Electronic Supplementary Information (ESI) for

Visible-light-promoted difluoroamidated oxindole synthesis *via* electron donor-acceptor complexes

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1. General information

Unless otherwise noted, all solvents and reagents were purchased from commercial suppliers and used without further purification. Anhydrous DMSO was purchased from Energy Chemical, and added to molecular sieves during use and stored at room temperature. The ¹H, ¹³C{¹H} and ¹⁹F{¹H} NMR spectra were recorded on a Bruker Ascend 400MHz spectrometer (400 MHz for ¹H NMR, 101 MHz for ¹³C{¹H} NMR, 377 MHz for ¹⁹F{¹H} NMR) or on a Bruker Ascend 500MHz spectrometer (500 MHz for ¹H NMR, 126 MHz for ¹³C{¹H} NMR, 471 MHz for ¹⁹F{¹H} NMR). The chemical shifts (δ) for ¹H, ¹³C{¹H} and ¹⁹F{¹H} are reported in ppm and are referenced to Me4Si (TMS) and the residual undeuterated solvent resonances (TMS at 0.00 ppm; CHCl₃ at 7.26 ppm ¹H NMR and 77.16 ppm ¹³C{¹H} NMR respectively). Data were reported as follows: chemical shift, multiplicity (s = singlet; d = doublet; dd = doublet; t= triplet; q = quartet; brs = broad singlet; m = multiplet), coupling constants (Hz), integration. All UV/vis absorption spectra were recorded in 1 cm path quartz cuvettes on a Shimadzu UV-2450 UV-VIS spectrophotometer. High resolution mass spectra (HRMS) were acquired using a Q-Exactive plus hybrid quadrupole-orbitrap mass spectrometer (Q-Orbitrap MS) (Thermo Scientific, San Jose, USA) with electrospray ionization (ESI) source. Column chromatography was carried out on silica gel (200-300 mesh, Petroleum PE/EtOAc solvent systems). A 440-450 nm Blue LED photoreaction lighting was employed as a visible light source without the use of filters.

2. General procedures for the preparation of N-phenylacrylamides and

bromodifluoroacetamides

N-phenylacrylamides 1a-1g, $^{1}1h$, $^{2}1i^{1}$, and the trifluoromethyl alkenes 2a, $^{3}2b^{3}$, 2c, $^{4}2d-2i^{3}$, 2j, $^{5}2k$, $^{5}2l$, $^{4}2m$, $^{5}2n$, $^{3}2p$, $^{5}2q^{5}$, and $2r^{6}$ were prepared according to the reported procedures.

Procedures for the preparation of compound 20

To a 10 mL flask were added methanamine (5 mmol) and $La(OTf)_3$ (0.25 mmol), then bromodifluoroacetate (6 mmol) was added to the mixture dropwise. When the reaction was completed as monitored by TLC, extracted with ethyl acetate three times. The combined organic layer was dried over anhydrous Na₂SO₄, filtered, and evaporated, and the resulting mixture was purified by column chromatography on silica gel to afford **20** as a white solid.

2-Bromo-2,2-difluoro-N-methylacetamide (20)

20

¹H NMR (400 MHz, CDCl₃) δ 6.98 (s, 1H), 2.92 (d, J = 5.2 Hz, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 161.04 (t, J = 27.4 Hz), 111.79 (t, J = 315.6 Hz), 77.16 (t, J = 32.0 Hz), 26.81; ¹⁹F{¹H} NMR (377 MHz, CDCl₃) δ -60.5; HRMS (ESI-TOF) m/z: [M + H]⁺ calcd for C₃H₅⁷⁹BrF₂N₂O, 187.9517; found, 187.9517.

Scheme S1. Structures of substrates



3. Experimental procedures

3.1 Experimental set-up



Figure S1. The set-up for the photochemical reactions.

3.2 Optimization of reaction conditions

Table S1. Screening of electron donor

	$H = \frac{1}{2}$	(NH ₄) ₂ S ₂ O ₈ , Electron Donor DMSO (0.1 M), r.t., N ₂ , 16 h Blue LED (440-450 nm)		
Entry ^a	$S_2O_8^{2-}$ (equiv.)	Electron Donor (equiv.)	Solvent	Yield ^b
1	$(NH_4)_2S_2O_8$ (2.0)	DBU (2.0)	DMSO	11%
2	(NH ₄) ₂ S ₂ O ₈ (2.0)	DMAP (2.0)	DMSO	27%
3	(NH ₄) ₂ S ₂ O ₈ (2.0)	Et ₃ N (2.0)	DMSO	24%
4	(NH ₄) ₂ S ₂ O ₈ (2.0)	ⁿ Bu ₃ N (2.0)	DMSO	14%
5	(NH ₄) ₂ S ₂ O ₈ (2.0)	DIPEA (2.0)	DMSO	34%
6	(NH ₄) ₂ S ₂ O ₈ (2.0)	DABCO (2.0)	DMSO	Trace
7	(NH ₄) ₂ S ₂ O ₈ (2.0)	TMEDA (2.0)	DMSO	62%
8	(NH ₄) ₂ S ₂ O ₈ (2.0)	PMDETA (2.0)	DMSO	38%
9	(NH ₄) ₂ S ₂ O ₈ (2.0)	Na ₂ CO ₃ (2.0)	DMSO	Trace
10	(NH ₄) ₂ S ₂ O ₈ (2.0)	Na ₂ HPO ₄ (2.0)	DMSO	Trace

^{*a*}Reactions were run under the conditions: **1a** (0.10 mmol, 1.0 equiv.), **2a** (1.0 equiv.), electron donor (2.0 equiv.), $(NH_4)_2S_2O_8$ (2.0 equiv.), DMSO (1.0 mL), r.t., 440-450 nm, under a nitrogen atmosphere, 16 h; ^{*b*1}H NMR yields with 1,3,5-trimethoxybenzene as an internal standard.

	$H_{F} + Br + Br + H_{F} + H_$			
	1a 2a		3a	
Entry ^a	$S_2O_8^{2-}$ (equiv.)	Electron Donor (equiv.)	Solvent	Yield ^b
1	(NH4)2S2O8 (2.0)	TMEDA (2.0)	DMSO	62%
2	(NH4)2S2O8 (2.0)	TMEDA (2.0)	DMF	47%
3	(NH4)2S2O8 (2.0)	TMEDA (2.0)	DCE	N.D.
4	(NH4)2S2O8 (2.0)	TMEDA (2.0)	THF	N.D.

^{*a*}Reactions were run under the conditions: **1a** (0.10 mmol, 1.0 equiv.), **2a** (1.0 equiv.), TMEDA (2.0 equiv.), (NH₄)₂S₂O₈ (2.0 equiv.), solvent (1.0 mL), r.t., 440-450 nm, under a nitrogen atmosphere, 16 h; ^{*b*1}H NMR yields with 1,3,5-trimethoxybenzene as an internal standard.

Table S3. Screening of equiv. of oxidant and electron donor

		(NH ₄) ₂ S ₂ O ₈ , TMEDA DMSO (0.1 M), r.t., N ₂ , 16 h Blue LED (440-450 nm)		
	1a 2a		3a	
Entry ^a	$S_2O_8^{2-}$ (equiv.)	Electron Donor (equiv.)	Solvent	Yield ^b
1	$(NH_4)_2S_2O_8(2.0)$	TMEDA (2.0)	DMSO	62%
2	$(NH_4)_2S_2O_8$ (4.0)	TMEDA (2.0)	DMSO	72%
3	(NH ₄) ₂ S ₂ O ₈ (6.0)	TMEDA (2.0)	DMSO	95%
4	(NH ₄) ₂ S ₂ O ₈ (8.0)	TMEDA (2.0)	DMSO	55%
5	(NH ₄) ₂ S ₂ O ₈ (10.0)	TMEDA (2.0)	DMSO	27%
6	(NH ₄) ₂ S ₂ O ₈ (2.0)	TMEDA (1.0)	DMSO	58%
7	(NH ₄) ₂ S ₂ O ₈ (2.0)	TMEDA (3.0)	DMSO	63%

^{*a*}Reactions were run under the conditions: **1a** (0.10 mmol, 1.0 equiv.), **2a** (1.0 equiv.), TMEDA, (NH₄)₂S₂O₈, DMSO (1.0 mL), r.t., 440-450 nm, under a nitrogen atmosphere, 16 h; ^{*b*1}H NMR yields with 1,3,5-trimethoxybenzene as an internal standard.

