ESI

Developing Design Tools for Introducing and Tuning Structural Order in Ionic Liquids: Asymmetrical 1-dodecyl-2-methyl-3-alkylimidazolium bromides

Olivier Renier[a], Guillaume Bousrez[a], Mei Yang[b], Milena Hölter[b], Bert Mallick[b], Volodymyr Smetana[a], Anja-Verena-Mudring[a,b]*

[a]Physical Materials Chemistry, Department of Materials and Environmental Chemistry, Stockholm University, Svante Arrhenius väg 16C, 10691 Stockholm, Sweden

[b]former affiliation: Anorganische Chemie III – Materials Engineering and Characterization, Fakultät für Chemie and Biochemie, Ruhr-Universität Bochum, 44780, Bochum, Germany.

Content:

I. Experimental details

Sample Preparation. Synthesis and sample handling of anhydrous salts were carried out using standard Schlenk and argon glove-box techniques. The water content was determined by TGA.

Synthesis.

Acetonitrile (99.5%), ethyl acetate (95%), dimethylsulfoxide (99%) were used as received from J.T.Backer (Deventer, Holland). Hydrobromic acid (47%) was obtained from Merck (Darmstadt, Germany). 1,2-dimethylimidazole (98%), 2-methylimidazole (99.5%), Potassium carbonate anhydrous (99%), and all 1-bromoalkanes were purchased from Sigma-Aldrich (Steinheim, Germany). All chemicals were used as received without further purification.

1-Dodecyl-2-methylimidazole was synthesized using the same route as reported for 1-alkylimidazole.[1]

Potassium hydroxide (100 mmol, 2.0 eq.) was added to a solution of 2-methylimidazole (50 mmol, 1.0 eq.) in DMSO (20 mL) and the mixture was stirred for 30 min at room temperature. Dodecyliodide (50 mmol, 1.0 eq.) was added portion-wise under vigorous stirring in a water bath and the stirring was continued overnight. The mixture was then quenched with water (200 mL) and extracted with diethyl ether (3 x 25 mL). The combined extracts were washed with water, dried over anhydrous magnesium sulfate and the solvent was evaporated off under reduced pressure.

General procedure

1-Dodecyl-2-methylimidazole (10 mmol, 1.0 eq.), alkyl bromide (11 mmol, 1.1 eq.) and acetonitrile (5 mL) were introduced in a Schlenk tube and heated under argon at 80 °C during 48 h. After cooling down the product was washed with ethyl acetate (3 x 20 mL). To obtain the precipitation of the final product the Schlenk tube is placed at -80 °C during one hour.

1-Dodecyl-2-methylimidazole. Orange oil. ^{1}H-NMR (400MHz, dmso-d_6): 0.83 (t, J_{H-H} = 6.8 Hz, 3H), 1.21 (s, 12H), 1.25 (s, 4H), 1.64-1.67 (m, 2H), 2.31 (s, 3H), 3.75 (t, J_{H-H} = 7.2 Hz, 2H), 6.75 (s, 1H), 6.84 (s, 1H). ν_{max} (cm^{-1}): 3105, 2922, 2852, 1524, 1498, 1465, 1423, 1375, 1276, 1142, 1109, 1078, 1037, 981, 920, 836, 720, 675, 622, 425.

1-Dodecyl-2,3-dimethylimidazolium bromide [$C_{12}C_1C_1$][Br]. White solid (Yield = 92%). ^{1}H-NMR (400MHz, dmso-d_6): 0.83 (t, J_{H-H} = 6.8 Hz, 3H), 1.22 (s, 18H), 1.68-1.70 (m, 2H), 2.62 (s, 3H), 3.79 (s,

3H), 4.14 (t, J_{H-H} = 7.2 Hz, 2H), 7.74 (s, 1H), 7.75 (s, 1H). ^{13}C-NMR (100MHz, dmso-d_6): 9.4, 13.8, 22.0, 25.5, 28.5, 28.7, 28.9, 28.9, 29.0, 29.0, 29.2, 31.2, 34.7, 47.4, 120.8, 122.2, 144.1. ν_{max} (cm^{-1}): 3105, 3037, 3018, 2955, 2917, 2870, 2849, 1809, 1713, 1588, 1539, 1517, 1470, 1429, 1416, 1378, 1363, 1341, 1301, 1287, 1267, 1247, 1175, 1143, 1115, 1092, 1055, 1039, 881, 818, 775, 749, 734, 719, 670, 634, 588, 521, 479. ESI-MS (positive) m/z = 265.3086 (calc. m/z = 265.2638).

1-Dodecyl-2-methyl-3-ethylimidazolium bromide [$C_{12}C_1C_2$][Br] . White solid (Yield = 87%). ^{1}H-NMR (400MHz, dmso-d_6): 0.82-0.84 (m, 3H), 1.22 (s, 18H), 1.34 (t, J_{H-H} = 7.2 Hz, 3H), 1.70 (s, 2H), 2.65 (s, 3H), 4.10-4.20 (m, 4H), 7.78 (s, 2H). ^{13}C-NMR (100MHz, dmso-d_6): 9.2, 13.9, 14.7, 22.0, 25.6, 28.5, 28.7, 28.8, 28.9, 29.0, 29.0, 29.1, 31.2, 42.7, 47.4, 120.6, 121.3, 143.4. ν_{max} (cm^{-1}): 3114, 3054, 2956, 2917, 2850, 1666, 1584, 1531, 1467, 1429, 1379, 1363, 1337, 1295, 1265, 1243, 1222, 1209, 1190, 1138, 1096, 1047, 956, 863, 806, 766, 749, 721, 684, 672, 639, 601, 477, 421. ESI-MS (positive) m/z = 279.3237 (calc. m/z = 279.2795).

1-Dodecyl-2-methyl-3-propylimidazolium bromide [$C_{12}C_1C_3$][Br]. White solid (Yield = 93%). ^{1}H-NMR (400MHz, dmso-d_6): 0.81-0.87 (m, 6H), 1.21 (s, 18H), 1.71-1.76 (m, 4H), 2.66 (s, 3H), 4.12-4.17 (m, 4H), 7.83 (s, 2H). ^{13}C-NMR (100MHz, dmso-d_6): 9.4, 10.3, 13.8, 22.0, 22.5, 25.5, 28.4, 28.6, 28.8, 28.9, 28.9, 29.0, 29.0, 31.2, 47.4, 48.7, 121.2, 121.3, 143.5. ν_{max} (cm^{-1}): 3115, 3084, 3051, 2960, 2918, 2872, 2850, 1743, 1643, 1582, 1528, 1470, 1425, 1372, 1333, 1285, 1264, 1236, 1196, 1173, 1139, 1091, 1047, 964, 896, 868, 799, 764, 735, 722, 678, 639, 585, 526, 481, 451. ESI-MS (positive) m/z = 293.3406 (calc. m/z = 293.2951).

1-Dodecyl-2-methyl-3-butylimidazolium bromide [$C_{12}C_1C_4$][Br]. White solid (Yield = 95%). ^{1}H-NMR (400MHz, dmso-d_6): 0.85 (t, J_{H-H} = 6.8 Hz, 3H), 0.90 (t, J_{H-H} = 7.2 Hz, 3H), 1.23 (s, 20H), 1.66-1.71 (m, 4H), 2.63 (s, 3H), 4.11-4.14 (m, 4H), 7.73 (s, 1H), 7.74 (s, 1H). ^{13}C-NMR (100MHz, dmso-d_6): 9.2, 13.4, 13.9, 18.9, 22.1, 25.6, 28.4, 28.7, 28.8, 28.9, 29.0, 29.0, 29.0, 31.1, 31.3, 47.2, 27.5, 121.2 (2C), 143.6. ν_{max} (cm^{-1}): 3126, 3085, 2958, 2919, 2851, 2765, 2730, 1658, 1579, 1529, 1507, 1480, 1467, 1427, 1375, 1336, 1293, 1271, 1248, 1181, 1163, 1142, 1134, 1092, 1065, 1043, 1012, 952, 878, 850, 779, 753, 721, 682, 638, 609, 478, 440, 403. ESI-MS (positive) m/z = 307.3564 (calc. m/z = 307.3108).

1-Dodecyl-2-methyl-3-pentylimidazolium bromide [$C_{12}C_1C_5$][Br]. Orange viscous oil (Yield = 89%). ^{1}H-NMR (400MHz, dmso-d_6): 0.84 (t, J_{H-H} = 6.8 Hz, 6H), 1.22 (s, 14H), 1.26 (s, 8H), 1.70-1.72 (m, 4H), 2.63 (s, 3H), 4.12 (t, J_{H-H} = 7.2 Hz, 4H), 7.76 (s, 2H). ^{13}C-NMR (100MHz, dmso-d_6):9.3, 13.8, 13.9, 21.9, 22.0, 25.2, 25.5, 28.5, 28.7, 28.8, 28.9, 29.0, 29.0, 29.0, 30.6, 31.3, 47.4 (2C), 121.3 (2C), 143.5. ν_{max} (cm^{-1}):

3052, 2955, 2922, 2853, 1738, 1672, 1583, 1530, 1465, 1465, 1465, 1377, 1337, 1273, 1244, 1179, 1135, 1089, 1044, 962, 889, 766, 724, 673, 474, 453, 407. ESI-MS (positive) m/z = 321.3783 (calc. m/z = 321.3264).

1-Dodecyl-2-methyl-3-hexylimidazolium bromide [$C_{12}C_1C_6$][Br]. White solid (Yield = 96%). ^{1}H-NMR (400MHz, dmso-d_6): 0.82-0.87 (m, 6H), 1.22 (s, 24H), 1.70-1.75 (m, 4H), 2.65 (s, 3H), 4.14 (t, J_{H-H} = Hz, 4H), 7.79 (s, 1H), 7.80 (s, 1H). ^{13}C-NMR (100MHz, dmso-d_6): 9.3, 13.7, 13.8, 21.6, 22.0, 25.5, 27.7, 28.4, 28.7, 28.7, 28.8, 28.9, 28.9, 29.0, 29.0, 31.2 (2C), 47.4, 47.4, 121.2 (2C), 143.5. ν_{max} (cm^{-1}): 3104, 3060, 2955, 2920, 2852, 1669, 1584, 1529, 1529, 1466, 1426, 1377, 1339, 1285, 1259, 1223, 1179, 1138, 1089, 1042, 931, 885, 782, 754, 735, 722, 677, 641, 503, 475. ESI-MS (positive) m/z = 335.3932 (calc. m/z = 335.3421).

1-Dodecyl-2-methyl-3-heptylimidazolium bromide [$C_{12}C_1C_7$][Br]. Orange viscous oil (Yield = 91%). ^{1}H-NMR (400MHz, dmso-d_6): 0.85 (t, J_{H-H} = 6.8 Hz, 6H), 1.23 (s, 26H), 1.71-1.72 (m, 4H), 2.62 (s, 3H), 4.11 (t, J_{H-H} = 7.2 Hz, 4H), 7.74 (s, 2H). ^{13}C-NMR (100MHz, dmso-d_6): 9.2, 13.9, 13.9, 22.0, 22.1, 25.5, 25.6, 28.1, 28.5, 28.7, 28.9, 28.9, 29.0, 29.0, 29.0, 29.0, 31.1, 31.3, 47.5 (2C), 121.3 (2C), 143.6. ν_{max} (cm^{-1}): 3053, 2956, 2922, 2853, 1738, 1583, 1530, 1466, 1466, 1374, 1339, 1238, 1176, 1134, 1094, 1046, 887, 767, 723, 673, 635, 606, 558, 479. ESI-MS (positive) m/z = 349.4054 (calc. m/z = 349.3577).

1-Dodecyl-2-methyl-3-octylimidazolium bromide [$C_{12}C_1C_8$][Br]. White solid (Yield = 95%). ^{1}H-NMR (400MHz, dmso-d_6): 0.84 (t, J_{H-H} = 6.8 Hz, 6H), 1.22 (s, 28H), 1.71-1.72 (m, 4H), 2.64 (s, 3H), 4.13 (t, J_{H-H} = 7.2 Hz, 4H), 7.78 (s, 2H). ^{13}C-NMR (100MHz, dmso-d_6): 9.3, 13.8, 13.8, 22.0, 22.0, 25.5 (2C), 28.4, 28.5, 28.5, 28.7, 28.8, 28.9, 29.0, 29.0, 29.0 (2C), 31.1, 31.2, 47.4 (2C), 121.3 (2C), 143.5. ν_{max} (cm^{-1}): 3096, 3044, 3004, 2952, 2918, 2850, 1676, 1582, 1527, 1509, 1465, 1424, 1376, 1362, 1334, 1286, 1263, 1248, 1212, 1180, 1167,1132, 1100, 1080, 1054, 990, 888, 864, 794, 753, 722, 701, 676, 599, 494, 448. ESI-MS (positive) m/z = 363.4214 (calc. m/z = 363.3734).

1-Dodecyl-2-methyl-3-nonylimidazolium bromide [$C_{12}C_1C_9$][Br]. White solid (Yield = 90%). ^{1}H-NMR (400MHz, dmso-d_6): 0.85 (t, J_{H-H} = 6.8 Hz, 6H), 1.23 (s, 30H), 1.69-1.74 (m, 4H), 2.62 (s, 3H), 4.11 (t, J_{H-H} = 7.2 Hz, 4H), 7.72 (s, 1H), 7.74 (s, 1H). ^{13}C-NMR (100MHz, dmso-d_6): 9.2, 13.9 (2C), 22.1, 22.1, 25.6 (2C), 28.5 (2C), 28.6, 28.7, 28.8, 28.9, 28.9, 29.0, 29.0, 29.0 (2C), 31.2, 31.3, 47.5 (2C), 121.3 (2C), 143.6. ν_{max} (cm^{-1}): 3084, 3084, 3055, 2917, 2849, 2761, 1735, 1653, 1575, 1530, 1501, 1467, 1426, 1409, 1375, 1353, 1328, 1287, 1268, 1243, 1217, 1178, 1128, 1099, 1076, 1050, 1028, 891, 778, 754, 743, 722, 705, 672, 632, 555, 500, 488, 450. ESI-MS (positive) m/z = 377.4417 (calc. m/z = 377.3890).

1-Dodecyl-2-methyl-3-decylimidazolium bromide [$C_{12}C_1C_{10}$][Br]. White solid (Yield = 75%). ^{1}H-NMR (400MHz, dmso-d_6): 0.84 (t, J_{H-H} = 6.8 Hz, 6H), 1.22 (s, 32H), 1.70-1.72 (m, 4H), 2.64 (s, 3H), 4.13 (t, J_{H-H} = 7.2 Hz, 4H), 7.78 (s, 2H). ^{13}C-NMR (100MHz, dmso-d_6): 9.3, 13.9 (2C), 22.1 (2C), 25.5 (2C), 28.5 (2C), 28.6, 28.7 (2C), 28.9 (2C), 28.9, 29.0, 29.0, 29.0 (2C), 31.2, 31.3, 47.4 (2C), 121.3 (2C), 143.5. ν_{max} (cm^{-1}): 3101, 3067, 3043, 2918, 2851, 1675, 1584, 1527, 1466, 1425, 1377, 1359, 1332, 1285, 1261, 1247, 1231, 1199, 1166, 1133, 1096, 1076, 1046, 968, 889, 789, 751, 722, 675, 561, 469, 426. ESI-MS (positive) m/z = 391.4596 (calc. m/z = 391.4047).

1-Dodecyl-2-methyl-3-undecylimidazolium bromide [$C_{12}C_1C_{11}$][Br]. White solid (Yield = 94%). ^{1}H-NMR (400MHz, dmso-d_6): 0.85 (t, J_{H-H} = 6.8 Hz, 6H), 1.23 (s, 34H), 1.71-1.72 (m, 4H), 2.62 (s, 3H), 4.11 (t, J_{H-H} = 7.2 Hz, 4H), 7.72 (s, 2H). ^{13}C-NMR (100MHz, dmso-d_6): 9.2, 13.9 (2C), 22.1 (2C), 25.6 (2C), 27.5, 28.1, 28.5, 28.7 (2C), 28.9, 28.9, 29.0, 29.0, 29.0, 29.0, 31.3 (2C), 32.2, 35.1, 47.5 (2C), 121.3 (2C), 143.6. ν_{max} (cm^{-1}): 3045, 3045, 2918, 2850, 2761, 1677, 1584, 1528, 1510, 1467, 1425, 1375, 1334, 1290, 1248, 1223, 1196, 1177, 1134, 1095, 1048, 967, 891, 793, 758, 722, 673, 652, 524, 483, 474, 434, 422. ESI-MS (positive) m/z = 405.4694 (calc. m/z = 405.4203).

1,3-Didodecyl-2-methylimidazolium bromide [$C_{12}C_1C_{12}$][Br]. White solid (Yield = 92%). ^{1}H-NMR (400MHz, dmso-d_6): 0.85 (t, J_{H-H} = 6.8 Hz, 6H), 1.23 (s, 36H), 1.70-1.72 (m, 4H), 2.61 (s, 3H), 4.10 (t, J_{H-H} = 7.2 Hz, 4H), 7.71 (s, 2H). ^{13}C-NMR (100MHz, dmso-d_6): 9.2, 13.9 (2C), 22.1 (2C), 25.6 (2C), 27.5, 28.1, 28.5, 28.7 (2C), 28.9 (2C), 28.9, 29.0 (2C), 29.0 (2C), 31.3 (2C), 32.2, 35.2, 47.5 (2C), 121.3 (2C), 143.6. ν_{max} (cm^{-1}): 3091, 3035, 2915, 2849, 1803, 1696, 1579, 1527, 1464, 1436, 1374, 1329, 1283, 1263, 1240, 1212, 1186, 1161, 1126, 1089, 1050, 989, 962, 924, 887, 859, 804, 775, 749, 720, 692, 675, 648, 519, 492, 468. ESI-MS (positive) m/z = 419.4930 (calc. m/z = 419.4360).

1-Dodecyl-2-methyl-3H-imidazolium bromide [$C_{12}C_1C_0$][Br].

[$C_{12}C_1C_0$]Br was prepared by dropwise addition of a slight excess of concentrated hydrobromic acid to 1-dodecyl-2-methylimidazole at 0 °C in diethyl ether. After two hours at room temperature, the solvent was removed under dynamic vacuum.

Brown solid (Yield = 96%). ^{1}H-NMR (400MHz, dmso-d_6): 0.83 (t, J_{H-H} = 6.8 Hz, 3H), 1.22 (s, 18H), 1.71-1.73 (m, 2H), 2.60 (s, 3H), 4.07 (t, J_{H-H} = 7.2 Hz, 2H), 7.59 (s, 1H), 7.69 (s, 1H), 14.02 (s, 1H). ^{13}C-NMR (100MHz, dmso-d_6): 10.3, 13.9, 22.1, 25.7, 28.5, 28.7, 28.9, 28.9, 29.0, 29.0 (2C), 31.3, 46.8, 117.9, 121.8, 143.8. ν_{max} (cm^{-1}): 3159, 3103, 3078, 3006, 2953, 2917, 2850, 1768, 1702, 1633, 1598, 1530, 1505, 1471, 1431, 1393, 1379, 1332, 1300, 1287, 1271, 1254, 1235, 1211, 1189, 1189, 1125, 1101,

1051, 1034, 1002, 928, 887, 856, 749, 721, 676, 659, 623, 579, 565, 503, 485, 477, 433, 409. ESI-MS (positive, ([%])) m/z = 251.2947 (calc. m/z = 251.2482).

ThermoGravimetric Analysis (TGA) was performed with a TG 449 F3 Jupiter (Netzsch, Selb, Germany). Measurements were carried out in aluminum oxide crucibles with a heating rate of 10 °C/min and nitrogen as purge gas.

Differential scanning calorimetry (DSC) was performed with a computer-controlled PhoenixDSC 204 F1 thermal analyzer (Netzsch, Selb, Germany). Measurements were carried out at a heating rate of 5 °C/min in sealed aluminium crucible with an nitrogen flow rate of 40 mL/min. The samples were placed in aluminium pans which were cold-sealed and punctured. Given temperatures correspond to the onset of the respective thermal process.

Optical analyses were made by **hot-stage polarized optical microscopy (POM)** with an Axio Imager A1 microscope (Carl Zeiss MicroImagingGmbH,Göttingen, Germany) equipped with a hot stage, THMS600 (LinkamScientificInstruments Ltd, Surrey, UK), and Linkam TMS 94 temperature controller (Linkam Scientific Instruments Ltd, Surrey, UK). Images were recorded at a magnification of 100× as a video with a digital camera. During heating and cooling, the sample was placed between two cover slips. Heating and cooling rates were 5 °C/min.

A SYNAPT G2-S HDMS Q-ToF **Mass Spectrometer** (Waters, Manchester, UK) with an ESI operated in the positive and negative ion mode, was used in this study. The ion source was set up as follows: capillary voltage: 2500 V, extractor: 1.0 V, RF lens: 0.5 V, ion source temperature: 120 °C and desolvation temperature 250 °C. Nitrogen was used as both the cone and desolvation gas at a flow of 70 L/h and 500 L/h, respectively. Argon was used as a collision gas at a pressure of $2.95 \cdot 10^{-4}$ mbar.

^{1}H and ^{13}C NMR spectra were recorded at room temperature in DMSO on a Bruker 400 MHz spectrometer equipped with a BBO probe. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm). The following abbreviations used for the observed multiplicities: s (singlet), d (doublet), t (triplet), q (quartet), p (pentuplet), h (hexuplet), m (multiplet for unresolved lines). ^{1}H NMR chemical shifts were referenced to the residual solvent signal for DMSO (2.50 ppm) and ^{13}C NMR chemical shifts were referenced to the solvent signal of DMSO (39.52 ppm).

Infrared spectra (IR) were collected on a Bruker Alpha-P ATR-spectrometer equipped with a diamond crystal (Karlsruhe, Germany) in attenuated total reflection configuration. The data evaluation was carried out with the program OPUS.

Single crystals of sufficient quality for **singe crystal X-ray structure determination** of $\mathbf{C_{12}C_1C_0}$ and $\mathbf{C_{12}C_1C_1}$ were obtained by recrystallization from ethyl acetate. The monohydrate of $\mathbf{C_{12}C_1C_{12}}$, could be crystallized from a dichloromethane solution of the anhydrous compound by isothermal evaporation in air at room temperature. All crystals, as a rule, appeared in the form of thin plates. 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 293 K) and Bruker Venture diffractometer using radiation Mo Kα radiation (λ = 0.71073 Å at 293 K). Crystal structure solution by direct methods using SIR 92[1] yielded the heavy atom positions. Refinement with SHELXL-97[2] 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[3] and numerical absorption correction was carried out with the program X-Shape.[4] To illustrate the crystal structures, the program Diamond[5] was used.

Temperature-dependent small angle X-ray scattering (SAXS) experiments were carried out at the A2 Beamline of DORIS III, Hasylab, DESY, Hamburg, Germany, at a fixed wavelength of 1.5 Å. The data were collected with a MarCCD detector. The detector was calibrated with silver behenate. The sample–detector position was fixed at 635.5 mm. For measurements, the samples were placed in a copper sample holder between aluminum foil. The sample temperature was controlled by a JUMO IMAGO 500 multi-channel process and program controller. Data reduction and analysis, correction or background scattering and transmission were carried out by using the program a2tool (Hasylab).

II. Single Crystal X-Ray Diffraction (SCXRD)

Table S1. Crystallographic and refinement details for **$C_{12}C_1C_0$**, **$C_{12}C_1C_1$**, and **$C_{12}C_1C_{12}$**·H_2O.

