

Supporting Information

Sensitization of europium(III) luminescence by benzophenone-containing ligands: Regioisomers, rearrangements and chelate ring size, and their influence on quantum yields

A. J. Wilkinson,^a D. Maffeo,^a A. Beeby,^a C. E. Foster,^b and J. A. G. Williams^{a,*}

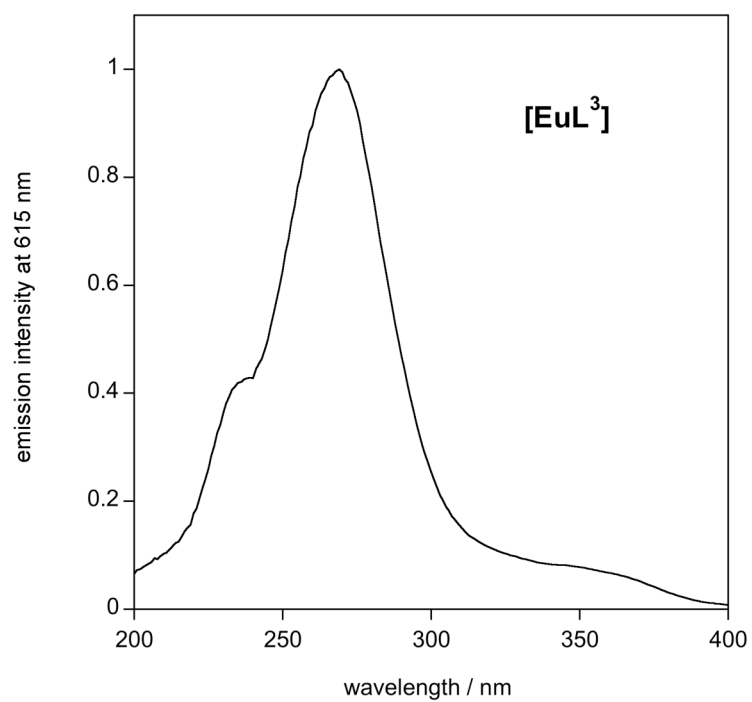
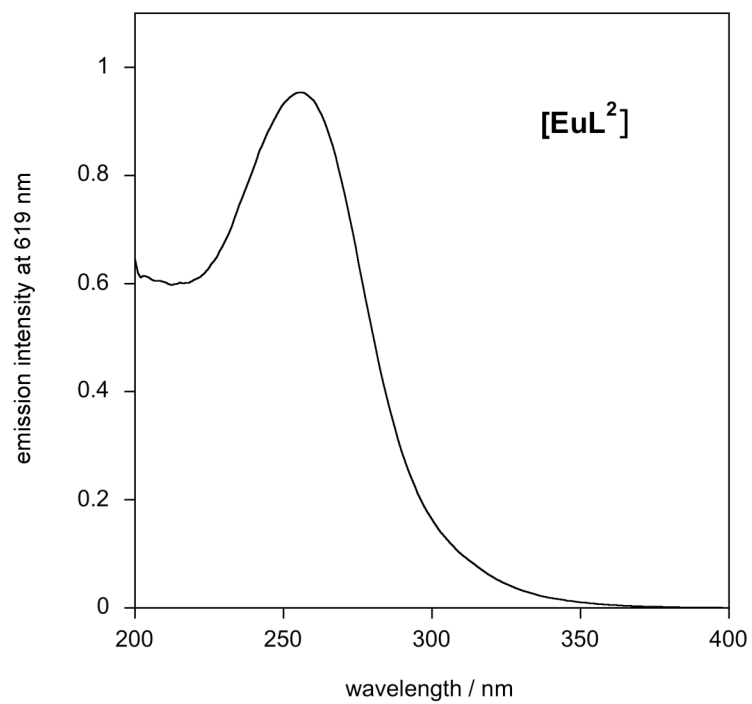
*(a) Department of Chemistry, University of Durham, South Road, Durham, DH1 3LE U.K.
and (b) Fujifilm Imaging Colorants Ltd, Hexagon House, Blackley, Manchester, M9 8ZS U.K.*