	$ \begin{array}{c} & & \\ & & $			
	1a 2a		3a	
Entry ^a	Oxidant (equiv.)	Electron Donor (equiv.)	Solvent	Yield ^b
1	(NH4)2S2O8 (6.0)	TMEDA (2.0)	DMSO	95%
2	$Na_2S_2O_8$ (6.0)	TMEDA (2.0)	DMSO	31%
3	TBHP (6.0)	TMEDA (2.0)	DMSO	6%
4	DTBP (6.0)	TMEDA (2.0)	DMSO	49%

^{*a*}Reactions were run under the conditions: **1a** (0.10 mmol, 1.0 equiv.), **2a** (1.0 equiv.), TMEDA (2.0 equiv.), Oxidant (6.0 equiv.), DMSO (1.0 mL), r.t., 440-450 nm, under a nitrogen atmosphere, 16 h; ^{*b*1}H NMR yields with 1,3,5-trimethoxybenzene as an internal standard.

3.3 General procedures for the preparation for compounds 3

General procedure for the synthesis and characterization of difluoroamidated oxindoles:

N-acrylamide **1** (1.0 equiv.), α -bromo acetamide **2** (1.0 equiv.) and (NH₄)₂S₂O₈ (6.0 equiv.) were added to a 25 mL transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and refilled with nitrogen (N₂) for three times. Then, DMSO (0.1 M), TMEDA (2.0 equiv.) were added via a gastight syringe under a nitrogen atmosphere. Afterward, the tube was sealed, and the reaction mixture was stirred under irradiation with a blue LED (440–450 nm, approximately 3.0 cm from the bulb) at room temperature for 16 h. The reaction mixture was washed with water and extracted with ethyl acetate (3 × 10 mL) to remove DMSO. The organic layers were combined and concentrated under vacuum. The desired product **3** was purified by flash column chromatography on silica gel.

3-(1,3-Dimethyl-2-oxoindolin-3-yl)-2,2-difluoro-N-(p-tolyl)propenamide (3a)



The compound **3a** was prepared according to the general method described above: *N*-acrylamide **1a** (0.20 mmol, 1.0 equiv.), α -bromo acetamide **2a** (1.0 equiv.), (NH₄)₂S₂O₈ (6.0 equiv.) and TMEDA (2.0 equiv.) were irradiated by blue LED (440–450 nm) in the solution of DMSO under a nitrogen atmosphere for 16 h. Then the reaction mixture was purified by flash column chromatography (petroleum ether/ethyl acetate = 10:1 to 4:1) and afforded the desired product as yellow solid, 59.7 mg, 83% yield.

¹H NMR (500 MHz, CDCl₃) δ 7.48 (s, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.21–7.13 (m, 3H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 7.5 Hz, 1H), 3.20 (s, 3H), 3.06–2.83 (m, 2H), 2.31 (s, 3H), 1.39 (s, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 179.2, 161.2 (t, *J* = 27.7 Hz), 142.9, 135.1, 133.2, 130.8, 129.4, 128.4, 124.3, 122.6, 120.2, 116.6 (dd, *J* = 257.5 Hz, 253.7 Hz), 108.1, 44.5 (d, *J* = 5.0 Hz), 40.2 (t, *J* = 23.3 Hz), 26.4, 25.7, 20.9; ¹⁹F{¹H} NMR (471 MHz, CDCl₃): δ = –97.9 (d, *J* = 260.0 Hz, 1F), –107.2 (d, *J* = 260.0 Hz, 1F); HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₂₀H₂₁F₂N₂O₂, 359.1566; found, 359.1573.

3-(1,3-Dimethyl-2-oxoindolin-3-yl)-2,2-difluoro-N-(4-isopropylphenyl)propenamide (3b)



The compound **3b** was prepared according to the general method described above: *N*-acrylamide **1a** (0.20 mmol, 1.0 equiv.), α -bromo acetamide **2b** (1.0 equiv.), (NH₄)₂S₂O₈ (6.0 equiv.) and TMEDA (2.0 equiv.) were irradiated by blue LED (440–450 nm) in the solution of DMSO under a nitrogen atmosphere for 16 h. Then the reaction mixture was purified by flash column chromatography (petroleum ether/ethyl acetate = 10:1 to 4:1) and afforded the desired product as yellow solid, 69.9 mg, 91% yield.

¹H NMR (500 MHz, CDCl₃) δ 7.43 (s, 1H), 7.26–7.20 (m, 3H), 7.20–7.13 (m, 3H), 6.94 (t, J = 7.5 Hz, 1H), 3.22 (s, 3H), 3.07–2.83 (m, 3H), 1.40 (s, 3H), 1.22 (d, J = 6.5 Hz, 6H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 179.3, 161.3 (t, J = 27.7 Hz), 146.3, 142.9, 133.4, 130.9, 128.4, 126.9, 124.3, 122.6, 120.3, 116.7 (dd, J = 257.3 Hz, 253.9 Hz), 108.1, 44.5 (d, J = 5.3 Hz), 40.2 (dd, J = 23.8 Hz, 22.6 Hz), 33.6, 26.5, 25.8, 24.0; ¹⁹F{¹H} NMR (471 MHz, CDCl₃): δ = –98.3 (d, J = 259.8 Hz, 1F), –107.1 (d, J = 259.8 Hz, 1F); HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₂₂H₂₅F₂N₂O₂, 387.1879; found, 387.1892.

N-(4-(*tert*-butyl)phenyl)-3-(1,3-dimethyl-2-oxoindolin-3-yl)-2,2-difluoropropanamide (3c)



The compound **3c** was prepared according to the general method described above: *N*-acrylamide **1a** (0.20 mmol, 1.0 equiv.), α -bromo acetamide **2c** (1.0 equiv.), (NH₄)₂S₂O₈ (6.0 equiv.) and TMEDA (2.0 equiv.) were irradiated by blue LED (440–450 nm) in the solution of DMSO under a nitrogen atmosphere for 16 h. Then the reaction mixture was purified by flash column chromatography (petroleum ether/ethyl acetate = 10:1 to 4:1) and afforded the desired product as orange solid, 69.2 mg, 87% yield.

¹H NMR (500 MHz, CDCl₃) δ 7.47 (s, 1H), 7.31 (d, J = 9.0 Hz, 2H), 7.27–7.21 (m, 3H), 7.18 (t, J = 7.8 Hz, 1H), 6.94 (t, J = 7.5 Hz, 1H), 6.82 (d, J = 7.6 Hz, 1H), 3.22 (s, 3H), 3.08–2.83 (m, 2H), 1.40 (s, 3H), 1.30 (s, 9H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 179.3, 161.3 (t, J = 27.9 Hz), 148.6, 142.9, 133.1, 131.0, 128.4, 125.8, 124.3, 122.6, 120.0, 116.7 (dd, J = 257.4 Hz, 254.0 Hz), 108.1, 44.5 (d, J = 5.0 Hz), 40.2 (dd, J = 23.9 Hz, 22.5 Hz), 34.5, 31.3, 26.5, 25.8; ¹⁹F{¹H} NMR (471 MHz, CDCl₃): δ = –98.4 (d, J = 259.3 Hz, 1F), –106.9 (d, J = 259.3 Hz, 1F); HRMS (ESI-TOF) m/z: [M + H]⁺ calcd for C₂₃H₂₇F₂N₂O₂, 401.2035; found, 401.2041.

3-(1,3-Dimethyl-2-oxoindolin-3-yl)-2,2-difluoro-N-(4-methoxyphenyl)propenamide (3d)



The compound **3d** was prepared according to the general method described above: *N*-acrylamide **1a** (0.10 mmol, 1.0 equiv.), α -bromo acetamide **2d** (1.0 equiv.), (NH₄)₂S₂O₈ (6.0 equiv.) and TMEDA (2.0 equiv.) were irradiated by blue LED (440–450 nm) in the solution of DMSO under a nitrogen atmosphere for 16 h. Then the reaction mixture was purified by flash column chromatography (petroleum ether/ethyl acetate = 10:1 to 4:1) and afforded

the desired product as brown solid, 26.9 mg, 72% yield.

