Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Planar Chiral Boron Difluoride Complexes showing Circularly Polarized Luminescence

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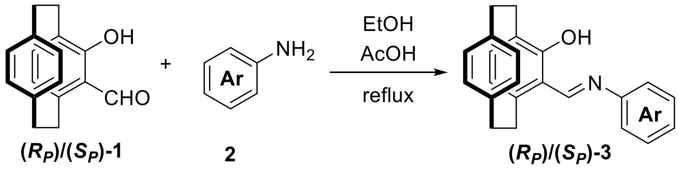
Contents

1. General Experimental Information

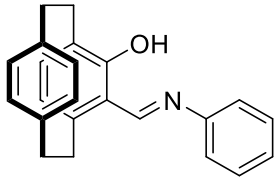
^{1}H NMR, ^{13}C NMR, ^{11}B NMR and ^{19}F NMR spectra were recorded at ambient temperature using Bruker ARX 400 MHz or 500 MHz spectrometer. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. High resolution mass spectra were acquired on an LTQ FT spectrometer, and were obtained by peak matching. Melting points were measured on a SGW X-4. Melting points are reported uncorrected. Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator. Chromatography was performed using with 300-400 mesh silica gel (SiO_2). Unless otherwise noted, all reagents and solvents were obtained from commercial sources and, where appropriate, purified prior to use. UV-*vis* absorption spectra were obtained by using a Hitashi U-3900 absorption spectrophotometer. Fluorescence spectra were measured by using a HORIBA Scientific Fluoromax-4 Spectrofluorometer. Circular dichroism (CD) spectra were obtained on a JASCO *J*-810 spectropolarimeter. Circularly polarized luminescence (CPL) spectra were recorded by a JASCO CPL-300 spectrofluoropolarimeter. Values of optical rotation were measured on Rudolph Automatic Polarimeter A21101 at the wavelength of the sodium D-line (589 nm). All measurements were performed at room temperature unless otherwise stated.

2. General Procedure for Preparation of (*R*$_P$)/(*S*$_P$)-3[1]:



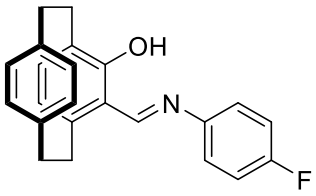
Optically pure 5-formyl-4-hydroxy[2.2]paracyclophane (***R*$_P$**)/(***S*$_P$**)-**1** (0.5 mmol) and aniline derivatives **2** (0.6 mmol) were added into 5 mL of EtOH, and then acetic acid (0.05 mmol) was added to the solution. The mixture was stirred for 8 h at 80 °C in an oil bath. After completion of the reaction, the reaction solvents were cooled to room

temperature. The solvent was removed under reduced pressure and the resulting residue was purified by columnar chromatography on silica gel (ethyl acetate/petroleum ether, 1/10) to deliver the reaction product (***R*****$_P$**)/(***S*****$_P$**)-**3**.



(*S*$_P$)-3a

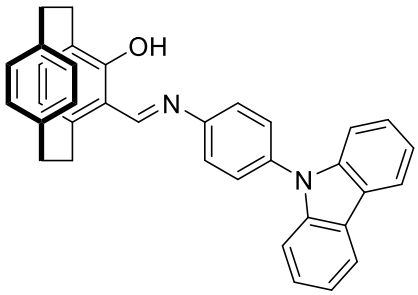
(*E*)-1^3-((phenylimino)methyl)-1,4(1,4)-dibenzenacyclohexaphan-1^2-ol ((*S*$_P$)-3a), yellow solid, 0.160 g, 98% yield. Mp: 112−113 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 14.06 (s, 1H), 8.54 (s, 1H), 7.49−7.45 (m, 2H), 7.33−7.30 (m, 3H), 6.96 (dd, *J* = 7.6 Hz, 2.0 Hz, 1H), 6.63−6.61 (m, 1H), 6.58 (d, *J* = 7.6 Hz, 1H), 6.47 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 6.30−6.27 (m, 2H), 3.58−3.53 (m, 2H), 3.29−3.15 (m, 2H), 3.09−3.02 (m, 1H), 2.97−2.92 (m, 1H), 2.82−2.75 (m, 1H), 2.66−2.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.6, 159.8, 148.7, 143.1, 140.1, 138.3, 137.4, 133.4, 132.1, 130.8, 129.5, 128.1, 126.9, 126.6, 124.7, 121.1, 119.8, 35.4, 33.8, 32.6, 29.9; HRMS (ESI) *m/z* calcd for $C_{23}H_{22}NO$ $(M+H)^+$ 328.1696, found 328.1700. $[\alpha]_D^{20}$ = *R*/*S* +673/-671 (c 0.5, $CHCl_3$).



(*S*$_P$)-3b

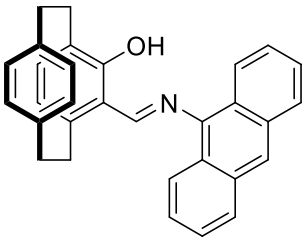
(*E*)-1^3-(((4-fluorophenyl)imino)methyl)-1,4(1,4)-dibenzenacyclohexaphan-1^2-ol ((*S*$_P$)-3b), yellow solid, 0.164 g, 95% yield. Mp: 103−104 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.87 (s, 1H), 8.49 (s, 1H), 7.29−7.25 (m, 2H), 7.17−7.12 (m, 2H), 6.94−6.92 (m, 1H), 6.62 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 6.57 (d, *J* = 7.6 Hz, 1H), 6.45−6.43 (m, 1H), 6.29 (d, *J* = 7.6 Hz, 1H), 6.26 (dd, *J* = 8.0 Hz, 2.4 Hz, 1H), 3.57−3.46 (m, 2H), 3.29−3.13 (m, 2H), 3.08−3.02 (m, 1H), 2.96−2.88 (m, 1H), 2.80−2.72 (m, 1H), 2.65−2.58 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7 (d, *J* = 244.6 Hz), 161.2, 159.7, 145.0, 143.1, 140.1, 138.3, 137.4, 133.5, 132.1, 130.8, 128.0,

126.8, 124.8, 122.5 (d, J = 9.0 Hz), 119.8, 116.4 (d, J = 22.6 Hz), 35.5, 33.9, 32.6, 29.9; HRMS (ESI) *m/z* calcd for $C_{23}H_{21}FNO$ $(M+H)^+$ 346.1602, found 346.1605. $[\alpha]_D^{20}$ = *R*/*S* +512/-514 (c 0.5, $CHCl_3$).



(S_P)-3c

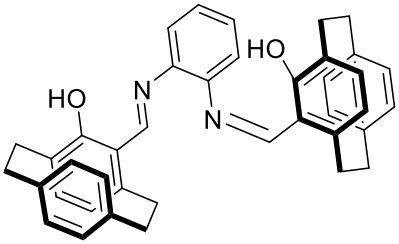
(*E*)-1^3-(((4-(9H-carbazol-9-yl)phenyl)imino)methyl)-1,4(1,4)-dibenzenacyclohexaphan-1^2-ol ((S_P)-3c), yellow solid, 0.239 g, 97% yield. Mp: 118−119 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.97 (s, 1H), 8.66 (s, 1H), 8.20−8.18 (m, 2H), 7.69−7.67 (m, 2H), 7.56−7.44 (m, 6H), 7.36−7.32 (m, 2H), 7.03−7.00 (m, 1H), 6.67−6.65 (m, 1H), 6.63 (d, J = 7.6 Hz, 1H), 6.50−6.48 (m, 1H), 6.38−6.35 (m, 1H), 6.34 (d, J = 7.6 Hz, 1H), 3.65−3.52 (m, 2H), 3.35−3.19 (m, 2H), 3.13−3.07 (m, 1H), 3.02−2.94 (m, 1H), 2.89−2.82 (m, 1H), 2.70−2.63 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5, 160.2, 147.7, 143.3, 140.8, 140.2, 138.6, 137.4, 136.1, 133.5, 132.1, 130.9, 128.2, 128.1, 126.9, 126.0, 124.9, 123.4, 122.5, 120.4, 120.1, 119.9, 109.7, 35.5, 33.9, 32.6, 29.9; HRMS (ESI) *m/z* calcd for $C_{35}H_{29}N_2O$ $(M+H)^+$ 493.2275, found 493.2276. $[\alpha]_D^{20}$ = *R*/*S* +621/-620 (c 0.5, $CHCl_3$).



(S_P)-3d

(*E*)-1^3-((anthracen-9-ylimino)methyl)-1,4(1,4)-dibenzenacyclohexaphan-1^2-ol ((S_P)-3d), yellow solid, 0.169 g, 79% yield. Mp: 125−126 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.96 (s, 1H), 8.58 (s, 1H), 8.34 (s, 1H), 8.20−8.18 (m, 2H), 8.07−8.04 (m, 2H), 7.54−7.48 (m, 4H), 7.27 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 6.68−6.65 (m, 2H), 6.57−6.53 (m, 2H), 6.35 (d, J = 7.6 Hz, 1H), 3.66−3.59 (m, 1H), 3.40−3.29 (m, 2H),

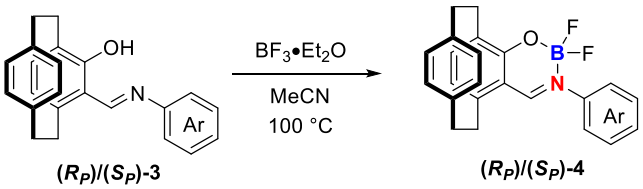
3.18−3.12 (m, 2H), 2.93−2.86 (m, 1H), 2.75−2.62 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 161.4, 143.7, 142.9, 140.4, 138.9, 137.7, 133.6, 132.4, 131.9, 131.2, 128.4, 128.3, 126.9, 125.7, 125.6, 125.0, 123.6, 123.4, 123.1, 119.8, 35.3, 34.0, 32.3, 29.9; HRMS (ESI) *m/z* calcd for $C_{31}H_{26}NO$ $(M+H)^+$ 428.2009, found 428.2003. $[\alpha]_D^{20}$ = *R*/*S* +476/-479 (c 0.5, $CHCl_3$).



(*S*$_P$)-3e

(*E*,*E*)-1,2-bis(13-((phenylimino)methyl)-1,4(1,4)-dibenzenacyclohexaphan-12-ol)benzene ((*S*$_P$)-3e), yellow solid, 0.254 g, 88% yield. Mp: 161−162 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 14.10 (s, 2H), 8.59 (s, 2H), 7.46−7.44 (m, 2H), 7.40−7.38 (m, 2H), 7.22−7.20 (m, 2H), 6.67−6.64 (m, 2H), 6.60 (d, *J* = 7.6 Hz, 2H), 6.52−6.49 (m, 2H), 6.42−6.40 (m, 2H), 6.29 (d, *J* = 7.6 Hz, 2H), 3.66−3.55 (m, 4H), 3.43−3.36 (m, 2H), 3.28−3.22 (m, 2H), 3.15−3.08 (m, 2H), 2.99−2.92 (m, 2H), 2.84−2.77 (m, 2H), 2.69−2.62 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.9, 160.4, 143.4, 143.4, 140.3, 138.7, 137.5, 133.2, 131.9, 131.3, 128.2, 127.8, 127.5, 124.7, 120.2, 119.6, 35.4, 34.2, 32.7, 29.7; HRMS (ESI) *m/z* calcd for $C_{40}H_{37}N_2O_2$ $(M+H)^+$ 577.2850, found 577.2855. $[\alpha]_D^{20}$ = *R*/*S* -1142/+1140 (c 0.5, $CHCl_3$).

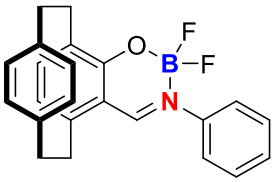
3. General Procedure for Preparation of (*R*$_P$)/(*S*$_P$)-4[2]:



(*R*$_P$)/(*S*$_P$)-3 (*R*$_P$)/(*S*$_P$)-4

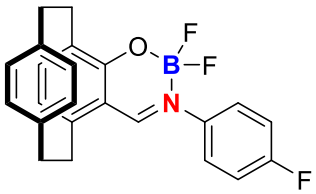
In a 10 mL Schlenk tube was charged with (***R*$_P$**)/(***S*$_P$**)-**3** (0.2 mmol, 1.0 equiv). The tube was evacuated and filled with nitrogen for three cycles. Then, dry acetonitrile and boron trifluoride diethyl ether (1.0 mmol, 5.0 equiv) were slowly added to the mixture via syringe at room temperature. The reaction was allowed to stir at

corresponding temperature in an oil bath for 8 hours. Upon completion, the reaction was cooled to room temperature, the mixture was extracted with dichloromethane, and the collected dichloromethane layer was washed with water and brine. The separated organic layer was dried over anhydrous Mg_2SO_4. After removal of the solvent, the crude reaction mixture was purified by columnar chromatography on silica gel (ethyl acetate/petroleum ether, 1/5) to afford the desired product (***R*****$_p$**)/(***S*****$_p$**)-**4**.



(*S*$_P$)-4a

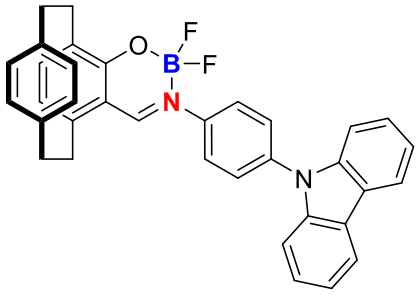
1^2,1^2-difluoro-1^3-phenyl-1^{2}H-1$^2\lambda^4$,1$^3\lambda^4$-1(5,8)-benzo[e][1,3,2]oxazaborinina-4(1,4)-benzenacyclohexaphane ((*S*$_P$)-4a), light yellow solid, 0.071 g, 94% yield. Mp: 135−137 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.59−7.46 (m, 5H), 7.04 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 6.67 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 6.51 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 6.37 (d, *J* = 7.6 Hz, 1H), 6.25−6.22 (m, 1H), 3.65−3.58 (m, 1H), 3.45−3.39 (m, 1H), 3.32−3.22 (m, 2H), 3.08−2.99 (m, 2H), 2.91−2.83 (m, 1H), 2.69−2.61 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 159.4, 144.2, 143.8, 142.9, 140.7, 137.0, 133.4, 132.4, 132.3, 130.2, 129.7, 129.0, 127.9, 126.0, 123.7, 35.5, 33.9, 32.0, 29.4; ^{19}F NMR (376 MHz, $CDCl_3$): -130.3, -130.4, -130.4, -130.5; ^{11}B NMR (160 MHz, $CDCl_3$): 0.79, 0.70, 0.62; HRMS (ESI) *m/z* calcd for $C_{23}H_{21}BF_2NO$ $(M+H)^+$ 376.1679, found 376.1688. $[\alpha]_D^{20}$ = *R*/*S* +830/-828 (c 0.5, $CHCl_3$).



(*S*$_P$)-4b

1^2,1^2-difluoro-1^3-(4-fluorophenyl)-1^{2}H-1$^2\lambda^4$,1$^3\lambda^4$-1(5,8)-benzo[e][1,3,2]oxazaborinina-4(1,4)-benzenacyclohexaphane ((*S*$_P$)-4b), light yellow solid, 0.076 g, 92% yield. Mp: 143−145 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (s, 1H), 7.59−7.56 (m, 2H),

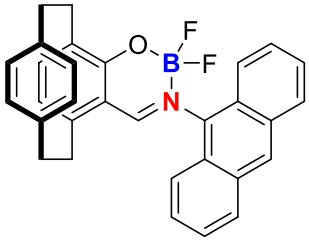
7.24−7.20 (m, 2H), 7.03−7.01 (m, 1H), 6.81 (d, *J* = 3.2 Hz, 1H), 6.68 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 6.52 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 6.38 (d, *J* = 7.6 Hz, 1H), 6.23 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 3.65−3.58 (m, 1H), 3.45−3.39 (m, 1H), 3.33−3.23 (m, 2H), 3.09−3.02 (m, 2H), 2.91−2.85 (m, 1H), 2.68−2.62 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.9 (d, *J* = 247.9 Hz), 159.9 (d, *J* = 2.9 Hz), 159.9, 159.3, 144.3, 144.0, 140.8, 139.0, 136.9, 133.4, 132.5, 132.4, 130.8, 130.3, 127.9 (d, *J* = 1.5 Hz), 126.1, 125.6 (d, *J* = 8.7 Hz), 125.5, 117.2, 116.8, 116.6, 35.6, 33.9, 32.0, 29.4; ^{19}F NMR (376 MHz, $CDCl_3$): -111.8, -129.8, -129.8, -129.8, -129.9, -130.0, -130.0, -130.0, -130.0, -130.6, -130.6, -130.7, -130.7, -130.8, -130.9, -130.9, -130.9; ^{11}B NMR (160 MHz, $CDCl_3$): 0.73, 0.65, 0.57; HRMS (ESI) *m/z* calcd for $C_{23}H_{19}BF_3NNaO$ $(M+Na)^+$ 416.1404, found 416.1389. $[\alpha]_D^{20}$ = *R*/*S* +673/-676 (c 0.5, $CHCl_3$).



