Supporting Information

Ionic Liquid-Based Dye Sensitized Solar Cells - Insights into Electrolyte and Redox Mediator Design

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I. Instrumentation

The measuring cell (Figure S1) for measuring electric conductivity consists of a pair of indium tin oxide (ITO) electrodes. The distance between the two electrodes is fixed by a Teflon spacer (∅ 3 mm, height 0.5 mm) which is filled with the sample. In addition, a multimeter and thermometer were connected to each electrode to allow for an accurate reading and temperature control. All the samples were heated in a tube furnace which was heated in a drying oven (Heraeus Function line T, Thermo Scientific) (Figure S1). The temperature was controlled with a handheld thermometer (Omega HH11B, Omega, Canada) equipped with a K-Type thermocouple, while the resistances were simultaneously measured with a Voltcraft VC 608 multimeter (Voltcraft Conrad Electronic, Germany) under constant 2.5 V.

The conductivity of the electrolytes σ was calculated from the temperature dependent resistance which was measured using an anisotropic conductivity analysis method[1]:

$$\boldsymbol{\sigma} = \frac{\boldsymbol{d}}{\boldsymbol{R_b A}} \quad (1)$$

where R_b, d, and A are the bulk resistance, the sample thickness, and the cross sectional area of the electrode, respectively.

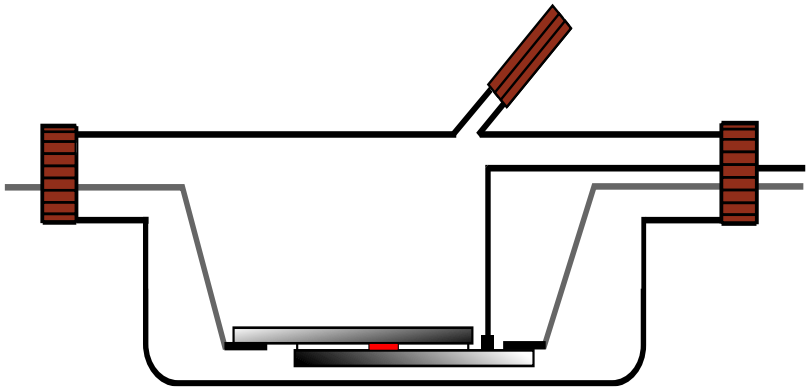

Figure S1. Setup of conductivity measurement, *grey lines*: contact for the multimeter, *black line* thermometer.

The DSSCs were manufactured as follows. For the preparation of the dye-absorbed photoelectrode, the TiO_2-layered ITO-glasses were immersed in a solution of 47 mg dye N719 ($RuL_2(NCS)_2 \cdot 2TBA$, OrganicaFeinchemie GmbH, Bitterfeld-Wolfen, Germany) in 100 mL ethanol for at least 24 h to allow the TiO_2 layer to absorb the dye. Prior to assembly of the DSSCs' photoelectrodes were dried in air. As counter-electrode, ITO-glasses were wetted with a solution of 20.5 mg chloroplatinic acid hydride (Sigma Aldrich) in 5 mL of 2-propanol. After drying in

ambient atmosphere for several minutes, the counter-electrode glasses were calcinated in at 450 °C for 2 h. Both electrodes were washed and dried carefully prior to use. As an appropriate electrolyte for the DSSCs, the studied ILs/ILCs were doped with 25 mol% of solid iodine (I_2) by stirring at room temperature for 24 h, to form the I^-/I_3^- redox couple. Then, a Parafilm© frame was placed onto the Pt-counter-electrode and filled with the electrolyte samples. In order to distribute the sample homogeneously on the glass substrate the Pt-electrode was heated on a hot plate. The photoelectrode was placed in staggered order on the counter-electrode to provide two contact surfaces for the connections. The DSSCs with hygroscopic electrolytes were built in the glovebox and glued with two-components glue (UHU plus 300, UHU GmbH & Co. KG, Germany) to prevent any exposition to moisture. For comparable conditions, all DSSCs were glued at the superimposed edged.

The solar cells were irradiated on the dye-coated working-electrode by a xenon lamp at 1 AM, from a Newport 190 Sol2A (model: 940042A), equipped with an IR cut-off filter. The irradiated area has a specific value of 0.12 cm^2. The working-electrode and the platinic-layered counter-electrode were connected together with a reference-electrode (Figure S2, *bottom*). The current-voltage curves were then recorded at a scan rate of 40.0 mV s^{-1}. From the photocurrent density-voltage characteristic of a DSSC, the overall *photoelectrical energy conversion efficiency* η can be calculated (2), where $\mathbf{I_{sc}}$ is the *short-circuit photocurrent*, $\mathbf{V_{oc}}$ the *open-circuit voltage*, $\mathbf{P_{in}}$ the *incident light power* (per area A) and **FF** the *fill factor*. The fill factor describes the ratio of maximum power (P_{max}, 3) per unit area of the solar cell, divided by the product of the short-circuit current (I_{sc}) and the open-circuit photovoltage (V_{oc}) (4). In other words, FF is the relation between a real photovoltaic cell and an *ideal* solar cell that is supposed to be a constant current source (Figure S3).[2]

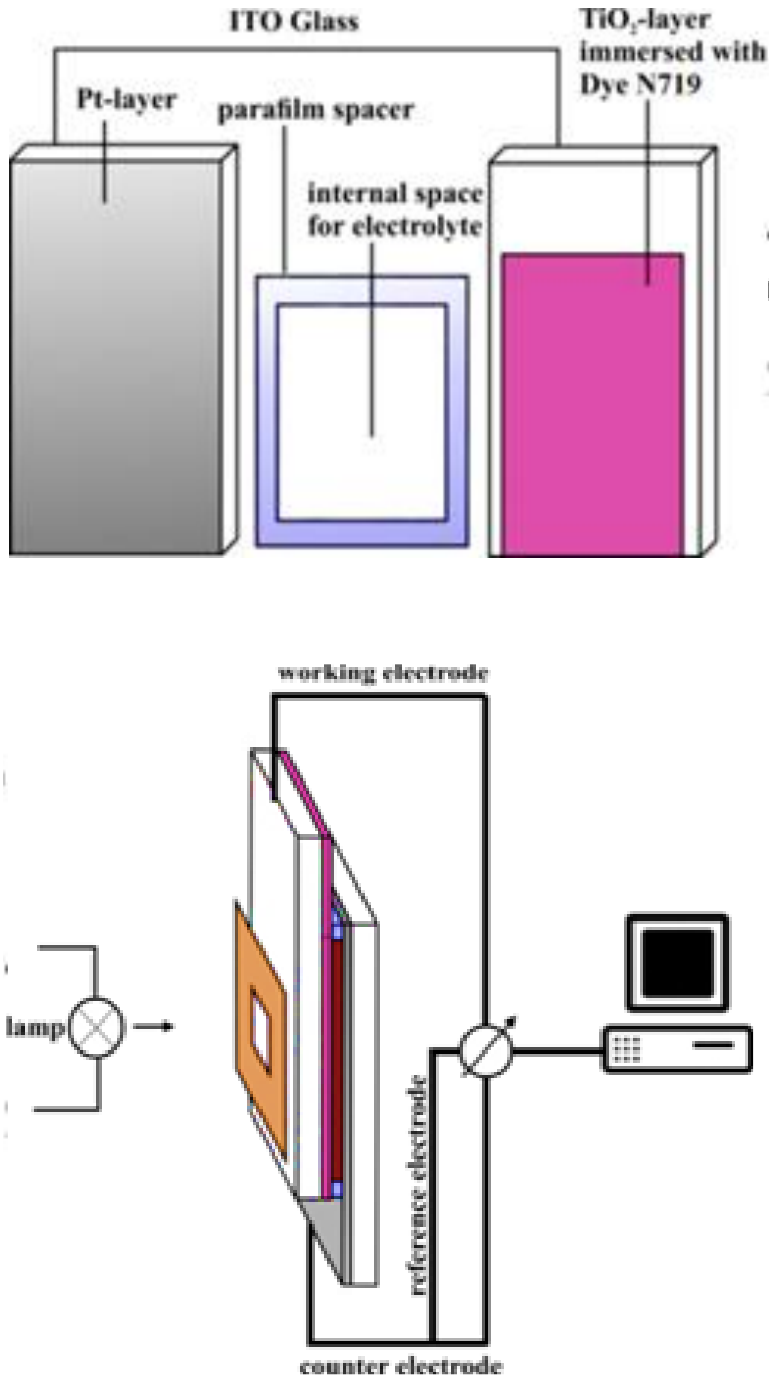

Figure S2. *Top*: Preparation of the electrodes. *Bottom*: Schematic setup for the solar-to-energy-conversion measurements.

$$\eta = \frac{I_{sc} * V_{oc} * FF}{P_{in} * A} \quad (2)$$

$$P_{max} = I_{mp} * U_{mp} \quad (3)$$

$$FF = \frac{P_{max} * A}{I_{sc} * V_{oc}} \quad (4)$$

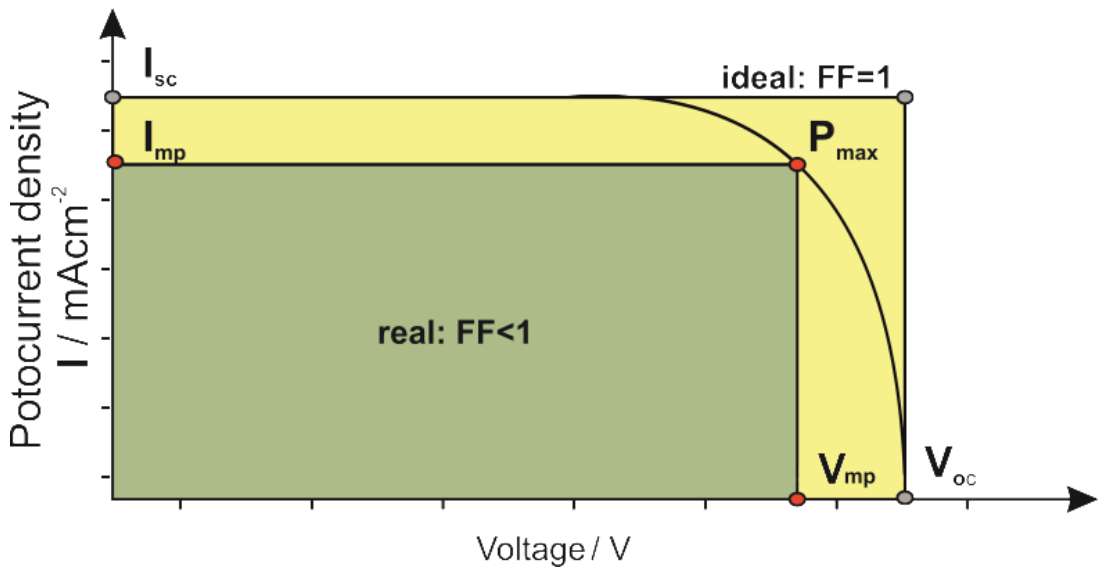

Figure S3. Photocurrent density-voltage characteristic of a DSSC.

II. Detailed synthetic procedures for compounds **1a-5a**, **1-10**

Synthesis

The alkylazides were synthesized according to a common literature method.[3] All other starting materials and solvents were purchased from standard commercial sources and were used without further purification. No protective atmosphere was required during synthesis.

Synthesis of 1-alkyl-1,2,3-triazole (**1a-4a**)

Alkylazide (25 mmol, 1 eq.) and vinyl acetate (100 mmol, 4 eq.) were heated at 80 °C in a closed glass tube for three days. Then n-hexane (200 mL) was added and the suspension was filtered off. The solution was cooled to -78 °C for 4 hours. The precipitated product was filtered off and dried overnight under vacuum.

Synthesis of 1-methyl-1,2,3-triazole (**5a**)

1-H-1,2,3-triazole (50 mmol, 1 eq.) and potassium carbonate (101 mmol, 2.02 eq.) were solved in tetrahydrofuran (50 mL). Methyl iodide (55 mmol, 1.1 eq.) was added and the mixture was stirred during 3 hours at room temperature. The solution was filtered and the filtrate was concentrated and the residue dried under vacuum.

Synthesis of 1-alkyl-3-alkyl-1,2,3-triazolium iodide (**1-8**)

1-Alkyl-1,2,3-triazole (**1a**–**5a**) (50 mmol, 1 eq.) and the respective alkyl iodide (55 mmol, 1.1 eq.) were heated under reflux in acetonitrile (10 mL) during 48 hours. After cooling to room temperature the solution was washed with ethyl acetate and put in a cold bath (-78 °C) to allow the crystallization of the product. The precipitate was washed many times and then dried under vacuum.

Synthesis of 1-alkyl-3-methylimidazolium iodide (**9**, **10**)

1-Methylimidazole (50 mmol, 1eq.), the respective alkyl iodide (55 mmol, 1.1 eq.) and acetonitrile (10 mL) were heated under reflux for three days. After cooling to room temperature the solution was washed with ethyl acetate and put in a cold bath (-78 °C) to allow the crystallization of the product. The precipitate was washed many times and then dried under vacuum.

1-Dodecyl-1,2,3-triazole (1a). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 0.84 (t, J_{H-H} = 6.8 Hz, 3H), 1.21 (s, 14H), 1.27 (s, 4H), 1.85-1.88 (m, 2H), 4.34 (t, J_{H-H} = 7.2 Hz, 2H), 7.52 (s, 1H), 7.65 (s, 1H). ν_{max} (cm^{-1}): 3126, 3074, 3042, 2992, 2954, 2916, 2872, 2846, 1794, 1709, 1628, 1529, 1463, 1444, 1428, 1374, 1353, 1311, 1273, 1254, 1228, 1205, 1193, 1129, 1088, 1052, 1039, 992, 899, 814, 751, 724, 690, 654, 635, 501, 430, 416.

1-Undecyl-1,2,3-triazole (2a). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 0.81 (t, J_{H-H} = 6.4 Hz, 3H), 1.18 (s, 12H), 1.25 (s, 4H), 1.83-1.85 (m, 2H), 4.33 (t, J_{H-H} = 7.2 Hz, 2H), 7.49 (s, 1H), 7.67 (s, 1H). ν_{max} (cm^{-1}): 3140, 3123, 2953, 2917, 2846, 1744, 1663, 1487, 1462, 1375, 1340, 1326, 1293, 1279, 1256, 1227, 1213, 1115, 1073, 1034, 987, 953, 923, 890, 811, 798, 772, 737, 725, 700, 649, 600, 507, 489, 437.

1-Decyl-1,2,3-triazole (3a). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 0.84 (t, J_{H-H} = 6.8 Hz, 3H), 1.22 (s, 10H), 1.28 (s, 4H), 1.85-1.89 (m, 2H), 4.35 (t, J_{H-H} = 7.2 Hz, 2H), 7.52 (s, 1H), 7.66 (s,

1H). ν_{max} (cm^{-1}): 3140, 3122, 2956, 2918, 2870, 2847, 1748, 1673, 1663, 1487, 1461, 1441, 1370, 1335, 1300, 1285, 1264, 1234, 1214, 1115, 1073, 1034, 1016, 1000, 968, 951, 890, 879, 812, 799, 757, 740, 726, 701, 649, 504, 477, 432.

1-Octyl-1,2,3-triazole (4a). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 0.87 (t, J_{H-H} = 6.8 Hz, 3H), 1.26-1.37 (m, 18H), 1.89-1.94 (m, 2H), 4.38 (t, J_{H-H} = 7.2 Hz, 2H), 7.53 (s, 1H), 7.70 (s, 1H). ν_{max} (cm^{-1}): 3119, 2956, 2924, 2855, 1533, 1465, 1377, 1280, 1261, 1215, 1113, 1073, 1027, 950, 922, 866, 795, 723, 702, 663, 638, 553, 511, 491, 456, 445, 425, 414.

1-Methyl-1,2,3-triazole (5a). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): 3.97 (s, 3H), 7.49 (s, 1H), 7.53 (s, 1H). ν_{max} (cm^{-1}): 3324, 3143, 3125, 2953, 2883, 1769, 1719, 1673, 1486, 1449, 1417, 1367, 1337, 1311, 1263, 1214, 1175, 1115, 1076, 1056, 1028, 990, 948, 920, 785, 701, 678, 635, 492.

1-Dodecyl-3-methyl-1,2,3-triazolium iodide (1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 0.79 (t, J_{H-H} = 6.8 Hz, 3H), 1.17 (s, 14H), 1.28 (s, 4H), 1.96-1.99 (m, 2H), 4.48 (s, 3H), 4.70 (t, J_{H-H} = 7.2 Hz, 2H), 9.31 (s, 1H), 9.37 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 14.0, 22.6, 26.0, 28.8, 29.2 (2C), 29.4, 29.5 (2C), 29.5, 31.8, 41.2, 54.4, 131.3, 132.2. ν_{max} (cm^{-1}): 3126, 3074, 3042, 2992, 2954, 2916, 2872, 2846, 1794, 1709, 1628, 1529, 1463, 1444, 1428, 1374, 1353, 1311, 1273, 1254, 1228, 1205, 1193, 1129, 1088, 1052, 1039, 992, 899, 814, 751, 724, 690, 654, 635, 501, 430, 416. ESI TOF *m/z* (positive mode) 252.2447 (calc. *m/z* = 252.2434).

1-Undecyl-3-methyl-1,2,3-triazolium iodide (2). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 0.81 (t, J_{H-H} = 6.8 Hz, 3H), 1.19 (s, 12H), 1.29 (s, 4H), 1.98-2.01 (m, 2H), 4.50 (s, 3H), 4.72 (t, J_{H-H} = 7.2 Hz, 2H), 9.33 (s, 1H), 9.40 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 14.0, 22.6, 26.0, 28.8, 29.2, 29.2, 29.4, 29.5, 29.6, 31.8, 41.2, 54.4, 131.3, 132.2. ν_{max} (cm^{-1}): 3116, 3072, 3040, 2989, 2953, 2919, 2846, 1791, 1700, 1624, 1528, 1461, 1436, 1388, 1372, 1345, 1313, 1297, 1281, 1260, 1232, 1208, 1195, 1130, 1090, 1043, 1029, 987, 923, 900, 884, 833, 806, 774, 756, 727, 686, 653, 634, 504, 436, 428. ESI TOF *m/z* (positive mode) 238.2264 (calc. *m/z* = 238.2278).

1-Decyl-3-methyl-1,2,3-triazolium iodide (3). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 0.80 (t, J_{H-H} = 6.4 Hz, 3H), 1.18 (s, 10H), 1.29 (s, 4H), 1.97-2.00 (m, 2H), 4.49 (s, 3H), 4.71 (t, J_{H-H} = 7.2 Hz, 2H), 9.32 (s, 1H), 9.38 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 14.0, 22.5, 26.0, 28.7, 29.1, 29.2, 29.3, 29.5, 31.7, 41.2, 54.4, 131.2, 132.1. ν_{max} (cm^{-1}): 3125, 3072, 3043, 2993, 2954, 2918, 2872, 2847, 1794, 1708, 1528, 1463, 1439, 1428, 1388, 1376, 1353, 1309, 1289, 1269, 1240, 1211, 1195, 1129, 1088, 1040, 1026, 972, 898, 814, 790, 750, 734, 723, 690, 653, 635, 501, 475, 427. ESI TOF *m/z* (positive mode) 224.2164 (calc. *m/z* = 224.2121).

1-Octyl-3-methyl-1,2,3-triazolium iodide (4). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 0.78 (t, J_{H-H} = 6.8 Hz, 3H), 1.17 (s, 6H), 1.27 (s, 4H), 1.95-1.98 (m, 2H), 4.48 (s, 3H), 4.70 (t, J_{H-H} = 7.2 Hz, 2H), 9.29 (s, 1H), 9.34 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 14.0, 22.5, 26.0, 29.7, 28.8, 29.5, 31.5, 41.2, 54.4, 131.3, 132.2. ν_{max} (cm^{-1}): 3124, 3070, 3043, 2991, 2953, 2921, 2871, 2849, 1795, 1708, 1627, 1529, 1463, 1448, 1430, 1389, 1375, 1354, 1307, 1287, 1257, 1223, 1198, 1129, 1089, 1041, 1027, 1003, 939, 899, 859, 813, 752, 723, 689, 654, 634, 492, 448, 429. ESI TOF *m/z* (positive mode) 196.1842 (calc. *m/z* = 196.1808).

1-Hexyl-3-methyl-1,2,3-triazolium iodide (5). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 0.77 (t, J_{H-H} = 6.8 Hz, 3H), 1.21-1.28 (m, 6H), 1.95 (p, J_{H-H} = 14.4 Hz, J_{H-H} = 7.2 Hz, 2H), 4.46 (s, 3H), 4.68 (t, J_{H-H} = 7.2 Hz, 2H), 9.26 (s, 1H), 9.29 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 13.7, 22.1, 25.5, 29.3, 30.7, 41.1, 54.2, 131.1, 131.9. ν_{max} (cm^{-1}): 3090, 3044, 2956, 2924, 2857, 1721, 1530, 1461, 1379, 1354, 1313, 1259, 1201, 1182, 1128, 1088, 1030, 891, 819, 795, 756, 727, 707, 685, 652, 633, 615, 431. ESI TOF *m/z* (positive mode) 168.1503 (calc. *m/z* = 168.1495).

