ELECTRONIC SUPPLEMENTARY INFORMATION

for the paper entitled

New Route to Amide-Functionalized *N*-Donor Ligands Enables Improved Selective Solvent Extraction of Trivalent Actinides

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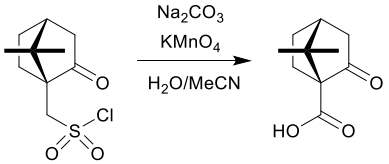
1: Experimental Procedures

General Procedures

All solvents and reagents were purchased from Sigma-Aldrich, Acros Organics, Fluorochem or Alfa-Aesar and used without further purification unless otherwise specified. Reactions were monitored by TLC using silica gel with UV_{254} fluorescent indicator. Uncorrected melting points were measured in open capillary tubes using an SRS DigiMelt MPA160 instrument with an upper limit of 260 ^{o}C. NMR spectra were recorded on a JEOL ECS400FT Delta spectrometer (399.78 MHz for ^{1}H NMR, 100.53 MHz for ^{13}C NMR). Chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane as internal standard. Coupling constants (*J*) are measured in hertz. Multiplets are reported as follows: b = broad, s = singlet, d = doublet, dd = double doublet, dt = double triplet, t = triplet, q = quartet, qu = quintet, m = multiplet, app d = apparent doublet, app t = apparent triplet. Low resolution mass spectra were obtained in methanol solutions on a Thermo Finnigan LCQ Advantage MS detector using electrospray ionisation (ESI). High resolution mass spectra were obtained on a Thermo Scientific LTQ Orbitrap XL Mass Spectrometer using electrospray ionization (ESI) at the EPSRC UK National Mass Spectrometry Service (University of Swansea). Column chromatography was conducted using 0.060–0.20 mm silica gel (70–230 mesh), and automated flash column chromatography was performed using a Biotage Isolera One ISO-1SV instrument. Bis-amidrazones **11**[1] and **15**[2] were synthesized following known procedures.

1*S*-(+)-Ketopinic acid 6[3]

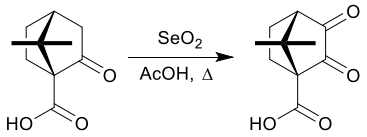


5 **6**

A solution of sodium carbonate (3.804 g, 35.893 mmol, 3 eq) and potassium permanganate (4.159 g, 26.322 mmol, 2.2 eq) in water (45 mL) and acetonitrile (30 mL) was prepared by dissolving both solids in water (45 mL) and then adding acetonitrile (30 mL). To this solution was added a solution of (+)-10-camphorsulfonyl chloride **5** (3.00 g, 11.964 mmol) in acetonitrile (15 mL) dropwise over 5 minutes. The solution was stirred at room temperature for 30 minutes and was then stirred at 70 ^{o}C for 3 hours. The solution was allowed to cool to room temperature and separate aqueous solutions of sulfuric acid (2 M, 25 mL) and sodium sulfite

(2 M, 50 mL) were successively added. Further quantities of sulfuric acid were added until the pH was approx. 2–3. The resulting clear colorless solution was extracted with diethyl ether (3 × 50 mL). The combined organic extracts were dried over magnesium sulfate, filtered and evaporated to afford pure 1*S*-(+)-ketopinic acid **6** as a white solid (1.594 g, 73%). ^{1}H NMR (399.8 MHz, $CDCl_3$, Me_4Si): δ 2.57 (1H, app d, *J* = 18.8 Hz, 3-CH_{2exo}), 2.37–2.43 (1H, m, C*H*), 2.13 (1H, app s, 4-C*H*), 2.06–2.10 (1H, m, C*H*), 2.01 (1H, d, *J* = 18.8 Hz, 3-CH_{2endo}), 1.76–1.82 (1H, m, C*H*), 1.40–1.46 (1H, m, C*H*), 1.18 (3H, s, CH_3), 1.10 (3H, s, CH_3) ppm.

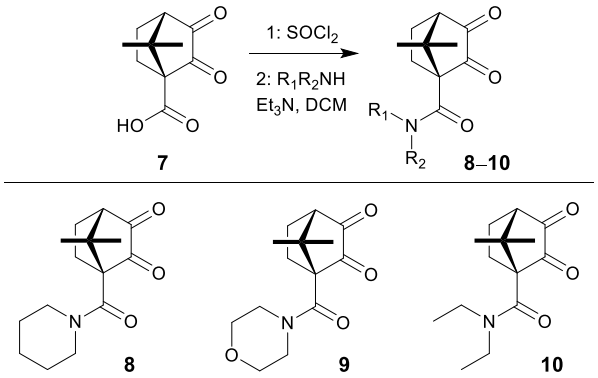
Compound 7[4]



6 **7**

(1*S*)-(+)-Ketopinic acid **6** (4.984 g, 27.351 mmol) was dissolved in acetic acid (50 mL) and SeO_2 (6.68 g, 60.201 mmol, 2.2 eq) was added. The reaction mixture was heated under reflux for 48 hours. The flask was allowed to cool to room temperature and the reaction mixture was filtered through celite and washed with EtOAc (100 mL). The filtrate was evaporated to afford the crude product **7** as a yellow solid. The solid was triturated with chloroform (100 mL) and the insoluble residue was filtered and washed with chloroform (50 mL), and the filtrate was evaporated to afford the product **7** as a yellow solid. The solid was again triturated with chloroform (50 mL) and the insoluble residue was filtered and washed with chloroform (20 mL), and the filtrate was evaporated to afford the pure product **7** as a yellow solid (5.288 g, 98%). ^{1}H NMR (399.8 MHz, $CDCl_3$, Me_4Si): δ 2.72 (1H, d, *J* = 5.04 Hz, 4-C*H*), 2.42 (1H, td, *J* = 12.82, 4.58 Hz, C*H*), 2.28 (1H, tt, *J* = 5.04, 4.58 Hz, C*H*), 2.03 (1H, tt, *J* = 5.04, 4.58 Hz, C*H*), 1.71 (1H, ddd, *J* = 5.04, 4.58 Hz, C*H*), 1.25 (3H, s, CH_3), 1.25 (3H, s, CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, Me_4Si): δ 201.0 (*C*=O), 199.5 (*C*=O), 172.6 (*C*O_2H), 67.3 (quat), 58.0 (4-*C*H), 44.8 (quat), 26.6 (*C*H_2), 22.1 (*C*H_3), 21.4 (*C*H_2), 18.4 (*C*H_3) ppm.

Diketones 8–10: General Procedure



Compound **7** was dissolved in thionyl chloride (10 mL per g of **7**) and the solution was heated under reflux for 2 hours. The excess thionyl chloride was evaporated and the residue was dissolved in DCM (20 mL per g of **7**). The solution was cooled to 0 °C and a solution of the appropriate amine (1.5 eq) and triethylamine (1.6 eq) in DCM (16 mL per g of **7**) was added slowly dropwise. The solution was allowed to warm to room temperature and stirring was continued for 24 hours. Water (100 mL) was added and the phases were mixed and separated. The organic phase was washed with water (100 mL) and aqueous hydrochloric acid solution (0.1 M, 50 mL), and was then dried over magnesium sulfate, filtered and evaporated to afford the pure diketone **8**–**10** which was used in the next step without further purification.

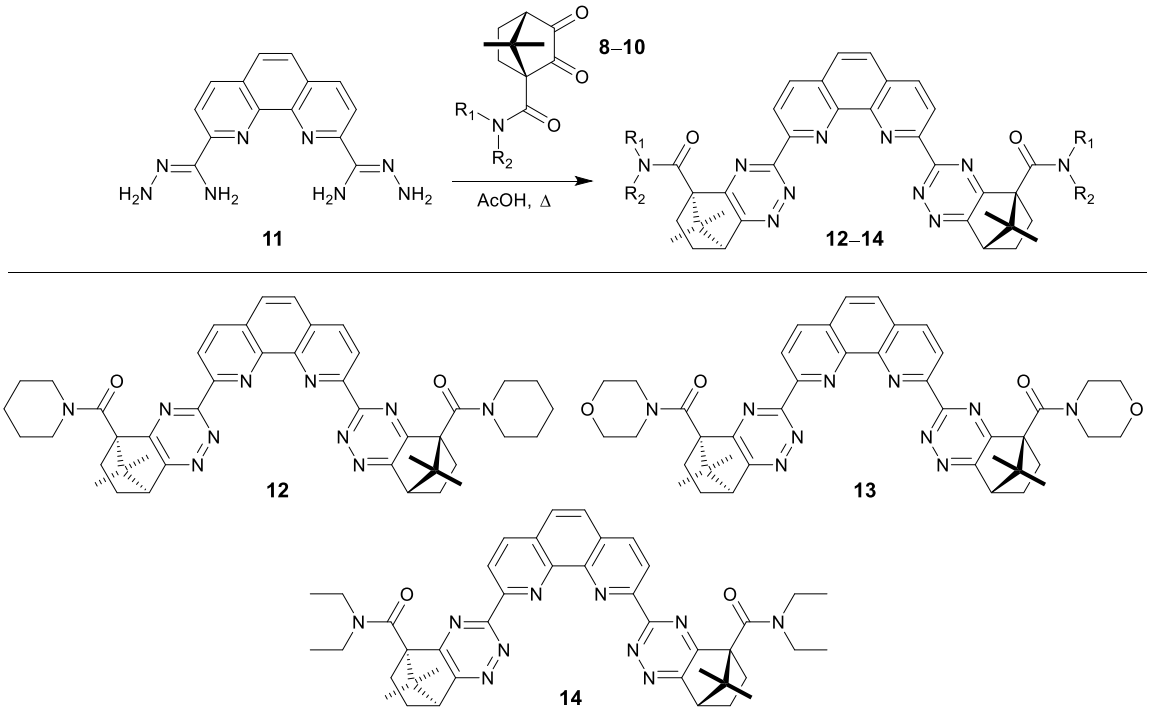
Diketone 8: Obtained from **7** (2.22 g, 11.326 mmol) and piperidine (1.68 mL, 16.989 mmol) as a yellow solid (2.87 g, 96%). Mp 131–133.5 °C (from DCM). Found C, 68.09; H, 8.00; N, 5.27%. $C_{15}H_{21}NO_3$ requires C, 68.42; H, 8.04; N, 5.32%. ^{1}H NMR (399.8 MHz, $CDCl_3$, Me_4Si): δ 3.57–3.37 (4H, m, 2 × C*H*$_2$), 2.55 (1H, d, *J* = 5.04 Hz, 4-C*H*), 2.46 (1H, ddd, *J* = 4.61, 4.58 Hz, C*H*), 2.32–2.13 (2H, m, 2 × C*H*), 2.05–1.95 (1H, m, C*H*) 1.76–1.60 (6H, m, 3 × C*H*$_2$), 1.34 (3H, s, C*H*$_3$), 1.26 (3H, s, C*H*$_3$) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$, Me_4Si): δ 200.7 (*C*=O), 198.1 (*C*=O), 165.0 (*C*ON), 65.9 (quat), 57.8 (4-*C*H), 45.8 (quat), 27.6 (*C*H$_2$), 24.5 (*C*H$_2$), 22.4 (*C*H$_3$), 19.5 (*C*H$_3$) ppm. *m*/*z* (HRMS, ESI) 264.1594 ([M + H]$^+$); $C_{15}H_{22}NO_3$ requires 264.1594.

Diketone 9: Obtained from **7** (0.56 g, 2.857 mmol) and morpholine (0.37 mL, 4.285 mmol) in 86% yield as a yellow solid. Mp 105–106.5 °C (from DCM). Found C, 62.97; H, 7.24; N, 5.59%. $C_{14}H_{19}NO_4$ requires C, 63.38; H, 7.22; N, 5.28%. ^{1}H NMR (399.8 MHz, $CDCl_3$, Me_4Si): δ 3.81–3.44 (8H, m, 4 × C*H*$_2$), 2.59 (1H, d, *J* = 5.04 Hz, C*H*), 2.46 (1H, td, *J* = 12.82, 4.58, 4.12 Hz, C*H*), 2.30 (1H, tt, *J* = 13.28, 5.04 Hz, C*H*), 2.17 (1H, ddd, *J* = 9.16, 4.58, 4.12 Hz, C*H*), 1.75 (1H, ddd, *J* = 9.16, 4.58, 4.12 Hz, C*H*), 1.37 (3H, s, C*H*$_3$), 1.28 (3H, s, C*H*$_3$)

ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$, Me_4Si): δ 200.1 (*C*=O), 198.0 (*C*=O), 165.3 (*C*ON), 67.0 (4 × *C*H_2), 57.7 (*C*H), 45.8 (quat), 27.3 (*C*H_2), 22.7 (*C*H_2), 22.3 (*C*H_3), 19.3 (*C*H_3) ppm. *m*/*z* (HRMS, ESI) 266.1389 ($[M + H]^+$); $C_{14}H_{20}NO_4$ requires 266.1387.

Diketone 10: Obtained from **7** (2.08 g, 10.612 mmol) and diethylamine (1.65 mL, 15.918 mmol, 1.5 eq) as a yellow solid (2.57 g, 96%). Mp 144–145.5 °C (from DCM). Found C, 66.62; H, 8.46; N, 5.62%. $C_{14}H_{21}NO_3$ requires C, 66.91; H, 8.42; N, 5.57%. ^{1}H NMR (399.8 MHz, $CDCl_3$, Me_4Si): δ 3.55 (1H, qu, *J* = 14.65, 7.33, 6.87 Hz, C*H*), 3.36 (1H, qu, *J* = 14.65, 7.33, 6.87 Hz, C*H*) 3.23 (2H, qu, *J* = 14.20, 7.33, 6.87 Hz, 2 × NC*H*), 2.56 (1H, d, *J* = 5.04 Hz, C*H*), 2.46 (1H, td, *J* = 13.28, 4.58, 4.12 Hz, C*H*), 2.29 (1H, tt, *J* = 13.74, 5.04 4.58 Hz, C*H*), 2.14 (1H, ddd, *J* = 9.16, 4.58 Hz, C*H*), 1.74 (1H, ddd, *J* = 5.04, 4.58, 4.12 Hz, C*H*), 1.34 (3H, s, CH_3), 1.29 (3H, s, CH_3), 1.18 (6H, sp, *J* = 7.33, 6.87, 6.41 Hz, 2 x CH_3) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$, Me_4Si): δ 200.7 (*C*=O), 198.2 (*C*=O), 165.7 (*C*ON), 67.5 (quat), 57.7 (*C*H), 45.9 (quat), 41.9 (*C*H_2N), 40.5 (*C*H_2N), 27.8 (*C*H_2), 22.7 (*C*H_2), 22.5 (*C*H_3), 19.2 (*C*H_3), 14.4 (*C*H_3), 12.7 (*C*H_3) ppm. *m*/*z* (HRMS, ESI) 252.1595 ($[M + H]^+$); $C_{14}H_{22}NO_3$ requires 252.1594.

BTPhen Ligands 12–14: General Procedure



1,10-Phenanthroline-2,9-bis-amidrazone **11** was dissolved in acetic acid (30 mL per g of **11**) and the appropriate diketone **8**–**10** (2 eq) was added. The solution was heated under reflux for 24 hours. The solution was allowed to cool to room temperature and the solvent was

evaporated. The residue was dissolved in DCM (100 mL per g of **11**) and the solution was washed with saturated aqueous sodium hydrogen carbonate (3 × 100 mL per g of **11**) and water (100 mL per g of **11**), and was then dried over magnesium sulfate, filtered and evaporated to afford the crude BTPhen ligand **12**–**14** as an orange solid. The crude product was dissolved in DCM (15 mL per g of **11**) and diethyl ether (150 mL per g of **11**) was added. The precipitated solid was filtered and washed with diethyl ether (100 mL per g of **10**), and the filtrate was evaporated to afford the crude BTPhen ligand **12**–**14**. The crude product was purified by short-path (ca. 20 cm) column chromatography, eluting with MeOH: DCM (1:10 volume ratio + 1% Et_3N) to afford the pure BTPhen ligand **12**–**14**.

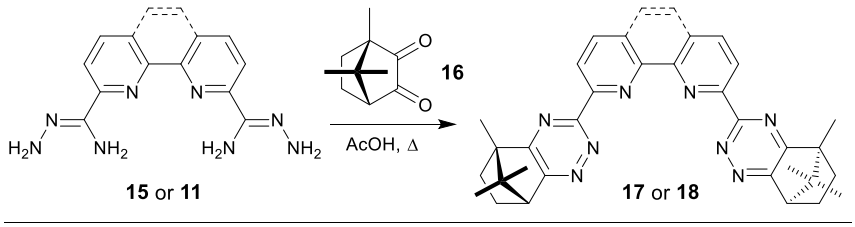
BTPhen Ligand 12: Obtained from 1,10-phenanthroline-2,9-bis-amidrazone **11** (1.604 g, 5.45627 mmol) and diketone **8** (2.87 g, 2 eq) as a yellow solid (1.80 g, 44%). Mp 240.4–241.6 ^{o}C (from DCM/diethyl ether). Found C, 70.17; H, 6.51; N, 18.57%. $C_{44}H_{48}N_{10}O_2$ requires C, 70.56; H, 6.46; N, 18.70%. ^{1}H NMR (399.8 MHz, $CDCl_3$, Me_4Si): δ 8.68 (2H, d, *J* = 8.24 Hz, 2 × ArC*H*), 8.48 (2H, d, *J* = 8.70 Hz, 2 × ArC*H*), 7.97 (2H, s, 2 × ArC*H*), 3.88–3.55 (8H, m, 4 × CH_2), 3.24 (2H, d, *J* = 4.12 Hz, 2 × C*H*), 2.72 (2H, td, *J* = 4.12, 3.66 Hz, 2 × CH_{exo}), 2.53–2.46 (2H, m, 2 × CH_{exo}), 1.95 (2H, ddd, *J* = 4.12, 3.66 Hz, 2 × CH_{endo}), 1.67 (12H, br s, 6 × CH_2), 1.57–1.50 (2H, m, 2 × CH_{endo}), 1.43 (6H, s, 2 × CH_3), 0.99 (6H, s, 2 × CH_3) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$, Me_4Si): δ 166.9 (2 × *C*ON), 166.2 (2 × quat), 164.9 (2 × quat), 162.1 (2 × quat), 154.1 (2 × quat), 146.7 (2 × quat), 137.0 (2 × Ar*C*H), 129.4 (2 × quat), 127.5 (2 × Ar*C*H), 123.3 (2 × Ar*C*H), 62.7 (2 × quat), 60.1 (2 × quat), 51.5 (2 × *C*H), 29.3 (2 × *C*H_2), 27.2 (2 × *C*H_2), 26.0 (2 × *C*H_2) 24.5 (2 × *C*H_2), 24.4 (2 × *C*H_2), 21.7 (2 × *C*H_3), 20.7 (2 × *C*H_3) ppm. *m*/*z* (HRMS, ESI) 749.4028 ($[M + H]^+$); $C_{44}H_{49}N_{10}O_2$ requires 749.4034.

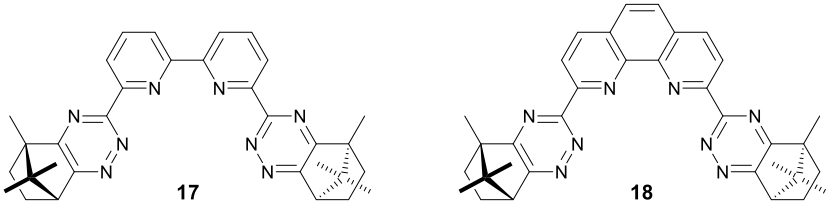
BTPhen Ligand 13: Obtained from 1,10-phenanthroline-2,9-bis-amidrazone **11** (0.0843 g, 0.2867 mmol) and diketone **9** (0.16 g, 0.6037 mmol) as a yellow solid (0.188 g, 86%). Mp 255–255.6 ^{o}C (from DCM/diethyl ether). Found C, 66.81; H, 6.02; N, 18.38%. $C_{42}H_{44}N_{10}O_4$ requires C, 67.00; H, 5.89; N, 18.60%. ^{1}H NMR (399.8 MHz, $CDCl_3$, Me_4Si): δ 8.56 (2H, d, *J* = 8.24 Hz, 2 × ArC*H*), 8.50 (2H, d, *J* = 8.24 Hz, 2 × ArC*H*), 7.98 (2H, s, 2 × ArC*H*), 4.1–3.4 (16H, m, 4 × CH_2O and 4 × CH_2N), 3.29 (2H, d, *J* = 4.12 Hz, 2 × C*H*), 2.70 (2H, td, *J* = 4.12, 3.66 Hz, 2 × C*H*), 2.53–2.46 (2H, m, 2 × C*H*), 2.05–1.94 (2H, m, 2 × C*H*), 1.59–1.50 (2H, m, 2 × C*H*), 1.43 (6H, s, 2 × CH_3), 1.03 (6H, s, 2 × CH_3) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$, Me_4Si): δ 166.8 (2 × *C*ON), 166.7 (2 × quat), 164.9 (2 × quat), 161.9 (2 × quat), 153.8 (2 × quat), 146.4

(2 × quat), 137.4 (2 × Ar*C*H), 129.6 (2 × quat), 127.6 (2 × Ar*C*H), 123.1 (2 × Ar*C*H), 67.2 (8 × *C*H_2), 62.4 (2 × quat), 60.2 (2 × quat), 51.4 (2 × *C*H), 28.9 (2 × *C*H_2), 24.3 (2 × *C*H_2), 21.6 (2 × *C*H_3), 20.5 (2 × *C*H_3) ppm. *m*/*z* (HRMS, ESI) 753.3614 ($[M + H]^+$); $C_{42}H_{45}N_{10}O_4$ requires 753.3620.

BTPhen Ligand 14: Obtained from 1,10-phenanthroline-2,9-bis-amidrazone **11** (1.505 g, 5.11952 mmol) and diketone **10** (2.57 g, 2 eq) as a yellow solid (1.96 g, 53%). Mp 195.2–195.8 °C (from DCM/diethyl ether). Found C, 69.32; H, 6.85; N, 19.21%. $C_{42}H_{48}N_{10}O_2$ requires C, 69.59; H, 6.67; N, 19.32%. ^{1}H NMR (399.8 MHz, $CDCl_3$, Me_4Si): δ 8.69 (2H, d, *J* = 8.70 Hz, 2 × ArC*H*), 8.46 (2H, d, *J* = 8.70 Hz, 2 × ArC*H*), 7.95 (2H, s, 2 × ArC*H*), 3.98–3.92 (2H, m, C*H*$_2$N), 3.76–3.70 (2H, m, C*H*$_2$N), 3.66–3.61 (2H, m, C*H*$_2$N), 3.48–3.43 (2H, m, C*H*$_2$N), 3.24 (2H, d, *J* = 4.12 Hz, 2 × C*H*), 2.70 (2H, ddd, *J* = 9.16, 8.70, 3.66 Hz, 2 × C*H*), 2.53–2.45 (2H, m, 2 × C*H*), 1.95–1.88 (2H, m, 2 × C*H*), 1.56 (2H, ddd, *J* = 9.16, 8.70, 3.66 Hz, 2 × C*H*), 1.42 (6H, s, 2 × C*H*$_3$), 1.30 (6H, t, *J* = 7.33 Hz, 2 × C*H*$_3$CH$_2$N), 1.25 (6H, t, *J* = 7.33 Hz, 2 × C*H*$_3$CH$_2$N), 1.01 (6H, s, 2 × C*H*$_3$) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$, Me_4Si): δ 167.0 (2 × *C*ON), 165.3 (4 × quat), 161.3 (2 × quat), 153.5 (2 × quat), 146.5 (2 × quat), 137.3 (2 × Ar*C*H), 129.7 (2 × quat), 127.6 (2 × Ar*C*H), 122.9 (2 × Ar*C*H), 62.7 (2 × quat), 60.3 (2 × quat), 51.4 (2 × *C*H), 43.0 (2 × *C*H_2), 40.9 (2 × *C*H_2), 29.3 (2 × *C*H_2), 24.3 (2 × *C*H_2), 21.8 (2 × *C*H_3), 20.3 (2 × *C*H_3), 15.3 (2 × *C*H_3), 13.1 (2 × *C*H_3) ppm. *m*/*z* (HRMS, ESI) 725.4028 ($[M + H]^+$); $C_{42}H_{49}N_{10}O_2$ requires 725.4034.

CA-BTBP 17 and CA-BTPhen 18: General Procedure





The appropriate bis-amidrazone **15** or **11** was dissolved in acetic acid (60 mL per g of **15** or **11**) and (1*S*)-(+)-camphorquinone **16** (2.1 eq) was added. The solution was heated under reflux for 24 hours. The solution was allowed to cool to room temperature and the solvent was

evaporated. The residue was dissolved in DCM (100 mL per g of **15** or **11**) and the solution was washed with saturated aqueous sodium hydrogen carbonate (3 × 100 mL per g of **15** or **11**) and water (100 mL per g of **15** or **11**), and was then dried over magnesium sulfate, filtered and evaporated to afford the crude ligand **17** or **18** as an orange solid. The crude solid was triturated with diethyl ether (100 mL per g of **15** or **11**) and the insoluble solid was filtered and washed with diethyl ether (250 mL per g of **15** or **11**) and hexane (10 mL per g of **15** or **11**) to afford the pure ligand **17** or **18**.

CA-BTBP 17: Obtained from 2,2'-bipyridine-6,6'-bis-amidrazone **15** (0.2037 g, 0.7544 mmol) and (1*S*)-(+)-camphorquinone **16** (0.263 g, 2.1 eq) as a yellow solid (0.203 g, 53%). Mp 176.3–178.0 °C (from diethyl ether). Found C, 72.15; H, 6.43; N, 20.89%. $C_{32}H_{34}N_8$ requires C, 72.43; H, 6.46; N, 21.12%. ^{1}H NMR (399.8 MHz, $CDCl_3$, Me_4Si): δ 8.93 (2H, d, *J* = 7.79 Hz, 2 × ArC*H*), 8.60 (2H, d, *J* = 7.79 Hz, 2 × ArC*H*), 8.08 (2H, t, *J* = 7.79 Hz, 2 × ArC*H*), 3.32 (2H, d, *J* = 4.12 Hz, 2 × C*H*), 2.39–2.32 (2H, m, 2 × CH_{exo}), 2.14–2.08 (2H, m, 2 × CH_{exo}), 1.52–1.41 (4H, m, 4 × CH_{endo}), 1.49 (6H, s, 2 × CH_3), 1.15 (6H, s, 2 × CH_3), 0.69 (6H, s, 2 × CH_3) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$, Me_4Si): δ 171.1 (2 × quat), 165.3 (2 × quat), 161.7 (2 × quat), 156.1 (2 × quat), 153.0 (2 × quat), 138.0 (2 × Ar*C*H), 124.3 (2 × Ar*C*H), 123.1 (2 × Ar*C*H), 55.6 (2 × quat), 54.5 (2 × quat), 51.2 (2 × *C*H), 31.1 (2 × *C*H_2), 24.3 (2 × *C*H_2), 20.2 (2 × *C*H_3), 18.4 (2 × *C*H_3), 9.3 (2 × *C*H_3) ppm. *m*/*z* (HRMS, ESI) 531.2972 ([M + H]$^+$); $C_{32}H_{35}N_8$ requires 531.2979.

CA-BTPhen 18:[5] Obtained from 1,10-phenanthroline-2,9-bis-amidrazone **11** (0.63 g, 2.142857 mmol) and (1*S*)-(+)-camphorquinone **16** (0.747 g, 2.1 eq) as a yellow solid (0.76 g, 64%). ^{1}H NMR (399.8 MHz, $CDCl_3$, Me_4Si): δ 8.87 (2H, d, *J* = 8.24 Hz, 2 × ArC*H*), 8.45 (2H, d, *J* = 8.24 Hz, 2 × ArC*H*), 7.94 (2H, s, 2 × ArC*H*), 3.31 (2H, d, *J* = 4.12 Hz, 2 × C*H*), 2.12 (2H, m, 2 × CH_{exo}), 2.12 (2H, td, *J* = 9.62, 3.66 Hz, 2 × CH_{exo}), 1.60 (6H, s, 2 × CH_3), 1.54 (2H, m, 2 × CH_{endo}), 1.45 (2H, m, 2 × CH_{endo}), 1.15 (6H, s, 2 × CH_3), 0.70 (6H, s, 2 × CH_3) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$, Me_4Si): δ 171.4 (2 × quat), 165.5 (2 × quat), 161.8 (2 × quat), 153.7 (2 × quat), 146.2 (2 × quat), 137.3 (2 × Ar*C*H), 129.7 (2 × quat), 127.6 (2 × Ar*C*H), 123.3 (2 × Ar*C*H), 55.6 (2 × quat), 54.7 (2 × quat), 51.2 (2 × *C*H), 31.1 (2 × *C*H_2), 24.3 (2 × *C*H_2), 20.3 (2 × *C*H_3), 18.4 (2 × *C*H_3), 9.6 (2 × *C*H_3) ppm. *m*/*z* (HRMS, ESI) 555.2971 ([M + H]$^+$); $C_{34}H_{35}N_8$ requires 555.2979.

Solubility Measurements

A small sample of each ligand **12**–**14**, **17** or **18** was accurately weighed in a sample tube to 4 decimal places by subtracting the mass of the sample tube from the mass of the sample tube + ligand. A few drops of 1-octanol were added and the sample was sonicated. This procedure was continued until complete dissolution of the ligand. At this point the mass of the sample tube was again taken to determine the mass of 1-octanol added, which was then converted to volume. The solubility was expressed as mol/L by calculating the mass (g) of each ligand dissolved in 1 L of 1-octanol and dividing by the molecular weight of each ligand. The sample was then left overnight to ensure the ligand remained in solution and did not crystallize.

Solvent Extraction Measurements

Aqueous solutions representing the composition of a typical DIAMEX feed solution were prepared for the solvent extraction experiments. The DIAMEX feed solution is obtained when spent nuclear fuel solutions have been processed through the PUREX and DIAMEX processes, and is then processed further in the SANEX process,[6] in which the trivalent minor actinides Am(III) and Cm(III) are separated from the trivalent lanthanides. The DIAMEX feed solution does not contain U or Pu as these have already been removed in the preceding PUREX and DIAMEX processes. The aqueous solutions were prepared by spiking nitric acid solutions (0.01–3 M) containing 1×10^{-5} M of each lanthanide (except Pm) and Y with stock solutions of ^{241}Am, ^{152}Eu and ^{244}Cm tracers (10 μL) in nitric acid. All the lanthanides were included even though the heavy lanthanides (Tb–Lu) are not fission products. We have chosen to include data for all the lanthanides as data on the extraction of all lanthanides by *N*-donor ligands could be relevant in other fields besides the field of nuclear reprocessing (eg: the field of lanthanide separation and purification). Ultrapure water (18.2 MΩcm) was used for all dilutions. The radiotracers ^{241}Am, ^{244}Cm and ^{152}Eu were supplied by Isotopendienst M. Blaseg GmbH, Waldburg (Germany), Oak Ridge National Laboratory, Oak Ridge (USA), and Eckert & Ziegler Nuclitec GmbH, Braunschweig (Germany), respectively. Solutions of the ligands **12**–**14**, **17** and **18** (0.01 M) were prepared by dissolving **12**–**14**, **17** or **18** in 1-octanol. 1-octanol was chosen as the diluent to minimize precipitate formation previously found with ligand **4** when using other diluents, and to allow direct comparison with previous results for ligands **1**–**3**. Each organic phase (500 μL) was shaken separately with each of the aqueous phases (500 μL) for one hour at 22 °C using a thermostatted aluminum block installed on an IKA Vibrax Orbital Shaker Model VXR (2,200 rpm). The contact time of one hour was sufficient to attain

the distribution equilibrium. After phase separation by centrifugation, 200 µL aliquots of each phase were withdrawn for radio analysis. Activity measurements of the γ-ray emitters ^{241}Am and ^{152}Eu were performed with a HPGe γ-ray spectrometer, EG & G Ortec, Munich (Germany). The γ-lines at 59.5 keV, and 121.8 keV were examined for ^{241}Am, and ^{152}Eu, respectively. The nuclides ^{241}Am and ^{244}Cm were measured by means of alpha spectrometry with an Alpha Spectrometer OctêteTM PC obtained from EG & G Ortec, Munich (Germany). Stable elements were determined by ICP-MS on a NexION 2000 obtained from Perkin Elmer Sciex, Rodgau-Jügesheim (Germany). The concentration of inactive elements in organic phases was measured via ICP-MS using Triton-X 100 as surfactant. The distribution ratio *D* was calculated as the ratio between the radioactivity/concentration in the organic and the aqueous phase. The separation factor SF is calculated as the ratio between the distribution ratios of the corresponding metals. Distribution ratios between 0.01 and 100 exhibit a maximum error of ± 5 %. The error may be up to ± 20 % for smaller and larger values.

NMR Titrations

Stock solutions (0.01 M) of each of the ligands **12**, **14** and **18**, and of the metal nitrate salts $La(NO_3)_3.6H_2O$, $Lu(NO_3)_3.H_2O$ and $Y(NO_3)_3.6H_2O$ (Aldrich) were prepared in CD_3CN (Fluorochem). A 0.5 mL aliquot of the appropriate ligand solution was placed in an NMR tube and the ^{1}H NMR spectrum was recorded at 399.8 MHz on a JEOL ECS400FT Delta spectrometer. The appropriate lanthanide salt solution was added to the NMR tube in 50 µL aliquots (ie: 0.1 equivalents each time) using a calibrated Gilson 100 µL micropipette. The tube was inverted several times to ensure full mixing and the ^{1}H NMR spectrum was recorded after each successive addition until the resonances of the free ligand had completely disappeared and/or until no further spectral changes were observed. Homogeneous solutions were obtained after each addition. The relative ratios of the different species present were calculated from the relative integrals of a suitable one-proton resonance of the ligand **12**, **14** or **18**. These values were normalized such that, for a given one-proton resonance, the total integration for all species present equalled unity. The species distributions at different metal:ligand ratios were calculated from these normalized relative ratios.

Kinetics and Interfacial Tension Measurements

The extraction kinetics of Am(III) and Eu(III) by BTPhen **12** in 1-octanol were studied using the rotating membrane cell (RMC) technique (Figure 1). The cell consists of a thin membrane that is glued on the base of a cylinder made of perspex. Membranes purchased from Millipore™

were used. Two types of Millipore membranes were used depending on the type of solution impregnating the membrane: a hydrophilic Omnipore JHWP (PTFE) membrane (thickness: 58 µm, porosity 0.8, tortuosity 2.51) for the 3M HNO_3 aqueous solution; a hydrophobic HVHP membrane (thickness: 102 µm, porosity 0.75, tortuosity 1.94) for the organic BTPhen **12** solution in 1-octanol.

The thickness of the membrane is in the range 50-120 µm and its diameter is ca. 8 mm. Depending on its type, it is impregnated with the aqueous or the organic phase. This phase, denoted by A, is spiked with the radioactive tracer to be extracted. The cell is mounted on a rotating-electrode spindle that can be rotated at a definite speed. Initially, it is set into rotation at 600 rpm and it is immersed into the outer phase B.

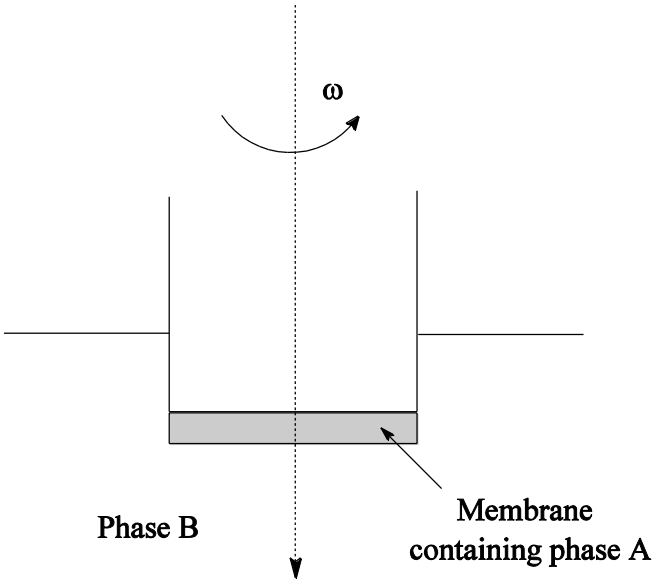


Figure 1. Sketch of the rotating membrane cell (RMC) technique.

