Electronic Supplementary Information

Amine Protection by *in situ* Formation of choline chloride-based Deep Eutectic Solvents

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Figure S1. FT-IR-DES_1

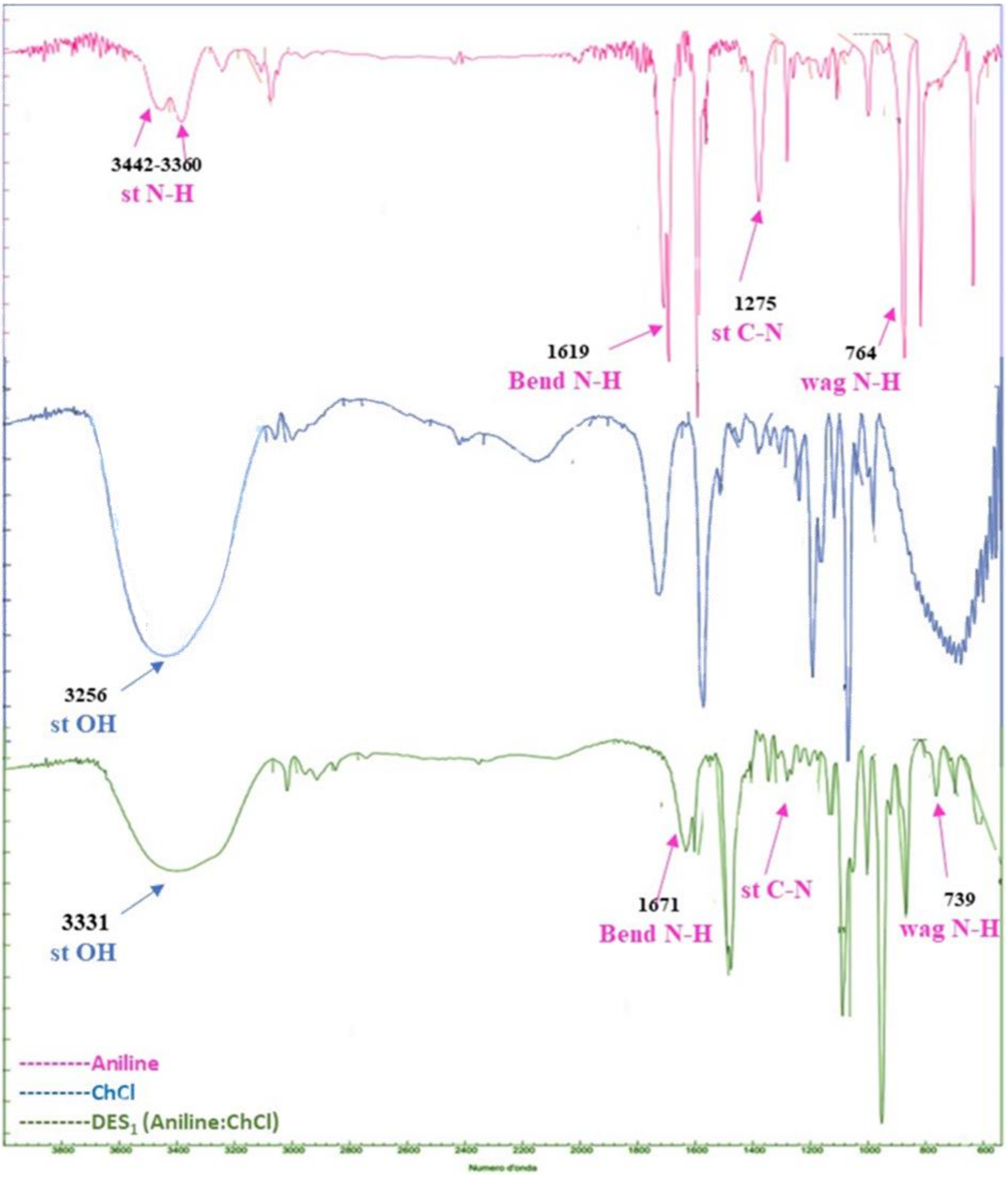


Figure S2. FT-IR-DES_2

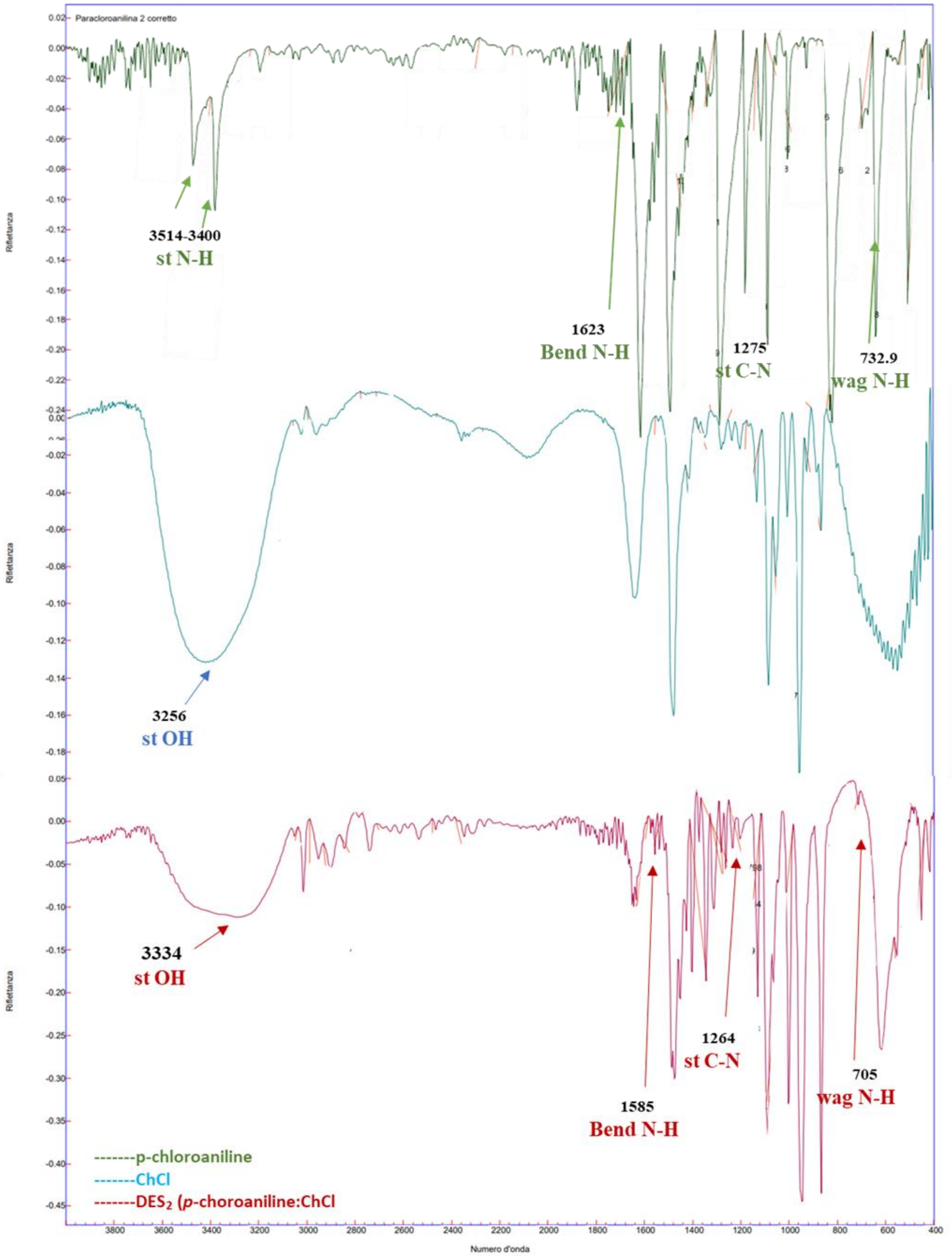


Figure S3. FT-IR-DES$_3$

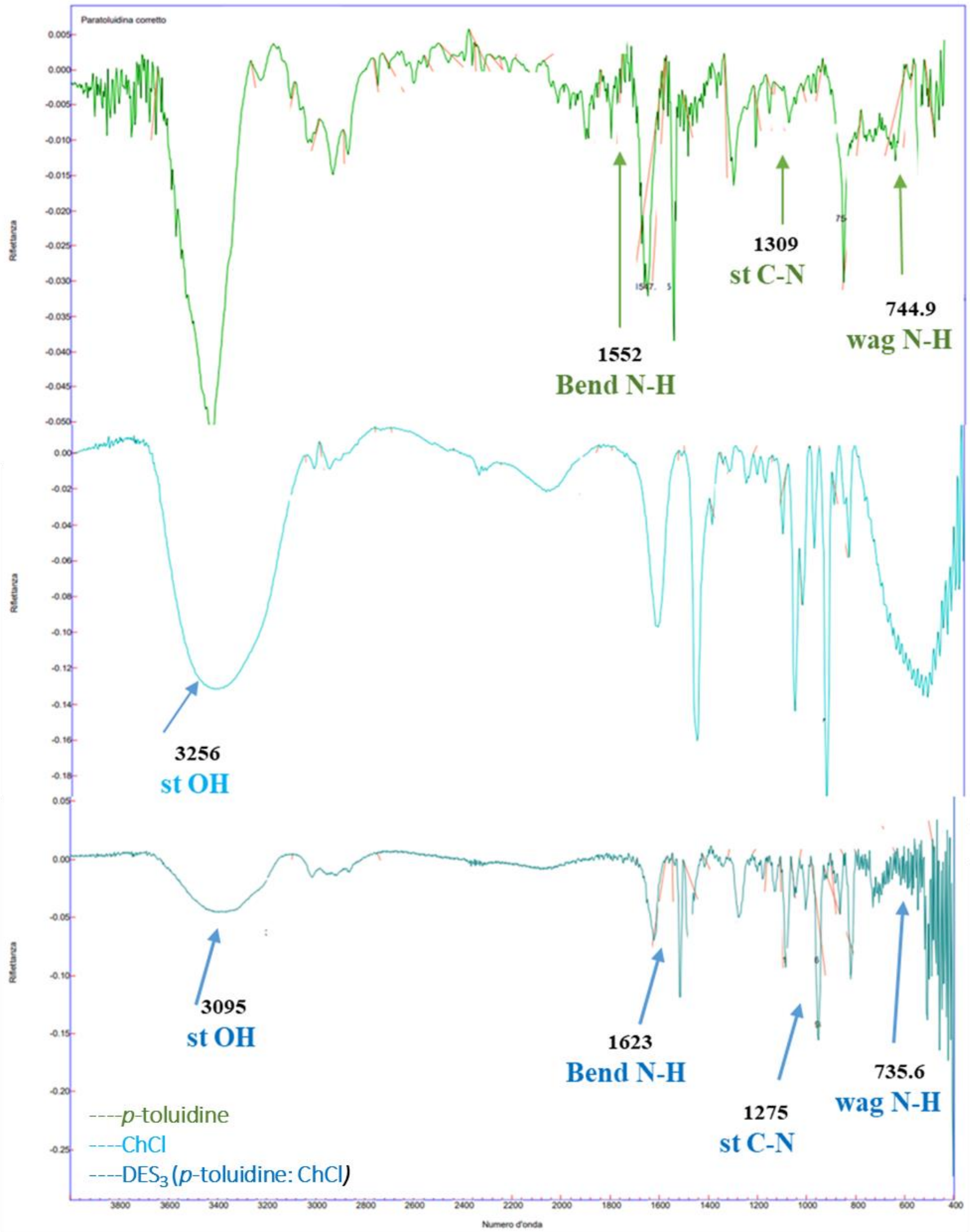


Figure S4. FT-IR-DES4

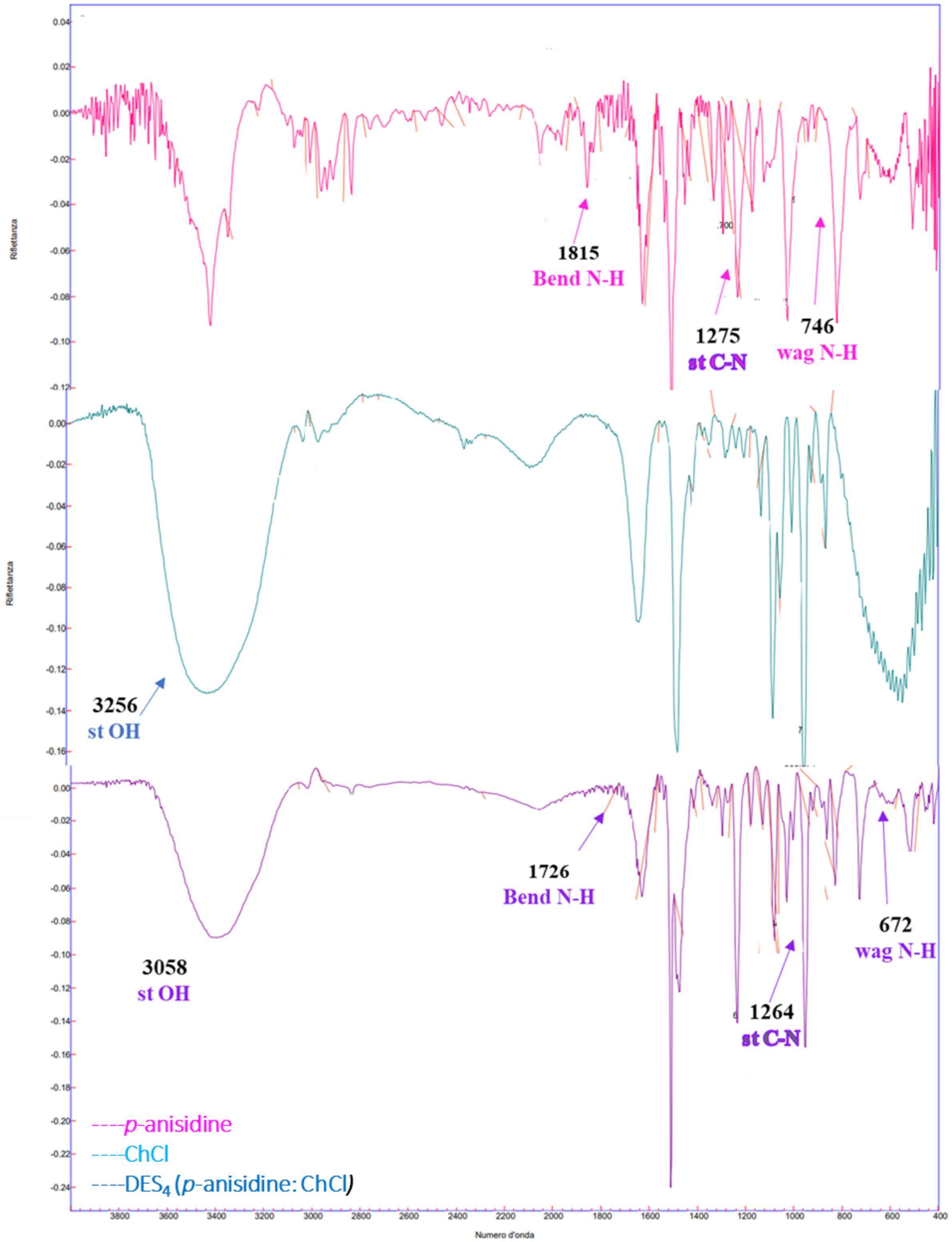


Figure S5. FT-IR- DES_5

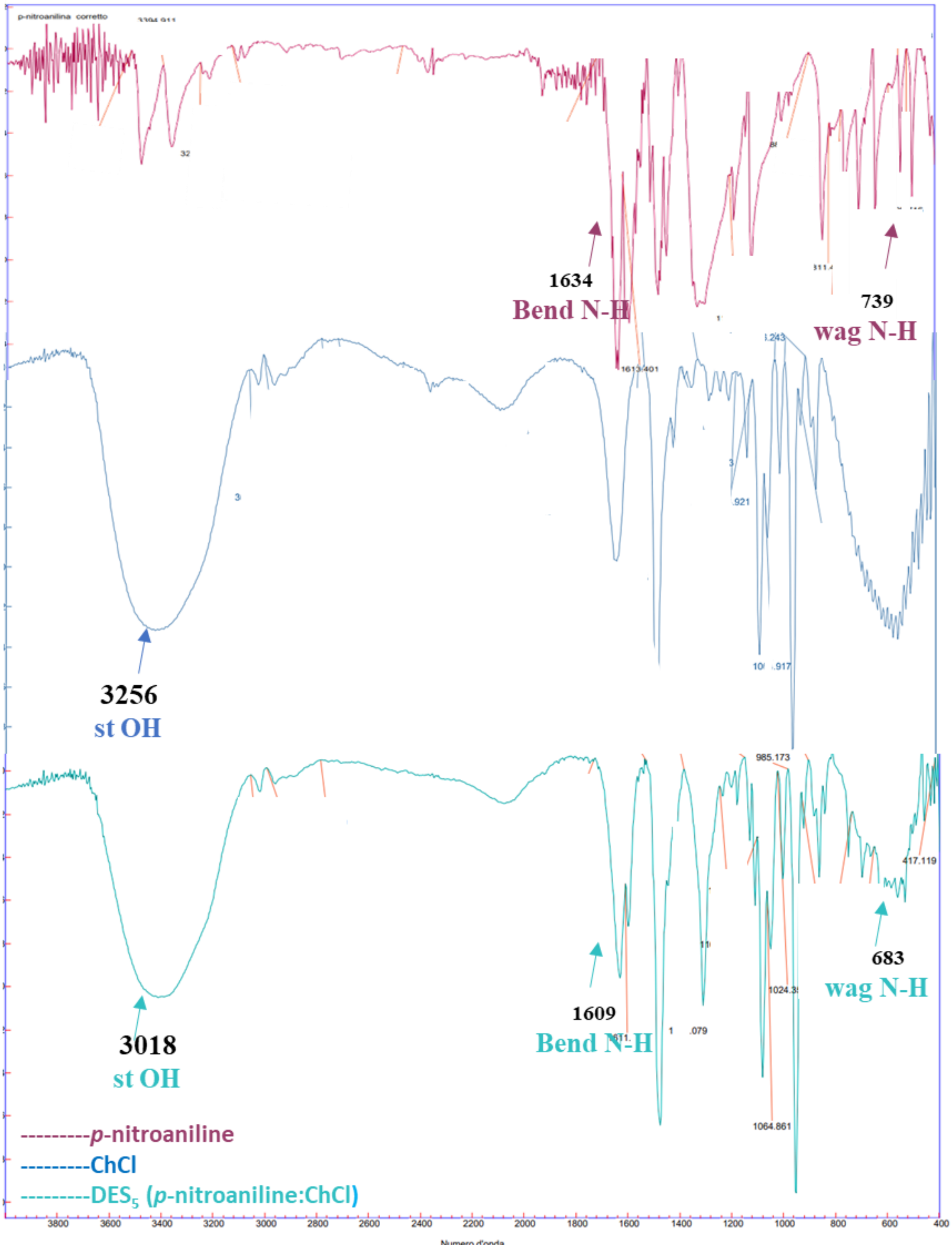


Figure S6. FT-IR-DES$_6$

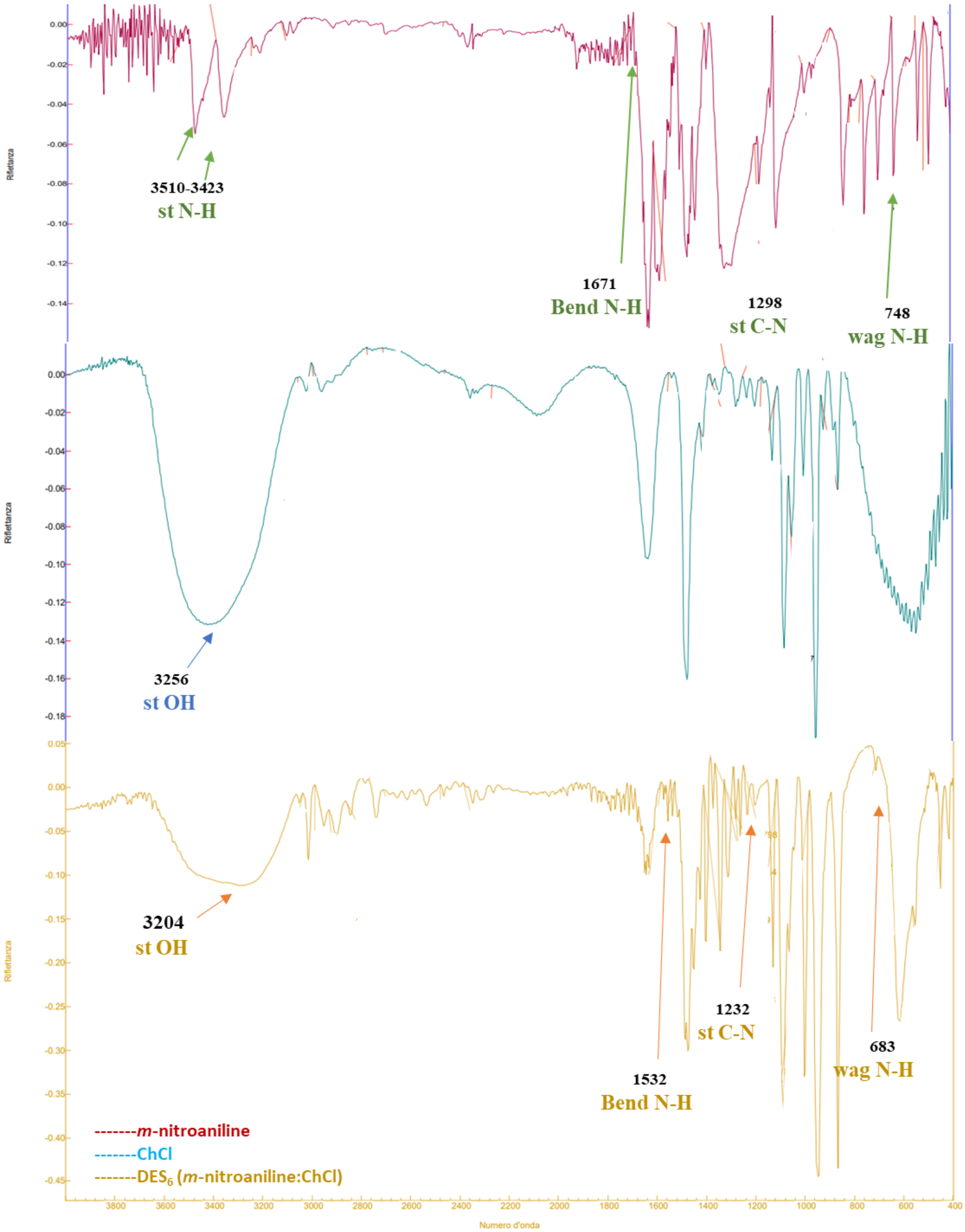


Figure S7. FT-IR-DES$_7$

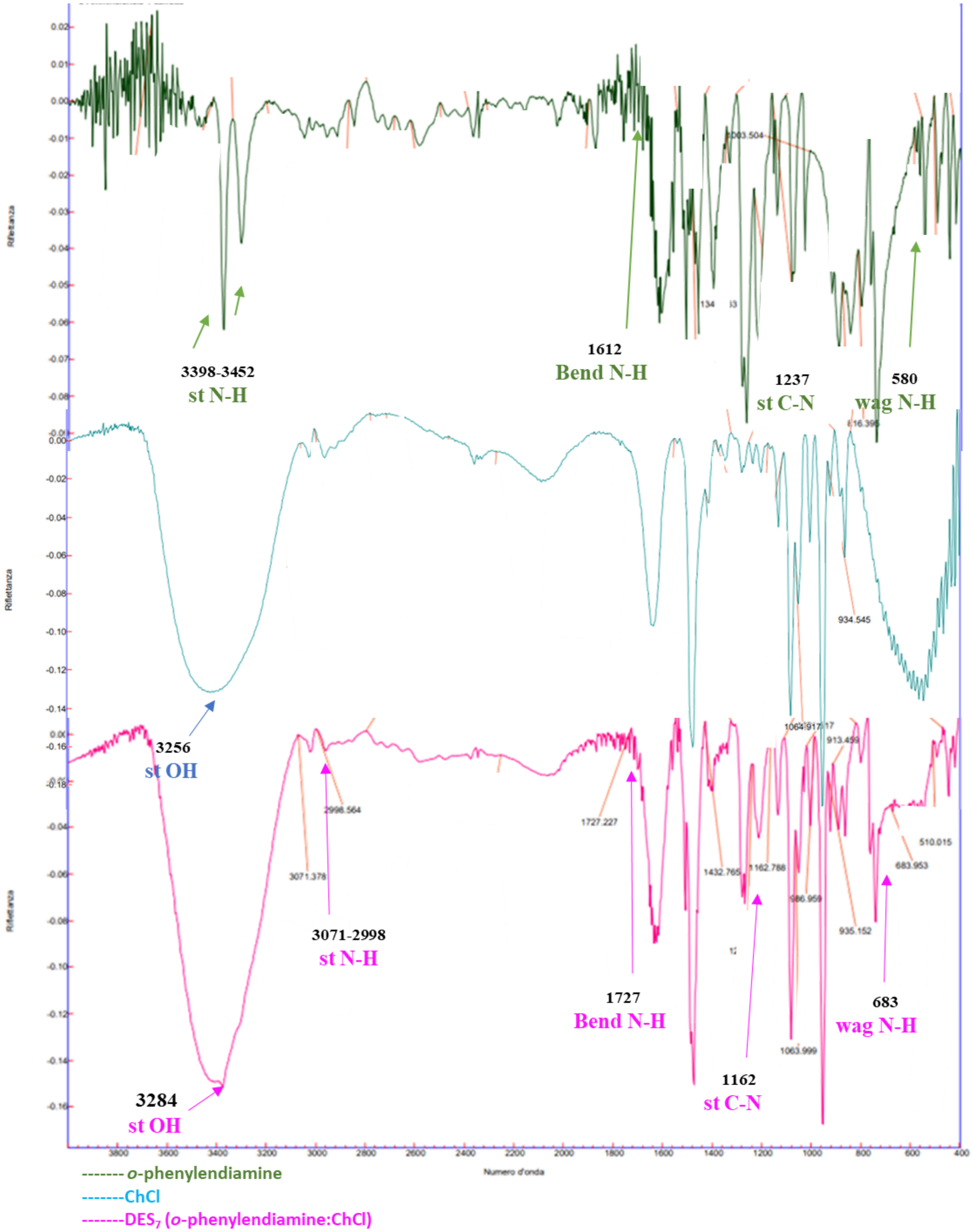


Figure S8. FT-IR-DES8

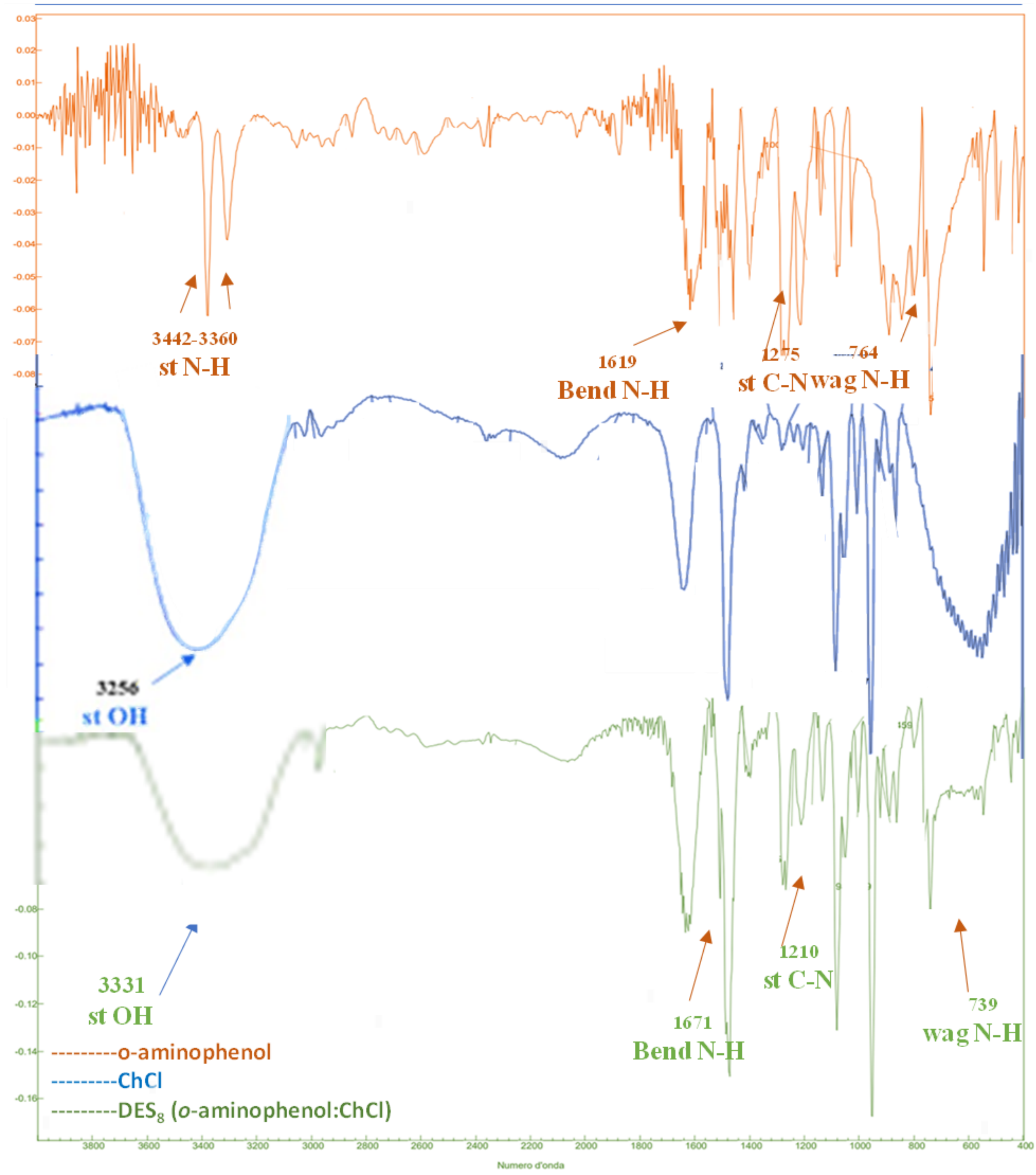


Figure S9. FT-IR-DES_9

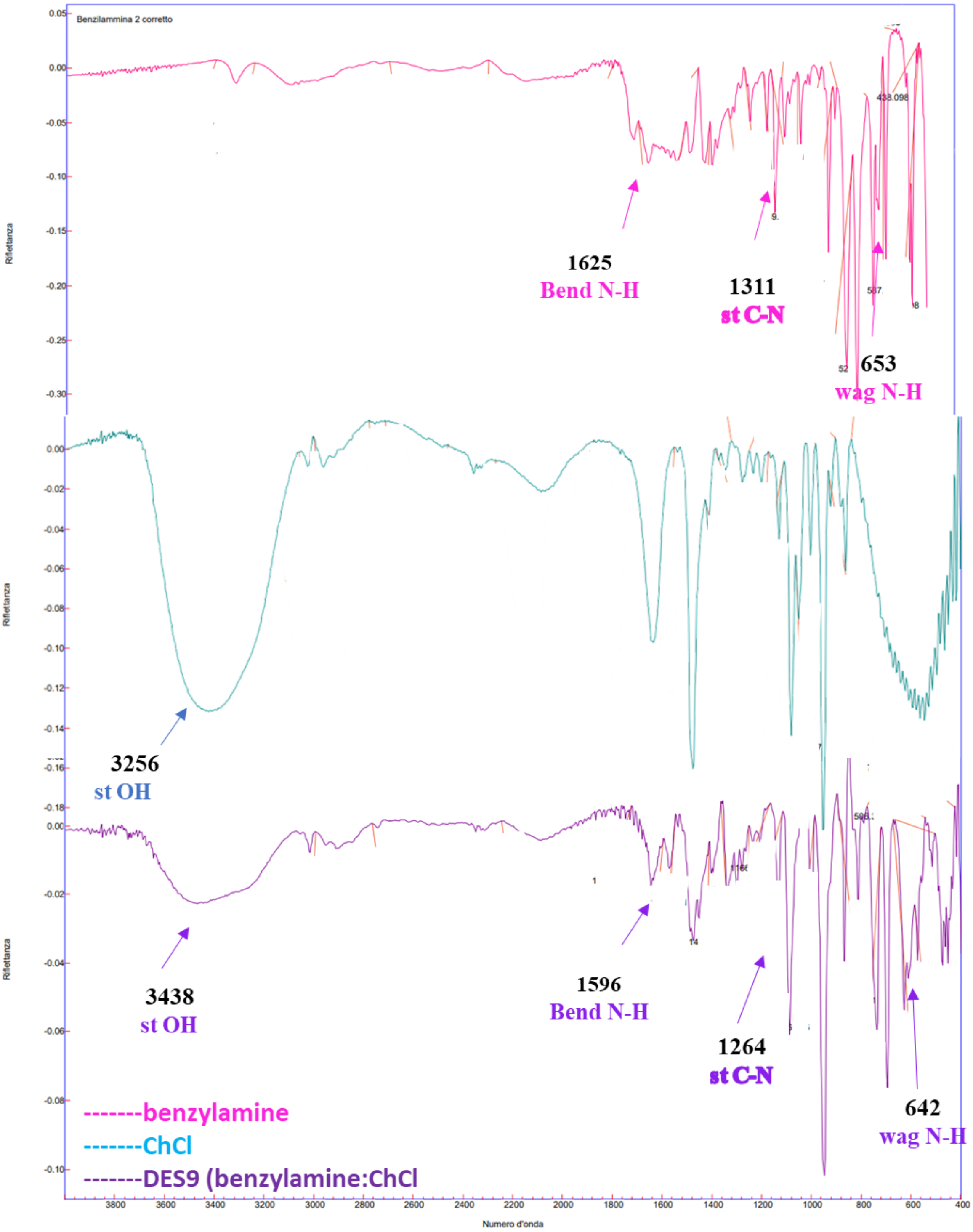


Figure S10. FT-IR-DES$_{10}$

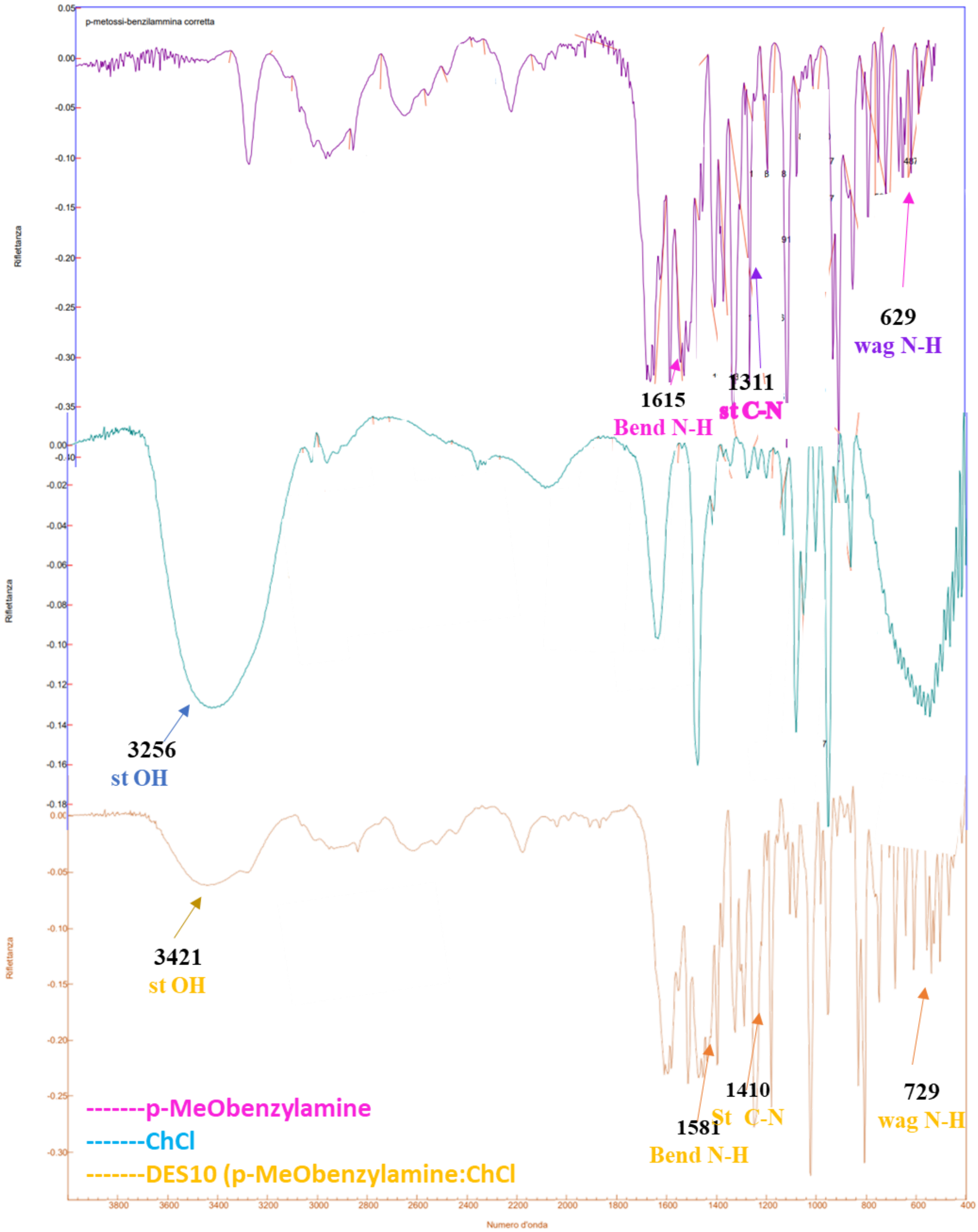


Figure S11. FT-IR-DES11

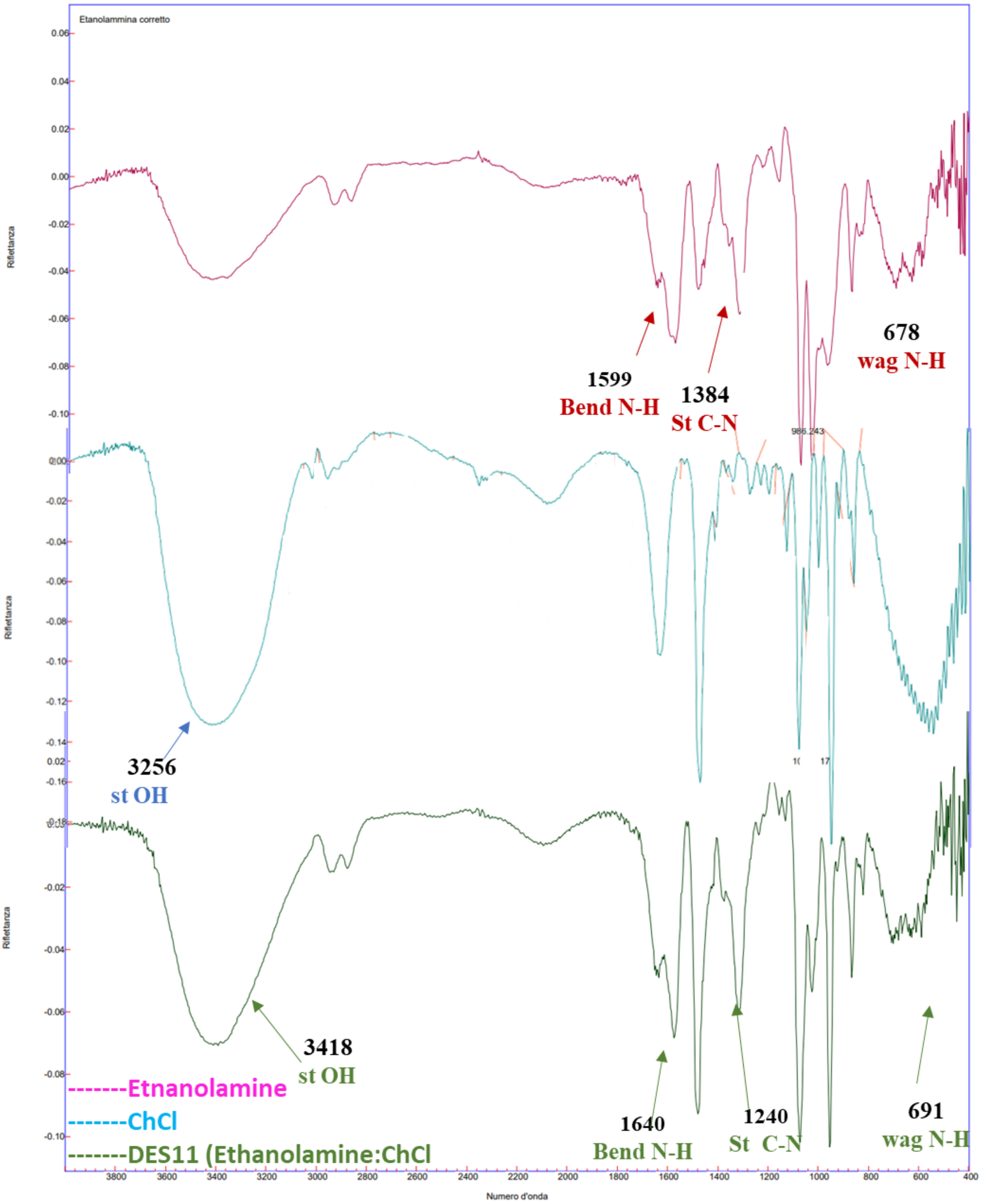


Figure S12. FT-IR-DES_{12}

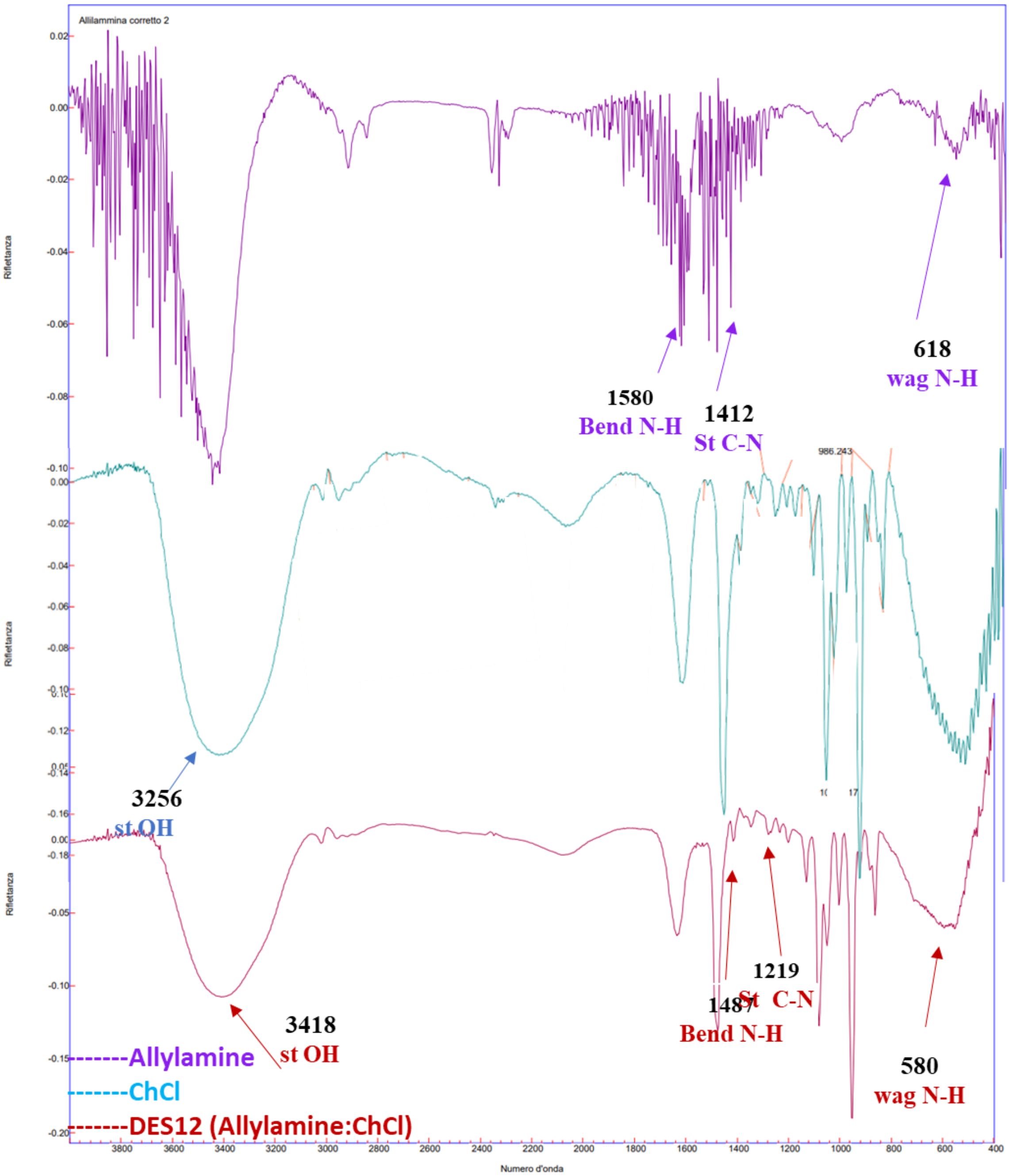


Figure S13. FT-IR-DES13

