Supporting Information

Photo-Driven Haloazidation Cyclization of 1,5-Enynes Having Cyano Groups with TMSN₃ and NIS/NCS/NBS under Metal-Free Conditions

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1. General considerations

All $^1$H NMR and $^{13}$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 δ 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, SiO₂.

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), TMSN₃ (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(PPh₃)₂Cl₂ (10 mol %), CuI (5 mol %), and Et₃N (2.0 mL). The reactants were degassed and filled with N₂ 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(PPh₃)₄ (5 mol %), K₂CO₃ (0.60 mmol, 3.0 equiv.), and 1,4-dioxane (2.0 mL). The reactants were degassed and filled with N₂ 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

![Chemical structure]

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), TMSN₃ (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)

![Chemical structure]

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), TMSN₃ (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)

![Chemical structure](image)

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), TMSN₃ (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⁺ 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
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.
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.

![Absorption spectra of 1a, 1y and 1z in DMF](image)

**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 TMSN₃ (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 TMSN₃ (2a) under the present reaction conditions (Figure S6 and Figure S7).

**Figure S5.** Quenching experiment of 1a by the addition of TMSN₃ (2a)

**Figure S6.** Quenching experiment of 1y by the addition of TMSN₃ (2a)
Figure S7. Quenching experiment of 1z by the addition of TMSN₃ (2a)

5. X-Ray single crystal diffraction analysis of 4a (CCDC: 1960896)
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You have not supplied any structure factors. As a result the full set of tests cannot be run.

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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)-dicarbonitrile (4a):
Yellow solid; m. p. 128.2–130.1 °C; ¹H NMR (600 MHz, CDCl₃) δ: 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); ¹³C NMR (150 MHz, CDCl₃) δ: 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) ([M+Na⁺]⁺) Calcd. for C₁₈H₁₀IN₅Na⁺: 445.9873, Found: 445.9873.

(E)-1-Azido-3-((4-fluorophenyl)iodomethylene)-1H-indene-2,2(3H)-dicarbonitrile (4b):
Yellow solid; m. p. 131.3–133.7 °C; ¹H NMR (600 MHz, CDCl₃) δ: 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); ¹³C NMR (150 MHz, CDCl₃) δ: 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) ([M+Na⁺]⁺) Calcd. for C₁₈H₉FIN₅Na⁺: 463.9779, Found: 463.9781.
*(E)-1-Azido-3-((4-chlorophenyl)iodomethylene)-1*H*-indene-2,2(3*H*)-dicarbonitrile (4c):* Yellow solid; m. p. 134.3–135.6 °C; *1*H NMR (600 MHz, CDCl3) 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); *13*C NMR (150 MHz, CDCl3) 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]+) Calcd. for C18H9ClIN5Na+: 479.9483, Found: 479.9483.

![Image of 4c structure]

*(E)-1-Azido-3-((4-cyanophenyl)iodomethylene)-1*H*-indene-2,2(3*H*)-dicarbonitrile (4d):* Yellow solid; m. p. 135.6–137.3 °C; *1*H NMR (600 MHz, CDCl3) δ: 8.66 (dd, *J*1 = 2.0 Hz, *J*2 = 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); *13*C NMR (150 MHz, CDCl3) 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]+) Calcd. for C19H10IN6+: 449.0006, Found: 449.0004.

![Image of 4d structure]

*(E)-1-Azido-3-(iodo(4-(trifluoromethyl)phenyl)methylene)-1*H*-indene-2,2(3*H*)-dicarbonitrile (4e):* Yellow solid; m. p. 127.6–129.7 °C; *1*H NMR (600 MHz, CDCl3) 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); *13*C NMR (150 MHz, CDCl3) 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]+) Calcd. for C19H9F3IN5Na+: 513.9747, Found: 513.9747.
(E)-1-Azido-3-((4-bromophenyl)iodomethylene)-1H-indene-2,2(3H)-dicarbonitrile (4f): Yellow solid; m. p. 136.8–139.5 °C; 1H NMR (600 MHz, 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); 13C NMR (150 MHz, 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) ([M+Na$^+$]) Calcd. for C$_{18}$H$_9$BrIN$_5$Na$: 523.8978$, Found: 523.8978.

