# Differentiation of enantiomeric anions by NMR spectroscopy with chiral bisurea receptors

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## 1. Determination of association constants by NMR titration

Association constants $K_1$ and $K_2$ of host–guest complexes is defined

$$H + G \overset{K_1}{\rightleftharpoons} HG$$

$$HG + G \overset{K_2}{\rightleftharpoons} HG_2$$

$$K_1 = \frac{[HG]}{[H][G]} \qquad K_2 = \frac{[HG_2]}{[HG][G]}$$

where [H], [G], [HG], and [$HG_2$] represent molar concentrations of the host, guest, 1:1 complex of host–guest, and 1:2 complex of host–guest, respectively.

The key equation for 1:2 equilibria is defined

$$\Delta\delta = \frac{\delta_{\Delta HG} K_1[G] + \delta_{\Delta HG_2} K_1 K_2 [G]^2}{1 + K_1[G] + K_1 K_2 [G]^2}$$

where $\Delta\delta$ represents the observed changes in the NMR chemical shift at a specific signal. $\Delta\delta_{HG}$ and $\Delta\delta_{HG2}$ are the variation of NMR chemical shift values of HG and $HG_2$ from that of the mixture of host and guest. The results were analysed by the nonlinear curve fitting program using Matlab.[1] Each titration experiments in $d_6$-acetone were carried out in triplicate. Titration experiments in $CDCl_3$ and $d_6$-DMSO were also carried out in duplicate and once, respectively. The results are summarized in Tables S1–S20 and Figs. S1–S10.

**Table S1.** Data tables for NMR titration of (*R*,*R*)-**2a** with (*R*)-TBAM in $d_6$-acetone.

**1st titration**

| $[(R)\text{-TBAM}]_0$ (mM) | $H_A$ (ppm) | $H_B$ (ppm) | $H_C$ (ppm) | $H_D$ (ppm) |
|---|---|---|---|---|
| 0.00 | 5.453 | 7.512 | 7.260 | 7.997 |
| 0.44 | 5.407 | 7.503 | 7.285 | 7.989 |
| 0.88 | 5.345 | 7.481 | 7.299 | 7.967 |
| 1.34 | 5.284 | 7.465 | 7.321 | 7.950 |
| 1.78 | 5.226 | 7.449 | 7.343 | 7.935 |
| 2.16 | 5.179 | 7.438 | 7.360 | 7.922 |
| 2.59 | 5.123 | 7.423 | 7.381 | 7.908 |
| 3.08 | 5.070 | 7.410 | 7.401 | 7.894 |
| 3.54 | 5.019 | 7.398 | 7.420 | 7.882 |
| 3.83 | 4.965 | 7.385 | 7.441 | 7.869 |
| 4.42 | 4.912 | 7.375 | 7.459 | 7.857 |
| 5.75 | 4.869 | 7.367 | 7.483 | 7.844 |
| 6.78 | 4.884 | 7.373 | 7.493 | 7.841 |
| 7.97 | 4.903 | 7.382 | 7.500 | 7.840 |
| 9.28 | 4.924 | 7.391 | 7.507 | 7.839 |
| 10.28 | 4.944 | 7.400 | 7.513 | 7.839 |
| 11.18 | 4.964 | 7.408 | 7.518 | 7.839 |
| 12.14 | 4.983 | 7.416 | 7.523 | 7.839 |
| 13.44 | 5.001 | 7.423 | 7.528 | 7.839 |
| 17.89 | 5.063 | 7.446 | 7.545 | 7.838 |
| 22.29 | 5.112 | 7.470 | 7.559 | 7.839 |
| 44.74 | 5.257 | 7.529 | 7.594 | 7.840 |
| 67.74 | 5.329 | 7.561 | 7.612 | 7.843 |
| 90.20 | 5.367 | 7.575 | 7.622 | 7.846 |
| 109.29 | 5.394 | 7.585 | 7.628 | 7.849 |

$[(R,R)\text{-}\mathbf{2a}]_0$ = 5.0 mM

**2nd titration**

| $[(R)\text{-TBAM}]_0$ (mM) | $H_A$ (ppm) | $H_B$ (ppm) | $H_C$ (ppm) | $H_D$ (ppm) |
|---|---|---|---|---|
| 0.00 | 5.455 | 7.514 | 7.254 | 7.999 |
| 0.51 | 5.386 | 7.494 | 7.278 | 7.980 |
| 1.00 | 5.318 | 7.475 | 7.303 | 7.961 |
| 1.44 | 5.253 | 7.457 | 7.327 | 7.944 |
| 1.96 | 5.183 | 7.438 | 7.353 | 7.926 |
| 2.49 | 5.121 | 7.422 | 7.376 | 7.910 |
| 3.03 | 5.061 | 7.408 | 7.399 | 7.894 |
| 3.43 | 5.002 | 7.393 | 7.421 | 7.880 |
| 4.07 | 4.943 | 7.378 | 7.445 | 7.865 |
| 4.43 | 4.895 | 7.367 | 7.464 | 7.853 |
| 4.98 | 4.873 | 7.362 | 7.477 | 7.846 |
| 6.22 | 4.865 | 7.365 | 7.492 | 7.839 |
| 7.40 | 4.890 | 7.373 | 7.501 | 7.838 |
| 8.66 | 4.915 | 7.384 | 7.509 | 7.837 |
| 9.81 | 4.939 | 7.398 | 7.515 | 7.837 |
| 11.00 | 4.963 | 7.408 | 7.522 | 7.837 |
| 12.31 | 4.985 | 7.417 | 7.528 | 7.837 |
| 13.61 | 5.006 | 7.426 | 7.533 | 7.836 |
| 14.78 | 5.026 | 7.433 | 7.539 | 7.837 |
| 19.93 | 5.091 | 7.461 | 7.555 | 7.836 |
| 24.51 | 5.141 | 7.482 | 7.569 | 7.837 |
| 47.10 | 5.280 | 7.539 | 7.604 | 7.839 |
| 73.11 | 5.344 | 7.565 | 7.619 | 7.842 |
| 98.87 | 5.378 | 7.580 | 7.627 | 7.845 |
| 130.50 | 5.404 | 7.590 | 7.632 | 7.848 |

$[(R,R)\text{-}\mathbf{2a}]_0$ = 5.0 mM

**3rd titration**

| $[(R)\text{-TBAM}]_0$ (mM) | $H_A$ (ppm) | $H_B$ (ppm) | $H_C$ (ppm) | $H_D$ (ppm) |
|---|---|---|---|---|
| 0.00 | 5.454 | 7.514 | 7.252 | 7.999 |
| 0.48 | 5.395 | 7.496 | 7.274 | 7.982 |
| 0.98 | 5.322 | 7.475 | 7.300 | 7.962 |
| 1.49 | 5.253 | 7.457 | 7.325 | 7.944 |
| 1.97 | 5.188 | 7.439 | 7.349 | 7.927 |
| 2.42 | 5.125 | 7.423 | 7.373 | 7.911 |
| 2.94 | 5.060 | 7.407 | 7.397 | 7.894 |
| 3.49 | 5.000 | 7.391 | 7.420 | 7.880 |
| 3.79 | 4.943 | 7.378 | 7.443 | 7.866 |
| 4.46 | 4.894 | 7.367 | 7.463 | 7.854 |
| 4.99 | 4.871 | 7.361 | 7.478 | 7.845 |
| 6.11 | 4.867 | 7.363 | 7.494 | 7.839 |
| 7.63 | 4.896 | 7.378 | 7.506 | 7.838 |
| 8.71 | 4.926 | 7.389 | 7.512 | 7.837 |
| 10.03 | 4.955 | 7.405 | 7.520 | 7.837 |
| 11.13 | 4.983 | 7.415 | 7.529 | 7.836 |
| 12.04 | 5.008 | 7.426 | 7.535 | 7.836 |
| 13.63 | 5.032 | 7.437 | 7.541 | 7.836 |
| 14.98 | 5.054 | 7.447 | 7.546 | 7.836 |
| 20.03 | 5.132 | 7.479 | 7.567 | 7.836 |
| 24.93 | 5.188 | 7.501 | 7.582 | 7.836 |
| 47.52 | 5.342 | 7.567 | 7.623 | 7.839 |
| 76.34 | 5.412 | 7.595 | 7.641 | 7.842 |
| 98.80 | 5.450 | 7.610 | 7.651 | 7.845 |
| 115.79 | 5.474 | 7.621 | 7.657 | 7.848 |

$[(R,R)\text{-}\mathbf{2a}]_0$ = 5.0 mM

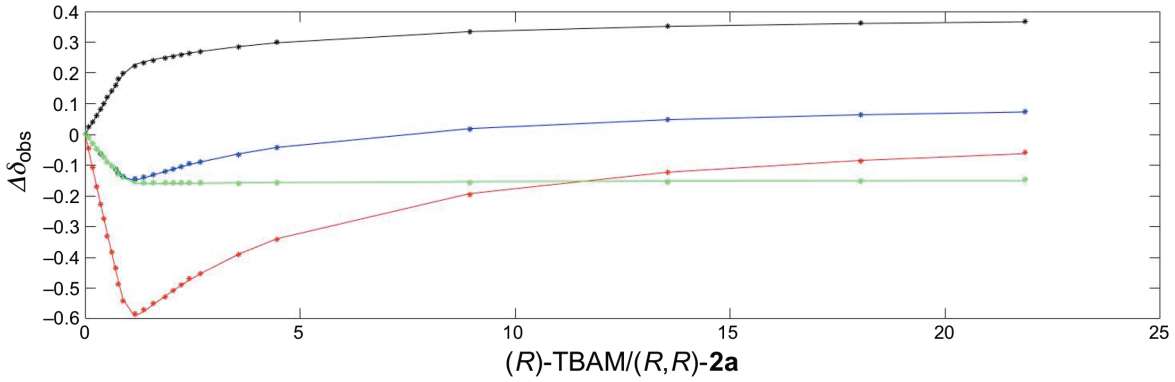



**Fig. S1** Typical fitted plots for the titration of (*R*,*R*)-**2a** with (*R*)-TBAM in $d_6$-acetone (1st titration).

**Table S2.** Association constants and error values obtained by curve-fitting analysis of NMR titration data of (*R*,*R*)-**2a** with (*R*)-TBAM in $d_6$-acetone.

| Entry | $K_1$ ($M^{-1}$) | $K_2$ ($M^{-1}$) | Standard error | Covariance of fit |
|---|---|---|---|---|
| 1st titration | 53423 | 48.7075 | 0.00392474 | 0.000278238 |
| 2nd titration | 31433.7 | 61.6698 | 0.00530838 | 0.000460578 |
| 3rd titration | 32621.2 | 62.92 | 0.00588963 | 0.000567245 |
| Average | $(3.9\pm1.4)\times10^4$ | $(5.8\pm0.9)\times10^1$ | | |

**Table S3.** Data tables for NMR titration of (*R*,*R*)-**2a** with (*S*)-TBAM in $d_6$-acetone.

**1st titration**

| $[(S)\text{-TBAM}]_0$ (mM) | $H_A$ (ppm) | $H_B$ (ppm) | $H_C$ (ppm) | $H_D$ (ppm) |
|---|---|---|---|---|
| 0.00 | 5.430 | 7.506 | 7.264 | 7.991 |
| 0.59 | 5.370 | 7.489 | 7.285 | 7.975 |
| 1.09 | 5.302 | 7.471 | 7.308 | 7.958 |
| 1.61 | 5.237 | 7.454 | 7.332 | 7.941 |
| 1.97 | 5.182 | 7.440 | 7.349 | 7.928 |
| 2.51 | 5.120 | 7.424 | 7.371 | 7.913 |
| 2.87 | 5.052 | 7.408 | 7.394 | 7.897 |
| 3.43 | 4.988 | 7.392 | 7.417 | 7.882 |
| 3.89 | 4.936 | 7.378 | 7.439 | 7.868 |
| 4.47 | 4.876 | 7.367 | 7.457 | 7.856 |
| 4.99 | 4.849 | 7.361 | 7.468 | 7.850 |
| 6.30 | 4.835 | 7.361 | 7.479 | 7.844 |
| 7.24 | 4.840 | 7.370 | 7.485 | 7.843 |
| 8.75 | 4.867 | 7.378 | 7.490 | 7.843 |
| 9.69 | 4.885 | 7.387 | 7.494 | 7.843 |
| 10.66 | 4.896 | 7.393 | 7.498 | 7.844 |
| 11.91 | 4.914 | 7.401 | 7.502 | 7.844 |
| 13.24 | 4.931 | 7.410 | 7.507 | 7.844 |
| 14.71 | 4.950 | 7.419 | 7.515 | 7.845 |
| 18.98 | 5.008 | 7.447 | 7.527 | 7.846 |
| 23.86 | 5.052 | 7.468 | 7.539 | 7.847 |
| 49.66 | 5.200 | 7.537 | 7.578 | 7.852 |
| 81.63 | 5.281 | 7.577 | 7.599 | 7.857 |
| 112.79 | 5.327 | 7.597 | 7.611 | 7.860 |
| 120.94 | 5.360 | 7.615 | 7.620 | 7.863 |

$[(R,R)\text{-}\mathbf{2a}]_0$ = 5.0 mM

**2nd titration**

| $[(S)\text{-TBAM}]_0$ (mM) | $H_A$ (ppm) | $H_B$ (ppm) | $H_C$ (ppm) | $H_D$ (ppm) |
|---|---|---|---|---|
| 0.00 | 5.451 | 7.512 | 7.256 | 7.997 |
| 0.48 | 5.387 | 7.494 | 7.278 | 7.980 |
| 1.01 | 5.316 | 7.475 | 7.302 | 7.961 |
| 1.48 | 5.249 | 7.457 | 7.324 | 7.944 |
| 2.00 | 5.183 | 7.440 | 7.348 | 7.928 |
| 2.56 | 5.118 | 7.424 | 7.370 | 7.912 |
| 3.14 | 5.052 | 7.407 | 7.393 | 7.897 |
| 3.63 | 4.988 | 7.392 | 7.416 | 7.881 |
| 4.12 | 4.927 | 7.378 | 7.437 | 7.868 |
| 4.61 | 4.875 | 7.366 | 7.456 | 7.856 |
| 5.14 | 4.843 | 7.359 | 7.469 | 7.848 |
| 6.52 | 4.835 | 7.361 | 7.479 | 7.844 |
| 7.56 | 4.840 | 7.370 | 7.485 | 7.843 |
| 8.60 | 4.868 | 7.379 | 7.490 | 7.843 |
| 9.74 | 4.886 | 7.388 | 7.495 | 7.843 |
| 11.42 | 4.905 | 7.397 | 7.500 | 7.844 |
| 12.73 | 4.921 | 7.405 | 7.504 | 7.844 |
| 13.58 | 4.938 | 7.413 | 7.508 | 7.844 |
| 15.47 | 4.953 | 7.420 | 7.513 | 7.845 |
| 19.30 | 5.009 | 7.447 | 7.527 | 7.846 |
| 25.68 | 5.053 | 7.468 | 7.543 | 7.847 |
| 49.08 | 5.200 | 7.537 | 7.578 | 7.852 |
| 80.48 | 5.281 | 7.578 | 7.599 | 7.857 |
| 110.62 | 5.327 | 7.598 | 7.611 | 7.860 |
| 126.94 | 5.357 | 7.614 | 7.619 | 7.863 |

$[(R,R)\text{-}\mathbf{2a}]_0$ = 5.0 mM

**3rd titration**

| $[(S)\text{-TBAM}]_0$ (mM) | $H_A$ (ppm) | $H_B$ (ppm) | $H_C$ (ppm) | $H_D$ (ppm) |
|---|---|---|---|---|
| 0.00 | 5.442 | 7.997 | 7.257 | 7.511 |
| 0.63 | 5.375 | 7.985 | 7.293 | 7.499 |
| 1.32 | 5.281 | 7.955 | 7.315 | 7.467 |
| 1.88 | 5.209 | 7.936 | 7.340 | 7.448 |
| 2.44 | 5.135 | 7.918 | 7.365 | 7.429 |
| 3.06 | 5.061 | 7.900 | 7.392 | 7.410 |
| 3.76 | 4.983 | 7.882 | 7.420 | 7.391 |
| 4.33 | 4.917 | 7.867 | 7.444 | 7.376 |
| 4.83 | 4.863 | 7.854 | 7.464 | 7.364 |
| 6.04 | 4.831 | 7.844 | 7.480 | 7.358 |
| 6.55 | 4.834 | 7.844 | 7.482 | 7.361 |
| 7.01 | 4.846 | 7.843 | 7.485 | 7.365 |
| 7.68 | 4.849 | 7.843 | 7.488 | 7.369 |
| 8.89 | 4.867 | 7.843 | 7.493 | 7.378 |
| 10.31 | 4.889 | 7.843 | 7.500 | 7.389 |
| 11.59 | 4.911 | 7.844 | 7.506 | 7.400 |
| 13.25 | 4.932 | 7.844 | 7.511 | 7.410 |
| 14.89 | 4.950 | 7.844 | 7.517 | 7.419 |
| 16.35 | 4.970 | 7.845 | 7.522 | 7.429 |
| 18.13 | 4.987 | 7.845 | 7.527 | 7.437 |
| 24.16 | 5.056 | 7.847 | 7.547 | 7.470 |
| 31.38 | 5.105 | 7.848 | 7.561 | 7.495 |
| 60.06 | 5.248 | 7.853 | 7.598 | 7.554 |
| 98.84 | 5.324 | 7.859 | 7.620 | 7.602 |
| 135.47 | 5.364 | 7.863 | 7.632 | 7.622 |
| 169.30 | 5.400 | 7.866 | 7.639 | 7.639 |

