Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information: Experimental procedures and characterization

Pursuing High Efficiency in Photocatalytic Oxidative Couplings of Heteroarenes and Aliphatic C-H bonds

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I. General information

All NMR spectra were acquired on Bruker 400 MHz spectrometers. ^{1}H NMR chemical shifts were recorded relative to TMS (δ 0.00) or residual protiated solvents ($CDCl_3$: δ 7.27). Multiplicities were given as: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). The number of protons (n) for a given resonance was indicated by nH. Coupling constants were reported as a *J* value in Hz. ^{13}C NMR spectra were obtained at 100 MHz on 400 MHz instruments and chemical shifts were recorded relative to solvent resonance ($CDCl_3$: δ 77.00). ^{19}F NMR spectra were recorded at 376 MHz on 400 MHz NMR spectrometers without any external standard. Proof of purity of new compounds was demonstrated with copies of ^{1}H, ^{13}C, and ^{19}F NMR spectra. Glassware was dried at 120 ^{o}C in an oven for at least 6 h before use.

Unless noted otherwise, commercially available chemicals were used as received without purification. The GC internal standard *n*-$C_{12}H_{26}$ was degassed with argon and dried over activated 4Å molecular sieve beads before use. CAS numbers are given in the characterization session of known compounds.

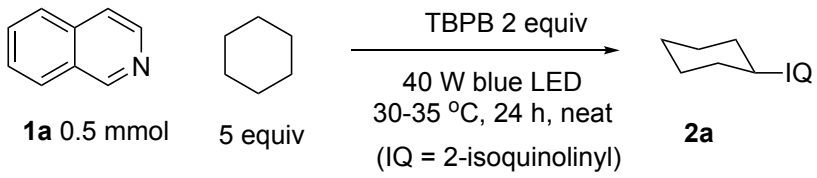
Flash chromatography was performed using Merck 40-63D 60Å silica gel. Gas chromatography (GC) analysis was performed on a Shimadzu GC-2010 instrument with Agilent J & W GC column DB-5MS-UI. GC/MS analysis was conducted on a Thermo Scientific DSQ II single quadrupole GC/MS instrument with Agilent J & W GC column DB-5MS-UI. GC/MS analysis was conducted on a Thermo Scientific DSQ II single quadrupole GC/MS instrument with Agilent J & W GC column DB-5MS-UI. ESI/MS analysis was conducted on a ThermoFinnigan LCQ Fleet MS spectrometer.

Time-Resolved Photoluminescence (TRPL) measurements were performed using femtosecond excitation pulses at 360 nm (>50 fs) which generated from a femtosecond laser system configured by Coherent Libra (50 fs; seed and amplifier integrated system) + OPerA Solo (optical parametric amplifier). The emitted light was collected at a backscattering angle by a spectrometer (Acton, SpectraPro-2500i) and an Optronis OptoScope streak camera system, which has an ultimate temporal resolution of 10 ps in TRPL measurements.

II. Condition optimization of oxidative alkylation of heteroarenes

*A typical procedure under blue LED irradiation***:** in an argon-filled glove box, a 10 mL Schlenk tube or a 10 mL Pyrex tube containing a magnetic stir bar was charged with isoquinoline (59 uL, 0.5 mmol), *tert*-butyl peroxybenzoate (1.0 mmol) and cyclohexane (275 uL, 2.5 mmol). The tube was capped tightly and the reaction mixture was vigorously stirred at 30-35 °C (with fan cooling) for 24 hours under 40 W blue LED (Kessil A160WE Tuna Blue. Setting: maximal light intensity and maximum spectral width/color. At the end of the reaction, 1 mL of dilute aq $NaHCO_3$ and GC standard *n*-dodecane (50 μL) were added. An aliquot of the reaction mixture was passed through a short plug of silica gel with ethyl acetate washings. The filtrate was subjected to GC to determine the conversion of isoquinoline and calibrated GC yield of the product.

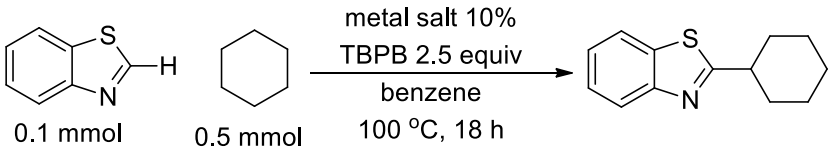
Table S1 Effect of transition metal salts on oxidative coupling of cyclohexane and benzothiazole under blue LED



Entry	Metal salt	Conv (%)	GC Yield (%)
1	None	**100**	**73**
2	$Cu(OTf)_2$	93	71
3	$Cu(OAc)_2$	65	58
4	$CoCl_2$	58	26
5	$CoBr_2$	40	16
6	$FeCl_2$	74	48
7	$FeCl_3$	90	54
8	$NiBr_2$	83	64
9	$Ni(OAc)_2$	95	66

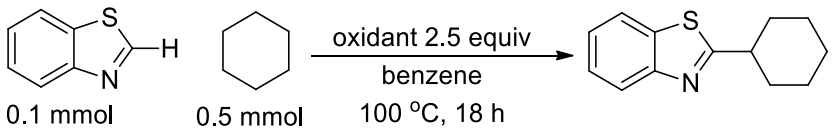
*A typical procedure under thermal heating (for comparison with LED conditions)**:*** in an argon-filled glove box, a 10 mL Schlenk tube or a 10 mL Pyrex tube containing a magnetic stir bar was charged with benzothiazole (0.1 mmol), *tert*-butyl peroxybenzoate (0.25 mmol) and cyclohexane (0.5 mmol) and benzene (0.2 mL). The tube was capped tightly and the reaction mixture was vigorously stirred in an oil bath at 100 °C for 18 hours. At the end of the reaction, 1 mL of dilute aq $NaHCO_3$ and GC standard *n*-dodecane (10 μL) were added. An aliquot of the reaction mixture was passed through a short plug of silica gel with ethyl acetate washings. The filtrate was subjected to GC to determine the conversion of benzothiazole and calibrated GC yield of the product.

Table S2 Effect of transition metal salts on thermal oxidative coupling of cyclohexane and benzothiazole



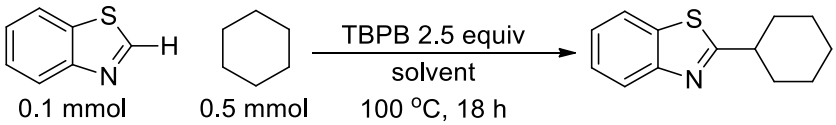
Entry	Metal salt	Conv (%)	GC Yield (%)
1	None	**100**	**61**
2	CuCl	100	5
3	CuBr	100	5
4	CuI	100	5
5	CuCN	100	12
6	$Cu(OAc)_2$	100	33
7	CuF_2	100	12
8	$CoCl_2$	100	39
9	$CoBr_2$	100	39
10	$FeCl_2$	100	23
11	$FeBr_2$	100	33
12	$NiBr_2$	100	55
13	$PdCl_2$	100	55

Table S3 Effect of peresters and peroxides on thermal oxidative coupling of cyclohexane and benzothiazole



Entry	Oxidant	Conv (%)	GC Yield (%)
1	H_2O_2	0	0
2	Oxone	5	0
3	$K_2S_2O_8$	10	0
4	*m*CPBA	15	0
5	$PhI(OAc)_2$	0	0
6	*t*BuOOH	90	42
7	di-*t*-Butyl peroxide	90	47
8	Dibenzoyl peroxide	80	14
9	*t*-Butyl peroxybenzoate	100	61

Table S4 Effect of solvents on thermal oxidative coupling of cyclohexane and benzothiazole



0.1 mmol 0.5 mmol

Entry	Solvent	Conv (%)	GC Yield (%)
1	THF	100	0
2	Dioxane	100	0
3	DMF	20	0
4	DMSO	20	0
5	MeCN	0	0
6	1,2-Dichlorobenzene	40	0
7	1,2-Dichloroethane	100	0
8	Toluene	20	5
9	PhCl	10	13
10	PhOMe	10	0
11	$PhCF_3$	100	**56**
12	Benzene	100	**61**

III. Oxidative alkylation of heteroarenes using 5 equiv of alkanes

A typical procedure under LED irradiation: in an argon-filled glove box, a 10 mL Schlenk tube or a 10 mL Pyrex tube containing a magnetic stir bar was charged with heteroarene (0.5 mmol), *tert*-butyl peroxybenzoate (1.0 mmol) and alkane (2.5 mmol). The tube was capped tightly and the reaction mixture was vigorously stirred at 30-35 °C (with fan cooling) for 48 hours under close irradiation of 40 W blue LED lamp (Kessil A160WE Tuna Blue. Setting: maximal light intensity and maximum spectral width/color. Position: ~1 cm away from the side of the tube). At the end of the reaction, 1 mL of dilute aq $NaHCO_3$ was added and the reaction mixture was extracted with EA (3 x 5 mL). The filtrate was dried over anhydrous Na_2SO_4 and purified by flash column chromatography on silica gel with hexanes/EA 10: 1 to obtain the desired product. The ratios of isomers of crude samples were determined by proton NMR spectrometry and confirmed by GCMS.

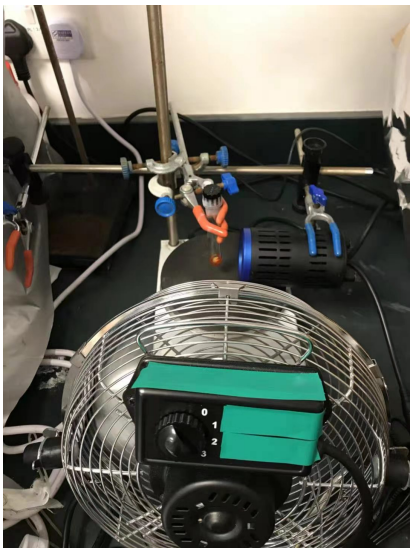
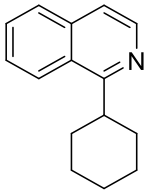


Figure S1. Configuration of LED experiments



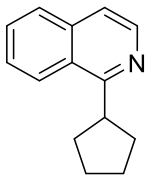
1-Cyclohexylisoquinoline [33538-11-3]

White solid, 77 mg, 73% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (d, *J* = 5.6 Hz, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.67-7.63 (m, 1H), 7.61-7.57 (m, 1H), 7.48 (d, *J* = 5.6 Hz, 1H), 3.57 (tt, *J* = 11.2, 3.2 Hz, 1H), 2.02-1.93 (m, 4H), 1.89-1.80 (m, 3H), 1.60-1.49 (m, 2H), 1.46-1.38 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 141.9, 136.4, 129.5, 127.5, 126.8, 126.3, 124.7, 118.8, 41.5, 32.6, 26.9, 26.2.

MS (EI) m/z: Calcd for $C_{15}H_{17}N$: 211.1; Found: 211.0.



