Electronic Supplementary Information

Mutually antagonistic molecular clips: symmetry-breaking non-covalent bonds at the chiral–nonchiral interface

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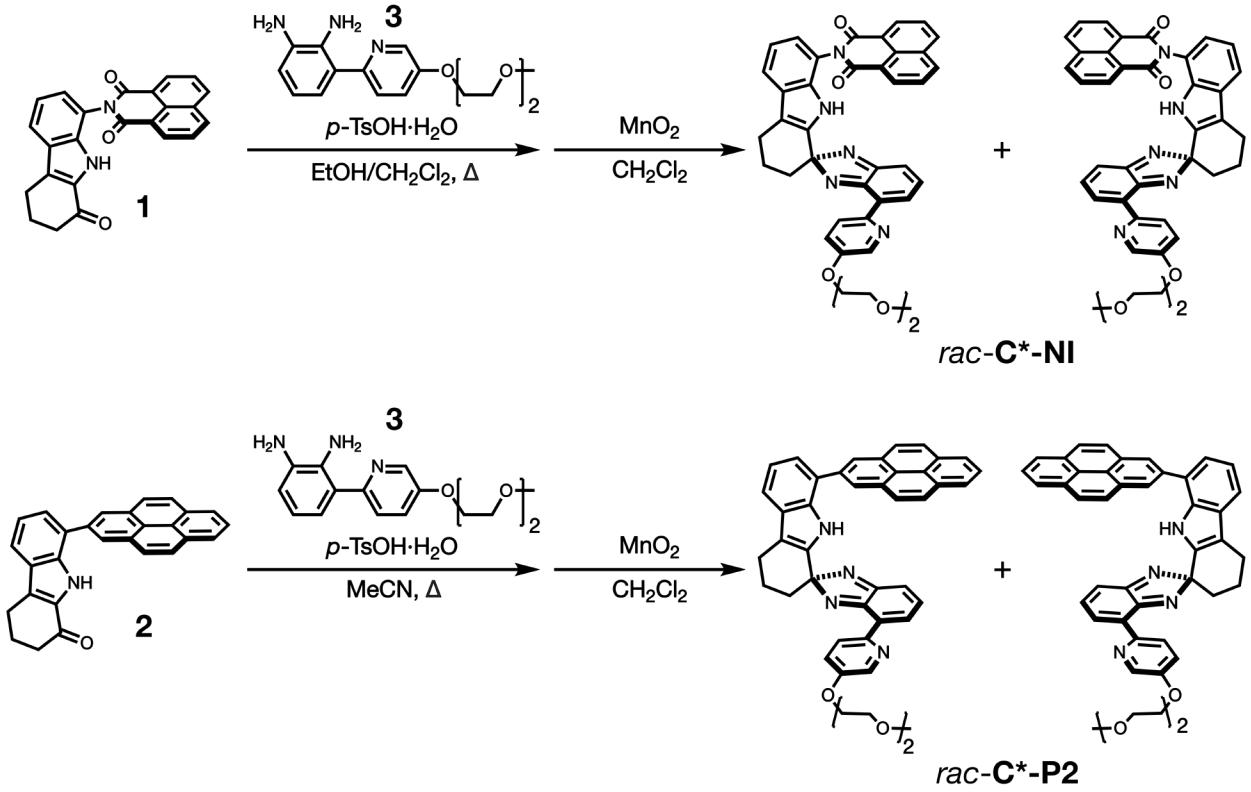
Experimental Section

General Considerations. Unless otherwise noted, all reagents were purchased from commercial suppliers and used as received. All air-sensitive manipulations were carried out under inert atmosphere by Schlenk-line techniques. All microwave-assisted synthesis was performed in a Biotage® Initiator+ microwave synthesizer. Spectroscopic grade chloroform and acetonitrile were used for circular dichroism (CD) measurements. Chiral HPLC separation was performed with a Daicel Chiralpak IM column on a Shimadzu LC-20AR Semi-Preparative Recycle System equipped with a fraction collector. The compounds benzo[*c*]-1,2,5-thiadiazole-4-(boronic acid pinacol ester),[1] 2-(1-oxo-2,3,4,9-tetrahydro-1*H*-carbazol-8-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione,[2] 8-(pyren-2-yl)-2,3,4,9-tetrahydro-1*H*-carbazol-1-one,[2] 2-(9-methyl-1-oxo-2,3,4,9-tetrahydro-1*H*-carbazol-8-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione,[2] and 9-methyl-8-(pyren-2-yl)-2,3,4,9-tetrahydro-1*H*-carbazol-1-one[2] were prepared according to literature procedures.

Physical Measurements. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Agilent 400-MR DD2 Magnetic Resonance System, a 500 MHz Varian/Oxford As-500 spectrometer, a 500 MHz Bruker Ascend^{TM} 500 spectrometer, or a 500 MHz Bruker Ascend Evo 500 spectrometer. Chemical shifts were referenced to internal standard of tetramethylsilane (as $\delta = 0.00$ ppm), or referenced to the residual solvent peaks. High-resolution electrospray ionization (ESI) mass spectra were obtained on a Thermo Scientific LTQ Orbitrap XL mass spectrometer. FT-IR spectra were recorded on a PerkinElmer Spectrum Two FT-IR spectrometer. CD spectra were measured with a Jasco J-1700 Circular Dichroism Spectrophotometer.

[1] P. Sonar, E. Williams, S. Singh, and S. Manzhos, *Phys. Chem. Chem. Phys.*, 2013, **15**, 17064–17069.
[2] H. Lee and D. Lee, *Commun. Chem.*, 2022, **5**, 180.

Scheme S1 Synthetic routes to *rac*-**C*-NI** and *rac*-**C*-P2**.

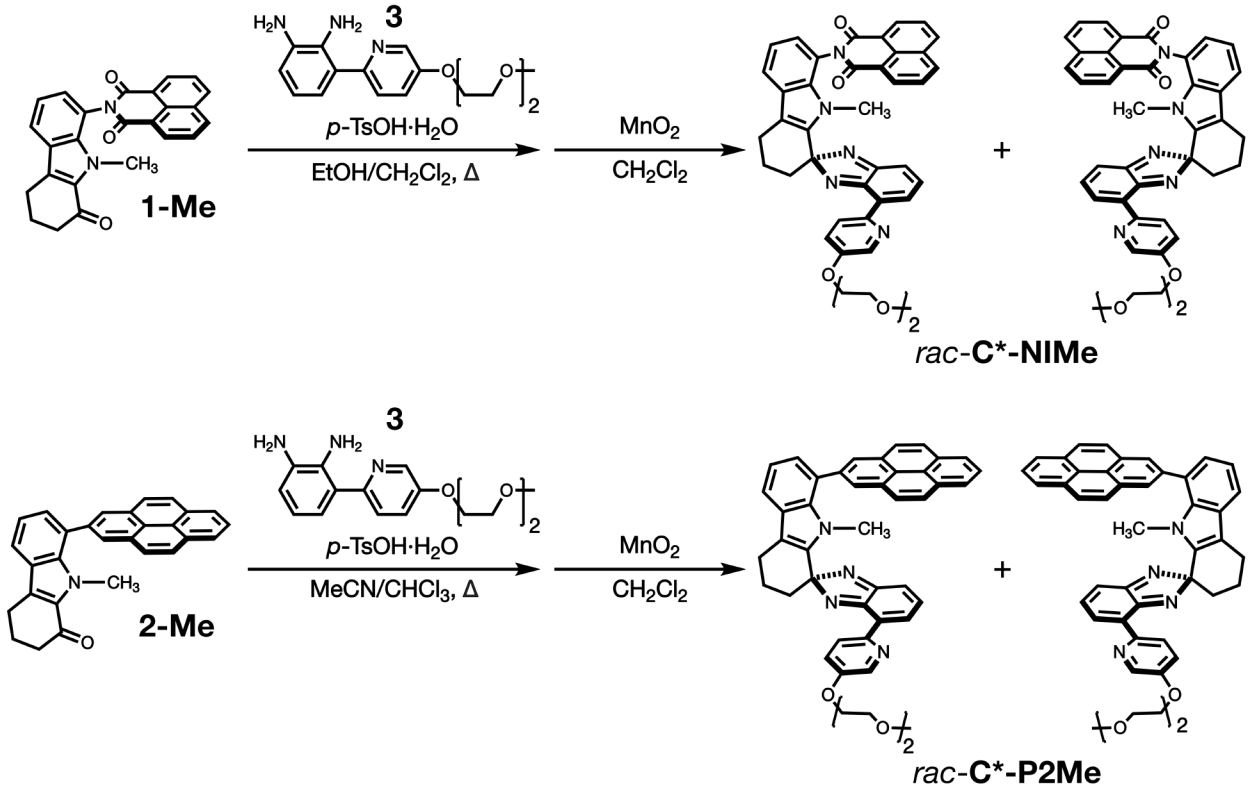


***rac*-2-(4-(5-(2-(2-Methoxyethoxy)ethoxy)pyridin-2-yl)-2′,3′,4′,9′-tetrahydrospiro[benzo[*d*]imidazole-2,1′-carbazol]-8′-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (*rac*-C*-NI).** An oven-dried 10–20 mL Biotage® Microwave Reaction Vial was loaded with **1** (0.441 g, 1.16 mmol), **3** (0.424 g, 1.40 mmol), *p*-toluenesulfonic acid monohydrate (27.5 mg, 145 μmol), anhyd EtOH (15 mL), and anhyd CH_2Cl_2 (6 mL). The mixture was heated by microwave irradiation at 90 °C with stirring for 16 h, cooled to r.t., and concentrated under reduced pressure. The residual material was transfered into an oven-dried 250 mL round-bottom flask loaded with oven-dried MnO_2 (1.01 g, 11.6 mmol) and CH_2Cl_2 (100 mL). The mixture was stirred at r.t. for 10 h, filtered through Celite, washed with water (100 mL × 3), dried over anhyd $MgSO_4$, filtered, and concentrated under reduced pressure. Flash column chromatography on SiO_2 (CH_2Cl_2:EtOAc = 100:1 to 1:2, v/v) furnished *rac*-**C*-NI** as a yellow-orange solid (0.226 g, 0.340 mmol, yield = 29%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 10.91 (s, 1H), 8.14 (d, J = 7.2 Hz, 1H), 7.89–7.83 (m, 2H), 7.77–7.69 (m, 3H), 7.50–7.42 (m, 2H), 7.22 (t, J = 7.7 Hz, 1H), 7.10–7.06 (m, 1H), 7.02 (d, J = 7.4 Hz, 1H), 6.62 (s, 1H), 6.41 (d, J = 8.9 Hz, 1H), 6.27 (d, J = 8.9 Hz, 1H), 6.06 (s, 1H), 4.14–4.06 (m, 1H), 3.99–3.90 (m, 1H), 3.87–3.82 (m, 2H), 3.80–3.68 (m, 2H), 3.63 (t, J = 4.6 Hz, 2H), 3.41 (s, 3H), 3.14 (t, J = 6.1 Hz, 2H), 2.46 (s, 2H), 2.15 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 164.30, 163.95, 161.56, 159.38, 154.35, 143.91, 138.01, 134.91, 134.76, 134.07, 133.62, 133.38, 131.25, 131.01, 130.01, 129.18, 128.37, 126.70, 126.49, 125.53, 125.44, 125.13, 123.14, 122.52, 122.37, 122.20, 119.81, 119.30, 119.19, 115.34, 104.48, 72.20, 70.96, 69.60, 68.09, 59.21, 31.34, 23.13, 21.84, 21.58. FT-IR (ATR, cm^{-1}): 3150, 3119, 3069, 2923, 2851, 1708, 1675, 1627, 1589, 1565, 1533, 1500, 1483, 1468, 1436, 1378, 1354, 1299, 1269, 1237, 1198, 1188, 1137, 1112, 1071, 1055, 1027, 984, 960, 901, 846, 813, 781, 745, 699, 645, 527, 510. HRMS (ESI) calcd for

$C_{40}H_{34}N_5O_5$ $[M + H]^+$ 664.2554, found 664.2570.

***rac*-4-(5-(2-(2-Methoxyethoxy)ethoxy)pyridin-2-yl)-8′-(pyren-2-yl)-2′,3′,4′,9′-tetrahydrospiro[benzo[*d*]imidazole-2,1′-carbazole] (*rac*-C*-P2).** An oven-dried 500 mL round-bottom flask was loaded with **2** (0.571 g, 1.48 mmol), **3** (0.473 g, 1.56 mmol), *p*-toluenesulfonic acid monohydrate (30.3 mg, 159 μmol), and anhyd MeCN (362 mL). The mixture was heated at reflux for 24 h, cooled to r.t., and concentrated under reduced pressure. The residual material was transfered into an oven-dried 500 mL round-bottom flask loaded with oven-dried MnO_2 (1.29 g, 14.8 mmol) and CH_2Cl_2 (244 mL). The residual material was stirred at r.t. for 4 h, filtered through Celite, washed with water (200 mL × 3), dried over anhyd $MgSO_4$, filtered, and concentrated under reduced pressure. Flash column chromatography on SiO_2 (hexane:CH_2Cl_2 = 100:1 to 7:3, v/v) furnished *rac*-**C*-P2** as a yellow-orange solid (0.210 g, 0.314 mmol, yield = 21%). ^{1}H NMR (500 MHz, $CDCl_3$, 20 mM, 298 K): δ 8.64 (s, 1H), 8.05–7.95 (m, 5H), 7.90 (t, J = 7.6 Hz, 1H), 7.81 (d, J = 8.9 Hz, 2H), 7.72–7.63 (m, 4H), 7.29–7.23 (m, 2H), 6.91 (s, 1H), 6.64 (d, J = 9.1 Hz, 2H), 6.42 (s, 1H), 4.00 (t, J = 4.7 Hz, 2H), 3.82 (t, J = 4.7 Hz, 2H), 3.75–3.68 (m, 2H), 3.62–3.56 (m, 2H), 3.40 (s, 3H), 3.23–3.07 (m, 2H), 2.57–2.48 (m, 2H), 2.25–2.14 (m, 1H), 2.04–1.93 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, 20 mM, 298 K): δ 161.72, 160.24, 154.35, 144.02, 137.50, 137.10, 135.76, 135.29, 132.60, 131.18, 131.09, 130.84, 128.09, 127.54, 127.30, 126.37, 126.11, 125.85, 125.27, 125.16, 124.98, 124.27, 123.93, 123.61, 123.24, 119.92, 119.46, 118.15, 114.96, 104.47, 72.06, 71.02, 69.62, 67.78, 59.27, 32.69, 23.22, 21.66. FT-IR (ATR, cm^{-1}): 3360, 3313, 3185, 3138, 3052, 2953, 2922, 2852, 1661, 1633, 1589, 1563, 1532, 1498, 1468, 1410, 1377, 1308, 1292, 1263, 1222, 1181, 1137, 1107, 1061, 1025, 969, 955, 880, 840, 811, 797, 746, 716, 644. HRMS (ESI) calcd for $C_{44}H_{37}N_4O_3$ $[M + H]^+$ 669.2860, found 669.2878.

Scheme S2 Synthetic routes to *rac*-**C*-NIMe** and *rac*-**C*-P2Me**.

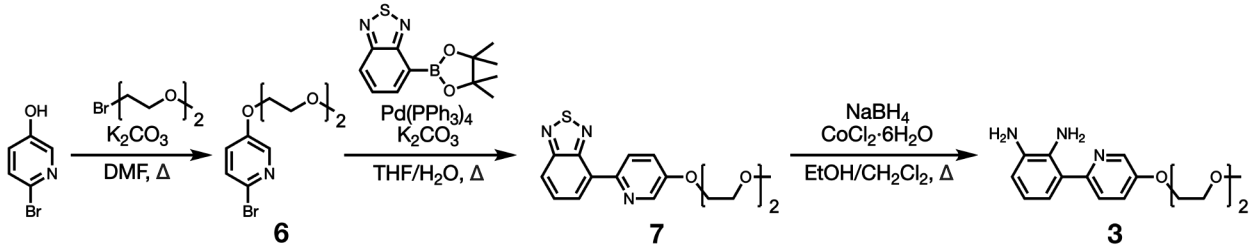


***rac*-2-(4-(5-(2-(2-Methoxyethoxy)ethoxy)pyridin-2-yl)-9′-methyl-2′,3′,4′,9′-tetrahydrospiro[benzo[*d*]imidazole-2,1′-carbazol]-8′-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (*rac*-C*-NIMe).** An oven-dried 10–20 mL Biotage® Microwave Reaction Vial was loaded with **1-Me** (0.378 g, 0.960 mmol), **3** (0.350 g, 1.15 mmol), *p*-toluenesulfonic acid monohydrate (26.2 mg, 138 μmol), anhyd EtOH (15.3 mL), and anhyd CH_2Cl_2 (4.9 mL). The mixture was heated by microwave irradiation at 90 °C with stirring for 16 h, cooled to r.t., and concentrated under reduced pressure. The residual material was transfered into a an oven-dried 250 mL round-bottom flask loaded with oven-dried MnO_2 (0.830 g, 9.55 mmol) and CH_2Cl_2 (65 mL). The mixture was stirred at r.t. for 18 h, filtered through Celite, washed with water (100 mL × 3), dried over anhyd $MgSO_4$, filtered, and concentrated under reduced pressure. Flash column chromatography on SiO_2 (CH_2Cl_2:EtOAc = 100:1 to 1:1, v/v) furnished *rac*-**C*-NIMe** as a yellow-orange solid (95.3 mg, 0.141 mmol, yield = 15%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 8.76 (d, J = 8.8 Hz, 1H), 8.64 (d, J = 7.4, 1H), 8.61 (d, J = 7.3 Hz, 1H), 8.37 (d, J = 3.0 Hz, 1H), 8.27–8.22 (m, 2H), 7.96 (d, J = 6.6 Hz, 1H), 7.81–7.72 (m, 3H), 7.32–7.20 (m, 3H), 7.15 (dd, J = 9.4, 6.7 Hz, 1H), 7.05 (d, J = 7.4 Hz, 1H), 4.24 (t, J = 4.7 Hz, 2H), 3.92 (t, J = 4.9 Hz, 2H), 3.79–3.74 (m, 2H), 3.65–3.60 (m, 2H), 3.43 (s, 3H), 3.21–3.08 (m, 2H), 2.69 (s, 3H), 2.46–2.37 (m, 2H), 2.07–1.98 (m, 1H), 1.87–1.78 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 164.65, 164.47, 161.99, 160.86, 154.98, 144.70, 138.47, 135.87, 134.32, 133.79, 133.49, 131.87, 131.85, 131.79, 131.59, 129.73, 128.57, 127.47, 127.03, 127.00, 125.79, 124.84, 123.74, 122.52, 122.50, 120.52, 119.89, 119.13, 119.01, 114.63, 105.44, 71.94, 70.86, 69.56, 67.86, 59.12, 36.45, 30.74, 23.68, 22.10. FT-IR (ATR, cm^{-1}): 3069, 2926, 2881, 1706, 1670, 1586, 1561, 1529, 1492, 1475, 1455, 1436, 1406, 1373, 1348, 1305, 1284, 1262, 1236, 1218, 1188, 1137, 1125, 1115, 1070, 1059, 1028, 965, 918, 901, 847, 816, 781,

759, 735, 701, 645, 617, 603, 594, 534, 505. HRMS (ESI) calcd for $C_{41}H_{36}N_5O_5$ $[M + H]^+$ 678.2711, found 678.2731.

***rac*-4-(5-(2-(2-Methoxyethoxy)ethoxy)pyridin-2-yl)-9′-methyl-8′-(pyren-2-yl)-2′,3′,4′,9′-tetrahydrospiro[benzo[*d*]imidazole-2,1′-carbazole] (*rac*-C*-P2Me).** An oven-dried 10–20 mL Biotage® Microwave Reaction Vial was loaded with **2-Me** (0.426 g, 1.07 mmol), **3** (0.338 g, 1.11 mmol), *p*-toluenesulfonic acid monohydrate (20.0 mg, 105 μmol), anhyd MeCN (17 mL), and $CHCl_3$ (3 mL). The mixture was heated by microwave irradiation at 90 °C with stirring for 28 h, cooled to r.t., and concentrated under reduced pressure. The residual material was transfered into an oven-dried 100 mL round-bottom flask loaded with oven-dried MnO_2 (4.250 g, 48.9 mmol) and CH_2Cl_2 (30 mL). The mixture was stirred at r.t. for 36 h, filtered through Celite, washed with water (100 mL × 3), dried over anhyd $MgSO_4$, filtered, and concentrated under reduced pressure. Flash column chromatography on SiO_2 (CH_2Cl_2:EtOAc = 100:1 to 2:3, v/v) furnished *rac*-**C*-P2Me** as a yellow-orange solid (8.6 mg, 0.013 mmol, yield = 1%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 8.67 (d, J = 8.6 Hz, 1H), 8.32 (d, J = 2.7 Hz, 1H), 8.19–8.11 (m, 4H), 8.09–7.93 (m, 5H), 7.89 (d, J = 6.5 Hz, 1H), 7.70 (dd, J = 7.8, 1.8 Hz, 1H), 7.24–7.16 (m, 4H), 7.11 (dd, J = 9.2, 6.8 Hz, 1H), 4.22–4.18 (m, 2H), 3.90–3.87 (m, 2H), 3.74–3.71 (m, 2H), 3.61–3.56 (m, 2H), 3.39 (s, 3H), 3.18 (t, J = 6.3 Hz, 2H), 2.48–2.40 (m, 2H), 2.25 (s, 3H), 2.03–1.90 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 162.32, 161.03, 155.06, 144.94, 138.75, 138.49, 136.13, 136.07, 133.89, 131.94, 131.17, 130.63, 128.00, 127.52, 127.42, 126.53, 126.43, 126.19, 125.98, 125.66, 125.25, 124.84, 124.63, 123.68, 120.71, 118.62, 118.35, 114.73, 105.68, 72.07, 71.00, 69.70, 67.98, 59.26, 36.45, 33.18, 23.91, 22.84, 22.25. FT-IR (ATR, cm^{-1}): 3364, 3315, 3297, 3182, 3040, 3000, 2951, 2919, 2876, 2852, 1733, 1661, 1632, 1597, 1585, 1564, 1539, 1493, 1470, 1463, 1427, 1408, 1401, 1368, 1365, 1312, 1288, 1261, 1240, 1220, 1202, 1190, 1180, 1139, 1115, 1086, 1062, 1048, 1027, 998, 986, 966, 942, 913, 883, 857, 843, 819, 813, 802, 798, 781, 745, 718, 704, 696, 693, 682, 667, 664, 648, 642, 633, 612, 596. HRMS (ESI) calcd for $C_{45}H_{39}N_4O_3$ $[M + H]^+$ 683.3017, found 683.3032.

Scheme S3 Synthetic route to **3**



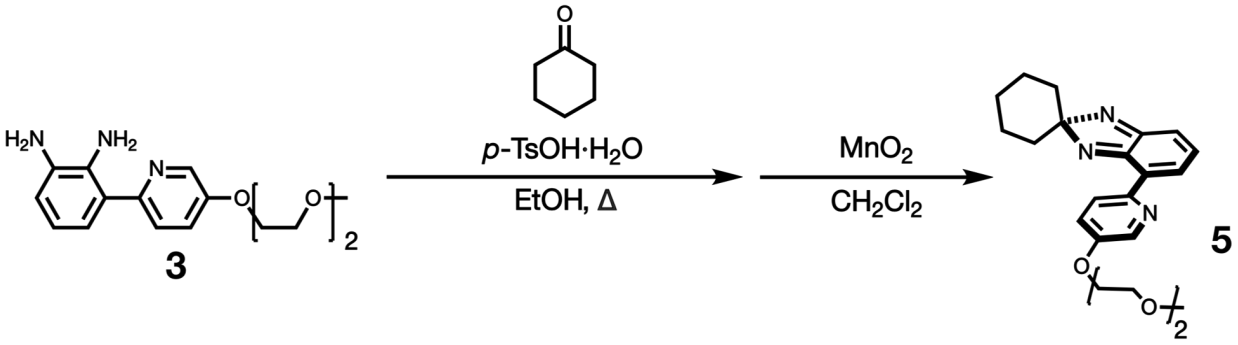
3-(5-(2-(2-Methoxyethoxy)ethoxy)pyridin-2-yl)benzene-1,2-diamine (3). To a solution of **7** (4.59 g, 13.8 mmol) in EtOH (280 mL) and CH_2Cl_2 (70 mL) in a 500 mL round-bottom flask at r.t. were added $NaBH_4$ (5.24 g, 139 mmol) and $CoCl_2{\cdot}6H_2O$ (0.682 g, 2.87 mmol) portionwise over a period of 10 min. The reaction mixture was stirred at 50 °C for 1 h. After cooling to r.t., H_2O (100 mL) was added, and the reaction mixture was stirred at r.t. for 10 min, filtered through Celite, and concentrated under reduced pressure. The residual material was taken up into CH_2Cl_2 (250 mL), washed with water (150 mL × 3), dried over anhyd $MgSO_4$, filtered, and concentrated under reduced pressure. Flash column chromatography on SiO_2 (CH_2Cl_2:EtOAc = 100:1 to 0:1 → EtOAc:MeOH = 1:0 to 98:2, v/v) furnished **3** as a yellow oil (3.25 g, 10.7 mmol, yield = 78%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 8.34 (d, J = 3.0 Hz, 1H), 7.59 (d, J = 8.8 Hz, 1H), 7.33 (dd, J = 8.7, 3.0 Hz, 1H), 7.04 (dd, J = 7.2, 2.2 Hz, 1H), 6.76–6.68 (m, 2H), 5.27 (br, 2H), 4.26–4.21 (m, 3H), 3.93–3.87 (m, 2H), 3.77–3.71 (m, 2H), 3.62–3.57 (m, 2H), 3.52–3.33 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 153.11, 152.32, 135.47, 135.34, 135.19, 123.62, 123.19, 122.90, 120.65, 118.36, 116.51, 71.97, 70.87, 69.70, 67.96, 59.13. FT-IR (ATR, cm^{-1}): 3407, 3338, 3255, 3061, 3030, 2980, 2926, 2879, 2823, 1734, 1611, 1560, 1489, 1461, 1386, 1355, 1267, 1243, 1219, 1200, 1125, 1105, 1053, 1026, 940, 923, 844, 802, 788, 752, 732, 674, 644, 609, 591, 552. HRMS (ESI) calcd for $C_{16}H_{22}N_3O_3$ $[M + H]^+$ 304.1656, found 304.1659.

4-(5-(2-(2-Methoxyethoxy)ethoxy)pyridin-2-yl)benzo[c][1,2,5]thiadiazole (7). A 250 mL round-bottom flask was loaded with benzo[*c*]-1,2,5-thiadiazole-4-(boronic acid pinacol ester) (3.41 g, 13.0 mmol), **6** (3.88 g, 14.1 mmol), $Pd(PPh_3)_4$ (0.813 g, 0.704 mmol), K_2CO_3 (5.43 g, 39.3 mmol) in THF (130 mL) and H_2O (26 mL). The mixture was bubbled with Ar for 5 min, and heated at reflux for 16 h, cooled to r.t., filtrated through Celite, and concentrated under reduced pressure. The residual material was taken up into CH_2Cl_2 (200 mL), washed with water (150 mL × 3), dried over anhyd $MgSO_4$, filtered, and concentrated under reduced pressure. Flash column chromatography on SiO_2 (hexane:EtOAc = 100:1 to 1:1, v/v) furnished **7** as a yellow solid (3.03 g, 9.14 mmol, yield = 70%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.63 (d, J = 8.8 Hz, 1H), 8.50 (d, J = 2.9 Hz, 1H), 8.36 (d, J = 6.8 Hz, 1H), 8.03 (d, J = 8.6 Hz, 1H), 7.73 (dd, J = 8.8, 7.1 Hz, 1H), 7.39 (dd, J = 8.7, 3.0 Hz, 1H), 4.28 (t, J = 4.8 Hz, 2H), 3.93 (t, J = 4.8 Hz, 2H), 3.77–3.70 (m, 2H), 3.64–3.57 (m, 2H), 3.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 155.97, 154.80, 153.04, 146.92, 138.43, 132.02, 129.94, 128.44, 125.41, 121.41, 121.33, 72.10, 71.03, 69.77, 68.09, 59.27. FT-IR (ATR, cm^{-1}): 3061, 2980, 2928, 2883, 2834, 2810, 2742, 2521, 1587, 1569, 1535, 1471, 1447, 1420, 1411, 1381, 1360, 1328, 1318, 1307, 1293, 1262, 1231, 1212, 1139, 1130, 1124, 1107, 1087, 1059, 1044, 1021, 932, 920, 912, 900, 855, 835, 819, 768, 749, 732, 647, 610, 552, 528, 505, 486, 465, 441, 415. HRMS (ESI) calcd for $C_{16}H_{18}N_3O_3S$ $[M + H]^+$ 332.1064, found 332.1069.

2-Bromo-5-(2-(2-methoxyethoxy)ethoxy)pyridine (6). A mixture of 6-bromopyridin-3-ol (3.74 g, 16.3 mmol), 1-bromo-2-(2-methoxyethoxy)ethane (2.6 mL, 19 mmol), and K_2CO_3 (8.89 g,

64.3 mmol) in DMF (50 mL) was heated at 80 °C for 16 h, cooled to r.t., and concentrated under reduced pressure. The residual material was taken up into CH_2Cl_2 (200 mL), washed with water (150 mL × 5), dried over anhyd $MgSO_4$, filtered, and concentrated under reduced pressure. Flash column chromatography on SiO_2 (hexane:EtOAc = 1:0 to 1:1, v/v) furnished **6** as a white solid (4.26 g, 15.4 mmol, yield = 72%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 8.07 (d, J = 3.2 Hz, 1H), 7.35 (d, J = 8.7 Hz, 1H), 7.13 (dd, J = 8.7, 3.2 Hz, 1H), 4.19–4.13 (m, 2H), 3.88–3.83 (m, 2H), 3.73–3.67 (m, 2H), 3.59–3.54 (m, 2H), 3.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 154.93, 137.76, 132.49, 128.25, 125.27, 72.07, 71.01, 69.69, 68.40, 59.26. FT-IR (ATR, cm^{-1}): 3088, 3067, 2983, 2926, 2894, 2817, 1577, 1566, 1470, 1449, 1368, 1355, 1270, 1235, 1226, 1200, 1136, 1123, 1103, 1091, 1055, 1027, 1010, 983, 946, 923, 891, 850, 839, 811, 722, 653, 620, 522, 422. HRMS (ESI) calcd for $C_{10}H_{15}BrNO_3$ $[M + H]^+$ 276.0230, found 276.0234.

Scheme S4 Synthetic route to **5**.



