Triazole–Pyridine Ligands: A Novel Approach to Chromophoric Iridium Arrays

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Supporting Information

Experimental Section

PRECAUTION: NaN_3 is extremely toxic and may explode if heated.

Materials. All chemicals and solvents were purchased from commercial sources and used without further purification unless stated otherwise. Solvents were distilled prior to use: THF, toluene (Na); CH_2Cl_2, Et_3N and MeOH (CaH_2). All cross-coupling and "click" reactions were performed under an argon atmosphere using Schlenk techniques and deoxygenated solvents (freeze–pump–thaw in 3 cycles, <0.4 mbar). Silica gel (0.035–0.070 mm) from Acros or silica gel (0.063–0.200 mm) from J. T. Baker were used for column chromatography and silica 60 F254 coated glass plates (Merck) were used for thin layer chromatography (TLC). Spacer molecule **16**[S1] and *meso*-Δ,Λ-$(C^{\wedge}N)_2Ir(\mu\text{-}Cl)_2Ir(C^{\wedge}N)_2$ ($C^{\wedge}N$ = 2-phenylpyridine or 2-(1*H*-pyrazol-1-yl)pyridine)[S2] are known from the literature and were prepared following the described procedures.

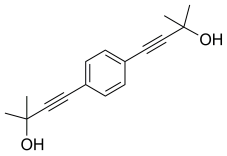
Instrumentation. FT-infrared spectra were recorded on a ThermoMattson IR300 spectrometer equipped with a Harrick ATR unit. UV–vis spectra were recorded on a Varian Cary 50 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded at 25 °C on a Bruker DPX-200 instrument operating at 200 and 50 MHz, respectively, on a Bruker DMX-300 instrument operating at 300 and 75 MHz, respectively, or on a Varian Inova 400 instrument operating at 400 MHz (^1H NMR). Chemical shifts (δ) are reported in parts per million (ppm) relative to the residual peak of the solvent (^1H and ^{13}C NMR, respectively): $CDCl_3$ (δ = 7.26 and 77.0 ppm) and DMSO-d_6 (δ = 2.50 and 39.5 ppm). Multiplicities of the ^1H NMR signals are assigned as following: s (singlet), d (doublet), t (triplet), m (multiplet), b (broad) or as a combination (e.g. bd (broad doublet), dd (doublet of doublets), etc.). Coupling constants are reported as a *J* value in Hertz (Hz). The number of protons (n) for a given resonance is indicated as *nH* and is based on spectral integration values. The resolution of the spectrum was increased, when necessary, by performing an exponential or TRAF apodisation of the FID. A number of ^{13}C NMR signals (n) that were overlapped within the resolution limits of the NMR technique (after apodisation) is indicated as *nC overlapped*. EIMS and HRMS (EI) measurements were performed on a Micromass VG7070E instrument. ESIMS measurements were performed on a Thermo Finnigan LCQ Advantage MAX instrument by using MeOH or MeOH/THF (95/5) as a solvent. HRMS (ESI) measurements were performed on a JEOL AccuTOF-CS instrument by using MeOH or MeOH/THF (95/5) as a solvent. GCMS measurements were performed on a Thermo Finnigan PolarisQ GS/MS instrument. MALDI-ToF MS measurements were performed on a Bruker BiFLEX III spectrometer using reflectron mode and dithranol (20 mg/mL in THF) as a matrix.

General procedure S1 for the Sonogashira cross-coupling reactions. Aryl halide, palladium catalyst and CuI were placed in a Schlenk tube equipped with a stirrer and the system was evacuated and filled with argon three times. After the addition of a mixture of Et_3N and THF, and terminal acetylene, the resulting mixture was heated in a closed system under an argon atmosphere before it was quenched with NH_4Cl (1M). The crude product was extracted with CH_2Cl_2 and the combined organic layers were dried over Na_2SO_4. After filtration, the solvents were evaporated and the residue was purified by column chromatography on silica gel to afford the pure product.

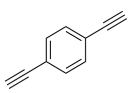
General procedure S2 for the CuAAC ("click") reactions. Azide, terminal acetylene and CuI were placed in a Schlenk tube equipped with a stirrer and the system was evacuated and filled with argon three times. After the addition of THF and PMDTA, the resulting mixture was stirred under an argon atmosphere before it was quenched with NH_4Cl (1M). The crude product was extracted with CH_2Cl_2 and the combined organic layers were dried over Na_2SO_4. After filtration, the solvents were evaporated and the residue was purified by column chromatography on silica gel to afford the pure product.

Synthesis of the mono- and difunctionalised precursors

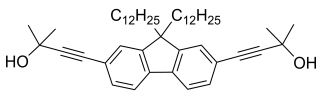
Azidocyclohexane. This compound was prepared following the literature procedure for 1-azidobutane.[S3] A mixture of bromocyclohexane (5.0 g, 31 mmol), NaN_3 (2.2 g, 34 mmol), MeOH (4 mL) and water (8 mL) was stirred at 90 °C for 16 h in a closed system before it was allowed to cool down to room temperature. The crude product was extracted with CH_2Cl_2 and the organic layer was washed three times with water and dried over Na_2SO_4. After filtration, the solvent was evaporated (150 mbar, 40 °C) and the residue was purified by column chromatography on silica gel using pentane to afford the pure product (0.76 g, 20%) as a colourless liquid. ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.49–3.22 (m, 1H, C*H*), 2.04–1.08 (m, 10H, CH_2). ^{13}C NMR (50 MHz, $CDCl_3$) δ 59.8, 31.6, 25.2, 24.2. IR (neat, cm^{-1}) 2935, 2859, 2093 (N_3), 1453, 1254, 907, 731. GCMS *m/z* (%) calcd for $C_6H_{11}N_3$ 125, found 83 ([$M^{+\bullet} - N_3$], 36), 55 (89), 41 (100).



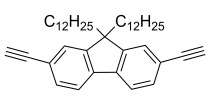
4,4′-(1,4-Phenylene)bis(2-methylbut-3-yn-2-ol) (32). See the General procedure S1 (p S2): 1,4-diiodobenzene (0.50 g, 1.5 mmol), $Pd(PPh_3)_4$ (88 mg, 76 μmol), CuI (15 mg, 76 μmol), Et_3N/THF (30 mL, 2/1), 2-methylbut-3-yn-2-ol (0.44 mL, 4.6 mmol), 60 °C, 20 h. Column chromatography on silica gel using pentane/ethyl acetate (4/1 to 1/1) afforded the pure product (0.36 g, 97%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (s, 4H, $C_{Ar}H$), 2.05 (s, 2H, O*H*), 1.61 (s, 12H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.5 (*C*H), 122.6, 95.4, 81.7, 65.6, 31.4 (*C*H_3). IR (neat, cm^{-1}) 3350 (O-H), 2980, 2920, 2855, 2146 (C≡C), 1519, 1506, 1463, 1377, 1359, 1273, 1185, 1161, 962, 907, 836, 612. GCMS *m/z* (%) 242 ([$M^{+\bullet}$], 36), 227 (100), 206 (40). HRMS (EI) *m/z* calcd for $C_{16}H_{18}O_2$ 242.1307, found 242.1307 ($|\Delta|$ = 0.1 ppm).



1,4-Diethynylbenzene (15). This compound is also commercially available. A mixture of **32** (0.35 g, 1.4 mmol), NaOH (0.58 g, 14 mmol) and toluene (30 mL) was refluxed for 17 h before the solvent was evaporated and the residue was purified by column chromatography on silica gel using pentane/ethyl acetate (95/5) to afford the pure product (79 mg, 44%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (s, 4H, $C_{Ar}H$), 3.17 (s, 2H, CC*H*). ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.0 (*C*H), 122.5, 83.0, 79.0 (*C*H). IR (neat, cm^{-1}) 3300 (CC-H), 2103 (C≡C), 1919, 1795, 1496, 1257, 837, 708, 676, 636, 546, 496.



4,4′-(9,9-Didodecyl-9*H*-fluorene-2,7-diyl)bis(2-methylbut-3-yn-2-ol) (33). See the General procedure S1 (p S2): 2,7-dibromo-9,9-didodecyl-9H-fluorene (1.0 g, 1.5 mmol), $Pd(PPh_3)_4$ (88 mg, 76 μmol), CuI (15 mg, 76 μmol), Et_3N/THF (30 mL, 2/1), 2-methylbut-3-yn-2-ol (0.44 mL, 4.5 mmol), 60 °C, 20 h. Column chromatography on silica gel using pentane/ethyl acetate (4/1) afforded the pure product (0.88 g, 87% yield) as a yellowish solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (dd, J = 7.8, 0.7 Hz, 2H, $C_{Ar}H$), 7.39 (dd, J = 7.8, 1.5 Hz, 2H, $C_{Ar}H$), 7.37 (dd, J = 1.4, 0.7 Hz, 2H, $C_{Ar}H$), 2.11 (s, 2H, O*H*), 1.96–1.88 (m, 4H, CCH_2), 1.66 (s, 12H, CCH_3), 1.34–0.96 (m, 36H, CH_2), 0.90–0.82 (m, 6H, CH_2CH_3), 0.60–0.48 (m, 4H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ (1C overlapped) 150.9, 140.6, 130.7 (*C*H), 126.0 (*C*H), 121.4, 119.8 (*C*H), 93.9, 83.0, 65.7, 55.1, 40.3 (*C*H_2), 31.9 (*C*H_2), 31.5 (*C*H_3), 30.0 (*C*H_2), 29.58 (*C*H_2), 29.56 (*C*H_2), 29.5 (*C*H_2), 29.31 (*C*H_2), 29.28 (*C*H_2), 23.7 (*C*H_2), 22.6 (*C*H_2), 14.1 (*C*H_3). IR (neat, cm^{-1}) 3330 (O-H), 2980, 2920, 2850, 2228 (C≡C), 1887, 1774, 1463, 1416, 1377, 1364, 1277, 1169, 966, 923, 888, 824, 724, 560. MALDI-ToF MS *m/z* calcd for $C_{47}H_{70}O_2$ 666.54, found 666.25.



9,9-Didodecyl-2,7-diethynyl-9*H*-fluorene (17). A mixture of **33** (0.83 g, 1.2 mmol), NaOH (0.50 g, 12 mmol) and toluene (50 mL) was refluxed for 40 h before the solvent was evaporated. Column chromatography on silica gel using pentane/ethyl acetate (95/5) afforded the pure product (0.64 g, 94%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (dd, J = 7.8 Hz, 0.6 Hz, 2H, $C_{Ar}H$), 7.48 (dd, J = 7.8 Hz, 1.5 Hz, 2H, $C_{Ar}H$), 7.46 (dd, J = 1.5 Hz, 0.6 Hz, 2H, $C_{Ar}H$), 3.15 (s, 2H, CC*H*), 1.98–1.88 (m, 4H, CCH_2),

1.34–0.96 (m, 36H, CH_2), 0.91–0.82 (m, 6H, CH_3), 0.62–0.48 (m, 4H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ (1C overlapped) 151.0, 141.0, 131.2 (*C*H), 126.5 (*C*H), 120.8, 119.9 (*C*H), 84.5, 77.3 (*C*H), 55.2, 40.2 (*C*H_2), 31.9 (*C*H_2), 30.0 (*C*H_2), 29.59 (*C*H_2), 29.58 (*C*H_2), 29.5 (*C*H_2), 29.3 (*C*H_2), 29.2 (*C*H_2), 23.7 (*C*H_2), 22.7 (*C*H_2), 14.1 (*C*H_3). IR (neat, cm^{-1}) 3309 (CC-H), 2924, 2850, 2106 (C≡C), 1464, 889, 821, 611. MALDI-ToF MS *m/z* calcd for $C_{41}H_{58}$ 550.45, found 550.47.

1,4-Diazidobenzene (24). A mixture of benzene-1,4-diamine (5.0 g, 49 mmol) and TFA (120 mL) was cooled down to −20 °C and $NaNO_2$ (10 g, 0.15 mol) was slowly added to the stirred solution. During the addition, the temperature was kept below −5 °C. After 1 h, NaN_3 (9.6 g, 0.15 mol) was slowly added to the solution and the mixture was stirred at −5 °C for an additional 1 h before it was diluted with water. The crude product was extracted with CH_2Cl_2 and the combined organic layers were washed with aq. NH_4Cl (1M) and dried over Na_2SO_4. After filtration, the solvent was evaporated and the residue was purified by column chromatography on silica gel using pentane/CH_2Cl_2 (9/1) to afford the pure product (1.8 g, 23%) as a yellow crystalline solid. The product is light and heat sensitive, and is stored at −20 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.01 (s, 4H, $C_{Ar}H$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.7, 120.3 (*C*H). IR (neat, cm^{-1}) 2140 (N_3), 2100 (N_3), 2071 (N_3), 1500, 1295, 1275, 1143, 829, 778, 582, 530. GCMS *m/z* (%) 160 ([M$^{+\bullet}$], 24), 132 (38), 104 (72), 77 (100), 52 (98). HRMS (EI) *m/z* calcd for $C_6H_4N_6$ 160.0498, found 160.0494 ($|\Delta|$ = 2.2 ppm).

Cyclohexane-1,4-diyl bis(4-methylbenzenesulfonate) (*cis*-34/*trans*-34, 1/1). A solution of tosyl chloride (7.2 g, 38 mmol) in CH_2Cl_2 (30 mL) was slowly added to a cooled solution (0 °C) of cyclohexane-1,4-diol (2.0 g, 17 mmol) in a 7/1 mixture of CH_2Cl_2 and Et_3N (80 mL) while stirring and the resulting mixture was kept at 0 °C overnight before the solvents were evaporated. The residue was purified by column chromatography on silica gel using pentane/CH_2Cl_2 (2/1) to remove the excess of tosyl chloride and CH_2Cl_2 to afford the pure product (3.0 g, 40%) as a white solid as a 1/1 mixture of *cis*- and *trans*-isomer.

Mixture (1/1) of *cis*-34 and *trans*-34. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79–7.72 (m, 8H, AA′ of AA′BB′), 7.35–7.28 (m, 8H, BB′ of AA′BB′), 4.65–4.46 (m, 4H, C*H*), 2.44 (s, 12H, CH_3), 1.94–1.74 (m, 16H, CH*H*), 1.69–1.52 (m, 16H, CH*H*). ^{13}C NMR (75 MHz, $CDCl_3$) δ (1C overlapped) 144.7, 144.6, 134.3, 134.1, 129.80, 129.78, 127.5, 127.4, 78.1, 77.7, 27.8, 26.6, 21.5. IR (neat, cm^{-1}) 3066, 3032, 2953, 2921, 2871, 1598, 1446, 1356, 1188, 1175, 1094, 908, 876, 859, 814, 786, 683, 669, 571, 556. HRMS (ESI) *m/z* calcd for $C_{20}H_{24}O_6S_2 + Na^+$ 447.09120, found 447.08924 ($|\Delta|$ = 4.38 ppm).

1,4-Diazidocyclohexane (*cis*-25/*trans*-25, 1/1). A mixture of **34** (2.0 g, 4.7 mmol), NaN_3 (0.76 g, 12 mmol) and MeOH (50 mL) was heated to reflux for 48 h before the solvent was evaporated and the residue was dried under the vacuum. After the addition of $CHCl_3$, the white precipitate was filtered off and washed with $CHCl_3$. The organic fractions were combined and after evaporation of the solvent, the residue was purified by column chromatography on silica gel using pentane/CH_2Cl_2 (3/1, 3/4 and 1/1) to afford the pure product (0.30 g, 40%) as a colourless oil as a 1/1 mixture of *cis*- and *trans*-isomer.

Mixture (1/1) of *cis*-25 and *trans*-25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.57–3.45 (m, 2H, C*H*), 3.44–3.30 (m, 2H, C*H*), 2.08–1.91 (m, 4H, CH*H*), 1.82–1.60 (m, 8H, CH*H*), 1.49–1.33 (m, 4H, CH*H*). ^{13}C NMR (75 MHz, $CDCl_3$) δ 58.2, 57.3, 28.6, 27.1. IR (neat, cm^{-1}) 2937, 2901, 2863, 2088 (N_3), 1445, 1369, 1253, 1015, 913. GCMS *m/z* (%) 82 ([M$^{+\bullet}$ − N_6], 26), 68 (40), 54 (98), 41 (100).

Synthesis of the monomeric building blocks 13 and 14

5-Bromo-2-((trimethylsilyl)ethynyl)pyridine (21). See the General procedure S1 (p S2): 2,5-dibromopyridine (2.0 g, 8.4 mmol), $Pd(PPh_3)_4$ (97 mg, 84 μmol), CuI (16 mg, 84 μmol), Et_3N/THF (40 mL, 2/1), (trimethylsilyl) acetylene (1.1 mL, 7.9 mmol), room temperature, 2.5 h. After the precipitate was filtered off and washed with THF, the solvent was evaporated and the residue containing the product was dried under vacuum. Column chromatography on silica gel using pentane/ethyl acetate (4/1) and crystallisation from MeOH/H_2O afforded the pure product (1.5 g, 71%) as a white crystalline solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.62 (dd, J = 2.4 Hz, 0.6 Hz, 1H, $C_{Ar}H$), 7.76 (dd, J = 8.4 Hz, 2.4 Hz, 1H, $C_{Ar}H$), 7.33 (dd, J = 8.4 Hz, 0.8 Hz, 1H, $C_{Ar}H$), 0.26 (s, 9H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.1 (*C*H), 141.4, 138.7 (*C*H), 128.2 (*C*H), 120.3, 102.6, 96.4, −0.4 (CH_3). IR (neat, cm^{-1}) 3031, 2957, 2897, 2165 (C≡C), 1562, 1542, 1448, 1248, 1092, 1002, 869, 842, 759, 680. GCMS *m/z* (%) 255 ([M$^{+\bullet}$ + 2], 35), 253 ([M$^{+\bullet}$], 34), 240 (98), 238 (100). HRMS (EI) *m/z* calcd for $C_{10}H_{12}BrNSi$ 252.9922, found 252.9923 (|Δ| = 0.3 ppm). ^{1}H NMR and MS data were in agreement with those previously described.[S4]

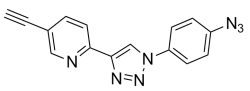
5-((Triisopropylsilyl)ethynyl)-2-((trimethylsilyl)ethynyl)pyridine (22). See the General procedure S1 (p S2): **21** (3.1 g, 12 mmol), $Pd(PPh_3)_4$ (0.28 g, 0.24 mmol), CuI (93 mg, 0.49 mmol), Et_3N/THF (30 mL, 2/1), (triisopropylsilyl)acetylene (3.0 mL, 13 mmol), 60 °C, 22 h. Column chromatography on silica gel using pentane/ethyl acetate (99/1) afforded the pure product (3.9 g, 90%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.61 (dd, J = 2.1 Hz, 0.8 Hz, 1H, $C_{Ar}H$), 7.68 (dd, J = 8.1 Hz, 2.1 Hz, 1H, $C_{Ar}H$), 7.38 (dd, J = 8.1 Hz, 0.9 Hz, 1H, $C_{Ar}H$), 1.16–1.09 (m, 21H, C*H*(CH_3)$_2$), 0.27 (s, 9H, SiCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.6 (*C*H), 141.5, 138.8 (*C*H), 126.4 (*C*H), 119.8, 103.4, 103.1, 96.9, 96.8, 18.6 (*C*H), 11.2 (CH_3), −0.4 (CH_3). IR (neat, cm^{-1}) 2959, 2942, 2891, 2865, 2159 (C≡C), 1462, 1247, 869, 842. GCMS *m/z* (%) 312 ([M$^{+\bullet}$ − C_3H_7], 100), 270 (46). HRMS (EI) *m/z* calcd for $C_{21}H_{33}NSi_2$ 355.2152, found 355.2157 (|Δ| = 1.5 ppm).

