## **RSC** Advances

## **Electronic Supplementary Information (ESI)**

# Effective cholesteric liquid crystal inducers based on axially chiral alleno-acetylenes

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### **Experimental section**

#### General methods and materials

Toluene and THF were purified by a solvent drying system from LC Technology Solutions Inc. SP-105 and degassed by purging with N<sub>2</sub> for 30 min. Chloroform was deacidified by filtration through an alumina column prior to use. N,N-Diisopropylethylamine (DIPEA) was dried by distillation from CaH<sub>2</sub> under a nitrogen atmosphere. (P)-(+)-5,7-Di-tert-butyl-2methylnona-5,6-diene-3,8-diyn-2-ol ((P)-(+)-1),<sup>1</sup> 2-iodonaphthalene,<sup>2</sup> azidophenyl<sup>3</sup> and 4azidobiphenyl<sup>4</sup> were prepared according to procedures described in literature. All other chemicals were commercial products and were used as received. To prevent photoracemization in the synthesis of (P)-(+)-2b-d, light was excluded as much as possible. Flash chromatography (FC) was performed using silica gel (SiO<sub>2</sub>) purchased from Fluka (particle size 0.040–0.063 mm, 230–400 mesh) and thin-layer chromatography (TLC) was carried out on aluminium sheets coated with silica 60 F254 obtained from Merck; compounds were visualised with a UV lamp (254 nm). Melting points (m.p.) were determined using a Büchi-B540 capillary melting point apparatus and are uncorrected. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Varian Mercury-300 and Bruker DRX-400 spectrometers at 298 K, and chemical shifts are reported in ppm relative to the residual solvent signal as internal reference. FT-IR spectra were recorded on a Bruker Equinox 55 instrument (resolution  $cm^{-1}$ ). UV/Vis Spectra were recorded on a Varian Cary-500 Scan spectrophotometer and CD spectra were measured on a JASCO Corp., J-715, Rev. 1.00 instrument in a 1 cm quartz cuvette. Optical rotations were measured on a Perkin-Elmer 241 Polarimeter. Mass spectrometry (ESI-MS) was performed on a Bruker maXis ESI-Q-TOF spectrometer. Elemental analyses were performed at the Laboratorium für Organische Chemie, ETH Zürich, with a LECO CHN/900 instrument.

#### Helical Twisting power measurements

Cholesteric solutions in E7 (Merck) and MBBA (Sigma-Aldrich) were prepared in a concentration range of 0.2 - 2.5% (w/w) by avoiding the daylight as much as possible. Cholesteric pitch and handedness were obtained at room temperature using the lens version of the Grandjean-Cano method<sup>5</sup> with a standard Zeiss microscope equipped with a JVC video camera. Keeping the light intensity very low, the orientation of the samples under the Grandjean–Cano boundary conditions was followed.

(P)-(+)-(3,5-Di-*tert*-butylhepta-3,4-dien-1,6-diyne-1,7-diyl)dibenzene ((P)-(+)-2a)



Dichlorobistriphenylphosphine palladium(II) (41 mg, 10 mol%), copper(I) iodide (11 mg, 10 mol%) and tetrabutylammonium iodide (22 mg, 10 mol%) were brought under a nitrogen atmosphere in a Schlenk tube via three vacuum-nitrogen cycles. Degassed toluene (0.6 mL) was added, and the resulting suspension was stirred and treated with bromobenzene (61  $\mu$ L, 0.58 mmol), a solution of (P)-(+)-1 (30 mg. 0.12 mmol) in degassed toluene (0.6 mL) and degassed 5M aqueous sodium hydroxide (0.5 mL). The heterogeneous mixture was heated to 80 °C for 16 h, cooled to r.t. and diluted with water (0.5 mL) and 1M aqueous HCl (0.5 mL). The aqueous layer was extracted with  $Et_2O$  (3×, 5 mL). The combined organic phases were dried over MgSO<sub>4</sub>, filtered over Celite and evaporated. FC (SiO<sub>2</sub>; pentane/CH<sub>2</sub>Cl<sub>2</sub> 39:1) afforded (*P*)-(+)-**2a** (28 mg, 68%) as a colourless oil.  $[\alpha]_D^{20}$  +579° (*c* 0.5, CHCl<sub>3</sub>);  $R_f = 0.45$ (SiO<sub>2</sub>; pentane/Et<sub>2</sub>O 99.5:0.5); IR (ATR)  $v_{max}$  (neat)/cm<sup>-1</sup> 2963 (s), 1598 (w), 1489 (m), 1361 (m), 753 (s), 689 (s); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{\rm H}$  1.24 (s, 18 H; *t*-Bu), 7.28-7.35 (m, 6 H; H–C(3'-5')), 7.45-7.49 (m, 4 H; H–C(2',6')); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta_{\rm C}$  29.3 (C(CH<sub>3</sub>)<sub>3</sub>), 35.9 (C(CH<sub>3</sub>)<sub>3</sub>), 83.4, 92.8 (C≡C), 103.6 (C=C−C), 123.9 (C(1')), 128.1 (C(4')), 128.4 (C(3')), 131.6 (C(2')), 211.7 (C=C=C); HRMS (ESI) *m/z* (%): 354.2293 (32) 353.2260  $(100, [M + H]^+, \text{ calcd for } C_{27}H_{29}^+: 353.2264).$ 

(P)-4,4''-(3,5-Di-*tert*-butylhepta-3,4-dien-1,6-diyne-1,7-diyl)di-1,1'-biphenyl ((P)-(+)-2b)



