Supporting Information

Asymmetric aza-Friedel–Crafts reaction of newly developed

ketimines: access to chiral indeno[1,2-b]quinoxaline

architectures

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1. General experimental information

Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Flash column chromatography was performed over silica gel (H, purchased from Qingdao Ocean Chemical Co., Ltd. Qingdao, China). Analytical thin layer chromatography (TLC) was performed on silica gel HSGF254 glass plates (purchased from Yantai Xinuo Chemical Co., Ltd. Yantai, China) containing a 254 nm fluorescent indicator. The enantiomeric excesses were determined by chiral HPLC analysis that was performed by Agilent HPLC systems using chiral columns described below in detail. Optical rotations were measured with a polarimeter. ¹H NMR spectra were measured on a Bruker AVANCE NEO 400 MHz spectrometer at the ambient temperature of 400 MHz. Proton chemical shifts are reported in parts per million (δ scale) and referenced using tetramethylsilane (TMS) as an internal standard or residual protium in the NMR solvent [CDCl₃: δ 7.26 (CHCl₃) or DMSO-d₆: δ 2.50 (CD_2HSOCD_3)]. Data are reported as follows: chemical shift [multi-plicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, td = triplet of doublets, brs = broad singlet), coupling constant(s) (Hz), integration]. ¹³C NMR spectra were also measured on a Bruker AVANCE NEO 400 MHz spectrometer at the ambient temperature of ¹³C at 101 MHz. Carbon chemical shifts are reported in parts per million (δ scale), and referenced using the carbon resonances of the solvent [δ 77.16 (CDCl₃) or δ 39.52 (DMSO- d_6)]. ¹⁹F NMR spectra were measured on a Bruker AVANCE NEO 400 MHz spectrometer at the ambient temperature of ¹⁹F at 377 MHz. Fluorine chemical shifts are reported in parts per million (δ scale), The melting points of products were recorded on a Büchi Melting Point B-545 and temperatures were not corrected. High-resolution mass spectra (HRMS) were recorded with Agilent 6545 LC/Q-TOF mass spectrometer by using an electrospray ionization (ESI) ionization source analyzed by quadrupole time-of-flight (Q-TOF). IR spectra were recorded with PerkinElmer FT-IR Spectrometer Spectrum 3 by using a PIKE MIRacle universal ATR.

2. Methods for the synthesis of substrates 1 and characterization data.

The starting substrate **1a** was synthesized according to the experimental procedure outlined below. Other substrates were prepared using analogous methods.



The ninhydrin (1.80 g, 10 mmol) and *o*-phenylenediamine (1.10, 10 mmol) were added to ethanol (15.0 mL)/acetic acid (2.0 mL). The mixture was heated under reflux for 2.0 h. The reaction contents were cooled to room temperature. The resulting yellow precipitates were filtered, washed with ethanol, and dried to yield 11H-indeno[1,2-*b*]quinoxalin-11-one **S1** (2.0 g).

The 11*H*-indeno[1,2-*b*]quinoxalin-11-one **S1** (1.20 g, 5.0 mmol) and *N*-Boc-imino-(triphenyl)phosphorane (2.3 g, 6.0 mmol) was added to toluene (15 mmol), the mixture was heated at 120 °C for 24 h, After completion of the reaction (monitored by TLC), the reaction mixture was directly purified by flash chromatography on silica gel (petroleum ether/ ethyl acetate) to give the indeno[1,2-*b*]quinoxalin-11-imine **1a** (0.9 g).

Tert-butyl (*E*)-(11*H*-indeno[1,2-*b*]quinoxalin-11-ylidene)carbamate (1a)



Yellow solid; 193.1 - 193.5 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.16 - 7.94 (m, 4H), 7.83 - 7.75 (m, 1H), 7.74 - 7.65 (m, 2H), 7.61 - 7.53 (m, 1H), 1.74 (s, 9H). HRMS (ESI) m/z: [M + Na]⁺ Calcd. for C₂₀H₁₇N₃O₂Na 354.1213; found: 354.1219

Tert-butyl (*E*)-(7,8-dimethyl-11*H*-indeno[1,2-*b*]quinoxalin-11-ylidene)carbamate (1b)



Yellow solid; m.p. 218.7 – 219.0 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, J = 7.6 Hz, 1H), 7.95 (s, 1H), 7.91 – 7.84 (m, 2H), 7.73 (td, J = 7.5, 1.1 Hz, 1H), 7.56 (td, J = 7.5, 0.8 Hz, 1H), 2.51 (s, 3H), 2.49 (s, 3H), 1.45 (s, 9H). HRMS (ESI) m/z: [M + H]⁺ Calcd. for C₂₂H₂₂N₃O₂ 360.1707; found: 360.1713.

Tert-butyl (*E*)-(7,8-difluoro-11*H*-indeno[1,2-*b*]quinoxalin-11-ylidene)carbamate (1c)



Yellow solid; m.p. 183.5 – 184.1 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.17 – 8.01 (m, 1H), 8.01 – 7.94 (m, 1H), 7.89 – 7.73 (m, 2H), 7.69 (t, J = 7.4 Hz, 1H), 7.64 – 7.53 (m, 1H), 1.73 (s, 9H).

HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{20}H_{15}F_2N_3O_2Na$ 390.1025; found: 390.1032.

Tert-butyl (E)-(7,8-dichloro-11H-indeno[1,2-b]quinoxalin-11-ylidene)carbamate (1d)



Yellow solid; m.p. 211.5 – 212.2 °C.

¹**H NMR (400 MHz, CDCl₃)** δ 8.33 (s, 1H), 8.25 (s, 1H), 8.11 (d, J = 7.6 Hz, 1H), 7.96 (d, J = 7.5 Hz, 1H), 7.81 (td, J = 7.6, 1.0 Hz, 1H), 7.66 (td, J = 7.5, 0.8 Hz, 1H), 1.45 (s, 9H).

HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{20}H_{16}Cl_2N_3O_2$ 400.0614, 402.0588; found: 400.0618, 402.0611.



Yellow solid; m.p. 217.3 – 217.9 °C.

¹**H NMR (400 MHz, CDCl**₃) δ 8.40 (s, 1H), 8.29 (s, 1H), 8.10 – 8.04 (m, 1H), 8.03 – 7.96 (m, 1H), 7.71 (t, *J* = 7.3 Hz, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 1.73 (s, 11H).

HRMS (ESI) m/z: [M + H]⁺ Calcd. for C₂₀H₁₆Br₂N₃O₂ 487.9604, 489.9584, 491.9567; found: 487.9617, 489.9585, 491.9562.

3. General procedure for the synthesis of the product 3



Indeno[1,2-b]quinoxalin-11-imine 1 (0.10 mmol), indoles 2 (0.20 mmol), chiral phosphoric acid IV (10 mol%), and 2-MeTHF (1.0 mL) were successively added to a vial. The resulting mixture was stirred at indicated temperature for the indicated time. After completion of the reaction (monitored by TLC), the reaction mixture was concentrated. The residue was dissolved with DCM, then directly subjected to flash column chromatography to give the corresponding product **3**.

Tert-butyl (11-(1*H*-indol-3-yl)-11*H*-indeno[1,2-*b*]quinoxalin-11-yl)carbamate (3a)



Pale yellow solid; Procedure A: 43.2 mg, 92% yield, 99% *ee*; $[\alpha]_D^{20} = -312.21$ (*c* 2.535, CH₂Cl₂); m.p. 126.2 - 127.5 °C.

¹**H NMR (400 MHz, CDCl₃)** δ 8.56 (s, 1H), 8.35 (s, 1H), 8.21 (d, *J* = 6.6 Hz, 1H), 8.05 (d, *J* = 7.3 Hz, 2H), 7.74 (d, *J* = 6.8 Hz, 1H), 7.67 – 7.46 (m, 4H), 7.24 – 7.12 (m, 3H), 6.49 (s, 1H), 6.05 (brs, 1H), 0.90 (brs, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 163.1, 154.2, 153.5, 150.1, 142.3, 141.4, 137.1, 136.8, 131.8, 129.7, 129.4, 129.3, 128.8, 128.8, 125.0, 124.6, 123.6, 122.7, 122.4, 122.0, 120.0, 115.6, 111.7, 80.4, 63.8, 27.9.
IR (ART) v 3287, 3058, 2974, 1687, 1478, 1455, 1363, 1335, 1246, 1160, 1103, 1048, 1015, 906, 875, 852, 740 cm⁻¹.

HPLC analysis: Chiralpak IA column (*n*-hexane/*i*-PrOH= 85/15; flow rate: 1.0 mL/min; $\lambda = 254$ nm; $t_{minor} = 12.6$ min, $t_{major} = 13.3$ min).

HRMS (ESI) m/z: [M + H]⁺ Calcd. for C₂₈H₂₅N₄O₂ 449.1972; found: 449.1979.

Tert-butyl (11-(4-fluoro-1*H*-indol-3-yl)-11*H*-indeno[1,2-*b*]quinoxalin-11-yl)carbamate (3b)



Pale yellow solid; Procedure A: 46.5 mg, 99% yield, 86% *ee*; Procedure B: 45.6 mg, 98% yield, 97% *ee*; $[\alpha]_D^{20} = -202.32$ (*c* 1.411, CH₂Cl₂, 97% *ee*); m.p. 216.5 - 217.4 °C.