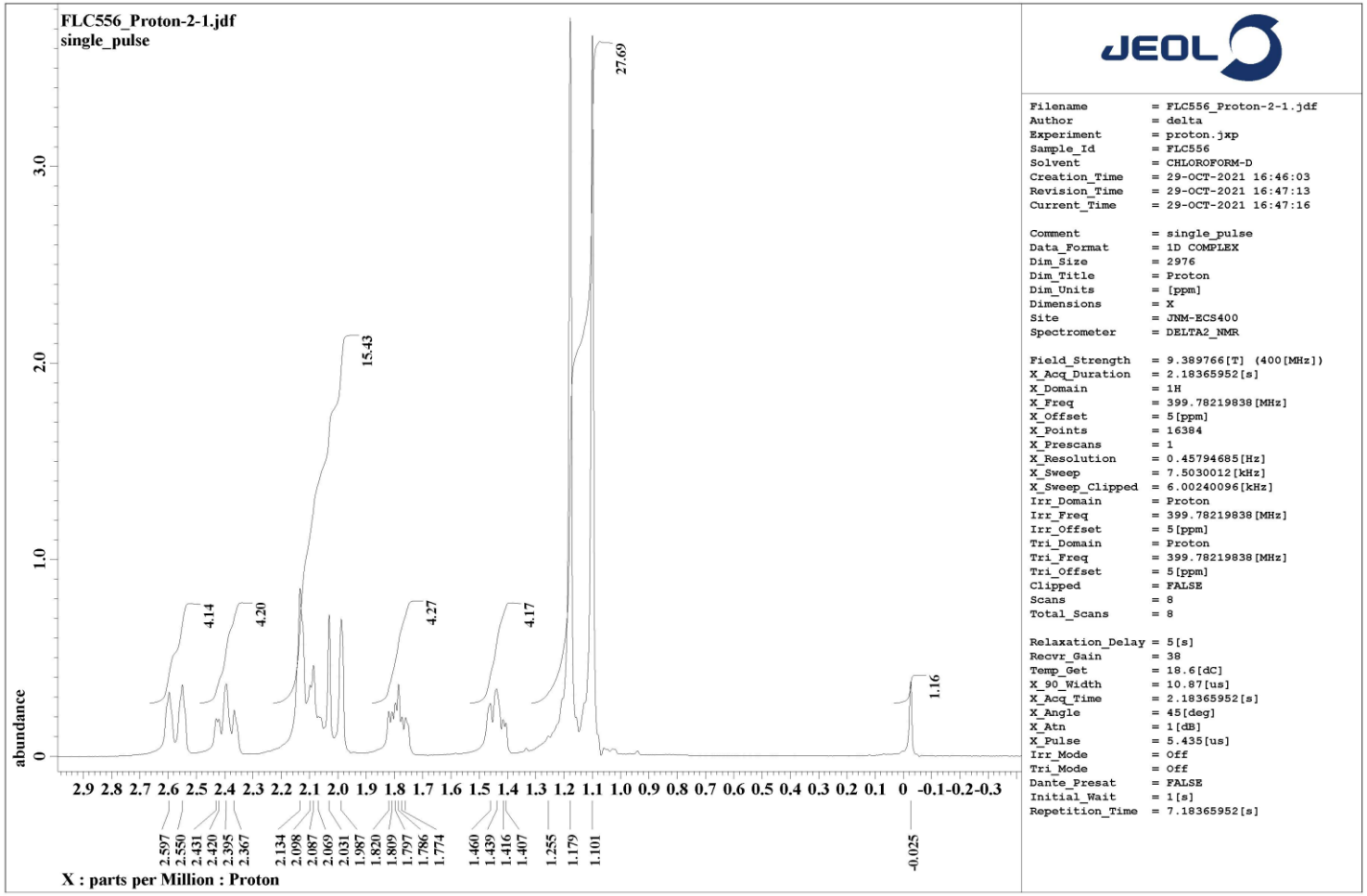
In phase A, transport in the pores of the membrane is purely diffusive and is governed by Fick's law. In phase B, rotating-disc hydrodynamics is promoted, which leads to a convective transport process which can be described following the theory of Levich.[7] The contributions of the transport processes in phases A and B can be assessed by measuring independently the diffusion coefficients of solute in the two phases. These quantities were determined using the closed capillary technique.[8] Formally, the contributions from the diffusive transport processes can be subtracted from the overall process, so yielding the contribution from interfacial transfer alone. ^{152}Eu(III) was purchased from LEA-CERCA (France). Two types of hydrophilic membranes were purchased from Millipore™: Durapore HVLP membranes (thickness ≈ 120 µm, measured porosity ≈ 71.0 %) and Omnipore JHWP membranes (thickness ≈ 50 µm, measured porosity ≈ 80.5 %). Both types have a pore size of ca. 0.45 µm. For reasons of

compatibility, the Durapore membrane was used with 1-octanol as the organic solvent. These membranes were glued on the plastic cylinder with polyvinyl chloride (PVC) and with a polyimide resin, respectively. It was verified that these compounds did not penetrate significantly into the membranes by measuring their free volume after gluing the membrane. The polyimide was Pyre-M.L.® RC-5019 (purchased from Aldrich, CAS no. 25038-81-7). An extraction experiment is conducted as follows. First, the membrane is impregnated with the radiolabelled phase A. In the case that A is an aqueous phase, a small drop of pure organic solvent is rapidly placed on top of the membrane in order to prevent evaporation of the aqueous phase. Then the cell is turned over, it is set into rotation at a known speed and, at $t = 0$, it is immersed into phase B. It is removed after a certain lapse of time and a sample of phase B is taken. The activity of this sample is counted in a radioactivity counter together with the activity of the cell bearing the membrane. The amount of extracted solute is deduced from these two results. In most cases, the kinetic experiments were carried out with radiolabelled organic phase placed in the membrane. This stripping configuration is much less extractant consuming than in the case of extraction because the free volume of the membrane is of the order of one thousand times smaller than that of the outer solution. Some experiments in the reverse configuration (by placing the radiolabeled aqueous phase in the membrane) were carried out to check that the same results for the rate constants were obtained.

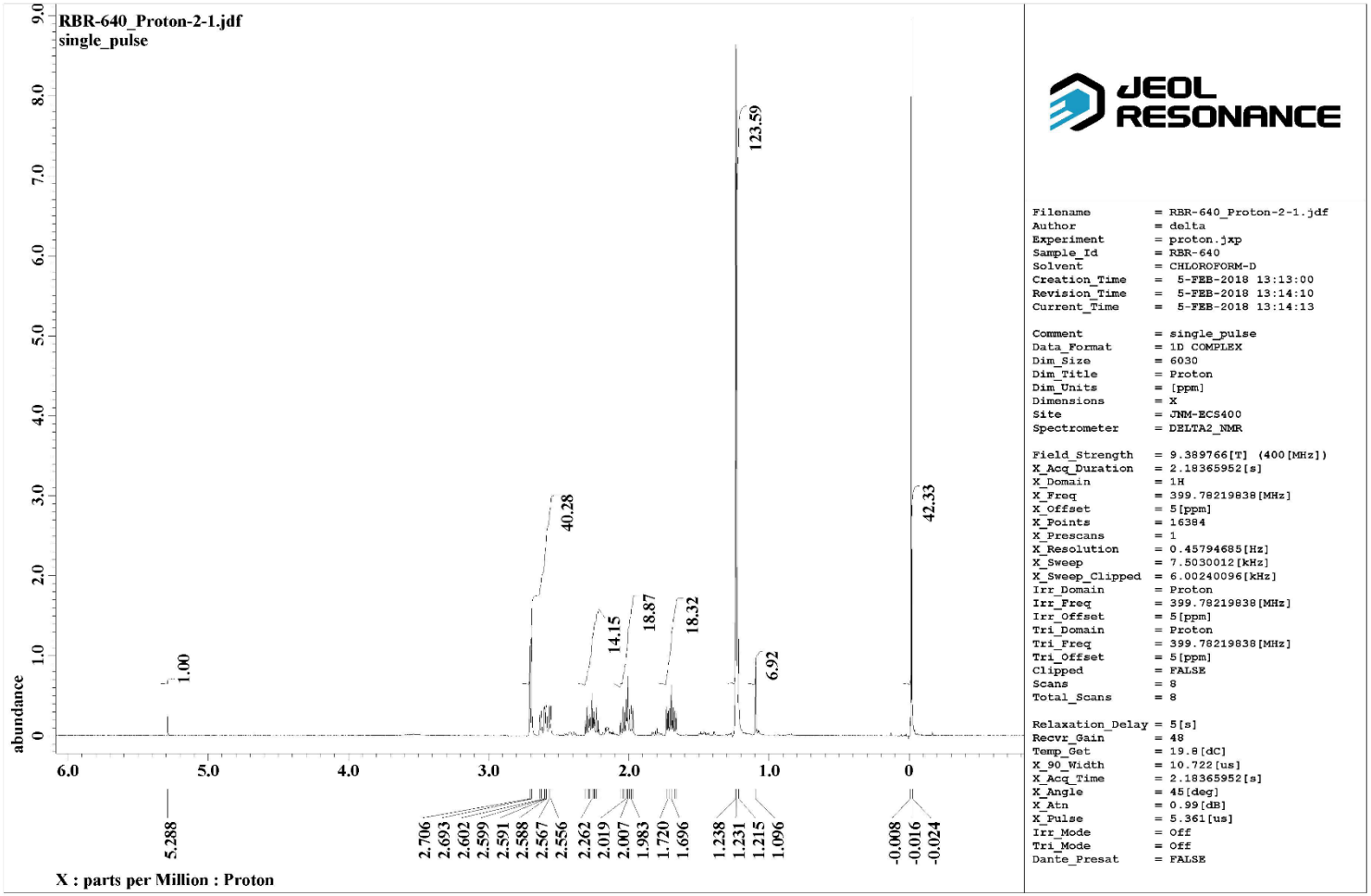
Interfacial tensions were measured using a K10 Krüss tensiometer and a platinum ring. The measurement was based on the du Noüy ring method in which the ring is detached from the interface at which it is placed initially. The interfacial tension is deduced from the maximum value of the force exerted to detach the ring. The measurements were made for solutions of BTPhen ligand **12** in 1-octanol as the organic phase and for 1 M nitric acid as the aqueous phase. The phases were pre-equilibrated by contacting them for one day. The absence of surface activity is shown by a flat profile in the plot of the interfacial tension as a function of the extractant concentration. On the contrary, the interfacial tension decreases when the extractant is surface active.

2: NMR Spectra

(+)-Ketopinic acid **6**



Compound **7**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2.602
2.599
2.591
2.588
2.567
2.556
2.262
2.019
2.007
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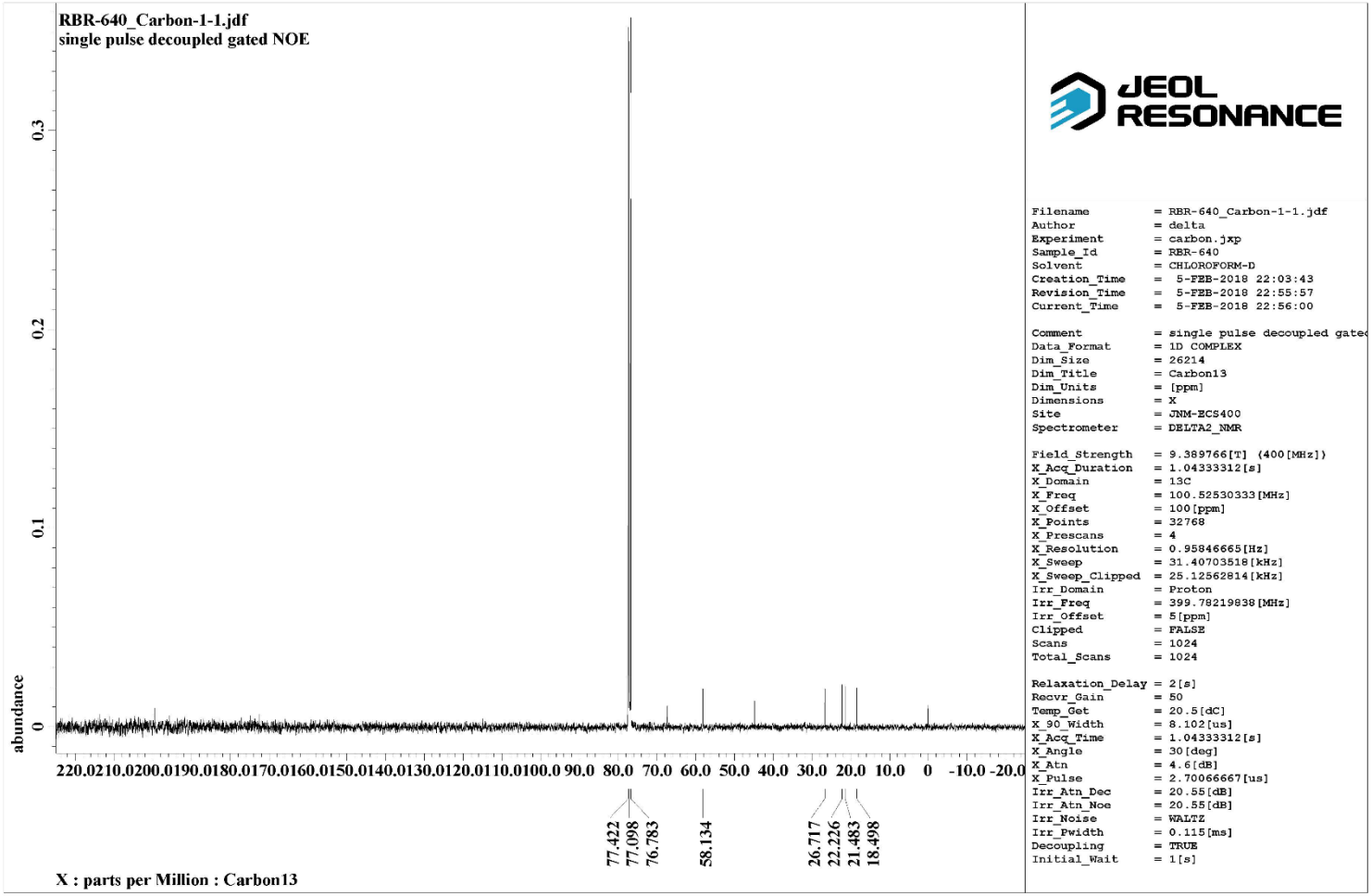
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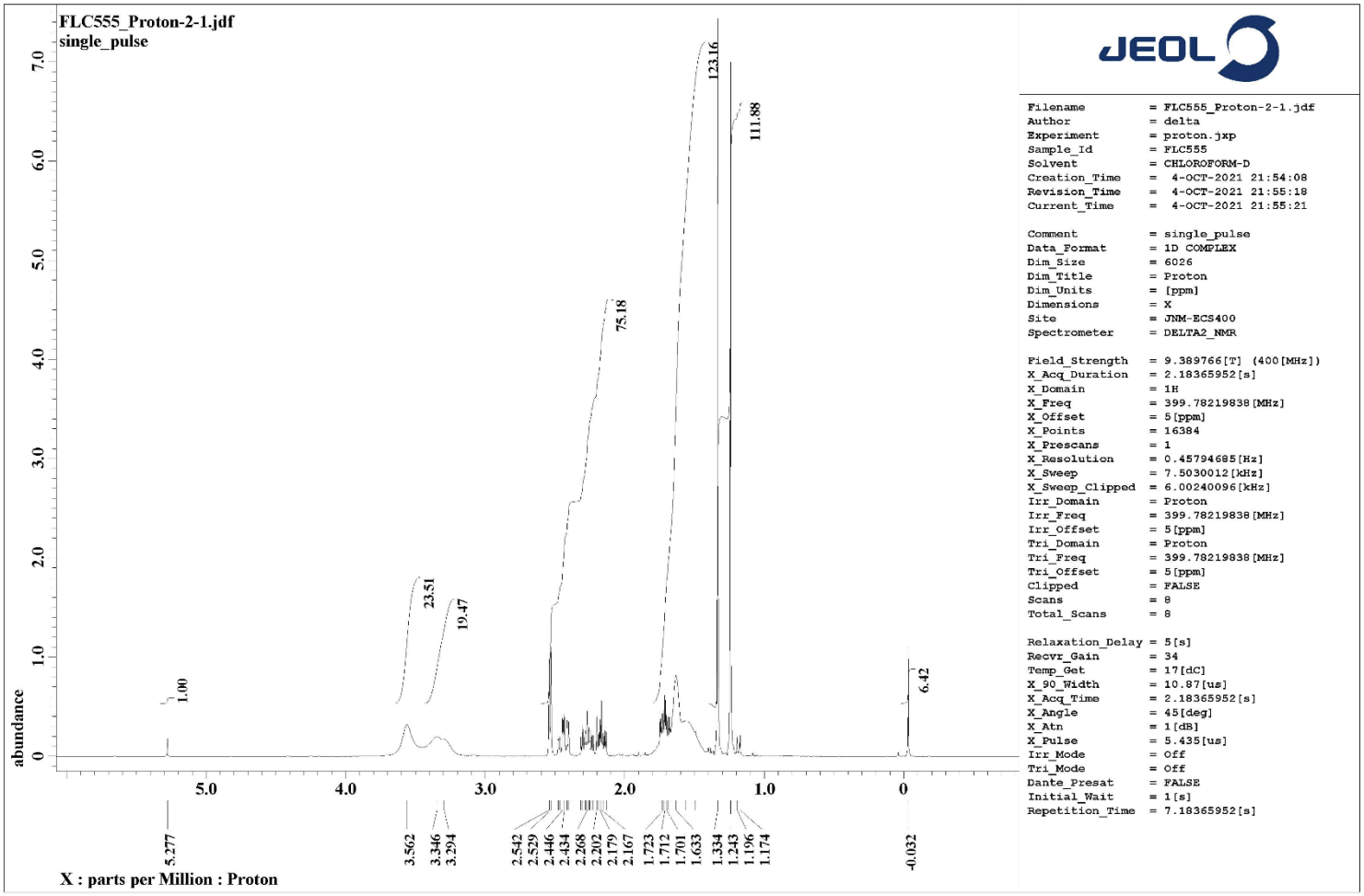
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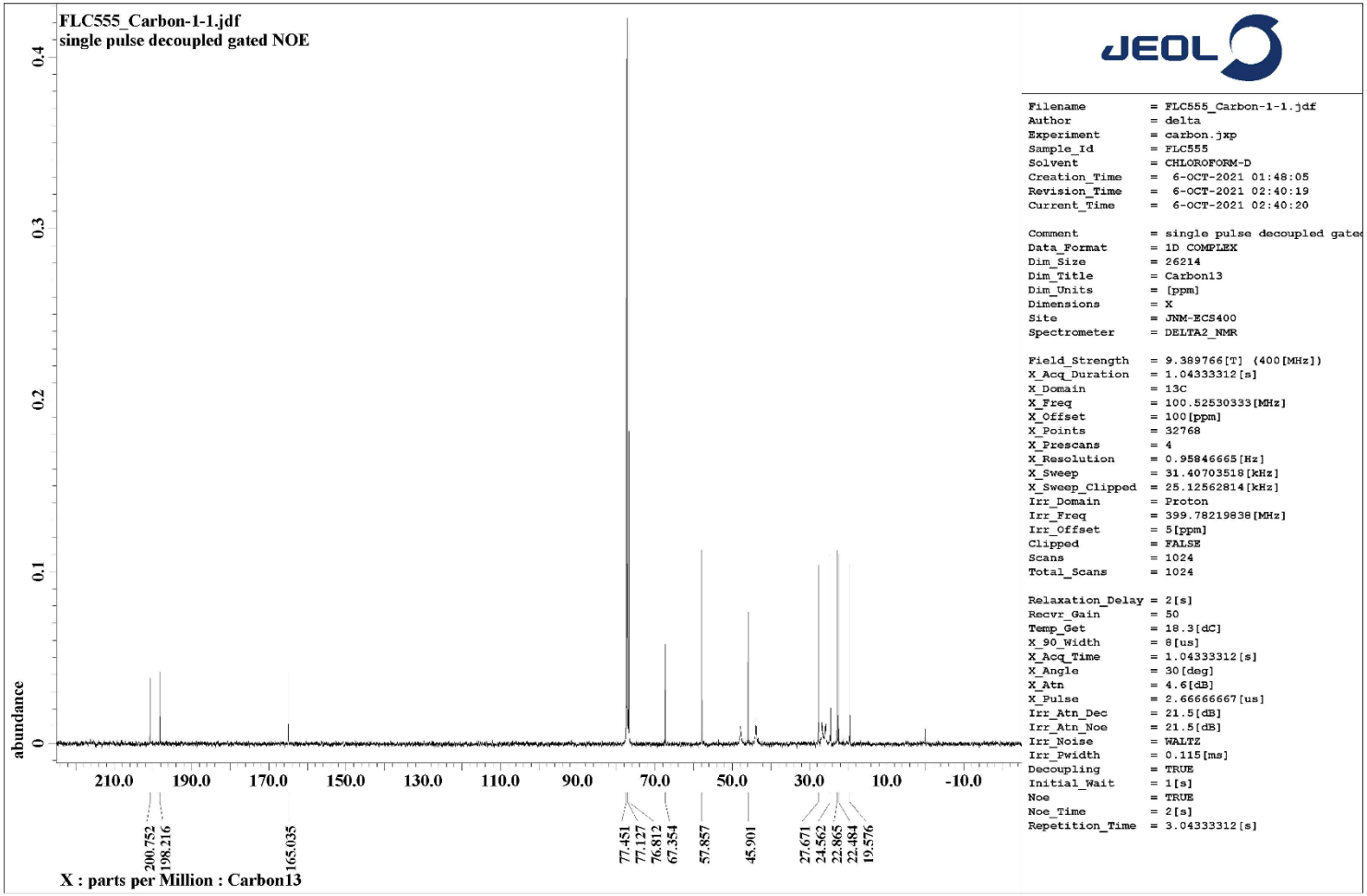
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70.0
50.0
30.0
10.0
-10.0
200.752
198.216
165.035
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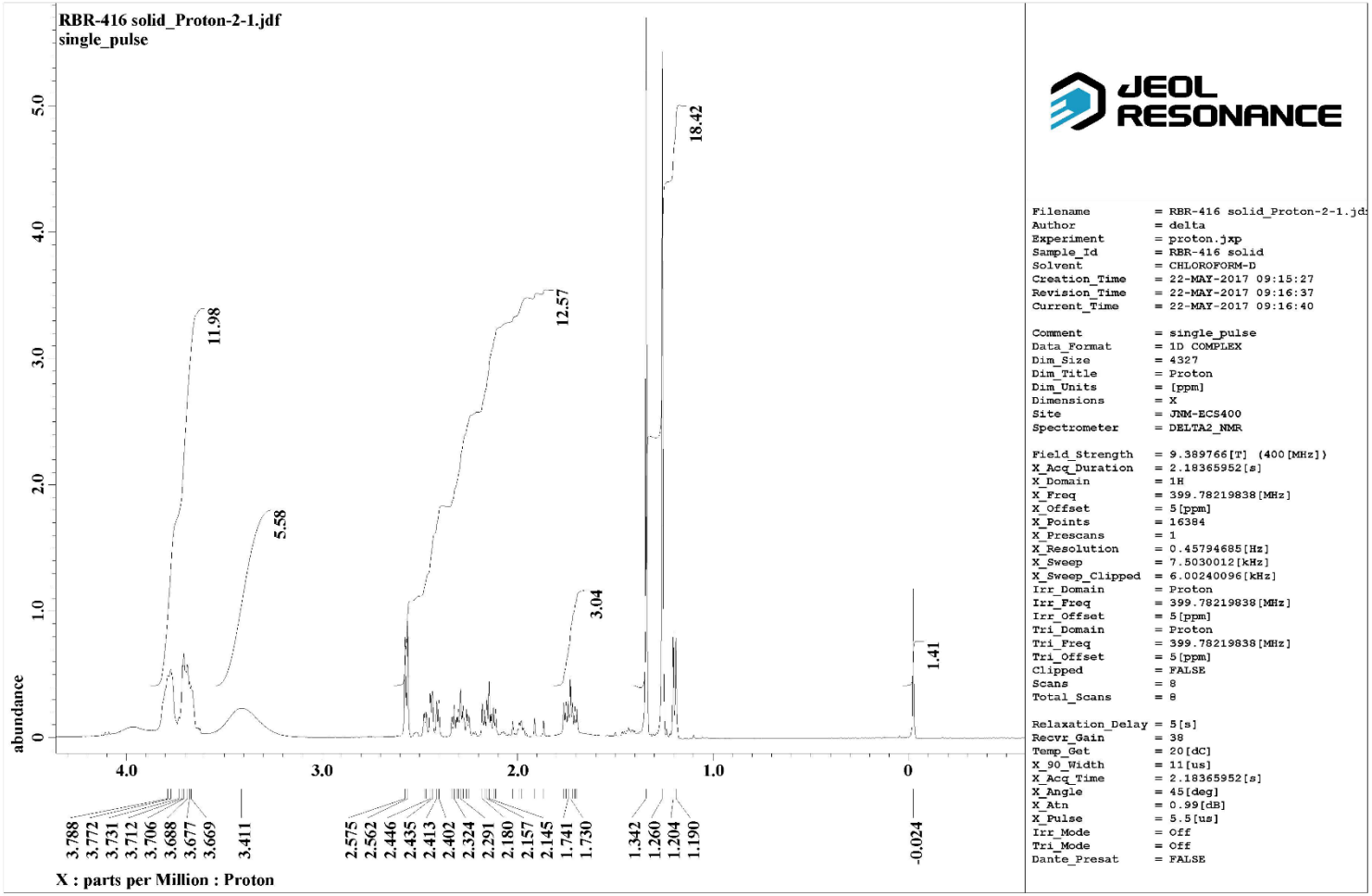
Compound **9**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3.669
3.411
2.575
2.562
2.446
2.435
2.413
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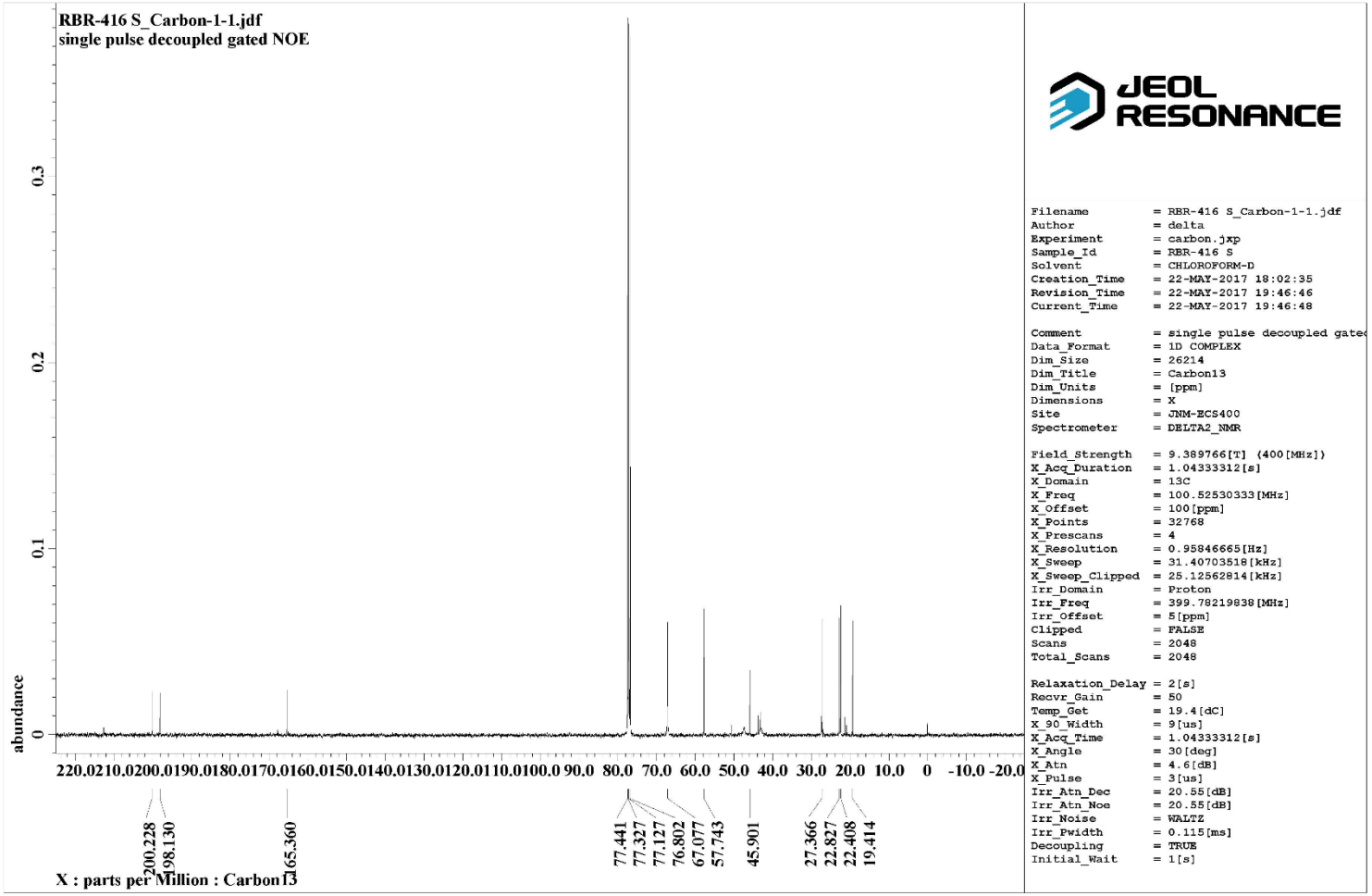
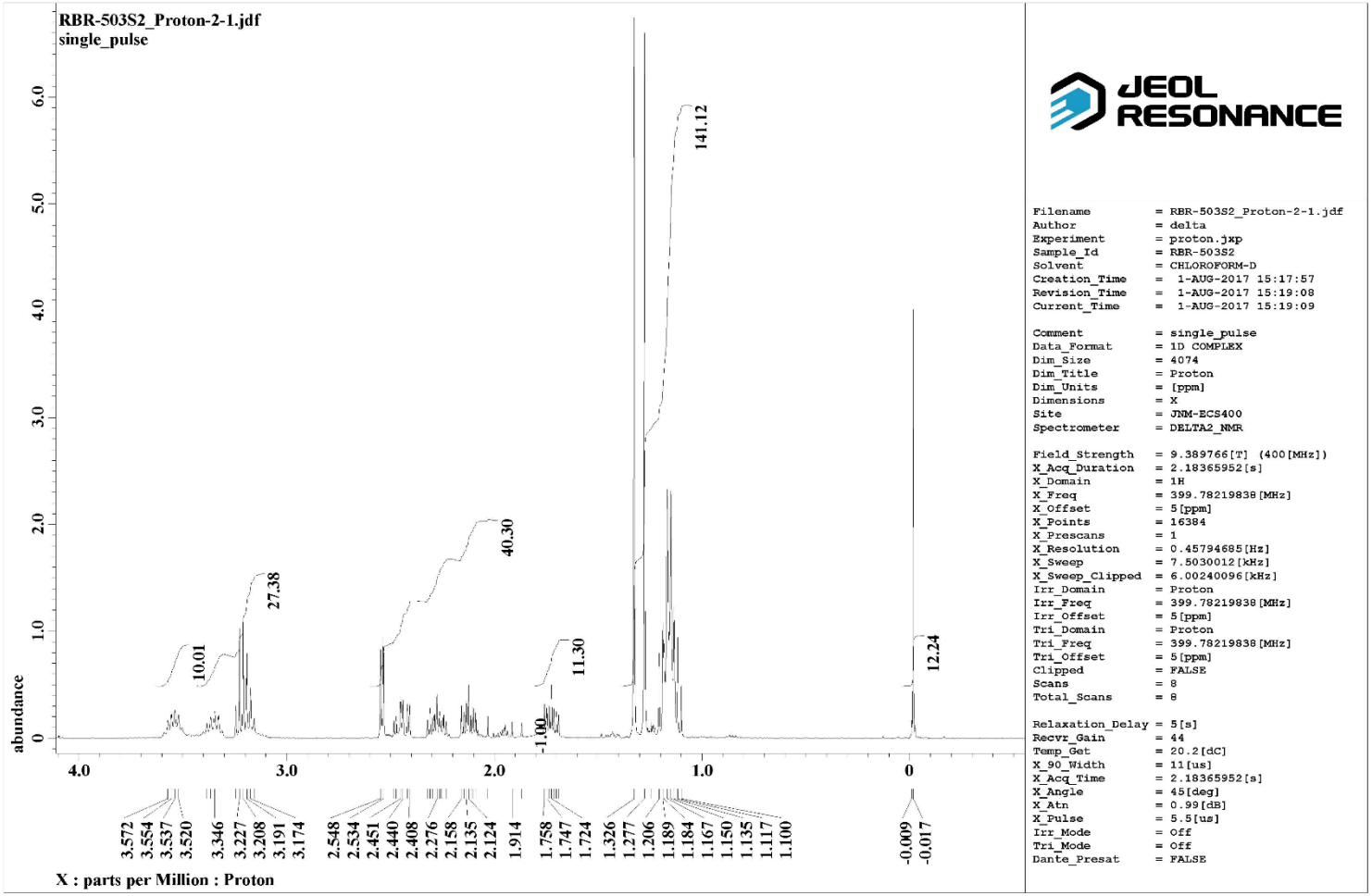
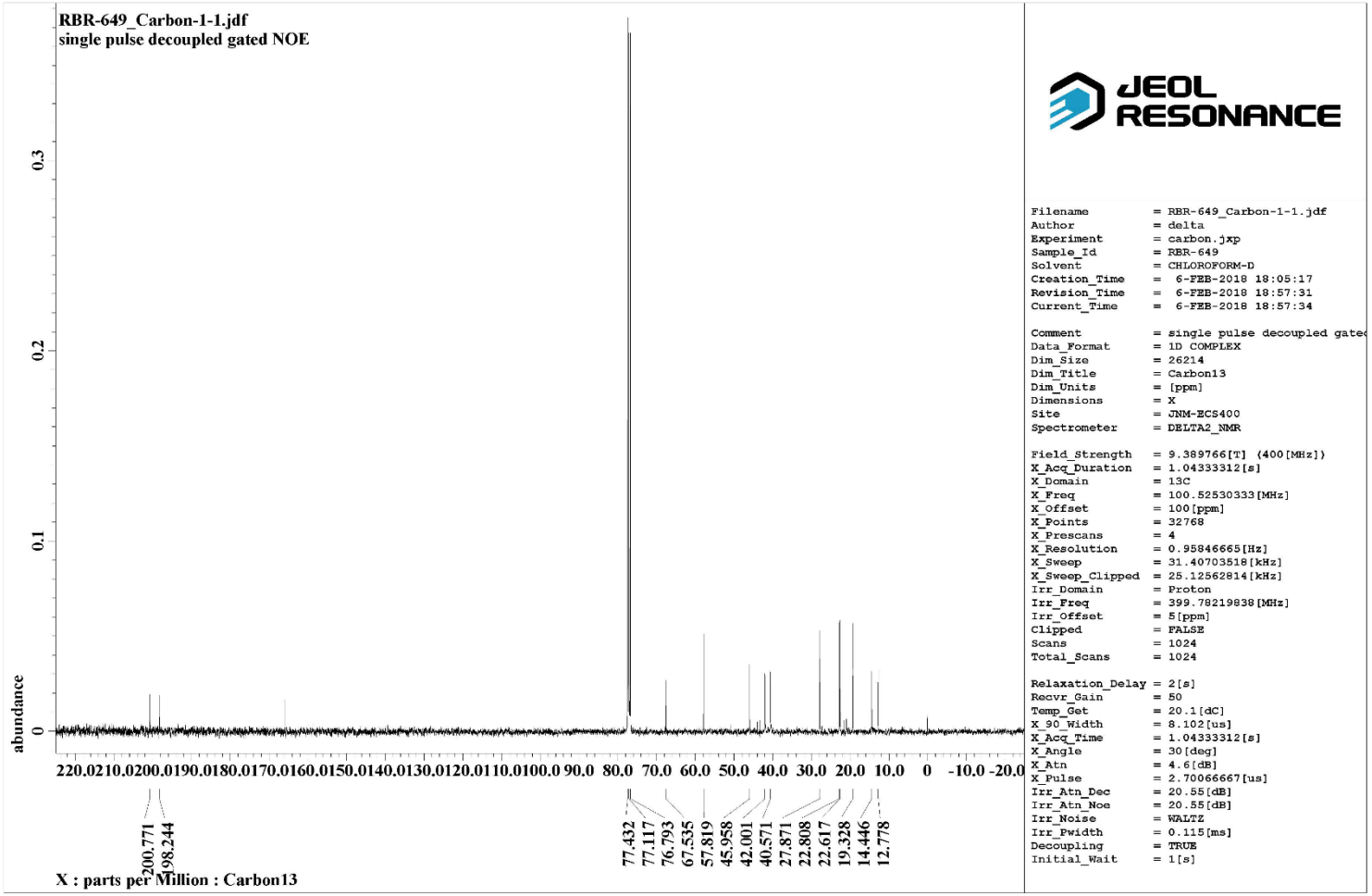
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 38
Temp_Get = 20[dC]
X_90_Width = 11[us]
X_Acq_Time = 2.18365952[s]
X_Angle = 45[deg]
X_Atn = 0.99[dB]
X_Pulse = 5.5[us]
Irr_Mode = Off
Tri_Mode = Off
Dante_Presat = FALSE

