Supporting Information

Tying a Molecular Overhand Knot of Single Handedness and Asymmetric Catalysis with the Corresponding Pseudo-D_3-Symmetric Trefoil Knot

Guzmán Gil-Ramírez, Steven Hoekman, Matthew O. Kitching, David A. Leigh,* Iñigo J. Vitorica-Yrezabal, and Gen Zhang

School of Chemistry, University of Manchester,

Oxford Road, Manchester, M13 9PL, United Kingdom

Email: david.leigh@manchester.ac.uk

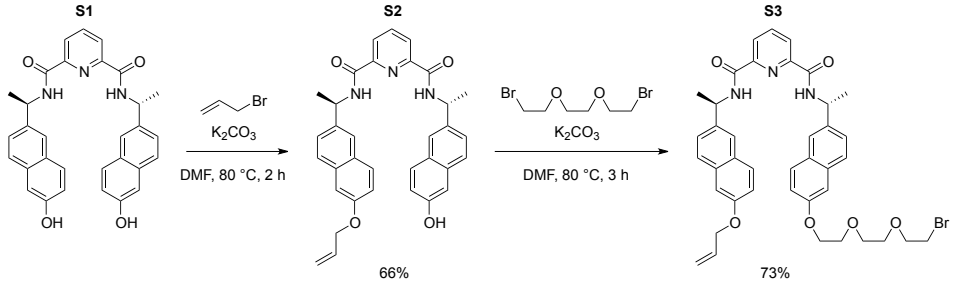
TABLE OF CONTENTS

1 GENERAL METHODS

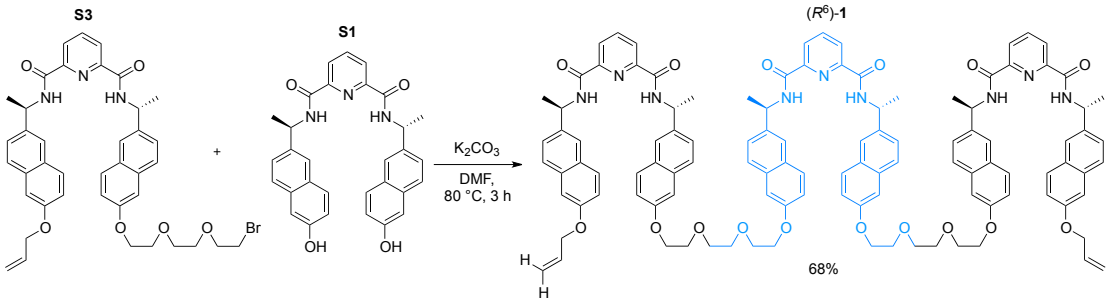
Unless stated otherwise, reagents were obtained from commercial sources and used without purification. Anhydrous THF (HPLC grade, Fischer scientific), CH_2Cl_2 (HPLC grade, Fischer scientific), and CH_3CN (HPLC grade, Fischer scientific) were obtained by passing the solvent through an activated alumina column on a Phoenix SDS (solvent drying system; JC Meyer Solvent Systems, CA, USA). DMF (Peptide synthesis grade, Merck) was used throughout. ^{1}H NMR spectra were recorded on a Bruker Avance III instrument with an Oxford AS600 magnet equipped with a cryoprobe [5mm CPDCH ^{13}C-^{1}H/D] (600 MHz). Chemical shifts are reported in parts per million (ppm) from high to low frequency using the residual solvent peak as the internal reference ($CDCl_3$ = 7.26 ppm, CD_3OD = 3.31 ppm and CD_3CN = 1.94).[S1,S2] All ^{1}H resonances are reported to the nearest 0.01 ppm. The multiplicity of ^{1}H signals are indicated as: s = singlet; d = doublet; t = triplet; q = quartet; sept = septet; m = multiplet; br = broad; app = apparent; or combinations of thereof. Coupling constants (*J*) are quoted in Hz and reported to the nearest 0.1 Hz. Where appropriate, averages of the signals from peaks displaying multiplicity were used to calculate the value of the coupling constant. ^{13}C NMR spectra were recorded on the same spectrometer with the central resonance of the solvent peak as the internal reference ($CDCl_3$ = 77.16 ppm, CD_3OD = 49.00 ppm and CD_3CN = 118.26 ppm).[S1,S2] ^{13}C resonances are reported to the nearest 0.01 ppm. DEPT, COSY, HSQC and HMBC experiments were used to aid structural determination and spectral assignment. Where necessary, ROESY or NOESY spectra were used to aid the assignment of ^{1}H spectra. Fully characterized compounds were chromatographically homogeneous. Flash column chromatography[S3] was carried out using Silica 60 Å (particle size 40-63 µm, Sigma Aldrich, UK) as the stationary phase. Preparative TLC was performed using PLC 20×20 cm, 60 F_{254} Prep plates (Merck), Silica Gel GF 20×20 cm or U_{254} Prep plates (Analtech) of various thicknesses and smaller quantities (< 10 mg of crude material) were purified on analytical TLC plates (0.25 mm thick, 60 F_{254}, Merck, Germany). TLC was visualized using both short and long waved ultraviolet light in combination with standard laboratory stains (acidic potassium permanganate, acidic ammonium molybdate and ninhydrin). Low resolution ESI mass spectrometry was performed with a Thermo Scientific LCQ Fleet Ion Trap Mass Spectrometer or an Agilent Technologies 1200 LC system with 6130 single quadrupole MS detector. High-resolution mass spectrometry was carried out by the EPSRC National Mass Spectrometry Service Centre (Swansea, UK) and the Mass Spectrometry Service at the University of Manchester (School of Chemistry). Melting points

(Mp) were determined using a Büchi M-565 apparatus and are corrected. Optical rotations were measured using a Rudolph Research Analytical Autopol I polarimeter with both AP Accuracy (±0.004°) and resolution upgrades with a built in thermoprobe for temperature measurement/control. Measurements were conducted using a sodium lamp (l 589 nm, D-line); $[\alpha]_{D}^{20}$ values were reported in 10 deg cm^2 g^{-1}, concentration (*c*) in g per 100 ml. Enantiomeric ratios were determined by HPLC on a Agilent 1260 Infinity system with UV detection at 254 nm. A Chiralpak IA (5 µm Particle size, 250×4.6 mm, Diacel Corporation) column and hexane/2-propanol as eluent (1 ml/min flow-rate) were used for separations unless otherwise indicated. Steady state emission spectra were recorded on an Edinburgh Instrument FP920 Phosphorescence Lifetime Spectrometer at 295 K equipped with a 450 watt xenon lamp and a red sensitive photomultiplier in peltier (air cooled) housing, (Hamamatsu R928P). Lifetime data were recorded following excitation into the ligand absorption bands with a 2 W xenon flash lamp (Edinburgh Instruments), using multichannel scaling. Lifetimes were obtained by tail fit on the data obtained, and quality of fit judged by minimization of reduced chi-squared and residuals squared. The inner sphere hydration numbers (*q*) were determined by recording lifetime data for the complexes in MeOH and MeOD using the Horrocks equation.

2 REACTION SCHEMES



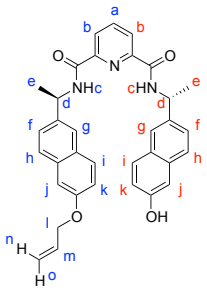
Scheme 1: Synthesis of **S3**.



Scheme 2: Synthesis of (R^6)-**1**.

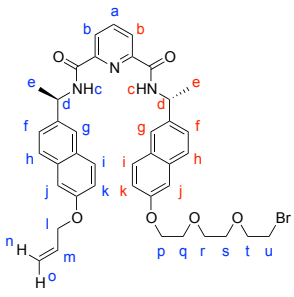
3 SYNTHETIC PROCEDURES AND CHARACTERIZATION DETAILS

S2



Diol **S1** (500 mg, 0.99 mmol) was taken up in DMF (10 mL) and K_2CO_3 (410 mg, 2.97 mmol) and allyl bromide (86 µL, 0.99 mmol) were added. The reaction mixture was stirred at 80 °C for 2 h under a nitrogen atmosphere. The mixture was concentrated under reduced pressure and purified by flash column chromatography (CH_2Cl_2/EtOAc, 10:1→5:1) to afford the title compound (357 mg, 0.65 mmol) as a colorless solid in 66% yield. Mp 153 °C. $[\alpha]_D^{20}$ −342.4 (*c* 1.15, MeOH). ^{1}H NMR (600 MHz, CD_3OD): δ 8.25–8.21 (m, 2H, H_b), 8.04 (app t, *J* =7.8 Hz, 1H, H_a), 7.73–7.70 (m, 2H, H_g), 7.69–7.63 (m, 3H, $H_{i+i,h}$), 7.59 (d, *J* = 8.6 Hz, 1H, H_h), 7.46 (d, *J* = 8.5 Hz, 1H, H_f), 7.42 (d, *J* = 8.6 Hz, 1H, H_f), 7.17–7.15 (m, 1H, H_j), 7,13–7.09 (m, 1H, H_k), 7.08–7.06 (m, 1H, H_j), 7.06–7.03 (m, 1H, H_k). 6.11 (app qd, *J* = 10.5, 5.2 Hz, 1H, H_m), 5.47–5.38 (m, 3H, $H_{n,d}$), 5.27 (d, *J* = 10.6 Hz, 1H, H_o), 4.61 (d, *J* = 5.2 Hz, 2H, H_l), 1.62 (m, 6H, H_e).[S4] ^{13}C NMR (151 MHz, CD_3OD): δ 165.29, 165.27, 157.98, 156.49, 150.58, 150.56, 140.22, 139.82, 139.00, 135.58, 135.20, 134.84, 130.44, 130.36, 130.23, 129.61, 128.27, 127.65, 126.39, 126.24, 126.18, 126.18, 125.39, 125.33, 120.12, 119.53, 117.56, 109.79, 107.86, 69.76, 50.14, 50.15, 21.64, 21.61. LRMS (ESI) m/z calc for $C_{34}H_{31}N_3NaO_4$ $[M+Na]^+$: 568.2, found 568.2. LRMS (ESI) measured isotopic distribution for $C_{34}H_{30}N_3O_4$ $[M-H]^-$: 544.2 (100), 545.2 (39), 546.2 (8). Calculated: 544.3 (100), 545.3 (39), 546.3 (8). HRMS (ESI) m/z calc for $C_{34}H_{32}N_3O_4$ $[M+H]^+$: 546.2387, found 546.2383.

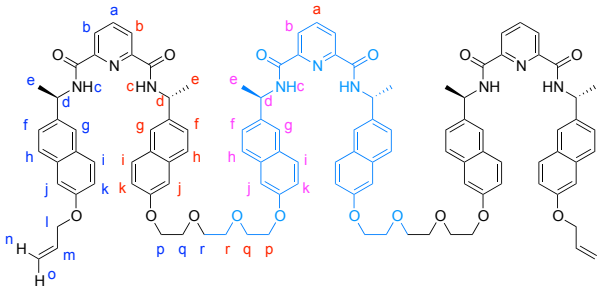
S3



DMF (5 mL) was added to a flask containing alcohol **S2** (250 mg, 0.46 mmol), 1,2-bis(2-bromoethoxy)ethane (253 mg, 0.92 mmol) and K_2CO_3 (190 mg, 1.37 mmol). The resulting suspension was stirred at 80 °C for 3 h under a nitrogen atmosphere. The mixture was concentrated under reduced pressure and purified by flash column chromatography to give bromide **S3** as a pale brown solid (249 mg, 0.34 mmol) in 73% yield. Mp 118 °C. $[\alpha]_D^{20}$ −165.0 (*c* 1.23, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.36 (app d, *J* = 7.8 Hz, 2H, H_b), 8.03 (m, 1H, H_a), 7.89–7.85 (m, 2H, H_c), 7.74–7.71 (m, 2H, H_g), 7.70–7.67 (m, 2H, H_i), 7.66–7.62 (m, 2H, H_h), 7.45–7.41 (m, 2H, H_f), 7.21–7.18 (m, 2H, H_k), 7.13-7.10 (m, 2H, H_j), 6.13 (ddt, *J* = 17.3, 10.6, 5.3 Hz, 1H, H_m), 5.48 (dd, *J* = 17.3, 1.6 Hz, 1H, H_n), 5.46–5.41 (m, 2H, H_d), 5.33 (dd, *J* = 10.5, 1.5 Hz, 1H, H_o), 4.66 (d, *J* = 5.4

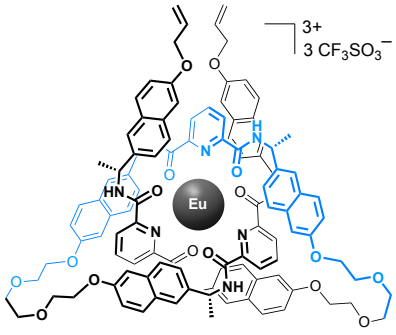
Hz, 2H, H_l), 4.26 (t, *J* = 4.7 Hz, 2H, H_p), 3.95 (t, *J* = 4.7 Hz, 2H, H_q), 3.82 (t, *J* = 6.3 Hz, 2H, H_t), 3.79–3.75 (m, 2H, H_r), 3.74–3.70 (m, 2H, H_s), 3.47 (t, *J* = 6.3 Hz, 2H, H_u), 1.66 (s, 3H, H_e), 1.65 (s, 3H, H_e).[S4] ^{13}C NMR (151 MHz, $CDCl_3$): δ 162.69, 162.69, 157.13, 156.90, 148.93, 148.93, 139.23, 138.02, 138.02, 134.03, 134.01, 133.17, 129.54, 129.50, 128.98, 128.96, 127.70, 127.70, 125.31, 125.31, 125.07, 125.02, 124.72, 124.72, 119.70, 119.66, 118.05, 107.00, 106.72, 71.40, 71.02, 70.75, 69.69, 68.99, 67.60, 49.19, 49.19, 30.49, 21.79, 21.75. LRMS (ESI) measured isotopic distribution for $C_{40}H_{42}BrN_3NaO_6$ $[M+Na]^+$: 762.3 (76), 763.3 (47), 764.3 (100), 765.3 (58). Calculated: 762.2 (93), 763.2 (42), 764.2 (100), 765.2 (43). HRMS (ESI) m/z calc for $C_{40}H_{43}BrN_3O_6$ $[M+H]^+$: 740.2330, found 740.2336.

(R^6)-**1**



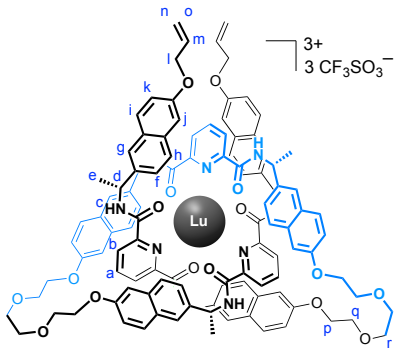
Bromide **S3** (40 mg, 0.054 mmol) and diol **S1** (14 mg, 0.027 mmol) were dissolved in DMF (3 mL). K_2CO_3 (11 mg, 0.081 mmol) was added and the reaction mixture was heated to 80 °C and stirred under nitrogen for 3 h. Upon completion, the mixture was concentrated under reduced pressure and purified by flash column chromatography (CH_2Cl_2/MeOH, 15:1→10:1) to afford chiral ligand (R^6)-**1** as a colorless solid (32 mg, 0.018 mmol) in 68% yield. Mp 115 °C. $[\alpha]_D^{20}$ −192.7 (*c* 0.45, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.31–8.25, (m, 6H, H_b), 8.06–8.01 (m, 6H, H_c), 7.95–7.88 (m, 3H, H_a), 7.65–7.56 (m, 18H, $H_{g,i,h}$), 7.40–7.35 (m, 6H, H_f), 7.17–7.11 (m, 6H, H_k), 7.09-7.05 (m, 6H, H_j), 6.12 (ddt, *J* = 17.3, 10.5, 5.3 Hz, 2H, H_m), 5.47 (dd, *J* = 17.3, 1.6 Hz, 2H, H_n), 5.42–5.33 (m, 6H, H_d), 5.32 (dd, *J* = 10.6, 1.5 Hz, 2H, H_o), 4.64 (d, *J* = 5.3 Hz, 4H, H_l), 4.24–4.29 (m, 8H, H_p), 3.95–3.89 (m, 8H, H_q), 3.79 (br s, 8H, H_r), 1.57 (d, *J* = 6.8 Hz, 6H, H_e), 1.54–1.48 (m, 12H, H_e).[S4] ^{13}C NMR (151 MHz, $CDCl_3$): δ 162.80, 162.80, 162.80, 157.07, 157.07, 156.82, 148.87, 148.84, 148.84, 139.05, 139.05, 138.05, 138.05, 138.05, 133.93, 133.91, 133.91, 133.17, 129.45, 129.41, 129.39, 128.90, 128.88, 128.86, 127.62, 127.59, 127.58, 125.24, 125.24, 125.22, 125.16, 125.14, 125.14, 124.61, 124.59, 124.59, 119.62, 119.62, 119.59, 118.02, 106.93, 106.75, 106.75, 71.07, 71.07, 69.93, 69.93, 68.95, 67.59, 67.59, 49.00, 48.98, 48.98, 21.59, 21.53, 21.52. LRMS (ESI) measured isotopic distribution for $C_{111}H_{109}N_9NaO_{16}$ $[M+Na]^+$: 1846.67 (80), 1847.58 (100), 1848.58 (65), 1849.58 (29), 1850.67 (12). Calculated: 1846.79 (80), 1847.79 (100), 1848.80 (65), 1849.80 (30), 1850.80 (11). HRMS (ESI) m/z calc for $C_{111}H_{110}N_9O_{16}$ $[M+H]^+$: 1825.8100, found 1825.8087.