(E)-1-Azido-3-(iodo(p-tolyl)methylene)-1H-indene-2,2(3H)-dicarbonitrile (4g): Yellow solid; m. p. 130.3–131.9 °C; 1H NMR (600 MHz, 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); 13C NMR (150 MHz, 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) ([M+Na$^+$]) Calcd. for C$_{19}$H$_{12}$IN$_5$Na$: 460.0030$, Found: 460.0030.

(E)-1-Azido-3-(iodo(4-methoxyphenyl)methylene)-1H-indene-2,2(3H)-dicarbonitrile (4h): Yellow solid; m. p. 135.3–137.7 °C; 1H NMR (600 MHz, 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); 13C
NMR (150 MHz, CDCl₃) δ: 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]+) Calcd. for C₁₉H₁₂IN₅NaO⁺: 475.9979, Found: 475.9979.

\((E)-1\text{-Azido-3-}\left(\text{4-}\text{(\text{tert}-\text{butyl})phenyl}ight)\text{iodomethylene-1H-indene-2,2(3H)-dicarbonitrile (4i)}\): Yellow solid; m. p. 151.6–153.3 °C; \(^1\text{H} \text{NMR (600 MHz, CDCl}_3\) δ: 8.63 (d, \(J = 7.7 \text{ Hz}, 1\text{H}\)), 7.53–7.47 (m, 3H), 7.44–7.40 (m, 4H), 5.19 (s, 1H), 1.29 (s, 9H); \(^{13}\text{C} \text{NMR (150 MHz, CDCl}_3\) δ: 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]+) Calcd. for C₂₂H₁₈IN₅Na⁺: 502.0499, Found: 502.0498.

\((E)-1\text{-}\left(\text{[1,1\text{-Biphenyl]}-4-}\text{yliodomethylene}\right)\text{-3-azido-1H-indene-2,2(3H)-dicarbonitrile (4j):}\) Yellow solid; m. p. 147.3–148.9 °C; \(^1\text{H} \text{NMR (600 MHz, CDCl}_3\) δ: 8.59 (d, \(J = 7.8 \text{ Hz}, 1\text{H}\)), 7.76 (d, \(J = 8.6 \text{ Hz}, 2\text{H}\)), 7.66 (t, \(J = 8.7 \text{ Hz}, 4\text{H}\)), 7.58 (t, \(J = 7.2 \text{ Hz}, 1\text{H}\)), 7.54 (td, \(J_1\text{=1.1 Hz}, J_2\text{=7.5 Hz}, 1\text{H}\)), 7.49 (d, \(J = 7.5 \text{ Hz}, 1\text{H}\)), 7.46 (t, \(J = 7.5 \text{ Hz}, 2\text{H}\)), 7.38 (td, \(J_1\text{=1.0 Hz}, J_2\text{=7.4 Hz}, 1\text{H}\)), 5.33 (s, 1H); \(^{13}\text{C} \text{NMR (150 MHz, CDCl}_3\) δ: 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]+) Calcd. for C₂₄H₁₄IN₅Na⁺: 522.0186, Found: 522.0186.
(E)-1-Azido-3-(iodo(m-tolyl)methylene)-1H-indene-2,2(3H)-dicarbonitrile (4k): Yellow solid; m. p. 130.5–132.7 °C; \(^1\)H NMR (600 MHz, 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); \(^{13}\)C NMR (150 MHz, 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) ([M+Na\(^+\)]\(^+\)) Calcd. for C\(_{19}\)H\(_{12}\)IN\(_5\)Na\(^+\): 460.0030, Found: 460.0031.

(E)-1-Azido-3-(iodo(3-methoxyphenyl)methylene)-1H-indene-2,2(3H)-dicarbonitrile (4l): Yellow solid; m. p. 134.3–135.7 °C; \(^1\)H NMR (600 MHz, 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); \(^{13}\)C NMR (150 MHz, 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) ([M+Na\(^+\)]\(^+\)) Calcd. for C\(_{19}\)H\(_{12}\)IN\(_5\)NaO\(^+\): 475.9979, Found: 475.9980.