(*S*$_P$)-4c

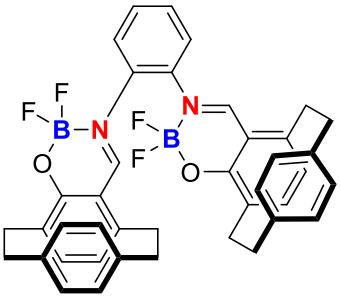
1^3-(4-(9H-carbazol-9-yl)phenyl)-1^2,1^2-difluoro-1^{2}H-1$^2\lambda^4$,1$^3\lambda^4$-1(5,8)-benzo[e][1,3,2]oxazaborinina-4(1,4)-benzenacyclohexaphane ((*S*$_P$)-4c), light yellow solid, 0.098 g, 87% yield. Mp: 156−157 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.22 (s, 1H), 8.09 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.43−7.36 (m, 4H), 7.28−7.24 (m, 2H), 7.00−6.99 (m, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.62−6.60 (m, 1H), 6.46−6.44 (m, 1H), 6.32 (d, *J* = 7.5 Hz, 1H), 6.31−6.20 (m, 1H), 3.59−3.55 (m, 1H), 3.44−3.39 (m, 1H), 3.28−3.22 (m, 2H), 3.03−3.00 (m, 2H), 2.87−2.85 (m, 1H), 2.62−2.60 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.1, 159.2, 144.4, 144.2, 141.4, 140.8, 140.4, 138.5, 136.9, 133.5, 132.5, 132.5, 130.3, 128.0, 127.9, 127.9, 126.2, 126.2, 125.2, 123.7, 120.5, 120.4, 120.4, 117.4, 109.6, 35.6, 33.9, 32.0, 29.4; ^{19}F NMR (471 MHz, $CDCl_3$): -133.8, -133.8, -133.9, -140.0, -134.7, -134.7, -134.7, -134.8, -134.9, -134.9, -134.9; ^{11}B NMR (160 MHz, $CDCl_3$): 0.81, 0.73; HRMS (ESI)

m/z calcd for $C_{35}H_{27}BF_2N_2NaO$ $(M+Na)^+$ 563.2077, found 563.2075. $[\alpha]_D^{20}$ = *R*/*S* +1771/-1772 (c 0.5, $CHCl_3$).



(S_P)-4d

1^3-(anthracen-9-yl)-1^2,1^2-difluoro-1^2H-$1^2\lambda^4$,$1^3\lambda^4$-1(5,8)-benzo[e][1,3,2]oxazaborinina-4(1,4)-benzenacyclohexaphane ((S_P)-4d), light yellow solid, 0.087 g, 92% yield. Mp: 162−164 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (s, 1H), 8.42 (d, *J* = 8.4 Hz, 1H), 8.14 (s, 1H), 8.42 (d, *J* = 8.8 Hz, 1H), 8.06−8.04 (m, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.72−7.69 (m, 1H), 7.60−7.56 (m, 1H), 7.51−7.45 (m, 2H), 7.32−7.30 (m, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.72−6.70 (m, 1H), 6.61−6.59 (m, 1H), 6.49−6.47 (m, 1H), 6.38 (d, *J* = 7.6 Hz, 1H), 3.78−3.72 (m, 1H), 3.43−3.36 (m, 1H), 3.15−3.10 (m, 3H), 3.02−2.94 (m, 1H), 2.78−2.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 160.7, 144.7, 144.5, 141.0, 137.3, 133.1, 132.8, 131.6, 131.4, 128.5, 128.3, 128.2, 127.8, 127.6, 127.5, 127.3, 126.8, 126.2, 125.9, 125.8, 123.2, 123.2, 123.0, 122.9, 35.4, 34.1, 31.6, 29.5; ^{19}F NMR (376 MHz, $CDCl_3$): -251.6, -251.6, -251.7, -251.7, -251.8, -251.9, -251.9, -252.0, -255.0, -255.1, -255.1, -255.3, -255.3, -255.4; ^{11}B NMR (160 MHz, $CDCl_3$): 0.98, 0.87; HRMS (ESI) *m/z* calcd for $C_{31}H_{25}BF_2NO$ $(M+H)^+$ 476.1992, found 476.1991. $[\alpha]_D^{20}$ = *R*/*S* -621/+618 (c 0.5, $CHCl_3$).



(S_P)-4e

1,2-bis(1^2,1^2-difluoro-1^2H-$1^2\lambda^4$,$1^3\lambda^4$-1(5,8)-benzo[e][1,3,2]oxazaborinina-4(1,4)-benzenacyclohexaphane-13-yl)benzene ((S_P)-4e), light yellow solid, 0.114 g, 85%

yield. Mp: 171−173 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (s, 2H), 7.88−7.86 (m, 2H), 7.68−7.66 (m, 2H), 7.02 (dd, *J* = 8.0 Hz, 1.6 Hz, 2H), 6.68 (d, *J* = 7.6 Hz, 2H), 6.58−6.56 (m, 2H), 6.41−6.39 (m, 2H), 6.21 (d, *J* = 7.2 Hz, 2H), 6.09 (dd, *J* = 7.6 Hz, 2.0 Hz, 2H), 3.55−3.48 (m, 2H), 3.38−3.32 (m, 2H), 3.25−3.11 (m, 4H), 3.06−2.99 (m, 2H), 2.86−2.29 (m, 2H), 2.72−2.64 (m, 2H), 2.60−2.53 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 165.1, 165.1, 159.6, 145.9, 144.6, 140.4, 137.6, 137.6, 133.6, 132.5, 132.1, 129.8, 129.7, 128.2, 127.3, 126.1, 116.6, 35.3, 33.7, 31.5, 29.5; ^{19}F NMR (376 MHz, $CDCl_3$): -247.8, -247.9, -248.0; ^{11}B NMR (160 MHz, $CDCl_3$): 0.27; HRMS (ESI) *m/z* calcd for $C_{40}H_{35}B_2F_4N_2O_2$ $(M+H)^+$ 673.2815, found 673.2821. $[\alpha]_D^{20}$ = *R*/*S* +1242/-1244 (c 0.5, $CHCl_3$).

4. References

[1] S. Ay, M. Nieger and S. Bräse, *Chem. -Eur. J*. 2008, **14**, 11539-11556.

[2] K. Li, X. Duan, Z. Jiang, D. Ding, Y. Chen, G.-Q. Zhang, Z. Liu, *Nat. Commun*., 2021, **12**, 2376.

5. Single-Crystal X-ray Analysis

Colourless crystals were grown by slow evaporation at room temperature from a solution in a mixture of hexane and dichloromethane. The crystals were removed from the vial and covered with a layer of a viscous perfluoropolyether (FomblinY). Suitable crystals, selected with the aid of a microscope, were mounted on a cryoloop and placed in the low temperature nitrogen stream of the diffractometer. The intensity data sets were collected at 200 K on a Bruker-Nonius KappaCCD diffractometer equipped with an Oxford Cryostream 700 unit. Crystallographic data for compounds **(*S*$_P$)-4a** are presented in **Table S1**.

Table S1. Crystal data and structure refinement for **(*S*$_P$)-4a**

Identification code	**(*S*$_P$)-4a**
Empirical formula	$C_{23}H_{20}BF_2NO$
Formula weight	375.21
Temperature/K	213.15
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	11.493(4)
b/Å	17.513(6)
c/Å	18.089(6)
α/°	90

β/°	90
γ/°	90
Volume/Å^3	3641(2)
Z	8
ρ_{calc}g/cm^3	1.369
μ/mm^{-1}	0.503
F(000)	1568.0
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	6.112 to 107.748
Index ranges	-13 ≤ h ≤ 13, -21 ≤ k ≤ 21, -21 ≤ l ≤ 21
Reflections collected	53808
Independent reflections	6626 [R_{int} = 0.0625, R_{sigma} = 0.0329]
Data/restraints/parameters	6626/0/506
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0330, wR_2 = 0.0798
Final R indexes [all data]	R_1 = 0.0354, wR_2 = 0.0822
Largest diff. peak/hole / e Å^{-3}	0.17/-0.15
Flack parameter	0.08(18)
CCDC	2077719

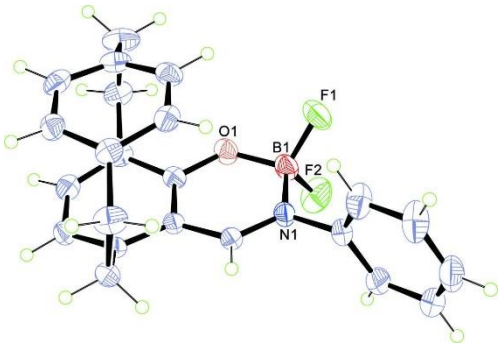
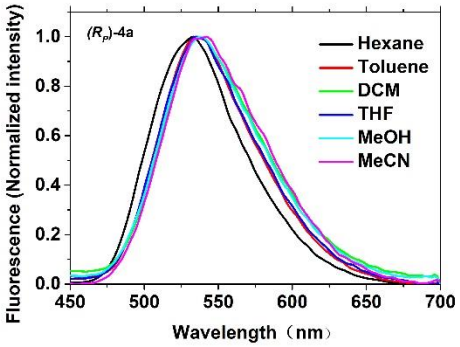
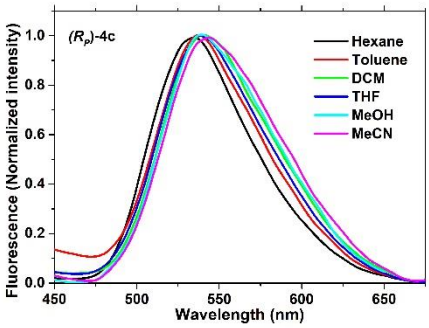


Fig. S1 X-ray structure and numbering scheme for (***S$_P$)*-4a**. Thermal ellipsoids are drawn at the 50% probability level.

6. Photophysical Properties





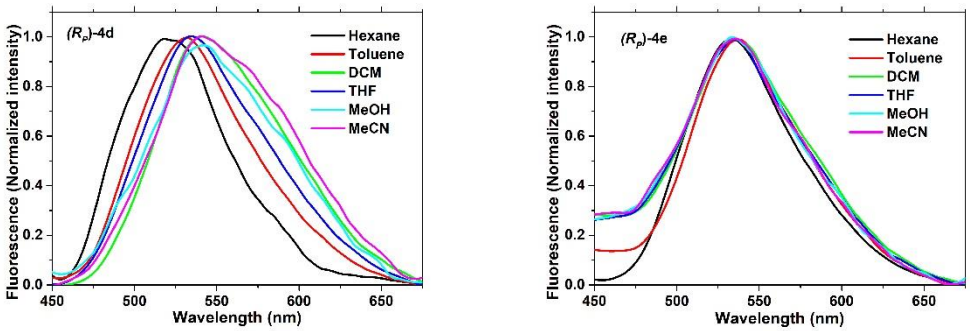


Fig. S2 Normalized fluorescence spectra of (***R*P**)-**4a,** (***R*P**)-**4c,** (***R*P**)-**4d** and (***R*P**)-**4e** (In 1x10^{-5} mol/L different solvents) with photophysical date.

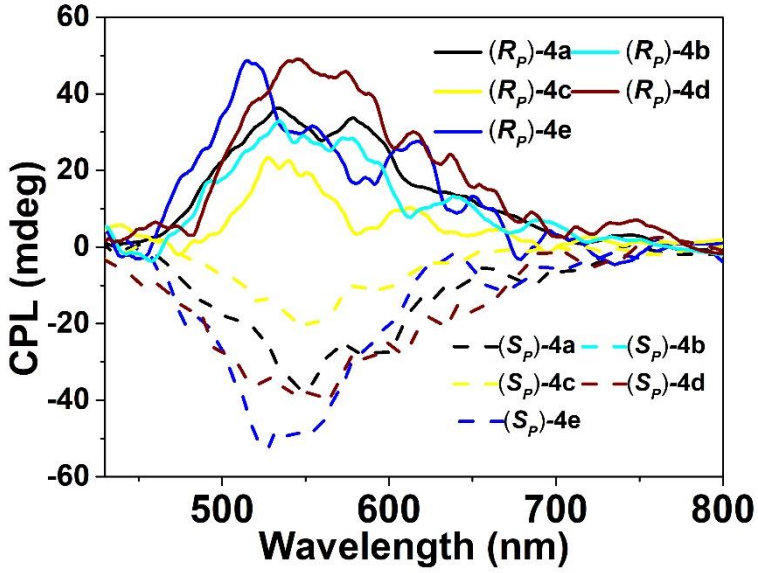


Figure S3. CPL spectra of (***R*P**/***S*P**)-**4a**-**4e** (10% PMMA film) with photophysical date.

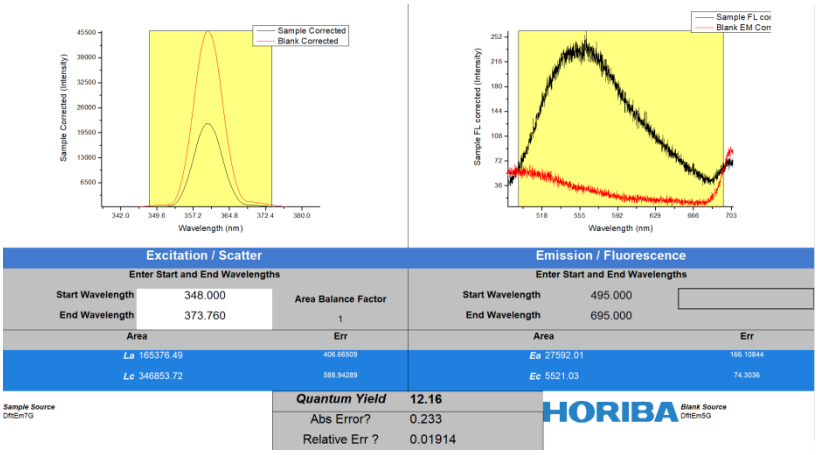


Fig. S4 PLQYs measurement of (***R*P**)-**4a** in THF solution (1×10^{-5} M).

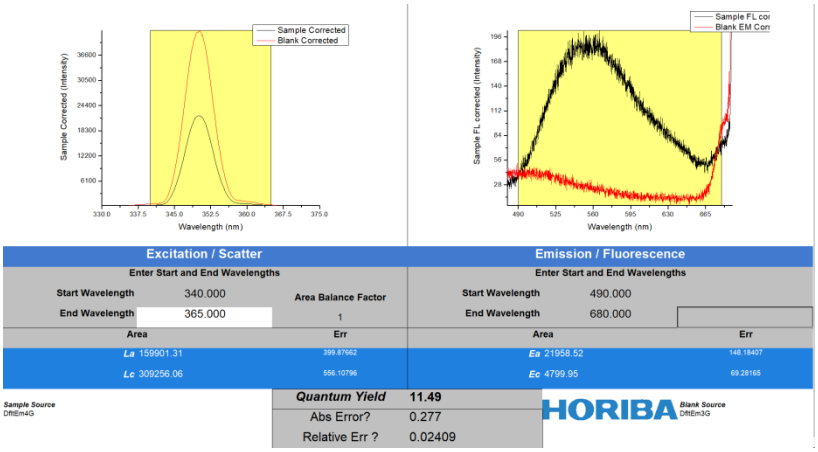


Fig. S5 PLQYs measurement of (***R*P)-4b** in THF solution (1×10^{-5} M).