Λ-Eu(R^6)-**1**$(CF_3SO_3)_3$



Dialkene (R^6)-**1** (45 mg, 0.0247 mmol) was dissolved in MeCN (5.0 mL) and treated with europium(III) triflate (15 mg, 0.054 mmol). The reaction mixture was stirred under an inert atmosphere at 80 °C for 12 h. The mixture was concentrated under reduced pressure and the resulting paste was suspended in CH_2Cl_2. The formed precipitate was filtered off and washed with CH_2Cl_2 (3 × 10 mL) to give complex Λ-Eu(R^6)-**1**$(CF_3SO_3)_3$ as a colorless powder (51 mg, 0.0210 mmol) in 85% yield. LRMS (ESI) m/z calc for $C_{112}H_{109}EuF_3N_9O_{19}S$ $[M-2OTf]^{2+}$: 1062.84, found 1062.92 (100), $C_{111}H_{109}EuN_9O_{16}$ $[M-3OTf]^{3+}$: 658.91, found 659.75 (51). HRMS (ESI) m/z calc for $C_{111}H_{109}EuN_9O_{16}$ $[M-3OTf]^{3+}$: 658.9070, found 658.9054.[S5]

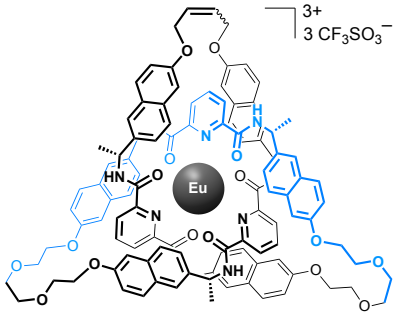
Λ-Lu(R^6)-**1**$(CF_3SO_3)_3$



Prepared as described as above starting from (R^6)-**1** (300 mg, 0.16 mmol) and lutetium(III) triflate (97 mg, 0.16 mmol) to give complex Λ-Lu(R^6)-**1**$(CF_3SO_3)_3$ as a colorless powder (354 mg, 0.14 mmol) in 90% yield. ^{1}H NMR (600 MHz, CD_3CN): δ 8.42 (d, *J* = 4.3 Hz, 2H, H_c), 8.38 (d, *J* = 6.3 Hz, 2H, H_c), 8.28 (d, *J* = 5.2 Hz, 2H, H_c), 7.64 (d, *J* = 9.7 Hz, 2H, H_i), 7.57–7.48 (m, 10H, $H_{b,h,i}$), 7.33–7.23 (m, 8H, $H_{h,k,j}$), 7.22–7.19 (m, 4H, $H_{g,j}$), 7.16–7.11 (m, 3H, $H_{a,k}$), 7.07 (s, 2H, H_j), 6.99 (s, 2H, H_g), 6.94–6.91 (m, 4H, $H_{b,g}$), 6.85 (d, *J* = 8.6 Hz, 2H, H_f), 6.84–6.80 (m, 4H, $H_{b,f}$), 6.66 (d, *J* = 8.5 Hz, 2H, H_f), 6.25 (app ddd, *J* = 22.4, 10.5, 5.2 Hz, 2H, H_m), 6.06 (t, *J* = 7.9 Hz, 2H, H_a), 5.58 (dd, *J* = 17.3, 1.5 Hz, 2H, H_n), 5.41 (d, *J* = 10.5 Hz, 2H, H_o), 4.86–4.80 (m, 4H, H_l), 4.78–4.73 (m, 2H, H_d), 4.70–4.59 (m, 4H, H_d), 4.42–4.29 (m, 4H, H_p), 4.26–4.20 (m, 4H, H_p), 4.10–4.01 (m, 4H, H_q), 3.99–3.93 (m, 4H, H_q), 3.91–3.78 (m, 8H, H_r), 1.58 (d, *J* = 7.0 Hz, 6H, H_e), 1.54 (d, *J* = 7.1 Hz, 6H, H_e), 1.48 (d, *J* = 7.0 Hz, 6H, H_e).[S4] ^{13}C NMR (151 MHz, CD_3CN): δ 167.57, 167.30, 167.05, 158.04, 157.86, 157.71, 145.30, 144.62, 144.58, 140.00, 139.33, 139.33, 139.00, 134.54, 134.54, 134.50, 134.30, 133.90, 130.10, 130.00, 129.76, 129.29, 129.28, 129.02, 128.12, 128.12, 127.87, 125.11, 124.46, 124.02, 124.02, 123.91, 123.38, 123.27, 123.21, 123.15, 120.40, 120.40, 120.31, 117.81, 108.15, 107.97, 107.95, 71.60, 71.51, 69.94, 69.93, 69.67, 69.28, 69.12, 54.13, 53.65, 52.91, 23.48, 23.29, 22.12. LRMS (ESI) m/z calc for $C_{112}H_{109}F_3LuN_9O_{19}S$

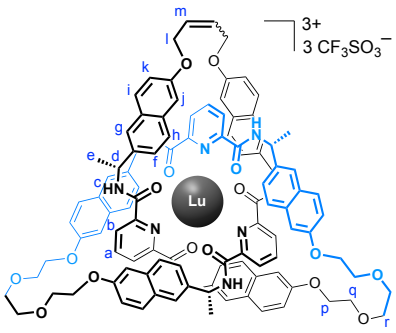
[M−2OTf]$^{2+}$: 1074.15, found 1074.00. HRMS (ESI) m/z calc for $C_{111}H_{109}LuN_9O_{16}$ [M−3OTf]$^{3+}$: 666.5805, found 666.5793.

Λ-Eu(R^6)-**2**$(CF_3SO_3)_3$



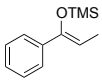
A degassed mixture of CH_2Cl_2 and $MeNO_2$ (3:1, 200 mL) was added to a flask containing Λ-Eu(R^6)-**1** (24 mg, 0.0101 mmol). Hoveyda-Grubbs (2nd generation) catalyst (3.1 mg, 0.005 mmol) was added under nitrogen and the mixture was heated to 50 °C for 18 h. The solution was allowed to cool to rt and was quenched with ethyl vinyl ether (0.75 mL). The mixture was stirred for another 30 min (the solution turned brown), concentrated (to ca. 2 mL) and diluted with CH_2Cl_2 (20 mL). The precipitate was filtered off and washed with CH_2Cl_2 (3 × 5 mL) to give knot Λ-Eu(R^6)-**2**$(CF_3SO_3)_3$ as a colorless powder (21 mg, 0.0091 mmol) in 90% yield. LRMS (ESI) m/z calc for $C_{110}H_{105}EuF_3N_9O_{19}S$ [M−2OTf]$^{2+}$: 1048.82, found 1048.92 (100), $C_{109}H_{105}EuN_9O_{16}$ [M−3OTf]$^{3+}$: 649.56, found 649.75 (56). HRMS (ESI) m/z calc for $C_{109}H_{105}EuN_9O_{16}$ [M−3OTf]$^{3+}$: 649.5631, found 649.5623.[S5]

Λ-Lu(R^6)-**2**$(CF_3SO_3)_3$



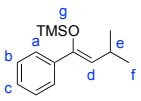
Prepared as described as above starting from complex Λ-Lu(R^6)-**1**$(CF_3SO_3)_3$ (127 mg, 0.053 mmol) to give Λ-Lu(R^6)-**2**$(CF_3SO_3)_3$ as a white powder (111 mg, 0.047 mmol) in 88% yield. ^{1}H NMR (600 MHz, CD_3CN, 345 K): δ 8.30 (d, J = 7.6 Hz, 6H, H_c), 7.62–7.54 (m, 6H, H_h), 7.55–7.42 (m, 6H, H_i), 7.28 (app d, J = 9.2 Hz, 6H, H_k), 7.22 (app d, J = 11.2 Hz, 6H, H_j), 7.06 (app d, J = 11.7 Hz, 6H, H_b), 6.94 (app d, J = 8.0 Hz, 6H, H_g), 6.92–6.85 (m, 6H, H_f), 6.42 (m, 2H, H_m), 6.26 (m, 3H, H_a), 5.15–4.90 (m, 6H, H_d), 4.80–4.67 (m, 4H, H_l), 4.43–4.31 (m, 8H, H_p), 4.15–4.08 (m, 4H, H_q), 4.06–3.98 (m, 4H, H_q), 3.97–3.85 (m, 8H, H_r), 1.70–1.56 (m, 18H, H_e).[S4] LRMS (ESI) m/z calc for $C_{110}H_{105}F_3LuN_9O_{19}S$ [M−2OTf]$^{2+}$: 1059.83, found 1059.32. HRMS (ESI) m/z calc for $C_{109}H_{105}LuN_9O_{16}$ [M−3OTf]$^{3+}$: 657.2367, found 657.2354.

Trimethyl(1-phenylpropenyloxy)silane



Propiophenone (1.34 g, 9.99 mmol) in THF (20 mL) was added dropwise to a stirred solution of LiHMDS (1 M in THF, 15 mL) over a period of 30 min at rt. The resulting solution was stirred for another 15 min before the addition of chlorotrimethylsilane (1.62 g, 14.9 mmol) in THF (10 mL). The reaction mixture was concentrated and the residue taken up in CH_2Cl_2 (50 mL). The resulting suspension was filtered and the filtrate concentrated under reduced pressure to afford the silyl enol ether (1.85 g, 8.69 mmol) as a yellow oil in 87% yield. The product was stored in the freezer and used without further purification.[S6] Characterization data was in agreement with the literature.[S7]

Trimethyl(3-methyl-1-phenylbutenyloxy)silane



Prepared as described as above starting from isovalerophenone (1.63 g, 10.05 mmol) to afford the silyl enol ether (1.77 g, 7.54 mmol) as a yellow oil in 75% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.47–7.44 (m, 2H, H_a). 7.31–7.27 (m, 2H, H_b), 7.25–7.21 (m, 1H, H_c), 5.08 (d, *J* = 9.6 Hz, 1H, H_d), 2.81 (dsept, *J* = 9.6, 6.7 Hz, 1H, H_e), 1.04 (d, *J* = 6.7 Hz, 6H, H_f), 0.13 (s, 9H, H_g). ^{13}C NMR (151 MHz, $CDCl_3$): δ 147.16, 139.46, 128.12, 127.42, 125.55, 119.32, 25.62, 23.34, 0.66. LRMS (ESI) m/z calc for $C_{14}H_{23}OS_i$ $[M+H]^+$: 235.15, found 235.08.

Mukaiyama aldol addition general procedures

General procedure A

A solution of europium catalyst (10 mol%) and aldehyde (0.066 mmol, 1 equiv.) in a mixture of dry MeOH/CH_3CN (5:2, 0.7 mL) was cooled to –10 °C. The silyl enol ether (0.066 mmol, 1 equiv.) was added dropwise and the reaction mixture was stirred at the same temperature for 4 d. The reaction mixture was concentrated and the remaining solid taken up in CH_2Cl_2. The suspension was filtered and the solution was concentrated under reduced pressure. The crude product was purified by preparative thin layer chromatography (PET/EtOAc, 5:1) to afford the aldol adduct.

General procedure B

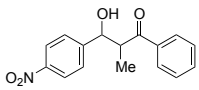
To a dry microwave vial equipped with a stirrer bar, the europium catalyst (10 mol%) was transferred from a stock solution (CH_3CN) and the solvent removed under reduced pressure. To this, the aldehyde (0.01 mmol, 1 equiv.) and silyl enol ether (0.015 mmol, 1.5 equiv.)

were added sequentially from separate stock solutions of dry MeOH/CH_3CN (5:2, 0.05 mL) at –10 °C. The resulting slurry was stirred at the same temperature for 4 d. The reaction mixture was concentrated and the remaining solid taken up in CH_2Cl_2. The suspension was filtered and the solution was concentrated under reduced pressure. The crude product was purified by preparative thin layer chromatography (PET/EtOAc, 5:1) to afford the aldol adduct, which was analyzed by ^{1}H NMR and chiral HPLC.

Synthesis of racemates

The silyl enol ether (0.066 mmol, 1 equiv.) was added dropwise to a solution of europium(III) triflate (79 mg, 0.132 mmol, 2 equiv,) and aldehyde (0.066 mmol, 1 equiv.) in a mixture of dry MeOH/CH_3CN (5:2, 0.7 mL) at rt and stirred overnight. The reaction mixture was concentrated and the crude product was purified by preparative thin layer chromatography (PET/EtOAc, 5:1) to afford the aldol adduct.

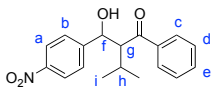
3-Hydroxy-2-methyl-3-(4-nitrophenyl)-1-phenylpropan-1-one (5)



Prepared as described employing general procedure A starting from trimethyl(1-phenylpropenyloxy)silane and 4-nitrobenzaldehyde. Characterization data was in agreement with the literature.[S8]

Enantiomeric excess was determined by HPLC with a Chiralpak IA (5 µm Particle size, 250×4.6 mm, Diacel Corperation) column (hexane/2-propanol, 95:5, 1 mL/min, 254 nm); *syn* diastereoisomer t_r = 31.5, 33.7 min, *anti* diastereoisomer t_r = 40.0, 68.2 min.

2-(Hydroxy(4-nitrophenyl)methyl)-3-methyl-1-phenylbutan-1-one (9)

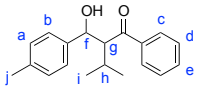


Prepared as described employing general procedure B starting from trimethyl(3-methyl-1-phenylbutenyloxy)silane and 4-nitrobenzaldehyde. ^{1}H NMR (600 MHz, $CDCl_3$): *syn* diastereoisomer δ 8.14 (d, *J* = 8.7 Hz, 2H, H_a), 7.80 (d, *J* = 7.4 Hz, 2H, H_c), 7.59 (d, *J* = 8.7 Hz, 2H, H_b), 7.54 (m, 1H, H_e), 7.42 (m, 2H, H_d), 5.28 (d, *J* = 6.4 Hz, 1H, H_f), 3.82 (dd, *J* = 6.2, 5.0 Hz, 1H, H_g), 3.12 (br s, 1H, OH), 2.44–2.35 (m, 1H, H_h), 1.23 (d, *J* = 6.9 Hz, 3H, H_i), 0.90 (d, *J* = 7.0 Hz, 3H, H_i). ^{13}C NMR (151 MHz, $CDCl_3$): *syn* diastereoisomer δ 203.75, 150.25, 147.34, 138.24, 133.69, 128.89, 128.37, 127.54, 123.68, 73.10, 57.55, 27.99, 22.52, 19.82. ^{1}H NMR (600 MHz, $CDCl_3$): *anti* diastereoisomer δ 8.05 (d, *J* = 8.7 Hz, 2H, H_a), 7.62 (d, *J* = 7.4 Hz, 2H, H_c), 7.48 (m, 1H, H_e), 7.44 (d, *J* = 8.6 Hz, 2H, H_b), 7.32 (dd, *J* = 8.4, 7.3 Hz, 2H, H_d), 5.24 (m, 1H, H_f), 4.56 (br s, 1H, OH), 3.57 (dd, *J* = 9.2, 3.5 Hz, 1H, H_g), 2.44–2.35 (m, 1H, H_h), 1.03 (d, *J* = 6.7 Hz, 3H, H_i), 0.86 (d, *J* = 6.8 Hz, 3H, H_i). ^{13}C NMR (151 MHz, $CDCl_3$):

anti diastereoisomer δ 207.07, 151.08, 147.09, 138.04, 134.05, 128.83, 128.14, 126.52, 123.65, 72.84, 57.96, 29.93, 21.60, 21.16. LRMS (ESI) m/z calc for $C_{36}H_{38}N_2NaO_8$ $[2M+Na]^+$: 649.3, found 649.3. HRMS (ESI) *syn* m/z calc for $C_{18}H_{20}NO_4$ $[M+H]^+$: 314.1387, found 314.1387. HRMS (ESI) *anti* m/z calc for $C_{18}H_{19}ClNO_4$ $[M+Cl]^-$: 348.0997, found 348.1000.

Enantiomeric excess was determined by HPLC with a Chiralpak IA (5 µm Particle size, 250×4.6 mm, Diacel Corperation) column (hexane/2-propanol, 95:5, 1 mL/min, 254 nm); *syn* diastereoisomer t_r = 27.4, 34.1 min, *anti* diastereoisomer t_r = 23.4, 39.4 min.