Tetrakis(triphenylphosphine) palladium(0) (74 mg, 10 mol%), copper(I) iodide (12 mg, 10 mol%) and tetrabutylammonium iodide (24 mg, 10 mol%) were brought under a nitrogen atmosphere in a Schlenk tube via three vacuum-nitrogen cycles. Degassed toluene (0.6 mL) was added, and the resulting suspension was stirred and treated with 4-iodobiphenyl (179 mg, 0.64 mmol), a solution of (P)-(+)-1 (33 mg. 0.13 mmol) in degassed toluene (0.6 mL) and degassed 5M aqueous sodium hydroxide (0.5 mL). The heterogeneous mixture was heated to 80 °C for 16 h, cooled to r.t. and diluted with water (0.5 mL) and 1M aqueous HCl (0.5 mL). The aqueous layer was extracted with  $Et_2O$  (3× 5 mL). The combined organic phases were dried over MgSO<sub>4</sub> and evaporated. FC (SiO<sub>2</sub>; pentane/CH<sub>2</sub>Cl<sub>2</sub> 39:1) afforded (P)-(+)-2b (21 mg, 33%, e.r. > 99:1) as a white solid. m.p. 145–147 °C;  $[\alpha]_D^{20}$  +819° (c 0.5, CHCl<sub>3</sub>);  $R_f =$ 0.31 (SiO<sub>2</sub>; pentane/CH<sub>2</sub>Cl<sub>2</sub> 9:1); IR (ATR)  $v_{max}$  (neat)/cm<sup>-1</sup> 3032 (w), 2963 (s, sh), 1487 (br. m), 1361 (w), 839 (s), 762 (s), 723 (w), 696 (s); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, assignment based on COSY)  $\delta_{\rm H}$  1.26 (s, 18 H; *t*-Bu), 7.35 (br. t, J = 7.4 Hz, 2 H; H–C(4<sup>''</sup>)), 7.45 (br. t, J  $= 7.5 \text{ Hz}, 4 \text{ H}; \text{H}-\text{C}(3^{\prime\prime},5^{\prime\prime}); 7.53-7.62 \text{ (m, 12 H; H}-\text{C}(2^{\prime},3^{\prime},5^{\prime},6^{\prime})), \text{H}-\text{C}(2^{\prime\prime},6^{\prime\prime})); ^{13}\text{C NMR}$ (100 MHz, CDCl<sub>3</sub>, assignment based on HSQC and HMBC)  $\delta_{\rm C}$  29.3 (C(CH<sub>3</sub>)<sub>3</sub>), 36.0  $(C(CH_3)_3)$ , 84.1 (C=C-Ar), 92.8 (C=C-Ar), 103.8 (C=C-C), 122.8 (C(4')), 127.1, 127.2 (C(2',3',5',6')), 127.7 (C(4'')), 129.0 (C(3'',5'')), 132.0 (C(2'',6'')), 140.6, 140.8(C(1',1'')), 211.9 (C=C=C); HRMS (ESI) m/z (%): 544.2481 (18), 543.2442 (43,  $[M+K]^+$ , calcd for  $C_{39}H_{36}K^+$ : 543.2449), 527.2704 (20,  $[M+Na]^+$ , calcd for  $C_{39}H_{36}Na^+$ : 527.2709), 506.2918 (45), 505.2882 (100,  $[M+H]^+$ , calcd for C<sub>39</sub>H<sub>37</sub><sup>+</sup>: 505.2890); elemental analysis calcd (%) for C<sub>39</sub>H<sub>36</sub>: C 92.81, H 7.19; found: C 91.99, H 7.34.

(P)-1,1'-(3,5-Di-tert-butylhepta-3,4-dien-1,6-diyne-1,7-diyl)dinaphthalene ((P)-(+)-2c)



Dichlorobistriphenylphosphine palladium(II) (40 mg, 10 mol%), copper(I) iodide (11 mg, 10 mol%) and tetrabutylammonium iodide (21 mg, 10 mol%) were brought under a nitrogen atmosphere in a Schlenk tube via three vacuum-nitrogen cycles. Degassed toluene (0.6 mL) was added, and the resulting suspension was stirred and treated with 1-bromonaphthalene (78  $\mu$ L, 0.56 mmol), a solution of (P)-(+)-1 (29 mg. 0.11 mmol) in degassed toluene (0.6 mL) and degassed 5M aqueous sodium hydroxide (0.5 mL). The heterogeneous mixture was heated at 80 °C for 16 h, cooled to r.t. and diluted with water (0.5 mL) and 1M aqueous HCl (0.5 mL). The aqueous phase was extracted with Et<sub>2</sub>O (3×, 5 mL), and the combined organic phases were dried over MgSO<sub>4</sub> and evaporated. FC (SiO<sub>2</sub>, pentane/CH<sub>2</sub>Cl<sub>2</sub> 39:1) gave (P)-(+)-2c (31 mg, 62%, e.r. = 88:12) as an amber oil.  $[\alpha]_D^{20}$  +505° (c 0.5, CHCl<sub>3</sub>);  $R_f = 0.52$ (SiO<sub>2</sub>, pentane/Et<sub>2</sub>O 99:1); IR (ATR)  $v_{max}$  (neat)/cm<sup>-1</sup> 3056 (w), 2963 (s), 1474 (m), 1459 (m), 1396 (m), 1361 (m), 1219 (br. w), 798 (s), 772 (s); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, assignment based on COSY)  $\delta_{\rm H}$  1.36 (s, 18 H; *t*-Bu), 7.43 (dd, J = 8.3, 7.2 Hz, 2 H; H–C(3')), 7.49-7.61 (m, 4 H; H–C(6',7')), 7.72 (dd, J = 7.2, 1.2 Hz, 2 H; H–C(2')), 7.79-7.87 (m, 4 H, H-C(4',5')), 8.37 (d, J = 8.8 Hz, 2 H, H-C(8')); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, assignment based on HSQC and HMBC) δ<sub>C</sub> 29.3 (C(CH<sub>3</sub>)<sub>3</sub>), 36.0 (C(CH<sub>3</sub>)<sub>3</sub>), 83.3 (C=C-Ar), 91.1 (C=C-Ar), 104.0 (C=C-C), 121.6 (C(1')), 125.4 (C(3')), 126.4 (C(8')), 126.5, 126.9 (C(6',7')), 128.4, 128.6 (C(4',5')), 130.4 (C(2')), 133.4 (2×) (C(9',10')), 212.3 (C=C=C); HRMS (ESI) m/z (%): 454.2602 (37), 453.2565 (100,  $[M + H]^+$ , calcd for C<sub>35</sub>H<sub>33</sub><sup>+</sup>: 453.2577), 398.1980 (26), 397.1938 (72,  $[M - t-Bu + H]^+$ , calcd for C<sub>31</sub>H<sub>25</sub><sup>+</sup>: 397.1956); elemental analysis calcd (%) for C<sub>35</sub>H<sub>32</sub>: C 92.87, H 7.13; found: C 92.91, H 7.26.

