Supporting Information for

Pd(II)-catalyzed annulation of terminal alkynes with 2-pyridinylsubstituted *p*-quinone methides: Direct access to indolizines

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Experimental Section

1. General methods

All reactions were carried out in an oven dried round bottom flask. All the solvents were distilled before use and stored under argon atmosphere. Most of the reagents, starting materials were purchased from commercial sources and used as such. Melting points were recorded on SMP20 melting point apparatus and are uncorrected. ¹H, ¹³C and ¹⁹F spectra were recorded in CDCl₃ (400, 100 and 376 MHz respectively) on Bruker FT–NMR spectrometer. Chemical shift (δ) values are reported in parts per million relative to TMS and the coupling constants (*J*) are reported in Hz. High resolution mass spectra were recorded on Waters Q–TOF Premier–HAB213 spectrometer. FT-IR spectra were recorded on a Perkin-Elmer FTIR spectrometer. Thin layer chromatography was performed on Merck silica gel 60 F₂₅₄ TLC pellets and visualised by UV irradiation and KMnO₄ stain. Column chromatography was carried out through silica gel (100–200 mesh) using EtOAc/hexane as an eluent.

General procedure for the reaction between terminal alkynes to 2-pyridinyl-substituted pquinone methides

Anhydrous MeCN (1.5 mL) was added to the mixture of *p*-quinone methide [*p*-QM] (30 mg, 1.0 equiv.), terminal alkyne (2.0 equiv.) and $Pd(OAc)_2$ (10 mol %) under argon atmosphere and the resulting suspension was stirred at 50 °C until the *p*-QM was completely consumed (based on TLC analysis). The reaction mixture was concentrated under reduced pressure and the residue was purified through a silica gel chromatography, using EtOAc/Hexane mixture as an eluent, to get the pure 1,3-disubstituted indolizine.

2. Table for optimization studies:

Table 1. Optimization Study^a

	^{<i>t</i>} Bu ^{<i>t</i>} Bu 1a (1 equiv.)	─────────────────────────────────────	atalyst (10 mol%) Solvent, temp.	N 3a Ph	∕ ^r Bu
Entry	Catalyst	Solvent	Temp. [°C]	Time [h]	Yield [%] ^b
1	Cu(OTf) ₂	MeCN	RT	24	n.r.
2	Cu(OTf) ₂	THF	RT	24	n.r.
3	Cu(OTf) ₂	PhMe	RT	24	Trace
4	Cu(OTf) ₂	PhMe	50	12	30
5 ^{<i>c</i>}	Cu(OTf) ₂	PhMe	50	12	32
6^d	Cu(OTf) ₂	PhMe	50	12	30
7	CuOTf.PhMe	PhMe	50	12	25
8	Pd(OAc) ₂	PhMe	50	12	56
9	Pd(OAc) ₂	1,2-DCE	50	12	73
10	Pd(OAc) ₂	1,4-Dioxane	50	10	75
11	Pd(OAc) ₂	THF	50	24	59
12	Pd(OAc) ₂	MeCN	50	7	90
13	PdCl ₂	MeCN	50	24	62
14	Pd(PPh ₃) ₄	MeCN	50	24	n.r.
15	AgOCOCF ₃	MeCN	50	24	n.r.
16	$AgSbF_6$	MeCN	50	24	n.r.
17	AgOAc	MeCN	50	24	n.r.
18	Pd(OAc) ₂	MeCN	RT	24	52
19		MeCN	50	48	n.r.
20	$Ni(C_5H_5)_2$	MeCN	50	24	n.r.
21	$[(C_6H_5)_3P]_3RhCl$	MeCN	50	24	n.r.
22	$[(C_{6}H_{5})_{2}P(CH_{2})_{3}P(C_{6}H_{5})_{2}]NiCl_{2}$	MeCN	50	24	n.r.
23	Cu(OAc) ₂	MeCN	50	24	Trace
24	CuBr ₂	MeCN	50	24	n.r.
25	FeCl ₂	MeCN	50	24	n.r.
26	Fe(OAc) ₂	MeCN	50	24	n.r.

он

^tBu、

^aReaction conditions: Reactions were carried out with 0.10 mmol of **1a**, 2 equiv. of **2a** with respect to **1a** and 10 mol % catalyst. bYields reported are isolated yields. ^c2 equiv. Of NEt3 was used, ^d2 equiv. of Pr_2NEt was used. 1,2-DCE = 1,2-Dichloroethane; n.r. = No reaction).

3. De-tert-butylation Reaction:

To further improve the substrate-scope of this transformation, **3a** was subjected to de-*tert*butylation reaction with AlCl₃ (6 equiv.) in benzene at 55 °C and, the resultant product **4** was obtained in 95% yield in an hour (scheme 1).



4. Large scale reaction:

To show the practical applicability of this transformation, a relatively large-scale reaction between 1a (0.5 g scale) and 2a was performed, and the desired product 3a was obtained in 82% yield (0.55 g) in 10 hours (scheme 2).



Scheme 2. Relatively large-scale reaction

5. Characterisation of 2-pyridinyl-substituted p-quinone methides (1b-f):

The 2-pyridinyl-substituted p-quinone methides **1b-f** were prepared by following a literature procedure.¹

2,6-di-*tert*-butyl-4-[(3-methylpyridin-2-yl)-methylene]-cyclohexa-2,5-dien-1-one (1b)



The reaction was performed at 4.127 mmol scale of 3-methylpicolinaldehyde; R_f = 0.5 (5% EtOAc in hexane); yellow solid (794 mg, 62% yield); m. p. = 154 – 156 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.57 – 8.56 (m, 1H), 8.34 (d, *J* = 1.9 Hz,

1H), 7.54 – 7.52 (m, 1H), 7.15 (dd, *J* = 7.7, 4.7 Hz, 1H), 7.12 (s, 1H), 7.00 (d, *J* = 2.0 Hz, 1H),

2.43 (s, 3H), 1.32 (s, 9H), 1.30 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 186.8, 153.7, 149.8, 148.6, 147.5, 138.3, 136.1, 135.5, 134.7, 134.4, 129.6, 123.1, 35.6, 35.2, 29.7, 29.67, 19.5; FT-IR (thin film, neat): 2952, 2857, 1739, 1604, 1540, 1372, 1237, 1045, 931, 740, 590 cm⁻¹; HRMS (ESI): m/z calcd for C₂₁H₂₈NO [M+H]⁺ : 310.2171; found : 310.2176.

2,6-di-*tert*-butyl-4-[(3-fluoropyridin-2-yl)-methylene]-cyclohexa-2,5-dien-1-one (1c)



The reaction was performed at 3.997 mmol scale of 3-fluoropicolinaldehyde; R_f = 0.5 (5% EtOAc in hexane); orange solid (826 mg, 66% yield); m. p. = 130 – 132 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.75 (d, *J* = 2.2 Hz, 1H), 8.53 (d, *J* = 4.5

Hz, 1H), 7.44 – 7.39 (m, 1H), 7.27 – 7.23 (m, 1H), 7.13 (d, J = 2.2 Hz, 1H), 6.98 (d, J = 2.2 Hz, 1H), 1.33 (s, 9H), 1.32 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 186.8, 158.9 (d, $J_{C-F} = 263.4$ Hz), 150.3, 149.0, 145.7 (d, $J_{C-F} = 5.4$ Hz), 144.1 (d, $J_{C-F} = 9.0$ Hz), 135.7 (d, $J_{C-F} = 1.6$ Hz), 135.5, 129.4, 128.8, 124.5 (d, $J_{C-F} = 4.1$ Hz), 123.3 (d, $J_{C-F} = 19.5$ Hz), 35.8, 35.2, 29.7, 29.69; ¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ –120.4; FT-IR (thin film, neat): 2983, 1738, 1618, 1451, 1372, 1235, 1044, 936, 787, 536 cm⁻¹; HRMS (ESI): m/z calcd for C₂₀H₂₅FNO [M+H]⁺ : 314.1920; found : 314.1913.

2,6-di-*tert*-butyl-4-[(5-methylpyridin-2-yl)-methylene]-cyclohexa-2,5-dien-1-one (1d)



The reaction was performed at 0.102 mmol scale of 5-methylpicolinaldehyde; $R_f = 0.5$ (5% EtOAc in hexane); yellow solid (820 mg, 64% yield); m. p. = 152 - 154 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.69 (d, J = 1.6 Hz, 1H), 8.57

(brs, 1H), 7.52 - 7.49 (m, 1H), 7.29 (d, J = 8.0 Hz 1H), 6.95 (d, J = 1.8 Hz, 1H), 6.92 (s, 1H), 2.36 (s, 3H), 1.33 (s, 9H), 1.31 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 186.8, 152.7, 150.9, 149.6, 148.4, 138.7, 136.9, 135.6, 133.9, 133.0, 129.3, 126.9, 35.7, 35.1, 29.7, 29.69, 18.6; FT-IR (thin film, neat): 3090, 2954, 2864, 2734, 1951, 1762, 1606, 1541, 1382, 1251, 1023, 950,

705, 644, 535 cm⁻¹; HRMS (ESI): m/z calcd for C₂₁H₂₈NO [M+H]⁺: 310.2171; found: 310.2180.

2,6-di-*tert*-butyl-4-[(5-chloropyridin-2-yl)-methylene]-cyclohexa-2,5-dien-1-one (1e)

The reaction was performed at 3.532 mmol scale of 5-chloropicolinaldehyde; $R_f = 0.5$ (5% EtOAc in hexane); yellow solid (842 mg, 72% yield); m. p. = 154 - 156 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.68 (d, J = 2.2 Hz, 1H), 8.63 (d, *J* = 1.7 Hz, 1H), 7.68 (dd, *J* = 8.4, 2.4 Hz 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 6.93 (d, *J* = 1.8 Hz, 1H), 6.86 (s, 1H), 1.32 (s, 9H), 1.31 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 186.7, 153.5, 150.2, 149.2, 149.0, 136.5, 136.3, 135.3, 135.1, 131.3, 128.8, 127.7, 35.8, 35.2, 29.7, 29.69; FT-IR (thin film, neat): 2984, 2925, 1737, 1618, 1448, 1372, 1234, 1044, 937, 736, 607, 512 cm⁻¹; HRMS (ESI): m/z calcd for C₂₀H₂₅ClNO [M+H]⁺ : 330.1625; found : 330.1624.

