  $J = 8.5$  Hz, 1H), 7.03 (dd,  $J_1 = 2.2$  Hz,  $J_2 = 8.5$  Hz, 1H), 5.10 (s, 1H), 3.83 (s, 3H);

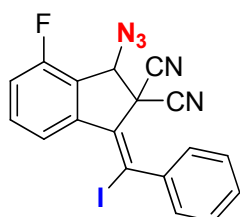
$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 160.8, 143.1, 137.6, 133.3, 130.4, 129.2, 128.2, 126.1, 119.0, 118.2, 112.7, 111.2, 108.4, 99.8, 70.0, 55.7, 47.9. HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd. for  $\text{C}_{19}\text{H}_{12}\text{IN}_5\text{NaO}^+$ : 475.9979, Found: 475.9979.



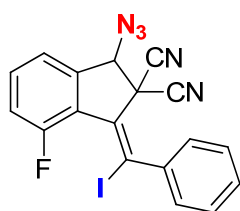
**(E)-3-Azido-1-(iodo(phenyl)methylene)-5-methoxy-1H-indene-2,2(3H)-dicyanonitrile (4s):** Yellow solid; m. p. 131.2–132.9 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.23 (d,  $J = 2.2$  Hz, 1H), 7.55 (d,  $J = 6.0$  Hz, 2H), 7.49 (t,  $J = 7.0$  Hz, 2H), 7.45 (d,  $J = 7.3$  Hz, 1H), 7.39 (d,  $J = 8.4$  Hz, 2H), 7.11 (dd,  $J_1 = 2.3$  Hz,  $J_2 = 8.5$  Hz, 1H), 5.18 (s, 1H), 3.91 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 162.2, 143.1, 140.4, 132.9, 130.2, 129.2, 128.4, 128.1, 116.4, 112.7, 111.4, 109.5, 96.4, 70.4, 55.9, 47.7. HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd. for  $\text{C}_{19}\text{H}_{12}\text{IN}_5\text{NaO}^+$ : 475.9979, Found: 475.9981.



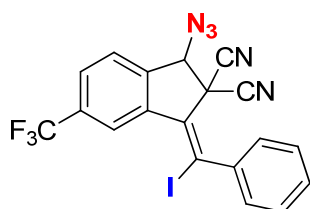
**(E)-3-Azido-1-(iodo(phenyl)methylene)-5-methyl-1H-indene-2,2(3H)-dicyanonitrile (4t):** Yellow solid; m. p. 131.9–133.8 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.53 (s, 1H), 7.55 (d,  $J = 7.2$  Hz, 2H), 7.49 (t,  $J = 8.2$  Hz, 2H), 7.46–7.43 (m, 1H), 7.38 (s, 2H), 5.19 (s, 1H), 2.50 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 143.2, 140.4, 136.2, 135.6, 133.5, 132.5, 130.4, 129.3, 127.0, 124.9, 112.7, 111.3, 99.4, 70.4, 47.8, 21.9. HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd. for  $\text{C}_{19}\text{H}_{12}\text{IN}_5\text{Na}^+$ : 460.0030, Found: 460.0030.



**(E)-3-Azido-4-fluoro-1-(iodo(phenyl)methylene)-1H-indene-2,2(3H)-dicyanitrile (4u):** Yellow solid; m. p. 129.7–130.5 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 7.49–7.43 (m, 3H), 7.35 (s, 2H), 7.06 (t, *J* = 2.8 Hz, 1H), 7.04 (d, *J* = 1.8 Hz, 1H), 6.00 (dd, *J*<sub>1</sub> = 2.6 Hz, *J*<sub>2</sub> = 6.4 Hz, 1H), 5.73 (s, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 159.1 (d, *J* = 251.5 Hz), 143.1, 137.7 (d, *J* = 3.3 Hz), 135.9 (d, *J* = 2.7 Hz), 132.9 (d, *J* = 7.3 Hz), 130.1, 129.6, 127.2 (d, *J* = 36.8 Hz), 124.7 (d, *J* = 16.9 Hz), 121.2 (d, *J* = 3.8 Hz), 116.9 (d, *J* = 19.0 Hz), 112.5, 109.9, 105.7, 67.8, 51.7. HRMS (ESI) ([M+Na]<sup>+</sup>) Calcd. for C<sub>18</sub>H<sub>9</sub>FIN<sub>5</sub>Na<sup>+</sup>: 463.9779, Found: 463.9776.