1-Butyl-3-methyl-1,2,3-triazolium iodide (6). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 0.87 (t, J_{H-H} = 8.0 Hz, 3H), 1.32 (h, J_{H-H} = 22.4 Hz, J_{H-H} = 14.8 Hz, J_{H-H} = 7.6 Hz, 2H), 1.94 (p, J_{H-H} = 14.8 Hz, J_{H-H} =7.2 Hz, 2H), 4.45 (s, 3H), 4.70 (t, J_{H-H} = 6.8 Hz, 2H), 9.24 (s, 1H), 9.26 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 13.2, 19.2, 31.3, 41.2, 54.0, 131.1, 131.9. ν_{max} (cm^{-1}): 3135, 3076, 3040, 2990, 2956, 2935, 2873, 1788, 1699, 1527, 1463, 1440, 1430, 1389, 1379, 1358, 1345, 1311, 1274, 1246, 1211, 1191, 1126, 1086, 1038, 1028, 1010, 947, 896, 806, 748, 732, 703, 687, 652, 634, 610, 504, 426. ESI TOF *m/z* (positive mode) 140.1189 (calc. *m/z* = 140.1182).

1,3-Didecyl-1,2,3-triazolium iodide (7). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 0.82 (t, J_{H-H} = 6.8 Hz, 6H), 1.20 (s, 20H), 1.29 (s, 8H), 1.99-2.02 (m, 4H), 4.75 (t, J_{H-H} = 7.2 Hz, 4H), 9.47 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 14.1 (2C), 22.7 (2C), 26.1 (2C), 28.9 (2C), 29.3 (2C), 29.3 (2C), 29.5 (2C), 29.7 (2C), 31.9 (2C), 54.4 (2C), 131.5 (2C). ν_{max} (cm^{-1}): 3135, 3080, 3041, 2955, 2912, 2873, 2847, 1790, 1701, 1527, 1469, 1442, 1412, 1375, 1351, 1335, 1320, 1309, 1288, 1247, 1223, 1213, 1196, 1173, 1133, 1121, 1087, 1060, 1043, 1031, 948, 891, 862, 823, 808, 775, 741, 718, 688, 643, 603, 540, 519, 461, 448. ESI TOF *m/z* (positive mode) 350.3515 (calc. *m/z* = 350.3530).

1,3-Dioctyl-1,2,3-triazolium iodide (8). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 0.82 (t, J_{H-H} = 6.8 Hz, 6H), 1.21 (s, 12H), 1.30 (s, 8H), 2.00-2.03 (m, 4H), 4.76 (t, J_{H-H} = 7.2 Hz, 4H), 9.48 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 14.0 (2C), 22.5 (2C), 26.0 (2C), 28.8 (2C), 28.9 (2C), 29.7 (2C), 31.6 (2C), 54.4 (2C), 131.4 (2C). ν_{max} (cm^{-1}): 3133, 3092, 3039, 2954, 2916, 2871, 2850, 1810, 1783, 1703, 1525, 1464, 1438, 1376, 1348, 1338, 1309, 1294, 1279, 1266, 1242, 1227, 1189, 1173, 1130, 1115, 1084, 1048, 972, 915, 893, 860, 811, 772, 722, 690, 645, 610, 528, 509, 494, 478, 416. ESI TOF *m/z* (positive mode) 294.2932 (calc. *m/z* = 294.2904).

1-Dodecyl-3-methylimidazolium iodide (9). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 0.82 (t, J_{H-H} = 6.8 Hz, 3H), 1.19 (s, 14H), 1.27 (s, 4H), 1.86-1.89 (m, 2H), 4.08 (s, 3H), 4.47 (t, J_{H-H} = 7.2 Hz, 2H), 7.43 (s, 1H), 7.57 (s, 1H), 9.96 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 14.1, 22.6, 26.2, 28.9, 29.3, 29.3, 29.4, 29.5 (2C), 30.2, 31.8, 37.1, 50.2, 122.7, 123.8, 136.6. ν_{max} (cm^{-1}): 3137, 3070, 2957, 2931, 2870, 1729, 1564, 1460, 1427, 1379, 1337, 1261, 1164, 1113, 1021, 948, 812, 749, 697, 647, 616, 410. ESI TOF *m/z* (positive mode) 251.2543 (calc. *m/z* = 251.2482).

1-Butyl-3-methylimidazolium iodide (10). Yellow viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): 0.81 (t, J_{H-H} = 7.2 Hz, 3H), 1.25 (h, J_{H-H} = 21.6 Hz, J_{H-H} = 14.4 Hz, J_{H-H} = 7.2 Hz, 2H), 1.78 (p, J_{H-H} = 14.8 Hz, J_{H-H} = 7.2 Hz, 2H), 3.99 (s, 3H), 4.21 (t, J_{H-H} = 7.2 Hz, 2H), 7.48 (s, 1H), 7.54 (s, 1H), 9.78 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 13.1, 19.0, 31.7, 36.7, 49.5, 122.1, 123.5, 136.0. ν_{max} (cm^{-1}): 3132, 3071, 3024, 2917, 2850, 1697, 1636, 1588, 1564, 1467, 1404, 1378, 1336, 1282, 1163, 1093, 1080, 1018, 827, 765, 736, 721, 699, 646, 622, 601, 409. ESI TOF *m/z* (positive mode) 139.1235 (calc. *m/z* = 139.1230).

III. ^{1}H and ^{13}C NMR spectra for compounds **1a-5a**, **1-10**

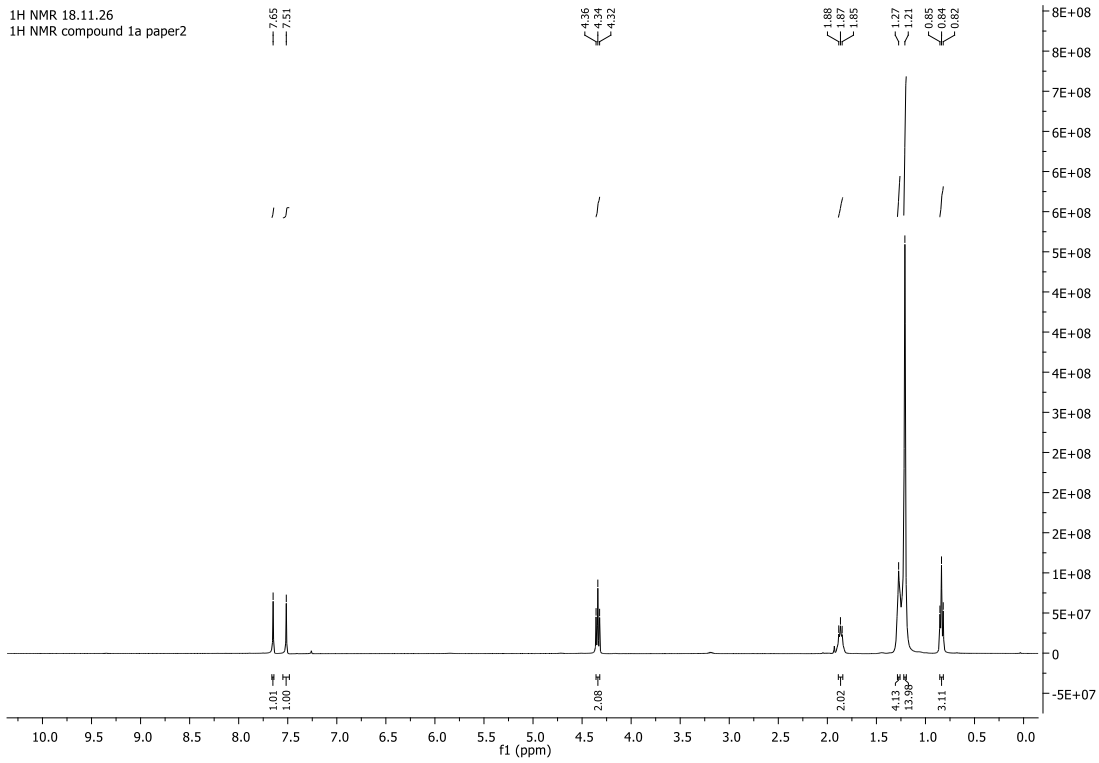

Figure S4. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of compound **1a**.

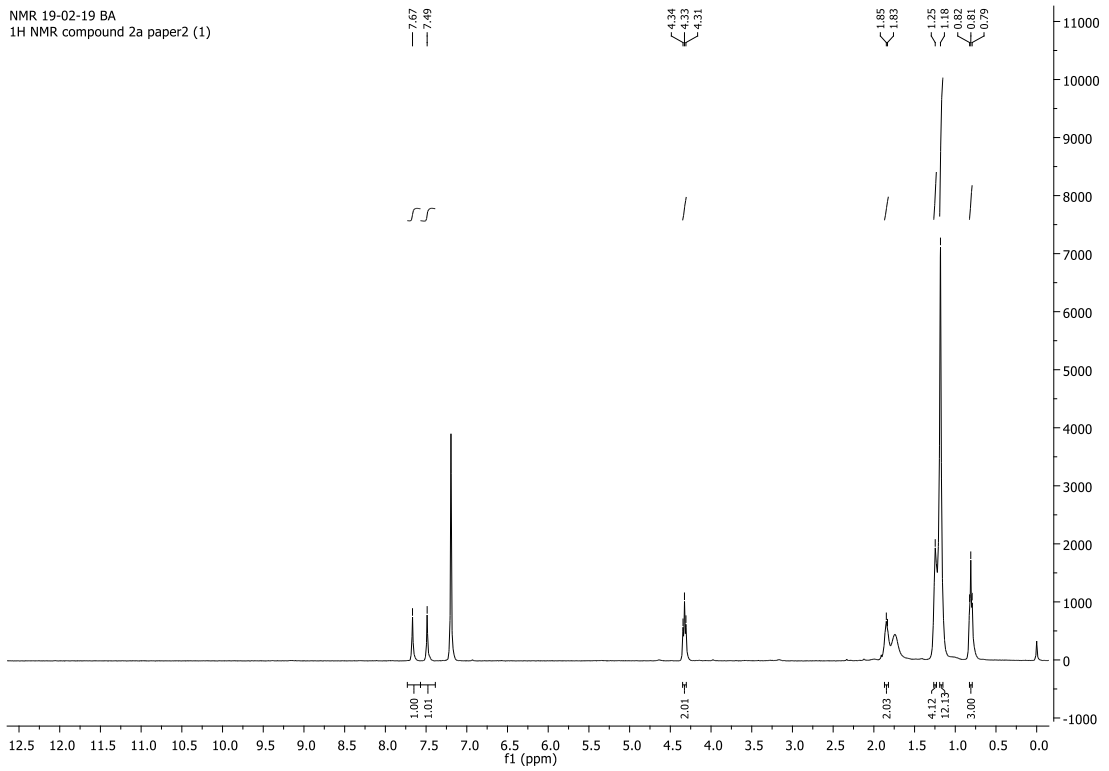

Figure S5. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of compound **2a**.

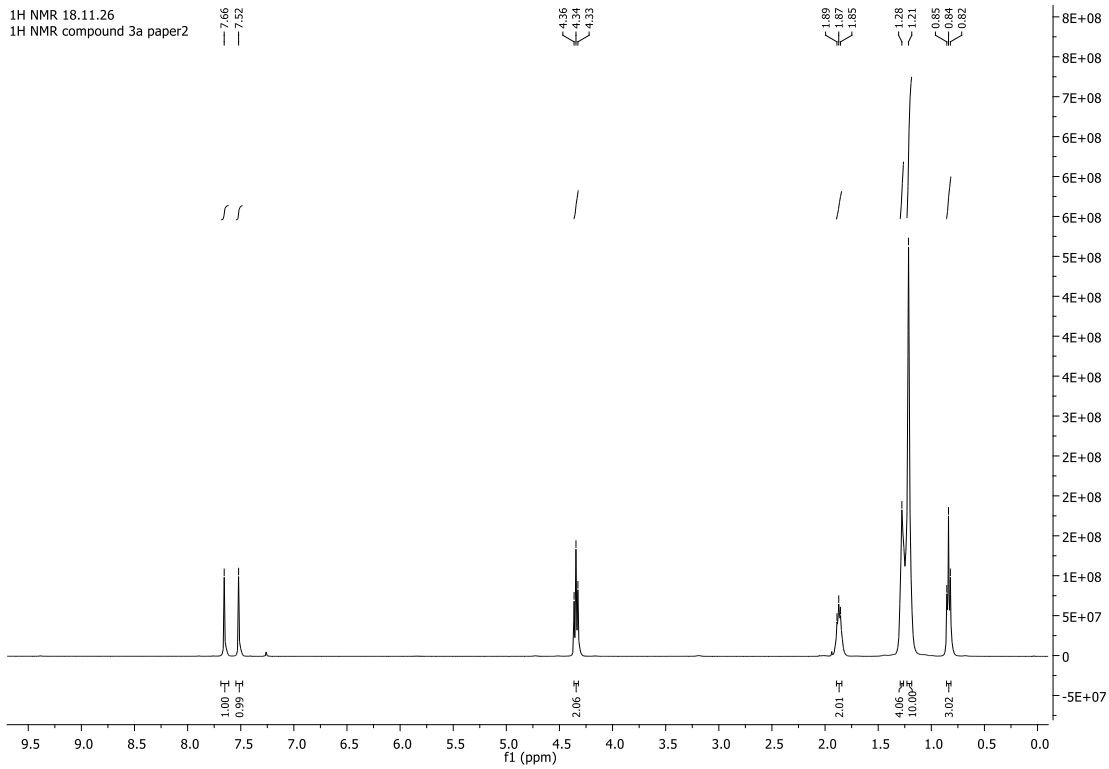

Figure S6. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of compound **3a**.

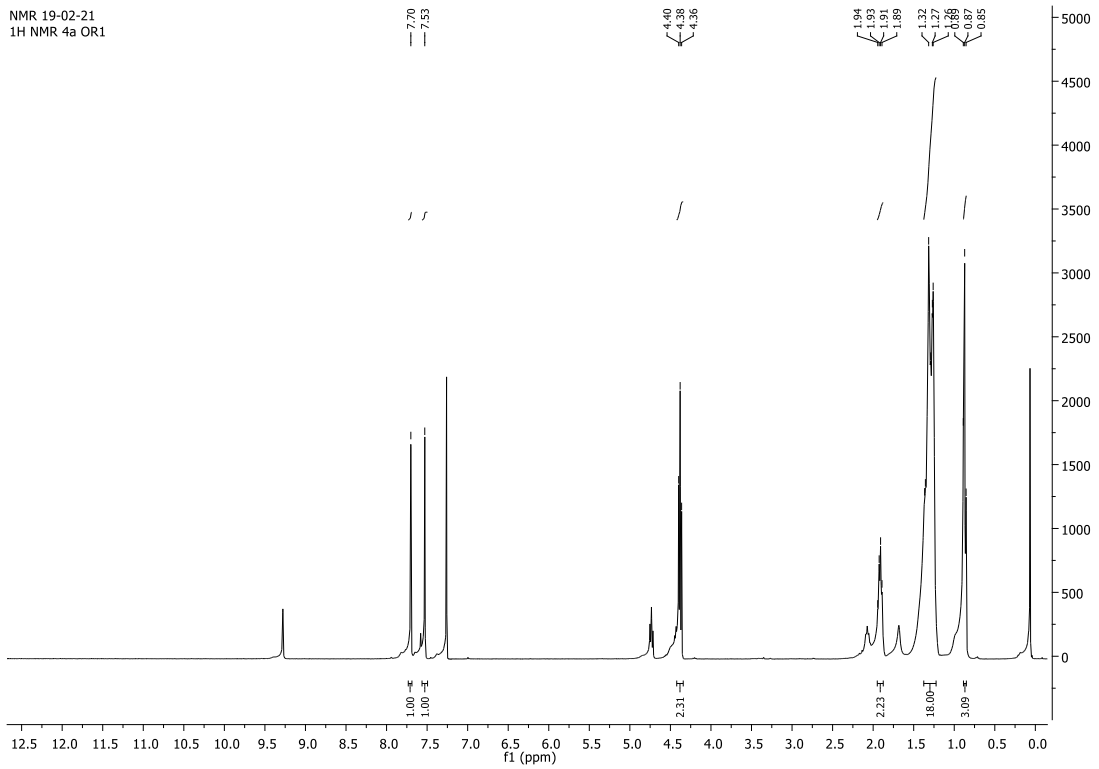

Figure S7. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of compound **4a**.

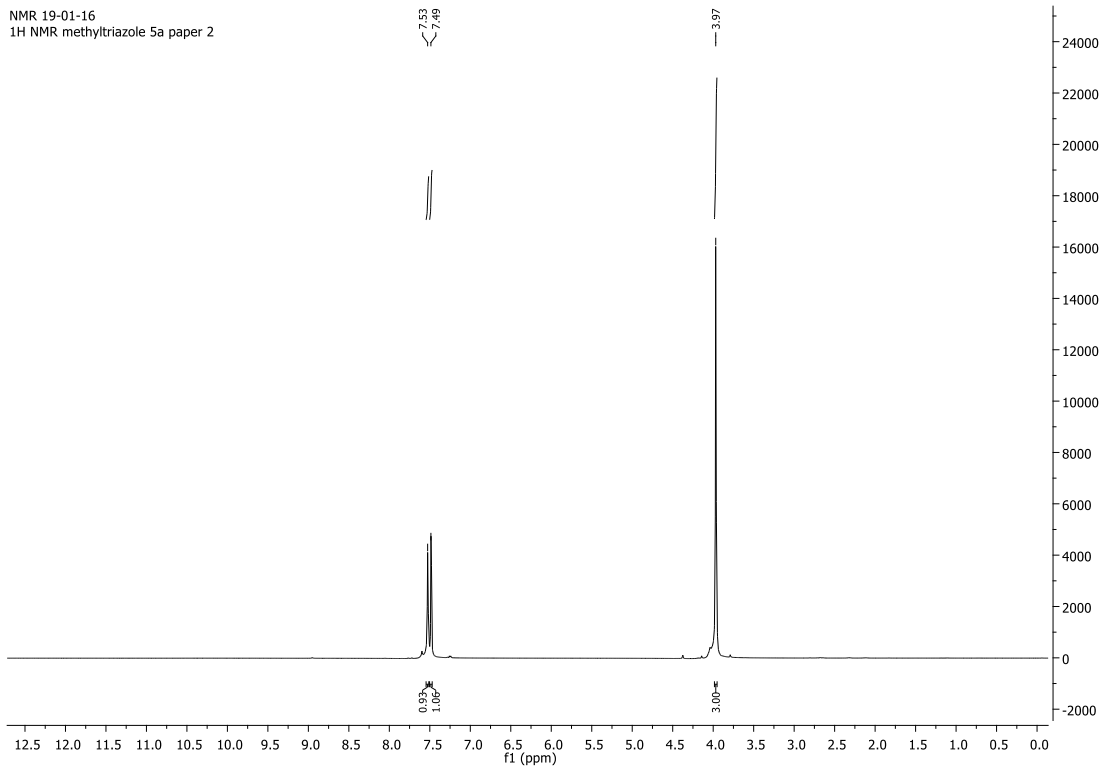

Figure S8. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of compound **5a**.

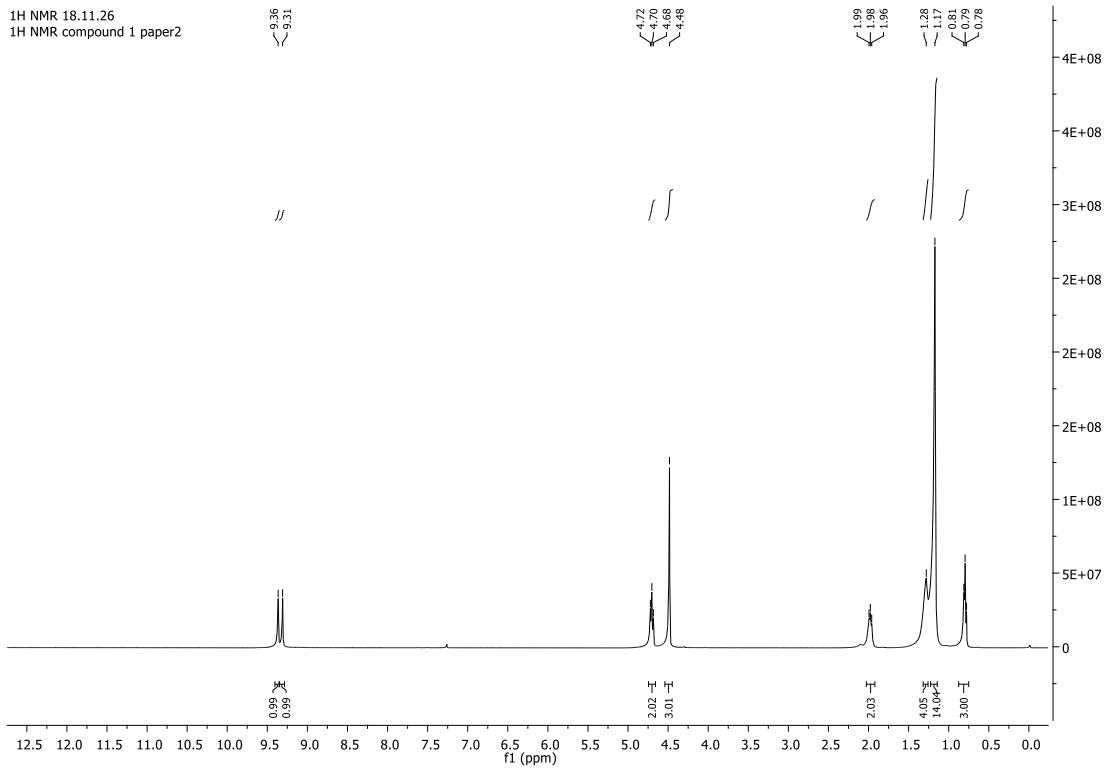

Figure S9. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of compound **1**.