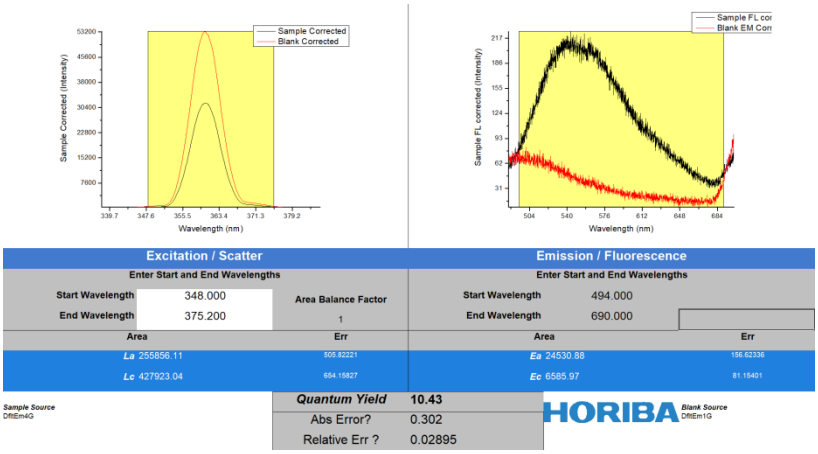


Fig. S6 PLQYs measurement of (***R*P)-4c** in THF solution (1×10^{-5} M).

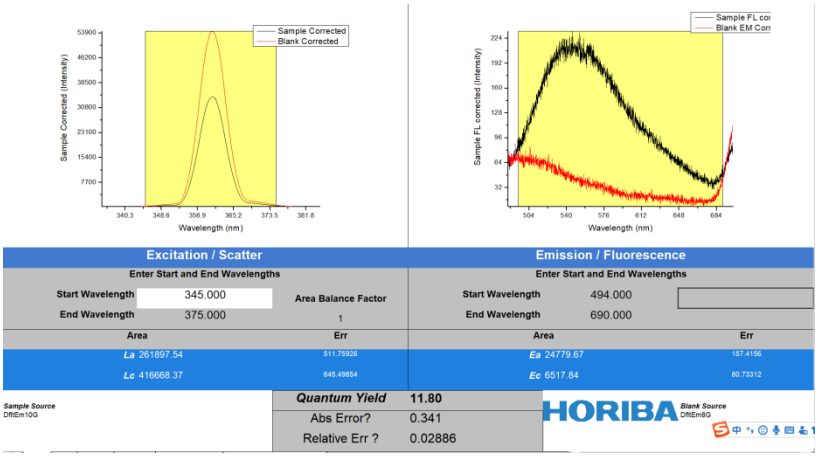


Fig. S7 PLQYs measurement of (***R*P)-4d** in THF solution (1×10^{-5} M).

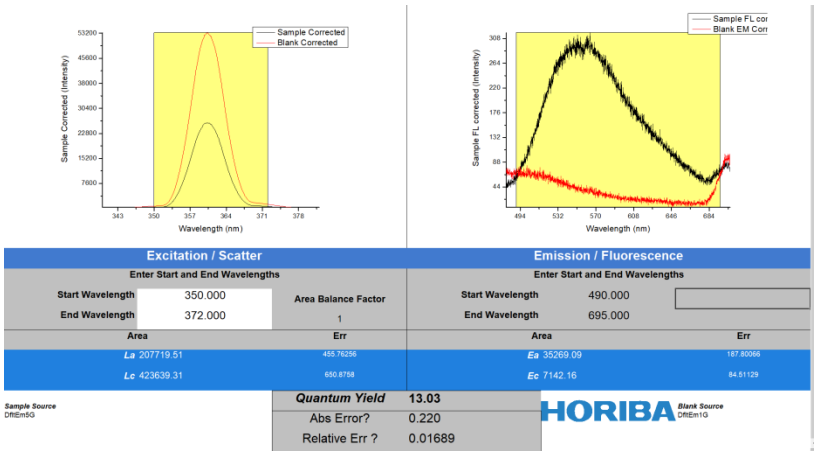
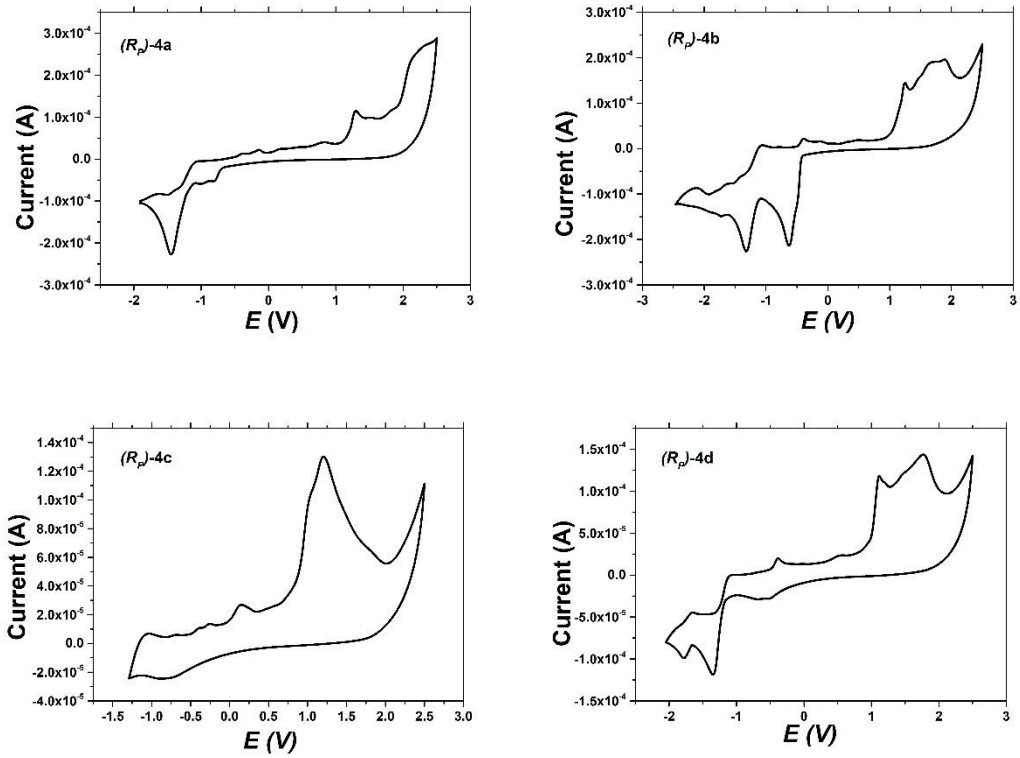


Fig. S8 PLQYs measurement of (***R*_P)-4e** in THF solution (1×10^{-5} M).

7. Electrochemical Measurements

Cyclic and difference pulse voltammograms were obtained under the following conditions; solvent: MeCN, electrolyte: 0.1 M Bu_4NPF_6, working electrode: Pt, counter electrode: Pt, reference electrode: $Ag/AgNO_3$. The scan rate was 100 mVs^{-1}. All potentials are referenced to the potential of ferrocene/ferrocenium cation couple.



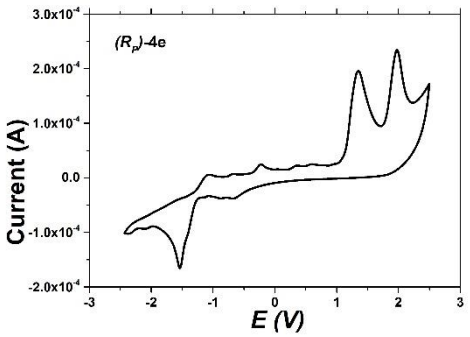


Fig. S9 CV curves of (***R*_P**)-**4a**-**4e** in MeCN solution ($2.5x10^{-3}$ mol/L)

8. Cartesian coordinates for TD-DFT calculations:

Table S2. ((*R*_P)-4a) Total Energy (B3LYP/6-31G)：-1242.872057 a. u.

	X	Y	Z
C	-2.941791	-1.079979	-2.465294
C	-2.844961	-2.312966	-1.81267
C	-1.69928	-2.64065	-1.06341
C	-0.554667	-1.844978	-1.251355
C	-0.651897	-0.616642	-1.915434
C	-1.88802	-0.149765	-2.396417
C	-2.143637	1.338951	-2.547565
C	-1.782125	-3.600577	0.109404
C	-3.977231	0.338236	0.177763
C	-3.899854	-0.917572	0.819593
C	-2.692213	-1.447366	1.267613
C	-1.598366	-0.55335	1.327729
C	-1.658315	0.724567	0.699661
C	-2.834339	1.099685	-0.031251
C	-2.769789	2.03546	-1.224427
C	-2.463837	-2.936145	1.413672
O	-0.455538	-0.979631	1.89305
B	0.846238	-0.272324	1.918387
N	0.661242	1.163057	1.252568

C	-0.488496	1.525863	0.705908
C	1.810495	2.032812	1.141507
C	2.653613	2.21976	2.247423
C	3.748114	3.080946	2.135116
C	4.011125	3.750875	0.934262
C	3.176257	3.547126	-0.170162
C	2.080139	2.686062	-0.07182
F	1.271382	-0.122956	3.265808
F	1.803781	-0.986529	1.148471
H	-3.886019	-0.789588	-2.919257
H	-3.716094	-2.962191	-1.771124
H	0.373316	-2.101379	-0.749264
H	0.215836	0.0383	-1.93775
H	-1.205591	1.85331	-2.787578
H	-2.837115	1.537916	-3.372821
H	-2.365196	-4.492497	-0.149313
H	-0.777459	-3.933519	0.38618
H	-4.903096	0.617149	-0.315052
H	-4.781182	-1.553008	0.82289
H	-2.192383	2.944516	-1.019233
H	-3.786333	2.364499	-1.462794
H	-3.42609	-3.429062	1.589882
H	-1.818606	-3.144292	2.271137
H	-0.524728	2.510267	0.250033
H	2.446917	1.692899	3.168411
H	4.396888	3.227227	2.992176
H	4.865053	4.415458	0.855693
H	3.385998	4.04204	-1.112649
H	1.462955	2.492486	-0.943096

Table S3. ((*R*$_P$)-4b Total Energy (B3LYP/6-31G)：-1342.085512 a. u.

	X	Y	Z
C	-3.460801	-1.263787	-2.491031
C	-3.338717	-2.539193	-1.929103
C	-2.129341	-2.950288	-1.337893
C	-0.984664	-2.177649	-1.60204
C	-1.10932	-0.903688	-2.167295
C	-2.372676	-0.371541	-2.480976
C	-2.58421	1.131441	-2.512693
C	-2.113496	-3.983825	-0.227319
C	-4.091152	-0.011337	0.346428
C	-3.953021	-1.300723	0.905593
C	-2.707635	-1.863251	1.177957
C	-1.602295	-0.981737	1.1537
C	-1.724677	0.335296	0.617936
C	-2.972639	0.755124	0.047149
C	-3.036183	1.758257	-1.088744
C	-2.490944	-3.360507	1.216467
O	-0.402233	-1.439286	1.558992
B	0.901084	-0.763972	1.370871
N	0.629355	0.755067	0.983319
C	-0.570733	1.156357	0.591159
C	1.722723	1.688544	1.049606
C	1.524621	2.978604	1.565874
C	2.585678	3.886674	1.606085
C	3.828835	3.475462	1.138498
C	4.053708	2.195316	0.639964
C	2.991561	1.292531	0.594815
F	1.662401	-0.817389	2.552321

F	1.608047	-1.367278	0.273865
F	4.887963	4.374482	1.179723
H	-4.437521	-0.917244	-2.819796
H	-4.22314	-3.163917	-1.830671
H	-0.016852	-2.492211	-1.225418
H	-0.226851	-0.272575	-2.234909
H	-1.657013	1.628396	-2.819887
H	-3.353753	1.407685	-3.242792
H	-2.82455	-4.791589	-0.43639
H	-1.119466	-4.434685	-0.147727
H	-5.065079	0.298319	-0.01857
H	-4.835422	-1.930373	0.978516
H	-2.419729	2.646343	-0.904898
H	-4.067933	2.111885	-1.183633
H	-3.404462	-3.849349	1.571927
H	-1.686122	-3.607869	1.912672
H	-0.658722	2.181849	0.244773
H	0.55974	3.261571	1.972056
H	2.461051	4.883751	2.009099
H	5.040821	1.917041	0.293163
H	3.128367	0.292167	0.205958

Table S4. ((R_P)-4c Total Energy(B3LYP/6-31G)：-1759.018146 a. u.

C	5.645471	1.651938	1.772297
C	6.259343	0.396628	1.716076
C	5.486763	-0.777755	1.643421
C	4.117093	-0.670043	1.944894
C	3.507341	0.588098	2.011823
C	4.242559	1.762397	1.771286
C	3.553382	3.009625	1.247928

C	6.029382	-2.029083	0.977646
C	5.360934	1.75119	-1.386603
C	6.002965	0.493741	-1.432434
C	5.329824	-0.69269	-1.150985
C	3.918355	-0.619684	-1.115428
C	3.247465	0.63768	-1.083181
C	4.015747	1.849346	-1.055222
C	3.506273	3.103777	-0.369672
C	6.03949	-1.925133	-0.633839
O	3.222114	-1.763894	-0.998312
B	1.763622	-1.903662	-0.787094
N	1.098169	-0.455722	-0.828996
C	1.837555	0.638055	-0.941643
C	-0.323455	-0.340106	-0.617493
C	-1.203602	-1.220561	-1.265891
C	-2.57851	-1.086524	-1.079733
C	-3.095528	-0.091703	-0.232737
C	-2.208769	0.770884	0.432874
C	-0.833521	0.64874	0.239294
F	1.215181	-2.709918	-1.821326
F	1.505296	-2.460518	0.494572
N	-4.496756	0.033309	-0.039246
C	-5.246918	1.220849	-0.178679
C	-6.612787	0.93245	0.09591
C	-6.694736	-0.481309	0.418259
C	-5.377381	-1.009449	0.325223
C	-7.753204	-1.323334	0.784875
C	-7.488651	-2.666209	1.059995
C	-6.17545	-3.169125	0.979961

C	-5.103029	-2.350164	0.615798
C	-4.832065	2.501013	-0.561353
C	-5.802769	3.503321	-0.644532
C	-7.156252	3.238077	-0.360011
C	-7.566827	1.954672	0.006135
H	6.255166	2.547998	1.686935
H	7.337483	0.337436	1.589052
H	3.495613	-1.560017	1.972503
H	2.426705	0.64288	2.119635
H	2.522042	3.045882	1.618284
H	4.053464	3.916516	1.606982
H	7.056421	-2.235807	1.301315
H	5.417125	-2.891783	1.256476
H	5.968209	2.649665	-1.428652
H	7.084084	0.467539	-1.537001
H	2.480654	3.359332	-0.660896
H	4.132254	3.946809	-0.679199
H	7.081058	-1.905702	-0.972366
H	5.574954	-2.831463	-1.030793
H	1.311915	1.587631	-0.939574
H	-0.805354	-1.987947	-1.914658
H	-3.258967	-1.745011	-1.60654
H	-2.597768	1.508516	1.124891
H	-0.157788	1.287144	0.798549
H	-8.764293	-0.935352	0.859525
H	-8.299221	-3.329172	1.343764
H	-5.988151	-4.21327	1.208778
H	-4.095264	-2.745458	0.570733
H	-3.795451	2.712901	-0.795192

H	-5.505038	4.504801	-0.938547
H	-7.88532	4.038307	-0.432092
H	-8.612661	1.750241	0.212982

Table S5. ((*R*$_P$)-4d) Total Energy (B3LYP/6-31G)：-1550.077292 a. u.