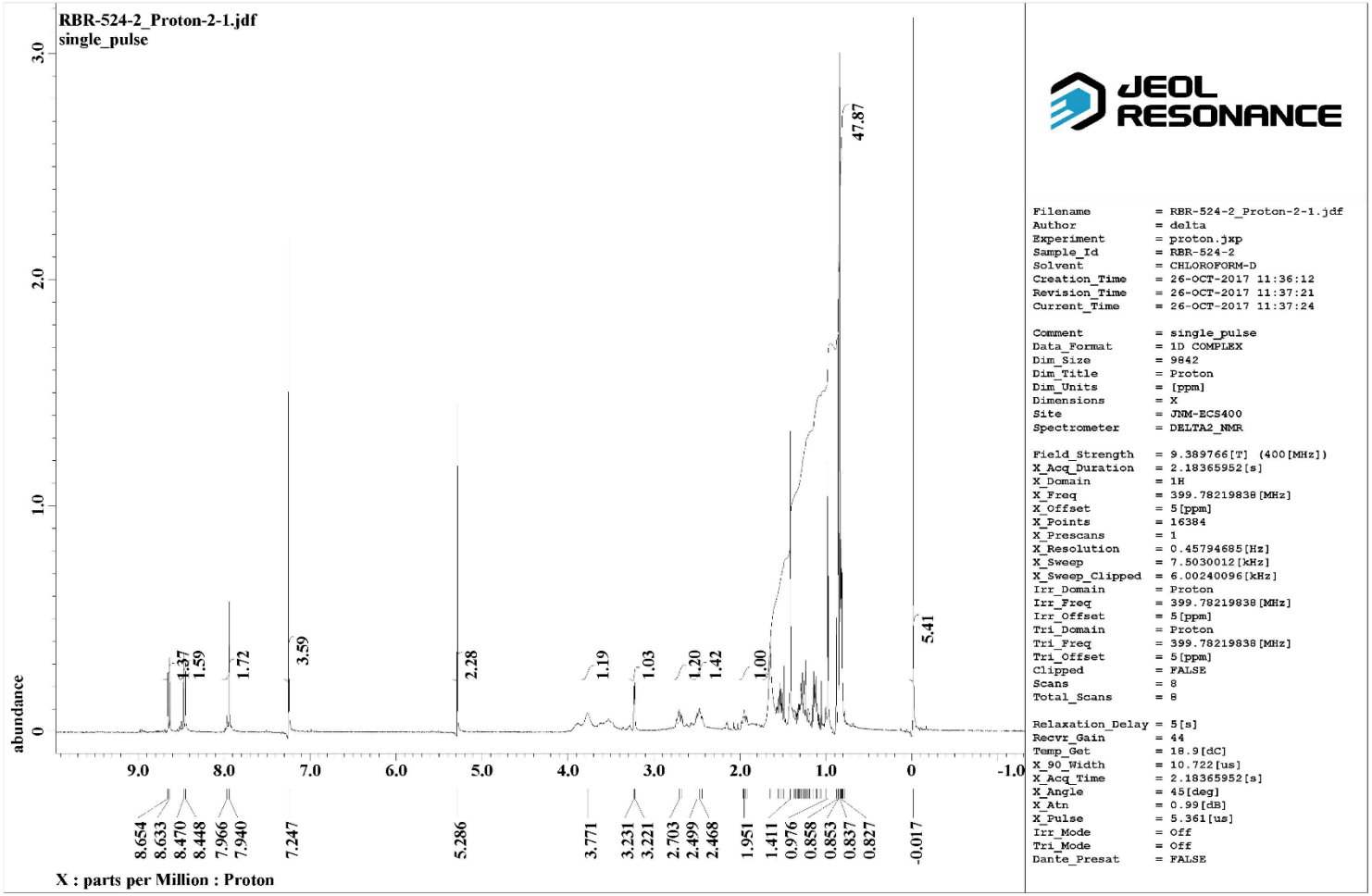

RBR-416 S_Carbon-1-1.jdf
single pulse decoupled gated NOE
abundance
0
0.1
0.2
0.3
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
200.228
198.130
165.360
77.441
77.327
77.127
76.802
67.077
57.743
45.901
27.366
22.827
22.408
19.414
X : parts per Million : Carbon13
JEOL RESONANCE
Filename = RBR-416 S_Carbon-1-1.jdf
Author = delta
Experiment = carbon.jxp
Sample_Id = RBR-416 S
Solvent = CHLOROFORM-D
Creation_Time = 22-MAY-2017 18:02:35
Revision_Time = 22-MAY-2017 19:46:46
Current_Time = 22-MAY-2017 19:46:48
Comment = single pulse decoupled gate
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 1.04333312[s]
X_Domain = 13C
X_Freq = 100.52530333[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 0.95846665[Hz]
X_Sweep = 31.40703518[kHz]
X_Sweep_Clipped = 25.12562814[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Clipped = FALSE
Scans = 2048
Total_Scans = 2048
Relaxation_Delay = 2[s]
Recvr_Gain = 50
Temp_Get = 19.4[dC]
X_90_Width = 9[us]
X_Acq_Time = 1.04333312[s]
X_Angle = 30[deg]
X_Atn = 4.6[dB]
X_Pulse = 3[us]
Irr_Atn_Dec = 20.55[dB]
Irr_Atn_Noe = 20.55[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 0.115[ms]
Decoupling = TRUE
Initial_Wait = 1[s]

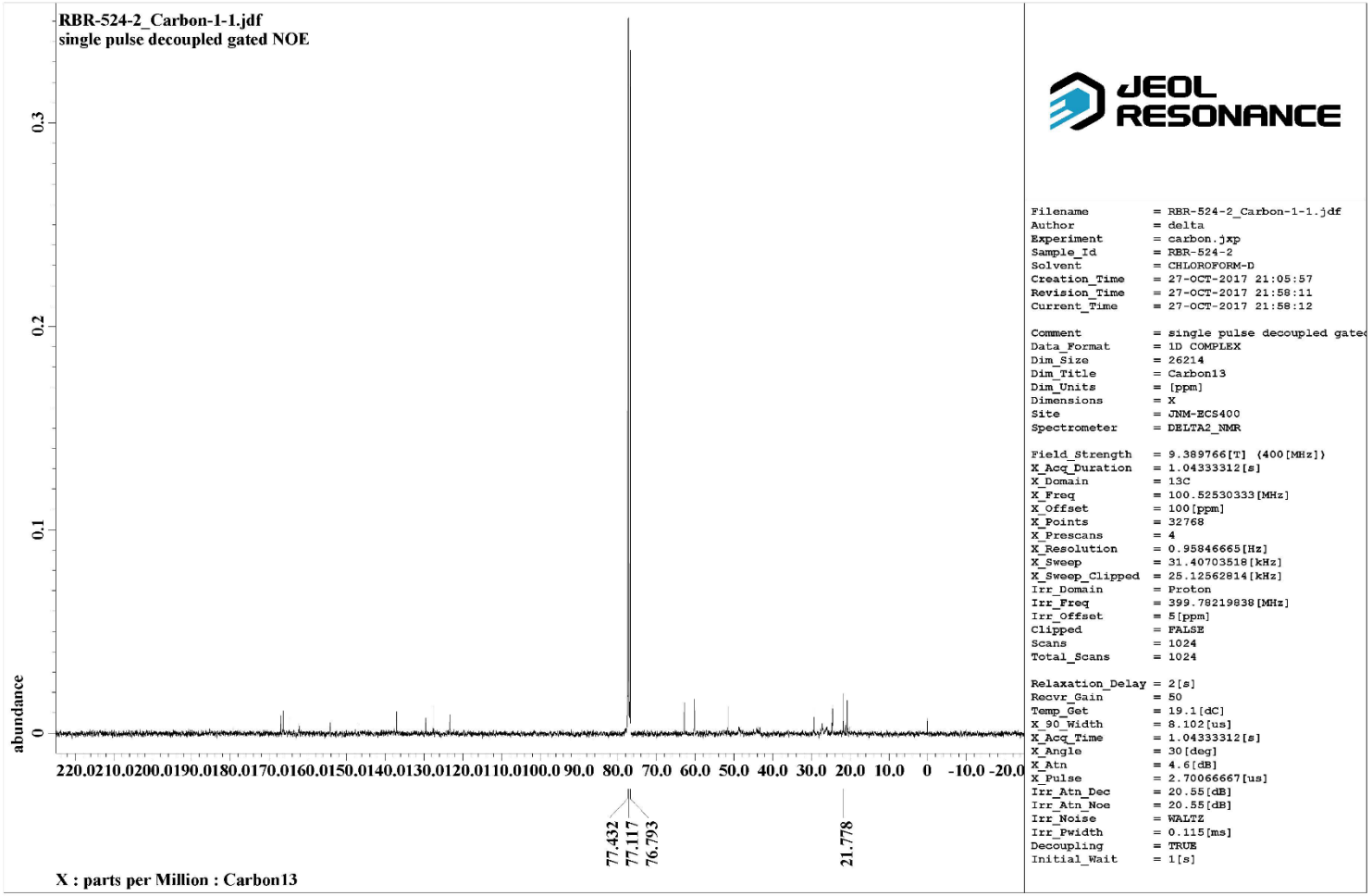
Compound **10**


RBR-503S2_Proton-2-1.jdf
single_pulse
abundance
X : parts per Million : Proton
10.01
27.38
40.30
11.30
141.12
12.24
1.00
3.572
3.554
3.537
3.520
3.346
3.227
3.208
3.191
3.174
2.548
2.534
2.451
2.440
2.408
2.276
2.158
2.135
2.124
1.914
1.758
1.747
1.724
1.326
1.277
1.206
1.189
1.184
1.167
1.150
1.135
1.117
1.100
-0.009
-0.017
Filename = RBR-503S2_Proton-2-1.jdf
Author = delta
Experiment = proton.jxp
Sample_Id = RBR-503S2
Solvent = CHLOROFORM-D
Creation_Time = 1-AUG-2017 15:17:57
Revision_Time = 1-AUG-2017 15:19:08
Current_Time = 1-AUG-2017 15:19:09
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 4074
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 2.18365952[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 16384
X_Prescans = 1
X_Resolution = 0.45794685[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 44
Temp_Get = 20.2[dC]
X_90_Width = 11[us]
X_Acq_Time = 2.18365952[s]
X_Angle = 45[deg]
X_Atn = 0.99[dB]
X_Pulse = 5.5[us]
Irr_Mode = Off
Tri_Mode = Off
Dante_Presat = FALSE

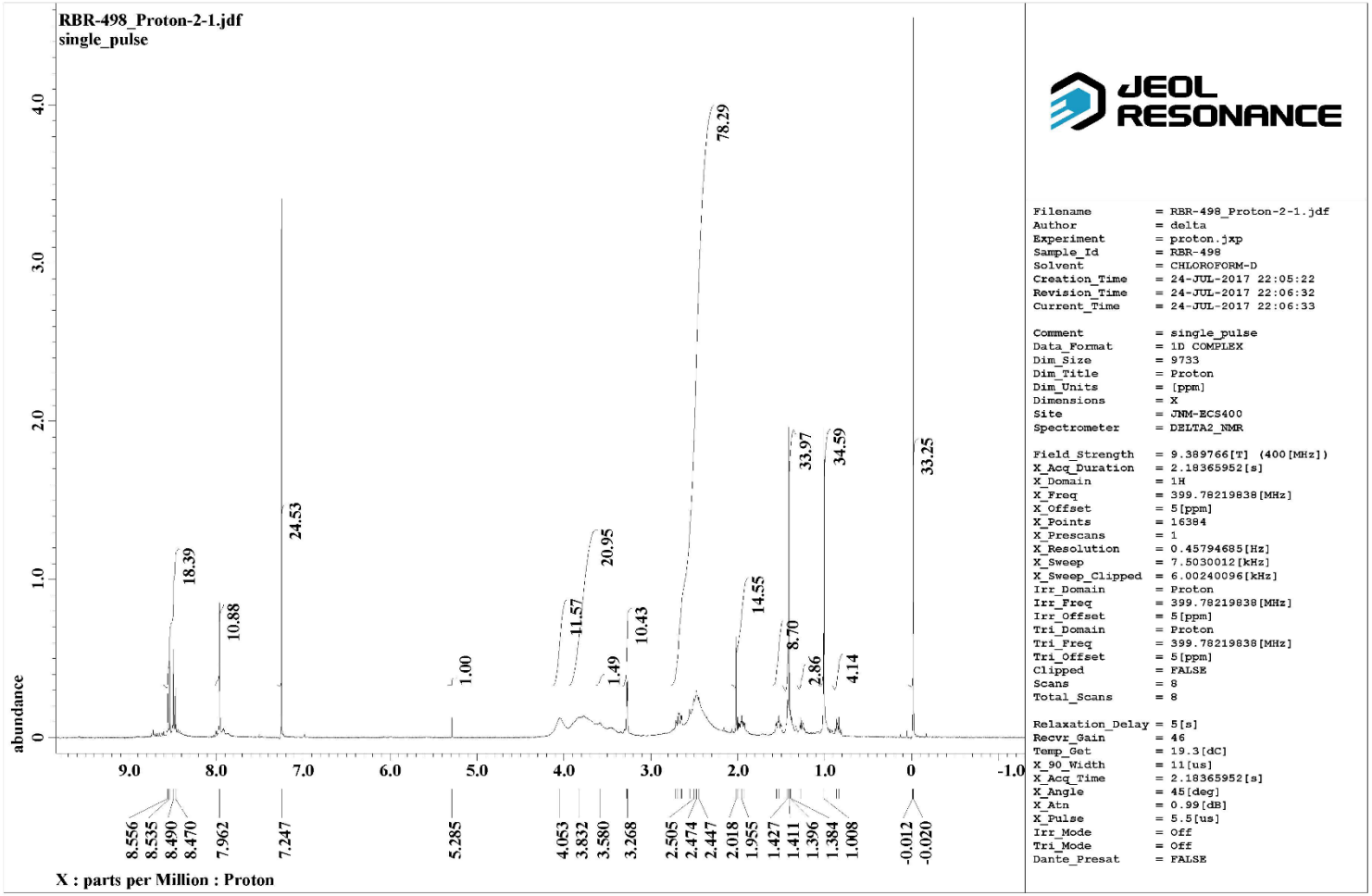

RBR-649_Carbon-1-1.jdf
single pulse decoupled gated NOE
abundance
0.3
0.2
0.1
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
200.771
198.244
77.432
77.117
76.793
67.535
57.819
45.958
42.001
40.571
27.871
22.808
22.617
19.328
14.446
12.778
X : parts per Million : Carbon13
JEOL RESONANCE
Filename = RBR-649_Carbon-1-1.jdf
Author = delta
Experiment = carbon.jxp
Sample_Id = RBR-649
Solvent = CHLOROFORM-D
Creation_Time = 6-FEB-2018 18:05:17
Revision_Time = 6-FEB-2018 18:57:31
Current_Time = 6-FEB-2018 18:57:34
Comment = single pulse decoupled gate
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 1.04333312[s]
X_Domain = 13C
X_Freq = 100.52530333[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 0.95846665[Hz]
X_Sweep = 31.40703518[kHz]
X_Sweep_Clipped = 25.12562814[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Clipped = FALSE
Scans = 1024
Total_Scans = 1024
Relaxation_Delay = 2[s]
Recvr_Gain = 50
Temp_Get = 20.1[dC]
X_90_Width = 8.102[us]
X_Acq_Time = 1.04333312[s]
X_Angle = 30[deg]
X_Atn = 4.6[dB]
X_Pulse = 2.70066667[us]
Irr_Atn_Dec = 20.55[dB]
Irr_Atn_Noe = 20.55[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 0.115[ms]
Decoupling = TRUE
Initial_Wait = 1[s]

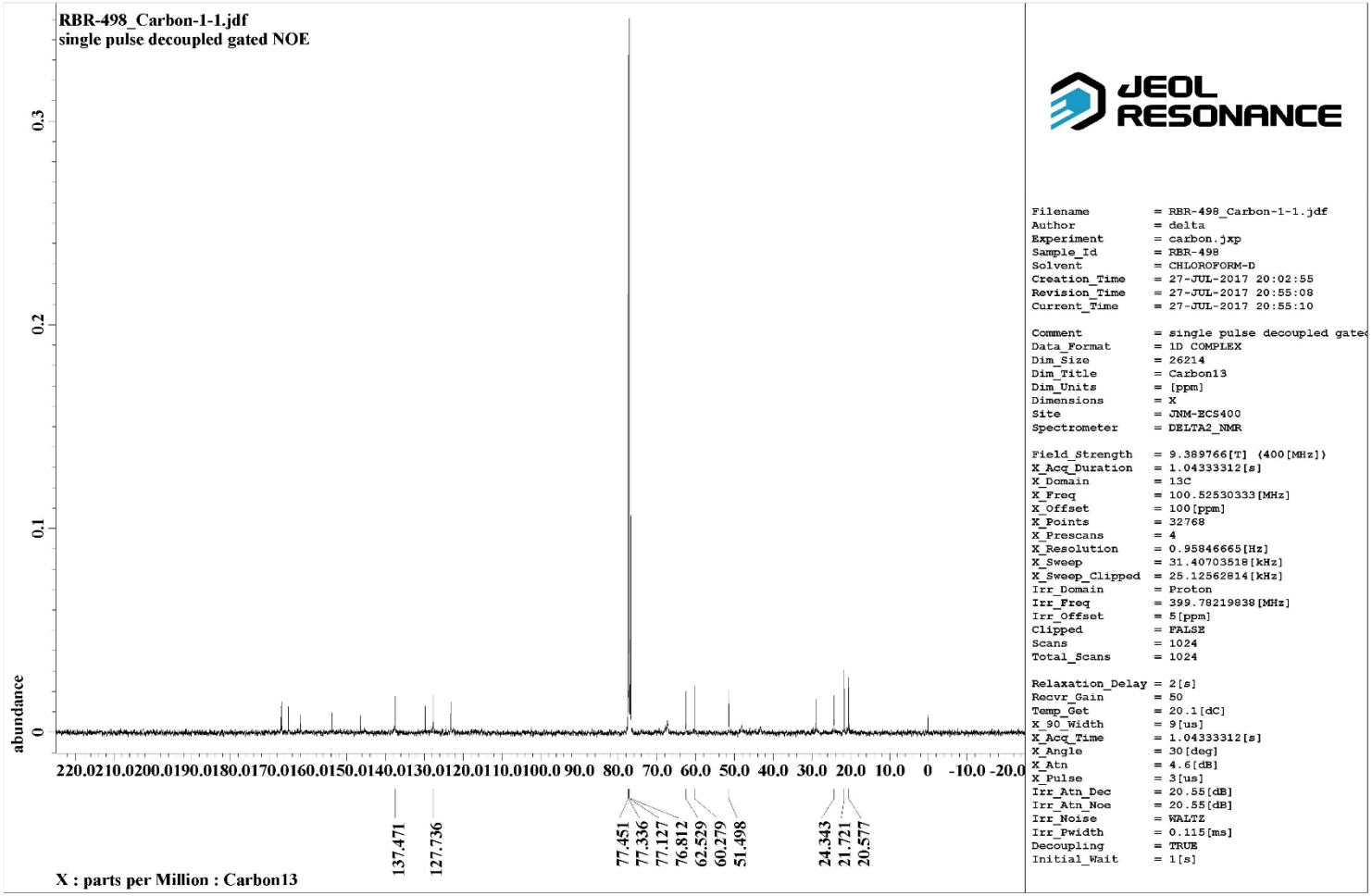
BTPhen ligand **12**



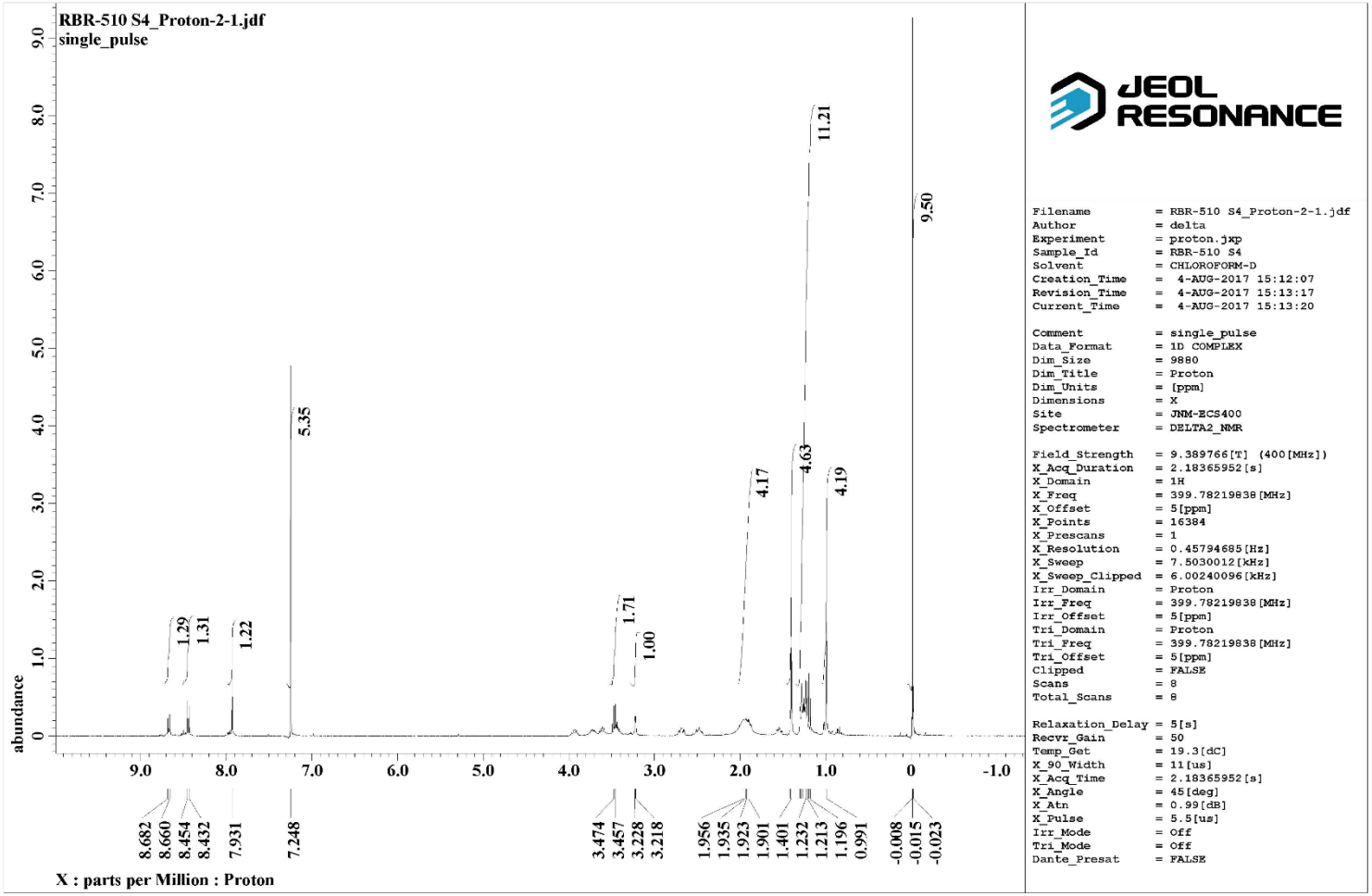

RBR-524-2_Carbon-1-1.jdf
single pulse decoupled gated NOE
abundance
0.3
0.2
0.1
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
77.432
77.117
76.793
21.778
X : parts per Million : Carbon13
JEOL RESONANCE
Filename = RBR-524-2_Carbon-1-1.jdf
Author = delta
Experiment = carbon.jxp
Sample_Id = RBR-524-2
Solvent = CHLOROFORM-D
Creation_Time = 27-OCT-2017 21:05:57
Revision_Time = 27-OCT-2017 21:58:11
Current_Time = 27-OCT-2017 21:58:12
Comment = single pulse decoupled gate
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 1.04333312[s]
X_Domain = 13C
X_Freq = 100.52530333[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 0.95846665[Hz]
X_Sweep = 31.40703518[kHz]
X_Sweep_Clipped = 25.12562814[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Clipped = FALSE
Scans = 1024
Total_Scans = 1024
Relaxation_Delay = 2[s]
Recvr_Gain = 50
Temp_Get = 19.1[dC]
X_90_Width = 8.102[us]
X_Acq_Time = 1.04333312[s]
X_Angle = 30[deg]
X_Atn = 4.6[dB]
X_Pulse = 2.70066667[us]
Irr_Atn_Dec = 20.55[dB]
Irr_Atn_Noe = 20.55[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 0.115[ms]
Decoupling = TRUE
Initial_Wait = 1[s]

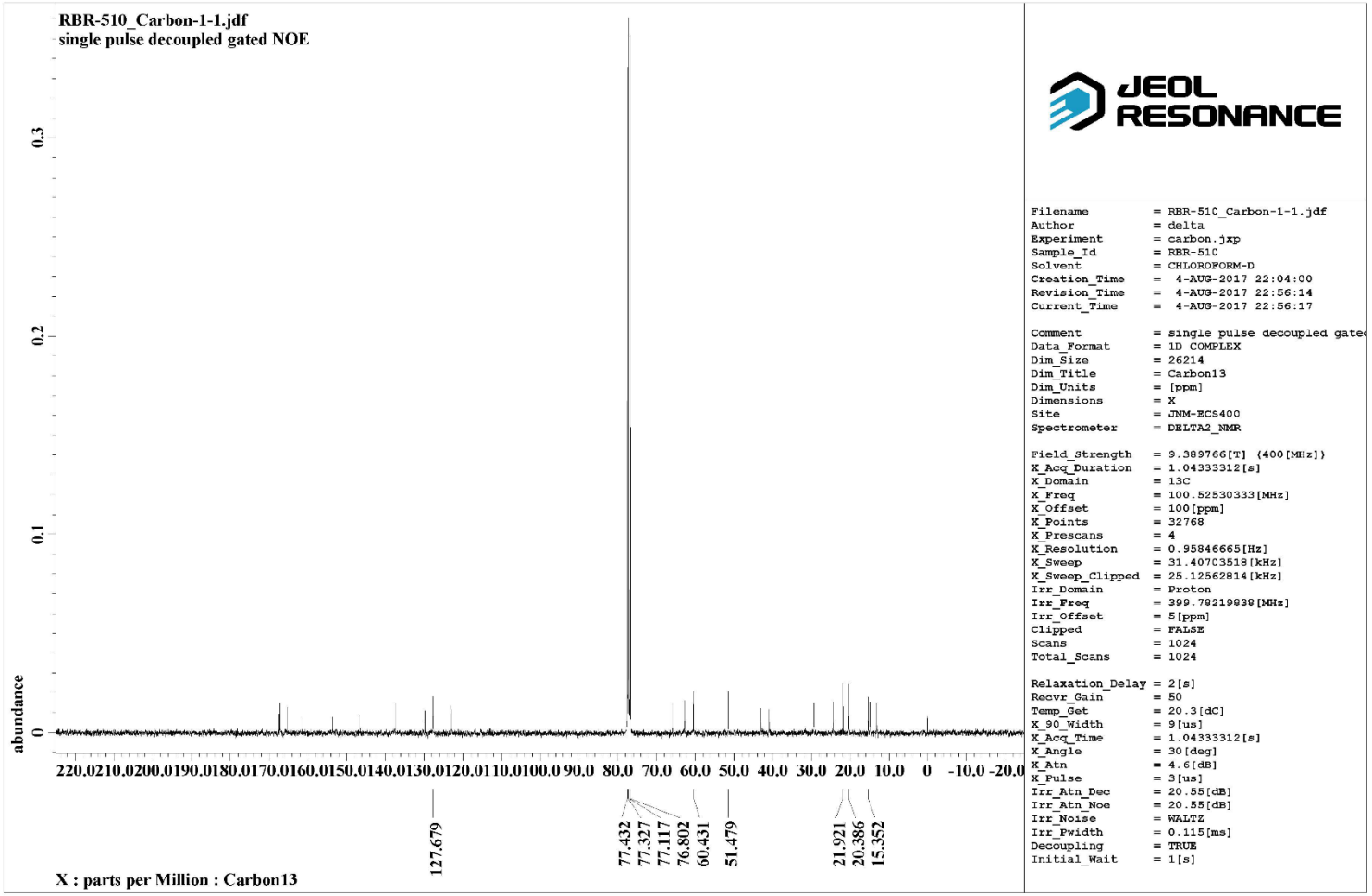
BTPhen ligand **13**



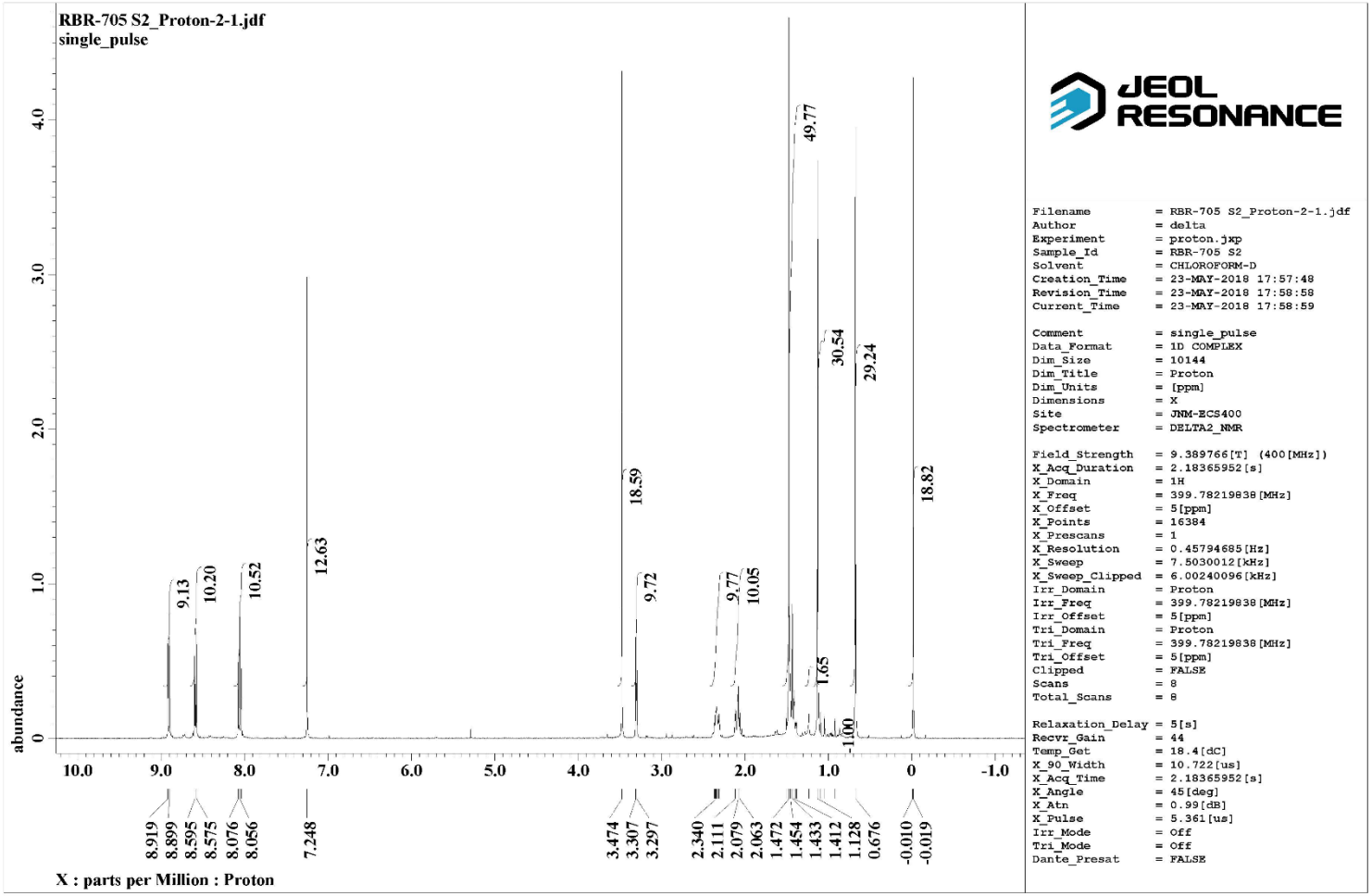

RBR-498_Carbon-1-1.jdf
single pulse decoupled gated NOE
abundance
0.3
0.2
0.1
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
137.471
127.736
77.451
77.336
77.127
76.812
62.529
60.279
51.498
24.343
21.721
20.577
X : parts per Million : Carbon13
JEOL RESONANCE
Filename = RBR-498_Carbon-1-1.jdf
Author = delta
Experiment = carbon.jxp
Sample_Id = RBR-498
Solvent = CHLOROFORM-D
Creation_Time = 27-JUL-2017 20:02:55
Revision_Time = 27-JUL-2017 20:55:08
Current_Time = 27-JUL-2017 20:55:10
Comment = single pulse decoupled gate
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 1.04333312[s]
X_Domain = 13C
X_Freq = 100.52530333[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 0.95846665[Hz]
X_Sweep = 31.40703518[kHz]
X_Sweep_Clipped = 25.12562814[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Clipped = FALSE
Scans = 1024
Total_Scans = 1024
Relaxation_Delay = 2[s]
Recvr_Gain = 50
Temp_Get = 20.1[dC]
X_90_Width = 9[us]
X_Acq_Time = 1.04333312[s]
X_Angle = 30[deg]
X_Atn = 4.6[dB]
X_Pulse = 3[us]
Irr_Atn_Dec = 20.55[dB]
Irr_Atn_Noe = 20.55[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 0.115[ms]
Decoupling = TRUE
Initial_Wait = 1[s]

