

Supporting Informations (SI) for

Luminescent Dansyl-based Ionic Liquids from amino acids and methylcarbonate onium salt precursors: Synthesis and Photobehaviour

Giulia Fiorani,^{a*} Maurizio Selva,^{a*} Alvise Perosa,^a Alvise Benedetti,^b Francesco Enrichi,^c Peter Licence,^d Timothy L. Easun^d

^{a,b} Department of Molecular Sciences and Nanosystems, Centre for Sustainable Technologies, University of Ca' Foscari Venezia, and INSTN and Centro di Microscopia Elettronica 25 "Giovanni Stevanato"
Calle Larga Santa Marta, Dorsoduro 2137, 30123 Venezia, and
Via Torino 155, 30172 Mestre (Venezia), Italy

^c Veneto Nanotech, Via delle Industrie 5, 30175 Marghera (Venezia), Italy

^d School of Chemistry, The University of Nottingham, University Park, Nottingham NG7 2RD, UK

email: selva@unive.it; tel. +39 041 234 8687

NMR characterization of:	Page
Trimethyloctylammonium methylcarbonate, [N ₁₁₁₈][H ₃ COCO ₂]	2
Phenylalanine methyl ester, 1a	2
Tryptophan methyl ester, 2a	2
Dansylated amino acid esters	
- Methyl (2-dansylamido-3-indolyl)propanoate, 1b	2
- Methyl (2-dansylamido-3-phenyl)propanoate, 2b	2
- Ethyl (2-dansylamido-3-oxo)amidoetanoate, 3b	3
Triethylammonium (2-dansylamido-3-indolyl)propanoate, 1'c	3
Triethylammonium(2-dansylamido-3-phenyl)propanoate, 2'c	3
3-Dansylamido-2-ossoaminoetanoic acid, 3c	3
Full characterization of LILs:	
Trioctylmethylphosphonium 3-indolyl-2-dansylamidopropanoate, [P ₁₈₈₈][DNS-Trp], 1d	4
Tributylmethylphosphonium 3-indolyl-2-dansylamidopropanoate, [P ₁₄₄₄][DNS-Trp], 1e	8
Trimethyloctylammonium 3-indolyl-2-dansylamidopropanoate, [N ₁₁₁₈][DNS-L-Trp], 1f	12
Trioctylmethylphosphonium 3-phenyl-2-dansylamidopropanoate, [P ₁₈₈₈][DNS-Phe], 2d	15
Methyltrioctylphosphonium 2-(3-dansylamido-2-oxo)aminoetanoate, [P ₁₈₈₈][DNS-Gly-Gly], 3d	19

Trimethyloctylammonium methylcarbonate, [N₁₁₁₈][H₃COCO₂]

¹H NMR (400 MHz, 298 K, CDCl₃) δ: 3.45 (dd, J = 13.8, 5.7 Hz, 3H, [H₃C(CO)O]⁻), 3.36 (s, 9H, -N(CH₃)₃), 1.72 (s, 2H, H-1 Octyl), 1.31 (dd, J = 20.5, 12.3 Hz, 10H, H-2 – H-7 Octyl), 0.88 (t, J = 6.7 Hz, 3H, -CH₃Octyl). Traces of the corresponding hydrogencarbonate anion (3.56 ppm). ¹³C NMR (101 MHz, 298 K, CDCl₃) δ: 170.36 ([HO(CO)O]⁻, hydrogencarbonate anion traces), 158.29 ([H₃CO(CO)O]⁻), 66.62 (C-1 Octyl), 52.88 ([H₃C(CO)O]⁻), 49.73 (N(CH₃)₃), 31.58 (C-3 Octyl), 29.10 (C-5 Octyl), 28.97 (C-4 Octyl), 26.19 (C-6 Octyl), 23.12 (C-7 Octyl), 22.49 (C-1 Octyl), 13.97 (C-8 Octyl).

Phenylalanine methyl ester, 1a

¹H NMR (400 MHz, 298 K, CDCl₃) δ: 7.34 – 7.28 (m, 2H, H-2 + H-6 Ph), 7.25 – 7.17 (m, 3H, H-3 + H-4 + H-5Ph), 3.76 (dd, ³J = 7.8, ²J = 5.2 Hz, 1H, H-2 Propyl), 3.72 (d, J = 3.3 Hz, 3H, -CO₂CH₃), 3.11 (dd, ³J = 13.6 Hz, ²J = 5.2 Hz, 1H, H-3 Propyl), 2.88 (dd, ³J = 13.5 Hz, ²J = 7.9 Hz, 1H, H-3 Propyl), 1.81 (s, 2H, -NH₂).

Tryptophan methyl ester, 2a

¹H NMR (400 MHz, 298 K, DMSO-d₆) δ: 7.48 (dd, ³J = 8.0 Hz, ⁴J = 0.5 Hz, 1H, H-7 Ind), 7.33 (dt, ³J = 8.1 Hz, ⁴J = 0.9 Hz, 1H, H-4 Ind), 7.11 (d, J = 2.3 Hz, 1H, H-2 Ind), 7.05 (ddd, ³J = 8.1 Hz, ³J = 7.1 Hz, ⁴J = 1.1 Hz, 1H, H-5 Ind), 6.97 (ddd, ³J = 8.0 Hz, ³J = 7.0 Hz, ⁴J = 1.0 Hz, 1H, H-6 Ind), 3.62 (t, J = 6.3 Hz, 1H, H-3 Propyl), 3.55 (s, 3H, -CO₂CH₃), 3.07 – 2.98 (m, 1H, H-2 Propyl), 2.97 – 2.89 (m, 1H, H-2 Propyl).

Methyl (2-dansylamido-3-indolyl)propanoate, 1b

1b: ¹H NMR (400 MHz, 333 K, CDCl₃) δ: 8.47 (d, J = 8.5 Hz, 1H, H-4 DNS), 8.25 – 8.10 (m, 2H, H-8 + H-2 DNS), 7.91 (s, 1H, -NH-Ind), 7.52 – 7.44 (m, 1H, H-3 DNS), 7.41 (dd, ³J = 8.5 Hz, ³J = 7.4 Hz, 1H, H-7 DNS), 7.35 (d, J = 8.0 Hz, 1H, H-6 DNS), 7.24 (s, 1H, H-4 Ind), 7.14 (m, 2H, H-6 + H-7 Ind), 7.05 – 6.97 (m, 1H, H-5 Ind), 6.86 (s, 1H, H-2 Ind), 5.35 (d, J = 8.7 Hz, 1H, -SO₂NH-), 4.24 (dd, ³J = 5.8 Hz, ²J = 2.9 Hz, 1H, H-2 Propyl), 3.28 (s, 3H, -CO₂CH₃), 3.15 (d, J = 5.6 Hz, 2H, H-3 Propyl), 2.87 (s, 6H, -N(CH₃)₂). ¹³C NMR (101 MHz, 323 K, CDCl₃) δ: 171.43 (-CO₂CH₃), 136.06 (C-5 DNS), 134.87 (C-1 DNS), 134.60 (C-9 Ind), 130.46 (C-9 DNS), 129.82 (C-4 DNS), 129.64 (C-7 DNS), 129.45 (C-8 Ind), 129.02 (C-3 DNS), 128.20 (C-2 DNS), 128.18 (C-8 DNS), 127.19 (C-2 Ind), 123.25 (C-5 Ind), 123.00 (C-10 DNS), 122.15 (C-7 DNS), 119.59 (C-7 Ind), 118.35 (C-6 Ind), 115.17 (C-6 DNS), 111.01 (C-4 Ind), 109.09 (C-1 Ind), 56.46 (C-2 Propyl), 52.13 (-CO₂CH₃), 45.37 (-N(CH₃)₂), 29.19 (C-3 Propyl).

Methyl (2-dansylamido-3-phenyl)propanoate, 2b

2b: ¹H NMR (400 MHz, 333 K, CDCl₃) δ: 8.55 (d, J = 8.6 Hz, 1H, H-8 DNS), 8.26 (d, J = 8.7 Hz, 1H, H-2 DNS), 8.18 (d, J = 7.2 Hz, 1H, H-3 DNS), 7.56 – 7.43 (m, 2H, H-3 + H-4 DNS), 7.20 (d, J = 7.6 Hz, 1H, H-6 DNS), 7.13 – 7.06 (m, 3H, H-3 Ph + H-5 Ph + H-7 DNS), 6.94 (dd, ³J = 6.4 Hz, ⁴J = 2.9 Hz, 2H, H-2 + H-6 Ph), 5.23 (d, J = 9.0 Hz, 1H, -SO₂NH-), 4.26 – 4.17 (m, 1H, H-2 Propyl), 3.38 (d, J = 2.0 Hz, 3H, -CO₂CH₃), 2.94 (d, J = 6.2 Hz, 2H, H-3 Propyl), 2.90 (s, 6H, -N(CH₃)₂). ¹³C NMR (101 MHz, 323 K, CDCl₃) δ: 171.23 (-CO₂CH₃), 151.75 (C-5 DNS), 135.15 (C-1 DNS), 135.06 (C-1 Ph), 130.74 (C-9 DNS), 130.05 (C-4 DNS), 129.87 (C-7 DNS), 129.66 (C-3 DNS), 129.36 (C-3 + C-5 Ph), 128.50 (C-2 + C-4 Ph),

128.45 (C-10 DNS), 127.23 (C-6 Ph), 123.29 (C-8 DNS), 119.52 (C-2 DNS), 115.56 (C-5 DNS), 57.24 (C-2 Propyl), 52.26 (-CO₂CH₃), 45.61 (-N(CH₃)₂), 39.45 (C-3 Propyl).

Ethyl (2-dansylamido-3-oxo)amidoetanoate, 3b

3b: ¹H NMR (400 MHz, 298 K, CDCl₃) δ: 8.55 (d, J = 8.5 Hz, 1H, H-4 DNS), 8.33 – 8.15 (m, 2H, H-8 + H-2 DNS), 7.65 – 7.42 (m, 2H, H-7 + H-6 DNS), 7.18 (dd, ³J = 10.4 Hz, ³J = 6.5 Hz, 1H, H-3 DNS), 6.29 (t, J = 6.2 Hz, 1H, -SO₂NH-), 4.15 (qd, ³J = 7.1 Hz, ²J = 1.5 Hz, 2H, -CO₂CH₂CH₃), 3.96 (d, J = 5.7 Hz, 2H, -(SO₂NH)CH₂(CONH)-), 3.57 (d, J = 6.4 Hz, 2H, -(NH)CH₂CO₂CH₂CH₃), 2.87 (d, J = 1.6 Hz, 6H, -N(CH₃)₂), 0.91 – 0.78 (m, 3H, -CO₂CH₂CH₃).

Triethylammonium (2-dansylamido-3-indolyl)propanoate, 1'c

¹H NMR (400 MHz, 298 K, CDCl₃) δ: 8.41 (d, J = 8.5 Hz, 1H, H-4 DNS), 8.30 (d, J = 8.7 Hz, 1H, H-8 DNS), 8.16 (dd, ³J = 7.3 Hz, ²J = 1.2 Hz, 1H, H-2 DNS), 7.90 (s, 1H, NH-Ind), 7.56 (d, J = 7.9 Hz, 1H, H-6 DNS), 7.40 (ddd, ³J = 25.3 Hz, ³J = 8.5 Hz, ³J = 7.5 Hz, 2H, H-3 + H-7 DNS), 7.19 (d, J = 8.0 Hz, 1H, H-4 Ind), 7.10 (d, J = 7.6 Hz, 1H, H-7 Ind), 7.08 – 7.01 (m, 1H, H-6 Ind), 6.99 – 6.92 (m, 1H, H-5 + H-2 Ind), 6.07 (s, 1H, -SO₂NH-), 4.00 (s, 1H, H-2 Propyl), 3.20 (qd, ⁴J = 14.6 Hz, ³J = 4.9 Hz, 2H, H-3 Propyl), 2.85 (s, 6H, -N(CH₃)₂), 2.69 (dt, J = ³J = 7.5 Hz, ³J = 6.3 Hz, 9H, [NH(CH₂CH₃)₃]⁺), 0.94 (t, J = 7.3 Hz, 12H, [NH(CH₂CH₃)₃]⁺).