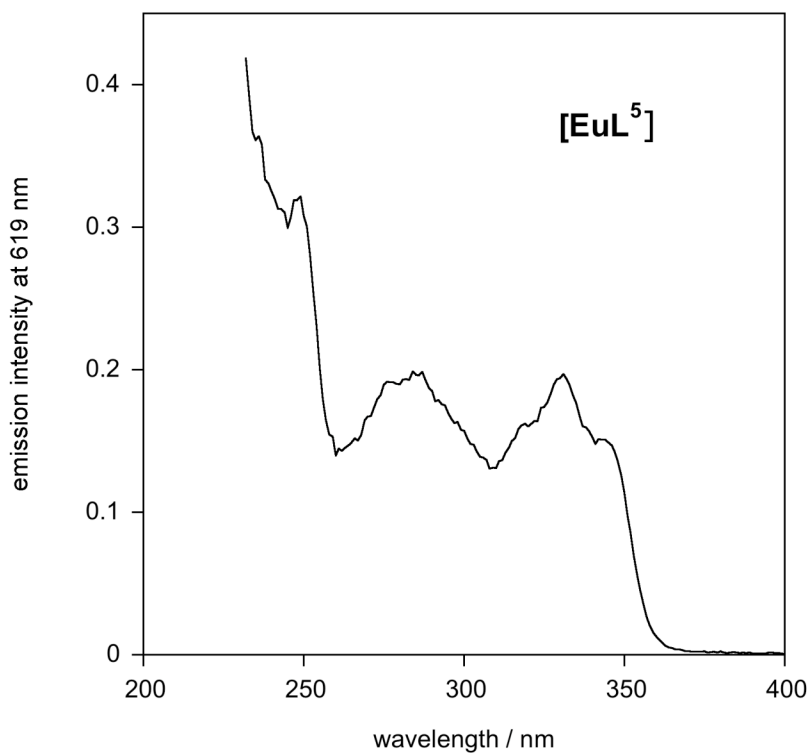
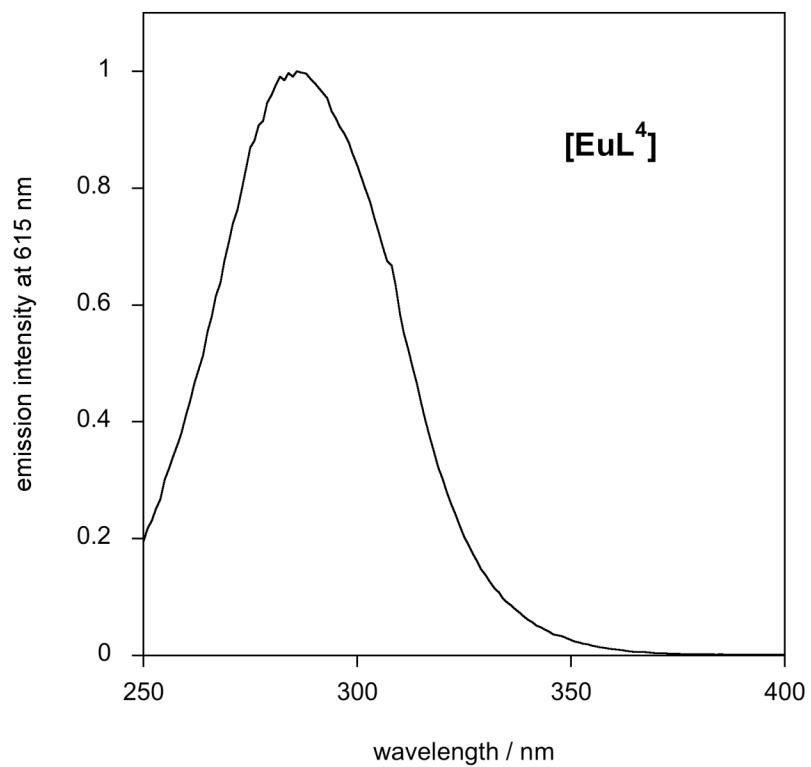
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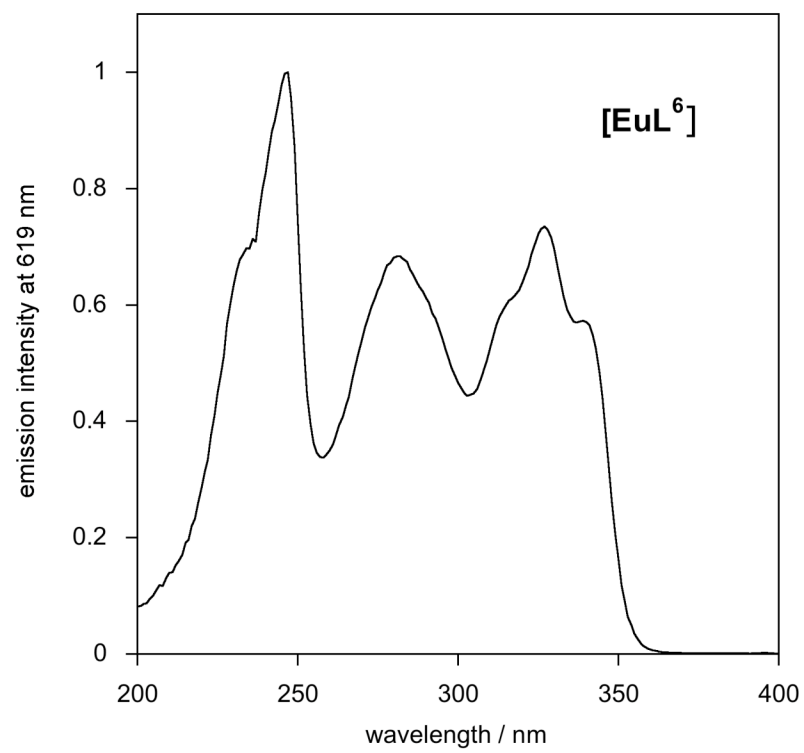