(P)-2,2'-(3,5-Di-tert-butylhepta-3,4-dien-1,6-diyne-1,7-diyl)dinaphthalene ((P)-(+)-2d)



Tetrakis(triphenylphosphine) palladium(0) (69 mg, 10 mol%), copper(I) iodide (11 mg, 10 mol%) and tetrabutylammonium iodide (22 mg, 10 mol%) were brought under a nitrogen atmosphere in a Schlenk tube via three vacuum-nitrogen cycles. Degassed toluene (0.6 mL) was added, and the resulting suspension was stirred and treated with 2-iodonaphthalene (153 mg, 0.60 mmol), a solution of (P)-(+)-1 (31 mg, 0.12 mmol) in degassed toluene (0.6 mL) and degassed 5M aqueous sodium hydroxide (0.5 mL). The heterogeneous mixture was heated to 80 °C for 16 h, cooled to r.t. and diluted with water (0.5 mL) and 1M aqueous HCl (0.5 mL). The aqueous layer was extracted with  $Et_2O$  (3×, 5 mL). The combined organic phases were dried over MgSO<sub>4</sub> and evaporated. FC (SiO<sub>2</sub>; pentane/CH<sub>2</sub>Cl<sub>2</sub> 39:1) afforded (P)-(+)-2d (8 mg, 15%, e.r. = 99:1) as a white solid. m.p. 152–153 °C;  $[\alpha]_D^{20}$  +896° (c 0.5, CHCl<sub>3</sub>);  $R_{\rm f} = 0.37$  (SiO<sub>2</sub>; pentane/CH<sub>2</sub>Cl<sub>2</sub> 24:1); IR (ATR)  $v_{\rm max}$  (neat)/cm<sup>-1</sup> 3057 (w), 2961 (m, sh), 1595 (w), 1498 (w), 1472 (w, sh), 1361 (w), 1241 (w), 1221 (w, sh), 951 (w), 895 (m), 859 (m), 819 (s), 744 (s); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, assignment based on COSY)  $\delta_{\rm H}$ 1.30 (s, 18 H; *t*-Bu), 7.45-7.50 (m, 4 H; H–C(6',7')), 7.53 (dd, J = 8.5, 1.6 Hz, 2 H; H–C(3')), 7.76-7.82 (m, 6 H; H–C(4',5',8')), 7.99 (br. s, 2H; H–C(1')); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, assignment based on HSQC and HMBC)  $\delta_C$  29.3 (C(CH<sub>3</sub>)<sub>3</sub>), 36.0 (C(CH<sub>3</sub>)<sub>3</sub>), 83.8 (C=C-Ar), 93.3 (C=C-Ar), 103.8 (C=C-C), 121.2 (C(10')), 126.6 (2x) (C(6',7')), 127.9 (2x), 128.0 (C(4',5',8')), 128.6 (C(3')), 131.3 (C(1')), 132.8 (C(2')), 128.6 (C(9')), 121.1 (C=C=C); HRMS (ESI) m/z (%): 492.2164 (24) 491.2129 (64,  $[M + K]^+$ , calcd for C<sub>35</sub>H<sub>32</sub>K<sup>+</sup>: 491.2136), 454.2605 (43), 453.2567 (100,  $[M + H]^+$ , calcd for C<sub>35</sub>H<sub>33</sub><sup>+</sup>: 453.2577); elemental analysis calcd (%) for C<sub>35</sub>H<sub>32</sub>·<sup>1</sup>/<sub>2</sub>H<sub>2</sub>O: C 91.06, H 7.21; found: C 90.74, H 7.27.

## (*P*)-5-(*tert*-Butyl)-2,8,8-trimethyl-7-(1-phenyl-1*H*-1,2,3-triazol-4-yl)nona-5,6-dien-3-yn-2-ol ((*P*)-(+)-3a)



A degassed solution of (P)-(+)-1 (42 mg, 0.16 mmol) and azidophenyl (21 mg, 0.18 mmol) in THF (1 mL) was treated with DIPEA (0.2 mL) and copper(I) iodide (6 mg, 20 mol%). Stirred under N<sub>2</sub> for 40 h and diluted with 1M aqueous HCl (1 mL). The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×, 2 mL), and the combined organic layers were dried over MgSO<sub>4</sub> and evaporated. FC (SiO<sub>2</sub>, cvclohexane/EtOAc 4:1) vielded (P)-(+)-3a (43 mg, 70%) as an amber oil.  $[\alpha]_D^{20}$  +218° (c 0.5, CHCl<sub>3</sub>);  $R_f = 0.32$  (SiO<sub>2</sub>, cyclohexane/EtOAc 4:1); IR (ATR)  $v_{max}$ (neat)/cm<sup>-1</sup> 3381 (br. m), 2963 (s), 1599 (m), 1501 (m), 1361 (m), 1220 (br. m), 1165 (br. m), 1034 (m), 757 (s), 690 (m); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, assignment based on COSY)  $\delta_{\rm H}$  1.16 (s, 9 H; *t*-Bu), 1.35 (s, 9 H; *t*-Bu); 1.56 (s, 6 H; (CH<sub>3</sub>)<sub>2</sub>OH), 2.01 (s, 1H; OH), 7.43 (tt, *J* = 7.4, 1.2 Hz, 1 H; H–C(4')), 7.49-7.54 (m, 2 H; H–C(3',5')), 7.72-7.76 (m, 2 H; H–C(2',6')), 7.78 (s, 1 H, triazolyl H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, assignment based on HSQC)  $\delta_{\rm C}$  29.2, 29.8 (C(CH<sub>3</sub>)<sub>3</sub>), 31.7 (C(CH<sub>3</sub>)<sub>2</sub>OH), 35.3, 35.5 (C(CH<sub>3</sub>)<sub>3</sub>), 65.9 (C(CH<sub>3</sub>)<sub>2</sub>OH), 76.4, 96.9 (C≡C), 102.4 (C=C-alkyl), 109.3 (C=C-triazolyl), 120.1 (N-CH), 120.6 (C(2',6')), 128.7 (C(4')), 129.8 (C(3',5')), 137.2 (C(1')), 144.6 (N-C=CH), 206.4 (C=C=C); HRMS (ESI) m/z (%):  $378.2557 (16, [M + H]^+, \text{ calcd for } C_{24}H_{32}N_3O^+: 378.2540), 361.2482 (23), 360.2453 (100, [M$  $- OH^{+}_{1}$ , calcd for C<sub>24</sub>H<sub>30</sub>N<sub>3</sub><sup>+</sup>: 360.2534).