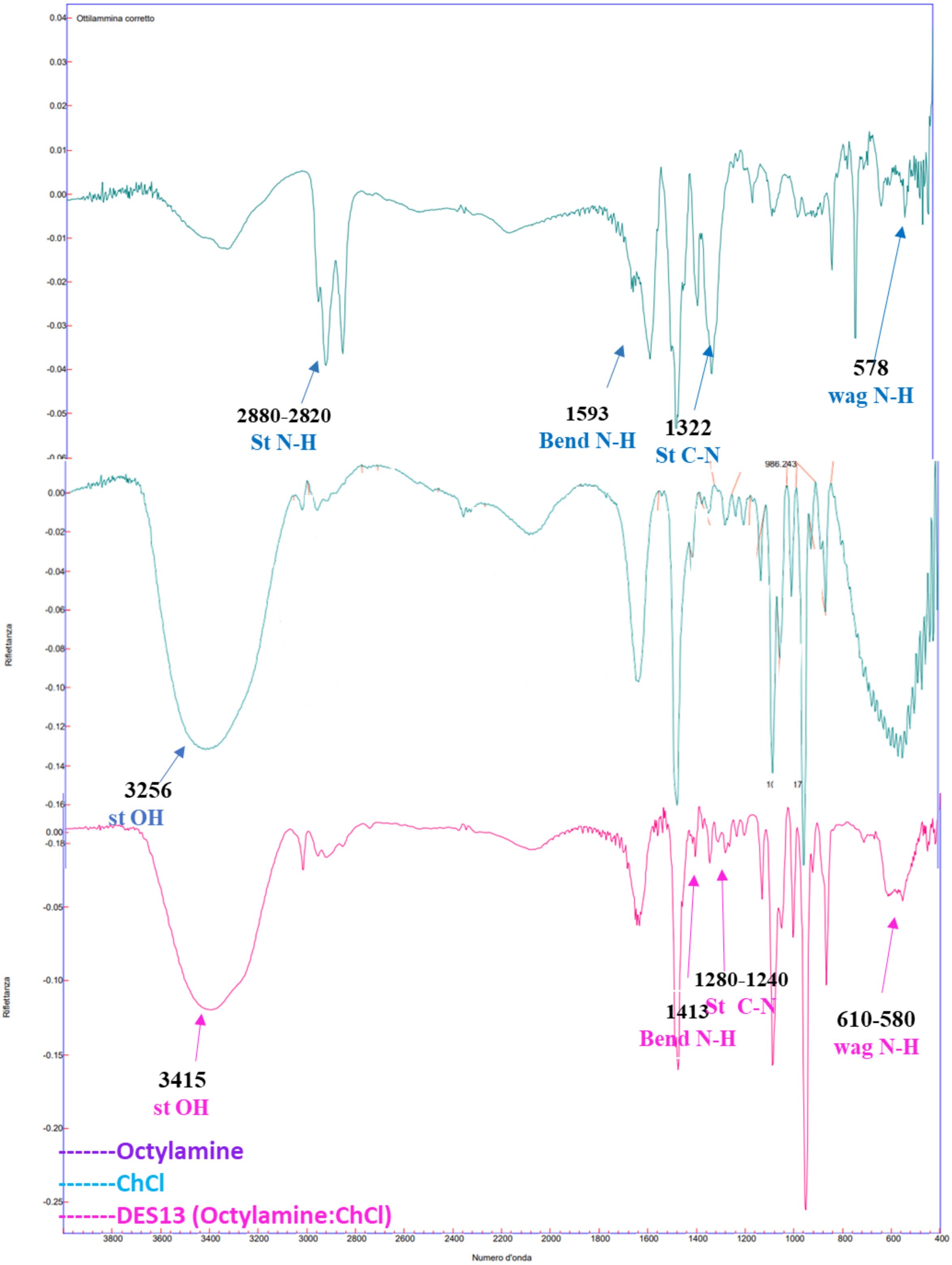


Figure S14. FT-IR-DES14

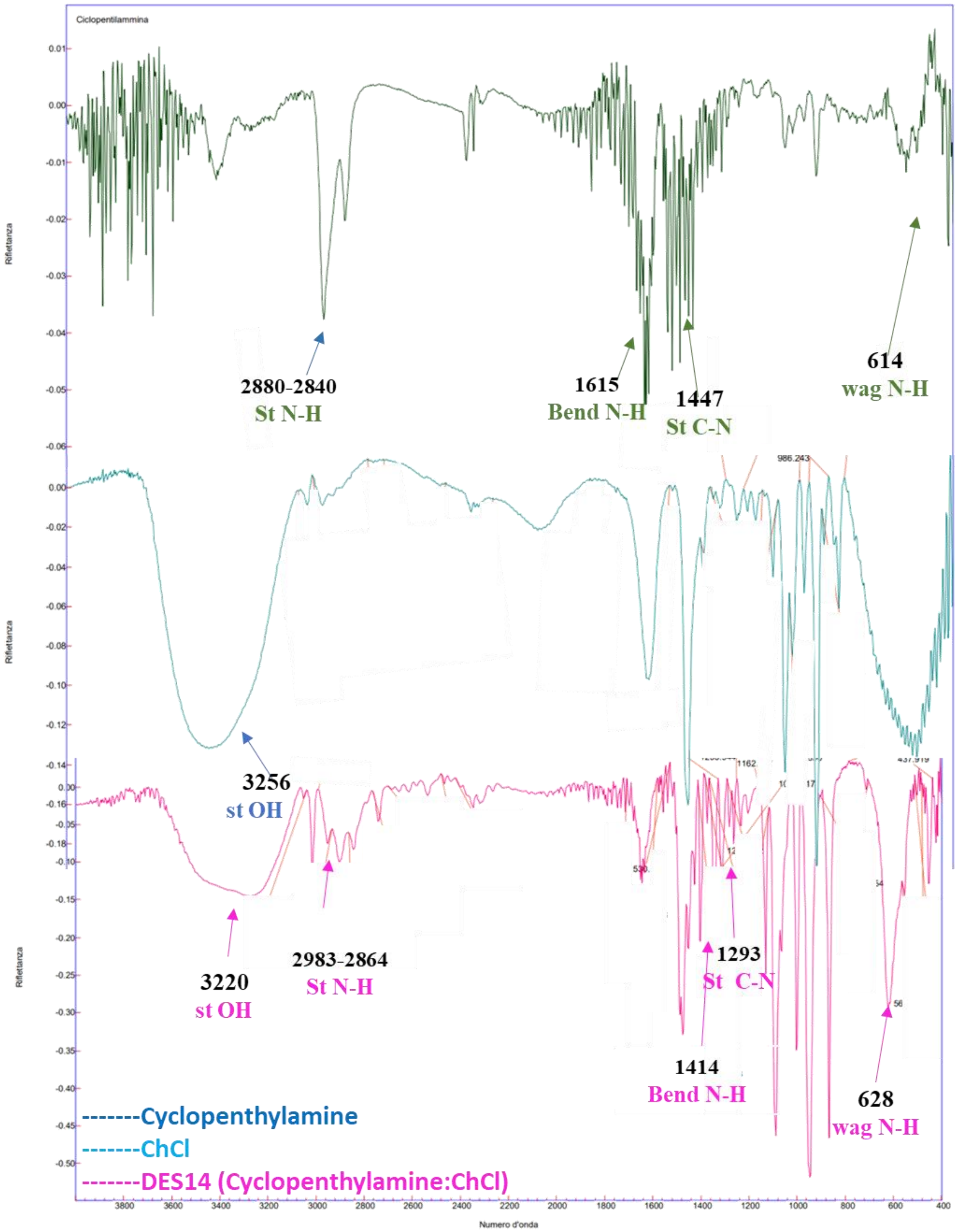
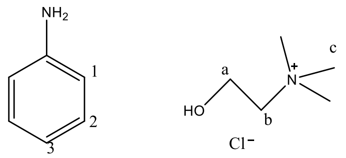
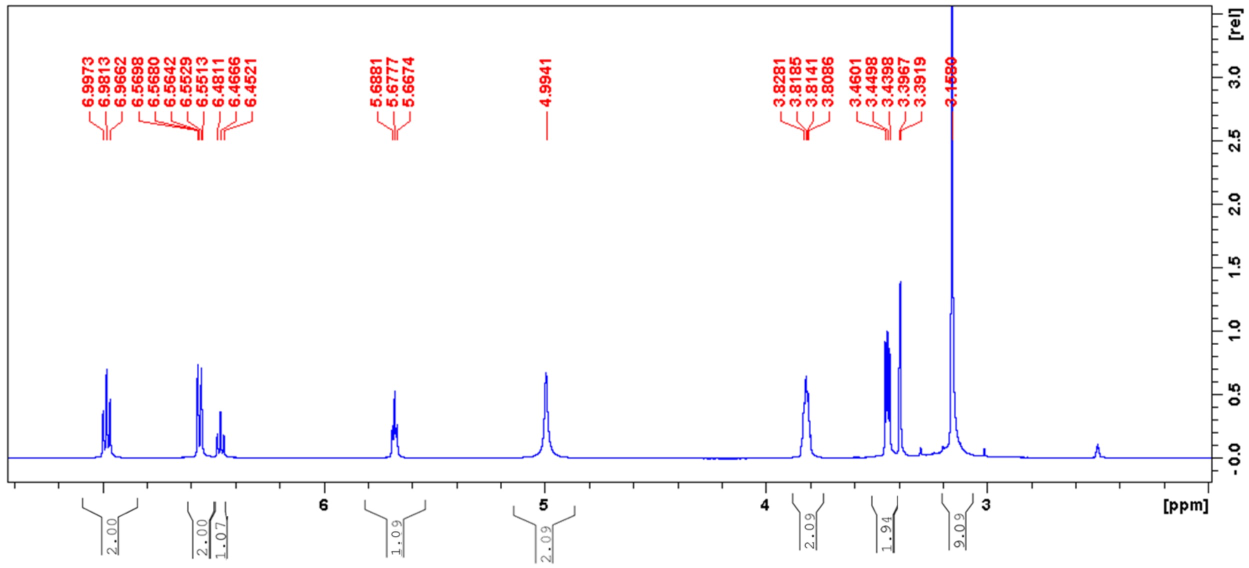
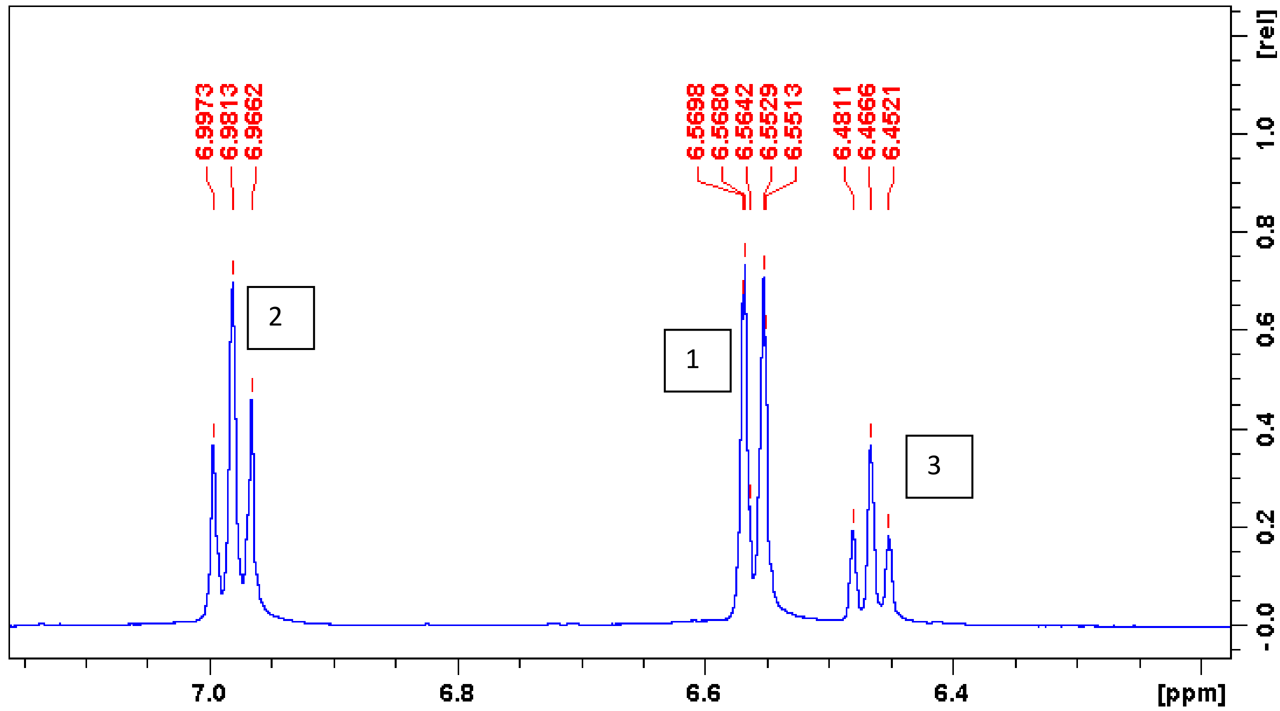
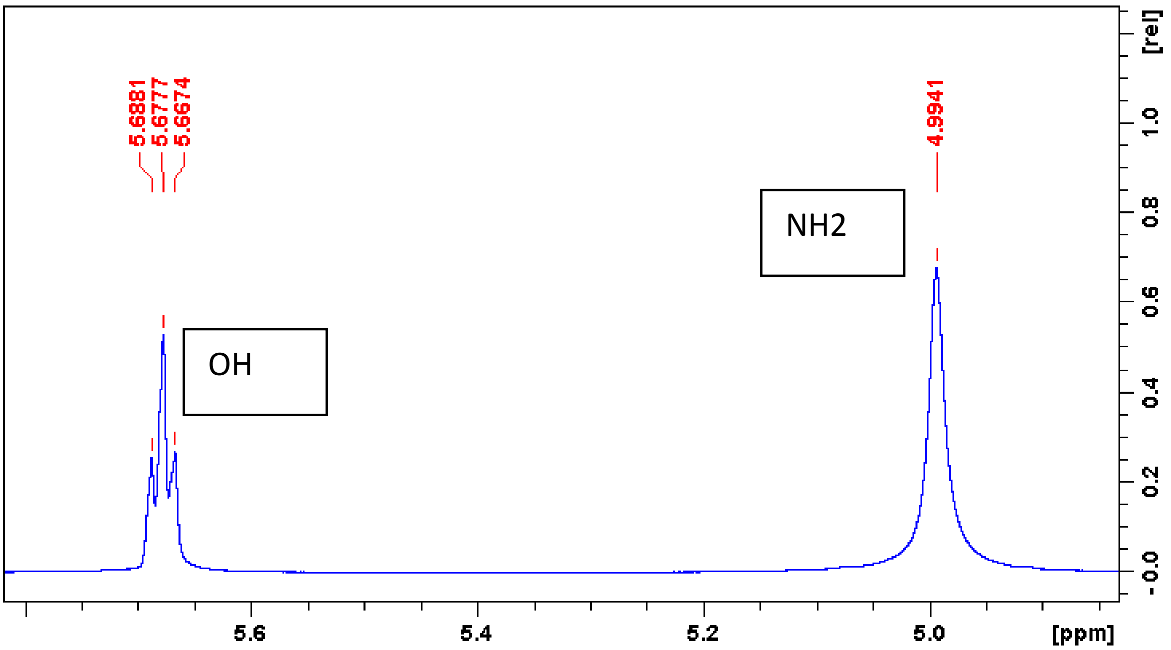


Figure S15. ^{1}H-NMR- DES$_1$





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5.6777
5.6674
4.9941
NH2
OH
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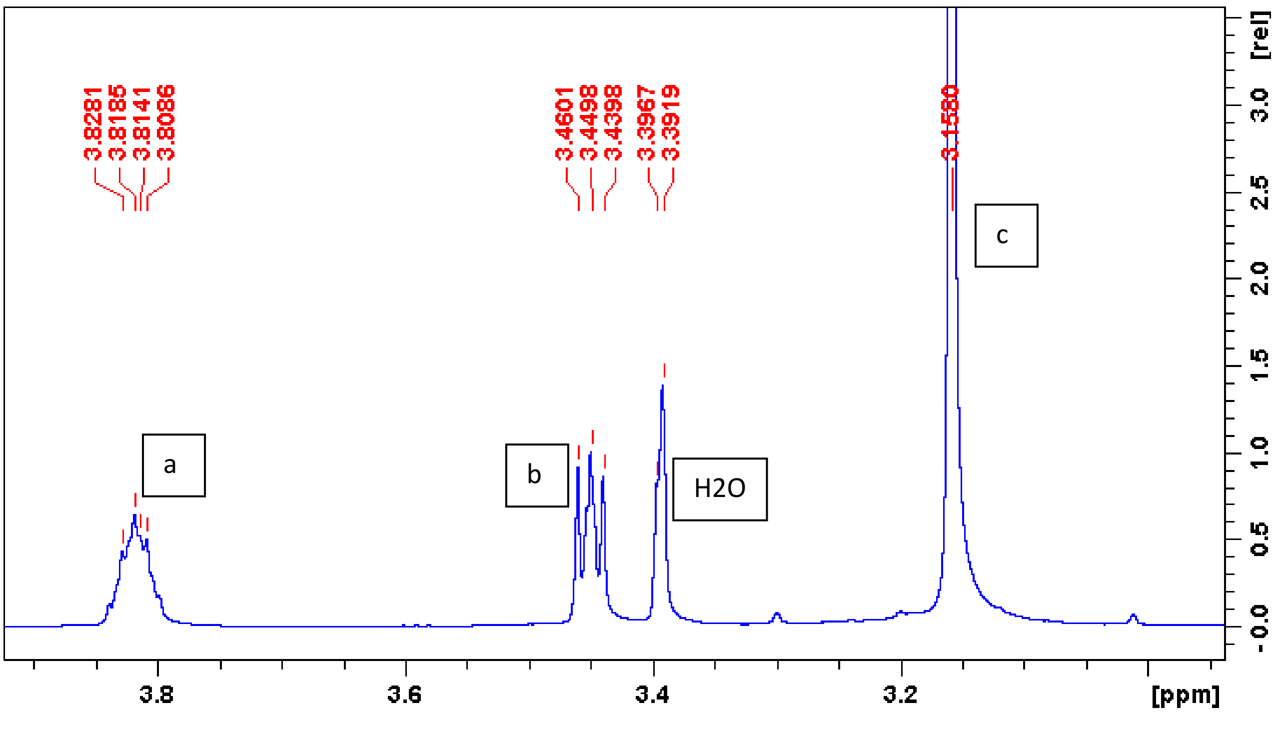
1.0
0.8
0.6
0.4
0.2
-0.0
5.6
5.4
5.2
5.0
[ppm]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3.8185
3.8141
3.8086
3.4601
3.4498
3.4398
3.3967
3.3919
3.1580
a
b
H2O
c
[rel]
3.0
2.5
2.0
1.5
1.0
0.5
-0.0
3.8
3.6
3.4
3.2
[ppm]

Figure S16. ^{13}C-NMR- DES$_1$

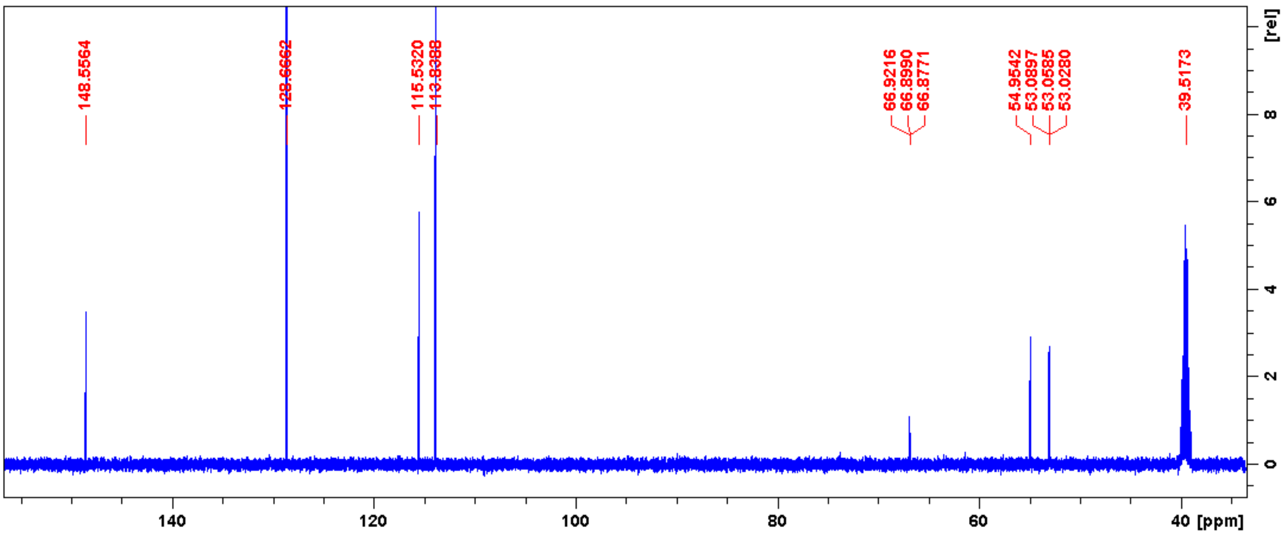


Figure S17. HMQC- DES$_1$

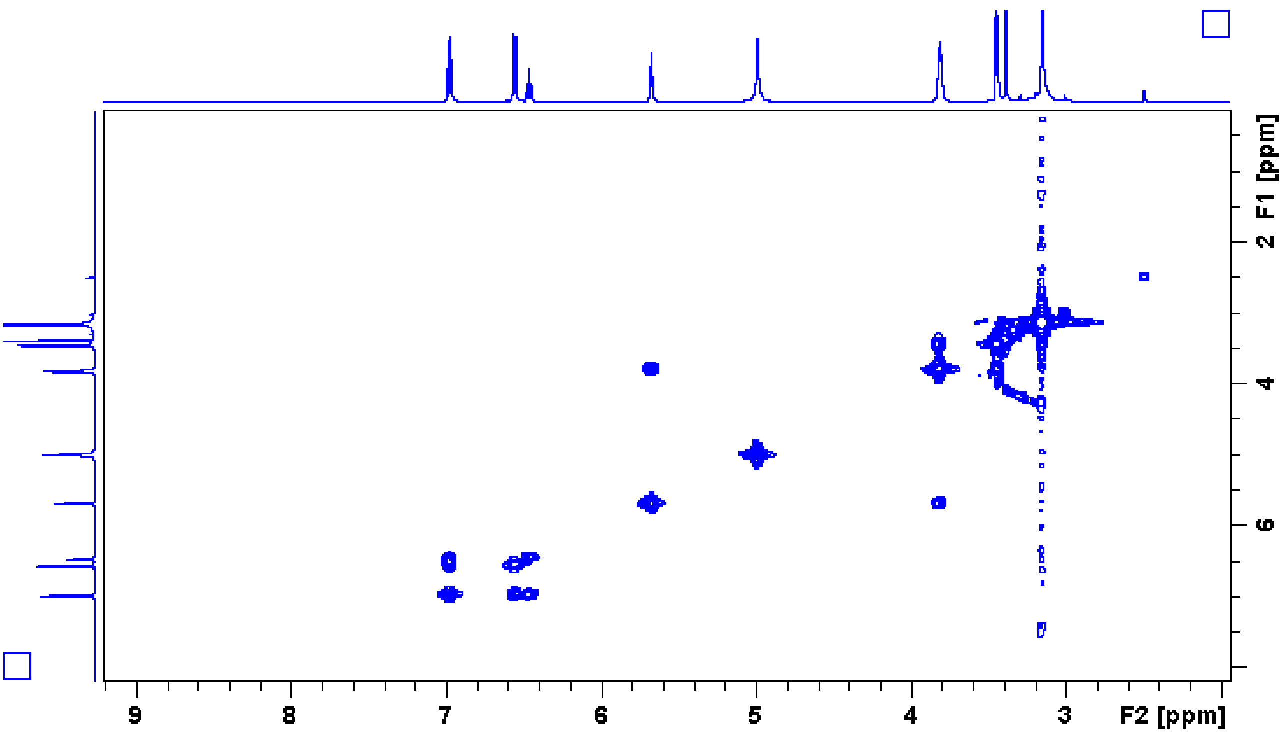


Figure S18. COSY- DES$_1$

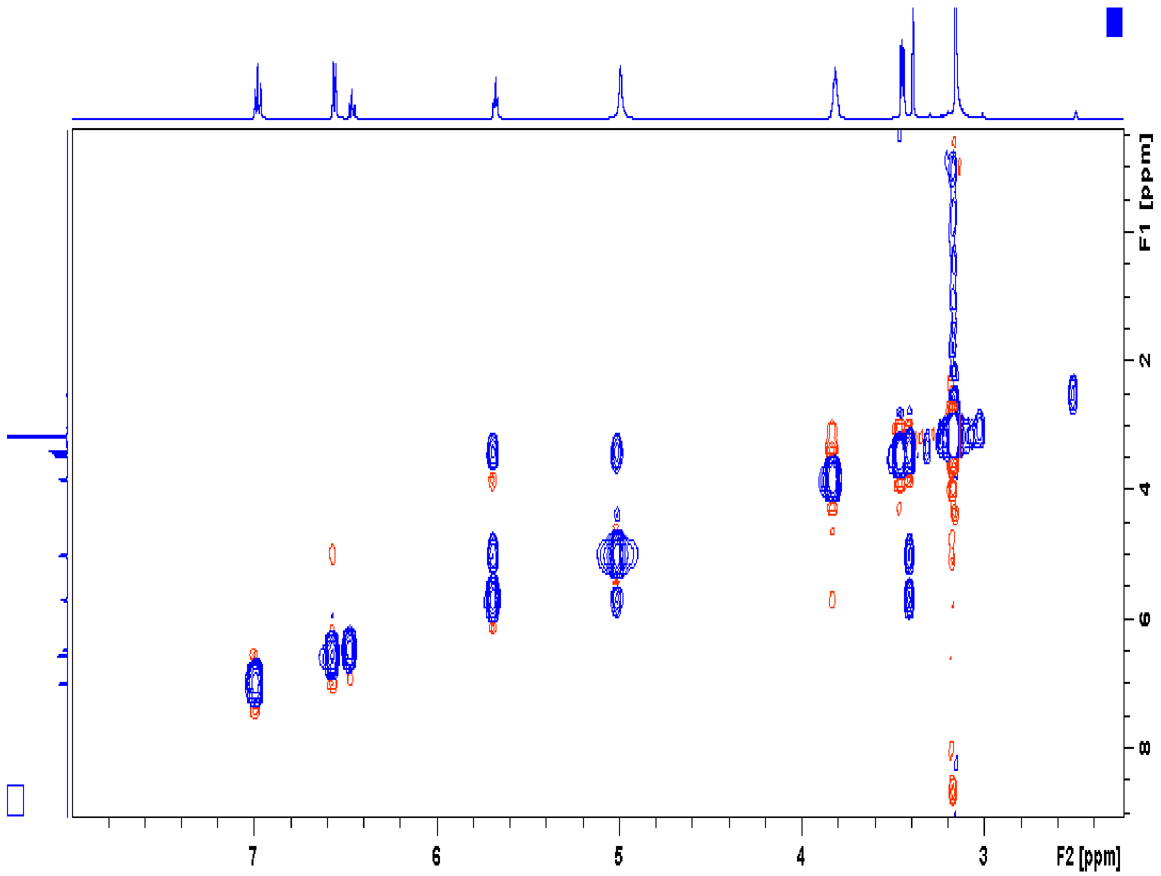
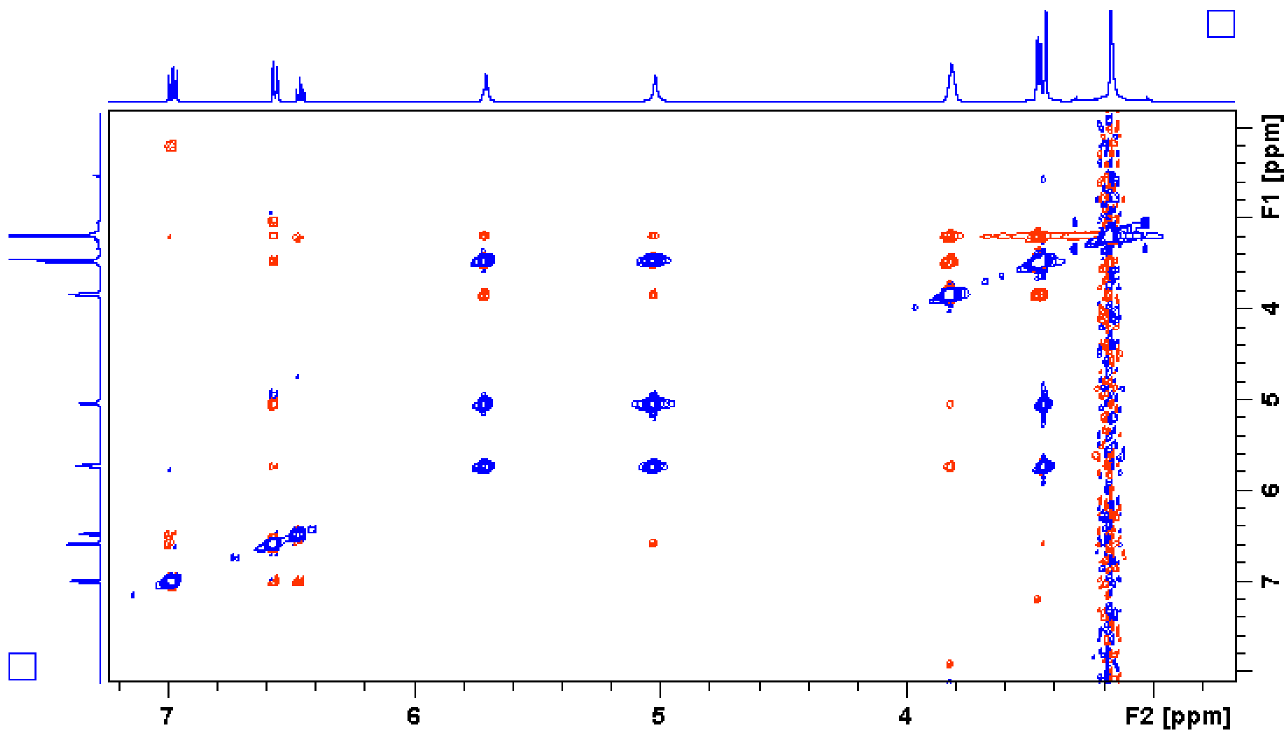
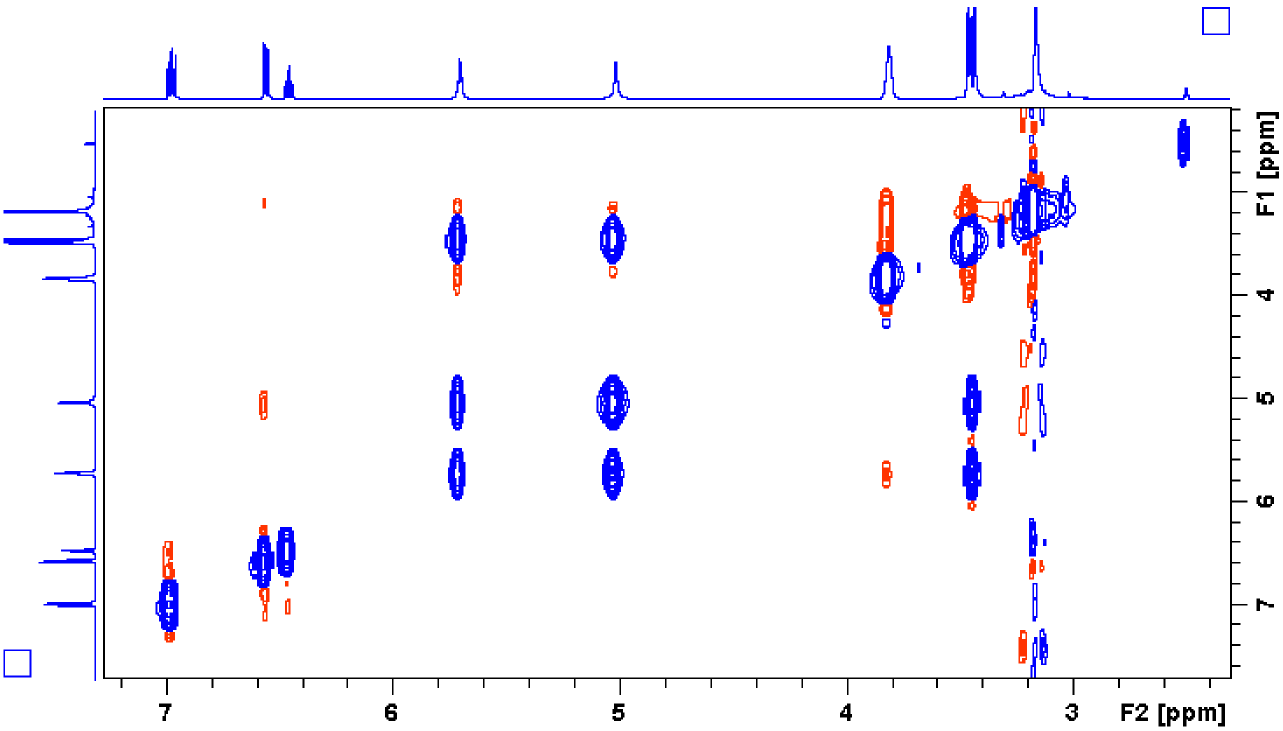