4-(5-(2-(2-Methoxyethoxy)ethoxy)pyridin-2-yl)spiro[benzo[*d*]imidazole-2,1′-cyclohexane] (5). An oven-dried 100 mL round-bottom flask was loaded with **3** (0.142 g, 0.468 mmol), cyclohexanone (46 μL, 0.44 mmol), *p*-toluenesulfonic acid monohydrate (9.4 mg, 49 μmol), and anhyd EtOH (34 mL). The mixture was heated at reflux for 19 h, cooled to r.t., and concentrated under reduced pressure. The residual material was transfered into an oven-dried 100 mL round-bottom flask loaded with oven-dried MnO_2 (0.390 g, 4.49 mmol) and CH_2Cl_2 (30 mL). The mixture was stirred at r.t. for 2 h, filtered through Celite, washed with water (100 mL $\times$ 3), dried over anhyd $MgSO_4$, filtered, and concentrated under reduced pressure. Flash column chromatography on SiO_2 (EtOAc isocratic flow) furnished **5** as a yellow-orange solid (54.0 mg, 0.142 mmol, yield = 32%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.70 (d, J = 8.7 Hz, 1H), 8.38 (d, J = 3.0 Hz, 1H), 7.94 (d, J = 6.5 Hz, 1H), 7.28 (dd, J = 8.8, 3.0 Hz, 1H), 7.22 (d, J = 9.2 Hz, 1H), 7.16 (dd, J = 9.3, 6.5 Hz, 1H), 4.23 (t, J = 4.8 Hz, 2H), 3.90 (t, J = 4.8 Hz, 2H), 3.73 (dd, J = 5.8, 3.5 Hz, 2H), 3.58 (dd, J = 5.7, 3.6 Hz, 2H), 3.39 (s, 3H), 2.05–1.92 (m, 4H), 1.87–1.51 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 160.18, 158.67, 154.92, 145.64, 138.39, 135.23, 134.25, 131.26, 125.53, 125.42, 120.79, 107.43, 72.07, 71.00, 69.74, 67.99, 59.23, 33.06, 25.86, 25.03. FT-IR (ATR, cm^{-1}): 3068, 2931, 2890, 2878, 2855, 2823, 2527, 1737, 1588, 1575, 1562, 1531, 1491, 1477, 1448, 1407, 1394, 1356, 1333, 1307, 1285, 1264, 1215, 1201, 1170, 1136, 1111, 1060, 1033, 957, 947, 914, 848, 830, 815, 789, 749, 705, 684, 641, 628, 566, 550, 528, 493, 460, 446, 417. HRMS (ESI) calcd for $C_{22}H_{28}N_3O_3$ $[M + H]^+$ 382.2126, found 382.2132.

X-ray Crystallographic Studies on *meso*-[C*-NI]$_2$. Single crystals of *meso*-[**C*-NI**]$_2$ were obtained by slow evaporation of a CH_2Cl_2–toluene (1:1, v/v) solution of *rac*-**C*-NI** at r.t. A yellow crystal (approximate dimensions 0.178 × 0.167 × 0.160 mm^3) was placed onto a nylon loop with Paratone-N oil, and mounted on a Bruker single Crystal X-ray diffractometer. The data collection was carried out using Mo Kα radiation, and the crystal was kept at 100.0 K. A total of 33857 reflections were measured ($4.224° \leq 2\theta \leq 52.720°$). The structure was solved with the SHELXT[3] structure solution program using intrinsic phasing, and refined with the SHELXL[4] refinement package of OLEX2..[5] The final refinements of *meso*-[**C*-NI**]$_2$ were performed using the SQUEEZE routine of PLATON package.[6] A total of 7569 unique reflections were used in all calculations. The final $R1$ was 0.0787 ($I \geq 2\sigma(I)$), and $wR2$ was 0.2743 (all data). $C_{40}H_{33}N_5O_5{\cdot}C_7H_8$, M = 755.88 g/mol, monoclinic, $P2_1/n$ (no. 14), a = 13.0754(15) Å, b = 19.067(2) Å, c = 15.680(2) Å, β = 104.258(4)°, V = 3788.7(8) Å^3, Z = 4, D_c = 1.325 g/cm^3. CCDC 2369723 contains the supplementary crystallographic data for this structure.

X-ray Crystallographic Studies on *meso*-[C*-P2]$_2$. Single crystals of *meso*-[**C*-P2**]$_2$ were obtained by vapor diffusion of methyl *tert*-butyl ether into a $CHCl_3$ solution of the material at r.t. A yellow crystal (approximate dimensions 0.171 × 0.074 × 0.035 mm^3) was coated with Immersion Oil Type NVH to mount on the micro-loop under cold nitrogen stream at T = 100 K. The diffraction data measured using synchrotron radiation (λ = 0.70000 Å) employing a PLSII-2D SMC on a Rayonix SX165 CCD area detector with high precision one-axis goniostat at Pohang Accelerator Laboratory, Korea. The PAL BL2D-SMDC program[7] was used for data collection, and HKL3000sm (Ver.717)[8] was used for cell refinement, reduction, and absorption correction. A total of 65136 reflections were measured ($3.718° \leq 2\theta \leq 59.526°$). The structure was solved with the SHELXT[3] structure solution program using intrinsic phasing, and refined with the SHELXL[4] refinement package of OLEX2.[5] A total of 9816 unique reflections were used in all calculations. The final $R1$ was 0.0564 ($I \geq 2\sigma(I)$), and $wR2$ was 0.1562 (all data). $C_{44}H_{36}N_4O_3$, M = 668.80 g/mol, orthorhombic, *Pbca* (no. 61), a = 15.283(3) Å, b = 14.723(3) Å, c = 30.471(6) Å, V = 6856(2) Å^3, Z = 8, D_c = 1.296 g/cm^3. CCDC 2369724 contains the supplementary crystallographic data for this structure.

X-ray Crystallographic Studies on (*R*)-C*-P2@(*S*)-C*-NI. Single crystals of (*R*)-**C*-P2**@(*S*)-**C*-NI** were obtained by vapor diffusion of Et_2O into a $CHCl_3$ solution of an equimolar mixture of (*R*)-**C*-P2** and (*S*)-**C*-NI** at r.t. A yellow crystal (approximate dimensions 0.271 × 0.221 × 0.065 mm^3) was coated with Immersion Oil Type NVH to mount on the micro-loop under cold nitrogen stream at T = 100 K. The diffraction data measured using synchrotron radiation (λ = 0.70000 Å) employing a PLSII-2D SMC on a Rayonix SX165 CCD area detector with high precision one-axis goniostat at Pohang Accelerator Laboratory, Korea. The PAL BL2D-SMDC program[7] was used for data collection, and HKL3000sm (Ver.717)[8] was used for cell refinement, reduction, and absorption correction. A total of 66130 reflections were measured ($2.974° \leq 2\theta \leq 59.462°$). The structure was solved with the SHELXT[3] structure solution program using intrinsic phasing, and refined with the SHELXL[4] refinement package of OLEX2.[5] A total of 18822 unique reflections were used in all calculations. The final $R1$ was 0.0682 ($I \geq 2\sigma(I)$), and $wR2$ was 0.1789 (all data).

[3] G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3–8.
[4] G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3–8.
[5] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339–341.
[6] A. L. Spek, *Acta Cryst.* 2009, **D65**, 148–155.
[7] J. W. Shin, K. Eom, and D. Moon, *J. Synchrotron Rad.*, 2016, **23**, 369–373.
[8] Z. Otwinowski, *Methods Enzymol.*, 1997, **276**, 307–326.

$C_{84}H_{69}N_9O_8$, M = 1331.53 g/mol, orthorhombic, $P2_12_12_1$ (no. 19), a = 14.434(3) Å, b = 15.041(3) Å, c = 30.493(6) Å, V = 6620(2) Å^3, Z = 4, D_c = 1.337 g/cm^3. CCDC 2369725 contains the supplementary crystallographic data for this structure.

X-ray Crystallographic Studies on *rac*-[C*-P2⊃PHD]. Single crystals of *rac*-[**C*-P2**⊃PHD] were obtained by vapor diffusion of pentane into a toluene solution of 1:4 molar ratio mixture of *rac*-**C*-P2** and 1,10-phenanthroline-5,6-dione at r.t. A red crystal (approximate dimensions 0.070 × 0.060 × 0.020 mm^3) was coated with Immersion Oil Type NVH to mount on the micro-loop under cold nitrogen stream at T = 100 K. The diffraction data measured using synchrotron radiation (λ = 0.70000 Å) employing a PLSII-2D SMC on a Rayonix SX165 CCD area detector with high precision one-axis goniostat at Pohang Accelerator Laboratory, Korea. The PAL BL2D-SMDC program[7] was used for data collection, and HKL3000sm (Ver.717)[8] was used for cell refinement, reduction, and absorption correction. A total of 46476 reflections were measured (3.006° ≤ 2θ ≤ 59.676°). The structure was solved with the SHELXT[3] structure solution program using intrinsic phasing, and refined with the SHELXL[4] refinement package of OLEX2.[5] A total of 23370 unique reflections were used in all calculations. The final $R1$ was 0.1025 ($I \geq 2\sigma(I)$), and $wR2$ was 0.3123 (all data). $C_{56}H_{42}N_6O_5$, M = 878.99 g/mol, triclinic, $P\bar{1}$ (no. 2), a = 8.4180(17) Å, b = 12.809(3) Å, c = 40.083(8) Å, V = 4131.5(17) Å^3, Z = 4, D_c = 1.413 g/cm^3. CCDC 2369726 contains the supplementary crystallographic data for this structure.

Table S1. Summary of X-Ray Crystallographic Data.

	meso-[**C*-NI**]$_2$	*meso*-[**C*-P2**]$_2$
Chemical formula	$C_{40}H_{33}N_5O_5 \cdot C_7H_8$	$C_{44}H_{36}N_4O_3$
Formula weight	755.88	668.80
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	$Pbca$
Color of crystal	Yellow	Yellow
a (Å)	13.0754(15)	15.283(3)
b (Å)	19.067(2)	14.723(3)
c (Å)	15.680(2)	30.471(6)
α (°)	-	-
β (°)	104.258(4)	-
γ (°)	-	-
Volume (Å^3)	3788.7(8)	6856(2)
Z	4	8
R_{int}	0.0715	0.1052
Final R indices	$R1 = 0.0787$,	$R1 = 0.0564$,
$[I \geq 2\sigma(I)]$	$wR2 = 0.2005$	$wR2 = 0.1427$
Final R indices	$R1 = 0.1369$,	$R1 = 0.0922$,
[all data]	$wR2 = 0.2743$	$wR2 = 0.1562$
GOF	1.084	1.020
	(*R*)-**C*-P2**@(*S*)-**C*-NI**	*rac*-[**C*-P2**⊃PHD]
Chemical formula	$C_{84}H_{69}N_9O_8$	$C_{56}H_{42}N_6O_5$
Formula weight	1331.53	878.99
Crystal system	orthorhombic	triclinic
Space group	$P2_12_12_1$	$P\bar{1}$
Color of crystal	Yellow	Red
a (Å)	14.434(3)	8.4180(17)
b (Å)	15.041(3)	12.809(3)
c (Å)	30.493(6)	40.083(8)
α (°)	-	91.42(3)
β (°)	-	92.29(3)
γ (°)	-	106.79(3)
Volume (Å^3)	6620(2)	4131.5(17)
Z	4	4
R_{int}	0.1244	0.0449
Final R indices	$R1 = 0.0682$,	$R1 = 0.1025$,
$[I \geq 2\sigma(I)]$	$wR2 = 0.1569$	$wR2 = 0.2804$
Final R indices	$R1 = 0.1040$,	$R1 = 0.1474$,
[all data]	$wR2 = 0.1789$	$wR2 = 0.3123$
GOF	1.036	1.046
Absolute structure parameter	–0.1(6)	-

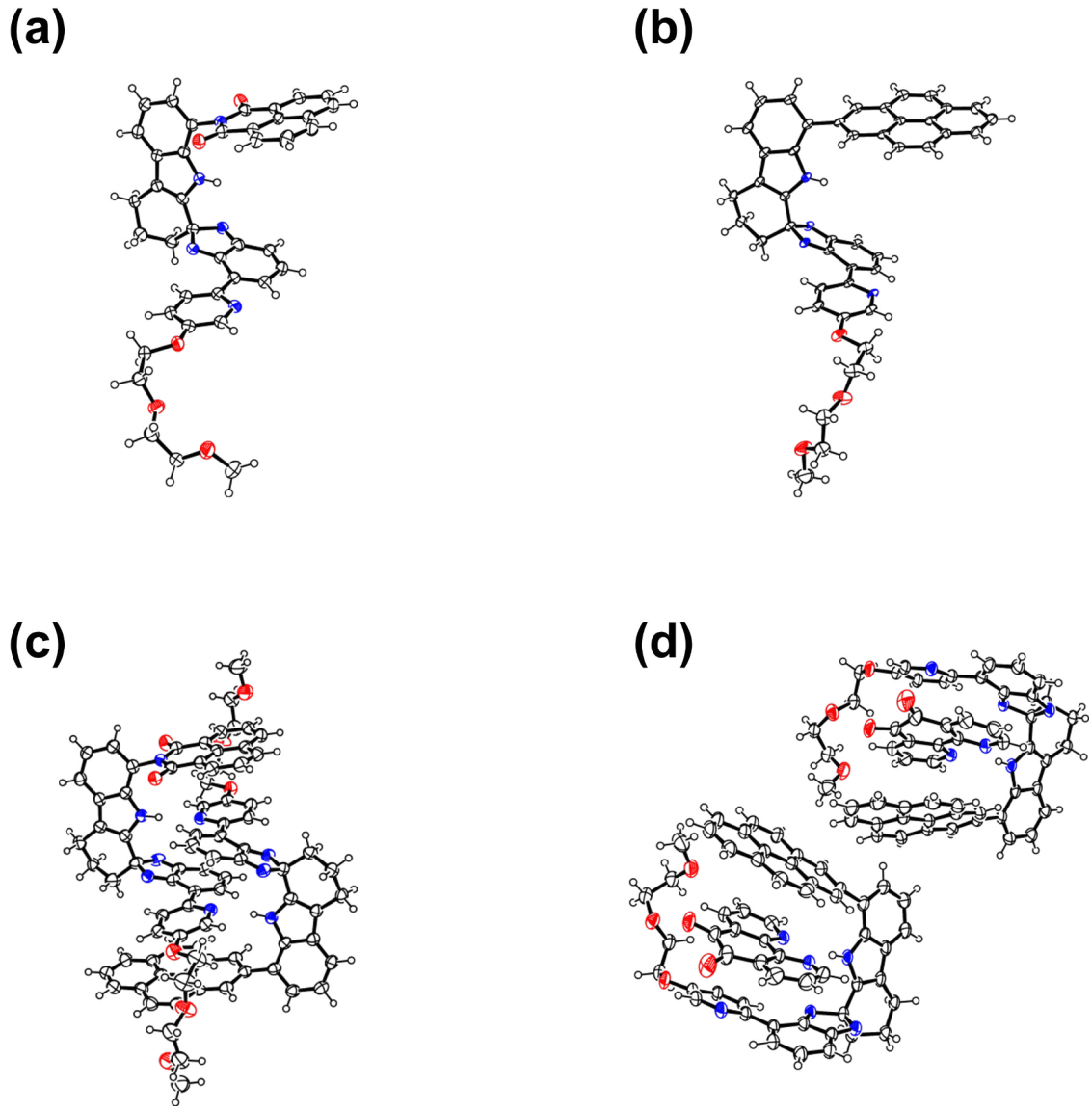


Fig. S1 ORTEP diagrams of (a) (*S*)-**C*-NI** component of *meso*-[**C*-NI**]$_2$, (b) (*S*)-**C*-P2** component of *meso*-[**C*-P2**]$_2$, (c) (*R*)-**C*-P2**@(*S*)-**C*-NI**, and (d) *rac*-[**C*-P2**⊃PHD] with thermal ellipsoids at the 50% probability level.

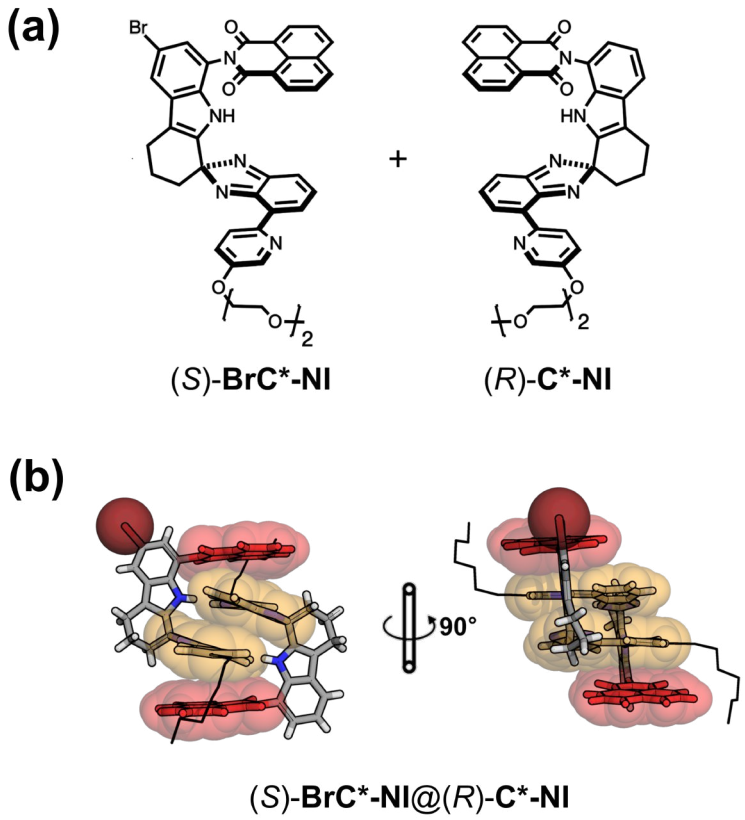


Fig. S2 (a) Chemical structure of (*S*)-**BrC*-NI** and (*R*)-**C*-NI**, (b) capped-stick representations of the X-ray structures of quasi-racemate (*S*)-**BrC*-NI**@(*R*)-**C*-NI** with vdW surfaces overlaid on the stacked aromatic regions and Br atom, and ether chains simplified as wireframes. Absolute structure parameter (Parson's q value) is 0.098(6). Space group $P1$ with $a = 16.540(3)$ Å, $b = 17.007(3)$ Å, $c = 17.482(4)$ Å, $\alpha = 63.23(3)°$, $\beta = 63.24(3)°$, $\gamma = 83.74(3)°$, $V = 3893(2)$ Å^3, $Z = 2$, $Z' = 2$, $R1 = 0.0840$, $wR2 = 0.2639$.

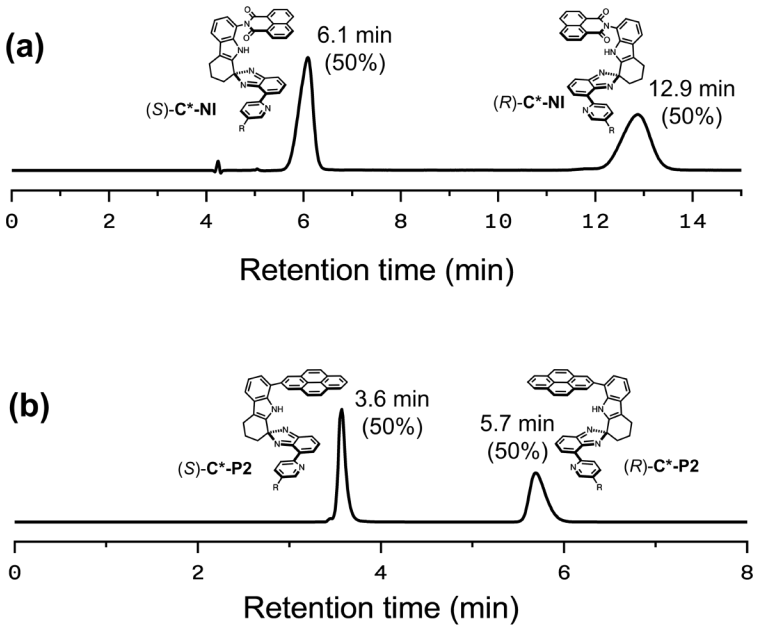


Fig. S3 HPLC chromatograms of (a) *rac*-**C*-NI** (n-hexane:$CHCl_3$:EtOH = 40:30:30, v/v/v, T = 298 K, flow rate = 0.8 mL/min) and (b) *rac*-**C*-P2** (n-hexane:$CHCl_3$:EtOH = 25:50:25, v/v/v, T = 298 K, flow rate = 1.0 mL/min) using a CHIRALPAK IM (ϕ=4.6 mm, l=250 mm) column and recorded as the absorption of 410 nm light. Retention time of each peak is provided along with the percentage of each peak area.

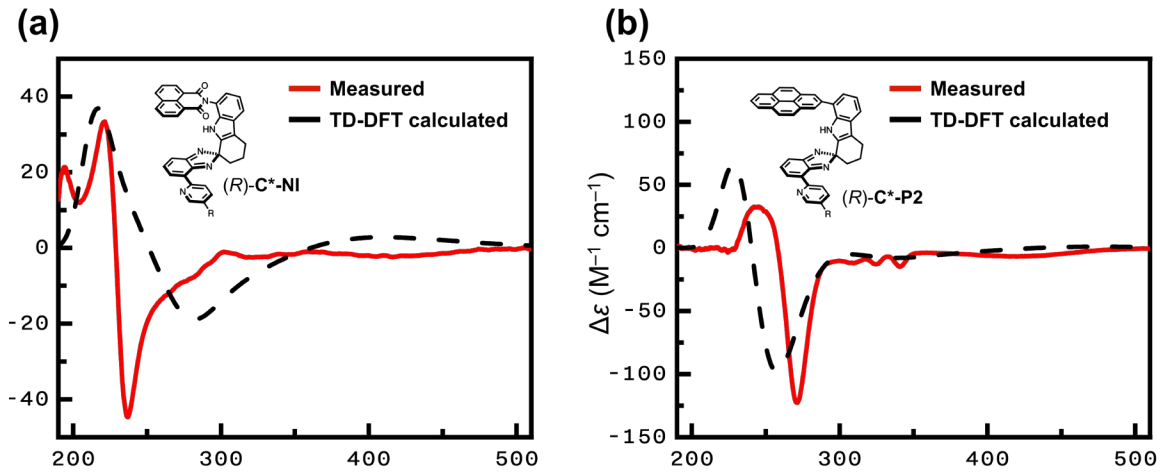


Fig. S4 CD spectra of (a) (*R*)-**C*-NI** measured in CH_3CN and (b) (*R*)-**C*-P2** measured in $CHCl_3$ at $T = 298$ K (red lines). Computed CD spectra using DFT functional BHandHLYP/def2TZVP are overlaid (black dashed lines). Solvation was considered by self-consistent reaction field (SCRF) calculations with conductor-like polarizable continuum model (CPCM) of CH_3CN ($\varepsilon = 35.7$) for (*R*)-**C*-NI** and $CHCl_3$ ($\varepsilon = 4.71$) for (*R*)-**C*-P2**.[9]

[9] J. Tomasi, B. Mennucci, and R. Cammi *Chem. Rev.*, 2005, **105**, 2999–3094.

Supplementary Note 1. Determining the Homochiral Dimerization (= Self-Association) Constant (K_{homo})

The self-association constant of enantiopure clip was determined by fitting the changes in the chemical shifts in the ^{1}H NMR spectra as a function of the sample concentration. The solution population reflects the following equilibrium. (R)-**C*** (= R) can self-associate to form R_2.

$$\mathsf{R} + \mathsf{R} \overset{K_{\mathsf{homo}}}{\rightleftarrows} \mathsf{R}_2$$

$$K_{\mathsf{homo}} = \frac{[\mathsf{R}_2]}{[\mathsf{R}]^2} \tag{1}$$

$$[\mathsf{R}] = \frac{\sqrt{1+8K_{\mathsf{homo}}[\mathsf{R}]_0}-1}{4K_{\mathsf{homo}}} \tag{2}$$

$$[\mathsf{R}_2] = K_{\mathsf{homo}}\left(\frac{\sqrt{1+8K_{\mathsf{homo}}[\mathsf{R}]_0}-1}{4K_{\mathsf{homo}}}\right)^2 \tag{3}$$

$$\delta_{obs} = \left(\frac{\sqrt{1+8K_{\mathsf{homo}}[\mathsf{R}]_0}-1}{4K_{\mathsf{homo}}}\right)\frac{\delta_{\mathsf{R}}}{[\mathsf{R}]_0} + 2K_{\mathsf{homo}}\left(\frac{\sqrt{1+8K_{\mathsf{homo}}[\mathsf{R}]_0}-1}{4K_{\mathsf{homo}}}\right)^2\frac{\delta_{\mathsf{R}_2}}{[\mathsf{R}]_0} \tag{4}$$

Here, the terms δ_{obs}, δ_{R}, and δ_{R_2} denote the observed chemical shift (resulting from the fast exchange between R and R_2), chemical shift of the (R)-form of the monomeric (= free) clip R, and chemical shift of the homochiral dimeric (= self-associated) R_2, respectively.

All ^{1}H NMR (400 MHz) spectra were obtained in $CDCl_3$ to monitor concentration-dependent changes in the δ_{obs} value of one or more distinguishable proton resonances at $T = 298$ K. A numerical fittings were carried out by using non-linear least-squares regression analysis[10] with eq (4) to obtain K_{homo}, δ_{R}, and δ_{R_2}. The K_{homo} value was determined as 6.2 M^{-1} for **C*****-P2** and 1.3×10^3 M^{-1} for **C*****-NI**, respectively.

[10]Non-linear least-squares regression analysis software was Origin2017; OriginLap Corp.: Northampton, MA.

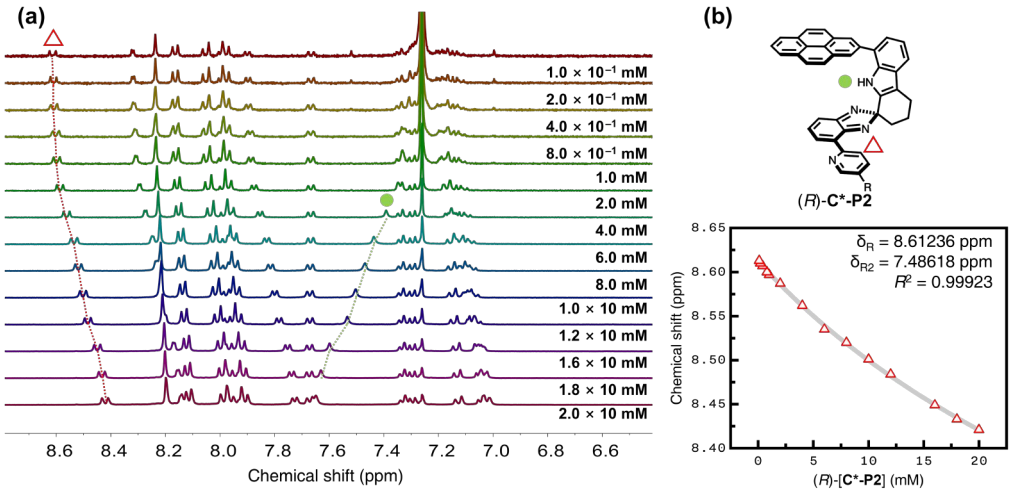


Fig. S5 (a) Partial ^{1}H NMR spectra of (*R*)-**C*-P2** at different concentrations in $CDCl_3$ measured at $T = 298$ K. (b) Changes in the chemical shift of the $H_{3\text{-pyridine}}$ proton resonance (△) as a function of the sample concentration [(*R*)-**C*-P2**]. The theoretical curve with $K_{\text{homo}} = 6.2$ M^{-1} is superimposed on the data points.

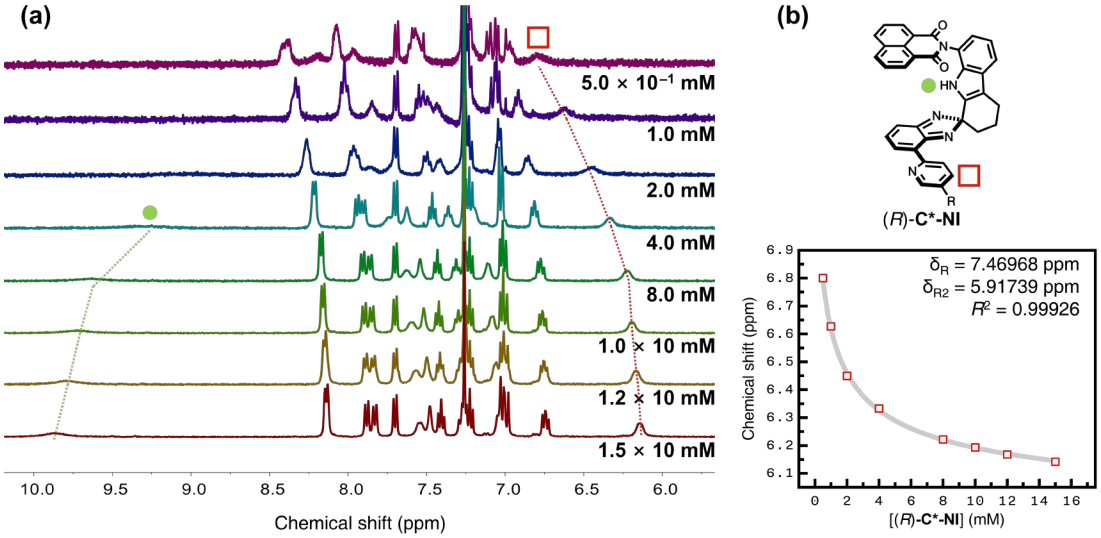
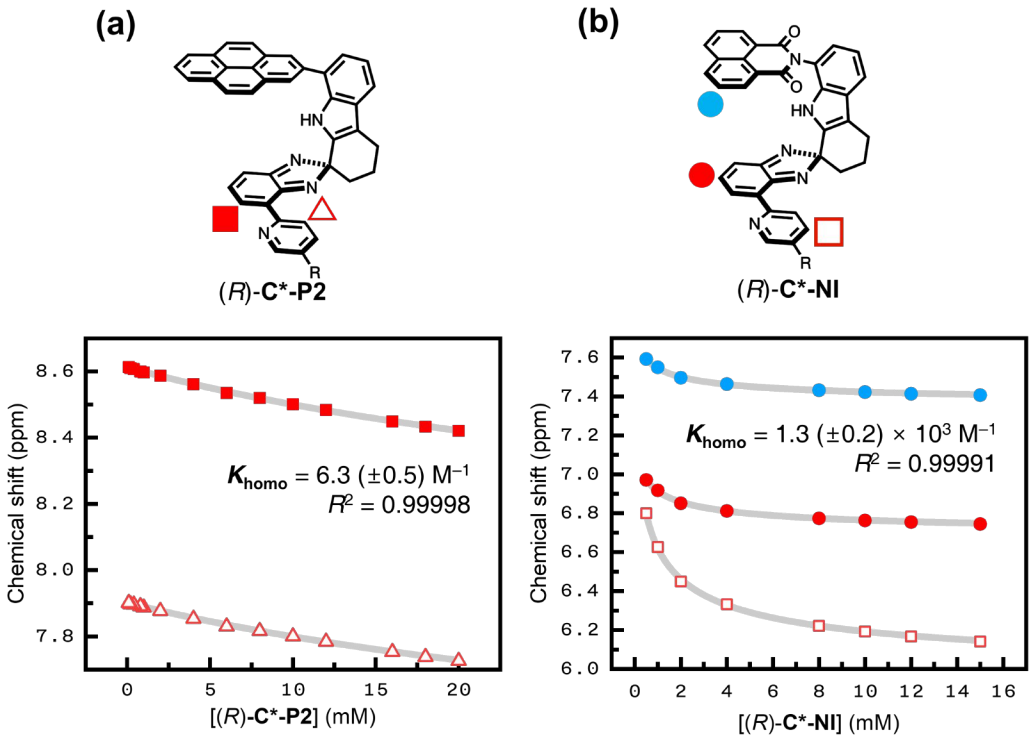


Fig. S6 (a) Partial ^{1}H NMR spectra of (*R*)-**C*-NI** at different concentrations in $CDCl_3$ measured at $T = 298$ K. (b) Changes in the chemical shift of the $H_{4\text{-pyridine}}$ proton resonance (□) as a function of the sample concentration [(*R*)-**C*-NI**]. The theoretical curve with $K_{\text{homo}} = 1.3 \times 10^3$ M^{-1} is superimposed on the data points.



method	K_{homo} (M^{-1})
global fitting	6.3 (±0.5)
single-point fitting	6.2 (±0.7)

method	K_{homo} (M^{-1})
global fitting	1.3 (±0.2) × 10^3
single-point fitting	1.3 (±0.3) × 10^3

Fig. S7 Changes in the chemical shifts of (a) (*R*)-**C*-P2**, and (b) (*R*)-**C*-NI** as a function of the sample concentration. In each plot, the theoretical curves with the dimerization constant K_{homo} are superimposed on the data points; results from global fitting and single-point fitting are compared in the table below. Proton resonances are labeled with the symbols denoted in the chemical structures.