	$C_{12}C_1C_0$	**$C_{12}C_1C_1$**	**$C_{12}C_1C_{12}$**·H_2O
CCDC	1912603	1912604	1912605
Empirical formula	$C_{16}H_{31}N_2Br$	$C_{17}H_{33}N_2Br$	$C_{28}H_{56}N_2Br_2O$
Formula weight	331.34	345.36	516.66
Crystal system	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
Unit cell dimensions	a = 6.989(1) Å	a = 22.453(1) Å	a = 7.595(7) Å
	b = 8.308(2) Å	b = 8.5697(5) Å	b = 9.979(9) Å
	c = 16.476(3) Å	c = 10.2184(7) Å	c = 20.82(2)Å
	α = 83.84(3) °	α = 90 °	α = 85.10(3) °
	β = 78.78(3) °	β = 91.870(2) °	β = 83.70(4) °
	γ = 79.10(3) °	γ = 90 °	γ = 84.22(3) °
Volume	919.0(3) Å^3	1965.1(2) Å^3	1556(3) Å^3
Z	2	4	2
Calculated density	1.197 g/cm^3	1.167 g/cm^3	1.105 g/cm^3
Absorption coefficient	2.229 mm^{-1}	2.087 mm^{-1}	1.928 mm^{-1}
Θ-range for data collection	2.9 to 25.1 °	2.5 to 28.3 °	2.1 to 44.7 °
Reflections collected / unique	7952 / 2953	24952 / 4880	7672 / 2425
Refinement method	Full-matrix least-squares on F^2		
Temperature	170 K		
Data / parameters	2953 / 175	4880 / 184	2425 / 291
Goodness-of-fit on F^2	1.00	1.02	1.17
Final R indices [I>2sigma(I)]	R_1 = 0.063	R_1 = 0.052	R_1 = 0.0610
	wR_2 = 0.156	wR_2 = 0.112	wR_2 = 0.124
R indices (all data)	R_1 = 0.091	R_1 = 0.116	R_1 = 0.082
	wR_2 = 0.173	wR_2 = 0.136	wR_2 = 0.132

III. H and ^{13}C NMR spectra

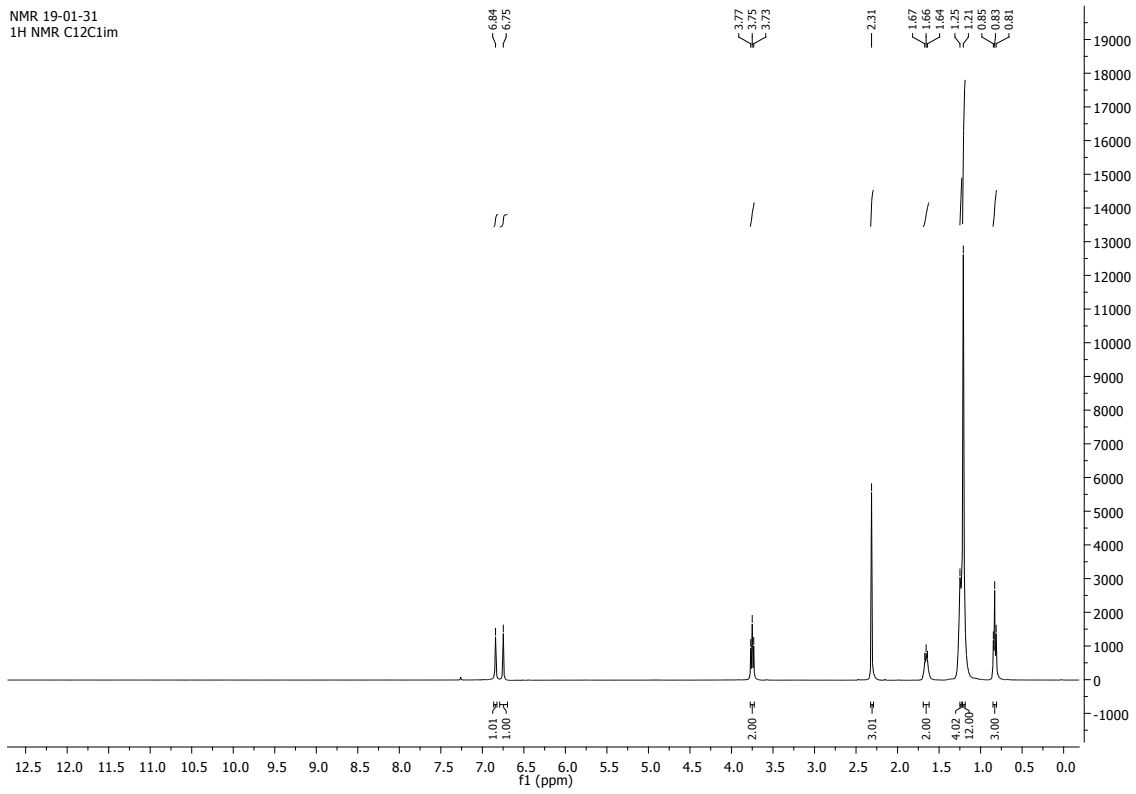

Figure S1: ^{1}H-NMR spectrum (400 MHz, DMSO) of 1-dodecyl-2-methylimidazole

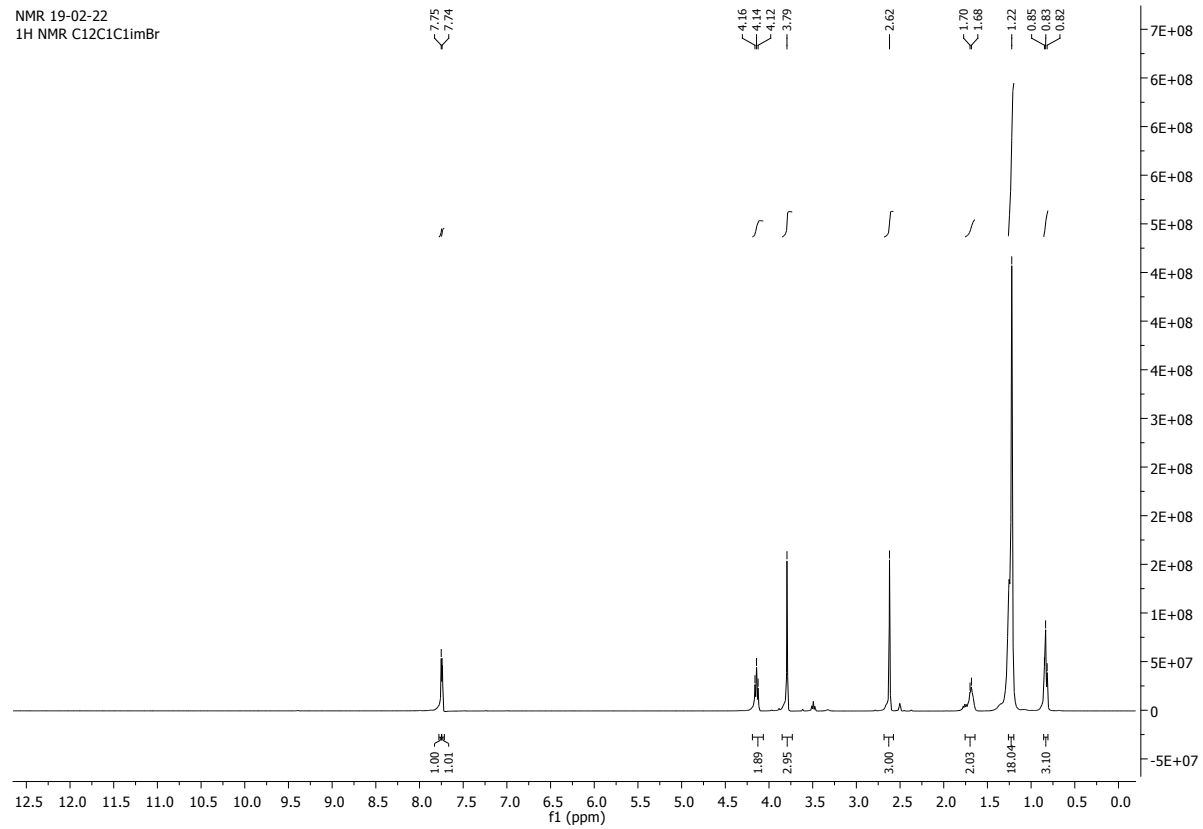

Figure S2: ^{1}H-NMR spectrum (400 MHz, DMSO) of compound $\mathbf{C_{12}C_1C_1}$

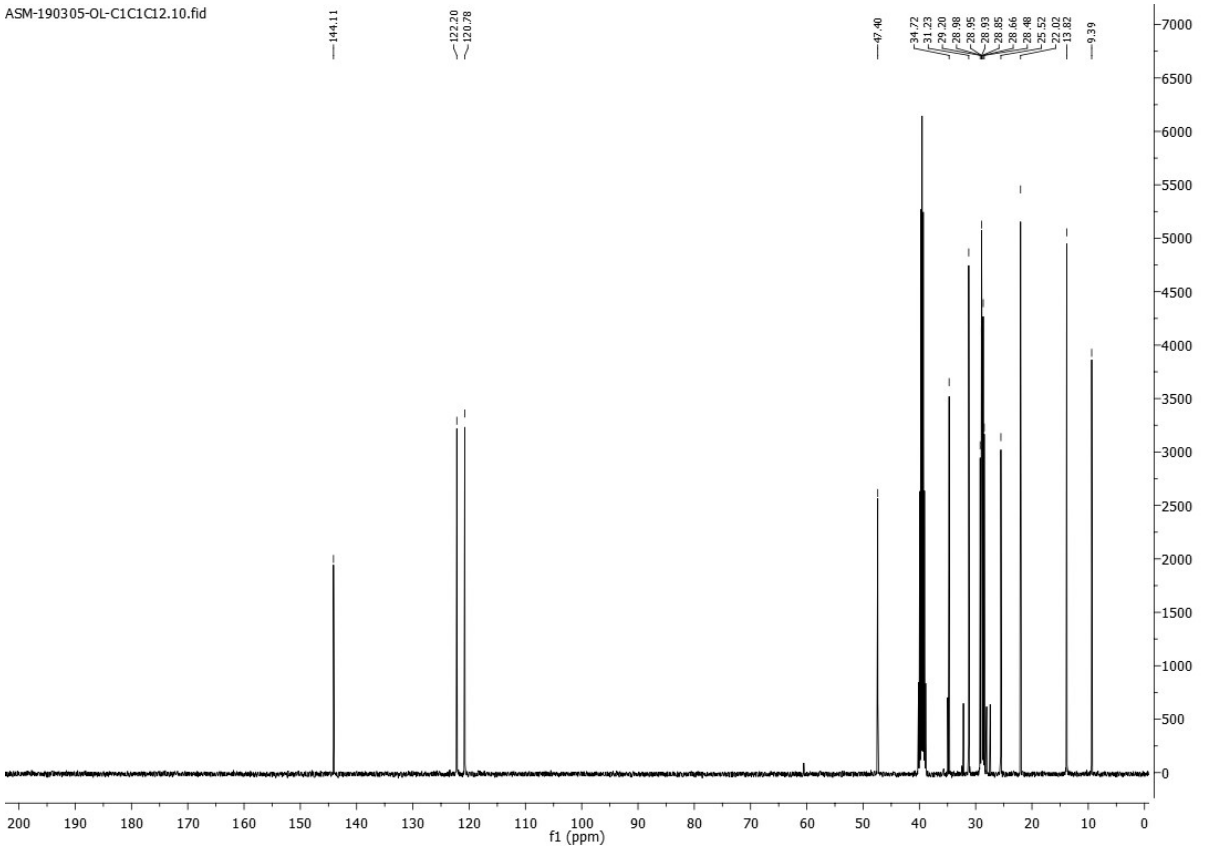

Figure S3: ^{13}C-NMR spectrum (100 MHz, DMSO) of compound $\mathbf{C_{12}C_1C_1}$

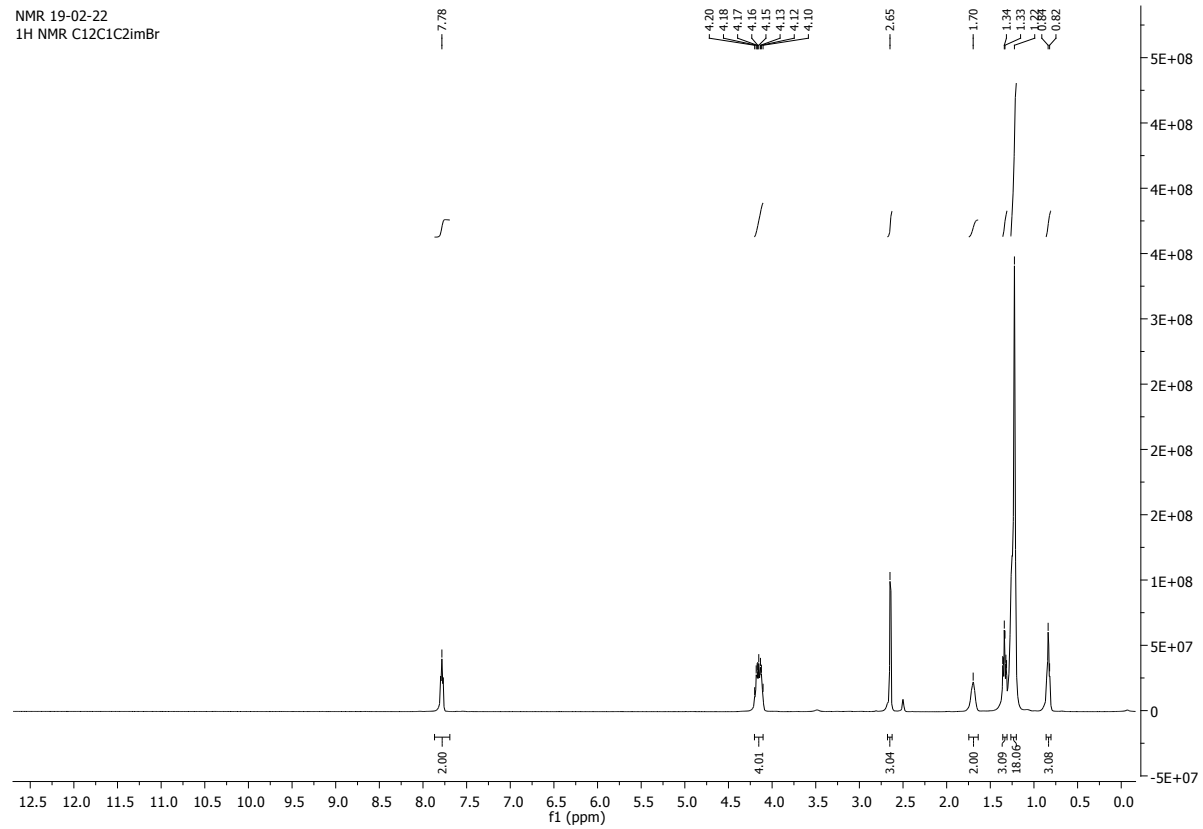

Figure S4: ^{1}H-NMR spectrum (400 MHz, DMSO) of compound $\mathbf{C_{12}C_1C_2}$

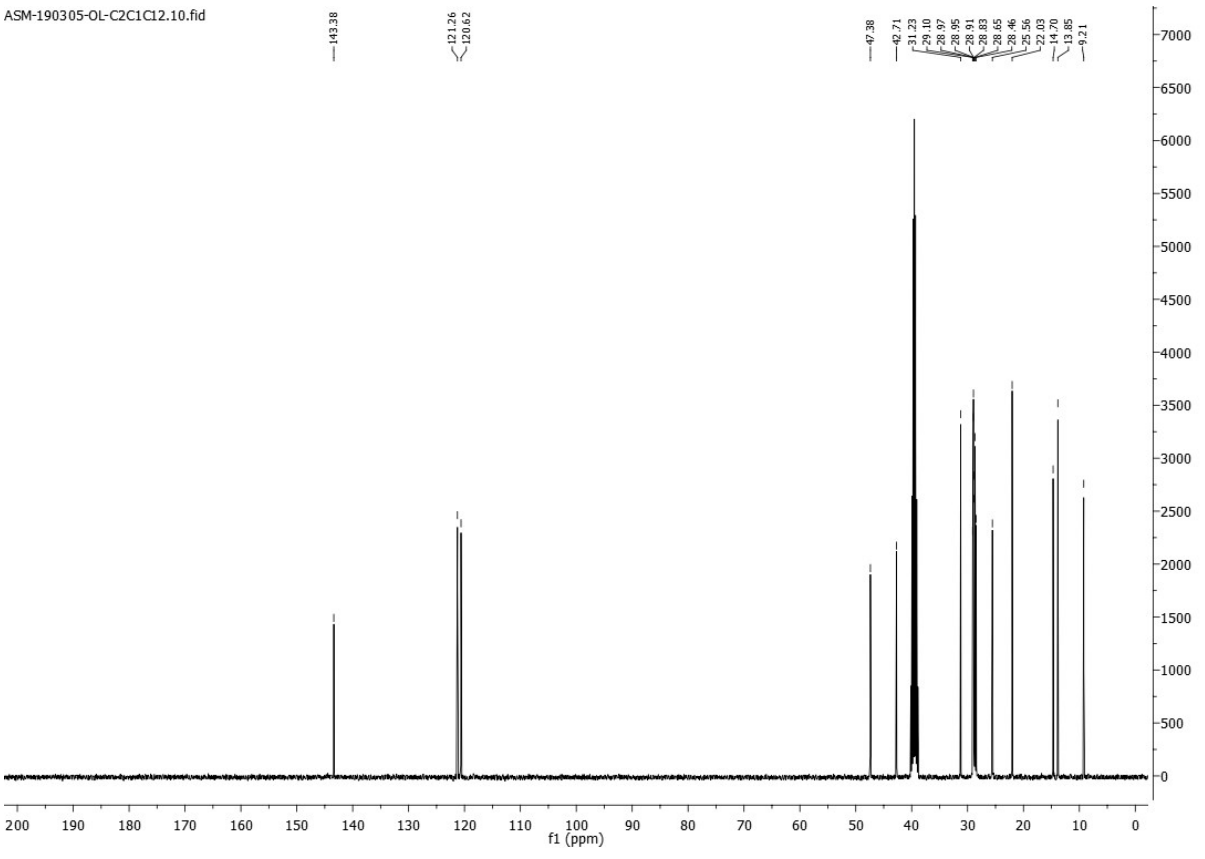

Figure S5: ^{13}C-NMR spectrum (100 MHz, DMSO) of compound $\mathbf{C_{12}C_1C_2}$

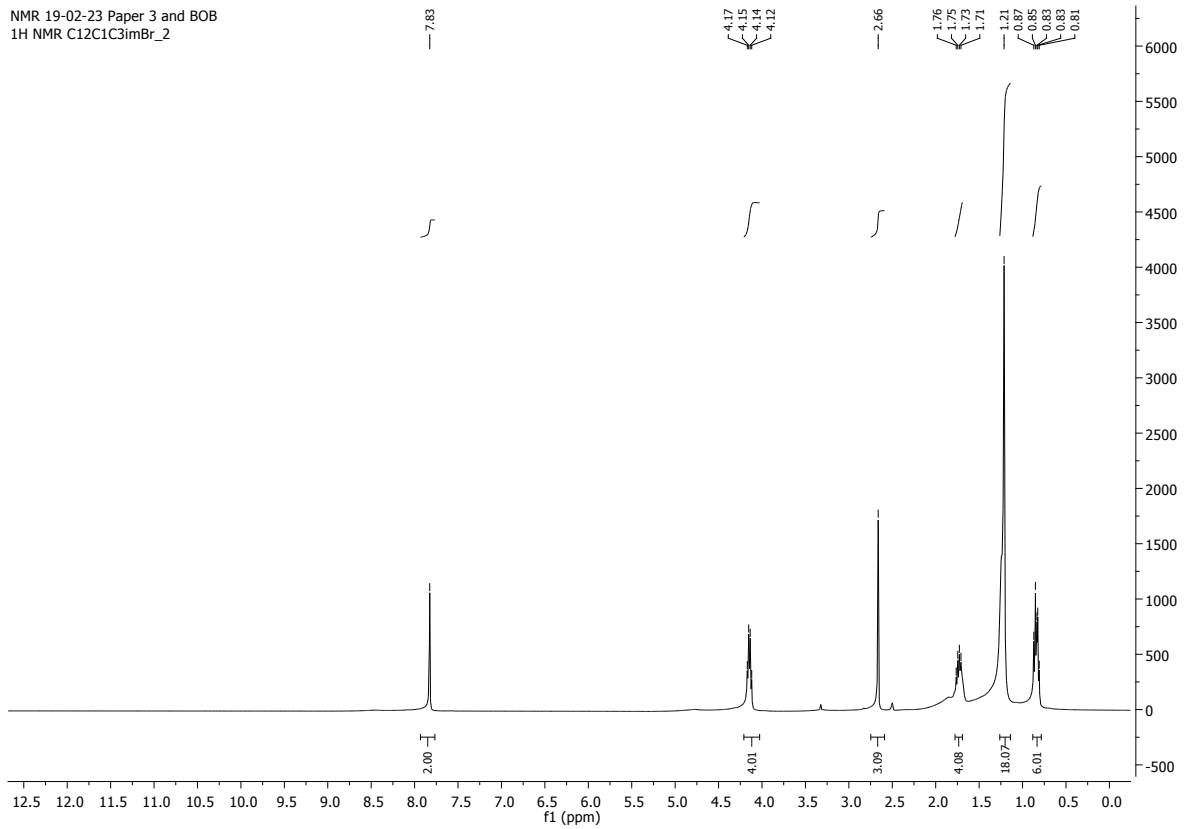

Figure S6: ^{1}H-NMR spectrum (400 MHz, DMSO) of compound $\mathbf{C_{12}C_1C_3}$

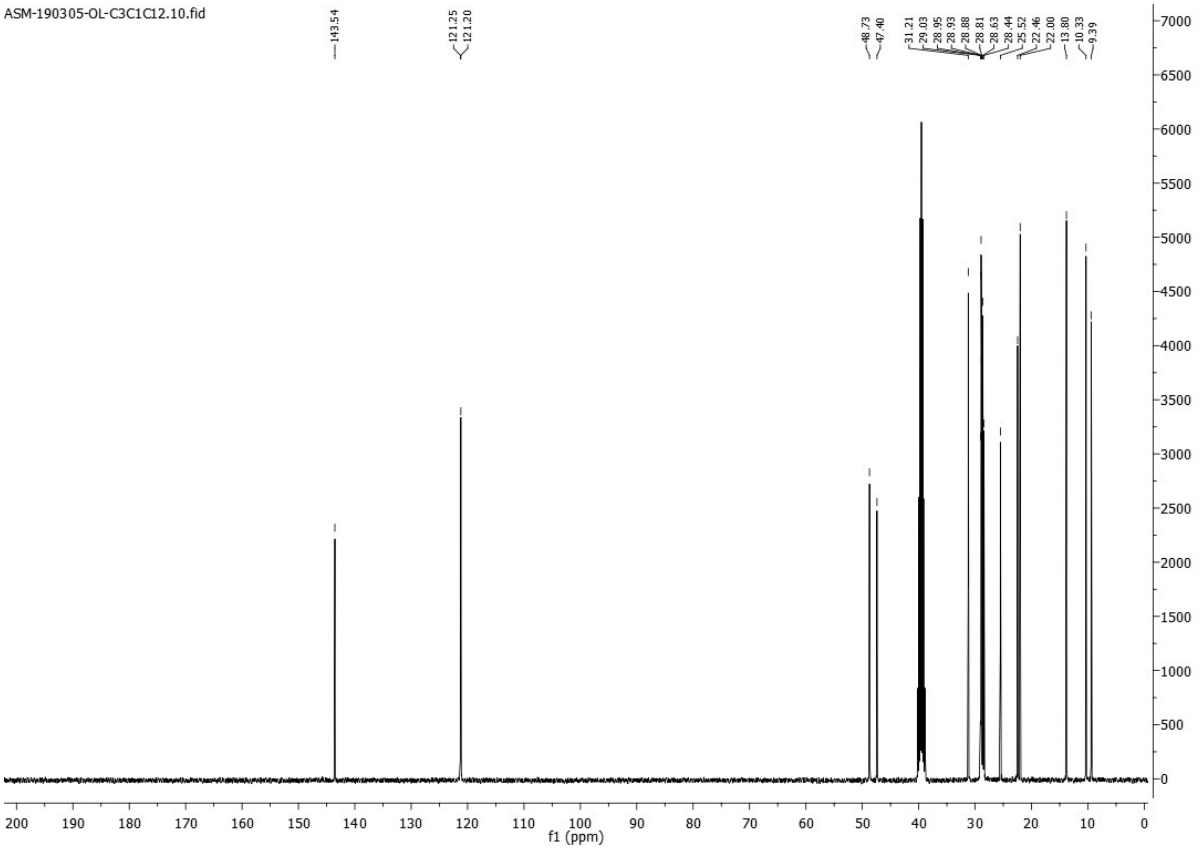

Figure S7: ^{13}C-NMR spectrum (100 MHz, DMSO) of compound $\mathbf{C_{12}C_1C_3}$

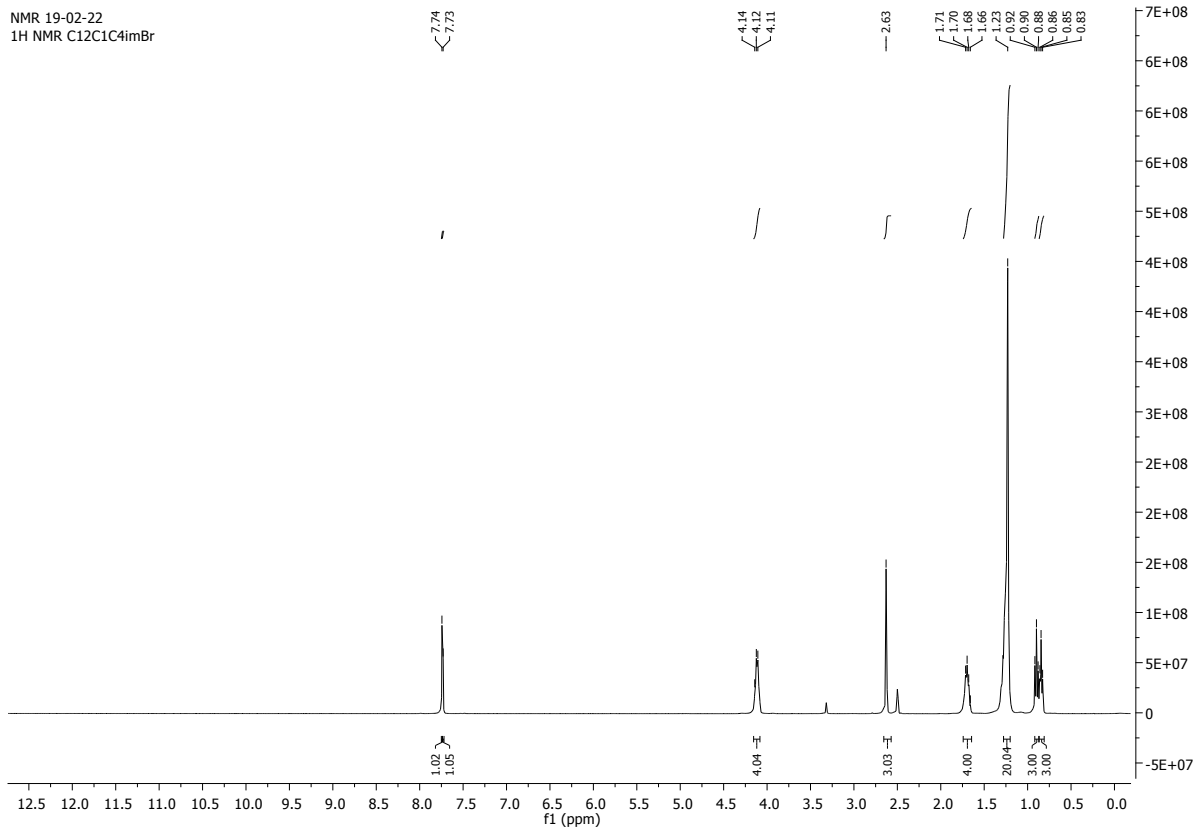

Figure S8: ^{1}H-NMR spectrum (400 MHz, DMSO) of compound $\mathbf{C_{12}C_1C_4}$

