Supplementary Information for:

Chiral fluorescent sensors based on cellulose derivatives bearing terthienyl pendants

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1. Materials

Anhydrous solvents (toluene, *N*,*N*-dimethylformamide (DMF), dichloromethane and tetrahydrofuran (THF)) and common organic solvents were purchased from Kanto Kagaku (Tokyo, Japan). 2-Bromothiophene was from Tokyo Kasei Kogyo (TCI) (Tokyo, Japan). 2-Iodothiophene (**3a**), tributyltin chloride, tetra-*n*-butylammonium fluoride (1.0 M in THF) and copper (I) iodide (CuI) were from Sigma-Aldrich (St. Louis, MO, USA). (Triisopropylsilyl)acetylene, *trans*-dichlorobis(triphenylphosphine)palladium(II) ($Pd(PPh_3)_2Cl_2$), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC-HCl), *N*,*N*-dimethyl-4-aminopyridine (DMAP) and *n*-butyllithium (1.6 M in *n*-hexane) were purchased from Wako Pure Chemical Industries (Osaka, Japan). Tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$) was purchased from Nacalai (Kyoto, Japan). Triethylamine was obtained from Kishida (Osaka, Japan). All starting materials for the synthesis of aromatic nitro compounds and their analogues (**5**–**9**) were purchased from Nacalai, Wako Pure Chemical Industries and TCI. 2-Bromo-5-(2-hexyldecyl)thiophene (**3f**) was prepared according to a literature procedure.[1]

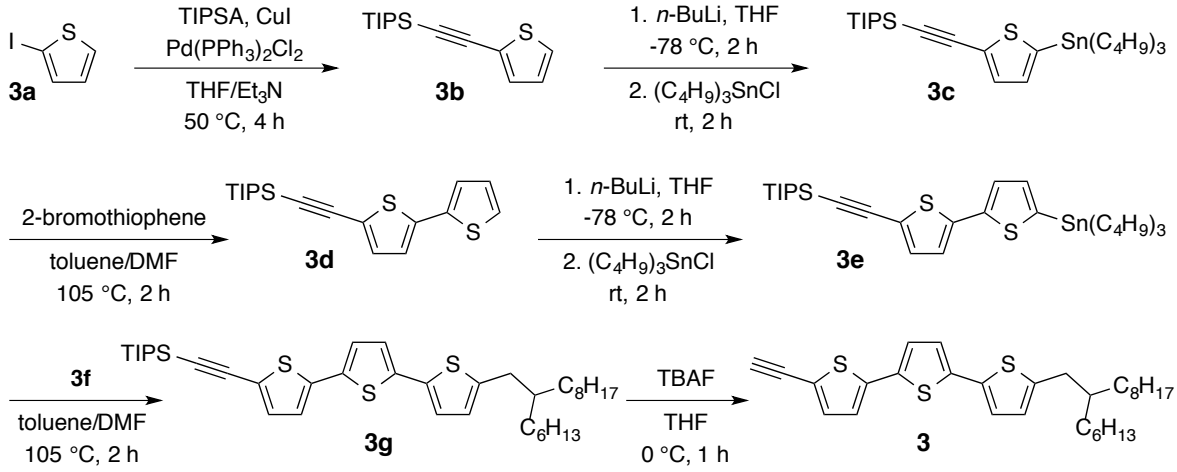
2. Instruments

NMR spectra were taken on a JNA-LA 400 (JEOL, Tokyo, Japan) (400 MHz for ^{1}H) or a JNM-ECA 500 (JEOL) (500 MHz for ^{1}H, 125 MHz for ^{13}C) or a JNM-ECA 600 (JEOL) (600 MHz for ^{1}H) spectrometer in $CDCl_3$, pyridine-d_5 and DMSO-d_6 using tetramethylsilane or a solvent residual peak as the internal standard. Melting points were measured on a Yanako melting point apparatus and were uncorrected. Microwave irradiation experiments were performed using an EYELA Wave Magic MWO-1000S (Tokyo Rikakikai, Tokyo, Japan). TGA was conducted with a TG/DTA6200 (SII NanoTechnology, Chiba, Japan) at a heating rate of 10 °C min^{-1} under a nitrogen flow. IR spectra were obtained using a JASCO (Hachioji, Japan) Fourier Transform IR-460 spectrophotometer with a KBr pellet. Absorption and circular dichroism (CD) spectra were measured at 25 °C in a 1.0 or 10 mm quartz cell using a JASCO V-570 and a JASCO J-725 spectrometers, respectively. The temperature was controlled using a JASCO ETC-505T (absorption spectroscopy) and a JASCO PTC-348WI apparatus (CD spectroscopy). Dynamic light scattering (DLS) measurements were performed on a Nano partica SZ-100 (Horiba, Kyoto, Japan) equipped with a 10 mW a diode pumped solid state laser (532 nm)

at 25 °C. Fluorescence emission spectra were measured with a JASCO FP-6300. Elemental analyses were performed by the Research Institute for Instrumental Analysis of Advanced Science Research Center, Kanazawa University, Kanazawa, Japan.

3. Synthesis

2,2':5',2''-Terthiophene derivative (**3**) was prepared according to Scheme S1. Aromatic nitro compounds and their analogues (**5**–**9**) were synthesized thorough common condensation reactions using the corresponding amine or alcohol compounds as starting materials.



Scheme S1 Synthesis of 2,2':5',2''-terthiophene derivative (**3**).

2-[(Triisopropylsilyl)ethynyl]thiophene (3b). To a solution of **3a** (20.0 g, 95.2 mmol), $Pd(PPh_3)_2Cl_2$ (3.34 g, 4.76 mmol) and CuI (0.91 g, 4.76 mmol) in degassed THF/triethylamine (3/1, v/v) (480 mL) was added (triisopropylsilyl)acetylene (22.3 mL, 99.9 mmol). The solution was stirred at 50 °C for 4 h. After cooling to room temperature, the reaction mixture was diluted with hexane and passed through Celite to remove the metal catalyst. The solution was washed with 1 N HCl aqueous solution and water, and then dried over Na_2SO_4. After removing the solvent by evaporation, the crude product was purified by silica gel chromatography using hexane as the eluent to give the desired product as a colorless oil (25.1 g, 99% yield). ^{1}H NMR (600 MHz, $CDCl_3$, rt): δ 7.23-7.20 (m, 2H, Ar-H), 6.95 (dd, J = 5.0, 3.6 Hz, 1H, Ar-H), 1.14-1.10 (m, 21H, TIPS).

2-(Tributyltin)-5-[(triisopropylsilyl)ethynyl]thiophene (3c). To a solution of **3b** (25.1 g, 95.1 mmol) in anhydrous THF (338 mL) was added dropwise *n*-butyllithium (1.6

M in hexane, 62 mL, 99 mmol) via syringe at –78 °C under nitrogen atmosphere. After the mixture was stirred at –78 °C for 2 h, tributyltin chloride (30 mL, 110 mmol) was added. The mixture was warmed to room temperature and stirred for 2 h. After quenching the reaction with water, the volatile species were evaporated in vacuo. The residue was extracted with hexane, and the organic layer was washed with water, dried over anhydrous Na_2SO_4 and concentrated. Compound **3c** (58.0 g) was obtained as a pale yellow oil and was used for the next step without further purification. ^{1}H NMR (600 MHz, $CDCl_3$, rt): δ 7.33 (d, J = 3.0 Hz, 1H, Ar-H), 6.99 (d, J = 3.6 Hz, 1H, Ar-H), 1.68-1.50 (m, 6H, $3CH_2$), 1.38-1.28 (m, 12H, $6CH_2$), 1.14-1.09 (m, 21H, TIPS), 0.94-0.87 (m, 9H, $3CH_3$).

5-[(Triisopropylsilyl)ethynyl]-2,2'-bithiophene (3d). To a solution of **3c** (10.0 g) and 2-bromothiophene (2.95 g, 18.1 mmol) in toluene/DMF (4/1, v/v) (80 mL) was added $Pd(PPh_3)_4$ (0.626 g, 0.542 mmol). The solution was stirred at 105 °C for 2 h under microwave heating. After cooling to room temperature, the reaction mixture was diluted with hexane, washed with water, and then dried over Na_2SO_4. After removing the solvent by evaporation, the crude product was purified by silica gel chromatography using hexane as the eluent to give the desired product as a pale yellow oil (4.03 g, 77% yield). ^{1}H NMR (600 MHz, $CDCl_3$, rt): δ 7.23 (d, J = 4.8 Hz, 1H, Ar-H), 7.17 (d, J = 3.8 Hz, 1H, Ar-H), 7.12 (d, J = 3.8 Hz, 1H, Ar-H), 7.01 (d, J = 3.8 Hz, 2H, Ar-H), 1.13 (s, 21H, TIPS).

5-(Tributyltin)-5'-[(triisopropylsilyl)ethynyl]-2,2'-bithiophene (3e). To a solution of **3d** (2.90 g, 8.37 mmol) in anhydrous THF (30 mL) was added dropwise *n*-butyllithium (1.6 M in hexane, 5.50 mL, 8.80 mmol) via syringe at –78 °C under nitrogen atmosphere. After the mixture was stirred at –78 °C for 2 h, tributyltin chloride (2.6 mL, 9.6 mmol) was added. The mixture was warmed to room temperature and stirred for 2 h. After quenching the reaction with water, the volatile species were evaporated in vacuo. The residue was extracted with hexane, and the organic layer was washed with water, dried over anhydrous Na_2SO_4 and concentrated. Compound **3e** (7.88 g) was obtained as a yellow oil and was used for the next step without further purification. ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 7.28 (d, J = 3.4 Hz, 1H, Ar-H), 7.11 (d, J = 4.0 Hz, 1H, Ar-H), 7.05 (d, J = 3.4 Hz, 1H, Ar-H), 7.00 (d, J = 4.0 Hz, 1H, Ar-H), 1.68-1.53 (m, 6H, $3CH_2$), 1.40-1.30 (m, 12H, $6CH_2$), 1.14-1.10 (m, 21H, TIPS), 0.93-0.88 (m, 9H, $3CH_3$).

5-(2-Hexyldecyl)-5''-[2-(triisopropylsilyl)ethynyl]-2,2':5',2''-terthiophene (3g). To a solution of **3e** (1.41 g) and **3f** (0.59 g, 2.1 mmol) in toluene/DMF (4/1, v/v) (8 mL) was

added $Pd(PPh_3)_4$ (63 mg, 0.055 mmol). The solution was stirred at 105 °C for 4 h under microwave heating. After cooling to room temperature, the reaction mixture was diluted with hexane, washed with water, and then dried over Na_2SO_4. After removing the solvent by evaporation, the crude product was purified by silica gel chromatography using hexane as the eluent to give the desired product as a pale yellow oil (0.98 g, 71% yield). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 7.11 (d, J = 4.0 Hz, 1H, Ar-H), 7.04 (d, J = 4.0 Hz, 1H, Ar-H), 7.00-6.95 (m, 3H, Ar-H), 6.66 (d, J = 3.2 Hz, 1H, Ar-H), 2.72 (d, J = 6.9 Hz, 2H, Ar-CH_2), 1.62 (br, 1H, CH), 1.37-1.19 (m, 24H, 12CH_2), 1.11 (s, 21H, TIPS), 0.92-0.84 (m, 6H, 2CH_3).

5-(2-Hexyldecyl)-5''-ethynyl-2,2':5',2''-terthiophene (3). To a solution of **3g** (0.98 g, 1.5 mmol) in THF (72 mL) was added tetra-*n*-butylammonium fluoride (1.0 M in THF, 2.2 mL, 2.2 mmol). The mixture was stirred at 0 °C for 1 h and was diluted with dichloromethane. The solution was washed with 1 N HCl aqueous solution and water, and then dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure and the crude product was then purified by silica gel chromatography using *n*-hexane–dichloromethane (9/1, v/v) as the eluent to give the desired product as a yellow solid (0.56 g, 75% yield). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 7.17 (d, J = 3.7 Hz, 1H, Ar-H), 7.06 (d, J = 3.7 Hz, 1H, Ar-H), 6.99 (d, J = 3.7 Hz, 3H, Ar-H), 6.66 (d, J = 3.2 Hz, 1H, Ar-H), 3.40 (s, 1H, C≡CH), 2.72 (d, J = 6.9 Hz, 2H, CH_2), 1.60 (br, 1H, CH), 1.37-1.07 (m, 24H, 12CH_2), 1.00-0.57 (m, 6H, 2CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 144.59, 139.11, 137.80, 134.37, 133.96, 125.97, 124.97, 123.58, 123.50, 122.88, 120.36, 82.26, 76.92, 39.96, 34.58, 33.19, 33.15, 31.90, 31.88, 29.93, 29.61, 29.32, 26.58, 22.68, 14.12. IR (KBr, cm^{-1}): 3307 (≡CH), 2100 (C≡C). Calcd for $C_{30}H_{40}S_3 \cdot 0.1H_2O$: C, 72.26; H, 8.13. Found: C, 71.99; H, 8.04.

(–)-*N*-(4-Nitrobenzoyl)-D-alanine methyl ester ((*R*)-5a). D-Alanine methyl ester hydrochloride (0.75 g, 5.4 mmol) and triethylamine (1.5 mL, 10.8 mmol) were dissolved in anhydrous THF (15 mL) and the solution was cooled to 0 °C. To this solution was added 4-nitrobenzoyl chloride (1.0 g, 5.4 mmol) dissolved in THF (15 mL) and the mixture was stirred at rt for 2 h. The mixture was diluted with THF, washed with brine, and then dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by silica gel chromatography using hexane–ethyl acetate (1/2, v/v) as the eluent, followed by recrystallization from a hexane–ethyl acetate mixture to give the desired

product as a white solid (0.99 g, 73% yield). Mp: 137.7–138.1 °C. $[\alpha]^{25}_{D}$ –4.1 (*c* 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$, rt): δ 8.34-8.28 (m, 2H, Ar-H), 8.01-7.95 (m, 2H, Ar-H), 6.81 (d, J = 5.5 Hz, 1H, NH), 4.84-4.77 (m, 1H, CH), 3.82 (s, 3H, OCH_3), 1.56 (s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 173.37, 164.75, 149.76, 139.43, 128.29, 123.87, 52.83, 48.79, 18.56. IR (KBr, cm^{-1}): 3296 (N-H), 1741 (C=O). Calcd for $C_{11}H_{12}N_2O_5$: C, 52.38; H, 4.80; N, 11.11. Found: C, 52.23; H, 4.89; N, 11.11.

(+)-*N*-(4-Nitrobenzoyl)-L-alanine methyl ester ((*S*)-5a). The title compound was prepared from L-alanine methyl ester hydrochloride in the same way as (*R*)-**5a** and obtained in 66% yield as a white solid. Mp: 137.9–138.4 °C. $[\alpha]^{25}_{D}$ +4.1 (*c* 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$, rt): δ 8.35-8.28 (m, 2H, Ar-H), 8.01-7.95 (m, 2H, Ar-H), 6.81 (d, J = 5.8 Hz, 1H, NH), 4.84-4.77 (m, 1H, CH), 3.82 (s, 3H, OCH_3), 1.57 (s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 173.37, 164.75, 149.77, 139.43, 128.29, 123.87, 52.83, 48.79, 18.56. IR (KBr, cm^{-1}): 3293 (N-H), 1741 (C=O). Calcd for $C_{11}H_{12}N_2O_5$: C, 52.38; H, 4.80; N, 11.11. Found: C, 52.37; H, 4.79; N, 11.12.

***N*-(4-Nitrobenzoyl)-DL-alanine methyl ester (*rac*-5a).** The title compound was prepared from DL-alanine methyl ester hydrochloride in the same way as (*R*)-**5a** and obtained in 43% yield as a white solid. Mp: 129.4–129.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 8.34-8.28 (m, 2H, Ar-H), 8.01-7.95 (m, 2H, Ar-H), 6.81 (d, J = 6.9 Hz, 1H, NH), 4.85-4.77 (m, 1H, CH), 3.82 (s, 3H, OCH_3), 1.59-1.54 (m, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 173.39, 164.81, 149.73, 139.42, 128.33, 123.85, 52.84 (q, J = 8.4 Hz), 48.79 (d, J = 9.6 Hz), 18.49 (d, J = 3.5 Hz). IR (KBr, cm^{-1}): 3296 (N-H), 1736 (C=O). Calcd for $C_{11}H_{12}N_2O_5$: C, 52.38; H, 4.80; N, 11.11. Found: C, 52.18; H, 4.80; N, 11.11.

***N*-Benzoyl-DL-alanine methyl ester (*rac*-5b).** The title compound was prepared from DL-alanine methyl ester hydrochloride and benzoyl chloride in the same way as (*R*)-**5a** and obtained in 26% yield as a white solid. Mp: 81.8–82.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 7.81 (d, J = 7.4 Hz, 2H, Ar-H), 7.55-7.49 (m, 1H, Ar-H), 7.48-7.42 (m, 2H, Ar-H), 6.78-6.64 (br, 1H, NH), 4.86-4.76 (m, 1H, CH), 3.80 (s, 3H, OCH_3), 1.53 (d, J = 7.4 Hz, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 173.69, 166.75, 133.91, 131.73, 128.58, 127.01, 52.59, 48.45, 18.70. IR (KBr, cm^{-1}): 3307 (N-H), 1751 (C=O). Calcd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32; N, 6.76. Found: C, 63.47; H, 6.32; N, 6.76.

(–)-*N*-(4-Nitrobenzoyl)-D-valine methyl ester ((*R*)-6). The title compound was

prepared from D-valine methyl ester hydrochloride in the same way as (*R*)-**5a** and obtained in 56% yield as a white solid. Mp: 125.8–126.2 °C. $[\alpha]^{25}_{D}$ –4.6 (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 8.34-8.29 (m, 2H, Ar-H), 8.00-7.94 (m, 2H, Ar-H), 6.68 (d, *J* = 8.6 Hz, 1H, NH), 4.83-4.76 (m, 1H, CH), 3.81 (s, 3H, OCH_3), 2.37-2.25 (m, 1H, CH), 1.02 (dd, *J* = 11.5, 6.9 Hz, 6H, $2CH_3$). ^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 172.38, 165.32, 149.73, 139.67, 128.30, 123.89, 57.70, 52.51, 31.62, 19.00, 17.97. IR (KBr, cm^{-1}): 3255 (N-H), 1747 (C=O). Calcd for $C_{13}H_{16}N_2O_5$: C, 55.71; H, 5.75; N, 10.00. Found: C, 55.49; H, 5.68; N, 9.94.

(+)-*N*-(4-Nitrobenzoyl)-L-valine methyl ester ((*S*)-6). The title compound was prepared from L-valine methyl ester hydrochloride in the same way as (*R*)-**5a** and obtained in 67% yield as a white solid. Mp: 125.7–126.0 °C. $[\alpha]^{25}_{D}$ +4.3 (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 8.36-8.28 (m, 2H, Ar-H), 8.02-7.94 (m, 2H, Ar-H), 6.69 (d, *J* = 8.0 Hz, 1H, NH), 4.82-4.76 (m, 1H, CH), 3.81 (s, 3H,OCH_3), 2.36-2.26 (m, 1H, CH), 1.02 (dd, *J* = 11.5, 6.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 172.38, 165.32, 149.73, 139.67, 128.30, 123.89, 57.70, 52.51, 31.62, 19.00, 17.97. IR (KBr, cm^{-1}): 3255 (N-H), 1747 (C=O). Calcd for $C_{13}H_{16}N_2O_5$: C, 55.71; H, 5.75; N, 10.00. Found: C, 55.60; H, 5.77; N, 9.99.

(–)-*N*-(4-Nitrobenzoyl)-D-leucine methyl ester ((*R*)-7). The title compound was prepared from D-leucine methyl ester hydrochloride in the same way as (*R*)-**5a** and obtained in 70% yield as a white solid. Mp: 106.6–106.9 °C. $[\alpha]^{25}_{D}$ –2.6 (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 8.34-8.29 (m, 2H, Ar-H), 8.00-7.94 (m, 2H, Ar-H), 6.58 (d, *J* = 7.4 Hz, 1H, NH), 4.91-4.81 (m, 1H, CH), 3.80 (s, 3H, OCH_3), 1.84-1.64 (m, 3H, $CHCH_2$), 1.00 (dd, *J* = 10.3, 6.3 Hz, 6H, $2CH_3$). ^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 173.53, 165.11, 149.71, 139.37, 128.31, 123.82, 52.63, 51.42, 41.67, 25.03, 22.81, 22.00. IR (KBr, cm^{-1}): 3313 (N-H), 1749 (C=O). Calcd for $C_{14}H_{18}N_2O_5$: C, 57.14; H, 6.16; N, 9.52. Found: C, 56.86; H, 6.11; N, 9.48.

(+)-*N*-(4-Nitrobenzoyl)-L-leucine methyl ester ((*S*)-7). The title compound was prepared from L-leucine methyl ester hydrochloride in the same way as (*R*)-**5a** and obtained in 70% yield as a white solid. Mp: 106.6–107.2 °C. $[\alpha]^{25}_{D}$ +2.6 (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 8.37-8.24 (m, 2H, Ar-H), 8.03-7.90 (m, 2H, Ar-H), 6.59 (d, *J* = 7.4 Hz, 1H, NH), 4.94-4.80 (m, 1H, CH), 3.80 (s, 3H, OCH_3), 1.87-1.62 (m, 3H, $CHCH_2$), 1.00 (dd, *J* = 10.3, 6.3 Hz, 6H, $2CH_3$). ^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 173.51, 165.10,

149.72, 139.39, 128.31, 123.83, 52.64, 51.41, 41.70, 25.03, 22.81, 22.00. IR (KBr, cm^{-1}): 3313 (N-H), 1747 (C=O). Calcd for $C_{14}H_{18}N_2O_5$: C, 57.14; H, 6.16; N, 9.52. Found: C, 57.06; H, 6.16; N, 9.47.

