Supplementary Data

Unsymmetrical Heptamethine Dyes for NIR Dye-Sensitized Solar Cells

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1 Synthesis

1.2 General information

Heterocycles **S1-S5** were prepared according to literature procedures[1]. Middle synthon **S6** was purchased from FEW Chemicals Gmbh and ORGANICA Feinchemie GmbH Wolfen. Compound **S7** was prepared following the synthetic route published elsewhere[2]. Synthesis procedure for the anchor group **S8** is described in literature[3] (Figure S1). Symmetric heptamethine dyes (**symHepta1-3**) were synthesized according to known literature procedures.

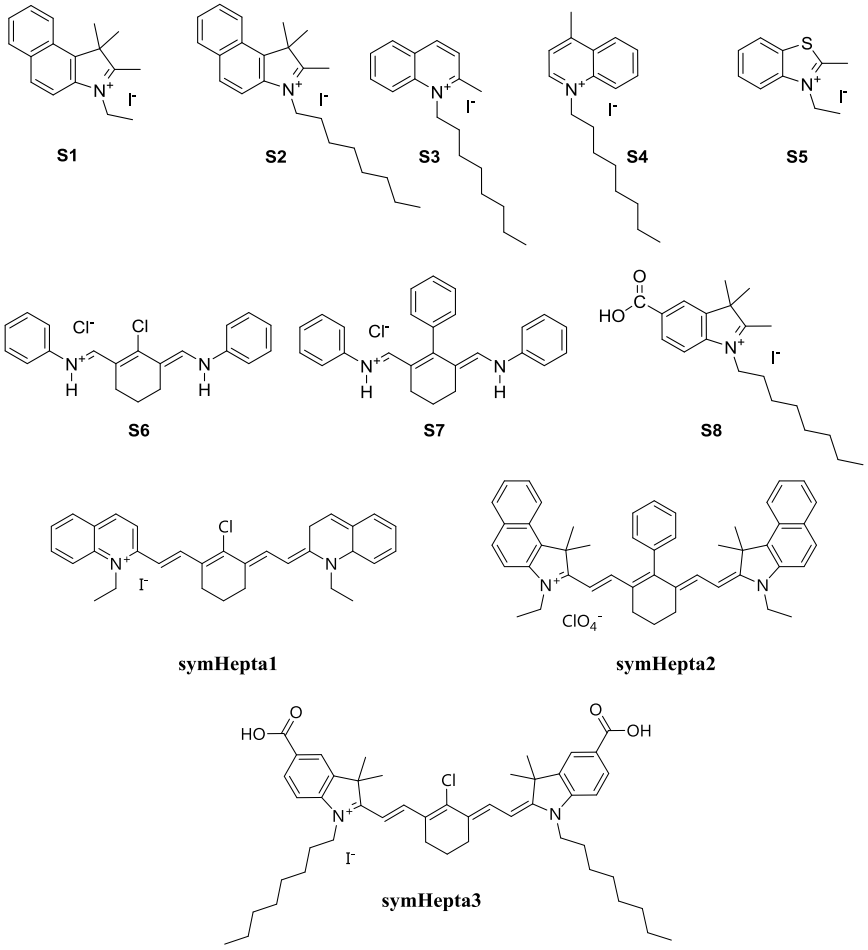
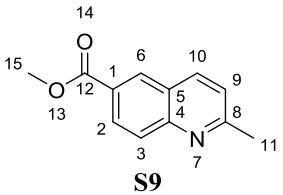


Figure S1 Used compounds and dyes

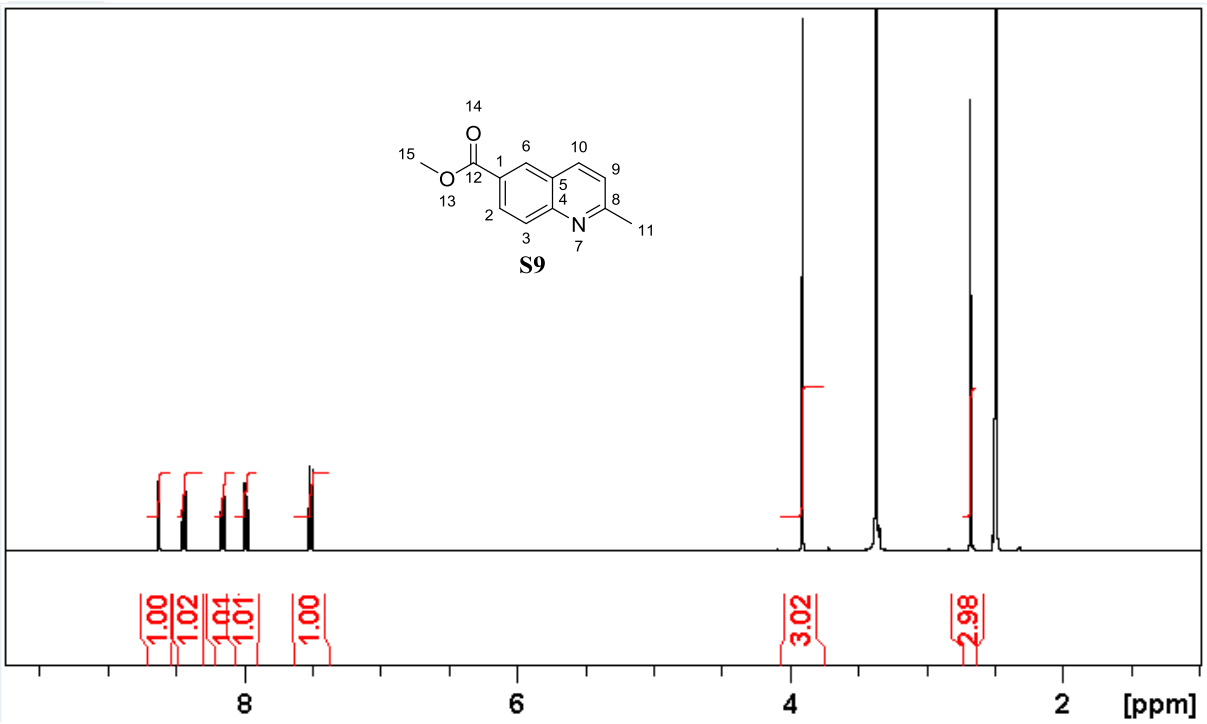
(1) Pardal, A. C.; Ramos, S. S.; Santos, P. F.; Reis, L. V., Almeida, P. *Molecules*, **2002**, 7, 320
(2) Salon, J.; Wolińska, E.; Raszkiewicz, A.; Patonay, G.; Strekowski, L. J. *Heterocyclic. Chem.*, **2005**, 42, 959
(3) Yum, J. H.; Walter, P.; Huber, S.; Rentsch, D.; Geiger, T.; Nuesch, F.; De Angelis, F.; Gratzel, M.; Nazeeruddin, M. K. *J. Am. Chem. Soc.*, **2007**, 129, 10320

1.2 Methyl 2-methylquinoline-6-carboxylate (S9)[4]

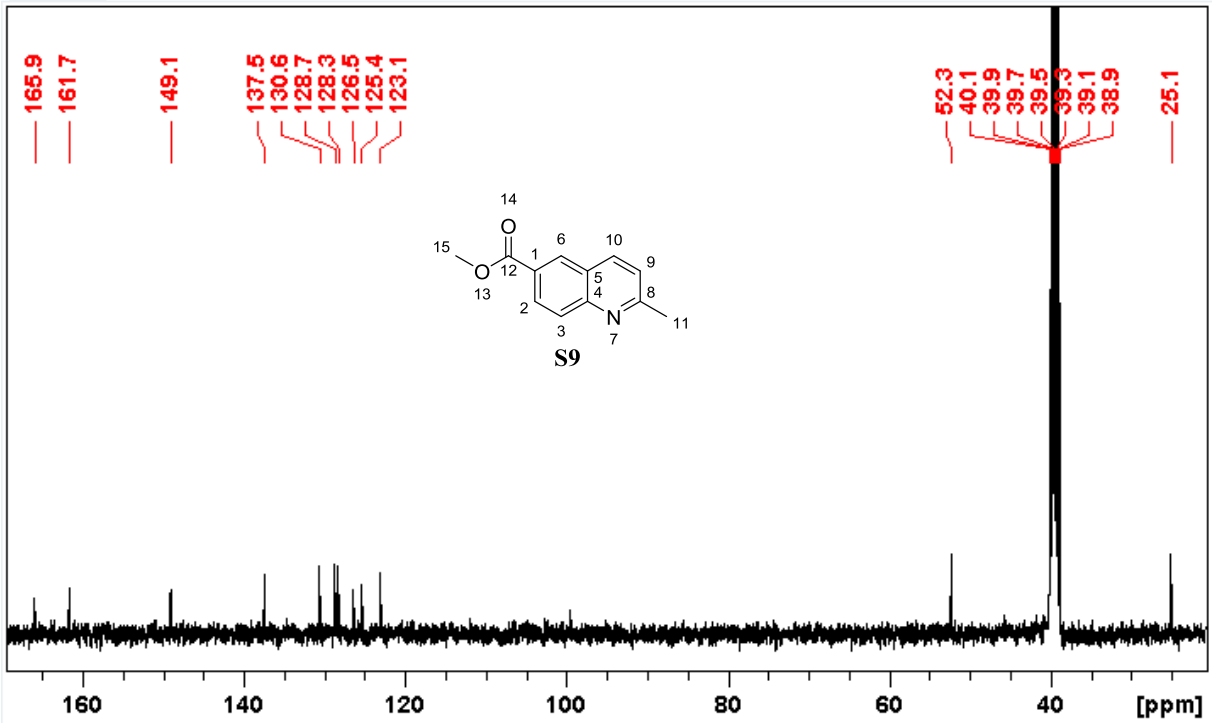


S9

2-Methylquinoline-6-carboxylic acid (22.7 g, 0.1 mol) and concentrated sulfuric acid (98%, 9 ml) were mixed in methanol (150 ml) and refluxed for 24 h. After the reaction, the mixture was cooled down to room temperature and poured into ice cold water (500 ml), stirred for 20 min and filtered. The obtained solution was neutralized with saturated $NaHCO_3$ solution (200 ml) and a precipitate formed. The suspension was stored at 4 °C for 12 hours and filtered. The white product was washed with water twice (50 ml each) and dried at 40 °C under reduced pressure for 12 h to yield pure methyl 2-methylquinoline-6-carboxylate **S9** (13.39 g, 69.2). m.p. 103 °C. ^{1}H NMR (DMSO-d_6, 400.1 MHz): δ 8.62 (d, J = 2.0, 1H), 8.44 (d, J = 8.5, 1H), 8.15 (dd, J = 8.8, 2.0, 1H), 7.99 (d, J = 8.8, 1H), 7.51 (d, J = 8.5, 1H), 3.91 (s, 3H), 2.68 (s, 3H). ^{13}C NMR (DMSO-d_6, 100.6 MHz, ppm): δ 165.9, 161.7, 149.1, 137.5, 130.7, 128.7, 128.4, 126.5, 125.5, 123.1, 52.3, 25.1. IR (ATR, cm^{-1}): λ_{max} 3028, 3000, 2953, 1705, 1439, 1275, 815, 790, 753, 639.

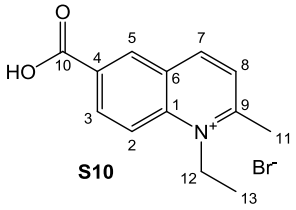


[4] Bottino, F. A.; Pasquale, G. D.; Pollicino, A.; Recca, A.; Staniland, P. A. *J. Heterocycl. Chem.* **1989**, 26, 929



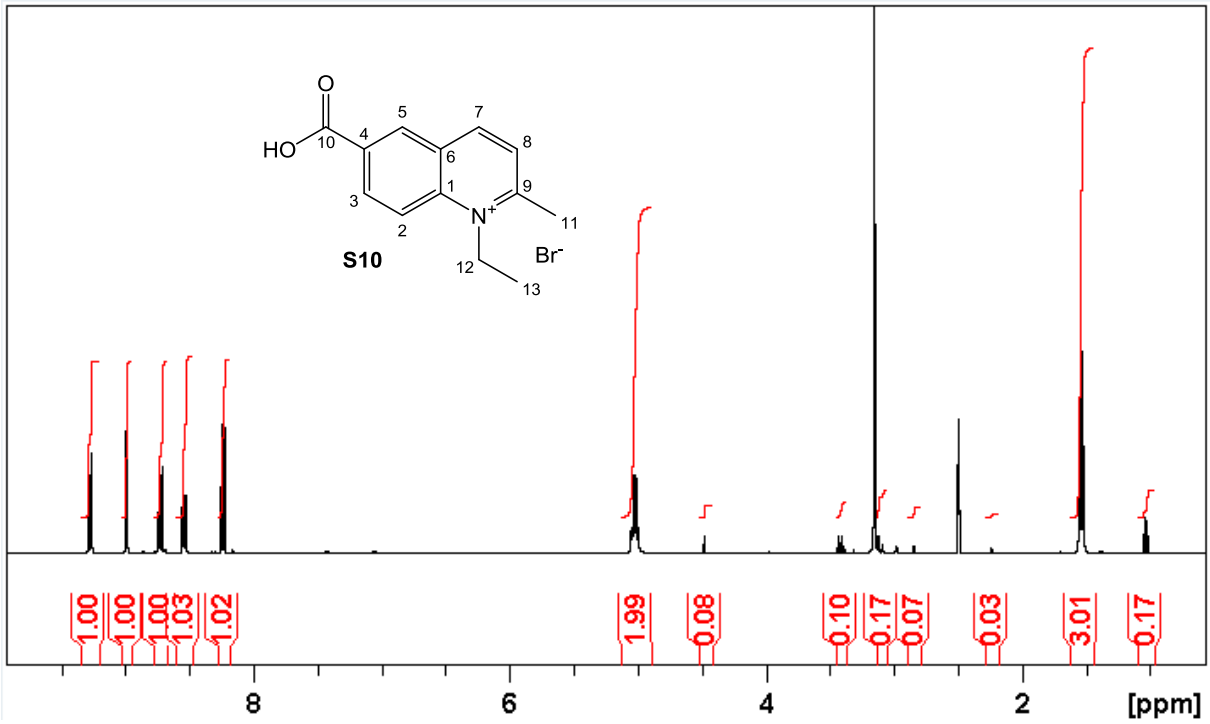
S9 ^{1}H and ^{13}C{^{1}H} NMR (DMSO-d$_6$)

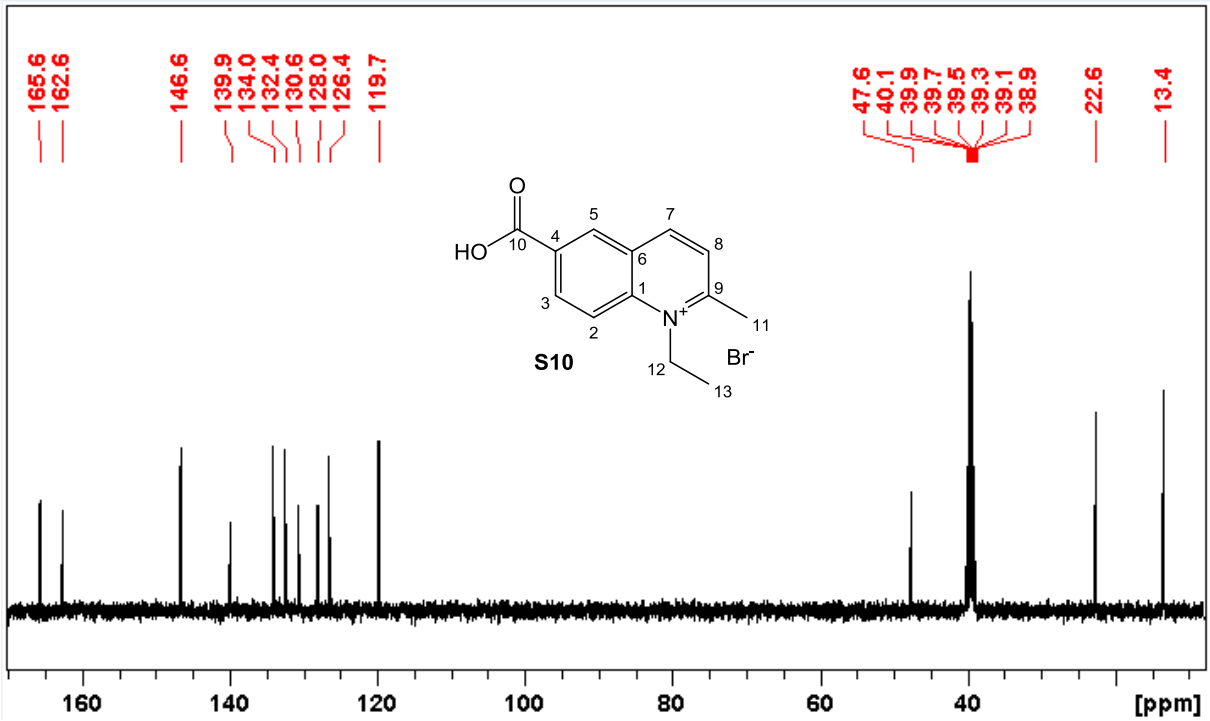
1.3 6-Carboxy-1-ethyl-2-methylquinolin-1-ium bromide (S10)

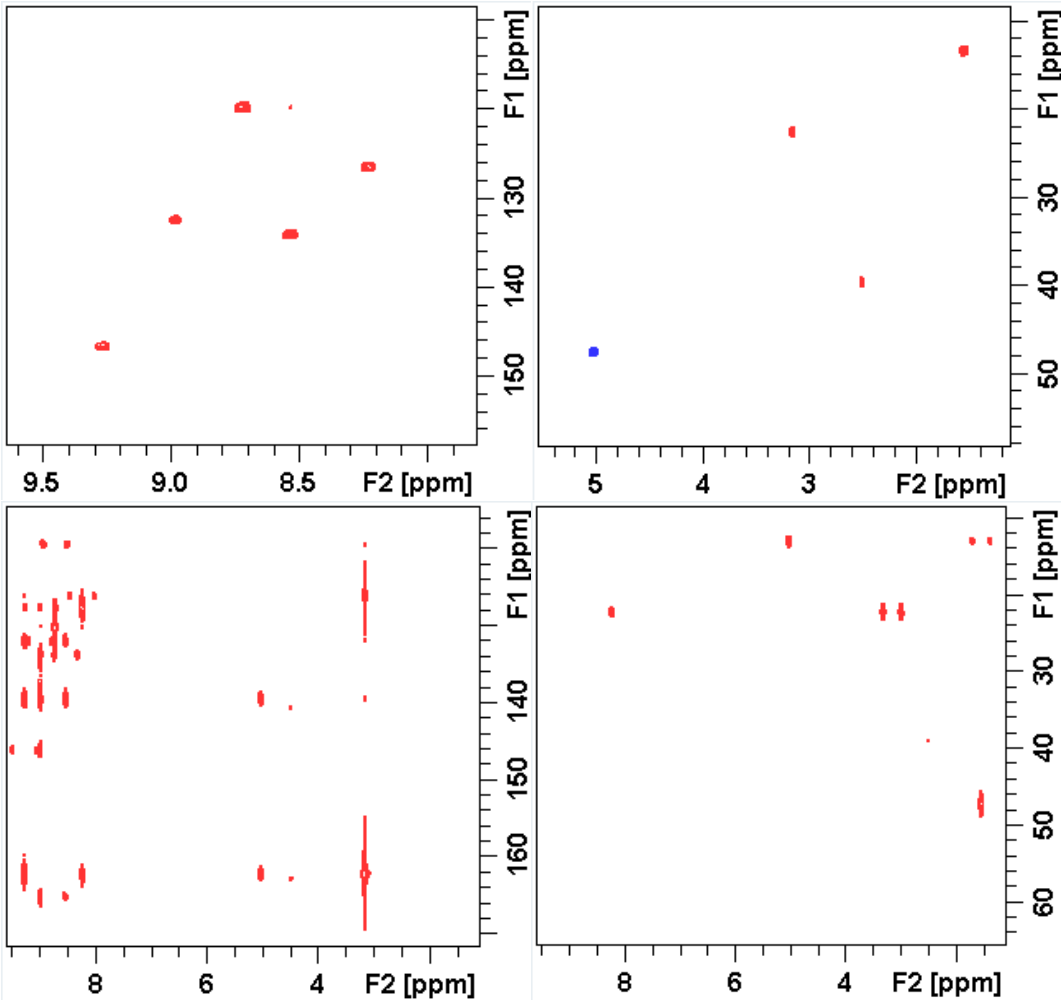


Methyl 2-methylquinoline-6-carboxylate **S9** (0.118 mol, 23.8 g) and ethyl *p*-toluene sulfonate (0.19 mol, 38.0 g) were combined in a dry flask and degassed by three cycles of vaccum pumping and argon ventilation. The reactants were heated to 140 °C under argon for 18 h. The melt was cooled to room temperature. Subsequently, the partially crystalline suspension was dissolved in chloroform (350 ml) and extracted with water four times (4 x 50 ml). The combined water phase was washed with chloroform (8 x 50 ml) in order to remove pink-colored impurities. Then, the water was completely removed by distillation under reduced pressure. For the ester cleavage, the light orange and highly viscous residue was dissolved in aqueous HBr (48 %, 30 ml) and heated to 140 °C for 2 h. Then, the aqueous HBr was completely removed by distillation under reduced pressure yielding an amorphous solid after 2 h. For further purification, the solid was dissolved in hot ethanol (80 ml) and stored at 0 °C for 24 h. The precipitated light pink-coloured crystals **S10** were isolated by filtration, washed with ethanol trice (30 ml) and dried under reduced pressure at 40 °C (12.3 g, 35 %). m.p. 256 °C. d.p. 283 °C. ^{1}H NMR (DMSO-d$_6$, 400.1 MHz): δ 13.80 (br, 1H, OH), 9.27 (d, J = 8.6, 1H, H-7), 8.97 (d, J = 2.0, 1H, H-5), 8.72 (d, J = 9.3, 1H, H-2), 8.53 (dd, J = 9.3, 2.0, 1H, H-3), 8.23 (d, J = 8.6, 1H, H-8), 5.02 (q, J = 7.3, 2H, H-12), 3.15 (s, 3H, H-11), 1.53 (t, J = 7.3, 3H, H-13). ^{13}C NMR (DMSO-d$_6$, 100.6 MHz): δ 165.6 (s, C-10), 162.6 (s, C-9), 146.6 (d, C-7), 139.9 (s, C-1), 134.0 (d, C-3), 132.4 (d, C-5), 130.6 (s, C-4), 128.0 (s, C-6), 126.4 (d, C-8), 119.7 (d, C-2), 47.6 (t, C-12), 22.6 (q, C-11), 13.4 (q, C-13). HMBC correlations: H-2 → C-(4, 6), H-3 → C-(1, 5, 10), H-5 → C-(1, 3, 7, 10), H-7 → C-(1, 5, 9), H-8 → C-(6, 9, 11), H-11 → C-(8, 9), H-12 → C-(1, 9, 13). HR-MS(ESI-QTOF): calculated for $C_{13}H_{14}NO_2$ [M-Br]$^{+}$: 216.1019. Found: 216.1018. Elemental analysis: calculated for $C_{13}H_{14}NO_2Br$: C, 52.72

%; H, 4.76 %; N, 4.73 %; O, 10.80%; Br, 26.98 %. Found: C, 52.56 %; H, 4.81 %; N, 4.75 %; O, 10.97 %; Br, 26.87 %. IR (ATR, cm^{-1}): λ_{max} 3034, 2754, 1701, 1599, 1374, 1245, 1192, 1163, 828, 774.