2-Ethynyl-5-((triisopropylsilyl)ethynyl)pyridine (23). A mixture of **22** (0.92 g, 2.6 mmol), K_2CO_3 (1.8 g, 13 mmol), THF (35 mL) and MeOH (35 mL) was stirred at room temperature for 16 h before K_2CO_3 was filtered off and washed with CH_2Cl_2. After the solvents were evaporated, the crude product was purified by column chromatography on silica gel using pentane/ethyl acetate (99/1) to afford the pure product (0.58 g, 80%) as a yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (dd, J = 2.1 Hz, 0.8 Hz, 1H, $C_{Ar}H$), 7.65 (dd, J = 8.2 Hz, 2.1 Hz, 1H, $C_{Ar}H$), 7.35 (dd, J = 8.0 Hz, 0.8 Hz, 1H, $C_{Ar}H$), 3.21 (s, 1H, CC*H*), 1.15–1.00 (m, 21H, C*H*(CH_3)$_2$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.6 (*C*H), 140.7, 138.7 (*C*H), 126.4 (*C*H), 120.1, 102.9, 97.0, 82.4, 78.7 (*C*H), 18.4 (*C*H), 11.0 (CH_3). IR (neat, cm^{-1}) 3303 (CC-H), 2942, 2890, 2862, 2155 (C≡C), 2110 (C≡C), 1540, 1465, 1361, 1229, 1018, 996, 882, 843, 744, 675, 654. GCMS *m/z* (%) 240 ([M$^{+\bullet}$ − C_3H_7], 100), 212 (46), 198 (50), 184 (73), 170 (66). HRMS (EI) *m/z* calcd for $C_{18}H_{25}NSi$ 283.1756, found 283.1756 (|Δ| = 0.1 ppm).

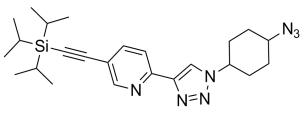
2-(1-(4-Azidophenyl)-1*H*-1,2,3-triazol-4-yl)-5-((triisopropylsilyl)ethynyl)pyridine (13). To a solution of **24** (0.57 g, 3.6 mmol) in THF (20 mL), a solution of **23** (0.10 g, 0.36 mmol), CuI (34 mg, 0.18 mmol) and PMDTA (37 mg, 0.21 mmol) in THF (80 mL) was added drop wise over a period of 3 h and the mixture was stirred for additional 12 h under an argon atmosphere before the solvent was evaporated. CH_2Cl_2 was added and the mixture was washed with aq. NH_4Cl (1M) and dried over Na_2SO_4. After filtration, the solvent was evaporated and the crude product was purified by column chromatography on silica gel using pentane/CH_2Cl_2 (1/1) to afford the unreacted **24** and CH_2Cl_2/ethyl acetate (99.5/0.5 to 97/3) to afford the pure product (0.14 g, 85%) as a yellowish solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (dd, J = 2.0 Hz, 0.6 Hz, 1H, $C_{Ar}H$), 8.56 (s, 1H, $C_{Ar}H$), 8.19 (dd, J = 8.2 Hz, 0.6 Hz, 1H, $C_{Ar}H$), 7.87 (dd, J = 8.2 Hz, 2.1 Hz, 1H, $C_{Ar}H$), 7.83–7.78 (m, 2H, AA′ of AA′XX′), 7.23–7.18 (m, 2H, XX′ of AA′XX′), 1.18–1.12 (m, 21H, C*H*(CH_3)$_2$). ^{13}C

NMR (75 MHz, $CDCl_3$) δ 152.5 (*C*H), 148.7, 148.5, 140.9, 139.8 (*C*H), 133.7, 122.0 (*C*H), 120.3 (*C*H), 120.2 (*C*H), 119.9, 119.5 (*C*H), 103.5, 95.6, 18.6 (*C*H), 11.3 (CH_3). IR (neat, cm^{-1}) 3054, 2958, 2940, 2921, 2865, 2158 (C≡C), 2130 (N_3), 2093 (N_3), 1598, 1516, 1471, 1364, 1285, 1235, 1197, 1031, 1020, 991, 886, 849, 833, 802, 674, 609. HRMS (ESI) *m/z* calcd for $C_{24}H_{29}N_7Si + H^+$ 444.23319, found 444.23207 ($|\Delta| = 2.54$ ppm).

2-(1-(4-Azidophenyl)-1*H*-1,2,3-triazol-4-yl)-5-ethynylpyridine (1). A mixture of **13** (0.23 g, 0.51 mmol), TBAF (0.25 mL, 1M in THF) and THF (30 mL) was stirred at room temperature in the dark for 24 h before the solvent was evaporated. The residue was purified by column chromatography on silica gel using pentane/ethyl acetate (5/1 and 3/2) to afford the pure product (90 mg, 62%) as a yellowish solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (dd, J = 2.1, 0.8 Hz, 1H, $C_{Ar}H$), 8.56 (s, 1H, $C_{Ar}H$), 8.21 (dd, J = 8.2, 0.9 Hz, 1H, $C_{Ar}H$), 7.89 (dd, J = 8.2, 2.1 Hz, 1H, $C_{Ar}H$), 7.83–7.77 (m, 2H, AA′ of AA′XX′), 7.23–7.17 (m, 2H, XX′ of AA′XX′), 3.28 (s, 1H, CC*H*). ^{13}C NMR (50 MHz, $CDCl_3$) δ 152.6, 149.1, 148.5, 140.9, 140.1, 133.6, 121.9, 120.28, 120.25, 119.6, 118.5, 81.1, 80.4. IR (neat, cm^{-1}) 3290 (CC-H), 2132 (N_3), 2096 (N_3), 1597, 1507, 1474, 1367, 1304, 1290, 1240, 1190, 1131, 1100, 1032, 990, 909, 848, 829, 803, 736, 656, 593, 533, 515, 493, 462. Molecular peak could not be detected by any of the available MS techniques (EI, ESI, GC, MALDI-ToF).



2-(1-(4-Azidocyclohexyl)-1*H*-1,2,3-triazol-4-yl)-5-((triisopropylsilyl)ethynyl)pyridine (*trans*-14/*cis*-14, 3/2). See the General procedure S2 (p S2): **23** (45 mg, 0.16 mmol), **25** (0.15 g, 0.90 mmol), CuI (6 mg, 0.03 mmol), THF (13 mL), PMDTA (7 mg, 0.04 mmol), room temperature, 20 h. Column chromatography on silica gel using CH_2Cl_2/ethyl acetate (99/1 to 4/1) afforded the pure product (55 mg, 77%) as a white solid as a 3/2 mixture of *trans*- and *cis*-isomer (the ratio was obtained from ^{1}H NMR).



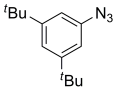
Major isomer *trans*-14. (Measured from a 3/2 mixture of *trans*-**14** and *cis*-**14**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65–8.59 (m, 1H, $C_{Ar}H$), 8.15 (s, 1H, $C_{Ar}H$), 8.11 (dd, J = 8.3, 0.5 Hz, 1H, $C_{Ar}H$), 7.82 (dd, J = 8.2, 2.1 Hz, 1H, $C_{Ar}H$), 4.51 (tt, J = 11.6, 4.1 Hz, 1H, NC*H*), 3.45 (tt, J = 11.2, 4.1 Hz, 1H, NC*H*), 2.41–2.32 (m, 2H, CH*H*), 2.25–2.17 (m, 2H, CH*H*), 1.95 (dddd, J = 13.5, 13.5, 11.6, 4.0 Hz, 2H, CH*H*), 1.59 (dddd, J = 13.7, 13.0, 11.3, 3.9 Hz, 2H, CH*H*), 1.20–1.05 (m, 21H, C*H*(CH_3)$_2$).

Minor isomer *cis*-14. (Measured from a 3/2 mixture of *trans*-**14** and *cis*-**14**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65–8.59 (m, 1H, $C_{Ar}H$), 8.20 (s, 1H, $C_{Ar}H$), 8.10 (dd, J = 8.1, 0.5 Hz, 1H, $C_{Ar}H$), 7.82 (dd, J = 8.2, 2.1 Hz, 1H, $C_{Ar}H$), 4.56 (tt, J = 10.8, 4.4 Hz, 1H, NC*H*), 3.93 (tt, J = 3.4, 3.2 Hz, 1H, NC*H*), 2.20–1.98 (m, 6H, CH*H*), 1.78 (dddd, J = 12.4, 7.1, 4.3, 3.1 Hz, 2H, CH*H*), 1.20–1.05 (m, 21H, C*H*(CH_3)$_2$).

Mixture (3/2) of *trans*-14 and *cis*-14. ^{13}C NMR (75 MHz, $CDCl_3$) δ (3C overlapped) 152.3, 149.0, 148.9, 147.7, 147.6, 139.8, 139.7, 120.3, 120.1, 119.5, 119.4, 119.22, 119.18, 103.6, 103.5, 95.24, 95.15, 58.62, 58.59, 58.3, 56.0, 31.1, 30.1, 28.5, 27.7, 18.6, 11.2. IR (neat, cm^{-1}) 2941, 2864, 2156 (C≡C), 2094 (N_3), 1594, 1470, 1361, 1255, 1227, 881, 835, 696, 676. HRMS (ESI) *m/z* calcd for $C_{24}H_{35}N_7Si + H^+$ 450.28014, found 450.27821 ($|\Delta| = 4.30$ ppm).

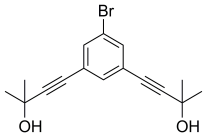
Synthesis of the blocking group 19

1-Azido-3,5-di-*tert*-butylbenzene (30). To a cooled solution (−10 °C) of 3,5-di-*tert*-butylaniline (0.50 g, 2.4 mmol) in TFA (20 mL), sodium nitrite (0.32 g, 4.6 mmol) was added in small portions over 15 min. The reaction mixture was stirred for additional 30 min at − 10 °C before sodium azide (0.33 g, 5.1 mmol) was added in small portions over 5 min and the reaction mixture was stirred for additional 2 h at −10 °C. After the addition of a mixture of ice and water, the reaction mixture was extracted with CH_2Cl_2. The combined organic extracts

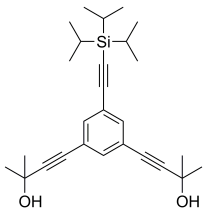


were washed with aq. Na_2CO_3 (10%) and dried over Na_2SO_4. After filtration, the solvent was evaporated and the crude product was purified by column chromatography on silica gel using pentane to afford the pure product (0.23 g, 41%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (t, J = 1.7 Hz, 1H, $C_{Ar}H$), 6.86 (d, J = 1.7 Hz, 2H, $C_{Ar}H$), 1.32 (s, 18H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.7, 139.1, 119.3, 114.3, 35.0, 31.3. IR (neat, cm^{-1}) 2962, 2098 (N_3), 1601, 1308, 703. GCMS *m/z* (%) 203 ([$M^{+\bullet} - N_2$], 48), 188 (100). HRMS (EI) *m/z* calcd for $C_{14}H_{21}N_3$ 231.1735, found 231.1727 ($|\Delta|$ = 3.7 ppm).

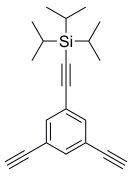
4,4′-(5-Bromo-1,3-phenylene)bis(2-methylbut-3-yn-2-ol) (27). See the General procedure S1 (p S2): 1,3,5-tribromobenzene (5.0 g, 16 mmol), CuI (1 mg, 6 μmol), $Pd(PPh_3)_4$ (7 mg, 6 μmol), Et_3N/THF (80 mL, 1/1), 2-methylbut-3-yn-2-ol (5.3 g, 63 mmol), 70 °C, 15 h. Column chromatography on silica gel using heptane/ethyl acetate (3/1 and 1/1) afforded the pure product (2.1 g, 41%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, J = 1.4 Hz, 2H, $C_{Ar}H$), 7.38 (t, J = 1.4 Hz, 1H, $C_{Ar}H$), 2.21 (s, 2H, O*H*), 1.59 (s, 12H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.0, 133.3, 124.7, 121.7, 95.6, 79.9, 65.5, 31.3. IR (neat, cm^{-1}) 3329 (O-H), 2978, 2932, 2866, 2247 (C≡C), 1584, 1552, 1424, 1363, 1241, 1164, 1147, 961, 945, 908, 863, 823, 731, 677, 566, 537. GCMS *m/z* (%) 322 ([$M^{+\bullet}$ + 2], 12), 320 ([$M^{+\bullet}$], 12), 307 (48), 305 (54), 289 (98), 287 (100). HRMS (EI) *m/z* calcd for $C_{16}H_{17}BrO_2$ 320.0412, found 320.0411 ($|\Delta|$ = 0.3 ppm).



4,4′-(5-((Triisopropylsilyl)ethynyl)-1,3-phenylene)bis(2-methylbut-3-yn-2-ol) (28). See the General procedure S1 (p S2): **27** (0.64 g, 2.0 mmol), CuI (15 mg, 80 μmol), $Pd(PPh_3)_4$ (59 mg, 50 μmol), Et_3N/THF (10 mL, 1/1), (triisopropylsilyl)acetylene (0.44 g, 2.4 mmol), 55 °C, 15 h. Column chromatography on silica gel using pentane/ethyl acetate (3/1) afforded the pure product (0.71 g, 85%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, J = 1.6 Hz, 2H, $C_{Ar}H$), 7.40 (t, J = 1.6 Hz, 1H, $C_{Ar}H$), 1.95 (s, 2H, O*H*), 1.60 (s, 12H, CCH_3), 1.12–1.10 (m, 21H, $CH(CH_3)_2$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.6, 134.3, 124.1, 123.2, 105.1, 94.8, 92.2, 80.6, 65.6, 31.4, 18.6, 11.2. IR (neat, cm^{-1}) 3334 (O-H), 2941, 2863, 2358, 2145 (C≡C), 1580, 1411, 1238, 1164, 949, 879, 677. GCMS *m/z* (%) 379 ([$M^{+\bullet} - C_3H_7$], 100), 351 (26), 337 (32), 309 (40). HRMS (EI) *m/z* calcd for $C_{27}H_{38}O_2Si - C_3H_7$ 379.2093, found 379.2101 ($|\Delta|$ = 2.0 ppm).



((3,5-Diethynylphenyl)ethynyl)triisopropylsilane (29). A mixture of **28** (0.69 g, 1.6 mmol), NaOH (0.66 g, 16 mmol) and toluene (50 mL) was heated to reflux overnight before water was added. Aqueous layer was extracted with CH_2Cl_2 and the combined organic layers (toluene and CH_2Cl_2) were dried over Na_2SO_4. After filtration, the solvents were evaporated and the residue was purified by column chromatography on silica gel using heptane to afford the pure product (0.48 g, 96%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, J = 1.5 Hz, 2H, $C_{Ar}H$), 7.53 (t, J = 1.5 Hz, 1H, $C_{Ar}H$), 3.10 (s, 2H, CCH), 1.12–1.10 (m, 21H, $CH(CH_3)_2$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.6, 135.1, 124.3, 122.7, 104.8, 92.7, 81.8, 78.4, 18.6, 11.2. IR (neat, cm^{-1}) 3300 (CC-H), 2957, 2941, 2923, 2889, 2862, 2158 (C≡C), 2121 (C≡C), 1780, 1580, 1459, 1414, 1384, 1364, 1294, 1237, 1072, 997, 966, 883, 677, 654, 627. GCMS *m/z* (%) 263 ([$M^{+\bullet} - C_3H_7$], 100), 235 (40), 221 (52), 207 (58), 193 (68). HRMS (EI) *m/z* calcd for $C_{21}H_{26}Si$ 306.1804, found 306.1804 ($|\Delta|$ = 0.1 ppm).



4,4′-(5-((Triisopropylsilyl)ethynyl)-1,3-phenylene)bis(1-(3,5-di-*tert*-butylphenyl)-1*H*-1,2,3-triazole) (31). See the General procedure S2 (p S2): **29** (0.13 g, 0.42 mmol), **30** (0.23 g, 0.99 mmol), CuI (20 mg, 0.10 mmol), THF (10 mL), PMDTA (18 mg, 0.10 mmol), 40 °C, 18 h. Column chromatography on silica gel using pentane/ethyl acetate (95/5) afforded the pure product (0.31 g, 95%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.46 (t, J = 1.6 Hz, 1H, $C_{Ar}H$), 8.35 (s, 2H, $C_{Ar}H$), 8.06 (d, J = 1.7 Hz, 2H, $C_{Ar}H$), 7.61 (d, J = 1.7 Hz, 4H, $C_{Ar}H$), 7.54 (t, J = 1.7 Hz, 2H, $C_{Ar}H$), 1.41 (s, 36H, CCH_3), 1.19–1.16 (m, 21H, $CH(CH_3)_2$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.9, 147.1, 136.7, 131.2, 128.9, 124.9, 123.2, 122.9, 118.7, 115.4, 106.3, 91.7, 35.2, 31.4, 18.7, 11.3. IR (neat, cm^{-1}) 2963, 2863, 2155 (C≡C), 1593, 1459, 1247, 1040, 879, 672. HRMS (ESI) *m/z* calcd for $C_{49}H_{68}N_6Si$ + H^+ 769.53530, found 569.53901 (|Δ| = 4.83 ppm).

