The Oxygen Switch in Visible-Light Photoredox Catalysis: Radical Additions and Cyclizations and Unexpected C-C-Bond Cleavage Reactions

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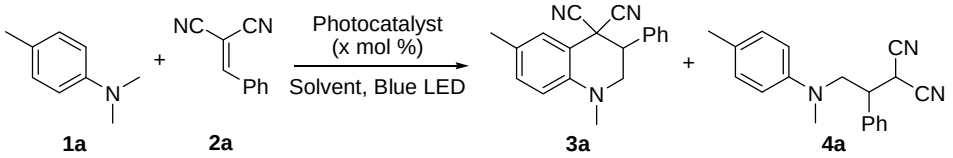
Supporting Information

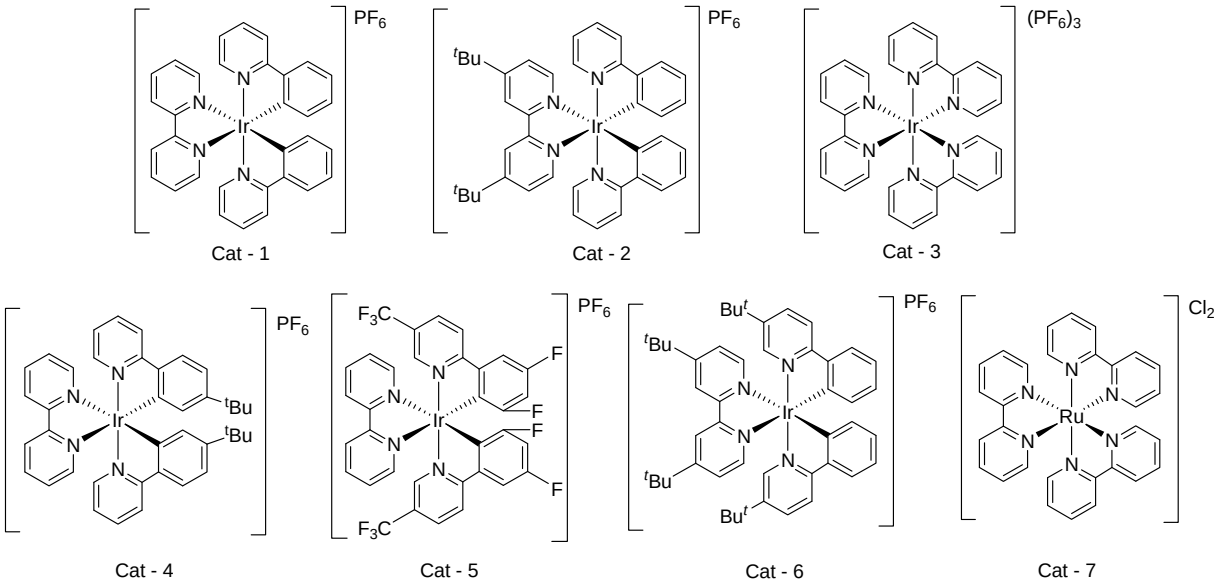
General: Unless otherwise noted, all commercially available compounds were used as provided without further purification. Solvents used in reactions were p.A. grade and dried only if indicated. Solvents for chromatography were technical grade and distilled prior to use. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel aluminium plates with F-254 indicator, visualised by irradiation with UV light. Column chromatography was performed using silica gel Merck 60 (particle size 0.063 – 0.2 mm). Solvent mixtures are understood as volume/volume.

^{1}H-NMR and ^{13}C-NMR were recorded on a Varian VNMR 400, VNMR 600 and Mercury 300 spectrometer in $CDCl_3$. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated br (broadened singlet), s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet); coupling constants (*J*) are in Hertz (Hz). Mass spectra (MS-EI, 70 eV) were conducted on Finnigan SSQ 7000. IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer and are reported in terms of frequency of absorption (cm^{-1}).

Table 1SI. Catalyst screening for the photoredox reaction.



1a **2a** **3a** **4a**



Cat - 1 Cat - 2 Cat - 3

Cat - 4 Cat - 5 Cat - 6 Cat - 7

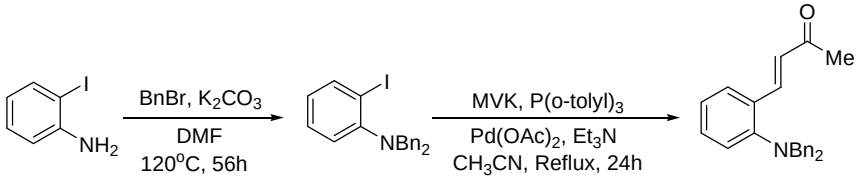
Entry[a]	Catalyst	time	Major product	Yield (%)[b]
1	Cat-1 (1 mol %)	32	**3a**	62
2	Cat-2 (1 mol %)	24	**3a**	54
3	Cat-3 (1 mol %)	28	**3a**	42
4	Cat-4 (1 mol %)	26	**3a**	47
5	Cat-5 (1 mol %)	24	**3a**	50
6	Cat-6 (1 mol %)	24	**3a**	54
7	Cat-7 (1 mol %)	24	**3a**	62
8[c]	Cat-1 (1 mol %)	48	--	0
9[d]	--	48	--	0
10	Cat-1 (5 mol %)	8	**3a**	68
11[e]	Cat-1 (1 mol %)	48	**4a**	67
12[e]	Cat-1 (5 mol %)	20	**4a**	91

[a] Reaction conditions: **1a** (0.26 mmol), **2a** (0.20 mmol), catalyst (1-5 mol%), Blue LED irradiation, MeCN (1.5 mL) and reaction mixture was degassed [b] Yield of the isolated product. [c] Reaction was carried out in the dark. [d] Reaction was carried out without catalyst. [e] Reaction was carried out under argon.

Representative procedure for the radical addition/cyclization reaction: An oven-dried test tube equipped with a stir bar was charged with $[Ir(ppy)_2bpy](PF_6)_2$ (5 mol%) and 2-benzylidenemalononitrile (**2a**; 0.2 mmol). The tube was sealed with a rubber stopper, evacuated and backfilled with argon for three times, then dry CH_3CN (1.5 mL) and *N*,*N*-dimethyl-4-methylaniline (**1a**; 0.26 mmol) were added under argon. The solution was stirred at room temperature under irradiation with visible light. After **2a** was completely consumed (monitored by TLC), the crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 20:1) to yield the corresponding product **3a**.

General procedure for radical addition of tertiary amines with electron-deficient alkenes: An oven-dried Schlenk tube was charged with 2-benzylidenemalononitrile (**2a**, 0.2 mmol) and $[Ir(ppy)_2bpy]PF_6$ (0.01 mmol) and was sealed with a rubber stopper, evacuated and backfilled with argon for three times, then dry CH_3CN (1.5 ml) and *N*,*N*-dimethyl-4-methylaniline (**1a**, 0.26 mmol) were added under argon. The solution was stirred at room temperature under irradiation with Blue LEDs. After **2a** was completely consumed (monitored by TLC), the crude mixture was purified by column chromatography (hexanes: ethyl acetate) to yield the corresponding product **4a**.

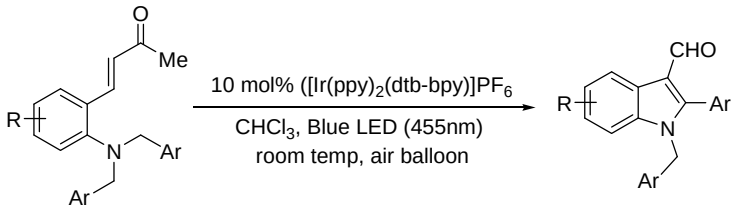
Experimental procedure for the synthesis of (*E)-4-(2-(dibenzylamino)phenyl)but-3-en-2-one*:



To a solution of *o*-iodoaniline (3.55 g, 16.2 mmol) in DMF (32.3 mL) was added K_2CO_3 (11.2 g, 80.8 mmol) and BnBr (7.69 mL, 64.6 mmol) at room temperature, followed by heating at 120 °C. After stirring for 48 h at 120 °C, the reaction was stopped by adding Et_2NH (4.20 mL, 40.4 mmol) at 0 °C. The crude products were extracted with ethyl acetate (x4) and the combined organic extracts were washed with brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 30/1) to afford dibenzylaniline (6.2 g, quant.) as a colorless oil.

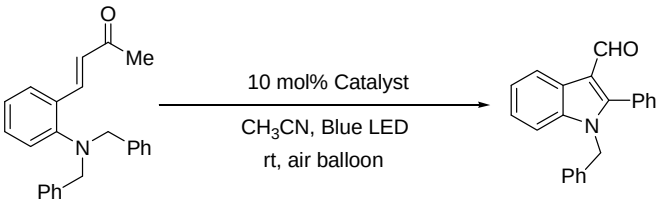
Mizoroki-Heck reaction of *N,N*-dibenzyl-2-iodoaniline: A N_2-purged 100 mL three-necked flask was charged with tri-*o*-tolyl phosphine (457 mg, 1.5 mmol), palladium (II) acetate (168 mg, 0.75 mmol), *N,N*-dibenzyl-2-iodoaniline (5.18 g, 13 mmol), methyl vinyl ketone (1.5 mL, 18 mmol), NEt_3 (2.29 mL, 16.5 mmol) and CH_3CN (60 mL). The system was immersed in an oil bath at reflux. After 24 h, it was removed from the oil bath, diluted with EtOAc (180 mL) and extracted with water (2 x 60 mL) and brine (60 mL). The organic layer was dried over Na_2SO_4 and volatiles were removed *in vacuo*. The residue was subjected to column chromatography on silica-gel (eluent; hexane/EtOAc = 5/1) to give (*E*)-4-(2-(dibenzylamino)phenyl)but-3-en-2-one (**5a**) (2.53 g, 7.41 mmol, 57% yield) as a viscous liquid.

Standard procedure for the photoredox catalyzed intramolecular Michael addition followed by oxidative cleavage reaction:

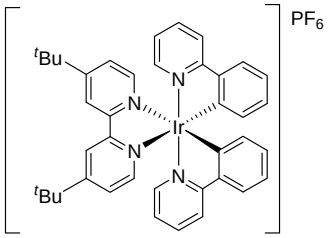


Photoredox catalyst $[Ir(ppy)_2(dtb\text{-}bpy)]PF_6$ (10 mol%) was transferred into a dried Schlenk tube. The sealed tube was fitted with an air balloon. A solution of the starting compound **5a** (0.2 mmol) in 2 mL chloroform (anhydrous) was added via syringe. After stirring for 22 h at room temperature, the reaction mixture was filtered through a short silica plug and the silica was washed with DCM. The organic solvents were evaporated *in vacuo* and the product was purified by column chromatography.

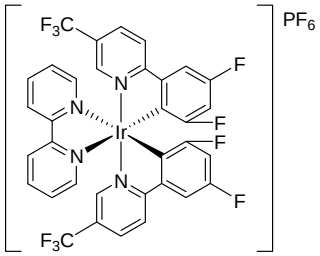
Table 2SI.