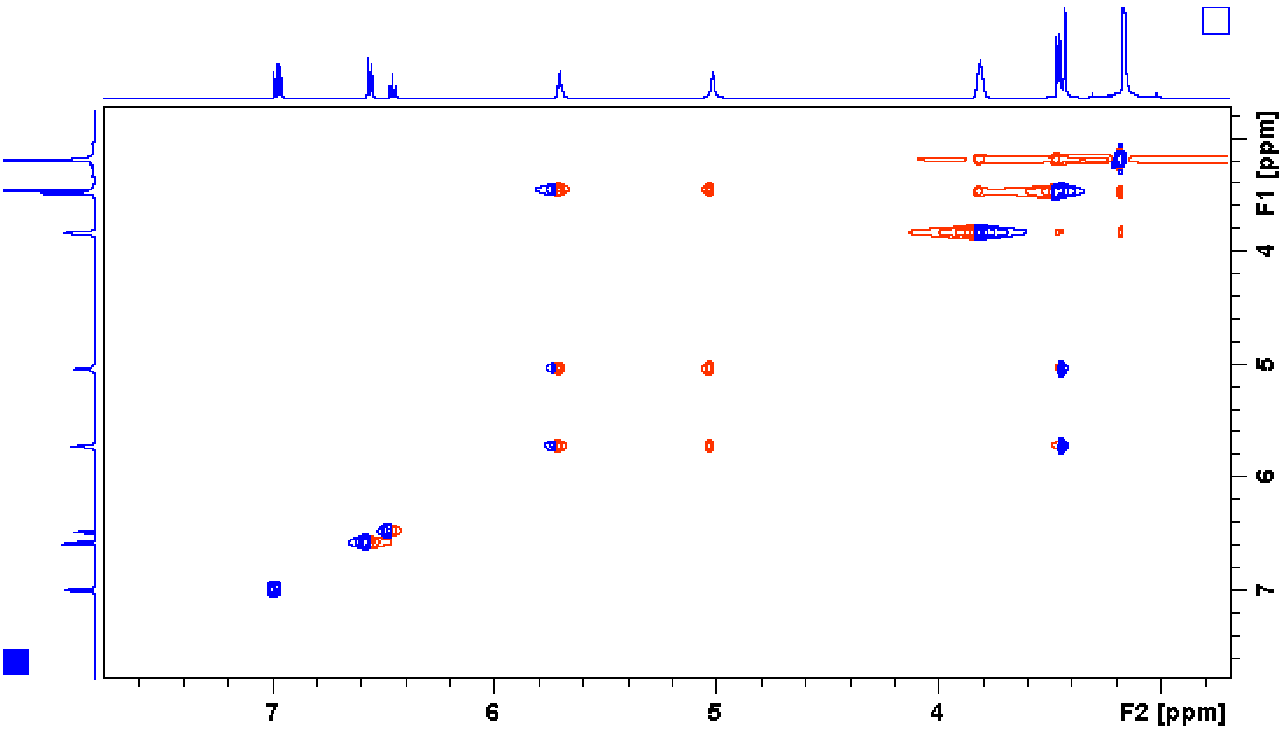
Figure S19. NOESY - DES$_1$



Noesy D8 = 900 ms

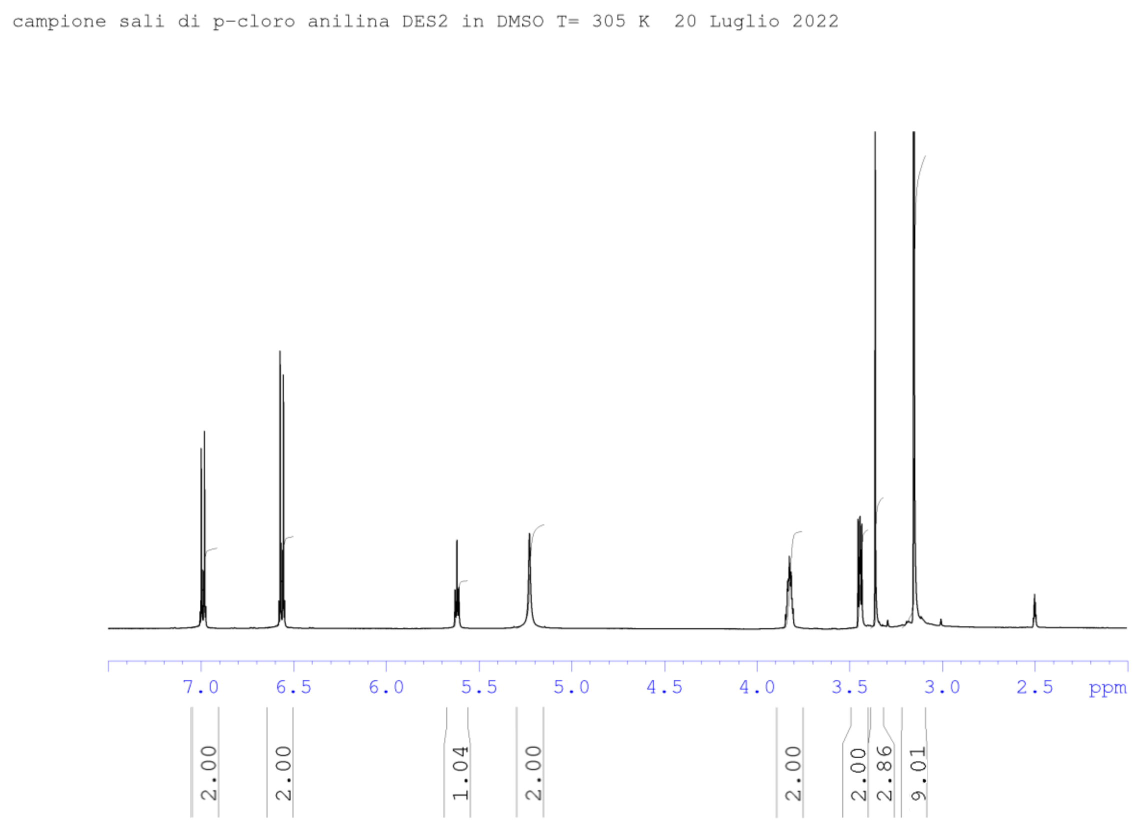


Noesy D8= 800 ms



Noesy D8 = 1.1 s

Figure S20. ^{1}H-NMR- DES$_2$



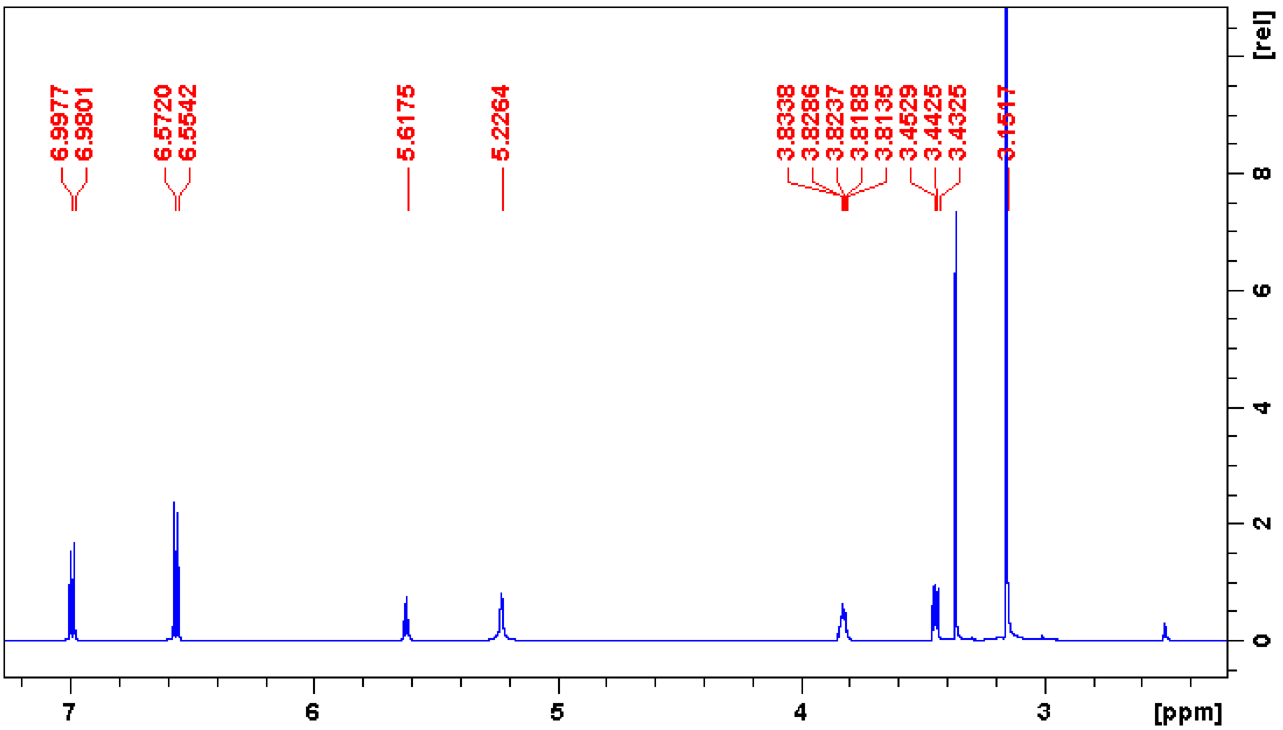


Figure S21. ^{13}C-NMR- DES_2

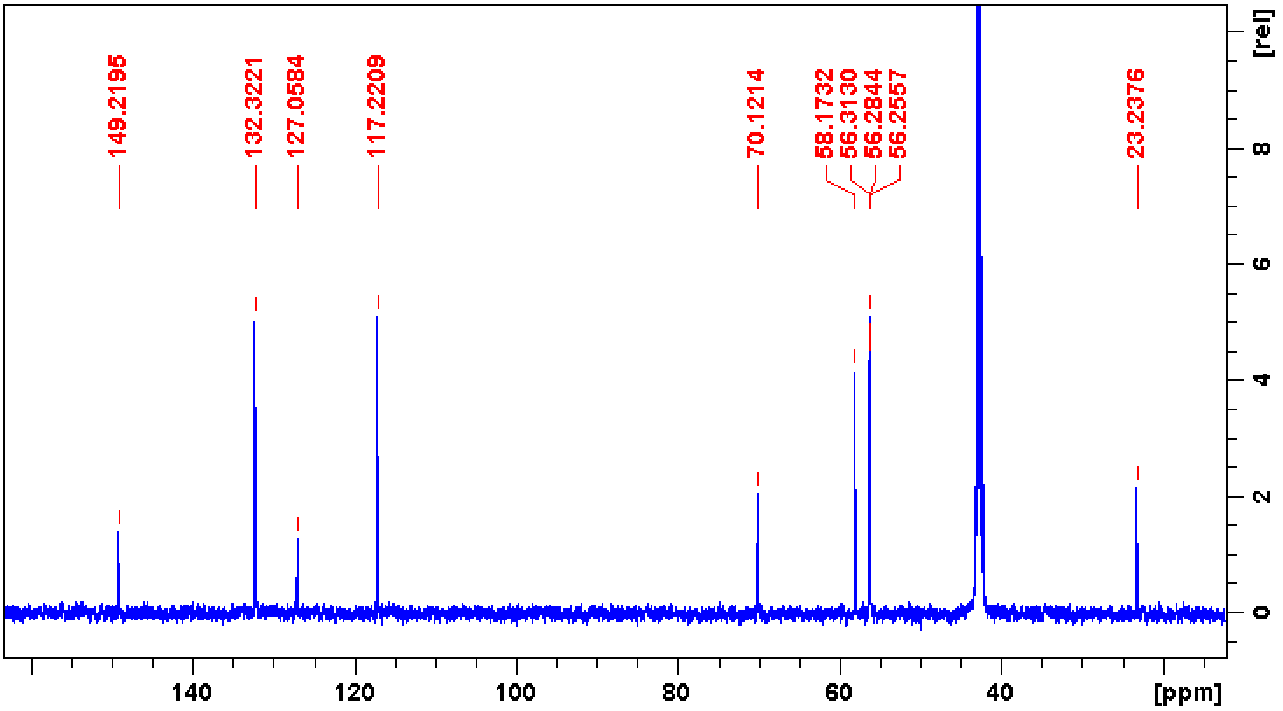
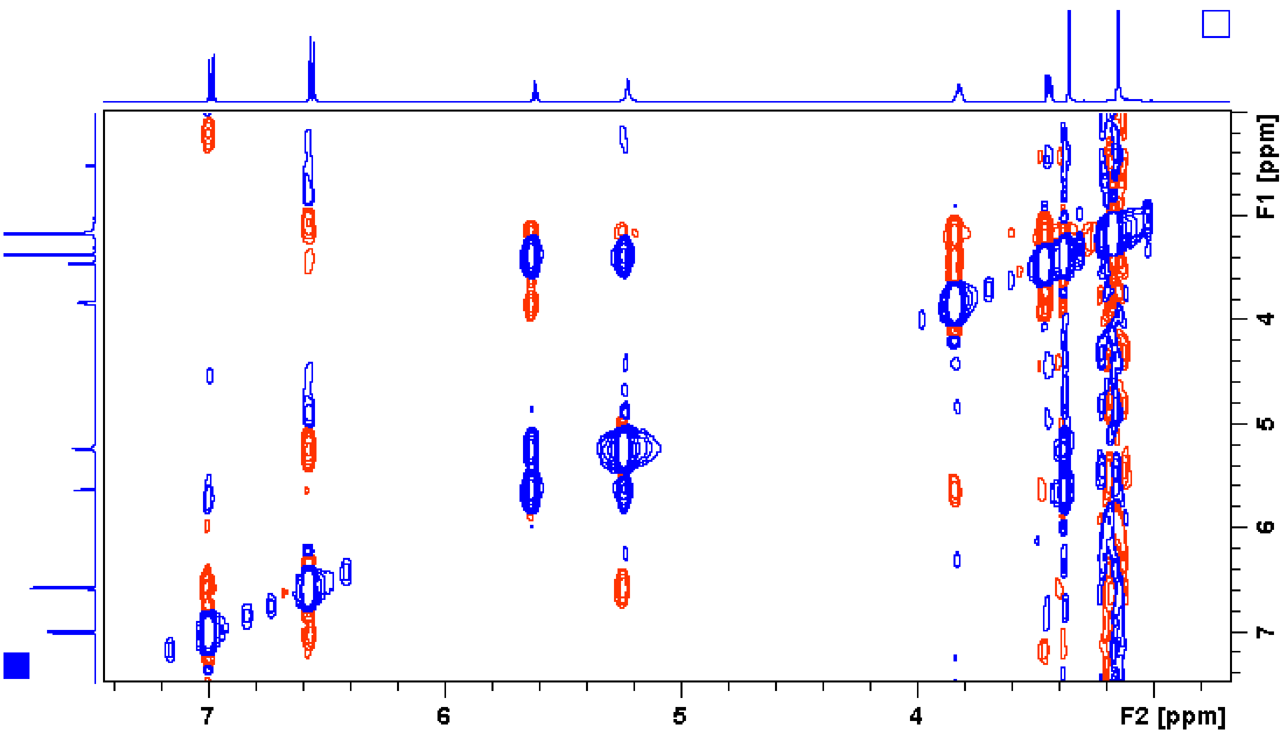
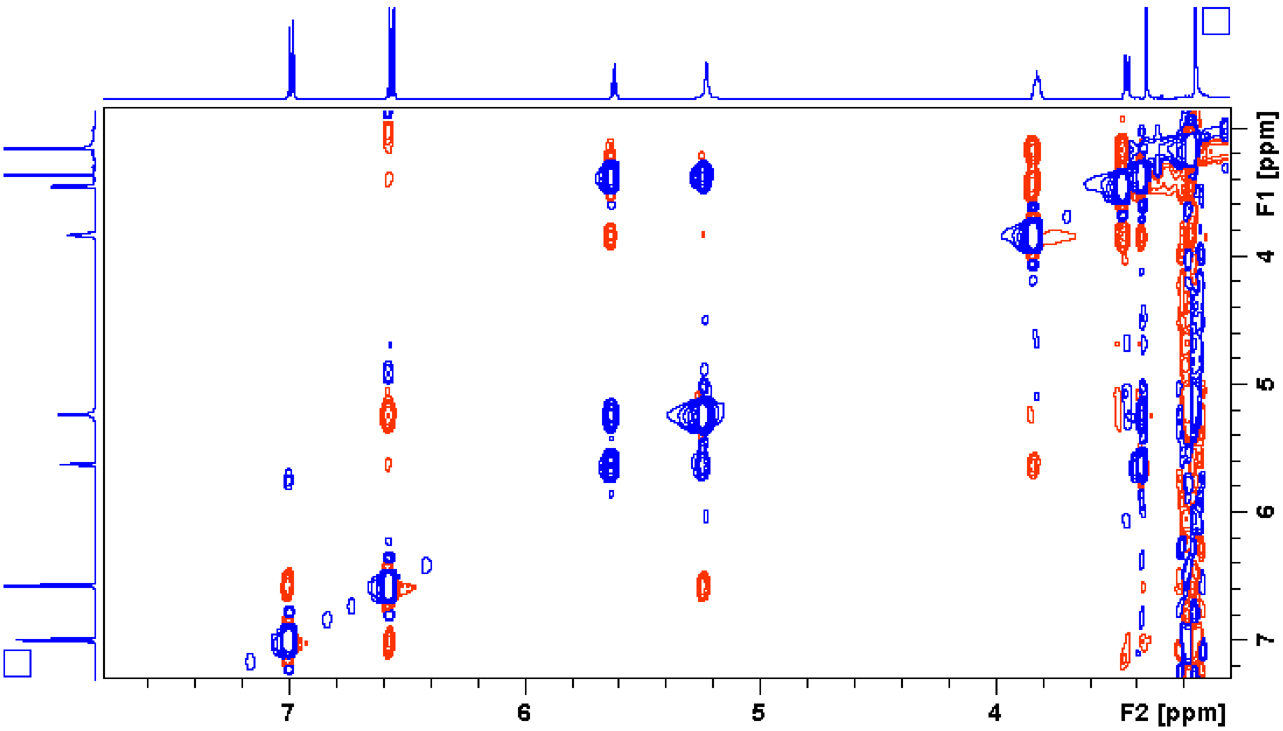


Figure S22. NOESY- DES_2

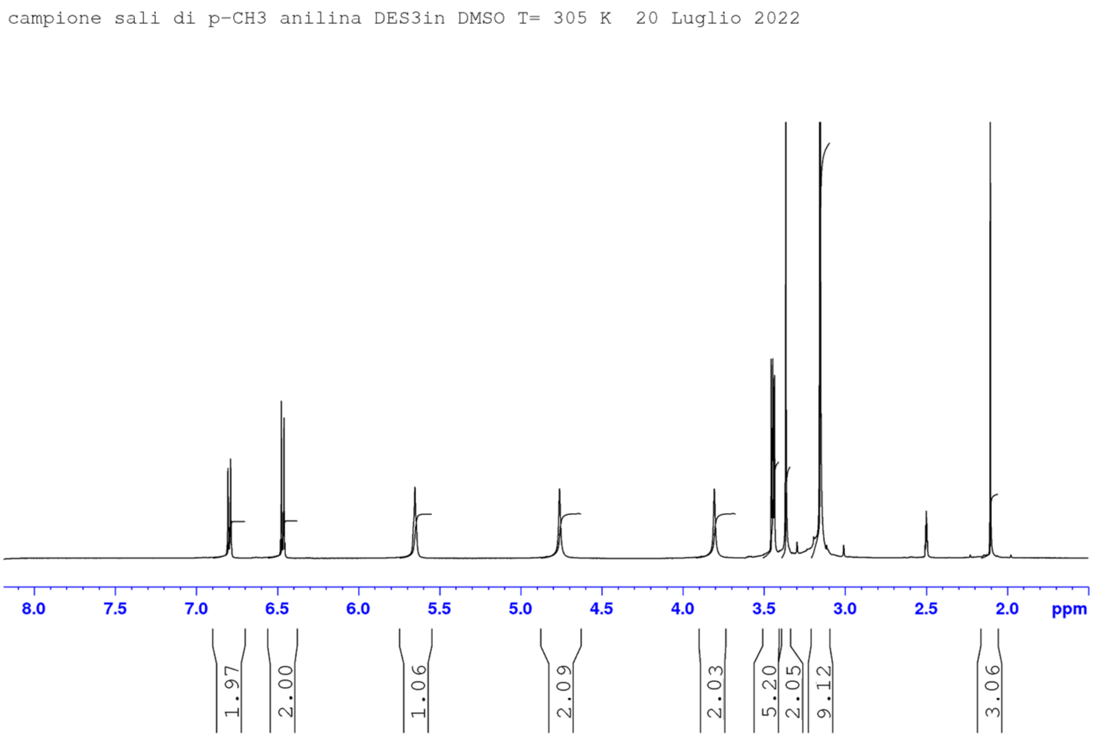


NOESY Tmix= 900 ms



NOESY Tmix= 1.2 s

Figure S23. ^{1}H-NMR – DES_3



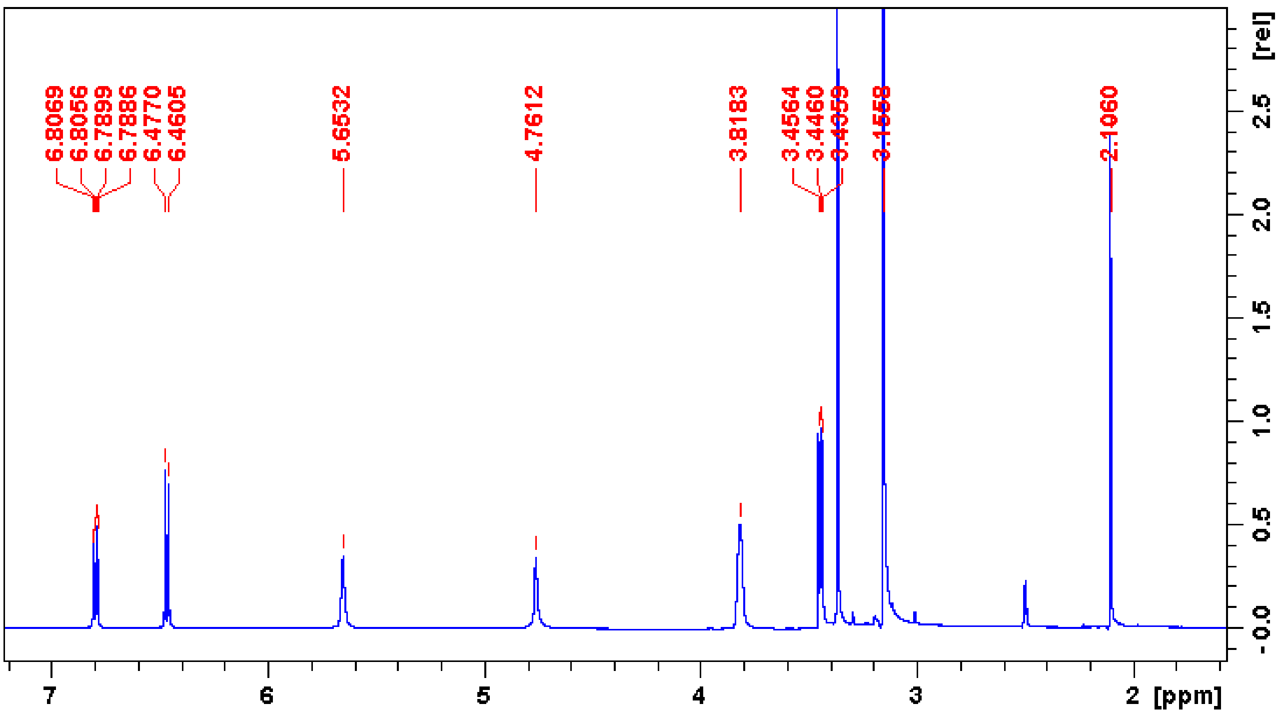


Figure S24. ^{13}C-NMR- DES_3

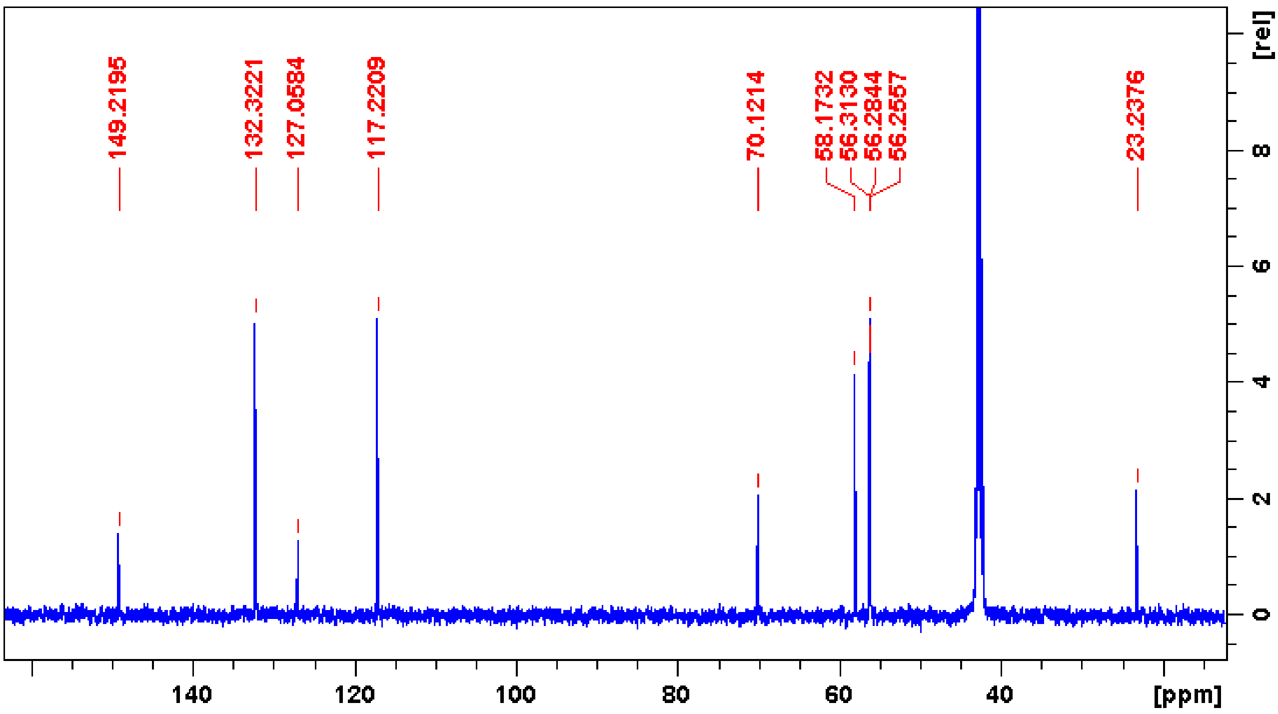
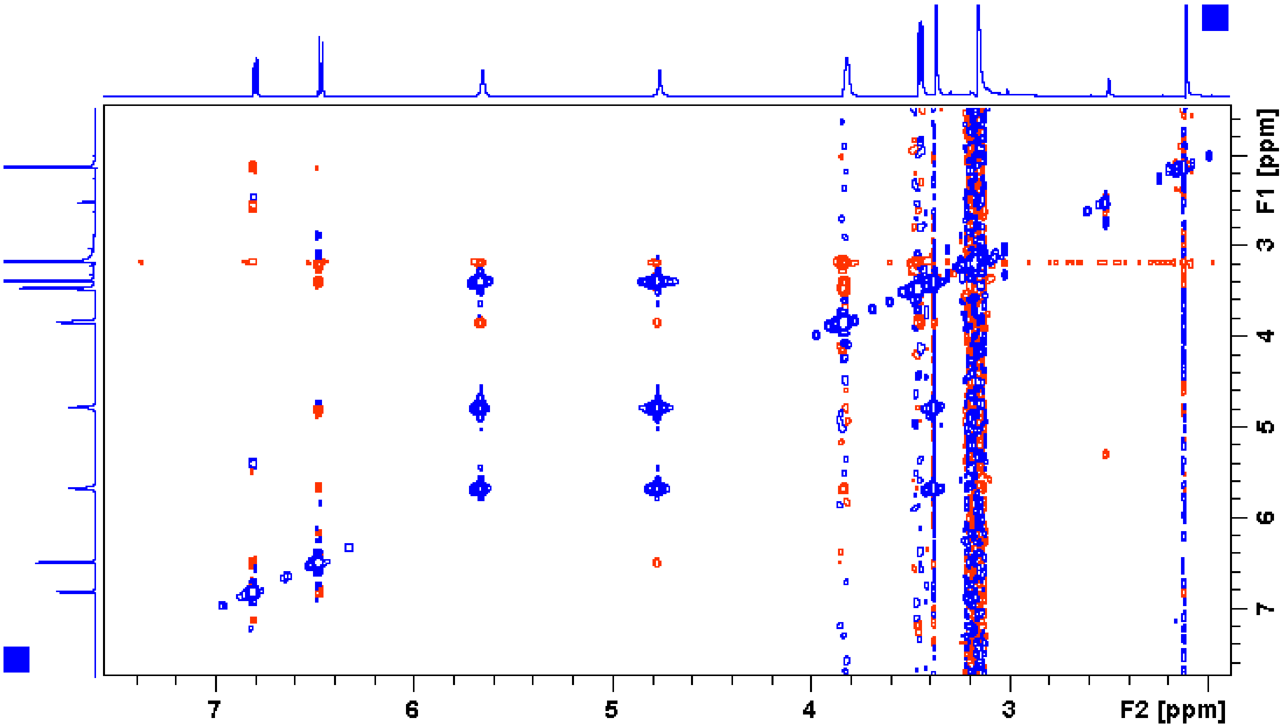
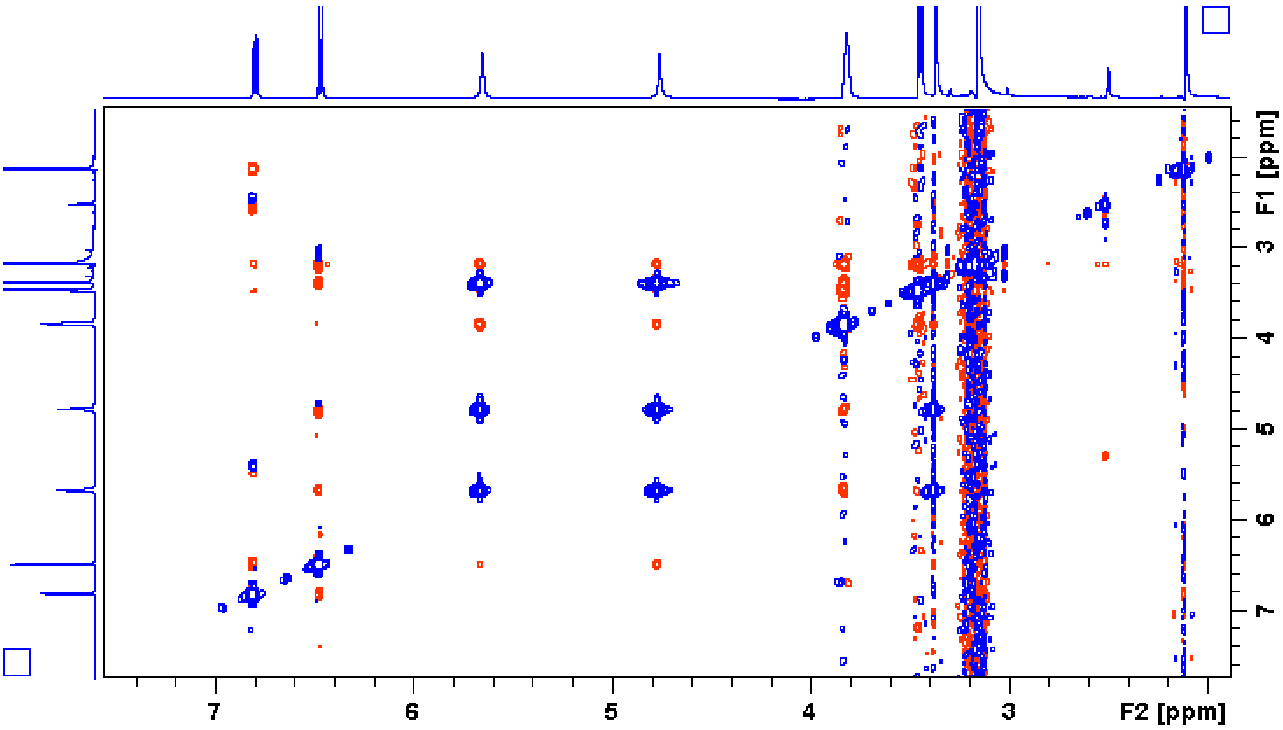