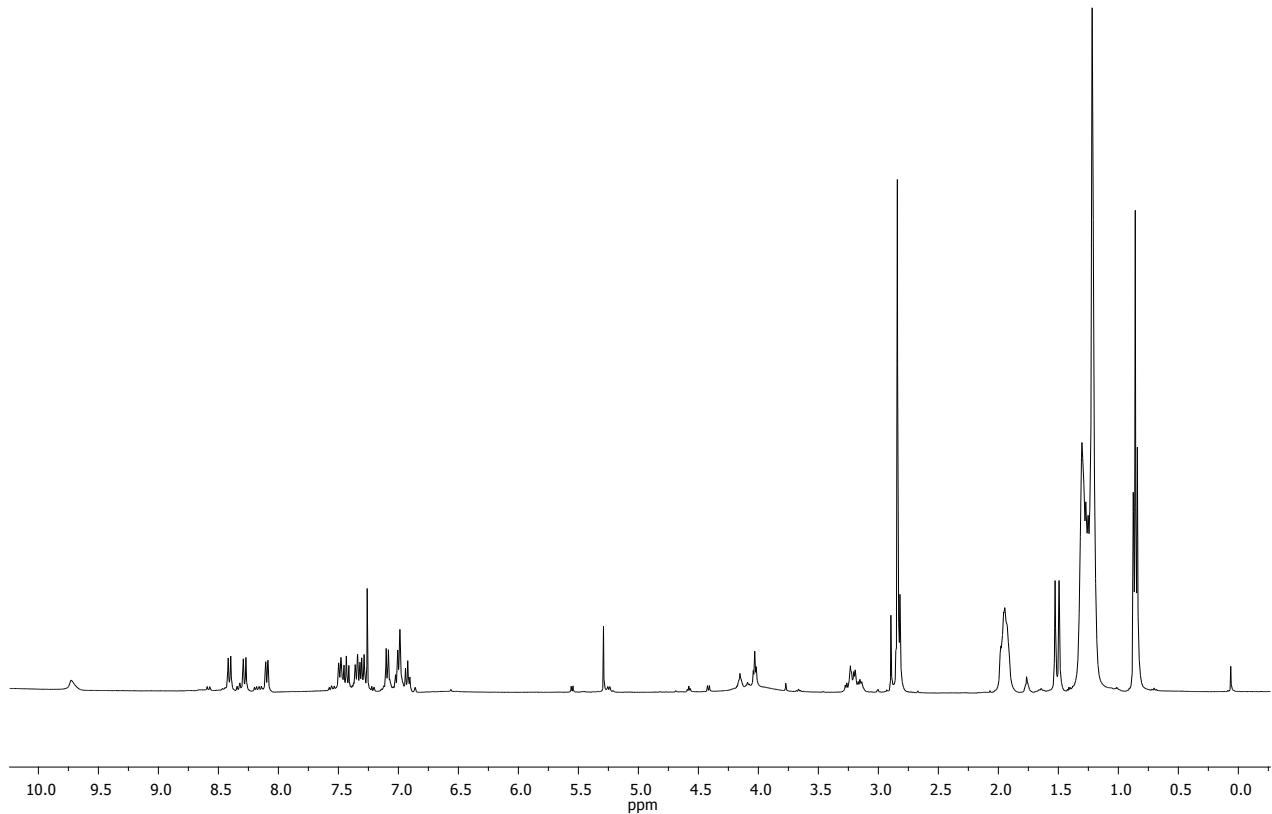
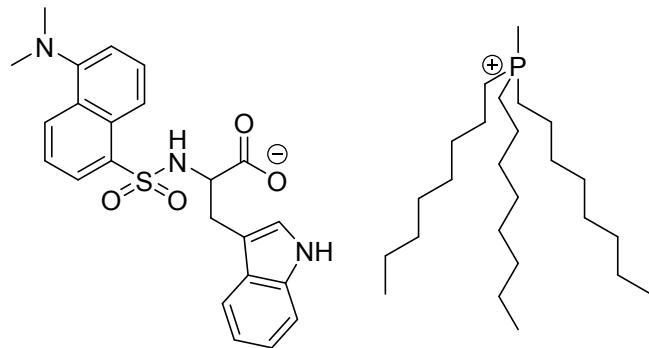
Triethylammonium(2-dansylamido-3-phenyl)propanoate, 2'c

¹H NMR (400 MHz, 298 K, CDCl₃) δ: 8.44 (d, J = 8.0 Hz, 1H, H-4 DNS), 8.22 (d, J = 8.3 Hz, 1H, H-8 DNS), 8.13 (d, J = 7.3 Hz, 1H, H-2 DNS), 7.43 (dt, ³J = 13.8 Hz, ³J = 8.0 Hz, 2H, H-3 + H-7 DNS), 7.11 (d, J = 7.6 Hz, 1H, H-6 DNS), 6.96 (d, J = 17.1 Hz, 5H, Ph), 5.81 (s, 1H, -NHSO₂-), 3.99 (d, J = 4.8 Hz, 1H, H-2 Propyl), 2.98 (dd, ⁴J = 13.7 Hz, ³J = 5.0 Hz, 2H, H-3 Propyl), 2.90 (s, 6H, -N(CH₃)₂), 2.87 – 2.79 (m, 6H, [NH(CH₂CH₃)₃]⁺), 1.14 (t, J = 7.3 Hz, 9H, [NH(CH₂CH₃)₃]⁺).

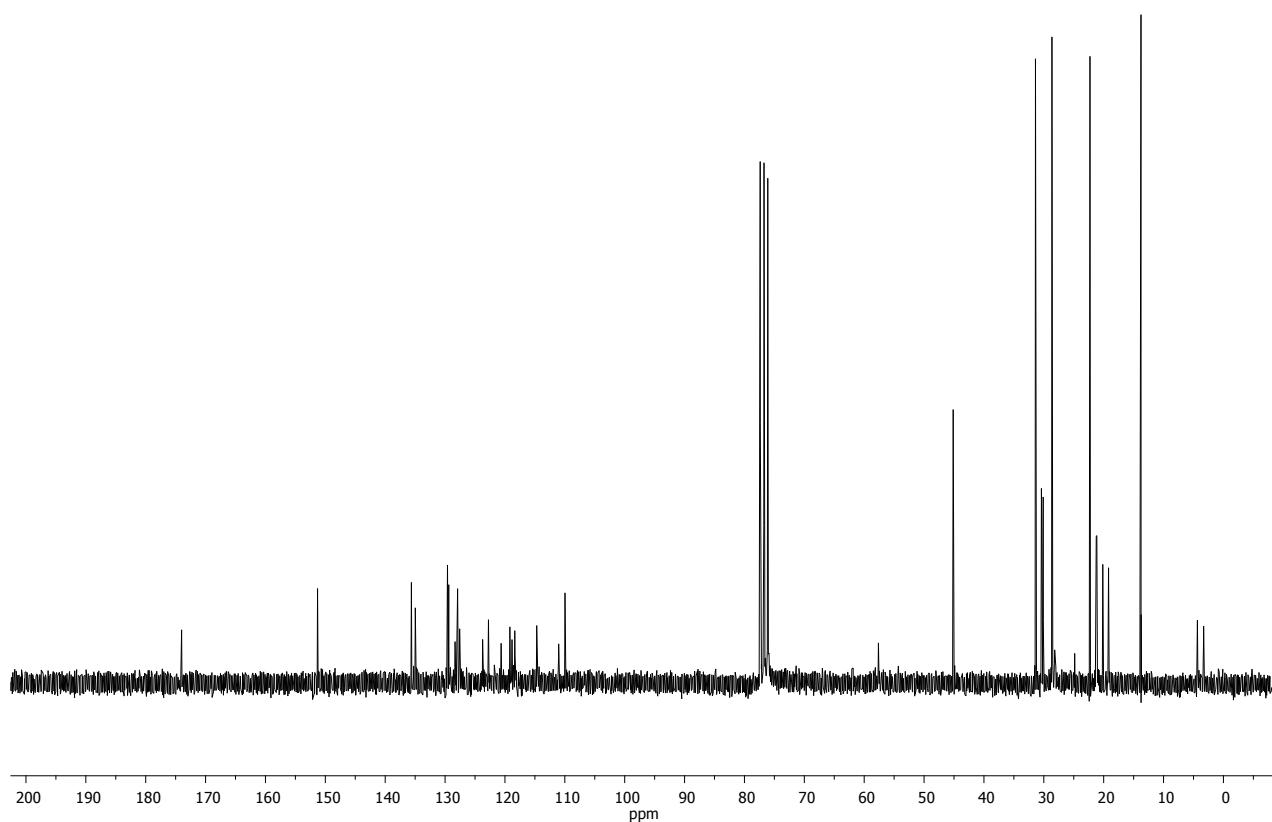
3-Dansylamido-2-ossoaminoetanoic acid, 3c

¹H NMR (400 MHz, 298 K, CDCl₃) δ: 8.42 (d, J = 7.9 Hz, 1H, H-4 DNS), 8.26 (d, J = 8.2 Hz, 1H, H-8 DNS), 8.09 (d, J = 6.1 Hz, 1H, H-2 DNS), 7.55 (s, 1H, -(CO)NH-CO₂H), 7.40 (d, J = 7.6 Hz, 2H, H-3 + H-7 DNS), 7.12 (d, J = 7.1 Hz, 1H, H-6 DNS), 6.94 (s, 1H, -SO₂NH-), 4.30 (-CO₂H), 4.12 (d, J = 7.1 Hz, 1H, -NHCH₂CO₂H), 3.77 (s, 2H, -NHCH₂CO₂H), 3.55 (s, 2H, -NHCH₂CONH-), 2.86 (d, J = 21.2 Hz, 6H, -N(CH₃)₂).

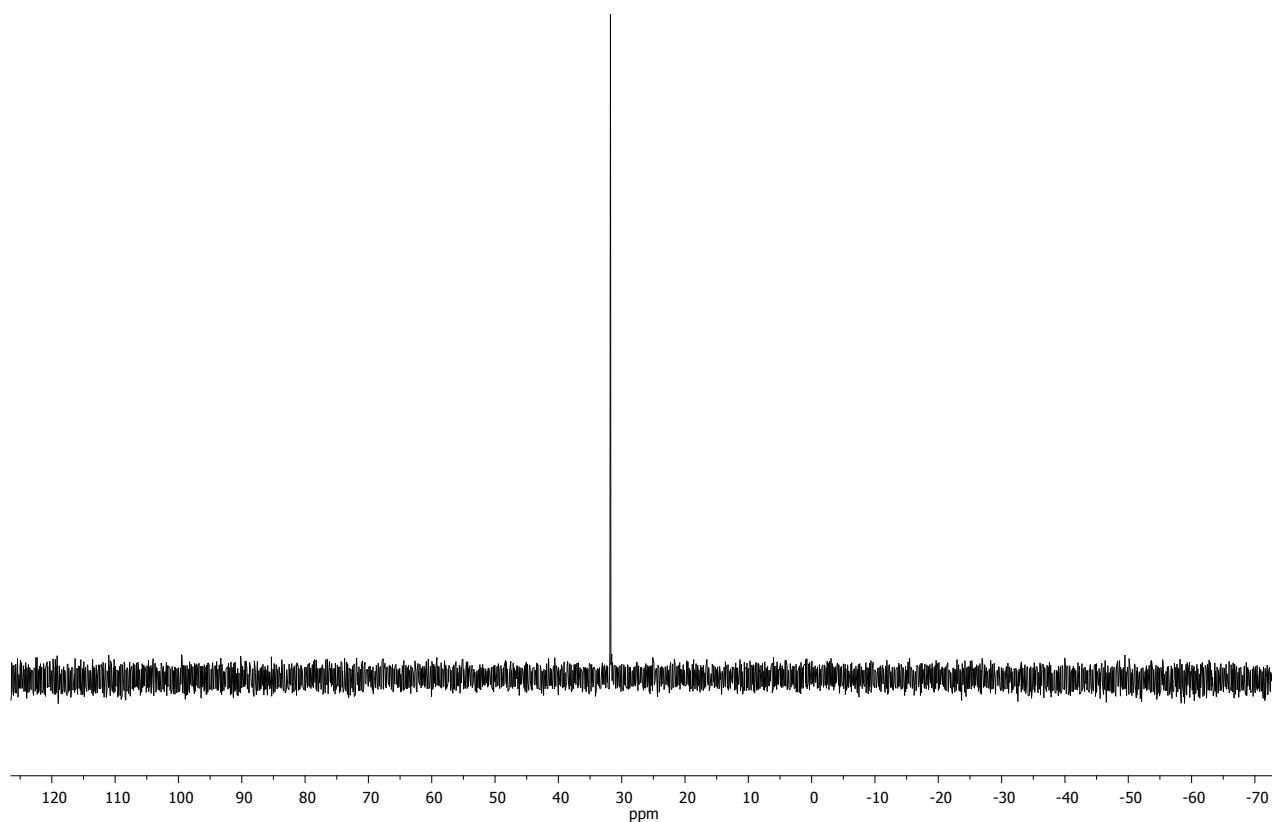
Trioctylmethylphosphonium 3-indolyl-2-dansylamidopropanoate, [P₁₈₈₈][DNS-Trp] (1d)



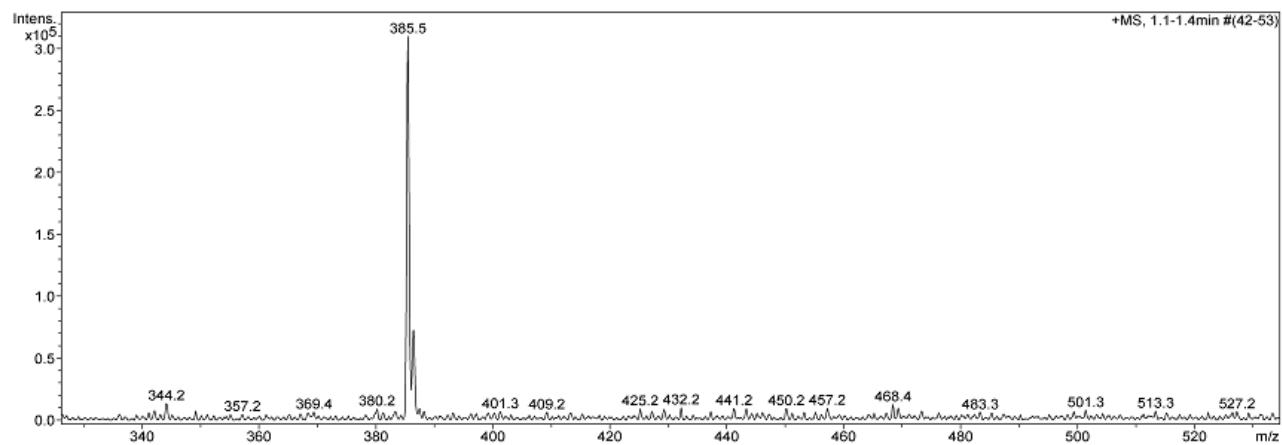
¹H NMR (400 MHz, 298 K, CDCl₃) δ: δ 9.73 (s, 1H, NH Ind), 8.41 (d, *J* = 8.5 Hz, 1H, H-4 DNS), 8.28 (d, *J* = 8.7 Hz, 1H, H-8 DNS), 8.10 (d, *J* = 7.2 Hz, 1H, H-2 DNS), 7.52 – 7.40 (m, 2H, H-3 + H-7 DNS), 7.39 – 7.27 (m, 2H, H-4 + H-7 Ind), 7.09 (d, *J* = 7.5 Hz, 1H, H-6 DNS), 7.00 (d, *J* = 7.2 Hz, 2H, H-5 + H-6 Ind), 6.93 (d, *J* = 7.5 Hz, 1H, H-2 Ind), 5.29 (s, 1H, SO₂NH-), 4.03 (t, *J* = 4.8 Hz, 1H, SO₂NH-CH-), 3.31 – 3.11 (m, 2H, Ind-(CH₂)-), 2.89 (m, 6H, -N(CH₃)₂), 2.09 – 1.86 (m, 6H, -CH₂-(CH₂)₆CH₃ [P₁₈₈₈]⁺), 1.51 (d, *J* = 13.3 Hz, 3H, -CH₃ [P₁₈₈₈]⁺), 1.43 – 1.06 (m, 42H, -(CH₂)₆CH₃ [P₁₈₈₈]⁺), 0.86 (t, *J* = 6.8 Hz, 3H, -(CH₂)₇CH₃ [P₁₈₈₈]⁺).