$[(R,R)\text{-}\mathbf{2a}]_0$ = 5.0 mM

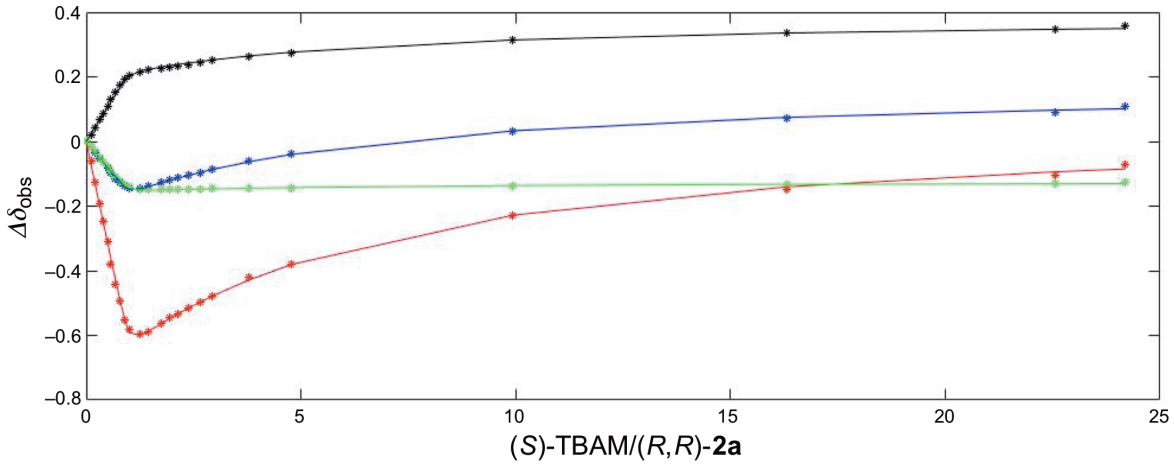



**Fig. S2** Typical fitted plots for the titration of (*R*,*R*)-**2a** with (*S*)-TBAM in $d_6$-acetone (1st titration).

**Table S4.** Association constants and error values obtained by curve-fitting analysis of NMR titration data of (*R*,*R*)-**2a** with (*S*)-TBAM in $d_6$-acetone.

| Entry | $K_1$ ($M^{-1}$) | $K_2$ ($M^{-1}$) | Standard error | Covariance of fit |
|---|---|---|---|---|
| 1st titration | 59506.7 | 33.8721 | 0.00525521 | 0.000469976 |
| 2nd titration | 44156.5 | 32.004 | 0.00346843 | 0.000188417 |
| 3rd titration | 35789.9 | 30.0576 | 0.00372195 | 0.000205844 |
| Average | $(4.7\pm1.3)\times10^4$ | $(3.2\pm0.2)\times10^1$ | | |

**Table S5.** Data tables for NMR titration of (*R*,*R*)-**2b** with (*R*)-TBAM in $d_6$-acetone.

**1st titration**

| $[(R)\text{-TBAM}]_0$ (mM) | $H_A$ (ppm) | $H_B$ (ppm) | $H_C$ (ppm) | $H_D$ (ppm) |
|---|---|---|---|---|
| 0.00 | 6.224 | 7.524 | 7.354 | 8.019 |
| 0.45 | 6.142 | 7.512 | 7.398 | 8.001 |
| 1.02 | 6.036 | 7.497 | 7.447 | 7.980 |
| 1.52 | 5.936 | 7.481 | 7.493 | 7.960 |
| 2.11 | 5.835 | 7.466 | 7.541 | 7.940 |
| 2.53 | 5.744 | 7.454 | 7.587 | 7.922 |
| 3.07 | 5.647 | 7.438 | 7.635 | 7.903 |
| 3.49 | 5.556 | 7.424 | 7.680 | 7.885 |
| 4.22 | 5.463 | 7.410 | 7.725 | 7.866 |
| 4.52 | 5.392 | 7.400 | 7.761 | 7.853 |
| 5.03 | 5.375 | 7.398 | 7.776 | 7.847 |
| 5.88 | 5.406 | 7.406 | 7.788 | 7.844 |
| 7.46 | 5.458 | 7.417 | 7.798 | 7.841 |
| 8.93 | 5.509 | 7.428 | 7.807 | 7.841 |
| 9.89 | 5.557 | 7.438 | 7.815 | 7.839 |
| 11.67 | 5.600 | 7.447 | 7.828 | 7.837 |
| 12.01 | 5.639 | 7.455 | 7.830 | 7.838 |
| 13.43 | 5.678 | 7.463 | 7.837 | 7.837 |
| 14.75 | 5.715 | 7.471 | 7.844 | 7.836 |
| 20.99 | 5.826 | 7.494 | 7.864 | 7.835 |
| 25.36 | 5.906 | 7.511 | 7.878 | 7.834 |
| 47.49 | 6.112 | 7.548 | 7.917 | 7.834 |
| 74.63 | 6.198 | 7.573 | 7.934 | 7.836 |
| 97.46 | 6.242 | 7.581 | 7.942 | 7.838 |
| 127.05 | 6.271 | 7.587 | 7.948 | 7.840 |

$[(R,R)\text{-}\mathbf{2b}]_0$ = 5.0 mM

**2nd titration**

| $[(R)\text{-TBAM}]_0$ (mM) | $H_A$ (ppm) | $H_B$ (ppm) | $H_C$ (ppm) | $H_D$ (ppm) |
|---|---|---|---|---|
| 0.00 | 6.219 | 7.524 | 7.360 | 8.017 |
| 0.49 | 6.130 | 7.510 | 7.401 | 7.999 |
| 0.96 | 6.036 | 7.496 | 7.444 | 7.981 |
| 1.38 | 5.954 | 7.485 | 7.485 | 7.964 |
| 1.98 | 5.859 | 7.470 | 7.532 | 7.945 |
| 2.34 | 5.774 | 7.457 | 7.574 | 7.927 |
| 2.90 | 5.678 | 7.442 | 7.619 | 7.909 |
| 3.36 | 5.589 | 7.429 | 7.661 | 7.892 |
| 3.72 | 5.509 | 7.417 | 7.702 | 7.876 |
| 4.25 | 5.420 | 7.404 | 7.747 | 7.858 |
| 4.65 | 5.376 | 7.398 | 7.770 | 7.849 |
| 5.08 | 5.371 | 7.398 | 7.779 | 7.846 |
| 5.58 | 5.383 | 7.401 | 7.784 | 7.844 |
| 5.96 | 5.398 | 7.404 | 7.787 | 7.844 |
| 6.90 | 5.436 | 7.412 | 7.795 | 7.842 |
| 8.18 | 5.483 | 7.422 | 7.803 | 7.841 |
| 9.24 | 5.531 | 7.431 | 7.812 | 7.840 |
| 10.26 | 5.573 | 7.441 | 7.819 | 7.837 |
| 11.42 | 5.615 | 7.450 | 7.825 | 7.837 |
| 13.19 | 5.653 | 7.457 | 7.833 | 7.836 |
| 14.15 | 5.688 | 7.465 | 7.837 | 7.837 |
| 18.19 | 5.798 | 7.488 | 7.859 | 7.835 |
| 23.25 | 5.881 | 7.506 | 7.874 | 7.834 |
| 47.83 | 6.095 | 7.549 | 7.913 | 7.833 |
| 71.42 | 6.187 | 7.571 | 7.931 | 7.835 |
| 98.09 | 6.233 | 7.579 | 7.940 | 7.837 |
| 126.97 | 6.261 | 7.586 | 7.946 | 7.839 |

$[(R,R)\text{-}\mathbf{2b}]_0$ = 5.0 mM

**3rd titration**

| $[(R)\text{-TBAM}]_0$ (mM) | $H_A$ (ppm) | $H_B$ (ppm) | $H_C$ (ppm) | $H_D$ (ppm) |
|---|---|---|---|---|
| 0.00 | 6.234 | 7.525 | 7.353 | 8.018 |
| 0.44 | 6.137 | 7.512 | 7.399 | 8.000 |
| 1.09 | 6.036 | 7.496 | 7.448 | 7.978 |
| 1.57 | 5.938 | 7.483 | 7.494 | 7.959 |
| 2.16 | 5.825 | 7.465 | 7.551 | 7.937 |
| 2.82 | 5.714 | 7.448 | 7.604 | 7.915 |
| 3.31 | 5.622 | 7.434 | 7.650 | 7.896 |
| 3.79 | 5.527 | 7.421 | 7.695 | 7.878 |
| 4.38 | 5.449 | 7.409 | 7.734 | 7.863 |
| 5.05 | 5.390 | 7.400 | 7.766 | 7.851 |
| 5.64 | 5.379 | 7.399 | 7.777 | 7.846 |
| 6.76 | 5.390 | 7.402 | 7.783 | 7.845 |
| 7.08 | 5.404 | 7.405 | 7.786 | 7.843 |
| 7.81 | 5.422 | 7.409 | 7.789 | 7.843 |
| 8.29 | 5.459 | 7.417 | 7.796 | 7.844 |
| 10.03 | 5.503 | 7.426 | 7.805 | 7.841 |
| 10.81 | 5.545 | 7.435 | 7.812 | 7.840 |
| 12.40 | 5.582 | 7.443 | 7.819 | 7.837 |
| 13.98 | 5.619 | 7.451 | 7.827 | 7.837 |
| 15.26 | 5.653 | 7.458 | 7.832 | 7.837 |
| 17.65 | 5.688 | 7.464 | 7.838 | 7.837 |
| 21.61 | 5.795 | 7.488 | 7.858 | 7.836 |
| 26.81 | 5.878 | 7.506 | 7.873 | 7.834 |
| 54.95 | 6.095 | 7.550 | 7.916 | 7.834 |
| 82.79 | 6.192 | 7.574 | 7.936 | 7.836 |
| 106.93 | 6.244 | 7.585 | 7.949 | 7.838 |
| 143.82 | 6.275 | 7.592 | 7.952 | 7.839 |

$[(R,R)\text{-}\mathbf{2b}]_0$ = 5.0 mM

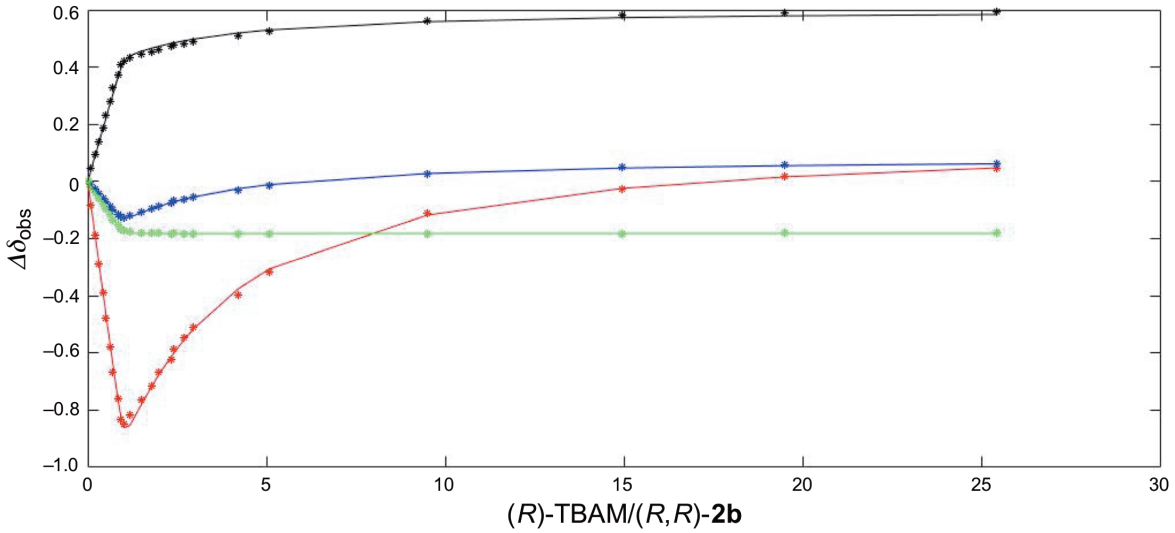



**Fig. S3** Typical fitted plots for the titration of (*R*,*R*)-**2b** with (*R*)-TBAM in $d_6$-acetone (1st titration).

**Table S6.** Association constants and error values obtained by curve-fitting analysis of NMR titration data of (*R*,*R*)-**2b** with (*R*)-TBAM in $d_6$-acetone.

| Entry | $K_1$ ($M^{-1}$) | $K_2$ ($M^{-1}$) | Standard error | Covariance of fit |
|---|---|---|---|---|
| 1st titration | 110315 | 75.4396 | 0.00967604 | 0.000715052 |
| 2nd titration | 105945 | 81.2486 | 0.0103111 | 0.000793198 |
| 3rd titration | 47210.3 | 52.3694 | 0.00710802 | 0.00035455 |
| Average | $(8.8\pm5.0)\times10^4$ | $(7.0\pm1.8)\times10^1$ | | |

**Table S7.** Data tables for NMR titration of (*R*,*R*)-**2b** with (*S*)-TBAM in $d_6$-acetone.

**1st titration**

| $[(S)\text{-TBAM}]_0$ (mM) | $H_A$ (ppm) | $H_B$ (ppm) | $H_C$ (ppm) | $H_D$ (ppm) |
|---|---|---|---|---|
| 0.00 | 6.212 | 7.523 | 7.366 | 8.016 |
| 0.50 | 6.130 | 7.512 | 7.399 | 8.000 |
| 1.01 | 6.043 | 7.499 | 7.438 | 7.982 |
| 1.43 | 5.956 | 7.488 | 7.475 | 7.965 |
| 1.94 | 5.874 | 7.475 | 7.515 | 7.948 |
| 2.49 | 5.792 | 7.462 | 7.553 | 7.932 |
| 3.09 | 5.703 | 7.450 | 7.591 | 7.915 |
| 3.28 | 5.618 | 7.440 | 7.629 | 7.898 |
| 4.06 | 5.533 | 7.426 | 7.668 | 7.881 |
| 4.38 | 5.457 | 7.416 | 7.702 | 7.867 |
| 4.81 | 5.428 | 7.412 | 7.716 | 7.860 |
| 5.98 | 5.430 | 7.415 | 7.728 | 7.856 |
| 7.68 | 5.456 | 7.425 | 7.736 | 7.856 |
| 8.84 | 5.495 | 7.432 | 7.743 | 7.855 |
| 9.84 | 5.527 | 7.441 | 7.750 | 7.854 |
| 11.43 | 5.557 | 7.448 | 7.757 | 7.854 |
| 13.06 | 5.587 | 7.457 | 7.764 | 7.853 |
| 13.47 | 5.615 | 7.464 | 7.771 | 7.853 |
| 14.21 | 5.641 | 7.471 | 7.777 | 7.853 |
| 20.56 | 5.734 | 7.495 | 7.800 | 7.853 |
| 23.86 | 5.805 | 7.514 | 7.816 | 7.852 |
| 45.19 | 6.007 | 7.564 | 7.866 | 7.852 |
| 70.17 | 6.104 | 7.593 | 7.890 | 7.854 |
| 84.58 | 6.155 | 7.605 | 7.904 | 7.856 |
| 150.11 | 6.187 | 7.614 | 7.912 | 7.858 |

$[(R,R)\text{-}\mathbf{2b}]_0$ = 5.0 mM

**2nd titration**

| $[(S)\text{-TBAM}]_0$ (mM) | $H_A$ (ppm) | $H_B$ (ppm) | $H_C$ (ppm) | $H_D$ (ppm) |
|---|---|---|---|---|
| 0.00 | 6.219 | 7.523 | 7.360 | 8.017 |
| 0.49 | 6.139 | 7.512 | 7.396 | 8.001 |
| 1.01 | 6.055 | 7.499 | 7.434 | 7.984 |
| 1.40 | 5.966 | 7.488 | 7.472 | 7.967 |
| 1.93 | 5.890 | 7.475 | 7.507 | 7.951 |
| 2.41 | 5.809 | 7.462 | 7.544 | 7.935 |
| 2.87 | 5.716 | 7.450 | 7.585 | 7.917 |
| 3.35 | 5.632 | 7.440 | 7.624 | 7.900 |
| 3.88 | 5.550 | 7.426 | 7.660 | 7.885 |
| 4.14 | 5.483 | 7.416 | 7.690 | 7.872 |
| 4.88 | 5.430 | 7.412 | 7.714 | 7.861 |
| 5.71 | 5.427 | 7.415 | 7.726 | 7.857 |
| 7.79 | 5.462 | 7.425 | 7.734 | 7.855 |
| 8.48 | 5.495 | 7.432 | 7.742 | 7.855 |
| 9.90 | 5.528 | 7.441 | 7.750 | 7.854 |
| 10.81 | 5.561 | 7.448 | 7.758 | 7.854 |
| 11.69 | 5.588 | 7.457 | 7.764 | 7.854 |
| 13.00 | 5.615 | 7.464 | 7.771 | 7.853 |
| 14.25 | 5.642 | 7.471 | 7.777 | 7.853 |
| 22.34 | 5.802 | 7.514 | 7.816 | 7.852 |
| 43.09 | 6.005 | 7.564 | 7.867 | 7.852 |
| 66.49 | 6.102 | 7.593 | 7.890 | 7.854 |
| 85.23 | 6.153 | 7.605 | 7.903 | 7.856 |
| 148.24 | 6.186 | 7.614 | 7.912 | 7.858 |

