Synthesis V. Hutskalova, C. Sparr THIEME OPEN ACCESS Paper

Control over Stereogenic N–N Axes by Pd-Catalyzed 5-*endo*-Hydroaminocyclizations

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Dedicated to Prof. Cristina Nevado, recipient of the 2021 Dr. Margaret Faul Women in Chemistry Award

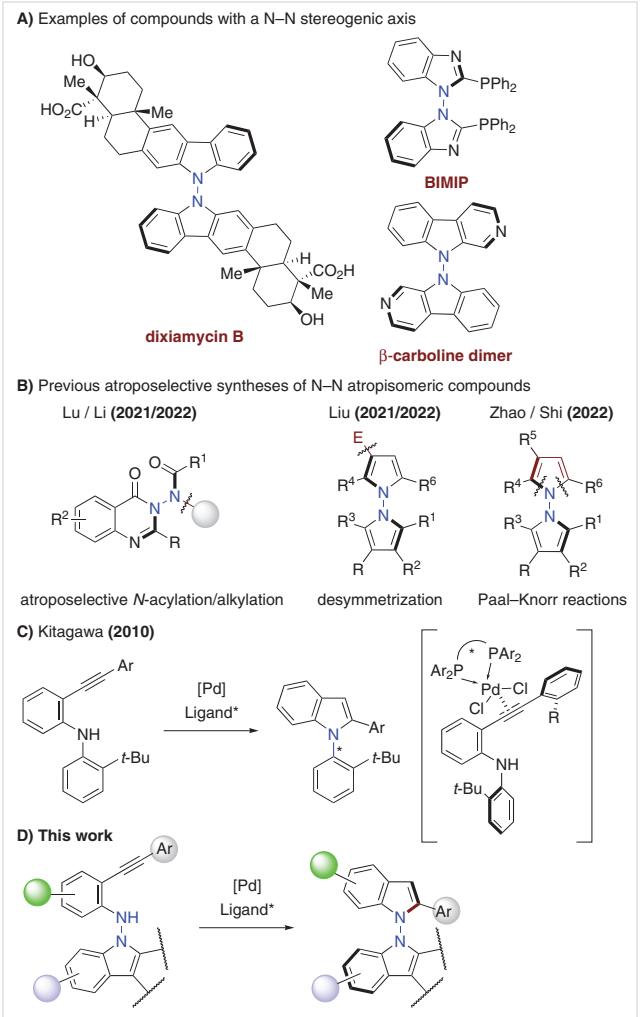
Published as part of the
Special Issue dedicated to Prof. Cristina Nevado, recipient of the 2021 Dr. Margaret Faul Women in Chemistry Award

Received: 23.09.2022
Accepted after revision: 06.12.2022
Published online: 06.12.2022 (Accepted Manuscript), 16.01.2023 (Version of Record)
DOI: 10.1055/a-1993-6899; Art ID: SS-2022-09-0460-OP

Abstract A novel approach for the stereoselective construction of N–N atropisomeric compounds by a Pd-catalyzed 5-*endo*-hydroaminocyclization is described herein. A broad range of bisheterocycles , connected by a configurationally stable N–N stereogenic axis, were prepared with catalyst control in enantioenriched form.

Key words palladium, cyclization, heterocycles, asymmetric catalysis, alkynes, atropisomers

Atropisomers, which arise from the restricted rotation about a single bond, have distinctly defined topologies and are frequently encountered in drug development campaigns.[1] Substituted biaryls possessing a C–C stereogenic axis are one of the most extensively explored and developed classes of atropisomers and they have found diverse applications, for instance as ligands in stereoselective catalysis.[2–6] In recent years, synthetic efforts have been increasingly devoted to methods for catalyst-controlled stereoselectivity to forge N–C atropisomers.[7–13] However, in contrast to the well-developed C–C and N–C atropisomers, scaffolds featuring N–N stereogenic axes have remained underexplored, despite an early report of N–N atropisomerism in 1931.[14] Currently, N–N atropisomers are represented by a small number of natural products and bioactive compounds, such as dixiamycins[15] and β-carboline dimers,[16] and they have also found applications as OLED materials[17] and ligands (Scheme 1A).[18] It was only recently that the first reports on the atroposelective synthesis of scaffolds possessing N–N stereogenic axes were disclosed.[19–24] with rare examples of indole-carbazole scaffolds obtained only with low enantioselectivities.[24b] Lu, Houk, and co-workers utilized a strategy based on a quinidine-catalyzed *N*-allylic alkylation reaction,[19] while Li and co-workers developed an organocatalytic atroposelective *N*-acylation[20] and a stereo-

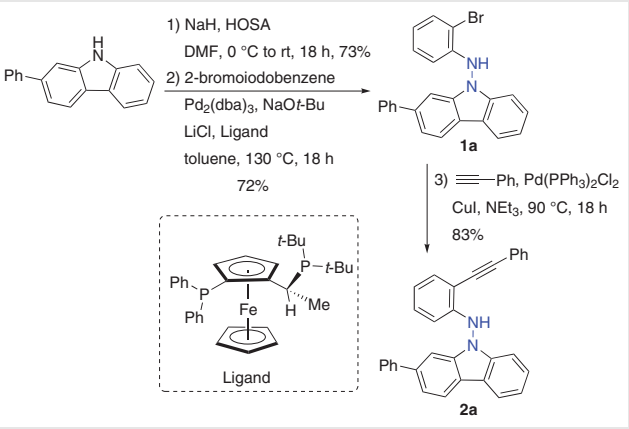


Scheme 1 Atropisomers with stereogenic N–N axes, recent methods for their stereoselective synthesis, and the synthetic strategy for our studies

selective *N*-alkylation via asymmetric phase-transfer catalysis (Scheme 1B).[21] Desymmetrization via stereoselective metal catalysis was also applied for the atroposelective synthesis of N–N biaryls by Liu and co-workers,[22] and the most recent strategies by Zhao and Shi are based on stereoselective Paal–Knorr reactions.[23] Despite these seminal strategies, efficient procedures to prepare N–N stereogenic compounds are still scarce. Inspired by the atroposelective synthesis of N–C atropisomeric indoles by the Kitagawa group,[25] we thus considered if the de novo construction of indole rings by a catalytic 5-*endo*-hydroaminocyclization[26] allows the configuration of N–N stereogenic axes to be controlled (Scheme 1).

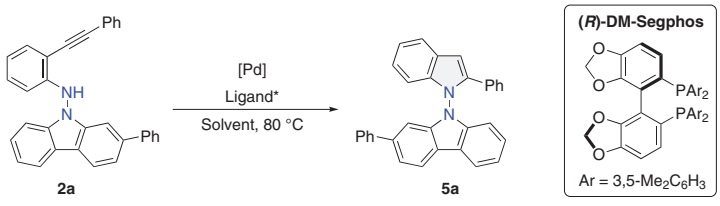
We initiated our studies with an expeditious precursor synthesis from readily available substrates by the formation of an *N*-aminocarbazole with HOSA, a subsequent Buchwald–Hartwig amination, and a Sonogashira coupling yielding **2a** (Scheme 2).

With the alkyne precursor in hand, we performed an extensive optimization to explore the impact of different parameters on the 5-*endo*-hydroaminocyclization (Table 1, see the Supporting Information for details). Initial investigations showed that Pd^{II} performs best among all tested transition metals (Au^{I}, Ag^{I}, Cu^{I}) (Table S1 in the Supporting Information) and that the presence of chloride is beneficial. The replacement of chloride by bromide caused a significant drop in atroposelectivity (Table 1, entry 14), while the utilization of $Pd(OAc)_2$ yielded a racemic product (entry 13).



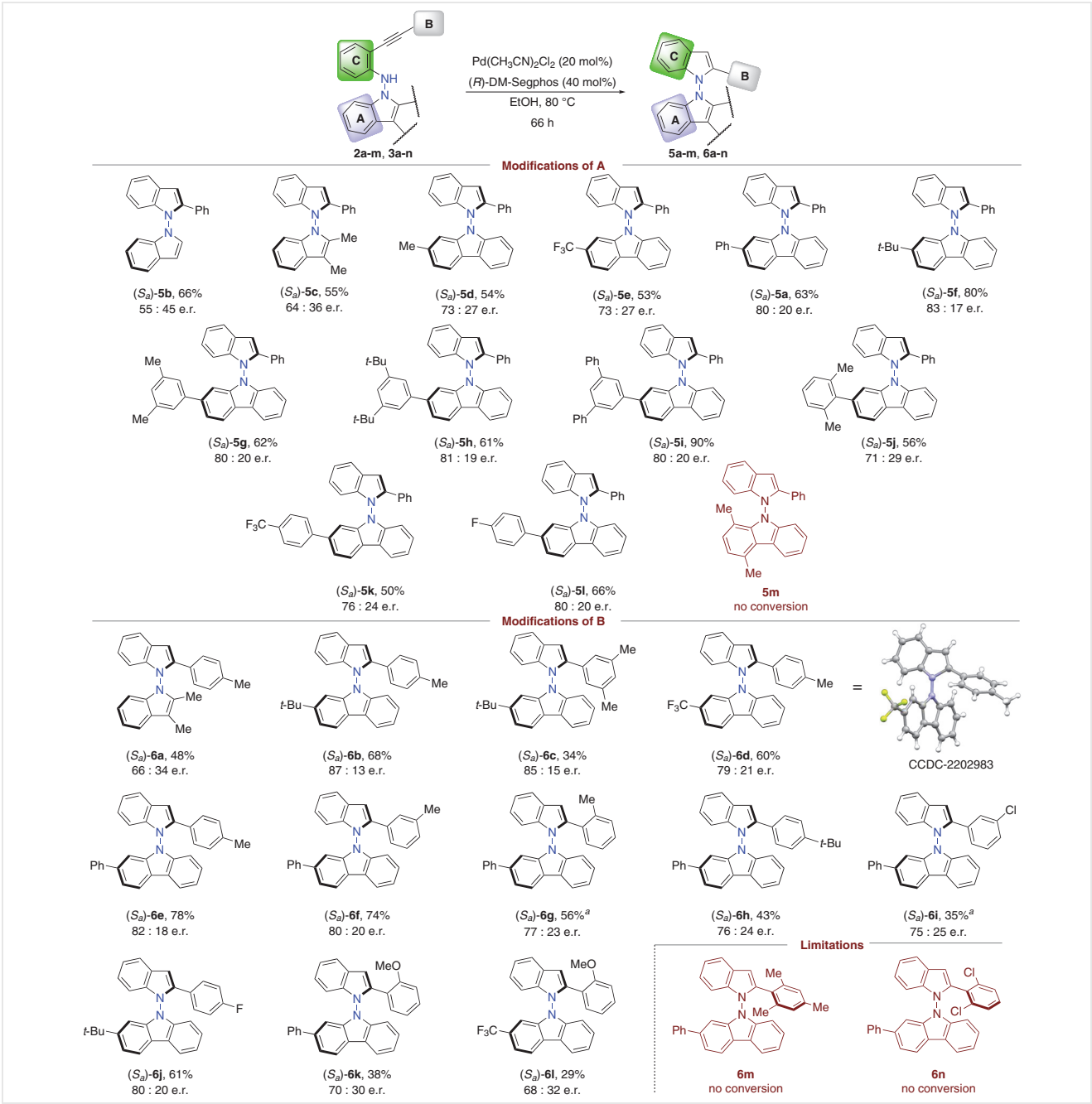
Scheme 2 Precursor synthesis, HOSA = hydroxylamine-*O*-sulfonic acid

Table 1 Optimization of the Reaction Conditions for Atroposelective 5-*endo*-Hydroaminocyclization[a]



Entry	[Pd]	[Pd] (equiv)	Ligand	Ligand (equiv)	Solvent	Additives/Deviations	Conversion[b] (%)	e.r.
1	$Pd(CH_3CN)_2Cl_2$	0.60	(*R*)-Monophos	1.2	EtOH	–	100	52:48
2	$Pd(CH_3CN)_2Cl_2$	0.60	(*S*)-BINAP	1.2	EtOH	–	26	49:51
3	$Pd(CH_3CN)_2Cl_2$	0.60	(*R*)-Tol-BINAP	1.2	EtOH	–	52	55:45
4	$Pd(CH_3CN)_2Cl_2$	0.60	(*S*)-SEGPHOS	1.2	EtOH	–	37	35:65
5	$Pd(CH_3CN)_2Cl_2$	0.60	(*S*)-DIFLUOROPHOS	1.2	EtOH	–	38	33:67
6	$Pd(CH_3CN)_2Cl_2$	0.60	(*R*)-DTBM-SEGPHOS	1.2	EtOH	–	5	52:48
7	$Pd(CH_3CN)_2Cl_2$	0.60	(*R*)-DM-SEGPHOS	1.2	EtOH	–	69	83:17
8	$Pd(CH_3CN)_2Cl_2$	0.30	(*R*)-DM-SEGPHOS	0.60	EtOH	–	66	81:19
9	$Pd(CH_3CN)_2Cl_2$	0.20	(*R*)-DM-SEGPHOS	0.40	EtOH	–	59	81:19
10	$Pd(CH_3CN)_2Cl_2$	0.20	(*R*)-DM-SEGPHOS	0.40	EtOH	42 h	100	80:20
11	$Pd(CH_3CN)_2Cl_2$	0.20	(*R*)-DM-SEGPHOS	0.40	EtOH	argon	47	82:18
12	$Pd(CH_3CN)_2Cl_2$	0.10	(*R*)-DM-SEGPHOS	0.20	EtOH	–	41	79:21
13	$Pd(OAc)_2$	0.30	(*R*)-DM-SEGPHOS	0.60	EtOH	–	100	50:50
14	$Pd(CH_3CN)_4(BF_4)_2$	0.30	(*R*)-DM-SEGPHOS	0.60	EtOH	TBAB (0.70 equiv)	62	56:44
15	$Pd(CH_3CN)_4(BF_4)_2$	0.30	(*R*)-DM-SEGPHOS	0.60	EtOH	CsF (0.66 equiv)	0	–
16	$Pd(CH_3CN)_2Cl_2$	0.30	(*R*)-DM-SEGPHOS	0.60	*i*PrOH	–	10	83:17

[a] Reaction conditions: Pd salt, additive, ligand, solvent (1.5 mL) were stirred for 1 h at r.t. Then **2a** (6.00 µmol) was added and the mixture was stirred at the indicated temperature for 18 h.
[b] Conversion and e.r. were determined by NP-HPLC (Chiralpak IG, 3 µm; heptane/*i*PrOH 97.5:2.5; 40 °C; 1 mL/min).



Scheme 3 Substrate scope. *Reagents and conditions*: **2a–m**, **3a–n** (40.0 µmol, 1.00 equiv), $Pd(CH_3CN)_2Cl_2$ (8.00 µmol, 20 mol%), (*R*)-DM-SEGPHOS (16.0 µmol, 40 mol%), EtOH (10 mL), 80 °C, 66 h; [a] 90 h.