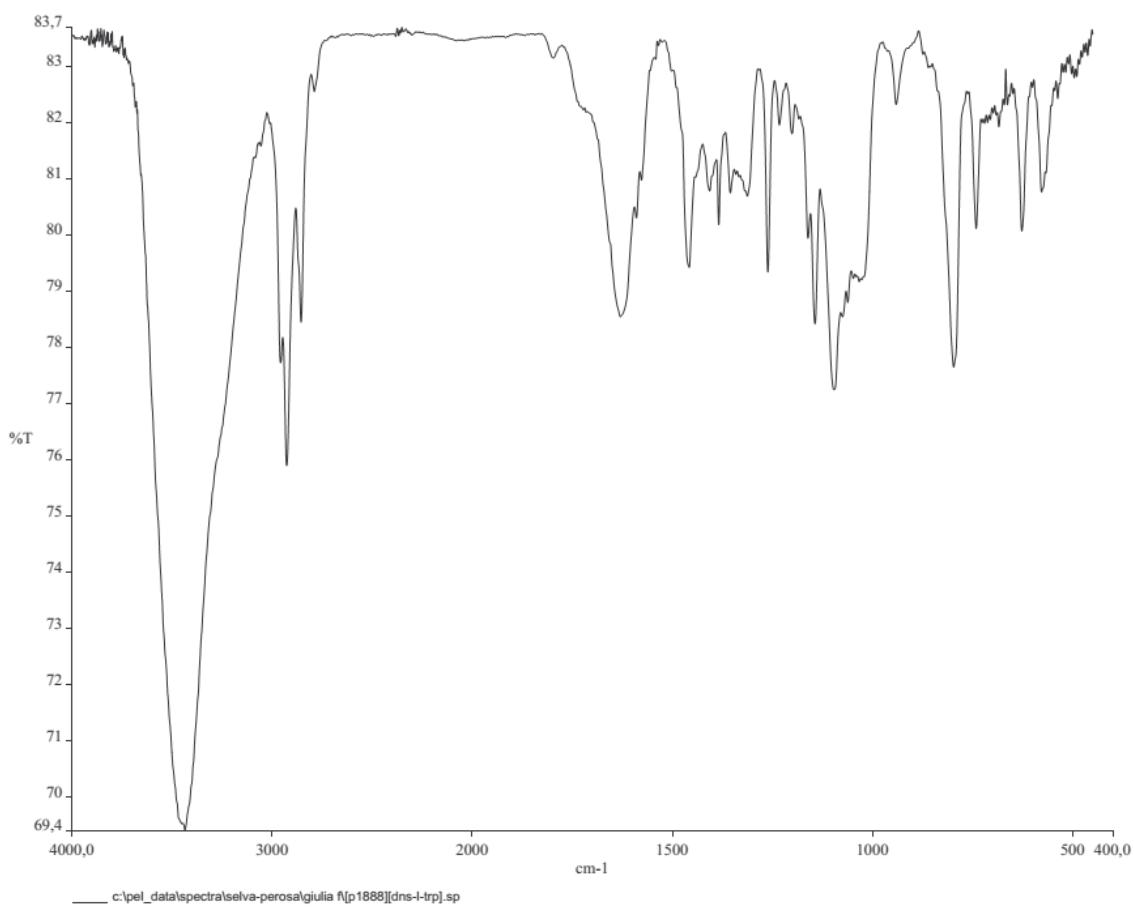
^{13}C NMR (50 MHz, 298 K, CDCl_3) δ : 174.01 ($-\text{CO}_2\text{H}$), 151.30 (C-5 DNS), 135.63 (C-9 Ind), 134.98 (C-1 DNS), 129.60 (C-4 DNS), 129.39 (C-7 DNS), 128.34 (C-9 DNS), 127.91 (C-4 DNS), 127.57 (C-8 Ind), 123.73 (C-3 DNS), 122.75 (C-2 DNS), 120.64 (C-2 Ind), 119.17 (C-8 DNS), 118.82 (C-5 Ind), 118.36 (C-7 Ind), 114.70 (C-6 DNS), 111.03 (C-4 Ind), 109.97 (C-1 Ind), 57.62 (C-3 Propyl), 45.14($-\text{N}(\text{CH}_3)_2$), 31.40 (C-2 Propyl), 30.40 (C-5 [$\text{P}_{1888}]^+$), 30.11 (C-4 [$\text{P}_{1888}]^+$), 28.60 ($-\text{CH}_2\text{CO}_2^-$), 22.29 (C-3 [$\text{P}_{1888}]^+$), 21.19 (d, C-2 [$\text{P}_{1888}]^+$), 20.15 (C-7 [$\text{P}_{1888}]^+$), 19.19 (t, C-1 [$\text{P}_{1888}]^+$), 13.75 (C-8 [$\text{P}_{1888}]^+$), 4.35 - 3.31 ($-\text{CH}_3$ [$\text{P}_{1888}]^+$).



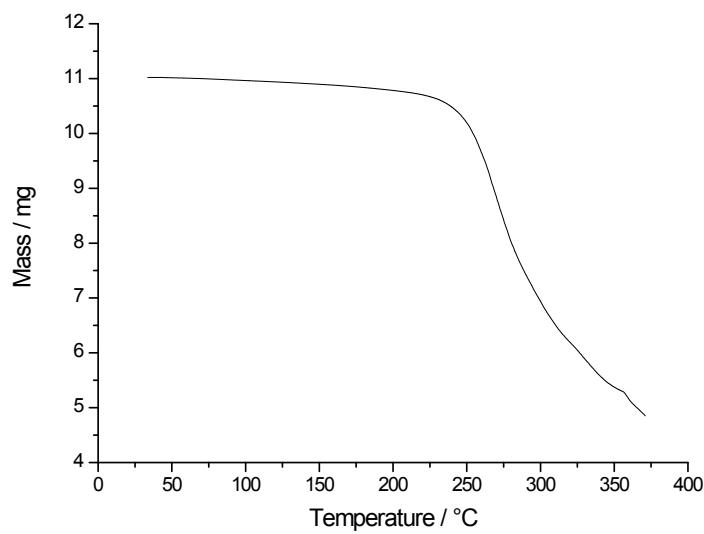
^{31}P NMR (81 MHz, 298 K , CDCl_3) δ : 31.77.



ESI-MS (FIA, CH_3CN): 385 ($[\text{P}_{1888}]^+$); 436 ($[\text{C}_{23}\text{H}_{22}\text{N}_3\text{O}_4\text{S}]^-$).

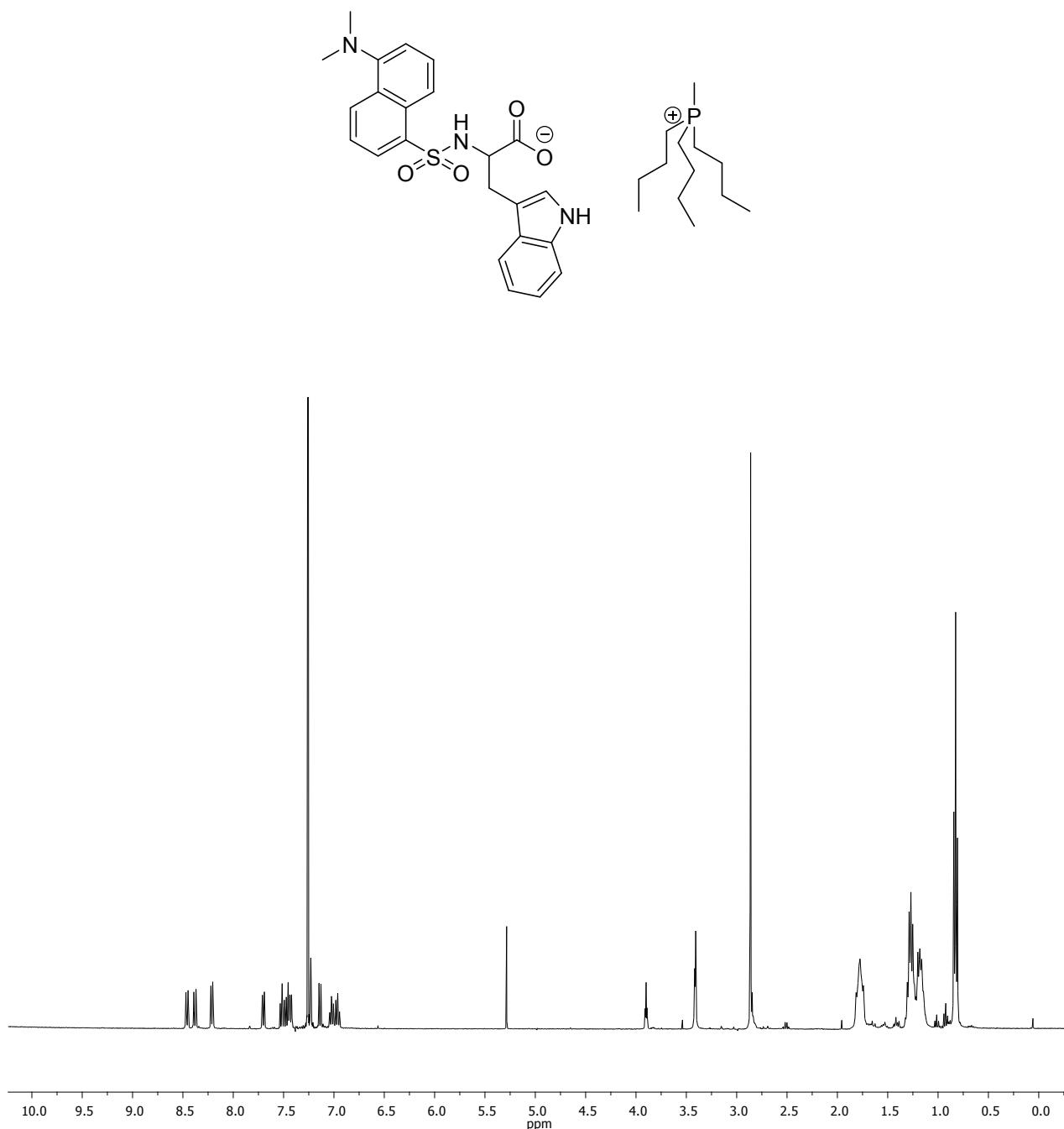


IR (KBr): 3435 (b), 2960, 2920, 2850 (m), 1640 (b), 1455 (sh), 1265 (sh), 1105 (b), 805 (sh).