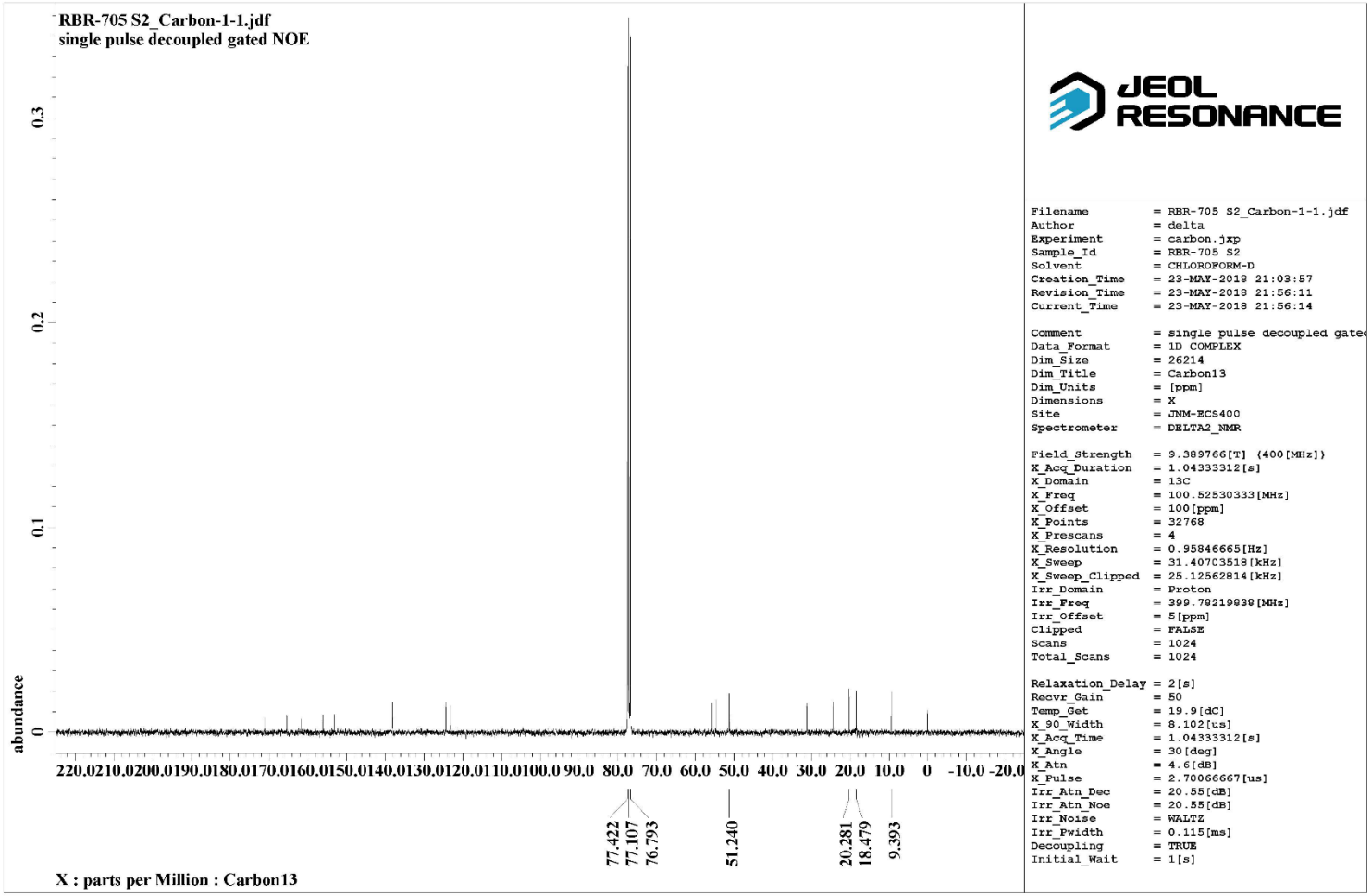
BTPhen ligand **14**



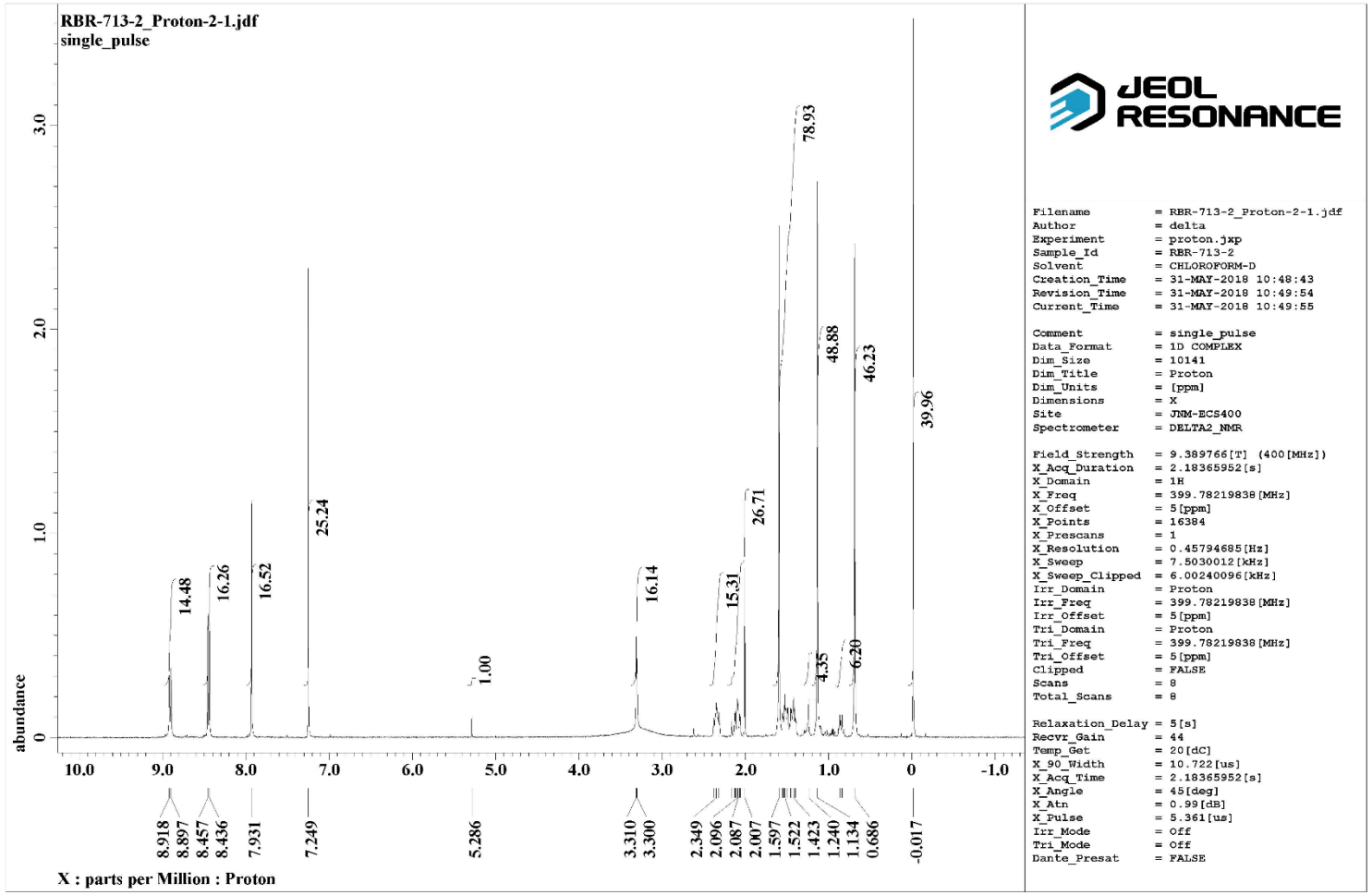

RBR-510_Carbon-1-1.jdf
single pulse decoupled gated NOE
abundance
0
0.1
0.2
0.3
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
127.679
77.432
77.327
77.117
76.802
60.431
51.479
21.921
20.386
15.352
X : parts per Million : Carbon13
JEOL RESONANCE
Filename = RBR-510_Carbon-1-1.jdf
Author = delta
Experiment = carbon.jxp
Sample_Id = RBR-510
Solvent = CHLOROFORM-D
Creation_Time = 4-AUG-2017 22:04:00
Revision_Time = 4-AUG-2017 22:56:14
Current_Time = 4-AUG-2017 22:56:17
Comment = single pulse decoupled gate
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 1.04333312[s]
X_Domain = 13C
X_Freq = 100.52530333[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 0.95846665[Hz]
X_Sweep = 31.40703518[kHz]
X_Sweep_Clipped = 25.12562814[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Clipped = FALSE
Scans = 1024
Total_Scans = 1024
Relaxation_Delay = 2[s]
Recvr_Gain = 50
Temp_Get = 20.3[dC]
X_90_Width = 9[us]
X_Acq_Time = 1.04333312[s]
X_Angle = 30[deg]
X_Atn = 4.6[dB]
X_Pulse = 3[us]
Irr_Atn_Dec = 20.55[dB]
Irr_Atn_Noe = 20.55[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 0.115[ms]
Decoupling = TRUE
Initial_Wait = 1[s]

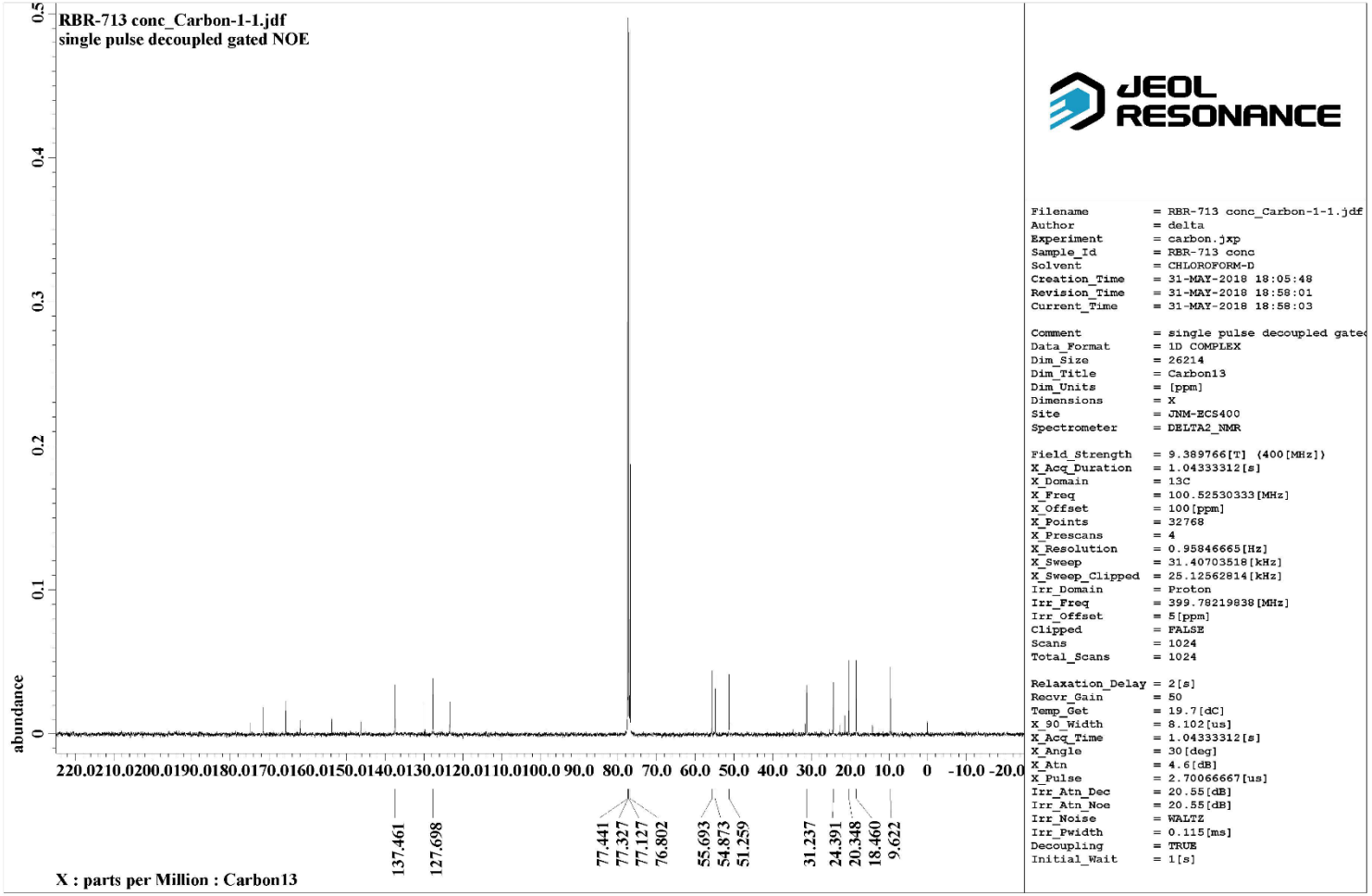
CA-BTBP ligand **17**




RBR-705 S2_Carbon-1-1.jdf
single pulse decoupled gated NOE
abundance
0.3
0.2
0.1
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
77.422
77.107
76.793
51.240
20.281
18.479
9.393
X : parts per Million : Carbon13
JEOL RESONANCE
Filename = RBR-705 S2_Carbon-1-1.jdf
Author = delta
Experiment = carbon.jxp
Sample_Id = RBR-705 S2
Solvent = CHLOROFORM-D
Creation_Time = 23-MAY-2018 21:03:57
Revision_Time = 23-MAY-2018 21:56:11
Current_Time = 23-MAY-2018 21:56:14
Comment = single pulse decoupled gate
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 1.04333312[s]
X_Domain = 13C
X_Freq = 100.52530333[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 0.95846665[Hz]
X_Sweep = 31.40703518[kHz]
X_Sweep_Clipped = 25.12562814[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Clipped = FALSE
Scans = 1024
Total_Scans = 1024
Relaxation_Delay = 2[s]
Recvr_Gain = 50
Temp_Get = 19.9[dC]
X_90_Width = 8.102[us]
X_Acq_Time = 1.04333312[s]
X_Angle = 30[deg]
X_Atn = 4.6[dB]
X_Pulse = 2.70066667[us]
Irr_Atn_Dec = 20.55[dB]
Irr_Atn_Noe = 20.55[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 0.115[ms]
Decoupling = TRUE
Initial_Wait = 1[s]

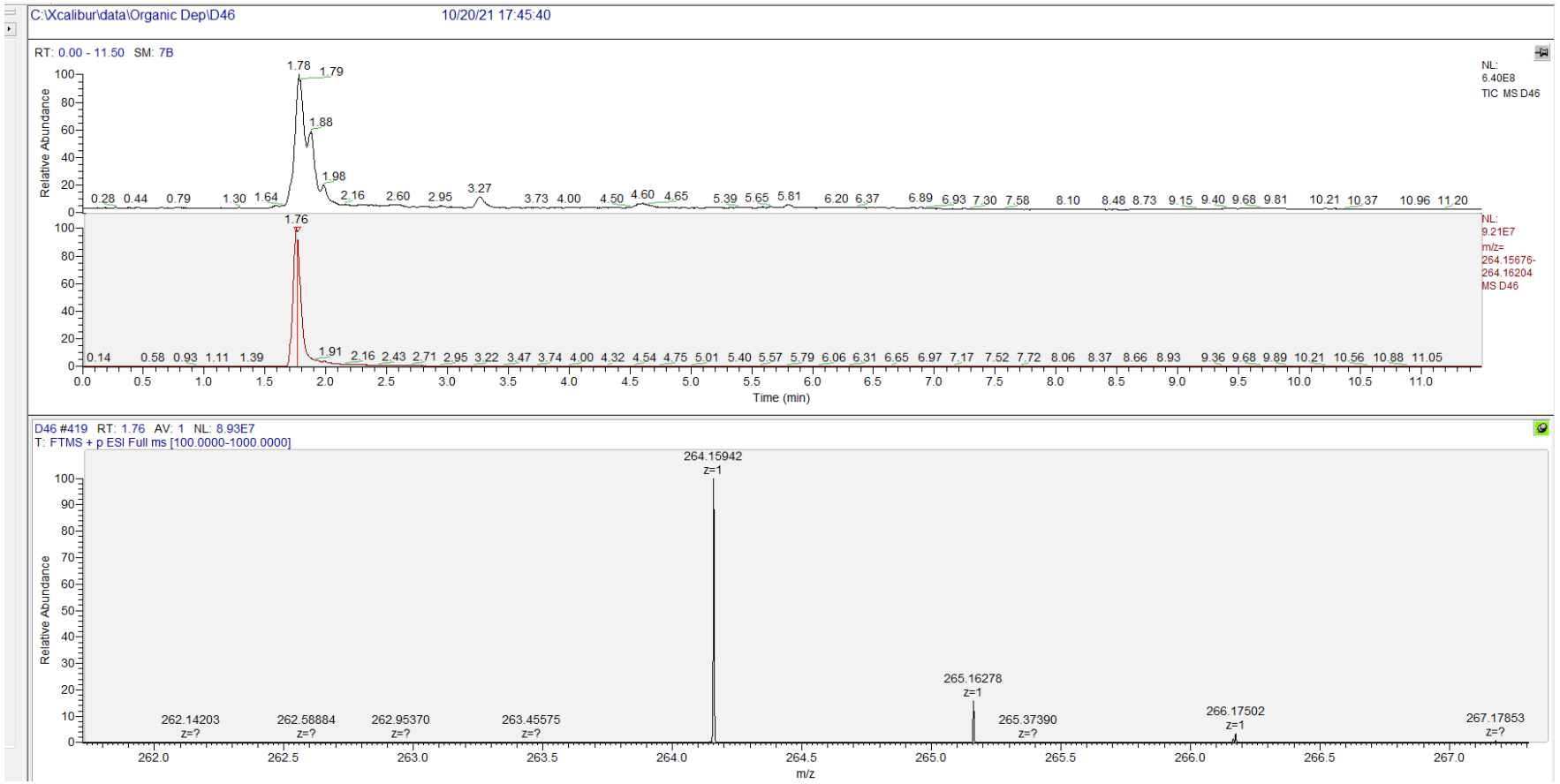
CA-BTPhen ligand **18**



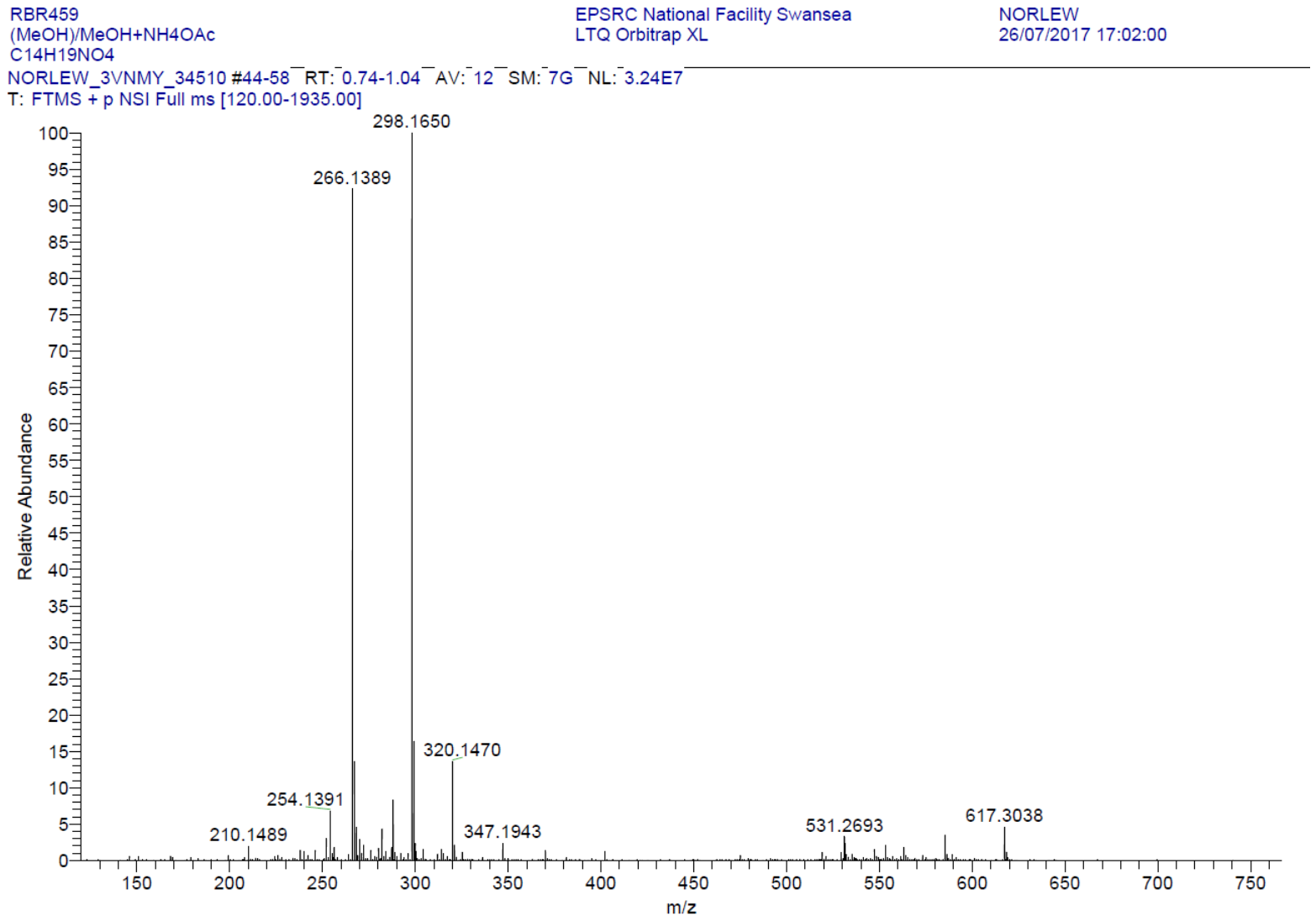

RBR-713 conc_Carbon-1-1.jdf
single pulse decoupled gated NOE
abundance
0.5
0.4
0.3
0.2
0.1
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
137.461
127.698
77.441
77.327
77.127
76.802
55.693
54.873
51.259
31.237
24.391
20.348
18.460
9.622
X : parts per Million : Carbon13
JEOL RESONANCE
Filename = RBR-713 conc_Carbon-1-1.jdf
Author = delta
Experiment = carbon.jxp
Sample_Id = RBR-713 conc
Solvent = CHLOROFORM-D
Creation_Time = 31-MAY-2018 18:05:48
Revision_Time = 31-MAY-2018 18:58:01
Current_Time = 31-MAY-2018 18:58:03
Comment = single pulse decoupled gate
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 1.04333312[s]
X_Domain = 13C
X_Freq = 100.52530333[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 0.95846665[Hz]
X_Sweep = 31.40703518[kHz]
X_Sweep_Clipped = 25.12562814[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Clipped = FALSE
Scans = 1024
Total_Scans = 1024
Relaxation_Delay = 2[s]
Recvr_Gain = 50
Temp_Get = 19.7[dC]
X_90_Width = 8.102[us]
X_Acq_Time = 1.04333312[s]
X_Angle = 30[deg]
X_Atn = 4.6[dB]
X_Pulse = 2.70066667[us]
Irr_Atn_Dec = 20.55[dB]
Irr_Atn_Noe = 20.55[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 0.115[ms]
Decoupling = TRUE
Initial_Wait = 1[s]

3: Mass Spectra

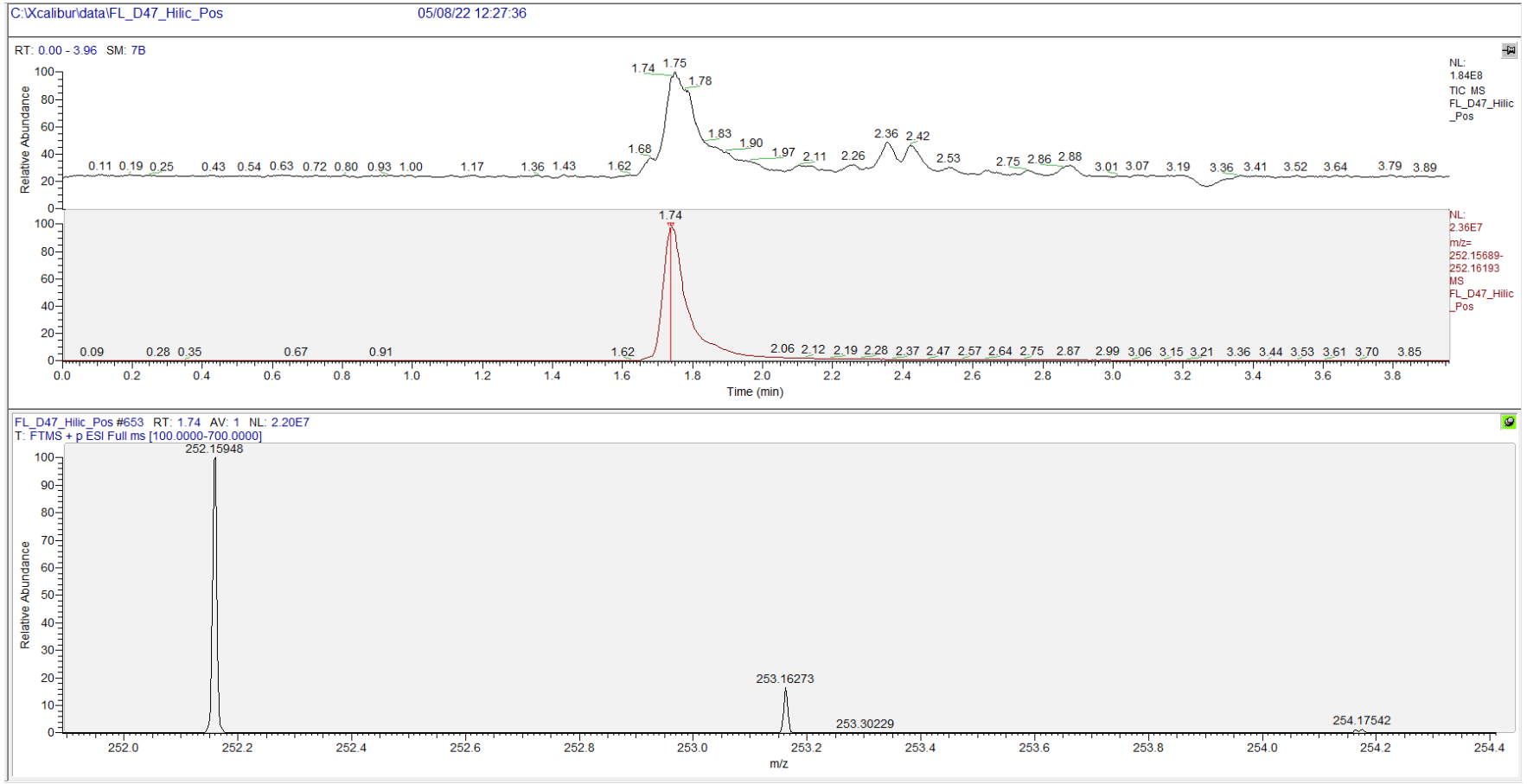
Compound **8**



Compound **9**


RBR459
(MeOH)/MeOH+NH4OAc
C14H19NO4
EPSRC National Facility Swansea
LTQ Orbitrap XL
NORLEW
26/07/2017 17:02:00
NORLEW_3VNMY_34510 #44-58 RT: 0.74-1.04 AV: 12 SM: 7G NL: 3.24E7
T: FTMS + p NSI Full ms [120.00-1935.00]
298.1650
266.1389
320.1470
254.1391
210.1489
347.1943
531.2693
617.3038
Relative Abundance
m/z

Compound **10**


C:\Xcalibur\data\FL_D47_Hilic_Pos 05/08/22 12:27:36
RT: 0.00 - 3.96 SM: 7B
Relative Abundance
NL: 1.84E8 TIC MS FL_D47_Hilic_Pos
NL: 2.36E7 m/z= 252.15689-252.16193 MS FL_D47_Hilic_Pos
Time (min)
FL_D47_Hilic_Pos #653 RT: 1.74 AV: 1 NL: 2.20E7
T: FTMS + p ESI Full ms [100.0000-700.0000]
252.15948
253.16273
253.30229
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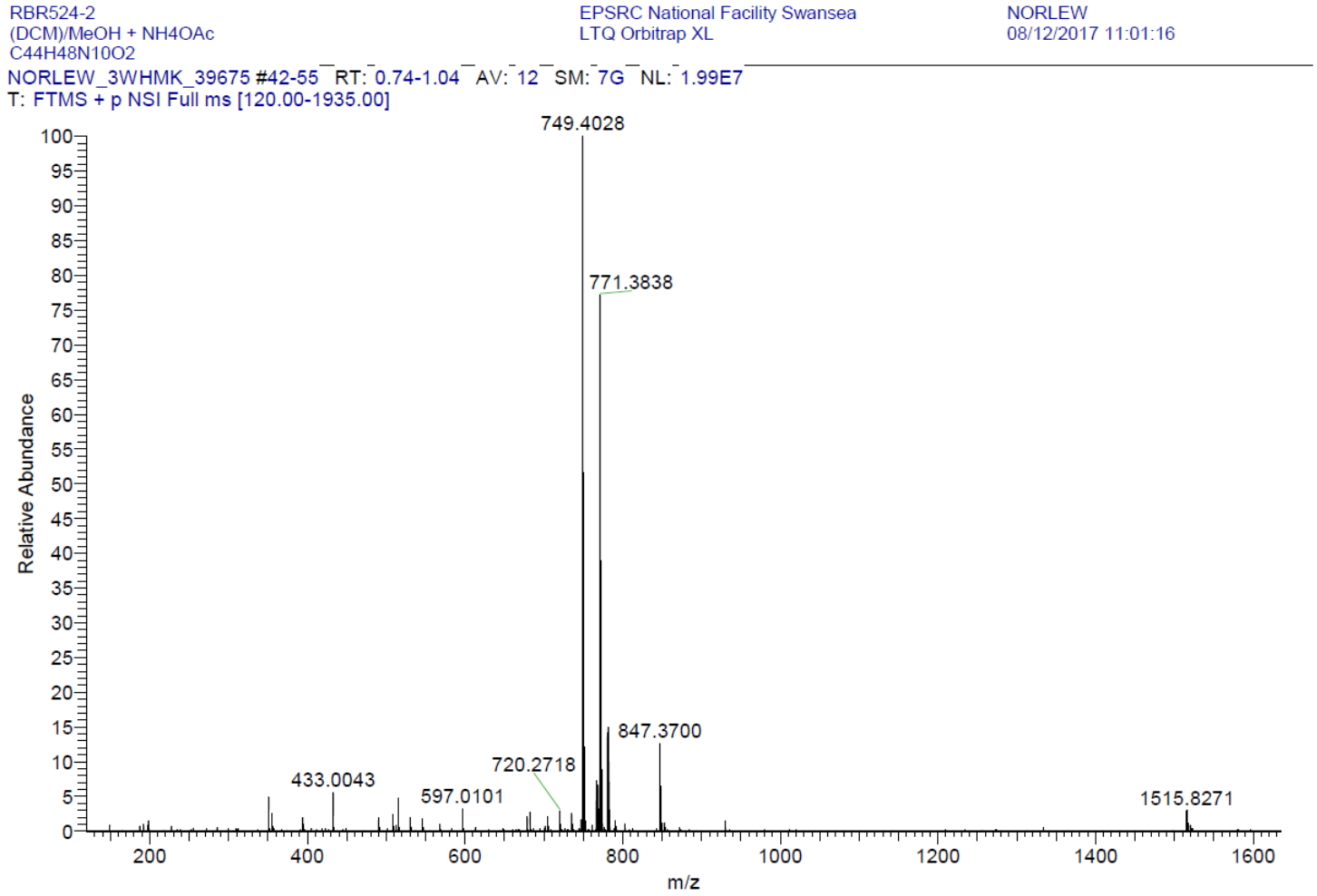
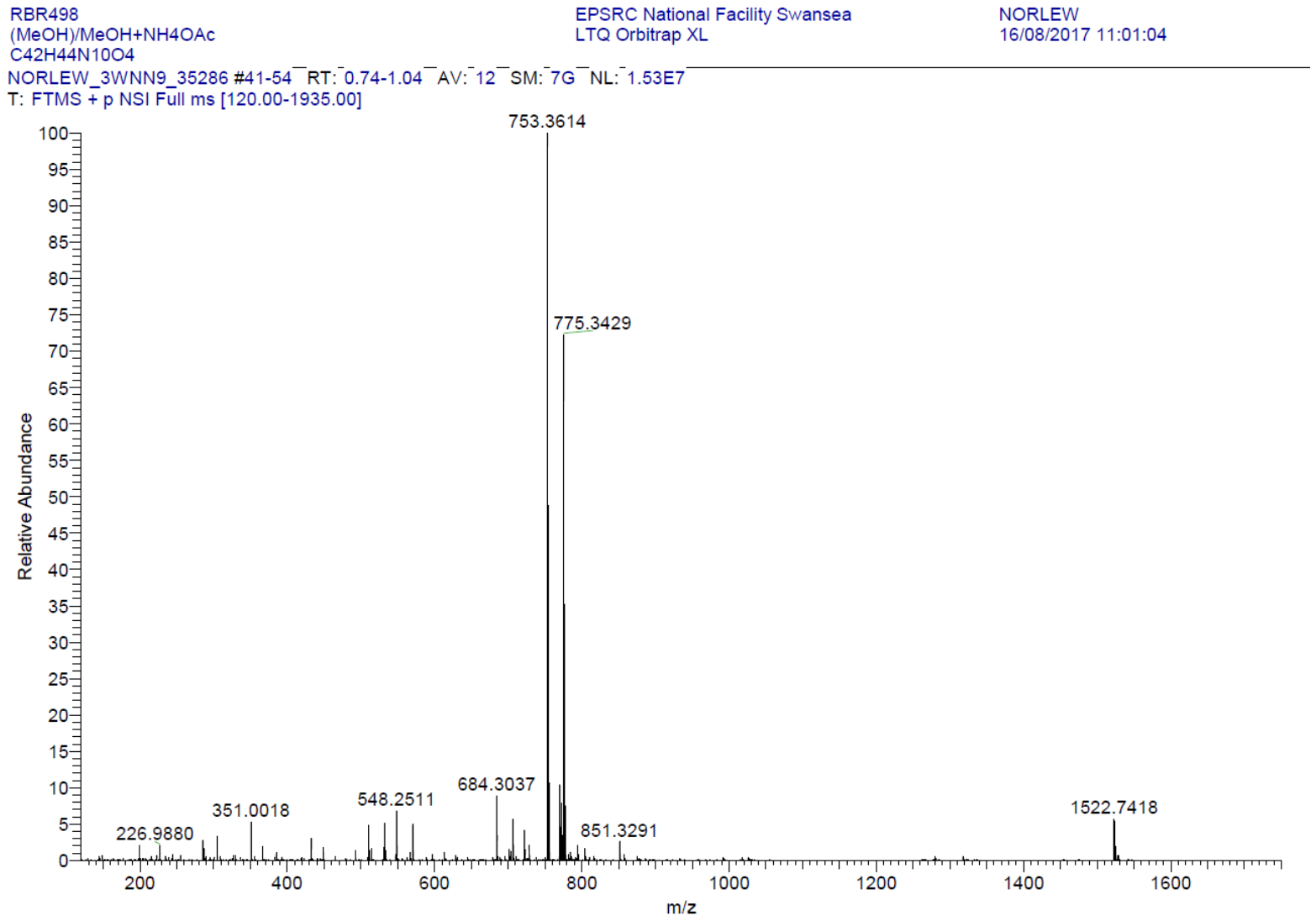
m/z