(*R*)-(+)-1,1'-Binaphthyl-2,2'-diyl bis(4-nitrobenzoate) ((*R*)-8a). (*R*)-1,1'-Bi-2-naphthol (1.00 g, 3.49 mmol), 4-nitrobenzoic acid (1.75 g, 10.5 mmol), DMAP (1.28 g, 10.5 mmol) were dissolved in anhydrous dichloromethane (18 mL) and the solution was cooled to 0 °C. To this solution was added EDC-HCl (2.01 g, 10.5 mmol) and the mixture was stirred at rt for 12 h. The mixture was diluted with dichloromethane, washed with 1 N HCl aqueous solution and water, and then dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by silica gel chromatography using hexane–dichloromethane (1/4, v/v) as the eluent to give the desired product as a pale yellow solid (2.00 g, 98% yield). Mp: 93.6–94.1 °C. $[\alpha]^{25}_D$ +4.9 (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 8.11-8.04 (m, 4H, Ar-H), 8.02 (d, J = 8.6 Hz, 2H, Ar-H), 7.95 (d, J = 8.6 Hz, 2H, Ar-H), 7.72-7.65 (m, 4H, Ar-H), 7.59-7.48 (m, 4H, Ar-H), 7.46-7.34 (m, 4H, Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 162.90, 150.54, 146.46, 134.41, 133.12, 131.68, 130.79, 130.04, 128.24, 127.30, 126.23, 125.87, 123.39, 121.24. IR (KBr, cm^{-1}): 1743 (C=O). Calcd for $C_{34}H_{20}N_2O_8 \cdot 0.01H_2O$: C, 69.84; H, 3.45; N, 4.79. Found: C, 69.54; H, 3.48; N, 4.75.

(*S*)-(–)-1,1'-Binaphthyl-2,2'-diyl bis(4-nitrobenzoate) ((*S*)-8a). The title compound was prepared from (*S*)-1,1'-bi-2-naphthol in the same way as (*R*)-**8a** and obtained in 99% yield as a pale yellow solid. Mp: 93.5–93.9 °C. $[\alpha]^{25}_D$ –4.7 (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 8.11-8.04 (m, 4H, Ar-H), 8.02 (d, J = 9.2 Hz, 2H, Ar-H), 7.95 (d, J = 8.0 Hz, 2H, Ar-H), 7.73-7.65 (m, 4H, Ar-H), 7.58-7.47 (m, 4H, Ar-H), 7.44-7.36 (m, 4H, Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 162.91, 150.55, 146.46, 134.41, 133.11, 131.68, 130.79, 130.04, 128.24, 127.29, 126.23, 125.87, 123.40, 121.24. IR (KBr, cm^{-1}): 1744 (C=O). Calcd for $C_{34}H_{20}N_2O_8$: C, 69.86; H, 3.45; N, 4.79. Found: C, 69.79; H, 3.58; N, 4.78.

***rac*-1,1'-Binaphthyl-2,2'-diyl bis(4-nitrobenzoate) (*rac*-8a).** The title compound was prepared from *rac*-1,1'-bi-2-naphthol in the same way as (*R*)-**8a** and obtained in 98% yield as a pale yellow solid. Mp: 173.5–173.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 8.09-8.04 (m, 4H, Ar-H), 8.02 (d, J = 9.2 Hz, 2H, Ar-H), 7.95 (d, J = 8.0 Hz, 2H, Ar-H), 7.71-7.66 (m, 4H, Ar-H), 7.57-7.49 (m, 4H, Ar-H), 7.44-7.37 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$, rt): δ

162.91, 150.55, 146.46, 134.41, 133.11, 131.68, 130.79, 130.04, 128.24, 127.29, 126.23, 125.87, 123.40, 121.24. IR (KBr, cm^{-1}): 1741 (C=O). Calcd for $C_{34}H_{20}N_2O_8$: C, 69.86; H, 3.45; N, 4.79. Found: C, 69.75; H, 3.58; N, 4.81.

***rac*-1,1'-Binaphthyl-2,2'-diyl bisbenzoate (*rac*-8b).** The title compound was prepared from *rac*-1,1'-bi-2-naphthol and benzoic acid in the same way as (*R*)-**8a** and obtained in 90% yield as a pale yellow solid. Mp: 164.5–164.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 7.98 (d, J = 8.6 Hz, 2H, Ar-H), 7.90 (d, J = 8.6 Hz, 2H, Ar-H), 7.64 (d, J = 7.4 Hz, 4H, Ar-H), 7.56 (d, J = 8.6 Hz, 2H, Ar-H), 7.44 (dd, J = 12.6, 7.4 Hz, 4H, Ar-H), 7.39 (d, J = 8.6 Hz, 2H, Ar-H), 7.36-7.30 (m, 2H, Ar-H), 7.28-7.20 (m, 4H, Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$, 55 °C): δ 164.67, 147.19, 133.55, 133.05, 131.67, 129.87, 129.49, 128.17, 128.01, 126.81, 126.22, 125.67, 123.80, 121.81. IR (KBr, cm^{-1}): 1736 (C=O). Calcd for $C_{34}H_{22}O_4$: C, 82.58; H, 4.48. Found: C, 82.29; H, 4.51.

(*R*)-(–)-5,5',6,6',7,7',8,8'-Octahydro-1,1'-binaphthyl-2,2'-diyl bis(4-nitrobenzoate) ((*R*)-9). The title compound was prepared from (*R*)-5,5',6,6',7,7',8,8'-octahydro-1,1'-bi-2-naphthol in the same way as (*R*)-**8a** and obtained in 83% yield as a pale yellow solid. Mp: 81.4–81.8 °C. $[\alpha]^{25}_D$ –7.4 (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 8.20 (d, J = 8.6 Hz, 4H, Ar-H), 7.90 (d, J = 8.6 Hz, 4H, Ar-H), 7.10 (q, J = 8.6 Hz, 4H, Ar-H), 2.90-2.68 (m, 4H, $2CH_2$), 2.52-2.21 (m, 4H, $2CH_2$), 1.86-1.61 (m, 8H, $4CH_2$). ^{13}C NMR (125 MHz, $CDCl_3$, 55 °C): δ 162.96, 150.84, 145.94, 137.51, 135.81, 135.23, 130.87, 129.49, 128.16, 123.41, 119.35, 29.53, 27.29, 22.92, 22.89. IR (KBr, cm^{-1}): 1742 (C=O). Calcd for $C_{34}H_{28}N_2O_8$: C, 68.91; H, 4.76; N, 4.73. Found: C, 68.92; H, 4.71; N, 4.69.

(*S*)-(+)-5,5',6,6',7,7',8,8'-Octahydro-1,1'-binaphthyl-2,2'-diyl bis(4-nitrobenzoate) ((*S*)-9). The title compound was prepared from (*S*)-5,5',6,6',7,7',8,8'-octahydro-1,1'-bi-2-naphthol in the same way as (*R*)-**8a** and obtained in 91% yield as a pale yellow solid. Mp: 81.7–82.2 °C. $[\alpha]^{25}_D$ +7.6 (*c* 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 8.19 (d, J = 9.2 Hz, 4H, Ar-H), 7.90 (d, J = 8.6 Hz, 4H, Ar-H), 7.10 (q, J = 8.6 Hz, 4H, Ar-H), 2.90-2.66 (m, 4H, $2CH_2$), 2.54-2.22 (m, 2H, $2CH_2$), 1.87-1.59 (m, 8H, $4CH_2$). ^{13}C NMR (125 MHz, $CDCl_3$, 55 °C): δ 162.96, 150.84, 145.94, 137.51, 135.81, 135.23, 130.87, 129.49, 128.15, 123.42, 119.35, 29.54, 27.29, 22.92, 22.89. IR (KBr, cm^{-1}): 1741 (C=O). Calcd for $C_{34}H_{28}N_2O_8$: C, 68.91; H, 4.76; N, 4.73. Found: C, 68.91; H, 4.80; N, 4.65.

Supporting data

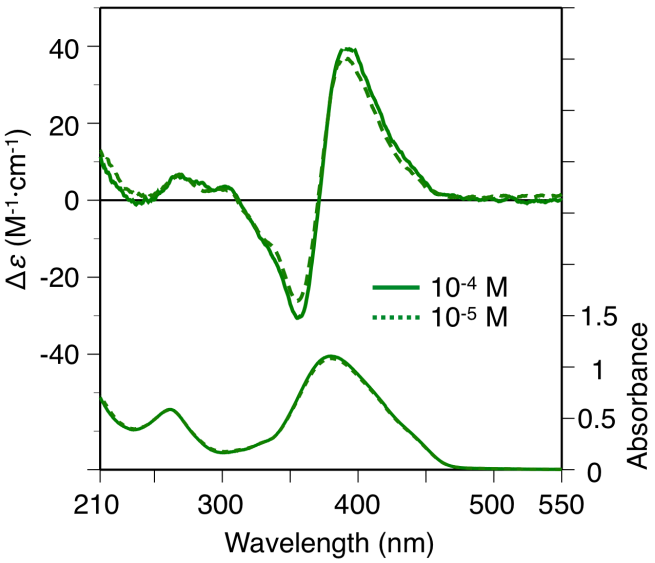


Fig. S1 CD and absorption spectra of Ce-**1b** in hexane/THF (75/25, v/v) at 25 °C. The spectra indicated by dashed and solid lines were obtained from polymer solutions of 1.0×10^{-5} M (cell length: 10 mm) and 1.0×10^{-4} M (cell length: 1.0 mm), respectively.

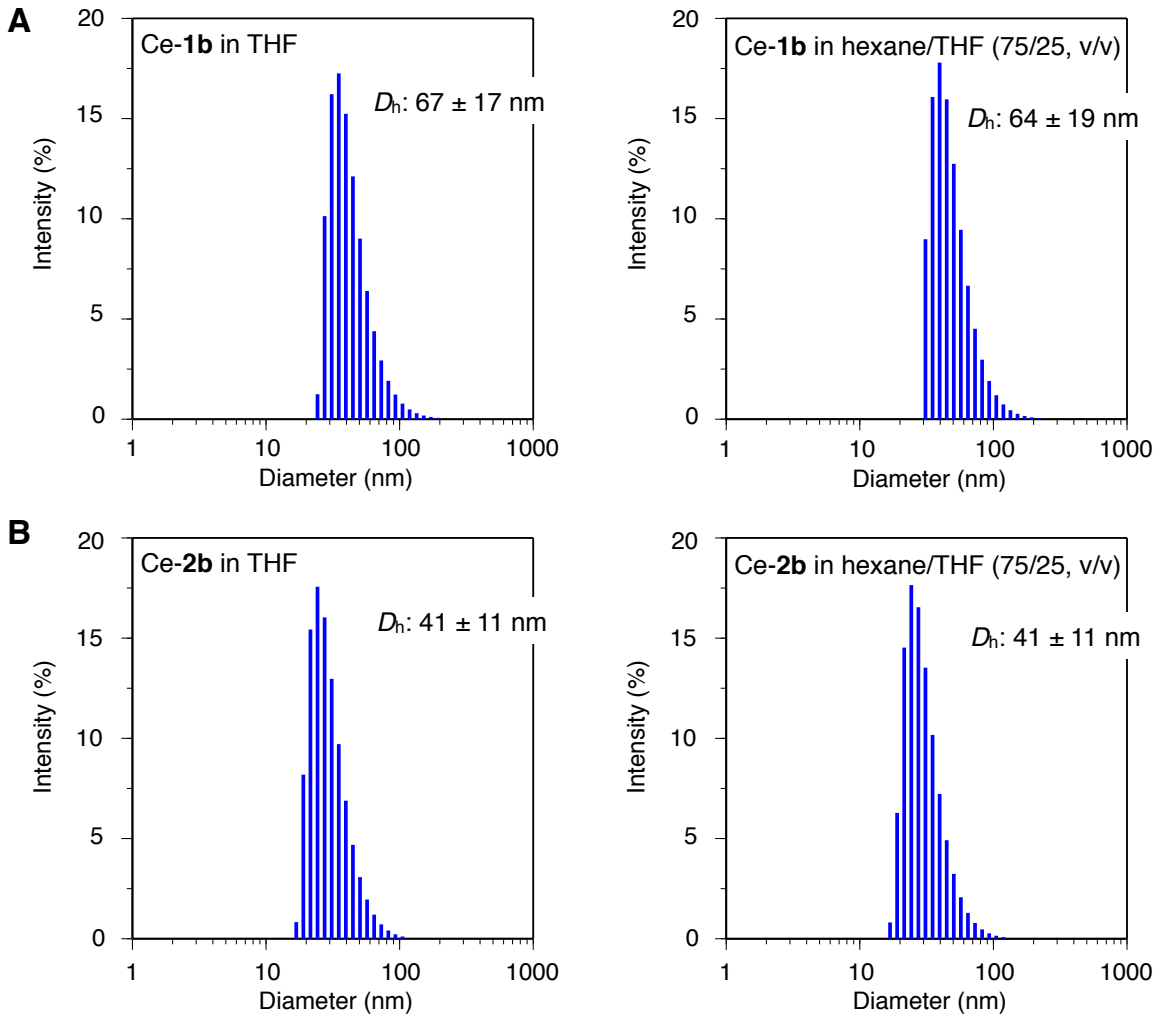


Fig. S2 Histogram analysis of the DLS measurements of Ce-**1b** (A) and Ce-**2b** (B) in THF (left) and hexane/THF (75/25, v/v) (right) at 30 °C after filtration through a membrane filter with a pore size of 0.45 μm. [glucose unit] = 1.0×10^{-4} M.

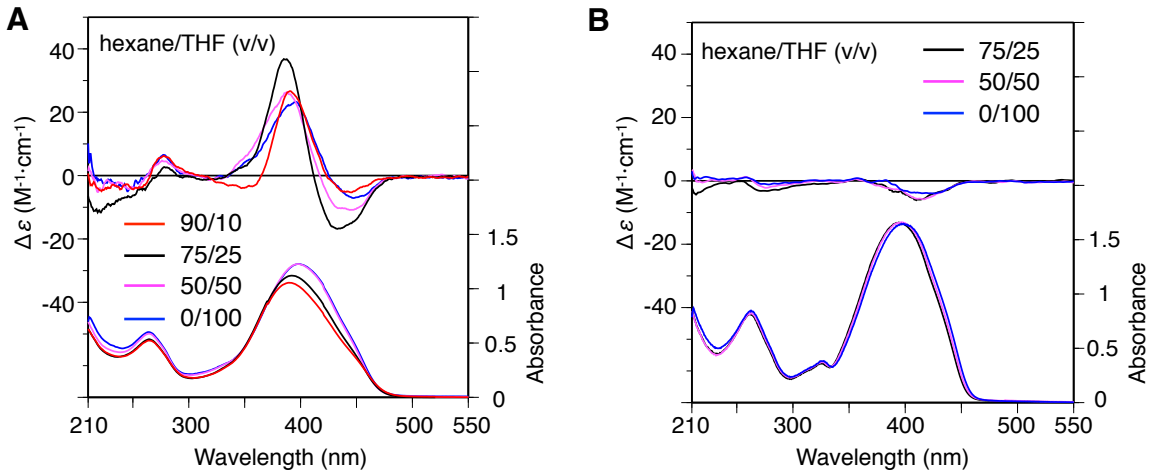


Fig. S3 CD and absorption spectra of Ce-**2b** (A) and Gl-**1b** (B) in hexane/THF (hexane: 0–90 vol %) at 25 °C. [glucose unit] = 1.0×10^{-5} M.

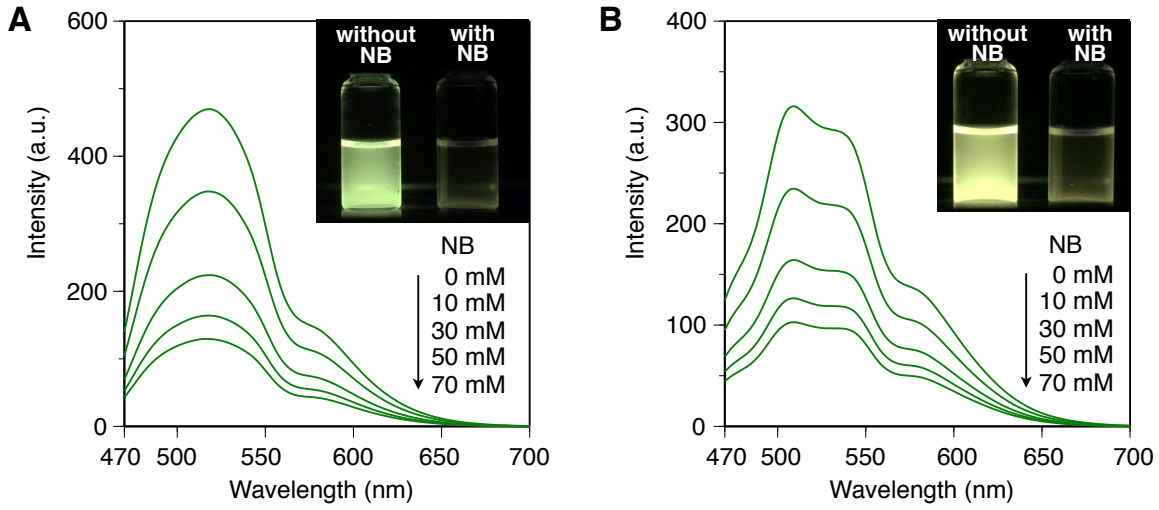


Fig. S4 Fluorescence spectra of Ce-**2b** (A) and Gl-**1b** (B) upon the addition of various amounts of NB (0–70 mM) in THF at rt. [glucose unit] = 1.0×10^{-5} M, λ_{ex} = 450 nm. Insets: Photographs of each fluorophore solution in the absence (left) and presence (right) of nitrobenzene (70 mM) under irradiation at 365 nm.

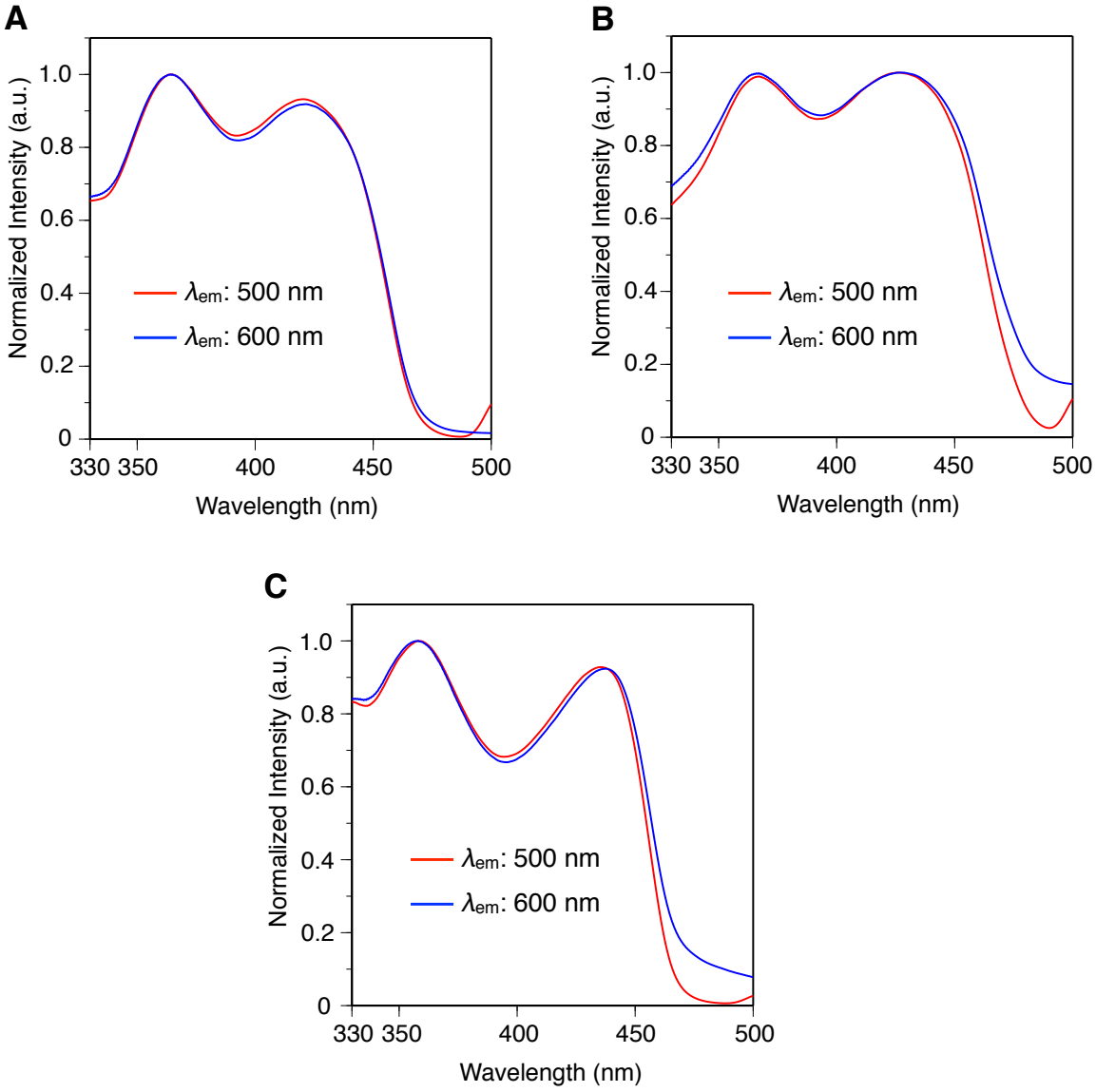


Fig. S5 Excitation spectra of Ce-**1b** (A), Ce-**2b** (B) and Gl-**1b** (C) recorded for 500 (red line) and 600 (blue line) nm emissions in THF at rt. [glucose unit] = 1.0×10^{-5} M.