Supplementary Note 2. Determining the Heterochiral Dimerization Constant (K_{hetero}) of C*-P2

The heterochiral dimerization constant of the racemic sample was determined by fitting the changes in the chemical shifts in the ^{1}H NMR spectra as a function of the sample concentration. The solution population reflects the following equilibrium. (*R*)-**C*** (= R) can either (i) self-associate to form $\mathsf{R_2}$, or (ii) associated with its mirror image clip (*S*)-**C*** (= S) to afford RS.

$$\mathsf{R} + \mathsf{R} \overset{K_{\mathsf{homo}}}{\rightleftarrows} \mathsf{R_2}$$

$$\mathsf{S} + \mathsf{S} \overset{K_{\mathsf{homo}}}{\rightleftarrows} \mathsf{S_2}$$

$$\mathsf{R} + \mathsf{S} \overset{K_{\mathsf{hetero}}}{\rightleftarrows} \mathsf{RS}$$

$$K_{\mathsf{homo}} = \frac{[\mathsf{R_2}]}{[\mathsf{R}]^2} \tag{1}$$

$$K_{\mathsf{homo}} = \frac{[\mathsf{S_2}]}{[\mathsf{S}]^2} \tag{5}$$

$$K_{\mathsf{hetero}} = \frac{[\mathsf{RS}]}{[\mathsf{R}][\mathsf{S}]} \tag{6}$$

$$[\mathsf{R}]_0 = [\mathsf{R}] + 2[\mathsf{R_2}] + [\mathsf{RS}] \tag{7}$$

Since it is a racemic molecule, the following relationships should also be satisfied:

$$[\mathsf{R}]_0 = [\mathsf{S}]_0 \tag{8}$$

$$[\mathsf{R}] = [\mathsf{S}] \tag{9}$$

$$[\mathsf{R_2}] = [\mathsf{S_2}] \tag{10}$$

The following equations are obtained from eqs (1), (6), (7) and (9):

$$[\mathsf{R}] = [\mathsf{S}] = \frac{\sqrt{1 + 4\left(2K_{\mathsf{homo}} + K_{\mathsf{hetero}}\right)[\mathsf{R}]_0} - 1}{2\left(2K_{\mathsf{homo}} + K_{\mathsf{hetero}}\right)} \tag{11}$$

$$[\mathsf{R_2}] = [\mathsf{S_2}] = K_{\mathsf{homo}} \left(\frac{\sqrt{1 + 4\left(2K_{\mathsf{homo}} + K_{\mathsf{hetero}}\right)[\mathsf{R}]_0} - 1}{2\left(2K_{\mathsf{homo}} + K_{\mathsf{hetero}}\right)} \right)^2 \tag{12}$$

$$[\mathsf{RS}] = 2K_{\mathsf{hetero}} \left(\frac{\sqrt{1 + 4\left(2K_{\mathsf{homo}} + K_{\mathsf{hetero}}\right)[\mathsf{R}]_0} - 1}{2\left(2K_{\mathsf{homo}} + K_{\mathsf{hetero}}\right)} \right)^2 \tag{13}$$

$$\delta_{obs} = \frac{\sqrt{1+4\left(2K_{\mathsf{homo}}+K_{\mathsf{hetero}}\right)[\mathsf{R}]_0}-1}{2\left(2K_{\mathsf{homo}}+K_{\mathsf{hetero}}\right)}\frac{\delta_{\mathsf{R}}}{[\mathsf{R}]_0} + 2K_{\mathsf{homo}}\left(\frac{\sqrt{1+4\left(2K_{\mathsf{homo}}+K_{\mathsf{hetero}}\right)[\mathsf{R}]_0}-1}{2\left(2K_{\mathsf{homo}}+K_{\mathsf{hetero}}\right)}\right)^2\frac{\delta_{\mathsf{R}_2}}{[\mathsf{R}]_0} + K_{\mathsf{hetero}}\left(\frac{\sqrt{1+4\left(2K_{\mathsf{homo}}+K_{\mathsf{hetero}}\right)[\mathsf{R}]_0}-1}{2\left(2K_{\mathsf{homo}}+K_{\mathsf{hetero}}\right)}\right)^2\frac{\delta_{\mathsf{RS}}}{[\mathsf{R}]_0} \tag{14}$$

Here, the terms δ_{obs}, δ_{R}, δ_{R_2}, and δ_{RS} denote the observed chemical shift (resulting from the fast exchange among R, R_2, and RS), chemical shift of the (*R*)-form of the monomeric (= free) clip R, (*R*,*R*)-form homochiral dimeric (= self-associated) R_2, and heterochiral dimeric RS as a *meso*-form, respectively. The values of K_{homo}, δ_{R}, and δ_{R_2} are already available from the independent experiments to determine the homochiral dimerization constants of **C*-P2** (see Supplementary Note 1). According to eq (8), numerical fitting was carried out by using half the concentration of the racemic clip as the variable.

All ^{1}H NMR (400 MHz) spectra were obtained in $CDCl_3$ to monitor concentration-dependent changes in the δ_{obs} value of the $H_{3\text{-pyridine}}$ proton (denoted with a blank triangle in the chemical structure shown next to the spectra) resonance at $T = 298$ K. A numerical fitting was carried out by using non-linear least-squares regression analysis[10] with eq (14) to obtain K_{hetero} and δ_{RS}. The K_{hetero} value was determined as 2.3×10^2 M^{-1} for **C*-P2**.

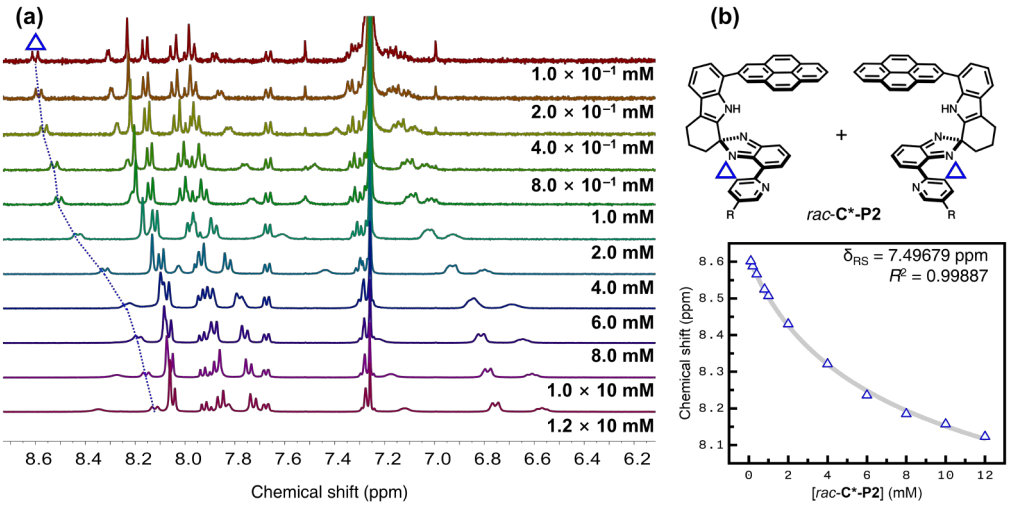


Fig. S8 (a) Partial ^{1}H NMR spectra of *rac*-**C*-P2** at different concentrations in $CDCl_3$ measured at $T = 298$ K. (b) Changes in the chemical shift of the $H_{3\text{-pyridine}}$ proton resonance (△) as a function of the sample concentration [*rac*-**C*-P2**]. The theoretical curve with $K_{\text{hetero}} = 2.3 \times 10^2$ M^{-1} is superimposed on the data points.

Supplementary Note 3. Selectivity Between Self-Association and Cross-Dimerization

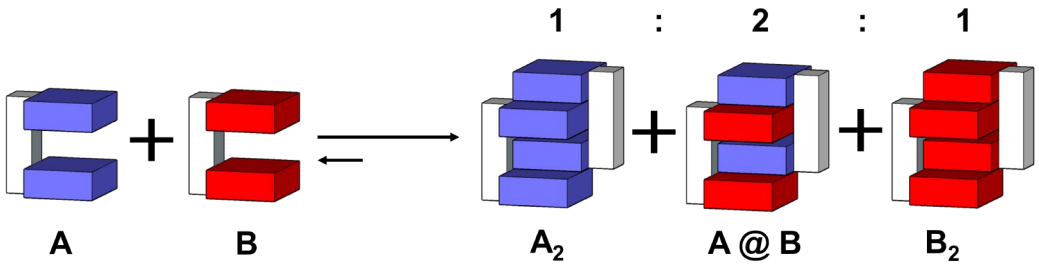


Fig. S9 Equilibrium distribution of self-dimerization and cross-dimerization in an equimolar mixture of molecular clips A and B without thermodynamic preference.

For two arbitrary molecular clips, A and B, we assume that any forms of dimerization between molecules A and B (i.e., A with A, B with B, and A with B) occur with identical binding affinity.

$$\mathsf{A} + \mathsf{A} \overset{K_{\mathsf{dimA}}}{\rightleftharpoons} \mathsf{A}_2$$

$$\mathsf{B} + \mathsf{B} \overset{K_{\mathsf{dimB}}}{\rightleftharpoons} \mathsf{B}_2$$

$$\mathsf{A} + \mathsf{B} \overset{K_{\mathsf{crossAB}}}{\rightleftharpoons} \mathsf{A@B}$$

$$K_{\mathsf{dimA}} = \frac{[\mathsf{A}_2]}{[\mathsf{A}]^2} \tag{15}$$

$$K_{\mathsf{dimB}} = \frac{[\mathsf{B}_2]}{[\mathsf{B}]^2} \tag{16}$$

$$K_{\mathsf{crossAB}} = \frac{[\mathsf{A@B}]}{[\mathsf{A}][\mathsf{B}]} \tag{17}$$

For equal initial amounts of A and B, the fraction of A@B, as depicted in Fig. S9, is twice the fractions of either A_2 or B_2. With the following relation,

$$[\mathsf{A}] = [\mathsf{B}] \tag{18}$$

$$2[\mathsf{A}_2] = 2[\mathsf{B}_2] = [\mathsf{A@B}] \tag{19}$$

the following relationships are established from eqs (15), (16), (17), (18), and (19):

$$2K_{\mathsf{dimA}} = 2K_{\mathsf{dimB}} = K_{\mathsf{crossAB}} \tag{20}$$

Since the enthalpy changes of the three different dimerization processes are the same, the twofold difference in the equilibrium constants result from the entropy difference of $R\ln 2$.

In such a case, there is no thermodynamic preference between self-dimerization and cross-dimerization, which is described by eq (21).

$$S_{\mathsf{crossAB,dimA}} = \frac{K_{\mathsf{crossAB}}}{2K_{\mathsf{dimA}}} = 1 \tag{21}$$

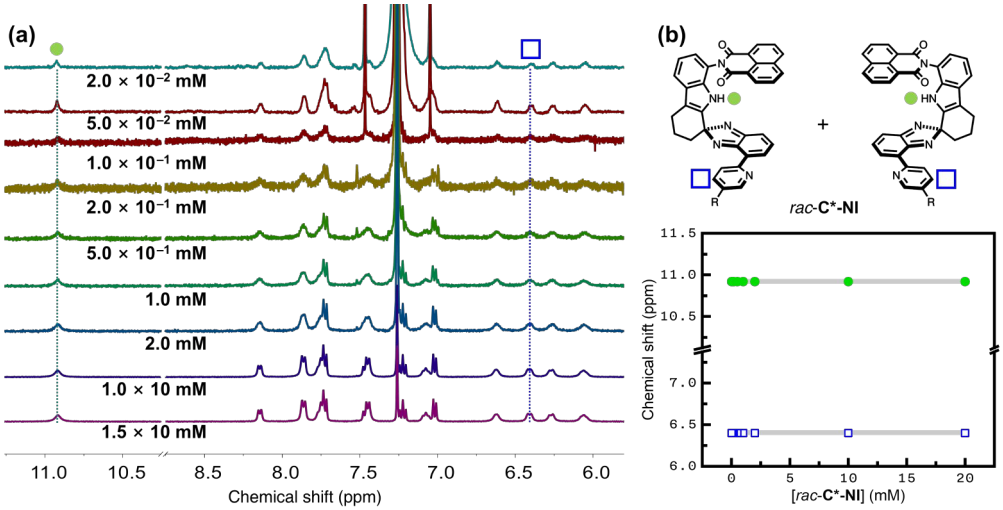


Fig. S10 (a) Partial ^{1}H NMR spectra of *rac*-**C*-NI** at different concentrations in $CDCl_3$ measured at $T = 298$ K. (b) Chemical shift of the $H_{3\text{-pyridine}}$ proton resonance (□) and N_{indole}–H proton resonance (●) as a function of the sample concentration [*rac*-**C*-NI**].

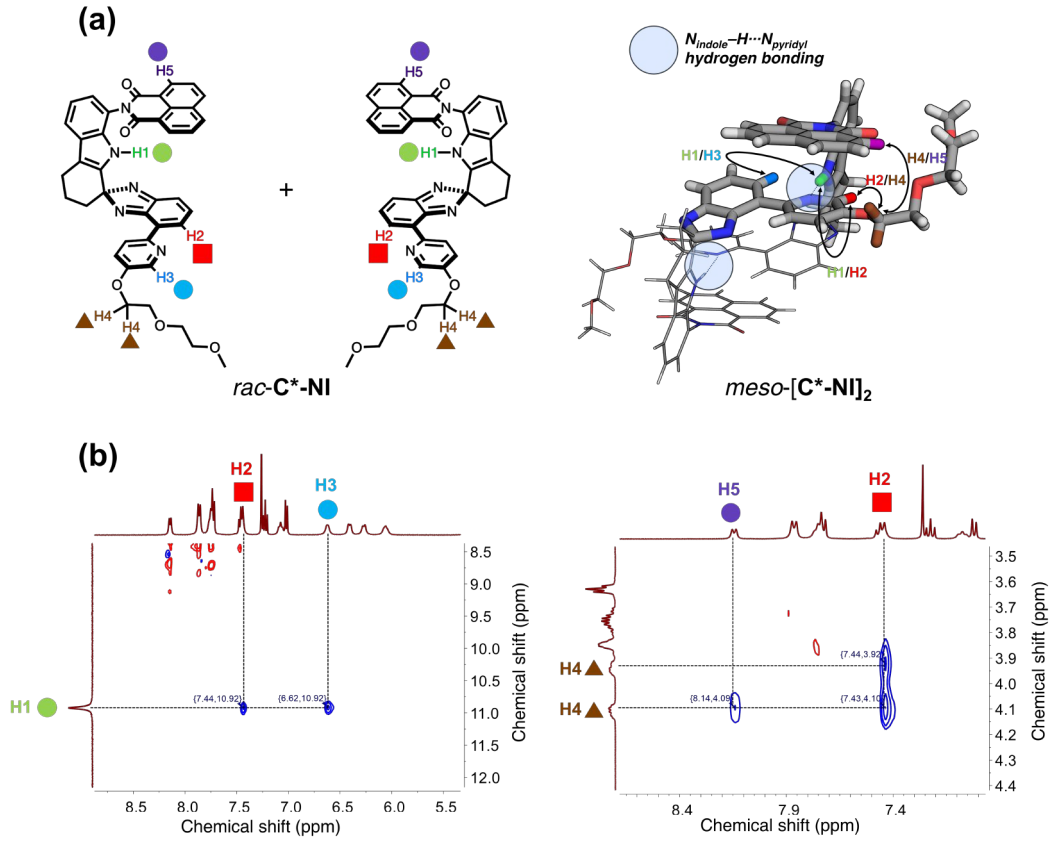


Fig. S11 (a) Chemical structure of *rac*-**C*-NI** and X-ray structure of *meso*-[**C*-NI**]$_2$ with NOE contacts denoted with double-headed arrows. The proton resonances of indole (H1), isobenzimidazole (H2), indole (H2), pyridine (H3), methoxyethyl ether chain (H4), and naphthaleneimide (H5) are labeled with symbols and color-coded. Highlighted in blue shaded circles are N_{indole}–H···$N_{pyridyl}$ hydrogen bonds inside the dimer cavity. (b) Partial 2D-NOESY contour plot of **C*-NI** (15 mM) in $CDCl_3$ at $T = 298$ K; the corresponding 1D spectrum is shown along the ordinate. The proton labeling scheme is provided in (a).

Supplementary Note 4. Numerical Simulations of the Enantiomeric Excess of Scalemic C*-NI

(*R*)-**C***-**NI** (= R) can either (i) self-associate to form R_2, or (ii) bind (*S*)-**C***-**NI** (= S) to afford RS.

$$R + R \overset{K_{homo}}{\rightleftharpoons} R_2$$

$$S + S \overset{K_{homo}}{\rightleftharpoons} S_2$$

$$R + S \overset{K_{hetero}}{\rightleftharpoons} RS$$

$$K_{homo} = \frac{[R_2]}{[R]^2} \tag{1}$$

$$K_{homo} = \frac{[S_2]}{[S]^2} \tag{5}$$

$$K_{hetero} = \frac{[RS]}{[R][S]} \tag{6}$$

$$[R]_0 = [R] + 2[R_2] + [RS] \tag{7}$$

$$[S]_0 = [S] + 2[S_2] + [RS] \tag{22}$$

The enantiomeric excess plot in Figure 4e was numerically simulated by using the experimentally determined homochiral dimerization constant ($K_{homo} = 1.3 \times 10^3$ M^{-1}), heterochiral dimerization constant ($K_{hetero} = 4.68 \times 10^5$ M^{-1}) and eqs (1), (5), (6), (7), and (22) using [(*R*)-**C***-**NI**]$_0$ = (1 + ee_0) × 5 mM and [(*S*)-**C***-**NI**]$_0$ = (1 – ee_0) × 5 mM with the ee_0 varied from 0 to 1.

ee_0, ee_{mono}, and ee_{total} are defined as the following equations.

$$ee_0 = \frac{[R]_0 - [S]_0}{[R]_0 + [S]_0} \tag{23}$$

$$ee_{mono} = \frac{[R] - [S]}{[R] + [S]} \tag{24}$$

$$ee_{total} = \frac{([R] + 2[R_2]) - ([S] + 2[S_2])}{([R] + 2[R_2]) + ([S] + 2[S_2])} \tag{25}$$

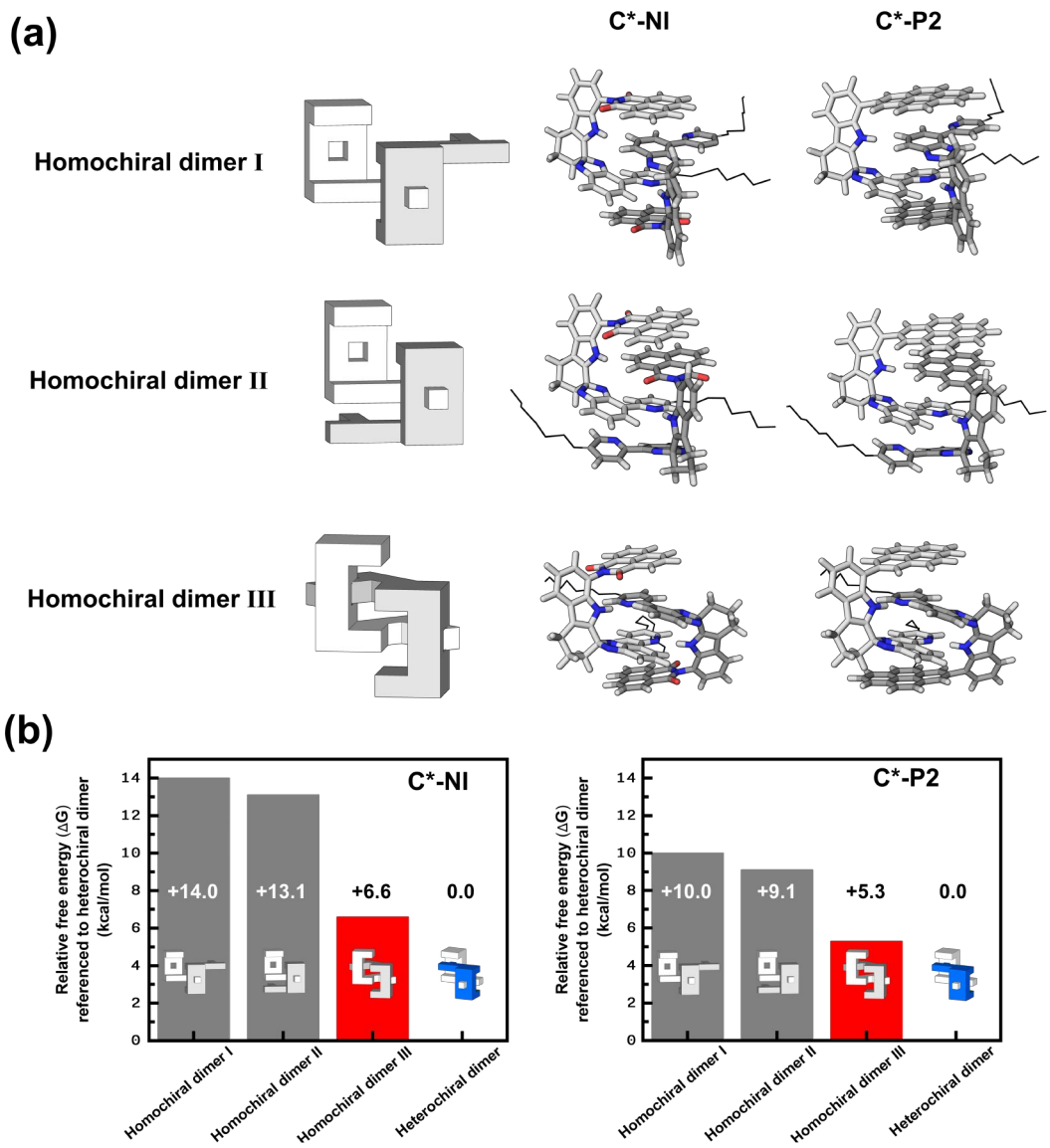


Fig. S12 (a) Schematic representations of computed homochiral dimers, (*R*,*R*)-[**C***]$_2$, along with the DFT energy-minimized structures calculated at the B3LYP-D3/6-31++G** level. Solvation was considered by self-consistent reaction field (SCRF) calculations with conductor-like polarizable continuum model (CPCM) of $CHCl_3$ ($\varepsilon = 4.71$).[9] (b) Bar graphs summarizing the computed free energies of homochiral dimer structures. The energies of the heterochiral dimers, calculated using the same basis set, were set as the reference points.

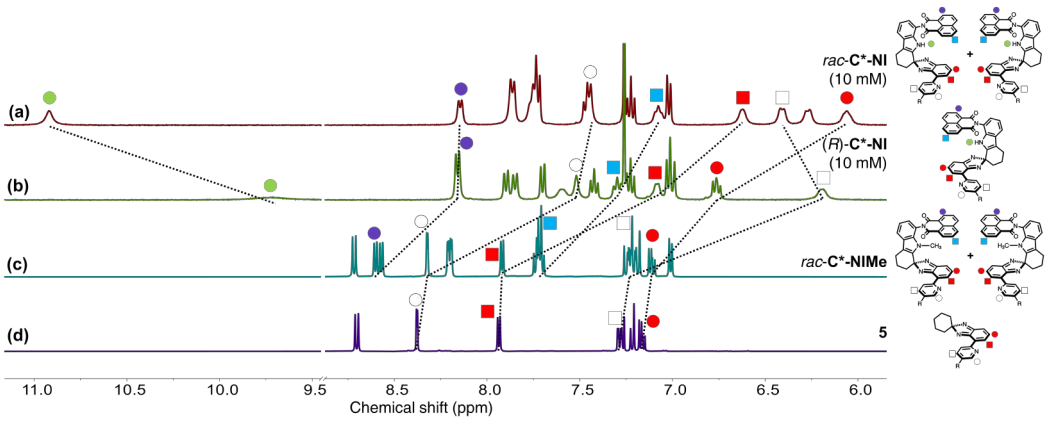


Fig. S13 Partial ^{1}H NMR spectra of (a) *rac*-**C*-NI** (10 mM), (b) (*R*)-**C*-NI** (10 mM), (c) *rac*-**C*-NIMe** (42 mM), and (d) **5** (23 mM) in $CDCl_3$ measured at $T = 298$ K. Proton resonances are labeled with the symbols denoted in the chemical structures.

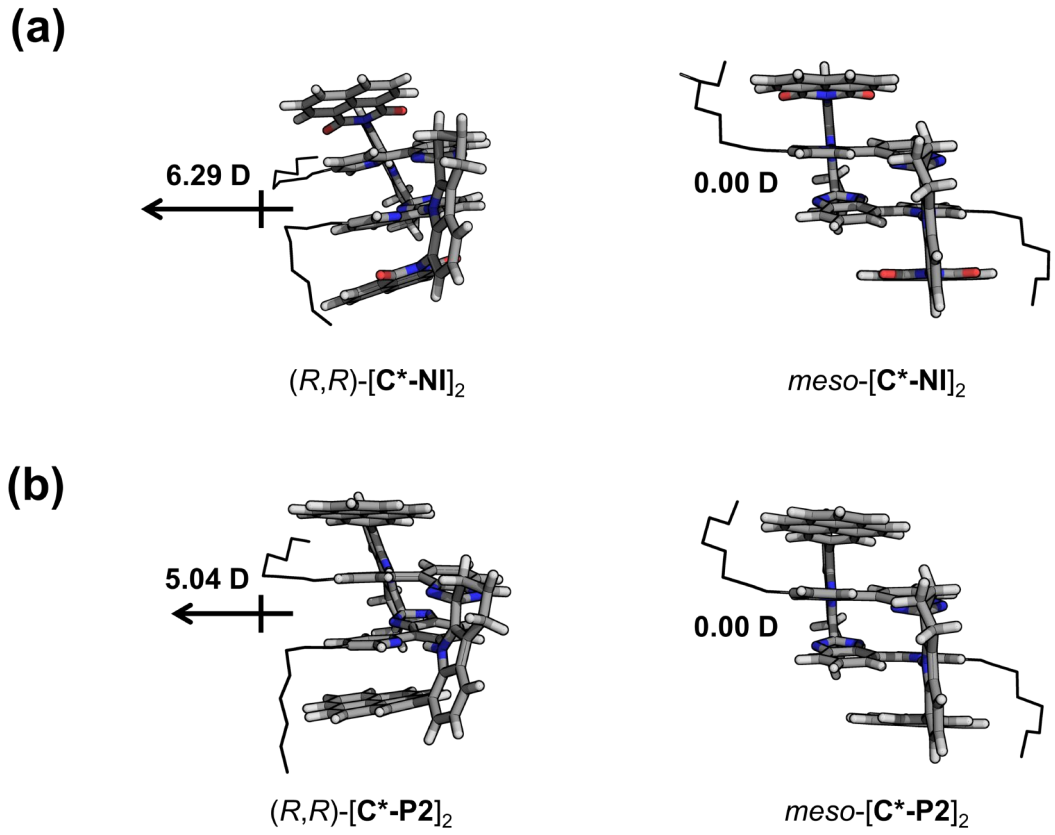


Fig. S14 Dipole moments of DFT energy-minimized structures of the homochiral dimer (*R*,*R*)-[**C***]$_2$ and heterochiral dimer *meso*-[**C***]$_2$ of (a) **C*****-NI** and (b) **C*****-P2** calculated at the B3LYP-D3/6-31++G** level. Solvation was considered by self-consistent reaction field (SCRF) calculations with conductor-like polarizable continuum model (CPCM) of $CHCl_3$ ($\varepsilon = 4.71$).[9]

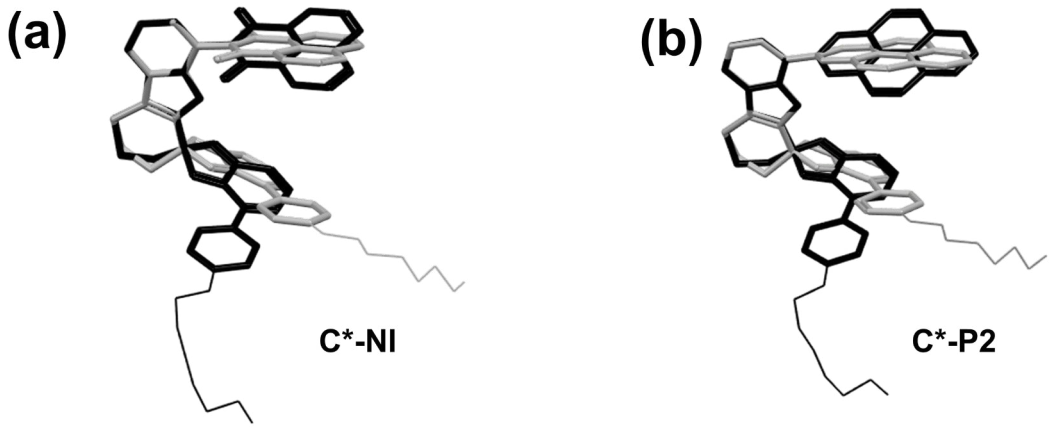


Fig. S15 Capped-stick representations of the DFT energy-minimized structures of monomers forming the heterochiral dimer (black) overlaid with monomers forming the homochiral dimer (gray) for (a) **C*-NI** and (b) **C*-P2**. DFT calculations were performed at the B3LYP-D3/6-31++G** level. Solvation was considered by self-consistent reaction field (SCRF) calculations with conductor-like polarizable continuum model (CPCM) of $CHCl_3$ ($\varepsilon = 4.71$).[9]

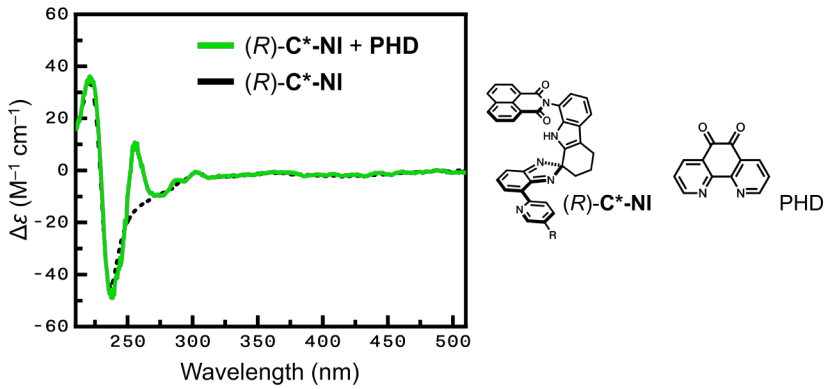


Fig. S16 CD spectra of (*R*)-**C*-NI** alone (black dashed line) and (*R*)-**C*-NI** treated with 10 eq PHD (green line) measured in CH_3CN at 298 K. Sample concentrations: [(*R*)-**C*-NI**] = 37.8 μM; [PHD] = 378 μM.

