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Ketosulfonylmethylenation and Sulfonylethylenation of

Imidazoheterocycles with Dimethylformamide as Methylene Source

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1 General Experimental

Unless otherwise mentioned, all materials were commercially obtained and used without further purification. imidazoheterocycles (**3**)¹ were synthesized according to previously described methods. The ¹H NMR, ¹³C NMR, and ¹⁹F NMR spectra were recorded at 500 MHz, 126 MHz, 471 MHz, respectively, on a Bruker AM500 MHz with chemical shift values in ppm relative to TMS (δ H 0.00 and δ C 0.0) as internal standard. The coupling constants *J*, are reported in Hertz (Hz). All melting points were determined on a SGW X-4A melting point instrument without correction. High-resolution mass spectra (HRMS) were recorded on Q-Exactive plus Orbitrap (ESI) or HP-5989A instrument. Infrared spectra (IR) were recorded on Spectrum TWO. Reactions were monitored by thin layer chromatography (TLC), on glass plates coated with silica gel with Fluorescent indicator (Huanghai, HSGF254) and visualized with UV light at 254 nm. Flash chromatography was performed on silica gel (Huanghai, 300-400) using petroleum ether (PE)-ethyl acetate (EA) as eluent. The structure of product **3c** (CCDC file number 2181031) was further confirmed by X-ray diffraction collected on a diffractometer with graphite-monochromated Cu K\alpha radiation.

∽Ph

2 Optimization of the reaction conditions

Table S1. Optimization of the reaction with alkynes/sodium sulfite

	Ph -	= + NaO ₂ S	1) Inducer, rt 2) Imidazopyric Catalyst B	dine 3a,	H ₂ C Ts	
	I	a 2a	Solvent, 14	0 °C	4a	
Entrya	Inducer	Catalyst	Base (2 equiv.)	Solvent	Temperature	Vield (%)b
Entry	Inducer	(0.2 equiv.)	Dase (2 equiv.)	(2 mL)	(°C)	1 leiu (70)°
1	I ₂	CoCl ₂ ·6H ₂ O	Na ₂ CO ₃	DMF	140	43
2	I_2	$CoCl_2 \cdot 6H_2O$	Na ₂ CO ₃	DMSO	140	22
3	I_2	$CoCl_2 \cdot 6H_2O$	Na ₂ CO ₃	DMAc	140	29
4	TBAI	$CoCl_2 \cdot 6H_2O$	Na ₂ CO ₃	DMF	140	0
5	NaI	CoCl ₂ ·6H ₂ O	Na ₂ CO ₃	DMF	140	0
6	I_2	$CoCl_2 \cdot 6H_2O$		DMF	140	0
7	I_2		Na ₂ CO ₃	DMF	140	0
8	I_2	CoCl ₂ ·6H ₂ O	NaHCO ₃	DMF	140	67
9	I_2	$CoCl_2 \cdot 6H_2O$	LiOBu	DMF	140	32
10	I_2	CoCl ₂ ·6H ₂ O	KOAc	DMF	140	75
11	I_2	CoCl ₂ ·6H ₂ O	NaOAc·3H ₂ O	DMF	140	86
12	I_2	$Co(OAc)_2$	$NaOAc \cdot 3H_2O$	DMF	140	43
13	I_2	$Co(acac)_2$	NaOAc·3H ₂ O	DMF	140	72
14	I_2	$Co(C_2O_4)_2$	$NaOAc \cdot 3H_2O$	DMF	140	56
15	I_2	$Co(C_2O_4)_2$	NaOAc·3H ₂ O	DMF	140	56
16	I_2	Fe(acac) ₂	$NaOAc \cdot 3H_2O$	DMF	140	46
17	I_2	Cu(OTf) ₂	NaOAc·3H ₂ O	DMF	140	0
18	I2	Ni(acac) ₂	NaOAc·3H ₂ O	DMF	140	0

19	I_2	$CoCl_2 \cdot 6H_2O$	$NaOAc \cdot 3H_2O$	DMF	150	84
20	I_2	$CoCl_2 \cdot 6H_2O$	NaOAc·3H ₂ O	DMF	130	62
21°	I_2	$CoCl_2 \cdot 6H_2O$	NaOAc·3H ₂ O	DMF	140	65
22 ^d	I_2	$CoCl_2 \cdot 6H_2O$	NaOAc·3H ₂ O	DMF	140	0

^{*a*}Reaction conditions: **1a** (0.4 mmol), **2a** (0.4 mmol), inducer (1.5 equiv.), and solvent in air reacted at room temperature for 3 h, followed by addition of **3a** (0.2 mmol), catalyst (0.2 equiv.), and base (2 equiv.) under stirring at 140 °C for another 12 h. ^{*b*}Isolated yield. ^{*c*} CoCl₂·6H₂O (0.1 equiv.) was used. ^{*d*}Under N₂.

Table S2 Optimization of the reaction conditions with styrene/sulfonylhydrazide



Entry ^a	Inducer	Oxidant	Catalyst (0.2 equiv.)	Base (2 equiv.)	Solvent (2 mL)	Temperatur e (°C)	Yield (%) ^b
1	I ₂		CoCl ₂ ·6H ₂ O	NaOAc·3H ₂ O	DMF	140	0
2	I_2	DTBP	CoCl ₂ ·6H ₂ O	NaOAc·3H ₂ O	DMF	140	64
3	I_2	TBHP	CoCl ₂ ·6H ₂ O	NaOAc·3H ₂ O	DMF	140	46
4	I_2	$K_2S_2O_8$	CoCl ₂ ·6H ₂ O	NaOAc·3H ₂ O	DMF	140	trace
5	I_2	DTBP	$Co(acac)_2$	NaOAc·3H ₂ O	DMF	140	53
6	I_2	DTBP	Cu(OTf) ₂	$NaOAc \cdot 3H_2O$	DMF	140	0
7	I_2	DTBP	$Ni(acac)_2$	NaOAc·3H ₂ O	DMF	140	0
8	I_2	DTBP	FeCl ₂	NaOAc·3H ₂ O	DMF	140	35
9	I_2	DTBP	FeCl ₃ ·6H ₂ O	$NaOAc \cdot 3H_2O$	DMF	140	78
10	I_2	DTBP	Fe(acac) ₃	NaOAc·3H ₂ O	DMF	140	83
11	I_2	DTBP	Fe(acac) ₃	Na ^t OBu	DMF	140	46
12	I_2	DTBP	Fe(acac) ₃	КОН	DMF	140	57
13	I_2	DTBP	Fe(acac) ₃	$NaOAc \cdot 3H_2O$	DMSO	140	51
14	I_2	DTBP	Fe(acac) ₃	$NaOAc \cdot 3H_2O$	DMAc	140	44
15	I_2	DTBP	Fe(acac) ₃	$NaOAc \cdot 3H_2O$	DMF	130	64
16	I_2	DTBP	Fe(acac) ₃	$NaOAc \cdot 3H_2O$	DMF	150	80
17	NaI	DTBP	Fe(acac) ₃	$NaOAc \cdot 3H_2O$	DMF	140	27
18	TBAI	DTBP	Fe(acac) ₃	NaOAc·3H ₂ O	DMF	140	16

^{*a*} Reaction conditions: **3a** (0.2 mmol), **7a** (0.5 mmol), **8a** (0.5 mmol), I₂ (1.5 equiv.), DTBP (3 equiv.), Fe(acac)₃ (0.2 equiv.), NaOAc·3H₂O (2 equiv.), and solvent in air reacted at room temperature for 3 h, followed by stirring at 140 °C for 12 h. ^{*b*} Isolated yield.

3 Deacylation and α-Allylation



Figure S1 Deacylation reveals the ethylene group.



Figure S2 α -Allylation of 4a.

4 Control experiments

Treatment of 1a, 2a, and I₂ in DMF afforded intermediate 11 in 93% yield. The addition of NaOAc·3H₂O transformed 11 into ketosulfone 12 (Figure S1a). The reaction of 7a and 8a without Fe(acac)₃ afforded 12 at a 63% yield (Figure S1b). Furthermore, the combination reaction of 12 and 3a at 140 °C with CoCl₂·6H₂O or Fe(acac)₃ provided 4a with yields of 91% and 88%, respectively (Figure S1c), indicating that 11 and 12 could be plausible reaction intermediates.



Figure S3 Control experiments

5 General procedure for the synthesis of 3-ketosulfonylmethylenated

heterocycles 4, 6 and 3-sulfonylethylated imidazoheterocycles 9

General procedure for synthesis of desired products 4/6 with Co-catalysts, alkynes and sodium sulfite

2 mL DMF, alkynes (1, 0.4 mmol (2.0 equiv.)), sodium sulfite (2, 0.4 mmol (2.0 equiv.)), and I_2 (76.1 mg, 0.3 mmol (1.5 equiv.)) were added into the dry thick-walled glass pressure tube and stirred in air at toom temperature for 3 h, followed by adding imidazoheterocycles (5, 0.2 mmol) or indoles/naphthols (0.2 mmol), CoCl₂·6H₂O (9.5 mg, 0.04mmol), NaOAc·3H₂O (54.4 mg, 0.4 mmol

(2.0 equiv.)) and stirring at in a preheated oil bath at 140 °C for in air for another 12 h. Then the reaction was cooled down to room temperature, diluted with 20 mL ethyl acetate and washed with 10 mL H₂O. The aqueous layer was extracted twice with ethyl acetate (5 mL) and the combined organic phase was dried over Na₂SO₄. After evaporation of the solvents the residue was purified by flash column chromatography (silica gel, petroleum ether–ethyl acetate, 2:1 to 1:1) to afford the desired products **4 or 6**.

General procedure for synthesis of desired products 4 with Fe-catalysts, styrenes and sulfonylhydrazides

2 mL DMF, styrenes (7, 0.5 mmol (2.5 equiv.)), sodium sulfite (8, 0.5 mmol (2.5 equiv.)), I_2 (76.1 mg, 0.3 mmol (1.5 equiv.)), DTBP (87.7 mg, 0.6mmol (3.0 equiv.)), Fe(acac)₃ (14.1 mg, 0.04mmol), NaOAc·3H₂O (54.4 mg, 0.4 mmol (2.0 equiv.)) and I_2 (0.3 mmol (1.5 equiv.)) were added into the dry thick-walled glass pressure tube and stirred in air at toom temperature for 3 h, followed by stirring at in a preheated oil bath at 140 °C for in air for another 12 h. Then the reaction was cooled down to room temperature, diluted with 20 mL ethyl acetate and washed with 10 mL H₂O. The aqueous layer was extracted twice with ethyl acetate (5 mL) and the combined organic phase was dried over Na₂SO₄. After evaporation of the solvents the residue was purified by flash column chromatography (silica gel, petroleum ether–ethyl acetate, 2:1 to 1:1) to afford the desired products **4**.