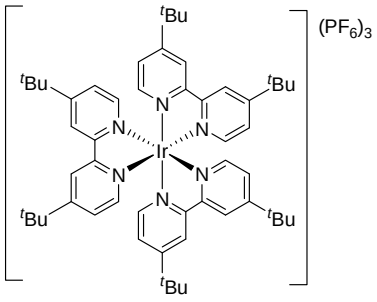
5a **6a**



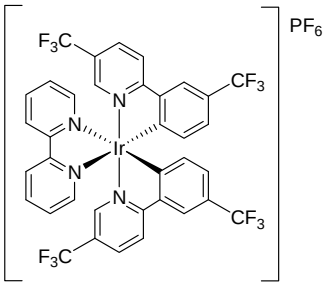
Cat-2



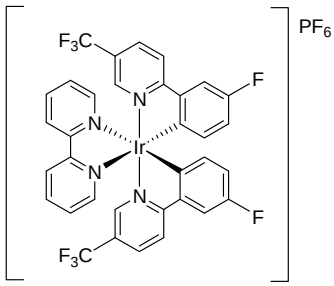
Cat-5



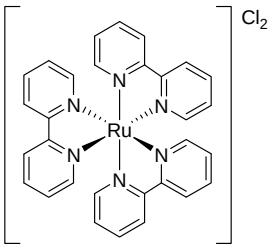
Cat-8



Cat-9



Cat-10



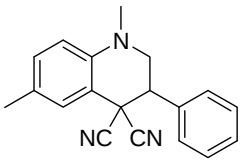
Cat-7

Entry[a]	Catalyst	Time[b] (h)	Yield[c] (%)
1.	**Cat-2**	**22**	**51**
2.	Cat-5	48	**5a** as mixture of E,Z-Isomer (1:1)
3.	Cat-8	48	**5a** as mixture of E,Z-Isomer (1:1)
4.	Cat-9	48	**5a** as mixture of E,Z-Isomer (1:1)
5.	Cat-10	48	**5a** as mixture of E,Z-Isomer (1:1)
6.	Cat-7	48	**5a** as mixture of E,Z-Isomer (1:1)
7.	TiO_2 (1.1 equiv.)	72	**5a** as mixture of E,Z-Isomer (1:1)
8.	ZnO (1.1 equiv.)	72	**5a** as mixture of E,Z-Isomer (1:1)

[a] Reaction conditions: 0.1 mmol substrate 10 mol% catalyst, 1 mL solvent.
[b] Refers to the time until all starting material is consumed.
[c] Yield of the isolated product.

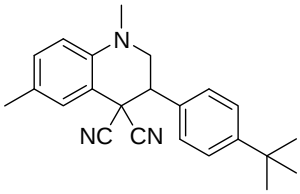
Photoredox radical addition/cyclization reaction:

1,6-dimethyl-3-phenyl-2,3-dihydroquinoline-4,4(1*H*)-dicarbonitrile (3a):



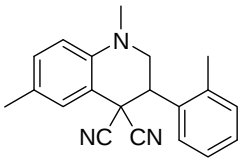
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.50 – 7.41 (m, 5H), 7.35 – 7.31 (m, 1H), 7.15 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.67 (d, *J* = 8.5 Hz, 1H), 3.90 (dd, *J* = 12.2, 11.4 Hz, 1H), 3.61 (dd, *J* = 11.4, 3.7 Hz, 1H), 3.48 (dd, *J* = 12.2, 3.7 Hz, 1H), 2.99 (s, 3H), 2.29 (s, 3H); ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ = 142.2, 135.1, 132.3, 129.5, 129.3, 128.6, 127.8, 127.4, 115.5, 114.4, 113.0, 112.8, 51.7, 45.9, 42.6, 39.1, 20.3; IR (neat): ν = 3361, 3035, 2919, 2850, 2230, 1960, 1888, 1816, 1706, 1622, 1520, 1454, 1294, 1212, 1118, 1000, 875, 809, 769, 700, 618, 500; MS-EI: *m/z*(%): 288 (23), 287 (100), 286 (10), 197 (12), 196 (86), 183 (20), 181 (15), 171 (14), 156 (10), 155 (10), 105 (11), 104 (15), 91 (23), 77 (14).

3-(4-(*tert*-butyl)phenyl)-1,6-dimethyl-2,3-dihydroquinoline-4,4(1*H*)-dicarbonitrile (3b):



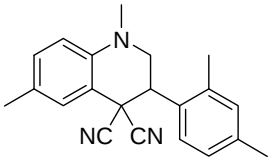
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.48 – 7.44 (m, 2H), 7.41 – 7.37 (m, 2H), 7.33 (s, 1H), 7.14 (dd, *J* = 8.5, 1.5 Hz, 1H), 6.66 (d, *J* = 8.5 Hz, 1H), 3.92 – 3.85 (m, 1H), 3.59 (dd, *J* = 11.5, 3.7 Hz, 1H), 3.46 (dd, *J* = 12.3, 3.7 Hz, 1H), 2.98 (s, 3H), 2.29 (s, 3H), 1.35 (s, 9H); ^{13}C-NMR (150.8 MHz, $CDCl_3$): δ = 152.4, 142.2, 132.5, 132.0, 129.3, 128.3, 127.3, 126.2, 115.7, 114.5, 112.9, 51.8, 45.5, 42.7, 39.1, 34.8, 31.4, 20.3; IR (neat): ν =3037, 2965, 2917, 2850, 2230, 1907, 1731, 1621, 1588, 1516, 1455, 1260, 1211, 1108, 1017, 887, 813, 705, 656; MS-EI: *m/z*(%): 344 (29), 343 (100), 328 (17), 197 (12), 196 (80), 181 (8), 171 (7), 164 (6), 145 (13), 117 (9), 115 (4), 105 (5), 91 (6), 77 (3).

1,6-dimethyl-3-(*o*-tolyl)-2,3-dihydroquinoline-4,4(1*H*)-dicarbonitrile (3c):



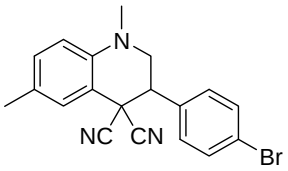
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.62 – 7.48 (m, 1H), 7.40 – 7.24 (m, 4H), 7.16 (ddd, *J* = 8.5, 2.1, 0.6 Hz, 1H), 6.68 (d, *J* = 8.5 Hz, 1H), 3.99 (dd, *J* = 11.3, 3.7 Hz, 1H), 3.90 – 3.81 (m, 1H), 3.37 (dd, *J* = 12.3, 3.7 Hz, 1H), 2.99 (s, 3H), 2.48 (s, 3H), 2.30 (s, 3H); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ = 142.0, 137.2, 133.7, 132.6, 131.5, 129.0, 128.9, 127.3, 127.1, 126.8, 115.5, 114.6, 113.5, 112.9, 52.3, 41.7, 40.6, 38.9, 20.3, 20.2; IR (neat): ν = 3029, 2852, 2333, 2242, 1815, 1708, 1622, 1574, 1521, 1459, 1384, 1344, 1292, 1248, 1208, 1164, 1121, 1075, 1000, 959, 911, 874, 769, 731, 622, 561, 512, 458; MS-EI: *m/z*(%): 302 (22), 301 (100), 300 (7), 286 (4), 197 (10), 196 (70), 195 (4), 183 (10), 182 (3), 181 (10), 171 (8), 169 (4), 168 (2) 156 (5), 155 (5), 130 (3), 129 (3), 128 (3), 118 (7), 117 (13), 116 (5), 115 (10), 105 (8), 103 (4), 102 (2), 91 (12), 89 (3), 79 (3), 78 (3), 77 (8), 65 (7), 63 (2), 51 (3).

3-(2,4-dimethylphenyl)-1,6-dimethyl-2,3-dihydroquinoline-4,4(1*H*)-dicarbonitrile (3d):



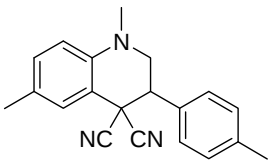
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.46 – 7.41 (m, 1H), 7.35 – 7.32 (m, 1H), 7.18 – 7.07 (m, 3H), 6.67 (d, *J* = 8.5 Hz, 1H), 3.95 (dd, *J* = 11.4, 3.4 Hz, 1H), 3.91 – 3.77 (m, 1H), 3.35 (dd, *J* = 11.9, 3.4 Hz, 1H), 2.98 (s, 3H), 2.44 (s, 3H), 2.34 (s, 3H), 2.30 (s, 3H); ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ = 142.0, 138.8, 137.0, 132.5, 132.2, 130.6, 128.9, 127.8, 127.2, 126.7, 115.4, 114.7, 113.5, 112.9, 52.4, 40.4, 38.9, 21.2, 20.3, 20.1; IR (neat): ν = 3312, 3026, 2920, 2832, 2239, 2086, 1900, 1693, 1621, 1575, 1518, 1448, 1411, 1380, 1344, 1291, 1255, 1213, 1168, 1112, 1071, 1034, 999, 947, 887, 808, 732, 680 MS-EI: *m/z*(%): 316 (16), 315 (80), 197 (14), 196 (100), 195 (7), 183 (9), 181 (11), 171 (8), 132 (9), 117 (12), 115 (10), 91 (9), 77 (4).

3-(4-bromophenyl)-1,6-dimethyl-2,3-dihydroquinoline-4,4(1*H*)-dicarbonitrile (3e):



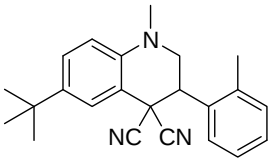
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 8.5 Hz, 2H), 7.35 – 7.30 (m, 3H), 7.15 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.67 (d, *J* = 8.5 Hz, 1H), 3.84 (dd, *J* = 12.2, 11.2 Hz, 1H), 3.59 (dd, *J* = 11.2, 3.7 Hz, 1H), 3.47 (dd, *J* = 12.2, 3.7 Hz, 1H), 2.99 (s, 3H), 2.29 (s, 3H); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ = 142.1, 134.1, 132.7, 132.5, 130.2, 129.3, 127.7, 123.8, 115.4, 114.2, 113.0, 112.4, 51.5, 45.4, 42.3, 39.1, 20.3; IR (neat): ν = 3426, 2922, 2852, 2051, 1903, 1708, 1620, 1568, 1520, 1487, 1448, 1406, 1346, 1294, 1239, 1213, 1113, 1072, 1005, 941, 873, 812, 726, 676; MS-EI: *m/z*(%): 368 (21), 367 (100), 366 (32), 365 (97), 364 (9), 197 (12), 196 (93), 184 (9), 183 (19), 182 (12), 181 (17), 171 (15), 169 (10), 156 (11) 155 (13), 129 (4), 128 (5), 115 (7), 105 (9), 103 (11), 102 (7), 91 (6), 90 (5), 89 (7), 77 (16), 76 (6), 75 (5), 63 (5), 51 (5), 50 (4).

1,6-dimethyl-3-(*p*-tolyl)-2,3-dihydroquinoline-4,4(1*H*)-dicarbonitrile (3f):



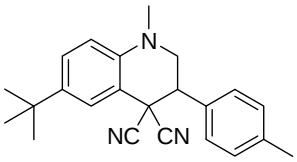
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.36 – 7.29 (m, 3H), 7.26 – 7.21 (m, 2H), 7.12 (ddd, *J* = 8.5, 2.0, 0.6 Hz Hz, 1H), 6.64 (d, *J* = 8.5 Hz, 1H), 3.86 (dd, *J* = 12.2, 11.5 Hz, 1H), 3.56 (dd, *J* = 11.5, 3.7 Hz, 1H), 3.44 (dd, *J* = 12.2, 3.7 Hz, 1H), 2.97 (s, 3H), 2.37 (s, 3H), 2.27 (s, 3H); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ = 142.2, 139.4, 132.5, 132.1, 123.0, 129.3, 128.4, 127.4, 115.6, 114.5, 112.9, 51.7, 45.6, 42.8, 39.1, 21.3, 20.3; IR (neat): ν =3025, 2920, 2854, 2248, 1904, 1806, 1719, 1621, 1519, 1456, 1345, 1293, 1252, 1208, 1118, 1000, 911, 812, 732, 569, 509; MS-EI: *m/z*(%): 302 (18), 301 (93), 300 (7), 197 (13), 196 (100), 195 (6), 182 (4), 171 (10), 118 (17), 117 (16), 105 (12), 91 (10), 77 (7).