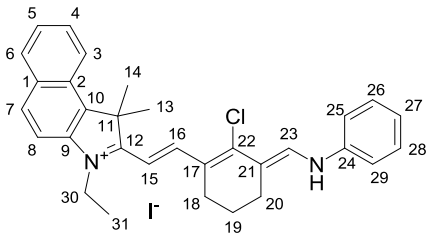






S10 ^{1}H, ^{13}C{^{1}H}, HSQC and HMBC NMR (DMSO-d$_6$)

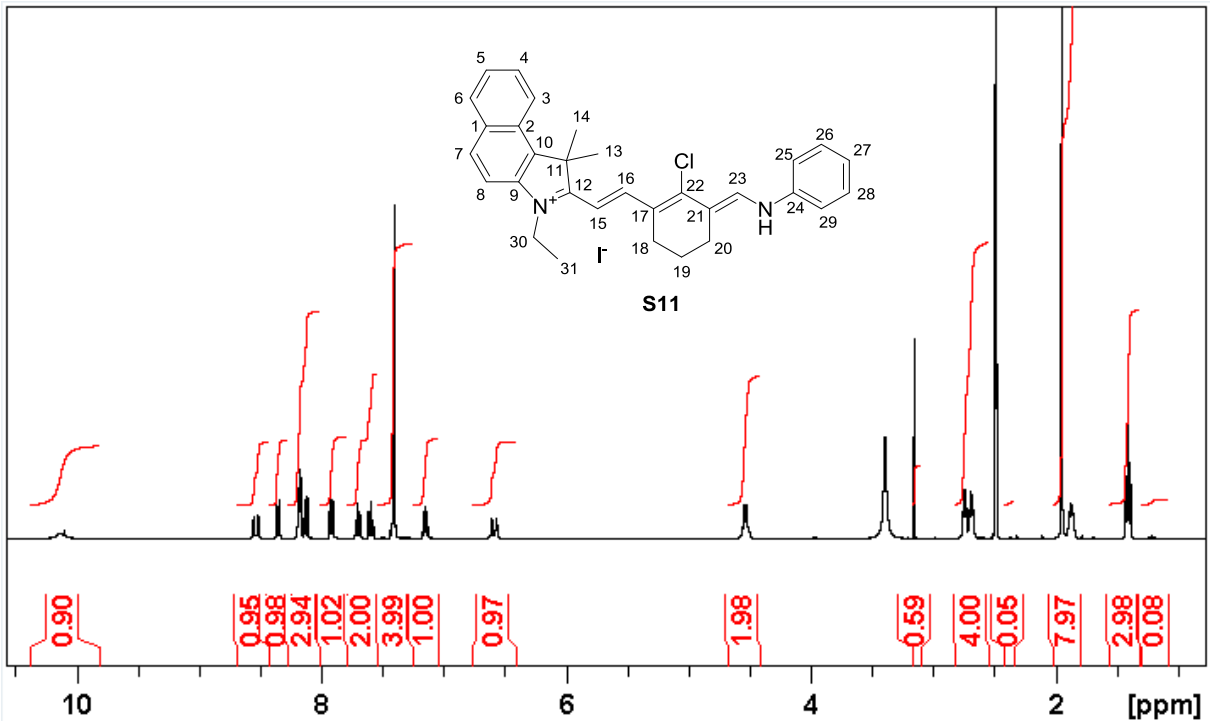
1.4 2-(2-(2-Chloro-3-((phenylamino)methylene)cyclohex-1-en-1-yl)vinyl)-3-ethyl-1,1-dimethyl-1*H*-benzo[e]indol-3-ium iodide (S11)

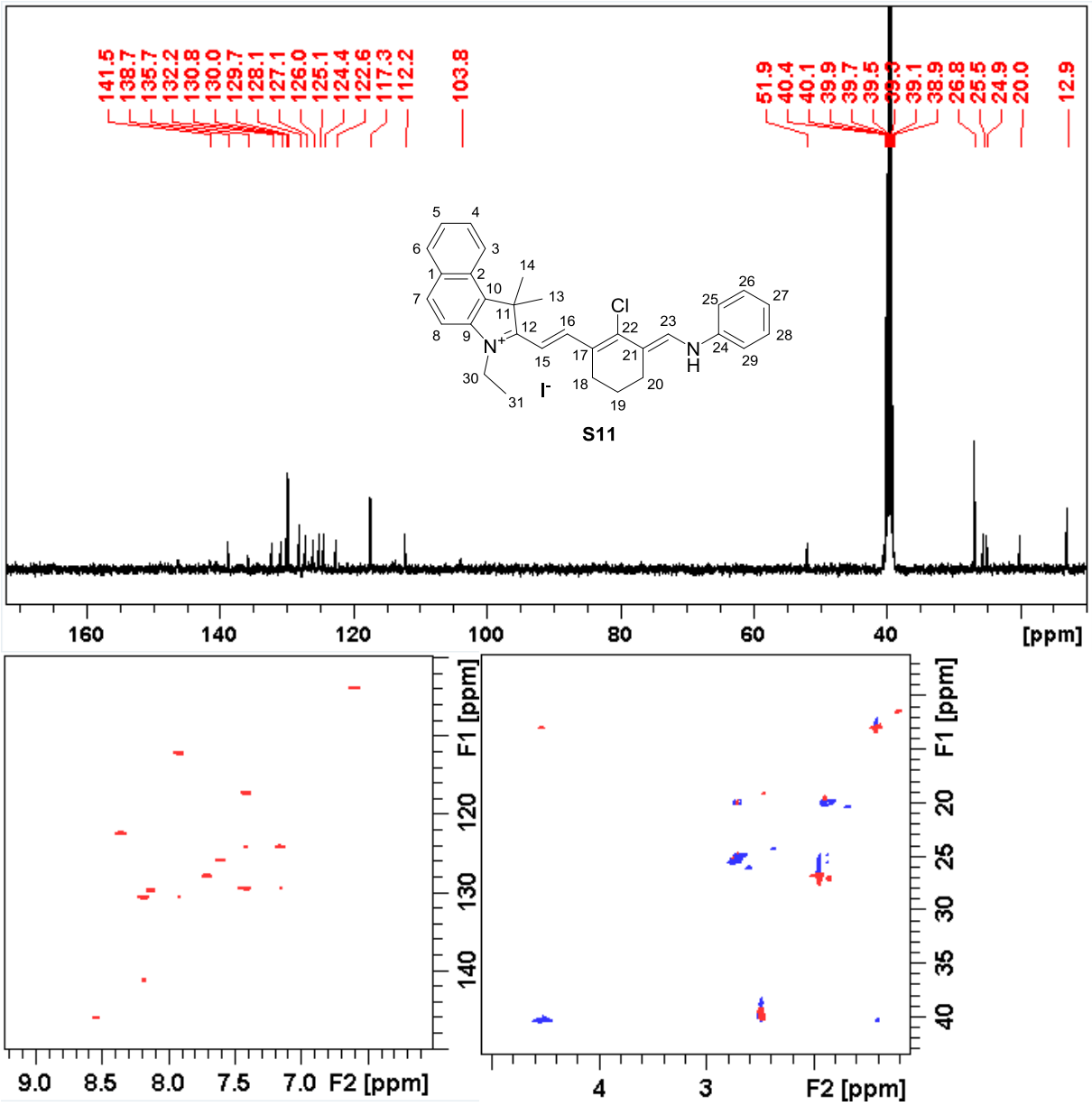


S11

A solution of 3-ethyl-1,1,2-trimethyl-1*H*-benzo[e]indol-3-ium iodide **S1** (20 mmol, 7.3 g) and *N*-((2-chloro-3-((phenylimino)methyl)cyclohex-2-en-1-ylidene)methyl)aniline hydrochloride **S6** (22 mmol, 7.9 g) in anhydrous ethanol (160 ml) were stirred at 80 °C for 20 h. After the reaction, the solution was cooled to 4 °C and unreacted starting material was removed. The filtrate was stored at 4 °C for 12 h. Finally, the product was collected by filtration. For further purification, the residue was washed with cold ethanol three times (30 ml) and dried under reduced pressure at 40 °C to yield shiny green crystals **S11** (4.05 g, 36%). m.p. 227 °C. d.p. 240 °C. ^{1}H NMR (DMSO-d$_6$, 400.1 MHz): δ 10.13 (br, 1H, NH), 8.54 (d, J = 14.8, 1H, H-16), 8.35 (d, J = 8.2, 1H, H-3), 8.18 (d, J = 8.8, 1H, H-7), 8.17 (d, J = 14.7, 1H, H-23), 8.12 (d, J = 8.9, 1H, H-6), 7.92 (d, J = 8.8, 1H, H-8), 7.71 (m, 1H, H-4), 7.61 (m, 1H, H-5), 7.41 (m, 2H,

H-26, 28), 7.41 (m, 2H, H-25, 29), 7.15 (m, 1H, H-27), 6.59 (d, *J* = 14.8, 1H, H-15), 4.53 (q, *J* = 7.1, 2H, H-35), 2.74 (t, *J* = 6.1, 2H, H-18), 2.69 (t, *J* = 6, 2H, H-20), 1.95 (s, 6H, H-13, 14), 1.87 (m, 2H, H-19), 1.41 (t, *J* = 7.1, 3H, H-36). ^{13}C NMR (DMSO-d_6, 100.6 MHz): δ 177.3 (s, C-12), 148.7 (s, C-22), 146.2 (d, C-16), 141.5 (d, C-23), 140.4 (s, C-24), 138.7 (s, C-9), 135.7 (s, C-10), 132.2 (s, C-1), 130.8 (d, C-7), 130.0 (d, C-6), 129.7 (d, C-26, 28), 128.1 (d, C-4), 127.1 (s, C-2), 126.0 (d, C-5), 125.1 (s, C-17), 124.4 (d, C-27), 122.6 (d, C-3), 117.3 (s, C-25, 29), 113.6 (s, C-21), 112.2 (d, C-8), 103.8 (d, C-15), 51.9 (s, C-11), 40.4 (t, C-35), 26.8 (q, C-13, 14), 25.4 (t, C-18), 24.9 (t, C-20), 20.0 (t, C-19), 12.9 (q, C-36). HMBC correlations: H-3 → C-(1, 2w, 5, 10), H-4 → C-(2, 6), H-5 → C-(1, 3), H-6 → C-(2, 4, 7), H-7 → C-(1w, 2, 6, 8w, 9), H-8 → C-(1, 10), H-13, 14 → C-(10, 11, 12, 13, 14), H-15 → C-(11, 17), H-16 → C-(12, 18, 22), H-18 → C-(16w, 17, 19, 20, 22), H-19 → C-(17, 21), H-20 → C-(18, 19, 21, 22, 23w), H-23 → C-(20, 22, 24), H-26, 28 → C-(24, 26, 28), H-27 → C-(25, 26, 28, 29), H-35 → C-(9, 12, 31), H-36 → C-(30). DQF-COSY correlations: H-3 → H-(4), H-4 → H-(3, 5), H-5 → H-(4, 6), H-6 → H-(5), H-7 → H-(8), H-8 → H-(7), H-15 → H-(16), H-16 → H-(15), H-18 → H-(19), H-19 → H-(18, 20), H-20 → H-(19), H-26, 28 → H-(27), H-27 → H-(26, 28), H-35 → H-(36), H-36 → H-(35). HR-MS(ESI-QTOF): calculated for $C_{31}H_{32}ClN_2$ [M-I$^-$]: 467.2249. Found: 467.2254. Elemental Analysis: Calculated for $C_{31}H_{32}N_2ClI$: [C] 62.58 %; [H] 5.42 %; [N] 4.71 %; [Cl] 5.96 %, [I] 21.33 %. Found: [C] 61.79 %; [H] 5.50 %; [N] 4.69 %; [Cl] 5.90 %, [I] 20.85 %. IR (ATR, cm^{-1}): λ_{max} 3197, 2957, 2872, 2324, 1708, 1547, 1430, 1350, 1233, 1122, 738. UV-Vis: λ_{max} 669.0 nm (in ethanol).

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60
40
[ppm]

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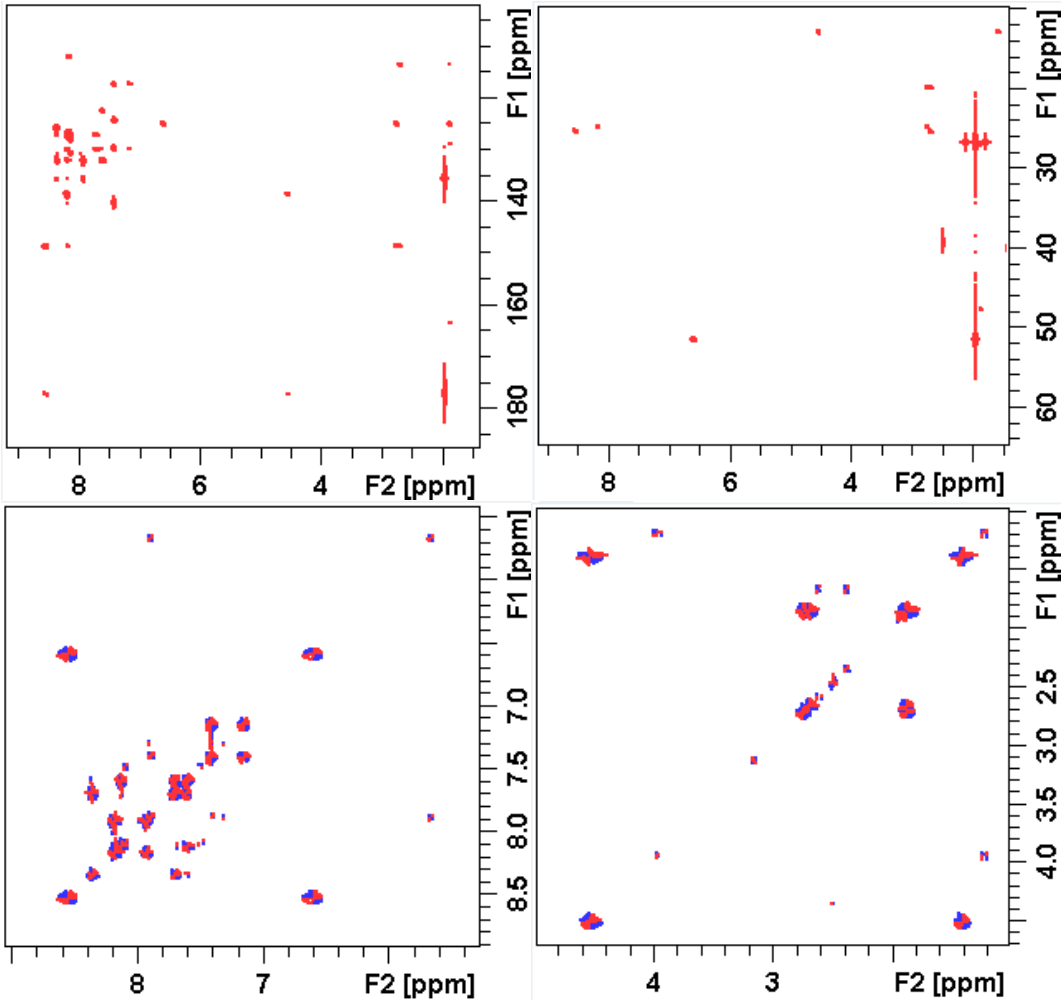
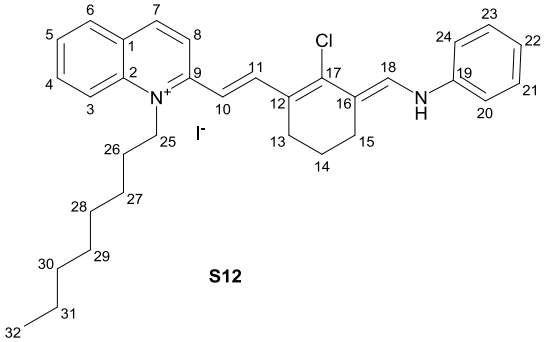


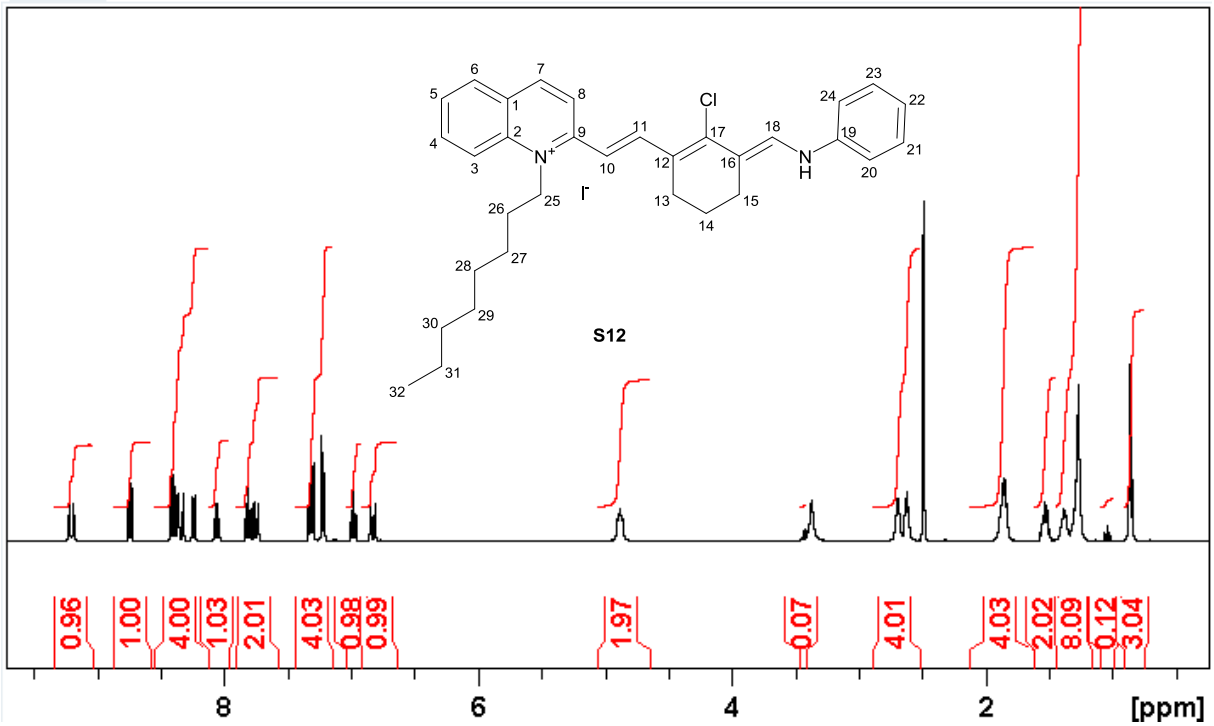
S11 ^{1}H, ^{13}C{^{1}H}, HSQC, HMBC and DQF-COSY NMR (DMSO-d$_6$)

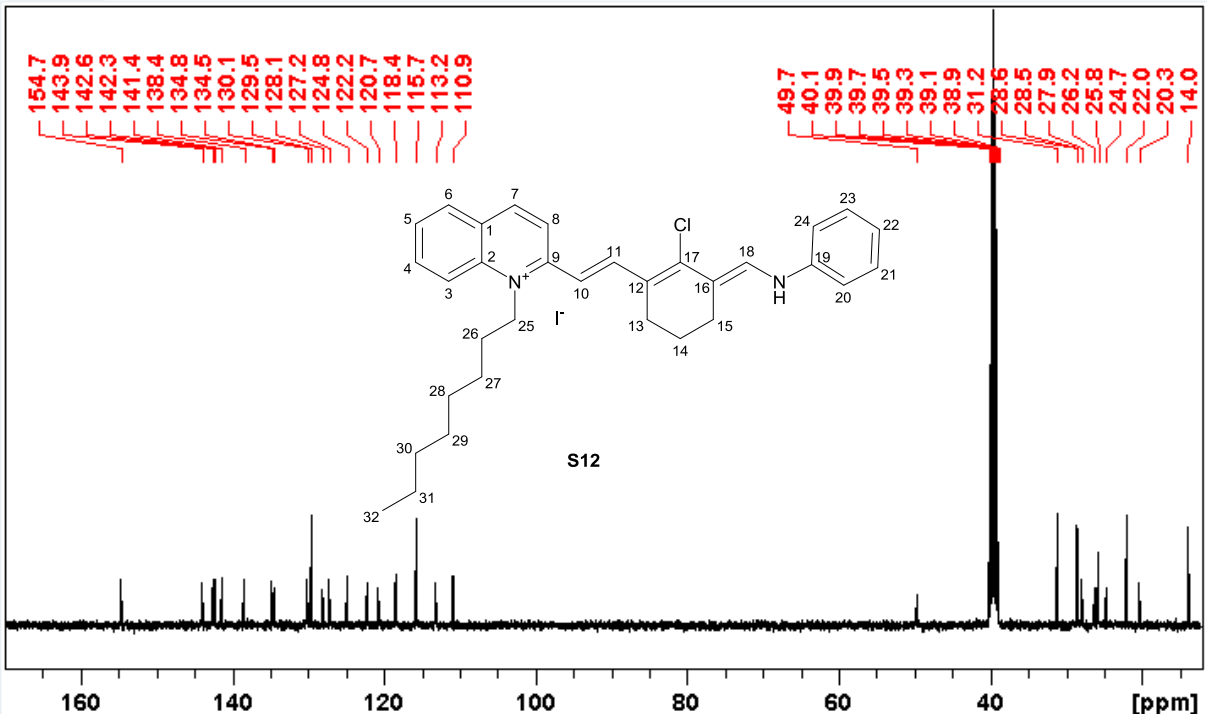
1.5 2-(2-(2-Chloro-3-((phenylamino)methylene)cyclohex-1-en-1-yl)vinyl)-1-octylquinolin-1-ium iodide (S12)



2-Methyl-1-octylquinolin-1-ium iodide **S3** (20 mmol, 7.66 g) and *N*-((2-chloro-3-((phenylimino)methyl) cyclohex-2-en-1-ylidene)methyl)aniline hydrochloride **S6** (22 mmol, 7.90 g) were dissolved in anhydrous ethanol (150 ml) and heated to 80 °C for 18 h. Afterwards, the crude product was isolated by hot filtration, washed with ethanol (50 ml) and dried under reduced pressure at 40 °C for 20 h to yield green shiny powder **S12** (7.46 g, 60.8%). d.p. 250 °C. ^{1}H NMR (DMSO-d$_6$, 400.1 MHz): δ 9.20 (d, J = 12.9, 1H, NH), 8.74 (d, J = 9.2, 1H, H-7), 8.40 (d, J = 9.2, 1H, H-8), 8.38 (d, J = 9.5, 1H, H-3), 8.34 (d, J = 14.9, 1H, H-11), 8.24 (dd, J = 8.1, 1.1, 1H, H-6), 8.06 (m, 1H, H-4), 7.81 (m, 1H, H-5), 7.75 (d, J = 12.9, 1H, H-18), 7.31 (m, 2H, H-21, 23), 7.22 (m, 2H, H-20, 24), 6.98 (m, 1H, H-22), 6.82 (d,

J = 14.9, 1H, H-10), 4.88 (m, 2H, H-25), 2.69 (t, *J* = 5.9, 2H, H-13), 2.62 (t, *J* = 5.9, 2H, H-15), 1.85 (m, 2H, H-26), 1.85 (m, 2H, H-14), 1.53 (m, 2H, H-27), 1.38 (m, 2H, H-28), 1.28 (m, 2H, H-29), 1.26 (m, 2H, H-31), 1.26 (m, 2H, H-30), 0.86 (t, *J* = 7.0, 3H, H-32). ^{13}C NMR (DMSO-d_6, 100.6 MHz): δ 154.7 (s, C-9), 143.9 (d, C-11), 142.6 (s, C-17), 142.3 (d, C-7), 141.4 (s, C-19), 138.4 (s, C-2), 134.8 (d, C-18), 134.5 (d, C-4), 130.1 (d, C-6), 129.5 (d, C-21, 23), 128.1 (d, C-5), 127.2 (s, C-1), 124.8 (s, C-12), 122.2 (d, C-22), 120.7 (d, C-8), 118.4 (d, C-3), 115.7 (d, C-20, 24), 113.2 (d, C-10), 110.9 (s, C-16), 49.7 (t, C-25), 31.2 (t, C-30), 28.6 (t, C-29), 28.5 (t, C-28), 27.9 (t, C-26), 26.2 (t, C-13), 25.8 (t, C-27), 24.7 (t, C-15), 22.0 (t, C-31), 20.3 (t, C-14), 14.0 (q, C-32). HMBC correlations: H-3 → C-(1, 5), H-4 → C-(2, 6), H-5 → C-(1, 2w, 3, 4, 6w), H-6 → C-(1w, 2, 4, 7), H-7 → C-(1, 2, 6, 8w, 9), H-8 → C-(1, 9, 10w), H-10 → C-(8, 11, 12), H-11 → C-(9, 10w, 13, 17), H-13 → C-(11w, 12, 14, 15, 17), H-14 → C-(12, 13, 15, 16), H-15 → C-(13, 14, 16, 17, 18), H-18 → C-(15, 17, 19), H-20, 24 → C-(20, 22, 24), H-21, 23 → C-(19, 21, 23), H-22 → C-(20, 21w, 23w, 24), H-25 → C-(2, 9, 26, 27), H-26 → C-(25, 27, 28), H-27 → C-(25, 26, 29), H-28 → C-(27, 29, 30), H-32 → C-(30, 31) , NH → C-(16, 19w, 20, 24). DQF-COSY correlations: H-3 → H-(4), H-4 → H-(3, 5), H-5 → H-(4, 6), H-6 → H-(5), H-7 → H-(8), H-8 → H-(7), H-10 → H-(11), H-11 → H-(10), H-13 → H-(14), H-14 → H-(13, 15), H-15 → H-(14), H-18 → NH, H-20, 24 → H-(21, 23), H-21, 23 → H-(20, 22, 24), H-22 → H-(21, 23), H-25 → H-(26), H-26 → H-(25, 27), H-27 → H-(26, 28), H-28 → H-(27, 29), H-31 → H-(32), H-32 → H-(31), NH → H-(18). HR-MS (ESI-QTOF): calculated for $C_{32}H_{38}ClN_2$ $[M-I]^+$: 485.2718. Found: 485.2707. Elemental analysis: calculated for $C_{32}H_{38}ClIN_2$: C, 62.70 %; H, 6.25 %; N, 4.57 %; Cl, 5.67 %; I, 20.70 %. Found: C, 62.54 %; H, 6.25 %; N, 4.52 %; Cl, 5.69%; I, 20.51 %. IR (ATR, cm^{-1}): λ_{max} 3194, 2925, 2853, 2524, 1627, 1479, 1354, 1219, 1147, 1050, 748. UV-Vis: λ_{max} 627 nm (in ethanol).