General procedure for synthesis of desired products 9.

1 mL THF and 1 mL MeOH, **4** (0.1 mmol), and NaBH₄ (0.1 mmol (3.8 mg, 1.0 equiv.)) were added into the dry thick-walled glass pressure tube and stirred in air at toom temperature for 30 minutes. After the evaporation of the solution, 2 mL of dry toluene was added, followed by stirring in a preheated oil bath at 110 °C for 12 h. Then the reaction was cooled down to room temperature, diluted with 20 mL ethyl acetate and washed with 10 mL H₂O. The aqueous layer was extracted twice with ethyl acetate (5 mL) and the combined organic phase was dried over Na₂SO₄. After evaporation of the solvents the residue was purified by flash column chromatography (silica gel, petroleum ether–ethyl acetate, 2:1 to 1:1) to afford the desired products **9**.

General procedure for synthesis of desired products 10.

2 mL of acetone, **4a** (48.1 mg, 0.1mmol), K_2CO_3 (27.6 mg, 0.2 mmol (2.0 equiv.)), cinnamyl bromide (39.4 mg, 0.2 mmol (2.0 equiv.)) were added into the dry thick-walled glass pressure tube and stirred in air in a preheated oil bath at 60 °C for 4 h. Then the reaction was cooled down to room temperature, diluted with 20 mL ethyl acetate and washed with 10 mL H₂O. The aqueous layer was extracted twice with ethyl acetate (5 mL) and the combined organic phase was dried over Na₂SO₄. After evaporation of the solvents the residue was purified by flash column chromatography (silica gel, petroleum ether–ethyl acetate, 2:1 to 1:1) to afford the desired products **10**.



1-phenyl-3-(2-phenylimidazo[1,2-a]pyridin-3-yl)-2-tosylpropan-1-one

4a was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to1:1). Yellow solid, mp 165-167 °C.

¹**H NMR (500 MHz, CDCl₃)** δ 8.15 (d, J = 7.0 Hz, 1H), 7.64 – 7.63 (m, 2H), 7.58 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 9.0 Hz, 1H), 7.43 – 7.37 (m, 4H), 7.29 (d, J = 7.5 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.16 (t, J = 7.5 Hz, 2H), 7.12 – 7.08 (m, 1H), 6.80 (t, J = 6.5 Hz, 1H), 5.37 (t, J = 7.0 Hz, 1H), 3.98 (d, J = 7.5 Hz, 2H), 2.38 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 191.9, 145.7, 144.8, 143.2, 136.4, 134.1, 133.9, 133.7, 129.8, 129.1, 128.8, 128.4, 128.0, 127.8, 124.4, 123.4, 117.3, 114.2, 112.4, 66.7, 22.1, 21.6.

IR (KBr): 2920, 1680, 1445, 1326, 1302, 1143, 1052, 743, 700, 678 cm⁻¹.

HRMS for C₂₉H₂₅N₂O₃S⁺(M+H)⁺: calcd. 481.15804, found 481.15820.



1-phenyl-3-(2-(p-tolyl)imidazo[1,2-a]pyridin-3-yl)-2-tosylpropan-1-one **4b** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1). Yellow solid, mp 128-130 °C.

¹**H NMR (500 MHz, CDCl₃)** δ 8.13 (d, J = 7.0 Hz, 1H), 7.59 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 9.0 Hz, 1H), 7.41 (t, J = 7.5 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.26 – 7.17 (m, 6H), 7.10 (d, J = 7.5 Hz, 1H), 6.80 (d, J = 6.5 Hz, 1H), 5.39 – 5.37 (m, 1H), 4.00 – 3.91 (m, 2H), 2.43 (s, 3H), 2.42 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 192.1, 145.7, 144.8, 143.4, 137.9, 136.5, 134.0, 133.7, 131.2, 129.8, 129.6, 129.3, 128.6, 128.5, 127.8, 124.4, 123.4, 117.3, 113.9, 112.4, 66.9, 22.3, 21.7, 21.4
IR (KBr): 2923, 1673, 1593, 1254, 1215, 1148, 1082, 932, 803, 679 cm⁻¹.

HRMS for $C_{30}H_{27}N_2O_3S^+(M+H)^+$: calcd. 495.17369, found 495.17404.



3-(2-(4-methoxyphenyl)imidazo[1,2-a]pyridin-3-yl)-1-phenyl-2-tosylpropan-1-one **4c** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1). Yellow solid, mp 66-68 °C.

¹**H NMR (500 MHz, CDCl₃)** δ 8.12 (d, *J* = 7.0 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 4H), 7.46 (d, *J* = 9.0 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 7.5 Hz, 2H), 7.11 – 7.08 (m, 1H), 6.95 (d, *J* = 9.0 Hz, 2H), 6.80 (d, *J* = 7.0 Hz, 1H), 5.39 – 5.36 (m, 1H), 3.98 – 3.92 (m, 2H), 3.87 (s, 3H), 2.40 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 192.0, 159.5, 145.7, 144.7, 143.1, 136.4, 134.0, 133.8, 129.8, 129.3,

129.1, 128.5, 128.5, 126.5, 124.3, 123.4, 117.1, 114.3, 113.5, 112.4, 66.8, 55.3, 22.2, 21.7 **IR (KBr):** 2922, 1676, 1447, 1302, 1250, 1145, 736, 682 cm⁻¹. **HRMS for C₃₀H₂₇N₂O₄S⁺ (M+H)⁺: calcd.** 511.16860, found 511.16824.



3-(2-(4-chlorophenyl)imidazo[1,2-a]pyridin-3-yl)-1-phenyl-2-tosylpropan-1-one **4d** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1). Yellow solid, mp 174-176 °C.

¹H NMR (500 MHz, CDCl₃) δ 8.16 (d, J = 7.0 Hz, 1H), 7.62 – 7.58 (m, 4H), 7.48 (d, J = 9.0 Hz, 1H), 7.43 (t, J = 7.0 Hz, 1H), 7.38 – 7.35 (m, 4H), 7.28 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 7.5 Hz, 2H), 7.14 (t, J = 8.0 Hz, 1H), 6.83 (t, J = 7.0 Hz, 1H), 5.30 – 5.28 (m, 1H), 4.02 – 3.93 (m, 2H), 2.43 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 191.9, 145.9, 144.9, 142.2, 136.3, 134.2, 134.0, 133.6, 132.6, 129.9, 129.3, 129.1, 129.0, 128.6, 128.5, 124.8, 123.5, 117.4, 114.5, 112.7, 67.0, 22.2, 21.8. IR (KBr): 2919, 1676, 1596, 1310, 1273, 1141, 1088, 822, 726, 685 cm⁻¹. HRMS for C₂₉H₂₄ClN₂O₃S⁺ (M+H)⁺: calcd. 515.11907, found 515.11938.



3-(2-(4-fluorophenyl)imidazo[1,2-a]pyridin-3-yl)-1-phenyl-2-tosylpropan-1-one **4e** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1). Yellow solid, mp 174-176 °C.

¹**H NMR (500 MHz, CDCl₃)** δ 8.16 (d, *J* = 7.0 Hz, 1H), 7.63 – 7.60 (m, 4H), 7.48 (d, *J* = 9.0 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 2H), 7.15 – 7.09 (m, 3H), 6.83 (t, *J* = 7.0 Hz, 1H), 5.31 – 5.29 (m, 1H), 4.01 – 3.93 (m, 2H), 2.41 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 191.9, 162.6 (d, $J_{C-F} = 246.4$ Hz), 145.9, 144.9, 142.5, 136.3, 134.1, 133.6, 130.2 (d, $J_{C-F} = 2.6$ Hz), 129.9, 129.7 (d, $J_{C-F} = 8.3$ Hz), 129.3, 128.6, 128.5, 124.7, 123.5, 117.4, 115.8 (d, $J_{C-F} = 20.6$ Hz), 114.1, 112.7, 66.9, 22.1, 21.7.

¹⁹F NMR (470 MHz, CDCl₃): δ -113.41.

IR (KBr): 2922, 1678, 1595, 1497, 1324, 1220, 1147, 855, 738, 669 cm⁻¹.

HRMS for C₂₉H₂₄FN₂O₃S⁺(M+H)⁺: calcd. 499.14862, found 499.14868.



3-(2-([1,1'-biphenyl]-4-yl)imidazo[1,2-a]pyridin-3-yl)-1-phenyl-2-tosylpropan-1-one **4f** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1). Yellow solid, mp 109-111 °C.

¹**H NMR (500 MHz, CDCl₃)** δ 8.15 (d, *J* = 7.0 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.66 (t, *J* = 9.0 Hz, 4H), 7.60 (d, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 8.0 Hz, 3H), 7.39 – 7.33 (m, 4H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.15 (t, *J* = 7.5 Hz, 2H), 7.10 (t, *J* = 8.0 Hz, 1H), 6.79 (t, *J* = 7.0 Hz, 1H), 5.44 – 5.41 (m, 1H), 4.04 – 3.97 (m, 2H), 2.35 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 192.0, 145.7, 144.8, 142.7, 140.5, 140.3, 136.3, 134.0, 133.7, 132.9, 129.8, 129.1, 128.9, 128.5, 128.4, 128.1, 127.5, 127.3, 126.9, 124.5, 123.4, 117.2, 114.4, 112.5, 66.8, 22.2, 21.6.

IR (KBr): 2924, 1678, 1595, 1453, 1285, 1147, 1083, 737, 706 cm⁻¹.

HRMS for C₃₅H₂₉N₂O₃S⁺(M+H)⁺: calcd. 557.18934, found 557.18915.



4-(3-(3-oxo-3-phenyl-2-tosylpropyl)imidazo[1,2-a]pyridin-2-yl)benzonitrile

4g was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1). Yellow solid, mp 190-192 °C.

¹**H NMR (500 MHz, CDCl₃)** δ 8.10 (d, *J* = 7.0 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 9.0 Hz, 1H), 7.35 (t, *J* = 7.0 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.15 – 7.09 (m, 3H), 6.79 (t, *J* = 7.0 Hz, 1H), 5.2 – 5.17 (m, 1H), 3.99 – 3.90 (m, 2H), 2.35 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 191.7, 146.1, 145.2, 141.2, 138.7, 136.2, 134.3, 133.3, 132.5, 130.0, 129.5, 128.6, 128.5, 128.2, 125.3, 123.6, 118.9, 117.7, 115.8, 113.2, 111.3, 67.1, 22.3, 21.8.

IR (KBr): 2922, 2225, 1694, 1381, 1203, 1089, 1045, 879, 766 cm⁻¹.

HRMS for $C_{30}H_{24}N_3O_3S^+(M+H)^+$: calcd. 506.15329, found 506.15280.



1-phenyl-2-tosyl-3-(2-(4-(trifluoromethyl)phenyl)imidazo[1,2-a]pyridin-3-yl)propan-1-one

4h was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1). Yellow solid, mp 172-174 °C.