6-(*tert*-butyl)-1-methyl-3-(*o*-tolyl)-2,3-dihydroquinoline-4,4(1*H*)-dicarbonitrile (3g):



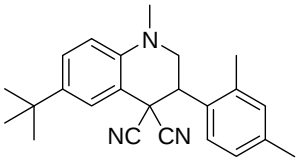
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.60 – 7.55 (m, 1H), 7.52 (d, *J* = 2.3 Hz, 1H), 7.39 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.34 – 7.29 (m, 3H), 6.72 (d, *J* = 8.8 Hz, 1H), 4.00 (dd, *J* = 11.5, 3.7 Hz, 1H), 3.94 – 3.85 (m, 1H), 3.36 (dd, *J* = 12.2, 3.7 Hz, 1H), 3.00 (s, 3H), 2.48 (s, 3H), 1.33 (s, 9H); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ = 141.9, 140.9, 137.2, 133.7, 131.5, 129.0, 127.1, 126.8, 125.2, 115.3, 114.7, 113.1, 112.6, 52.3, 42.1, 40.7, 38.8, 34.2, 31.5, 20.3; IR (neat): ν = 3434, 2922, 2246, 1735, 1618, 1521, 1460, 1373, 1292, 1216, 1119, 907, 757, 668, 577, 457; MS-EI: *m/z*(%): 344 (13), 343 (53), 342 (3), 330 (3), 329 (24), 328 (100), 327 (4), 182 (3), 169 (2), 160 (6), 117 (5), 116 (2), 115 (4), 105 (4), 91 (4), 77 (3), 65 (2), 57 (5).

6-(*tert*-butyl)-1-methyl-3-(*p*-tolyl)-2,3-dihydroquinoline-4,4(1*H*)-dicarbonitrile (3h):



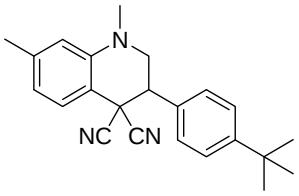
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 2.3 Hz, 1H), 7.29 (dd, *J* = 8.7, 2.3 Hz, 3H), 7.24 – 7.15 (m, 3H), 6.63 (d, *J* = 8.7 Hz, 1H), 3.89 – 3.77 (m, 1H), 3.50 (dd, *J* = 11.5, 3.7 Hz, 1H), 3.37 (dd, *J* = 12.2, 3.7 Hz, 1H), 2.92 (s, 3H), 2.32 (s, 3H), 1.24 (s, 9H); ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ = 142.1, 141.0, 139.4, 132.1, 130.0, 129.0, 128.4, 127.8, 125.6, 114.4, 112.7, 51.7, 45.7, 39.0, 31.4, 31.1, 21.4; IR (neat): ν = 3438, 2919, 2853, 2421, 2237, 1731, 1675, 1617, 1579, 1540, 1462, 1382, 1248, 1201, 1113, 926, 876, 819, 725, 525, 459; MS-EI: *m/z*(%): 344 (13), 343 (53), 342 (3), 330 (3), 329 (24), 328 (100), 327 (4), 182 (3), 169 (2), 160 (6), 117 (5), 116 (2), 115 (4), 105 (4), 91 (4), 77 (3), 65 (2), 57 (5).

6-(*tert*-butyl)-3-(2,4-dimethylphenyl)-1-methyl-2,3-dihydroquinoline-4,4(1*H*)-dicarbonitrile (3i):



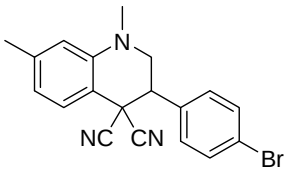
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 2.3 Hz, 1H), 7.45 (d, *J* = 8.7 Hz, 1H), 7.38 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.10 – 7.15 (m, 2H), 6.71 (d, *J* = 8.7 Hz, 1H), 3.96 (dd, *J* = 11.5, 3.5 Hz, 1H), 3.91 – 3.83 (m, 1H), 3.34 (dd, *J* = 12.0, 3.5 Hz, 1H), 3.00 (s, 3H), 2.44 (s, 3H), 2.35 (s, 3H), 1.32 (s, 9H); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ = 141.9, 140.8, 138.8, 137.0, 132.3, 130.7, 128.9, 127.8, 126.7, 125.2, 115.3, 114.7, 113.1, 112.6, 52.4, 42.2, 40.4, 38.8, 34.2, 31.5, 21.2, 20.2; IR (neat): ν = 3427, 2959, 2855, 2243, 1896, 1705, 1617, 1578, 1520, 1461, 1383, 1347, 1293, 1218, 1127, 1000, 961, 883, 817, 757, 665, 620, 546, 518, 459; MS-EI: *m/z*(%): 359 (3), 358 (20), 357 (72), 356 (7), 344 (4), 343 (21), 342 (100), 341 (4), 238 (6), 182 (7), 160 (4), 157 (2), 132 (2), 131 (2), 119 (3), 117 (4), 115 (3), 91 (3), 57 (8).

3-(4-(tert-butyl)phenyl)-1,7-dimethyl-2,3-dihydroquinoline-4,4(1H)-dicarbonitrile (3j):



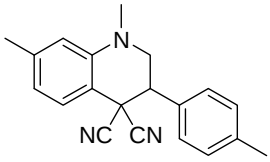
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.47 – 7.44 (m, 2H), 7.41 – 7.38 (m, 3H), 6.64 (d, *J* = 7.8 Hz, 1H), 6.54 (s, 1H), 3.93 (t, *J* = 11.8Hz, 1H), 3.56 (dd, *J* = 3.8, *J* = 11.5 Hz, 1H), 3.47 (dd, *J* = 3.8, 12.4 Hz 1H), 3.01 (s, 3H), 2.34 (s, 3H), 1.34 (s, 9H); ^{13}C-NMR (150.8 MHz, $CDCl_3$): δ = 152.3, 143.9, 141.9, 131.8, 128.7, 128.1, 126.0, 118.6, 115.4, 114.3, 113.0, 110.2, 51.5, 45.2, 42.3, 38.8, 34.7, 31.2, 21.8; IR (neat): ν = 3742, 2957, 2865, 2324, 1736, 1606, 1508, 1360, 1250, 1112, 1019, 836, 785, 687; MS-EI: m/z = 196 (83), 197 (12), 343 (100), 344 (28), 345 (5).

3-(4-bromophenyl)-1,7-dimethyl-2,3-dihydroquinoline-4,4(1H)-dicarbonitrile (3k):



^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.59 – 7.57 (m, 2H), 7.39 (d, *J* = 7.9, 1H), 7.34 – 7.32 (m, 2H), 6.66 (d, *J* = 8.7 Hz, 1H), 6.55 (s, 1H), 3.88 (dd, *J* = 11.3, *J* = 12.3 Hz, 1H), 3.56 (dd, *J* = 3.8, *J* = 11.2 Hz, 1H), 3.48 (dd, *J* = 3.8, *J* = 12.4 Hz 1H), 3.01 (s, 3H), 2.35 (s, 3H); ^{13}C-NMR (150.8 MHz, $CDCl_3$): δ = 143.8, 142.2, 133.8, 132.3, 130.0, 128.7, 123.7, 118.9, 115.1, 114.0, 113.1, 109.7, 51.2, 45.2, 41.9, 38.8, 21.8; IR (neat): ν = 2923, 2852, 1695, 1605, 1570, 1490, 1459, 1305, 1246, 1109, 1074, 1008, 950, 804, 728, 661; MS-EI: m/z = 196 (92), 197 (13), 365 (100), 366 (26), 367 (99), 368 (23).

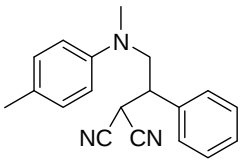
1,7-dimethyl-3-(p-tolyl)-2,3-dihydroquinoline-4,4(1H)-dicarbonitrile (3l):



^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 1H), 6.64 (d, *J* = 7.9 Hz, 1H), 6.54 (s, 1H), 3.91 (t, *J* = 11.5Hz, 1H), 3.57 (dd, *J* = 3.8, *J* = 11.4 Hz, 1H), 3.48 (dd, *J* = 3.9, *J* = 12.4 Hz 1H), 3.01 (s, 3H), 2.39 (s, 3H), 2.34 (s, 3H); ^{13}C-NMR (150.8 MHz, $CDCl_3$): δ = 143.9, 142.0, 139.2, 131.8, 129.8, 128.7, 128.3, 118.6, 115.4, 114.3, 113.0, 110.1, 51.5, 45.3, 42.4, 38.8, 21.8, 21.2; IR (neat): ν = 3741, 3208, 2924, 2842, 2606, 2330, 2157, 1607, 1571, 1508, 1412, 1301, 1245, 1114, 1016, 809, 725, 668; MS-EI: m/z = 117 (19), 196 (100), 197 (14), 301 (100), 302 (25).

Photoredox radical addition reaction:

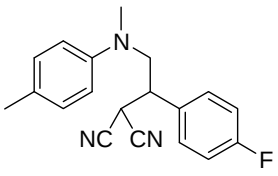
2-(2-(methyl(*p*-tolyl)amino)-1-phenylethyl)malononitrile (4a):



^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.49 – 7.38 (m, 5H), 7.12 (d, *J* = 8.7 Hz, 2H), 6.76 (d, *J* = 8.7 Hz, 2H), 4.29 (d, *J* = 4.3 Hz, 1H), 3.89 – 3.75 (m, 1H), 3.70 – 3.54 (m, 2H), 2.95 (s, 3H), 2.30 (s, 3H); ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ = 146.7, 135.0, 130.3, 129.5, 129.5, 128.8, 128.3, 114.8, 112.4, 111.9, 55.7, 45.0, 41.5, 27.1, 20.5; IR (neat): ν = 3435, 2919, 2850, 2254, 1882, 1724, 1616, 1577, 1519, 1452, 1382, 1240, 1183,

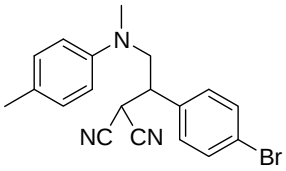
1119, 1031, 806, 760, 700, 611, 524; MS-EI: *m/z*(%): 290 (2), 289 (10), 135 (9), 134 (100), 119 (6), 118 (7), 91 (12), 78 (3), 77 (6), 65 (5).

2-(1-(4-fluorophenyl)-2-(methyl(*p*-tolyl)amino)ethyl)malononitrile (4b):



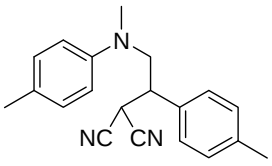
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.42 – 7.36 (m, 2H), 7.17 – 7.10 (m, 4H), 6.75 (d, *J* = 8.5 Hz, 2H), 4.31 – 4.28 (m, 1H), 3.81 – 3.73 (m, 1H), 3.64 – 3.56 (m, 2H), 2.95 (s, 3H), 2.29 (s, 3H); ^{13}C-NMR (150.8 MHz, $CDCl_3$): δ = 163.3 (d, J_{CF} = 249 Hz), 146.7, 130.3, 130.1, 129.1, 116.6, 116.5, 115.0, 112.3, 111.73, 55.8, 44.3, 41.6, 27.1, 20.5; IR (neat): ν = 3436, 2920, 2851, 2230, 1890, 1726, 1608, 1515, 1457, 1382, 1235, 1163, 1120, 1045, 942, 835, 809, 760, 604, 524; MS-EI: *m/z*(%): 307 (6), 135 (10), 134 (100), 119 (7), 118 (7), 91 (11), 77 (3), 65 (5).