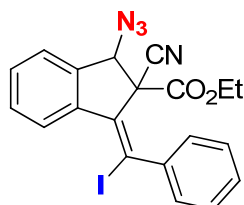


**(Z)-1-Azido-4-fluoro-3-(iodo(phenyl)methylene)-1H-indene-2,2(3H)-dicyanitrile (4v):** Yellow solid; m. p. 130.3–132.1 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 7.60 (s, 2H), 7.55–7.52 (m, 1H), 7.47 (s, 3H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 9.2 Hz, 1H), 5.31 (s, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 156.4 (d, *J* = 260.2 Hz), 142.7, 139.4 (d, *J* = 2.6 Hz), 133.1 (d, *J* = 7.9 Hz), 131.4 (d, *J* = 4.6 Hz), 131.0, 129.1, 124.8 (d, *J* = 13.4 Hz), 120.7 (d, *J* = 3.2 Hz), 119.3 (d, *J* = 21.8 Hz), 111.6, 111.0, 104.9, 71.3, 49.7. HRMS (ESI) ([M+Na]<sup>+</sup>) Calcd. for C<sub>18</sub>H<sub>9</sub>FIN<sub>5</sub>Na<sup>+</sup>: 463.9779, Found: 463.9776.

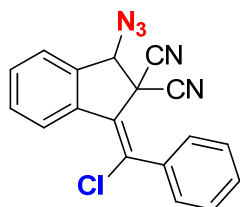


**(E)-1-Azido-3-(iodo(phenyl)methylene)-5-(trifluoromethyl)-1H-indene-2,2(3H)-dicyanitrile (4w):** Yellow solid; m. p. 128.1–129.9 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 8.74 (d, *J* = 7.7 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 7.6 Hz, 2H), 7.61 (t, *J* = 7.6 Hz, 2H), 7.50 (d, *J* = 7.2 Hz, 1H), 5.29 (s, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ:

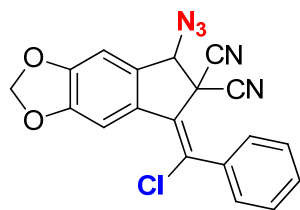
146.3, 138.6, 135.6, 134.6, 132.1, 132.0 (q,  $J = 33.0$  Hz), 130.1, 126.6, 126.3 (q,  $J = 3.1$  Hz), 125.3, 123.5 (q,  $J = 271.1$  Hz), 112.5, 111.1, 96.8, 70.5, 47.4. HRMS (ESI) ( $[M+Na]^+$ ) Calcd. for  $C_{19}H_9F_3IN_5Na^+$ : 513.9747, Found: 513.9747.



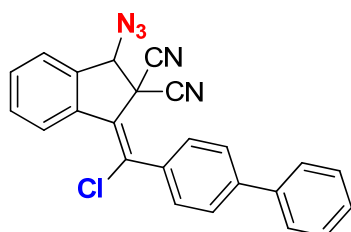
**(E)-Ethyl 1-azido-2-cyano-3-(iodo(phenyl)methylene)-2,3-dihydro-1H-indene-2-carboxylate (4x):** Yellow solid; m. p. 136.7–138.9 °C;  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$ : 8.76 (d,  $J = 7.3$  Hz, 1H), 7.54–7.49 (m, 3H), 7.42 (d,  $J = 7.3$  Hz, 1H), 7.38 (t,  $J = 7.6$  Hz, 3H), 7.31 (t,  $J = 7.6$  Hz, 1H), 5.30 (s, 1H), 3.87–3.82 (m, 1H), 3.57–3.51 (m, 1H), 1.07 (t,  $J = 7.1$  Hz, 3H);  $^{13}C$  NMR (150 MHz,  $CDCl_3$ )  $\delta$ : 165.9, 143.7, 139.8, 137.9, 137.3, 130.9, 129.1, 129.0, 128.4, 125.9, 124.4, 115.2, 96.8, 70.7, 63.6, 62.4, 13.4. HRMS (ESI) ( $[M+Na]^+$ ) Calcd. for  $C_{20}H_{15}IN_4NaO_2^+$ : 493.0132, Found: 493.0133.