¹**H NMR (400 MHz, CDCl**₃) δ 9.05 (s, 1H), 8.16 – 7.96 (m, 3H), 7.85 (d, *J* = 7.4 Hz, 1H), 7.61 (dt, *J* = 25.4, 6.8 Hz, 2H), 7.49 – 7.30 (m, 2H), 7.06 – 6.91 (m, 1H), 6.91 – 6.83 (m, 1H), 6.81 – 6.72 (m, 1H), 6.28 (s, 2H), 1.04 (brs, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 163.8, 155.5 (d, J = 246.2 Hz, 1C), 154.4, 154.3, 151.1, 142.6, 141.4, 140.1 (d, J = 11.0 Hz, 1C), 136.2, 132.2, 129.6, 129.5, 129.1, 129.0, 128.9, 124.7, 124.6, 123.5, 123.1 (d, J = 8.3 Hz, 1C), 114.3 (d, J = 2.8 Hz, 1C), 113.6 (d, J = 19.9 Hz, 1C), 108.2 (d, J = 3.3 Hz, 1C), 105.7 (d, J = 22.1 Hz, 1C), 80.3, 62.9, 28.0.

¹⁹F NMR (377 MHz, CDCl₃) δ -135.02.

IR (ART) *v* 3241, 2976, 2921, 2851, 1697, 1433, 1364, 1338, 1257, 1205, 1158, 1098, 1076, 1047, 1017, 889, 757, 732 cm⁻¹.

HPLC analysis: Chiralpak IA column (*n*-hexane/*i*-PrOH= 85/15; flow rate: 1.0 mL/min; $\lambda = 254$ nm; $t_{major} = 10.7$ min, $t_{minor} = 15.8$ min).

HRMS (ESI) m/z: [M + K]⁺ Calcd. for C₂₈H₂₃FN₄O₂K 505.1437; found: 505.1405.

Tert-butyl (11-(4-chloro-1*H*-indol-3-yl)-11*H*-indeno[1,2-*b*]quinoxalin-11-yl)carbamate (3c)



Pale yellow solid; Procedure A: 44.5 mg, 92% yield, 42% *ee*; Procedure C: 31.4 mg, 65% yield, 78% *ee*; $[\alpha]_D^{20} = -88.74$ (*c* 1.256, CH₂Cl₂, 78% *ee*); m.p. 147.2 - 148.0 °C.

¹**H NMR (400 MHz, CDCl**₃) δ 9.55 (s, 1H), 8.27 – 7.97 (m, 3H), 7.88 (s, 1H), 7.75 – 7.64 (m, 1H), 7.63 – 7.54 (m, 1H), 7.44 (s, 2H), 7.07 – 6.74 (m, 3H), 6.56 (brs, 1H), 6.26 (brs, 1H), 1.11 (brs, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 164.0, 154.7, 154.1, 151.3, 142.5, 141.2, 139.4, 136.6, 132.0, 129.7, 129.4, 129.2, 129.1, 128.9, 126.3, 125.9, 124.7, 122.7, 122.6, 122.4, 122.1, 114.0, 110.7, 80.2, 63.5, 28.2. **IR** (ART) *v* 3421, 3281, 2968, 2923, 2853, 1690, 1615, 1486, 1364, 1334, 1256, 1242, 1157, 1097, 1044, 1017, 942, 899, 874, 852, 757, 735 cm⁻¹.

HPLC analysis: Chiralpak IG column (*n*-hexane/*i*-PrOH= 85/15; flow rate: 1.0 mL/min; $\lambda = 254$ nm; $t_{minor} = 11.5 \text{ min}, t_{major} = 13.2 \text{ min}$).

HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{28}H_{24}ClN_4O_2$ 483.1582, 485.1566; found: 483.1588, 485.1574.

Tert-butyl (11-(4-methoxyl-1H-indol-3-yl)-11H-indeno[1,2-b]quinoxalin-11-yl)carbamate (3d)



Pale yellow solid; Procedure A: 40.4 mg, 85% yield, 98% *ee*; $[\alpha]_D^{20} = +192.43$ (*c* 1.616, CH₂Cl₂); m.p. 134.1 – 135.2 °C.

¹**H** NMR (400 MHz, CDCl₃) δ 8.78 (s, 1H), 8.09 (dd, J = 12.3, 8.3 Hz, 2H), 8.02 (d, J = 8.1 Hz, 1H), 7.77 (d, J = 7.3 Hz, 1H), 7.75 – 7.62 (m, 2H), 7.62 – 7.55 (m, 1H), 7.42 – 7.28 (m, 2H), 7.02 (t, J = 7.9 Hz, 1H), 6.81 (d, J = 8.1 Hz, 1H), 6.56 (d, J = 7.8 Hz, 1H), 6.10 (s, 1H), 4.05 (s, 3H), 1.02 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 164.9, 155.0, 154.8, 152.4, 152.2, 142.5, 141.4, 139.0, 136.0, 132.1, 129.5, 129.4, 129.0, 128.7, 128.5, 124.6, 123.2, 122.1, 122.1, 116.2, 115.5, 105.8, 100.6, 79.6, 63.3, 55.5. IR (ART) *v* 3305, 3005, 2970, 2926, 1693, 1618, 1576, 1507, 1463, 1364, 1326, 1275, 1258, 1241, 1159, 1090, 1042, 1017, 966, 936, 909, 751, 731 cm⁻¹.

HPLC analysis: Chiralpak IA column (*n*-hexane/*i*-PrOH= 85/15; flow rate: 1.0 mL/min; $\lambda = 254$ nm; $t_{major} = 11.3 \text{ min}, t_{minor} = 12.5 \text{ min}$).

HRMS (ESI) m/z: [M + H]⁺ Calcd. for C₂₉H₂₇N₄O₃ 479.2078; found: 479.2084.

Tert-butyl (11-(5-chloro-1*H*-indol-3-yl)-11*H*-indeno[1,2-b]quinoxalin-11-yl)carbamate (3e)



Pale yellow solid; Procedure A: 41.4 mg, 85% yield, 89% *ee*; Procedure A: 47.8 mg, 99% yield, 90% *ee*; $[\alpha]_D^{20} = -481.89$ (*c* 1.932, CH₂Cl₂, 90% *ee*); m.p. 160.9 – 161.8 °C.

¹**H NMR (400 MHz, CDCl**₃) δ 8.62 (s, 1H), 8.48 (s, 1H), 8.15 (s, 1H), 8.09 – 7.85 (m, 2H), 7.73 (d, J = 7.0 Hz, 1H), 7.67 – 7.47 (m, 4H), 7.11 – 7.04 (m, 1H), 7.00 (d, J = 8.6 Hz, 1H), 6.43 (d, J = 2.4 Hz, 1H), 5.92 (brs, 1H), 1.01 (brs, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 162.6, 154.2, 153.2, 149.6, 142.3, 141.3, 136.9, 135.5, 131.8, 129.7, 129.5, 129.4, 128.9, 128.9, 126.1, 125.7, 125.0, 124.6, 123.1, 122.4, 121.7, 115.2, 112.6, 80.6, 63.5, 28.0. IR (ART) *v* 3414, 3290, 2975, 2926, 1691, 1571, 1463, 1365, 1338, 1274, 1259, 1158, ,1102, 1045, 1016, 938, 908, 892, 796, 752 cm⁻¹.

HPLC analysis: Chiralpak IG column (*n*-hexane/EtOH= 85/15; flow rate: 1.0 mL/min; $\lambda = 254$ nm; $t_{minor} = 5.8$ min, $t_{major} = 7.2$ min).

HRMS (ESI) m/z: [M + H]⁺ Calcd. for C₂₈H₂₄ClN₄O₂ 483.1582, 485.1566; found: 483.1592, 485.1579.

Tert-butyl (11-(5-bromo-1H-indol-3-yl)-11H-indeno[1,2-b]quinoxalin-11-yl)carbamate (3f)



Pale yellow solid; Procedure A: 51.5 mg, 98% yield, 89% *ee*; Procedure B: 48.4 mg, 92% yield, 85% *ee*; $[\alpha]_D^{20} = -452.41$ (*c* 2.260, CH₂Cl₂, 89% *ee*); m.p. 165.6 - 166.7 °C.

¹**H NMR (400 MHz, CDCl**₃) δ 8.83 – 8.52 (m, 2H), 8.32 – 7.82 (m, 3H), 7.79 – 7.68 (m, 1H), 7.67 – 7.33 (m, 4H), 7.24 – 7.12 (m, 1H), 7.04 – 6.86 (m, 1H), 6.46 – 6.31 (m, 1H), 5.91 (brs, 1H), 1.04 (brs, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 162.6, 154.2, 153.1, 149.6, 142.3, 141.3, 136.9, 135.8, 131.8, 129.7, 129.5, 129.4, 128.9, 128.8, 126.8, 125.7, 124.9, 124.8, 124.6, 122.4, 115.1, 113.4, 113.0, 80.6, 63.5, 27.9.
IR (ART) v 3411, 3291, 2974, 2924, 1688, 1453, 1364, 1337, 1274, 1259, 1158, 1101, 1016, 938, 906, 884, 794, 751 cm⁻¹.