¹H NMR (500 MHz, CDCl₃) δ 7.42 (bs, 1H), 7.26–7.20 (m, 3H), 7.17 (td, *J* = 7.8 Hz, 1.0 Hz, 1H), 6.93 (td, *J* = 7.5 Hz, 1.0 Hz, 1H), 6.84–6.80 (m, 3H), 3.79 (s, 3H), 3.22 (s, 3H), 3.07–2.84 (m, 2H), 1.40 (s, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 179.4, 161.2 (t, *J* = 27.7 Hz), 157.2, 143.0, 131.0, 128.9, 128.5, 124.4, 122.7, 122.0, 116.8 (dd, *J* = 257.4 Hz, 253.6 Hz), 114.1, 108.2, 55.6, 44.6 (d, *J* = 5.5 Hz), 40.4 (dd, *J* = 24.0 Hz, 22.6 Hz), 26.6, 25.9; ¹⁹F{¹H} NMR (471 MHz, CDCl₃): δ = -97.8 (d, *J* = 259.8 Hz, 1F), -107.4 (d, *J* = 259.8 Hz, 1F); HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₂₀H₂₁F₂N₂O₃, 375.1515; found, 375.1518.

3-(1,3-Dimethyl-2-oxoindolin-3-yl)-2,2-difluoro-*N*-phenylpropanamide (3e)



The compound **3e** was prepared according to the general method described above: *N*-acrylamide **1a** (0.20 mmol, 1.0 equiv.), α -bromo acetamide **2e** (1.0 equiv.), (NH₄)₂S₂O₈ (6.0 equiv.) and TMEDA (2.0 equiv.) were irradiated by blue LED (440–450 nm) in the solution of DMSO under a nitrogen atmosphere for 16 h. Then the reaction mixture was purified by flash column chromatography (petroleum ether/ethyl acetate = 10:1 to 4:1) and afforded the desired product as yellow liquid, 46.0 mg, 67% yield.

¹H NMR (500 MHz, CDCl₃) δ 7.51 (s, 1H), 7.32 (d, J = 9.5 Hz, 2H), 7.30 (d, J = 9.0 Hz, 2H), 7.24 (d, J = 9.0 Hz, 1H), 7.14 (t, J = 9.3 Hz, 2H), 6.90 (t, J = 9.5 Hz, 1H), 6.80 (d, J = 9.5 Hz, 1H), 3.21 (s, 3H), 3.08–2.82 (m, 2H), 1.40 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 179.2, 161.3 (t, J = 27.9 Hz), 142.9, 135.8, 130.8, 128.9, 128.4, 125.4, 124.3, 122.6, 120.1, 116.6 (dd, J = 257.5 Hz, 253.9 Hz), 108.1, 44.5 (d, J = 5.3 Hz), 40.3 (dd, J = 23.8 Hz, 22.8 Hz), 26.4, 25.7; ¹⁹F{¹H} NMR (377 MHz, CDCl₃): δ = –97.8 (d, J = 260.0 Hz, 1F), –107.2 (d, J = 260.0 Hz, 1F); HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₁₉H₁₉F₂N₂O₂, 345.1409; found, 345.1416.





The compound **3f** was prepared according to the general method described above: *N*-acrylamide **1a** (0.20 mmol, 1.0 equiv.), α -bromo acetamide **2f** (1.0 equiv.), (NH₄)₂S₂O₈ (6.0 equiv.) and TMEDA (2.0 equiv.) were irradiated by blue LED (440–450 nm) in the solution of DMSO under a nitrogen atmosphere for 16 h. Then the reaction mixture was purified by flash column chromatography (petroleum ether/ethyl acetate = 10:1 to 4:1) and afforded the desired product as yellow solid, 72.3 mg, 99% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.61 (s, 1H), 7.28–7.34 (m, 2H), 7.23 (d, J = 7.2 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 6.98 (t, J = 8.6 Hz, 2H), 6.91 (t, J = 7.4 Hz, 1H), 6.81 (d, J = 7.6 Hz, 1H), 3.21 (s, 3H), 3.07–2.81 (m, 2H), 1.39 (s, 3H); ¹³C {¹H} NMR (101 MHz, CDCl₃) δ 179.2, 161.4 (t, J = 27.9 Hz), 161.2, 158.7, 142.9, 131.9 (d, J = 2.8 Hz), 130.8, 128.5, 124.3, 122.6, 122.0 (d, J = 8.0 Hz), 116.6 (dd, J = 257.4 Hz, 253.7 Hz), 115.8, 115.5, 108.1, 44.5 (d, J = 5.0 Hz), 40.2 (dd, J = 24.3 Hz, 23.3 Hz), 26.5, 25.8; ¹⁹F {¹H} NMR (377 MHz, CDCl₃): δ = –97.7 (d, J = 260.3 Hz, 1F), –116.2 (s, 1F); HRMS (ESI-TOF) *m*/*z*: [M + H]⁺ calcd for C₁₉H₁₈F₃N₂O₂, 363.1315; found, 363.1312.

N-(4-chlorophenyl)-3-(1,3-dimethyl-2-oxoindolin-3-yl)-2,2-difluoropropanamide (3g)



The compound **3g** was prepared according to the general method described above: *N*-acrylamide **1a** (0.20 mmol, 1.0 equiv.), α -bromo acetamide **2g** (1.0 equiv.), (NH₄)₂S₂O₈ (6.0 equiv.) and TMEDA (2.0 equiv.) were irradiated by blue LED (440–450 nm) in the solution of DMSO under a nitrogen atmosphere for 16 h. Then the reaction mixture was purified by flash column chromatography (petroleum ether/ethyl acetate = 4:1) and afforded the desired product as yellow solid, 57.6 mg, 76% yield.

¹H NMR (500 MHz, CDCl₃) δ 7.68 (s, 1H), 7.30 (d, *J* = 9.0 Hz, 2H), 7.25 (d, *J* = 9.0 Hz, 2H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.14 (t, *J* = 7.8 Hz, 1H), 6.90 (t, *J* = 7.3 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 3.20 (s, 3H), 3.06–2.82 (m, 2H), 1.39 (s, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 179.2, 161.5 (t, *J* = 28.1 Hz), 142.9, 134.5, 130.7, 130.5, 129.0, 128.5, 124.3, 122.7, 121.5, 116.6 (dd, *J* = 257.5 Hz, 253.8 Hz), 108.1, 44.5 (d, *J* = 5.4 Hz), 40.3 (dd, *J* = 24.1 Hz, 22.5 Hz), 26.5, 25.7; ¹⁹F{¹H} NMR (471 MHz, CDCl₃): δ = –97.5 (d, *J* = 260.5 Hz, 1F), –107.4 (d, *J* = 260.5 Hz, 1F); HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₁₉H₁₈³⁵ClF₂N₂O₂, 379.1019; found, 379.1027.

N-(4-bromophenyl)-3-(1,3-dimethyl-2-oxoindolin-3-yl)-2,2-difluoropropanamide (3h)



The compound **3h** was prepared according to the general method described above: *N*-acrylamide **1a** (0.20 mmol, 1.0 equiv.), α -bromo acetamide **2h** (1.0 equiv.), (NH₄)₂S₂O₈ (6.0 equiv.) and TMEDA (2.0 equiv.) were irradiated by blue LED (440–450 nm) in the solution of DMSO under a nitrogen atmosphere for 16 h. Then the reaction mixture was purified by flash column chromatography (petroleum ether/ethyl acetate = 10:1 to 4:1) and afforded the desired product as yellow solid, 81.8 mg, 97% yield.