¹**H** NMR (500 MHz, CDCl₃) δ 8.20 (d, J = 6.5 Hz, 1H), 7.78 (d, J = 8.0 Hz, 2H), 7.65 – 7.61 (m, 4H), 7.51 (d, J = 9.0 Hz, 1H), 7.43 (t, J = 7.0 Hz, 1H), 7.35 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 7.0 Hz, 2H), 7.22 – 7.16 (m, 3H), 6.87 (t, J = 6.5 Hz, 1H), 5.29 – 5.27 (m, 1H), 4.07 – 3.98 (m, 2H), 2.43 (s, 3H).

¹³**C** NMR (126 MHz, CDCl₃) δ 191.8, 146.1, 145.1, 141.8, 137.7, 136.3, 134.3, 133.6, 130.0, 129.8 (q, $J_{C-F} = 32.5 \text{ Hz}$), 129.4, 128.7, 128.5, 128.1, 125.7 (q, $J_{C-F} = 3.4 \text{ Hz}$), 125.1, 124.2 (q, $J_{C-F} = 270.3 \text{ Hz}$), 123.7, 117.7, 115.3, 113.0, 67.1, 22.3, 21.7.

¹⁹F NMR (470 MHz, CDCl₃): δ -62.42.

IR (KBr): 2921, 1673, 1625, 1324, 1255, 1138, 1073, 746, 727, 680 cm⁻¹. **HRMS for C_{30}H_{24}F_{3}N_2O_3S^+(M+H)^+: calcd.** 549.14542, found 549.14569.



3-(2-(3-bromophenyl)imidazo[1,2-a]pyridin-3-yl)-1-phenyl-2-tosylpropan-1-one **4i** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1). Yellow solid, mp 80-82 °C.

¹**H NMR (500 MHz, CDCl₃)** δ 8.17 (d, J = 7.0 Hz, 1H), 7.79 (m, 1H), 7.58 – 7.54 (m, 3H), 7.51 – 7.48 (m, 2H), 7.43 (t, J = 7.0 Hz, 1H), 7.34 (d, J = 7.5 Hz, 2H), 7.28 – 7.19 (m, 5H), 7.14 (t, J = 7.5 Hz, 1H), 6.84 (d, J = 7.0 Hz, 1H), 5.32 (t, J = 7.0 Hz, 1H), 3.96 (d, J = 7.0 Hz, 2H), 2.39 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 191.8, 145.8, 144.9, 141.8, 136.2, 136.2, 134.1, 133.6, 131.2, 131.0, 130.2, 129.9, 129.2, 128.6, 128.5, 126.1, 124.9, 123.6, 123.1, 117.5, 114.8, 112.8, 66.8, 22.1, 21.7. IR (KBr): 2923, 1677, 1622, 1549, 1352, 1145, 1092, 732, 682 cm⁻¹.

HRMS for C₂₉H₂₄BrN₂O₃S⁺(M+H)⁺: calcd. 559.06855, found 559.06873.



3-(2-(3-nitrophenyl)imidazo[1,2-a]pyridin-3-yl)-1-phenyl-2-tosylpropan-1-one **4j** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1). Yellow solid, mp 171-173 °C.

¹**H NMR (500 MHz, CDCl₃)** δ 8.45 (s, 1H), 8.24 – 8.20 (m, 2H), 7.97 (d, *J* = 7.5 Hz, 1H), 7.63 – 7.53 (m, 4H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.40 (d, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 8.0 Hz, 3H), 6.92 (t, *J* = 7.0 Hz, 1H), 5.28 – 5.25 (m, 1H), 4.08 – 3.97 (m, 2H), 2.43 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 191.6, 148.5, 146.2, 145.2, 141.2, 136.2, 135.9, 134.4, 133.6, 133.2, 130.0, 129.8, 129.4, 128.7, 128.5, 125.4, 123.6, 123.1, 122.7, 117.8, 115.3, 113.3, 67.1, 22.3, 21.8.

IR (KBr): 2921, 1672, 1523, 1347, 1283, 1146, 738, 703, 682 cm⁻¹. **HRMS for C₂₉H₂₄N₃O₅S⁺ (M+H)⁺:** calcd. 526.14312, found 526.14325.



1-phenyl-3-(2-(thiophen-2-yl)imidazo[1,2-a]pyridin-3-yl)-2-tosylpropan-1-one **4k** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1). Yellow solid, mp 220-222 °C.

¹H NMR (500 MHz, CDCl₃) δ 8.14 (d, J = 7.0 Hz, 1H), 7.70 (d, J = 8.0 Hz, 2H), 7.48 – 7.40 (m, 5H), 7.38 (d, J = 5.0 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.21 (t, J = 7.5 Hz, 2H), 7.15 – 7.13 (m, 1H), 7.09 (t, J = 7.5 Hz, 1H), 6.78 (t, J = 7.0 Hz, 1H), 5.55 – 5.52 (m, 1H), 4.02 – 3.96 (m, 2H), 2.43 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 192.5, 146.0, 144.9, 138.3, 137.4, 136.5, 134.2, 133.5, 130.0, 129.6, 128.6, 128.3, 126.0, 124.9, 124.2, 123.6, 117.1, 113.3, 112.6, 66.5, 22.4, 21.8.

IR (KBr): 2921, 1672, 1523, 1347, 1283, 1145, 738, 703, 682 cm⁻¹.

HRMS for C₂₇H₂₃N₂O₃S₂⁺(M+H)⁺: calcd. 487.11446, found 487.11465.



3-(2-(naphthalen-2-yl)imidazo[1,2-a]pyridin-3-yl)-1-phenyl-2-tosylpropan-1-one **41** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1). Yellow solid, mp 160-162 °C.

¹**H NMR (500 MHz, CDCl₃)** δ 8.18 – 8.16 (m, 2H), 7.91 – 7.87 (m, 4H), 7.54 – 7.51 (m, 5H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 7.5 Hz, 2H), 7.16 – 7.11 (m, 3H), 7.06 (t, *J* = 7.5 Hz, 2H), 6.81 (t, *J* = 7.0 Hz, 1H), 5.44 – 5.42 (m, 1H), 4.14 – 4.00 (m, 2H), 2.36 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 192.1, 145.7, 145.0, 143.1, 136.3, 134.0, 133.7, 133.5, 132.9, 131.5, 129.8, 129.2, 128.6, 128.5, 128.5, 128.4, 127.7, 126.9, 126.5, 126.4, 125.6, 124.6, 123.5, 117.4, 114.7, 112.6, 66.9, 22.3, 21.7.

IR (KBr): 2921, 1678, 1594, 1408, 1303, 1146, 1082, 812, 793, 753 cm⁻¹. **HRMS for C₃₃H₂₇N₂O₃S⁺ (M+H)⁺:** calcd. 531.17369, found 531.17407.



3-(7-methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)-1-phenyl-2-tosylpropan-1-one **4m** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1). Yellow solid, mp 152-154 °C.

¹**H NMR (500 MHz, CDCl₃)** δ 8.05 (d, J = 7.0 Hz, 1H), 7.63 – 7.58 (m, 4H), 7.42 – 7.38 (m, 4H), 7.31 – 7.24 (m, 5H), 7.18 (t, J = 7.5 Hz, 2H), 6.66 (d, J = 7.0 Hz, 1H), 5.35 (t, J = 7.0 Hz, 1H), 3.95 (d, J = 7.0 Hz, 2H), 2.41 (s, 3H), 2.34 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 192.0, 145.7, 145.3, 142.8, 136.5, 135.6, 134.1, 134.0, 133.8, 129.9, 129.3, 128.9, 128.5, 128.5, 128.0, 127.8, 122.7, 115.7, 115.2, 113.7, 66.8, 22.1, 21.7, 21.3.

IR (KBr): 1669, 1587, 1445, 1326, 1307, 1171, 1034, 851, 760, 716 cm⁻¹.

HRMS for C₃₀H₂₇N₂O₃S⁺ (M+H)⁺: calcd. 495.17369, found 495.17398.



3-(7-methoxy-2-phenylimidazo[1,2-a]pyridin-3-yl)-1-phenyl-2-tosylpropan-1-one **4n** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 1:1 to 1:2). Yellow solid, mp 228-230 °C.

¹**H NMR (500 MHz, CDCl₃)** δ 7.99 (d, J = 7.5 Hz, 1H), 7.65 – 7.61 (m, 4H), 7.45 – 7.39 (m, 4H), 7.34 (d, J = 7.5 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.21 (t, J = 7.5 Hz, 2H), 6.76 (d, J = 2.0 Hz, 1H), 6.56 – 6.54 (m, 1H), 5.38 – 5.35 (m, 1H), 3.97 – 3.87 (m, 2H), 3.80 (s, 3H), 2.44 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 192.2, 157.9, 146.4, 145.8, 142.6, 136.6, 134.2, 134.1, 133.8, 129.9, 129.4, 128.9, 128.6, 128.6, 127.9, 127.7, 124.1, 113.2, 107.6, 94.6, 67.1, 55.6, 22.3, 21.8.

IR (KBr): 2921, 2852, 1651, 1447, 1211, 1172, 1080, 945, 704, 682 cm⁻¹.

HRMS for C₃₀H₂₇N₂O₄S⁺ (M+H)⁺: calcd. 511.16860, found 511.16873.



3-(6-methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)-1-phenyl-2-tosylpropan-1-one **40** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1). Yellow solid, mp 110-112 °C.

¹**H NMR (500 MHz, CDCl₃)** δ 7.93 (s, 1H), 7.59 (d, *J* = 7.5 Hz, 4H), 7.42 – 7.38 (m, 5H), 7.29 – 7.24 (m, 4H), 7.18 (t, *J* = 7.5 Hz, 2H), 6.97 (d, *J* = 9.0 Hz, 1H), 5.38 – 5.35 (m, 1H), 4.02 – 3.91 (m, 2H), 2.41 (s, 3H), 2.35 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 192.0, 145.7, 144.0, 143.1, 136.5, 134.3, 134.0, 134.0, 129.9, 129.2, 128.8, 128.5, 128.0, 127.9, 127.7, 122.2, 121.1, 116.8, 114.0, 66.7, 22.2, 21.8, 18.6.

IR (KBr): 2920, 2851, 1678, 1446, 1312, 1182, 1148, 803, 707 cm⁻¹.



3-(6-fluoro-2-phenylimidazo[1,2-a]pyridin-3-yl)-1-phenyl-2-tosylpropan-1-one **4p** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1). Yellow solid, mp 170-172 °C.

