Supporting Information

Photo-Induced 1,2-Alkylarylation/Cyclization of Alkenes, Alkyl Halides and *N*-Alkylindoles via an EDA-Complex

Tao Ju*, Min Ge, Li-Hang Ren, Ai-Ling Lu, Zhi-Hao Wang, Shi-Ji He, Jing Sun, Ying Han, and Chao-Guo Yan*

School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 250002, P. R. China.

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1. General information

All reactions were carried out under a nitrogen atmosphere in Schlenk tubes. Anhydrous solvent (including DCM, 99.9%, Water< 30 ppm) were purchased from Adamas, and used as received. Commercially available compounds were obtained from Adamas, Bidepharm, Energy Chemical and used as received unless otherwise stated.

¹H NMR and proton-decoupled ¹³C NMR were recorded on Agilent 400-MR DD2 (400 MHz) spectrometers at ambient temperature (¹H: 400 MHz, ¹³C: 101 MHz). ¹H NMR, ¹³C NMR and ¹⁹F NMR were recorded on Bruker AVANCE III (600 MHz) spectrometers at ambient temperature (¹H: 600 MHz, ¹³C: 151 MHz, ¹⁹F: 564 MHz). Chemical shifts (δ) for ¹H and ¹³C NMR spectra are given in ppm relative to TMS (δ = 0.00 ppm), and the residual solvent signals were used as references for ¹H and ¹³C NMR spectra and the chemical shifts converted to the TMS scale (CDCl₃: δ H = 7.26 ppm, δ C = 77.16 ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad.

TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm. High-resolution mass spectra were recorded on a Bruker maXis instrument using ESI technique. The UV-Vis spectrum (UV-Vis) was determined by Shimadzu UV2550. X-ray data was collected with a Bruker Smart Apex II diffractometer with MoKα radiation.

2. Additional reaction optimization tables

Ph Br +	Ph Ph +		Base (2 equiv) Zn(OAc) ₂ (3 equiv) DCM, blue LEDs, rt, 48 h	PhPh
1a	2a	3a		4a
Entry		Ba	ase	4a/Yield
1		K ₂ H	90	
2		Nał	80	
3		K ₃	79	
4		KH	36	
5		КС	61	
6		D	<10	

Table S1. Screening of bases

Reaction conditions: **1a** (0.4 mmol, 2.0 equiv), **2a** (0.6 mmol, 3.0 equiv), **3a** (0.2 mmol), base (0.4 mmol, 2.0 equiv), $Zn(OAc)_2$ (0.6 mmol, 3.0 equiv) in 2 mL DCM under N₂ atmosphere, 30 W blue LEDs, room temperature (rt, about 40 °C), 48 h. DCM = Dichloromethane.

Table S2. Screening of solvents

Ph∕→Br + 1a	Ph Ph 2a	+ (), 3a	K ₂ HPO ₄ (2 equiv) Zn(OAc) ₂ (3 equiv) Solvent, blue LEDs, rt, 48 h	Ph Ph Ph Ph Ph 4a
Entry		Solvent		4a/Yield
1		DCM		90
2		DCE		88
3		MeCN		39
4			N.D.	

Reaction conditions: **1a** (0.4 mmol, 2.0 equiv), **2a** (0.6 mmol, 3.0 equiv), **3a** (0.2 mmol), K_2 HPO₄ (0.4 mmol, 2.0 equiv), Zn(OAc)₂ (0.6 mmol, 3.0 equiv) in 2 mL solvent under N₂ atmosphere, 30 W blue LEDs, rt (about 40 °C), 48 h. DCE = Dichloroethane, DMF = *N*,*N*-Dimethylformamide.

Table S3. Screening of lewis acids

Ph Br +	Ph Ph 2a	+ , N	K ₂ HPO ₄ (2 equiv) Lewis acid (3 equiv) DCM, blue LEDs, rt, 48 h	Ph Ph Ph 4a
Entry		Lev	vis acid	4a/Yield
1		Zn(OAc) ₂		90
2		ZnCl ₂		42
3		FeCl₃		24
4		(CuCl	trace

Reaction conditions: **1a** (0.4 mmol, 2.0 equiv), **2a** (0.6 mmol, 3.0 equiv), **3a** (0.2 mmol), K_2HPO_4 (0.4 mmol, 2.0 equiv), Lewis acid (0.6 mmol, 3.0 equiv) in 2 mL DCM under N₂ atmosphere, 30 W blue LEDs, rt (about 40 °C), 48 h.

Table S4. Screening of equivs

Ph Br +	Ph Ph 2a	+ , N	K ₂ HPO ₄ (2 equiv) Zn(OAc) ₂ (x equiv) DCM, blue LEDs, rt, 48 h	Ph Ph Ph Ph 4a
Entry		Zn(OA	c) ₂ (x equiv)	4a/Yield
1		3	equiv	90
2		4	80	
3		2 equiv		82
4		1	80	
5		0.9	5 equiv	78

Reaction conditions: **1a** (0.4 mmol, 2.0 equiv), **2a** (0.6 mmol, 3.0 equiv), **3a** (0.2 mmol), K₂HPO₄ (0.4 mmol, 2.0 equiv), Zn(OAc)₂ (2x mmol, x equiv) in 2 mL DCM under N₂ atmosphere, 30 W blue LEDs, rt (about 40 °C), 48 h.

3 Synthesis of starting materials

3.1 Synthesis of alkenes 2

The alkenes 2 in **Table 3** were prepared according to the Wittig reaction.

Note: Ketone: *n*-BuLi^[1] (2a, 2b, 2c, 2d, 2g, 2h, 2k, 2l, 2m, 2n) or KO'Bu^[2] (2e, 2f, 2i, 2j) as a strong base.

General procedures A:

To a stirred solution of Ph_3PCH_3Br (1.2 equiv) in THF (0.30 M) at 0 °C was added *n*-BuLi (1.2 equiv). The reaction mixture was stirred for 2.5 hours at room temperature. Ketone (20 mmol) in THF (10 mL) was added dropwise to the cooled reaction mixture at 0 °C. The reaction was then stirred at room temperature for 12 h, and then quenched with saturated NH₄Cl (40 mL), diluted with water (30 mL) and extracted with EtOAc (3 x 30 mL). The combined organic extracts were washed with brine (2 x 30 mL), dried over Na₂SO₄ and concentrated under reduced pressure. The product was isolated by flash column chromatography (eluent: PE).

General procedures B:



 Ph_3PCH_3Br (2.0 equiv) was added to a flame-dried round-bottom flask, evacuated, backfilled with N₂ three times, and suspended in THF (0.30 M). To this vigorously stirring heterogeneous solution was added KO'Bu (2.0 equiv), and the reaction was allowed to stirred at room temperature for 15 min until a bright yellow heterogeneous mixture was achieved. The resulting solution was cooled to 0 °C, and the ketone (20 mmol) was added slowly. Upon complete addition, the cooling bath was removed, and the reaction was allowed to stir for 12 h, and then quenched with saturated NH_4CI (40 mL), diluted with water (30 mL) and extracted with EtOAc (3 x 30 mL). The combinedorganic extracts were washed with brine (2 x 30 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The product was isolated by flash column chromatography (eluent: PE).

3.2 Synthesis of N-alkyl indoles 3

The N-alkyl indoles 3 in Table 3 were prepared according to the general procedure.^[3]

General Procedure:



To a well-stirred solution of indole derivatives (10 mmol) in DMF (20 mL) at 0 °C was added sodium hydride (60% in mineral oil, 16 mmol, 1.6 equiv). The reaction was warmed to room temperature and allowed to stir for 30 min. After 30 min, the reaction flask was cooled again to 0 °C and alkyl iodides (12 mmol, 1.2 equiv) was

added dropwise. The reaction mixture was warmed to room temperature and allowed to stir untill the reaction completed (monitored by TLC) and then cooled to 0 °C and quenched with saturated aqueous NH_4CI . The product was extracted with diethyl ether (3 x 20 mL) and dried over anhydrous Na_2SO_4 . The organic phase was concentrated in vacuum to obtain the crude mixture which was further purified by column chromatography (eluent: PE/EA = 30 : 1).

4. Experimental procedures and characterization data

General procedure for the synthesis of 4a-4t, 5a-5o and 6a-6m:

An oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with K_2HPO_4 (69.7 mg, 0.4 mmol, 2 equiv) and Zn(OAc)₂ (110.1 mg, 0.6 mmol, 3 equiv). The tube was then connected to a vacuum line where it was evacuated and back-filled with N₂ for 3 times. Then DCM (2 mL), benzyl halides (0.4 mmol, 2 equiv), alkenes (0.6 mmol, 3 equiv) and indoles (0.2 mmol, 1 equiv) were added under N₂ flow. Finally, the reaction mixture in sealed tube was placed in water bath and irradiated with a 30 W blue LED lamp (1 ~ 2 cm away, with cooling fan to keep the reaction temperature at 40~45 °C) for 48 hours (wavelength: 460 nm). Then, the mixture was quenched with 2 mL of H₂O, extracted with AcOEt, then concentrated in vacuo. The residue was purified by silica gel flash chromatography (petroleum ether/dichloromethane $30/1 \sim 3/1$) to give the pure desired product.



Figure S1. Blue LED Photoreactor

1-methyl-3-(1,1,3-triphenylpropyl)-1H-indole (4a)



72.3 mg, 0.180 mmol, 90%;

Pure white solid;

R_f(PE/DCM 10/1): 0.26;

¹**H NMR** (400 MHz, CDCl₃) δ 7.43 (d, *J* = 7.4 Hz, 4H), 7.30 – 7.26 (m, 3H), 7.26 – 7.21 (m, 4H), 7.21 – 7.15 (m, 4H), 7.15 – 7.05 (m, 3H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.73 (s, 1H), 3.74 (s, 3H), 3.01 – 2.93 (m, 2H), 2.45 – 2.37 (m, 2H);

¹³**C NMR** (101 MHz, CDCl₃) δ 147.15, 142.98, 137.70, 128.99, 128.67, 128.35, 128.27, 127.85, 127.02, 125.79, 125.68, 122.32, 121.30, 120.72, 118.56, 109.21, 52.25, 42.33, 32.79, 32.56;

Exact Mass ESI-MS: calculated m/z for [C₃₀H₂₇NNa]⁺: 424.2036, found: 424.2040.

3-(1,1-diphenyl-3-(p-tolyl)propyl)-1-methyl-1*H*-indole (4b)

70.6 mg, 0.170 mmol, 85%;

Pure white solid;

R_f (PE/DCM 5/1): 0.32;

¹**H NMR** (600 MHz, CDCl₃) δ 7.42 (d, *J* = 7.4 Hz, 4H), 7.30 – 7.22 (m, 6H), 7.18 – 7.13 (m, 4H), 7.05 (d, *J* = 7.8 Hz, 2H), 6.99 (d, *J* = 7.9 Hz, 2H), 6.91 (t, *J* = 7.2 Hz, 1H), 3.73 (s, 3H), 2.97 – 2.92 (m, 2H), 2.39 – 2.35 (m, 2H), 2.29 (s, 3H);

¹³C NMR (151 MHz, CDCl₃) δ 147.30, 139.99, 137.81, 135.19, 129.13, 129.06, 128.79, 128.24, 127.92, 127.14, 125.86, 122.43, 121.37, 120.90, 118.64, 109.28, 52.36, 42.63, 32.83, 32.17, 21.10; Exact Mass ESI-MS: calculated m/z for [C₃₁H₂₉NNa]⁺: 438.2192, found: 438.2195.

3-(3-([1,1'-biphenyl]-4-yl)-1,1-diphenylpropyl)-1-methyl-1H-indole (4c)



69.5 mg, 0.146 mmol, 73%; Pure white solid;

R_f(PE/DCM 6/1): 0.22;

¹**H NMR** (400 MHz, CDCl₃) δ 7.56 (d, *J* = 7.5 Hz, 2H), 7.52 – 7.34 (m, 8H), 7.33 – 7.24 (m, 6H), 7.22 – 7.07 (m, 6H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.75 (s, 1H), 3.74 (s, 3H), 3.05 - 2.96 (m, 2H), 2.50 - 2.41 (m, 2H); ¹³**C NMR** (101 MHz, CDCl₃) δ 147.17, 142.14, 141.13, 138.69, 137.74, 129.07, 128.75, 128.73, 128.70, 127.92, 127.12, 127.02, 125.86, 122.35, 121.36, 120.70, 118.63, 109.28, 52.31, 42.27, 32.82, 32.23; **Exact Mass ESI-MS:** calculated m/z for [C₃₆H₃₁Na]⁺: 500.2349, found: 500.2346.

1-methyl-3-(3-(4-nitrophenyl)-1,1-diphenylpropyl)-1H-indole (4d)

61.2 mg, 0.137 mmol, 69%;

Ph Ph

R_f (PE/EA 20/1): 0.24;

Pale yellow solid;

¹**H NMR** (400 MHz, CDCl₃) δ 8.06 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 7.5 Hz, 4H), 7.31 – 7.25 (m, 5H), 7.24-7.14 (m, 5H), 7.12 (d, *J* = 8.0 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.70 (s, 1H), 3.74 (s, 3H), 3.02 – 2.94 (m, 2H), 2.58 – 2.50 (m, 2H);

¹³**C NMR** (101 MHz, CDCl₃) δ 150.94, 146.80, 146.16, 137.75, 129.21, 129.04, 128.49, 128.04, 126.85, 126.05, 123.57, 122.12, 121.52, 120.19, 118.76, 109.39, 52.31, 41.47, 32.83, 32.74;

Exact Mass ESI-MS: calculated m/z for $[C_{30}H_{26}N_2O_2Na]^+$: 469.1886, found: 469.1887.

methyl 4-(3-(1-methyl-1H-indol-3-yl)-3,3-diphenylpropyl)benzoate (4e)

89.1 mg, 0.194 mmol, 97%;

Pure white solid;

R_f (PE/EA 10/1): 0.27;

¹**H NMR** (400 MHz, CDCl₃) δ 7.90 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 7.5 Hz, 4H), 7.30 – 7.24 (m, 5H), 7.22 – 7.09 (m, 6H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.71 (s, 1H), 3.88 (s, 3H), 3.74 (s, 3H), 3.01 – 2.93 (m, 2H), 2.50 – 2.43 (m, 2H);

¹³C NMR (101 MHz, CDCl₃) δ 167.15, 148.59, 146.97, 137.72, 129.71, 129.06, 128.59, 128.32, 127.94, 127.67, 126.93, 125.91, 122.23, 121.40, 120.48, 118.65, 109.29, 52.28, 51.99, 41.82, 32.81, 32.75; **Exact Mass ESI-MS:** calculated m/z for [C₃₂H₂₉NO₂Na]⁺: 482.2091, found: 482.2098.