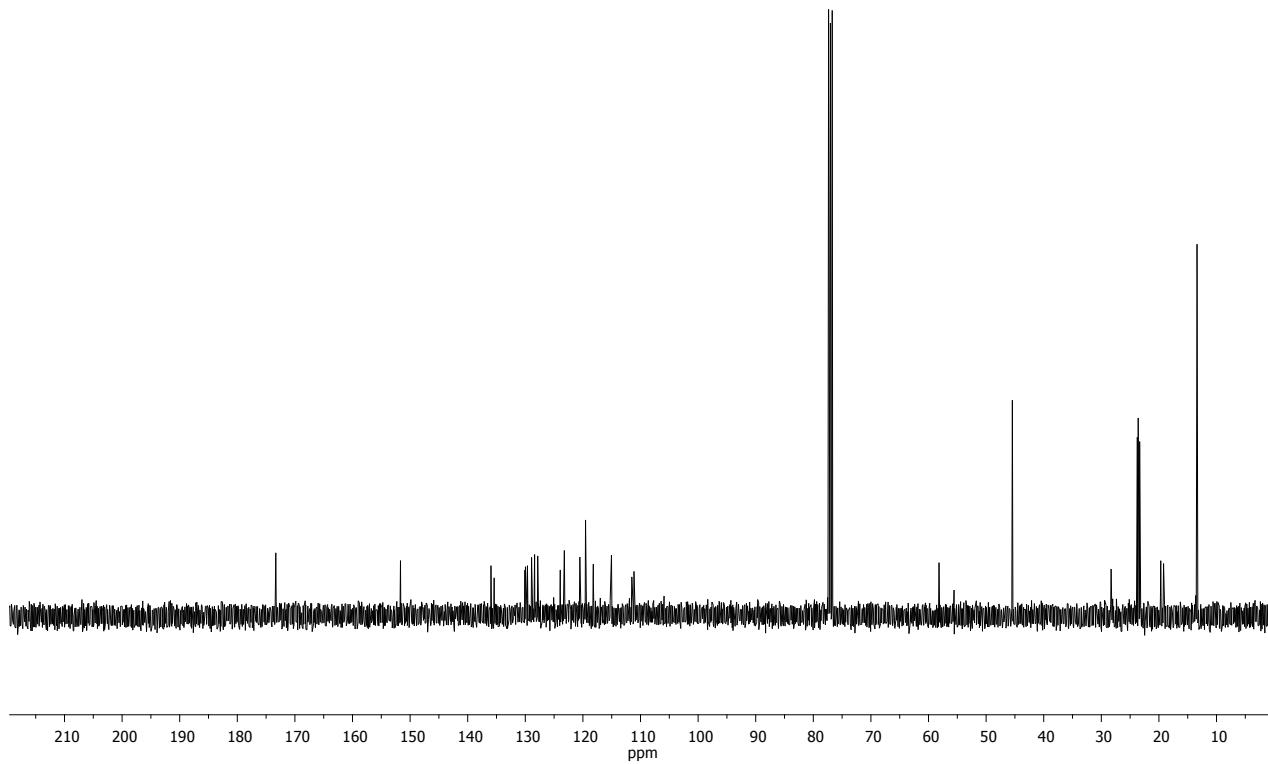


TGA

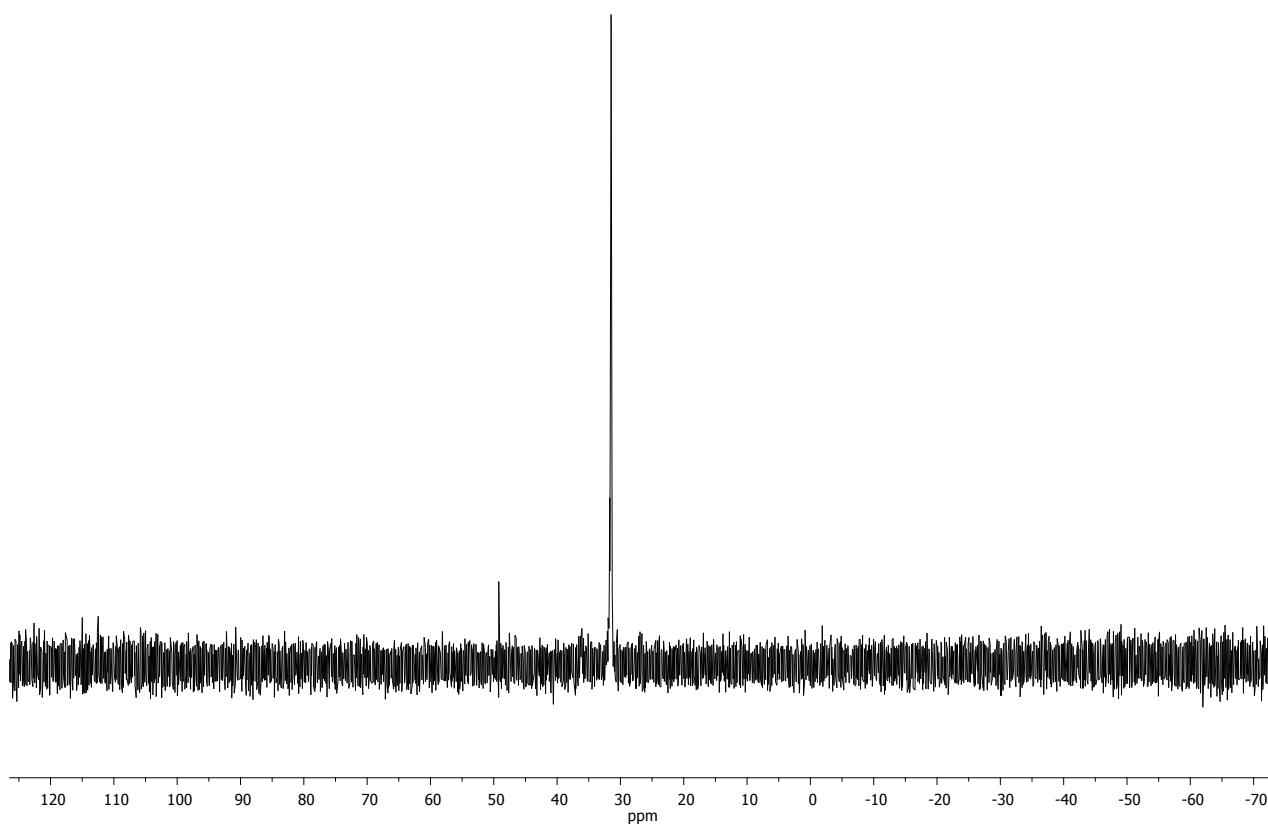
*Tributylmethylphosphonium 3-indolyl-2-dansylamidopropanoate, [P₁₄₄₄][DNS-Trp] (**1e**)*



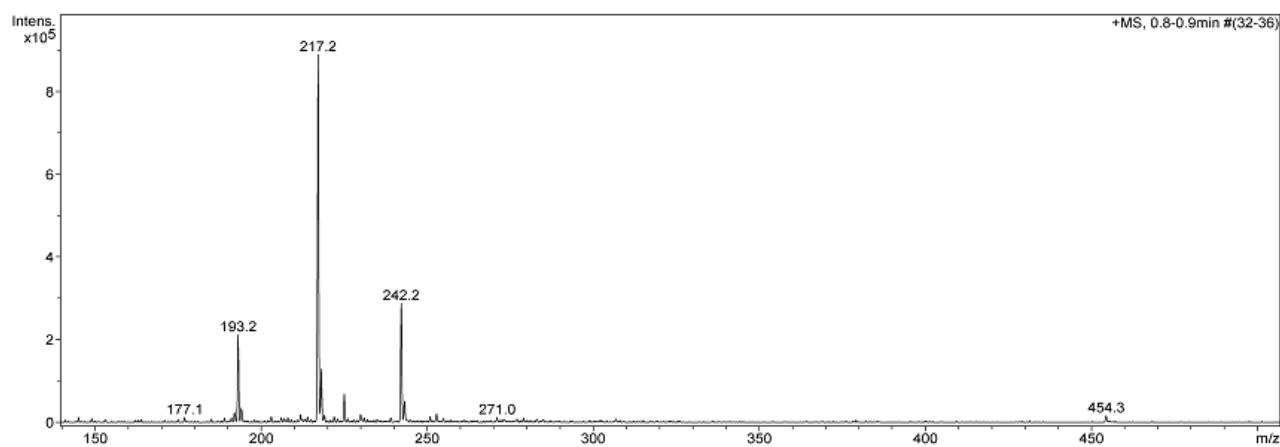
¹H NMR (400 MHz, 298 K, CDCl₃) δ: 8.46 (d, *J* = 9.2 Hz, 1H, H-4 DNS), 8.38 (d, *J* = 8.6 Hz, 1H, H-8 DNS), 8.21 (d, *J* = 7.3 Hz, 1H, H-2 DNS), 7.70 (d, *J* = 7.7 Hz, 1H, H-3 DNS), 7.51 (s, 1H, H-7 DNS), 7.45 (m, 2H, H-6 DNS + H-4 Ind), 7.23 (s, 1H, SO₂NH), 7.14 (d, *J* = 7.6 Hz, 1H, H-5 Ind), 7.02 (dd, *J* = 13.6, 5.7 Hz, 1H, H-6 Ind), 6.96 (t, *J* = 7.4 Hz, 1H, H-7 Ind), 5.29 (d, *J* = 1.2 Hz, 1H, -NH Ind), 3.90 (s, 1H, -SO₂NH-CH-), 3.41 (t, *J* = 2.7 Hz, 2H, Ind-(CH₂)-), 2.86 (s, 6H, -N(CH₃)₂), 1.76 (m, 3H, -CH₃ [P₁₄₄₄]⁺), 1.24 (m, 18H, -(CH₂)₃CH₃ [P₁₈₈₈]⁺), 0.83 (t, *J* = 7.1 Hz, 3H, -(CH₂)₃CH₃ [P₁₄₄₄]⁺).



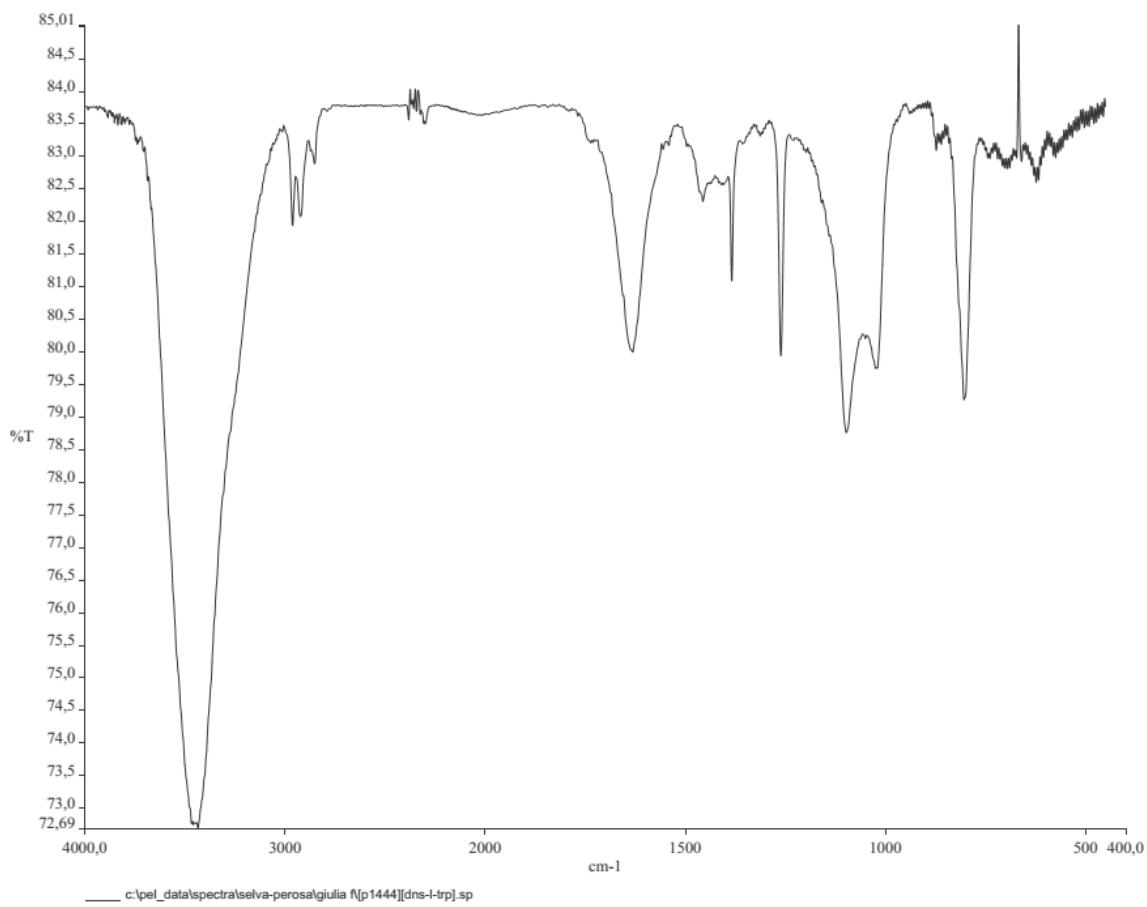
¹³C NMR (101 MHz, 298 K, CDCl₃) δ: 173.32 (-CO₂H), 151.67 (C-5 DNS), 136.40 (C-9 Ind), 135.27 (C-9 DNS), 132.47 (C-1 DNS), 130.08 (C-4 DNS), 129.94 (C-7 DNS), 129.63 (C-2 DNS), 128.88 (C-8 Ind), 128.39 (C-10 DNS), 127.85 (C-2 Ind), 123.93 (C-3 DNS), 123.22 (C-5 Ind), 120.53 (C-6 Ind), 119.54 (C-7 Ind), 118.19 (C-8 DNS), 115.04 (C-6 Ind), 111.51 (C-4 Ind), 111.13 (C-1 Ind), 58.17 (C-2 Propyl), 45.44 (-N(CH₃)₂), 28.30 (-CH₂-Ind), 23.60 (t, C-1 [P₁₄₄₄]⁺), 19.68 (d, C-2 [P₁₄₄₄]⁺) 13.38 (C-3 [P₁₄₄₄]⁺).



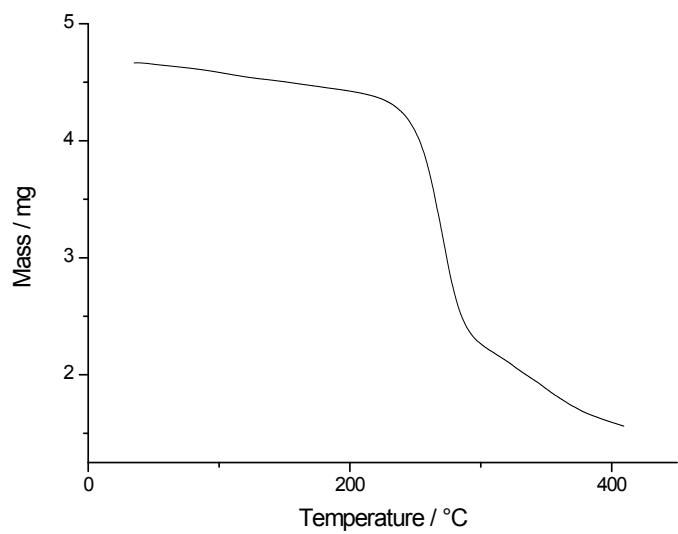
^{31}P NMR (81 MHz, 298 K, CDCl_3) δ : 31.48.