$[(R,R)\text{-}\mathbf{2b}]_0$ = 5.0 mM

**3rd titration**

| $[(S)\text{-TBAM}]_0$ (mM) | $H_A$ (ppm) | $H_B$ (ppm) | $H_C$ (ppm) | $H_D$ (ppm) |
|---|---|---|---|---|
| 0.00 | 6.202 | 7.522 | 7.370 | 8.014 |
| 0.51 | 6.123 | 7.511 | 7.404 | 7.998 |
| 1.01 | 6.031 | 7.497 | 7.445 | 7.981 |
| 1.59 | 5.942 | 7.485 | 7.485 | 7.963 |
| 2.11 | 5.850 | 7.472 | 7.525 | 7.945 |
| 2.56 | 5.774 | 7.461 | 7.562 | 7.929 |
| 3.09 | 5.680 | 7.447 | 7.604 | 7.911 |
| 3.46 | 5.608 | 7.438 | 7.637 | 7.897 |
| 4.13 | 5.530 | 7.426 | 7.671 | 7.882 |
| 4.39 | 5.456 | 7.416 | 7.705 | 7.868 |
| 5.02 | 5.426 | 7.412 | 7.729 | 7.867 |
| 5.55 | 5.427 | 7.412 | 7.734 | 7.865 |
| 5.98 | 5.429 | 7.415 | 7.730 | 7.857 |
| 6.53 | 5.442 | 7.418 | 7.733 | 7.857 |
| 7.59 | 5.472 | 7.426 | 7.740 | 7.856 |
| 8.89 | 5.507 | 7.436 | 7.748 | 7.856 |
| 10.07 | 5.541 | 7.445 | 7.756 | 7.855 |
| 10.80 | 5.573 | 7.454 | 7.764 | 7.855 |
| 12.34 | 5.631 | 7.470 | 7.777 | 7.854 |
| 15.08 | 5.659 | 7.476 | 7.783 | 7.854 |
| 19.79 | 5.750 | 7.503 | 7.805 | 7.853 |
| 22.95 | 5.818 | 7.519 | 7.821 | 7.853 |
| 52.21 | 6.021 | 7.571 | 7.870 | 7.854 |
| 71.64 | 6.116 | 7.598 | 7.894 | 7.855 |
| 111.39 | 6.166 | 7.610 | 7.907 | 7.858 |
| 122.93 | 6.196 | 7.616 | 7.914 | 7.858 |

$[(R,R)\text{-}\mathbf{2b}]_0$ = 5.0 mM

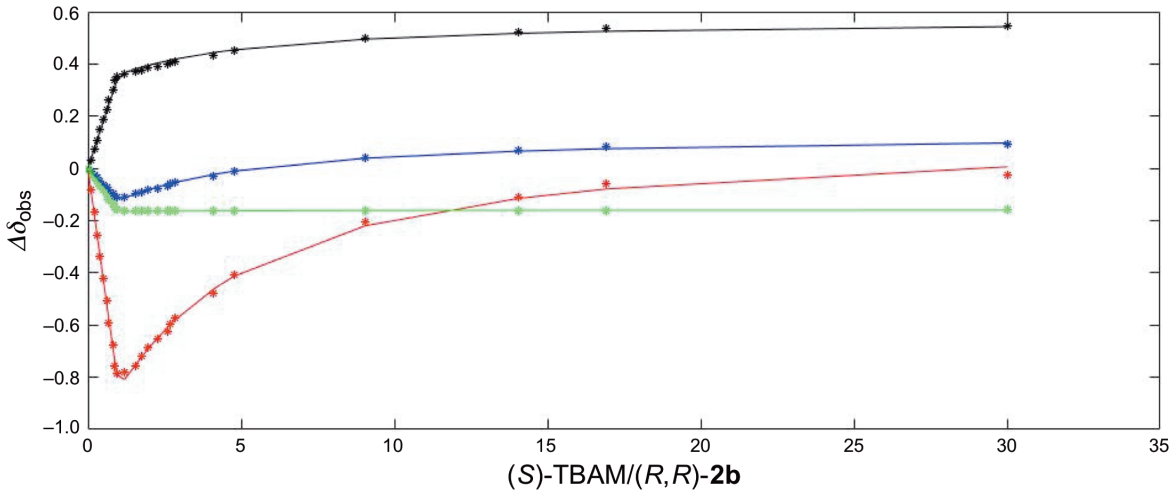



**Fig. S4** Typical fitted plots for the titration of (*R*,*R*)-**2b** with (*S*)-TBAM in $d_6$-acetone (1st titration).

**Table S8.** Association constants and error values obtained by curve-fitting analysis of NMR titration data of (*R*,*R*)-**2b** with (*S*)-TBAM in $d_6$-acetone.

| Entry | $K_1$ ($M^{-1}$) | $K_2$ ($M^{-1}$) | Standard error | Covariance of fit |
|---|---|---|---|---|
| 1st titration | 138013 | 48.6614 | 0.0100559 | 0.000905094 |
| 2nd titration | 70047.6 | 58.4541 | 0.00925406 | 0.000757775 |
| 3rd titration | 119420 | 53.515 | 0.00823091 | 0.00059642 |
| Average | $(1.1\pm0.4)\times10^5$ | $(5.4\pm0.6)\times10^1$ | | |

**Table S9.** Data tables for NMR titration of (*R*,*R*)-**2c** with (*R*)-TBAM in $d_6$-acetone.

**1st titration**

| $[(R)\text{-TBAM}]_0$ (mM) | $H_A$ (ppm) | $H_B$ (ppm) | $H_C$ (ppm) | $H_D$ (ppm) |
|---|---|---|---|---|
| 0.00 | 5.222 | 7.446 | 7.714 | 8.035 |
| 0.49 | 5.180 | 7.428 | 7.720 | 8.014 |
| 1.07 | 5.120 | 7.404 | 7.729 | 7.990 |
| 1.62 | 5.064 | 7.384 | 7.737 | 7.968 |
| 2.16 | 4.988 | 7.359 | 7.747 | 7.944 |
| 2.69 | 4.927 | 7.340 | 7.754 | 7.924 |
| 2.96 | 4.861 | 7.319 | 7.763 | 7.902 |
| 3.57 | 4.796 | 7.297 | 7.771 | 7.881 |
| 4.36 | 4.744 | 7.280 | 7.777 | 7.863 |
| 4.84 | 4.728 | 7.272 | 7.778 | 7.853 |
| 5.29 | 4.742 | 7.272 | 7.777 | 7.848 |
| 7.32 | 4.813 | 7.279 | 7.768 | 7.842 |
| 7.83 | 4.886 | 7.290 | 7.760 | 7.839 |
| 9.36 | 4.968 | 7.299 | 7.755 | 7.836 |
| 11.34 | 5.017 | 7.307 | 7.750 | 7.834 |
| 12.10 | 5.061 | 7.314 | 7.747 | 7.832 |
| 14.17 | 5.095 | 7.319 | 7.744 | 7.831 |
| 15.81 | 5.118 | 7.323 | 7.742 | 7.830 |
| 17.23 | 5.138 | 7.327 | 7.741 | 7.829 |
| 20.86 | 5.191 | 7.337 | 7.738 | 7.827 |
| 28.68 | 5.216 | 7.342 | 7.737 | 7.826 |
| 48.18 | 5.255 | 7.353 | 7.738 | 7.827 |
| 83.74 | 5.265 | 7.359 | 7.741 | 7.830 |
| 103.32 | 5.270 | 7.361 | 7.744 | 7.832 |
| 146.31 | 5.271 | 7.362 | 7.746 | 7.834 |

$[(R,R)\text{-}\mathbf{2c}]_0$ = 5.0 mM

**2nd titration**

| $[(R)\text{-TBAM}]_0$ (mM) | $H_A$ (ppm) | $H_B$ (ppm) | $H_C$ (ppm) | $H_D$ (ppm) |
|---|---|---|---|---|
| 0.00 | 5.226 | 8.035 | 7.713 | 7.447 |
| 0.47 | 5.187 | 8.016 | 7.720 | 7.428 |
| 1.05 | 5.127 | 7.993 | 7.729 | 7.407 |
| 1.56 | 5.068 | 7.971 | 7.737 | 7.386 |
| 1.98 | 5.008 | 7.951 | 7.745 | 7.366 |
| 2.52 | 4.947 | 7.931 | 7.752 | 7.346 |
| 3.06 | 4.891 | 7.913 | 7.759 | 7.327 |
| 3.29 | 4.825 | 7.895 | 7.768 | 7.308 |
| 3.73 | 4.807 | 7.886 | 7.770 | 7.301 |
| 4.59 | 4.735 | 7.862 | 7.778 | 7.277 |
| 5.41 | 4.723 | 7.852 | 7.779 | 7.269 |
| 5.86 | 4.740 | 7.847 | 7.777 | 7.269 |
| 6.36 | 4.773 | 7.845 | 7.773 | 7.273 |
| 7.82 | 4.846 | 7.841 | 7.766 | 7.283 |
| 9.10 | 4.933 | 7.837 | 7.758 | 7.295 |
| 10.13 | 4.989 | 7.835 | 7.753 | 7.303 |
| 12.46 | 5.038 | 7.833 | 7.749 | 7.311 |
| 13.51 | 5.074 | 7.831 | 7.746 | 7.317 |
| 14.75 | 5.100 | 7.830 | 7.744 | 7.321 |
| 21.21 | 5.183 | 7.827 | 7.739 | 7.336 |
| 26.43 | 5.212 | 7.826 | 7.738 | 7.342 |
| 52.84 | 5.255 | 7.827 | 7.739 | 7.354 |
| 75.86 | 5.266 | 7.830 | 7.742 | 7.359 |
| 102.89 | 5.269 | 7.832 | 7.744 | 7.362 |
| 122.62 | 5.272 | 7.834 | 7.747 | 7.363 |

$[(R,R)\text{-}\mathbf{2c}]_0$ = 5.0 mM

**3rd titration**

| $[(R)\text{-TBAM}]_0$ (mM) | $H_A$ (ppm) | $H_B$ (ppm) | $H_C$ (ppm) | $H_D$ (ppm) |
|---|---|---|---|---|
| 0.00 | 5.230 | 7.447 | 7.713 | 8.036 |
| 0.50 | 5.185 | 7.431 | 7.720 | 8.017 |
| 0.96 | 5.140 | 7.412 | 7.727 | 7.997 |
| 1.49 | 5.081 | 7.391 | 7.735 | 7.975 |
| 2.00 | 5.023 | 7.370 | 7.743 | 7.956 |
| 2.37 | 4.968 | 7.352 | 7.751 | 7.937 |
| 2.94 | 4.903 | 7.331 | 7.758 | 7.917 |
| 3.58 | 4.846 | 7.312 | 7.766 | 7.897 |
| 4.06 | 4.788 | 7.293 | 7.772 | 7.878 |
| 4.38 | 4.749 | 7.279 | 7.778 | 7.864 |
| 5.05 | 4.730 | 7.272 | 7.780 | 7.853 |
| 5.42 | 4.742 | 7.270 | 7.778 | 7.849 |
| 5.92 | 4.766 | 7.273 | 7.775 | 7.845 |
| 6.63 | 4.799 | 7.277 | 7.772 | 7.843 |
| 8.61 | 4.854 | 7.285 | 7.766 | 7.840 |
| 9.11 | 4.921 | 7.295 | 7.760 | 7.838 |
| 10.48 | 4.986 | 7.304 | 7.755 | 7.835 |
| 12.68 | 5.030 | 7.311 | 7.752 | 7.833 |
| 13.41 | 5.068 | 7.318 | 7.749 | 7.833 |
| 13.96 | 5.095 | 7.322 | 7.747 | 7.831 |
| 15.08 | 5.120 | 7.326 | 7.746 | 7.831 |
| 19.95 | 5.179 | 7.337 | 7.742 | 7.829 |
| 28.96 | 5.208 | 7.343 | 7.740 | 7.827 |
| 59.10 | 5.252 | 7.356 | 7.740 | 7.828 |
| 79.99 | 5.269 | 7.361 | 7.744 | 7.831 |
| 105.19 | 5.273 | 7.365 | 7.747 | 7.834 |
| 119.10 | 5.274 | 7.367 | 7.749 | 7.837 |

$[(R,R)\text{-}\mathbf{2c}]_0$ = 5.0 mM

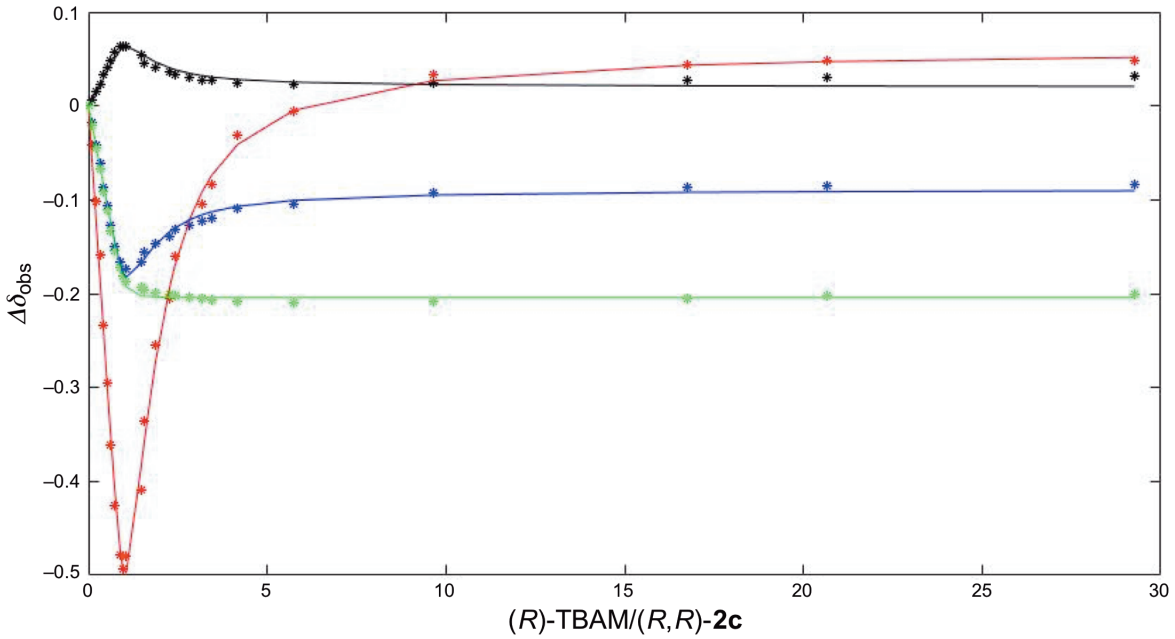



**Fig. S5** Typical fitted plots for the titration of (*R*,*R*)-**2c** with (*R*)-TBAM in $d_6$-acetone (1st titration).

**Table S10.** Association constants and error values obtained by curve-fitting analysis of NMR titration data of (*R*,*R*)-**2c** with (*R*)-TBAM in $d_6$-acetone.

| Entry | $K_1$ ($M^{-1}$) | $K_2$ ($M^{-1}$) | Standard error | Covariance of fit |
|---|---|---|---|---|
| 1st titration | 80974.9 | 445.198 | 0.00894311 | 0.00427439 |
| 2nd titration | 112884 | 382.6 | 0.00696565 | 0.00235563 |
| 3rd titration | 90421.5 | 332.219 | 0.00811029 | 0.00316993 |
| Average | $(9.5\pm1.9)\times10^4$ | $(3.9\pm0.7)\times10^2$ | | |

**Table S11.** Data tables for NMR titration of (*R*,*R*)-**2c** with (*S*)-TBAM in $d_6$-acetone.

**1st titration**

| $[(S)\text{-TBAM}]_0$ (mM) | $H_A$ (ppm) | $H_B$ (ppm) | $H_C$ (ppm) | $H_D$ (ppm) |
|---|---|---|---|---|
| 0.00 | 5.231 | 8.038 | 7.712 | 7.448 |
| 0.43 | 5.194 | 8.020 | 7.718 | 7.433 |
| 0.89 | 5.144 | 8.002 | 7.725 | 7.415 |
| 1.32 | 5.099 | 7.985 | 7.731 | 7.396 |
| 1.75 | 5.041 | 7.968 | 7.738 | 7.379 |
| 2.35 | 4.988 | 7.950 | 7.744 | 7.362 |
| 2.68 | 4.929 | 7.932 | 7.752 | 7.343 |
| 3.19 | 4.875 | 7.916 | 7.757 | 7.326 |
| 3.58 | 4.821 | 7.899 | 7.764 | 7.306 |
| 4.08 | 4.768 | 7.883 | 7.770 | 7.303 |
| 4.57 | 4.729 | 7.870 | 7.774 | 7.300 |
| 5.69 | 4.731 | 7.856 | 7.772 | 7.283 |
| 7.67 | 4.793 | 7.852 | 7.766 | 7.277 |
| 7.82 | 4.865 | 7.848 | 7.760 | 7.286 |
| 9.47 | 4.915 | 7.846 | 7.755 | 7.294 |
| 9.72 | 4.969 | 7.843 | 7.752 | 7.302 |
| 11.02 | 5.007 | 7.841 | 7.749 | 7.308 |
| 13.13 | 5.041 | 7.839 | 7.747 | 7.313 |
| 14.40 | 5.068 | 7.838 | 7.745 | 7.318 |
| 17.94 | 5.138 | 7.835 | 7.742 | 7.330 |
| 22.22 | 5.175 | 7.833 | 7.740 | 7.338 |
| 44.38 | 5.237 | 7.831 | 7.741 | 7.353 |
| 61.28 | 5.253 | 7.833 | 7.744 | 7.360 |
| 88.32 | 5.260 | 7.833 | 7.747 | 7.362 |
| 112.82 | 5.264 | 7.834 | 7.749 | 7.364 |