HPLC analysis: Chiralpak IG column (*n*-hexane/EtOH= 85/15; flow rate: 1.0 mL/min; $\lambda = 254$ nm; $t_{minor} = 5.8$ min, $t_{major} = 6.8$ min).

HRMS (ESI) m/z: [M + H]⁺ Calcd. for C₂₈H₂₄BrN₄O₂ 527.1077, 529.1061; found: 527.1089, 529.1075.

Methyl 3-(11-((*tert*-butoxycarbonyl)amino)-11*H*-indeno[1,2-*b*]quinoxalin-11-yl)-1*H*-indole-5carboxylate (3g)



Pale yellow solid; Procedure A: 48.5 mg, 96% yield, 88% *ee*; Procedure B: 49.8 mg, 99% yield, 94% *ee*; $[\alpha]_D^{20} = -519.09$ (*c* 2.004, CH₂Cl₂, 94% *ee*); m.p. 166.8 – 167.6 °C.

¹**H NMR (400 MHz, CDCl**₃) δ 9.12 (d, J = 14.9 Hz, 2H), 8.15 (s, 1H), 8.08 – 7.90 (m, 2H), 7.85 – 7.71 (m, 2H), 7.68 – 7.40 (m, 4H), 7.10 (d, J = 8.6 Hz, 1H), 6.65 – 6.46 (m, 1H), 6.03 (brs, 1H), 3.99 (s, 3H), 0.94 (brs, 9H).b

¹³C NMR (101 MHz, CDCl₃) δ 168.4, 162.6, 154.3, 153.3, 149.7, 142.3, 141.3, 139.8, 136.8, 131.8, 129.7, 129.5, 129.4, 128.9, 128.9, 125.3, 125.2, 124.7, 124.7, 124.0, 122.5, 122.0, 116.7, 111.4, 80.6, 63.5, 52.1, 27.9.

IR (ART) *v* 3300, 2974, 1687, 1615, 1434, 1364, 1316, 1273, 1257, 1158, 1106, 1047, 1014, 898, 808, 750 cm⁻¹.

HPLC analysis: Chiralpak IA column (*n*-hexane/*i*-PrOH= 85/15; flow rate: 1.0 mL/min; $\lambda = 254$ nm; $t_{minor} = 8.2 \text{ min}, t_{major} = 12.9 \text{ min}$).

HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{30}H_{27}N_4O_4$ 507.2027; found: 507.2035.

Tert-butyl (11-(5-methyl-1*H*-indol-3-yl)-11*H*-indeno[1,2-b]quinoxalin-11-yl)carbamate (3h)



Pale yellow solid; Procedure A: 45.7 mg, 99% yield, 95% *ee*; $[\alpha]_D^{20} = -414.30$ (*c* 1.828, CH₂Cl₂); m.p. 127.3 – 128.2 °C.

¹**H** NMR (400 MHz, CDCl₃) δ 8.39 (s, 1H), 8.31 – 7.91 (m, 4H), 7.82 – 7.70 (m, 1H), 7.70 – 7.38 (m, 4H), 7.10 (d, J = 8.3 Hz, 1H), 6.99 (d, J = 8.3 Hz, 1H), 6.44 (s, 1H), 6.00 (brs, 1H), 2.53 (s, 3H), 0.85 (brs, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 163.2, 154.3, 153.5, 150.3, 142.3, 141.4, 136.8, 135.5, 131.7, 129.7, 129.3, 129.2, 128.9, 128.8, 125.3, 124.6, 124.4, 123.7, 122.3, 121.6, 115.1, 111.3, 80.3, 63.8, 27.9, 21.8. **IR (ART)** *v* 3397, 3302, 2968, 2917, 2853, 1689, 1578, 1479, 1463, 1362, 1335, 1273, 1257, 1158, 1100, 1018, 905, 795, 758 cm⁻¹.

HPLC analysis: Chiralpak IG column (*n*-hexane/EtOH= 85/15; flow rate: 1.0 mL/min; $\lambda = 254$ nm; $t_{minor} = 6.7$ min, $t_{major} = 8.7$ min).

HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{29}H_{27}N_4O_2$ 463.2129; found: 463.2136.

Tert-butyl (11-(5-methoxyl-1*H*-indol-3-yl)-11*H*-indeno[1,2-*b*]quinoxalin-11-yl)carbamate (3i)



Pale yellow solid; Procedure A: 45.4 mg, 98% yield, 93% *ee*; $[\alpha]_D^{20} = -400.7$ (*c* 2.092, CH₂Cl₂); m.p. 139.6 – 140.3 °C.

¹**H** NMR (400 MHz, CDCl₃) δ 8.47 (s, 1H), 8.20 (d, J = 6.5 Hz, 1H), 8.12 – 7.96 (m, 2H), 7.88 (s, 1H), 7.80 – 7.70 (m, 1H), 7.69 – 7.39 (m, 4H), 7.07 (d, J = 8.8 Hz, 1H), 6.81 (dd, J = 8.8, 2.3 Hz, 1H), 6.51 (d, J = 2.1 Hz, 1H), 5.97 (brs, 1H), 3.96 (s, 3H), 0.85 (brs, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 163.0, 154.3, 154.0, 153.4, 150.1, 142.3, 141.3, 136.9, 132.2, 131.7, 129.7, 129.4, 129.3, 128.9, 128.8, 125.5, 124.7, 124.4, 122.4, 115.0, 113.3, 112.3, 103.7, 80.3, 63.7, 56.1, 27.9.

IR (ART) *v* 3312, 2974, 2927, 1691, 1623, 1578, 1623, 1481, 1454, 1335, 1257, 1218, 1158, 1102, 1045, 1016, 903, 797, 756 cm⁻¹.

HPLC analysis: Chiralpak IG column (*n*-hexane/EtOH= 85/15; flow rate: 1.0 mL/min; $\lambda = 254$ nm; $t_{minor} = 13.3$ min, $t_{major} = 15.6$ min).

HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{29}H_{27}N_4O_3$ 479.2078; found: 479.2089.

Tert-butyl (11-(5-ethoxyl-1H-indol-3-yl)-11H-indeno[1,2-b]quinoxalin-11-yl)carbamate (3j)



Pale yellow solid; Procedure A: 48.5 mg, 98% yield, 92% *ee*; $[\alpha]_D^{20} = -452.71$ (*c* 2.044, CH₂Cl₂); m.p. 119.3 – 120.0 °C.

¹**H** NMR (400 MHz, CDCl₃) δ 8.45 (s, 1H), 8.20 (d, J = 5.0 Hz, 1H), 8.02 (dd, J = 18.5, 6.9 Hz, 2H), 7.85 (s, 1H), 7.73 (d, J = 6.4 Hz, 1H), 7.67 – 7.45 (m, 4H), 7.06 (d, J = 8.8 Hz, 1H), 6.81 (d, J = 8.8 Hz, 1H), 6.48 (s, 1H), 5.97 (brs, 1H), 4.19 (q, J = 6.5 Hz, 2H), 1.51 (t, J = 6.7 Hz, 3H), 0.87 (brs, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 163.1, 154.3, 153.5, 153.3, 150.1, 142.4, 141.3, 136.9, 132.2, 131.7, 129.6, 129.4, 129.2, 128.9, 128.8, 125.5, 124.7, 124.3, 122.4, 115.1, 113.9, 112.3, 104.7, 80.3, 64.3, 63.7, 27.9, 15.2.

IR (ART) *v* 3310, 2976, 2927, 1689, 1621, 1576, 1473, 1461, 1364, 1337, 1259, 1201, 1158, 1201, 1158, 1102, 1045, 1018, 962, 903, 853, 797, 760 cm⁻¹.

HPLC analysis: Chiralpak IA column (*n*-hexane/*i*-PrOH= 85/15; flow rate: 1.0 mL/min; $\lambda = 254$ nm; $t_{minor} = 28.8 \text{ min}, t_{major} = 34.9 \text{ min}$).

HRMS (ESI) m/z: [M + H]⁺ Calcd. for C₃₀H₂₉N₄O₃ 493.2234; found: 493.2239.

Tert-butyl (11-(4-fluoro-1H-indol-3-yl)-11H-indeno[1,2-b]quinoxalin-11-yl)carbamate (3k)



Pale yellow solid; Procedure A: 46.5 mg, 99% yield, 97% *ee*; $[\alpha]_D^{20} = -353.28$ (*c* 2.196, CH₂Cl₂); m.p. 140.1 – 140.8 °C.

¹**H NMR (400 MHz, CDCl**₃) δ 8.67 – 8.50 (m, 1H), 8.32 (s, 1H), 8.17 (d, J = 5.7 Hz, 1H), 8.10 – 7.90 (m, 2H), 7.72 (d, J = 7.4 Hz, 1H), 7.66 – 7.42 (m, 4H), 6.94 (td, J = 9.3, 2.3 Hz, 1H), 6.80 (dd, J = 9.4, 2.1 Hz, 1H), 6.43 (d, J = 2.6 Hz, 1H), 6.00 (brs, 1H), 0.95 (brs, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 162.9, 160.2 (d, J = 240.1 Hz, 1C), 154.3, 153.3, 149.8, 142.3, 141.3, 137.2 (d, J = 12.3 Hz, 1C), 136.9, 131.8, 129.7, 129.5, 129.4, 128.9, 124.6, 124.0 (d, J = 3.1 Hz, 1C), 123.1 (d, J = 8.7 Hz, 1C), 122.4, 121.7, 115.7, 108.8 (d, J = 24.1 Hz, 1C), 97.8 (d, J = 26.0 Hz, 1C), 80.5, 63.6, 27.9.