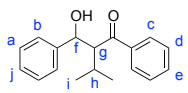
2-(hydroxyl(*p*-tolyl)methyl)-3-methyl-1-phenylbutan-1-one (10)[S9]



Prepared as described employing general procedure B starting from trimethyl(3-methyl-1-phenylbutenyloxy)silane and *p*-tolualdehyde. ^{1}H NMR (600 MHz, $CDCl_3$): *syn* diastereoisomer δ 7.77 (d, *J* = 7.5 Hz, 2H, H_c), 7.49 (m, 1H, H_e), 7.38 (m, 2H, H_d), 7.27 (m, 2H, H_b), 7.06 (d, *J* = 7.9 Hz, 2H, H_a), 5.14 (d, *J* = 7.4 Hz, 1H, H_f), 3.87 (dd, *J* = 7.5, 4.7 Hz, 1H, H_g), 2.42 (m, 1H, H_h), 2.26 (s, 3H, H_j), 1.06 (d, *J* = 6.9 Hz, 3H, H_i), 0.88 (d, *J* = 7.0 Hz, 3H, $H_{i'}$).). ^{13}C NMR (151 MHz, $CDCl_3$): *syn* diastereoisomer δ 203.77, 139.91, 138.97, 137.36, 132.98, 129.15, 128.59, 128.28, 126.61, 73.77, 57.90, 28.19, 22.38, 21.23, 19.41. ^{1}H NMR (600 MHz, $CDCl_3$): *anti* diastereoisomer δ 7.68 (dd, *J* = 8.3, 1.1 Hz, 2H, H_c), 7.47 (m, 1H, H_e), 7.34 (dd, *J* = 8.1, 7.6 Hz, 2H, H_d), 7.17 (d, *J* = 8.0 Hz, 2H, H_b), 7.03 (d, *J* = 7.9 Hz, 2H, H_a), 5.13 (d, *J* = 4.7 Hz, 1H, H_f), 3.84 (br s, 1H, OH), 3.60 (dd, *J* = 8.2, 4.8 Hz, 1H, H_g), 2.23 (m, 4H, $H_{h,j}$), 1.11 (d, *J* = 6.7 Hz, 3H, H_i), 0.86 (d, *J* = 6.8 Hz, 3H, $H_{i'}$). ^{13}C NMR (151 MHz, $CDCl_3$): *anti* diastereoisomer δ 207.42, 140.24, 139.05, 136.97, 133.22, 129.11, 128.54, 128.25, 125.75, 73.60, 58.68, 29.67, 21.46, 21.15, 20.95. HRMS (ESI) *anti* m/z calc for $C_{19}H_{22}NaO_2$ $[M+Na]^+$: 305.1512, found 305.1507.

Enantiomeric excess was determined by HPLC with a Chiralpak IA (5 µm Particle size, 250×4.6 mm, Diacel Corperation) column (hexane/2-propanol, 95:5, 1 mL/min, 254 nm); *syn* diastereoisomer t_r = 13.8, 15.2 min, *anti* diastereoisomer t_r = 16.9, 17.3 min.

2-(hydroxyl(phenyl)methyl)-3-1-phenylbutan-1-one (11)



Prepared as described employing general procedure B starting from trimethyl(3-methyl-1-phenylbutenyloxy)silane and benzaldehyde. ^{1}H NMR (600 MHz, $CDCl_3$): *syn* diastereoisomer δ 7.76 (d, *J* = 7.3 Hz, 2H, H_c), 7.49 (m, 1H, H_e), 7.40–7.35 (m, 4H, $H_{d,b}$), 7.25 (m, 2H, H_a), 7.17 (m, 1H, H_j), 5.18 (d, *J* = 7.3 Hz, H_f), 3.87 (dd, *J* = 7.3, 4.7 Hz, 1H, H_g), 3.59 (br s, 1H, OH), 2.43 (m, 1H, H_h), 1.06 (d, *J* = 6.9 Hz, 3H, H_i), 0.88 (d, *J* = 7.1 Hz, 3H, $H_{i'}$). ^{13}C NMR (151 MHz, $CDCl_3$): *syn* diastereoisomer δ 203.92, 142.89, 138.91,

133.06, 128.62, 128.47, 128.26, 127.73, 126.69, 73.94, 57.95, 28.14, 22.40, 19.44. ^{1}H NMR (600 MHz, $CDCl_3$): *anti* diastereoisomer δ 7.64 (dd, *J* = 8.3, 1.1 Hz, 2H, H_c), 7.46 (m, 1H, H_e), 7.31 (dd, *J* = 8.1, 7.5 Hz, 2H, H_d), 7.27 (m, 2H, H_b), 7.22 (m, 2H, H_a), 7.11 (m, 1H, H_j), 5.17 (d, *J* = 4.3 Hz, 1H, H_f), 4.04 (br s, 1H, OH), 3.59 (dd, *J* = 8.5, 4.4 Hz, 1H, H_g), 2.29 (m, 1H, H_h), 1.15 (d, *J* = 6.7 Hz, 3H, H_i), 0.86 (d, *J* = 6.8 Hz, 3H, $H_{i'}$). ^{13}C NMR (151 MHz, $CDCl_3$): *anti* diastereoisomer δ 207.54, 143.27, 138.90, 133.31, 128.53, 128.42, 128.20, 127.36, 125.74, 73.60, 58.79, 29.70, 21.35, 21.17. HRMS (ESI) *syn* m/z calc for $C_{18}H_{20}NaO_2$ $[M+Na]^+$: 291.1356, found 291.1353. HRMS (ESI) *anti* m/z calc for $C_{18}H_{20}NaO_2$ $[M+Na]^+$: 291.1356, found 291.1350. Characterization data was in agreement with the literature.[S10]

Enantiomeric excess was determined by HPLC with a Chiralpak IA (5 μm Particle size, 250×4.6 mm, Diacel Corperation) column (hexane/2-propanol, 9:1, 1 mL/min, 254 nm); *syn* diastereoisomer t_r = 8.4, 9.0 min, *anti* diastereoisomer t_r = 10.4, 11.8 min.

4 HIGH-RESOLUTION MASS SPECTRA

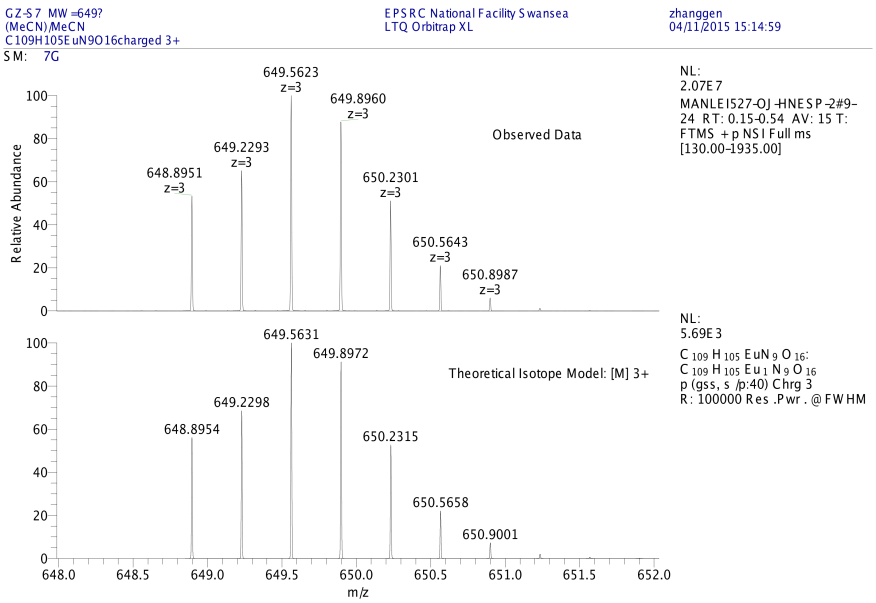


Figure 1: ESI found (top) and simulated (bottom) isotopic distribution of Λ-Eu(R^6)-**2**$(CF_3SO_3)_3$.

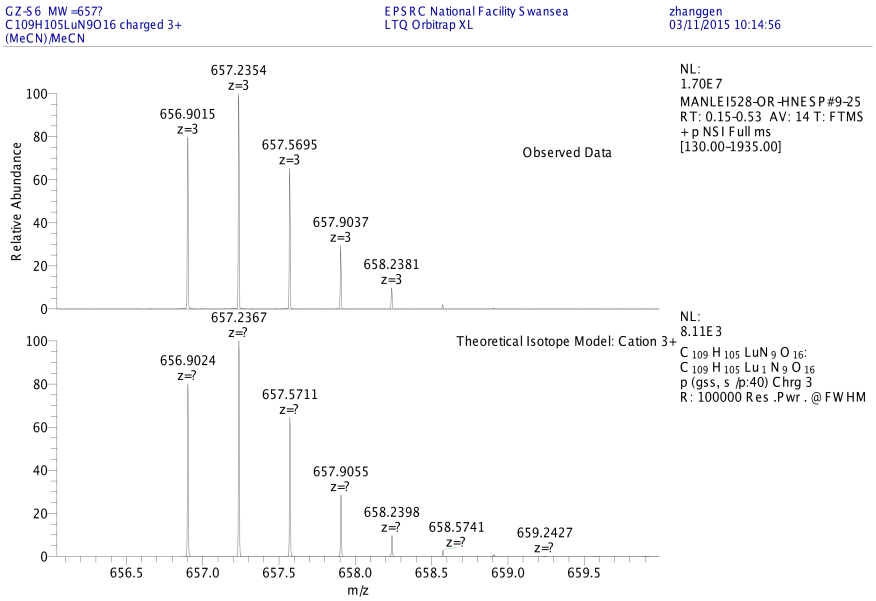
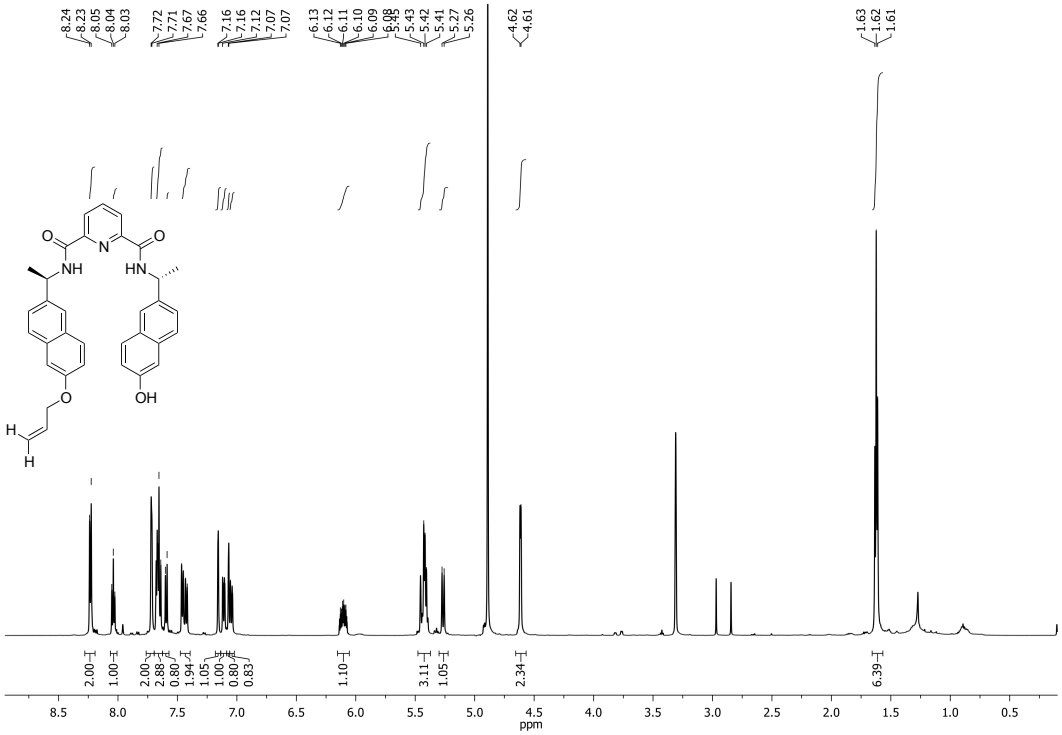
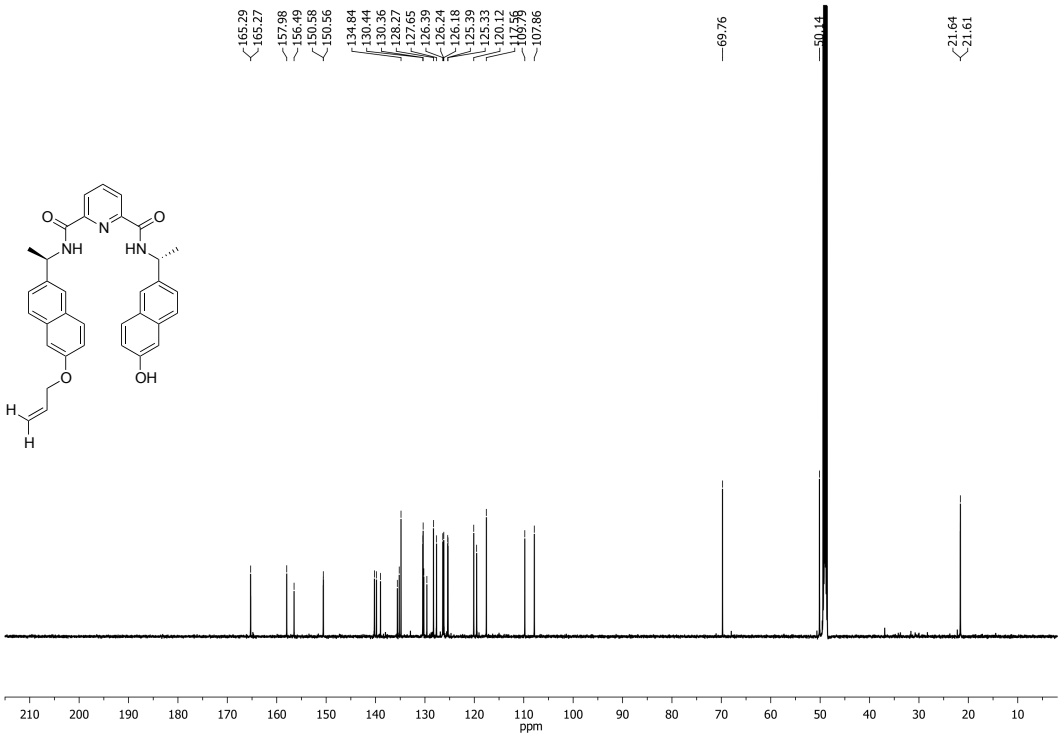


Figure 2: ESI found (top) and simulated (bottom) isotopic distribution of Λ-Lu(R^6)-**2**$(CF_3SO_3)_3$.

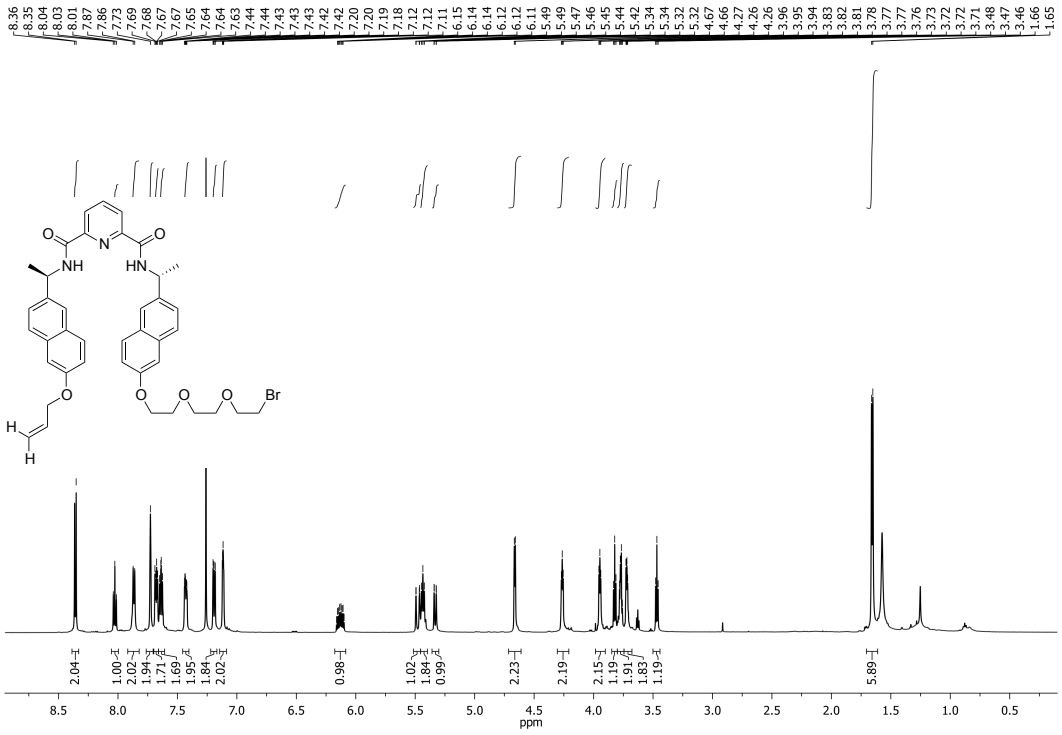
5 NMR SPECTRA



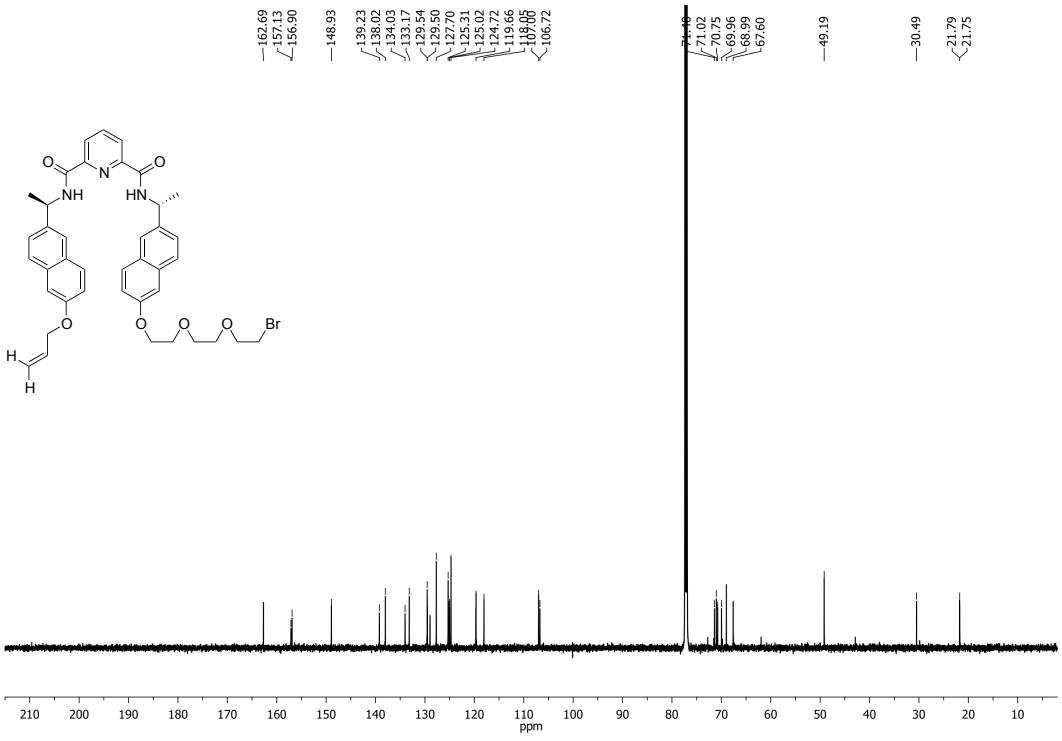
^{1}H NMR (600 MHz, MeOD)