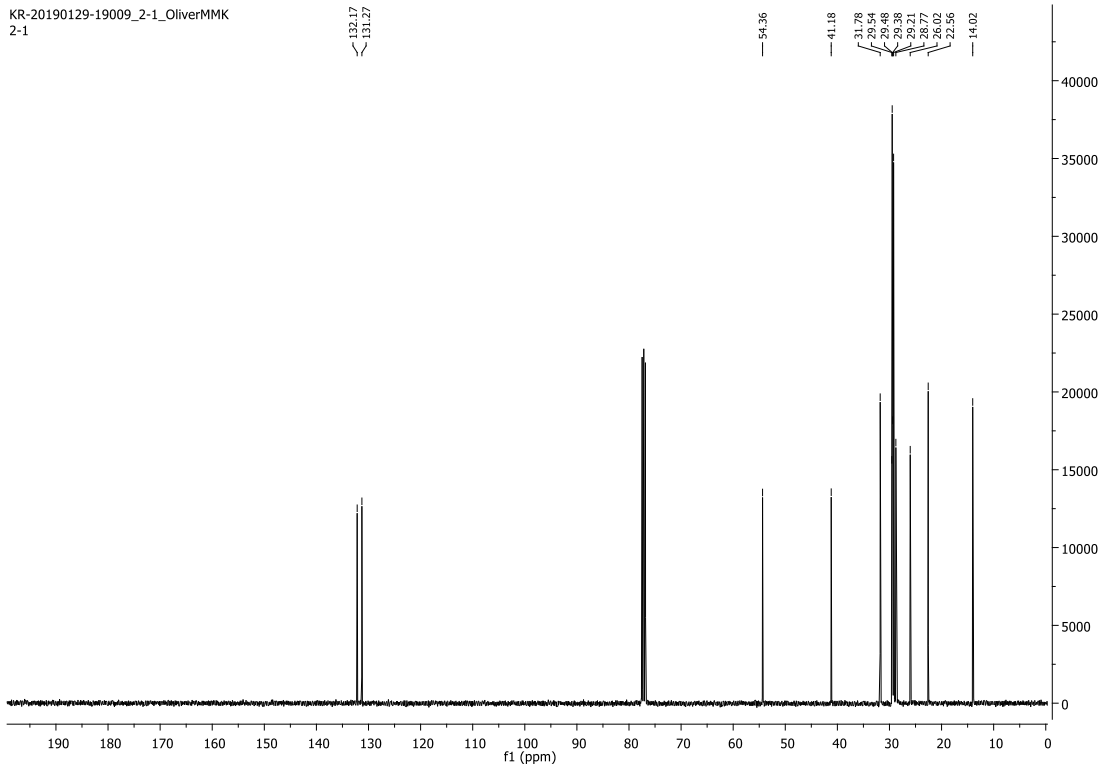

Figure S10. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of compound **1**.

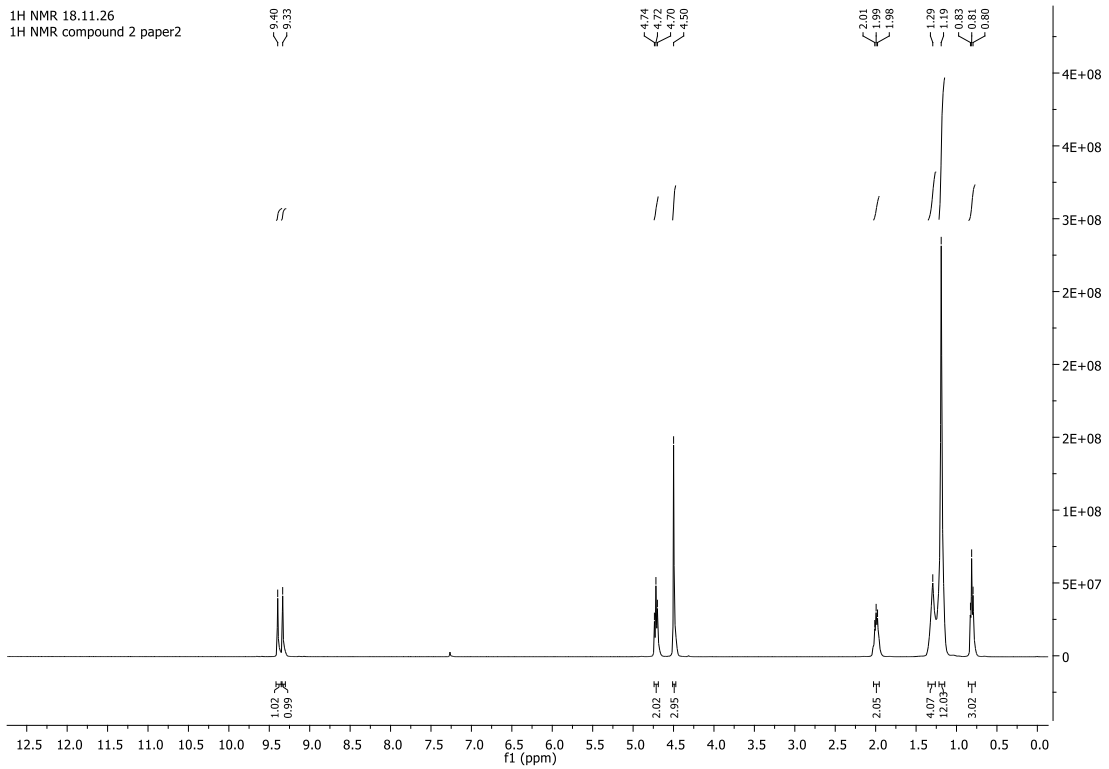

Figure S11. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of compound **2**.

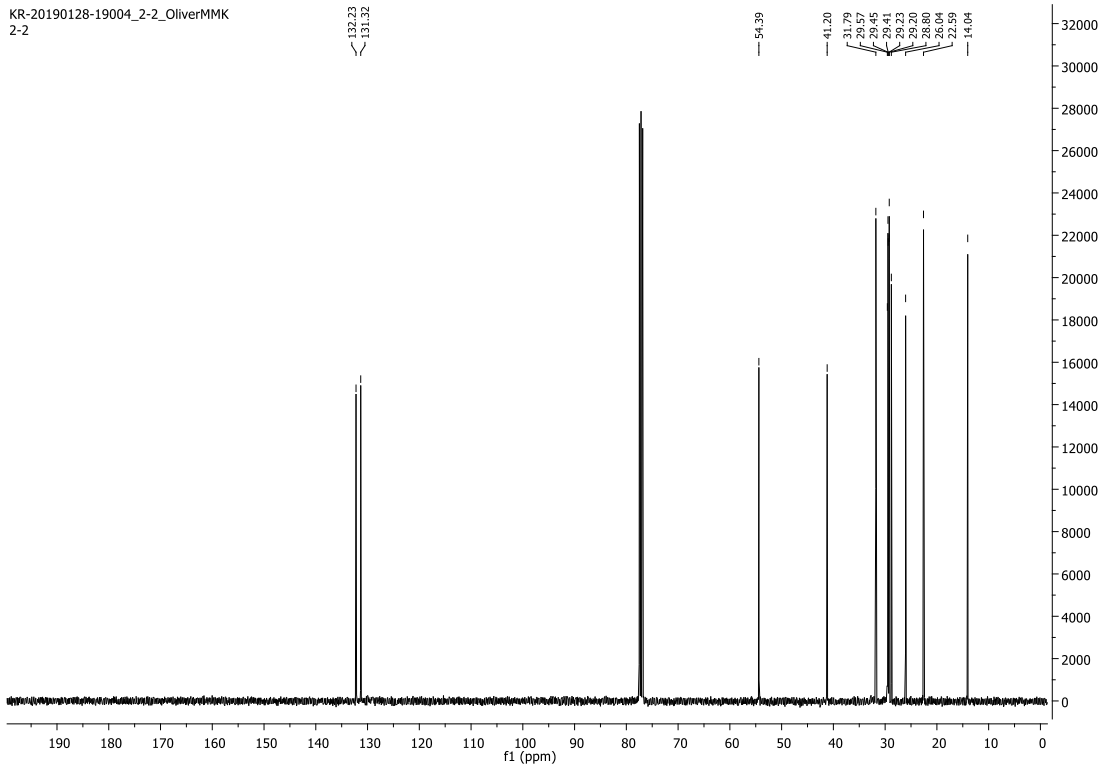

Figure S12. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of compound **2**.

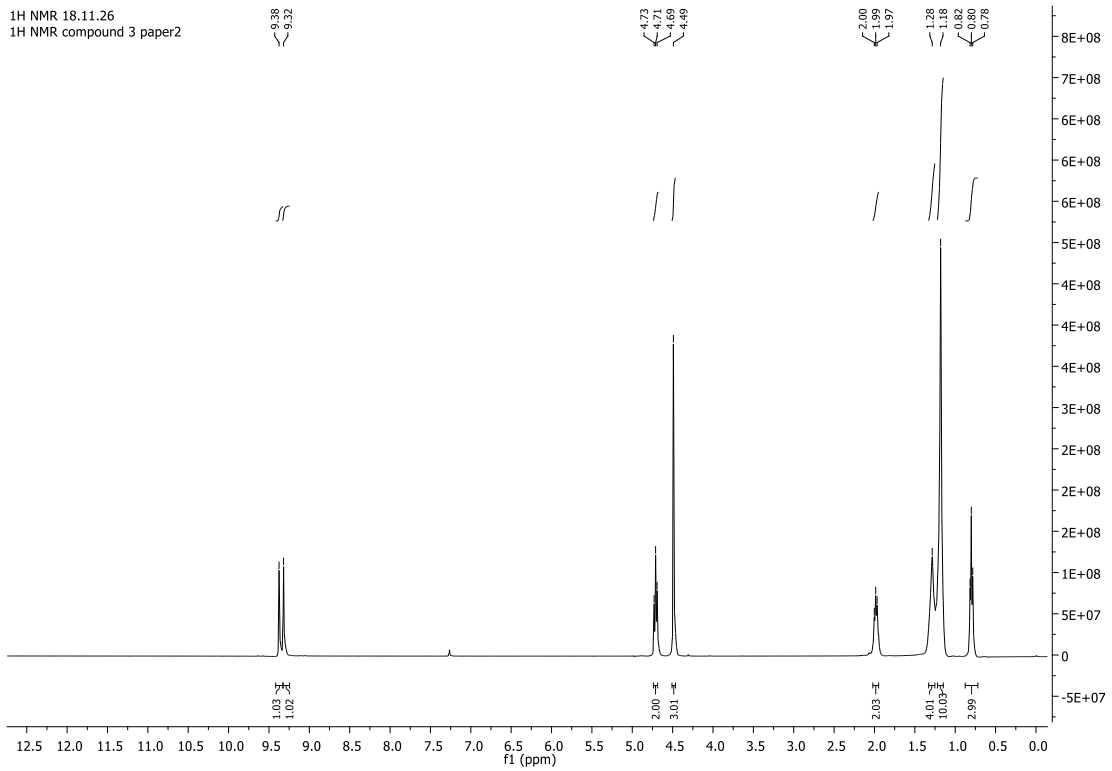

Figure S13. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of compound **3**.

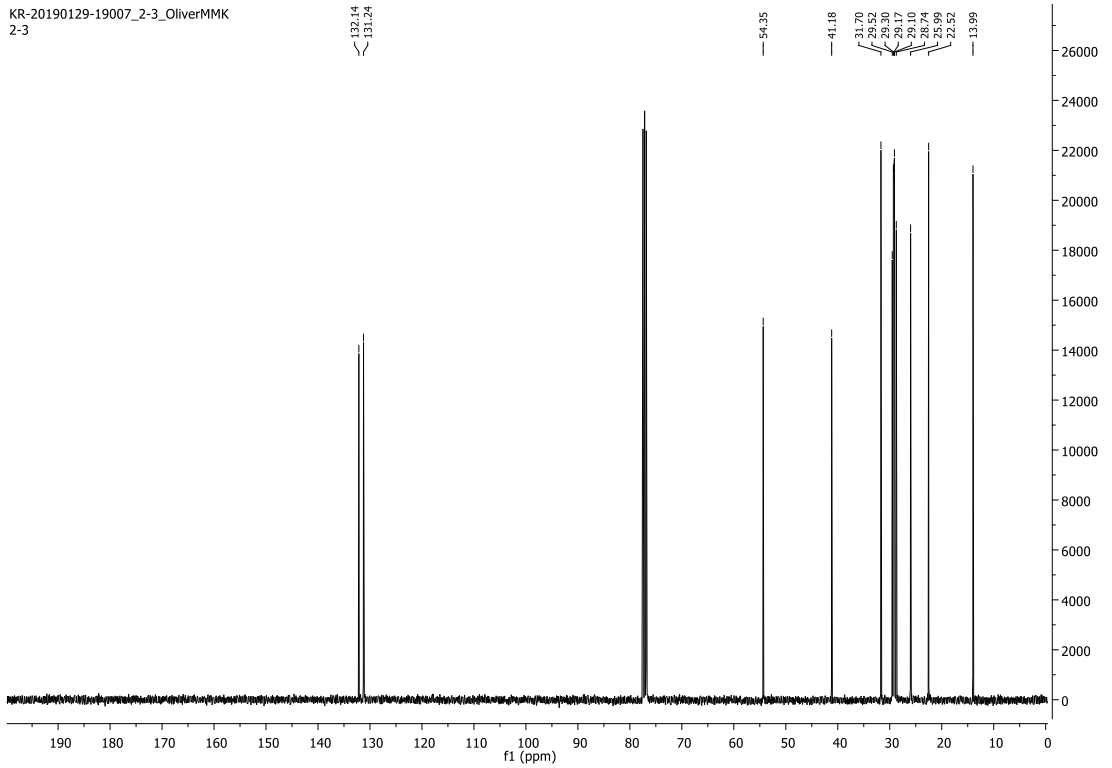

Figure S14. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of compound **2**.

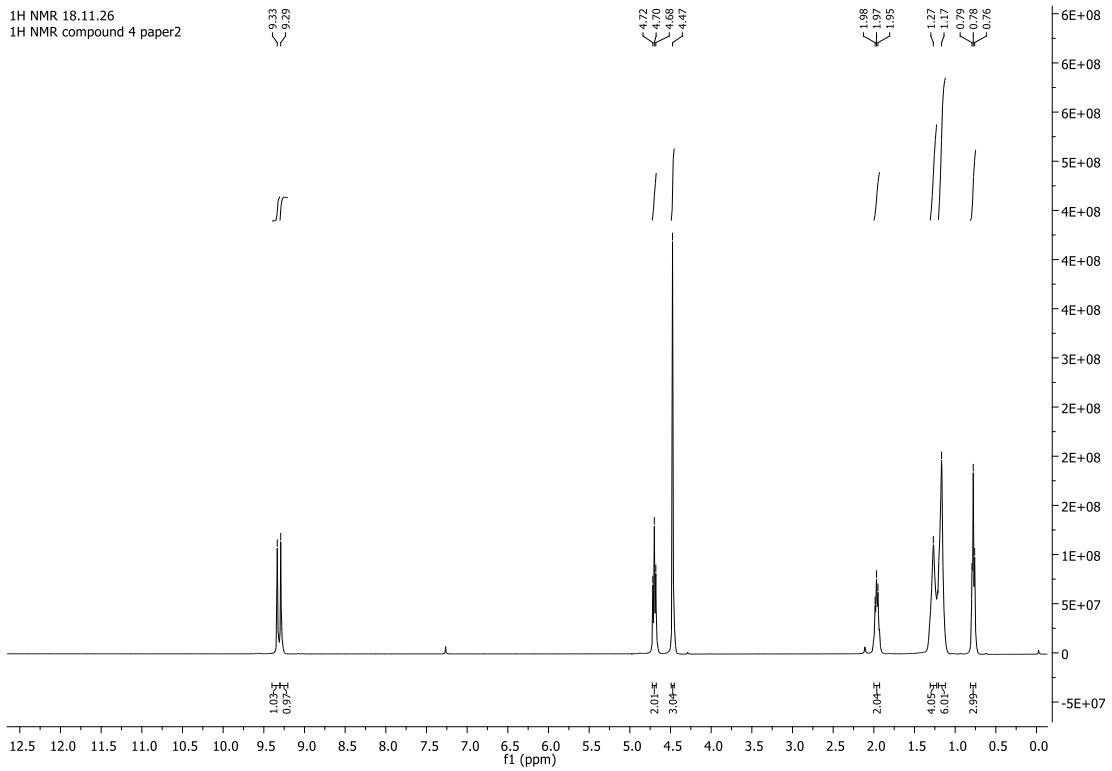

Figure S15. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of compound **4**.

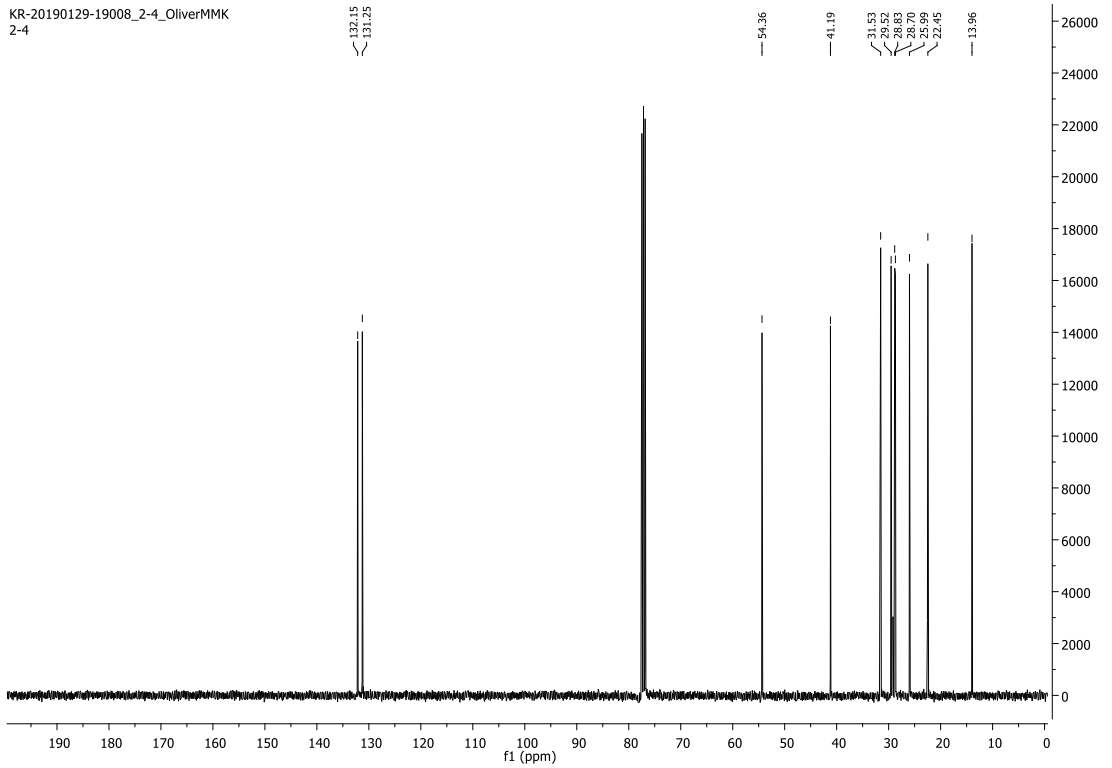

Figure S16. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of compound **4**.

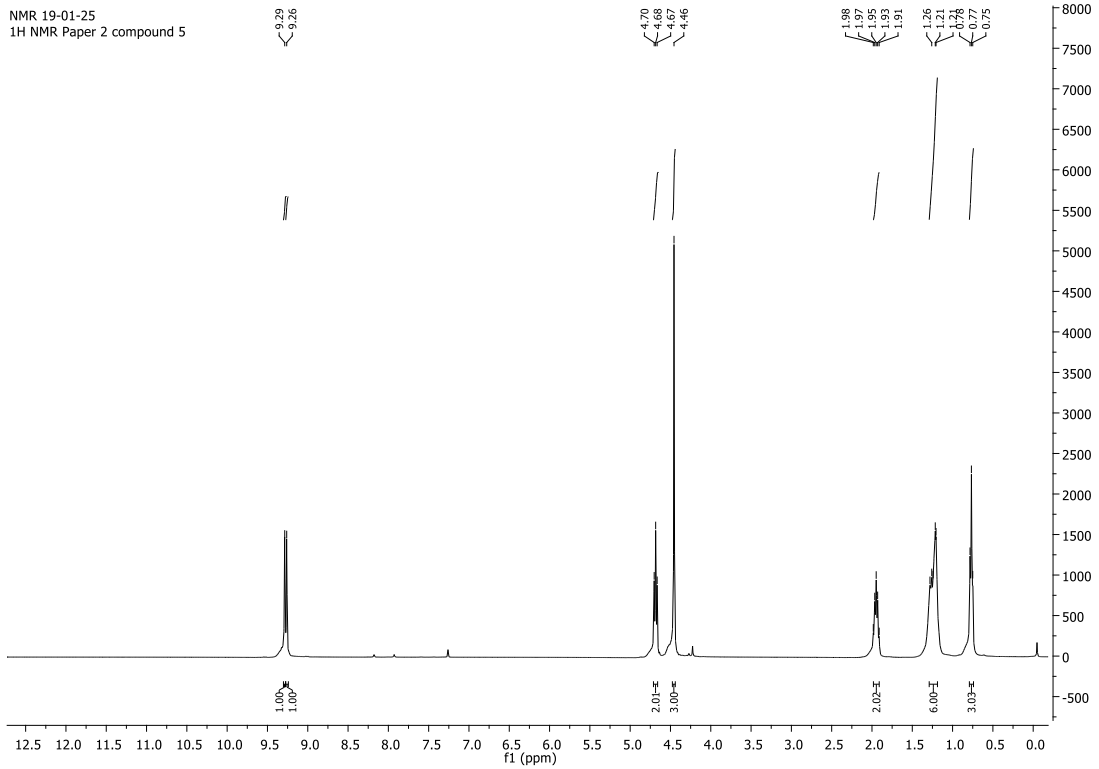

Figure S17. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of compound **5**.