$[(R,R)\text{-}\mathbf{2c}]_0$ = 5.0 mM

**2nd titration**

| $[(S)\text{-TBAM}]_0$ (mM) | $H_A$ (ppm) | $H_B$ (ppm) | $H_C$ (ppm) | $H_D$ (ppm) |
|---|---|---|---|---|
| 0.00 | 5.226 | 8.034 | 7.714 | 7.445 |
| 0.48 | 5.185 | 8.016 | 7.720 | 7.429 |
| 1.12 | 5.131 | 7.996 | 7.727 | 7.409 |
| 1.49 | 5.075 | 7.977 | 7.734 | 7.390 |
| 2.04 | 5.012 | 7.957 | 7.742 | 7.369 |
| 2.57 | 4.957 | 7.939 | 7.748 | 7.352 |
| 2.81 | 4.934 | 7.932 | 7.751 | 7.343 |
| 3.19 | 4.878 | 7.915 | 7.757 | 7.325 |
| 3.66 | 4.816 | 7.897 | 7.764 | 7.304 |
| 4.19 | 4.766 | 7.881 | 7.770 | 7.303 |
| 4.94 | 4.722 | 7.867 | 7.774 | 7.299 |
| 6.33 | 4.744 | 7.855 | 7.771 | 7.279 |
| 7.37 | 4.812 | 7.851 | 7.764 | 7.278 |
| 9.41 | 4.880 | 7.847 | 7.758 | 7.287 |
| 10.71 | 4.934 | 7.845 | 7.753 | 7.296 |
| 11.94 | 4.983 | 7.842 | 7.750 | 7.303 |
| 13.33 | 5.021 | 7.840 | 7.748 | 7.310 |
| 13.35 | 5.052 | 7.839 | 7.746 | 7.315 |
| 15.58 | 5.079 | 7.838 | 7.745 | 7.319 |
| 23.08 | 5.146 | 7.835 | 7.741 | 7.332 |
| 25.91 | 5.177 | 7.833 | 7.740 | 7.338 |
| 47.90 | 5.236 | 7.831 | 7.741 | 7.353 |
| 76.92 | 5.253 | 7.832 | 7.744 | 7.359 |
| 108.67 | 5.259 | 7.833 | 7.747 | 7.362 |
| 117.81 | 5.263 | 7.834 | 7.749 | 7.365 |

$[(R,R)\text{-}\mathbf{2c}]_0$ = 5.0 mM

**3rd titration**

| $[(S)\text{-TBAM}]_0$ (mM) | $H_A$ (ppm) | $H_B$ (ppm) | $H_C$ (ppm) | $H_D$ (ppm) |
|---|---|---|---|---|
| 0.00 | 5.221 | 8.034 | 7.714 | 7.445 |
| 0.64 | 5.170 | 8.010 | 7.721 | 7.424 |
| 1.27 | 5.099 | 7.985 | 7.731 | 7.398 |
| 1.93 | 5.032 | 7.963 | 7.740 | 7.376 |
| 2.63 | 4.957 | 7.940 | 7.749 | 7.350 |
| 3.38 | 4.892 | 7.917 | 7.757 | 7.326 |
| 3.81 | 4.816 | 7.894 | 7.766 | 7.302 |
| 4.38 | 4.760 | 7.876 | 7.772 | 7.297 |
| 5.18 | 4.730 | 7.863 | 7.776 | 7.293 |
| 5.83 | 4.739 | 7.858 | 7.773 | 7.281 |
| 6.49 | 4.769 | 7.854 | 7.770 | 7.272 |
| 7.24 | 4.803 | 7.853 | 7.767 | 7.275 |
| 7.76 | 4.839 | 7.851 | 7.764 | 7.280 |
| 7.94 | 4.873 | 7.849 | 7.761 | 7.284 |
| 9.51 | 4.926 | 7.847 | 7.756 | 7.294 |
| 10.41 | 4.994 | 7.844 | 7.752 | 7.304 |
| 13.07 | 5.037 | 7.841 | 7.748 | 7.309 |
| 14.86 | 5.075 | 7.840 | 7.745 | 7.315 |
| 16.76 | 5.103 | 7.838 | 7.743 | 7.320 |
| 17.57 | 5.127 | 7.837 | 7.742 | 7.324 |
| 20.01 | 5.144 | 7.836 | 7.741 | 7.326 |
| 29.02 | 5.196 | 7.834 | 7.738 | 7.335 |
| 31.09 | 5.221 | 7.834 | 7.737 | 7.341 |
| 59.65 | 5.260 | 7.835 | 7.738 | 7.350 |
| 92.73 | 5.274 | 7.837 | 7.741 | 7.355 |
| 130.45 | 5.284 | 7.839 | 7.744 | 7.356 |
| 166.69 | 5.281 | 7.841 | 7.747 | 7.357 |

$[(R,R)\text{-}\mathbf{2c}]_0$ = 5.0 mM

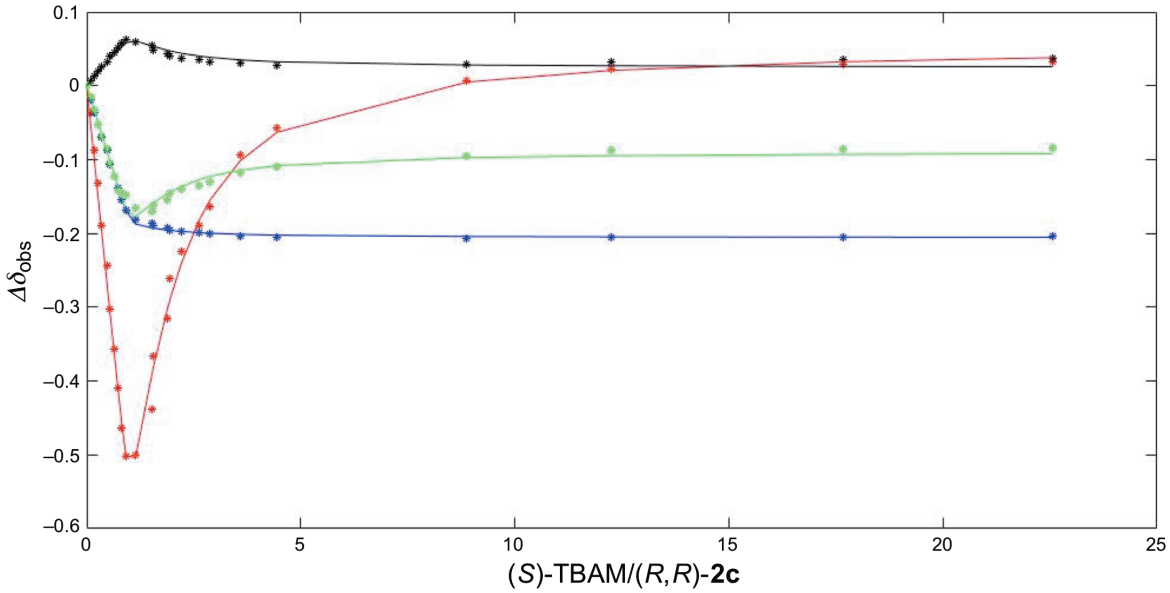



**Fig. S6** Typical fitted plots for the titration of (*R*,*R*)-**2c** with (*S*)-TBAM in $d_6$-acetone (1st titration).

**Table S12.** Association constants and error values obtained by curve-fitting analysis of NMR titration data of (*R*,*R*)-**2c** with (*S*)-TBAM in $d_6$-acetone.

| Entry | $K_1$ ($M^{-1}$) | $K_2$ ($M^{-1}$) | Standard error | Covariance of fit |
|---|---|---|---|---|
| 1st titration | 201995 | 321.076 | 0.00924234 | 0.00442789 |
| 2nd titration | 131035 | 233.947 | 0.00855427 | 0.00396013 |
| 3rd titration | 212539 | 255.983 | 0.00800423 | 0.00330207 |
| Average | $(1.8\pm0.5)\times10^5$ | $(2.7\pm0.5)\times10^2$ | | |

**Table S13.** Data tables for NMR titration of (*R*,*R*)-**2a** with (*R*)-TBAM in $CDCl_3$.

**1st titration**

| $[(R)\text{-TBAM}]_0$ (mM) | $H_A$ (ppm) | $H_B$ (ppm) | $H_C$ (ppm) | $H_D$ (ppm) |
|---|---|---|---|---|
| 0.00 | 5.486 | 7.163 | 7.837 | 7.154 |
| 0.43 | 5.444 | 7.170 | 7.822 | 7.134 |
| 0.89 | 5.400 | 7.171 | 7.808 | 7.112 |
| 1.48 | 5.356 | 7.193 | 7.794 | 7.090 |
| 1.97 | 5.316 | 7.205 | 7.783 | 7.075 |
| 2.56 | 5.281 | 7.217 | 7.774 | 7.060 |
| 3.03 | 5.247 | 7.229 | 7.766 | 7.047 |
| 3.68 | 5.211 | 7.244 | 7.758 | 7.034 |
| 4.30 | 5.186 | 7.254 | 7.754 | 7.026 |
| 4.90 | 5.162 | 7.266 | 7.749 | 7.019 |
| 5.63 | 5.145 | 7.274 | 7.746 | 7.014 |
| 6.09 | 5.132 | 7.280 | 7.745 | 7.012 |
| 6.79 | 5.121 | 7.286 | 7.743 | 7.009 |
| 7.08 | 5.113 | 7.292 | 7.742 | 7.008 |
| 8.41 | 5.098 | 7.299 | 7.740 | 7.005 |
| 9.84 | 5.087 | 7.305 | 7.739 | 7.004 |
| 11.60 | 5.079 | 7.309 | 7.738 | 7.003 |
| 12.71 | 5.070 | 7.312 | 7.737 | 7.003 |
| 13.93 | 5.066 | 7.315 | 7.737 | 7.003 |
| 16.69 | 5.060 | 7.317 | 7.736 | 7.003 |
| 17.84 | 5.057 | 7.320 | 7.737 | 7.004 |
| 23.49 | 5.042 | 7.325 | 7.733 | 7.005 |
| 28.38 | 5.033 | 7.328 | 7.732 | 7.007 |
| 43.54 | 5.012 | 7.337 | 7.731 | 7.014 |
| 73.33 | 5.007 | 7.342 | 7.730 | 7.016 |
| 91.71 | 5.005 | 7.346 | 7.730 | 7.021 |

$[(R,R)\text{-}\mathbf{2a}]_0$ = 5.0 mM

**2nd titration**

| $[(R)\text{-TBAM}]_0$ (mM) | $H_A$ (ppm) | $H_B$ (ppm) | $H_C$ (ppm) | $H_D$ (ppm) |
|---|---|---|---|---|
| 0.00 | 5.483 | 7.163 | 7.835 | 7.158 |
| 0.48 | 5.441 | 7.170 | 7.821 | 7.134 |
| 0.89 | 5.395 | 7.182 | 7.807 | 7.111 |
| 1.37 | 5.361 | 7.192 | 7.796 | 7.095 |
| 1.99 | 5.322 | 7.204 | 7.784 | 7.077 |
| 2.42 | 5.287 | 7.214 | 7.775 | 7.062 |
| 2.96 | 5.255 | 7.225 | 7.767 | 7.050 |
| 3.43 | 5.228 | 7.232 | 7.762 | 7.041 |
| 3.89 | 5.205 | 7.247 | 7.757 | 7.033 |
| 4.34 | 5.185 | 7.254 | 7.753 | 7.026 |
| 4.86 | 5.167 | 7.264 | 7.750 | 7.021 |
| 5.38 | 5.153 | 7.271 | 7.747 | 7.018 |
| 5.86 | 5.139 | 7.278 | 7.745 | 7.013 |
| 6.48 | 5.127 | 7.283 | 7.743 | 7.011 |
| 6.89 | 5.119 | 7.288 | 7.743 | 7.009 |
| 8.31 | 5.103 | 7.296 | 7.740 | 7.006 |
| 9.47 | 5.092 | 7.302 | 7.740 | 7.005 |
| 10.88 | 5.083 | 7.307 | 7.738 | 7.004 |
| 11.87 | 5.076 | 7.311 | 7.738 | 7.004 |
| 13.21 | 5.071 | 7.313 | 7.738 | 7.004 |
| 15.05 | 5.066 | 7.316 | 7.737 | 7.004 |
| 19.08 | 5.052 | 7.322 | 7.735 | 7.006 |
| 24.14 | 5.041 | 7.326 | 7.735 | 7.006 |
| 53.19 | 5.017 | 7.337 | 7.732 | 7.013 |
| 77.84 | 5.008 | 7.343 | 7.731 | 7.018 |
| 117.65 | 5.005 | 7.348 | 7.731 | 7.020 |

$[(R,R)\text{-}\mathbf{2a}]_0$ = 5.0 mM

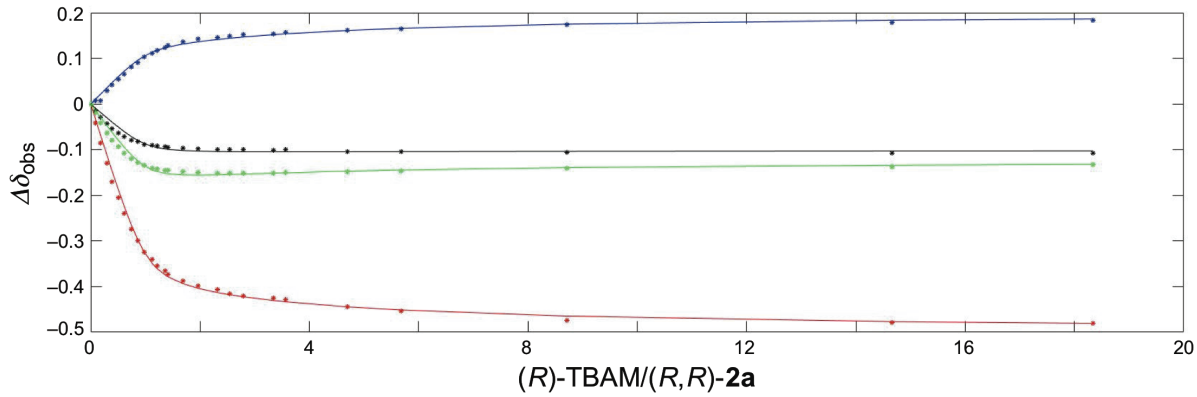



**Fig. S7** Typical fitted plots for the titration of (*R*,*R*)-**2a** with (*R*)-TBAM in $CDCl_3$ (1st titration).

**Table S14.** Association constants and error values obtained by curve-fitting analysis of NMR titration data of (*R*,*R*)-**2a** with (*R*)-TBAM in $CDCl_3$.

| Entry | $K_1$ ($M^{-1}$) | $K_2$ ($M^{-1}$) | Standard error | Covariance of fit |
|---|---|---|---|---|
| 1st titration | 5544 | 58.1559 | 0.00761385 | 0.00163728 |
| 2nd titration | 5815.96 | 72.0007 | 0.00760955 | 0.001758 |
| Average | $(5.7\pm0.3)\times10^3$ | $(6.5\pm1.4)\times10^1$ | | |

**Table S15.** Data tables for NMR titration of (*R*,*R*)-**2a** with (*S*)-TBAM in $CDCl_3$.

**1st titration**

| $[(S)\text{-TBAM}]_0$ (mM) | $H_A$ (ppm) | $H_B$ (ppm) | $H_C$ (ppm) | $H_D$ (ppm) |
|---|---|---|---|---|
| 0.00 | 5.478 | 7.160 | 7.841 | 7.155 |
| 0.41 | 5.428 | 7.166 | 7.823 | 7.135 |
| 0.88 | 5.379 | 7.178 | 7.807 | 7.111 |
| 1.46 | 5.333 | 7.186 | 7.793 | 7.090 |
| 1.91 | 5.288 | 7.198 | 7.781 | 7.073 |
| 2.41 | 5.252 | 7.210 | 7.772 | 7.060 |
| 2.84 | 5.216 | 7.221 | 7.765 | 7.048 |
| 3.41 | 5.184 | 7.233 | 7.760 | 7.039 |
| 3.99 | 5.157 | 7.244 | 7.756 | 7.032 |
| 4.51 | 5.137 | 7.251 | 7.753 | 7.027 |
| 4.92 | 5.121 | 7.261 | 7.752 | 7.024 |
| 5.06 | 5.107 | 7.268 | 7.751 | 7.022 |
| 5.56 | 5.095 | 7.273 | 7.750 | 7.019 |
| 6.72 | 5.085 | 7.278 | 7.749 | 7.018 |
| 7.64 | 5.069 | 7.284 | 7.747 | 7.015 |
| 8.98 | 5.057 | 7.292 | 7.747 | 7.014 |
| 9.71 | 5.049 | 7.296 | 7.747 | 7.014 |
| 10.93 | 5.041 | 7.300 | 7.747 | 7.015 |
| 12.60 | 5.035 | 7.301 | 7.747 | 7.014 |
| 13.82 | 5.030 | 7.304 | 7.745 | 7.014 |
| 15.48 | 5.025 | 7.305 | 7.752 | 7.014 |
| 20.58 | 5.011 | 7.311 | 7.746 | 7.016 |
| 25.34 | 5.000 | 7.314 | 7.745 | 7.018 |
| 45.28 | 4.973 | 7.322 | 7.743 | 7.023 |
| 91.64 | 4.962 | 7.327 | 7.743 | 7.027 |
| 131.72 | 4.956 | 7.329 | 7.742 | 7.029 |
| 168.65 | 4.954 | 7.330 | 7.742 | 7.031 |

$[(R,R)\text{-}\mathbf{2a}]_0$ = 5.0 mM

**2nd titration**

| $[(S)\text{-TBAM}]_0$ (mM) | $H_A$ (ppm) | $H_B$ (ppm) | $H_C$ (ppm) | $H_D$ (ppm) |
|---|---|---|---|---|
| 0.00 | 5.477 | 7.159 | 7.841 | 7.153 |
| 0.46 | 5.426 | 7.167 | 7.822 | 7.132 |
| 0.93 | 5.374 | 7.178 | 7.805 | 7.106 |
| 1.48 | 5.324 | 7.187 | 7.790 | 7.085 |
| 2.06 | 5.280 | 7.197 | 7.778 | 7.068 |
| 2.44 | 5.244 | 7.208 | 7.770 | 7.055 |
| 2.98 | 5.208 | 7.220 | 7.763 | 7.044 |
| 3.44 | 5.177 | 7.231 | 7.757 | 7.034 |
| 3.91 | 5.150 | 7.242 | 7.753 | 7.028 |
| 4.61 | 5.126 | 7.252 | 7.750 | 7.022 |
| 4.79 | 5.107 | 7.262 | 7.749 | 7.018 |
| 5.49 | 5.090 | 7.270 | 7.747 | 7.015 |
| 5.86 | 5.078 | 7.277 | 7.747 | 7.013 |
| 6.59 | 5.068 | 7.282 | 7.745 | 7.012 |
| 7.94 | 5.054 | 7.289 | 7.745 | 7.011 |
| 8.99 | 5.042 | 7.295 | 7.745 | 7.011 |
| 9.99 | 5.034 | 7.299 | 7.745 | 7.011 |
| 10.99 | 5.028 | 7.302 | 7.745 | 7.011 |
| 13.28 | 5.022 | 7.304 | 7.745 | 7.011 |
| 14.87 | 5.018 | 7.306 | 7.745 | 7.012 |
| 17.10 | 5.014 | 7.308 | 7.745 | 7.013 |
| 21.61 | 5.000 | 7.312 | 7.743 | 7.014 |
| 25.00 | 4.991 | 7.315 | 7.742 | 7.017 |
| 55.14 | 4.967 | 7.323 | 7.742 | 7.023 |
| 67.24 | 4.958 | 7.328 | 7.742 | 7.027 |
| 106.72 | 4.954 | 7.330 | 7.742 | 7.030 |