(*P*)-7-{1-[(1,1'-Biphenyl)-4-yl]-1*H*-1,2,3-triazol-4-yl}-5-(*tert*-butyl)-2,8,8-trimethylnona-5,6-dien-3-yn-2-ol ((*P*)-(+)-3b)



A degassed solution of (P)-(+)-1 (49 mg, 0.19 mmol) and 4-azidobiphenyl (41 mg, 0.21 mmol) in THF (1 mL) was treated with DIPEA (0.2 mL) and copper(I) iodide (8 mg, 20 mol%). Stirred under N<sub>2</sub> for 40 h and diluted with 1M aqueous HCl (1 mL). The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×, 2 mL), and the combined organic layers were dried over MgSO<sub>4</sub> and evaporated. FC (SiO<sub>2</sub>, cyclohexane/EtOAc 4:1) yielded (P)-(+)-**3b** (73 mg, 85%) as an amber oil.  $[\alpha]_D^{20}$  +218° (*c* 0.5, CHCl<sub>3</sub>);  $R_f = 0.39$  (SiO<sub>2</sub>, cyclohexane/EtOAc 4:1); IR (ATR)  $v_{\text{max}}$  (neat)/cm<sup>-1</sup> 3393 (br. m), 2963 (s, sh), 1524 (m), 1490 (m, sh), 1392 (w), 1362 (m), 1220 (br. m), 1166 (br. m), 1032 (br. m), 989 (w), 956 (w), 841 (m), 763 (s), 697 (m); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, assignment based on COSY)  $\delta_{\rm H}$  1.18 (s, 9 H; *t*-Bu), 1.36 (s, 9 H; *t*-Bu), 1.57 (s, 6 H; (CH<sub>3</sub>)<sub>2</sub>OH), 1.98 (br. s, 1H; OH), 7.40 (tt, J = 7.2, 1.3 Hz, 1 H; H–C(4<sup>''</sup>)), 7.48 (br. t, J = 7.5 Hz, 2 H; H–C(3<sup>''</sup>,5<sup>''</sup>)), 7.61-7.64 (m, 2 H; H–C(2<sup>''</sup>,6<sup>''</sup>)), 7.72-7.76 (m, 2 H; H–C(2',6')), 7.80-7.84 (m, 3 H; H–C(3',5'), triazolyl H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, assignment based on HSQC and HMBC)  $\delta_{\rm C}$  27.1, 29.3 (C(CH\_3)\_3), 31.7 (C(CH\_3)\_2OH), 35.3, 35.6 (*C*(CH<sub>3</sub>)<sub>3</sub>), 65.9 (*C*(CH<sub>3</sub>)<sub>2</sub>OH), 76.5 (*C*=C–H), 97.0 (C=C–H), 102.5 (C=C–alkyl), 109.3 (C=C-triazolyl), 120.0 (N-CH), 120.9 (C(3',5')), 127.2 (C(2'',6'')), 128.1 (C(4'')), 128.5 (C(2',6')), 129.1 (C(3'',5'')), 136.3 (C(1')), 139.8 (C(1'')), 141.8 (C(4')), 144.7 (N-C=CH), 206.4 (C=C=C); HRMS (ESI) m/z (%): 476.2670 (11,  $[M + Na]^+$ , calcd for C<sub>30</sub>H<sub>35</sub>N<sub>3</sub>NaO<sup>+</sup>: 476.2672), 455.2880 (12), 454.2850 (34,  $[M + H]^+$ , calcd for C<sub>30</sub>H<sub>36</sub>N<sub>3</sub>O<sup>+</sup>: 454.2853),  $437.2773 (37), 436.2748 (100, [M - OH]^+, calcd for C_{30}H_{34}N_3^+: 436.2747).$ 

## (*P*)-4-[5-(*tert*-Butyl)-2,2-dimethylhepta-3,4-dien-6-yn-3-yl]-1-phenyl-1*H*-1,2,3-triazole ((*P*)-(+)-4a)



Under a N<sub>2</sub> atmosphere, (*P*)-(+)-**3a** (54 mg, 0.14 mmol) in toluene (4 mL) was added to sodium hydroxide powder (18 mg, 0.45 mmol). The solution was heated under reflux for 3 h., diluted with brine (2 mL) and extracted with EtOAc (3×, 5 mL). The combined extracts were dried over MgSO<sub>4</sub> and evaporated. FC (SiO<sub>2</sub>, cyclohexane/EtOAc 95:5) gave (*P*)-(+)-**4a** (45 mg, 98%) as a colourless oil.  $[a]_{D}^{20}$  +118° (*c* 0.5, CHCl<sub>3</sub>);  $R_{f} = 0.49$  (SiO<sub>2</sub>, cyclohexane/EtOAc 9:1); IR (ATR)  $\nu_{max}$  (neat)/cm<sup>-1</sup> 3309 (br. w), 2963 (s), 1600 (m), 1502 (s), 1476 (m), 1460 (m), 1362 (m), 1218 (m), 1034 (s), 759 (s), 689 (m); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, assignment based on COSY)  $\delta_{H}$  1.19 (s, 9 H; *t*-Bu), 1.37 (s, 9 H; *t*-Bu), 2.99 (s, 1 H; C=C-H), 7.46 (tt, *J* = 7.4, 1.2 Hz, 1 H; H–C(4')), 7.50-7.55 (m, 2 H; H–C(3',5')), 7.72-7.76 (m, 2 H; H–C(2',6')), 7.80 (s, 1 H; triazolyl H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, assignment based on HSQC and HMBC)  $\delta_{C}$  29.1, 29.8 (C(CH<sub>3</sub>)<sub>3</sub>), 35.3 (*C*(CH<sub>3</sub>)<sub>3</sub>), 78.3 (*C*=C-H), 80.1 (C=*C*-H), 102.1 (C=*C*-alkyl), 109.9 (C=*C*-triazolyl), 120.1 (N–CH), 120.6 C(2',6'), 128.8 C(4'), 129.8 C(3',5'), 137.2 (C(1')), 144.4 (N–C=CH), 207.3 (C=*C*=C); HRMS (ESI) *m/z* (%): 359.1703 (27), 358.1677 (100, [*M* + K]<sup>+</sup>, calcd for C<sub>21</sub>H<sub>25</sub>N<sub>3</sub>K<sup>+</sup>: 358.1668), 343.1965 (26), 342.1935 (89, [*M* + Na]<sup>+</sup>, calcd for C<sub>21</sub>H<sub>25</sub>N<sub>3</sub>A<sup>+</sup>: 342.1941).