¹H NMR (500 MHz, CDCl₃) δ 7.60 (s, 1H), 7.40 (d, J = 8.5 Hz, 2H), 7.23 (m, 3H), 7.15 (t, J = 7.8 Hz, 1H), 6.90 (t, J = 7.5 Hz, 1H), 6.81 (d, J = 8.0 Hz, 1H), 3.21 (s, 3H), 3.07–2.82 (m, 2H), 1.39 (s, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 179.2, 161.5 (t, J = 28.2 Hz), 142.9, 135.0, 131.9, 130.7, 128.5, 124.3, 122.7, 121.7, 118.2, 116.5 (dd, J = 257.5 Hz, 253.7 Hz), 108.1, 44.5 (d, J = 5.7 Hz), 40.3 (dd, J = 24.2 Hz, 22.6 Hz), 26.5, 25.7; ¹⁹F{¹H} NMR (471 MHz, CDCl₃): δ = -97.5 (d, J = 260.3 Hz, 1F), -107.5 (d, J = 260.3 Hz, 1F); HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₁₉H₁₈⁷⁹BrF₂N₂O₂, 423.0514; found, 423.0523.

Methyl 4-(3-(1,3-dimethyl-2-oxoindolin-3-yl)-2,2-difluoropropanamido)benzoate (3i)



The compound **3i** was prepared according to the general method described above: *N*-acrylamide **1a** (0.10 mmol, 1.0 equiv.), α -bromo acetamide **2i** (1.0 equiv.), (NH₄)₂S₂O₈ (6.0 equiv.) and TMEDA (2.0 equiv.) were irradiated by blue LED (440–450 nm) in the solution of DMSO under a nitrogen atmosphere for 16 h. Then the reaction mixture was purified by flash column chromatography (petroleum ether/ethyl acetate = 10:1 to 4:1) and afforded

the desired product as yellow solid, 38.0 mg, 95% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, J = 8.8 Hz, 2H), 7.80 (s, 1H), 7.44 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 7.2 Hz, 1H), 7.10 (t, J = 7.6 Hz, 1H), 6.86 (t, J = 7.2 Hz, 1H), 6.80 (d, J = 8.0 Hz, 1H), 3.91 (s, 3H), 3.20 (s, 3H), 3.09–2.83 (m, 2H), 1.40 (s, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 179.2, 166.5, 161.7 (t, J = 28.1 Hz), 143.0, 140.1, 130.7, 130.7, 128.6, 126.9, 124.4, 122.7, 117.6 (dd, J = 258.2 Hz, 254.1 Hz), 108.2, 52.3, 44.6 (d, J = 5.7 Hz), 40.4 (dd, J = 24.7 Hz, 22.2 Hz), 26.6, 25.8; ¹⁹F{¹H} NMR (471 MHz, CDCl₃) δ –97.3 (d, J = 260.9 Hz, 1F); -107.5 (d, J = 260.9 Hz, 1F); HRMS (ESI-TOF) m/z: [M + Na]⁺ calcd for C₂₁H₂₁F₂N₂O₄, 425.1283; found, 425.1297.

3-(1,3-Dimethyl-2-oxoindolin-3-yl)-2,2-difluoro-*N*-(*o*-tolyl)propenamide (3j)



The compound **3j** was prepared according to the general method described above: *N*-acrylamide **1a** (0.20 mmol, 1.0 equiv.), α -bromo acetamide **2j** (1.0 equiv.), (NH₄)₂S₂O₈ (6.0 equiv.) and TMEDA (2.0 equiv.) were irradiated by blue LED (440–450 nm) in the solution of DMSO under a nitrogen atmosphere for 16 h. Then the reaction mixture was purified by flash column chromatography (petroleum ether/ethyl acetate = 10:1 to 4:1) and afforded the desired product as yellow solid, 48.2 mg, 67% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, J = 8.4 Hz, 1H), 7.38 (s, 1H), 7.25 (d, J = 7.2 Hz, 1H), 7.21–7.05 (m, 4H), 6.93 (t, J = 7.6 Hz, 1H), 6.81 (d, J = 7.6 Hz, 1H), 3.23 (s, 3H), 3.12–2.85 (m, 2H), 2.05 (s, 3H), 1.41 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 179.2, 161.3 (t, J = 27.7 Hz), 143.0, 133.8, 131.0, 130.5, 128.5, 128.3, 126.8, 125.9, 124.4, 122.6, 122.1, 116.9 (dd, J = 257.5 Hz, 253.8 Hz), 108.0, 44.5 (d, J = 5.4 Hz), 40.1 (dd, J = 24.0 Hz, 22.2 Hz), 26.5, 25.9, 17.2; ¹⁹F{¹H} NMR (377 MHz, CDCl₃): δ = –97.6 (d, J = 261.7 Hz, 1F), –107.2 (d, J = 261.7 Hz, 1F); HRMS (ESI-TOF) m/z: [M + H]⁺ calcd for C₂₀H₂₁F₂N₂O₂, 359.1566; found, 359.1568.

3-(1,3-Dimethyl-2-oxoindolin-3-yl)-2,2-difluoro-*N*-(*m*-tolyl)propenamide (3k)



The compound **3k** was prepared according to the general method described above: *N*-acrylamide **1a** (0.20 mmol, 1.0 equiv.), α -bromo acetamide **2k** (1.0 equiv.), (NH₄)₂S₂O₈ (6.0 equiv.) and TMEDA (2.0 equiv.) were irradiated by blue LED (440–450 nm) in the solution of DMSO under a nitrogen atmosphere for 16 h. Then the reaction mixture was purified by flash column chromatography (petroleum ether/ethyl acetate = 9:1 to 4:1) and afforded the desired product as yellow solid, 57.6 mg, 80% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.44 (s, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.20–7.13 (m, 3H), 7.09 (d, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 1H), 6.91 (t, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 3.22 (s, 3H), 3.08–2.82 (m, 2H), 2.32 (s, 3H), 1.40 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 179.2, 161.3 (t, *J* = 27.8 Hz), 142.9, 138.9, 135.7, 130.9, 128.7, 128.4, 126.3, 124.3, 122.6, 120.8, 117.3, 116.6 (dd, *J* = 257.4 Hz, 253.8 Hz), 108.1, 44.5 (d, *J* = 5.9 Hz), 40.3 (dd, *J* = 24.2 Hz, 22.5 Hz), 26.5, 25.8, 21.4; ¹⁹F{¹H} NMR (377 MHz, CDCl₃): δ = –98.0 (d, *J* = 259.4 Hz, 1F); HRMS (ESI-TOF) *m*/*z*: [M + H]⁺ calcd for C₂₀H₂₁F₂N₂O₂, 359.1566; found, 359.1571.

3-(1,3-Dimethyl-2-oxoindolin-3-yl)-2,2-difluoro-N-(3-methoxyphenyl)propenamide (31)



The compound **31** was prepared according to the general method described above: *N*-acrylamide **1a** (0.20 mmol, 1.0 equiv.), α -bromo acetamide **2l** (1.0 equiv.), (NH₄)₂S₂O₈ (6.0 equiv.) and TMEDA (2.0 equiv.) were irradiated by blue LED (440–450 nm) in the solution of DMSO under a nitrogen atmosphere for 16 h. Then the reaction mixture was purified by flash column chromatography (petroleum ether/ethyl acetate = 10:1 to 4:1) and afforded the desired product as yellow solid, 58.5 mg, 78% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.49 (s, 1H), 7.24 (d, J = 7.6 Hz, 1H), 7.19 (d, J = 8.0 Hz, 1H), 7.15 (d, J = 6.8 Hz, 1H), 7.07 (s, 1H), 6.92 (t, J = 7.6 Hz, 1H), 6.80 (t, J = 7.0 Hz, 2H), 6.69 (dd, J = 8.2 Hz, 1.8 Hz, 1H), 3.79 (s, 3H), 3.22 (s, 3H), 3.07–2.82 (m, 2H), 1.40 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 179.2, 161.4 (t, J = 28.0 Hz), 160.0, 142.9, 137.0, 130.8, 129.6, 128.5, 124.3, 122.6, 116.6 (dd, J = 257.6 Hz, 254.0 Hz), 112.4, 111.3, 108.1, 105.9, 55.4, 44.5 (d, J = 5.4 Hz), 40.3 (dd, J = 24.2 Hz, 22.5 Hz), 26.5, 25.8; ¹⁹F{¹H} NMR (377 MHz, CDCl₃): δ = -98.1 (d, J = 259.6 Hz, 1F), -107.1 (d, J = 259.6 Hz, 1F); HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₂₀H₂₁F₂N₂O₃, 375.1515; found, 375.1514.