4,4′-(5-Ethynyl-1,3-phenylene)bis(1-(3,5-di-*tert*-butylphenyl)-1*H*-1,2,3-triazole) (19). A mixture of **31** (0.13 g, 0.12 mmol), TBAF (12 µL, 1M in THF), THF (25 mL) and 5 drops of water was stirred at room temperature for 2.5 h before the solvent was evaporated. Precipitation of the residue from CH_2Cl_2 in MeOH afforded the pure product (0.10 g, 93%) as a yellowish solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.51 (t, J = 1.6 Hz, 1H, $C_{Ar}H$), 8.34 (s, 2H, $C_{Ar}H$), 8.08 (d, J = 1.7 Hz, 2H, $C_{Ar}H$), 7.61 (d, J = 1.7 Hz, 4H, $C_{Ar}H$), 7.54 (t, J = 1.7 Hz, 2H, $C_{Ar}H$), 3.17 (s, 1H, CCH), 1.41 (s, 36H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.9, 146.9, 136.7, 131.4, 128.9, 123.5, 123.3, 123.2, 118.7, 115.4, 83.0, 78.0, 35.2, 31.4. IR (neat, cm^{-1}) 3301 (CC-H), 2962, 2905, 2868, 2108 (C≡C), 1593, 1481, 1456, 1363, 1247, 1231, 1056, 1037, 879, 851, 789, 705, 617. HRMS (ESI) *m/z* calcd for $C_{40}H_{48}N_6$ + H^+ 613.40187, found 613.39996 (|Δ| = 3.11 ppm).

Synthesis of the ligands 3a–10a and 12a

1,4-Bis(4-(5-((triisopropylsilyl)ethynyl)pyridin-2-yl)-1*H*-1,2,3-triazol-1-yl)benzene (3a). See the General procedure S2 (p S2): **23** (0.11 g, 0.40 mmol), **24** (32 mg, 0.20 mmol), CuI (15 mg, 80 µmol), THF (20 mL), PMDTA (21 mg, 0.12 mmol), room temperature, 14 h. Column chromatography on silica gel using CH_2Cl_2/ethyl acetate (97/3) afforded the pure product (0.13 g, 92%) as a yellowish solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (dd, J = 2.1, 0.8 Hz, 2H, $C_{Ar}H$), 8.68 (s, 2H, $C_{Ar}H$), 8.20 (dd, J = 8.2, 0.8 Hz, 2H, $C_{Ar}H$), 8.04 (s, 4H, $C_{Ar}H$), 7.88 (dd, J = 8.2 Hz, 2.1 Hz, 2H, $C_{Ar}H$), 1.18–1.12 (m, 42H, $CH(CH_3)_2$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.5, 148.9, 148.2, 139.8, 136.8, 121.6, 120.1, 120.0, 119.5, 103.5, 95.7, 18.6, 11.2. IR (neat, cm^{-1}) 3127, 3045, 2941, 2888, 2863, 2154 (C≡C), 1592, 1523, 1473, 1406, 1363, 1255, 1236, 1025, 990, 881, 836, 699, 673. HRMS (ESI) *m/z* calcd for $C_{42}H_{54}N_8Si_2$ + H^+ 727.40882, found 727.40675 (|Δ| = 2.85 ppm).

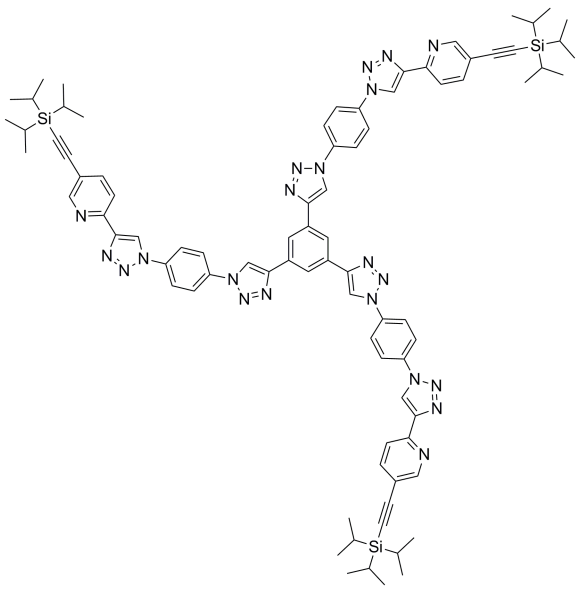
1,4-Bis(1-(4-(4-(5-((triisopropylsilyl)ethynyl)pyridin-2-yl)-1*H*-1,2,3-triazol-1-yl)phenyl)-1*H*-1,2,3-triazol-4-yl)benzene (4a). See the General procedure S2 (p S2): **15** (24 mg, 0.19 mmol), **13** (0.17 g, 0.38 mmol), CuI (7 mg, 0.04 mmol), THF (8 mL), PMDTA (8 mg, 0.05 mmol), 40 °C, 46 h. After extraction with $CHCl_3$, the organic layers were combined and washed several times with demineralised water. Due to the low solubility of the product, no further purification and characterisation could be carried out and the crude product (0.19 g,

98%), obtained after evaporation of the solvent as a yellowish solid, was used in further experiments. ESIMS analysis of a mixture, obtained after the reaction of a small fraction of the crude product with an excess of $(C^{\wedge}N)_2Ir(\mu\text{-}Cl)_2Ir(C^{\wedge}N)_2$ (see the General procedure S3 (p S13)), showed that the crude product contained also the monoclicked product and the unreacted **13**.

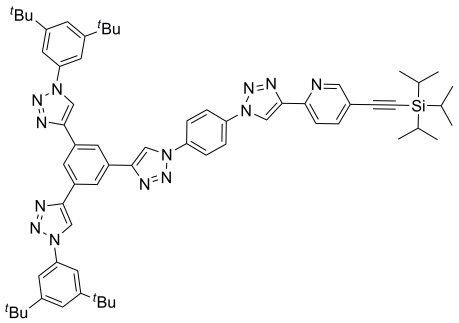
6,6′-(1,1′-(4,4′-(4,4′-(2,5-Bis(dodecyloxy)-1,4-phenylene)bis(1*H*-1,2,3-triazole-4,1-diyl))bis(4,1-phenylene))bis(1*H*-1,2,3-triazole-4,1-diyl))bis(3-((triisopropylsilyl)ethynyl)pyridine) (5a). See the General procedure S2 (p S2): **13** (80 mg, 0.18 mmol), **16** (43 mg, 86 μmol), CuI (3 mg, 0.02 mmol), THF (10 mL), PMDTA (3 mg, 0.02 mmol), 40 °C, 17 h. Size exclusion chromatography using CH_2Cl_2 and subsequent crystallisation from CH_2Cl_2/MeOH afforded the pure product (55 mg, 47%) as a white crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (dd, J = 2.1 Hz, 0.7 Hz, 2H, $C_{Ar}H$), 8.61 (s, 2H, $C_{Ar}H$), 8.55 (s, 2H, $C_{Ar}H$), 8.17 (dd, J = 8.2, 0.7 Hz, 2H, $C_{Ar}H$), 8.06 (s, 2H, $C_{Ar}H$), 8.01–7.91 (m, 8H, AA′BB′), 7.85 (dd, J = 8.2 Hz, 2.1 Hz, 2H, $C_{Ar}H$), 4.26 (t, J= 6.6 Hz, 4H, OCH_2), 1.99 (tt, J = 6.8, 6.6 Hz, 4H, CH_2), 1.64–1.54 (m, 4H, CH_2) 1.50–1.40 (m, 4H, CH_2), 1.41–1.20 (m, 28H, CH_2), 1.19–1.08 (m, 42H, $CH(CH_3)_2$), 0.87–0.82 (m, 6H, CH_2CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.5, 149.6, 148.9, 148.3, 144.1, 139.8, 137.0, 136.4, 121.4, 121.2, 120.7, 119.97, 119.96, 119.5, 118.9, 110.7, 103.5, 95.7, 69.0, 31.9, 29.8, 29.72, 29.69, 29.66, 29.63, 29.60, 29.4, 26.5, 22.7, 18.6, 14.1, 11.3. IR (neat, cm^{-1}) 2923, 2864, 2155 (C≡C), 1736, 1594, 1525, 1237, 1023, 826, 700. MALDI-ToF MS *m/z* calcd for $C_{82}H_{112}N_{14}O_2Si_2$ + H^+ 1381.86, found 1381.68.

6,6′-(1,1′-(4,4′-(4,4′-(9,9-Didodecyl-9*H*-fluorene-2,7-diyl)bis(1*H*-1,2,3-triazole-4,1-diyl))bis(4,1-phenylene))bis(1*H*-1,2,3-triazole-4,1-diyl))bis(3-((triisopropylsilyl)ethynyl)pyridine) (6a). See the General procedure S2 (p S2): **17** (70 mg, 0.13 mmol), **13** (0.11 g, 0.25 mmol), CuI (15 mg, 76 μmol), THF (8 mL), PMDTA (15 mg, 89 μmol), 40 °C, 21 h. Column chromatography on silica gel using $CHCl_3$/ethyl acetate (9/1 to 6/4) afforded the pure product (0.16 g, 88%) as a yellowish solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (dd, J = 2.0, 0.8 Hz, 2H, $C_{Ar}H$), 8.70 (s, 2H, $C_{Ar}H$), 8.35 (s, 2H, $C_{Ar}H$), 8.22 (dd, J = 8.2, 0.8 Hz, 2H, $C_{Ar}H$), 8.07–8.06 (m, 8H, AA′BB′), 8.00 (dd, J = 1.5, 0.6 Hz, 2H, $C_{Ar}H$), 7.89 (dd, J = 8.2, 2.1 Hz, 2H, $C_{Ar}H$), 7.89 (dd, J = 7.8, 1.6 Hz, 2H, $C_{Ar}H$), 7.81 (dd, J = 7.9, 0.6 Hz, 2H, $C_{Ar}H$), 2.16–2.06 (m, 4H, CCH_2), 1.29–0.95 (m, 78H, CH_2 + $CH(CH_3)_2$), 0.85–0.80 (m, 6H, CH_2CH_3), 0.74–0.64 (m, 4H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.5, 151.9, 149.3, 148.9, 148.2, 141.2, 139.9, 137.0, 136.7, 128.8, 124.8, 121.64, 121.62, 120.4, 120.3, 120.2, 120.1, 119.6, 117.3, 103.4, 95.8, 55.6, 40.5, 31.8, 30.0, 29.58, 29.57, 29.56, 29.5, 29.33, 29.27, 23.9, 22.6, 18.6, 14.1, 11.2. IR (neat, cm^{-1}) 2921, 2856, 2156 (C≡C), 1592, 1523, 1463, 1402, 1363, 1234, 1023, 993, 882, 837, 696, 674. MALDI-ToF MS *m/z* calcd for $C_{89}H_{116}N_{14}Si_2$ + H^+ 1437.90, found 1437.69.

1,3,5-Tris(1-(4-(4-(5-((triisopropylsilyl)ethynyl)pyridin-2-yl)-1*H*-1,2,3-triazol-1-yl)phenyl)-1*H*-1,2,3-triazol-4-yl) benzene (7a). See the General procedure S2 (p S2): **13** (90 mg, 0.20 mmol), **18** (10 mg, 63 μmol), CuI (4 mg, 19 μmol), THF (10 mL), PMDTA (3 mg, 19 μmol), 40 °C, 17 h. Size exclusion chromatography (SEC) using CH_2Cl_2 afforded the product as a yellowish solid. Aggregation in solution disabled both qualitative and quantitative identification of the product by NMR. A small fraction of each collected SEC fraction was reacted with an excess of $(C^{\wedge}N)_2Ir(\mu\text{-}Cl)_2Ir(C^{\wedge}N)_2$ (see the General procedure S3 (p S13)) and analysed by ESIMS. The SEC fractions, where the presence of the product was proven by the ESIMS of the corresponding complex **7b**, were combined (43 mg, 51%) and used for further experiments.



2-(1-(4-(4-(3,5-Bis(1-(3,5-di-*tert*-butylphenyl)-1*H*-1,2,3-triazol-4-yl)phenyl)-1*H*-1,2,3-triazol-1-yl)phenyl)-1*H*-1,2,3-triazol-4-yl)-5-((triisopropylsilyl)ethynyl)pyridine (8a). See the General procedure S2 (p S2): **13** (0.14 g, 0.32 mmol), **19** (0.20 g, 0.32 mmol), CuI (30 mg, 0.16 mmol), THF (10 mL), PMDTA (28 mg, 0.16 mmol), 40 °C, 17 h. Column chromatography on silica gel using CH_2Cl_2/ethyl acetate (95/5) afforded the pure product (0.18 g, 52%) as a yellowish solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (dd, J = 2.1, 0.8 Hz, 1H, $C_{Ar}H$), 8.69 (s, 1H, $C_{Ar}H$), 8.56 (t, J = 1.6 Hz, 1H, $C_{Ar}H$), 8.55 (s, 1H, $C_{Ar}H$), 8.53 (d, J = 1.6 Hz, 2H, $C_{Ar}H$), 8.50 (s, 2H, $C_{Ar}H$), 8.21 (dd, J = 8.2, 0.9 Hz, 1H, $C_{Ar}H$), 8.08–8.06 (m, 4H, AA′BB′), 7.88 (dd, J = 8.2 Hz, 2.1 Hz, 1H, $C_{Ar}H$), 7.65 (d, J = 1.7 Hz, 4H, $C_{Ar}H$), 7.55 (t, J = 1.7 Hz, 2H, $C_{Ar}H$), 1.42 (s, 36H, CCH_3), 1.18–1.14 (m, 21H, $CH(CH_3)_2$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.9, 152.5, 148.8, 148.3, 148.0, 147.3, 139.8, 136.8, 136.6, 131.8, 131.1, 123.1, 122.8, 122.5, 121.5, 120.1, 119.9, 119.5, 118.9, 118.2, 115.3, 103.5, 95.6, 77.2, 35.2, 31.3, 29.6, 18.6, 11.2. IR (neat, cm^{-1}) 3137, 2959, 2864, 2155 (C≡C), 1594, 1523, 1473, 1457, 1363, 1232, 1038, 987, 695. MALDI-ToF MS *m/z* calcd for $C_{64}H_{77}N_{13}Si + H^+$ 1056.62, found 1056.35.



2-(1-(4-(4-(3,5-Bis(1-(3,5-di-*tert*-butylphenyl)-1*H*-1,2,3-triazol-4-yl)phenyl)-1*H*-1,2,3-triazol-1-yl)phenyl)-1*H*-1,2,3-triazol-4-yl)-5-ethynylpyridine (9a). A mixture of **8a** (0.13 g, 0.12 mmol), TBAF (12 μL, 1M in THF), THF (25 mL) and 5 drops of water was stirred at room temperature for 2.5 h before the solvent was evaporated. Precipitation of the residue from CH_2Cl_2 in MeOH afforded the pure product (0.10 g, 93%) as a yellowish solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.74 (dd, J = 2.1 Hz, 0.8 Hz, 1H, $C_{Ar}H$), 8.70 (s, 1H, $C_{Ar}H$), 8.58 (t, J = 1.6 Hz, 1H, $C_{Ar}H$), 8.57 (s, 1H, $C_{Ar}H$), 8.55 (d, J = 1.5 Hz, 2H, $C_{Ar}H$), 8.50 (s, 2H, $C_{Ar}H$), 8.25 (dd, J = 8.2 Hz, 0.9 Hz, 1H, $C_{Ar}H$), 8.11–8.07 (m, 4H, AA′BB′), 7.92 (dd, J = 8.2 Hz, 2.1 Hz, 1H, $C_{Ar}H$), 7.65 (d, J = 1.7 Hz, 4H, $C_{Ar}H$), 7.56 (t, J = 1.7 Hz, 2H, $C_{Ar}H$), 3.29 (s, 1H, CCH), 1.43 (s, 36H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.0, 152.6, 148.9, 148.8, 148.2, 147.3,

140.1, 137.0, 136.8, 136.7, 131.9, 131.2, 123.2, 122.9, 122.6, 121.69, 121.68, 120.3, 119.6, 119.0, 118.6, 118.2, 115.3, 81.2, 80.4, 35.3, 31.4. IR (neat, cm^{-1}) 3299 (CC-H), 3139, 2962, 2903, 2866, 2108 (C≡C), 1592, 1522, 1475, 1360, 1246, 1035, 786, 701. MALDI-ToF MS *m/z* calcd for $C_{55}H_{57}N_{13}$ + H^+ 900.49, found 900.32.

2-(1-(4-(4-(3,5-Bis(1-(3,5-di-*tert*-butylphenyl)-1*H*-1,2,3-triazol-4-yl)phenyl)-1*H*-1,2,3-triazol-1-yl)phenyl)-1*H*-1,2,3-triazol-4-yl)-5-(1-(4-(4-(5-((triisopropylsilyl)ethynyl)pyridin-2-yl)-1*H*-1,2,3-triazol-1-yl)phenyl)-1*H*-1,2,3-triazol-4-yl)pyridine (10a). See the General procedure S2 (p S2): **9a** (81 mg, 89 μmol), **13** (44 mg, 99 μmol), CuI (9 mg, 0.05 mmol), THF (10 mL), PMDTA (8 mg, 0.05 mmol), 40 °C, 17 h. Size exclusion chromatography (SEC) using CH_2Cl_2 afforded the product as a yellowish solid. Aggregation in solution disabled both qualitative and quantitative identification of the product by NMR. A small fraction of each collected SEC fraction was reacted with an excess of $(C^{\wedge}N)_2Ir(\mu\text{-}Cl)_2Ir(C^{\wedge}N)_2$ (see the General procedure S3 (p S13)) and analysed by ESIMS. The SEC fractions, where the presence of the product was proven by the ESIMS of the corresponding complexes **10b** and **10c**, were combined (69 mg, 57%) and used for further experiments.