Figure S25. NOESY- DES3

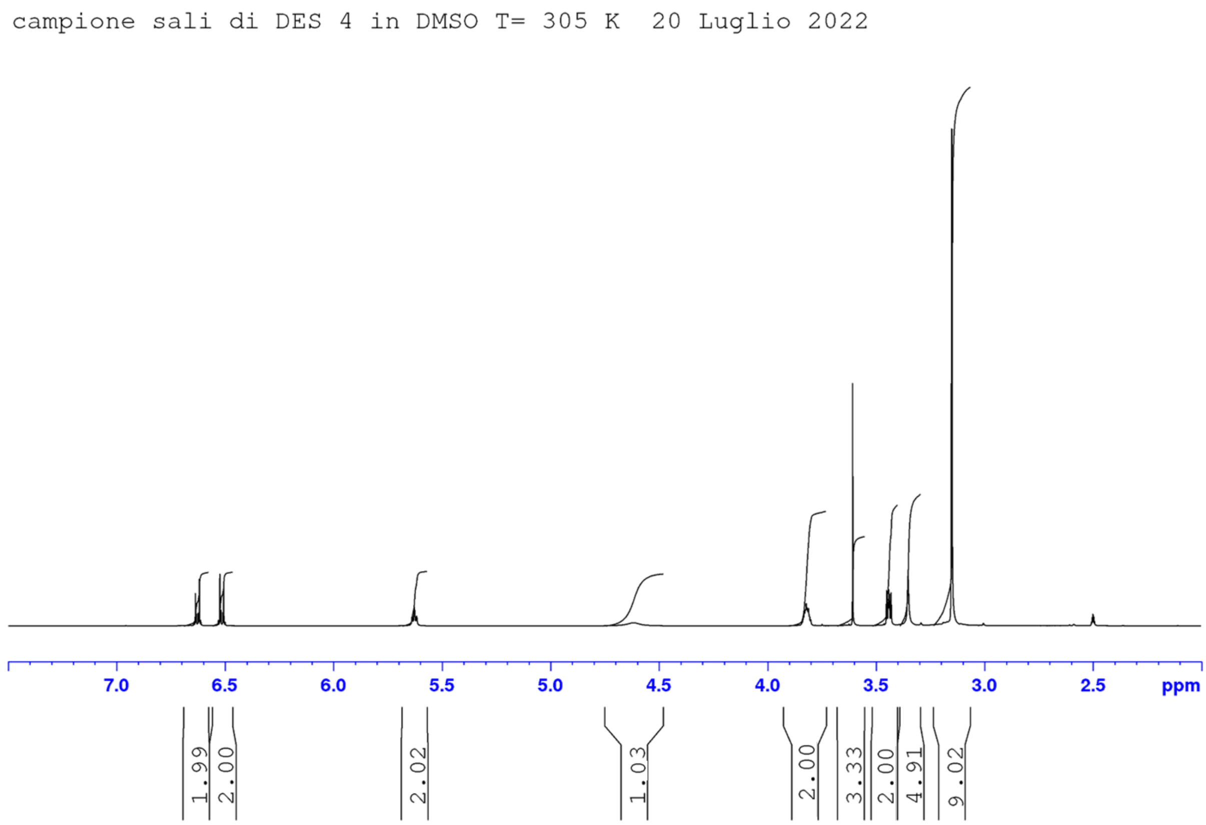


NOESY Tmix= 900 ms



NOESY Tmix= 1.2 s

Figure S26. ^{1}H-NMR – DES_4



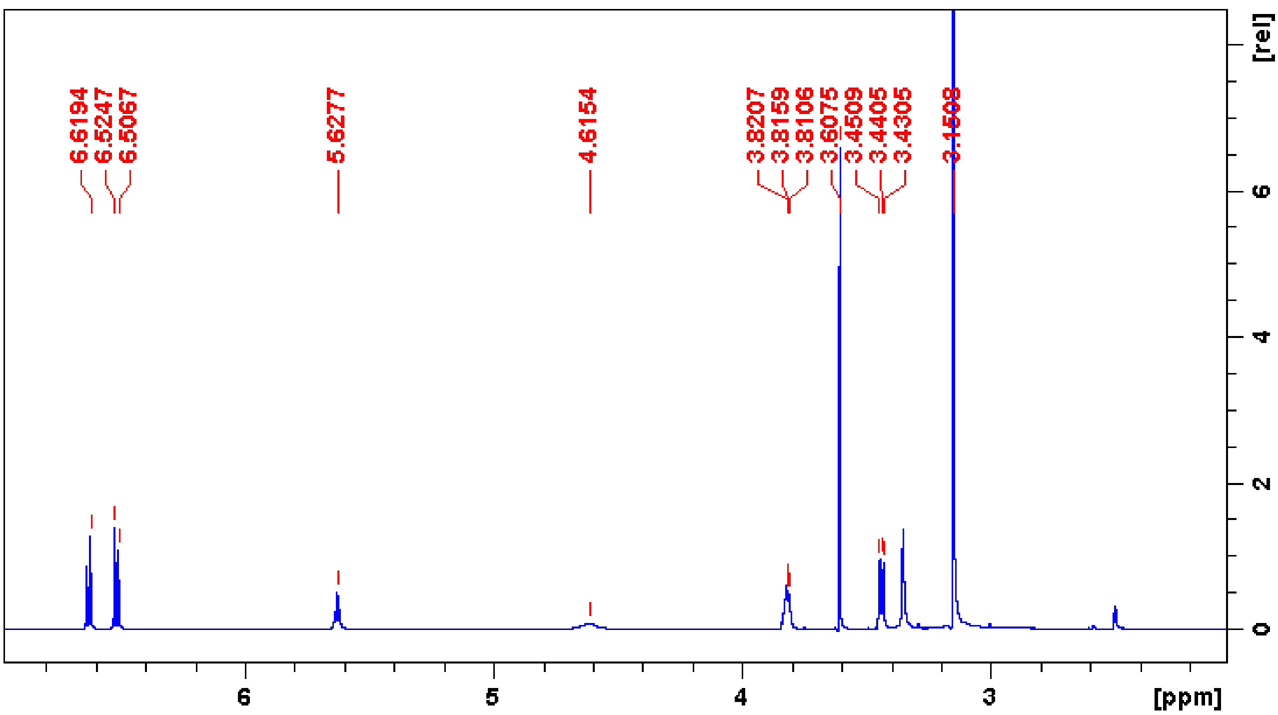


Figure S27. ^{13}C-NMR- DES$_4$

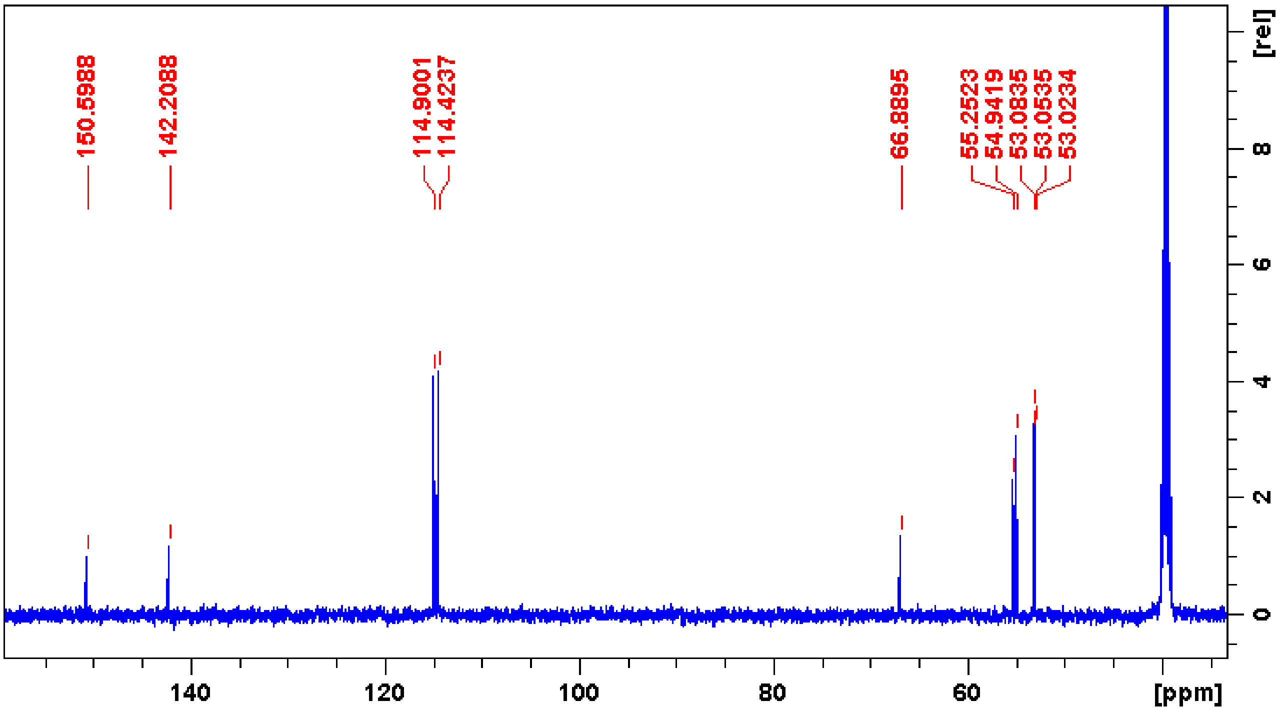
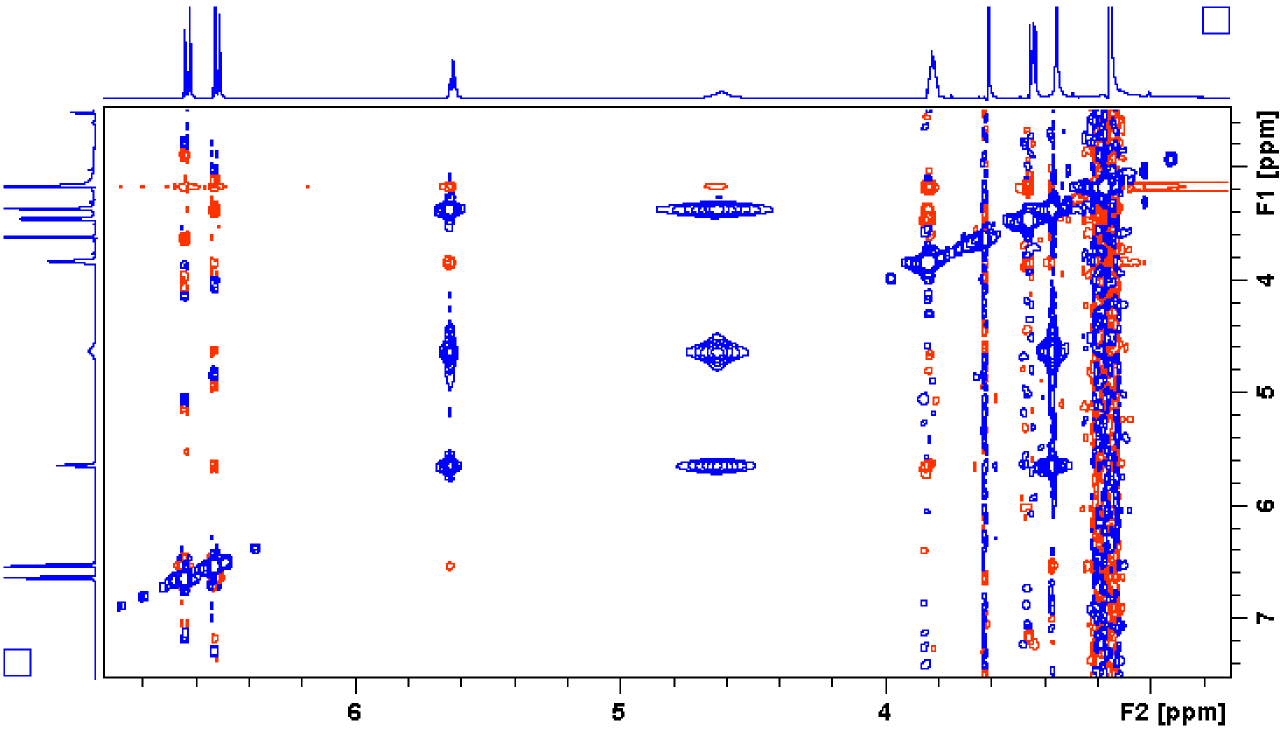
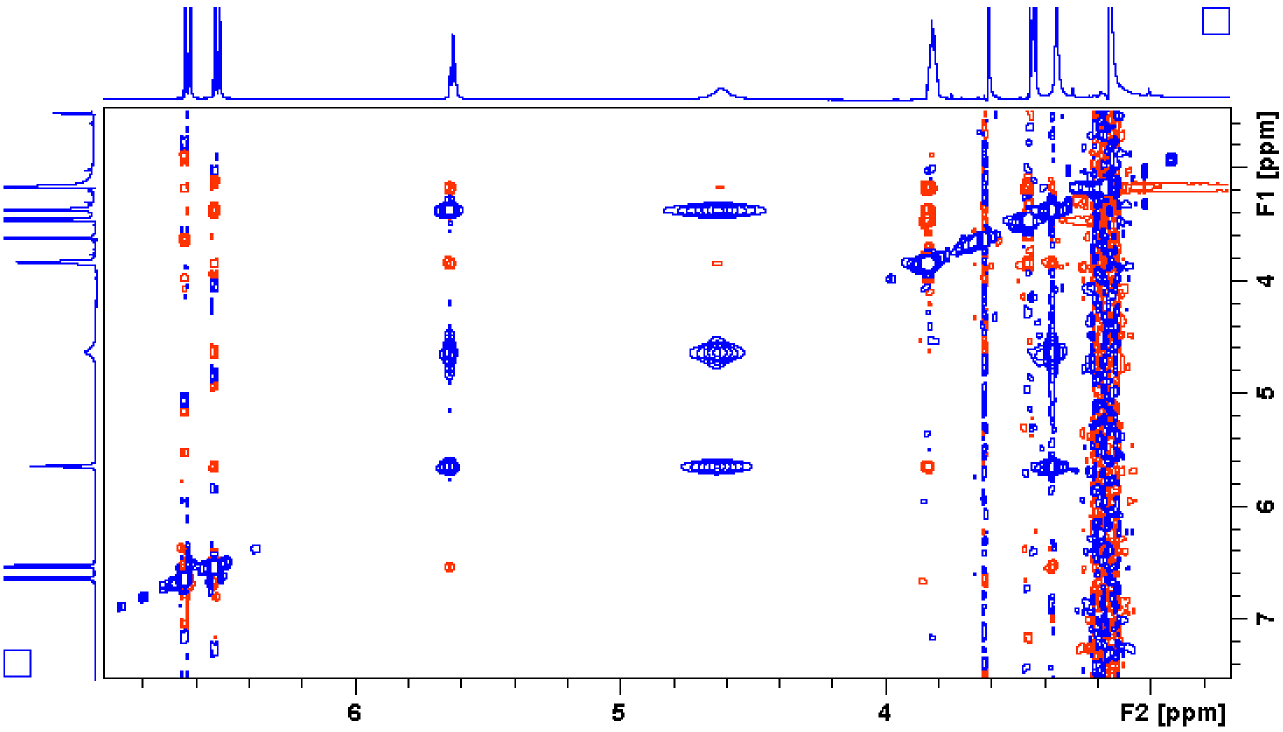


Figure S28. NOESY- DES$_4$

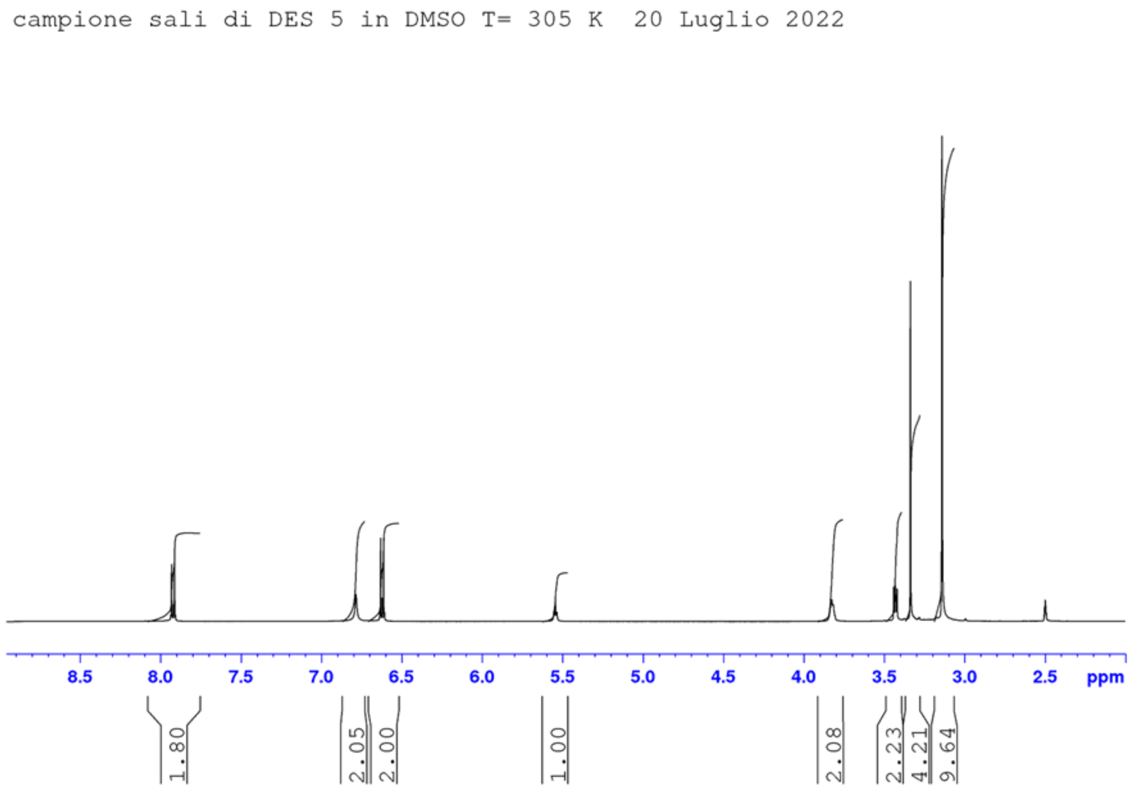


Noesy d8 = 900 ms



Noesy Tmix = 1.2 s

Figure S29. ^{1}H-NMR – DES_5



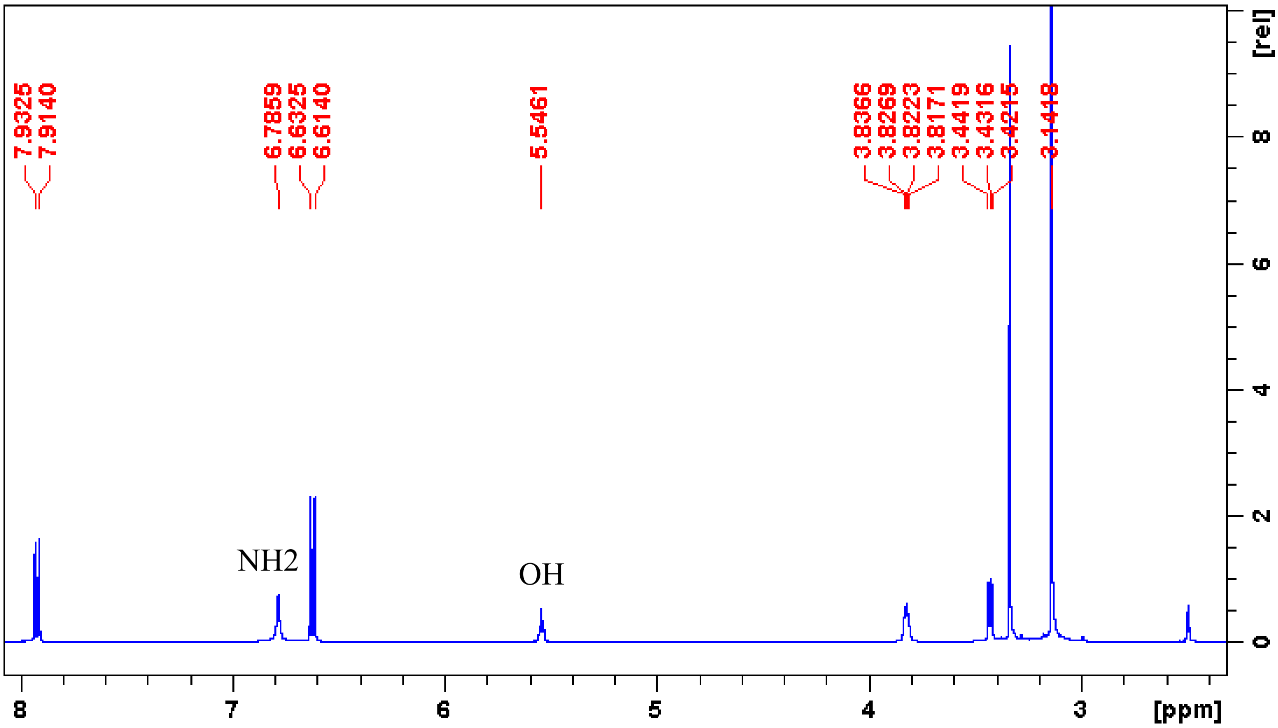


Figure S30. ^{13}C-NMR- DES_5

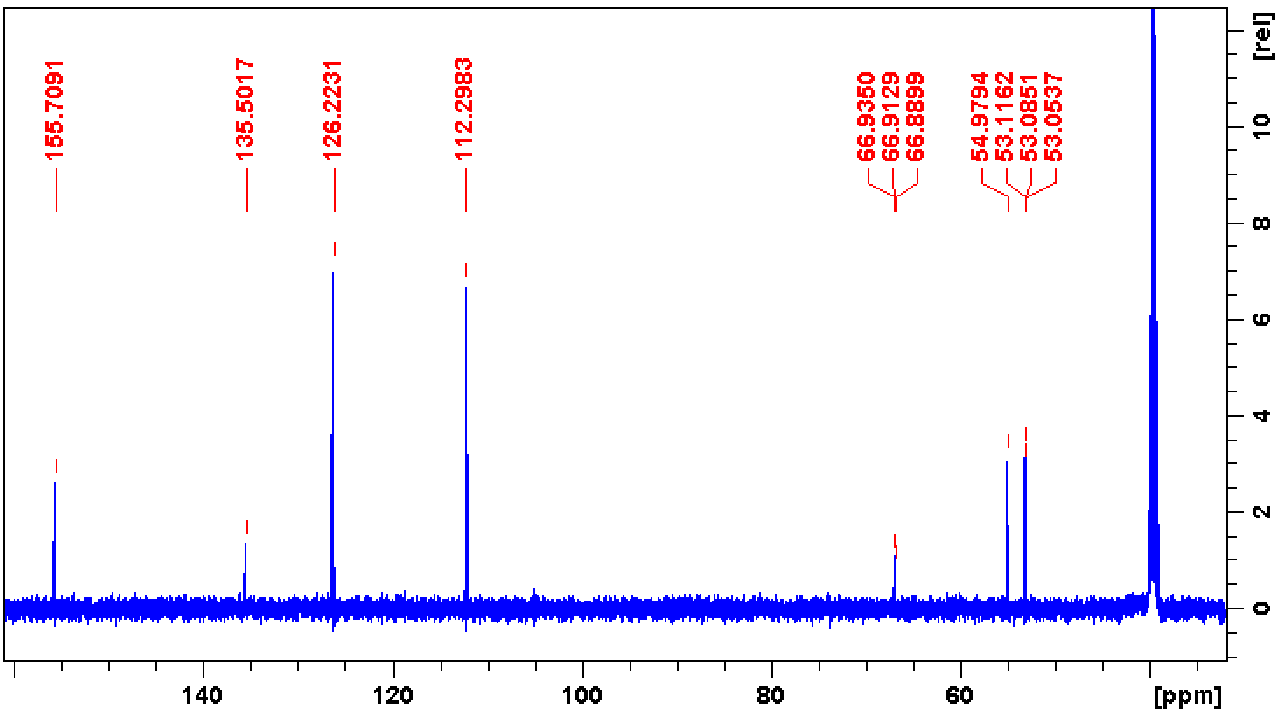
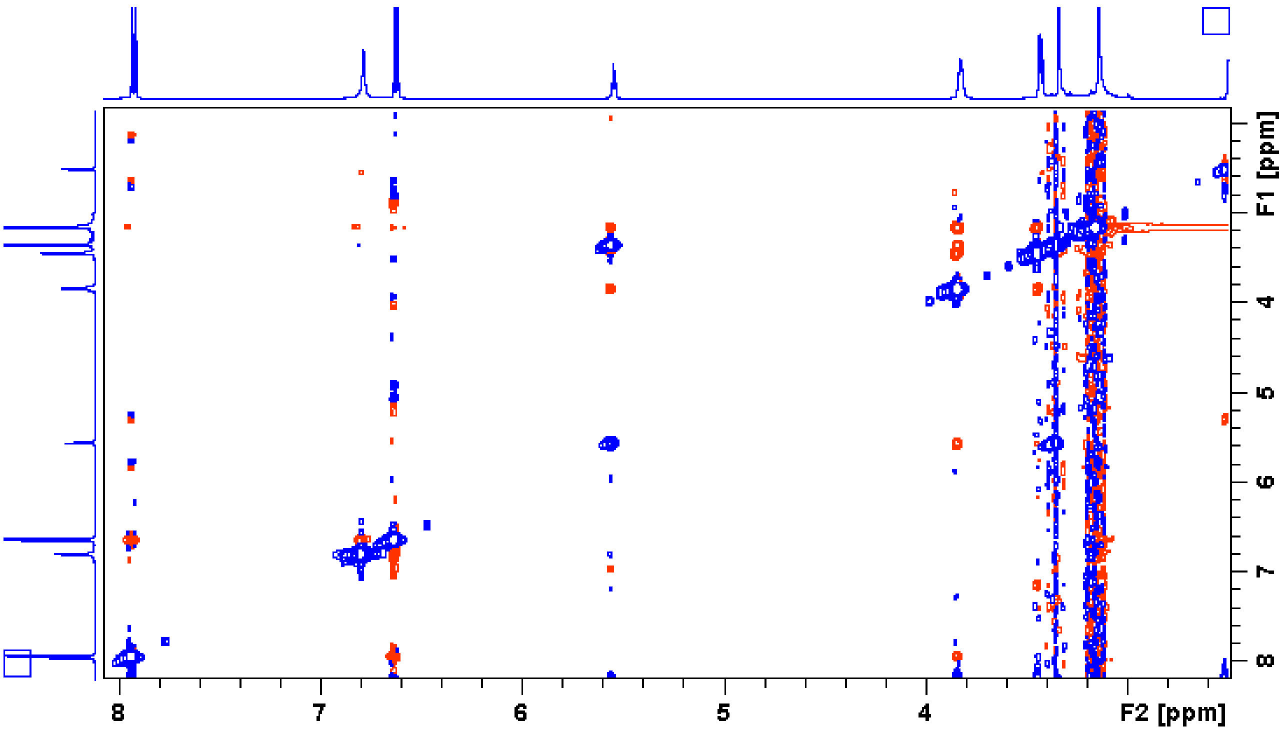
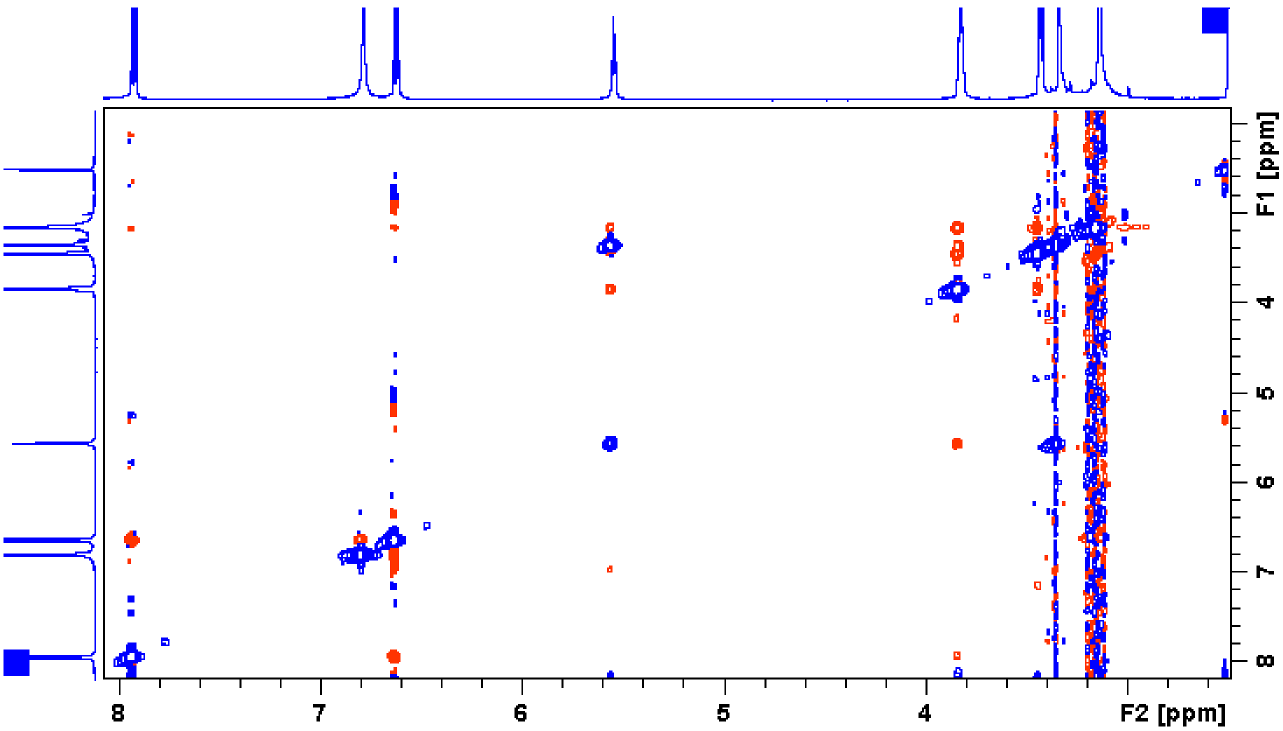


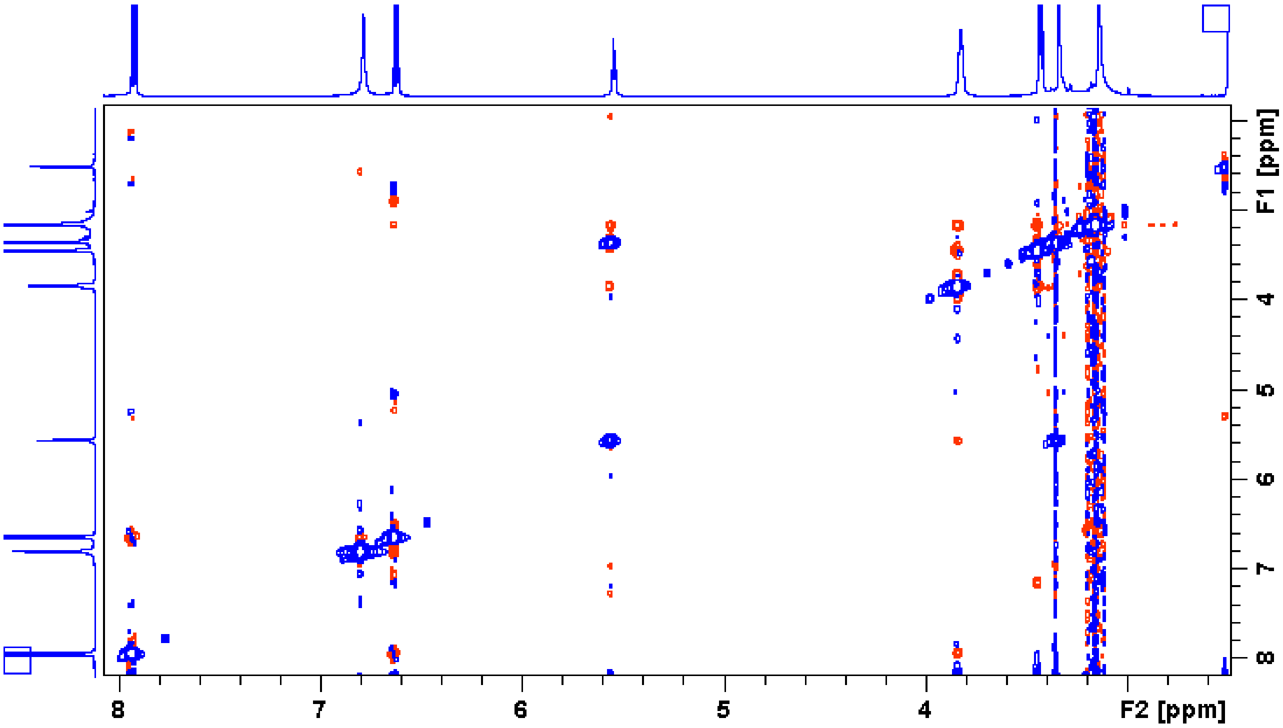
Figure S31. NOESY- DES$_5$



Noesy Tmix = 900 ms



Noesy Tmix = 1.2 s



Noesy Tmix = 400 ms

Figure S32. ^{1}H-NMR – DES_6

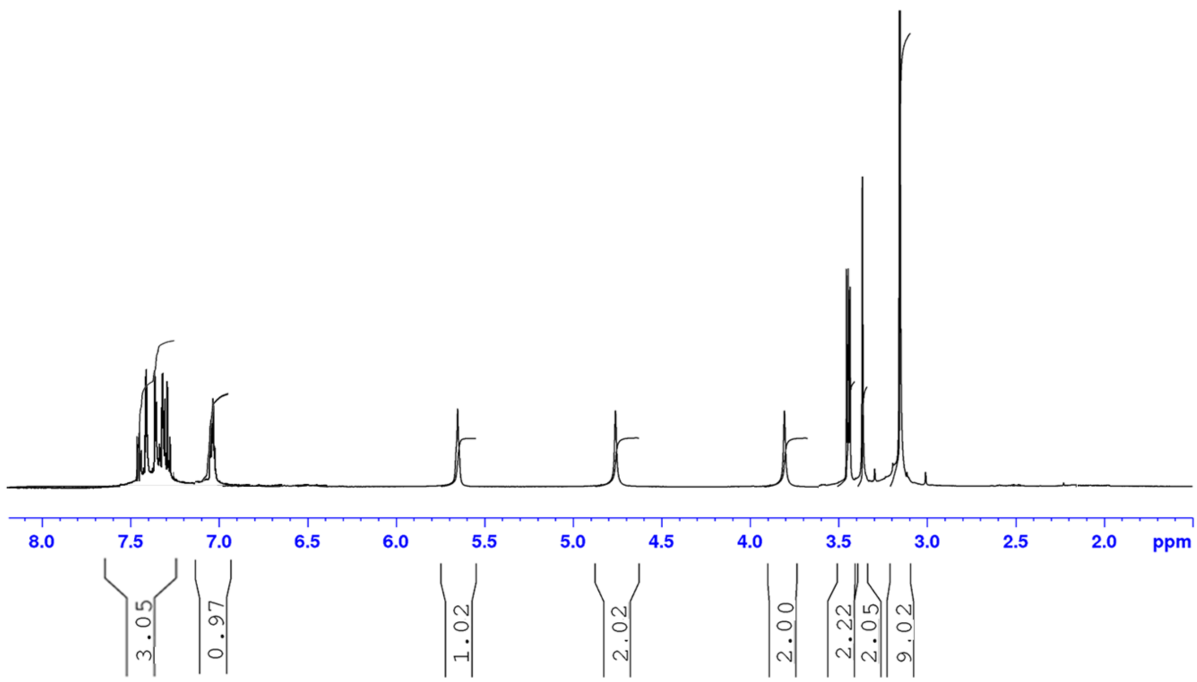


Figure S33. ^{13}C-NMR- DES_6

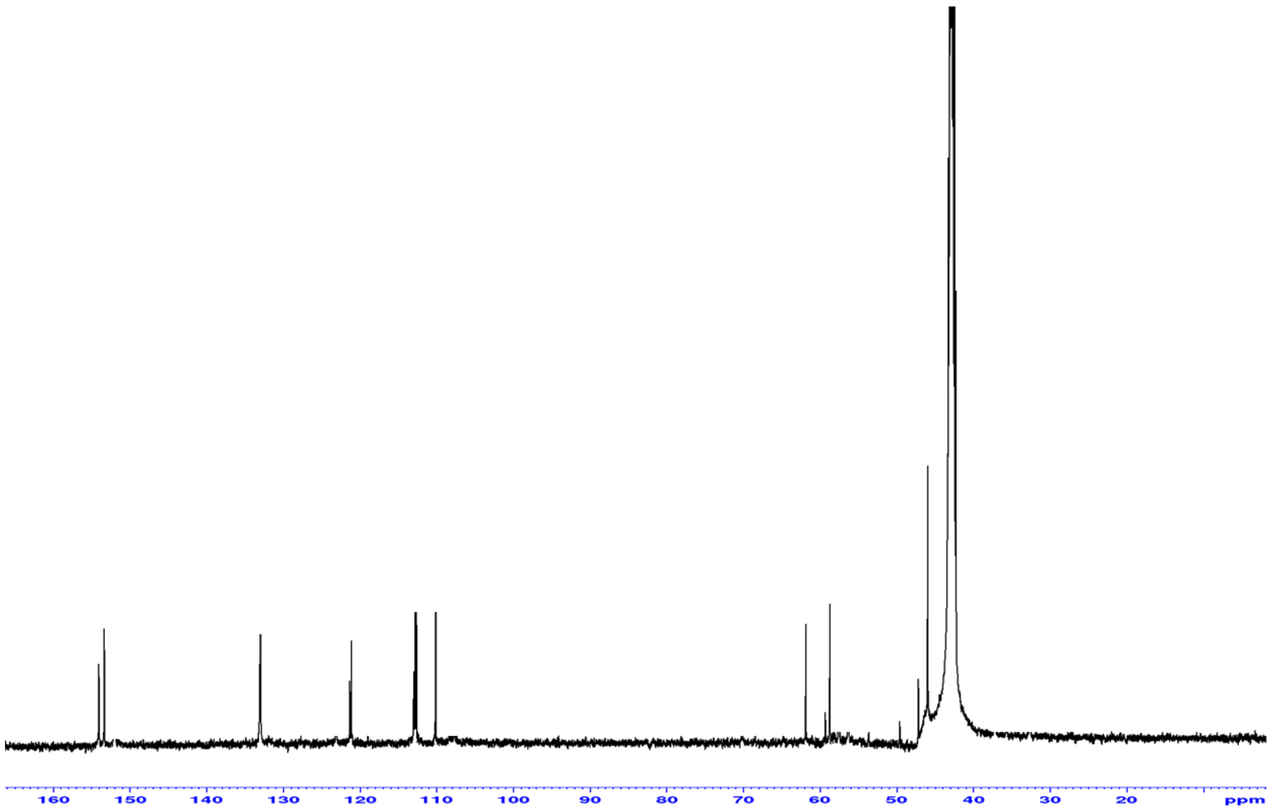
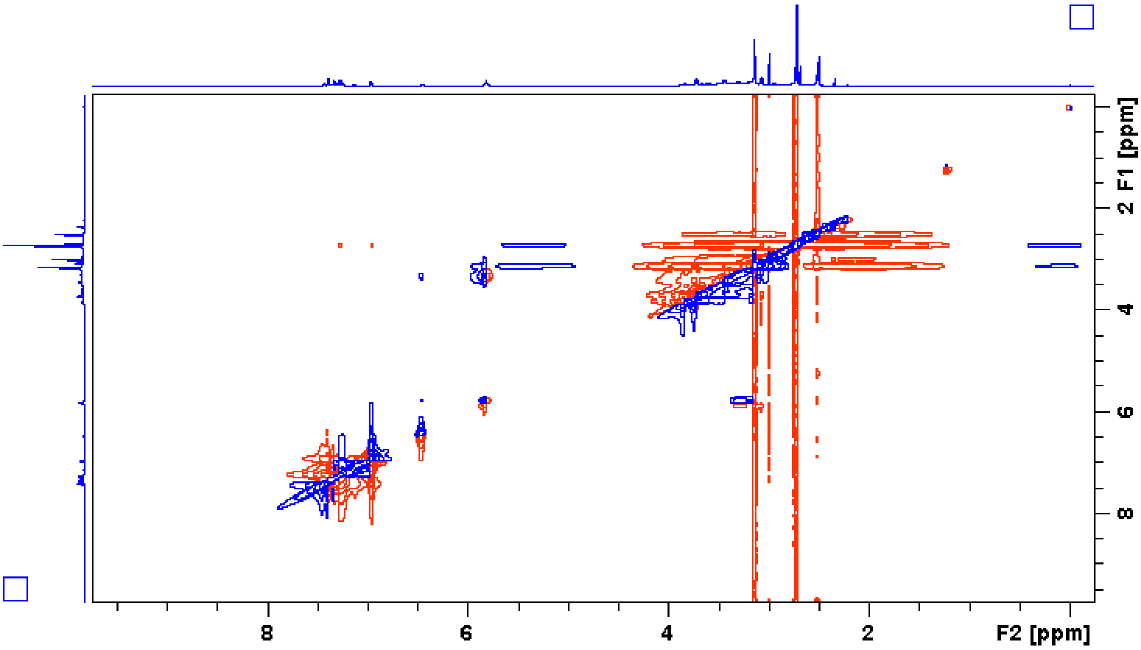


Figure S34. NOESY- DES_6



D8 =900 ms

Figure S35. ^{1}H-NMR – DES_7

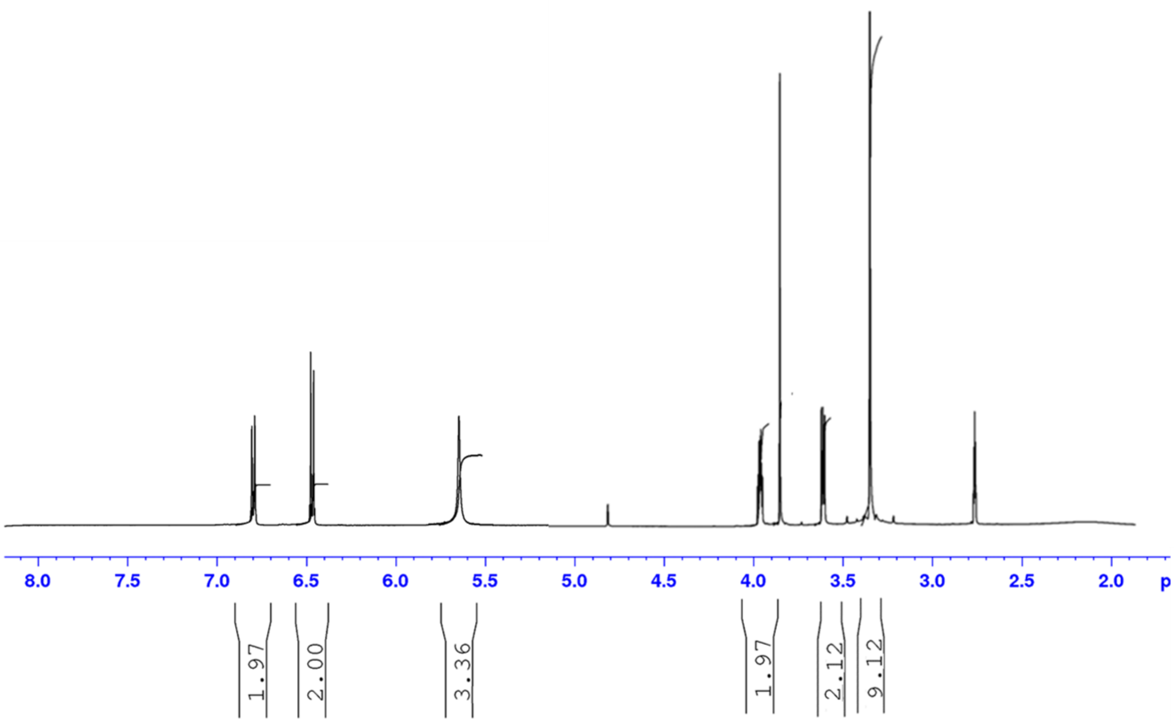


Figure S36. ^{13}C-NMR- DES$_7$

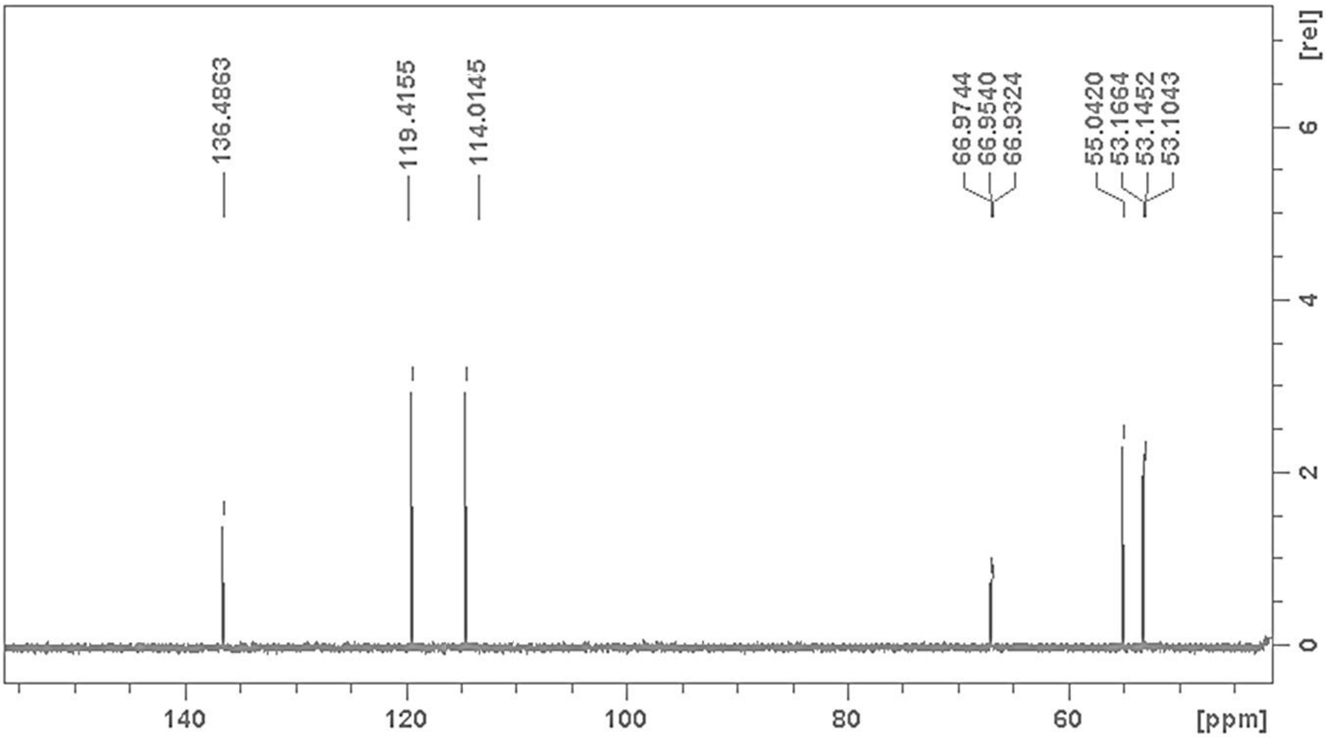
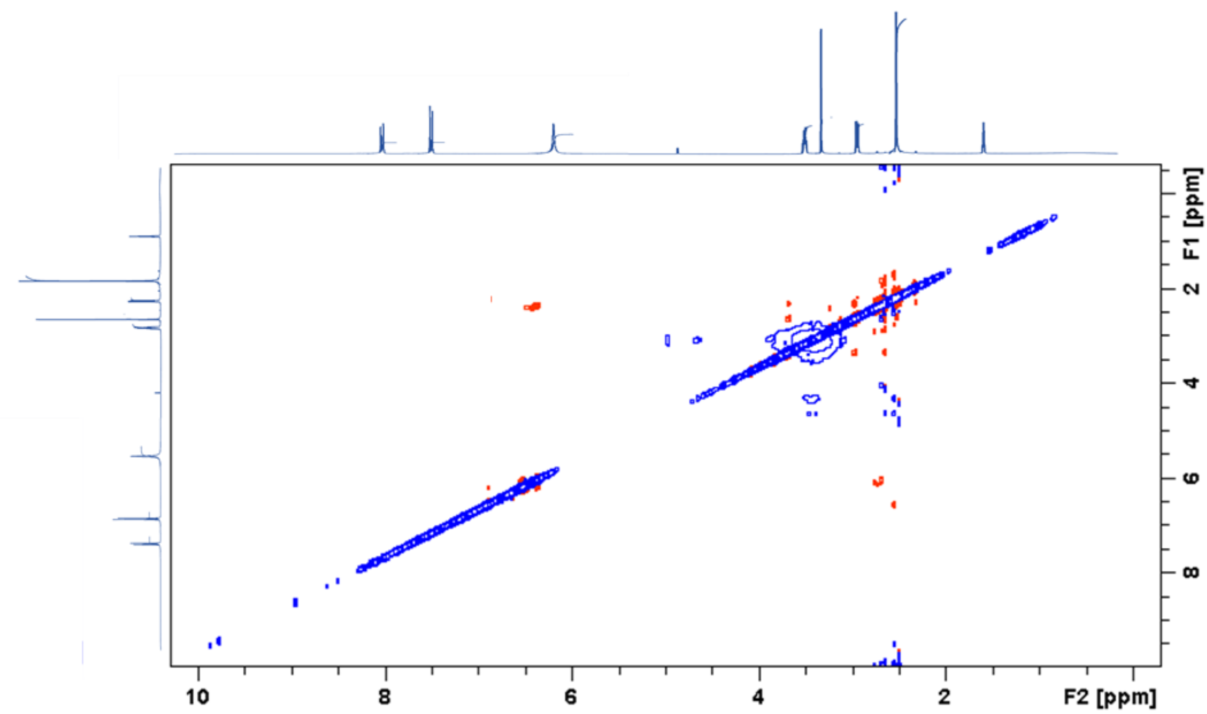
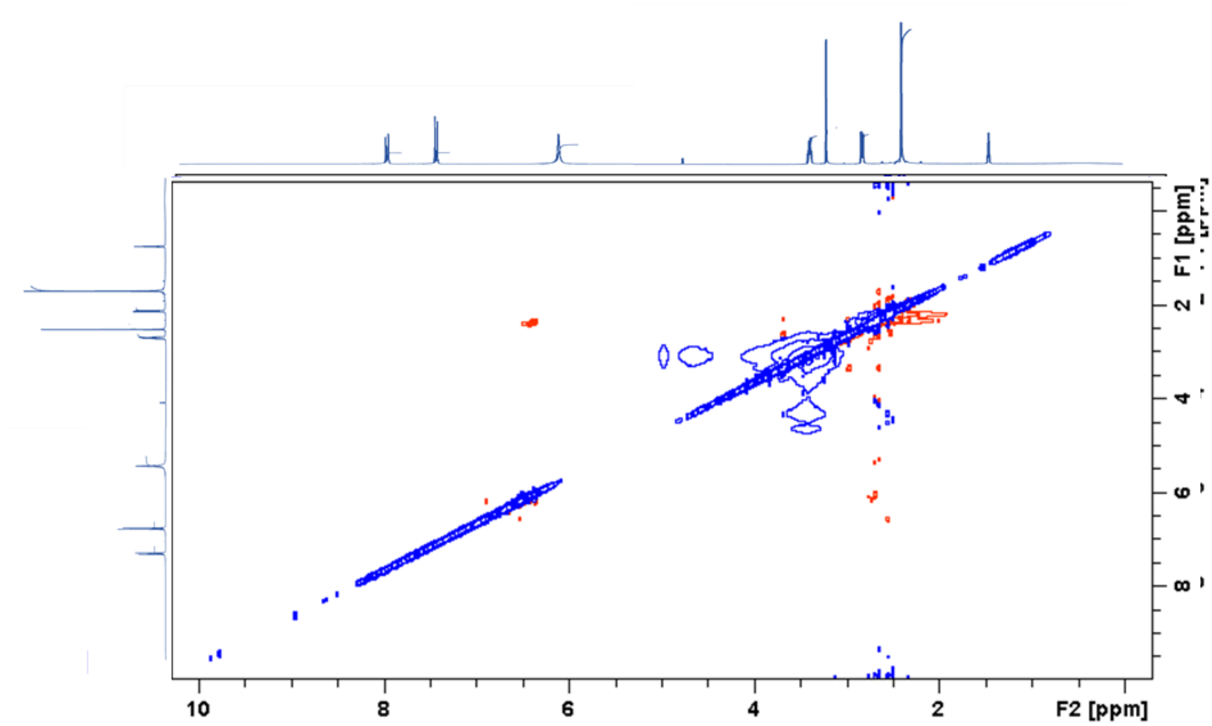