4-[(5-bromopyridin-2-yl)methylene]-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (1f)



The reaction was performed at 2.855 mmol scale of 5-bromopicolinaldehyde; $R_f = 0.5$ (5% EtOAc in hexane); yellow solid (760 mg, 75% yield); m. p. = $168 - 170 \text{ °C}; ^{1}\text{H} \text{ NMR} (400 \text{ MHz}, \text{CDCl}_{3}) \delta 8.78 \text{ (d, } J = 2.3 \text{ Hz}, 1\text{H}), 8.63$ (d, J = 2.3 Hz, 1H), 7.83 (dd, J = 8.3, 2.4 Hz, 1H), 7.27 (d, J = 8.2 Hz, 1H), 6.93 (d, J = 2.2 Hz)Hz, 1H), 6.84 (s, 1H), 1.32 (s, 9H), 1.31 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 186.8, 153.7, 151.3, 150.2, 149.0, 139.2, 136.6, 135.3, 135.1, 128.8, 128.1, 120.2, 35.8, 35.2, 29.72, 29.68; FT-IR (thin film, neat): 3053, 2917, 2865, 1733, 1607, 1455, 1329, 1232, 1022, 742, 534 cm⁻ ¹; HRMS (ESI): m/z calcd for C₂₀H₂₅BrNO [M+H]⁺: 374.1120; found : 374.1109.

6. Characterisation of 2-pyridinyl-substituted p-quinone methides (1g-h):

The 2-pyridinyl-substituted *p*-quinone methides **1g-h** were prepared by following a literature procedure 2 by the coupling of corresponding boronic acid and p-QM (1f)

4-{6-[(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl]-pyridin-3-yl}-

benzaldehyde (1g)



The reaction was performed at 0.801 mmol scale of 1f; $R_f = 0.3$ (10% EtOAc in hexane); yellow solid (134mg, 41% yield); m. p. = 174 - 176 °C; ¹H NMR

 $(400 \text{ MHz}, \text{CDCl}_3) \delta 10.1 \text{ (s, 1H)}, 9.04 \text{ (d, } J = 2.2 \text{ Hz}, 1\text{H}), 8.79 \text{ (d, } J = 2.0 \text{ Hz})$ Hz, 1H), 8.01 (d, J = 8.4 Hz, 2H), 7.97 (dd, J = 8.2, 2.4 Hz, 1H), 7.82 (d, J = 8.2, Hz, 2H), 7.51 $(d, J = 8.1 \text{ Hz}, 1\text{H}), 6.98 (d, J = 2.2 \text{ Hz} 1\text{H}), 6.97 (s, 1\text{H}), 1.35 (s, 9\text{H}), 1.33 (s, 9\text{H}); {}^{13}\text{C NMR}$ $(100 \text{ MHz}, \text{CDCl}_3) \delta$ 191.7, 186.8, 155.3, 150.2, 148.9, 148.8, 143.1, 137.3, 136.1, 135.5, 134.9, 135.3, 133.9, 130.7, 129.1, 127.7, 127.4, 35.8, 35.3, 29.8, 29.7; FT-IR (thin film, neat): 2998, 2955, 2866, 2731, 1699, 1604, 1535, 1359, 1251, 1089, 953, 818, 738 cm⁻¹; HRMS (ESI): m/z calcd for C₂₇H₃₀NO₂ [M+H]⁺: 400.2277; found: 400.2257.

2,6-di-tert-butyl-4-{(5-[3-(trifluoromethyl)phenyl]pyridin-2-yl)methylene}-cyclohexa-2,5-dien-1-one (1h)



The reaction was performed at 0.801 mmol scale of 1f; $R_f = 0.5$ (5% EtOAc in hexane); yellow solid (138 mg, 39% yield); m. p. = 122-124 °C; ¹H NMR $(400 \text{ MHz}, \text{CDCl}_3) \delta 9.00 \text{ (d}, J = 2.2 \text{ Hz}, 1\text{H}), 8.81 \text{ (d}, J = 2.2 \text{ Hz}, 1\text{H}), 7.93$ (dd, J = 8.1, 2.4 Hz, 1H), 7.88 (s, 1H), 7.85 (d, J = 7.6 Hz, 1H), 7.69 – 7.68 (m, 1H), 7.62 (t, J = 7.7 Hz 1H), 7.50 (d, J = 8.1 Hz, 1H), 6.98 (d, J = 2.2 Hz, 1H), 6.97 (s, 1H), 1.36 (s, 9H), 1.33 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 186.8, 155.0, 150.2, 148.9, 148.7, 138.1, 137.4, 135.5, 135.1, 134.7, 134.0, 13.8 (q, J_{C-F} = 32.2 Hz), 130.42, 130.41, 129.9, 127.4, 125.2 (q, J_{C-F} = 3.7 Hz), 124.1 (q, $J_{C-F} = 270.8$ Hz) 123.9 (q, $J_{C-F} = 3.8$ Hz), 35.8, 35.2, 29.8, 29.7; ¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ -62.7; FT-IR (thin film, neat): 2956, 2866, 1613, 1537, 1440, 1360, 1265, 1129, 1048, 933, 737 cm⁻¹; HRMS (ESI): m/z calcd for C₂₇H₂₉F₃NO [M+H]⁺: 440.2201; found: 440.2187.

7. Characterisation of 2-pyridinyl-substituted p-quinone methide (1i):

The 2-pyridinyl-substituted p-quinone methide 1i was prepared by following a literature procedure ³

2,6-di-iso-propyl-4-(pyridin-2-ylmethylene)-cyclohexa-2,5-dien-1-one (1i)

 $R_f = 0.3$ (10% EtOAc in hexane); greenish gummy solid; ¹H NMR (400 MHz, CDCl₃) $\delta 8.74 - 8.73$ (m, 1H), 8.64 - 8.63 (m, 1H), 7.71 (td, J = 7.7, 1.8 Hz, 1H), 7.39 (d, J = 7.8 Hz, 1H), 7.22 – 7.19 (m, 1H), 6.96 (s, 1H), 6.92 (d, J = 2.3 Hz, 1H), 3.20 - 3.13 (m, 2H), 1.16 (d, J = 6.9 Hz, 6H), 1.14 (d, J = 6.9 Hz, 6H); 13 C NMR (100) MHz, CDCl₃) δ 185.6, 155.2, 150.3, 147.8, 146.6, 138.7, 136.6, 135.3, 134.6, 128.9, 127.4, 123.0, 27.3, 26.6, 22.13, 22.12; FT-IR (thin film, neat): 3053, 2961, 2867, 1611, 1590, 1464, 1383, 1265, 1115, 993, 735, 703 cm⁻¹; HRMS (ESI): m/z calcd for C₁₈H₂₁NNaO [M+Na]⁺: 290.1521; found: 290.1518.

8. Characterisation of 1,3-disubstituted indolizines (3a-3z and 3aa-3an)

2,6-di-tert-butyl-4-(3-phenylindolizin-1-yl)-phenol (3a)



The reaction was performed at 0.102 mmol scale of **1a**; $R_f = 0.6$ (5% EtOAc in hexane); pale green solid (36.4 mg, 90% yield); m. p. = 108 - 110 °C; ¹H NMR $(400 \text{ MHz}, \text{CDCl}_3) \delta 8.29 \text{ (d}, J = 7.2 \text{ Hz}, 1\text{H}), 7.70 \text{ (d}, J = 9.1 \text{ Hz}, 1\text{H}), 7.64 - 7.62 \text{ (d}, J = 9.1 \text{ Hz}, 1\text{Hz}, 1\text{Hz}), 7.64 - 7.62 \text{ (d}, J = 9.1 \text{ Hz}, 1\text{Hz}), 7.64 - 7.62 \text{ (d}, J = 9.1 \text{ Hz}, 1\text{Hz}), 7.64 - 7.62 \text{ (d}, J = 9.1 \text{ Hz}, 1\text{Hz}), 7.64 - 7.62 \text{ (d}, J = 9.1 \text{ Hz}, 1\text{Hz}), 7.64 - 7.62 \text{ (d}, J = 9.1 \text{ Hz}, 1\text{Hz}), 7.64 - 7.62 \text{ (d}, J = 9.1 \text{ Hz}), 7.64 - 7.62 \text{ (d}, J = 9.1 \text{ Hz}), 7.64 - 7.62 \text{ (d}, J = 9.1 \text{ Hz}), 7.64 - 7.62 \text{ (d}, J = 9.1 \text{ Hz}), 7.64 - 7.62 \text{ (d}, J = 9.1 \text{ Hz}), 7.64 - 7.62 \text{ (d}, J = 9.1 \text{ Hz}), 7.64 - 7.62 \text{ (d}, J = 9.1 \text{ Hz}), 7.64 - 7.62 \text{ (d}, J = 9.1 \text{ Hz}), 7.64 - 7.62 \text{ (d}, J = 9.1 \text{ Hz}), 7.64 - 7.62$ (m, 2H), 7.52 – 7.48 (m, 3H), 7.44 (s, 2H), 7.38 – 7.34 (m, 1H), 7.00 (s, 1H), 6.74 – 6.70 (m, 1H), 6.52 - 6.47 (m, 1H), 5.18 (s, 1H), 1.52 (s, 18H); ¹³C NMR (100 MHz, CDCl₃) δ 152.3, 136.4, 132.5, 130.0, 129.1, 128.3, 127.4, 127.3, 125.4, 124.7, 122.6, 118.8, 117.5, 116.5, 113.9, 111.0, 34.6, 30.6; FT-IR (thin film, neat): 3635, 2956, 1600, 1407, 1302, 1233, 1155, 1013,

737, 699 cm⁻¹; HRMS (ESI): m/z calcd for C₂₈H₃₂NO [M+H]⁺ : 398.2484; found : 398.2492.

2,6-di-*tert*-butyl-4-[3-(*p*-tolyl)-indolizin-1-yl]-phenol (3b)



The reaction was performed at 0.102 mmol scale of **1a**; $R_f = 0.6$ (5% EtOAc in hexane); green solid (38.1 mg, 91% yield); m. p. = 180 - 182 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.25 (d, J = 7.2 Hz, 1H), 7.70 (d, J = 9.1 Hz, 1H), 7.52 (d, J = 8 Hz, 2H), 7.44(s, 2H), 7.31 (d, J = 7.9 Hz, 2H), 7.00 (s, 1H), 6.72 – 6.68 (m, 1H), 6.50 – 6.46

(m, 1H), 5.18 (s, 1H), 2.44 (s, 3H), 1.52 (s, 18H); ¹³C NMR (100 MHz, CDCl₃) δ 152.2, 137.2, 136.3, 129.8, 129.78, 129.6, 128.3, 127.5, 125.5, 124.7, 122.7, 118.8, 117.3, 116.3, 113.6, 110.9, 34.6, 30.6, 21.5; FT-IR (thin film, neat): 3451, 2956, 2870, 1641, 1451, 1360, 1233, 1154, 1119, 886, 738 cm⁻¹; HRMS (ESI): *m/z* calcd for C₂₉H₃₄NO [M+H]⁺: 412.2640; found : 412.2631.