	X	Y	Z
C	4.558381	1.426667	-1.015300
C	5.025244	0.78041	0.134689
C	4.172315	0.568297	1.233933
C	2.963225	1.285908	1.262595
C	2.503143	1.938245	0.113697
C	3.230292	1.886198	-1.08826
C	2.518746	2.039367	-2.419826
C	4.38737	-0.597039	2.181645
C	3.283246	-1.244109	-2.108869
C	3.779652	-1.890728	-0.956068
C	3.118116	-1.840771	0.268895
C	1.784371	-1.369185	0.243914
C	1.255977	-0.728269	-0.917294
C	2.099572	-0.519963	-2.059836
C	1.903797	0.654133	-2.99889
C	3.851308	-1.999965	1.583073
O	1.04117	-1.470314	1.363024
B	-0.249906	-0.769696	1.607324
N	-0.857426	-0.367157	0.199515
C	-0.093713	-0.292109	-0.878197
C	-2.271409	-0.039668	0.080679
C	-2.690486	1.295845	0.259588
C	-4.087201	1.612055	0.036371

C	-4.980069	0.59073	-0.314642
C	-4.565227	-0.741259	-0.448395
C	-3.171658	-1.077142	-0.243046
F	-1.145084	-1.615058	2.283737
F	-0.00549	0.437659	2.340885
C	-5.48262	-1.785125	-0.795898
C	-5.059578	-3.084757	-0.92506
C	-3.689014	-3.416917	-0.706101
C	-2.77315	-2.447296	-0.376069
C	-1.805419	2.354256	0.65044
C	-2.26565	3.642796	0.778376
C	-3.634038	3.96134	0.527635
C	-4.517505	2.971488	0.175508
H	5.187491	1.458822	-1.901511
H	6.010987	0.321654	0.123983
H	2.303557	1.20559	2.120359
H	1.50782	2.375223	0.117169
H	1.693938	2.754523	-2.324563
H	3.200458	2.433105	-3.182223
H	5.450995	-0.722006	2.416395
H	3.862951	-0.412399	3.124217
H	3.926206	-1.16015	-2.979097
H	4.782403	-2.307794	-0.988444
H	0.847534	0.830407	-3.231198
H	2.400813	0.435019	-3.949596
H	4.712232	-2.661423	1.43713
H	3.199207	-2.458497	2.330371
H	-0.562032	0.080039	-1.785244
H	-6.024633	0.838131	-0.484533

H	-6.525052	-1.52279	-0.951224
H	-5.76425	-3.867761	-1.185224
H	-3.372308	-4.451311	-0.790231
H	-1.742971	-2.716196	-0.181772
H	-0.783152	2.110181	0.907023
H	-1.585702	4.42857	1.091168
H	-3.972437	4.986962	0.632491
H	-5.56486	3.199189	-0.000176

Table S6. ((*R*$_P$)-4e) Total Energy (B3LYP/6-31G)：-2253.531667 a. u.

	X	Y	Z
C	-6.654614	-0.900656	0.570957
C	-6.502492	-1.635993	-0.609938
C	-5.631327	-1.19509	-1.623916
C	-5.166908	0.129241	-1.547428
C	-5.317921	0.860586	-0.364658
C	-5.938798	0.295395	0.763611
C	-5.598312	0.799256	2.154946
C	-4.974353	-2.180666	-2.571297
C	-4.059277	-2.239622	1.773326
C	-3.884399	-2.93651	0.5563
C	-3.307615	-2.344436	-0.564505
C	-2.631295	-1.119141	-0.348795
C	-2.765474	-0.414178	0.887332
C	-3.648207	-0.920644	1.901037
C	-4.379503	-0.000071	2.859222
C	-3.61184	-2.813986	-1.971043
O	-1.912533	-0.585891	-1.352784
B	-1.422173	0.819791	-1.409587
N	-1.307097	1.346849	0.095776

C	-2.056897	0.800951	1.044683
C	-0.645492	2.607461	0.359816
C	0.75548	2.767547	0.270731
C	1.313756	4.033634	0.513229
C	0.504773	5.12034	0.840899
C	-0.882327	4.962576	0.928311
C	-1.448833	3.71167	0.683029
F	-0.175092	0.864185	-2.047533
F	-2.386511	1.655577	-2.04679
N	1.654654	1.70161	-0.063902
B	2.835268	2.015846	-1.087576
O	3.322166	0.737116	-1.64665
C	1.547052	0.49822	0.476678
C	6.10807	-2.244017	0.762389
C	5.302444	-2.348923	1.901736
C	4.530435	-1.254403	2.332971
C	4.824119	0.00015	1.769144
C	5.632693	0.108388	0.632628
C	6.160363	-1.044919	0.026979
C	6.476278	-1.052116	-1.45681
C	3.254497	-1.452128	3.132405
C	3.596482	-2.817145	-1.054139
C	2.787796	-2.977705	0.093032
C	2.264702	-1.873769	0.75085
C	2.303397	-0.620117	0.053629
C	3.156092	-0.47154	-1.081451
C	3.915086	-1.562987	-1.568348
C	5.171721	-1.319216	-2.375916
C	1.998036	-1.949571	2.241823

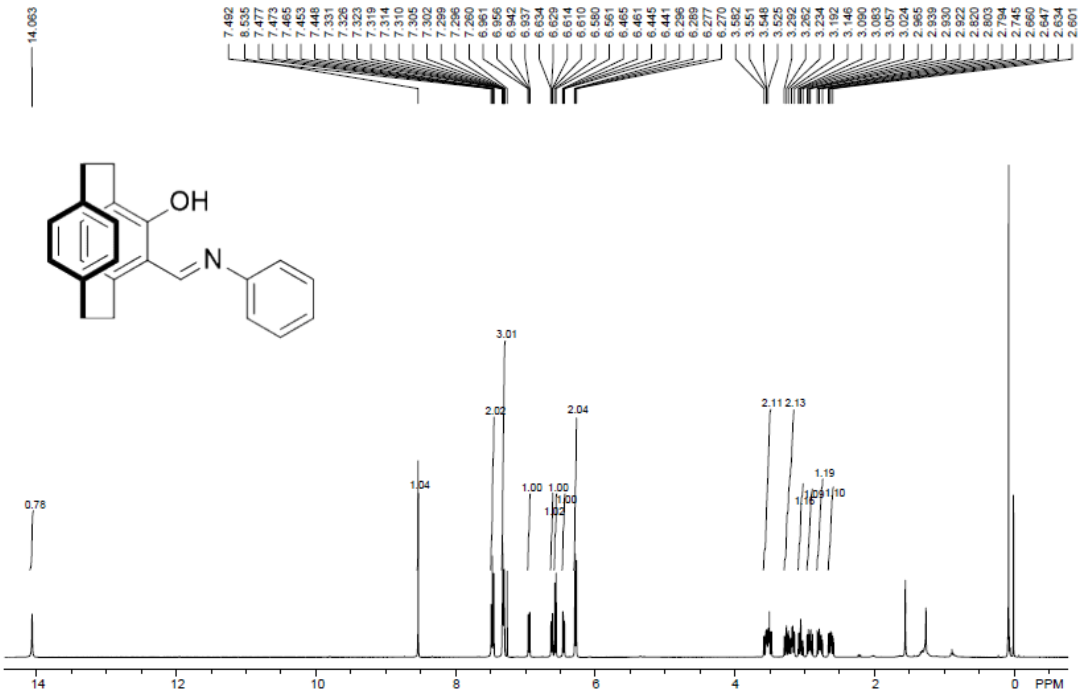
F	2.403772	2.881673	-2.098408
F	3.886195	2.631866	-0.306196
H	-7.228266	-1.323425	1.392216
H	-6.960548	-2.619042	-0.687273
H	-4.547909	0.538822	-2.338421
H	-4.825302	1.826216	-0.286361
H	-5.321523	1.858601	2.103621
H	-6.460272	0.725675	2.828268
H	-5.657398	-3.00727	-2.798167
H	-4.724004	-1.693632	-3.519234
H	-4.686235	-2.681224	2.541088
H	-4.35679	-3.908666	0.445812
H	-3.719165	0.74168	3.324805
H	-4.791552	-0.60348	3.67452
H	-3.710853	-3.904886	-1.982818
H	-2.787874	-2.545808	-2.635664
H	-2.082144	1.309336	2.005185
H	2.388746	4.13927	0.445779
H	0.958622	6.088359	1.021222
H	-1.520122	5.806858	1.165382
H	-2.52556	3.583325	0.694884
H	0.817399	0.365856	1.267227
H	6.591584	-3.134994	0.369133
H	5.173296	-3.319074	2.375605
H	4.309964	0.888592	2.1259
H	5.705612	1.069197	0.134684
H	6.906539	-0.092488	-1.761321
H	7.214175	-1.829439	-1.687105
H	3.394235	-2.190847	3.930584

H	2.974735	-0.508142	3.614185
H	4.112447	-3.687989	-1.449137
H	2.733229	-3.955358	0.560995
H	5.376455	-2.188091	-3.010911
H	5.029549	-0.454543	-3.027609
H	1.121091	-1.36492	2.546497
H	1.782805	-2.990573	2.504244
C	-6.654614	-0.900656	0.570957

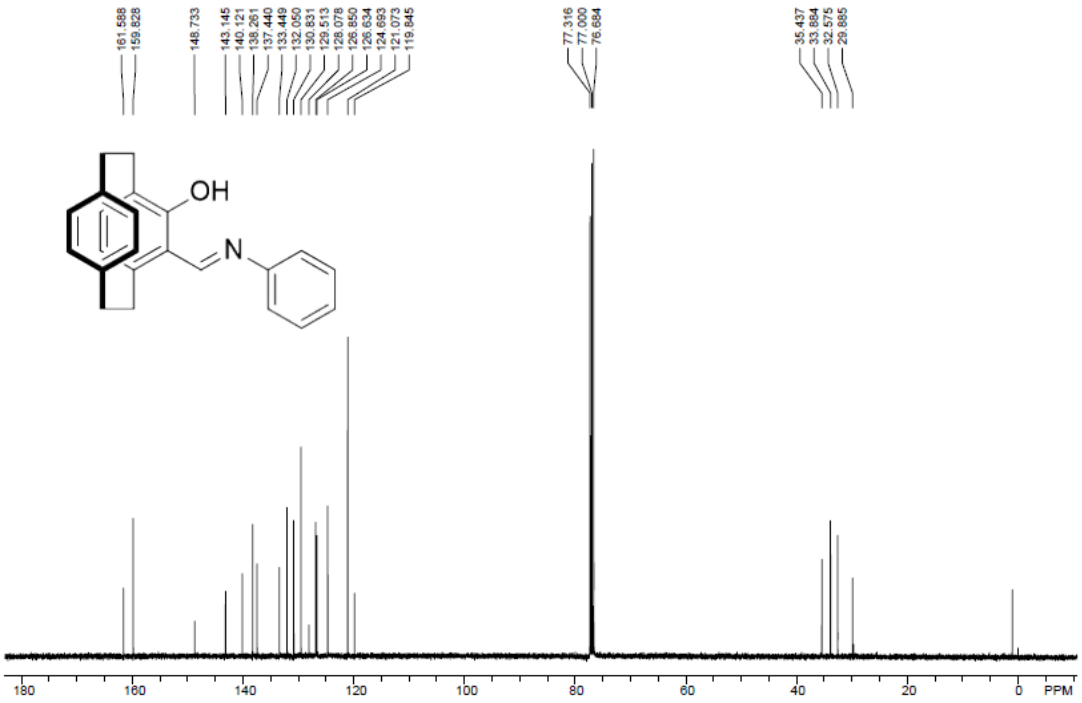
Table S7. ((*R*$_P$)-4a-4e) in S1 State at TD-DFT, B3LYP/6-31G level in THF Solvent.

	E/eV	**λ/nm**	***f***
(*R*$_P$)-4a	3.39	365	0.1529
(*R*$_P$)-4b	3.36	369	0.1154
(*R*$_P$)-4c	2.96	419	0.0382
(*R*$_P$)-4d	3.07	404	0.0670
(*R*$_P$)-4e	2.98	417	0.0298

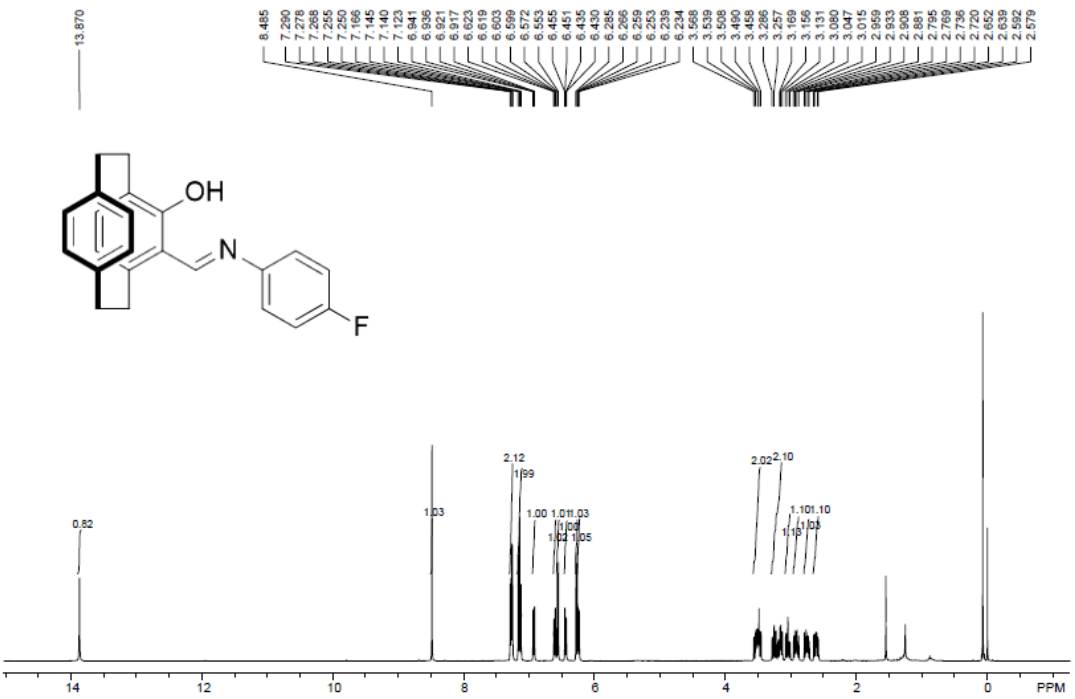
9. NMR spectra of (S_P)-3 and (S_P)-4



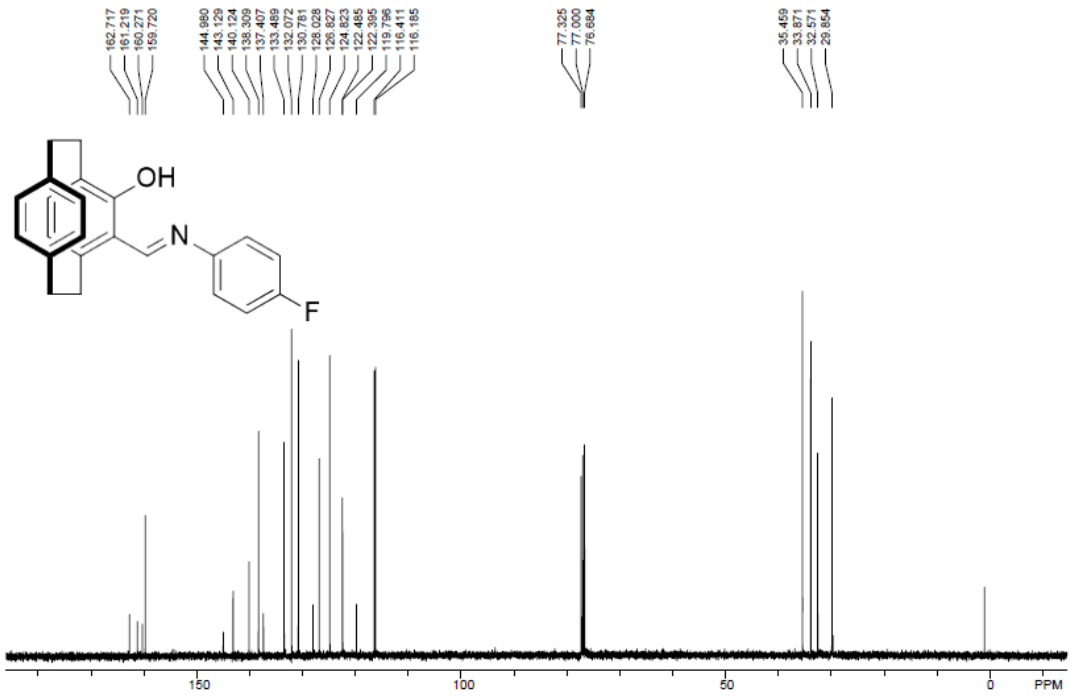
^{1}H NMR spectrum of (S_P)-**3a** (400 MHz, $CDCl_3$)