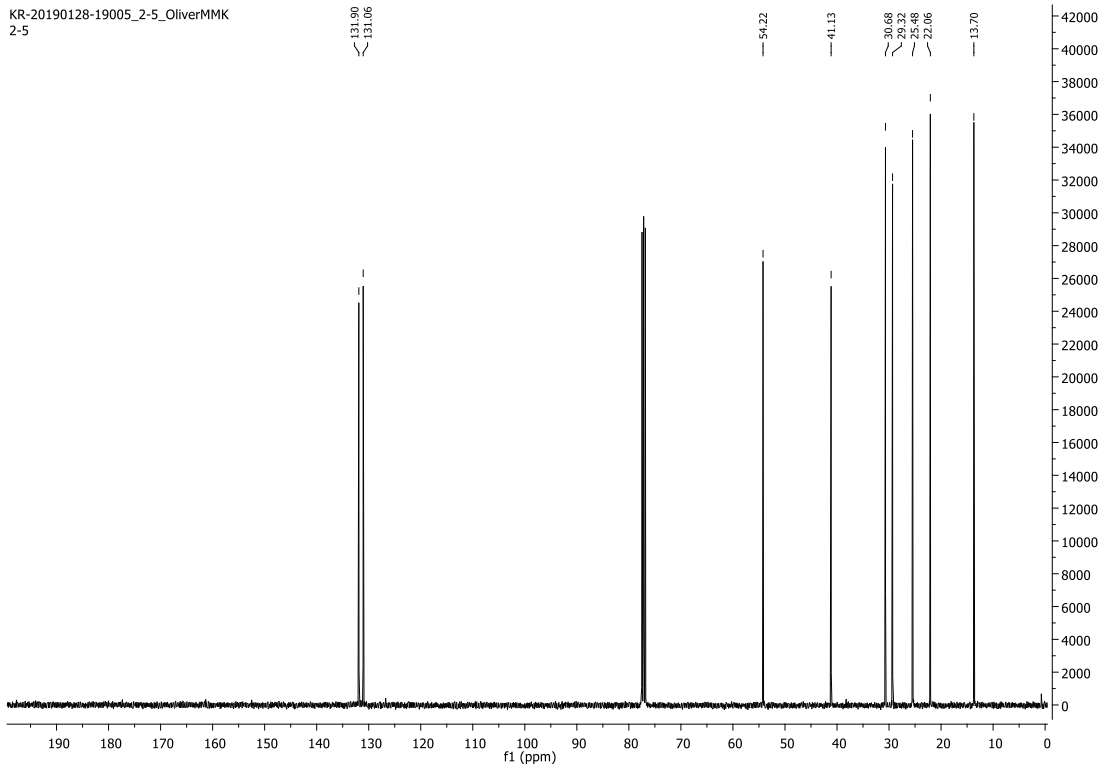

Figure S18. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of compound **5**.

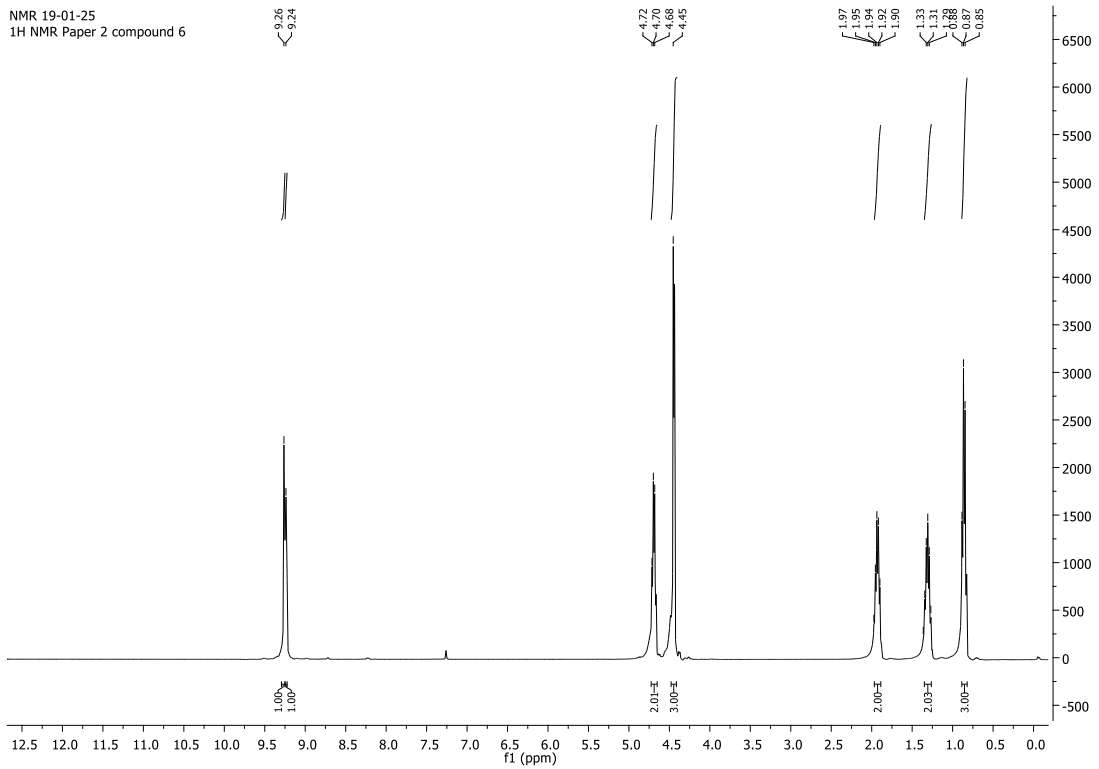

Figure S19. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of compound **6**.

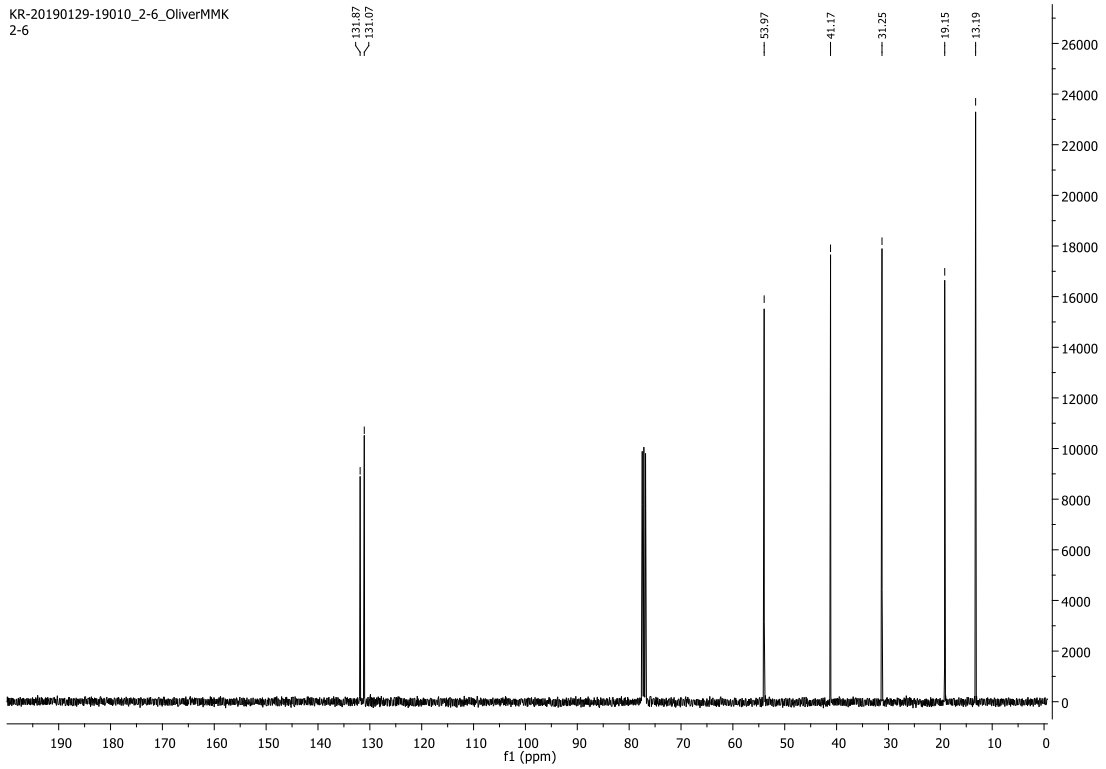

Figure S20. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of compound **6**.

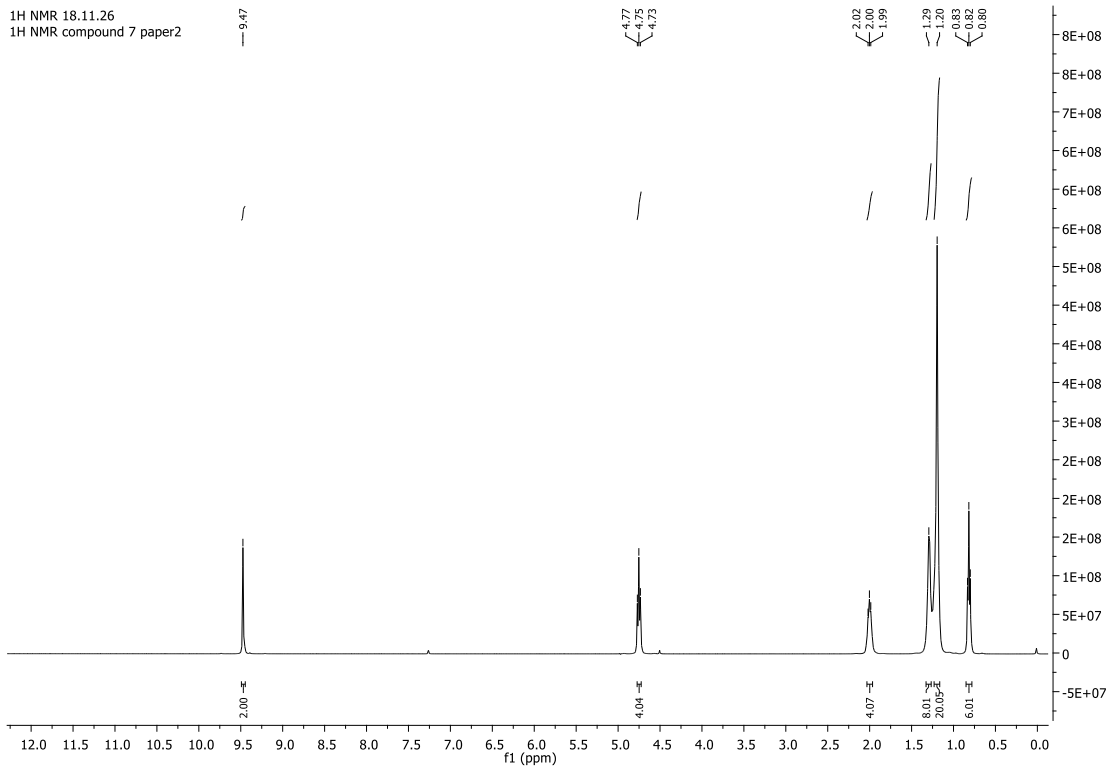

Figure S21. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of compound **7**.

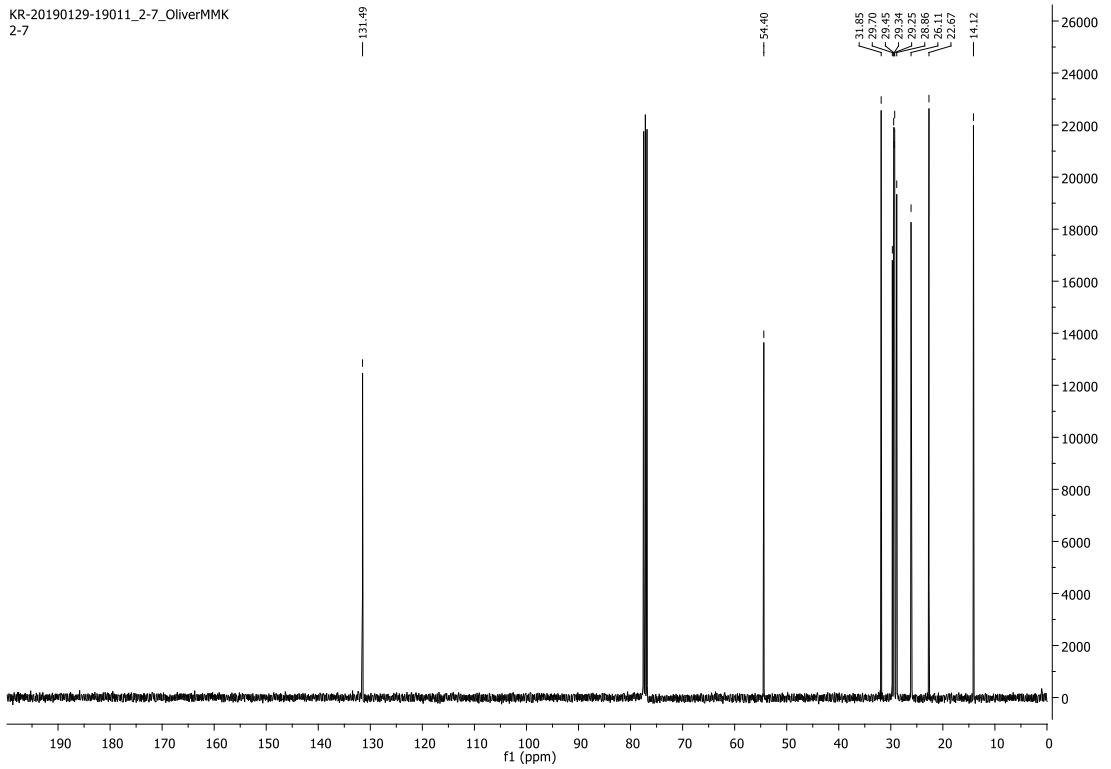

Figure S22. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of compound **7**.

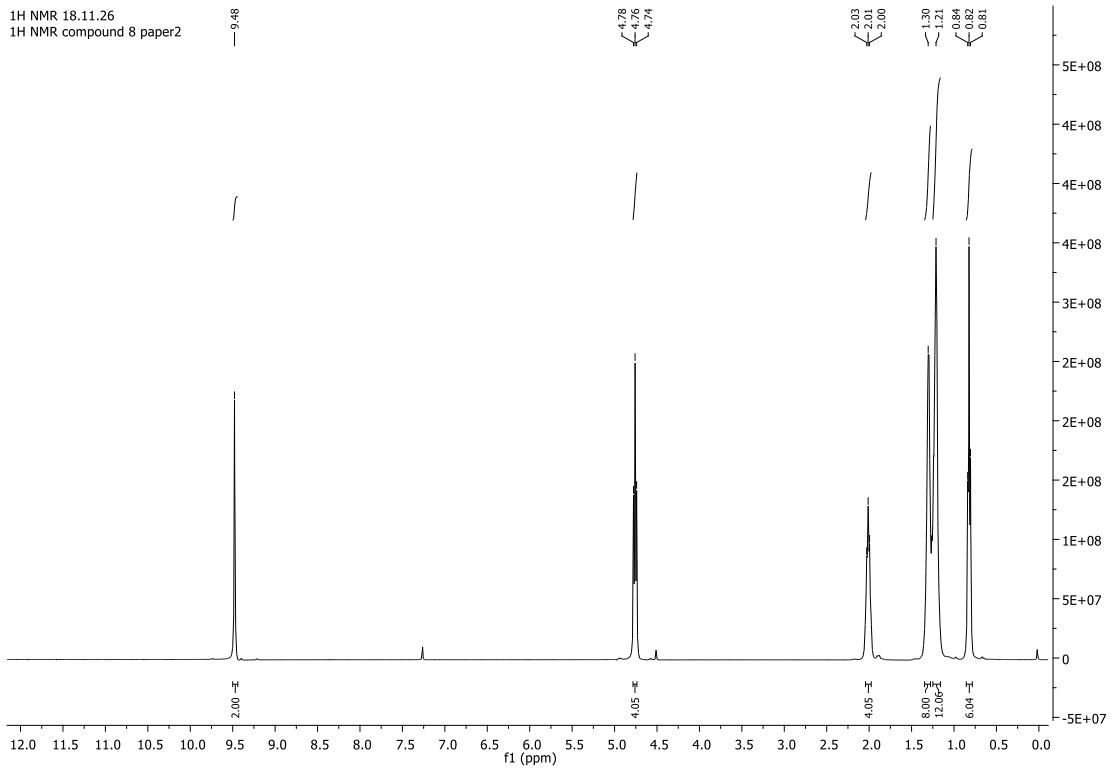

Figure S23. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of compound **8**.

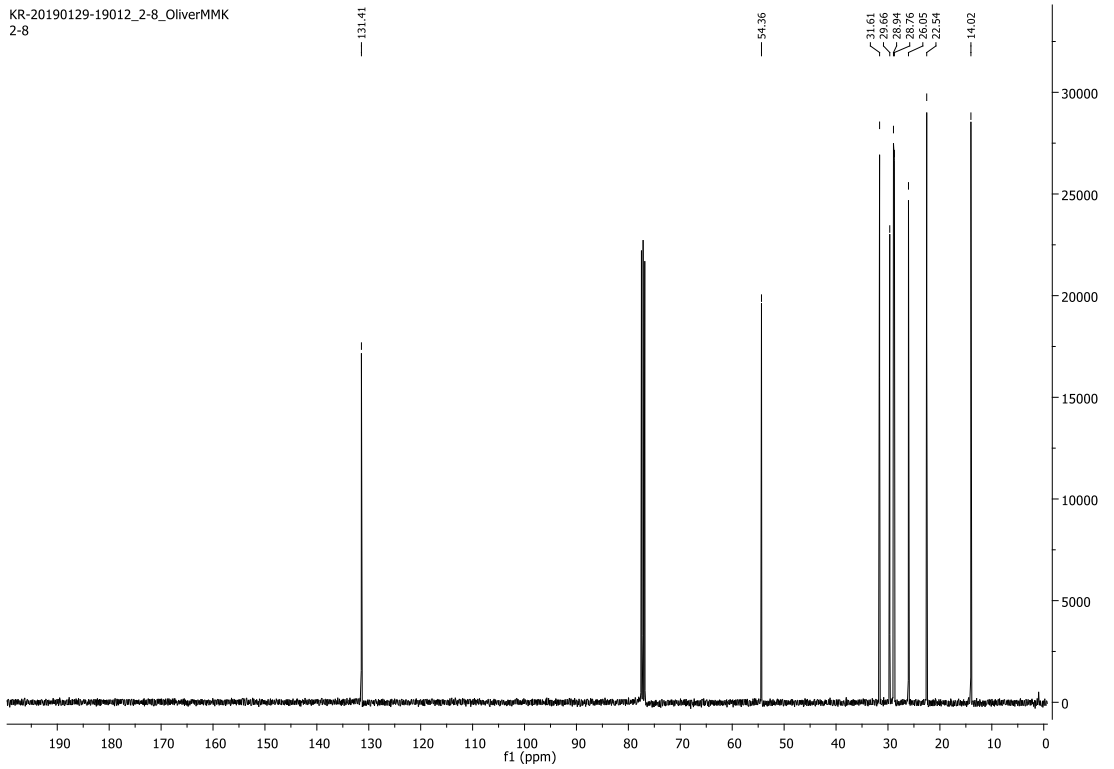

Figure S24. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of compound **8**.

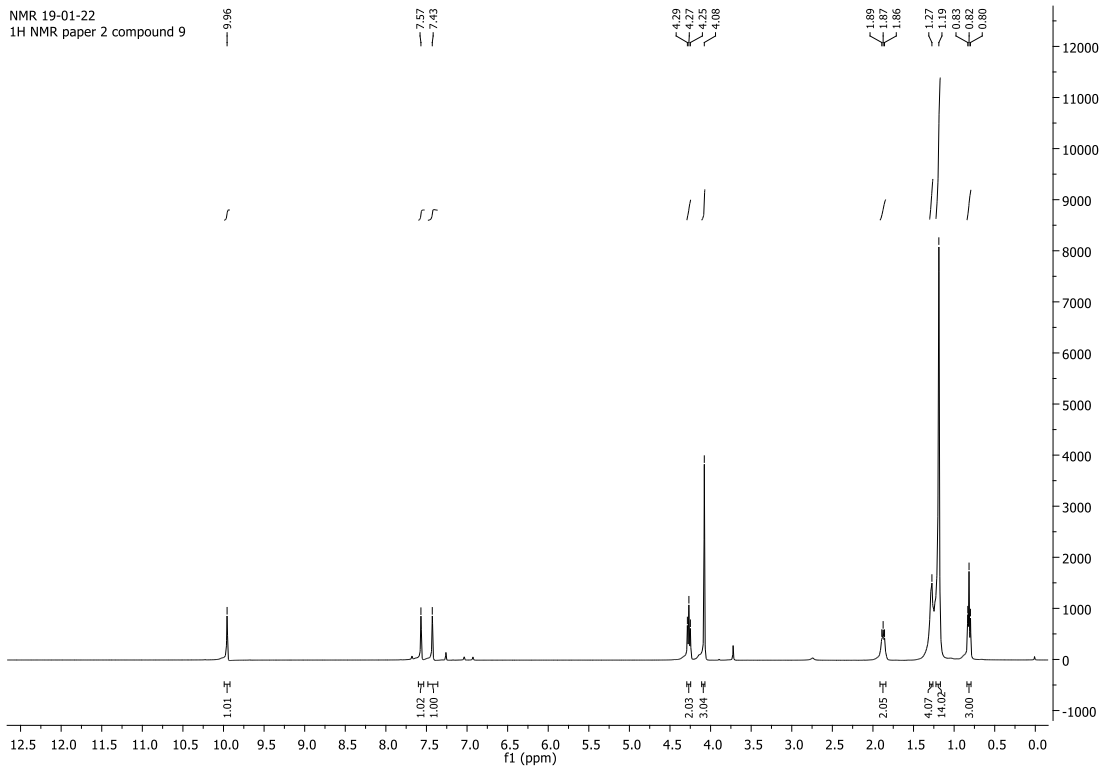

Figure S25. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of compound **9**.