1-methyl-3-(3-(4-nitrophenyl)-1,1-diphenylpropyl)-1H-indole (4f)



82.9 mg, 0.176 mmol, 88%; Pure white solid;

R_f(PE/DCM 10/1): 0.31;

¹**H NMR** (600 MHz, CDCl₃) δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 7.6 Hz, 4H), 7.29 – 7.25 (m, 5H), 7.19 – 7.15 (m, 5H), 7.13 (d, *J* = 8.1 Hz, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.70 (s, 1H), 3.73 (s, 3H), 2.99 – 2.94 (m, 2H), 2.50 – 2.45 (m, 2H);

¹³**C NMR** (101 MHz, CDCl₃) δ 147.11 (q, *J* = 1.3 Hz), 146.95, 137.74, 129.10, 128.57, 127.97, 127.85 (q, *J* = 32.3 Hz), 126.92, 125.95, 125.21 (q, *J* = 3.7 Hz), 124.51 (q, *J* = 300.0 Hz), 122.20, 121.44, 120.42, 118.68, 109.32, 52.28, 41.86, 32.80, 32.55;

¹⁹**F NMR** (564 MHz, CDCl₃) δ -62.26;

Exact Mass ESI-MS: calculated m/z for $[C_{31}H_{26}F_3NNa]^+$: 492.1910, found: 492.1919.

3-(1,1-diphenyl-3-(4-(trifluoromethoxy)phenyl)propyl)-1-methyl-1H-indole (4g)

86.2 mg, 0.178 mmol, 89%; Pure white solid;

^{F3} R_f (PE): 0.40;

¹**H NMR** (400 MHz, CDCl₃) δ 7.42 (d, J = 7.4 Hz, 4H), 7.29 – 7.22 (m, 5H), 7.20 – 7.12 (m, 4H), 7.06 (s, 4H), 6.92 (t, J = 7.5 Hz, 1H), 6.70 (s, 1H), 3.72 (s, 3H), 2.99 – 2.91 (m, 2H), 2.46 – 2.38 (m, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 147.35, 147.12, 141.80, 137.84, 129.54, 129.14, 128.69, 128.02, 127.05, 125.99,

122.32, 121.50, 121.00, 120.64, 120.62 (q, J = 256.5 Hz), 118.74, 109.37, 52.36, 42.21, 32.82, 32.04; ¹⁹**F NMR** (564 MHz, CDCl₃) δ -57.92;

Exact Mass ESI-MS: calculated m/z for [C₃₁H₂₆F₃NONa]⁺: 508.1859, found: 508.1858.

3-(3-(4-fluorophenyl)-1,1-diphenylpropyl)-1-methyl-1*H*-indole (4h)

55.8 mg, 0.133 mmol, 67%;

Pure white solid;

R_f(PE/EA 5/1): 0.25;

¹**H NMR** (600 MHz, CDCl₃) δ 7.41 (d, *J* = 7.5 Hz, 4H), 7.29 – 7.24 (m, 5H), 7.17 (t, *J* = 7.3 Hz, 3H), 7.13 (d, *J* = 8.1 Hz, 1H), 7.05 – 7.00 (m, 2H), 6.94 – 6.89 (m, 3H), 6.70 (s, 1H), 3.73 (s, 3H), 2.96 – 2.91 (m, 2H), 2.41 – 2.36 (m, 2H);

¹³**C NMR** (101 MHz, CDCl₃) δ 161.41 (d, J = 249.5 Hz), 146.06, 142.79, 137.68, 133.51 (d, J = 11.4 Hz), 130.78 (d, J = 4.3 Hz), 128.37, 128.29, 128.24, 127.74, 127.12, 125.93, 125.73, 123.46 (d, J = 3.3 Hz), 122.06, 121.37, 119.30, 118.73, 116.51 (d, J = 23.9 Hz), 109.32, 51.24, 41.06 (d, J = 4.4 Hz), 32.86, 32.81; ¹⁹**F NMR** (564 MHz, CDCl₃) δ -117.96;

Exact Mass ESI-MS: calculated m/z for [C₃₀H₂₆FNNa]⁺: 442.1941, found: 442.1938.

3-(3-(4-chlorophenyl)-1,1-diphenylpropyl)-1-methyl-1*H*-indole (4i)



82.9 mg, 0.190 mmol, 95%;

Pure white solid;

R_f (PE/DCM 5/1): 0.33;

¹**H NMR** (400 MHz, CDCl₃) δ 7.45 – 7.36 (m, 4H), 7.29 (d, *J* = 8.9 Hz, 2H), 7.25 (d, *J* = 5.7 Hz, 3H), 7.21 – 7.10 (m, 6H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 11.1, 4.0 Hz, 1H), 6.70 (s, 1H), 3.74 (s, 3H), 2.99 – 2.89 (m, 2H), 2.42 – 2.34 (m, 2H);

¹³C NMR (101 MHz, CDCl₃) δ 147.07, 141.43, 137.76, 131.37, 129.65, 129.05, 128.63, 128.43, 127.94, 126.99, 125.91, 122.26, 121.41, 120.59, 118.67, 109.30, 52.29, 42.23, 32.81, 32.03; Exact Mass ESI-MS: calculated m/z for [C₃₀H₂₆CINNa]⁺: 458.1646, found: 458.1642.

3-(3-(4-bromophenyl)-1,1-diphenylpropyl)-1-methyl-1H-indole (4j)

70.6 mg, 0.174 mmol, 87%; Pure white solid;

R_f (PE/DCM 5/1): 0.33;

¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, *J* = 7.6 Hz, 4H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.30 – 7.23 (m, 5H), 7.20 – 7.10 (m, 4H), 6.98 – 6.88 (m, 3H), 6.70 (s, 1H), 3.73 (s, 3H), 2.97 – 2.89 (m, 2H), 2.40 – 2.32 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 147.11, 142.00, 137.79, 131.44, 130.15, 129.14, 128.68, 128.03, 127.01, 125.99, 122.31, 121.48, 120.58, 119.45, 118.74, 109.40, 52.32, 42.19, 32.86, 32.15; Exact Mass ESI-MS: calculated m/z for [C₃₀H₂₆BrNNa]⁺: 502.1141, found: 502.1144.

3-(3-(3-methoxyphenyl)-1,1-diphenylpropyl)-1-methyl-1*H*-indole (4k)

Ph Ph N OMe

63.3 mg, 0.146 mmol, 73%; Pure white solid;

R_f (PE/DCM 5/1): 0.23;

¹**H NMR** (400 MHz, CDCl₃) δ 7.43 (d, *J* = 8.2 Hz, 4H), 7.30 – 7.24 (m, 5H), 7.21 – 7.10 (m, 5H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.76 – 6.66 (m, 3H), 6.63 (s, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 3.01 – 2.92 (m, 2H), 2.39 (dd, *J* = 10.5, 6.3 Hz, 2H);

¹³C NMR (101 MHz, CDCl₃) δ 159.60, 147.15, 144.68, 137.72, 129.32, 129.05, 128.68, 127.89, 127.00, 125.83, 122.32, 121.33, 120.71, 120.66, 118.58, 114.14, 110.85, 109.25, 55.15, 52.26, 42.17, 32.81, 32.63; **Exact Mass ESI-MS:** calculated m/z for [C₃₁H₂₉NONa]⁺: 454.2141, found: 454.2141.

3-(1,1-diphenyl-3-(4-(trifluoromethyl)phenyl)propyl)-1-methyl-1H-indole (4)

70.0 mg, 0.149 mmol, 75%;

Pure white solid; R_f(PE/DCM 10/1): 0.25;

¹**H NMR** (400 MHz, CDCl₃) δ 7.54 – 7.36 (m, 5H), 7.35 – 7.23 (m, 8H), 7.22 – 7.11 (m, 4H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.72 (s, 1H), 3.75 (s, 3H), 3.03 – 2.94 (m, 2H), 2.53 – 2.45 (m, 2H);

¹³**C NMR** (151 MHz, CDCl₃) δ 147.02, 143.90, 137.82, 131.75, 130.62 (q, *J* = 31.9 Hz), 129.13, 128.77, 128.68, 128.03, 127.01, 126.01, 124.99 (q, *J* = 3.5 Hz), 124.33 (q, *J* = 272.3 Hz), 122.63 (q, *J* = 3.4 Hz), 122.31, 121.51, 120.54, 118.75, 109.37, 52.39, 42.04, 32.83, 32.56;

¹⁹**F NMR** (564 MHz, $CDCI_3$) δ -62.47;

Exact Mass ESI-MS: calculated m/z for $[C_{31}H_{26}F_3NNa]^+$: 492.1910, found: 492.1912.

3-(1,1-diphenyl-3-(o-tolyl)propyl)-1-methyl-1H-indole (4m)



74.2 mg, 0.168 mmol, 84%;

Pure white solid;

R_f (PE/DCM 10/1): 0.23;

¹**H NMR** (400 MHz, CDCl₃) δ 7.47 (d, *J* = 7.7 Hz, 4H), 7.35 – 7.22 (m, 5H), 7.21 – 7.13 (m, 4H), 7.09 (d, *J* = 17.3 Hz, 4H), 6.91 (t, *J* = 6.4 Hz, 1H), 6.79 (s, 1H), 3.75 (s, 3H), 2.94 – 2.84 (m, 2H), 2.43 – 2.34 (m, 2H), 2.02 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 147.11, 141.18, 137.73, 135.97, 130.17, 128.90, 128.70, 128.23, 128.13, 127.86, 127.01, 125.98, 125.82, 122.44, 121.33, 120.84, 118.53, 109.20, 52.36, 40.97, 32.80, 29.82, 19.15; **Exact Mass ESI-MS:** calculated m/z for [C₃₁H₂₉NNa]⁺: 438.2192, found: 438.2194.

1-methyl-3-(3-(naphthalen-2-yl)-1,1-diphenylpropyl)-1H-indole (4n)

56.6 mg, 0.125 mmol, 63%;

Ph Ph

Pure white solid; R_f (PE/DCM 30/1): 0.24;

¹**H NMR** (400 MHz, CDCl₃) δ 7.81 – 7.68 (m, 3H), 7.53 (s, 1H), 7.46 (d, *J* = 7.5 Hz, 4H), 7.43 – 7.32 (m, 2H), 7.31 – 7.24 (m, 5H), 7.24 – 7.11 (m, 5H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.76 (s, 1H), 3.74 (s, 3H), 3.11 – 3.02 (m, 2H), 2.63 – 2.54 (m, 2H);

¹³**C NMR** (101 MHz, CDCl₃) δ 147.21, 140.55, 137.77, 133.68, 131.95, 129.10, 128.74, 127.96, 127.91, 127.65, 127.40, 127.07, 126.10, 125.93, 125.90, 125.11, 122.39, 121.39, 120.75, 118.66, 109.31, 52.38, 42.26, 32.84, 32.80;

Exact Mass ESI-MS: calculated m/z for [C₃₄H₂₉NNa]⁺: 474.2192, found: 474.2188.

3-(1,1-diphenyl-3-(thiophen-3-yl)propyl)-1-methyl-1H-indole (40)



43.9 mg, 0.108 mmol, 54%; Pure white solid;

R_f (PE/DCM 10/1): 0.24;

¹**H NMR** (400 MHz, CDCl₃) δ 7.41 (d, J = 7.6 Hz, 4H), 7.31 – 7.26 (m, 3H), 7.26 – 7.11 (m, 7H), 6.98 – 6.81 (m, 3H), 6.71 (s, 1H), 3.74 (s, 3H), 3.00 (dd, J = 10.3, 6.6 Hz, 2H), 2.49 – 2.39 (m, 2H);

¹³**C NMR** (151 MHz, CDCl₃) δ 147.16, 143.09, 137.76, 129.01, 128.70, 128.25, 127.92, 127.07, 125.87, 125.26, 122.34, 121.36, 120.71, 119.66, 118.63, 109.25, 52.22, 40.97, 32.82, 27.13;

Exact Mass ESI-MS: calculated m/z for [C₂₈H₂₅NSNa]⁺: 430.1600, found: 430.1595.

methyl 4-(1-methyl-1*H*-indol-3-yl)-2,4,4-triphenylbutanoate (X = Br, 4p)



COOMe

50.2 mg, 0.109 mmol, 55%;

Pure white solid;

R_f(PE/EA 20/1): 0.26;

 ^{1}H NMR (400 MHz, CDCl_3) δ 7.42 – 7.37 (m, 4H), 7.28 (s, 2H), 7.27 – 7.18 (m, 8H), 7.16 –

7.10 (m, 3H), 7.01 (d, *J* = 8.1 Hz, 1H), 6.88 (t, *J* = 7.6 Hz, 1H), 6.74 (s, 1H), 3.72 (s, 3H), 3.68 (d, *J* = 7.2 Hz, 2H), 3.26 (q, *J* = 11.9 Hz, 1H), 2.85 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 173.52, 146.18, 146.13, 141.22, 137.62, 129.52, 128.62, 128.01, 127.88, 127.06, 126.92, 125.95, 122.59, 121.29, 119.62, 118.51, 108.98, 52.88, 51.39, 49.58, 32.70;

Exact Mass ESI-MS: calculated m/z for $[C_{32}H_{29}NO_2Na]^+$: 482.2091, found: 482.2082.

phenyl 4-(1-methyl-1H-indol-3-yl)-4,4-diphenylbutanoate (4q)

54.1 mg, 0.121 mmol, 61%;