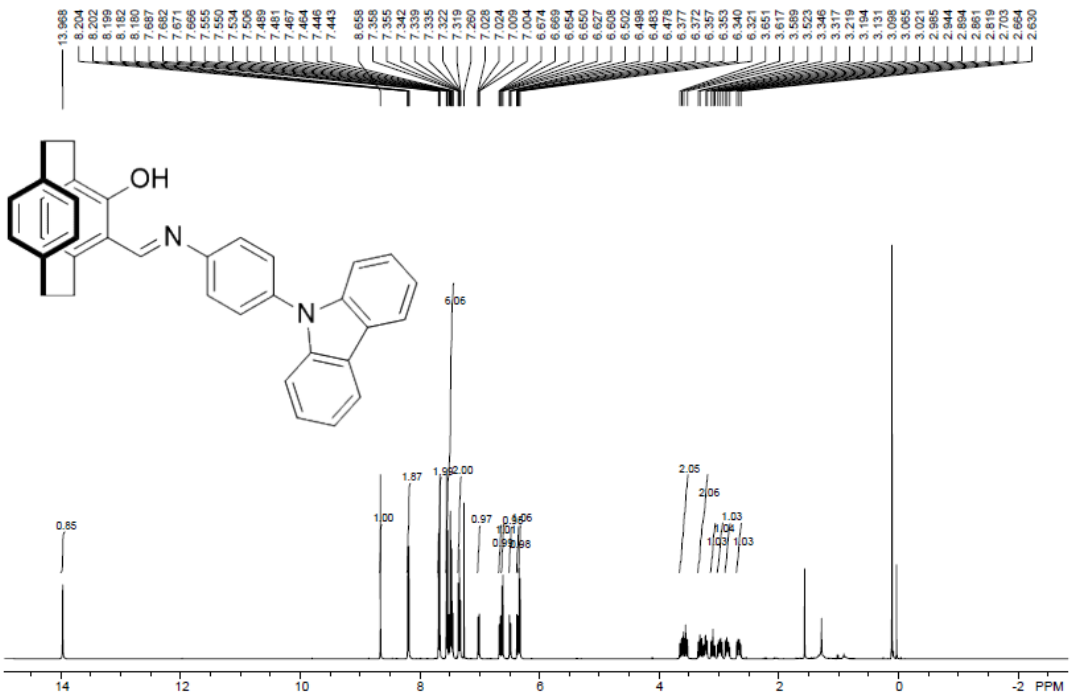
^{13}C NMR spectrum of (S_P)-**3a** (100 MHz, $CDCl_3$)



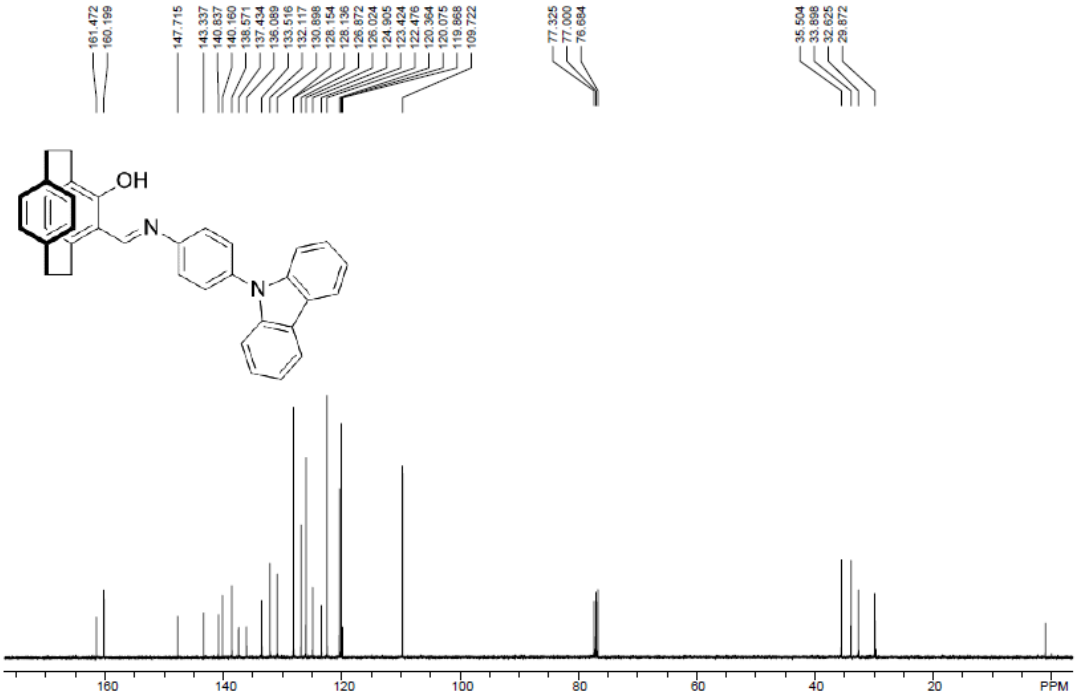
^{1}H NMR spectrum of (***S*$_P$**)-**3b** (400 MHz, $CDCl_3$)



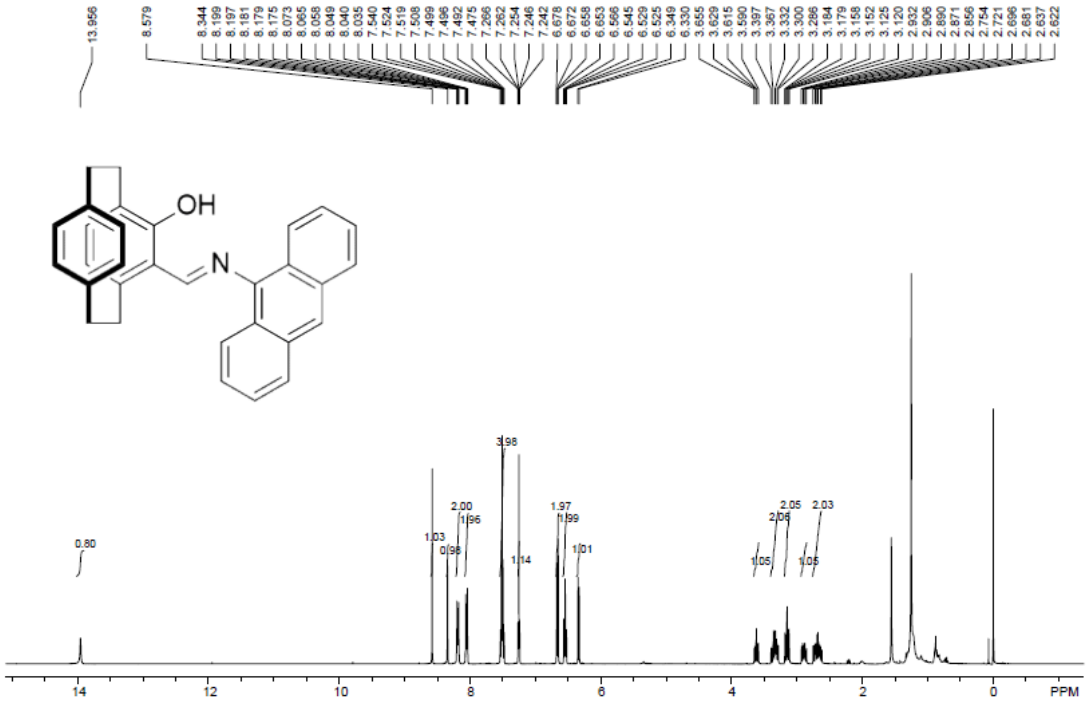
^{13}C NMR spectrum of (***S*$_P$**)-**3b** (100 MHz, $CDCl_3$)



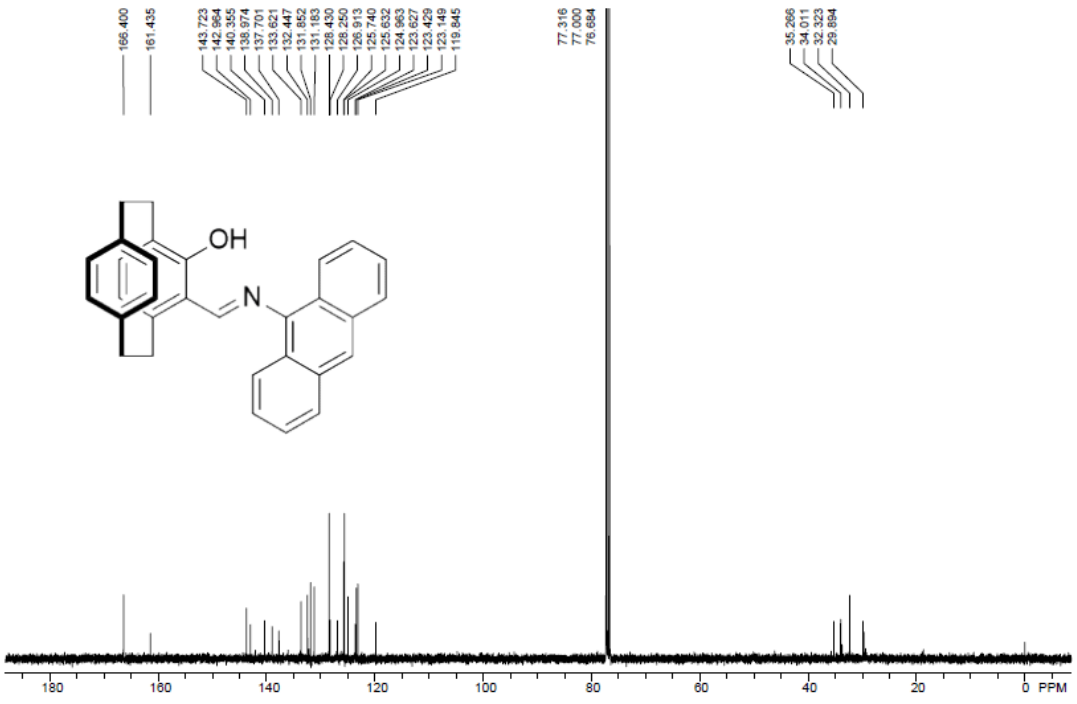
^{1}H NMR spectrum of (***S$_P$)*-3c** (400 MHz, $CDCl_3$)



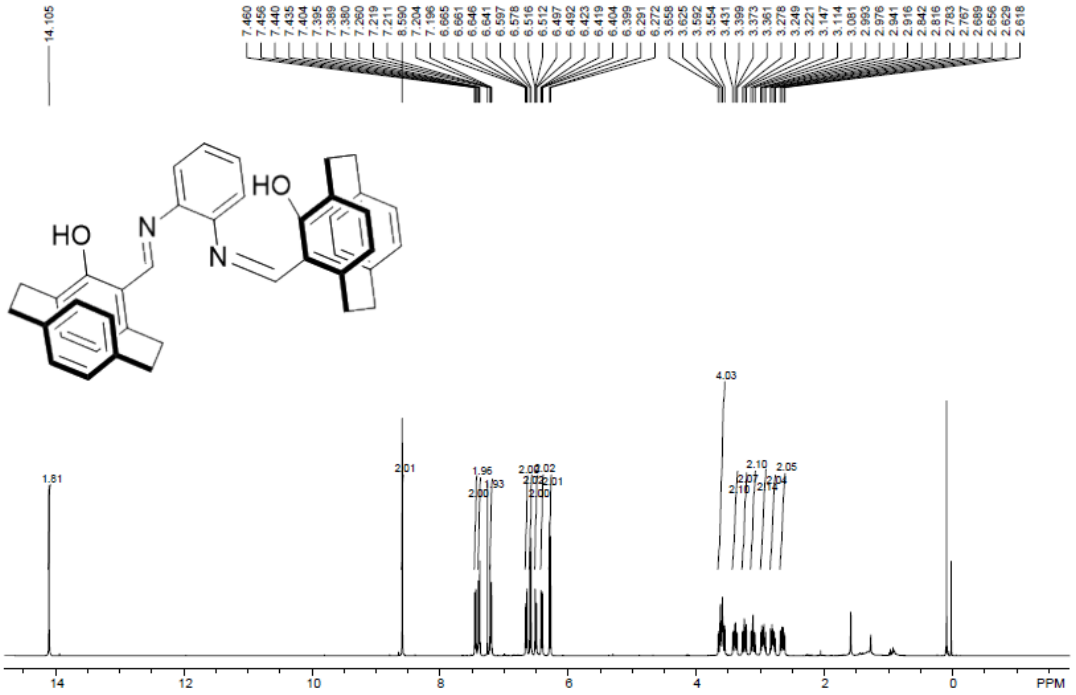
^{13}C NMR spectrum of (***S$_P$)*-3c** (100 MHz, $CDCl_3$)



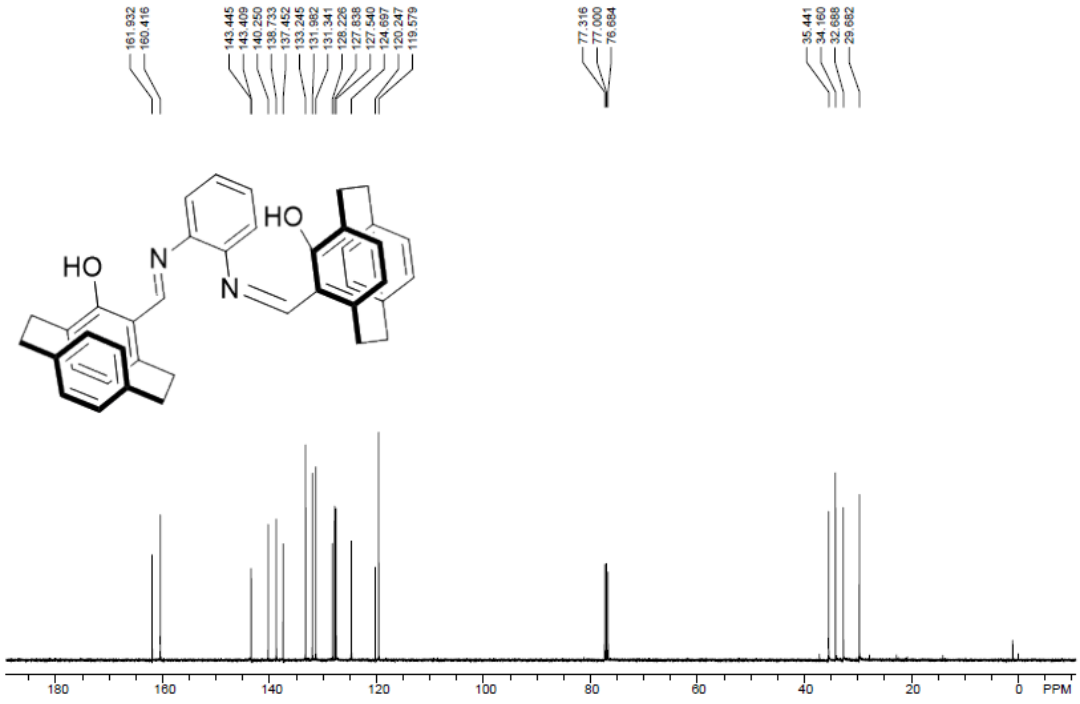
^{1}H NMR spectrum of (***S*$_P$)**-**3d** (400 MHz, $CDCl_3$)



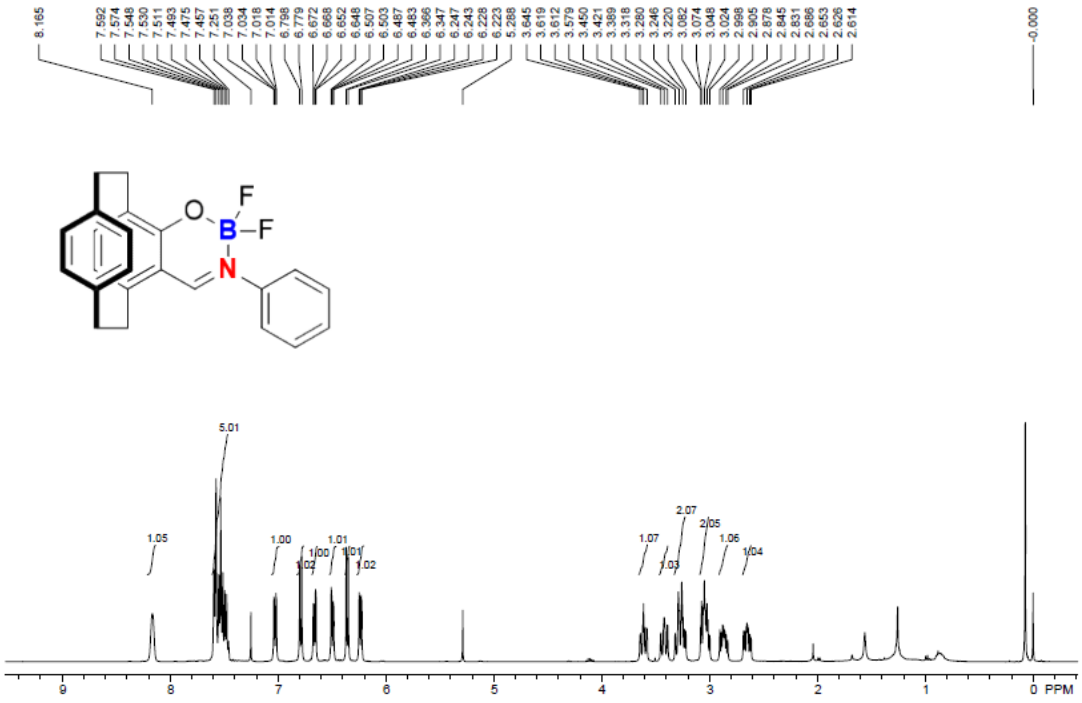
^{13}C NMR spectrum of (***S*$_P$)**-**3d** (100 MHz, $CDCl_3$)