N-(3,4-Dimethoxyphenyl)-3-(1,3-dimethyl-2-oxoindolin-3-yl)-2,2-difluoropropanamide (3m)



The compound **3m** was prepared according to the general method described above: *N*-acrylamide **1a** (0.20 mmol, 1.0 equiv.), α -bromo acetamide **2m** (1.0 equiv.), (NH₄)₂S₂O₈ (6.0 equiv.) and TMEDA (2.0 equiv.) were irradiated by blue LED (440–450 nm) in the solution of DMSO under a nitrogen atmosphere for 16 h. Then the reaction mixture was purified by flash column chromatography (petroleum ether/ethyl acetate = 4:1 to 1:1) and afforded the desired product as colourless liquid, 71.9 mg, 89% yield.

¹H NMR (500 MHz, CDCl₃) δ 7.59 (bs, 1H), 7.25 (d, *J* = 7.0 Hz, 1H), 7.19 (t, *J* = 8.0 Hz, 1H), 7.10 (s, 1H), 6.95 (d, *J* = 7.3 Hz, 1H), 6.82 (d, *J* = 7.5 Hz, 1H), 6.76 (s, 2H), 3.85 (s, 6H), 3.21 (s, 3H), 3.07–2.83 (m, 2H), 1.40 (s, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 179.3, 161.2 (t, *J* = 27.7 Hz), 148.8, 146.6, 142.9, 130.9, 129.3, 128.4, 124.3, 122.6, 116.7 (dd, *J* = 257.1 Hz, 253.9 Hz), 112.4, 110.9, 108.1, 104.9, 56.0, 44.5 (d, *J* = 4.9 Hz), 40.3 (t, *J* = 23.3 Hz), 26.5, 25.8; ¹⁹F{¹H} NMR (471 MHz, CDCl₃): δ = -98.2 (d, *J* = 259.3 Hz, 1F), -107.1 (d, *J* = 259.3 Hz, 1F); HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₂₁H₂₃F₂N₂O₄, 405.1620; found, 405.1623.

3-(1,3-Dimethyl-2-oxoindolin-3-yl)-2,2-difluoro-N-(naphthalen-1-yl)propenamide (3n)



The compound **3n** was prepared according to the general method described above: *N*-acrylamide **1a** (0.20 mmol, 1.0 equiv.), α -bromo acetamide **2n** (1.0 equiv.), (NH₄)₂S₂O₈ (6.0 equiv.) and TMEDA (2.0 equiv.) were irradiated by blue LED (440–450 nm) in the solution of DMSO under a nitrogen atmosphere for 16 h. Then the reaction mixture was purified by flash column chromatography (petroleum ether/ethyl acetate = 10:1 to 4:1) and afforded the desired product as reddish brown solid, 62.7 mg, 80% yield.

¹H NMR (500 MHz, CDCl₃) δ 7.98 (s, 1H), 7.88–7.83 (m, 1H), 7.78 (d, J = 7.5 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.52–7.41 (m, 4H), 7.29–7.25 (m, 1H), 7.10 (t, J = 7.5 Hz, 1H), 6.92 (t, J = 7.3 Hz, 1H), 6.77 (d, J = 8.0 Hz, 1H), 3.24 (s, 3H), 3.17–2.93 (m, 2H), 1.43 (s, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 179.3, 161.9 (t, J = 27.7 Hz), 143.0, 133.9, 130.9, 130.1, 128.8, 128.5, 126.7, 126.6, 126.4, 126.3, 125.5, 124.4, 122.6, 120.4, 120.1, 117.1 (dd, J = 257.8 Hz, 253.7 Hz), 108.2, 44.6 (d, J = 5.4 Hz), 40.1 (dd, J = 24.2 Hz, 22.1 Hz), 26.5, 26.0; ¹⁹F{¹H} NMR (471 MHz, CDCl₃): δ = –97.0 (d, J = 262.6 Hz, 1F), –106.8 (d, J = 262.6 Hz, 1F); HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₂₃H₂₁F₂N₂O₂, 395.1566; found, 395.1573.

3-(1,3-Dimethyl-2-oxoindolin-3-yl)-2,2-difluoro-N-methylpropanamide (30)



The compound **30** was prepared according to the general method described above: *N*-acrylamide **1a** (0.20 mmol, 1.0 equiv.), α -bromo acetamide **20** (1.0 equiv.), (NH₄)₂S₂O₈ (6.0 equiv.) and TMEDA (2.0 equiv.) were irradiated by blue LED (440–450 nm) in the solution of DMSO under a nitrogen atmosphere for 16 h. Then the reaction mixture was purified by flash column chromatography (petroleum ether/ethyl acetate = 6:1) and afforded the desired product as white solid, 36.0 mg, 64% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.30–7.22 (m, 2H), 7.06 (td, J = 7.5 Hz, 0.9 Hz, 1H), 6.86 (d, J = 8.0 Hz, 1H), 5.92 (s, 1H), 3.23 (s, 3H), 3.06–2.89 (m, 1H), 2.84–2.72 (m, 1H), 2.54 (d, J = 5.2 Hz, 3H), 1.38 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 179.4, 164.3 (t, J = 27.9 Hz), 143.0, 130.8, 128.4, 124.6, 122.4, 116.6 (dd, J = 256.5 Hz, 251.5 Hz), 108.1, 44.5 (d, J = 6.5 Hz), 40.2 (dd, J = 24.9 Hz, 22.0 Hz), 26.1 (t, J = 36.6 Hz); ¹⁹F{¹H} NMR (377 MHz, CDCl₃): δ = –97.6 (d, J = 260.7 Hz, 1F), –110.1 (d, J = 260.7 Hz, 1F); HRMS (ESI-TOF) *m*/*z*: [M + H]⁺ calcd for C₁₄H₁₇F₂N₂O₂, 283.1253; found, 283.1249.

3-(1,3-Dimethyl-2-oxoindolin-3-yl)-2,2-difluoro-N-isopropylpropanamide (3p)



The compound **3p** was prepared according to the general method described above: *N*-acrylamide **1a** (0.20 mmol, 1.0 equiv.), α -bromo acetamide **2p** (1.0 equiv.), (NH₄)₂S₂O₈ (6.0 equiv.) and TMEDA (2.0 equiv.) were irradiated by blue LED (440–450 nm) in the solution of DMSO under a nitrogen atmosphere for 16 h. Then the reaction mixture was purified by flash column chromatography (petroleum ether/ethyl acetate = 6:1) and afforded the desired product as white solid, 27.3 mg, 44% yield.

¹H NMR (500 MHz, CDCl₃) δ 7.28 (d, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 8.5 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 5.72 (s, 1H), 3.78–3.69 (m, 1H), 3.24 (s, 3H), 3.05–2.93 (m, 1H), 2.83–2.72 (m, 1H), 1.38 (s, 3H), 1.07 (d, *J* = 6.5 Hz, 3H), 0.92 (d, *J* = 6.5 Hz, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 179.4, 162.6 (t, *J* = 27.9 Hz), 143.0, 131.1, 128.3, 124.5, 122.4, 116.6 (dd, *J* = 256.8 Hz, 252.0 Hz), 108.0, 44.5 (d, *J* = 5.8 Hz), 41.8, 39.8 (dd, *J* = 24.5 Hz, 21.8 Hz), 26.4, 25.9, 22.15, 22.10; ¹⁹F{¹H} NMR (471 MHz, CDCl₃): δ = –98.0 (d, *J* = 261.7 Hz, 1F); HRMS (ESI-TOF) *m*/*z*: [M + H]⁺ calcd for C₁₆H₂₁F₂N₂O₂, 311.1566; found, 311.1571.