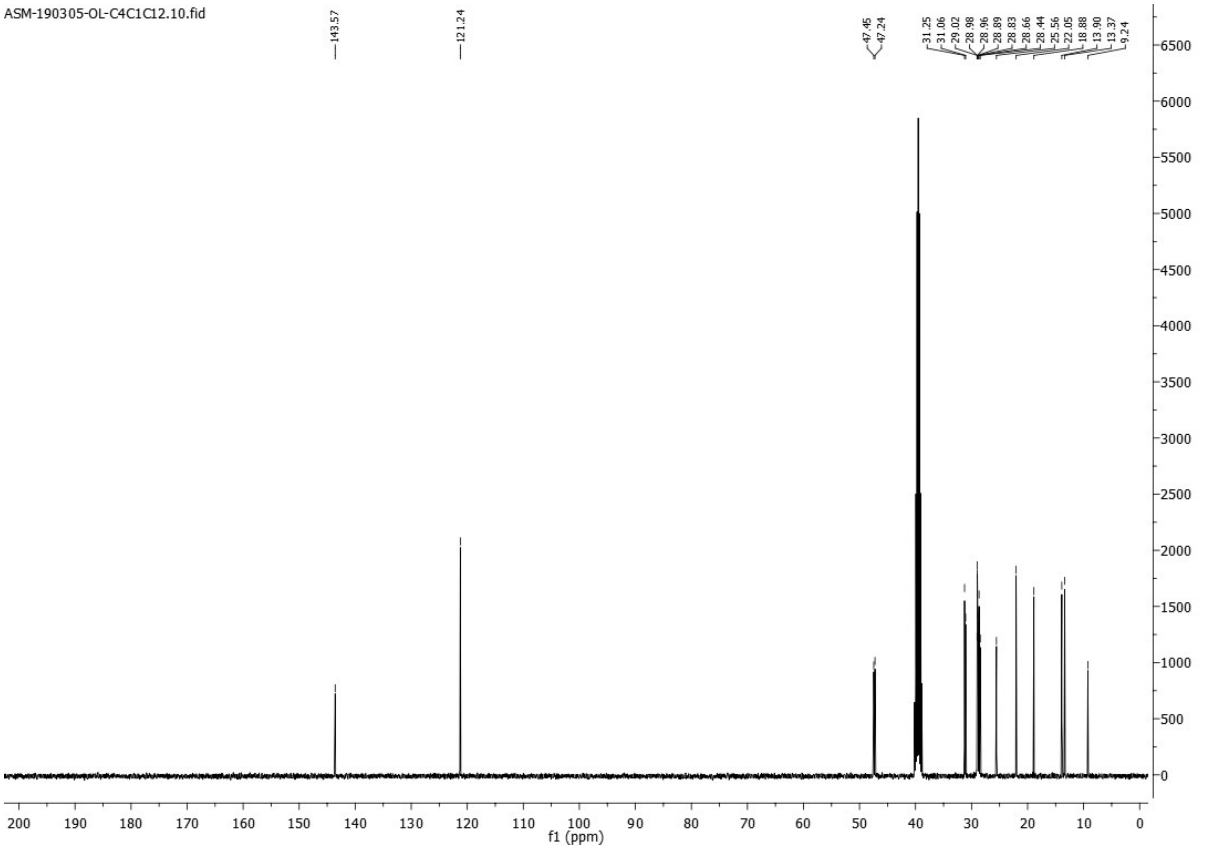

Figure S9: ^{13}C-NMR spectrum (100 MHz, DMSO) of compound $\mathbf{C_{12}C_1C_4}$

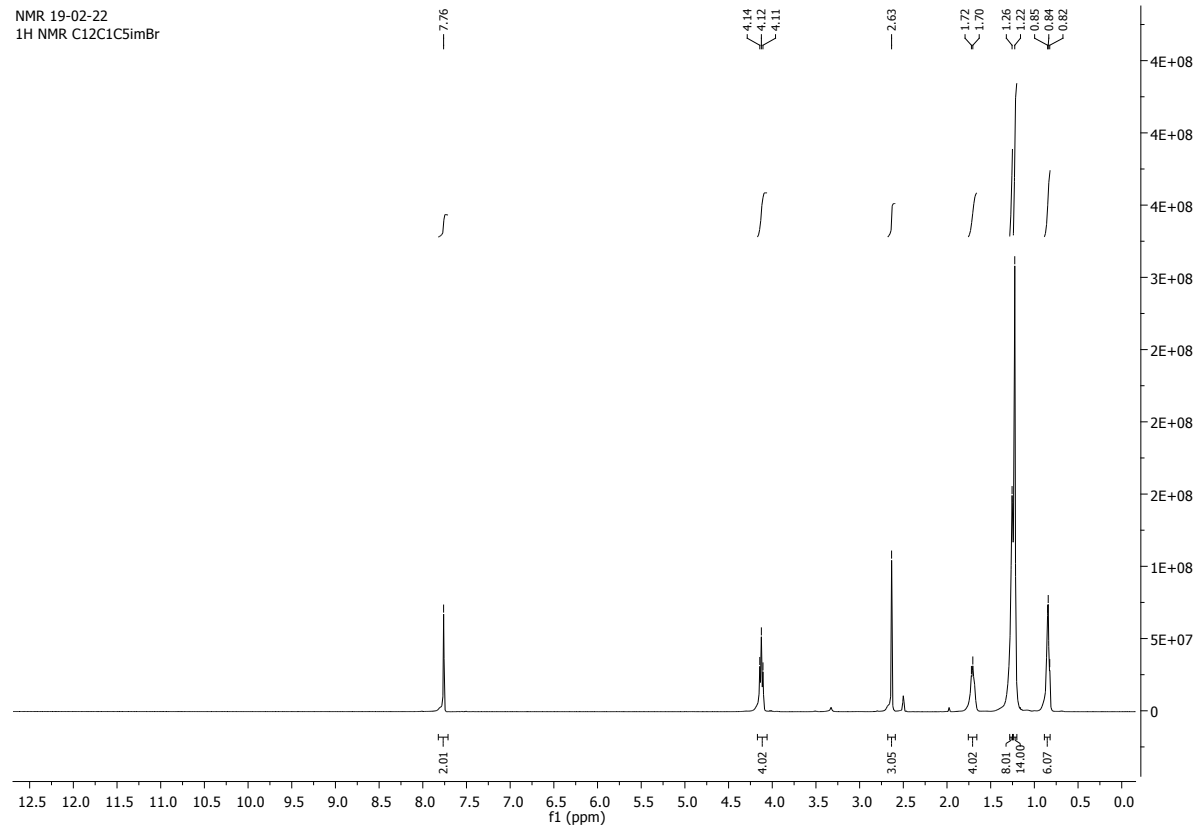

Figure S10: ^{1}H-NMR spectrum (400 MHz, DMSO) of compound $\mathbf{C_{12}C_1C_5}$

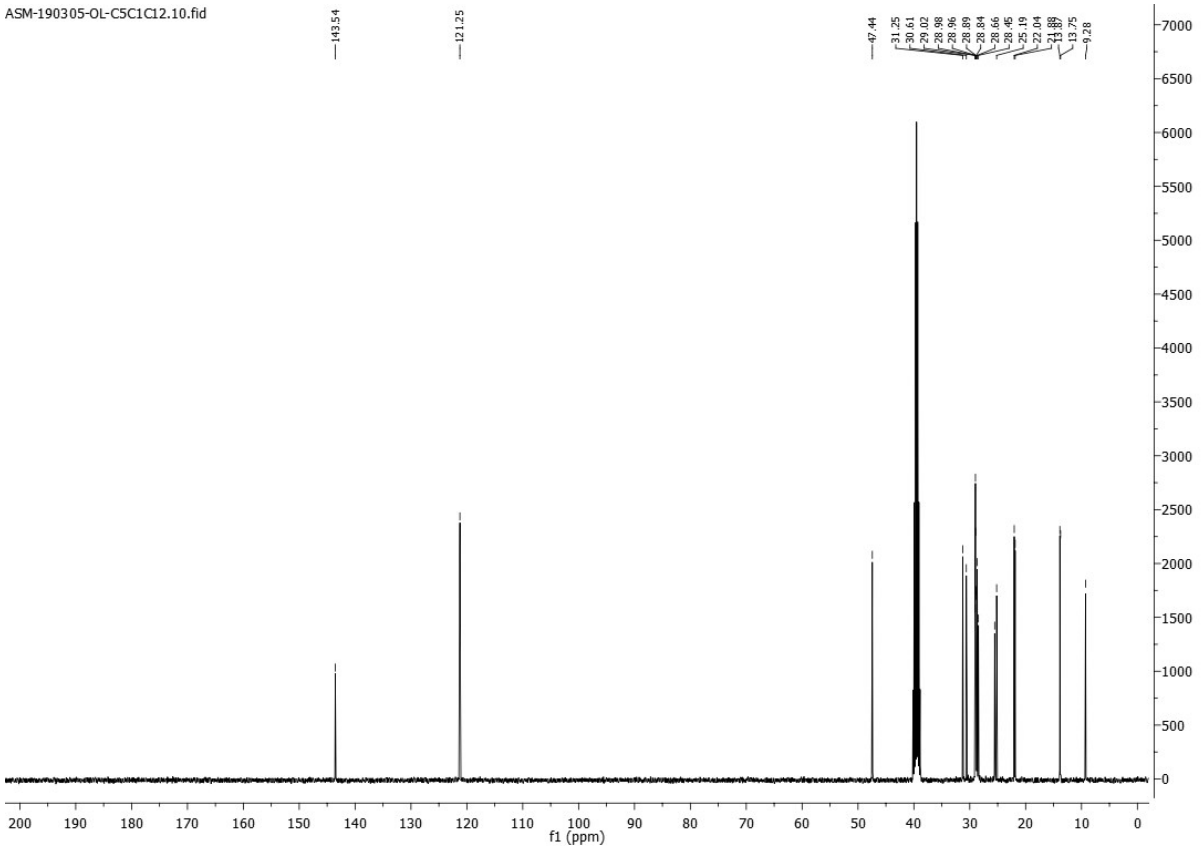

Figure S11: ^{13}C-NMR spectrum (100 MHz, DMSO) of compound $\mathbf{C_{12}C_1C_5}$

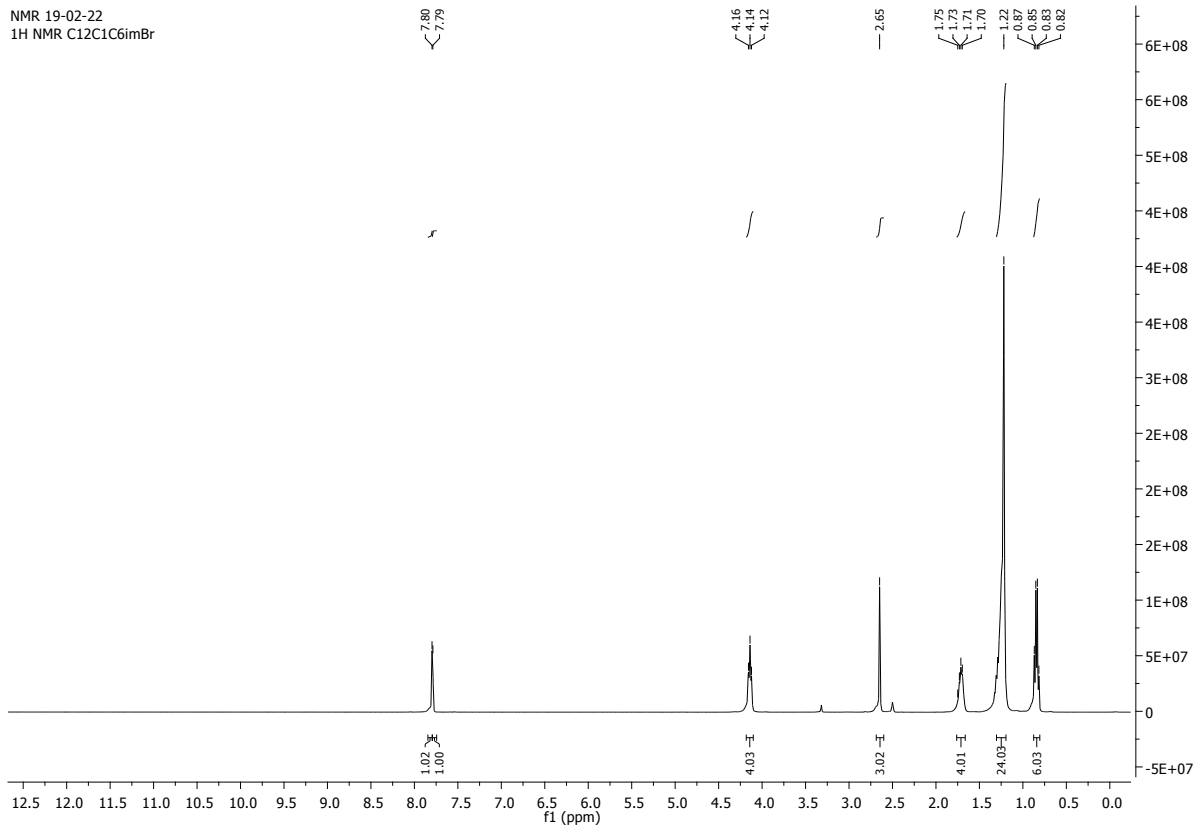

Figure S12: ^{1}H-NMR spectrum (400 MHz, DMSO) of compound $\mathbf{C_{12}C_1C_6}$

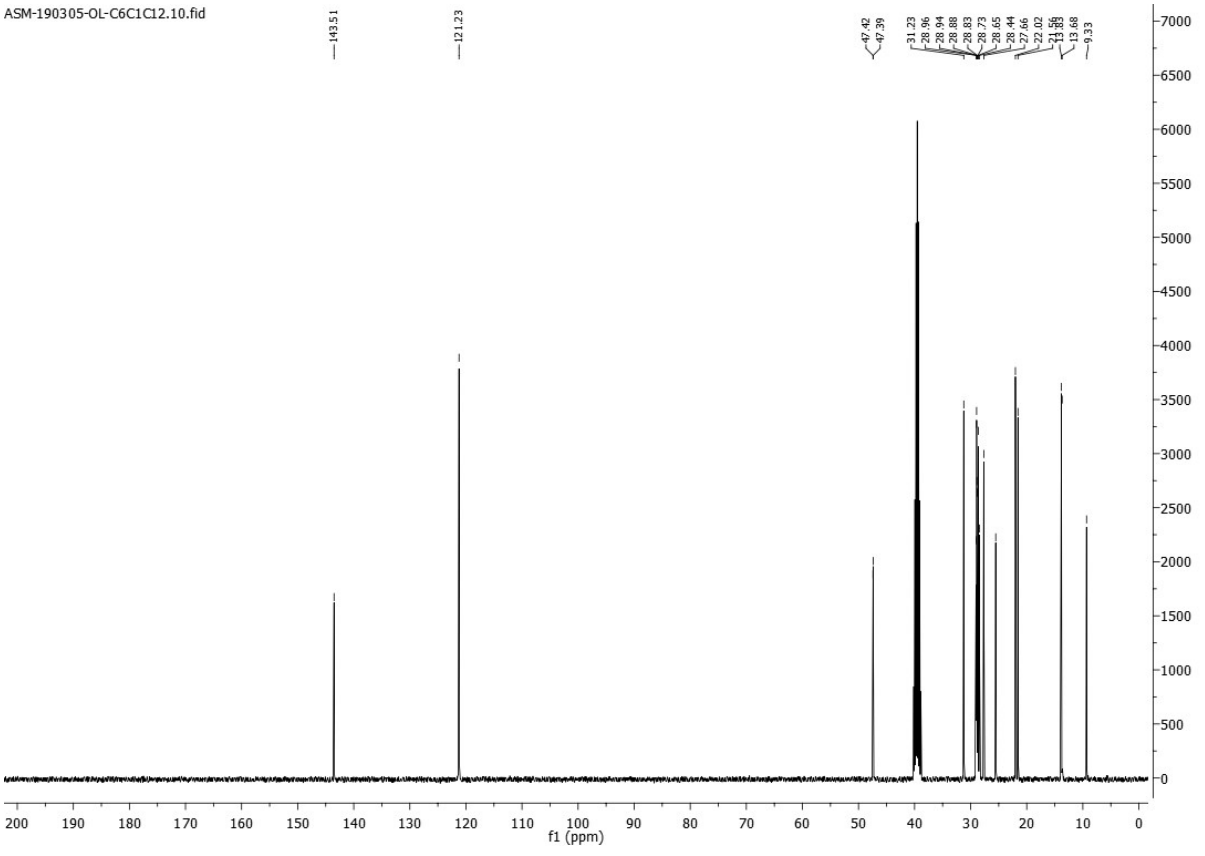

Figure S13: ^{13}C-NMR spectrum (100 MHz, DMSO) of compound $\mathbf{C_{12}C_1C_6}$

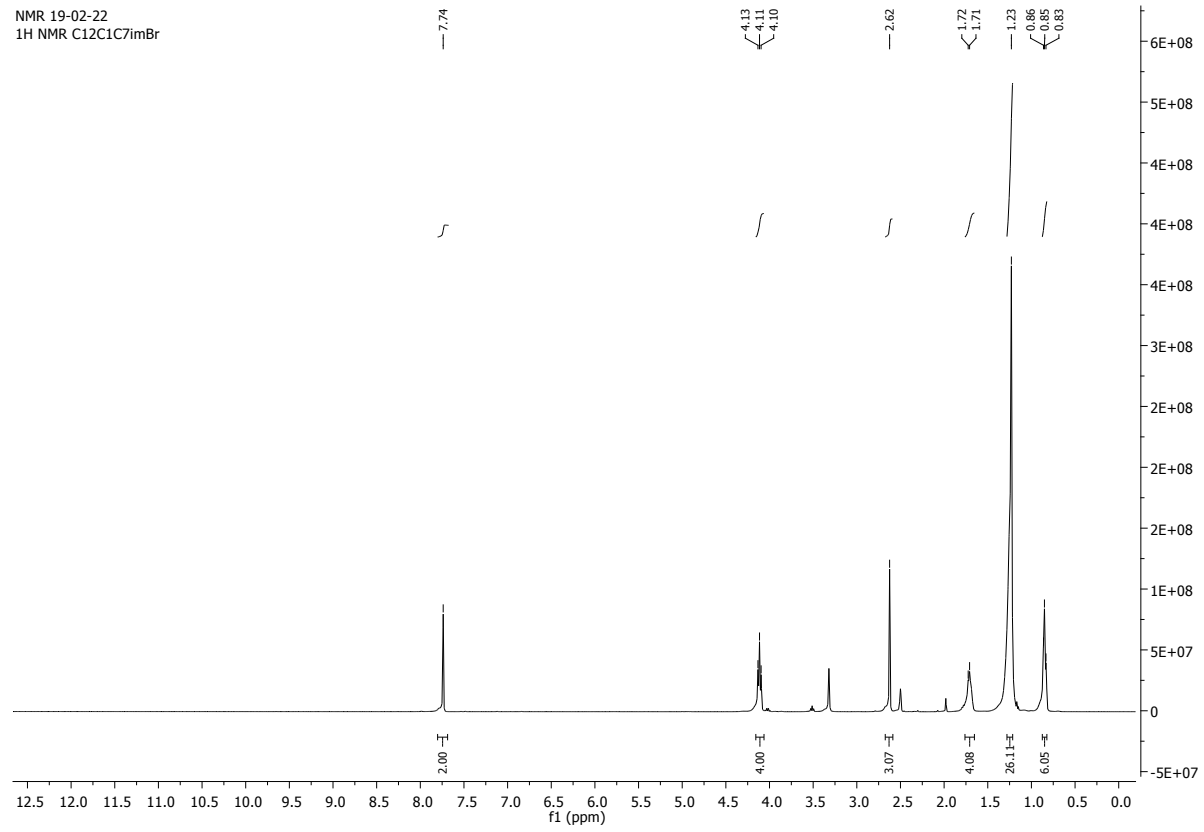

Figure S14: ^{1}H-NMR spectrum (400 MHz, DMSO) of compound $\mathbf{C_{12}C_1C_7}$

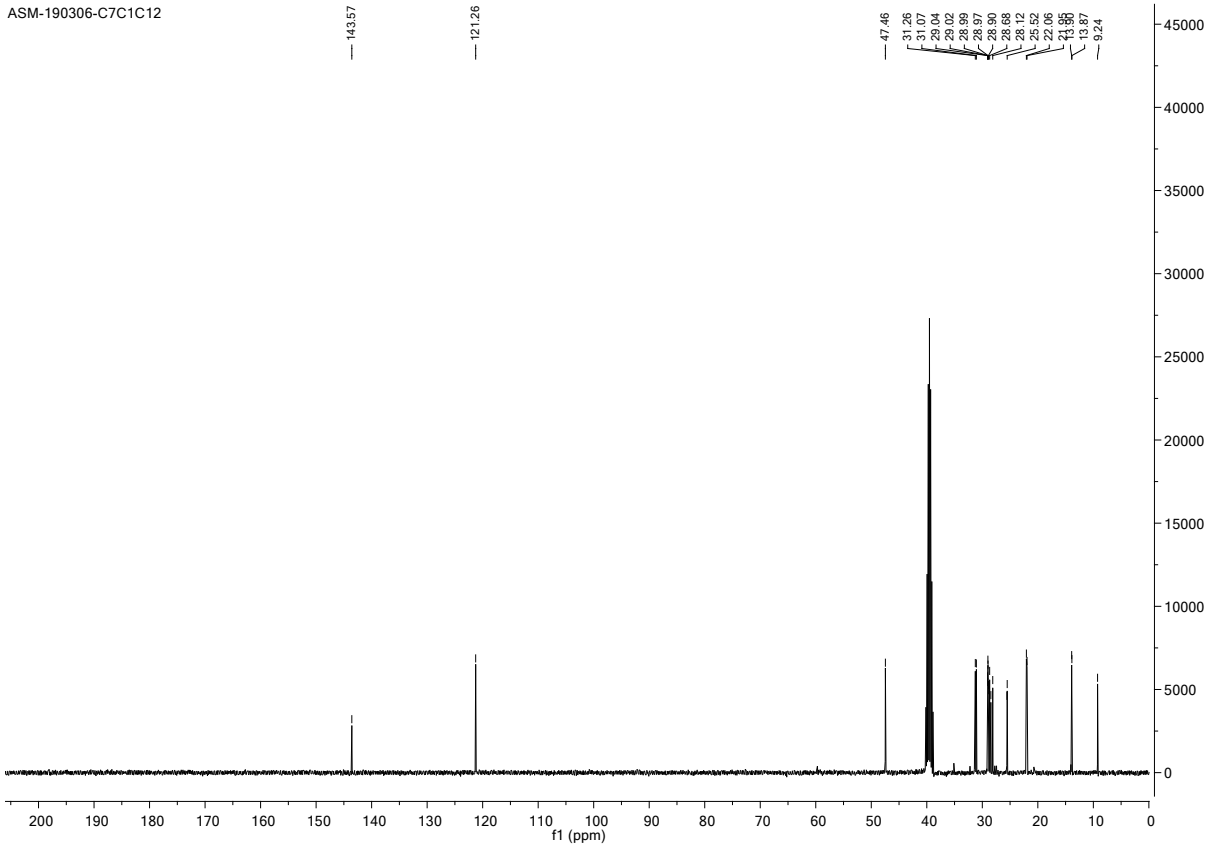

Figure S15: ^{13}C-NMR spectrum (100 MHz, DMSO) of compound $\mathbf{C_{12}C_1C_7}$

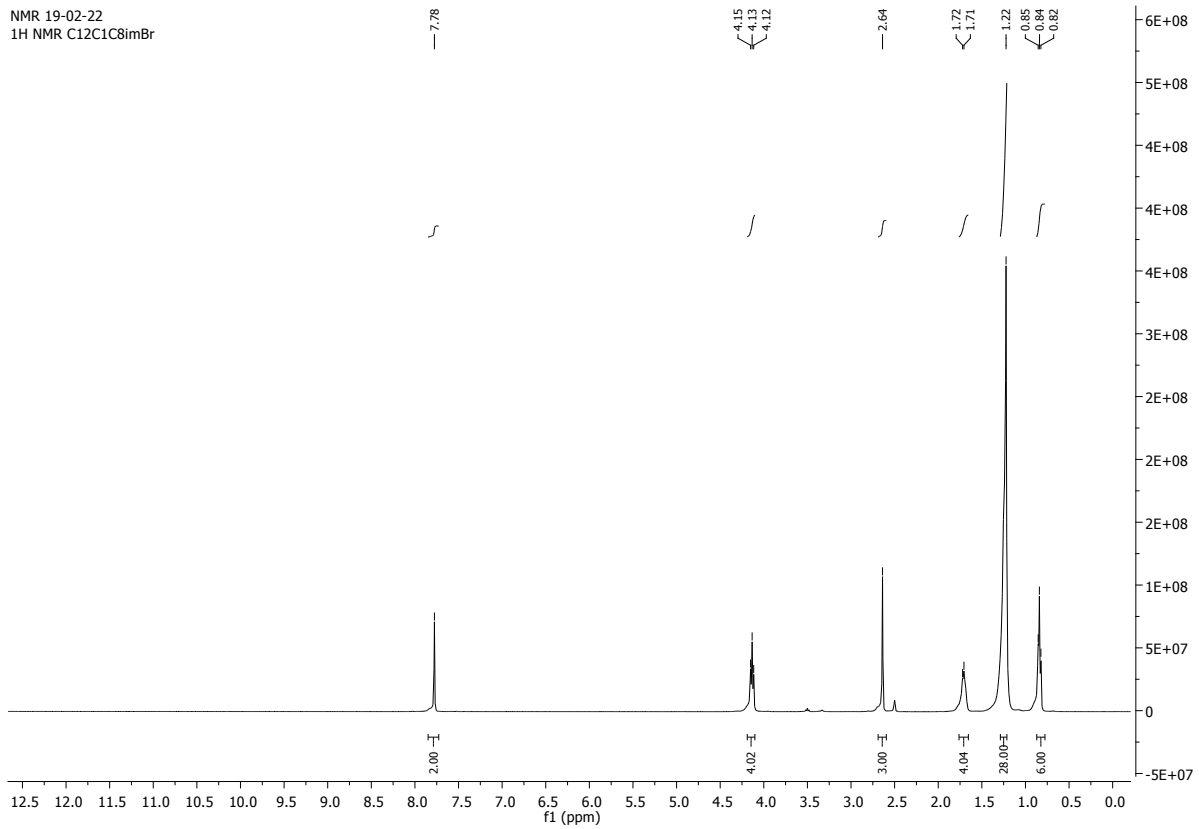

Figure S16: ^{1}H-NMR spectrum (400 MHz, DMSO) of compound $\mathbf{C_{12}C_1C_8}$