2-(1-(4-(4-(3,5-Bis(1-(3,5-di-*tert*-butylphenyl)-1*H*-1,2,3-triazol-4-yl)phenyl)-1*H*-1,2,3-triazol-1-yl)phenyl)-1*H*-1,2,3-triazol-4-yl)-5-(1-(4-(4-(5-((triisopropylsilyl)ethynyl)pyridin-2-yl)-1*H*-1,2,3-triazol-1-yl)cyclohexyl)-1*H*-1,2,3-triazol-4-yl)pyridine (*trans*-12a/*cis*-12a, 3/2). See the General procedure S2 (p S2): **9a** (13 mg, 14 μmol), **14** (7 mg, 0.02 mmol), CuI (3 mg, 0.02 mmol), THF (6 mL), PMDTA (3 mg, 0.02 mmol), 40 °C, 23 h. Column chromatography on silica gel using CH_2Cl_2/MeOH (99/1 to 97.5/2.5) afforded the pure product (14 mg, 72%) as a colourless solid film as a 3/2 mixture of *trans*- and *cis*-isomer (the ratio was obtained from ^1H NMR).

Major isomer *trans*-12a. (Measured from a 3/2 mixture of *trans*-**12a** and *cis*-**12a**) ^1H NMR (400 MHz, $CDCl_3$) δ 9.11–9.07 (m, 1H, $C_{Ar}H$), 8.73 (s, 1H, $C_{Ar}H$), 8.65 (d, J = 1.4 Hz, 1H, $C_{Ar}H$), 8.61–8.49 (m, 6H, $C_{Ar}H$), 8.33 (d, J = 8.3 Hz, 1H, $C_{Ar}H$), 8.28 (dd, J = 8.4, 1.8 Hz, 1H, $C_{Ar}H$), 8.24 (s, 1H, $C_{Ar}H$), 8.14 (d, J = 8.2 Hz, 1H, $C_{Ar}H$), 8.10–8.04 (m, 4H, AA′BB′), 7.98 (s, 1H, $C_{Ar}H$), 7.85 (dd, J = 8.2, 2.0 Hz, 1H, $C_{Ar}H$), 7.65 (d, J = 1.4 Hz, 4H, $C_{Ar}H$), 7.55 (t, J = 1.5 Hz, 2H, $C_{Ar}H$), 4.77–4.63 (m, 1H, NC*H*), 4.77–4.63 (m, 1H, NC*H*), 2.64–1.54 (m, 8H, CH*H*), 1.42 (s, 36H, CCH_3), 1.18–1.11 (m, 21H, C*H*(CH_3)$_2$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.0, 152.3, 149.1, 149.0, 148.8, 148.2, 147.8, 147.3, 146.8, 144.4, 139.9, 136.9, 136.8, 136.7, 133.9, 131.9, 131.2, 126.2, 123.2, 122.9, 122.6, 121.64, 121.58, 120.54, 120.50, 119.9, 119.7, 119.3, 119.0, 118.30, 118.25, 115.3, 103.5, 95.4, 58.7, 58.5, 35.2, 31.71, 31.69, 31.4, 18.6, 11.3.

Minor isomer *cis*-12a. (Measured from a 3/2 mixture of *trans*-**12a** and *cis*-**12a**) ^1H NMR (400 MHz, $CDCl_3$) δ 9.11–9.07 (m, 1H, $C_{Ar}H$), 8.74 (s, 1H, $C_{Ar}H$), 8.63 (d, J = 2.0 Hz, 1H, $C_{Ar}H$), 8.61–8.49 (m, 6H, $C_{Ar}H$), 8.33 (d, J = 8.3 Hz, 1H, $C_{Ar}H$), 8.28 (dd, J = 8.4, 1.8 Hz, 1H, $C_{Ar}H$), 8.26 (s, 1H, $C_{Ar}H$), 8.13 (d, J = 8.2 Hz, 1H, $C_{Ar}H$), 8.10–8.04 (m, 4H, AA′BB

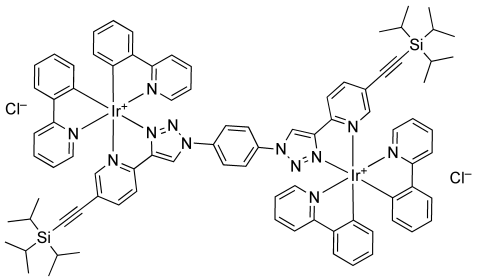
′), 7.97 (s, 1H, $C_{Ar}H$), 7.85 (dd, J = 8.2, 2.0 Hz, 1H, $C_{Ar}H$), 7.65 (d, J = 1.4 Hz, 4H, $C_{Ar}H$), 7.55 (t, J = 1.5 Hz, 2H, $C_{Ar}H$), 4.89–4.77 (m, 1H, NCH), 4.77–4.63 (m, 1H, NCH), 2.64–1.54 (m, 8H, CHH), 1.42 (s, 36H, CCH_3), 1.18–1.11 (m, 21H, CH(CH_3)$_2$). The high noise to signal ratio and overlap of some signals with the signals of the *trans*-isomer did not allow for a reliable description of the ^{13}C NMR signals of the *cis*-isomer.

Mixture (3/2) of *trans*-12a and *cis*-12a. IR (neat, cm^{-1}) 2957, 2925, 2862, 2155 (C≡C), 1594, 1523, 1467, 1364, 1261, 1233, 1036, 989, 883, 837, 809, 699, 669. MALDI-ToF MS *m/z* calcd for $C_{79}H_{92}N_{20}Si$ + H^+ 1349.76, found 1349.47.

Synthesis of the iridium complexes 3b–8b, 10b, 3c–6c and 8c–12c

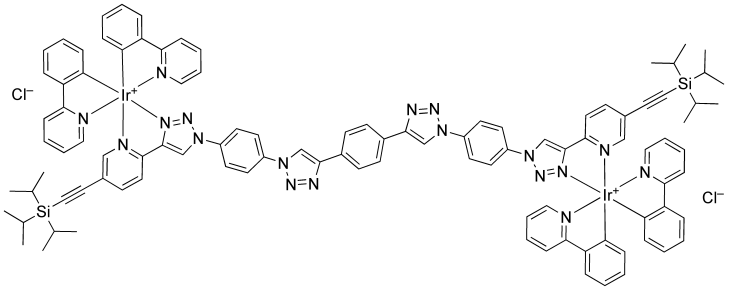
General procedure S3. A mixture of the ligand (**3a–10a** and **12a**; 1 eq), *meso*-Δ,Λ-(C^N)$_2$Ir(μ-Cl)$_2$Ir(C^N)$_2$ (C^N = 2-phenylpyridine for the **b** series; C^N = 2-(1*H*-pyrazol-1-yl)pyridine for the **c** series; 1.1 eq (**8a** and **9a**); 2.2 eq (**3a–6a**, **10a** and **12a**); 3.3 eq (**7a**)) and a 3/1 mixture of $CHCl_3$ and MeOH (5 mL/25 μmol of the ligand) was heated to 50 °C for 2–5 h (140 h in the case of **4b**) before the solvents were evaporated. The residue was purified by flash column chromatography on silica gel using $CHCl_3$/MeOH (99/1) to remove the excess of *meso*-Δ,Λ-(C^N)$_2$Ir(μ-Cl)$_2$Ir(C^N)$_2$ and $CHCl_3$/MeOH (97/3 to 8/2) to afford the pure product. Since no reason or evidence for the formation of the diastereomerically pure or diastereomerically enriched binuclear products were found, it is presumed that all binuclear iridium complexes were obtained as a 1/1 mixture of *rel*-Δ,Δ- and *meso*-Δ,Λ-diastereomer (**3b–6b** and **3c–6c**) or as a 1/1 mixture of *rel*-Δ,Δ- and *rel*-Δ,Λ-diastereomer (**10b**, **10c** and **12c**). Except for **3b** and **3c**, the ^{1}H and ^{13}C NMR signals of the diastereomers of all binuclear products overlap within the resolution limits of both NMR techniques; in the case of **3b** and **3c**, some individual ^{1}H and ^{13}C NMR signals are visible. The small or the lack of difference in the chemical shifts between the two diastereomers is most likely due to the long distance between the two chiral centres.

Compound 3b (*rel*-Δ,Δ-3b/*meso*-Δ,Λ-3b, 1/1). See the General procedure S3 (p S13). Column chromatography on silica gel using ethyl acetate/MeOH (95/5 to 8/2) afforded the pure product (70 mg, 92%) as a yellow solid.



Mixture (1/1) of *rel*-Δ,Δ-3b and *meso*-Δ,Λ-3b. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.78 (s, 2H, $C_{Ar}H$), 11.78 (s, 2H, $C_{Ar}H$), 9.04 (d, J = 8.2 Hz, 2H, $C_{Ar}H$), 9.04 (d, J = 8.2 Hz, 2H, $C_{Ar}H$), 8.32 (s, 4H, $C_{Ar}H$), 8.31 (s, 4H, $C_{Ar}H$), 7.96 (bd, J = 8.8 Hz, 2H, $C_{Ar}H$), 7.96 (bd, J = 8.8 Hz, 2H, $C_{Ar}H$), 7.94 (bd, J = 9.1 Hz, 2H, $C_{Ar}H$), 7.94 (bd, J = 9.1 Hz, 2H, $C_{Ar}H$), 7.90 (bd, J = 9.1 Hz, 2H, $C_{Ar}H$), 7.90 (bd, J = 9.1 Hz, 2H, $C_{Ar}H$), 7.80–7.66 (m, 20H, $C_{Ar}H$), 7.64 (bd, J = 7.9 Hz, 2H, $C_{Ar}H$), 7.64 (bd, J = 7.9 Hz, 2H, $C_{Ar}H$), 7.52 (bd, J = 5.9 Hz, 2H, $C_{Ar}H$), 7.52 (bd, J = 5.9 Hz, 2H, $C_{Ar}H$), 7.07–6.95 (m, 16H, $C_{Ar}H$), 6.90 (bdd, J = 8.0, 7.9 Hz, 2H, $C_{Ar}H$), 6.90 (bdd, J = 8.0, 7.9 Hz, 2H, $C_{Ar}H$), 6.88 (bdd, J = 8.0, 7.9 Hz, 2H, $C_{Ar}H$), 6.88 (bdd, J = 8.0, 7.9 Hz, 2H, $C_{Ar}H$), 6.37 (bdd, J = 7.4, 2.2 Hz, 2H, $C_{Ar}H$), 6.37 (bdd, J = 7.4, 2.2 Hz, 2H, $C_{Ar}H$), 6.29 (bd, J = 7.6 Hz, 2H, $C_{Ar}H$), 6.29 (bd, J = 7.6 Hz, 2H, $C_{Ar}H$), 1.13–0.93 (m, 42H, CH(CH_3)$_2$), 1.13–0.93 (m, 42H, CH(CH_3)$_2$). ^{13}C NMR (75 MHz, $CDCl_3$) δ (29C overlapped) 168.43, 168.40, 167.54, 167.53, 152.5 (*C*H), 149.5 (*C*H), 149.38, 149.36, 149.08, 149.07, 148.4, 148.3 (*C*H), 145.01, 144.99, 143.6, 143.32, 143.29, 141.5 (*C*H), 138.1 (*C*H), 138.0 (*C*H), 136.4, 131.78 (*C*H), 131.75 (*C*H), 131.7 (*C*H), 130.7 (*C*H), 130.31 (*C*H), 130.27 (*C*H), 127.4 (*C*H), 124.6 (*C*H), 124.3 (*C*H), 123.3 (*C*H), 122.9, 122.8 (*C*H), 122.7 (*C*H), 121.9 (*C*H), 119.6 (*C*H), 119.5 (*C*H), 101.1, 99.7, 18.5 (*C*H), 11.0 (*C*H$_3$). IR (neat, cm^{-1}) 3054, 2955, 2938, 2924, 2864, 2156 (C≡C), 1718, 1607, 1582, 1523, 1476, 1266, 1227, 1163, 1066, 1033, 883, 846, 756, 735, 702, 669. HRMS (ESI) *m/z* calcd for $C_{86}H_{86}Ir_2N_{12}Si_2^+$ 1728.58954, found 1728.58986 (|Δ| = 0.19 ppm).

Compound 4b (*rel*-Δ,Δ-4b/*meso*-Δ,Λ-4b, 1/1). See the General procedure S3 (p S13). Column chromatography on silica gel using $CHCl_3$/MeOH (93/7 to 87/13) afforded the pure product (22 mg, 43%) as a yellow solid.

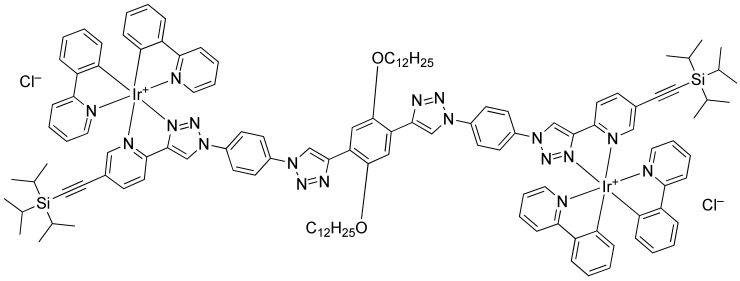


***rel*-Δ,Δ-4b.** (Measured from a 1/1 mixture of *rel*-Δ,Δ-**4b** and *meso*-Δ,Λ-**4b**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.95 (s, 2H, $C_{Ar}H$), 9.20 (dd, J = 8.4, 0.5 Hz, 2H, $C_{Ar}H$), 8.42–8.36 (m, 4H, AA′ of AA′XX′), 8.32 (s, 2H, $C_{Ar}H$), 8.02 (s, 4H, $C_{Ar}H$), 8.02–7.97 (m, 4H, XX′ of AA′XX′), 8.00 (dd, J = 8.2, 1.9 Hz, 2H, $C_{Ar}H$), 7.96 (ddd, J = 8.6, 1.4, 0.7 Hz, 2H, $C_{Ar}H$), 7.94 (ddd, J = 8.8, 1.4, 0.6 Hz, 2H, $C_{Ar}H$), 7.81 (ddd, J = 8.6, 7.4, 1.6 Hz, 2H, $C_{Ar}H$), 7.81 (dd, J = 5.9, 1.8 Hz, 2H, $C_{Ar}H$), 7.79 (ddd, J = 8.9, 7.4, 1.6 Hz, 2H, $C_{Ar}H$), 7.69 (ddd, J = 8.2, 1.3, 0.5 Hz, 2H, $C_{Ar}H$), 7.69 (dd, J = 1.9, 0.7 Hz, 2H, $C_{Ar}H$), 7.67 (ddd, J = 8.0, 1.1, 0.5 Hz, 2H, $C_{Ar}H$), 7.56 (ddd, J = 5.9, 1.5, 0.7 Hz, 2H, $C_{Ar}H$), 7.08 (ddd, J = 7.4, 5.9, 1.4 Hz, 2H, $C_{Ar}H$), 7.05 (ddd, J = 7.3, 5.9, 1.4 Hz, 2H, $C_{Ar}H$), 7.04 (ddd, J = 7.8, 7.2, 1.2 Hz, 2H, $C_{Ar}H$), 7.03 (ddd, J = 7.9, 7.4, 1.2 Hz, 2H, $C_{Ar}H$), 6.92 (ddd, J = 7.6, 7.2, 1.3 Hz, 2H, $C_{Ar}H$), 6.92 (ddd, J = 7.6, 7.3, 1.5 Hz, 2H, $C_{Ar}H$), 6.34 (ddd, J = 7.6, 1.3, 0.5 Hz, 2H, $C_{Ar}H$), 6.34 (ddd, J = 7.6, 1.3, 0.5 Hz, 2H, $C_{Ar}H$), 1.08–1.01 (m, 42H, CH(CH_3)$_2$). ^{13}C NMR (50 MHz, DMSO-d_6, 48 °C) δ (2C overlapped) 166.9, 166.2, 152.0, 150.0, 149.5, 148.6, 148.3, 148.0, 147.1, 145.4, 143.92, 143.86, 141.7, 138.9, 138.6, 137.2, 135.3, 131.3, 130.7, 130.0, 129.8, 129.3, 126.1, 125.9, 124.7, 124.4, 123.9, 123.7, 122.5, 121.8, 121.7, 121.2, 121.1, 119.8, 119.6, 101.6, 98.1, 18.2, 10.4.

***meso*-Δ,Λ-4b.** ^{1}H and ^{13}C NMR data are identical to *rel*-Δ,Δ-**4b** within the resolution limits of both NMR techniques.

Mixture (1/1) of *rel*-Δ,Δ-4b and *meso*-Δ,Λ-4b. IR (neat, cm^{-1}) 3049, 2956, 2940, 2923, 2863, 2159 (C≡C), 1605, 1583, 1524, 1477, 1422, 1266, 1227, 1163, 1064, 1032, 990, 881, 841, 757, 731, 696, 669. HRMS (ESI) *m/z* calcd for $C_{102}H_{96}Ir_2N_{18}Si_2^+$ 2010.68157, found 2010.68102 ($|\Delta|$ = 0.27 ppm).

Compound 5b (*rel*-Δ,Δ-5b/*meso*-Δ,Λ-5b, 1/1). See the General procedure S3 (p S13). Column chromatography on silica gel using $CHCl_3$/MeOH (9/1) afforded the pure product (29 mg, 97%) as a yellow solid.