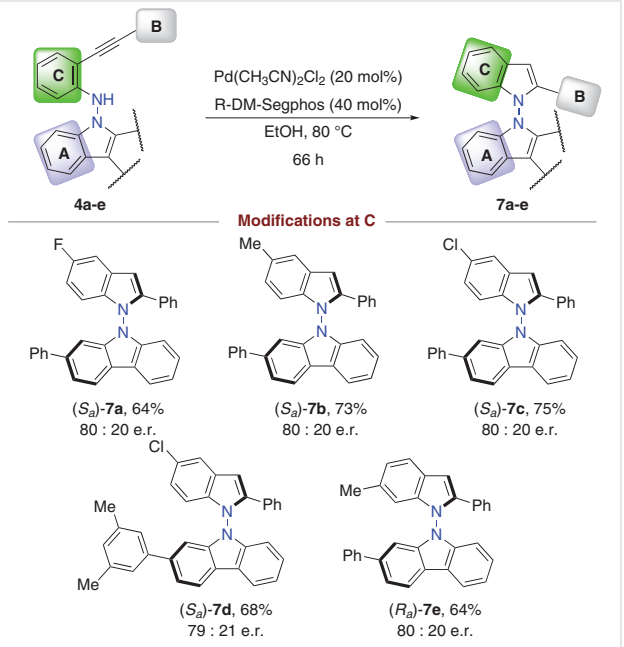
The examination of a wide range of ligands revealed (*R*)-DM-SEGPHOS in EtOH as the best system (entries 1–12). Notably, the application of an aprotic reaction medium or their combination with protic solvents resulted in reaction suppression (Table S3 in the Supporting Information) and the switch from EtOH to *i*PrOH caused a slight increase in atroposelectivity, but with drastically decreased reaction efficiency (entry 16). As a control experiment, separately prepared and purified Pd((*R*)-DM-SEGPHOS)Cl_2 was directly subjected to the 5-*endo*-hydroaminocyclization. The results were comparable as with the *in situ* generated Pd^{II} complex, indicating that the catalyst is efficiently formed prior to the cyclization (Table S3 in the Supporting Information). After establishing the optimal reaction conditions (Table 1, entry 10), we set out to investigate the scope of the developed methodology (Scheme 3). The modularity of the

divergent synthetic strategy was confirmed by dividing the target scaffold into three structural segments. Since altering the steric features and electronic nature of the substituents at all three segments can substantially affect atroposelectivity, we initiated a systematic investigation of each variable. In particular, the alkyne precursors possessing indole moieties showed considerably lower enantioselectivities upon cyclization ((S_a)-**5b**/**5c**/**6a**) than the carbazole-substituted analogues ((S_a)-**5d**).

The examination of the substituents at the 2-position of the carbazole moiety showed that bulky groups lead to higher selectivities. This tendency is further observed for compounds (S_a)-**5a–f**, where, for instance, the replacement of the methyl ((S_a)-**5d**) with a *tert*-butyl group ((S_a)-**5f**) caused an increase of enantioenrichment from 73:27 to 83:17 e.r. However, our method was found to be incompatible with substituents at the 1-position of the carbazole (**5m**). Variations at the alkyne (site B) revealed that the introduction of a *p*-methyl group had a favorable effect on selectivity ((S_a)-**5a**/(S_a)-**6e**, (S_a)-**5e**/(S_a)-**6d**, (S_a)-**5f**/(S_a)-**6b**).

However, a methyl group located at closer proximity to the reaction center ((S_a)-**6g**) led to decreased atroposelectivity (77:23 e.r.) and longer reaction times. In contrast, the presence of a methoxy group at the same position resulted in lower enantioselectivity ((S_a)-**6k**, (S_a)-**6l**), whereas the introduction of two substituents at the *o*-positions of the aromatic ring yielded alkyne precursors that were unreactive under the standard conditions (**6m**, **6n**). To confirm the configurational stability of the synthesized N–N atropisomers, we evaluated the rotational barriers of substrates **5b** and **6d**. While **6d** proved to be configurationally stable at 160 °C after 7 hours ($\Delta G^{\ddagger}$ >140 kJ·mol^{-1}), a slow racemization of **5b** was observed at 120 °C with a rotational barrier at 129 kJ·mol^{-1} (see the Supporting Information for details). Finally, modifications of the aniline moiety (site C) were performed (Scheme 4). Substrates possessing F, Cl, Me groups at different positions smoothly underwent the cyclization with almost identical enantioselectivities, indicating that substituents at the modulation site C do not have a strong impact on the reaction outcome. Interestingly, the common side product of the cyclization step was the carbazole arising from N–N bond cleavage. To shed some light on this undesired process, we explored the 2-phenyl-9*H*-carbazole formation for products (S_a)-**5a** and (S_a)-**6k** (see the Supporting Information).

In particular, control experiments demonstrated that the alkyne precursor is inert towards N–N bond cleavage upon reflux in EtOH and treatment with (*R*)-DM-SEGPHOS (Table S5). The cyclization product (S_a)-**5a** also proved to be stable towards Pd^{II} salts, (*R*)-DM-SEGPHOS, and heating, as neither decomposition nor kinetic resolution was detected. These results support the notion that N–N bond cleavage is a Pd-catalyzed process involving the alkyne precursor and competing with the desired cyclization (up to 35% conversion of the alkyne precursor to the side product). Based on the mechanistic proposal by Kitagawa,[25b] this side reaction for a N–N bond activation could be initiated by coordination of nitrogen to Pd that competes with the formation of the alkyne-Pd complex.



Scheme 4 Substrate scope. *Reagents and conditions*: **4a–e** (40.0 µmol, 1.00 equiv), $Pd(CH_3CN)_2Cl_2$ (8.00 µmol, 20 mol%), (*R*)-DM-SEGPHOS (16.0 µmol, 40 mol%), EtOH (10 mL), 80 °C, 66 h.

In summary, a concise and practical enantioselective approach to atropisomers possessing an N–N stereogenic axis by a Pd-catalyzed 5-*endo*-hydroaminocyclization was developed. The structural modularity of the method allowed the preparation of a broad range of N–N-linked bisindoles and indolyl-carbazoles with up to 87:13 atroposelectivity and 90% yield.

All reaction solvents and reagents were obtained from commercial suppliers and used without further purification unless otherwise stated. Solvents for extractions and chromatography were technical grade. Syringes were used to transfer air- and moisture-sensitive liquids and solutions. Analytical thin layer chromatography (Merck silica gel 60 F_{254} plates) was utilized for monitoring reactions and visualized by UV light (254 nm and 350 nm). Flash chromatography was performed with SiliCycle silica gel 60 (230–400 mesh) or otherwise stated stationary columns. Concentration *in vacuo* was performed by rotary evaporation to ~10 mbar at 40 °C and drying at ~ 10^{-2} mbar at r.t.

^{1}H NMR spectra were recorded on Bruker DPX 400 MHz or Bruker DRX 500 MHz spectrometers at 298 K in the indicated deuterated solvent supplied by *Cambridge Isotope Laboratories*. ^{1}H NMR spectra are referenced to the residual solvent peak (δ = 7.26 for $CDCl_3$ and δ = 2.50 for DMSO-d_6). ^{13}C and 2D NMR spectra were recorded with ^{1}H-decoupling on Bruker DRX 500 MHz spectrometers at 298 K in the indicated

deuterated solvent supplied by *Cambridge Isotope Laboratories*. ^{13}C NMR spectra are referenced to the residual solvent peak (δ = 77.16 for $CDCl_3$ and δ = 39.52 for DMSO-d_6).

Melting points were measured on a Büchi B-565 melting point apparatus and are uncorrected. IR spectroscopy was measured on an ATR Varian Scimitar 800 FT-IR spectrometer. High-resolution mass spectrometry (HRMS-ESI) was recorded by Dr. Michael Pfeffer at the University of Basel on a *Bruker MaXis 4G QTOF* ESI mass spectrometer. Optical rotations were measured at 296 K on a Jasco P-2000 digital polarimeter with a path length of 10.0 cm, using the 589.3 nm sodium D-line and concentrations are reported in g/100 mL. UV/Vis spectra were measured in MeCN solution on a Jasco V-770 spectrometer with a 10-mm sample cell at 20 °C. Circular dichroism (CD) spectra were acquired in MeCN solution on a Jasco J-1500 CD spectrometer using a 10-mm quartz cuvette at 20 °C.

Synthesis of 5a–5l/6a–6n/7a–7e; General Procedure

$Pd(CH_3CN)_2Cl_2$ (2.08 mg, 8.00 µmol, 20 mol%) and (*R*)-DM-SEGPHOS (11.6 mg, 16.0 µmol, 40 mol%) were transferred to a vial and dry EtOH (5.0 mL) was added. The resulting mixture was stirred for 1 h at r.t. before the corresponding alkyne precursor (**2a–2l**, **3a–3n**, **4a–4e**) (40.0 µmol, 1.00 equiv) and additional dry EtOH (5 mL) were added. The reaction mixture was stirred for 66 h (unless otherwise noted) at 80 °C. The reaction completion was checked by NP-HPLC analysis and then the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel, cyclohexane/CH_2Cl_2 from 1:0 to 10:1) or preparative TLC (silica gel) to yield the product.

(*S*$_a$)-2-Phenyl-9-(2-phenyl-1*H*-indol-1-yl)-9*H*-carbazole ((*S*$_a$)-5a)

Prepared according to the general procedure using 2-phenyl-*N*-(2-(phenylethynyl)phenyl)-9*H*-carbazol-9-amine (**2a**; 17.4 mg, 40.0 µmol, 1.00 equiv) followed by column chromatography (silica gel) to give (*S*$_a$)-**5a** (11.0 mg, 25.3 µmol, 63%) as a beige solid; mp 120.7–121.2 °C; $[\alpha]_D^{22}$ –17.7 (*c* 0.6, $CHCl_3$); R_f = 0.51 (cyclohexane/EtOAc 20:1).

IR (neat): 3058w, 3051w, 2961w, 2925w, 2860w, 1731w, 1607m, 1454s, 1334w, 1259m, 1248m, 1076w, 1016m, 908w, 797m, 742s cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.16 (d, ^3J = 8.1 Hz, 1 H, C4′*H*), 8.13–8.08 (m, 1 H, C5′*H*), 7.74 (d, ^3J = 7.9 Hz, 1 H, C4*H*), 7.57–7.50 (m, 3 H, C2‴*H*, C6‴*H*, C3′*H*), 7.44–7.37 (m, 2 H, C2″*H*, C6″*H*), 7.38–7.28 (m, 5 H, C6′*H*, C7′*H*, C3‴*H*, C5‴*H*, C4‴*H*), 7.24–7.18 (m, 2 H, C1′*H*, C5*H*), 7.15–7.10 (m, 3 H, C3″*H*, C5″*H*, C4″*H*), 7.08–7.03 (m, 1 H, C6*H*), 7.00–6.94 (m, 2 H, C8′*H*, C3*H*), 6.68–6.60 (m, 1 H, C7*H*).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 141.25 (C1‴), 141.20 (C2), 141.18 (C9a′), 141.0 (C8a′), 140.3 (C2′), 137.8 (C7a), 130.5 (C1″), 128.7 (C3‴, C5‴), 128.6 (C3″, C5″), 128.2 (C4″), 127.5 (C2‴, C6‴), 127.30 (C4‴), 127.26 (C2″, C6″), 126.70 (C7′), 126.68 (C3a), 123.3 (C6), 121.9 (C5), 121.5 (C4b′), 121.2 (C6′), 121.0 (C4), 120.9 (C4′), 120.7 (C3′), 120.6 (C5′), 109.7 (C7), 109.1 (C8′), 107.3 (C1′), 102.2 (C3).

HRMS (ESI): *m*/*z* $[M]^+$ calcd for $C_{32}H_{22}N_2$: 434.1778; found: 434.1769.

The e.r. of 80:20 for (*S*$_a$)-**5a** was determined by NP-HPLC (Chiralpak IG analytical column; 1.0 mL·min^{-1}, heptane/*i*PrOH 97.5:2.5; 40 °C): t_R = 6.60 (major), 6.97 min (minor).

(*S*$_a$)-2-Phenyl-1,1′-biindole ((*S*$_a$)-5b)

Prepared according to the general procedure using *N*-(2-(phenylethynyl)phenyl)-1*H*-indol-1-amine (**2b**; 12.3 mg, 40.0 µmol, 1.00 equiv) followed by preparative TLC (silica gel, cyclohexane/CH_2Cl_2, 65:35) to give (*S*$_a$)-**5b** (8.10 mg, 26.3 µmol, 66%) as a viscous yellow solid; $[\alpha]_D^{24}$ –4.8 (*c* 0.4, $CHCl_3$); R_f = 0.60 (cyclohexane/CH_2Cl_2 65:35).

IR (neat): 3106w, 3057w, 2660w, 2925w, 2853w, 1731w, 1601w, 1488w, 1452s, 1331m, 1272w, 1236w, 1213w, 1179w, 1102w, 1026w, 1009w, 922w, 848w, 800w, 758m, 738 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.70 (d, ^3J = 7.9 Hz, 1 H, C4*H*), 7.68–7.66 (m, 1 H, C4′*H*), 7.29–7.26 (m, 2 H, C2″*H*, C6″*H*), 7.23–7.12 (m, 8 H, C5*H*, C6*H*, C3″*H*, C4″*H*, C5″*H*, C5′*H*, C6′*H*, C2′*H*), 6.96 (d, ^3J = 7.5 Hz, 1 H, C7′*H*), 6.87 (s, 1 H, C3*H*), 6.77 (d, ^3J = 8.1 Hz, 1 H, C7*H*), 6.62 (d, ^3J = 3.2 Hz, 1 H, C3′*H*).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 140.5 (C2), 138.8 (C7a), 136.7 (C7a′), 130.3 (C1″), 128.6 (C3″, C5″), 128.18 (C4″), 128.15 (C2′), 127.2 (C2″, C6″), 126.2 (C3a′), 125.9 (C3a), 123.41 (C6), 123.35 (C6′), 121.8 (C5), 121.4 (C4′), 121.1 (C5′), 120.9 (C4), 109.4 (C7), 109.3 (C7′), 102.5 (C3′), 101.8 (C3).

HRMS (ESI): *m*/*z* $[M - H]^-$ calcd for $C_{22}H_{15}N_2$: 307.1241; found: 307.1244.

The e.r. of 55:45 for (*S*$_a$)-**5b** was determined by NP-HPLC (Chiralpak IA analytical column; 1.0 mL·min^{-1}, heptane/*i*PrOH 97.5:2.5; 40 °C): t_R = 5.58 (major), 6.03 min (minor).

(*S*$_a$)-2,3-Dimethyl-2′-phenyl-1,1′-biindole ((*S*$_a$)-5c)

Prepared according to the general procedure using 2,3-dimethyl-*N*-(2-(phenylethynyl)phenyl)-1*H*-indol-1-amine (**2c**; 13.5 mg, 40.0 µmol, 1.00 equiv) followed by preparative TLC (silica gel, cyclohexane/CH_2Cl_2, 3:1) to give (*S*$_a$)-**5c** (7.40 mg, 22.0 µmol, 55%) as a beige viscous solid; $[\alpha]_D^{24}$ +4.4 (*c* 0.5, $CHCl_3$); R_f = 0.64 (cyclohexane/CH_2Cl_2 3:1).