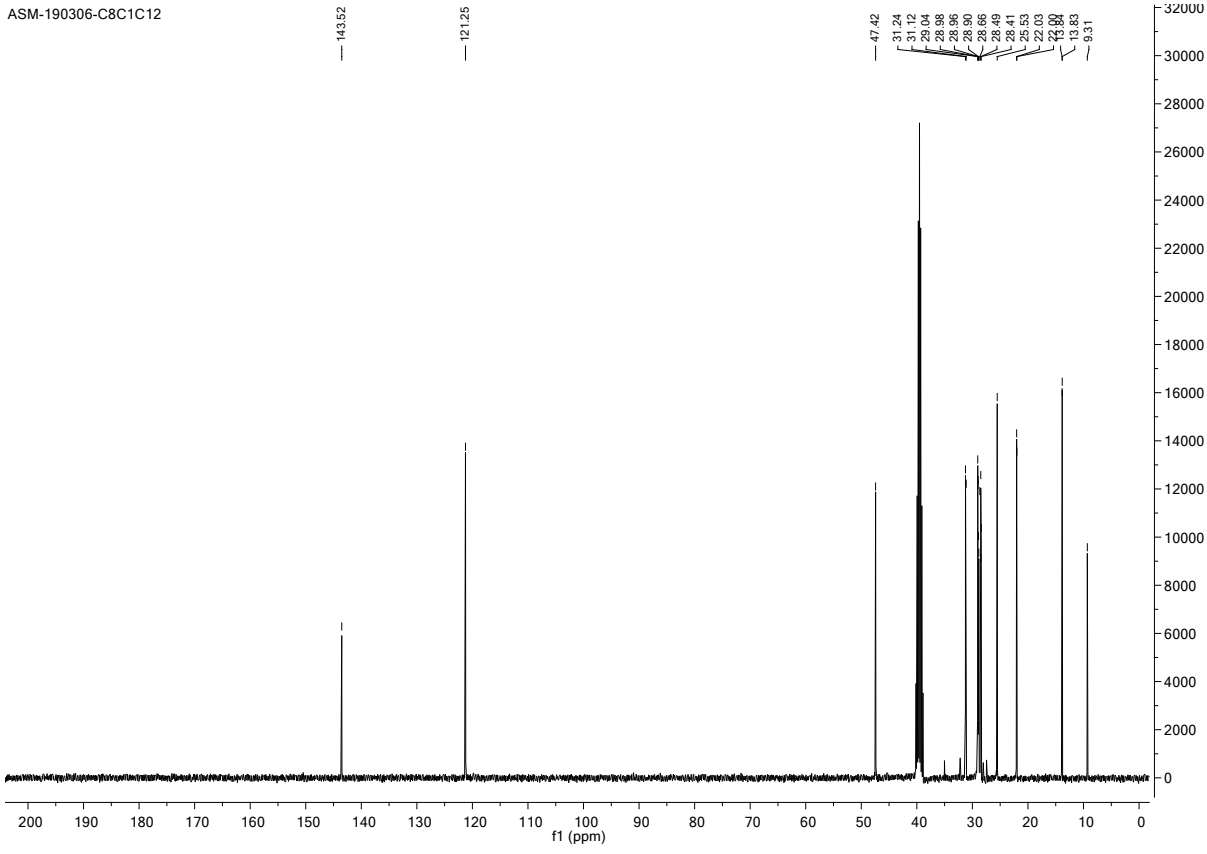

Figure S17: ^{13}C-NMR spectrum (100 MHz, DMSO) of compound $\mathbf{C_{12}C_1C_8}$

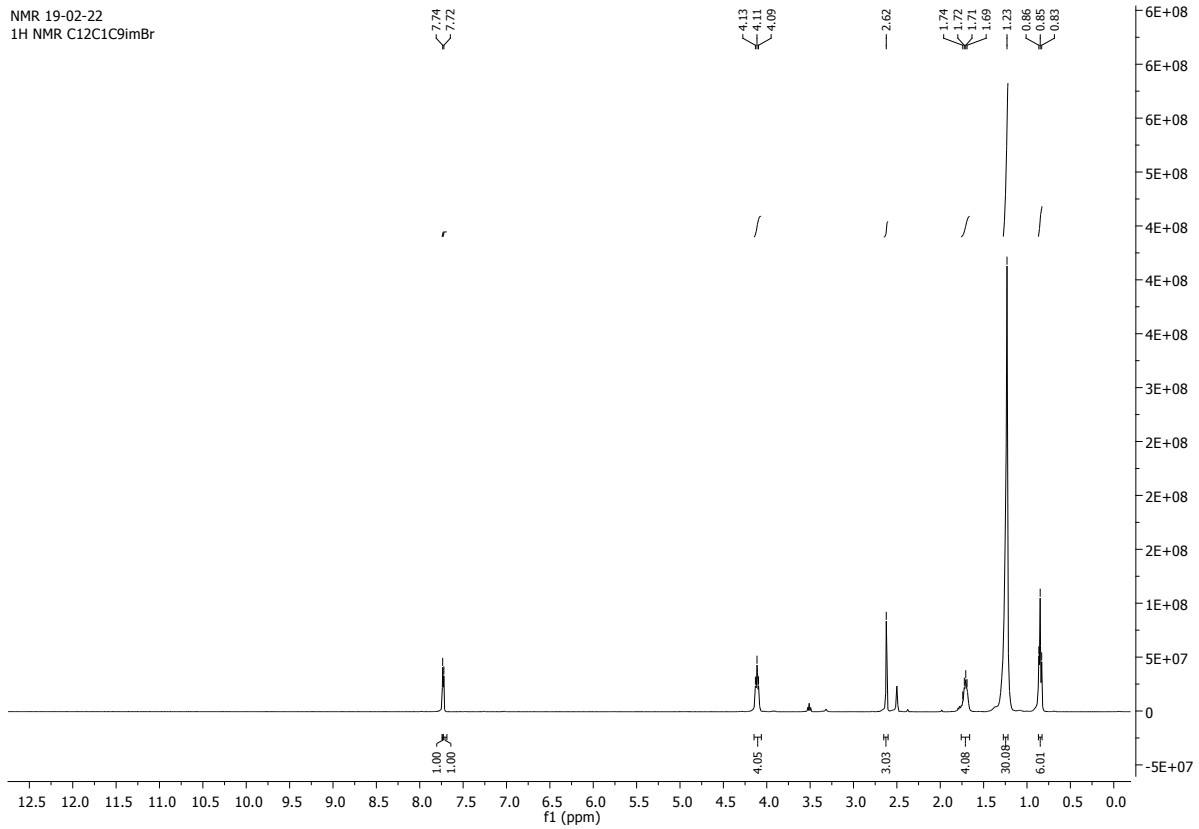

Figure S18: ^{1}H-NMR spectrum (400 MHz, DMSO) of compound $\mathbf{C_{12}C_1C_9}$

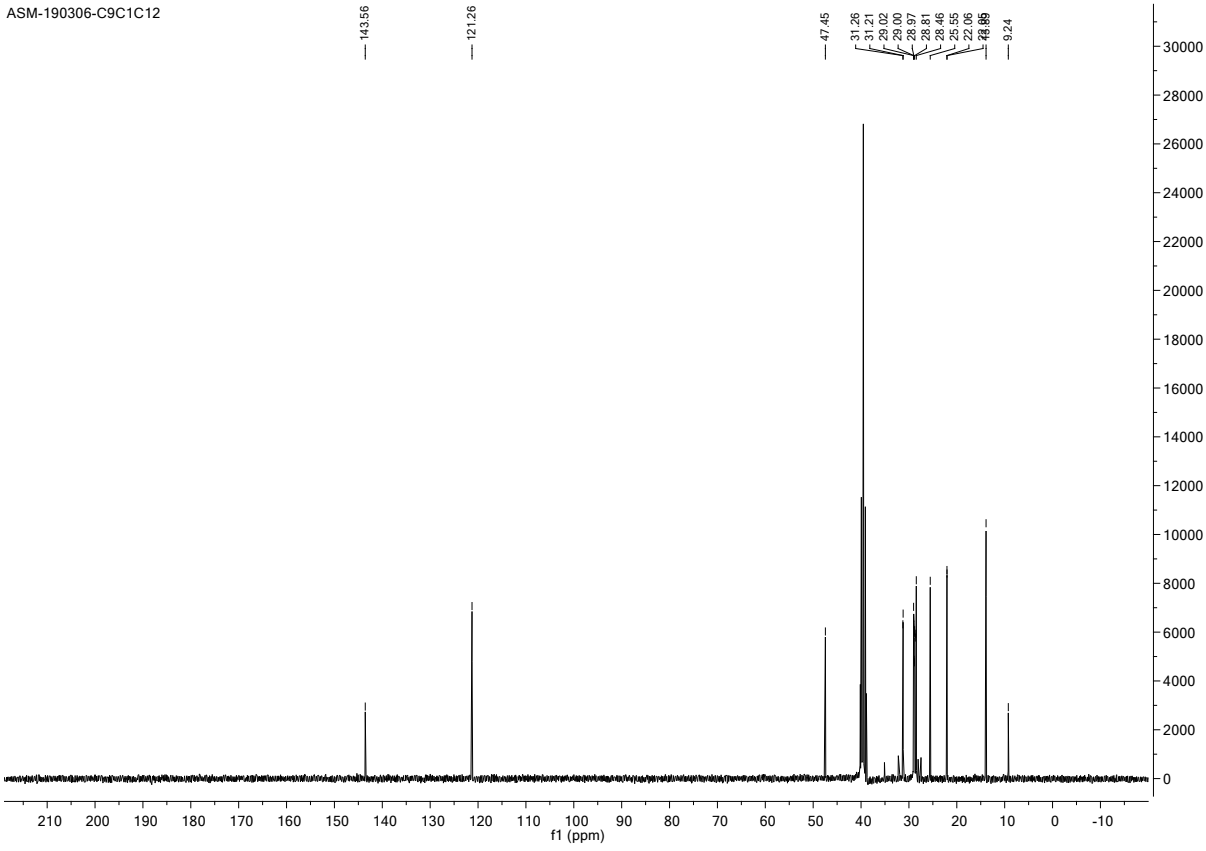

Figure S19: ^{13}C-NMR spectrum (100 MHz, DMSO) of compound $\mathbf{C_{12}C_1C_9}$

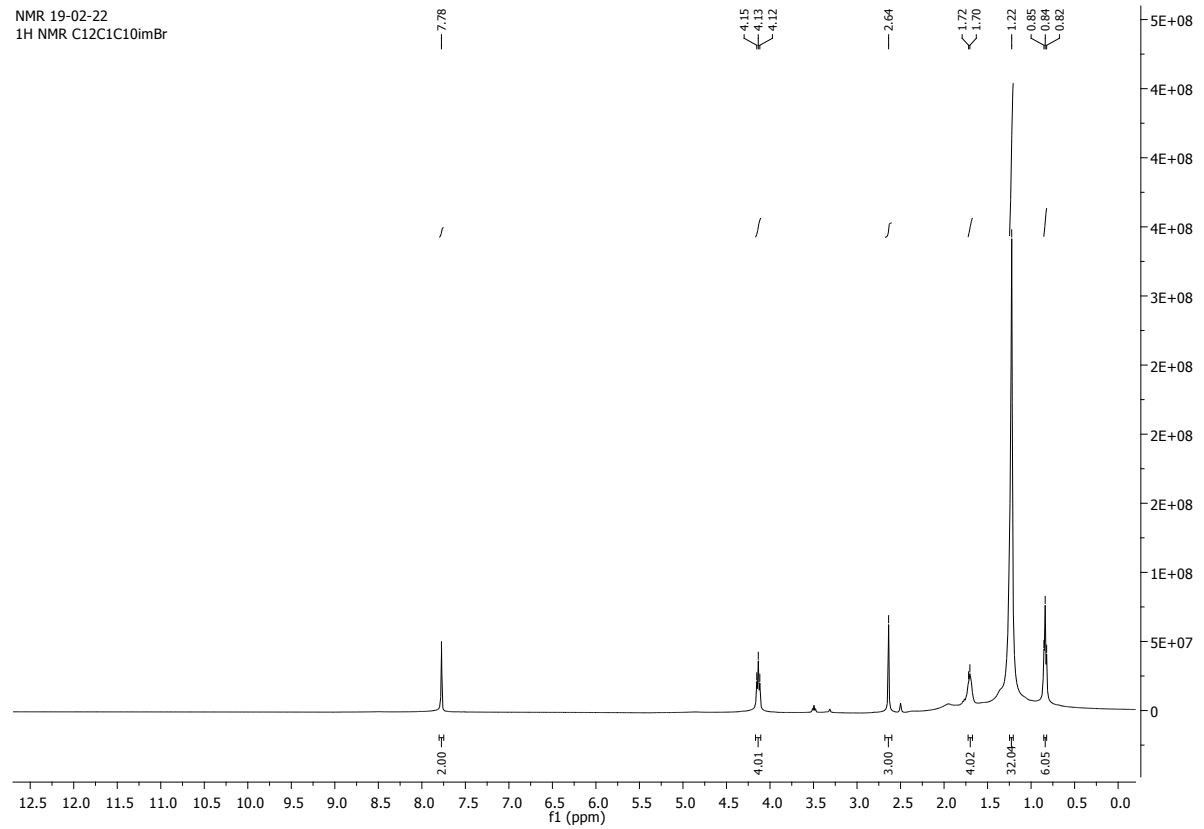

Figure S20: ^{1}H-NMR spectrum (400 MHz, DMSO) of compound $\mathbf{C_{12}C_1C_{10}}$

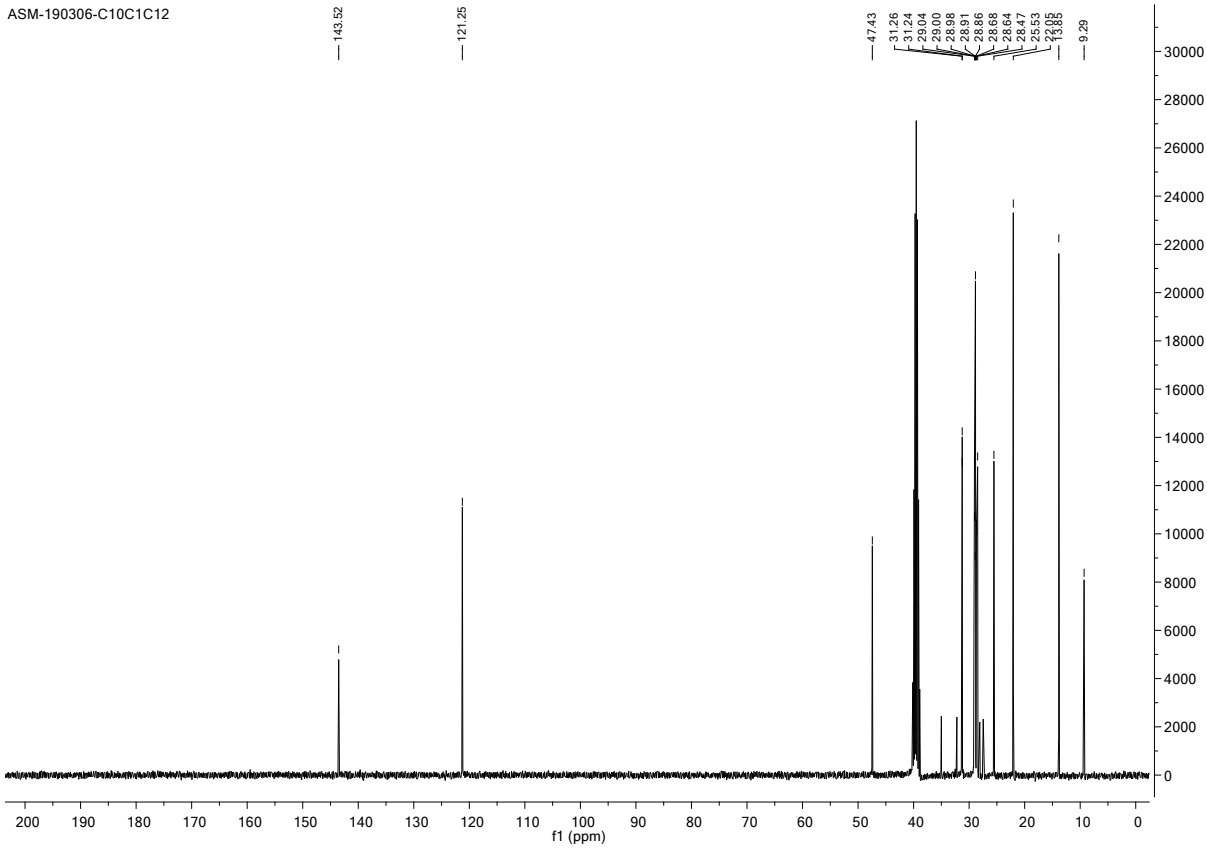

Figure S21: ^{13}C-NMR spectrum (100 MHz, DMSO) of compound $\mathbf{C_{12}C_1C_{10}}$

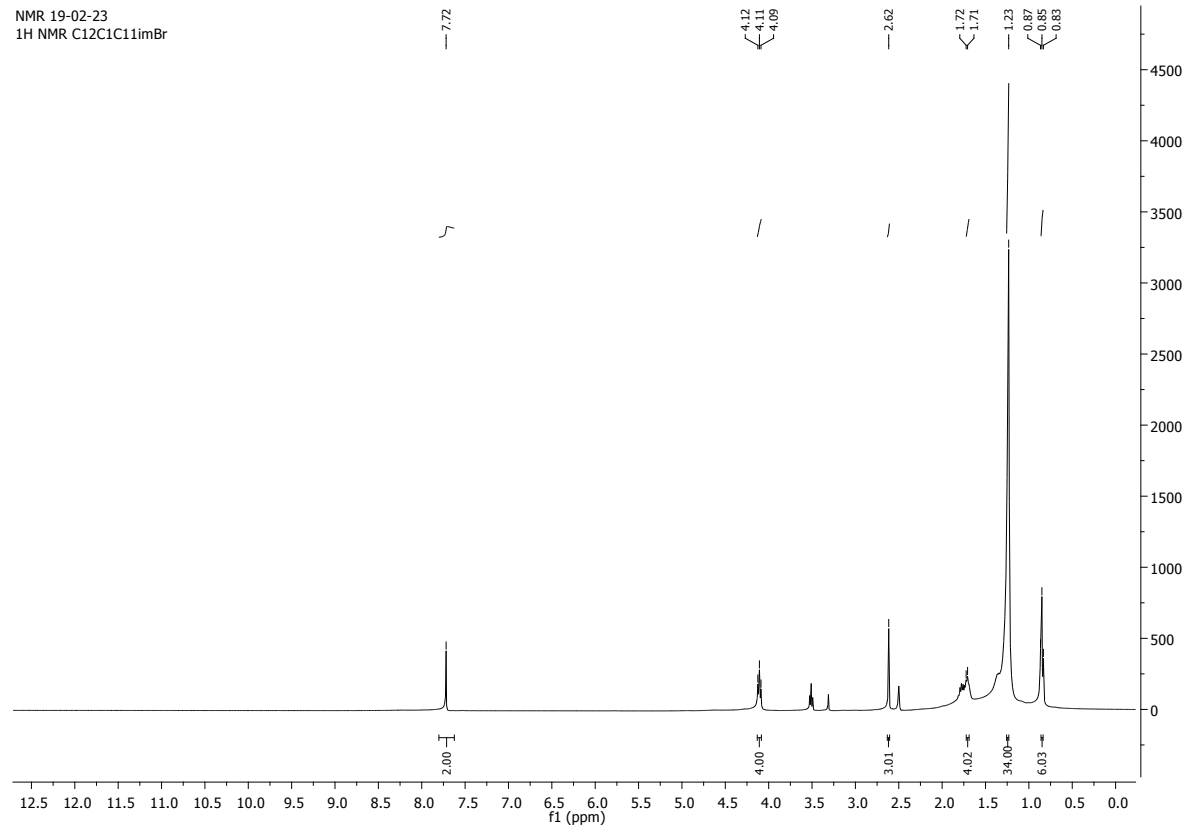

Figure S22: ^{1}H-NMR spectrum (400 MHz, DMSO) of compound $\mathbf{C_{12}C_1C_{11}}$

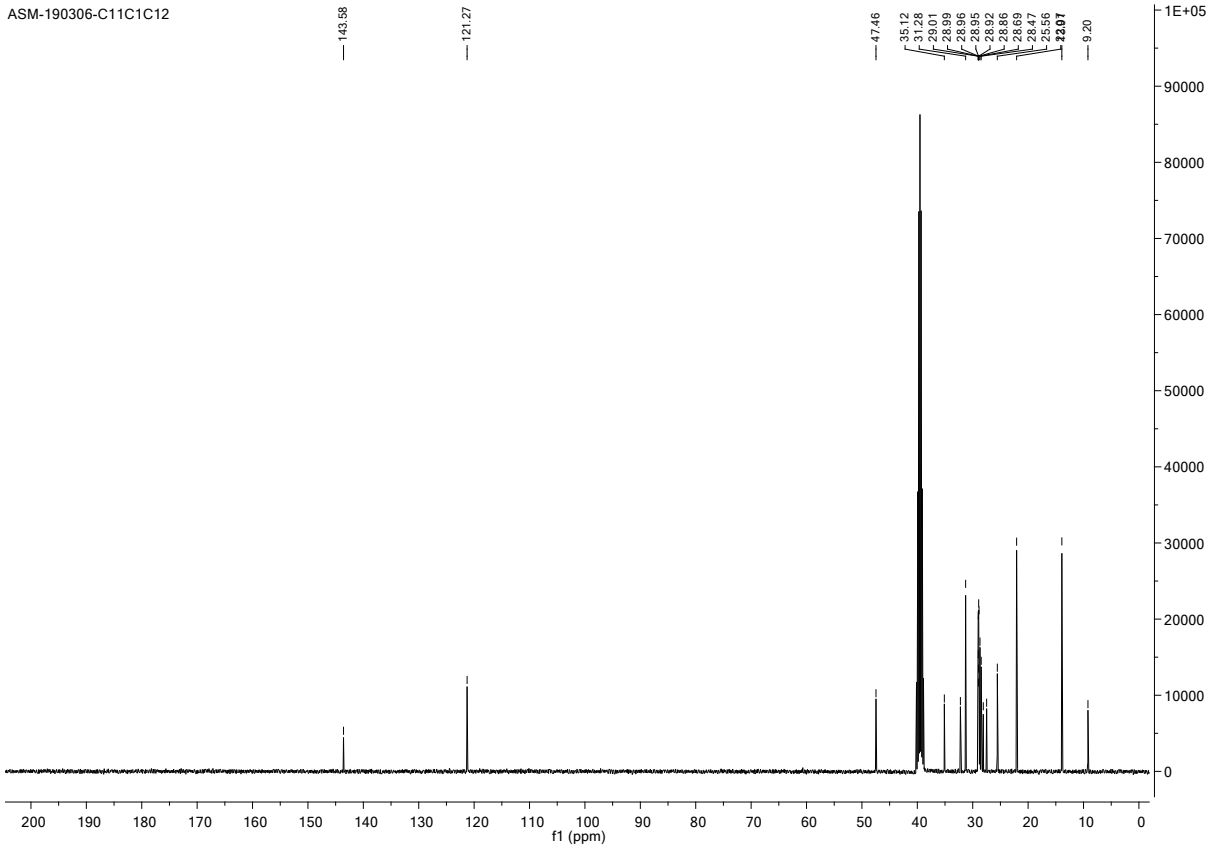

Figure S23: ^{13}C-NMR spectrum (100 MHz, DMSO) of compound $\mathbf{C_{12}C_1C_{11}}$