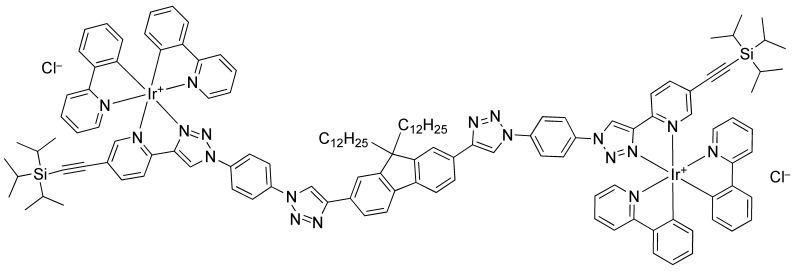


***rel*-Δ,Δ-5b.** (Measured from a 1/1 mixture of *rel*-Δ,Δ-**5b** and *meso*-Δ,Λ-**5b**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.99 (s, 2H, $C_{Ar}H$), 9.25 (dd, J = 8.3, 0.5 Hz, 2H, $C_{Ar}H$), 8.60 (s, 2H, $C_{Ar}H$), 8.42–8.33 (m, 4H, AA′ of AA′XX′), 8.09 (s, 2H, $C_{Ar}H$), 8.02 (dd, J = 8.3, 1.6 Hz, 2H, $C_{Ar}H$), 8.00–7.95 (m, 4H, XX′ of AA′XX′), 7.94 (bd, J = 8.2 Hz, 2H, $C_{Ar}H$), 7.93 (bdd, J = 8.6, 1.1 Hz, 2H, $C_{Ar}H$), 7.83–7.75 (m, 6H, $C_{Ar}H$), 7.71–7.64 (m, 6H, $C_{Ar}H$), 7.56 (bd, J = 5.5 Hz, 2H, $C_{Ar}H$), 7.10–6.99 (m, 8H, $C_{Ar}H$), 6.92 (ddd, J = 7.8, 7.3, 1.3 Hz, 2H, $C_{Ar}H$), 6.90 (ddd, J = 7.9, 7.3, 1.6 Hz, 2H, $C_{Ar}H$), 6.34 (dd, J = 7.6, 0.9 Hz, 2H, $C_{Ar}H$), 6.34 (dd, J = 7.6, 0.9 Hz, 2H, $C_{Ar}H$), 4.25 (t, J = 7.0 Hz, 4H, OCH_2), 1.97 (tt, J = 7.0, 7.0 Hz, 4H, CH_2), 1.57–1.47 (m, 4H, CH_2), 1.45–1.35 (m, 4H, CH_2), 1.34–1.16 (m, 28H, CH_2), 1.07–0.99 (m, 42H, CH(CH_3)$_2$), 0.88–0.79 (m, 6H, CH_2CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.3, 167.6, 152.5, 149.6, 149.4, 149.3, 149.1, 148.5, 148.4, 145.7, 144.2, 143.56, 143.55, 141.8, 138.1, 138.0, 137.7, 135.6, 131.9, 131.6, 130.8, 130.1, 127.3, 124.7, 124.59, 124.58, 124.4, 123.3, 123.0, 122.9, 122.3, 121.8, 121.3, 120.7, 119.6, 119.5, 118.9, 110.9, 101.1, 99.8, 69.0, 31.9, 29.63, 29.59, 29.56, 29.5, 29.4, 29.29, 29.26, 26.0, 22.6, 18.5, 14.1, 11.1.

***meso*-Δ,Λ-5b.** ^{1}H and ^{13}C NMR data are identical to *rel*-Δ,Δ-**5b** within the resolution limits of both NMR techniques.

Mixture (1/1) of *rel*-Δ,Δ-5b and *meso*-Δ,Λ-5b. IR (neat, cm^{-1}) 3048, 2922, 2852, 2160 (C≡C), 1720, 1606, 1582, 1524, 1478, 1420, 1267, 1247, 1228, 1204, 1064, 1030, 879, 840, 760, 731, 695, 669. HRMS (ESI) *m/z* calcd for $C_{126}H_{144}Ir_2N_{18}O_2Si_2^+$ 2379.04700, found 2379.04833 (|Δ| = 0.56 ppm).

Compound 6b (*rel*-Δ,Δ-6b/*meso*-Δ,Λ-6b, 1/1). See the General procedure S3 (p S13). Column chromatography on silica gel using $CHCl_3$/MeOH (95/5 to 9/1) afforded the pure product (52 mg, >99%) as a yellow solid.

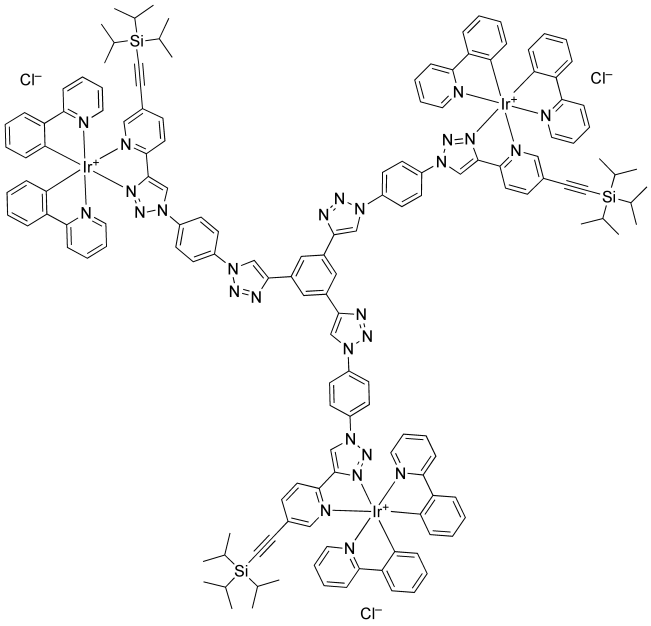


***rel*-Δ,Δ-6b.** (Measured from a 1/1 mixture of *rel*-Δ,Δ-**6b** and *meso*-Δ,Λ-**6b**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.89 (s, 2H, $C_{Ar}H$), 9.19 (d, J = 8.1 Hz, 2H, $C_{Ar}H$), 8.43–8.35 (m, 4H, AA′ of AA′XX′), 8.32 (s, 2H, $C_{Ar}H$), 8.02–7.98 (m, 4H, XX′ of AA′XX′), 8.01 (dd, J = 8.3, 1.9 Hz, 2H, $C_{Ar}H$), 7.97 (dd, J = 1.5, 0.6 Hz, 2H, $C_{Ar}H$), 7.96–7.91 (m, 4H, $C_{Ar}H$), 7.85 (dd, J = 7.8, 1.5 Hz, 2H, $C_{Ar}H$), 7.82–7.77 (m, 4H, $C_{Ar}H$), 7.78 (ddd, J = 8.3, 7.4, 1.5 Hz, 2H, $C_{Ar}H$), 7.78 (dd, J = 7.9, 0.6 Hz, 2H, $C_{Ar}H$), 7.70–7.65 (m, 4H, $C_{Ar}H$), 7.69 (dd, J = 1.9, 0.6 Hz, 2H, $C_{Ar}H$), 7.55 (ddd, J = 5.9, 1.5, 0.7 Hz, 2H, $C_{Ar}H$), 7.07 (ddd, J = 7.3, 5.9, 1.5 Hz, 2H, $C_{Ar}H$), 7.06–7.02 (m, 2H, $C_{Ar}H$), 7.02 (ddd, J = 7.8, 7.4, 1.4 Hz, 2H, $C_{Ar}H$), 7.02 (ddd, J = 7.9, 7.3, 1.4 Hz, 2H, $C_{Ar}H$), 6.92 (ddd, J = 7.5, 7.5, 1.4 Hz, 2H, $C_{Ar}H$), 6.90 (ddd, J = 7.5, 7.4, 1.4 Hz, 2H, $C_{Ar}H$), 6.34 (ddd, J = 7.7, 1.2, 0.5 Hz, 2H, $C_{Ar}H$), 6.34 (ddd, J = 7.7, 1.3, 0.5 Hz, 2H, $C_{Ar}H$), 2.15–2.03 (m, 4H, CCH_2), 1.36–0.95 (m, 78H, CH_2 + $CH(CH_3)_2$), 0.84–0.77 (m, 6H, CH_2CH_3), 0.73–0.60 (m, 4H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.3, 167.6, 152.5, 151.9, 149.4, 149.30, 149.27, 149.0, 148.5, 148.3, 145.6, 143.6, 141.8, 141.1, 138.2, 138.0, 137.5, 135.7, 131.9, 131.6, 130.8, 130.1, 128.7, 127.2, 124.8, 124.7, 124.5, 124.40, 124.36, 123.3, 123.02, 122.96, 122.9, 122.4, 121.9, 121.5, 120.3, 120.2, 119.64, 119.55, 117.4, 101.1, 99.9, 55.5, 40.5, 31.8, 30.0, 29.6, 29.52, 29.50, 29.47, 29.3, 29.2, 23.9, 22.6, 18.5, 14.0, 11.1.

***meso*-Δ,Λ-6b.** ^{1}H and ^{13}C NMR data are identical to *rel*-Δ,Δ-**6b** within the resolution limits of both NMR techniques.

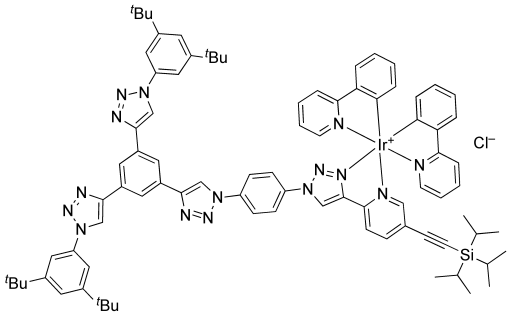
Mixture (1/1) of *rel*-Δ,Δ-6b and *meso*-Δ,Λ-6b. IR (neat, cm^{-1}) 3060, 3046, 2920, 2851, 2160 (C≡C), 1605, 1581, 1523, 1476, 1269, 1226, 1064, 1031, 844, 758, 730. HRMS (ESI) *m/z* calcd for $C_{133}H_{148}Ir_2N_{18}Si_2^+$ 2435.08847, found 2435.09522 (|Δ| = 2.77 ppm).

Compound 7b. See the General procedure S3 (p S13). Column chromatography on silica gel using $CHCl_3$/MeOH (9/1 to 8/2) afforded the product (10 mg, 48%) as a yellow solid. Significant broadening of the ^1H and ^{13}C NMR signals, most likely due to the aggregation, disabled the interpretation of the ^1H and ^{13}C NMR spectra. Presuming that during the purification no diastereomerical enrichment occured, the product was obtained as a 1/1/1/1 mixture of *rel*-Δ,Δ,Δ-**7b**, *rel*-Δ,Δ,Λ-**7b**, *rel*-Δ,Λ,Δ-**7b** and *rel*-Δ,Λ,Λ-**7b** diastereomers.

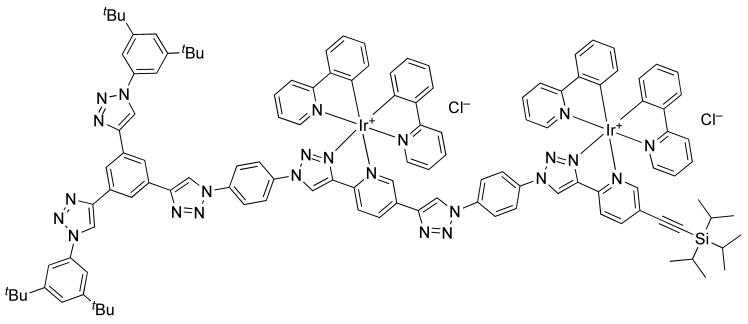


Mixture (1/1/1/1) of *rel*-Δ,Δ,Δ-7b, *rel*-Δ,Δ,Λ-7b, *rel*-Δ,Λ,Δ-7b and *rel*-Δ,Λ,Λ-7b. IR (neat, cm^{-1}) 3063, 2952, 2921, 2853, 2160 (C≡C), 1730, 1607, 1583, 1520, 1463, 1377, 1230, 1163, 1068, 1040, 847, 760, 736, 698, 667. HRMS (ESI) *m/z* calcd for $C_{150}H_{141}{}^{191}Ir_2{}^{193}IrN_{27}Si_3{}^+$ 2979.00121, found 2979.00055 (|Δ| = 0.22 ppm).

Compound 8b. See the General procedure S3 (p S13). Column chromatography on silica gel using $CHCl_3$/MeOH (9/1) afforded the pure product (92 mg, >99%) as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 11.88 (s, 1H, $C_{Ar}H$), 9.12 (d, *J* = 7.9 Hz, 1H, $C_{Ar}H$), 8.67 (s, 1H, $C_{Ar}H$), 8.59 (s, 2H, $C_{Ar}H$), 8.56 (t, *J* = 1.5 Hz, 1H, $C_{Ar}H$), 8.53 (d, *J* = 1.4 Hz, 2H, $C_{Ar}H$), 8.38–8.32 (m, 2H, AA′ of AA′XX′), 8.03–7.98 (m, 2H, XX′ of AA′XX′), 7.95 (bd, *J* = 8.1 Hz, 1H, $C_{Ar}H$), 7.94 (bd, *J* = 8.0 Hz, 1H, $C_{Ar}H$), 7.90 (bd, *J* = 8.5 Hz, 1H, $C_{Ar}H$), 7.87 (bd, *J* = 5.5 Hz, 1H, $C_{Ar}H$), 7.82 (ddd, *J* = 8.3, 7.7, 1.6 Hz, 1H, $C_{Ar}H$), 7.78 (ddd, *J* = 8.2, 7.5, 1.6 Hz, 1H, $C_{Ar}H$), 7.71–7.65 (m, 3H, $C_{Ar}H$), 7.67 (d, *J* = 1.6 Hz, 4H, $C_{Ar}H$), 7.56–7.53 (m, 1H, $C_{Ar}H$), 7.54 (t, *J* = 1.7 Hz, 2H, $C_{Ar}H$), 7.13 (bdd, *J* = 6.5, 6.4 Hz, 1H, $C_{Ar}H$), 7.10–7.05 (m, 1H, $C_{Ar}H$), 7.04 (ddd, *J* = 7.7, 7.2, 1.2 Hz, 1H, $C_{Ar}H$), 7.02 (ddd, *J* = 7.9, 7.2, 1.2 Hz, 1H, $C_{Ar}H$), 6.92 (ddd, *J* = 7.8, 7.2, 1.6 Hz, 1H, $C_{Ar}H$), 6.92 (ddd, *J* = 7.8, 7.1, 1.4 Hz, 1H, $C_{Ar}H$), 6.35 (ddd, *J* = 7.8, 1.4, 0.5 Hz, 1H, $C_{Ar}H$), 6.34 (ddd, *J* = 7.8, 1.1, 0.5 Hz, 1H, $C_{Ar}H$), 1.43 (s, 36H, CCH_3), 1.06–1.01 (m, 21H, $CH(CH_3)_2$). ^{13}C NMR (75 MHz, $CDCl_3$) δ (1C overlapped) 168.2, 167.4, 152.8, 152.6, 149.9, 149.1, 149.0, 148.5, 148.0, 147.9, 147.3, 145.7, 143.8, 143.6, 141.1, 138.1, 137.9, 137.1, 136.7, 135.4, 131.9, 131.8, 131.6, 131.2, 130.6, 130.0, 126.5, 124.5, 124.3, 123.7, 123.6, 123.0, 122.9, 122.8, 122.6, 122.5, 122.3, 121.7, 121.2, 119.6, 119.5, 119.3, 119.0, 115.1, 101.1, 99.4, 35.2, 31.4, 18.5, 11.0. IR (neat, cm^{-1}) 3059, 3048, 2955, 2924, 2864, 2162 (C≡C), 1719, 1607, 1522, 1477, 1361, 1317, 1229, 1061, 1037, 878, 847, 789, 757, 732, 696, 669. HRMS (ESI) *m/z* calcd for $C_{86}H_{93}IrN_{15}Si^+$ 1556.71368, found 1556.72109 (|Δ| = 4.76 ppm).

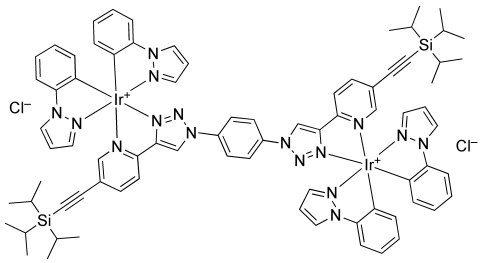


Compound 10b (*rel*-Δ,Δ-10b/*rel*-Δ,Λ-10b, 1/1). See the General procedure S3 (p S13). Column chromatography on silica gel using $CHCl_3$/MeOH (96/4 to 85/15) afforded the product (16 mg, 45%) as a yellow solid. Significant broadening of the ^1H and ^{13}C NMR signals, most likely due to the aggregation, disabled the interpretation of the ^1H and ^{13}C NMR spectra.



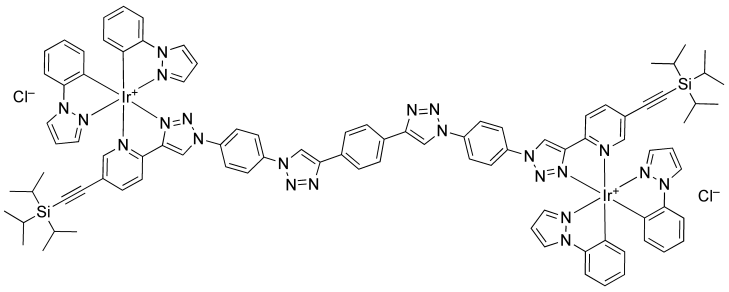
Mixture (1/1) of *rel*-Δ,Δ-10b and *rel*-Δ,Λ-10b. IR (neat, cm^{-1}) 3053, 2958, 2922, 2865, 1713, 1607, 1523, 1480, 1423, 1258, 1230, 1097, 1063, 1031, 845, 804, 757, 732, 705, 669, 612. HRMS (ESI) *m/z* calcd for $C_{123}H_{118}Ir_2N_{24}Si^+$ 2340.89523, found 2340.89408 ($|\Delta|$ = 0.49 ppm).

Compound 3c (*rel*-Δ,Δ-3c/*meso*-Δ,Λ-3c, 1/1). See the General procedure S3 (p S13). Column chromatography on silica gel using $CHCl_3$/MeOH (95/5 to 9/1) afforded the pure product (60 mg, 92%) as a yellow solid.