Supplementary Note 5. Determining the Host–Guest Complexation Constant (K_{HG})

^{1}H NMR titration studies were carried out in $CDCl_3$ at $T = 298$ K (Fig. 6b, c; S16 and S18). The initial concentration of the guest PHD was set at 0.45 mM (=$[\mathsf{G}]_{\mathsf{initial}}$) in a 600 μL solution. Aliquots of the enantiopure host molecule were delivered from a stock solution (18 mL). The NMR tube was sonicated to ensure homogeneous mixing. Spectra were measured after the temperature was stabilized at $T = 298$ K.

The host (*R*)-**C*** (= H) can either (i) self-associate to form $\mathsf{H_2}$, or (ii) bind the guest (= G) to afford HG.

$$\mathsf{H} + \mathsf{H} \overset{K_{\mathsf{homo}}}{\rightleftarrows} \mathsf{H_2}$$

$$\mathsf{H} + \mathsf{G} \overset{K_{\mathsf{HG}}}{\rightleftarrows} \mathsf{HG}$$

$$K_{\mathsf{homo}} = \frac{[\mathsf{H_2}]}{[\mathsf{H}]^2} \tag{26}$$

$$K_{\mathsf{HG}} = \frac{[\mathsf{HG}]}{[\mathsf{H}][\mathsf{G}]} \tag{27}$$

$$[\mathsf{H}]_0 = [\mathsf{H}] + 2[\mathsf{H_2}] + [\mathsf{HG}] \tag{28}$$

From eqs (26) and (28), the following equation is obtained.

$$[\mathsf{H}] = \frac{\sqrt{1 - 8K_{\mathsf{homo}}\left([\mathsf{HG}] - [\mathsf{H}]_0\right)} - 1}{4K_{\mathsf{homo}}} \tag{29}$$

By combining eqs (27) and (29), we obtain

$$K_{\mathsf{HG}} = \frac{4K_{\mathsf{homo}}[\mathsf{HG}]}{(\sqrt{1 - 8K_{\mathsf{homo}}\left([\mathsf{HG}] - [\mathsf{H}]_0\right)} - 1)[\mathsf{G}]} \tag{30}$$

For the guest G,

$$[\mathsf{G}]_0 = [\mathsf{G}] + [\mathsf{HG}] \tag{31}$$

$$[\mathsf{G}] = \left(\frac{\delta_{obs} - \delta_{\mathsf{HG}}}{\delta_{\mathsf{G}} - \delta_{\mathsf{HG}}}\right)[\mathsf{G}]_0 \tag{32}$$

$$[\mathsf{HG}] = \left(1 - \frac{\delta_{obs} - \delta_{\mathsf{HG}}}{\delta_{\mathsf{G}} - \delta_{\mathsf{HG}}}\right)[\mathsf{G}]_0 \tag{33}$$

, where δ_{obs}, δ_{HG}, and δ_{G} denote the observed chemical shift, chemical shift of the host–guest complex, and chemical shift of the unbound guest, respectively.

From eqs (30), (32), and (33), the following relationship is established:

$$[\mathsf{H}]_0 = \frac{\left\{1 + \left(4K_{\mathsf{homo}}\dfrac{1-\dfrac{\delta_{obs}-\delta_{\mathsf{HG}}}{\delta_{\mathsf{G}}-\delta_{\mathsf{HG}}}}{K_{\mathsf{HG}}\dfrac{\delta_{obs}-\delta_{\mathsf{HG}}}{\delta_{\mathsf{G}}-\delta_{\mathsf{HG}}}}\right)\right\}^2 + 8K_{\mathsf{homo}}\left(1-\dfrac{\delta_{obs}-\delta_{\mathsf{HG}}}{\delta_{\mathsf{G}}-\delta_{\mathsf{HG}}}\right)[\mathsf{G}]_0 - 1}{8K_{\mathsf{homo}}} \tag{34}$$

To take into account the volume change and sample dilution during the titration, the following correction was made.

$$[\mathsf{G}]_0 = \left(1 - \frac{[\mathsf{H}]_0}{[\mathsf{H}]_{\mathsf{stock}}}\right)[\mathsf{G}]_{\mathsf{initial}} \tag{35}$$

By rearranging eqs (34) and (35) and using Solve function of Wolfram Mathematica 14,[11] an explicit function is obtained for$[\mathsf{H}]_0$:

$$[\mathsf{H}]_0 = -\frac{[\mathsf{H}]_{\mathsf{stock}}\left(\delta_{\mathsf{G}}-\delta_{obs}\right)\left(2K_{\mathsf{homo}}\left(\delta_{\mathsf{G}}-\delta_{obs}\right)\left(\delta_{\mathsf{G}}-\delta_{\mathsf{HG}}\right)+K_{\mathsf{HG}}\left(\delta_{obs}-\delta_{\mathsf{HG}}\right)\left(\delta_{\mathsf{G}}+[\mathsf{G}]_0K_{\mathsf{HG}}\left(\delta_{obs}-\delta_{\mathsf{HG}}\right)-\delta_{\mathsf{HG}}\right)\right)}{K_{\mathsf{HG}}^2\left(\delta_{obs}-\delta_{\mathsf{HG}}\right)^2\left([\mathsf{G}]_0\left(-\delta_{\mathsf{G}}+\delta_{obs}\right)+[\mathsf{H}]_{\mathsf{stock}}\left(-\delta_{\mathsf{G}}+\delta_{\mathsf{HG}}\right)\right)} \tag{36}$$

Using eq (36), numerical global fittings were carried out by non-linear least-squares regression analysis[10] to obtain K_{HG} and δ_{HG}. The value of K_{homo} is already available from the independent experiments to determine the homochiral dimerization constants of **C*-P2** and **C*-NI** (see Supplementary Note 1).

All ^{1}H NMR (400 MHz) spectra were obtained in $CDCl_3$ to monitor changes in the δ_{obs} value of the $H_{2\text{-PHD}}$ proton (denoted with a green filled circle in the chemical structure shown next to the spectra) resonances at $T = 298$ K. The K_{HG} values were determined as 1.22×10^2 M^{-1} for **C*-P2** and 4.9×10^2 M^{-1} for **C*-NI**, respectively.[10]

The dashed lines in Fig. 6b and c, which denote the expected titration curves (δ_{sim}; simulated chemical shifts) in the absence of host dimerization, were numerically obtained using the experimentally determined host–guest complexation constant (K_{HG}), the chemical shift of the unbound guest (δ_{G}), and the chemical shift of the host–guest complex (δ_{HG}). By taking the limit of eq (36) with the homochiral dimerization constant approaching zero (i.e., $K_{\mathsf{homo}} \to 0$), the following relationship is obtained. Note that the notation δ_{obs} in eq (36) has been replaced with δ_{sim}.

$$\lim_{K_{\mathsf{homo}}\to 0}[\mathsf{H}]_0 = -\frac{[\mathsf{H}]_{\mathsf{stock}}\left(\delta_{\mathsf{G}}-\delta_{sim}\right)\left(K_{\mathsf{HG}}\left(\delta_{sim}-\delta_{\mathsf{HG}}\right)\left(\delta_{\mathsf{G}}+[\mathsf{G}]_0K_{\mathsf{HG}}\left(\delta_{sim}-\delta_{\mathsf{HG}}\right)-\delta_{\mathsf{HG}}\right)\right)}{K_{\mathsf{HG}}^2\left(\delta_{sim}-\delta_{\mathsf{HG}}\right)^2\left([\mathsf{G}]_0\left(-\delta_{\mathsf{G}}+\delta_{sim}\right)+[\mathsf{H}]_{\mathsf{stock}}\left(-\delta_{\mathsf{G}}+\delta_{\mathsf{HG}}\right)\right)} \tag{37}$$

The speciation plot Fig. 7a was numerically simulated by using the experimentally determined homochiral dimerization constant ($K_{\mathsf{homo}} = 1.3 \times 10^3$ M^{-1}), host–guest complexation constant ($K_{\mathsf{HG}} = 4.9 \times 10^2$ M^{-1}), and eqs (26), (27), and (28), using $[(R)$-**C*-NI**$]_0 = 10$ mM and the concentration of PHD guest varied.

[11] Mathematica 14.0; Wolfram Research: Champaign, IL.

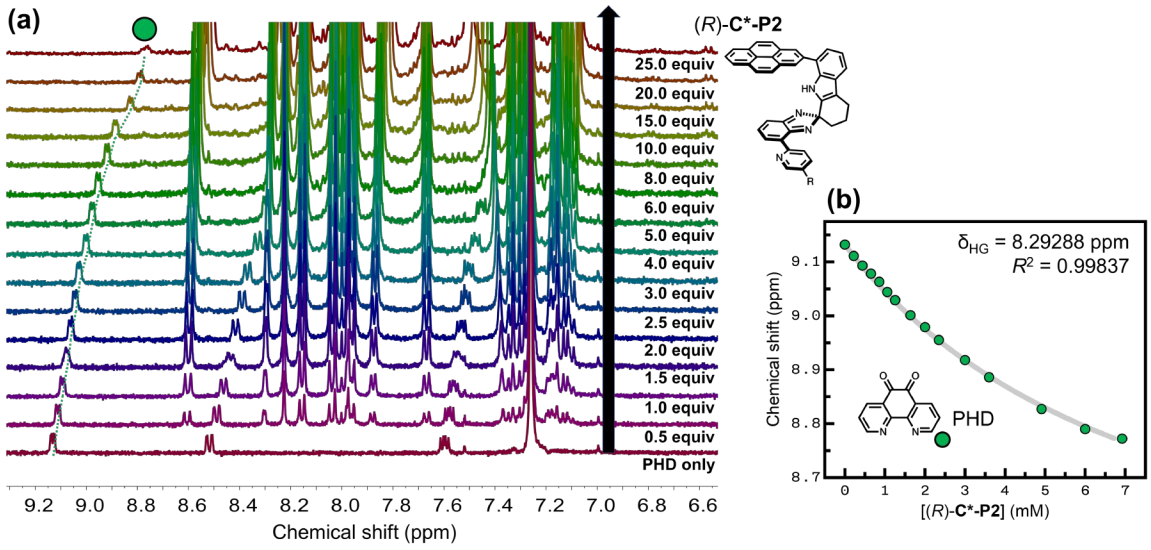


Fig. S17 (a) Partial ^{1}H NMR spectra of PHD in $CDCl_3$ obtained in the presence of (*R*)-**C*-P2** at T = 298 K. (b) Changes in the chemical shift of the proton resonance (●) as a function of the concentration [(*R*)-**C*-P2**]. The theoretical curve with K_{HG} = 1.22 × 10^2 M^{-1} is superimposed on the data points.

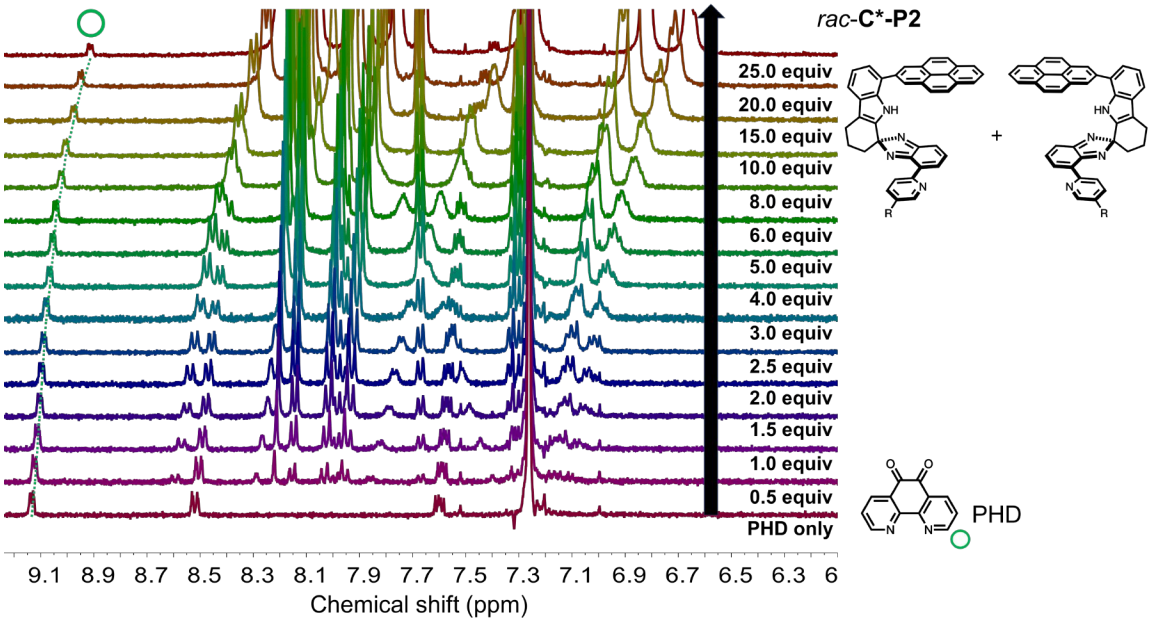


Fig. S18 Partial ^{1}H NMR spectra of PHD in $CDCl_3$ obtained in the presence of an increasing amount of *rac*-**C*-P2** at T = 298 K.

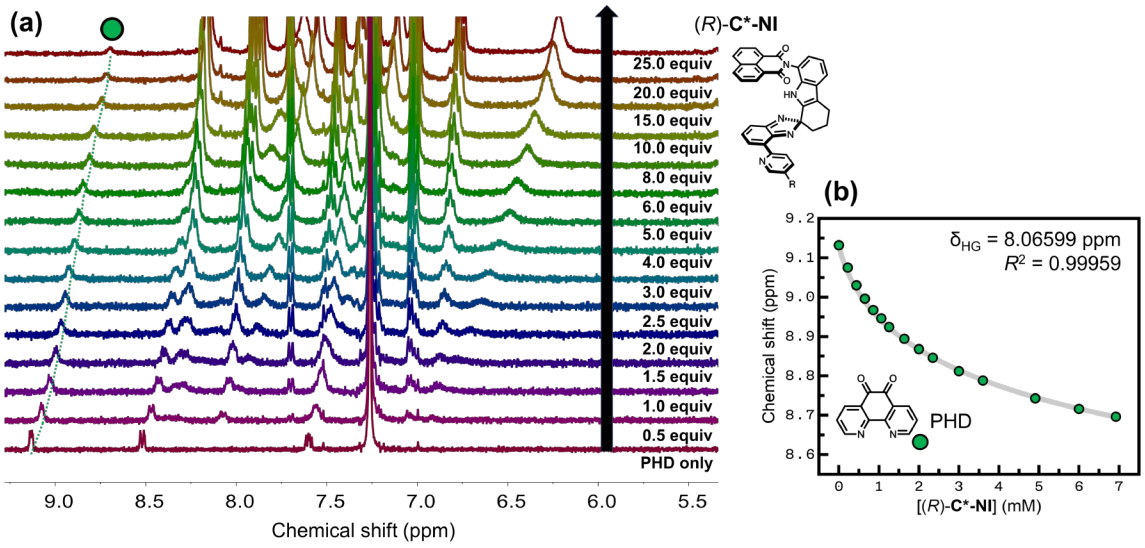


Fig. S19 (a) Partial ^{1}H NMR spectra of PHD in $CDCl_3$ obtained in the presence of (*R*)-**C*-NI** at $T = 298$ K. (b) Changes in the chemical shift of the proton resonance (●) as a function of the concentration [(*R*)-**C*-NI**]. The theoretical curve with $K_{HG} = 4.9 \times 10^2$ M^{-1} is superimposed on the data points.

Supplementary Note 6. Determining the Heterochiral Dimerization Constants (K_{hetero}) of C*-NI

^{1}H NMR competitions studies were carried out in $CDCl_3$ at $T = 298$ K (Fig. 6c and S19). The initial concentration of the guest PHD was set at 0.45 mM (=$[\mathsf{G}]_{\mathsf{initial}}$) in a 600 μL solution sample. Aliquots of *rac*-**C*-NI** host molecule were delivered from a stock solution ($[\mathsf{R}]_{\mathsf{stock}}$+$[\mathsf{S}]_{\mathsf{stock}}$=18 mM). The NMR tube was sonicated to ensure homogeneous mixing. Spectra were measured after the temperature was stabilized at $T = 298$ K.

(*R*)-**C*-NI** (= R) can either (i) self-associate to form R_2, (ii) bind the guest (= G) to afford RG, or (iii) associated with its mirror image clip (*S*)-**C*-NI** (= S) to afford RS.

$$\mathsf{R} + \mathsf{R} \overset{K_{\mathsf{homo}}}{\rightleftharpoons} \mathsf{R}_2$$

$$\mathsf{S} + \mathsf{S} \overset{K_{\mathsf{homo}}}{\rightleftharpoons} \mathsf{S}_2$$

$$\mathsf{R} + \mathsf{G} \overset{K_{\mathsf{RG}}}{\rightleftharpoons} \mathsf{RG}$$

$$\mathsf{S} + \mathsf{G} \overset{K_{\mathsf{SG}}}{\rightleftharpoons} \mathsf{SG}$$

$$\mathsf{R} + \mathsf{S} \overset{K_{\mathsf{hetero}}}{\rightleftharpoons} \mathsf{RS}$$

$$K_{\mathsf{homo}} = \frac{[\mathsf{R}_2]}{[\mathsf{R}]^2} \tag{1}$$

$$K_{\mathsf{homo}} = \frac{[\mathsf{S}_2]}{[\mathsf{S}]^2} \tag{5}$$

$$K_{\mathsf{RG}} = \frac{[\mathsf{RG}]}{[\mathsf{R}][\mathsf{G}]} \tag{38}$$

$$K_{\mathsf{SG}} = \frac{[\mathsf{SG}]}{[\mathsf{S}][\mathsf{G}]} \tag{39}$$

$$K_{\mathsf{hetero}} = \frac{[\mathsf{RS}]}{[\mathsf{R}][\mathsf{S}]} \tag{6}$$

$$[\mathsf{R}]_0 = [\mathsf{R}] + 2[\mathsf{R}_2] + [\mathsf{RG}] + [\mathsf{RS}] \tag{40}$$

Since it is a racemic molecule, the following relationships should also be satisfied:

$$[\mathsf{R}]_0 = [\mathsf{S}]_0 \tag{8}$$

$$[\mathsf{R}] = [\mathsf{S}] \tag{9}$$

$$[\mathsf{R}_2] = [\mathsf{S}_2] \tag{28}$$

$$[\mathsf{RG}] = [\mathsf{SG}] \tag{41}$$

From eqs (1), (6), (9), and (39), the following equation is obtained.

$$[\mathsf{R}] = [\mathsf{S}] = \frac{\sqrt{1 - 4\left(2K_{\mathsf{homo}} + K_{\mathsf{hetero}}\right)\left([\mathsf{RG}] - [\mathsf{R}]_0\right)} - 1}{2\left(2K_{\mathsf{homo}} + K_{\mathsf{hetero}}\right)} \tag{42}$$

By combining eqs (9), (37), (38), (41), and (42), we obtain

$$K_{\mathsf{RG}} = K_{\mathsf{SG}} = \frac{2\left(2K_{\mathsf{homo}} + K_{\mathsf{hetero}}\right)[\mathsf{RG}]}{\left(\sqrt{1 - 4\left(2K_{\mathsf{homo}} + K_{\mathsf{hetero}}\right)\left([\mathsf{RG}] - [\mathsf{R}]_0\right)} - 1\right)[\mathsf{G}]} \tag{43}$$

For the guest G,

$$[\mathsf{G}]_0 = [\mathsf{G}] + [\mathsf{RG}] + [\mathsf{SG}] = [\mathsf{G}] + 2[\mathsf{RG}] \tag{44}$$

$$\delta_{\mathrm{obs}} = [\mathsf{G}]\frac{\delta_{\mathsf{G}}}{[\mathsf{G}]_0} + [\mathsf{RG}]\frac{\delta_{\mathsf{RG}}}{[\mathsf{G}]_0} + [\mathsf{SG}]\frac{\delta_{\mathsf{SG}}}{[\mathsf{G}]_0} = [\mathsf{G}]\frac{\delta_{\mathsf{G}}}{[\mathsf{G}]_0} + 2[\mathsf{RG}]\frac{\delta_{\mathsf{RG}}}{[\mathsf{G}]_0} \tag{45}$$

, where δ_{obs}, δ_{RG} ($= \delta_{\mathsf{SG}}$), and δ_{G} denote the observed chemical shift, chemical shift of (*R*)-**C***-**NI**⊃PHD (= chemical shift of (*S*)-**C***-**NI**⊃PHD), and chemical shift of the unbound guest, respectively.

By combining eqs (44) and (45), we obtain

$$[\mathsf{G}] = \left(\frac{\delta_{obs} - \delta_{\mathsf{RG}}}{\delta_{\mathsf{G}} - \delta_{\mathsf{RG}}}\right)[\mathsf{G}]_0 \tag{46}$$

$$[\mathsf{RG}] = [\mathsf{SG}] = \left(\frac{1 - \dfrac{\delta_{obs} - \delta_{\mathsf{RG}}}{\delta_{\mathsf{G}} - \delta_{\mathsf{RG}}}}{2}\right)[\mathsf{G}]_0 \tag{47}$$

From eqs (43), (46), and (47), the following relationship is established:

$$[\mathsf{R}]_0 = [\mathsf{S}]_0 = \frac{\left\{1 + \left((2K_{\mathsf{homo}} + K_{\mathsf{hetero}})\dfrac{1 - \dfrac{\delta_{obs} - \delta_{\mathsf{RG}}}{\delta_{\mathsf{G}} - \delta_{\mathsf{RG}}}}{K_{\mathsf{RG}}\dfrac{\delta_{obs} - \delta_{\mathsf{RG}}}{\delta_{\mathsf{G}} - \delta_{\mathsf{RG}}}}\right)\right\}^2 + 2\left(2K_{\mathsf{homo}} + K_{\mathsf{hetero}}\right)\left(1 - \dfrac{\delta_{obs} - \delta_{\mathsf{RG}}}{\delta_{\mathsf{G}} - \delta_{\mathsf{RG}}}\right)[\mathsf{G}]_0 - 1}{4\left(2K_{\mathsf{homo}} + K_{\mathsf{hetero}}\right)} \tag{48}$$

To take into account volume changes and sample dilution during the titration, the following correction was made.

$$[\mathsf{G}]_0 = \left(1 - \frac{[\mathsf{R}]_0}{[\mathsf{R}]_{\mathsf{stock}}}\right)[\mathsf{G}]_{\mathsf{initial}} \tag{49}$$

By rearranging eqs (48) and (49) and using the Solve function of Wolfram Mathematica 14,[11] an explicit function is obtained for $[\mathsf{R}]_0$ ($= [\mathsf{S}]_0$):

$$[\mathsf{R}]_0 = [\mathsf{S}]_0 = -\frac{1}{2}\cdot\frac{[\mathsf{R}]_{\mathsf{stock}}(\delta_{\mathsf{G}} - \delta_{obs})\,(K_{\mathsf{hetero}}(\delta_{\mathsf{G}} - \delta_{obs})(\delta_{\mathsf{G}} - \delta_{\mathsf{RG}}) + 2K_{\mathsf{homo}}(\delta_{\mathsf{G}} - \delta_{obs})(\delta_{\mathsf{G}} - \delta_{\mathsf{RG}}) + 2K_{\mathsf{RG}}(\delta_{obs} - \delta_{\mathsf{RG}})(\delta_{\mathsf{G}} + [\mathsf{G}]_0 K_{\mathsf{RG}}(\delta_{obs} - \delta_{\mathsf{RG}}) - \delta_{\mathsf{RG}}))}{K_{\mathsf{RG}}^2(\delta_{obs} - \delta_{\mathsf{RG}})^2\,([\mathsf{G}]_0(-\delta_{\mathsf{G}} + \delta_{obs}) + 2[\mathsf{R}]_{\mathsf{stock}}(-\delta_{\mathsf{G}} + \delta_{\mathsf{RG}}))} \tag{50}$$

Using eq (50), numerical global fittings were carried out by non-linear least-squares regression analysis[10] to obtain K_{hetero}. The values of K_{homo}, K_{RG} ($= K_{\mathsf{HG}}$), and δ_{RG} ($= \delta_{\mathsf{HG}}$) are already available from the independent experiments to determine the homochiral dimerization constant and host–guest complexation constant of **C*-NI** (see Supplementary Notes 1 and 5). According to eq (8),numerical fitting was carried out by using half the concentration of the racemic clip as the variable.

All ^{1}H NMR (400 MHz) spectra were obtained in $CDCl_3$ to monitor changes in the δ_{obs} value of the $H_{2\text{-PHD}}$ proton (denoted with a green hollow circle in the chemical structure shown next to the spectra) resonance at $T = 298$ K. The K_{hetero} value was determined as 4.68×10^5 M^{-1} for **C*-NI**.

The speciation plot Fig. 7b was numerically simulated by using the experimentally determined homochiral dimerization constant ($K_{\mathsf{homo}} = 1.3 \times 10^3$ M^{-1}), host–guest complexation constant ($K_{\mathsf{HG}} = 4.9 \times 10^2$ M^{-1}), heterochiral dimerization constant ($K_{\mathsf{hetero}} = 4.68 \times 10^5$ M^{-1}), and eqs (1), (5), (37), (38),(6), (39), (8), (9), (28), and (41), using [*rac*-**C*-NI**]$_0$ = 10 mM and the concentration of PHD guest varied.

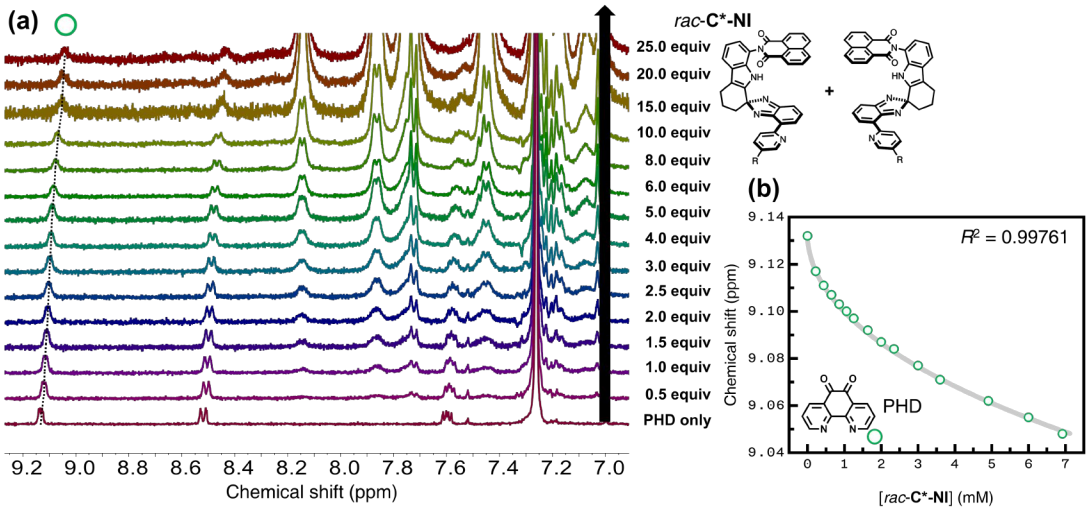


Fig. S20 (a) Partial ^{1}H NMR spectra of PHD in $CDCl_3$ obtained in the presence of *rac*-**C*****-NI** at $T = 298$ K. (b) Changes in the chemical shift of the proton resonance (○) as a function of the host concentration [*rac*-**C*****-NI**]. The theoretical curve with $K_{\text{hetero}} = 4.68 \times 10^5$ M^{-1} is superimposed on the data points.

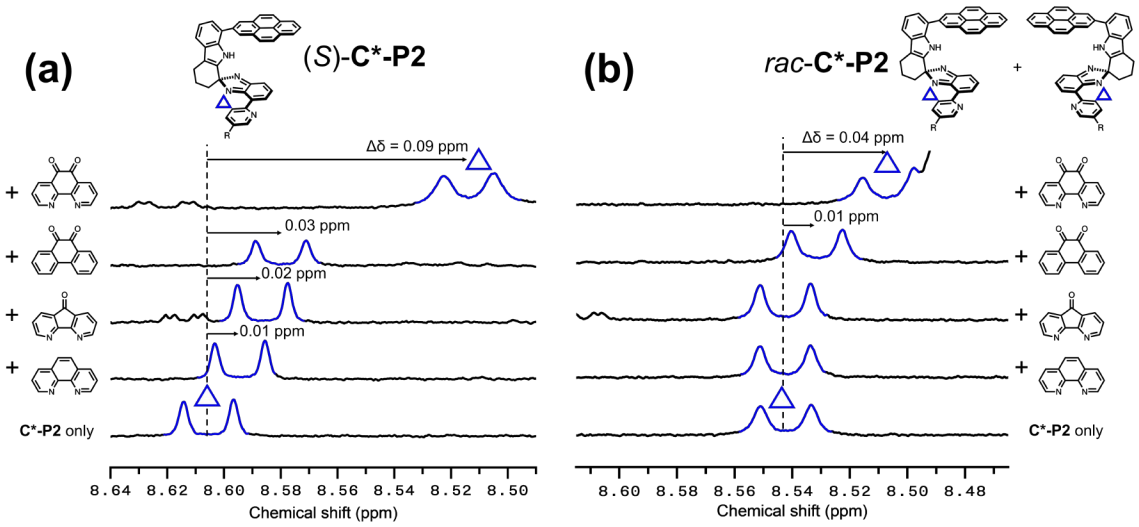


Fig. S21 Aromatic region in the ^{1}H NMR spectra of (a) (*S*)-**C*-P2** and (b) *rac*-**C*-P2** obtained in the presence of various poly(hetero)aromatic guests (G) in $CDCl_3$ at $T = 298$ K ([**C*-P2**] = 1.0 mM; [G] = 20.0 mM). The pyridyl proton (denoted with blue triangle in the chemical structure of **C*-P2**) resonances are colored in blue.