ESI-MS (FIA, CH_3CN): 217 ($[\text{P}_{1444}]^+$); 436 ($[\text{C}_{23}\text{H}_{22}\text{N}_3\text{O}_4\text{S}]^-$).

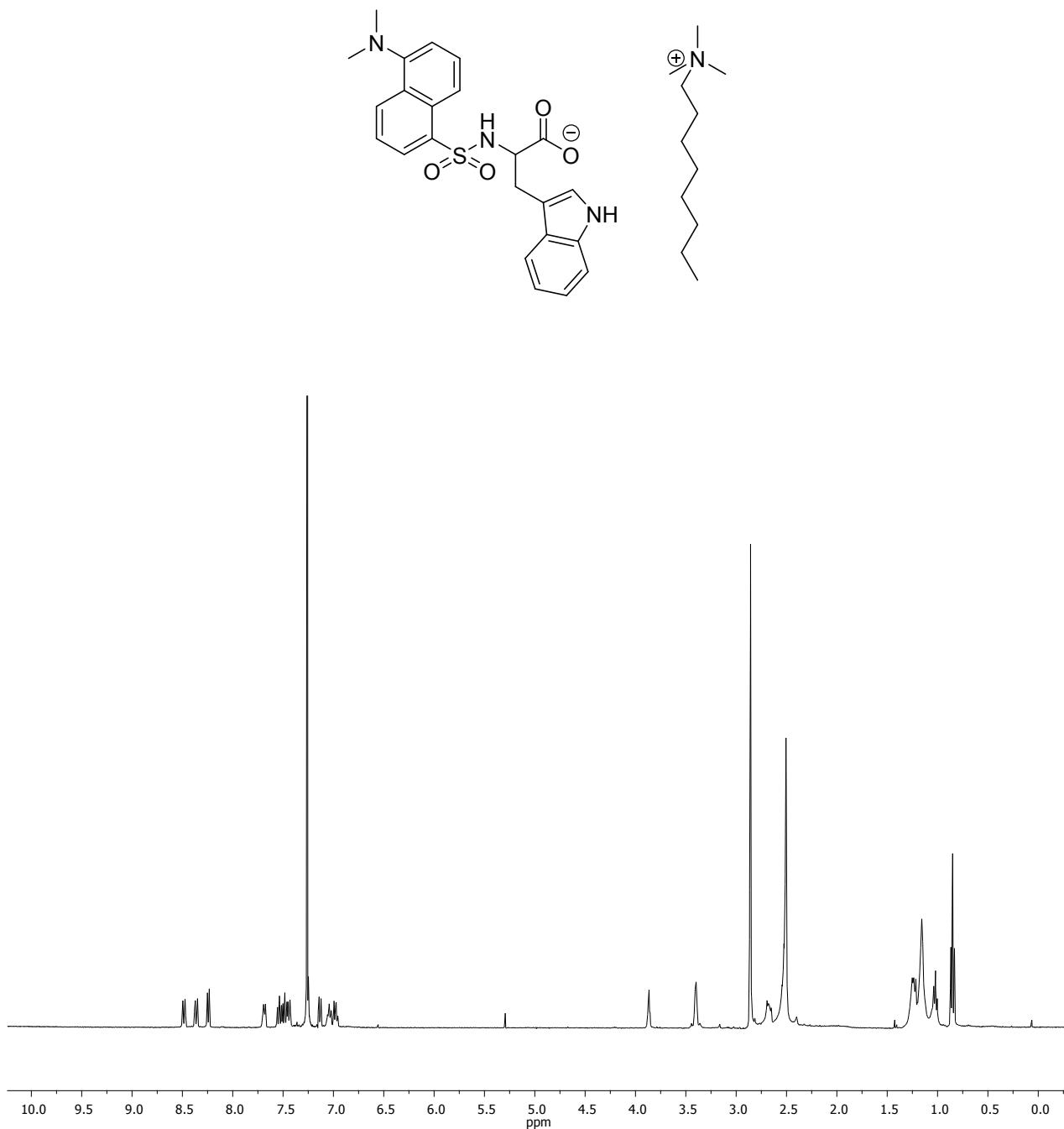


IR (KBr): 3430 (b), 2970, 2920, 2860 (w), 1640 (b), 1385 (sh), 1260 (sh), 1105, 1030 (b), 810 (sh).

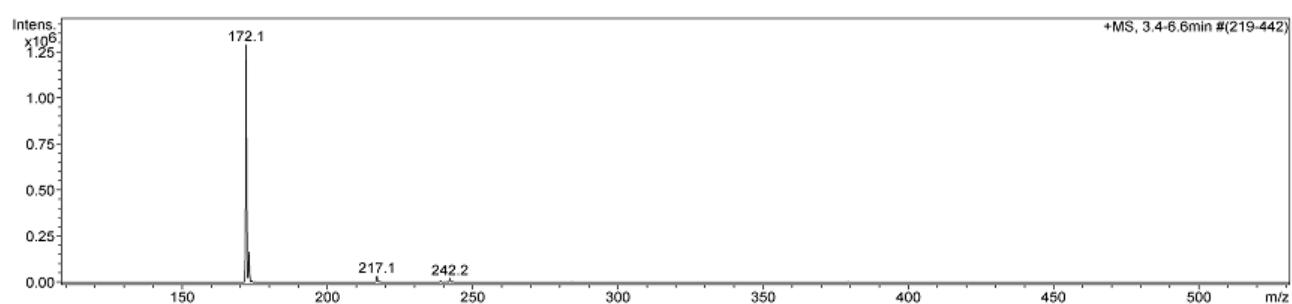
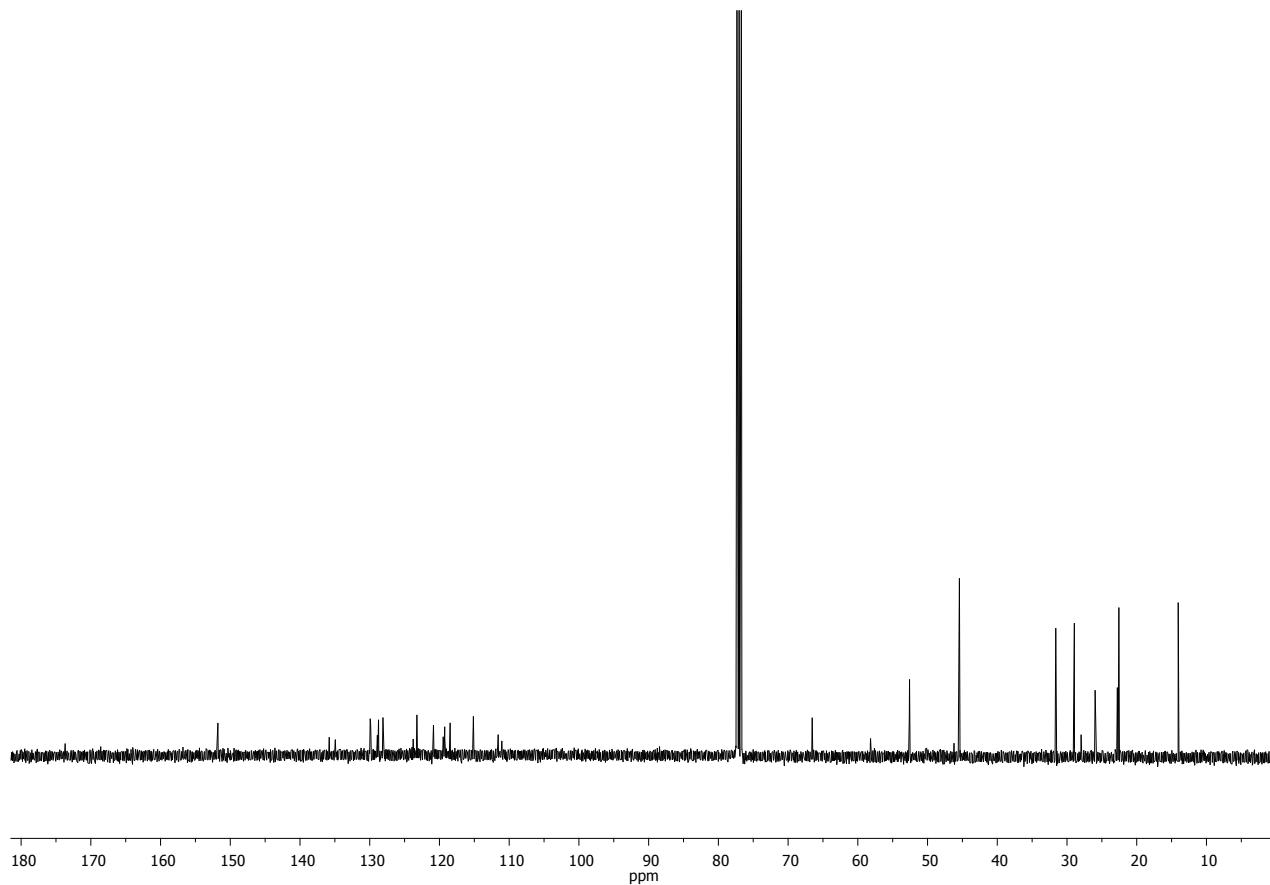


TGA

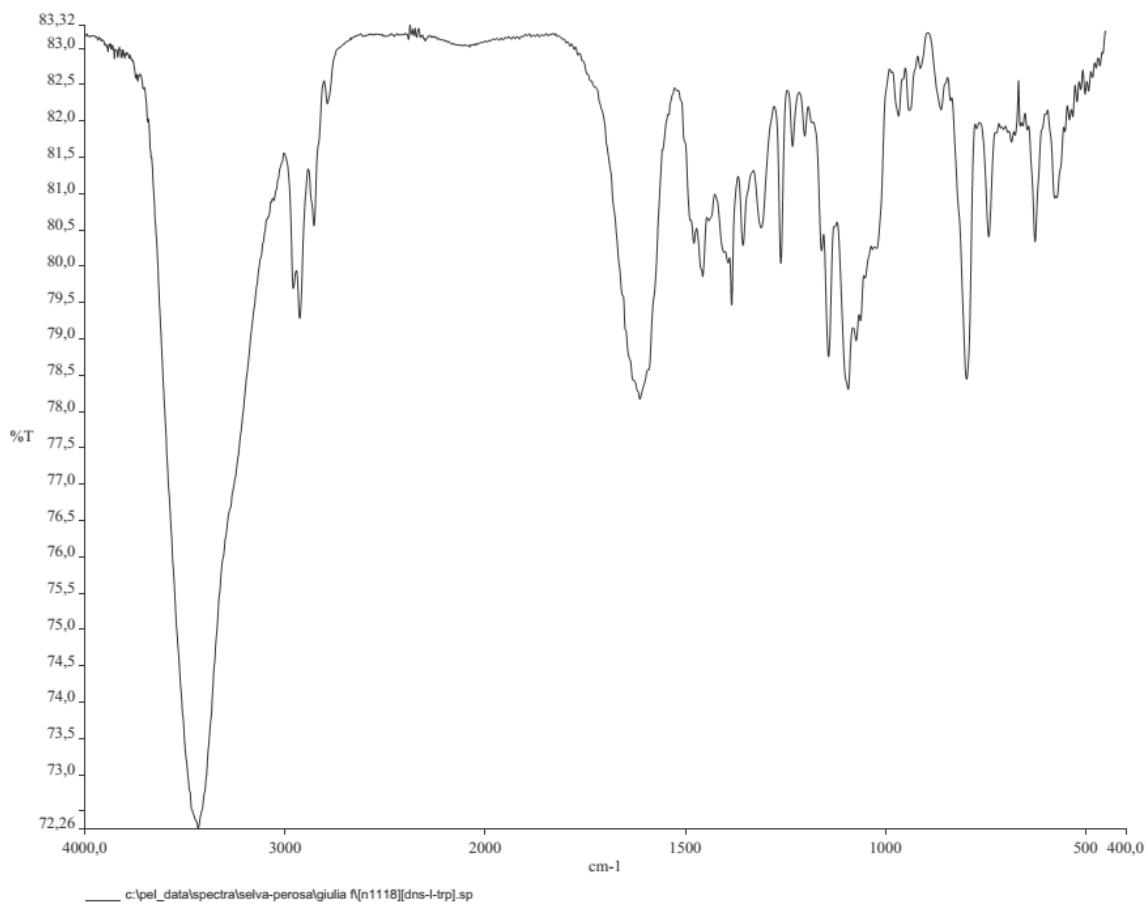
Trimethyloctylammonium 3-indolyl-2-dansylamidopropanoate, [N₁₁₁₈][DNS-L-Trp] (1f)



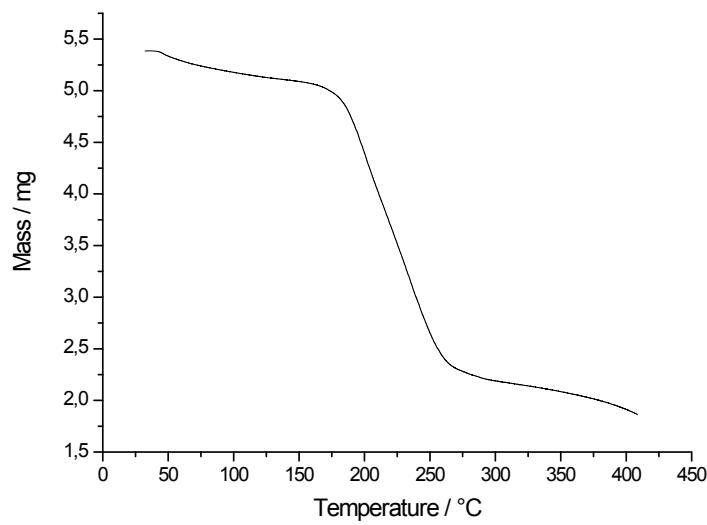
^1H NMR (400 MHz, 298 K, CDCl_3) δ : 8.50 – 8.45 (m, 1H, H-4 DNS), 8.36 (d, J = 8.7 Hz, 1H, H-8 DNS), 8.24 (dd, J = 7.3, 1.3 Hz, 1H, H-2 DNS), 7.68 (d, J = 7.8 Hz, 1H, H-3 DNS), 7.58 – 7.41 (m, 4H, H-7 DNS + H-6 DNS + H-4 Ind), 7.26 (H-2 Ind), 7.14 (dd, J = 7.6, 2.7 Hz, 1H, H-5 Ind), 7.04 (t, J = 7.5 Hz, 1H, H-6 Ind), 7.01 – 6.94 (m, 1H, H-7 Ind), 5.29 (d, J = 1.1 Hz, 1H, -NH Ind), 3.86 (d, J = 4.2 Hz, 1H, -SO₂NH-CH-), 3.40 (d, J = 3.0 Hz, 2H, Ind-(CH₂)-), 2.85 (s, 6H, -N(CH₃)₂), 2.76 – 2.63 (m, 2H, -CH₂-(CH₂)₂CH₃ [N_{1118}^+]), 2.52 (s, 9H, -CH₃ [N_{1118}^+]), 1.23 (dd, J = 12.2, 3.6 Hz, 4H, -(CH₂)₂-(CH₂)₄CH₃ [N_{1118}^+]), 1.16 (s, 6H, -(CH₂)₂-CH₂CH₃ [N_{1118}^+]), 1.09 – 0.98 (m, 2H), 0.85 (td, J = 7.0, 1.3 Hz, 3H, -(CH₂)₇CH₃ [N_{1118}^+]).