N-(tert-butyl)-3-(1,3-dimethyl-2-oxoindolin-3-yl)-2,2-difluoropropanamide (3q)



The compound **3q** was prepared according to the general method described above: *N*-acrylamide **1a** (0.20 mmol, 1.0 equiv.), α -bromo acetamide **2q** (1.0 equiv.), (NH₄)₂S₂O₈ (6.0 equiv.) and TMEDA (2.0 equiv.) were irradiated by blue LED (440–450 nm) in the solution of DMSO under a nitrogen atmosphere for 16 h. Then the reaction mixture was purified by flash column chromatography (petroleum ether/ethyl acetate = 10:1 to 4:1) and afforded the desired product as yellow solid, 32.2 mg, 50% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.30–7.24 (m, 2H), 7.05 (t, J = 7.6 Hz, 1H), 6.85 (t, J = 7.6 Hz, 1H), 5.76 (s, 1H), 3.24 (s, 3H), 3.00–2.69 (m, 2H), 1.38 (s, 3H), 1.22 (s, 9H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 179.5, 162.7 (t, J = 27.2 Hz), 143.0, 131.7, 128.2, 124.3, 122.8, 116.7 (dd, J = 257.7 Hz, 254.0 Hz), 108.2, 51.8, 44.7 (d, J = 4.5 Hz), 39.8 (dd, J = 24.0 Hz, 22.0 Hz), 28.4, 26.5, 26.1; ¹⁹F{¹H} NMR (377 MHz, CDCl₃): δ = –99.3 (d, J = 259.8 Hz, 1F), -105.7 (d, J = 259.8 Hz, 1F); HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₁₇H₂₃F₂N₂O₂, 325.1722; found, 325.1732.

3-(2,2-Difluoro-3-morpholino-3-oxopropyl)-1,3-dimethylindolin-2-one (3r)



The compound **3r** was prepared according to the general method described above: *N*-acrylamide **1a** (0.20 mmol, 1.0 equiv.), α -bromo acetamide **2r** (1.0 equiv.), (NH₄)₂S₂O₈ (6.0 equiv.) and TMEDA (2.0 equiv.) were irradiated by blue LED (440–450 nm) in the solution of DMSO under a nitrogen atmosphere for 16 h. Then the reaction mixture was purified by flash column chromatography (petroleum ether/ethyl acetate = 10:1 to 4:1) and afforded the desired product as yellow solid, 48.0 mg, 71%.

¹H NMR (500 MHz, CDCl₃) δ 7.30 (td, J = 7.6 Hz, 1.2 Hz, 1H), 7.26 (d, J = 8.5 Hz, 1H), 7.07 (td, J = 7.5 Hz, 1.0 Hz, 1H), 6.87 (d, J = 7.5 Hz, 1H), 3.67–3.46 (m, 8H), 3.24 (s, 3H), 3.10–2.98 (m, 1H), 2.89–2.76 (m, 1H), 1.41 (s, 3H). The NMR data agreed with those in a literature report.⁷

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{21}F_2N_2O_3$, 339.1515; found, 339.1518. **2,2-Difluoro-3-(5-fluoro-1,3-dimethyl-2-oxoindolin-3-yl)**-*N*-(*p*-tolyl)propenamide (3s)



The compound **3s** was prepared according to the general method described above: *N*-acrylamide **1b** (0.20 mmol, 1.0 equiv.), α -bromo acetamide **2a** (1.0 equiv.), (NH₄)₂S₂O₈ (6.0 equiv.) and TMEDA (2.0 equiv.) were irradiated by blue LED (440–450 nm) in the solution of DMSO under a nitrogen atmosphere for 16 h. Then the reaction mixture was purified by flash column chromatography (petroleum ether/ethyl acetate = 10:1 to 4:1) and afforded the desired product as brown solid, 45.1 mg, 60% yield.

¹H NMR (500 MHz, CDCl₃) δ 7.61 (s, 1H), 7.25 (d, J = 8.5 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 7.03 (dd, J = 8.0 Hz, 2.5 Hz, 1H), 6.86 (td, J = 8.8 Hz, 2.5 Hz, 1H), 6.73 (dd, J = 8.5 Hz, 4.0 Hz, 1H), 3.20 (s, 3H), 3.02–2.83 (m, 2H), 2.31 (s, 3H), 1.40 (s, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 178.9, 161.1 (t, J = 27.8 Hz), 159.1 (d, J = 241.0

Hz), 138.8 (d, J = 1.5 Hz), 135.3, 133.1, 132.6 (d, J = 8.0 Hz), 129.5, 120.1, 116.5 (dd, J = 257.1 Hz, 254.5 Hz), 114.7 (d, J = 23.6 Hz), 112.5 (d, J = 24.9 Hz), 108.6 (d, J = 8.2 Hz), 45.0 (d, J = 4.4 Hz), 40.1 (dd, J = 23.8 Hz, 22.6 Hz), 26.6, 25.7, 20.9; ¹⁹F{¹H} NMR (471 MHz, CDCl₃): $\delta = -99.5$ (d, J = 259.1 Hz, 1F), -106.2 (d, J = 259.1 Hz, 1F), -120.2 (s, 1F); HRMS (ESI-TOF) m/z: [M + H]⁺ calcd for C₂₀H₂₀F₃N₂O₂, 377.1471; found, 377.1475.

3-(5-Chloro-1,3-dimethyl-2-oxoindolin-3-yl)-2,2-difluoro-N-(p-tolyl)propenamide (3t)



The compound **3t** was prepared according to the general method described above: *N*-acrylamide **1c** (0.20 mmol, 1.0 equiv.), α -bromo acetamide **2a** (1.0 equiv.), (NH₄)₂S₂O₈ (6.0 equiv.) and TMEDA (2.0 equiv.) were irradiated by blue LED (440–450 nm) in the solution of DMSO under a nitrogen atmosphere for 16 h. Then the reaction mixture was purified by flash column chromatography (petroleum ether/ethyl acetate = 10:1 to 4:1) and afforded the desired product as yellow solid, 78.4 mg, 99% yield.

¹H NMR (500 MHz, CDCl₃) δ 7.59 (s, 1H),7.28–7.22 (m, 3H), 7.15–7.08 (m, 3H), 6.73 (d, J = 8.0 Hz, 1H), 3.20 (s, 3H), 3.02–2.82 (m, 2H), 2.32 (s, 3H), 1.40 (s, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 178.8, 161.0 (t, J = 27.7 Hz), 141.5, 135.3, 133.1, 132.6, 129.5, 128.4, 128.1, 124.9, 120.2, 116.5 (dd, J = 257.2 Hz, 254.3 Hz), 109.1, 44.8 (d, J = 5.0 Hz), 40.1 (t, J = 23.3 Hz), 26.6, 25.7, 21.0; ¹⁹F{¹H} NMR (377 MHz, CDCl₃): δ = –99.1 (d, J = 259.2 Hz, 1F), –106.5 (d, J = 259.2 Hz, 1F); HRMS (ESI-TOF) m/z: [M + H]⁺ calcd for C₂₀H₂₀³⁵ClF₂N₂O₂, 393.1176; found, 393.1184.

3-(5-Bromo-1,3-dimethyl-2-oxoindolin-3-yl)-2,2-difluoro-*N*-(*p*-tolyl)propenamide (3u)



The compound **3u** was prepared according to the general method described above: *N*-acrylamide **1a** (0.20 mmol, 1.0 equiv.), α -bromo acetamide **2a** (1.0 equiv.), (NH₄)₂S₂O₈ (6.0 equiv.) and TMEDA (2.0 equiv.) were irradiated by blue LED (440–450 nm) in the solution of DMSO under a nitrogen atmosphere for 16 h. Then the reaction mixture was purified by flash column chromatography (petroleum ether/ethyl acetate = 10:1 to 4:1) and afforded the desired product as yellow solid, 69.9 mg, 80% yield.

¹H NMR (500 MHz, CDCl₃) δ 7.61 (s, 1H), 7.38 (d, J = 1.5 Hz, 1H), 7.30–7.22 (m, 3H), 7.11 (d, J = 8.0 Hz, 2H), 6.68 (d, J = 8.0 Hz, 1H), 3.19 (s, 3H), 3.02–2.82 (m, 2H), 2.31 (s, 3H), 1.39 (s, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 178.6, 161.0 (t, J = 27.7 Hz), 142.0, 135.3, 133.1, 133.0, 131.3, 129.5, 127.6, 120.2, 116.5 (dd, J = 254.2 Hz, 257.3 Hz), 115.4, 109.6, 44.7 (d, J = 4.9 Hz), 40.1 (dd, J = 23.9 Hz, 22.5 Hz), 26.6, 25.7, 21.0; ¹⁹F{¹H} NMR (471 MHz, CDCl₃): δ = –98.9 (d, J = 259.8 Hz, 1F), –106.5 (d, J = 259.8 Hz, 1F); HRMS (ESI-TOF) m/z: [M + H]⁺ calcd for C₂₀H₂₁⁷⁹BrF₂N₂O₂, 437.0671; found, 437.0679.