¹**H NMR (500 MHz, CDCl₃)** δ 8.11 (m, 1H), 7.63 – 7.58 (m, 4H), 7.47 – 7.40 (m, 5H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 2H), 7.06 – 7.02 (m, 1H), 5.36 – 5.34 (m, 1H), 3.97 – 3.87 (m, 2H), 2.41 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 191.8, 153.3 (d, $J_{C-F} = 235.5$ Hz), 145.8, 144.5 (d, $J_{C-F} = 1.4$ Hz), 142.5, 136.3, 134.1, 133.7 (d, $J_{C-F} = 25.9$ Hz), 129.9, 129.2, 128.9, 128.6, 128.5, 128.3, 127.8, 117.8 (d, $J_{C-F} = 8.9$ Hz), 116.5 (d, $J_{C-F} = 24.9$ Hz), 115.8 (d, $J_{C-F} = 2.1$ Hz), 110.6, 110.3, 66.7, 22.2, 21.7.

¹⁹F NMR (470 MHz, CDCl₃): δ -138.99.

IR (KBr): 2922, 1674, 1592, 1506, 1447, 1299, 1212, 1112, 874, 679 cm⁻¹.

HRMS for $C_{29}H_{24}FN_2O_3S^+(M+H)^+$: calcd. 499.14862, found 499.14865.



1-phenyl-3-(6-phenylimidazo[2,1-b]thiazol-5-yl)-2-tosylpropan-1-one

4q was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1). Yellow solid, mp 147-149 °C..

¹**H NMR (500 MHz, CDCl₃)** δ 7.60 (t, *J* = 8.0 Hz, 4H), 7.48 – 7.44 (m, 4H), 7.39 (t, *J* = 7.0 Hz, 2H), 7.35 – 7.33 (m, 1H), 7.28 – 7.23 (m, 4H), 6.75 (d, *J* = 4.5 Hz, 1H), 5.36 – 5.34 (m, 1H), 3.95 – 3.80 (m, 2H), 2.43 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 192.2, 148.7, 145.8, 144.2, 136.6, 134.3, 134.2, 133.8, 129.9, 129.3, 128.9, 128.7, 128.7, 127.6, 126.9, 117.8, 116.1, 112.5, 67.4, 23.9, 21.8.

IR (KBr): 2921, 1671, 1596, 1322, 1205, 1149, 1082, 783, 761, 678 cm⁻¹.

HRMS for C₂₇H₂₃N₂O₃S₂⁺(M+H)⁺: calcd. 487.11446, found 487.11459.



1-phenyl-3-(2-phenylimidazo[1,2-a]pyridin-3-yl)-2-(phenylsulfonyl)propan-1-one **4r** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1). Yellow solid, mp 69-71 °C.

¹**H NMR (500 MHz, CDCl₃)** δ 8.16 (d, J = 7.0 Hz, 1H), 7.69 (d, J = 7.5 Hz, 2H), 7.63 – 7.58 (m, 3H), 7.49 – 7.37 (m, 7H), 7.27 (d, J = 7.5 Hz, 2H), 7.16 (d, J = 7.5 Hz, 2H), 7.13 – 7.10 (t, J = 7.5 Hz, 1H), 6.82 (t, J = 6.5 Hz, 1H), 5.38 (t, J = 7.5 Hz, 1H), 4.00 (d, J = 7.0 Hz, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 191.8, 144.9, 143.3, 136.9, 136.3, 134.5, 134.1, 129.2, 129.1, 128.9, 128.5, 128.4, 128.1, 127.9, 124.5, 123.5, 117.4, 114.1, 112.5, 66.6, 22.1.

IR (KBr): 2920, 1676, 1479, 1309, 1145, 1081, 863, 769, 679 cm⁻¹.

HRMS for C₂₈H₂₃N₂O₃S⁺(M+H)⁺: calcd. 467.14239, found 467.14218.



2-((4-chlorophenyl)sulfonyl)-1-phenyl-3-(2-phenylimidazo[1,2-a]pyridin-3-yl)propan-1-one **4s** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1). Yellow solid, mp 160-162 °C.

¹**H NMR (500 MHz, CDCl₃)** δ 8.13 (d, *J* = 7.0 Hz, 1H), 7.65 – 7.59 (m, 4H), 7.51 – 7.48 (m, 1H), 7.46 – 7.40 (m, 6H), 7.29 – 7.27 (m, 2H), 7.21 – 7.18 (m, 2H), 7.15 – 7.11 (m, 1H), 6.83 (td, *J* = 7.0, 1.0 Hz, 1H), 5.38 – 5.35 (m, 1H), 4.03 – 3.92 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 191.8, 145.0, 143.5, 141.4, 136.2, 135.1, 134.3, 134.1, 130.7, 129.5, 129.0, 128.7, 128.5, 128.2, 128.0, 124.6, 123.4, 117.5, 113.9, 112.7, 66.9, 22.2.

IR (KBr): 2923, 2887, 1645, 1379, 1087, 7044, 879, 709 cm⁻¹.

HRMS for $C_{28}H_{22}CIN_2O_3S^+(M+H)^+$: calcd. 501.10342, found 501.10364.



2-((4-nitrophenyl)sulfonyl)-1-phenyl-3-(2-phenylimidazo[1,2-a]pyridin-3-yl)propan-1-one **4t** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1). Yellow solid, mp 167-169 °C.

¹**H NMR** (500 **MHz**, **CDCl**₃) δ 8.22 (d, J = 9.0 Hz, 2H), 8.08 (d, J = 7.0 Hz, 1H), 7.80 (d, J = 9.0 Hz, 2H), 7.62 – 7.60 (m, 2H), 7.49 – 7.40 (m, 5H), 7.31 – 7.28 (m, 2H), 7.21 (t, J = 7.5 Hz, 2H), 7.15 – 7.12 (m, 1H), 6.83 (td, J = 7.0, 1.0 Hz, 1H), 5.43 – 5.41 (m, 1H), 4.08 – 4.04 (m, 1H), 3.92 – 3.87 (m, 1H). ¹³**C NMR** (126 MHz, **CDCl**₃) δ 191.4, 151.0, 144.9, 143.6, 142.1, 135.9, 134.6, 133.9, 130.6, 129.0, 128.8, 128.5, 128.4, 127.9, 124.7, 124.2, 123.2, 117.5, 113.5, 112.7, 66.9, 22.3. **IR** (KBr): 2922, 1676, 1593, 1530, 1333, 1150, 1080, 733, 700 cm⁻¹. **HRMS for** C₂₈H₂₂N₃O₅S⁺ (M+H)⁺: calcd. 512.12747, found 512.12750.



2-(naphthalen-2-ylsulfonyl)-1-phenyl-3-(2-phenylimidazo[1,2-a]pyridin-3-yl)propan-1-one **4u** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1). Yellow solid, mp 87-89 °C.

¹**H NMR (500 MHz, CDCl₃)** δ 8.24 (s, 1H), 8.17 (d, *J* = 7.0 Hz, 1H), 7.88 (t, *J* = 8.5 Hz, 3H), 7.69 – 7.57 (m, 5H), 7.45 (d, *J* = 9.0 Hz, 1H), 7.33 – 7.29 (m, 6H), 7.13 – 7.08 (m, 3H), 6.81 (t, *J* = 7.0 Hz, 1H), 5.46 – 5.43 (m, 1H), 4.08 – 4.01 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 191.9, 144.9, 143.3, 136.5, 135.6, 134.1, 134.0, 133.9, 131.9, 131.3, 129.8, 129.6, 129.5, 128.9, 128.5, 128.5, 128.1, 128.0, 127.9, 124.6, 123.5, 123.3, 117.4, 114.3, 112.6, 66.9, 22.2.

IR (KBr): 2919, 1677, 1593, 1445, 1314, 1145, 749, 680 cm⁻¹.

HRMS for $C_{32}H_{25}N_2O_3S^+(M+H)^+$: calcd. 517.15804, found 517.15808.



2-(methylsulfonyl)-1-phenyl-3-(2-phenylimidazo[1,2-a]pyridin-3-yl)propan-1-one

4v was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1). Yellow solid, mp 178-180 °C.

¹**H NMR (500 MHz, CDCl₃)** δ 8.20 (d, *J* = 7.0 Hz, 1H), 7.66 (d, *J* = 7.0 Hz, 2H), 7.55 (d, *J* = 9.0 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 3H), 7.44 – 7.40 (m, 3H), 7.25 (t, *J* = 8.0 Hz, 2H), 7.19 (t, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 7.0 Hz, 1H), 5.15 (d, *J* = 9.0 Hz, 1H), 4.16 – 4.03 (m, 2H), 3.02 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 193.4, 145.1, 144.0, 136.0, 134.7, 133.8, 128.9, 128.8, 128.7, 128.4, 128.2, 124.8, 123.2, 117.8, 113.8, 113.0, 66.1, 38.3, 23.3.

IR (KBr): 2921, 2852, 1680, 1447, 1304, 1141, 962, 787, 743 cm⁻¹.

HRMS for $C_{23}H_{21}N_2O_3S^+(M+H)^+$: calcd. 405.12674, found 405.12680.



1-(4-methoxyphenyl)-3-(2-phenylimidazo[1,2-a]pyridin-3-yl)-2-tosylpropan-1-one **4w** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1). Yellow solid, mp 75-77 °C.

¹**H** NMR (500 MHz, CDCl₃) δ 8.14 (d, J = 7.0 Hz, 1H), 7.65 (d, J = 7.0 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 9.0 Hz, 1H), 7.43 – 7.38 (m, 3H), 7.33 (d, J = 8.5 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 7.5 Hz, 1H), 6.78 (t, J = 6.5 Hz, 1H), 6.64 (d, J = 9.0 Hz, 2H), 5.32 – 5.29 (m, 1H), 3.98 – 3.91 (m, 2H), 3.72 (s, 3H), 2.40 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 189.8, 164.3, 145.6, 144.8, 143.2, 134.1, 133.7, 131.1, 129.7, 129.4, 129.2, 128.8, 128.0, 127.9, 124.4, 123.5, 117.2, 114.4, 113.7, 112.4, 66.4, 55.5, 22.2, 21.7.

IR (KBr): 2921, 1645, 1380, 1247, 1088, 1044, 879, 619 cm⁻¹.

HRMS for $C_{30}H_{27}N_2O_4S^+(M+H)^+$: calcd. 511.16860, found 511.16849.



4-(3-(2-phenylimidazo[1,2-a]pyridin-3-yl)-2-tosylpropanoyl)benzonitrile

4x was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1). Yellow solid, mp 104-106 °C.

¹**H NMR (500 MHz, CDCl₃)** δ 8.11 (d, *J* = 7.0 Hz, 1H), 7.57 – 7.54 (m, 4H), 7.50 – 7.46 (m, 3H), 7.40 – 7.39 (m, 3H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.16 – 7.13 (m, 1H), 6.84 (t, *J* = 6.5 Hz, 1H), 5.33 – 5 31 (m, 1H), 3.98 – 3.91 (m, 2H), 2.44 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 191.1, 146.2, 145.0, 143.2, 139.2, 134.0, 133.4, 132.3, 130.0, 129.2, 129.0, 128.8, 128.3, 127.9, 124.7, 123.3, 117.5, 117.5, 117.0, 113.8, 112.7, 67.1, 22.1, 21.8.