¹⁹F NMR (377 MHz, CDCl₃) δ -119.91.

IR (ART) *v* 3300, 2974, 2921, 1689, 1625, 1481, 1454, 1364, 1333, 1259, 1242, 1156, 1100, 1047, 1016, 954, 905, 802, 754, 736 cm⁻¹.

HPLC analysis: Chiralpak IG column (*n*-hexane/EtOH= 85/15; flow rate: 1.0 mL/min; $\lambda = 254$ nm; $t_{minor} = 7.5$ min, $t_{major} = 11.0$ min).

HRMS (ESI) m/z: [M + Na]⁺ Calcd. for C₂₈H₂₃FN₄O₂Na 489.1697; found: 489.1704.

Tert-butyl (11-(6-chloro-1H-indol-3-yl)-11H-indeno[1,2-b]quinoxalin-11-yl)carbamate (31)



Pale yellow solid; Procedure A: 48.6mg, 99% yield, 95% *ee*; $[\alpha]_D^{20} = -340.62$ (*c* 1.944, CH₂Cl₂); m.p. 161.6 - 162.1 °C.

¹**H NMR (400 MHz, CDCl**₃) δ 8.69 (s, 1H), 8.30 (d, J = 7.1 Hz, 1H), 8.15 (s, 1H), 8.02 (s, 2H), 7.71 (d, J = 7.2 Hz, 1H), 7.66 – 7.42 (m, 4H), 7.13 (dd, J = 8.6, 1.8 Hz, 1H), 7.07 (s, 1H), 6.42 (d, J = 2.4 Hz, 1H), 6.01 (s, 1H), 1.00 (brs, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 162.8, 154.3, 153.3, 149.7, 142.3, 141.3, 137.5, 136.9, 131.8, 129.6,

129.5, 129.4, 128.9, 128.8, 128.6, 124.6, 124.3, 123.6, 123.0, 122.4, 120.7, 115.7, 111.5, 80.6, 63.5, 27.9. **IR (ART)** *v* 3284, 2970, 2925, 1687, 1617, 1477, 1454, 1364, 1329, 1259, 1158, 1102, 1047, 1018, 905, 800, 756 cm⁻¹.

HPLC analysis: Chiralpak IG column (*n*-hexane/EtOH= 85/15; flow rate: 1.0 mL/min; $\lambda = 254$ nm; $t_{minor} = 12.6$ min, $t_{major} = 15.1$ min).

HRMS (ESI) m/z: $[M + H]^+$ Calcd. for C₂₈H₂₄ClN₄O₂ 483.1582, 485.1566; found: 483.1592, 485.1574.

Tert-butyl (11-(6-(trifluoromethyl)-1*H*-indol-3-yl)-11*H*-indeno[1,2-*b*]quinoxalin-11-yl)carbamate (3m)



Pale yellow solid; Procedure A: 44.9 mg, 87% yield, 85% *ee*; Procedure B: 47.9 mg, 93% yield, 94% *ee*; $[\alpha]_D^{20} = -342.28$ (*c* 1.916, CH₂Cl₂, 94% *ee*); m.p. 162.8 - 163.3 °C.

¹**H NMR (400 MHz, CDCl₃)** δ 8.90 (s, 1H), 8.49 (d, J = 7.1 Hz, 1H), 8.15 (s, 1H), 7.98 (d, J = 27.8 Hz, 2H), 7.77 – 7.68 (m, 1H), 7.64 – 7.46 (m, 4H), 7.40 (d, J = 6.9 Hz, 2H), 6.58 (s, 1H), 6.06 (s, 1H), 1.02 (brs, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 162.7, 154.4, 153.2, 149.5, 142.3, 141.3, 136.9, 136.1, 131.9, 129.6, 129.5, 129.0, 128.9, 127.4, 126.2, 125.1 (q, *J* = 272.8 Hz, 1C), 124.6, 124.5, 122.6, 122.5, 116.6 (q, *J* = 3.2 Hz, 1C), 115.9, 109.2 (q, *J* = 4.1 Hz, 1C), 80.7, 63.5, 27.9.

¹⁹**F** NMR (**377** MHz, CDCl₃) δ -60.87.

IR (ART) *v* 3289, 2966, 2925, 1687, 1510, 1457, 1362, 1331, 1277, 1257, 1222, 1160, 1108, 1049, 1014, 917, 874, 818, 752 cm⁻¹.

HPLC analysis: Chiralpak IA column (*n*-hexane/EtOH= 85/15; flow rate: 1.0 mL/min; $\lambda = 254$ nm; t_{major} = 7.1 min, t_{minor} = 8.3 min).

HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{29}H_{23}F_3N_4O_2Na$ 539.1665; found: 539.1673.

Tert-butyl (11-(6-(methyl)-1*H*-indol-3-yl)-11*H*-indeno[1,2-*b*]quinoxalin-11-yl)carbamate (3n)



Pale yellow solid; Procedure A: 45.8 mg, 99% yield, 82% *ee*; Procedure B: 45.2 mg, 98% yield, 90% *ee*; $[\alpha]_D^{20} = -367.62$ (*c* 1.848, CH₂Cl₂, 90% *ee*); m.p. 144.0 – 144.7 °C.

¹**H NMR (400 MHz, CDCl**₃) δ 8.51 – 8.35 (m, 1H), 8.30 – 8.13 (m, 2H), 8.05 (d, *J* = 7.6 Hz, 2H), 7.81 – 7.69 (m, 1H), 7.67 – 7.48 (m, 4H), 7.01 (d, *J* = 8.2 Hz, 1H), 6.97 (s, 1H), 6.45 – 6.37 (m, 1H), 6.03 (s, 1H), 2.40 (s, 3H), 0.92 (brs, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 163.2, 154.2, 153.6, 150.2, 142.3, 141.4, 137.6, 136.8, 132.6, 131.7, 129.7, 129.3, 129.2, 128.9, 128.7, 124.6, 122.9, 122.8, 122.3, 121.8, 121.5, 115.5, 111.5, 80.3, 63.8, 27.9, 21.7.

IR (ART) v 3314, 2974, 2919, 1689, 1506, 1477, 1450, 1364, 1333, 1257, 1158, 1102, 1018, 935, 907,

851, 800, 756 cm⁻¹.

HPLC analysis: Chiralpak IA column (*n*-hexane/*i*-PrOH= 85/15; flow rate: 1.0 mL/min; $\lambda = 254$ nm; t_{minor} = 15.5 min, t_{major} = 17.0 min).

HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{29}H_{27}N_4O_2$ 463.2129; found: 463.2132.

Tert-butyl (11-(7-fluoro-1*H*-indol-3-yl)-11*H*-indeno[1,2-*b*]quinoxalin-11-yl)carbamate (30)



Pale yellow solid; Procedure A: 45.7 mg, 98% yield, 90% *ee*; $[\alpha]_D^{20} = -297.04$ (*c* 2.004, CH₂Cl₂); m.p. 233.1 - 233.9 °C.

¹**H NMR (400 MHz, CDCl**₃) δ 8.81 (s, 1H), 8.28 – 8.16 (m, 1H), 8.14 – 7.96 (m, 3H), 7.81 – 7.71 (m, 1H), 7.68 – 7.47 (m, 4H), 7.07 (td, *J* = 8.0, 4.9 Hz, 1H), 6.86 (dd, *J* = 11.0, 7.9 Hz, 1H), 6.56 (d, *J* = 2.6 Hz, 1H), 6.04 (brs, 1H), 0.97 (brs, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 162.9, 154.2, 153.4, 149.9, 149.6 (d, J = 245.4 Hz, 1C), 142.4, 141.4, 136.9, 131.8, 129.7, 129.5, 129.4, 129.0, 128.9, 128.6 (d, J = 4.9 Hz, 1C), 125.7 (d, J = 13.7 Hz, 1C), 124.7, 124.2, 122.4, 120.3 (d, J = 6.1 Hz, 1C), 117.8, 116.7, 107.5 (d, J = 15.6 Hz, 1C), 80.5, 63.5, 27.9. ¹⁹F NMR (377 MHz, CDCl₃) δ -134.87.

IR (ART) *v* 3304, 2970, 2921, 2851, 1694, 1640, 1578, 1484, 1366, 1331, 1276, 1236, 1159, 1101, 1084, 1046, 1017, 976, 898, 863, 785, 766, 752 cm⁻¹.

HPLC analysis: Chiralpak IA column (*n*-hexane/*i*-PrOH= 85/15; flow rate: 1.0 mL/min; $\lambda = 254$ nm; $t_{major} = 11.5$ min, $t_{major} = 13.6$ min).

HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{28}H_{24}FN_4O_2$ 467.1878; found: 467.1883.