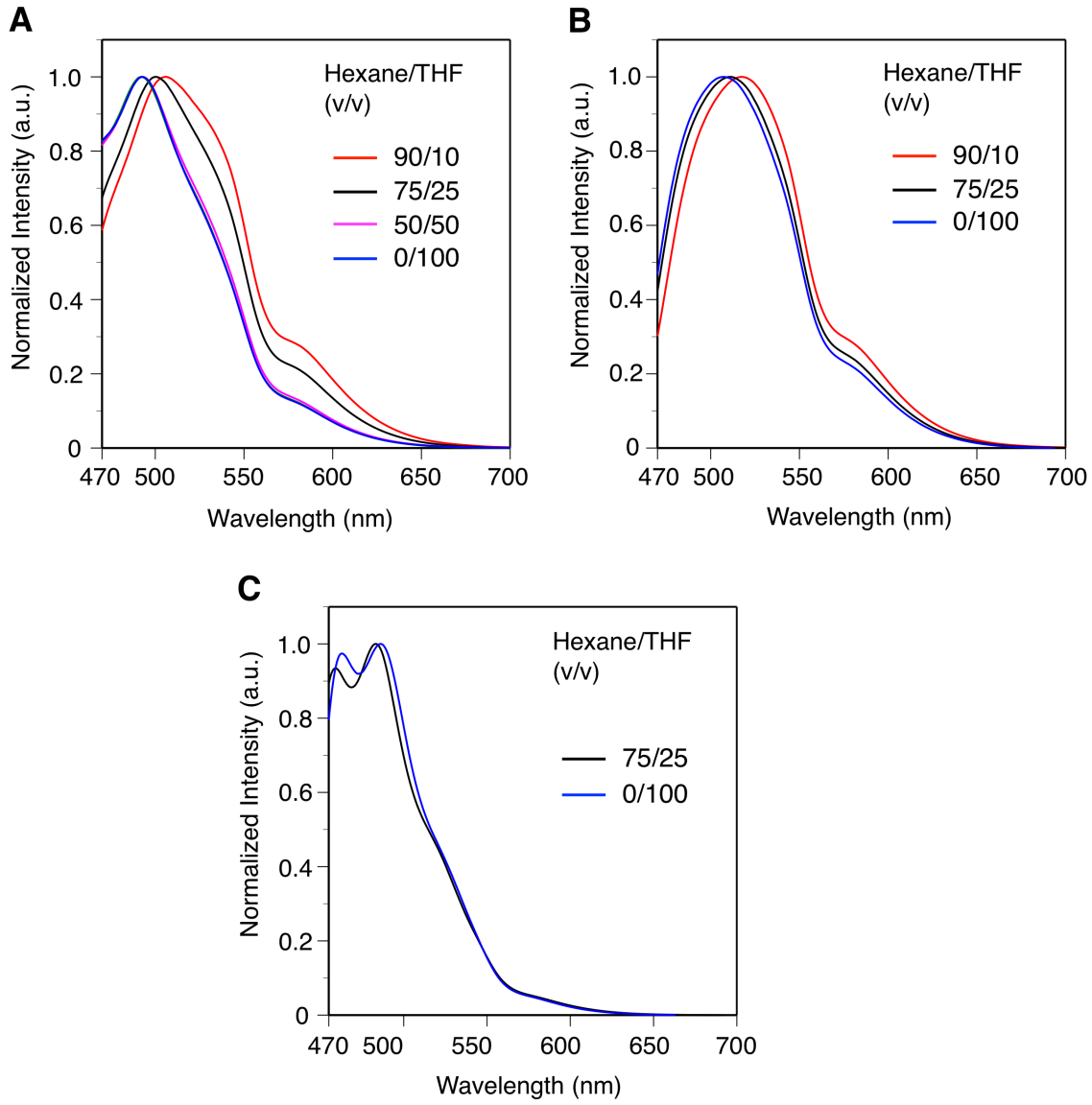


Fig. S6 Fluorescence spectra of Ce-**1b** (A), Ce-**2b** (B) and Gl-**1b** (C) in hexane/THF (hexane: 0–90 vol %) at rt. [glucose unit] = 1.0×10^{-5} M, λ_{ex} = 450 nm.

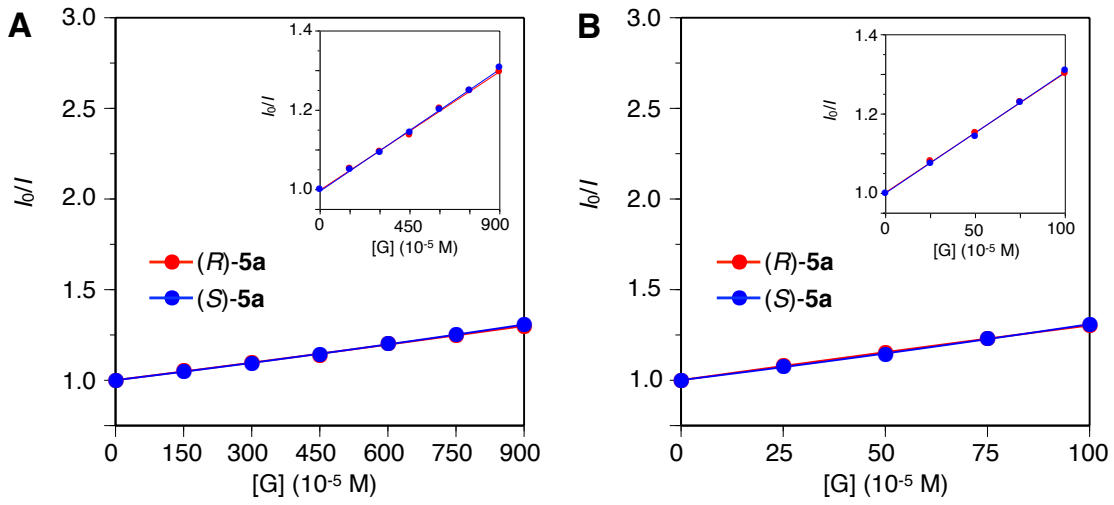


Fig. S7 Stern-Volmer plots for the fluorescence quenching of Gl-**1b** (A) and Ce-**2b** (B) by (*R*)-**5a** (red) and (*S*)-**5a** (blue) in hexane/THF (75/25 for Gl-**1b** and 90/10 for Ce-**2b**, v/v) at rt. [glucose unit] = 1.0×10^{-5} M, λ_{ex} = 450 nm. The insets show expanded detail of the Stern-Volmer plots.

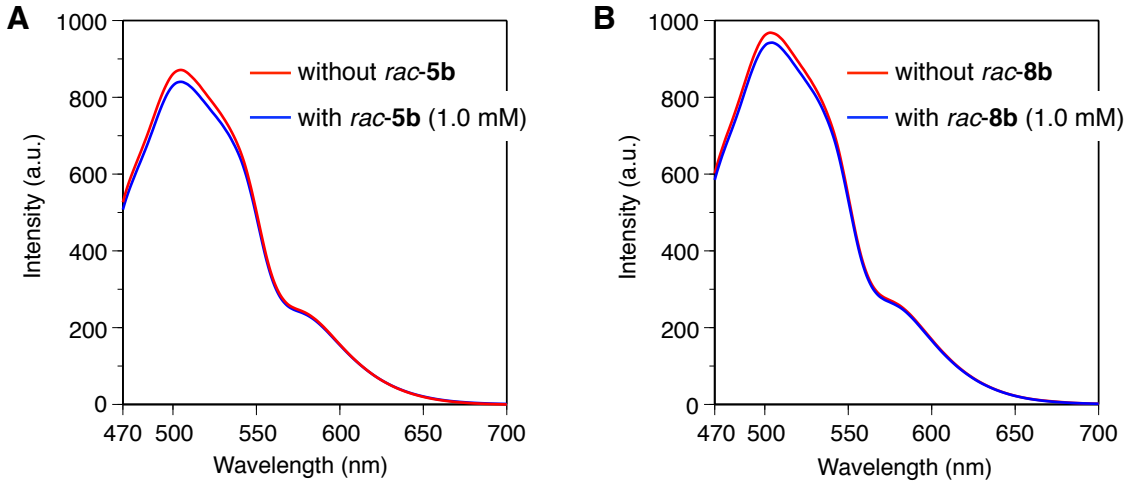


Fig. S8 Fluorescence spectra of Ce-**1b** (λ_{ex} = 450 nm) in the absence (red line) and presence (blue line) of *rac*-**5b** (A) and *rac*-**8b** (B) in hexane/THF (90/10, v/v) at rt. [glucose unit] = 1.0×10^{-5} M.

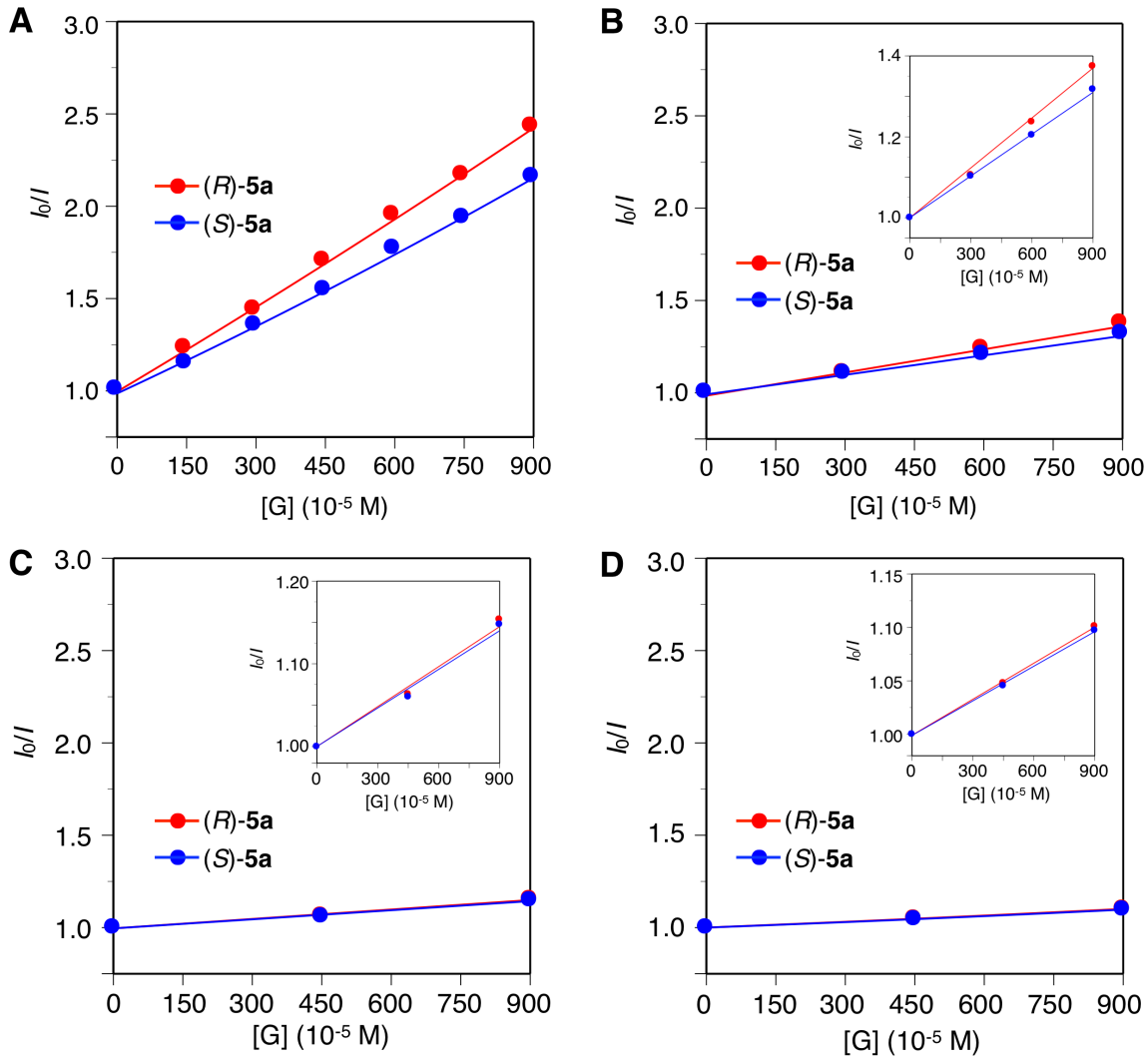


Fig. S9 Stern-Volmer plots for the fluorescence quenching of Ce-**1b** (λ_{ex} = 450 nm) by (*R*)-**5a** (red) and (*S*)-**5a** (blue) in hexane/THF (hexane: 75 (A), 50 (B), 25 (C) and 0 (D) vol %) at rt. [glucose unit] = 1.0×10^{-5} M. The insets in B–D show expanded detail of the Stern-Volmer plots.

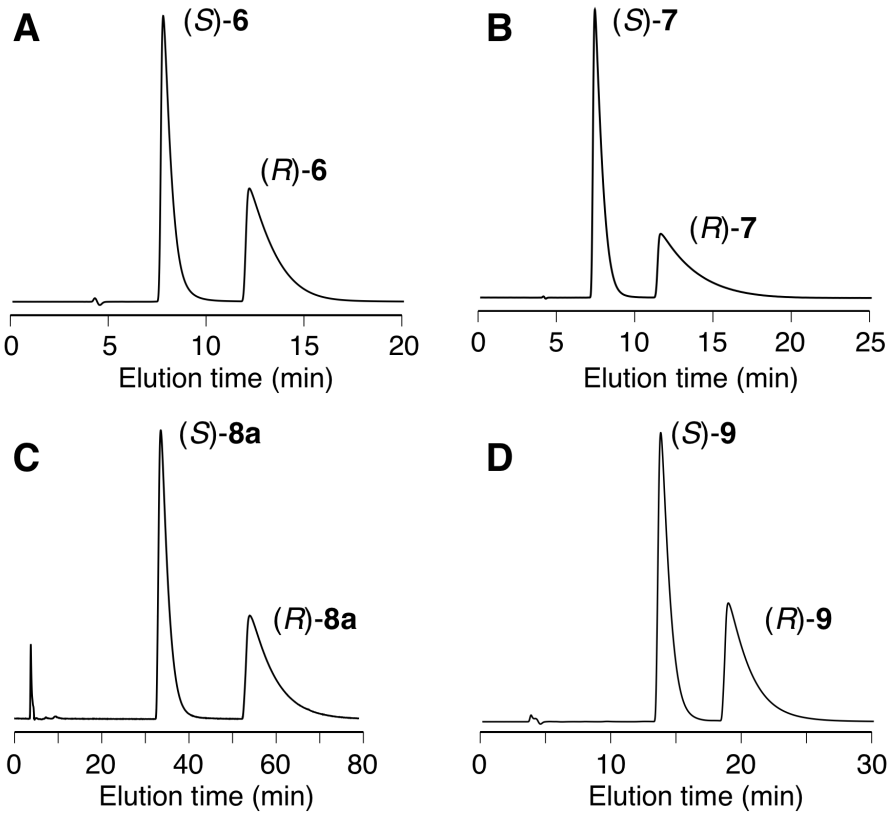


Fig. S10 Chromatograms for the resolutions of **6** (A), **7** (B), **8a** (C) and **9** (D) on Ce-**1b**-based CSP (column, 25 cm × 0.20 cm (i.d.); eluent, hexane/2-propanol (90/10, v/v); flow rate, 0.2 mL/min).

Table S1 Resolutions of racemates on CTPC-based CSP

H/I (v/v) [a]	90/10 [b]		70/30 [c]		50/50 [d]	
Racemate	k_1	α	k_1	α	k_1	α
5a	14.9 (*S*)	1.11	2.62 (*S*)	1.06	1.28	1.0
6	7.12 (*R*)	1.22	1.38 (*R*)	1.23	0.69 (*R*)	1.25
7	8.37 (*S*)	1.06	1.99	1.0	1.08	1.0
8a	19.2 (*R*)	1.50	10.4 (*R*)	1.42	7.15 (*R*)	1.38
9	4.02 (*S*)	1.51	2.00 (*S*)	1.48	1.76 (*S*)	1.48

Column: 25 cm × 0.20 cm (i.d.). [a]Eluent: H = hexane; I = 2-propanol. Flow rate: [b]0.2 mL min^{-1}; [c]0.1 mL min^{-1}; [d]0.05 mL min^{-1}. The characters in parentheses represent the absolute configuration of the first-eluted enantiomer.

NMR spectral data

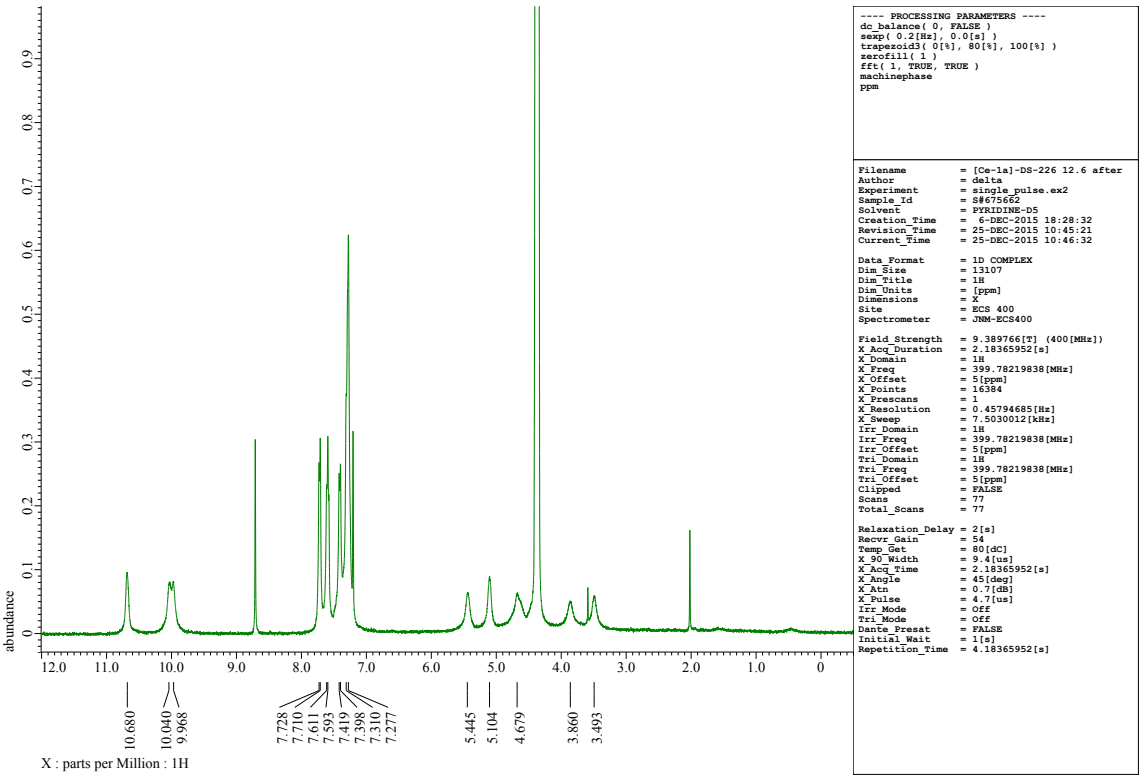


Fig. S11 ^{1}H NMR (pyridine-d_5, 400 MHz) spectrum of Ce-**1a**.

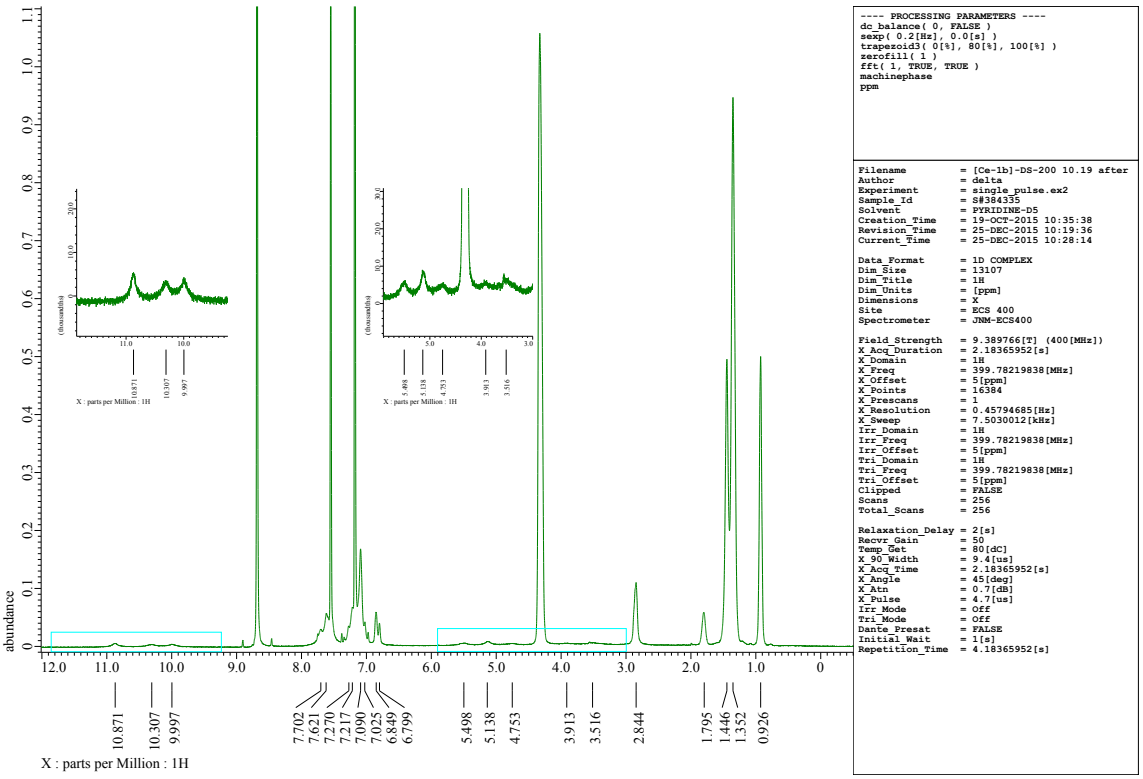


Fig. S12 ^{1}H NMR (pyridine-d_5, 400 MHz) spectrum of Ce-**1b**.