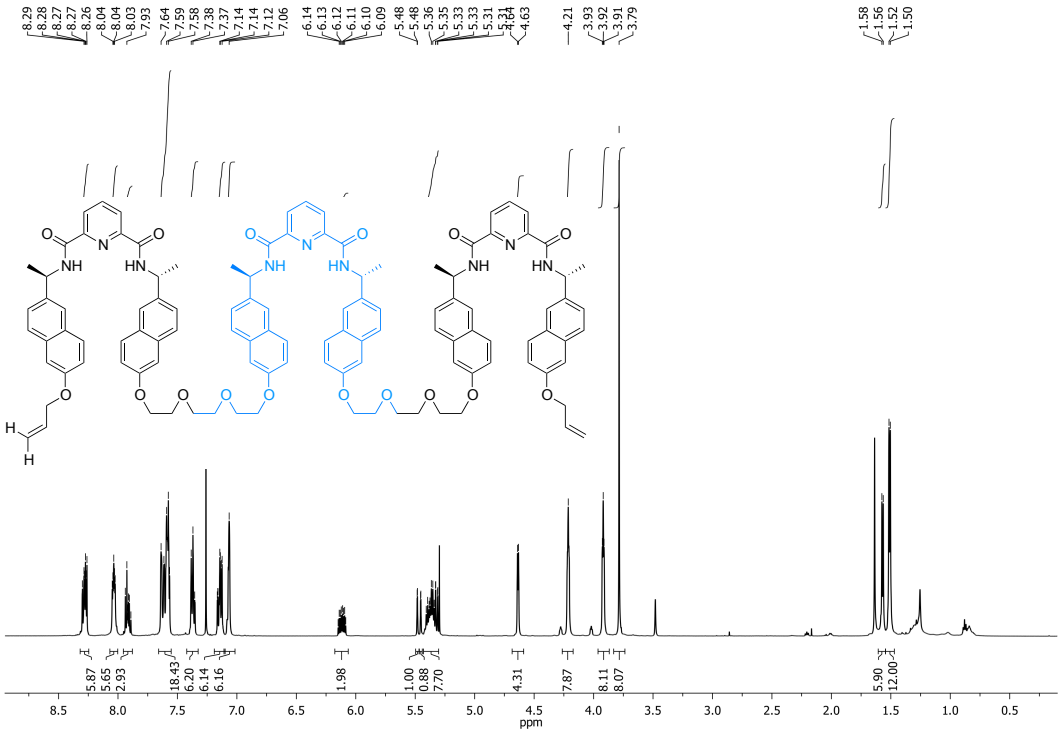
^{13}C NMR (151 MHz, MeOD)



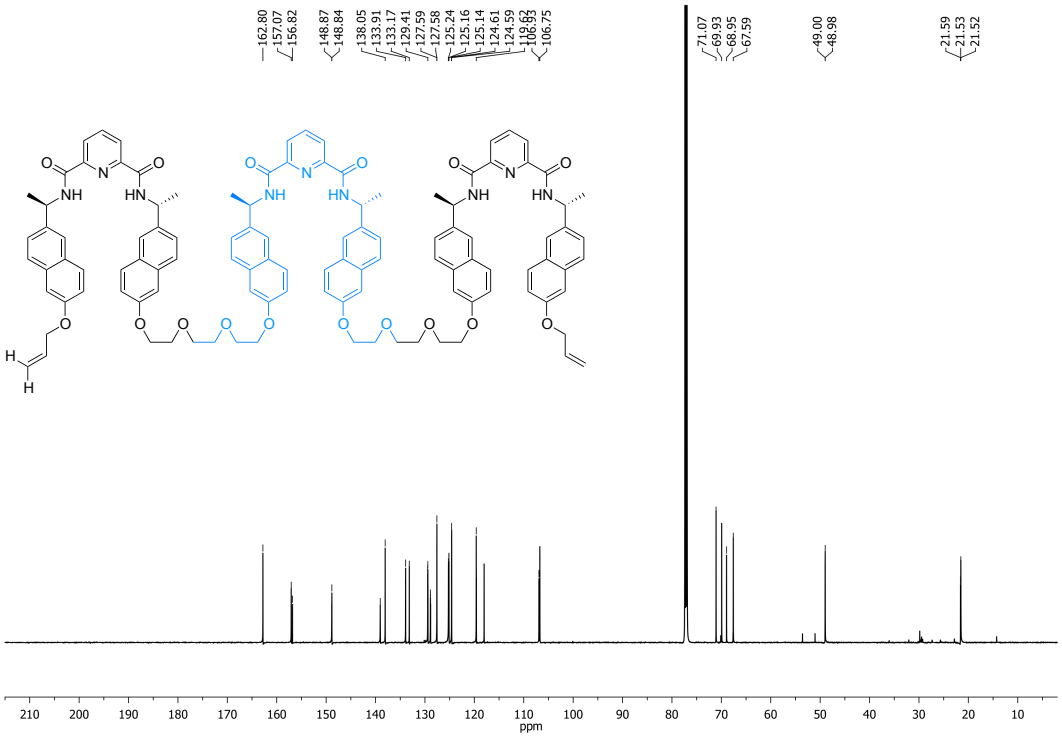
^{1}H NMR (600 MHz, $CDCl_3$)



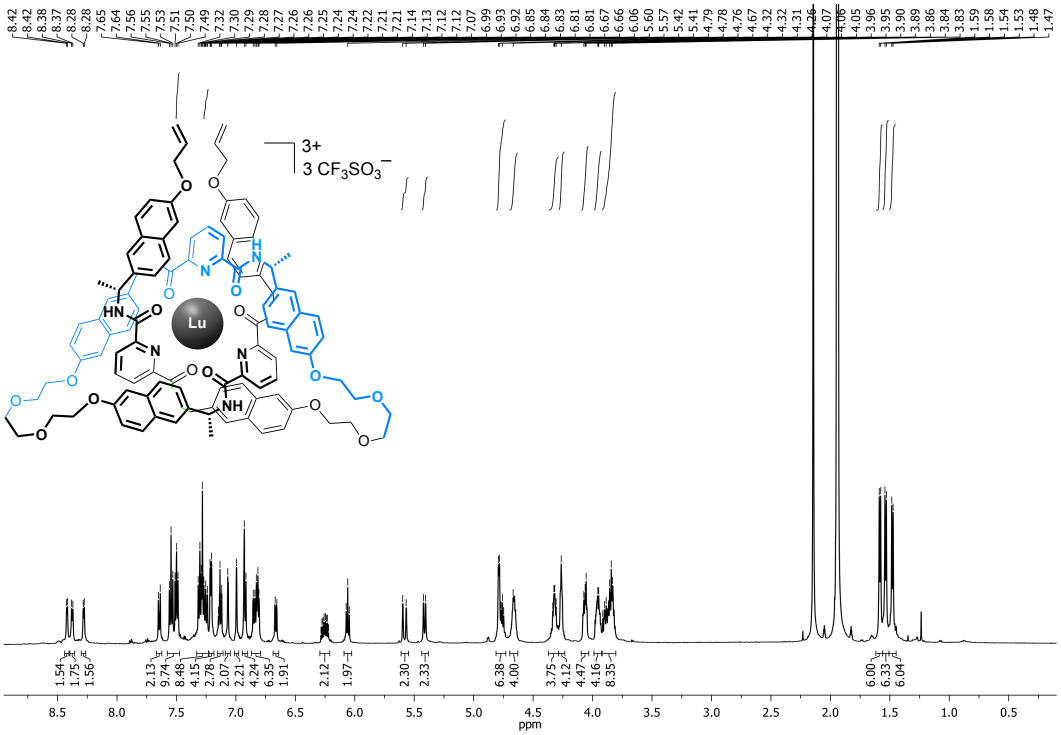
^{13}C NMR (151 MHz, $CDCl_3$)



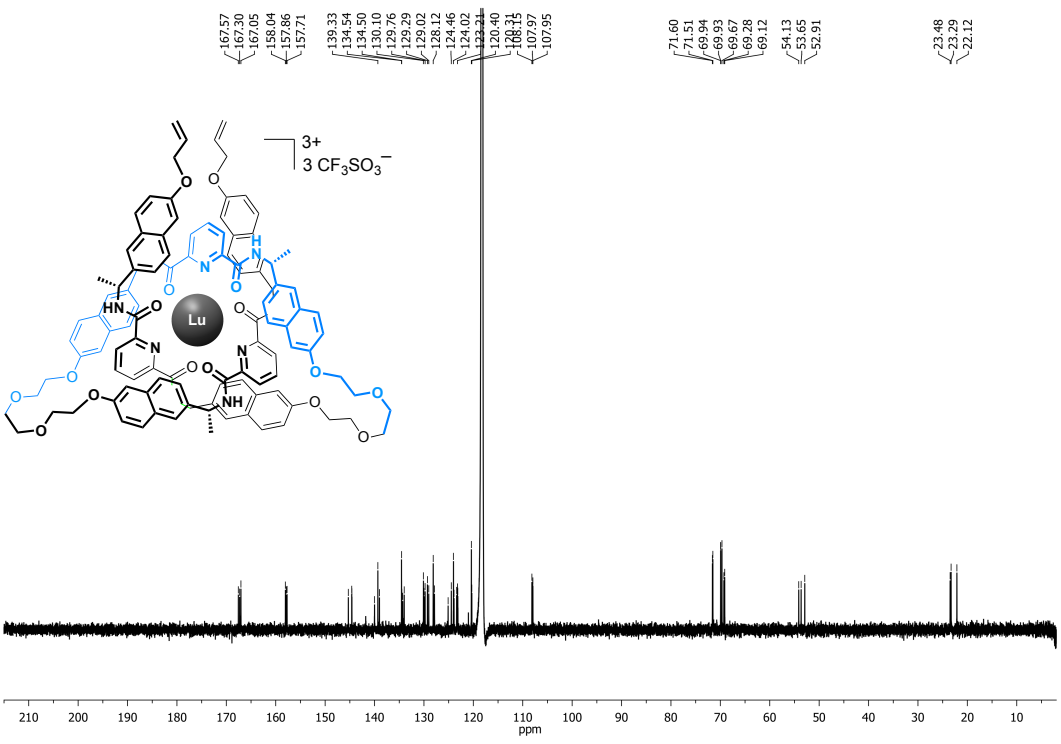
^{1}H NMR (600 MHz, $CDCl_3$)



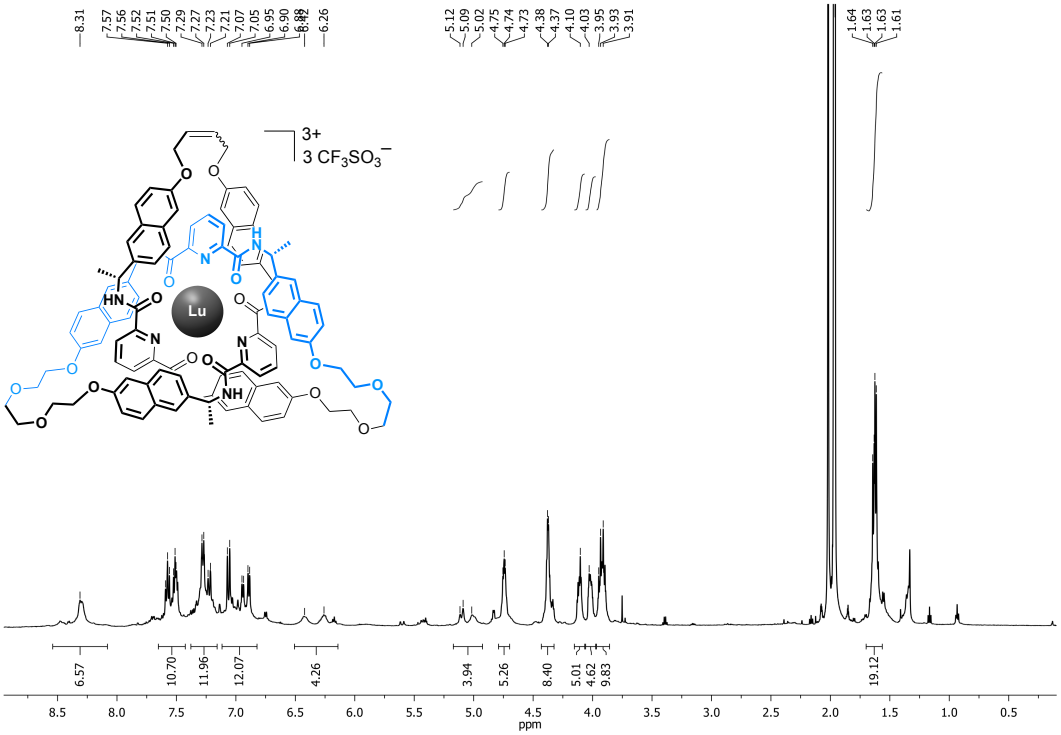
^{13}C NMR (151 MHz, $CDCl_3$)



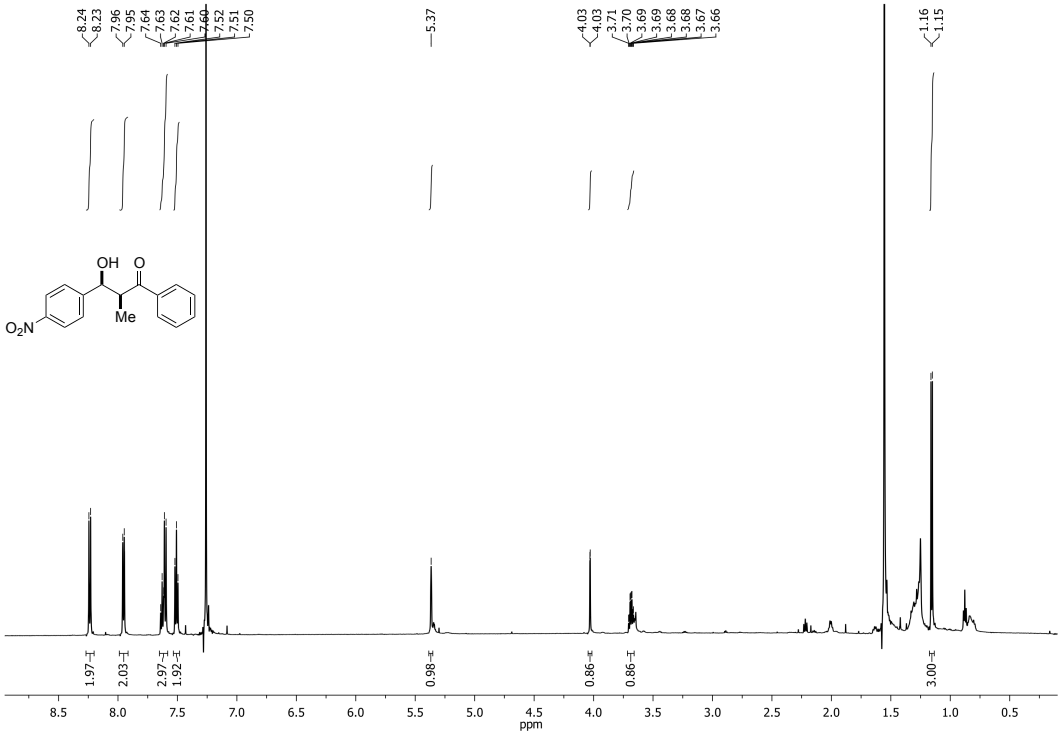
^{1}H NMR (600 MHz, CD_3CN)