(E)-1-Azido-3-(iodo(2-methoxyphenyl)methylene)-1H-indene-2,2(3H)-dicarbonitrile (4m): Yellow solid; m. p. 152.7–152.9 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\): 8.68 (d, \(J = 7.8\) Hz, 1H), 7.63 (t, \(J = 7.7\) Hz, 1H), 7.56 (t, \(J = 6.7\) Hz, 1H), 7.48 (td, \(J_1 = 1.0\) Hz, \(J_2 = 7.5\) Hz, 1H), 7.40 (d, \(J = 7.5\) Hz, 1H), 7.32–7.28 (m, 3H), 7.17 (d, \(J = 7.3\) Hz, 1H), 5.14 (s, 1H), 2.30 (s, 3H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\): 144.2, 139.3, 138.4, 136.1, 133.1, 131.4, 131.2, 130.5, 129.8, 129.1, 126.4, 125.0, 112.6, 111.3, 100.2, 70.5, 47.7, 21.3. HRMS (ESI) ([M+Na\(^+\)]\(^+\)) Calcd. for C\(_{19}\)H\(_{12}\)IN\(_5\)Na\(^+\): 460.0030, Found: 460.0031.
**rile (4m):** Yellow solid; m. p. 132.3–133.6 °C; $^1$H NMR (600 MHz, CDCl$_3$) δ: 8.67 (d, $J = 7.8$ Hz, 1H), 7.56 (t, $J = 6.9$ Hz, 1H), 7.52 (td, $J_1 = 1.0$ Hz, $J_2 = 7.5$ 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); $^{13}$C NMR (150 MHz, CDCl$_3$) 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$^+$]) Calcd. for C$_{19}$H$_{12}$IN$_5$NaO$: 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; $^1$H NMR (600 MHz, CDCl$_3$) 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); $^{13}$C NMR (150 MHz, CDCl$_3$) 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$^+$]) Calcd. for C$_{17}$H$_9$IN$_6$Na$: 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; $^1$H NMR (600 MHz, CDCl$_3$) 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); $^{13}$C NMR (150 MHz, CDCl$_3$) 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$^+$]) Calcd. for C$_{19}$H$_{10}$IN$_5$NaO$_2$: 489.9771, Found: 489.9770.
\((E)-1\)-Azido-3-(cyclopropyliodomethylene)-1\(H\)-indene-2,2(3\(H\))-dicarbonitrile (4p): Yellow solid; m. p. 123.4–125.3 °C; \(^1\)H NMR (600 MHz, 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); \(^{13}\)C NMR (150 MHz, 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) ([M+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-1\(H\)-indene-2,2(3\(H\))-dicarbonitrile (4q): Yellow solid; m. p. 131.2–133.1 °C; \(^1\)H NMR (600 MHz, 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); \(^{13}\)C NMR (150 MHz, 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) ([M+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-1\(H\)-indene-2,2(3\(H\))-dicarbonitrile (4r): Yellow solid; m. p. 133.7–135.1 °C; \(^1\)H NMR (600 MHz, 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);
$^{13}$C NMR (150 MHz, CDCl$_3$) δ: 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) ([M+Na$^+$]) Calcd. for C$_{19}$H$_{12}$IN$_5$NaO$: 475.9979$, Found: 475.9979.

(E)-3-Azido-1-(iodo(phenyl)methylene)-5-methoxy-$1H$-indene-2,2(3$H$)-dicarbonitrile (4s): Yellow solid; m. p. 131.2–132.9 °C; $^1$H NMR (600 MHz, CDCl$_3$) δ: 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); $^{13}$C NMR (150 MHz, CDCl$_3$) δ: 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) ([M+Na$^+$]) Calcd. for C$_{19}$H$_{12}$IN$_5$NaO$: 475.9979$, Found: 475.9981.