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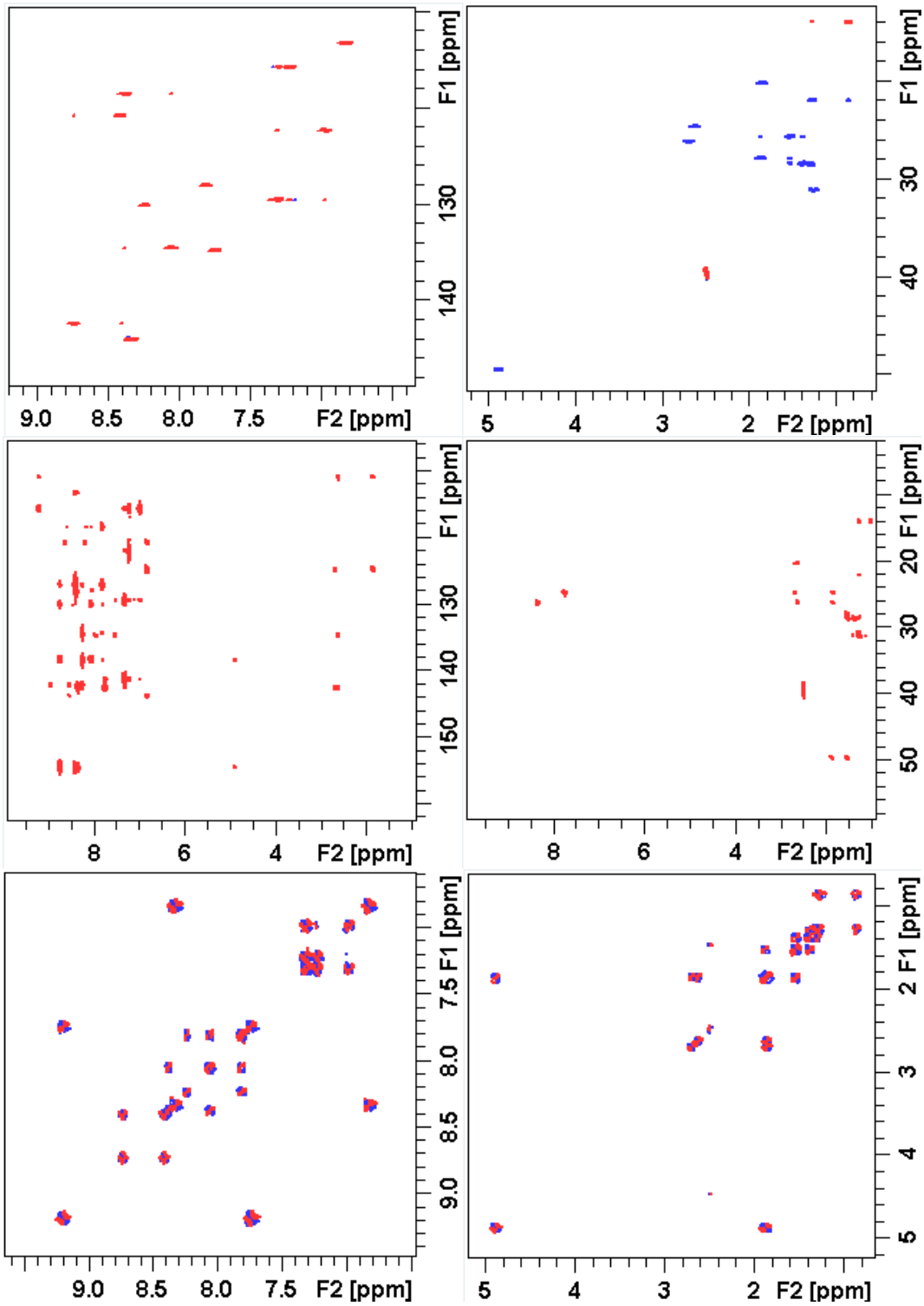
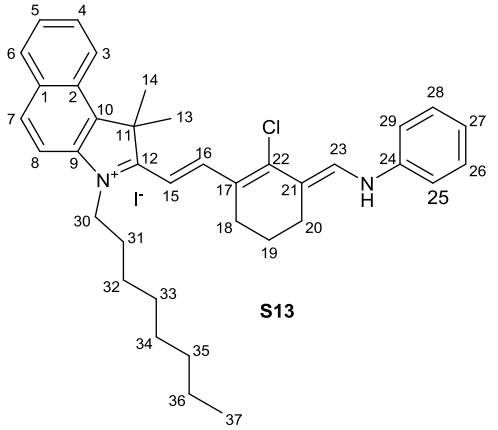
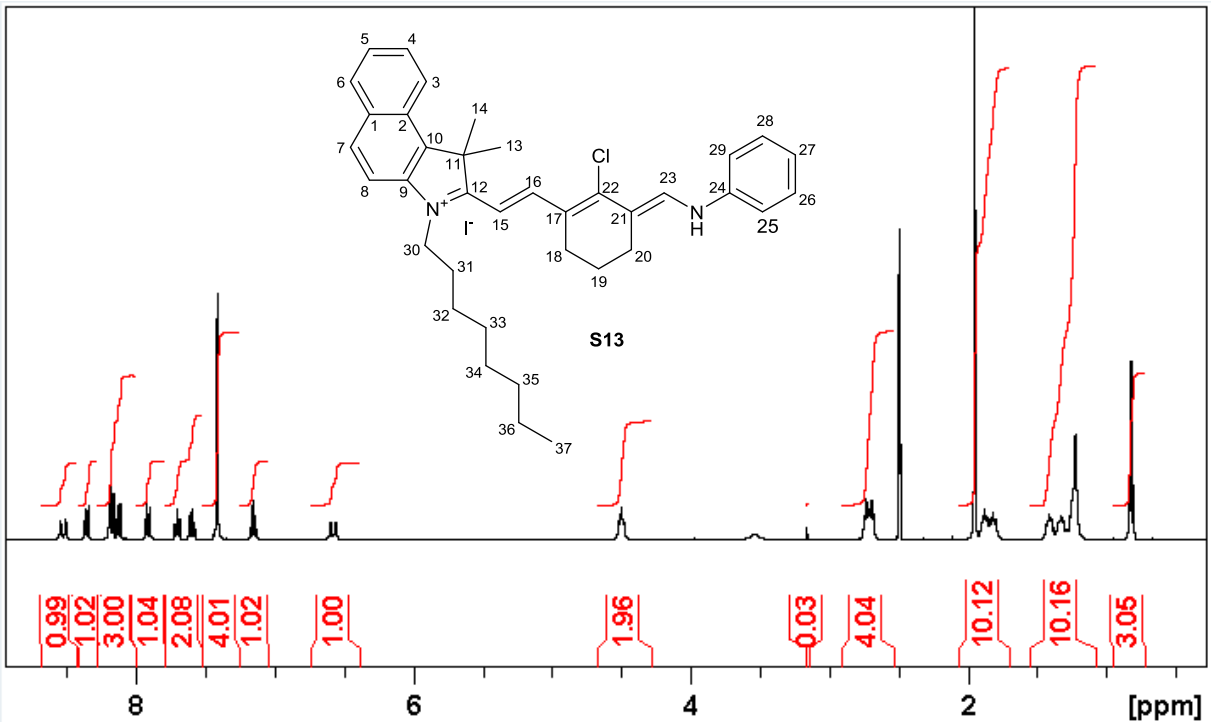


S12 ^{1}H, ^{13}C{^{1}H}, HSQC, HMBC and DQF-COSY NMR (DMSO-d_6)

1.6 2-(2-(2-Chloro-3-((phenylamino)methylene)cyclohex-1-en-1-yl)vinyl)-1,1-dimethyl-3-octyl-1*H*-benzo[e]indol-3-ium iodide (S13)



1,1,2-Trimethyl-3-octyl-1*H*-benzo[e]indol-3-ium iodide **S2** (20 mmol, 7.66 g) and *N*-((2-chloro-3-((phenylimino)methyl)cyclohex-2-en-1-ylidene)methyl)aniline hydrochloride **S6** (22 mmol, 7.90 g) were dissolved in anhydrous ethanol (150 ml) and heated to 80 °C for 20 h. Subsequently, the reaction mixture was slowly cooled to room temperature and then stored at 4 °C for 20 h. Precipitated starting material was removed by filtration and the filtrate was stored at 4 °C for an additional 48 h. Finally, the crude product precipitated and was isolated by filtration. Further purification by recrystallization from methanol three times (50 ml) and drying under reduced pressure at 40 °C yielded shiny green crystals **S13** (3.97 g, 29.2%). d.p. 218 °C. ^{1}H NMR (DMSO-d$_6$, 400.1 MHz): δ 10.15 (s(br), 1H, NH), 8.53 (d, *J* = 14.9, 1H, H-16), 8.35 (d, *J* = 8.5, 1H, H-3), 8.18 (s, 1H, H-23), 8.17 (d, *J* = 8.9, 1H, H-7), 8.12 (d, *J* = 8.2, 1H, H-6), 7.91 (d, *J* = 8.9, 1H, H-8), 7.70 (m, 1H, H-4), 7.60 (m, 1H, H-5), 7.41 (m, 2H, H-26, 28), 7.41 (m, 2H, H-25, 29), 7.15 (m, 1H, H-27), 6.58 (d, *J* = 14.9, 1H, H-15), 4.49 (t, *J* = 7.4, 2H, H-30), 2.73 (m, 2H, H-18), 2.69 (m, 2H, H-20), 1.95 (s, 6H, H-13, 14), 1.88 (m, 2H, H-19), 1.81 (m, 2H, H-31), 1.39 (m, 2H, H-32), 1.32 (m, 2H, H-33), 1.23 (m, 2H, H-34), 1.22 (m, 2H, H-36), 1.21 (m, 2H, H-35), 0.82 (t, *J* = 6.9, 3H, H-37). ^{13}C NMR (DMSO-d$_6$, 100.6 MHz): δ 177.7 (s, C-12), 148.9 (s, C-22), 146.1 (d, C-16), 141.5 (d, C-23), 140.4 (s, C-24), 139.1 (s, C-9), 135.5 (s, C-10), 132.1 (s, C-1), 130.7 (d, C-7), 129.9 (d, C-6), 129.7 (d, C-26, 28), 128.1 (d, C-4), 127.1 (s, C-2), 126.0 (d, C-5), 125.0 (s, C-17), 124.4 (d, C-27), 122.6 (d, C-3), 117.4 (d, C-25, 29), 113.6 (s, C-21), 112.4 (d, C-8), 104.0 (d, C-15), 51.8 (s, C-11), 44.9 (t, C-30), 31.1 (t, C-35), 28.6 (t, C-34), 28.5 (t, C-33), 28.2 (q, C-13, 14), 27.6 (t, C-31), 25.9 (t, C-32), 25.5 (t, C-18), 24.9 (t, C-20), 22.0 (t, C-36), 20.0 (t, C-19), 13.9 (q, C-37). HMBC correlations: H-3 → C-(1, 5, 10), H-4 → C-(2, 6), H-5 → C-(1, 3), H-6 → C-(2, 4 7), H-7 → C-(2, 6, 9), H-8 → C-(1, 10), H-13, 14 → C-(10, 11, 12, 13, 14), H-15 → C-(11, 17), H-16 → C-(12, 18, 22), H-18 → C-(17, 19, 20, 22), H-19 → C-(17, 18, 20, 21), H-20 → C-(18, 19, 21, 22), H-23 → C-(20, 22, 24), H-25, 29 → C-(25, 27, 29), H-26, 28 → C-(24, 26, 28), H-27 → C-(25, 26, 28, 29), H-30 → C-(9, 12, 31, 32), H-31 → C-(30), H-32 → C-(33, 34), H-35 → C-(36, 37), H-36 → C-(35, 37), H-37 → C-(35, 36). DQF-COSY correlations: H-3 → H-(4), H-4 → H-(3, 5), H-5 → H-(4, 6), H-6 → H-(5), H-7 → H-(8), H-8 → H-(7), H-15 → H-(16), H-16 → H-(15), H-18 → H-(19), H-19 → H-(18, 20), H-20 → H-(19), H-26, 28 → H-(27), H-27 → H-(26, 28), H-30 → H-(31), H-31 → H-(30, 32), H-32 → H-(31, 33), H-33 → H-(32), H-36 → H-(37), H-37 → H-(36). HR-MS (ESI-QTOF): calculated for $C_{37}H_{44}ClN_2$ [M-I]$^{+}$: 551.3188. Found: 551.3189. Elemental analysis: calculated for $C_{37}H_{44}ClIN_2$: C, 65.44 %; H, 6.53 %; N, 4.12 %; Cl, 5.22 %; I, 18.69 %. Found: C, 56.29 %; H, 5.66 %; N, 3.49 %. IR (ATR, cm^{-1}): λ_{max} 2921, 2853, 1624, 1548, 1430, 1231, 892, 745. UV-Vis: λ_{max} 670 nm (in ethanol).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3.05
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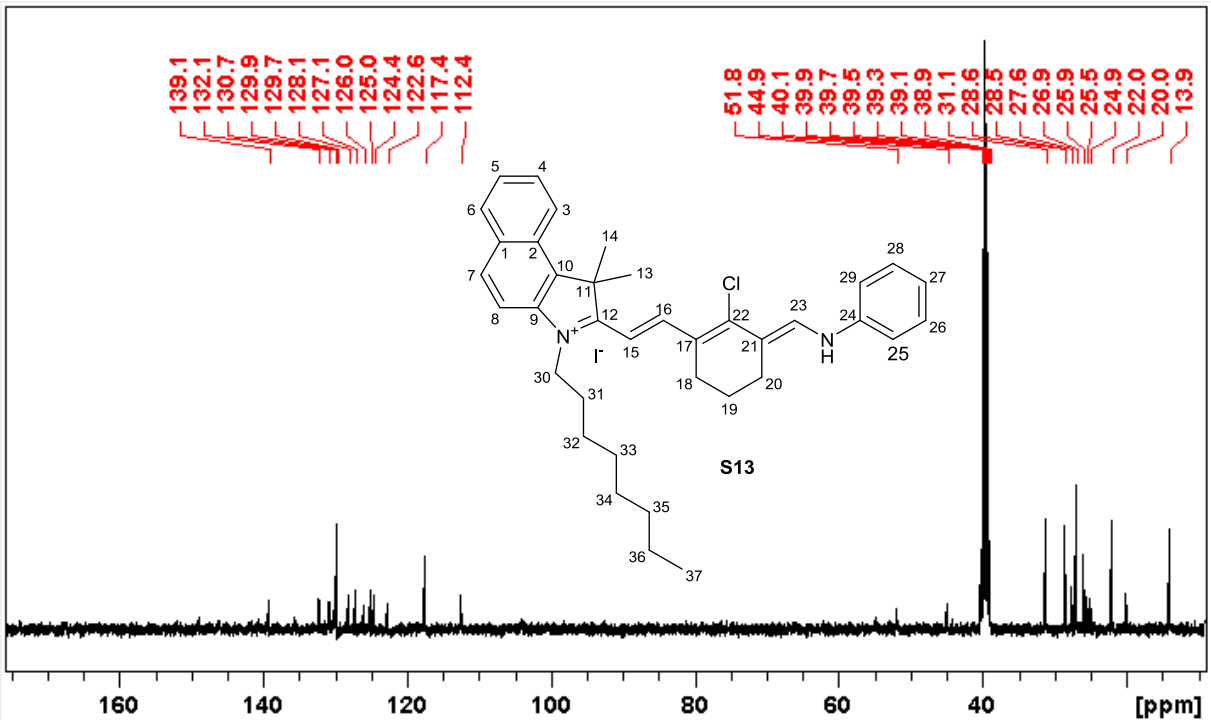
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44.9
40.1
39.9
39.7
39.5
39.3
39.1
38.9
31.1
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28.5
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26.9
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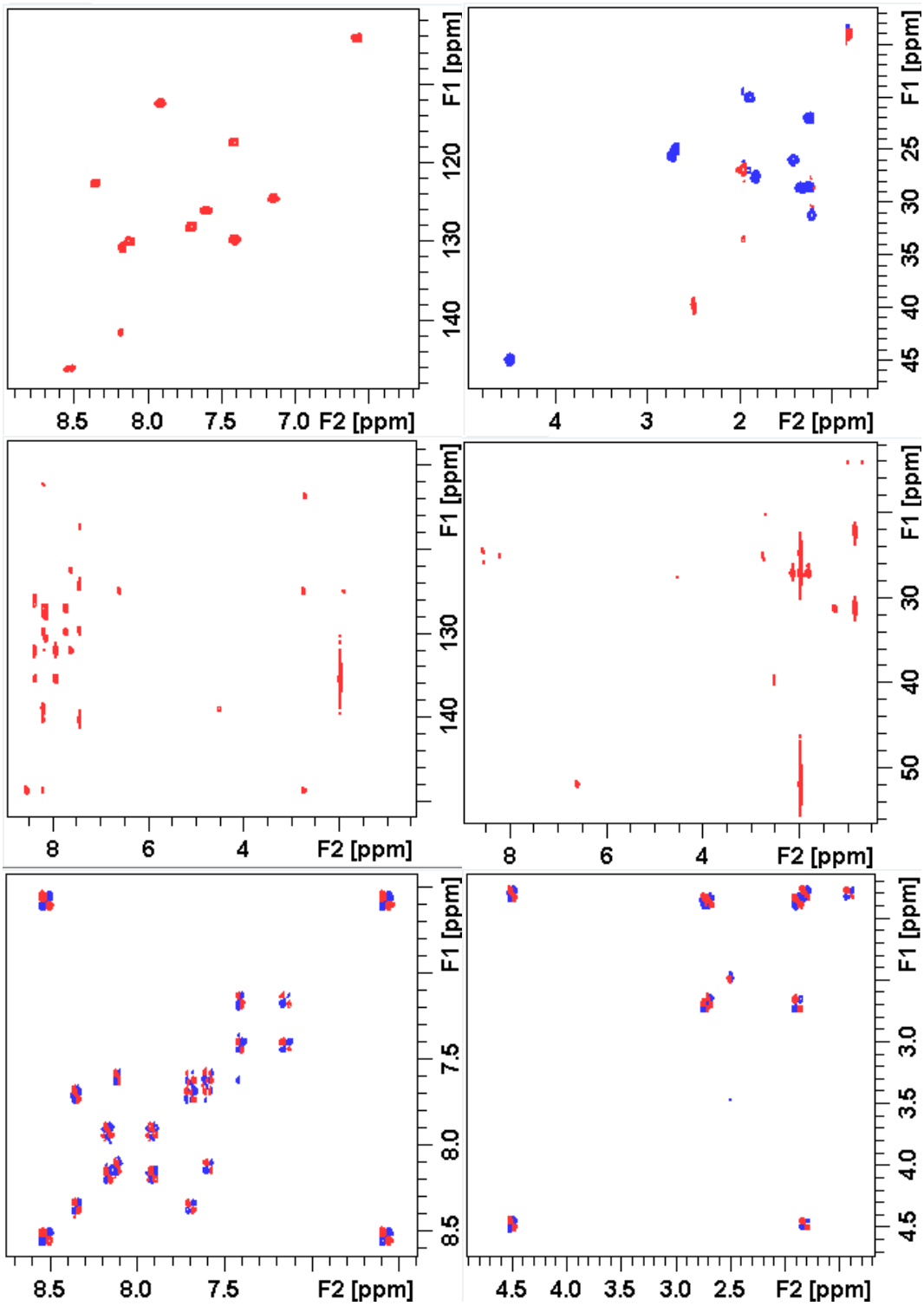
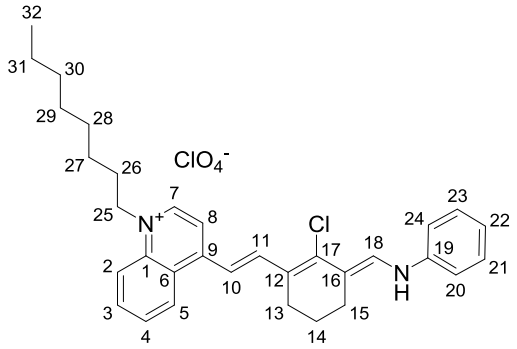


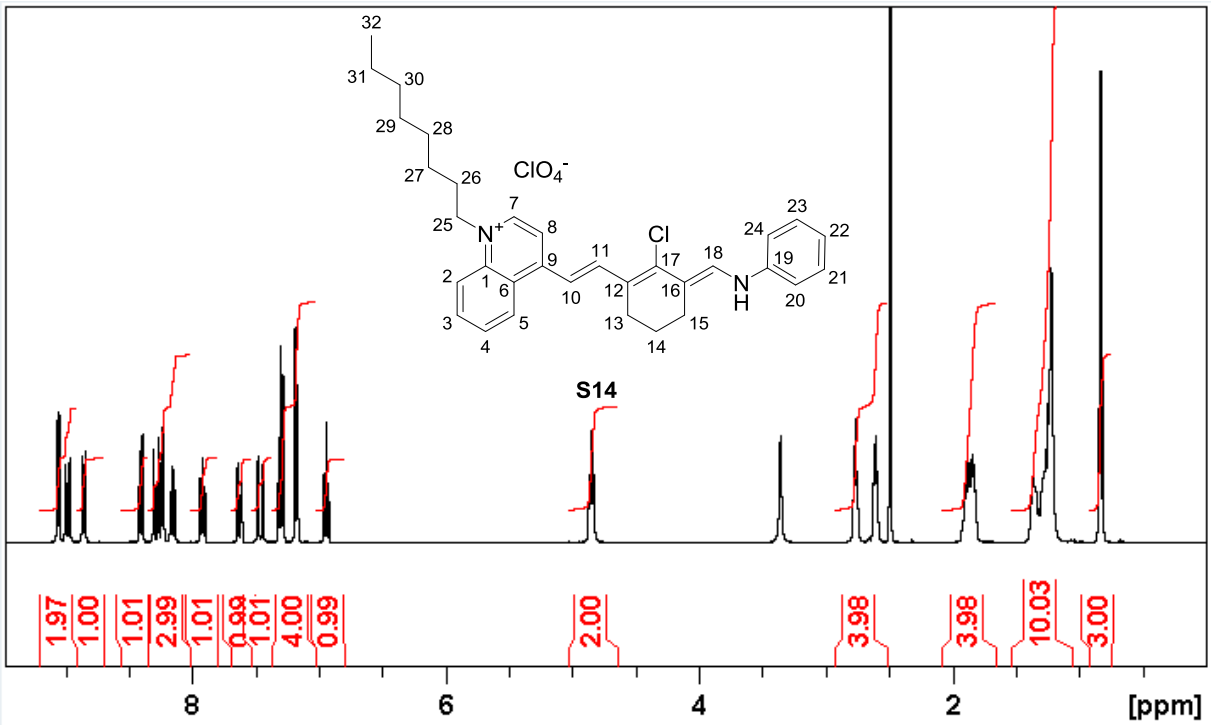
S13 ^{1}H, ^{13}C{^{1}H}, HSQC, HMBC and DQF-COSY NMR (DMSO-d_6)

1.7 4-(2-(2-Chloro-3-((phenylamino)methylene)cyclohex-1-en-1-yl)vinyl)-1-octylquinolin-1-ium iodide (S14)



S14

4-Methyl-1-octylquinolin-1-ium iodide **S4** (26.5 mmol, 10.15 g) and *N*-((2-chloro-3-((phenylimino)methyl)cyclohex-2-en-1-ylide-ne)methyl)aniline hydrochloride **S6** (29.1 mmol, 10.46 g) were dissolved in anhydrous ethanol (150 ml) and heated to 80 °C for 48 h. After the reaction, the solution was cooled to room temperature and the product precipitated. The precipitate was collected by filtration, washed with cold ethanol twice (50 ml each) and dried under reduced pressure at 40 °C for 20 h to yield green shiny crystals **S14** (10.87 g, 70%). d.p. 263 °C. ^{1}H NMR (DMSO-d$_6$, 400.1 MHz): δ 9.05 (d, *J* = 6.8, 1H, H-7), 8.98 (d, *J* = 12.7, 1H, NH), 8.85 (dd, *J* = 8.9, 1.0, 1H, H-5), 8.40 (d, *J* = 8.9, 1H, H-2), 8.28 (d, *J* = 15.1, 1H, H-11), 8.23 (d, *J* = 6.8, 1H, H-8), 8.15 (m, 1H, H-3), 7.92 (m, 1H, H-4), 7.62 (d, *J* = 12.7, 1H, H-18), 7.46 (d, *J* = 15.1, 1H, H-10), 7.29 (m, 2H, H-21, 23), 7.17 (m, 2H, H-20, 24), 6.94 (m, 1H, H-22), 4.85 (t, *J* = 7.4, 2H, H-25), 2.76 (t, *J* = 5.9, 2H, H-13), 2.60 (t, *J* = 5.9, 2H, H-15), 1.88 (m, 2H, H-26), 1.84 (m, 2H, H-14), 1.36 (m, 2H, H-27), 1.32 (m, 2H, H-28), 1.23 (m, 2H, H-29), 1.22 (m, 2H, H-31), 1.20 (m, 2H, H-30), 0.83 (t, *J* = 6.9, 3H, H-32). ^{13}C NMR (DMSO-d$_6$, 100.6 MHz): δ 152.4 (s, C-9), 146.2 (d, C-7), 141.8 (s, C-19), 140.2 (s, C-17), 140.2 (d, C-11), 137.7 (s, C-1), 134.7 (d, C-3), 132.8 (d, C-18), 129.5 (d, C-21, 23), 128.6 (d, C-4), 126.4 (d, C-5), 126.2 (s, C-6), 125.7 (s, C-12), 121.6 (d, C-22), 118.9 (d, C-2), 116.1 (d, C-10), 115.3 (d, C-20, 24), 114.7 (d, C-8), 110.7 (s, C-16), 55.9 (t, C-25), 31.0 (t, C-30), 29.3 (t, C-26), 28.5 (t, C-29), 28.5 (t, C-28), 26.4 (t, C-13), 25.8 (t, C-27), 24.8 (t, C-15), 22.0 (t, C-31), 20.4 (t, C-14), 13.9 (q, C-32). HMBC correlations: H-3 → C-(1, 5), H-4 → C-(2, 6), H-5 → C-(1, 2w, 3, 4, 6w), H-6 → C-(1w, 2, 4, 7), H-7 → C-(1, 2, 6, 8w, 9), H-8 → C-(1, 9, 10w), H-10 → C-(8, 11, 12), H-11 → C-(9, 10w, 13, 17), H-13 → C-(11w, 12, 14, 15, 17), H-14 → C-(12, 13, 15, 16), H-15 → C-(13, 14, 16, 17, 18), H-18 → C-(15, 17, 19), H-20, 24 → C-(20, 22, 24), H-21, 23 → C-(19, 21, 23), H-22 → C-(20, 21w, 23w, 24), H-25 → C-(2, 9, 26, 27), H-26 → C-(25, 27, 28), H-27 → C-(25, 26, 29), H-28 → C-(27, 29, 30), H-32 → C-(30, 31), NH → C-(16, 19w, 20, 24). DQF-COSY correlations: H-3 → H-(4), H-4 → H-(3, 5), H-5 → H-(4, 6), H-6 → H-(5), H-7 → H-(8), H-8 → H-(7), H-10 → H-(11), H-11 → H-(10), H-13 → H-(14), H-14 → H-(13, 15), H-15 → H-(14), H-18 → NH, H-20, 24 → H-(21, 23), H-21, 23 → H-(20, 22, 24), H-22 → H-(21, 23), H-25 → H-(26), H-26 → H-(25, 27), H-27 → H-(26, 28), H-28 → H-(27, 29), H-31 → H-(32), H-32 → H-(31), NH → H-(18). HR-MS (ESI-QTOF): calculated for $C_{32}H_{38}ClN_2$ $[M-I]^+$: 485.2718. Found: 485.2716. Elemental analysis: calculated for $C_{32}H_{38}ClIN_2$: C, 62.70 %; H, 6.25 %; N, 4.57 %; Cl, 5.78 %; I, 20.70 %. Found: C, 62.73 %; H, 6.23 %; N, 4.52 %; Cl, 5.72 %; I, 20.46 %. IR (ATR, cm^{-1}): λ_{max} 3208, 3045, 2914, 2849, 1775, 1627, 1598, 1552, 1251, 1169, 749, 691. UV-Vis: λ_{max} 641 nm (in ethanol).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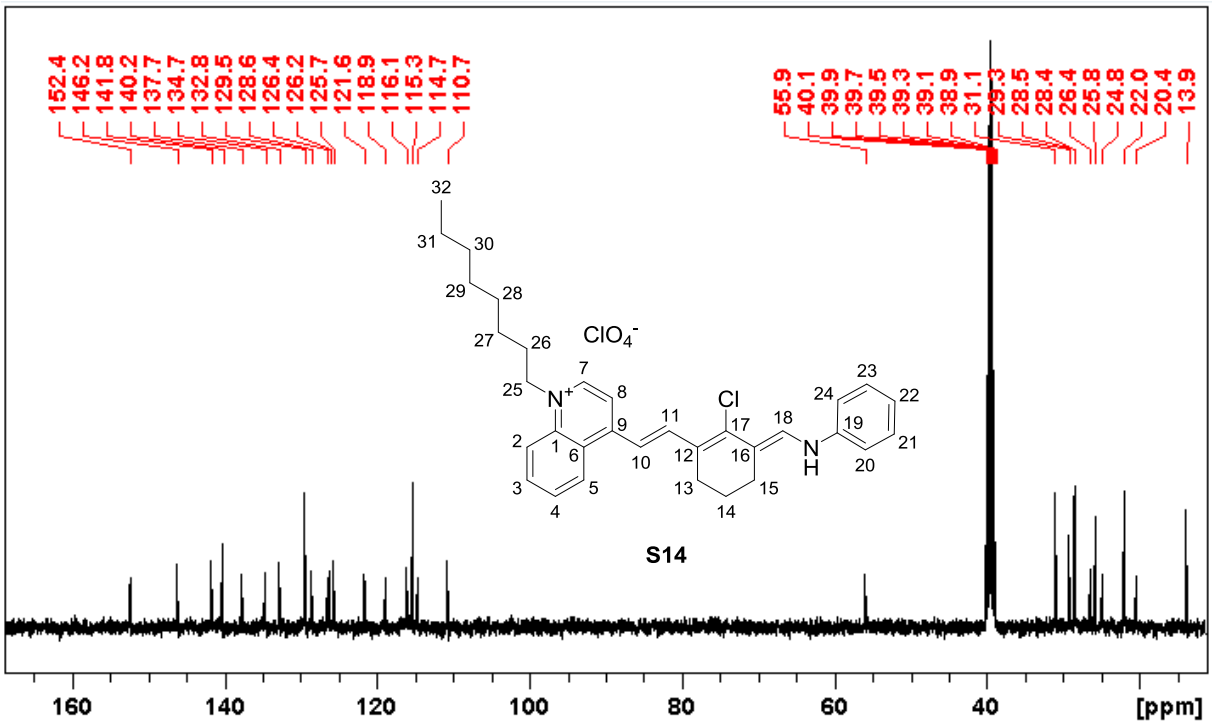
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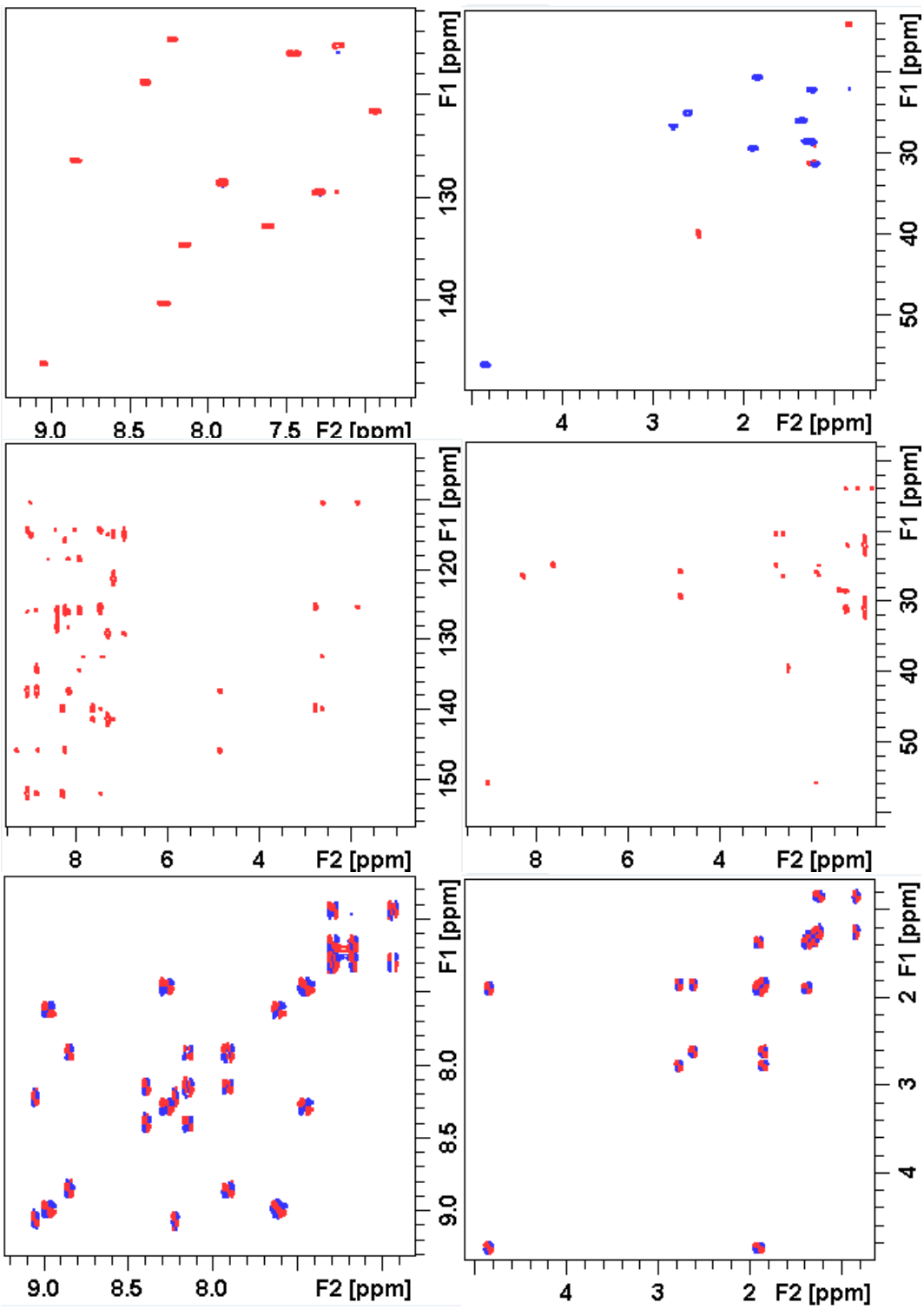
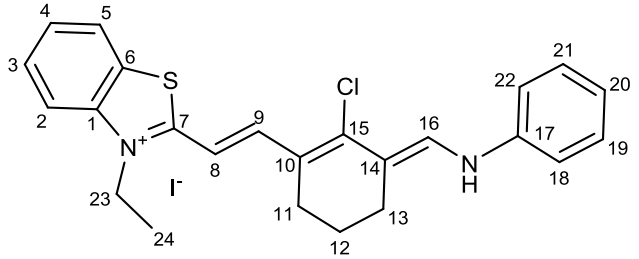