Pure white solid;

R_f (PE/EA 15/1): 0.23;

¹**H NMR** (400 MHz, CDCl₃) δ 7.42 (d, *J* = 7.6 Hz, 4H), 7.34 – 7.23 (m, 7H), 7.20 – 7.14 (m, 4H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 7.9 Hz, 2H), 6.91 (t, *J* = 7.6 Hz, 1H), 6.77 (s, 1H), 3.70 (s, 3H), 3.20 –

3.10 (m, 2H), 2.47 - 2.39 (m, 2H);

¹³C NMR (101 MHz, CDCl₃) δ 172.49, 150.68, 146.45, 137.77, 129.35, 128.92, 128.53, 128.06, 126.79, 126.06, 125.71, 122.26, 121.53, 121.48, 119.98, 118.76, 109.31, 51.62, 34.73, 32.78, 31.75; Exact Mass ESI-MS: calculated m/z for $[C_{31}H_{27}NO_2Na]^+$: 468.1934, found: 468.1939.

methyl 4-(1-methyl-1H-indol-3-yl)-2,4,4-triphenylbutanoate (X = Cl, 4r)

-COOMe 79.0 mg, 0.172 mmol, 86%;



Pure white solid; R_f (PE/EA 20/1): 0.26;

 $N_{\rm f}$ (FL/LA 20/1). 0.20,

¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.37 (m, 4H), 7.28 (s, 2H), 7.27 – 7.18 (m, 8H), 7.16 – 7.10 (m, 3H), 7.01 (d, J = 8.1 Hz, 1H), 6.88 (t, J = 7.6 Hz, 1H), 6.74 (s, 1H), 3.72 (s, 3H), 3.68 (d, J = 7.2 Hz, 2H), 3.26 (q, J = 11.9 Hz, 1H), 2.85 (s, 3H);

¹³**C NMR** (101 MHz, CDCl₃) δ 173.52, 146.18, 146.13, 141.22, 137.62, 129.52, 128.62, 128.01, 127.88, 127.06, 126.92, 125.95, 122.59, 121.29, 119.62, 118.51, 108.98, 52.88, 51.39, 49.58, 32.70;

Exact Mass ESI-MS: calculated m/z for $[C_{32}H_{29}NO_2Na]^+$: 482.2091, found: 482.2082.

ethyl 4-(1-methyl-1*H*-indol-3-yl)-2,4,4-triphenylbutanoate (X = Cl, 4s)

53.6 mg, 0.113 mmol, 57%;



R_f(PE/EA 20/1): 0.31;

Pale yellow solid;

¹**H NMR** (400 MHz, CDCl₃) δ 7.38 (s, 4H), 7.27 (s, 4H), 7.24 – 7.18 (m, 6H), 7.16 – 7.10 (m, 3H), 7.00 (d, *J* = 7.9 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.74 (s, 1H), 3.71 (s, 3H), 3.70 – 3.59 (m, 2H), 3.28 – 3.17 (m, 3H), 0.82 (t, *J* = 7.0 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 173.22, 146.27, 146.13, 141.42, 137.60, 129.40, 128.76, 128.56, 128.03, 127.87, 126.97, 125.94, 122.60, 121.28, 119.72, 118.47, 108.95, 60.31, 52.93, 49.72, 43.22, 32.73, 13.60; **Exact Mass ESI-MS:** calculated m/z for [C₃₃H₃₁NO₂Na]⁺: 496.2247, found: 496.2241.

methyl 4-(1-methyl-1*H*-indol-3-yl)-2,4,4-triphenylbutanoate (X = CI, 4t)

MeOOC

44.6 mg, 0.100 mmol, 50%;

Pure white solid;

^N R_f(PE/DAM 4/1): 0.20;

¹**H NMR** (400 MHz, CDCl₃) δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 4H), 7.30 – 7.24 (m, 5H), 7.22 – 7.07 (m, 6H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.71 (s, 1H), 3.89 (s, 3H), 3.74 (s, 3H), 3.01 – 2.92 (m, 2H), 2.51 – 2.42 (m, 2H);

¹³C NMR (101 MHz, CDCl₃) δ 167.15, 148.59, 146.96, 137.72, 129.70, 129.06, 128.58, 128.30, 127.92, 127.66, 126.93, 125.90, 122.22, 121.39, 120.48, 118.64, 109.27, 52.28, 51.99, 41.82, 32.81, 32.74; Exact Mass ESI-MS: calculated m/z for [C₃₂H₂₉NO₂Na]⁺: 482.2091, found: 482.2088.

3-(1,3-diphenyl-1-(p-tolyl)propyl)-1-methyl-1H-indole (5a)

71.5 mg, 0.172 mmol, 86%; Pure white solid;

R_f(PE/DCM 10/1): 0.29;

¹**H NMR** (400 MHz, CDCl₃) δ 7.42 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 7.7 Hz, 3H), 7.27 – 7.23 (m, 4H), 7.19 – 7.14 (m, 4H), 7.08 (d, 4H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.73 (s, 1H), 3.73 (s, 3H), 2.99 – 2.91 (m, 2H), 2.43 – 2.37 (m, 2H), 2.30 (s, 3H);

¹³C NMR (101 MHz, CDCl₃)δ 147.40, 144.18, 143.08, 137.73, 135.21, 128.98, 128.65, 128.60, 128.56, 128.36, 128.31, 127.85, 127.06, 125.75, 125.68, 122.39, 121.28, 120.90, 118.53, 109.21, 51.93, 42.37, 32.78, 32.58, 20.98:

Exact Mass ESI-MS: calculated m/z for [C₃₁H₂₉NNa]⁺: 438.2192, found: 438.2192.

3-(1-([1,1'-biphenyl]-4-yl)-1,3-diphenylpropyl)-1-methyl-1H-indole (5b)

76.8 mg, 0.160 mmol, 80%;

R_f(PE/DCM 5/1): 0.20;

Pure white solid;

¹**H NMR** (400 MHz, CDCl₃) δ 7.58 (d, *J* = 7.3 Hz, 2H), 7.52 – 7.44 (m, 6H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.32 - 7.23 (m, 6H), 7.22 - 7.15 (m, 4H), 7.12 (d, J = 7.4 Hz, 2H), 6.93 (t, J = 7.5 Hz, 1H), 6.78 (s, 1H), 3.75 (s, 3H), 3.04 - 2.96 (m, 2H), 2.49 - 2.41 (m, 2H);

¹³C NMR (101 MHz, CDCl₃) δ 147.04, 146.29, 142.95, 140.77, 138.37, 137.71, 129.04, 129.02, 128.98, 128.69, 128.36, 128.28, 127.90, 127.05, 126.98, 126.92, 126.48, 125.86, 125.70, 122.34, 121.33, 120.62, 118.59, 109.23, 52.05, 42.32, 32.84, 32.56;

Exact Mass ESI-MS: calculated m/z for [C₃₆H₃₁NNa]⁺: 500.2349, found: 500.2340.

ethyl4-(1-(1-methyl-1H-indol-3-yl)-1,3-diphenylpropyl)benzoate (5c)

79.0 mg, 0.166 mmol, 83%;

Pure white solid;

R_f (PE/DCM 10/1): 0.26;

¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.45 – 7.39 (m, 2H), 7.30 – 7.23 (m, 4H), 7.23 – 7.14 (m, 4H), 7.13 – 7.07 (m, 3H), 6.92 (t, J = 7.5 Hz, 1H), 6.74 (s, 1H), 4.33 (q, J = 7.1 Hz, 2H), 3.72 (s, 3H), 3.03 – 2.92 (m, 2H), 2.46 – 2.33 (m, 2H), 1.35 (t, J = 7.1 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃)δ 166.61, 152.52, 146.27, 142.66, 137.75, 129.21, 128.96, 128.93, 128.66, 128.43, 128.26, 128.07, 128.03, 126.78, 126.13, 125.82, 122.10, 121.51, 120.02, 118.78, 109.36, 60.80, 52.57, 42.20, 32.84, 32.49, 14.39;

Exact Mass ESI-MS: calculated m/z for [C₃₃H₃₁NO₂Na]⁺: 496.2247, found: 496.2246.

3-(1-(4-fluorophenyl)-1,3-diphenylpropyl)-1-methyl-1*H*-indole (5d)

60.0 mg, 0.143 mmol, 72%;

Pure white solid;

R_f(PE/DCM 10/1): 0.26;

¹**H NMR** (600 MHz, CDCl₃) δ 7.41 (d, *J* = 7.6 Hz, 2H), 7.37 (dd, *J* = 8.7, 5.4 Hz, 2H), 7.29 –

7.23 (m, 5H), 7.19 - 7.08 (m, 6H), 6.95 - 6.91 (m, 3H), 6.72 (s, 1H), 3.74 (s, 3H), 3.03 - 2.89 (m, 2H), 2.47 -2.34 (m, 2H);

¹³C NMR (101 MHz, CDCl₃) δ 146.89, 142.97, 142.77 (d, J = 1.4 Hz), 137.72, 130.17 (d, J = 8.0 Hz), 128.89, 128.55, 128.39, 128.24, 127.95, 126.83, 125.94, 125.75, 122.16, 121.41, 120.56, 118.68, 114.55 (d, J = 20.8 Hz), 109.99, 109.30, 51.78, 42.53, 32.80, 32.53;

¹⁹F NMR (564 MHz, CDCl₃) δ -117.62;

Exact Mass ESI-MS: calculated m/z for [C₃₀H₂₆FNNa]⁺: 442.1941, found: 442.1934.

3-(1-(4-chlorophenyl)-1,3-diphenylpropyl)-1-methyl-1H-indole (5e)

66.5 mg, 0.152 mmol, 76%;

Pure white solid;

R_f (PE/DCM 20/1): 0.20;

¹**H NMR** (400 MHz, CDCl₃) δ 7.41 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 7.5 Hz, 2H), 7.33 – 7.24 (m, 5H), 7.24 – 7.16 (m, 5H), 7.15 – 7.06 (m, 3H), 6.94 (t, J = 7.5 Hz, 1H), 6.73 (s, 1H), 3.75 (s, 3H), 3.01 – 2.86 (m, 2H), 2.46 – 2.31 (m, 2H);

¹³C NMR (101 MHz, CDCl₃) δ 146.54, 145.82, 142.68, 137.71, 131.53, 130.07, 128.90, 128.55, 128.40, 128.23, 127.99, 127.97, 126.76, 126.02, 125.78, 122.12, 121.45, 120.18, 118.72, 109.32, 51.91, 32.82, 32.47; **Exact Mass ESI-MS:** calculated m/z for [C₃₀H₂₆ClNNa]⁺: 458.1646, found: 458.1655.

3-(1-(3-bromophenyl)-1,3-diphenylpropyl)-1-methyl-1*H*-indole (5f)

93.0 mg, 0.194 mmol, 97%;

Ph N

Pure white solid; ^h R_f(PE/DCM 10/1): 0.28;

¹**H NMR** (400 MHz, CDCl₃) δ 7.58 (d, *J* = 1.8 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 2H), 7.37 – 7.33 (m, 1H), 7.31 – 7.16 (m, 9H), 7.14 – 7.07 (m, 4H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.72 (d, *J* = 1.4 Hz, 1H), 3.74 (s, 3H), 2.97 – 2.89 (m, 2H), 2.43 – 2.34 (m, 2H);

¹³**C NMR** (101 MHz, CDCl₃) δ 149.89, 146.18, 142.64, 137.73, 131.41, 129.41, 128.96, 128.63, 128.41, 128.25, 128.02, 127.52, 126.74, 126.11, 125.80, 122.18, 122.06, 121.47, 119.91, 118.77, 109.33, 52.25, 42.25, 32.83, 32.48;

Exact Mass ESI-MS: calculated m/z for [C₃₀H₂₆BrNNa]⁺: 502.1141, found: 502.1147.

3-(1,3-diphenyl-1-(m-tolyl) propyl)-1-methyl-1H-indole (5g)



68.7 mg, 0.165 mmol, 83%;

Pure white solid;

R_f (PE/DCM 30/1): 0.26;

¹**H NMR** (400 MHz, CDCl₃) δ 7.43 (d, *J* = 8.3 Hz, 2H), 7.30 – 7.25 (m, 4H), 7.24 – 7.20 (m, 3H), 7.20 – 7.13 (m, 5H), 7.10 (d, *J* = 7.7 Hz, 2H), 6.99 (d, *J* = 7.4 Hz, 1H), 6.92 (dd, *J* = 8.0, 7.1 Hz, 1H), 6.72 (s, 1H), 3.74 (s, 3H), 2.98 – 2.93 (m, 2H), 2.42 – 2.37 (m, 2H), 2.28 (s, 3H);

¹³**C NMR** (101 MHz, CDCl₃) δ 147.27, 147.16, 143.12, 137.73, 137.23, 129.24, 129.06, 128.73, 128.39, 128.33, 127.87, 127.71, 127.09, 126.58, 125.96, 125.78, 125.71, 122.40, 121.29, 120.78, 118.56, 109.22, 52.21, 42.36, 32.80, 32.64, 21.85;

Exact Mass ESI-MS: calculated m/z for [C₃₁H₂₉NNa]⁺: 438.2192, found: 438.2196.

3-(1-(2-fluorophenyl)-1,3-diphenylpropyl)-1-methyl-1*H*-indole (5h)

76.0 mg, 0.181 mmol, 91%;



Pure white solid;

R_f (PE/DCM 5/1): 0.23;

¹**H NMR** (400 MHz, CDCl₃) δ 7.39 (t, J = 8.0 Hz, 3H), 7.32 – 7.21 (m, 7H), 7.21 – 7.16 (m, 3H), 7.12 (d, J = 7.9 Hz, 2H), 7.04 – 6.91 (m, 3H), 6.75 (s, 1H), 3.75 (s, 3H), 3.18 – 3.11 (m, 1H), 3.01 (td, J = 13.4, 5.1 Hz, 1H), 2.49 (td, J = 13.3, 4.4 Hz, 1H), 2.30 (td, J = 13.0, 6.7 Hz, 1H);

¹³**C NMR** (101 MHz, CDCl₃) δ 161.38 (d, *J* = 249.4 Hz), 146.04, 142.77, 137.65, 133.48 (d, *J* = 11.2 Hz), 130.75 (d, *J* = 4.6 Hz), 128.55 (d, *J* = 3.1 Hz), 128.42, 128.35, 128.27, 128.22, 127.72, 127.10, 125.80 (d, *J* = 20.2 Hz), 123.44 (d, *J* = 3.2 Hz), 122.04, 121.34, 119.27, 118.70, 116.61, 116.37, 109.30, 51.22 (d, *J* = 2.3 Hz), 41.06, 41.01, 32.82;

¹⁹**F NMR** (564 MHz, CDCl₃) δ -104.79;

Exact Mass ESI-MS: calculated m/z for $[C_{30}H_{26}FNNa]^+$: 442.1941, found: 442.1940.