IR (neat): 3053w, 2968w, 2916w, 1729w, 1606w, 1457m, 1410w, 1334w, 1284w, 1230m, 1075m, 907s, 799w, 736s, 695m, 614m cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.69 (dt, ^3J = 7.9, ^4J = 0.7 Hz, 1 H, C4*H*), 7.57 (dt, ^3J = 7.6, ^4J = 1.0 Hz, 1 H, C4′*H*), 7.30–7.26 (m, 2 H, C2″*H*, C6″*H*), 7.23–7.18 (m, 4 H, C5*H*, C3″*H*, C4″*H*, C5″*H*), 7.18–7.16 (m, 1 H, C5′*H*), 7.15–7.11 (m, 1 H, C6′*H*), 7.11–7.08 (m, 1 H, C6*H*), 7.00–6.96 (m, 1 H, C7′*H*), 6.89 (d, ^4J = 0.7 Hz, 1 H, C3*H*), 6.65–6.61 (m, 1 H, C7*H*), 2.27–2.20 (3 H, C3′-CH_3), 1.82 (3 H, C2′-CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 140.8 (C2), 138.6 (C7a), 136.7 (C7a′), 133.3 (C2′), 130.8 (C1″), 128.8 (C3″, C5″), 128.2 (C4″), 127.34 (C2″, C6″), 127.26 (C3a′), 126.2 (C3a), 123.4 (C6), 122.4 (C6′), 121.8 (C5), 120.9 (C4), 120.6 (C5′), 118.5 (C4′), 109.6 (C7), 108.9 (C7′), 107.5 (C3′), 101.6 (C3), 9.0 (C3′-CH_3), 8.9 (C2′-CH_3).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{24}H_{21}N_2$: 337.1699; found: 337.1699.

The e.r. of 64:36 for (*S*$_a$)-**5c** was determined by NP-HPLC (Chiralpak IA analytical column; 1.0 mL·min^{-1}, heptane/*i*PrOH 97.5:2.5; 40 °C): t_R = 4.33 (major), 4.67 min (minor).

(*S*$_a$)-2-Methyl-9-(2-phenyl-1*H*-indol-1-yl)-9*H*-carbazole ((*S*$_a$)-5d)

Prepared according to the general procedure using 2-methyl-*N*-(2-(phenylethynyl)phenyl)-9*H*-carbazol-9-amine (**2d**; 14.9 mg, 40.0 µmol, 1.00 equiv) followed by column chromatography (silica gel, cyclohexane/EtOAc from 1:0 to 10:1) to give (*S*$_a$)-**5d** (8.00 mg, 21.5 µmol, 54%) as a brown solid; mp 111.9–113.0 °C; $[\alpha]_D^{24}$ –0.5 (*c* 0.4, $CHCl_3$); R_f = 0.65 (cyclohexane/EtOAc 10:1).

IR (neat): 3056w, 3032w, 2959w, 2920w, 2852w, 1629w, 1605m, 1581w, 1490m, 1452s, 1409w, 1329m, 1285m, 1261w, 1230s, 1179w, 1099w, 1022m, 912w cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.05 (d, ^3J = 6.8 Hz, 1 H, C5′*H*), 7.98 (d, ^3J = 7.9 Hz, 1 H, C4′*H*), 7.74 (d, ^3J = 7.7 Hz, 1 H, C4*H*), 7.43–7.35 (m, 2 H, C2″*H*, C6″*H*), 7.32–7.27 (m, 2 H, C6′*H*, C7′*H*), 7.20 (t, ^3J = 7.3 Hz, 1 H, C5*H*), 7.16–7.08 (m, 4 H, C3″*H*, C4″*H*, C5″*H*, C3′*H*), 7.07–7.01 (m, 1 H, C6*H*), 6.95 (s, 1 H, C3*H*), 6.93 (d, ^3J = 7.3 Hz, 1 H, C8′*H*), 6.80 (s, 1 H, C1′*H*), 6.56 (d, ^3J = 8.2 Hz, 1 H, C7*H*), 2.39 (s, 3 H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 141.24 (C2), 141.21 (C9a′), 140.7 (C8a′), 137.9 (C7a), 137.4 (C2′), 130.7 (C1″), 128.7 (C3″, C5″), 128.3 (C4″), 127.4 (C2″, C6″), 126.8 (C3a), 126.3 (C7′), 123.4 (C6), 122.8 (C3′), 121.9 (C5), 121.1 (C4b′), 121.1 (C6′), 120.41 (C4′), 120.34 (C5′), 119.6 (C4a′), 109.8 (C7), 109.3 (C1′), 109.1 (C8′), 102.1 (C3), 22.2 (CH_3).

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{27}H_{19}N_2$: 371.1554; found: 371.1552.

The e.r. of 73:27 for (S_a)-**5d** was determined by NP-HPLC (Chiralpak IB analytical column; 1.0 mL·min^{-1}, heptane/*i*PrOH 97.5:2.5; 20 °C): t_R = 5.37 (major), 5.13 min (minor).

(S_a)-9-(2-Phenyl-1*H*-indol-1-yl)-2-(trifluoromethyl)-9*H*-carbazole ((S_a)-5e)

Prepared according to the general procedure using *N*-(2-(phenylethynyl)phenyl)-2-(trifluoromethyl)-9*H*-carbazol-9-amine (**2e**; 17.1 mg, 40.0 µmol, 1.00 equiv) followed by column chromatography (silica gel) to give (S_a)-**5e** (9.00 mg, 21.1 µmol, 53%) as a yellow solid; mp 149.9–150.2 °C; $[\alpha]_D^{23}$ +7.1 (*c* 0.4, $CHCl_3$); R_f = 0.81 (*n*-hexane/EtOAc 15:1).

IR (neat): 3059w, 3028w, 2947w, 2909w, 1581w, 1482w, 1446m, 1322s, 1265m, 1233m, 1161m, 1122s, 1057m, 952m, 871w, 738w, 696w cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.22 (d, ^3J = 8.2 Hz, 1 H, C4′*H*), 8.18 (d, ^3J = 7.8 Hz, 1 H, C5′*H*), 7.80 (dt, ^3J = 7.9, ^4J = 0.8 Hz, 1 H, C4*H*), 7.60–7.56 (m, 1 H, C3′*H*), 7.45 (ddd, ^3J = 8.3, ^3J = 7.3, ^4J = 1.2 Hz, 1 H, C7′*H*), 7.40–7.33 (m, 3 H, C2″*H*, C6″*H*, C6′), 7.32–7.30 (m, 1 H, C1′), 7.30–7.25 (m, 1 H, C5*H*), 7.19–7.10 (m, 4 H, C3″*H*, C4″*H*, C5″*H*, C6*H*), 7.07–7.04 (m, 1 H, C8′*H*), 7.01 (d, ^4J = 0.8 Hz, 1 H, C3*H*), 6.63 (dd, ^3J = 8.2, ^4J = 0.8 Hz, 1 H, C7*H*).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 141.6 (C8a′), 141.2 (C2), 139.9 (C9a′), 137.9 (C7a), 130.4 (C1″), 128.8 (C3″, C5″), 128.5 (C4″), 128.2 (C7′), 127.4 (C2″, C6″), 126.9 (C3a), 124.3 (C4a′), 123.7 (C6)122.4 (C5), 121.9 (C6′), 121.4 (C4), 121.3 (C5′), 121.2 (C4′), 120.7 (C4b′), 118.1 (q, $^3J_{CF}$ = 3.7 Hz, C3′), 109.54 (C7), 109.5 (C8′), 106.4 (q, $^3J_{CF}$ = 4.3 Hz, C1′), 102.8 (C3).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –61.1 (CF_3).

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{27}H_{16}F_3N_2$: 425.1271; found: 425.1267.

The e.r. of 73:27 for (S_a)-**5e** was determined by NP-HPLC (Chiralpak IB analytical column; 1.0 mL·min^{-1}, heptane/*i*PrOH 97.5:2.5; 40 °C): t_R = 4.78 (major), 5.12 min (minor).

(S_a)-2-*tert*-Butyl-9-(2-phenyl-1*H*-indol-1-yl)-9*H*-carbazole ((S_a)-5f)

Prepared according to the general procedure using 2-*tert*-butyl-*N*-(2-(phenylethynyl)phenyl)-9*H*-carbazol-9-amine (**2f**; 16.6 mg, 40.0 µmol, 1.00 equiv) followed by column chromatography (silica gel) to give (S_a)-**5f** (13.2 mg, 31.8 µmol, 80%) as a yellow solid; mp 128.4–130.0 °C; $[\alpha]_D^{23}$ +13.7 (*c* 0.6, $CHCl_3$); R_f = 0.63 (cyclohexane/EtOAc 20:1).

IR (neat): 3058w, 2961s, 2907w, 2863w, 1608m, 1491w, 1455s, 1330m, 1245m, 1235m, 1091w, 1024w, 817w, 743s cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.09–8.03 (m, 1 H, C5′*H*), 8.00 (d, ^3J = 7.7 Hz, 1 H, C4′*H*), 7.75 (d, ^3J = 7.9 Hz, 1 H, C4*H*), 7.38–7.27 (m, 5 H, C3′*H*, C7′*H*, C2″*H*, C6″*H*, C4″*H*), 7.25–7.19 (m, 2 H, C6′*H*, C5*H*), 7.13–7.09 (m, 2 H, C3″*H*, C5″*H*), 7.09–7.04 (m, 1 H, C6*H*), 6.98 (d, ^4J = 1.4 Hz, 1 H, C1′*H*), 6.95 (d, ^4J = 0.7 Hz, 1 H, C3*H*), 6.91 (d, ^3J = 7.3 Hz, 1 H, C8′*H*), 6.65 (d, ^3J = 8.2 Hz, 1 H, C7*H*), 1.26 (s, 9 H, C(CH_3)$_3$).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 150.9 (C2′), 141.4 (C2), 140.9 (C9a′), 140.8 (C8a′), 138.0 (C7a), 130.8 (C1″), 128.6 (C3″, C5″), 128.2 (C4″), 127.4 (C2″, C6″), 126.8 (C3a), 126.2 (C7′), 123.3 (C6), 121.9 (C5), 121.8 (C4b′), 121.1 (C6′), 121.0 (C4), 120.4 (C5′), 120.1 (C4′), 119.4 (C4a′), 119.0 (C3′), 109.9 (C7), 109.0 (C8′), 105.7 (C1′), 102.2 (C3), 35.3 (*C*(CH_3)$_3$), 31.8 (C(*C*H$_3$)$_3$).

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{30}H_{25}N_2$: 413.2023; found: 413.2025.

The e.r. of 83:17 for (S_a)-**5f** was determined by NP-HPLC (Chiralpak IB analytical column; 1.0 mL·min^{-1}, heptane/*i*PrOH 97.5:2.5; 20 °C): t_R = 4.78 (major), 4.60 min (minor).

(S_a)-2-(3,5-Dimethylphenyl)-9-(2-phenyl-1*H*-indol-1-yl)-9*H*-carbazole ((S_a)-5g)

Prepared according to the general procedure using 2-(3,5-dimethylphenyl)-*N*-(2-(phenylethynyl)phenyl)-9*H*-carbazol-9-amine (**2g**; 18.5 mg, 40.0 µmol, 1.00 equiv) followed by column chromatography (silica gel) to give (S_a)-**5g** (11.5 mg, 24.9 µmol, 62%) as a beige solid; mp 78.7–79.0 °C; $[\alpha]_D^{23}$ –19.8 (*c* 0.5, $CHCl_3$); R_f = 0.72 (cyclohexane/EtOAc 17:2).

IR (neat): 3058w, 3026w, 2921w, 2853w, 1603m, 1453s, 1329m, 1260m, 1232m, 1150w, 1096w, 1029m, 907s, 797s, 740s, 695m, 636s cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.14 (d, ^3J = 8.1 Hz, 1 H, C4′*H*), 8.11–8.08 (m, 1 H, C5′*H*), 7.76–7.73 (m, 1 H, C4*H*), 7.54 (dd, ^3J = 8.1, ^4J = 1.5 Hz, 1 H, C3′*H*), 7.42–7.37 (m, 2 H, C2″*H*, C6″*H*), 7.33–7.25 (m, 3 H, C1′*H*, C6′*H*, C7′*H*), 7.23–7.19 (m, 1 H, C5*H*), 7.16 (s, 2 H, C2‴*H*, C6‴*H*), 7.14–7.11 (m, 3 H, C3″*H*, C4″*H*, C5″*H*), 7.05 (ddd, ^3J = 8.2, ^3J = 7.2, ^4J = 1.1 Hz, 1 H, C6*H*), 6.97 (d, ^4J = 0.8 Hz, 1 H, C3*H*), 6.95 (s, 1 H, C4‴*H*), 6.91–6.87 (m, 1 H, C8′*H*), 6.65–6.61 (m, 1 H, C7*H*), 2.33 (s, 6 H, 2 × CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 141.28 (C9a′), 141.21 (C1‴), 141.18 (C2), 140.9 (C8a′), 140.6 (C2′), 138.3 (C3‴, C5‴), 137.9 (C7a), 130.5 (C1″), 129.0 (C4‴), 128.6 (C3″, C5″), 128.2 (C4″), 127.3 (C2″, C6″), 126.7 (C3a), 126.6 (C7′), 125.4 (C2‴, C6‴), 123.4 (C6), 121.9 (C5), 121.5 (C4b′), 121.2 (C6′), 121.0 (C4), 120.9 (C3′), 120.78 (C4′), 120.76 (C4a′), 120.5 (C5′), 109.8 (C7), 109.0 (C8′), 107.3 (C1′), 102.1 (C3), 21.4 (CH_3).

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{34}H_{25}N_2$: 461.2023; found: 461.2021.

The e.r. of 80:20 for (S_a)-**5g** was determined by NP-HPLC (Chiralpak IA analytical column; 1.0 mL·min^{-1}, heptane/*i*PrOH 97.5:2.5; 20 °C): t_R = 5.77 (major), 6.48 min (minor).

(S_a)-2-(3,5-Di-*tert*-butylphenyl)-9-(2-phenyl-1*H*-indol-1-yl)-9*H*-carbazole ((S_a)-5h)

Prepared according to the general procedure using 2-(3,5-di-*tert*-butylphenyl)-*N*-(2-(phenylethynyl)phenyl)-9*H*-carbazol-9-amine (**2h**; 21.9 mg, 40.0 µmol, 1.00 equiv) followed by column chromatography (silica gel) to give (S_a)-**5h** (13.3 mg, 24.3 µmol, 61%) as a yellow solid; mp 123.3–124.5 °C; $[\alpha]_D^{23}$ –1.7 (*c* 0.4, $CHCl_3$); R_f = 0.58 (cyclohexane/CH_2Cl_2 3:1).