2,6-di-*tert*-butyl-4-[3-(*o*-tolyl)-indolizin-1-yl]-phenol (3c)



The reaction was performed at 0.102 mmol scale of **1a**; $R_f = 0.6$ (5% EtOAc in hexane); green solid (28.1 mg, 67% yield); m. p. = $128 - 130 \text{ }^{\circ}\text{C}$;¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, J = 9.1 Hz, 1H), 7.56 (d, J = 7.1 Hz, 1H), 7.47 (s, 2H), 7.43 (d, J = 7.2 Hz, 1H), 7.37 – 7.36 (m, 2H), 7.34 – 7.29 (m, 1H), 6.93 (s, 1H); 6.73 – 6.70 (m, 1H), 6.45 (t, J = 6.6 Hz, 1H), 5.17 (s, 1H), 2.20 (s, 3H) 1.53 (s, 18H); ¹³C NMR (100 MHz, CDCl₃) δ 152.1, 138.4, 136.4, 131.7, 131.4, 130.6, 128.8, 128.5, 127.7, 126.2, 124.5, 123.1, 118.6, 117.0, 115.49, 115.48, 114.0, 110.6, 34.6, 30.6, 20.0; FT-IR (thin film, neat): 3635, 2957, 2869, 1601, 1550, 1455, 1330, 1233, 1147, 884, 699, 599 cm⁻¹; HRMS (ESI): *m/z* calcd for C₂₉H₃₄NO [M+H]⁺ : 412.2640; found : 412.2620.

2,6-di-*tert*-butyl-4-{3-[4-(*tert*-butyl) phenyl] indolizin-1-yl}-phenol (3d)



The reaction was performed at 0.102 mmol scale of **1a**; $R_f = 0.6$ (5% EtOAc in hexane); brown solid (38.1 mg, 82% yield); m. p. = 112 - 114 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.31 (d, J = 7.2 Hz, 1H), 7.73 (d, J = 9.1 Hz, 1H), 7.59 (d, J = 8.4

Hz 2H) 7.55 (d, J = 8.5 Hz 2H) 7.48 (s, 2H), 7.02 (s, 1H), 6.74 – 6.71 (m, 1H), 6.52 – 6.48 (m, 1H) 5.20 (s, 1H), 1.55 (s, 18H), 1.42 (s, 9H); 13 C NMR (100 MHz, CDCl₃) δ 152.2, 150.3, 136.3, 129.8, 129.6, 128.0, 127.6, 126.0, 125.4, 124.7, 122.8, 118.8, 117.3, 116.3, 113.7, 110.8, 34.8, 34.6, 31.5, 30.6; FT-IR (thin film, neat): 3640, 2961, 1737, 1604, 1515, 1407, 1362, 1262, 1146, 1097, 1022, 826, 708 cm⁻¹; HRMS (ESI): m/z calcd for C₃₂H₄₀NO [M+H]⁺ : 454.3110; found : 454.3109.

2,6-di-*tert*-butyl-4-[3-(2,4,5-trimethylphenyl)-indolizin-1-yl]-phenol (3e)



The reaction was performed at 0.102 mmol scale of **1a**; $R_f = 0.6$ (5% EtOAc in hexane); green solid (36.1 mg, 80% yield); m. p. = 118-120 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, J = 9.1 Hz, 1H), 7.59 (d, J = 7.1 Hz, 1H), 7.50 (s, 2H), 7.22 (s, 1H), 7.17 (s, 1H), 6.92 (s, 1H), 6.73 - 6.70 (m, 1H), 6.47 - 6.44 (m, 1H), 5.18 (s, 1H), 2.35 (s, 3H), 2.31 (s, 3H), 2.15 (s, 3H), 1.55 (s, 18H); ¹³C NMR (100 MHz, CDCl₃) δ 152.0, 136.9, 136.3, 135.6, 134.2, 132.5, 131.9, 129.0, 128.7, 127.8, 124.7, 124.5, 123.2, 118.5, 116.8, 115.4, 113.9, 110.4, 34.6, 30.6, 19.7, 19.4 (2C); FT-IR (thin film, neat): 3639, 2956, 2869, 1602, 1515, 1451, 1410, 1360, 1304, 1264, 1199, 1150, 1114, 1009, 885, 831, 740, 726 cm⁻¹; HRMS (ESI): *m*/*z* calcd for C₃₁H₃₈NO [M+H]⁺ : 440.2953; found : 440.2955.

2,6-di-tert-butyl-4-[3-(4-methoxyphenyl)-indolizin-1-yl]-phenol (3f)



The reaction was performed at 0.102 mmol scale of **1a**; $R_f = 0.5$ (5% EtOAc in hexane); pale green solid (37.5 mg, 86% yield); m. p. = 148-150 °C; ¹H NMR $(400 \text{ MHz}, \text{CDCl}_3) \delta 8.18 \text{ (d, } J = 7.2 \text{ Hz}, 1\text{H}), 7.69 \text{ (d, } J = 9.1 \text{ Hz}, 1\text{H}), 7.56 -$ 7.52 (m, 2H), 7.45 (s, 2H), 7.10 – 7.03 (m, 2H), 6.94 (s, 1H), 6.71 – 6.67 (m, 1H), 6.49 – 6.45 (m, 1H), 5.18 (s, 1H), 3.89 (s, 3H), 1.52 (s, 18H); 13 C NMR (100 MHz, CDCl₃) δ 159.0, 152.2, 136.3, 129.8, 129.5, 127.6, 125.2, 124.9, 124.7, 122.6, 118.7, 117.2, 116.1, 114.5, 113.4, 110.8, 55.5, 34.6, 30.6; FT-IR (thin film, neat): 3632, 2962, 1732, 1601, 1504, 1462, 1291, 1258,

1169, 1096, 830, 799 cm⁻¹; HRMS (ESI): *m/z* calcd for C₂₉H₃₄NO₂ [M+H]⁺ : 428.2590; found : 428.2597.

2,6-di-tert-butyl-4-[3-(4-methoxy-2-methylphenyl)-indolizin-1-yl]-phenol (3g)



The reaction was performed at 0.102 mmol scale of 1a; $R_f = 0.5$ (5% EtOAc in hexane); green solid (35.0 mg, 78% yield); m. p. = 157–159 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, J = 9.1 Hz, 1H), 7.55 (d, J = 7.1 Hz, 1H), 7.49 (s, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 6.93 (d, *J* = 2.3 Hz, 1H), 6.91 (s, 2H), 6.88 (dd, *J* = 8.4, 2.5 Hz 1H), 6.71 (dd, J = 8.9, 6.4 Hz 1H), 6.45 (t, J = 6.8 Hz, 1H), 5.18 (s, 1H), 3.89 (s, 3H), 2.17 (s, 3H) 1.54 (s, 18H); ¹³C NMR (100 MHz, CDCl₃) δ 159.8, 152.1, 140.1, 136.3, 132.6, 128.6, 127.7, 124.5, 124.3, 124.1, 123.0, 118.5, 116.9, 115.9, 115.3, 114.0, 111.5, 110.4, 55.4, 34.6, 30.6,

20.2; FT-IR (thin film, neat): 3635, 2956, 2870, 1607, 1567, 1515, 1463, 1413, 1304, 1238, 1160, 1119, 1045, 885, 819, 741 cm⁻¹; HRMS (ESI): m/z calcd for C₃₀H₃₆NO₂ [M+H]⁺: 442.2746; found : 442.2746.

2,6-di-tert-butyl-4-{3-[4-(trifluoromethoxy)phenyl]indolizin-1-yl}-phenol (3h)



The reaction was performed at 0.102 mmol scale of 1a; $R_f = 0.5$ (5% EtOAc in hexane); green solid (30.3 mg, 62% yield); m. p. = 178-180 °C;¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, J = 7.2 Hz, 1H), 7.70 (d, J = 9.1 Hz, 1H), 7.64 (d, J = 8.6

Hz, 2H), 7.43 (s, 2H), 7.34 (d, J = 8.2 Hz, 2H), 7.00 (s, 1H), 6.76 – 6.72 (m, 1H), 6.52 (t, J =6.9 Hz, 1H), 5.19 (s, 1H), 1.52 (s, 18H); ${}^{13}C{}^{1}H$ NMR (100 MHz, CDCl₃) δ 152.4, 148.2 (q, $J_{C-F} = 1.8$ Hz), 136.4, 131.3, 130.3, 129.5, 127.2, 124.7, 123.9, 122.3, 121.7, 120.7 (q, $J_{C-F} =$ 255.7 Hz), 118.9, 117.8, 116.7, 114.2, 111.4, 34.6, 30.6; ${}^{19}F{}^{1}H$ NMR (376 MHz, CDCl₃) δ -57.78; FT-IR (thin film, neat): 3641, 2957, 2871, 1603, 1548, 1481, 1407, 1340, 1258, 1164, 1119, 1013, 921, 854, 780, 738 cm⁻¹; HRMS (ESI): m/z calcd for C₂₉H₃₁F₃NO₂ [M+H]⁺: 482.2307; found : 482.2284.

2,6-di-tert-butyl-4-[3-(4-phenoxyphenyl)indolizin-1-yl]-phenol (3i)



The reaction was performed at 0.102 mmol scale of 1a; $R_f = 0.5$ (5% EtOAc in hexane); brown solid (43.2 mg, 86% yield); m. p. = 110-112 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, J = 7.1 Hz, 1H), 7.71 (d, J = 9.1 Hz, 1H), 7.6 (d, J = 8.6 Hz, 2H), 7.46 (s, 2H), 7.42 – 7.38 (m, 2H), 7.18 – 7.16 (m, 2H), 7.13 – 7.11 (m, 3H), 7.00 (s, 1H), 6.74 – 6.70 (m, 1H), 6.53 – 6.48 (m, 1H), 5.19 (s, 1H), 1.54 (s, 18H); ¹³C NMR (100 MHz,

CDCl₃) *δ* 157.1, 156.7, 152.3, 136.4, 130.0, 129.84, 129.79, 129.4, 127.5, 127.4, 124.8, 124.7, 123.7, 122.5, 119.3, 118.8, 117.4, 116.3, 113.7, 111.0, 34.6, 30.6; FT-IR (thin film, neat): 3449, 2958, 1640, 1484, 1338, 1145, 828, 762, 739, 696 cm⁻¹; HRMS (ESI): *m/z* calcd for C₃₄H₃₆NO₂ [M-H]⁺ : 490.2746; found : 490.2758.

2,6-di-tert-butyl-4-[3-(4-pentylphenyl)indolizin-1-yl]-phenol (3j)



The reaction was performed at 0.102 mmol scale of **1a**; $R_f = 0.6$ (5% EtOAc in hexane); green solid (34.4 mg, 85% yield); m. p. = $116 - 118 \,^{\circ}$ C; ¹H NMR (400 MHz, CDCl₃) δ 8.28 (d, J = 7.2 Hz, 1H), 7.71 (d, J = 9.1 Hz, 1H), 7.55 (d, J = (CH₂)₄CH₂ 8.0 Hz, 2H), 7.46 (s, 1H), 7.32 (d, J = 8.1 Hz, 2H), 7.0 (s, 1H), 6.73 – 6.69 (m, 1H), 6.51 – 6.47 (m, 1H), 5.19 (s, 1H), 2.69 (t, J = 7.6 Hz, 2H), 1.74 - 1.67 (m, 2H), 1.54 (s, 18H), 1.43 - 1.38(m, 4H), 0.95 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 152.2, 142.2, 136.3, 129.8, 129.1, 128.2, 127.5, 125.5, 124.7, 122.7, 118.8, 117.3, 116.3, 113.7, 110.8, 35.9, 34.6, 31.7, 31.3, 30.6, 22.7, 14.2; FT-IR (thin film, neat): 3451, 2956, 1641, 1451, 1407, 1304, 1233, 1143, 1012, 827, 739 cm⁻¹; HRMS (ESI): m/z calcd for C₃₃H₄₂NO [M+H]⁺ : 468.3266; found : 468.3270.