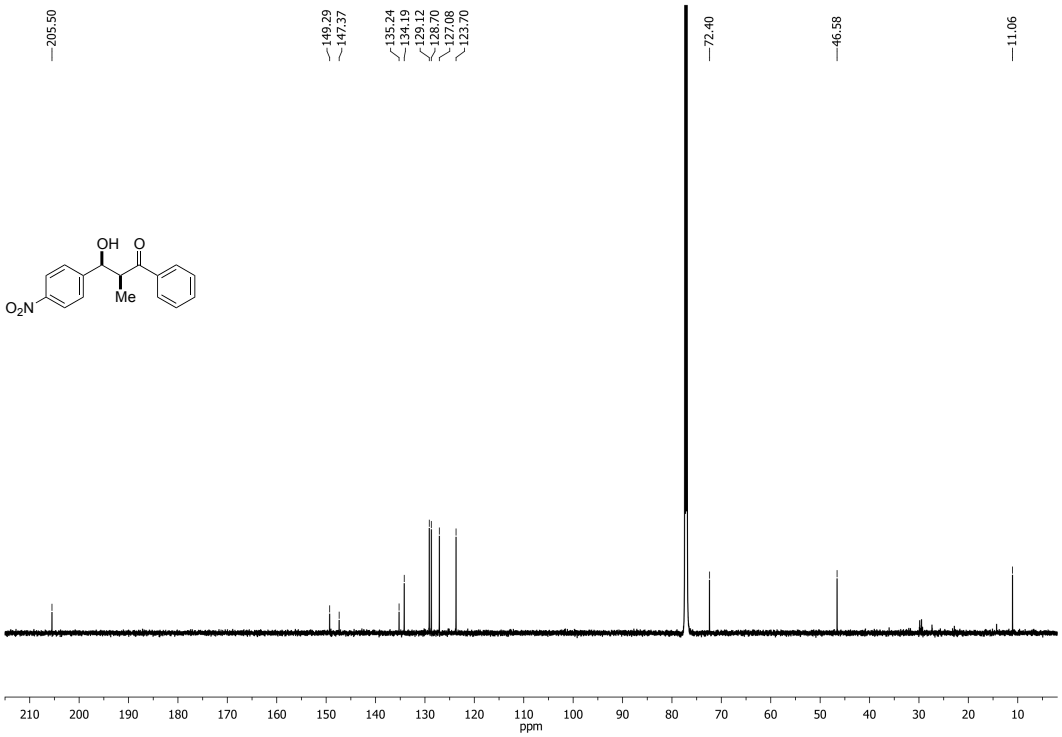
^{13}C NMR (151 MHz, CD_3CN)



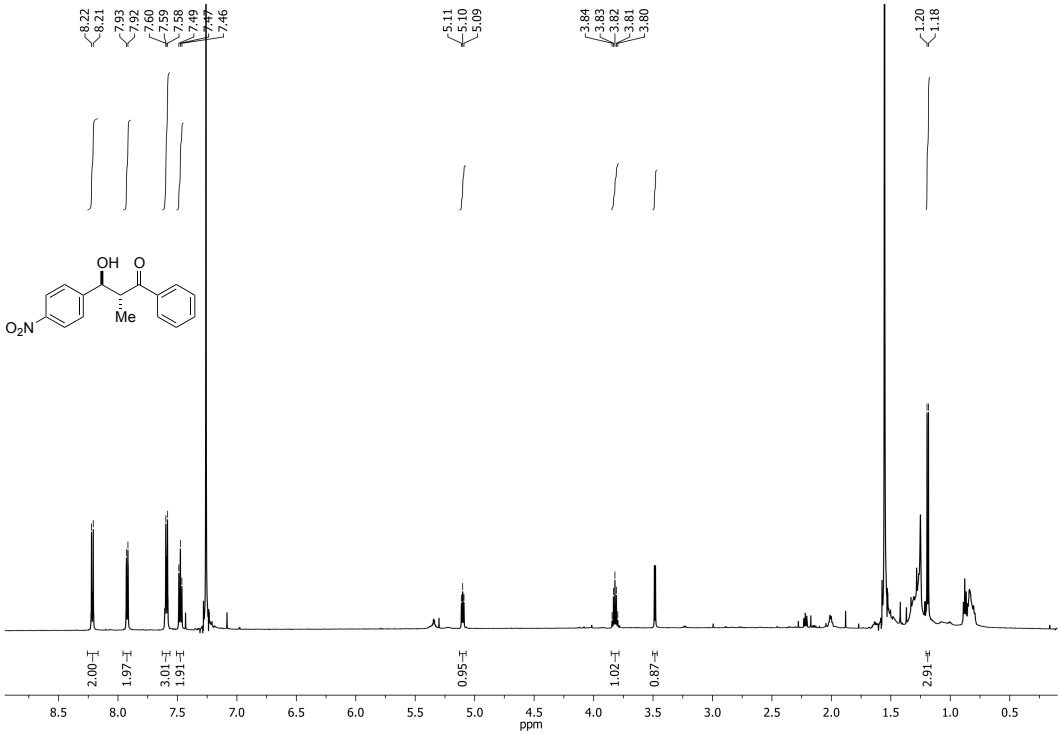
^{1}H NMR (600 MHz, CD_3CN, 345 K)



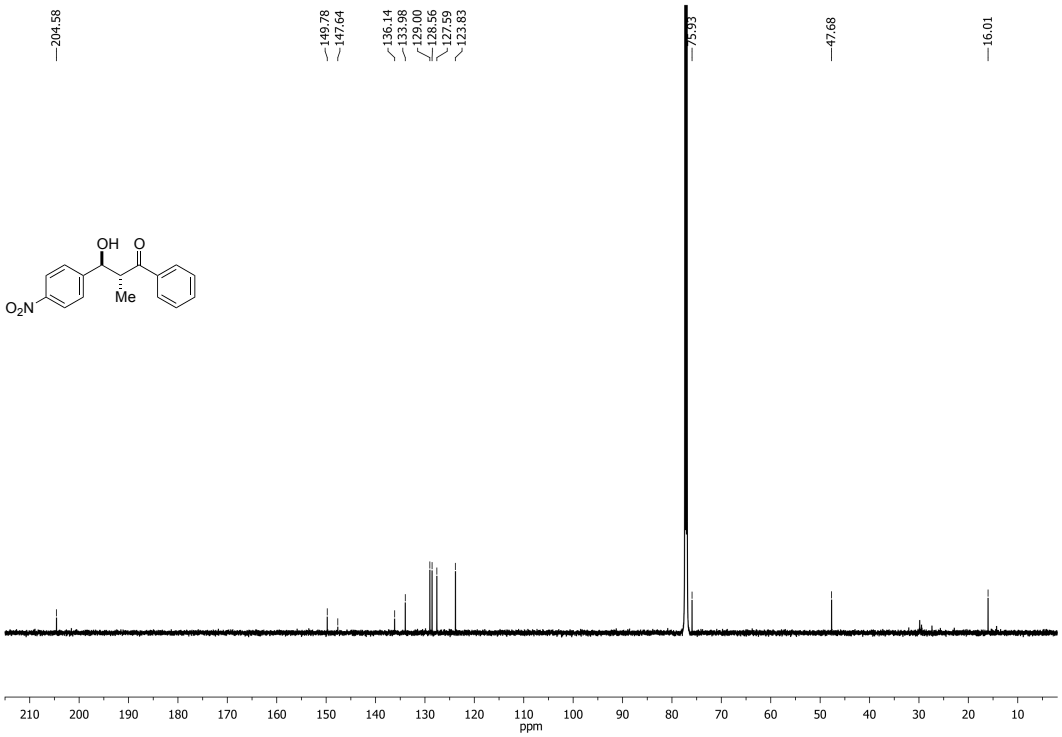
^{1}H NMR (600 MHz, $CDCl_3$)



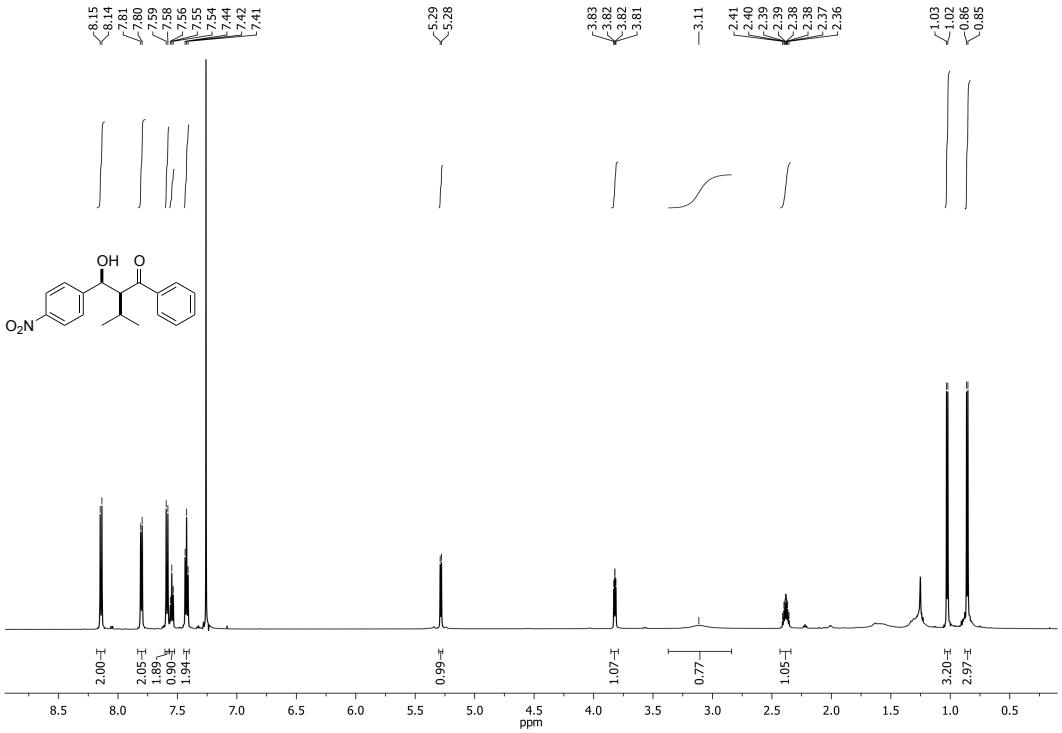
^{13}C NMR (151 MHz, $CDCl_3$)



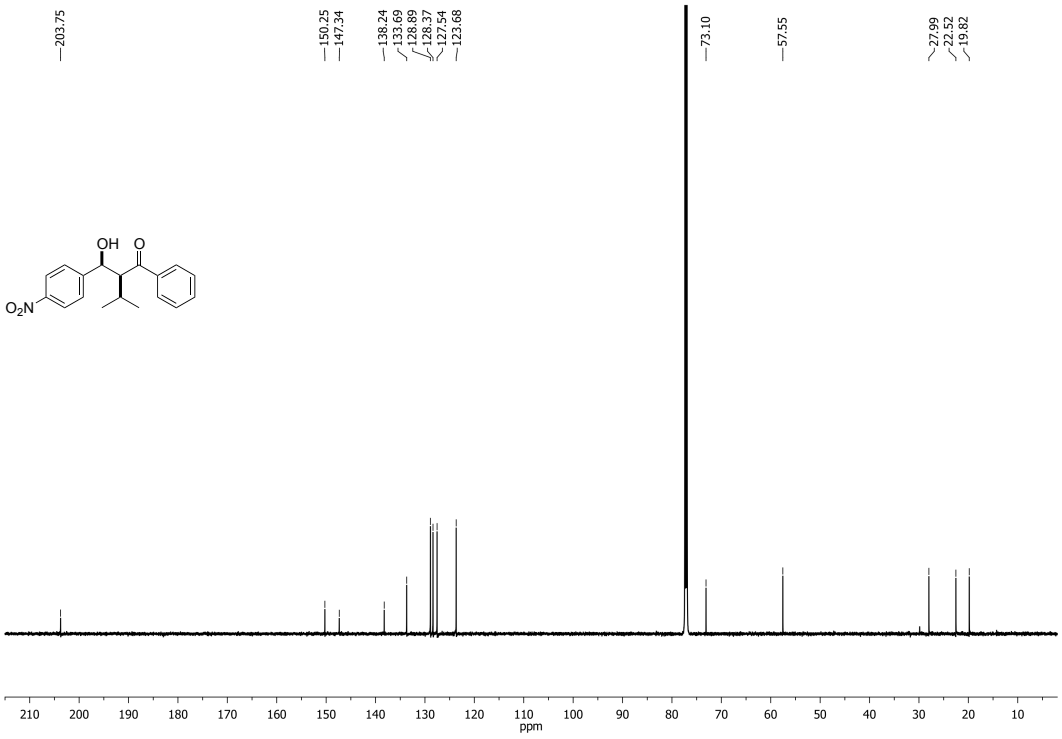
^{1}H NMR (600 MHz, $CDCl_3$)



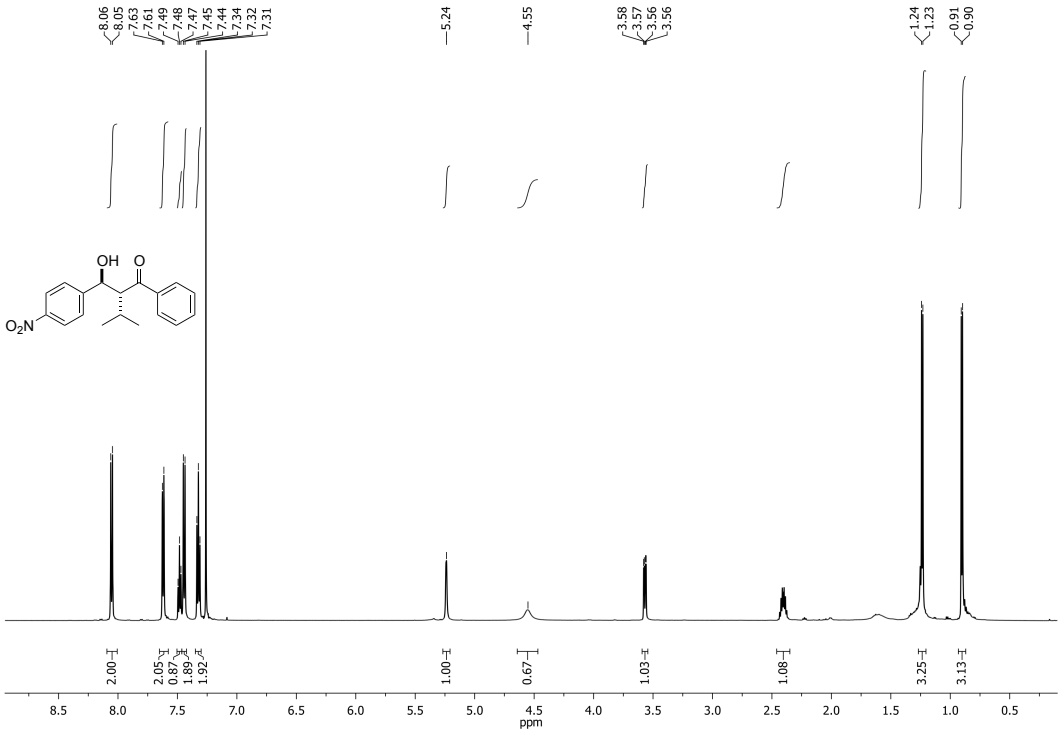
^{13}C NMR (151 MHz, $CDCl_3$)



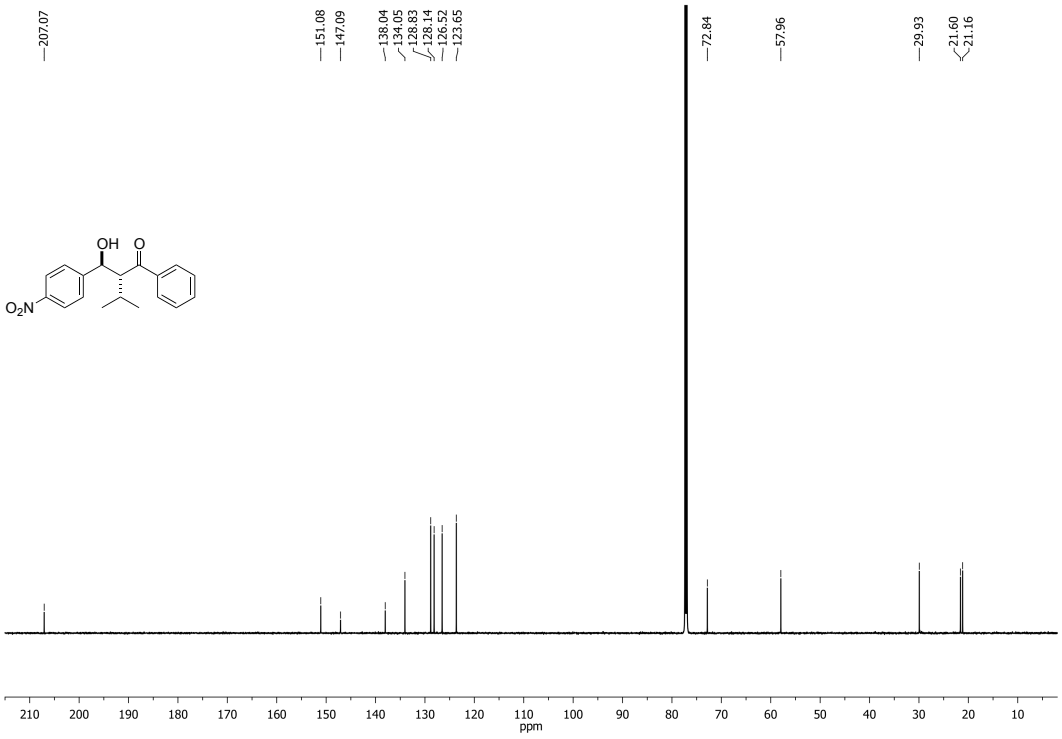
^{1}H NMR (600 MHz, $CDCl_3$)