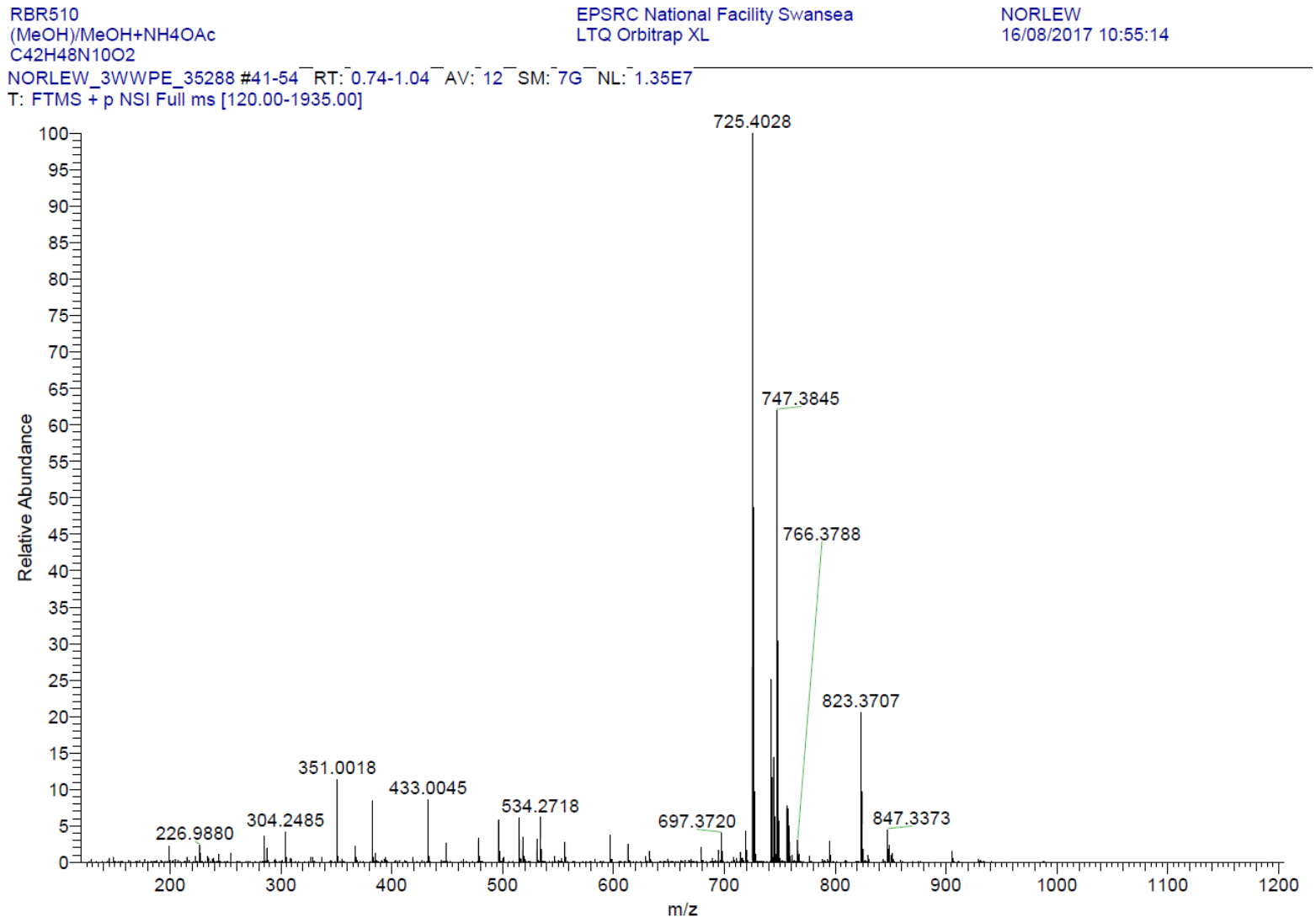
BTPhen ligand **12**



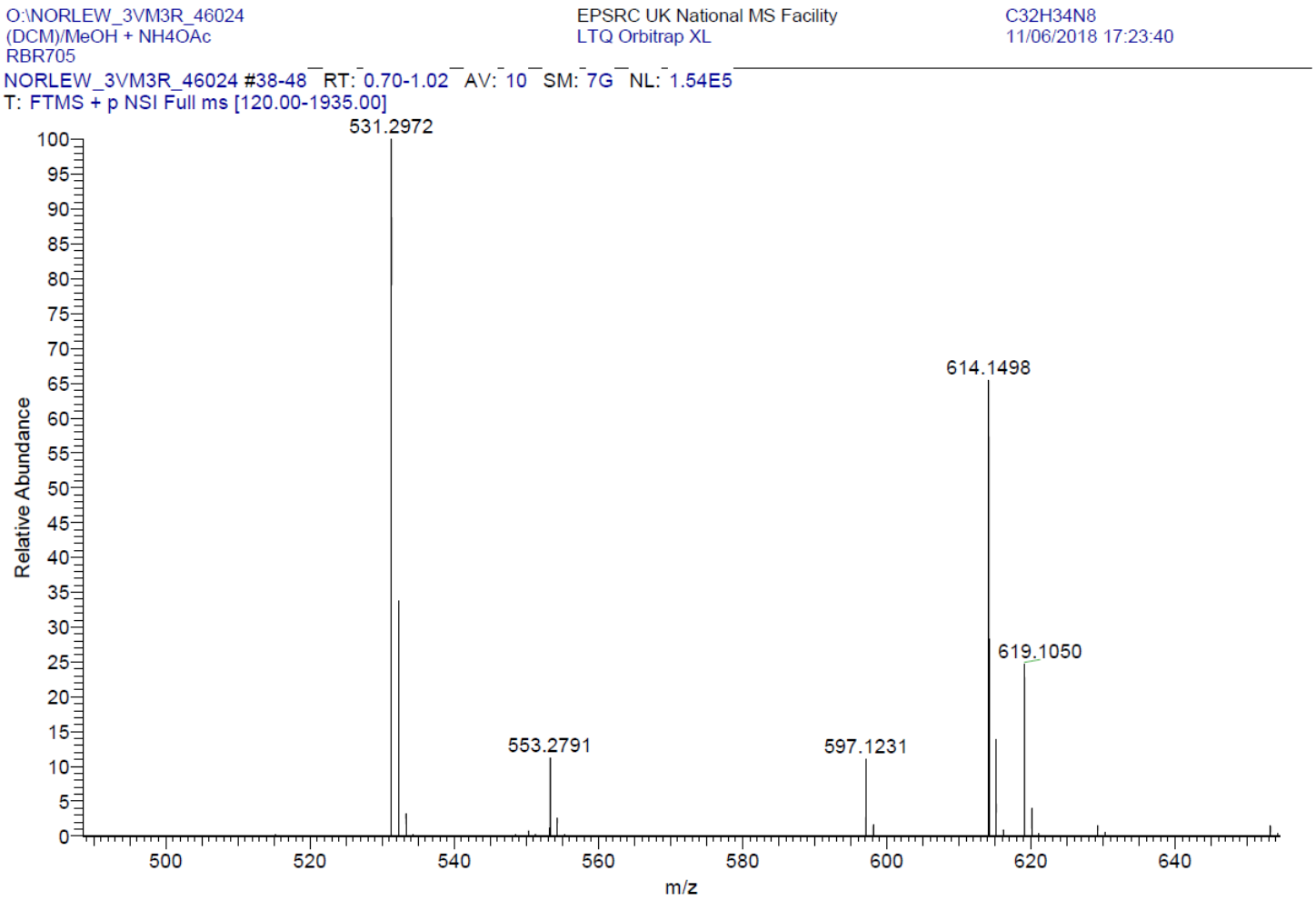
BTPhen ligand **13**



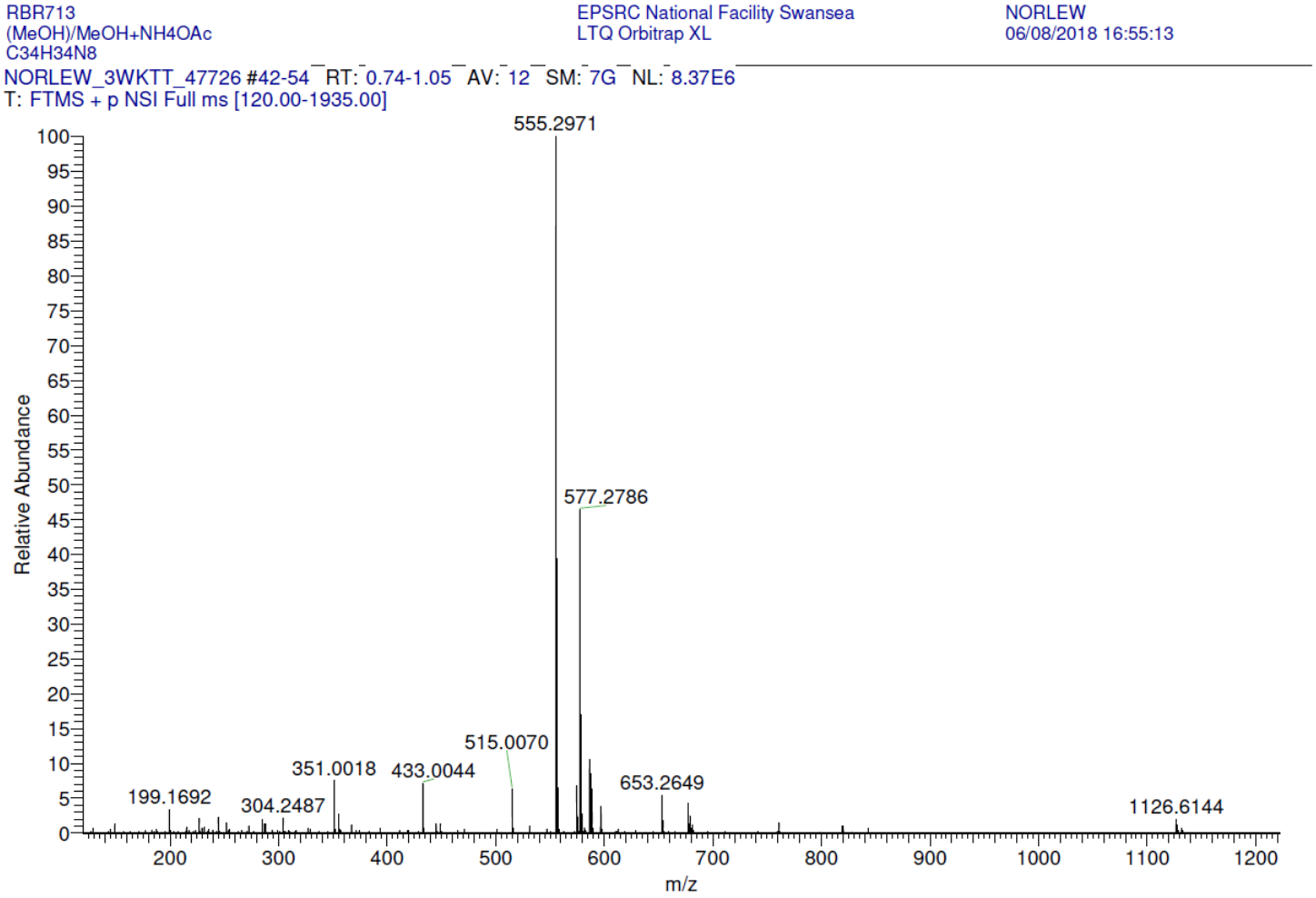
BTPhen ligand **14**



CA-BTBP ligand **17**



CA-BTPhen ligand **18**



4: Solubility Measurements

Table 1. Measured solubilities of ligands **12**–**14**, **17** and **18** in 1-octanol.

Ligand	Solubility (mM)
12	40.9
13	41.8
14	50.4
CA-BTP **4**	200[a]
CA-BTBP **17**	58.1
CA-BTPhen **18**	18.6[b]

[a] Taken from ref. 9. [b] Taken from ref. 5.

5: Calculated Log*P* Values

Table 2. Calculated Log*P* (cLog*P*) values of ligands **12**–**14**, CA-BTP **4**, CA-BTBP **17** and CA-BTPhen **18** in the 2-phase system water/1-octanol.

Ligand	cLog*P*[a]	cLog*P*[b]
12	5.95 ± 1.43	5.15
13	3.84 ± 1.47	3.45
14	5.12 ± 1.42	5.12
CA-BTP **4**	6.91 ± 0.62	4.35
CA-BTBP **17**	7.19 ± 0.63	4.89
CA-BTPhen **18**	7.69 ± 1.40	5.50
$CyMe_4$-BTBP **2**	8.59 ± 0.63	5.56
$CyMe_4$-BTPhen **3**	9.09 ± 1.40	6.03

[a] Calculated using ACD-Labs ChemSketch software (www.acdlabs.com).

[b] Calculated using SwissADME (www.swissadme.ch).

6: Solvent Extraction Studies

6.1 Extraction Studies for BTPhen Ligand 12

Table 3. Extraction of Am(III) and Eu(III) by 10 mM BTPhen ligand **12** into 1-octanol as a function of the initial nitric acid concentration of the aqueous phase. Results are from gamma spectrometry (*D* = distribution ratio, SF = separation factor, contact time: 60 min, temperature: 22 °C ± 1 °C).

[HNO_3] initial (mol/L)	D_{Am}	D_{Eu}	$SF_{Am/Eu}$
0.01	2.0	0.18	11.4
0.11	18.9	0.45	42.1
0.30	44.2	0.87	51.1
0.70	54.9	0.75	73.6
1.03	55.2	0.59	94.1
3.11	43.0	0.19	230.9

Table 4. Extraction of Am(III) and Cm(III) by 10 mM BTPhen ligand **12** into 1-octanol as a function of the initial nitric acid concentration of the aqueous phase. Results are from alpha spectrometry (*D* = distribution ratio, SF = separation factor, contact time: 60 min, temperature: 22 °C ± 1 °C).

[HNO_3] initial (mol/L)	D_{Am}	D_{Cm}	$SF_{Am/Cm}$
0.01	1.6	1.2	1.4
0.11	9.5	9.1	1.1
0.30	28.1	24.4	1.2
0.70	16.4	14.8	1.1
1.03	19.3	16.8	1.2
3.11	31.6	16.6	1.9

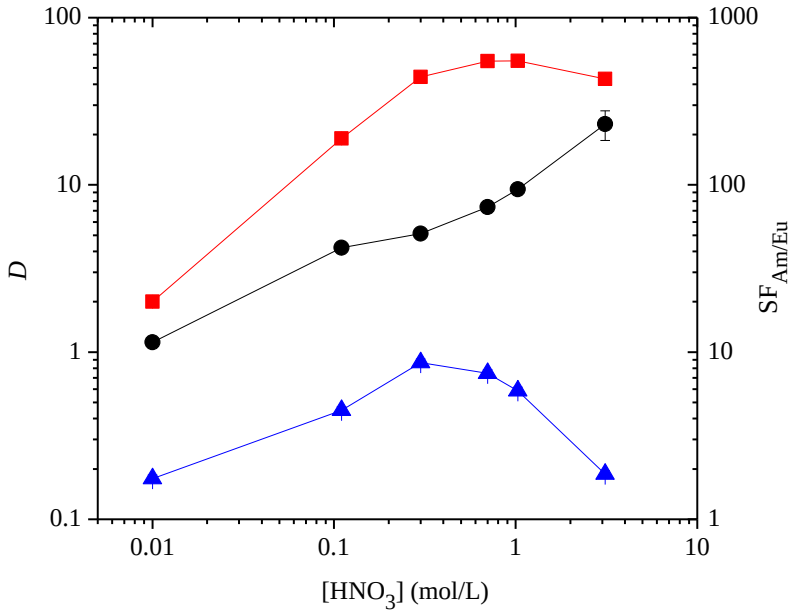


Figure 2. Extraction of Am(III) and Eu(III) by BTPhen ligand **12** (0.01 M) into 1-octanol as a function of the initial nitric acid concentration of the aqueous phase (D = distribution ratio, SF = separation factor, ■ = D_{Am}, ▲ = D_{Eu}, ● = $SF_{Am/Eu}$, contact time: 60 min, temperature: 22 °C ± 1 °C).

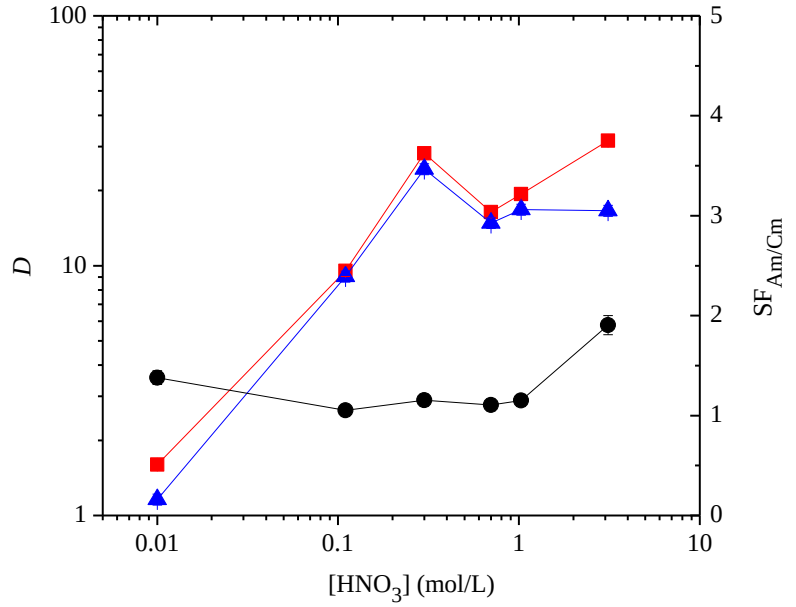


Figure 3. Extraction of Am(III) and Cm(III) by BTPhen ligand **12** (0.01 M) into 1-octanol as a function of the initial nitric acid concentration of the aqueous phase (D = distribution ratio, SF = separation factor, ■ = D_{Am}, ▲ = D_{Cm}, ● = $SF_{Am/Cm}$, contact time: 60 min, temperature: 22 °C ± 1 °C).

Table 5. Extraction of Am(III) and Eu(III) from 1.03 M nitric acid by 10 mM BTPhen ligand **12** into 1-octanol as a function of contact time. Results are from gamma spectrometry (*D* = distribution ratio, SF = separation factor, temperature: 22 °C ± 1 °C).

Contact time (min)	D_{Am}	D_{Eu}	$SF_{Am/Eu}$
5	59.8	0.89	67.4
10	59.9	0.87	69.1
15	66.9	0.91	73.5
30	67.8	0.87	78.1
60	121.7	1.72	70.8
120	74.1	0.89	82.9

Table 6. Extraction of Am(III) and Cm(III) from 1.03 M nitric acid by 10 mM BTPhen ligand **12** into 1-octanol as a function of contact time. Results are from alpha spectrometry (*D* = distribution ratio, SF = separation factor, temperature: 22 °C ± 1 °C).

Contact time (min)	D_{Am}	D_{Cm}	$SF_{Am/Cm}$
5	39.8	33.7	1.2
10	17.1	15.9	1.1
15	36.7	31.6	1.2
30	59.6	45.7	1.3
60	21.0	18.1	1.2
120	32.2	28.1	1.2

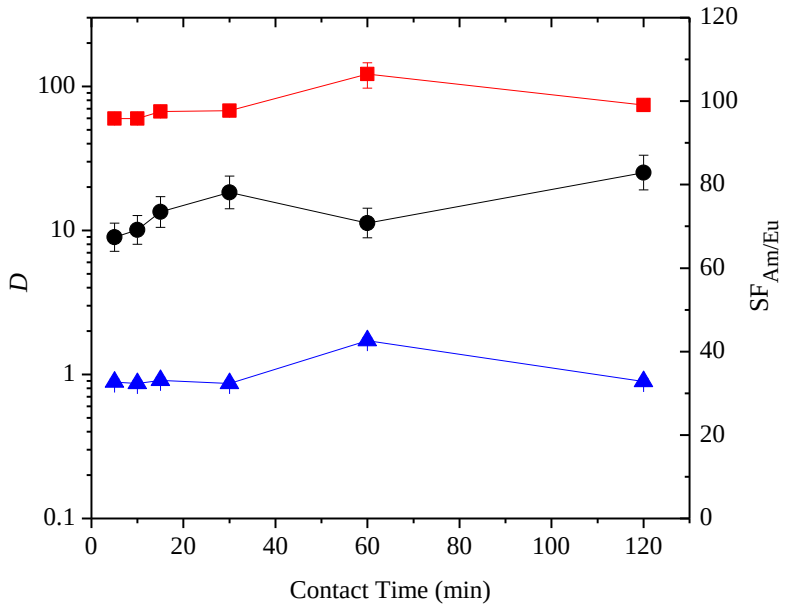


Figure 4. Extraction of Am(III) and Eu(III) from 1.03 M nitric acid by BTPhen ligand **12** (0.01 M) into 1-octanol as a function of contact time (*D* = distribution ratio, SF = separation factor, ■ = D_{Am}, ▲ = D_{Eu}, ● = $SF_{Am/Eu}$, temperature: 22 °C ± 1 °C).

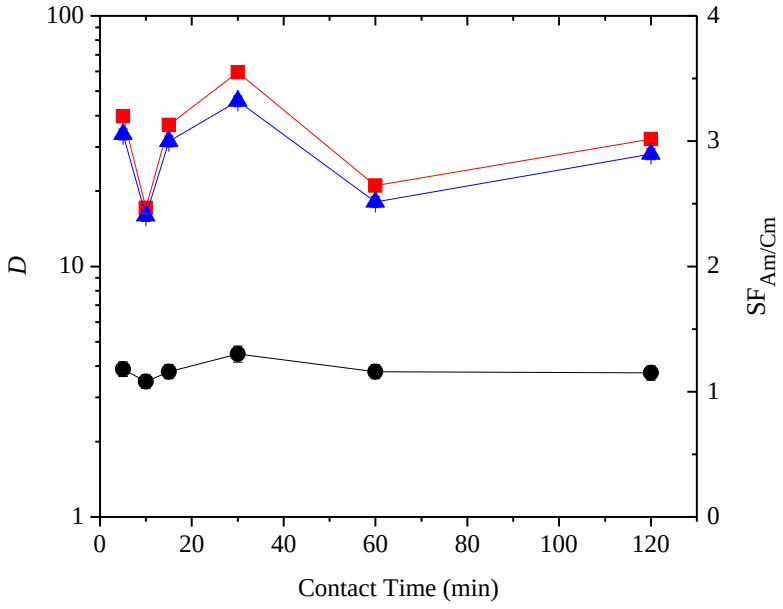


Figure 5. Extraction of Am(III) and Cm(III) from 1.03 M nitric acid by BTPhen ligand **12** (0.01 M) into 1-octanol as a function of contact time (*D* = distribution ratio, SF = separation factor, ■ = D_{Am}, ▲ = D_{Cm}, ● = $SF_{Am/Cm}$, temperature: 22 °C ± 1 °C).

Table 7. Extraction of Y(III) and all the trivalent lanthanides (except Pm) by 10 mM BTPhen ligand **12** into 1-octanol as a function of the initial nitric acid concentration of the aqueous phase. Results are from ICP-MS (*D* = distribution ratio, SF = separation factor, contact time: 60 min, temperature: 22 ºC ± 1 ºC).

[HNO_3] (mol/L)		0.01	0.11	0.30	0.70	1.03	3.11
Element	**Atomic Number**	*D*	*D*	*D*	*D*	*D*	*D*
Y	39	0.01	0.02	0.03	0.03	0.03	0.03
La	57	0.01	0.04	0.08	0.06	0.06	0.03
Ce	58	0.06	0.22	0.42	0.31	0.32	0.09
Pr	59	0.13	0.42	0.82	0.59	0.62	0.17
Nd	60	0.18	0.57	1.09	0.78	0.83	0.22
Sm	62	0.27	0.67	1.29	0.90	0.93	0.26
Eu	63	0.24	0.57	1.09	0.78	0.80	0.22
Gd	64	0.16	0.32	0.63	0.47	0.49	0.15
Tb	65	0.17	0.42	0.89	0.69	0.74	0.25
Dy	66	0.14	0.43	0.92	0.75	0.84	0.31
Ho	67	0.11	0.43	0.91	0.77	0.88	0.35
Er	68	0.10	0.46	0.98	0.81	0.93	0.40
Tm	69	0.09	0.51	0.97	0.73	0.80	0.36
Yb	70	0.09	0.68	1.06	0.62	0.62	0.26
Lu	71	0.11	0.70	0.99	0.47	0.43	0.16

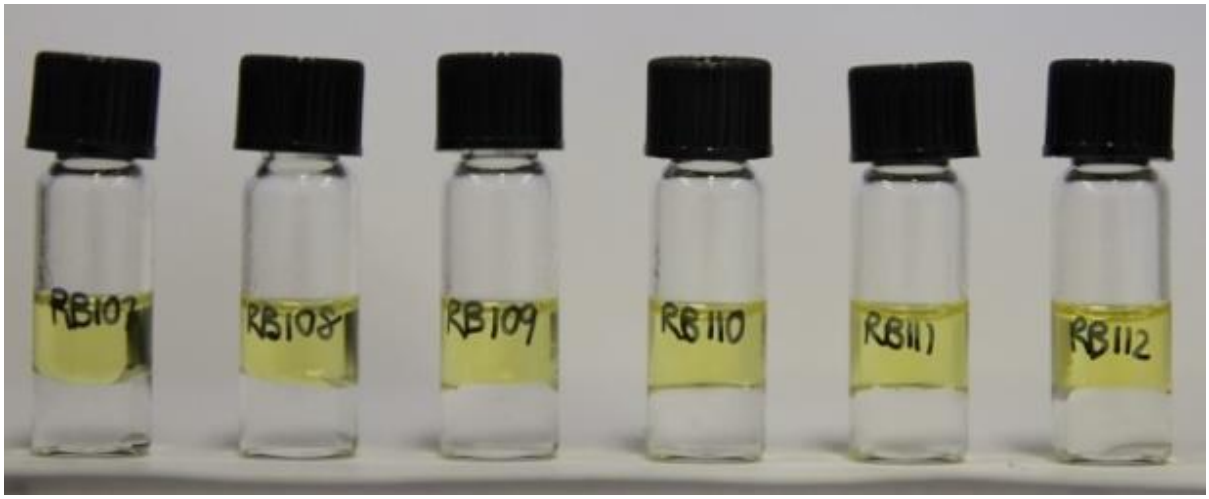


Figure 6. Photograph of the sample tubes from the extraction of Am(III), Cm(III) and Eu(III) by 10 mM BTPhen ligand **12** into 1-octanol as a function of the initial nitric acid concentration of the aqueous phase, with increasing [HNO_3] going from left to right.

6.2 Extraction Studies for BTPhen Ligand 13

Table 8. Extraction of Am(III) and Eu(III) by 10 mM BTPhen ligand **13** into 1-octanol as a function of the initial nitric acid concentration of the aqueous phase. Results are from gamma spectrometry (*D* = distribution ratio, SF = separation factor, contact time: 60 min, temperature: 22 °C ± 1 °C). Results from alpha spectrometry for ligand **13** were not obtained due to the precipitation observed during the extraction experiments.

[HNO_3] initial (mol/L)	**D_{Am}**	**D_{Eu}**	**$SF_{Am/Eu}$**
0.01	0.01	0.11	0.1
0.11	0.03	0.05	0.7
0.30	0.06	0.09	0.7
0.70	0.08	0.10	0.8
1.03	0.08	0.09	0.9
3.11	0.19	0.04	5.1

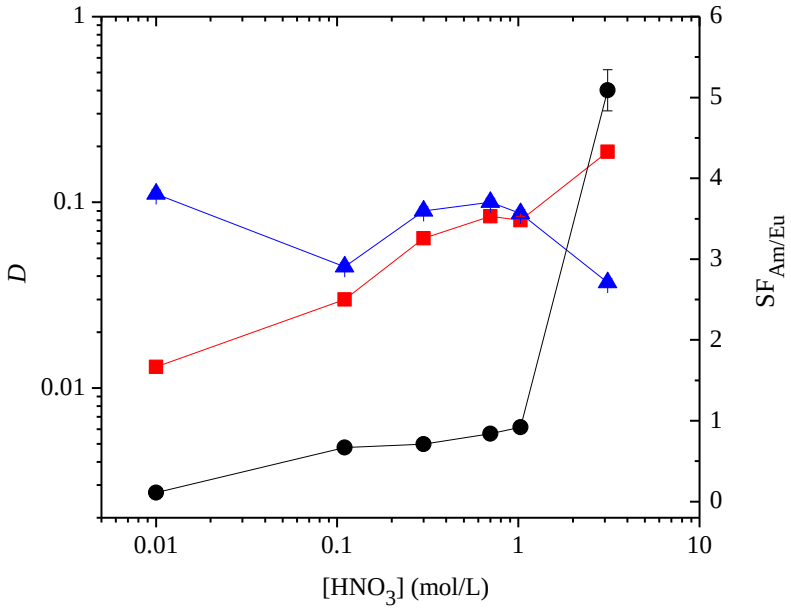


Figure 7. Extraction of Am(III) and Eu(III) by BTPhen ligand **13** (0.01 M) into 1-octanol as a function of the initial nitric acid concentration of the aqueous phase (*D* = distribution ratio, SF = separation factor, ■ = D_{Am}, ▲ = D_{Eu}, ● = $SF_{Am/Eu}$, contact time: 60 min, temperature: 22 °C ± 1 °C). Results from alpha spectrometry for ligand **13** were not obtained due to the precipitation observed during the extraction experiments.

Table 9. Extraction of Y(III) and all the trivalent lanthanides (except Pm) by 10 mM BTPhen ligand **13** into 1-octanol as a function of the initial nitric acid concentration of the aqueous phase. Results are from ICP-MS (*D* = distribution ratio, SF = separation factor, contact time: 60 min, temperature: 22 ºC ± 1 ºC).

[HNO_3] (mol/L)		0.01	0.11	0.30	0.70	1.03	3.11
Element	**Atomic Number**	*D*	*D*	*D*	*D*	*D*	*D*
Y	39	0.05	0.01	0.03	0.02	0.02	0.01
La	57	0.04	0.02	0.02	0.02	0.02	0.01
Ce	58	0.05	0.02	0.03	0.03	0.03	0.02
Pr	59	0.05	0.02	0.03	0.03	0.03	0.03
Nd	60	0.05	0.02	0.04	0.04	0.05	0.03
Sm	62	0.11	0.04	0.09	0.09	0.09	0.05
Eu	63	0.15	0.06	0.12	0.13	0.11	0.05
Gd	64	0.16	0.06	0.14	0.13	0.11	0.04
Tb	65	0.16	0.07	0.17	0.17	0.15	0.06
Dy	66	0.13	0.07	0.16	0.16	0.14	0.07
Ho	67	0.09	0.06	0.14	0.14	0.13	0.06
Er	68	0.07	0.06	0.13	0.14	0.13	0.08
Tm	69	0.07	0.06	0.13	0.13	0.13	0.08
Yb	70	0.07	0.06	0.13	0.13	0.12	0.07
Lu	71	0.08	0.06	0.13	0.12	0.11	0.06

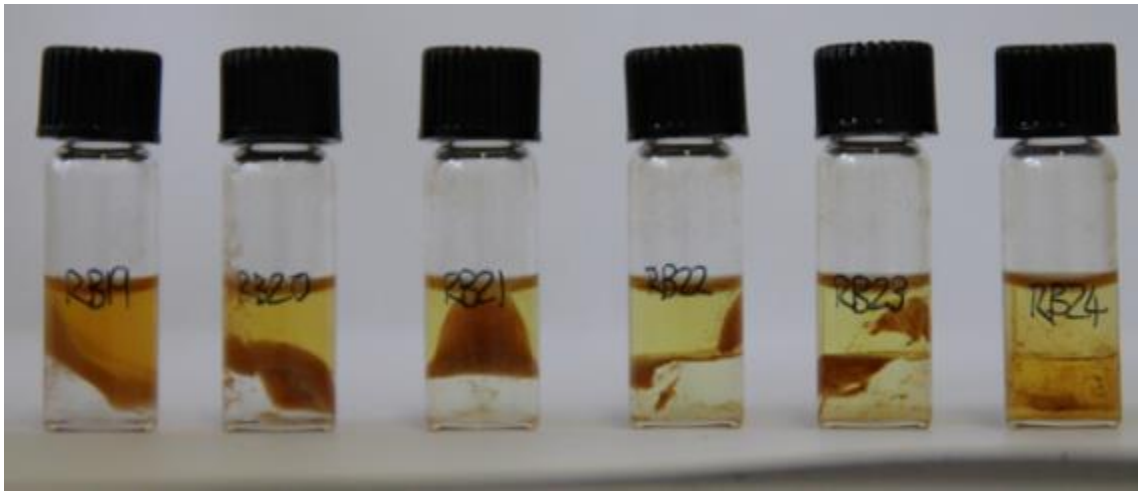


Figure 8. Photograph of the sample tubes from the extraction of Am(III), Cm(III) and Eu(III) by 10 mM BTPhen ligand **13** into 1-octanol as a function of the initial nitric acid concentration of the aqueous phase, with increasing [HNO_3] going from left to right.

6.3 Extraction Studies for BTPhen Ligand 14

Table 10. Extraction of Am(III) and Eu(III) by 10 mM BTPhen ligand **14** into 1-octanol as a function of the initial nitric acid concentration of the aqueous phase. Results are from gamma spectrometry (*D* = distribution ratio, SF = separation factor, contact time: 60 min, temperature: 22 °C ± 1 °C).

[HNO_3] initial (mol/L)	D_{Am}	D_{Eu}	$SF_{Am/Eu}$
0.01	0.96	0.12	8.3
0.11	11.4	1.42	8.0
0.30	28.4	2.76	10.3
0.70	35.6	2.21	16.1
1.03	41.8	1.74	24.1
3.11	70.0	0.63	111.8

Table 11. Extraction of Am(III) and Cm(III) by 10 mM BTPhen ligand **14** into 1-octanol as a function of the initial nitric acid concentration of the aqueous phase. Results are from alpha spectrometry (*D* = distribution ratio, SF = separation factor, contact time: 60 min, temperature: 22 °C ± 1 °C).

[HNO_3] initial (mol/L)	D_{Am}	D_{Cm}	$SF_{Am/Cm}$
0.01	0.94	0.92	1.0
0.11	9.2	12.7	0.8
0.30	18.0	19.0	0.9
0.70	30.3	29.6	1.0
1.03	33.0	31.1	1.1
3.11	49.6	44.4	1.1

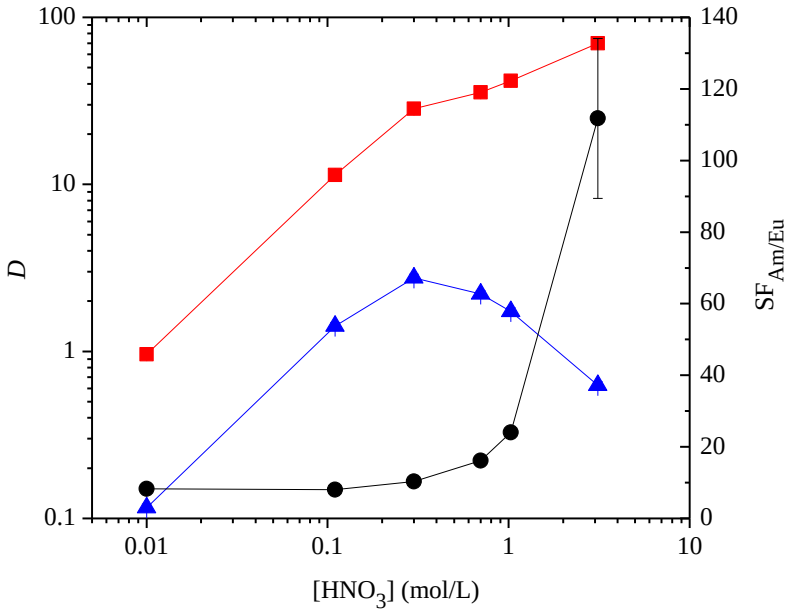


Figure 9. Extraction of Am(III) and Eu(III) by BTPhen ligand **14** (0.01 M) into 1-octanol as a function of the initial nitric acid concentration of the aqueous phase (D = distribution ratio, SF = separation factor, ■ = D_{Am}, ▲ = D_{Eu}, ● = $SF_{Am/Eu}$, contact time: 60 min, temperature: 22 °C ± 1 °C).

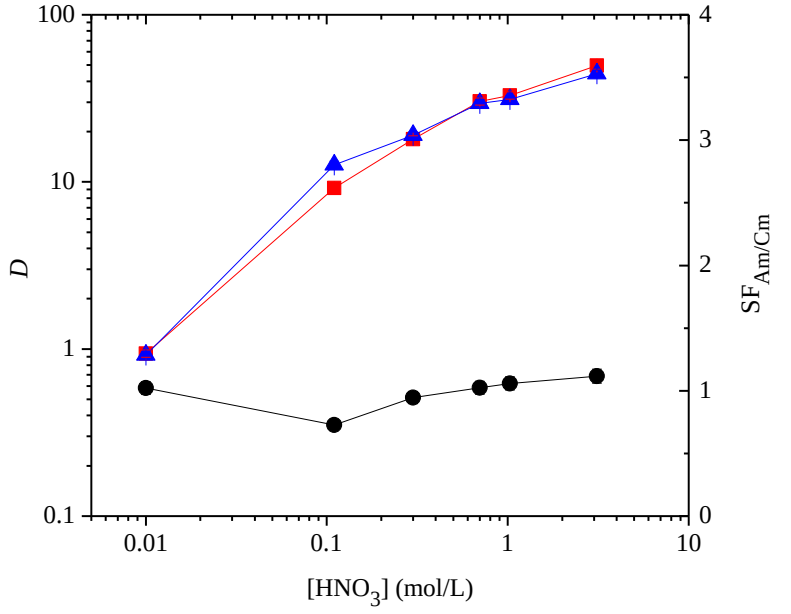


Figure 10. Extraction of Am(III) and Cm(III) by BTPhen ligand **14** (0.01 M) into 1-octanol as a function of the initial nitric acid concentration of the aqueous phase (D = distribution ratio, SF = separation factor, ■ = D_{Am}, ▲ = D_{Cm}, ● = $SF_{Am/Cm}$, contact time: 60 min, temperature: 22 °C ± 1 °C).

Table 12. Extraction of Am(III) and Eu(III) from 1.03 M nitric acid by 10 mM BTPhen ligand **14** into 1-octanol as a function of contact time. Results are from gamma spectrometry (*D* = distribution ratio, SF = separation factor, temperature: 22 °C ± 1 °C).

Contact time (min)	D_{Am}	D_{Eu}	$SF_{Am/Eu}$
5	38.0	1.70	22.5
10	34.2	1.63	21.0
30	31.8	1.61	19.7
60	33.1	1.58	21.0
120	37.4	1.55	24.1

Table 13. Extraction of Am(III) and Cm(III) from 1.03 M nitric acid by 10 mM BTPhen ligand **14** into 1-octanol as a function of contact time. Results are from alpha spectrometry (*D* = distribution ratio, SF = separation factor, temperature: 22 °C ± 1 °C).

Contact time (min)	D_{Am}	D_{Cm}	$SF_{Am/Cm}$
5	33.2	30.5	1.1
10	32.0	29.1	1.1
30	33.0	32.6	1.0
60	38.0	33.7	1.1
120	37.0	31.8	1.2

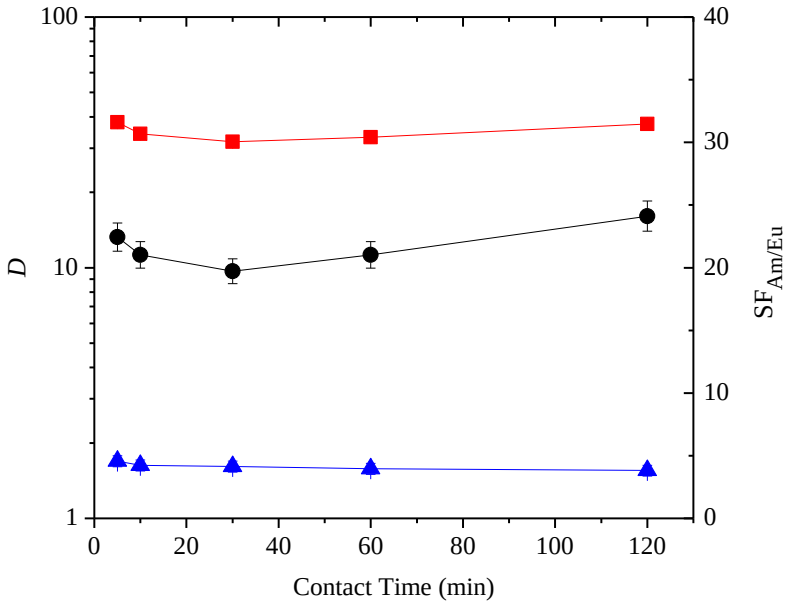


Figure 11. Extraction of Am(III) and Eu(III) from 1.03 M nitric acid by BTPhen ligand **14** (0.01 M) into 1-octanol as a function of contact time (*D* = distribution ratio, SF = separation factor, ■ = D_{Am}, ▲ = D_{Eu}, ● = $SF_{Am/Eu}$, temperature: 22 °C ± 1 °C).

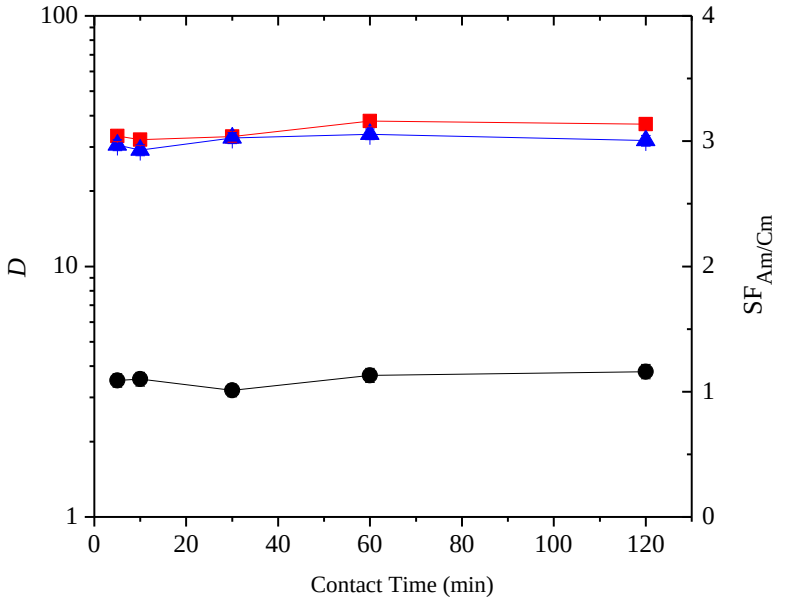


Figure 12. Extraction of Am(III) and Cm(III) from 1.03 M nitric acid by BTPhen ligand **14** (0.01 M) into 1-octanol as a function of contact time (*D* = distribution ratio, SF = separation factor, ■ = D_{Am}, ▲ = D_{Cm}, ● = $SF_{Am/Cm}$, temperature: 22 °C ± 1 °C).