(*P*)-1-[(1,1'-Biphenyl)-4-yl]-4-[5-(*tert*-butyl)-2,2-dimethylhepta-3,4-dien-6-yn-3-yl]-1*H*-1,2,3-triazole ((*P*)-(+)-4b)



Under a N<sub>2</sub> atmosphere, (P)-(+)-3b (60 mg, 0.13 mmol) in toluene (4 mL) was added to sodium hydroxide powder (16 mg, 0.40 mmol). The solution was heated under reflux for 3 h., diluted with brine (2 mL) and extracted with EtOAc (3×, 5 mL). The combined extracts were dried over MgSO<sub>4</sub> and evaporated. FC (SiO<sub>2</sub>, cyclohexane/EtOAc 95:5) gave (P)-(+)-4b (42 mg, 80%) as a white solid. m.p. 123–124 °C;  $[\alpha]_D^{20}$  +146° (*c* 0.5, CHCl<sub>3</sub>);  $R_f = 0.37$  (SiO<sub>2</sub>, cyclohexane/EtOAc 19:1); IR (ATR)  $v_{max}$  (neat)/cm<sup>-1</sup> 3289 (w), 3270 (w), 2961 (m, sh), 1523-1361 (m), 1239 (m), 1217 (br. m), 1051 (m), 1035 (m), 936 (w), 841 (m), 807 (w), 769 (s), 721 (m), 699 (s), 667 (s, sh), 624 (m); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{\rm H}$  1.20 (s, 9 H; *t*-Bu), 1.38 (s, 9 H; *t*-Bu), 3.01 (s, 1 H; C=C-H), 7.40 (tt, J = 7.4, 1.3 Hz, 1 H; H–C(4<sup>''</sup>)), 7.49 (br. t, J = 7.6 Hz, 2 H; H–C(3<sup>''</sup>,5<sup>''</sup>)), 7.61-7.64 (m, 2 H; H–C(2<sup>''</sup>,6<sup>''</sup>)), 7.72-7.76 (m, 2 H; H– C(2',6')), 7.80-7.85 (m, 3 H; H-C(3',5'), triazolyl H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, assignment based on HSQC and HMBC)  $\delta_{C}$  29.1, 29.8 (C(CH\_3)\_3), 35.3 (2×) (C(CH\_3)\_3), 78.2 (C=C-H), 80.1 (C=C-H), 102.1 (C=C-alkyl), 109.8 (C=C-triazolyl), 120.0 (N-CH), 120.9 (C(3',5')), 127.2 (C(2'',6'')), 128.1 (C(4'')), 128.4 (C(2',6')), 129.1 (C(3'',5'')), 136.1(C(1')), 139.8 (C(1'')), 141.7 (C(4')), 144.4 (N-C=CH), 207.3 (C=C=C); HRMS (ESI) m/z (%): 397.2479 (16), 396.2441 (54,  $[M + H]^+$ , calcd for C<sub>27</sub>H<sub>30</sub>N<sub>3</sub><sup>+</sup>: 396.2434), 369.2415 (26),  $368.2379 (100, [M - 2Me + 3H]^+, calcd for C_{25}H_{26}N_3^+: 368.2121).$ 

## (*P*)-4,4'-(2,2,6,6-Tetramethylhepta-3,4-diene-3,5-diyl)bis(1-phenyl-1*H*-1,2,3-triazole) ((*P*)-(+)-5a)



A degassed solution of (*P*)-(+)-**4a** (30 mg, 0.094 mmol) and azidophenyl (12 mg, 0.10 mmol) in THF (1 mL) was treated with DIPEA (0.2 mL) and copper(I) iodide (4 mg, 20 mol%). Stirred under N<sub>2</sub> for 24 h and diluted with aqueous 1M HCl (1 mL). The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×, 5 mL), and the combined organic layers were dried over MgSO<sub>4</sub> and evaporated. FC (SiO<sub>2</sub>, cyclohexane/EtOAc 85:15) afforded (*P*)-(+)-**5a** (37 mg, 90%) as a white solid. m.p. 130–131 °C;  $[\alpha]_D^{20}$  +405° (*c* 0.5, CHCl<sub>3</sub>);  $R_f = 0.50$  (SiO<sub>2</sub>, cyclohexane/EtOAc 4:1); IR (ATR)  $v_{max}$  (neat)/cm<sup>-1</sup> 2960 (br. m), 1599 (m), 1500 (s), 1218 (br. m), 1034 (s), 1056 (s), 732 (m), 689 (s); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, assignment based on COSY)  $\delta_H$  1.40 (s, 18 H; *t*-Bu), 7.42 (tt, *J* = 7.4, 1.2 Hz, 2 H; H–C(4′)), 7.48-7.54 (m, 4 H; H–C(3′,5′)), 7.72-7.77 (m, 4 H; H–C(2′,6′)), 7.91 (s, 2 H; triazolyl H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, assignment based on HSQC and HMBC)  $\delta_C$  30.0 (C(*C*H<sub>3</sub>)<sub>3</sub>), 35.1 (*C*(CH<sub>3</sub>)<sub>3</sub>), 109.1 (C=*C*-triazolyl), 119.9 (N–CH), 120.6 C(2′,6′), 128.7 C(4′), 129.8 C(3′,5′), 137.2 (C(1′)), 145.1 (N–*C*=CH), 202.5 (C=*C*=C); HRMS (ESI) *m/z* (%): 440.2637 (32), 439.2604 (100, [*M* + H]<sup>+</sup>, calcd for C<sub>27</sub>H<sub>31</sub>N<sub>6</sub><sup>+</sup>: 439.2605).

#### (P)-4,4'-(2,2,6,6-Tetramethylhepta-3,4-diene-3,5-diyl)bis{1-[(1,1'-biphenyl)-4-yl]-1H-

1,2,3-triazole} ((*P*)-(+)-5b)