$[(R,R)\text{-}\mathbf{2a}]_0$ = 5.0 mM

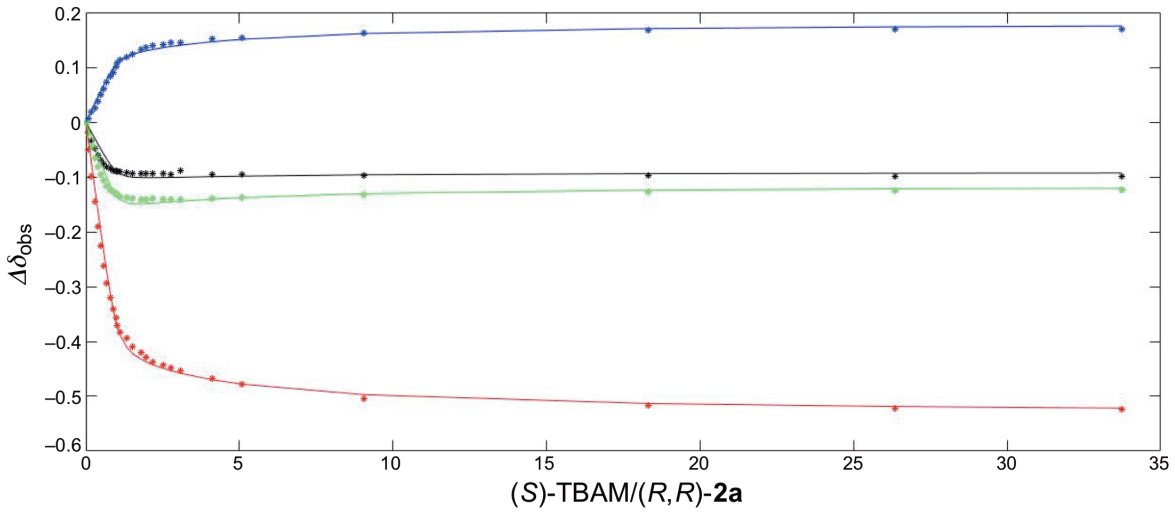



**Fig. S8** Typical fitted plots for the titration of (*R*,*R*)-**2a** with (*S*)-TBAM in $CDCl_3$ (1st titration).

**Table S16.** Association constants and error values obtained by curve-fitting analysis of NMR titration data of (*R*,*R*)-**2a** with (*S*)-TBAM in $CDCl_3$.

| Entry | $K_1$ ($M^{-1}$) | $K_2$ ($M^{-1}$) | Standard error | Covariance of fit |
|---|---|---|---|---|
| 1st titration | 9659.05 | 53.8387 | 0.011105 | 0.00320859 |
| 2nd titration | 9949.76 | 64.897 | 0.0105355 | 0.00284926 |
| Average | $(9.8\pm0.3)\times10^3$ | $(5.9\pm1.1)\times10^1$ | | |

**Table S17.** Data tables for NMR titration of (*R*,*R*)-**2a** with (*R*)-TBAM in $d_6$-DMSO.

| $[(R)\text{-TBAM}]_0$ (mM) | $H_A$ (ppm) | $H_B$ (ppm) | $H_C$ (ppm) | $H_D$ (ppm) |
|---|---|---|---|---|
| 0.00 | 8.025 | 7.183 | 6.871 | 0.915 |
| 0.29 | 8.021 | 7.180 | 6.869 | 0.912 |
| 1.13 | 8.020 | 7.180 | 6.866 | 0.911 |
| 1.52 | 8.018 | 7.178 | 6.865 | 0.909 |
| 1.93 | 8.018 | 7.176 | 6.861 | 0.905 |
| 2.50 | 8.016 | 7.175 | 6.859 | 0.903 |
| 2.83 | 8.015 | 7.174 | 6.858 | 0.902 |
| 3.42 | 8.012 | 7.172 | 6.856 | 0.901 |
| 3.78 | 8.011 | 7.171 | 6.855 | 0.899 |
| 4.37 | 8.009 | 7.170 | 6.853 | 0.897 |
| 4.88 | 8.008 | 7.169 | 6.851 | 0.895 |
| 5.37 | 8.006 | 7.167 | 6.849 | 0.894 |
| 5.66 | 8.004 | 7.166 | 6.848 | 0.893 |
| 6.33 | 8.003 | 7.165 | 6.846 | 0.891 |
| 7.48 | 8.000 | 7.163 | 6.844 | 0.889 |
| 8.14 | 7.994 | 7.162 | 6.841 | 0.887 |
| 9.53 | 7.995 | 7.159 | 6.839 | 0.885 |
| 10.91 | 7.992 | 7.157 | 6.836 | 0.883 |
| 12.36 | 7.990 | 7.156 | 6.834 | 0.881 |
| 13.02 | 7.988 | 7.154 | 6.832 | 0.880 |
| 14.19 | 7.986 | 7.153 | 6.832 | 0.879 |
| 18.13 | 7.979 | 7.148 | 6.824 | 0.875 |
| 22.75 | 7.974 | 7.146 | 6.821 | 0.872 |
| 50.71 | 7.958 | 7.134 | 6.803 | 0.870 |
| 79.18 | 7.950 | 7.127 | 6.800 | 0.874 |
| 90.32 | 7.947 | 7.128 | 6.798 | 0.879 |
| 134.74 | 7.944 | 7.128 | 6.796 | 0.884 |

$[(R,R)\text{-}\mathbf{2a}]_0$ = 5.0 mM

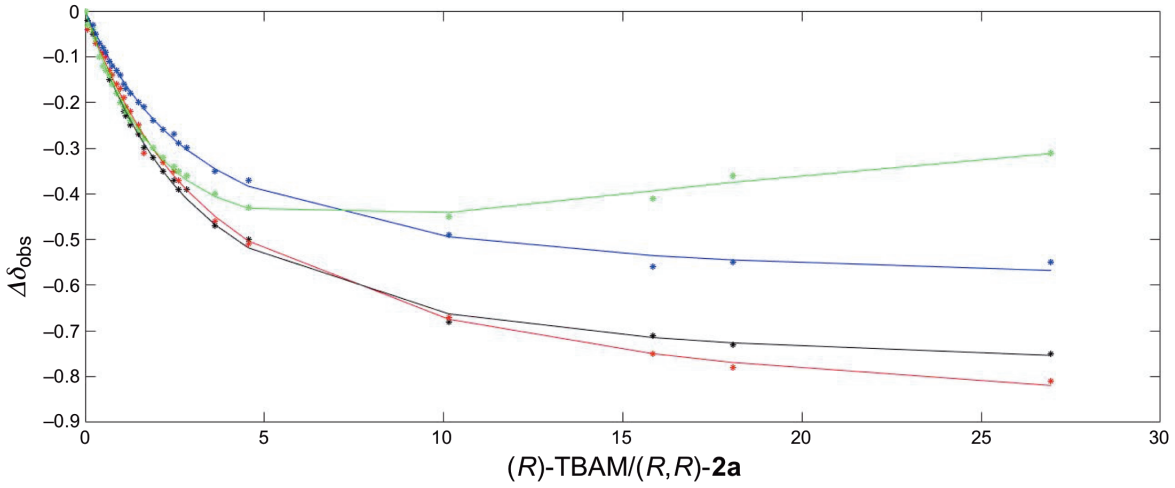



**Fig. S9** Typical fitted plots for the titration of (*R*,*R*)-**2a** with (*R*)-TBAM in $d_6$-DMSO.

**Table S18.** Association constants and error values obtained by curve-fitting analysis of NMR titration data of (*R*,*R*)-**2a** with (*R*)-TBAM in $d_6$-DMSO.

| $K_1$ ($M^{-1}$) | $K_2$ ($M^{-1}$) | Standard error | Covariance of fit |
|---|---|---|---|
| 97.4263 | 11.5272 | 0.000995454 | 0.00241527 |

**Table S19.** Data tables for NMR titration of (*R*,*R*)-**2a** with (*S*)-TBAM in $d_6$-DMSO.

| $[(S)\text{-TBAM}]_0$ (mM) | $H_A$ (ppm) | $H_B$ (ppm) | $H_C$ (ppm) | $H_D$ (ppm) |
|---|---|---|---|---|
| 0.00 | 8.026 | 7.183 | 6.867 | 0.912 |
| 0.52 | 8.022 | 7.181 | 6.867 | 0.909 |
| 0.99 | 8.020 | 7.178 | 6.864 | 0.905 |
| 1.38 | 8.018 | 7.176 | 6.862 | 0.903 |
| 1.89 | 8.017 | 7.175 | 6.860 | 0.899 |
| 2.38 | 8.015 | 7.173 | 6.858 | 0.897 |
| 2.83 | 8.013 | 7.171 | 6.856 | 0.894 |
| 3.11 | 8.012 | 7.170 | 6.855 | 0.892 |
| 3.56 | 8.009 | 7.168 | 6.853 | 0.889 |
| 4.10 | 8.009 | 7.168 | 6.853 | 0.888 |
| 4.51 | 8.006 | 7.165 | 6.849 | 0.884 |
| 5.10 | 8.005 | 7.165 | 6.848 | 0.883 |
| 5.36 | 8.002 | 7.162 | 6.846 | 0.879 |
| 6.21 | 8.002 | 7.161 | 6.845 | 0.879 |
| 7.41 | 7.999 | 7.159 | 6.842 | 0.875 |
| 8.43 | 7.997 | 7.157 | 6.840 | 0.870 |
| 9.68 | 7.994 | 7.154 | 6.836 | 0.867 |
| 11.26 | 7.991 | 7.152 | 6.834 | 0.863 |
| 11.84 | 7.990 | 7.151 | 6.832 | 0.862 |
| 12.93 | 7.987 | 7.148 | 6.830 | 0.858 |
| 14.16 | 7.986 | 7.148 | 6.828 | 0.856 |
| 19.36 | 7.980 | 7.142 | 6.822 | 0.849 |
| 22.85 | 7.975 | 7.136 | 6.818 | 0.844 |
| 50.30 | 7.962 | 7.128 | 6.804 | 0.836 |
| 82.04 | 7.960 | 7.129 | 6.803 | 0.838 |
| 91.33 | 7.957 | 7.126 | 6.798 | 0.842 |
| 125.01 | 7.956 | 7.127 | 6.798 | 0.844 |

$[(R,R)\text{-}\mathbf{2a}]_0$ = 5.0 mM

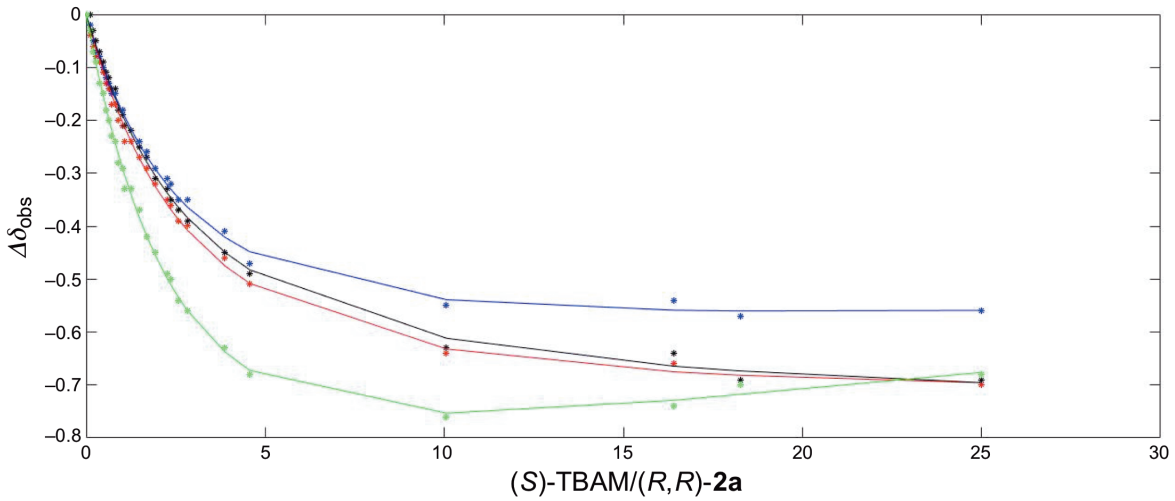



**Fig. S10** Typical fitted plots for the titration of (*R*,*R*)-**2a** with (*S*)-TBAM in $d_6$-DMSO (1st titration).

**Table S20.** Association constants and error values obtained by curve-fitting analysis of NMR titration data of (*R*,*R*)-**2a** with (*S*)-TBAM in $d_6$-DMSO.

| $K_1$ ($M^{-1}$) | $K_2$ ($M^{-1}$) | Standard error | Covariance of fit |
|---|---|---|---|
| 99.9613 | 8.40613 | 0.00106614 | 0.00237843 |

## 2. Distribution of guest molecules calculated from association constants

Association constants $K_1$ and $K_2$ for 1:1 and 1:2 complaxation of host and guest compounds are defined

$$H + G \overset{K_1}{\rightleftharpoons} HG$$

$$HG + G \overset{K_2}{\rightleftharpoons} HG_2$$

$$K_1 = \frac{[HG]}{[H][G]} \quad (1) \qquad K_2 = \frac{[HG_2]}{[HG][G]} \quad (2)$$

where [H], [G], [HG], and [$HG_2$] represent molar concentrations of the host, guest, 1:1 complex of host-guest, and 1:2 complex of host-guest, respectively.

The initial concentrations of host and guest compounds $[H]_0$ and $[G]_0$ are expressed as follows.

$$[H]_0 = [H] + [HG] + [HG_2] \quad (3)$$

$$[G]_0 = [G] + [HG] + 2[HG_2] \quad (4)$$

From equations (1)–(4), the cubic equation (5) is derived.

$$K_1K_2[G]^3 + \{K_1(2K_2[H]_0 - K_2[G]_0+1)\}[G]^2 + \{K_1([H]_0-[G]_0) + 1\}[G] - [G]_0 = 0 \quad (5)$$

The smallest positive real solution of the equation (5) corresponds to the concentration of the guest compound [G]. After the concentration of guest compound [G] is obtained, the concentration of host compound [H] can be calculated from equation (6).

$$[H] = \frac{[H]_0}{1 + K_1[G] + K_1K_2[G]^2} \quad (6)$$

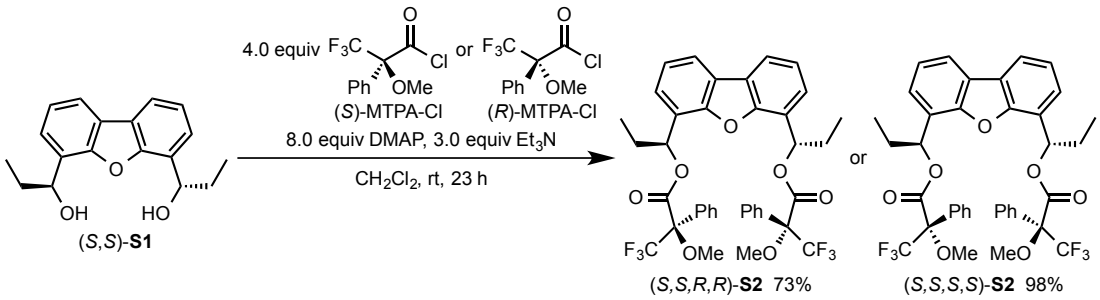
Once [H] and [G] are known, the concentration of 1:1 complex [HG] and 1:2 complex [$HG_2$] can also be calculated from equations (7) and (8).

$$[HG] = K_1[H][G] \quad (7) \qquad [HG_2] = K_2[HG][G] \quad (8)$$

The distribution of guest molecules shown in Tables 5–7 was obtained from the calculated [G], [HG], and [$HG_2$].

## 3. Determination of the absolute configuration of chiral diol (*S*,*S*)-S1

Chiral diamine (*R*,*R*)-**1** was derived from chiral diol (*S*,*S*)-**S1**.[2] The absolute configuration of (*S*,*S*)-**S1** was determined based on the stereochemical course of the asymmetric ethylation[2] and further confirmed by the modified Mosher ester analysis.[3] Diastereomeric diesters (*S*,*S*,*R*,*R*)-**S2** and (*S*,*S*,*S*,*S*)-**S2** were synthesized by the reaction of (*S*,*S*)-**S1** with (*S*)- or (*R*)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (MTPA-Cl) in the presence of DMAP and $Et_3N$ (Scheme S1).




**Scheme S1** Synthesis of MTPA esters (*S*,*S*,*R*,*R*)-**S2** and (*S*,*S*,*S*,*S*)-**S2**

As the $^1$H NMR signals of ethyl groups of (*S*)-MTPA ester **S2** appeared upfield relative to those of (*R*)-MTPA ester **S2** owing to the diamagnetic effect of the phenyl group of MTPA, the absolute configuration of chiral diol **S1** was determined as (*S*,*S*)-configuration (Fig. S7).