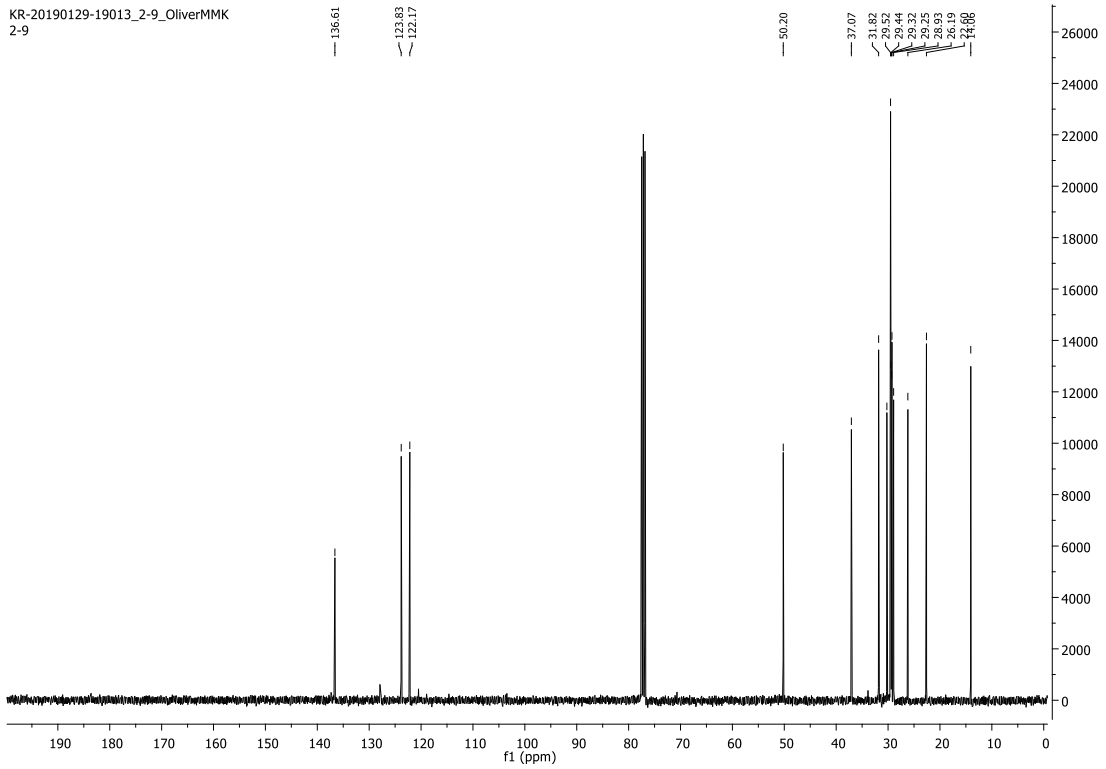

Figure S26. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of compound **9**.

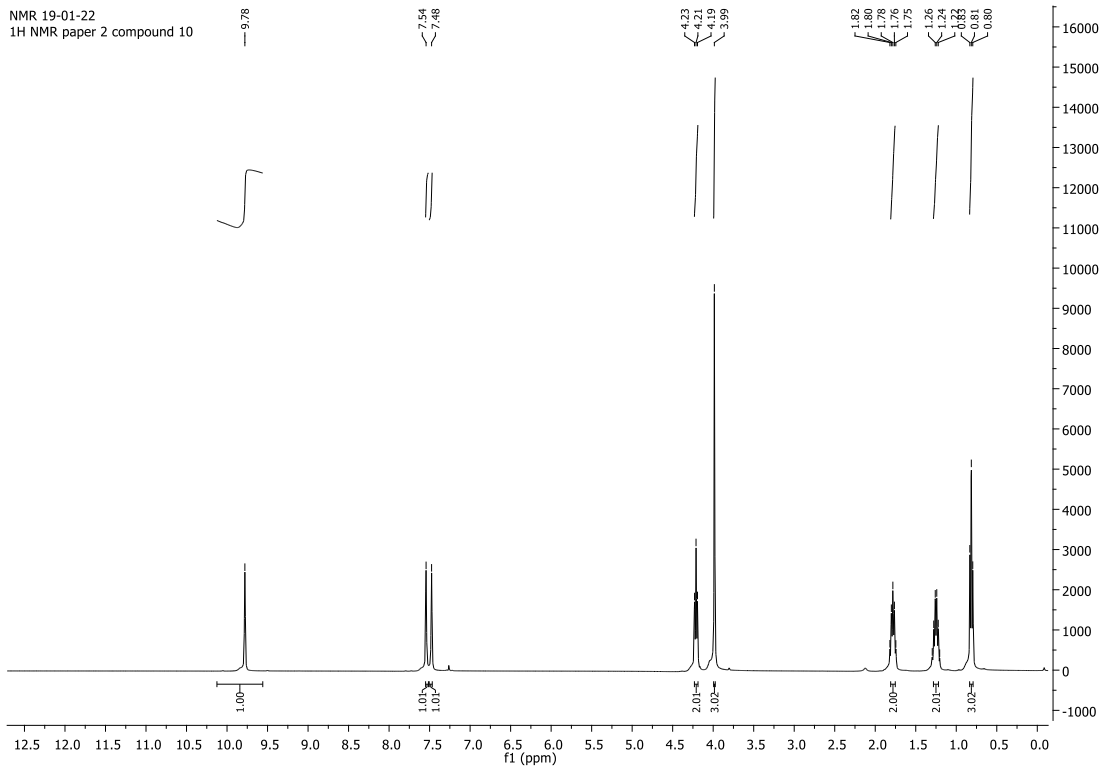

Figure S27. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of compound **10**.

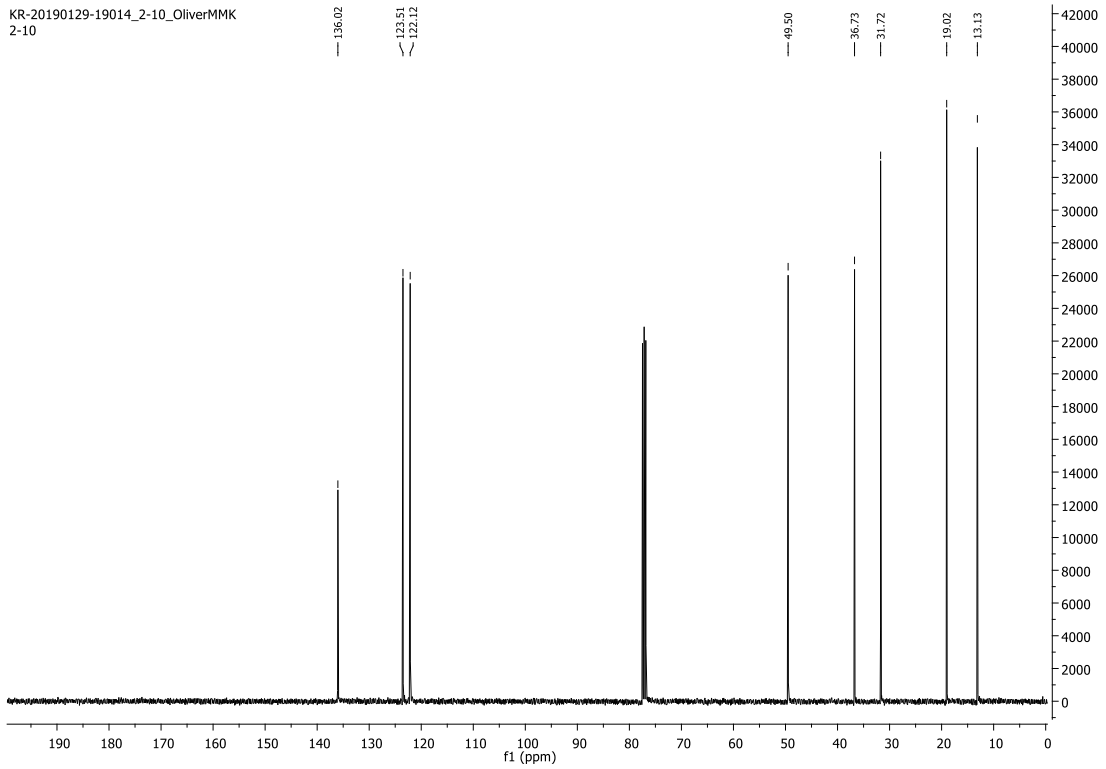

Figure S28. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of compound **10**.

IV. <u>Infrared spectra for compounds **1a-5a**, **1-10**</u>

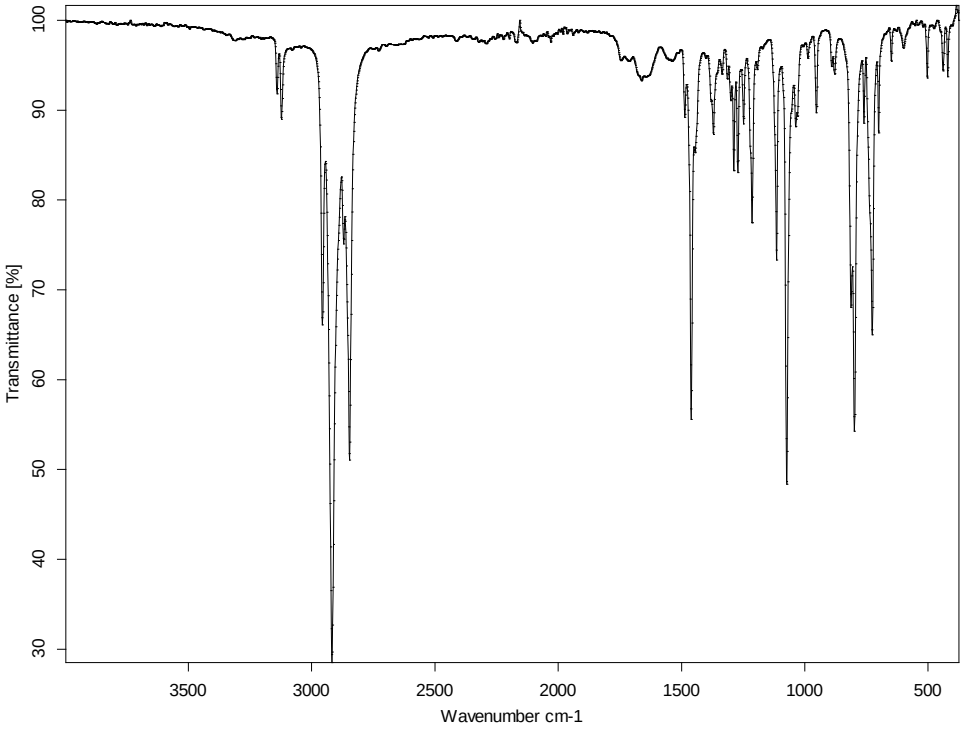

Figure S29. Infrared spectrum of compound **1a**.

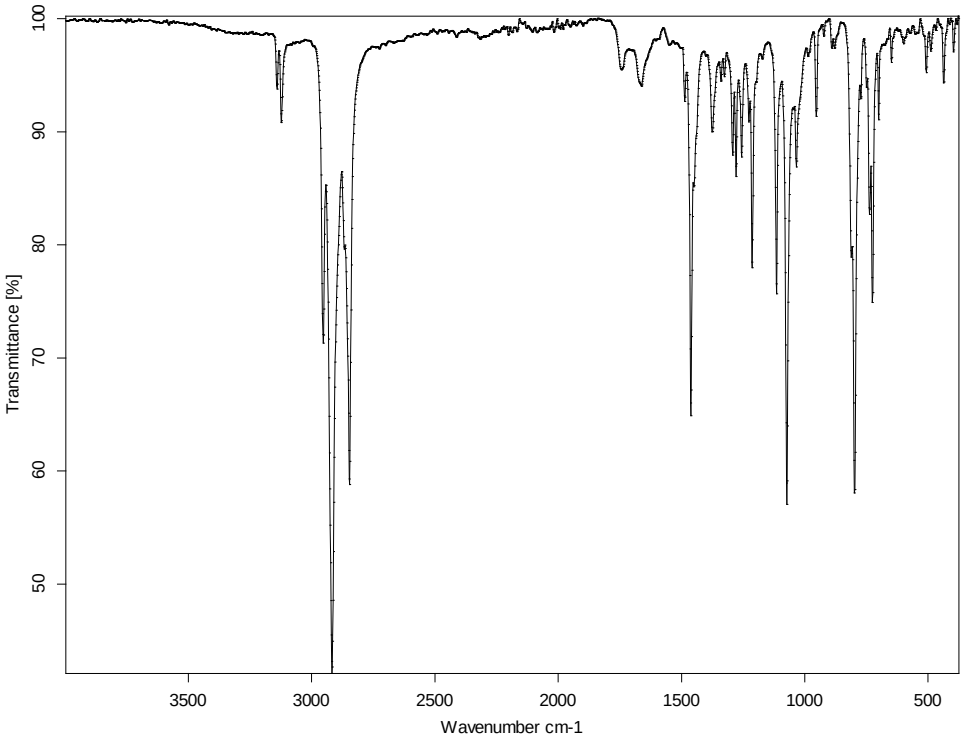

Figure **S30.** Infrared spectrum of compound **2a**.

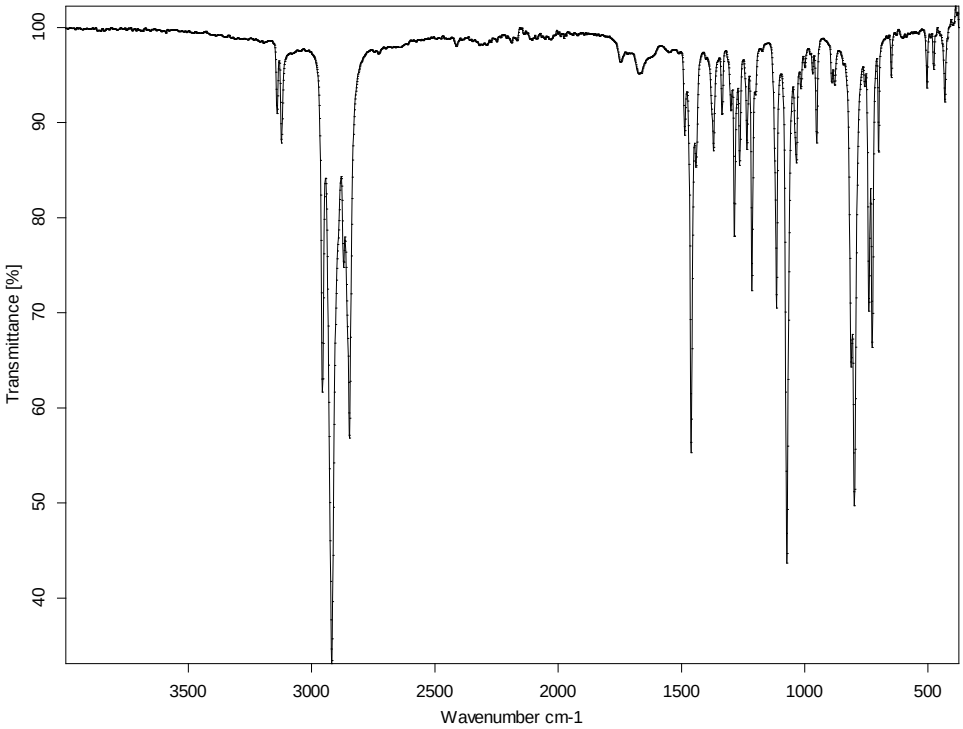

Figure S31. Infrared spectrum of compound **3a**.

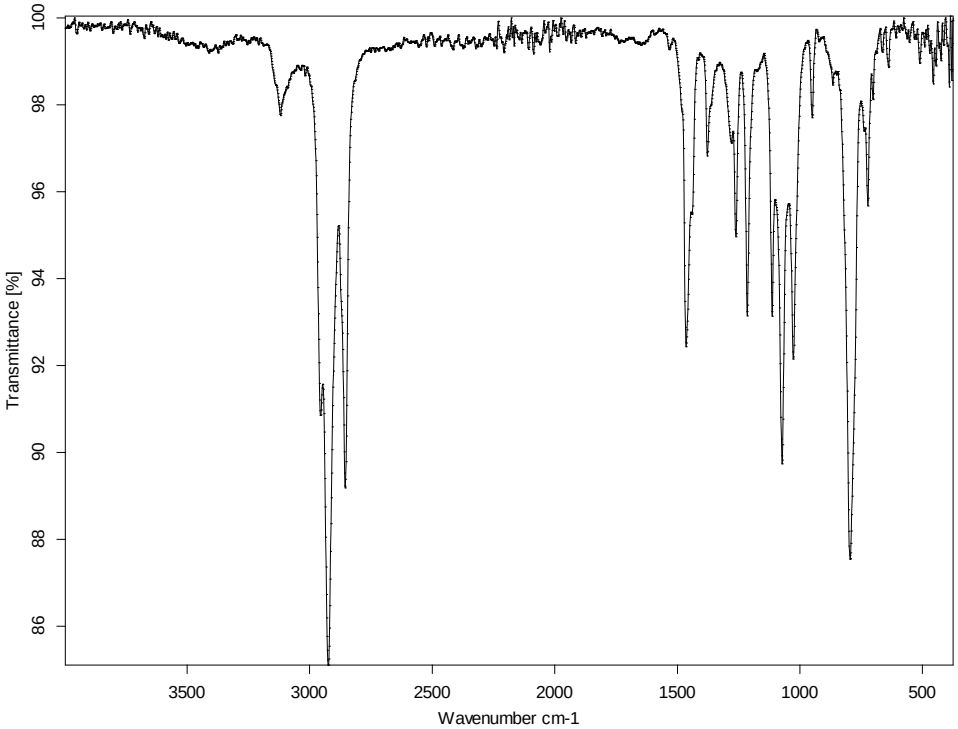

Figure S32. Infrared spectrum of compound **4a**.

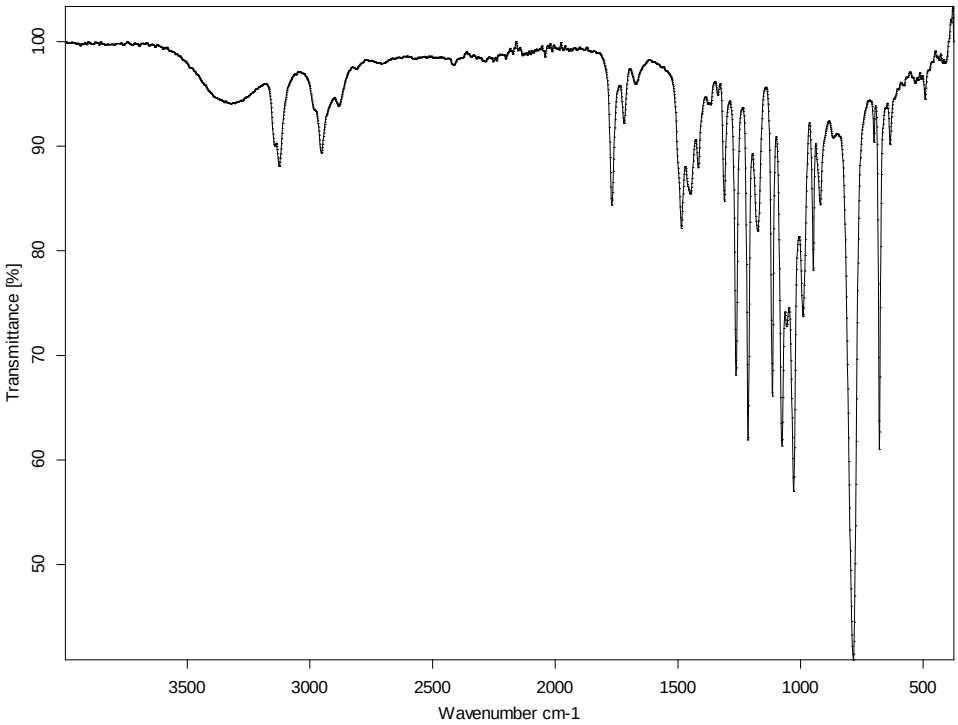

Figure S33. Infrared spectrum of compound **5a**.