3-(1-(2-chlorophenyl)-1,3-diphenylpropyl)-1-methyl-1H-indole (5i)



62.6 mg, 0.143 mmol, 72%; Pure white solid;

R_f(PE/DCM 5/1): 0.25;

¹**H NMR** (400 MHz, CDCl₃) δ 7.54 – 7.47 (m, 1H), 7.44 – 7.30 (m, 3H), 7.30 – 7.21 (m, 6H), 7.17 (ddd, *J* = 15.3, 9.1, 4.2 Hz, 6H), 6.94 (dd, *J* = 8.0, 7.1 Hz, 1H), 6.76 (s, 1H), 3.75 (s, 3H), 3.38 – 3.29 (m, 1H), 3.16 (td, *J* = 13.5, 5.2 Hz, 1H), 2.51 (td, *J* = 13.3, 3.8 Hz, 1H), 2.25 (td, *J* = 13.2, 5.0 Hz, 1H);

¹³**C NMR** (101 MHz, CDCl₃) δ 146.10, 142.86, 142.77, 137.64, 134.89, 132.10, 132.00, 128.70, 128.50, 128.41, 128.30, 127.95, 127.64, 127.26, 126.16, 125.78, 125.71, 122.14, 121.35, 119.65, 118.80, 109.35, 53.36, 40.29, 33.03, 32.90;

Exact Mass ESI-MS: calculated m/z for $[C_{30}H_{26}CINNa]^+$: 458.1646, found: 458.1638.

3-(1-(2-bromophenyl)-1,3-diphenylpropyl)-1-methyl-1H-indole (5j)

Ph Br N Ph

Pure white solid;

55.0 mg, 0.114 mmol, 57%;

R_f(PE/DCM 10/1): 0.21;

¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, *J* = 7.7 Hz, 1H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.40 (d, *J* = 7.6 Hz, 2H), 7.36 – 6.97 (m, 13H), 6.94 (t, *J* = 7.4 Hz, 1H), 6.79 (s, 1H), 3.75 (s, 3H), 3.41 – 3.31 (m, 1H), 3.28 – 3.17 (m, 1H), 2.56 – 2.46 (m, 1H), 2.25 (td, *J* = 13.2, 5.0 Hz, 1H);

¹³**C NMR** (101 MHz, CDCl₃) δ 146.10, 144.01, 142.72, 137.60, 135.76, 132.66, 128.68, 128.39, 128.27, 128.07, 127.61, 127.20, 126.64, 125.76, 125.64, 124.64, 122.16, 121.30, 119.76, 118.75, 109.31, 54.06, 40.11, 33.00, 32.87;

Exact Mass ESI-MS: calculated m/z for [C₃₀H₂₆BrNNa]⁺: 502.1141, found: 502.1145.

3-(1,3-diphenyl-1-(4-(prop-2-yn-1-yloxy)phenyl)propyl)-1-methyl-1H-indole (5k)

74.9 mg, 0.164 mmol, 82%;

Pure white solid;

^J R_f (PE/DCM 3/1): 0.20;

¹**H NMR** (400 MHz, CDCl₃) δ 7.42 (d, J = 7.9 Hz, 2H), 7.33 (d, J = 8.7 Hz, 2H), 7.30 – 7.22 (m, 5H), 7.20 – 7.12 (m, 4H), 7.10 (d, J = 7.3 Hz, 2H), 6.92 (t, 1H), 6.85 (d, J = 8.8 Hz, 2H), 6.72 (s, 1H), 4.60 (d, J = 2.3 Hz, 2H), 3.73 (s, 3H), 2.99 – 2.89 (m, 2H), 2.47 – 2.37 (m, 2H), 1.85 (t, J = 2.2 Hz, 3H);

¹³**C NMR** (101 MHz, CDCl₃) δ 155.93, 147.48, 143.06, 139.99, 137.77, 129.73, 128.96, 128.65, 128.41, 128.33, 127.90, 127.07, 125.81, 125.73, 122.40, 121.35, 121.06, 118.60, 114.06, 109.26, 83.64, 74.34, 56.48, 51.68, 42.63, 32.81, 32.66, 3.81;

Exact Mass ESI-MS: calculated m/z for [C₃₄H₃₁NONa]⁺: 492.2298, found: 492.2306.

1-methyl-3-(1-(naphthalen-2-yl)-1,3-diphenylpropyl)-1H-indole (5l)

76.5 mg, 0.169 mmol, 85%; Pure white solid; R_f (PE/DCM 5/1): 0.22; ¹**H NMR** (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.79 – 7.73 (m, 2H), 7.70 (d, J = 8.7 Hz, 1H), 7.54 – 7.45 (m, 3H), 7.43 (dd, J = 6.2, 3.3 Hz, 2H), 7.31 – 7.24 (m, 5H), 7.21 – 7.10 (m, 6H), 6.90 (t, J = 7.6 Hz, 1H), 6.75 (s, 1H), 3.74 (s, 3H), 3.07 (dd, J = 9.9, 7.2 Hz, 2H), 2.46 (td, J = 7.0, 3.0 Hz, 2H);

¹³**C NMR** (101 MHz, CDCl₃) δ 146.96, 144.66, 143.03, 137.76, 133.21, 131.87, 129.18, 129.17, 128.83, 128.45, 128.36, 128.30, 128.21, 127.97, 127.38, 127.10, 126.22, 125.97, 125.81, 125.79, 125.65, 122.37, 121.41, 120.48, 118.73, 109.31, 52.49, 42.38, 32.83, 32.72;

Exact Mass ESI-MS: calculated m/z for [C₃₄H₂₉NNa]⁺: 474.2192, found: 474.2192.

3-(1-(benzofuran-2-yl)-1,3-diphenylpropyl)-1-methyl-1H-indole (5m)

38.3 mg, 0.086 mmol, 43%;

Pure white solid; R_f (PE/DCM 5/1): 0.34;

¹**H NMR** (400 MHz, CDCl₃) δ 7.50–7.38 (m, 4H), 7.31 – 7.25 (m, 4H), 7.24 – 7.21 (m, 2H), 7.21 – 7.11 (m, 7H), 6.94 – 6.89 (m, 2H), 6.48 (d, *J* = 0.7 Hz, 1H), 3.77 (s, 3H), 3.04 – 2.91 (m, 2H), 2.70 – 2.59 (m, 2H);

¹³**C NMR** (101 MHz, CDCl₃) δ 163.15, 154.69, 144.60, 142.80, 137.56, 128.45, 128.39, 128.31, 128.22, 128.02, 126.77, 126.53, 125.77, 123.49, 122.54, 122.04, 121.43, 120.72, 118.79, 118.51, 111.23, 109.24, 104.60, 104.56, 49.61, 41.94, 32.85, 32.82, 32.30;

Exact Mass ESI-MS: calculated m/z for [C₃₂H₂₇NONa]⁺: 464.1985, found: 464.1977.

1-methyl-3-(9-phenethyl-9H-thioxanthen-9-yl)-1H-indole (5n)

44.5 mg, 0.103 mmol, 52%;

Pure white solid;

R_f (PE/DCM 5/1): 0.22;

¹**H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 4H), 7.21 (t, *J* = 7.3 Hz, 2H), 7.16 – 7.09 (m, 4H), 7.04 (d, *J* = 7.0 Hz, 2H), 6.94 – 6.86 (m, 4H), 6.75 (t, *J* = 7.2 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 3.92 (s, 3H), 2.60 – 2.51 (m, 2H), 2.47 – 2.39 (m, 2H);

¹³C NMR (101 MHz, CDCl₃) δ 142.42, 138.93, 137.94, 136.86, 136.72, 131.66, 130.76, 130.28, 129.90, 128.18, 127.20, 126.90, 126.36, 125.79, 125.54, 124.47, 121.64, 119.76, 49.85, 49.42, 33.08, 31.59; **Exact Mass ESI-MS:** calculated m/z for [C₃₀H₂₅NSNa]⁺: 454.1600, found: 454.1613.

3-(2,4-diphenylbutan-2-yl)-1-methyl-1H-indole (50)



35.7 mg, 0.105 mmol, 53%;

Pure white solid;

R_f (PE/DCM 20/1): 0.26;

¹**H NMR** (400 MHz, CDCl₃) δ 7.37 – 7.32 (m, 2H), 7.27 – 7.20 (m, 5H), 7.17–7.11 (m, 3H), 7.08 – 7.01 (m, 3H), 6.96 (s, 1H), 6.88 – 6.83 (m, 1H), 3.75 (s, 3H), 2.60 – 2.52 (m, 1H), 2.45 – 2.36 (m, 3H), 1.79 (s, 3H); ¹³**C NMR** (101 MHz, CDCl₃) δ 148.80, 143.19, 137.76, 128.42, 128.30, 128.00, 127.01, 126.48, 126.31, 125.64, 125.59, 123.05, 121.36, 121.25, 118.43, 109.11, 44.01, 42.50, 32.75, 31.38, 27.70;

Exact Mass ESI-MS: calculated m/z for $[C_{25}H_{25}NNa]^+$: 362.1879, found: 362.1886.

1-ethyl-3-(1,1,3-triphenylpropyl)-1*H*-indole (6a)

64.8 mg, 0.156 mmol, 78%; Pure white solid; R_f(PE/DCM 5/1):0.33; ¹**H NMR** (400 MHz, CDCl₃) δ 7.43 (d, J = 7.4 Hz, 4H), 7.32 (d, J = 8.2 Hz, 1H), 7.29 – 7.25 (m, 5H), 7.25 – 7.22 (m, 2H), 7.20 – 7.13 (m, 4H), 7.12 – 7.08 (m, 2H), 6.90 (t, J = 7.4 Hz, 1H), 6.80 (s, 1H), 4.13 (q, J = 7.3 Hz, 2H), 3.01 – 2.93 (m, 2H), 2.43 – 2.36 (m, 2H), 1.43 (t, J = 7.2 Hz, 3H);

 $^{13}\textbf{C NMR} \ (101 \ \text{MHz}, \text{CDCl}_3) \ \delta \ 147.20, \ 143.06, \ 136.79, \ 128.71, \ 128.38, \ 128.32, \ 127.88, \ 127.29, \ 127.23, \ 125.81, \ 125.71, \ 122.46, \ 121.17, \ 120.82, \ 118.51, \ 109.31, \ 52.38, \ 42.36, \ 40.91, \ 32.59, \ 15.57;$

Exact Mass ESI-MS: calculated m/z for $[C_{31}H_{29}NNa]^+$: 438.2192, found: 438.2193.

benzyl-3-(1,1,3-triphenylpropyl)-1H-indole (6b)

Ph_Ph 59.8 mg, 0.125 mmol, 63%;

th Pure white solid;

R_f (PE/DCM 5/1): 0.29;

¹**H NMR** (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.1 Hz, 4H), 7.30 – 7.20 (m, 10H), 7.20 – 7.13 (m, 4H), 7.11 (d, J = 7.3 Hz, 1H), 7.07 (d, J = 6.9 Hz, 4H), 6.91 (t, J = 7.5 Hz, 1H), 6.87 (s, 1H), 5.29 (s, 2H), 3.02 – 2.93 (m, 2H), 2.45 – 2.36 (m, 2H);

¹³C NMR (101 MHz, CDCl₃) δ 147.02, 142.93, 137.72, 137.38, 128.76, 128.62, 128.55, 128.35, 128.25, 127.88, 127.49, 127.31, 126.43, 125.82, 125.68, 122.41, 121.56, 121.30, 118.86, 109.78, 52.31, 49.94, 42.22, 32.55; **Exact Mass ESI-MS:** calculated m/z for [C₃₆H₃₁NNa]⁺: 500.2349, found: 500.2346.

4-fluoro-1-methyl-3-(1,1,3-triphenylpropyl)-1H-indole (6c)

Ph Ph N-Ph 55.0 mg, 0.131 mmol, 66%;

Pure white solid;

^{Ph} R_f (PE/DCM 5/1): 0.23;

¹**H NMR** (400 MHz, CDCl₃) δ 7.39 (d, *J* = 8.1 Hz, 4H), 7.24 (q, *J* = 6.9, 6.5 Hz, 6H), 7.19 – 7.04 (m, 7H), 6.67 (dd, *J* = 11.5, 7.4 Hz, 1H), 6.52 (s, 1H), 3.70 (s, 3H), 3.09 – 3.00 (m, 2H), 2.48 – 2.38 (m, 2H);

¹³**C NMR** (101 MHz, CDCl₃) δ 156.42 (d, *J* = 249.0 Hz), 148.23, 142.95, 140.73 (d, *J* = 11.7 Hz), 130.08 (d, *J* = 5.8 Hz), 128.38, 128.34, 128.27, 127.79, 125.68, 122.28 (d, *J* = 8.2 Hz), 119.85 (d, *J* = 3.9 Hz), 115.92 (d, *J* = 19.9 Hz), 105.41 (d, *J* = 3.6 Hz), 105.26, 105.03, 51.97, 41.82, 33.16, 33.11;

¹⁹F NMR (564 MHz, CDCl₃) δ -112.09;

Exact Mass ESI-MS: calculated m/z for $[C_{30}H_{26}FNNa]^+$: 442.1941, found: 442.1944.