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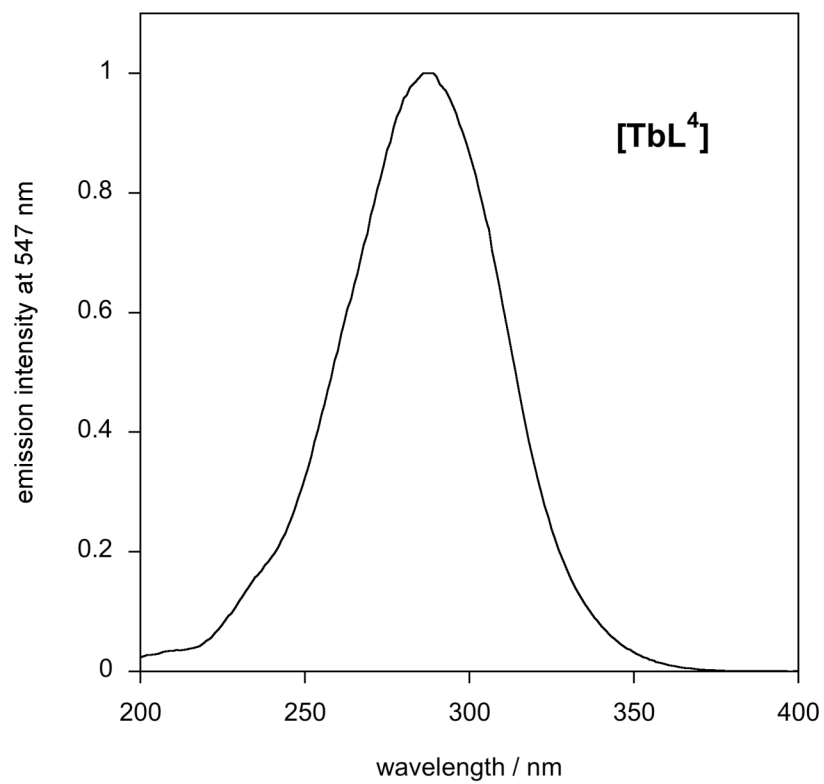
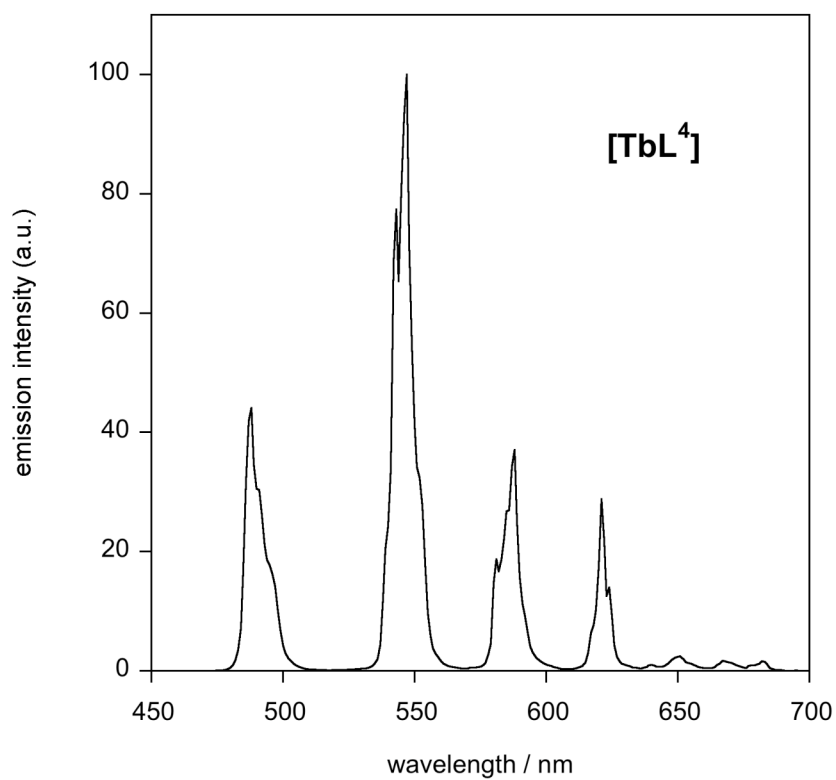
* Corresponding author: E-mail: j.a.g.williams@durham.ac.uk