Mixture (1/1) of *rel*-Δ,Δ-3c and *meso*-Δ,Λ-3c. ^1H NMR (400 MHz, $CDCl_3$) δ 11.84 (s, 2H, $C_{Ar}H$), 11.84 (s, 2H, $C_{Ar}H$), 9.04 (d, J = 8.2 Hz, 2H, $C_{Ar}H$), 9.04 (d, J = 8.2 Hz, 2H, $C_{Ar}H$), 8.35 (s, 4H, $C_{Ar}H$), 8.35 (s, 4H, $C_{Ar}H$), 8.12 (dd, J = 3.0, 0.7 Hz, 2H, $C_{Ar}H$), 8.11 (dd, J = 3.0, 0.8 Hz, 2H, $C_{Ar}H$), 8.11 (dd, J = 3.0, 0.6 Hz, 2H, $C_{Ar}H$), 8.10 (dd, J = 3.0, 0.6 Hz, 2H, $C_{Ar}H$), 7.97 (dd, J = 8.2, 1.9 Hz, 2H, $C_{Ar}H$), 7.97 (dd, J = 8.2, 1.9 Hz, 2H, $C_{Ar}H$), 7.86 (dd, J = 1.9, 0.6 Hz, 2H, $C_{Ar}H$), 7.86 (dd, J = 1.9, 0.6 Hz, 2H, $C_{Ar}H$), 7.28 (ddd, J = 8.0, 1.2, 0.5 Hz, 2H, $C_{Ar}H$), 7.28 (ddd, J = 8.0, 1.1, 0.4 Hz, 2H, $C_{Ar}H$), 7.26 (ddd, J = 8.2, 1.3, 0.5 Hz, 2H, $C_{Ar}H$), 7.26 (ddd, J = 8.1, 1.2, 0.5 Hz, 2H, $C_{Ar}H$), 7.09 (dd, J = 2.3, 0.6 Hz, 2H, $C_{Ar}H$), 7.08 (dd, J = 2.3, 0.6 Hz, 2H, $C_{Ar}H$), 7.03 (ddd, J = 8.0, 7.3, 1.3 Hz, 2H, $C_{Ar}H$), 7.03 (ddd, J = 7.9, 7.4, 1.2 Hz, 2H, $C_{Ar}H$), 7.01 (ddd, J = 8.1, 7.4, 1.3 Hz, 2H, $C_{Ar}H$), 7.01 (ddd, J = 8.0, 7.3, 1.3 Hz, 2H, $C_{Ar}H$), 6.89 (dd, J = 2.3, 0.6 Hz, 2H, $C_{Ar}H$), 6.89 (dd, J = 2.3, 0.6 Hz, 2H, $C_{Ar}H$), 6.85 (ddd, J = 7.5, 7.4, 1.2 Hz, 2H, $C_{Ar}H$), 6.85 (ddd, J = 7.5, 7.4, 1.2 Hz, 2H, $C_{Ar}H$), 6.84 (ddd, J = 7.6, 7.5, 1.2 Hz, 2H, $C_{Ar}H$), 6.83 (ddd, J = 7.5, 7.5, 1.2 Hz, 2H, $C_{Ar}H$), 6.57 (dd, J = 2.9, 2.3 Hz, 2H, $C_{Ar}H$), 6.56 (dd, J = 2.9, 2.3 Hz, 2H, $C_{Ar}H$), 6.53 (dd, J = 2.9, 2.3 Hz, 2H, $C_{Ar}H$), 6.52 (dd, J = 2.9, 2.3 Hz, 2H, $C_{Ar}H$), 6.38 (ddd, J = 7.5, 1.2, 0.6 Hz, 2H, $C_{Ar}H$), 6.38 (ddd, J = 7.5, 1.2, 0.6 Hz, 2H, $C_{Ar}H$), 6.29 (ddd, J = 7.6, 1.2, 0.6 Hz, 2H, $C_{Ar}H$), 6.29 (ddd, J = 7.6, 1.2, 0.6 Hz, 2H, $C_{Ar}H$), 1.06–1.00 (m, 42H, $CH(CH_3)_2$), 1.06–1.00 (m, 42H, $CH(CH_3)_2$). ^{13}C NMR (75 MHz, $CDCl_3$) δ (31C overlapped) 152.6, 149.5, 148.8, 142.7, 142.5, 141.7, 138.9, 137.6, 136.3, 133.4, 133.1, 131.1, 126.9, 126.8, 126.7, 126.6, 126.44, 126.42, 124.0, 123.43, 123.36, 122.5, 121.8, 111.5, 111.3, 108.2, 107.9, 101.0, 99.7, 18.4, 10.9. IR (neat, cm^{-1}) 3058, 2956, 2941, 2921, 2865, 2160 (C≡C), 2040, 1714, 1607, 1579, 1520, 1481, 1467, 1411, 1336, 1274, 1263, 1230, 1058, 1033, 883, 845, 748, 730, 701, 667, 656. HRMS (ESI) *m/z* calcd for $C_{78}H_{82}Ir_2N_{16}Si_2^+$ 1680.56587, found 1680.56964 ($|\Delta|$ = 2.25 ppm).

Compound 4c (*rel*-Δ,Δ-4c/*meso*-Δ,Λ-4c, 1/1). See the General procedure S3 (p S13). Column chromatography on silica gel using $CHCl_3$/MeOH (96/4 to 9/1) afforded the pure product (17 mg, 43%) as a yellow solid.

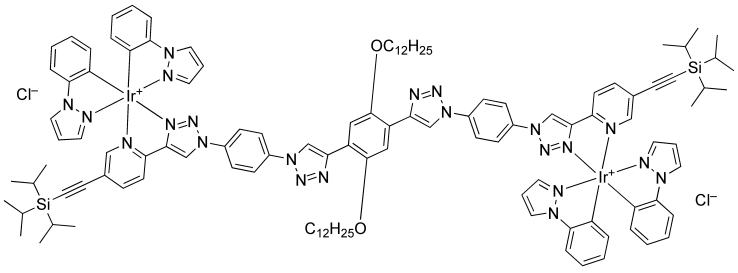


***rel*-Δ,Δ-4c.** (Measured from a 1/1 mixture of *rel*-Δ,Δ-**4c** and *meso*-Δ,Λ-**4c**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.95 (s, 2H, $C_{Ar}H$), 9.19 (d, J = 8.1 Hz, 2H, $C_{Ar}H$), 8.39–8.34 (m, 6H, $C_{Ar}H$), 8.15 (dd, J = 3.0, 0.5 Hz, 2H, $C_{Ar}H$), 8.14 (dd, J = 2.9, 0.5 Hz, 2H, $C_{Ar}H$), 8.00–7.95 (m, 10H, $C_{Ar}H$), 7.86 (dd, J = 1.9, 0.7 Hz, 2H, $C_{Ar}H$), 7.30–7.27 (m, 4H, $C_{Ar}H$), 7.13 (dd, J = 2.3, 0.5 Hz, 2H, $C_{Ar}H$), 7.06–7.00 (m, 4H, $C_{Ar}H$), 6.95 (dd, J = 2.4, 0.4 Hz, 2H, $C_{Ar}H$), 6.87 (ddd, J = 7.5, 7.5, 1.1 Hz, 2H, $C_{Ar}H$), 6.84 (ddd, J = 7.5, 7.5, 1.1 Hz, 2H, $C_{Ar}H$), 6.59 (dd, J = 2.8, 2.3 Hz, 2H, $C_{Ar}H$), 6.57 (dd, J = 2.9, 2.4 Hz, 2H, $C_{Ar}H$), 6.35 (ddd, J = 7.4, 1.1, 0.6 Hz, 2H, $C_{Ar}H$), 6.33 (ddd, J = 7.6, 1.2, 0.5 Hz, 2H, $C_{Ar}H$), 1.07–1.02 (m, 42H, CH(CH_3)$_2$). ^{13}C NMR (75 MHz, $CDCl_3$/CD_3OD (3/1)) δ 153.0, 149.3, 147.90, 147.85, 142.50, 142.46, 141.1, 138.5, 137.6, 137.4, 135.2, 133.1, 132.5, 130.0, 129.5, 127.0, 126.8, 126.5, 126.3, 125.9, 125.7, 123.9, 123.4, 122.8, 122.7, 122.2, 121.6, 121.0, 118.4, 111.4, 110.9, 108.0, 107.8, 100.3, 100.0, 17.8, 10.6.

***meso*-Δ,Λ-4c.** ^{1}H and ^{13}C NMR data are identical to *rel*-Δ,Δ-**4c** within the resolution limits of both NMR techniques.

Mixture (1/1) of *rel*-Δ,Δ-4b and *meso*-Δ,Λ-4b. IR (neat, cm^{-1}) 3057, 2959, 2939, 2924, 2862, 2160 (C≡C), 1524, 1480, 1467, 1412, 1264, 1064, 1034, 1017, 801, 747, 697, 669. HRMS (ESI) *m/z* calcd for $C_{94}H_{92}Ir_2N_{22}Si_2^+$ 1970.66723, found 1970.66850 (|Δ| = 0.65 ppm).

Compound 5c (*rel*-Δ,Δ-5c/*meso*-Δ,Λ-5c, 1/1). See the General procedure S3 (p S13). Column chromatography on silica gel using $CHCl_3$/MeOH (85/15) afforded the pure product (23 mg, >99%) as a yellow solid.

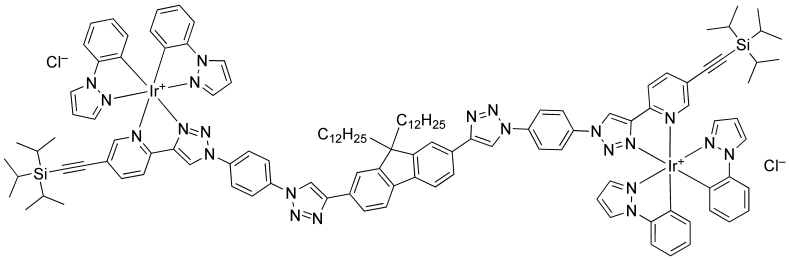


***rel*-Δ,Δ-5c.** (Measured from a 1/1 mixture of *rel*-Δ,Δ-**5c** and *meso*-Δ,Λ-**5c**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.81 (s, 2H, $C_{Ar}H$), 9.20 (dd, J = 8.4, 0.5 Hz, 2H, $C_{Ar}H$), 8.61 (s, 2H, $C_{Ar}H$), 8.40–8.34 (m, 4H, AA′ of AA′XX′), 8.14–8.11 (m, 4H, $C_{Ar}H$), 8.09 (s, 2H, $C_{Ar}H$), 8.03 (dd, J = 8.3, 1.8 Hz, 2H, $C_{Ar}H$), 8.01–7.95 (m, 4H, XX′ of AA′XX′), 7.87 (dd, J = 1.9, 0.6 Hz, 2H, $C_{Ar}H$), 7.28 (ddd, J = 7.9, 1.4, 0.4 Hz, 2H, $C_{Ar}H$), 7.28 (ddd, J = 8.1, 1.2, 0.5 Hz, 2H, $C_{Ar}H$), 7.13 (dd, J = 2.3, 0.5 Hz, 2H, $C_{Ar}H$), 7.05 (ddd, J = 8.1, 7.5, 1.4 Hz, 2H, $C_{Ar}H$), 7.04 (ddd, J = 7.9, 7.4, 1.3 Hz, 2H, $C_{Ar}H$), 6.95 (dd, J = 2.4, 0.5 Hz, 2H, $C_{Ar}H$), 6.88 (ddd, J = 7.5, 7.5, 1.0 Hz, 2H, $C_{Ar}H$), 6.86 (ddd, J = 7.5, 7.4, 1.0 Hz, 2H, $C_{Ar}H$), 6.60 (dd, J = 2.7, 2.4 Hz, 2H, $C_{Ar}H$), 6.58 (dd, J = 2.8, 2.4 Hz, 2H, $C_{Ar}H$), 6.36 (ddd, J = 7.4, 1.2, 0.5 Hz, 2H, $C_{Ar}H$), 6.35 (ddd, J = 7.5, 1.3, 0.6 Hz, 2H, $C_{Ar}H$), 4.26 (t, J = 6.9 Hz, 4H, OCH_2), 1.98 (tt, J = 7.1, 7.0 Hz, 4H, CH_2), 1.57–1.47 (m, 4H, CH_2), 1.46–1.35 (m, 4H, CH_2), 1.35–1.17 (m, 28H, CH_2), 1.08–1.00 (m, 42H, CH(CH_3)$_2$), 0.87–0.81 (m, 6H, CH_2CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.7, 149.8, 149.6, 148.9, 144.2, 142.7, 142.0, 138.9, 137.9, 137.7, 135.6, 133.6, 133.1, 131.0, 127.2, 127.0, 126.9, 126.7, 126.5, 126.3, 124.3, 123.6, 123.0, 122.6, 121.8, 121.4, 120.8, 118.9, 111.6, 111.2, 110.91, 110.89, 108.3, 108.1, 101.0, 99.8, 69.0, 31.9, 29.63, 29.58, 29.56, 29.5, 29.4, 29.28, 29.26, 26.0, 22.6, 18.5, 14.1, 11.1.

***meso*-Δ,Λ-5c.** ^{1}H and ^{13}C NMR data are identical to *rel*-Δ,Δ-**5c** within the resolution limits of both NMR techniques.

Mixture (1/1) of *rel*-Δ,Δ-5b and *meso*-Δ,Λ-5b. IR (neat, cm^{-1}) 3055, 2922, 2857, 2160 (C≡C), 1607, 1578, 1523, 1481, 1464, 1408, 1337, 1246, 1201, 1061, 1033, 881, 844, 750, 696, 670. HRMS (ESI) *m/z* calcd for $C_{118}H_{140}Ir_2N_{22}O_2Si_2^+$ 2335.02799, found 2335.04193 (|Δ| = 5.97 ppm).

Compound 6c (*rel*-Δ,Δ-6c/*meso*-Δ,Λ-6c, 1/1). See the General procedure S3 (p S13). Column chromatography on silica gel using $CHCl_3$/MeOH (96/4 to 92/8) afforded the pure product (43 mg, 99%) as a yellow solid.

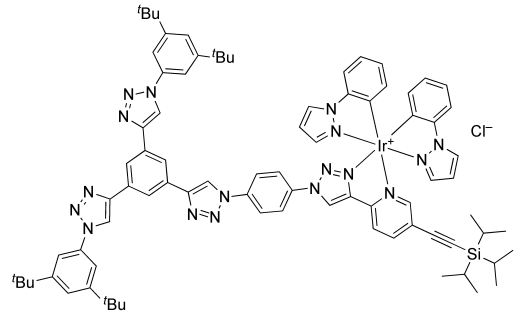


***rel*-Δ,Δ-6c.** (Measured from a 1/1 mixture of *rel*-Δ,Δ-**6c** and *meso*-Δ,Λ-**6c**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.01 (s, 2H, $C_{Ar}H$), 9.23 (dd, J = 8.2, 0.4 Hz, 2H, $C_{Ar}H$), 8.45–8.39 (m, 4H, AA′ of AA′XX′), 8.31 (s, 2H, $C_{Ar}H$), 8.13 (dd, J = 3.0, 0.6 Hz, 2H, $C_{Ar}H$), 8.13 (dd, J = 3.0, 0.6 Hz, 2H, $C_{Ar}H$), 8.03 (dd, J = 8.1, 2.0 Hz, 2H, $C_{Ar}H$), 8.03–7.99 (m, 4H, XX′ of AA′XX′), 7.98 (dd, J = 2.1, 0.5 Hz, 2H, $C_{Ar}H$), 7.88 (dd, J = 1.9, 0.7 Hz, 2H, $C_{Ar}H$), 7.87 (dd, J = 7.6, 1.8 Hz, 2H, $C_{Ar}H$), 7.80 (dd, J = 7.6, 0.6 Hz, 2H, $C_{Ar}H$), 7.31–7.27 (m, 4H, $C_{Ar}H$), 7.13 (dd, J = 2.4, 0.6 Hz, 2H, $C_{Ar}H$), 7.05 (ddd, J = 7.9, 7.4, 1.3 Hz, 2H, $C_{Ar}H$), 7.04 (ddd, J = 7.9, 7.4, 1.3 Hz, 2H, $C_{Ar}H$), 6.94 (dd, J = 2.3, 0.6 Hz, 2H, $C_{Ar}H$), 6.88 (ddd, J = 7.5, 7.5, 1.2 Hz, 2H, $C_{Ar}H$), 6.86 (ddd, J = 7.5, 7.5, 1.2 Hz, 2H, $C_{Ar}H$), 6.60 (dd, J = 2.8, 2.3 Hz, 2H, $C_{Ar}H$), 6.58 (dd, J = 2.9, 2.3 Hz, 2H, $C_{Ar}H$), 6.36 (dd, J = 7.4, 1.3 Hz, 2H, $C_{Ar}H$), 6.35 (dd, J = 7.5, 1.3 Hz, 2H, $C_{Ar}H$), 2.15–2.04 (m, 4H, CCH_2), 1.33–0.92 (m, 78H, CH_2 + $CH(CH_3)_2$), 0.85–0.77 (m, 6H, CH_2CH_3), 0.72–0.61 (m, 4H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.7, 151.9, 149.8, 149.2, 148.9, 142.7, 141.9, 141.1, 138.9, 137.9, 137.5, 135.6, 133.6, 133.1, 130.9, 128.8, 127.1, 127.0, 126.92, 126.85, 126.6, 126.2, 124.82, 124.81, 124.3, 123.6, 123.0, 122.6, 121.8, 121.4, 120.3, 120.2, 117.4, 111.6, 111.2, 108.3, 108.0, 101.0, 99.9, 55.5, 40.4, 31.8, 30.0, 29.6, 29.51, 29.49, 29.46, 29.3, 29.2, 23.9, 22.6, 18.5, 14.0, 11.0.

***meso*-Δ,Λ-6c.** ^{1}H and ^{13}C NMR data are identical to *rel*-Δ,Δ-**6c** within the resolution limits of both NMR techniques.

Mixture (1/1) of *rel*-Δ,Δ-6c and *meso*-Δ,Λ-6c. IR (neat, cm^{-1}) 3058, 2923, 2852, 2160 (C≡C), 2043, 1610, 1582, 1521, 1481, 1462, 1408, 1337, 1265, 1225, 1061, 1034, 994, 884, 840, 746, 733, 699, 670, 657. HRMS (ESI) *m/z* calcd for $C_{125}H_{144}Ir_2N_{22}Si_2^+$ 2391.06946, found 2391.07614 (|Δ| = 2.79 ppm).