Table 14. Extraction of Am(III) and Eu(III) from 0.3 M nitric acid by 10 mM BTPhen ligand **14** into 1-octanol as a function of contact time. Results are from gamma spectrometry (*D* = distribution ratio, SF = separation factor, temperature: 22 °C ± 1 °C).

Contact time (min)	D_{Am}	D_{Eu}	$SF_{Am/Eu}$
5	24.0	2.89	8.3
10	25.1	3.04	8.3
20	26.6	2.98	8.9
30	24.6	3.01	8.2
45	25.8	3.05	8.5
60	25.4	3.05	8.3

Table 15. Extraction of Am(III) and Cm(III) from 0.3 M nitric acid by 10 mM BTPhen ligand **14** into 1-octanol as a function of contact time. Results are from alpha spectrometry (*D* = distribution ratio, SF = separation factor, temperature: 22 °C ± 1 °C).

Contact time (min)	D_{Am}	D_{Cm}	$SF_{Am/Cm}$
5	22.9	22.2	1.0
10	23.9	23.7	1.0
20	24.2	24.3	1.0
30	24.8	24.9	1.0
45	19.8	19.6	1.0
60	24.4	24.4	1.0

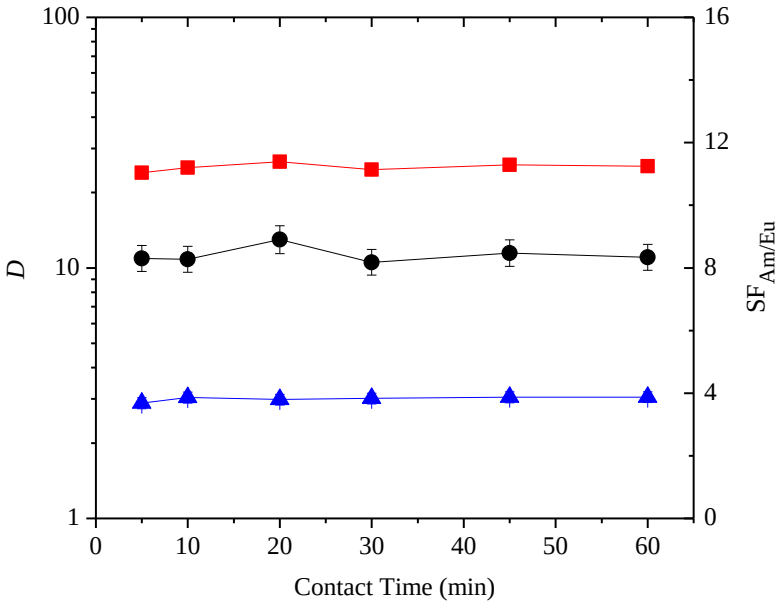


Figure 13. Extraction of Am(III) and Eu(III) from 0.3 M nitric acid by BTPhen ligand **14** (0.01 M) into 1-octanol as a function of contact time (*D* = distribution ratio, SF = separation factor, ■ = D_{Am}, ▲ = D_{Eu}, ● = $SF_{Am/Eu}$, temperature: 22 °C ± 1 °C).

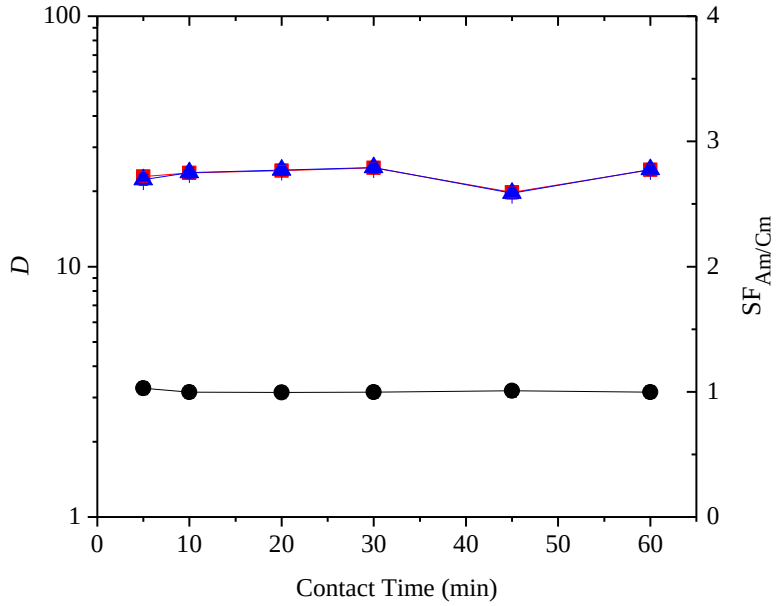


Figure 14. Extraction of Am(III) and Cm(III) from 0.3 M nitric acid by BTPhen ligand **14** (0.01 M) into 1-octanol as a function of contact time (*D* = distribution ratio, SF = separation factor, ■ = D_{Am}, ▲ = D_{Cm}, ● = $SF_{Am/Cm}$, temperature: 22 °C ± 1 °C).

Table 16. Extraction of Y(III) and all the trivalent lanthanides (except Pm) by 10 mM BTPhen ligand **14** into 1-octanol as a function of the initial nitric acid concentration of the aqueous phase. Results are from ICP-MS (*D* = distribution ratio, SF = separation factor, contact time: 60 min, temperature: 22 °C ± 1 °C).

[HNO_3] (mol/L)		0.01	0.11	0.30	0.70	1.03	3.11
Element	**Atomic Number**	*D*	*D*	*D*	*D*	*D*	*D*
Y	39	0.01	0.05	0.11	0.10	0.09	0.06
La	57	0.02	0.22	0.42	0.33	0.23	0.07
Ce	58	0.08	1.11	2.21	1.74	1.22	0.34
Pr	59	0.15	2.02	4.02	3.17	2.3	0.67
Nd	60	0.19	2.51	4.96	3.99	2.94	0.91
Sm	62	0.20	2.51	4.76	3.77	2.68	0.99
Eu	63	0.17	2.0	3.77	2.99	2.19	0.88
Gd	64	0.10	1.14	2.16	1.74	1.31	0.57
Tb	65	0.13	1.45	2.96	2.55	1.97	0.96
Dy	66	0.14	1.57	3.26	2.94	2.38	1.27
Ho	67	0.13	1.61	3.43	3.23	2.62	1.53
Er	68	0.14	1.65	3.51	3.27	2.70	1.46
Tm	69	0.12	1.15	2.15	1.81	1.45	0.71
Yb	70	0.12	0.65	1.04	0.83	0.65	0.33
Lu	71	0.12	0.36	0.49	0.38	0.31	0.16

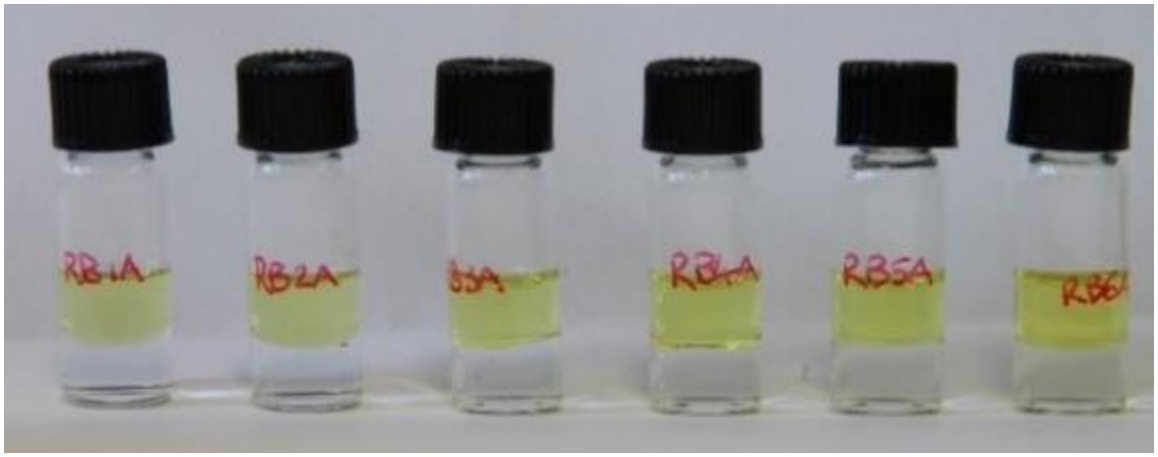


Figure 15. Photograph of the sample tubes from the extraction of Am(III), Cm(III) and Eu(III) by 10 mM BTPhen ligand **14** into 1-octanol as a function of the initial nitric acid concentration of the aqueous phase, with increasing [HNO_3] going from left to right.

6.4 Extraction Studies for CA-BTBP Ligand 17

Table 17. Extraction of Am(III) and Eu(III) by 10 mM CA-BTBP ligand **17** into 1-octanol as a function of the initial nitric acid concentration of the aqueous phase. Results are from gamma spectrometry (*D* = distribution ratio, SF = separation factor, contact time: 60 min, temperature: 22 °C ± 1 °C).

[HNO_3] initial (mol/L)	D_{Am}	D_{Eu}	$SF_{Am/Eu}$
0.001	0.02	0.003	5.77
0.013	0.17	0.003	49.0
0.296	0.84	0.007	128.5
0.796	3.06	0.020	153.4
1.031	7.71	0.058	133.4
3.000	0.11	0.005	22.0

Table 18. Extraction of Am(III) and Cm(III) by 10 mM CA-BTBP ligand **17** into 1-octanol as a function of the initial nitric acid concentration of the aqueous phase. Results are from alpha spectrometry (*D* = distribution ratio, SF = separation factor, contact time: 60 min, temperature: 22 °C ± 1 °C).

[HNO_3] initial (mol/L)	D_{Am}	D_{Cm}	$SF_{Am/Cm}$
0.001	0.02	0.01	2.1
0.013	0.14	0.06	2.4
0.296	0.72	0.31	2.3
0.796	2.51	1.10	2.3
1.031	3.75	1.75	2.2
3.000	0.14	0.07	2.1

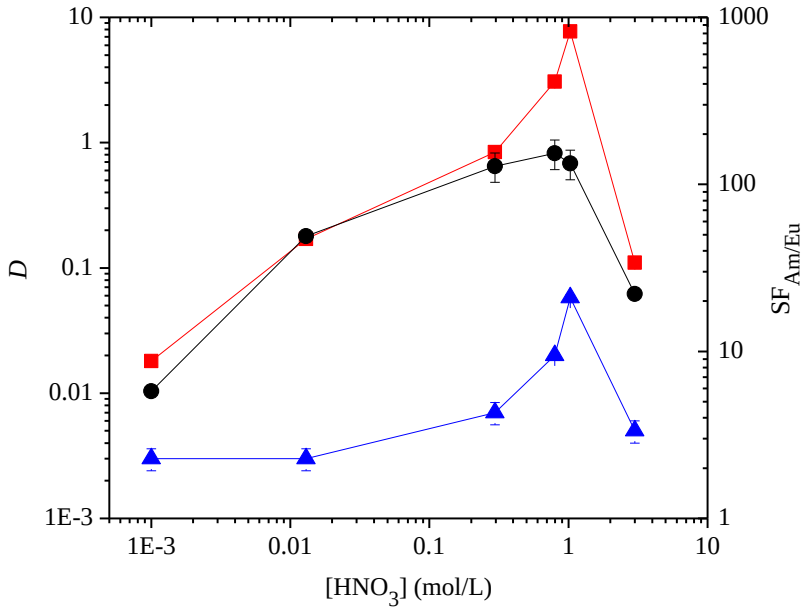


Figure 16. Extraction of Am(III) and Eu(III) by CA-BTBP **17** (0.01 M) into 1-octanol as a function of the initial nitric acid concentration of the aqueous phase (*D* = distribution ratio, SF = separation factor, ■ = D_{Am}, ▲ = D_{Eu}, ● = $SF_{Am/Eu}$, contact time: 60 min, temperature: 22 °C ± 1 °C).

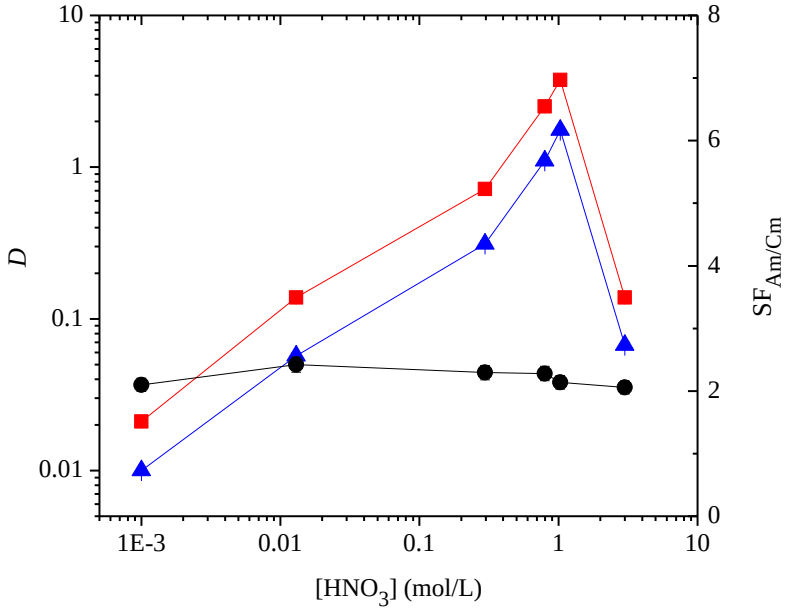


Figure 17. Extraction of Am(III) and Cm(III) by CA-BTBP **17** (0.01 M) into 1-octanol as a function of the initial nitric acid concentration of the aqueous phase (*D* = distribution ratio, SF = separation factor, ■ = D_{Am}, ▲ = D_{Cm}, ● = $SF_{Am/Cm}$, contact time: 60 min, temperature: 22 °C ± 1 °C).

Table 19. Extraction of Y(III) and all the trivalent lanthanides (except Pm) by 10 mM CA-BTBP ligand **17** into 1-octanol as a function of the initial nitric acid concentration of the aqueous phase. Results are from ICP-MS (*D* = distribution ratio, SF = separation factor, contact time: 60 min, temperature: 22 °C ± 1 °C).

[HNO_3] (mol/L)		0.01	0.11	0.30	0.70	1.03	3.11
Element	**Atomic Number**	*D*	*D*	*D*	*D*	*D*	*D*
Y	39	≤0.001	≤0.001	≤0.001	0.002	0.001	0.002
La	57	≤0.001	≤0.001	≤0.001	0.001	0.001	0.002
Ce	58	≤0.001	0.001	0.001	0.004	0.002	0.002
Pr	59	≤0.001	≤0.001	0.002	0.008	0.004	0.002
Nd	60	≤0.001	0.001	0.003	0.012	0.006	0.003
Sm	62	≤0.001	0.001	0.004	0.018	0.008	0.003
Eu	63	≤0.001	0.001	0.004	0.017	0.008	0.003
Gd	64	≤0.001	≤0.001	0.003	0.012	0.006	0.003
Tb	65	≤0.001	0.001	0.004	0.021	0.009	0.004
Dy	66	≤0.001	0.001	0.006	0.029	0.014	0.005
Ho	67	≤0.001	0.001	0.007	0.036	0.016	0.006
Er	68	≤0.001	0.001	0.008	0.043	0.022	0.008
Tm	69	≤0.001	0.001	0.008	0.043	0.020	0.009
Yb	70	0.001	0.001	0.007	0.040	0.020	0.009
Lu	71	0.001	0.001	0.007	0.037	0.018	0.010

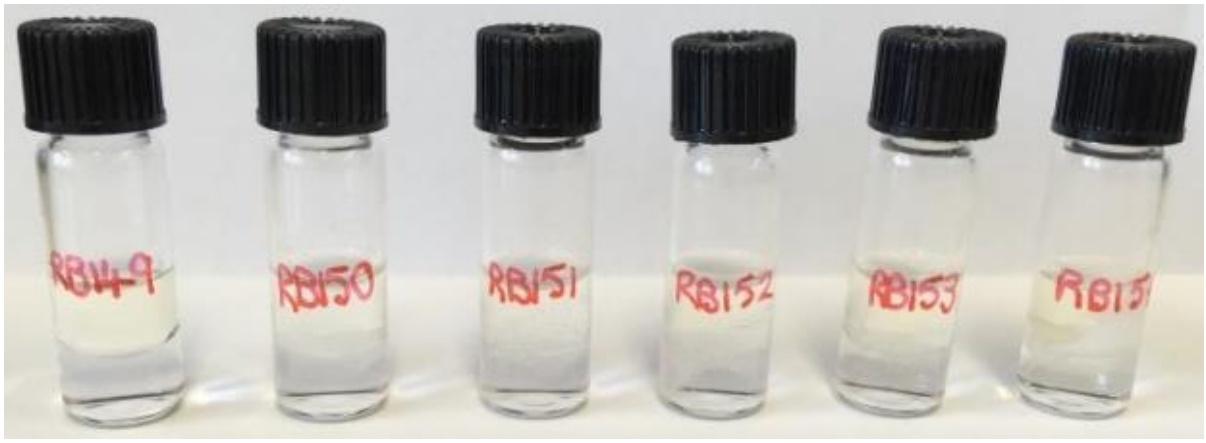


Figure 18. Photograph of the sample tubes from the extraction of Am(III), Cm(III) and Eu(III) by 10 mM CA-BTBP ligand **17** into 1-octanol as a function of the initial nitric acid concentration of the aqueous phase, with increasing [HNO_3] going from left to right.

6.5 Extraction Studies for CA-BTPhen Ligand 18

Table 20. Extraction of Am(III) and Eu(III) by 10 mM CA-BTPhen ligand **18** into 1-octanol as a function of the initial nitric acid concentration of the aqueous phase. Results are from gamma spectrometry (*D* = distribution ratio, SF = separation factor, contact time: 60 min, temperature: 22 °C ± 1 °C).

[HNO_3] initial (mol/L)	D_{Am}	D_{Eu}	$SF_{Am/Eu}$
0.001	2.19	0.02	129.7
0.013	15.0	0.07	223.3
0.296	40.4	0.15	264.6
0.796	47.0	0.18	264.4
1.031	25.1	0.24	105.5
3.000	7.91	0.04	211.7

Table 21. Extraction of Am(III) and Cm(III) by 10 mM CA-BTPhen ligand **18** into 1-octanol as a function of the initial nitric acid concentration of the aqueous phase. Results are from alpha spectrometry (*D* = distribution ratio, SF = separation factor, contact time: 60 min, temperature: 22 °C ± 1 °C).

[HNO_3] initial (mol/L)	D_{Am}	D_{Cm}	$SF_{Am/Cm}$
0.001	1.99	0.83	2.4
0.013	9.70	4.92	2.0
0.296	10.8	7.70	1.4
0.796	23.7	12.2	1.9
1.031	22.3	12.1	1.8
3.000	4.86	2.66	1.8

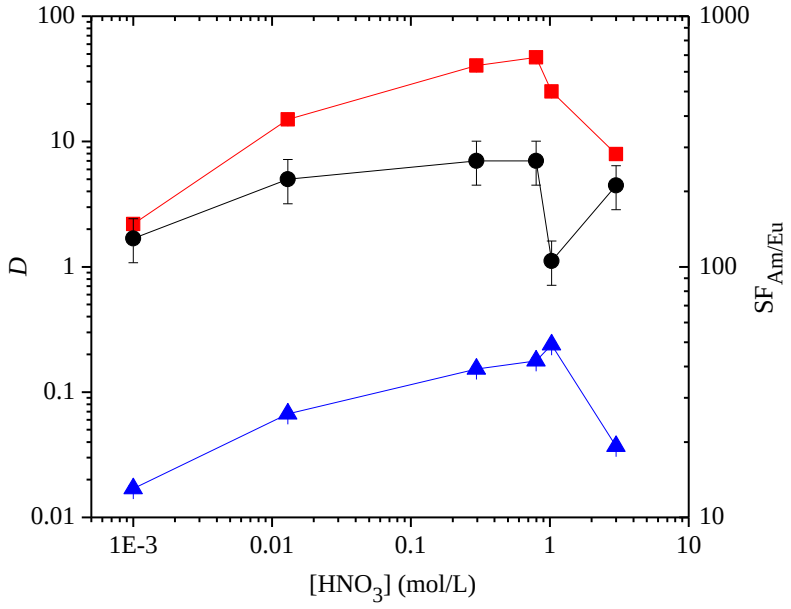


Figure 19. Extraction of Am(III) and Eu(III) by CA-BTPhen **18** (0.01 M) into 1-octanol as a function of the initial nitric acid concentration of the aqueous phase (*D* = distribution ratio, SF = separation factor, ■ = D_{Am}, ▲ = D_{Eu}, ● = $SF_{Am/Eu}$, contact time: 60 min, temperature: 22 °C ± 1 °C).

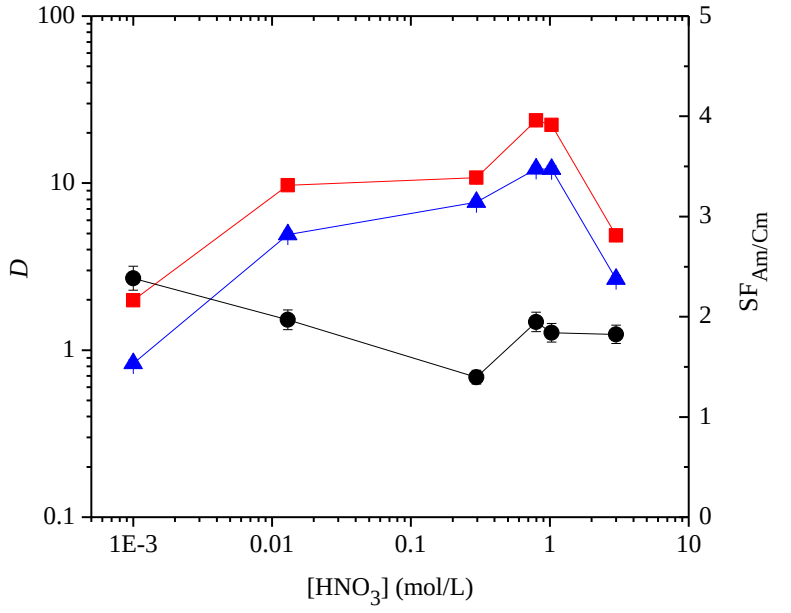


Figure 20. Extraction of Am(III) and Cm(III) by CA-BTPhen **18** (0.01 M) into 1-octanol as a function of the initial nitric acid concentration of the aqueous phase (*D* = distribution ratio, SF = separation factor, ■ = D_{Am}, ▲ = D_{Cm}, ● = $SF_{Am/Cm}$, contact time: 60 min, temperature: 22 °C ± 1 °C).

Table 22. Extraction of Y(III) and all the trivalent lanthanides (except Pm) by 10 mM CA-BTPhen ligand **18** into 1-octanol as a function of the initial nitric acid concentration of the aqueous phase. Results are from ICP-MS (*D* = distribution ratio, SF = separation factor, contact time: 60 min, temperature: 22 °C ± 1 °C).

[HNO_3] (mol/L)		0.01	0.11	0.30	0.70	1.03	3.11
Element	**Atomic Number**	*D*	*D*	*D*	*D*	*D*	*D*
Y	39	0.002	0.002	0.004	0.006	0.007	0.005
La	57	0.011	0.011	0.019	0.019	0.017	0.004
Ce	58	0.031	0.043	0.090	0.092	0.074	0.011
Pr	59	0.038	0.072	0.171	0.173	0.141	0.020
Nd	60	0.034	0.087	0.231	0.237	0.187	0.029
Sm	62	0.024	0.085	0.232	0.244	0.205	0.041
Eu	63	0.017	0.063	0.179	0.197	0.167	0.041
Gd	64	0.009	0.032	0.094	0.109	0.095	0.026
Tb	65	0.011	0.039	0.117	0.147	0.129	0.044
Dy	66	0.012	0.038	0.119	0.152	0.136	0.053
Ho	67	0.012	0.037	0.115	0.156	0.142	0.060
Er	68	0.014	0.036	0.115	0.157	0.144	0.070
Tm	69	0.014	0.029	0.093	0.129	0.120	0.067
Yb	70	0.016	0.024	0.074	0.105	0.097	0.062
Lu	71	0.018	0.019	0.059	0.081	0.077	0.053

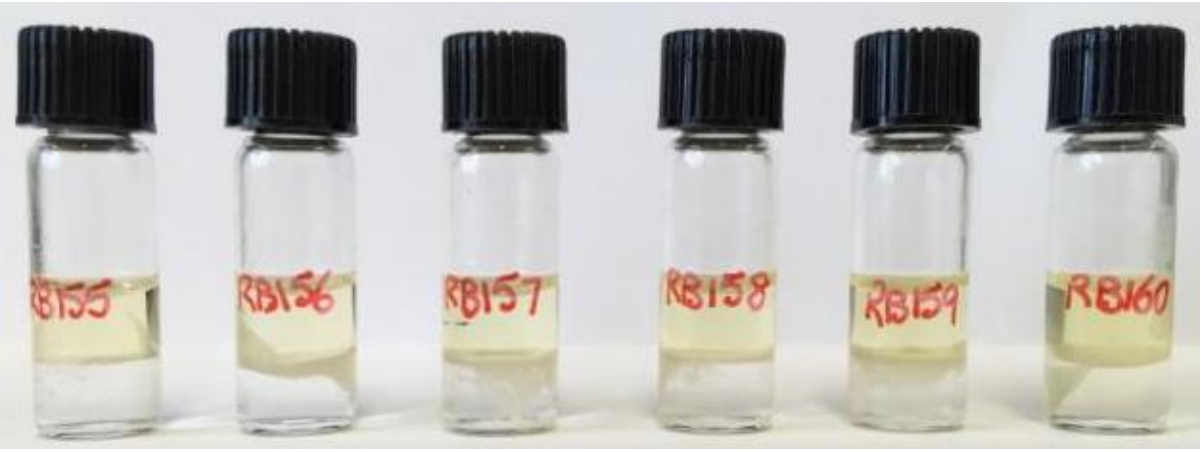
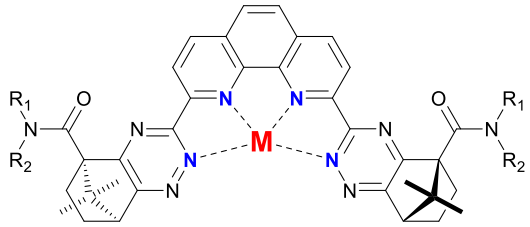
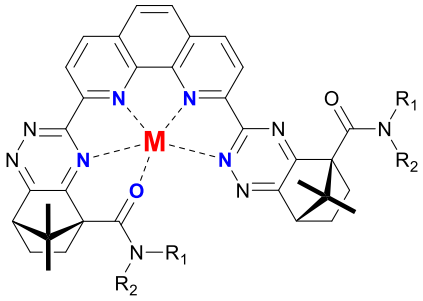


Figure 21. Photograph of the sample tubes from the extraction of Am(III), Cm(III) and Eu(III) by 10 mM CA-BTPhen ligand **18** into 1-octanol as a function of the initial nitric acid concentration of the aqueous phase, with increasing [HNO_3] going from left to right.

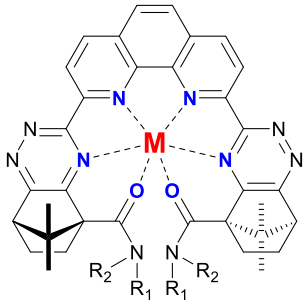
7: NMR Titrations with Metal Salts



Species A:
(symmetrical tetradentate coordination mode)



Species B:
(unsymmetrical pentadentate coordination mode)



Species C:
(symmetrical hexadentate coordination mode)

Figure 22. The three possible coordination modes of BTPhen ligands **12**–**14** with lanthanide ions **M** in their 1:1 metal:ligand complexes (species A: symmetrical tetradentate coordination mode, species B: unsymmetrical pentadentate coordination mode, species C: symmetrical hexadentate coordination mode). These species are labelled as follows in the species distribution diagrams; species A = ●, species B = ▼, species C = ◀. Species B can be distinguished from species A and C by ^{1}H NMR spectroscopy.

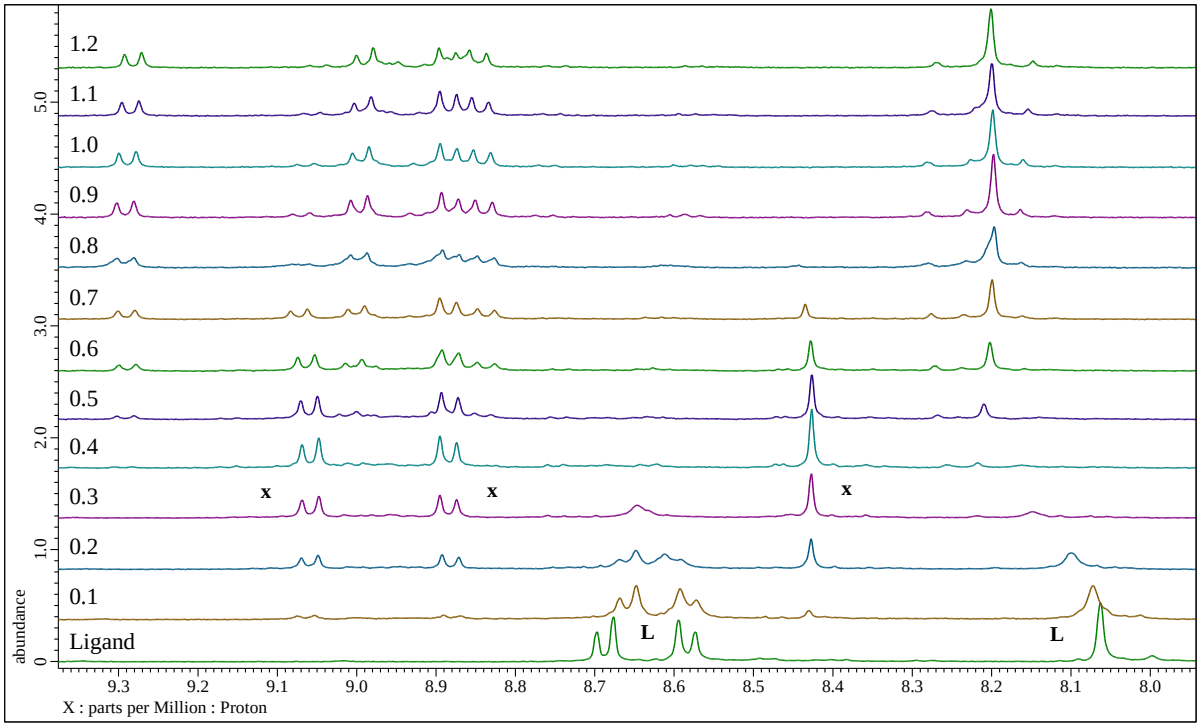


Figure 23. Aromatic region of the stack plot for the ^{1}H NMR titration of BTPhen ligand **12** with $La(NO_3)_3$ in CD_3CN. Bottom spectrum = free ligand. Each preceding spectrum corresponds to the addition of 0.1 equivalents of metal salt solution (L = free ligand, x = 1:2 complex $[La(\mathbf{12})_2(NO_3)]^{2+}$).

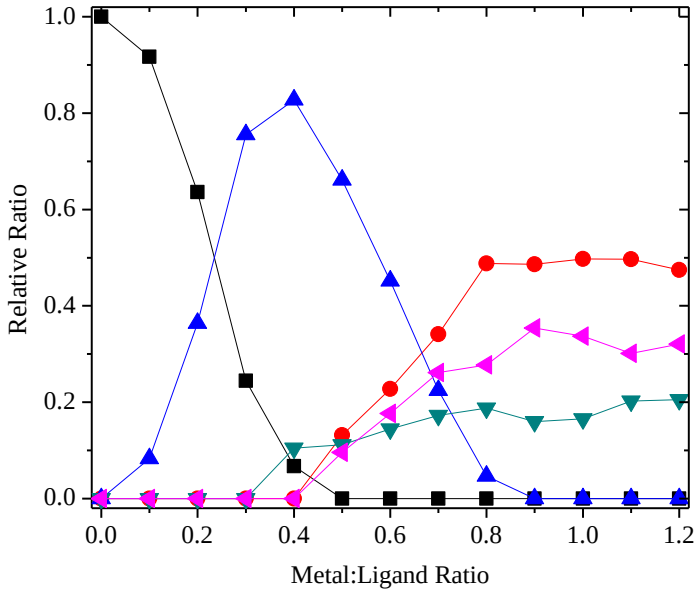


Figure 24. Species distribution for the ^{1}H NMR titration of BTPhen **12** with $La(NO_3)_3$ in CD_3CN (■ = free ligand, ▲ = 1:2 complex, ● = species A, ▼ = species B, ◀ = species C).

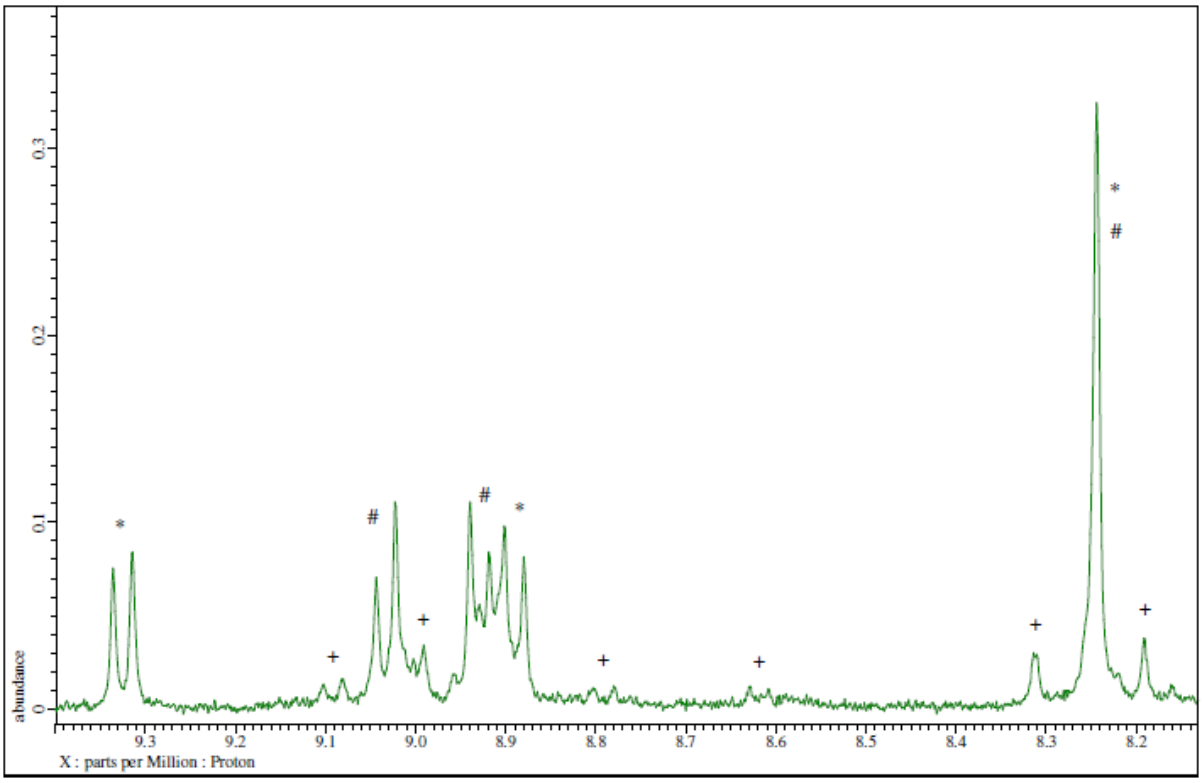


Figure 25. Enlargement of the aromatic region of the ^{1}H NMR spectrum of a mixture of BTPhen ligand **12** with $La(NO_3)_3$ (1.2 equivalents) in CD_3CN. Assignments: * = species A (symmetrical 1:1 complex with tetradentate coordination of ligand), + = species B (unsymmetrical 1:1 complex with pentadentate coordination of ligand), # = species C (symmetrical 1:1 complex with hexadentate coordination of ligand).