A degassed solution of (P)-(+)-4b (28 mg, 0.071 mmol) and 4-azidobiphenyl (15 mg, 0.078 mmol) in THF (1 mL) was treated with DIPEA (0.2 mL) and copper(I) iodide (3 mg, 20 mol%), stirred under N<sub>2</sub> for 24 h and diluted with aqueous 1M HCl (1 mL). The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×, 5 mL), and the combined organic layers were dried over MgSO<sub>4</sub> and evaporated. FC (SiO<sub>2</sub>, cyclohexane/EtOAc 85:15) afforded (P)-(+)-5b (36 mg, 86%) as a colourless glassy solid or white foam. m.p. 103–106 °C;  $[\alpha]_D^{20}$  +488° (*c* 0.5, CHCl<sub>3</sub>);  $R_{\rm f} = 0.31$  (SiO<sub>2</sub>, cyclohexane/EtOAc 9:1); IR (ATR)  $v_{\rm max}$  (neat)/cm<sup>-1</sup> 3060 (br. w), 2961 (m, sh), 2248 (w), 1608 (w), 1523 (m), 1489 (m, sh), 1431-1361 (w), 1217 (br. m), 1032 (br. m, sh), 908 (m), 840 (m), 761 (s), 730 (s), 696 (s); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{\rm H}$ 1.42 (s, 18 H; *t*-Bu), 7.39 (tt, J = 7.4, 1.3 Hz, 2 H; H–C(4'')), 7.48 (br. t, J = 7.5 Hz, 4 H; H– C(3'',5''), 7.60-7.64 (m, 4 H; H–C(2'',6'')), 7.73 (br. d, J = 8.7 Hz, 4 H; H–C(2',6')), 7.83 (br. d, J = 8.7 Hz, 4 H; H–C(3',5')), 7.95 (s, 2 H, triazolyl H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, assignment based on HSQC and HMBC)  $\delta_C$  30.0 (C(CH<sub>3</sub>)<sub>3</sub>), 35.2 (C(CH<sub>3</sub>)<sub>3</sub>), 109.2 (C=Ctriazolyl), 119.9 (N-CH), 120.9 (C(3',5')), 127.2 (C(2'',6'')), 128.1 (C(4'')), 128.5 (C(2',6')), 129.1 (C(3'',5'')), 136.3 (C(1')), 139.8 (C(1'')), 141.8 (C(4')), 145.2 (N-C=CH), 202.6 (C=C=C); HRMS (ESI) m/z (%): 593.3289 (12), 592.3259 (53), 591.244 (100, [M +  $H_{1}^{+}$ , calcd for  $C_{39}H_{39}N_{6}^{+}$ : 591.3231).

## UV/Vis and CD spectra of title compounds



Fig. 1-ESI. CD (top) and UV/Vis (bottom) absorption spectra of (*P*)-(+)-2a-d and (*P*)-(+)-5a-b measured at  $1 \times 10^{-5}$  M in CHCl<sub>3</sub> (*T* = 298 K). Note that for (*P*)-(+)-2c e.r. = 88:12.



## CD spectra measured in time upon daylight exposure

**Fig. 2-ESI.** CD spectra of a  $1 \times 10^{-5}$  M solution of (*P*)-(+)-**2a** in CHCl<sub>3</sub> measured in time upon standing in the daylight.



**Fig. 3-ESI.** CD spectra of a  $1 \times 10^{-5}$  M solution of (*P*)-(+)-**2b** in CHCl<sub>3</sub> measured in time upon standing in the daylight.



**Fig. 4-ESI.** CD spectra of a  $1 \times 10^{-5}$  M solution of (*P*)-(+)-2c in CHCl<sub>3</sub> measured in time upon standing in the daylight. Note that e.r. (t = 0) = 88:12.



**Fig. 5-ESI.** CD spectra of a  $1 \times 10^{-5}$  M solution of (*P*)-(+)-2d in CHCl<sub>3</sub> measured in time upon standing in the daylight.



**Fig. 6-ESI.** CD spectra of a  $1 \times 10^{-5}$  M solution of (*P*)-(+)-**5a** in CHCl<sub>3</sub> measured in time upon standing in the daylight.



**Fig. 7-ESI.** CD spectra of a  $1 \times 10^{-5}$  M solution of (*P*)-(+)-**5b** in CHCl<sub>3</sub> measured in time upon standing in the daylight.

### Single-crystal X-ray analysis of (P)-(+)-2b and (±)-5a

(*P*)-(+)-2b: Single crystals were grown upon cooling of a solution in hot MeCN. The X-ray intensity data were measured on a Bruker Nonius Kappa APEX-II CCD system equipped with a fine-focus sealed X-ray tube (MoK $\alpha$ ,  $\lambda = 0.71073$  Å) with graphite monochromator. Collected data was processed with the Bruker SAINT software package<sup>6</sup> using a narrow frame algorithm and corrected for absorption effects using the multi-scan method (SADABS). The structure was solved and refined using the OLEX2<sup>7</sup> and SHELX<sup>8</sup> Software Package. Crystallographic data:  $C_{39}H_{36}$ ;  $M_w = 504.68$ ; crystal size  $0.40 \times 0.14 \times 0.09$  mm; monoclinic; space group  $P2_1$ ; a = 5.8859(5) Å, b = 27.177(2) Å, c = 18.490(2) Å;  $\alpha = 90^\circ$ ,  $\beta$ = 94.200(3)°,  $\gamma = 90°$ ; V = 2949.8(4) Å<sup>3</sup>; Z = 4;  $\rho_{calcd} = 1.136 \text{ mg/m}^{-3}$ ;  $\mu(Mo_{K_a}) = 0.064 \text{ mm}^{-1}$ ;  $T = 100 \text{ K}; \theta(\min/\max) = 2.67/27.68^{\circ}; 48103 \text{ reflections collected}; 13507 \text{ unique reflections}$  $F^2$ . 0.0490): refinement method: full-matrix least-squares on  $(R_{int})$ = data/restraints/parameters: 13507/1/991; GoF on  $F^2 = 0.996$ ; R1 = 0.0453 and wR2 = 0.0867 $[10201 \text{ I}>2\sigma(\text{I})]; R1 = 0.0756 \text{ and } wR2 = 0.0976 \text{ (all data)}; \text{ largest diff. peak and hole: } 0.173$ and -0.223 eÅ<sup>3</sup>.