3-(1,3-Dimethyl-2-oxo-5-(trifluoromethyl)indolin-3-yl)-2,2-difluoro-*N*-(*p*-tolyl)propenamide (3v)



The compound **3v** was prepared according to the general method described above: *N*-acrylamide **1e** (0.20 mmol, 1.0 equiv.), α -bromo acetamide **2a** (1.0 equiv.), (NH₄)₂S₂O₈ (6.0 equiv.) and TMEDA (2.0 equiv.) were irradiated by blue LED (440–450 nm) in the solution of DMSO under a nitrogen atmosphere for 16 h. Then the reaction mixture was purified by flash column chromatography (petroleum ether/ethyl acetate = 10:1 to 4:1) and afforded the desired product as light yellow solid, 63.5 mg, 75% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.54–7.44 (m, 3H), 7.22 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 6.89 (d, J = 8.4 Hz, 2H), 3.26 (s, 3H), 3.09–2.86 (m, 2H), 2.31 (s, 3H), 1.44 (s, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 179.1, 160.8 (t, J = 27.9 Hz), 145.9, 135.4, 133.0, 131.6, 129.5, 126.3 (q, J = 3.9 Hz), 124.9 (q, J = 32.9 Hz), 124.2 (q, J = 271.6 Hz), 121.4 (q, J = 3.3 Hz), 120.0, 116.5 (dd, J = 256.7 Hz, 254.9 Hz), 107.9, 44.5 (d, J = 4.5 Hz), 40.1 (t, J = 23.1 Hz), 26.7, 25.7, 20.9; ¹⁹F{¹H} NMR (377 MHz, CDCl₃): δ = -61.4 (s, 1F), -99.8 (d, J = 259.6 Hz, 1F), -105.3 (d, J = 259.6 Hz, 1F); HRMS (ESI-TOF) m/z: [M + H]⁺ calcd for C₂₁H₂₀F₅N₂O₂, 427.1439; found, 427.1449.

2,2-Difluoro-*N*-(*p*-tolyl)-3-(1,3,5-trimethyl-2-oxoindolin-3-yl)propenamide (3w)



The compound **3w** was prepared according to the general method described above: *N*-acrylamide **1f** (0.20 mmol, 1.0 equiv.), α -bromo acetamide **2a** (1.0 equiv.), (NH₄)₂S₂O₈ (6.0 equiv.) and TMEDA (2.0 equiv.) were irradiated by blue LED (440–450 nm) in the solution of DMSO under a nitrogen atmosphere for 16 h. Then the reaction mixture was purified by flash column chromatography (petroleum ether/ethyl acetate = 10:1 to 4:1) and afforded the desired product as reddish brown solid, 38.7 mg, 52% yield.

¹H NMR (500 MHz, CDCl₃) δ 7.32 (s, 1H), 7.18 (d, J = 8.5 Hz, 2H), 7.08 (d, J = 8.5 Hz, 2H), 7.02 (s, 1H), 6.90 (d, J = 7.5 Hz, 1H), 6.70 (d, J = 8.0 Hz, 1H), 3.21 (s, 3H), 3.09–2.97 (m, 1H), 2.92–2.82 (m, 1H), 2.31 (s, 3H), 2.04 (s, 3H), 1.37 (s, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 179.3, 161.3 (t, J = 27.7 Hz), 140.5, 135.1, 133.2, 132.3, 130.5, 129.3, 128.8, 125.3, 119.9, 116.6 (dd, J = 258.1 Hz, 252.7 Hz), 107.7, 44.5 (d, J = 6.2 Hz), 40.2 (dd, J = 24.8 Hz, 22.2 Hz), 26.5, 25.7, 20.9, 20.8; ¹⁹F{¹H} NMR (471 MHz, CDCl₃): δ = –96.1 (d, J = 259.8 Hz, 1F); HRMS (ESI-TOF) m/z: [M + H]⁺ calcd for C₂₁H₂₃F₂N₂O₂, 373.1722; found, 373.1720.

2,2-Difluoro-3-(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)-N-(p-tolyl)propenamide (3x)



The compound **3x** was prepared according to the general method described above: *N*-acrylamide **1g** (0.20 mmol, 1.0 equiv.), α -bromo acetamide **2a** (1.0 equiv.), (NH₄)₂S₂O₈ (6.0 equiv.) and TMEDA (2.0 equiv.) were irradiated

by blue LED (440–450 nm) in the solution of DMSO under a nitrogen atmosphere for 16 h. Then the reaction mixture was purified by flash column chromatography (petroleum ether/ethyl acetate = 10:1 to 4:1) and afforded the desired product as yellow solid, 66.2 mg, 85% yield.

¹H NMR (500 MHz, CDCl₃) δ 7.47 (s, 1H), 7.21 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 2.5 Hz, 1H), 6.71 (d, *J* = 8.5 Hz, 1H), 6.63 (dd, *J* = 8.5 Hz, 2.5 Hz, 1H), 3.56 (s, 3H), 3.19 (s, 3H), 3.05–2.82 (m, 2H), 2.31 (s, 3H), 1.38 (s, 3H); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 178.9, 161.3 (t, *J* = 27.8 Hz), 155.9, 136.4, 135.1, 133.2, 132.0, 129.4, 120.1, 116.7 (dd, *J* = 257.8 Hz, 253.4 Hz), 112.9, 111.8, 108.4, 55.5, 44.9 (d, *J* = 5.9 Hz), 40.2 (dd, *J* = 24.5 Hz, 22.6 Hz), 26.6, 25.8, 20.9; ¹⁹F{¹H} NMR (471 MHz, CDCl₃): δ = –96.9 (d, *J* = 259.8 Hz, 1F), -108.6 (d, *J* = 259.8 Hz, 1F); HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₂₁H₂₃F₂N₂O₃, 389.1671; found, 389.1677.

3.4 Scale-up reaction



N-acrylamide **1a** (5 mmol, 1.0 equiv.), α -bromo acetamide **2a** (1.0 equiv.), (NH₄)₂S₂O₈ (6.0 equiv.) and TMEDA (2.0 equiv.) were irradiated by blue LED (440–450 nm) in the solution of DMSO (30 mL) under a nitrogen atmosphere for 16 h. Then, the reaction mixture was diluted with ethyl acetate (35 mL), washed with brine (30 mL × 3), dried over anhydrous Na₂SO₄, filtered, concentrated under reduced pressure, the resulting mixture purified by flash column chromatography (petroleum ether/ethyl acetate = 10:1 to 4:1) to afford the desired product as yellow solid, 916.0 mg, 51% yield.

4. Mechanistic investigations

4.1 UV-vis absorption spectra as evidence of the EDA complexes



Figure S2. UV/vis absorptions of 1a (0.1 M), 2a (0.1 M) and their mixture in DMSO solution.

The UV/vis absorption spectra of DMSO solution of 1a (0.1 M), 2a (0.1 M), and a mixture of 1a (0.1 M) and 2a (0.1 M) are shown in Figure S2. In Figure S2, we don't really see a bathochromic shift. Upon mixing 1a + 2a, the new curve is completely superimposable to the sum of 1a and 2a. This observation excludes the formation of electron donor-acceptor (EDA) complexes.



Figure S3. UV/vis absorptions of 1a (0.1 M), TMEDA (0.2 M) and their mixture in DMSO solution.

The UV/vis absorption spectra of DMSO solution of **1a** (0.1 M), **TMEDA** (0.2 M), and a mixture of **1a** (0.1 M) and **TMEDA** (0.2 M) are shown in Figure S3. In Figure S3, we don't really see a bathochromic shift. Upon mixing **1a** + **TMEDA**, the new curve is completely superimposable to the sum of **1a** and **TMEDA**. This observation excludes the formation of electron donor-acceptor (EDA) complexes.