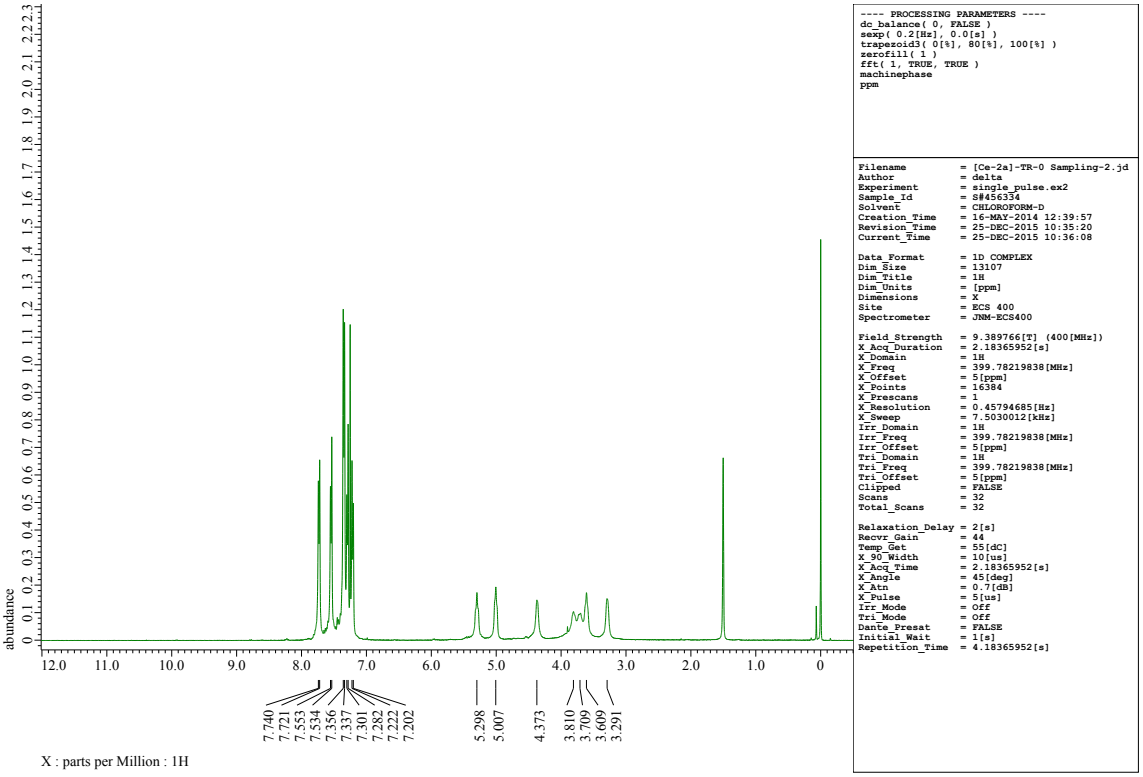


Fig. S13 ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of Ce-**2a**.

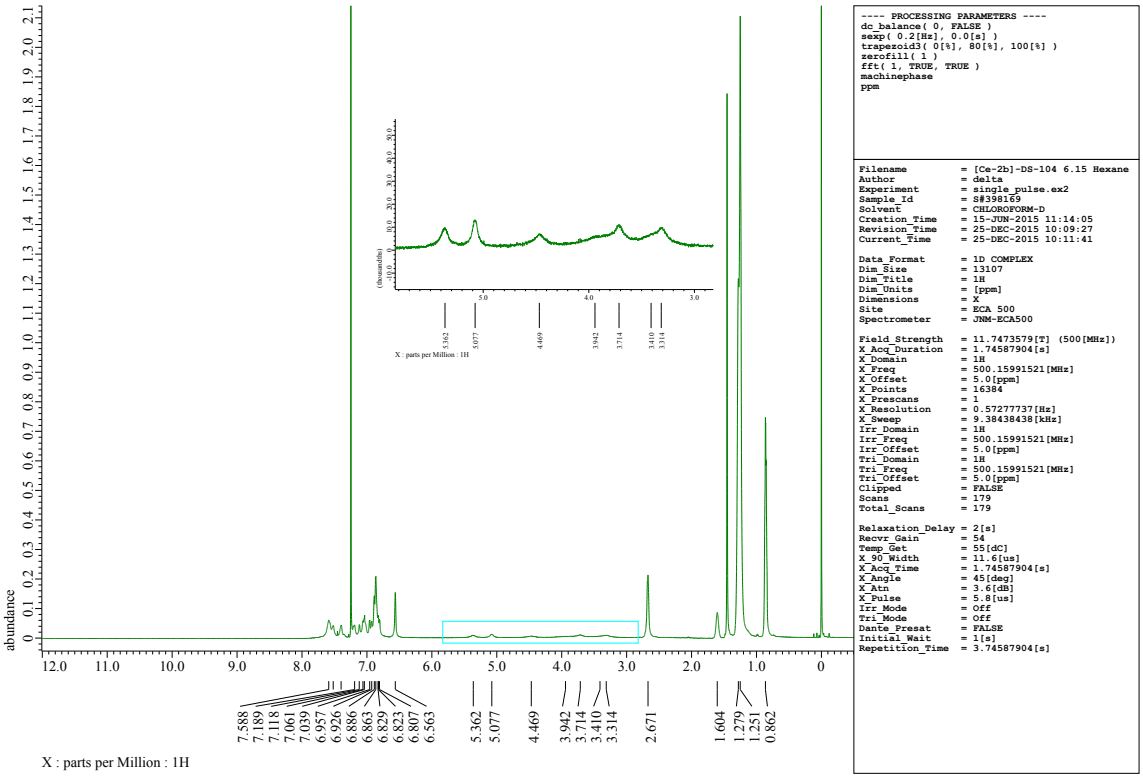


Fig. S14 ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of Ce-**2b**.

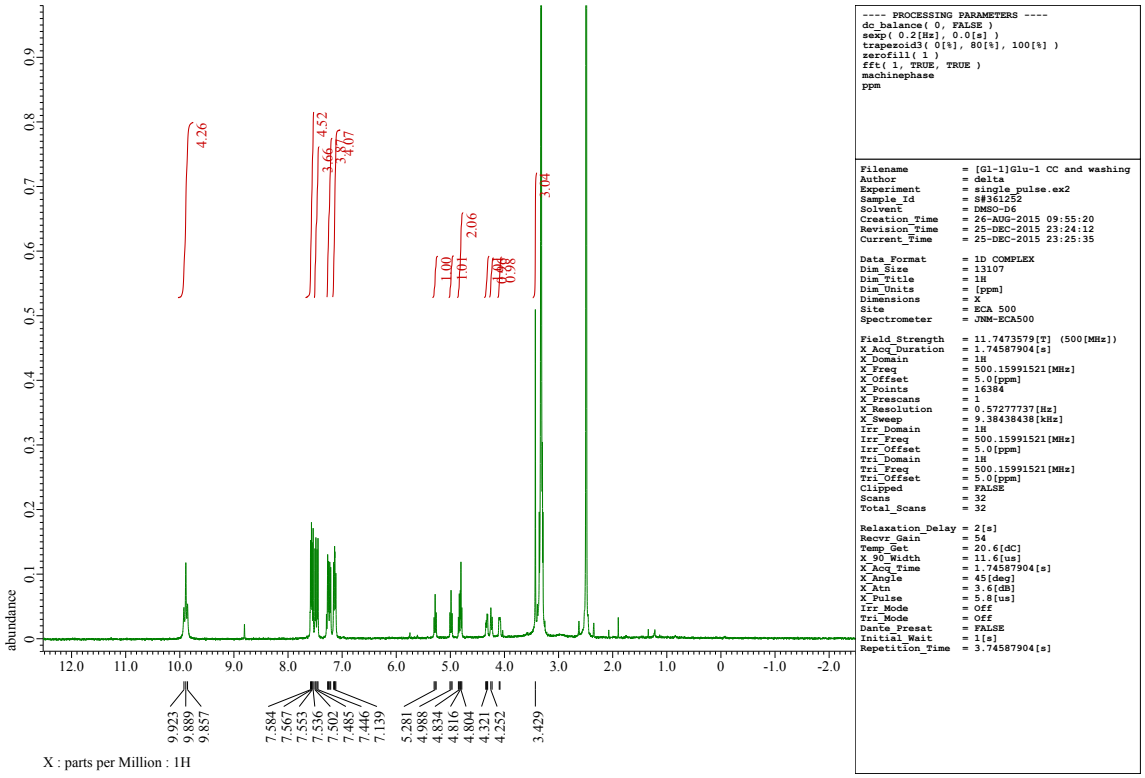


Fig. S15 ^{1}H NMR (DMSO-d_6, 500 MHz) spectrum of Gl-**1a**.

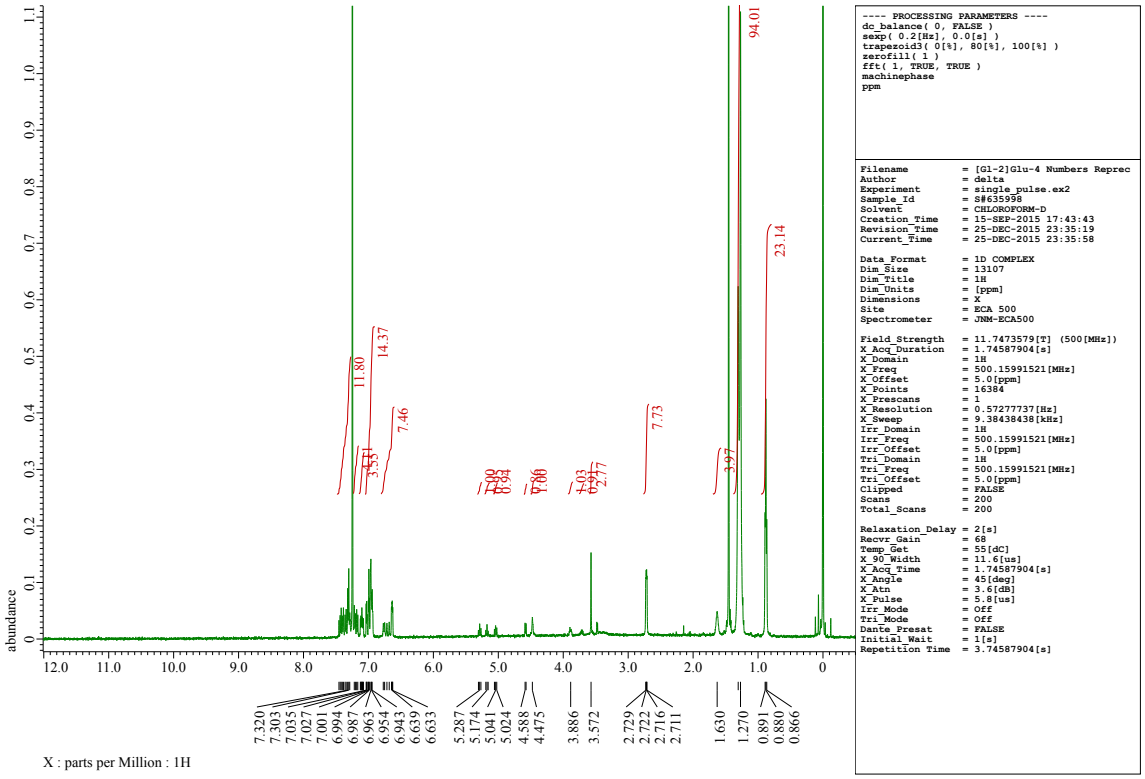


Fig. S16 ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of Gl-**1b**.

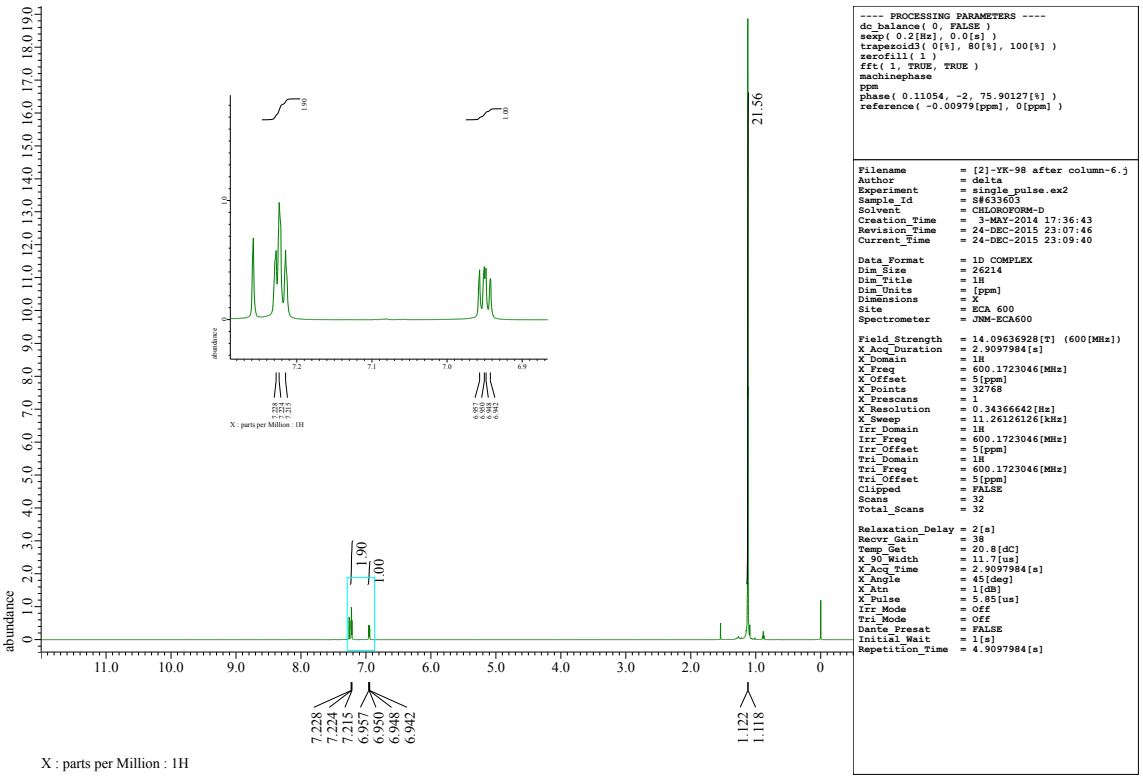


Fig. S17 ^{1}H NMR ($CDCl_3$, 600 MHz) spectrum of **3b**.

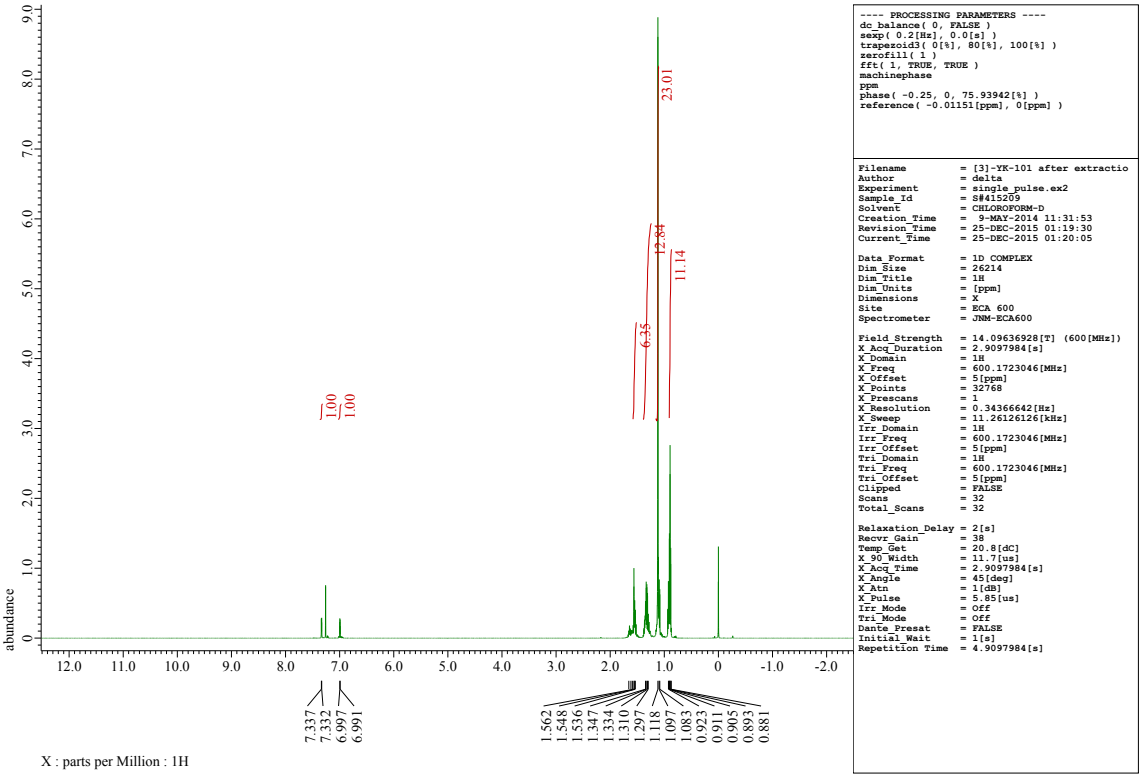


Fig. S18 ^{1}H NMR ($CDCl_3$, 600 MHz) spectrum of **3c**.

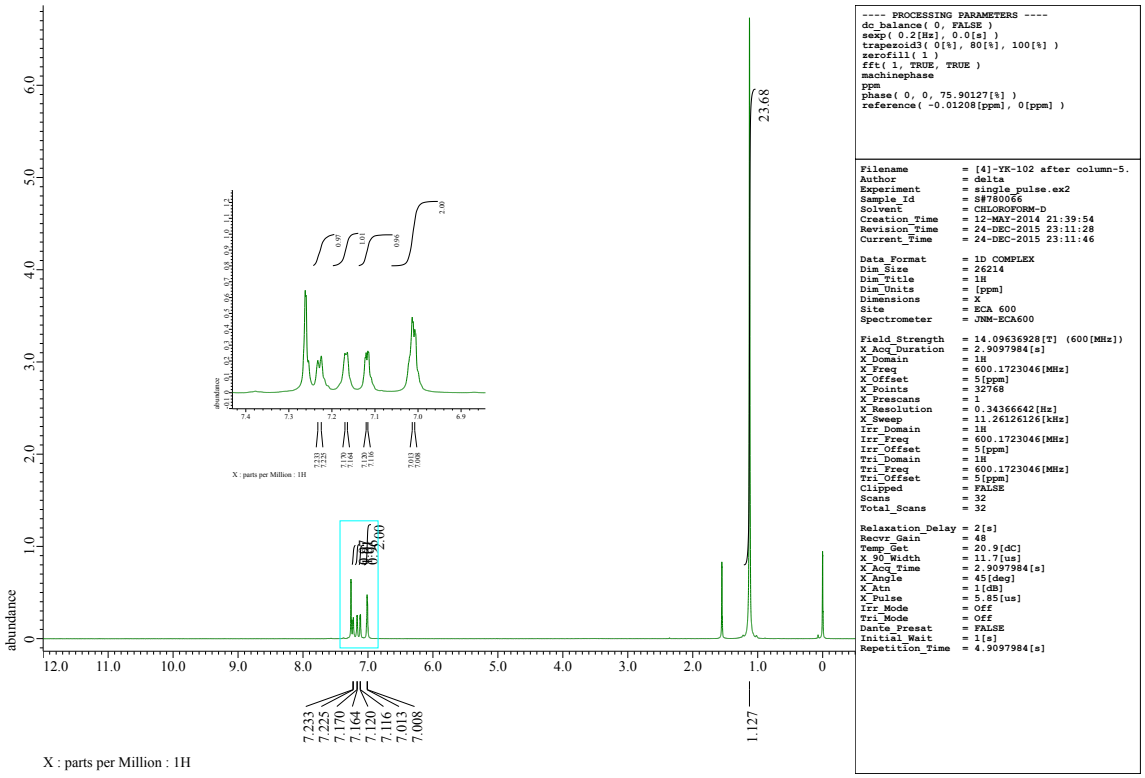


Fig. S19 ^{1}H NMR ($CDCl_3$, 600 MHz) spectrum of **3d**.

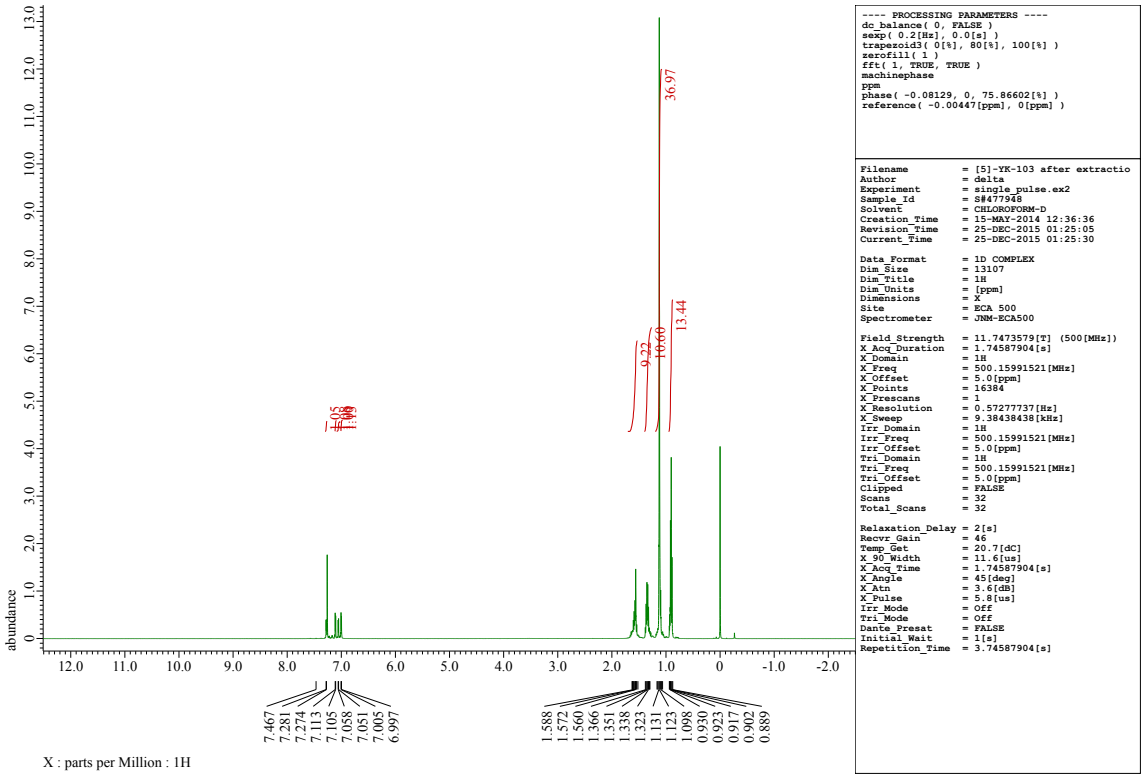


Fig. S20 ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of **3e**.