IR (neat): 3059w, 2961s, 2906w, 2867w, 1736w, 1596m, 1477m, 1452s, 1328w, 1233s, 1226m, 1151w, 1025w, 907m, 858w, 819w, 740s cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.15–8.09 (m, 2 H, C4′*H*, C5′*H*), 7.73 (dt, ^3J = 7.9, ^4J = 0.9 Hz, 1 H, C4*H*), 7.49 (dd, ^3J = 8.1, ^4J = 1.5 Hz, 1 H, C3′*H*), 7.45–7.41 (m, 2 H, C2″*H*, C6″*H*), 7.40–7.34 (m, 2 H, C7′*H*, C4‴*H*), 7.34–7.29 (m, 1 H, C6′*H*), 7.28 (d, ^4J = 1.8 Hz, 2 H, C2‴*H*, C6‴*H*), 7.22–7.17 (m, 1 H, C5*H*), 7.17–7.13 (m, 3 H, C3″*H*, C4″*H*, C5″*H*), 7.10–7.07 (m, 1 H, C1′*H*), 7.07–7.02 (m, 2 H, C6*H*, C8′*H*), 6.96 (d, ^3J = 0.8 Hz, 1 H, C3*H*), 6.68–6.60 (m, 1 H, C7*H*), 1.33 (s, 18 H, $C(CH_3)_3$).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 151.2 (C3‴, C5‴), 141.8 (C2′), 141.6 (C2), 141.14 (C9a′), 141.09 (C8a′), 140.99 (C1‴), 138.2 (C7a), 130.8 (C1″), 128.8 (C3″, C5″), 128.4 (C4″), 127.5 (C2″, C6″), 126.9 (C3a), 126.7 (C7′), 123.4 (C6), 122.2 (C5), 122.1 (C2‴, C6‴), 121.7 (C4a′/C4b′), 121.6 (C4‴), 121.27 (C6′), 121.26 (C4), 121.1 (C3′), 120.7 (C4′/C5′), 110.0 (C7), 109.2 (C8′), 107.8 (C1′), 102.3 (C3), 35.1 ($C(CH_3)_3$), 31.6 ($C(CH_3)_3$).

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{40}H_{37}N_2$: 545.2962; found: 545.2955.

The e.r. of 81:19 for (S_a)-**5h** was determined by NP-HPLC (Chiralpak IG analytical column; 1.0 mL·min^{-1}, heptane/*i*PrOH 97.5:2.5; 40 °C): t_R = 3.95 (major), 3.72 min (minor).

(S_a)-2-([1,1′:3′,1″-Terphenyl]-5′-yl)-9-(2-phenyl-1*H*-indol-1-yl)-9*H*-carbazole ((S_a)-5i)

Prepared according to the general procedure using 2-([1,1′:3′,1″-terphenyl]-5′-yl)-*N*-(2-(phenylethynyl)phenyl)-9*H*-carbazol-9-amine (**2i**; 23.5 mg, 40.0 µmol, 1.00 equiv) followed by column chromatography (silica gel) to give (S_a)-**5i** (21.1 mg, 36.0 µmol, 90%) as a beige viscous solid; $[\alpha]_D^{23}$ –6.0 (*c* 0.9, $CHCl_3$); R_f = 0.58 (cyclohexane/CH_2Cl_2 1:1).

IR (neat): 3058w, 3035w, 2960w, 2928w, 2856w, 1891w, 1730m, 1577, 1596m, 1494m, 1453s, 1411m, 1330m, 1262m, 1230m, 1095w, 1025w, 795s, 758s cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.19 (d, ^3J = 8.1 Hz, 1 H, C4′*H*), 8.13 (d, ^3J = 7.7 Hz, 1 H, C5′*H*), 7.75–7.71 (m, 2 H, C4*H*, C4‴*H*), 7.69 (d, ^4J = 1.4 Hz, 2 H, C2‴*H*, C6‴*H*), 7.67–7.60 (m, 5 H, 2 × C10*H*, 2 × C14*H*, C3′*H*), 7.50–7.43 (m, 4 H, 2 × C11*H*, 2 × C13*H*), 7.42–7.39 (m, 2 H, C2″*H*, C6″*H*), 7.39–7.31 (m, 3 H, 2 × C12*H*, C7′*H*), 7.31–7.28 (m, 2 H, C1′*H*, C6′*H*), 7.22–7.18 (m, 1 H, C5*H*), 7.16–7.11 (m, 3 H, C3″*H*, C4″*H*, C5″*H*), 7.09–7.02 (m, 1 H, C6*H*), 7.00–6.93 (m, 2 H, C3*H*, C8′*H*), 6.66 (d, ^3J = 8.2 Hz, 1 H, C7*H*).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 142.7 (C1‴), 142.5 (C3‴, C5‴), 141.28 (C2), 141.26 (C9a′), 141.23 (C15), 141.12 (C8a′), 140.4 (C2′), 138.1 (C7a), 130.7 (C1″), 128.9 (C11, C13), 128.8 (C3″, C5″), 128.4 (C4″), 127.7 (C12), 127.5 (C10, C14), 127.4 (C2″, C6″), 127.0 (C7′), 126.9 (C3a), 125.7 (C2‴, C6‴), 125.4 (C4‴), 123.5 (C6), 122.1 (C5), 121.6 (C4b′), 121.4 (C6′), 121.23 (C3′), 121.20 (C4), 121.12 (C4a′), 121.09 (C4′), 120.8 (C5′), 109.9 (C7), 109.3 (C8′), 107.7 (C1′), 102.5 (C3).

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{44}H_{29}N_2$: 585.2336; found: 585.2324.

The e.r. of 80:20 for (S_a)-**5i** was determined by NP-HPLC (Chiralpak IA analytical column; 1.0 mL·min^{-1}, heptane/*i*PrOH 96.5:3.5; 40 °C): t_R = 14.5 (major), 16.3 min (minor).

(S_a)-2-(2,6-Dimethylphenyl)-9-(2-phenyl-1*H*-indol-1-yl)-9*H*-carbazole ((S_a)-5j)

Prepared according to the general procedure using 2-(2,6-dimethylphenyl)-*N*-(2-(phenylethynyl)phenyl)-9*H*-carbazol-9-amine (**2j**; 18.5 mg, 40.0 µmol, 1.00 equiv) followed by column chromatography (silica gel) to give (S_a)-**5j** (10.3 mg, 22.3 µmol, 56%) as a beige viscous solid; $[\alpha]_D^{23}$ +6.9 (*c* 0.6, $CHCl_3$); R_f = 0.50 (cyclohexane/CH_2Cl_2 3:1).

IR (neat): 3059w, 2954w, 2921w, 2853w, 1725w, 1608m, 1491w, 1454s, 1316m, 1285w, 1231m, 1153w, 1126w, 1014w, 940w, 908w, 744s cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.17–8.12 (m, 2 H, C4′*H*, C5′*H*), 7.70 (d, ^3J = 7.9 Hz, 1 H, C4*H*), 7.42–7.36 (m, 1 H, C7′*H*), 7.36–7.30 (m, 3 H, C6′*H*, C2″*H*, C6″*H*), 7.23–7.16 (m, 1 H, C5*H*), 7.14–7.00 (m, 9 H, C6*H*, C3″*H*, C4″*H*, C5″*H*, C3‴*H*, C4‴*H*, C5‴*H*, C3′*H*, C8′*H*), 6.89 (s, 1 H, C3*H*), 6.78–6.69 (m, 2 H, C1′*H*, C7*H*), 1.90 (s, 3 H, C2‴-CH_3), 1.79 (s, 3 H, C6‴-CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 141.9 (C1‴), 141.1 (C2), 140.9 (C2′), 140.8 (C9a′), 139.9 (C8a′), 137.9 (C7a), 136.3 (C2‴/C6‴), 136.2 (C2‴/C6‴), 130.6 (C1″), 128.6 (C3″, C5″), 128.2 (C4″), 127.4 (C2″, C6″), 127.2 (C3‴, C5‴), 126.75, (C7′), 126.73 (C3a), 123.4 (C6), 122.3 (C3′), 121.9 (C5), 121.7 (C4‴), 121.3 (C4), 121.2 (C6′), 120.67 (C5′), 120.63 (C4′), 120.30 (C4a′), 109.7 (C7), 109.6 (C1′), 109.2 (C8′), 102.3 (C3), 20.9 (C2‴-CH_3/C6‴-CH_3), 20.65 (C2‴-CH_3/C6‴-CH_3).

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{34}H_{25}N_2$: 461.2023; found: 461.2026.

The e.r. of 71:29 for (S_a)-**5j** was determined by NP-HPLC (Chiralpak IB analytical column; 1.0 mL·min^{-1}, heptane/*i*PrOH 97.5:2.5; 20 °C): t_R = 5.42 (major), 4.93 min (minor).

(S_a)-9-(2-Phenyl-1*H*-indol-1-yl)-2-(4-(trifluoromethyl)phenyl)-9*H*-carbazole ((S_a)-5k)

Prepared according to the general procedure using *N*-(2-(phenylethynyl)phenyl)-2-(4-(trifluoromethyl)phenyl)-9*H*-carbazol-9-amine (**2k**; 20.1 mg, 40.0 µmol, 1.00 equiv) followed by column chromatography (silica gel) to give (S_a)-**5k** (10.1 mg, 20.1 µmol, 50%) as a yellow solid; mp 77.8–78.5 °C; $[\alpha]_D^{24}$ –5.4 (*c* 0.5, $CHCl_3$); R_f = 0.52 (cyclohexane/CH_2Cl_2 3:1).

IR (neat): 3060w, 2953w, 2929w, 1730w, 1613m, 1491w, 1453m, 1406w, 1322s, 1233m, 1165s, 1121s, 1069s, 1014s, 906s, 816m, 813s cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.18 (d, ^3J = 8.1 Hz, 1 H, C4′*H*), 8.15–8.11 (m, 1 H, C5′*H*), 7.81–7.73 (m, 1 H, C4*H*), 7.65–7.59 (m, 4 H, C2‴*H*, C3‴*H*, C5‴*H*, C6‴*H*), 7.54 (d, ^3J = 8.1 Hz, 1 H, C3′*H*), 7.41–7.28 (m, 4 H, C2″*H*, C6″*H*, C6′*H*, C7′*H*), 7.24–7.20 (m, 1 H, C5*H*), 7.20–7.17 (m, 1 H, C1′*H*), 7.16–7.10 (m, 3 H, C3″*H*, C5″*H*, C4″*H*), 7.09–7.04 (m, 1 H, C6*H*), 7.02–6.99 (m, 1 H, C8′*H*), 6.98 (s, 1 H, C3*H*), 6.63 (d, ^3J = 8.2 Hz, 1 H, C7*H*).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 144.9 (C1‴), 141.26 (C9a′, C2), 141.24 (C8a′), 138.8 (C2′), 138.0 (C7a), 130.6 (C1″), 128.8 (C3‴, C5″), 128.4 (C4″), 127.9 (C2‴, C6‴), 127.4 (C2″, C6″), 127.3 (C7′), 126.9 (C3a), 125.86–125.66 (m, C3‴, C5‴), 123.6 (C6), 122.2 (C5), 121.7 (C4a′), 121.6 (C6′), 121.4 (C4b′), 121.27 (C4), 121.25 (C4′), 120.9 (C5′), 120.8 (C3′), 109.7 (C7), 109.3 (C8′), 107.6 (C1′), 102.5 (C3).

^{19}F NMR (471 MHz, $CDCl_3$): δ = –62.42.

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{33}H_{20}F_3N_2$: 501.1584; found: 501.1580.

The e.r. of 76:24 for (S_a)-**5k** was determined by NP-HPLC (Chiralpak IG analytical column; 1.0 mL·min^{-1}, heptane/*i*PrOH 97.5:2.5; 40 °C): t_R = 6.03 (major), 5.78 min (minor).

((S_a)-2-(4-Fluorophenyl)-9-(2-phenyl-1*H*-indol-1-yl)-9*H*-carbazole ((S_a)-5l)

Prepared according to the general procedure using 2-(4-fluorophenyl)-*N*-(2-(phenylethynyl)phenyl)-9*H*-carbazol-9-amine (**2l**; 18.1 mg, 40.0 µmol, 1.00 equiv) followed by column chromatography (silica gel) to give (S_a)-**5l** (12.0 mg, 26.5 µmol, 66%) as a yellow viscous solid; $[\alpha]_D^{19}$ –19.8 (*c* 0.3, $CHCl_3$); R_f = 0.47 (cyclohexane/EtOAc 20:1).

IR (neat): 3059w, 2953w, 2922w, 2858w, 1892w, 1605m, 1516m, 1491m, 1453s, 1404w, 1330w, 1231s, 1159m, 1098w, 1013w, 907s, 815s, 730s, 694m, 637m cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.15 (dd, ^3J = 8.1, ^5J = 0.5 Hz, 1 H, C4′*H*), 8.13–8.10 (m, 1 H, C5′*H*), 7.75 (dt, ^3J = 7.9, ^4J = 0.9 Hz, 1 H, C4*H*), 7.50–7.46 (m, 3 H, C3′*H*, C2‴*H*, C6‴*H*), 7.42–7.38 (m, 2 H, C2″*H*, C6″*H*), 7.36–7.32 (m, 1 H, C7′*H*), 7.30 (td, ^3J = 7.4, ^4J = 1.2 Hz, 1 H, C6′*H*), 7.22 (ddd, ^3J = 8.0, ^3J = 7.2, ^4J = 1.0 Hz, 1 H, C5*H*), 7.15–7.12 (m, 4 H, C3″*H*, C4″*H*, C5″*H*, C1′*H*), 7.09–7.03 (m, 3 H, C6*H*, C3‴*H*, C5‴*H*), 6.99–6.95 (m, 2 H, C3*H*, C8′*H*), 6.63 (dq, ^3J = 8.2, ^4J = 1.0 *H*z, 1 H, C7*H*).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 162.6 (d, $^1J_{CF}$ = 246.8 Hz, C4‴), 141.30 (C2), 141.25 (C9a′), 141.13 (C8a′), 139.4 (*C*2′), 137.9 (C7a), 137.50 (d, $^4J_{CF}$ = 3.0 Hz, C1‴), 130.6 (C1″), 129.16 (d, $^3J_{CF}$ = 8.2 Hz, C2‴, C6‴), 128.8 (C4″), 128.4 (C3″, C5″), 127.4 (C2″, C6″), 126.9 (C7′), 126.8 (C3a), 123.5 (C6), 122.1 (C5), 121.5 (C4b′), 121.4 (C6′), 121.2 (C4), 121.1 (C4′), 121.0 (C5′), 120.7 (C3′), 115.71 (d, $^2J_{CF}$ = 21.6 Hz, C3‴, C5‴), 109.8 (C7), 109.2 (C8′), 107.2 (C1′), 102.4 (C3).

^{19}F NMR (471 MHz, $CDCl_3$): δ = –115.67.

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{32}H_{20}FN_2$: 451.1616; found: 451.1613.

The e.r. of 80:20 for (S_a)-**5l** was determined by NP-HPLC (Chiralpak IG analytical column; 1.0 mL·min^{-1}, heptane/*i*PrOH 97.5:2.5; 40 °C): t_R = 6.75 (major), 7.10 min (minor).