1-Cyclopentylisoquinoline [76518-71-3]

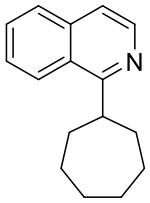
White solid, 69 mg, 70% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 5.6 Hz, 1H), 8.26 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.68-7.64

(m, 1H), 7.61-7.57 (m, 1H), 7.49 (d, *J* = 5.6 Hz, 1H), 4.04 (ψquintet, *J* = 8.4 Hz, 1H), 2.20-2.06 (m, 4H), 1.89-1.80 (m, 3H), 1.97-1.86 (m, 2H), 1.84-1.73 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.8, 141.8, 136.3, 129.5, 127.4, 127.2, 126.7, 125.2, 118.9, 43.0, 32.8, 26.1.

MS (EI) m/z: Calcd for $C_{14}H_{15}N$: 197.1; Found: 197.0.



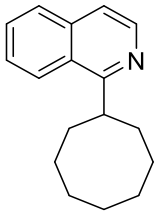
1-Cycloheptylisoquinoline [2130837-96-4]

Colorless oil, 93 mg, 83% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 5.6 Hz, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.68-7.64 (m, 1H), 7.61-7.57 (m, 1H), 7.47 (d, *J* = 6.0 Hz, 1H), 3.74 (tt, *J* = 10.0, 3.6 Hz, 1H), 2.11-1.98 (m, 4H), 1.96-1.90 (m, 2H), 1.80-1.63 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 141.9, 136.4, 129.5, 127.5, 126.8, 126.0, 124.8, 118.9, 43.2, 34.6, 28.0, 27.5.

MS (EI) m/z: Calcd for $C_{16}H_{19}N$: 225.1; Found: 225.0.



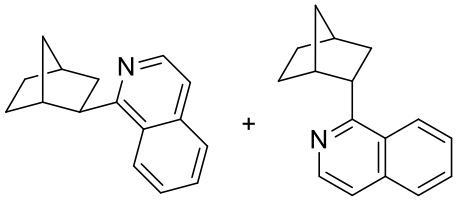
1-Cyclooctylisoquinoline [1123206-28-9]

Colorless oil, 72 mg, 60% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 6.0 Hz, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.68-7.64 (m, 1H), 7.62-7.57 (m, 1H), 7.47 (d, *J* = 5.6 Hz, 1H), 3.88-3.82 (m, 1H), 2.13-1.98 (m, 4H), 1.92-1.88 (m, 2H), 1.80-1.66 (m, 8H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.8, 141.8, 136.5, 129.5, 127.6, 126.8, 126.0, 124.9, 118.7, 41.1, 33.1, 26.8, 26.7, 26.3.

MS (EI) m/z: Calcd for $C_{17}H_{21}N$: 239.1; Found: 239.1.



The ratio of two isomers was determined to be 5:1 by GC of the crude reaction mixture and confirmed by GCMS and proton NMR spectroscopy. Combined yield 51%.

***exo*-1-(1-Isoquinolyl)bicyclo[2.2.1]heptane [2366139-50-4]**

Colorless oil, 48.1 mg, 43% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (d, *J* = 5.7 Hz, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.67-7.62 (m, 1H), 7.60-7.56 (m, 1H), 7.46 (d, *J* = 5.8 Hz, 1H), 3.61-3.57 (m, 1H), 2.60-2.59 (m, 1H), 2.44-2.37 (m, 2H), 1.76-1.55 (m, 5H), 1.44-1.38 (m, 1H), 1.21-1.17 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4, 141.4, 136.4, 129.6, 127.5, 127.1, 126.8, 125.5, 118.9, 45.6, 43.1, 36.9, 36.2, 36.0, 30.4, 29.7.

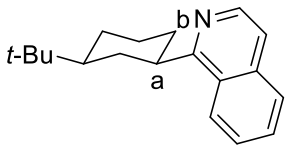
***endo*-1-(1-Isoquinolyl)bicyclo[2.2.1]heptane**

Colorless oil, 8.8 mg, 8% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, *J* = 5.7 Hz, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.66-7.62 (m, 1H), 7.59-7.55 (m, 1H), 7.48 (d, *J* = 5.7 Hz, 1H), 4.15-4.11 (m, 1H), 2.70 (d, *J* = 4.5 Hz, 1H), 2.50 (ddd, *J* = 12.1, 5.1, 2.5 Hz, 1H), 2.41 (d, *J* = 4.5 Hz, 1H), 1.89-1.77 (m, 2H), 1.57-1.49 (m, 3H), 1.18-1.09 (m, 1H), 0.99-0.92 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.2, 141.5, 136.3, 129.5, 128.1, 127.5, 126.8, 125.6, 119.1, 45.0, 43.6, 41.8, 37.9, 31.9, 29.5, 23.8.

MS (EI) m/z: Calcd for $C_{16}H_{17}N$: 223.1; Found: 223.2.



1-(3-(*tert*-Butyl)cyclohexyl)isoquinoline and 1-(4-(*tert*-butyl)cyclohexyl)isoquinoline

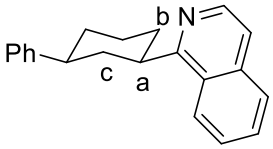
Colorless oil, 87.2 mg, 62% combined yield of two isomers. The ratio (a:b = 2.8:1) of two isomers was determined by GC of the crude reaction mixture and confirmed by GCMS and proton NMR spectroscopy.

^{1}H NMR of two isomers (400 MHz, $CDCl_3$): δ 8.52-8.49 (m, 3.4H), 8.26-8.22 (m, 3.7H), 7.84-7.82 (m, 3.5H), 7.69-7.64 (m, 3.6H), 7.62-7.58 (m, 3.7H), 7.51-7.44 (m, 3.7H), 3.60 (tt, *J* = 11.6, 3.2 Hz, 2.8H), 3.53 (ψtt, *J* = 11.8, 3.5 Hz, 1.0H), 2.11-1.89 (m, 17.0H), 1.87-1.75 (m, 3.9H), 1.62-1.50 (m, 6.0H), 1.40-1.31 (m, 5.9H), 1.27-1.10 (m, 5.9H), 0.95

(s, 9.2H), 0.92 (s, 26.0H).

^{13}C NMR of two isomers (100 MHz, $CDCl_3$): δ 166.0, 165.8, 142.13, 142.10, 136.54, 136.49, 129.7, 129.6, 127.70, 127.67, 127.0, 126.9, 126.6, 126.4, 124.9, 124.8, 119.00, 118.98, 48.9, 47.9, 42.1, 41.7, 33.9, 33.0, 32.9, 32.7, 32.5, 27.81, 27.79 (two overlapping signals), 27.3, 27.2.

MS (EI) m/z: Calcd for $C_{19}H_{25}N$: 267.2; Found: 267.3.



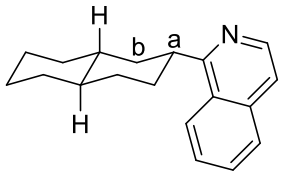
1-(3-(Phenylcyclohexyl))isoquinoline and 1-(4-(phenylcyclohexyl))isoquinoline

Colorless oil, 63.0 mg, 44% combined yield of two main isomers. The ratio 2.6:1 of isomers was determined by GC of the crude reaction mixture and confirmed by GCMS and proton NMR spectroscopy.

^{1}H NMR of two isomers (400 MHz, $CDCl_3$): δ 8.51-8.48 (m, 3.8H), 8.42 (d, *J* = 5.8 Hz, 0.8H), 8.28-8.24 (m, 4.0H), 8.12 (d, *J* = 8.4 Hz, 0.8H), 7.84-7.80 (m, 4.0H), 7.69-7.58 (m, 9.6H), 7.55-7.44 (m, 6.7H), 7.36-7.28 (m, 17.1H), 7.24-7.15 (m, 5.6H), 7.08 (d, *J* = 7.7 Hz, 2.1H), 6.95 (t, *J* = 7.5 Hz, 1.8H), 6.84 (t, *J* = 7.3 Hz, 1.0H), 3.92-3.86 (m, 1.0H), 3.78 (tt, *J* = 11.1, 3.1 Hz, 3.1H), 3.71-3.64 (m, 1.7H), 3.49-3.42 (m, 1.0H), 2.87 (tt, *J* = 11.8, 3.2 Hz, 3.1H), 2.78-2.71 (m, 1.7H), 2.18-2.00 (m, 25.4H), 1.98-1.88 (m, 7.0H), 1.84-1.70 (m, 8.6H), 1.68-1.61 (m, 5.4H).

^{13}C NMR of two isomers (100 MHz, $CDCl_3$): δ 165.4, 165.2, 164.6, 147.7, 147.5, 142.3, 142.2, 142.0, 137.1, 136.7, 136.4, 130.7, 129.8, 129.5, 128.61, 128.56, 127.9, 127.8, 127.7, 127.5, 127.21, 127.16, 127.1, 126.8, 126.6, 126.5, 126.2, 125.6, 124.9, 124.8, 124.6, 119.3, 118.8, 48.5, 46.0, 45.1, 44.3, 41.9, 41.2, 40.0, 35.7, 34.7, 34.4, 32.9, 32.2, 27.2, 27.0, 26.9.

MS (EI) m/z: Calcd for $C_{21}H_{21}N$: 287.2; Found: 287.2.



1-(Decahydronaphthalen-2-yl)isoquinoline and 1-(decahydronaphthalen-1-yl)isoquinoline

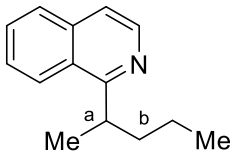
Colorless oil, 86.0 mg, 65% combined yield of two isomers. The ratio (a:b = 1.4:1) of two isomers was determined by GC of the crude reaction mixture and confirmed by GCMS and proton NMR spectroscopy.

^{1}H NMR of two isomers (400 MHz, $CDCl_3$): δ 8.53 (d, *J* = 5.7 Hz, 0.8H), 8.48 (d, *J* = 5.7 Hz, 1.4H), 8.27-8.22 (m,

2.5H), 7.82-7.80 (m, 2.4H), 7.67-7.63 (m, 2.4H), 7.60-7.55 (m, 2.5H), 7.49-7.46 (m, 2.5H), 3.65 (ψtt, *J* = 11.8, 3.4 Hz, 1.7H), 3.39-3.32 (m, 1.0H), 2.02-1.96 (m, 1.8H), 1.92-1.78 (m, 8.8H), 1.76-1.78 (m, 13.7H), 1.37-1.00 (m, 18.7H), 0.88-0.75 (m, 1.8H).

^{13}C NMR of two isomers (100 MHz, $CDCl_3$): δ 165.62, 165.60, 142.4, 142.1, 136.5, 136.4, 129.69, 129.67, 127.8, 127.7, 127.6, 126.94, 126.88, 126.5, 124.92, 124.88, 119.0, 118.6, 47.1, 46.1, 43.7, 43.5, 43.1, 41.6, 39.7, 34.4, 34.33, 34.27, 34.1, 32.7, 31.5, 27.0, 26.9, 26.8, 26.73, 26.68.

MS (EI) m/z: Calcd for $C_{19}H_{23}N$: 265.2; Found: 265.3.



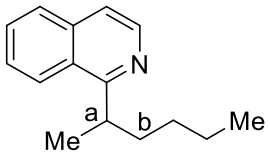
1-(2-Pentyl)isoquinoline [1821161-15-2] and 1-(3-pentyl)isoquinoline [76518-78-0]

Colorless oil, 70 mg, 70% combined yield of two isomers. The ratio (a:b = 5:1) of two isomers was determined by GC of the crude reaction mixture and confirmed by GCMS and proton NMR spectroscopy.