ESI-MS (FIA, CH₃CN): 172 ([N₁₁₁₈]⁺); 436 ([C₂₃H₂₂N₃O₄S]⁻).

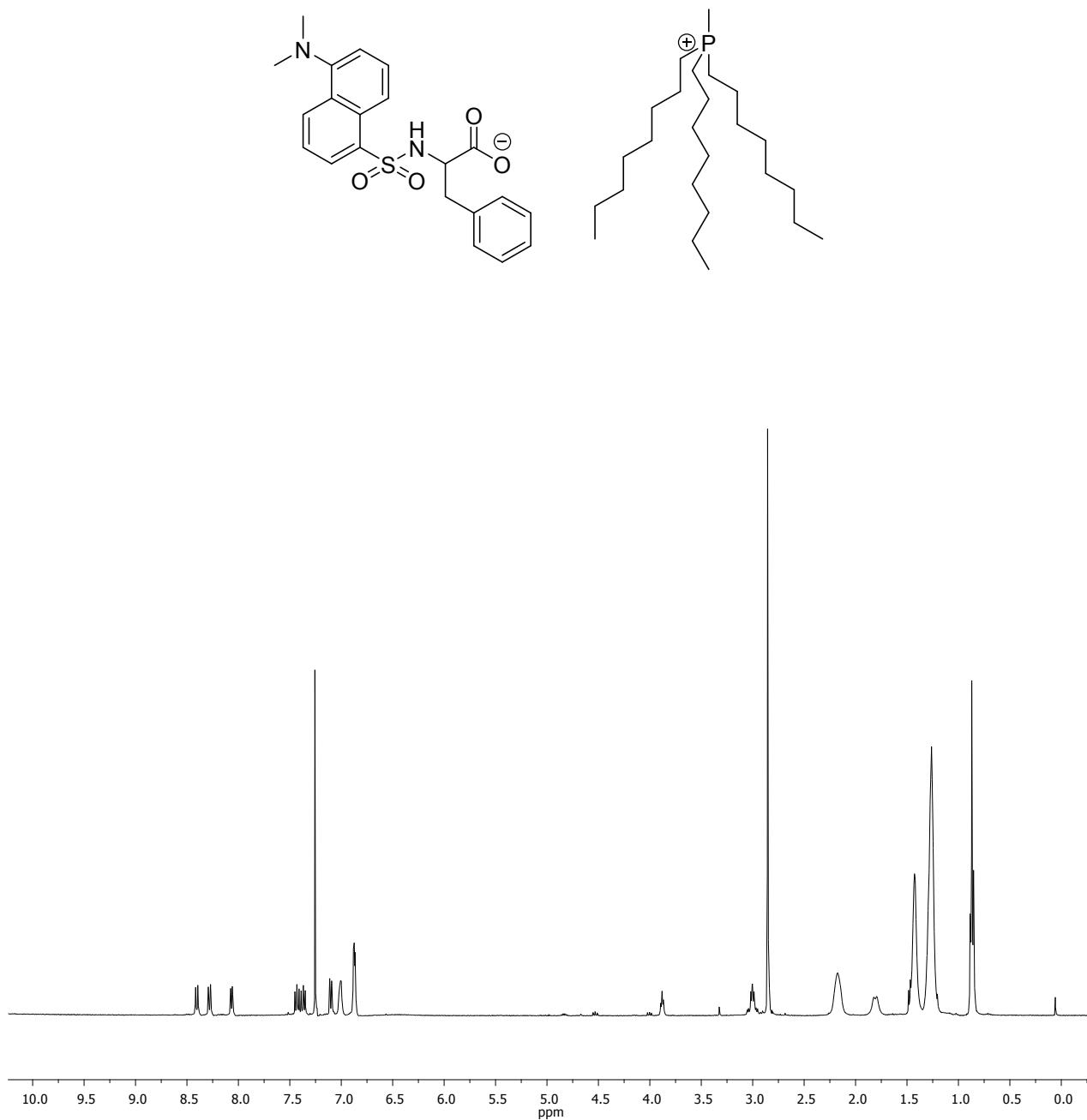


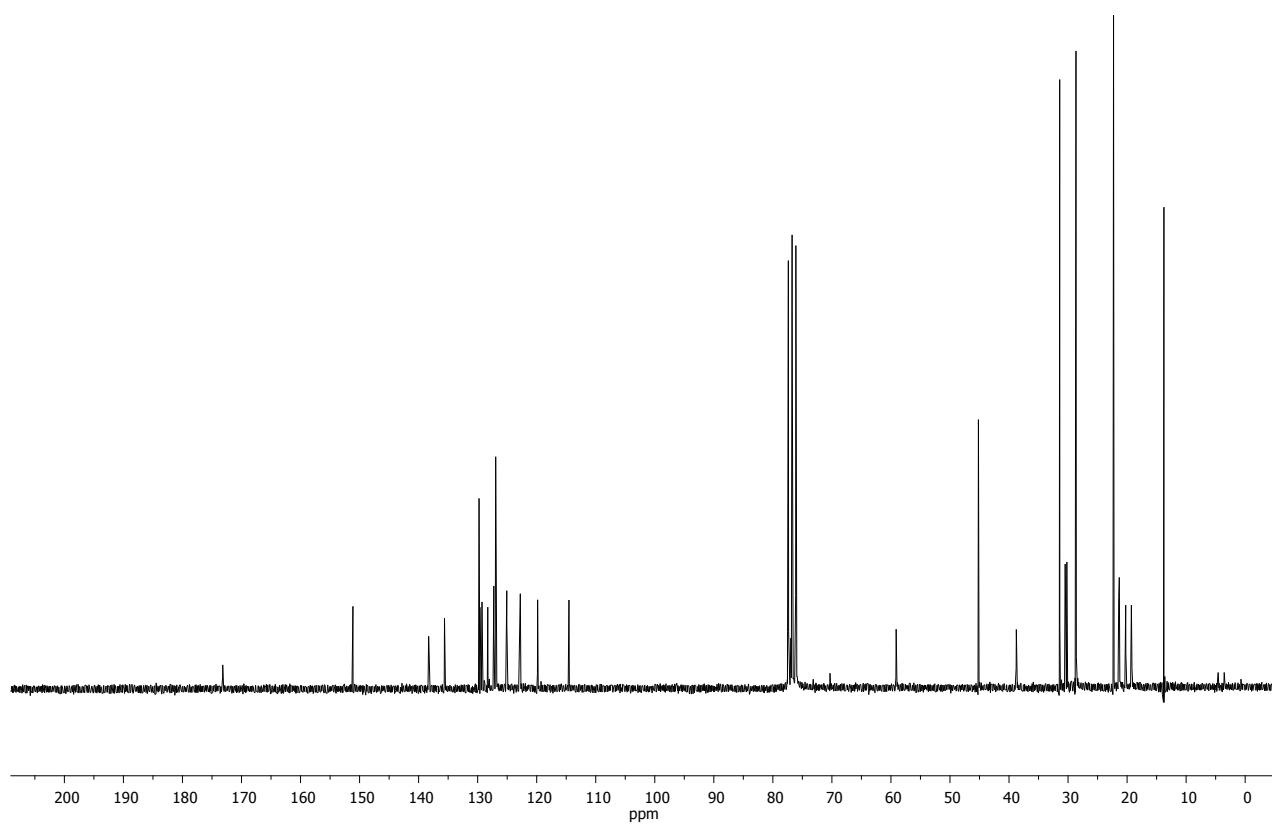
IR (KBr): 3455 (b), 2955 (m), 2960, 2930, 2860 (w), 1620 (b), 1145 (sh), 1090 (m), 795 (sh).



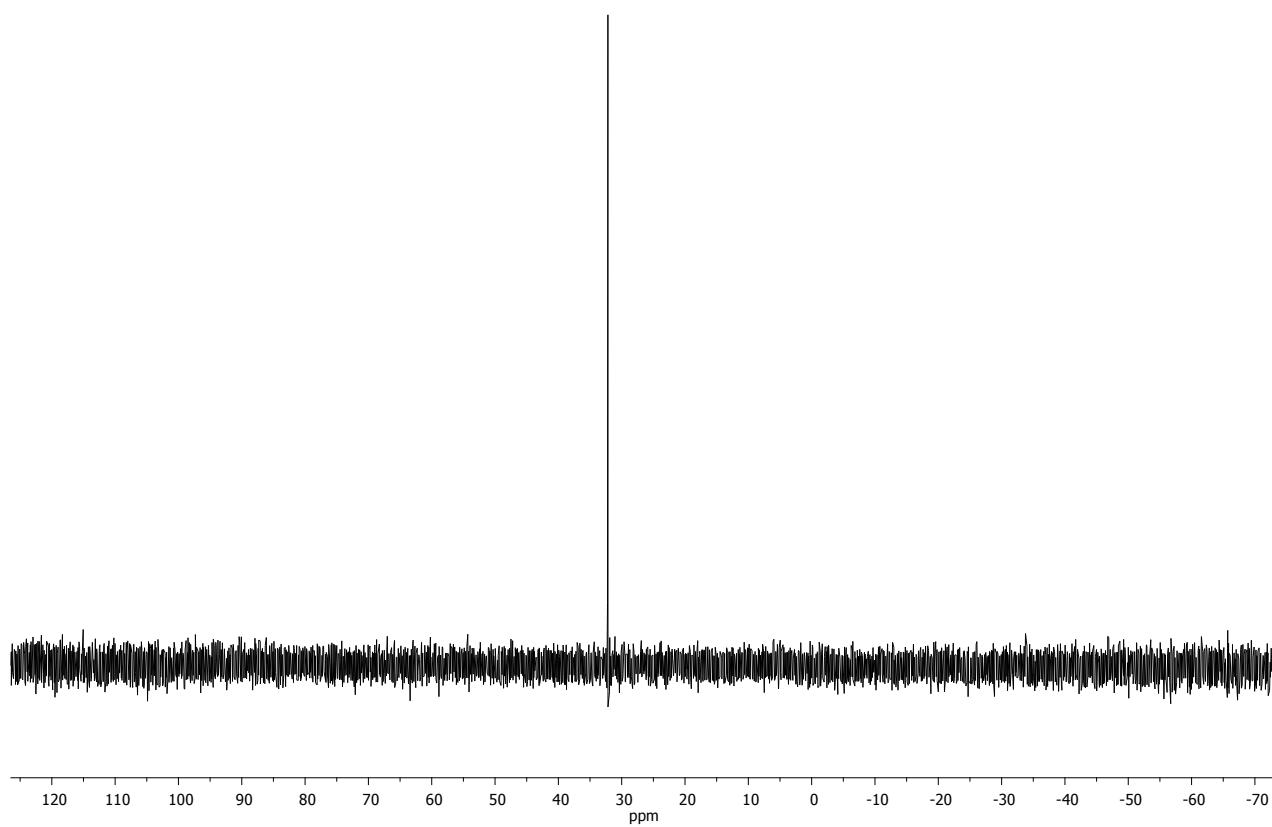
TGA

Trioctylmethylphosphonium 3-phenyl-2-dansylamidopropanoate, [P₁₈₈₈][DNS-Phe] (2d)