4-chloro-1-methyl-3-(1,1,3-triphenylpropyl)-1H-indole (6d)



52.4 mg, 0.120 mmol, 60%;

Pure white solid;

^{Ph} R_f (PE/DCM 5/1): 0.29;

¹**H NMR** (400 MHz, CDCl₃) δ 7.37 (d, *J* = 7.6 Hz, 4H), 7.26 – 7.22 (m, 7H), 7.21 – 7.11 (m, 6H), 7.09 (t, *J* = 7.7 Hz, 1H), 6.37 (s, 1H), 3.69 (s, 3H), 3.34 – 3.26 (m, 2H), 2.49 – 2.39 (m, 2H);

¹³**C NMR** (101 MHz, CDCl₃) δ 149.68, 142.97, 139.72, 132.47, 128.40, 128.33, 127.77, 126.50, 125.64, 125.58, 124.64, 122.05, 121.63, 120.05, 108.12, 51.79, 34.06, 33.15, 33.12;

Exact Mass ESI-MS: calculated m/z for [C₃₀H₂₆CINNa]⁺: 458.1646, found: 458.1641.

1,5-dimethyl-3-(1,1,3-triphenylpropyl)-1*H*-indole (6e)

52.6 mg, 0.126 mmol, 63%; Pure white solid; R_f (PE/DCM 10/1): 0.26; ¹**H NMR** (400 MHz, CDCl₃) δ 7.41 (d, *J* = 7.8 Hz, 4H), 7.28 – 7.22 (m, 6H), 7.20 – 7.13 (m, 4H), 7.11 (d, *J* = 7.4 Hz, 2H), 7.00 (d, *J* = 8.3 Hz, 1H), 6.93 (s, 1H), 6.65 (s, 1H), 3.70 (s, 3H), 2.99 – 2.93 (m, 2H), 2.45 – 2.39 (m, 2H), 2.29 (s, 3H);

 $^{13}\textbf{C} \ \textbf{NMR} \ (151 \ \textbf{MHz}, \textbf{CDCl}_3) \ \delta \ 147.41, \ 143.14, \ 136.25, \ 129.25, \ 128.77, \ 128.38, \ 128.34, \ 127.86, \ 127.66, \ 127.35, \ 125.79, \ 125.70, \ 123.01, \ 122.00, \ 120.08, \ 108.90, \ 52.36, \ 42.35, \ 32.83, \ 32.64, \ 21.64;$

Exact Mass ESI-MS: calculated m/z for $[C_{31}H_{29}NNa]^+$: 438.2192, found: 438.2192.

5-methoxy-1-methyl-3-(1,1,3-triphenylpropyl)-1H-indole (6f)

82.2 mg, 0.190 mmol, 95%;

Pure white solid;

R_f(PE/DCM 5/1): 0.26;

¹**H NMR** (400 MHz, CDCl₃) δ 7.43 (d, *J* = 7.9 Hz, 4H), 7.29 – 7.22 (m, 6H), 7.22 – 7.14 (m, 4H), 7.11 (d, *J* = 7.3 Hz, 2H), 6.83 (dd, *J* = 8.8, 2.2 Hz, 1H), 6.74 (s, 1H), 6.51 (d, *J* = 2.2 Hz, 1H), 3.71 (s, 3H), 3.57 (s, 3H), 3.00 – 2.89 (m, 2H), 2.48 – 2.39 (m, 2H);

¹³**C NMR** (101 MHz, CDCl₃) δ 153.06, 147.08, 143.05, 133.13, 129.54, 128.73, 128.41, 128.32, 127.90, 127.41, 125.85, 125.75, 120.17, 111.39, 109.86, 104.52, 55.80, 52.23, 42.42, 33.01, 32.62;

Exact Mass ESI-MS: calculated m/z for $[C_{31}H_{29}NONa]^+$: 454.2141, found: 454.2149.

5-fluoro-1-methyl-3-(1,1,3-triphenylpropyl)-1H-indole (6g)

MeO

52.6 mg, 0.125 mmol, 63%;

Pure white solid;

R_f (PE/DCM 5/1): 0.25;

¹**H NMR** (400 MHz, CDCl₃) δ 7.41 (d, *J* = 8.1 Hz, 4H), 7.29 – 7.23 (m, 6H), 7.22 – 7.14 (m, 4H), 7.11 (d, *J* = 7.6 Hz, 2H), 6.91 (t, *J* = 9.0 Hz, 1H), 6.80 (s, 1H), 6.76 (d, *J* = 10.6 Hz, 1H), 3.73 (s, 3H), 2.97 – 2.89 (m, 2H), 2.43 – 2.36 (m, 2H);

¹³**C NMR** (101 MHz, CDCl₃) δ 157.01 (d, *J* = 233.4 Hz), 146.67, 142.78, 134.34, 130.42, 128.58, 128.39, 128.24, 127.96, 127.16 (d, *J* = 9.8 Hz), 125.94, 125.76, 120.74 (d, *J* = 4.9 Hz), 109.79 (d, *J* = 9.9 Hz) 109.75 (d, *J* = 26.4 Hz), 107.03 (d, *J* = 24.0 Hz), 52.11, 42.22, 33.08, 32.49;

¹⁹**F NMR** (564 MHz, CDCl₃) δ -125.11;

Exact Mass ESI-MS: calculated m/z for $[C_{30}H_{26}FNNa]^+$: 442.1941, found: 442.1951.

5-chloro-1-methyl-3-(1,1,3-triphenylpropyl)-1H-indole (6h)



47.3mg, 0.108 mmol, 54%;

Pure white solid;

R_f (PE/DCM 5/1): 0.28;

¹**H NMR** (400 MHz, CDCl₃) δ 7.39 (d, J = 7.8 Hz, 3H), 7.32-7.22 (m, 7H), 7.22 – 7.15 (m, 4H), 7.15 – 7.06 (m, 4H), 6.76 (s, 1H), 3.72 (s, 3H), 2.98 – 2.88 (m, 2H), 2.44 – 2.33 (m, 2H);

¹³**C NMR** (101 MHz, CDCl₃) δ 146.69, 142.72, 136.11, 130.20, 128.57, 128.40, 128.24, 127.98, 127.93, 125.99, 125.77, 124.44, 121.72, 121.40, 120.53, 110.28, 52.14, 42.27, 32.98, 32.50;

Exact Mass ESI-MS: calculated m/z for [C₃₀H₂₆CINNa]⁺: 458.1646, found: 458.1645.

5-bromo-1-methyl-3-(1,1,3-triphenylpropyl)-1H-indole (6i)

52.3 mg, 0.108 mmol, 54%; Pure white solid; R_f(PE/DCM 5/1): 0.27;

¹**H NMR** (400 MHz, CDCl₃) δ 7.39 (d, *J* = 8.1 Hz, 4H), 7.30 – 7.23 (m, 8H), 7.22 – 7.14 (m, 4H), 7.11 (d, *J* = 7.7 Hz, 2H), 6.74 (s, 1H), 3.72 (s, 3H), 2.99 – 2.87 (m, 2H), 2.44 – 2.33 (m, 2H);

¹³**C NMR** (101 MHz, CDCl₃) δ 146.69, 142.69, 136.35, 130.09, 130.04, 128.55, 128.38, 128.23, 127.96, 125.98, 125.75, 124.43, 124.26, 120.50, 112.14, 110.72, 52.15, 42.30, 32.98, 32.52;

Exact Mass ESI-MS: calculated m/z for [C₃₀H₂₆BrNNa]⁺: 502.1141, found: 502.1140.

6-methoxy-1-methyl-3-(1,1,3-triphenylpropyl)-1H-indole (6j)

MeO Ph Ph N Ph

59.6 mg, 0.138 mmol, 69%; Pure white solid;

R_f (PE/DCM 5/1): 0.23;

¹**H NMR** (400 MHz, CDCl₃) δ 7.42 (d, J = 7.9 Hz, 4H), 7.28 – 7.22 (m, 6H), 7.17 (t, J = 7.2 Hz, 3H), 7.10 (d, J = 7.6 Hz, 2H), 7.00 (d, J = 8.8 Hz, 1H), 6.73 (s, 1H), 6.64 – 6.55 (m, 2H), 3.85 (s, 3H), 3.68 (s, 3H), 2.98 – 2.89 (m, 2H), 2.46 – 2.37 (m, 2H);

¹³**C NMR** (101 MHz, CDCl₃) δ 155.95, 147.21, 143.04, 138.46, 128.68, 128.38, 128.31, 127.92, 127.87, 125.81, 125.71, 122.94, 121.43, 120.81, 108.40, 92.63, 55.60, 52.23, 42.44, 32.83, 32.58;

Exact Mass ESI-MS: calculated m/z for [C₃₁H₂₉NONa]⁺: 454.2141, found: 454.2145.

7-methoxy-1-methyl-3-(1,1,3-triphenylpropyl)-1H-indole (6k)



76.1 mg, 0.176 mmol, 88%;

Pure white solid;

R_f (PE/DCM 5/1): 0.27;

¹**H NMR** (400 MHz, CDCl₃) δ 7.42 (d, J = 7.4 Hz, 4H), 7.27 – 7.22 (m, 6H), 7.16 (t, J = 6.5 Hz, 3H), 7.11 (d, J = 7.0 Hz, 2H), 6.78 (t, J = 7.9 Hz, 1H), 6.70 (d, J = 7.7 Hz, 1H), 6.59 (s, 1H), 6.55 (d, J = 7.5 Hz, 1H), 3.99 (s, 3H), 3.90 (s, 3H), 2.99 – 2.90 (m, 2H), 2.44 – 2.35 (m, 2H);

¹³**C NMR** (101 MHz, CDCl₃) δ 147.71, 147.20, 143.07, 130.25, 129.33, 128.68, 128.35, 128.31, 127.85, 127.41, 125.75, 125.67, 120.48, 118.89, 115.22, 101.99, 55.27, 52.18, 42.21, 36.67, 32.60;

Exact Mass ESI-MS: calculated m/z for [C₃₁H₂₉NONa]⁺: 454.2141, found: 454.2131.

1,2-dimethyl-3-(1,1,3-triphenylpropyl)-1*H*-indole (6l)

69.6 mg, 0.167 mmol, 84%;

N Ph

R_f(PE/DCM 5/1): 0.27;

Pure white solid;

¹**H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, J = 7.8 Hz, 4H), 7.27 – 7.20 (m, 7H), 7.13 (t, J = 7.2 Hz, 3H), 7.08 (t, J = 5.8 Hz, 3H), 6.77 (t, J = 7.6 Hz, 1H), 6.51 (d, J = 8.1 Hz, 1H), 3.63 (s, 3H), 3.08 – 3.01 (m, 2H), 2.46 – 2.39 (m, 2H), 1.79 (s, 3H);

¹³**C NMR** (101 MHz, CDCl₃) δ 148.49, 143.05, 136.85, 134.96, 128.32, 128.20, 128.09, 128.07, 127.89, 125.66, 122.10, 122.01, 120.12, 118.23, 115.95, 108.40, 52.50, 40.94, 32.53, 29.43, 13.47;

Exact Mass ESI-MS: calculated m/z for $[C_{31}H_{29}NNa]^+$: 438.2192, found: 438.2196.

1-(1,1,3-triphenylpropyl)-5,6-dihydro-4*H*-pyrrolo[3,2,1-ij]quinoline (6m)

65.0 mg, 0.152 mmol, 76%; Pure white solid; R_f(PE/DCM 6/1): 0.26; ¹**H NMR** (400 MHz, CDCl₃) δ 7.44 (d, *J* = 8.0 Hz, 4H), 7.29 – 7.22 (m, 6H), 7.21 – 7.09 (m, 5H), 6.95 (d, *J* = 7.5 Hz, 1H), 6.90 – 6.78 (m, 2H), 6.76 (s, 1H), 4.09 (t, *J* = 5.5 Hz, 2H), 3.03 – 2.89 (m, 4H), 2.49 – 2.39 (m, 2H), 2.27 – 2.19 (m, 2H);

¹³C NMR (101 MHz, CDCl₃) δ 147.37, 143.07, 135.05, 128.74, 128.33, 128.30, 127.80, 126.06, 125.73, 125.65, 124.71, 121.56, 121.14, 119.88, 118.86, 118.29, 52.43, 44.00, 42.59, 32.52, 24.78, 22.80; Exact Mass ESI-MS: calculated m/z for [C₃₂H₂₉NNa]⁺: 450.2192, found: 450.2195.

General procedure for the synthesis of 8a-8n:

The 2-bromoacetophenones (0.4 mmol, if solid), KHCO₃ (40.0 mg, 0.4 mmol, 2 equiv) and Zn(OAc)₂ (73.4 mg, 0.4 mmol, 2 equiv) was added to an oven-dried Schlenk tube (10 mL). The Schlenk tube was then connected to a vacuum line where it was evacuated and back-filled with N₂ for 3 times. Then anhydrous DCM (1 mL), alkenes (0.6 mmol, 3 equiv) and indoles (0.2 mmol) were added via syringe under N₂ atmosphere. Finally, the reaction mixture in sealed tube was placed at a distance of 1 ~ 2 cm from a 30 W blue LED (wavelength: 460 nm) and stirred at room temperature (40~45 °C) for 24 h. Then, the mixture was quenched with 1 mL of H₂O, extracted with AcOEt, then concentrated in vacuo. The residue was purified by silica gel flash chromatography (petroleum ether/AcOEt 30/1 ~ 7/1) to give the pure desired product.

4-(1-methyl-1H-indol-3-yl)-1,4,4-triphenylbutan-1-one (8a)

62.5 mg, 0.145 mmol, 73%; Pure white solid;

R_f(PE/DCM 3/1): 0.20;

¹H NMR (400 MHz, CDCl₃) δ 7.56 – 7.43 (m, 5H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.30 – 7.20 (m, 4H), 7.20 – 7.08 (m, 7H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.89 (s, 1H), 3.67 (s, 3H), 2.82 – 2.65 (m, 3H), 2.62 – 2.54 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 147.98, 147.61, 147.20, 137.63, 128.02, 127.79, 127.68, 126.46, 126.44, 126.34, 126.19, 126.15, 126.10, 125.99, 121.35, 121.29, 121.20, 118.87, 109.04, 89.21, 86.98, 37.49, 32.72; Exact Mass ESI-MS: calculated m/z for [C₃₁H₂₇NONa]⁺: 452.1985, found: 452.1980.