(±)-5a: Single crystals were obtained by slow evaporation of a solution in CH<sub>2</sub>Cl<sub>2</sub>/hexane. Data was collected with a Bruker Kappa Apex-II Duo system equipped with a fine-focus sealed X-ray tube (MoK $\alpha$ ,  $\lambda = 0.71073$  Å) with graphite monochromator. Collected data was processed with the Bruker SAINT software package<sup>6</sup> using a narrow-frame algorithm and corrected for absorption effects using the multi-scan method (SADABS). The structure was solved and refined using the OLEX2<sup>7</sup> and SHELX<sup>8</sup> Software Package. Crystallographic data: C<sub>54</sub>H<sub>60</sub>N<sub>12</sub>;  $M_w = 877.14$ ; crystal size 0.08 × 0.06 × 0.04 mm; monoclinic; space group *P2*<sub>1</sub>/c; a = 11.2921(6) Å, b = 18.910(1) Å, c = 11.3518(8) Å;  $a = 90^{\circ}$ ,  $b = 96.286(4)^{\circ}$ ,  $\gamma = 90^{\circ}$ ; V = 2409.5(3) Å<sup>3</sup>; Z = 4;  $\rho_{calcd} = 1.209$  mg/m<sup>-3</sup>;  $\mu$ (Mo<sub>K-</sub>) = 0.074 mm<sup>-1</sup>; T = 100 K;  $\theta$ (min/max) = 1.81/27.52°; 20460 reflections collected; 5460 unique reflections ( $R_{int} = 0.0612$ ); refinement method: full-matrix least-squares on  $F^2$ ; data/restraints/parameters: 5460/0/418; GoF on  $F^2 = 0.985$ ; R1 = 0.0494 and wR2 = 0.0911 [3288 I>2 $\sigma$ (I)]; R1 = 0.1081 and wR2 = 0.1101 (all data); largest diff. peak and hole: 0.196 and -0.223 eÅ<sup>3</sup>.

CCDC-926555 ((*P*)-(+)-**2b**) and CCDC-926554 (( $\pm$ )-**5a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.



Fig. 8-ESI. Crystal packing of (*P*)-(+)-2b



Fig. 9-ESI. Crystal packing of (±)-5a

#### Torsional potentials and molecular geometries

The geometry of dopants was determined by quantum mechanical optimization with DFT at the B3LYP/6-31G(d,p) level.<sup>9</sup> The allene twist angle was found to be close to 90° for all dopants. Torsional potentials were calculated by relaxed scans of single dihedrals; the absence of correlations between  $\phi_1$  and  $\phi_2$  (see Fig. 10-ESI) was verified for (*P*)-(+)-**2a**. All calculations were performed in vacuum.

Fig. 10-ESI shows the torsional potential calculated for the rotation of aryl groups in (*P*)-(+)-**2a** and (*P*)-(+)-**2c**. The results obtained for (*P*)-(+)-**2b** and (*P*)-(+)-**2d** are very similar to those for (*P*)-(+)-**2a**. In the case of (*P*)-**2c**, there is a small energy difference between the two planar states: the conformation with the naphthyl group pointing inwards is slightly preferred over the other. For all dopants, almost free rotation of the aromatic rings is predicted, with only some preference for the planar geometry (allene bonds in the same plane of the aryl group). This behaviour is in line with experimental and theoretical results for the rotation around C<sub>ar</sub>-C<sub>sp</sub> bonds in diphenylacetylene.<sup>10</sup>



**Fig. 10-ESI.** Structure of (*P*)-(+)-**2a** showing the  $\phi_1, \phi_2$  dihedrals (left) and torsional potential (right) for the  $\phi$  dihedrals of (*P*)-(+)-**2a** (blue) and (*P*)-(+)-**2c** (red, dashed). For  $\phi = 0^\circ$  and  $\phi = 180^\circ$ , the allene bonds lie in the plane of the aryl ring; the naphthyl group points outwards for  $\phi = 0^\circ$  and inwards for  $\phi = 180^\circ$ .

In (*P*)-(+)-**5a-b**, the replacement of ethynyls by triazolyls has the effect of reducing the rotational freedom of the lateral wings. A single triazole substituent has a preferred conformation with the allene bonds approximately in the ring plane and the triazole hydrogen pointing inwards. The other conformation, which differs for having outwards pointing hydrogen, is higher in energy by about 3 kcal mol<sup>-1</sup>. The most stable state of (*P*)-(+)-**5a-b** (I, see Fig. 11-ESI) has both triazole rings in their lowest energy conformation. However, there

is some correlation between the two triazoles and in the di-substituted compound there is a second conformation (II) that is only about 0.75 kcal mol<sup>-1</sup> higher in energy than the (I) conformation. It has one triazolyl with inwards pointing hydrogen and the triazolyl-allene dihedral is about  $-30^{\circ}$  (+30°); the other triazolyl has outwards pointing hydrogen and triazolyl-allene dihedral of about +120° (-120°).



Fig. 11-ESI. Different core conformations I (left) and II (right) of (P)-(+)-5b.

Fig. 12-ESI shows the torsional potential for the triazole-phenyl twist angle and the molecular fragment used for calculations. The twist angle is mostly confined within a range of  $\pm 40^{\circ}$  around the planar configuration.



**Fig. 12-ESI.** Torsional potential for the phenyl-triazole twist angle (left) and molecular fragment used for calculations (right). Because of the symmetry, only one half of the torsional range is shown. For  $\chi=0^{\circ}$  and  $\chi=180^{\circ}$ , the triazole and phenyl rings are coplanar.

#### **Chirality parameter calculations**

The chirality parameter Q, defined in the Surface Chirality model,<sup>11</sup> was calculated for each molecular geometry as outlined in ref. [12]. In all calculations, the orienting strength  $\xi = 2.5$  nm<sup>-2</sup> was assumed. The molecular surface was generated using the program MSMS, with a rolling sphere radius equal to 0.3 nm and a density of vertices equal to 500 nm<sup>-2</sup>.<sup>13</sup> The following van der Waals radii were used:  $r_{\rm H} = 0.1$  nm,  $r_{\rm N} = 0.15$  nm and  $r_{\rm C} = 0.185$  nm.<sup>14</sup>

Q values of the chiral dopants were calculated by averaging over a finite number of conformers or over continuous torsional angles, according to the Boltzmann distribution.<sup>15</sup> Potential energies obtained by quantum chemical calculations were used (see previous section), and the temperature T = 300 K was assumed.

(*P*)-(+)-**2a**-d: the chirality parameter, *Q*, was calculated as a function of the ( $\phi_1$ ,  $\phi_2$ ) dihedrals. Molecular conformations were generated starting from structures obtained by geometry optimization (see previous section), with the allene twist angle set equal to 100°, in agreement with the crystal structures of (*P*)-(+)-**2b** (see main text). Fig. 13-ESI and Fig. 14-ESI show the chirality parameter *Q*, calculated for (*P*)-(+)-**2a** and (*P*)-(+)-**2c-d** as a function of the ( $\phi_1$ ,  $\phi_2$ ) dihedrals.



**Fig. 13-ESI.** Chirality parameter *Q* calculated for (*P*)-(+)-2**a** as a function of the  $\phi_1$  and  $\phi_2$  dihedrals. For  $\phi = 0^\circ$  and  $\phi = 180^\circ$ , the allene bonds are in the plane of the phenyl ring.



