Supporting Information for

Decarboxylative 1,4-Carbocyanation of 1,3-Enynes to Access Tetrasubstituted Allenes via Copper/Photoredox Dual Catalysis

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1. General information

Unless otherwise noted, all experiments were carried out under an atmosphere of nitrogen and anhydrous conditions. ¹H NMR and ¹³C NMR spectra were recorded on Bruker AMX 400 Spectrometer (¹H 400 MHz and ¹³C 100 MHz, respectively) and Bruker AMX 500 Spectrometer (¹H 500 MHz and ¹³C 125 MHz, respectively). Chemical shifts (δ) were given in ppm and were referenced to residual solvent or TMS peaks. All high resolution mass spectra were obtained on a Bruker micrOTOFQ II (ESI). All the solvents were purified according to the standard procedures. Substrates of NHP ester were synthesized according to the modified literature methods.^[1] All other chemicals which are commercially available were employed without further purification.

2. Optimization of reaction conditions

C ₆ H ₁₁ +	2a	Cu] (5 mol%) ppy) ₃ (1 mol%) pp (7 mol%) IF, N ₂ , rt, 12 h lue LEDs 3a	CN C_5H_{11}
Entry	[Cu]	Yield (%) ^[b]	
1	Cu(CH ₃ CN) ₄ PF ₆	74	
2	CuOAc	73	
3	CuCl	50	
4	CuBr	32	
5	CuI	66	
6	CuCN	68	
7	Cu(OTf) ₂	70	
8	CuCl ₂	16	

Table S1. Screening of copper catalysts [a]

[a] Reaction conditions: 1a (0.2 mmol), 2a (0.2 mmol) and TMSCN (0.4 mmol) in 1.0 mL DMF,
[Cu] (5 mol%), bpy (7 mol%), Ir(ppy)₃ (1 mol%), at room temperature, 30 W blue LEDs, 12 h. [b]
Determined by ¹H NMR analysis of crude product with CH₂Br₂ as an internal standard.

Table S2. Screening of ligands^[a]



[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol) and TMSCN (0.4 mmol) in 1.0 mL DMF, Cu(CH₃CN)₄PF₆ (5 mol%), ligand (7 mol%), Ir(ppy)₃ (1 mol%), at room temperature, 30 W blue LEDs, 12 h. [b] Determined by ¹H NMR analysis of crude product with CH₂Br₂ as an internal standard.

Table S3. S	creening of s	solvents ^[a]
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<u>_</u>	+ C ₅ H ₁₁ +	Poor + TMSCN 2a	$\begin{array}{c} Cu(CH_3CN)_4PF_6 (5 \text{ mol}\%) \\ Ir(ppy)_3 (1 \text{ mol}\%) \\ \hline \textbf{bpy} (7 \text{ mol}\%) \\ solvent, N_2, rt, 12 h \\ blue LEDs \\ \hline \textbf{3a} \end{array}$
	Entry	Solvent	Yield (%) ^[b]
-	1	DMF	74
	2	DMSO	70
	3	DMA	86
	4	NMP	81
	5	CH ₃ CN	trace
	6	MeOH	trace

7	THF	15
8	EA	trace
9	DCM	trace
10	PhCl	18
11 ^[c]	DMA	88 (82)

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol) and TMSCN (0.4 mmol) in 1.0 mL solvent, Cu(CH₃CN)₄PF₆ (5 mol%), bpy (7 mol%), Ir(ppy)₃ (1 mol%), at room temperature, 30 W blue LEDs, 12 h. [b] Determined by ¹H NMR analysis of crude product with CH₂Br₂ as an internal standard. Yield of the isolated product given within parentheses. [c] Cu(CH₃CN)₄PF₆ (2.5 mol%), bpy (3.5 mol%).

3. General procedure for the synthesis of 1,3-enynes^[2]



Under nitrogen atmosphere, *n*-BuLi (2.0 M in hexane, 5 mmol, 2.5 mL) was added dropwise to a solution of alkyne (5 mmol) in anhydrous THF (20 mL) at -78 °C. After addition, the resulting solution was stirred at room temperature for one hour. Then, cooled to -78 °C again, ketone (5 mmol) in THF (10 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and was monitored by TLC for completion. Once completion the reaction was quenched with saturated aqueous NH₄Cl and extracted with EtOAc three times. The combined organic layer was dried over Na₂SO₄ and concentrated under reduced pressure to afford the crude propargyl alcohol.

The resulting propargyl alcohol was dissolved in DCM (30 mL), and the mixture was cooled to 0 °C. TEA (25 mmol, 5 equiv) was added to this solution and methylsulfonyl chloride (12.5 mmol, 2.5 equiv) sequentially. After one hour the reaction was monitored by TLC for completion. Once completion the reaction was quenched with saturated aqueous NH₄Cl. The aqueous layer was extracted with DCM and the combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude material was purified by flash chromatography to yield the 1,3-enyne.

 $1b^{[2a]}, 1j^{[2d]}, 1k^{[2b]}, 1l^{[2d]}, 1m^{[2b]}, 1n^{[2c]}, 1o^{[2d]}, 1p^{[2c]}, 1r^{[2e]}, 1t^{[2f]}, 11^{[2c]}, 13^{[2c]}$ are known compounds in the references.





1-methoxy-4-(non-1-en-3-yn-2-yl)benzene (1a): Pale yellow oil, isolated yield 50%. ¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, J = 9.2 Hz, 2H), 6.79 (d, J = 8.8 Hz, 2H), 5.65 (d, J = 1.2 Hz, 1H), 5.40 (d, J = 1.2 Hz, 1H), 3.73 (s,

3H), 2.32 (t, *J* = 7.0 Hz, 2H), 1.56 – 1.49 (m, 2H), 1.40 – 1.25 (m, 4H), 0.85 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 159.7, 130.6, 130.4, 127.4, 117.5, 113.7, 91.9, 80.1, 55.4, 31.3, 28.6, 22.4, 19.5, 14.1.



1-methyl-4-(non-1-en-3-yn-2-yl)benzene (1c): Pale yellow oil, isolated yield 50%. ¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.17-7.15 (m, 2H), 5.81 (d, *J* = 1.2 Hz, 1H), 5.54 (d, *J* = 1.2 Hz, 1H), 2.42 (t, *J* = 7.2 Hz, 2H), 2.37

(s, 3H), 1.65 – 1.56 (m, 2H), 1.49 – 1.34 (m, 4H), 0.94 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 138.1, 135.2, 130.9, 129.1, 126.1, 118.5, 92.0, 80.0, 31.3, 28.6, 22.4, 21.3, 19.5, 14.2.



1-fluoro-4-(non-1-en-3-yn-2-yl)benzene (1d): Pale yellow oil, isolated yield 59%. ¹H NMR (400 MHz, CDCl₃) δ 7.64 – 7.61 (m, 2H), 7.05 – 7.00 (m, 2H), 5.77 (d, *J* = 1.2 Hz, 1H), 5.56 – 5.55 (m, 1H), 2.41 (t, *J* = 7.0 Hz, 2H), 1.64 –

1.58 (m, 2H), 1.46 – 1.33 (m, 4H), 0.93 (t, J = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 162.9 (d, J_{C-F} = 246.0 Hz), 134.1 (d, J_{C-F} = 3.0 Hz), 130.1, 127.9 (d, J_{C-F} = 8.0 Hz), 119.2 (d, J_{C-F} = 1.0 Hz), 115.2 (d, J_{C-F} = 22.0 Hz), 92.5, 79.7, 31.3, 28.6, 22.4, 19.5, 14.2.



1-chloro-4-(non-1-en-3-yn-2-yl)benzene (1e): Pale yellow oil, isolated yield 68%. ¹H NMR (400 MHz, CDCl₃) δ 7.54 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 5.77 (d, J = 0.8 Hz, 1H), 5.55 (d, J = 0.8 Hz, 1H), 2.37 (t, J = 7.2

Hz, 2H), 1.59 – 1.52 (m, 2H), 1.43 – 1.29 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 136.5, 134.1, 130.1, 128.5, 127.5, 119.8, 92.7, 79.5, 31.3, 28.5, 22.4, 19.5, 14.1.



1-bromo-4-(non-1-en-3-yn-2-yl)benzene (1f): Pale yellow oil, isolated yield 49%. ¹H NMR (400 MHz, CDCl₃) δ 7.53 – 7.50 (m, 2H), 7.48 – 7.45 (m, 2H), 5.82 (d, J = 0.8Hz, 1H), 5.59 (m, 1H), 2.40 (t, J = 7.2 Hz, 2H), 1.63 – 1.58

(m, 2H), 1.45 – 1.33 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 136.9, 131.5, 130.2, 127.9, 122.3, 119.9, 92.7, 79.4, 31.3, 28.5, 22.4, 19.5, 14.2.



1-methyl-3-(non-1-en-3-yn-2-yl)benzene (1g): Pale yellow oil, isolated yield 55%. ¹H NMR (500 MHz, CDCl₃) δ 7.51 – 7.48 (m, 2H), 7.28 – 7.24 (m, 1H), 7.15 – 7.13 (m, 1H), 5.85 (d, *J* = 1.5 Hz, 1H), 5.59 (d, *J* = 1.0 Hz, 1H), 2.44 (t, *J* = 7.0 Hz,

2H), 2.40 (s, 3H), 1.68 – 1.62 (m, 2H), 1.51 – 1.45 (m, 2H), 1.42 – 1.37 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 137.9, 131.2, 129.0, 128.3, 127.0, 123.3, 119.3, 92.1, 80.0, 31.3, 28.6, 22.4, 21.6, 19.5, 14.2.