2,6-di-tert-butyl-4-[3-(4-propylphenyl)indolizin-1-yl]-phenol (3k)



The reaction was performed at 0.102 mmol scale of **1a**; $R_f = 0.6$ (5% EtOAc in hexane); brown solid (39.4 mg, 88% yield); m. p. = 124–126 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.28 (d, J = 7.2 Hz, 1H), 7.71 (d, J = 9.1 Hz, 1H), 7.55 (d, J =

7.9 Hz, 2H), 7.46 (s, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.01 (s, 1H), 6.73 – 6.69 (m, 1H), 6.49 (t, J = 6.6 Hz, 1H), 5.19 (s, 1H), 2.68 (t, J = 7.5 Hz, 2H), 1.78 – 1.68 (m, 2H), 1.54 (s, 18H), 1.02 (t, J = 7.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 152.2, 142.0, 136.3, 129.81, 129.78, 129.2, 128.2, 127.6, 125.5, 124.7, 122.7, 118.8, 117.3, 116.3, 113.7, 110.8, 38.0, 34.6, 30.6, 24.7, 14.1 ; FT-IR (thin film, neat): 3633, 2955, 2859, 1654, 1547, 1453, 1408, 1304, 1233, 1152, 1017, 965, 887, 737, 591, 535, 512 cm⁻¹; HRMS (ESI): m/z calcd for C₃₁H₃₈NO [M+H]⁺ : 440.2953; found : 440.2953.

4-{3-[(1,1'-biphenyl)-4-yl]-indolizin-1-yl}-2,6-di-tert-butylphenol (3l)

The reaction was performed at 0.102 mmol scale of **1a**; $R_f = 0.6$ (5% EtOAc in hexane); green solid (39.7 mg, 82% yield); m. p. = 248–250 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.37 (d, J = 7.2 Hz, 1H), 7.77 – 7.71 (m, 5H), 7.70 – 7.68 (m, 2H), 7.52 – 7.48 (m, 4H), 7.42 – 7.38 (m, 1H), 7.10 (s, 1H), 6.77 – 6.73 (m, 1H), 6.56 – 6.52 (m, 1H), 5.21 (s, 1H), 1.55 (s, 18H); ¹³C NMR (100 MHz, CDCl₃) δ 152.3, 140.8, 140.0, 136.4, 131.4, 130.2, 129.0, 128.5, 127.8, 127.5, 127.4, 127.1, 125.1, 124.7, 122.7, 118.9, 117.6, 116.7, 114.0, 111.1, 34.6, 30.6; FT-IR (thin film, neat): 3449, 2957, 1640, 1484, 1446, 1360, 1306, 1233, 1145, 1007, 885, 696 cm⁻¹; HRMS (ESI): m/z calcd for C₃₄H₃₆NO [M+H]⁺ : 474.2797; found : 474.2780.

2,6-di-*tert*-butyl- 4-[3-(4-fluorophenyl)-indolizin-1-yl]-phenol (3m)



The reaction was performed at 0.102 mmol scale of **1a**; $R_f = 0.6$ (5% EtOAc in hexane); off white solid (24.2 mg, 57% yield); m. p. = $176-178 \text{ }^{\circ}\text{C}$; ¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, J = 7.2 Hz, 1H), 7.72 (d, J = 9.1 Hz, 1H), 7.61 – 7.57 (m,

2H), 7.45 (s, 2H), 7.23 – 7.18 (m, 2H), 7.00 (s, 1H), 6.75 – 6.71 (m, 1H), 6.52 – 6.49 (m, 1H), 5.20 (s, 1H), 1.54 (s, 18H); ¹³C NMR (100 MHz, CDCl3) δ 162.1 (d, J_{C-F} = 245.5 Hz), 152.3, 136.4, 130.5 (d, $J_{C-F} = 7.9$ Hz), 129.9, 128.6 (d, $J_{C-F} = 3.2$ Hz), 127.3, 124.7, 124.3, 122.4, 118.8, 117.5, 116.4, 116.1 (d, $J_{C-F} = 21.4 \text{ Hz}$), 113.9, 111.1, 34.6, 30.6; ¹⁹F{¹H} NMR (376) MHz, CDCl₃) δ –114.32; FT-IR (thin film, neat): 3636, 3440, 2957, 1603, 1521, 1451, 1360, 1304, 1233, 1157, 1119, 1013, 887, 739 cm⁻¹; HRMS (ESI): *m/z* calcd for C₂₈H₃₁FNO [M+H]⁺ : 416.2390; found : 416.2378.

2,6-di-tert-butyl-4-[3-(3-fluorophenyl)indolizin-1-yl]-phenol (3n)



The reaction was performed at 0.102 mmol scale of **1a**; $R_f = 0.6$ (5% EtOAc in hexane); brown solid (22.0 mg, 52% yield); m. p. = 152-154 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.29 (d, J = 7.2 Hz, 1H), 7.70 (d, J = 9.1 Hz, 1H), 7.46 - 7.40 (m, 4H), 7.34 - 7.31 (m, 1H), 7.06 - 7.01 (m, 2H), 6.76 - 6.72 (m, 1H), 6.53 (t, J = 7.0 Hz, 1H), 5.19 (s, 1H), 1.52 (s, 18H); ¹³C NMR (100 MHz, CDCl3) δ 163.3 (d, J_{C-F} = 244.8 Hz), 152.4, 136.4, 134.6 (d, $J_{C-F} = 8.3 \text{ Hz}$), 130.6, (d, $J_{C-F} = 8.7 \text{ Hz}$), 130.5, 127.2, 124.7, 124.1 (d, $J_{C-F} = 8.7 \text{ Hz}$) 2.4 Hz), 123.6 (d, J_{C-F} = 2.7 Hz), 122.5, 118.9, 117.9, 116.8, 114.8 (d, J_{C-F} = 21.9 Hz), 114.3 (d, $J_{C-F} = 1.1$ Hz), 114.0, (d, $J_{C-F} = 21.0$ Hz), 111.4, 34.6, 30.6; ${}^{19}F{}^{1}H{}$ NMR (376 MHz, CDCl₃) δ -112.35; FT-IR (thin film, neat): 3636, 2924, 1603, 1521, 1482, 1408, 1304, 1233, 1119, 887, 739 cm⁻¹; HRMS (ESI): m/z calcd for C₂₈H₃₁FNO [M+H]⁺: 416.2390; found : 416.2387.

2,6-di-*tert*-butyl-4-[3-(4-chlorophenyl)indolizin-1-yl]-phenol (30)

The reaction was performed at 0.102 mmol scale of 1a; $R_f = 0.6$ (5% EtOAc in hexane); green solid (32.1 mg, 73% yield); m. p. = $216 - 218 \text{ }^{\circ}\text{C}$;¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, J = 7.2 Hz, 1H), 7.72 – 7.69 (m, 1H), 7.59 – 7.56 (m, 1H),

7.55 – 7.54 (m, 1H), 7.48 – 7.45 (m, 2H) 7.43 (s, 2H), 7.00 (s, 1H); 6.75 – 6.71 (m, 1H), 6.53 -7.50 (m, 1H), 5.19 (s, 1H)), 1.52 (s, 18H); ¹³C NMR (100 MHz, CDCl₃) δ 152.4, 136.4, 132.9, 130.9, 130.3, 129.4, 129.3, 127.2, 124.7, 124.1, 122.4, 118.9, 117.8, 116.7, 114.1, 111.3, 34.6, 30.5; FT-IR (thin film, neat): 3627, 2954, 1511, 1450, 1304, 1231, 1141, 1009, 829, 726 cm⁻¹; HRMS (ESI): m/z calcd for C₂₈H₃₁ClNO [M+H]⁺ : 432.2094; found : 432.2097.

2,6-di-tert-butyl-4-[3-(2-chlorophenyl)indolizin-1-yl]-phenol (3p)

The reaction was performed at 0.102mmol scale of 1a; $R_f = 0.6$ (5% EtOAc in hexane); brown solid (24.4 mg, 55% yield); m. p. = 165-167 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.77 – 7.74 (m, 1H), 7.67 – 7.66 (m, 1H), 7.58 – 7.53 (m, 2H), 7.48 (s, 2H), 7.40 – 7.37 (m, 2H), 7.04 (s, 1H); 6.80 – 6.76 (m, 1H), 6.55 – 6.51 (m, 1H), 5.19 (s, 1H)), 1.54 (s, 18H); ¹³C NMR (100 MHz, CDCl₃) δ 152.2, 136.3, 134.8, 133.1, 131.3, 130.2, 129.6, 129.5, 127.4, 127.1, 124.7, 123.7, 122.3, 118.5, 117.6, 115.9, 114.9, 110.6, 34.6, 30.6; FT-IR (thin film, neat): 3634, 2957, 1598, 1443, 1306, 1262, 1150, 1034, 833, 654 cm⁻¹; HRMS (ESI): *m*/*z* calcd for C₂₈H₃₁ClNO [M+H]⁺ : 432.2094; found : 432.2094.

4-[3-(4-bromophenyl)-indolizin-1-yl]-2,6-di-tert-butylphenol (3q)



The reaction was performed at 0.102 mmol scale of 1a; $R_f = 0.5$ (5% EtOAc in hexane); green solid (28.3 mg, 58% yield); m. p. = 230–232 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, *J* = 7.2 Hz, 1H), 7.70 (d, *J* = 9.1 Hz, 1H), 7.63 – 7.60 (m, 2H), 7.51 – 7.48 (m, 2H), 7.42 (s, 2H), 6.98 (s, 1H), 6.75 – 6.71 (m, 1H), 6.53 – 6.50 (m, 1H),

5.19 (s, 1H), 1.52 (s, 18H); ¹³C NMR (100 MHz, CDCl₃) δ 152.4, 136.4, 132.3, 131.4, 130.3,

129.7, 127.2, 124.7, 124.1, 122.4, 121.0, 118.9, 117.8, 116.8, 114.1, 111.4, 34.6, 30.5; FT-IR (thin film, neat): 3437, 2956, 2850, 1633, 1510, 1485, 1450, 1361, 1304, 1233, 1144, 1071, 1009, 822, 723 cm⁻¹; HRMS (ESI): m/z calcd for C₂₈H₃₁BrNO [M+H]⁺ : 476.1589; found : 476.1570.