^{1}H NMR of two isomers (400 MHz, $CDCl_3$): δ 8.54 (d, *J* = 5.6 Hz, 0.9H), 8.51 (d, *J* = 5.7 Hz, 2.7H), 8.27-8.23 (m, 4.3H), 7.82 (d, *J* = 8.4 Hz, 3.9H), 7.68-7.64 (m, 4.1H), 7.61-7.57 (m, 4.1H), 7.49 (d, *J* = 5.7 Hz, 4.1H), 3.87-3.78 (m, 3.5H), 3.58-3.51 (m, 1.0H), 2.02-1.94 (m, 5.5H), 1.90-1.80 (m, 2.5H), 1.77-1.68 (m, 4.3H), 1.42 (d, *J* = 6.8 Hz, 10.7H), 1.39-1.21 (m, 8.6H), 0.91 (t, *J* = 7.3 Hz, 10.7H), 0.80 (t, *J* = 7.4 Hz, 6.1H).

^{13}C NMR of two isomers (100 MHz, $CDCl_3$): δ 166.1, 165.0, 142.1, 142.0, 136.3, 136.2, 129.5, 129.5, 127.5, 127.4, 126.89, 126.8, 126.7, 124.9, 124.7, 118.8, 118.6, 44.8, 39.0, 35.8, 28.2, 21.0, 20.5, 14.3, 12.3.

MS (EI) m/z: Calcd for $C_{12}H_{18}N$: 199.1; Found: 199.2.



1-(2-Hexyl)isoquinoline [2366139-51-5] and 1-(3-hexyl)isoquinoline [2366139-52-6]

Colorless oil, 72.6 mg, 68% combined yield of two isomers. The ratio (a:b = 2:1) of two isomers was determined by GC of the crude reaction mixture and confirmed by GCMS and proton NMR spectroscopy.

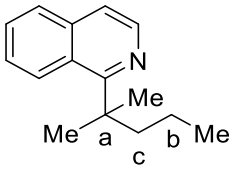
^{1}H NMR of two isomers (400 MHz, $CDCl_3$): δ 8.53 (d, *J* = 5.6 Hz, 0.8H), 8.50 (d, *J* = 5.6 Hz, 2.3H), 8.26-8.22 (m, 3.6H), 7.81 (d, *J* = 8.1 Hz, 3.3H), 7.67-7.63 (m, 3.5H), 7.60-7.56 (m, 3.5H), 7.48 (d, *J* = 5.7 Hz, 3.5H), 3.83-3.75 (m,

3.0H), 3.66-3.59 (m, 1.0H), 2.04-1.92 (m, 4.9H), 1.88-1.81 (m, 1.0H), 1.79-1.69 (m, 4.1H), 1.41 (d, *J* = 6.8 Hz, 9.0H), 1.35-1.27 (m, 10.4H), 1.24-1.18 (m, 3.3H), 1.16-1.11 (m, 1.2H), 0.87-0.83 (m, 12.3H), 0.78 (t, *J* = 7.4 Hz, 2.8H).

^{13}C NMR of two isomers (100 MHz, $CDCl_3$): δ 166.1, 165.0, 142.1, 142.0, 136.3, 136.2, 129.5, 129.5, 127.5, 127.4, 126.89, 126.8, 126.7, 124.9, 124.7, 118.8, 118.6, 44.8, 39.0, 35.8, 28.2, 21.0, 20.5, 14.3, 12.3.

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.3, 142.2, 136.5, 136.4, 129.7, 127.7, 127.6, 127.0, 126.92, 126.90, 125.0, 124.9, 118.9, 118.8, 37.8, 36.7, 36.2, 30.3, 28.7, 23.1, 21.1, 20.7, 14.5, 14.2, 12.5.

MS (EI) m/z: Calcd for $C_{15}H_{19}N$: 213.2; Found: 213.2.



The ratio (a:b = 1.2:1) of two main isomers was determined by GC of the crude reaction mixture and confirmed by GCMS and proton NMR spectroscopy. Combined yield 61%.

2-(1-Isoquinolyl)-2-methylpentane

Colorless oil, 35 mg, 33% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (d, *J* = 8.8 Hz, 1H), 8.45 (d, *J* = 7.6 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.64-7.61 (m, 1H), 7.57- 7.53 (m, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 2.11-2.07 (m, 2H), 1.64 (s, 6H), 1.11-1.01 (m, 2H), 0.79 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 140.6, 137.2, 128.8, 128.2, 126.8, 126.6, 125.7, 119.6, 45.7, 43.5, 29.8, 18.3, 14.8.

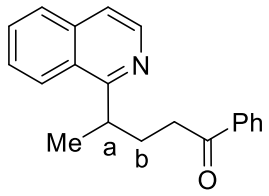
2-(1-Isoquinolyl)-4-methylpentane [2253895-74-6] with some isomer

Colorless oil, 30 mg, 28% yield.

^{1}H NMR of two isomers (400 MHz, $CDCl_3$): δ 8.55 (d, *J* = 5.6 Hz, 1.0H), 8.51 (d, *J* = 5.7 Hz, 3.5H), 8.26 (d, *J* = 8.5 Hz, 4.5H), 7.82 (d, *J* = 8.1 Hz, 4.6H), 7.68-7.64 (m, 4.8H), 7.62-7.58 (m, 4.9H), 7.49 (d, *J* = 5.6 Hz, 4.7H), 3.96-3.87 (m, 4.0H), 3.37-3.31 (m, 1.0H), 2.28-2.19 (m, 1.1H), 2.12-1.99 (m, 2.1H), 2.94-1.88 (m, 4.1H), 1.64-1.56 (m, 8.1H), 1.40 (d, *J* = 6.8 Hz, 12.2H), 1.07 (d, *J* = 6.7 Hz, 3.1H), 0.95 (d, *J* = 6.2 Hz, 12.2H), 0.90 (d, *J* = 6.2 Hz, 12.1H), 0.72 (d, *J* = 6.7 Hz, 3.0H), 0.65 (t, *J* = 7.4 Hz, 3.0H).

^{13}C NMR of two isomers (100 MHz, $CDCl_3$): δ 166.2, 165.0, 142.0, 142.0, 136.4, 136.2, 129.5, 129.4, 128.8, 127.6, 127.5, 126.8, 126.7, 126.6, 125.1, 124.6, 118.8, 118.5, 45.9, 33.7, 33.2, 25.9, 24.9, 23.1, 22.6, 21.7, 20.7, 20.5, 12.4.

MS (EI) m/z: Calcd for $C_{15}H_{19}N$: 213.1; Found: 213.0.



tert-Butyl peroxybenzoate (4.0 equiv) was used. The ratio (a:b = 3:1) of two isomers was determined by GC of the crude reaction mixture and confirmed by GCMS and proton NMR spectroscopy. Combined yield 47%

4-(1-Isoquinolyl)-1-phenylpentan-1-one

Colorless oil, 52.2 mg, 36% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (d, *J* = 5.7 Hz, 1H), 8.24 (d, *J* = 8.5 Hz, 1H), 7.88-7.86 (m, 2H), 7.67-7.63 (m, 2H), 7.59-7.55 (m, 2H), 7.52-7.47 (m, 2H), 7.4-7.36 (m, 2H), 4.02-3.94 (m, 1H), 3.08-3.00 (m, 1H), 2.90-2.82 (m, 1H), 2.58-2.49 (m, 1H), 2.24-2.15 (m, 1H), 1.46 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 200.7, 164.9, 142.1, 137.1, 136.5, 133.0, 129.8, 128.6, 128.2, 127.7, 127.2, 127.0, 124.8, 119.3, 36.6, 35.5, 30.8, 21.0.

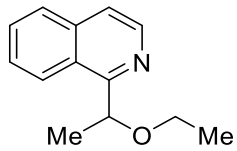
3-(Isoquinolin-1-yl)-1-phenylpentan-1-one

Colorless oil, 15.3 mg, 11% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 8.42 (d, *J* = 7.1 Hz, 2H), 7.98 (d, *J* = 7.5 Hz, 2H), 7.80 (d, *J* = 7.7 Hz, 1H), 7.67-7.61 (m, 2H), 7.54-7.50 (m, 1H), 7.47 (d, *J* = 5.5 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 4.49-4.42 (m, 1H), 3.98 (ψdd, *J* = 17.6, 7.9 Hz, 1H), 3.41 (ψdd, *J* = 17.6, 5.3 Hz, 1H), 2.05-1.94 (m, 1H), 1.92-1.81 (m, 1H), 0.86 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 199.9, 164.1, 141.8, 137.4, 136.5, 133.0, 129.8, 128.6, 128.3, 127.6, 127.5, 127.2, 125.3, 119.3, 43.3, 38.3, 29.1, 12.3.

MS (EI) m/z: Calcd for $C_{20}H_{19}NO$: 289.1; Found: 289.2.



1-(1-Ethoxyethyl)isoquinoline [33357-71-0]

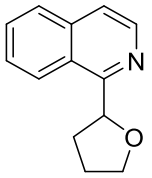
White oil, 80.4 mg, 80% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (d, *J* = 8.6 Hz, 1H), 8.47 (d, *J* = 5.6 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.70-7.66 (m, 1H), 7.61-7.57 (m, 2H), 5.18 (q, *J* = 6.8 Hz, 1H), 3.56-3.49 (m, 1H), 3.44-3.36 (m, 1H), 1.71 (d, *J* = 6.8 Hz, 3H),

1.20 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.8, 141.5, 136.8, 129.9, 127.4, 126.8, 126.1, 80.1, 64.5, 21.6, 15.5.

MS (EI) m/z: Calcd for $C_{13}H_{13}NO$: 201.1; Found: 201.0.



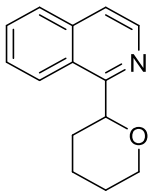
1-(Tetrahydrofuran-2-yl)isoquinoline [115885-68-2]

Yellow oil, 77 mg, 78% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (d, *J* = 6.0 Hz, 1H), 8.34 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.69-7.65 (m, 1H), 7.62-7.60 (m, 1H), 7.58-7.56 (m, 1H), 5.72 (t, *J* = 7.2 Hz, 1H), 4.19 (dd, *J* = 14.8, 7.6 Hz, 1H), 4.07-4.01 (m, 1H), 2.58-2.49 (m, 1H), 2.45-2.36 (m, 1H), 2.23-2.06 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 141.6, 136.5, 129.7, 127.3, 127.0, 126.6, 125.2, 120.4, 79.1, 68.9, 30.7, 26.1.

MS (EI) m/z: Calcd for $C_{13}H_{13}NO$: 199.1; Found: 199.0.



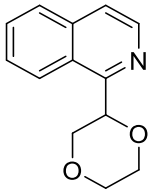
1-(Tetrahydro-2H-pyran-2-yl)isoquinoline [1798823-56-9]

White solid, 87 mg, 82% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (d, *J* = 5.6 Hz, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.69-7.65 (m, 1H), 7.62-7.57 (m, 2H), 5.20 (dd, *J* = 11.0, 2.4 Hz, 1H), 4.38-4.26 (m, 1H), 3.83-3.77 (ψtd, *J* = 11.6, 2.3 Hz, 1H), 2.19-1.99 (m, 3H), 1.95-1.76 (m, 2H), 1.70-.67 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 141.8, 136.7, 129.7, 127.4, 127.0, 126.0, 125.3, 120.5, 79.3, 69.4, 31.1, 25.9, 23.9.