(E)-3-Azido-1-(iodo(phenyl)methylene)-5-methyl-$1H$-indene-2,2(3$H$)-dicarbonitrile (4t): Yellow solid; m. p. 131.9–133.8 °C; $^1$H NMR (600 MHz, CDCl$_3$) δ: 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); $^{13}$C NMR (150 MHz, CDCl$_3$) δ: 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) ([M+Na$^+$]) Calcd. for C$_{19}$H$_{12}$IN$_5$Na$: 460.0030$, Found: 460.0030.
(E)-3-Azido-4-fluoro-1-(iodo(phenyl)methylene)-1H-indene-2,2(3H)-dicarbonitrile (4u): Yellow solid; m. p. 129.7–130.5 °C; $^1$H NMR (600 MHz, CDCl$_3$) 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, $J_1$ = 2.6 Hz, $J_2$ = 6.4 Hz, 1H), 5.73 (s, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) 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]$^+$) Calcd. for C$_{18}$H$_9$FNI$_5$Na$: 463.9779$, Found: 463.9776.

(Z)-1-Azido-4-fluoro-3-(iodo(phenyl)methylene)-1H-indene-2,2(3H)-dicarbonitrile (4v): Yellow solid; m. p. 130.3–132.1 °C; $^1$H NMR (600 MHz, CDCl$_3$) 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); $^{13}$C NMR (150 MHz, CDCl$_3$) 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]$^+$) Calcd. for C$_{18}$H$_9$FNI$_5$Na$: 463.9779$, Found: 463.9776.

(E)-1-Azido-3-(iodo(phenyl)methylene)-5-(trifluoromethyl)-1H-indene-2,2(3H)-dicarbonitrile (4w): Yellow solid; m. p. 128.1–129.9 °C; $^1$H NMR (600 MHz, CDCl$_3$) 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); $^{13}$C NMR (150 MHz, CDCl$_3$) 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\(_9\)F\(_3\)IN\(_5\)Na\(^+\): 513.9747, Found: 513.9747.

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\begin{align*}
&\text{N}_3 \\
&\text{C} \quad \text{CN} \\
&\text{CO}_2\text{Et} \\
&\text{I}\end{align*}
\]

\((E)-\text{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; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \):
\begin{align*}
&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\(_4\)NaO\(_2\)\(^+\): 493.0132, Found: 493.0133.

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\begin{align*}
&\text{N}_3 \\
&\text{C} \quad \text{CN} \\
&\text{CN} \\
&\text{Cl} \\
&\text{CO}_2\text{Et}\end{align*}
\]

\((E)-\text{1-Azido-3-(chloro(phenyl)methylene)-1H-indene-2,2(3H)-dicarbonitrile (4y):} Yellow solid; m. p. 138.5–149.1 °C; \(^1\)H 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\(_{12}\)ClIN\(_3\)Na\(^+\): 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; $^1$H NMR (600 MHz, CDCl$_3$) δ: 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); $^{13}$C NMR (150 MHz, CDCl$_3$) δ: 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) ([M+Na]$^+$) Calcd. for C$_{19}$H$_{10}$ClN$_5$O$_2$: 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; $^1$H NMR (600 MHz, CDCl$_3$) δ: 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); $^{13}$C NMR (150 MHz, CDCl$_3$) δ: 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) ([M+Na]$^+$) Calcd. for C$_{24}$H$_{14}$ClN$_5$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; $^1$H NMR (600 MHz, CDCl$_3$) δ:
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); $^{13}$C NMR (150 MHz, 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) ([M+Na]$^+$) Calcd. for C$_{22}$H$_{18}$ClN$_5$Na$: 410.1143, Found: 410.1145.

**($E$)-1-Azido-3-((chloro(m-tolyl)methylene)-$^{1}H$-indene-2,2(3$H$)-dicarbonitride (4ac):**

Yellow solid; m. p. 139.8–140.4 °C; $^1$H NMR (600 MHz, 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); $^{13}$C NMR (150 MHz, 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) ([M+Na]$^+$) Calcd. for C$_{19}$H$_{12}$ClN$_5$Na$: 368.0673, Found: 368.0675.