Excitation spectra of europium complexes in D₂O solution at 298K









Details of synthesis and characterisation of the aromatic precursors

N-(3-Benzoyl-phenyl)-2-bromo-acetamide, **2**

Bromoacetyl bromide (2.84 g, 14.1 mmol) was added dropwise to a solution of 3-aminobenzophenone (2.19 g, 11.1 mmol) and triethylamine (1.36 g, 13.4 mmol) in diethyl ether (100 mL) at -10°C, ensuring that the temperature did not rise above 0°C. After warming to room temperature, the precipitated solid was isolated by filtration, redissolved in dichloromethane and washed with HCl (1 mol dm⁻³, 3 × 50 mL). Drying over MgSO₄, removal of solvent under reduced pressure and drying under vacuum gave the desired product **2** as a pale brown solid (2.42 g, 68%). ¹H-NMR (CDCl₃, 400 MHz) δ = 8.32 (1H, br s, NH), 7.94 (1H, d, J = 7.8, H⁶), 7.85 (1H, s, H²), 7.81 (2H, d, J = 5.6, H^{2'}), 7.61 (1H, tt, J = 7.4, 1.4, H^{4'}), 7.57 (1H, dt, J = 7.7, 1.3, H⁴), 7.46-7.53 (3H, m, H⁵ & H^{3'}), 4.03 (2H, s, CH₂). ¹³C{¹H}-NMR (CDCl₃, 101 MHz) δ = 196.1 (C=O), 163.8 (C=O), 138.7 (C^q), 137.3 (C^q), 137.3 (C^q), 132.9 (C^{4'}), 130.2 (C^{2'}), 129.3 (C⁵), 128.6 (C^{3'}), 126.9 (C⁴), 124.1 (C⁶), 121.4 (C²), 29.4 (CH₂). MS(EI) *m/z* = 317/319 (M⁺), 240/242 (M⁺ - Ph), 238 (M⁺ - Br), 197 (PhCOC₆H₄NH₂⁺), 105 (PhCO⁺), 77 (Ph⁺). IR (KBr disc) $\bar{\nu}$ = 1662 cm⁻¹ (ketone, C=O stretch), 1655 cm⁻¹ (amide, C=O stretch).