MS (EI) m/z: Calcd for $C_{14}H_{15}NO$: 213.1; Found: 213.1.



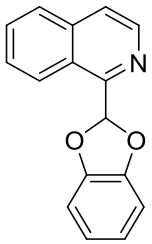
1-(1,4-Dioxan-2-yl)isoquinoline [33787-81-4]

White solid, 77 mg, 72% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, *J* = 5.6 Hz, 1H), 8.33 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.72-7.68 (m, 1H), 7.66-7.62 (m, 2H), 5.49 (dd, *J* = 9.6, 2.8 Hz, 1H), 4.21-4.07 (m, 4H), 3.92-3.88 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.0, 141.9, 136.4, 130.0, 127.4 (two overlapping signals), 126.5, 124.7, 121.0, 75.8, 70.2, 67.5, 66.5.

MS (EI) m/z: Calcd for $C_{13}H_{13}NO_2$: 215.1; Found: 215.0.



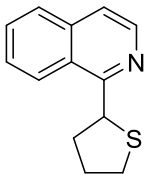
1-(Benzo[1,3]dioxol-2-yl)isoquinoline

White solid, 96 mg, 77% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59 (d, *J* = 5.6 Hz, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 5.6 Hz, 1H), 7.71 (ψt, *J* = 7.6 Hz, 1H), 7.59 (ψt, *J* = 7.7 Hz, 1H), 7.45 (s, 1H), 7.01-6.94 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.4, 147.4, 141.6, 137.0, 130.3, 128.0, 127.5, 126.3, 124.6, 123.0, 122.2, 111.1, 109.1.

MS (EI) m/z: Calcd for $C_{16}H_{11}NO_2$: 249.1; Found: 249.0.



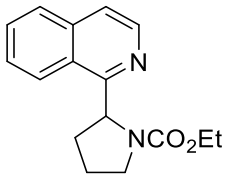
1-(Tetrahydrothiophen-2-yl)isoquinoline

Light yellow oil, 80 mg, 74% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 6.0 Hz, 1H), 8.34 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 7.2 Hz, 1H), 7.69-7.59 (m, 2H), 7.52 (d, *J* = 6.4 Hz, 1H), 3.18-3.12 (m, 1H), 3.08-3.03 (m, 1H), 2.99-2.91 (m, 1H), 2.56-2.47 (m, 1H), 2.38-2.30 (m, 1H), 2.26-2.16 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.7, 141.7, 136.3, 129.8, 127.4, 127.2, 127.0, 124.9, 119.8, 48.7, 34.5, 34.0, 31.3.

MS (EI) m/z: Calcd for $C_{13}H_{13}NS$: 215.1; Found: 215.1.



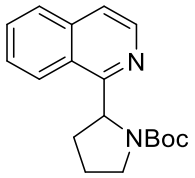
***N*-Ethoxycarbonyl 2-(isoquinolin-1-yl)pyrrolidine**

Yellow oil 95 mg, 70% yield.

^{1}H NMR of two rotamers (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 5.2 Hz, 1H), 8.23-8.15 (m, 1H), 7.85-7.79 (m, 1H), 7.69-7.62 (m, 1H), 7.60-7.57 (m, 1H), 7.54-7.50 (m, 1H), 5.64 (dd, *J* = 7.6, 5.2 Hz, 1H), 3.90-3.84 (m, 1H), 3.77-3.70 (m, 1H), 2.55-2.43 (m, 1H), 2.17-2.04 (m, 2H), 2.07-1.94 (m, 2H),1.45 (s, 3H), 0.92 (s, 6H).

^{13}C NMR of two rotamers (100 MHz, $CDCl_3$): δ 161.2, 160.8, 155.2, 155.2, 141.8, 136.4, 136.3, 129.6, 127.5, 127.4, 126.9, 126.9, 125.7, 125.5, 124.3, 124.1, 119.8, 119.6, 60.9, 60.4, 58.7, 47.4, 47.0, 33.8, 32.9, 24.1, 23.4, 14.7, 14.2.

MS (EI) m/z: Calcd for $C_{16}H_{18}N_2O_2$: 270.1; Found: 270.1.

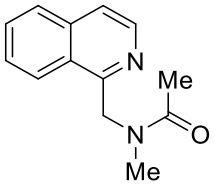


***N*-Boc-2-(isoquinolin-1-yl)pyrrolidine [2244464-38-6]**

Yellow oil 80 mg, 54% yield.

^{1}H NMR of major rotamer (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 5.2 Hz, 1H), 8.23-8.15 (m, 1H), 7.85-7.79 (m, 1H), 7.69-7.62 (m, 1H), 7.60-7.57 (m, 1H), 7.54-7.50 (m, 1H), 5.64 (dd, *J* = 7.6, 5.2 Hz, 1H), 3.90-3.84 (m, 1H), 3.77-3.70 (m, 1H), 2.55-2.43 (m, 1H), 2.17-2.04 (m, 2H), 2.07-1.94 (m, 2H),1.45 (s, 3H), 0.92 (s, 6H).

^{13}C NMR of two rotamers (100 MHz, $CDCl_3$): δ 162.1, 161.0, 154.6, 154.3, 141.7, 1141.7, 136.4, 136.2, 129.6, 127.5, 126.9, 125.6, 124.3, 124.0, 119.8, 119.5, 79.2, 78.7, 59.5, 58.6, 47.3, 47.1, 33.9, 32.9, 28.5, 28.0, 27.9, 24.0, 23.8.



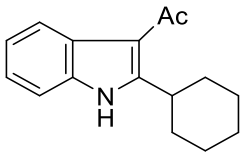
***N*-(1-Isoquinolyl)methyl-*N*-methylacetamide [2055127-13-2]**

Yellow oil, 106 mg, 91% yield.

^{1}H NMR of major rotamer (400 MHz, $CDCl_3$): δ 8.44 (d, *J* = 6.0 Hz, 1H), 8.35 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.69-7.65 (m, 1H), 7.62-7.58 (m, 2H), 5.22 (s, 2H), 2.95 (s, 3H), 2.15 (s, 3H).

^{13}C NMR of two rotamers (100 MHz, $CDCl_3$): δ 170.4, 156.5, 141.5, 142.2, 136.3, 136.1, 130.2, 130.1, 127.7, 127.5, 127.1, 126.8, 125.4, 126.1, 123.1, 120.7, 120.3, 50.3, 53.3, 35.4, 34.4, 21.8, 21.5.

MS (EI) m/z: Calcd for $C_{13}H_{14}N_2O$: 214.1; Found: 214.1.



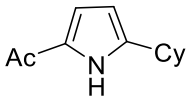
3-Acetyl-2-cyclohexylindole [1801761-20-5]

White solid, 70 mg, 50% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (br s, NH), 7.95 (d, *J* = 7.6 Hz, 1H), 7.39-7.37 (m, 1H), 7.27-7.20 (m, 2H), 3.78 (tt, *J* = 11.8, 3.0 Hz, 1H), 2.70 (s, 3H), 2.09 (d, *J* = 12.0 Hz, 2H), 1.90-1.87 (m, 2H), 1.84-1.80 (m, 1H), 1.58-1.51 (m, 1H), 1.49-1.37 (m, 2H), 1.34-1.22 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 194.8, 152.8, 134.5, 126.9, 122.2, 121.9, 120.8, 113.0, 36.7, 32.3, 31.7.4, 26.4, 26.1.

MS (EI) m/z: Calcd for $C_{16}H_{19}NO$: 241.1; Found: 241.1.



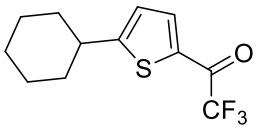
2-Acetyl-5-cyclohexylpyrrole.

Colorless oil, 28.7 mg, 30%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.03 (s, 1H), 6.84 (dd, *J* = 3.6, 2.8 Hz, 1H), 6.02-6.00 (m, 1H), 2.63-2.57 (m, 1H), 2.39 (s, 3H), 2.00-1.96 (m, 2H), 1.86-1.80 (m, 2H), 1.76-1.72 (m, 1H), 1.42-1.35 (m, 4H), 1.28-1.25 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 187.1, 145.7, 130.7, 117.5, 106.7, 36.9, 32.7, 26.1, 25.9, 25.0.

MS (EI) m/z: Calcd for $C_{12}H_{18}N_2$: 191.1; Found: 191.2.



2-Cyclohexyl-5-trifluoroacetylthiophene [2006336-68-9]

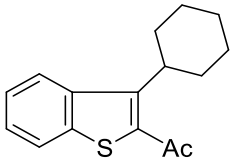
Colorless oil, 79 mg, 60% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 2.0 Hz, 1H), 6.96 (d, J = 4.0 Hz, 1H), 2.89 (td, J = 11.0, 3.1 Hz, 1H), 2.08 (d, J = 10.8 Hz, 2H), 1.87 (dd, J = 9.8, 2.6 Hz, 2H), 1.77 (d, J = 12.4 Hz, 1H), 1.53-1.38 (m, 4H), 1.33-1.23 (m, 1H).

^{19}F NMR (377 MHz, $CDCl_3$): δ 71.99 (s).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.2 (q, J_{CF} = 36.0 Hz), 167.4, 137.0 (q, J_{CF} = 3.0 Hz), 116.6 (q, J_{CF} = 288.7 Hz), 40.3, 35.0, 26.2, 25.6.

MS (EI) m/z: Calcd for $C_{12}H_{13}F_3OS$:262.1; Found: 262.1.



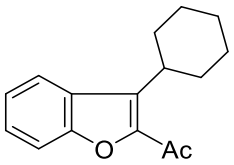
2-Acetyl-3-cyclohexylbenzothiophene [1801761-05-6]

Colorless oil, 98 mg, 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, J = 8.4 Hz, 1H), 7.84(d, J = 8.0, 1H), 7.47-7.43 (m, 1H), 7.41-7.37 (m, 1H), 4.06 (tt, J = 12.6, 3.3 Hz, 1H), 2.65 (s, 3H), 2.17-2.08 (m, 2H), 1.90 (d, J = 12.8 Hz, 2H), 1.85-1.78 (m, 3H), 1.54-1.39 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 193.7, 148.3, 140.4, 139.2, 134.9, 126.7, 126.3, 124.0, 122.9, 38.9, 31.3, 31.0, 29.7, 27.0, 26.2.

MS (EI) m/z: Calcd for $C_{16}H_{18}OS$:258.1; Found: 258.1.



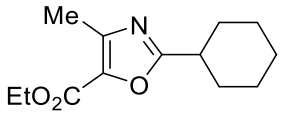
2-Acetyl-3-cyclohexylbenzofuran [1801761-07-8]

White solid, 61 mg, 51% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 8.4 Hz, 1H), 7.46-7.42 (m, 1H), 7.28-7.24 (m, 1H), 3.84-3.76 (m, 1H), 2.62 (s, 3H), 1.92-1.80 (m, 7H), 1.49-1.34 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 191.8, 154.3, 147.0, 133.3, 127.7, 127.6, 123.8, 122.7, 112.4, 35.2, 31.9, 28.3, 26.6, 26.2.