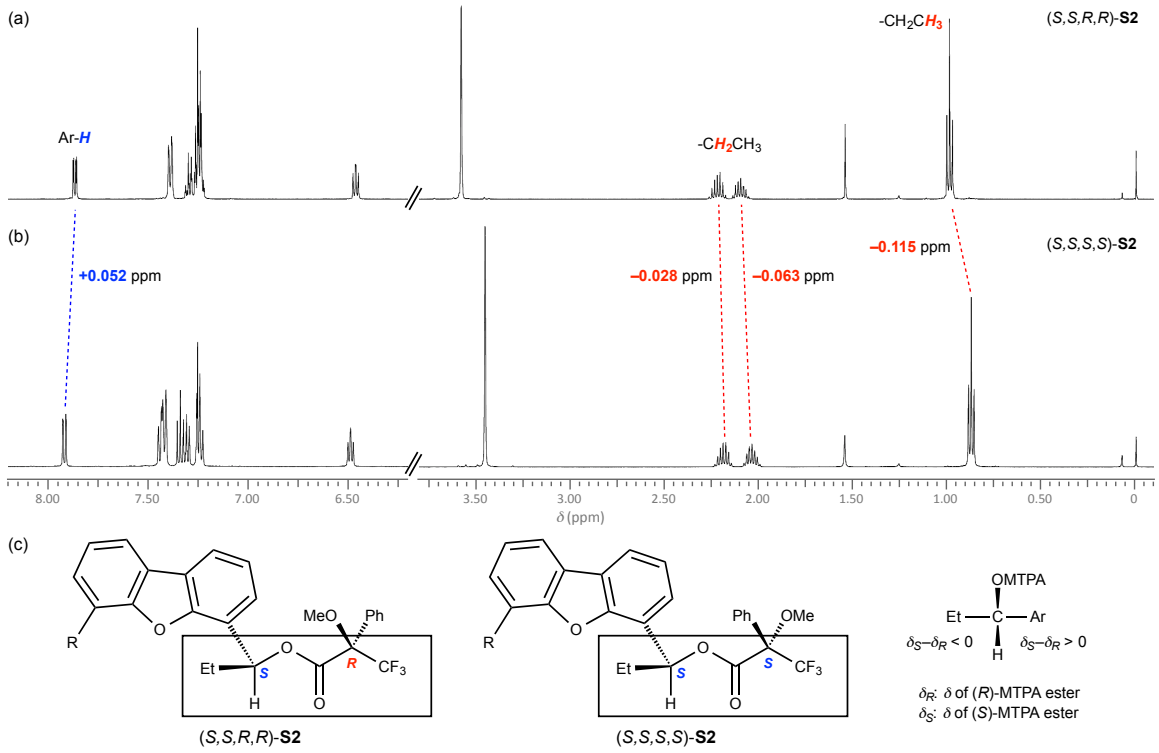



**Fig. S11** $^1$H NMR spectra of (*S*,*S*,*R*,*R*)-**S2** (a) and (*S*,*S*,*S*,*S*)-**S2** (b). Configurational correlation model for (*S*,*S*,*R*,*R*)-**S2** and (*S*,*S*,*S*,*S*)-**S2** (c).

**4,6-Bis((*S*)-1-{[(*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoyl]oxy}propyl)dibenzo[*b*,*d*]furan [(*S*,*S*,*R*,*R*)-S2]** To a stirred solution of (*S*,*S*)-**S1** (12.0 mg, 0.041 mmol) in dichloromethane (5.0 mL) was added DMAP (40.0 mg, 0.33 mmol), $Et_3N$ (170 μL, 0.12 mmol), and (*S*)-MTPA-Cl (30 μL, 0.16 mmol). The reaction mixture was stirred at room temperature for 23 h. To the mixture was added $N^1$,$N^1$-dimethylpropane-1,3-diamine (20 μL, 0.16 mmol), and the mixture was stirred at room temperature for 10 min. After removal of solvent under reduced pressure, crude product was purified by preparative thin-layer chromatography (hexane/$CH_2Cl_2$/AcOEt = 8:1:1) to give (*R*)-MTPA ester (*S*,*S*,*R*,*R*)-**S2** (21.0 mg, 73%) as colorless oil. $[\alpha]_D^{28}$ +9.8 (*c* 0.86, $CHCl_3$); IR (neat): $\nu_{max}$ 3065, 3034, 2975, 2947, 2881, 2850, 1747, 1715, 1588, 1491, 1452, 1436, 1422, 1362, 1270, 1252, 1185, 1123, 1082, 1058, 1018, 994, 965, 918, 890, 866, 846, 813, 781, 766, 749, 719, 697, 647 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ (ppm) 7.88–7.85 (m, 2H), 7.39 (d, *J* = 7.8 Hz, 4H), 7.32–7.22 (m, 10H), 6.46 (dd, *J* = 7.3, 6.0 Hz, 2H), 3.58 (s, 6H), 2.27–2.17 (m, 2H), 2.15–2.05 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 6H); $^{13}C$ NMR (126 MHz, $CDCl_3$): $\delta$ (ppm) 165.8, 152.9, 132.2, 129.4, 128.2, 127.3, 125.1, 124.2, 123.5, 123.3 (q, $^1J_{C\text{-}F}$ = 289 Hz), 122.9, 120.4, 84.6 (q, $^2J_{C\text{-}F}$ = 28 Hz), 75.3, 55.6, 28.0, 9.8; HRMS-ESI (*m*/*z*): $[M+Na]^+$ Calcd for $C_{38}H_{34}O_7F_6Na$, 739.2101; Found, 739.2115.

**4,6-Bis((*S*)-1-{[(*S*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoyl]oxy}propyl)dibenzo[*b*,*d*]furan [(*S*,*S*,*S*,*S*)-S2]** According to the same procedure as the synthesis of (*S*,*S*,*R*,*R*)-**S2**, the reaction of (*S*,*S*)-**S1** and (*R*)-MTPA-Cl afforded (*S*)-MTPA ester (*S*,*S*,*S*,*S*)-**S2** (29.0 mg, 98%) as colorless oil. $[\alpha]_D^{28}$ –70.3 (*c* 1.2, $CHCl_3$); IR (neat): $\nu_{max}$ 3065, 3037, 2975, 2947, 2881, 2849, 1748, 1715, 1588, 1491, 1452, 1437, 1422, 1362, 1270, 1242, 1186, 1122, 1082, 1058, 1017, 994, 965, 918, 893, 869, 847, 812, 782, 766, 749, 719, 697, 647$cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ (ppm) 7.93–7.91 (m, 2H), 7.45–7.41 (m, 6H), 7.36–7.29 (m, 4H), 7.26–7.22 (m, 4H), 6.49 (t, *J* = 6.6 Hz, 2H), 3.45 (s, 6H), 2.23–2.14 (m, 2H), 2.08–1.99 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 6H); $^{13}C$ NMR (126 MHz, $CDCl_3$): $\delta$ (ppm) 165.9, 153.1, 132.3, 129.5, 128.3, 127.4, 125.7, 124.3, 123.5, 123.4 (q, $^1J_{C\text{-}F}$ = 289 Hz) 123.1, 120.7, 84.6 (q, $^2J_{C\text{-}F}$ = 28 Hz), 75.4, 55.3, 27.7, 9.6; HRMS-ESI (*m*/*z*): $[M+Na]^+$ Calcd for $C_{38}H_{34}O_7F_6Na$, 739.2101; Found, 739.2110.

## 4. Reference

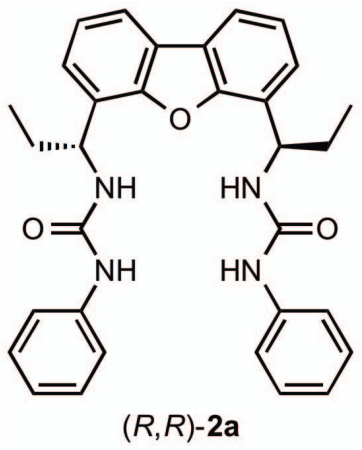

1) P. Thordarson, *Chem. Soc. Rev.*, 2011, **40**, 1305.

2) S. Ito, K. Ikeda, M. Asami, *Chem. Lett.*, 2016, **45**, 1379.

3) I. Ohtani, T. Kusumi, Y. Kashman, H. Kakisawa, *J. Am. Chem. Soc.*, 1991, **113**, 4092.

## $^1$H NMR (500 MHz, in $CDCl_3$)

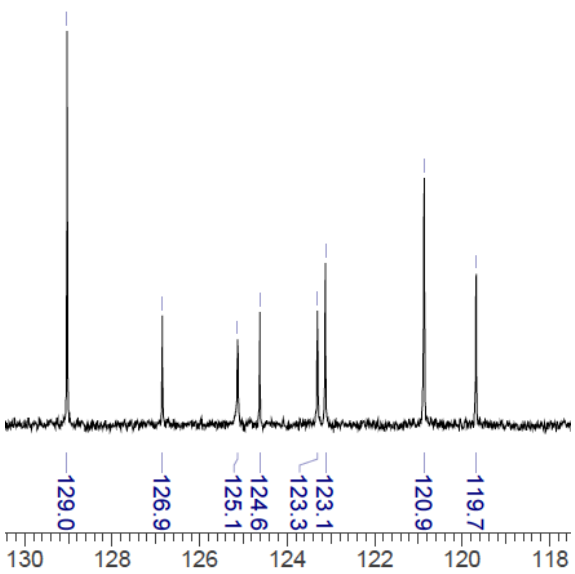
| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Acquisition Time (sec)** | 3.1719 | **Comment** | U 0628-2 | **D** | 3.827959 | **D1** | 3.827959 | **DE** | 6 |
| **DS** | 2 | **Date** | 28 Jun 2017 17:00:44 | | | **Date Stamp** | 28 Jun 2017 17:00:44 | | |
| **File Name** | F:¥NMR¥U 0628-2¥1¥PDATA¥1¥1r | | | **Frequency (MHz)** | 500.1300 | **GB** | 0 | **INSTRUM** | <spect> |
| **LB** | 0.1 | **NS** | 8 | **Nucleus** | 1H | **Number of Transients** | 8 | **Origin** | spect |
| **Original Points Count** | 32768 | **Owner** | root | **PC** | 1 | **PROBHD** | <5 mm BBO BB-1H Z-GRD Z859001/0006 > | | |
| **PULPROG** | <zg30> | **Points Count** | 32768 | **Pulse Sequence** | zg30 | **Receiver Gain** | 362.00 | **SF** | 500.130006648269 |
| **SFO1** | 500.133088507478 | | | **SI** | 32768 | **SSB** | 0 | **SW(cyclical) (Hz)** | 10330.58 |
| **SWH** | 10330.5785123967 | | | **Solvent** | CHLOROFORM-d | | | **Spectrum Offset (Hz)** | 3065.8052 |
| **Spectrum Type** | standard | **Sweep Width (Hz)** | 10330.26 | **TD** | 65536 | **TD0** | 1 | **TE** | 323.2 |
| **Temperature (degree C)** | 50.200 | **WDW** | 1 | | | | | | |




(*R*,*R*)-**2a**

## $^{13}$C NMR (126 MHz, in $CDCl_3$)

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Acquisition Time (sec)** | 1.0912 | **Comment** | U 0628 13C | | | **D** | 0.00345 | **D1** | 2 |
| **DE** | 6 | **DS** | 4 | **Date** | 28 Jun 2017 18:03:50 | | | **Date Stamp** | 28 Jun 2017 18:03:50 |
| **File Name** | F:¥NMR¥U 0628 13C¥1¥PDATA¥1¥1r | | | **Frequency (MHz)** | 125.7578 | **GB** | 0 | **INSTRUM** | <spect> |
| **LB** | 1 | **NS** | 1024 | **Nucleus** | 13C | **Number of Transients** | 1024 | **Origin** | spect |
| **Original Points Count** | 32768 | **Owner** | root | **PC** | 1.4 | **PROBHD** | <5 mm BBO BB-1H Z-GRD Z859001/0006 > | | |
| **PULPROG** | <zgpg30> | **Points Count** | 32768 | **Pulse Sequence** | zgpg30 | **Receiver Gain** | 8192.00 | **SF** | 125.757789 |
| **SFO1** | 125.770364304853 | | | **SI** | 32768 | **SSB** | 0 | **SW(cyclical) (Hz)** | 30030.03 |
| **SWH** | 30030.03003003 | | | **Solvent** | CHLOROFORM-d | | | **Spectrum Offset (Hz)** | 12583.4375 |
| **Spectrum Type** | standard | **Sweep Width (Hz)** | 30029.11 | **TD** | 65536 | **TD0** | 1 | **TE** | 323.2 |
| **Temperature (degree C)** | 50.200 | **WDW** | 1 | | | | | | |







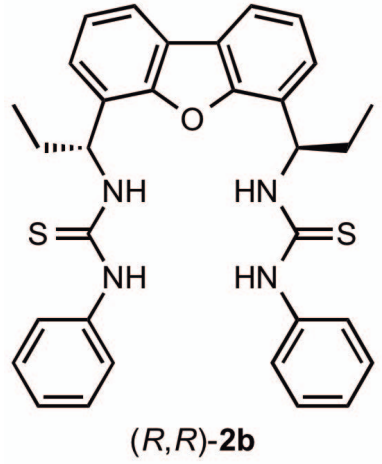



(*R*,*R*)-**2a**

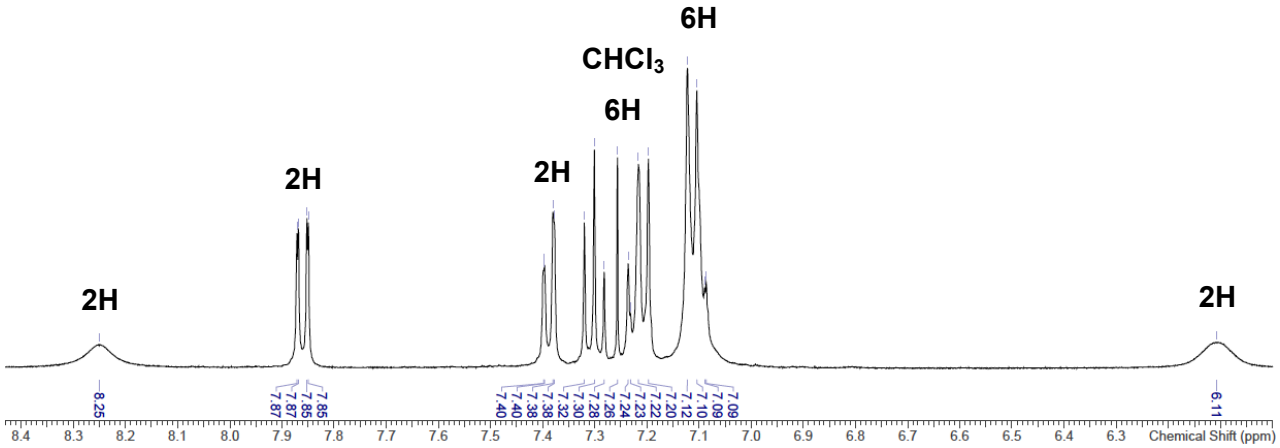
## $^1$H NMR (400 MHz, in $CDCl_3$)

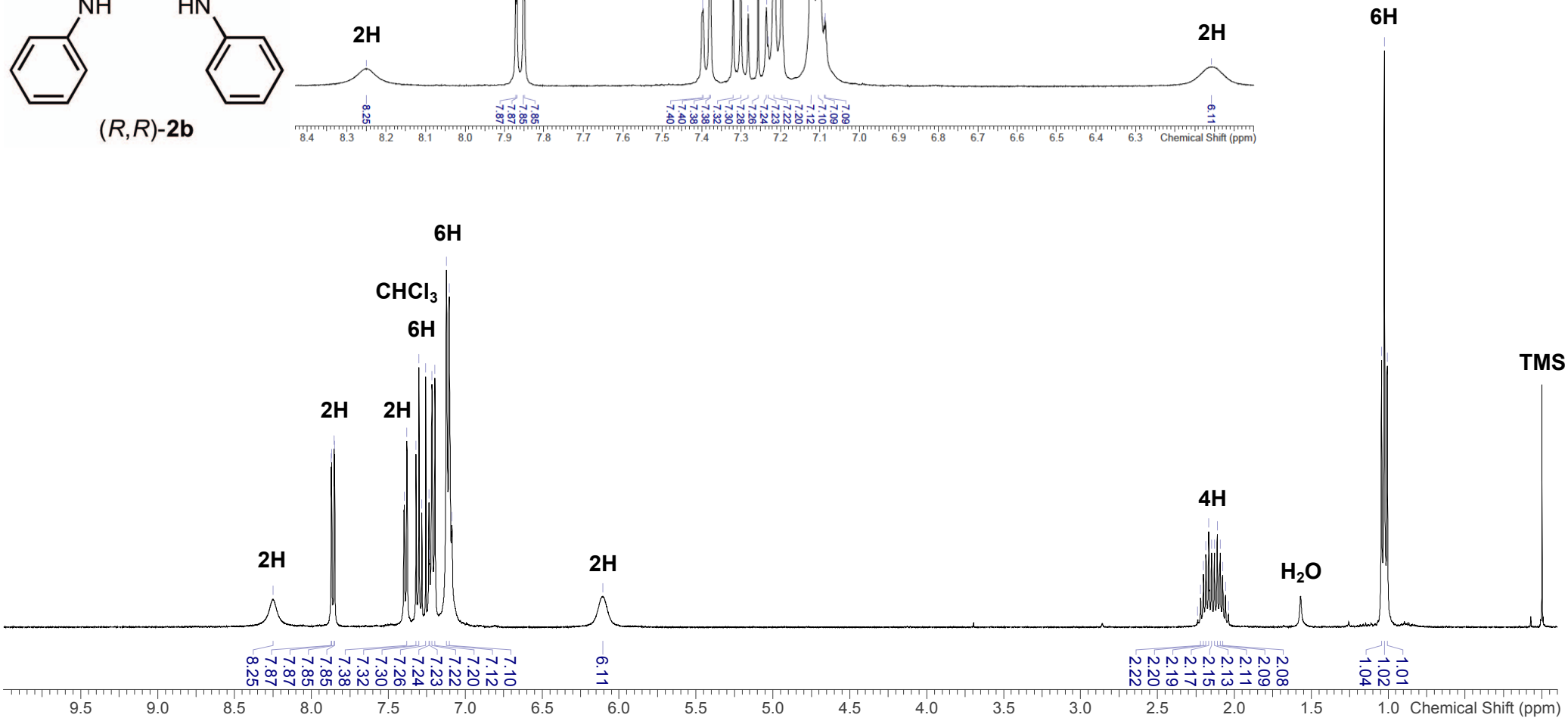
| | | | |
|---|---|---|---|
| **Multiplets Integrals Sum** | 31.55 | **Number of Nuclei** | 34 H's |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Acquisition Time (sec)** | 4.3673 | **Comment** | single_pulse | **Date** | 29 Dec 2016 13:17:18 | | **Date Stamp** | 29 Dec 2016 13:15:51 |
| **File Name** | F:¥NMR¥oku309 7-9_proton-1-1.jdf | | | **Frequency (MHz)** | 399.7822 | **Nucleus** 1H | **Number of Transients** | 8 |
| **Origin** | JNM-ECX400 | | | **Original Points Count** | 32768 | **Owner** delta | **Points Count** | 32768 |
| **Pulse Sequence** | proton.jxp | **SW(cyclical) (Hz)** | 7503.00 | **Solvent** | CHLOROFORM-d | | **Spectrum Offset (Hz)** | 2001.1609 |
| **Sweep Width (Hz)** | 7503.00 | **Temperature (degree C)** | 25.000 | | | | | |