2-(1-(4-bromophenyl)-2-(methyl(*p*-tolyl)amino)ethyl)malononitrile (4c):



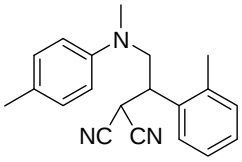
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.59 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.75 (d, *J* = 8.5 Hz, 2H), 4.29 (d, *J* = 4.4 Hz, 1H), 3.77 (dd, *J* = 14.7, 10.5 Hz, 1H), 3.60 (dd, *J* = 14.7, 5.0 Hz, 1H), 3.58 – 3.54 (m, 1H), 2.94 (s, 3H), 2.29 (s, 3H); ^{13}C-NMR (150.8 MHz, $CDCl_3$): δ = 146.0, 133.9, 132.7, 130.3, 129.9, 129.1, 123.7, 115.0, 112.2, 111.6, 55.6, 44.5, 41.6, 26.9, 20.5; IR (neat): ν = 2914, 2254, 1901, 1708, 1616, 1519, 1488, 1346, 1238, 1183, 1122, 1074, 1010, 910, 811, 732, 520; MS-EI: *m/z*(%): 369 (4), 367 (4), 135 (11), 134 (100), 133 (4), 119 (7), 118 (7), 91 (12), 77 (4), 65 (6).

2-(2-(methyl(*p*-tolyl)amino)-1-(*p*-tolyl)ethyl)malononitrile (4d):



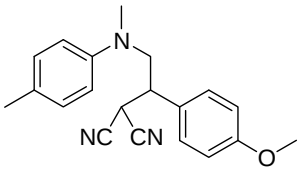
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.31 – 7.14 (m, 4H), 7.04 (d, *J* = 8.7 Hz, 2H), 6.68 (d, *J* = 8.7 Hz, 2H), 4.19 (d, *J* = 4.1 Hz, 1H), 3.77 – 3.67 (m, 1H), 3.59 – 3.45 (m, 2H), 2.87 (s, 3H), 2.31 (s, 3H), 2.21 (s, 3H); ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ = 146.8, 139.4, 132.0, 130.2, 130.1, 128.7, 128.1, 114.8, 112.5, 112.0, 55.8, 44.7, 41.5, 27.2, 21.3, 20.5; IR (neat): ν = 3665, 3031, 2917, 2228, 1908, 1802, 1709, 1615, 1587, 1518, 1451, 1349, 1240, 1185, 1119, 1043, 911, 811, 731, 613, 520; MS-EI: *m/z*(%): 304 (2), 303 (9), 135 (11), 134 (100), 119 (6), 118 (6), 117 (3), 91 (10), 77 (3), 65 (5).

2-(2-(methyl(*p*-tolyl)amino)-1-(*o*-tolyl)ethyl)malononitrile (4e):



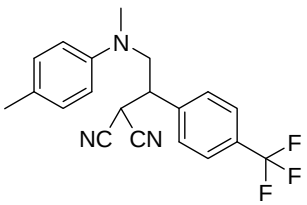
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.43 – 7.37 (m, 1H), 7.27 – 7.15 (m, 3H), 7.03 (dd, *J* = 8.8, 0.7 Hz, 2H), 6.64 (d, *J* = 8.8 Hz, 2H), 4.08 (d, *J* = 5.5 Hz, 1H), 3.97 – 3.86 (m, 1H), 3.76 (dd, *J* = 14.7, 9.4 Hz, 1H), 3.50 (dd, *J* = 14.7, 5.4 Hz, 1H), 2.82 (s, 3H), 2.25 (s, 3H), 2.20 (s, 3H); ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ = 146.4, 137.1, 134.0, 131.6, 130.2, 128.9, 128.3, 127.2, 126.2, 114.4, 112.4, 112.1, 56.2, 41.544, 39.2, 26.6, 20.4, 19.9; IR (neat): ν = 3411, 3065, 3032, 2956, 2920, 2850, 2229, 1711, 1622, 1528, 1519, 1457, 1384, 1345 ,1294, 1209, 1163, 1121, 1032, 998, 911, 874, 809, 733, 618, 479; MS-EI: *m/z*(%): 302 (20), 301 (100), 300 (6), 286 (4), 273 (3), 197 (11), 196 (77), 183 (10), 181 (12), 171 (9), 169 (4), 167 (3), 156 (5), 155 (5), 130 (6), 118 (6), 117 (12), 115 (9), 105 (9), 103 (5), 91 (9), 77 (8), 65 (5).

2-(1-(4-methoxyphenyl)-2-(methyl(*p*-tolyl)amino)ethyl)malononitrile (4f):



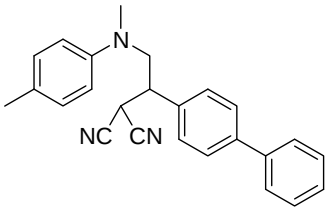
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.33 (d, *J* = 8.7 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 6.97 (d, *J* = 8.7 Hz, 2H), 6.75 (d, *J* = 8.7 Hz, 2H), 4.26 (d, *J* = 4.2 Hz, 1H), 3.86 – 3.74 (m, 4H), 3.64 – 3.52 (m, 2H), 2.94 (s, 3H), 2.29 (s, 3H); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ = 160.2, 146.6, 133.4, 130.1, 129.3, 128.5, 126.7, 114.7, 114.6, 114.5, 112.4, 111.8, 55.7, 55.3, 44.2, 41.3, 27.2, 20.3; IR (neat): ν = 3434, 3011, 2919, 2849, 2226, 2053, 1882, 1713, 1615, 1579, 1515, 1460, 1381, 1252, 1180, 1117, 1030, 808, 730, 528, 461; MS-EI: *m/z*(%): 319 (6), 317 (3), 196 (4), 135 (10), 134 (100), 133 (7), 119 (7), 118 (6), 91 (10), 77 (3), 65 (4).

2-(2-(methyl(*p*-tolyl)amino)-1-(4-(trifluoromethyl)phenyl)ethyl)malononitrile (4g):



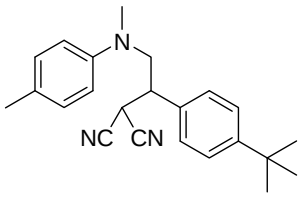
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 6.76 (d, *J* = 8.6 Hz, 2H), 4.35 (d, *J* = 4.3 Hz, 1H), 3.81 (dd, *J* = 15.7, 11.7 Hz, 1H), 3.69 – 3.61 (m, 2H), 2.95 (s, 3H), 2.30 (s, 3H); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ = 146.6, 138.9, 132.7, 132.0, 130.4, 129.4, 128.9, 126.5 (q, J_{CF} = 4 Hz), 115.2, 112.0, 111.5, 55.6, 44.7, 41.8, 26.8, 20.5; IR (neat): ν =2919, 2234, 1708, 1618, 1575, 1519, 1426, 1382, 1325, 1241, 1173, 1115, 1069, 1017, 840, 809, 731, 610, 517; MS-EI: *m/z*(%): 358 (2), 357 (10), 135 (10), 134 (100), 119 (7), 118 (8), 91 (14), 77 (4), 65 (6).

2-(1-([1,1'-biphenyl]-4-yl)-2-(methyl(*p*-tolyl)amino)ethyl)malononitrile (4h):



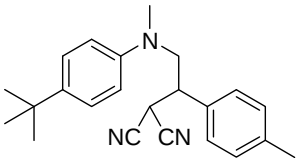
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 8.3 Hz, 2H), 7.63 – 7.59 (m, 2H), 7.51 – 7.44 (m, 4H), 7.41 – 7.36 (m, 1H), 7.13 (d, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 4.33 (d, *J* = 4.3 Hz, 1H), 3.91 – 3.80 (m, 1H), 3.72 – 3.61 (m, 2H), 2.98 (s, 3H), 2.30 (s,3H); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ = 146.8, 142.4, 140.3, 133.9, 130.3, 129.0, 128.9, 128.7, 128.1, 127.9, 127.3, 114.9, 112.4, 111.9, 55.8, 44.7, 41.6, 27.1, 20.5; IR (neat): ν = 3437, 3030, 2918, 2854, 2254, 1882, 1710, 1616, 1576, 1519, 1450, 1381, 1339, 1215, 1189, 1116, 836, 807, 761, 697, 514; MS-EI: *m/z*(%): 366 (2), 365 (8), 230 (3), 165 (3), 135 (10), 134 (100), 119 (6), 118 (5), 91 (8), 77(3), 65 (3), 57 (3).

2-(1-(4-(*tert*-butyl)phenyl)-2-(methyl(*p*-tolyl)amino)ethyl)malononitrile (4i):



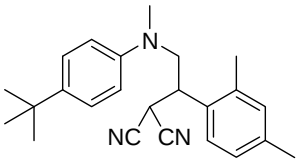
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.7 Hz, 2H), 6.76 (d, *J* = 8.7 Hz, 2H), 4.29 (d, *J* = 4.2 Hz, 1H), 3.79 (dd, *J* = 14.7, 10.8 Hz, 1H), 3.67 – 3.54 (m, 2H), 2.96 (s, 3H), 2.29 (s, 3H), 1.34 (s, 9H); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ = 152.5, 146.8, 131.9, 130.3, 128.7, 128.0, 126.4, 114.9, 112.5, 112.0, 55.7, 44.6, 41.5, 34.8, 31.4, 27.2, 20.5; IR (neat): ν =3435, 2961, 2919, 2255, 1706, 1616, 1574, 1518, 1461, 1367, 1269, 1212, 1188, 1113, 1018, 807, 757, 569, 516; MS-EI: *m/z*(%): 346 (2), 345 (8), 135 (10), 134 (100), 133 (2), 119 (5), 118 (5), 117 (2), 91 (7), 77 (2), 65 (2), 57 (2).

2-(2-((4-(*tert*-butyl)phenyl)(methyl)amino)-1-(*p*-tolyl)ethyl)malononitrile (4j):



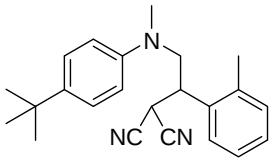
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.36 – 7.29 (m, 4H), 7.26 (d, *J* = 7.3 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 4.28 (d, *J* = 4.4 Hz, 1H), 3.82 (dd, *J* = 14.8, 10.6 Hz, 1H), 3.65 (dd, *J* = 14.8, 4.9 Hz, 1H), 3.62 – 3.57 (m, 1H), 2.97 (s, 3H), 2.40 (s, 3H), 1.32 (s, 9H); ^{13}C-NMR (151.8 MHz, $CDCl_3$): δ = 146.4, 141.7, 139.2, 131.8, 130.0, 128.0, 126.4, 113.9, 112.4, 111.9, 55.6, 44.6, 41.0, 33.9, 31.5, 27.1, 21.2; IR (neat): ν = 3436, 3020, 2960, 2920, 2856, 1713, 1613, 1518, 1215, 757, 668; MS-EI: *m/z*(%): 345 (8), 328 (10), 177 (13), 176 (100), 161 (5), 146 (10), 118 (4), 91 (3), 77 (2).

2-(2-((4-(*tert*-butyl)phenyl)(methyl)amino)-1-(2,4-dimethylphenyl)ethyl)malononitrile (4k):



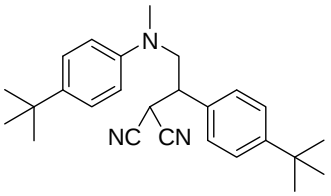
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 8.9 Hz, 2H), 7.17 – 7.08 (m, 2H), 6.76 (d, *J* = 8.9 Hz, 2H), 4.19 (d, *J* = 5.4 Hz, 1H), 3.99 (m, 1H), 3.82 (dd, *J* = 14.9, 9.7 Hz, 1H), 3.59 (dd, *J* = 14.9, 5.2 Hz, 1H), 2.95 (s, 3H), 2.34 (s, 3H), 2.33 (s, 3H), 1.32 (s, 9H); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ = 146.2, 141.5, 138.6, 136.7, 132.2, 130.7, 127.7, 126.3, 126.0, 113.5, 112.3, 112.1, 56.1, 41.2, 39.1, 33.9, 31.4, 26.6, 21.0, 19.7; IR (neat): ν = 3440, 2958, 2252, 1881, 1708, 1613, 1518, 1460, 1372, 1203, 1126, 1038, 912, 819, 732, 560; MS-EI: *m/z*(%): 359 (8), 177 (13), 176 (100), 146 (9), 91 (3), 77 (2).