2,6-di-tert-butyl-4-[3-(2,4-dichlorophenyl)-indolizin-1-yl]-phenol (3r)



The reaction was performed at 0.102 mmol scale of 1a; $R_f = 0.5$ (5% EtOAc in hexane); brown solid (24.0 mg, 50% yield); m. p. = 152-154 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, J = 9.1 Hz, 1H), 7.62 (d, J = 7.1 Hz, 1H), 7.58 (d, J = 2.1 Hz, 1H), 7.48 – 7.45 (m, 3H), 7.37 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.00 (s, 1H), 6.80 – 6.76 (m, 1H),

6.55 - 6.51 (m, 1H), 5.19 (s, 1H), 1.52 (s, 18H); ¹³C NMR (100 MHz, CDCl₃) δ 152.3, 136.4, 135.4, 134.6, 133.7, 130.1, 130.0, 129.9, 127.5, 127.2, 124.7, 123.5, 121.0, 118.6, 117.9, 116.1, 115.1, 110.9, 34.6, 30.6; FT-IR (thin film, neat): 3635, 3452, 2956, 2870, 1631, 1548, 1443, 1408, 1360, 1233, 1154, 1101, 1056, 822, 724 cm⁻¹; HRMS (ESI): *m/z* calcd for C₂₈H₃₀Cl₂NO [M+H]⁺ : 466.1704; found : 466.1687.

2,6-di-*tert*-butyl-4-{3-[4-(trifluoromethyl)phenyl]indolizin-1-yl}-phenol (3s)



The reaction was performed at 0.102 mmol scale of **1a**; $R_f = 0.6$ (5% EtOAc in hexane); off white solid (23.0 mg, 48% yield); m. p. = 220-222 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.30 (d, J = 7.2 Hz, 1H), 7.74 – 7.71 (m, 5H), 7.43 (s, 2H), 7.05 (s, 1H), 6.79 - 6.75 (m, 1H), 6.57 - 6.53 (m, 1H), 5.21 (s, 1H), 1.52 (s, 18H); ¹³C NMR (100) MHz, CDCl₃) δ 152.5, 136.4, 136.0 (apparent q, $J_{C-F} = 0.9$ Hz), 130.9, 128.8 (q, $J_{C-F} = 32.4$ Hz), 127.9, 127.0, 126.1 (q, $J_{C-F} = 3.7$ Hz), 124.7, 124.3 (q, $J_{C-F} = 270.2$ Hz), 123.9, 122.4, 119.0, 118.3, 117.2, 114.8, 111.7, 34.6, 30.5; ¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ -62.41; FT-IR (thin film, neat): 3453, 2957, 2855, 1615, 1456, 1408, 1324, 1235, 1167, 1127, 1067, 1017, 841, 722, 684 cm⁻¹; HRMS (ESI): m/z calcd for C₂₉H₃₁F₃NO [M+H]⁺ : 466.2358; found : 466.2349.

methyl 4-[1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)indolizin-3-yl]-benzoate (3t)



The reaction was performed at 0.102 mmol scale of 1a; $R_f = 0.4$ (5% EtOAc in hexane); brown solid (17.3 mg, 37% yield); m. p. = 204-206 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.36 (d, J = 7.2 Hz, 1H), 8.15 (d, J = 8.3 Hz, 2H), 7.71 (d, J = 8.3 Hz, 2H),

Hz, 3H), 7.42 (s, 2H), 7.07 (s, 1H), 6.79 – 6.75 (m, 1H), 6.57 – 6.54 (m, 1H), 5.20 (s, 1H), 3.96 (s, 3H) 1.52 (s, 18H); 13 C NMR (100 MHz, CDCl₃) δ 167.0, 152.5, 136.9, 136.4, 131.2, 130.5, 128.2, 127.2, 127.0, 124.7, 124.3, 122.7, 119.0, 118.4, 117.3, 114.9, 111.7, 52.3, 34.6, 30.5; FT-IR (thin film, neat): 3633, 3078, 2955, 1719, 1605, 1517, 1407, 1235, 1146, 1014, 832, 704 cm⁻¹; HRMS (ESI): m/z calcd for C₃₀H₃₄NO₃ [M+H]⁺ : 456.2539; found : 456.2541.

4-[1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)indolizin-3-yl]-benzaldehyde (3u)



The reaction was performed at 0.102 mmol scale of 1a; $R_f = 0.4$ (5% EtOAc in hexane); brown solid (14.8 mg, 34% yield); m. p. = $234-236 \text{ }^{\circ}\text{C}$;¹H NMR (400 MHz, CDCl₃) δ 10.04 (s, 1H), 8.41 (d, J = 7.2 Hz, 1H), 8.00 (d, J = 8.3 Hz, 2H), 7.81 (d, J = 8.2 Hz, 2H), 7.73 (d, J = 9.1 Hz, 1H), 7.43 (s, 2H), 7.12 (s, 1H), 6.82 - 6.78 (m, 1H), 6.61 – 6.58 (m, 1H), 5.22 (s, 1H), 1.52 (s, 18H); ¹³C NMR (100 MHz, CDCl₃) δ 191.6, 152.6, 138.5, 136.5, 134.5, 131.7, 130.7, 127.5, 126.8, 124.8, 124.1, 122.7, 119.1, 118.8, 117.7, 115.4, 112.0, 34.6, 30.5; FT-IR (thin film, neat): 3522, 2924, 2864, 2730, 1685, 1591, 1458, 1401, 1291, 1222, 1103, 1023, 943, 822, 730, 666 cm⁻¹; HRMS (ESI): *m/z* calcd for C₂₉H₃₂NO₂ [M+H]⁺ : 426.2433; found : 426.2443.

2,6-di-tert-butyl-4-[3-(naphthalen-1-yl)-indolizin-1-yl]-phenol (3v)



The reaction was performed at 0.102 mmol scale of **1a**; $R_f = 0.6$ (5% EtOAc in hexane); green solid (33.7 mg, 74% yield); m. p. = $139-141 \text{ }^{\circ}\text{C}$; ¹H NMR (400 MHz, CDCl₃) δ 8.0 (d, J = 8.1 Hz, 2H), 7.80 (d, J = 9.1 Hz, 1H), 7.70 – 7.66 (m,

2H), 7.63 – 7.59 (m, 2H), 7.56 – 7.52 (m, 3H), 7.47 – 7.43 (m, 1H), 7.14 (s, 1H), 6.78 – 6.74

(m, 1H), 6.42 - 6.39 (m, 1H), 5.21 (s, 1H), 1.56 (s, 18H); 13 C NMR (100 MHz, CDCl₃) δ 152.2, 136.4, 134.1, 132.4, 129.9, 129.4, 129.0, 128.8, 128.7, 127.6, 126.7, 126.3, 126.1, 125.8, 124.6, 123.5, 123.3, 118.6, 117.4, 115.9, 115.4, 110.6, 34.6, 30.6; FT-IR (thin film, neat): 3633, 3056, 2957, 2870, 1599, 1545, 1451, 1410, 1361, 1303, 1264, 1234, 1154, 1112, 1017, 886, 777, 740 cm⁻¹; HRMS (ESI): *m/z* calcd for C₃₂H₃₄NO [M+H]⁺ : 448.2640; found : 448.2644.

2,6-di-*tert*-butyl-4-[3-(6-methoxynaphthalen-2-yl)indolizin-1-yl]-phenol (3w)



The reaction was performed at 0.102 mmol scale of **1a**; $R_f = 0.5$ (5% EtOAc in hexane); brown solid (40.4 mg, 83% yield); m. p. = 190–192 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.38 (d, J = 7.2 Hz, 1H), 8.03 (s, 1H), 7.87 (d, J = 8.5 Hz 1H),

7.81 (d, J = 8.6 Hz, 1H), 7.78 – 7.72 (m, 2H), 7.52 (s, 2H), 7.25 – 7.22 (m, 2H), 7.12 (s, 1H), 6.78 – 6.74 (m, 1H), 6.55 – 6.51 (m, 1H), 5.22 (s, 1H), 3.98 (s, 3H), 1.39 (s, 18H); ¹³C NMR $(100 \text{ MHz}, \text{CDCl}_3) \delta$ 158.0, 152.2, 136.4, 133.8, 130.0, 129.6, 129.3, 127.6, 127.54, 127.51, 127.1, 126.6, 125.5, 124.7, 122.6, 119.4, 118.8, 117.5, 116.5, 114.0, 111.1, 105.9, 55.5, 34.6, 30.6; FT-IR (thin film, neat): 3630, 2956, 1732, 1606, 1494, 1302, 1220, 1135, 890, 739 cm⁻¹; HRMS (ESI): m/z calcd for C₃₃H₃₆NO₂ [M+H]⁺: 478.2746; found : 478.2742.

4-[3-(anthracen-9-yl)-indolizin-1-yl]-2,6-di-tert-butylphenol (3x)



The reaction was performed at 0.102 mmol scale of 1a; $R_f = 0.5$ (5% EtOAc in hexane); green solid (34.4 mg, 68% yield); m. p. = 154-156 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.62 (s, 1H), 8.12 (d, J = 8.4 Hz, 2H), 7.91 (d, J = 9.1 Hz, 1H), 7.69 (d, J = 8.7 Hz, 2H), 7.64 (s, 2H), 7.53 – 7.49 (m, 2H), 7.43 – 7.38 (m, 2H), 7.28 (s, 1H), 7.18 (d, J = 7.1 Hz, 1H), 6.81 – 6.77 (m, 1H), 6.35 – 6.31 (m, 1H), 5.23 (s, 1H), 1.58 (s, 18H); ¹³C NMR (100 MHz, CDCl₃) δ 152.2, 136.5, 132.0, 131.8, 129.3, 128.8, 128.4, 127.7, 126.6, 126.5, 126.1, 125.6, 124.5, 123.5, 120.3, 118.6, 117.4, 116.8, 115.9, 110.6, 34.7, 30.6; FT-IR (thin film, neat): 3633, 3401, 2957, 2870, 1622, 1511, 1454, 1361, 1324, 1233, 1152, 1115, 1013, 887, 791, 737 cm⁻¹; HRMS (ESI): *m*/*z* calcd for C₃₆H₃₅NNaO [M+Na]⁺ : 520.2616; found : 520.2596.

2,6-di-*tert*-butyl-4-[3-(phenanthren-9-yl) indolizin-1-yl]-phenol (3y)



The reaction was performed at 0.102 mmol scale of **1a**; $R_f = 0.5$ (5% EtOAc in hexane); green solid (39.6 mg, 78% yield); m. p. = 136–138 °C; 8.83 (d, J = 8.2

Hz, 1H), 8.78 (d, J = 8.2 Hz, 1H), 8.00 (s, 1H), 7.95 (dd, J = 7.8, 0.9 Hz, 1H), 7.83 (d, J = 9.2 Hz, 1H), 7.76 – 7.73 (m, 1H), 7.72 – 7.71 (m, 1H), 7.70 – 7.68 (m, 1H), 7.67 – 7.65 (m, 1H), 7.60 – 7.53 (m, 4H), 7.21 (s, 1H), 6.80 – 6.75 (m, 1H), 6.42 – 6.39 (m, 1H), 5.22 (s, 1H), 1.57 (s, 18H); ¹³C NMR (100 MHz, CDCl3) δ 152.2, 136.4, 131.8, 131.2, 130.9, 130.6, 130.3, 129.4, 129.0, 128.6, 127.6, 127.3, 127.2, 127.1, 127.0, 126.9, 124.6, 123.7, 123.3, 123.2, 122.8, 118.6, 117.4, 115.9, 115.3, 110.6, 34.7, 30.6; FT-IR (thin film, neat): 3635, 3450, 2957, 1642, 1450, 1442, 1336, 1233, 1153, 886, 727 cm⁻¹; HRMS (ESI): m/z calcd for C₃₆H₃₆NO [M+H]⁺: 498.2797; found : 498.2788.