**($E$)-1-Azido-3-((4-bromophenyl)chloromethylene)-$^{1}H$-indene-2,2(3$H$)-dicarbonitride (4ad):**

Yellow solid; m. p. 141.2–143.1 °C; $^1$H NMR (600 MHz, 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); $^{13}$C NMR (150 MHz, 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) ([M+Na]$^+$) Calcd. for C$_{19}$H$_9$BrClN$_5$Na$: 431.9622, Found: 431.9622.
(E)-1-Azido-3-(chloro(phenyl)methylene)-1H-indene-2,2(3H)-dicarbonitrile (4ae):
Yellow solid; m. p. 135.7–137.8 °C; \(^1\)H NMR (600 MHz, 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); \(^1\)\(^3\)C NMR (150 MHz, 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) ([M+Na]+) Calcd. for C\(_{18}\)H\(_{10}\)BrN\(_5\)Na\(^+\): 398.0012, Found: 398.0010.

(\(E\))-1-([1,1'-Biphenyl]-4-ylbromomethylene)-3-azido-1H-indene-2,2(3H)-dicarbonitrile (4af):
Yellow solid; m. p. 143.6–144.1 °C; \(^1\)H NMR (600 MHz, 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); \(^1\)\(^3\)C NMR (150 MHz, 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) ([M+Na]+) Calcd. for C\(_{24}\)H\(_{14}\)BrN\(_5\)Na\(^+\): 474.0325, Found: 474.0326.

(\(E\))-1-Azido-3-(bromo(4-(\(\text{tert}-\text{butyl})\)phenyl)methylene)-1H-indene-2,2(3H)-dicarbonitrile:

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onitrile (4ag): Yellow solid; m. p. 157.8–159.4 °C; $^1$H NMR (600 MHz, 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); $^{13}$C NMR (150 MHz, 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) ([M+Na]$^+$) Calcd. for C$_{22}$H$_{18}$BrN$_5$Na$: 454.0638$, Found: 454.0636.

![onitrile structure](image)

(E)-1-Azido-3-(bromo(m-tolyl)methylene)-1H-indene-2,2(3H)-dicarbonitrile (4ah): Yellow solid; m. p. 136.9–138.3 °C; $^1$H NMR (600 MHz, 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); $^{13}$C NMR (150 MHz, 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) ([M+Na]$^+$) Calcd. for C$_{19}$H$_{12}$BrN$_5$Na$: 412.0168$, Found: 412.0171.

![structure of 4ah](image)

(E)-1-Azido-3-(bromo(4-bromophenyl)methylene)-1H-indene-2,2(3H)-dicarbonitrile (4ai): Yellow solid; m. p. 137.9–139.0 °C; $^1$H NMR (600 MHz, 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); $^{13}$C NMR (150 MHz, 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) ([M+Na]$^+$) Calcd. for C$_{18}$H$_9$Br$_2$N$_5$Na$: 475.9117$, Found: 475.9117.
(E)-5-Azido-7-(bromo(phenyl)methylene)-5H-indeno[5,6-d][1,3]dioxole-6,6(7H)-dicyanocarbonitrile (4aj): Yellow solid; m. p. 145.6–147.1 °C; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$: 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); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$: 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$^+$]) Calcd. for C$_{19}$H$_{10}$BrN$_5$NaO$_2$: 441.9910, Found: 441.9909.

(E)-1-Azido-3-(1-phenyl-3-(p-tolyl)prop-2-yn-1-ylidene)-1H-indene-2,2(3H)-dicyanocarbonitrile (6a): Yellow solid; m. p. 121.9–123.0 °C; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$: 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); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$: 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$^+$]) Calcd. for C$_{27}$H$_{17}$N$_5$Na$: 434.1376, Found: 434.1379.

1-Azido-3-(diphenylmethylene)-1H-indene-2,2(3H)-dicyanocarbonitrile (8a): Yellow
solid; m. p. 118.3–120.1 °C; $^1$H NMR (600 MHz, CDCl$_3$) 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); $^{13}$C NMR (150 MHz, CDCl$_3$) δ: 146.4, 140.0, 139.8, 136.9, 136.8, 130.3, 129.9, 129.7, 129.3, 129.1, 129.0, 127.9, 126.5, 125.1, 113.9, 111.9, 71.3, 47.4. HRMS (ESI) ([M+Na]$^+$) Calcd. for C$_{24}$H$_{15}$N$_5$Na$: 396.1220$, Found: 396.1222.
7. $^1$H and $^{13}$C NMR spectra of the products