(S_a)-2,3-Dimethyl-2′-(*p*-tolyl)-1,1′-biindole ((S_a)-6a)

Prepared according to the general procedure using 2,3-dimethyl-*N*-(2-(*p*-tolylethynyl)phenyl)-1*H*-indol-1-amine (**3a**; 14.0 mg, 40.0 µmol, 1.00 equiv) followed by column chromatography (silica gel) to give (S_a)-**6a** (6.70 mg, 19.1 µmol, 48%) as a beige viscous solid; mp 78.7–79.0 °C; $[\alpha]_D^{24}$ +1.5 (*c* 0.3, $CHCl_3$); R_f = 0.44 (cyclohexane/CH_2Cl_2 4:1).

IR (neat): 3054w, 2953w, 2919w, 2849w, 1722w, 1503w, 1457m, 1333m, 1284m, 1186w, 1104w, 908w, 739s cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.68 (dt, ^3J = 7.9, ^4J = 0.9 Hz, 1 H, C4*H*), 7.56 (d, ^3J = 7.7 Hz, 1 H, C4′*H*), 7.20–7.15 (m, 4 H, C5*H*, C5′*H*, C2″*H*, C6″*H*), 7.14–7.05 (m, 2 H, C6*H*, C6′*H*), 7.02–6.98 (m, 2 H, C3″*H*, C5″H), 6.97 (dt, ^3J = 7.9, ^4J = 0.9 Hz, 1 H, C7′*H*), 6.85 (d, ^4J = 0.9 Hz, 1 H, C3*H*), 6.64–6.59 (m, 1 H, C7*H*), 2.26 (s, 3 H, C4′-CH_3), 2.25 (s, 3 H, C2′-CH_3), 1.82 (s, 3 H, C3′-CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 140.8 (C2), 138.4 (C7a), 137.9 (C4″), 136.6 (C7a′), 133.1 (C2′), 129.4 (C3″, C5″), 127.7 (C1″), 127.09 (C3a′), 127.06 (C2″, C6″), 126.2 (C3a), 123.0 (C6), 122.2 (C6′), 121.6 (C5), 120.7 (C4), 120.4 (C5′), 118.3 (C4′), 109.4 (C7), 108.8 (C7′), 107.2 (C3′), 100.9 (C3), 21.2 (C4″-CH_3), 8.9 (C2′-CH_3), 8.8 (C3′-CH_3).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{25}H_{23}N_2$: 351.1865; found: 351.1857.

The e.r. of 66:34 for (S_a)-**6a** was determined by NP-HPLC (Chiralpak IG analytical column; 1.0 mL·min^{-1}, heptane/*i*PrOH 97.5:2.5; 40 °C): t_R = 4.68 (major), 5.27 min (minor).

(S_a)-2-*tert*-Butyl-9-(2-(*p*-tolyl)-1*H*-indol-1-yl)-9*H*-carbazole ((S_a)-6b)

Prepared according to the general procedure using 2-*tert*-butyl-*N*-(2-(*p*-tolylethynyl)phenyl)-9*H*-carbazol-9-amine (**3b**; 17.1 mg, 40.0 µmol, 1.00 equiv) followed by column chromatography (silica gel) to give (S_a)-**6b** (11.7 mg, 27.3 µmol, 68%) as a beige viscous solid; $[\alpha]_D^{19}$ –15.8 (*c* 0.4, $CHCl_3$); R_f = 0.50 (cyclohexane/EtOAc 21:1).

IR (neat): 3039w, 3025w, 2961m, 2664m, 1629w, 1609m, 1504m, 1454s, 1331m, 1235m, 1020w, 907w, 818m, 743s cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.11–8.03 (m, 1 H, C5′*H*), 8.01 (d, ^3J = 8.2 Hz, 1 H, C4′*H*), 7.73 (d, ^3J = 7.9 Hz, 1 H, C4*H*), 7.35 (dd, ^3J = 8.3, ^4J = 1.6 Hz, 1 H, C3′*H*), 7.30–7.26 (m, 2 H, C6′*H*, C7′*H*), 7.25–7.22 (m, 2 H, C2″*H*, C6″), 7.22–7.18 (m, 1 H, C5*H*), 7.08–7.02 (m, 1 H, C6*H*), 6.99 (d, ^4J = 1.4 Hz, 1 H, C1′*H*), 6.94–6.86 (m, 4 H, C3*H*, C8′*H*, C3″*H*, C5″*H*), 6.61 (d, ^3J = 8.2 Hz, 1 H, C7*H*), 2.17 (s, 3 H, C4″-CH_3), 1.26 (s, 9 H, C(CH_3)$_3$).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 150.9 (C2′), 141.6 (C2), 140.9 (C9a′), 140.8 (C8′a), 138.1 (C4″), 137.9 (C7a), 129.4 (C3″, C5″), 127.9 (C1″), 127.3 (C2″, C6″), 126.9 (C3a), 126.2 (C7′), 123.1 (C6), 121.9 (C5), 121.7 (C4b′), 120.96 (C6′), 120.92 (C4), 120.3 (C5′), 120.1 (C4′), 119.3 (C4a′), 118.9 (C3′), 109.9 (C7), 109.1 (C8′), 105.7 (C1′), 101.7 (C3), 35.3 (C4″-CH_3), 31.8 (C(CH_3)$_3$), 21.3 (C(CH_3)$_3$).

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{31}H_{27}N_2$: 427.2180; found: 427.2185.

The e.r. of 87:13 for (S_a)-**6b** was determined by NP-HPLC (Chiralpak IA analytical column; 1.0 mL·min^{-1}, heptane/*i*PrOH 97.5:2.5; 20 °C): t_R = 4.33 (major), 4.53 min (minor).

(S_a)-2-*tert*-Butyl-9-(2-(3,5-dimethylphenyl)-1*H*-indol-1-yl)-9*H*-carbazole ((S_a)-6c)

Prepared according to the general procedure using 2-*tert*-butyl-*N*-(2-((3,5-dimethylphenyl)ethynyl)phenyl)-9*H*-carbazol-9-amine (**3c**; 17.7 mg, 40.0 µmol, 1.00 equiv) followed by column chromatography (silica gel) to give (S_a)-**6c** (6.00 mg, 13.6 µmol, 34%) as a yellow viscous solid; $[\alpha]_D^{24}$ +36.5 (*c* 0.3, $CHCl_3$); R_f = 0.60 (cyclohexane/CH_2Cl_2 3:1).

IR (neat): 3057w, 2962w, 2865w, 1734w, 1606m, 1454s, 1333m, 1240m, 1166w, 1095w, 1013w, 960w, 907m, 850m, 818m, 739s cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.03 (d, ^3J = 7.6 Hz, 1 H, C5′*H*), 7.99 (d, ^3J = 8.2 Hz, 1 H, C4′*H*), 7.74 (d, ^3J = 7.8 Hz, 1 H, C4*H*), 7.33 (dd, ^3J = 8.2, ^4J = 1.3 Hz, 1 H, C3′*H*), 7.30–7.18 (m, 3 H, C5*H*, C6′*H*, C7′*H*), 7.07 (t, ^3J = 7.6 Hz, 1 H, C6*H*), 7.04 (s, 1 H, C1′*H*), 6.93 (s, 2 H, C2″*H*, C6″*H*), 6.89 (s, 1 H, C3*H*), 6.85 (d, ^3J = 7.8 Hz, 1 H, C8′*H*), 6.76–6.70 (m, 2 H, C7*H*, C4″*H*), 2.00 (s, 6 H, C3″-CH_3, C5″-CH_3), 1.28 (s, 9 H, C(CH_3)$_3$).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 150.6 (C2′), 142.1 (C2), 141.0 (C8a′/C9a′), 140.9 (C8a′/C9a′), 138.1 (C7a), 137.7 (C3″, C5″), 130.4 (C1″), 129.8 (C4″), 126.7 (C3a), 126.0 (C7′), 125.4 (C2″, C6″), 123.1 (C6), 121.7 (C5), 121.6 (C4b′), 120.8 (C4), 120.7 (C6′), 120.1 (C5′), 119.9 (C4′), 119.2 (C4a′), 118.7 (C3′), 109.9 (C7), 108.9 (C8′), 105.7 (C1′), 101.9 (C3), 35.1 (*C*(CH_3)$_3$), 31.6 (C(CH_3)$_3$), 21.0 (C3″-CH_3, C5″-CH_3).

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{32}H_{29}N_2$: 441.2336; found: 441.2332.

The e.r. of 85:15 for (S_a)-**6c** was determined by NP-HPLC (Chiralpak IG analytical column; 1.0 mL·min^{-1}, heptane/*i*PrOH 97.5:2.5; 40 °C): t_R = 5.53 (major), 4.10 min (minor).

(S_a)-9-(2-(*p*-Tolyl)-1*H*-indol-1-yl)-2-(trifluoromethyl)-9*H*-carbazole ((S_a)-6d)

Prepared according to the general procedure using *N*-(2-(*p*-tolylethynyl)phenyl)-2-(trifluoromethyl)-9*H*-carbazol-9-amine (**3d**; 17.6 mg, 40.0 µmol, 1.00 equiv) followed by column chromatography (silica gel) to give (S_a)-**6d** (10.5 mg, 23.8 µmol, 60%) as an orange solid; mp 119.9–120.9 °C; $[\alpha]_D^{22}$ +5.0 (*c* 0.5, $CHCl_3$); R_f = 0.44 (cyclohexane/EtOAc 20:1).

IR (neat): 3059w, 3052w, 2922w, 2863w, 1598w, 1490w, 1447w, 1444w, 1323s, 1263m, 1228m, 1164m, 1119s, 1057m, 1052w, 951w, 821m, 809w, 741s, 662w cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.20 (d, ^3J = 8.1 Hz, 1 H, C4′*H*), 8.15 (d, ^3J = 7.8 Hz, 1 H, C5′*H*), 7.75 (d, ^3J = 7.9 Hz, 1 H, C4*H*), 7.55 (dd, ^3J = 8.8, ^4J = 1.6 Hz, 1 H, C3′*H*), 7.44–7.40 (m, 1 H, C7′*H*), 7.37–7.32 (m, 1 H, C6′*H*), 7.29 (d, ^4J = 1.6 Hz, 1 H, C1′*H*), 7.25–7.18 (m, 3 H, C2″*H*, C6″*H*, C5*H*), 7.07 (ddd, ^3J = 8.2, ^3J = 7.2, ^4J = 1.2 Hz, 1 H, C6*H*), 7.04–6.99 (m, 1 H, C8′*H*), 6.95–6.89 (m, 3 H, C3*H*, C3″*H*, C5″*H*), 6.58 (dd, ^3J = 8.2, ^3J = 1.0 Hz, 1 H, C7*H*), 2.19 (s, 3 H, C4″-CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 141.5 (C8′a), 141.3 (C1″), 139.8 (C9′a), 138.3 (C4″), 137.7 (C7a), 129.4 (C3″, C5″), 128.8–128.7 (C2′), 128.1 (C7′), 127.3 (C2), 127.1 (C2″, C6″), 126.8 (C3a), 124.2 (C4′a), 123.4 (C6), 122.2 (C5), 121.7 (C6′), 121.2 (C5′), 121.1 (C4), 121.0 (C4′), 120.6 (C4′b), 118.2–117.6 (m, C3′), 109.4 (C8′), 109.3 (C7), 106.5–105.9 (m, C1′), 102.2 (C3), 21.1 (CH_3).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –61.09.

HRMS (ESI): *m*/*z* $[M]^+$ calcd for $C_{28}H_{19}F_3N_2$: 440.1495; found: 440.1486.

The e.r. of 79:21 for (S_a)-**6d** was determined by NP-HPLC (Chiralpak IB analytical column; 1.0 mL·min^{-1}, heptane/*i*PrOH 97.5:2.5; 20 °C): t_R = 4.73 (major), 5.48 min (minor).

(S_a)-2-Phenyl-9-(2-(*p*-tolyl)-1*H*-indol-1-yl)-9*H*-carbazole ((S_a)-6e)

Prepared according to the general procedure using 2-phenyl-*N*-(2-(*p*-tolylethynyl)phenyl)-9*H*-carbazol-9-amine (**3e**; 17.9 mg, 40.0 µmol, 1.00 equiv) followed by column chromatography (silica gel) to give (S_a)-**6e** (14.0 mg, 31.2 µmol, 78%) as a beige viscous solid; $[\alpha]_D^{22}$ –1.9 (*c* 0.7, $CHCl_3$); R_f = 0.48 (cyclohexane/CH_2Cl_2 3:1).

IR (neat): 3052w, 3027w, 2921w, 2856w, 1730w, 1608w, 1484w, 1454s, 1316w, 1233m, 1111w, 1018w, 745s cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.16 (d, ^3J = 8.1 Hz, 1 H, C4′*H*), 8.12 (d, ^3J = 7.3 Hz, 1 H, C5′*H*), 7.73 (d, ^3J = 7.9 Hz, 1 H, C4*H*), 7.59–7.50 (m, 3 H, C2‴*H*, C6‴*H*, C3′*H*), 7.38 (t, ^3J = 7.6 Hz, 2 H, C3‴*H*, C5‴*H*), 7.36–7.27 (m, 5 H, C2″*H*, C6″*H*, C6′*H*, C7′*H*, C4‴*H*), 7.23–7.16 (m, 2 H, C1′*H*, C5*H*), 7.04 (t, ^3J = 7.7 Hz, 1 H, C6*H*), 6.99–6.91 (m, 4 H, C3*H*, C3″*H*, C5″*H*, C8′*H*), 6.61 (d, ^3J = 8.2 Hz, 1 H, C7*H*), 2.19 (s, 3 H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 141.34 (C2), 141.26 (C1‴), 141.19 (C9a′), 141.0 (C8a′), 140.2 (C2′), 138.1 (C4″), 137.8 (C7a), 129.4 (C3″, C5″), 128.7 (C3‴, C5‴), 127.5 (C2‴, C6‴), 127.3 (C4‴), 127.1 (C2″, C6″), 126.8 (C3a), 126.7 (C7′), 123.1 (C6), 121.9 (C5), 121.4 (C4b′), 121.2 (C6′), 120.87 (C4a′), 120.85 (C4/C4′), 120.7 (C5′), 120.5 (C3′), 109.6 (C7), 109.1 (C8′), 107.3 (C1′), 101.7 (C3), 21.1 (CH_3).

HRMS (ESI): *m*/*z* $[M - H]^-$ calcd for $C_{33}H_{23}N_2$: 447.1867; found: 447.1871.

The e.r. of 82:18 for (S_a)-**6e** was determined by NP-HPLC (Chiralpak IB analytical column; 1.0 mL·min^{-1}, heptane/*i*PrOH 97.5:2.5; 20 °C): t_R = 5.23 (major), 5.45 min (minor).

(S_a)-2-Phenyl-9-(2-(*m*-tolyl)-1*H*-indol-1-yl)-9*H*-carbazole ((S_a)-6f)

Prepared according to the general procedure using 2-phenyl-*N*-(2-(*m*-tolylethynyl)phenyl)-9*H*-carbazol-9-amine (**3f**; 17.9 mg, 40.0 µmol, 1.00 equiv) followed by column chromatography (silica gel) to give (S_a)-**6f** (13.2 mg, 29.4 µmol, 74%) as a yellow solid; mp 86.7–88.0 °C; $[\alpha]_D^{24}$ –11.6 (*c* 0.6, $CHCl_3$); R_f = 0.53 (cyclohexane/CH_2Cl_2 3:1).