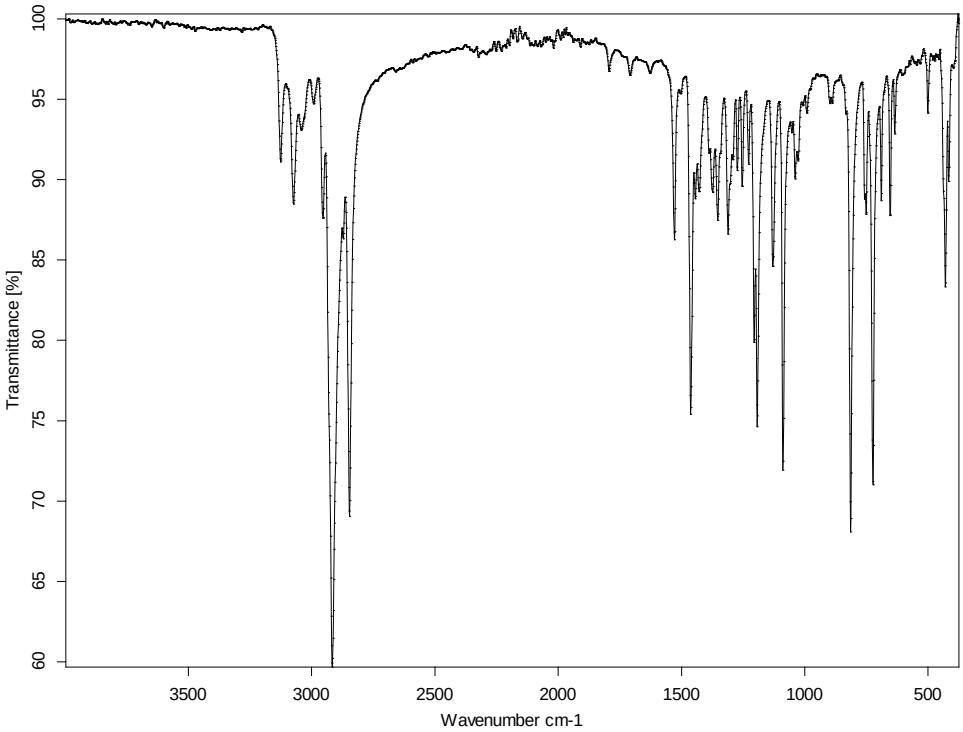

Figure S34. Infrared spectrum of compound **1**.

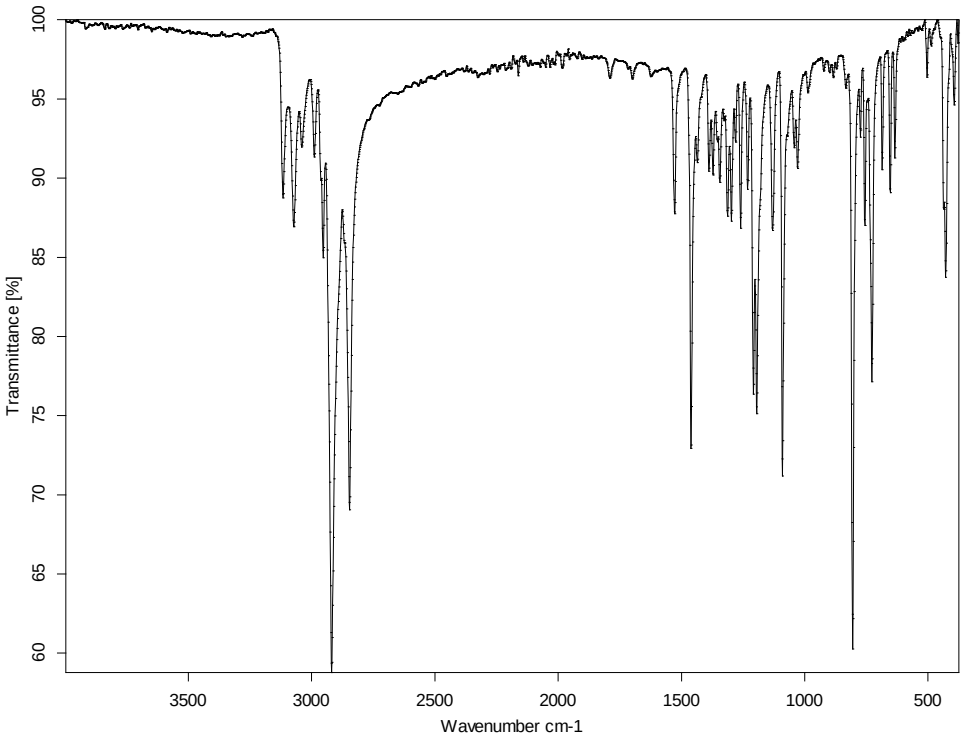

Figure S35. Infrared spectrum of compound **2**.

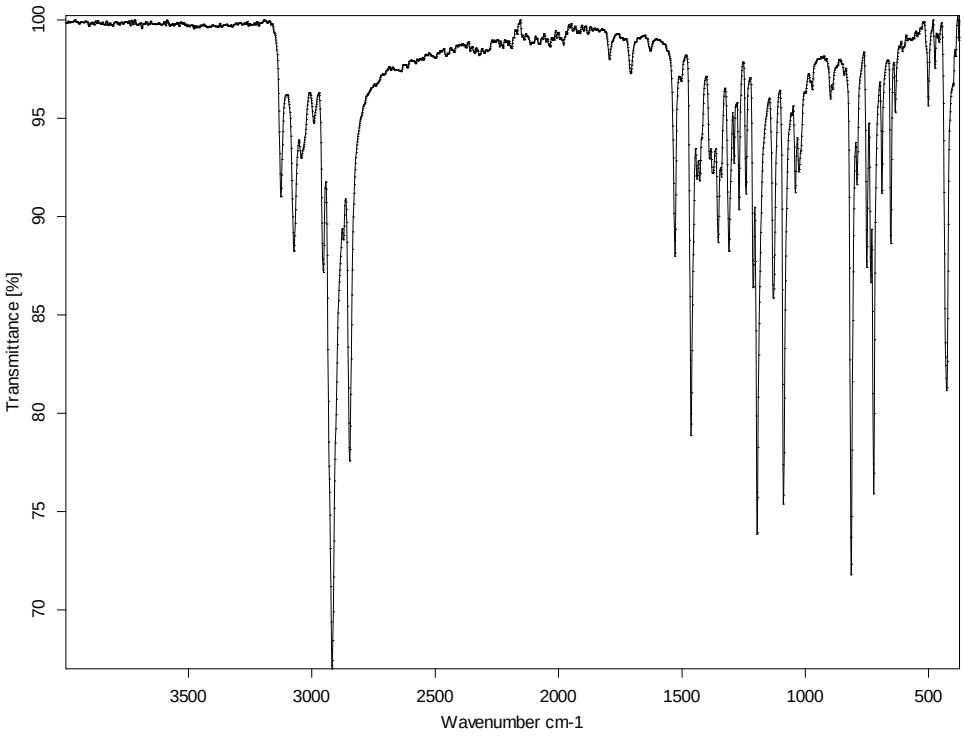

Figure S36. Infrared spectrum of compound **3**.

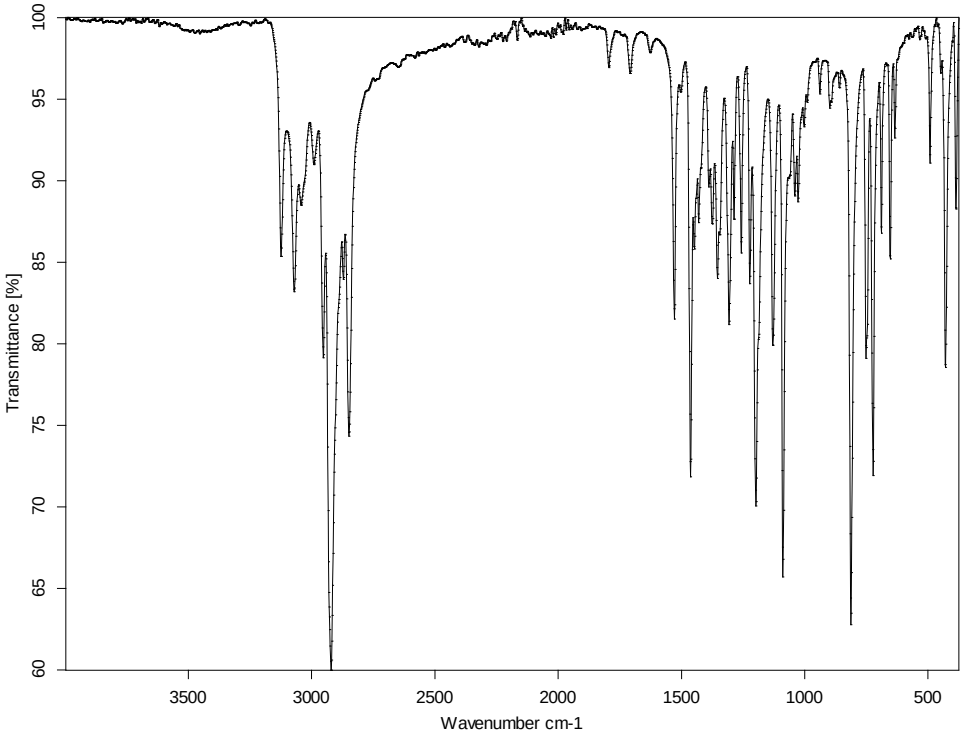

Figure S37. Infrared spectrum of compound **4**.

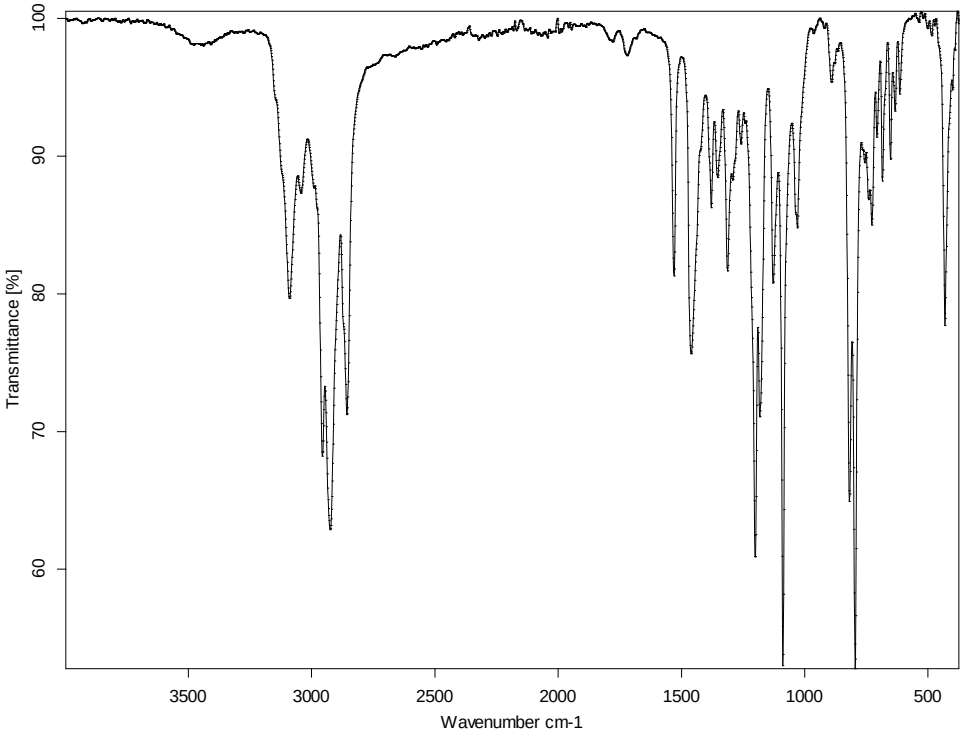

Figure S38. Infrared spectrum of compound **5**.

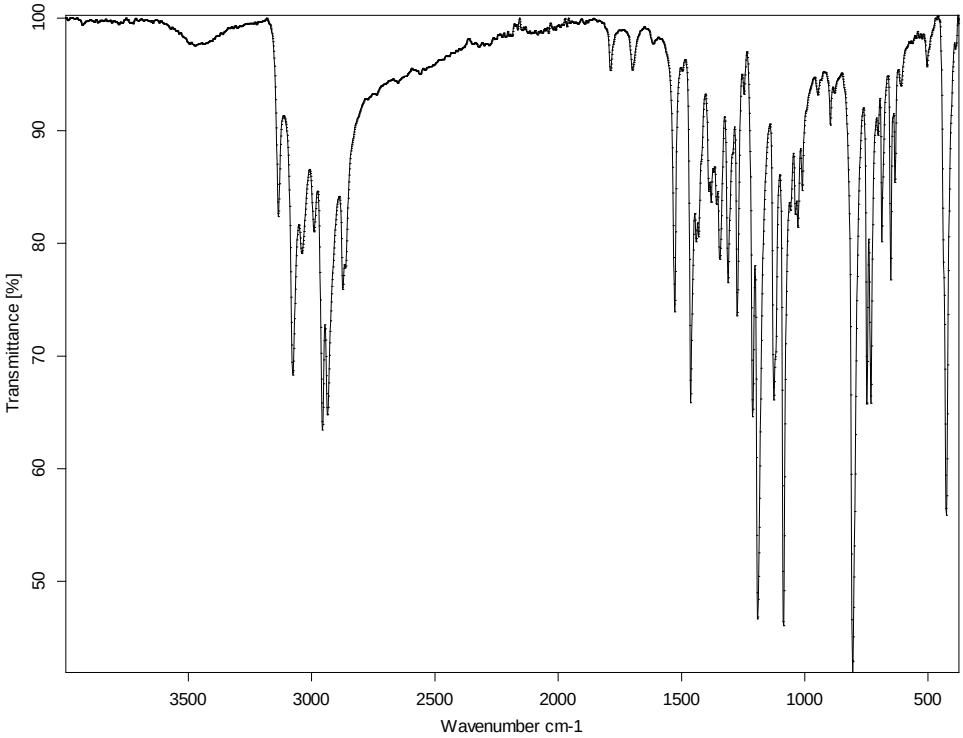

Figure S39. Infrared spectrum of compound **6**.

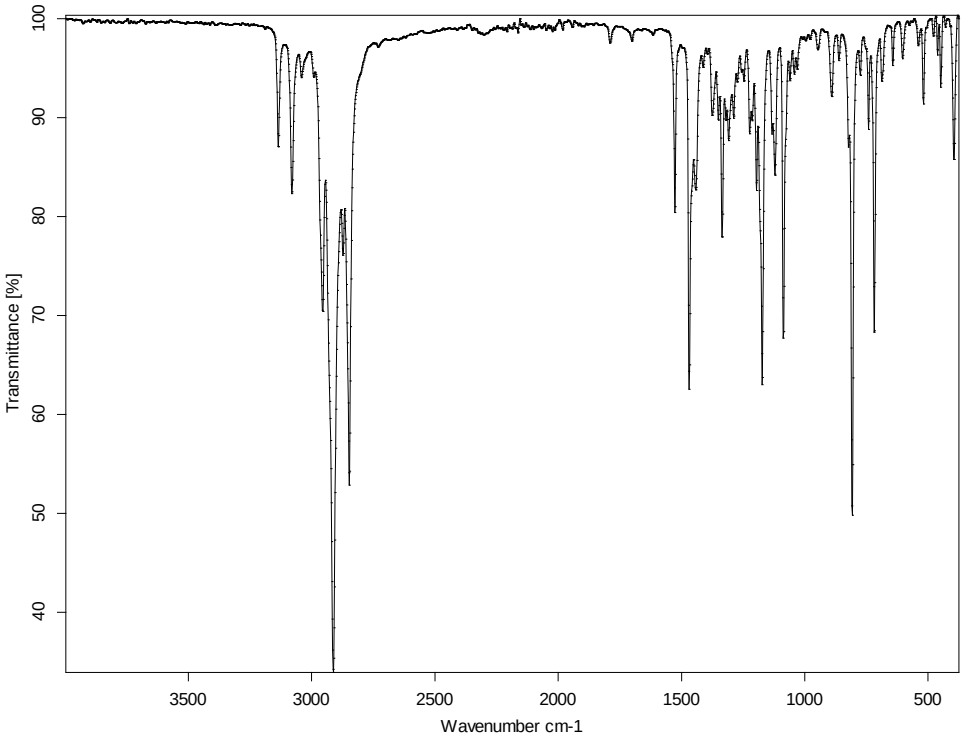

Figure S40. Infrared spectrum of compound **7**.

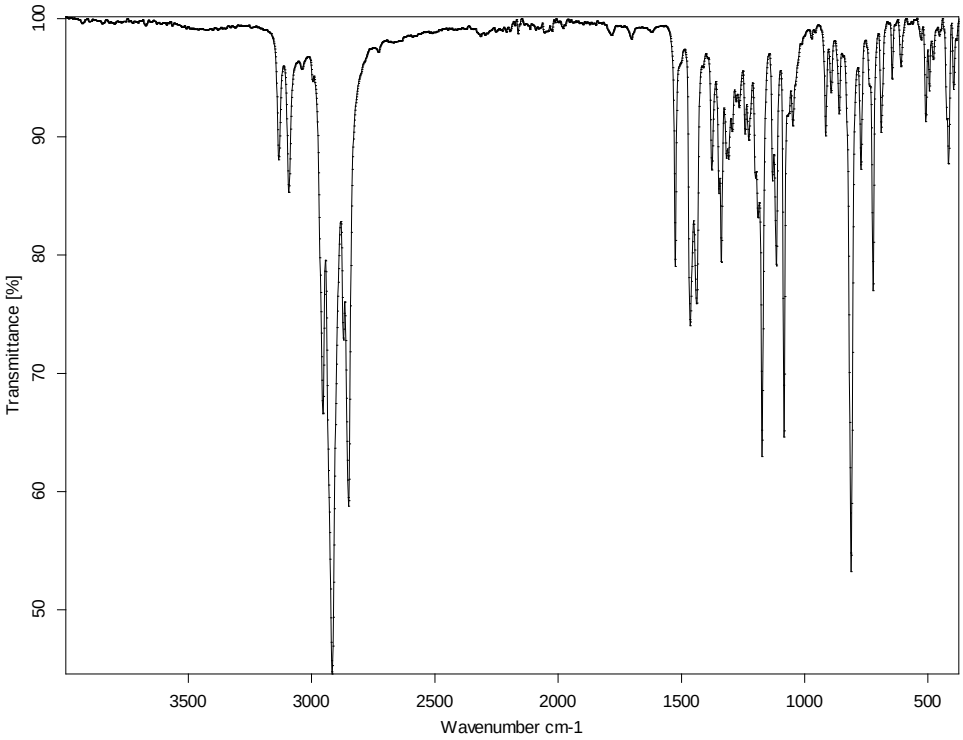

Figure S41. Infrared spectrum of compound **8**.

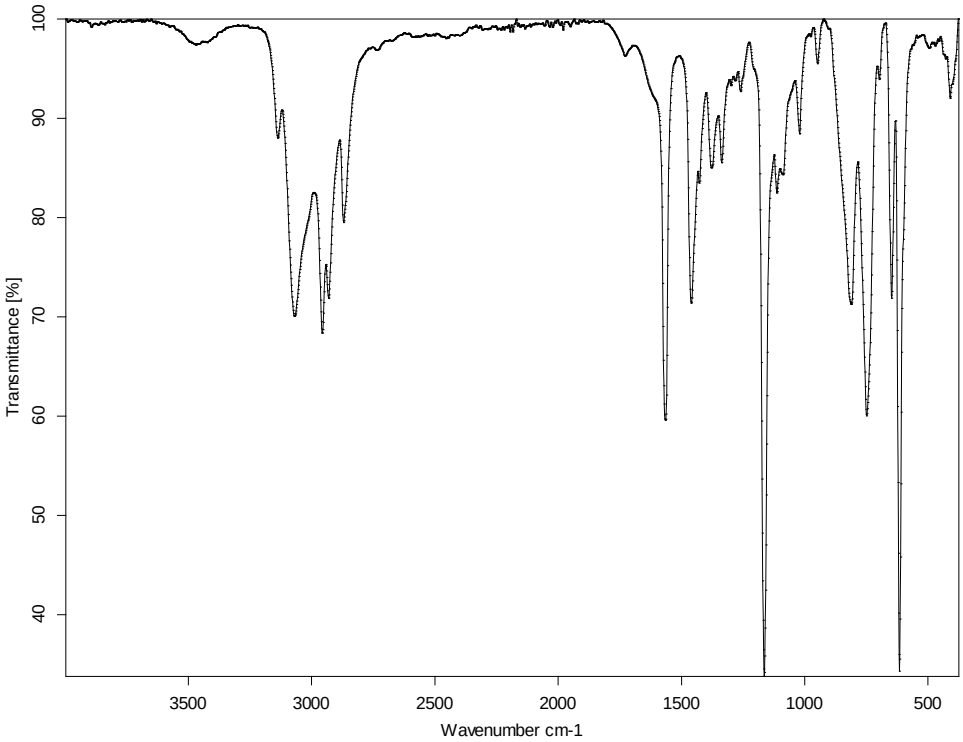

Figure S42. Infrared spectrum of compound **9**.

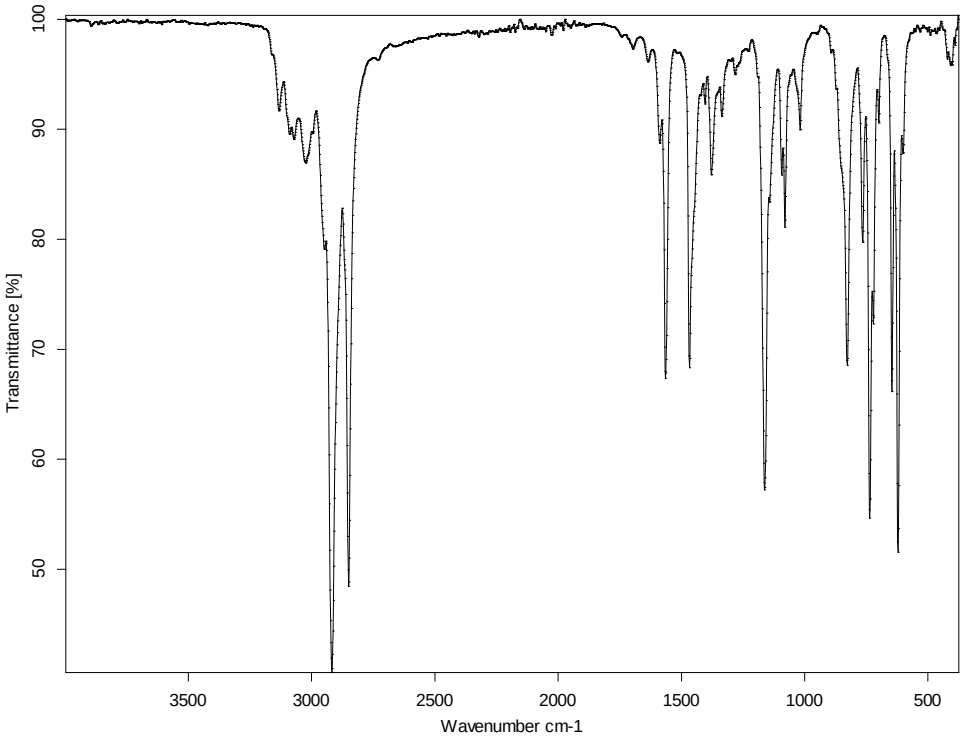

Figure S43. Infrared spectrum of compound **10**.