MS (EI) m/z: Calcd for $C_{16}H_{18}O_2$:242.1; Found: 242.1.



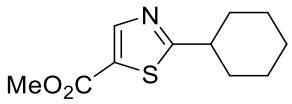
2-Cyclohexyl-5-ethoxycarbonyl-4-methyloxazole [933782-12-8]

Colorless oil, 65 mg, 55% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.47 (q, 7.1 Hz, 2H), 3.39 (t, *J* = 11.2 Hz, 1H), 2.78 (s, 3H), 2.22 (d, *J* = 9.6 Hz, 2H), 1.94-1.78 (m, 5H), 1.51-1.34 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 159.0, 145.7, 136.9, 60.9, 37.7, 30.4, 25.6 (2C), 14.4, 13.3.

MS (EI) m/z: Calcd for $C_{13}H_{19}NO_3$:237.1; Found: 237.1.



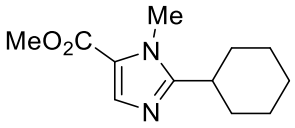
2-Cyclohexyl-5-methoxycarbonylthiazole [1514220-02-0]

White solid, 80 mg, 71% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (s, 1H), 3.89 (s, 3H), 3.01 (tt, *J* = 11.6, 3.6 Hz, 1H), 2.16 (dd, *J* = 13.0, 2.4 Hz, 2H), 1.89-1.84 (m, 2H), 1.79-1.73 (m, 1H), 1.59-1.50 (m, 2H), 1.48-1.37 (m, 2H), 1.34-1.24 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 183.3, 162.0, 148.1, 127.6, 52.3, 43.0, 33.5, 25.9, 25.7.

MS (EI) m/z: Calcd for $C_{16}H_{18}OS$: 225.1; Found: 225.1.



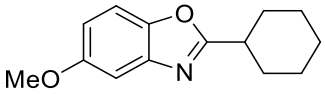
2-Cyclohexyl-5-methoxycarbonyl-1-methylimidazole [2115848-81-0]

Colorless oil, 51 mg, 46% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (s, 1H), 3.86 (s, 3H), 3.83 (s, 3H), 2.72-2.65 (m, 1H), 1.90-1.87 (m, 4H), 1.77-1.63 (m, 4H), 1.37-1.33 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.3, 157.5, 136.5, 122.3, 51.2, 36.0, 31.6, 31.2, 26.2, 25.7.

MS (EI) m/z: Calcd for $C_{12}H_{18}N_2$: 222.1; Found: 222.1.



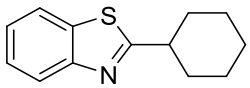
2-Cyclohexyl-5-methoxybenzoxazole [1268121-40-9]

Colorless oil, 88 mg, 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 2.4 Hz, 1H), 6.88 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.84 (s, 3H), 2.93 (tt, *J* = 11.2, 3.6 Hz, 1H), 2.16 (dd, *J* = 13.0, 3.0 Hz, 2H), 1.89-1.84 (m, 2H), 1.76-1.65 (m, 3H), 1.48-1.26 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 157.0, 145.2, 142.1, 112.6, 110.3, 102.9, 55.9, 38.0, 30.5, 25.8, 25.6.

MS (EI) m/z: Calcd for $C_{14}H_{17}NO_2$: 231.1; Found: 231.0.



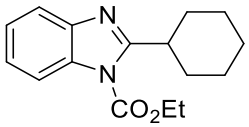
2-Cyclohexylbenzothiazole [40115-03-5]

Colorless oil, 90 mg, 83% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.47-7.43 (m, 1H), 7.37-7.33 (m, 1H), 3.12 (tt, *J* = 11.6, 3.6 Hz, 1H), 2.22 (dd, *J* = 13.2, 1.2 Hz, 2H), 1.93-1.89 (m, 2H), 1.80-1.76 (m, 1H), 1.71-1.61 (m, 2H), 1.52-1.41 (m, 2H), 1.38-1.31 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.6, 153.1, 134.5, 129.5, 125.8, 124.5, 122.6, 121.5, 43.4, 33.4, 26.1, 25.8.

MS (EI) m/z: Calcd for $C_{13}H_{15}NS$: 217.1; Found: 217.0.



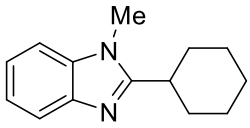
***N*-Ethoxycarbonyl-2-cyclohexylbenzoimidazole [1801760-93-9]**

Colorless oil, 87.1 mg, 64% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 2.4 Hz, 1H), 6.88 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.84 (s, 3H), 2.93 (tt, *J* = 11.2, 3.6 Hz, 1H), 2.16 (dd, *J* = 13.0, 3.0 Hz, 2H), 1.89-1.84 (m, 2H), 1.76-1.65 (m, 3H), 1.48-1.26 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.7, 150.5, 142.3, 132.8, 124.2 (2 overlapping signals), 119.6, 115.0, 63.9, 38.7, 31.9, 26.3, 26.0, 14.2.

MS (EI) m/z: Calcd for $C_{16}H_{20}N_2O_2$: 272.2; Found: 272.2.



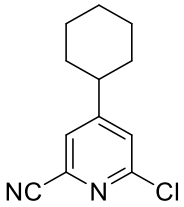
2-Cyclohexyl-1-methylbenzoimidazole [106380-62-5]

White solid, 48.3 mg, 45% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81-7.76 (m, 1H), 7.32-7.28 (m, 1H), 7.28-7.22 (m, 2H), 3.75 (s, 3H), 2.86 (tt, *J* = 11.7, 3.5 Hz, 1H), 2.04-2.00 (m, 2H), 1.96-1.92 (m, 2H), 1.89-1.79 (m, 3H), 1.50-1.36 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9, 142.4, 135.5, 121.9, 121.7, 119.2, 108.8, 36.3, 31.4, 29.5, 26.3, 25.8.

MS (EI) m/z: Calcd for $C_{14}H_{18}N_2$: 214.1; Found: 214.2.



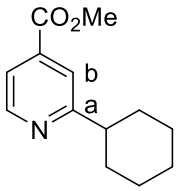
6-Chloro-4-cyclohexylpicolinonitrile [106719-06-6]

White solid, 70 mg, 64% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 3.01 (tt, *J* = 11.8, 2.8 Hz, 1H), 1.96-1.89 (m, 4H), 1.83 (d, *J* = 13.2 Hz, 1H), 1.53-1.42 (m, 2H), 1.38-1.25 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.1, 146.3, 136.5, 130.2, 127.6, 116.2, 40.7, 32.5, 26.4, 25.8.

MS (EI) m/z: Calcd for $C_{12}H_{13}ClN_2$: 220.1; Found: 220.1.



The ratio (a:b = 1.5:1) of two isomers was determined by GC of the crude reaction mixture and confirmed by GCMS and proton NMR spectroscopy. Combined yield 56%

Methyl 2-cyclohexylisonicotinate [137655-83-5]

Colorless oil, 38.2 mg, 35% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (d, *J* = 1.2 Hz, 1H), 7.72 (s, 1H), 7.64 (d, *J* = 4.4 Hz, 1H), 3.94 (s, 3H), 2.79 (t, *J* = 12.0 Hz, 1H), 1.96 (d, *J* = 12.8 Hz, 2H), 1.88-1.84 (m, 2H), 1.78-1.73 (m, 1H), 1.54 (ψqd, *J* = 12.2, 2.9 Hz, 2H), 1.46-1.36 (m, 2H), 1.30 (ψtt, *J* = 12.6, 3.3 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 166.2, 150.0, 137.8, 120.5, 120.3, 52.7, 46.7, 33.0, 26.6, 26.1.

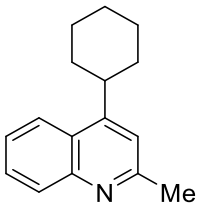
Methyl 3-cyclohexylisonicotinate [2113960-93-1]

Colorless oil, 22.8 mg, 21% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (s, 1H), 8.52 (d, *J* = 5.1 Hz, 1H), 7.52 (d, *J* = 5.0 Hz, 1H), 3.93 (s, 3H), 3.21 (ψtt, *J* = 11.8, 3.1 Hz, 1H), 1.90-1.84 (m, 4H), 1.79-1.74 (m, 1H), 1.55-1.35 (m, 4H), 1.33-1.25 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 149.8, 147.4, 141.7, 137.1, 122.8, 52.6, 39.0, 34.1, 27.0, 26.2.

MS (EI) m/z: Calcd for $C_{13}H_{17}NO_2$: 219.1; Found: 219.2.



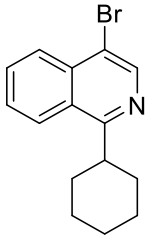
4-Cyclohexyl-2-methylquinoline [37597-46-9]

Colorless oil, 93.6 mg, 83% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05-8.04 (m, 1H), 8.03-8.02 (m, 1H), 7.68-7.63 (m, 1H), 7.51-7.47 (m, 1H), 7.18 (s, 1H), 3.33-3.27 (m, 1H), 2.73 (s, 3H), 2.03-2.01 (m, 2H), 1.96-1.93 (m, 2H), 1.40-1.33 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 153.3, 148.2, 129.6, 128.7, 125.2 (2 overlapping signals), 122.8, 119.3, 38.8, 33.6, 26.9, 26.3, 25.5.

MS (EI) m/z: Calcd for $C_{16}H_{19}N$: 225.1; Found: 225.1.



4-Bromo-1-cyclohexylisoquinoline [1809217-60-4]

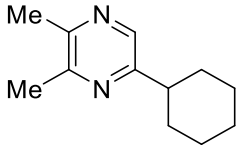
White solid, 94 mg, 65% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (s, 1H), 8.24-8.19 (m, 2H), 7.79-7.75 (m, 1H), 7.87-7.83 (m, 1H), 3.56-3.49 (m,

1H), 1.99-1.92 (m, 4H), 1.86-1.76 (m, 3H), 1.59-1.48 (m, 2H), 1.44-1.33 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 143.7, 134.9, 130.8, 127.7, 127.6, 126.9, 125.1, 117.5, 41.5, 32.5, 26.8, 26.2.

MS (EI) m/z: Calcd for $C_{15}H_{16}NBr$: 290.0; Found: 290.1.



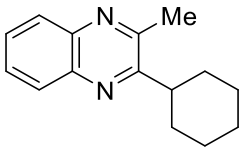
5-Cyclohexyl-2,3-dimethylpyrazine [73570-41-9]

Colorless oil, 66.5 mg, 70% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (s, 1H), 2.65 (tt, *J* = 11.8, 3.3 Hz, 1H), 2.50 (s, 3H), 2.48 (s, 3H), 1.93-1.90 (m, 2H), 1.87-1.82 (m, 2H), 1.77-1.71 (m, 1H), 1.57-1.47 (m, 2H), 1.45-1.34 (m, 2H), 1.33-1.25 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.8, 151.1, 149.2, 139.0, 43.8, 32.6, 26.4, 25.9, 21.6.

MS (EI) m/z: Calcd for $C_{12}H_{18}N_2$: 190.1; Found: 190.1.