1-methyl-2-(non-1-en-3-yn-2-yl)benzene (**1h**): Pale yellow oil, isolated yield 46%. ¹H NMR (400 MHz, CDCl₃) δ 7.29-7.26 (m, 1H), 7.23-7.17 (m, 3H), 5.71-5.70 (m, 1H), 5.41-5.40 (m, 1H), 2.46-2.45 (m, 3H), 2.37-2.32 (m, 2H), 1.59 – 1.53 (m,

2H), 1.42 – 1.31 (m, 4H), 0.95 – 0.90 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 140.1, 135.6, 132.4, 130.4, 128.8, 127.8, 125.9, 123.9, 92.1, 80.8, 31.3, 28.5, 22.3, 20.3, 19.6, 14.1.



2-(non-1-en-3-yn-2-yl)naphthalene (**1i**): Pale yellow oil, isolated yield 40%. ¹H NMR (400 MHz, CDCl₃) δ 8.18 (m, 1H), 7.90-7.78 (m, 4H), 7.52-7.47 (m, 2H), 6.01 (d, *J* = 0.8

Hz, 1H), 5.71 (d, J = 1.2 Hz, 1H), 2.50 (t, J = 7.0 Hz, 3H),

1.73-1.66 (m, 2H), 1.56 – 1.49 (m, 2H), 1.47 – 1.39 (m, 2H), 0.98 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 135.2, 133.4, 133.3, 131.1, 128.5, 128.0, 127.7, 126.4, 126.3, 126.1, 123.6, 119.8, 92.4, 79.9, 31.4, 28.6, 22.4, 19.6, 14.2.



1-methyl-4-(5-phenylpent-1-en-3-yn-2-yl)benzene (1q): Pale yellow oil, isolated yield 45%. ¹H NMR (400 MHz, CDCl₃) δ 7.58 (d, J = 8.4 Hz, 2H), 7.44-7.41 (m, 2H), 7.38-7.34 (m, 2H), 7.29-7.25 (m, 1H), 7.18-7.16 (m, 2H), 5.87 (d, J = 1.2 Hz,

1H), 5.62 (d, *J* = 0.8 Hz, 1H), 3.86 (s, 2H), 2.37 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 138.2, 136.9, 135.0, 130.7, 129.1, 128.7, 128.1, 126.8, 126.1, 119.3, 88.9, 82.2, 25.9, 21.3.



1-(5,5-dimethylhex-1-en-3-yn-2-yl)-4-methylbenzene (1s): Pale yellow oil, isolated yield 80%. ¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.17-7.15 (m, 2H), 5.79 (d, *J* = 1.2 Hz, 1H), 5.52 (d, *J* = 1.6 Hz, 1H), 2.36 (s, 3H), 1.33 (s, 9H);

¹³C NMR (100 MHz, CDCl₃) δ 138.1, 135.3, 130.8, 129.1, 126.1, 118.4, 100.0, 78.5, 31.2, 28.2, 21.3.

4. General procedure for 1,4-carbocyanation of 1,3-enynes



General procedure : In a 10 mL sealed tube, $Cu(CH_3CN)_4PF_6$ (0.005 mmol, 2.5 mol%), bpy (0.007 mmol, 3.5 mol%), Ir(ppy)₃ (0.002 mmol, 1.0 mol%) and NHP ester (0.2 mmol, 1.0 equiv) were added in degassed DMA under a nitrogen atmosphere, and the mixture was stirred at room temperature for 30 minutes. Then 1,3-enyne (0.2 mmol, 1.0 equiv) and TMSCN (0.4 mmol, 2.0 equiv) were sequentially added. The reaction mixture was stirred at room temperature under 30 W blue LEDs irradiation for 12 hours. After the reaction completion, the reaction mixture was diluted with EtOAc, then washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc) to afford the corresponding products.

The analytical data of the products are summarized below. **4e** is known compound in the references.^[2d]



2-(3-cyclopentyl-2-(4-methoxyphenyl)prop-1-en-1ylidene)heptanenitrile (3a): Pale yellow oil, 52.8 mg, isolated yield 82%. ¹H NMR (400 MHz, CDCl₃) δ 7.27 (d, J H₁₁ = 9.2 Hz, 2H), 6.89 (d, J = 9.2 Hz, 2H), 3.82 (s, 3H), 2.49 (d, J = 7.2 Hz, 2H), 2.29 - 2.26 (m, 2H), 2.06 - 2.02 (m, 1H),

1.84 - 1.79 (m, 2H), 1.66 - 1.51 (m, 6H), 1.35 - 1.32 (m, 4H), 1.27 - 1.19 (m, 2H), $0.90 - 0.87 \text{ (m, 3H)}; {}^{13}\text{C}$ NMR (100 MHz, CDCl₃) δ 212.8, 159.8, 128.0, 126.0, 116.0, 114.3, 111.2, 84.5, 55.5, 38.2, 37.2, 32.9, 32.1, 31.1, 27.7, 25.4, 25.4, 22.4, 14.1. HRMS (ESI): m/z calcd. for C₂₂H₂₉NONa⁺([M+Na]⁺) = 346.2165, found = 346.2159.



 $(100 \text{ MHz}, \text{CDCl}_3) \delta 212.8, 134.0, 128.9, 128.4, 126.8, 115.9, 111.6, 84.7, 38.2, 37.1, 32.9, 32.9, 32.0, 31.1, 27.6, 25.4, 25.4, 22.4, 14.1. HRMS (ESI): m/z calcd. for C₂₁H₂₇NNa⁺([M+Na]⁺) = 316.2036, found = 316.2038.$



2-(3-cyclopentyl-2-(p-tolyl)prop-1-en-1-

ylidene)heptanenitrile (3c): Colorless oil, 54.0 mg, isolated
yield 88%. ¹H NMR (400 MHz, CDCl₃) δ 7.24 (d, J = 6.8 Hz,
2H), 7.17 (d, J = 8.0 Hz, 2H), 2.50 (d, J = 7.6 Hz, 2H), 2.36 (s, 3H), 2.30 – 2.26 (m, 2H), 2.06 – 2.01 (m, 1H), 1.86 – 1.79 (m,

2H), 1.67 - 1.50 (m, 6H), 1.37 - 1.29 (m, 4H), 1.27 - 1.19 (m, 2H), 0.90 - 0.87 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 212.8, 138.4, 130.9, 129.6, 126.7, 116.0, 111.4, 84.5, 38.2, 37.1, 32.9, 32.0, 31.1, 27.6, 25.4, 25.4, 22.4, 21.3, 14.1. HRMS (ESI): m/z calcd. for C₂₂H₂₉NNa⁺([M+Na]⁺) = 330.2192, found = 330.2201.



2-(3-cyclopentyl-2-(4-fluorophenyl)prop-1-en-1-

ylidene)heptanenitrile (3d): Pale yellow oil, 49.9 mg,
isolated yield 80%. ¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.29
H₁₁ (m, 2H), 7.07 – 7.03 (m, 2H), 2.49 (d, J = 7.2 Hz, 2H), 2.31 – 2.27 (m, 2H), 2.05 – 1.99 (m, 1H), 1.86 – 1.78 (m, 2H), 1.67 –

1.52 (m, 6H), 1.35 – 1.31 (m, 4H), 1.26 – 1.19 (m, 2H), 0.90 – 0.86 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 212.6 (d, $J_{C-F} = 2.0$ Hz), 162.7 (d, $J_{C-F} = 247.0$ Hz), 130.0 (d, $J_{C-F} = 4.0$ Hz), 128.5 (d, $J_{C-F} = 8.0$ Hz), 115.9 (d, $J_{C-F} = 21.0$ Hz), 115.7, 110.8, 84.9, 38.1, 37.3, 32.9, 32.9, 32.0, 31.1, 27.6, 25.4, 25.4, 22.4, 14.1. HRMS (ESI): m/z calcd. for C₂₁H₂₆FNNa⁺([M+Na]⁺) = 334.1941, found = 334.1951.



2-(2-(4-chlorophenyl)-(3-cyclopentylprop-1-en-1ylidene)heptanenitrile (3e): Pale yellow oil, 54.2 mg,

isolated yield 83%. ¹H NMR (400 MHz, CDCl₃) δ 7.34 - 7.31

(m, 2H), 7.28 - 7.25 (m, 2H), 2.49 (d, J = 7.2 Hz, 2H), 2.31 -

3e 2.27 (m, 2H), 2.06 – 2.00 (m, 1H), 1.86 – 1.76 (m, 2H), 1.65 – 1.53 (m, 6H), 1.37 – 1.29 (m, 4H), 1.26 – 1.17 (m, 2H), 0.90 – 0.86 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 212.6, 134.3, 132.5, 129.1, 128.1, 115.6, 110.8, 85.2, 38.1, 37.1, 32.9, 32.9, 31.9, 31.1, 27.6, 25.4, 25.4, 22.4, 14.1. HRMS (ESI): m/z calcd. for C₂₁H₂₆ClNNa⁺([M+Na]⁺) = 350.1646, found = 350.1645.



2-(2-(4-bromophenyl)-(3-cyclopentylprop-1-en-1ylidene)heptanenitrile (3f): Pale yellow oil, 57.9 mg, isolated yield 78%. ¹H NMR (400 MHz, CDCl₃) δ 7.48 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 2.49 (d, J = 7.6 Hz, 2H), 2.31 – 2.27 (m, 2H), 2.06 – 1.98 (m, 1H), 1.85 – 1.78 (m,

2H), 1.67 - 1.51 (m, 6H), 1.35 - 1.31 (m, 4H), 1.24 - 1.18 (m, 2H), 0.88 (t, J = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 212.6, 133.0, 132.0, 128.4, 122.4, 115.5, 110.9, 85.2, 38.1, 37.0, 32.9, 32.9, 31.9, 31.1, 27.6, 25.4, 25.4, 22.4, 14.1. HRMS (ESI): m/z calcd. for C₂₁H₂₆BrNNa⁺([M+Na]⁺) = 394.1141, found = 394.1150.