Tert-butyl (11-(7-chloro-1H-indol-3-yl)-11H-indeno[1,2-b]quinoxalin-11-yl)carbamate (3p)



Pale yellow solid; Procedure A: 48.1 mg, 99% yield, 73% *ee*; Procedure B: 17.2 mg, 36% yield, 75% *ee*; $[\alpha]_D^{20} = -283.77$ (*c* 0.684, CH₂Cl₂, 75% *ee*); m.p. 222.7 - 223.3 °C.

¹H NMR (400 MHz, DMSO-*d*₆) δ 11.45 (s, 1H), 8.51 – 8.05 (m, 3H), 7.97 (d, J = 7.6 Hz, 1H), 7.82 – 7.61 (m, 5H), 7.54 (s, 1H), 7.12 (d, J = 7.5 Hz, 1H), 7.03 (s, 1H), 6.93 (t, J = 7.7 Hz, 1H), 1.06 (brs, 9H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 163.7, 154.1, 153.4, 150.7, 141.5, 140.6, 136.3, 133.7, 132.3, 129.5, 129.4, 129.2, 129.1, 128.8, 127.0, 125.3, 124.6, 121.7, 120.9, 120.2, 119.8, 116.0, 115.4, 78.5, 63.1, 27.7. IR (ART) *v* 3300, 2974, 2960, 2919, 2853, 1697, 1619, 1561, 1481, 1435, 1365, 1337, 1275, 1258, 1238, 1206, 1157, 1098, 1074, 1048, 1017, 889, 855, 834, 783, 763, 752, 731 cm⁻¹.

HPLC analysis: Chiralpak IA column (*n*-hexane/*i*-PrOH= 85/15; flow rate: 1.0 mL/min; $\lambda = 254$ nm; $t_{minor} = 13.1 \text{ min}, t_{major} = 20.9 \text{ min}$).

HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{28}H_{24}CIN_4O_2$ 483.1582, 485.1566; found: 483.1592, 485.1569.



Pale yellow solid; Procedure A: 31.4 mg, 60% yield, 67% *ee*; Procedure B: 32.9 mg, 62% yield, 66% *ee*; $[\alpha]_D^{20} = -139.57$ (*c* 1.047, CH₂Cl₂, 70% *ee*); m.p. 223.9 - 224.7 °C.

¹**H NMR (400 MHz, DMSO-***d*₆) δ 11.31 (d, J = 2.4 Hz, 1H), 8.64 – 7.83 (m, 4H), 7.82 – 7.38 (m, 6H), 7.26 (d, J = 7.5 Hz, 1H), 6.99 (s, 1H), 6.88 (t, J = 7.8 Hz, 1H), 1.10 (brs, 9H).

¹³C NMR (101 MHz, DMSO-*d₆*) δ 163.7, 154.2, 153.4, 150.7, 141.6, 140.7, 136.3, 135.2, 132.4, 129.6, 129.5, 129.3, 129.1, 128.8, 126.8, 125.3, 124.7, 124.1, 121.8, 120.7, 120.3, 115.5, 104.3, 78.6, 63.2, 27.8.
IR (ART) *v* 3393, 3208, 3117, 2960, 2919, 2848, 1695, 1615, 1559, 1433, 1378, 1363, 1335, 1258, 1204, 1160, 1093, 1071, 1044, 1016, 879, 856, 798, 781, 757, 747, 731 cm⁻¹.

HPLC analysis: Chiralpak IA column (*n*-hexane/EtOH= 85/15; flow rate: 1.0 mL/min; λ = 254 nm; t_{major} = 10.8 min, t_{minor} = 12.3 min).

HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{28}H_{24}BrN_4O_2$ 527.1077, 529.1061; found: 527.1082, 529.1064.

Tert-butyl (11-(7-methyl-1*H*-indol-3-yl)-11*H*-indeno[1,2-*b*]quinoxalin-11-yl)carbamate (3r)



Pale yellow solid; Procedure A: 45.7 mg, 99% yield, 73% *ee*; Procedure B: 38.8 mg, 84% yield, 71% *ee*; $[\alpha]_D^{20} = -155.18$ (*c* 0.940, CH₂Cl₂, 73% *ee*); m.p. 217.3 – 217.7 °C.

¹**H NMR (400 MHz, DMSO-***d*₆) δ 11.07 (d, J = 2.3 Hz, 1H), 8.33 – 8.00 (m, 3H), 7.95 (d, J = 7.9 Hz, 1H), 7.79 – 7.58 (m, 5H), 7.30 – 7.02 (m, 2H), 6.80 (d, J = 7.0 Hz, 1H), 6.74 (t, J = 7.5 Hz, 1H), 2.36 (s, 3H), 1.07 (brs, 9H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 164.1, 154.2, 153.7, 151.2, 141.5, 140.7, 136.4, 136.3, 132.2, 129.5, 129.3, 129.1, 129.0, 128.8, 124.7, 124.6, 123.8, 121.8, 121.6, 120.8, 119.0, 118.2, 114.3, 78.5, 63.4, 27.7, 16.7.

IR (ART) *v* 3306, 2964, 2919, 2851, 1696, 1617, 1454, 1364, 1337, 1257, 1160, 1104, 1083, 1046, 1006, 937, 897, 812, 762, 750, 739 cm⁻¹.

HPLC analysis: Chiralpak IA column (*n*-hexane/*i*-PrOH= 85/15; flow rate: 1.0 mL/min; $\lambda = 254$ nm; $t_{major} = 11.4$ min, $t_{minor} = 16.9$ min).

HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{29}H_{27}N_4O_2$ 463.2129; found: 463.2136.

Tert-butyl (11-(7-methoxyl-1H-indol-3-yl)-11H-indeno[1,2-b]quinoxalin-11-yl)carbamate (3s)



Pale yellow solid; Procedure A: 44.4 mg, 93% yield, 80% *ee*; Procedure B: 32.3 mg, 88% yield, 80% *ee*; $[\alpha]_D^{20} = -173.78$ (*c* 1.776, CH₂Cl₂, 80% *ee*); m.p. 220.8 - 221.3 °C.

¹**H NMR (400 MHz, DMSO-***d*₆) δ 11.18 (s, 1H), 8.28 – 7.89 (m, 4H), 7.69 (q, *J* = 30.1, 15.3, 6.4 Hz, 5H), 6.97 (s, 2H), 6.77 (t, *J* = 7.7 Hz, 1H), 6.57 (d, *J* = 7.6 Hz, 1H), 3.82 (s, 3H), 1.05 (brs, 9H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 164.0, 154.1, 153.6, 151.2, 146.1, 141.5, 140.7, 136.2, 132.1, 129.4, 129.2, 129.0, 128.7, 127.1, 126.3, 124.6, 123.6, 121.6, 119.2, 114.4, 113.4, 101.8, 78.4, 63.3, 55.2, 27.7. **IR** (ART) *v* 3397, 3215, 3119, 2927, 1697, 1632, 1580, 1497, 1445, 1416, 1378, 1364, 1330, 1257, 1164, 1155, 1101, 1089, 1053, 1015, 992, 784, 760, 747, 731 cm⁻¹.

HPLC analysis: Chiralpak IG column (*n*-hexane/EtOH= 85/15; flow rate: 1.0 mL/min; $\lambda = 254$ nm; $t_{minor} = 19.4$ min, $t_{major} = 25.9$ min).

HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{29}H_{27}N_4O_3$ 479.2078; found: 479.2085.

Tert-butyl (11-(5,6-difluoro-1*H*-indol-3-yl)-11*H*-indeno[1,2-*b*]quinoxalin-11-yl)carbamate (3t)



Pale yellow solid; Procedure A: 47.9 mg, 99% yield, 86% *ee*; Procedure B: 46.7 mg, 96% yield, 91% *ee*; $[\alpha]_D^{20} = -393.44$ (*c* 1.924, CH₂Cl₂, 91% *ee*); m.p. 170.6 – 171.3 °C.

¹**H NMR (400 MHz, CDCl**₃) δ 8.75 – 8.64 (m, 1H), 8.37 – 8.22 (m, 1H), 8.21 – 7.80 (m, 3H), 7.78 – 7.68 (m, 1H), 7.67 – 7.42 (m, 4H), 6.83 (dd, *J* = 10.3, 6.8 Hz, 1H), 6.43 (s, 1H), 5.93 (brs, 1H), 0.90 (brs, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 162.6, 154.3, 153.1, 148.3 (dd, J = 243.5, 16.2 Hz, 1C), 146.4 (dd, J = 238.9, 14.6 Hz, 1C), 142.3, 141.2, 136.9, 132.3 (d, J = 10.3 Hz, 1C), 131.8, 129.6, 129.4, 129.0, 128.9, 125.1 (d, J = 3.1 Hz, 1C), 124.6, 122.5, 120.4 (d, J = 8.3 Hz, 1C), 115.6 (d, J = 3.8 Hz, 1C), 109.1 (d, J = 21.6 Hz, 1C), 99.3 (d, J = 21.7 Hz, 1C), 80.7, 63.4, 28.0.

¹⁹F NMR (377 MHz, CDCl₃) δ -142.34, -146.09.

IR (ART) v 3421, 3289, 2966, 2927, 1687, 1592, 1540, 1475, 1364, 1335, 1284, 1259, 1156, 1101, 1038, 1016, 937, 907, 844, 797, 757 cm⁻¹.