2-(2-((4-(*tert*-butyl)phenyl)(methyl)amino)-1-(*o*-tolyl)ethyl)malononitrile (4l):



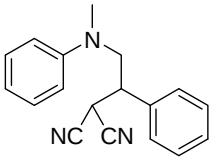
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.52 – 7.45 (m, 1H), 7.36 – 7.23 (m, 5H), 6.75 (d, *J* = 8.9 Hz, 2H), 4.19 (d, *J* = 5.5 Hz, 1H), 4.06 – 3.98 (m, 1H), 3.84 (dd, *J* = 14.9, 9.6 Hz, 1H), 3.60 (dd, *J* = 14.9, 5.3 Hz, 1H), 2.93 (s, 3H), 2.36 (s, 3H), 1.31 (s, 9H); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ = 146.2, 141.5, 134.0, 133.8, 131.4, 128.8, 127.0, 126.4, 126.1, 113.6, 112.2, 112.0, 56.1, 41.2, 39.3, 33.9, 31.4, 26.5, 19.8; IR (neat): ν = 3468, 3031, 2960, 2568, 2253, 1879, 1710, 1613, 1519, 1462, 1363, 1205, 1130, 1048, 911, 818, 732, 649, 555, 498; MS-EI: *m/z*(%): 345 (12), 177 (14), 176 (100), 146 (12), 118 (5), 91 (3), 77 (2).

2-(1-(4-(*tert*-butyl)phenyl)-2-((4-(*tert*-butyl)phenyl)(methyl)amino)ethyl)malononitrile (4m):



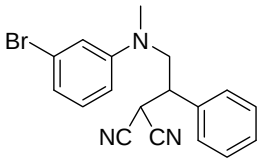
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 8.5 Hz, 2H), 7.38 – 7.31 (m, 4H), 6.79 (d, *J* = 8.9 Hz, 2H), 4.30 (d, *J* = 4.2 Hz, 1H), 3.81 (dd, *J* = 14.8, 10.8 Hz, 1H), 3.69 – 3.57 (m, 2H), 2.99 (s, 3H), 1.35 (s, 9H), 1.31 (s, 9H); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ = 152.3, 146.4, 141.7, 131.6, 127.8, 126.4, 126.2, 113.9, 112.4, 111.9, 55.5, 44.6, 41.1, 34.7, 33.9, 31.4, 31.2, 27.0; IR (neat): ν = 3437, 3020, 2919, 2401, 1580, 1519, 1425, 1383, 1215, 1034, 928, 758, 669; MS-EI: *m/z*(%): 387 (7), 177 (13), 176 (100), 161 (5), 160 (3), 146 (8), 57 (7).

2-(2-(methyl(phenyl)amino)-1-phenylethyl)malononitrile (4n):



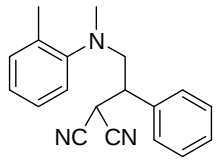
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.51 – 7.39 (m, 5H), 7.36 – 7.28 (m, 2H), 6.91 – 6.79 (m, 3H), 4.24 (d, *J* = 4.6 Hz, 1H), 3.92 (dd, *J* = 14.8, 10.1 Hz, 1H), 3.76 – 3.59 (m, 2H), 2.98 (s, 3H); ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ = 148.7, 135.0, 129.7, 129.5, 128.2, 127.7, 118.9, 114.0, 112.3, 111.9, 55.5, 44.9, 41.0, 27.1; IR (neat): ν = 3063, 3034, 2895, 2254, 1709, 1599, 1502, 1453, 1353, 1198, 1122, 1034, 993 911, 752, 698, 518; MS-EI: *m/z*(%): 276 (2), 275 (7), 121 (10), 120 (100), 119 (3), 105 (5), 104 (6), 103 (2), 91 (4), 77 (13), 51 (4).

2-(2-((3-bromophenyl)(methyl)amino)-1-phenylethyl)malononitrile (4o):



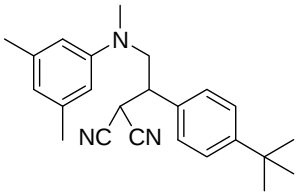
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.48 – 7.36 (m, 5H), 7.14 (t, *J* = 8.2 Hz, 1H), 6.99 – 6.93 (m, 1H), 6.88 (t, *J* = 2.3 Hz, 1H), 6.70 (dd, *J* = 8.2, 2.3 Hz, 1H), 4.14 (d, *J* = 4.9 Hz, 1H), 3.94 (dd, *J* = 15.0, 9.3 Hz, 1H), 3.71 (dd, *J* = 15.0, 5.7 Hz, 1H), 3.66 – 3.56 (m, 1H), 2.93 (s, 3H); ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ = 149.7, 134.9, 130.9, 129.6, 128.1, 127.7, 123.9, 121.3, 116.3, 112.0, 111.9, 111.8, 55.3, 44.7, 40.7, 27.1; IR (neat): ν = 3658, 3469, 3069, 3033, 2904, 2579, 2377, 2255, 1814, 1708, 1593, 1555, 1493, 1454, 1428, 1357, 1292, 1243, 1181, 1125, 986, 911, 836, 799, 763, 733, 700, 571, 522; MS-EI: *m/z*(%): 355 (8), 353 (8), 201 (8), 200 (100), 199 (14), 198 (98), 197 (4), 184 (3), 183 (3), 182 (3), 157 (3), 155 (3).

2-(2-(methyl(*o*-tolyl)amino)-1-phenylethyl)malononitrile (4p):



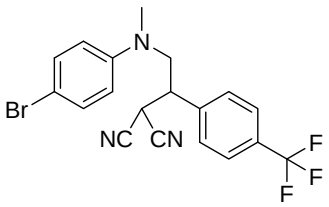
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.46 – 7.34 (m, 5H), 7.28 – 7.19 (m, 2H), 7.13 – 7.07 (m, 2H), 4.44 (d, *J* = 4.3 Hz, 1H), 3.56 (dd, *J* = 13.1, 4.9 Hz, 1H), 3.51 – 3.41 (m, 1H), 3.38 – 3.28 (m, 1H), 2.71 (s, 3H), 2.33 (s, 3H); ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ = 149.5, 135.3, 134.2, 131.9, 129.3, 129.3, 128.2, 127.2, 125.1, 120.6, 112.6, 111.7, 56.3, 44.9, 44.5, 27.0, 18.0; IR (neat): ν = 3660, 3064, 3029, 2950, 2916, 2851, 2801, 2255, 1705, 1594, 1495, 1454, 1380, 1290, 1217, 1169, 1113, 1050, 984, 936, 763, 700, 667, 579,459; MS-EI: *m/z*(%): 289 (3), 135 (11), 134 (100), 133 (3), 119 (3), 118 (9), 91 (10), 77 (4), 65 (6).

2-(1-(4-(*tert*-butyl)phenyl)-2-((3,5-dimethylphenyl)(methyl)amino)ethyl)malononitrile (4q):



^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 6.53 (s, 1H), 6.45 (s, 2H), 4.24 (d, *J* = 4.3 Hz, 1H), 3.85 (dd, *J* = 14.9, 10.5 Hz, 1H), 3.66 (dd, *J* = 14.9, 4.7 Hz, 1H), 3.62 – 3.56 (m, 1H), 2.97 (s, 3H), 2.30 (s, 6H), 1.34 (s, 9H); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ = 152.5, 148.9, 139.4, 131.9, 128.0, 126.4, 120.9, 112.5, 112.0, 55.4, 44.8, 41.1, 34.8, 31.4, 27.2, 21.9; IR (neat): ν = 3781, 3435, 2960, 2918, 2254, 1906, 1721, 1598, 1481, 1379, 1269, 1233, 1178, 1114, 1045, 918, 824, 757, 691, 563; MS-EI: *m/z*(%): 360 (2), 359 (9), 149 (11), 148 (100), 147 (5), 133 (4), 132 (3), 117 (2), 105 (3), 91 (4), 79 (2), 77 (2), 57 (2).

2-(2-((4-bromophenyl)(methyl)amino)-1-(4-(trifluoromethyl)phenyl)ethyl)malononitrile (4r):

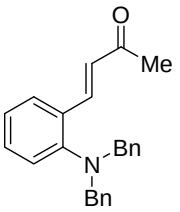


^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.1 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 9.2 Hz, 2H), 6.66 (d, *J* = 9.2 Hz, 2H), 4.21 (d, *J* = 4.4 Hz, 1H), 3.97 – 3.86 (m, 1H), 3.75 – 3.62 (m, 2H), 2.94 (s, 3H); ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ = 147.4, 138.7, 132.6, 131.9 (q, J_{CF} = 33 Hz), 128.8,

127.8, 126.6 (q, J_{CF} = 4 Hz), 125.6, 115.6, 111.7, 111.4, 55.2, 44.5, 41.1, 26.8; IR (neat): ν = 3079, 2907, 2256, 1925, 1867, 1804, 1709, 1591, 1499, 1425, 1327, 1240, 1171, 1116, 1070, 911, 839, 811, 733, 604, 517; MS-EI: *m/z*(%): 422 (13), 420 (13), 201 (8), 200 (100), 199 (5), 198 (100), 185 (5), 184 (6), 183 (7), 182 (6), 157 (4), 155 (5), 119 (19), 118 (27), 104 (8), 103 (4), 91 (4), 90 (4), 78 (4), 77 (10), 76 (7), 75 (9), 69 (5), 63 (6), 57 (4), 51 (4), 50 (4).

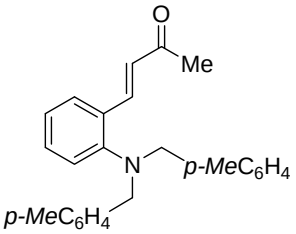
Characterization of substrates 5a-m and products 5a' and 6a-l

(E)-4-(2-(dibenzylamino)phenyl)but-3-en-2-one (5a):



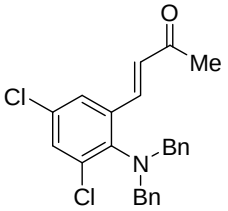
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 16.5 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.33 – 7.20 (m, 11H), 7.07 (t, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 16.5 Hz, 1H), 4.21 (s, 4H), 2.31 (s, 3H); ^{13}C NMR (151.8 MHz, $CDCl_3$): δ = 199.2, 151.1, 141.5, 137.8, 130.8, 129.9, 128.5, 128.5, 127.9, 127.6, 127.3, 123.6, 122.5, 58.0, 26.9; IR (neat): ν =3248, 2921, 1734, 1667, 1597, 1456, 1362, 989, 757cm^{-1}; EI-MS: m/z = 342 (M^++1, 8%), 341 (M^+, 29%), 250 (53%), 208 (56%), 91 (100%).