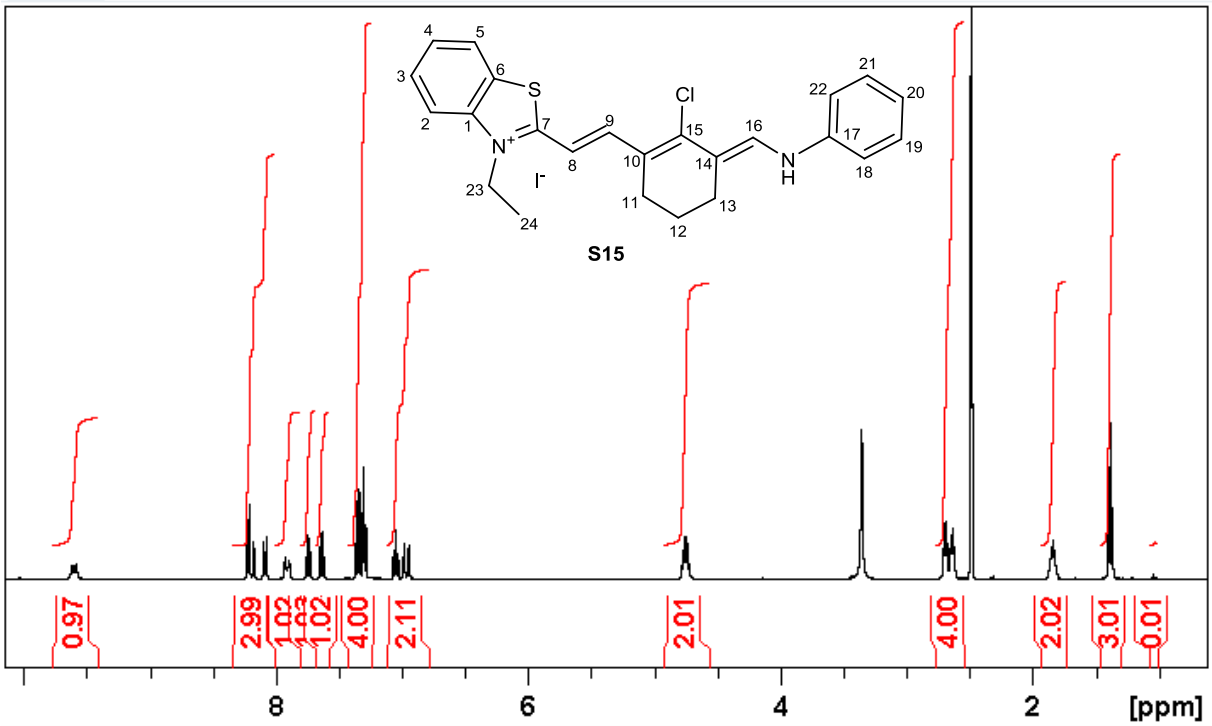
S14 ^{1}H, ^{13}C{^{1}H}, HSQC, HMBC and DQF-COSY NMR (DMSO-d_6)

1.8 2-(2-(2-Chloro-3-((phenylamino)methylene)cyclohex-1-en-1-yl)vinyl)-3-ethylbenzothiazol-3-ium iodide (S15)



S15

3-Ethyl-2-methylbenzo[*d*]thiazol-3-ium iodide **S5** (32.8 mmol, 10.00 g) and *N*-((2-chloro-3-((phenylimino)methyl)cyclohex-2-en-1-ylidene) methyl)aniline hydrochloride **S6** (34.4 mmol, 12.36 g) were dissolved in anhydrous ethanol (150 ml) and heated to 80 °C for 18 h. Then, the precipitate was separated by hot filtration and dried under reduced pressure at 40 °C for 20 h. For further purification, the residue was washed with hot ethanol (40 ml) to yield shiny green crystalline powder **S15** (15.21 g, 87%). d.p. 252 °C. ^{1}H NMR (DMSO-d$_6$, 400.1 MHz): δ 9.60 (d (br), *J* = 12.7, 1H, NH), 8.22 (d, *J* = 8.1, 1H, H-5), 8.20 (d, *J* = 14.5, 1H, H-9), 8.09 (d, *J* = 8.5, 1H, H-2), 7.91 (d, *J* = 12.7, 1H, H-16), 7.74 (m, 1H, H-3), 7.63 (m, 1H, H-4), 7.35 (m, 2H, H-19, 21), 7.29 (m, 2H, H-18, 22), 7.05 (m, 1H, H-20), 6.96 (d, *J* = 14.5, 1H, H-8), 4.75 (q, *J* = 7.2, 2H, H-23), 2.69 (t, *J* = 6.0, 2H, H-11), 2.64 (t, *J* = 6.1, 2H, H-13), 1.84 (m, 2H, H-12), 1.39 (t, *J* = 7.2, 3H, H-24). ^{13}C NMR (DMSO-d$_6$, 100.6 MHz): δ 169.5 (s, C-7), 144.9 (s, C-15), 144.7 (d, C-9), 141.1 (s, C-1), 140.9 (s, C-17), 137.7 (d, C-16), 129.6 (d, C-19, 21), 129.0 (d, C-3), 127.3 (d, C-4), 127.0 (s, C-6), 124.4 (s, C-10), 123.9 (d, C-5), 123.2 (d, C-20), 116.4 (d, C-18, 22), 115.5 (d, C-2), 111.7 (s, C-14), 106.4 (d, C-8), 43.2 (t, C-23), 26.1 (t, C-11), 24.8 (t, C-13), 20.0 (t, C-12), 13.6 (q, C-24). HMBC correlations: H-2 → C-(4, 6), H-3 → C-(1, 5), H-4 → C-(2, 6), H-5 → C-(1, 3), H-8 → C-(7, 10), H-9 → C-(7, 11, 15), H-11 → C-(9, 10, 12, 13, 15), H-12 → C-(10, 11, 13, 14), H-13 → C-(11, 12, 14, 15, 16), H-16 → C-(13, 15, 17), H-18, 22 → C-(18, 20, 22), H-19, 21 → C-(17, 19, 21), H-20 → C-(18, 19w, 21w, 22), H-23 → C-(1, 7, 24), H-24 → C-(23). DQF-COSY correlations: H-2 → H-(3), H-3 → H-(2, 4), H-4 → H-(3, 5), H-5 → H-(4), H-8 → H-(9), H-9 → H-(8), H-11 → H-(12), H-12 → H-(11, 13), H-13 → H-(12), H-16 → NH, H-18, 22 → H-(19, 21), H-19, 21 → H-(18, 20, 22), H-20 → H-(19, 21), H-23 → H-(24), H-24 → H-(23), NH → H-(16). HR-MS (ESI-QTOF): calculated for $C_{24}H_{24}ClN_2S$ $[M-I]^+$: 407.1343. Found: 407.1335. Elemental analysis: calculated for $C_{24}H_{24}ClIN_2S$: C, 53.89 %; H, 4.52 %; N, 5.24 %; S, 5.99%; Cl, 6.63 %; I, 23.73 %. Found: C, 53.95 %; H, 4.64 %; N, 5.18 %; S, 5.93%; Cl, 6.65 %; I, 23.43 %. IR (ATR, cm-1): λ_{max} 3182, 2924, 1862, 1625, 1538, 1433, 1178, 926, 767, 699. UV-Vis (nm): λ_{max} 635 (in ethanol).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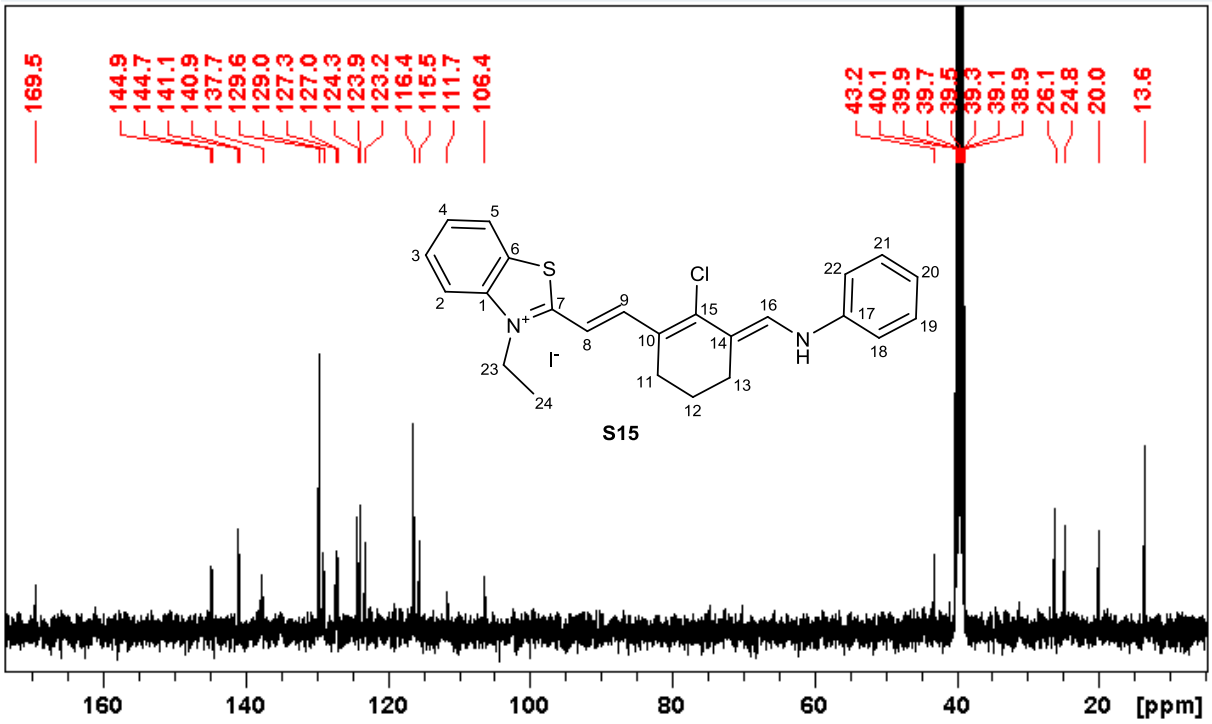
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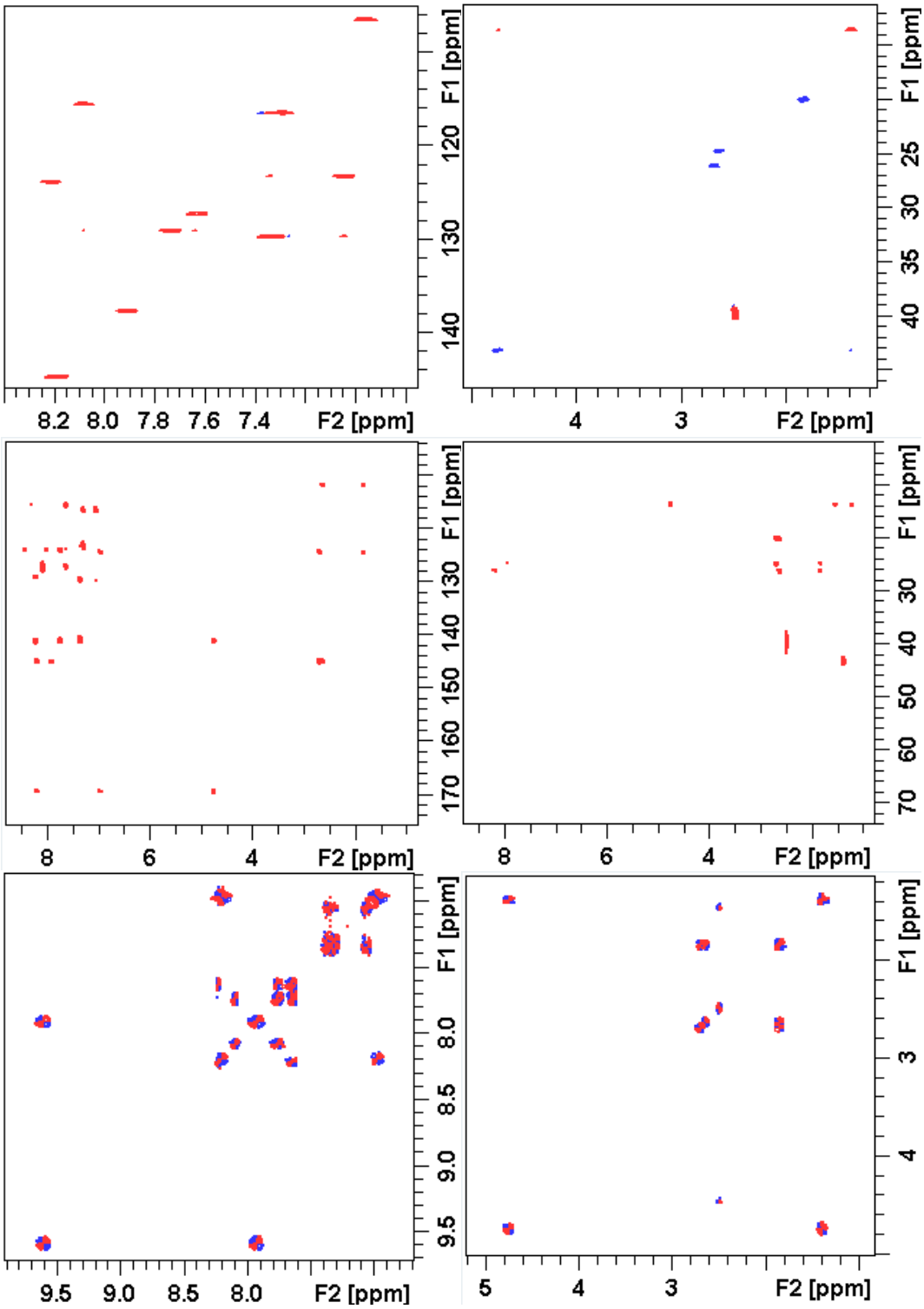
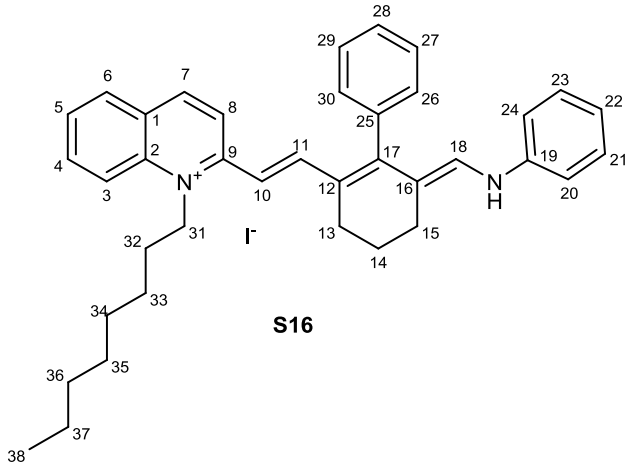
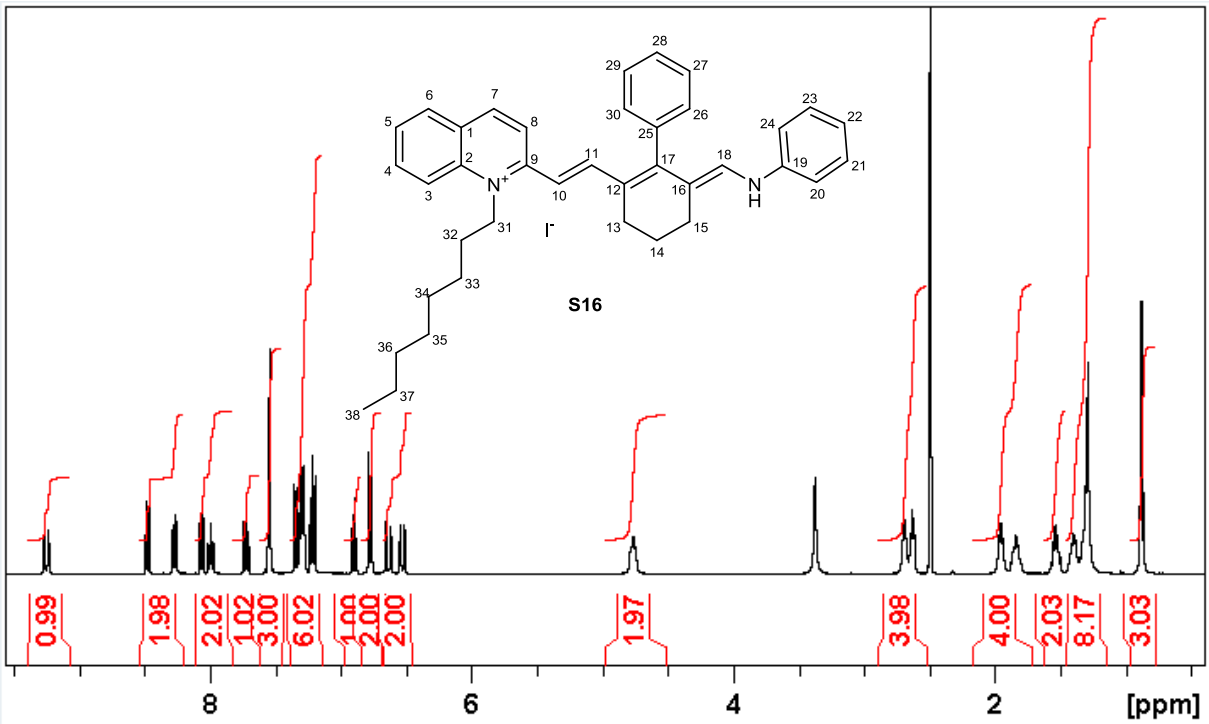


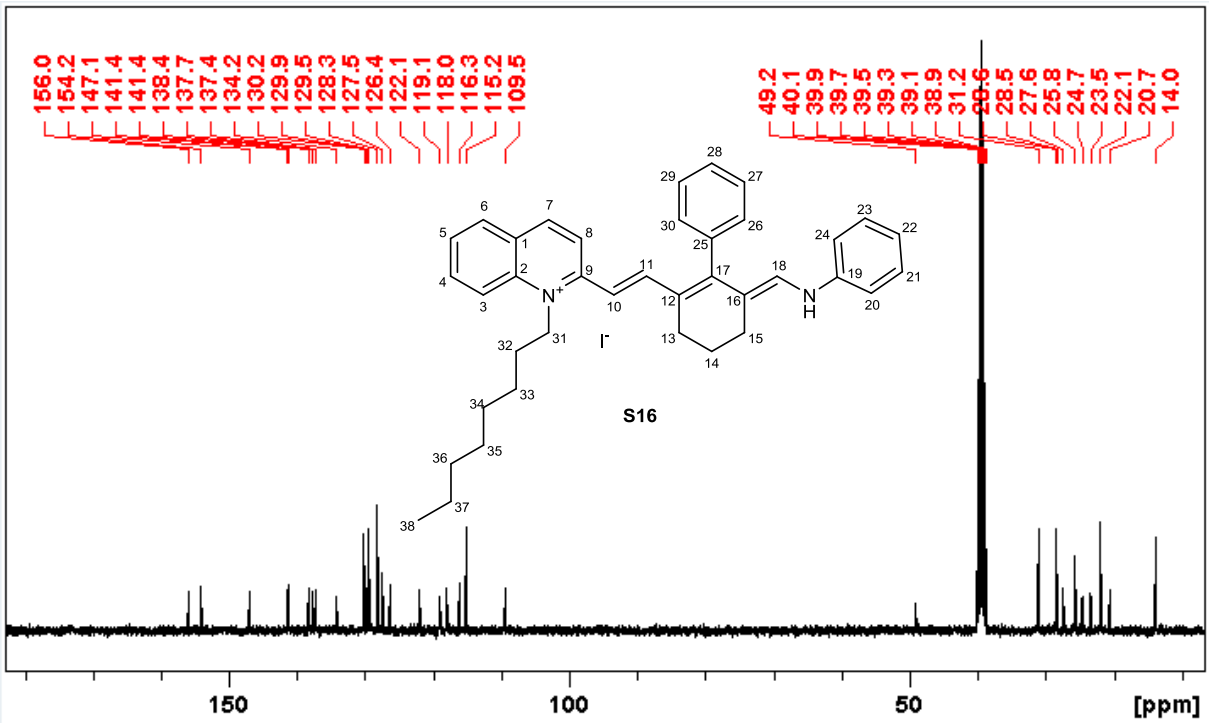
S15 ^{1}H, ^{13}C{^{1}H}, HSQC, HMBC and DQF-COSY NMR (DMSO-d_6)