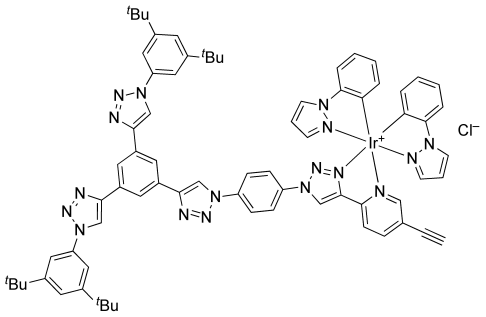
Compound 8c. See the General procedure S3 (p S13). Column chromatography on silica gel using $CHCl_3$/MeOH (99/1 and 95/5) and subsequent crystallisation from CH_2Cl_2/MeCN afforded the pure product (16 mg, 50%) as a yellow solid.



^{1}H NMR (400 MHz, $CDCl_3$) δ 11.46 (s, 1H, $C_{Ar}H$), 8.92 (s, 1H, $C_{Ar}H$), 8.82–8.70 (m, 1H, $C_{Ar}H$), 8.75 (s, 2H, $C_{Ar}H$), 8.50 (d, J = 1.4 Hz, 2H, $C_{Ar}H$), 8.46 (t, J = 1.6 Hz, 1H, $C_{Ar}H$), 8.29–8.23 (m, 2H, AA′ of AA′XX′), 8.16 (dd, J = 2.7, 0.4 Hz, 1H, $C_{Ar}H$), 8.09 (dd, J = 2.8, 0.6 Hz, 1H, $C_{Ar}H$), 8.03–7.98 (m, 2H, XX′ of AA′XX′), 7.75 (dd, J = 1.9, 0.6 Hz, 1H, $C_{Ar}H$), 7.72–7.67 (m, 1H, $C_{Ar}H$), 7.70 (d, J = 1.7 Hz, 4H, $C_{Ar}H$), 7.56–7.52 (m, 1H, $C_{Ar}H$), 7.54 (t, J = 1.7 Hz, 2H, $C_{Ar}H$), 7.32 (dd, J = 8.1, 0.9 Hz, 1H, $C_{Ar}H$), 7.27–7.23 (m, 1H, $C_{Ar}H$), 7.04 (ddd, J = 7.8, 7.3, 1.2 Hz, 1H, $C_{Ar}H$), 7.02 (ddd, J = 8.0, 7.3, 1.2 Hz, 1H, $C_{Ar}H$), 6.89–6.82 (m, 3H, $C_{Ar}H$), 6.70 (dd, J = 2.6, 2.4 Hz, 1H, $C_{Ar}H$), 6.56 (dd, J = 2.6, 2.6 Hz, 1H, $C_{Ar}H$), 6.38 (dd, J = 7.6, 1.2 Hz, 1H, $C_{Ar}H$), 6.32 (dd, J = 7.4, 1.2 Hz, 1H, $C_{Ar}H$), 1.43 (s, 36H, CCH_3), 1.03–0.94 (m, 21H, $CH(CH_3)_2$). ^{13}C NMR (75 MHz, $CDCl_3$) δ (3C overlapped) 152.9, 152.8,

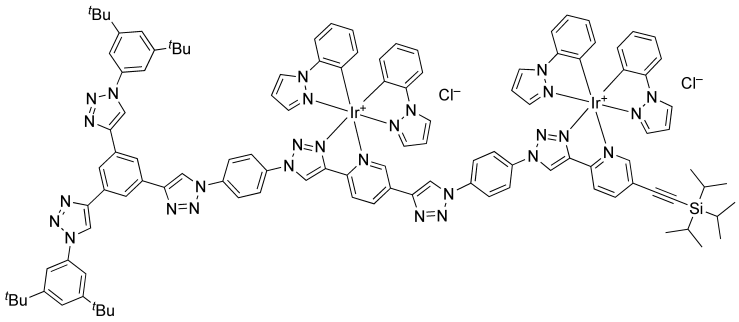
149.7, 148.7, 148.0, 147.3, 142.9, 142.8, 141.4, 139.6, 137.8, 137.2, 136.7, 135.5, 133.7, 133.1, 131.8, 131.2, 131.1, 127.3, 127.0, 126.8, 126.5, 126.3, 123.6, 123.5, 122.9, 122.6, 122.3, 121.9, 121.4, 119.2, 118.9, 115.2, 111.6, 111.2, 108.4, 108.1, 101.1, 99.5, 35.2, 31.4, 18.5, 11.0. IR (neat, cm^{-1}) 3057, 2961, 2864, 2159 (C≡C), 1593, 1521, 1479, 1464, 1409, 1363, 1249, 1231, 1060, 1035, 993, 879, 847, 788, 749, 696, 671. HRMS (ESI) *m/z* calcd for $C_{82}H_{91}IrN_{17}Si^+$ 1534.70418, found 1534.69669 ($|\Delta|$ = 4.88 ppm).

Compound 9c. See the General procedure S3 (p S13). Column chromatography on silica gel using $CHCl_3$/MeOH (95/5 and 9/1) afforded the pure product (10 mg, 64%) as a yellow solid.



^1H NMR (400 MHz, $CDCl_3$) δ 11.09 (s, 1H, $C_{Ar}H$), 9.15 (s, 1H, $C_{Ar}H$), 8.86 (s, 2H, $C_{Ar}H$), 8.48–8.42 (m, 2H, $C_{Ar}H$), 8.42–8.35 (m, 1H, $C_{Ar}H$), 8.35–8.32 (m, 1H, $C_{Ar}H$), 8.20 (d, J = 2.8 Hz, 1H, $C_{Ar}H$), 8.19–8.13 (m, 2H, AA′ of AA′BB′), 8.05 (d, J = 2.8 Hz, 1H, $C_{Ar}H$), 8.02–7.95 (m, 2H, BB′ of AA′BB′), 7.91–7.84 (m, 1H, $C_{Ar}H$), 7.72 (d, J = 1.6 Hz, 4H, $C_{Ar}H$), 7.70–7.67 (m, 1H, $C_{Ar}H$), 7.57 (bd, J = 7.9 Hz, 1H, $C_{Ar}H$), 7.54 (t, J = 1.6 Hz, 2H, $C_{Ar}H$), 7.30 (d, J = 7.7 Hz, 1H, $C_{Ar}H$), 7.22 (d, J = 8.0 Hz, 1H, $C_{Ar}H$), 7.01 (ddd, J = 7.7, 7.6, 1.1 Hz, 1H, $C_{Ar}H$), 6.98 (ddd, J = 7.9, 7.6, 1.1 Hz, 1H, $C_{Ar}H$), 6.88 (ddd, J = 7.5, 7.4, 0.9 Hz, 1H, $C_{Ar}H$), 6.84–6.79 (m, 2H, $C_{Ar}H$), 6.74–6.71 (m, 1H, $C_{Ar}H$), 6.51 (dd, J = 2.5, 2.4 Hz, 1H, $C_{Ar}H$), 6.38 (ddd, J = 7.8, 1.0, 0.5 Hz, 1H, $C_{Ar}H$), 6.24 (ddd, J = 7.4, 1.3, 0.5 Hz, 1H, $C_{Ar}H$), 3.07 (s, 1H, CC*H*), 1.45 (s, 36H, CCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.8, 152.4, 149.3, 149.2, 147.7, 147.1, 143.0, 142.7, 142.0, 140.4, 137.6, 136.9, 136.8, 135.1, 133.7, 132.9, 131.8, 131.0, 130.9, 127.2, 126.50, 126.46, 126.3, 125.9, 123.46, 123.45, 122.9, 122.81, 122.80, 122.4, 121.64, 121.62, 121.2, 120.5, 119.6, 119.4, 115.2, 111.6, 111.1, 108.6, 108.0, 83.4, 78.4, 35.3, 31.5. IR (neat, cm^{-1}) 3298 (CC-H), 3059, 2963, 2930, 2867, 2118 (C≡C), 2048, 1609, 1592, 1521, 1479, 1414, 1365, 1261, 1062, 1038, 848, 800, 749, 705, 608. HRMS (ESI) *m/z* calcd for $C_{73}H_{71}IrN_{17}^+$ 1376.56842, found 1376.56449 ($|\Delta|$ = 2.86 ppm).

Compound 10c (*rel*-Δ,Δ-10c/*rel*-Δ,Λ-10c, 1/1). See the General procedure S3 (p S13). Column chromatography on silica gel using $CHCl_3$/MeOH (9/1 to 8/2) afforded the pure product (20 mg, 33%) as a yellow solid.



***rel*-Δ,Δ-10c.** (Measured from a 1/1 mixture of *rel*-Δ,Δ-**10c** and *rel*-Δ,Λ-**10c**) ^1H NMR (400 MHz, DMSO-d_6) δ 10.40 (s, 1H, $C_{Ar}H$), 10.37 (s, 1H, $C_{Ar}H$), 9.83 (s, 1H, $C_{Ar}H$), 9.66 (s, 2H, $C_{Ar}H$), 9.64 (s, 1H, $C_{Ar}H$), 8.94 (d, J = 2.8 Hz, 1H, $C_{Ar}H$), 8.93–8.89 (m, 3H, $C_{Ar}H$), 8.72–8.59 (m, 6H, $C_{Ar}H$), 8.45 (d, J = 7.9 Hz, 1H, $C_{Ar}H$), 8.40–8.32 (m, 3H, $C_{Ar}H$), 8.22–8.06 (m, 6H, $C_{Ar}H$), 7.84 (d, J = 1.4 Hz, 4H, $C_{Ar}H$), 7.80 (d, J = 1.3 Hz, 1H, $C_{Ar}H$), 7.75–7.61 (m, 6H, $C_{Ar}H$), 7.59–7.56 (m, 1H, $C_{Ar}H$), 7.56 (t, J = 1.4 Hz, 2H, $C_{Ar}H$), 7.50–7.46 (m, 1H, $C_{Ar}H$), 7.11 (dd, J = 8.1, 7.5 Hz, 1H, $C_{Ar}H$), 7.06 (dd, J = 8.1, 7.4 Hz, 1H, $C_{Ar}H$), 7.03–6.96 (m, 2H, $C_{Ar}H$), 6.93 (dd, J = 7.5, 7.3 Hz, 1H, $C_{Ar}H$), 6.86 (dd, J = 7.6, 7.3 Hz, 1H, $C_{Ar}H$), 6.84–6.71 (m, 6H, $C_{Ar}H$), 6.25 (d, J = 2.5 Hz, 1H, $C_{Ar}H$), 6.24 (d, J = 2.4 Hz, 1H, $C_{Ar}H$), 6.20 (d, J = 7.4 Hz, 1H, $C_{Ar}H$), 6.20 (d, J = 7.4 Hz, 1H, $C_{Ar}H$), 1.40 (s, 36H, CCH_3), 1.04–0.99 (m, 21H, C*H*(CH_3)$_2$). ^{13}C NMR (75 MHz, DMSO-d_6) δ 152.5, 149.3, 148.9, 148.63, 148.58, 147.2, 146.6, 146.3, 143.12, 143.07, 143.03, 143.00, 142.0, 140.1–139.0 (m), 137.3, 136.8, 136.4, 135.8, 135.5, 133.3–132.8 (m), 132.4, 132.2, 132.0, 131.4, 131.1, 131.0, 129.0–128.3 (m), 127.7, 127.4, 126.4, 126.3, 126.0, 125.7, 125.4, 123.4, 122.9, 122.73, 122.68, 122.4, 122.0, 121.4, 121.2, 120.6, 114.6, 112.2, 111.8, 111.7, 108.6, 108.5, 101.8, 97.9, 35.0, 31.1, 18.3, 10.5.

***rel*-Δ,Λ-10c.** ^{1}H and ^{13}C NMR data are identical to *rel*-Δ,Δ-**10c** within the resolution limits of both NMR techniques.

Mixture (1/1) of *rel*-Δ,Δ-10c and *rel*-Δ,Λ-10c. IR (neat, cm^{-1}) 3054, 2957, 2918, 2849, 2161 (C≡C), 1722, 1596, 1524, 1482, 1464, 1411, 1260, 1063, 1032, 843, 804, 747, 699. HRMS (ESI) *m/z* calcd for $C_{115}H_{114}Ir_2N_{28}Si^+$ 2296.87623, found 2296.87427 (|Δ| = 0.85 ppm).

Compound 11c. See the General procedure S2 (p S2): **9c** (8 mg, 6 μmol), azidocyclohexane (14 mg, 0.11 mmol), CuI (2 mg, 0.01 mmol), THF (2 mL), PMDTA (3 mg, 0.02 mmol), room temperature, 21 h. Column chromatography on silica gel using CH_2Cl_2 and CH_2Cl_2/MeOH (97.5/2.5) afforded the pure product (5.3 mg, 61%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.35 (s, 1H, $C_{Ar}H$), 9.35 (s, 1H, $C_{Ar}H$), 8.68 (m, 2H, $C_{Ar}H$), 8.42–8.33 (m, 2H, $C_{Ar}H$), 8.30–8.19 (m, 3H, $C_{Ar}H$), 8.13 (d, J = 2.7 Hz, 1H, $C_{Ar}H$), 8.11–8.03 (m, 4H, AA′BB′), 8.11–8.03 (m, 1H, $C_{Ar}H$), 8.01 (d, J = 2.7 Hz, 1H, $C_{Ar}H$), 7.82–7.79 (m, 1H, $C_{Ar}H$), 7.76 (d, J = 1.4 Hz, 4H, $C_{Ar}H$), 7.58–7.53 (m, 1H, $C_{Ar}H$), 7.56 (t, J = 1.6 Hz, 2H, $C_{Ar}H$), 7.19 (d, J = 8.1 Hz, 1H, $C_{Ar}H$), 7.08 (d, J = 8.0 Hz, 1H, $C_{Ar}H$), 7.00 (ddd, J = 7.8, 7.6, 1.2 Hz, 1H, $C_{Ar}H$), 6.92–6.80 (m, 3H, $C_{Ar}H$), 6.81 (ddd, J = 7.4, 7.4, 1.2 Hz, 1H, $C_{Ar}H$), 6.70–6.66 (m, 1H, $C_{Ar}H$), 6.45 (dd, J = 2.7, 2.4 Hz, 1H, $C_{Ar}H$), 6.45–6.42 (m, 1H, $C_{Ar}H$), 6.27 (dd, J = 7.1, 1.5 Hz, 1H, $C_{Ar}H$), 4.32 (tt, J = 11.5, 3.5 Hz, 1H, C*H*), 2.16–2.06 (m, 2H, CH*H*), 1.94–1.83 (m, 2H, CH*H*), 1.82–1.21 (m, 6H, CH*H*), 1.48 (s, 36H, CCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ (1C overlapped) 152.9, 149.8, 147.9, 147.3, 147.1, 146.6, 142.9, 142.7, 142.0, 140.9, 137.6, 137.0, 136.8, 135.0, 133.8, 133.0, 131.8, 131.3, 131.0, 128.8, 127.6, 127.2, 126.5, 126.4, 124.1, 123.4, 123.2, 123.0, 122.84, 122.80, 122.3, 122.0, 121.2, 120.2, 119.9, 119.73, 119.68, 115.3, 111.4, 111.0, 108.3, 107.8, 60.4, 35.4, 33.3, 31.5, 25.1, 22.7. IR (neat, cm^{-1}) 3062, 2959, 2936, 2863, 1592, 1524, 1480, 1449, 1414, 1362, 1247, 1230, 1061, 1036, 846, 749. HRMS (ESI) *m/z* calcd for $C_{79}H_{82}IrN_{20}^+$ 1501.66372, found 1501.66956 (|Δ| = 3.89 ppm).

Compound 12c (*rel*-Δ,Δ-*trans*-12c and *rel*-Δ,Λ-*trans*-12c, 1/1). See the General procedure S3 (p S13). Column chromatography on silica gel using $CHCl_3$/MeOH (99/1) and $CHCl_3$/MeOH (8/2) afforded the pure product as a mixture of *cis*- and *trans*-isomer. The major *trans*-isomer was separated from the minor *cis*-isomer by a preparative TLC using $CHCl_3$/MeOH (92/18). Subsequent purification by column chromatography on silica gel using $CHCl_3$/MeOH (99.5/0.5, 99/1, 95/5, 9/1 and 8/2) afforded the pure *trans*-isomer (7.0 mg, 30%) as a yellow solid. The high noise to signal ratio did not allow for a reliable description of the ^{13}C NMR signals.

***rel*-Δ,Δ-*trans*-12c.** (Measured from a 1/1 mixture of *rel*-Δ,Δ-*trans*-**12c** and *rel*-Δ,Λ-*trans*-**12c**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.41 (s, 1H, $C_{Ar}H$), 10.31 (s, 1H, $C_{Ar}H$), 8.98 (s, 1H, $C_{Ar}H$), 8.73–8.56 (m, 3H, $C_{Ar}H$), 8.56–8.45 (m, 1H, $C_{Ar}H$), 8.43–8.27 (m, 4H, $C_{Ar}H$), 8.18–7.91 (m, 11H, $C_{Ar}H$), 7.87–7.84 (m, 1H, $C_{Ar}H$), 7.76–7.64 (m, 5H, $C_{Ar}H$), 7.54–7.50 (m, 2H, $C_{Ar}H$), 7.29–7.25 (m, 2H, $C_{Ar}H$), 7.23 (d, J = 8.1 Hz, 1H, $C_{Ar}H$), 7.18 (bd, J = 8.0 Hz, 1H, $C_{Ar}H$), 7.06–6.79 (m, 11H, $C_{Ar}H$), 6.76–6.71 (m, 1H, $C_{Ar}H$), 6.62–6.55 (m, 2H, $C_{Ar}H$), 6.52–6.47 (m, 1H, $C_{Ar}H$), 6.41 (d, J = 7.5 Hz, 1H, $C_{Ar}H$), 6.34 (d, J = 7.5 Hz, 1H, $C_{Ar}H$), 6.30 (d, J = 7.3 Hz, 1H, $C_{Ar}H$), 6.30 (d, J = 7.3 Hz, 1H, $C_{Ar}H$), 4.77–4.67 (m, 1H, NC*H*), 4.67–4.57 (m, 1H, NC*H*), 2.47–1.53 (m, 8H, CH*H*), 1.43 (s, 36H, CCH_3), 1.09–1.00 (m, 21H, C*H*(CH_3)$_2$).

***rel*-Δ,Λ-*trans*-12c.** ^{1}H NMR data are identical to *rel*-Δ,Δ-*trans*-**10c** within the resolution limits of the NMR technique.