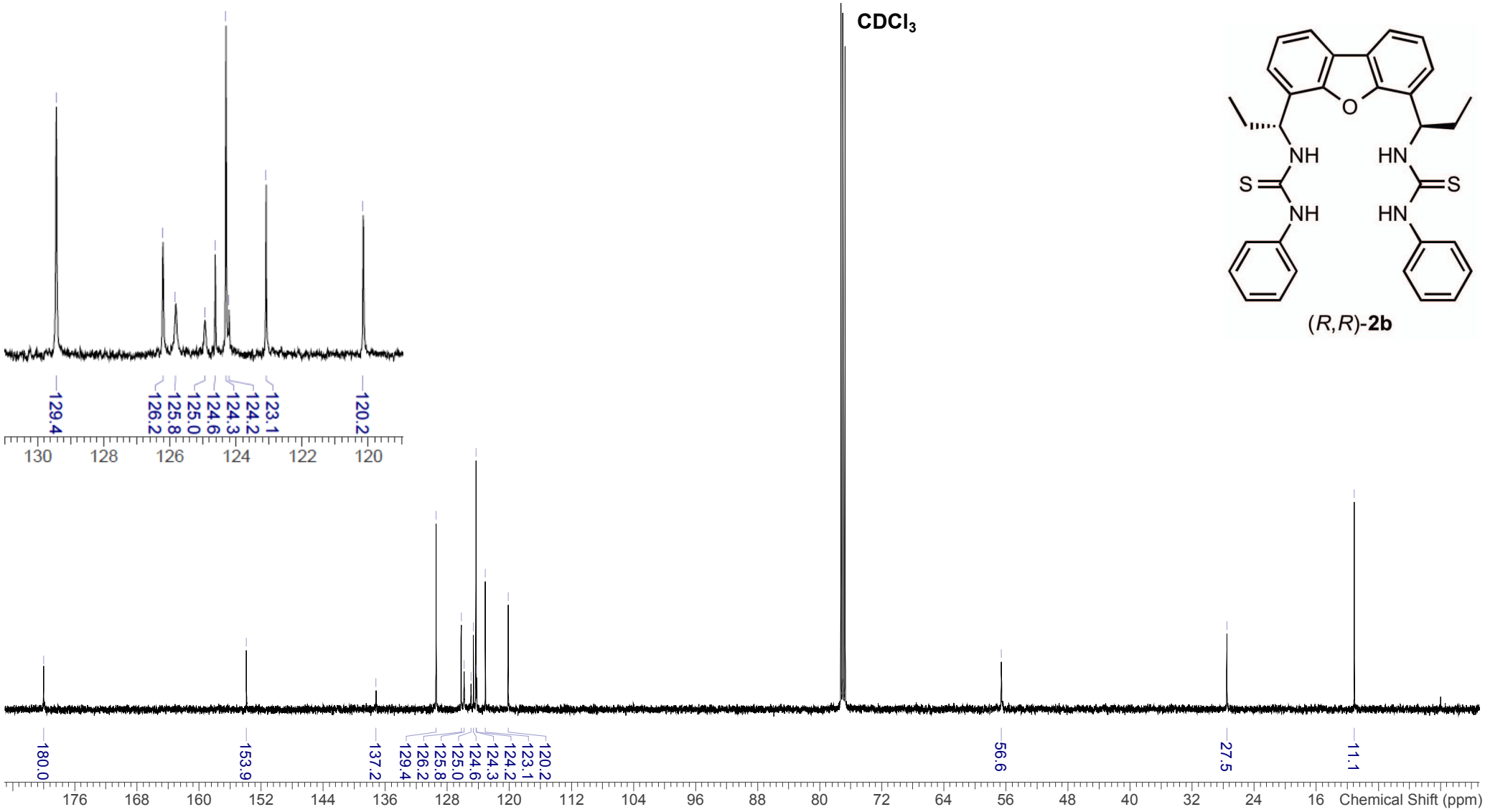

(*R*,*R*)-**2b**



## $^{13}C$ NMR (126 MHz, in $CDCl_3$)

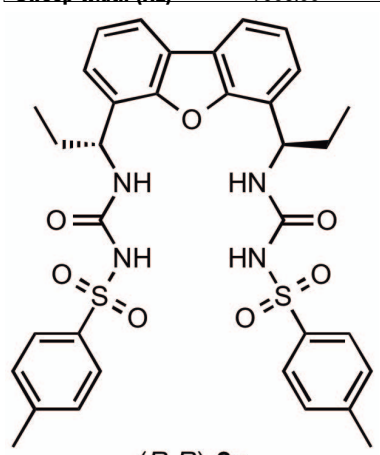
| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Acquisition Time (sec)** | 1.0912 | **Comment** | TU 1104 13C | | | **D** | 0.00345 | **D1** | 2 |
| **DE** | 6 | **DS** | 4 | **Date** | 04 Nov 2016 17:27:33 | | | **Date Stamp** | 04 Nov 2016 17:27:33 |
| **File Name** | K:¥NMR¥TU 1104 13C¥1¥PDATA¥1¥1r | | | **Frequency (MHz)** | 125.7578 | **GB** | 0 | **INSTRUM** | <spect> |
| **LB** | 1 | **NS** | 512 | **Nucleus** | 13C | **Number of Transients** | 512 | **Origin** | spect |
| **Original Points Count** | 32768 | **Owner** | root | **PC** | 1.4 | **PROBHD** | <5 mm BBO BB-1H Z-GRD Z859001/0006 > | | |
| **PULPROG** | <zgpg30> | **Points Count** | 32768 | **Pulse Sequence** | zgpg30 | **Receiver Gain** | 5792.60 | **SF** | 125.757789 |
| **SFO1** | 125.770364304853 | | | **SI** | 32768 | **SSB** | 0 | **SW(cyclical) (Hz)** | 30030.03 |
| **SWH** | 30030.03003003 | | | **Solvent** | CHLOROFORM-d | | | **Spectrum Offset (Hz)** | 12569.6924 |
| **Spectrum Type** | standard | **Sweep Width (Hz)** | 30029.11 | **TD** | 65536 | **TD0** | 1 | **TE** | 298.8 |
| **Temperature (degree C)** | 25.800 | **WDW** | 1 | | | | | | |



## $^1$H NMR (400 MHz, in $CDCl_3$)

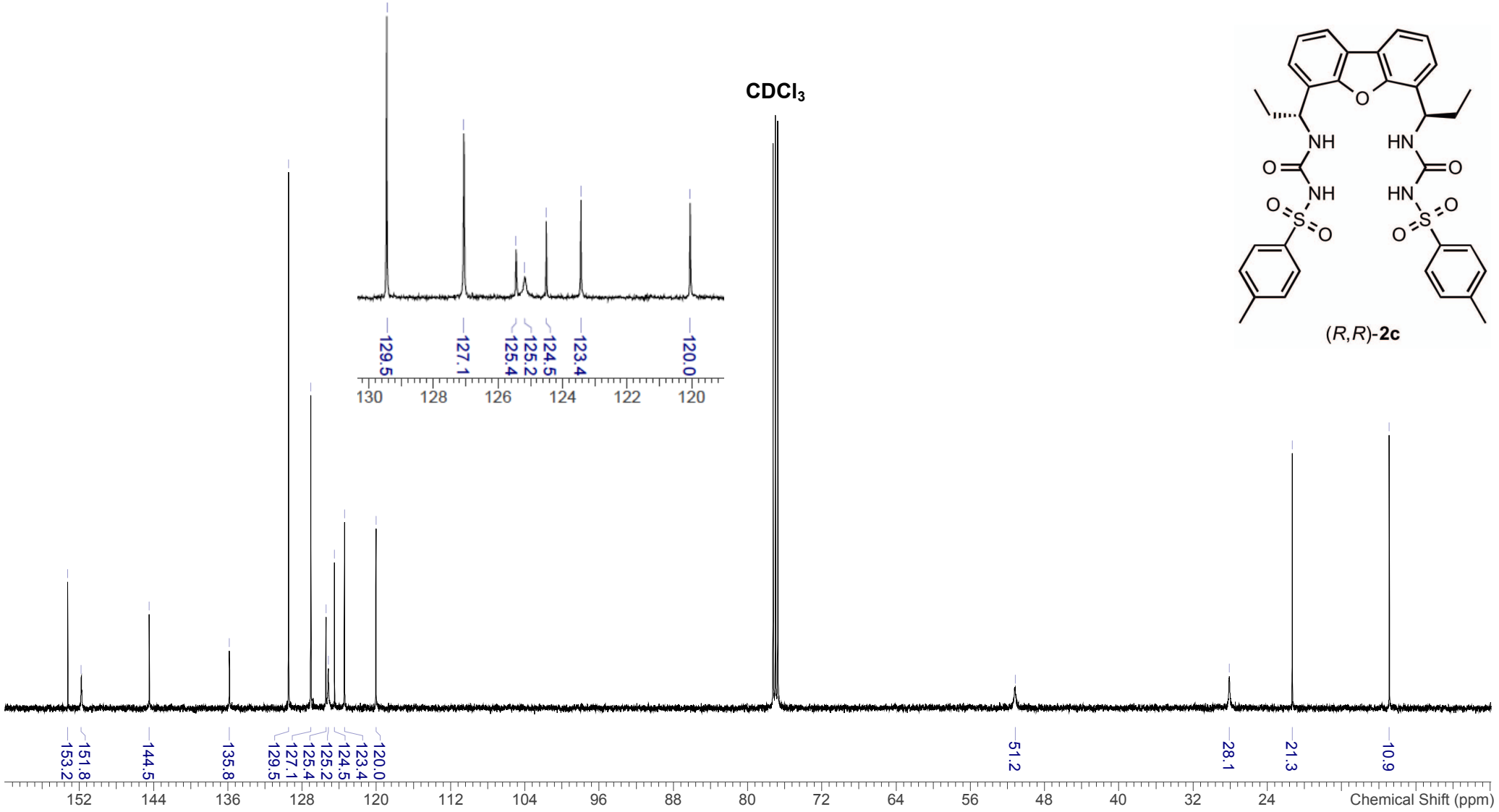
| | | | |
|---|---|---|---|
| **Multiplets Integrals Sum** | 17.59 | **Number of Nuclei** | 18 H's |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Acquisition Time (sec)** | 4.3673 | **Comment** | single_pulse | **Date** | 27 Jun 2017 17:21:46 | | **Date Stamp** | 27 Jun 2017 17:20:19 |
| **File Name** | G:¥NMR¥SU 0627 proton-1-1.jdf | | | **Frequency (MHz)** | 399.7822 | **Nucleus** 1H | **Number of Transients** | 8 |
| **Origin** | JNM-ECX400 | | | **Original Points Count** | 32768 | **Owner** delta | **Points Count** | 32768 |
| **Pulse Sequence** | proton.jxp | **SW(cyclical) (Hz)** | 7503.00 | **Solvent** | CHLOROFORM-d | | **Spectrum Offset (Hz)** | 2002.7772 |
| **Sweep Width (Hz)** | 7503.00 | **Temperature (degree C)** | 22.700 | | | | | |



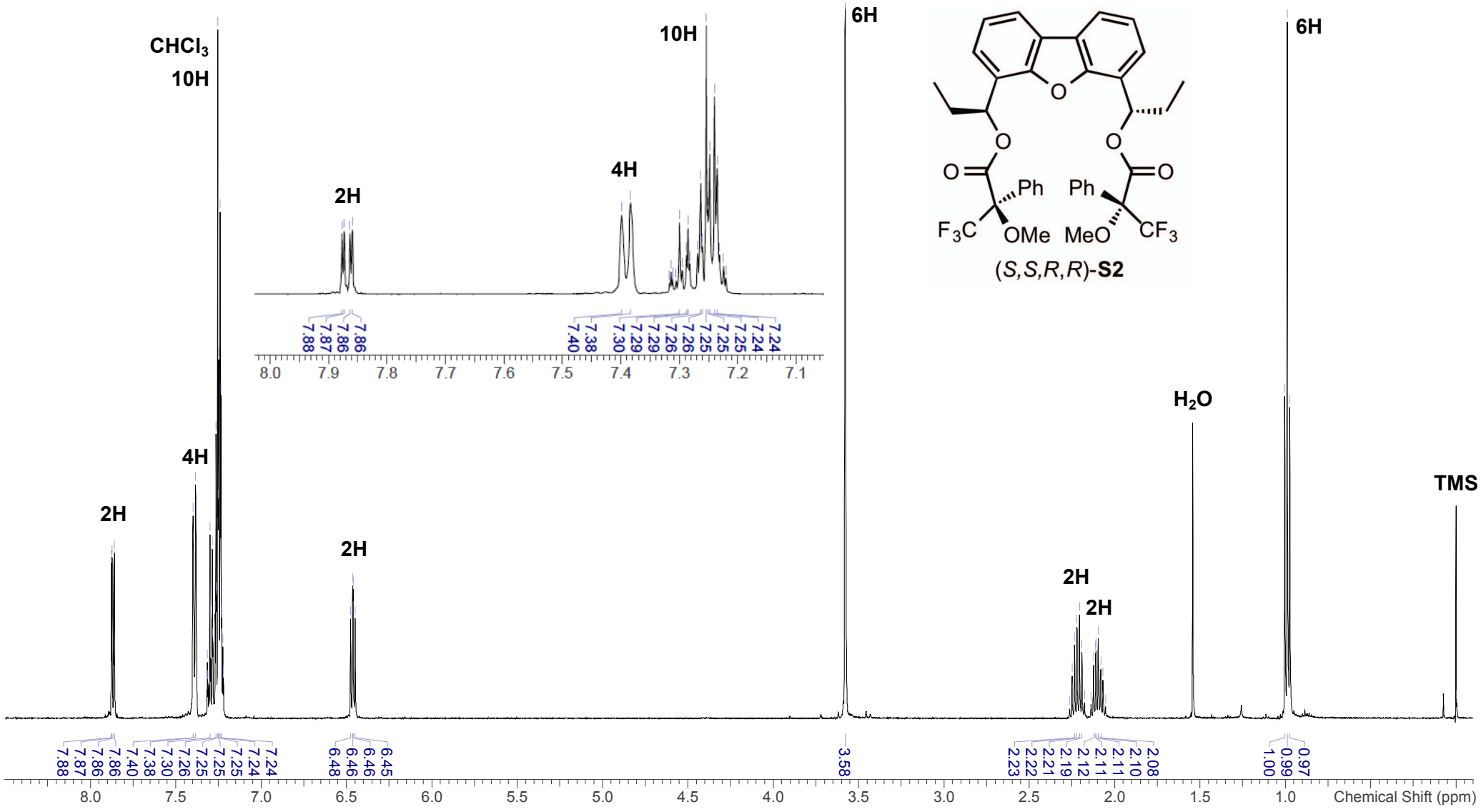
## $^{13}$C NMR (126 MHz, in $CDCl_3$)

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Acquisition Time (sec)** | 1.0912 | **Comment** | SU 0208 13C | | | **D** | 0.00345 | **D1** | 2 |
| **DE** | 6 | **DS** | 4 | **Date** | 08 Feb 2017 15:10:17 | | | **Date Stamp** | 08 Feb 2017 15:10:17 |
| **File Name** | F:¥NMR¥SU 0208 13C¥10¥PDATA¥1¥1r | | | **Frequency (MHz)** | 125.7578 | **GB** | 0 | **INSTRUM** | <spect> |
| **LB** | 1 | **NS** | 512 | **Nucleus** | 13C | **Number of Transients** | 512 | **Origin** | spect |
| **Original Points Count** | 32768 | **Owner** | root | **PC** | 1.4 | **PROBHD** | <5 mm BBO BB-1H Z-GRD Z859001/0006 > | | |
| **PULPROG** | <zgpg30> | **Points Count** | 32768 | **Pulse Sequence** | zgpg30 | **Receiver Gain** | 10321.30 | **SF** | 125.757789 |
| **SFO1** | 125.770364304853 | | | **SI** | 32768 | **SSB** | 0 | **SW(cyclical) (Hz)** | 30030.03 |
| **SWH** | 30030.03003003 | | | **Solvent** | CHLOROFORM-d | | | **Spectrum Offset (Hz)** | 12567.8574 |
| **Spectrum Type** | standard | **Sweep Width (Hz)** | 30029.11 | **TD** | 65536 | **TD0** | 1 | **TE** | 298.4 |
| **Temperature (degree C)** | 25.400 | **WDW** | 1 | | | | | | |