IR (neat): 3057w, 3030w, 2961w, 2922w, 2855w, 1607m, 1484m, 1453s, 1316m, 1234m, 1149w, 1093w, 1027w, 906s, 861w, 782m, 730s, 633w cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.15 (d, ^3J = 8.1 Hz, 1 H, C4′*H*), 8.13–8.08 (m, 1 H, C5′*H*), 7.73 (d, ^3J = 7.9 Hz, 1 H, C4*H*), 7.56–7.49 (m, 3 H, C2‴*H*, C6‴*H*, C3′*H*), 7.40–7.36 (m, 2 H, C3‴*H*, C5‴*H*), 7.33 (td, ^3J = 7.6, ^4J = 1.3 Hz, 1 H, C7′*H*), 7.31–7.26 (m, 3 H, C6′*H*, C2″*H*, C4‴*H*), 7.22–7.17 (m, 2 H, C5*H*, C1′*H*), 7.13 (d, ^3J = 7.6 Hz, 1 H, C6″*H*), 7.05 (ddd, ^3J = 8.2, ^3J = 7.2, ^4J = 1.0 Hz, 1 H, C6*H*), 7.00–6.91 (m, 4 H, C3*H*, C8′*H*, C4″*H*, C5″*H*), 6.68–6.63 (m, 1 H, C7*H*), 2.12 (s, 3 H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 141.4 (C2), 141.3 (C1‴), 141.2 (C9a′), 141.1 (C8a′), 140.2 (C2′), 138.0 (C3″), 137.9 (C7a), 130.4 (C1″), 128.9 (C4″), 128.7 (C3‴, C5‴), 128.4 (C5″), 128.2 (C2″), 127.5 (C6‴, C2‴), 127.3 (C4‴), 126.7 (C7′), 124.1 (C6″), 123.3 (C6), 121.9 (C5), 121.4 (C4b′), 121.2 (C6′), 120.96 (C4), 120.85 (C4a′), 120.81 (C4′), 120.7 (C3′), 120.5 (C5′), 109.7 (C7), 109.1 (C8′), 107.3 (C1′), 102.1 (C3), 21.3 (CH_3).

HRMS (ESI): *m*/*z* $[M - H]^-$ calcd for $C_{33}H_{23}N_2$: 447.1867; found: 447.1861.

The e.r. of 80:20 for (S_a)-**6f** was determined by NP-HPLC (Chiralpak IA analytical column; 1.0 mL·min^{-1}, heptane/*i*PrOH 97.5:2.5; 40 °C): t_R = 6.05 (major), 6.67 min (minor).

(S_a)-2-Phenyl-9-(2-(*o*-tolyl)-1*H*-indol-1-yl)-9*H*-carbazole ((S_a)-6g)

Prepared according to a modified general procedure (90 h reaction time) using 2-phenyl-*N*-(2-(*o*-tolylethynyl)phenyl)-9*H*-carbazol-9-amine (**3g**; 17.9 mg, 40.0 µmol, 1.00 equiv) followed by column chromatography (silica gel) to give (S_a)-**6g** (10.0 mg, 22.3 µmol, 56%) as a yellow viscous solid; $[\alpha]_D^{22}$ –5.7 (*c* 0.6, $CHCl_3$); R_f = 0.36 (cyclohexane/CH_2Cl_2 3:1).

^1H NMR (500 MHz, $CDCl_3$): δ = 8.07 (d, ^3J = 8.1 Hz, 1 H, C4′*H*), 8.04 (d, ^3J = 7.7 Hz, 1 H, C5′*H*), 7.77–7.72 (m, 1 H, C4*H*), 7.57–7.52 (m, 2 H, C2‴*H*, C6‴*H*), 7.50 (dd, ^3J = 8.1, ^4J = 1.5 Hz, 1 H, C3′*H*), 7.43–7.37 (m, 2 H, C3‴*H*, C5‴*H*), 7.36–7.26 (m, 3 H, C4‴*H*, C6′*H*, C7′*H*), 7.25–7.23 (m, 1 H, C1′*H*), 7.23–7.19 (m, 2 H, C5*H*, C6″*H*), 7.11 (d, ^3J = 7.6 Hz, 1 H, C3″*H*), 7.07 (td, ^3J = 7.7, ^4J = 1.0 Hz, 1 H, C6*H*), 7.05–6.99 (m, 2 H, C4″*H*, C8′*H*), 6.82 (t, ^3J = 7.6 Hz, 1 H, C5″*H*), 6.79 (d, ^4J = 0.8 Hz, 1 H, C3*H*), 6.69–6.64 (m, 1 H, C7*H*), 2.51 (s, 3 H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 141.5 (C1‴), 141.3 (C8a′), 140.1 (C2′), 139.9 (C9a′/C2), 137.4 (C2″), 136.8 (C7a), 130.5 (C3″), 130.2 (C6″), 129.8 (C1″), 128.9 (C3‴, C5‴), 128.7 (C4″), 127.6 (C2‴, C6‴), 127.4 (C4‴), 126.57 (C7′), 126.56 (C3a), 125.4 (C5″), 123.2 (C6), 121.8 (C5), 121.5 (C4b′), 121.2 (C6′), 121.1 (C4), 120.94 (C4a′), 120.87 (C4′), 120.7 (C3′), 120.6 (C5′), 109.8 (C7), 109.2 (C8′), 107.4 (C4′), 104.2 (C3), 20.9 (CH_3).

HRMS (ESI): *m*/*z* $[M - H]^-$ calcd for $C_{33}H_{23}N_2$: 447.1867; found: 447.1864.

The e.r. of 77:23 for (S_a)-**6g** was determined by NP-HPLC (Chiralpak IG analytical column; 1.0 mL·min^{-1}, heptane/*i*PrOH 97.5:2.5; 40 °C): t_R = 5.98 (major), 6.48 min (minor).

(S_a)-9-(2-(4-*tert*-Butylphenyl)-1*H*-indol-1-yl)-2-phenyl-9*H*-carbazole ((S_a)-6h)

Prepared according to the general procedure using *N*-(2-((4-*tert*-butylphenyl)ethynyl)phenyl)-2-phenyl-9*H*-carbazol-9-amine (**3h**; 19.6 mg, 40.0 µmol, 1.00 equiv) followed by column chromatography (silica gel) to give (S_a)-**6h** (8.40 mg, 17.1 µmol, 43%) as a beige solid; mp 212.0–214.7 °C; $[\alpha]_D^{24}$ +6.4 (*c* 0.4, $CHCl_3$); R_f = 0.57 (cyclohexane/CH_2Cl_2 3:1).

IR (neat): 3057w, 3035w, 2961s, 2924s, 2903s, 2860s, 1725w, 1609m, 1570w, 1454s, 1415w, 1333w, 1259s, 1097w, 1015m, 907m, 837w, 739w cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.18 (d, ^3J = 8.1 Hz, 1 H, C4′*H*), 8.15–8.11 (m, 1 H, C5′*H*), 7.72 (d, ^3J = 7.9 Hz, 1 H, C4*H*), 7.57 (dd, ^3J = 8.1, ^4J = 1.5 Hz, 1 H, C3′*H*), 7.55–7.52 (m, 2 H, C2‴*H*, C6‴*H*), 7.40–7.35 (m, 4 H, C7′*H*, C3‴*H*, C4‴*H*, C5‴*H*), 7.34–7.27 (m, 3 H, C6′*H*, C2″*H*, C6″*H*), 7.22 (d, ^4J = 1.0 Hz, 1 H, C3*H*), 7.20–7.13 (m, 3 H, C5*H*, C3″*H*, C5″*H*), 7.04–6.99 (m, 1 H, C6*H*), 6.98–6.94 (m, 2 H, C1′*H*, C8′*H*), 6.54 (d, ^3J = 8.2 Hz, 1 H, C7*H*), 1.18 (s, 9 H, $C(CH_3)_3$).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 151.3 (C4″), 141.5 (C8a′), 141.4 (C9a′), 141.31 (C2), 141.29 (C1‴), 140.4 (C2′), 137.9 (C7a), 128.9 (C2″, C6″), 127.69 (C4‴), 127.62 (C2‴, C6‴), 127.4 (C1″), 126.91 (C3a), 126.90 (C3‴, C5‴), 126.88 (C7′), 125.8 (C3″, C5″), 123.3 (C6), 122.0 (C5), 121.7 (C4b′), 121.4 (C6′), 121.1 (C4a′), 121.0 (C4, C4′), 120.8 (C3′), 120.7 (C5′), 109.7 (C7), 109.4 (C8′), 107.6 (C3), 101.9 (C1′), 34.7 ($C(CH_3)_3$), 31.2 ($C(CH_3)_3$).

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{36}H_{29}N_2$: 489.2336; found: 489.2344.

The e.r. of 76:24 for (S_a)-**6h** was determined by NP-HPLC (Chiralpak IG analytical column; 1.0 mL·min^{-1}, heptane/*i*PrOH 97.5:2.5; 40 °C): t_R = 4.48 (major), 5.22 min (minor).

(S_a)-9-(2-(3-Chlorophenyl)-1*H*-indol-1-yl)-2-phenyl-9*H*-carbazole ((S_a)-6i)

Prepared according to a modified general procedure (90 h reaction time) using 2-(3-chlorophenyl)-*N*-(2-(phenylethynyl)phenyl)-9*H*-carbazol-9-amine (**3i**; 18.8 mg, 40.0 µmol, 1.00 equiv) followed by column chromatography (silica gel) to give (S_a)-**6i** (6.50 mg, 13.9 µmol, 35%) as an orange viscous solid; $[\alpha]_D^{24}$ –2.6 (*c* 0.4, $CHCl_3$); R_f = 0.54 (cyclohexane/CH_2Cl_2 3:1).

IR (neat): 3060w, 3026w, 2954w, 2925w, 2852w, 1725m, 1597m, 1571m, 1453s, 1430m, 1316m, 1259m, 1231m, 1096m, 1014m, 907s, 785m, 731s cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.17 (d, ^3J = 8.1 Hz, 1 H, C4′*H*), 8.13 (d, ^3J = 7.0 Hz, 1 H, C5′*H*), 7.75 (d, ^3J = 7.9 Hz, 1 H, C4*H*), 7.56 (dd, ^3J = 8.1, ^4J = 1.5 Hz, 1 H, C3′*H*), 7.55–7.51 (m, 2 H, C2‴*H*, C6‴*H*), 7.50 (t, ^4J = 1.9 Hz, 1 H, C2″*H*), 7.42–7.27 (m, 5 H, C3‴*H*, C5‴*H*, C6′*H*, C8′*H*, C4‴*H*), 7.24–7.20 (m, 1 H, C5*H*), 7.18 (d, ^4J = 1.4 Hz, 1 H, C1′*H*), 7.17–7.14 (m, 1 H, C6″*H*), 7.12–7.04 (m, 2 H, C4″*H*, C6*H*), 7.02–6.97 (m, 2 H, C3*H*, C5″*H*), 6.94 (d, ^3J = 7.4 Hz, 1 H, C8′*H*), 6.65 (d, ^3J = 8.2 Hz, 1 H, C7*H*).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 141.4 (C9a′), 141.3 (C1‴), 141.1 (C8a′), 140.6 (C2′), 139.7 (C2), 138.2 (C7a), 134.6 (C3″), 132.3 (C1″), 130.0 (C5″), 128.9 (C3‴, C5‴), 128.3 (C4″), 127.7 (C2‴, C6‴), 127.6 (C2″), 127.5 (C4‴), 127.0 (C7′), 126.6 (C3a), 125.0 (C6″), 123.9 (C6), 122.3 (C5), 121.7 (C6′), 121.6 (C4b′), 121.4 (C4), 121.11 (C4a′/C3′), 121.07 (C4′), 120.8 (C5′), 109.9 (C7), 109.1 (C8′), 107.3 (C1′), 103.1 (C3).

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{32}H_{20}ClN_2$: 467.1320; found: 467.1328.

The e.r. of 75:25 for (S_a)-**6i** was determined by NP-HPLC (Chiralpak IB analytical column; 1.0 mL·min^{-1}, heptane/*i*PrOH 97.5:2.5; 40 °C): t_R = 5.08 (major), 5.48 min (minor).

(S_a)-2-*tert*-Butyl-9-(2-(4-fluorophenyl)-1*H*-indol-1-yl)-9*H*-carbazole ((S_a)-6j)

Prepared according to the general procedure using 2-*tert*-butyl-*N*-(2-((4-fluorophenyl)ethynyl)phenyl)-9*H*-carbazol-9-amine (**3j**; 17.3 mg, 40.0 µmol, 1.00 equiv) followed by column chromatography (silica gel) to give (S_a)-**6j** (10.6 mg, 24.5 µmol, 61%) as a white solid; mp 159.1–160.9 °C; $[\alpha]_D^{24}$ +10.6 (*c* 0.5, $CHCl_3$); R_f = 0.51 (cyclohexane/CH_2Cl_2 3:1).

IR (neat): 3052w, 2962w, 2926w, 2849w, 1604w, 1504m, 1454w, 1330w, 1260w, 1232m, 1157w, 1092w, 1044w, 907w, 782s, 738s, 630s cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.07–8.04 (m, 1 H, C5′*H*), 8.01 (d, ^3J = 8.1 Hz, 1 H, C4′*H*), 7.75 (dt, ^3J = 7.9, ^4J = 1.0 Hz, 1 H, C4*H*), 7.35 (dd, ^3J = 8.1, ^4J = 1.8 Hz, 1 H, C3′*H*), 7.32–7.24 (m, 4 H, C7′H, C6′*H*, C2″*H*, C6″*H*), 7.22 (ddd, ^3J = 8.0, ^3J = 7.2, ^4J = 1.0 Hz, 1 H, C5*H*), 7.08 (ddd, ^3J = 8.0, ^3J = 7.5, ^4J = 1.0 Hz, 1 H, C6*H*), 6.95 (d, ^4J = 1.5 Hz, 1 H, C1′*H*), 6.91–6.88 (m, 2 H, C3*H*, C8′*H*), 6.82–6.75 (m, 2 H, C3″*H*, C5″*H*), 6.66 (dd, ^3J = 7.9, ^4J = 1.0 Hz, 1 H, C7*H*), 1.26 (s, 9 H, 3 × CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 162.7 (d, $^1J_{CF}$ = 248.4 Hz, C4″), 151.0 (C2′), 140.8 (C9a′), 140.7 (C8a′), 140.4 (C1″), 138.4 (C2), 137.9 (C7a), 129.27 (d, $^3J_{CF}$ = 8.2 Hz, C2″, C6″), 126.7 (C3a), 126.3 (C7′), 123.5 (C6), 122.0 (C5), 121.8 (C4b′), 121.2 (C6′), 121.1 (C4), 120.5 (C5′), 120.2 (C4′), 119.4 (C4a′), 119.1 (C3′), 115.8 (d, $^2J_{CF}$ = 21.6 Hz, C3″, C5″), 110.0 (C7), 108.9 (C3), 105.5 (C1′), 102.1 (C8′), 35.3 ($C(CH_3)_3$), 31.8 ($C(CH_3)_3$).