2-(3-cyclopentyl-2-(*m*-tolyl)prop-1-en-1-

ylidene)heptanenitrile (3g): Pale yellow oil, 45.8 mg, isolated
yield 75%. ¹H NMR (400 MHz, CDCl₃) δ 7.25 - 7.22 (m, 1H),
7.15 - 7.09 (m, 3H), 2.50 (d, J = 7.2 Hz, 2H), 2.36 (s, 3H), 2.28 (t, J = 7.6 Hz, 2H), 2.07 - 2.00 (m, 1H), 1.88 - 1.76 (m, 2H), 1.65

- 1.50 (m, 6H), 1.38 - 1.17 (m, 6H), 0.89 - 0.86 (m, 3H); ¹³C NMR (100 MHz, CDCl₃)
δ 212.8, 138.5, 133.9, 129.2, 128.7, 127.5, 123.9, 115.9, 111.6, 84.5, 38.2, 37.2, 32.9,
32.9, 32.0, 31.1, 27.6, 25.4, 25.4, 22.4, 21.6, 14.1. HRMS (ESI): m/z calcd. for

 $C_{22}H_{29}NNa^{+}([M+Na]^{+}) = 330.2192$, found = 330.2189.



2-(3-cyclopentyl-2-(o-tolyl)prop-1-en-1-

ylidene)heptanenitrile (3h): Pale yellow oil, 25.0 mg, isolated CN yield 41%. ¹H NMR (400 MHz, CDCl₃) δ 7.22 – 7.17 (m, 4H), Ċ₅H₁₁ 2.42 - 2.39 (m, 2H), 2.36 (s, 3H), 2.22 - 2.18 (m, 2H), 1.98 - 1.92 (m, 1H), 1.85 – 1.78 (m, 2H), 1.65 – 1.60 (m, 2H), 1.59 – 1.51 (m, 4H), 1.33 – 1.26 (m, 4H), 1.25 – 1.17 (m, 2H), 0.88 – 0.84 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 210.2, 135.9, 134.9, 130.9, 128.1, 128.0, 126.2, 116.1, 110.5, 82.0, 40.9, 38.0, 32.9, 32.9, 31.6, 31.0, 27.5, 25.5, 25.5, 22.4, 20.4, 14.1. HRMS (ESI): m/z calcd. for $C_{22}H_{29}NNa^+([M+Na]^+) = 330.2192$, found = 330.2194.



2-(3-cyclopentyl-2-(naphthalen-2-yl)prop-1-en-1-

ylidene)heptanenitrile (3i): Pale yellow oil, 38.2 mg, isolated yield 56%. ¹H NMR (400 MHz, CDCl₃) δ 7.85 – 7.78 (m, 4H), 7.52 - 7.44 (m, 3H), 2.66 (d, J = 7.2 Hz, 2H), 2.36 - 2.32 (m, 2H), 2.17 – 2.09 (m, 1H), 1.88 – 1.84 (m, 2H), 1.70 – 1.55 (m,

6H), 1.42 - 1.24 (m, 6H), 0.89 (t, J = 7.0 Hz, 3H); 13 C NMR (100 MHz, CDCl₃) δ 213.4, 133.5, 133.2, 131.2, 128.5, 128.3, 127.8, 126.7, 126.6, 125.3, 125.1, 115.9, 111.8, 85.0, 38.3, 37.1, 33.0, 32.1, 31.1, 27.6, 25.4, 25.4, 22.4, 14.1. HRMS (ESI): m/z calcd. for $C_{25}H_{29}NNa^{+}([M+Na]^{+}) = 366.2192$, found = 366.2196.

2-(3-cyclopentyl)-2-(thiophen-2-yl)-prop-1-en-1ylidene)octanenitrile (3j): Pale yellow oil, 31.4 mg, isolated yield CN 50%. ¹H NMR (500 MHz, CDCl₃) δ 7.28 (dd, J = 5.0, 1.5 Hz, 1H), $C_{6}H_{13}$ 7.03 - 7.00 (m, 2H), 2.52 - 2.50 (m, 2H), 2.31 - 2.28 (m, 2H), 3j 2.14 - 2.08 (m, 1H), 1.86 - 1.82 (m, 2H), 1.66 - 1.53 (m, 6H),

1.41 – 1.19 (m, 8H), 0.89 – 0.87 (m, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 212.4, 137.9,

127.8, 126.3, 125.3, 115.3, 107.1, 85.5, 38.4, 38.2, 32.9, 32.9, 32.3, 31.6, 28.6, 27.9, 25.4, 22.7, 14.2. HRMS (ESI): m/z calcd. for $C_{20}H_{27}NNaS^+([M+Na]^+) = 336.1756$, found = 336.1759.

5-Pr CN C 3k 11

5-cyclopentyl-4-methyl-2-phenylpenta-2,3-dienenitrile (3k): Pale yellow oil, 21.0 mg, isolated yield 44%. ¹H NMR (400 MHz, CDCl₃) δ 7.47 – 7.44 (m, 2H), 7.41 – 7.36 (m, 2H), 7.32 – 7.28 (m, 1H), 2.21 (t, *J* = 7.6 Hz, 2H), 2.07 – 2.00 (m, 1H), 1.92 (s, 3H), 1.88 – 1.83 (m, 1H), 1.79 – 1.74 (m, 1H), 1.63 – 1.49 (m, 6H); ¹³C

NMR (100 MHz, CDCl₃) δ 209.7, 130.8, 129.0, 128.4, 125.7, 115.1, 110.3, 85.2, 40.8, 37.8, 33.0, 25.5, 18.4. HRMS (ESI): m/z calcd. for C₁₇H₁₉NNa⁺([M+Na]⁺) = 260.1410, found = 260.1412.



5-cyclopentyl-4-cyclopropyl-2-phenylpenta-2,3-dienenitrile

(31): Colorless oil, 22.8 mg, isolated yield 43%. ¹H NMR (500 MHz, CDCl₃) δ 7.44 – 7.41 (m, 2H), 7.39 – 7.36 (m, 2H), 7.32 – 7.29 (m, 1H), 2.34 – 2.25 (m, 2H), 2.12 – 2.06 (m, 1H), 1.89 – 1.83 (m, 1H), 1.80 – 1.74 (m, 1H), 1.63 – 1.57 (m, 2H), 1.55 –

1.51 (m, 2H), 1.35 – 1.30 (m, 1H), 1.21 – 1.15 (m, 2H), 0.86 – 0.82 (m, 2H), 0.57 – 0.51 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 209.5, 130.7, 129.1, 128.5, 125.5, 119.0, 114.9, 87.7, 39.6, 38.1, 33.1, 33.0, 25.5, 12.7, 7.6, 7.5. HRMS (ESI): m/z calcd. for C₁₉H₂₁NNa⁺([M+Na]⁺) = 286.1566, found = 286.1573.



5-cyclopentyl-2-propyl-4-(p-tolyl)penta-2,3-dienenitrile

(3m): Colorless oil, 50.2 mg, isolated yield 90%. ¹H NMR (500 MHz, CDCl₃) δ 7.24 (d, J = 8.5 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 2.51 (d, J = 7.0 Hz, 2H), 2.36 (s, 3H), 2.29 – 2.26 (m, 2H), 2.08 – 2.02 (m, 1H), 1.86 – 1.78 (m, 2H), 1.65 – 1.53 (m, 6H),

1.26 - 1.19 (m, 2H), 0.99 (t, J = 7.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 212.9,

138.4, 130.9, 129.6, 126.7, 115.9, 111.4, 84.3, 38.2, 37.1, 34.0, 32.9, 25.4, 25.4, 21.3, 21.3, 13.5. HRMS (ESI): m/z calcd. for $C_{20}H_{25}NNa^+([M+Na]^+) = 302.1879$, found = 302.1886.



2-(3-cyclopentyl-2-(p-tolyl)prop-1-en-1-

ylidene)octanenitrile (3n): Colorless oil, 54.0 mg, isolated yield 84%. ¹H NMR (400 MHz, CDCl₃) δ 7.16 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 2.43 (d, *J* = 7.2 Hz, 2H), 2.28 (s, 3H), 2.22 – 2.19 (m, 2H), 2.01 – 1.93 (m, 1H), 1.75 – 1.69 (m,

2H), 1.59 - 1.44 (m, 6H), 1.30 - 1.12 (m, 8H), 0.82 - 0.78 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 212.8, 138.4, 131.0, 129.6, 126.7, 116.0, 111.5, 84.5, 38.2, 37.1, 32.9, 32.1, 31.6, 28.6, 27.9, 25.4, 25.4, 22.7, 21.3, 14.1. HRMS (ESI): m/z calcd. for $C_{23}H_{31}NNa^{+}([M+Na]^{+}) = 344.2349$, found = 344.2351.



2-(cyclohexylmethyl)-5-cyclopentyl-4-phenylpenta-2,3dienenitrile (30): Colorless oil, 45.9 mg, isolated yield 72%. ¹H NMR (500 MHz, CDCl₃) δ 7.38 – 7.33 (m, 4H), 7.31 – 7.28 (m, 1H), 2.52 (d, *J* = 7.5 Hz, 2H), 2.17 (dd, *J* = 7.3, 1.8 Hz, 2H), 2.08 – 2.02 (m, 1H), 1.85 – 1.79 (m, 4H), 1.74 – 1.53 (m,

8H), 1.32 - 1.13 (m, 5H), 1.00 - 0.92 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 213.4, 134.0, 128.9, 128.3, 126.9, 116.0, 110.9, 83.3, 39.7, 38.2, 37.1, 36.7, 33.0, 32.9, 32.9, 32.9, 26.4, 26.1, 25.4, 25.3. HRMS (ESI): m/z calcd. for C₂₃H₂₉NNa⁺([M+Na]⁺) = 342.2192, found = 342.2200.