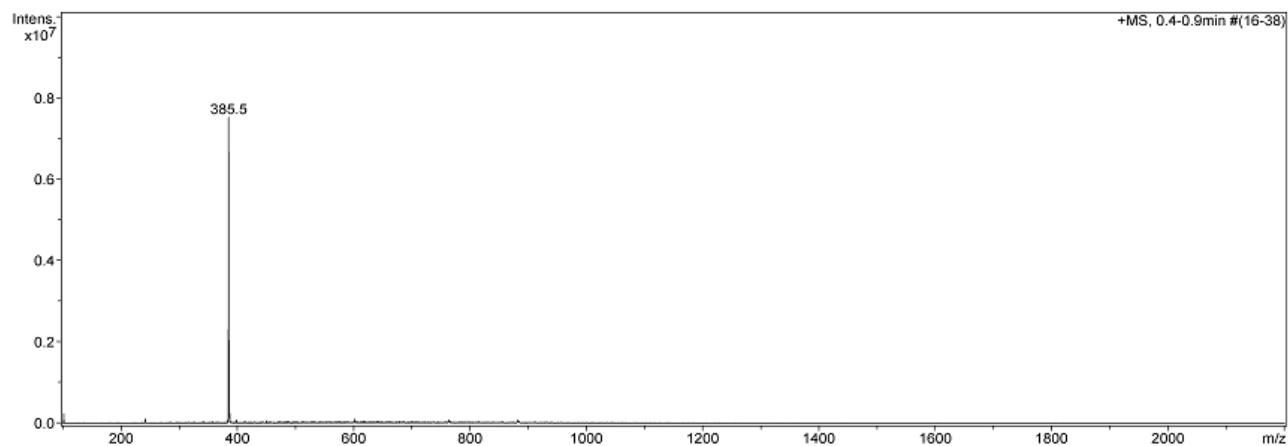




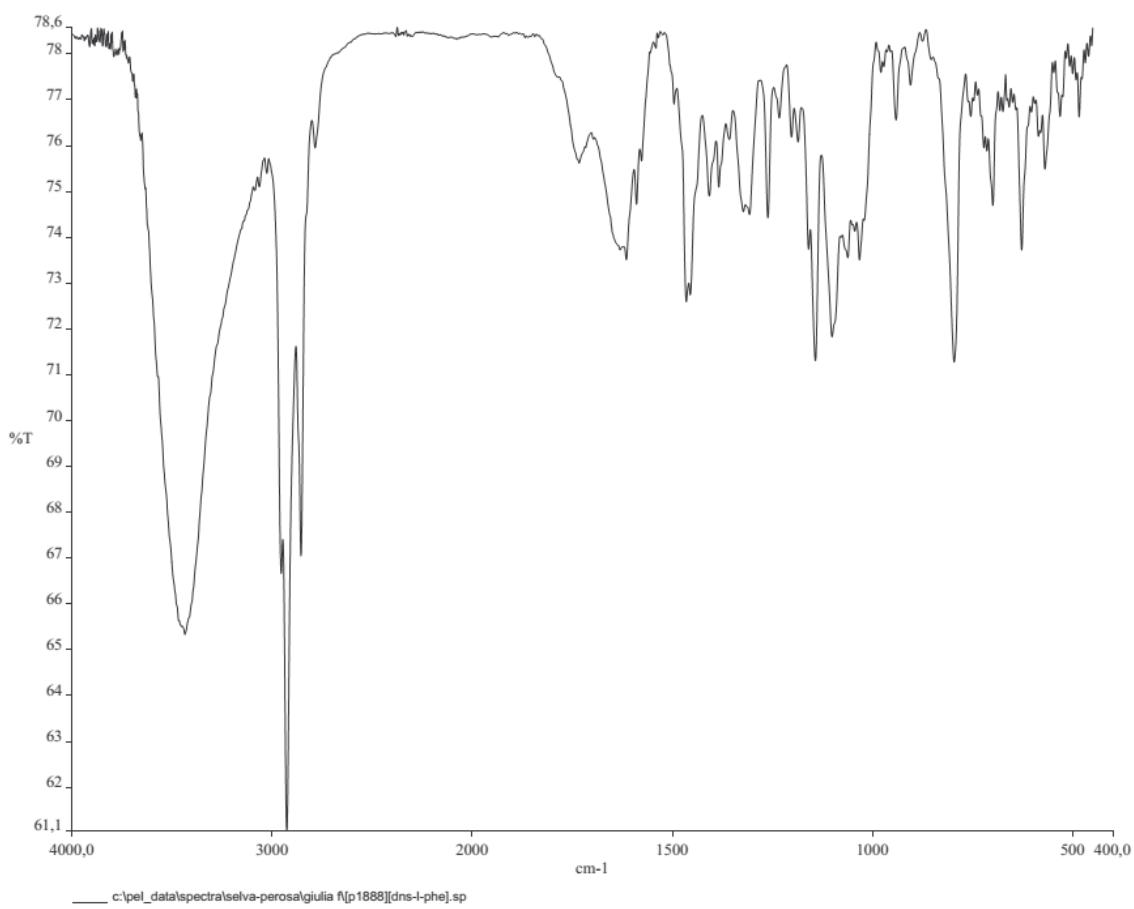
^{13}C NMR (50 MHz, 298 K, CDCl_3) δ : 173.18 ($-\text{CO}_2\text{H}$), 151.13 (C-5 DNS), 138.30 (C-1 DNS), 135.62 (C-1 Ph), 129.76 (C-8 DNS), 129.62 (C-3 Ph), 129.59 (C-5 Ph), 129.26 (C-4 DNS), 128.29 (C-6 DNS), 127.27 (C-2 + C-6 Ph), 126.95 (C-3 DNS), 125.07 (C-4 Ph), 122.77 (C-7 DNS), 119.84 (C-10 DNS), 114.53 (C-5 DNS), 59.12 (C-2 Propile), 45.18 ($-\text{N}(\text{CH}_3)_2$), 31.39 (C-6 $[\text{P}_{1888}]^+$), 30.49 (C-5 $[\text{P}_{1888}]^+$), 30.20 (C-4 $[\text{P}_{1888}]^+$), 28.64 ($-\text{CH}_2\text{CO}_2^-$), 22.31 (C-3 $[\text{P}_{1888}]$), 21.36 (d, C-2 $[\text{P}_{1888}]^+$), 20.24 (C-7 $[\text{P}_{1888}]^+$), 19.27 (t, C-1 $[\text{P}_{1888}]^+$), 13.75 (C-8 $[\text{P}_{1888}]^+$), 4.59 – 3.55 (d, $-\text{CH}_3$ $[\text{P}_{1888}]^+$).



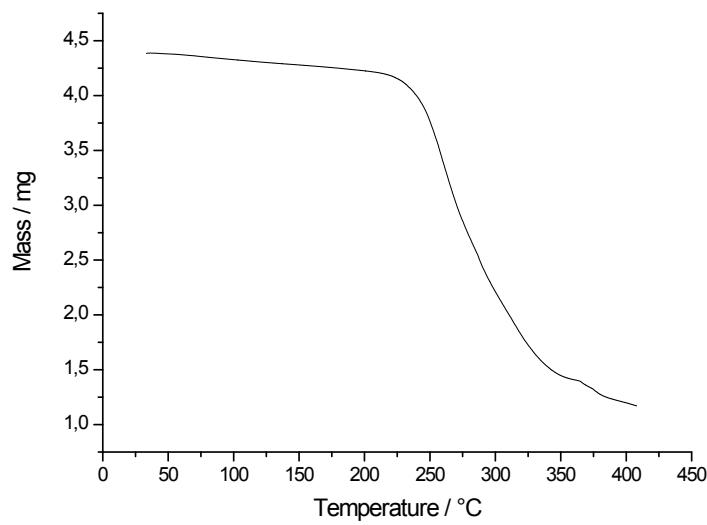
^{31}P NMR (811 MHz, 298 K, CDCl_3) δ : 32.18.



ESI-MS (FIA, CH_3CN): 385 ($[\text{P}_{1888}]^+$); 397 ($[\text{C}_{21}\text{H}_{21}\text{N}_2\text{O}_4\text{S}]^-$).

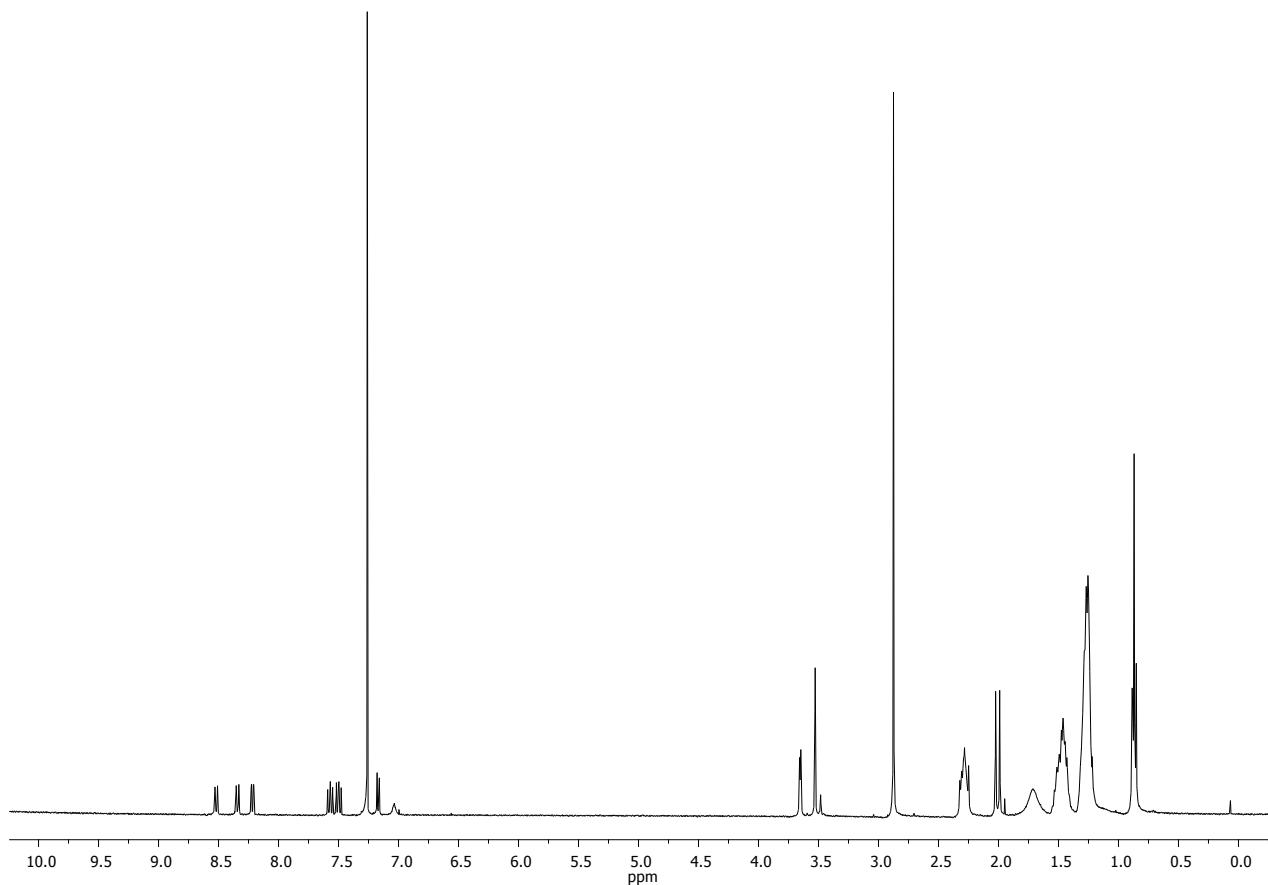
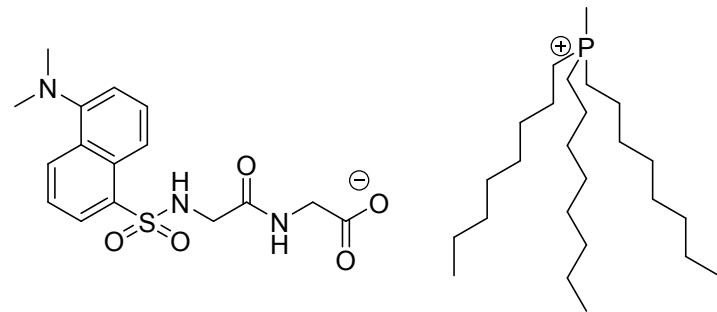


IR (KBr): 3440 (b), 2955, 2935, 2860 (sh), 1745, 1640 (b), 1460 (sh), 111500 (sh), 1090 (b), 790 (sh).