N-(2-Benzoyl-phenyl)-2-bromo-acetamide, **3**

Bromoacetyl bromide (2.89 g, 14.3 mmol) was added dropwise to a solution of 2-aminobenzophenone (2.19 g, 11.1 mmol) and triethylamine (1.50 g, 14.8 mmol) in diethyl ether (100 mL) at -10°C, ensuring that the temperature did not rise above 0°C. After warming to room temperature, the reaction mixture was washed with HCl (1 mol dm⁻³, 3 × 50 mL) and dried over MgSO₄. Removal of solvent under reduced pressure and drying under vacuum gave the desired product, **3**, as a pale brown solid (3.30 g, 93%). ¹H-NMR (CDCl₃, 500 MHz) δ = 11.50 (1H, br s, NH), 8.59 (1H, d, J = 8.2, H⁶), 7.72 (2H, d, J = 7.9, H^{2'}), 7.58-7.63 (3H, m, H³, H⁵ & H^{4'}), 7.49 (2H, t, J = 7.6, H^{3'}), 7.16 (1H, t, J = 7.6, H⁴), 4.03 (2H, s, CH₂). ¹³C{¹H}-NMR (CDCl₃, 126 MHz) δ = 199.4 (C=O), 165.2 (NHC=O), 139.6 (C^q), 138.4 (C^q), 134.3 (C³ or C⁵ or C^{4'}), 133.7 (C³ or C⁵ or C^{4'}), 132.8 (C³ or C⁵ or C^{4'}), 130.1 (C^{2'}), 128.5 (C^{3'}), 124.2 (C^q), 123.2 (C⁴), 121.7 (C⁶), 29.6 (CH₂). MS(EI) *m/z* = 317/319 (M⁺), 240/242 (M⁺ - Ph), 238 (M⁺ - Br), 224 (M⁺ - CH₂Br), 212/214 (M⁺ - PhCO), 196 (M⁺ - COCH₂Br), 105 (PhCO⁺), 77 (Ph⁺). IR (KBr disc) $\bar{\nu}$ = 1684 cm⁻¹ (ketone, C=O stretch), 1630 cm⁻¹ (amide, C=O stretch).