IR (KBr): 2923, 2886, 2205, 1651, 1380, 1256, 1045, 879, 614 cm⁻¹.

HRMS for $C_{30}H_{24}N_3O_3S^+(M+H)^+$: calcd. 506.15329, found 506.15375.



1-(3-fluorophenyl)-3-(2-phenylimidazo[1,2-a]pyridin-3-yl)-2-tosylpropan-1-one
4y was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1).
Yellow solid, mp 170-172 °C.

¹**H NMR (500 MHz, CDCl₃)** δ 8.14 (d, J = 7.0 Hz, 1H), 7.61 – 7.56 (m, 4H), 7.49 (d, J = 9.0 Hz, 1H), 7.43 – 7.39 (m, 3H), 7.25 (d, J = 8.0 Hz, 2H), 7.17 – 7.08 (m, 3H), 7.01 (d, J = 7.5 Hz, 1H), 6.96 (d, J = 9.0 Hz, 1H), 6.83 (td, J = 7.0, 1.0 Hz, 1H), 5.31 – 5.28 (m, 1H), 4.01 – 3.94 (m, 2H), 2.41 (s, 3H). ¹³**C NMR (126 MHz, CDCl₃)** δ 190.8 (d, J_{C-F} = 2.3 Hz), 162.4 (d, J_{C-F} = 248.3 Hz), 145.9, 144.9, 143.3, 138.3 (d, $J_{C-F} = 6.5$ Hz), 134.0, 133.6, 130.2 (d, $J_{C-F} = 8.0$ Hz), 129.9, 129.2, 128.9, 128.1, 127.9, 124.6, 124.3 (d, $J_{C-F} = 2.7$ Hz), 123.4, 121.0 (d, $J_{C-F} = 20.9$ Hz), 117.4, 115.0 (d, $J_{C-F} = 22.8$ Hz), 114.0, 112.6, 67.0, 22.0, 21.7.

¹⁹F NMR (470 MHz, CDCl₃): δ -111.33.

IR (KBr): 2920, 1682, 1590, 1441, 1303, 1258, 1142, 791, 723, 669 cm⁻¹. **HRMS for C₂₉H₂₄FN₂O₃S⁺ (M+H)⁺:** calcd. 499.14862, found 499.14896.



3-(2-phenylimidazo[1,2-a]pyridin-3-yl)-1-(thiophen-2-yl)-2-tosylpropan-1-one 4z was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1). Yellow solid, mp 174-176 °C.

¹**H NMR (500 MHz, CDCl₃)** δ 8.16 (d, J = 7.0 Hz, 1H), 7.67 – 7.63 (m, 4H), 7.55 – 7.52 (m, 2H), 7.45 – 7.39 (m, 3H), 7.29 (d, J = 8.0 Hz, 2H), 7.17 – 7.14 (m, 1H), 7.01 – 7.00 (m, 1H), 6.87 – 6.83 (m, 2H), 5.10 – 5.07 (m, 1H), 4.02 – 3.92 (m, 2H), 2.44 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 183.7, 145.9, 145.0, 143.6, 143.4, 136.5, 134.4, 134.0, 133.7, 129.9, 129.5, 128.9, 128.5, 128.2, 128.0, 124.7, 123.6, 117.5, 114.3, 112.7, 69.0, 22.2, 21.8.

IR (KBr): 2921, 1654, 1516, 1411, 1328, 1259, 1146, 1071, 831, 725 cm⁻¹.

HRMS for C₂₇H₂₃N₂O₃S₂⁺(M+H)⁺: calcd. 487.11446, found 487.11472.



1-(naphthalen-2-yl)-3-(2-phenylimidazo[1,2-a]pyridin-3-yl)-2-tosylpropan-1-one **4aa** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1). Yellow solid, mp 95-97 °C.

¹**H NMR (500 MHz, CDCl**₃) δ 8.19 (d, *J* = 6.5 Hz, 1H), 7.70 – 7.67 (m, 3H), 7.61 – 7.54 (m, 4H), 7.52 – 7.43 (m, 8H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.81 (t, *J* = 6.5 Hz, 1H), 5.57 – 5.54 (m, 1H), 4.08 – 4.05 (m, 2H), 2.24 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 191.6, 145.7, 144.9, 143.2, 135.6, 134.3, 133.8, 131.8, 131.0, 129.8, 129.1, 129.1, 128.9, 128.4, 128.1, 128.1, 127.6, 126.9, 124.4, 123.5, 123.3, 117.4, 114.4, 112.5, 66.8, 21.9, 21.5.

IR (KBr): 2920, 1672, 1625, 1594, 1355, 1317, 1083, 810, 750, 703 cm⁻¹.

HRMS for $C_{33}H_{27}N_2O_3S^+(M+H)^+$: calcd. 531.17369, found 531.17383.



1-cyclopropyl-3-(2-phenylimidazo[1,2-a]pyridin-3-yl)-2-tosylpropan-1-one **4ab** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 1:1 to 1:2). Yellow solid, mp 141-143 °C.

¹**H NMR (500 MHz, CDCl₃)** δ 8.08 (d, J = 6.5 Hz, 1H), 7.69 (m, 4H), 7.57 (d, J = 9.5 Hz, 1H), 7.42 (t, J = 7.5 Hz, 2H), 7.37 – 7.33 (m, 3H), 7.19 – 7.16 (m, 1H), 6.83 (t, J = 7.0 Hz, 1H), 4.53 – 4.51 (m, 1H), 3.94 – 3.79 (m, 2H), 2.46 (s, 3H), 1.86 – 1.81 (m, 1H), 0.90 – 0.86 (m, 1H), 0.72 – 0.68 (m, 2H), 0.53 – 0.49 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 201.6, 145.9, 145.0, 143.5, 134.1, 133.8, 130.0, 129.2, 128.8, 128.0, 128.0, 124.6, 123.6, 117.6, 114.3, 112.5, 73.0, 23.1, 21.8, 21.3, 14.1, 13.1.

IR (KBr): 2917, 1679, 1447, 1305, 1142, 963, 783, 689 cm⁻¹.

HRMS for C₂₆H₂₅N₂O₃S⁺(M+H)⁺: calcd. 445.15804, found 445.15823.



3-(1H-indol-3-yl)-1-phenyl-2-tosylpropan-1-one

6a was purified by silica gel chromatography (petroleum ether/ethyl acetate = 4:1 to 2:1). Yellow solid, mp 173-175 °C.

¹**H NMR (500 MHz, DMSO-d₆)** δ 10.8 (s, 1H), 7.90 (d, J = 7.5 Hz, 2H), 7.79 (d, J = 8.0 Hz, 2H), 7.58 (t, J = 7.5 Hz, 1H), 7.45 (d, J = 8.0 Hz, 2H), 7.43 – 7.40 (m, 3H), 7.25 (d, J = 8.0 Hz, 1H), 7.05 – 7.02 (m, 2H), 6.97 (t, J = 7.0 Hz, 1H), 6.02 – 5.99 (m, 1H), 3.55 – 3.49 (m, 1H), 3.70 – 3.34 (m, 1H), 2.42 (s, 3H).

¹³C NMR (126 MHz, DMSO-d₆) δ 192.2, 145.2, 136.8, 135.9, 134.0, 133.9, 129.8, 129.3, 128.9, 128.6, 126.5, 123.5, 121.2, 118.7, 117.9, 111.5, 108.3, 68.2, 23.2, 21.1.

IR (KBr): 2923, 1673, 1594, 1457, 1289, 1128, 1201, 1084, 866, 744 cm⁻¹.

HRMS for C₂₄H₂₀NO₃S⁻(M-H)⁻: calcd. 402.11584, found 402.11649.



3-(5-methoxy-1H-indol-3-yl)-1-phenyl-2-tosylpropan-1-one

6b was purified by silica gel chromatography (petroleum ether/ethyl acetate = 4:1 to 2:1). Yellow solid, mp 168-170 °C.

¹**H NMR (500 MHz, DMSO-d₆)** δ 10.7 (s, 1H), 7.95 (d, J = 7.5 Hz, 2H), 7.87 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 7.5 Hz, 1H), 7.46 – 7.41 (m, 4H), 7.18 (d, J = 8.5 Hz, 1H), 7.00 (d, J = 1.5 Hz, 1H), 6.82 (d, J = 1.5 Hz, 1H), 6.71 (dd, J = 8.5, 2.0 Hz, 1H), 5.97 (dd, J = 11.5, 2.5 Hz, 1H), 3.75 (s, 3H), 3.61 – 3.56 (m, 1H), 3.36 – 3.33 (m, 1H), 2.39 (s, 3H).

¹³C NMR (126 MHz, DMSO-d₆) δ 192.6, 153.7, 145.7, 137.3, 134.7, 134.4, 131.5, 130.3, 129.7, 129.4, 129.1, 127.3, 124.6, 112.7, 112.0, 108.6, 100.0, 68.7, 55.7, 23.9, 21.6.

IR (KBr): 2922, 1678, 1593, 1447, 1316, 1206, 1145, 1071, 746 cm⁻¹.

HRMS for C₂₅H₂₂NO₄S⁻ (M-H)⁻: calcd. 432.12641, found 432.12585



3-(5-bromo-1H-indol-3-yl)-1-phenyl-2-tosylpropan-1-one

6c was purified by silica gel chromatography (petroleum ether/ethyl acetate = 3:1 to 1:1). Yellow solid, mp 171-173 °C.

¹**H NMR (500 MHz, CDCl₃)** δ 11.0 (s, 1H), 7.94 (d, *J* = 7.5 Hz, 2H), 7.82 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.54 – 7.52 (m, 1H), 7.45 – 7.40 (m, 4H), 7.24 (d, *J* = 8.5 Hz, 1H), 716 – 7.13 (m, 2H), 6.61 (dd, *J* = 11.5, 3.0 Hz, 1H), 3.56 – 3.51 (m, 1H), 3.38 – 3.35 (m, 1H), 2.40 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 192.3, 145.2, 136.8, 134.6, 134.1, 134.0, 129.8, 129.3, 129.0, 128.6, 128.4, 125.3, 123.7, 120.4, 113.5, 111.4, 108.4, 68.4, 23.0, 21.2.

IR (KBr): 2924, 2883, 1651, 1381, 1207, 1087, 1044, 879, 627 cm⁻¹.

HRMS for C₂₄H₁₉BrNO₃S⁻(M-H)⁻: calcd. 480.02635, found 480.02612



3-(5-iodo-1H-indol-3-yl)-1-phenyl-2-tosylpropan-1-one

6d was purified by silica gel chromatography (petroleum ether/ethyl acetate = 3:1 to 1:1). Yellow solid, mp 180-182 °C.