Figure S37. NOESY- DES$_7$

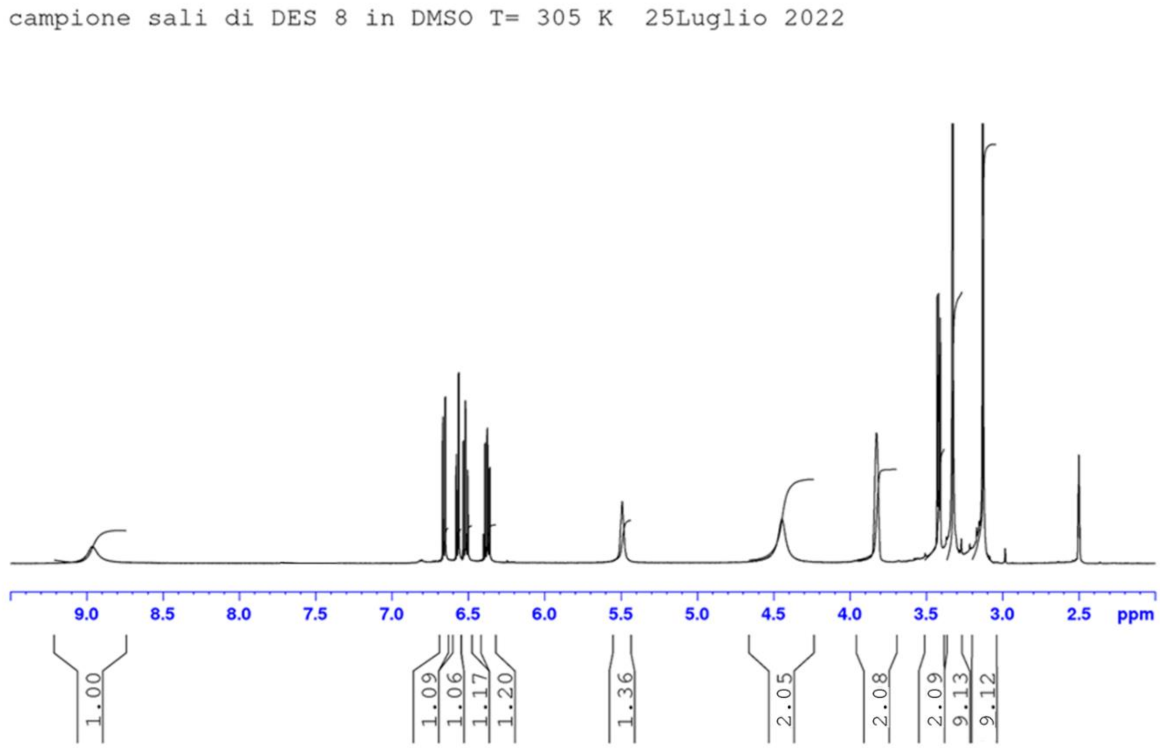


D8 = 900 ms



D8 = 700 ms

Figure S38. ^{1}H-NMR – DES$_8$



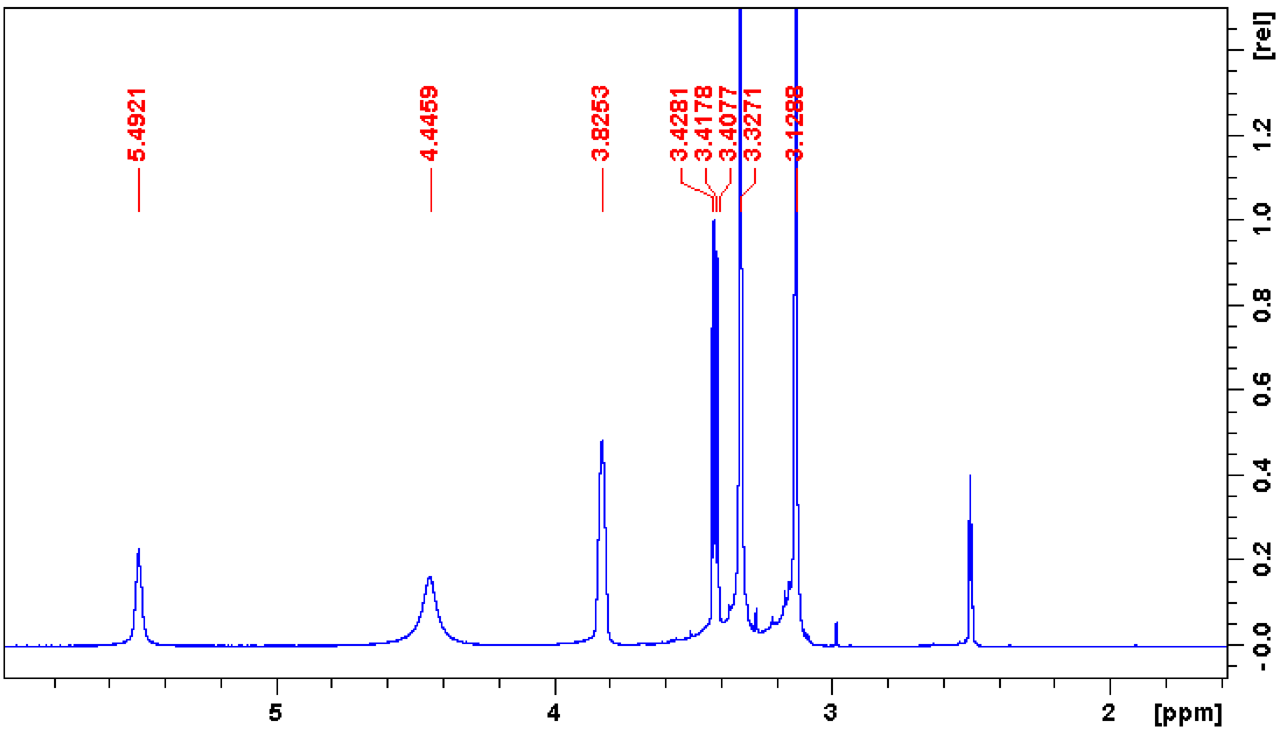


Figure S39. ^{13}C-NMR- DES_8

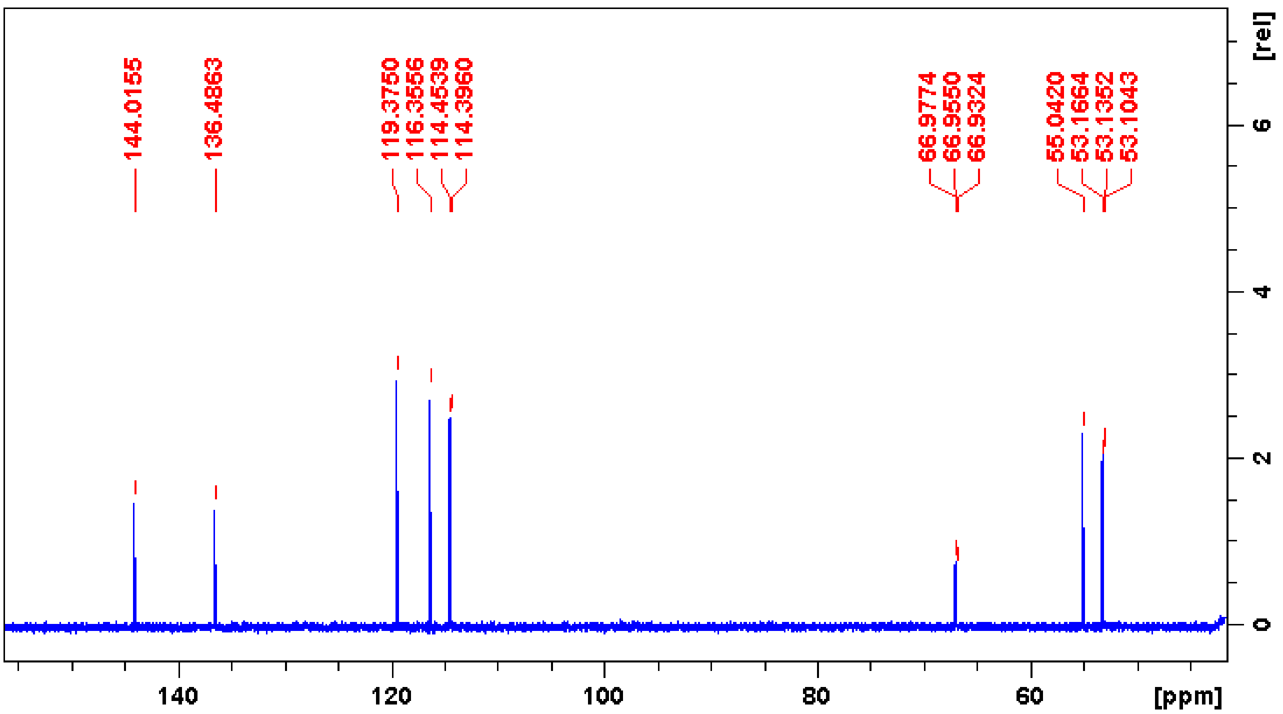
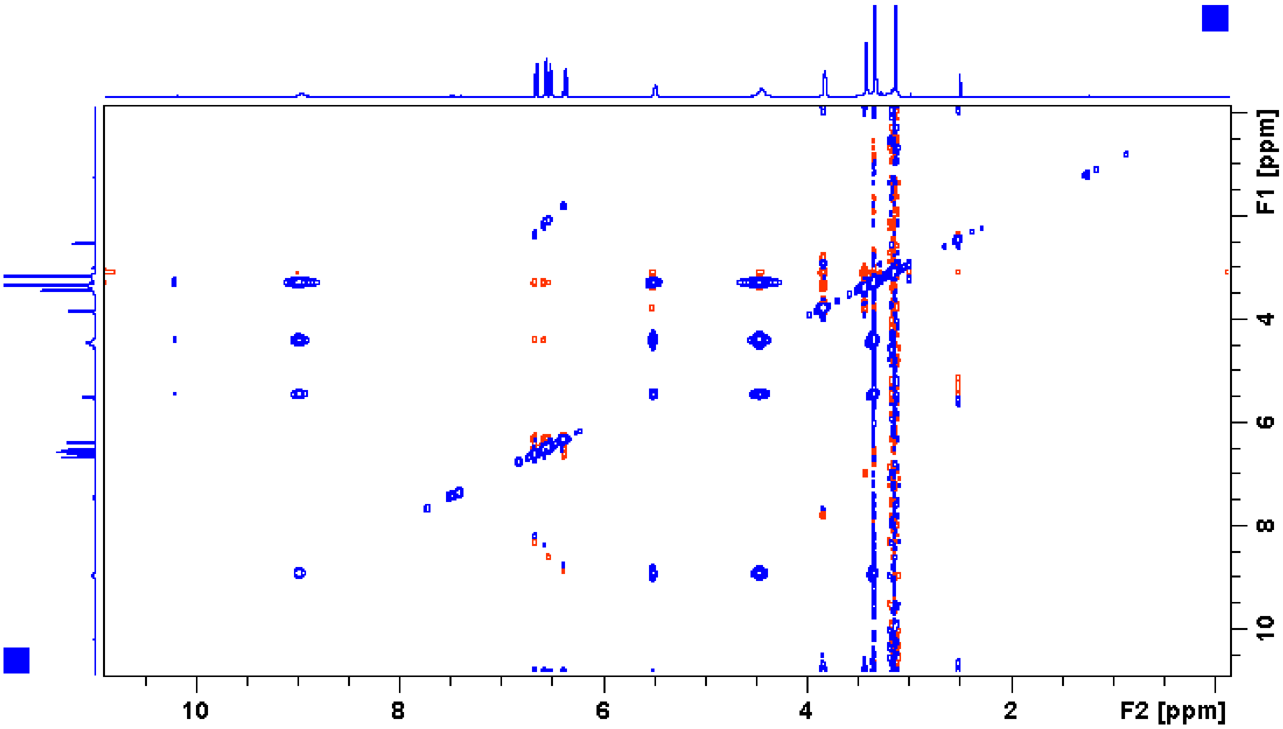
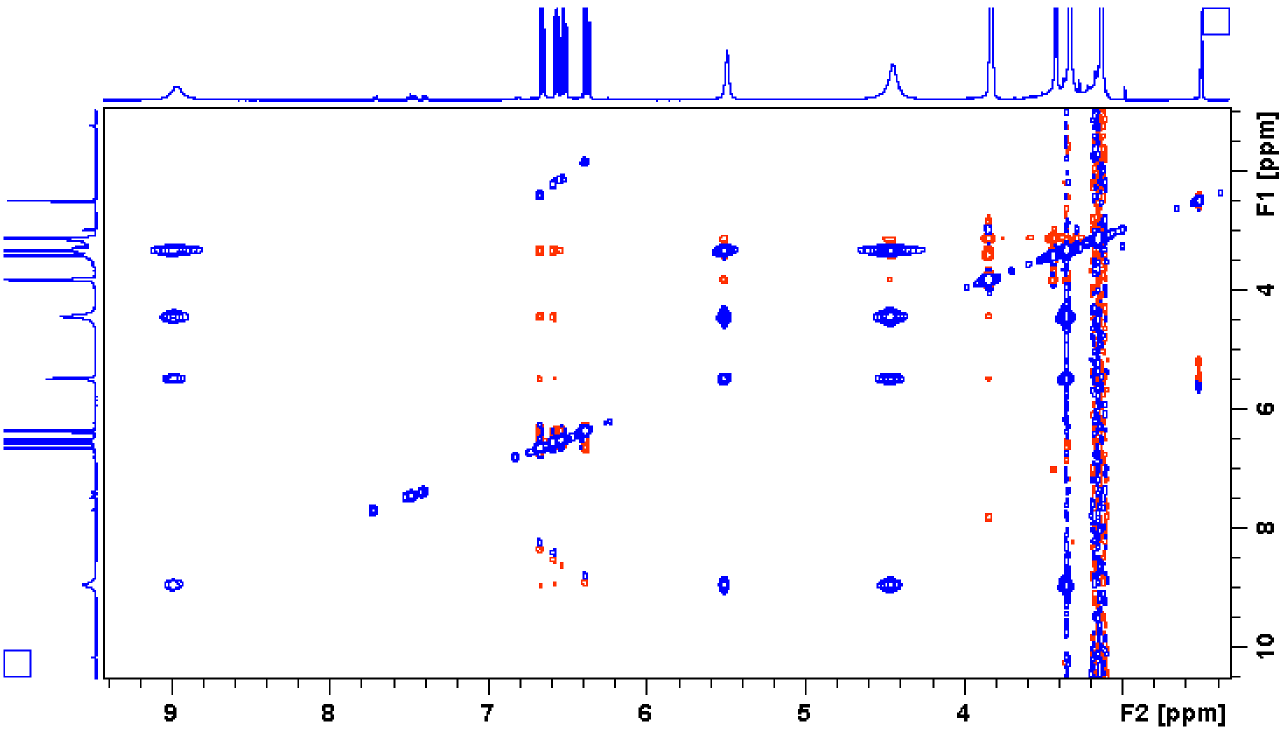