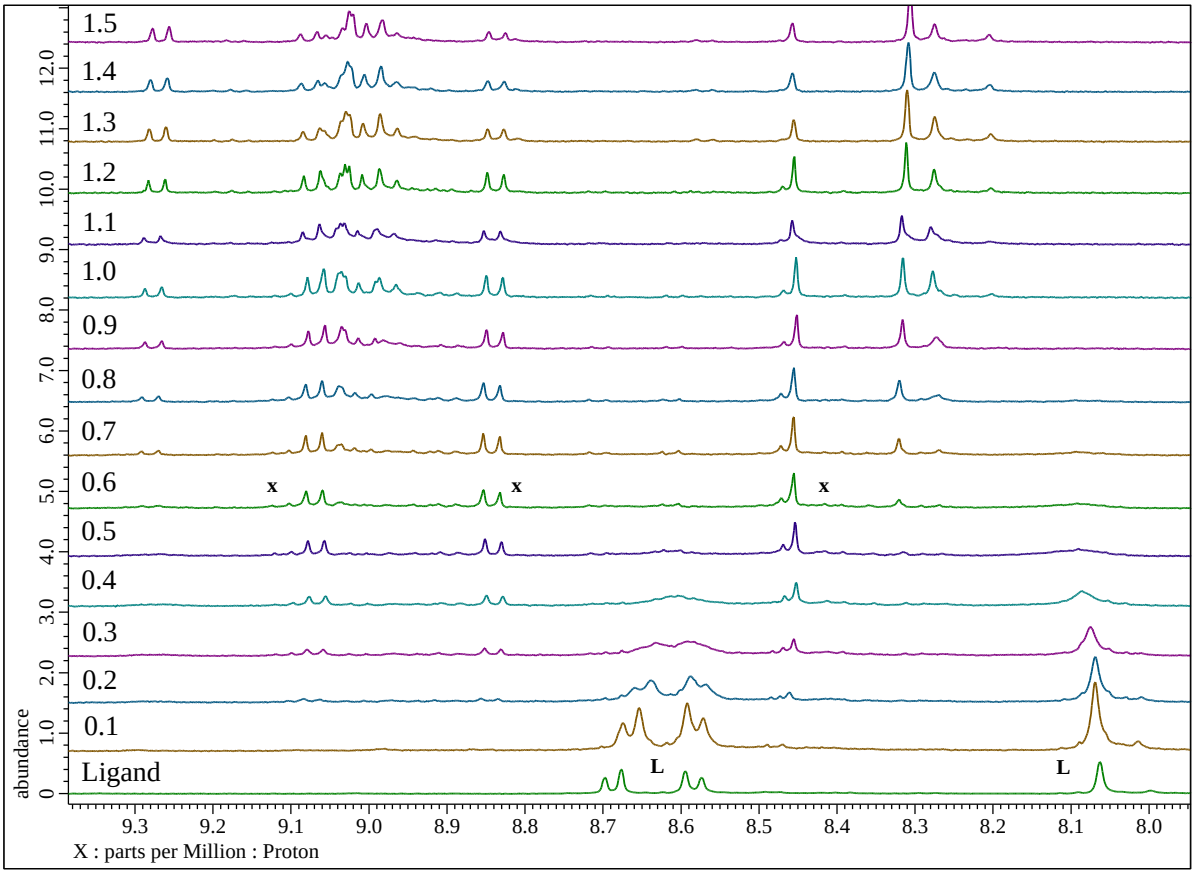


Figure 26. Aromatic region of the stack plot for the ^{1}H NMR titration of BTPhen ligand **12** with $Lu(NO_3)_3$ in CD_3CN. Bottom spectrum = free ligand. Each preceding spectrum corresponds to the addition of 0.1 equivalents of metal salt solution (L = free ligand, x = 1:2 complex $[Lu(\mathbf{12})_2(NO_3)]^{2+}$).

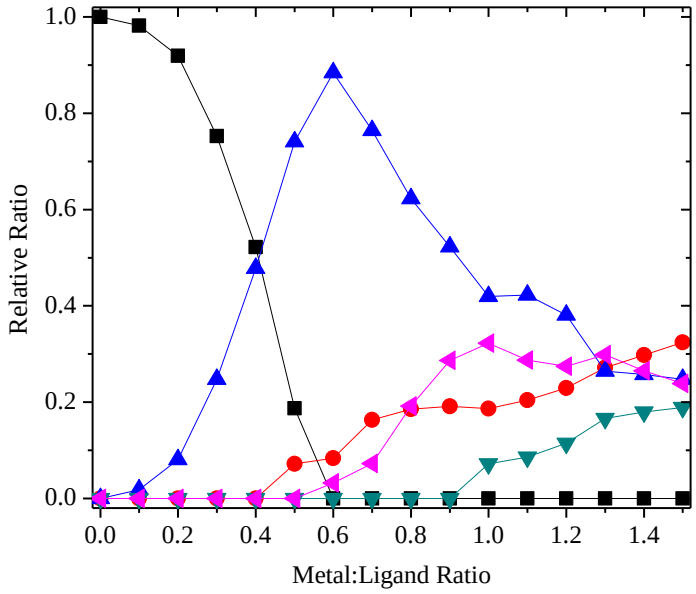


Figure 27. Species distribution for the ^{1}H NMR titration of BTPhen **12** with $Lu(NO_3)_3$ in CD_3CN (■ = free ligand, ▲ = 1:2 complex, ● = species A, ▼ = species B, ◀ = species C).

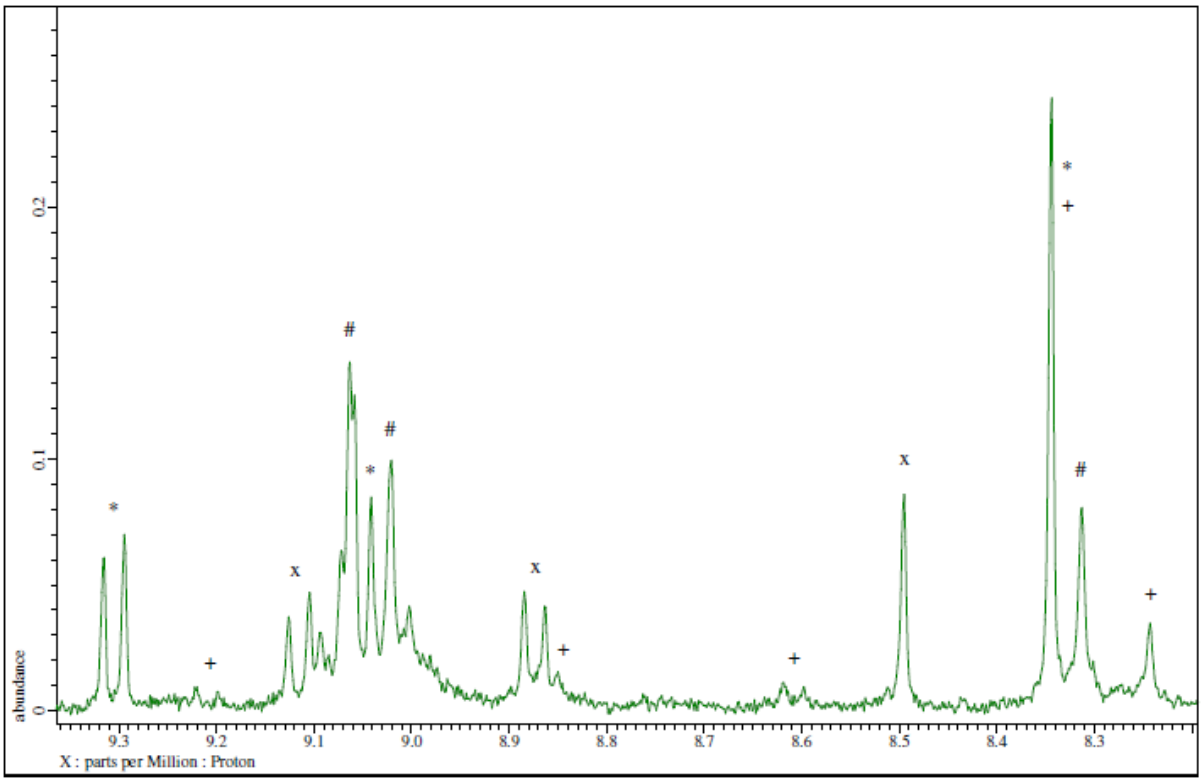


Figure 28. Enlargement of the aromatic region of the ^{1}H NMR spectrum of a mixture of BTPhen ligand **12** with $Lu(NO_3)_3$ (1.5 equivalents) in CD_3CN. Assignments: x = 1:2 complex, * = species A (symmetrical 1:1 complex with tetradentate coordination of ligand), + = species B (unsymmetrical 1:1 complex with pentadentate coordination of ligand), # = species C (symmetrical 1:1 complex with hexadentate coordination of ligand).

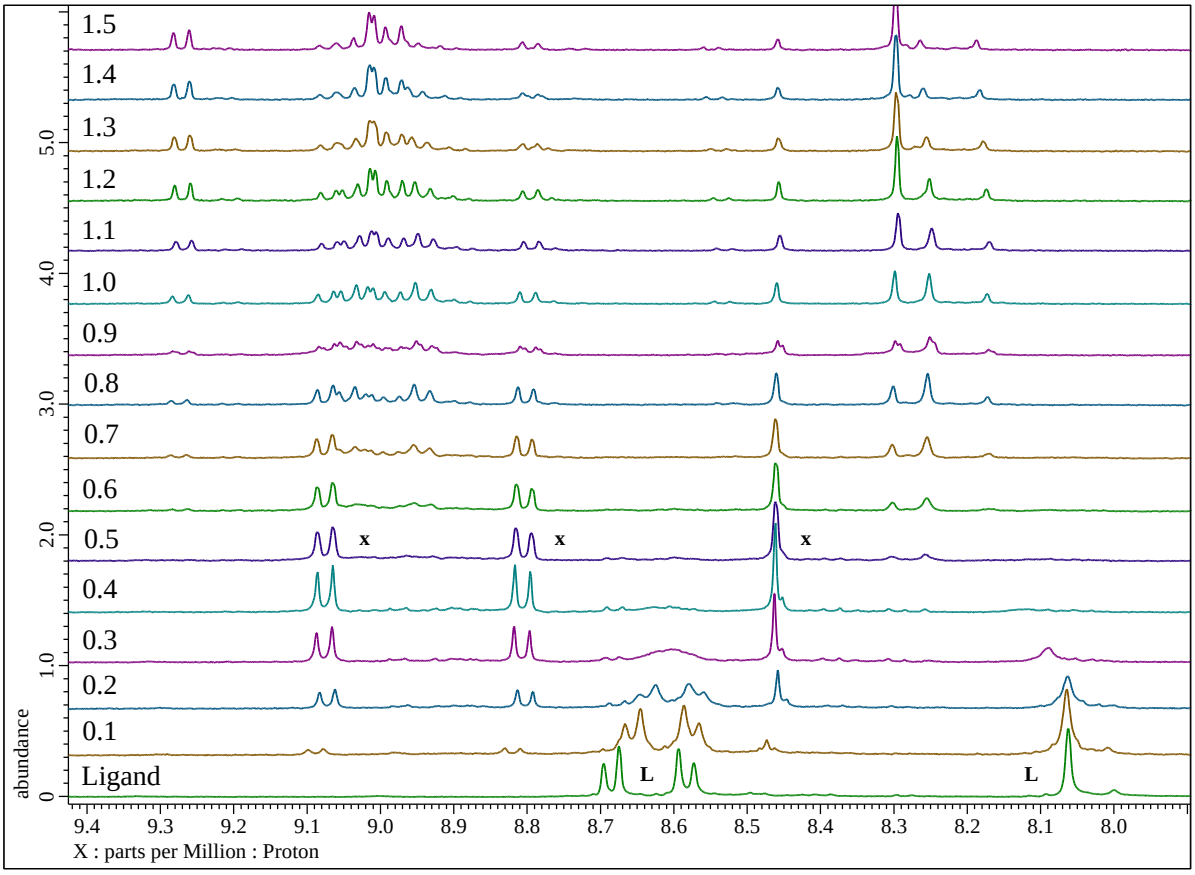


Figure 29. Aromatic region of the stack plot for the ^{1}H NMR titration of BTPhen ligand **12** with $Y(NO_3)_3$ in CD_3CN. Bottom spectrum = free ligand. Each preceding spectrum corresponds to the addition of 0.1 equivalents of metal salt solution (L = free ligand, x = 1:2 complex $[Y(\mathbf{12})_2(NO_3)]^{2+}$).

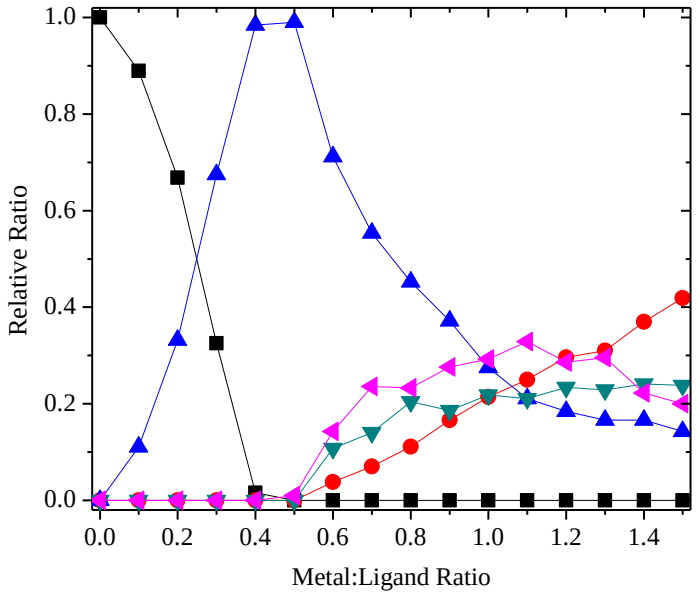


Figure 30. Species distribution for the ^{1}H NMR titration of BTPhen **12** with $Y(NO_3)_3$ in CD_3CN (■ = free ligand, ▲ = 1:2 complex, ● = species A, ▼ = species B, ◀ = species C).

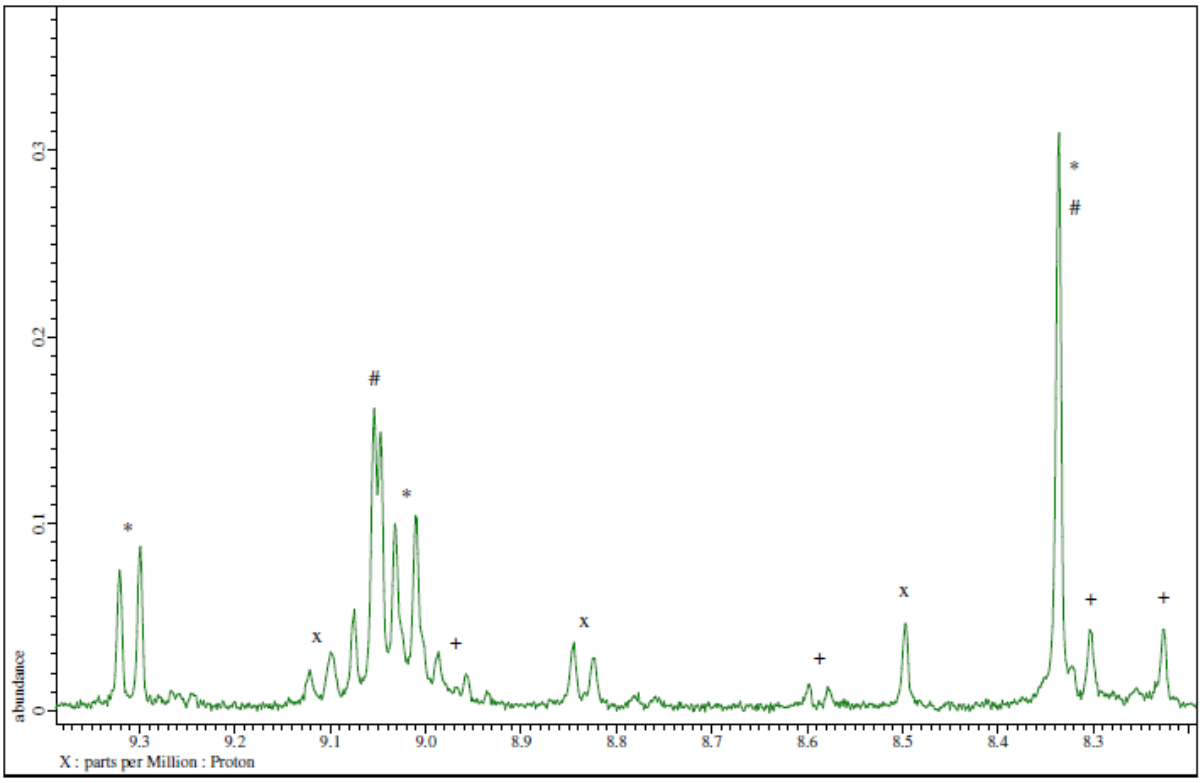


Figure 31. Enlargement of the aromatic region of the ^{1}H NMR spectrum of a mixture of BTPhen ligand **12** with $Y(NO_3)_3$ (1.5 equivalents) in CD_3CN. Assignments: x = 1:2 complex, * = species A (symmetrical 1:1 complex with tetradentate coordination of ligand), + = species B (unsymmetrical 1:1 complex with pentadentate coordination of ligand), # = species C (symmetrical 1:1 complex with hexadentate coordination of ligand).

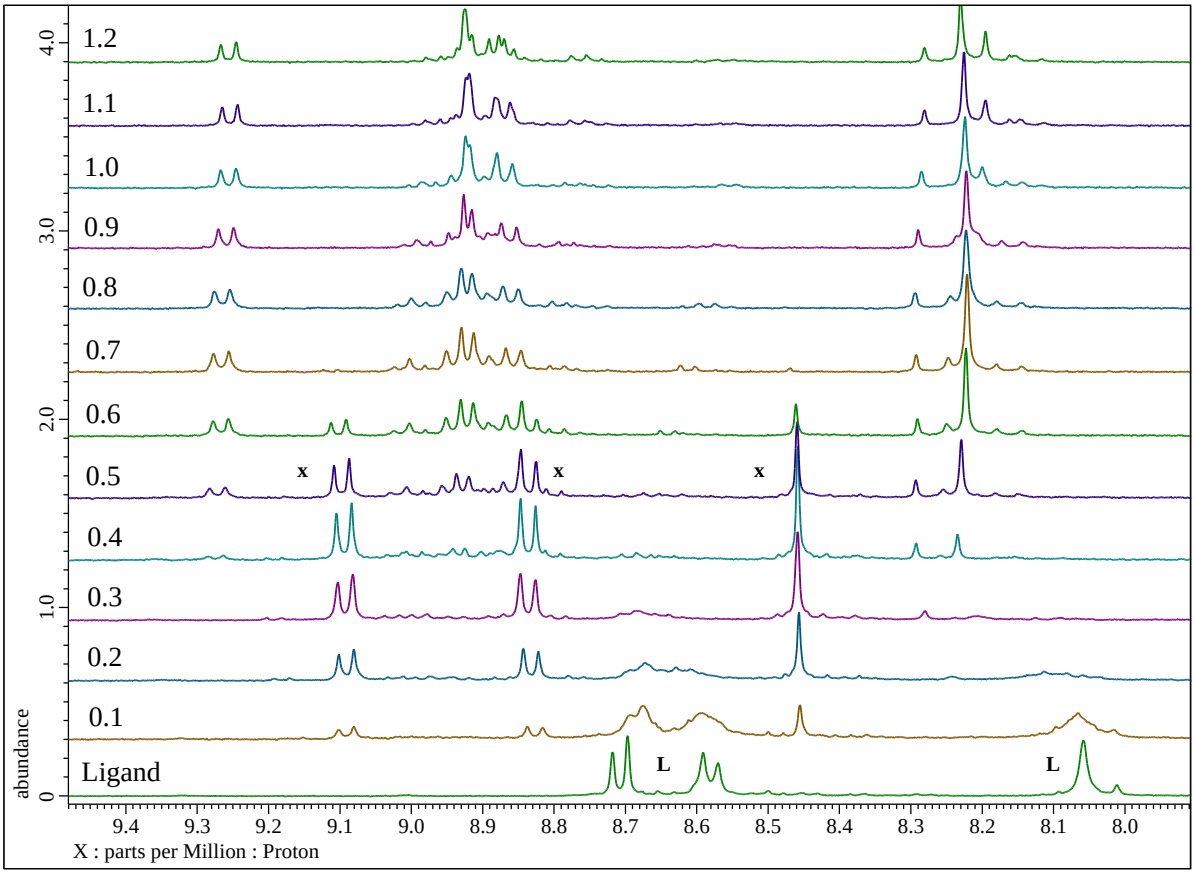


Figure 32. Aromatic region of the stack plot for the ^{1}H NMR titration of BTPhen ligand **14** with $La(NO_3)_3$ in CD_3CN. Bottom spectrum = free ligand. Each preceding spectrum corresponds to the addition of 0.1 equivalents of metal salt solution (L = free ligand, x = 1:2 complex $[La(\mathbf{14})_2(NO_3)]^{2+}$).

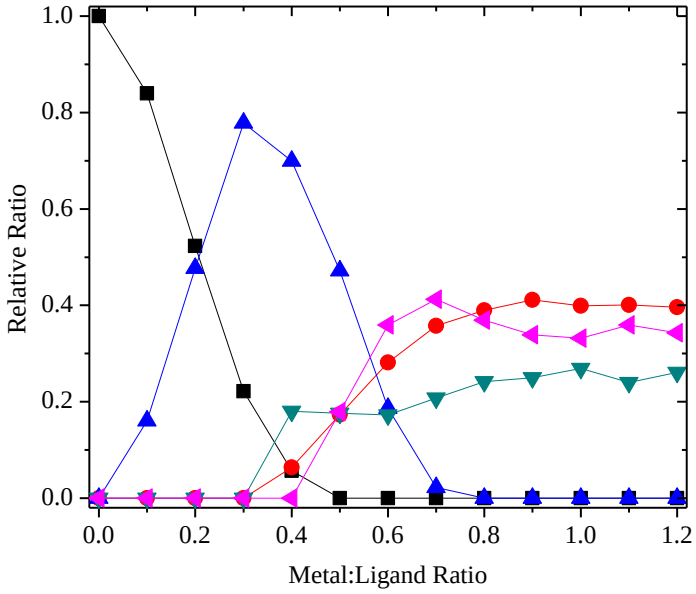


Figure 33. Species distribution for the ^{1}H NMR titration of BTPhen **14** with $La(NO_3)_3$ in CD_3CN (■ = free ligand, ▲ = 1:2 complex, ● = species A, ▼ = species B, ◀ = species C).

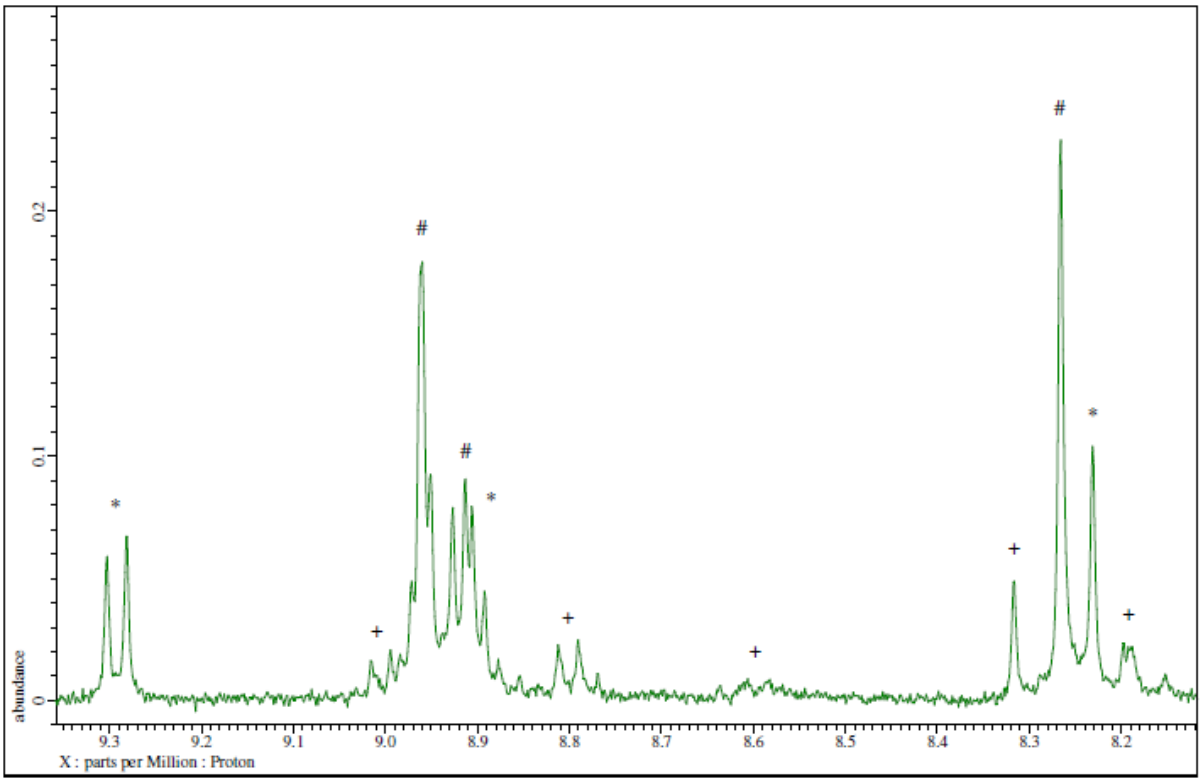


Figure 34. Enlargement of the aromatic region of the ^{1}H NMR spectrum of a mixture of BTPhen ligand **14** with $La(NO_3)_3$ (1.2 equivalents) in CD_3CN. Assignments: * = species A (symmetrical 1:1 complex with tetradentate coordination of ligand), + = species B (unsymmetrical 1:1 complex with pentadentate coordination of ligand), # = species C (symmetrical 1:1 complex with hexadentate coordination of ligand).

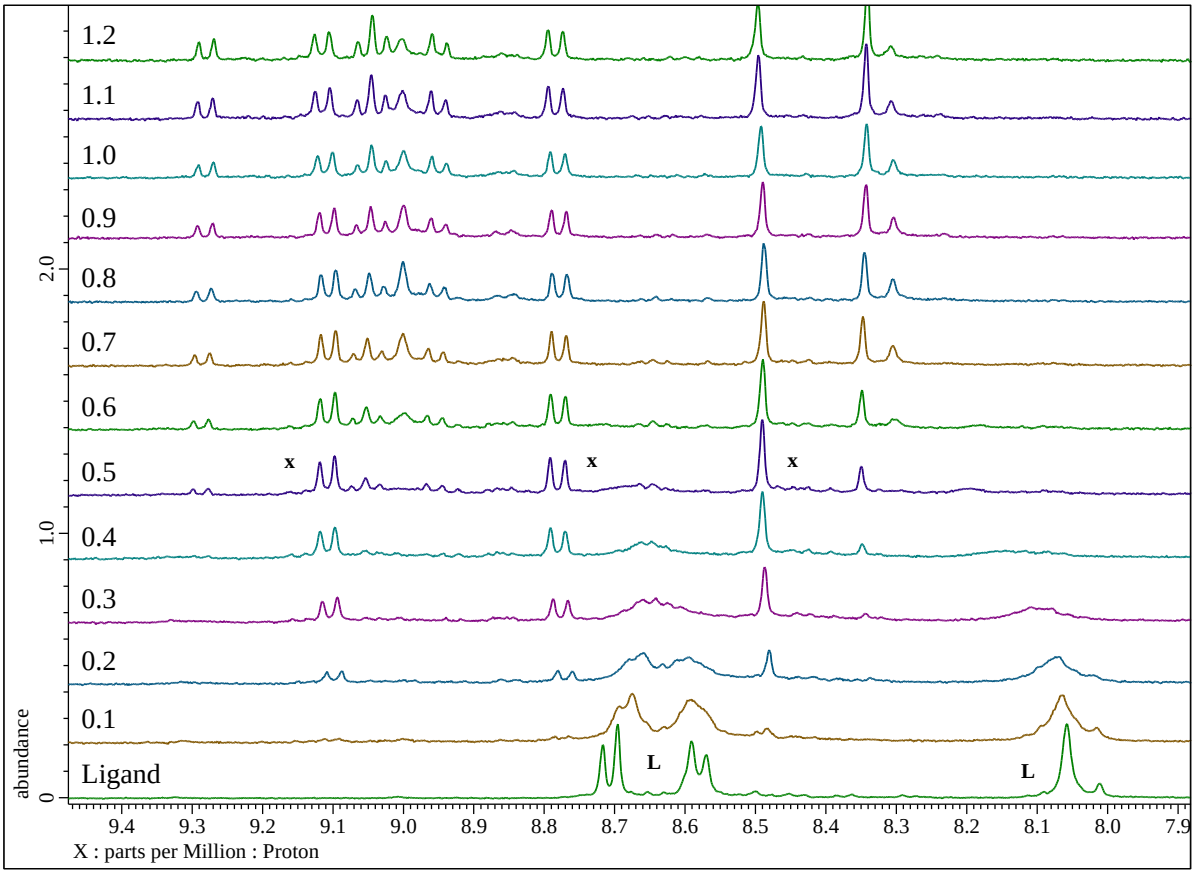


Figure 35. Aromatic region of the stack plot for the ^{1}H NMR titration of BTPhen ligand **14** with $Lu(NO_3)_3$ in CD_3CN. Bottom spectrum = free ligand. Each preceding spectrum corresponds to the addition of 0.1 equivalents of metal salt solution (L = free ligand, x = 1:2 complex $[Lu(\mathbf{14})_2(NO_3)]^{2+}$).

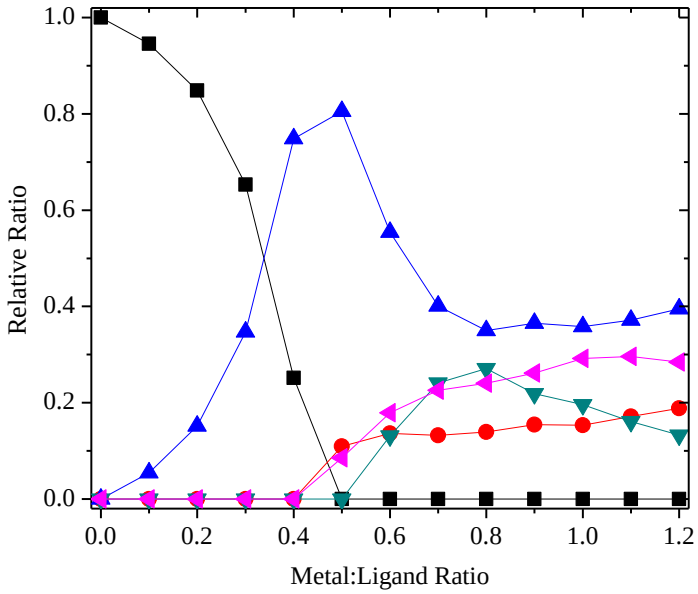


Figure 36. Species distribution for the ^{1}H NMR titration of BTPhen **14** with $Lu(NO_3)_3$ in CD_3CN (■ = free ligand, ▲ = 1:2 complex, ● = species A, ▼ = species B, ◀ = species C).

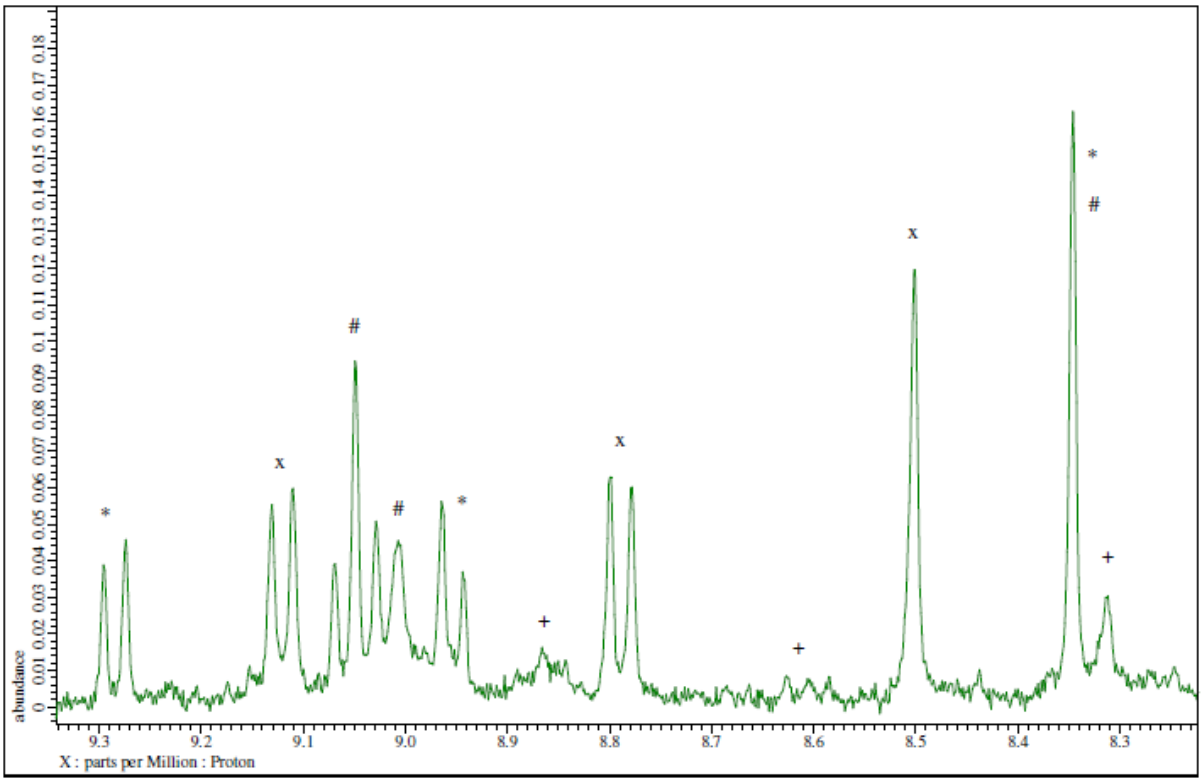


Figure 37. Enlargement of the aromatic region of the ^{1}H NMR spectrum of a mixture of BTPhen ligand **14** with $Lu(NO_3)_3$ (1.2 equivalents) in CD_3CN. Assignments: x = 1:2 complex, * = species A (symmetrical 1:1 complex with tetradentate coordination of ligand), + = species B (unsymmetrical 1:1 complex with pentadentate coordination of ligand), # = species C (symmetrical 1:1 complex with hexadentate coordination of ligand).

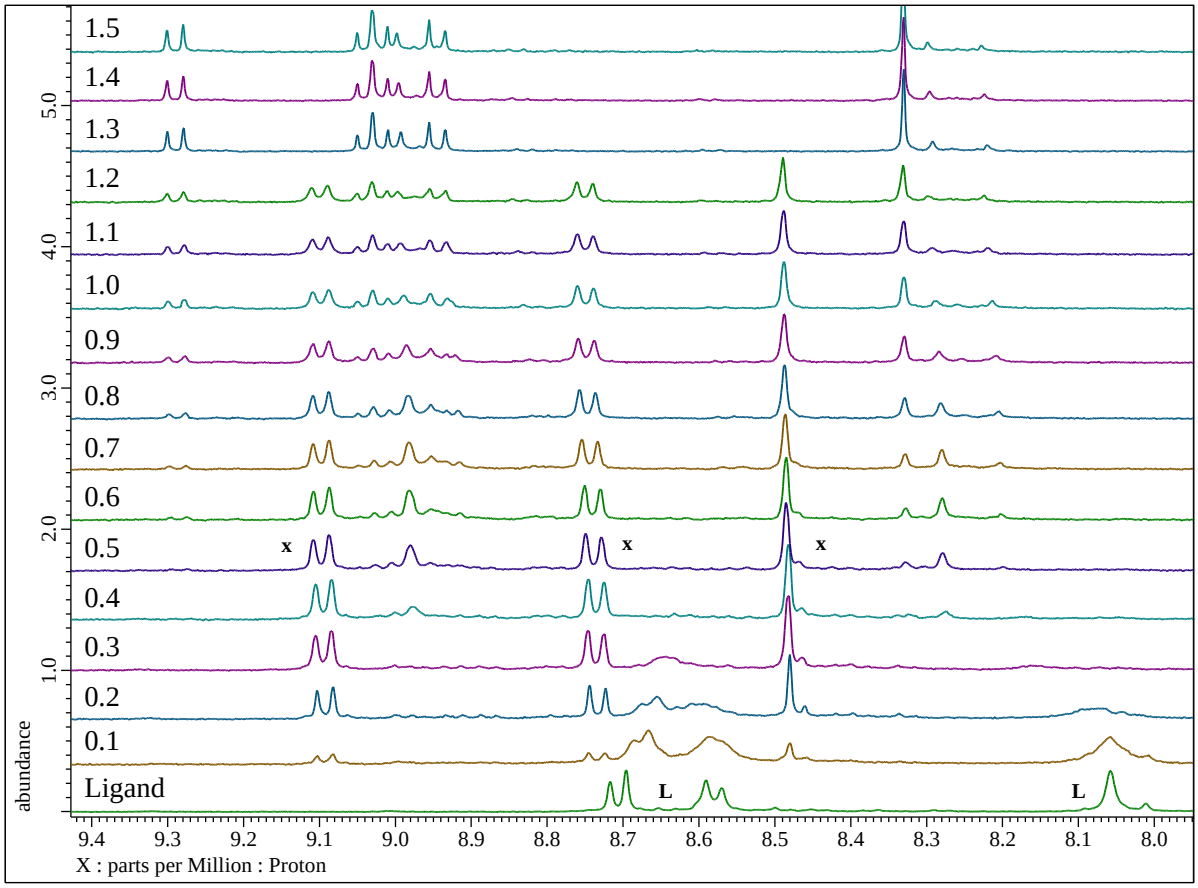


Figure 38. Aromatic region of the stack plot for the ^{1}H NMR titration of BTPhen ligand **14** with $Y(NO_3)_3$ in CD_3CN. Bottom spectrum = free ligand. Each preceding spectrum corresponds to the addition of 0.1 equivalents of metal salt solution (L = free ligand, x = 1:2 complex $[Y(\mathbf{14})_2(NO_3)]^{2+}$). The titration was stopped at a metal:ligand ratio of 1.2 and then resumed again after 1 week. After 1 week, the ^{1}H NMR spectrum at a metal:ligand ratio of 1.2 showed that all of the remaining 1:2 complex had dissociated to give the corresponding 1:1 complexes (species A, B and C).