(E)-4-(2-(bis(4-methylbenzyl)amino)phenyl)but-3-en-2-one (5b):



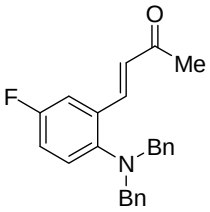
^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.27 (d, *J* = 16.6 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.40 – 7.27 (m, 1H), 7.25 – 7.01 (m, 10H), 6.72 (dd, *J* = 16.6, 1.5 Hz, 1H), 4.23 (s, 4H), 2.41(s, 3H), 2.40 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.1, 151.2, 141.6, 136.8, 134.7, 130.6, 129.8, 129.1, 129.0, 128.6, 128.5, 127.7, 127.3, 123.3, 122.5, 57.5, 26.8, 21.2; IR (neat): ν = 3246, 2921, 1733, 1667, 1599, 1255, 755 cm^{-1}; EI-MS: m/z = 370.2 (M^++1, 16%), 369.1 (M^+, 32%), 264.1 (39%), 222.2 (29%), 105.2 (100%).

(E)-4-(3,5-dichloro-2-(dibenzylamino)phenyl)but-3-en-2-one (5c):



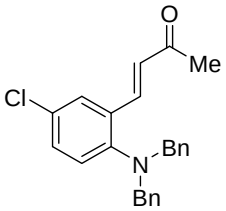
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (s, 1H), 7.43 (d, *J* = 16.0 Hz, 1H), 7.30 – 7.22 (m, 9H), 7.17 (m, 4H), 6.20 (d, *J* = 16.0 Hz, 1H), 4.26 (s, 4H), 2.14 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 198.5, 145.3, 140.8, 138.4, 138.3, 136.2, 132.0, 131.8, 129.4, 129.3, 129.2, 128.5, 127.7, 125.6, 57.4, 26.5; IR (neat): ν = 3247, 2920, 1731, 1459, 1216, 756 cm^{-1}; EI-MS: m/z = 411 (M^++2, 7%), 410 (M^+1, 4%), 409 (M^+, 11%), 276 (13%), 91.2 (100%).

(E)-4-(2-(dibenzylamino)-5-fluorophenyl)but-3-en-2-one (5d):



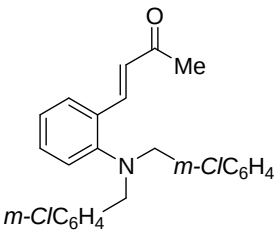
^{1}H NMR (600MHz, $CDCl_3$): δ = 8.12 (*d, J* = 16.6 Hz, 1H), 7.32-7.26 (*m*, 4H), 7.25-7.18 (*m*, 7H),7.01-6.93 (*m,* 2H), 6.53 (*d, J* = 16.5 Hz, 1H), 4.12 (*s*, 4H), 2.32 (*s*, 3H); ^{13}C NMR (150MHz, $CDCl_3$): δ =198.6, 159.1(*d*, $^1J_{C\text{-}F}$ = 243.5 Hz), 146.9, 139.8, 137.4, 128.6, 128.4, 128.3, 128.2, 127.3, 124.5 (*d*, $^3J_{C\text{-}F}$ = 8.3 Hz), 117.4 (*d*, $^2J_{C\text{-}F}$ = 22.5 Hz), 113.4 (*d*, $^2J_{C\text{-}F}$ = 22.8 Hz), 58.5, 27.0; IR (neat): ν = 3433, 3064, 3021, 1668, 1606, 1488, 1452, 1216, 757 cm^{-1}; EI-MS: m/z = 360.3 (M^+ +1, 15%), 359.2 (M^+, 41%), 268.2 (47%), 226.2 (47.3%), 91.1 (100%).

(E)-4-(5-chloro-2-(dibenzylamino)phenyl)but-3-en-2-one (5e)



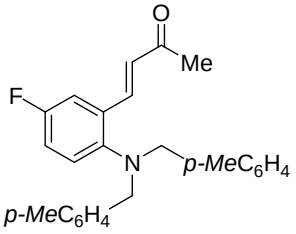
^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 16.5 Hz, 1H), 7.54 (d, *J* = 2.5 Hz, 1H), 7.41 – 7.14 (m, 11H), 6.94 (d, *J* = 8.7 Hz, 1H), 6.63 (d, *J* = 16.5 Hz, 1H), 4.20 (s, 4H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.5, 149.4, 139.7, 137.3, 131.6, 130.3, 128.8, 128.7, 128.5, 128.5, 128.2, 127.5, 123.9, 58.0, 27.3; IR (neat): ν = 3304, 2921, 1732, 1668, 1475, 1215, 756 cm^{-1}; EI-MS: m/z = 376 (M^++1, 7%), 369.1 (M^+, 19%), 284 (17%), 242 (26%), 91 (100%).

(E)-4-(2-(1,3-bis(3-chlorophenyl)propan-2-yl)phenyl)but-3-en-2-one (5f)



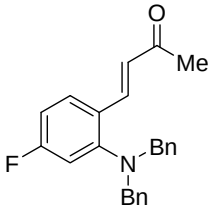
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 16.5 Hz, 1H), 7.57 (dd, *J* = 1.5, 7.8 Hz, 1H), 7.29 (m, 1H), 7.22 (dd, *J* = 0.9, 4.8 Hz, 6H), 7.12 (d, *J* =7.8 Hz, 1H), 7.07 (m, 2H), 7.00 (dd, *J* = 1.0, 8.1 Hz, 1H), 6.62 (d, *J* = 16.5 Hz, 1H), 4.12 (s, 4H), 2.35 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 197.9, 148.6, 138.8, 135.4, 133.3, 131.8, 130.4, 130.0, 129.9, 129.4, 128.7, 128.6, 128.0, 127.5, 127.9, 57.2, 27.9; IR (neat): = ν = 3440, 3059, 2924, 2850, 1944, 1672, 1598, 1472, 1369 cm^{-1}; EI-MS: m/z = 410 (M^+ +1, 7%), 409 (M^+, 20%), 284 (46%), 242 (70%), 125 (100%).

(E)-4-(2-(bis(4-methylbenzyl)amino)-5-fluorophenyl)but-3-en-2-one (5g):



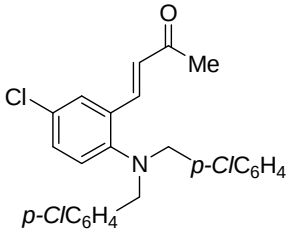
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.15 (dd, *J* = 16.6, 1.3 Hz, 1H), 7.28 – 7.18 (m, 1H), 7.13-7.11 (m, 8H), 7.04 – 6.89 (m, 2H), 6.56 (d, *J* = 16.6 Hz, 1H), 4.09 (s, 4H), 2.37 (s, 3H), 2.33 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 198.7, 159.1 (d, J_{CF} = 241.8 Hz), 147.1, 140.0 (d, J_{CF} = 1.59 Hz), 136.9, 134.5, 132.3 (d, J_{CF} = 7.38 Hz), 129.1, 128.7, 128.1, 124.6 (d, J_{CF} = 8.12 Hz), 117.4 (d, J_{CF} = 22.35 Hz), 113.4 (d, J_{CF} = 22.64 Hz), 58.2, 27.0, 21.2; IR (neat): ν = 3458, 2923, 1739, 1671, 1484, 1178, 812 cm^{-1}; EI-MS: m/z = 388 (M^++1, 5%), 387 (M^+, 14%), 282 (14%), 240 (12%), 105 (100%).

(E)-4-(2-(dibenzylamino)-4-fluorophenyl)but-3-en-2-one (5h):



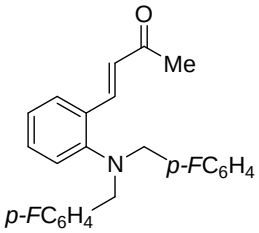
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 16.5 Hz, 1H), 7.54 (dd, *J* = 8.6, 6.7 Hz, 1H), 7.33-7.30 (m, 4H), 7.27 – 7.23 (m, 4H), 6.76 (dt, *J* = 8.3, 2.4 Hz, 1H), 6.68 (dd, *J* = 10.8, 2.4 Hz, 1H), 6.60 (d, *J* = 16.5 Hz, 1H), 4.20 (s, 4H), 2.28 (s, 3H); ^{13}C NMR (151.8 MHz, $CDCl_3$): δ = 198.9, 164.4 (d, *J* = 249.0 Hz), 153.1 (d, *J* = 9.0 Hz), 153.1, 140.5, 137.3, 129.5 (d, *J* = 9.0 Hz), 128.6, 128.4, 127.5, 127.1 (d, *J* = 1.5 Hz), 125.7 (d, *J* = 3.0 Hz), 110.6 (d, *J* = 22.5 Hz), 109.5 (d, *J* = 22.5 Hz), 57.8, 27.0; IR (neat): ν = 3437, 2920, 1733, 1578, 1385, 1072, 721 cm^{-1}; EI-MS: m/z = 360 (M^++1, 4%), 359 (M^+, 12%), 268 (29%), 226 (31%), 91 (100%).

(E)-4-(2-(bis(4-chlorobenzyl)amino)-5-chlorophenyl)but-3-en-2-one (5i):



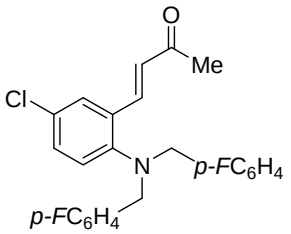
H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 16.4 Hz, 1H), 7.05(*d, J* = 2.5 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 4H), 7.18 (dd, *J* = 2.5, 8.6 HZ, 1H), 7.08 (d, *J* = 8.4 Hz, 4H), 6.83 (d, *J* = 8.7 Hz, 1H), 6.62 (d, *J* = 16.3 Hz, 1H), 4.05 (s, 4H), 2.32 (S, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 197.9, 148.6, 138.8, 135.4, 133.3, 131.8, 130.4, 129.95, 129.87, 129.4, 128.7, 128.6, 128.0, 127.5, 123.9, 55.2, 27.9; IR (neat): ν = 3426, 2922, 2852, 1897, 1672, 1605, 1464, 1384, 1090 cm^{-1}; EI-MS: m/z = 444.1 (M^+ +1, 7%), 443.1 (M^+, 20%), 318.2 (18%), 276. 1 (33%), 125 (100%).

(E)-4-(2-(bis(4-fluorobenzyl)amino)phenyl)but-3-en-2-one (5j):



^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 16.5 Hz, 1H), 7.57 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.30 – 7.21 (m, 1H), 7.18 – 7.11 (m, 4H), 7.11 – 7.03 (m, 1H), 7.01 – 6.91 (m, 5H), 6.66 (d, *J* = 16.4 Hz, 1H), 4.11 (s, 4H), 2.35 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 198.8, 162.2 (d, *J* = 244.0 Hz), 150.6, 140.9, 133.3 (d, *J* = 3.0 Hz), 130.8, 130.2 (d, *J* = 244.0 Hz), 127.9, 127.4, 124.0, 122.8, 115.4 (d, *J* = 244.0 Hz), 57.2, 27.4; IR (neat): ν = 3302, 2922, 1668, 1602, 1507, 1222, 830, 756 cm^{-1}; EI-MS: m/z = 378 (M^++1, 30%), 377 (M^+, 49%), 268 (48%), 226 (53%), 109 (100%).