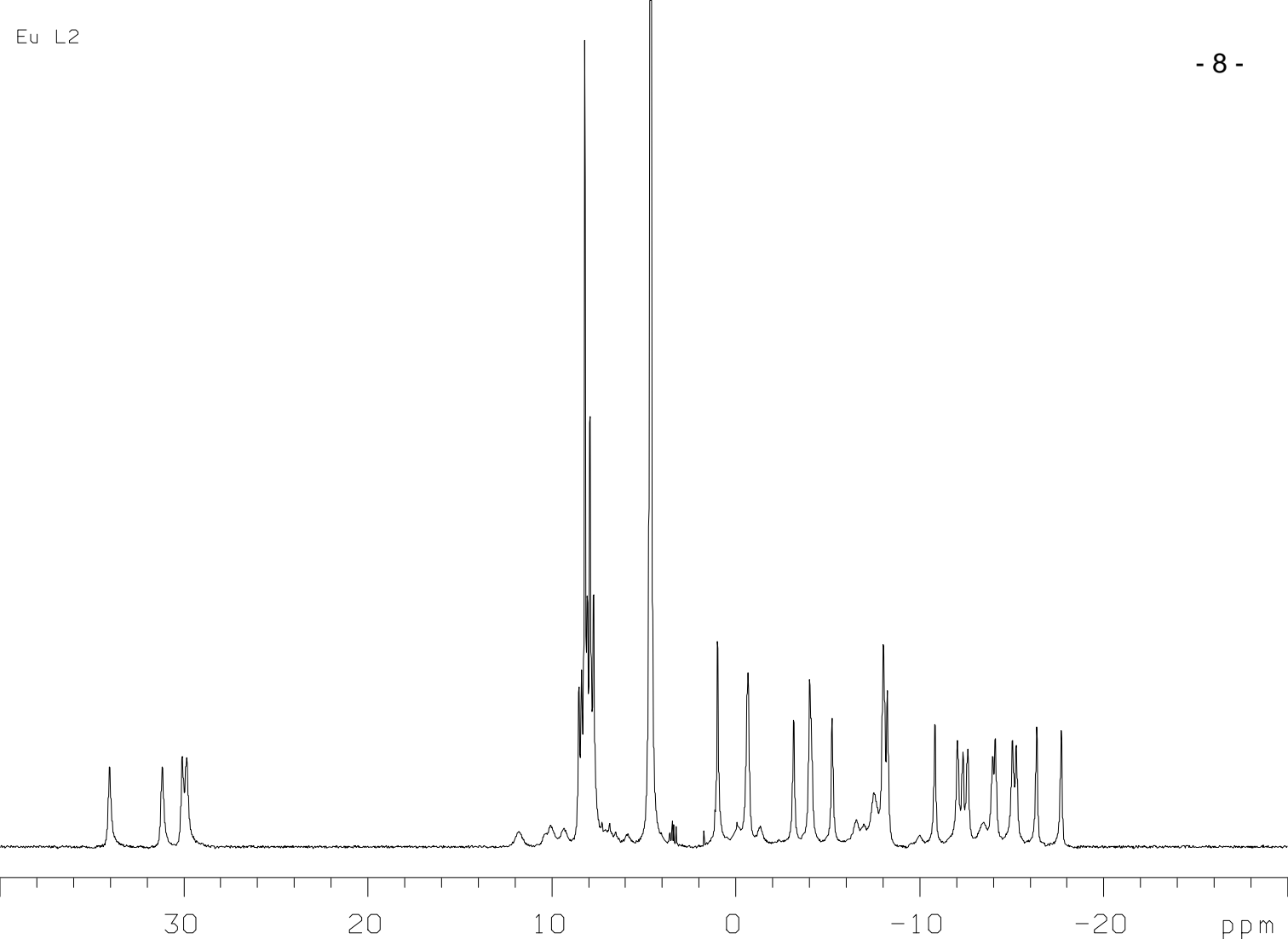
N-(2-Acetyl-phenyl)-2-bromo-acetamide

Bromoacetyl bromide (2.89 g, 14.3 mmol) was added dropwise to a solution of 2-aminoacetophenone (1.34 g, 11.1 mmol) and triethylamine (1.50 g, 14.8 mmol) in diethyl ether (100 mL) at -10°C, ensuring

that the temperature did not rise above 0°C. After warming to room temperature, the precipitated solid was removed by filtration and washed with diethyl ether (100 mL). The combined filtrates were washed with HCl solution (1 mol dm⁻³, 3 × 50 mL) and dried over MgSO₄. Removal of solvent under reduced pressure and drying under vacuum gave the desired product as a pale brown oil that solidified upon standing (2.26 g, 79%). ¹H-NMR (CDCl₃, 400 MHz) δ = 12.37 (1H, br s, NH), 8.71 (1H, dd, J = 8.5, 1.0, arom), 7.94 (1H, dd, J = 8.0, 1.6, arom), 7.59 (1H, ddd, J = 8.4, 7.4, 1.6, arom), 7.20 (1H, ddd, J = 7.8, 6.8, 1.1, arom), 4.03 (2H, s, CH₂), 2.70 (3H, s, CH₃). ¹³C{¹H}-NMR (CDCl₃, 101 MHz) δ = 202.8 (C=O), 165.7 (CONH), 140.1 (C^q), 135.2 (CH), 131.8 (CH), 123.6 (CH), 122.7 (C^q), 121.0 (CH), 29.7 (CH₂), 28.6 (CH₃). MS(EI) *m/z* = 255/257 (M⁺), 240/242 (M⁺ - CH₃), 212/214 (M⁺ - COCH₃), 176 (M⁺ - Br), 162 (M⁺ - CH₂Br), 135 (H₂NC₆H₄COCH₃⁺), 133 (M⁺ - COCH₃, Br), 120 (C₆H₃COCH₃⁺), 77 (C₆H₅⁺), 65 (C₅H₅⁺), 43 (CH₃CO⁺). IR (KBr disc) $\bar{\nu}$ = 1670 cm⁻¹ (ketone, C=O stretch), 1655 cm⁻¹ (amide, C=O stretch).