^{19}F NMR (471 MHz, $CDCl_3$): δ = –113.15.

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{30}H_{24}FN_2$: 431.1929; found: 431.1927.

The e.r. of 80:20 for (S_a)-**6j** was determined by NP-HPLC (Chiralpak IB analytical column; 1.0 mL·min^{-1}, heptane/*i*PrOH 97.5:2.5; 20 °C): t_R = 4.25 (major), 4.42 min (minor).

(S_a)-9-(2-(2-Methoxyphenyl)-1*H*-indol-1-yl)-2-phenyl-9*H*-carbazole ((S_a)-6k)

Prepared according to the general procedure using *N*-(2-((2-methoxyphenyl)ethynyl)phenyl)-2-phenyl-9*H*-carbazol-9-amine (**3k**; 18.6 mg, 40.0 µmol, 1.00 equiv) followed by preparative TLC (silica gel, cyclohexane/EtOAc, 6:1) to give (S_a)-**6k** (7.00 mg, 15.1 µmol, 38%) as a viscous beige solid; $[\alpha]_D^{24}$ –5.9 (*c* 0.4, $CHCl_3$); R_f = 0.60 (cyclohexane/EtOAc 6:1).

IR (neat): 3058w, 2954w, 2930w, 2845w, 1730w, 1607m, 1586w, 1484w, 1454s, 1317w, 1254s, 1238w, 1180w, 1121w, 1025w, 907s cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.07 (d, ^3J = 8.1 Hz, 1 H, C4′*H*), 8.04 (d, ^3J = 7.7 Hz, 1 H, C5′*H*), 7.75 (d, ^3J = 7.9 Hz, 1 H, C4*H*), 7.58–7.53 (m, 2 H, C2‴*H*, C6‴*H*), 7.49 (dd, ^3J = 8.1, ^4J = 1.5 Hz, 1 H, C3′*H*), 7.41–7.36 (m, 2 H, C3‴*H*, C5‴*H*), 7.35–7.26 (m, 4 H, C4‴*H*, C7′*H*, C6″*H*, C1′*H*), 7.25–7.18 (m, 2 H, C5*H*, C6′*H*), 7.11 (td, ^3J = 8.3, ^4J = 1.7 Hz, 1 H, C4″*H*), 7.08–7.03 (m, 2 H, C6*H*, C8′*H*), 6.89 (s, 1 H, C3*H*), 6.72 (t, ^3J = 7.5 Hz, 1 H, C5″*H*), 6.68 (d, ^3J = 8.2 Hz, 1 H, C7*H*), 6.65 (d, ^3J = 8.3 Hz, 1 H, C3″*H*), 3.39 (s, 3 H, OCH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 157.6 (C2″), 141.5 (C1‴), 141.3 (C9a′), 141.2 (C8a′), 139.7 (C2′), 138.3 (C2), 137.1 (C7a), 131.7 (C6″), 130.2 (C4″), 128.8 (C3‴, C5‴), 127.5 (C2‴, C6‴), 127.3 (C4‴), 126.8 (C3a), 126.4 (C7′), 123.0 (C6), 121.6 (C5), 121.4 (C4b′), 121.1 (C6′), 120.9

(C4), 120.8 (C4a′), 120.6 (C3″), 120.4 (C5′/C4′), 120.32 (C5″), 120.30 (C3′), 119.8 (C1″), 110.6 (C3″), 109.72 (C7), 109.67 (C8′), 108.0 (C1′), 103.9 (C3), 55.1 (OCH_3).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{33}H_{25}N_2O$: 465.1961; found: 465.1951.

The e.r. of 70:30 for (S_a)-**6k** was determined by NP-HPLC (Chiralpak IG analytical column; 1.0 mL·min^{-1}, heptane/*i*PrOH 97.5:2.5; 40 °C): t_R = 7.57 (major), 9.50 min (minor).

(S_a)-9-(2-(2-Methoxyphenyl)-1*H*-indol-1-yl)-2-(trifluoromethyl)-9*H*-carbazole ((S_a)-6l)

Prepared according to the general procedure using *N*-(2-((2-methoxyphenyl)ethynyl)phenyl)-2-(trifluoromethyl)-9*H*-carbazol-9-amine (**3l**; 18.3 mg, 40.0 µmol, 1.00 equiv) followed by preparative TLC (silica gel, cyclohexane/CH_2Cl_2 2:1) to give (S_a)-**6l** (5.20 mg, 11.4 µmol, 29%) as a white solid; mp 167.5–170.0 °C; $[\alpha]_D^{24}$ +8.1 (*c* 0.3, $CHCl_3$); R_f = 0.48 (cyclohexane/CH_2Cl_2, 4:1).

IR (neat): 3062w, 2961w, 2921w, 2843w, 1631w, 1608w, 1583w, 1485w, 1448m, 1415w, 1321s, 1295w, 1261m, 1235m, 1160w, 1115s, 1054m, 1020m, 951m, 876w, 820w, 738m, 723m cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.10 (d, ^3J = 8.2 Hz, 1 H, C4′*H*), 8.06 (d, ^3J = 7.8 Hz, 1 H, C5′*H*), 7.77 (d, ^3J = 7.9 Hz, 1 H, C4*H*), 7.48 (d, ^3J = 8.2 Hz, 1 H, C3′*H*), 7.42–7.35 (m, 2 H, C1′*H*, C7′*H*), 7.31–7.26 (m, 2 H, C6′*H*, C6″*H*), 7.25–7.21 (m, 1 H, C5*H*), 7.14–7.06 (m, 2 H, C6*H*, C4″*H*), 7.02 (d, ^3J = 8.2 Hz, 1 H, C8′*H*), 6.85 (d, ^4J = 0.7 Hz, 1 H, C3*H*), 6.72 (td, ^3J = 7.5, ^4J = 0.9 Hz, 1 H, C5″*H*), 6.62 (d, ^3J = 8.2 Hz, 2 H, C3″*H*, C7*H*), 3.40 (s, 3 H, OCH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 157.5 (C2″), 141.5 (C8a′), 139.7 (C9a′), 138.3 (C2), 136.9 (C7a), 131.8 (C6″), 130.3 (C4″), 127.5 (C7′), 126.8 (C3a), 123.9 (C4a′), 123.1 (C6), 121.7 (C5), 121.3 (C6′), 121.1 (C4), 120.8 (C5′), 120.6 (C4′), 120.4 (C4b′), 120.1 (C5″), 119.3 (C1″), 117.52–117.31 (m, C3′), 110.3 (C3″), 109.8 (C8′), 109.2 (C7), 107.18 (q, $^3J_{CF}$ = 4.2 Hz, C1′), 103.9 (C3), 54.8 (OCH_3).

^{19}F NMR (471 MHz, $CDCl_3$): δ = –61.04.

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{28}H_{18}F_3N_2O$: 455.1377; found: 455.1373.

The e.r. of 68:32 for (S_a)-**6l** was determined by NP-HPLC (Chiralpak IB analytical column; 1.0 mL·min^{-1}, heptane/*i*PrOH 97.5:2.5; 40 °C): t_R = 5.30 (major), 5.72 min (minor).

9-(2-Mesityl-1*H*-indol-1-yl)-2-phenyl-9*H*-carbazole (*rac*-6m)

N-(2-(Mesitylethynyl)phenyl)-2-phenyl-9*H*-carbazol-9-amine (**3m**; 19.1 mg, 40.0 µmol, 1.00 equiv) and $Pd(CH_3CN)_2Cl_2$ (2.08 mg, 8.00 µmol, 1.00 equiv) were dissolved in dry EtOH (10 mL) and the resulting mixture was stirred at 80 °C for 48 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, cyclohexane/CH_2Cl_2 from 1:0 to 10:1) to give *rac*-**6m** (15.3 mg, 32.1 µmol, 80%) as a beige viscous solid; R_f = 0.51 (cyclohexane/CH_2Cl_2, 3:1).

IR (neat): 3055w, 3012w, 2959w, 2921w, 2860w, 1729w, 1609m, 1567w, 1484w, 1454s, 1312m, 1229m, 1150w, 1076w, 1037w, 907m, 853m, 803w, 735s, 697s cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.07 (d, ^3J = 8.1 Hz, 1 H, C4′*H*), 8.05–8.02 (m, 1 H, C5′*H*), 7.76–7.73 (m, 1 H, C4*H*), 7.54–7.46 (m, 3 H, C3′*H*, C2‴*H*, C6‴*H*), 7.39 (t, ^3J = 7.7 Hz, 2 H, C3‴*H*, C5‴*H*), 7.32–7.26 (3 H, C4‴*H*, C6′*H*, C7′*H*), 7.24–7.22 (m, 1 H, C1′*H*), 7.22–7.18 (m, 1 H, C5*H*), 7.05–6.97 (m, 2 H, C6*H*, C8′*H*), 6.72 (d, ^3J = 6.7 Hz, 2 H, C3″*H*, C5″*H*), 6.67 (d, ^4J = 0.8 Hz, 1 H, C3*H*), 6.51–6.47 (m, 1 H, C7*H*), 2.30 (s, 3 H, C2″-CH_3), 2.22 (s, 3 H, C6″-CH_3), 2.13 (s, 3 H, C4″-CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 141.4 (C1‴), 141.1 (C2′), 140.9 (C9a′), 139.4 (C8a′), 138.8 (C2), 138.7 (C6″), 138.6 (C2″), 138.4 (C4″), 136.3 (C7a), 128.7 (C3‴, C5‴), 128.2 (C5″), 128.1 (C3″), 127.4 (C2‴, C6‴), 127.2 (C4‴), 126.9 (C1″), 126.3 (C3a), 125.9 (C7′), 122.7 (C5), 121.6 (C4b′), 121.3 (C6/C6′), 121.1 (C4a′), 120.9 (C4), 120.6 (C3′), 120.5 (C4′), 120.3 (C5′), 110.1 (C8′), 109.7 (C7), 108.4 (C1′), 104.2 (C3), 21.6 (C2″-CH_3), 21.4 (C6″-CH_3), 21.0 (C4″-CH_3).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{35}H_{29}N_2$: 477.2325; found: 477.2318.

9-(2-(2,6-Dichlorophenyl)-1*H*-indol-1-yl)-2-phenyl-9*H*-carbazole (*rac*-6n)

N-(2-((2,6-Dichlorophenyl)ethynyl)phenyl)-2-phenyl-9*H*-carbazol-9-amine (**3n**; 20.1 mg, 40.0 µmol, 1.00 equiv) and $Pd(CH_3CN)_2Cl_2$ (2.08 mg, 8.00 µmol, 1.00 equiv) were dissolved in dry EtOH (10 mL) and the resulting mixture was stirred at 80 °C for 48 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, cyclohexane/CH_2Cl_2 from 1:0 to 10:1) to give *rac*-**6n** (17.0 mg, 33.8 µmol, 84%) as a yellow viscous solid; R_f = 0.60 (cyclohexane/EtOAc, 15:2).

IR (neat): 3059w, 2954w, 2924w, 2852w, 1721w, 1607w, 1557w, 1455s, 1427s, 1316m, 1230m, 1152w, 1096w, 1014w, 907w, 867w, 823w, 784w, 734s cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.09–8.06 (m, 1 H, C4′*H*), 8.05 (dt, ^3J = 7.6, ^4J = 0.9 Hz, 1 H, C5′*H*), 7.79 (dt, ^3J = 7.9, ^4J = 1.0 Hz, 1 H, C4*H*), 7.59–7.55 (m, 2 H, C2‴*H*, C6‴*H*), 7.53–7.49 (m, 2 H, C1′*H*, C3′*H*), 7.41–7.36 (m, 2 H, C3‴*H*, C5‴*H*), 7.33–7.27 (m, 3 H, C6′*H*, C7′*H*, C4‴*H*), 7.25–7.18 (m, 4 H, C5*H*, C8′*H*, C3″*H*, C5″*H*), 7.11 (t, ^3J = 8.1 Hz, 1 H, C4″*H*), 7.05 (td, ^3J = 7.7, ^4J = 1.0 Hz, 1 H, C6*H*), 6.88 (d, ^4J = 0.8 Hz, 1 H, C3*H*), 6.50–6.43 (m, 1 H, C7*H*).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 141.6 (C9a′), 141.5 (C8a′), 141.3 (C1‴), 139.7 (C2′), 137.5 (C2″/C6″), 137.35 (C2″/C6″), 136.3 (C7a), 134.4 (C2), 130.9 (C4″), 129.5 (C1″), 128.8 (C3‴, C5‴), 128.3 (C3″/C5″), 128.2 (C3″/C5″), 127.6 (C2‴, C6‴), 127.3 (C4‴), 126.10 (C3a), 126.08 (C7′), 123.7 (C6), 121.9 (C4b′), 121.70 (C4), 121.68 (C5), 121.4 (C6′), 121.35 (C4a′), 120.9 (C3′), 120.6 (C4′), 120.3 (C5′), 111.1 (C8′), 109.9 (C7), 109.1 (C1′), 105.7 (C3).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{32}H_{21}Cl_2N_2$: 503.1076; found: 503.1068.

(S_a)-9-(5-Fluoro-2-phenyl-1*H*-indol-1-yl)-2-phenyl-9*H*-carbazole ((S_a)-7a)

Prepared according to the general procedure using *N*-(4-fluoro-2-(phenylethynyl)phenyl)-2-phenyl-9*H*-carbazol-9-amine (**4a**; 18.1 mg, 40.0 µmol, 1.00 equiv) followed by column chromatography (silica gel) to give (S_a)-**7a** (11.5 mg, 25.4 µmol, 64%) as a white solid; mp 95.6–97.0 °C; $[\alpha]_D^{22}$ –16.1 (*c* 0.6, $CHCl_3$); R_f = 0.36 (cyclohexane/CH_2Cl_2 3:1).