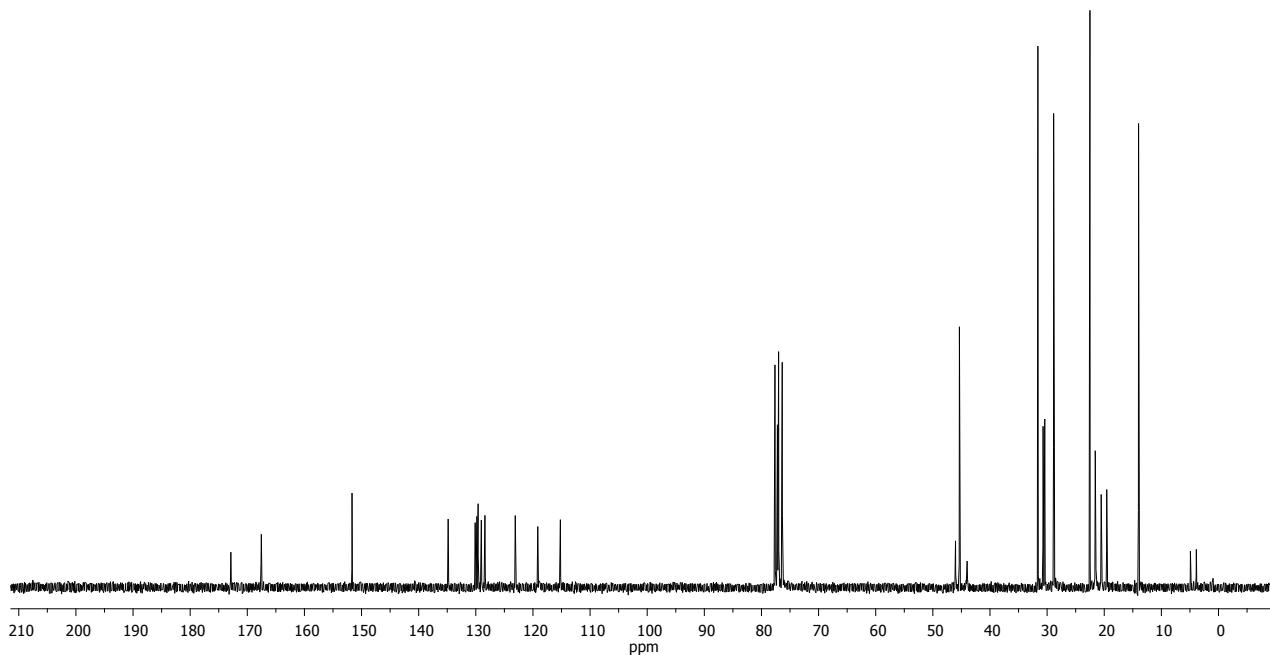


TGA

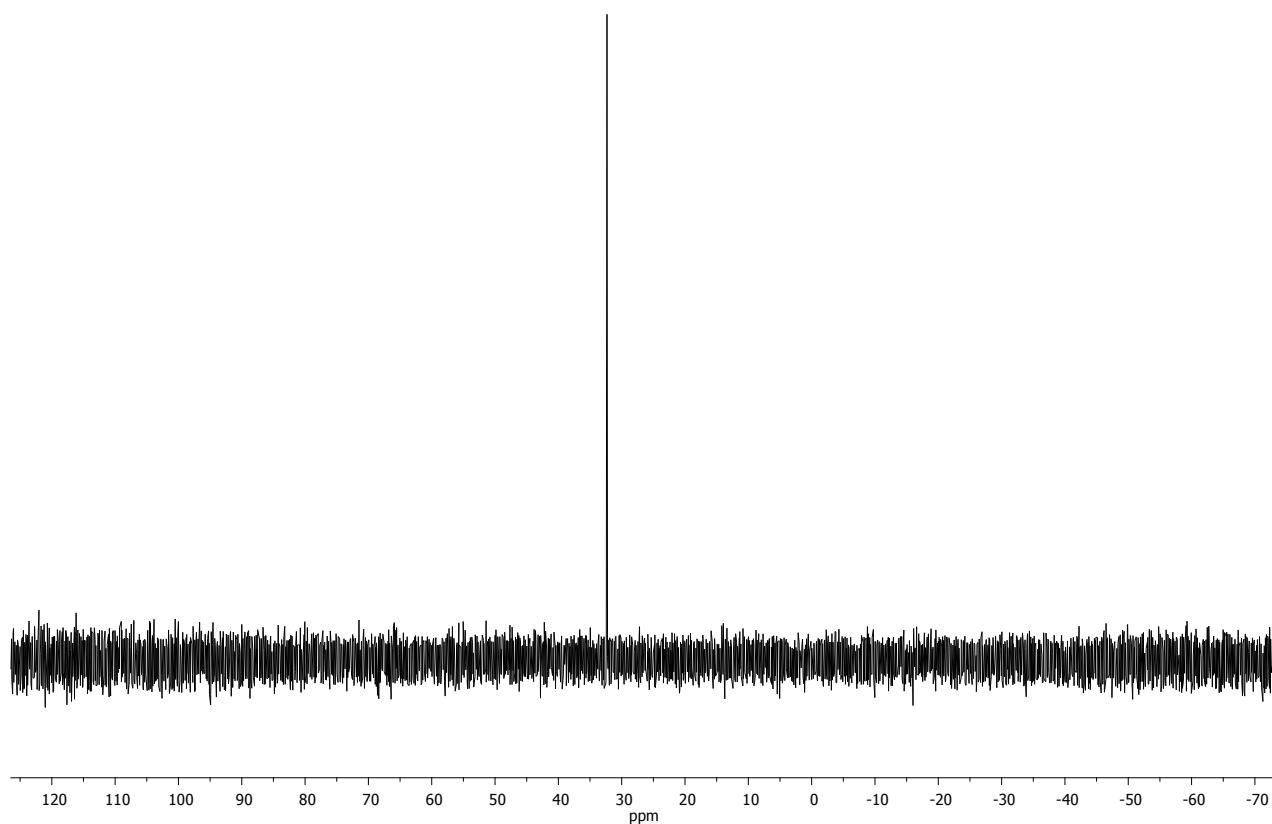
Methyltriocetylphosphonium 2-(3-dansylamido-2-oxo)aminoetanoate, [P₁₈₈₈][DNS-Gly-Gly] (3d)



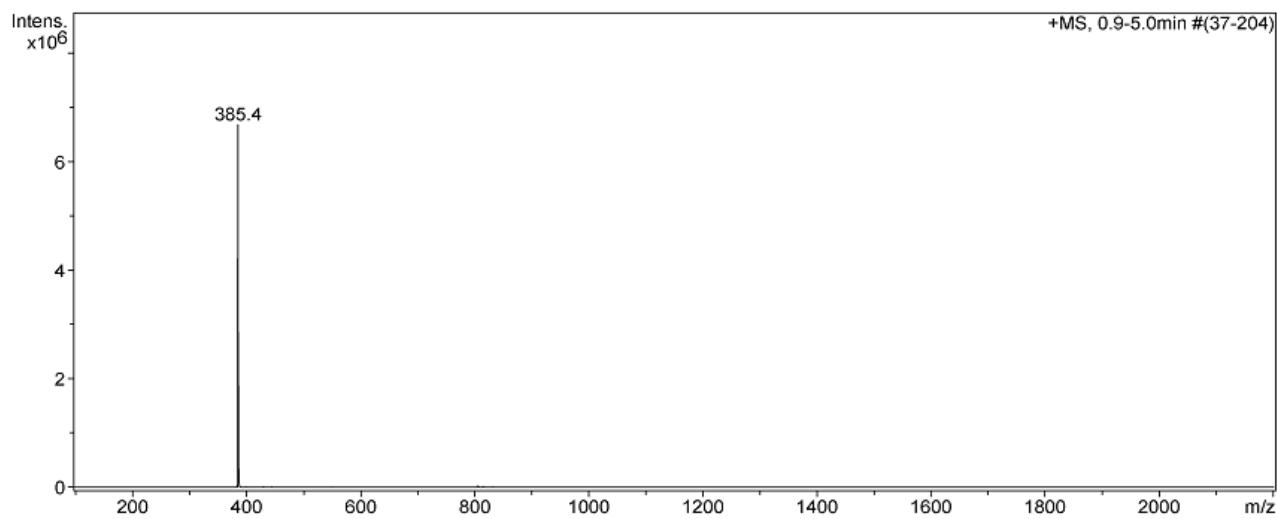
¹H NMR (400 MHz, 298 K, CDCl₃) δ 8.52 (d, *J* = 8.5 Hz, 1H), 8.34 (d, *J* = 8.7 Hz, 1H), 8.22 (dd, *J* = 7.3, 1.1 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.50 (dd, *J* = 8.5, 7.4 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 3.65 (d, *J* = 3.9 Hz, 2H), 3.53 (s, 2H), 2.87 (s, 6H), 2.36 – 2.22 (m, 6H), 2.01 (d, *J* = 13.5 Hz, 3H), 1.60 – 1.38 (m, 13H), 1.25 (t, *J* = 9.7 Hz, 27H), 0.87 (t, *J* = 6.8 Hz, 9H).



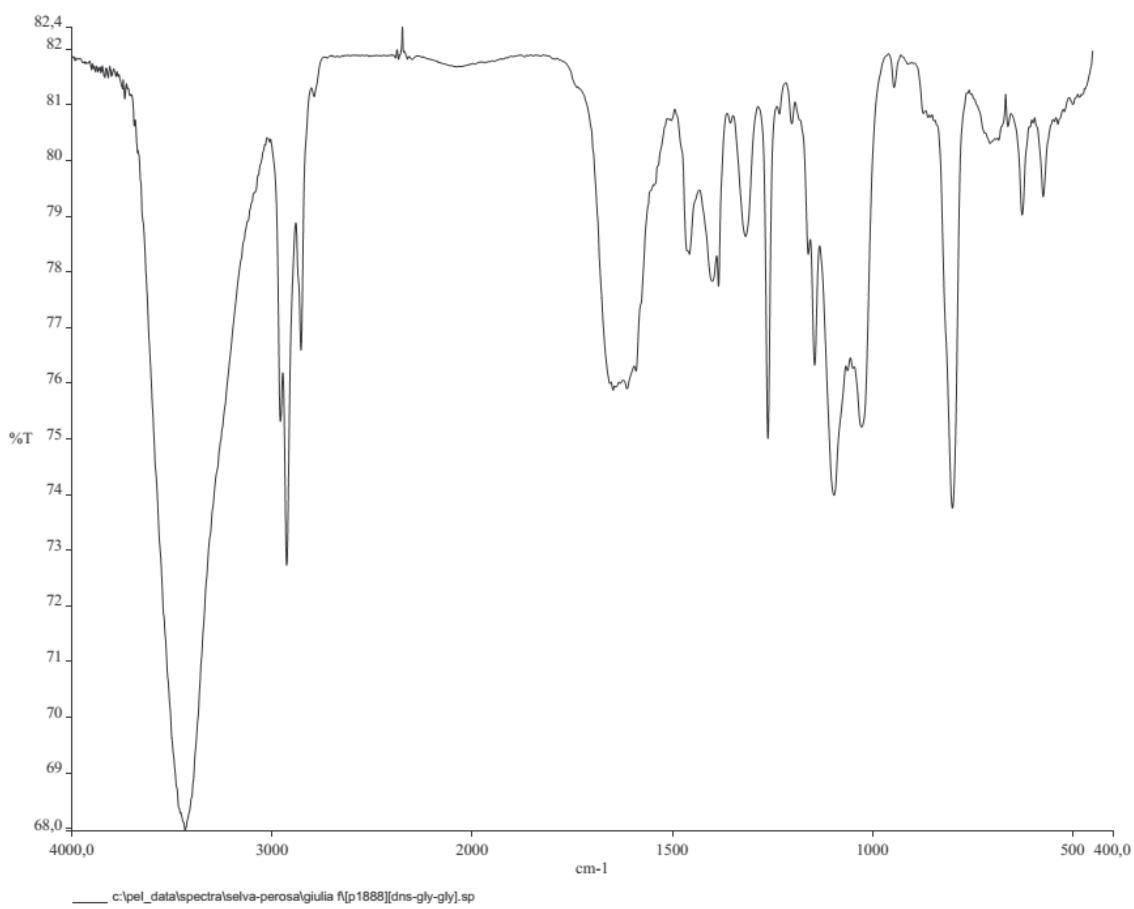
¹³C NMR (50 MHz, 298 K, CDCl₃) δ: 172.88 (-CO₂H), 167.54 (-HN(CO)-), 151.67(C-5 DNS), 134.84 (C-1 DNS), 130.12 (C-9 DNS), 129.81 (C-4 DNS), 129.59 (C-7 DNS), 129.03 (C-3 DNS), 128.40 (C-2 DNS), 123.10 (C-8 DNS), 119.16 (C-10 DNS), 115.20 (C-6 DNS), 46.03 (SO₂NH-CH₂), 45.35 (-N(CH₃)₂), 31.61 (C-6 [P₁₈₈₈]), 30.71 (C-5 [P₁₈₈₈]), 30.41 (C-4 [P₁₈₈₈]), 28.86 (-CH₂CO₂⁻), 22.50 (C-3 [P₁₈₈₈]), 21.48 (d, C-2 [P₁₈₈₈]), 20.53 (C-7 [P₁₈₈₈]), 19.56 (t, C-1 [P₁₈₈₈]), 13.98 (C-8 [P₁₈₈₈]), 4.92-3.88 (-CH₃ [P₁₈₈₈]).



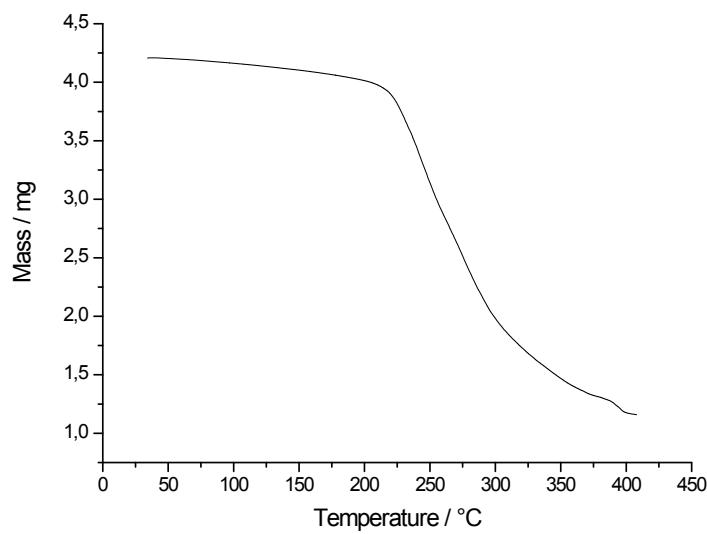
^{31}P NMR (811 MHz, 298 K, CDCl_3) δ : 32.24.



ESI-MS (FIA, CH_3CN): 385 ($[\text{P}_{1888}]^+$); 364 ($[\text{C}_{16}\text{H}_{18}\text{N}_3\text{O}_5\text{S}]^-$).



IR (KBr): 3440 (w), 2955 (m), 2920 (m), 2850 (sh), 1635 (b), 1265 (sh), 1105, 1025 (m), 795 (sh).



TGA