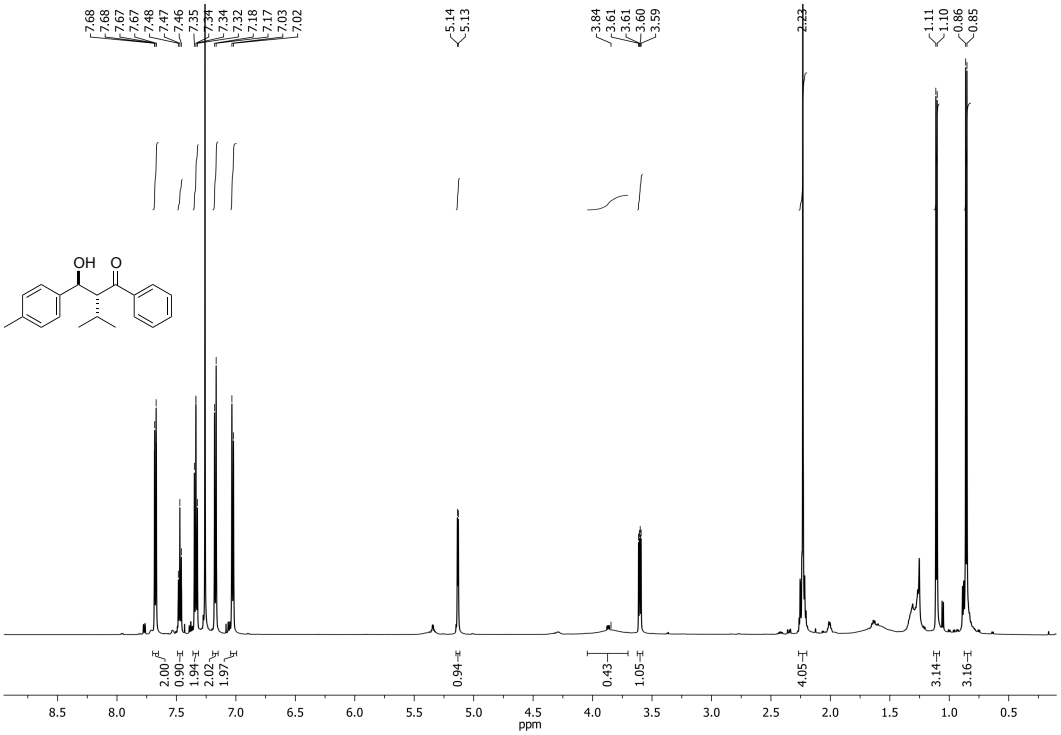
^{13}C NMR (151 MHz, $CDCl_3$)



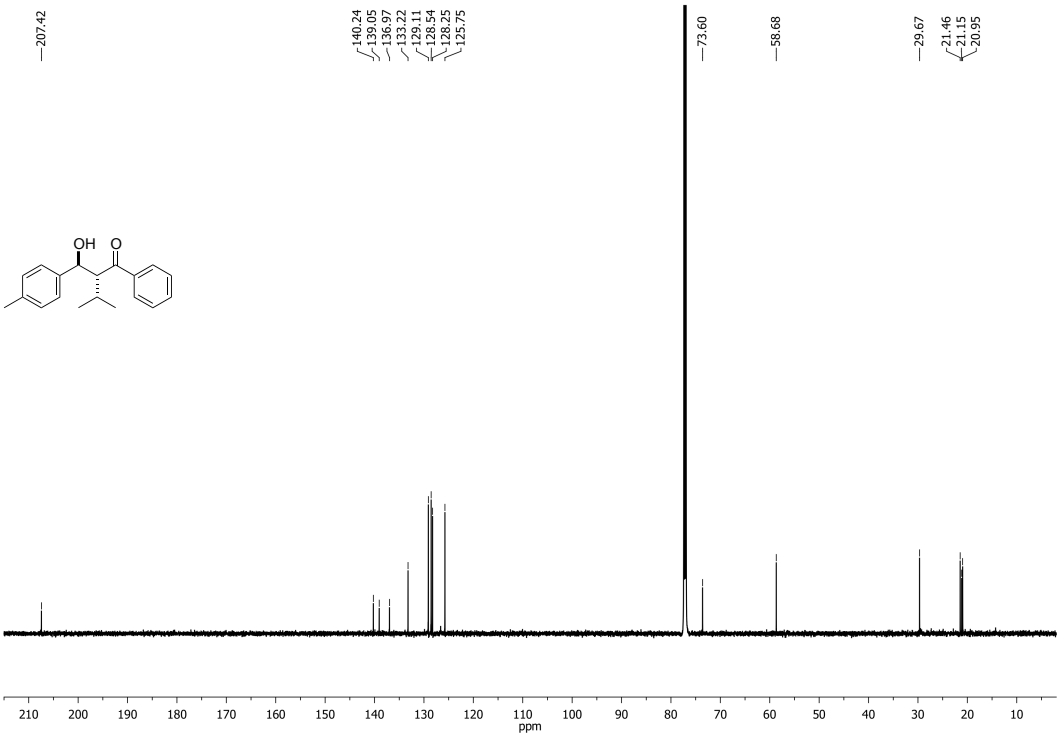
^{1}H NMR (600 MHz, $CDCl_3$)



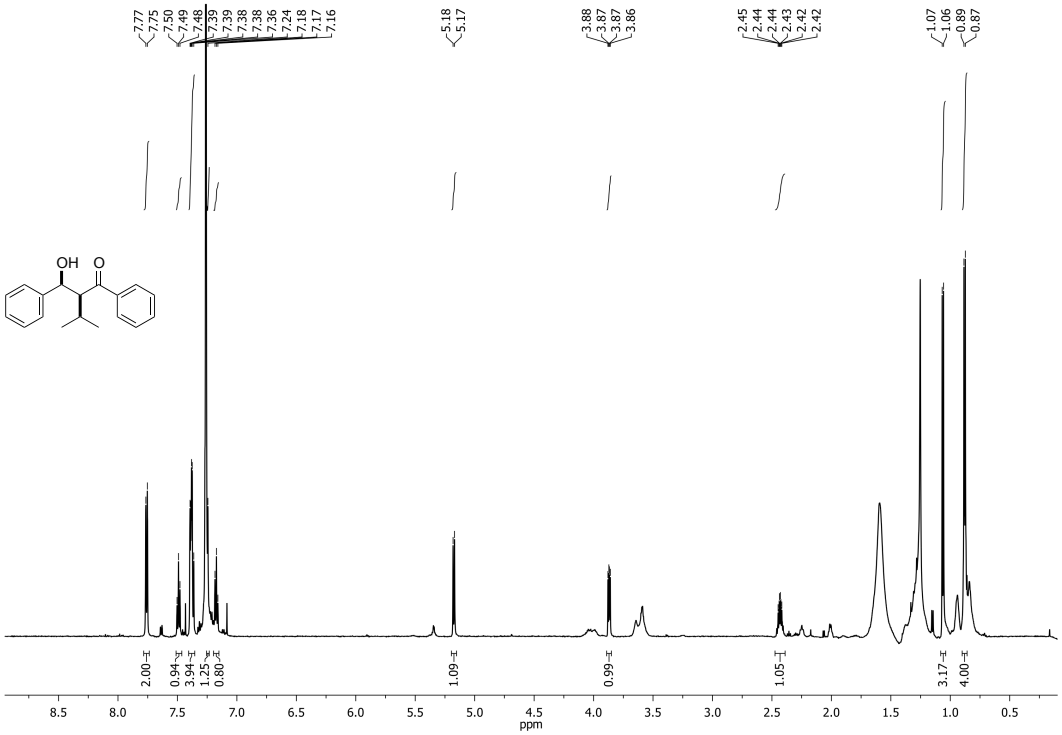
^{13}C NMR (151 MHz, $CDCl_3$)



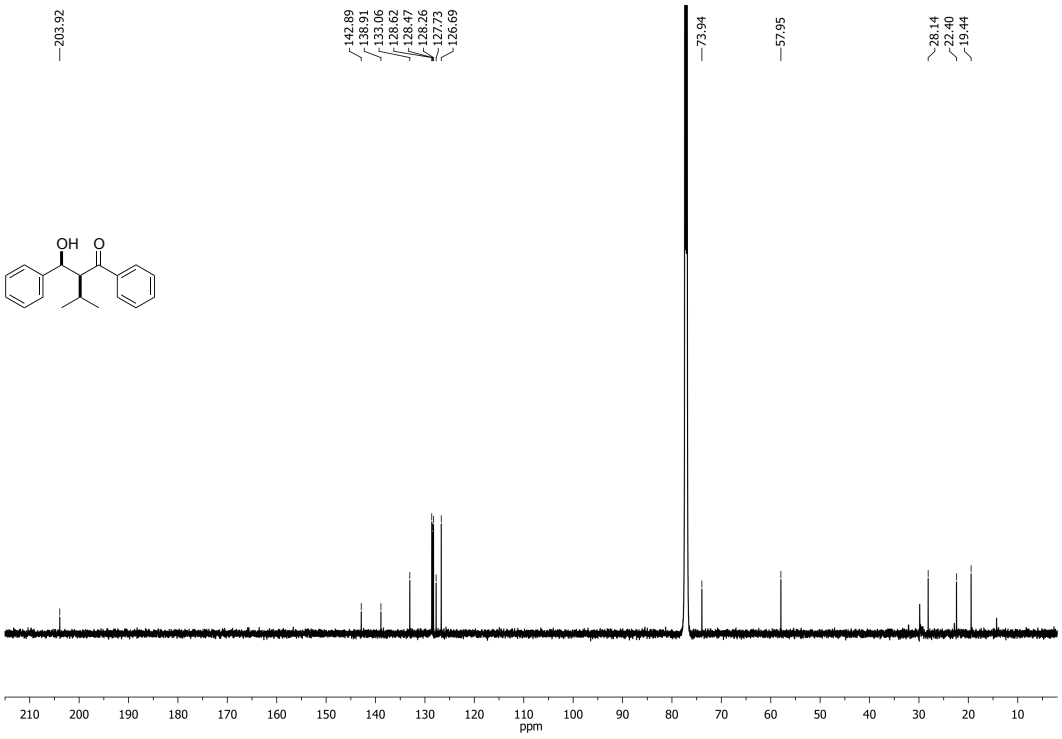
^{1}H NMR (600 MHz, $CDCl_3$)



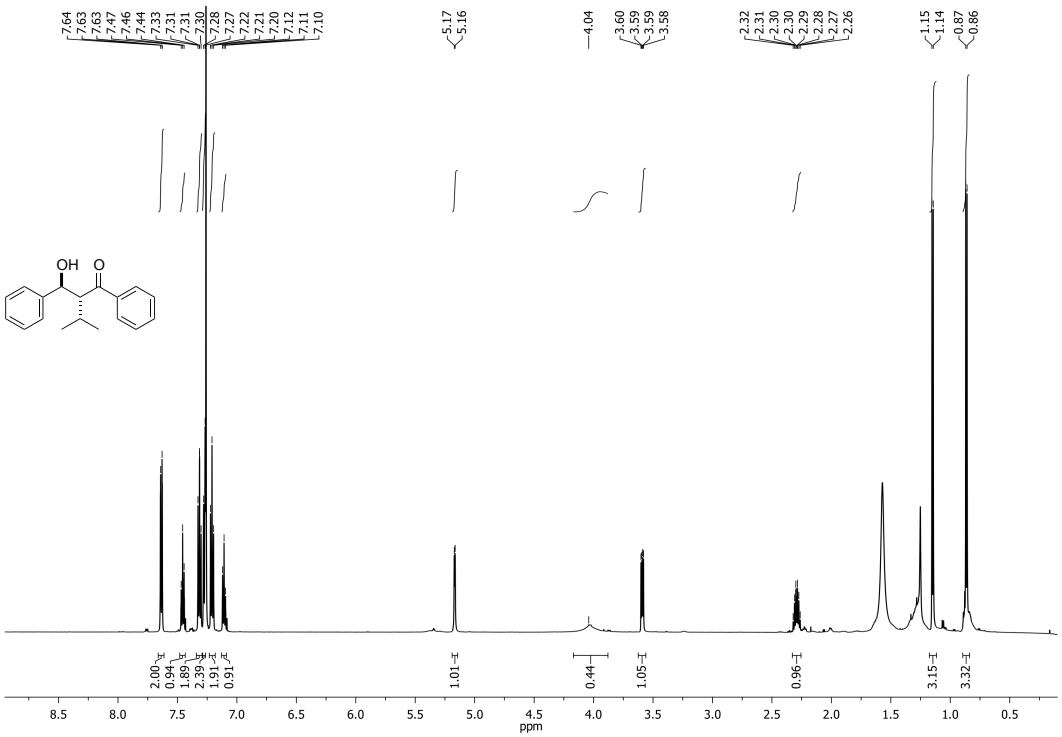
^{13}C NMR (151 MHz, $CDCl_3$)



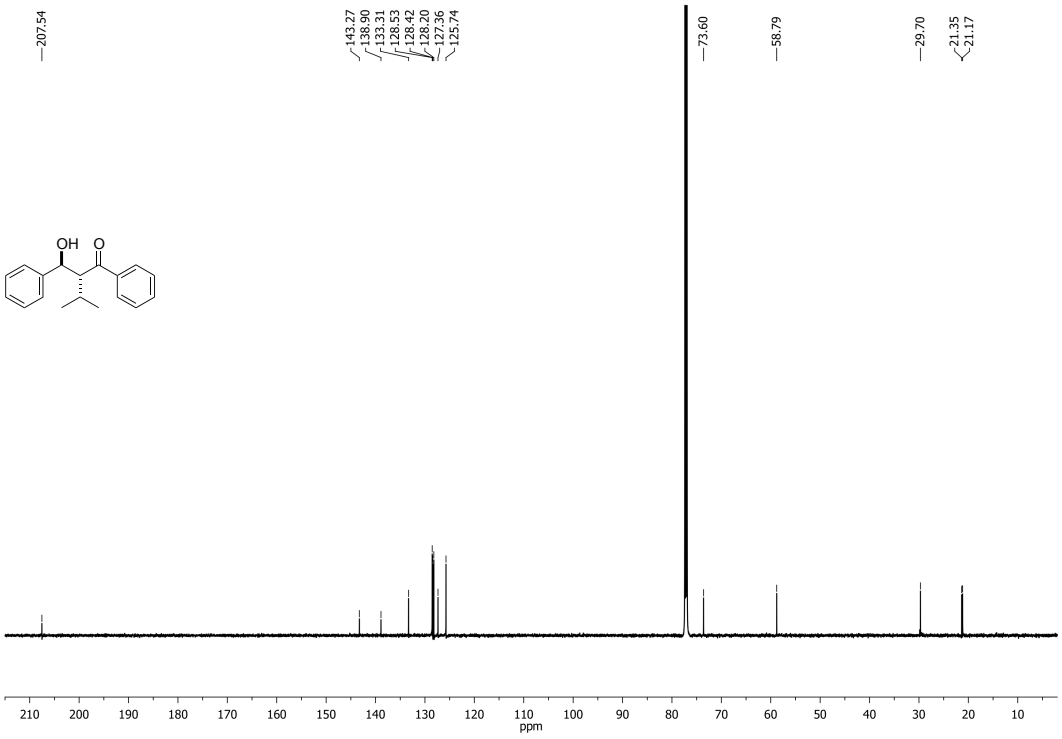
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)

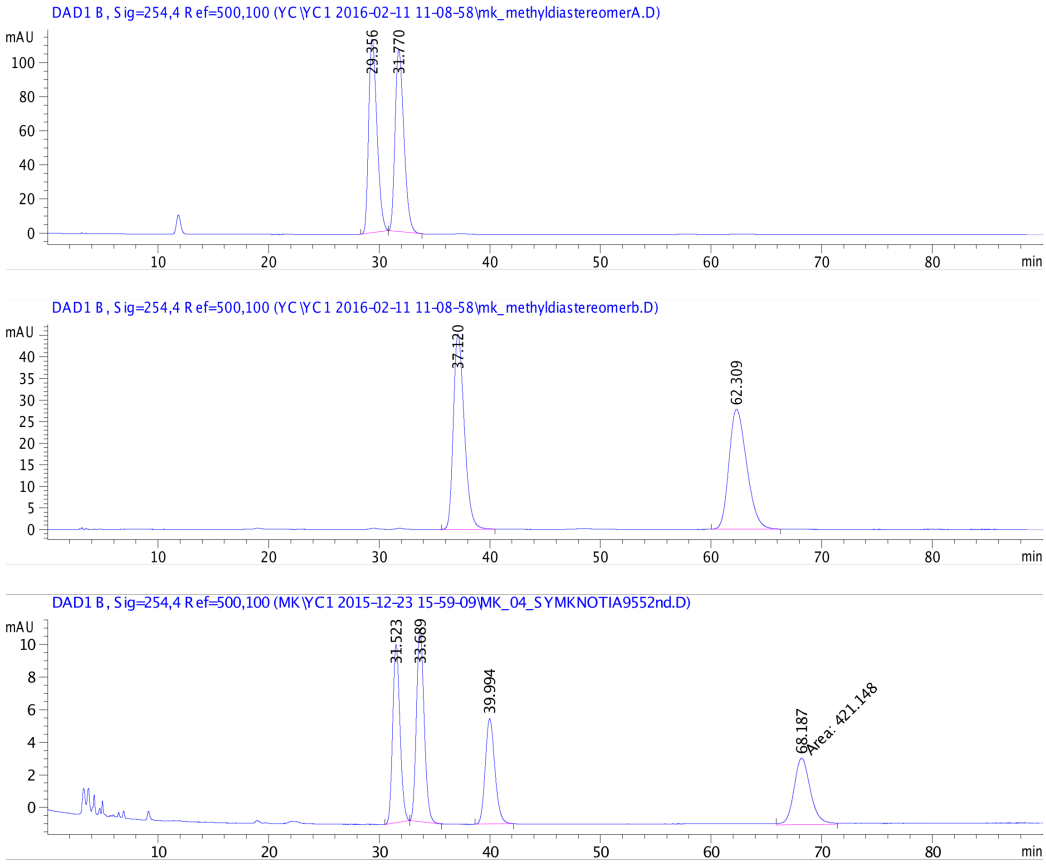


^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)

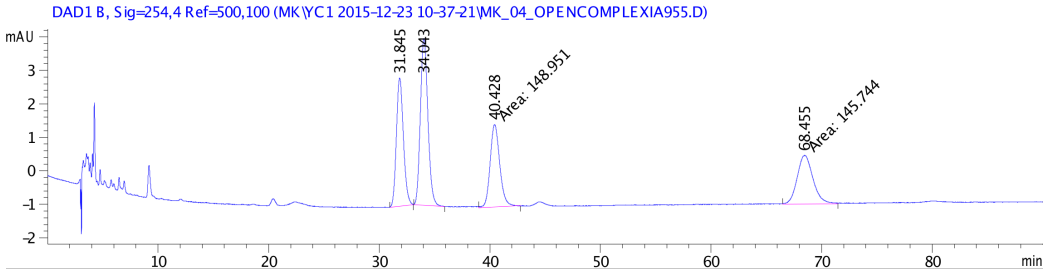
6 HPLC TRACES



Signal 2: DAD1 B, Sig=254,4 Ref=500,100

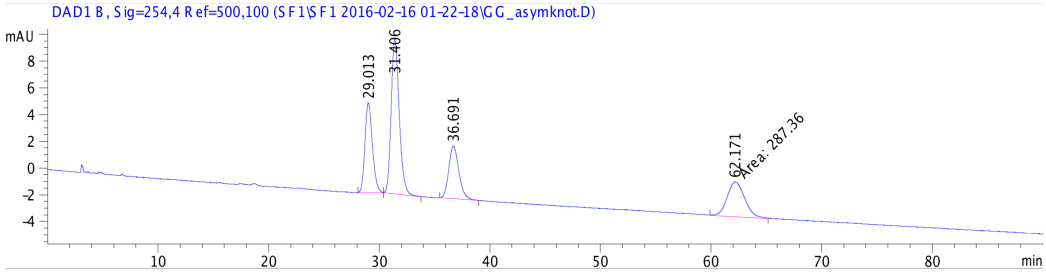
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.523	BB	0.6902	498.33713	10.92502	26.4405
2	33.689	BB	0.7331	573.84869	11.80616	30.4469
3	39.994	BB	0.7914	391.41675	6.47388	20.7676
4	68.187	MM	1.7231	421.14847	4.07363	22.3450
Totals :				1884.75104	33.27868	

Figure 3: HPLC trace of product **5** obtained using catalyst Λ-Eu-**7** (bottom). The top and middle trace show the corresponding *syn* and *anti* racemates.