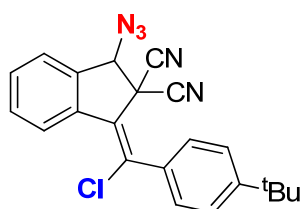
**(E)-1-Azido-3-(chloro(phenyl)methylene)-1H-indene-2,2(3H)-dicarbonitrile (4y):** Yellow solid; m. p. 138.5–149.1 °C;  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$ : 8.42 (d,  $J = 7.9$  Hz, 1H), 7.63 (dd,  $J_1 = 3.5$  Hz,  $J_2 = 7.2$  Hz, 2H), 7.59 (td,  $J_1 = 0.6$  Hz,  $J_2 = 7.5$  Hz, 1H), 7.55–7.53 (m, 3H), 7.51 (d,  $J = 7.2$  Hz, 1H), 7.41 (s, 1H), 5.33 (s, 1H);  $^{13}C$  NMR (150 MHz,  $CDCl_3$ )  $\delta$ : 138.7, 137.6, 135.0, 131.0, 130.6, 130.4, 129.6, 129.0, 128.4, 126.8, 124.9, 124.7, 112.3, 111.1, 70.5, 47.4. HRMS (ESI) ( $[M+Na]^+$ ) Calcd. for  $C_{18}H_{10}ClN_5Na^+$ : 354.0517, Found: 354.0517.



**(E)-5-Azido-7-(chloro(phenyl)methylene)-5H-indeno[5,6-d][1,3]dioxole-6,6(7H)-dicarbonitrile (4z):** Yellow solid; m. p. 139.7–142.1 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.95 (s, 1H), 7.51 (d,  $J = 6.4$  Hz, 2H), 7.49–7.42 (m, 3H), 6.83 (s, 1H), 6.06 (s, 2H), 5.11 (s, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 150.8, 149.3, 143.2, 133.6, 132.9, 130.6, 130.3, 129.3, 112.7, 111.3, 106.3, 104.9, 102.9, 96.9, 70.2, 47.9. HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd. for  $\text{C}_{19}\text{H}_{10}\text{ClN}_5\text{NaO}_2^+$ : 398.0415, Found: 398.0415.

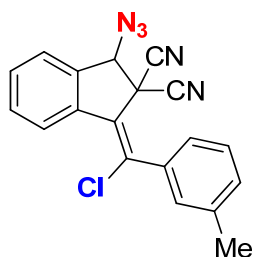


**(E)-1-([1,1'-Biphenyl]-4-ylchloromethylene)-3-azido-1H-indene-2,2(3H)-dicarbonitrile (4aa):** Yellow solid; m. p. 145.3–147.2 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.37 (d,  $J = 7.8$  Hz, 1H), 7.70 (d,  $J = 8.2$  Hz, 2H), 7.63 (d,  $J = 8.2$  Hz, 2H), 7.59 (t,  $J = 7.2$  Hz, 2H), 7.53 (t,  $J = 7.2$  Hz, 1H), 7.48 (t,  $J = 7.4$  Hz, 1H), 7.46 (t,  $J = 7.6$  Hz, 1H), 7.40 (t,  $J = 7.5$  Hz, 2H), 7.32 (t,  $J = 7.4$  Hz, 1H), 5.29 (s, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 143.9, 139.8, 137.2, 135.6, 134.9, 131.1, 130.9, 129.1, 128.9, 128.1, 127.9, 127.3, 127.2, 125.5, 125.1, 112.9, 111.4, 71.3, 47.1. HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd. for  $\text{C}_{24}\text{H}_{14}\text{ClN}_5\text{Na}^+$ : 430.0830, Found: 430.0831.