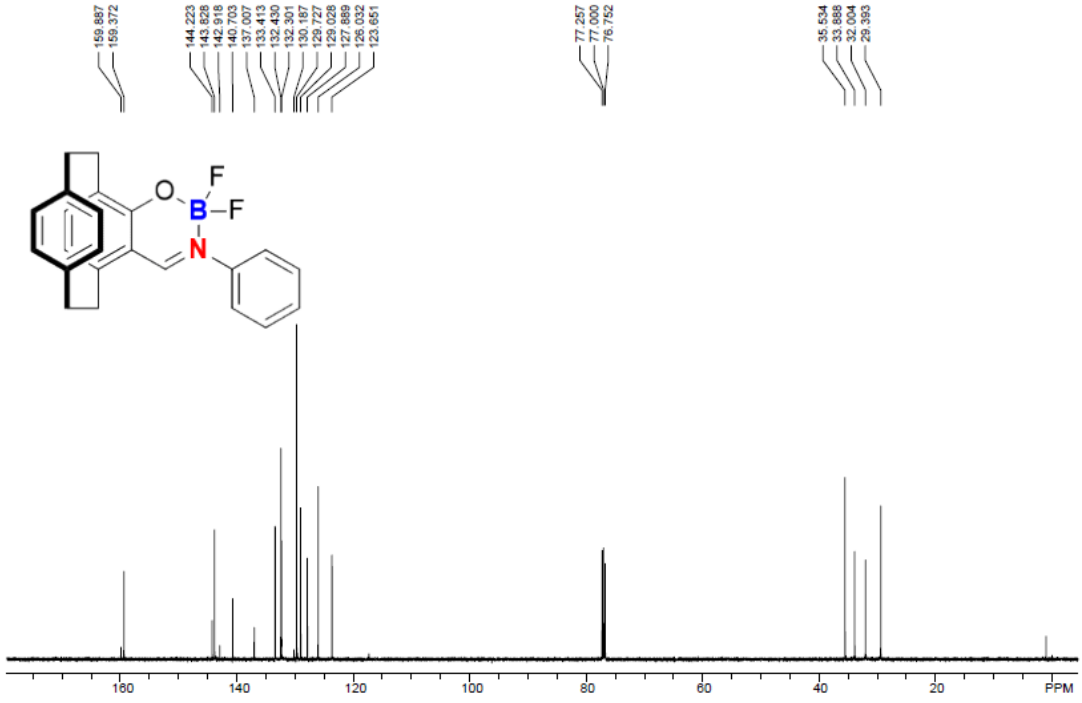
^{1}H NMR spectrum of (***S$_P$)*-3e** (400 MHz, $CDCl_3$)



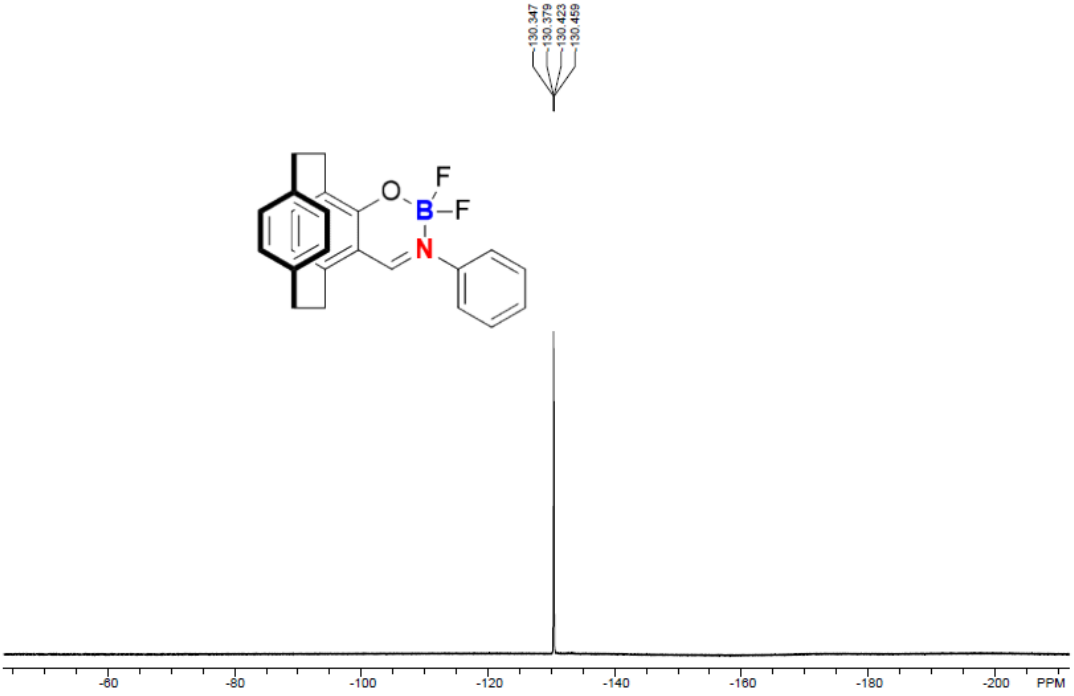
^{13}C NMR spectrum of (***S$_P$)*-3e** (100 MHz, $CDCl_3$)



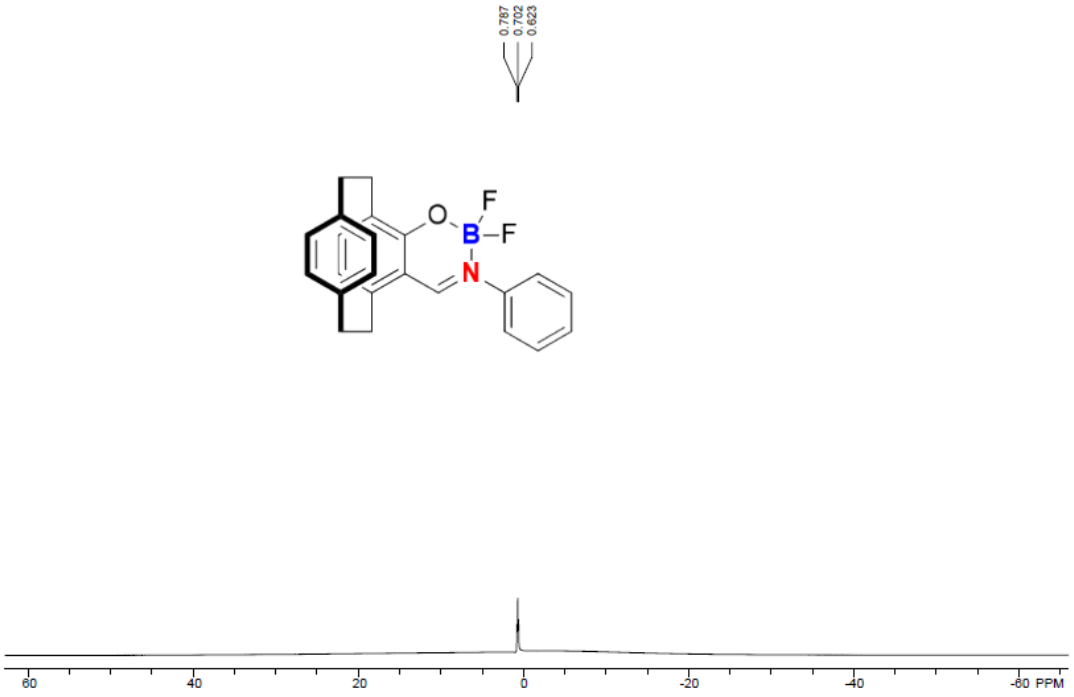
^{1}H NMR spectrum of (***S*$_P$)-4a** (400 MHz, $CDCl_3$)



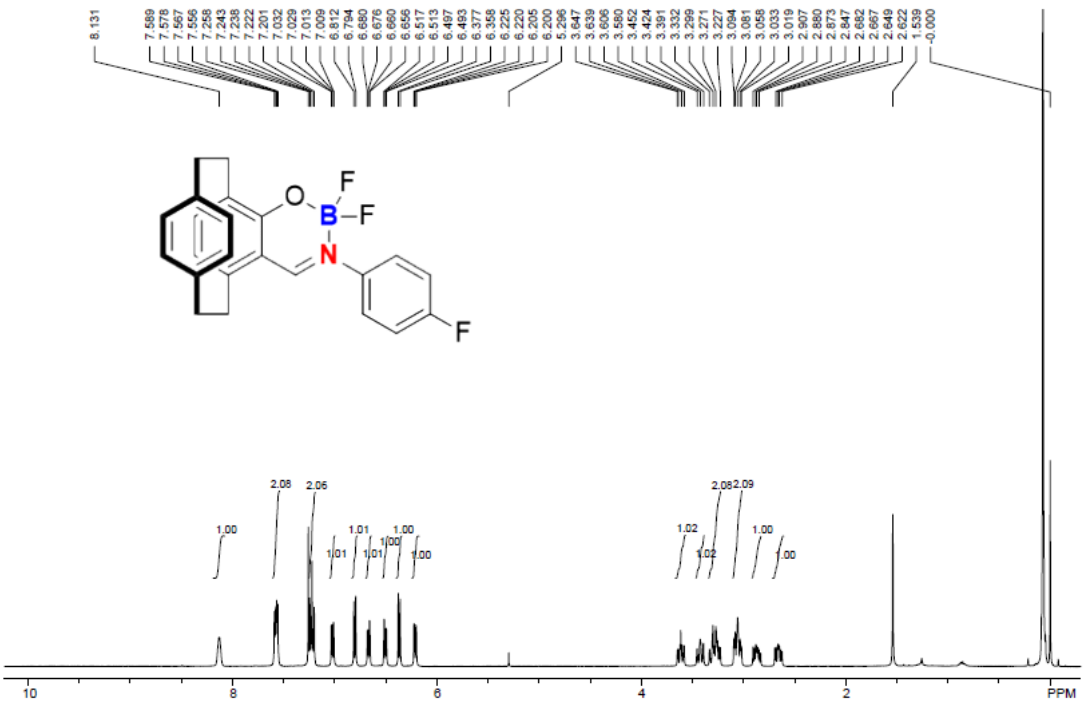
^{13}C NMR spectrum of (***S*$_P$)-4a** (100 MHz, $CDCl_3$)



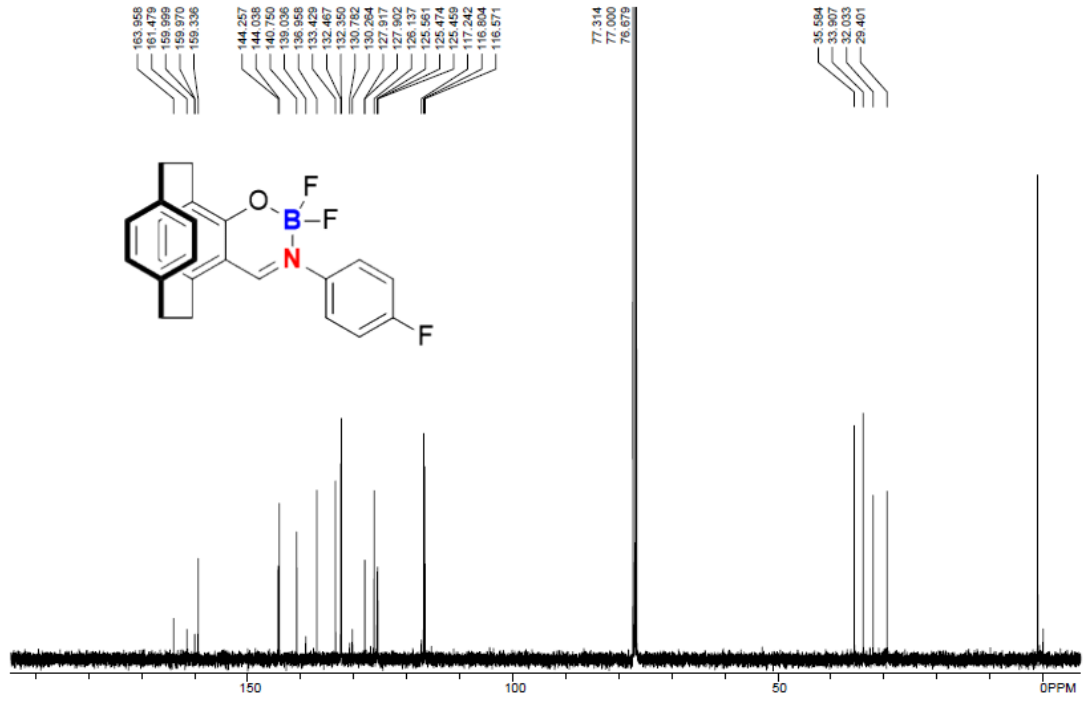
^{19}F NMR spectrum of (***S*$_P$)-4a** (376 MHz, $CDCl_3$)



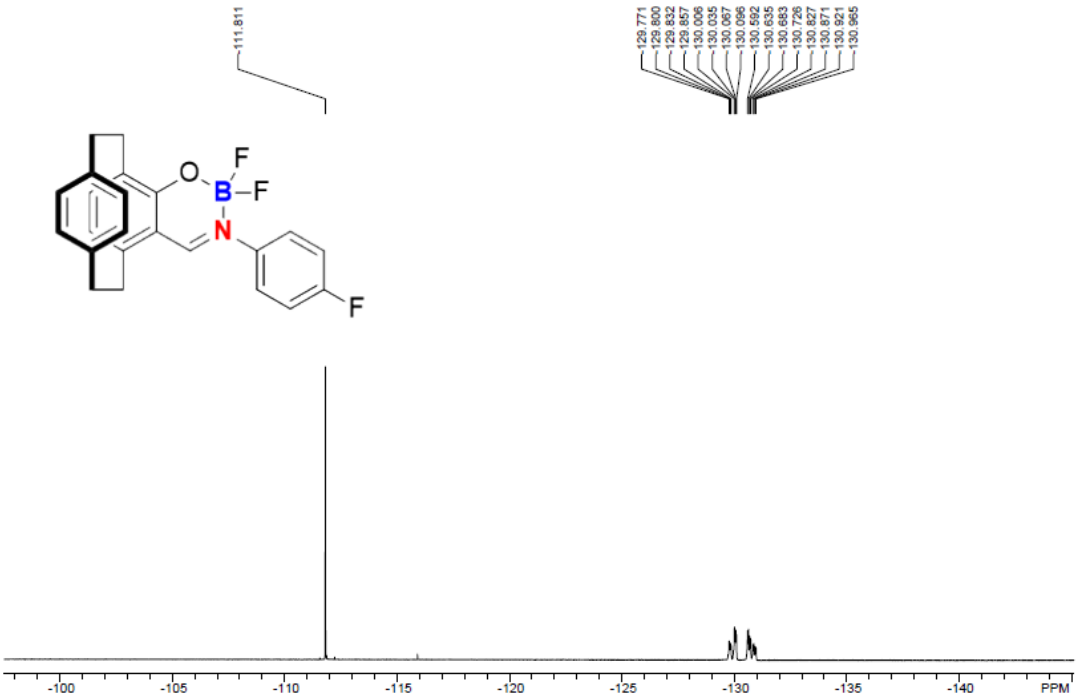
^{11}B NMR spectrum of (***S*$_P$)-4a** (160 MHz, $CDCl_3$)