IR (neat): 3055w, 2971w, 2904w, 1606w, 1499m, 1453s, 1408w, 1316m, 1232s, 1219m, 1074s, 908w, 860w, 818w, 691s cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.15 (d, ^3J = 8.1 Hz, 1 H, C4′*H*), 8.13–8.08 (m, 1 H, C5′*H*), 7.55 (dd, ^3J = 8.1, ^4J = 1.6 Hz, 1 H, C3′*H*), 7.54–7.51 (m, 2 H, C2‴*H*, C6‴*H*), 7.42–7.36 (m, 5 H, C3‴*H*, C5‴*H*, C2″*H*, C6″*H*, C4*H*), 7.34 (td, ^3J = 7.7, ^4J = 1.3 Hz, 1 H, C7′*H*), 7.32–7.28 (m, 2 H, C6′*H*, C4‴*H*), 7.18 (d, ^4J = 1.1 Hz, 1 H, C1′*H*), 7.16–7.11 (m, 3 H, C3″*H*, C4″*H*, C5″*H*), 6.95 (d, ^3J = 7.7 Hz, 1 H, C8′*H*), 6.92 (d, ^4J = 0.6 Hz, 1 H, C3*H*), 6.79 (td, ^3J = 9.1, ^4J = 2.4 Hz, 1 H, C6*H*), 6.53 (dd, ^3J = 8.9, ^4J = 4.3 Hz, 1 H, C7*H*).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 159.3 (d, $^1J_{CF}$ = 236.8 Hz, C5), 142.9 (C2), 141.3 (C1‴), 141.2 (C9a′), 141.0 (C8a′), 140.5 (C2′), 134.3 (C7a), 130.3 (C1″), 128.9 (C3″, C5″), 128.8 (C2″, C6″), 128.6 (C4″), 127.6 (C2‴, C6‴), 127.5 (C4‴), 127.4 (C3‴, C5‴), 127.3 (C3a), 126.9 (C7′), 121.7 (C4b′), 121.5 (C6′), 121.09 (C4′), 121.06 (C4a′), 121.02 (C3′), 120.8 (C5′), 111.70 (d, $^2J_{CF}$ = 26.4 Hz, C6), 110.6 (d, $^3J_{CF}$ = 9.6 Hz, C7), 109.1 (C8′), 107.3 (C1′), 106.33 (d, $^2J_{CF}$ = 24.1 Hz, C4), 102.16 (d, $^4J_{CF}$ = 4.4 Hz, C3).

^{19}F NMR (471 MHz, $CDCl_3$): δ = –122.09.

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{32}H_{20}FN_2$: 451.1616; found: 451.1620.

The e.r. of 80:20 for (*S*$_a$)-**7a** was determined by NP-HPLC (Chiralpak IB analytical column; 1.0 mL·min^{-1}, heptane/*i*PrOH 97.5:2.5; 40 °C): t_R = 5.63 (major), 5.42 min (minor).

(*S*$_a$)-9-(5-Methyl-2-phenyl-1*H*-indol-1-yl)-2-phenyl-9*H*-carbazole ((*S*$_a$)-7b)

Prepared according to the general procedure using *N*-(4-methyl-2-(phenylethynyl)phenyl)-2-phenyl-9*H*-carbazol-9-amine (**4b**; 17.9 mg, 40.0 µmol, 1.00 equiv) followed by column chromatography (silica gel) to give (*S*$_a$)-**7b** (13.0 mg, 29.0 µmol, 73%) as a white solid; mp 126.0–127.7 °C; $[\alpha]_D^{22}$ –23.7 (*c* 0.7, $CHCl_3$); R_f = 0.40 (cyclohexane/CH_2Cl_2 3:1).

IR (neat): 3058w, 3023w, 2917w, 1729w, 1607m, 1454m, 1316m, 1233m, 1132w, 1074w, 1013w, 906s, 870w, 798m, 728s, 694s cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.14 (dd, ^3J = 8.1, ^4J = 0.6 Hz, 1 H, C4′*H*), 8.13–8.07 (m, 1 H, C5′*H*), 7.58–7.50 (m, 4 H, C4*H*, C2‴*H*, C6‴*H*, C3′*H*), 7.43–7.27 (m, 7 H, C2″*H*, C6″*H*, C3‴*H*, C5‴*H*, C6′*H*, C7′*H*, C4‴*H*), 7.22–7.18 (m, 1 H, C1′*H*), 7.15–7.05 (m, 3 H, C3″*H*, C4″*H*, C5″*H*), 6.96 (dt, ^3J = 8.4, ^4J = 0.8 Hz, 1 H, C8′*H*), 6.89 (d, ^4J = 0.8 Hz, 1 H, C3*H*), 6.88–6.86 (m, 1 H, C6*H*), 6.52 (d, ^3J = 8.3 Hz, 1 H, C7*H*), 2.44 (s, 3 H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 141.41 (C9a′/C2/C1‴), 141.40 (C9a′/C2/C1‴), 141.39 (C9a′/C2/C1‴), 141.2 (C8a′), 140.4 (C2′), 136.4 (C7a), 131.5 (C5), 130.8 (C1″), 128.8 (C3″/C5″), 128.7 (C3‴/C5‴), 128.2 (C4″), 127.6 (C2‴/C6‴), 127.4 (C4‴), 127.3 (C2″/C6″), 127.1 (C3a), 126.9 (C7′), 124.9 (C6), 121.6 (C4b′), 121.3 (C6′), 121.0 (C4′/C3′), 120.9 (C4a′), 120.8 (C4), 120.7 (C5′), 109.5 (C7), 109.2 (C8′), 107.4 (C1′), 101.9 (C3), 21.6 (*C*H$_3$).

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{33}H_{23}N_2$: 447.1867; found: 447.1873.

The e.r. of 80:20 for (*S*$_a$)-**7b** was determined by NP-HPLC (Chiralpak IB analytical column; 1.0 mL·min^{-1}, heptane/*i*PrOH 97.5:2.5; 40 °C): t_R = 5.13 (major), 5.37 min (minor).

(*S*$_a$)-9-(5-Chloro-2-phenyl-1*H*-indol-1-yl)-2-phenyl-9*H*-carbazole ((*S*$_a$)-7c)

Prepared according to the general procedure using *N*-(4-chloro-2-(phenylethynyl)phenyl)-2-phenyl-9*H*-carbazol-9-amine (**4c**; 18.8 mg, 40.0 µmol, 1.00 equiv) followed by preparative TLC (silica gel, cyclohexane/CH_2Cl_2 3:1) to give (*S*$_a$)-**7c** (14.0 mg, 29.9 µmol, 75%) as a beige viscous solid; $[\alpha]_D^{22}$ –41.9 (*c* 0.7, $CHCl_3$); R_f = 0.45 (cyclohexane/CH_2Cl_2 3:1).

IR (neat): 3059w, 3037w, 1607w, 154w, 1488m, 1454s, 1412w, 1317w, 1233m, 1179w, 1063w, 908w, 864w, 795m, 755s, 695s cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.15 (d, ^3J = 8.1 Hz, 1 H, C4′*H*), 8.11 (d, ^3J = 7.2 Hz, 1 H, C5′*H*), 7.71 (d, ^4J = 1.8 Hz, 1 H, C4*H*), 7.56 (dd, ^3J = 8.1, ^4J = 1.5 Hz, 1 H, C3′*H*), 7.54–7.50 (m, 2 H, C2‴*H*, C6‴*H*), 7.41–7.36 (m, 4 H, C2″*H*, C6″*H*, C3‴*H*, C5‴*H*), 7.36–7.27 (m, 3 H, C6′*H*, C7′*H*, C4‴*H*), 7.16 (d, ^4J = 1.1 Hz, 1 H, C1′*H*), 7.16–7.12 (m, 3 H, C3″*H*, C5″*H*, C4″*H*), 7.00 (dd, ^3J = 8.6, ^4J = 1.8 Hz, 1 H, C6*H*), 6.94 (d, ^3J = 7.6 Hz, 1 H, C8′*H*), 6.90 (d, ^4J = 0.5 Hz, 1 H, C3*H*), 6.54 (d, ^3J = 8.6 Hz, 1 H, C7*H*).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 142.6 (C2), 141.3 (C1‴), 141.2 (C9a′), 140.9 (C8a′), 140.6 (C2′), 136.2 (C7a), 130.1 (C1″), 128.9 (C3″, C5″), 128.8 (C2″, C6″), 128.7 (C4″), 127.8 (C3a), 127.7 (C5), 127.6 (C2‴, C6‴), 127.5 (C4‴), 127.4 (C3‴, C5‴), 126.9 (C7′), 123.7 (C6), 121.7 (C4b′), 121.6 (C6′), 121.11 (C4a′), 121.08 (C4′), 121.07 (C3′), 120.8 (C5′), 120.7 (C4), 110.9 (C7), 109.1 (C8′), 107.3 (C1′), 101.7 (C3).

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{32}H_{20}ClN_2$: 467.1320; found: 467.1321.

The e.r. of 80:20 for (*S*$_a$)-**7b** was determined by NP-HPLC (Chiralpak IG analytical column; 1.0 mL·min^{-1}, heptane/*i*PrOH 97.5:2.5; 40 °C): t_R = 7.80 (major), 7.45 min (minor).

(*S*$_a$)-9-(5-Chloro-2-phenyl-1*H*-indol-1-yl)-2-(3,5-dimethylphenyl)-9*H*-carbazole ((*S*$_a$)-7d)

Prepared according to the general procedure using *N*-(4-chloro-2-(phenylethynyl)phenyl)-2-(3,5-dimethylphenyl)-9*H*-carbazol-9-amine (**4d**; 19.9 mg, 40.0 µmol, 1.00 equiv) followed by preparative TLC (silica gel, cyclohexane/CH_2Cl_2, 3:1) to give (*S*$_a$)-**7d** (13.5 mg, 27.2 µmol, 68%) as a beige viscous solid; $[\alpha]_D^{23}$ –46.3 (*c* 0.7, $CHCl_3$); R_f = 053 (cyclohexane/CH_2Cl_2 3:1).

IR (neat): 3051w, 2961w, 2919w, 2842w, 1729w, 1604m, 1443s, 1326w, 1269w, 1232m, 1177w, 1102w, 1063w, 999w, 906sm, 848m, 819m, 728s cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.13 (d, ^3J = 8.1 Hz, 1 H, C4′*H*), 8.11–8.08 (m, 1 H, C5′*H*), 7.71 (d, ^4J = 1.9 Hz, 1 H, C4*H*), 7.58–7.50 (m, 1 H, C3′*H*), 7.43–7.35 (m, 2 H, C2″*H*, C6″*H*), 7.34–7.26 (m, 2 H, C6′*H*, C7′*H*), 7.19 (s, 1 H, C1′*H*), 7.17–7.10 (m, 5 H, C3″*H*, C4″*H*, C5″*H*,, C2‴*H*, C6‴*H*), 7.00 (dd, ^3J = 8.7, ^4J = 1.9 Hz, 1 H, C6*H*), 6.96 (s, 1 H, C4‴*H*), 6.91 (s, 1 H, C3*H*), 6.87 (d, ^3J = 7.2 Hz, 1 H, C8′*H*), 6.54 (^3J = 8.7 Hz, 1 H, C7H), 2.34 (s, 6 H, 2 × *C*H$_3$).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 142.5 (C2), 141.2 (C1‴), 141.0 (C9a′), 140.8 (C8a′), 138.3 (C3‴, C5‴), 136.1 (C7a), 129.9 (C1″), 129.1 (C4‴), 128.7 (C3″, C5″), 128.6 (C4″), 127.7 (C5), 127.6 (C3a), 127.3 (C2″, C6″), 126.7 (C7′), 125.4 (C2‴, C6‴), 123.6 (C6), 121.6 (C4b′), 121.4 (C6′), 121.1 (C3′), 120.9 (C4′), 120.8 (C4a′), 120.6 (C5′), 120.5 (C4), 110.8 (C7), 108.8 (C8′), 107.1 (C1′), 101.5 (C3), 21.4 (*C*H$_3$).

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{34}H_{24}C_lN_2$: 495.1634; found: 495.1635.

The e.r. of 79:21 for (*S*$_a$)-**7d** was determined by NP-HPLC (Chiralpak IG analytical column; 1.0 mL·min^{-1}, heptane/*i*PrOH 97.5:2.5; 40 °C): t_R = 6.83 (major), 5.60 min (minor).

(*R*$_a$)-9-(6-Methyl-2-phenyl-1*H*-indol-1-yl)-2-phenyl-9*H*-carbazole ((*R*$_a$)-7e)

Prepared according to the general procedure using *N*-(5-methyl-2-(phenylethynyl)phenyl)-2-phenyl-9*H*-carbazol-9-amine (**4e**; 17.9 mg, 40.0 µmol, 1.00 equiv) followed by preparative TLC (silica gel, cyclohexane/CH_2Cl_2 3:1) to give (*R*$_a$)-**7e** (11.5 mg, 25.6 µmol, 64%) as a beige solid; mp 84.3–85.5 °C; $[\alpha]_D^{24}$ –36.6 (*c* 0.6, $CHCl_3$); R_f = 056 (cyclohexane/CH_2Cl_2 3:1).

IR (neat): 3058w, 3023w, 2954w, 2920w, 2860w, 1729w, 1605m, 1468m, 1454s, 1317m, 1233s, 1075w, 1029w, 907s, 817m, 731s cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.17 (d, ^3J = 8.1 Hz, 1 H, C4′*H*), 8.12 (d, ^3J = 7.5 Hz, 1 H, C5′*H*), 7.62 (d, ^3J = 8.0 Hz, 1 H, C4*H*), 7.58–7.52 (m, 3 H, C3′*H*, C2‴*H*, C6‴*H*), 7.42–7.34 (m, 4 H, C2″*H*, C6″*H*, C3‴*H*, C5‴*H*), 7.34–7.28 (m, 3 H, C7′*H*, C4‴*H*, C6′*H*), 7.22 (s, 1 H, C1′*H*), 7.14–7.07

(m, 3 H, C3″*H*, C4″*H*, C5″*H*), 7.04 (d, ^3J = 8.0 Hz, 1 H, C5*H*), 6.98 (d, ^3J = 7.9 Hz, 1 H, C8′*H*), 6.92 (s, 1 H, C3*H*), 6.43 (s, 1 H, C7*H*), 2.25 (s, 3 H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 141.4 (C1‴), 141.3 (C9a′), 141.1 (C8a′), 140.7 (C2), 140.4 (C2′), 138.5 (C7a), 133.7 (C6), 130.8 (C1″), 128.9 (C2″, C6″), 128.7 (C3″, C5″), 128.1 (C4″), 127.6 (C2‴, C6‴), 127.4 (C4‴), 127.2 (C3‴, C5‴), 126.9 (C7′), 124.6 (C3a), 123.9 (C5), 121.5 (C4b′), 121.3 (C6′), 120.99 (C4′), 120.9 (C4a′), 120.8 (C4), 120.74 (C5′), 120.68 (C3′), 109.7 (C7), 109.2 (C8′), 107.4 (C1′), 102.3 (C3), 21.8 (CH_3).

HRMS (ESI): *m*/*z* [M – H]$^-$ calcd for $C_{33}H_{23}N_2$: 447.1867; found: 447.1861.

The e.r. of 80:20 for (R_a)-**7e** was determined by NP-HPLC (Chiralpak IG analytical column; 1.0 mL·min^{-1}, heptane/*i*PrOH 97.5:2.5; 40 °C): t_R = 5.93 (major), 5.17 min (minor).

Conflict of Interest

The authors declare no conflict of interest.

Funding Information

We gratefully acknowledge the Schweizerischer Nationalfonds zur Förderung der Wissenschaftlichen Forschung (175746) and the National Centre of Competence in Research, Molecular Systems Engineering (NCCR MSE) (182895) for financial support. This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 (H2020) research and innovation programme (grant agreement No. 101002471).

Acknowledgment

We thank E. Hamon for experimental support, Dr. A. Prescimone for X-ray crystallographic analysis, Prof. O. Baudoin and Solvias for helpful discussions and the generous donation of ligands.

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/a-1993-6899.

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