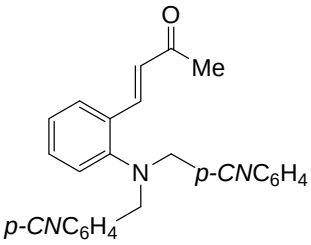
(E)-4-(2-(bis(4-fluorobenzyl)amino)-5-chlorophenyl)but-3-en-2-one (5k):



^{1}H NMR (600 MHz, $CDCl_3$ as E:Z= 1.6:1): δ = 8.05 (d, *J* = 16.4 Hz, 1H), 7.53 (d, *J* = 2.4 Hz, 1H), 7.28 – 7.23 (m, 2H), 7.22 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.18 – 7.12 (m, 4H), 7.09 (d, *J* = 2.2 Hz, 1H), 7.02 – 6.93 (m, 6H), 6.88 (d, *J* = 8.6 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 6.65 (d, *J* = 16.4 Hz, 1H), 4.09 (s, 4H), 4.00

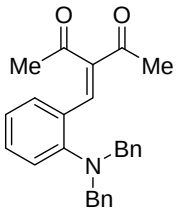
(s, 4H), 2.36 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (151.8 MHz, $CDCl_3$): δ = 206.2, 198.2, 162.2 (d, J_{CF} = 245.0 Hz), 162.2 (d, J_{CF} = 244.0 Hz), 149.0, 145.9, 139.1, 137.1, 133.4 (d, J_{CF} = 2.97 Hz), 132.8 (d, J_{CF} = 3.06 Hz), 131.9, 130.6, 130.4, 130.4 (d, J_{CF} = 7.97 Hz), 130.2 (d, J_{CF} = 7.89 Hz), 129.4, 128.1, 127.6, 124.8, 124.7, 124.4, 124.2, 115.5 (d, J_{CF} = 21.20 Hz), 115.1 (d, J_{CF} = 21.1 Hz), 57.2, 56.0, 30.2, 27.9; IR (neat): ν = 3301, 2921, 1726, 1671, 1604, 1470, 1222, 828, 758 cm^{-1}; EI-MS: m/z = 412 (M^++1, 3%), 411 (M^+, 11%), 109 (100%), 43 (35%).

(E)-4,4'-(2-(3-oxobut-1-enyl)phenylazanediyl)bis(methylene)dibenzonitrile (5l):



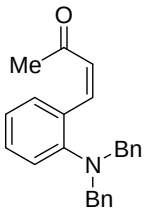
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, J = 16.3 Hz, 1H), 7.57 (d, J = 12.0 Hz, 4H), 7.32 (d, J = 12 Hz, 4H), 7.27-7.23 (m, 1H), 7.10 (t, J = 8.0 Hz, 1H), 6.92 (dd, J = 8.0, 1.0 Hz, 1H), 6.69 (d, J = 16.3 Hz, 1H), 4.20 (s, 4H), 2.32 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 198.2, 149.4, 142.7, 139.7, 132.4, 130.9, 130.1, 129.2, 128.1, 127.5, 124.6, 122.3, 118.6, 111.5, 57.9, 28.1; IR (neat): ν = 3243, 2919, 1731, 1468, 1215, 756 cm^{-1}; EI-MS: m/z = 392 (M^++1, 5%), 391 (M^+, 17%), 275 (30%), 233 (51%), 116 (61%), 43 (100%).

3-(2-(Dibenzylamino)benzylidene)pentane-2,4-dione (5m):



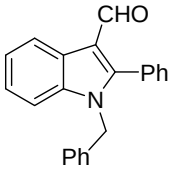
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (s, 1H), 7.34 – 7.20 (m, 12H), 7.05 – 6.97 (m, 2H), 4.23 (s, 4H), 2.34 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 205.0, 196.9, 151.3, 141.8, 139.5, 137.6, 131.1, 130.2, 128.6, 128.5, 128.4, 127.5, 123.3, 122.3, 57.8, 31.6, 26.7; IR (neat): ν = 3438, 2922, 1706, 1382, 1216, 756 cm^{-1}; EI-MS: m/z = 384 (M^++1, 17%), 383 (M^+1, 47%), 340 (50%), 283 (47%), 91(100%).

(Z)-4-(2-(dibenzylamino)phenyl)but-3-en-2-one (5a'):



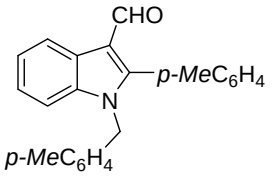
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, J = 12.3 Hz, 1H), 7.38 (dd, J = 7.6, 1.4 Hz, 1H), 7.34 – 7.28 (m, 4H), 7.28 – 7.20 (m, 7H), 7.01 (m, 1H), 6.93 (dd, J = 8.1, 0.9 Hz, 1H), 6.25 (d, J = 12.3 Hz, 1H), 4.18 (s, 4H), 2.17 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 200.9, 150.2, 140.4, 137.8, 131.6, 130.7, 129.7, 128.8, 128.5, 128.4, 127.3, 122.5, 121.6, 56.9(2C), 30.6; IR (neat): ν = 3433, 2922, 1736, 1666, 1596, 1216, 757 cm^{-1}; EI-MS: m/z = 342 (M^++1, 11%), 341 (M^+, 47%), 250 (31%), 208 (50%), 91 (100%).

1-Benzyl-2-phenyl-1H-indole-3-carbaldehyde (6a):[1]



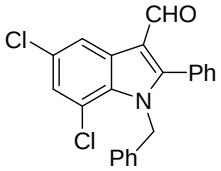
reaction time: 20h, ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.79 (s, 1H), 8.49 (d, *J* = 7.9 Hz, 1H), 7.53 (m,1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.44 (m, 2H), 7.37 (t, *J*= 7.5 Hz, 1H), 7.32 – 7.24 (m, 5H), 6.99 (dd, *J* = 7.3, 0.8 Hz, 2H), 5.31 (s, 2H);^{13}C NMR (151.8 MHz, $CDCl_3$): δ = 187.0, 151.8, 137.0, 136.6, 130.9, 130.1, 129.1, 128.8, 128.7, 127.9, 126.1, 125.6, 124.4, 123.5, 122.4, 116.4, 110.9, 47.9; IR (neat): ν = 3433, 2921, 2254, 1714, 1648, 1461, 1384, 908, 734 cm^{-1}; EI-MS: m/z = 312 (M^++1, 100%).

1-(4-Methylbenzyl)-2-p-tolyl-1H-indole-3-carbaldehyde (6b):



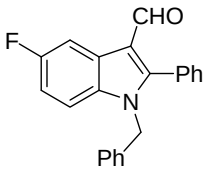
reaction time: 34h, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.78 (s, 1H), 8.46 (d, *J* = 7.8 Hz, 1H), 7.36 – 7.21 (m, 7H), 7.08 (d, *J* = 8.2 Hz, 2H), 6.88 (d, *J* = 8.2 Hz, 2H), 5.25 (s, 2H), 2.44 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 187.1, 152.1, 140.3, 137.5, 137.0, 133.6, 130.9, 129.7, 129.5, 126.0, 125.7, 124.2, 123.4, 122.3, 116.2, 111.0, 47.7, 21.6, 21.2; IR (neat): ν = 3437, 2919, 1733, 1577, 1385, 1071, 721 cm^{-1}; EI-MS: m/z = 340 (M^++1, 31%), 339 (M^+, 100%), 238 (28%), 105 (96%).

1-Benzyl-5,7-dichloro-2-phenyl-1H-indole-3-carbaldehyde (6c):



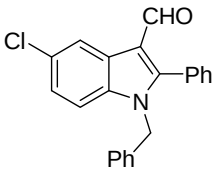
reaction time: 30h, ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.67 (s, 1H), 8.46 (d, *J* = 2.0 Hz, 1H), 7.56 – 7.49 (m, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.36 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.27- 7.23 (m, 4H), 6.81 – 6.75 (m, 2H), 5.65 (s, 2H); ^{13}C NMR (151.8 MHz, $CDCl_3$): δ = 186.5, 154.3, 138.1, 131.2, 130.9, 130.6, 130.6, 129.4, 129.0, 128.9, 127.8, 127.7, 126.3, 125.4, 120.7, 117.9, 116.1, 49.3; IR (neat): ν = 3438, 2921, 1578, 1544, 1436, 1215, 757 cm^{-1}; EI-MS: m/z = 381 (M^++2, 22%), 379 (M^+, 34%), 91 (100%).

1-Benzyl-5-fluoro-2-phenyl-1H-indole-3-carbaldehyde (6d):



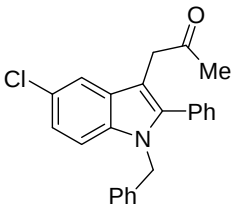
reaction time: 30h, ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 9.74 (*s*, 1H), 8.14 (dd, *J* = 2.5, 9.2 Hz, 2H), 7.48 (m, 7H), 7.28 (m, 7H), 7.14 (dd, *J* = 8.9, 4.3 Hz, 2H), 7.02 (dd, *J* = 9.0, 2.7 Hz, 1H), 6.96 (dd, *J* = 7.7, 1.9 Hz, 3H), 5.28 (*s*, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 186.6, 160.1 (*d*, $J_{C\text{-}F}$ = 239.6 Hz), 152.5, 136.1, 133.3, 130.1, 130.2, 129.0, 128.8, 127.8, 125.9, 116.1, 112.5 (*d*, $J_{C\text{-}F}$ = 26.2 Hz), 111.7 (d, $J_{C\text{-}F}$ = 9.6 Hz), 107.8 (d, $J_{C\text{-}F}$ = 24.9 Hz), 48.0; IR (neat): ν = 3435, 2931, 2853, 1634, 1452, 1384, 1153, 1068 cm^{-1}; EI-MS: m/z =330.3 (M^++1, 26%), 329.3 (M^+, 87%), 238.3(15%), 183.2(11%), 91.3(100%).

1-Benzyl-5-chloro-2-phenyl-1H-indole-3-carbaldehyde (6e):



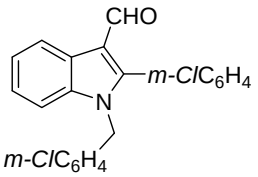
reaction time: 34h, ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.74 (s, 1H), 8.46 (d, *J* = 1.99 Hz, 1H), 7.55 – 7.42 (m, 5H), 7.32 – 7.26 (m, 3H), 6.93(dd, *J* = 8.92, 1.99 Hz, 1H), 7.13 (d, *J* = 8.92 Hz, 1H), 6.94 (d, *J* = 5.94 Hz, 2H), 5.27 (s, 2H); ^{13}C NMR (151.8 MHz, $CDCl_3$): δ = 186.5, 152.3, 136.0, 135.2, 130.7, 130.2, 129.3, 129.0, 128.9, 128.8, 128.1, 127.9, 126.4, 125.9, 124.6, 121.9, 111.8, 47.9; IR (neat): ν = 3305, 2920, 1734, 1579, 1459, 1052, 723 cm^{-1}; EI-MS: m/z = 347 (M^++2, 28%), 346 (M^++1, 33%), 345 (M^+, 100%), 91 (99%).

1-(1-Benzyl-5-chloro-2-phenyl-1H-indol-3-yl)propan-2-one (7e):



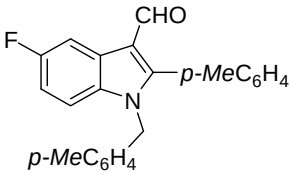
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 1.0 Hz, 1H), 7.44 – 7.39 (m, 3H), 7.29 (dd, *J* = 6.4, 3.0 Hz, 2H), 7.26-7.21 (m, 3H), 7.12 – 7.09 (m, 2H), 6.90 (d, *J* = 6.8 Hz, 2H), 5.21 (s, 2H), 3.71 (s, 2H), 2.10 (s, 3H); ^{13}C NMR (151.8 MHz, $CDCl_3$): δ = 207.1, 140.9, 137.8, 135.3, 130.9, 130.5, 129.1, 129.0, 128.9, 127.5, 126.1, 126.0, 122.8, 118.6, 111.7, 106.6, 48.0, 40.5, 29.3; IR (neat): ν = 3246, 2920, 1732, 1577, 1384, 1053, 720 cm^{-1}; EI-MS: m/z = 375 (M^++2, 8%), 373 (M^+, 22%), 332 (25%), 330 (62%), 91 (100).