V. Details on the single crystal structure analysis for **1**, **3**, **4**

Crystals of 1-dodecyl-3-methyltriazolium iodide (**1**), 1-decyl-3-methyltriazolium iodide (**3**) and 1-octyl-3-methyltriazolium iodide (**4**) were obtained from recrystallization of the compound in cold dichloromethane. Measurements were carried out on a Stoe IPDS-I single-crystal X-Ray diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å at 100 K). Crystal structure solution by direct methods using SIR 92[4] yielded the heavy atom positions. Refinement with SHELXL-97[5] allowed for the localization of the remaining atom positions. Hydrogen atoms were added and treated with the riding atom mode. Data reduction was performed with the program package X-Red[6] and numerical absorption correction was carried out with the program X-Shape.[7] To illustrate the crystal structures, the program Diamond[8] was used.

Table S1. Crystallographic and refinement details for compounds **1**, **3** and **4**.

Compound	$(C_{12}C_1Tr)I$ (**1**)	$(C_{10}C_1Tr)I$ (**3**)	$(C_8C_1Tr)I$ (**4**)
CCDC	1909213	1035964	1035963
Empirical formula	$C_{15}H_{30}N_3I$	$C_{13}H_{26}N_3I$	$C_{11}H_{22}N_3I$
M_w **(g/mol)**	379.32	351.27	323.22
Temperature (K)	170	170	170
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a[Å]	5.6056(6)	5.621(1)	5.597(1)
b[Å]	8.907(1)	8.830(1)	8.783(1)
c[Å]	19.523(3)	17.258(3)	15.111(2)
α [°]	79.80(2)	82.42(2)	86.84(2)
β [°]	83.50(2)	93.86(2)	89.34(2)

γ [°]	81.78(2)	98.49(2)	81.14(2)
Volume	945.6(2)	838.8(2)	732.8(2)
Z	2	2	2
ρ_{calcd} [Mg m^{-3}]	1.33	1.39	1.46
μ [mm^{-1}]	1.688	1.897	2.164
θ [°]	2.34 to 25.0	2.35 to 25.0	3.48 to 25.0
Index ranges	$-6 \leq h \leq 6$	$-6 \leq h \leq 6$	$-6 \leq h \leq 6$
	$-10 \leq k \leq 10$	$-10 \leq k \leq 10$	$-10 \leq k \leq 10$
	$-23 \leq l \leq 23$	$-20 \leq l \leq 20$	$-17 \leq l \leq 17$
Reflections collected	8211	7592	6544
Independent reflections	3342	2781	2424
Refinement method	Full-matrix least-squares on F^2		
Data / parameters	3342 / 173	2715 / 154	2424 / 144
Goodness-of-fit on F^2	0.987	0.827	0.995
R_{int}	0.063	0.098	0.085
Final R indices (I>2σ(I))	R_1 = 0.045 wR_2=0.071	R_1 = 0.055 wR_2=0.118	R_1= 0.045 wR_2=0.111
R indices (all data)	R_1 = 0.077 wR_2=0.082	R_1 = 0.086 wR_2 = 0.124	R_1 = 0.053 wR_2 = 0.114

VI. Thermogravimetric analysis for compounds **1-8**

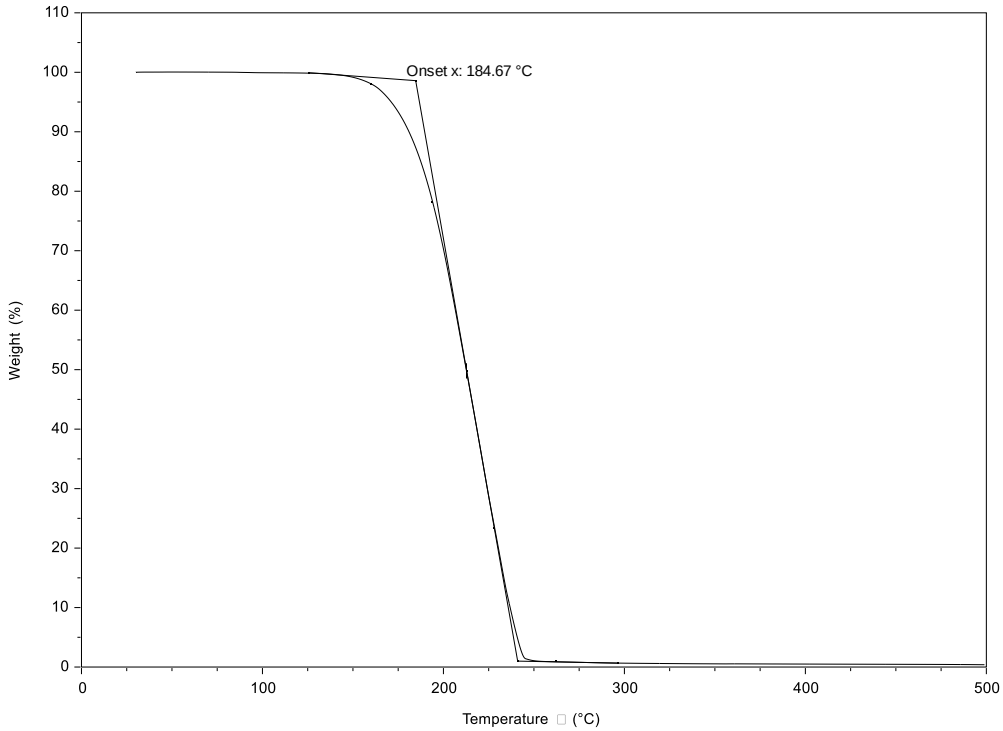

Figure S44. TGA thermogram of compound **1**.

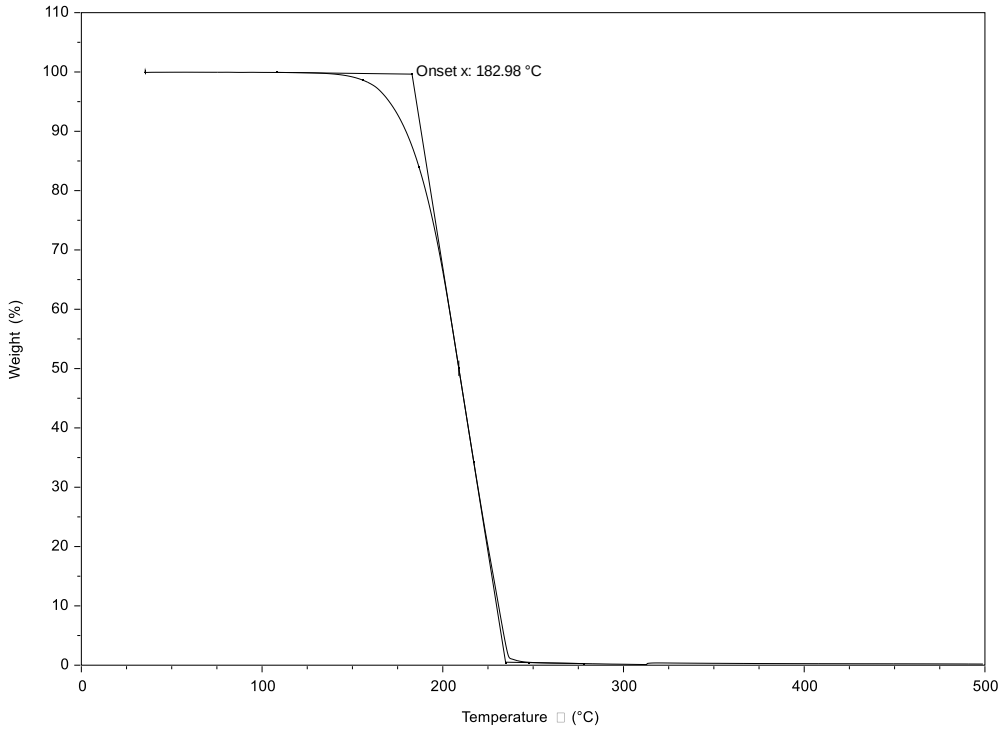

Figure S45. TGA thermogram of compound **2**.

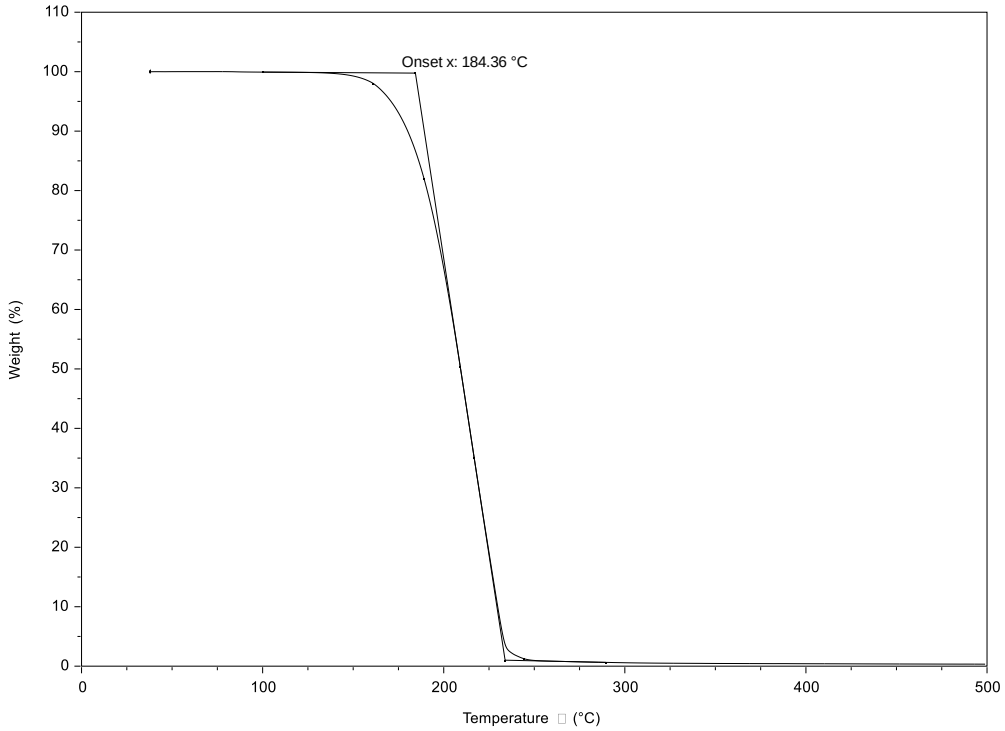

Figure S46. TGA thermogram of compound **3**.

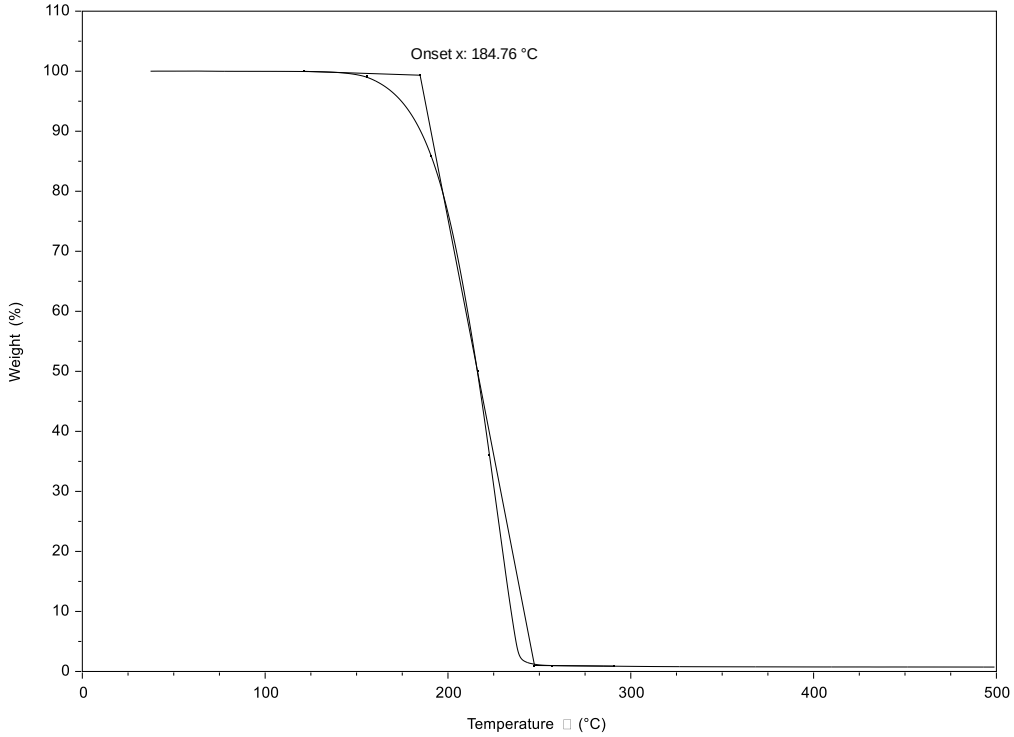

Figure S47. TGA thermogram of compound **4**.

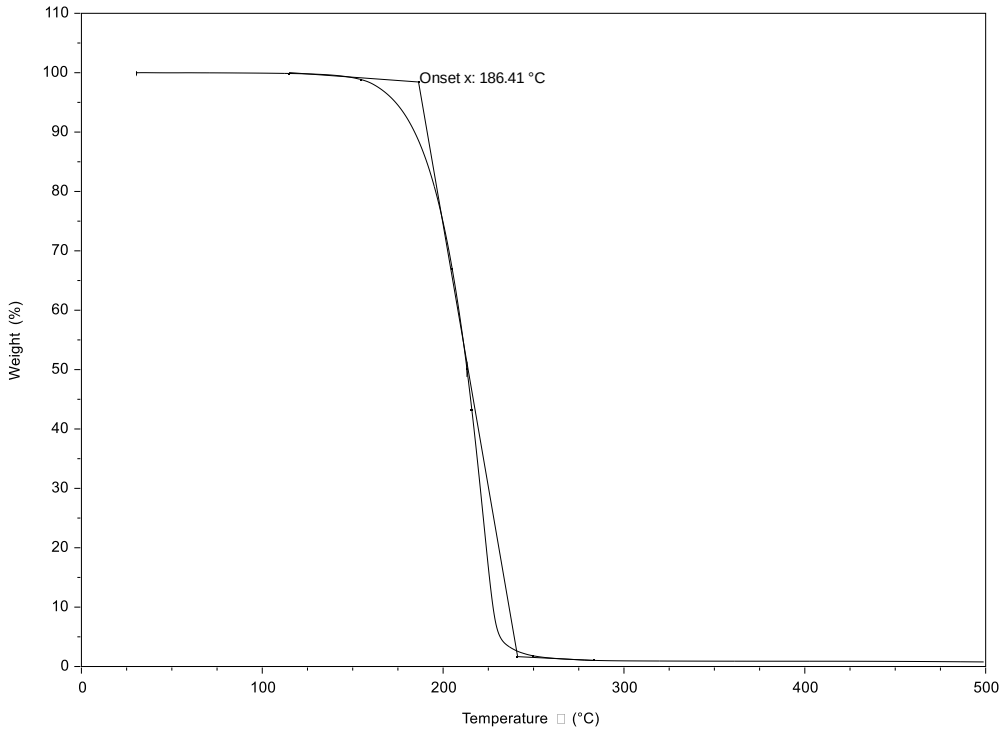

Figure S48. TGA thermogram of compound **5**.

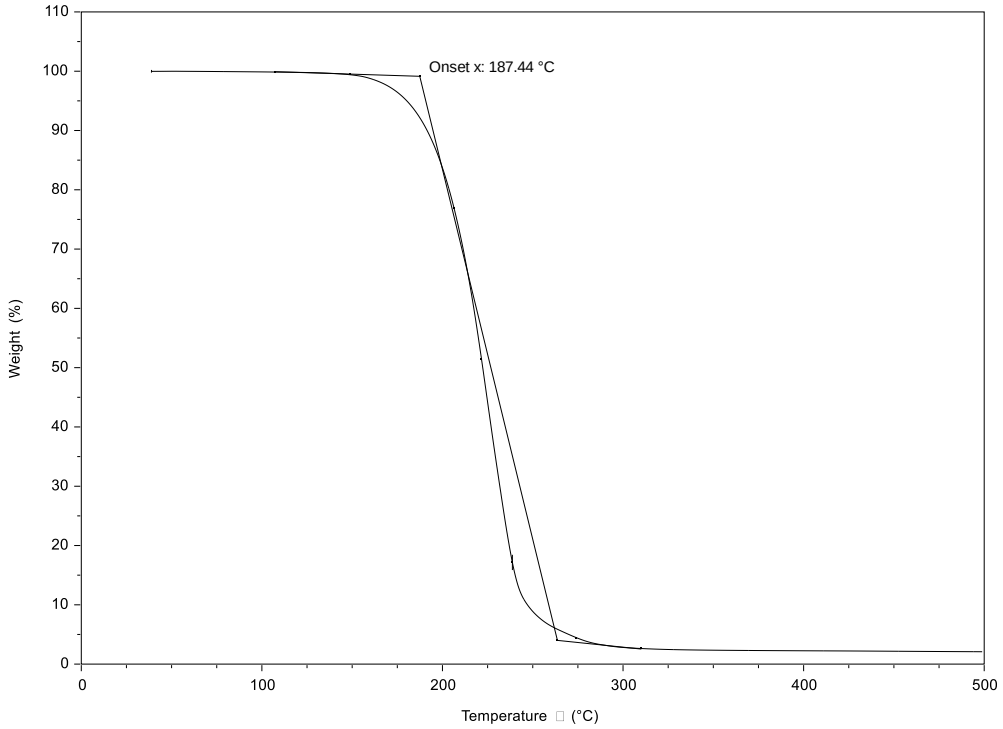

Figure S49. TGA thermogram of compound **6**.

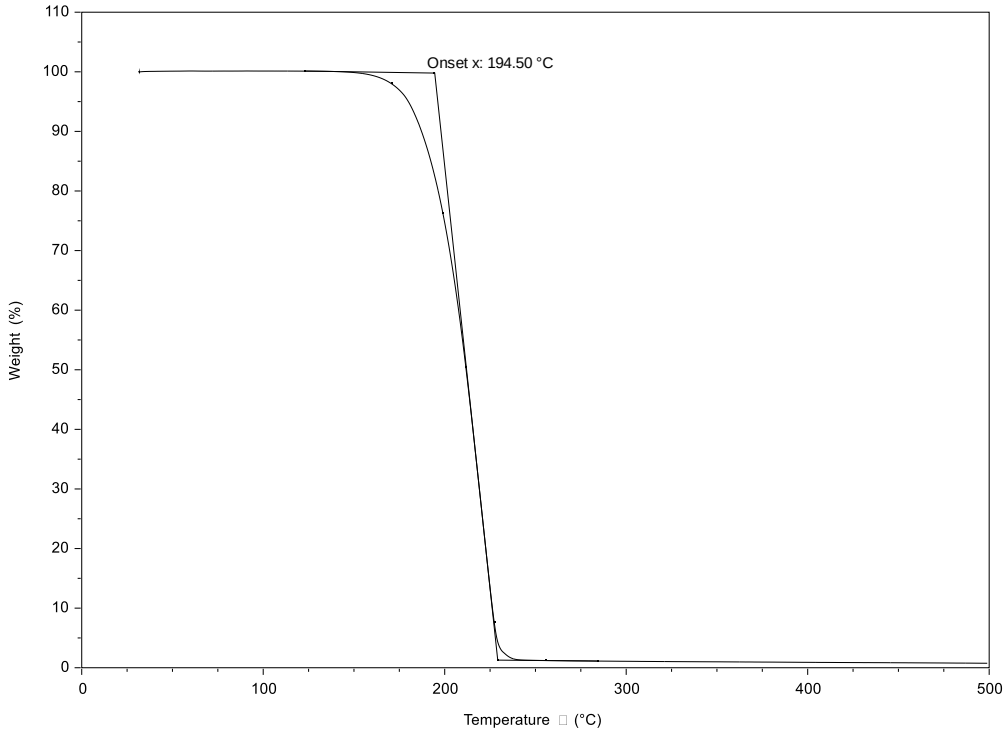

Figure S50. TGA thermogram of compound **7**.