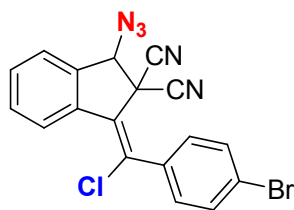
**(E)-1-Azido-3-((4-(tert-butyl)phenyl)chloromethylene)-1H-indene-2,2(3H)-dicarbonitrile (4ab):** Yellow solid; m. p. 153.6–155.2 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ :

8.49 (d,  $J = 7.8$  Hz, 1H), 7.50 (t,  $J = 7.1$  Hz, 1H), 7.47 (s, 1H), 7.46 (s, 4H), 7.41 (d,  $J = 7.4$  Hz, 1H), 5.24 (s, 1H), 1.29 (s, 9H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 154.6, 137.7, 136.0, 135.4, 131.0, 130.4, 129.4, 128.4, 127.1, 126.2, 125.5, 125.1, 112.5, 111.2, 71.0, 47.7, 35.0, 31.1. HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd. for  $\text{C}_{22}\text{H}_{18}\text{ClN}_5\text{Na}^+$ : 410.1143, Found: 410.1145.



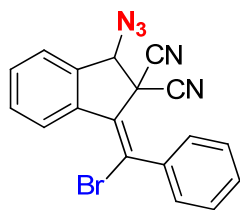
**(*E*)-1-Azido-3-(chloro(*m*-tolyl)methylene)-1*H*-indene-2,2(3*H*)-dicyanitrile (4ac):**

Yellow solid; m. p. 139.8–140.4 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.71 (d,  $J = 7.8$  Hz, 1H), 7.59 (t,  $J = 7.2$  Hz, 1H), 7.54 (td,  $J_1 = 0.8$  Hz,  $J_2 = 7.5$  Hz, 1H), 7.48 (d,  $J = 7.4$  Hz, 1H), 7.38–7.36 (m, 3H), 7.26 (d,  $J = 7.2$  Hz, 1H), 5.24 (s, 1H), 2.41 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 143.0, 139.2, 138.2, 136.1, 133.1, 131.4, 131.2, 130.0, 129.1, 126.6, 125.6, 125.1, 112.6, 111.3, 100.2, 70.5, 47.7, 21.3. HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd. for  $\text{C}_{19}\text{H}_{12}\text{ClN}_5\text{Na}^+$ : 368.0673, Found: 368.0675.



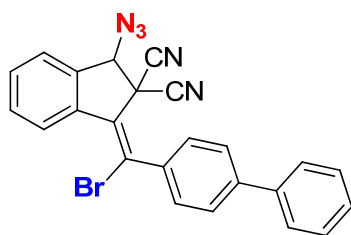
**(*E*)-1-Azido-3-((4-bromophenyl)chloromethylene)-1*H*-indene-2,2(3*H*)-dicyanitrile (4ad):**

Yellow solid; m. p. 141.2–143.1 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.49 (d,  $J = 6.9$  Hz, 1H), 7.58 (d,  $J = 8.5$  Hz, 2H), 7.52–7.49 (m, 2H), 7.43 (d,  $J = 6.8$  Hz, 1H), 7.38 (d,  $J = 8.4$  Hz, 2H), 5.26 (s, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 137.7, 137.6, 135.1, 132.5, 131.6, 130.7, 130.4, 130.1, 127.1, 125.3, 125.1, 123.4, 112.5, 111.0, 70.8, 47.4. HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd. for  $\text{C}_{18}\text{H}_9\text{BrClN}_5\text{Na}^+$ : 431.9622, Found: 431.9622.



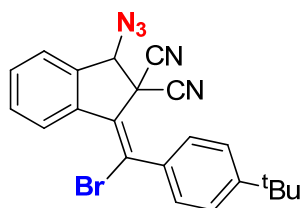
**(E)-1-Azido-3-(chloro(phenyl)methylene)-1H-indene-2,2(3H)-dicyanide (4ae):**

Yellow solid; m. p. 135.7–137.8 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.56 (d,  $J = 7.9$  Hz, 1H), 7.57 (d,  $J = 6.3$  Hz, 2H), 7.52 (t,  $J = 7.4$  Hz, 1H), 7.51 (t,  $J = 7.4$  Hz, 1H), 7.47 (t,  $J = 6.0$  Hz, 3H), 7.44 (d,  $J = 7.4$  Hz, 1H), 5.26 (s, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 138.7, 137.5, 135.1, 131.1, 130.7, 130.3, 129.6, 129.1, 128.4, 126.9, 124.9, 124.7, 112.4, 111.0, 70.5, 47.3. HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd. for  $\text{C}_{18}\text{H}_{10}\text{BrN}_5\text{Na}^+$ : 398.0012, Found: 398.0010.