¹H NMR (500 MHz, DMSO-d₆) δ 11.0 (s, 1H), 7.94 (d, J = 7.5 Hz, 2H), 7.81 (d, J = 8.0 Hz, 2H), 7.67 (s, 1H), 7.57 (t, J = 7.5 Hz, 1H), 7.46 – 7.40 (m, 4H), 7.28 (d, J = 8.5 Hz, 1H), 7.12 (d, J = 8.0 Hz, 1H), 7.06 (s, 1H), 6.00 (dd, J = 11.0, 2.5 Hz, 1H), 3.52 – 3.37 (m, 1H), 3.33 – 3.03 (m, 1H), 2.31 (s, 3H). ¹³C NMR (126 MHz, DMSO-d₆) δ 192.7, 145.7, 137.3, 135.4, 134.5, 134.5, 130.3, 129.8, 129.6, 129.5, 129.1, 127.0, 125.3, 114.4, 108.5, 83.0, 68.8, 23.5, 21.7. **IR (KBr):** 2921, 1664, 1595, 1273, 1446, 1240, 1077, 746, 683cm⁻¹. **HRMS for C₂₄H₁₉INO₃S⁻ (M-H)⁻**: calcd. 528.01248, found 528.01251.



3-(5-nitro-1H-indol-3-yl)-1-phenyl-2-tosylpropan-1-one

6e was purified by silica gel chromatography (petroleum ether/ethyl acetate = 5:1 to 3:1). Yellow solid, mp 194-196 °C.

¹**H NMR (500 MHz, DMSO-d₆)** δ 11.6 (s, 1H), 8.39 (d, *J* = 2.0 Hz, 1H), 7.94 – 7.91 (m, 3H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.46 – 7.39 (m, 5H), 7.32 (d, *J* = 2.0 Hz, 1H), 6.11 – 6.08 (m, 1H), 3.59 – 3.53 (m, 1H), 3.44 – 3.41 (m, 1H), 2.42 (s, 3H).

¹³C NMR (126 MHz, DMSO-d₆) δ 192.3, 145.3, 140.5, 139.0, 136.7, 134.0, 134.0, 129.8, 129.2, 129.0, 128.6, 127.8, 125.9, 116.6, 115.6, 111.9, 111.5, 68.3, 22.8, 21.1.

IR (KBr): 2923, 1653, 1329, 1141, 1079, 811, 738, 680 cm⁻¹.

HRMS for C₂₄H₁₉N₂O₅S⁻(M-H)⁻: calcd. 447.10092, found 447.10168.

3-(3-oxo-3-phenyl-2-tosylpropyl)-1H-indole-5-carbonitrile

6f was purified by silica gel chromatography (petroleum ether/ethyl acetate = 5:1 to 3:1). Yellow solid, mp 81-83 °C.

¹**H NMR (500 MHz, DMSO-d₆)** δ 11.4 (s, 1H), 7.91 (d, J = 7.5 Hz, 2H), 7.78 – 7.77 (m, 3H), 7.62 (d, J = 8.0 Hz, 1H), 7.57 (t, J = 7.5 Hz, 1H), 7.43 – 7.39 (m, 5H), 7.32 (dd, J = 8.0, 1.0 Hz, 1H), 6.10 (dd, J = 11.0, 3.0 Hz, 1H), 3.59 – 3.54 (m, 1H), 3.44 – 3.40 (m, 1H), 2.38 (s, 3H).

¹³C NMR (126 MHz, DMSO-d₆) δ 192.2, 145.2, 136.7, 134.6, 134.0, 134.0, 129.8, 129.6, 129.3, 128.9, 128.6, 128.5, 121.4, 120.6, 119.4, 116.5, 109.6, 102.6, 68.2, 22.8, 21.1.

IR (KBr): 2922, 2217, 1675, 1594, 1301, 1233, 1144, 1082, 747, 711 cm⁻¹.

HRMS for C₂₅H₁₉N₂O₃S⁻(M-H)⁻: calcd.427.11109, found 427.11047



3-(2-hydroxynaphthalen-1-yl)-1-phenyl-2-tosylpropan-1-one

6g was purified by silica gel chromatography (petroleum ether/ethyl acetate = 4:1 to 2:1). Yellow solid, mp 173-175 °C.

¹**H NMR (500 MHz, CDCl₃)** δ 7.87 (d, *J* = 8.5 Hz, 1H), 7.74 – 7.70 (m, 5H), 7.58 – 7.51 (m, 2H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.34 – 7.31 (m, 3H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.01 (d, *J* = 8.5 Hz, 1H), 6.90 (s, 1H), 5.62 – 5.59 (m, 1H), 3.88 – 3.84 (m, 1H), 3.76 – 3.70 (m, 1H), 2.44 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 194.5, 152.0, 146.0, 136.4, 134.6, 133.1, 132.7, 129.9, 129.8, 129.7, 129.6, 129.4, 129.0, 128.6, 127.4, 123.5, 121.7, 119.2, 113.0, 69.6, 23.6, 21.8.

IR (KBr): 2923, 1676, 1595, 1438, 1287, 1209, 1138, 992, 808, 742 cm⁻¹.

HRMS for C₂₆H₂₁O₄S⁻(M-H)⁻: calcd. 429.11551, found 429.11618.



 $\label{eq:2-by-constraint} 3-(6-bromo-2-hydroxynaphthalen-1-yl)-1-phenyl-2-tosylpropan-1-one$

6h was purified by silica gel chromatography (petroleum ether/ethyl acetate = 4:1 to 2:1). Yellow solid, mp 165-167 °C.

¹**H NMR (500 MHz, DMSO-d₆)** δ 10.2 (s, 1H), 7.94 (d, J = 1.5 Hz, 1H), 7.84 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 11.0 Hz, 1H), 7.59 – 7.56 (m, 3H), 7.53 – 7.50 (m, 2H), 7.45 (d, J = 8.0 Hz, 2H), 7.33 (t, J = 7.5 Hz, 2H), 7.06 (d, J = 9.5 Hz, 1H), 5.81 – 5.78 (m, 1H), 3.81 – 3.76 (m, 1H), 3.55 – 3.52 (m, 1H), 2.42 (s, 3H).

¹³C NMR (126 MHz, DMSO-d₆) δ 192.3, 153.7, 145.2, 136.9, 134.5, 133.8, 131.2, 130.0, 129.9, 129.3, 129.2, 128.6, 128.1, 128.1, 124.7, 118.6, 115.3, 113.4, 66.9, 23.9, 21.2.

IR (KBr): 2922, 1675, 1501, 1273, 1199, 808, 753, 668 cm⁻¹.

HRMS for C₂₆H₂₀BrO₄S⁻(M-H)⁻: calcd. 507.02602, found 507.02655.



3-(2-hydroxy-7-methylnaphthalen-1-yl)-1-phenyl-2-tosylpropan-1-one 6i was purified by silica gel chromatography (petroleum ether/ethyl acetate = 4:1 to 2:1). Yellow solid, mp 202-204 °C. ¹**H NMR (500 MHz, DMSO-d₆)** δ 9.87 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.59 – 7.48 (m, 7H), 7.36 (s, 1H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.06 (d, *J* = 8.5 Hz, 1H), 6.89 (d, *J* = 9.0 Hz, 1H), 5.69 (dd, *J* = 10.0, 2.0 Hz, 1H), 3.86 – 3.81 (m, 1H), 3.49 – 3.45 (m, 1H), 2.43 (s, 3H), 2.37 (s, 3H).

¹³C NMR (126 MHz, DMSO-d₆) δ 192.3, 153.4, 145.3, 137.1, 135.7, 134.7, 133.8, 132.8, 130.1, 129.3, 128.7, 128.6, 128.4, 128.2, 126.3, 124.6, 121.1, 116.5, 112.2, 67.2, 24.1, 22.0, 21.3.

IR (KBr): 2924, 2881, 1650, 1381, 1087, 1044, 879, 763 cm⁻¹.

HRMS for C₂₇H₂₃O₄S⁻ (M-H)⁻: calcd. 443.13116, found 443.13104.



2-phenyl-3-(2-tosylethyl)imidazo[1,2-a]pyridine

9a was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1). Yellow solid, mp 180-182 °C.

¹**H NMR (500 MHz, CDCl₃)** δ 7.84 (d, *J* = 6.5 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 9.0 Hz, 1H), 7.47 (d, *J* = 7.0 Hz, 2H), 7.28 – 7.23 (m, 5H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.77 (t, *J* = 7.0 Hz, 1H), 3.46 – 3.43 (m, 2H), 3.28 – 3.25 (m, 2H), 2.36 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 145.2, 144.8, 143.3, 135.4, 134.0, 130.1, 128.7, 128.0, 127.9, 127.9, 124.4, 122.7, 117.8, 115.3, 112.8, 53.2, 21.7, 17.7.

IR (KBr) 2920, 1595, 1449, 1358, 1288, 1138, 1085, 812, 777, 730 cm⁻¹.

HRMS for C₂₂H₂₁N₂O₂S⁺ (M+H)⁺: calcd. 377.13183, found 377.13199.



2-(p-tolyl)-3-(2-tosylethyl)imidazo[1,2-a]pyridine

9b was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1). Yellow solid, mp 203-205 °C.

¹**H NMR (500 MHz, CDCl₃)** δ 7.84 (d, *J* = 7.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 9.0 Hz, 1H), 7.37 (d, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.12 – 7.07 (m, 3H), 6.77 (t, *J* = 7.0 Hz, 1H), 3.46 – 3.43 (m, 2H), 3.29 – 3.25 (m, 2H), 2.38 (s, 3H), 2.30 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 145.2, 144.8, 143.4, 137.7, 135.5, 131.2, 130.1, 129.5, 128.0, 127.7, 124.3, 122.6, 117.8, 115.0, 112.8, 53.2, 21.8, 21.3, 17.8.

IR (KBr) 2920, 1501, 1404, 1355, 1290, 1232, 1142, 1084, 822, 734 cm⁻¹.

HRMS for C₂₃H₂₃N₂O₂S⁺(M+H)⁺: calcd. 391.14748, found 391.14713



2-(3-bromophenyl)-3-(2-tosylethyl)imidazo[1,2-a]pyridine

9c was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1). Yellow solid, mp 181-183 °C.

¹**H NMR (500 MHz, CDCl₃)** δ 7.87 (d, J = 7.0 Hz, 1H), 7.72 (s, 1H), 7.63 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 9.0 Hz, 1H), 7.35 (t, J = 7.5 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.14 – 7.10 (m, 2H), 6.79 (t, J = 7.0 Hz, 1H), 3.45 – 3.42 (m, 2H), 3.28 – 3.24 (m, 2H), 2.36 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 145.3, 144.9, 141.7, 136.2, 135.3, 131.0, 130.8, 130.2, 127.8, 126.1, 124.8, 123.0, 122.8, 117.9, 115.7, 113.1, 53.1, 21.7, 17.7.