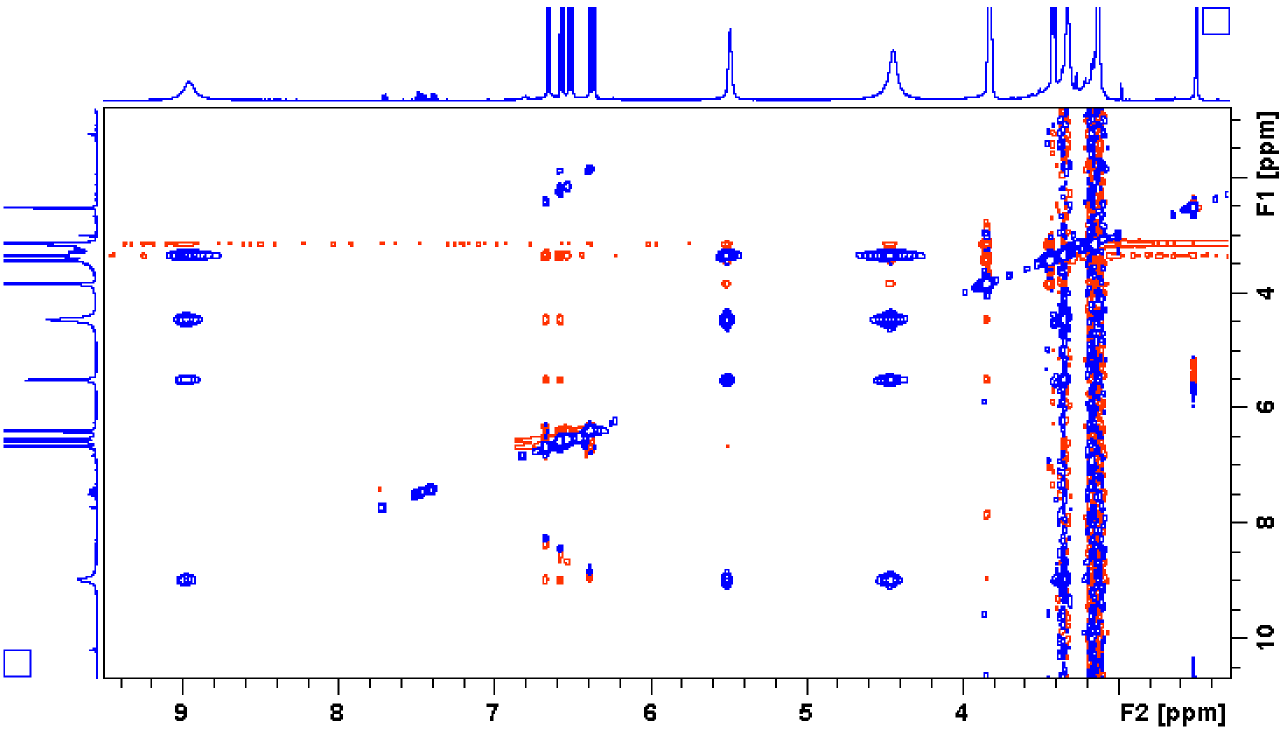
Figure S40. NOESY- DES_8



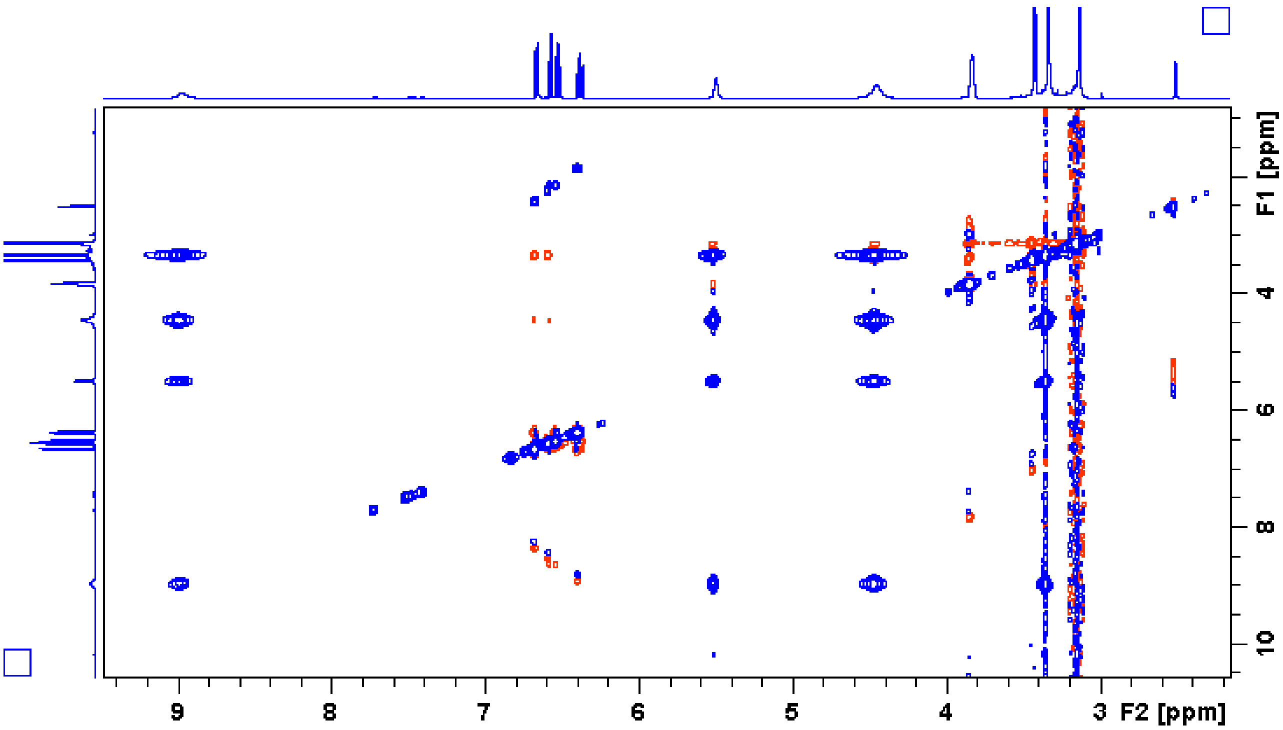
Noesy Tmix = 900 ms



Noesy Tmix = 1.2 s

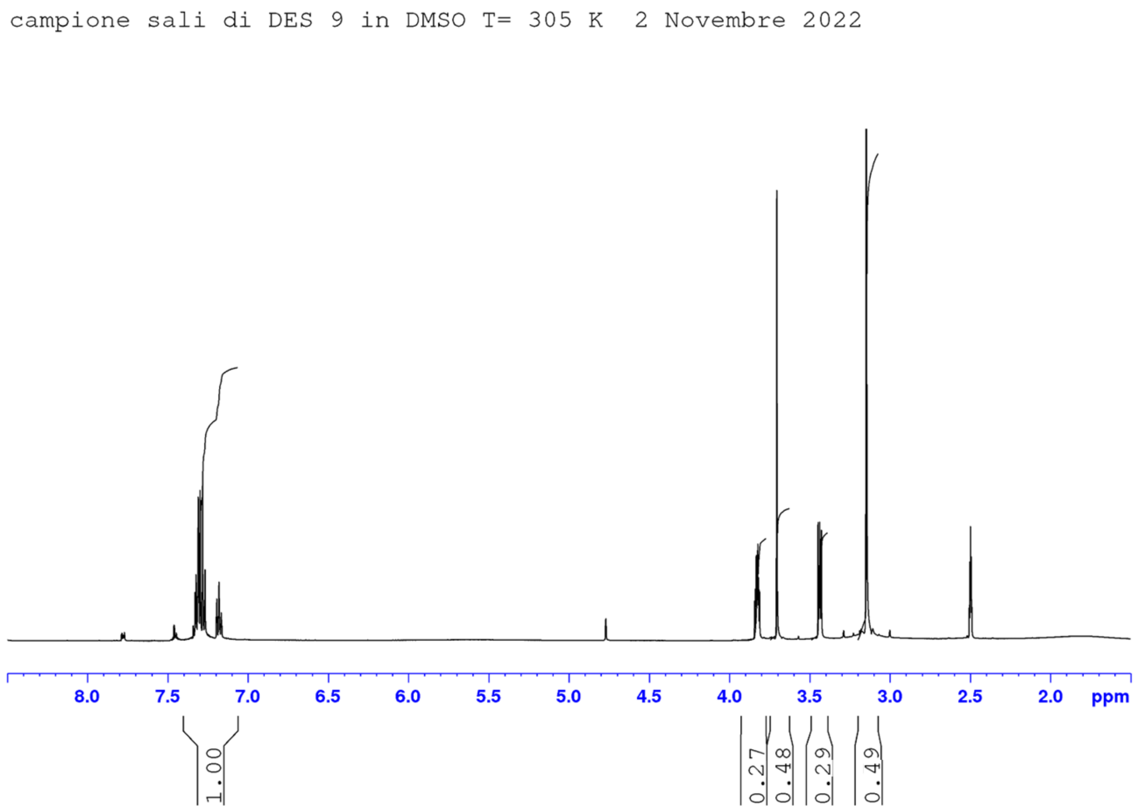


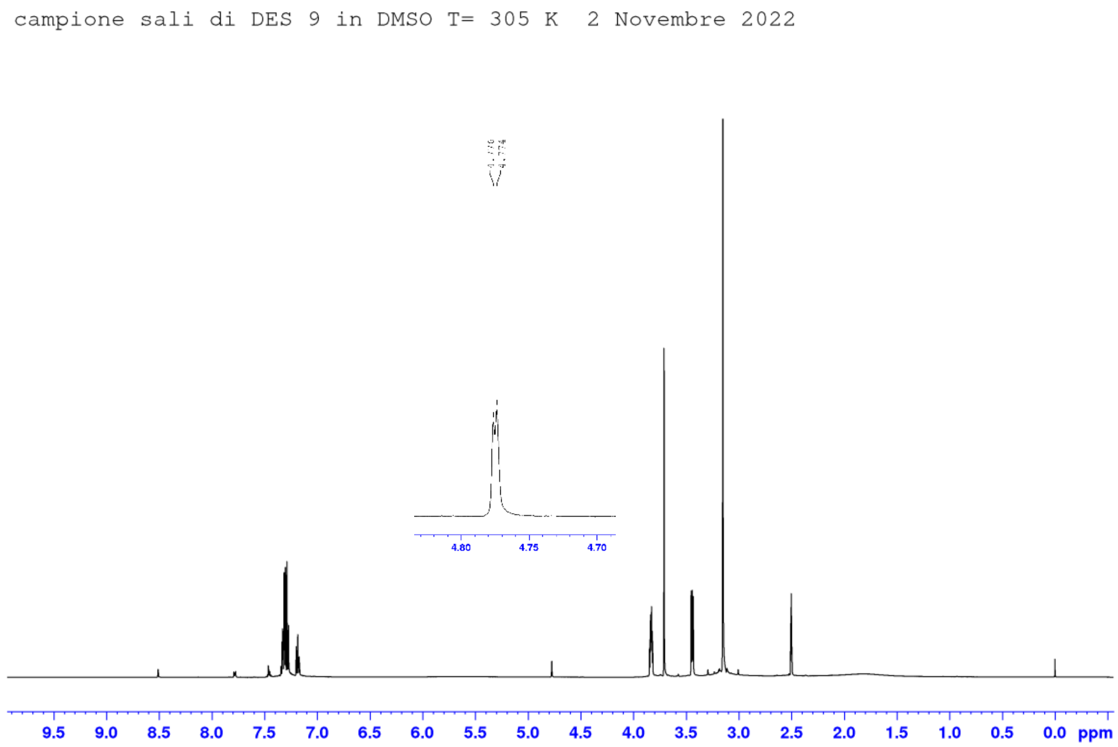
Noesy Tmix = 1.5 s



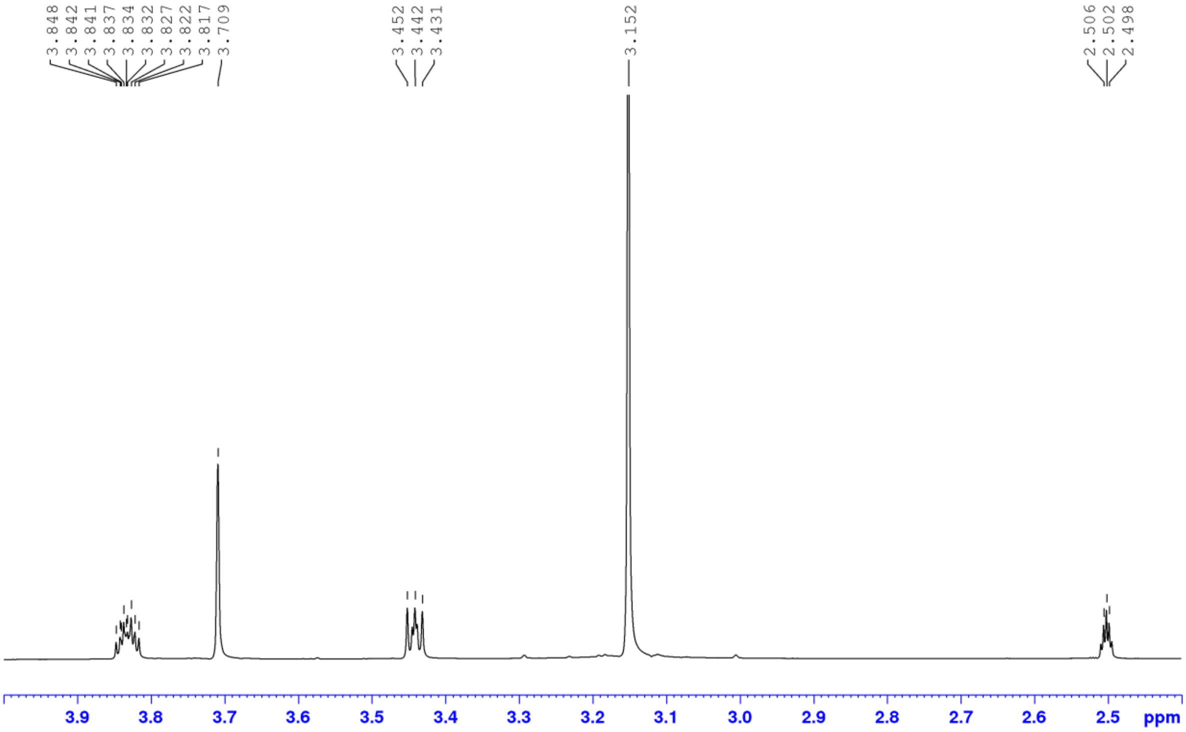
Noesy Tmix= 500 ms

Figure S41. ^{1}H-NMR – DES$_9$





campione sali di DES 9 in DMSO T= 305 K 2 Novembre 2022



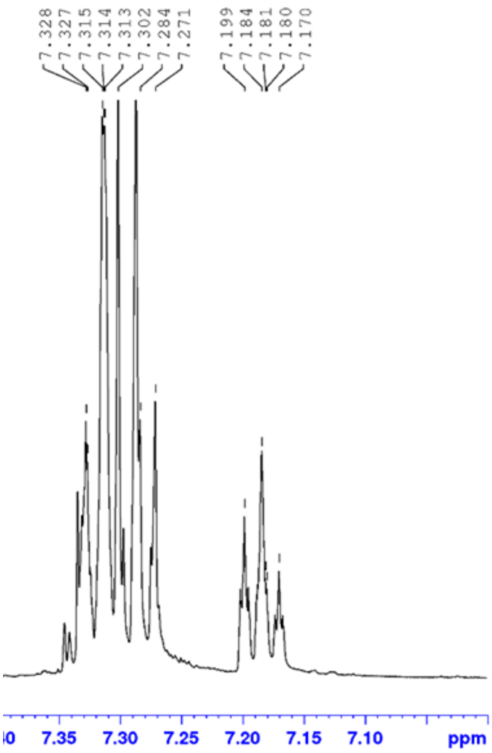


Figure S42. ^{13}C-NMR- DES$_9$

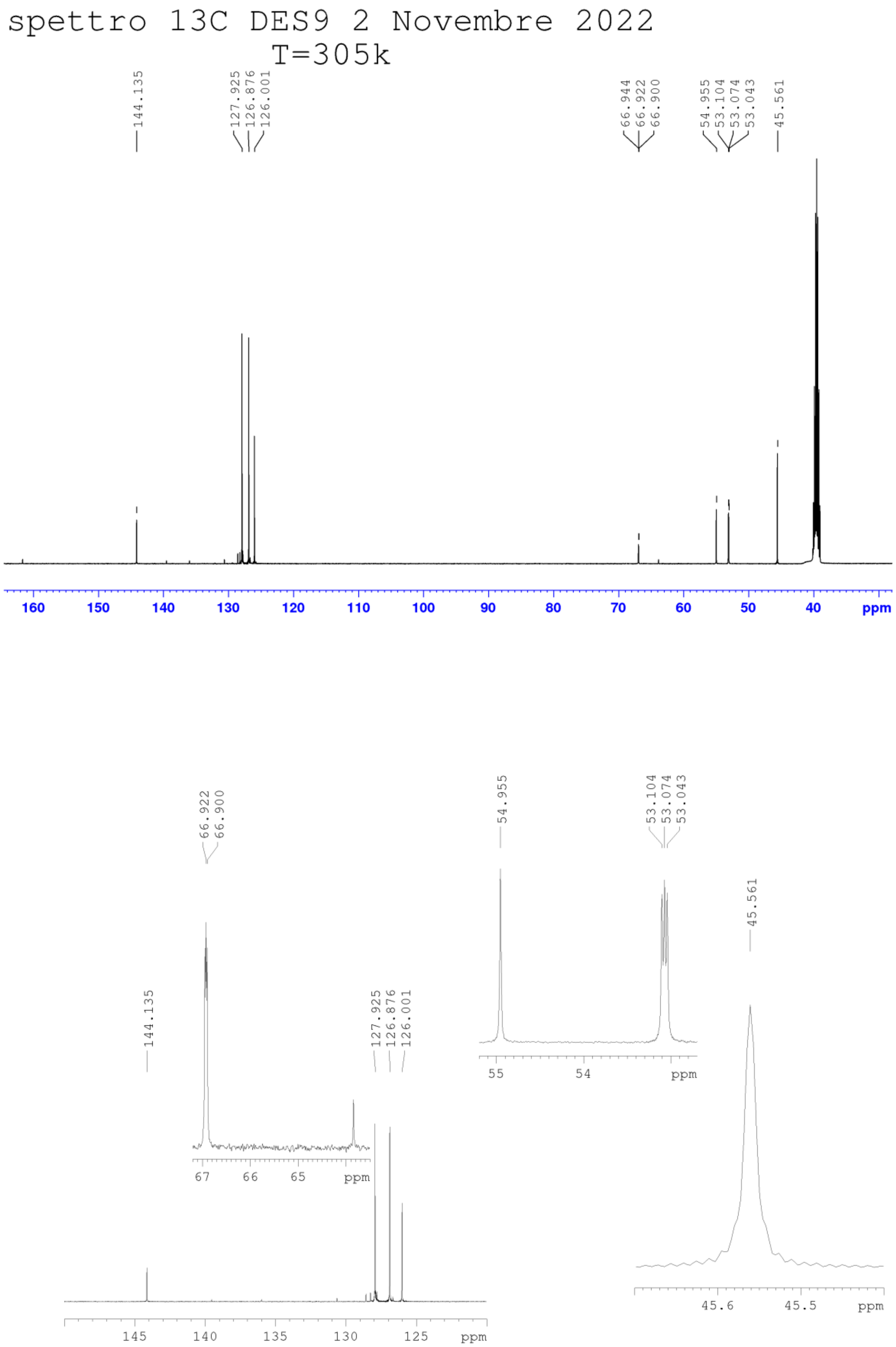
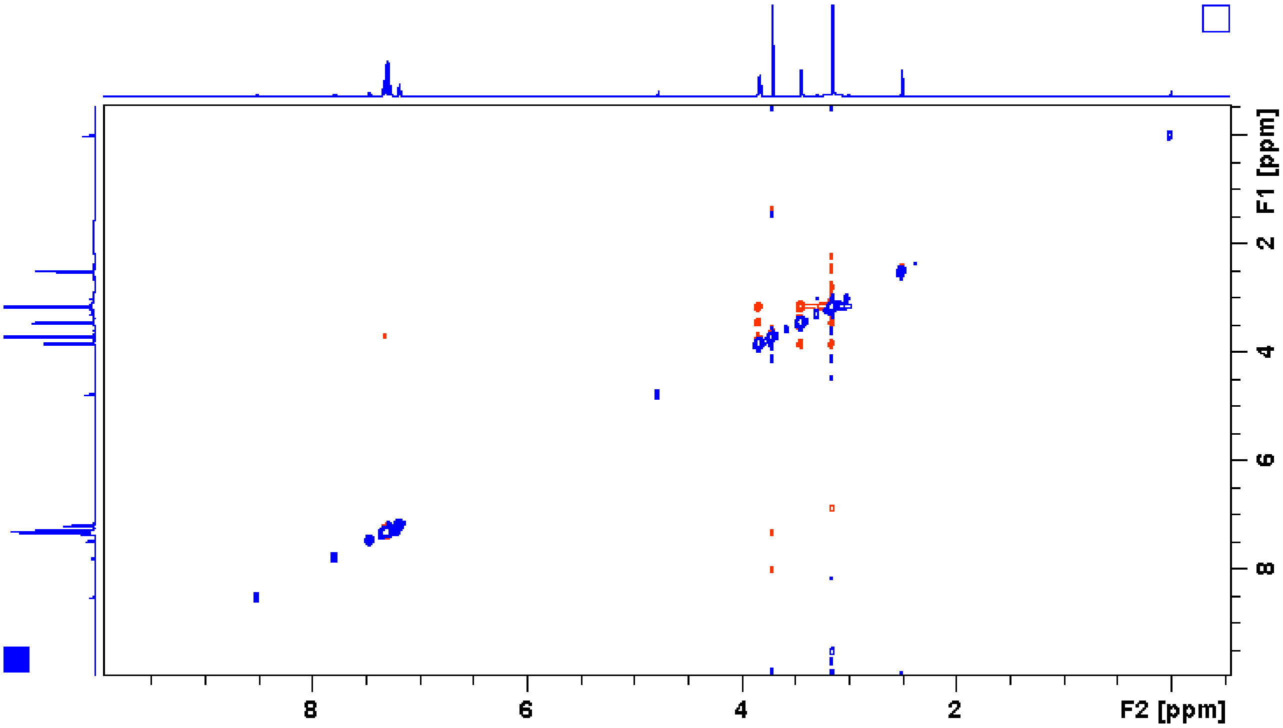
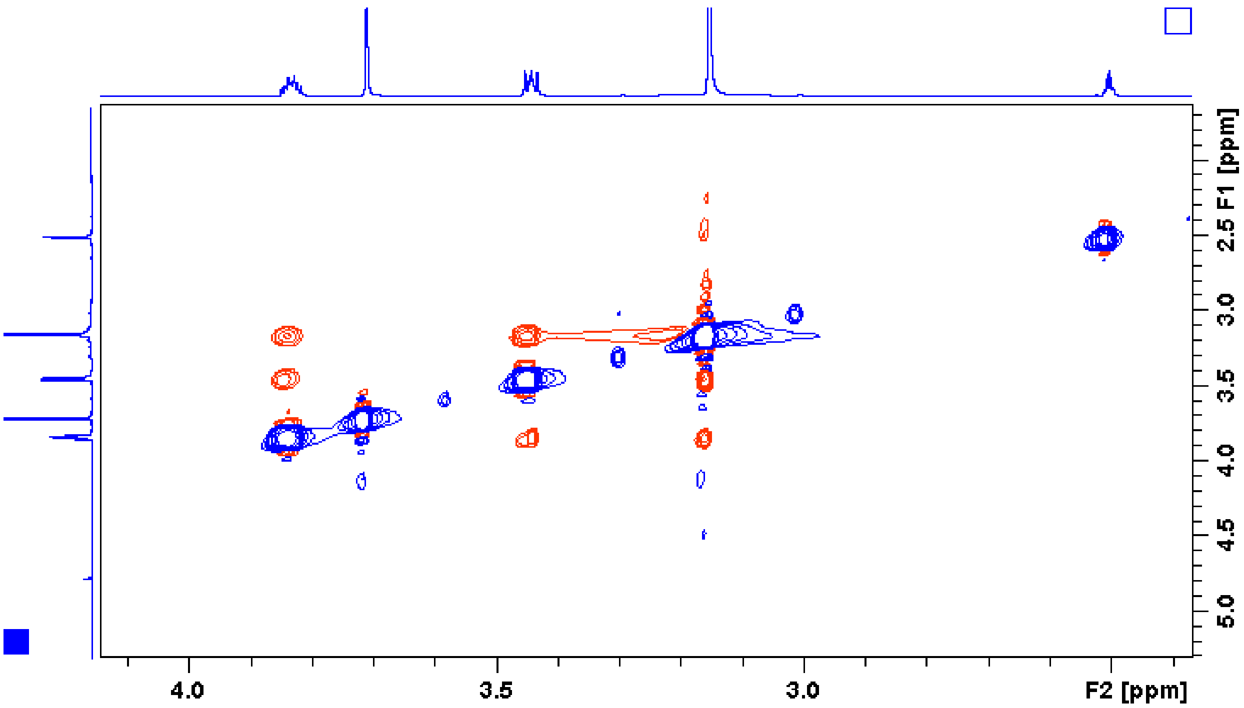
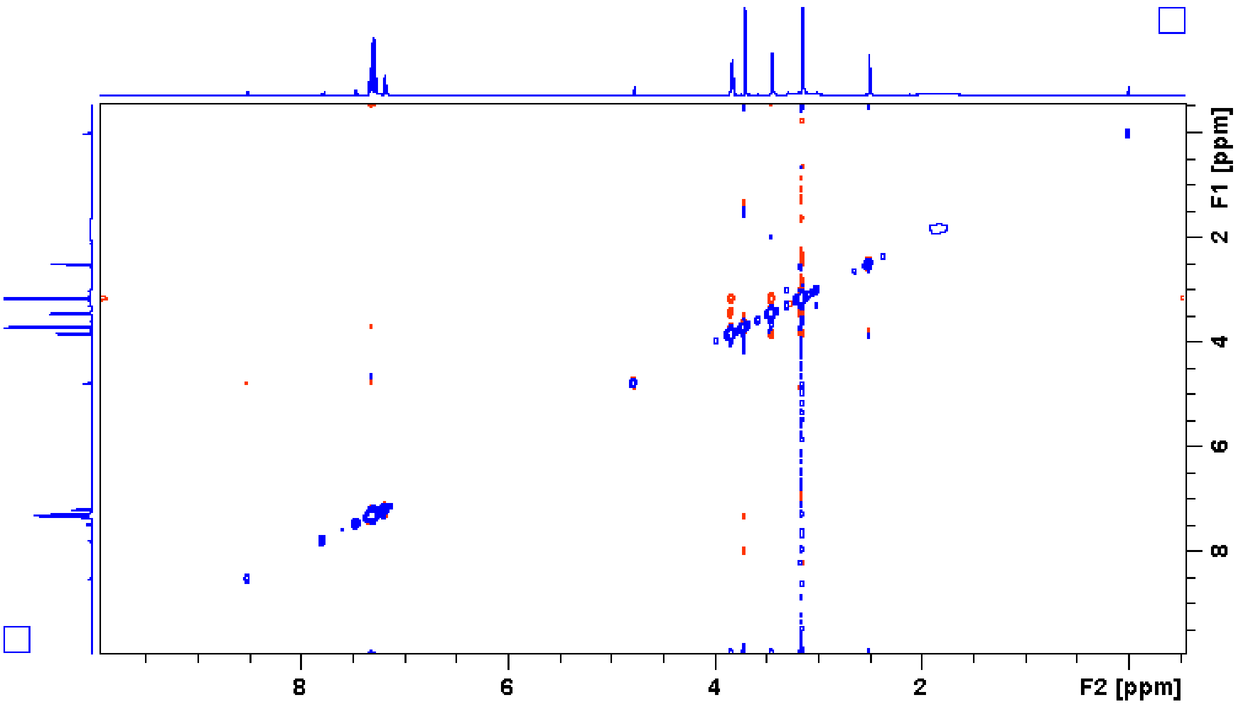


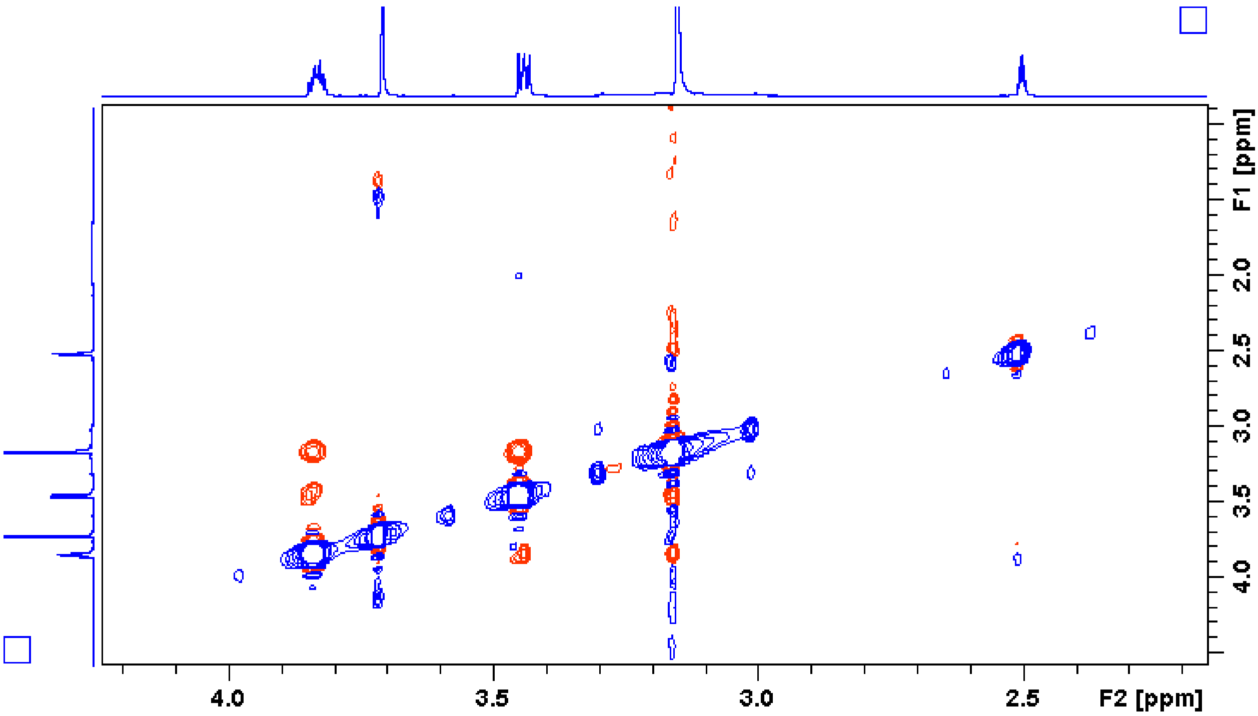
Figure S43. NOESY- DES_9



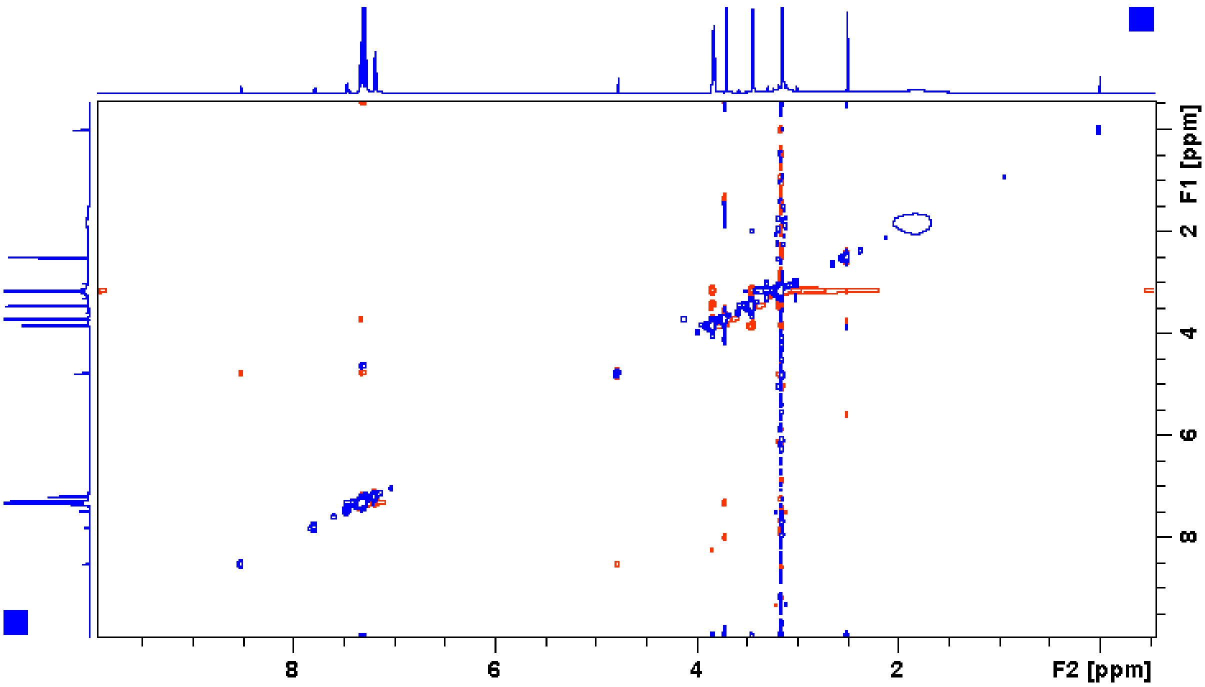


D8 = 900 ms





D= 500 ms



D8 = 700 ms

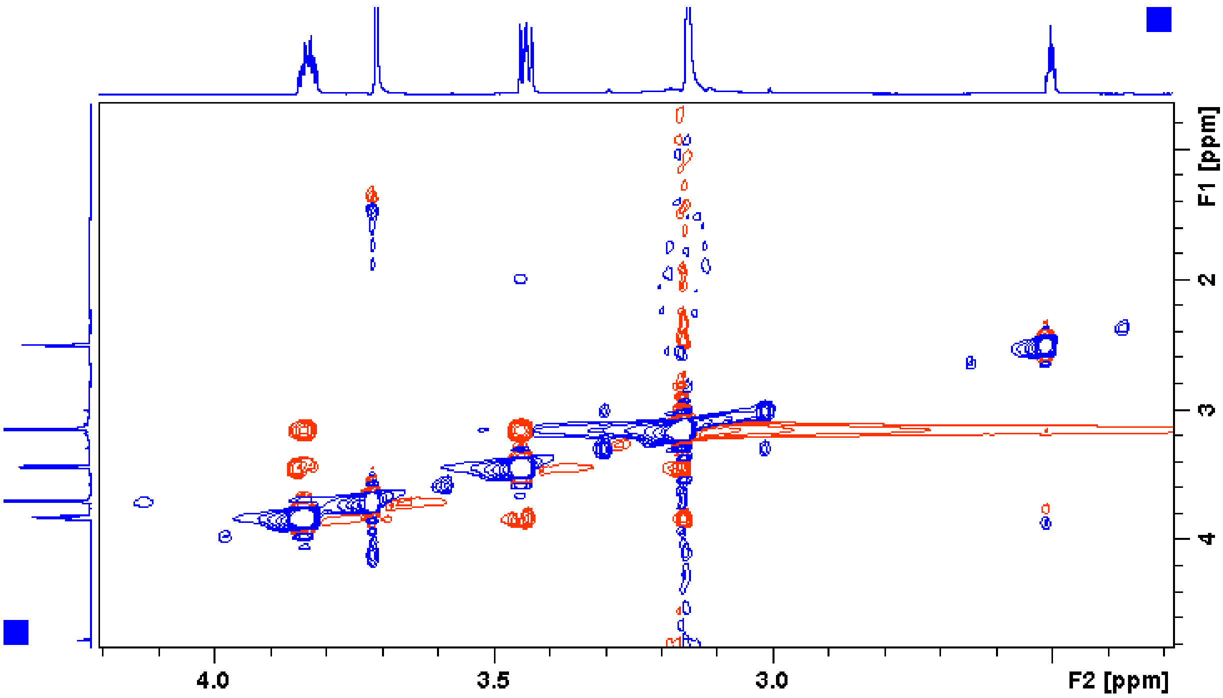


Figure S44. ^{1}H-NMR – DES$_{10}$

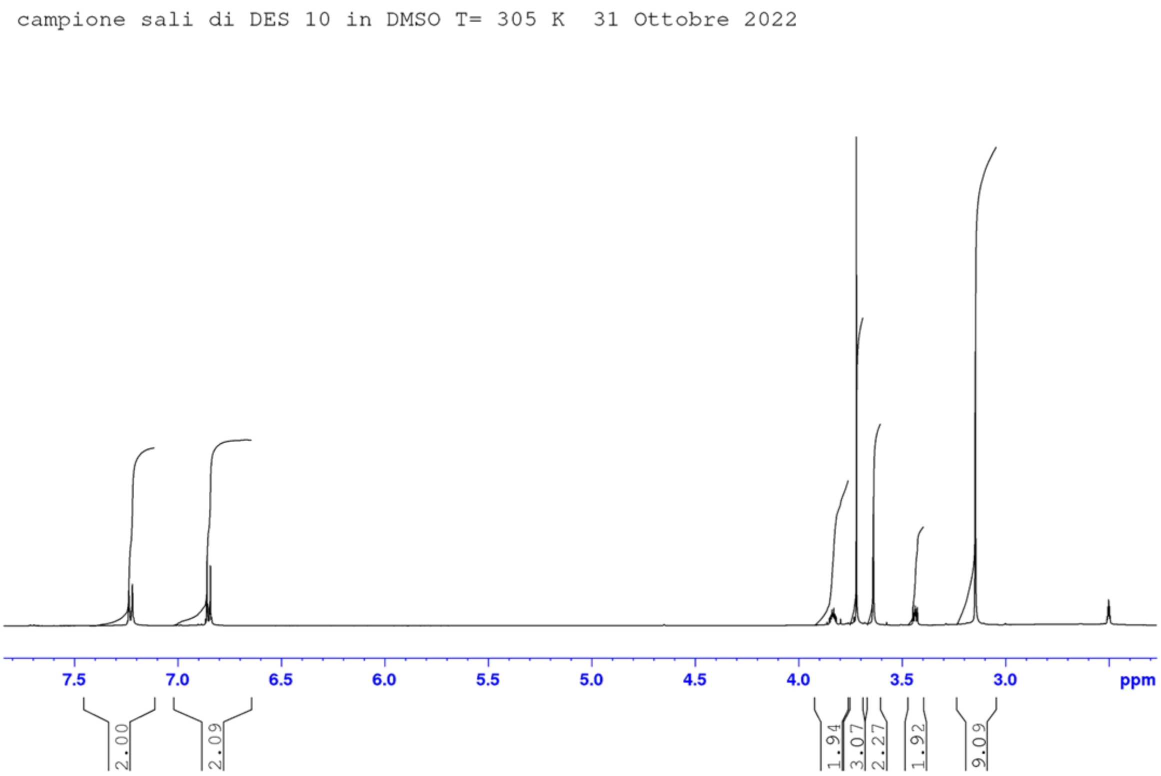
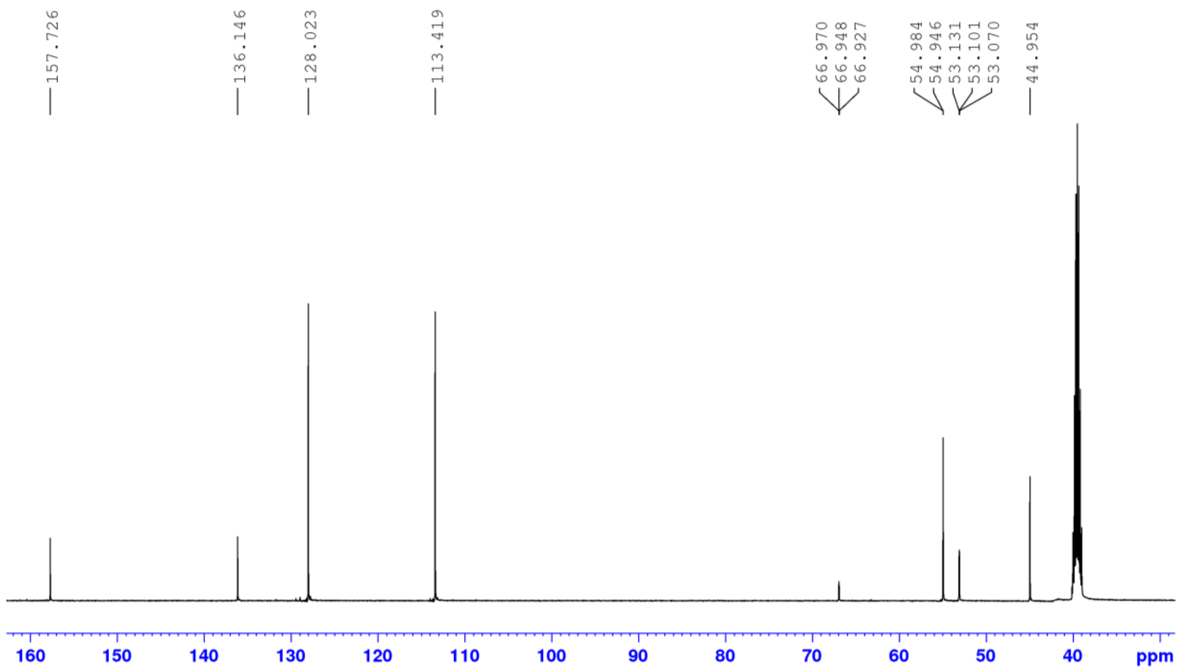


Figure S45. ^{13}C-NMR- DES$_{10}$



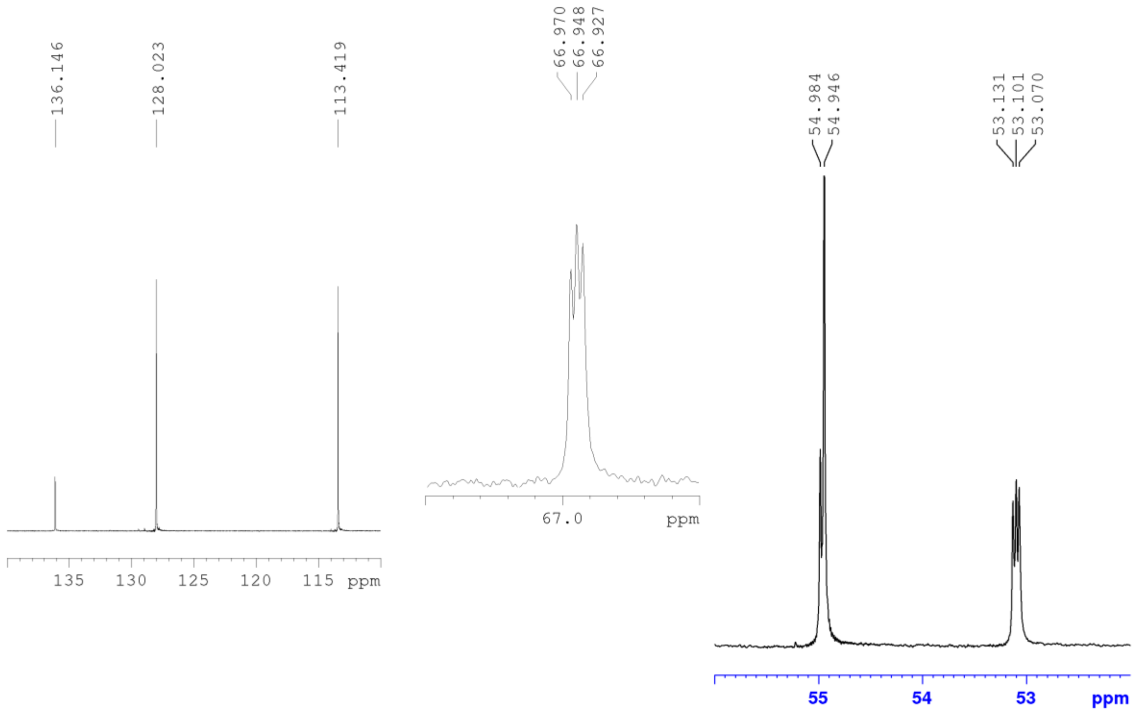
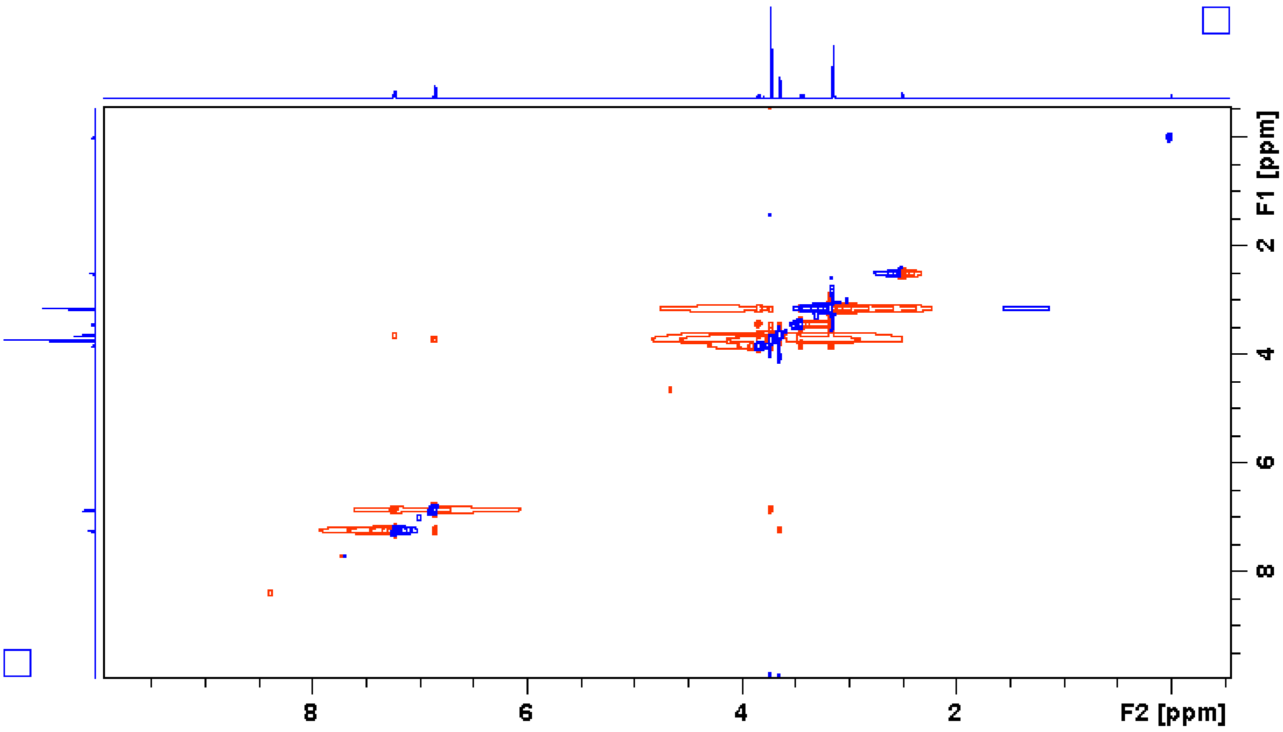
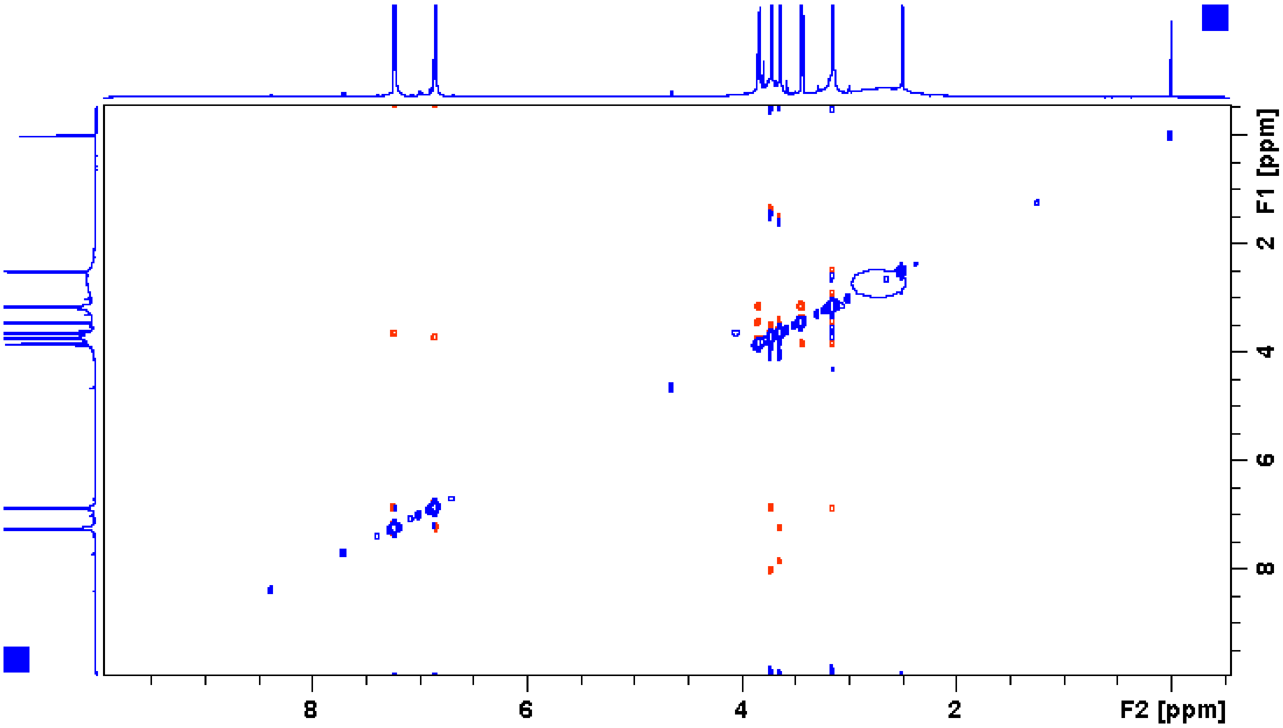


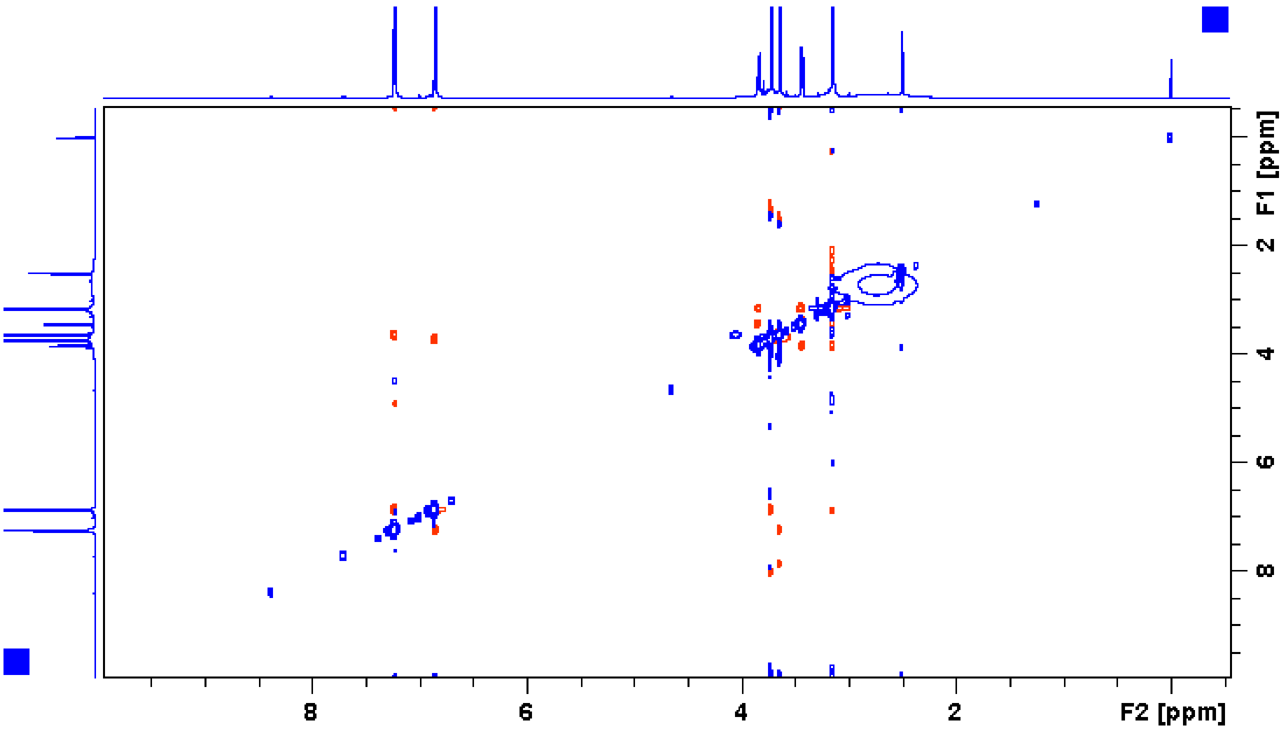
Figure S46. NOESY- DES_{10}



D= 900 ms



D8 =500 ms



D8 = 700 ms

Figure S47. ^{1}H-NMR – DES_{11}

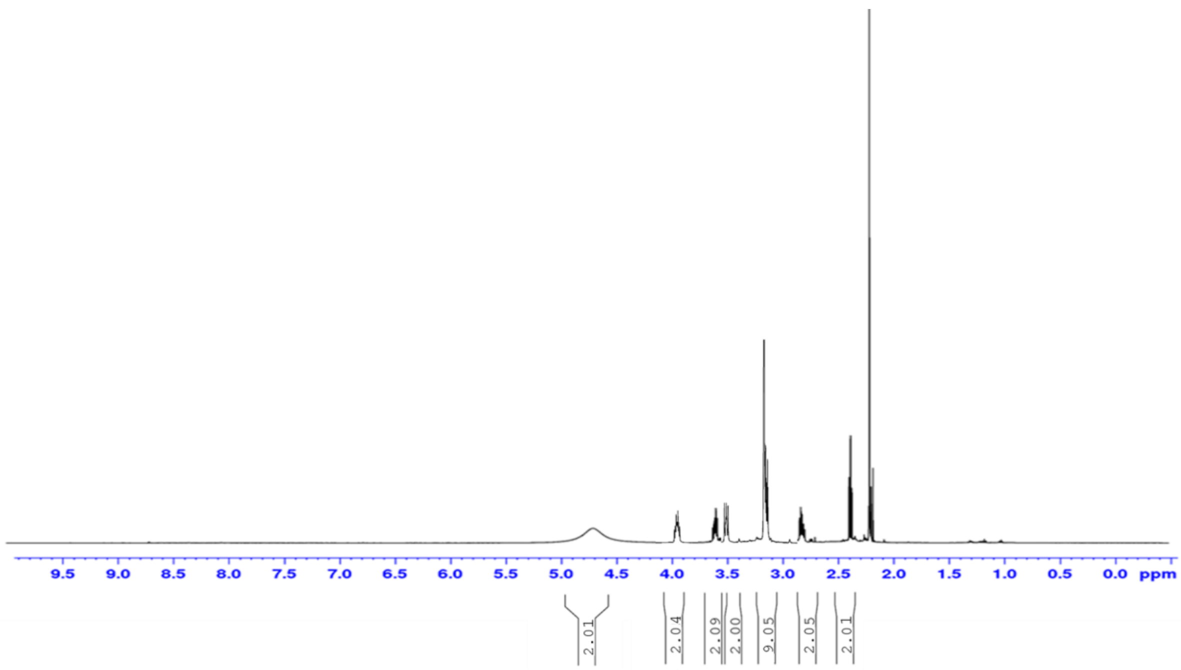


Figure S48. ^{13}C-NMR- DES_{11}

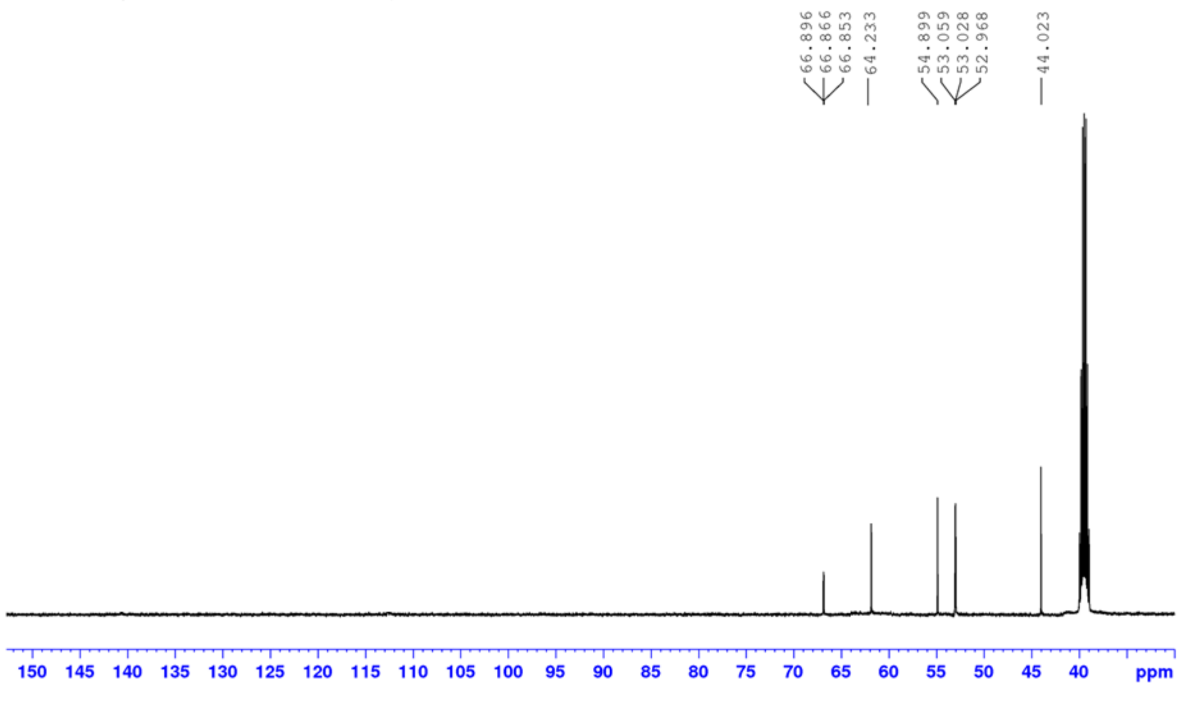
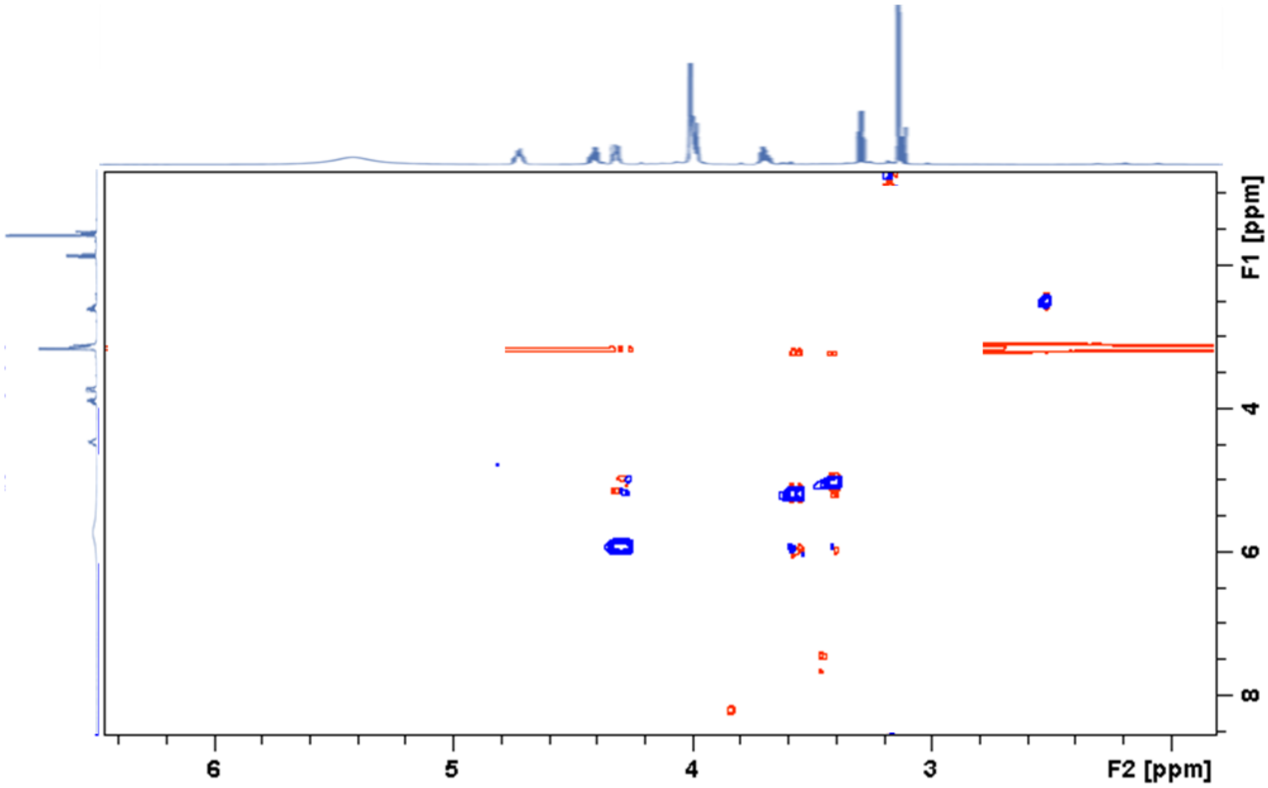