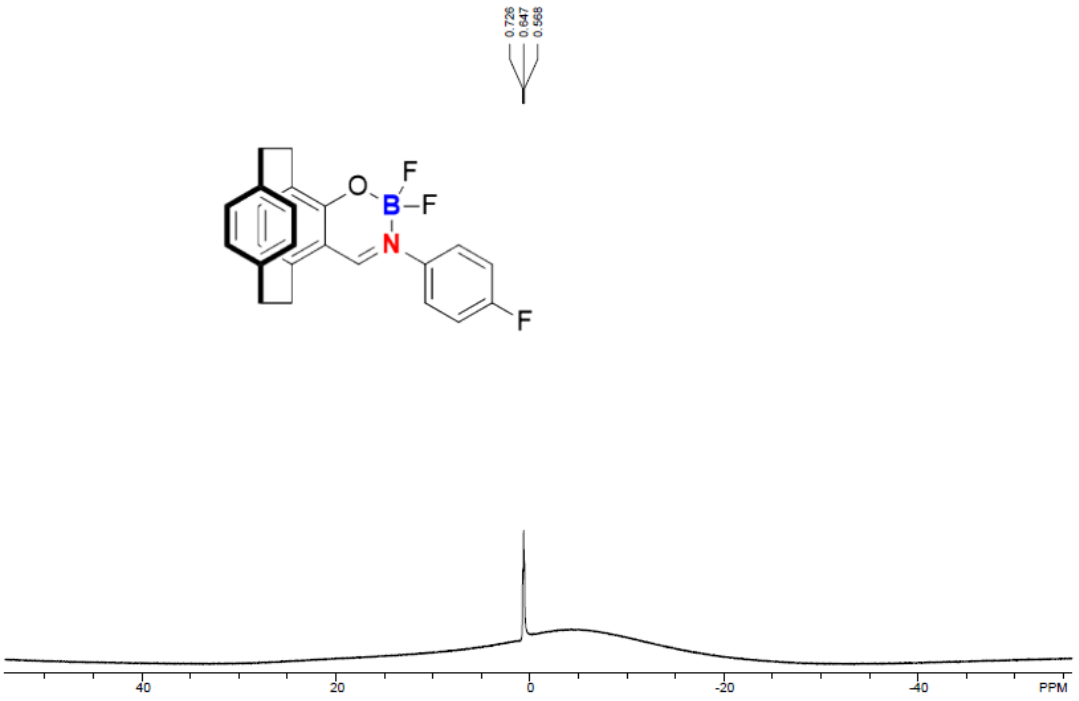
^{1}H NMR spectrum of (***S*$_P$)-4b** (400 MHz, $CDCl_3$)



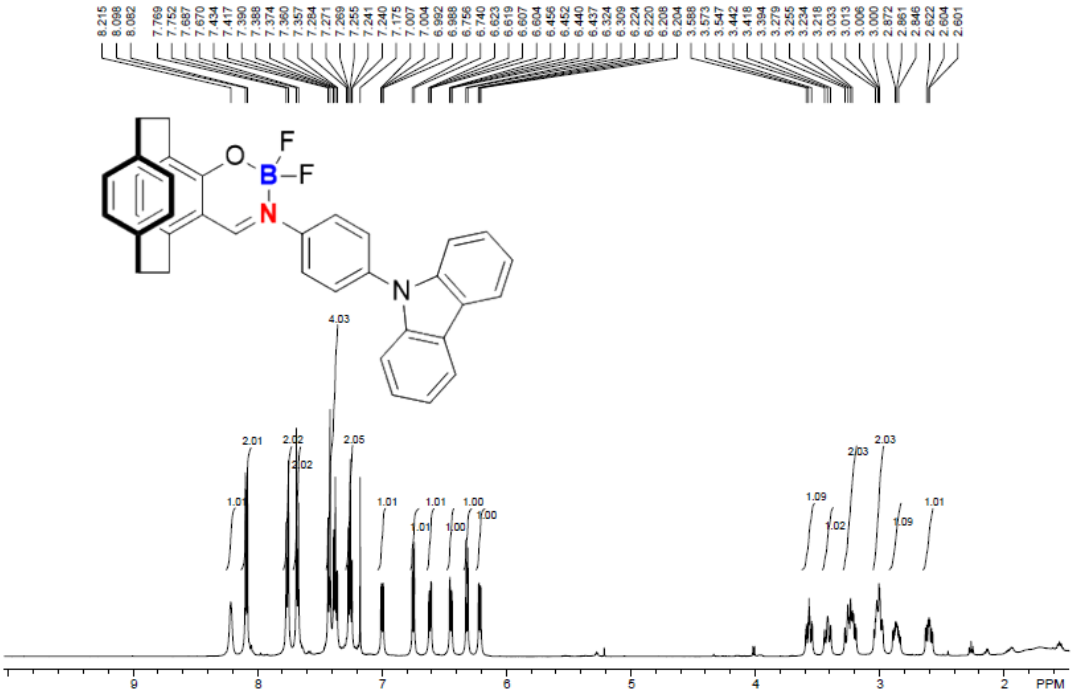
^{13}C NMR spectrum of (***S*$_P$)-4b** (100 MHz, $CDCl_3$)



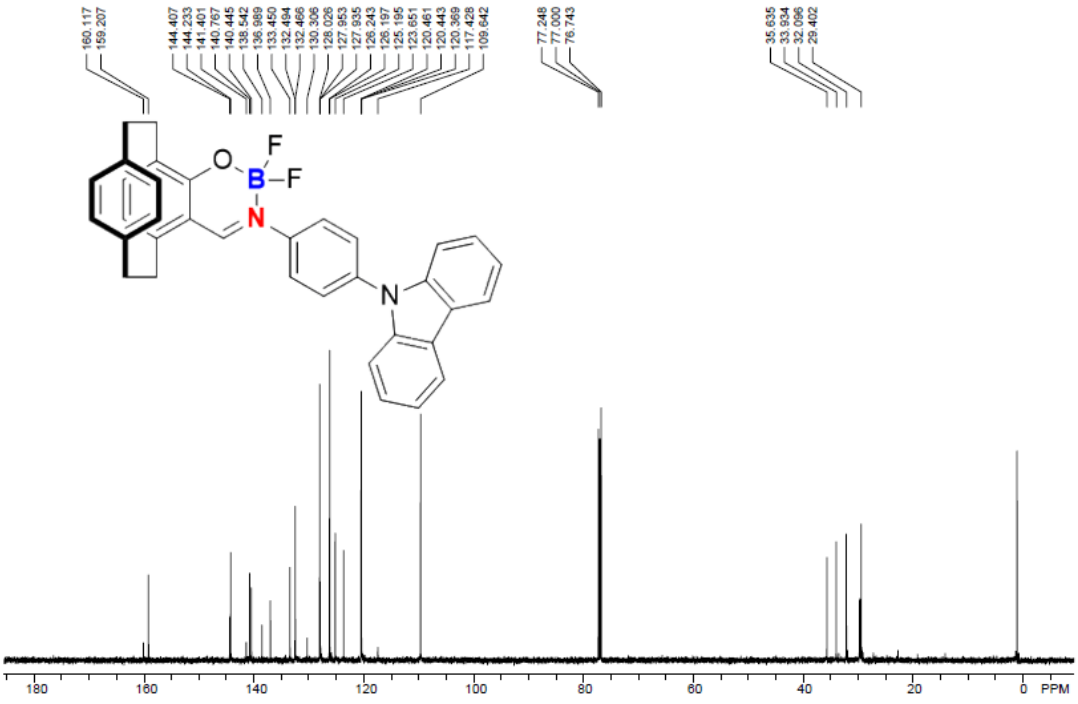
^{19}F NMR spectrum of (***S*$_P$)-4b** (376 MHz, $CDCl_3$)



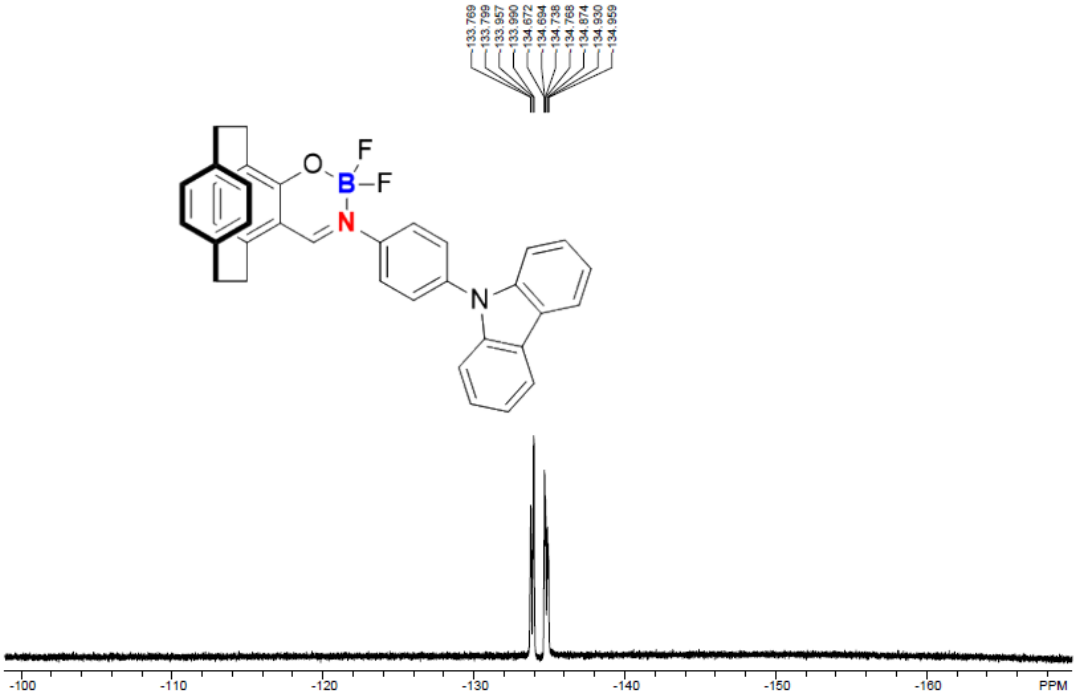
^{11}B NMR spectrum of (***S*$_P$)-4b** (160 MHz, $CDCl_3$)



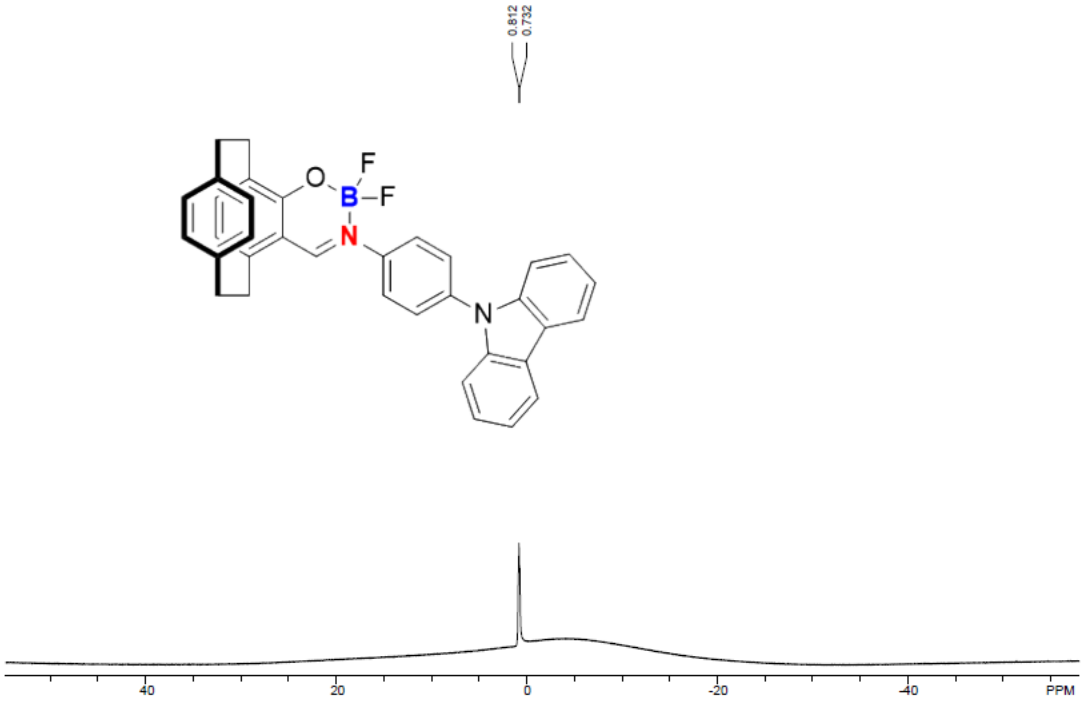
^{1}H NMR spectrum of (***S*$_P$**)-**4c** (500 MHz, $CDCl_3$)



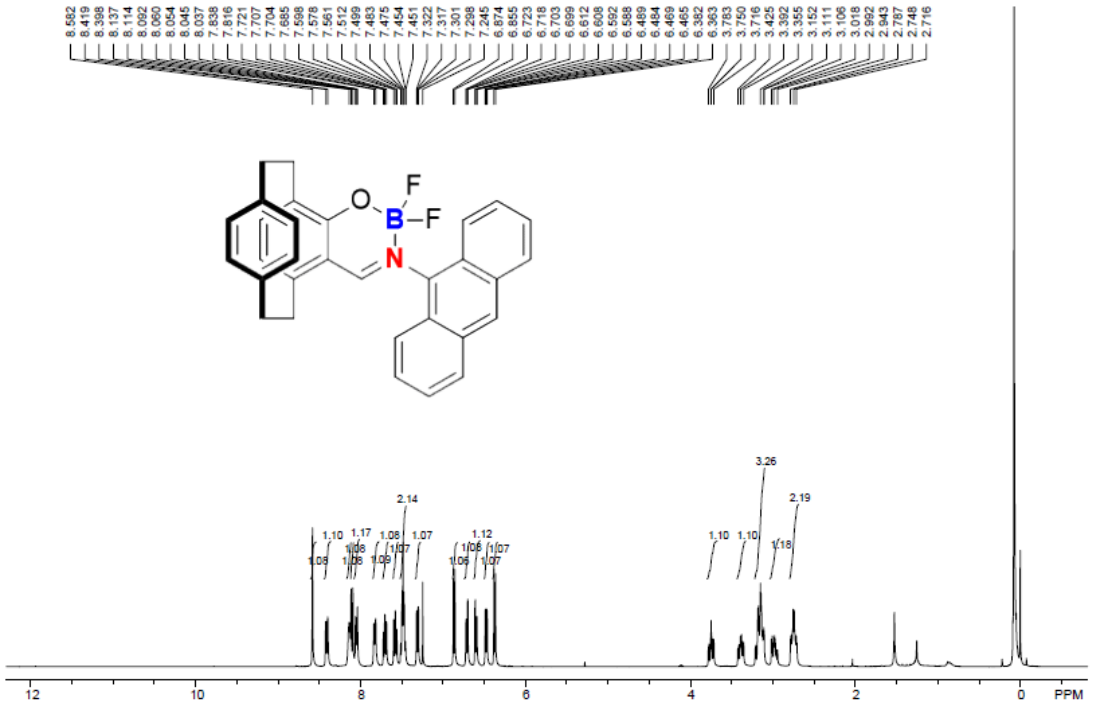
^{13}C NMR spectrum of (***S*$_P$**)-**4c** (125 MHz, $CDCl_3$)



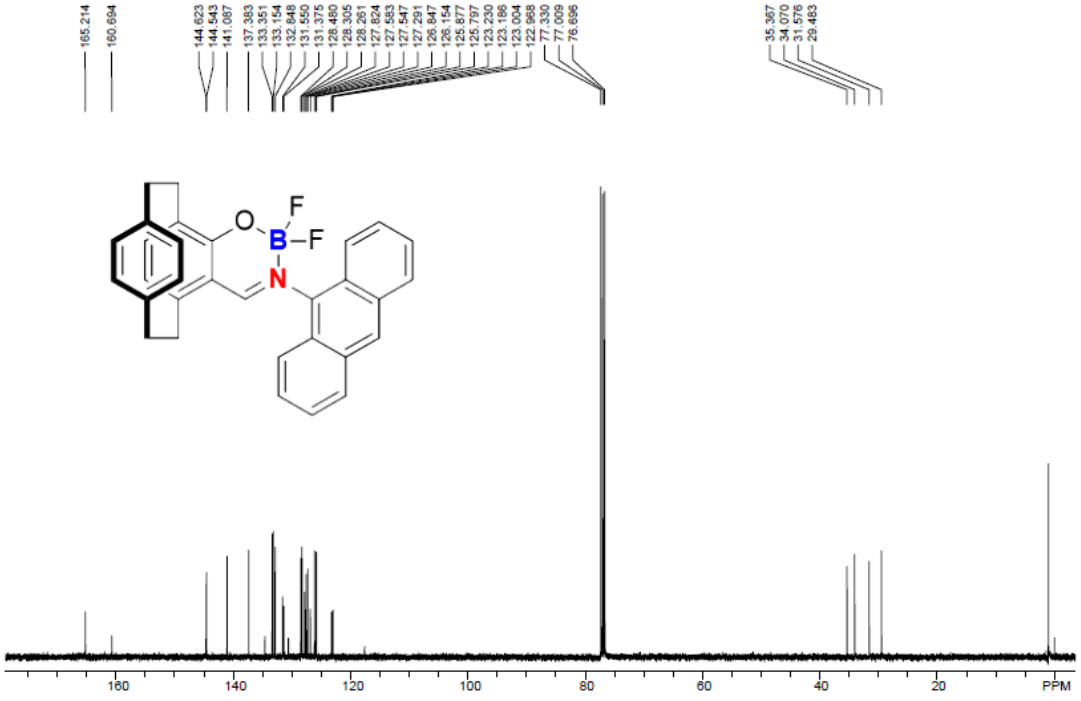
^{19}F NMR spectrum of (***S*$_P$)-4c** (471 MHz, $CDCl_3$)