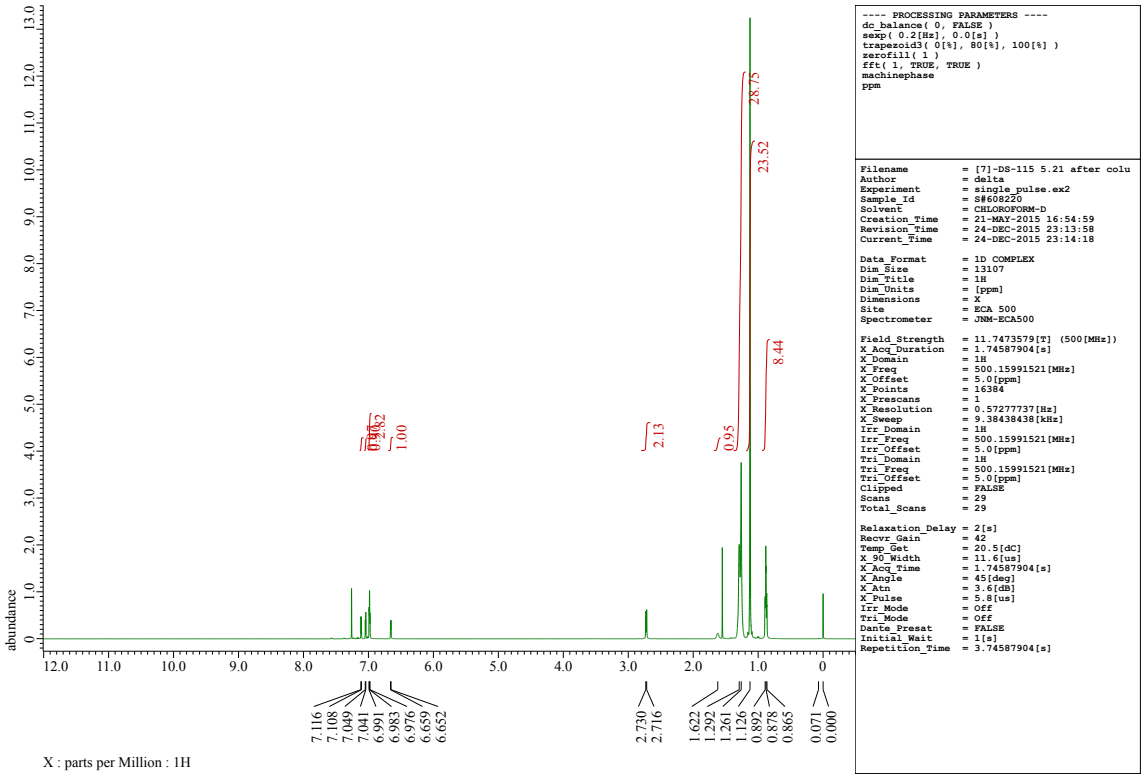


Fig. S21 ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of **3g**.

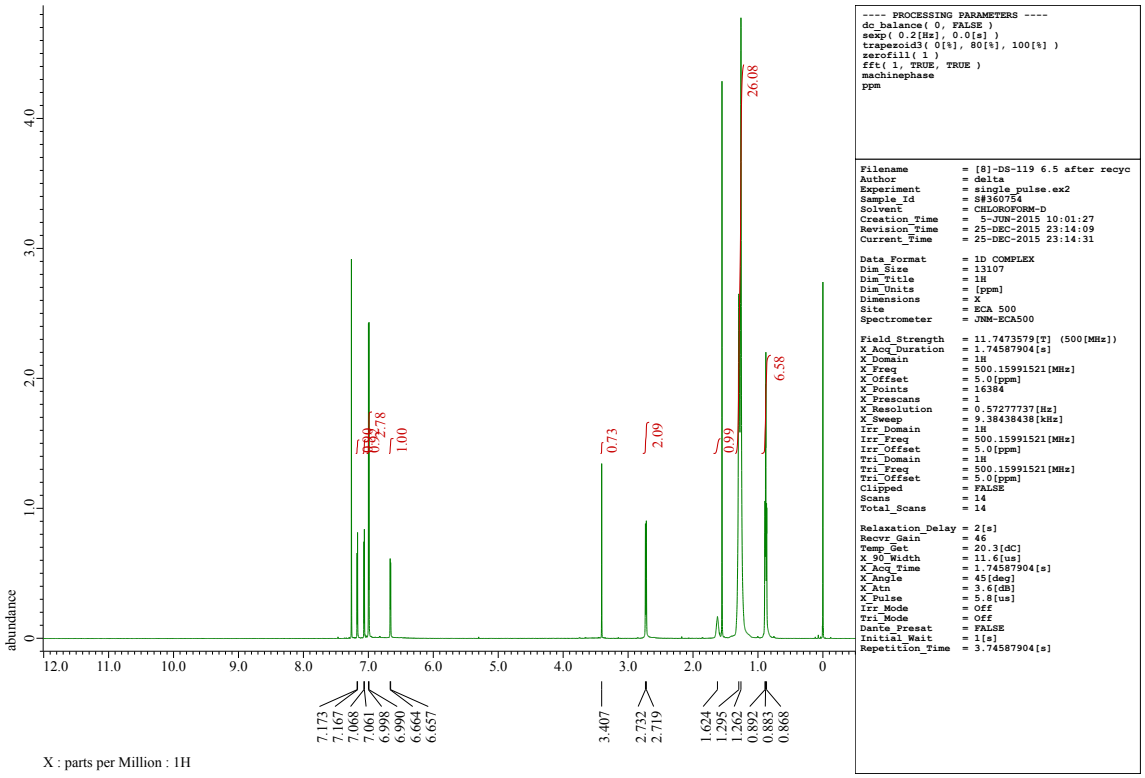


Fig. S22 ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of **3**.

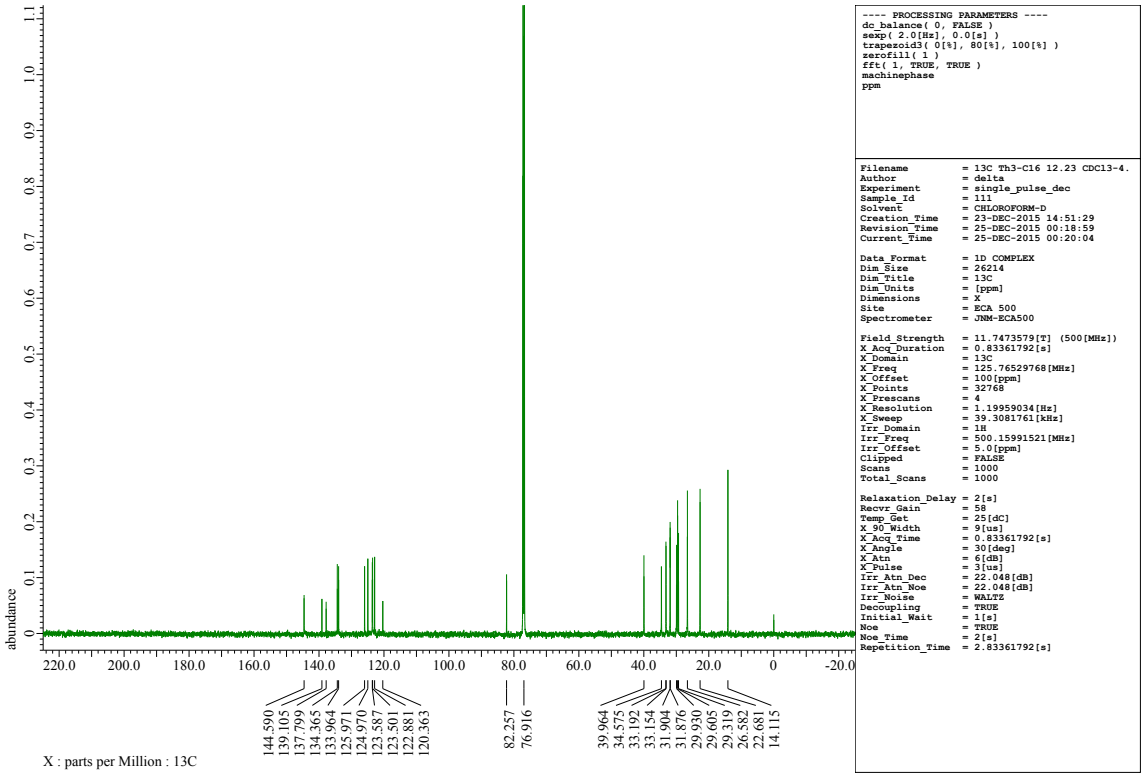


Fig. S23 ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of **3**.

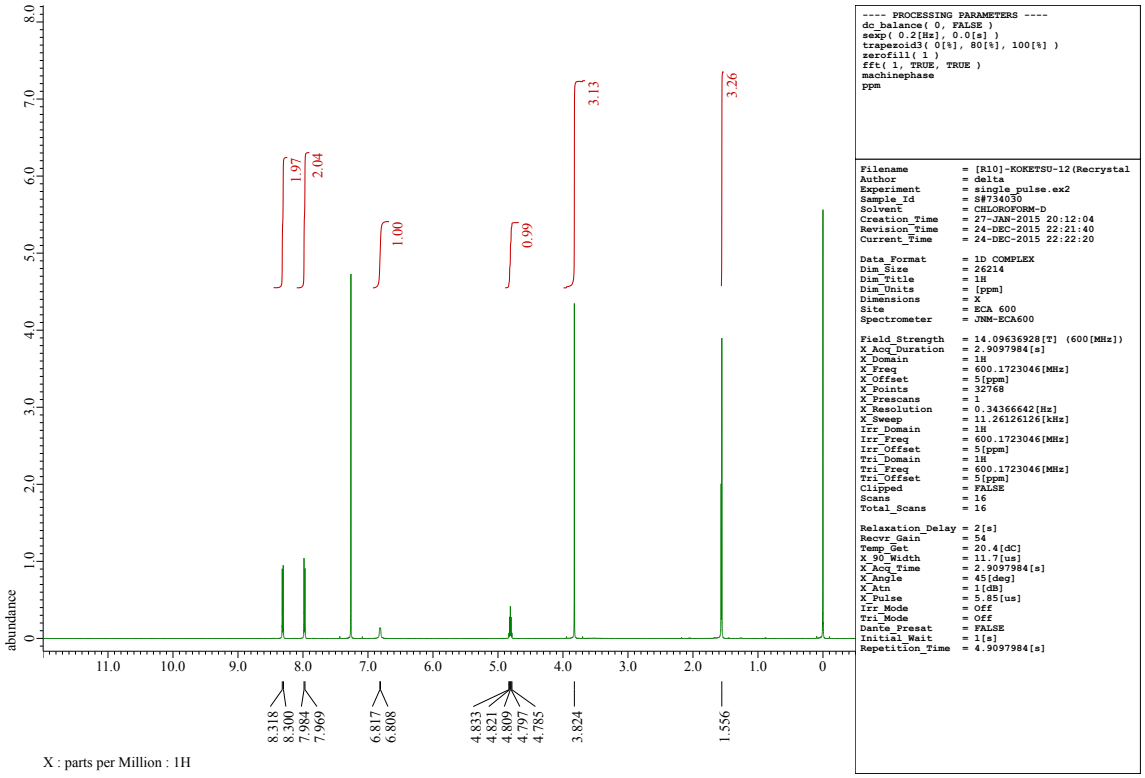


Fig. S24 ^{1}H NMR ($CDCl_3$, 600 MHz) spectrum of (*R*)-**5a**.

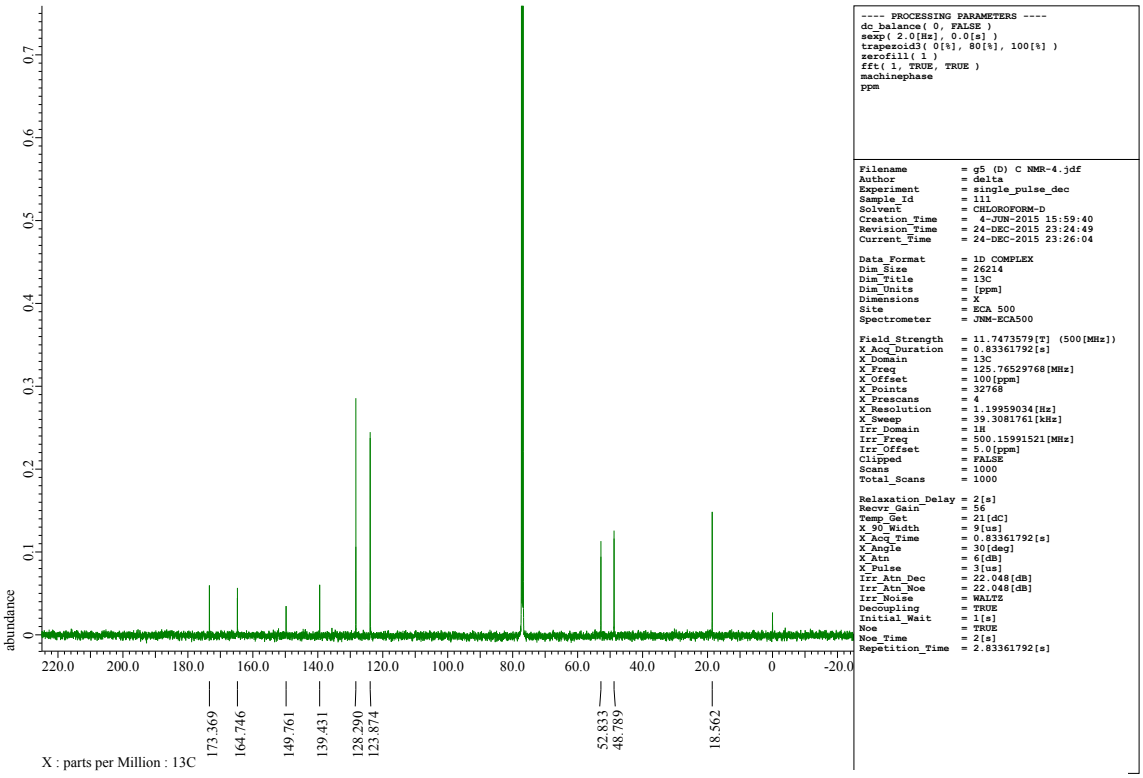


Fig. S25 ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of (*R*)-**5a**.

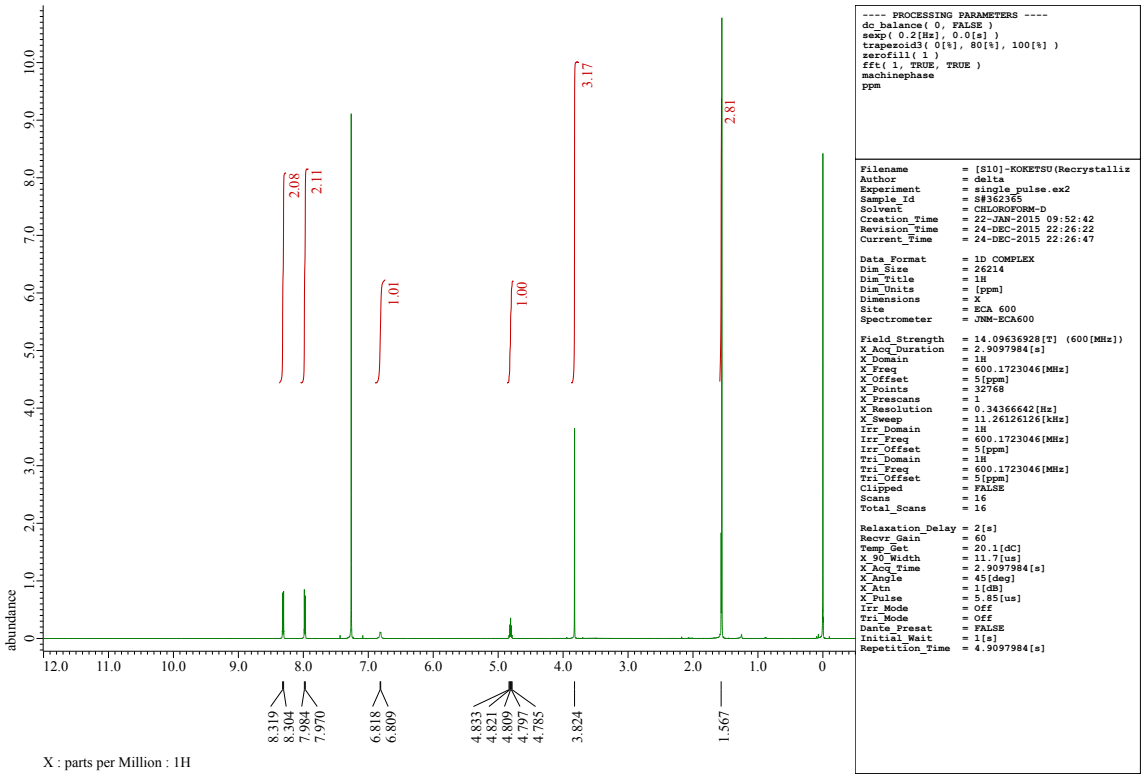


Fig. S26 ^{1}H NMR ($CDCl_3$, 600 MHz) spectrum of (*S*)-**5a**.

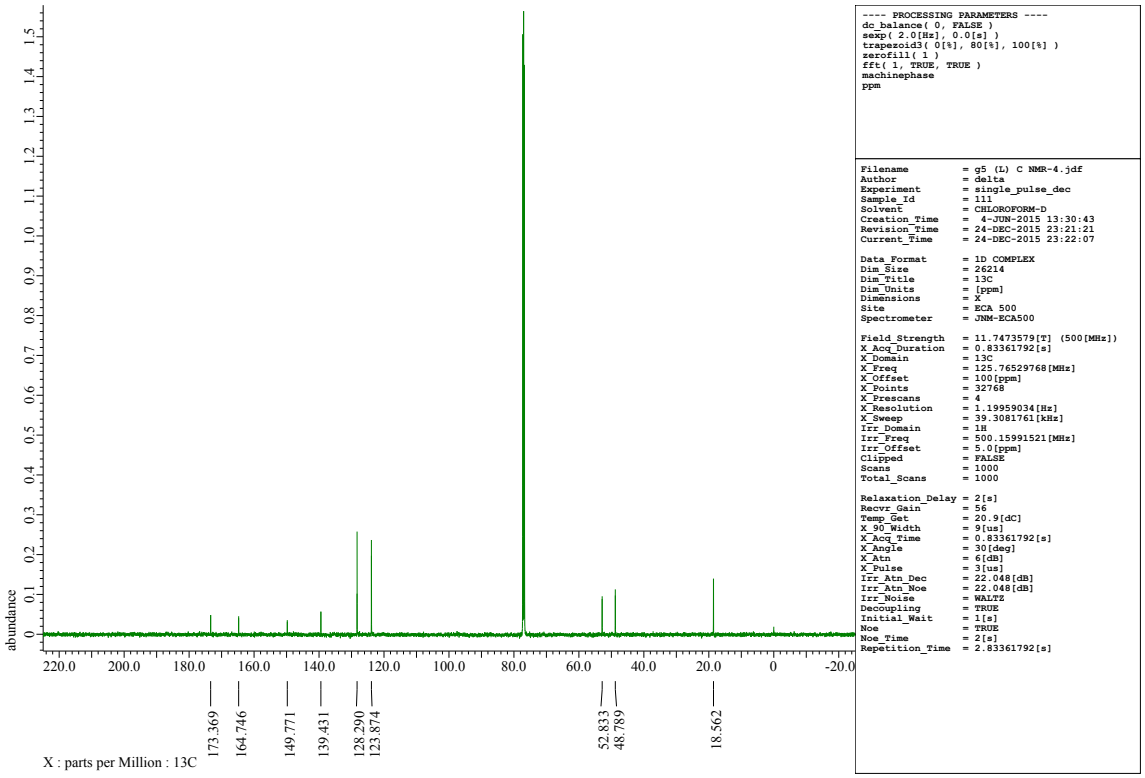


Fig. S27 ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of (*S*)-**5a**.

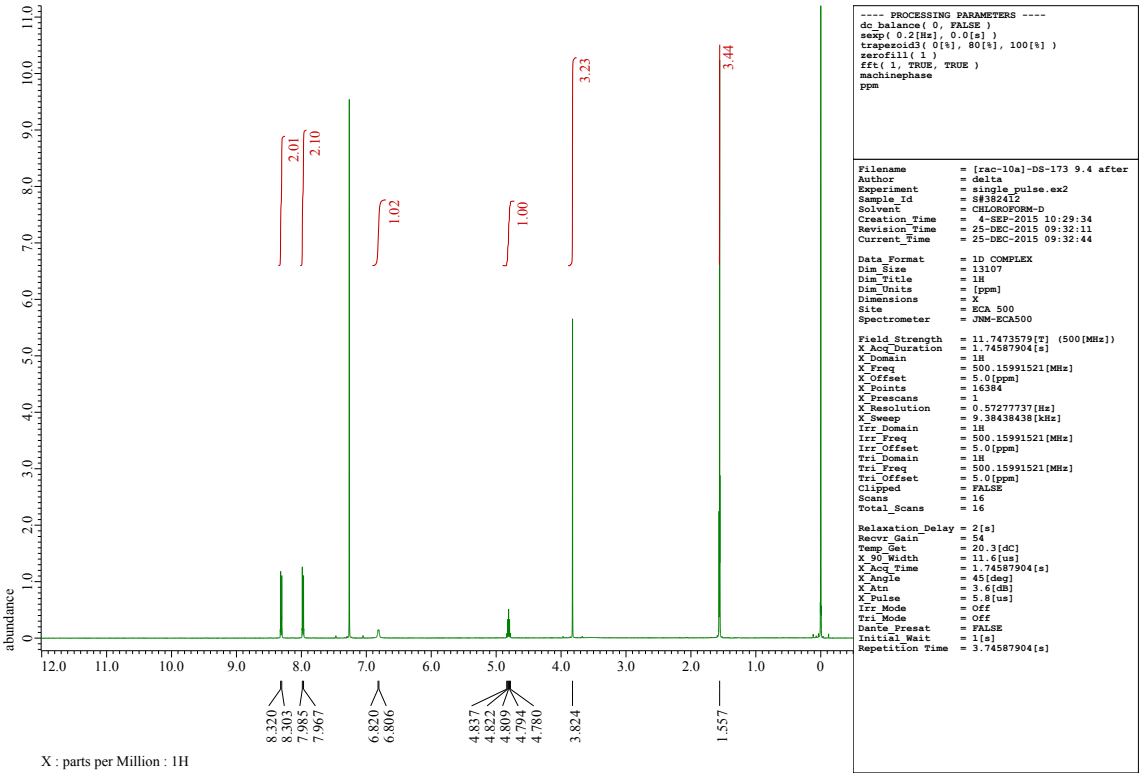


Fig. S28 ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of *rac*-**5a**.