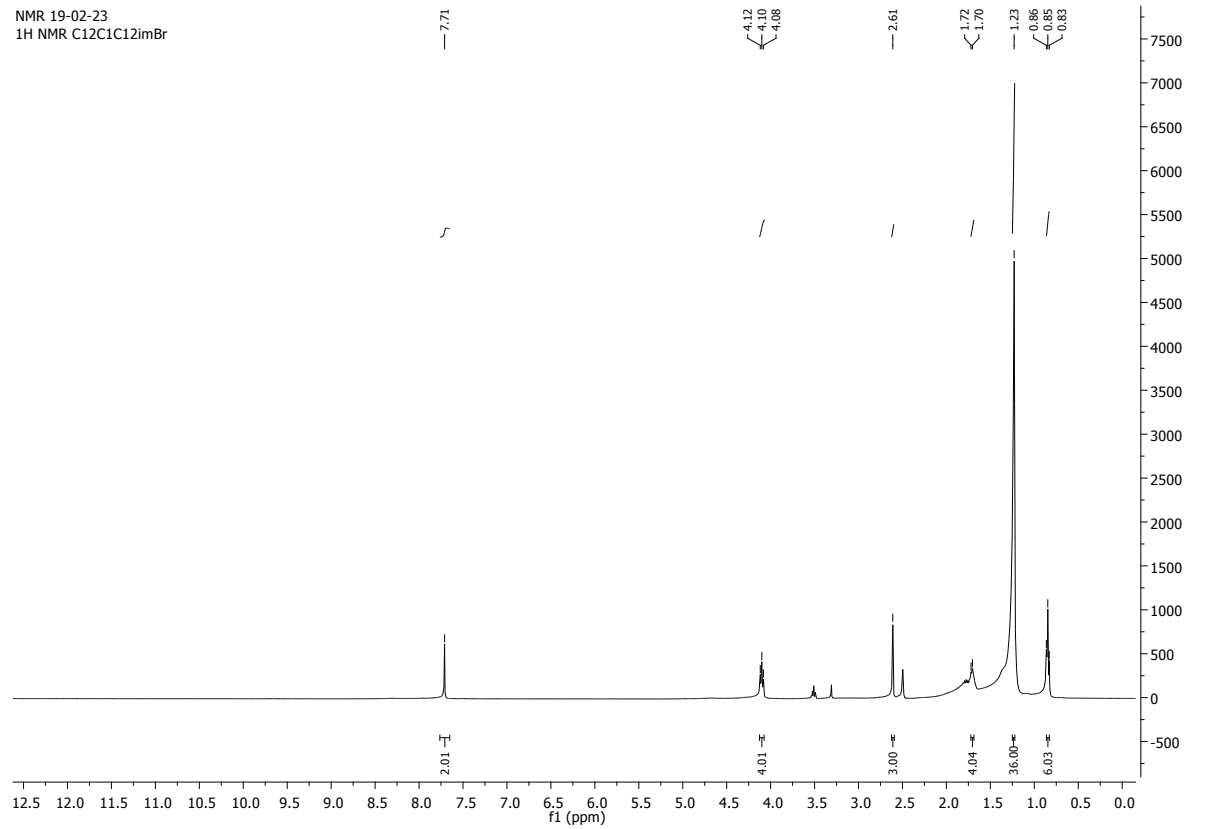

Figure S24: ^{1}H-NMR spectrum (400 MHz, DMSO) of compound $\mathbf{C_{12}C_1C_{12}}$

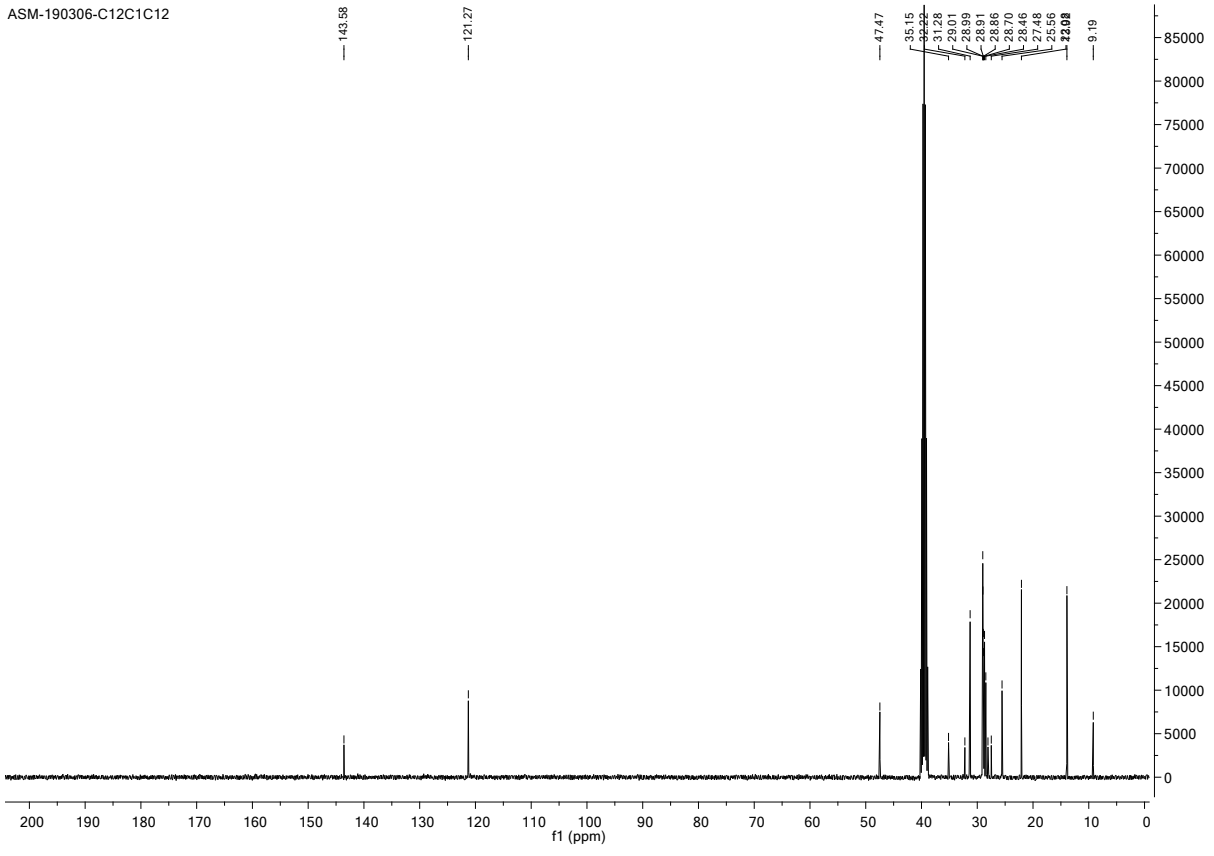

Figure S25: ^{13}C-NMR spectrum (100 MHz, DMSO) of compound $\mathbf{C_{12}C_1C_{12}}$

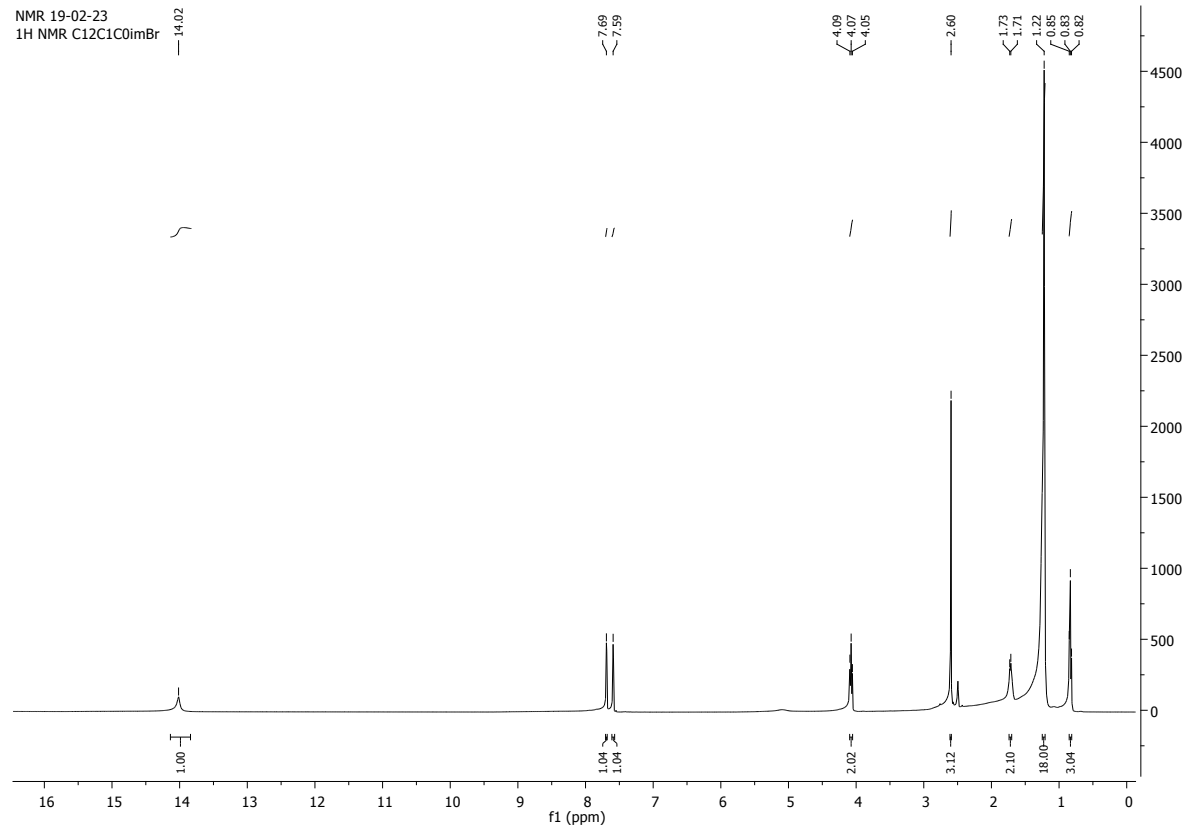

Figure S26: ^{1}H-NMR spectrum (400 MHz, DMSO) of compound $\mathbf{C_{12}C_1C_0}$

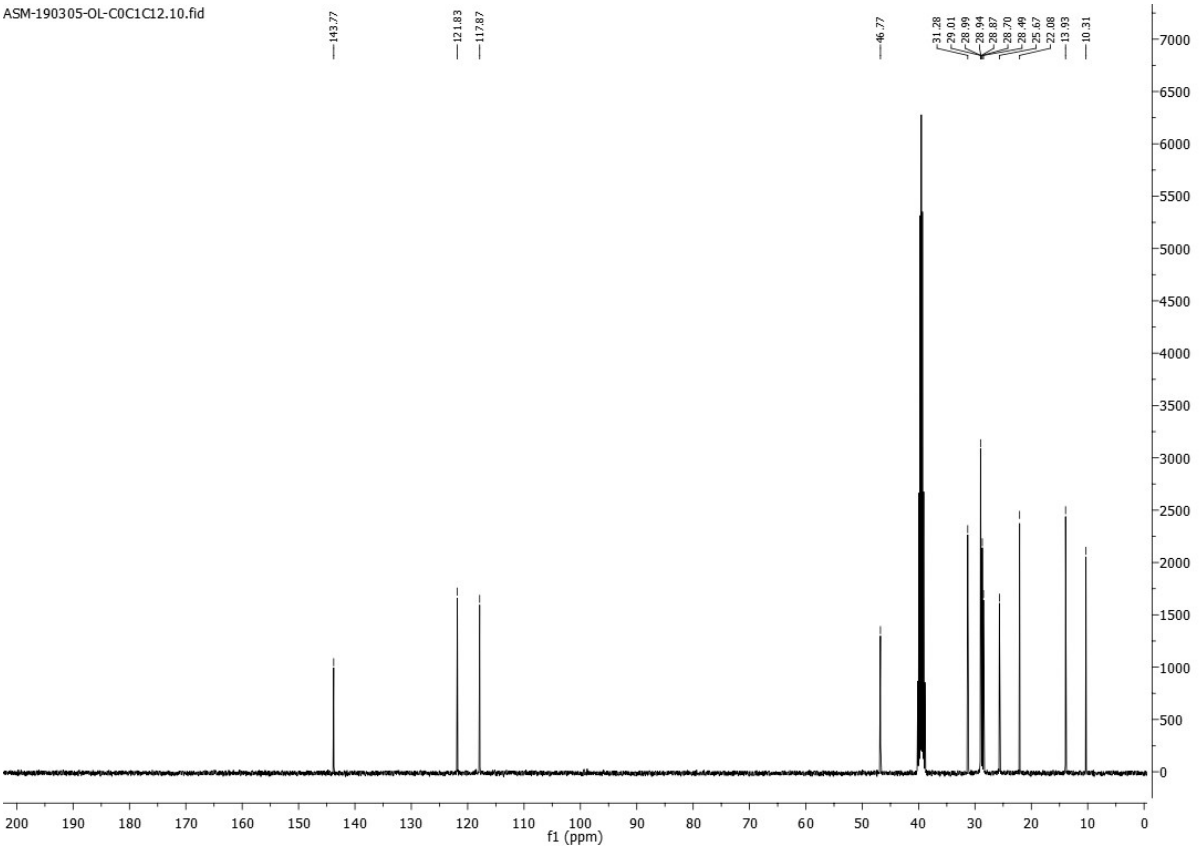

Figure S27: ^{13}C-NMR spectrum (100 MHz, DMSO) of compound $\mathbf{C_{12}C_1C_0}$

IV. Infrared Spectra

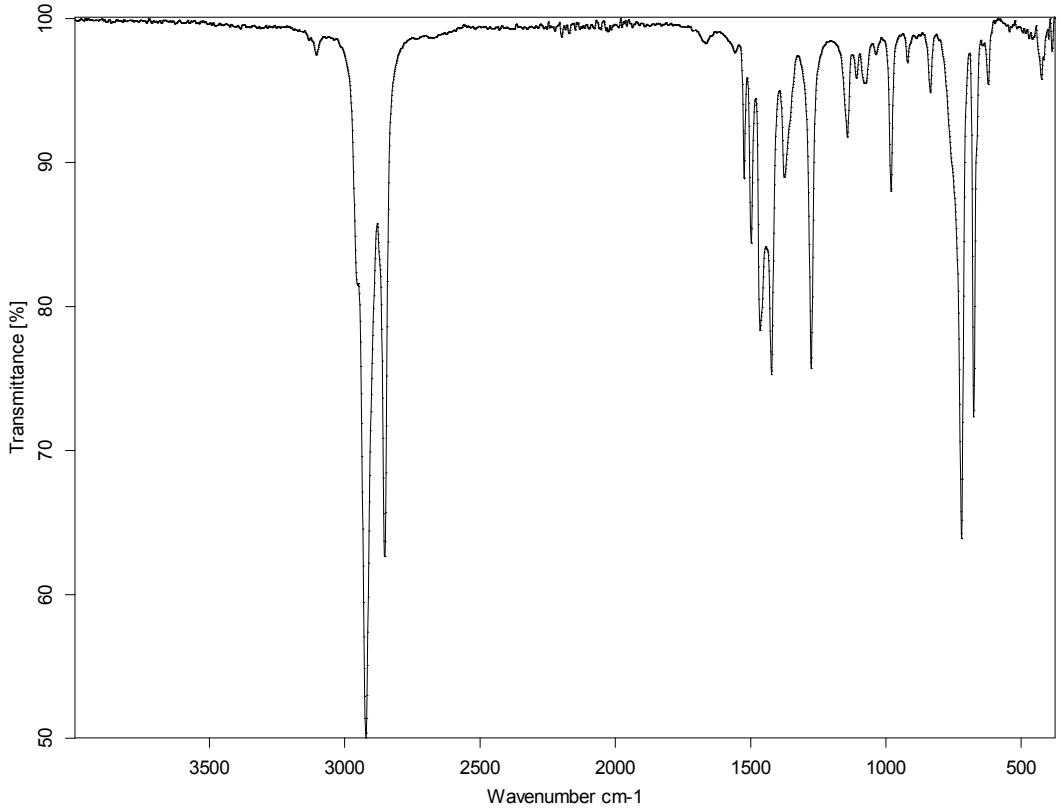

Figure S28: Infrared spectrum of 1-dodecyl-2-methylimidazole ($C_{12}C_1$im)