Figure S49. NOESY– DES_{11}



D8= 900 ms

Figure S50. ^{1}H-NMR – DES_{12}

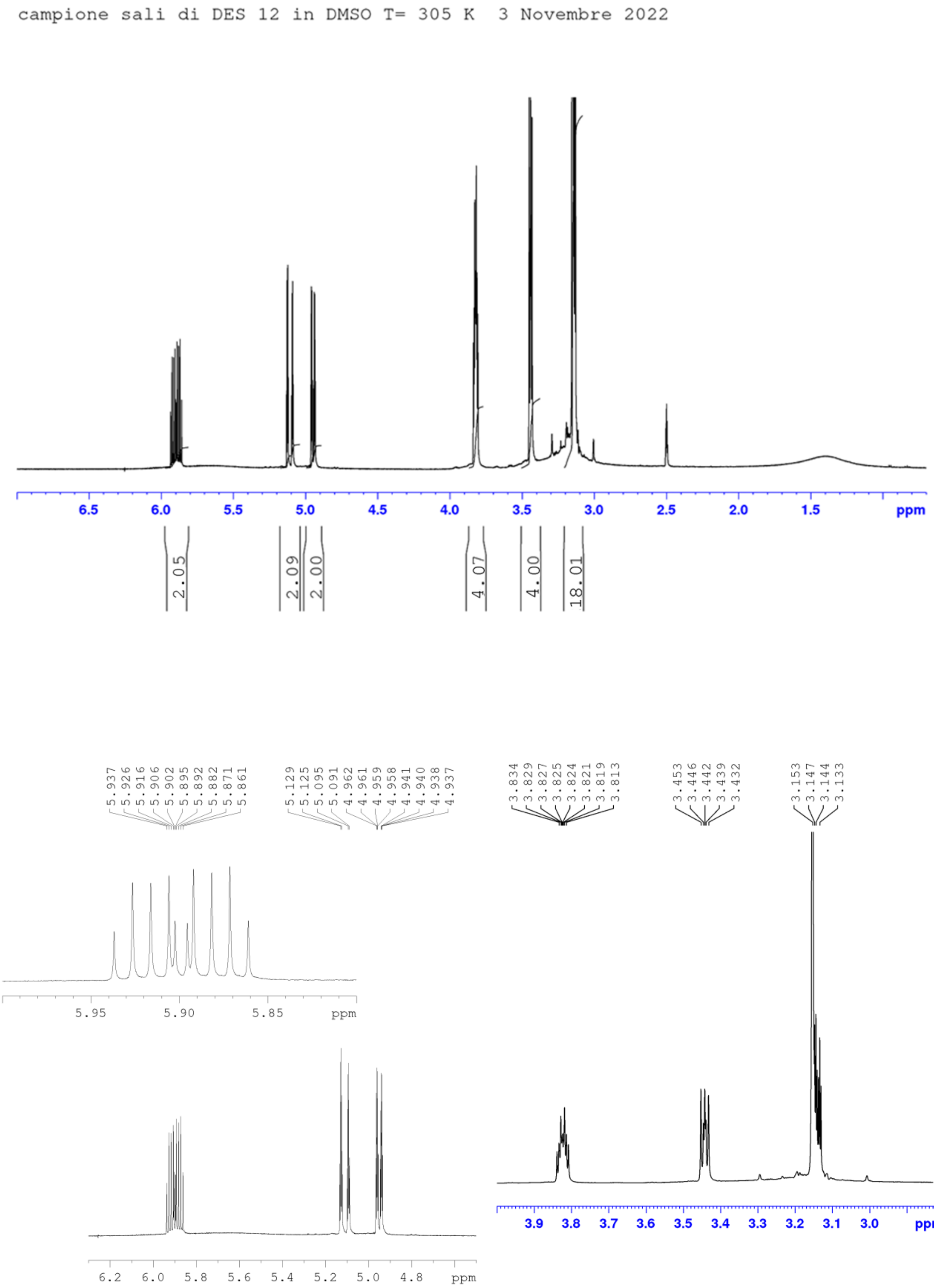


Figure S51. ^{13}C-NMR- DES_{12}

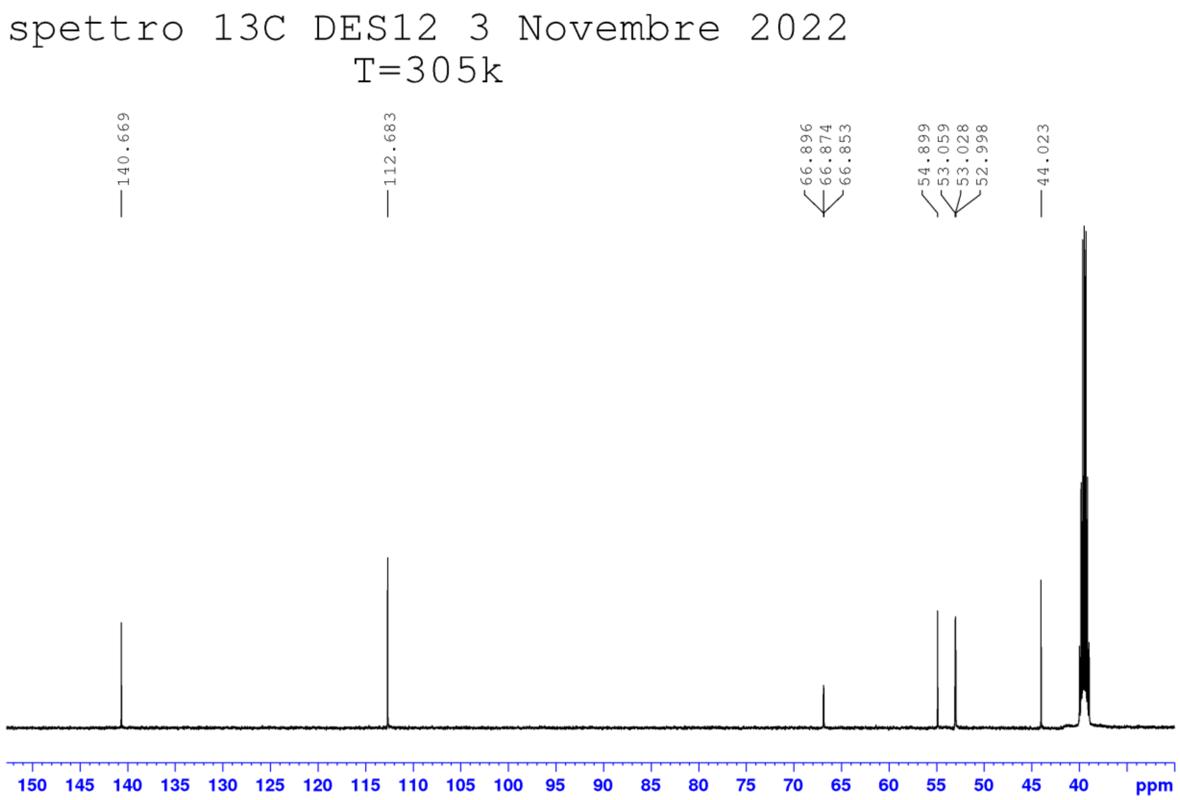
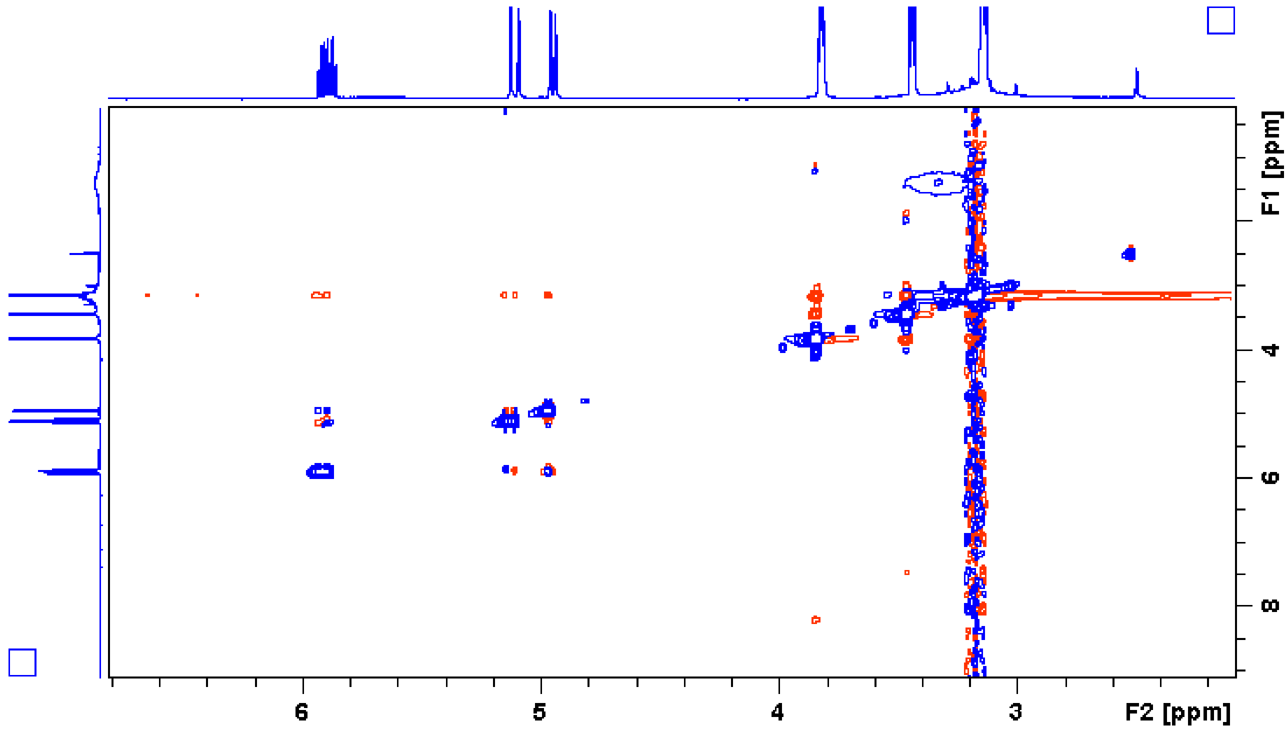
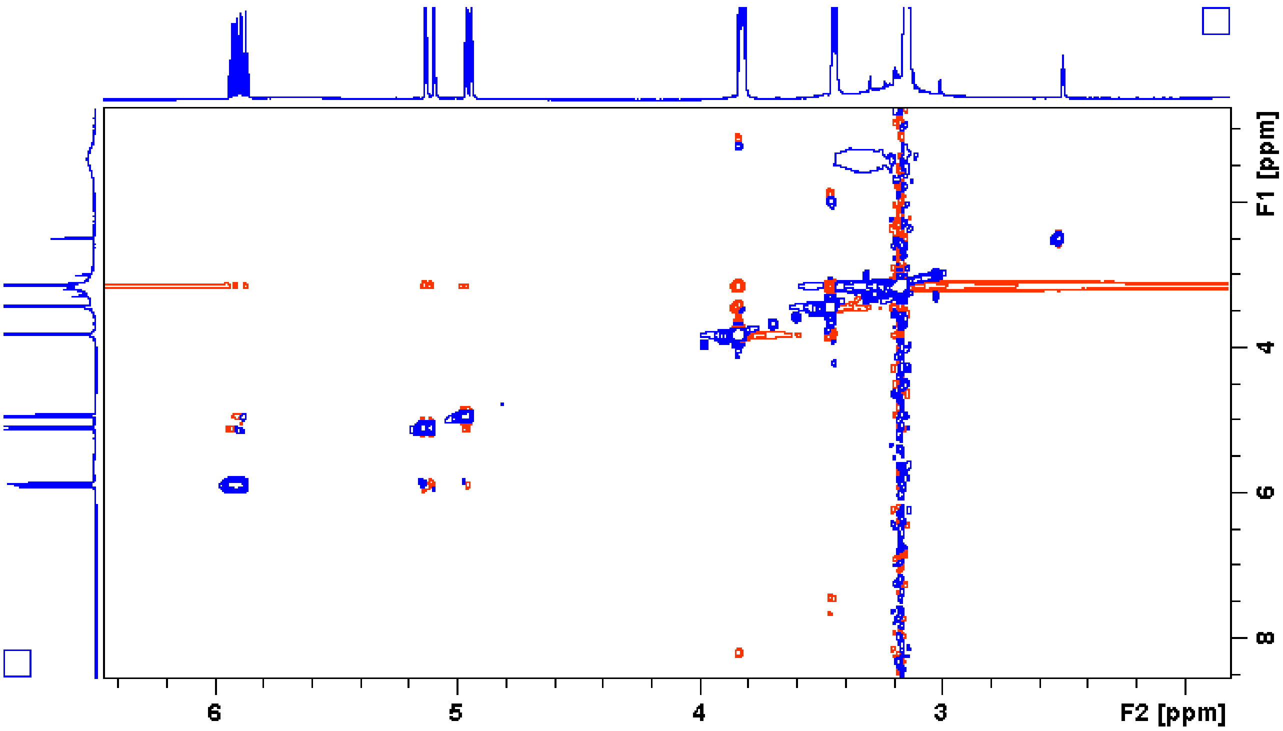


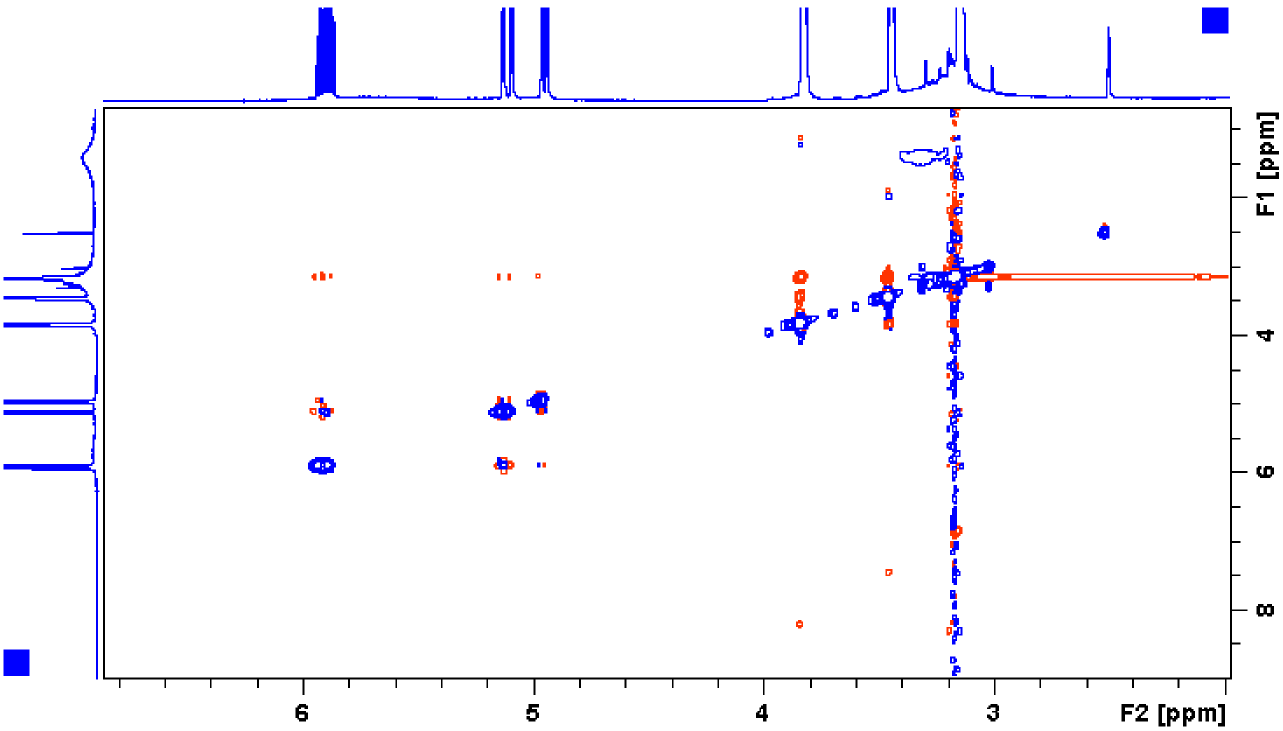
Figure S52. NOESY- DES_{12}



D8= 900 ms

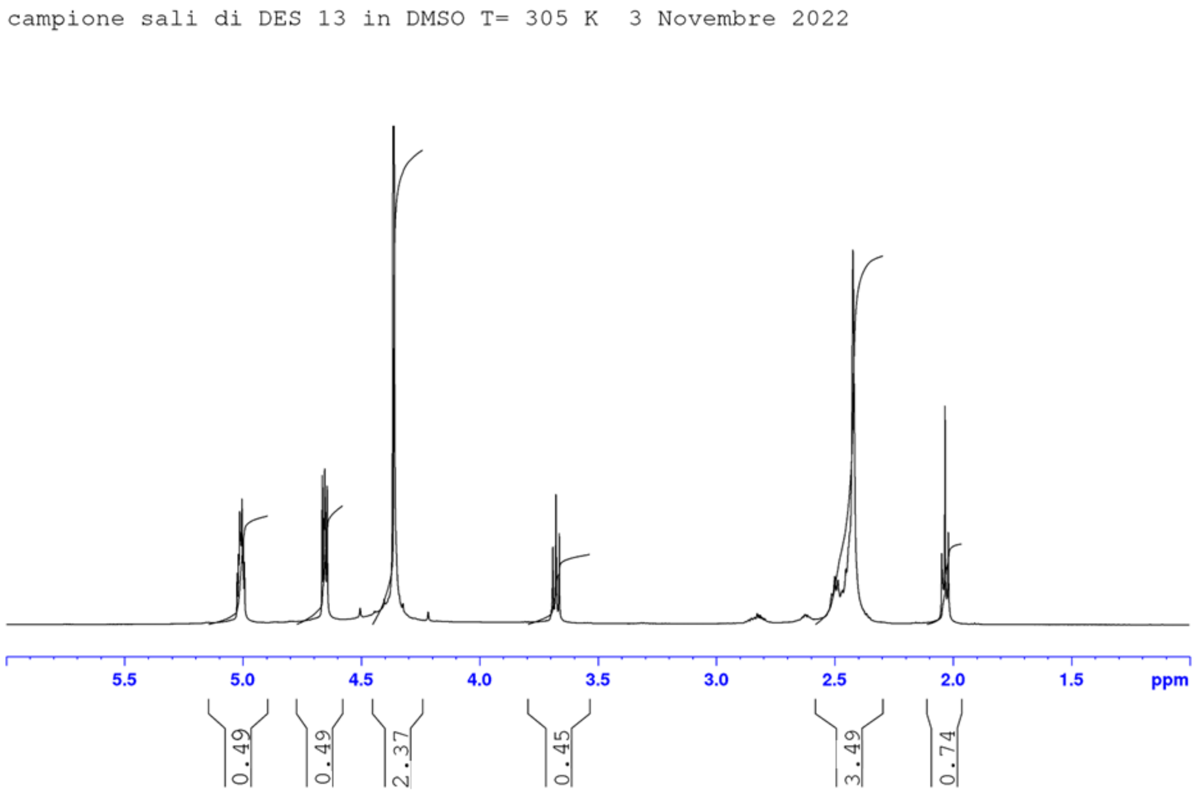


D8 = 500 ms



D8= 700 ms

Figure S53. ^{1}H-NMR – DES_{13}



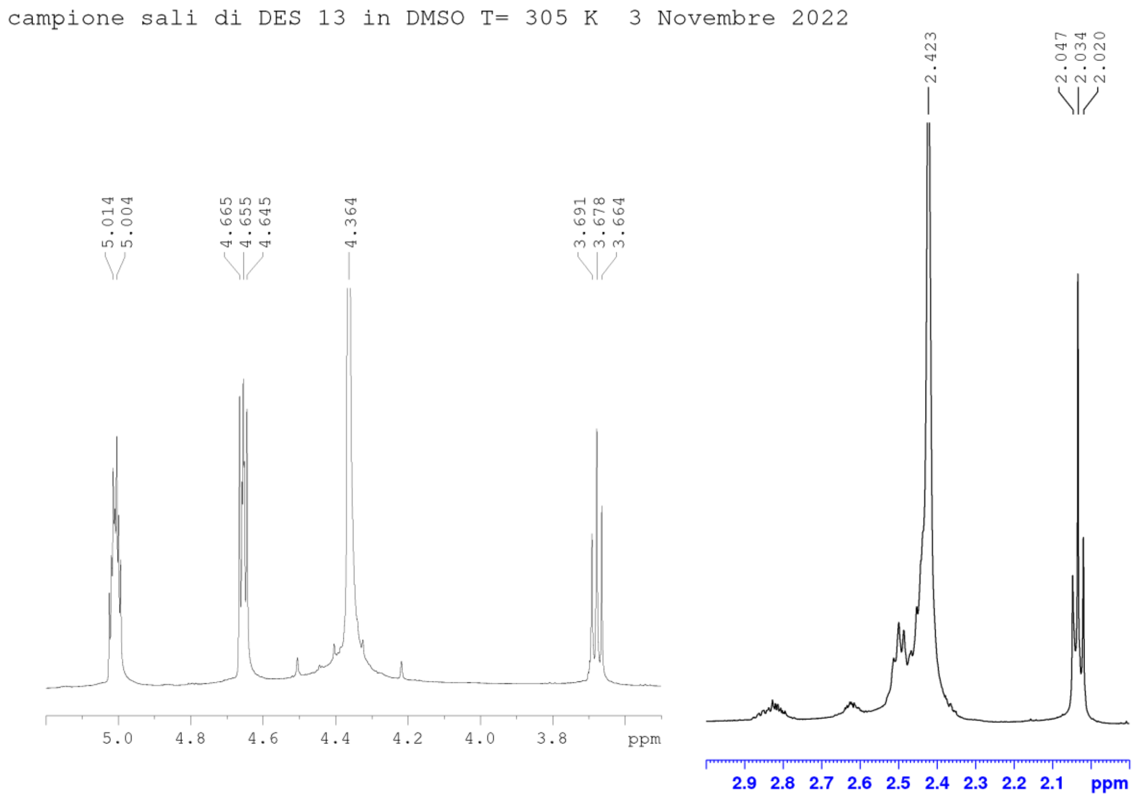


Figure S54. ^{13}C-NMR- DES_{13}

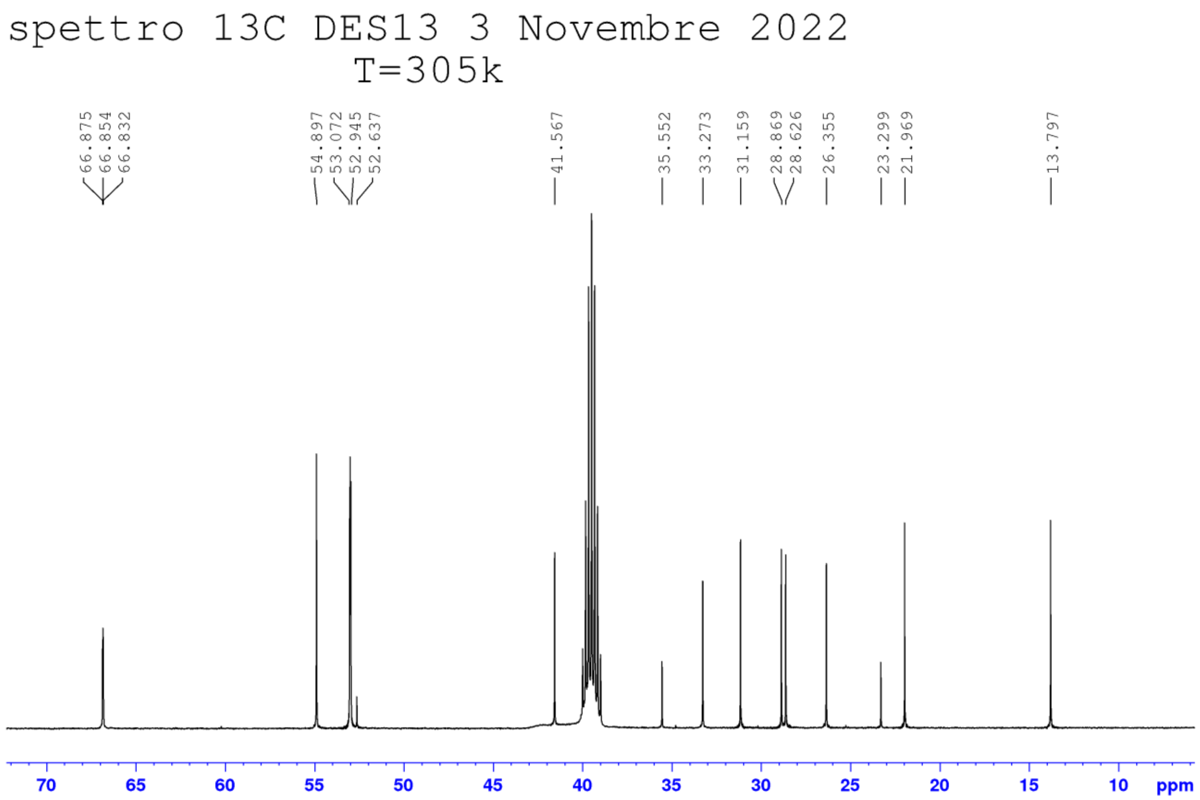
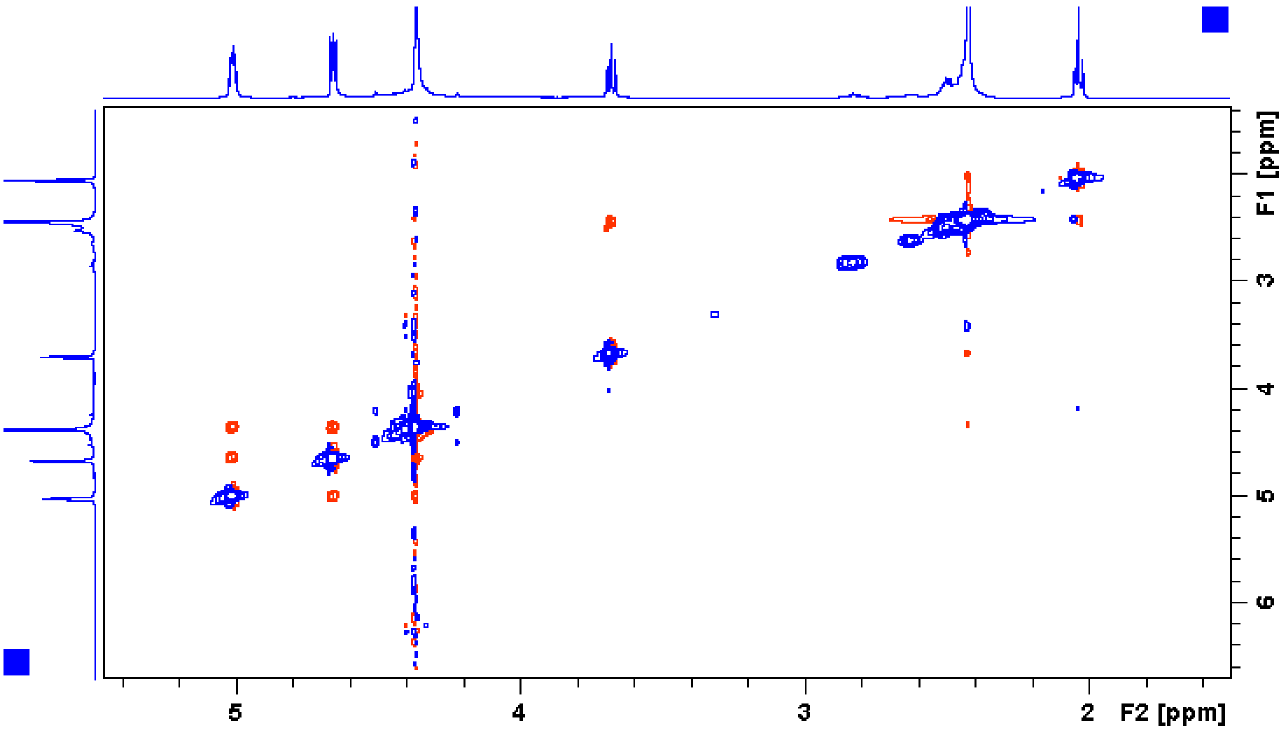
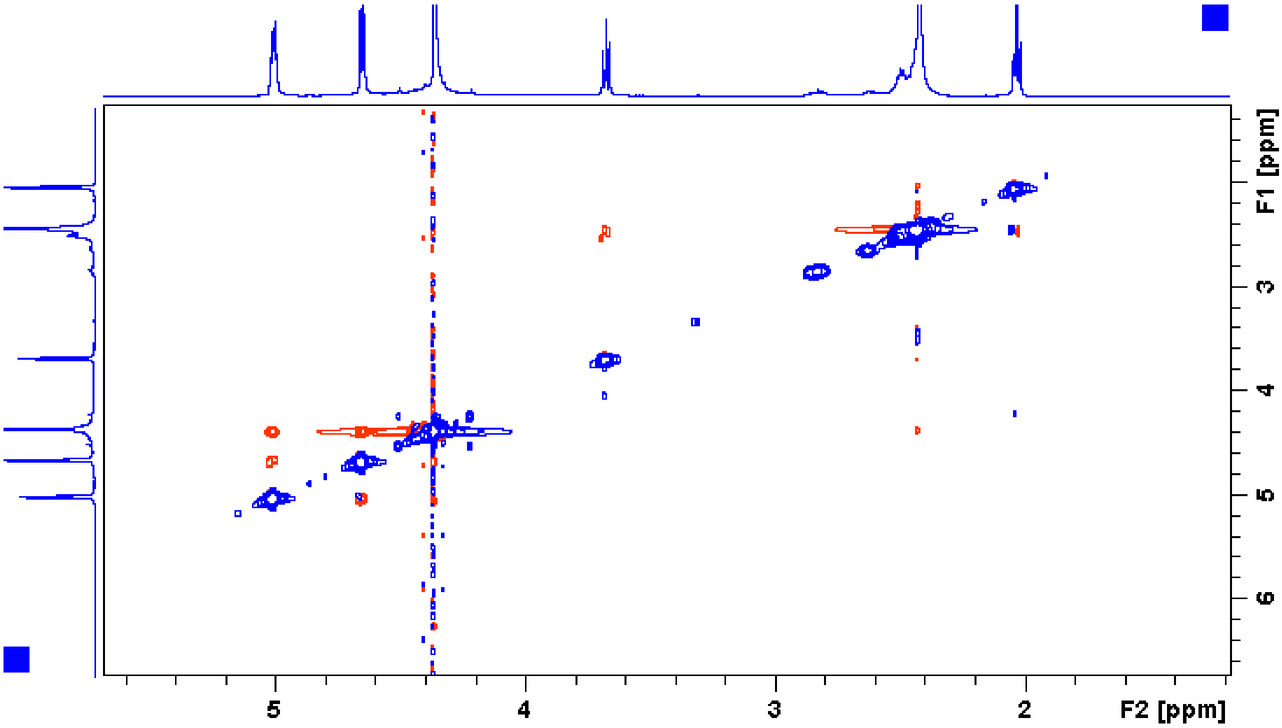