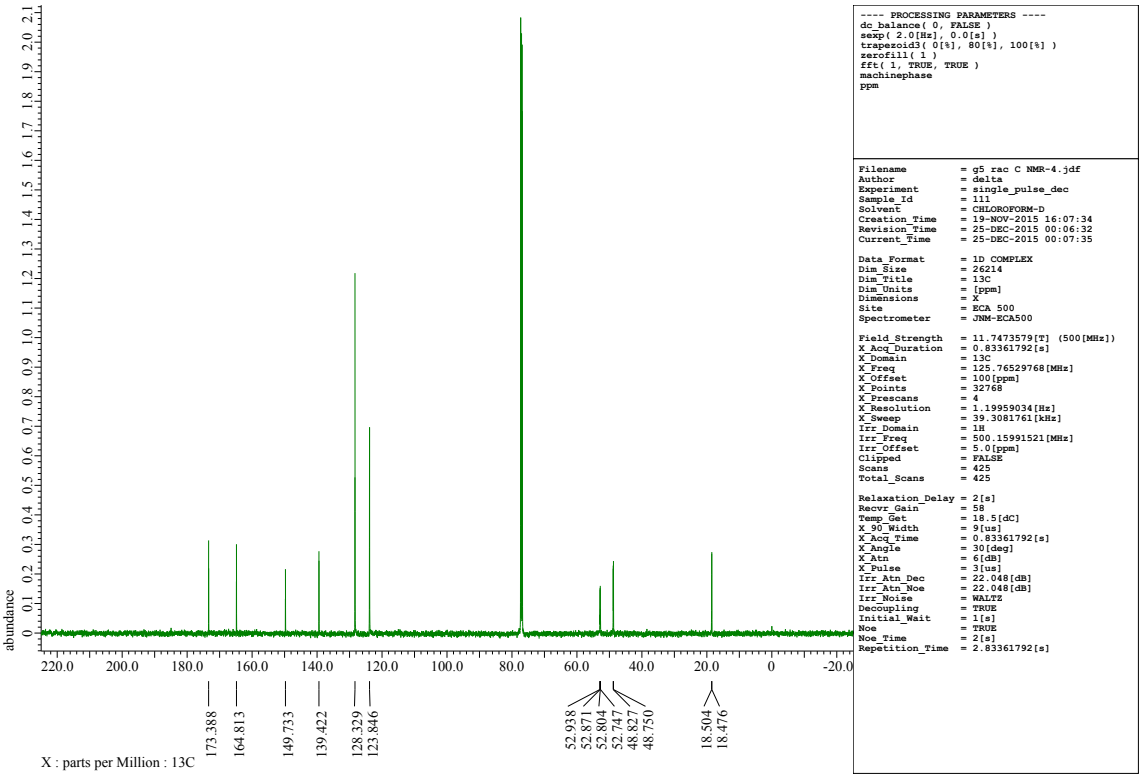


Fig. S29 ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of *rac*-**5a**.

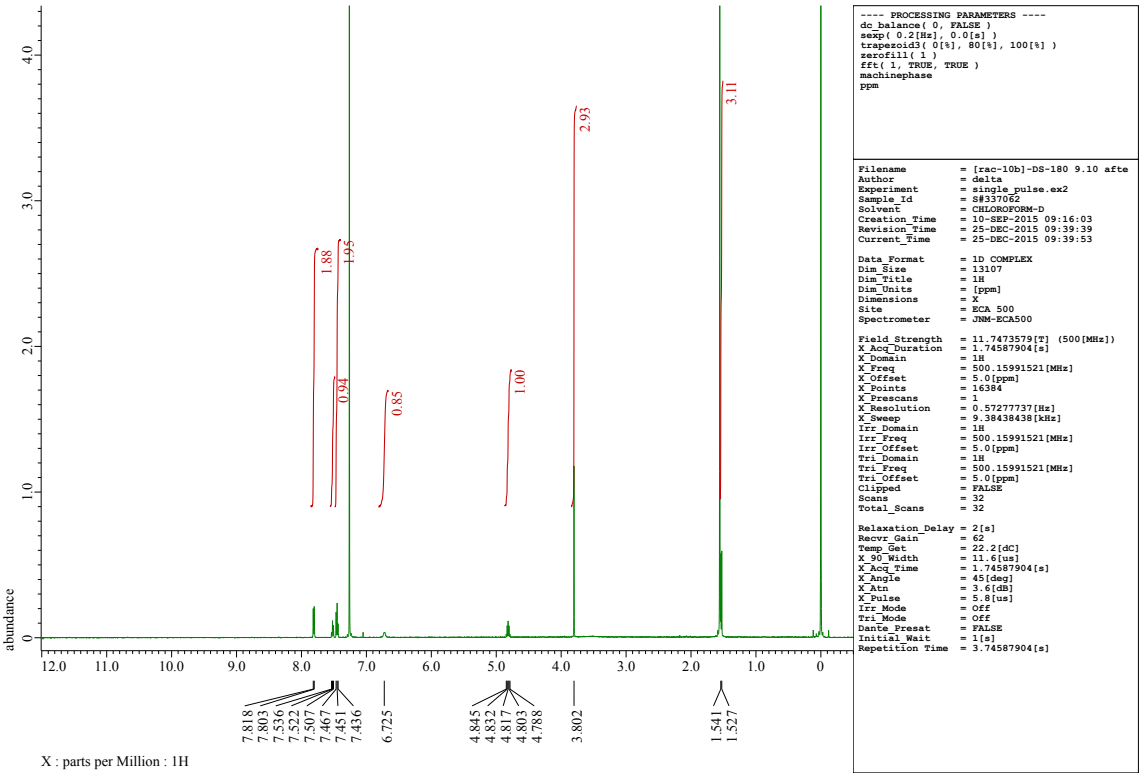


Fig. S30 ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of *rac*-**5b**.

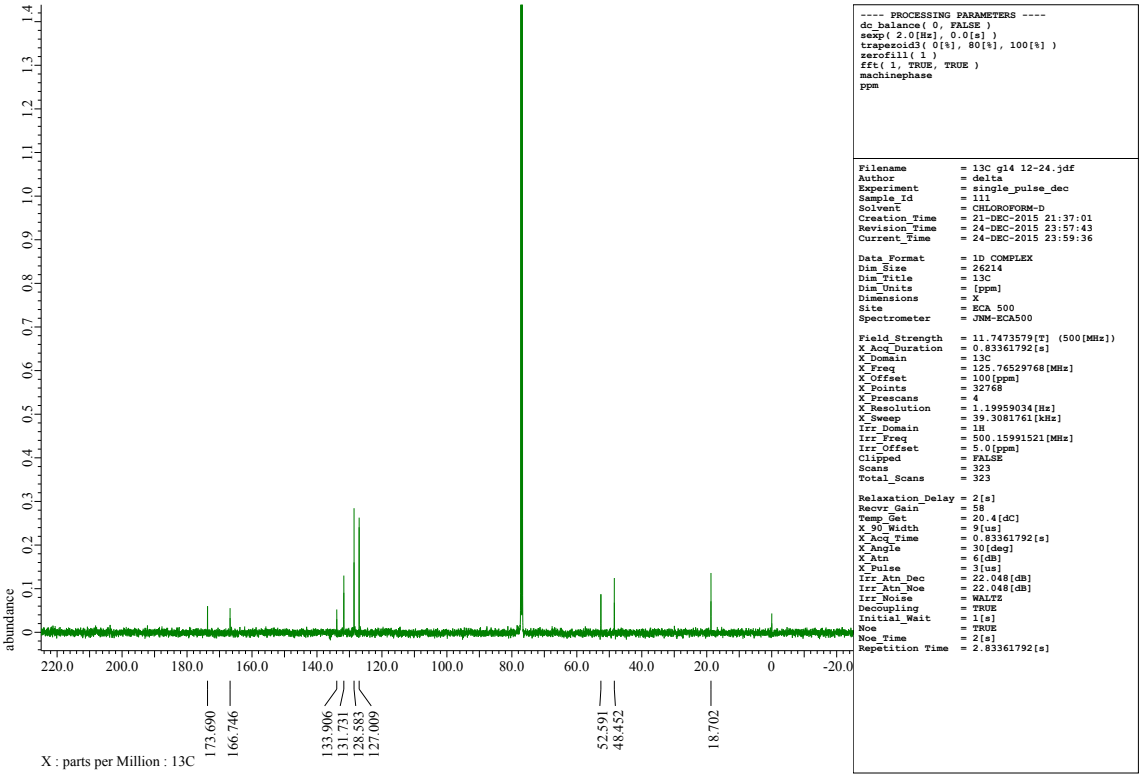


Fig. S31 ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of *rac*-**5b**.

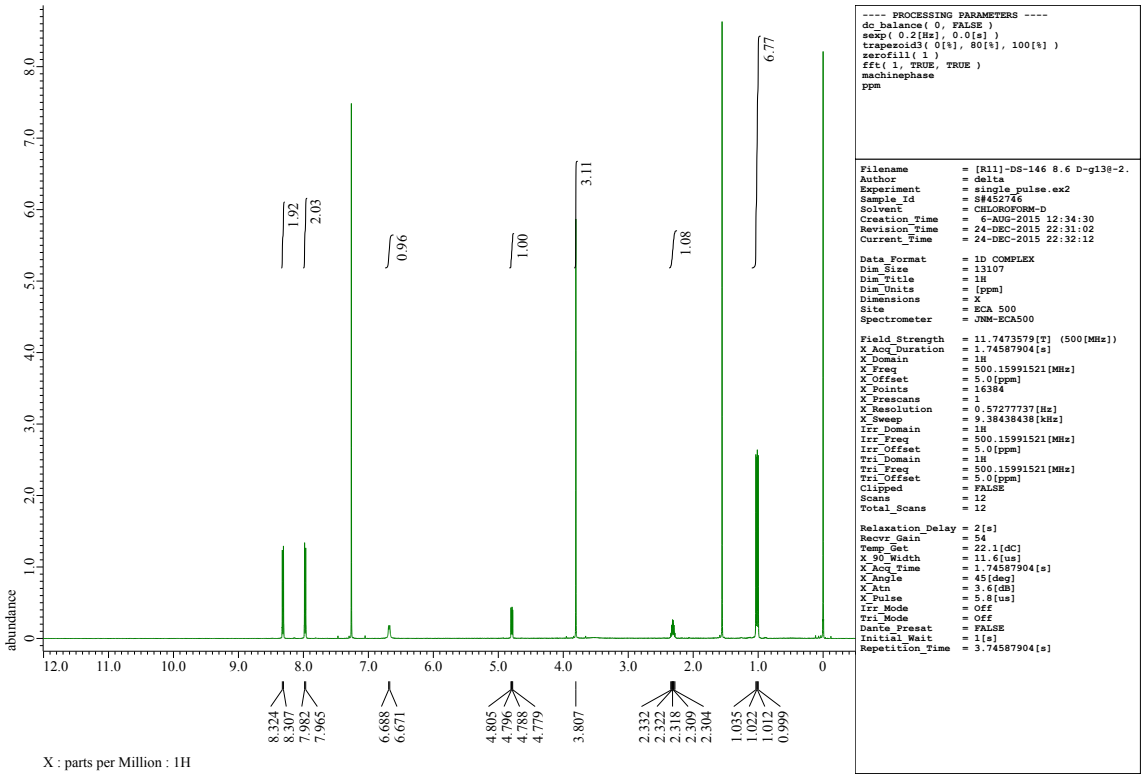


Fig. S32 ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (*R*)-**6**.

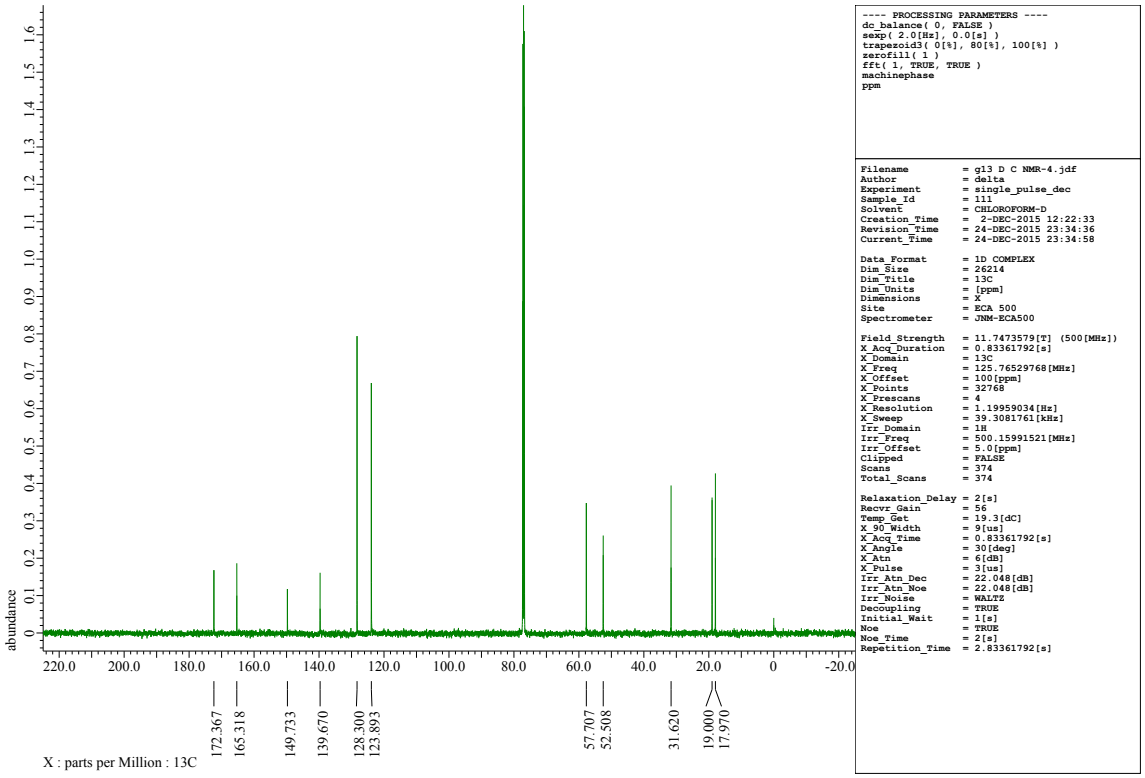


Fig. S33 ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of (*R*)-**6**.

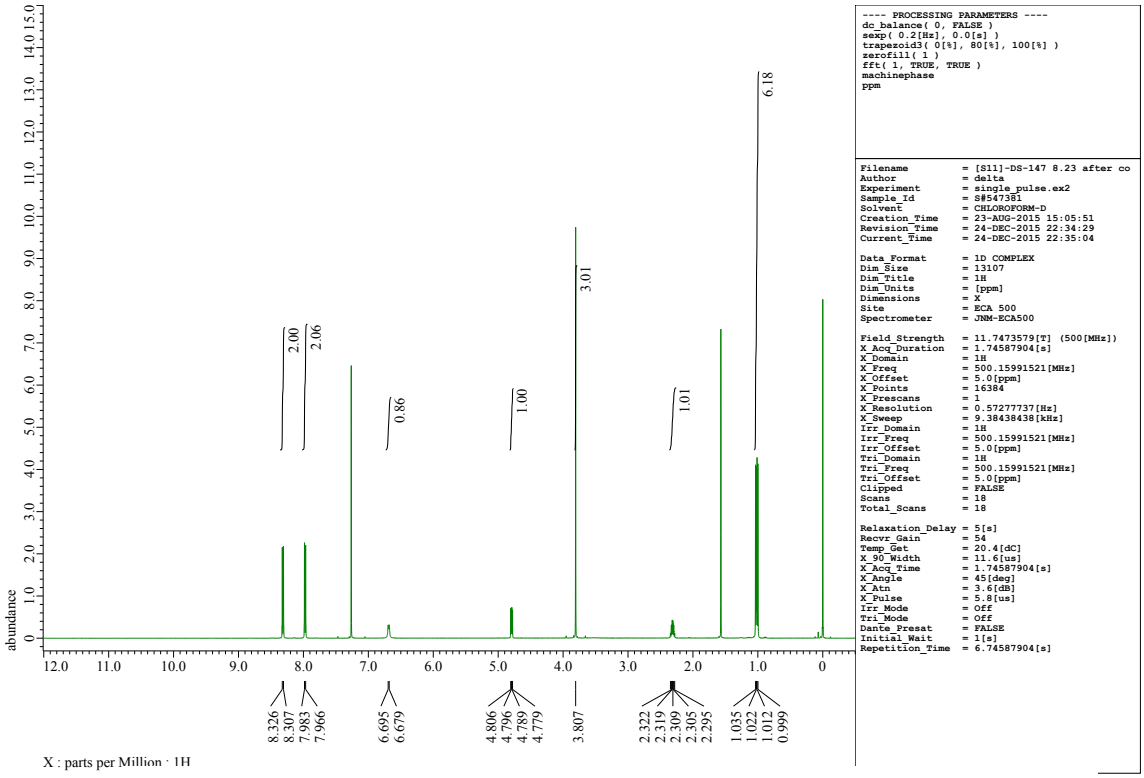


Fig. S34 ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (*S*)-**6**.

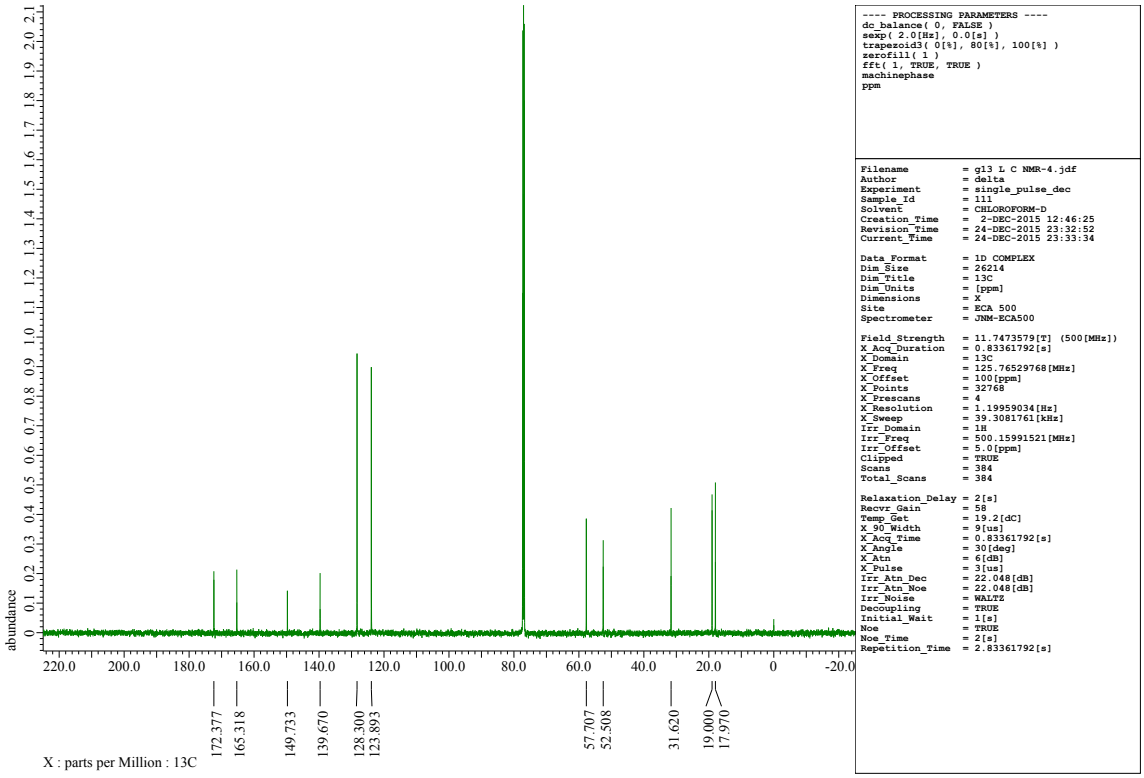


Fig. S35 ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of (*S*)-**6**.

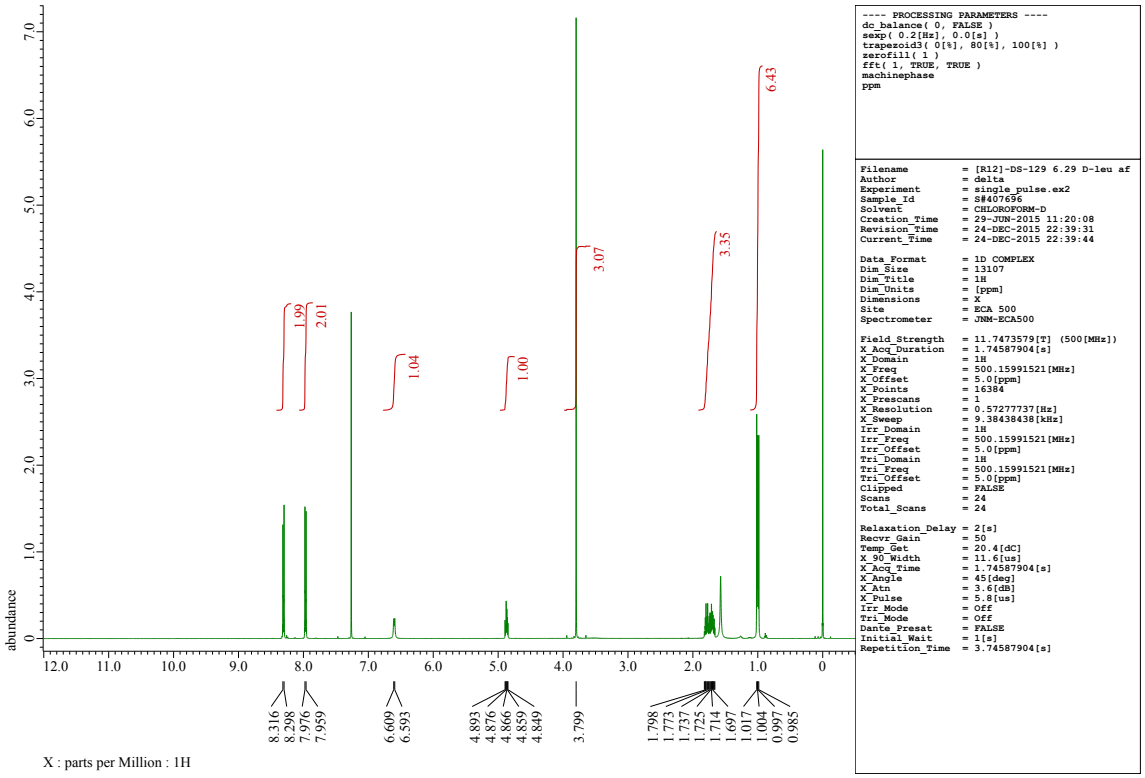


Fig. S36 ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (*R*)-**7**.