HPLC analysis: Chiralpak IG column (*n*-hexane/EtOH= 85/15; flow rate: 1.0 mL/min; $\lambda = 254$ nm; $t_{minor} = 5.4$ min, $t_{major} = 8.6$ min).

HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{28}H_{23}F_2N_4O_2$ 485.1784; found: 485.1792.

Tert-butyl (11-(1*H*-indol-3-yl)-7,8-dimethyl-11*H*-indeno[1,2-*b*]quinoxalin-11-yl)carbamate (3u)



Pale yellow solid; Procedure A: 42.9 mg, 90% yield, 99% *ee*; $[\alpha]_D^{20} = -320.98$ (*c* 1.716, CH₂Cl₂); m.p. 149.7 – 150.2 °C.

¹**H NMR (400 MHz, CDCl**₃) δ 8.60 (s, 1H), 8.27 (s, 1H), 8.20 – 8.08 (m, 1H), 7.79 (s, 2H), 7.74 – 7.67 (m, 1H), 7.50 (s, 2H), 7.24 – 7.07 (m, 3H), 6.46 (d, *J* = 2.4 Hz, 1H), 6.01 (brs, 1H), 2.41 (s, 3H), 2.39 (s, 3H), 0.87 (brs, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 162.3, 154.3, 152.5, 149.9, 140.9, 140.2, 139.6, 139.1, 137.1, 137.0, 131.3, 129.2, 129.0, 128.1, 125.0, 124.6, 123.4, 122.6, 122.1, 121.9, 119.9, 115.7, 111.7, 80.2, 63.7, 27.9, 20.3, 20.2.

IR (ART) *v* 3403, 3306, 2972, 2923, 2853, 1689, 1496, 1483, 1454, 1364, 1335, 1259, 1158, 1111, 1051, 1014, 907, 874, 789, 762, 735, 700 cm⁻¹.

HPLC analysis: Chiralpak IG column (*n*-hexane/EtOH= 85/15; flow rate: 1.0 mL/min; $\lambda = 254$ nm; $t_{minor} = 10.5$ min, $t_{major} = 12.8$ min).

HRMS (ESI) m/z: [M + Na]⁺ Calcd. for C₃₀H₂₈N₄O₂Na 499.2104; found: 499.2115.

Tert-butyl (7,8-difluoro-11-(1*H*-indol-3-yl)-11*H*-indeno[1,2-*b*]quinoxalin-11-yl)carbamate (3v)



Yellow solid; Procedure A: 46.2 mg, 95% yield, 98% *ee*; $[\alpha]_D^{20} = -356.19$ (*c* 1.848, CH₂Cl₂); m.p. 138.0 - 138.5 °C.

¹**H NMR (400 MHz, CDCl₃)** δ 8.49 – 8.27 (m, 2H), 8.15 (s, 1H), 7.90 – 7.43 (m, 5H), 7.25 – 7.10 (m, 3H), 6.53 – 6.40 (m, 1H), 6.06 (brs, 1H), 1.05 (brs, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 163.5, 154.1, 153.7, 151.6 (dd, J = 252.3, 14.2 Hz, 1C), 151.2 (dd, J = 254.1, 14.7 Hz, 1C), 139.4 (d, J = 10.7 Hz, 1C), 138.3 (d, J = 10.2 Hz, 1C), 137.1, 136.5, 132.1, 129.5, 124.8 (d, J = 35.9 Hz, 1C), 123.7, 122.9, 122.3 (d, J = 42.4 Hz, 1C), 120.1, 115.7 (d, J = 17.2 Hz, 1C), 115.2, 114.8 (d, J = 17.6 Hz, 1C), 111.7, 80.5, 63.7, 27.9.

¹⁹F NMR (**377** MHz, CDCl₃) δ -132.21, -132.78.

IR (ART) *v* 3403, 3312, 3053, 2968, 2925, 2855, 1691, 1582, 1520, 1478, 1432, 1366, 1332, 1250, 1236, 1193, 1158, 1102, 1048, 1015, 929, 906, 874, 852, 792, 762, 739 cm⁻¹.

HPLC analysis: Chiralpak IG column (*n*-hexane/*i*-PrOH= 70/30; flow rate: 1.0 mL/min; $\lambda = 254$ nm; $t_{minor} = 3.6$ min, $t_{major} = 4.9$ min).

HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{28}H_{23}F_2N_4O_2$ 485.1784; found: 485.1790.

Tert-butyl (7,8-dichloro-11-(1H-indol-3-yl)-11H-indeno[1,2-b]quinoxalin-11-yl)carbamate (3w)



Pale yellow solid; Procedure A: 42.8 mg, 83% yield, 98% *ee*; $[\alpha]_D^{20} = -364.90$ (*c* 1.712, CH₂Cl₂); m.p. 169.2 - 170.0 °C.

¹**H NMR (400 MHz, CDCl₃)** δ 8.42 (d, *J* = 7.4 Hz, 1H), 8.28 (s, 1H), 8.15 (s, 3H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.70 – 7.45 (m, 2H), 7.27 – 7.10 (m, 3H), 6.43 (s, 1H), 6.07 (brs, 1H), 1.05 (brs, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 164.2, 154.3, 154.1, 150.1, 141.2, 140.1, 137.1, 136.4, 133.4, 132.8, 132.3, 130.4, 129.6, 129.5, 124.9, 124.6, 123.8, 123.0, 122.7, 122.1, 120.2, 115.2, 111.6, 80.6, 63.7, 28.0. IR (ART) *v* 3407, 3306, 2974, 2929, 2855, 1693, 1613, 1481, 1470, 1459, 1410, 1392, 1364, 1331, 1253, 1160, 1122, 1047, 1015, 976, 902, 878, 814, 765, 739 cm⁻¹.

HPLC analysis: Chiralpak IC column (*n*-hexane/EtOH= 85/15; flow rate: 1.0 mL/min; λ = 254 nm; t_{minor} = 4.5 min, t_{major} = 6.3 min).

HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for C₂₈H₂₂Cl₂N₄O₂Na 539.1012, 541.0989; found: 539.1021. 541.1001.

Tert-butyl (7,8-dibromo-11-(1H-indol-3-yl)-11H-indeno[1,2-b]quinoxalin-11-yl)carbamate (3x)



Yellow solid; Procedure A: 59.1 mg, 97% yield, 98% *ee*; $[\alpha]_D^{20} = -272.46$ (*c* 2.364, CH₂Cl₂); m.p. 147.3 - 147.9 °C.

¹**H NMR (400 MHz, CDCl₃)** δ 8.72 – 7.89 (m, 5H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.69 – 7.44 (m, 2H), 7.25 – 7.11 (m, 3H), 6.40 (s, 1H), 6.10 (s, 1H), 1.05 (brs, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 154.4, 154.1, 150.1, 141.7, 140.6, 137.1, 136.3, 133.7, 132.9, 132.4, 129.6, 125.3, 124.9, 124.8, 124.6, 123.8, 122.9, 122.7, 122.1, 120.2, 115.0, 111.6, 80.6, 63.7, 28.0.

IR (ART) *v* 3409, 3314, 3057, 2972, 2923, 1689, 1609, 1481, 1467, 1457, 1402, 1389, 1364, 1333, 1257, 1159, 1115, 1100, 1090, 1048, 1016, 950, 901, 879, 854, 812, 803, 764, 739 cm⁻¹.

HPLC analysis: Chiralpak IC column (*n*-hexane/EtOH= 90/10; flow rate: 1.0 mL/min; $\lambda = 254$ nm; t_{minor} = 6.4 min, t_{major} = 9.1 min).

HRMS (ESI) m/z: [M + H]⁺ Calcd. for C₂₈H₂₃Br₂N₄O₂ 605.0182, 607.0164, 609.0149; found: 605.0195. 607.0171, 609.0163.

4. Scale-up experiment of 3a.



Indeno[1,2-b]quinoxalin-11-imine 1a (0.99 g, 3.0 mmol), indole 2a (0.42 g, 3.6 mmol), chiral

phosphoric acid IV (87 mg, 5.0 mol%), and 2-MeTHF (30.0 mL) were successively added to a 50 mL vial. The resulting mixture was stirred at 25 °C for the 6 h. After completion of the reaction (monitored by TLC), the reaction mixture was concentrated. The residue was dissolved with DCM, then directly subjected to flash column chromatography, giving the corresponding product 3a (1.30 g, 96% yield).

5. Transformation of product.



The compound **3a** (44.9 mg, 0.1 mmol) in DMF (2.0 mL) was stirred at 30 °C, then add the K_2CO_3 (0.25 mmol) and CH₃I (0.5 mmol). After being stirred at 30 °C for 72 h, After completion of the reaction (monitored by TLC). The mixture was diluted with 20 mL DCM and washed with water (20 mL × 3). The organic phase was dried over anhydrous Mg₂SO₄ and filtered. The filtrate was collected and concentrated in vacuum to remove the solvent. The residue was purified by silica gel column chromatography (petroleum ether / ethyl acetate) to afford compound **4**.