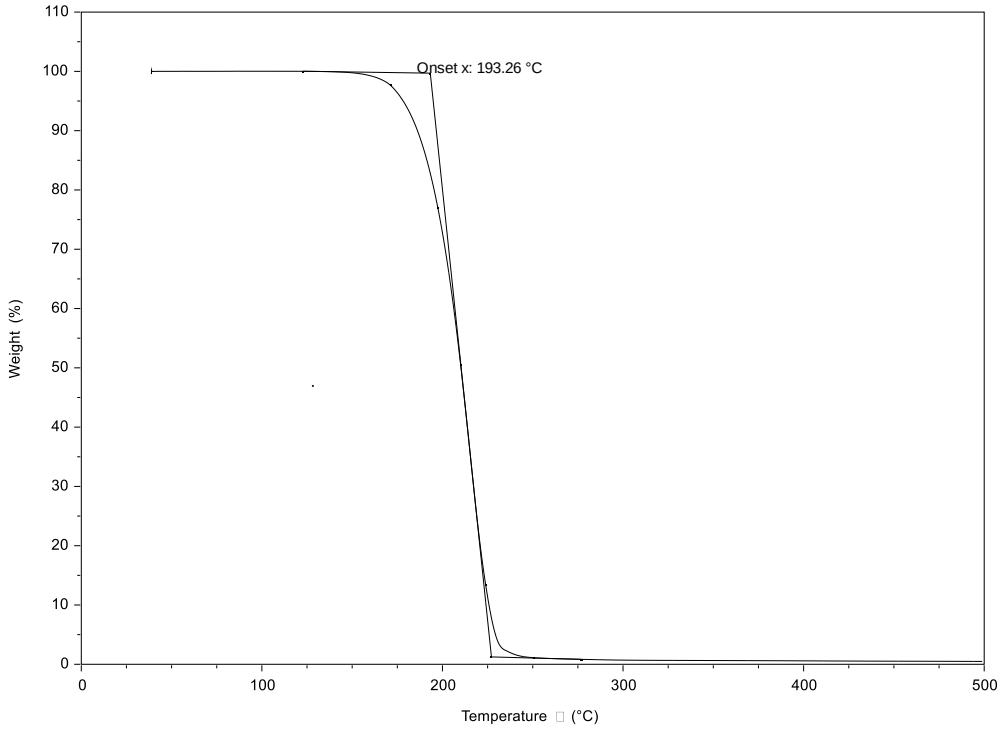

Figure S51. TGA thermogram of compound **8**.

VII. DSC thermograms for compounds **1-8, 10**, $[C_{10}C_1Im]I$, $[C_8C_1Im]I$, $[C_6C_1Im]I$

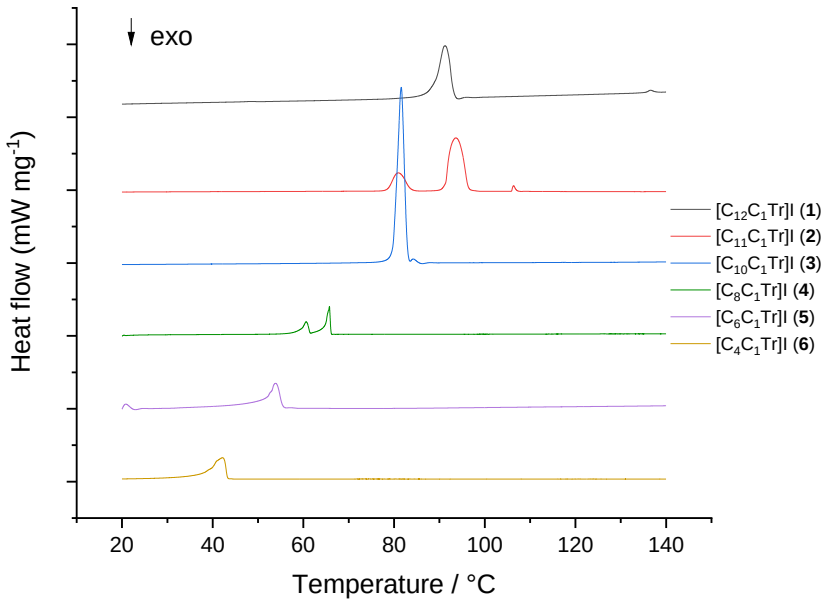

Figure S52. DSC heating traces of 1-alkyl-3-methyltriazolium iodides (**1-6**). *To avoid an overlap of thermal events, for compound **4** a thermal ramp of 1 °C min^{-1} is chosen, all other compounds have been measured at 5 °C min^{-1}.

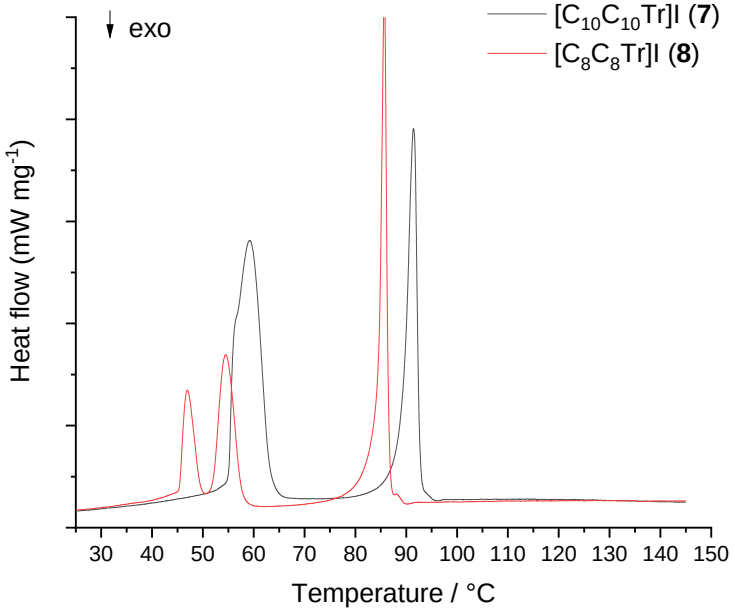

Figure S53. DSC heating traces of the 1,3-dialkyltriazolium iodides **7** and **8**.

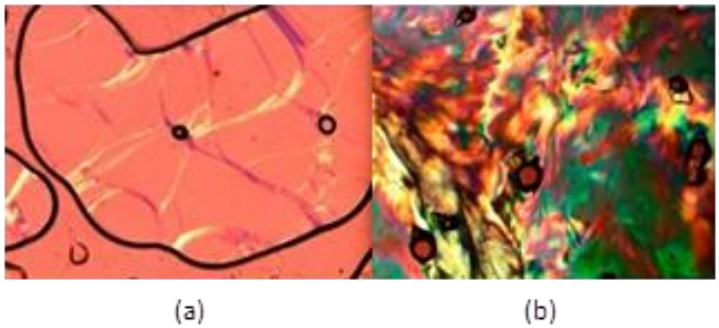

Figure S54. Representative textures as seen between crossed polarizers under an optical microscope. (a) SmA phase of **1** at 97.4 °C; (b) SmC phase of **8** at 58.2 °C.

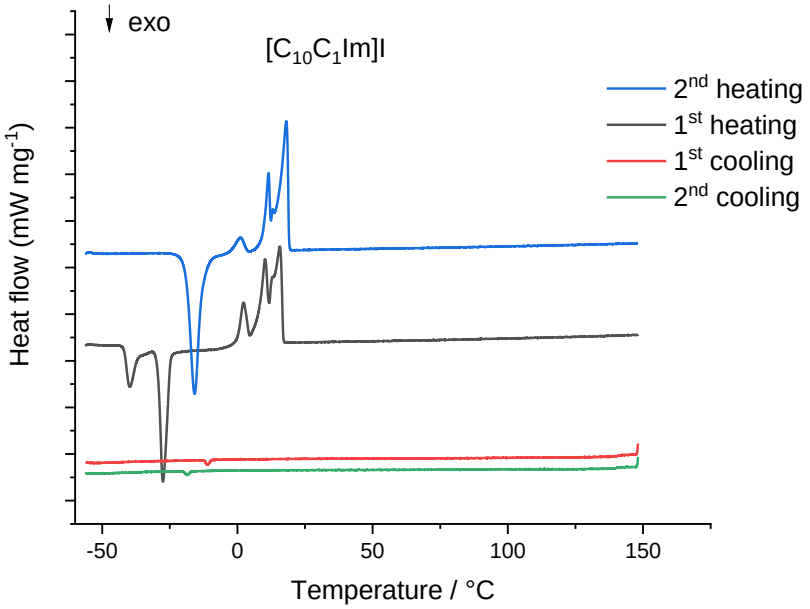

Figure S55. DSC thermogram of $[C_{10}C_1Im]I$.

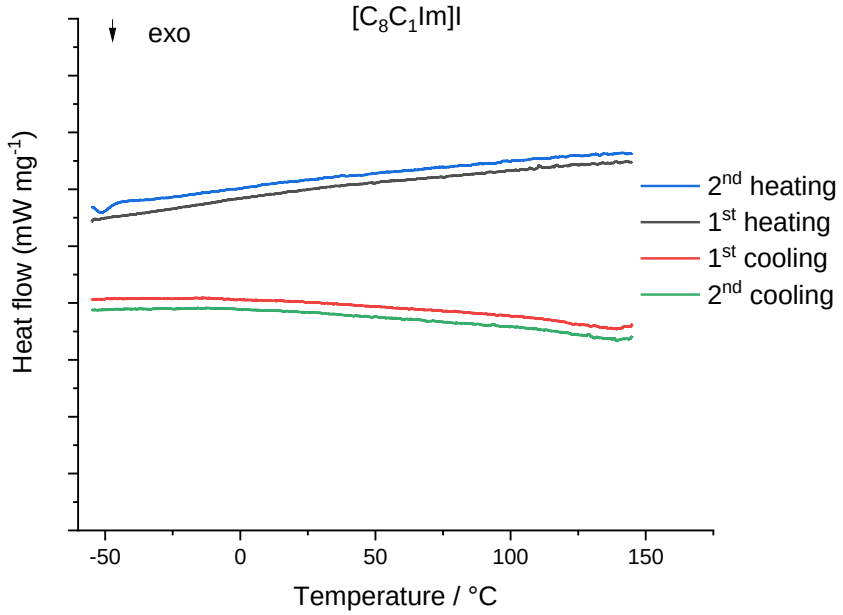

Figure S56. DSC thermogram of $[C_8C_1Im]I$.

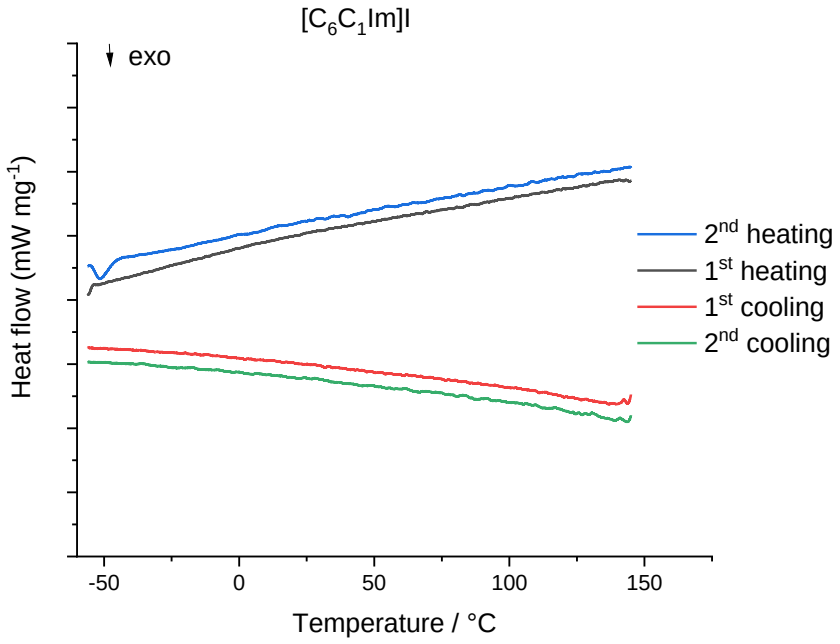

Figure S57. DSC thermogram of $[C_6C_1Im]I$.

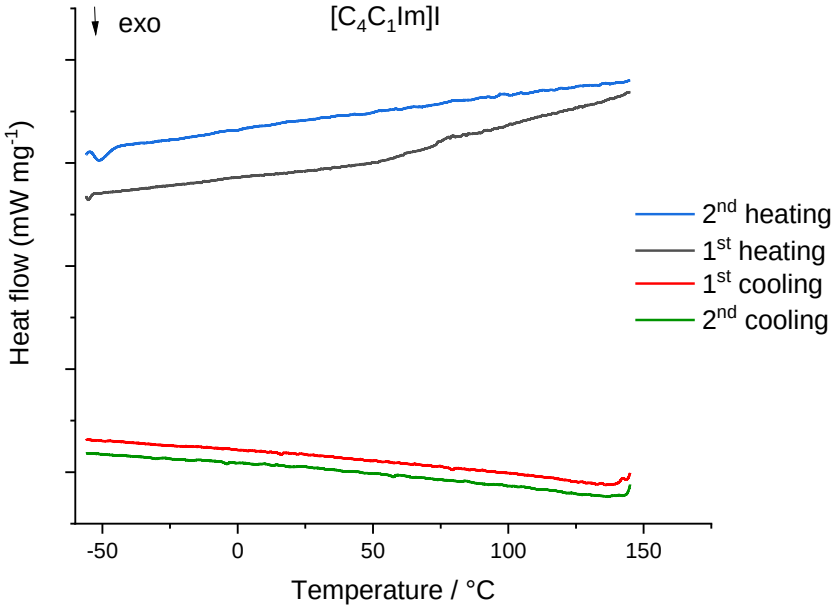

Figure S58. DSC thermogram of **10**.

VIII. Cyclic voltammetry

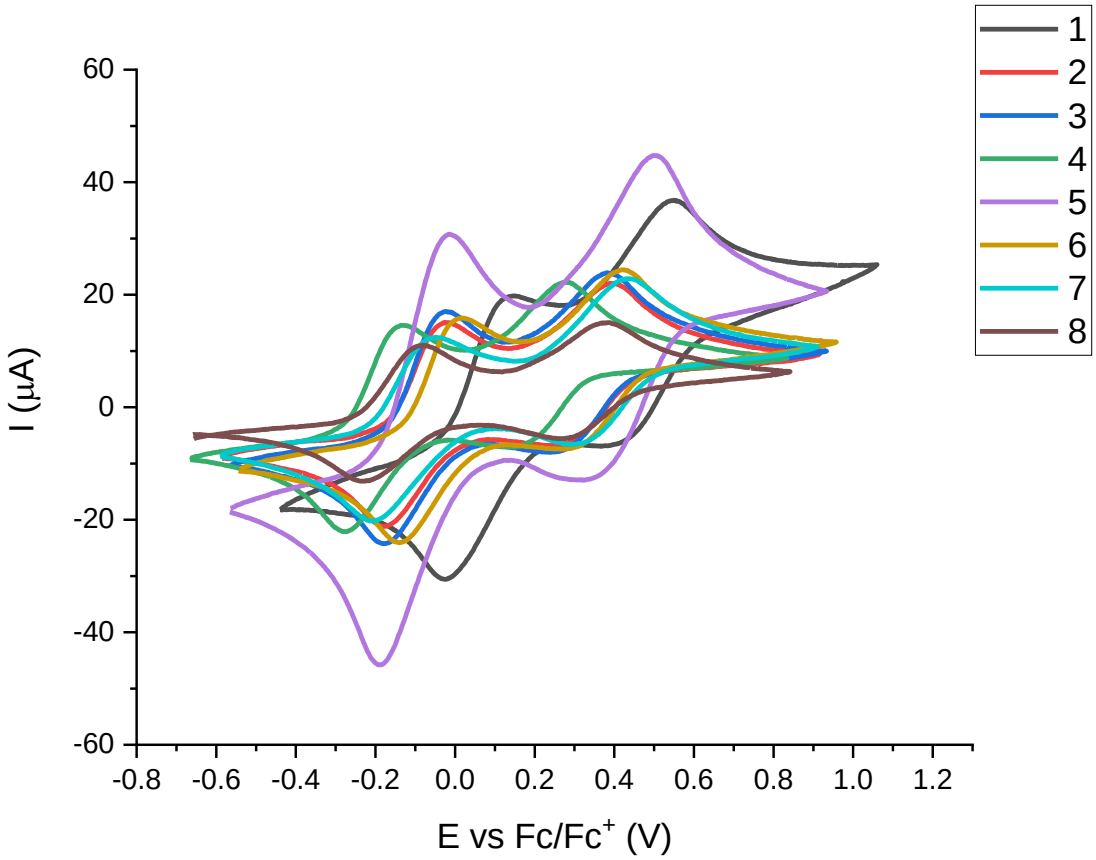

Figure S59. Cyclic voltammetry of compounds **1-8**.

Table S2. Observed redox potentials.

	$E_{1/2}$ vs Fc/Fc^+ (mV)	$E_{1/2}$ vs Fc/Fc^+ (mV)	E_{Max1} vs Fc/Fc^+ (mV)	E_{min1} Fc/Fc^+ (mV)	Δ_1 (mV)	E_{Max2} vs Fc/Fc^+ (mV)	E_{min2} vs Fc/Fc^+ (mV)	Δ_2 (mV)	Δ_2-Δ_1 (mV)
$(C_{12}C_1Tr)I$ (**1**)	114.4	508.5	201.4	27.4	174.0	601.5	415.4	162.1	394.1

($C_{11}C_1Tr$)I (**2**)	-97.6	318.5	-14.6	-180.6	166.0	399.5	237.5	162.0	416.1
($C_{10}C_1Tr$)I (**3**)	-106.2	242.0	-13.1	-181.1	168.0	391.0	236.9	154.1	348.2
(C_8C_1Tr)I (**4**)	-205.2	210.0	-128.2	-282.2	154.0	278.0	142.0	136.0	415.2
(C_6C_1Tr)I (**5**)	-102.9	384.2	-15.9	-189.9	174.0	504.2	162.1	240.1	487.1
(C_4C_1Tr)I (**6**)	-61.1	309.0	16.9	-139.1	156.0	433.0	184.9	248.1	370.1
($C_{10}C_{10}Tr$)I (**7**)	-131.2	360.9	-48.2	-214.2	166.0	443.9	277.8	166.1	492.1
(C_8C_8Tr)I (**8**)	-154.4	309.7	-76.4	-232.4	156.0	389.7	229.6	160.1	464.1

Table S3. Photovoltaic characteristic parameters of the solar cells fabricated with various electrolytes at t0. Data were obtained from five independent measurements, standard deviations in brackets.

Compound	J_{sc} /mAcm^{-2}	V_{oc} /V	P_{max} /mW	FF	η %
($C_{12}C_1Tr$)I (**1**)	9.73 (0.08)	0.25 (0.01)	0.09 (0.03)	0.33 (0.03)	0.91 (0.02)
($C_{11}C_1Tr$)I (**2**)	6.58 (0.14)	0.72 (0.02)	0.28 (0.06)	0.51 (0.02)	2.68 (0.08)
($C_{10}C_1Tr$)I (**3**)	4.60 (0.11)	0.69 (0.01)	0.14 (0.03)	0.37 (0.01)	1.34 (0.02)
(C_8C_1Tr)I (**4**)	10.36 (0.11)	0.67 (0.02)	0.31 (0.04)	0.37 (0.02)	2.87 (0.20)
(C_6C_1Tr)I (**5**)	3.50 (0.04)	0.62 (0.01)	0.05 (0.01)	0.21 (0.03)	0.57 (0.11)
(C_4C_1Tr)I (**6**)	12.49 (0.10)	0.73 (0.02)	0.69 (0.05)	0.64 (0.04)	6.63 (0.15)

($C_{10}C_{10}$Tr)I (**7**)	15.02 (0.16)	0.61 (0.05)	0.35 (0.03)	0.32 (0.02)	3.32 (0.09)
(C_8C_8Tr)I (**8**)	22.34 (0.35)	0.63 (0.05)	0.60 (0.04)	0.35 (0.02)	5.59 (0.14)
($C_{12}C_1$Im)I (**9**)	10.35 (0.25)	0.73 (0.06)	0.54 (0.07)	0.60 (0.01)	5.11 (0.12)
(C_4C_1Im)I (**10**)	5.87 (0.29)	0.79 (0.07)	0.17 (0.02)	0.30 (0.02)	1.72 (0.08)

Table S4. Photovoltaic characteristic parameters of the solar cells fabricated with various electrolytes at t+2 months. Data were obtained from five independent measurements, standard deviations in brackets.

Compound	J_{sc} /mAcm^{-2}	V_{oc} /V	P_{max} /mW	FF	η %
($C_{12}C_1$Tr)I (**1**)	9.70 (0.07)	0.25 (0.01)	0.09 (0.03)	0.33 (0.03)	0.90 (0.05)
($C_{11}C_1$Tr)I (**2**)	6.52 (0.26)	0.72 (0.02)	0.28 (0.06)	0.51 (0.02)	2.66 (0.06)
($C_{10}C_1$Tr)I (**3**)	4.55 (0.07)	0.69 (0.01)	0.14 (0.03)	0.37 (0.01)	1.29 (0.04)
(C_8C_1Tr)I (**4**)	10.31 (0.14)	0.67 (0.02)	0.31 (0.04)	0.37 (0.02)	2.84 (0.15)
(C_6C_1Tr)I (**5**)	3.42 (0.02)	0.62 (0.01)	0.05 (0.01)	0.21 (0.03)	0.49 (0.09)
(C_4C_1Tr)I (**6**)	12.40 (0.08)	0.73 (0.02)	0.69 (0.05)	0.64 (0.04)	6.44 (0.21)
($C_{10}C_{10}$Tr)I (**7**)	14.91 (0.21)	0.61 (0.05)	0.35 (0.03)	0.32 (0.02)	3.23 (0.05)
(C_8C_8Tr)I (**8**)	21.85 (0.45)	0.63 (0.05)	0.60 (0.04)	0.35 (0.02)	5.35 (0.11)

($C_{12}C_1Im$)I (**9**)	10.28 (0.31)	0.73 (0.06)	0.54 (0.07)	0.60 (0.01)	5.00 (0.15)
(C_4C_1Im)I (**10**)	5.81 (0.14)	0.79 (0.07)	0.17 (0.02)	0.30 (0.02)	1.53 (0.06)

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