2,6-di-tert-butyl-4-[3-(pyren-1-yl)indolizin-1-yl]-phenol (3z)



The reaction was performed at 0.102 mmol scale of **1a**; $R_f = 0.5$ (5% EtOAc in hexane); green solid (33.1 mg, 62% yield); m. p. = 128–130 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.30 (d, J = 7.9 Hz, 1H), 8.24 (d, J = 7.6 Hz, 1H), 8.21 – 8.16

(m, 2H), 8.15 (s, 2H), 8.06 – 8.02 (m, 2H), 7.92 (d, J = 9.2 Hz, 1H), 7.83 (d, J = 9.1 Hz, 1H), 7.69 (d, J = 7.1 Hz, 1H), 7.56 (s, 2H), 7.25 (s, 1H), 6.80 – 6.76 (m, 1H), 6.43 – 6.40 (m, 1H), 5.21 (s,1H), 1.55 (s, 18H) ¹³C NMR (100 MHz, CDCl₃) δ 152.3, 136.5, 131.5, 131.3, 131.1, 129.9, 129.7, 128.8, 128.2, 127.9, 127.6, 127.5, 127.0, 126.3, 125.52, 125.49, 125.4, 125.3, 125.1, 124.9, 124.7, 123.7, 123.2, 118.7, 117.6, 116.3, 115.9, 110.8, 34.7, 30.6; FT-IR (thin film, neat): 3465, 2924, 1640, 1462, 1432, 1303, 1234, 1116, 844, 716 cm⁻¹; HRMS (ESI): m/z calcd for C₃₈H₃₆NO [M+H]⁺ : 522.2797; found : 522.2772.

4-[3-(9H-fluoren-2-yl)indolizin-1-yl]-2,6-di-tert-butylphenol (3aa)



The reaction was performed at 0.102 mmol scale of 1a; $R_f = 0.6$ (5% EtOAc in hexane); light green solid (37.6 mg, 76% yield); m. p. = 196-198 °C; ¹H NMR $(400 \text{ MHz}, \text{CDCl}_3) \delta 8.36 \text{ (d, } J = 7.1 \text{ Hz}, 1\text{H}), 7.91 \text{ (d, } J = 7.8 \text{ Hz}, 1\text{H}), 7.85 \text{ (d, } J$

= 7.5 Hz, 1H), 7.81 (s, 1H), 7.74 (d, J = 9.1 Hz, 1H), 7.67 (d, J = 7.9, Hz, 1H), 7.60 (d, J = 7.4 Hz, 1H), 7.50 (s, 2H), 7.43 (t, J = 7.4 Hz, 1H), 7.35 (t, J = 7.4, Hz, 1H), 7.10 (s, 1H), 6.76 – 6.73 (m, 1H), 6.53 (t, J = 6.8 Hz, 1H), 5.21 (s, 1H), 4.01 (s, 2H), 1.55 (s, 18H); ¹³C NMR (100 MHz, CDCl₃) δ 152.3, 144.1, 143.5, 141.5, 140.9, 136.4, 130.8, 130.0, 127.5, 127.0, 126.9 (2C), 125.8, 125.2, 124.8, 124.7, 122.8, 120.4, 120.0, 118.8, 117.5, 116.5, 113.9, 111.0, 37.1, 34.6, 30.6; FT-IR (thin film, neat): 3633, 2957, 2870, 1612, 1547, 1422, 1337, 1152, 1014, 827, 703, 653 cm⁻¹; HRMS (ESI): *m/z* calcd for C₃₅H₃₆NO [M+H]⁺ : 486.2797; found : 486.2785.

2,6-di-tert-butyl-4-[3-(thiophen-2-yl)-indolizin-1-yl]-phenol (3ab)



The reaction was performed at 0.102 mmol scale of 1a; $R_f = 0.5$ (5% EtOAc in hexane); brown solid (32.0 mg, 78% yield); m. p. = $138 - 140 \text{ }^{\circ}\text{C}$;¹H NMR (400 MHz, CDCl₃) δ 8.38 (d, J = 7.2 Hz, 1H), 7.72 (d, J = 9.1 Hz, 1H), 7.45 (s, 2H), 7.37 (dd, J = 5.2, 1.0 Hz, 1H), 7.31 - 7.30 (m, 1H), 7.20 - 7.18 (m, 1H), 7.10 (s, 1H), 6.79 - 6.75(m, 1H), 6.61 - 6.57 (m, 1H), 5.21 (s, 1H) 1.54 (s, 18H); 13 C NMR (100 MHz, CDCl₃) δ 152.4, 136.4, 134.0, 130.5, 127.7, 127.1, 124.8, 124.74, 124.70, 123.2, 118.7, 118.3, 117.8, 116.6, 115.0, 111.4, 34.6, 30.6, FT-IR (thin film, neat): 3633, 3452, 2870, 1758, 1566, 1416, 1399, 1248, 1139, 853, 724, 664 cm⁻¹; HRMS (ESI): m/z calcd for C₂₆H₃₀NOS [M+H]⁺: 404.2048; found : 404.2034.

2,6-di-*tert*-butyl-4-[3-(thiophen-3-yl)indolizin-1-yl]-phenol (3ac)



The reaction was performed at 0.102 mmol scale of **1a**; $R_f = 0.5$ (5% EtOAc in hexane); brown solid (33.6 mg, 82% yield); m. p. = 140–142 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.25 (d, J = 7.2 Hz, 1H), 7.71 (d, J = 9.1 Hz, 1H), 7.49 – 7.47 (m,

2H), 7.44 (s, 2H), 7.40 (dd, J = 4.7, 1.4 Hz, 1H), 7.03 (s, 1H), 6.74 – 6.70 (m, 1H), 6.56 – 6.52 (m, 1H), 5.19 (s, 1H), 1.53 (s, 18H); ¹³C NMR (100 MHz, CDCl₃) δ 152.3, 136.4, 132.8, 129.8, 127.7, 127.4, 126.2, 124.7, 123.0, 121.2, 120.8, 118.7, 117.3, 116.2, 113.8, 111.2, 34.6, 30.6; FT-IR (thin film, neat): 3632,3452, 2956, 2870, 1642, 1566, 1452, 1416, 1399, 1360, 1331, 1264, 1248, 1139, 887, 783, 663 cm⁻¹; HRMS (ESI): m/z calcd for C₂₆H₃₀NOS [M+H]⁺ : 404.2048; found : 404.2037.

4-{3-(benzo[b]thiophen-2-yl)indolizin-1-yl}-2,6-di-tert-butylphenol (3ad)

The reaction was performed at 0.102 mmol scale of **1a**; $R_f = 0.5$ (5% EtOAc in hexane); brown solid (29.1 mg, 63% yield); m. p. = 126–128 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.55 (d, J = 7.2 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 7.5 Hz, 1H), 7.73 (d, J = 9.0 Hz, 1H), 7.50 (s, 1H), 7.43 (s, 1H), 7.41 – 7.31(m, 3H), 7.19 (s, 1H), 6.82 – 6.78 (m, 1H), 6.67 – 6.63 (m, 1H), 5.22 (s, 1H) 1.53 (s, 18H); ¹³C NMR (100 MHz, CDCl₃) δ 152.5, 140.6, 138.9, 136.4, 134.4, 131.3, 126.9, 124.8, 124.7, 124.3, 123.5, 123.3, 122.1, 119.7, 118.8, 118.5, 118.3, 117.2, 115.8, 111.9, 34.6, 30.6; FT-IR (thin film, neat): 3632, 2957, 2922, 2871, 1597, 1578, 1434, 1360, 1238, 1157, 1025, 889, 748, 665 cm⁻¹; HRMS (ESI): m/z calcd for C30H₃₂NOS [M+H]⁺ : 454.2205; found : 454.2226.

2,6-di-*tert*-butyl-4-[3-(4-ethynylphenyl)indolizin-1-yl]-phenol (3ae)



The reaction was performed at 0.102 mmol scale of **1a**; $R_f = 0.5$ (5% EtOAc in hexane); brown solid (24.0 mg, 56% yield); m. p. = 118–120 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.29 (d, J = 7.2 Hz, 1H), 7.70 (d, J = 9.1 Hz, 1H), 7.63 – 7.58 (m,

4H), 7.43 (s, 2H)), 7.02 (s, 1H), 6.76 – 6.72 (m, 1H), 6.55 – 6.51 (m, 1H), 5.19 (s, 1H), 3.16 (s, 1H), 1.52 (s, 18H); ¹³C NMR (100 MHz, CDCl₃) δ 152.4, 136.4, 132.91, 132.88, 130.6, 127.6, 127.2, 124.7, 124.6, 122.6, 120.5, 118.9, 118.0, 117.0, 114.4, 111.4, 83.7, 77.9, 34.6, 30.6; FT-IR (thin film, neat): 3643, 3306, 3267, 3066, 2923, 2870, 1657, 1484, 1365, 1243, 1154, 1025, 918, 684 cm⁻¹; HRMS (ESI): m/z calcd for C₃₀H₃₂NO [M+H]⁺ : 422.2484; found : 422.2472.

2,6-di-tert-butyl-4-(3-cyclopropylindolizin-1-yl)-phenol (3af)



The reaction was performed at 0.102 mmol scale of **1a**; $R_f = 0.6$ (5% EtOAc in hexane); brown gummy solid (7.6 mg, 20% yield); ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, J = 7.1 Hz, 1H), 7.64 (d, J = 9.1 Hz, 1H), 7.37 (s, 2H), 6.71 - 6.66 (m, 2H),6.57 - 6.53 (m, 1H), 5.12 (s, 1H), 1.91 - 1.85 (m, 1H), 1.50 (s, 18H), 1.03 - 0.98 (m, 2H), 0.76 -0.72 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 152.0, 136.3, 128.7, 127.9, 126.1, 124.5, 122.7, 118.4, 116.7, 114.3, 111.4, 110.2, 34.6, 30.6, 6.3, 5.5; FT-IR (thin film, neat): 3630, 3500, 3055, 2871, 1605, 1499, 1407, 1338, 1301, 1157, 1030, 928, 808, 676, 556 cm⁻¹; HRMS (ESI): m/z calcd for C₂₅H₃₂NO [M+H]⁺: 362.2484; found : 362.2498.