IR (KBr) 1592, 1505, 1355, 1298, 1284, 1150, 1086, 891, 807, 731 cm⁻¹.

HRMS for C₂₂H₂₀BrN₂O₂S⁺ (M+H)⁺: calcd. 455.04234, found 455.04208



2-(naphthalen-2-yl)-3-(2-tosylethyl)imidazo[1,2-a]pyridine

9d was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1). Yellow solid, mp 199-201 °C.

¹**H NMR (500 MHz, CDCl₃)** δ 7.97 (s, 1H), 7.90 (d, J = 6.5 Hz, 1H), 7.75 (d, J = 8.0 Hz, 2H), 7.72 – 7.71 (m, 1H), 7.68 – 7.64 (m, 3H), 7.57 (d, J = 9.0 Hz, 1H), 7.42 – 7.41 (m, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.15 (t, J = 8.0 Hz, 1H), 6.81 (d, J = 7.0 Hz, 1H), 3.57 – 3.54 (m, 2H), 3.32 – 3.29 (m, 2H), 2.35 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 145.3, 145.1, 143.3, 135.5, 133.5, 132.9, 131.5, 130.2, 128.5, 128.4, 128.0, 127.8, 126.9, 126.4, 126.4, 125.8, 124.6, 122.7, 118.0, 115.7, 113.0, 53.3, 21.8, 18.0.

IR (KBr) 2923, 1496, 1363, 1299, 1230, 1145, 1083, 889, 861, 757 cm⁻¹.

HRMS for C₂₆H₂₃N₂O₂S⁺ (M+H)⁺: calcd. 427.14748, found 427.14731



7-methyl-2-phenyl-3-(2-tosylethyl)imidazo[1,2-a]pyridine 9e was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1). Yellow solid, mp 195-197 °C. ¹**H NMR (500 MHz, CDCl₃)** δ 7.75 (d, *J* = 7.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.48 – 7.46 (m, 2H), 7.29 – 7.22 (m, 6H), 6.63 (dd, *J* = 7.0, 1.0 Hz, 1H), 3.45 – 3.42 (m, 2H), 3.28 – 3.25 (m, 2H), 2.39 (s, 3H), 2.33 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 145.2, 145.1, 142.8, 135.4, 134.2, 130.1, 128.7, 128.0, 127.8, 127.7, 121.9, 116.2, 115.4, 114.6, 53.3, 21.7, 21.3, 17.7.

IR (KBr) 2922, 1444, 1359, 1308, 1232, 1140, 1086, 816, 772, 693 cm⁻¹.

HRMS for C₂₃H₂₃N₂O₂S⁺(M+H)⁺: calcd. 391.14748, found 391.14749



2-phenyl-3-(2-(phenylsulfonyl)ethyl)imidazo[1,2-a]pyridine

9f was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1). Yellow solid, mp 180-182 °C.

¹**H NMR (500 MHz, CDCl₃)** δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 7.5 Hz, 2H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.52 (d, *J* = 9.0 Hz, 1H), 7.48 – 7.45 (m, 4H), 7.29 – 7.22 (m, 3H), 7.13 – 7.10 (m, 1H), 6.80 – 6.77 (m, 1H), 3.49 – 3.46 (m, 2H), 3.31- 3.27 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 144.9, 143.4, 138.4, 134.1, 134.0, 129.5, 128.8, 128.0, 127.9, 124.5, 122.6, 117.9, 115.1, 112.9, 53.1, 17.7.

IR (KBr) 2921, 1597, 1447, 1358, 1295, 1235, 1083, 804, 731 cm⁻¹.

HRMS for C₂₁H₁₉N₂O₂S⁺(M+H)⁺: calcd. 363.11617, found 363.11624



3-(2-((4-chlorophenyl)sulfonyl)ethyl)-2-phenylimidazo[1,2-a]pyridine

9g was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1). Yellow solid, mp 203-205 °C.

¹**H NMR (500 MHz, CDCl₃)** δ 7.89 (d, *J* = 7.0 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 9.0 Hz, 1H), 7.49 – 7.47 (m, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.33 – 7.28 (m, 3H), 7.16 – 7.13 (m, 1H), 6.82 (t, *J* = 6.5 Hz, 1H), 3.52 – 3.48 (m, 2H), 3.31 – 3.28 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 144.9, 143.5, 141.0, 136.9, 134.0, 129.8, 129.4, 128.9, 128.1, 127.9, 124.5, 122.6, 118.0, 115.0, 113.0, 53.3, 17.7.

IR (KBr) 2920, 1581, 1394, 1358, 1321, 1147, 1086, 836, 766 cm⁻¹.

HRMS for C₂₁H₁₈ClN₂O₂S⁺(M+H)⁺: calcd. 397.07720, found 397.07721



3-(2-(naphthalen-2-ylsulfonyl)ethyl)-2-phenylimidazo[1,2-a]pyridine **9h** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1). Yellow solid, mp 176-178 °C. **¹H NMR (500 MHz, CDCl₃)** δ 8.30 (s, 1H), 7.85 – 7.80 (m, 4H), 7.65 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.42 – 7.37 (m, 3H), 7.13 – 7.08 (m, 3H), 7.02 (t, *J* = 7.5 Hz,

1H), 6.71 (t, *J* = 6.5 Hz, 1H), 3.48 – 3.44 (m, 2H), 3.35 – 3.32 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 144.7, 143.2, 135.3, 135.1, 133.9, 132.0, 129.8, 129.7, 129.5, 129.5, 128.6, 128.0, 127.9, 127.8, 127.7, 124.4, 122.6, 122.3, 117.7, 115.1, 112.7, 53.1, 17.7.

IR (KBr) 2995, 1502, 1449, 1361, 1237, 1145, 1128, 1071, 817, 734 cm⁻¹.

HRMS for C₂₅H₂₁N₂O₂S⁺(M+H)⁺: calcd. 413.13183, found 413.13150



(E)-1,5-diphenyl-2-((2-phenylimidazo[1,2-a]pyridin-3-yl)methyl)-2-tosylpent-4-en-1-one Yellow solid, mp 79-81 °C.

10 was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1). **¹H NMR (500 MHz, CDCl₃)** δ 8.40 (d, *J* = 6.5 Hz, 1H), 7.77 (d, *J* = 7.0 Hz, 2H), 7.46 (d, *J* = 9.0 Hz, 1H), 7.37 – 7.32 (m, 3H), 7.28 – 7.22 (m, 3H), 7.19 – 7.14 (m, 3H), 6.99 – 6.95 (m, 7H), 6.88 (d, *J* = 8.0 Hz, 2H), 6.70 (t, *J* = 7.0 Hz, 1H), 5.86 (d, *J* = 16.0 Hz, 1H), 5.35 – 5.29 (m, 1H), 4.43 (s, 2H), 3.75 (d, *J* = 6.5 Hz, 2H), 2.22 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 165.9, 144.4, 143.9, 143.2, 138.8, 135.7, 135.2, 134.8, 131.4, 130.3, 130.2, 129.1, 129.0, 128.6, 128.5, 128.2, 127.9, 127.5, 126.9, 126.7, 124.6, 123.7, 122.8, 118.9, 117.4, 117.0, 112.0, 70.2, 22.7, 21.5

IR (KBr) 1612, 1590, 1488, 1306, 1250, 1149, 1126, 1070, 965, 772 cm⁻¹. **HRMS for C₃₈H₃₃N₂O₃S⁺ (M+H)⁺:** calcd. 597.22064, found .597.22089

(E)-1-((2-iodo-2-phenylvinyl)sulfonyl)-4-methylbenzene² Yellow solid, mp 78-80 °C.

¹H NMR (500 MHz, CDCl₃) δ 7.44 (d, J = 8.0 Hz, 2H), 7.36 (s, 1H), 7.30 – 7.25 (m, 3H), 7.23 – 7.21

(m, 2H), 7.17 (d, J = 8.5 Hz, 2H), 2.37 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 144.6, 141.3, 139.7, 137.3, 129.8, 129.7, 128.0, 127.9, 127.7, 114.3, 21.7.

IR (KBr): 2922, 2179, 1584, 1441, 1326, 1140, 1082, 858, 766, 748 cm⁻¹.

1-phenyl-2-tosylethan-1-one³

Yellow solid, mp 99-101 °C.

¹**H NMR (500 MHz, CDCl₃)** δ 7.93 – 7.91 (m, 2H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.58 (t, *J* = 8.5 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 4.73 (s, 2H), 2.41 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 188.2, 145.3, 135.8, 135.7, 134.3, 129.8, 129.3, 128.8, 128.6, 63.5, 21.7. IR (KBr): 2923, 1676, 1595, 1447, 1317, 1269, 1147, 992, 823, 736 cm⁻¹.

6 X-ray diffraction analysis of compound 4j

Sample preparation:

The method for crystal growth is slow volatilization using petroleum ether (PE)-ethyl acetate (EA) mixture as a solvent.

Crystal measurement for compound 4j:

A specimen of $C_{29}H_{23}N_3O_5S$, approximate dimensions 0.150 mm x 0.200 mm x 0.250 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured ($\lambda = 0.71073$ Å).

The integration of the data using a triclinic unit cell yielded a total of 31127 reflections to a maximum θ angle of 27.55° (0.77 Å resolution), of which 5555 were independent (average redundancy 5.603, completeness = 97.9%, $R_{int} = 6.02\%$, $R_{sig} = 4.41\%$) and 4432 (79.78%) were greater than $2\sigma(F^2)$. The final cell constants of $\underline{a} = 7.1153(4)$ Å, $\underline{b} = 12.1904(7)$ Å, $\underline{c} = 14.8931(8)$ Å, $\alpha = 79.211(2)^\circ$, $\beta = 77.257(2)^\circ$, $\gamma = 80.078(2)^\circ$, volume = 1226.09(12) Å^3, are based upon the refinement of the XYZ-centroids of reflections above 20 $\sigma(I)$. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9560 and 0.9740.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P -1, with Z = 2 for the formula unit, $C_{29}H_{23}N_3O_5S$. The final anisotropic full-matrix least-squares refinement on F² with 344 variables converged at R1 = 4.23%, for the observed data and wR2 = 11.50% for all data. The goodness-of-fit was 1.030. The largest peak in the final difference electron density synthesis was 0.345 e⁻/Å³ and the largest hole was -0.380 e⁻/Å³ with an RMS deviation of 0.054 e⁻/Å³. On the basis of the final model, the calculated density was 1.424 g/cm³ and F(000), 548 e⁻.



Plots are drawn at 50% probability level.