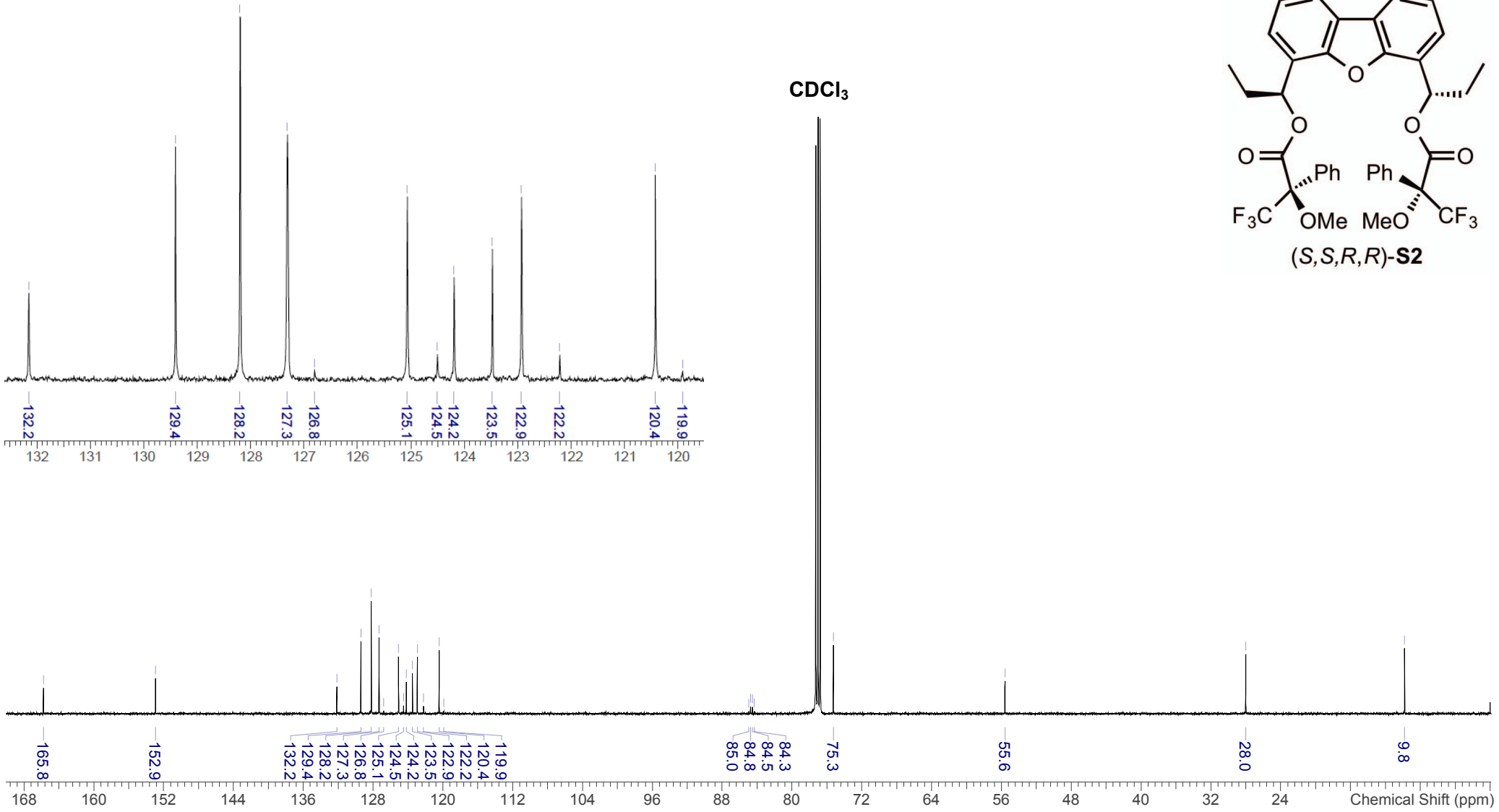
## $^1$H NMR (500 MHz, in $CDCl_3$)

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Acquisition Time (sec)** | 3.1719 | **Comment** | 362 S | **D** | 3.827959 | **D1** | 3.827959 | **DE** | 6 |
| **DS** | 2 | **Date** | 05 Jul 2017 18:35:46 | | | **Date Stamp** | 05 Jul 2017 18:35:46 | | |
| **File Name** | F:¥oku362 S¥1¥PDATA¥1¥1r | | | **Frequency (MHz)** | 500.1300 | **GB** | 0 | **INSTRUM** | <spect> |
| **LB** | 0.1 | **NS** | 8 | **Nucleus** | 1H | **Number of Transients** | 8 | **Origin** | spect |
| **Original Points Count** | 32768 | **Owner** | root | **PC** | 1 | **PROBHD** | <5 mm BBO BB-1H Z-GRD Z859001/0006 > | | |
| **PULPROG** | <zg30> | **Points Count** | 32768 | **Pulse Sequence** | zg30 | **Receiver Gain** | 256.00 | **SF** | 500.130006648269 |
| **SFO1** | 500.133088507478 | | | **SI** | 32768 | **SSB** | 0 | **SW(cyclical) (Hz)** | 10330.58 |
| **SWH** | 10330.5785123967 | | | **Solvent** | CHLOROFORM-d | | | **Spectrum Offset (Hz)** | 3071.4568 |
| **Spectrum Type** | standard | **Sweep Width (Hz)** | 10330.26 | **TD** | 65536 | **TD0** | 1 | **TE** | 300.2 |
| **Temperature (degree C)** | 27.200 | **WDW** | 1 | | | | | | |



## $^{13}$C NMR (126 MHz, in $CDCl_3$)

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Acquisition Time (sec)** | 1.0912 | **Comment** | A.13C_np CDCl3 {C:¥YNU} asmlab 1 | | | **D** | 0.00345 | **D1** | 2 |
| **DE** | 6 | **DS** | 4 | **Date** | 07 Sep 2017 03:30:35 | | | **Date Stamp** | 07 Sep 2017 03:30:35 |
| **File Name** | F:¥NMR¥oku362 R ester 0906¥2¥PDATA¥1¥1r | | | **Frequency (MHz)** | 125.7578 | **GB** | 0 | **INSTRUM** | <spect> |
| **LB** | 1 | **NS** | 7000 | **Nucleus** | 13C | **Number of Transients** | 7000 | **Origin** | spect |
| **Original Points Count** | 32768 | **Owner** | DRX500 | **PC** | 1.4 | **PROBHD** | <5 mm BBO BB-1H Z-GRD Z859001/0006 > | | |
| **PULPROG** | <zgpg30> | **Points Count** | 32768 | **Pulse Sequence** | zgpg30 | **Receiver Gain** | 9195.20 | **SF** | 125.757788800476 |
| **SFO1** | 125.770364304853 | | | **SI** | 32768 | **SSB** | 0 | **SW(cyclical) (Hz)** | 30030.03 |
| **SWH** | 30030.03003003 | | | **Solvent** | CHLOROFORM-d | | | **Spectrum Offset (Hz)** | 12575.5029 |
| **Spectrum Type** | standard | **Sweep Width (Hz)** | 30029.11 | **TD** | 65536 | **TD0** | 1 | **TE** | 299.2 |
| **Temperature (degree C)** | 26.200 | **WDW** | 1 | | | | | | |



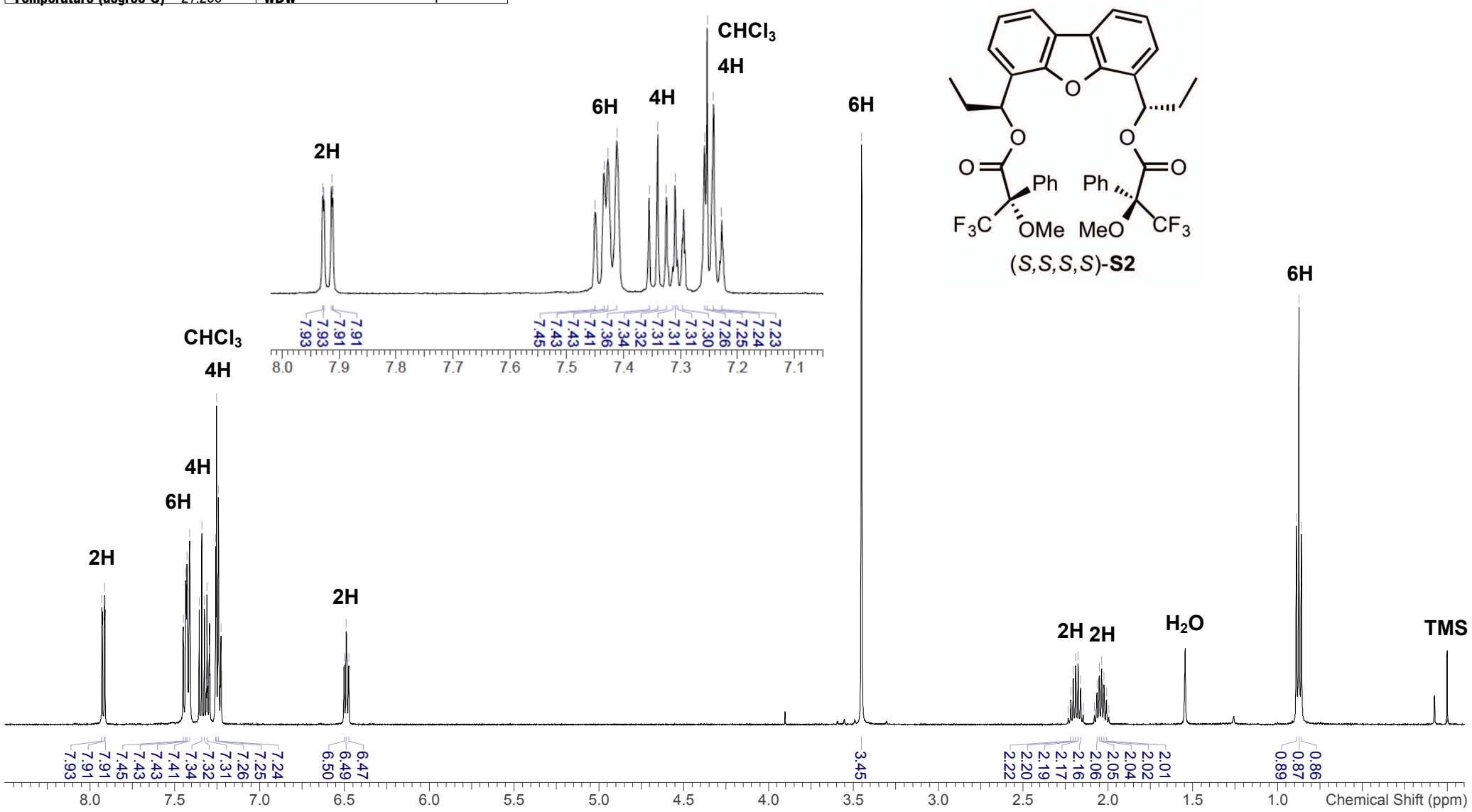




(*S*,*S*,*R*,*R*)-**S2**

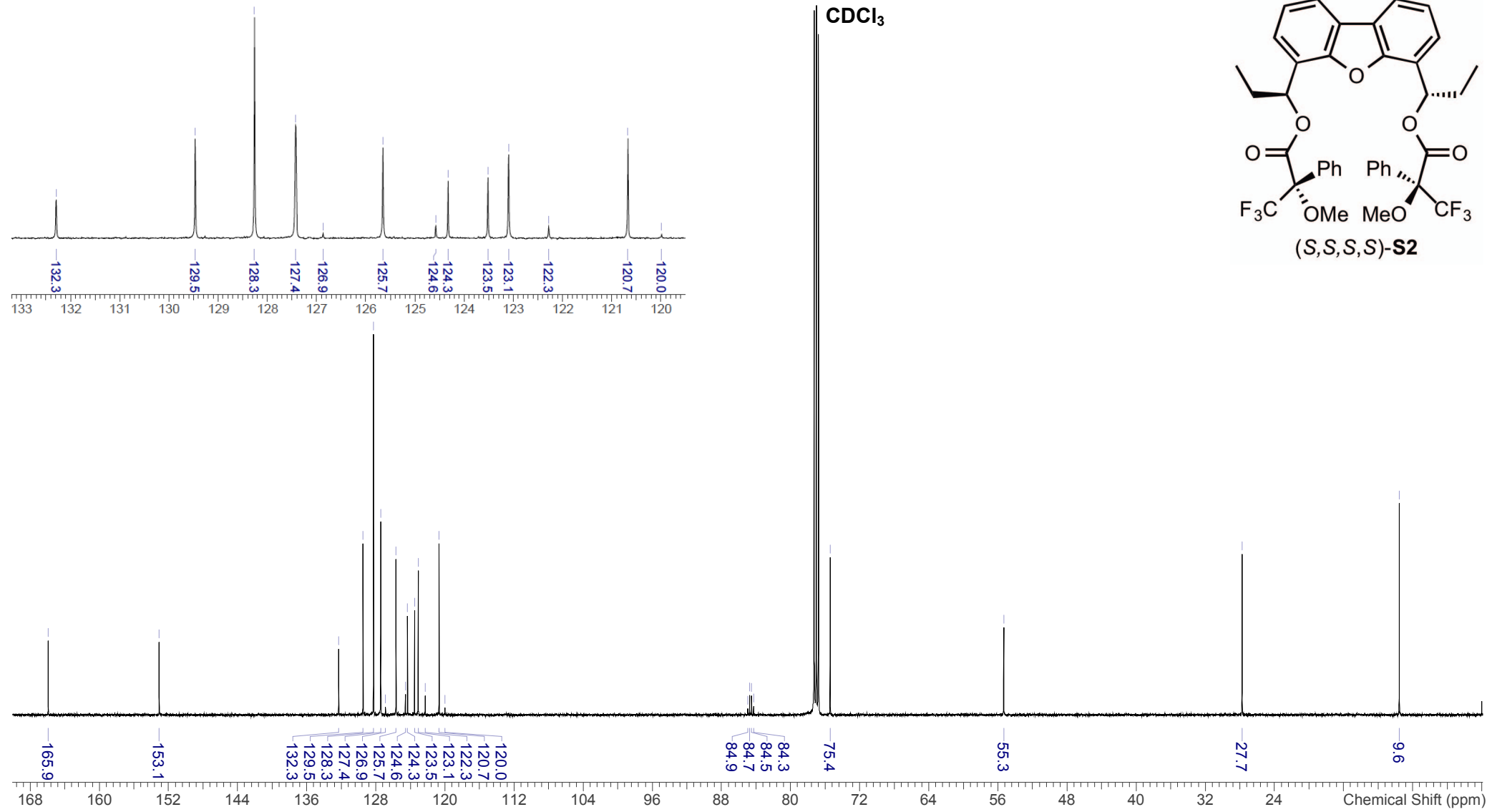
## $^1$H NMR (500 MHz, in $CDCl_3$)

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Acquisition Time (sec)** | 3.1719 | **Comment** | 363 R | **D** | 3.827959 | **D1** | 3.827959 | **DE** | 6 |
| **DS** | 2 | **Date** | 05 Jul 2017 18:40:09 | | | **Date Stamp** | 05 Jul 2017 18:40:09 | | |
| **File Name** | F:¥oku363 R¥1¥PDATA¥1¥1r | | | **Frequency (MHz)** | 500.1300 | **GB** | 0 | **INSTRUM** | <spect> |
| **LB** | 0.1 | **NS** | 8 | **Nucleus** | 1H | **Number of Transients** | 8 | **Origin** | spect |
| **Original Points Count** | 32768 | **Owner** | root | **PC** | 1 | **PROBHD** | <5 mm BBO BB-1H Z-GRD Z859001/0006 > | | |
| **PULPROG** | <zg30> | **Points Count** | 32768 | **Pulse Sequence** | zg30 | **Receiver Gain** | 181.00 | **SF** | 500.130006648269 |
| **SFO1** | 500.133088507478 | | | **SI** | 32768 | **SSB** | 0 | **SW(cyclical) (Hz)** | 10330.58 |
| **SWH** | 10330.5785123967 | | | **Solvent** | CHLOROFORM-d | | | **Spectrum Offset (Hz)** | 3071.1565 |
| **Spectrum Type** | standard | **Sweep Width (Hz)** | 10330.26 | **TD** | 65536 | **TD0** | 1 | **TE** | 300.2 |
| **Temperature (degree C)** | 27.200 | **WDW** | 1 | | | | | | |



## $^{13}$C NMR (126 MHz, in $CDCl_3$)

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Acquisition Time (sec)** | 1.0912 | **Comment** | A.13C_np CDCl3 {C:¥YNU} asmlab 2 | | | **D** | 0.00345 | **D1** | 2 |
| **DE** | 6 | **DS** | 4 | **Date** | 07 Sep 2017 09:46:42 | | | **Date Stamp** | 07 Sep 2017 09:46:42 |
| **File Name** | F:¥NMR¥oku363 S ester 0906¥2¥PDATA¥1¥1r | | | **Frequency (MHz)** | 125.7578 | **GB** | 0 | **INSTRUM** | <spect> |
| **LB** | 1 | **NS** | 7000 | **Nucleus** | 13C | **Number of Transients** | 7000 | **Origin** | spect |
| **Original Points Count** | 32768 | **Owner** | DRX500 | **PC** | 1.4 | **PROBHD** | <5 mm BBO BB-1H Z-GRD Z859001/0006 > | | |
| **PULPROG** | <zgpg30> | **Points Count** | 32768 | **Pulse Sequence** | zgpg30 | **Receiver Gain** | 5792.60 | **SF** | 125.757788761098 |
| **SFO1** | 125.770364304853 | | | **SI** | 32768 | **SSB** | 0 | **SW(cyclical) (Hz)** | 30030.03 |
| **SWH** | 30030.03003003 | | | **Solvent** | CHLOROFORM-d | | | **Spectrum Offset (Hz)** | 12575.5391 |
| **Spectrum Type** | standard | **Sweep Width (Hz)** | 30029.11 | **TD** | 65536 | **TD0** | 1 | **TE** | 299.3 |
| **Temperature (degree C)** | 26.300 | **WDW** | 1 | | | | | | |







(*S*,*S*,*S*,*S*)-**S2**