**Fig. 14-ESI.** Chirality parameter *Q* calculated for (*P*)-(+)-2c (left) and (*P*)-(+)-2d (right) as a function of the  $\phi_1$  and  $\phi_2$  dihedrals. For  $\phi = 0^\circ$  and  $\phi = 180^\circ$ , the allene bonds lie in the naphthyl plane. For  $\phi = 0^\circ$ , the naphthyl group points outwards in (*P*)-(+)-2c, the second  $\beta$ -carbon of the innermost rings points inwards in (*P*)-(+)-2d.

(*P*)-(+)-**2b** has additional torsional degrees of freedom in the biphenyl moieties. The torsional potential for biphenyl in liquid solution has minima corresponding to twist angles close to  $\pm 45^{\circ}$ , separated by barriers of about 2 kcal mol<sup>-1</sup>.<sup>16</sup> For simplicity in our calculations, we kept biphenyls frozen in conformations with ( $\tau_1$ ,  $\tau_2$ ) equal to  $\pm 45^{\circ}$ . For each of the biphenyl conformations defined in this way, the chirality parameter *Q* was calculated as a function of the dihedral angles  $\phi_1$  and  $\phi_2$ ; the results are shown in Fig. 15-ESI. Table 1-ESI reports the average chirality parameter *Q* calculated separately for each conformation of biphenyls.

**Table 1-ESI.** Chirality parameter Q calculated for conformations of (P)-(+)-**2b** with biphenyls frozen in  $(\tau_1, \tau_2)$  twist angles, by averaging over the  $(\phi_1, \phi_2)$  torsional angle distribution. Average values calculated assuming uniform dihedral probability are reported between brackets.

$\tau_1, \tau_2$	$Q(10^{-3} \text{nm}^3)$
-45°,-45°	-7 (-15)
-45°,+45°	-18 (-31)
+45°,+45°	-25 (-46)



**Fig. 15-ESI.** Chirality parameter *Q* calculated for (*P*)-(+)-**2b** as a function of the  $\phi_1$  and  $\phi_2$  dihedrals. Each of the plots was obtained with biphenyls frozen in a given conformation ( $\tau_1$ ,  $\tau_2$ ): top left (-45°,-45°), top right (-45°,+45°), bottom (+45°,+45°). For  $\phi=0^\circ$  and  $\phi=180^\circ$  the allene bonds lie on the same plane of the innermost phenyl rings.

(*P*)-(+)-**5a**-**b**: the chirality parameter was calculated by averaging over a finite number of conformers, generated in the following way. For the core, the two conformations denoted in the previous section as (I) and (II) were assumed. In view of the torsional potential for the  $\chi$  dihedral shown in Fig. 12-ESI, two values were considered:  $\chi$ =+25° and  $\chi$ =+155°. For the biphenyl twist angles in (*P*)-(+)-**5b**, the same choices already discussed for (*P*)-(+)-**2b** were taken. Thus, for (*P*)-(+)-**5a** a total number of eight conformers was assumed (four for each core geometry). For (*P*)-(+)-**5b**, the total number amounts to 32, with 16 conformers for each of the two core geometries.





**Fig. 16-ESI.** 400 MHz <sup>1</sup>H NMR (top) and 100 MHz <sup>13</sup>C NMR (bottom) spectra of (*P*)-(+)-2a recorded at 298 K in CDCl<sub>3</sub>.



**Fig. 17-ESI.** 400 MHz <sup>1</sup>H NMR (top) and 100 MHz <sup>13</sup>C NMR (bottom) spectra of (P)-(+)-**2b** recorded at 298 K in CDCl<sub>3</sub>.



**Fig. 18-ESI.** 400 MHz <sup>1</sup>H NMR (top) and 100 MHz <sup>13</sup>C NMR (bottom) spectra of (*P*)-(+)-2c recorded at 298 K in CDCl<sub>3</sub>.



**Fig. 19-ESI.** 400 MHz <sup>1</sup>H NMR (top) and 100 MHz <sup>13</sup>C NMR (bottom) spectra of (P)-(+)-2d recorded at 298 K in CDCl<sub>3</sub>.



**Fig. 20-ESI.** 400 MHz <sup>1</sup>H NMR (top) and 100 MHz <sup>13</sup>C NMR (bottom) spectra of (*P*)-(+)-**3a** recorded at 298 K in CDCl<sub>3</sub>.



**Fig. 21-ESI.** 400 MHz <sup>1</sup>H NMR (top) and 100 MHz <sup>13</sup>C NMR (bottom) spectra of (P)-(+)-**3b** recorded at 298 K in CDCl<sub>3</sub>.



**Fig. 22-ESI.** 400 MHz <sup>1</sup>H NMR (top) and 100 MHz <sup>13</sup>C NMR (bottom) spectra of (P)-(+)-4a recorded at 298 K in CDCl<sub>3</sub>.



**Fig. 23-ESI.** 400 MHz <sup>1</sup>H NMR (top) and 100 MHz <sup>13</sup>C NMR (bottom) spectra of (P)-(+)-4**b** recorded at 298 K in CDCl<sub>3</sub>.



**Fig. 24-ESI.** 400 MHz <sup>1</sup>H NMR (top) and 100 MHz <sup>13</sup>C NMR (bottom) spectra of (P)-(+)-**5a** recorded at 298 K in CDCl<sub>3</sub>.



**Fig. 25-ESI.** 400 MHz <sup>1</sup>H NMR (top) and 100 MHz <sup>13</sup>C NMR (bottom) spectra of (P)-(+)-**5b** recorded at 298 K in CDCl<sub>3</sub>.





**Fig. 26-ESI.** HPLC traces of (±)-2b (top) and (*P*)-(+)-2b (bottom) [Chiralpak IA, hexane, 1.5 mL/min,  $t_R(M) = 8.79 \text{ min.}, t_R(P) = 11.11 \text{ min.}$ ].



**Fig. 27-ESI.** HPLC traces of  $(\pm)$ -2c (top) and partially racemized (*P*)-(+)-2c (bottom) [Chiralpak IA, hexane, 0.7 mL/min,  $t_R(M) = 7.67 \text{ min.}, t_R(P) = 8.38 \text{ min.}].$ 



**Fig. 28-ESI.** HPLC traces of (±)-2d (top) and (*P*)-(+)-2d (bottom) [Chiralpak IA, hexane, 0.7 mL/min,  $t_R(M) = 9.20$  min.,  $t_R(P) = 9.89$  min.].

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