2,6-di-tert-butyl-4-(3-cyclohexylindolizin-1-yl)-phenol (3ag)



The reaction was performed at 0.102 mmol scale of 1a; $R_f = 0.6$ (5% EtOAc in hexane); brown gummy solid (10.1 mg, 24% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, *J* = 7.2 Hz, 1H), 7.64 (d, *J* = 9.1 Hz, 1H), 7.38 (s, 2H), 6.69 (s, 1H), 6.65 – 6.61 (m, 1H), 6.52 – 6.47 (m, 1H), 5.12 (s, 1H), 2.86 – 2.80 (m, 1H), 2.18 – 2.13 (m, 4H), 1.92 -1.80 (m, 3H), 1.61 - 1.54 (m, 3H), 1.50 (s, 18H); 13 C NMR (100 MHz, CDCl₃) δ 151.9, 136.2, 130.1, 128.4, 128.0, 124.6, 122.1, 118.8, 115.9, 114.8, 110.2, 109.4, 35.4, 34.6, 31.9, 30.6, 29.9, 26.8; FT-IR (thin film, neat): 3451, 2927, 2853, 1644, 1453, 1407, 1360, 1336,

1234, 1155, 1118, 888, 735, 721 cm⁻¹; HRMS (ESI): m/z calcd for C₂₈H₃₈NO [M+H]⁺ : 404.2953; found : 404.2960.

2,6-di-tert-butyl-4-(8-methyl-3-phenylindolizin-1-yl)-phenol (3ah)

The reaction was performed at 0.0969 mmol scale of **1b**; $R_f = 0.6$ (5% EtOAc in hexane); green solid (32.8 mg, 82% yield); m. p. = 158-160 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.23 (d, J = 6.3 Hz, 1H), 7.66 – 7.64 (m, 2H); 7.53 – 7.49 (m, 2H); 7.40 – 7.35 (m, 1H), 7.30 (s, 2H), 6.89 (s, 1H), 6.47 – 6.42 (m, 2H), 5.22 (s, 1H), 2.18 (s, 3H), 1.53 (s, 18H); ¹³C NMR (100 MHz, CDCl₃) δ 152.6, 134.8, 132.7, 130.0, 129.8, 129.1, 128.8, 128.5, 127.8, 127.2, 124.7, 120.7, 118.0, 117.8, 116.5, 110.6, 34.5, 30.6, 20.9; FT-IR (thin film, neat): 3635, 2955, 2870, 1601, 1544, 1395, 1333, 1231, 1154, 1026, 833, 736, 627, 590 cm⁻¹; HRMS (ESI): *m/z* calcd for C₂₉H₃₄NO [M+H]⁺ : 412.2640; found : 412.2638.

2,6-di-tert-butyl-4-(8-fluoro-3-phenylindolizin-1-yl)-phenol (3ai)

^{/Bu} / ^{/Bu}
F

The reaction was performed at 0.0957 mmol scale of 1c; $R_f = 0.6$ (5% EtOAc in hexane); brown solid (30.3 mg, 76% yield); m. p. = 160-160 °C;¹H NMR (400 MHz, CDCl₃) δ 8.07 – 8.05 (m, 1H), 7.63 – 7.61 (m, 2H), 7.54 – 7.50 (m, 2H), 7.46 (d, J = 3.3 Hz, 2H), 7.43 – 7.39 (m, 1H), 7.00 (s, 1H), 6.42 – 6.38 (m, 2H), 5.21 (s, 1H), 1.53 (s, 18H); ¹³C NMR (100 MHz, CDCl₃) δ 155.9 (d, J_{C-F} = 247.9 Hz) 152.6, 135.5, 132.1, 129.2, 128.6, 127.8, 127.4, 126.7, 126.3 (d, $J_{C-F} = 4.1$ Hz), 121.0 (d, $J_{C-F} = 32.1$ Hz), 119.1 (d, J_{C-F} = 32.1 Hz), 119.1 (d, $J_{C-F} = 32.1$ Hz), 119.1 (d, J_{C-F} = 32.1 Hz), 119.1 (d, J_{C-F} 4.0 Hz), 117.1 (d, J_{C-F} = 4.7 Hz), 115.5, 109.5 (d, J_{C-F} = 8.1 Hz), 100.1 (d, J_{C-F} = 19.4 Hz), 34.6, 30.6; ${}^{19}F{}^{1}H{}$ NMR (376 MHz, CDCl₃) δ –120.04; FT-IR (thin film, neat): 3638, 2941, 2856, 2742, 1601, 1527, 1437, 1396, 1264, 1152, 1078, 924, 831, 731, 623, 516 cm⁻¹; HRMS (ESI): m/z calcd for C₂₈H₃₀NaFNO [M+H]⁺: 438.2209; found : 438.2204.

2,6-di-tert-butyl-4-(6-methyl-3-phenylindolizin-1-yl)-phenol (3aj)



The reaction was performed at 0.0969 mmol scale of **1d**; $R_f = 0.6$ (5% EtOAc in hexane); brown solid (33.6 mg, 84% yield); m. p. = 146–148 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.09 (s, 1H), 7.66 – 7.63 (m, 3H), 7.53 – 7.49 (m, 2H), 7.46 (s,

2H), 7.39 - 7.35 (m, 1H), 7.00 (s, 1H), 6.61 (d, J = 9.1 Hz, 1H), 5.18 (s, 1H), 2.23 (s, 3H), 1.53 (s, 18H); 13 C NMR (100 MHz, CDCl₃) δ 152.2, 136.3, 132.7, 129.1, 129.0, 128.3, 127.6, 127.2, 125.1, 124.6, 120.9, 120.3, 120.0, 118.3, 116.2, 113.4, 34.6, 30.6, 18.7; FT-IR (thin film, neat): 3633, 3056, 2954, 2869, 1884, 1729, 1514, 1413, 1301, 1199, 1072, 884, 785, 698, 627, 574, 536 cm⁻¹; HRMS (ESI): m/z calcd for C₂₉H₃₄NO [M+H]⁺ : 412.2640; found : 412.2644.

2,6-di-*tert*-butyl-4-(6-chloro-3-phenylindolizin-1-yl)-phenol (3ak)



The reaction was performed at 0.0909 mmol scale of **1e**; $R_f = 0.6$ (5% EtOAc in hexane); brown gummy solid (29.2 mg, 74% yield); ¹H NMR (400 MHz, CDCl₃) δ 8.293 – 8.287 (m, 1H), 7.66 – 7.60 (m, 3H), 7.55 – 7.51 (m, 2H), 7.42 – 7.38

(m, 3H), 7.00 (s, 1H), 6.68 (dd, J = 9.5, 1.7 Hz, 1H), 5.23 (s, 1H), 1.53 (s, 18H); ¹³C NMR (100 MHz, CDCl₃) δ 152.6, 136.5, 131.8, 129.3, 128.6, 128.3, 127.8, 126.8, 126.1, 124.7, 120.2, 119.5, 119.4, 118.7, 117.9, 114.4, 34.6, 30.5; FT-IR (thin film, neat): 3633, 2955, 2869, 1601, 1455, 1313, 1233, 1152, 1112, 887, 757, 671 cm⁻¹; HRMS (ESI): m/z calcd for C₂₈H₃₁ClNO [M+H]⁺: 432.2094; found : 432.2084.

4-[1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-phenyl-indolizin-6-yl]-benzaldehyde (3al)



The reaction was performed at 0.075 mmol scale of **1g**; $R_f = 0.3$ (10% EtOAc in hexane); brown solid (18.0 mg, 47% yield); m. p. = 102–104 °C; ¹H NMR (400 MHz, CDCl₃) δ 10.04 (s, 1H), 8.56 (s, 1H), 7.94 (d, J = 8.3 Hz, 1H), 7.81

(dd, J = 9.3, 0.5 Hz, 1H), 7.71 (d, J = 8.2 Hz, 2H), 7.68 – 7.65 (m, 2H), 7.54 (t, J = 7.6 Hz, 2H), 7.47 (s, 2H), 7.43 – 7.39 (m, 1H), 7.06 (s, 1H), 7.04 (dd, J = 7.8, 1.6 Hz, 1H), 5.23 (s, 1H), 1.54 (s, 18H); ¹³C NMR (100 MHz, CDCl₃) δ 191.8, 152.5, 144.8, 136.5, 135.2, 132.1,

130.6, 129.3, 129.0, 128.4, 127.7, 127.0, 126.5, 124.7, 123.8, 121.1, 119.3, 117.4, 117.2, 115.07, 115.05, 34.6, 30.5; FT-IR (thin film, neat): 3627, 2955, 2826, 1701, 1603, 1565, 1462, 1396, 1265, 839, 702, cm⁻¹; HRMS (ESI): *m*/*z* calcd for C₃₅H₃₄NO₂ [M–H]⁻: 500.2590; found: 500.2586.

2,6-di-tert-butyl-4-{3-phenyl-6-[3-(trifluoromethyl)phenyl]-indolizin-1-yl}-phenol (3am)



The reaction was performed at 0.068 mmol scale of **1h**; $R_f = 0.5$ (5% EtOAc in hexane); brown gummy solid (17 mg, 46% yield); ¹H NMR (400 MHz, CDCl₃) δ 8.48 (s, 1H), 7.81 (dd, J = 8.6, 0.7 Hz, 1H), 7.78 (s, 1H), 7.71 (d, J = 7.6 Hz, 1H) 7.68 – 7.66 (m, 2H), 7.59 (d, J = 7.8

Hz, 1H), 7.76–7.52 (m, 3H), 7.48 (s, 2H), 7.43 – 7.38 (m, 1H), 7.06 (s, 1H), 7.00 (dd, J = 9.4, 1.5 Hz, 1H), 5.22 (s, 1H), 1.54 (s, 18H); ¹³C NMR (100 MHz, CDCl₃) δ 152.5, 139.7, 136.5, 132.2, 131.6, 131.3, 130.0, 129.5, 129.3, 129.1, 128.4, 127.7, 127.1, 126.3, 124.7, 124.0 (q, $J_{C-F} = 5.1$ Hz), 124.2 (q, $J_{C-F} = 270.8$ Hz), 123.5 (q, $J_{C-F} = 3.8$ Hz), 120.5, 119.3, 117.7, 117.0, 114.9, 34.7, 30.6; ¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ –62.6; FT-IR (thin film, neat): 3641, 2956, 2859, 1736, 1602, 1517, 1458, 1364, 1235, 1038, 889, 788, 701 cm⁻¹; HRMS (ESI): m/z calcd for C₃₅H₃₃F₃NO [M-H]⁻ : 540.2514; found : 540.2518.