3-(5,5-diphenyl-2-(p-tolyl)tetrahydrofuran-2-yl)-1-methyl-1H-indole (8b)

58.8 mg, 0.132 mmol, 66%; Pure white solid;

R_f(PE/EA 30/1): 0.28;

¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, *J* = 7.5 Hz, 3H), 7.39 (d, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 2H), 7.20 – 7.08 (m, 6H), 7.00 – 6.91 (m, 3H), 6.85 (s, 1H), 3.60 (s, 3H), 2.81 – 2.63 (m, 3H), 2.59 – 2.53 (m, 1H), 2.23 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 148.08, 147.76, 144.23, 137.66, 135.77, 128.41, 128.01, 127.79, 126.49, 126.41, 126.30, 126.18, 126.14, 126.03, 121.36, 121.33, 118.84, 109.04, 89.13, 86.98, 37.58, 37.47, 32.70, 21.02;
Exact Mass ESI-MS: calculated m/z for [C₃₂H₂₉NONa]⁺: 466.2141, found: 466.2159.

3-(2-([1,1'-biphenyl]-4-yl)-5,5-diphenyltetrahydrofuran-2-yl)-1-methyl-1H-indole (8c)

61.8 mg, 0.122 mmol, 61%;

Pure white solid; R_f (PE/EA 20/1): 0.23;

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¹**H NMR** (400 MHz, CDCl₃) δ 7.62 – 7.45 (m, 7H), 7.40 (d, J = 6.9 Hz, 4H), 7.35 (t, J = 7.6 Hz, 2H), 7.28 (t, J = 7.6 Hz, 3H), 7.23 – 7.08 (m, 6H), 6.97 (t, J = 7.3 Hz, 1H), 6.91 (s, 1H), 3.64 (s, 3H), 2.85 – 2.70 (m, 3H), 2.61 (dd, J = 10.7, 5.8 Hz, 1H);

¹³**C NMR** (101 MHz, CDCl₃) δ 147.98, 147.61, 146.35, 140.99, 139.01, 137.66, 128.65, 128.06, 127.81, 126.99, 126.78, 126.49, 126.43, 126.21, 126.16, 126.14, 126.00, 121.43, 121.36, 121.10, 118.92, 109.10, 89.29, 86.92, 37.59, 37.57, 32.71;

Exact Mass ESI-MS: calculated m/z for [C₃₇H₃₁NONa]⁺: 528.2298 found: 528.2300.

3-(2-(1-methyl-1H-indol-3-yl)-5,5-diphenyltetrahydrofuran-2-yl)benzonitrile (8d)

50.4 mg, 0.110 mmol, 55%; Pure white solid;

R_f(PE/EA 10/1):0.30;

¹H NMR (400 MHz, CDCl₃) δ 7.54 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.35 – 7.27 (m, 4H), 7.26 – 7.16 (m, 4H), 7.15 – 7.06 (m, 3H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.95 (s, 1H), 3.71 (s, 3H), 2.86 – 2.64 (m, 3H), 2.56 – 2.48 (m, 1H);

¹³**C NMR** (151 MHz, CDCl₃) δ 153.01, 147.44, 146.92, 137.70, 131.72, 128.24, 127.86, 126.99, 126.82, 126.36, 126.18, 125.98, 125.91, 125.82, 121.81, 120.93, 119.92, 119.29, 119.11, 110.11, 109.30, 89.79, 86.60, 37.65, 37.30, 32.82;

Exact Mass ESI-MS: calculated m/z for [C₃₂H₂₆N₂ONa]⁺: 477.1937, found: 477.1947.

methyl 4-(2-(1-methyl-1H-indol-3-yl)-5,5-diphenyltetrahydrofuran-2-yl)benzoate (8e)



61.6 mg, 0.126 mmol, 63%;

R_f(PE/EA 7/1): 0.22;

Pure white solid;

¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.66 – 7.40 (m, 5H), 7.37 (d, *J* = 6.9 Hz, 2H), 7.31 – 7.08 (m, 8H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.93 (s, 1H), 3.84 (s, 3H), 3.69 (s, 3H), 2.85 – 2.64 (m, 3H), 2.57 (dt, *J* = 11.2, 5.7 Hz, 1H);

¹³**C NMR** (101 MHz, CDCl₃) δ 167.08, 152.64, 147.68, 147.20, 137.63, 129.13, 128.15, 128.09, 127.80, 126.61, 126.30, 126.26, 126.01, 125.97, 125.89, 121.56, 121.06, 120.39, 119.05, 109.13, 89.48, 86.78, 51.95, 51.90, 37.42, 32.77;

Exact Mass ESI-MS: calculated m/z for $[C_{33}H_{29}NO_3Na]^+$: 510.2040, found: 510.2049.

3-(2-(3-chlorophenyl)-5,5-diphenyltetrahydrofuran-2-yl)-1-methyl-1H-indole (8f)

68.6 mg, 0.148 mmol, 74%;

R_f (PE/EA 15/1): 0.35;

Pure white solid;

¹**H NMR** (400 MHz, CDCl₃) δ 7.56 – 7.46 (m, 3H), 7.44 – 7.32 (m, 4H), 7.31 – 7.07 (m, 10H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.90 (s, 1H), 3.68 (s, 3H), 2.82 – 2.66 (m, 3H), 2.57 – 2.51 (m, 1H);

¹³**C NMR** (101 MHz, CDCl₃) δ 149.59, 147.72, 147.24, 137.67, 133.63, 128.95, 128.10, 127.81, 126.75, 126.68, 126.62, 126.51, 126.30, 125.99, 125.91, 124.41, 121.55, 121.16, 121.12, 120.53, 119.07, 109.16, 89.48, 86.62, 37.54, 37.42, 32.77;

Exact Mass ESI-MS: calculated m/z for [C₃₁H₂₆CINONa]⁺: 486.1595, found: 486.1652.

3-(2-(3-bromophenyl)-5,5-diphenyltetrahydrofuran-2-yl)-1-methyl-1H-indole (8g)



70.6 mg, 0.138 mmol, 69%; Pure white solid; R_f (PE/EA 25/1): 0.23;

¹**H NMR** (400 MHz, CDCl₃) δ 7.57 (s, 1H), 7.53 – 7.47 (m, 3H), 7.38 (t, *J* = 8.6 Hz, 3H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.08 (m, 7H), 7.05 – 6.97 (m, 2H), 6.90 (s, 1H), 3.69 (s, 3H), 2.82 – 2.67 (m, 3H), 2.54 (dt, *J* = 10.8, 5.5 Hz, 1H);

¹³**C NMR** (151 MHz, CDCl₃) δ 149.85, 147.74, 147.24, 137.70, 129.65, 129.45, 129.30, 128.14, 127.84, 126.67, 126.34, 126.30, 126.09, 126.01, 125.94, 124.88, 122.04, 121.59, 121.17, 120.51, 119.10, 109.17, 89.51, 86.60, 37.58, 37.44, 32.78;

Exact Mass ESI-MS: calculated m/z for [C₃₁H₂₆NBrNONa]⁺: 530.1090, found: 530.1123.

3-(2-(3-methoxyphenyl)-5,5-diphenyltetrahydrofuran-2-yl)-1-methyl-1H-indole (8h)

41.2 mg, 0.090 mmol, 45%;



Pure white solid;

R_f(PE/EA 15/1): 0.28;

¹**H NMR** (400 MHz, CDCl₃) δ 7.59 – 7.50 (m, 3H), 7.37 (d, *J* = 7.0 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.23 (s, 1H), 7.20 – 7.03 (m, 7H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.94 – 6.87 (m, 2H), 6.64 (dd, *J* = 8.1, 1.7 Hz, 1H), 3.70 (s, 3H), 3.48 (s, 3H), 2.83 – 2.68 (m, 3H), 2.59 – 2.53 (m, 1H);

¹³C NMR (151 MHz, CDCl₃) δ 159.04, 149.33, 148.10, 147.75, 137.67, 128.66, 128.14, 127.81, 126.54, 126.40, 126.32, 126.27, 126.19, 125.98, 121.51, 121.46, 120.92, 118.96, 118.72, 112.45, 111.66, 109.07, 89.32, 87.15, 54.88, 37.86, 37.49, 32.76;

Exact Mass ESI-MS: calculated m/z for $[C_{32}H_{29}NO_2Na]^+$: 482.2091, found: 482.2097.

1-methyl-3-(2-(naphthalen-2-yl)-5,5-diphenyltetrahydrofuran-2-yl)-1H-indole (8i)



61.8 mg, 0.128 mmol, 64%; Pure white solid;

R_f(PE/EA 20/1): 0.22;

Nf (1 L/LA 20/1). 0.22

¹H NMR (400 MHz, CDCl₃) δ 7.94 (s, 1H), 7.74 – 7.69 (m, 1H), 7.63 (d, J = 8.7 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.55 – 7.48 (m, 3H), 7.43 (d, J = 7.2 Hz, 2H), 7.40 – 7.32 (m, 2H), 7.28 (t, J = 7.6 Hz, 2H), 7.26 – 7.08 (m, 7H), 6.96 (s, 1H), 6.91 (t, J = 7.5 Hz, 1H), 3.69 (s, 3H), 2.90 – 2.83 (m, 1H), 2.80 – 2.62 (m, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 148.01, 147.62, 144.50, 137.67, 132.88, 132.27, 128.31, 128.03, 127.83, 127.67, 127.37, 126.61, 126.53, 126.24, 126.22, 126.19, 126.05, 125.65, 125.45, 124.58, 121.42, 121.28, 120.77, 118.94, 109.05, 89.33, 87.19, 37.49, 37.20, 32.76;

Exact Mass ESI-MS: calculated m/z for [C₃₅H₂₉NONa]⁺: 502.2141, found: 502.2143.

3-(5,5-diphenyl-2-(thiophen-2-yl)tetrahydrofuran-2-yl)-1-methyl-1H-indole (8j)



46.2 mg, 0.106 mmol, 53%;

Pure white solid;

R_f(PE/EA 25/1): 0.29;

¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, J = 7.3 Hz, 2H), 7.48 – 7.41 (m, 3H), 7.31 – 7.26 (m, 2H), 7.23 (s, 1H), 7.21 – 7.09 (m, 6H), 6.99 (t, J = 7.4 Hz, 1H), 6.87 – 6.79 (m, 3H), 3.64 (s, 3H), 2.86 – 2.76 (m, 3H), 2.74 – 2.66 (m, 1H);

¹³C NMR (151 MHz, CDCl₃) δ 152.18, 147.64, 147.58, 137.63, 127.96, 127.93, 127.11, 126.47, 126.40, 126.23, 126.11, 126.01, 125.95, 124.56, 124.54, 121.45, 120.98, 120.66, 119.02, 109.19, 89.34, 84.65, 38.94, 37.85, 32.74.

Exact Mass ESI-MS: calculated m/z for [C₂₉H₂₅NOSNa]⁺: 458.1549, found: 458.1563.

1-methyl-3-(4-methyl-2,5,5-triphenyltetrahydrofuran-2-yl)-1H-indole (8k)

41.1 mg, 0.092 mmol, 46%; Pure white solid;

R_f(PE/EA 20/1): 0.24;

 $R_{f}(PE/EA 20/1). 0.24,$

¹**H NMR** (400 MHz, CDCl₃) δ 7.63 (dd, J = 8.2, 1.1 Hz, 2H), 7.39 – 7.33 (m, 3H), 7.30 (d, J = 8.2 Hz, 1H), 7.27 – 7.22 (m, 4H), 7.20 – 7.16 (m, 1H), 7.10 – 7.07 (m, 4H), 7.03 – 6.97 (m, 4H), 6.96 – 6.92 (m, 1H), 3.78 (s, 3H), 3.09 – 3.02 (m, 1H), 2.80 (dd, J = 11.8, 5.5 Hz, 1H), 2.49 (t, J = 12.2 Hz, 1H), 0.85 (d, J = 6.8 Hz, 3H);

¹³**C NMR** (101 MHz, CDCl₃) δ 148.51, 147.39, 144.33, 137.70, 128.19, 127.80, 127.53, 127.51, 127.04, 126.57, 126.23, 126.04, 125.85, 125.67, 125.48, 122.48, 121.55, 120.74, 118.92, 108.78, 88.49, 87.41, 45.03, 40.62, 32.81, 15.91;

Exact Mass ESI-MS: calculated m/z for [C₃₂H₂₉NONa]⁺: 466.2141, found: 466.2147.

3-(2-(3-chlorophenyl)-5,5-diphenyltetrahydrofuran-2-yl)-1-methyl-1H-indole (8I)



72.0 mg, 0.150 mmol, 75%;

Pure white solid;

R_f (PE/EA 30/1): 0.30;

¹**H NMR** (400 MHz, CDCl₃) δ 7.61 (d, *J* = 7.2 Hz, 2H), 7.44 – 7.34 (m, 3H), 7.32 – 7.19 (m, 6H), 7.12 – 7.05 (m, 2H), 6.99 (s, 6H), 3.79 (s, 3H), 3.05 (d, *J* = 6.5 Hz, 1H), 2.79 (d, *J* = 6.4 Hz, 1H), 2.50 – 2.42 (m, 1H), 0.88 (d, *J* = 6.3 Hz, 3H);

¹³**C NMR** (151 MHz, CDCl₃) δ 148.25, 147.06, 146.76, 137.75, 133.21, 128.35, 128.28, 128.01, 127.60, 127.28, 126.78, 126.50, 126.07, 126.04, 125.97, 125.64, 125.47, 122.32, 121.75, 120.06, 119.13, 108.92, 88.28, 87.65, 45.07, 40.73, 32.86, 15.92;

Exact Mass ESI-MS: calculated m/z for [C₃₂H₂₈CINONa]⁺: 500.1752, found: 500.1759.