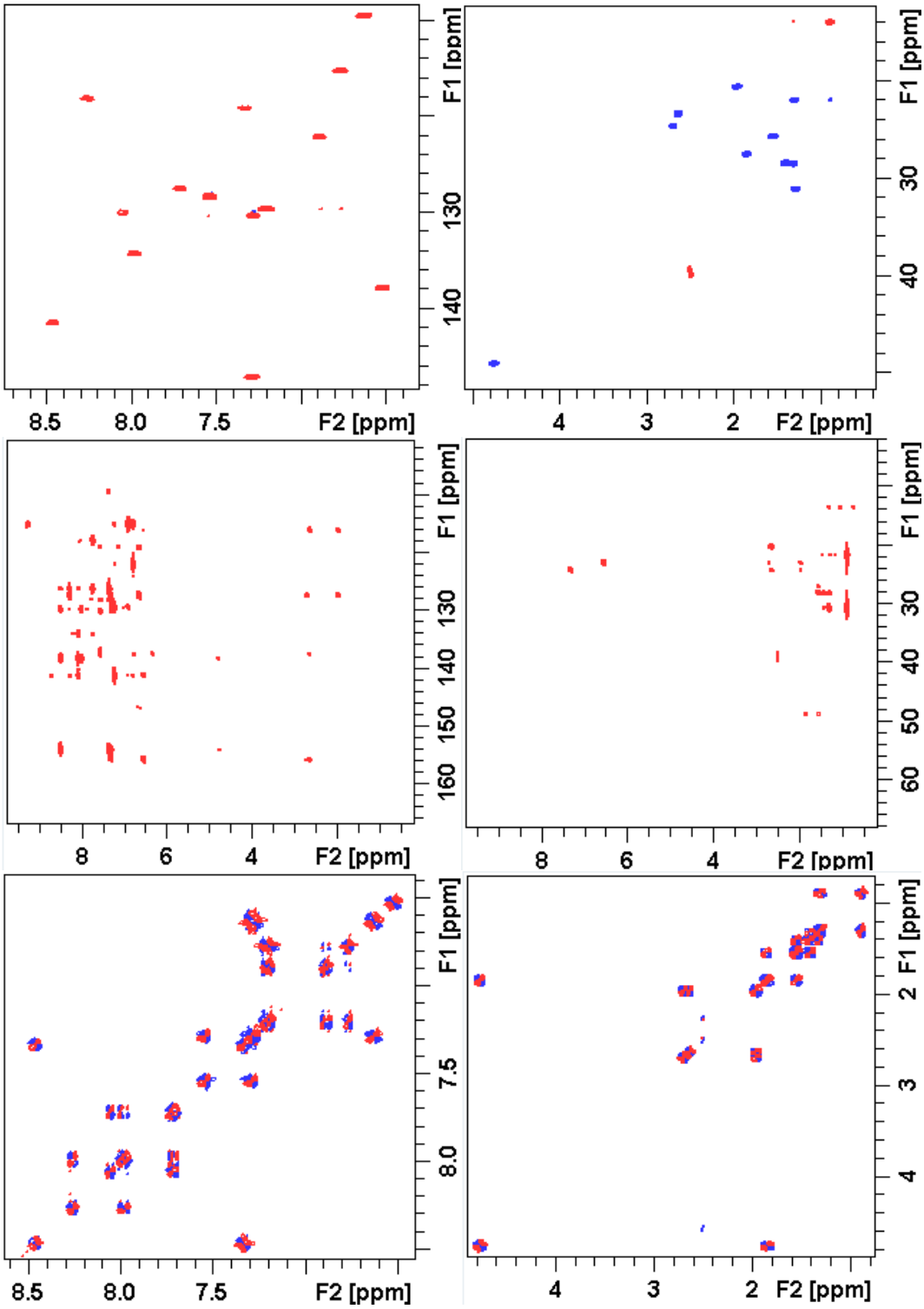
1.9 1-Octyl-2-(2-(6-((phenylamino)methylene)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)vinyl)quinolin-1-ium iodide (S16)



2-Methyl-1-octylquinolin-1-ium iodide **S3** (10.4 mmol, 4.00 g) and *N*-((6-((phenylamino) methylene)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl) methylene)aniline hydrochloride **S7** (10.9 mmol, 4.39g) were dissolved in anhydrous ethanol (80 ml) and heated to 85 °C for 72 h. Then, the solution was cooled to room temperature and stored at 4 °C for 20 h. Precipitated starting material was removed by filtration and the filtrate was stored at 4 °C for 48 h. Subsequently, precipitated crystals were filtered and recrystallized from ethanol (60 ml) to yield the desired half dye **S16** (1.24g, 18.2 %). d.p. 223 °C. ^{1}H NMR (DMSO-d$_6$, 400.1 MHz): δ 9.24 (d, *J* = 12.9, 1H, NH), 8.47 (d, *J* = 9.4, 1H, H-7), 8.26 (d, *J* = 8.9, 1H, H-3), 8.06 (dd, *J* = 8.0, 1.5, 1H, H-6), 7.99 (m, 1H, H-4), 7.72 (m, 1H, H-5), 7.33 (d, *J* = 9.4, 1H, H-8), 7.29 (d, *J* = 14.7, 1H, H-11), 7.21 (m, 2H, H-21, 23), 6.89 (m, 1H, H-22), 6.77 (m, 2H, H-20, 24), 6.63 (d, *J* = 14.7, 1H, H-10), 6.52 (d, *J* = 12.9, 1H, H-18), 4.76 (m, 2H, H-31), 2.69 (t, *J* = 5.9, 2H, H-13), 2.63 (t, *J* = 6.0, 2H, H-15), 1.94 (m, 2H, H-14), 1.83 (m, 2H, H-32), 1.53 (m, 2H, H-33), 1.40 (m, 2H, H-34), 1.31 (m, 2H, H-35), 1.29 (m, 2H, H-37), 1.29 (m, 2H, H-36), 0.87 (t, *J* = 6.8, 3H, H-38). ^{13}C NMR (DMSO-d$_6$, 100.6 MHz): δ 156.0 (s, C-17), 154.2 (s, C-9), 147.1 (d, C-11), 141.4 (d, C-7), 141.3 (s, C-19), 138.4 (s, C-2), 137.7 (d, C-18), 137.4 (s, C-25), 134.2 (d, C-4), 129.9 (d, C-6), 129.5 (d, C-21, 23), 127.5 (s, C-12), 127.5 (d, C-5), 126.4 (s, C-1), 122.1 (d, C-22), 119.1 (d, C-8), 118.0 (d, C-3), 116.3 (s, C-16), 115.2 (d, C-20, 24), 109.5 (d, C-10), 49.2 (t, C-31), 31.2 (t, C-36), 28.6 (t, C-35), 28.5 (t, C-34), 27.6 (t, C-32), 25.8 (t, C-33), 24.7 (t, C-13), 23.5 (t, C-15), 22.1 (t, C-37), 20.7 (t, C-14), 14.0 (q, C-38). HMBC correlations: H-3 → C-(1, 5), H-4 → C-(2, 6), H-5 → C-(1, 3, 4w), H-6 → C-(1, 2, 4, 7), H-7 → C-(1, 2, 6, 9), H-8 → C-(1, 9, 10w), H-10 → C-(8, 11w, 12), H-11 → C-(9, 13, 17), H-13 → C-(12, 14, 15, 17), H-14 → C-(12, 13, 15, 16), H-15 → C-(13, 14, 16, 17, 18), H-18 → C-(15, 16w, 17, 19), H-20, 24 → C-(19, 20, 22, 24), H-21, 23 → C-(19, 20w, 21, 23, 24w), H-22 → C-(19w, 20, 21w, 23w, 24), H-31 → C-(2, 9, 32), H-32 → C-(31, 33, 34w), H-33 → C-(31, 32, 34), H-34 → C-(33, 35, 36), H-35 → C-(34, 36), H-36 → C-(35, 37, 38), H-37 → C-(36, 38), H-38 → C-(36, 37), NH → C-(16w, 20, 24). DQF-COSY correlations: H-3 → H-(4), H-4 → H-(3, 5), H-5 → H-(4, 6), H-6 → H-(5), H-7 → H-(8), H-8 → H-(7), H-10 → H-(11), H-11 → H-(10), H-13 → H-(14), H-14 → H-(13, 15), H-15 → H-(14), H-18 → NH, H-20, 24 → H-(21, 23), H-21, 23 → H-(20, 22, 24), H-22 → H-(21, 23), H-31 → H-(32), H-32 → H-(31, 33), H-33 → H-(32, 34), H-34 → H-(33, 35), H-35 → H-(34), H-37 → H-(38), H-38 → H-(37), NH → H-(18). HR-MS (ESI-QTOF): calculated for $C_{38}H_{43}N_2$ $[M-I]^+$: 527.3421. Found: 527.3420. Elemental analysis: calculated for $C_{38}H_{43}IN_2$: C, 69.72 %; H, 6.62 %; N, 4.28 %; I, 19.38 %. Found: C, 68.29 %; H, 6.49 %; N, 4.13 %. IR (ATR, cm-1): λ_{max} 3044, 2922, 2853, 1624, 1599, 1368, 1217, 1142, 962, 748. UV-Vis: λ_{max} 645 nm (in ethanol).

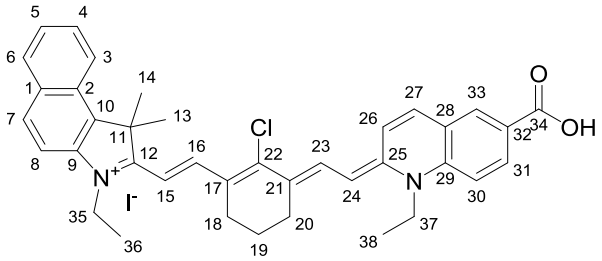

S16
0.99
1.98
2.02
1.02
3.00
6.02
1.00
2.00
2.00
1.97
3.98
4.00
2.03
8.17
3.03
8
6
4
2
[ppm]


156.0
154.2
147.1
141.4
141.4
138.4
137.7
137.4
134.2
130.2
129.9
129.5
128.3
127.5
126.4
122.1
119.1
118.0
116.3
115.2
109.5
49.2
40.1
39.9
39.7
39.5
39.3
39.1
38.9
31.2
28.5
27.6
25.8
24.7
23.5
22.1
20.7
14.0
S16
150
100
50
[ppm]

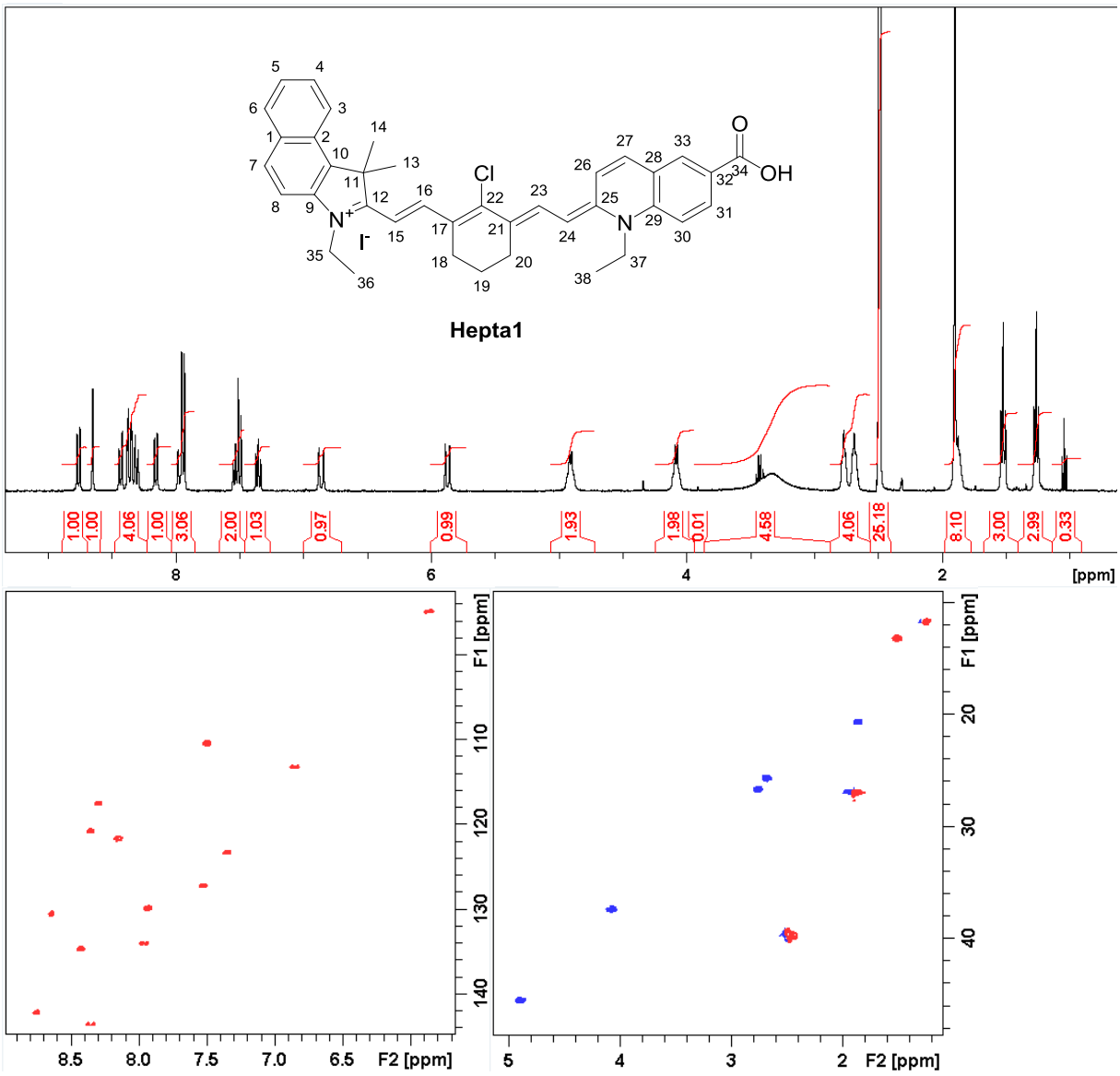


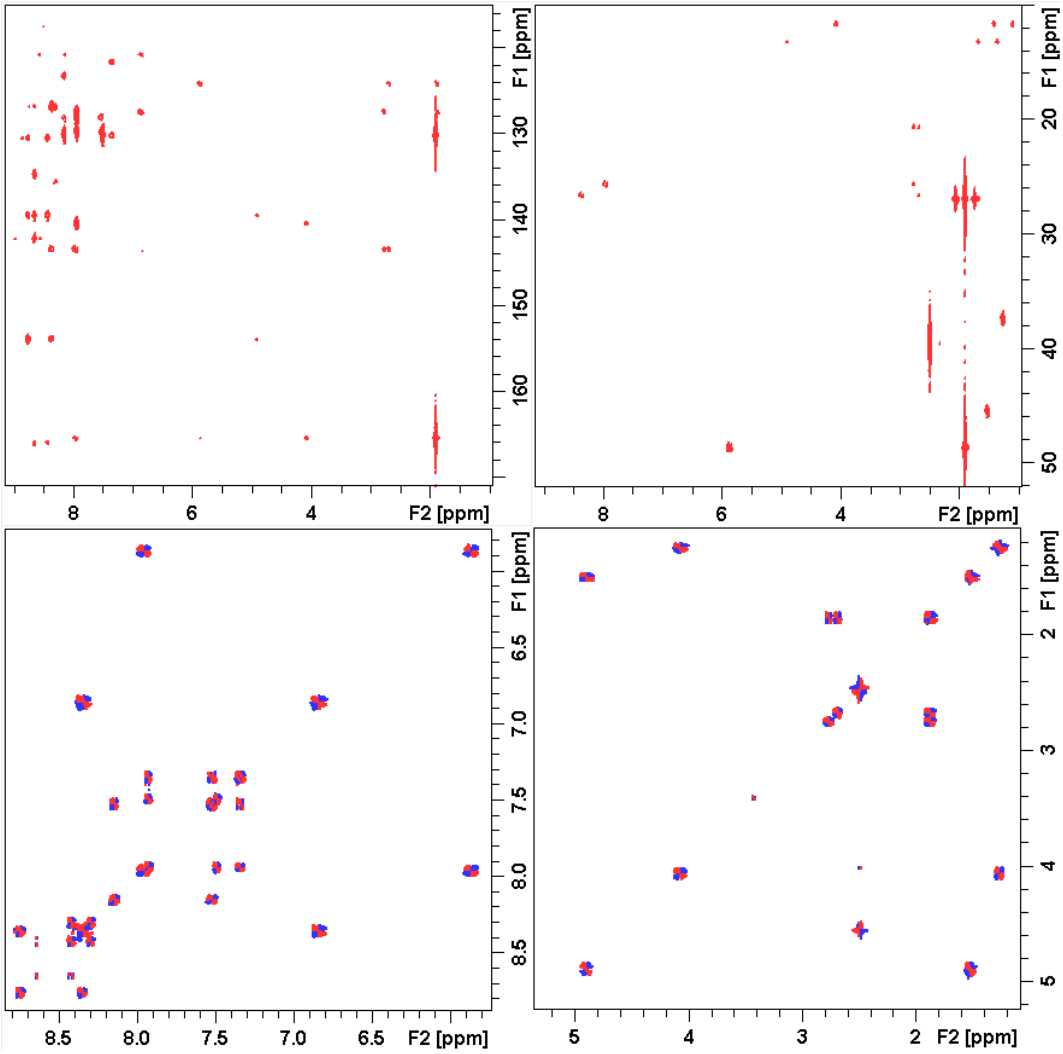
S16 ^{1}H, ^{13}C{^{1}H}, HSQC, HMBC and DQF-COSY NMR (DMSO-d_6)

1.10 2-(2-(3-(2-(6-carboxy-1-ethylquinolin-2(1*H*)-ylidene)ethylidene)-2-chlorocyclohex-1-en-1-yl)vinyl)-3-ethyl-1,1-dimethyl-1*H*-benzo[e]indol-3-ium iodide (Hepta1)



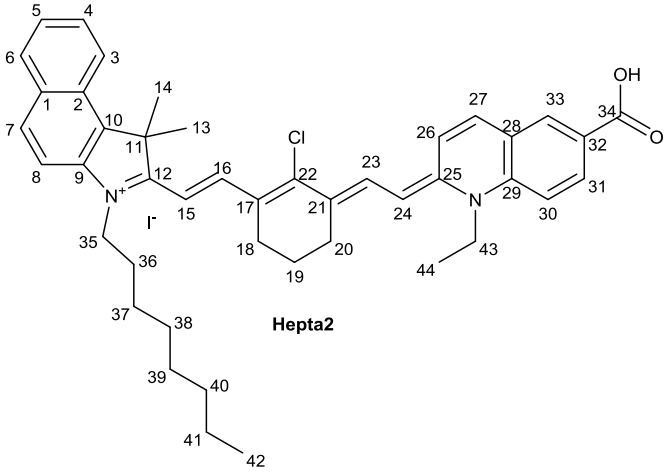
Hepta1

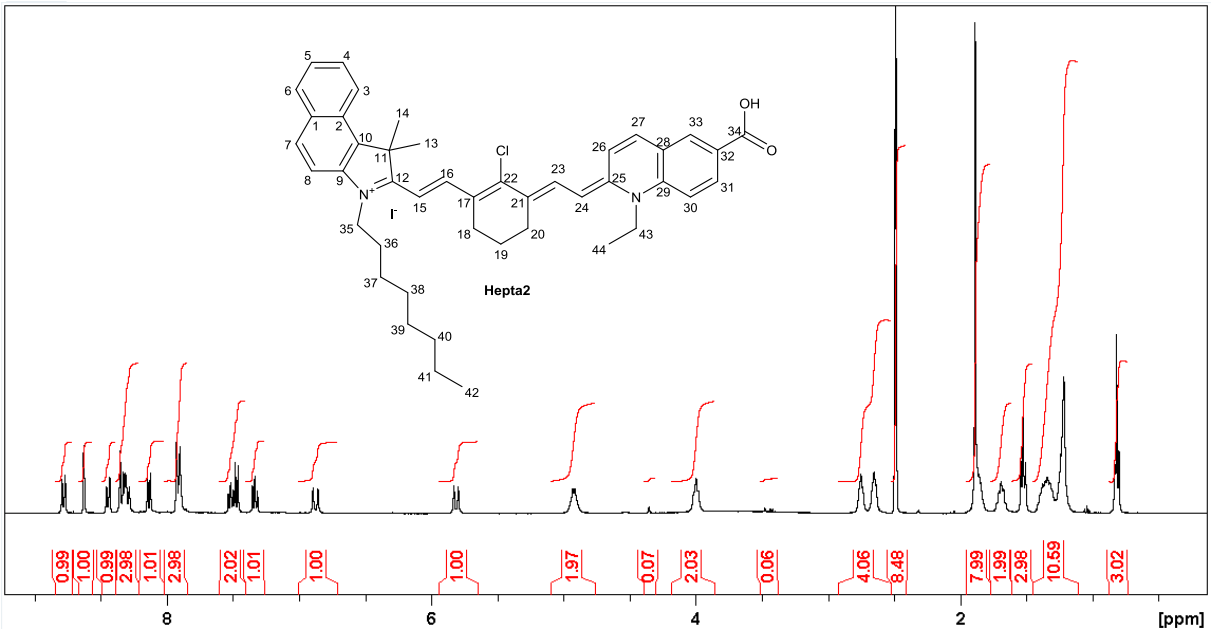


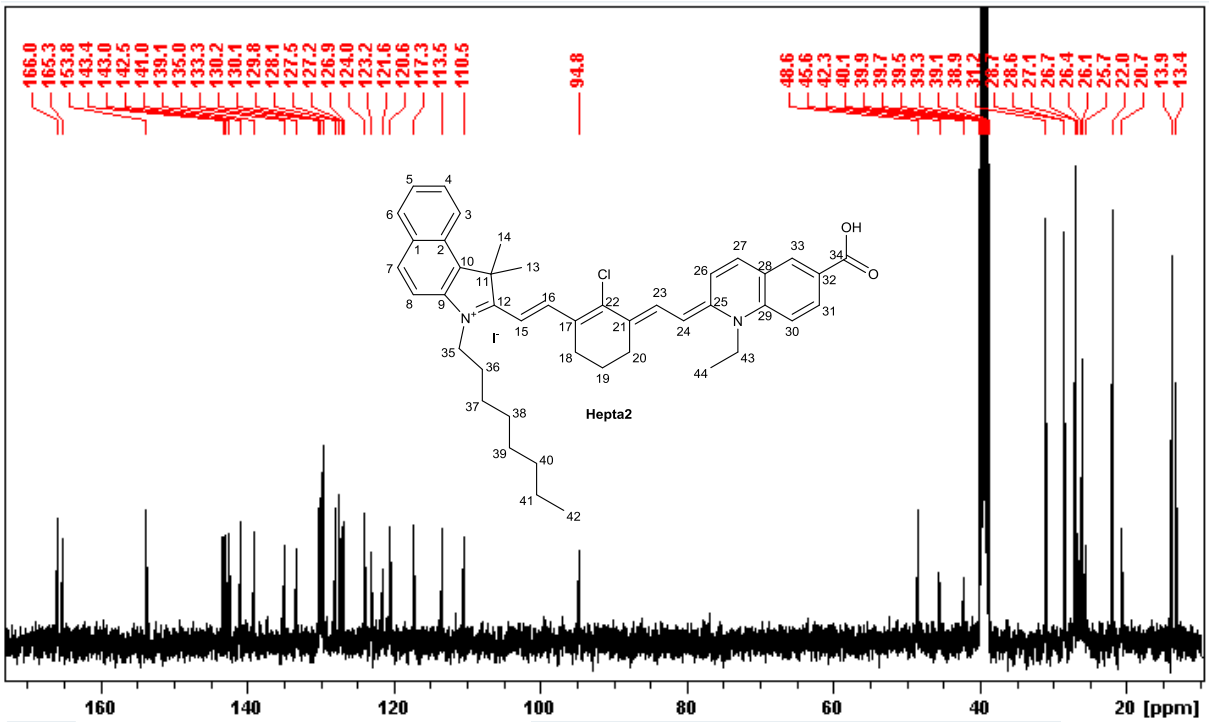


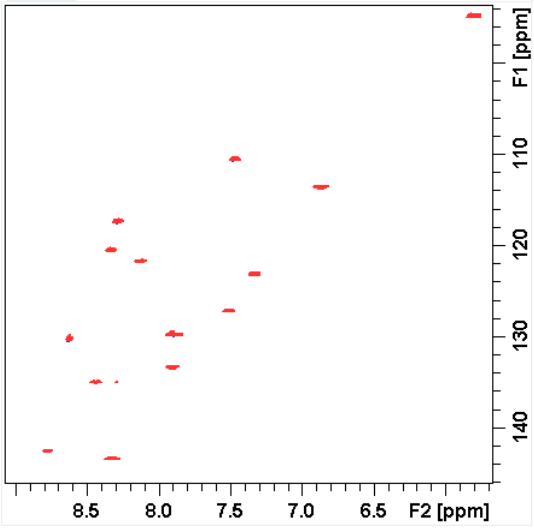
Hepta1 ^{1}H, HSQC, HMBC and DQF-COSY NMR (DMSO-d_6)

1.11 2-(2-(3-(2-(6-carboxy-1-ethylquinolin-2(1*H*)-ylidene)ethylidene)-2-chlorocyclohex-1-en-1-yl)vinyl)-1,1-dimethyl-3-octyl-1*H*-benzo[e]indol-3-ium iodide (Hepta2)




Hepta2
0.99
1.00
0.99
2.98
1.01
2.98
2.02
1.01
1.00
1.00
1.97
0.07
2.03
0.06
4.06
8.48
7.99
1.99
2.98
10.59
3.02
8
6
4
2
[ppm]


166.0
165.3
153.8
143.4
143.0
142.5
141.0
139.1
135.0
133.3
130.2
130.1
129.8
128.1
127.5
127.2
126.9
124.0
123.2
121.6
120.6
117.3
113.5
110.5
94.8
48.6
45.6
42.3
40.1
39.9
39.7
39.5
39.3
39.1
38.9
31.2
28.7
28.6
27.1
26.7
26.4
26.1
25.7
22.0
20.7
13.9
13.4
Hepta2
160
140
120
100
80
60
40
20 [ppm]