Tert-butyl (11-(1-methyl-1H-indol-3-yl)-11H-indeno[1,2-b]quinoxalin-11-yl)carbamate (4)



Yellow solid; 23.6 mg, 51% yield, 96% *ee*; $[\alpha]_D^{20} = -241.42$ (*c* 0.948, CH₂Cl₂); m.p. 83.1 – 83.7 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.41 (s, 1H), 8.32 – 8.20 (m, 1H), 8.17 – 8.01 (m, 2H), 7.86 – 7.77 (m, 1H), 7.71 – 7.57 (m, 4H), 7.26 – 7.18 (m, 3H), 6.47 (s, 1H), 6.02 (brs, 1H), 3.59 (s, 3H), 0.89 (brs, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 163.2, 154.1, 153.5, 150.4, 142.4, 141.5, 137.9, 136.9, 131.8, 129.9, 129.4, 129.3, 129.0, 128.8, 127.9, 125.6, 124.7, 122.5, 122.4, 122.3, 119.8, 114.3, 109.7, 80.3, 63.8, 32.9, 27.9.

IR (ART) *v* 2960, 2923, 2853, 1695, 1462, 1362, 1330, 1256, 1157, 1104, 1049, 1014, 936, 899, 853, 803, 761, 738 cm⁻¹.

HPLC analysis: Chiralpak IA column (*n*-hexane/*i*-PrOH= 85/15; flow rate: 1.0 mL/min; $\lambda = 254$ nm; $t_{major} = 9.1$ min, $t_{minor} = 16.8$ min).

HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{29}H_{27}N_4O_2$ 463.2129; found: 463.2132.



The compound **3a** (44.9 mg, 0.1 mmol), Boc_2O (0.4 mmol) in CHCl₃ (1.0 mL), DMAP (0.5 mmol) was added and the mixture stirred for 0.5 h. After completion of the reaction (monitored by TLC), the mixture was purified by silica gel column chromatography (petroleum ether / ethyl acetate) to afford compound **5**.

Tert-butyl 3-(11-((*tert*-butoxycarbonyl)amino)-11*H*-indeno[1,2-*b*]quinoxalin-11-yl)-1*H*-indole-1-carboxylate (5)



White solid; 48.4 mg, 88% yield, 97% *ee*; $[a]_D^{20} = -266.74$ (*c* 1.936, CH₂Cl₂); m.p. 119.1 – 119.7 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.53 – 8.15 (m, 2H), 8.12 (dd, *J* = 8.2, 1.2 Hz, 1H), 8.09 – 7.95 (m, 2H), 7.89 – 7.78 (m, 1H), 7.72 – 7.58 (m, 4H), 7.39 – 7.26 (m, 2H), 7.18 (s, 1H), 6.02 (s, 1H), 1.58 (s, 9H), 1.01 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 162.1, 154.0, 153.4, 149.4, 149.1, 142.5, 141.3, 137.0, 136.1, 132.0, 129.8, 129.7, 129.5, 129.0, 128.9, 127.7, 124.9, 124.6, 122.7, 122.4, 120.4, 115.3, 84.3, 80.5, 63.3, 28.1, 27.9, 27.8.

IR (ART) *v* 2974, 2927, 1722, 1697, 1475, 1451, 1365, 1339, 1307, 1255, 1236, 1149, 1095, 1077, 1015, 940, 851, 760, 745 cm⁻¹.

HPLC analysis: Chiralpak IA column (*n*-hexane/*i*-PrOH= 85/15; flow rate: 1.0 mL/min; $\lambda = 254$ nm; $t_{major} = 5.9$ min, $t_{minor} = 6.8$ min).

HRMS (ESI) m/z: [M + H]⁺ Calcd. for C₃₃H₃₃N₄O₄ 549.2496; found: 549.2504.

6. ¹H NMR spectra for compounds 1.









7. ¹H, ¹³C NMR spectra for compounds 1, 3, and 4.



S20





Detector	VWD1A,Wavelength=254 nm			
Peak	Ret.Time [min]	Area	Height	Area%
	12.641	17821.06	739.72	49.85
	13.977	17931.41	678.04	50.15
		35752.46		100.00

Condition A:



Detector	VWD1A.	Wavelength=254 nm	
	· · · · · · · · · · · · · · · · · · ·	navorongon bor nm	

Peak	Ret.Time [min]	Area	Height	Area%
	12.562	429.12	25.92	0.72
	13.315	59526.20	2252.03	99.28
		59955.32		100.00



S22





Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	10.921	14033.75	600.31	50.14
	15.892	13952.80	440.05	49.86
		27986.55		100.00

Condition A:



Detector	or VWD1A,Wavelength=254 nm			
Peak	Ret,Time [min] Area Height Area%			
	10.726	65891.20	2871.97	93.01
	15.770	4952.50	164.87	6.99
		70843.70		100.00

Condition B:



Detector	VWD1A,Wavelength=254 nm				
Peak	Ret,Time [min]	Area	Area%		
	10.915	23978.27	1049.25	98.57	
	15.683	348.08	11.59	1.43	
		24326.35		100.00	



HPLC spectra of 3c



Detector VWD1A, Wavelength=254 nm

	, 0			
Peak	Ret.Time [min]	Area	Height	Area%
	11.480	25272.94	630.32	49.48
	13.153	25807.99	527.84	50.52
		51080.93		100.00

Condition A:



Detector VWD1A,Wavelength=254 nm Ret.Time [min] Peak Height Area% Area 11.553 9331.92 244.94 28.97 494.42 13.207 22880.41 71.03 32212.33 100.00

Condition C:



Detector	VWD1A,	Wavel	ength=254	nm
			-	

Peak	Ret.Time [min]	Area	Height	Area%
	11.451	1181.13	31.36	10.95
	12.928	9609.27	210.79	89.05
		10790.40		100.00







Detector	YWD1A,Wavelength=254 nm			
Peak	Ret.Time [min]	Area	Height	Area%
	11.411	20253.03	819.78	49.37
	12.492	20770.81	722.21	50.63
		41023.84		100.00

Condition A:



Detector	VWD1A,Waveleng	th=254 nm					
Peak	Ret.Time [min] Area Height Area%						
	11.300	44346.20	1791.11	98.85			
	12.536	513.91	17.51	1.15			
		44860.10		100.00			







VWD1A,Wavelength=254 nm Detector Peak Ret,Time [min] Area Height Area% 1039.49 50.07 5.796 15317.26 617.16 49.93 7.274 15274.63 30591.89 100.00

Condition A:



Detector	VWD1A,Wavelength=254 nm					
Peak	Ret.Time [min] Area Height Area%					
	5.794	1996.30	140.10	5.68		
	7.247	33153.86	1349.75	94.32		
		35150.16		100.00		

Condition B:



Detector	VWD1A,Wavelength=254 nm					
Peak	Ret.Time [min]	Area	Height	Area%		
	5.773	1135.04	85.48	5.52		
	7.227	19413.12	826.17	94.48		
		20548.16		100.00		







Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	5.787	9154.39	601.49	49.88
	6.858	9197.13	432.45	50.12
		18351.52		100.00

Condition A:



Detector VWD1A,Wavelength=254 nm Ret.Time [min] Peak Area Height Area% 137.24 5.783 2075.39 6.16 6.834 31604.08 1502.34 93.84 33679.47 100.00

Condition B:



Detector	VWD1A, Wavelength=254	nm
1		

Peak	Ret.Time [min]	Area	Height	Area%
	5.780	1236.41	97.09	7.40
	6.842	15475.98	791.16	92.60
		16712.39		100.00

¹H NMR (400 MHz, CDCl₃) of **3g**







Detector	VWD1A,Wavelength=254 nm				
Peak	Ret.Time [min]	Area	Height	Area%	
	7.926	13887.80	640.91	50.06	
	12.499	13855.11	226.80	49.94	
		27742.90		100.00	

Condition A:



Detector	VWD1A,Wavelength=254 nm					
Peak	Ret.Time [min]	Area	Height	Area%		
	8.210	1088.28	53.29	6.14		
	12.899	16648.59	281.43	93.86		
		17736.88		100.00		

Condition B:



Detector	VWD1A, Wavelength=254 nm				
Peak	Ret.Time [min]	Area	Height	Area%	
	8.094	599.77	29,29	3.06	
	12.606	18974.88	318.42	96.94	
		19574.64		100.00	

¹H NMR (400 MHz, CDCl₃) of **3h**







Detector	VWD1A,Wavelength=254 nm					
Peak	Ret.Time [min]	Area	Height	Area%		
	6.733	9858.10	545.02	50.21		
	8.797	9774.16	345.72	49.79		
		19632.26		100.00		

Condition A:



Detector	VWD1A,Wavelength=254	nn

Peak	Ret.Time [min]	Area	Height	Area%
	6.727	1064.36	66.62	2.54
	8.729	40811.99	1480.52	97.46
		41876.35		100.00






Detector	VWD1A, Wavelength=254 nm			
Peak	Ret.Time [min]	Area	Height	Area%
	13.579	8669.20	267.23	50.19
	16.127	8601.84	205.89	49.81
		17271.04		100.00



Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	13.303	988.88	35.09	3.53
	15.620	27015.24	685.76	96.47
		28004.11		100.00









Detector	VWD1A,Wavelength=254 nm				
Peak	Ret.Time [min]	Area	Height	Area%	
	12.459	6443.80	228.75	49.93	
	14.039	6462.83	190.33	50.07	
		12906.63		100.00	