2-benzyl-5-cyclopentyl-4-(p-tolyl)penta-2,3-dienenitrile

(3p): Colorless oil, 42.0 mg, isolated yield 64%. ¹H NMR
(400 MHz, CDCl₃) δ 7.35 - 7.31 (m, 2H), 7.29 - 7.25 (m, 3H), 7.19 - 7.14 (m, 4H), 3.59 (s, 2H), 2.47 (d, *J* = 7.2 Hz, 2H), 2.36 (s, 3H), 2.02 - 1.94 (m, 1H), 1.81 - 1.74 (m, 2H),

1.64 - 1.60 (m, 2H), 1.53 - 1.49 (m, 2H), 1.21 - 1.14 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 213.4, 138.6, 136.7, 130.6, 129.6, 129.0, 128.9, 127.4, 126.8, 115.7, 112.3, 84.3, 38.6, 38.2, 37.1, 33.0, 32.8, 25.4, 25.3, 21.3. HRMS (ESI): m/z calcd. for $C_{24}H_{25}NNa^{+}([M+Na]^{+}) = 350.1879$, found = 350.1873.



2-(3-chloropropyl)-5-cyclopentyl-4-phenylpenta-2,3dienenitrile (3q): Colorless oil, 46.0 mg, isolated yield 77%. ¹H NMR (500 MHz, CDCl₃) δ 7.40 – 7.30 (m, 5H), 3.59 (t, *J* = 6.3 Hz, 2H), 2.55 (d, *J* = 7.5 Hz, 2H), 2.51 – 2.48 (m, 2H), 2.08 – 2.03 (m, 3H), 1.84 – 1.83 (m, 2H), 1.66 – 1.63 (m, 2H), 1.59 –

$$\begin{split} &1.53 \ (m, 2H), \ 1.27 - 1.21 \ (m, 2H); \ ^{13}C \ NMR \ (125 \ MHz, CDCl_3) \ \delta \ 213.0, \ 133.6, \ 129.0 \ , \\ &128.6, \ 126.8, \ 115.4, \ 112.5, \ 83.2, \ 43.6, \ 38.1, \ 37.2, \ 32.9, \ 30.5, \ 29.2, \ 25.4, \ 25.4. \ HRMS \\ &(ESI): \ m/z \ calcd. \ for \ C_{19}H_{22}ClNNa^+([M+Na]^+) = \ 322.1333, \ found = \ 322.1341. \end{split}$$



2-(tert-butyl)-5-cyclopentyl-4-(p-tolyl)penta-2,3-

dienenitrile (3r): White solid, 45.1 mg, isolated yield 77%. ¹H NMR (400 MHz, CDCl₃) δ 7.24 (d, J = 8.4 Hz, 2H), 7.18 – 7.16 (m, 2H), 2.52 (dd, J = 7.2, 4.4 Hz, 2H), 2.36 (s, 3H), 2.06 – 2.00 (m, 1H), 1.87 – 1.81 (m, 2H), 1.67 – 1.60 (m, 2H), 1.59 – 1.51

(m, 2H), 1.23 (s, 11H); ¹³C NMR (100 MHz, CDCl₃) δ 210.3, 138.3, 131.1, 129.6, 126.5, 115.1, 112.8, 95.8, 38.3, 37.7, 35.3, 33.2, 33.0, 29.1, 25.5, 25.3, 21.3. HRMS (ESI): m/z calcd. for C₂₁H₂₇NNa⁺([M+Na]⁺) = 316.2036, found = 316.2044.



5-cyclopentyl-4-phenylpenta-2,3-dienenitrile (3s): Pale yellow oil, 33.1 mg, isolated yield 74%. ¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.30 (m, 5H), 5.55 (t, *J* = 3.0 Hz, 1H), 2.57 – 2.53 (m, 2H), 2.11 – 2.04 (m, 1H), 1.87 – 1.81 (m, 2H), 1.67 – 1.53 (m, 4H), 1.26 – 1.21 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 217.3, 132.8,

129.0, 128.7, 126.9, 113.6, 112.2, 69.7, 38.1, 36.8, 32.9, 32.8, 25.4, 25.4. HRMS (ESI):

m/z calcd. for C₁₆H₁₇NNa⁺([M+Na]⁺) = 246.1253, found = 246.1258.



2-(2-(p-tolyl)but-1-en-1-ylidene)heptanenitrile (4a): Pale yellow oil, 42.0 mg, isolated yield 83%. ¹H NMR (500 MHz, CDCl₃) δ 7.25 – 7.23 (m, 2H), 7.18 – 7.16 (m, 2H), 2.53 (q, J =7.3 Hz, 2H), 2.36 (s, 3H), 2.29 (t, *J* = 7.8 Hz, 2H), 1.61 – 1.55 (m, 2H), 1.37 - 1.31 (m, 4H), 1.16 (t, J = 7.3 Hz, 3H), 0.88 (t, J = 7.0 Hz, 3H); ${}^{13}C$

NMR (125 MHz, CDCl₃) δ 212.1, 138.4, 130.9, 129.6, 126.6, 116.1, 113.8, 85.7, 32.0, 31.1, 27.6, 23.5, 22.4, 21.3, 14.1, 12.3. HRMS (ESI): m/z calcd. for $C_{18}H_{23}NNa^{+}([M+Na]^{+}) = 276.1723$, found = 276.1726.



2-pentyl-4-(p-tolyl)hepta-2,3-dienenitrile (4b): Pale yellow oil, 42.1 mg, isolated yield 79%. ¹H NMR (400 MHz, CDCl₃) δ 7.25 – 7.22 (m, 2H), 7.18 – 7.16 (m, 2H), 2.48 (t, J = 7.6 Hz, 2H), 2.36 (s, 3H), 2.28 (t, J = 7.6 Hz, 2H), 1.60 – 1.54 (m, 4H), 1.36 - 1.31 (m, 4H), 1.01 (t, J = 7.4 Hz, 3H), 0.88 (t, J = 7.2

Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 212.3, 138.4, 130.8, 129.6, 126.7, 116.0, 111.8, 84.9, 32.4, 32.0, 31.1, 27.6, 22.4, 21.3, 21.0, 14.1, 14.0. HRMS (ESI): m/z calcd. for $C_{19}H_{25}NNa^{+}([M+Na]^{+}) = 290.1879$, found = 290.1878.



2-pentyl-4-(p-tolyl)octa-2,3-dienenitrile (4c): Pale yellow oil, 46.1 mg, isolated yield 82%. ¹H NMR (400 MHz, CDCl₃) δ 7.23 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 2.50 (t, J =7.4 Hz, 2H), 2.36 (s, 3H), 2.30 – 2.26 (m, 2H), 1.60 – 1.50 (m, 4H), 1.45 - 1.39 (m, 2H), 1.36 - 1.31 (m, 4H), 0.94 (t, J = 7.4

Hz, 3H), 0.88 (t, J = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 212.3, 138.4, 130.9, 129.6, 126.7, 116.0, 112.0, 84.9, 32.0, 31.1, 30.0, 29.9, 27.6, 22.5, 22.4, 21.3, 14.1, 14.0. HRMS (ESI): m/z calcd. for $C_{20}H_{27}NNa^+([M+Na]^+) = 304.2036$, found = 304.2042.



2-pentyl-4-(*p*-tolyl)deca-2,3-dienenitrile (4d): Pale yellow
oil, 45.1 mg, isolated yield 73%. ¹H NMR (400 MHz, CDCl₃)
δ 7.23 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 7.6 Hz, 2H), 2.49 (t, J = 7.4 Hz, 2H), 2.36 (s, 3H), 2.28 (t, J = 7.6 Hz, 2H), 1.60

 $-1.50 \text{ (m, 4H)}, 1.41 - 1.29 \text{ (m, 10H)}, 0.91 - 0.86 \text{ (m, 6H)}; {}^{13}\text{C NMR} (100 \text{ MHz, CDCl}_3)$ $\delta 212.3, 138.4, 130.9, 129.6, 126.7, 116.0, 112.0, 84.9, 32.0, 31.8, 31.1, 30.3, 29.1, 27.7,$ $27.6, 22.8, 22.5, 21.3, 14.2, 14.1. \text{ HRMS (ESI)}: \text{m/z calcd. for } \text{C}_{22}\text{H}_{31}\text{NNa}^+([\text{M+Na}]^+)$ = 332.2349, found = 332.2348.



2-hexyl-4-(4-methoxyphenyl)deca-2,3-dienenitrile (4e): Colorless oil, 46.7 mg, isolated yield 69%. ¹H NMR (400 MHz, CDCl₃) δ 7.27 (d, J = 8.8 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 3.82 (s, 3H), 2.48 (t, J = 7.4 Hz, 2H), 2.28 (t, J = 7.4 Hz,

2H), 1.60 – 1.52 (m, 4H), 1.39 – 1.26 (m, 12H), 0.92 – 0.86 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 212.2, 159.8, 128.0, 125.9, 116.1, 114.3, 111.7, 84.9, 55.5, 32.1, 31.8, 31.6, 30.4, 29.1, 28.6, 27.9, 27.7, 22.8, 22.7, 14.2, 14.1. These data matches with reported values.^[2d]



2-(4-ethoxy-2-(p-tolyl)but-1-en-1-ylidene)heptanenitrile

(4f): Pale yellow oil, 39.8 mg, isolated yield 67%. ¹H NMR
CN (400 MHz, CDCl₃) δ 7.24 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.0 H₁₁ Hz, 2H), 3.60 (t, J = 6.8 Hz, 2H), 3.50 (q, J = 7.1 Hz, 2H), 2.78 (t, J = 6.6 Hz, 2H), 2.35 (s, 3H), 2.29 (t, J = 7.6 Hz, 2H), 1.61

-1.57 (m, 2H), 1.34 - 1.32 (m, 4H), 1.21 (t, J = 7.0 Hz, 3H), 0.90 - 0.86 (m, 3H); 13 C NMR (100 MHz, CDCl₃) δ 212.3 , 138.5, 130.5, 129.6, 126.6, 115.8, 108.9, 85.3, 68.3, 66.6, 32.0, 31.1, 30.7, 27.5, 22.4, 21.3, 15.3, 14.1. HRMS (ESI): m/z calcd. for $C_{20}H_{27}NONa^+([M+Na]^+) = 320.1985$, found = 320.1992.