F1 [ppm]
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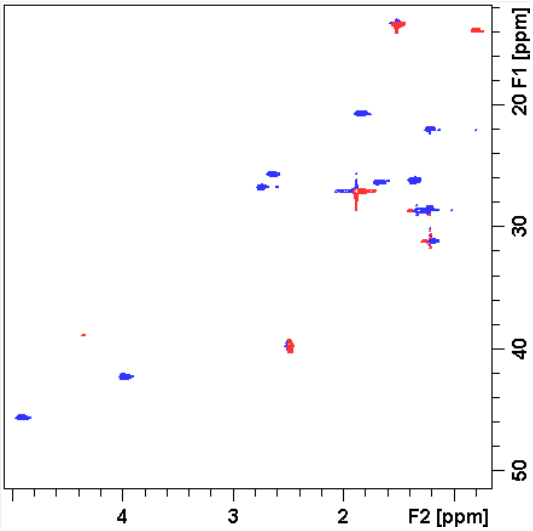
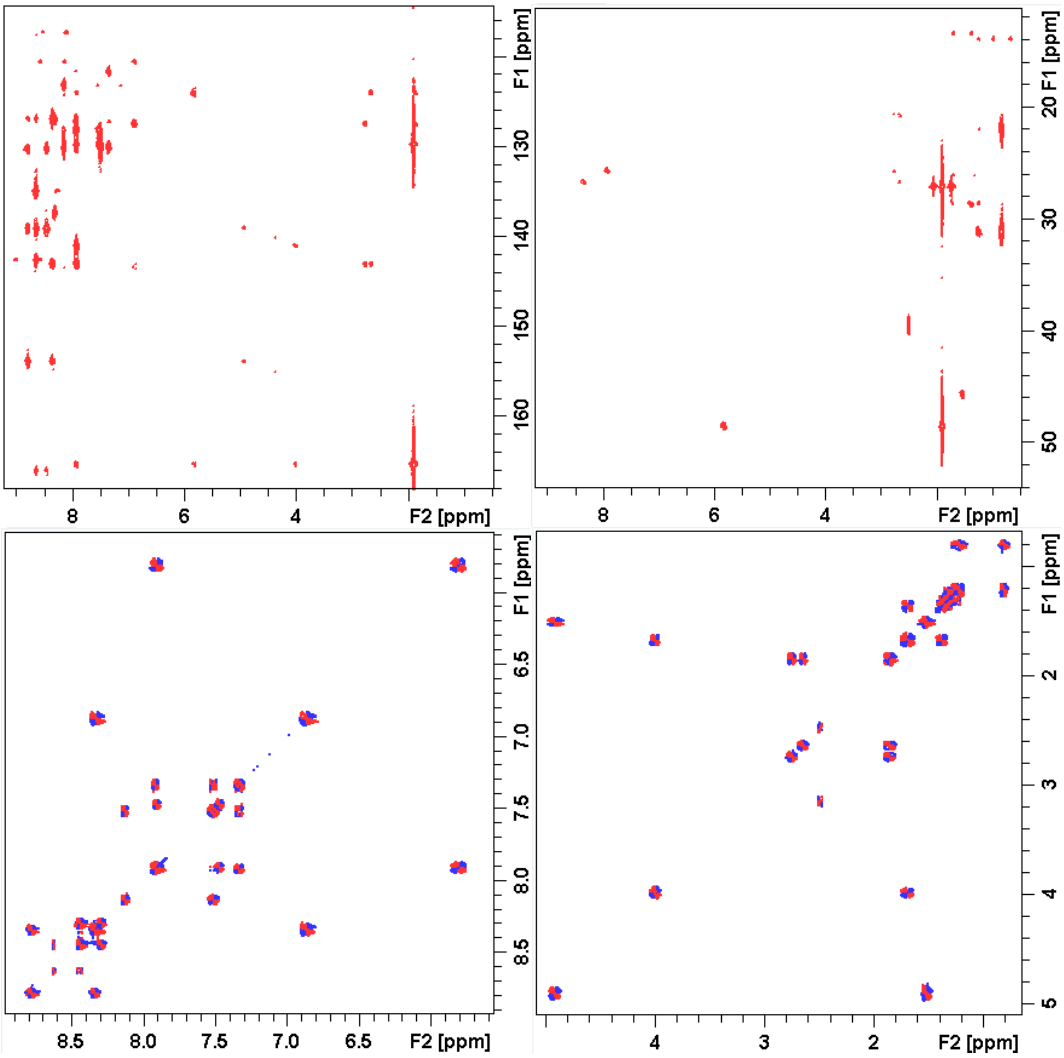
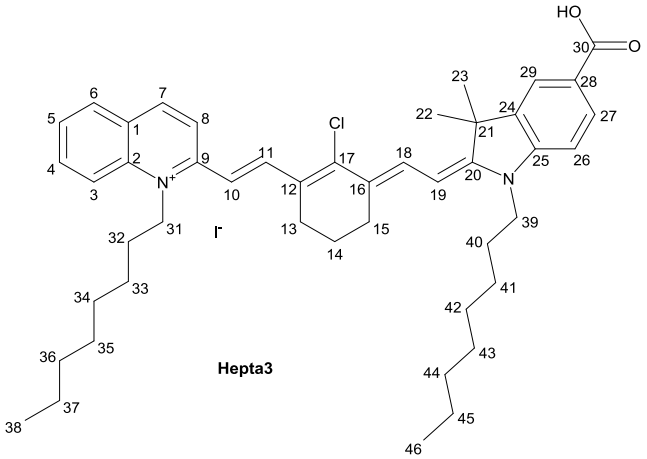
120
130
140
8.5
8.0
7.5
7.0
6.5
F2 [ppm]

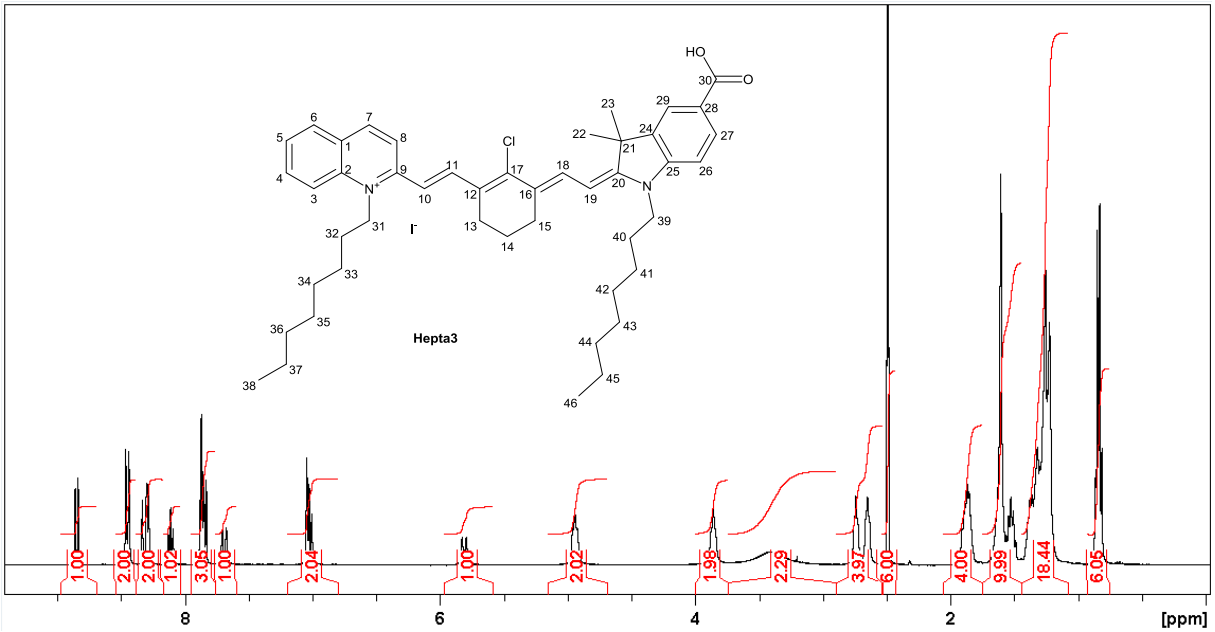

20 F1 [ppm]
30
40
50
4
3
2
F2 [ppm]

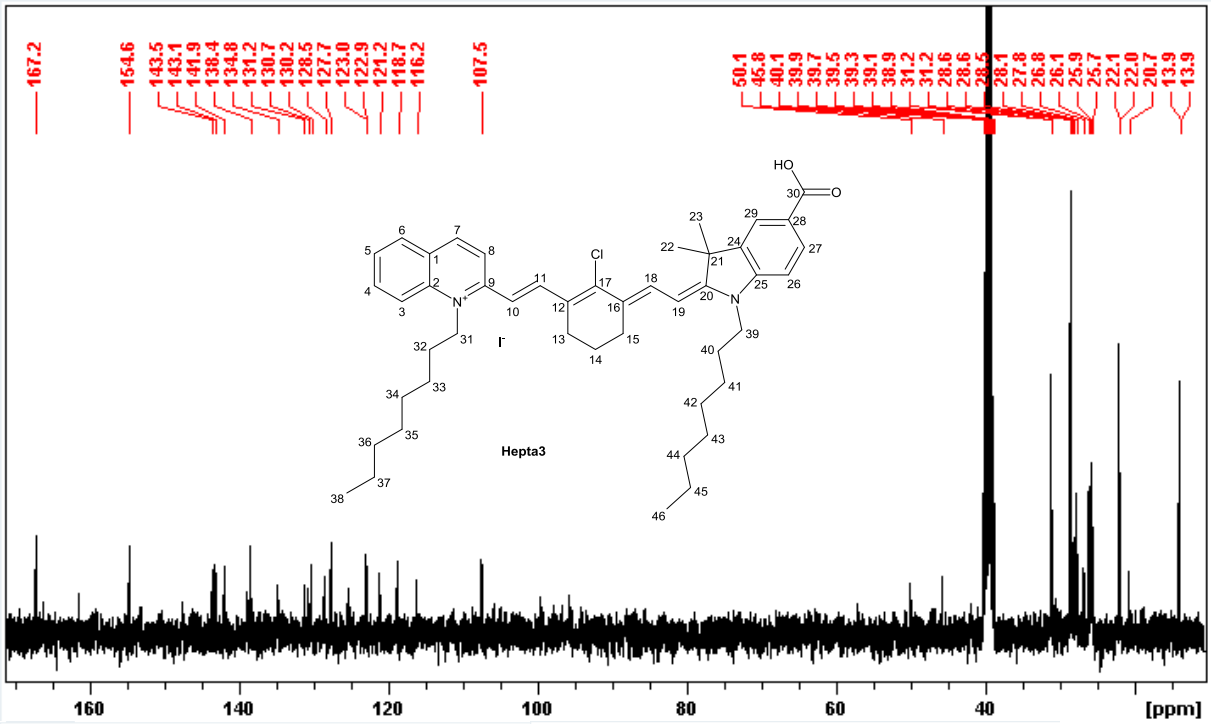


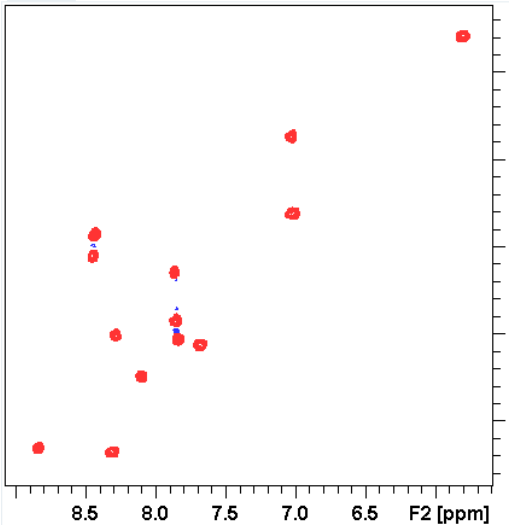
Hepta2 ^{1}H, $^{13}C\{^{1}H\}$, HSQC, HMBC and DQF-COSY NMR (DMSO-d_6)

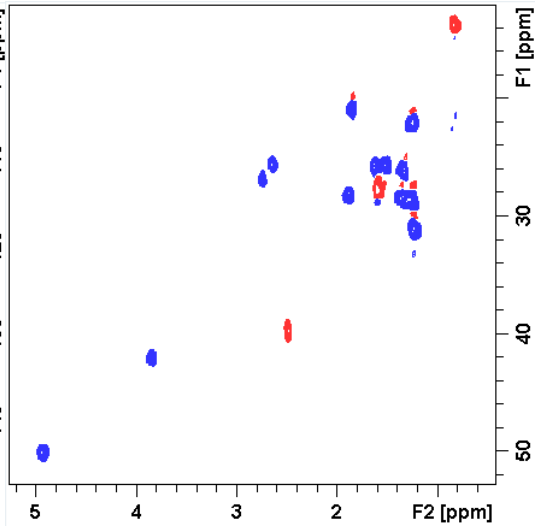
1.12 2-(2-(3-(2-(5-carboxy-3,3-dimethyl-1-octylindolin-2-ylidene)ethylidene)-2-chlorocyclohex-1-en-1-yl)vinyl)-1-octylquinolin-1-ium iodide (Hepta3)

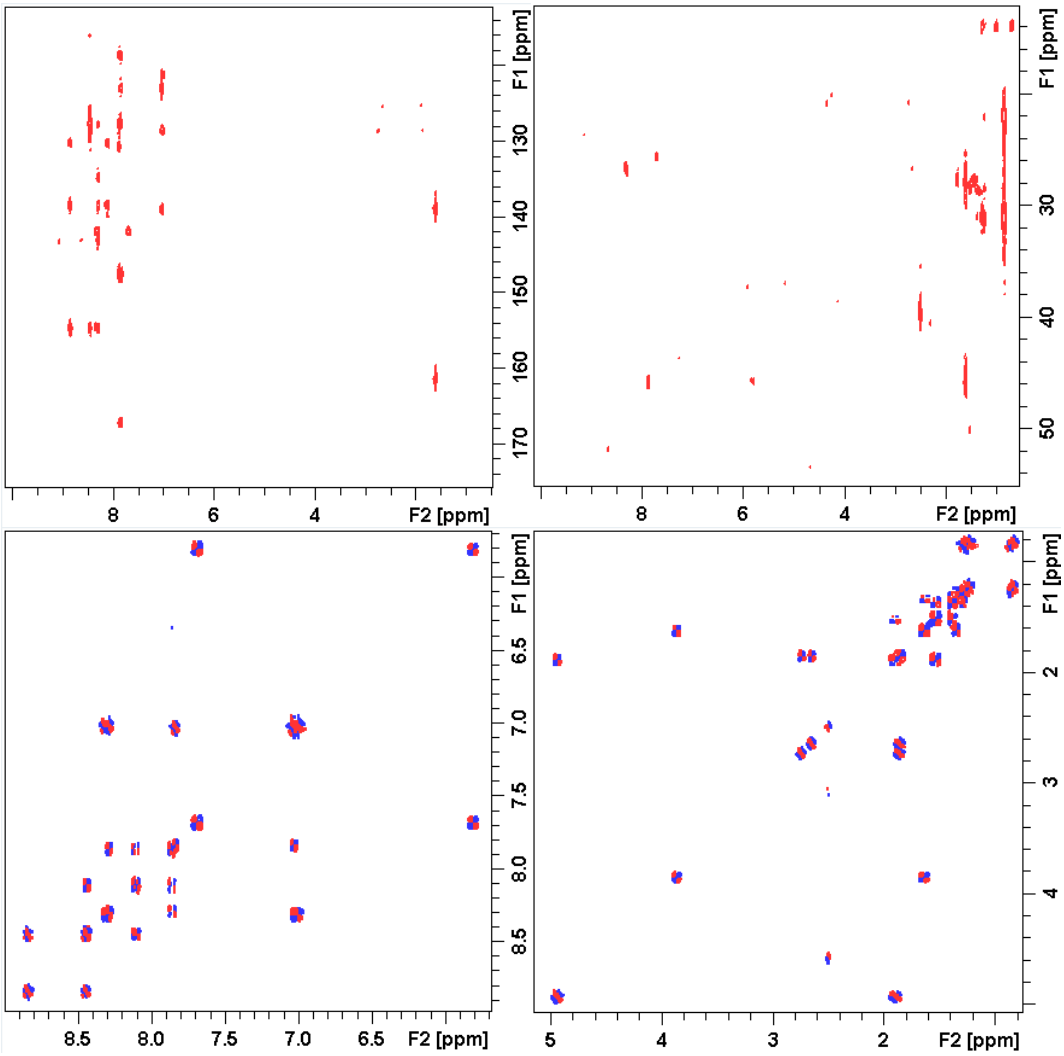



Hepta3
1.00
2.00
2.00
1.02
3.05
1.00
2.04
1.00
2.02
1.98
2.29
3.97
6.00
4.00
9.99
18.44
6.05
8
6
4
2
[ppm]


167.2
154.6
143.5
143.1
141.9
138.4
134.8
131.2
130.7
130.2
128.5
127.7
123.0
122.9
121.2
118.7
116.2
107.5
50.1
45.8
40.1
39.9
39.7
39.5
39.3
39.1
38.9
31.2
31.2
28.6
28.6
28.5
28.1
27.8
26.8
26.1
25.9
25.7
22.1
22.0
20.7
13.9
13.9
Hepta3
160
140
120
100
80
60
40
[ppm]

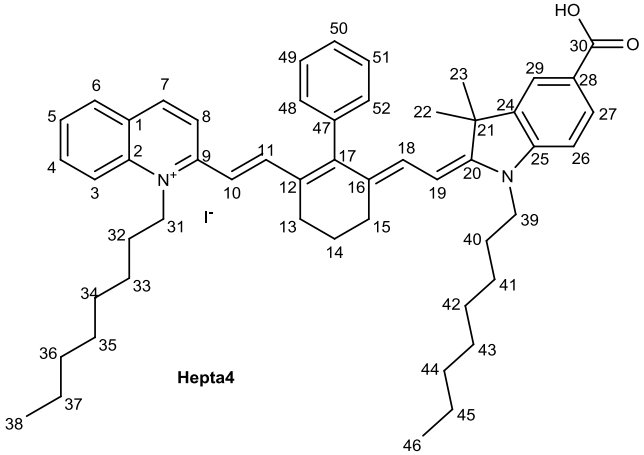

F1 [ppm]
110
120
130
140
8.5
8.0
7.5
7.0
6.5
F2 [ppm]

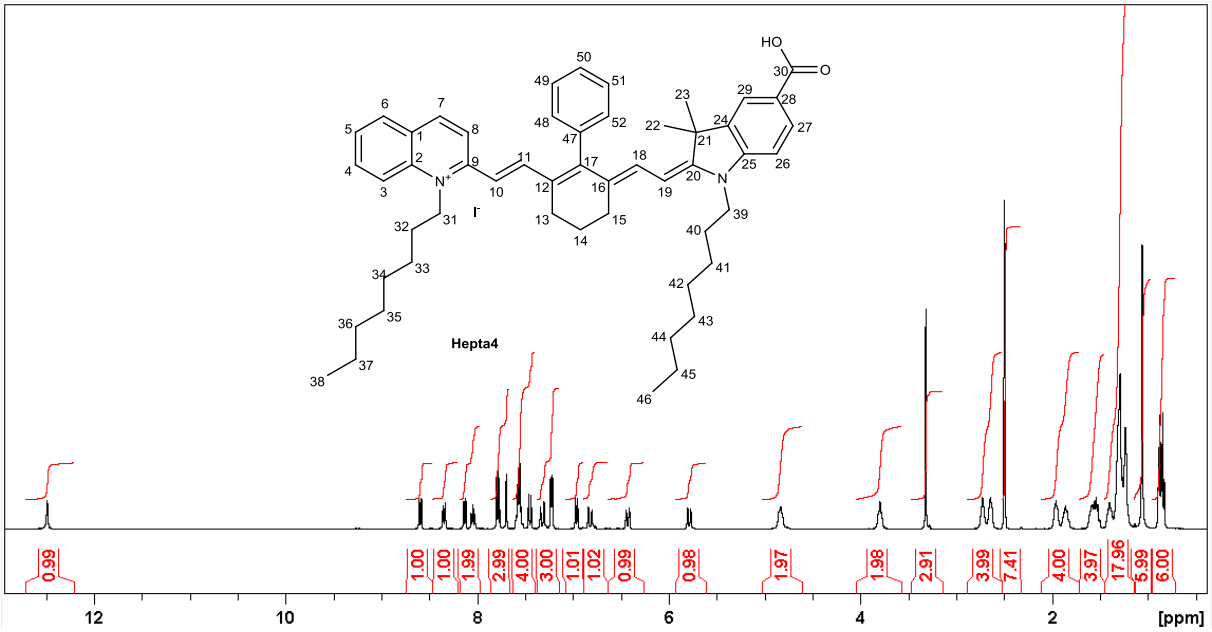

F1 [ppm]
30
40
50
5
4
3
2
F2 [ppm]

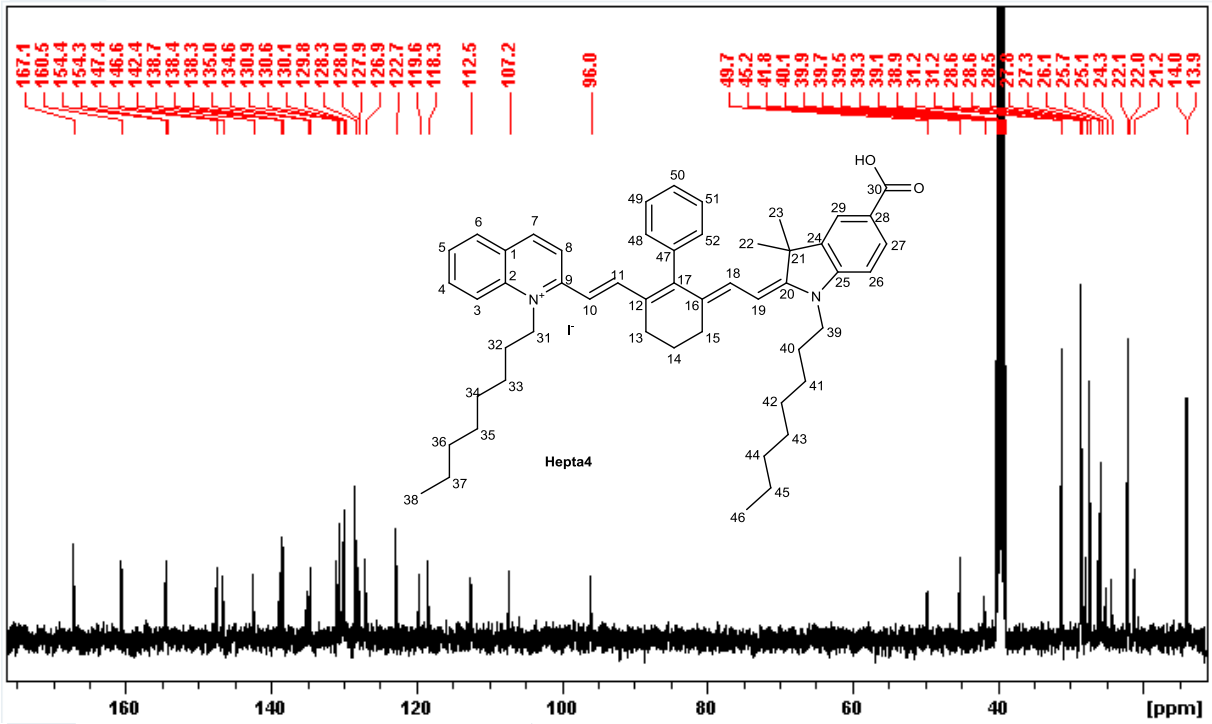


Hepta3 ^{1}H, $^{13}C\{^{1}H\}$, HSQC, HMBC and DQF-COSY NMR (DMSO-d_6)

1.13 2-(2-(6-(2-(5-carboxy-3,3-dimethyl-1-octylindolin-2-ylidene)ethylidene)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)vinyl)-1-octylquinolin-1-ium iodide (Hepta4)




Hepta4
0.99
1.00
1.00
1.99
2.99
4.00
3.00
1.01
1.02
0.99
0.98
1.97
1.98
2.91
3.99
7.41
4.00
3.97
17.96
6.99
6.00
12
10
8
6
4
2
[ppm]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154.4
154.3
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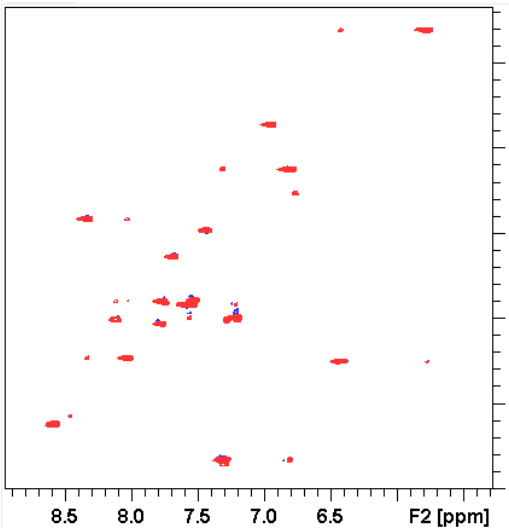
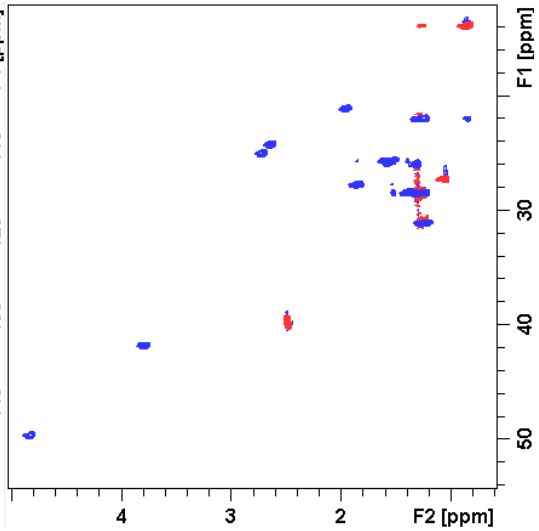
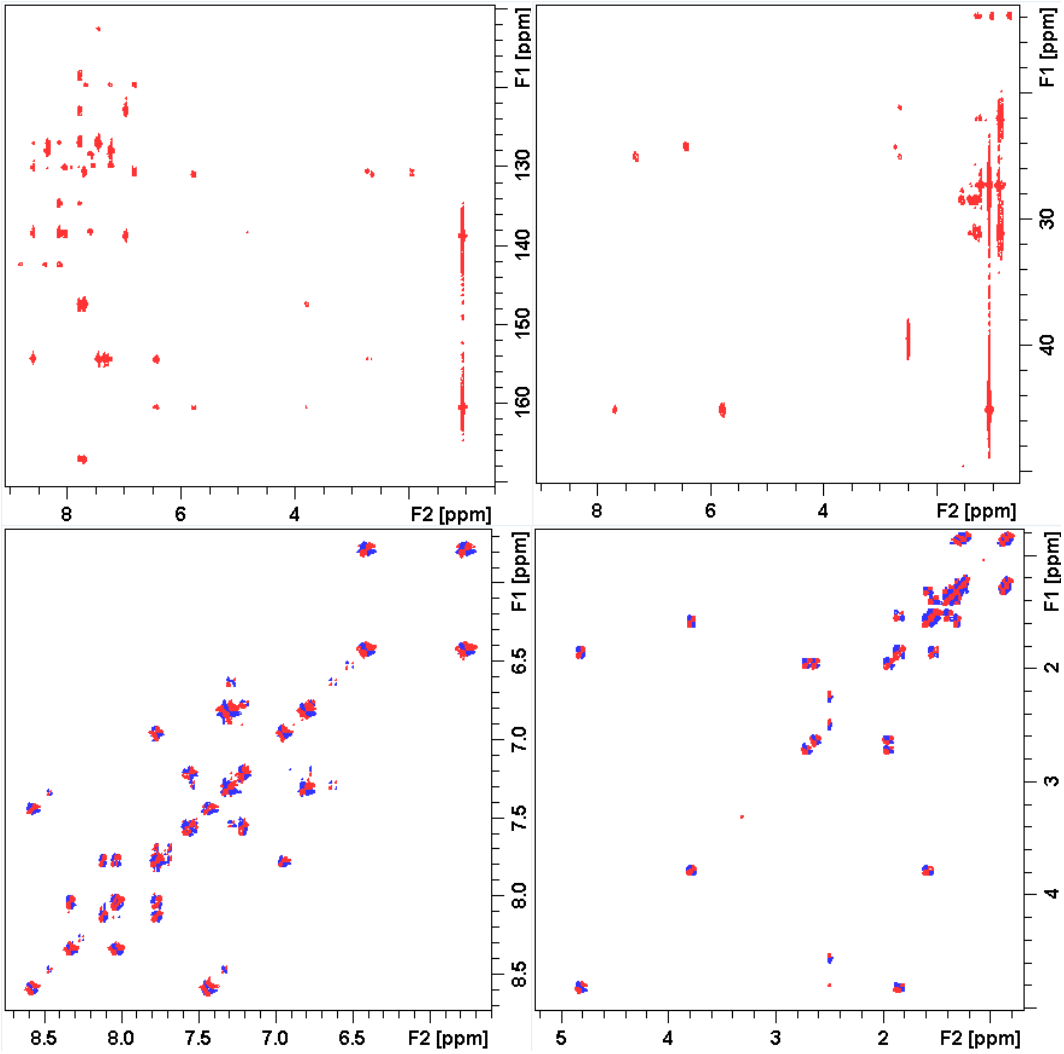
146.6
142.4
138.7
138.4
138.3
135.0
134.6
130.9
130.6
130.1
129.8
128.3
128.0
127.9
126.9
122.7
119.6
118.3
112.5
107.2
96.0
49.7
45.2
41.8
40.1
39.9
39.7
39.5
39.3
39.1
38.9
31.2
31.2
28.6
28.6
28.5
27.3
26.1
25.7
25.1
24.3
22.1
22.0
21.2
14.0
13.9
Hepta4
160
140
120
100
80
60
40
[ppm]