Supplementary Note 7. Numerical Simulations of the Enantiomeric Excess of Scalemic C*-NI⊃PHD Host–Guest Complex

(*R*)-**C*-NI** (= R) can either (i) self-associate to form R_2, or (ii) bind (*S*)-**C*-NI** (= S) to afford RS.

$$R + R \overset{K_{homo}}{\rightleftharpoons} R_2$$

$$S + S \overset{K_{homo}}{\rightleftharpoons} S_2$$

$$R + G \overset{K_{RG}}{\rightleftharpoons} RG$$

$$S + G \overset{K_{SG}}{\rightleftharpoons} SG$$

$$R + S \overset{K_{hetero}}{\rightleftharpoons} RS$$

$$K_{homo} = \frac{[R_2]}{[R]^2} \tag{1}$$

$$K_{homo} = \frac{[S_2]}{[S]^2} \tag{5}$$

$$K_{RG} = \frac{[RG]}{[R][G]} \tag{37}$$

$$K_{SG} = \frac{[SG]}{[S][G]} \tag{38}$$

$$K_{hetero} = \frac{[RS]}{[R][S]} \tag{6}$$

$$[R]_0 = [R] + 2[R_2] + [RG] + [RS] \tag{39}$$

$$[S]_0 = [S] + 2[S_2] + [SG] + [RS] \tag{51}$$

$$[G]_0 = [G] + [RG] + [SG] \tag{52}$$

The enantiomeric excess plot in Fig. 7c and d were numerically simulated by using the experimentally determined homochiral dimerization constant ($K_{homo} = 1.3 \times 10^3$ M^{-1}), heterochiral dimerization constant ($K_{hetero} = 4.68 \times 10^5$ M^{-1}), $K_{HG} = 4.9 \times 10^2$ M^{-1} and eqs (1), (5), (37), (38), (6), (39), (51), and (52). For Fig. 7c, the initial conditions were $[(R)\text{-}\mathbf{C^*\text{-}NI}]_0 = (1 + ee_0) \times 5$ mM, $[(S)\text{-}\mathbf{C^*\text{-}NI}]_0 = (1 - ee_0) \times 5$ mM, and $[PHD]_0 = 2$ mM with the ee_0 varied from 0 to 1.

For Fig. 7d, the initial conditions were $[(R)\text{-}\mathbf{C^*\text{-}NI}]_0 = 6$ mM and $[(S)\text{-}\mathbf{C^*\text{-}NI}]_0 = 4$ mM with the $[\mathrm{PHD}]_0$ varied from 0 to 10 mM.

ee_0 and ee_{HG} are defined as following equations.

$$ee_0 = \frac{[\mathsf{R}]_0 - [\mathsf{S}]_0}{[\mathsf{R}]_0 + [\mathsf{S}]_0} \tag{23}$$

$$ee_{\mathsf{HG}} = \frac{[\mathsf{RG}] - [\mathsf{SG}]}{[\mathsf{RG}] + [\mathsf{SG}]} \tag{53}$$

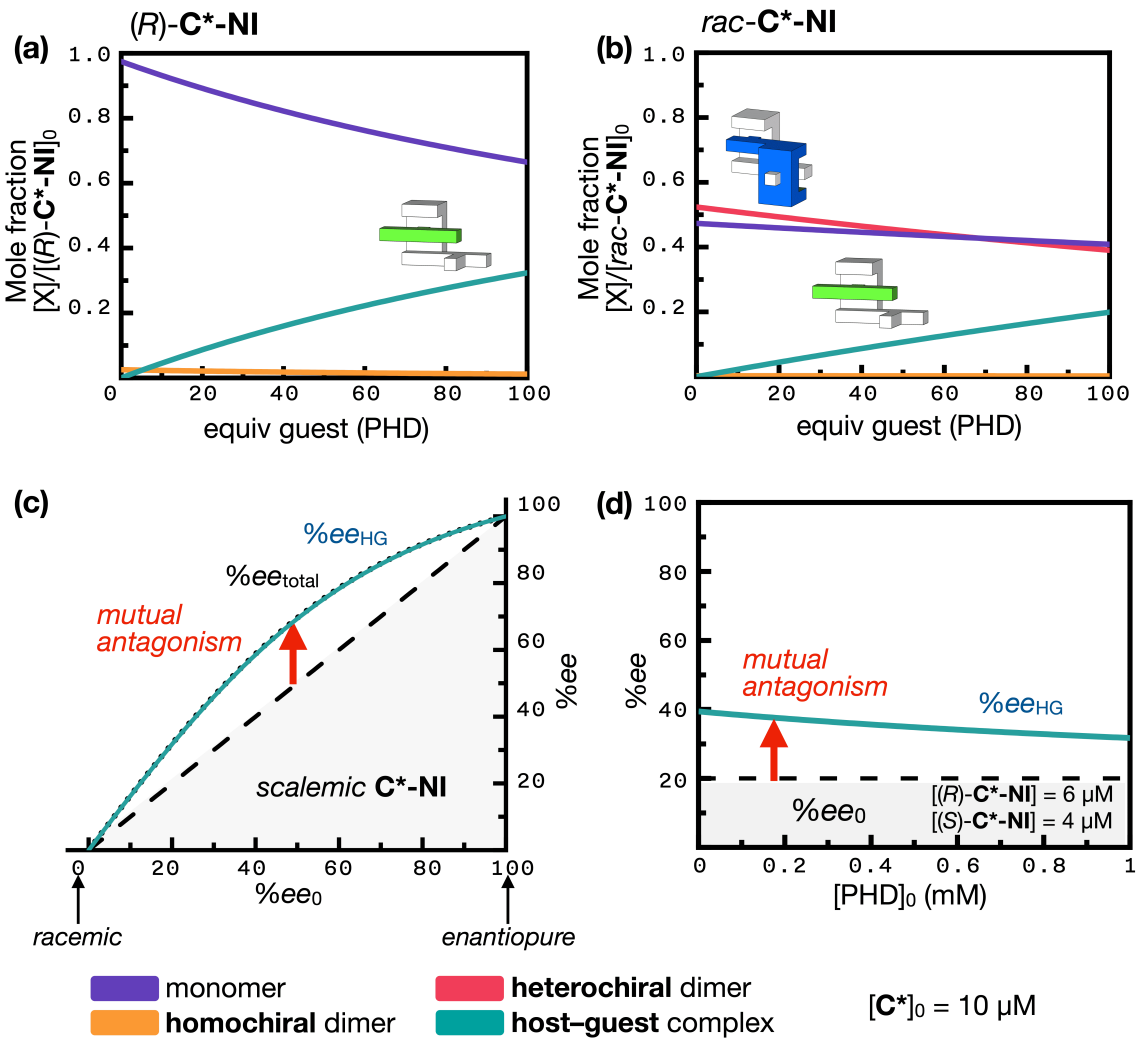


Fig. S22. Simulated speciation plots showing changes in the fractions of individual species originating from (a) (*R*)-**C*-NI**, and (b) *rac*-**C*-NI** clip (unbound (*R*)-**C*-NI** and (*S*)-**C*-NI**, violet line; homochiral dimeric (*R*,*R*)-[**C*-NI**]$_2$ and (*S*,*S*)-[**C*-NI**]$_2$, orange line; host–guest complex (*R*)-**C*-NI**⊃PHD and (*S*)-**C*-NI**⊃PHD, cyan line; heterochiral dimeric *meso*-[**C*-NI**]$_2$, magenta line) with the supply of the guest PHD into [**C*-NI**]$_0$ = 10 μM. (c) Plot of the enantiomeric excess of the host–guest complex (ee_{HG}) **C*-NI**⊃PHD (cyan line) as a function of the initial enantiomeric excess (ee_0) of **C*-NI** in a mixture of [PHD]$_0$ (1 mM) and [**C*-NI**]$_0$ (10 μM). The black dotted lines represent the relationship between ee_0 and ee_{total} (enantiomeric excess of both the monomer and homochiral dimer) in the absence of PHD; the black dashed lines indicate the relationship between ee_0 and ee_{HG} in the absence of host dimerization. (d) Simulated plot illustrating the ee_{HG} (cyan line) of a mixture of [(*R*)-**C*-NI**] and [(*S*)-**C*-NI**] as a function of the guest (PHD) concentration. Dashed lines denote the expected relationship in the absence of host dimerization. See Fig. 3 and 6 for the K_{homo}, K_{hetero}, and K_{HG} values used and Supplementary Notes 5, 6, and 7 for details on the numerical simulation.

Computational Details. All density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were performed using the Gaussian 16 suite of programs.[12] Ground-state geometry optimizations and vibrational frequency calculations were carried out with the B3LYP hybrid functional, incorporating Grimme's D3 dispersion correction[13] (B3LYP-D3), and employing the 6-31++G** basis set.[14,15] Vibrational frequency calculations were conducted to ensure that all optimized geometries correspond to minima on the potential energy surface. Zero-point and thermal corrections were applied to the electronic energies to derive the Gibbs free energies of the optimized geometries. The electronic energy of each monomer within the dimer was determined by performing single-point energy calculations on the monomers, utilizing the optimized structures of the dimers. TD-DFT calculations were executed with the BHandHLYP hybrid functional[16] and the Def2TZVP basis set,[17] based on the optimized structures obtained at the B3LYP-D3/6-31++G** level. Solvation effects were considered through self-consistent reaction field (SCRF) calculations, using the conductor-like polarizable continuum model (CPCM) with solvent parameters for $CHCl_3$ ($\varepsilon = 4.71$) or CH_3CN ($\varepsilon = 35.7$).[9] Unless otherwise specified, all calculations were performed using the CPCM model with $CHCl_3$ as the solvent.

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Table S2. Cartesian coordinates of computed DFT model of (*R*)-**C*-NI**, CPCM model with $CHCl_3$, *E*(B3LYP) = –2194.24583798 Hartree.

C	0.573675	–2.391867	0.576992	H	1.134598	1.559335	–2.083739
C	2.815640	–1.791120	0.566900	C	1.223905	1.985210	–1.090841
C	1.561412	–1.565415	–1.468692	C	0.076889	2.396932	–0.430089
C	0.457305	–2.061350	–0.788885	C	2.594632	2.645400	0.793266
N	1.751496	–2.261786	1.219536	C	0.161398	2.944503	0.876384
C	2.769946	–1.408547	–0.784769	C	2.486818	2.109917	–0.475572
C	–0.580216	–2.828957	1.402137	C	1.440114	3.076895	1.501214
C	–2.839904	–3.332402	3.253314	C	–1.005047	3.355648	1.573193
C	–1.957222	–2.845897	0.911982	H	3.369653	1.772428	–1.006462
C	–0.434344	–3.128620	2.733461	H	2.477126	3.733994	3.284899
C	–1.535490	–3.404921	3.635726	H	3.567405	2.739794	1.267697
C	–3.092572	–3.022459	1.869570	C	–0.902015	3.891475	2.848087
N	–4.227956	–2.871368	1.262315	H	–1.806066	4.196021	3.364036
N	–2.420341	–2.664768	–0.286502	C	0.359068	4.032305	3.465041
C	–3.879378	–2.598508	–0.144476	H	0.421618	4.454380	4.462642
C	–4.294403	–1.201423	–0.539726	C	1.506733	3.630834	2.807601
C	–4.625639	–3.585829	–1.078089	C	–1.238868	2.238297	–1.085078
C	–6.123976	–3.246111	–1.157681	C	–2.340963	3.186123	0.957459
C	–6.386756	–1.858524	–1.783644	O	–1.373627	1.764889	–2.208533
C	–5.403938	–0.849670	–1.263760	O	–3.384557	3.485448	1.527234
C	–5.320915	0.579114	–1.464660	H	–3.664170	–3.492105	3.939675
C	–4.117773	1.006217	–0.834110	O	3.813686	–0.879254	–1.479978
N	–3.528722	–0.085837	–0.248139	C	5.062279	–0.676139	–0.805866
C	–3.662432	2.322854	–0.913381	H	4.931417	–0.003431	0.051079
C	–6.103290	1.537933	–2.132795	H	5.455986	–1.634783	–0.448586
C	–5.662713	2.861006	–2.178371	C	5.996481	–0.034786	–1.831206
C	–4.442576	3.253068	–1.585993	H	6.136759	–0.711363	–2.686185
H	3.729940	–1.706299	1.145346	H	5.545501	0.891598	–2.199019
H	1.498474	–1.284822	–2.515094	O	7.242463	0.323657	–1.250836
H	–0.491809	–2.176219	–1.294664	C	8.160581	–0.756436	–1.083343
H	0.566114	–3.117804	3.151032	H	8.302026	–1.290843	–2.033984
H	–1.286596	–3.640166	4.666224	H	7.804953	–1.475380	–0.332807
H	–4.161409	–3.514824	–2.067451	H	–2.594947	–0.115599	0.131249
H	–4.471432	–4.601808	–0.702327	C	9.478957	–0.154070	–0.623403
H	–6.634407	–4.017295	–1.744228	H	9.856176	0.547505	–1.383477
H	–6.544690	–3.277438	–0.146613	H	9.327751	0.405828	0.312741
H	–6.297412	–1.919988	–2.878173	O	10.390333	–1.225464	–0.428141
H	–7.418191	–1.546624	–1.578699	C	11.672270	–0.787779	0.006834
H	–7.032206	1.251580	–2.617175	H	12.137329	–0.119898	–0.733066
H	–6.258402	3.607779	–2.694110	H	11.607013	–0.259684	0.969539
H	–4.100040	4.280155	–1.658049	H	12.292693	–1.678376	0.126874
N	–2.373501	2.634150	–0.340847				

Table S3. Cartesian coordinates of computed DFT model of (*R*)-**C*-NI**, CPCM model with CH_3CN, *E*(B3LYP) = –2194.25265566 Hartree.

C	0.578046	–2.374888	0.558958	H	1.130647	1.658339	–2.113344
C	2.822975	–1.781469	0.551463	C	1.216931	2.037518	–1.101399
C	1.564272	–1.523779	–1.477807	C	0.068091	2.415714	–0.422498
C	0.460136	–2.024817	–0.801698	C	2.584995	2.609082	0.812799
N	1.758415	–2.257591	1.200031	C	0.150967	2.901219	0.908488
C	2.775502	–1.380712	–0.795276	C	2.479018	2.134684	–0.480505
C	–0.575788	–2.818275	1.381060	C	1.429274	3.004988	1.539261
C	–2.836233	–3.332768	3.229754	C	–1.015704	3.277952	1.624494
C	–1.952735	–2.836818	0.890185	H	3.363048	1.824125	–1.025423
C	–0.430874	–3.122996	2.711445	H	2.466208	3.576454	3.352104
C	–1.531784	–3.404928	3.612185	H	3.557095	2.681209	1.292073
C	–3.088404	–3.018332	1.847238	C	–0.912406	3.752828	2.924010
N	–4.223942	–2.866848	1.239521	H	–1.815402	4.032135	3.455676
N	–2.416436	–2.653895	–0.307920	C	0.348098	3.864960	3.546997
C	–3.875619	–2.590287	–0.166742	H	0.410588	4.238825	4.563508
C	–4.291882	–1.191797	–0.556262	C	1.495920	3.495802	2.870652
C	–4.619272	–3.575204	–1.104965	C	–1.246189	2.283693	–1.081586
C	–6.117204	–3.235596	–1.191360	C	–2.349134	3.134586	1.001970
C	–6.376935	–1.846418	–1.814789	O	–1.384560	1.861553	–2.226441
C	–5.399593	–0.837956	–1.283183	O	–3.396728	3.404233	1.583188
C	–5.319878	0.592650	–1.472746	H	–3.659699	–3.496775	3.916053
C	–4.120686	1.018410	–0.832971	O	3.819001	–0.848441	–1.486163
N	–3.529641	–0.076499	–0.255490	C	5.069443	–0.650534	–0.810845
C	–3.668812	2.337373	–0.897983	H	4.938370	0.016470	0.050081
C	–6.101634	1.555532	–2.136848	H	5.462151	–1.612009	–0.461224
C	–5.664842	2.880597	–2.168002	C	6.001867	–0.003631	–1.834272
C	–4.448441	3.271660	–1.565734	H	6.139935	–0.674817	–2.693652
H	3.739066	–1.707181	1.128301	H	5.551914	0.926142	–2.194379
H	1.499506	–1.228291	–2.519980	O	7.250885	0.349077	–1.254788
H	–0.490379	–2.128969	–1.306819	C	8.165964	–0.735210	–1.093429
H	0.568478	–3.111842	3.131327	H	8.305530	–1.263462	–2.047688
H	–1.282721	–3.643820	4.641681	H	7.806567	–1.457163	–0.347876
H	–4.152009	–3.502678	–2.092792	H	–2.606082	–0.102028	0.149236
H	–4.466516	–4.592025	–0.731141	C	9.485560	–0.139018	–0.628873
H	–6.623888	–4.004971	–1.783150	H	9.864022	0.568733	–1.382381
H	–6.544645	–3.270363	–0.183101	H	9.336714	0.411493	0.312936
H	–6.278420	–1.904611	–2.908561	O	10.397497	–1.213103	–0.444202
H	–7.410299	–1.536242	–1.617803	C	11.678979	–0.777840	–0.001283
H	–7.026977	1.270908	–2.628992	H	12.143443	–0.100843	–0.732805
H	–6.260114	3.629933	–2.680530	H	11.610008	–0.260842	0.966810
H	–4.107999	4.300158	–1.628509	H	12.300917	–1.668502	0.109970
N	–2.381216	2.641992	–0.319254				

Table S4. Cartesian coordinates of computed DFT model of (*R*,*R*)-[**C*-NI**]$_2$ **I**, E(B3LYP) = –4388.55796842 Hartree.

C	–2.023165	–1.152772	1.158715	C	1.554692	1.323203	–1.447321
C	–3.840828	–2.107751	0.077207	C	–0.682550	1.635947	–0.889378
C	–4.236389	–0.840995	2.078974	C	–0.163850	0.480134	–2.923993
C	–2.869202	–0.610650	2.146910	C	1.180041	0.648608	–2.624119
N	–2.526358	–1.889151	0.147758	N	0.613393	1.809749	–0.612520
C	–4.749352	–1.603274	1.024903	C	–1.128119	0.972864	–2.040480
C	–0.554547	–0.968427	1.175250	C	2.969786	1.522676	–1.063977
C	2.393486	–0.740376	1.140269	C	5.753802	1.942540	–0.143711
C	0.130618	–0.037841	2.067810	C	4.053841	0.685187	–1.572233
C	0.257475	–1.653620	0.310985	C	3.344624	2.471657	–0.149717
C	1.698843	–1.537507	0.284638	C	4.706647	2.691924	0.293779
C	1.621158	0.066829	2.047633	C	5.452679	0.893365	–1.084200
N	2.028752	0.973621	2.879738	N	6.252882	0.016563	–1.605924
N	–0.356038	0.815047	2.913244	N	4.020779	–0.317604	–2.395172
C	0.799259	1.536851	3.469522	C	5.400544	–0.816757	–2.474242
C	0.692962	2.999841	3.108284	C	5.454634	–2.256495	–2.026223
C	0.797628	1.404324	5.019674	C	5.914282	–0.755287	–3.941902
C	1.613760	2.503851	5.710713	C	7.197011	–1.578002	–4.132445
C	1.004853	3.894967	5.450442	C	6.960655	–3.080421	–3.877681
C	0.750664	4.058310	3.980563	C	6.150549	–3.271997	–2.629027
C	0.571266	5.247880	3.187706	C	5.895223	–4.463170	–1.854029
C	0.434998	4.815658	1.834256	C	5.022629	–4.081389	–0.795185
N	0.500760	3.442982	1.810293	N	4.762528	–2.737775	–0.925139
C	0.273774	5.736189	0.793333	C	4.534897	–5.008389	0.129522
C	0.520280	6.622147	3.478442	C	6.301522	–5.805340	–1.948979
C	0.342294	7.529326	2.435293	C	5.840479	–6.719654	–1.002823
C	0.225340	7.089718	1.100147	C	4.958969	–6.327137	0.025781
H	–4.181701	–2.695097	–0.769186	H	–1.379791	2.035317	–0.160516
H	–4.914952	–0.432155	2.820808	H	–0.480277	–0.029052	–3.828183
H	–2.451500	–0.010397	2.943810	H	1.940915	0.259236	–3.285868
H	–0.202636	–2.333415	–0.395799	H	2.593255	3.113825	0.284212
H	2.213767	–2.124794	–0.468077	H	4.868739	3.492391	1.008734
H	–0.246287	1.462391	5.344895	H	5.115202	–1.145680	–4.580800
H	1.171896	0.409577	5.270050	H	6.072619	0.295783	–4.201350
H	1.646317	2.300599	6.786820	H	7.569496	–1.426974	–5.151349
H	2.646057	2.479255	5.341630	H	7.965341	–1.205095	–3.445993
H	0.070753	4.003357	6.021548	H	6.435454	–3.526314	–4.735194
H	1.680031	4.680396	5.810693	H	7.920413	–3.604944	–3.798988
H	0.619123	6.971594	4.502132	H	6.964296	–6.125145	–2.747594
H	0.299556	8.593559	2.645273	H	6.150075	–7.758442	–1.060986
H	0.104405	7.806189	0.293829	H	4.583057	–7.057564	0.734728
N	0.206421	5.271804	–0.573286	N	3.558624	–4.601000	1.113986
H	–3.215216	4.326804	–2.540343	H	–0.426595	–5.306631	0.753549
C	–2.299124	4.135481	–3.088442	C	–0.137489	–4.735455	1.628786
C	–1.084390	4.439687	–2.492901	C	1.206963	–4.462030	1.837639
C	–1.169183	3.301094	–5.060887	C	–0.739085	–3.503696	3.622665
C	0.129449	4.203538	–3.188848	C	1.614110	–3.702336	2.962950
C	–2.340826	3.566905	–4.377756	C	–1.112578	–4.256489	2.526273
C	0.092725	3.614016	–4.489152	C	0.628144	–3.210826	3.872442
C	1.380091	4.526107	–2.603514	C	2.982064	–3.394936	3.180887

H	–3.299647	3.322741	–4.822753	H	–2.160789	–4.461372	2.337201
H	1.296187	2.886375	–6.134850	H	0.303669	–2.060036	5.676349
H	–1.200079	2.845108	–6.046333	H	–1.491197	–3.115563	4.303358
C	2.560037	4.257738	–3.280102	C	3.360321	–2.635937	4.277746
H	3.504140	4.501219	–2.805917	H	4.410244	–2.404856	4.420197
C	2.528511	3.659778	–4.556807	C	2.391155	–2.161244	5.185775
H	3.460316	3.443749	–5.069021	H	2.704200	–1.564971	6.036444
C	1.320484	3.347572	–5.151525	C	1.052257	–2.438396	4.986209
C	–1.057549	4.953452	–1.104923	C	2.206106	–4.923014	0.849657
C	1.433547	5.119279	–1.252627	C	4.009628	–3.851704	2.219930
O	–2.069246	5.083373	–0.422019	O	1.904869	–5.538152	–0.166867
O	2.482918	5.445245	–0.706440	O	5.202537	–3.587232	2.336313
H	3.473769	–0.646915	1.138274	H	6.772105	2.099922	0.194310
O	–6.091142	–1.805627	1.001142	O	–2.430310	0.777288	–2.364741
C	–6.678436	–2.391952	–0.170008	C	–3.439360	1.163146	–1.419981
H	–6.415636	–1.797943	–1.051269	H	–3.312346	0.607690	–0.485387
H	–6.320626	–3.420688	–0.294042	H	–3.366160	2.236073	–1.212245
C	–8.189234	–2.357144	0.051974	C	–4.778638	0.796051	–2.061286
H	–8.449553	–2.910681	0.965557	H	–5.064157	1.547302	–2.812785
H	–8.510795	–1.319894	0.175209	H	–4.670659	–0.171089	–2.559639
O	–8.890995	–2.869002	–1.073815	O	–5.809247	0.626886	–1.100343
C	–8.964052	–4.292269	–1.139132	C	–6.142623	1.802352	–0.365097
H	–9.405095	–4.696597	–0.216227	H	–6.377735	2.633088	–1.047097
H	–7.971071	–4.742762	–1.272536	H	–5.314149	2.112575	0.286435
C	–9.842341	–4.639685	–2.330925	C	–7.350376	1.455120	0.489773
H	–10.845306	–4.205877	–2.196258	H	–8.198473	1.176981	–0.156010
H	–9.408577	–4.217323	–3.250726	H	–7.109768	0.592578	1.128214
O	–9.911197	–6.056084	–2.410500	O	–7.667741	2.596572	1.272728
C	–10.710334	–6.510259	–3.496339	C	–8.775180	2.377164	2.137916
H	–11.747922	–6.157416	–3.402424	H	–9.684426	2.135019	1.567910
H	–10.305185	–6.167209	–4.459750	H	–8.572045	1.558750	2.844394
H	–10.698549	–7.601915	–3.470002	H	–8.936817	3.301990	2.695727
H	0.570891	2.854034	0.970145	H	4.335907	–2.163570	–0.218179

Table S5. Cartesian coordinates of computed DFT model of (*R*,*R*)-[**C*-NI**]$_2$ **II**, E(B3LYP) = –4388.55932614 Hartree.

C	–0.360063	–4.748001	–0.603561	C	0.105508	–1.167119	–0.788166
C	–2.622023	–4.393098	–0.936393	C	2.367588	–0.894731	–1.252763
C	–1.929678	–5.646794	0.994758	C	0.793130	–0.602430	–3.035955
C	–0.620711	–5.473325	0.576236	C	–0.214941	–0.896656	–2.131518
N	–1.357645	–4.244144	–1.349410	N	1.391659	–1.175659	–0.383802
C	–2.962786	–5.077628	0.241950	C	2.119503	–0.579571	–2.594188
C	1.023917	–4.499083	–1.063551	C	–0.930255	–1.442444	0.229630
C	3.774611	–4.011763	–2.018872	C	–2.916387	–2.026389	2.343217
C	2.119558	–4.326388	–0.117889	C	–2.325663	–1.041028	0.067654
C	1.353662	–4.368001	–2.385172	C	–0.632899	–2.080728	1.404087
C	2.707116	–4.132202	–2.856052	C	–1.604320	–2.372993	2.439304
C	3.508131	–4.085631	–0.604051	C	–3.318599	–1.333610	1.146897
N	4.320628	–3.935222	0.396613	N	–4.492587	–0.886934	0.820486
N	2.089610	–4.299839	1.177311	N	–2.908127	–0.405798	–0.903350
C	3.474014	–4.057103	1.601033	C	–4.312835	–0.256141	–0.501444
C	3.572694	–2.788111	2.411383	C	–4.686268	1.205089	–0.434958
C	3.943744	–5.251873	2.484728	C	–5.245315	–0.920949	–1.555336
C	5.189780	–4.916619	3.313076	C	–6.713532	–0.530188	–1.338242
C	4.900424	–3.788177	4.321037	C	–6.941425	0.979101	–1.552036
C	4.207118	–2.655546	3.621406	C	–5.850283	1.767596	–0.889321
C	4.117466	–1.262942	3.977583	C	–5.744333	3.187556	–0.644843
C	3.440833	–0.612848	2.902585	C	–4.468319	3.403737	–0.050954
N	3.113355	–1.559295	1.959501	N	–3.838389	2.185083	0.062089
C	3.275915	0.776761	2.889683	C	–4.004812	4.687802	0.253637
C	4.569274	–0.504440	5.070720	C	–6.583559	4.289151	–0.880430
C	4.350134	0.871580	5.073517	C	–6.141951	5.561374	–0.518725
C	3.721620	1.507548	3.984027	C	–4.861448	5.761448	0.034945
H	–3.381621	–3.936917	–1.562354	H	3.376381	–0.918472	–0.854382
H	–2.168716	–6.190451	1.902862	H	0.571947	–0.377238	–4.074168
H	0.196690	–5.876959	1.158917	H	–1.248514	–0.901202	–2.447107
H	0.565850	–4.453719	–3.126194	H	0.380659	–2.421552	1.573527
H	2.854365	–4.056405	–3.929251	H	–1.246438	–2.900695	3.317992
H	3.112616	–5.503992	3.151467	H	–4.903449	–0.591434	–2.541892
H	4.116359	–6.107238	1.824763	H	–5.109176	–2.003583	–1.503437
H	5.521193	–5.818147	3.840064	H	–7.347757	–1.102667	–2.022756
H	6.001541	–4.611757	2.642399	H	–7.002951	–0.806293	–0.318697
H	4.276955	–4.174542	5.140940	H	–6.962329	1.204336	–2.628525
H	5.833159	–3.439885	4.780585	H	–7.922924	1.270854	–1.159080
H	5.087354	–0.983484	5.896480	H	–7.559717	4.151899	–1.336120
H	4.690559	1.473708	5.910261	H	–6.781730	6.422425	–0.684923
H	3.615526	2.585395	3.970711	H	–4.515544	6.764096	0.261408
N	2.779049	1.437286	1.704827	N	–2.639606	4.890892	0.681596
H	–1.080928	1.502114	0.549332	H	0.189403	6.712485	–1.600826
C	–0.405104	1.989032	–0.141598	C	0.544975	6.319296	–0.654896
C	0.936938	2.026199	0.189193	C	–0.356335	5.688577	0.189953
C	0.020897	3.122125	–2.231980	C	2.355950	5.906241	0.898064
C	1.868321	2.610645	–0.704486	C	0.084602	5.147199	1.423115
C	–0.867777	2.534290	–1.354932	C	1.904558	6.428481	–0.299118
C	1.408056	3.172940	–1.934485	C	1.461012	5.256460	1.788296
C	3.251823	2.628890	–0.400210	C	–0.817009	4.473188	2.286111

H	–1.923212	2.480354	–1.592384	H	2.597537	6.913243	–0.978295
H	2.010374	4.185842	–3.748856	H	2.931733	4.776761	3.298572
H	–0.333746	3.552558	–3.163858	H	3.405498	5.977652	1.168421
C	4.153556	3.200738	–1.285962	C	–0.365209	3.923376	3.475898
H	5.209311	3.195557	–1.037705	H	–1.066465	3.394114	4.111019
C	3.703170	3.768324	–2.495688	C	0.990710	4.038799	3.846095
H	4.421209	4.211221	–3.178046	H	1.329309	3.593543	4.775264
C	2.357969	3.753639	–2.814789	C	1.885046	4.691786	3.020680
C	1.391715	1.420839	1.459495	C	–1.767948	5.546791	–0.225890
C	3.747321	1.998767	0.843032	C	–2.234991	4.317801	1.903601
O	0.626359	0.915835	2.272638	O	–2.186078	5.956369	–1.302259
O	4.939309	1.943944	1.127449	O	–3.046867	3.697135	2.587062
H	4.783434	–3.843236	–2.379893	H	–3.642603	–2.252032	3.116245
O	–4.226446	–5.232726	0.722552	O	3.077797	–0.248611	–3.498094
C	–5.288178	–4.483423	0.116745	C	4.433961	–0.129286	–3.042148
H	–5.085771	–3.410920	0.208202	H	4.495988	0.581536	–2.210960
H	–5.379818	–4.751308	–0.942045	H	4.800757	–1.106563	–2.708769
C	–6.562075	–4.823125	0.891298	C	5.236343	0.401724	–4.227141
H	–6.894252	–5.844978	0.654902	H	5.170122	–0.296121	–5.074158
H	–6.350384	–4.764103	1.962109	H	4.817146	1.362985	–4.538063
O	–7.598966	–3.883577	0.641861	O	6.589264	0.644361	–3.866624
C	–8.088968	–3.872658	–0.696921	C	7.416120	–0.518425	–3.830207
H	–8.351125	–4.890010	–1.023196	H	7.395647	–1.033517	–4.801837
H	–7.340022	–3.470835	–1.392476	H	7.085496	–1.225500	–3.057567
C	–9.310088	–2.966709	–0.719533	C	8.828823	–0.051294	–3.517435
H	–10.144256	–3.426587	–0.168119	H	9.169784	0.654826	–4.290486
H	–9.062622	–2.013180	–0.230016	H	8.843613	0.470082	–2.547765
O	–9.658366	–2.756607	–2.080868	O	9.659192	–1.202999	–3.483818
C	–10.747824	–1.855345	–2.237582	C	11.015308	–0.897853	–3.180791
H	–11.653415	–2.232696	–1.740424	H	11.450941	–0.226501	–3.935473
H	–10.503796	–0.864613	–1.826539	H	11.105571	–0.425466	–2.191601
H	–10.938175	–1.763433	–3.308975	H	11.564845	–1.841543	–3.179732
H	2.429525	–1.427279	1.202670	H	–3.088183	2.006557	0.710861

Table S6. Cartesian coordinates of computed DFT model of (*R*,*R*)-[**C*-NI**]$_2$ **III**, E(B3LYP) = –4388.57797520 Hartree.