3-(2,8-diphenyl-1-oxaspiro[4.5]decan-2-yl)-1-methyl-1H-indole (8m)

68.3 mg, 0.162 mmol, 81%;

Pure white solid;

R_f(PE/EA 20/1): 0.24;

¹**H NMR** (400 MHz, CDCl₃) δ 7.69 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 7.3 Hz, 2H), 7.31 – 7.28 (m, 2H),

7.27 – 7.23 (m, 3H), 7.22 – 7.15 (m, 5H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.82 (s, 1H), 3.72 (s, 3H), 2.90 (dd, *J* = 12.8, 6.9 Hz, 1H), 2.59 (ddd, *J* = 22.0, 13.2, 5.4 Hz, 3H), 2.08 (dd, *J* = 13.2, 6.1 Hz, 1H), 2.03 – 1.98 (m, 1H), 1.88 (dd, *J* = 15.5, 8.2 Hz, 6H);

¹³**C NMR** (101 MHz, CDCl₃) δ 147.68, 146.84, 137.72, 128.33, 127.76, 126.88, 126.86, 126.78, 126.48, 126.26, 125.99, 121.40, 121.30, 118.89, 109.12, 85.09, 84.27, 43.48, 39.27, 39.06, 38.79, 34.56, 32.74, 32.70, 32.51; **Exact Mass ESI-MS:** calculated m/z for [C₃₀H₃₁NONa]⁺: 444.2298, found: 444.2300.

ethyl 2-(1-methyl-1*H*-indol-3-yl)-2-phenyl-1-oxaspiro[4.5]decane-8-carboxylate (8n) 52.0 mg, 0.124 mmol, 62%;

Colourless oil;



R_f(PE/EA 10/1): 0.27;

¹**H NMR** (400 MHz, CDCl₃) δ 7.64 (d, J = 8.0 Hz, 1H), 7.57 – 7.46 (m, 2H), 7.31 – 7.20 (m, 3H), 7.20 – 7.06 (m, 2H), 7.03 – 6.96 (m, 1H), 6.80 (s, 1H), 4.10 (q, J = 7.1 Hz, 2H), 3.70 (s, 3H), 2.88 – 2.80 (m, 1H), 2.55 (dt, J = 12.7, 7.3 Hz, 1H), 2.33 (tt, J = 10.5, 3.8

Hz, 1H), 2.05 - 1.85 (m, 4H), 1.77 - 1.68 (m, 3H), 1.64 - 1.44 (m, 3H), 1.23 (t, J = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 175.81, 147.66, 137.68, 127.73, 126.54, 126.50, 126.42, 126.24, 126.06, 121.39, 121.27, 118.85, 109.07, 85.25, 83.54, 60.18, 41.89, 38.66, 37.56, 37.35, 35.12, 26.93, 26.85, 14.24, 14.22; Exact Mass ESI-MS: calculated m/z for [C₂₇H₃₁NO₃Na]⁺: 440.2196, found: 440.2199.

5. Some unsuccessful substrates

Standard Conditions R Ŕ X = CI, Br Benzyl halides Ph Br Br Ph² `CI Ph NC MeO N.D. 17% trace trace Alkenes P٢ Ph' OMe 18% N.D. trace trace Heteroaromatic hydrocarbon OMe Ŕ' R' = Ac, trace Y = O, N.D. 32% N.D. R' = Bz, N.D. Y = S, N.D.

1,2-Alkylarylation of alkenes, alkyl halides and *N*-alkylindoles



1,2-Alkylarylation cyclization of alkenes, alkyl halides and N-alkylindoles

6. Mechanistic studies

6.1. Radical inhibition experiments



An oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with K_2HPO_4 (69.7 mg, 0.4 mmol, 2 equiv), $Zn(OAc)_2$ (110.1 mg, 0.6 mmol, 3 equiv) and the radical scavenger (0.8 mmol, 3 equiv). The Schlenk tube was then connected to a vacuum line where it was evacuated and back-filled with N₂ for 3 times. Then anhydrous DCM (2 mL), benzyl bromide (48 µL, 0.4 mmol, 2 equiv), 1,1-diphenylethylene (106 µL, 0.6 mmol, 3 equiv) and 1-methylindole (26 µL, 0.2 mmol) were added via syringe under N₂ atmosphere. Finally, the reaction mixture in sealed tube was placed at a distance of 1 ~ 2 cm from a 30 W blue LED (wavelength: 460 nm) and stirred at room temperature for 48 h. Then, the mixture was quenched with 2 mL of H₂O, extracted with AcOEt, then concentrated in vacuo. The residue was purified by silica gel flash chromatography (petroleum ether/dichloromethane 5/1) to give the pure desired product.



NMR analysis of the diphenyl diselenide adduct:

An oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with K_2HPO_4 (69.7 mg, 0.4 mmol, 2 equiv), $Zn(OAc)_2$ (110.1 mg, 0.6 mmol, 3 equiv) and diphenyl diselenide (249.7 mg, 0.8 mmol, 4 equiv). The Schlenk tube was then connected to a vacuum line where it was evacuated and back-filled with N₂ for 3 times. Then anhydrous DCM (2 mL), benzyl bromide (48 µL, 0.4 mmol, 2 equiv), 1,1-diphenylethylene (106 µL, 0.6 mmol, 3 equiv) and 1-methylindole (26 µL, 0.2 mmol) were added via syringe under N₂ atmosphere. Finally, the reaction mixture in sealed tube was placed at a distance of 1 ~ 2 cm from a 30 W blue LED (wavelength: 460 nm) and stirred at room temperature for 48 h. Then, the mixture was quenched with 2 mL of H₂O, extracted with AcOEt, then concentrated in vacuo. The obtained residue was purified by silica gel flash column chromatography to give the pure product in 31% yield. The obtained product was confirmed to be benzyl(phenyl)selane by ¹H NMR. The formation of the benzyl(phenyl)selane indicating the generation of the benzylic radical from substrate **1a**.

benzyl(phenyl)selane^[4]

 $^1\!H$ NMR (400 MHz, CDCl_3) δ 7.49 – 7.35 (m, 2H), 7.35 – 6.95 (m, 8H), 4.10 (s, 2H).



6.2. UV/vis monitoring studies

Benzyl bromide 1a: Benzyl bromide 1a (96 µL, 0.8 mmol, 2 equiv) was dissolved in DCM (4 mL).

1,1-Diphenylethylene 2a: 1,1-Diphenylethylene 2a (212 µL, 1.2 mmol, 3 equiv) was dissolved in DCM (4 mL).

The mixture of **1a** and **2a**: Under nitrogen atmosphere, a mixture of **1a** (96 μL, 0.8 mmol, 2 equiv), **2a** (212 μL, 1.2 mmol, 3 equiv) in DCM (4 mL) was stirred at room temperature for 30 minutes.

The mixture of **1a**, **2a** and Zn(OAc)₂: Under nitrogen atmosphere, a mixture of **1a** (96 μ L, 0.8 mmol, 2 equiv), **2a** (212 μ L, 1.2 mmol, 3 equiv) and Zn(OAc)₂ (220.2 mg, 1.2 mmol, 3 equiv) in DCM (4 mL) was stirred at room temperature for 30 minutes.

The mixture of **1a**, **2a** and K₂HPO₄: Under nitrogen atmosphere, a mixture of **1a** (96 μ L, 0.8 mmol, 2 equiv), **2a** (212 μ L, 1.2 mmol, 3 equiv) and K₂HPO₄ (139.4 mg, 0.8 mmol, 2 equiv) in DCM (4 mL) was stirred at room temperature for 30 minutes.



Figure S2. Comparison of the UV/Vis absorption spectra of 1a, 2a,1a+2a, 1a+2a+Zn(OAc)₂, 1a+2a+K₂HPO₄.

Benzyl bromide 1a: Benzyl bromide 1a (96 µL, 0.8 mmol, 2 equiv) was dissolved in DCM (4 mL).

1-Methylindole 3a: 1-methylindole 3a (52 µL, 0.4 mmol) was dissolved in DCM (4 mL).

The mixture of **1a** and **3a**: Under nitrogen atmosphere, a mixture of **1a** (96 μ L, 0.8 mmol, 2 equiv), **3a** (52 μ L, 0.4 mmol) in DCM (4 mL) was stirred at room temperature for 30 minutes.

The mixture of **1a**, **3a** and Zn(OAc)₂: Under nitrogen atmosphere, a mixture of **1a** (96 μ L, 0.4 mmol, 2 equiv), **3a** (52 μ L, 0.4 mmol) and Zn(OAc)₂ (220.2 mg, 1.2 mmol, 3 equiv) in DCM (4 mL) was stirred at room temperature for 30 minutes.

The mixture of **1a**, **3a** and K₂HPO₄: Under nitrogen atmosphere, a mixture of **1a** (96 μ L, 0.8 mmol, 2 equiv), **3a** (52 μ L, 0.4 mmol) and K₂HPO₄ (139.4 mg, 0.8 mmol, 2 equiv) in DCM (4 mL) was stirred at room temperature for 30 minutes.



Figure S3. Comparison of the UV/Vis absorption spectra of 1a, 3a,1a+3a, 1a+3a+Zn(OAc)₂, 1a+3a+K₂HPO₄.

1,1-Diphenylethylene 2a: 1,1-Diphenylethylene 2a (212 µL, 1.2 mmol, 3 equiv) was dissolved in DCM (4 mL).

1-Methylindole 3a: 1-methylindole 3a (52 µL, 0.4 mmol) was dissolved in DCM (4 mL).

The mixture of **2a** and **3a**: Under nitrogen atmosphere, a mixture of **2a** (212 μ L, 1.2 mmol, 3 equiv), **3a** (52 μ L, 0.4 mmol) in DCM (4 mL) was stirred at room temperature for 30 minutes.

The mixture of **2a**, **3a** and Zn(OAc)₂: Under nitrogen atmosphere, a mixture of **2a** (212 μ L, 1.2 mmol, 3 equiv), **3a** (52 μ L, 0.4 mmol) and Zn(OAc)₂ (220.2 mg, 1.2 mmol, 3 equiv) in DCM (4 mL) was stirred at room temperature for 30 minutes.

The mixture of **2a**, **3a** and K₂HPO₄: Under nitrogen atmosphere, a mixture of **2a** (212 μ L, 1.2 mmol, 3 equiv), **3a** (52 μ L, 0.4 mmol) and K₂HPO₄ (139.4 mg, 0.8 mmol, 2 equiv) in DCM (4 mL) was stirred at room temperature for 30 minutes.



Figure S4. Comparison of the UV/Vis absorption spectra of 2a, 3a, 2a+3a, 2a+3a+Zn(OAc)₂, 2a+3a+K₂HPO₄.



Figure S5. Photographs of (1) mixture of benzyl bromide **1a**, 1,1-diphenylethylene **2a**, K_2HPO_4 , and $Zn(OAc)_2$ after ca. 10 minutes of photoirradiation (Ex = 455 nm); (2) mixture of benzyl bromide **1a**, 1-methylindole **3a**, K_2HPO_4 , and $Zn(OAc)_2$ after ca. 10 minutes of photoirradiation (Ex = 455 nm); (3) mixture of **2a**, **3a**, K_2HPO_4 , and $Zn(OAc)_2$ after ca. 10 minutes of photoirradiation (Ex = 455 nm); (4) mixture of **1a**, **2a**, **3a**, K_2HPO_4 and $Zn(OAc)_2$ after ca. 10 minutes of photoirradiation (Ex = 455 nm); (4) mixture of **1a**, **2a**, **3a**, K_2HPO_4 and $Zn(OAc)_2$ after ca. 10 minutes of photoirradiation (Ex = 455 nm); (4) mixture of **1a**, **2a**, **3a**, K_2HPO_4 and $Zn(OAc)_2$ after ca. 10 minutes of photoirradiation (Ex = 455 nm). All solutions are prepared and illuminated under air atmosphere.

From the UV/Vis spectra of **1a**, **2a**, **3a**, we found 1-methylindole **3a** at high concentrations (0.1 M) exhibits weak absorption in the visible light region, which explained why the reaction has 46% yield of **4a** when without $Zn(OAc)_2$. In addition, the UV/Vis spectra of **1a**+**3a**+ $Zn(OAc)_2$ has a significant red shift in the visible light region. This result also suggest this reaction was driven by the photochemical activity of electron donor–acceptor (EDA) complexes, formed by association of benzyl bromide **1a** and 1-methylindole **3a** under the assistance of $Zn(OAc)_2$.

6.3. Control experiments

6.3.1. the reaction of 1a and 3a



To an oven-dried Schlenk tube (10 mL) equipped with a magnetic stir bar was added K_2HPO_4 (69.7 mg, 0.4 mmol, 2 equiv) and $Zn(OAc)_2$ (110.1 mg, 0.6 mmol, 3 equiv), then the Schlenk tube was charged with N₂ three times. Anhydrous DCM (2 mL), benzyl bromide (48 µL, 0.4 mmol, 2 equiv) and 1-methylindole (26 µL, 0.2 mmol) were added via syringe under N₂ atmosphere and stirred at room temperature for 20 min. The reaction mixture was quenched with 2 mL of H₂O, extracted with AcOEt, then concentrated in vacuo. The characteristic peaks of newly generated substance was confirmed to be 3-benzyl-1-methyl-1*H*-indolecan by ¹H NMR and then the residue was further purified by silica gel flash column chromatography to obtain the pure product with 9% yield. **3-benzyl-1-methyl-1***H***-indole (9)**^[5]

Ph 4.0 mg, 0.018 mmol, 9%; Pure white solid;

R_f(PE): 0.22;

¹**H NMR** (400 MHz, CDCl₃) δ 7.49 (d, *J* = 7.9 Hz, 1H), 7.29 – 7.20 (m, 5H), 7.20 – 7.12 (m, 2H), 7.07 – 7.02 (m, 1H), 6.67 (s, 1H), 4.06 (s, 2H), 3.60 (s, 3H);

¹³**C NMR** (101 MHz, CDCl₃) δ 141.58, 137.30, 128.84, 128.47, 127.99, 127.25, 125.98, 121.71, 119.35, 118.92, 114.39, 109.29, 32.63, 31.68.