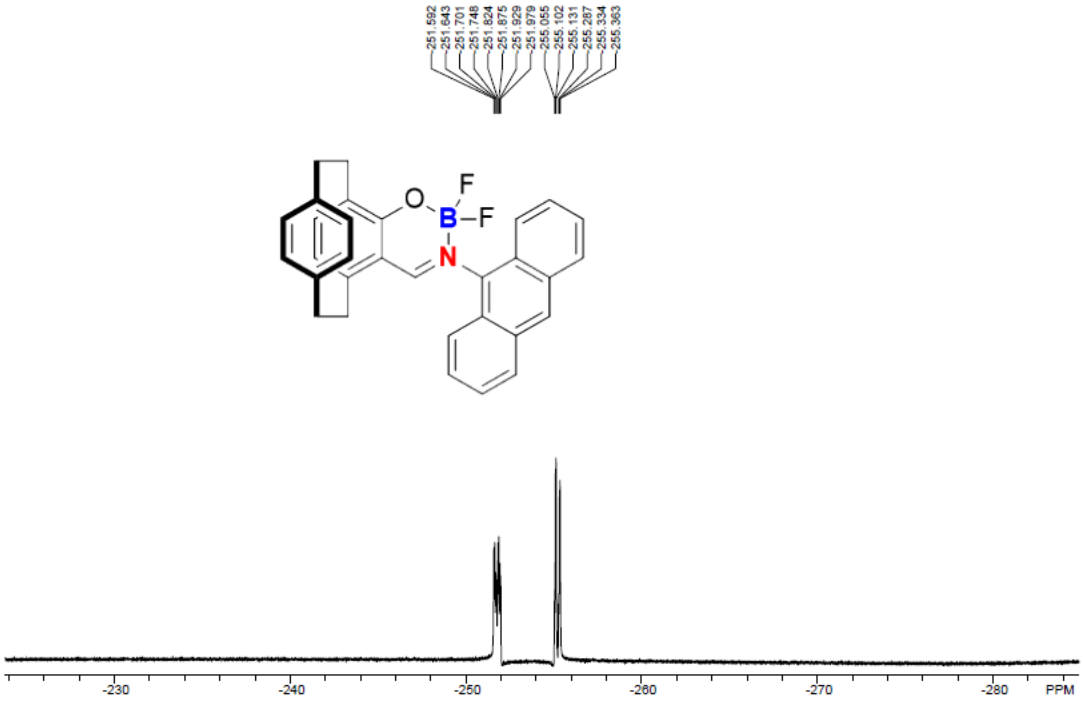
^{11}B NMR spectrum of (***S*$_P$)-4c** (160 MHz, $CDCl_3$)



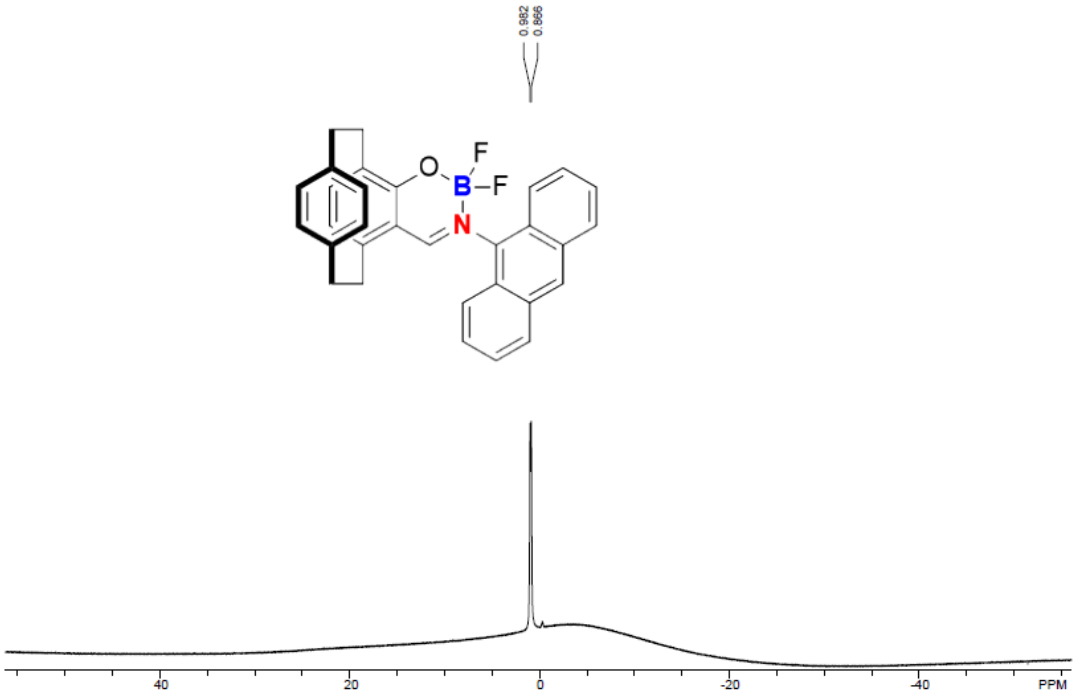
^{1}H NMR spectrum of (***S*$_P$)-4d** (400 MHz, $CDCl_3$)



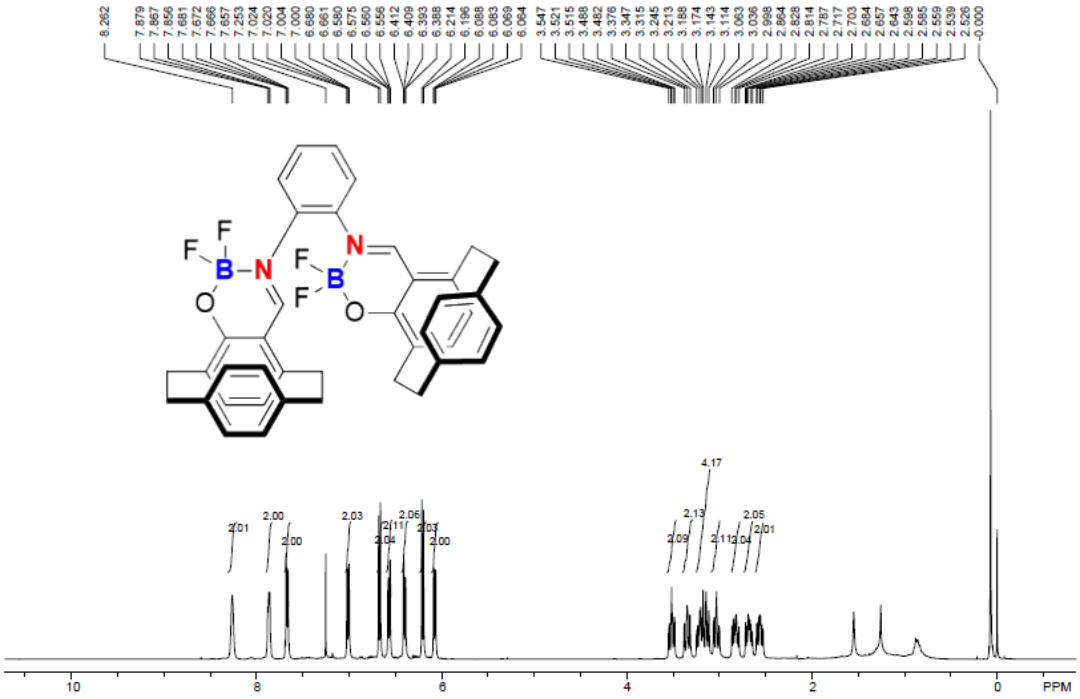
^{13}C NMR spectrum of (***S*$_P$)-4d** (100 MHz, $CDCl_3$)



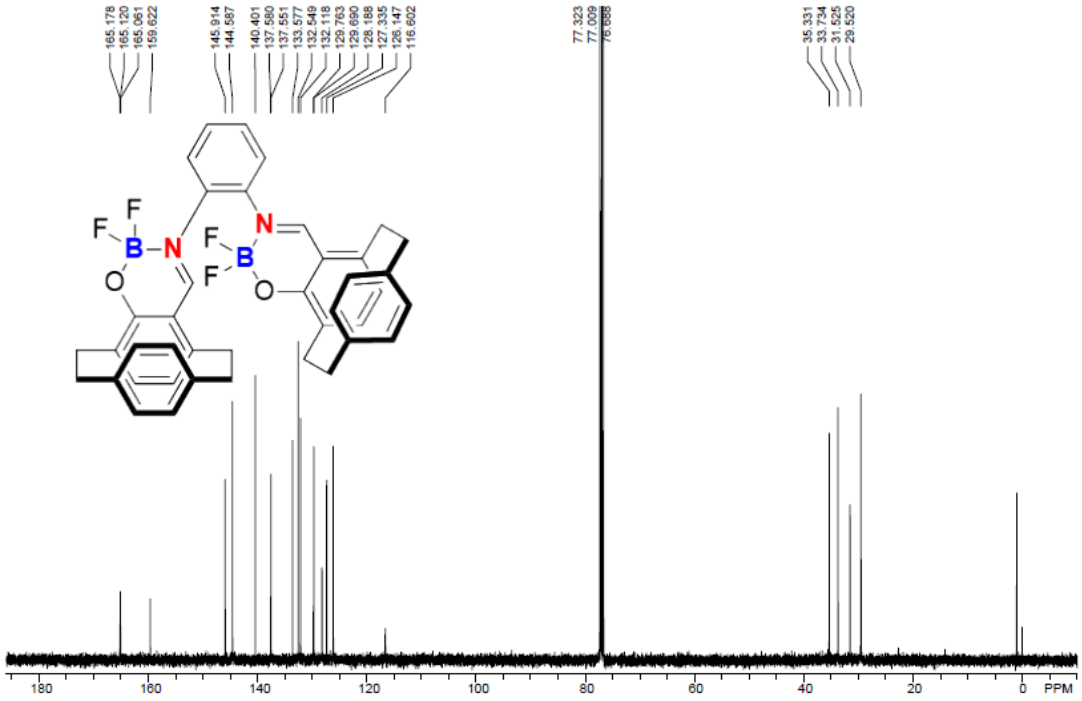
^{19}F NMR spectrum of (***S*$_P$)-4d** (376 MHz, $CDCl_3$)



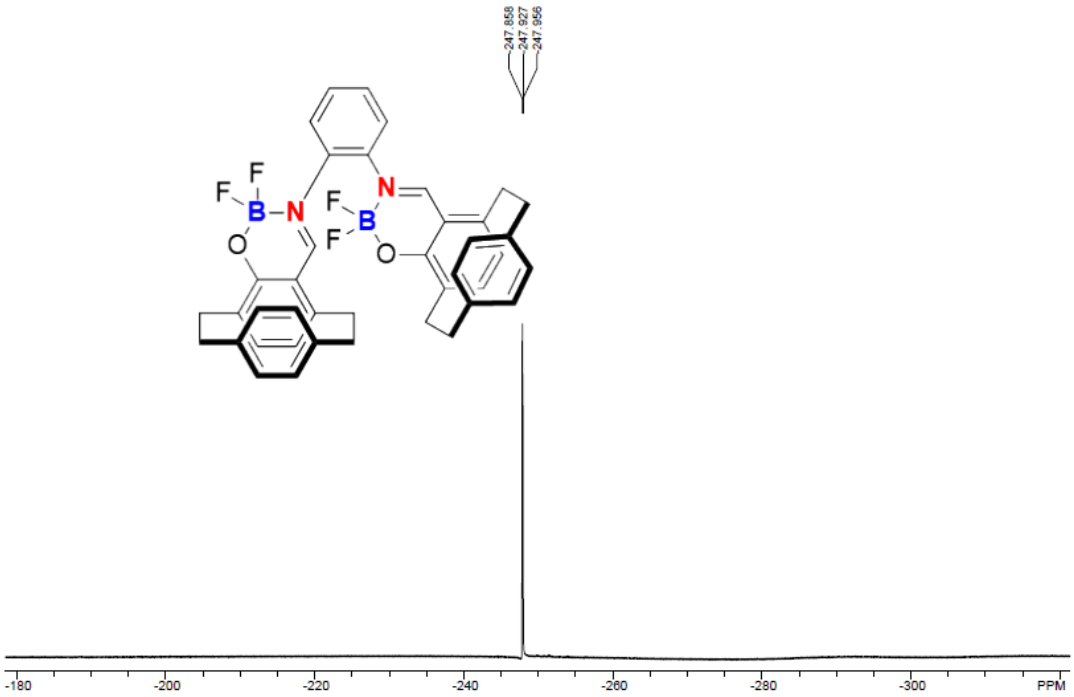
^{11}B NMR spectrum of (***S*$_P$)-4d** (160 MHz, $CDCl_3$)



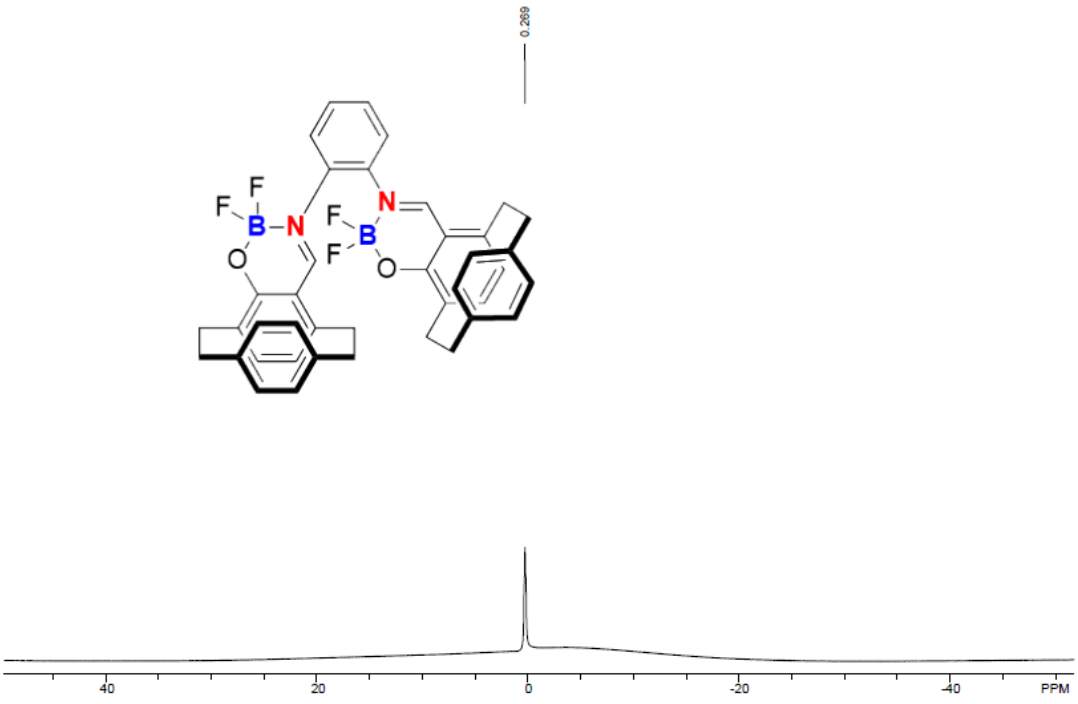
^{1}H NMR spectrum of (***S*$_P$)-4e** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of (***S*$_P$)-4e** (100 MHz, $CDCl_3$)



^{19}F NMR spectrum of (***S*$_P$)-4e** (376 MHz, $CDCl_3$)



^{11}B NMR spectrum of (***S*$_P$)-4e** (160 MHz, $CDCl_3$)