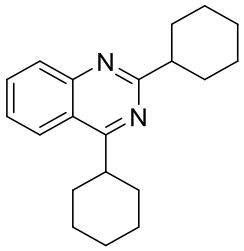
2-Cyclohexyl-3-methylquinoxaline [1466541-52-5]

White solid, 80 mg, 71% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04-8.00 (m, 1H), 7.98-7.94 (m, 1H), 7.67-7.63 (m, 2H), 3.05 (tt, *J* = 11.6, 3.2 Hz, 1H), 2.80 (s, 3H), 1.96-1.91 (m, 4H), 1.83-1.74 (m, 3H), 1.53-1.37 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 152.6, 141.4, 140.6, 128.7, 128.6, 128.5, 128.2, 42.6, 31.6, 26.6, 26.0, 22.7.

MS (EI) m/z: Calcd for $C_{15}H_{18}N_2$: 226.1; Found: 226.0.



2,4-Dicyclohexylbenzopyrimidine [1466541-56-9]

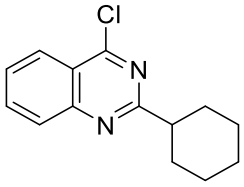
Benzopyrimidine (0.25 mmol), cyclohexane (10 equiv, 2.5 mmol) and TBPB (4 equiv, 1.0 mmol) were used. Colorless

oil, 52 mg, 71% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.81-7.77 (m, 1H), 7.54-7.50 (m, 1H), 3.51 (tt, *J* = 11.0, 2.8 Hz, 1H), 2.99 (tt, *J* = 11.8, 3.4 Hz, 1H), 2.08-2.05 (m, 2H), 1.96-1.77 (m, 12H), 1.54-1.34 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 174.4, 170.2, 150.6, 132.6, 128.9, 126.0, 123.9, 121.4, 47.9, 41.3, 32.0, 31.9, 26.5, 26.3, 26.2, 26.1.

MS (EI) m/z: Calcd for $C_{20}H_{26}N_2$: 294.2; Found: 294.2.



4-Chloro-2-cyclohexylquinazoline [284486-58-4]

White solid, 82 mg, 67% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, *J* = 8.0 Hz, 1H), 7.77 (ψt, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.47 (ψt, *J* = 7.4 Hz, 1H), 2.75-2.67 (m, 1H), 2.07 (d, *J* = 11.6 Hz, 2H), 1.94 (d, *J* = 12.8 Hz, 2H), 1.83-1.78 (m, 1H), 1.74-1.69 (m, 2H), 1.51-1.36 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.3, 160.2, 149.6, 134.6, 127.4, 126.2 (2C), 120.8, 44.8, 30.5, 26.0, 25.7.

MS (EI) m/z: Calcd for $C_{14}H_{15}ClN_2$: 246.1; Found: 246.0.

IV. Oxidative alkylation of heteroarenes using 1.5 equiv of alkanes

A typical procedure under LED irradiation: in an argon-filled glove box, a 10 mL Schlenk tube or 10 mL Pyrex tube containing a magnetic stir bar was charged with heteroarene (0.5 mmol), *t*-butyl peroxybenzoate (1.0 mmol), alkane (0.75 mmol) and *9,10-dichloroanthracene* DCA (2.5 mg, 0.01 mmol). The tube was capped tightly and the reaction mixture was vigorously stirred at ~40 °C (with fan cooling) for 24 hours under close irradiation of 40 W blue LED lamp (Kessil A160WE Tuna Blue. Setting: maximal light intensity and maximal spectral width/color. Position: ~1 cm away from the side of the tube). At the end of the reaction, 1 mL of dilute aq $NaHCO_3$ was added, the reaction mixture was extracted with DCM (3 x 3 mL). The filtrate was dried over anhydrous Na_2SO_4 and concentrated in vacuo. 1,3,5-$(MeO)_3C_6H_3$ (0.1 mmol) was added to determine the conversion and NMR yields in the crude products. The crude product was purified by flash column chromatography over silica gel with hexanes/EA 10: 1 to obtain the desired product. The ratios of isomers of crude samples were determined by proton NMR spectrometry and

confirmed by GCMS. For the dialkylation of benzopyrimidine (0.5 mmol), *t*-butyl peroxybenzoate (4 equiv, 2.0 mmol), alkane (3 equiv, 1.5 mmol) and *9,10-dichloroanthracene* DCA (5 mg, 0.02 mmol) were used (24 h). The characterization of all the isolated products are described above.

V. Mechanistic studies

A typical procedure under LED irradiation: in an argon-filled glove box, a 10-mL Schlenk tube containing a magnetic stir bar was charged with isoquinoline (59 uL, 0.5 mmol), TBPB (1.0 mmol) and cyclohexane (275 uL, 2.5 mmol). The tube was capped tightly and the reaction mixture was vigorously at 30-35 °C (with fan cooling) under 40 W blue LED (Kessil A160WE Tuna Blue) for heating for 24 hours. At the end of the reaction, NMR standard 1,3,5-trimethoxybenzene (0.2 mmol) and 0.5 mL of chloroform-*d* were added down the wall of the tube. After mixing, an aliquot was taken and diluted in an NMR tube to 0.6 mL for acquisition of crude NMR spectra. Calibrated NMR yields were calculated based on integration of signals of interest versus the standard. A complex black mixture of cyclohexylated oligo(isoquinoline)s **6** were isolated via silica gel chromatography (eluted with MeOH/DCM).

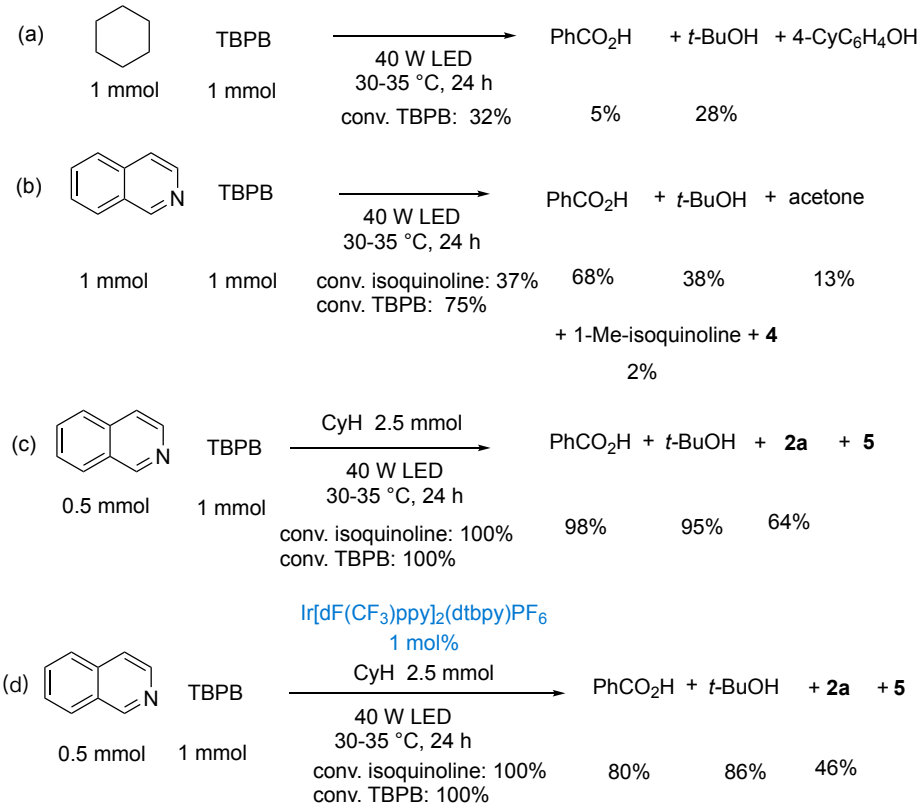


Fig S1 Mechanistic studies

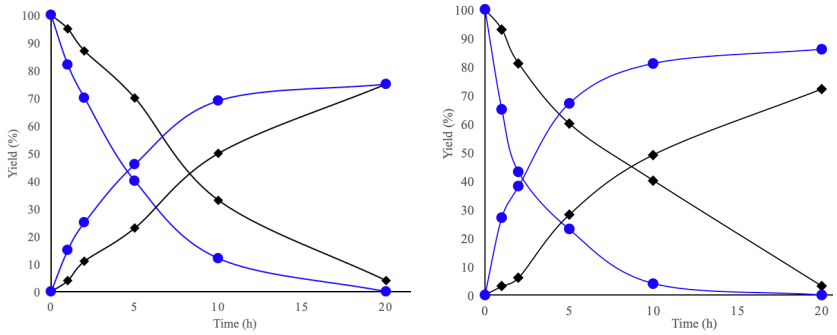


Fig S2 Kinetics of oxidative coupling of isoquinoline (0.5 mmol), cyclohexanes (2.5 mmol) and TBPB (1.0 mmol) to produce **2a** (conversions and yields) in the absence (black) and presence of a photocatalyst (blue): (a) **5** (10 mg at 35-40 °C) and (b) 9,10-dichloroanthrocene (2 mol% at 40 °C).

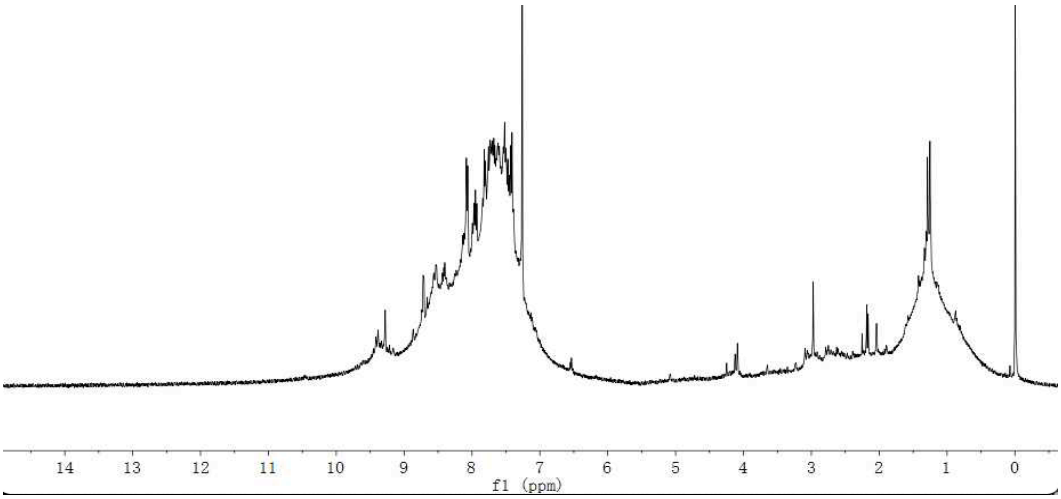


Fig S3. ^{1}H NMR spectrum of isolated black polar fractions (tBuO)(isoquinolyl)n **4** ($CDCl_3$, 400 MHz)