Signal 2: DAD1 B, Sig=254,4 Ref=500,100

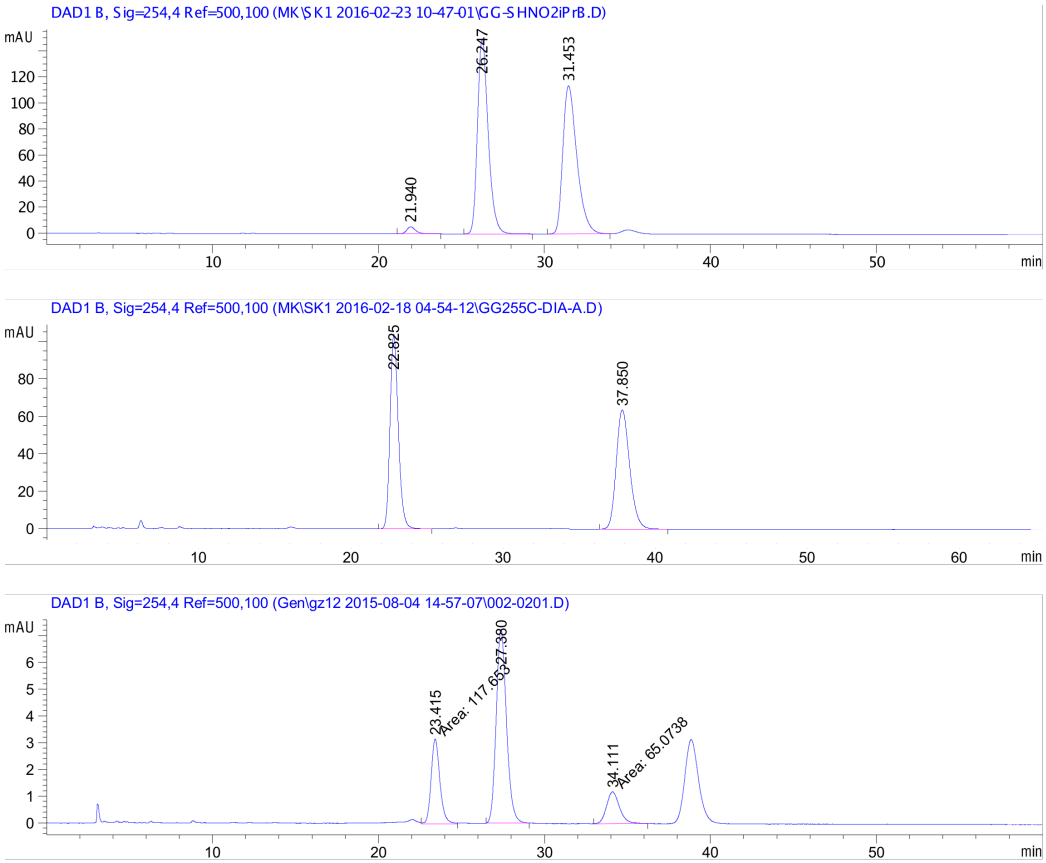
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.845	BB	0.6082	168.53781	3.82398	24.1378
2	34.043	BB	0.6752	234.99814	4.97414	33.6562
3	40.428	MM	1.0067	148.95100	2.46610	21.3326
4	68.455	MM	1.6668	145.74388	1.45729	20.8733
Totals :				698.23083	12.72152	



Signal 2: DAD1 B, Sig=254,4 Ref=500,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.013	BB	0.6897	315.16281	6.71352	21.8567
2	31.406	BB	0.7483	587.73688	11.61694	40.7598
3	36.691	BB	0.7744	251.69334	3.94454	17.4550
4	62.171	MM	1.8394	287.35999	2.60368	19.9285
Totals :				1441.95302	24.87869	

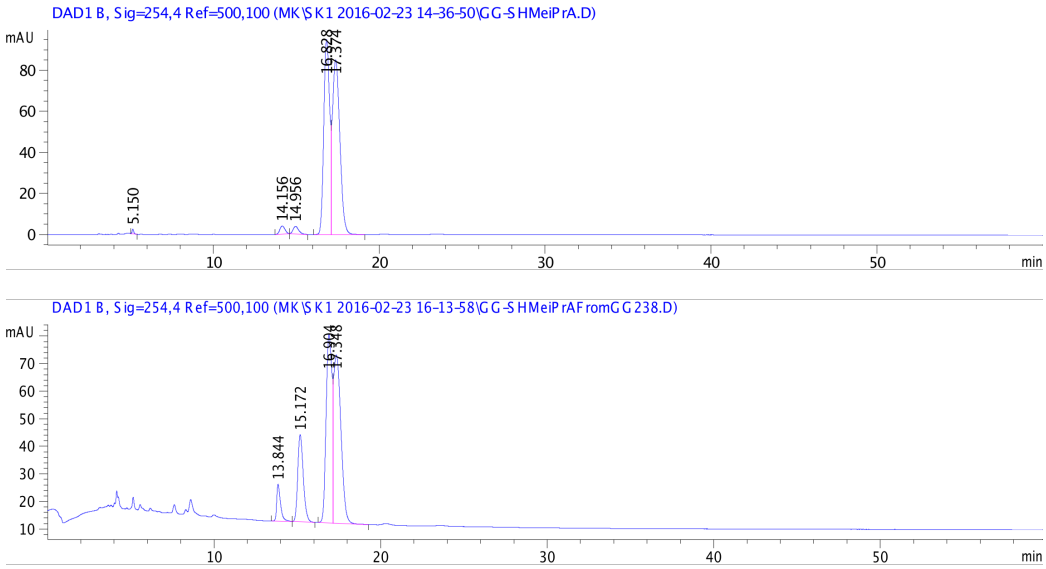
Figure 4: HPLC trace of product **5** obtained using catalysts Λ-Eu-**6** (top) and Λ-Eu(R^6)-**2**$(CF_3SO_3)_3$ (bottom).



Signal 2: DAD1 B, Sig=254,4 Ref=500,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.415	MM	0.6165	117.65346	3.18051	23.7480
2	27.380	BB	0.6328	312.69736	7.25575	63.1170
3	34.111	MM	0.9073	65.07378	1.19531	13.1350
Totals :				495.42459	11.63157	

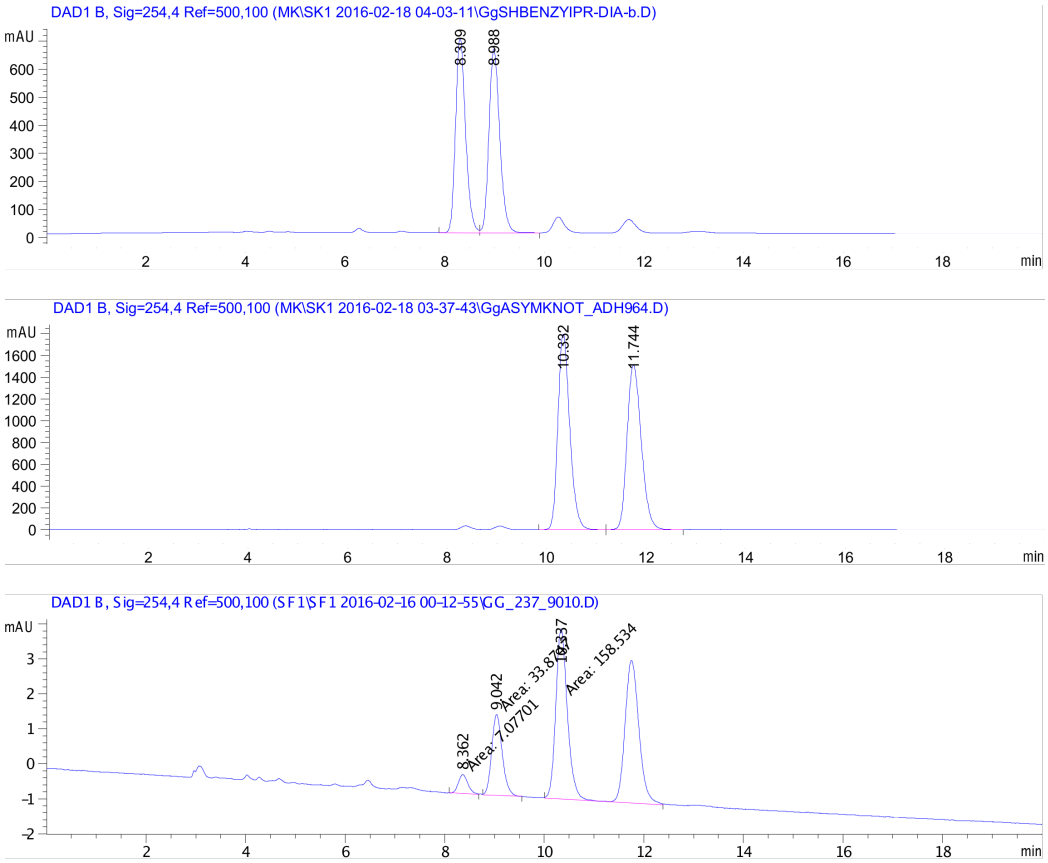
Figure 5: HPLC trace of product **9** obtained using catalyst Λ-Eu(R^6)-**2**$(CF_3SO_3)_3$ (bottom). The top and middle trace show the corresponding *syn* and *anti* racemates.



Signal 2: DAD1 B, Sig=254,4 Ref=500,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.844	BB	0.2333	212.87898	13.40374	4.7271
2	15.172	BB	0.3557	729.48419	31.55913	16.1986
3	16.904	BV	0.3665	1670.12378	68.49757	37.0860
4	17.348	VB	0.4738	1890.89307	60.98232	41.9883
Totals :				4503.38002	174.44276	

Figure 6: HPLC trace of product **10** obtained using catalyst Λ-Eu(R^6)-**2**$(CF_3SO_3)_3$ (bottom). The top trace shows the corresponding *anti* racemate.

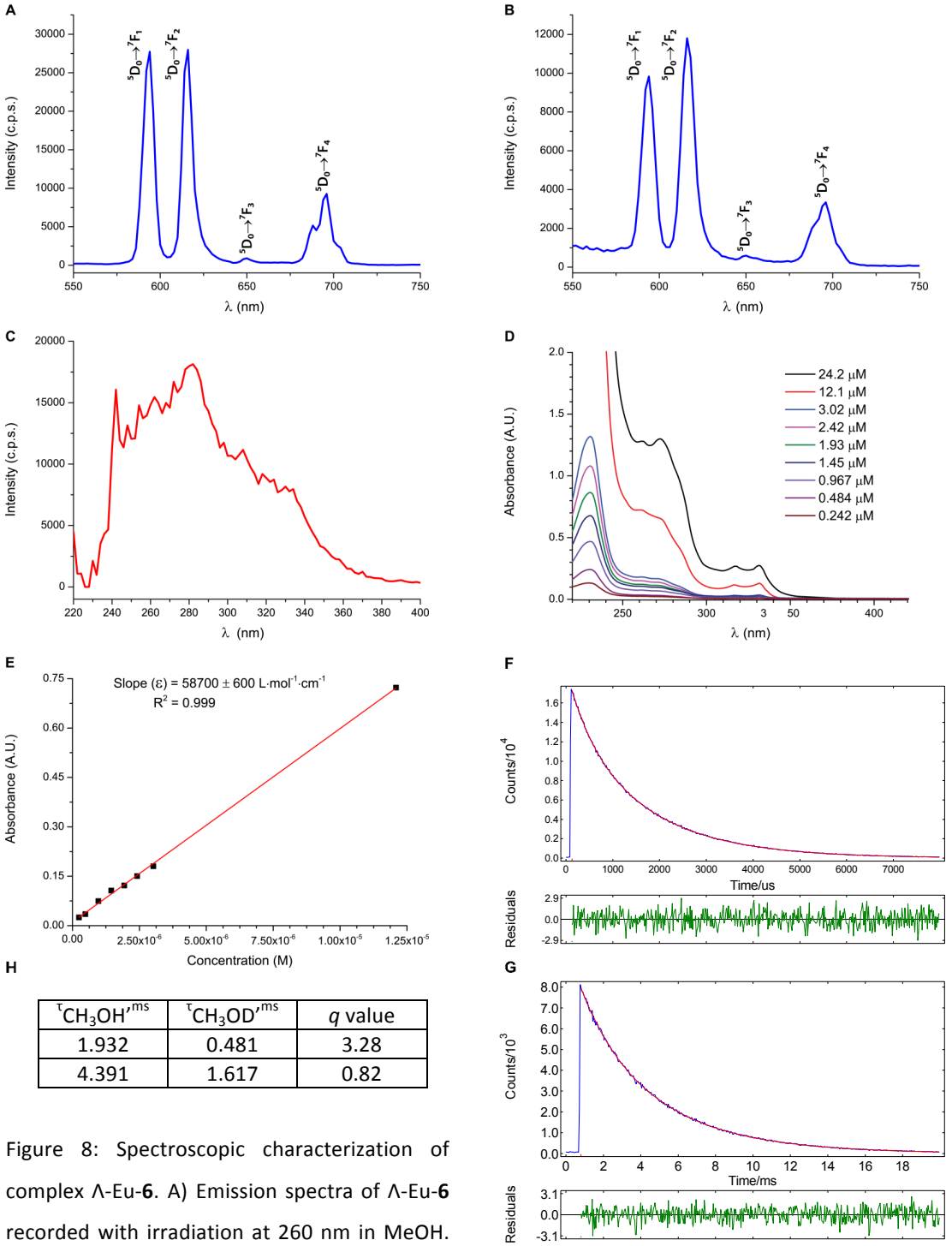


Signal 2: DAD1 B, Sig=254,4 Ref=500,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.362	MM	0.2190	7.07701	5.38633e-1	3.5476
2	9.042	MM	0.2448	33.87472	2.30596	16.9810
3	10.337	MM	0.5429	158.53400	4.86725	79.4713
Totals :				199.48573	7.71184	

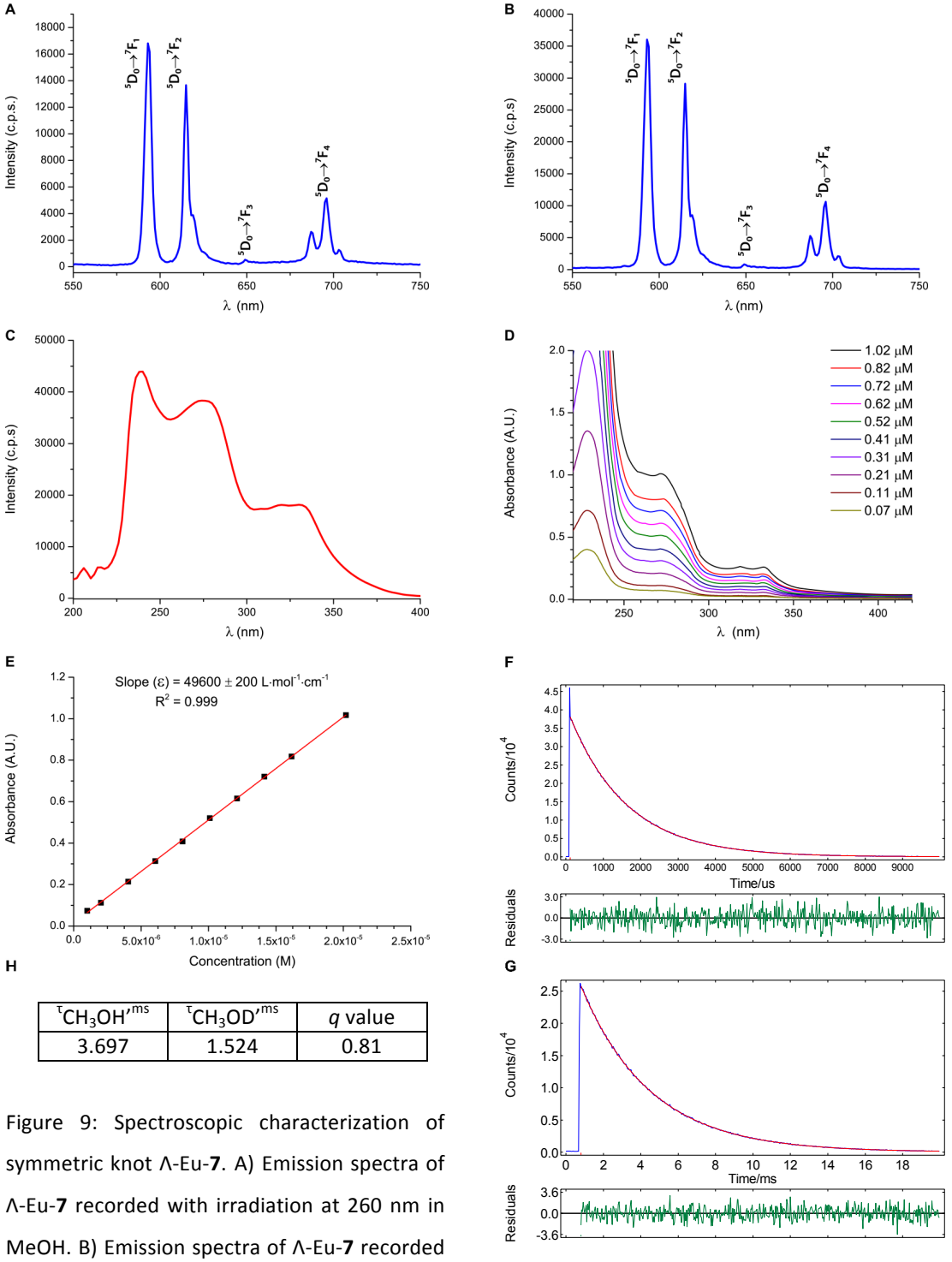
Figure 7: HPLC trace of product **11** obtained using catalyst Λ-Eu(R^6)-**2**$(CF_3SO_3)_3$ (bottom). The top and middle trace show the corresponding *syn* and *anti* racemates.