Mixture (1/1) of *rel*-Δ,Δ-*trans*-12c and *rel*-Δ,Λ-*trans*-12c. IR (neat, cm^{-1}) 3054, 2959, 2924, 2863, 2163 (C≡C), 1724, 1591, 1523, 1482, 1412, 1260, 1083, 1060, 1036, 1018, 798, 752, 700, 669. HRMS (ESI) *m/z* calcd for $C_{115}H_{120}Ir_2N_{28}Si^+$ 2302.92318, found 2302.93289 ($|\Delta| = 4.21$ ppm).

Photophysical Characterisation

Table S1. *Photophysical characterisation data of the studied iridium complexes.*

Cmpd	Absorbance[a]	Emission at room temperature[a,b]					Emission at 77 K[b]
	ε_{355} ($\times 10^4$ M^{-1} cm^{-1})	λ_{max} (nm)	Φ_{air}	Φ_{argon}	τ_{air} (μs)	τ_{argon} (μs)	τ (μs)
3b	0.57	551	0.01	0.05	0.16	0.20	4.1
4b	0.66	513	0.02	0.08	1.3 (18%) 0.34 (82%)	1.8 (25%) 0.78 (75%)	4.3
5b	1.2	553	0.03	0.14	1.53 (60%) 0.40 (40%)	2.10 (23%) 0.91 (77%)	[c]
6b	2.2	546	0.01	0.03	2.1 (3%) 0.50 (97%)	8.0 (1%) 1.6 (99%)	[c]
7b	0.47	543	0.03	0.08	1.82 (10%) 0.80 (90%)	1.78 (20%) 0.69 (80%)	[c]
8b	0.27	550	0.03	0.19	0.14	0.21	4.4
10b	0.63	518	0.02	0.05	0.17 (17%) 0.04 (83%)	1.6 (61%) 0.31 (39%)	4.5 (25%) 1.7 (75%)
3c	0.34	539	0.02	0.05	0.43 (31%) 0.20 (69%)	0.31 (75%) 0.11 (11%)	15.0 (40%) 4.0 (60%)
4c	0.41	547	0.04	0.05	0.54 (12%) 0.20 (88%)	2.10 (24%) 0.86 (76%)	17.5 (22%) 5.43 (78%)
5c	1.3	540	0.01	0.04	0.54 (10%) 0.2 (90%)	0.69 (4%) 0.19 (90%)	[c]
6c	2.0	544	0.001	0.005	0.34 (62%) 0.05 (38%)	2.00 (11%) 0.47 (89%)	[c]
8c	0.15	540	0.02	0.08	0.58 (25%) 0.19 (75%)	0.56 (51%) 0.25 (49%)	17.0 (44%) 4.8 (56%)
10c	0.63	511	0.04	0.34	0.42 (74%) 0.10 (26%)	0.66 (30%) 0.18 (70%)	14.0 (30%) 3.3 (70%)
11c	0.22	507	0.01	0.03	0.5 (3%) 0.17 (97%)	1.0 (13%) 0.3 (87%)	24.0 (23%) 5.0 (77%)
12c	0.10	507	0.03	0.10	2.3 (39%) 0.7 (61%)	2.3 (15%) 0.84 (85%)	17.0 (50%) 4.5 (50%)

[a] Measured in THF/CH_2Cl_2 (9/1). [b] Excitation at 355 nm. [c] These compounds showed a very high scattering in the rigid matrix that did not allow a good statistical analysis of the time resolved data.

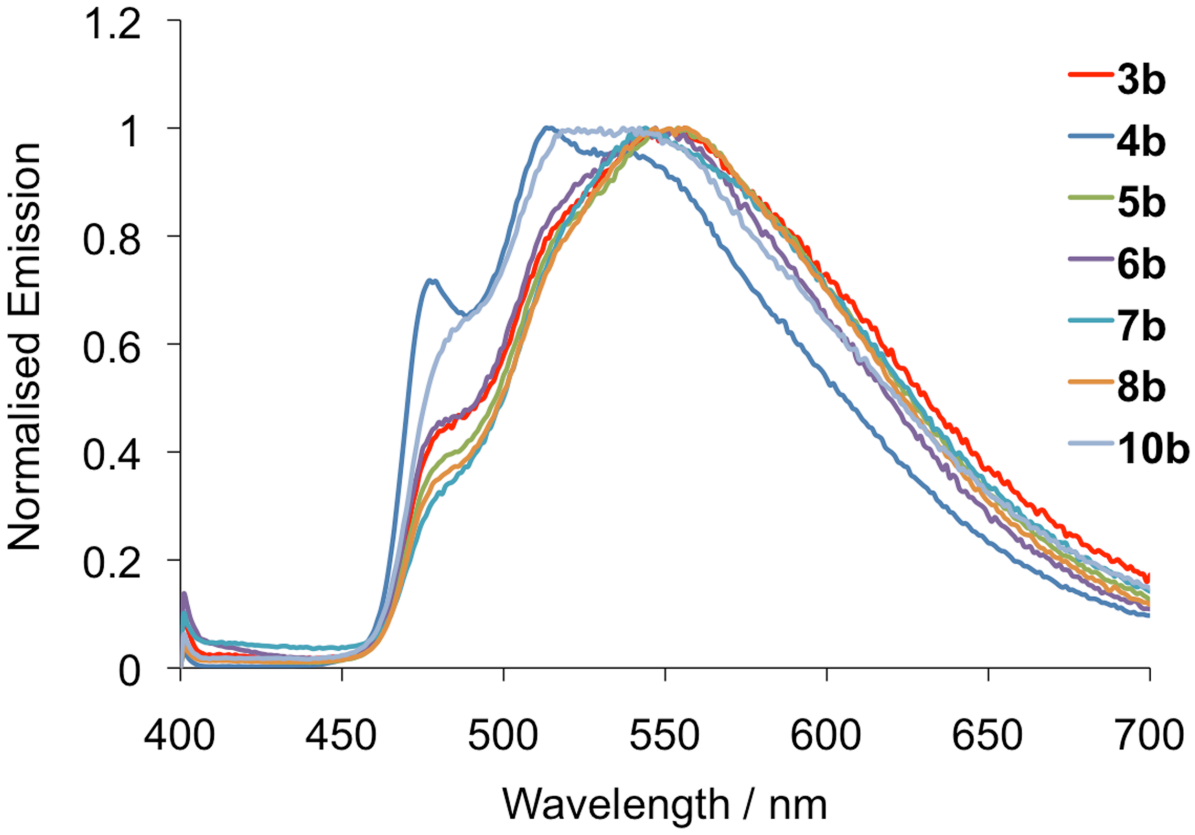


Figure S1. *Emission profiles at room temperature of compounds **3b**–**8b** and **10b** (excitation at 355 nm).*

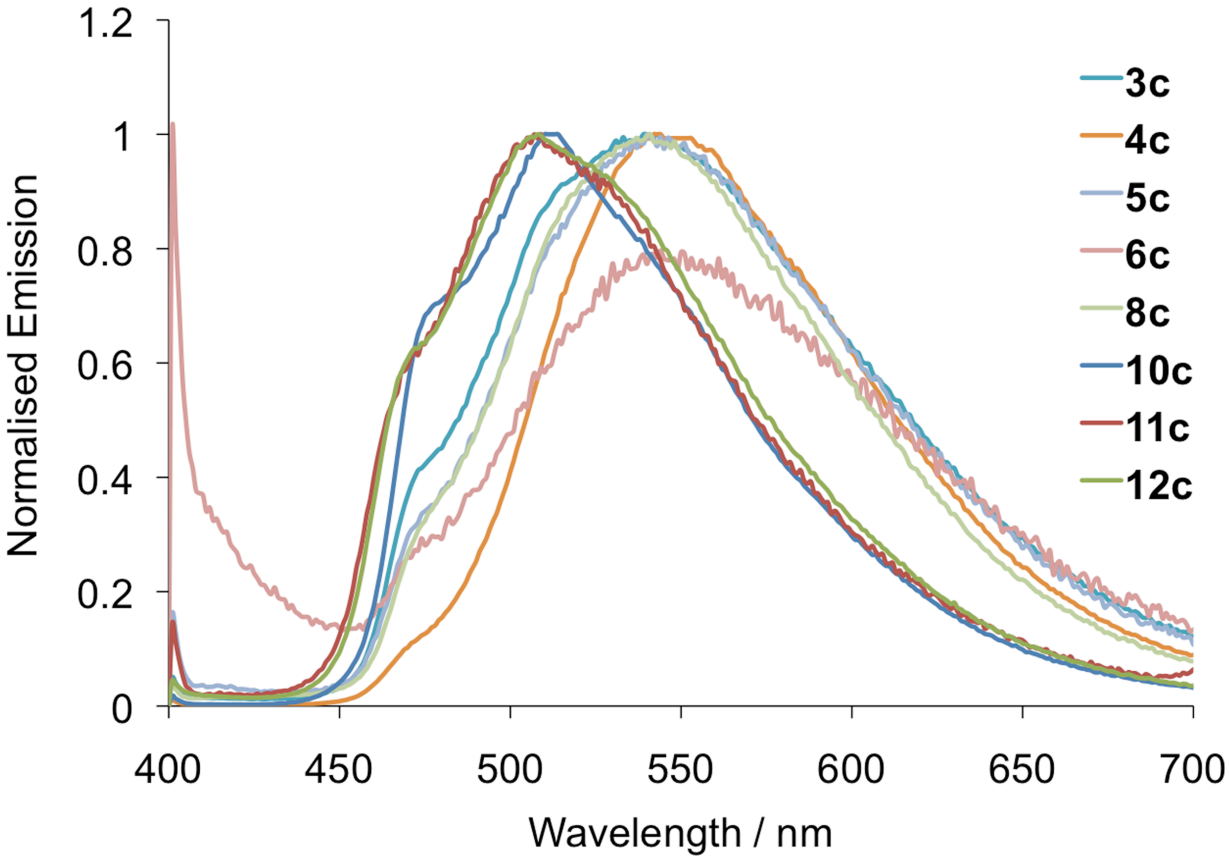


Figure S2. *Emission profiles at room temperature of compounds* ***3c–8c*** *and* ***10c–12c*** *(excitation at 355 nm).*

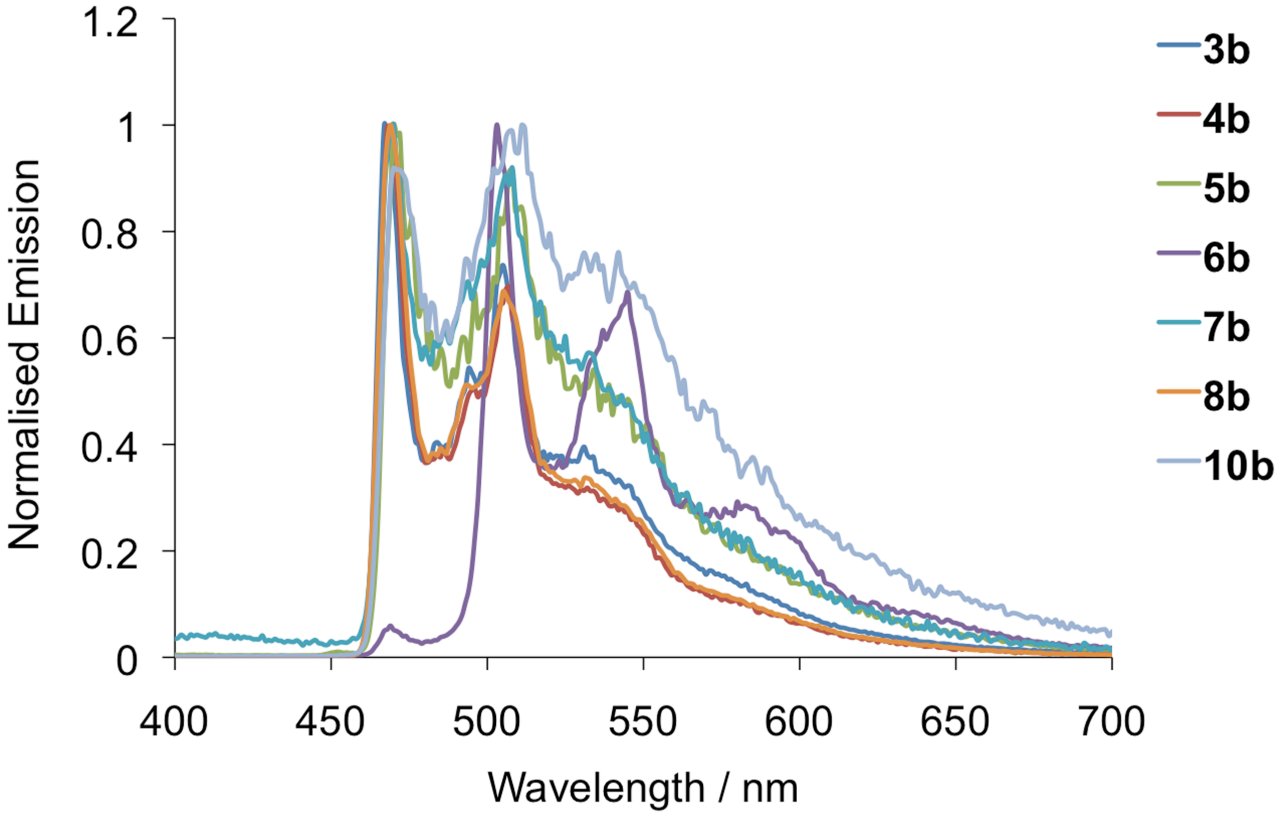


Figure S3. *Emission profiles at 77 K of compounds **3b–8b** and **10b** (excitation at 355 nm).*

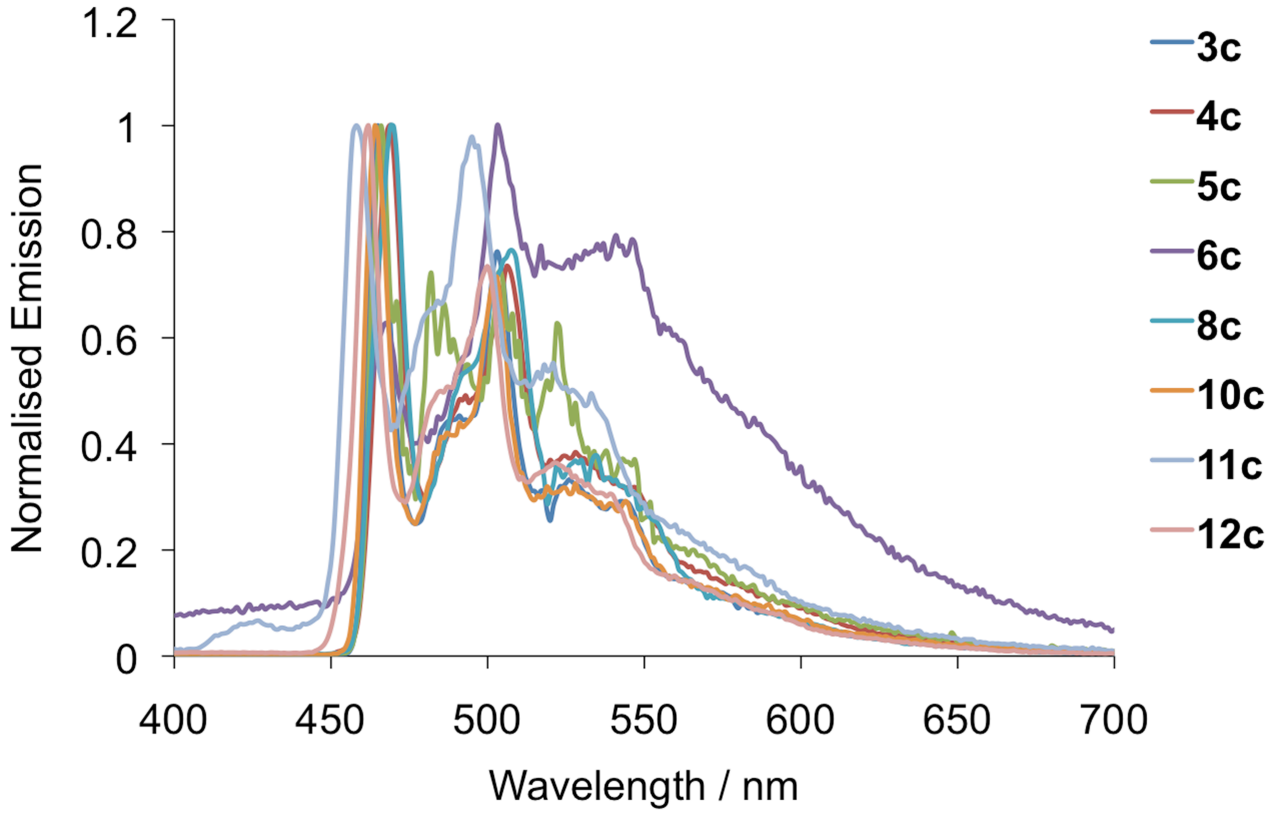


Figure S4. *Emission profiles at 77 K of compounds* ***3c–8c*** *and* ***10c–12c*** *(excitation at 355 nm).*

Electrochemical Characterisation

Table S2. *Cyclic voltammetry characterisation data of the selected iridium complexes.*[a]

Entry	Cmpd	Oxidation		Reduction
		E_{ox} (V)	$E_{1/2}$ (V)	E_{red} (V)
1	**3b**	[b]	[c]	-1.83[d]
2	**5b**	[b]	[c]	[b]
3	**6b**	[b]	[c]	-1.80[d]
4	**8b**	[b]	[c]	-1.84[d]
5	**3c**	+1.01[e]	+0.98	-1.83[d]
6	**5c**	[b]	[c]	[b]
7	**6c**	[b]	[c]	[b]
8	**8c**	[b]	[c]	-1.85[d]

[a] Cyclic voltammetry measurements were performed on an Eco Chemie Autolab PGSTAT20 instrument at a scan rate of 0.1 V s^{-1} using MeCN as a solvent. A conventional three-electrode cell with Pt working and auxiliary electrodes, and $Ag/AgNO_3$ reference electrode was used. A solution of tetrabutylammonium hexafluorophosphate(V) (TBAH) in MeCN (0.1M) was used as an electrolyte. [b] Not reproducible. [c] Not applicable. [d] Irreversible. [e] Irreversible oxidation of Cl^- was observed at +0.54 V.

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