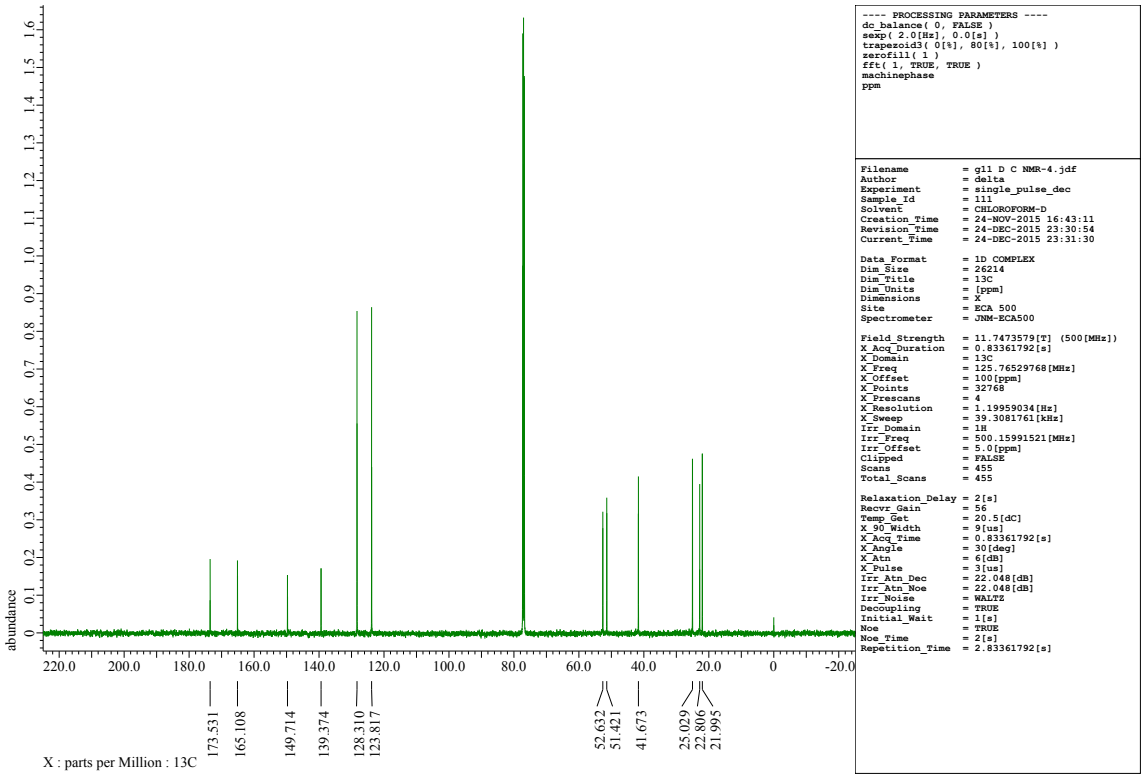


Fig. S37 ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of (*R*)-**7**.

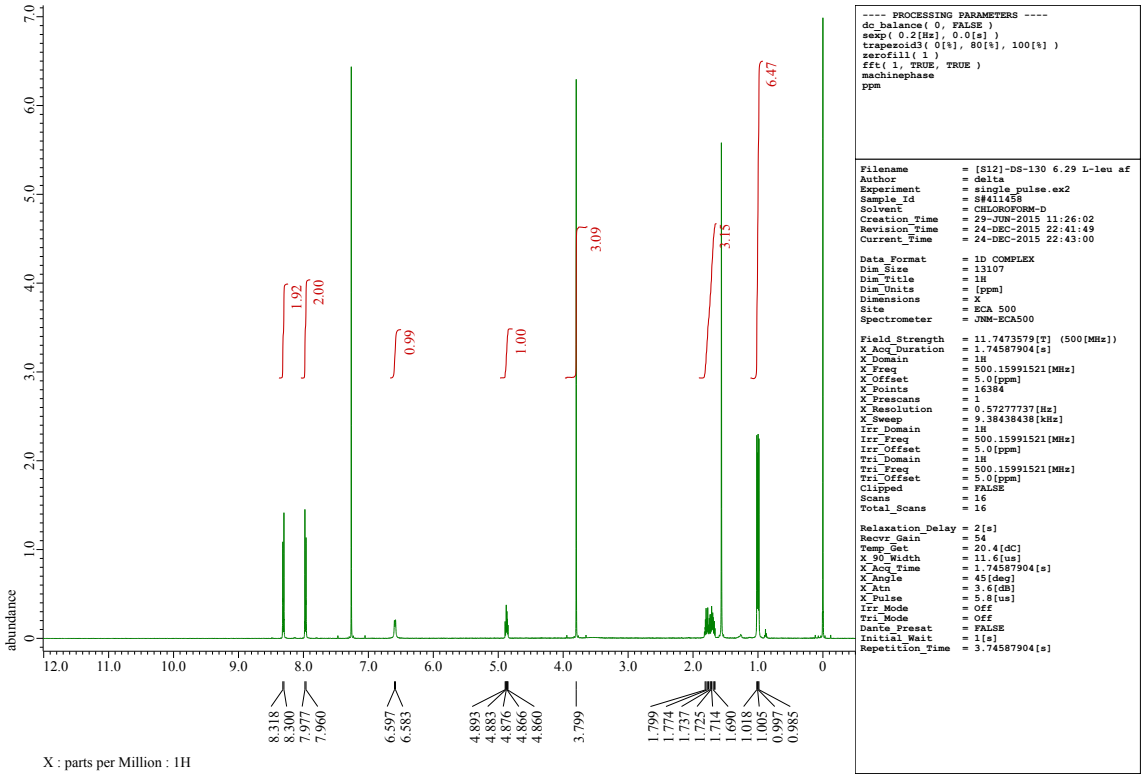


Fig. S38 ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (*S*)-**7**.

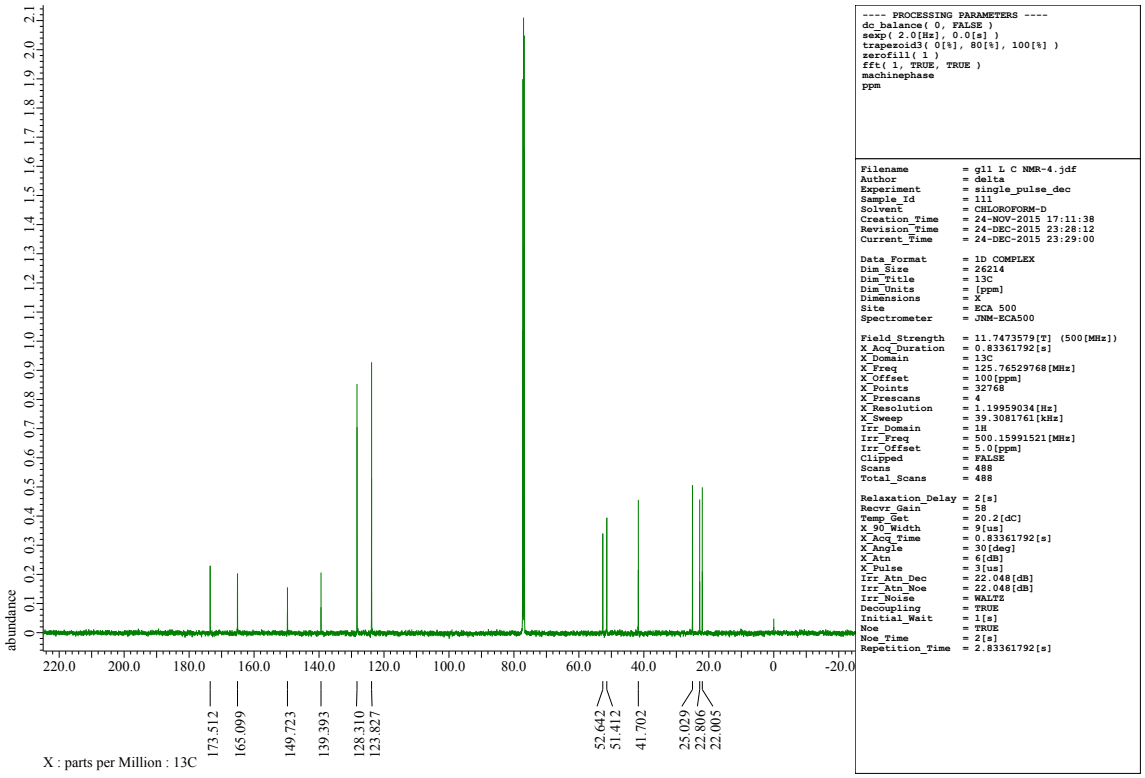


Fig. S39 ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of (*S*)-**7**.

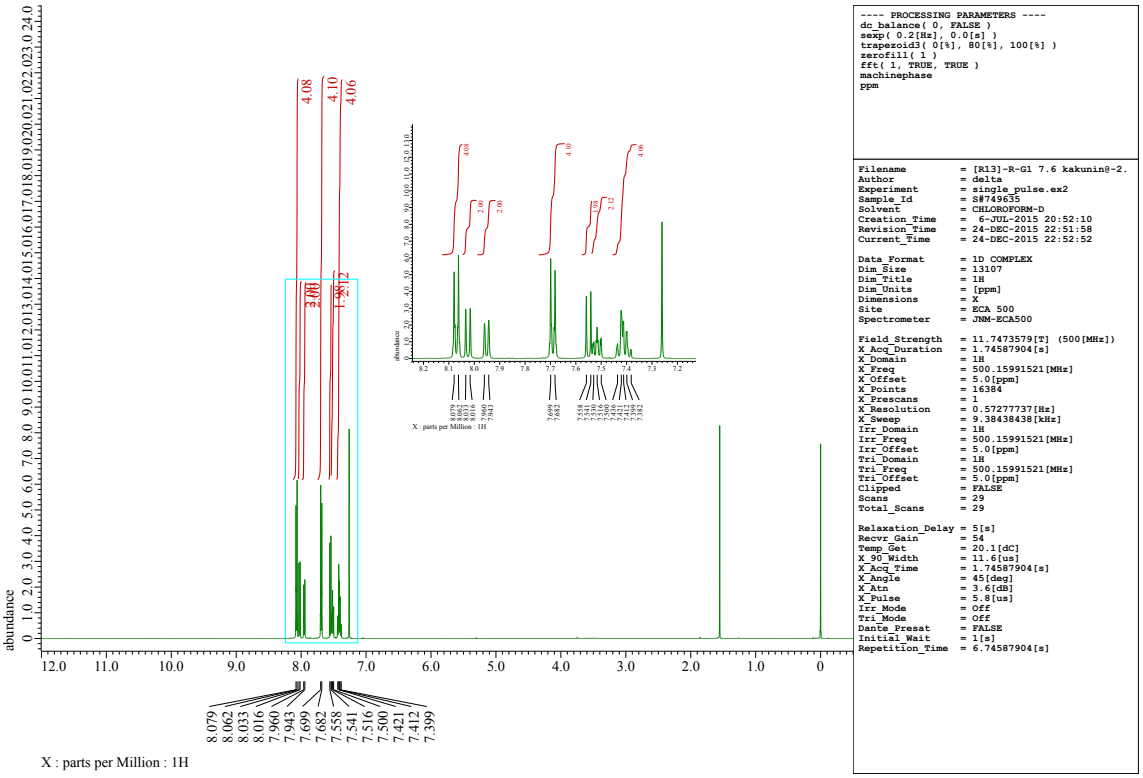


Fig. S40 ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (*R*)-**8a**.

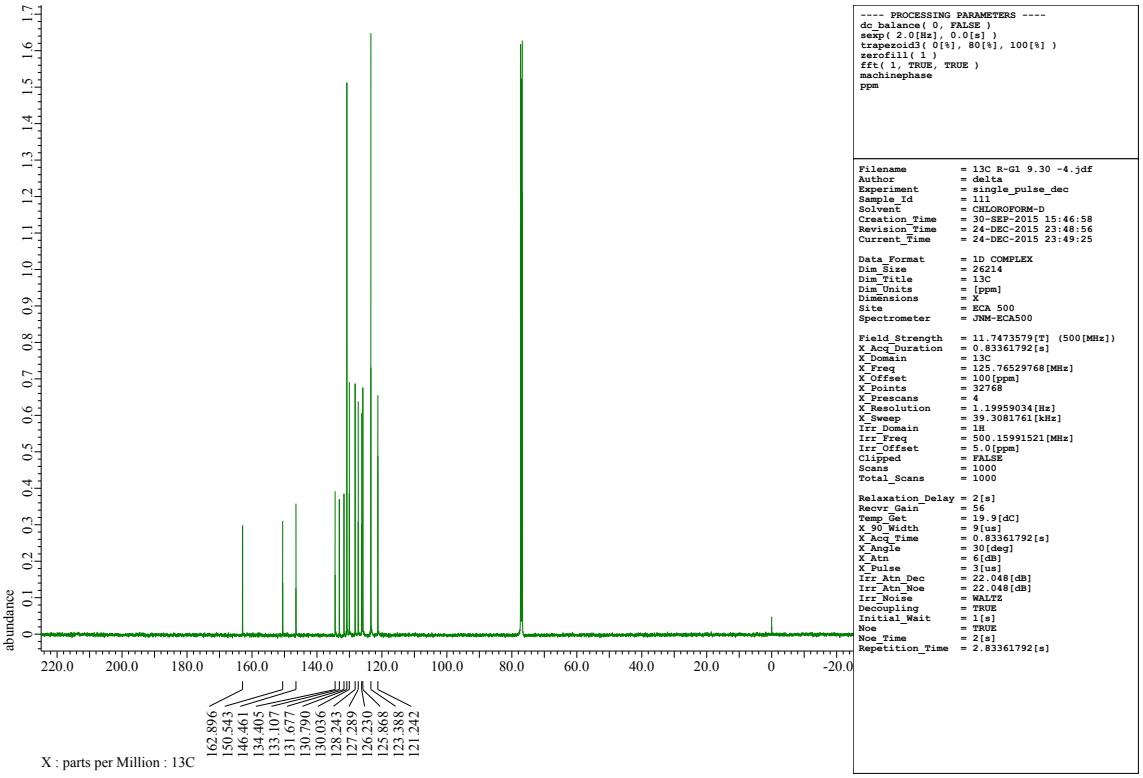


Fig. S41 ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of (*R*)-**8a**.

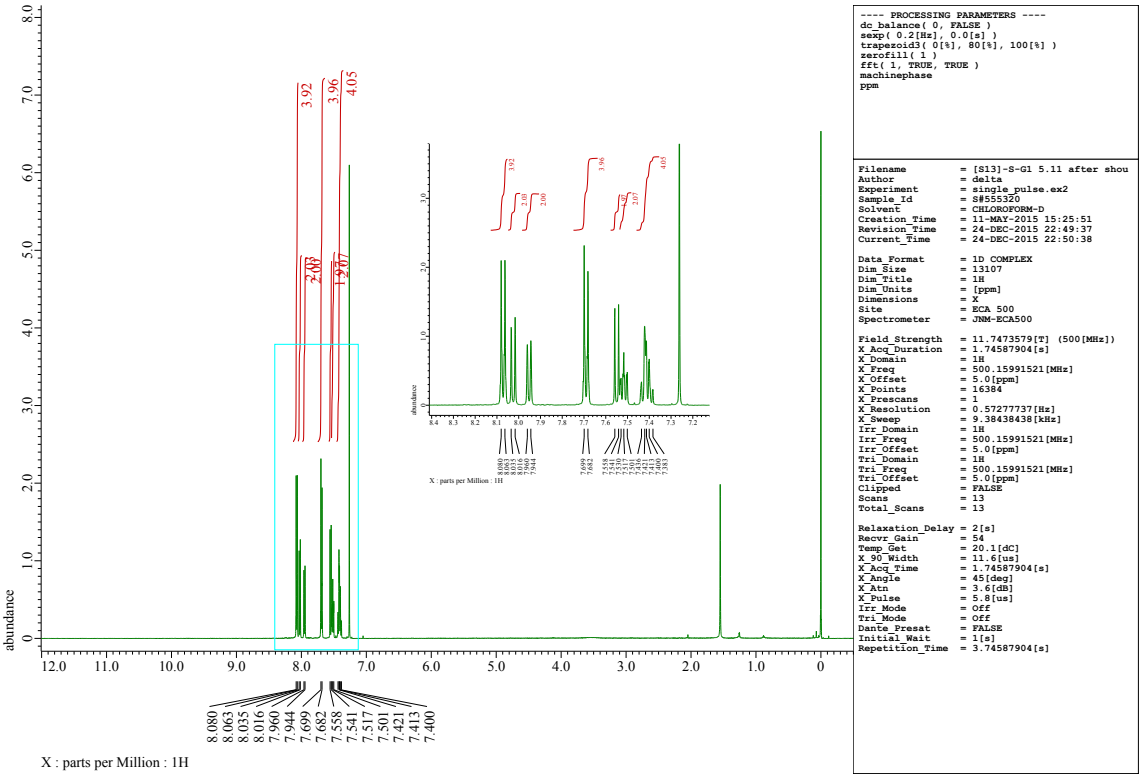


Fig. S42 ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (*S*)-**8a**.

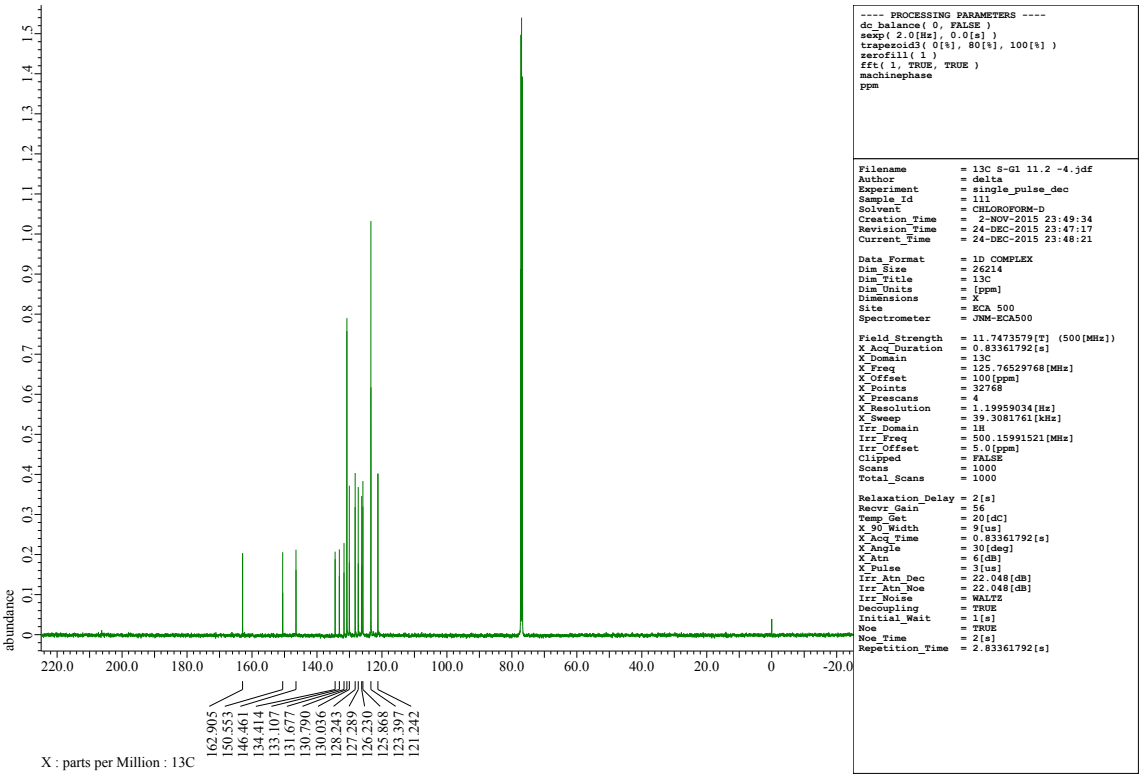


Fig. S43 ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of (*S*)-**8a**.