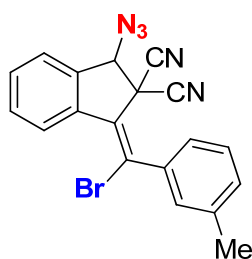
**(E)-1-([1,1'-Biphenyl]-4-ylbromomethylene)-3-azido-1H-indene-2,2(3H)-dicyanide (4af):**

Yellow solid; m. p. 143.6–144.1 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.59 (d,  $J = 7.7$  Hz, 1H), 7.75 (d,  $J = 8.5$  Hz, 2H), 7.68–7.65 (m, 4H), 7.58 (t,  $J = 7.4$  Hz, 1H), 7.54 (t,  $J = 7.0$  Hz, 1H), 7.49 (d,  $J = 7.6$  Hz, 1H), 7.46 (t,  $J = 7.4$  Hz, 2H), 7.38 (t,  $J = 7.4$  Hz, 1H), 5.32 (s, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 143.6, 139.7, 137.7, 137.6, 135.4, 131.3, 130.5, 129.8, 129.2, 128.9, 128.0, 127.8, 127.2, 125.1, 124.9, 112.7, 112.2, 71.0, 47.7. HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd. for  $\text{C}_{24}\text{H}_{14}\text{BrN}_5\text{Na}^+$ : 474.0325, Found: 474.0326.



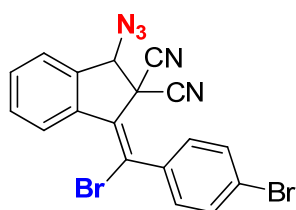
**(E)-1-Azido-3-(bromo(4-(tert-butyl)phenyl)methylene)-1H-indene-2,2(3H)-dicarb**

**onitrile (4ag):** Yellow solid; m. p. 157.8–159.4 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.57 (d,  $J = 7.8$  Hz, 1H), 7.58 (d,  $J = 7.2$  Hz, 1H), 7.55 (s, 1H), 7.53 (s, 4H), 7.49 (d,  $J = 7.4$  Hz, 1H), 5.31 (s, 1H), 1.37 (s, 9H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 154.5, 137.6, 136.1, 135.5, 131.1, 130.5, 129.5, 128.3, 127.1, 126.2, 125.4, 125.0, 112.6, 111.2, 70.9, 47.8, 34.9, 31.1. HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd. for  $\text{C}_{22}\text{H}_{18}\text{BrN}_5\text{Na}^+$ : 454.0638, Found: 454.0636.



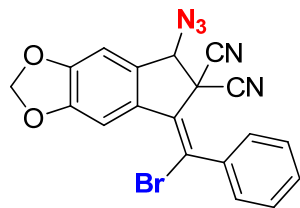
**(E)-1-Azido-3-(bromo(*m*-tolyl)methylene)-1*H*-indene-2,2(3*H*)-dicyanitrile**

**(4ah):** Yellow solid; m. p. 136.9–138.3 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.63 (d,  $J = 7.8$  Hz, 1H), 7.51 (t,  $J = 7.2$  Hz, 1H), 7.48 (t,  $J = 6.6$  Hz, 1H), 7.40 (d,  $J = 7.6$  Hz, 1H), 7.29 (t,  $J = 7.4$  Hz, 3H), 7.18 (d,  $J = 7.2$  Hz, 1H), 5.17 (s, 1H), 2.33 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 143.0, 139.2, 138.3, 136.1, 133.1, 131.4, 131.2, 130.5, 129.9, 129.1, 126.6, 125.1, 112.6, 111.3, 100.2, 70.5, 47.7, 21.3. HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd. for  $\text{C}_{19}\text{H}_{12}\text{BrN}_5\text{Na}^+$ : 412.0168, Found: 412.0171.