Detector VWD1A, Wavelength=254 r

Peak	Ret.Time [min]	Area	Height	Area%
	12.455	1419.41	56.51	3.88
	13.918	35158.03	1019.75	96.12
		36577.44		100.00







Detector	VWD1A,Wavelength=254 nm			
Peak	Ret,Time [min]	Area	Height	Area%
	7.508	6600.05	213.82	50.05
	11.061	6588.02	129.28	49.95
		13188.07		100.00



Detector	VWD1A,	Wavelength=254	nm	
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Peak	Ret,Time [min]	Area	Height	Area%
	7.504	229.79	8.33	1.48
	11.024	15299.99	299.68	98.52
		15529.78		100.00







Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	12.520	13485.08	237.02	49.80
	15.076	13592.14	233.09	50.20
		27077.22		100.00



Detector	VWD1A,Wavelength=254	nm

Peak	Ret.Time [min]	Area	Height	Area%
	12.590	776.10	14.77	2.57
	15.062	29428.94	508.49	97.43
		30205.04		100.00







Detector VWD1A,Wavelength=254 nm Peak Ret.Time [min] Area Height Area% 7.120 36980.04 2325.26 49.81 8.272 37262.54 2046.78 50.19 74242.58 100.00



Detector	VWD1A, Wavelength=254 nm					
Peak	Ret,Time [min] Area Height Area%					
	7.104	22177.33	1437.47	92.43		
	8.284	1816.92	108.88	7.57		
		23994.25		100.00		

Condition B:



Detector	VWD1A,Waveleng	th=254 nm	
Peak	Ret.Time [min]	Area	Height
	7.131	17337.52	1227.09

7.131	17337.52	1227.09	96.91
8.307	553.56	37.13	3.09
	17891.08		100.00

Area%







Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	15.411	14814.95	502.56	50.00
	17.016	14812.66	449.65	50.00
		29627.60		100.00



Detector	VWD1A,Wavelength=254 nm				
Peak	Ret.Time [min]	Area	Height	Area%	
	15.471	3244.68	121.46	8.85	
	16.998	33439.08	1019.75	91.15	
		36683.76		100.00	

Condition B:



Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	15.048	817.46	31.14	5.02
	16.737	15454.90	479.70	94.98
		16272.36		100.00









Peak	Ret,Time [min]	Area	Height	Area%
	11.513	24060.20	1098.65	50.70
	13.614	23392.44	926.57	49.30
		47452.64		100.00



Detector VWD1A, Wavelength=254 nm	m
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Peak	Ret.Time [min]	Area	Height	Area%
	11.525	59671.52	2666.93	94.89
	13.590	3212.53	140.95	5.11
		62884.05		100.00







VWD1A,Wavelength=254 nm Detector Peak Ret.Time [min] Area Height Area% 13.002 15866.96 651.52 50.09 21.155 15810.59 369.99 49.91

31677.56

100.00

Condition A:



VWD1A,Wavelength=254 nm Detector Ret.Time [min] Area Height Peak

^v eak	Ret.Time [min]	Area	Height	Area%
	13.062	29644.39	1121.32	86.55
	20.858	4607.66	130.21	13.45
		34252.04		100.00



Detector VWDIA, Wavelength=254 nm	Detector	VWD1A,Wavelength=254	nm
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Peak	Ret.Time [min]	Area	Height	Area%
	13.007	8317.82	354.28	87.59
	20.102	1177.99	34.84	12.41
		9495.81		100.00







Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	10.786	5386.68	176.03	50.03
	12.219	5379.78	218.48	49.97
		10766.47		100.00



Detector VWD1A,Wavelength=254 nm Ret.Time [min] Height Area% Peak Area 10.824 8649.91 286.36 83.73 12.281 1681.16 69.59 16.27 10331.07 100.00

Condition B:



Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	10.601	7125.97	238.84	82.80
	11.947	1479.93	66.62	17.20
		8605.90		100.00







Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	11.360	12957.90	561.88	50.01
	16.793	12952.08	399.48	49.99
		25909.97		100.00





40607.83

100.00

Condition B:



Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	11.361	9872.45	445.25	85.42
	16.356	1685.70	59.36	14.58
		11558.15		100.00







Detector VWD1A, Wavelength=254 nm

Peak	Ret,Time [min]	Area	Height	Area%
	19.437	11387.95	171.99	59.21
	26.146	7845.32	108.83	40.79
		19233.27		100.00



Detector VWD1A,Wavelength=254 nm Area% Peak Ret,Time [min] Area Height 19.407 3312.09 48.12 9.95 25.960 29988.53 408.25 90.05 33300.62 100.00



D1A,Wavelength=254 nm	Detector

Peak	Ret.Time [min]	Area	Height	Area%
	19.027	1229.88	19.53	10.22
	25.592	10804.69	150.38	89.78
		12034.57		100.00



S58





VWD1A,Wavelength=254 nm Detector Peak Ret.Time [min] Area Height Area% 5.453 19964.35 1016.47 50.01 8.579 19953.31 451.53 49.99 39917.66 100.00

Condition A:



Detector	VWD1A,Wavelength=254 nm				
Peak	Ret.Time [min]	Area	Height	Area%	
	5.426	2656.10	2656.10 136.59	7.22	
	8.585	34113.20	760.47	92.78	
		36769.31		100.00	



Detector	VWD1A,Wavelength=254 nm			
Peak	Ret.Time [min]	Area	Height	Area%
	5.418	761.21	54.78	4.63
	8.550	15676.93	353.67	95.37
		16438.14		100.00







Detector	VWD1A,Wavelength=254 nm			
Peak	Ret.Time [min]	Area	Height	Area%
	10.574	7669.78	161.33	49.78
	12.938	7739.06	133.61	50.22
		15408.84		100.00



Detector	VWD1A,Wavelength=254	nm
Decestor	input g autorougou Bor	

Peak	Ret.Time [min]	Area	Height	Area%
	10.517	115.37	2.77	0.69
	12.812	16570.02	296.38	99.31
		16685.39		100.00









Detector	VWD1A,Wavelength=254 nm				
Peak	Ret.Time [min]	Area	Height	Area%	
	3.625	14412.00	2151.55	49.68	
	4.934	14598.40	1332.03	50.32	
		29010.40		100.00	



Detector	VWD1A, Wavelength=254	nm
	, , , , , , , , , , , , , , , , , , , ,	

Peak	Ret.Time [min]	Area	Height	Агеа%
	3.624	396.01	70.03	1.09
	4.930	35960.59	3242.37	98.91
		36356.60		100.00

¹H NMR (400 MHz, CDCl₃) of 3w







Detector	VWD1A,Waveleng	th=254 nm		
Peak	Ret.Time [min]	Area	Height	Area%
	4.583	15381.99	1871.17	49.61
	6.337	15622.74	1298.87	50.39

31004.74

100.00





Detector	VWD1A,Wavelength=254	nm
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Peak	Ret.Time [min]	Area	Height	Area%
	4.562	176.41	24.78	1.10
	6.291	15923.83	1352.35	98.90
		16100.24		100.00







Detector	VWD1A,Wavelength=254 nm				
Peak	Ret.Time [min]	Area	Height	Area%	
	6.446	5716.47	473.32	50.04	
	9.193	5707.59	317.92	49.96	
		11424.06		100.00	



Detector VWD1A, Wavelength=254 nm	Detector	VWD1A,Wavelength=254	nm
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Peak	Ret.Time [min]	Area	Height	Area%
	6.427	203.91	20.02	1.03
	9.169	19658.03	1106.41	98.97
		19861.93		100.00







Detector	VWD1A,Waveleng	th=254 nm		
Peak	Ret.Time [min]	Area	Height	Area%
	9.176	3465.15	189.27	50.13
	16.883	3447.39	108.38	49.87
		6912.55		100.00



Detterter		en Bor mi		
Peak	Ret.Time [min]	Area	Height	Area%
	9.132	3170.50	170.56	98.00
	16.808	64.81	2.37	2.00
		3235.31		100.00

Detector VWD1A, Wavelength=254 nm



S70





Detector	VWD1A,Waveleng	th=254 nm		
Peak	Ret.Time [min]	Area	Height	Area%
	6.118	9169.47	776.92	50.05
	7.192	9152.13	595.42	49.95
		18321.61		100.00



Detector	VWD1A,Wavelength=254 nm	

Peak	Ret.Time [min]	Area	Height	Area%
	5.932	26516.67	2320.46	98.45
	6.779	418.49	38.71	1.55
		26935.17		100.00
8. ¹⁹F NMR spectra for compounds 3b, 3k, 3m, 3o, 3t, and 3v



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





¹⁹F spectrum of **3t**

— -142.335 — -146.093



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



--132.214







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

9. IR spectra for compounds 3



IR spectrum of 3b







IR spectrum of 3d



IR spectrum of 3e



IR spectrum of 3f







IR spectrum of 3h







IR spectrum of 3j







IR spectrum of 31



IR spectrum of 3m



IR spectrum of 3n



IR spectrum of 30



IR spectrum of 3p







IR spectrum of 3r







IR spectrum of 3t



IR spectrum of 3u



IR spectrum of 3v







IR spectrum of 3x







IR spectrum of 5