1-(3-Chlorobenzyl)-2-(3-chlorophenyl)-1H-indole-3-carbaldehyde (6f):



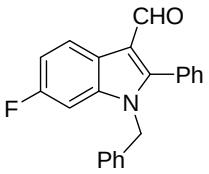
reaction time: 36h, ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.78 (s, 1H), 8.47 (d, *J* = 7.7 Hz, 1H), 7.54 – 7.50 (m, 1H), 7.43 (t, *J* = 7.9 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.36 – 7.32 (m, 1H), 7.31 – 7.27 (m, 1H), 7.25-7.23 (m, 2H), 7.21 (t, *J* = 7.8 Hz, 1H), 6.98 (s, 1H), 6.79 (d, *J* = 7.5 Hz, 1H), 5.25 (s, 2H); ^{13}C NMR (151.8 MHz, $CDCl_3$): δ = 186.4, 149.4, 138.4, 137.0, 135.2, 135.0, 130.9, 130.5, 130.3, 130.2, 129.0, 128.4, 126.4, 125.4, 124.9, 124.2, 123.9, 122.7, 116.8, 110.6, 47.4; IR (neat): ν = 3438, 2921, 1733, 1655, 1384, 1084, 752 cm^{-1}; EI-MS: m/z = 381 (M^++2, 60%), 380 (M^++1, 47%), 379 (M^+, 100%), 378 (48%), 125 (95%).

5-Fluoro-1-(4-methylbenzyl)-2-p-tolyl-1H-indole-3-carbaldehyde (6g):



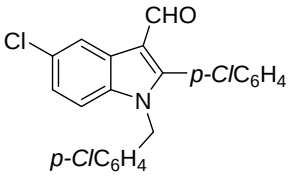
reaction time: 34h, ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.75 (s, 1H), 8.12 (dd, *J* = 9.3, 2.5 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.14 – 7.07 (m, 3H), 6.98 (dt, *J* = 9.0, 2.6 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 2H), 5.23 (s, 2H), 2.44 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (151.8 MHz, $CDCl_3$): δ = 186.8, 160.2 (d, J_{CF} = 238.35 Hz), 153.0, 140.5, 137.7, 133.4 (d, J_{CF} = 18.98 Hz), 133.3, 130.7, 129.8, 129.6, 126.3, 126.0, 125.4, 116.1, 112.4 (d, J_{CF} = 26.03 Hz), 111.8 (d, J_{CF} = 9.48 Hz), 107.8 (d, J_{CF} = 24.75 Hz), 47.9, 21.6, 21.2; IR (neat): ν = 3436, 2920, 1579, 1545, 1439, 1215, 758 cm^{-1}; EI-MS: m/z = 358 (M^++1, 15%), 357 (M^+, 54%), 105 (100%).

1-Benzyl-6-fluoro-2-phenyl-1H-indole-3-carbaldehyde (6h):



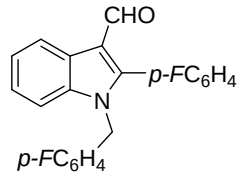
reaction time: 28h, ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.65 (s, 1H), 8.30 (dd, *J* = 8.7, 5.5 Hz, 1H), 7.44-7.42 (m, 1H), 7.40 – 7.35 (m, 2H), 7.35 – 7.31 (m, 2H), 7.22 – 7.14 (m, 3H), 7.02 – 6.96 (m, 1H), 6.89 – 6.85 (m, 2H), 6.80 (dd, *J* = 9.3, 2.1 Hz, 1H), 5.14 (s, 2H); ^{13}C NMR (151.8 MHz, $CDCl_3$): δ = 186.9, 160.8 (d, J_{CF} = 240.23 Hz), 152.2, 136.0, 130.9, 130.3, 129.2, 128.9, 128.7, 128.4, 128.1, 126.1, 123.6 (d, J_{CF} = 9.7 Hz), 121.9, 116.2, 112.0 (d, J_{CF} = 23.63 Hz), 97.8 (d, J_{CF} = 26.5Hz), 48.1; IR (neat): ν = 3437, 2920, 1737, 1654, 1384, 1078, 705 cm^{-1}; EI-MS: m/z = 330 (M^++1, 12%), 329 (M^+, 52%), 328 (23%), 91 (100%).

5-Chloro-1-(4-chlorobenzyl)-2-(4-chlorophenyl)-1H-indole-3-carbaldehyde (6i):



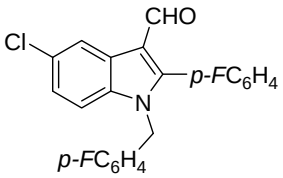
reaction time: 30h, ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 9.73 (d, *J* = 2.2, 1H), 8.46 (t, *J* = 2.0 Hz, 1H), 7.49-7.46 (m, 2H), 7.33 (td, *J* = 8.9, 2.4 Hz, 2H), 7.29-7.24 (m, 4H), 7.12 (dd, *J* = 8.7, 1.9 Hz, 1H), 6.85 (d, *J* = 8.5 Hz, 2H), 5.21 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 185.9, 150.4, 136.9, 135.1, 134.3, 134.0, 131.8, 129.6, 129.3, 129.2, 129.0, 127.1, 125.0, 122.0, 116.0, 111.6, 47.3; IR (neat): ν = 3433, 2920, 2854, 1650, 1582, 1450, 1384, 1070 cm^{-1}; EI-MS: m/z = 414.1 (M^++1, 7%), 413.1 (M^+, 15%), 253.2 (10%), 139.1 (16%), 125.1 (100%).

1-(4-Fluorobenzyl)-2-(4-fluorophenyl)-1H-indole-3-carbaldehyde (6j):



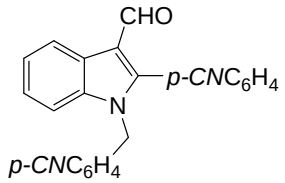
reaction time: 34h, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.75 (s, 1H), 8.46 (dd, *J* = 7.0, 1.0 Hz, 1H), 7.41 – 7.34 (m, 3H), 7.34 – 7.29 (m, 1H), 7.28 – 7.23 (m, 2H), 7.18 (t, *J* = 8.6 Hz, 1H), 7.00 – 6.88 (m, 4H), 5.24 (s, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 186.5, 163.9 (d, J_{CF} = 250.0 Hz), 162.4 (d, J_{CF} = 245.0 Hz), 150.2, 136.9, 132.8 (d, J_{CF} = 9.0 Hz), 132.2 (d, J_{CF} = 3.0 Hz), 127.8 (d, J_{CF} =8.0 Hz), 125.5, 124.6, 123.9, 123.7, 122.5, 116.7, 116.3 (d, J_{CF} = 5.0 Hz), 116.0 (d, J_{CF} = 5.0 Hz), 110.7, 47.2; IR (neat): ν = 3342, 2919, 1737, 1385, 838, 747 cm^{-1}; EI-MS: m/z = 348 (M^++1, 31%), 347 (M^+, 89%), 346 (44%), 109 (100%).

5-Chloro-1-(4-fluorobenzyl)-2-(4-fluorophenyl)-1H-indole-3-carbaldehyde (6k):



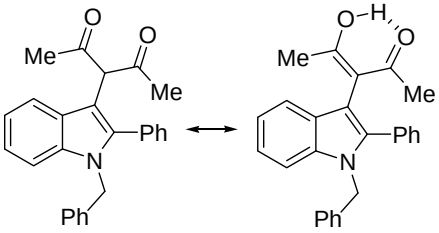
reaction time: 30h, ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.71 (s, 1H), 8.45 (d, *J* = 1.9 Hz, 1H), 7.41 – 7.35 (m, 2H), 7.28 – 7.23 (m, 1H), 7.22 – 7.16 (m, 2H), 7.14 (d, *J* = 8.7 Hz, 1H), 7.01 – 6.94 (m, 2H), 6.91 – 6.87 (m, 2H), 5.22 (s, 2H); ^{13}C NMR (151.8 MHz, $CDCl_3$): δ = 186.2, 164.0 (d, J_{CF} = 250.62 Hz), 162.4 (d, J_{CF} = 245.94 Hz), 150.9, 135.3, 132.7 (d, J_{CF} = 8.51 Hz), 131.7 (d, J_{CF} = 3.15 Hz), 129.7, 127.7 (d, J_{CF} = 8.15Hz), 126.5, 125.0, 124.2 (d, J_{CF} = 3.39 Hz), 122.1, 116.4 (d, J_{CF} = 21.74 Hz), 116.2 (d, J_{CF} = 21.68 Hz), 116.2, 111.7, 47.3; IR (neat): ν = 3338, 2920, 1736, 1584, 1451, 1227, 838 cm^{-1}; EI-MS: m/z = 383 (M^++2, 18%), 382 (M^++1, 16%), 381 (M^+, 43%), 109 (100%).

4-(1-(4-Cyanobenzyl)-3-formyl-1H-indol-2-yl)benzonitrile (6l):



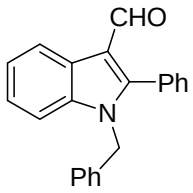
reaction time: 36h, ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.78 (s, 1H), 8.48 (d, *J* = 7.8 Hz, 1H), 7.79 (dd, *J* = 6.7, 1.7 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.52 (dd, *J* = 6.7, 1.7 Hz, 2H), 7.43 – 7.33 (m, 2H), 7.20 (d, *J* = 8.2 Hz, 1H), 7.04 (d, *J* = 8.5 Hz, 2H), 5.33 (s, 2H); ^{13}C NMR (151.8 MHz, $CDCl_3$): δ = 185.8, 148.0, 141.3, 137.0, 133.1, 133.1, 132.7, 131.5, 126.6, 125.4, 124.3, 122.9, 118.2, 117.8, 117.2, 114.4, 112.4, 110.4, 47.6; IR (neat): ν = 3304, 2920, 2232, 1730, 1656, 1422, 1216, 756 cm^{-1}; EI-MS: m/z = 362 (M^++1, 26%), 361 (M^+, 88%), 360 (49%), 116 (100%).

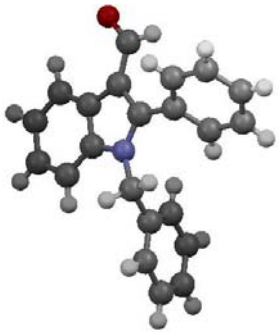
3-(1-Benzyl-2-phenyl-1H-indol-3-yl)pentane-2,4-dione (6m):



^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.41 (d, *J* = 7.9 Hz, 1H), 7.70 (dd, *J* = 7.0, 1.0 Hz, 1H), 7.55 – 7.34 (m, 11H), 7.34 – 7.15 (m, 14H), 6.95 (m, 4H), 6.15 (s, 1H), 5.25 (s, 2H), 5.23(s, 2H), 2.21 (s, 3H), 2.08 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (151.8 MHz, $CDCl_3$): δ = 201.5, 201.2, 191.2, 170.6, 149.4, 141.8, 139.9, 137.6, 137.0, 137.0, 136.3, 130.9, 130.8, 130.6, 130.3, 130.2, 129.8, 129.5, 129.2, 129.1, 129.0, 128.9, 128.6, 127.9, 127.5, 127.1, 126.2, 126.2, 124.4, 123.7, 123.1, 122.4, 121.2, 120.3, 111.0, 110.8, 75.6, 48.0, 47.9, 26.4, 26.0, 21.0; IR (neat): ν = 3338, 2920, 1736, 1584, 1451, 1227, 838 cm^{-1}; EI-MS: m/z = 382 (M^++1, 14%), 354 (87%), 338 (100%).

Crystal structure of **6a**.





1. Wu, C.-Y.; Hu, M.; Liu, Y.; Song, R.-J.; Lei, Y.; Tang, B.-X.; Li, R.-J.; Li, J.-H. *Chem. Commun.* **2012**, *48*, 3197.