8-oxo-2-pentyl-4-(*p*-tolyl)nona-2,3-dienenitrile (4g): Colorless oil, 26.0 mg, isolated yield 42%. ¹H NMR (400 MHz, CDCl₃) δ 7.24 – 7.21 (m, 2H), 7.18 – 7.16 (m, 2H), 2.55 – 2.51 (m, 4H), 2.35 (s, 3H), 2.30 – 2.26 (m, 2H), 2.16 (s, 3H), 1.86 – 1.78 (m, 2H), 1.60 – 1.55 (m, 2H), 1.35 – 1.31 (m, 4H), 0.89 – 0.86 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 212.1, 208.2,

138.6, 130.3, 129.7, 126.7, 115.8, 111.4, 85.4, 42.6, 32.0, 31.1, 30.2, 29.5, 27.6, 22.4, 21.6, 21.3, 14.1. HRMS (ESI): m/z calcd. for C₂₁H₂₇NONa⁺([M+Na]⁺) = 332.1985, found = 332.1988.



2-pentyl-4-(*p*-tolyl)nona-2,3,8-trienenitrile (4h): Colorless oil, 47.6 mg, isolated yield 81%. ¹H NMR (400 MHz, CDCl₃) δ 7.23 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.87 – 5.76 (m, 1H), 5.08 – 4.99 (m, 2H), 2.53 – 2.50 (m, 2H), 2.36 (s, 3H), 2.30 – 2.26 (m, 2H), 2.19 – 2.13 (m, 2H), 1.68 – 1.54 (m, 4H), 1.37 – 1.29 (m, 4H), 0.90 – 0.87 (m, 3H); ¹³C NMR (100 MHz,

CDCl₃) δ 212.2, 138.5, 138.0, 130.8, 129.6, 126.7, 115.9, 115.4, 111.8, 85.1, 33.4, 32.0, 31.1, 29.6, 27.6, 26.9, 22.4, 21.3, 14.1. HRMS (ESI): m/z calcd. for C₂₁H₂₇NNa⁺([M+Na]⁺) = 316.2036, found = 316.2024.



2-(4-cyclohexyl-2-(*p***-tolyl)but-1-en-1ylidene)heptanenitrile (4i):** Pale yellow oil, 57.0 mg, isolated yield 85%. ¹H NMR (400 MHz, CDCl₃) δ 7.23 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 2.51 (t, *J* = 7.8 Hz, 2H), 2.36 (s, 3H), 2.28 (t, *J* = 7.6 Hz, 2H), 1.75 – 1.69 (m, 5H), 1.60 – 1.56 (m, 2H), 1.43 – 1.38 (m, 2H), 1.37 – 1.14 (m, 8H), 0.98 – 0.87

(m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 212.3, 138.4, 130.9, 129.6, 126.6, 116.0, 112.2, 84.9, 37.4, 35.3, 33.4, 33.4, 32.0, 31.1, 27.7, 27.6, 26.7, 26.5, 22.5, 21.3, 14.1. HRMS (ESI): m/z calcd. for C₂₄H₃₃NNa⁺([M+Na]⁺) = 358.2505, found = 358.2508.



MHz, CDCl₃) δ 212.2, 141.7, 138.5, 130.7, 129.6, 128.6, 128.6, 126.6, 126.1, 115.9, 111.8, 85.2, 35.5, 32.0, 31.1, 29.7, 29.3, 27.6, 22.4, 21.3, 14.1. HRMS (ESI): m/z calcd. for C₂₅H₂₉NNa⁺([M+Na]⁺) = 366.2192, found = 366.2199.



2-pentyl-8-phenyl-4-(*p*-tolyl)octa-2,3-dienenitrile (4k): Pale yellow oil, 62.1 mg, isolated yield 87%. ¹H NMR (400 MHz, CDCl₃) δ 7.23 – 7.08 (m, 9H), 2.58 (t, *J* = 7.6 Hz, 2H), 2.45 (t, *J* = 7.4 Hz, 2H), 2.28 (s, 3H), 2.18 (t, *J* = 7.6 Hz, 2H), 1.69 – 1.62 (m, 2H), 1.55 – 1.44 (m, 4H), 1.27 – 1.19 (m, 4H), 0.81 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 212.1, 142.3, 138.4, 130.8, 129.6, 128.5, 128.4, 126.6, 125.9, 115.9, 111.9,

85.1, 35.8, 32.0, 31.1, 31.1, 30.1, 27.6, 27.3, 22.4, 21.3, 14.1. HRMS (ESI): m/z calcd. for C₂₆H₃₁NNa⁺([M+Na]⁺) = 380.2349, found = 380.2356.



7-(furan-2-yl)-2-pentyl-4-(*p***-tolyl)hepta-2,3-dienenitrile (4l):** Pale yellow oil, 53.2 mg, isolated yield 80%. ¹H NMR (500 MHz, CDCl₃) δ 7.32 – 7.31 (m, 1H), 7.23 – 7.21 (m, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 6.30– 6.29 (m, 1H), 6.03 – 6.02 (m, 1H), 2.75 – 2.72 (m, 2H), 2.57 – 2.53 (m, 2H), 2.36 (s, 3H), 2.30 – 2.27 (m, 2H), 1.91 – 1.87 (m, 2H), 1.60 – 1.55 (m, 2H), 1.35 –

1.29 (m, 4H), 0.88 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 212.1, 155.3, 141.2, 138.5, 130.6, 129.6, 126.6, 115.9, 111.6, 110.3, 105.4, 85.3, 32.0, 31.1, 29.6,

27.6, 27.5, 26.2, 22.4, 21.3, 14.0. HRMS (ESI): m/z calcd. for C₂₃H₂₇NONa⁺([M+Na]⁺) = 356.1985, found = 356.1986.



2-pentyl-7-(thiophen-2-yl)- 4-(*p***-tolyl)hepta-2,3-dienenitrile (4m):** Pale yellow oil, 57.2 mg, isolated yield 82%. ¹H NMR (500 MHz, CDCl₃) δ 7.23 – 7.21 (m, 2H), 7.19 – 7.17 (m, 2H), 7.14 (dd, *J* = 5.0, 1.0 Hz, 1H), 6.94 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.83 – 6.82 (m, 1H), 2.97 – 2.93 (m, 2H), 2.58 (t, *J* = 7.5 Hz, 2H), 2.37 (s, 3H), 2.31 – 2.28 (m, 2H), 1.97 – 1.90 (m, 2H),

 $1.61 - 1.56 \text{ (m, 2H)}, 1.37 - 1.30 \text{ (m, 4H)}, 0.88 \text{ (t, } J = 7.0 \text{ Hz}, 3\text{H}\text{)}; {}^{13}\text{C} \text{ NMR} (125 \text{ MHz}, \text{CDCl}_3) \delta 212.1, 144.4, 138.5, 130.6, 129.6, 126.9, 126.6, 124.6, 123.3, 115.9, 111.5, 85.3, 32.0, 31.1, 29.7, 29.4, 27.6, 22.4, 21.3, 14.0. HRMS (ESI): m/z calcd. for <math>C_{23}H_{27}\text{NSNa}^+([\text{M+Na}]^+) = 372.1756$, found = 372.1766.



2-(2,4-di-*p***-tolybut-1-en-1-ylidene)heptanenitrile (4n):** Pale yellow oil, 20.6 mg, isolated yield 30%. ¹H NMR (400 MHz, CDCl₃) δ 7.25 – 7.23 (m, 2H), 7.19 – 7.17 (m, 2H), 7.13 – 7.07 (m, 4H), 2.85 – 2.76 (m, 4H), 2.37 (s, 3H), 2.33 (s, 3H), 2.16 – 2.12 (m, 2H), 1.51 – 1.44 (m, 2H), 1.31 – 1.27 (m, 4H), 0.90 – 0.86 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 212.2, 138.5, 137.9, 135.9, 130.6, 129.7, 129.3, 128.4, 126.7, 115.8, 111.3,

85.3, 33.4, 32.1, 31.9, 31.1, 27.6, 22.4, 21.3, 21.2, 14.1. HRMS (ESI): m/z calcd. for C₂₅H₂₉NNa⁺([M+Na]⁺) = 366.2192, found = 366.2199.



2-(3-cyclobutyl-2-(p-tolyl)prop-1-en-1-

ylidene)heptanenitrile (40): Colorless oil, 48.0 mg, isolated yield 82%. ¹H NMR (500 MHz, CDCl₃) δ 7.22 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 2.61 – 2.59 (m, 2H), 2.54 – 2.47 (m, 1H), 2.35 (s, 3H), 2.28 – 2.25 (m, 2H), 2.18 – 2.08 (m, 2H), 1.91 – 1.86 (m, 2H), 1.74 – 1.69 (m, 2H), 1.61 – 1.55 (m, 2H), 1.36 – 1.30 (m, 4H), 0.89 (t, J = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 212.5, 138.4, 130.9, 129.6, 126.6, 116.0, 110.4, 84.8, 37.5, 34.1, 32.1, 31.2, 28.5, 28.4, 27.6, 22.4, 21.3, 18.5, 14.1. HRMS (ESI): m/z calcd. for C₂₁H₂₇NNa⁺([M+Na]⁺) = 316.2036, found = 316.2034.