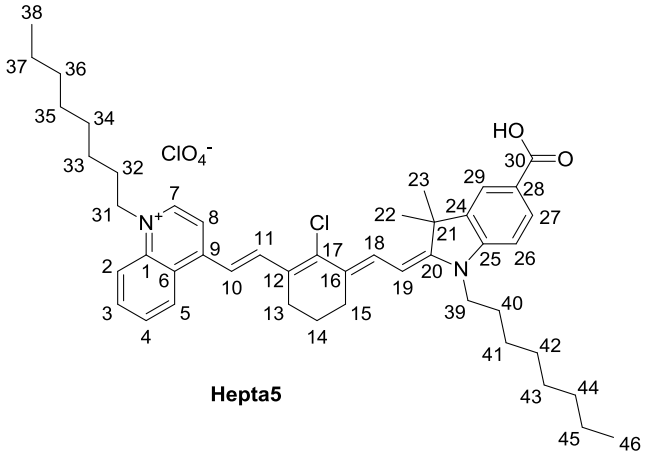

F1 [ppm]
110
120
130
140
8.5
8.0
7.5
7.0
6.5
F2 [ppm]


F1 [ppm]
30
40
50
4
3
2
F2 [ppm]

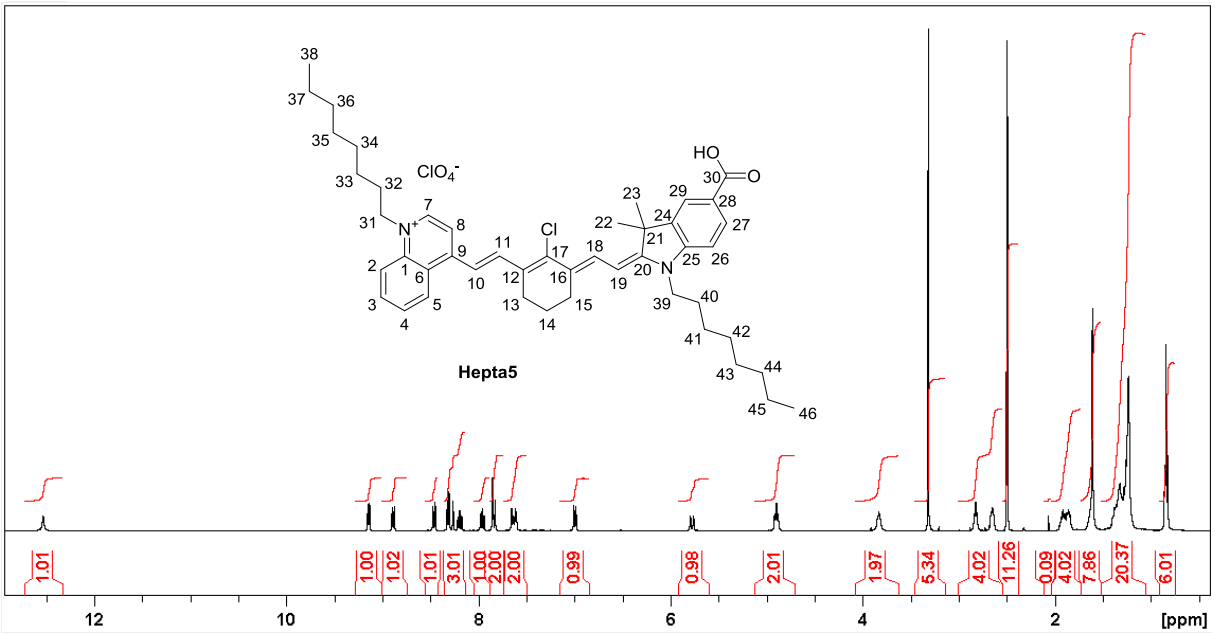


Hepta4 ^{1}H, $^{13}C\{^{1}H\}$, HSQC, HMBC and DQF-COSY NMR (DMSO-d_6)

1.14 4-(2-(3-(2-(5-carboxy-3,3-dimethyl-1-octylindolin-2-ylidene)ethylidene)-2-chlorocyclohex-1-en-1-yl)vinyl)-1-octylquinolin-1-ium perchlorate (Hepta5)



Hepta5


Hepta5
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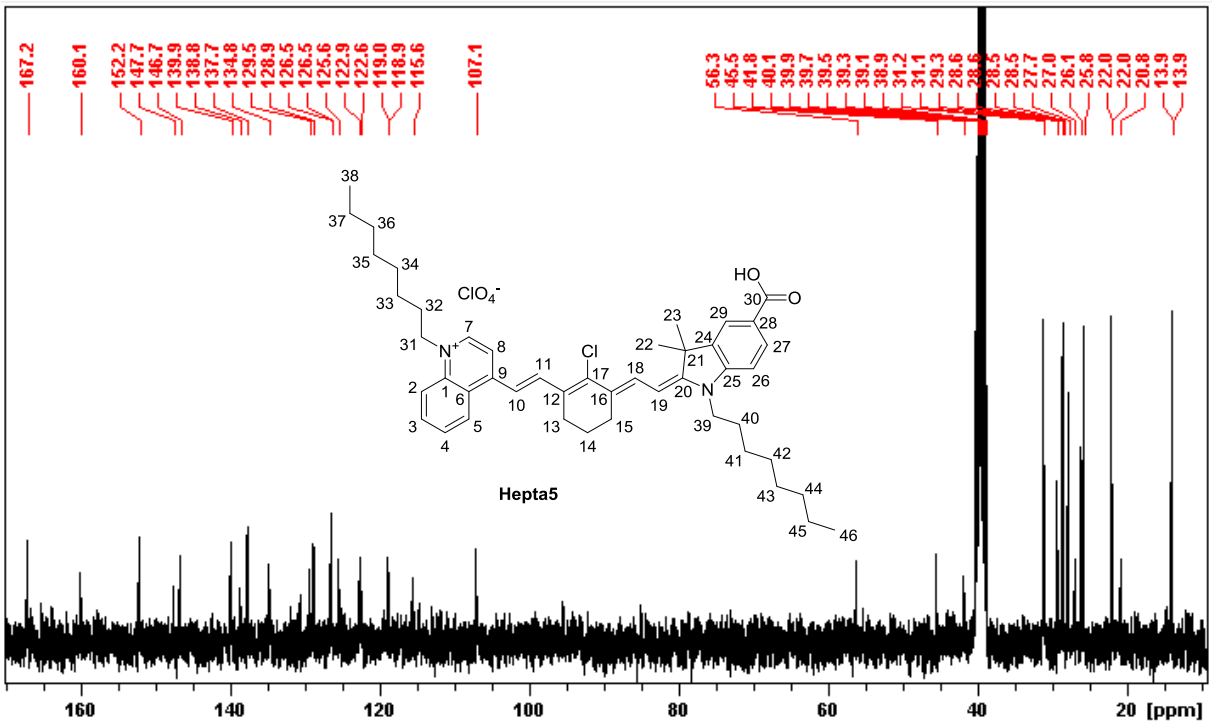
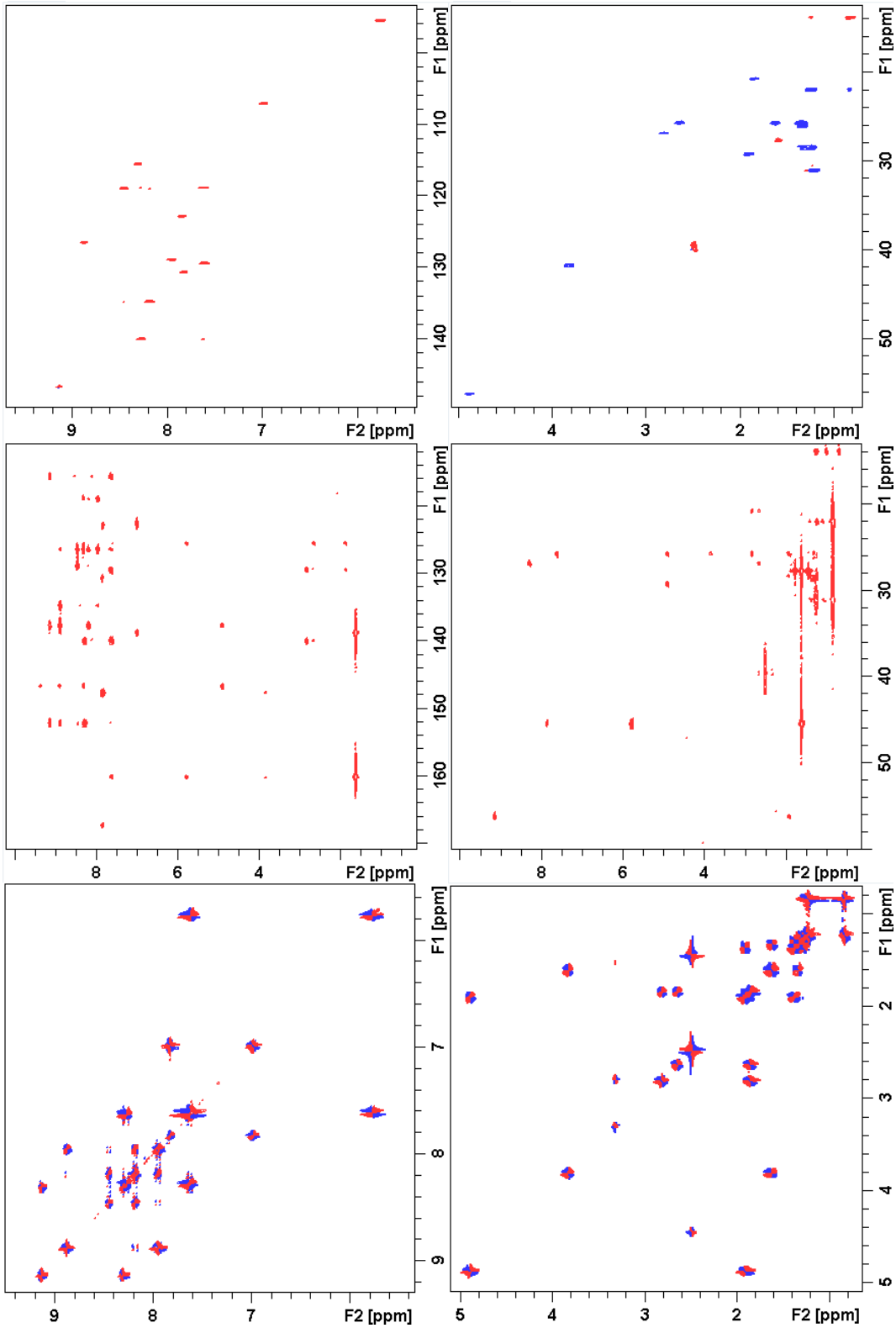
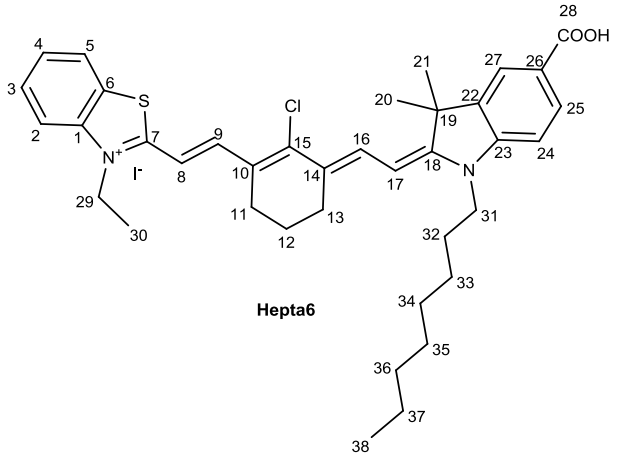
1.00
1.02
1.01
3.01
1.00
2.00
2.00
0.99
0.98
2.01
1.97
5.34
4.02
11.26
0.09
4.02
7.86
20.37
6.01
12
10
8
6
4
2
[ppm]

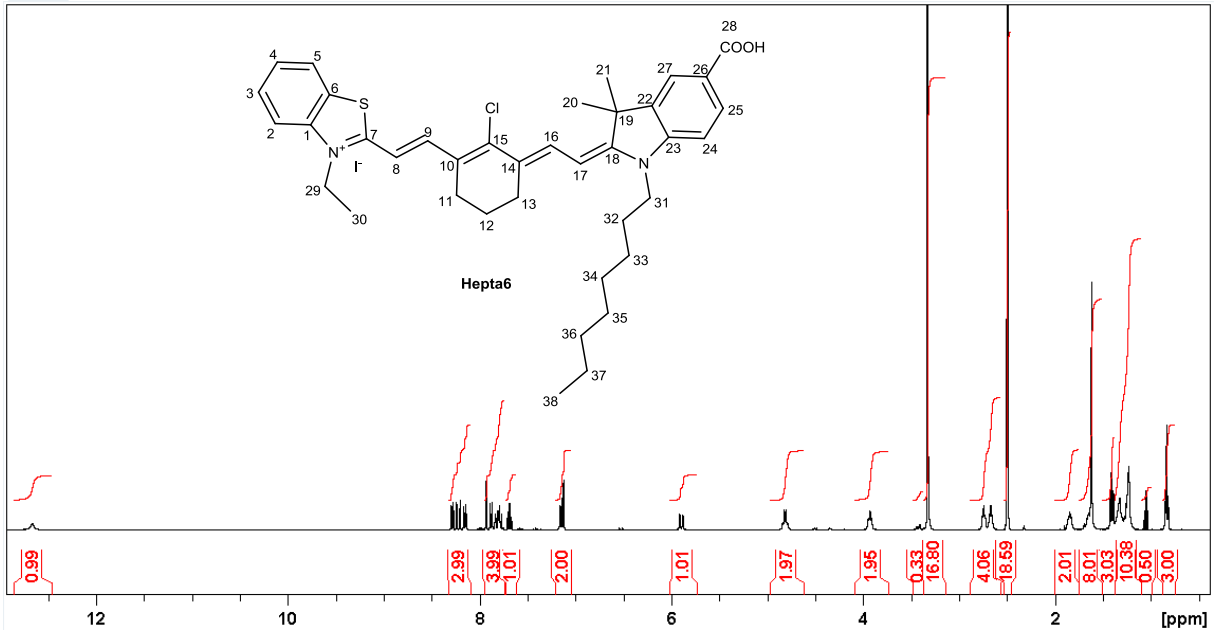

167.2
160.1
152.2
147.7
146.7
139.9
138.8
137.7
134.8
129.5
128.9
126.5
126.5
125.6
122.9
122.6
119.0
118.9
115.6
107.1
56.3
45.5
41.8
40.1
39.9
39.7
39.5
39.3
39.1
38.9
31.2
31.1
29.3
28.6
28.5
28.5
27.7
27.0
26.1
25.8
22.0
22.0
20.8
13.9
13.9
Hepta5
160
140
120
100
80
60
40
20
[ppm]

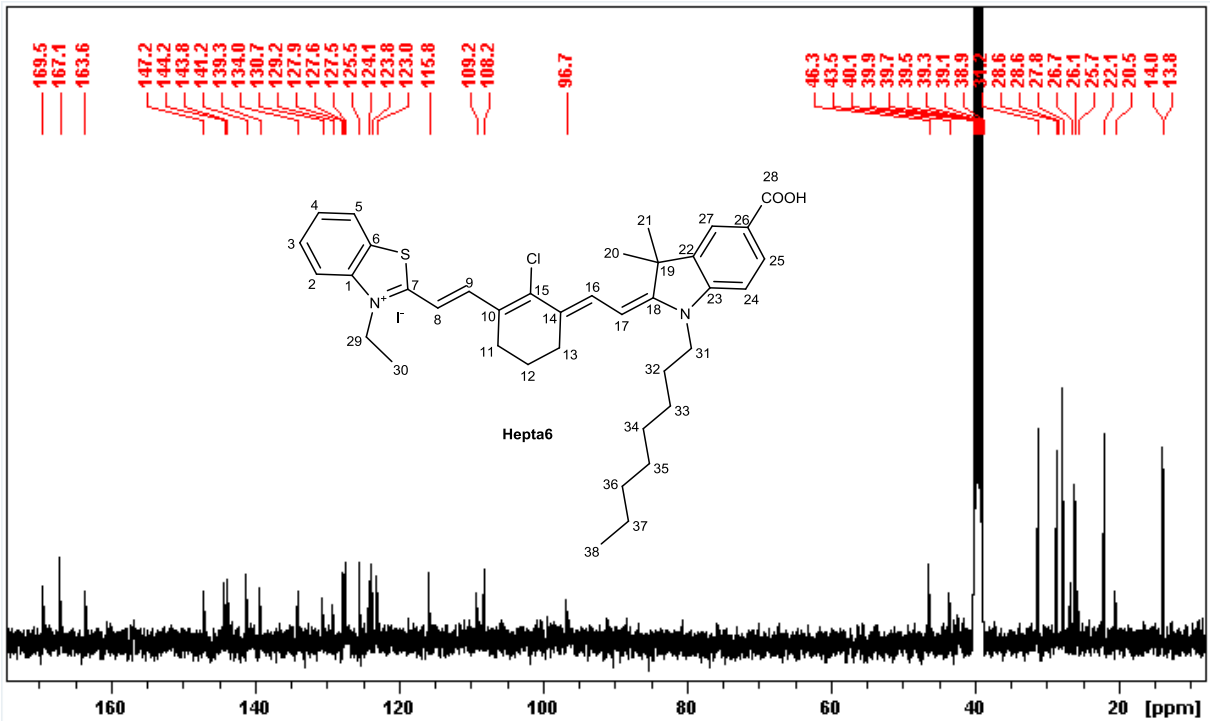


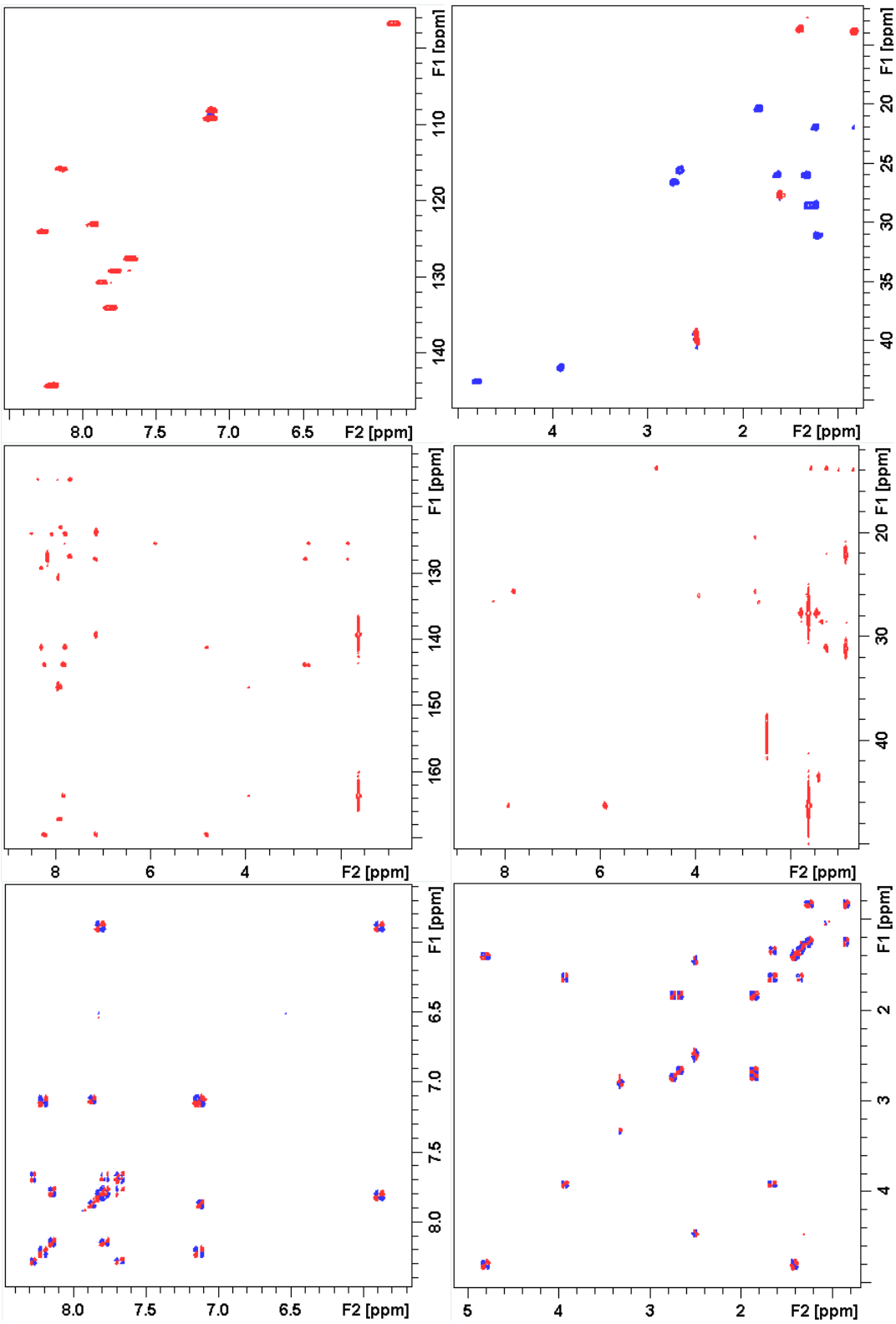
Hepta5 ^{1}H, ^{13}C{^{1}H}, HSQC, HMBC and DQF-COSY NMR (DMSO-d_6)

1.15 2-(2-(3-(2-(5-carboxy-3,3-dimethyl-1-octylindolin-2-ylidene)ethylidene)-2-chlorocyclohex-1-en-1-yl)vinyl)-3-ethylbenzo[d]thiazol-3-ium iodide (Hepta6)



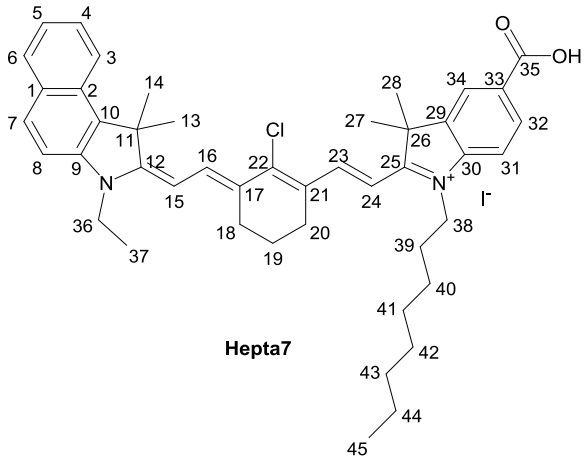


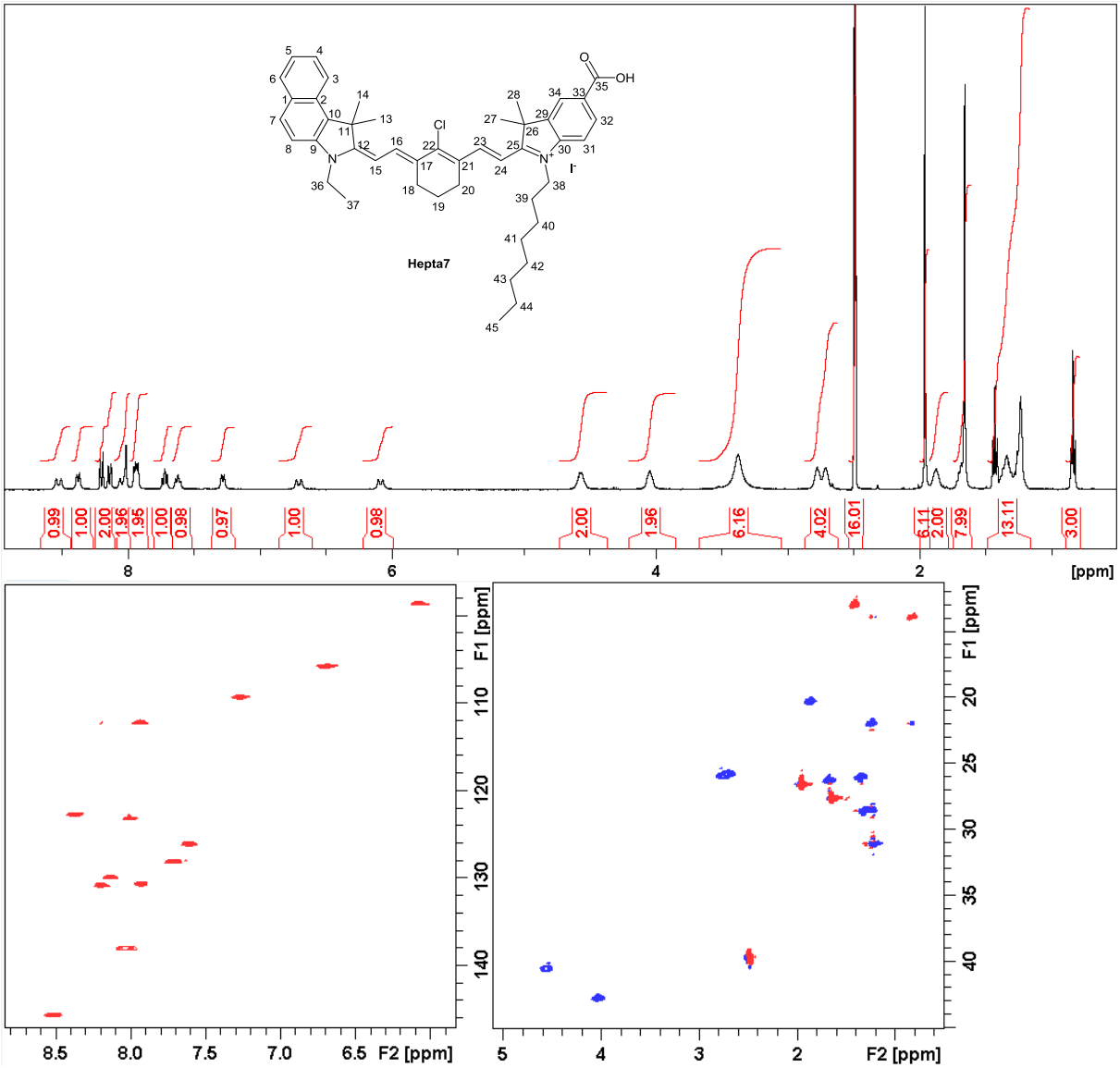

169.5
167.1
163.6
147.2
144.2
143.8
141.2
139.3
134.0
130.7
129.2
127.9
127.6
127.5
125.5
124.1
123.8
123.0
115.8
109.2
108.2
96.7
46.3
43.5
40.1
39.9
39.7
39.5
39.3
39.1
38.9
28.6
28.6
27.8
26.7
26.1
25.7
22.1
20.5
14.0
13.8
COOH
Cl
Hepta6
160
140
120
100
80
60
40
20
[ppm]