4.2 Free radical-trapping experiments

1a (0.10 mmol, 1.0 equiv.), 2a (0.10 mmol, 1.0 equiv.), (NH₄)₂S₂O₈ (6.0 equiv.), and TEMPO (2,2,6,6-tetramethylpiperidinooxy, 0.20 mmol, 2.0 equiv.) were added to a 25 mL transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and refilled with nitrogen (N₂) three times. Then, TMEDA (2.0 equiv.) and anhydrous DMSO (1.0 mL) were added via a gastight syringe under nitrogen atmosphere, and the tube was sealed and the mixture was stirred under irradiation with blue LED (440-450 nm, distance approximately 3.0 cm from the lamp) at room temperature for 16 h. The reaction mixture was analyzed by HRMS with ESI source, no desired product **3a** was detected, indicating that the reaction was completely inhibited by TEMPO. Meanwhile, free radical-trapping adduct TEMPO–**2a** was observed with HRMS analysis of the reaction solution (Figure S4). HRMS (ESI-TOF) m/z: [M + H]⁺ calcd for C₁₈H₂₆F₂N₂O₂, 341.2035; found, 341.2032.





Figure S4. HRMS of radical trapping experiment with TEMPO.

1a (0.20 mmol, 1.0 equiv.), 2a (0.20 mmol, 1.0 equiv.), $(NH_4)_2S_2O_8$ (6.0 equiv.), and BHT (butylated hydroxytoluene, 0.4 mmol, 2.0 equiv.) were added to a 25 mL transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and refilled with nitrogen (N₂) three times. Then, TMEDA (2.0 equiv.) and anhydrous DMSO (2.0 mL) were added via a gastight syringe under nitrogen atmosphere, and the tube was sealed and the mixture was stirred under irradiation with blue LED (440-450 nm, distance approximately 3.0 cm from the lamp) at room temperature for 16 h. The reaction mixture was analyzed by HRMS with ESI source, desired product **3a** was in 17% yield, indicating that the reaction was inhibited by BHT. Meanwhile, free radical-trapping adduct TEMPO–**2a** was observed with HRMS analysis of the reaction solution (Figure S5). HRMS (ESI-TOF) m/z: [M + H]⁺ calcd for C₂₄H₃₂F₂NO₂, 404.2396; found, 404.2387.



Figure S5. HRMS of radical trapping experiment with BHT.

1a (0.20 mmol, 1.0 equiv.), 2a (0.20 mmol, 1.0 equiv.), (NH₄)₂S₂O₈ (6.0 equiv.), and 1,1-diphenylethylene (0.4 mmol, 2.0 equiv.) were added to a 25 mL transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and refilled with nitrogen (N₂) three times. Then, TMEDA (2.0 equiv.) and anhydrous DMSO (2.0 mL) were added via a gastight syringe under nitrogen atmosphere, and the tube was sealed and the mixture was stirred under irradiation with blue LED (440-450 nm, distance approximately 3.0 cm from the lamp) at room temperature for 16 h. The reaction mixture was analyzed by HRMS with ESI source, no desired product **3a** was detected, indicating that the reaction was completely inhibited by 1,1-diphenylethylene. Meanwhile, free radical-trapping adduct 1,1-diphenylethylene–**2a** was observed with HRMS analysis of the reaction solution (Figure S6). HRMS (ESI-TOF) m/z: [M + H]⁺ calcd for C₂₃H₂₀F₂NO, 364.1507; found, 364.1516.



Figure S6. HRMS of radical trapping experiment with 1,1-diphenylethylene.

Note that product **3a** was isolated in 11% yield without light, and this reaction was probably initiated by the formation of non-covalent interactions between **2a** and TMEDA during the removal of solvent occurring during spin evaporation.



Scheme S2 Plausible thermal reaction mechanism

4.3 ¹H NMR titration experiments

The CDCl₃ solutions were mixed with 2a (0.10 mmol, 1.0 equiv.) and TMEDA by molar ratio from 1:0, 1:0.5, 1:1 to 1:2. The ¹H NMR experiments of different combinations of 2a and TMEDA were performed at 400 MHz.

5. References

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6. NMR spectra of related compounds

¹H NMR Spectra of compound **20** (400 MHz, CDCl₃)





 $^{13}C\{^{1}H\}$ NMR Spectra of compound 3a (126 MHz, CDCl_3)



¹H NMR Spectra of compound **3b** (500 MHz, CDCl₃)











¹⁹F{¹H} NMR Spectra of compound **3d** (471 MHz, CDCl₃)



S28

5.0 f1 (ppm)

4.5

4.0

5.5

6.0

0.86

7.5

8.0

8.5

.5 10.0

9.5

9.0

92299

6.5

7.0

3.05-

1.5

1.0

0.5

0.0 -0

2.0

2.5

3.05_ 2.12

3.0

3.5

¹³C{¹H} NMR Spectra of compound **3e** (101 MHz, CDCl₃)



10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)

¹H NMR Spectra of compound **3f** (400 MHz, CDCl₃)



 $^{13}C\{^{1}H\}$ NMR Spectra of compound **3f** (101 MHz, CDCl₃)





 $^{13}C\{^{1}\text{H}\}$ NMR Spectra of compound $3g~(126~\text{MHz}, \text{CDCl}_{3})$



S32

¹H NMR Spectra of compound **3h** (500 MHz, CDCl₃)







¹H NMR Spectra of compound **3i** (400 MHz, CDCl₃)



¹³C{¹H} NMR Spectra of compound **3i** (126 MHz, CDCl₃)



¹H NMR Spectra of compound **3j** (400 MHz, CDCl₃)



 $^{13}C\{^{1}H\}$ NMR Spectra of compound **3j** (101 MHz, CDCl₃)



¹⁹F{¹H} NMR Spectra of compound **3j** (377 MHz, CDCl₃)



¹³C{¹H} NMR Spectra of compound **3k** (101 MHz, CDCl₃)



¹H NMR Spectra of compound **3l** (400 MHz, CDCl₃)



 $^{13}C\{^{1}H\}$ NMR Spectra of compound **3l** (101 MHz, CDCl₃)



¹⁹F{¹H} NMR Spectra of compound **3l** (377 MHz, CDCl₃)



¹H NMR Spectra of compound **3m** (500 MHz, CDCl₃)



 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR Spectra of compound 3m (126 MHz, CDCl_3)



¹H NMR Spectra of compound **3n** (500 MHz, CDCl₃)





 $^{19}\mathrm{F}\{^{1}\mathrm{H}\}$ NMR Spectra of compound **3n** (471 MHz, CDCl₃)



 $^{13}C\{^{1}H\}$ NMR Spectra of compound 3o~(101 MHz, CDCl_3)



¹H NMR Spectra of compound **3p** (500 MHz, CDCl₃)



 $^{13}C\{^{1}H\}$ NMR Spectra of compound **3p** (126 MHz, CDCl₃)



¹⁹F{¹H} NMR Spectra of compound **3p** (471 MHz, CDCl₃)



¹³C{¹H} NMR Spectra of compound **3q** (126 MHz, CDCl₃)





¹H NMR Spectra of compound **3s** (500 MHz, CDCl₃)



¹³C{¹H} NMR Spectra of compound **3s** (126 MHz, CDCl₃)



¹H NMR Spectra of compound **3t** (500 MHz, CDCl₃)



¹⁹F{¹H} NMR Spectra of compound **3t** (377 MHz, CDCl₃)







!0 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22 f1 (ppm) ¹H NMR Spectra of compound **3v** (400 MHz, CDCl₃)



 $^{13}C\{^{1}H\}$ NMR Spectra of compound 3v (126 MHz, CDCl₃)



¹⁹F{¹H} NMR Spectra of compound **3v** (377 MHz, CDCl₃)





¹³C{¹H} NMR Spectra of compound **3w** (126 MHz, CDCl₃)



¹H NMR Spectra of compound **3x** (500 MHz, CDCl₃)





 $^{19}\mathrm{F}\{^{1}\mathrm{H}\}$ NMR Spectra of compound 3x (471 MHz, CDCl₃)