2- (3-cyclopropyl-2-(*p*-tolyl)prop-1-en-1-ylidene) heptanenitrile (4p): Colorless oil, 42.6 mg, isolated yield 76%. ¹H NMR (500 MHz, CDCl₃) δ 7.23 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 2.43 – 2.41 (m, 2H), 2.36 (s, 3H), 2.30 (t, *J* =

7.8 Hz, 2H), 1.61 – 1.58 (m, 2H), 1.36 – 1.32 (m, 4H), 0.94 –

0.91 (m, 1H), 0.88 (t, J = 7.0 Hz, 3H), 0.59 – 0.53 (m, 2H), 0.24 – 0.16 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 212.9, 138.4, 130.9, 129.6, 126.6, 116.1, 112.1, 85.3, 35.5, 32.1, 31.2, 27.6, 22.4, 21.3, 14.1, 9.4, 5.2, 5.1. HRMS (ESI): m/z calcd. for C₂₀H₂₅NNa⁺([M+Na]⁺) = 302.1879, found = 302.1878.



2-(3-(tetrahydro-2*H***-pyran-4-yl)-2-(***p***-tolyl)prop-1-en-1ylidene)heptanenitrile (4q): Colorless oil, 41.6 mg, isolated yield 64%. ¹H NMR (400 MHz, CDCl₃) \delta 7.22 (d,** *J* **= 8.4 Hz, 2H), 7.18 (d,** *J* **= 8.0 Hz, 2H), 3.98 – 3.94 (m, 2H), 3.35 – 3.33 (m, 2H), 2.51 – 2.40 (m, 2H), 2.36 (s, 3H), 2.29 – 2.26 (m, 2H),**

1.73 - 1.65 (m, 3H), 1.62 - 1.56 (m, 2H), 1.38 - 1.30 (m, 6H), 0.90 - 0.86 (m, 3H); ${}^{13}C$ NMR (100 MHz, CDCl₃) δ 212.4, 138.6, 130.5, 129.7, 126.7, 115.7, 109.3, 84.4, 68.0, 67.9, 37.9, 33.7, 33.3, 33.1, 32.0, 31.1, 27.6, 22.4, 21.3, 14.1. HRMS (ESI): m/z calcd. for C₂₂H₂₉NONa⁺([M+Na]⁺) = 346.2141, found = 346.2150.



1.70 (m, 2H), 1.65 – 1.55 (m, 3H), 1.45 (s, 9H), 1.35 – 1.31 (m, 4H), 1.21 – 1.13 (m, 2H), 0.90 – 0.86 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 212.4, 154.9, 138.6, 130.4, 129.7, 126.7, 115.7, 109.4, 84.3, 79.5, 37.5, 34.7, 32.3, 32.2, 31.9, 31.0, 28.6, 27.6, 22.4, 21.3, 14.0. HRMS (ESI): m/z calcd. for C₂₇H₃₈N₂O₂Na⁺([M+Na]⁺) = 445.2825, found = 445.2819.



6-methyl-2-pentyl-4-(*p*-tolyl)hepta-2,3-dienenitrile (4s): Colorless oil, 44.6 mg, isolated yield 79%. ¹H NMR (500 MHz, CDCl₃) δ 7.23 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 7.5 Hz, 2H), 2.43 – 2.34 (m, 5H), 2.29 – 2.26 (m, 2H), 1.85 – 1.79 (m, 1H), 1.62 – 1.56 (m, 2H), 1.36 – 1.30 (m, 4H), 0.99 – 0.97 (m, 6H), 0.89

(t, J = 7.3 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 212.6, 138.4, 130.8, 129.6, 126.8, 115.9, 110.6, 84.1, 39.8, 32.0, 31.1, 27.6, 27.0, 22.8, 22.7, 22.4, 21.3, 14.1. HRMS (ESI): m/z calcd. for C₂₀H₂₇NNa⁺([M+Na]⁺) = 304.2036, found = 304.2040.



6-ethyl-2-pentyl-4-(*p*-tolyl)deca-2,3-dienenitrile (4t): Colorless oil, 45.0 mg, isolated yield 67%, dr = 1:1. ¹H NMR (400 MHz, CDCl₃) δ 7.24 – 7.21 (m, 2H), 7.18 – 7.16 (m, 2H), 2.44 – 2.42 (m, 2H), 2.36 (s, 3H), 2.29 – 2.25 (m, 2H), 1.61 – 1.55 (m, 2H), 1.52 – 1.47 (m, 1H), 1.39 – 1.26 (m, 12H), 0.91 – 0.86 (m, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 212.6, 138.4,

131.0, 131.0, 129.6, 126.8, 115.9, 110.8, 110.8, 84.1, 84.0, 37.5, 37.5, 35.0, 35.0, 33.0, 32.8, 32.0, 31.1, 29.0, 28.9, 27.7, 26.1, 25.9, 23.3, 22.4, 21.3, 14.3, 14.1, 10.8, 10.7. HRMS (ESI): m/z calcd. for C₂₄H₃₅NNa⁺([M+Na]⁺) = 360.2662, found = 360.2662.



 $0.89 - 0.86 \text{ (m, 3H)}; {}^{13}\text{C} \text{ NMR} (100 \text{ MHz, CDCl}_3) \delta 212.5, 138.6, 134.0, 130.4, 129.6, 126.7, 117.8, 115.8, 110.6, 85.5, 34.7, 32.0, 31.0, 27.5, 22.4, 21.3, 14.1. HRMS (ESI): m/z calcd. for C₁₉H₂₄N⁺([M+H]⁺) = 266.1903, found = 266.1897.$



4-cyano-2-(*p***-tolyl)nona-2,3-dien-1-yl acrylate (4u'):** Pale yellow oil, 16.7 mg, isolated yield 27%. ¹H NMR (400 MHz, CDCl₃) δ 7.24 – 7.18 (m, 4H), 6.45 (dd, *J* = 17.4, 1.4 Hz, 1H), 6.14 (dd, *J* = 17.2, 10.4 Hz, 1H), 5.89 (dd, *J* = 10.4, 1.2 Hz, 1H), 5.12 (q, *J* = 13.1 Hz, 2H), 2.37 (s, 3H), 2.30 (t, *J* = 7.6 Hz, 2H),

1.60 - 1.55 (m, 2H), 1.35 - 1.28 (m, 4H), 0.87 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 211.9, 165.5, 139.2, 131.9, 129.9, 128.1, 127.9, 126.7, 114.9, 108.2, 87.3, 61.6, 31.9, 31.0, 27.4, 22.4, 21.4, 14.0. HRMS (ESI): m/z calcd. for $C_{20}H_{23}NO_2Na^+([M+Na]^+) = 332.1621$, found = 332.1623.



6,6-dimethyl-2-pentyl-4-(*p*-tolyl)hepta-2,3-dienenitrile (4v): Pale yellow oil, 50.7 mg, isolated yield 86%. ¹H NMR (400 MHz, CDCl₃) δ 7.24 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 2.51 – 2.38 (m, 2H), 2.35 (s, 3H), 2.28 – 2.24 (m, 2H), 1.59 – 1.56 (m, 2H), 1.34 – 1.30 (m, 4H), 0.93 (s, 9H), 0.89 –

0.85 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 213.8, 138.2, 132.3, 129.5, 127.0, 116.0, 109.6, 83.0, 43.9, 32.6, 31.9, 31.1, 30.0, 27.5, 22.4, 21.3, 14.1. HRMS (ESI): m/z calcd. for C₂₁H₂₉NNa⁺([M+Na]⁺) = 318.2192, found = 318.2198.



ylidene)heptanenitrile (4w): Colorless oil, 50.8 mg, isolated yield 83%. ¹H NMR (400 MHz, CDCl₃) δ 7.23 (d, *J* = 8.4 Hz, 2H), 7.17 – 7.15 (m, 2H), 2.62 (d, *J* = 0.8 Hz, 2H), 2.35 (s, 3H), 2.27 – 2.23 (m, 2H), 1.93 – 1.69 (m, 6H), 1.61 – 1.55 (m, 2H),

2-(3-(1-methylcyclobutyl)-2-(p-tolyl)prop-1-en-1-

1.34 - 1.31 (m, 4H), 1.18 (s, 3H), 0.89 - 0.86 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 213.2, 138.3, 131.9, 129.5, 126.8, 115.9, 109.1, 84.3, 42.8, 38.9, 33.8, 33.8, 32.0, 31.2, 27.5, 26.3, 22.4, 21.3, 15.4, 14.1. HRMS (ESI): m/z calcd. for C₂₂H₂₉NNa⁺([M+Na]⁺) = 330.2192, found = 330.2196.