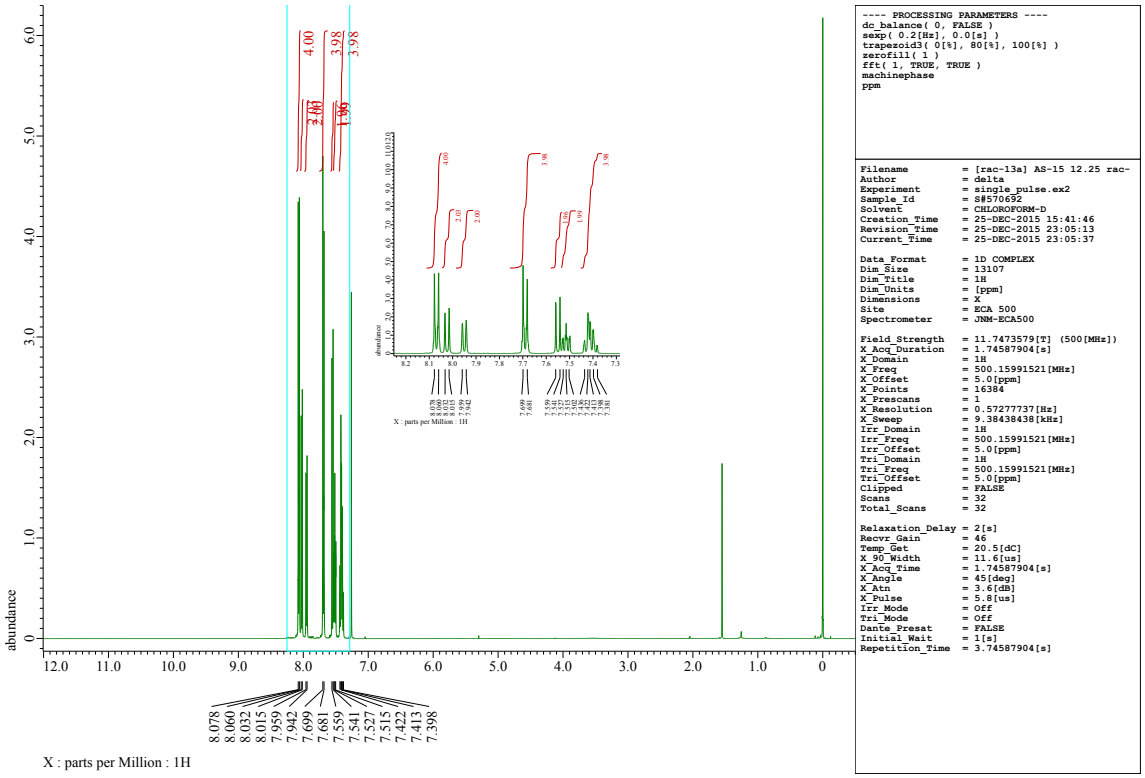


Fig. S44 ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of *rac*-**8a**.

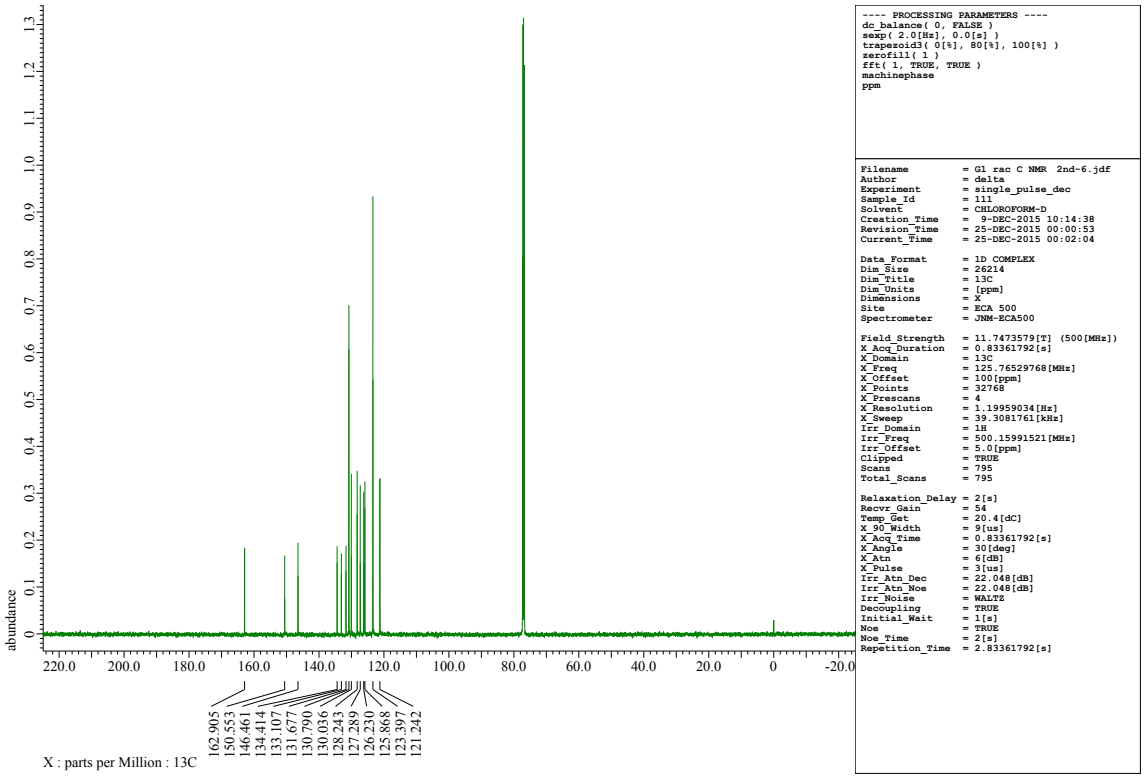


Fig. S45 ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of *rac*-**8a**.

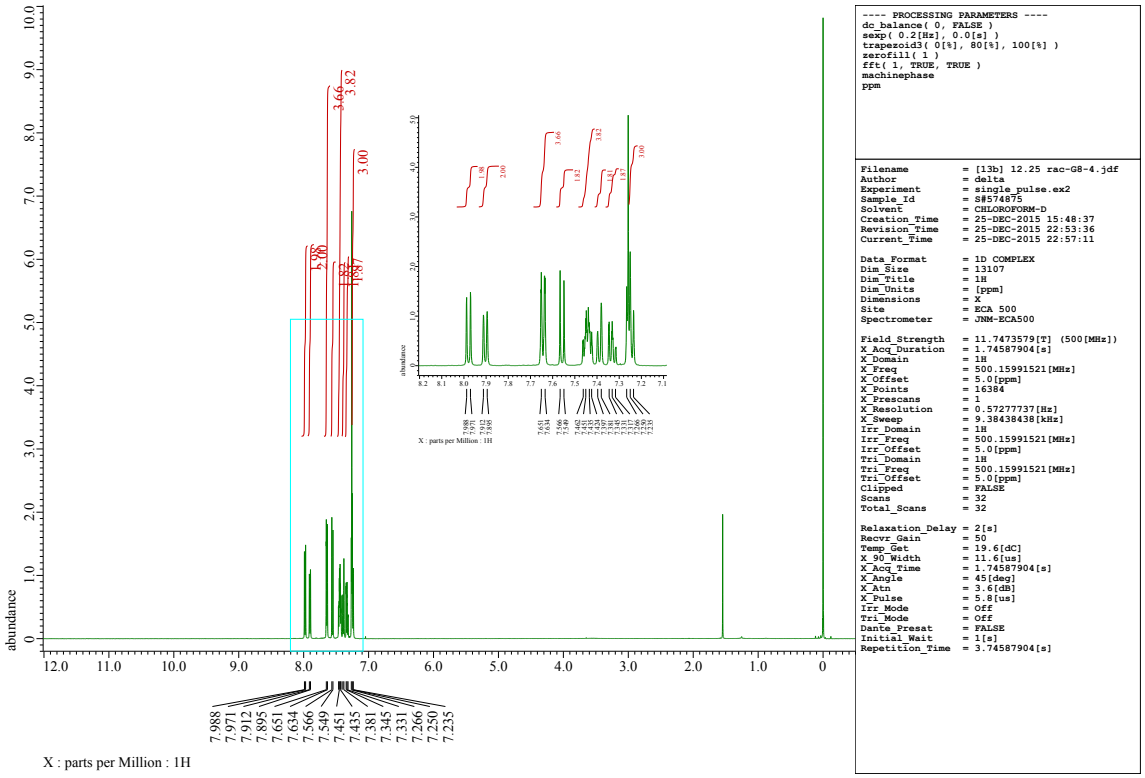


Fig. S46 ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of *rac*-**8b**.

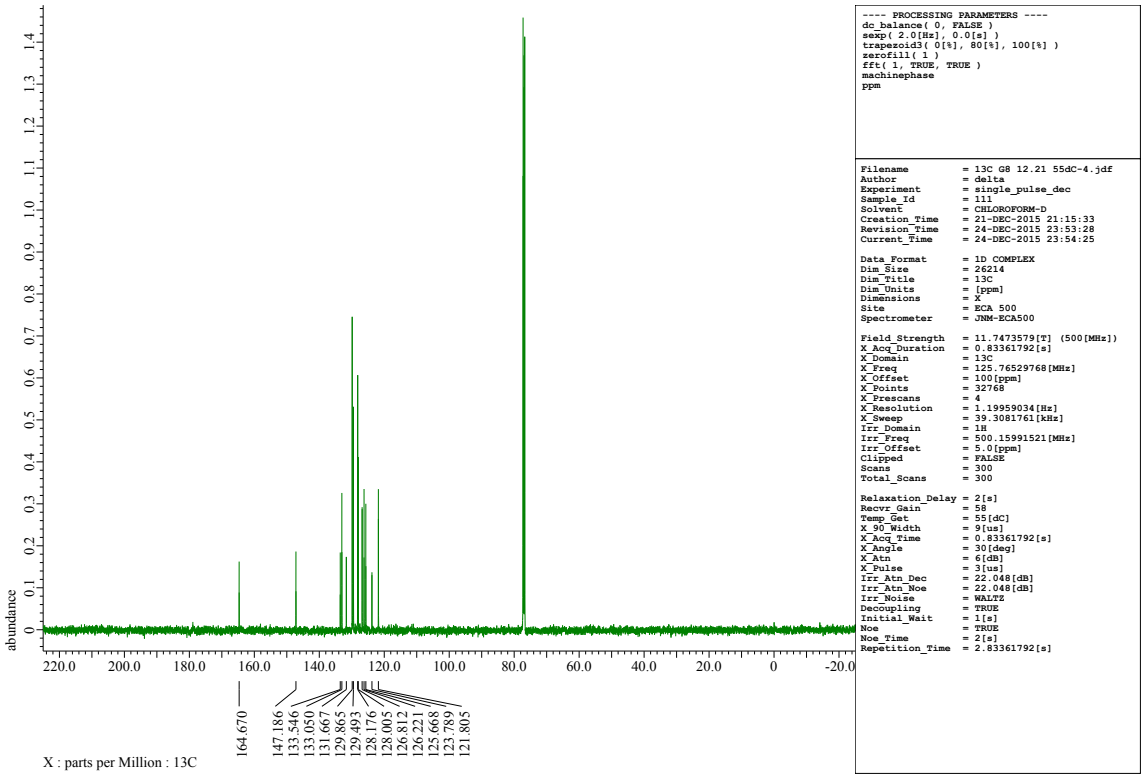


Fig. S47 ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of *rac*-**8b**.

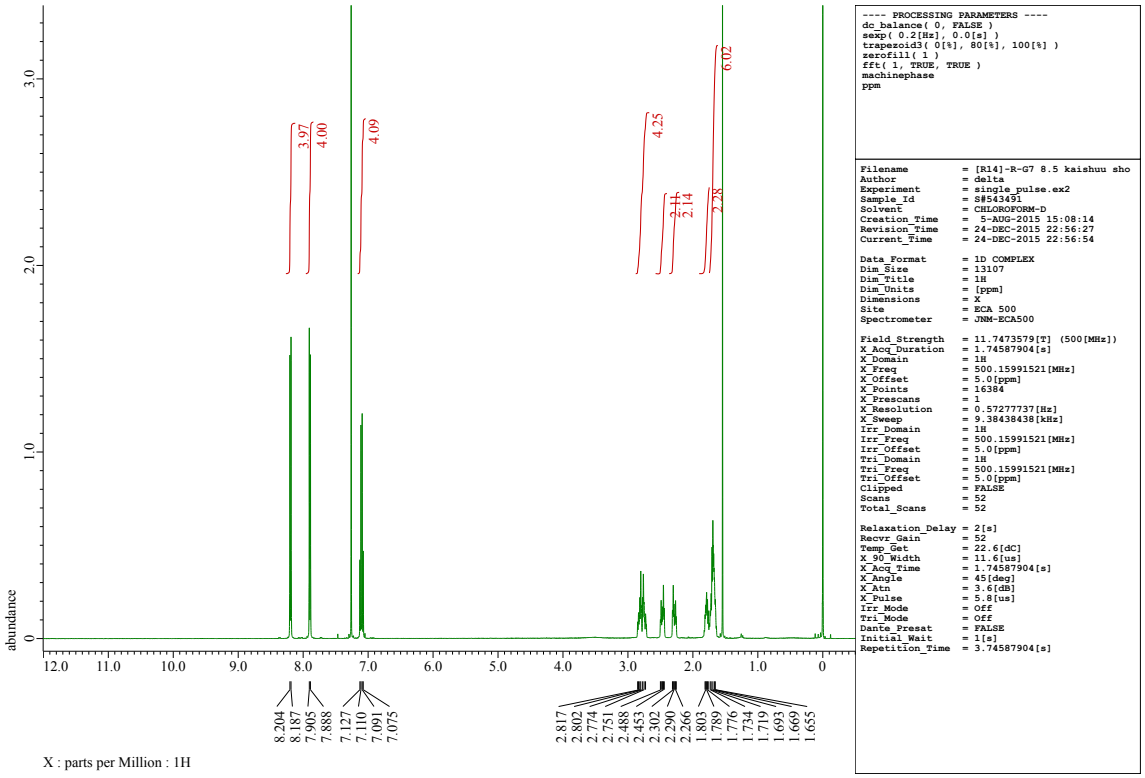


Fig. S48 ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (*R*)-**9**.

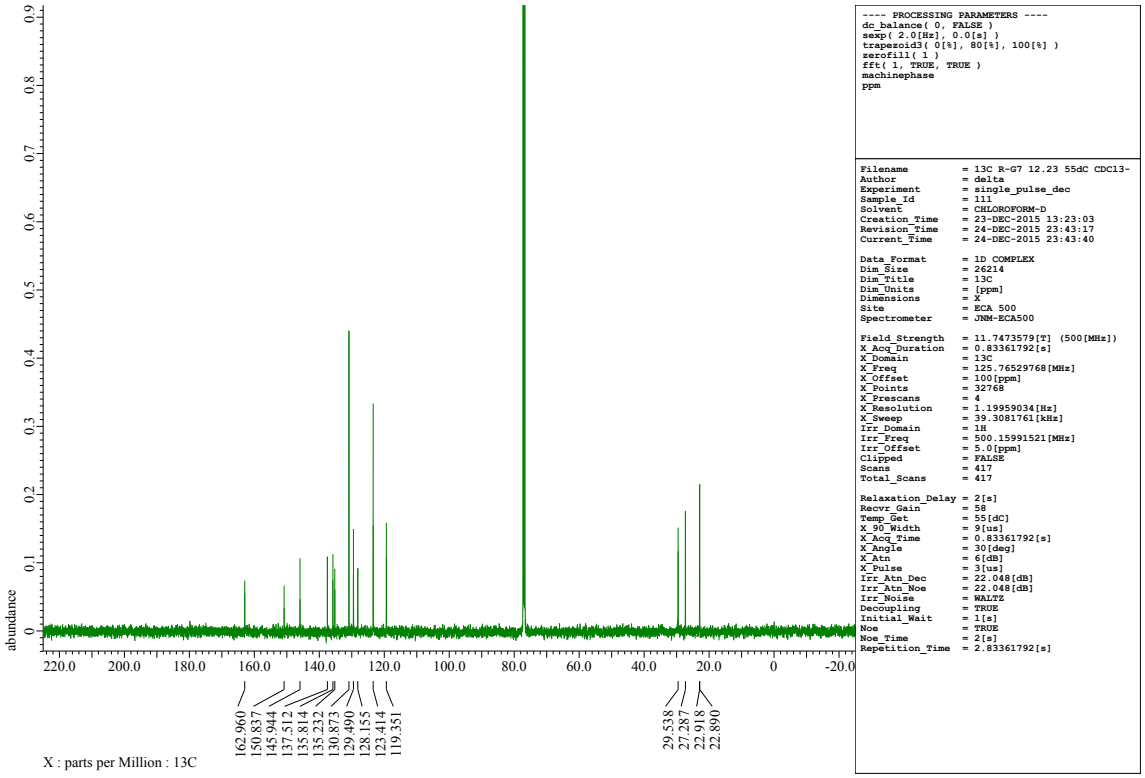


Fig. S49 ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of (*R*)-**9**.

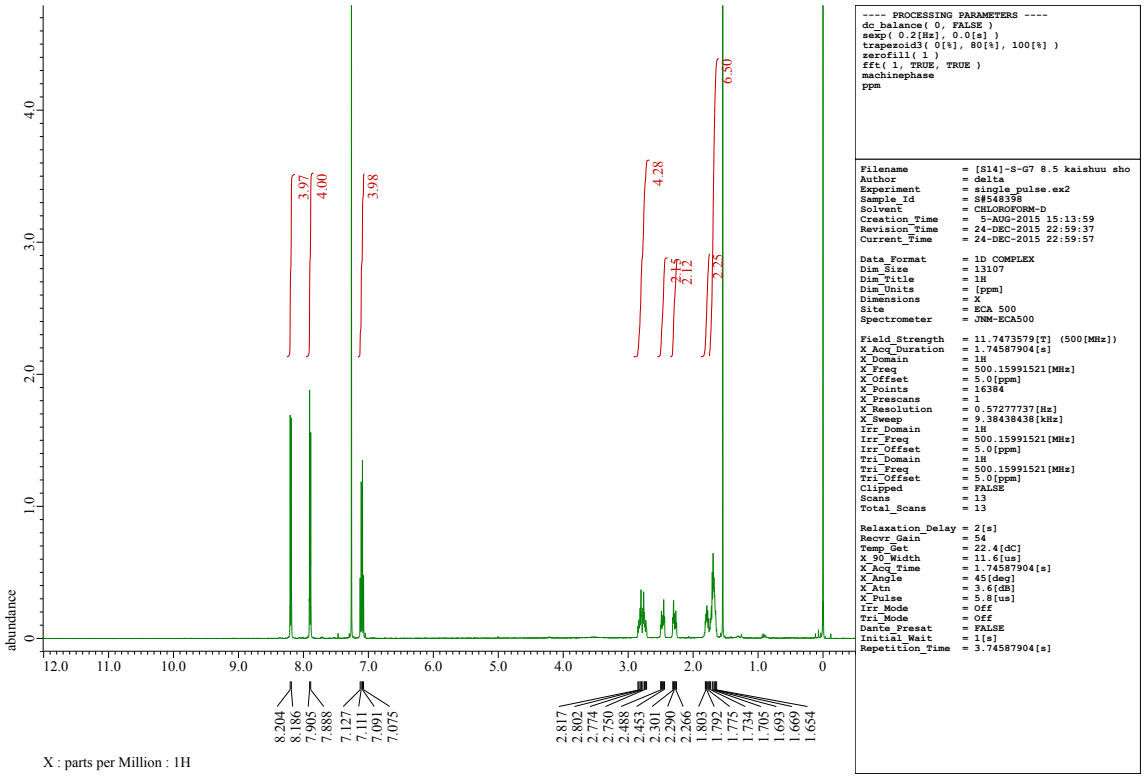


Fig. S50 ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (*S*)-**9**.

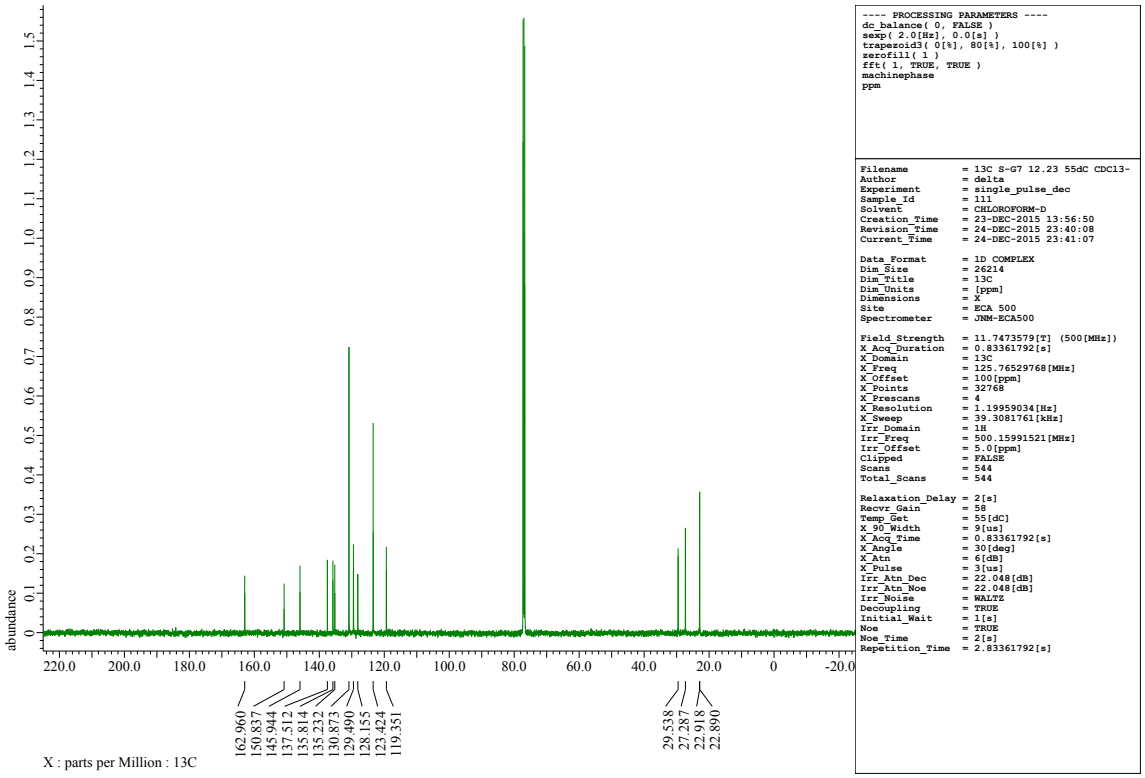


Fig. S51 ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of (*S*)-**9**.

Reference

1. J. Zhou, Y. Zuo, X. Wan, G. Long, Q. Zhang, W. Ni, Y. Liu, Z. Li, G. He, C. Li, B. Kan, M. Li and Y. Chen, *J. Am. Chem. Soc.*, 2013, **135**, 8484-8487.