C	–1.103489	0.101098	1.234185	C	0.901097	–1.264613	–1.108296
C	–2.474900	0.708368	–0.532768	C	2.249884	0.599924	–0.809412
C	–0.828916	2.284477	0.217495	C	0.627937	0.637250	–2.575993
C	–0.462393	1.346248	1.179147	C	0.251341	–0.639196	–2.189731
N	–2.129857	–0.176103	0.393219	N	1.901921	–0.638715	–0.455927
C	–1.830619	1.947447	–0.691959	C	1.636156	1.290476	–1.865040
C	–0.691337	–0.965835	2.165675	C	0.520284	–2.606245	–0.624000
C	0.125275	–3.238979	3.873719	C	–0.216930	–5.216275	0.550129
C	0.582679	–0.937379	2.879458	C	–0.763885	–3.224926	–0.942626
C	–1.458561	–2.083217	2.379355	C	1.336932	–3.334403	0.203399
C	–1.072128	–3.187771	3.230692	C	0.987735	–4.622302	0.764575
C	1.003214	–2.112024	3.699843	C	–1.143251	–4.519379	–0.303690
N	2.184227	–1.919090	4.199346	N	–2.339419	–4.870189	–0.660988
N	1.499099	–0.019227	2.925400	N	–1.721241	–2.820829	–1.720571
C	2.570926	–0.564478	3.758613	C	–2.779620	–3.826251	–1.607491
C	3.874813	–0.588555	3.001659	C	–4.075972	–3.193459	–1.166575
C	2.786460	0.317187	5.025889	C	–3.042325	–4.503040	–2.987827
C	4.030984	–0.128938	5.808459	C	–4.276742	–5.415985	–2.933776
C	5.329882	0.018893	4.988292	C	–5.572472	–4.640396	–2.615640
C	5.112714	–0.384184	3.558607	C	–5.326286	–3.586749	–1.575133
C	6.068167	–0.551547	2.495657	C	–6.262838	–2.738896	–0.884941
C	5.318214	–0.831551	1.312421	C	–5.489533	–1.840153	–0.087938
N	3.984136	–0.864370	1.647870	N	–4.160626	–2.148879	–0.261074
C	5.963291	–1.013563	0.082536	C	–6.109409	–0.851647	0.688566
C	7.471219	–0.500110	2.432484	C	–7.665179	–2.650514	–0.866988
C	8.101731	–0.724717	1.211155	C	–8.270962	–1.682809	–0.068307
C	7.351797	–0.971572	0.043999	C	–7.498002	–0.789051	0.699849
H	–3.285358	0.441472	–1.206844	H	3.038858	1.053229	–0.219798
H	–0.311554	3.234591	0.170696	H	0.140575	1.143246	–3.402485
H	0.341194	1.563685	1.867887	H	–0.548995	–1.153211	–2.702710
H	–2.425476	–2.159618	1.901247	H	2.311941	–2.941220	0.460105
H	–1.776366	–4.008441	3.324772	H	1.726314	–5.102246	1.399043
H	2.889556	1.354136	4.688793	H	–3.182382	–3.702409	–3.721835
H	1.886134	0.248077	5.644392	H	–2.146376	–5.067171	–3.265171
H	4.104995	0.461899	6.727962	H	–4.380833	–5.931530	–3.894766
H	3.900449	–1.174863	6.104446	H	–4.110286	–6.183069	–2.170524
H	5.672388	1.063973	5.018324	H	–5.952708	–4.160395	–3.529655
H	6.130010	–0.575266	5.446669	H	–6.354696	–5.338204	–2.292095
H	8.053564	–0.290310	3.325001	H	–8.266210	–3.328107	–1.466547
H	9.184730	–0.692332	1.145153	H	–9.353287	–1.603668	–0.038321
H	7.851688	–1.108930	–0.909244	H	–7.980951	–0.023717	1.298400
N	5.200000	–1.186768	–1.130834	N	–5.323530	0.111512	1.424167
H	4.755627	1.704021	–3.946455	H	–5.035575	4.051702	0.449906
C	4.194245	0.794043	–4.126347	C	–4.396835	3.722834	1.260568
C	4.300484	–0.252169	–3.221593	C	–4.442388	2.398676	1.670940
C	2.621889	–0.472825	–5.462866	C	–2.716034	4.221039	2.934041
C	3.577055	–1.454011	–3.431074	C	–3.646767	1.960989	2.759547
C	3.353360	0.681581	–5.251454	C	–3.530191	4.635316	1.895690
C	2.715986	–1.568059	–4.564684	C	–2.758764	2.880234	3.397982
C	3.681496	–2.535619	–2.519626	C	–3.719358	0.622003	3.220892

H	3.274636	1.512048	–5.945247	H	–3.503423	5.666879	1.559165
H	1.303761	–2.849800	–5.590052	H	–1.256447	3.103089	4.942209
H	1.961927	–0.554541	–6.321909	H	–2.037724	4.921287	3.413648
C	2.954779	–3.697444	–2.729581	C	–2.934404	0.208238	4.285683
H	3.044224	–4.509102	–2.016899	H	–3.002326	–0.820638	4.619496
C	2.092302	–3.809408	–3.839822	C	–2.038346	1.105214	4.904136
H	1.516608	–4.718399	–3.979559	H	–1.413712	0.758482	5.720770
C	1.972629	–2.766249	–4.738156	C	–1.948846	2.413157	4.468056
C	5.123146	–0.084224	–2.005501	C	–5.296004	1.438064	0.938969
C	4.529841	–2.413150	–1.317054	C	–4.600399	–0.350524	2.542063
O	5.696709	0.967268	–1.731979	O	–5.940567	1.751433	–0.057092
O	4.647569	–3.308866	–0.485872	O	–4.698755	–1.521971	2.897016
H	0.427319	–4.080038	4.487932	H	–0.490588	–6.166549	0.995152
O	–2.234182	2.695811	–1.745558	O	1.947471	2.559984	–2.237507
C	–1.639385	3.985945	–1.939091	C	3.030666	3.201105	–1.544930
H	–1.819788	4.605754	–1.053144	H	2.765062	3.360018	–0.492235
H	–0.554436	3.892881	–2.081783	H	3.922293	2.570603	–1.603473
C	–2.253526	4.589563	–3.198373	C	3.279160	4.543399	–2.223546
H	–1.881583	5.621280	–3.299863	H	3.595208	4.384364	–3.264783
H	–1.927571	4.018120	–4.071645	H	2.356778	5.131182	–2.229396
O	–3.672228	4.541671	–3.232455	O	4.239036	5.314051	–1.510667
C	–4.346311	5.304582	–2.235984	C	5.590349	4.837928	–1.560085
H	–4.385656	6.365675	–2.522316	H	6.236714	5.716377	–1.657434
H	–3.844768	5.234709	–1.263805	H	5.749164	4.197413	–2.437388
H	3.196671	–0.954899	0.997272	C	5.962383	4.080764	–0.286128
C	–5.742215	4.715148	–2.097413	H	5.728700	4.699743	0.594785
H	–6.316467	4.850771	–3.026570	H	5.394815	3.144615	–0.207977
H	–5.659427	3.638343	–1.892909	O	7.352589	3.796763	–0.348822
O	–6.378105	5.380170	–1.010634	C	7.753021	2.837829	0.627835
C	–7.656605	4.827642	–0.702960	H	7.565132	3.206831	1.647453
H	–8.342465	4.919091	–1.557784	H	7.224516	1.887772	0.484496
H	–7.566536	3.769515	–0.423124	H	8.825489	2.675198	0.499503
H	–8.056132	5.397006	0.139222	H	–3.366596	–1.585950	0.068964

Table S7. Cartesian coordinates of computed DFT model of *meso*-[**C*-NI**]$_2$, E(B3LYP) = –4388.58717457 Hartree.

O	3.204308	–1.652151	–3.449395	O	–3.203787	1.652197	3.448928
O	–5.277066	–1.606818	–2.281056	O	5.276695	1.606816	2.280928
O	6.741570	–1.513399	–0.552375	O	–6.741661	1.513150	0.552665
O	–8.049279	–2.342447	–2.304527	O	8.048840	2.342707	2.305589
N	4.973014	–1.573301	–2.002676	N	–4.972799	1.573204	2.002586
O	–9.477107	–0.139749	–1.157976	O	9.476577	0.139775	1.159396
N	3.146693	–2.842766	0.016499	N	–3.146750	2.842781	–0.016761
H	2.956509	–1.832275	0.025848	H	–2.956656	1.832277	–0.026254
N	–2.820023	–0.033657	–0.200089	N	2.819885	0.033740	0.199631
N	0.243442	–2.950457	1.134488	N	–0.243531	2.950563	–1.134878
N	1.943563	–2.360553	2.704709	N	–1.943715	2.360692	–2.705048
C	5.962161	–0.887909	–1.263517	C	–5.962066	0.887726	1.263667
C	5.022270	1.244761	–2.199662	C	–5.021752	–1.244867	2.199558
C	4.026376	–0.964681	–2.848879	C	–4.025903	0.964658	2.848562
C	4.868179	–3.001079	–1.810169	C	–4.868093	3.000990	1.810046
C	3.990275	–3.502361	–0.843463	C	–3.990296	3.502328	0.843270
C	0.061014	–1.734715	1.546672	C	–0.061084	1.734852	–1.547151
C	2.492345	–3.787476	0.786456	C	–2.492450	3.787526	–0.786712
C	5.978559	0.586102	–1.382146	C	–5.978317	–0.586289	1.382301
C	2.888030	–5.056394	0.440158	C	–2.888135	5.056427	–0.440342
C	3.864800	–4.904332	–0.608376	C	–3.864840	4.904312	0.608242
C	–2.054355	–1.067324	0.228572	C	2.054298	1.067434	–0.229105
C	4.061162	0.508981	–2.938527	C	–4.060530	–0.509007	2.938193
C	–4.188988	–1.545236	–1.478548	C	4.188726	1.545274	1.478277
C	–0.956536	–0.756566	1.167977	C	0.956518	0.756716	–1.168566
C	–2.333978	–2.372456	–0.202792	C	2.333919	2.372560	0.202281
H	–1.709465	–3.188763	0.131595	H	1.709473	3.188891	–0.132171
C	1.455289	–3.429792	1.823424	C	–1.455425	3.429900	–1.823734
C	6.895951	1.320912	–0.645980	C	–6.895865	–1.321180	0.646404
H	7.594093	0.812764	0.009598	H	–7.594301	–0.813106	–0.008917
C	2.325882	–6.293647	1.077834	C	–2.326035	6.293714	–1.077992
C	5.006389	2.672251	–2.253709	C	–5.005720	–2.672357	2.253585
C	–3.834133	–0.262863	–1.024573	C	3.833905	0.262914	1.024234
H	–4.417909	0.593601	–1.353675	H	4.417629	–0.593566	1.353384
C	5.621912	–3.898450	–2.554416	C	–5.621772	3.898321	2.554396
H	6.305228	–3.514420	–3.305197	H	–6.305002	3.514256	3.305237
C	1.124652	–1.370580	2.532014	C	–1.124761	1.370737	–2.532456
C	4.638901	–5.796934	–1.370781	C	–4.638891	5.796869	1.370751
H	4.562184	–6.868385	–1.209332	H	–4.562187	6.868331	1.209360
C	–3.407795	–2.621368	–1.056997	C	3.407635	2.621437	1.056622
H	–3.616571	–3.635968	–1.373740	H	3.616426	3.636030	1.373371
C	1.157508	–0.057994	3.123356	C	–1.157599	0.058185	–3.123873
H	1.927188	0.201831	3.841316	H	–1.927308	–0.201626	–3.841807
C	–0.818415	0.478754	1.744974	C	0.818439	–0.478567	–1.745652
H	–1.522439	1.259979	1.497382	H	1.522509	–1.259777	–1.498133
C	5.968772	3.393389	–1.496846	C	–5.968243	–3.393578	1.496980
H	5.956409	4.479408	–1.533004	H	–5.955776	–4.479595	1.533133
C	5.506847	–5.287844	–2.335608	C	–5.506756	5.287726	2.335621
H	6.110044	–5.966117	–2.931270	H	–6.109920	5.965965	2.931354
C	6.893649	2.729928	–0.714178	C	–6.893410	–2.730194	0.714588

H	7.608612	3.280442	–0.113566	H	–7.608507	–3.280759	0.114184
C	3.109661	1.168576	–3.702332	C	–3.108770	–1.168522	3.701745
H	2.373244	0.583954	–4.241875	H	–2.372261	–0.583838	4.241096
C	–10.095089	–1.338545	–1.604464	C	10.094672	1.338437	1.606090
H	–11.133761	–1.146128	–1.917666	H	11.133219	1.145814	1.919570
H	–10.114354	–2.084958	–0.794318	H	10.114308	2.084866	0.795962
C	0.209952	0.823467	2.705602	C	–0.209970	–0.823260	–2.706243
H	0.197085	1.835463	3.097539	H	–0.197088	–1.835231	–3.098248
C	–7.125590	–2.679045	–3.327964	C	7.124722	2.678992	3.328742
C	–5.769186	–2.892132	–2.691939	C	5.768542	2.892096	2.692237
H	–5.867103	–3.550427	–1.821722	H	5.866731	3.550584	1.822194
H	–5.075109	–3.342027	–3.412809	H	5.074141	3.341770	3.412931
C	4.013308	3.314443	–3.039442	C	–4.012369	–3.314466	3.039045
H	3.989418	4.400296	–3.069198	H	–3.988368	–4.400317	3.068784
C	1.136598	–4.699963	2.662525	C	–1.136790	4.700113	–2.662797
C	–9.308637	–1.880959	–2.779371	C	9.307985	1.880989	2.780786
H	–9.869616	–2.703020	–3.251480	H	9.868978	2.702939	3.253070
H	–9.167756	–1.084414	–3.525226	H	9.166737	1.084464	3.526587
C	3.083541	2.577029	–3.749088	C	–3.082490	–2.576973	3.748463
H	2.322236	3.078963	–4.337251	H	–2.320977	–3.078841	4.336412
C	–10.073937	0.404702	0.012762	C	10.073836	–0.404930	–0.011003
H	–10.054350	–0.319951	0.840756	H	10.054783	0.319628	–0.839091
H	–11.116208	0.703915	–0.171933	H	11.115959	–0.704343	0.174210
H	–9.479756	1.276572	0.291776	H	9.479599	–1.276702	–0.290203
H	–7.060403	–1.873877	–4.074947	H	7.059309	1.873654	4.075521
H	–7.430006	–3.603593	–3.843554	H	7.428861	3.603452	3.844655
C	1.001385	–5.955710	1.790462	C	–1.001562	5.955826	–1.790686
H	3.040421	–6.710853	1.802959	H	–3.040613	6.710933	–1.803070
H	0.214146	–5.793922	1.044663	H	–0.214296	5.794010	–1.044922
H	1.956521	–4.828437	3.376841	H	–1.956744	4.828603	–3.377075
H	0.222018	–4.506001	3.231464	H	–0.222230	4.506189	–3.231781
H	2.162084	–7.073298	0.324074	H	–2.162216	7.073342	–0.324211
H	0.687975	–6.796049	2.419805	H	–0.688182	6.796194	–2.420004

Table S8. Cartesian coordinates of computed DFT model of (*R*)-**C*-P2**, E(B3LYP) = –2143.28019601 Hartree.

C	3.468803	2.034529	–3.799089	C	–6.494634	–1.068663	0.278851
C	1.832019	3.615083	–2.171543	C	–7.739858	–1.937978	0.214857
C	2.877009	3.211376	–4.302305	O	–8.477448	–1.513029	–0.920636
C	3.259968	1.600856	–2.483761	C	–9.682206	–2.246146	–1.113872
C	2.435214	2.417180	–1.685778	H	4.086977	1.428851	–4.455418
C	2.056659	4.004804	–3.503666	H	3.062070	3.493976	–5.334522
N	2.071831	2.280618	–0.360961	H	1.602846	4.909360	–3.898226
C	1.279610	3.355853	–0.003552	H	0.903035	6.320065	–0.986009
C	1.089774	4.187525	–1.077401	H	–0.361259	5.531791	–1.917280
C	0.253521	5.432642	–1.014446	H	–1.073653	6.397199	0.413548
C	–0.645175	5.404384	0.238236	H	–1.479910	4.713066	0.075793
C	0.129698	4.966351	1.489485	H	0.998382	5.614739	1.644211
C	0.660627	3.509336	1.362127	H	–0.496243	5.020528	2.385290
C	3.874155	0.358136	–1.953005	H	2.056929	–0.355244	–1.028392
C	5.052259	–2.006635	–0.922104	H	5.825090	0.772220	–2.771159
C	3.113232	–0.547607	–1.194886	H	1.862034	–2.435709	0.300999
C	5.225580	0.069828	–2.198812	H	2.885696	–4.482457	1.207554
C	5.828921	–1.096325	–1.702344	H	8.637012	–4.865500	–0.314962
C	3.675745	–1.721664	–0.671113	H	7.271065	–6.433629	1.034806
C	2.909586	–2.655571	0.113000	H	4.879075	–5.956185	1.478886
C	3.477370	–3.789535	0.615257	H	7.804747	–0.709761	–2.533056
C	4.863416	–4.101051	0.380062	H	8.832532	–2.755070	–1.629391
C	5.646428	–3.192768	–0.398123	H	–0.761294	–0.758501	4.641348
C	7.024937	–3.473500	–0.651361	H	1.381827	–0.040427	5.582210
C	7.589433	–4.648476	–0.124483	H	–2.321693	1.497469	0.882994
C	6.818455	–5.530794	0.635520	H	–4.338855	–2.151005	3.441514
C	5.470856	–5.263405	0.886720	H	–4.477230	0.566437	0.099939
C	7.215413	–1.404442	–1.940658	H	–5.894310	–1.197125	–0.630110
C	7.784750	–2.538141	–1.439359	H	–6.772992	–0.012273	0.377426
N	–0.455196	2.554525	1.496757	H	–7.454889	–2.996941	0.125004
N	1.643633	3.231613	2.414055	H	–8.330474	–1.817073	1.135291
C	1.160948	2.228171	3.080406	H	–9.466266	–3.315661	–1.255501
C	–0.151769	1.798360	2.505524	H	–10.343881	–2.140978	–0.241132
C	–0.877532	0.671926	3.093019	H	2.449403	1.601377	0.282250
C	–0.265847	0.083689	4.171939	H	2.674416	1.863979	4.631657
C	1.003712	0.510305	4.726019	C	–10.362279	–1.684491	–2.352440
C	1.722355	1.549218	4.218753	H	–10.575195	–0.613592	–2.209678
C	–2.173742	0.171564	2.576865	H	–9.697266	–1.787058	–3.224082
C	–4.584324	–0.878542	1.717262	O	–11.564159	–2.415881	–2.546437
C	–2.790711	0.689034	1.427690	C	–12.298914	–1.979273	–3.683667
N	–2.747511	–0.839728	3.274435	H	–12.593603	–0.923958	–3.586380
C	–3.902209	–1.341194	2.860798	H	–11.713117	–2.099915	–4.606841
C	–4.007653	0.162371	0.988698	H	–13.196272	–2.598656	–3.744199
O	–5.757847	–1.500026	1.429035				

Table S9. Cartesian coordinates of computed DFT model of (*R*,*R*)-[**C*-P2**]$_2$ **I**, E(B3LYP) = –4286.62485327 Hartree.

C	–2.079844	–1.125336	1.024563	C	3.626436	2.201676	0.495468
C	–3.976961	–1.745048	–0.160805	C	4.965073	2.217015	1.050473
C	–4.258297	–0.696731	1.980909	N	5.677653	0.651740	–0.602238
C	–2.875444	–0.622986	2.073729	N	6.452789	–0.163911	–1.247263
N	–2.647722	–1.675085	–0.067955	C	4.261587	–0.163438	–2.202929
C	–4.837120	–1.267795	0.843693	C	5.611981	–0.730710	–2.317479
C	–0.600360	–1.093378	1.058186	C	5.556322	–2.234659	–2.217096
C	2.353698	–1.168907	1.036067	C	6.217531	–0.368494	–3.706925
C	0.168652	–0.389276	2.081547	C	7.458596	–1.213103	–4.027331
C	0.144677	–1.716864	0.092538	C	7.112564	–2.710039	–4.152547
C	1.590523	–1.748908	0.073082	C	6.213300	–3.128725	–3.026113
C	1.661583	–0.443232	2.066059	C	5.815552	–4.444657	–2.592407
N	2.156485	0.259890	3.035708	N	4.915144	–4.267176	–1.502441
N	–0.231487	0.362536	3.059257	C	4.786276	–2.911356	–1.288452
C	0.988688	0.838334	3.727592	C	4.255033	–5.335170	–0.871641
C	1.073305	2.344468	3.663652	C	6.092436	–5.750272	–3.037685
C	0.964559	0.404382	5.220640	C	5.457315	–6.820182	–2.411120
C	1.959654	1.194736	6.079062	H	4.544051	–6.614486	–1.353198
C	1.604234	2.693334	6.113407	H	–1.111174	2.081517	0.183511
C	1.353114	3.182322	4.716572	H	–0.109046	0.713812	–3.772096
C	1.390089	4.515626	4.175146	H	2.288438	0.757222	–3.076533
C	1.137320	4.397729	2.775450	H	2.888709	2.811771	0.994689
N	0.924967	3.063551	2.491769	H	5.133855	2.849705	1.916677
C	1.147329	5.506317	1.910804	H	5.437817	–0.543963	–4.455440
C	1.633562	5.788854	4.721965	H	6.450324	0.700539	–3.704698
C	1.633810	6.894098	3.874279	H	7.904418	–0.853172	–4.960927
C	1.399879	6.752682	2.488007	H	8.202263	–1.071495	–3.235039
H	–4.368700	–2.183563	–1.072835	H	6.616000	–2.897604	–5.116234
H	–4.897759	–0.315067	2.770537	H	8.030437	–3.310388	–4.159026
H	–2.404677	–0.179469	2.940348	H	6.778371	–5.918653	–3.862961
H	–0.379130	–2.232879	–0.702401	H	5.656603	–7.834560	–2.744237
H	2.050864	–2.281523	–0.751823	H	4.050636	–7.468086	–0.897034
H	–0.054545	0.564101	5.588224	C	–0.803115	–5.476707	–0.384005
H	1.167744	–0.667277	5.256829	C	–0.507671	–5.075719	0.581768
H	1.961006	0.782996	7.094592	C	0.897058	–4.940568	0.866070
H	2.969741	1.065809	5.672574	C	–1.083415	–4.135256	2.760526
H	0.715566	2.848346	6.743610	C	1.292698	–4.405211	2.128753
H	2.415094	3.266562	6.579123	C	–1.452033	–4.685053	1.483771
H	1.824175	5.905602	5.785209	C	0.304553	–4.008737	3.077900
H	1.822611	7.884368	4.278788	H	2.679552	–4.228772	2.419146
H	1.418643	7.630766	1.848423	C	–2.508176	–4.767769	1.243368
H	–2.759066	5.130682	–1.356078	H	3.051175	–3.690084	3.700742
C	–1.912553	4.895003	–1.995712	C	4.107293	–3.560604	3.921166
C	–0.589036	4.969281	–1.434910	H	2.107298	–3.333059	4.618383
C	–1.006854	4.190256	–4.152923	C	2.406874	–2.921819	5.578694
C	0.527602	4.685399	–2.278368	C	0.701704	–3.467347	4.339133
C	–2.111418	4.519492	–3.291314	C	1.885038	–5.272398	–0.075390
C	0.320404	4.291945	–3.633306	H	3.631506	–4.552481	1.437463
H	1.850918	4.760196	–1.748977	H	6.983549	1.478056	0.961134
C	–3.118704	4.448284	–3.692871	H	–2.098078	1.286642	–2.257784

H	2.959899	4.450202	–2.611306	O	–3.136480	1.592304	–1.319463
C	3.964282	4.503456	–2.200502	C	–3.091042	0.910924	–0.464216
H	2.762199	4.068351	–3.905469	H	–3.022722	2.623156	–0.968987
C	3.609188	3.817942	–4.538713	H	–4.452991	1.389813	–2.068611
C	1.438782	3.967185	–4.461564	C	–4.626718	2.220369	–2.769083
H	–0.365288	5.266413	–0.080591	H	–4.389797	0.460036	–2.640280
H	2.025965	5.084698	–0.395037	H	–5.555625	1.233000	–1.187429
O	3.436994	–1.202693	1.047217	O	–5.857186	2.377906	–0.393810
C	–6.193927	–1.323058	0.798986	C	–6.002801	3.263870	–1.030012
H	–6.826547	–1.732479	–0.422502	H	–5.050268	2.592505	0.320233
H	–6.519996	–1.068036	–1.237189	H	–7.129511	2.055601	0.372284
C	–6.548563	–2.765767	–0.661071	C	–7.953004	1.862785	–0.333555
H	–8.329843	–1.610804	–0.179720	H	–6.973072	1.147376	0.972338
H	–8.627654	–2.247992	0.665478	H	–7.428609	3.169120	1.201909
O	–8.572145	–0.574673	0.069646	O	–8.592185	2.964329	1.994161
C	–9.075119	–1.930384	–1.347640	C	–9.479673	2.803403	1.364339
H	–9.236788	–3.326212	–1.594058	H	–8.471038	2.099035	2.662485
H	–9.665880	–3.824683	–0.712463	H	–8.736577	3.865097	2.594487
H	–8.278674	–3.808752	–1.830366	H	4.213709	–2.487926	–0.577528
C	–10.179454	–3.463583	–2.779400	H	1.586845	–5.659888	–1.045783
H	–11.150654	–3.002872	–2.541096	C	4.686270	–4.396029	1.648346
H	–9.759485	–2.941639	–3.653363	H	–1.215066	5.441562	0.573868
O	–10.330231	–4.850638	–3.045297	C	3.030802	5.126137	0.014950
C	–11.197366	–5.111611	–4.142492	C	0.930164	5.308989	0.447992
H	–12.208880	–4.723676	–3.952056	C	3.246004	–5.069133	0.192405
H	–10.813536	–4.660570	–5.069434	H	–1.189492	3.760092	–5.478641
H	–11.245577	–6.195829	–4.263786	C	–2.197893	3.675982	–5.874829
C	0.879272	2.646434	1.553640	H	2.055800	3.287260	–6.412199
C	1.848937	1.444890	–1.077331	H	1.208162	3.541196	–5.781316
C	–0.394241	1.781590	–0.572734	C	–0.092238	3.437637	–6.280204
C	0.180172	1.008932	–2.768935	C	–0.251678	3.102998	–7.301040
N	1.510897	1.041583	–2.381859	C	–3.094175	–3.780747	3.448178
C	0.889641	1.818640	–0.205463	H	–2.039309	–3.707119	3.697068
C	–0.806117	1.369030	–1.847234	C	–0.290880	–3.070609	5.252592
C	3.247176	1.465605	–0.596268	H	0.005461	–2.661271	6.214289
C	5.984281	1.474566	0.539784	H	–1.644228	–3.183322	4.929307
C	4.304028	0.653162	–1.195498	C	–2.396155	–2.855650	5.641089

Table S10. Cartesian coordinates of computed DFT model of (*R*,*R*)-[**C*-P2**]$_2$ **II**, *E*(B3LYP) = –4286.62685674 Hartree.