6.3.2. the reaction of 1a and 3a without light



To an oven-dried Schlenk tube (10 mL) equipped with a magnetic stir bar was added K_2HPO_4 (69.7 mg, 0.4 mmol, 2 equiv) and $Zn(OAc)_2$ (110.1 mg, 0.6 mmol, 3 equiv), then the Schlenk tube was charged with N₂ three times. Anhydrous DCM (2 mL), benzyl bromide (48 µL, 0.4 mmol, 2 equiv) and 1-methylindole (26 µL, 0.2 mmol) were added via syringe under N₂ atmosphere and stirred at room temperature for 48 h without light. After the reaction was finished, the reaction mixture was quenched with 2 mL of H₂O, extracted with AcOEt, then concentrated in vacuo. This reaction has no conversion and no product, which confirmed by ¹H NMR.

6.3.3. the reaction of 1a and 2a



To an oven-dried Schlenk tube (10 mL) equipped with a magnetic stir bar was added K_2HPO_4 (69.7 mg, 0.4 mmol) and $Zn(OAc)_2$ (110.1 mg, 0.6 mmol), then the Schlenk tube was charged with N_2 three times. Anhydrous DCM (2 mL), benzyl bromide (48 μ L, 0.4 mmol) and 1,1-diphenylethylene (106 μ L, 0.6 mmol) were added via syringe under N_2 atmosphere and stirred at room temperature for 48 h. After the reaction was finished, the

reaction mixture was quenched with 2 mL of H_2O , extracted with AcOEt, then concentrated in vacuo. This reaction has no conversion and no product, which confirmed by ¹H NMR.

First, when the reaction between **1a** and **3a** under the standard reaction conditions for 20 min, the crosscoupling product 3-benzyl-1-methyl-1*H*-indole (**9**) was generated in 9% yield. However, no product **9** was observed in this reaction without blue light. These two reactions provide significant evidence for the interaction between **1a** and **3a** via the SET process under blue light irradiation. Second, not any product could be detected when the reaction of **1a** and **2a** were conducted under the standard reaction conditions, which excluding the process of photo promoted homolytic fragmentation of alkyl halides.

7. The application of the reaction

7.1. Synthesis of 4a in gram scale



Following the general procedure, the reaction with **1a** (1.0 mL, 8 mmol, 2 equiv), **2a** (2.1 mL, 12 mmol, 3 equiv), **3a** (0.5 mL, 4 mmol), K₂HPO₄ (1.4 g, 8 mmol, 2 equiv), Zn(OAc)₂ (2.2 g, 12 mmol, 3 equiv) and DCM (30 mL) under N₂ for 48 h at at room temperature (about 40 °C) afforded **4a** as white solid (1.0 g, 63% yield).

7.2. Derivatization reaction of 4a

Synthesis of the prop-1-ene-1,1,3-triyltribenzene 10



A 10 mL Schlenk tube were charged with **4a** (85 mg, 0.2 mmol) and CuBr₂ (89 mg, 0.4 mmol, 2 equiv) with H₂O (80.0 μ L, 0.4 mmol, 2 equiv) in DCE (2.0 mL). Then, the system reacts at 70 °C for overnight. When the reaction was finished, the mixture was quenched with 2 mL of H₂O, extracted with AcOEt, then concentrated in vacuo. The residue was purified by silica gel flash chromatography (PE) to afford the pure desired product with 86% yield.

prop-1-ene-1,1,3-triyltribenzene (10) [6]

Ph ¹H NMR (400 MHz, CDCl₃) δ 7.48 – 7.12 (m, 15H), 6.27 (t, *J* = 7.6 Hz, 1H), 3.47 (d, *J* = 7.6 Hz, Ph 2H);

¹³**C NMR** (101 MHz, CDCl₃) δ 142.49, 140.97, 139.84, 129.96, 128.44, 128.33, 128.14, 127.37, 127.09, 126.03, 35.97.

Synthesis of the 1-methyl-2-tosyl-3-(1,1,3-triphenylpropyl)-1H-indole 11



A 10 mL Schlenk tube were charged with **4a** (85 mg, 0.2 mmol), Tosyl chloride (76 μ L, 0.4 mmol, 2 equiv), *fac*-Ir(ppy)₃ (3 mg, 0.004 mmol, 2 mol%) and Na₂CO₃ (64 mg, 0.6 mmol, 3 equiv) in MeCN (2.0 mL). Then, the system reacts at room temperature for overnight. When the reaction was finished, the mixture was quenched with 2 mL of H₂O, extracted with AcOEt, then concentrated in vacuo. The residue was purified by silica gel flash chromatography (PE/EA = 5:1) to afford the pure desired product with 52% yield.

1-methyl-2-tosyl-3-(1,1,3-triphenylpropyl)-1H-indole (11)

^{Ph} Ph Ph Ph Ph Ts 1 **H NMR** (400 MHz, CDCl₃) δ 7.98 (s, 1H), 7.84 (d, J = 8.1 Hz, 2H), 7.38 – 7.32 (m, 5H), 7.28 – 7.21 (m, 7H), 7.17 (dd, J = 16.8, 8.4 Hz, 5H), 7.05 (d, J = 7.4 Hz, 2H), 6.97 (s, 1H), 3.81 (s, 3H), 2.96 – 2.90 (m, 2H), 2.37 (s, 3H), 2.34 (m, J = 5.6 Hz, 2H);

¹³**C NMR** (151 MHz, CDCl₃) δ 146.42, 143.59, 142.50, 139.71, 136.64, 134.19, 132.78, 130.21, 129.80, 128.57, 128.44, 128.22, 128.09, 127.61, 126.15, 125.87, 122.96, 121.91, 117.38, 109.85, 52.19, 42.37, 33.22, 32.46, 21.58.

Synthesis of the 2-bromo-1-methyl-3-(1,1,3-triphenylpropyl)-1H-indole 12



A 10 mL Schlenk tube were charged with **4a** (85 mg, 0.2 mmol) and NBS (39 mg, 0.22 mmol) in DMSO (1.0 mL) and DCE (1.0 mL). Then, the system reacts at room temperature for overnight. When the reaction was finished, the mixture was quenched with 2 mL of H_2O , extracted with AcOEt, then concentrated in vacuo. The residue was purified by silica gel flash chromatography (PE/DCM = 10:1) to afford the pure desired product with 60% yield.

2-bromo-1-methyl-3-(1,1,3-triphenylpropyl)-1H-indole (12)

Ph Ph Ph Ph Ph Ph **1H NMR** (400 MHz, CDCl₃) δ 7.57 - 7.45 (m, 4H), 7.28 - 7.21 (m, 7H), 7.19 - 7.08 (m, 6H), Br 6.81 - 6.76 (m, 1H), 6.47 (d, J = 8.2 Hz, 1H), 3.74 (s, 3H), 3.20 - 3.12 (m, 2H), 2.48 - 2.40 (m, 2H);

¹³**C NMR** (101 MHz, CDCl₃) δ 146.94, 142.77, 136.97, 128.60, 128.53, 128.33, 127.97, 127.67, 125.89, 125.69, 122.35, 121.47, 118.94, 118.00, 114.90, 109.19, 52.81, 40.41, 32.42, 31.62;



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9. NMR spectra

1-methyl-3-(1,1,3-triphenylpropyl)-1*H*-indole (4a)







3-(3-([1,1'-biphenyl]-4-yl)-1,1-diphenylpropyl)-1-methyl-1H-indole (4c)

40 30

100 90 f1 (ppm)

160 150 140

120 110

--1



1-methyl-3-(3-(4-nitrophenyl)-1,1-diphenylpropyl)-1H-indole (4d)





methyl 4-(3-(1-methyl-1H-indol-3-yl)-3,3-diphenylpropyl)benzoate (4e)
1-methyl-3-(3-(4-nitrophenyl)-1,1-diphenylpropyl)-1H-indole (4f)





3-(1,1-diphenyl-3-(4-(trifluoromethoxy)phenyl)propyl)-1-methyl-1H-indole (4g)











3-(3-(4-chlorophenyl)-1,1-diphenylpropyl)-1-methyl-1H-indole (4i)





3-(3-(4-bromophenyl)-1,1-diphenylpropyl)-1-methyl-1*H*-indole (4j)





3-(3-(3-methoxyphenyl)-1,1-diphenylpropyl)-1-methyl-1*H*-indole (4k)





3-(1,1-diphenyl-3-(4-(trifluoromethyl)phenyl)propyl)-1-methyl-1H-indole (4l)

























methyl 4-(1-methyl-1H-indol-3-yl)-2,4,4-triphenylbutanoate (4r)





110 100 f1 (ppm) 190 180 150 140

-1







3-(1,3-diphenyl-1-(p-tolyl)propyl)-1-methyl-1*H*-indole (5a)





3-(1-([1,1'-biphenyl]-4-yl)-1,3-diphenylpropyl)-1-methyl-1*H*-indole (5b)





3-(1-(4-fluorophenyl)-1,3-diphenylpropyl)-1-methyl-1H-indole (5d)





3-(1-(4-chlorophenyl)-1,3-diphenylpropyl)-1-methyl-1*H*-indole (5e)





3-(1-(3-bromophenyl)-1,3-diphenylpropyl)-1-methyl-1*H*-indole (5f)





3-(1,3-diphenyl-1-(m-tolyl) propyl)-1-methyl-1*H*-indole (5g)





3-(1-(2-fluorophenyl)-1,3-diphenylpropyl)-1-methyl-1*H*-indole (5h)





3-(1-(2-chlorophenyl)-1,3-diphenylpropyl)-1-methyl-1*H*-indole (5i)



3-(1-(2-bromophenyl)-1,3-diphenylpropyl)-1-methyl-1H-indole (5j)



3-(1,3-diphenyl-1-(4-(prop-2-yn-1-yloxy)phenyl)propyl)-1-methyl-1H-indole (5k)



1-methyl-3-(1-(naphthalen-2-yl)-1,3-diphenylpropyl)-1H-indole (5l)



3-(1-(benzofuran-2-yl)-1,3-diphenylpropyl)-1-methyl-1*H*-indole (5m)



1-methyl-3-(9-phenethyl-9H-thioxanthen-9-yl)-1H-indole (5n)



3-(2,4-diphenylbutan-2-yl)-1-methyl-1*H*-indole (50)



1-ethyl-3-(1,1,3-triphenylpropyl)-1H-indole (6a)



benzyl-3-(1,1,3-triphenylpropyl)-1H-indole (6b)



4-fluoro-1-methyl-3-(1,1,3-triphenylpropyl)-1H-indole (6c)




4-chloro-1-methyl-3-(1,1,3-triphenylpropyl)-1*H*-indole (6d)





1,5-dimethyl-3-(1,1,3-triphenylpropyl)-1*H*-indole (6e)





5-methoxy-1-methyl-3-(1,1,3-triphenylpropyl)-1*H*-indole (6f)





5-fluoro-1-methyl-3-(1,1,3-triphenylpropyl)-1*H*-indole (6g)





5-chloro-1-methyl-3-(1,1,3-triphenylpropyl)-1*H*-indole (6h)



5-bromo-1-methyl-3-(1,1,3-triphenylpropyl)-1H-indole (6i)



6-methoxy-1-methyl-3-(1,1,3-triphenylpropyl)-1*H*-indole (6j)



7-methoxy-1-methyl-3-(1,1,3-triphenylpropyl)-1H-indole (6k)



1,2-dimethyl-3-(1,1,3-triphenylpropyl)-1*H*-indole (6l)

160 150

40 30

10 0

100 90 f1 (ppm)



1-(1,1,3-triphenylpropyl)-5,6-dihydro-4*H*-pyrrolo[3,2,1-ij]quinoline (6m)



4-(1-methyl-1H-indol-3-yl)-1,4,4-triphenylbutan-1-one (8a)



3-(5,5-diphenyl-2-(p-tolyl)tetrahydrofuran-2-yl)-1-methyl-1H-indole (8b)



3-(2-([1,1'-biphenyl]-4-yl)-5,5-diphenyltetrahydrofuran-2-yl)-1-methyl-1H-indole (8c)



3-(2-(1-methyl-1H-indol-3-yl)-5,5-diphenyltetrahydrofuran-2-yl)benzonitrile (8d)

120 110

190

180 170 160 150 140 130

100 90 f1 (ppm) 80 70 60 50

0

10

40 30 20



methyl 4-(2-(1-methyl-1H-indol-3-yl)-5,5-diphenyltetrahydrofuran-2-yl)benzoate (8e)



3-(2-(3-chlorophenyl)-5,5-diphenyltetrahydrofuran-2-yl)-1-methyl-1H-indole (8f)



3-(2-(3-bromophenyl)-5,5-diphenyltetrahydrofuran-2-yl)-1-methyl-1H-indole (8g)



3-(2-(3-methoxyphenyl)-5,5-diphenyltetrahydrofuran-2-yl)-1-methyl-1H-indole (8h)



1-methyl-3-(2-(naphthalen-2-yl)-5,5-diphenyltetrahydrofuran-2-yl)-1H-indole (8i)



3-(5,5-diphenyl-2-(thiophen-2-yl)tetrahydrofuran-2-yl)-1-methyl-1H-indole (8j)



1-methyl-3-(4-methyl-2,5,5-triphenyltetrahydrofuran-2-yl)-1H-indole (8k)



3-(2-(3-chlorophenyl)-5,5-diphenyltetrahydrofuran-2-yl)-1-methyl-1H-indole (8l)



3-(2,8-diphenyl-1-oxaspiro[4.5]decan-2-yl)-1-methyl-1H-indole (8m)



ethyl 2-(1-methyl-1H-indol-3-yl)-2-phenyl-1-oxaspiro[4.5]decane-8-carboxylate (8n)



3-benzyl-1-methyl-1*H*-indole (9)





prop-1-ene-1,1,3-triyltribenzene (10)



1-methyl-2-tosyl-3-(1,1,3-triphenylpropyl)-1*H*-indole (11)



2-bromo-1-methyl-3-(1,1,3-triphenylpropyl)-1*H*-indole (12)