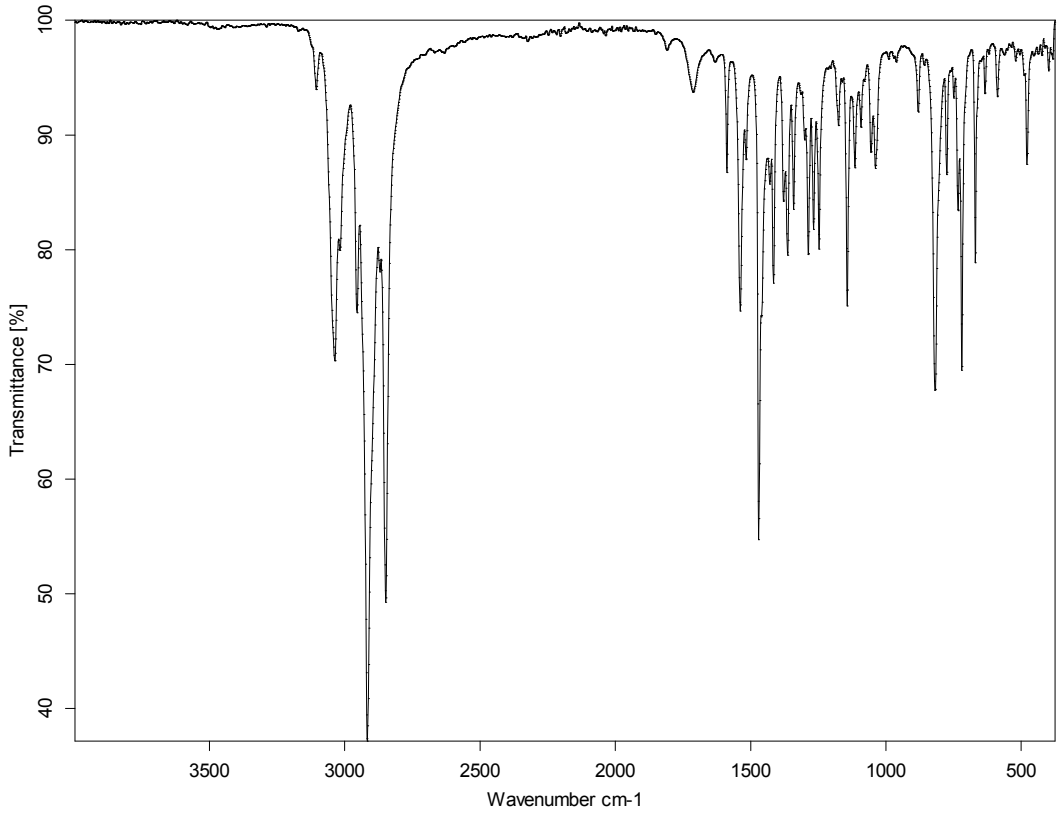

Figure S29: Infrared spectrum of compound **$C_{12}C_1C_1$**

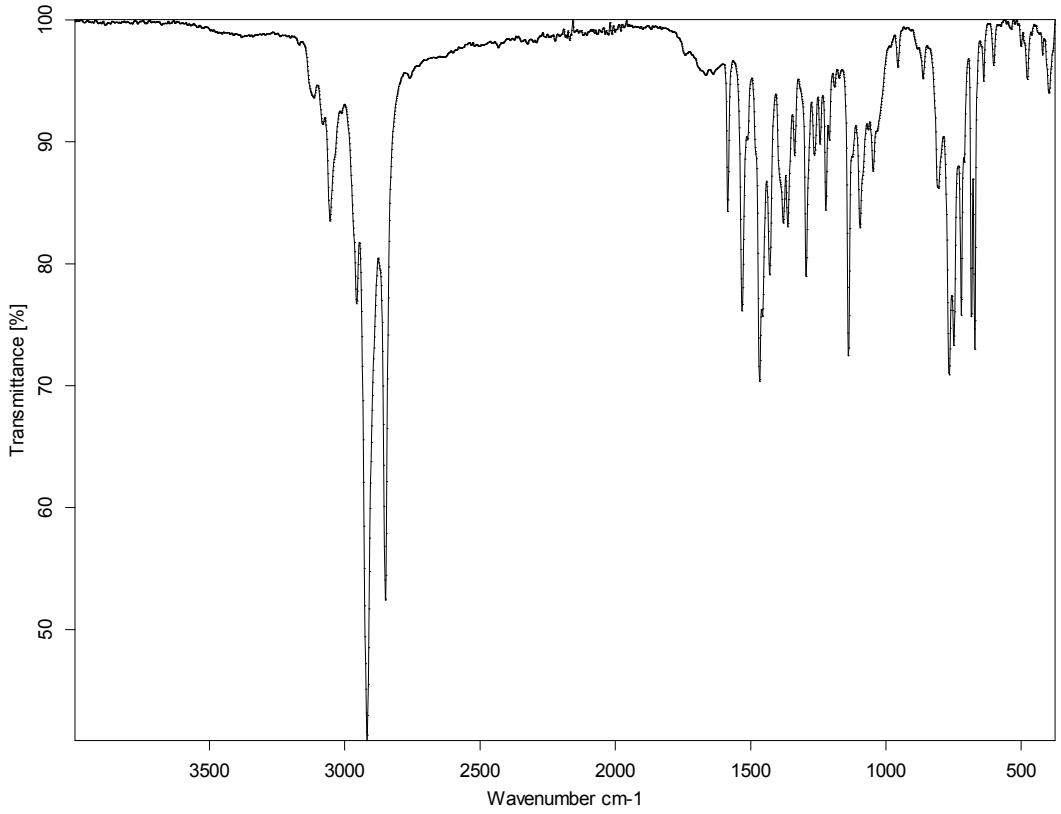

Figure S30: Infrared spectrum of compound $\mathbf{C_{12}C_1C_2}$

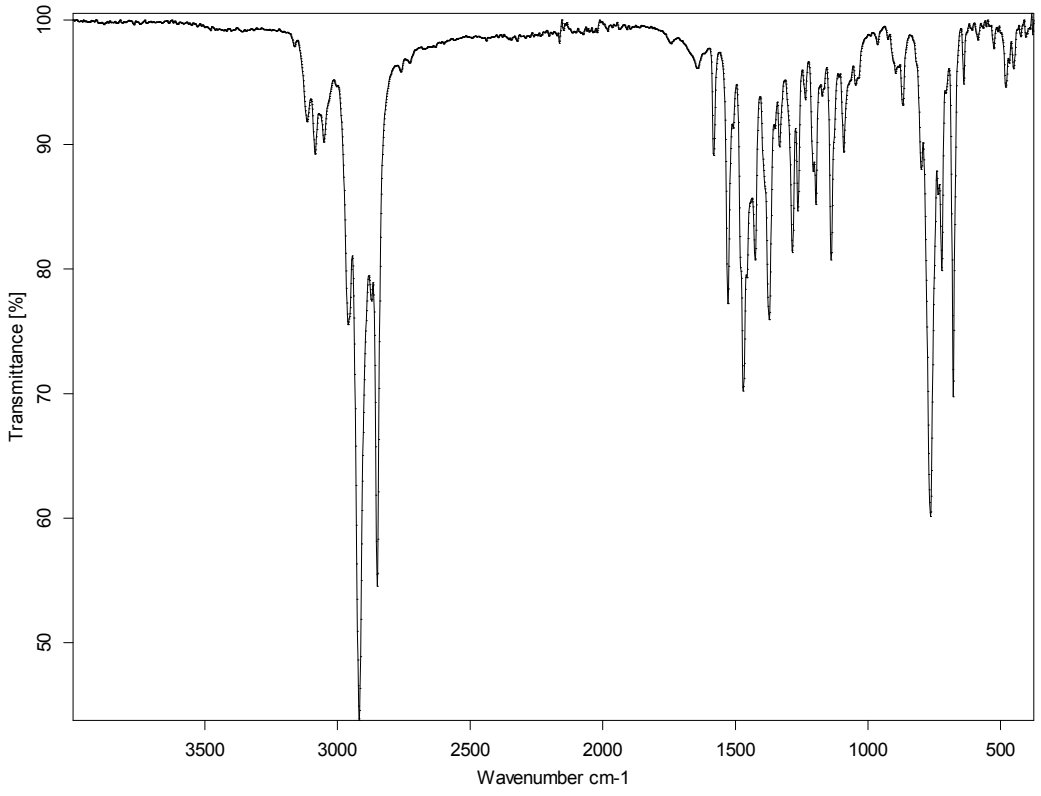

Figure S31:Infrared spectrum of compound $C_{12}C_1C_3$

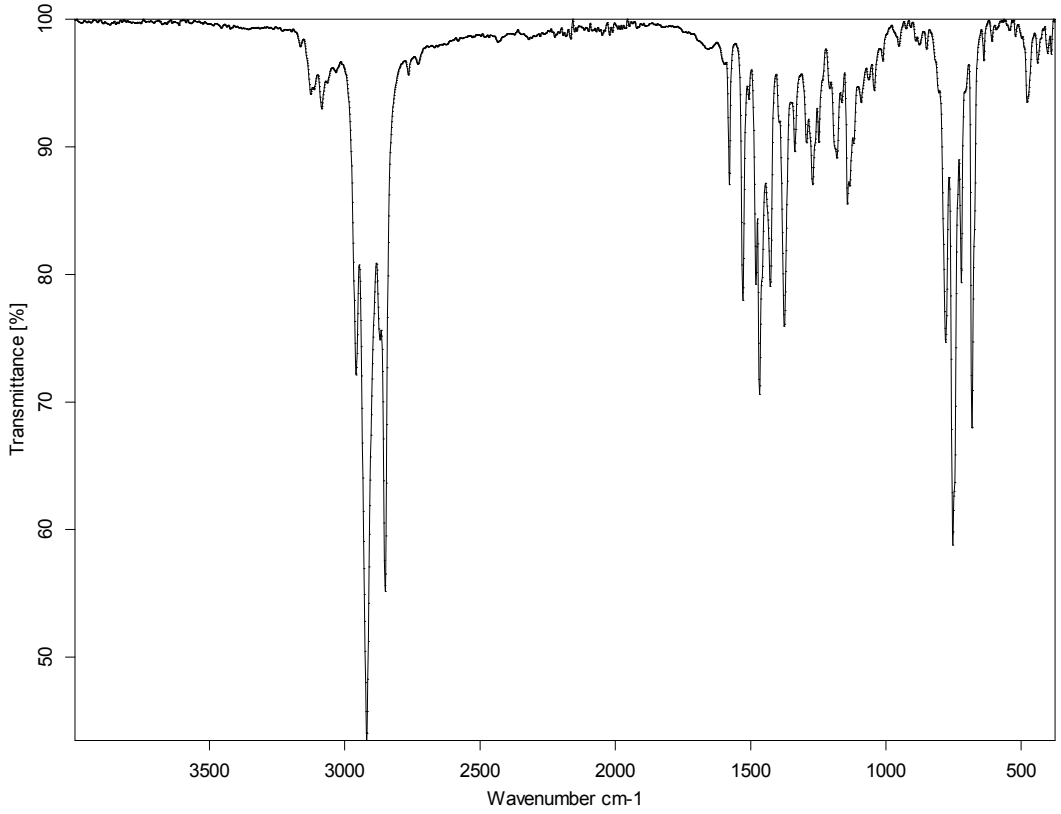

Figure S32: Infrared spectrum of compound $C_{12}C_1C_4$

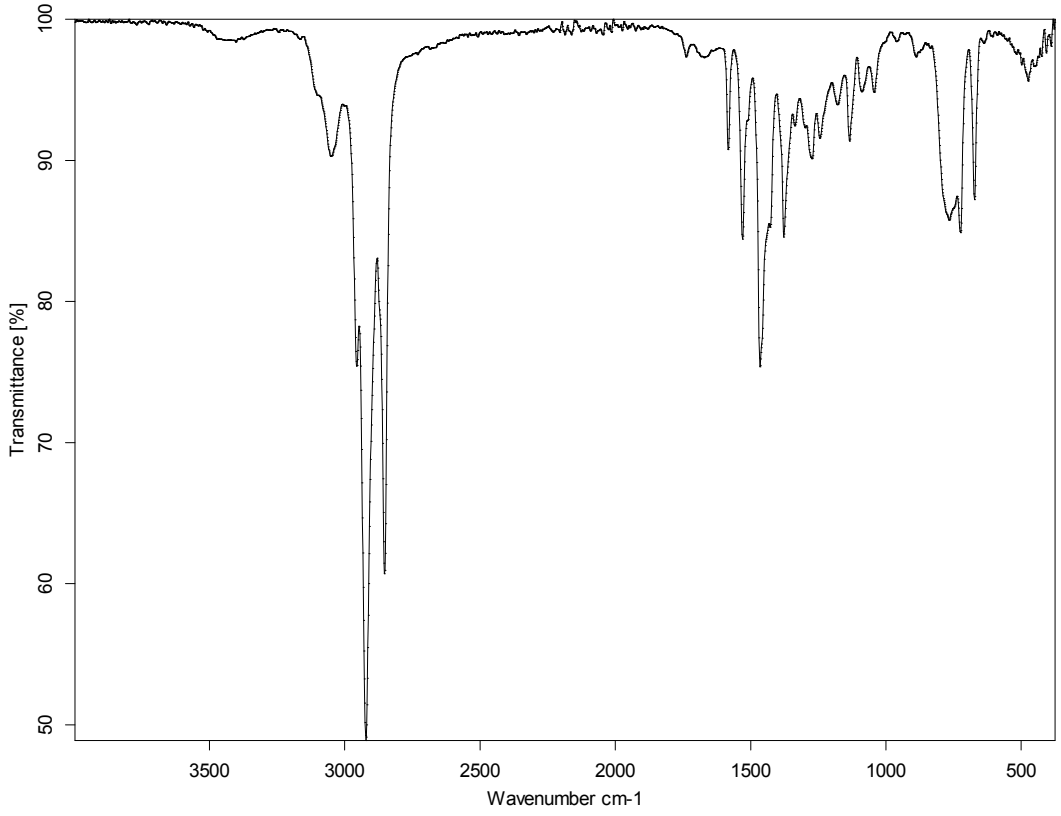

Figure S33: Infrared spectrum of compound $\mathbf{C_{12}C_1C_5}$

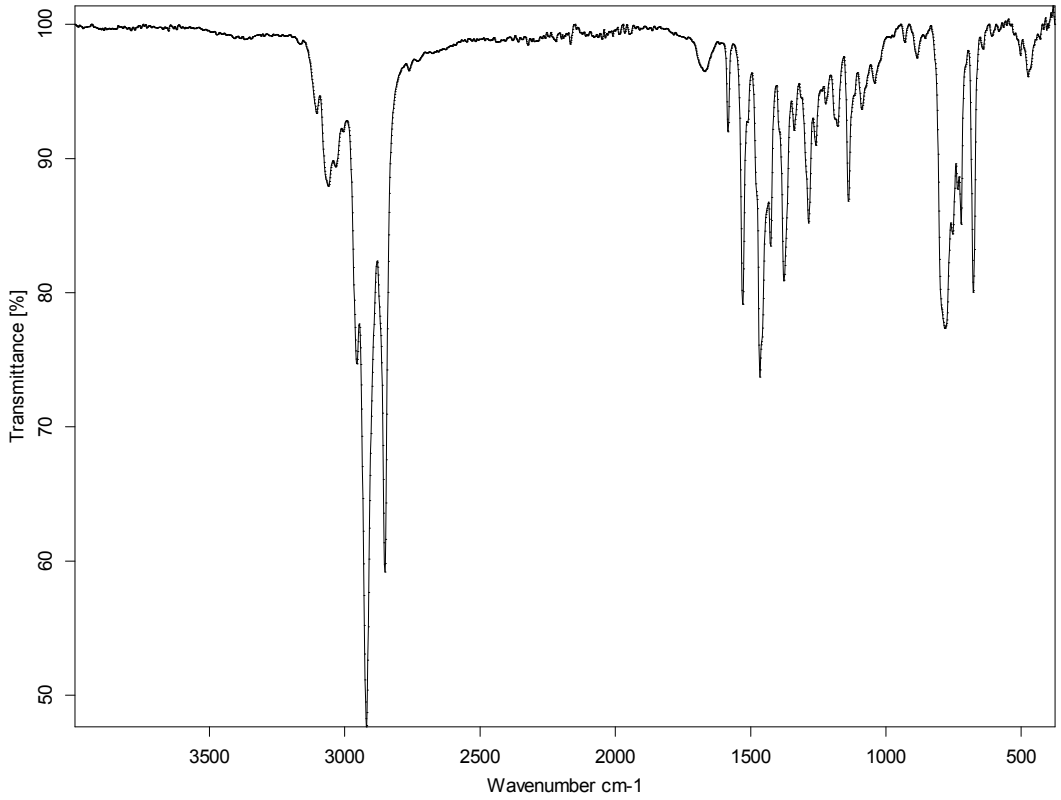

Figure S34: Infrared spectrum of compound $\mathbf{C_{12}C_1C_6}$

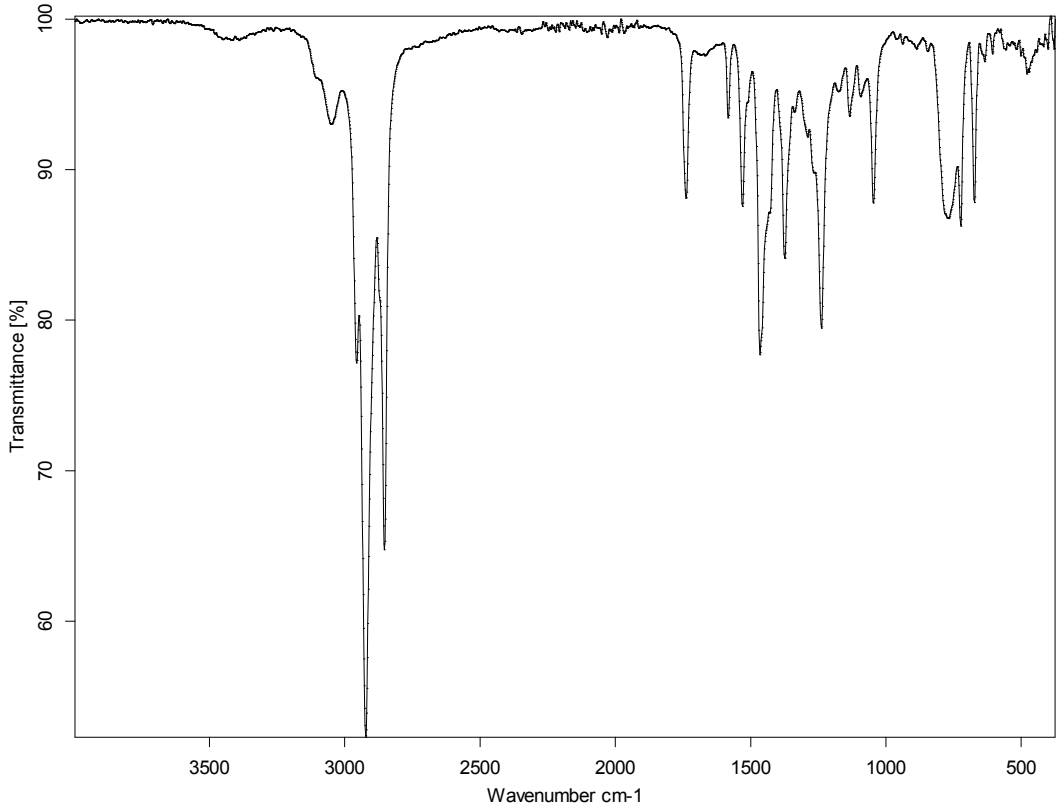

Figure S35: Infrared spectrum of compound $\mathbf{C_{12}C_1C_7}$

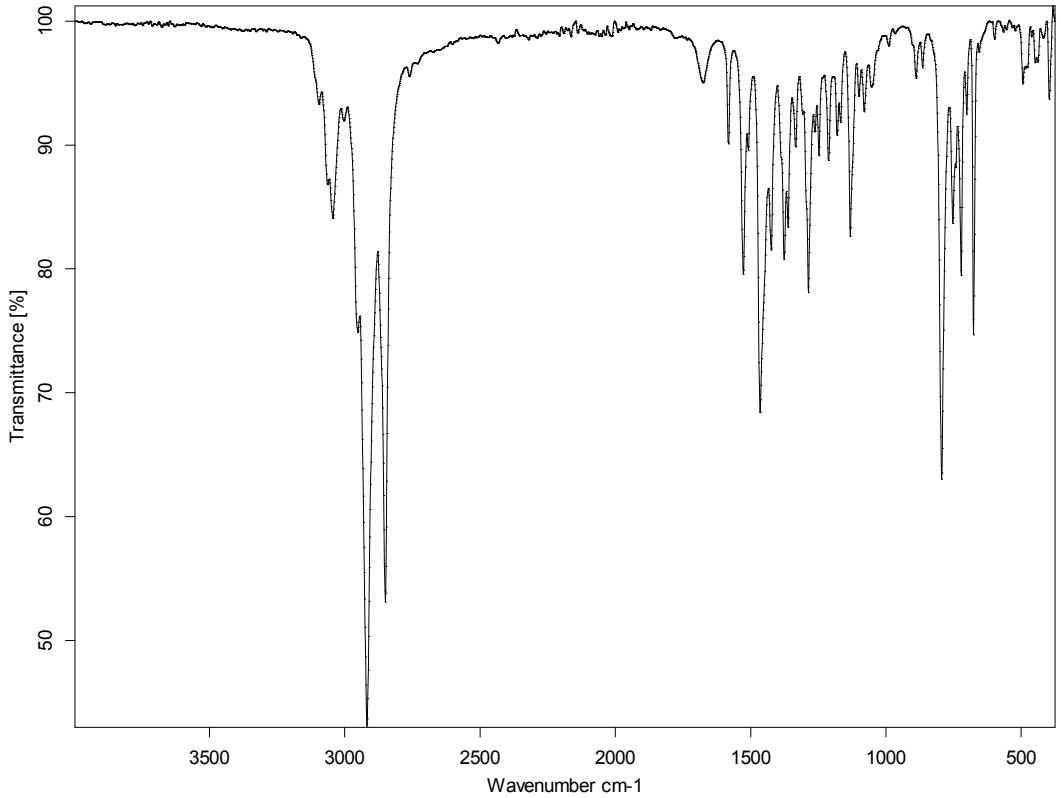

Figure S36: Infrared spectrum of compound $\mathbf{C_{12}C_1C_8}$

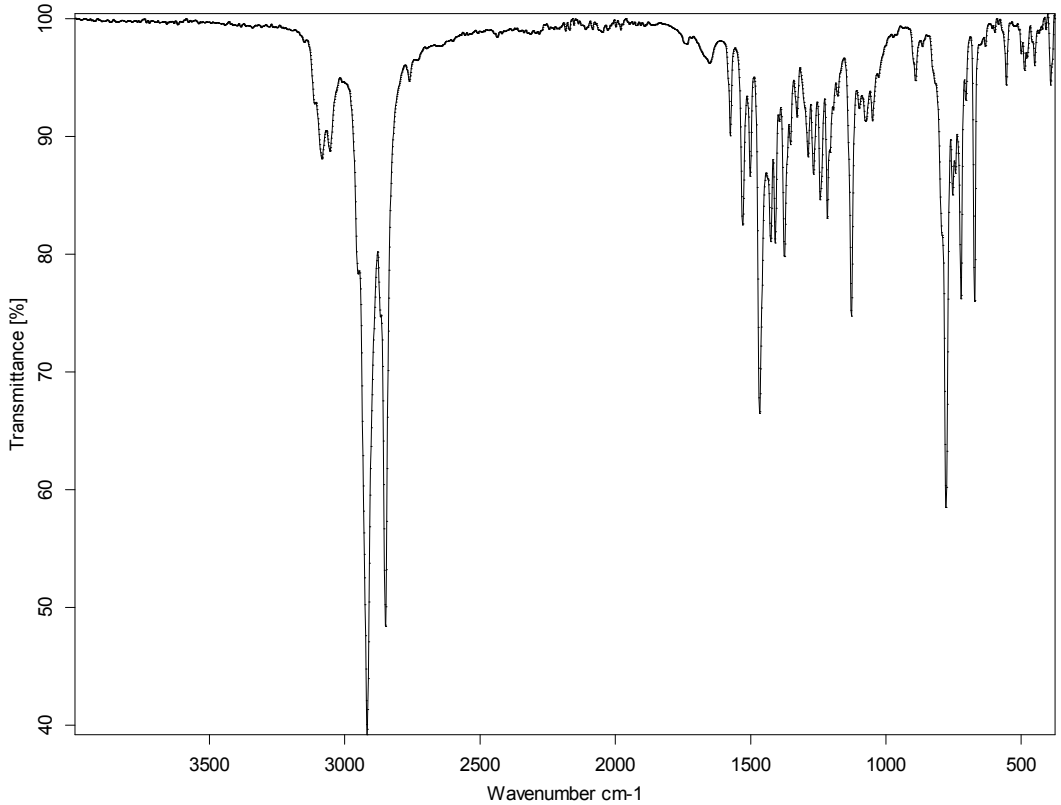

Figure S37: Infrared spectrum of compound $\mathbf{C_{12}C_1C_9}$

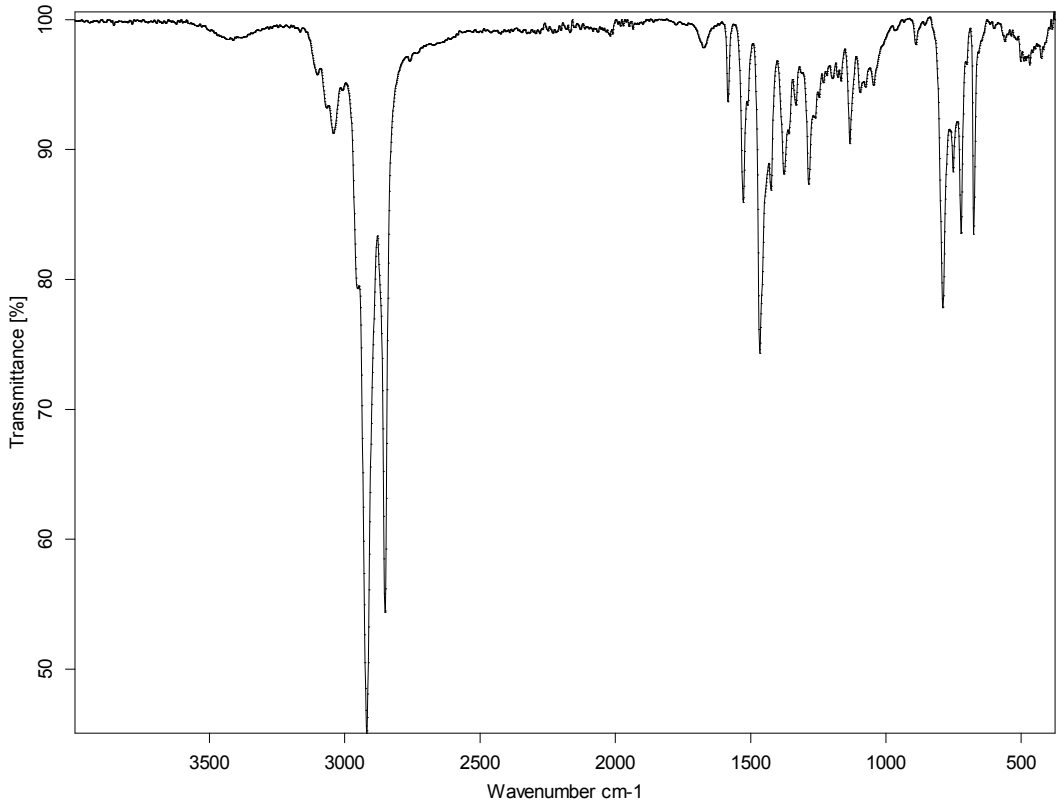

Figure S38: Infrared spectrum of compound $\mathbf{C_{12}C_1C_{10}}$

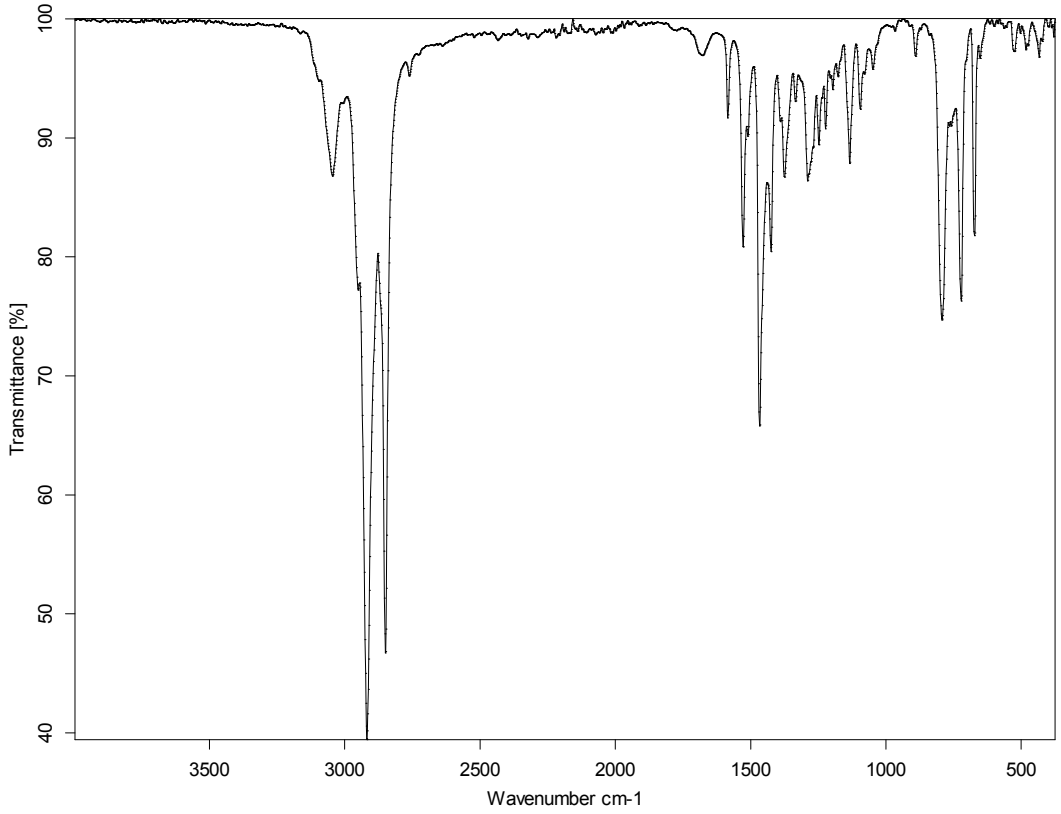

Figure S39: Infrared spectrum of compound $C_{12}C_1C_{11}$

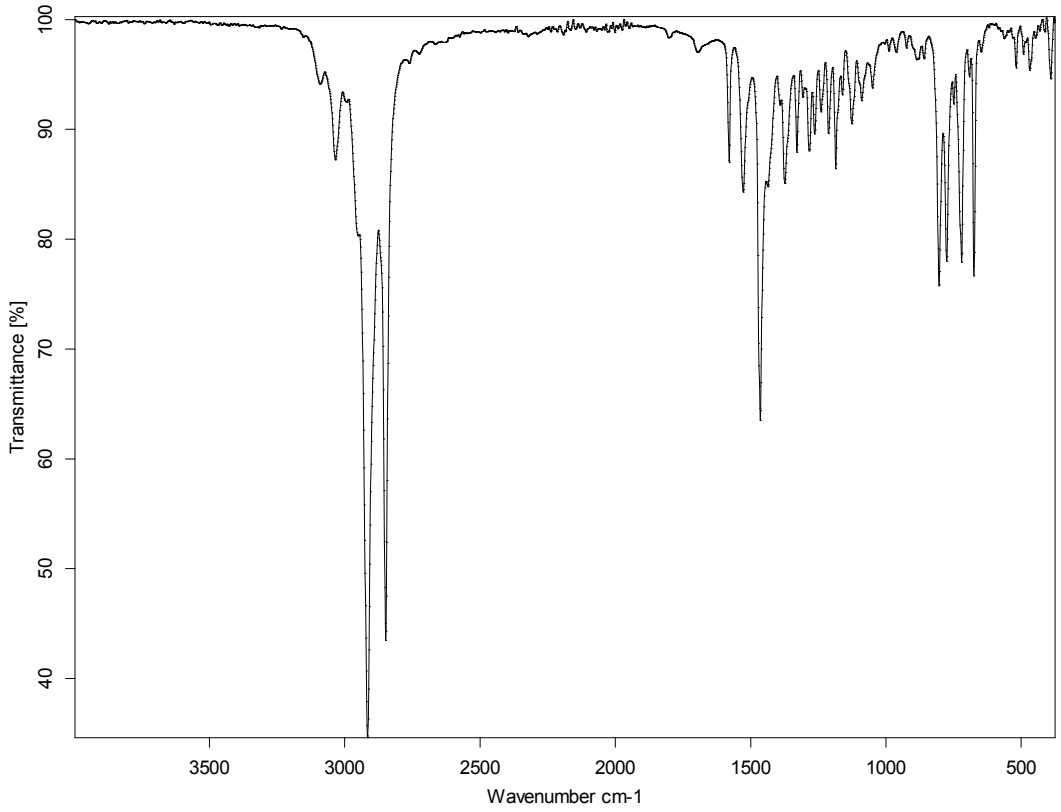

Figure S40: Infrared spectrum of compound $C_{12}C_1C_{12}$

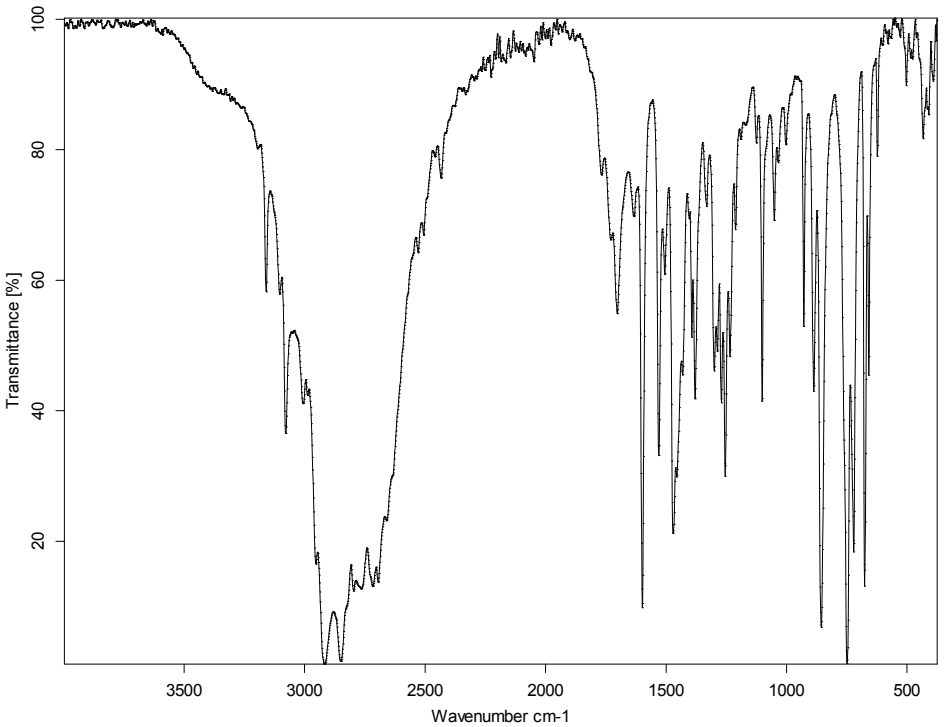

Figure S41: Infrared spectrum of compound $C_{12}C_1C_0$

V. Thermogravimetry analysis (TGA)

Due to experimental limitations, it was not possible to transfer the compounds under strict inert conditions into the thermal analyzer. This resulted in some water uptake for some samples. This becomes evident through a mass loss around 100 °C.

Table S2: Decomposition temperatures and water content of compounds $\mathbf{C_{12}C_1C_0}$- $\mathbf{C_{12}C_1C_{12}}$

Compound	T decomposition (°C)	Water content* (wt%)	Water content (mol eq.)
$\mathbf{C_{12}C_1C_0}$	262	-	-
$\mathbf{C_{12}C_1C_1}$	273	7.94	1.33
$\mathbf{C_{12}C_1C_2}$	266	-	-
$\mathbf{C_{12}C_1C_3}$	268	-	-
$\mathbf{C_{12}C_1C_4}$	271	-	-
$\mathbf{C_{12}C_1C_5}$	269	-	-
$\mathbf{C_{12}C_1C_6}$	269	-	-
$\mathbf{C_{12}C_1C_7}$	270	4.06	0.81
$\mathbf{C_{12}C_1C_8}$	266	2.54	0.55
$\mathbf{C_{12}C_1C_9}$	259	5.06	1.14
$\mathbf{C_{12}C_1C_{10}}$	266	7.38	1.74
$\mathbf{C_{12}C_1C_{11}}$	264	13.27	3.52
$\mathbf{C_{12}C_1C_{12}}$	263	7.11	1.79

* Water content was calculated from the sample weight loss between 60 °C to 120 °C.