C	–1.650773	–4.718184	–0.876475	C	–1.058022	–2.198910	1.237087
C	–3.811678	–3.918798	–1.088136	C	–2.061709	–2.419579	2.258479
C	–3.322417	–5.431975	0.712996	N	–3.584178	–1.012345	1.083955
C	–2.015908	–5.478100	0.252609	N	–4.672540	–0.359856	0.814308
N	–2.553537	–3.974550	–1.538463	C	–3.037706	0.007251	–0.888212
C	–4.245903	–4.615056	0.051437	C	–4.399611	0.340531	–0.454719
C	–0.261073	–4.695982	–1.383297	C	–4.543637	1.831126	–0.271668
C	2.489628	–4.646594	–2.453791	C	–5.430145	–0.088128	–1.539581
C	0.884083	–4.840004	–0.493803	C	–6.824120	0.483047	–1.247269
C	0.034696	–4.494163	–2.704390	C	–6.840706	2.022924	–1.317057
C	1.386746	–4.468390	–3.232195	C	–5.625028	2.590894	–0.644079
C	2.270633	–4.828423	–1.040957	C	–5.295134	3.956447	–0.322735
N	3.137875	–4.963551	–0.085383	N	–3.991177	3.944510	0.252551
N	0.915243	–4.950770	0.797113	C	–3.567715	2.632322	0.290603
C	2.336365	–5.051719	1.152226	C	–3.296489	5.117530	0.598131
C	2.758795	–3.949546	2.093398	C	–5.946124	5.189520	–0.509936
C	2.562703	–6.427159	1.852864	C	–5.278529	6.358836	–0.152546
C	3.883733	–6.488360	2.627523	H	–3.971260	6.322846	0.378879
C	3.894802	–5.465267	3.778184	H	3.081766	–1.655386	–0.969182
C	3.464515	–4.123922	3.259531	H	0.512288	0.095510	–3.945558
C	3.761116	–2.807933	3.756758	H	–1.410331	–0.373146	–2.421870
C	3.221023	–1.877953	2.817056	H	–0.115751	–2.713841	1.365206
N	2.604631	–2.601190	1.814796	H	–1.792410	–3.074497	3.081479
C	3.451890	–0.492735	2.922722	H	–5.058203	0.277442	–2.502167
C	4.486681	–2.336214	4.865332	H	–5.450818	–1.179040	–1.585857
C	4.683327	–0.964899	4.999194	H	–7.541954	0.071563	–1.964345
C	4.189469	–0.064983	4.031281	H	–7.135643	0.153070	–0.250725
H	–4.487112	–3.284319	–1.651038	H	–6.866248	2.347211	–2.367925
H	–3.635909	–5.991916	1.588037	H	–7.758583	2.408850	–0.856532
H	–1.276018	–6.076779	0.767292	H	–6.943349	5.228215	–0.938886
H	–0.784467	–4.351424	–3.401307	H	–5.763809	7.320456	–0.292095
H	1.501565	–4.304294	–4.299469	H	–3.470069	7.253206	0.630700
H	1.724624	–6.577943	2.541203	C	1.237159	6.847458	–0.889842
H	2.508717	–7.203466	1.083685	C	1.511374	6.258098	–0.019675
H	4.020715	–7.502396	3.019569	C	0.464201	5.617386	0.730167
H	4.717286	–6.284674	1.945259	C	3.207855	5.318734	1.466030
H	3.224431	–5.805953	4.581399	C	0.819600	4.810274	1.852401
H	4.896202	–5.398587	4.220219	C	2.820861	6.109146	0.328105
H	4.899525	–3.031966	5.590480	C	2.188015	4.668396	2.226546
H	5.243966	–0.576837	5.844861	H	–0.200711	4.135503	2.589293
H	4.399098	0.994601	4.129502	C	3.601596	6.582929	–0.260553
H	–0.734846	1.389693	0.685738	H	0.184151	3.331505	3.719371
C	0.044403	1.856875	0.091783	C	–0.593506	2.812007	4.273133
C	1.405653	1.578575	0.453693	H	1.491369	3.210851	4.089263
C	0.766436	3.246566	–1.775548	C	1.765744	2.593378	4.940379
C	2.447217	2.172652	–0.318656	C	2.539768	3.875149	3.361349
C	–0.263197	2.647770	–0.972810	C	–0.886529	5.728213	0.368698
C	2.130851	3.002512	–1.433663	H	–1.538462	4.265132	2.181940
H	3.809250	1.920605	0.022632	H	–4.054287	–2.031861	2.972147
C	–1.297502	2.831037	–1.245346	H	2.982683	–0.359443	–3.386276

H	4.844412	2.529063	–0.770624	O	4.325691	–0.490294	–2.894145
C	5.880236	2.335355	–0.505308	C	4.416211	–0.024186	–1.907423
H	4.543070	3.319821	–1.839562	H	4.593278	–1.550874	–2.820175
C	5.337225	3.765161	–2.433222	H	5.214152	0.252223	–3.889106
C	3.178047	3.584886	–2.212165	C	5.108311	–0.182052	–4.893519
H	1.737830	0.719998	1.513409	H	4.900473	1.298838	–3.926809
H	4.093585	1.068573	1.098998	H	6.573171	0.248762	–3.470556
O	3.496919	–4.630865	–2.855531	O	7.286385	–0.951287	–3.763474
C	–5.500368	–4.549473	0.575797	C	7.255914	–1.162546	–4.842554
H	–6.397953	–3.548476	0.073518	H	6.862792	–1.813992	–3.231579
H	–5.959177	–2.553204	0.204586	H	8.723312	–0.735800	–3.315339
C	–6.596876	–3.724601	–0.989797	C	9.158106	0.122095	–3.851412
H	–7.676411	–3.645867	0.906505	H	8.748827	–0.513253	–2.237195
H	–8.234314	–4.559429	0.653069	H	9.442632	–1.926711	–3.601321
O	–7.405082	–3.686032	1.964797	O	10.811014	–1.850166	–3.220222
C	–8.493514	–2.492894	0.751640	C	11.329563	–1.042049	–3.756988
H	–9.087639	–2.345881	–0.536175	H	10.914170	–1.680121	–2.138365
H	–9.642150	–3.254717	–0.813224	H	11.271227	–2.806100	–3.479057
H	–8.330289	–2.156041	–1.308108	H	–2.659014	2.324108	0.597179
C	–10.021295	–1.148074	–0.462611	H	3.072110	0.452311	1.836569
H	–10.866746	–1.359230	0.209938	C	0.941025	0.250973	2.083247
H	–9.473252	–0.283296	–0.059785	H	5.129465	0.863760	1.354961
O	–10.477957	–0.882477	–1.781354	C	–0.561928	4.262529	–3.134482
C	–11.304006	0.273386	–1.854788	C	0.476287	4.067745	–2.878913
H	–12.203573	0.161718	–1.231865	C	2.841701	4.395333	–3.309860
H	–10.757447	1.171537	–1.531224	H	1.261630	5.267312	–4.483817
H	–11.602492	0.390347	–2.898725	C	1.504107	4.634250	–3.635095
C	2.023980	–2.215467	1.060906	H	3.635712	4.840673	–3.903625
C	–0.170052	–1.229274	–0.876991	H	–1.155077	6.314883	–0.505334
C	2.106207	–1.348376	–1.331071	C	–2.314036	3.746819	2.740283
C	0.660943	–0.384757	–2.983994	C	–1.890695	5.052188	1.075561
N	–0.404824	–0.649443	–2.137765	C	3.893122	3.768512	3.723266
C	1.077595	–1.595759	–0.517626	H	4.162493	3.184948	4.598763
C	1.955985	–0.703284	–2.566213	C	5.328640	5.645283	1.267033
C	–1.244920	–1.425993	0.120276	H	4.550249	5.163525	1.852372
C	–3.299967	–1.858689	2.212579	H	4.885419	4.402283	2.973063
C	–2.558870	–0.790912	0.016753	C	5.927187	4.297868	3.261956

Table S11. Cartesian coordinates of computed DFT model of (*R*,*R*)-[**C*****-P2**]$_2$ **III**, *E*(B3LYP) = –4286.63843700 Hartree.

C	–1.170490	–0.273613	–1.149451	C	1.265393	4.077809	–2.565711
C	–2.558195	–0.145286	0.699342	C	–0.838994	4.545315	–1.542227
C	–1.047454	–2.002598	0.543140	N	–2.002940	5.085523	–1.349547
C	–0.618529	–1.467968	–0.669155	N	–1.505765	3.531502	0.394432
N	–2.150947	0.355783	–0.456599	C	–2.492815	4.500373	–0.085844
C	–2.025696	–1.318626	1.261820	C	–3.847504	3.853291	–0.249231
C	–0.725865	0.360416	–2.403498	C	–2.652921	5.656064	0.950986
C	0.119307	1.760953	–4.869617	C	–3.827397	6.575145	0.586129
C	0.508486	–0.017983	–3.086891	C	–5.179707	5.833958	0.616116
C	–1.434080	1.375567	–2.995433	C	–5.049076	4.457399	0.031707
C	–1.036599	2.047740	–4.211812	C	–6.068727	3.481306	–0.247298
C	0.944572	0.726746	–4.305692	C	–5.401499	2.301745	–0.695577
N	2.087957	0.281786	–4.726812	N	–4.042819	2.561840	–0.711725
N	1.377240	–0.938754	–2.801407	C	–6.098235	1.111377	–0.985147
C	2.426843	–0.827121	–3.813526	C	–7.469397	3.478630	–0.118618
C	3.777500	–0.617739	–3.174989	C	–8.165723	2.308234	–0.409110
C	2.507096	–2.139031	–4.653211	C	–7.487258	1.142494	–0.824319
C	3.713540	–2.118810	–5.603237	H	2.925629	–0.961003	0.478504
C	5.057506	–2.033900	–4.849655	H	0.125512	0.385422	3.459855
C	4.960643	–1.110102	–3.669878	H	–0.406166	2.301117	1.948163
C	5.994331	–0.648832	–2.783543	H	2.456019	2.506255	–1.666288
C	5.353343	0.106166	–1.754927	H	2.017184	4.229462	–3.334324
N	3.997231	0.127988	–2.028085	H	–2.812444	5.194699	1.931334
C	6.070534	0.633668	–0.663371	H	–1.710590	6.211623	0.985521
C	7.390560	–0.819872	–2.751408	H	–3.851174	7.418987	1.284460
C	8.109488	–0.262496	–1.698430	H	–3.653451	6.986239	–0.413816
C	7.454427	0.436408	–0.662952	H	–5.535513	5.751860	1.654135
H	–3.337989	0.392336	1.233227	H	–5.938793	6.418718	0.081566
H	–0.604730	–2.920443	0.908486	H	–7.994425	4.369750	0.214008
H	0.154660	–1.965851	–1.235989	H	–9.247392	2.283849	–0.312680
H	–2.363481	1.694553	–2.545417	H	–8.054227	0.240325	–1.036917
H	–1.695408	2.825574	–4.585815	H	–5.226135	–3.500005	0.969266
H	2.578638	–2.974465	–3.948600	C	–4.583465	–3.511880	0.094389
H	1.569273	–2.243110	–5.207914	C	–4.625567	–2.384938	–0.798793
H	3.694181	–3.020965	–6.224570	C	–2.870627	–4.590339	–1.275451
H	3.613399	–1.260314	–6.275138	C	–3.799742	–2.404601	–1.963050
H	5.349544	–3.034377	–4.496684	C	–3.745182	–4.563403	–0.132631
H	5.850473	–1.713201	–5.536802	C	–2.922048	–3.503398	–2.201020
H	7.894062	–1.383147	–3.532118	C	–3.823919	–1.297173	–2.863692
H	9.187980	–0.383318	–1.654858	H	–3.721182	–5.404799	0.554874
H	8.033490	0.829003	0.168173	C	–2.992323	–1.347322	–4.036642
H	5.077383	–0.439673	4.197466	H	–3.020465	–0.508615	–4.725881
C	4.489289	0.462081	4.050819	C	–2.146380	–2.392381	–4.261337
C	4.584231	1.143684	2.787278	H	–1.501455	–2.397056	–5.135991
C	3.832832	2.343414	2.599263	C	–2.064459	–3.498285	–3.344136
C	3.669779	0.917638	5.040789	C	–5.406649	–1.248554	–0.533108
C	2.983486	2.826419	3.637724	C	–4.605321	–0.175109	–2.546203
C	3.906317	3.035561	1.352500	H	–6.001386	–1.214010	0.375562
H	3.595153	0.378520	5.981456	H	–4.594911	0.683679	–3.211618
C	3.152658	4.250087	1.194017	H	–0.093512	5.548846	–3.348881

H	3.218051	4.778844	0.247912	O	1.773243	–1.511980	2.911701
C	2.338623	4.712151	2.185465	C	2.824372	–2.411807	2.550684
H	1.755197	5.617080	2.037996	H	2.552294	–2.979042	1.651510
C	5.345545	0.639620	1.720712	H	3.735043	–1.838447	2.349531
C	4.665353	2.483285	0.308370	C	3.039417	–3.358162	3.726971
H	5.894296	–0.290570	1.847063	H	3.325107	–2.779837	4.617518
H	0.429436	2.282413	–5.768398	H	2.112131	–3.894279	3.946304
O	–2.514066	–1.672023	2.477545	O	4.015506	–4.352021	3.430961
C	–1.979899	–2.844139	3.106947	C	5.353869	–3.869448	3.271241
H	–2.120892	–3.710734	2.450645	H	6.018112	–4.557917	3.803412
H	–0.904538	–2.716179	3.291409	H	5.471198	–2.874897	3.721158
C	–2.699360	–3.024840	4.434339	C	5.740644	–3.814326	1.793881
H	–2.235233	–3.867990	4.968989	H	5.757364	–4.831198	1.371248
H	–2.576866	–2.121612	5.038515	H	5.003796	–3.231996	1.221871
O	–4.103366	–3.217235	4.307265	O	7.019890	–3.206977	1.705591
C	–4.487384	–4.486392	3.790419	C	7.445070	–3.026104	0.356842
H	–4.165377	–5.293690	4.465249	H	7.530486	–3.991037	–0.164263
H	–4.044213	–4.670182	2.803828	H	6.751203	–2.378218	–0.195068
H	3.258879	0.472231	–1.404182	H	8.422724	–2.543089	0.387760
C	–6.001232	–4.474865	3.649429	H	–3.308131	1.840354	–0.744815
H	–6.481765	–4.415771	4.637980	C	5.364729	1.281319	0.474860
H	–6.307753	–3.588249	3.072134	H	4.696652	2.991132	–0.651630
O	–6.372772	–5.668618	2.975802	C	2.877750	2.106840	4.867793
C	–7.773289	–5.757638	2.741061	C	2.210043	4.010667	3.434902
H	–8.337396	–5.748750	3.685159	C	1.998751	2.576006	5.859816
H	–8.122866	–4.926958	2.110548	H	1.912667	2.028397	6.794577
H	–7.953302	–6.702214	2.223580	C	1.342602	4.441626	4.453875
C	0.987633	1.676312	0.423662	H	0.747275	5.337570	4.299516
C	2.186641	–0.260292	0.850043	H	0.560526	4.074347	6.425130
C	0.618784	0.499287	2.500462	C	1.238431	3.728658	5.650255
C	0.330133	1.564103	1.662478	C	–5.375204	–0.129545	–1.375727
N	1.916621	0.771893	0.051748	C	–1.165275	–4.562975	–3.527718
C	1.553508	–0.449391	2.087779	H	–0.503678	–4.555232	–4.389872
C	0.690898	2.762573	–0.529848	C	–1.959444	–5.637308	–1.501819
C	0.117223	4.808192	–2.585317	H	–1.915057	–6.463546	–0.797174
C	–0.537245	3.552499	–0.468985	H	–0.411073	–6.430933	–2.769057
C	1.531036	3.060430	–1.571893	C	–1.113970	–5.617723	–2.613308

Table S12. Cartesian coordinates of computed DFT model of *meso*-[**C*-P2**]$_2$, E(B3LYP) = –4286.64771682 Hartree.

C	–5.311917	–0.643214	–2.636202	C	–1.602344	2.977618	–2.287817
C	–8.156043	–0.993289	–2.607975	C	–5.813782	1.014087	1.403052
C	4.820937	–1.596081	–2.200275	N	–5.005310	–1.217797	1.983024
C	–9.241220	1.115996	–0.980499	N	–3.949481	0.770573	2.923713
N	2.847904	–3.094046	–0.439445	C	–4.629118	3.076759	2.220391
C	2.756635	–2.086994	–0.248692	C	–3.677791	3.675203	1.374067
C	–2.759287	0.292220	–0.303255	C	0.162112	1.972429	–1.215424
C	–0.076210	–3.106401	0.592933	C	–2.097576	4.089633	–0.155189
C	1.602343	–2.977620	2.287812	C	–5.925786	–0.382009	1.280537
C	5.813783	–1.014088	–1.403052	C	–2.408084	5.317300	0.380191
C	5.005313	1.217797	–1.983021	C	–3.436181	5.082534	1.360857
C	3.949483	–0.770571	–2.923714	C	2.151612	0.881379	0.005870
N	4.629119	–3.076758	–2.220394	N	–4.020818	–0.628411	2.831251
N	3.677791	–3.675202	–1.374071	C	4.263302	0.839675	1.800531
C	–0.162113	–1.972430	1.215420	C	1.061270	0.844344	–0.988363
C	2.097575	–4.089633	0.155184	C	2.584072	2.070269	0.611748
C	5.925788	0.382008	–1.280535	C	2.092635	3.002123	0.371035
C	2.408083	–5.317300	–0.380197	H	–1.054247	3.819308	–1.213803
C	3.436180	–5.082533	–1.360863	H	–6.902299	–0.996220	0.421611
C	–2.151613	–0.881380	–0.005873	H	–7.579127	–0.360847	–0.140135
C	4.020821	0.628413	–2.831250	H	–1.717380	6.587279	–0.025626
C	–4.263305	–0.839675	–1.800532	H	–5.039956	–2.632578	1.802113
N	–1.061271	–0.844345	0.988359	H	3.764741	–0.310906	1.166157
C	–2.584075	–2.070270	–0.611750	H	4.223738	–1.272885	1.380560
C	–2.092639	–3.002124	–0.371036	H	–5.348743	3.932084	3.057448
C	1.054246	–3.819309	1.213798	H	–6.092188	3.506062	3.725596
C	6.902301	0.996218	–0.421608	H	–0.886944	1.896509	–2.276733
H	7.579127	0.360843	0.140139	H	–4.177470	5.910367	2.224187
H	1.717379	–6.587279	0.025618	H	–4.014153	6.984542	2.234524
H	5.039959	2.632578	–1.802109	H	3.646929	2.057743	1.514344
H	–3.764742	0.310906	–1.166159	H	3.978812	2.985197	1.964938
H	–4.223738	1.272885	–1.380563	H	–1.021923	0.714735	–3.088559
H	5.348744	–3.932083	–3.057452	C	–1.780449	0.662561	–3.861438
H	6.092189	–3.506061	–3.725599	C	0.819195	–0.259613	–1.763305
H	0.886943	–1.896511	2.276728	C	1.431800	–1.139711	–1.625461
H	4.177470	–5.910367	–2.224193	C	–6.010292	–3.216225	0.930944
H	4.014152	–6.984541	–2.234532	C	–5.126899	5.328062	3.060749
H	–3.646933	–2.057744	–1.514344	C	–5.709769	5.952463	3.731918
H	–3.978818	–2.985198	–1.964937	C	–6.944619	–2.349927	0.262692
H	1.021922	–0.714737	3.088555	H	–7.674804	–2.789363	–0.410893
H	1.780448	–0.662564	3.861434	C	–3.091902	–1.490168	3.512741
H	–0.819196	0.259612	1.763301	H	–2.340248	–1.037180	4.152723
C	–1.431800	1.139710	1.625457	C	10.022200	–0.126337	1.641082
C	6.010296	3.216224	–0.930939	H	11.026282	–0.519068	1.866742
C	5.126899	–5.328060	–3.060754	C	10.136510	0.761253	0.999041
C	5.709769	–5.952462	–3.731924	C	–0.195059	–0.325159	–2.794829
C	6.944621	2.349924	–0.262687	C	–0.277504	–1.255335	–3.348921
C	7.674806	2.789359	0.410899	H	7.324782	1.296293	3.717793
H	3.091905	1.490172	–3.512739	H	5.993050	1.780908	3.185975
C	2.340251	1.037184	–4.152722	H	6.160805	2.530473	2.405852

H	–10.022200	0.126340	–1.641071	O	5.391827	2.220183	3.991949
C	–11.026283	0.519072	–1.866728	C	–4.078165	–3.461138	2.458493
H	–10.136510	–0.761250	–0.999029	H	–0.580329	5.177402	–1.806584
C	0.195059	0.325158	2.794826	H	9.334153	0.267139	2.931322
C	0.277504	1.255333	3.348917	C	10.018109	0.883968	3.535973
H	–7.324789	–1.296293	–3.717788	H	9.083041	–0.636438	3.507387
H	–5.993055	–1.780908	–3.185973	H	–3.112664	–2.840642	3.327243
O	–6.160809	–2.530473	–2.405850	O	–2.383114	–3.473248	3.825965
C	–5.391835	–2.220184	–3.991948	C	9.759473	–1.470566	–0.295593
H	4.078169	3.461139	–2.458488	H	9.767961	–0.605552	–0.975205
H	0.580328	–5.177403	1.806577	H	10.780809	–1.871125	–0.216281
C	–9.334158	–0.267137	–2.931312	C	9.102645	–2.240173	–0.706615
H	–10.018116	–0.883965	–3.535962	H	7.170224	0.405943	4.345522
H	–9.083045	0.636439	–3.507379	H	7.775513	2.084030	4.341961
O	3.112668	2.840645	–3.327239	O	–0.387058	6.251946	–0.728528
C	2.383118	3.473252	–3.825960	C	–2.354526	7.175956	–0.702720
H	–9.759465	1.470570	0.295603	H	0.340233	5.895713	0.010706
H	–9.767953	0.605556	0.975215	H	–1.343932	5.501931	–2.521217
H	–10.780801	1.871130	0.216294	H	0.344870	4.995930	–2.362283
C	–9.102635	2.240176	0.706623	H	–1.533781	7.220516	0.851006
H	–7.170231	–0.405943	–4.345518	C	0.032219	7.152079	–1.191856
H	–7.775521	–2.084029	–4.341956	H	6.487410	–1.650428	–0.835790
O	0.387057	–6.251947	0.728521	C	3.182153	–1.222353	–3.546225
C	2.354524	–7.175957	0.702712	C	4.096137	4.846852	–2.222434
H	–0.340234	–5.895712	–0.010713	C	3.358913	5.478018	–2.711575
H	1.343930	–5.501933	2.521210	H	5.045133	5.410631	–1.366120
H	–0.344871	–4.995932	2.362277	C	5.043310	6.482918	–1.192911
C	1.533780	–7.220515	–0.851014	H	6.728606	5.055381	–0.064102
C	–0.032221	–7.152080	1.191848	H	5.994998	4.608358	–0.729979
C	5.311913	0.643214	2.636203	C	–3.182151	1.222356	3.546223
C	8.156039	0.993289	2.607981	C	–6.487409	1.650426	0.835789
N	–4.820936	1.596082	2.200274	C	–5.994994	–4.608360	0.729986
C	9.241223	–1.115994	0.980508	H	–6.728602	–5.055384	0.064110
C	–2.847904	3.094046	0.439441	C	–3.358908	–5.478016	2.711582
C	–2.756635	2.086994	0.248688	H	–4.096132	–4.846851	2.222440
C	2.759287	–0.292221	0.303252	H	–5.045128	–5.410632	1.366127
C	0.076209	3.106400	–0.592938	C	–5.043304	–6.482918	1.192920

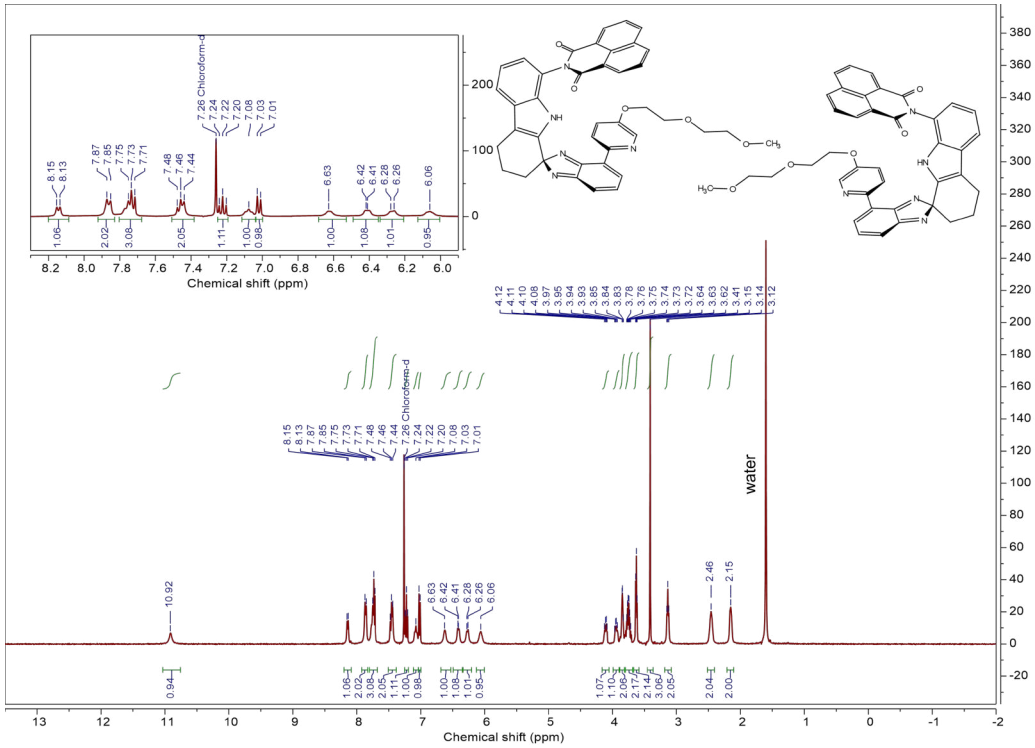

Fig. S23 ^{1}H NMR (400 MHz) spectrum of *rac*-**C*-NI** in $CDCl_3$ (T = 298 K).

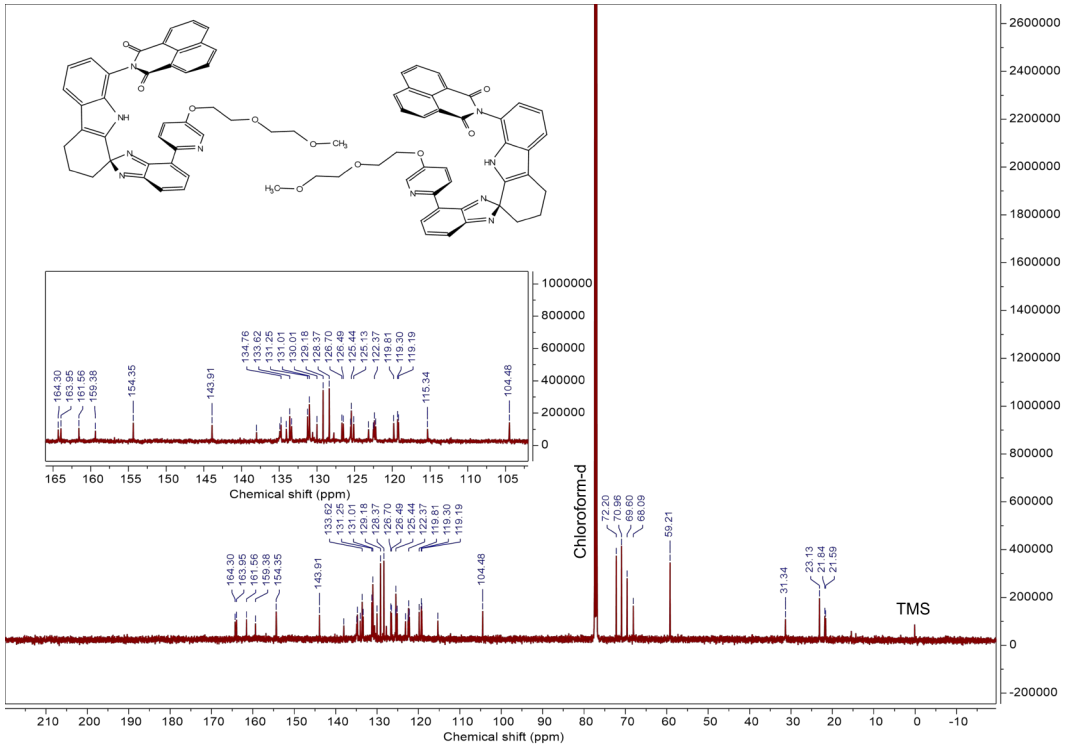

Fig. S24 ^{13}C NMR (125 MHz) spectrum of *rac*-**C*-NI** in $CDCl_3$ (T = 298 K).

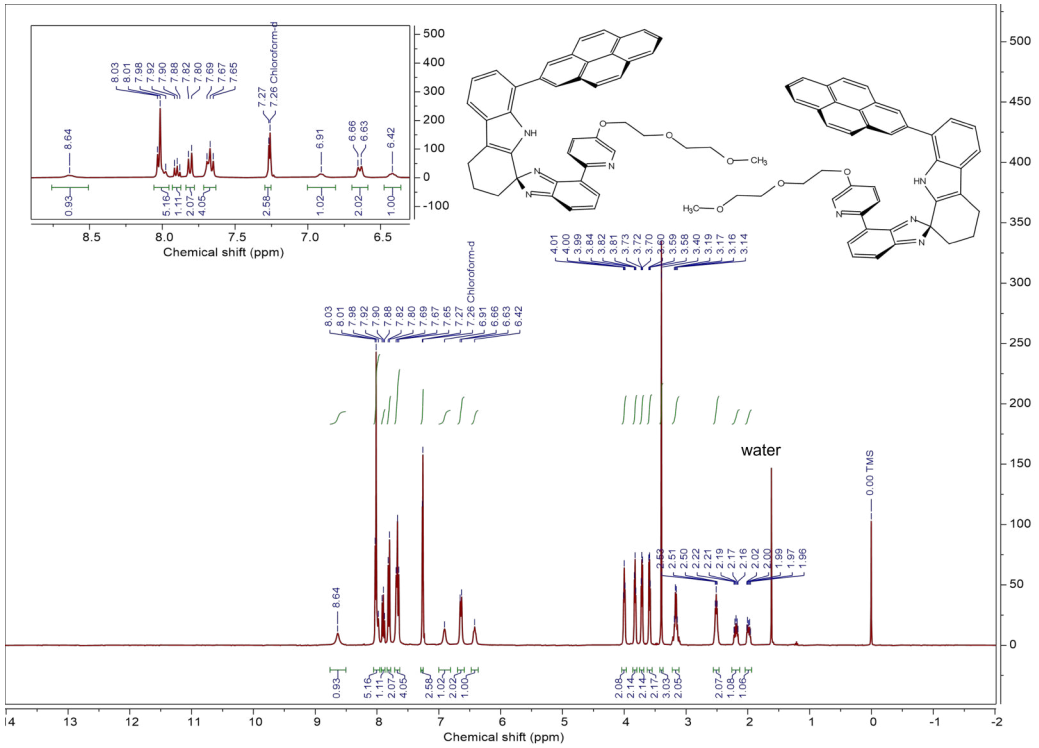

Fig. S25 ^{1}H NMR (500 MHz) spectrum of *rac*-**C*-P2** in $CDCl_3$ (T = 298 K).

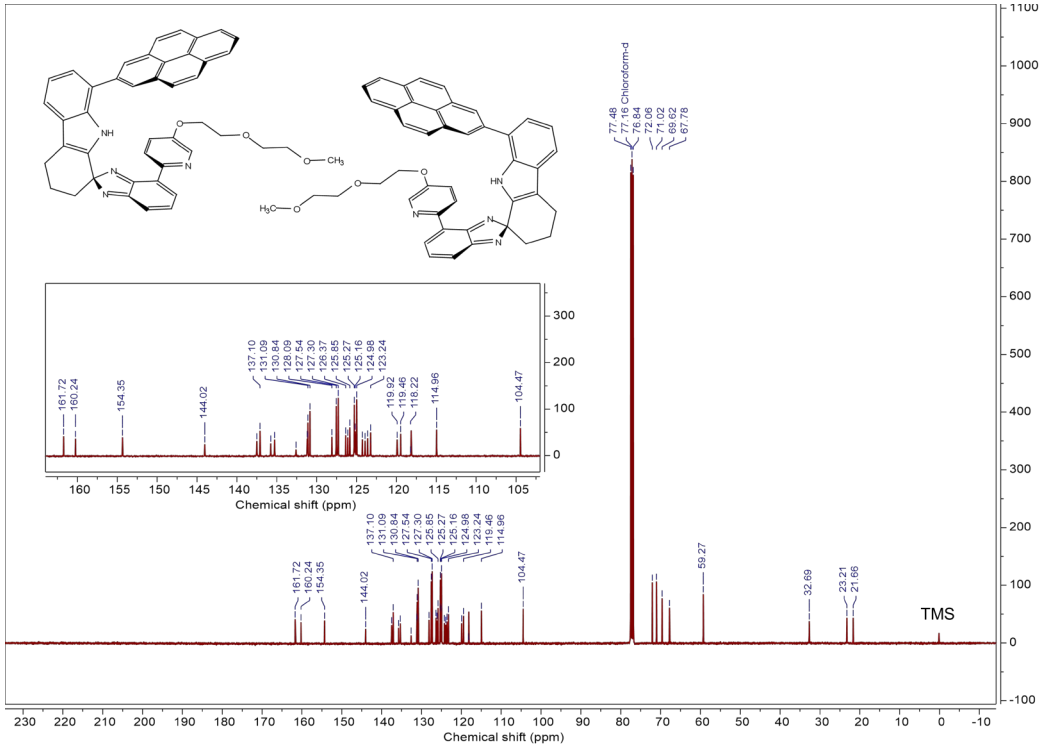

Fig. S26 ^{13}C NMR (100 MHz) spectrum of *rac*-**C*-P2** in $CDCl_3$ (T = 298 K).