2,6-di-*iso*-propyl-4-(3-phenylindolizin-1-yl)-phenol (3an)



The reaction was performed at 0.112 mmol scale of **1i**; $R_f = 0.3$ (5% EtOAc in hexane); brown gummy solid (32.3 mg, 78% yield); ¹H NMR (400 MHz, CDCl₃) δ 8.32 (d, J = 7.0 Hz, 1H), 7.74 (d, J = 9.1 Hz, 1H), 7.67 (d, J = 7.3 Hz, 2H), 7.53 (t,

J = 7.5 Hz, 1H), 7.40 (d, J = 7.4 Hz, 1H), 7.37 (s, 2H), 7.07 (s, 1H), 6.76 (t, J = 7.1 Hz, 1H), 6.54 – 6.51 (m, 1H), 4.83 (s, 1H), 3.28 (septet, J = 5.8 Hz, 2H), 1.39 (d, J = 6.8 Hz, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 148.4, 134.1, 132.5, 130.0, 129.1, 128.6, 128.3, 127.3, 125.5, 123.2, 122.6, 118.8, 117.6, 116.2, 113.9, 111.0, 27.4, 23.0; FT-IR (thin film, neat): 3053, 2960, 2869, 1654, 1601, 1547, 1341, 1263, 1014, 938, 833, 700 cm⁻¹; HRMS (ESI): *m/z* calcd for C₂₆H₂₆NO [M-H]⁻: 368.2014; found: 368.2014.

9. Experimental procedure for the de-tert-butylation of 3a:



AlCl₃ (100.6 mg, 0.755 mmol) was added to a solution of **3a** (50 mg, 0.126 mmol) in benzene (2.0 mL) and the mixture was stirred at 55 °C for 1 h . The reaction mixture was then quenched with cold ice water and extracted with Ethyl acetate, and the organic part was concentrated under reduced pressure. The residue was purified through a neutral alumina column using EtOAc/Hexane mixture as an eluent to get the pure product **4** (34.2 mg, 95%) as brown gummy solid; $R_f = 0.5$ (50% EtOAc in hexane); ¹H NMR (400 MHz, DMSO-d₆) δ 9.32 (s, 1H), 8.29 (d, *J* = 7.2 Hz, 1H), 7.64 (d, *J* = 9.1 Hz, 1H), 7.57 (d, *J* = 7.3 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.00 (s, 1H), 6.80 (d, *J* = 8.5 Hz, 2H), 6.73 – 7.70 (m, 1H), 6.54 (t, *J* = 6.9 Hz, 1H); ¹³C NMR (100 MHz, DMSO-d₆) δ 155.5, 131.6, 129.2, 129.1, 128.3, 127.7, 127.2, 126.4, 124.7, 122.6, 118.3, 118.0, 115.7, 114.8, 113.5, 111.4; FT-IR (thin film, neat): 3386, 3255, 2956, 2257, 1653, 1552, 1515, 1267, 1023, 572 cm⁻¹; HRMS (ESI): m/z calcd for C₂₀H₁₆NO [M+H]⁺ : 286.1232; found : 286.1227.

10. (a) Experimental Procedure for the reaction between phenylacetylene to 1a in a mixture of MeCN and D₂O:

Anhydrous MeCN (1.25 mL) and D₂O (0.25 mL) was added to the mixture of *p*-quinone methide **1a** (30 mg, 1.0 equiv.), phenylacetylene (2.0 equiv.) and Pd(OAc)₂ (10 mol %) under argon atmosphere and the resulting suspension was stirred at 50 °C until the *p*-QM **1a** was

completely consumed (based on TLC analysis). The reaction mixture was concentrated under reduced pressure and the residue was purified through a silica gel chromatography, using EtOAc/Hexane mixture as an eluent, to get the pure **3a'**.

(b) Experimental Procedure for the reaction between phenylacetylene-d to 1a:

The phenylacetylene-d was prepared by following a literature procedure ⁴

Anhydrous MeCN (1.5 mL) was added to the mixture of *p*-quinone methide **1a** (30 mg, 1.0 equiv.), phenylacetylene-d (2.0 equiv.) and Pd(OAc)₂ (10 mol %) under argon atmosphere and the resulting suspension was stirred at 50 °C until the *p*-QM **1a** was completely consumed (based on TLC analysis). The reaction mixture was concentrated under reduced pressure and the residue was purified through a silica gel chromatography, using EtOAc/Hexane mixture as an eluent, to get the pure **3a**'.

11. Characterisation of product 3a':

2,6-di-tert-butyl-4-(3-phenylindolizin-1-yl-2-d)-phenol (3a')



2,6-di-*tert*-butyl-4-(3-phenylindolizin-1-yl-2-d)-phenol (3a')

The reaction was performed at 0.102 mmol scale of **1a**; $R_f = 0.5$ (5% EtOAc in hexane); brown gummy solid (34.2 mg, 84% yield); ¹H NMR (400 MHz, CDCl₃) δ 8.30 (d, J = 7.2 Hz, 1H), 7.72 (d, J = 9.1 Hz, 1H), 7.65 – 7.63 (m, 2H), 7.51 (t, J = 7.5 Hz, 2H), 7.46 (s, 2H), 7.39 – 7.35 (m, 1H), 7.02 (s, 0.60H), 6.75 – 6.71 (m, 1H), 6.50 (td, J = 7.4, 1.2 Hz, 1H), 5.20 (s,1H), 1.54 (s, 18H); ¹³C NMR (100 MHz, CDCl₃) δ 152.3, 136.4, 132.5, 130.0, 129.1, 128.3, 127.4, 127.3, 125.4, 124.7, 122.6, 118.8, 117.5, 116.4, 113.9, 111.0, 34.6, 30.6.

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13. X-ray crystallographic analysis for compound 3f:

Complex	XII-FZ-23
Chemical formula	C ₂₉ H ₃₃ NO ₂
molar mass	427.56
Crystal system	Monoclinic
Space group	$P2_{1}/c$
<i>T</i> [K]	150.02(10)
<i>a</i> [Å]	12.5189(4)
<i>b</i> [Å]	10.2586(4)
c[Å]	18.1361(7)
α [°]	90.00
β [°]	97.843(4)
γ [°]	90.00
V [Å ³]	2307.37(15)
Ζ	4
$D(\text{calcd.}) [\text{g} \cdot \text{cm}^{-3}]$	1.231
μ (Mo-K _{α}) [mm ⁻¹]	0.076
Reflections collected	16666
Independent reflections	7963
Data/restraints/parameters	7963/0/300
$R1, wR_2[I > 2\sigma(I)]^{[a]}$	0.0708, 0.1848
$R1$, wR_2 (all data) ^[a]	0.0955, 0.2251
GOF	1.062
CCDC	2132083

Table S1. Crystal data and structure refinement for compound 3f (CCDC 2132083)



¹H NMR (400 MHz, CDCl₃) spectrum of (**1b**)



¹H NMR (400 MHz, CDCl₃) spectrum of (**1c**)





$^{13}C{^{1}H}$ NMR (100 MHz, CDCl₃) spectrum of (1d)



$^{13}C{^{1}H}$ NMR (100 MHz, CDCl₃) spectrum of (1e)





$^{13}C{^{1}H}$ NMR (100 MHz, CDCl₃) spectrum of (1f)



¹³C{¹H} NMR (100 MHz, CDCl₃) spectrum of (**1g**)


$^{13}C{^{1}H}$ NMR (100 MHz, CDCl₃) spectrum of (1h)



¹H NMR (400 MHz, CDCl₃) spectrum of (1i)



¹H NMR (400 MHz, CDCl₃) spectrum of (**3a**)



 $^{13}C{^{1}H}$ NMR (100 MHz, CDCl₃) spectrum of (**3a**)



¹H NMR (400 MHz, CDCl₃) spectrum of (**3b**)



¹H NMR (400 MHz, CDCl₃) spectrum of (**3c**)



¹H NMR (400 MHz, CDCl₃) spectrum of (**3d**)











¹H NMR (400 MHz, CDCl₃) spectrum of (**3h**)











$^{13}C\{^{1}H\}$ NMR (100 MHz, CDCl₃) spectrum of (**3k**)





S51



S52

¹H NMR (400 MHz, CDCl₃) spectrum of (**3n**)





¹³C{¹H} NMR (100 MHz, CDCl₃) spectrum of (**30**)



¹³C{¹H} NMR (100 MHz, CDCl₃) spectrum of (**3p**)



¹H NMR (400 MHz, CDCl₃) spectrum of (3q)



$^{13}C{^{1}H}$ NMR (100 MHz, CDCl₃) spectrum of (**3**q)







¹H NMR (400 MHz, CDCl₃) spectrum of (**3t**)



¹H NMR (400 MHz, CDCl₃) spectrum of (**3u**)



¹H NMR (400 MHz, CDCl₃) spectrum of (3v)



¹H NMR (400 MHz, CDCl₃) spectrum of (**3**w)



¹H NMR (400 MHz, CDCl₃) spectrum of (**3**x)



¹H NMR (400 MHz, CDCl₃) spectrum of (**3y**)



 $^{13}C{^{1}H}$ NMR (100 MHz, CDCl₃) spectrum of (**3y**)



¹H NMR (400 MHz, CDCl₃) spectrum of (**3**z)





¹H NMR (400 MHz, CDCl₃) spectrum of (**3ab**)



¹H NMR (400 MHz, CDCl₃) spectrum of (**3ac**)



¹H NMR (400 MHz, CDCl₃) spectrum of (**3ad**)



¹H NMR (400 MHz, CDCl₃) spectrum of (3ae)



¹H NMR (400 MHz, CDCl₃) spectrum of (**3af**)


¹H NMR (400 MHz, CDCl₃) spectrum of (3ag)



¹H NMR (400 MHz, CDCl₃) spectrum of (**3ah**)



¹H NMR (400 MHz, CDCl₃) spectrum of (3ai)





$^{13}C\{^1H\}$ NMR (100 MHz, CDCl₃) spectrum of (3aj)



¹³C{¹H} NMR (100 MHz, CDCl₃) spectrum of (**3ak**)



$^{13}C\{^1H\}$ NMR (100 MHz, CDCl₃) spectrum of (3al)





¹H NMR (400 MHz, CDCl₃) spectrum of (3an)



¹H NMR (400 MHz, DMSO-d₆) spectrum of (4)







¹H NMR (400 MHz, CDCl₃) spectrum of (**3a'**)



¹H NMR (400 MHz, CDCl₃) spectrum of (**3a'**) -1.5378 1.08 -2:03 $1.09 \pm$ 1.07 + 18.06-0.60 g 5.0 f1 (ppm) 10.0 9.5 6.5 6.0 5.5 4.5 2.0 1.5 0.0 9.0 8.5 8.0 7.5 7.0 4.0 3.5 3.0 2.5 1.0 0.5 ¹³C{¹H} NMR (100 MHz, CDCl₃) spectrum of (3a')
 136.3507

 136.3507

 132.9346

 132.9341

 122.91118

 122.9118

 122.2118

 122.2118

 122.2118

 122.2118

 122.2118

 123.2118

 123.2118

 123.2118

 123.2118

 123.2128

 123.2131

 123.2131

 123.2132

 123.2132

 123.2132

 111.512.6200

 111.512.6201

 111.3.9219

 111.3.9219

 111.1.0103
77.4771 77.1596 76.8422 ----- 34.6258 ---- 30.5652