2-(3-(1-methylcyclohexyl)-2-(*p***-tolyl)prop-1-en-1-ylidene) heptanenitrile (4x):** Colorless oil, 58.1 mg, isolated yield 87%. ¹H NMR (500 MHz, CDCl₃) δ 7.26 – 7.23 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 2.51 – 2.42 (m, 2H), 2.35 (s, 3H), 2.26 – 2.23 (m, 2H), 1.59 – 1.56 (m, 2H), 1.46 – 1.41 (m, 5H), 1.33 – 1.25 (m,

9H), 0.89 – 0.86 (m, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 213.7, 138.1, 132.7, 129.5, 127.0, 116.1, 109.0, 82.7, 42.6, 38.2, 38.1, 35.1, 31.9, 31.1, 27.5, 26.4, 25.3, 22.4, 22.2, 21.3, 14.1. HRMS (ESI): m/z calcd. for C₂₄H₃₃NNa⁺([M+Na]⁺) = 358.2505, found = 358.2504.



ylidene)heptanenitrile (4y): Colorless oil, 58.0 mg, isolated yield 78%. ¹H NMR (400 MHz, CDCl₃) δ 7.26 – 7.24 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 2.39 – 2.35 (m, 4H), 2.27 – 2.23 (m,

2-(3-(adamantan-1-yl)-2-(p-tolyl)prop-1-en-1-

 $C_{5}\Pi_{11}$ (d, 0 = 0.0 Hz, 2H), 2.55 (m, H), 2.27 = 2.25 (m, 3H), 1.94 - 1.91 (m, 3H), 1.68 - 1.56 (m, 8H), 1.53 - 1.44 (m,

6H), 1.34 - 1.29 (m, 4H), 0.89 - 0.85 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 213.7, 138.1, 132.4, 129.5, 127.0, 116.2, 108.2, 82.8, 44.6, 43.0, 37.0, 34.6, 32.0, 31.1, 28.8, 27.6, 22.4, 21.3, 14.1. HRMS (ESI): m/z calcd. for C₂₇H₃₅NNa⁺([M+Na]⁺) = 396.2662, found = 396.2666.



Methyl 3-(4-cyano-2-(p-tolyl)nona-2,3-dien-1yl)bicyclo[1.1.1]pentane-1-carboxylate (4z): Pale yellow oil, 60.2 mg, isolated yield 83%. ¹H NMR (400 MHz, CDCl₃) δ 7.20 – 7.14 (m, 4H), 3.63 (s, 3H), 2.73 (s, 2H), 2.35 (s, 3H), 2.30 – 2.26 (m, 2H), 1.93 (s, 6H),

1.62 - 1.54 (m, 2H), 1.35 - 1.32 (m, 4H), 0.90 - 0.86 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 212.9, 170.3, 138.6, 130.3, 129.6, 126.7, 115.7, 108.8, 84.6, 52.4, 51.7, 38.9, 38.0, 32.9, 32.1, 31.1, 27.5, 22.4, 21.3, 14.1. HRMS (ESI): m/z calcd. for $C_{24}H_{29}NO_2Na^+([M+Na]^+) = 386.2091$, found = 386.2082.



2H), 1.76 - 1.72 (m, 6H), 1.58 - 1.54 (m, 2H), 1.44 - 1.39 (m, 6H), 1.33 - 1.28 (m, 4H), 0.89 - 0.85 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 213.6, 178.3, 138.3, 131.9, 129.6, 127.0, 115.9, 108.6, 83.1, 51.7, 41.5, 38.9, 32.8, 32.0, 31.1, 31.0, 28.6, 27.5, 22.4, 21.3, 14.1. HRMS (ESI): m/z calcd. for C₂₇H₃₅NO₂Na⁺([M+Na]⁺) = 428.2560, found = 428.2565.



1.45 (s, 9H), 1.35 – 1.30 (m, 4H), 0.89 – 0.86 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 212.0, 155.9, 138.8, 130.0, 129.8, 126.6, 115.6, 85.6, 39.0, 32.1, 31.1, 28.5, 27.6, 22.4, 21.3, 14.1. HRMS (ESI): m/z calcd. for $C_{23}H_{32}N_2O_2Na^+([M+Na]^+) = 391.2356$, found = 391.2355.



2-pentyl-4-(*p*-tolyl)hexadeca-2,3-dienenitrile (5b): Pale yellow oil, 52.2 mg, isolated yield 66%. ¹H NMR (400 MHz, CDCl₃) δ 7.23 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 2.49 (t, J = 7.4 Hz, 2H), 2.36 (s, 3H), 2.28 (t, J = 7.6 Hz, 2H), 1.60 - 1.49 (m, 4H), 1.39 - 1.26 (m, 22H), 0.90 - 0.87 (m, 6H).; ¹³C NMR (100 MHz, CDCl₃) δ 212.3, 138.4, 130.9,

129.6, 126.7, 116.0, 112.1, 84.9, 32.1, 32.0, 31.1, 30.3, 29.8, 29.8, 29.8, 29.6, 29.5, 29.5, 27.8, 27.6, 22.8, 22.5, 21.3, 14.3, 14.1. HRMS (ESI): m/z calcd. for $C_{28}H_{43}NNa^+([M+Na]^+) = 416.3288$, found = 416.3290.



(Z)-2-pentyl-4-(*p*-tolyl)docosa-2,3,13-trienenitrile (5c): Pale yellow oil, 66.4 mg, isolated yield 70%. ¹H NMR (400 MHz, CDCl₃) δ 7.23 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.36 – 5.34 (m, 2H), 2.49 (t, *J* = 7.4 Hz, 2H), 2.36 (s, 3H), 2.28 (t, *J* = 7.6 Hz, 2H), 2.04 – 1.99 (m,

4H), 1.60 - 1.50 (m, 4H), 1.35 - 1.26 (m, 25H), 0.90 - 0.87 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 212.2, 138.4, 130.9, 130.1, 130.0, 129.6, 126.7, 116.0, 112.0, 84.9, 32.1, 32.0, 31.1, 30.3, 29.9, 29.9, 29.7, 29.7, 29.6, 29.5, 29.4, 27.8, 27.6, 27.4, 22.8, 22.5, 21.3, 14.3, 14.1. HRMS (ESI): m/z calcd. for C₃₄H₅₃NNa⁺([M+Na]⁺) = 498.4070, found = 498.4082.

(E)-10-(4-hydroxy-6-methoxy-7-methyl-3-oxo-1,3-dihydroisobenzofuran-5-yl)-8-



70.2, 61.1, 39.2, 32.0, 31.1, 29.6, 27.6, 25.8, 22.8, 22.4, 21.3, 16.2, 14.1, 11.7. HRMS (ESI): m/z calcd. for C₃₃H₃₉NO₄Na⁺([M+Na]⁺) = 536.2771, found = 536.2770.



tert-butyl((1-(5-cyano-3-(*p*-tolyl))deca-3,4-dien-1-yl)cyclohexyl)methyl)carbamate (5e): Pale yellow oil, 56.8 mg, isolated yield 61%. ¹H NMR (500 MHz, CDCl₃) δ
7.23 (d, J = 8.0 Hz, 2H), 7.16(d, J = 8.0 Hz, 2H), 4.47 (br, s, 1H), 3.12 - 3.10 (m, 2H), 2.46 (t, J = 8.3 Hz, 2H), 2.35 (s, 3H), 2.28 (t, J = 7.8 Hz, 2H), 1.59 - 1.54 (m, 2H), 1.49 -

1.41 (m, 17H), 1.34 – 1.31 (m, 8H), 0.88 (t, J = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 212.1, 156.3, 138.5, 130.8, 129.6, 126.7, 116.0, 112.8, 85.0, 79.4, 46.7, 36.4, 33.7, 33.6, 33.6, 32.1, 31.1, 28.5, 27.6, 26.3, 24.1, 22.5, 21.6, 21.3, 14.1. HRMS (ESI): m/z calcd. for C₃₀H₄₄N₂O₂Na⁺([M+Na]⁺) = 487.3295, found = 487.3286.

8-(4-(bis(2-chloroethyl)amino)phenyl)-2-pentyl-4-(p-tolyl)octa-2,3-dienenitrile



(5f): Pale yellow oil, 56.0 mg, isolated yield 56%. ¹H
NMR (400 MHz, CDCl₃) δ 7.22 (d, J = 8.4 Hz, 2H),
7.17 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 8.4 Hz, 2H), 6.63
(d, J = 8.8 Hz, 2H), 3.72 - 3.68 (m, 4H), 3.64 - 3.60
(m, 4H), 2.58 - 2.50 (m, 4H), 2.36 (s, 3H), 2.28 - 2.24

(m, 2H), 1.71 - 1.65 (m, 2H), 1.62 - 1.53 (m, 4H), 1.35 - 1.31 (m, 4H), 0.88 (t, J = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 212.2, 144.3, 138.4, 131.6, 130.8, 129.7, 129.6, 126.7, 116.0, 112.3, 111.9, 85.1, 53.8, 40.7, 34.6, 32.0, 31.4, 31.1, 30.1, 27.6, 27.3, 22.4, 21.3, 14.1. HRMS (ESI): m/z calcd. for C₃₀H₃₈N₂Cl₂Na⁺([M+Na]⁺) = 519.2304, found = 519.2306.

5. Scale-up syntheses and further transformations

5.1 Scale-up reaction



In a 100 mL sealed tube, Cu(CH₃CN)₄PF₆ (0.05 mmol, 2.5 mol%), bpy (0.07 mmol, 3.5 mol%), Ir(ppy)₃ (0.02 mmol, 1.0 mol%) and NHP ester **2a** (2.0 mmol, 1.0 equiv) were added in degassed DMA (10 mL) under a nitrogen atmosphere, and the mixture was stirred at room temperature for 30 minutes. Then 1,3-enyne **1c** (2.0 mmol, 1.0 equiv) and TMSCN (4.0 mmol, 2.0 equiv) were sequentially added. The reaction mixture was stirred at room temperature under 30 W blue LEDs irradiation for 12 hours. After the reaction completion, the reaction mixture was diluted with EtOAc, then washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc) to afford the product **3c** (0.510 g, 83% yield).

5.2 Further transformations



TFA (0.4 mmol, 30 μ L) was added dropwise to a suspension of NaBH₄ (0.8 mmol, 30.4 mg) and **3c** (0.2 mmol, 61.4 mg) in dry THF (4 mL) at 0 °C. The reaction mixture was stirred at room temperature overnight. Then the mixture was cautiously added water at 0 °C and extracted with DCM. The combined organic layer was dried over Na₂SO₄, and concentrated under reduced pressure and then was purified by flash chromatography on silica gel (hexane/EtOAc) to afford the product **6** in 84% yield.