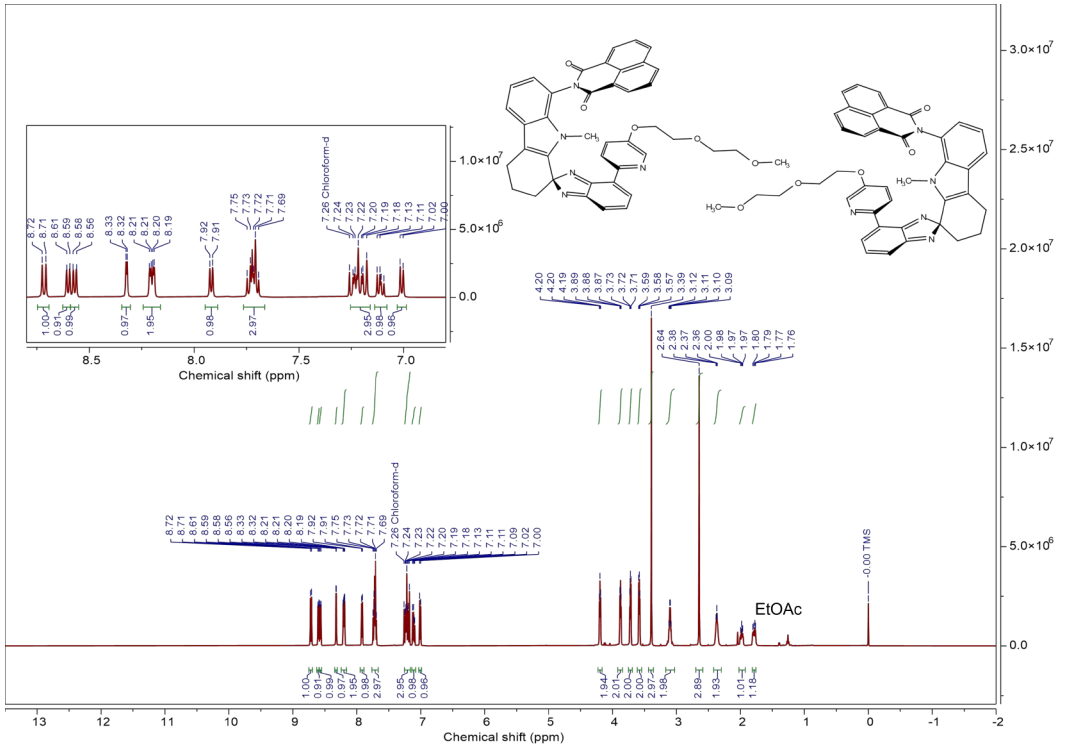

Fig. S27 ^{1}H NMR (500 MHz) spectrum of *rac*-**C*-NIMe** in $CDCl_3$ (T = 298 K).

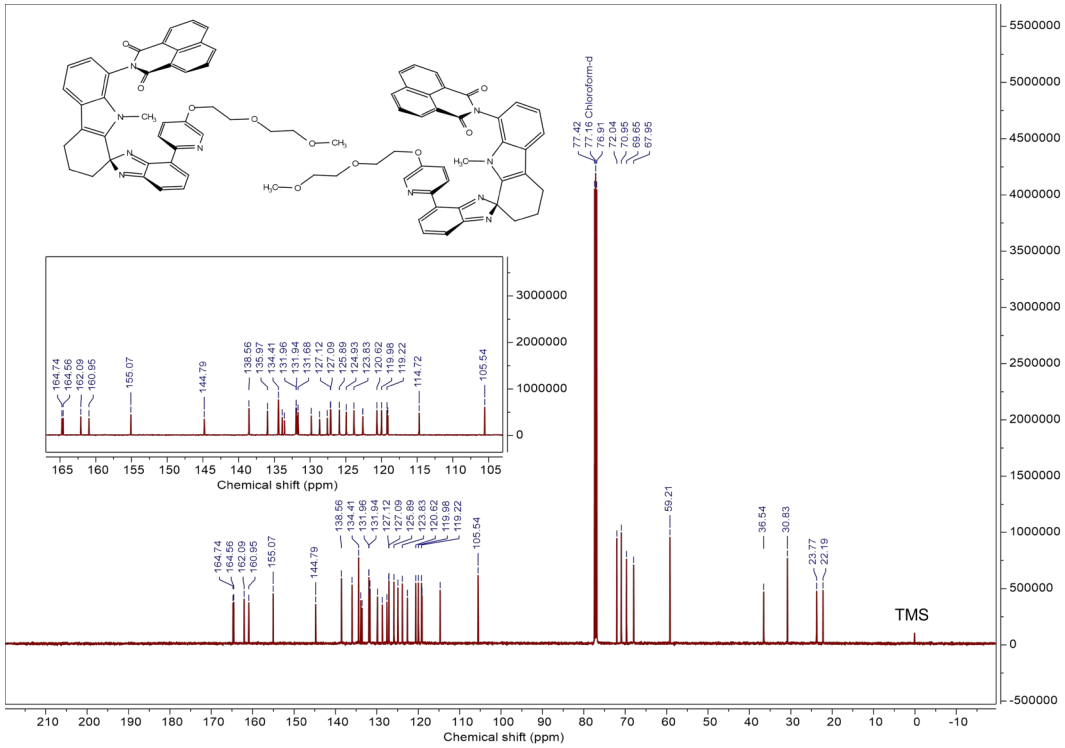

Fig. S28 ^{13}C NMR (125 MHz) spectrum of *rac*-**C*-NIMe** in $CDCl_3$ (T = 298 K).

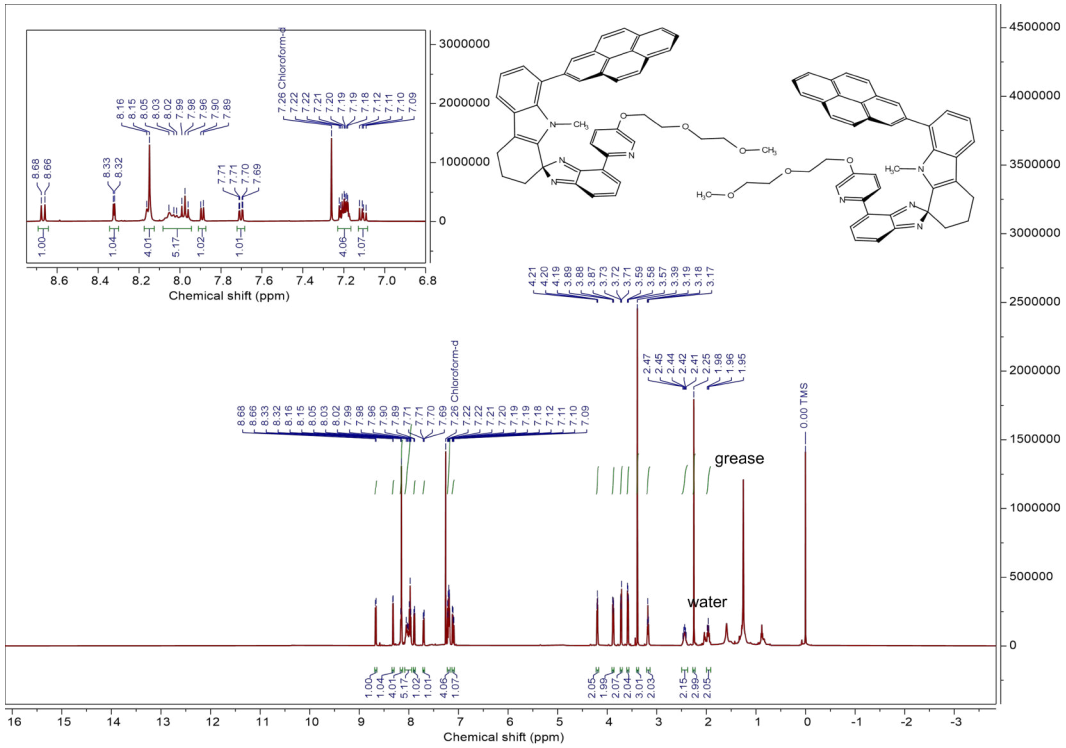

Fig. S29 ^{1}H NMR (500 MHz) spectrum of *rac*-**C*-P2Me** in $CDCl_3$ (T = 298 K).

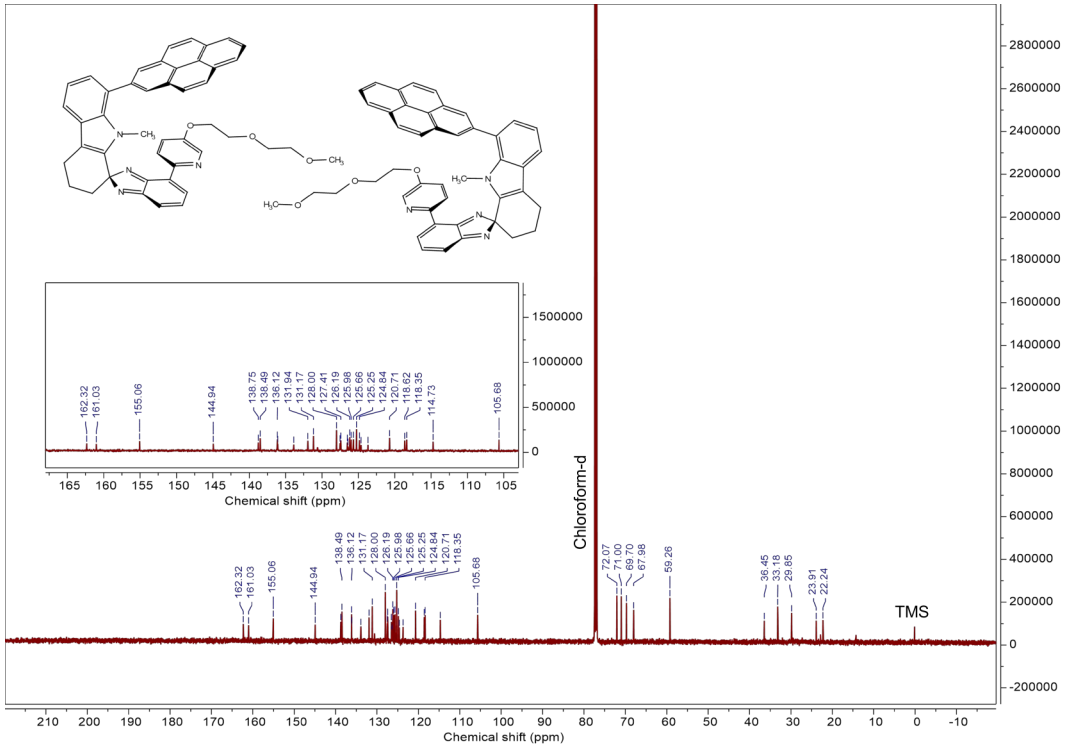

Fig. S30 ^{13}C NMR (125 MHz) spectrum of *rac*-**C*-P2Me** in $CDCl_3$ (T = 298 K).

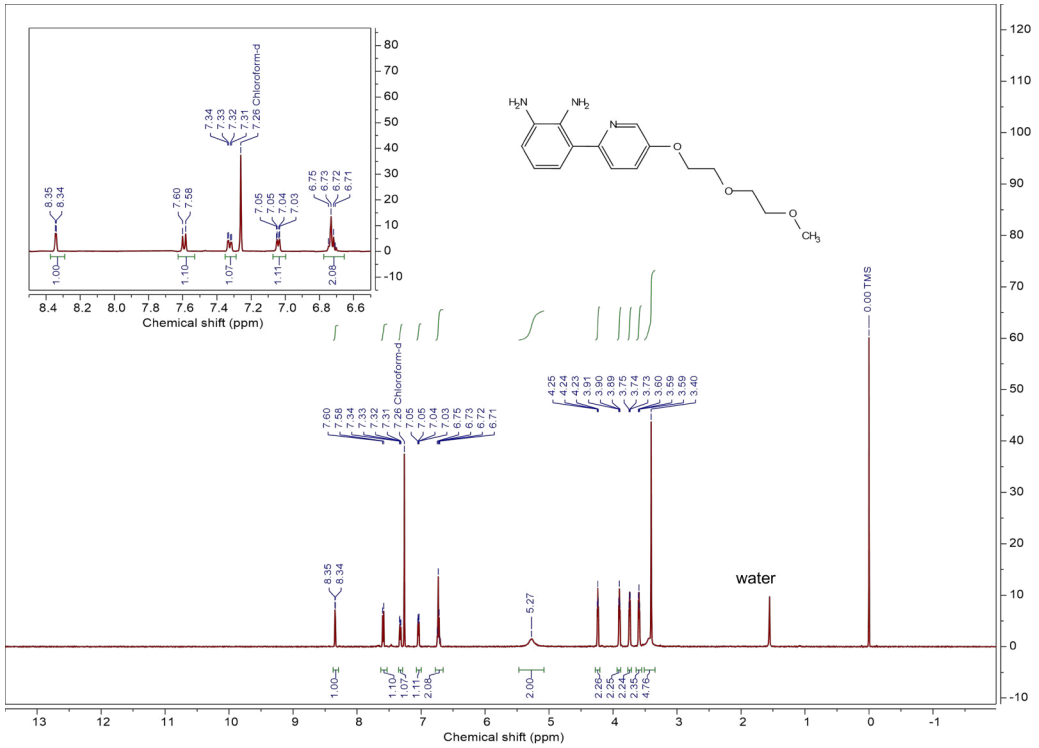

Fig. S31 ^{1}H NMR (500 MHz) spectrum of **3** in $CDCl_3$ (T = 298 K).

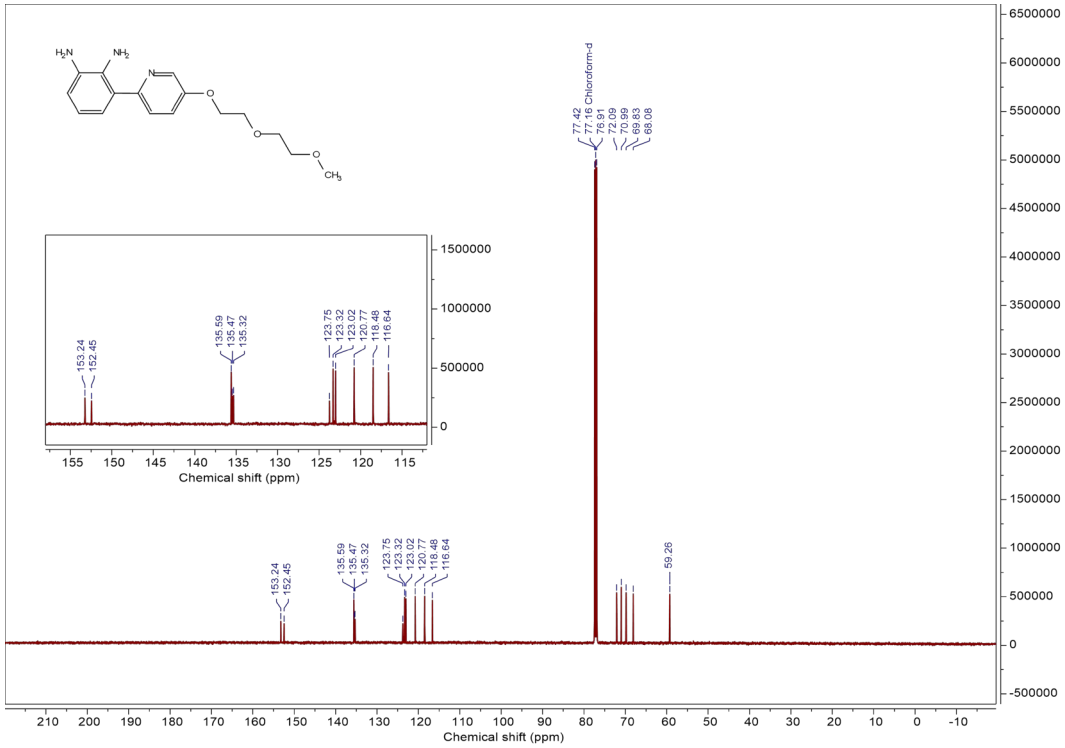

Fig. S32 ^{13}C NMR (125 MHz) spectrum of **3** in $CDCl_3$ (T = 298 K).

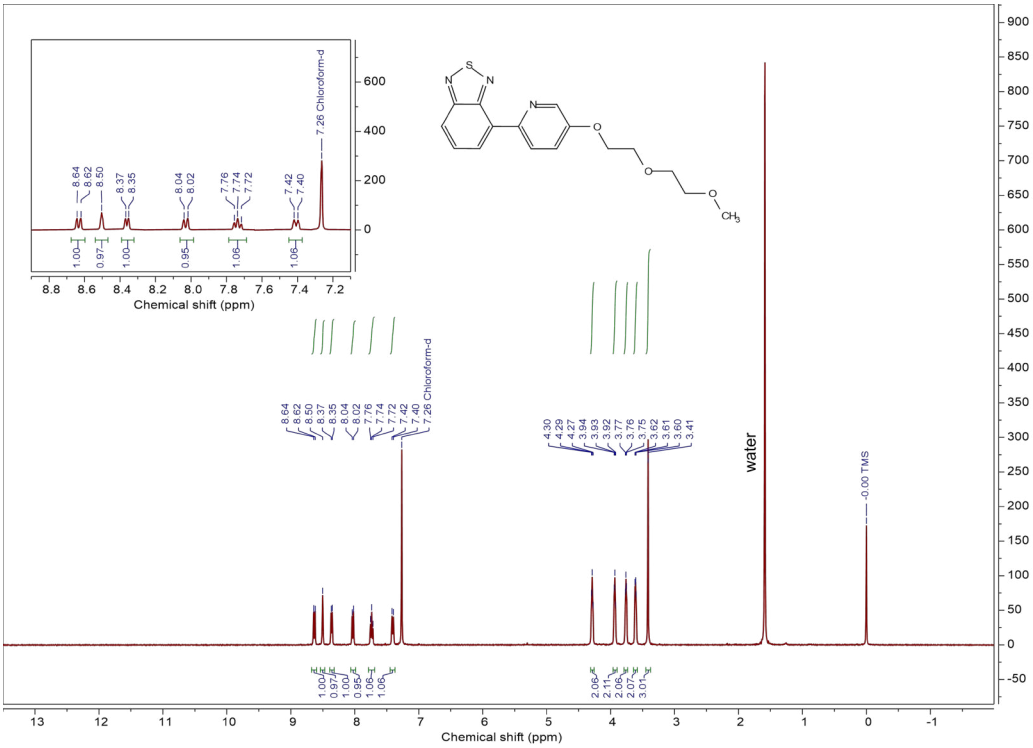

Fig. S33 ^{1}H NMR (400 MHz) spectrum of **7** in $CDCl_3$ (T = 298 K).

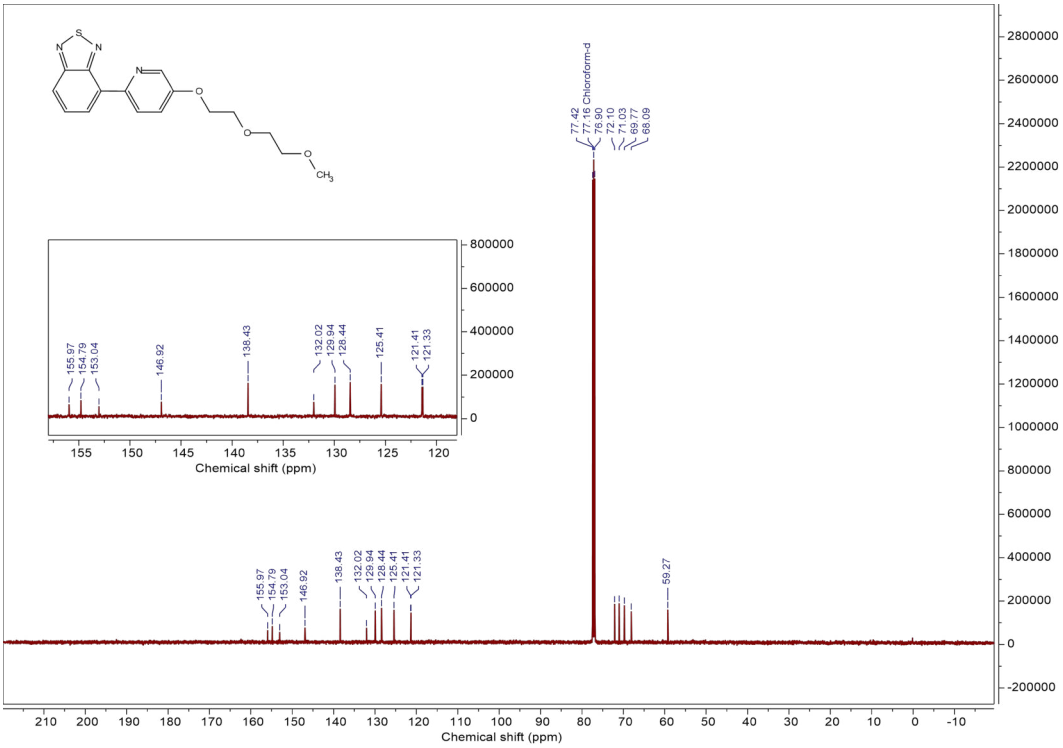

Fig. S34 ^{13}C NMR (125 MHz) spectrum of **7** in $CDCl_3$ (T = 298 K).

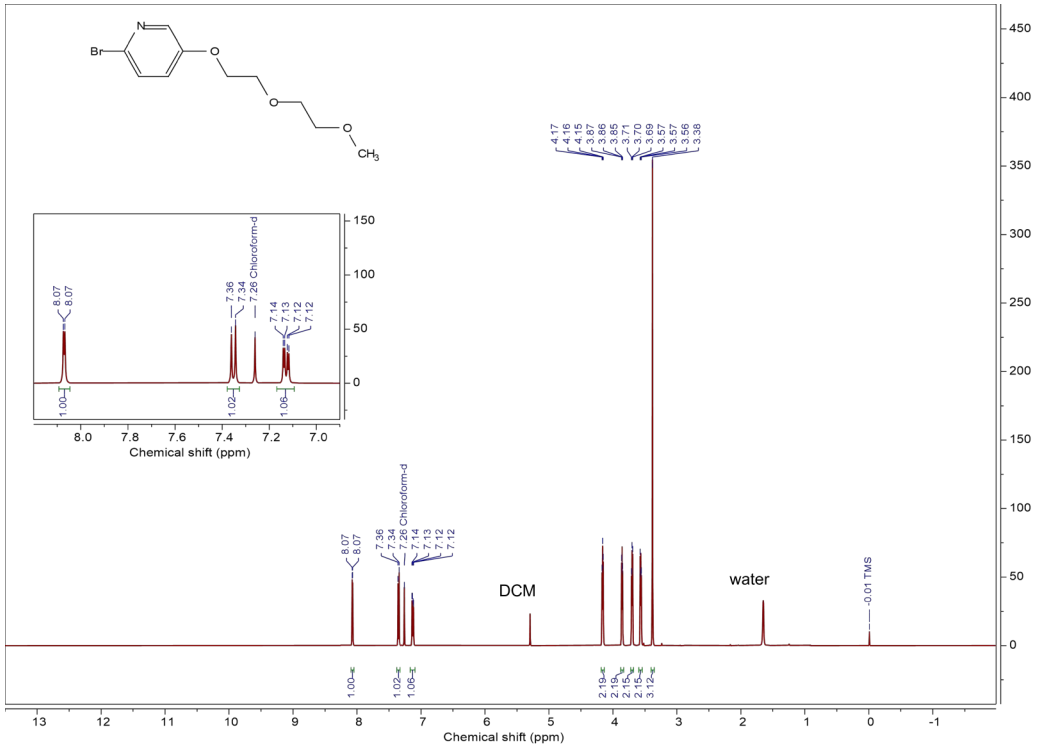

Fig. S35 ^{1}H NMR (500 MHz) spectrum of **6** in $CDCl_3$ (T = 298 K).

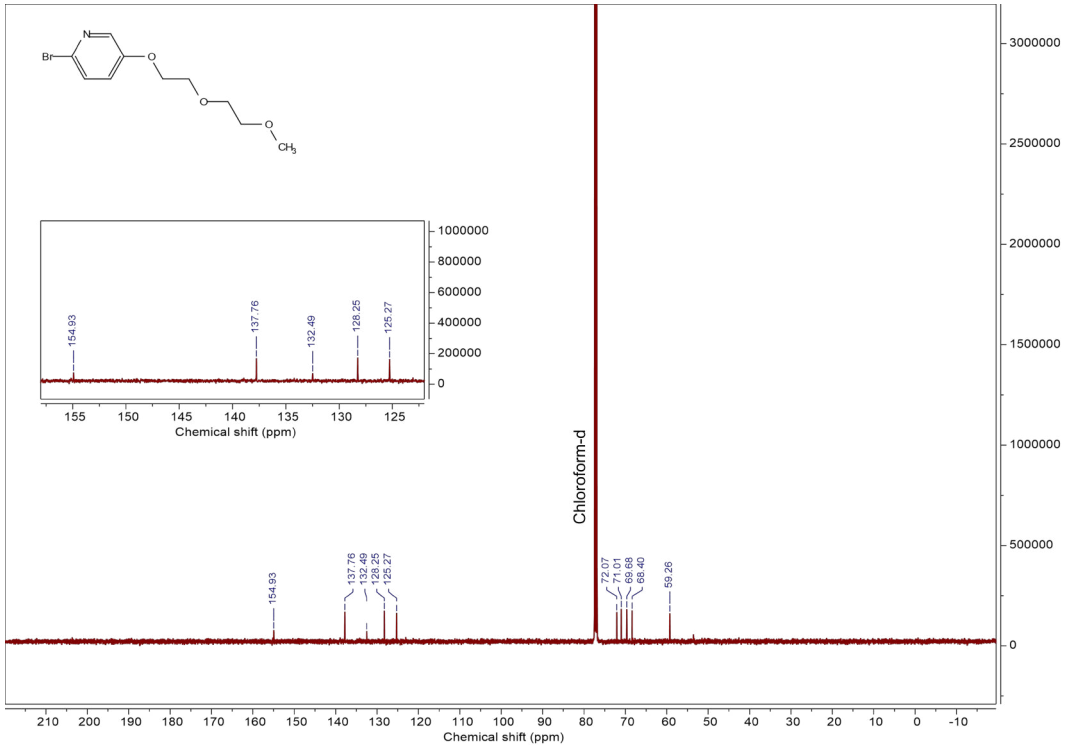

Fig. S36 ^{13}C NMR (125 MHz) spectrum of **6** in $CDCl_3$ (T = 298 K).

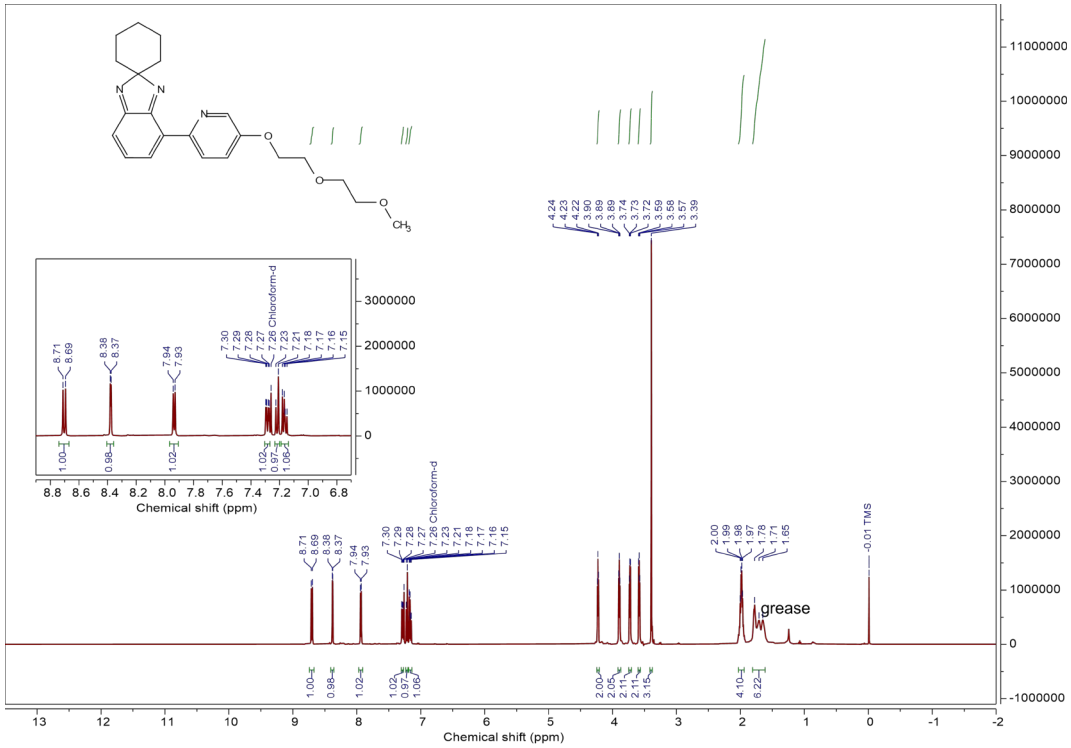

Fig. S37 ^{1}H NMR (400 MHz) spectrum of **5** in $CDCl_3$ (T = 298 K).

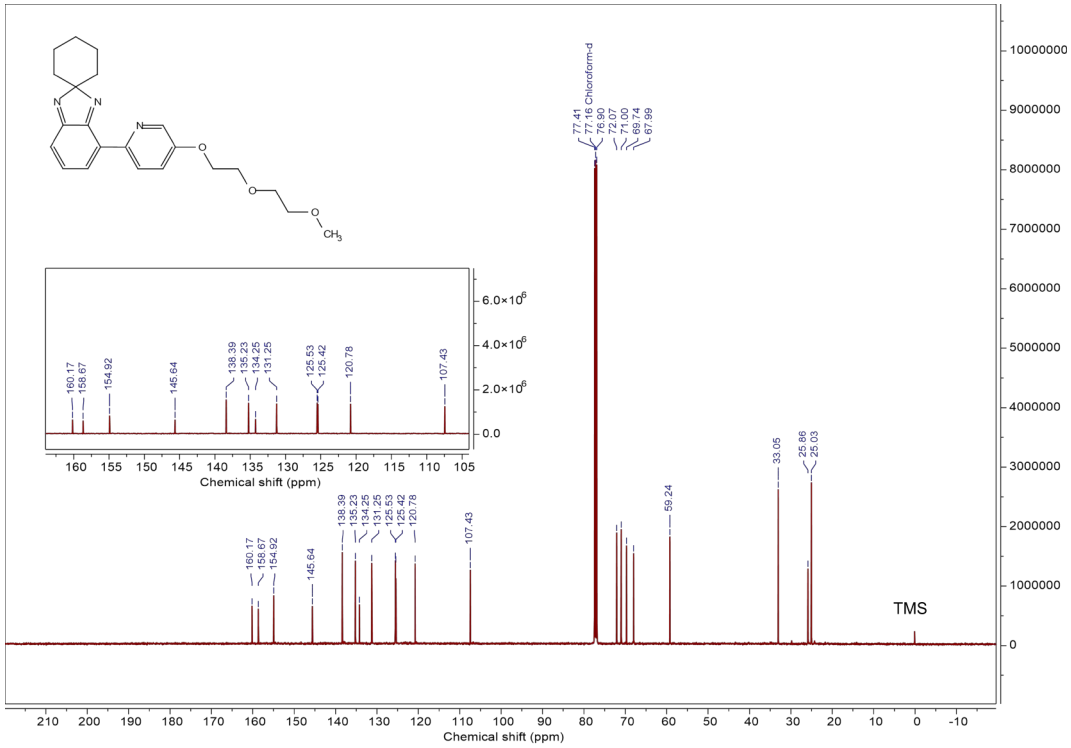

Fig. S38 ^{13}C NMR (125 MHz) spectrum of **5** in $CDCl_3$ (T = 298 K).