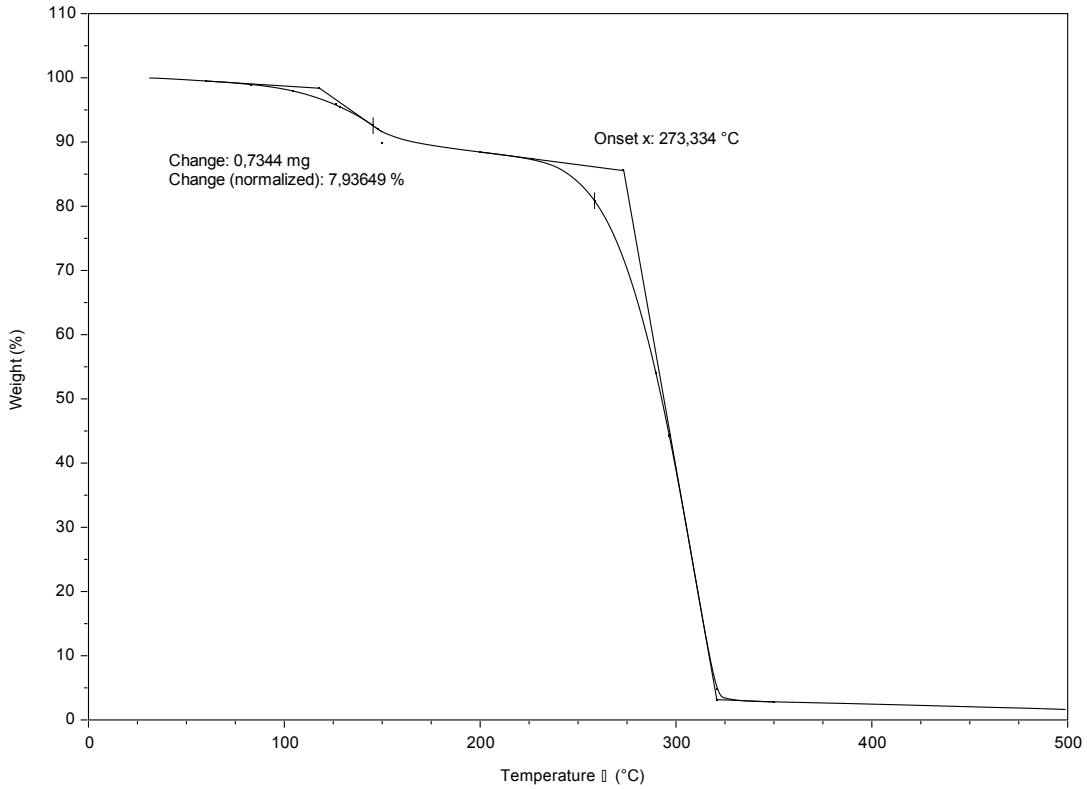

Figure S42: TGA trace of compound $\mathbf{C_{12}C_1C_1}$ (10 °C/min)

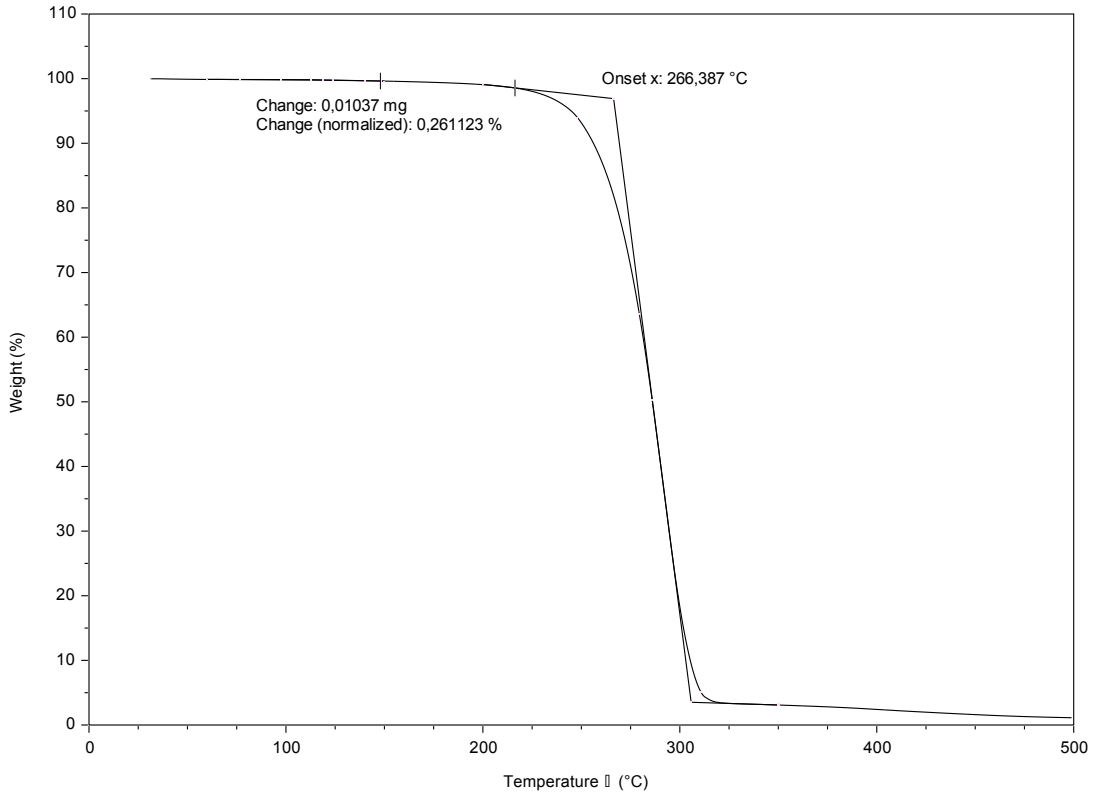

Figure S43: TGA trace of compound $\mathbf{C_{12}C_1C_2}$ (10 °C/min)

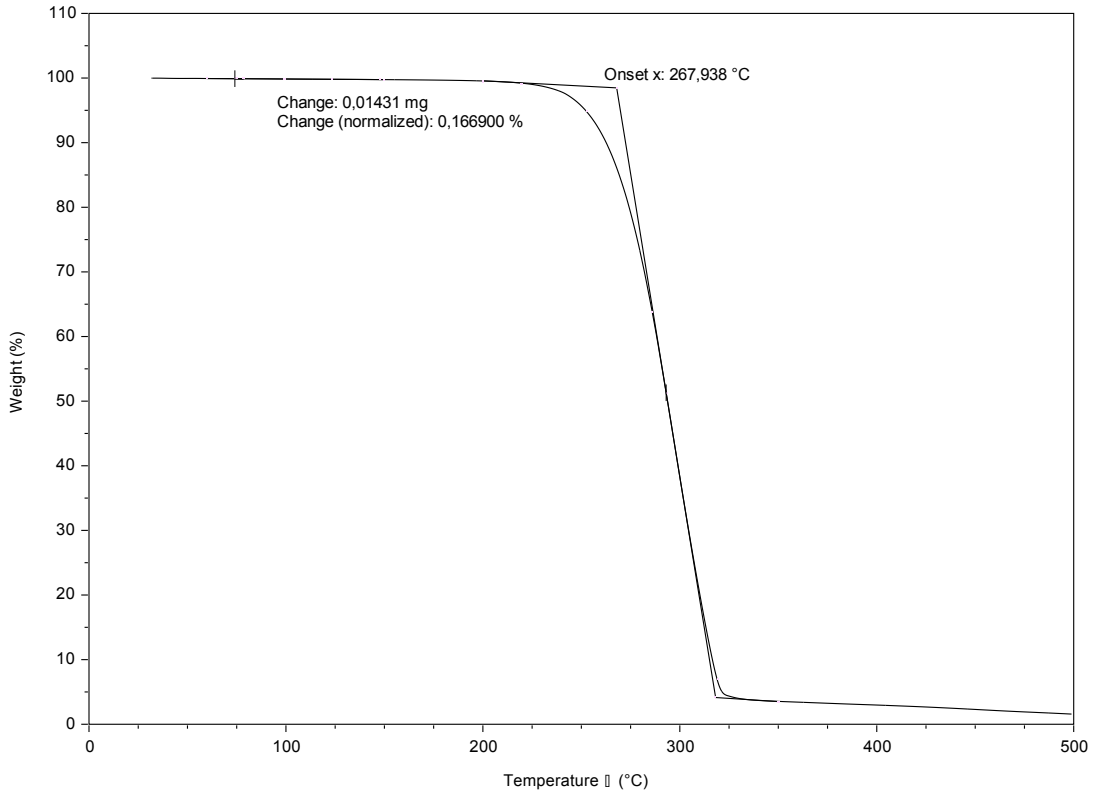

Figure S44: TGA trace of compound $\mathbf{C_{12}C_1C_3}$ (10 °C/min)

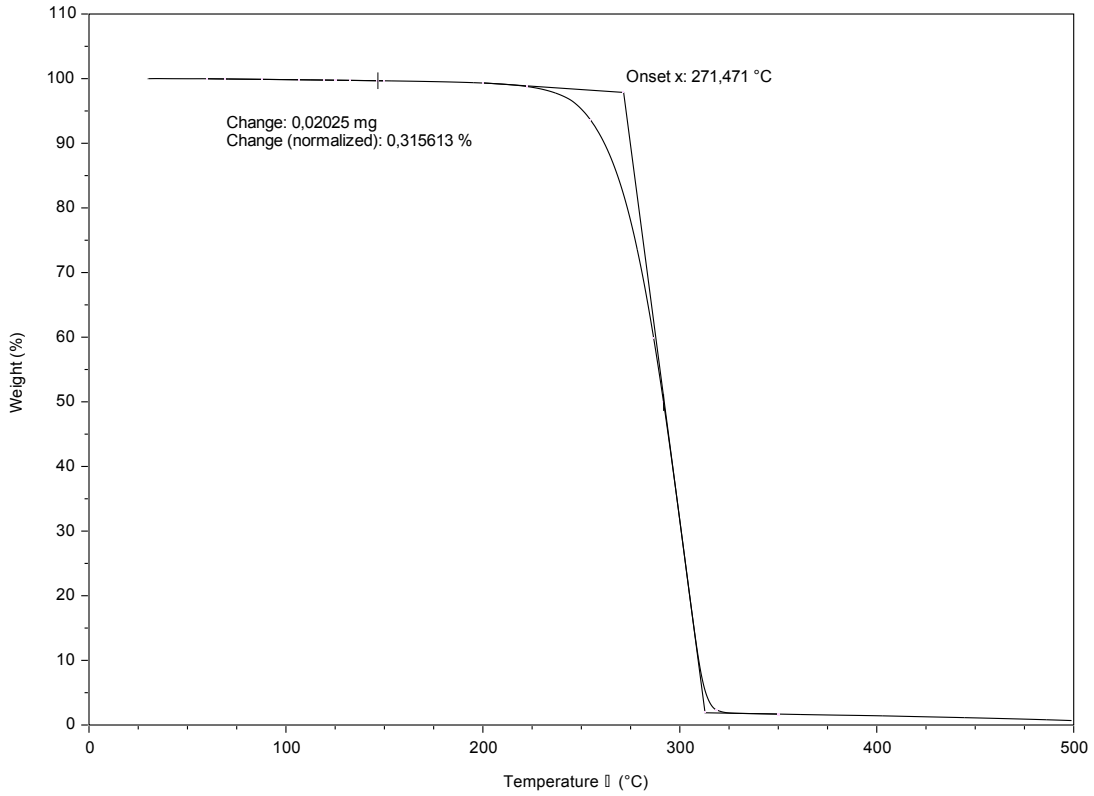

Figure S45: TGA trace of compound $\mathbf{C_{12}C_1C_4}$ (10 °C/min)

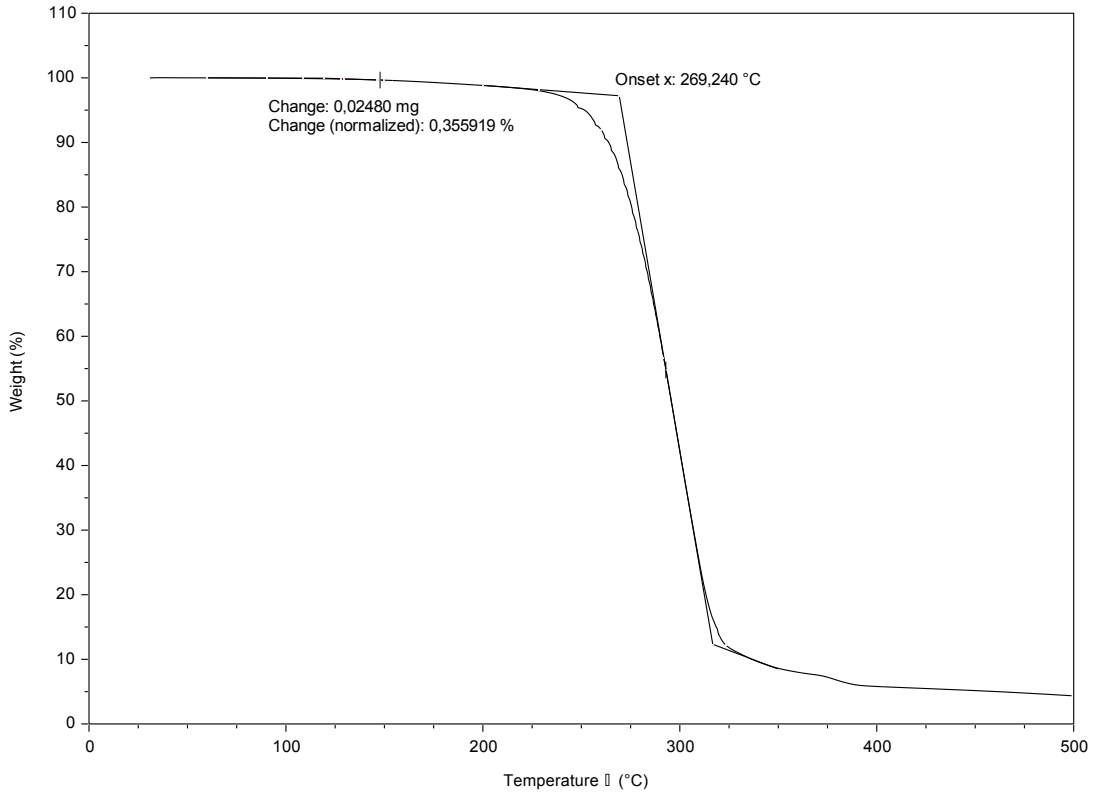

Figure S46: TGA trace of compound $\mathbf{C_{12}C_1C_5}$ (10 °C/min)

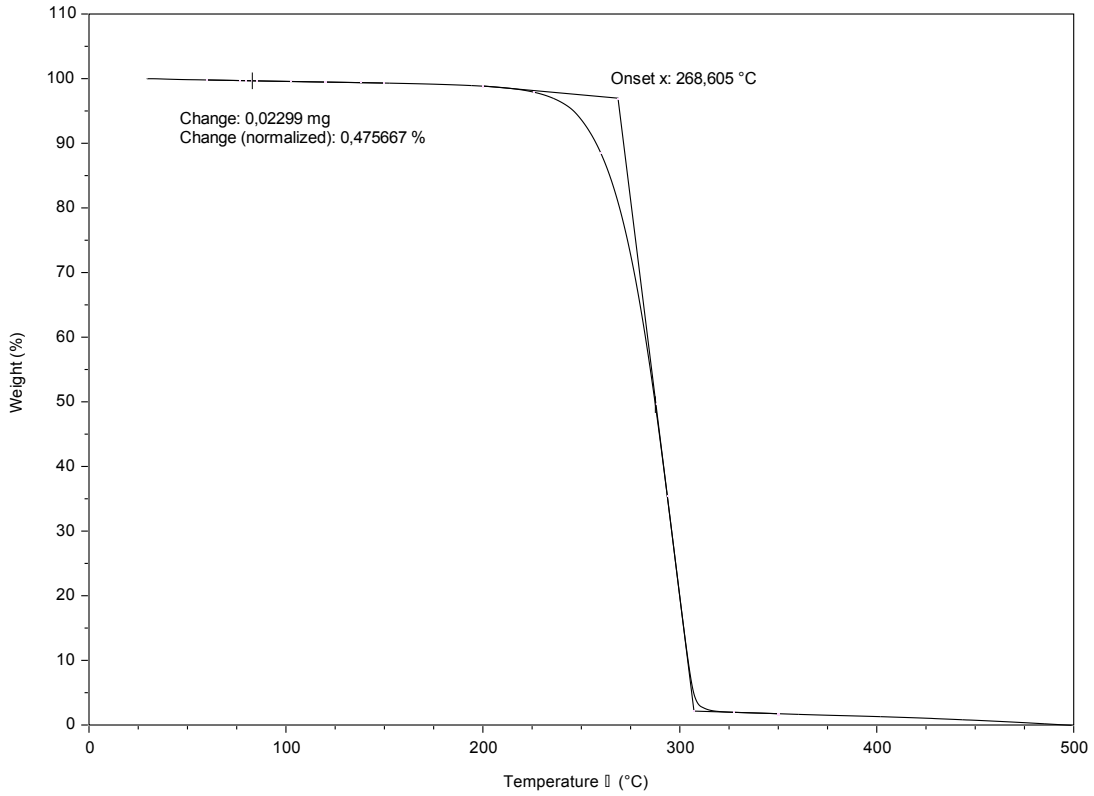

Figure S47: TGA trace of compound $\mathbf{C_{12}C_1C_6}$ (10 °C/min)

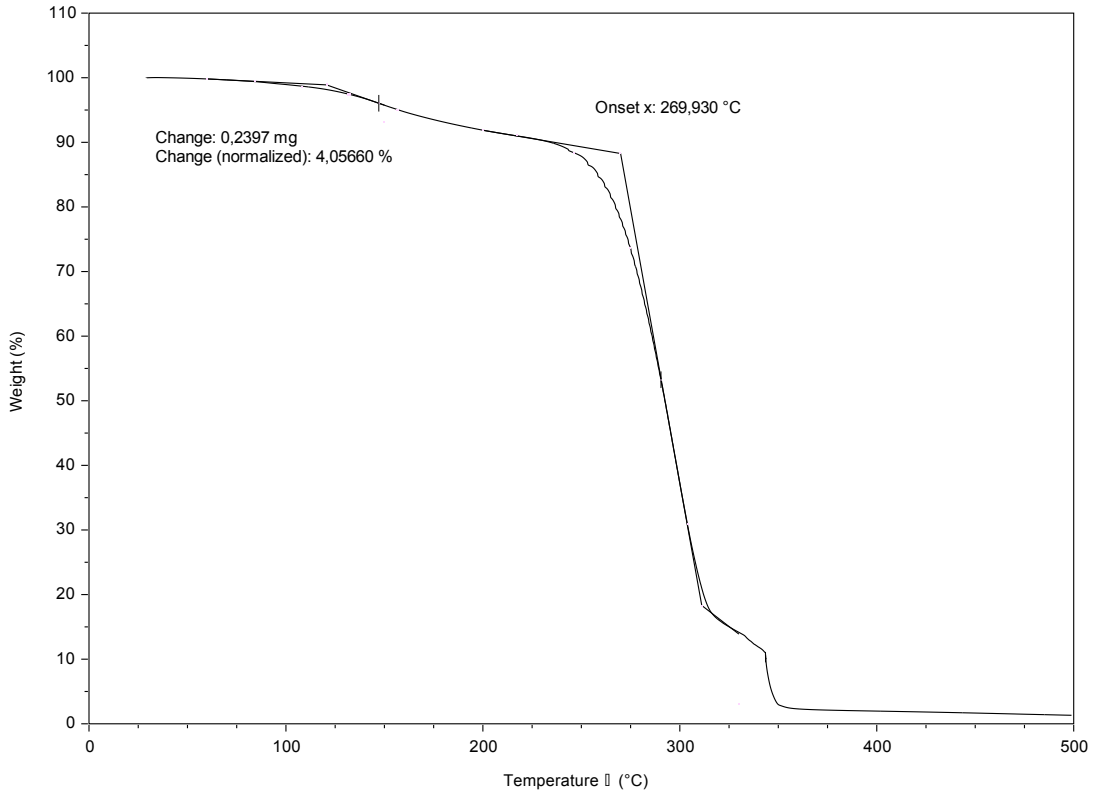

Figure S48: TGA trace of compound $\mathbf{C_{12}C_1C_7}$ (10 °C/min)

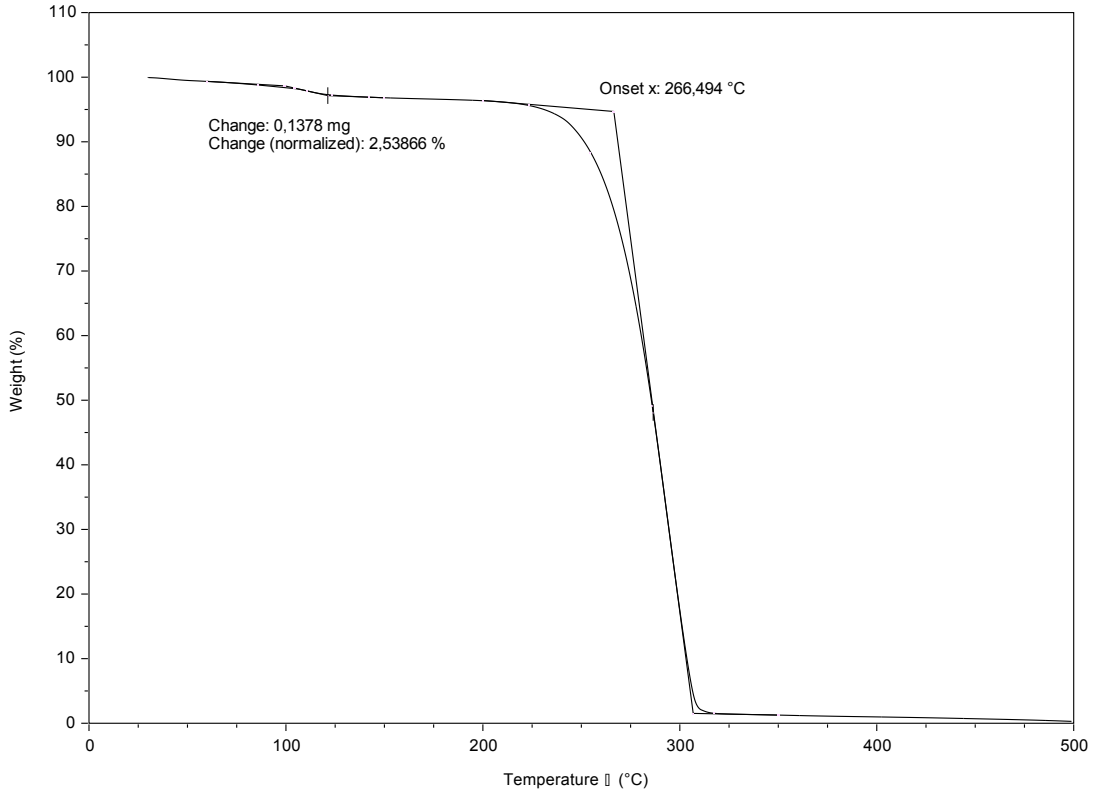

Figure S49: TGA trace of compound $\mathbf{C_{12}C_1C_8}$ (10 °C/min)

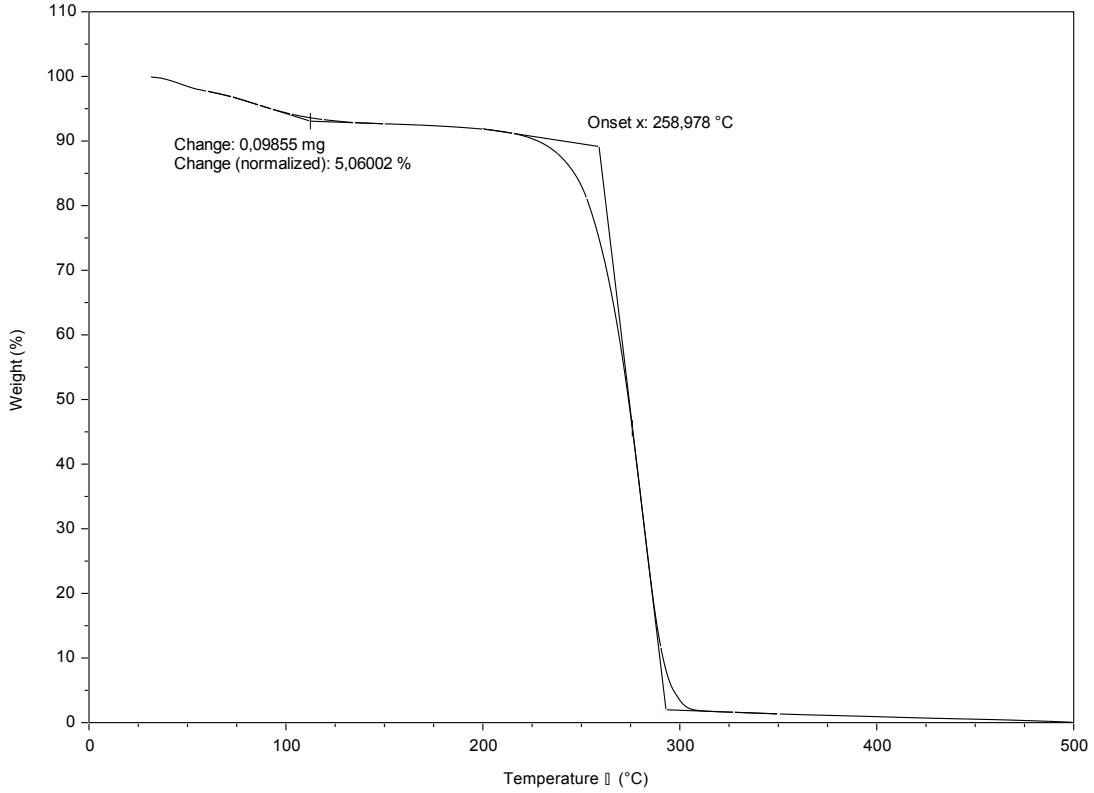

Figure S50: TGA trace of compound $\mathbf{C_{12}C_1C_9}$ (10 °C/min)