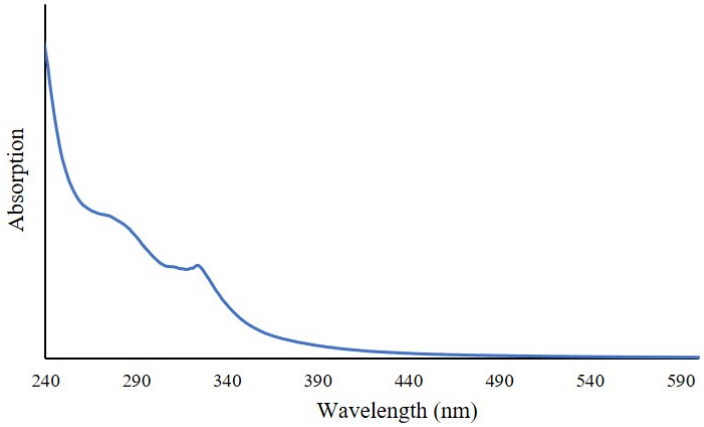


Fig S4. UV-vis absorption spectrum of isolated black polar fractions (*t*-BuO)(isoquinolyl)n **4** in dichloromethane

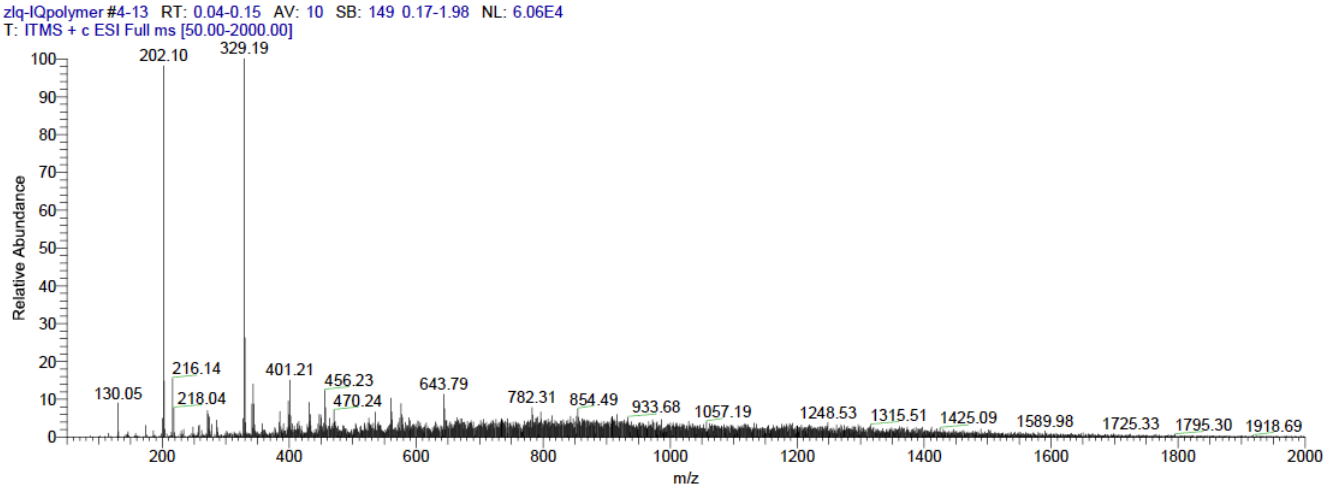


Fig S5. ESI-MS of isolated black polar fractions (tBuO)(isoquinolyl)n **4** (m/z 202 n= 1; m/z 329 n=2; m/z 456 n = 3)

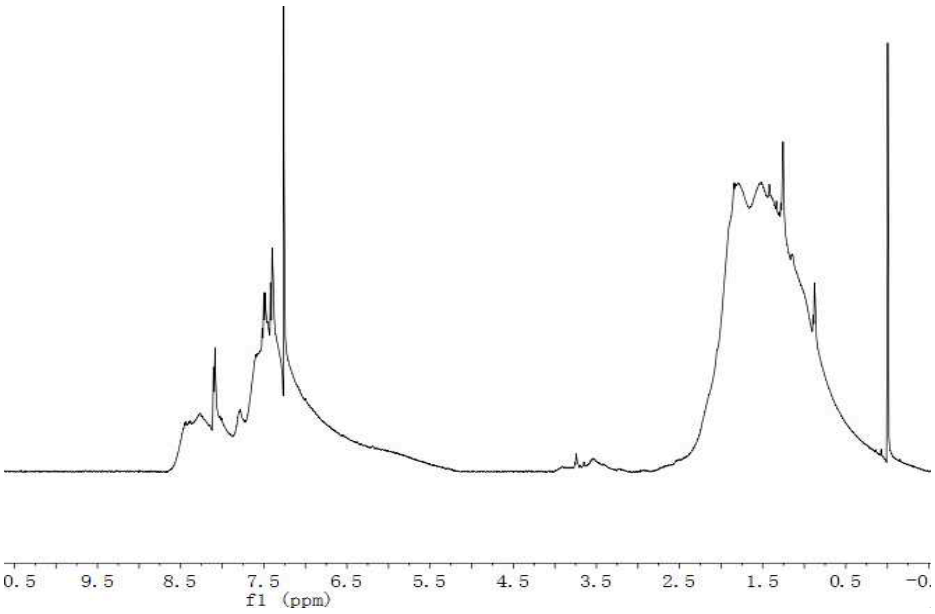


Fig S6. ^{1}H NMR spectrum of isolated black polar fractions $(isoquinolyl)_m(Cy)_n$ **5** ($CDCl_3$, 400 MHz)

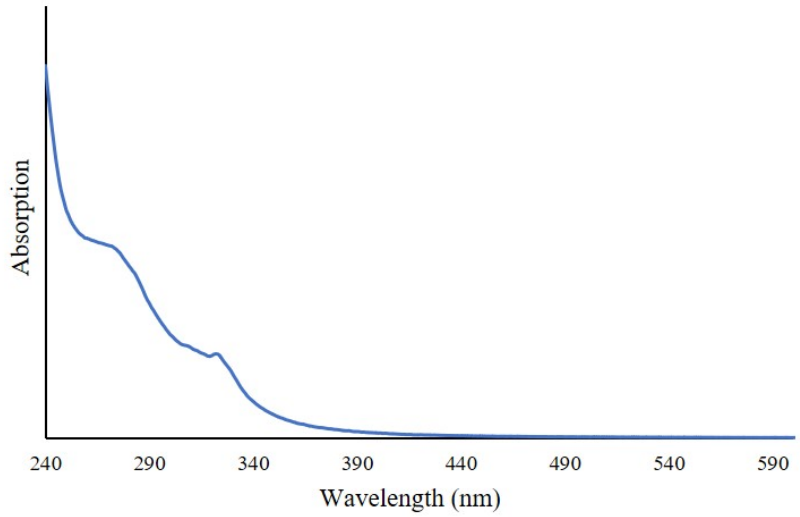


Fig S7. UV-vis absorption spectrum of isolated black polar fractions $(isoquinolyl)_m(Cy)_n$ **5** in dichloromethane

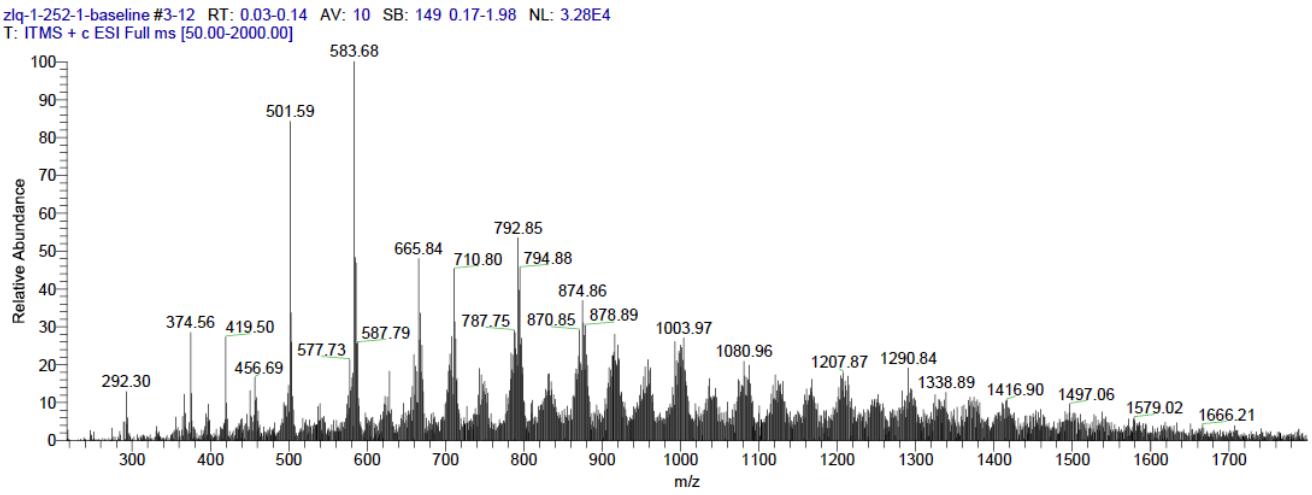
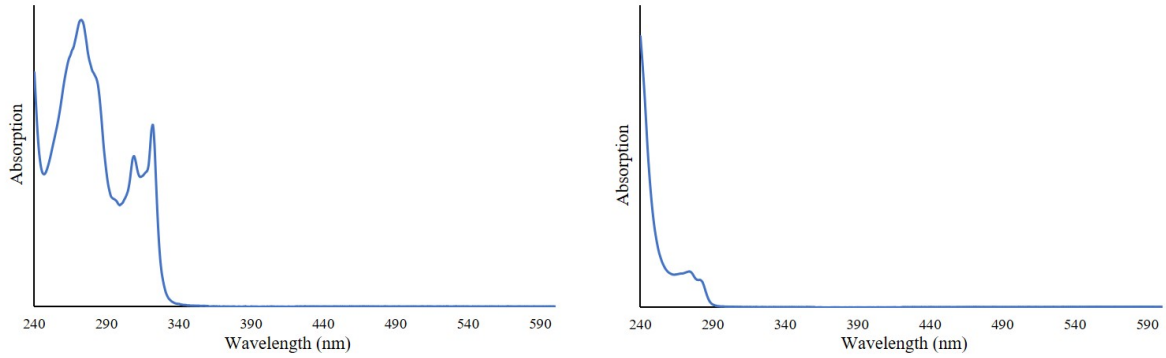


Fig S8. ESI-MS of isolated black polar fractions **5** $(isoquinolyl)_m(Cy)_n$ (m/z 292 m=1 n=2; m/z 374 m=2 n=2; m/z 501: m=2 n=3; m/z 583 m =2 n=4, m/z 666 m =2 n=5; m/z 711 m =3 n=4, etc)



(a) (b)

Fig S9. UV-vis absorption spectra of (a) 2-cyclohexylbenzoxazole **2a** and (b) *t*-butyl peroxybenzoate in dichloromethane