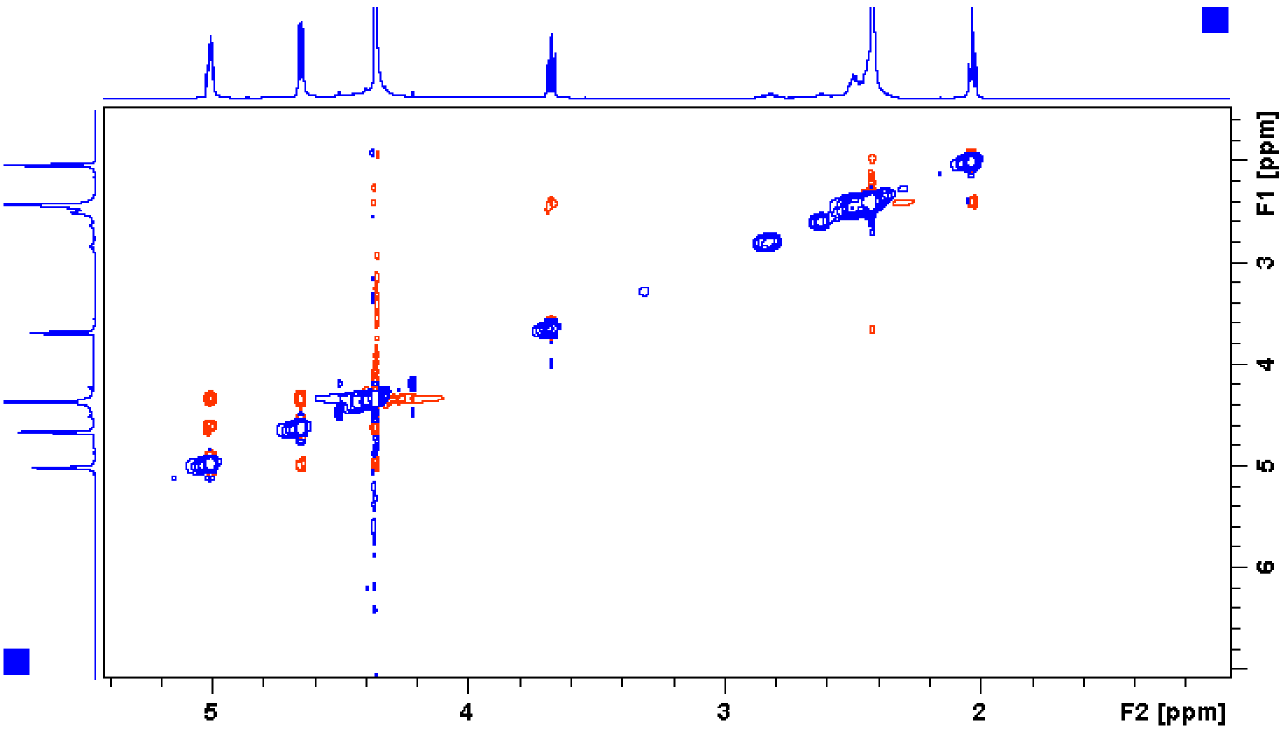
Figure S55. NOESY- DES_{13}



D8 =900 ms



D8 = 500 ms



D8 = 700 ms

Figure S56. ^{1}H-NMR – DES$_{14}$

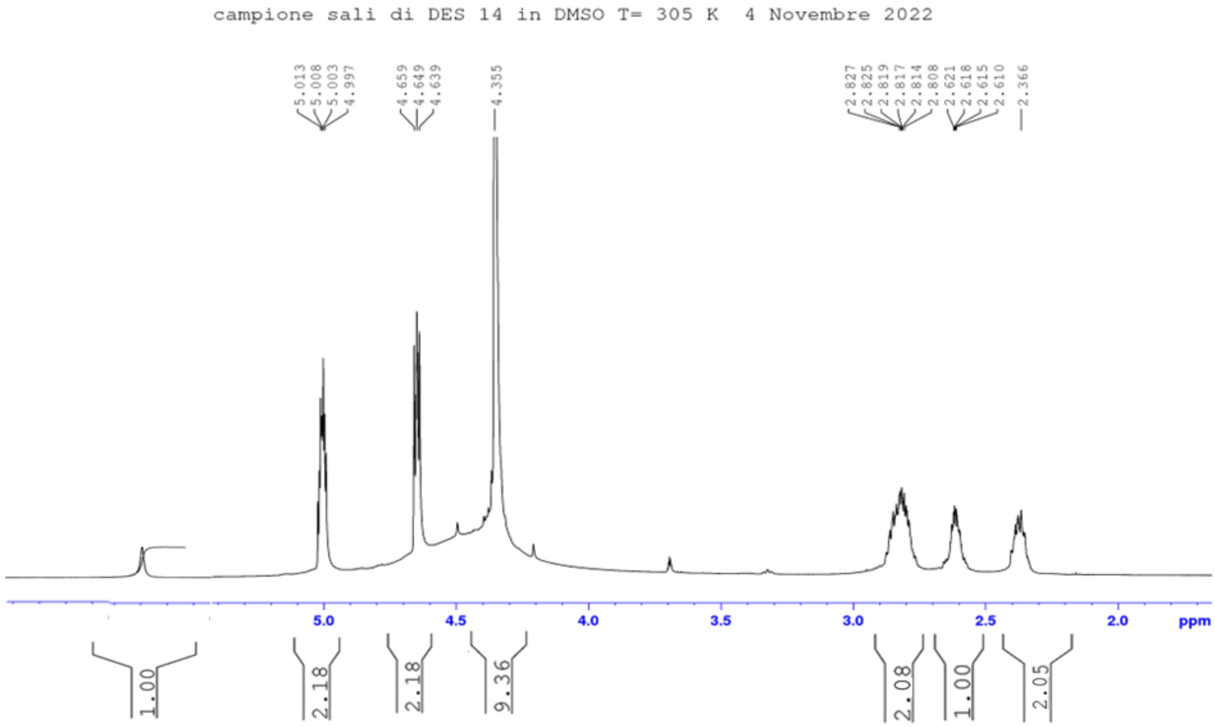


Figure S57. ^{13}C-NMR- DES$_{14}$

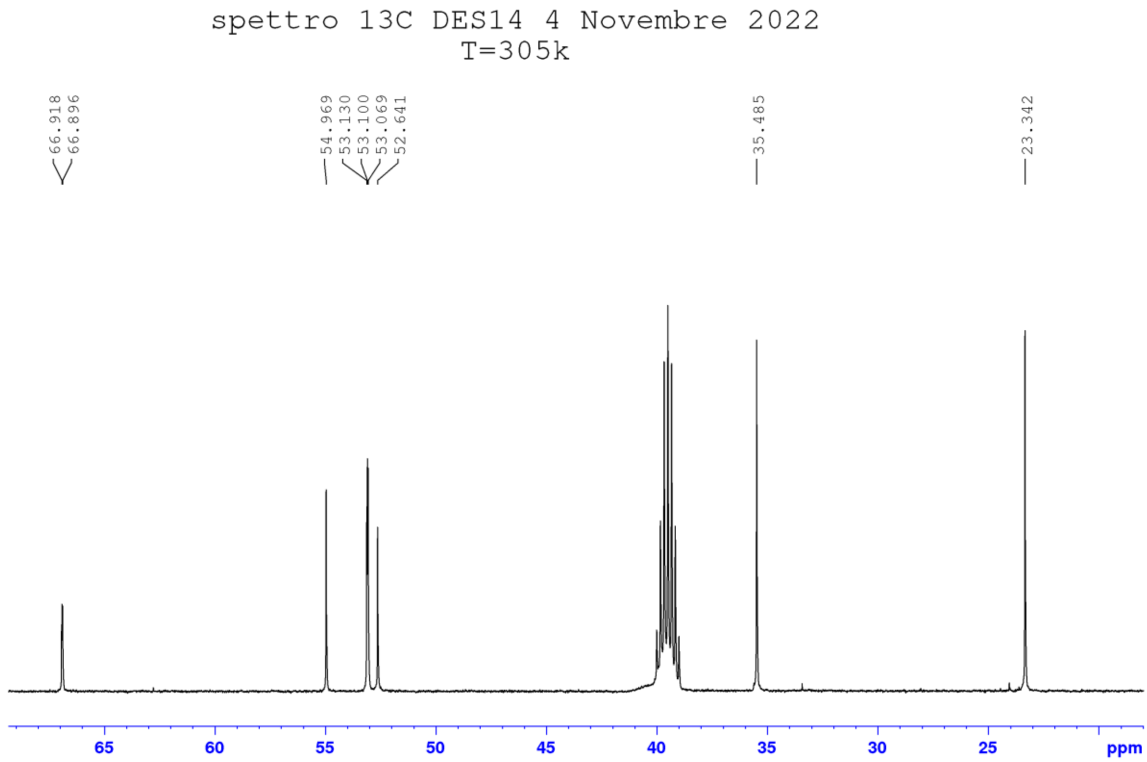
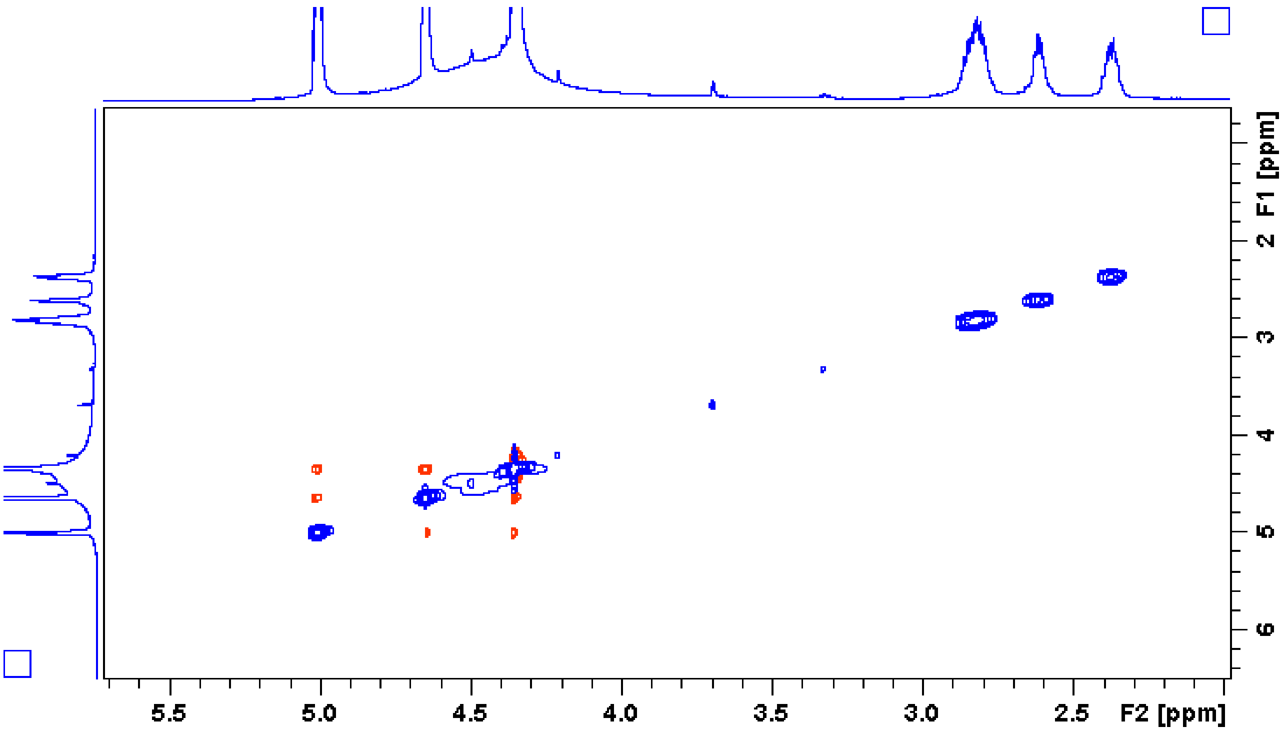
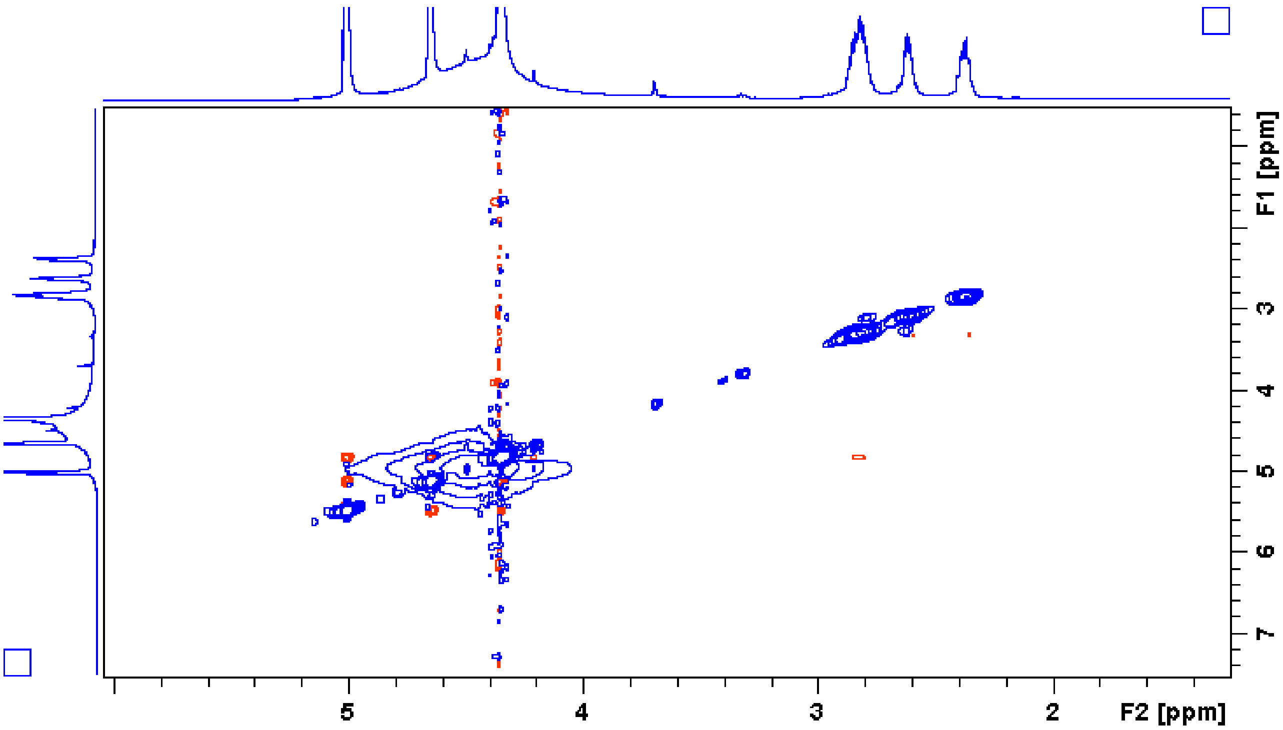


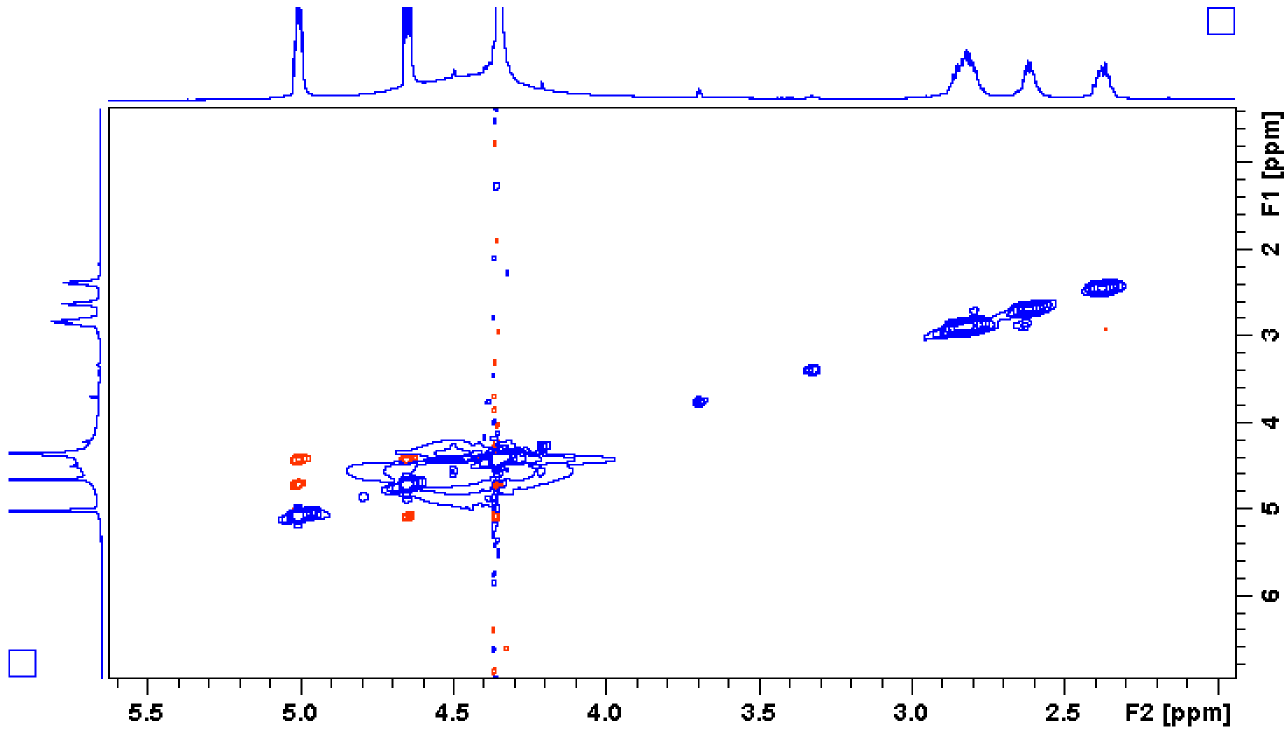
Figure S58. NOESY- DES$_{14}$



D8 = 900 ms



D8 = 500 ms



D8 = 700 ms

Characterization data for products 1a-14d

***N*-(9-Fluorenylmethoxycarbonyl) aniline (1a):** Spectroscopic data reported in the literature.[1] Brown solid obtained in quantitative yield; (mp 191-192° C)
***N*-(*tert*-Butoxycarbonyl) aniline (1b):** Spectroscopic data compared to those of the pure product. White solid obtained in quantitative yield (mp 133-137° C)
***N*-Phenyl-*p*-toluenesulfonamide (1c):** Spectroscopic data compared to those of the pure product. White solid obtained in 85% yield (mp 101-103 ˚C).
***N*-Acetyl aniline (1d):** Spectroscopic data compared to those of the pure product. White solid obtained in 97% yield (mp 114-116 °C).
***N*-(9-Fluorenylmethoxycarbonyl) *p*-chloroaniline (2a):** ^{1}H NMR (300 MHz, $CDCl_3$) δ =7.79 (d, 2H, J=7.5 Hz), 7.61 (d, 2H, J=7.3 Hz), 7.55-7.33 (m, 8H), 7.27 (m, 2H), 6.65 (br s, 1H), 4.55 (d, 2H, J=6.3 Hz), 4.24 (t, 1H, J=6.3Hz). ^{13}C NMR ($CDCl_3$) δ = 47.0, 66.8 120.4, 125.0, 126.2, 127.1, 127.8, 129.0, 133.0, 136.5, 141.4, 143.6, 153.2. MSEI(+) m/z: 349 $[M]^+$, 178 $[\text{9-methyl-9H-fluorene-H}]^+$, 152.9 $[C_7H_4ClNO]^+$, 126 $[C_7H_4ClNH]^+$. Yellow solid obtained in quantitative yield (mp 162-163°C).
***N*-(*tert*-Butoxycarbonyl) *p*-chloroaniline (2b):** Spectroscopic data compared to those of the pure product. Yellow solid obtained in 97% yield (mp 102-103°C).
***N*-*p*-chloroaniline-*p*-toluenesulfonamide (2c):** Spectroscopic data compared to those of the pure product. Yellow solid obtained in 97% yield (mp 122-123°C).
***N*-*p*-chloroaniline-acetamide (2d):** Spectroscopic data compared to those of the pure product. Yellow solid obtained in 98% yield (mp 171-172°C).
***N*-(9-Fluorenylmethoxycarbonyl) toluidine (3a):** Spectroscopic data compared to those reported in the literature.[1] Colorless solid obtained in 94% yield (mp 195-197 °C).
***N*-(*tert*-Butoxycarbonyl)-toluidine (3b):** Spectroscopic data compared to those of the pure product. Colorless solid obtained in 95% yield (mp 86-88 °C).
***N*-Toluidine *p*-toluenesulfonamide (3c):** Spectroscopic data compared to those of the pure product. Coloress oil obtained in 89% yield.
***N*-toluidine-acetamide (3d):** Spectroscopic data compared to those of the pure product. White solid obtained in 96% yield (mp 152-153 °C).
***N*-(9-Fluorenylmethoxycarbonyl) anisidine (4a):** Spectroscopic data compared to those of the pure product. White solid obtained in 95% yield (mp 192-193 °C).
***N*-(*tert*-Butoxycarbonyl) anisidine (4b):** Spectroscopic data compared to those of the pure product. White solid obtained in 92% yield (mp 94-95° C).
***N*-anisidine *p*-toluenesulfonamide (4c):** Spectroscopic data compared to those reported in the literature.[2] Cream solid obtained in 90% yield (mp 115–116°C).
***N*-acetyl-anisidine (4d):** Spectroscopic data compared to those of the pure product. White solid obtained in 91% yield (mp 132-133 °C).
***N*-(9-Fluorenylmethoxycarbonyl) *p*-nitro-aniline (5a):** Spectroscopic data compared to those reported in the literature.[3] Yellow solid obtained in 92% yield (mp 181-183 °C).
***N*-(*tert*-Butoxycarbonyl) *p*-nitro-aniline (5b):** Spectroscopic data compared to those of the pure product. Yellow oil obtained in 93% yield.
***N*-*p*-nitro-aniline-*p*-toluenesulfonamide (5c):** Spectroscopic data compared to those reported in the literature.[4] White solid obtained in 91% yield (mp 181-183 °C).

***N*-*p*-nitro-aniline acetamide (5d):** Spectroscopic data compared to those of the pure product. Solid yellow obtained in 92% yield (mp 214-216 °C).

***N*-(9-Fluorenylmethoxycarbonyl) *m*-nitro-aniline (6a):** Spectroscopic data compared to those reported in the literature.[4] Yellow solid obtained in 79% yield. (mp 178-179 °C).

***N*-(*tert*-Butoxycarbonyl) *m*-nitroaniline (6b):** Spectroscopic data compared to those reportd in the literature.[5] Yellow oil obtained in 75% yield.

***N*-*m*-nitroaniline-*p*-toluenesulfonamide (6c):** Spectroscopic data compared to those of the pure product. Yellow solid obtained in 78% yield (mp 125-127 °C).

***N*-*m*-nitro-aniline acetamide (6d):** Spectroscopic data compared to those of the pure product. Yellow solid obtained in 85% yield (mp 151-153 °C).

***N*-(9-Fluorenylmethoxycarbonyl) -*o*-phenylenediamine (7a):** ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 4.27 (t, 1H, J = 7.2 Hz, CH), 4.47 (d, 2H, J = 7.2 Hz, CH_2), 7.41-7.28 (m, 5H, ArH e NH), 7.57 (d, J = 7.4 Hz, 2H, ArH), 7.68-7.66 (m, 2H, ArH), 7.91-7.85 (m, 4H, ArH), 8.98 (s, 2H, NH) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 47.2, 67.2, 114.6, 118.8, 120.1, 122.7, 124.9, 125.2, 125.5, 127.0, 127.8, 141., 143.8, 150.1, 153.4. MSEI(+) m/z: 330 $[M]^+$, 178 [9-methyl-9H-fluorene-H]$^+$, 135 $[C_7H_7N_2O]^+$, 107 $[C_7H_4N_2H_2]^+$. White solid obtained in 79% yield. (mp 180-182 °C).

***N*-(*tert*-Butoxycarbonyl) -*o*-phenylenediamine (7b):** Spectroscopic data compared to those of the pure product. Brown solid obtained in 80% yield (mp 110-114 °C).

***N*-*p*-toluenesulfonamide-*o*-phenylenediamine (7c):** Spectroscopic data compared to those of the pure product. White solid obtained in 78% yield (mp 111-113 °C).

***o*-amino Acetanilide (7d):** Spectroscopic data compared to those of the pure product. White solid obtained in 81% yield (mp 111-113 °C).

***N*-(9-Fluorenylmethoxycarbonyl)-*o*-aminophenol (8a)**: Spectroscopic data compared to those reported in the literature.[5]

Yellow solid obtained in 88% yield (mp 167-169 °C).

***N*-(*tert*-Butoxycarbonyl)-*o*-amminophenol (8b):** Spectroscopic data compared to those of the pure product. Yellow solid obtained in 87% yield (mp 143-147 °C).

***N*-*p*-toluenesulfonamide-*o*-aminophenol (8c):** Spectroscopic data compared to those of the pure product. Dark pink solid obtained in 91% yield (mp 102-103 °C).

***o*-hydroxy Acetanilide (8d):** Spectroscopic data compared to those of the pure product. Bright brown solid obtained in 92% yield (mp 207-210 °C).

***N*-(9-Fluorenylmethoxycarbonyl) benzylamine (9a):** Spectroscopic data compared to those reported in the literature. [1] Colorless solid obtained in 90% yield (mp 192-193 °C).

***N*-(*tert*-Butoxycarbonyl) benzylamine (9b):** Spectroscopic data compared to those of the pure product. White solid obtained in 90% yield (mp 55-57 °C).

***N*-Benzyl-*p*-toluenesulfonamide (9c):** Spectroscopic data compared to those of the pure product. Yellow solid obtained in 88% yield (mp 115-116 °C).

***N*-benzylacetamide (9d):** Spectroscopic data compared to those of the pure product. Yellow solid obtained in 90% yield (mp 60-62 °C).

***N*-(9-Fluorenylmethoxycarbonyl) *p*-methoxybenzylamine (10a):** Spectroscopic data compared to those reported in the literature.[2] White solid obtained in 95% in yield. (mp. 182-184 °C).

***N*-(tert-Butoxycarbonyl) *p*-methoxybenzylamine (10b):** Spectroscopic data compared to those reported in the literature. [2] Colourless oil 94% yield.

***N*-*p*-toluenesulfonamide- *p*-methoxybenzylamine (10c):** Spectroscopic data compared to those reported in the literature.[2] White solid obtained in 92% yield (mp 180-182 °C).

***p*-Methoxybenzyl acetamide (10d):** Spectroscopic data compared to those of the pure product. Yellow oil obtained in 96% yield.

***N*-(9-Fluorenylmethoxycarbonyl) ethanolamine (11a):** Spectroscopic data compared to those of the pure product. Colorless solid obtained in 92% yield (mp 145-147 °C).

***N*-(*tert*-Butoxycarbonyl) ethanolamine (11b):** Spectroscopic data compared to those of the pure product Colourless oil obtained in 94% yield.

***N*- *p*-toluenesulfonamide- ethanolamine (11c):** Spectroscopic data compared to those of the pure product. Dark brown solid obtained in the 94% yield (mp 55-57 °C).

***N*-acetyl-ethanolamine (11d):** Spectroscopic data compared to those of the pure product. Colourless oil obtained in 94% yield.

***N*-(9-Fluorenylmethoxycarbonyl)-allylamine (12a):** Spectroscopic data compared to those of the pure product. Pale yellow solid obtained in 93% yield.

***N*-(*tert*-Butoxycarbonyl)-allylamine (12b):** Spectroscopic data compared to those of the pure product. White solid obtained in 95% yield (mp 35-38 °C).

***N*- *p*-toluenesulfonamide-allylamine (12c):** Spectroscopic data compared to those of the pure product. Dark brown solid obtained in the 96% yield (mp 55-57 °C).

***N*-acetyl- allylamine (12d):** Spectroscopic data compared to those of the pure product. Brown solid obtained in 94% yield (mp 64-65 °C).

***N*-(9-Fluorenylmethoxycarbonyl) octylamine (13a):** Spectroscopic data compared to those reported in the literature.[3] Pale yellow solid obtained in 86% yield (mp 91-93 °C).

***N*-(*tert*-Butoxycarbonyl) octylamine (13b):** Spectroscopic data compared to those reported in the literature.[3] Colourless oil obtained in 85% yield.

***N*-Octyl *p*-toluenesulfonamide (13c):** Spectroscopic data compared to those reported in the literature.[3] Yellow oil obtained in 80% yield.

N-Octyl acetamide (13d): Spectroscopic data compared to those of the pure product. Colorless oil obtained in 86% yield.

***N*-(9-Fluorenylmethoxycarbonyl)-cyclopentylamine (14a):** Spectroscopic data compared to those reported in the literature.[6] Pale yellow solid obtained in 86% yield (mp 111-113 °C).

***N*-(*tert*-Butoxycarbonyl)-cyclopentylamine (14b):** Spectroscopic data compared to those of the pure product. Pale yellow solid obtained in 86% yield (mp 74-76 °C).

***N*- *p*-toluenesulfonamide cyclopentylamine (14c):** Spectroscopic data compared to those of the pure product. Pale yellow solid obtained in 78% yield (mp 89-91 °C).

N-cyclopentylacetamide (14d): Spectroscopic data compared to those of the pure product. Pale yellow solid obtained in 83% yield (mp 78-81 °C).

References

1 M. B. Gawande, P. S. Branco *Green Chem*., 2011, **13**, 3355 -3359.
2 M. A. K. Zarchi, M. Aslani, *J. Appl. Polym. Sci*, 2012, **124**, 3456-3462.
3 M. Nardi, N. Herrera Cano, P. Costanzo, M. Oliverio, G. Sindona, A. Procopio, *RSC Adv*., 2015, **5**, 18751-18760.
4 M. Nasrollahzadeh, A. Ehsani, A. Rostami-Vartouni, *Ultrason Sonochem*, 2014, **21**, 275-282.
5 D. Procopio, C. Siciliano, R. De Rose, S. Trombino, R. Cassano, M.L. Di Gioia *Catalysts*. 2022; **12**(11):1480.
6 M. Godoi, G. V. Botteselle, J. Rafique, M. S. T. Rocha, J. M. Pena, A. L. Braga *Asian J. Org. Chem.*, 2013, **2** (9), 746-749.

Figure S59. ^{1}H-NMR **(2a).**

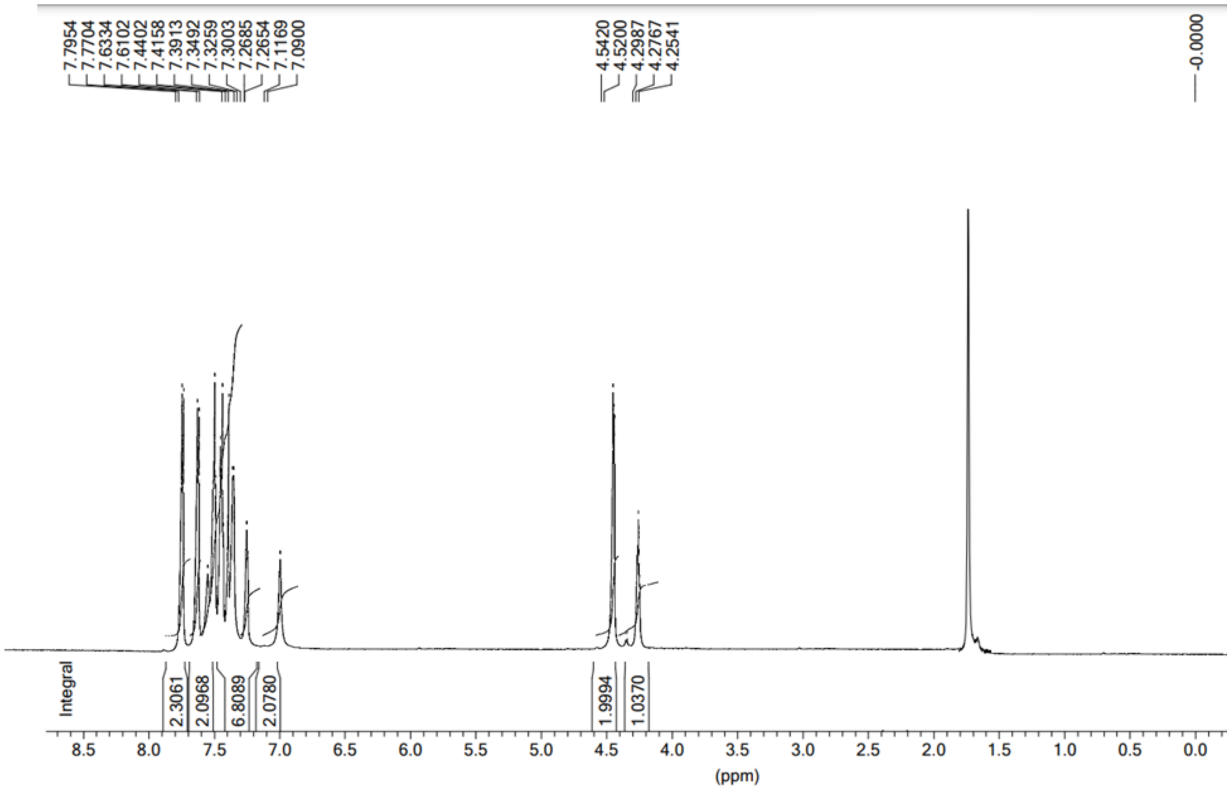


Figure S60. ^{13}C-NMR **(2a).**

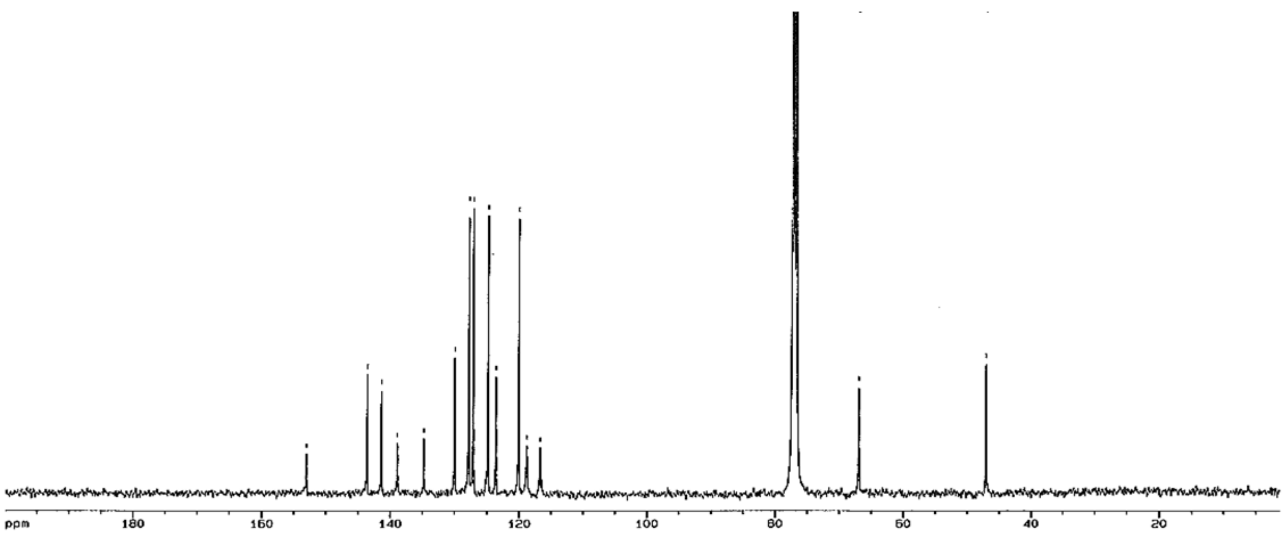


Figure S61. MSEI (+) **(2a).**

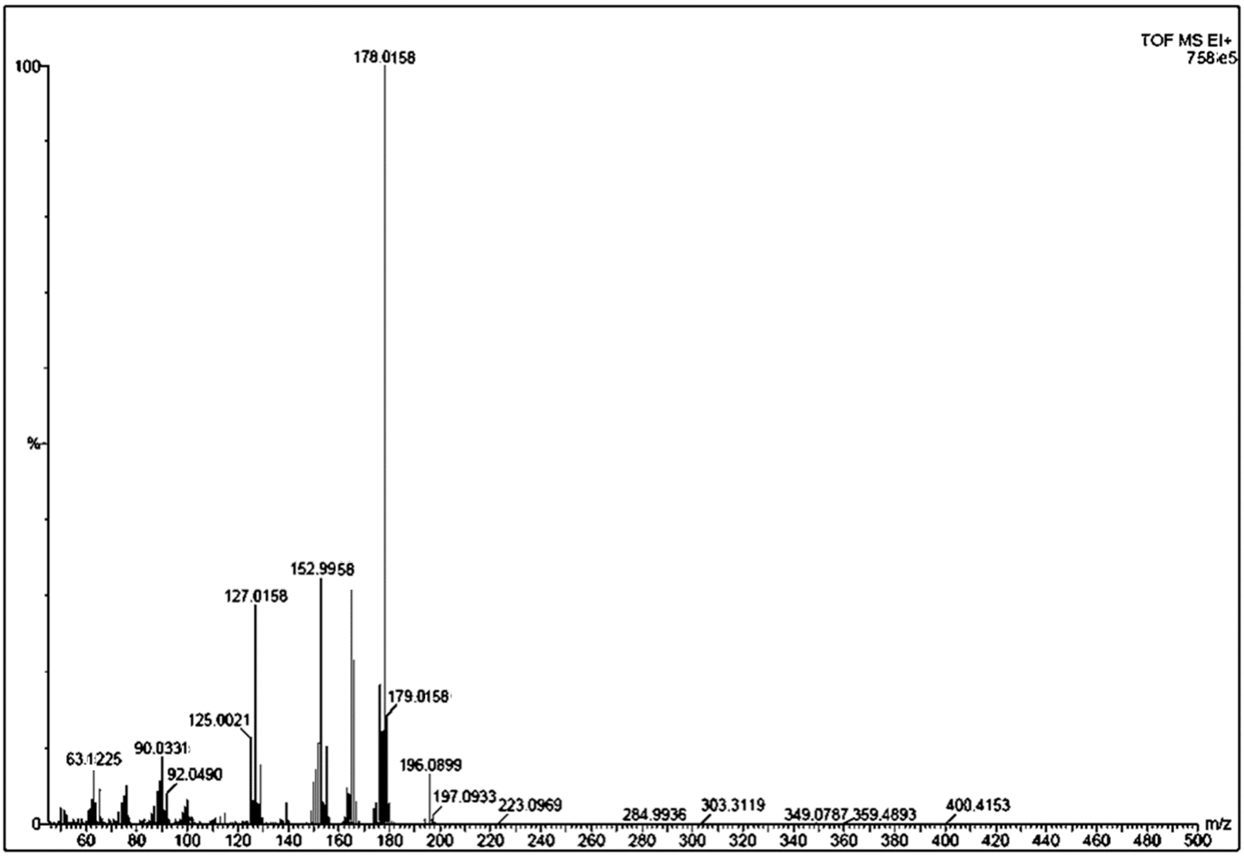


Figure S62. ^{1}H-NMR **(7a)**

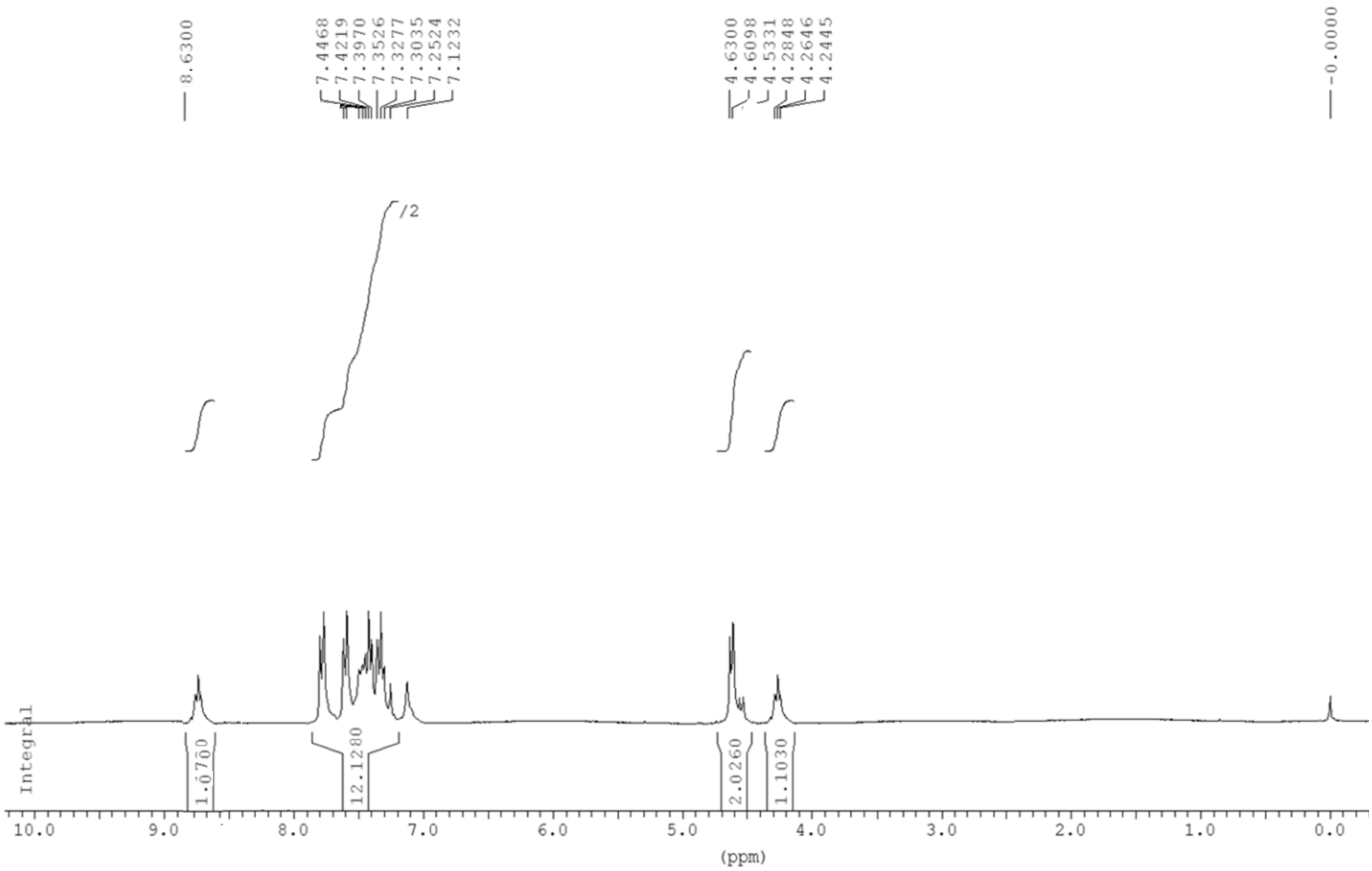


Figure S63. ^{13}C-NMR**(7a).**

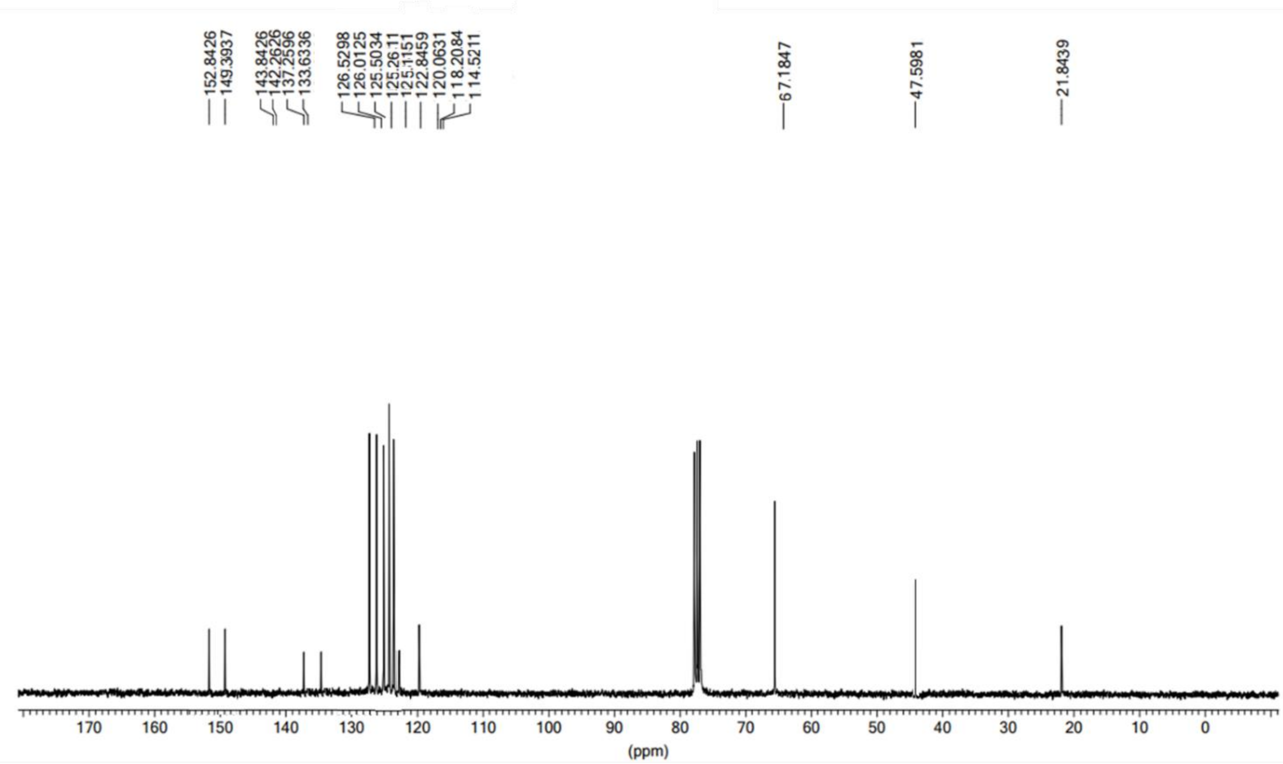


Figure S64. MSEI (+) **(7a)**