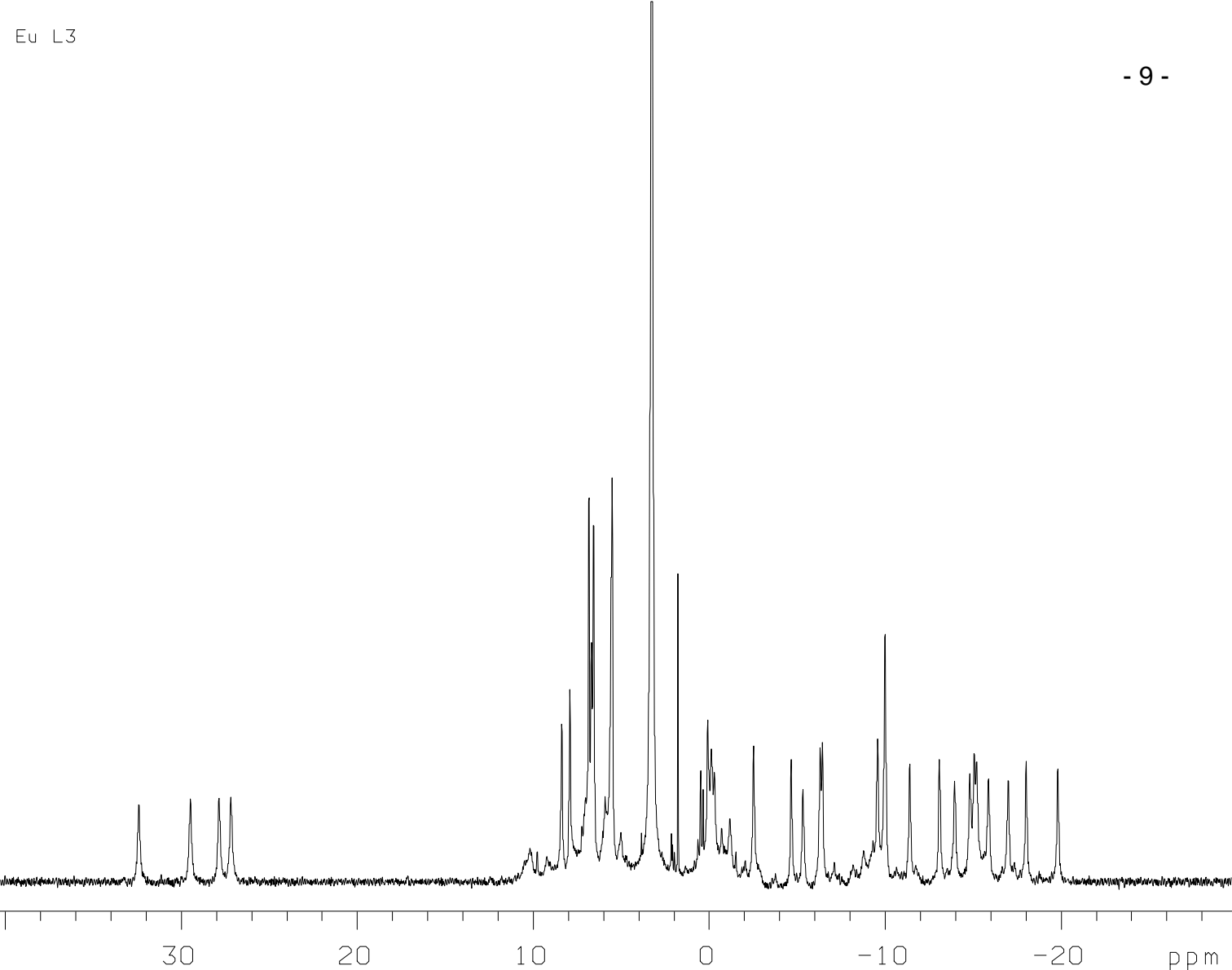
N-(4-Benzoylphenyl)acrylamide, 4

A solution of triethylamine (2.02 g, 19.7 mmol) and 4-aminobenzophenone (2.65 g, 13.2 mmol) in dichloromethane (50 mL) was stirred at 0° and a solution of acryloyl chloride (1.11 mL, 13.2 mmol) in dichloromethane (25 mL) was added dropwise. After 24 h, the solution was washed twice with water (50 mL) and the solvent was removed under vacuum to give the desired compound **4** (3.03 g, 92%). ¹H-NMR (CDCl₃, 200 MHz) δ = 10.48 (1H, s, NH), 8.02 (2H, d, J = 8.7, arom), 7.74 (4H, td, J = 8.7, 7.8, arom), 7.55 (1H, t, J = 7.8, arom), 7.45 (2H, t, 7.8, arom), 6.81 (1H, q, J = 16.4, 10.4, CH₂=CH), 6.42 (1H, d, J = 16.9, HCH=CH trans), 6.68 (1H, d, J = 10.4, HCH=CH cis). ¹³C{¹H}-NMR (CDCl₃, 126 MHz) δ = 195.5, 164.4, 143.1, 137.6, 131.9, 131.8, 131.5, 130.9, 129.4, 128.0, 127.1, 118.9. MS(ES⁻): *m/z* = 250 (M⁻), 286 (M+Cl⁻).



Eu L3

- 9 -



EuL4

- 10 -