Table S3.	Crystal	data ar	d structur	e refineme	ent for 4j

Identification code	20220910ge1			
Chemical formula	$C_{29}H_{23}N_3O_5S$			
Formula weight	525.56 g/mol			
Temperature	294(2) K			
Wavelength	0.71073 Å			
Crystal size	0.150 x 0.200 x 0.250 mm			
Crystal system	triclinic			
Space group	P -1			
Unit cell dimensions	$a = 7.1153(4) \text{ Å} \alpha = 79.211(2)^{\circ}$			
	$b = 12.1904(7) \text{ Å} \beta = 77.257(2)^{\circ}$			
	$c = 14.8931(8) \text{ Å}$ $\gamma = 14.8931(8)^{\circ}$			
Volume	1226.09(12) Å ³			
Ζ	2			
Density (calculated)	1.424 g/cm ³			
Absorption coefficient	0.180 mm^{-1}			
F(000)	548			
Theta range for data collection	2.39 to 27.55°			
Index ranges	-9<=h<=9, -15<=k<=15, -18<=l<=19			
Reflections collected	31127			
Independent reflections	5555 [R(int) = 0.0602]			
Max. and min. transmission	0.9740 and 0.9560			
Structure solution technique	direct methods			
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)			

Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	5555 / 0 / 344
Goodness-of-fit on F ²	1.030
$\Delta \sigma_{\rm max}$	0.001
Final R indices	4432 data; I> 2σ (I) R1 = 0.0423, wR2 = 0.1072
	all data $R1 = 0.0580$, $wR2 = 0.1150$
Weightige och and	$w=1/[\sigma^2(F_o^2)+(0.0647P)^2+0.1359P]$
weighting scheme	where $P = (F_o^2 + 2F_c^2)/3$
Largest diff. peak and hole	0.345 and -0.380 eÅ ⁻³
R.M.S. deviation from mean	0.054 eÅ ⁻³

Reference:

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- Mohan, D. C.; Donthiri, R. R.; Rao, S. N.; Adimurthya, S. Copper(I) iodide-catalysed aerobic oxidative synthesis of imidazo[1,2-a]pyridines from 2-aminopyridines and methyl ketones, *Adv. Synth. Catal.* 2013, 355, 2217-2221.
- (2) Zhou, C.; Zeng, X. Iodosulfonylation of alkynes under ultrasound irradiation, *Synthesis*, **2021**, *53*, 4614-4620.
- (3) Reddy, R. J.; Kumar, J. J.; Kumari, A. H. Unprecedented reactivity of β-iodovinyl sulfones: an efficient synthesis of β-keto sulfones and β-keto thiosulfones. *Eur. J. Org. Chem.*, **2019**, 3771-3775.

7 Copies of ¹H and ¹³C NMR Spectra

¹H NMR (500 MHz, CDCl₃) of 4a







¹³C NMR (126 MHz, CDCl₃) of 4a











¹H NMR (500 MHz, CDCl₃) of **4b**





¹³C NMR (126 MHz, CDCl₃) of **4b**







¹H NMR (500 MHz, CDCl₃) of 4c







¹³C NMR (126 MHz, CDCl₃) of **4c**







¹H NMR (500 MHz, CDCl₃) of **4d**



¹³C NMR (126 MHz, CDCl₃) of 4d




0. 98. I 0.95-I 2. 02. 2.94.T 1. 00-I 4.0 2.5 9.5 9.0 8.5 8.0 7.5 7.0 5.0 4.5 f1 (ppm) 6.5 3.5 3.0 2.0 1.5 1.0 0.5 0.0 6.0 5.5

¹³C NMR (126 MHz, CDCl₃) of 4e







H NMR (500 MHz, CDCl₃) of 4f







¹³C NMR (126 MHz, CDCl₃) of 4f





¹³C NMR (126 MHz, CDCl₃) of 4g

72	122232222442222222222222222222222222222	വം രം	
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 $<^{22.26}_{21.75}$



¹H NMR (500 MHz, CDCl₃) of **4h**



¹³C NMR (126 MHz, CDCl₃) of **4h**





¹H NMR (500 MHz, CDCl₃) of 4i



¹³C NMR (126 MHz, CDCl₃) of **4i**



¹H NMR (500 MHz, CDCl₃) of 4j



¹³C NMR (126 MHz, CDCl₃) of **4**j





- 22.299 - 21.785



¹H NMR (500 MHz, CDCl₃) of **4**k







¹³C NMR (126 MHz, CDCl₃) of 4k



¹H NMR (500 MHz, CDCl₃) of **4**I









¹H NMR (500 MHz, CDCl₃) of **4m**





¹³C NMR (126 MHz, CDCl₃) of **4m**



¹H NMR (500 MHz, CDCl₃) of **4n**





¹³C NMR (126 MHz, CDCl₃) of **4n**







¹H NMR (500 MHz, CDCl₃) of 40







¹³C NMR (126 MHz, CDCl₃) of 40













¹H NMR (500 MHz, CDCl₃) of 4q



¹³C NMR (126 MHz, CDCl₃) of **41**



¹H NMR (500 MHz, CDCl₃) of 4r















- 22.074

¹H NMR (500 MHz, CDCl₃) of 4s



¹³C NMR (126 MHz, CDCl₃) of 4s



¹H NMR (500 MHz, CDCl₃) of 4t







191.419







¹H NMR (500 MHz, CDCl₃) of 4u






¹³C NMR (126 MHz, CDCl₃) of 4u



¹H NMR (500 MHz, CDCl₃) of 4v





3.018



³C NMR (126 MHz, CDCl₃) of 4v







38.282

- 23.323





NMR (500 MHz, CDCl₃) of 4w



¹³C NMR (126 MHz, CDCl₃) of **4w**



¹H NMR (500 MHz, CDCl₃) of 4x







¹³C NMR (126 MHz, CDCl₃) of **4**x







H NMR (500 MHz, CDCl₃) of 4y









¹H NMR (500 MHz, CDCl₃) of 4z













¹³C NMR (126 MHz, CDCl₃) of 4aa





 $<^{21.85}_{21.50}$



¹H NMR (500 MHz, CDCl₃) of **4ab**



¹³C NMR (126 MHz, CDCl₃) of 4ab



¹H NMR (500 MHz, DMSO-d₆) of **6a**







¹H NMR (500 MHz, DMSO-d₆) of **6b**



¹³C NMR (126 MHz, DMSO-d₆) of **6b**







¹H NMR (500 MHz, DMSO- d_6) of **6**c





¹³C NMR (126 MHz, DMSO-d₆) of **6c**



¹H NMR (500 MHz, DMSO- d_6) of **6d**



¹³C NMR (126 MHz, DMSO-d₆) of **6d**





¹H NMR (500 MHz, DMSO-d₆) of **6e**







¹³C NMR (126 MHz, DMSO-d₆) of **6f**

191	2219 551 551 551 533 551 533 551 533 551 533 551 533 551 535 535	595 369 461	596	606	1 ^k	20 20 20 20 20 20 20 20 20 20 20 20 20 2	37
192.	1128.88 128.1233.44 128.1239.45 128.1239.45 128.1239.45 128.1239.45 129.1339.45 129.1457.55 129.1457.55 129.157.557.55 10	120. 119. 116.	109.	102.	68. 2	23.23.23.20 23.23.23.20 23.23.23.20 23.23.23.20 23.23.23.20 23.23.23.20 23.23.23.20 23.23.23.20 23.23.23.20 23.23.23.20 23.23.23.20 23.23.23.20 23.23.23.20 23.23.23.20 23.23.23.20 23.23.23.20 23.23.20 23.23.20 23.23.20 23.23.20 23.23.20 23.23.20 23.23.20 23.23.20 23.23.20 23.23.20 23.23.20 23.23.20 23.23.20 20.20 20.	22.8
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¹³C NMR (126 MHz, CDCl₃) of **6g**











ms2 133.4-2000_220707155742 #10 RT: 0.09 AV: 1 NL: 7.59E6

m/z

¹H NMR (500 MHz, DMSO- d_6) of **6h**



13 C NMR (126 MHz, DMSO-d₆) of **6h**



¹H NMR (500 MHz, DMSO-d₆) of **6i**







¹³C NMR (126 MHz, DMSO-d₆) of **6i**

32	36	531633262332733273326533355332533253325332533355333253335553335553335553335553335553335553335553335553335553335553335553335553335553335553335553335555	20	5	866886688	38 22
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¹³C NMR (126 MHz, CDCl₃) of 9a















¹³C NMR (126 MHz, CDCl₃) of **9b**

186 391 391 391 391 391 391 391 391 391 391	404 150 895	208	752 349 803
1145 122 1337 1345 1117 122 1229 1117 1229 1117 1229 1117 11	77.75.	53.	21.21.
VZ II SIZZZI III	\checkmark		VI









¹³C NMR (126 MHz, CDCl₃) of **9c**

250 8699 1641 164 160 160 160 160 160 160 160 160 160 160	396 396	260	736
144.5. 135.1.122.2.2.1330.135.144.5. 135.1117.1222.1226.1330.1355.144.5.	77. 7	23. [21. 2
11-2-21/11V 111	\vee		L. L.

-17, 676









5.5 5.0 4.5 f1 (ppm)

6.0

2.0 1.5

¹³C NMR (126 MHz, CDCl₃) of **9d**

2267 2507 2507 2507 2517 2517 2507 2517 2517 2517 2517 2517 2517 2517 251	896 104	203	63
	77. 1	22	21.7
	\checkmark	1	1 1





¹H NMR (500 MHz, CDCl₃) of **9e**



¹³C NMR (126 MHz, CDCl₃) of **9e**

228	41 15 15 15 15 15 15 15 15 15 15 15 15 15	339 339	021	9	500
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222	12 12 13 13	== :	20.72	23	1221
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¹³C NMR (126 MHz, CDCl₃) of **9f**

$\begin{array}{c} 88\\ 87\\ 87\\ 87\\ 87\\ 87\\ 87\\ 87\\ 87\\ 87\\$	900 90	13	68
112244	77. 76.	23.	17.
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¹³C NMR (126 MHz, CDCl₃) of **9g**

5259532555555555	8886	0 4 5	9
22,28,88,82,28,80,23	12 12 18	5.8	c2
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111 June 11	())		







¹³C NMR (126 MHz, CDCl₃) of **9h**

$\begin{array}{c} 715\\ 214\\ 235\\ 075\\ 903\\ 796\\ 742\\ 548\\ 548\\ 756\\ 756\\ 756\\ 756\\ 756\\ 756\\ 756\\ 756$	617 010 879 814 737 737 737 737 737 737 737 738 738 738
144. 135. 135. 129. 129. 129.	128. 127. 127. 127. 117. 117.
L'LLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLL	X11/11

-53, 063

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¹³C NMR (126 MHz, CDCl₃) of **10**

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~ 22.69





¹H NMR (500 MHz, CDCl₃) of **12a**