2.04 – 1.96 (m, 1H), 1.76 – 1.72 (m, 2H), 1.65 – 1.59 (m, 2H), 1.55 – 1.47 (m, 4H), 1.36 – 1.26 (m, 4H), 1.23 – 1.15 (m, 2H), 0.89 – 0.86 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 198.1, 137.5, 133.4, 129.5, 126.1, 112.1, 105.5, 49.7, 38.4, 37.7, 33.2, 33.0, 31.8, 31.7, 27.5, 25.5, 25.4, 22.6, 21.2, 14.1. HRMS (ESI): m/z calcd. for C₂₂H₃₄N⁺([M+H]⁺) = 312.2686, found = 312.2689.



 $7^{[3a]}$: H₂O₂ (0.8 mmol, 30% aqueous solution) was added dropwise to a suspension of NaOH (0.4 mmol, 92 mg) and **3c** (0.2 mmol, 61.4 mg) in dry EtOH (2 mL) at room temperature. Then the reaction mixture was stirred at 80 °C for 4 h. After cooling to room temperature, the mixture was quenched with aqueous solution of sodium thiosulfate and extracted with ethyl acetate. The combined organic layer was dried over Na₂SO₄, and concentrated under reduced pressure and then was purified by flash chromatography on silica gel (hexane/EtOAc) to afford 40.3 mg product **7** in 62% yield.

8^[3b]: Under nitrogen atmosphere, a mixture of 7 (0.12 mmol, 40.3 mg) and CuBr₂ (0.48 mmol, 107 mg) in dry THF (1 mL) was stirred at room temperature overnight. After removal of THF, an aqueous solution of NaOH (1 M, 2 mL) was added. Copper salts were removed by filtration through a Celite pad. The filtrate was extracted with ethyl acetate. The combined organic layer was dried over Na₂SO₄, and concentrated under reduced pressure and then was purified by flash chromatography on silica gel



2-(3-cyclopentyl-2-(*p***-tolyl)prop-1-en-1ylidene)heptanamide (7):** Pale yellow solid, 40.3 mg, isolated yield 62%. ¹H NMR (400 MHz, CDCl₃) δ 7.28 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 5.88 (br, s, 1H), 5.38 (br, s, 1H), 2.54 (dd, J = 7.6, 1.6 Hz, 2H), 2.41 – 2.33

(m, 5H), 2.12 - 2.05 (m, 1H), 1.83 - 1.80 (m, 2H), 1.65 - 1.59 (m, 2H), 1.57 - 1.46 (m, 4H), 1.34 - 1.18 (m, 6H), 0.85 (t, J = 7.0 Hz, 3H); 13 C NMR (100 MHz, CDCl₃) δ 207.2, 168.8, 137.7, 132.0, 129.6, 126.2, 110.9, 105.3, 38.3, 37.3, 33.3, 33.1, 31.8, 28.4, 28.2, 25.5, 25.5, 22.6, 21.3, 14.2. HRMS (ESI): m/z calcd. for C₂₂H₃₂NO⁺([M+H]⁺) = 326.2478, found = 326.2475.



4-bromo-5-(cyclopentylmethyl)-3-pentyl-5-(p-tolyl)-1H-

pyrrol-2(5*H***)-one (8):** Pale yellow oil, 41.8 mg, isolated yield 86%. ¹H NMR (400 MHz, CDCl₃) δ 7.29 (d, *J* = 8.4 Hz, 2H), 7.17 – 7.15 (m, 2H), 2.39 – 2.35 (m, 2H), 2.34 (s, 3H), 2.29 – 2.27 (m,

8 2H), 1.80 - 1.68 (m, 3H), 1.62 - 1.54 (m, 4H), 1.48 - 1.42 (m, 2H), 1.36 - 1.28 (m, 4H), 1.22 - 1.13 (m, 2H), 0.88 (t, J = 7.0 Hz, 3H); 13 C NMR (100 MHz, CDCl₃) δ 169.6, 141.9, 138.3, 136.6, 133.4, 129.3, 125.7, 92.7, 42.1, 35.8, 34.2, 34.1, 31.8, 27.1, 25.8, 25.3, 25.1, 22.6, 21.3, 14.2. HRMS (ESI): m/z calcd. for $C_{22}H_{31}BrNO^{+}([M+H]^{+}) = 404.1584$, found = 404.1583.

6. Control experiment

6.1 Radical trapping experiment



In a 10 mL sealed tube, Cu(CH₃CN)₄PF₆ (0.005 mmol, 2.5 mol%), bpy (0.007 mmol, 3.5 mol%), Ir(ppy)₃ (0.002 mmol, 1.0 mol%) and NHP ester **2a** (0.2 mmol, 1.0 equiv) were added in degassed DMA under a nitrogen atmosphere, and the mixture was stirred at room temperature for 30 minutes. Then TEMPO (0.2 mmol, 1.0 equiv), 1,3-enyne **1c** (0.2 mmol, 1.0 equiv) and TMSCN (0.4 mmol, 2.0 equiv) were sequentially added. The reaction mixture was stirred at room temperature under 30 W blue LEDs irradiation for 12 hours. The decarboxylative 1,4-carbocyanation was completely inhibited, and the TEMPO-captured **9** was detected by HRMS analysis. HRMS (ESI): m/z calcd. for C₁₄H₂₈NO⁺([M+H]⁺) = 226.2165, found = 226.2169.



Fig. S1 HRMS of TEMPO-captured 9





In a 10 mL sealed tube, $Cu(CH_3CN)_4PF_6$ (0.005 mmol, 2.5 mol%), bpy (0.007 mmol, 3.5 mol%), Ir(ppy)₃ (0.002 mmol, 1.0 mol%) and NHP ester **10** (0.2 mmol, 1.0 equiv) were added in degassed DMA under a nitrogen atmosphere, and the mixture was stirred at room temperature for 30 minutes. Then 1,3-enyne **1c** (0.2 mmol, 1.0 equiv) and TMSCN (0.4 mmol, 2.0 equiv) were sequentially added. The reaction mixture was stirred at room temperature under 30 W blue LEDs irradiation for 12 hours. After the reaction completion, the reaction mixture was diluted with EtOAc, then washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc) to afford the product **4h** (45.7 mg, 78% yield).



In a 10 mL sealed tube, $Cu(CH_3CN)_4PF_6$ (0.005 mmol, 2.5 mol%), bpy (0.007 mmol, 3.5 mol%), $Ir(ppy)_3$ (0.002 mmol, 1.0 mol%) and NHP ester **2a** (0.2 mmol, 1.0 equiv) were added in degassed DMA under a nitrogen atmosphere, and the mixture was stirred at room temperature for 30 minutes. Then 1,3-enyne **11** (0.2 mmol, 1.0 equiv) and TMSCN (0.4 mmol, 2.0 equiv) were sequentially added. The reaction mixture was stirred at room temperature under 30 W blue LEDs irradiation for 12 hours. After the reaction completion, the reaction mixture was diluted with EtOAc, then washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc) to afford the product **12** in 56% yield.



0.67 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 212.2, 133.9, 128.9, 128.5, 126.8, 114.7, 113.2, 88.2, 38.1, 37.3, 32.9, 32.9, 25.5, 25.4, 11.8, 6.5, 6.4. HRMS (ESI): m/z calcd. for C₁₉H₂₁NNa⁺([M+Na]⁺) = 286.1566, found = 286.1565.

6.3 Ring-closing experiment



In a 10 mL sealed tube, $Cu(CH_3CN)_4PF_6$ (0.005 mmol, 2.5 mol%), bpy (0.007 mmol, 3.5 mol%), Ir(ppy)₃ (0.002 mmol, 1.0 mol%) and NHP ester **2a** (0.2 mmol, 1.0 equiv) were added in degassed DMA under a nitrogen atmosphere, and the mixture was stirred at room temperature for 30 minutes. Then 1,3-enyne **13** (0.2 mmol, 1.0 equiv) and TMSCN (0.4 mmol, 2.0 equiv) were sequentially added. The reaction mixture was stirred at room temperature under 30 W blue LEDs irradiation for 12 hours. After the reaction completion, the reaction mixture was diluted with EtOAc, then washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc) to afford the product **14** in 45% yield.



(*E*)-2-(3-cyclopentyl-2-phenylprop-1-en-1-ylidene)-7phenylhept-6-enenitrile (14): Pale yellow oil, 33.1 mg, isolated yield 45%. ¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.34 (m, 4H), 7.33 – 7.27 (m, 5H), 7.22 – 7.18 (m, 1H), 6.36 – 6.32 (m, 1H), 6.19 – 6.12 (m, 1H), 2.53 (d, *J* = 7.6 Hz, 2H), 2.37 – 2.26 (m, 4H), 2.09 – 2.01 (m, 1H), 1.86 – 1.75 (m, 4H), 1.66 – 1.60 (m, 2H), 1.55 – 1.51 (m, 2H),

 $1.29 - 1.20 \text{ (m, 2H)}; {}^{13}\text{C NMR} (100 \text{ MHz, CDCl}_3) \delta 212.9, 137.6, 133.9, 131.1, 129.4, 128.9, 128.6, 128.5, 127.2, 126.9, 126.1, 115.8, 111.9, 84.4, 38.2, 37.2, 33.0, 32.9, 32.2, 31.4, 27.6, 25.4, 25.4. HRMS (ESI): m/z calcd. for C₂₇H₂₉NNa⁺([M+Na]⁺) = 390.2192, found = 390.2199.$
7. X-ray crystallography of 3r



CCDC 2034197 (**3r**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Date Centre via <u>www.ccdc.cam.ac.uk/data_request/cif</u>.

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9. Copy of NMR spectra

Feb06-2020-cy-s1-74.10.fid



Feb25-2020-cy-s1-96.10.fid

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