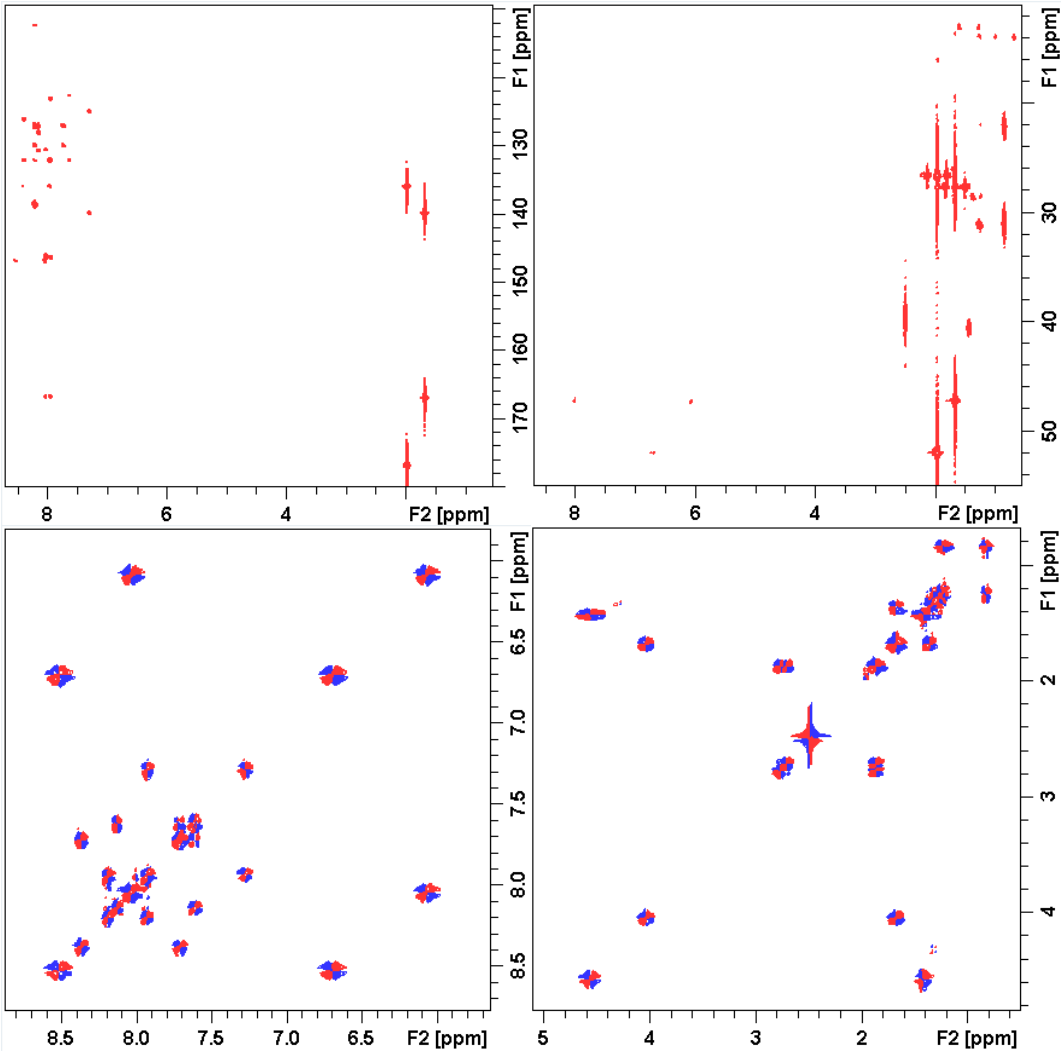


Hepta6 ^{1}H, $^{13}C\{^{1}H\}$, HSQC, HMBC and DQF-COSY NMR (DMSO-d_6)

1.16 5-carboxy-2-(2-(2-chloro-3-(2-(3-ethyl-1,1-dimethyl-1,3-dihydro-2*H*-benzo[e]indol-2-ylidene)ethylidene)cyclohex-1-en-1-yl)vinyl)-3,3-dimethyl-1-octyl-3*H*-indol-1-ium (Hepta7)

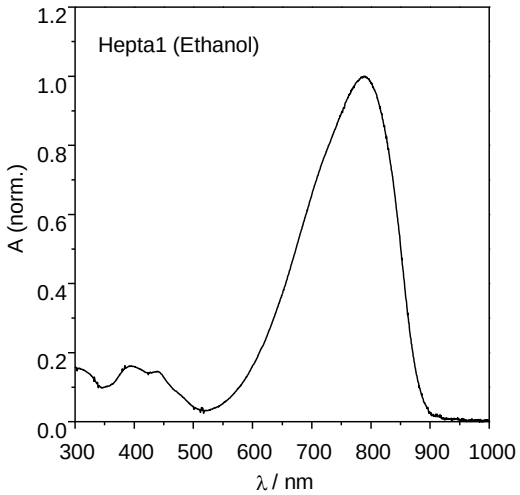


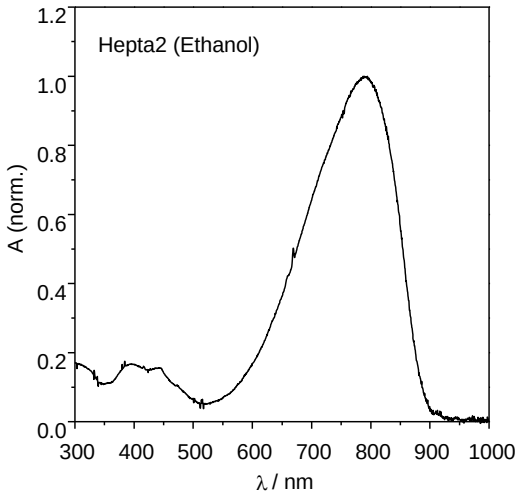


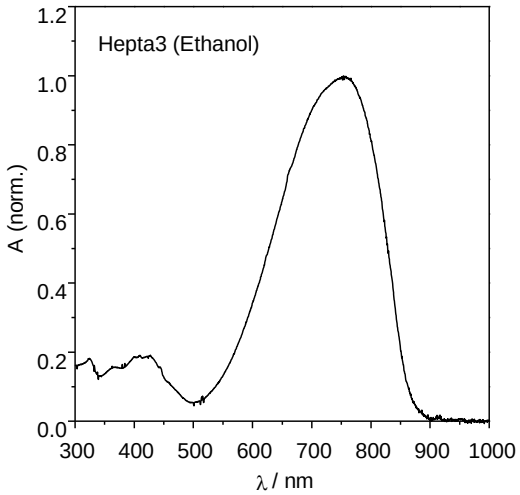


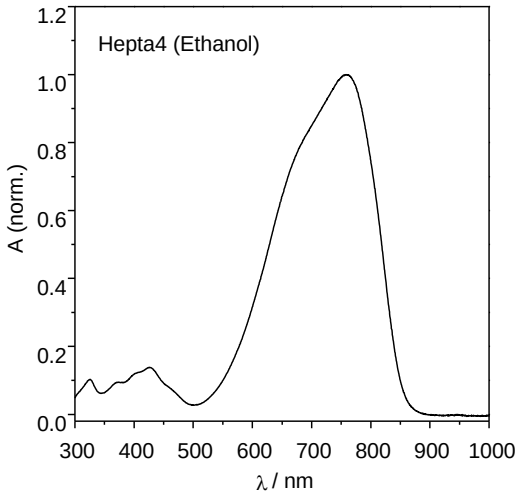
Hepta7 ^{1}H, HSQC, HMBC and DQF-COSY NMR (DMSO-d_6)

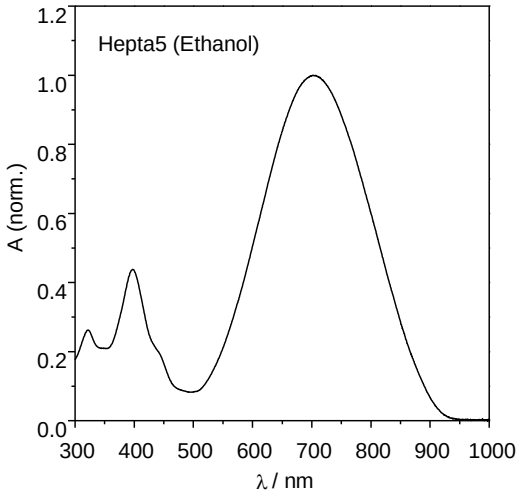
2 UV-vis spectroscopy

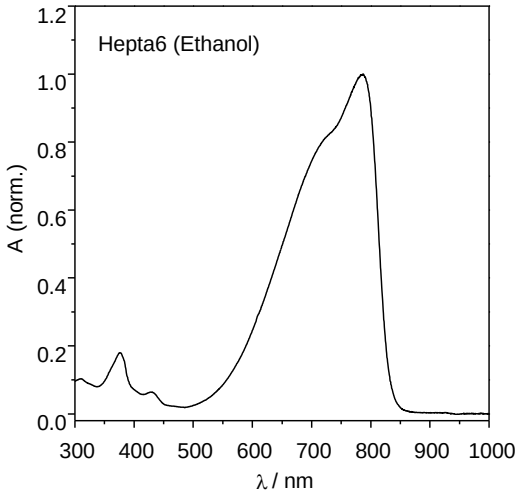


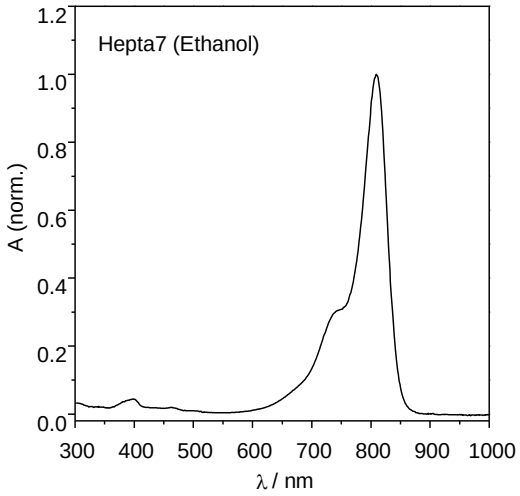


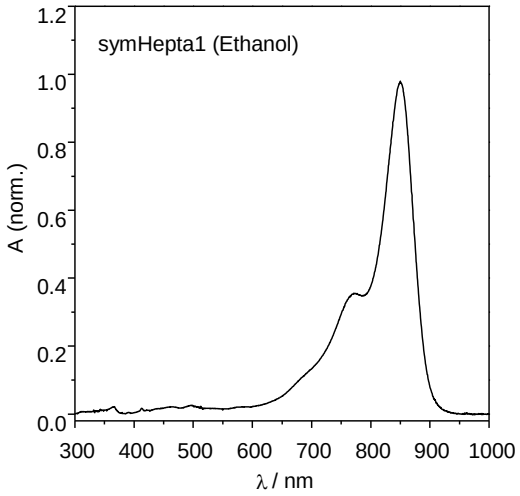


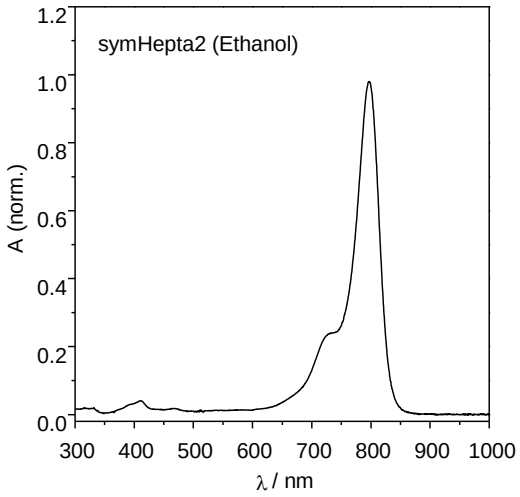


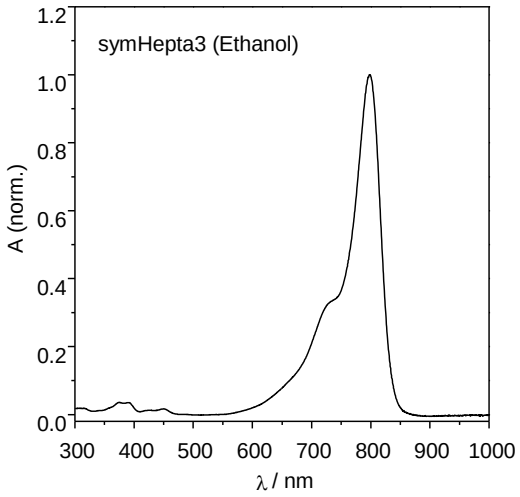




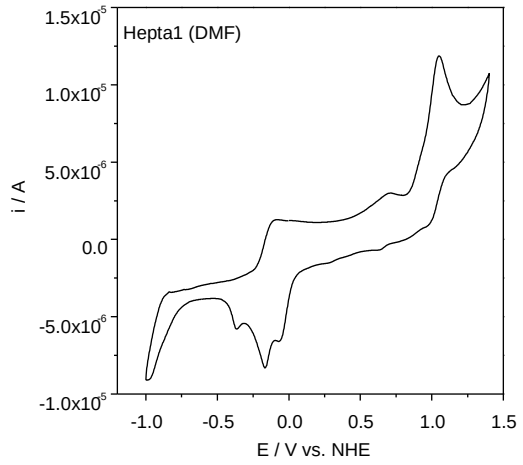

Hepta7 (Ethanol)
A (norm.)
λ / nm
1.2
1.0
0.8
0.6
0.4
0.2
0.0
300
400
500
600
700
800
900
1000

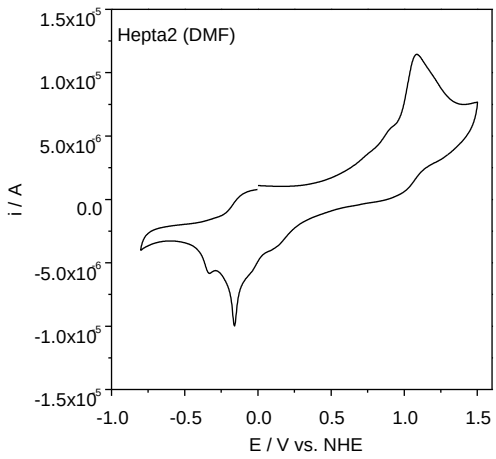

symHepta1 (Ethanol)
A (norm.)
λ / nm
1.2
1.0
0.8
0.6
0.4
0.2
0.0
300
400
500
600
700
800
900
1000

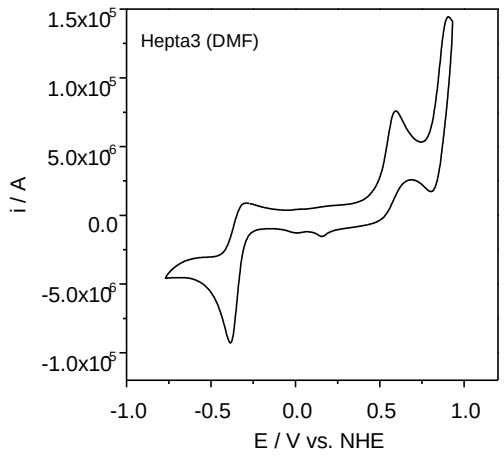

symHepta2 (Ethanol)
A (norm.)
λ / nm
1.2
1.0
0.8
0.6
0.4
0.2
0.0
300
400
500
600
700
800
900
1000

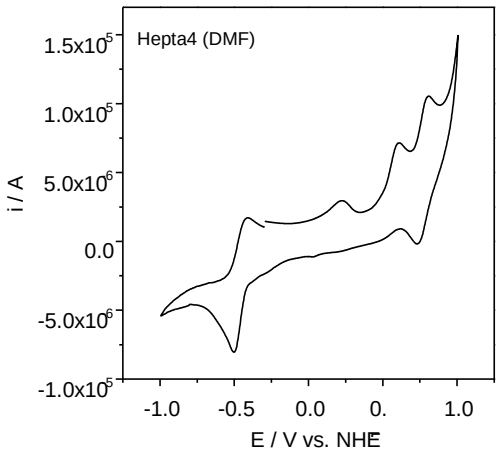

symHepta3 (Ethanol)
A (norm.)
λ / nm
1.2
1.0
0.8
0.6
0.4
0.2
0.0
300
400
500
600
700
800
900
1000

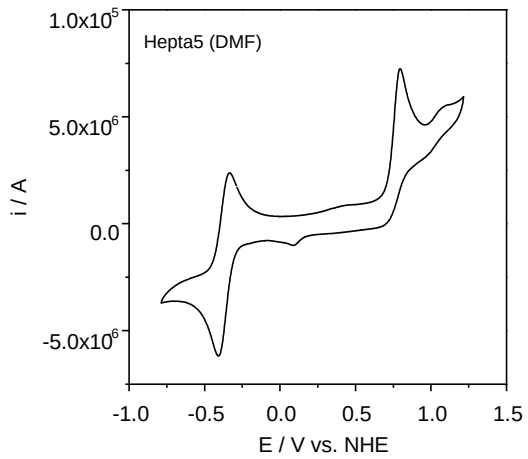
3 Cyclic Voltammetry

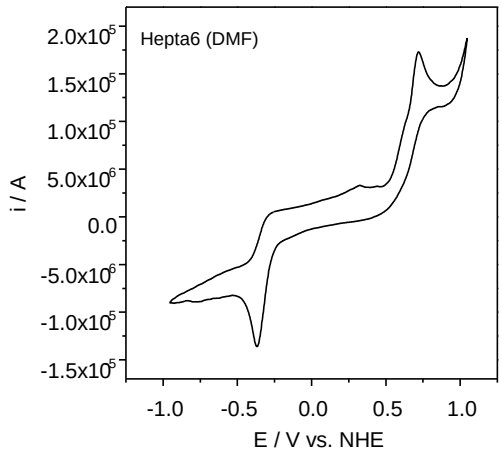


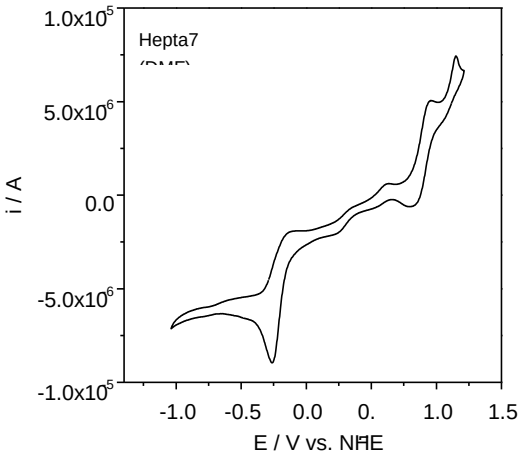


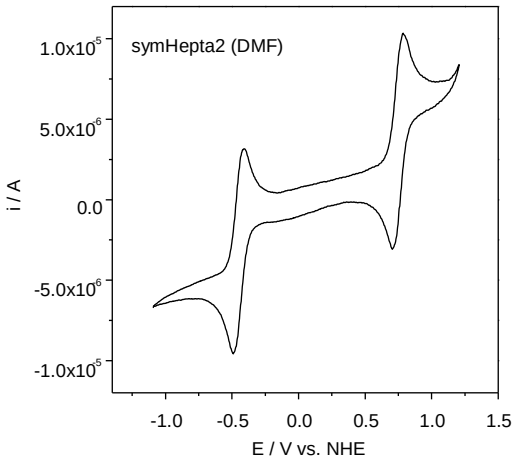




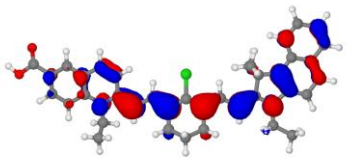
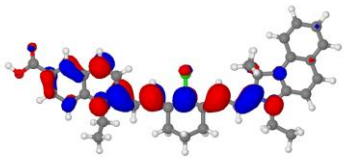
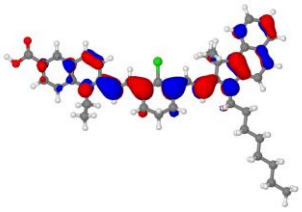
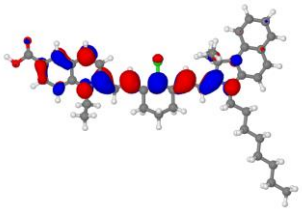
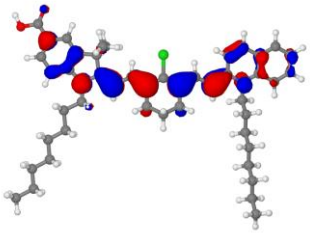
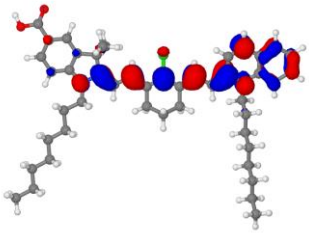
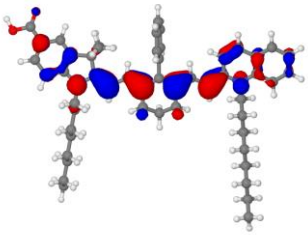
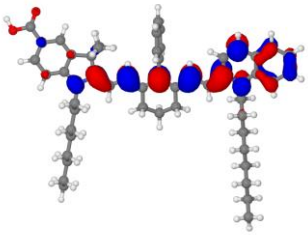
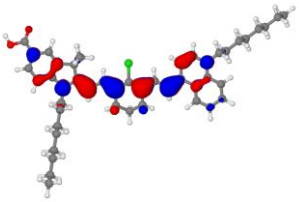
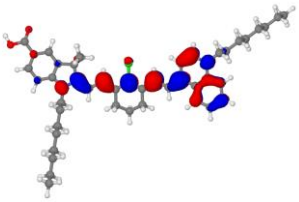


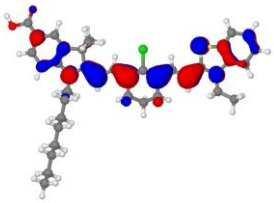
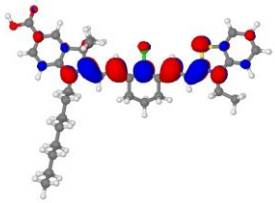
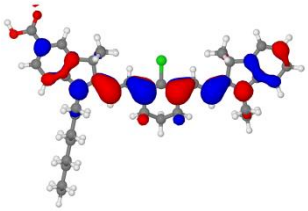
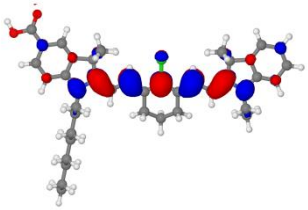



Hepta7
(DMF)
1.0x10^5
5.0x10^6
0.0
-5.0x10^6
-1.0x10^5
i / A
-1.0
-0.5
0.0
0.
1.0
1.5
E / V vs. NHE


symHepta2 (DMF)
1.0x10^5
5.0x10^6
0.0
-5.0x10^6
-1.0x10^5
i / A
-1.0
-0.5
0.0
0.5
1.0
1.5
E / V vs. NHE

4 Molecular Modelling

	HOMO	LUMO
Hepta1		
Hepta2		
Hepta3		
Hepta4		
Hepta5		

Hepta6		
Hepta7		

5 Dye sensitized solar cell preparation

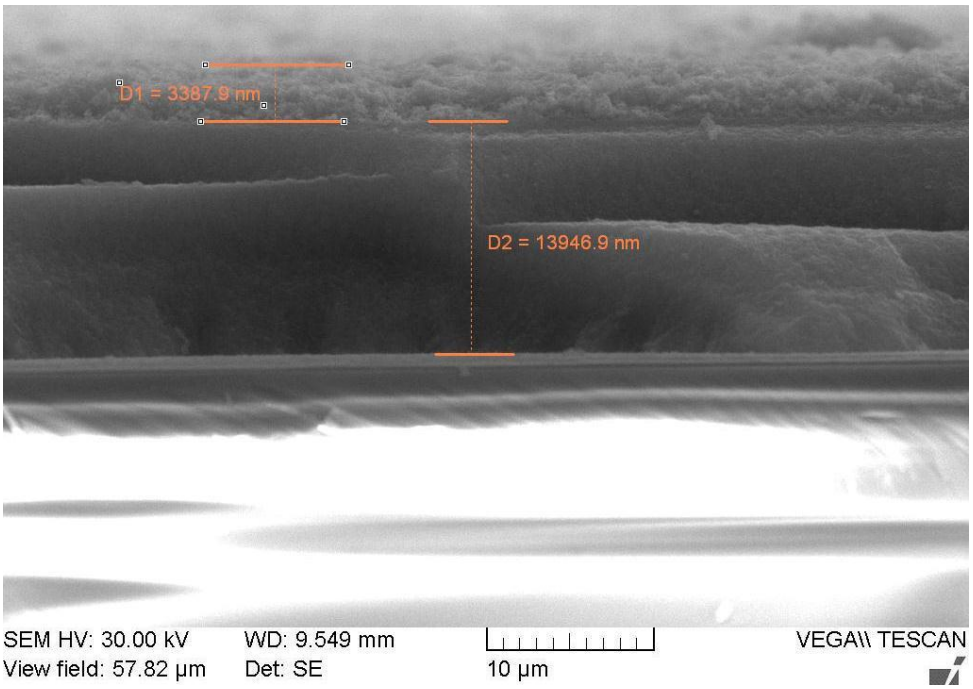


Figure S2 SEM cross section image of mesoporous titania photo anode.