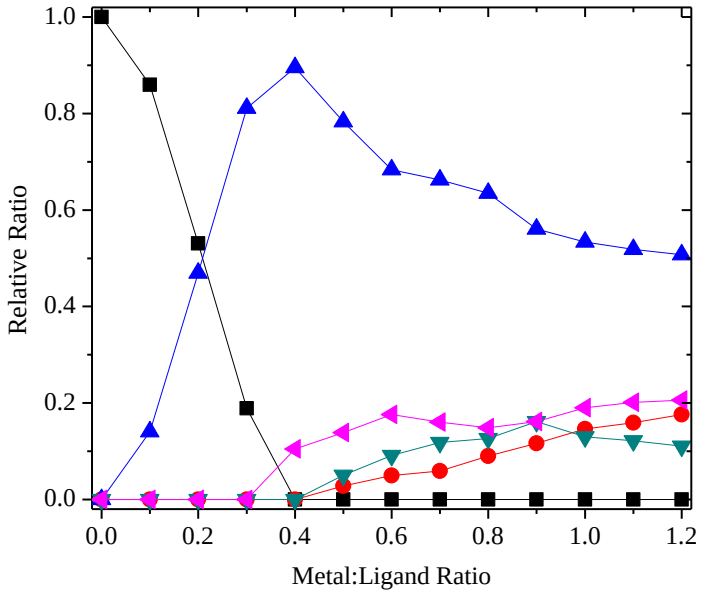


Figure 39. Species distribution for the ^{1}H NMR titration of BTPhen **14** with $Y(NO_3)_3$ in CD_3CN (■ = free ligand, ▲ = 1:2 complex, ● = species A, ▼ = species B, ◀ = species C).

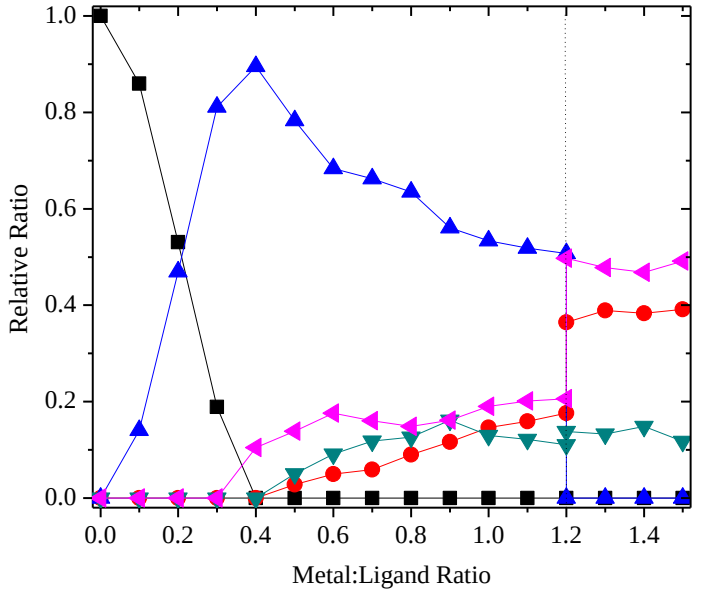


Figure 40. Species distribution for the ^{1}H NMR titration of BTPhen **14** with $Y(NO_3)_3$ in CD_3CN (■ = free ligand, ▲ = 1:2 complex, ● = species A, ▼ = species B, ◀ = species C). The dashed vertical line at a metal:ligand ratio of 1.2 indicates the titration was stopped at this point and then resumed again after 1 week. The ^{1}H NMR spectrum at a metal:ligand ratio of 1.2 was acquired again after 1 week before the titration was resumed.

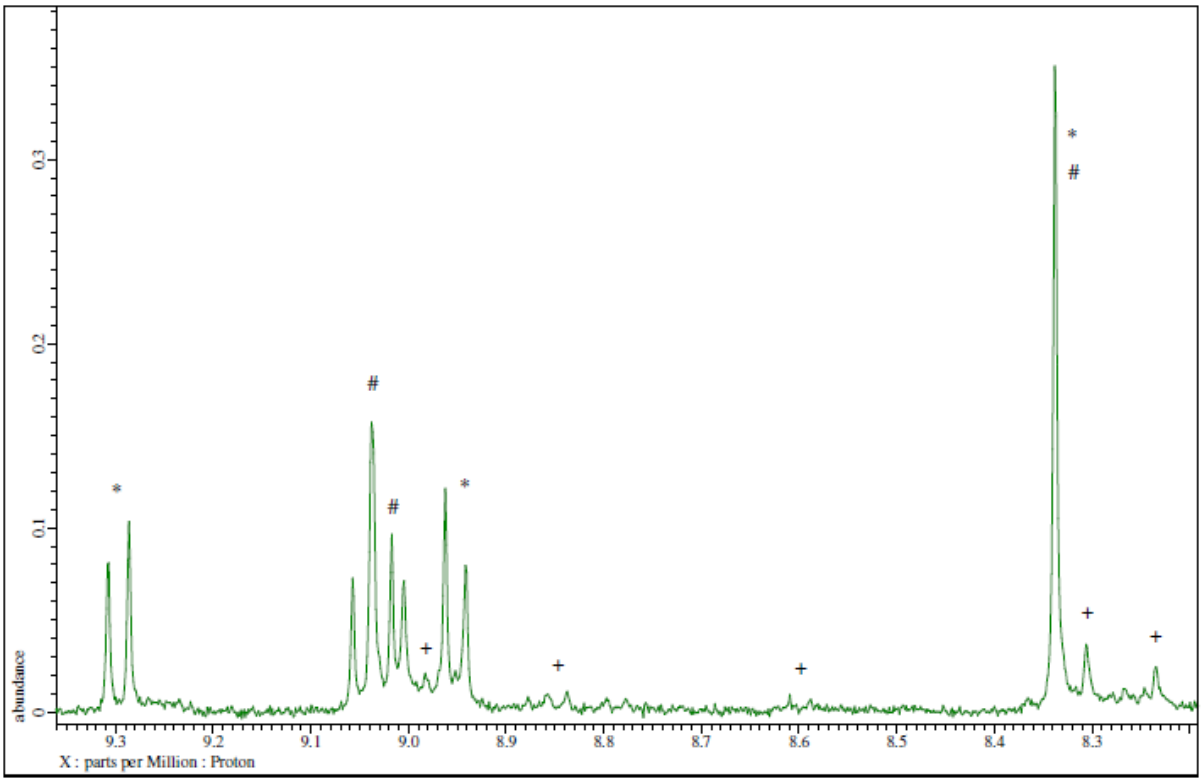


Figure 41. Enlargement of the aromatic region of the ^{1}H NMR spectrum of a mixture of BTPhen ligand **14** with $Y(NO_3)_3$ (1.5 equivalents) in CD_3CN. Assignments: * = species A (symmetrical 1:1 complex with tetradentate coordination of ligand), + = species B (unsymmetrical 1:1 complex with pentadentate coordination of ligand), # = species C (symmetrical 1:1 complex with hexadentate coordination of ligand).

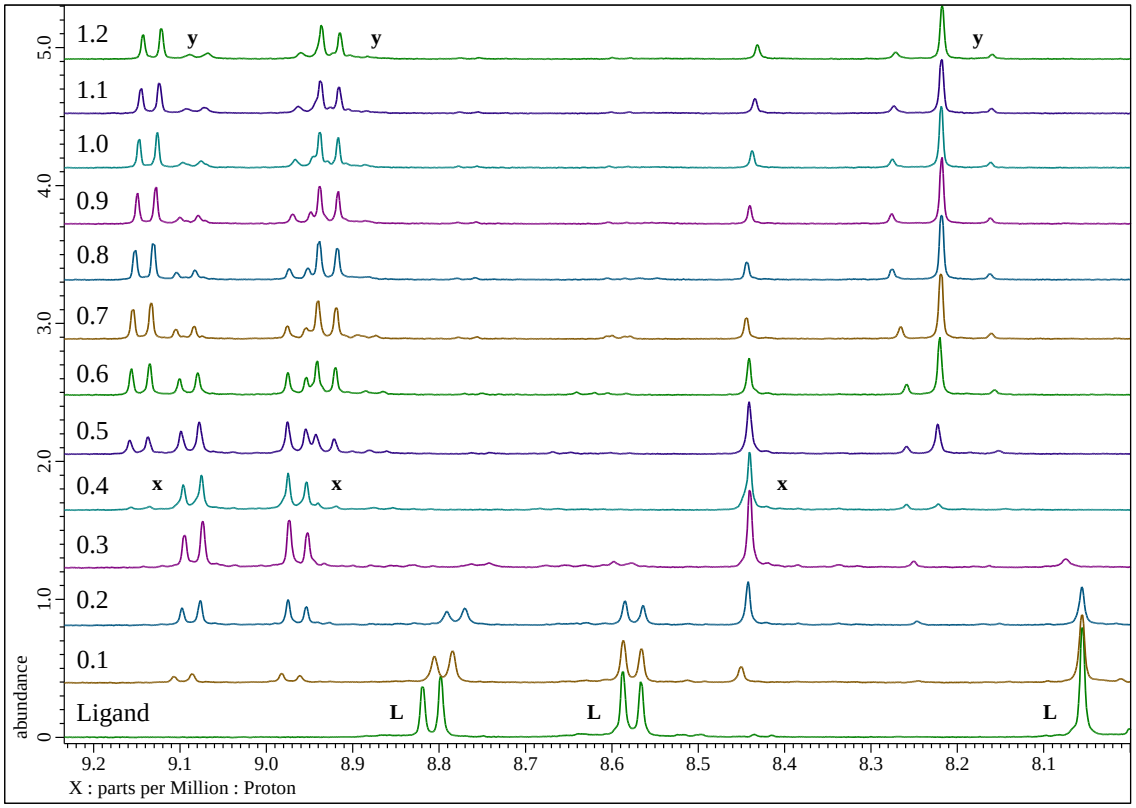


Figure 42. Aromatic region of the stack plot for the ^{1}H NMR titration of CA-BTPhen ligand **18** with $La(NO_3)_3$ in CD_3CN. Bottom spectrum = free ligand. Each preceding spectrum corresponds to the addition of 0.1 equivalents of metal salt solution (L = free ligand, x = 1:2 complex $[La(\mathbf{18})_2(NO_3)]^{2+}$, y = 1:1 complex $[La(\mathbf{18})(NO_3)_3]$).

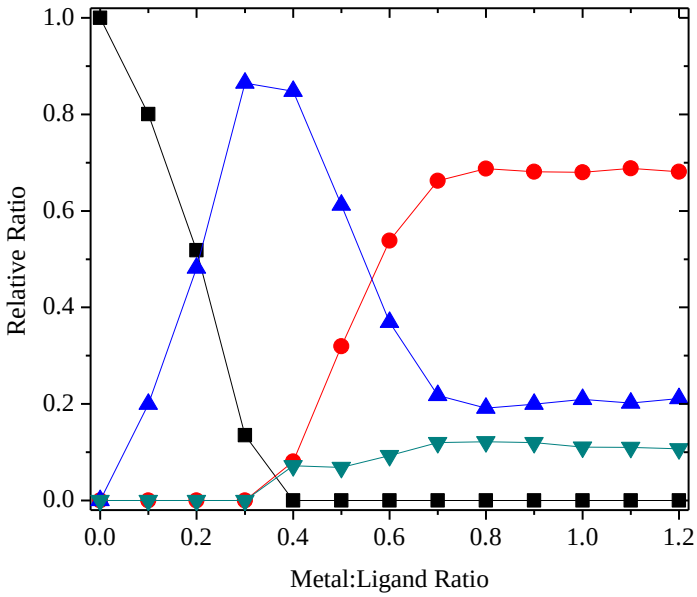


Figure 43. Species distribution for the ^{1}H NMR titration of CA-BTPhen **18** with $La(NO_3)_3$ in CD_3CN (■ = free ligand, ▲ = 1:2 complex, ● = symmetrical 1:1 complex with tetradentate coordination of ligand, ▼ = unsymmetrical 1:1 complex with pentadentate coordination of ligand).

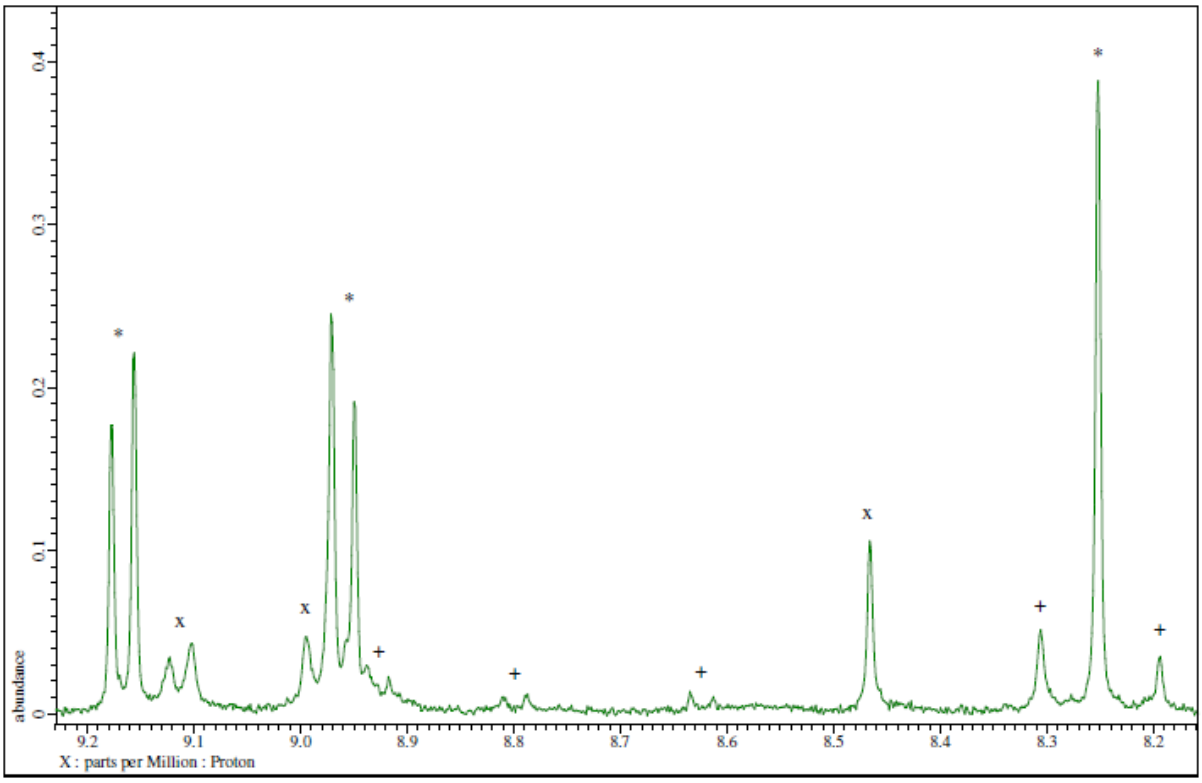


Figure 44. Enlargement of the aromatic region of the ^{1}H NMR spectrum of a mixture of CA-BTPhen ligand **18** with $La(NO_3)_3$ (1.2 equivalents) in CD_3CN. Assignments: x = 1:2 complex, * = symmetrical 1:1 complex with tetradentate coordination of ligand, + = unsymmetrical 1:1 complex with pentadentate coordination of ligand.

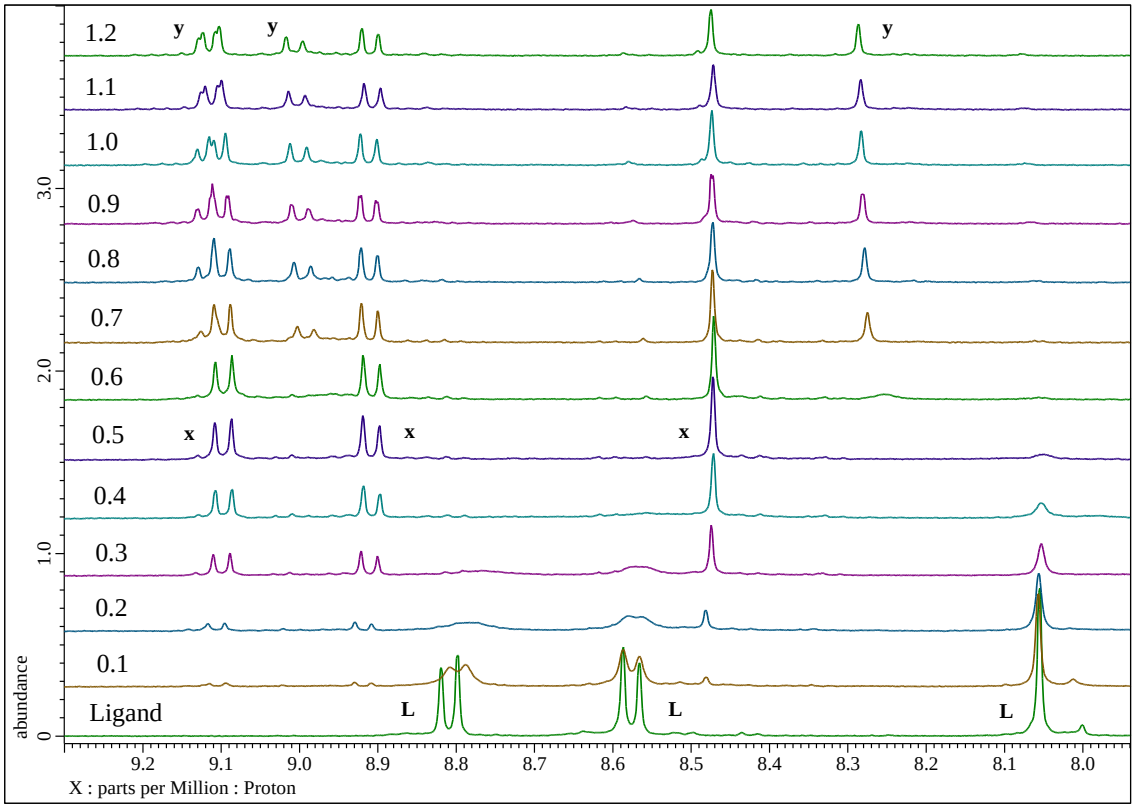


Figure 45. Aromatic region of the stack plot for the ^{1}H NMR titration of CA-BTPhen ligand **18** with $Lu(NO_3)_3$ in CD_3CN. Bottom spectrum = free ligand. Each preceding spectrum corresponds to the addition of 0.1 equivalents of metal salt solution (L = free ligand, x = 1:2 complex $[Lu(\mathbf{18})_2(NO_3)]^{2+}$, y = 1:1 complex $[Lu(\mathbf{18})(NO_3)_3]$).

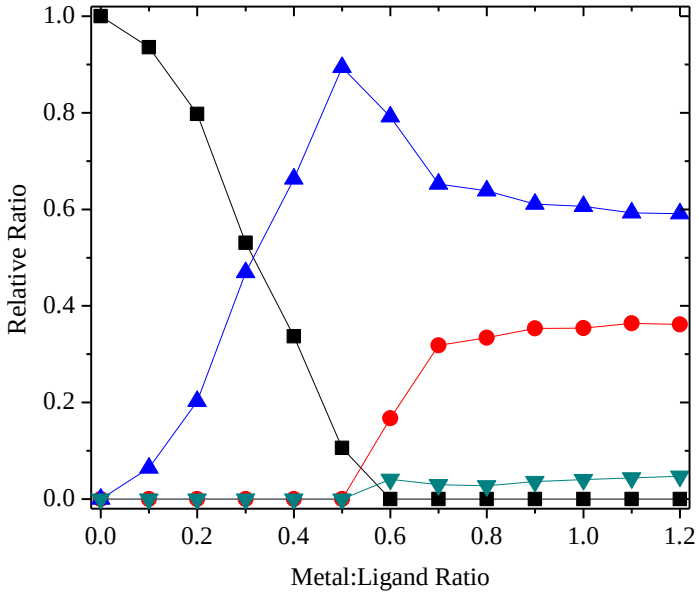


Figure 46. Species distribution for the ^{1}H NMR titration of CA-BTPhen **18** with $Lu(NO_3)_3$ in CD_3CN (■ = free ligand, ▲ = 1:2 complex, ● = symmetrical 1:1 complex with tetradentate coordination of ligand, ▼ = unsymmetrical 1:1 complex with pentadentate coordination of ligand).

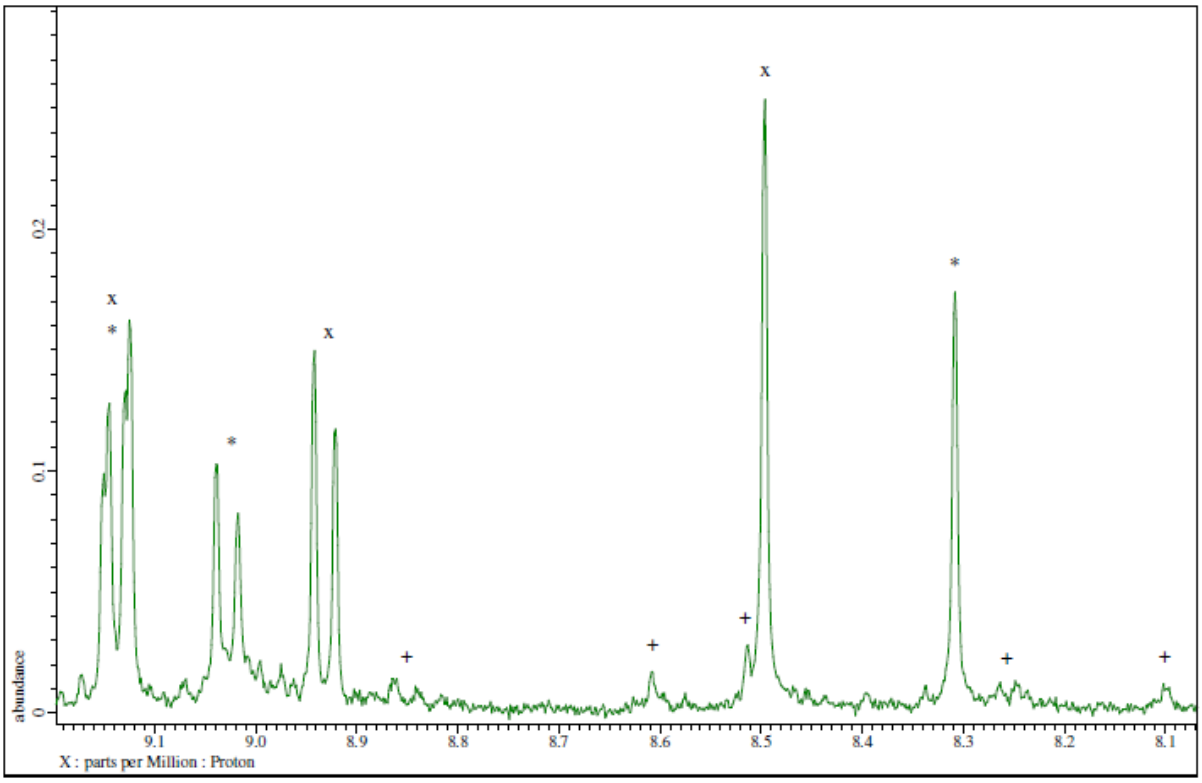


Figure 47. Enlargement of the aromatic region of the ^{1}H NMR spectrum of a mixture of CA-BTPhen ligand **18** with $Lu(NO_3)_3$ (1.2 equivalents) in CD_3CN. Assignments: x = 1:2 complex, * = symmetrical 1:1 complex with tetradentate coordination of ligand, + = unsymmetrical 1:1 complex with pentadentate coordination of ligand.

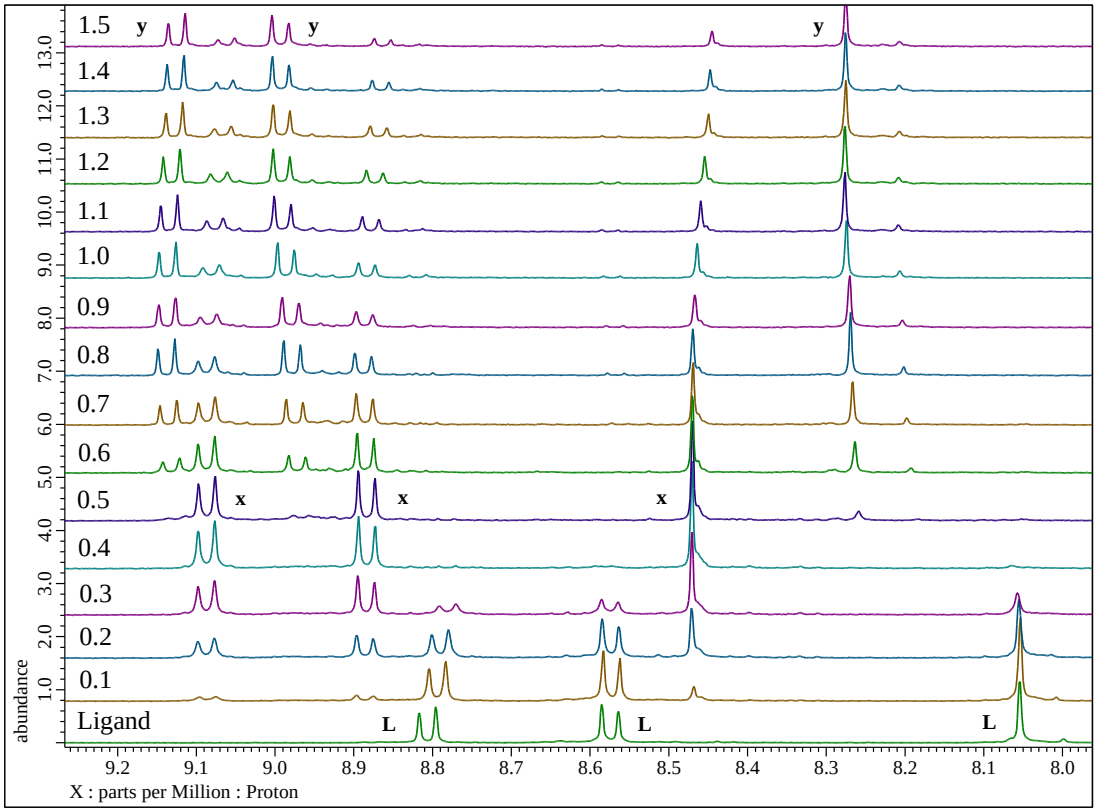


Figure 48. Aromatic region of the stack plot for the ^{1}H NMR titration of CA-BTPhen ligand **18** with $Y(NO_3)_3$ in CD_3CN. Bottom spectrum = free ligand. Each preceding spectrum corresponds to the addition of 0.1 equivalents of metal salt solution (L = free ligand, x = 1:2 complex $[Y(\mathbf{18})_2(NO_3)]^{2+}$, y = 1:1 complex $[Y(\mathbf{18})(NO_3)_3]$).

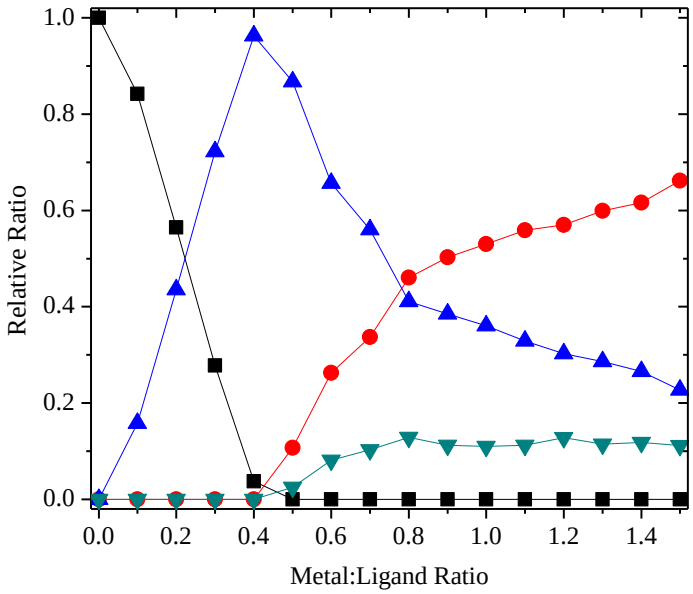


Figure 49. Species distribution for the ^{1}H NMR titration of CA-BTPhen **18** with $Y(NO_3)_3$ in CD_3CN (■ = free ligand, ▲ = 1:2 complex, ● = symmetrical 1:1 complex with tetradentate coordination of ligand, ▼ = unsymmetrical 1:1 complex with pentadentate coordination of ligand).

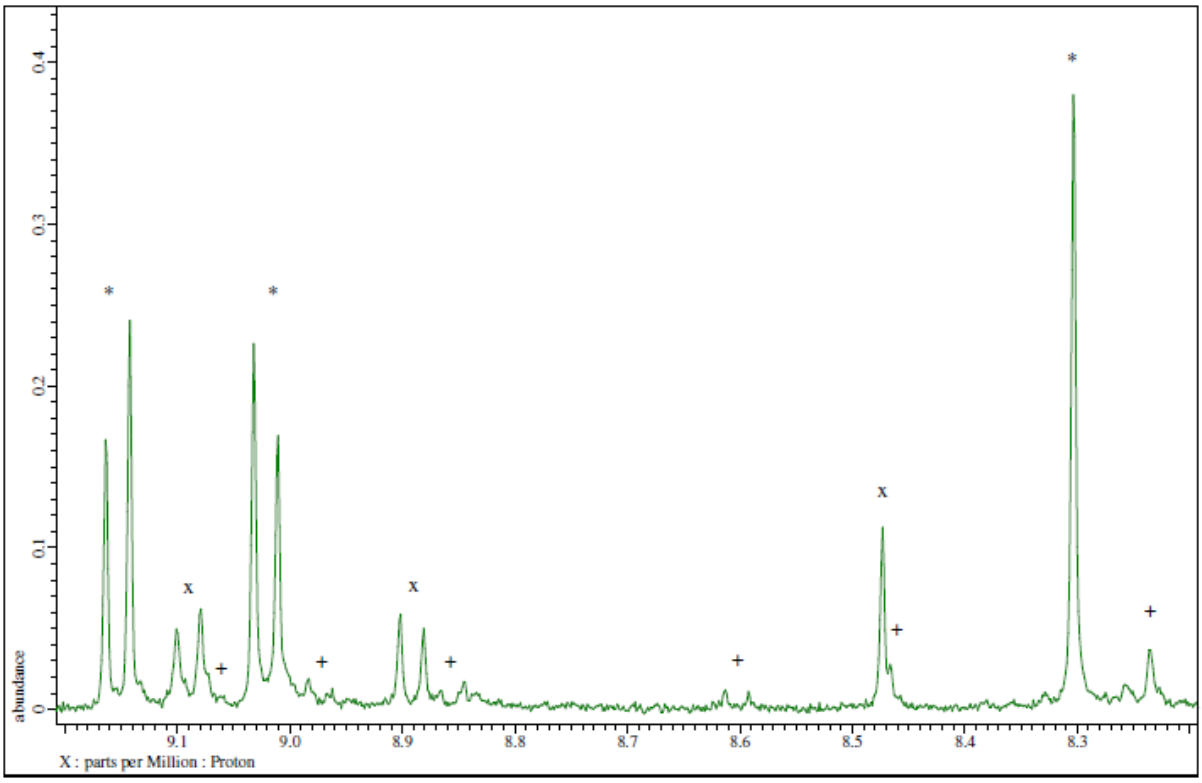


Figure 50. Enlargement of the aromatic region of the ^{1}H NMR spectrum of a mixture of CA-BTPhen ligand **18** with $Y(NO_3)_3$ (1.5 equivalents) in CD_3CN. Assignments: x = 1:2 complex, * = symmetrical 1:1 complex with tetradentate coordination of ligand, + = unsymmetrical 1:1 complex with pentadentate coordination of ligand.

Table 23. Percentage of the 1:2 complex that is present at the end of the ^{1}H NMR titrations of each of the BTPhen ligands **3a**, **3b**, **12**, **14** and **18** with La(III), Lu(III) and Y(III) in CD_3CN.

Ligand	La(III)	Lu(III)	Y(III)
BTPhen **3a**[a]	73%	79%	95%
BTPhen **3b**[b]	64%	70%	82%
BTPhen **12**	0%	25%	14%
BTPhen **14**	0%	39%	50%[c]
CA-BTPhen **18**	21%	59%	23%

[a] Taken from ref. 10. [b] Taken from ref. 11. [c] This decreased to 0% after 1 week, see **Figure 40**.

8: Kinetics and Interfacial Tension Measurements

Table 24. Interfacial tension measurements for BTPhen **12** in 1-octanol as a function of the ligand concentration (organic phase: pre-equilibrated solutions of **12** in 1-octanol; aqueous phase: pre-equilibrated 1 M HNO_3 at 22–23 ºC).

[BTPhen 12] (mM)	Measured σ (mN/m)	Absolute σ (mN/m)
12.0	0.2	0.2
10.0	0.5	0.4
7.5	3.4	3.0
7.5	3.2	2.8
6.7	4.1	3.6
5.0	4.8	4.2
2.3	4.9	4.3
1.02	5.4	4.8
0.442	5.6	5.0
0.121	5.6	5.0
0.012	5.4	4.8
0.000	5.6	5.0

Table 25. Interfacial tension measurements for BTPhen **3a** in 1-octanol as a function of the ligand concentration (organic phase: pre-equilibrated solutions of **3a** in 1-octanol; aqueous phase: pre-equilibrated 1 M HNO_3 at 22–23 ºC, data taken from ref. 12).

[BTPhen 3a] (mM)	Measured σ (mN/m)	Absolute σ (mN/m)
10	0.4	0.3
10	0.3	0.3
7.61	1.2	1.0
6.2	3.4	3.0
0.698	4.2	3.7
0.123	4.6	4.0
0.0125	4.9	4.3
0	5.3	4.7

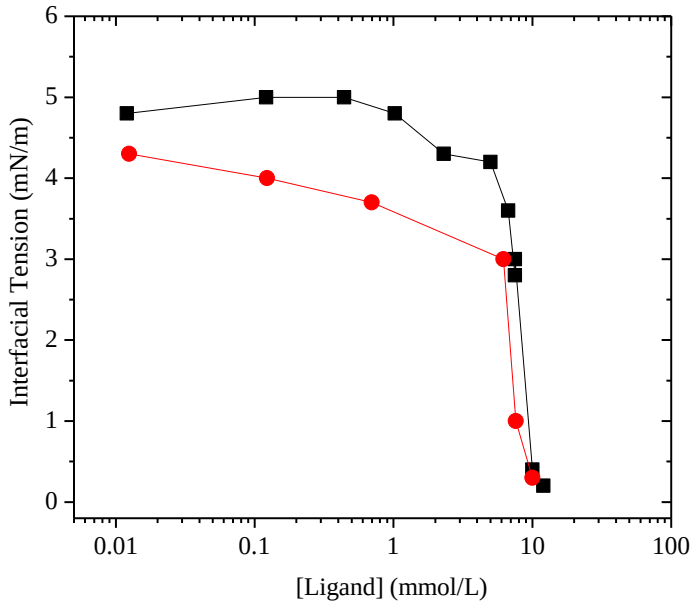


Figure 51. Interfacial tension measurements for BTPhen ligands **12** and **3a** in 1-octanol as a function of the ligand concentration (■ = BTPhen **12**, ● = BTPhen **3a**, organic phase: pre-equilibrated solutions of **12** or **3a** in 1-octanol, aqueous phase: pre-equilibrated 1 M HNO_3 at 22–23 °C). Data for BTPhen **3a** taken from ref. 12.

Table 26. Extraction (k_{ext}) and back-extraction (k_{str}) rate constants for the extraction/back-extraction of ^{241}Am(III) and ^{152}Eu(III) by BTPhen ligands **12** and **3a** (organic phase: 10 mM **12** or **3a** in 1-octanol. aqueous phase: 3 M HNO_3).

Ligand	**Metal**	***D***	**k_{ext} (cm/s)**	**k_{str} (cm/s)**
12[a]	Eu(III)	0.334	2.7×10^{-5}	8.2×10^{-5}
12[b]	Eu(III)	0.334	2.2×10^{-5}	6.4×10^{-5}
12[a]	Am(III)	74.5	9.6×10^{-5}	1.3×10^{-6}
3a[a,c]	Eu(III)	9.0	3.8×10^{-6}	0.43×10^{-6}
3a[a,c,d]	Eu(III)	12.6	1.85×10^{-5}	1.47×10^{-6}

[a] Results measured for extraction. [b] Results measured for back-extraction. [c] Data taken from ref. 12. [d] 0.01 M TODGA (*N*,*N*,*N*',*N*'-tetraoctyldiglycolamide) was added to the organic phase.

9: References

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