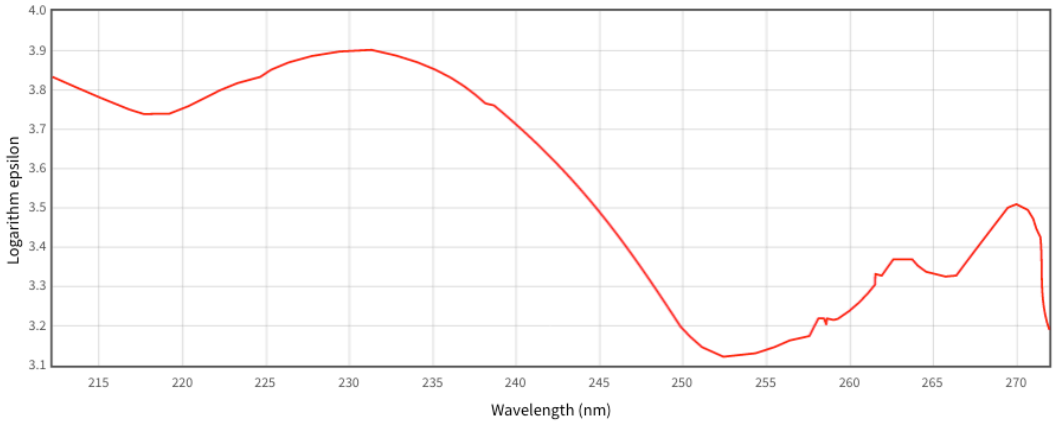


Fig S10. UV-vis absorption spectrum of benzoxazole (source: https://webbook.nist.gov/chemistry)

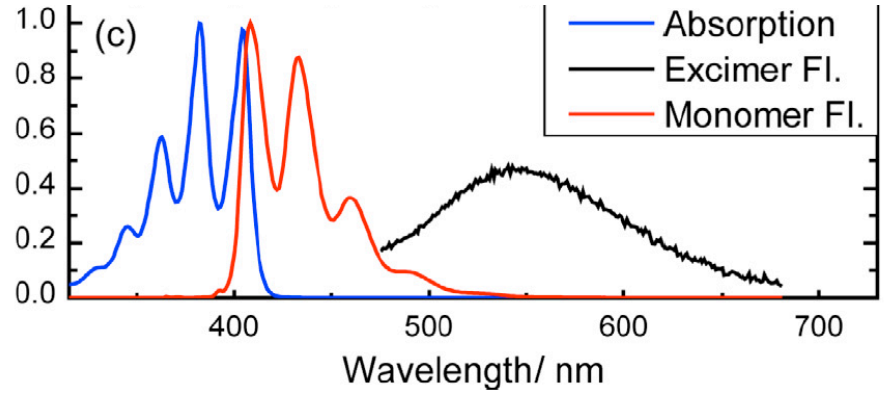


Fig S11. Steady state absorption (blue) and fluorescence emission (red) spectra of 9,10-dichloroanthracene in a dilute solution in benzene and the excimer spectrum (Source: F. J. Lederer et al. *Chem. Phys.*, 2014, **428**, 82)

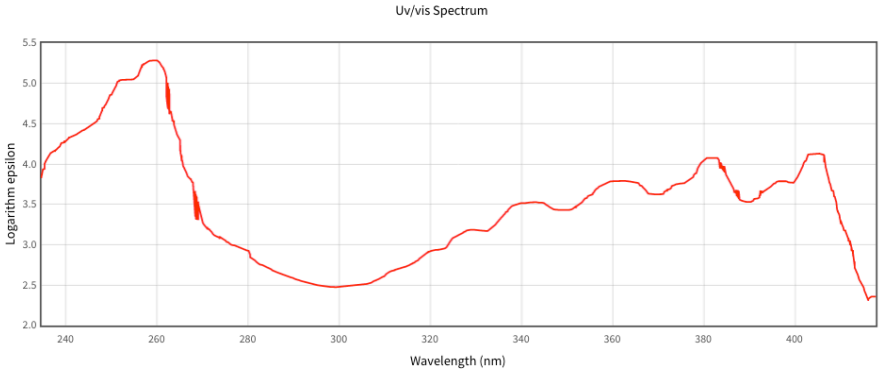


Fig S12. UV-vis absorption spectrum of 9,10-dichloroanthracene in benzene (source: https://webbook.nist.gov/chemistry)

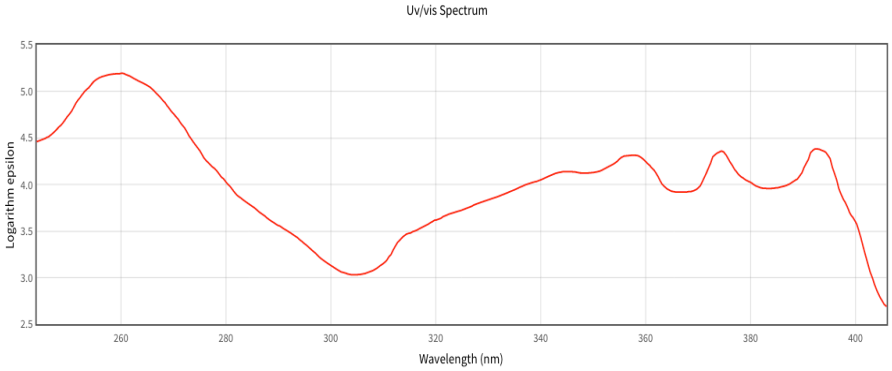


Fig S13. UV-vis absorption spectrum of 9,10-diphenylanthracene in benzene (source: https://webbook.nist.gov/chemistry)

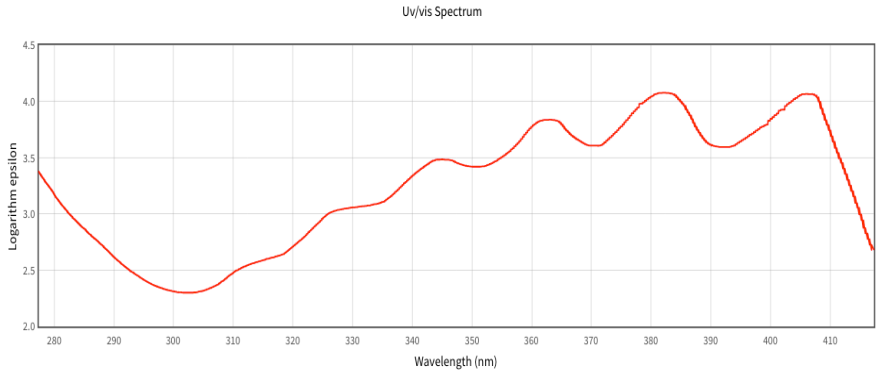
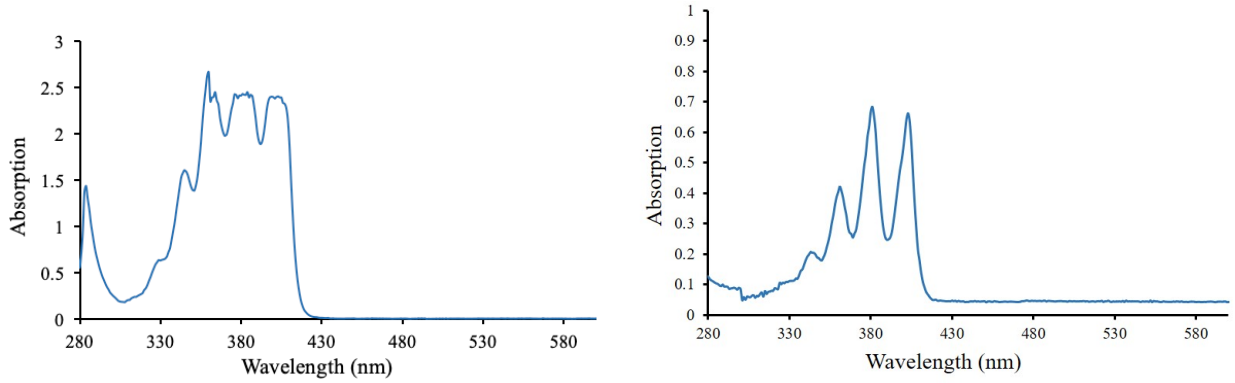
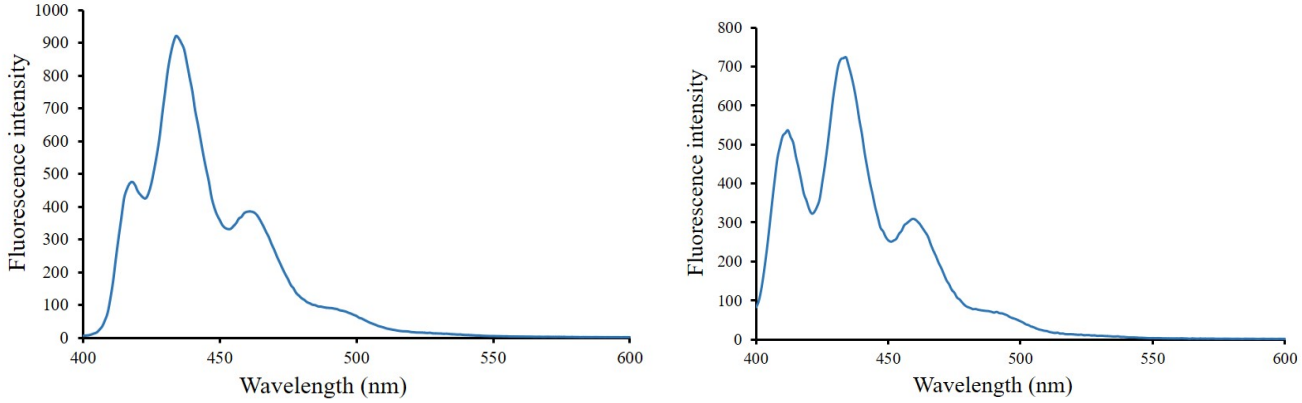


Fig S14. UV-vis absorption spectrum of 9,10-dibromoanthracene in benzene (source: https://webbook.nist.gov/chemistry)



(a) (b)

Fig S15. UV-vis absorption spectra of 9,10-dichloroanthracene (0.5 mM) in (a) toluene and (b) dichloromethane



(a) (b)

Fig S16. Emission spectra of 9,10-dichloroanthracene (0.5 mM) excited at 360 nm in (a) toluene and (b) dichloromethane

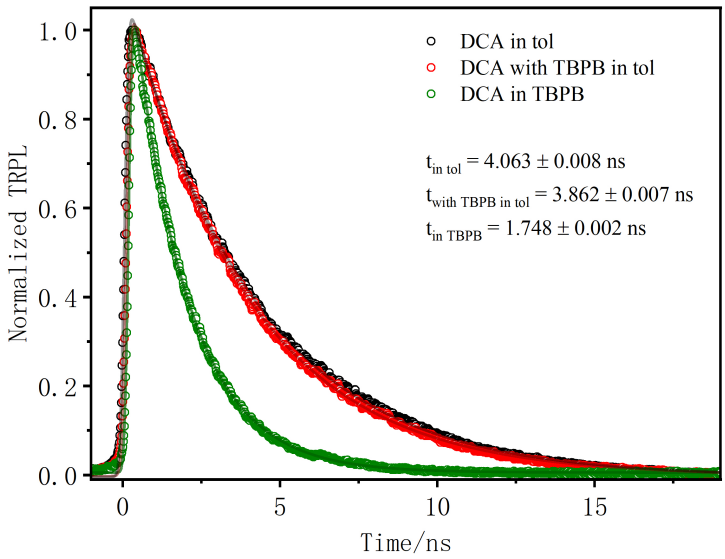


Fig S17. Time-resolved photoluminescence (TRPL) spectra of 9,10-dichloroanthracene (DCA, 0.5 mM) recorded at excitation wavelength of 360 nm in toluene (black), DCA (0.5 mM) and TBPB (100 equiv) in toluene (red), and DCA (1 mM) in neat TBPB (green).