7 LIFETIME DECAY MEASUREMENTS



$^{\tau}CH_3OH'^{ms}$	$^{\tau}CH_3OD'^{ms}$	*q* value
1.932	0.481	3.28
4.391	1.617	0.82

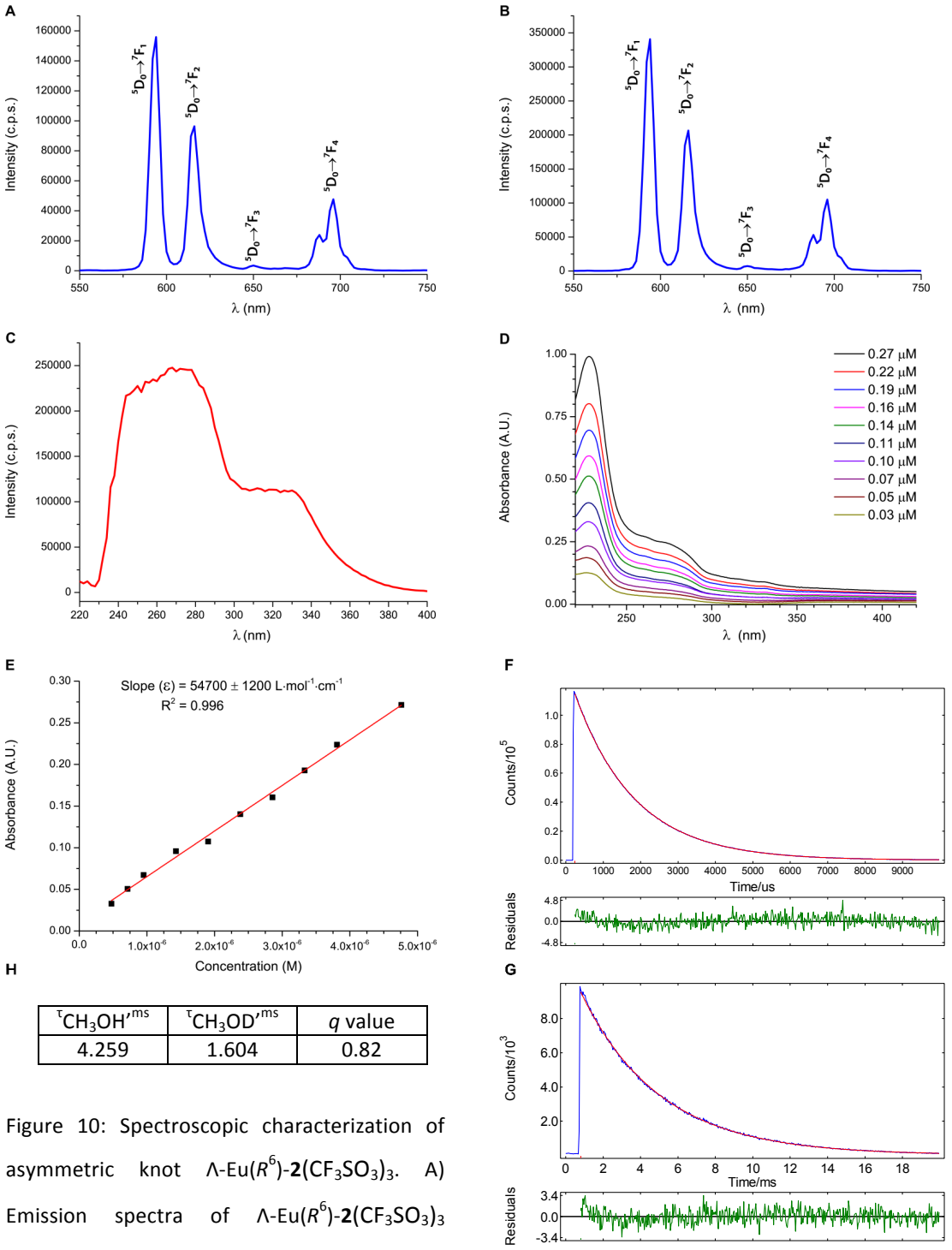
Figure 8: Spectroscopic characterization of complex Λ-Eu-**6**. A) Emission spectra of Λ-Eu-**6** recorded with irradiation at 260 nm in MeOH. B) Emission spectra of Λ-Eu-**6** recorded with irradiation at 260 nm in d_4-MeOD. C) Excitation/emission spectra of Λ-Eu-**6** in d_4-MeOD monitoring emission at 617 nm. D) UV-Vis absorption of Λ-Eu-**6** in MeOH. E) Calculation of the absorption co-efficient of Λ-Eu-**6** in MeOH at 260 nm. F) Lifetime decay profile of Λ-Eu-**6** in MeOH (λ_{ex} = 260 nm, λ_{em} = 617 nm) at 298 K. G) Lifetime decay profile of Λ-Eu-**6** in d_4-MeOD (λ_{ex} = 260 nm, λ_{em} = 617 nm) at 298 K. H) *q* Value calculations and summary data table.



H

$^{\tau}CH_3OH'^{ms}$	$^{\tau}CH_3OD'^{ms}$	*q* value
3.697	1.524	0.81

Figure 9: Spectroscopic characterization of symmetric knot Λ-Eu-**7**. A) Emission spectra of Λ-Eu-**7** recorded with irradiation at 260 nm in MeOH. B) Emission spectra of Λ-Eu-**7** recorded with irradiation at 260 nm in d_4-MeOD. C) Excitation/emission spectra of Λ-Eu-**7** in d_4-MeOD monitoring emission at 617 nm. D) UV-Vis absorption of Λ-Eu-**7** in MeOH. E) Calculation of the absorption co-efficient of Λ-Eu-**7** in MeOH at 260 nm. F) Lifetime decay profile of Λ-Eu-**7** in MeOH (λ_{ex} = 260 nm, λ_{em} = 617 nm) at 298 K. G) Lifetime decay profile of Λ-Eu-**7** in d_4-MeOD (λ_{ex} = 260 nm, λ_{em} = 617 nm) at 298 K. H) *q* Value calculations and summary data table.



H

$^{\tau}CH_3OH'^{ms}$	$^{\tau}CH_3OD'^{ms}$	*q* value
4.259	1.604	0.82

Figure 10: Spectroscopic characterization of asymmetric knot Λ-Eu(R^6)-**2**$(CF_3SO_3)_3$. A) Emission spectra of Λ-Eu(R^6)-**2**$(CF_3SO_3)_3$ recorded with irradiation at 260 nm in MeOH. B) Emission spectra of Λ-Eu(R^6)-**2**$(CF_3SO_3)_3$ recorded with irradiation at 260 nm in d_4-MeOD. C) Excitation/emission spectra of Λ-Eu(R^6)-**2**$(CF_3SO_3)_3$ in d_4-MeOD monitoring emission at 617 nm. D) UV-Vis absorption of Λ-Eu(R^6)-**2**$(CF_3SO_3)_3$ in MeOH. E) Calculation of the absorption co-efficient of Λ-Eu(R^6)-**2**$(CF_3SO_3)_3$ in MeOH at 260 nm. F) Lifetime decay profile of Λ-Eu(R^6)-**2**$(CF_3SO_3)_3$ in MeOH (λ_{ex} = 260 nm, λ_{em} = 617 nm) at 298 K. G) Lifetime decay profile of Λ-Eu(R^6)-**2**$(CF_3SO_3)_3$ in d_4-MeOD (λ_{ex} = 260 nm, λ_{em} = 617 nm) at 298 K. H) *q* Value calculations and summary data table.

8 CRYSTALLOGRAPHY

Data Collection: Synchrotron X-ray data were collected at beamline I19 (λ = 0.6889 Å) Diamond Light Source[S11] for Λ-Eu(R^6)-**2**$(CF_3SO_3)_3$ at temperature of 100 K. Data were measured using CrystalClear-SM Expert 2.0 r5 suite of programs.

Crystal structure determinations and refinements: X-Ray data were processed and reduced using the CrysAlisPro suite of programs. Absorption correction was performed using empirical methods based upon symmetry-equivalent reflections combined with measurements at different azimuthal angles.[S12] The crystal structure was solved and refined against all F^2 values using the SHELXL suite of programs and Olex2.[S13] Atoms corresponding to the aliphatic chains were refined isotropically due to the high disorder of these moieties. The disorders in the aliphatic groups were modelled over two positions. The occupancies of the aliphatic chains were set to be 2/3 for the polyethoxy moieties and 1/3 for the ethene group. Hydrogen atoms were placed in calculated positions refined using idealized geometries (riding model) and assigned fixed isotropic displacement parameters. The phenyl groups were restrained to have idealized geometries using AFIX commands. The C-C, C-O, C-F, C-S and S-O distances in the aliphatic chains and triflates ions were restrained using DFIX and SADI command. The atomic displacement parameters (adp) of the ligands have been restrained using RIGU, EADP and SIMU commands.

The crystal of compound Λ-Eu(R^6)-**2**$(CF_3SO_3)_3$ was twinned. The TwinRotMax protocol inside PLATON suites was used to account the twin components.[S14] A large number B alerts were found due to high disorder found in the aliphatic chains.

CCDC 1494803 Λ-Eu(R^6)-**2**$(CF_3SO_3)_3$ contains the supplementary crystallographic data for this paper. This data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

Table S1: Crystallographic information for Λ-Eu(R^6)-**2**$(CF_3SO_3)_3$.

Crystal colour	Colorless
Crystal size (mm)	0.20 × 0.05 × 0.05
Crystal system	Trigonal
Space group, *Z*	P321, *2*
a (Å)	22.777(1)
c (Å)	12.8368(6)
V (Å^3)	5767.6(6)
Density (Mg.m^{-3})	1.390
Wavelength (Å)	0.6889
Temperature (K)	100
μ(Mo-Kα) (mm^{-1})	0.635
2Θ range (°)	4.634 to 49.034
Reflns collected	47487
Independent reflns (R_{int})	6885 (0.0609)
L.S. parameters, *p*	372
No. of restraints, *r*	790
*R*1 (*F*)^a *I* > 2.0σ*(I)*	0.1144
*wR*2(F^2), ^{a} all data	0.3394
S(F^2), ^{a} all data	1.093
Flack p.	0.05(2)

^{a} R1(F) = Σ(|F_o| − |F_c|)/Σ|F_o|; [b] $wR^2(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{½}$; [c] $S(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/(n + r - p)]^{½}$

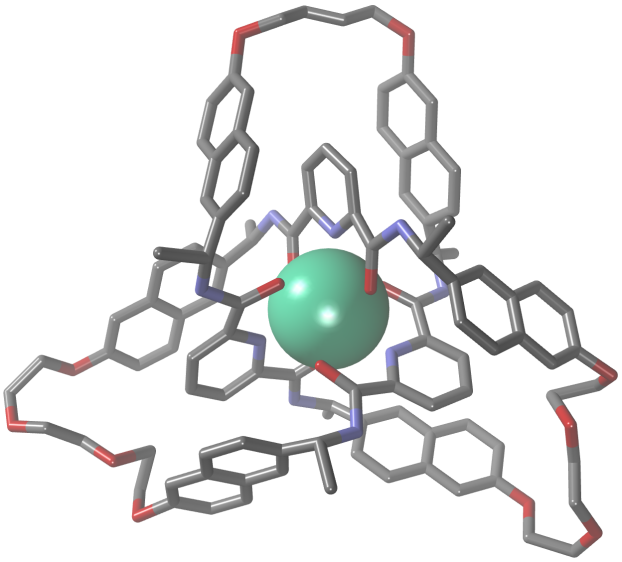


Figure 11: Stick representation of the X-ray crystal structure of Λ-Eu(R^6)-**2**$(CF_3SO_3)_3$.

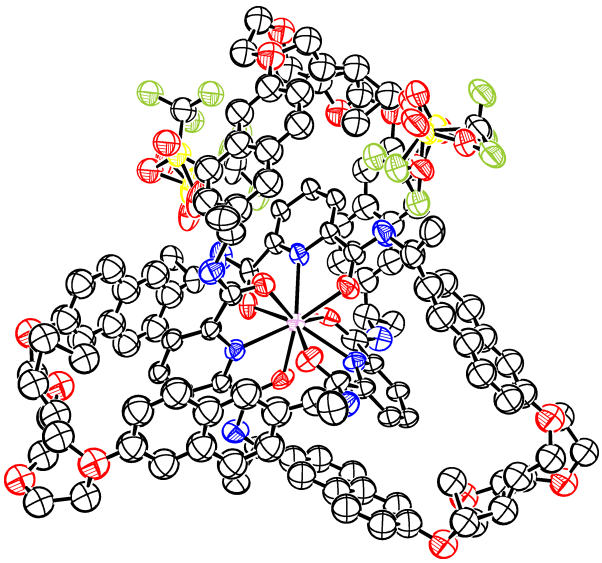


Figure 12: ORTEP representation (ellipsoids at 10% probability) of the X-ray crystal structure of Λ-Eu(R^6)-**2**$(CF_3SO_3)_3$.

9 REFERENCES

(S1) Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512–7515.

(S2) Budavari, S.; O'Neil, M. J.; Smith, A.; Heckelman, P. E. *The Merck Index, an Encyclopedia of Chemicals, Drugs, and Biologicals - Eleventh Edition*; Merck Co., Inc.: Rahway, NJ, 1989.

(S3) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.

(S4) 2D NMR experiments were not adequate to aid in the assignment of the distinct pseudo symmetrical regions of molecule.

(S5) No NMR data is given because the europium-metal caused the spectra to appear very broad.

(S6) Wiles, C.; Watts, P.; Haswell, S. J.; Pombo-Villar, E. *Tetrahedron*. **2005**, *61*, 10757–10773.

(S7) Kerr, W. J.; Watson, A. J. B.; Hayes, D. *Chem*. *Commun*. **2007**, 5049–5051.

(S8) Shibata, I.; Suwa, T.; Sakakibara, H.; Baba, A. *Org*. *Lett*. **2002**, *4*, 301–303.

(S9) The diastereoisomers proved difficult to separate and only the *anti*-diastereoisomer was isolated without contamination of the other.

(S10) Ohtsuka, Y.; Koyasu, K.; Ikeno, T.; Yamada, T. *Org*. *Lett*. **2001**, *3*, 2543–2546.

(S11) Nowell, H.; Barnett, S. A.; Christensen, K. E.; Teat, S. J.; Allan, D. R. *J. Synchrotron Rad*. **2012**, *19*, 435–441.

(S12) a) Sheldrick, G. M. SADABS, University of Göttingen, 1995, Empirical absorption correction program based upon the method of Blessing. b) Blessing, R. H. *Acta Cryst*. **1995**, *A51*, 33–38.

(S13) a) Sheldrick, G. M. *Acta Cryst*. **2008**, *A64*, 112–122. b) G. M. Sheldrick, *Acta Cryst*. **2015**, *A71*, 3–8. c) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl*. *Cryst*. **2009**, *42,* 339–341.

(S14) PLATON, A Multipurpose Crystallographic Tool (Utrecht University, Utrecht, The Netherlands, 2008).