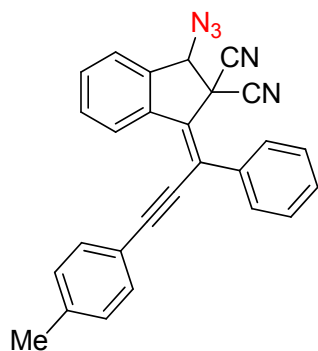


**(E)-1-Azido-3-(bromo(4-bromophenyl)methylene)-1*H*-indene-2,2(3*H*)-dicyanitrile (4ai):** Yellow solid; m. p. 137.9–139.0 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.57 (d,  $J = 7.1$  Hz, 1H), 7.66 (d,  $J = 8.5$  Hz, 2H), 7.61–7.56 (m, 2H), 7.51 (d,  $J = 6.8$  Hz, 1H), 7.46 (d,  $J = 8.5$  Hz, 2H), 5.33 (s, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$ : 137.8, 137.7, 135.1, 132.6, 131.5, 130.6, 130.4, 130.2, 127.2, 125.3, 125.2, 123.4, 112.5, 111.1, 70.8, 47.3. HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd. for  $\text{C}_{18}\text{H}_9\text{Br}_2\text{N}_5\text{Na}^+$ : 475.9117, Found: 475.9117.

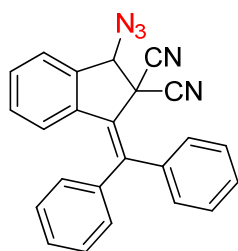




**(E)-5-Azido-7-(bromo(phenyl)methylene)-5H-indeno[5,6-d][1,3]dioxole-6,6(7H)-dicarbonitrile (4aj):** Yellow solid; m. p. 145.6–147.1 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 8.01 (s, 1H), 7.58 (d, *J* = 6.8 Hz, 2H), 7.51 (d, *J* = 7.4 Hz, 3H), 6.89 (s, 1H), 6.13 (s, 2H), 5.18 (s, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 150.5, 149.8, 138.9, 132.7, 130.7, 129.7, 129.2, 128.7, 122.2, 112.7, 111.0, 106.6, 104.8, 102.7, 70.4, 47.8. HRMS (ESI) ([M+Na]<sup>+</sup>) Calcd. for C<sub>19</sub>H<sub>10</sub>BrN<sub>5</sub>NaO<sub>2</sub><sup>+</sup>: 441.9910, Found: 441.9909.



**(E)-1-Azido-3-(1-phenyl-3-(p-tolyl)prop-2-yn-1-ylidene)-1H-indene-2,2(3H)-dicarbonitrile (6a):** Yellow solid; m. p. 121.9–123.0 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 8.50 (s, 1H), 7.79 (d, *J* = 8.4 Hz, 3H), 7.64–7.62 (m, 2H), 7.56–7.54 (m, 1H), 7.45 (t, *J* = 2.6 Hz, 3H), 7.42 (t, *J* = 4.6 Hz, 3H), 7.38 (s, 1H), 2.32 (s, 3H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ: 144.3, 143.5, 136.1, 134.4, 132.2, 131.4, 129.9, 129.7, 129.2, 129.1, 128.7, 127.1, 124.4, 121.9, 121.8, 94.9, 85.9, 59.7, 21.0, 14.0. HRMS (ESI) ([M+Na]<sup>+</sup>) Calcd. for C<sub>27</sub>H<sub>17</sub>N<sub>5</sub>Na<sup>+</sup>: 434.1376, Found: 434.1379.



**1-Azido-3-(diphenylmethylene)-1H-indene-2,2(3H)-dicarbonitrile (8a):** Yellow

solid; m. p. 118.3–120.1 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 7.49–7.45 (m, 6H), 7.38 (d, *J* = 9.2 Hz, 2H), 7.33 (s, 1H), 7.23 (d, *J* = 16.0 Hz, 3H), 7.13 (t, *J* = 6.7 Hz, 1H), 6.59 (d, *J* = 7.6 Hz, 1H), 5.31 (s, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 146.4, 140.0, 139.8, 136.9, 136.8, 130.3, 129.9, 129.7, 129.3, 129.2, 129.1, 129.0, 127.9, 126.5, 125.1, 113.9, 111.9, 71.3, 47.4. HRMS (ESI) ([M+Na]<sup>+</sup>) Calcd. for C<sub>24</sub>H<sub>15</sub>N<sub>5</sub>Na<sup>+</sup>: 396.1220, Found: 396.1222.

## 7. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of the products