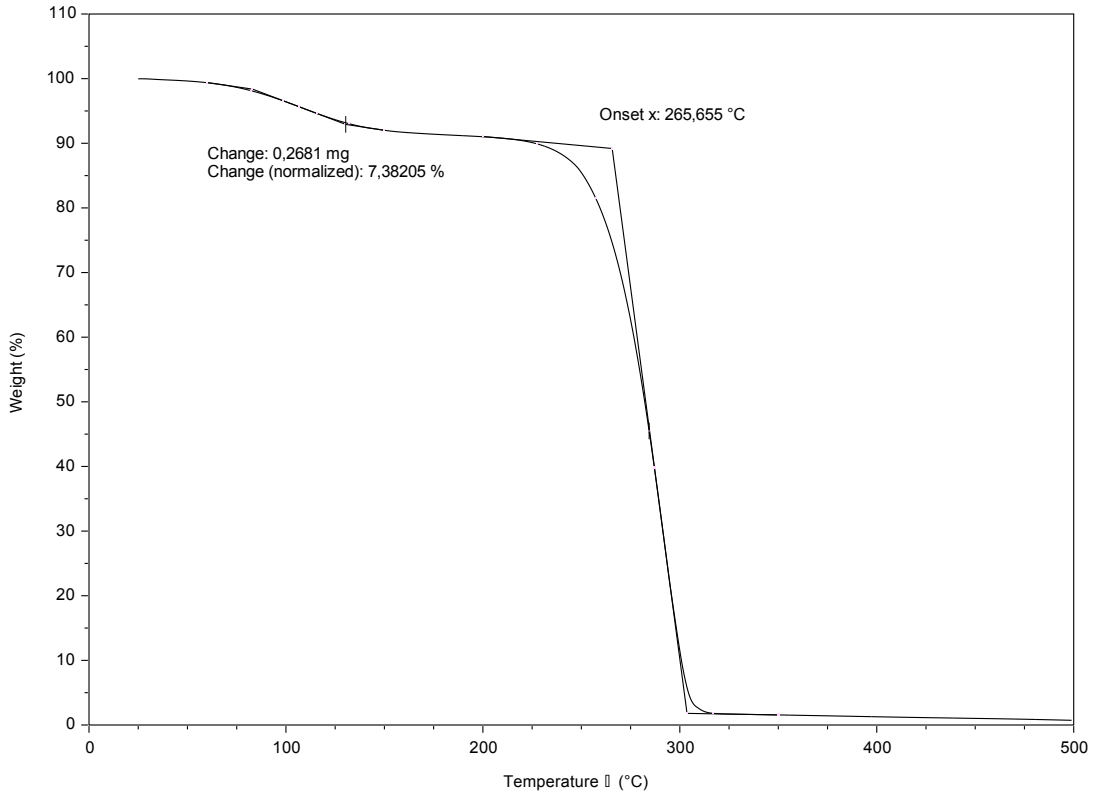

Figure S51: TGA trace of compound $\mathbf{C_{12}C_1C_{10}}$ (10 °C/min)

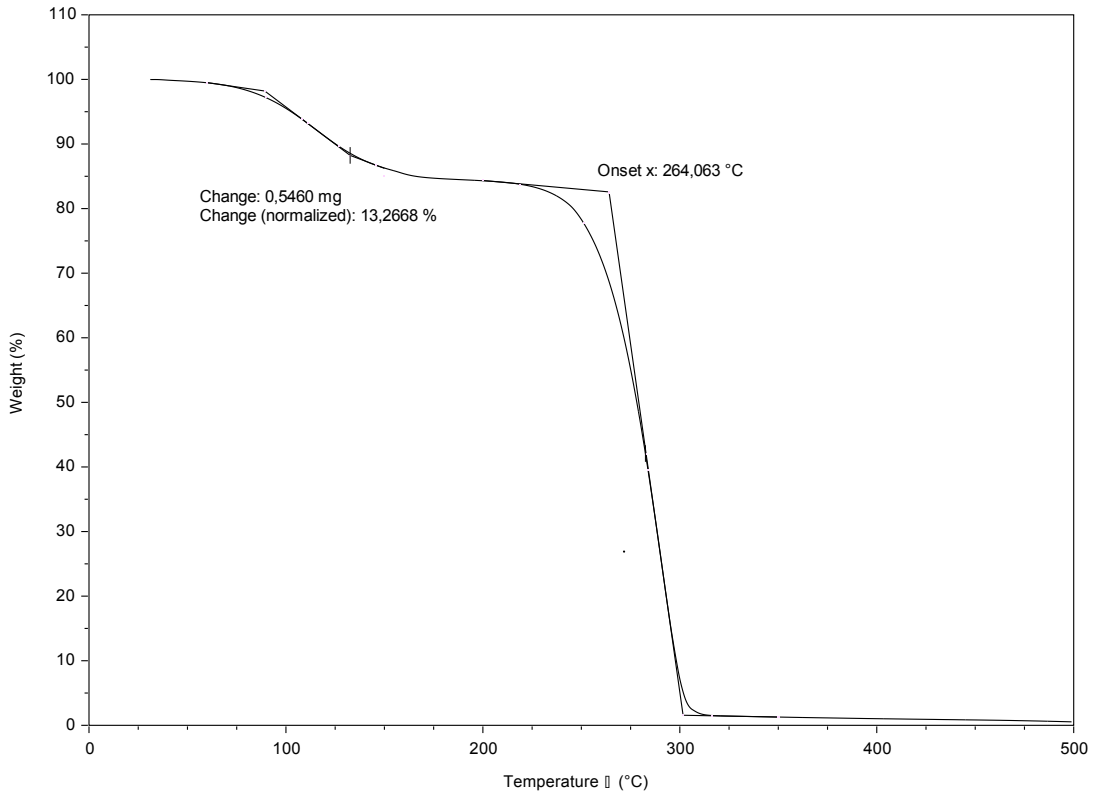

Figure S52: TGA trace of compound $\mathbf{C_{12}C_1C_{11}}$ (10 °C/min)

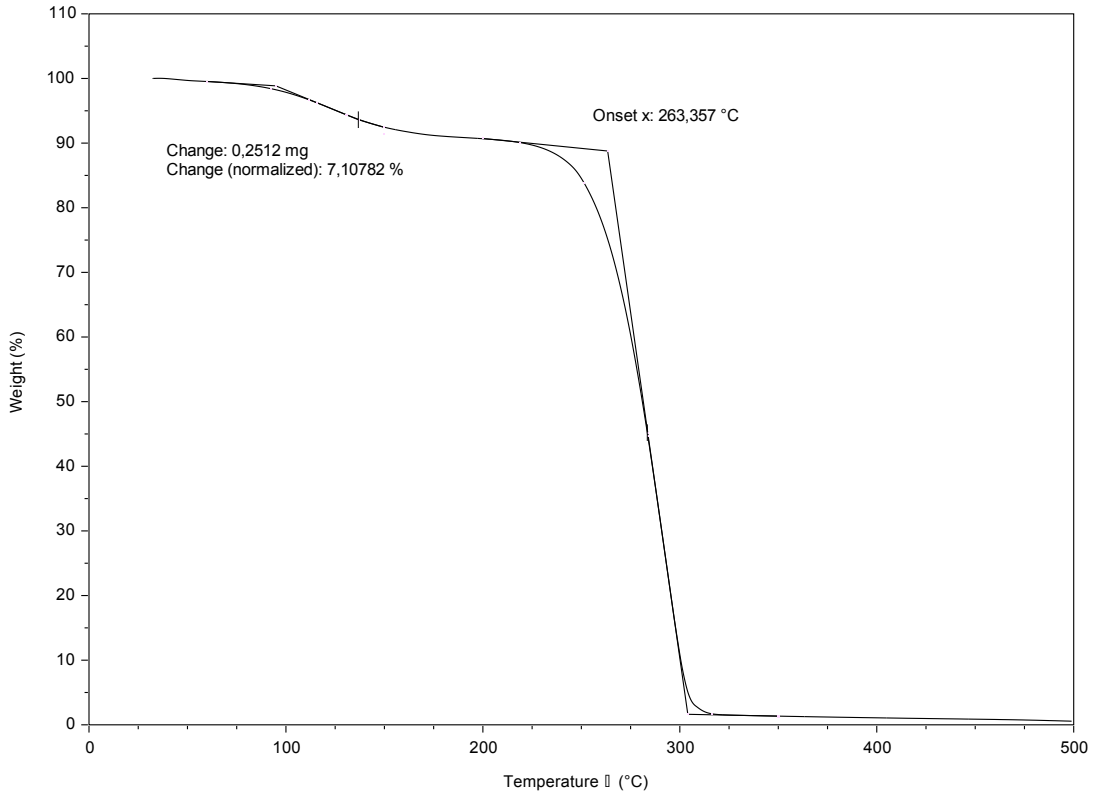

Figure S53: TGA trace of compound $\mathbf{C_{12}C_1C_{12}}$ (10 °C/min)

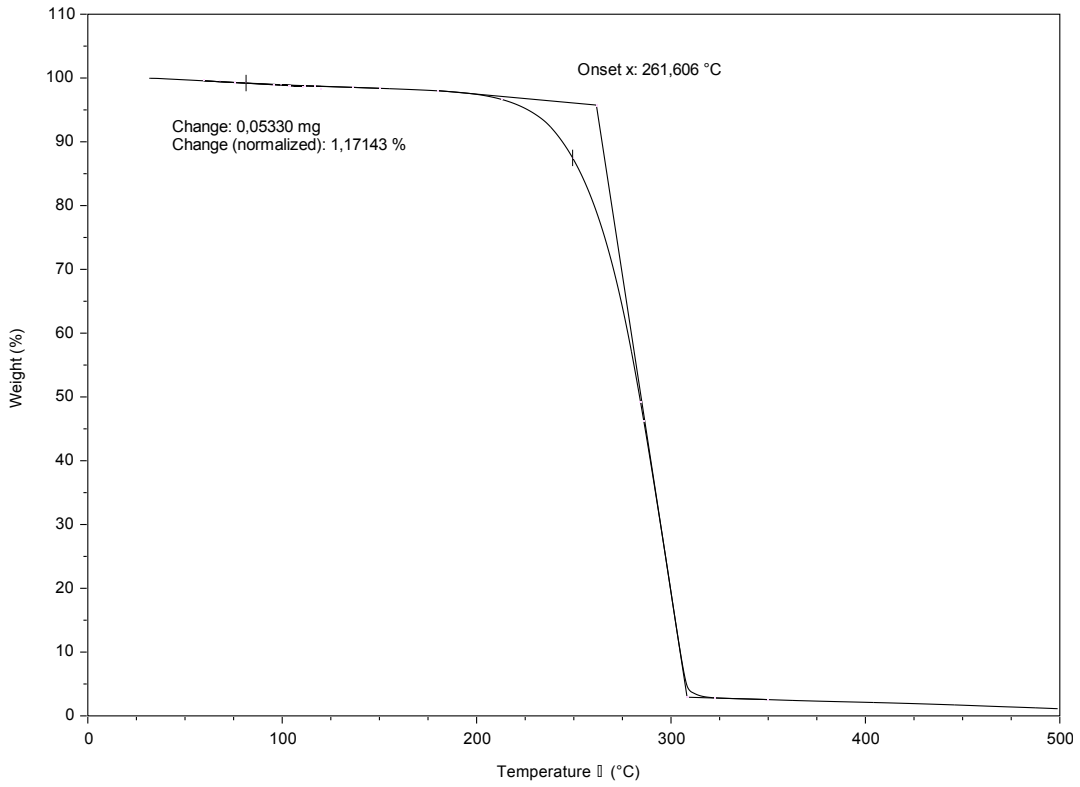

Figure S54: TGA trace of compound $\mathbf{C_{12}C_1C_0}$ (10 °C/min)

VI. Differential Scanning Calorimetry (DSC)

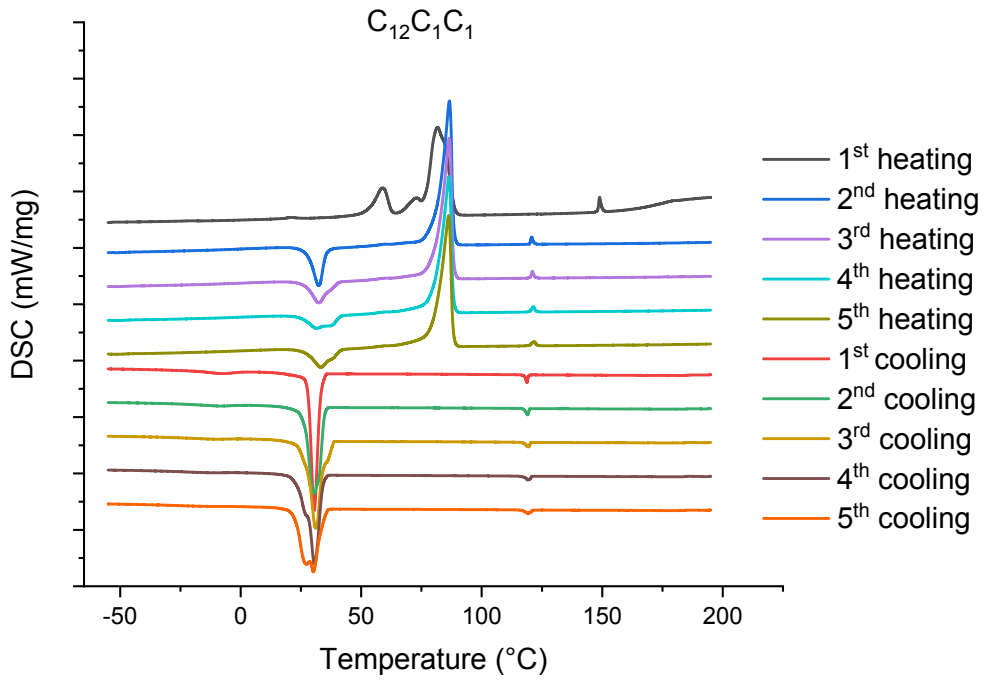

Figure S55: DSC traces of compound **$C_{12}C_1C_1$** (5 °C/min)

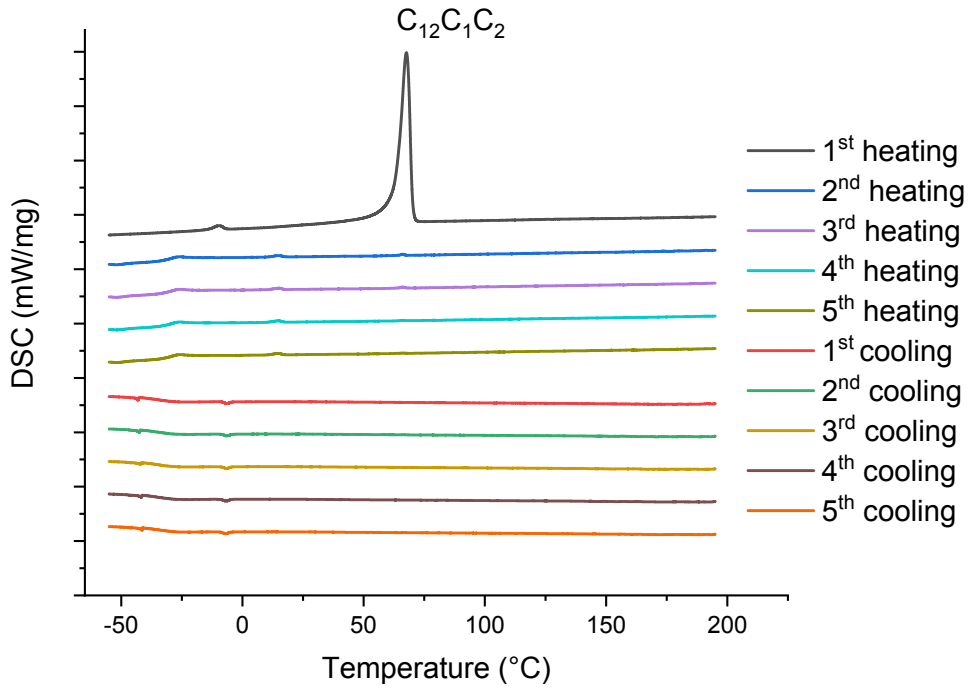

Figure S56: DSC traces of compound **$C_{12}C_1C_2$** (5 °C/min)

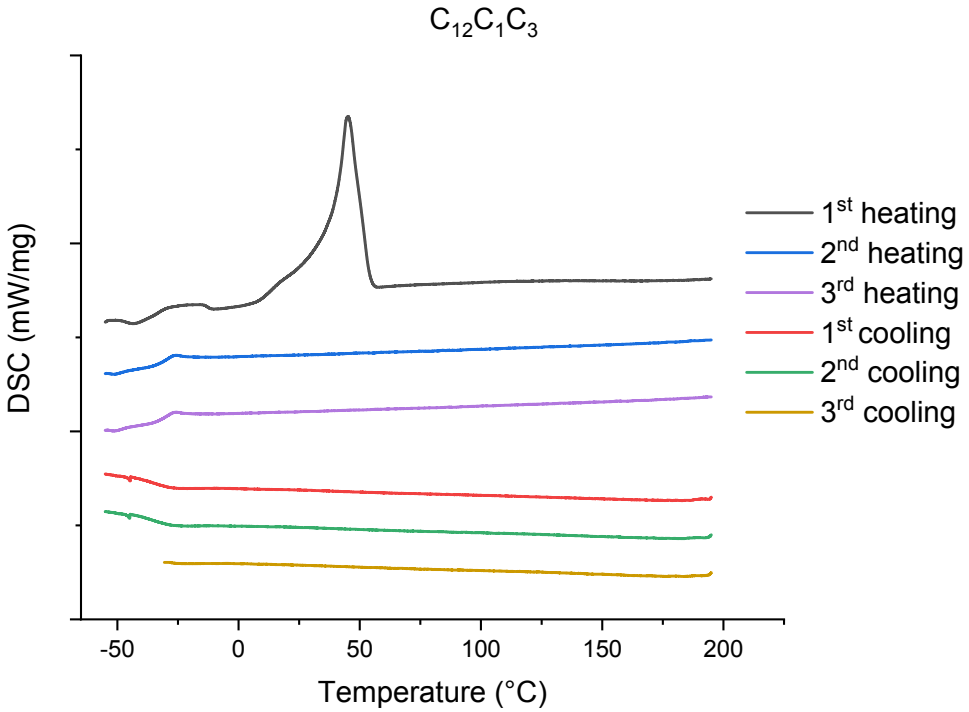

Figure S57: DSC traces of compound **$C_{12}C_1C_3$** (5 °C/min)

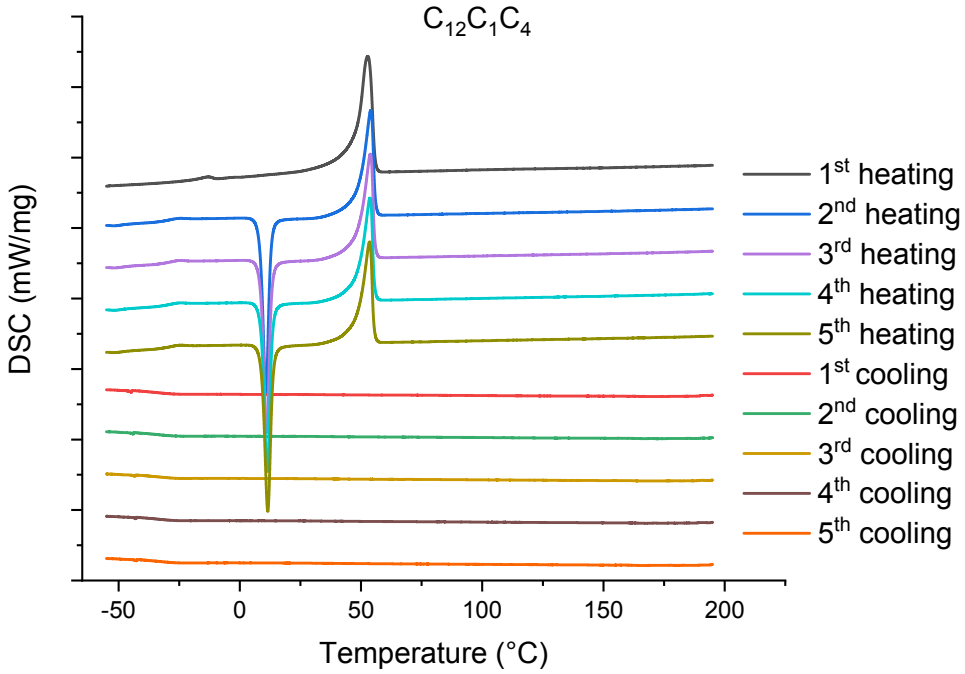

Figure S58: DSC traces of compound **$C_{12}C_1C_4$** (5 °C/min)

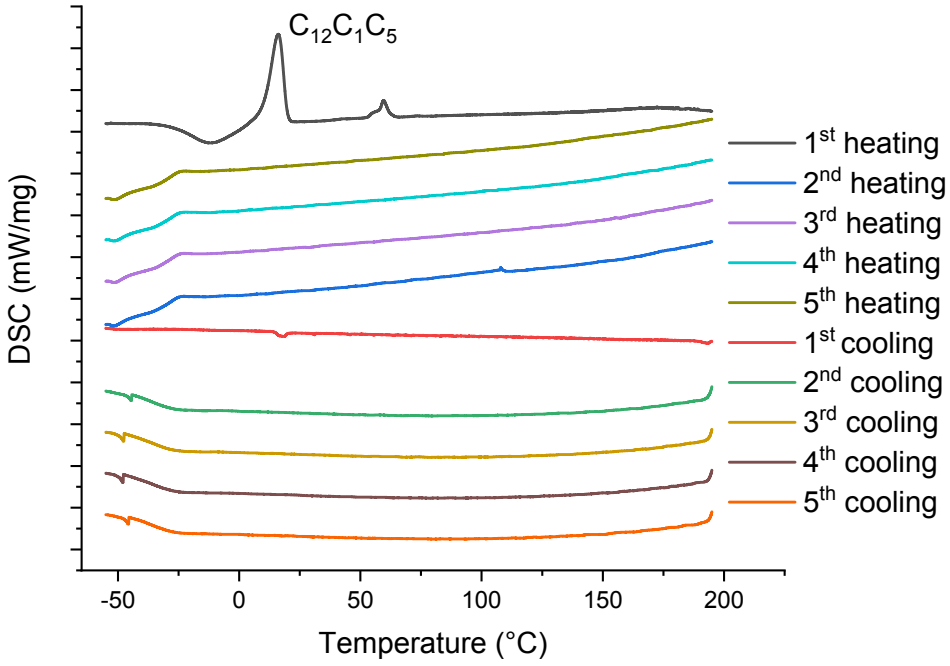

Figure S59: DSC traces of compound $\mathbf{C_{12}C_1C_5}$ (5 °C/min)

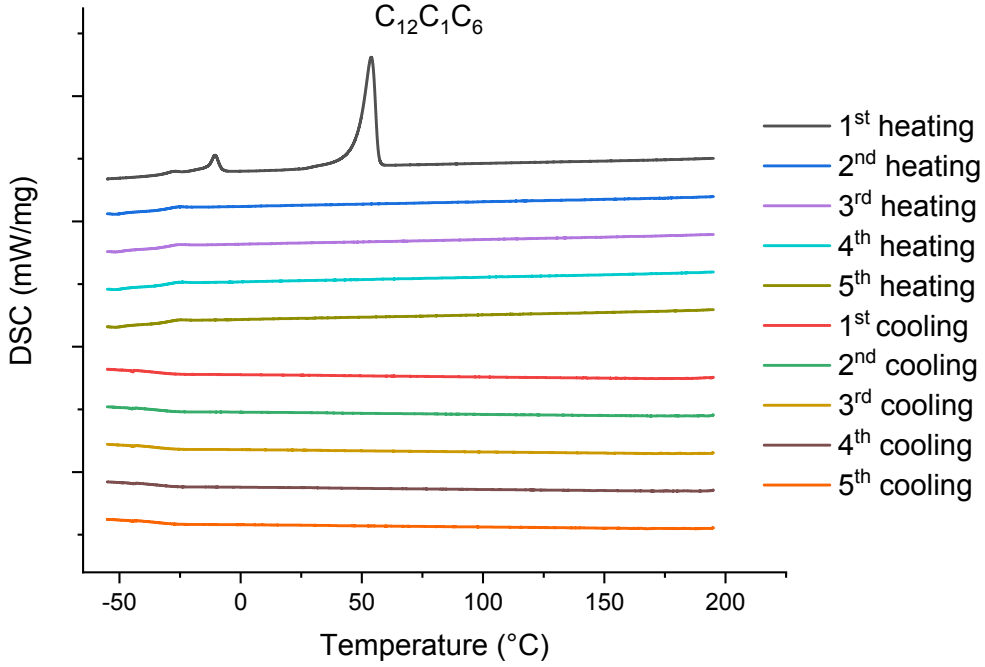

Figure S60: DSC traces of compound $\mathbf{C_{12}C_1C_6}$ (5 °C/min)

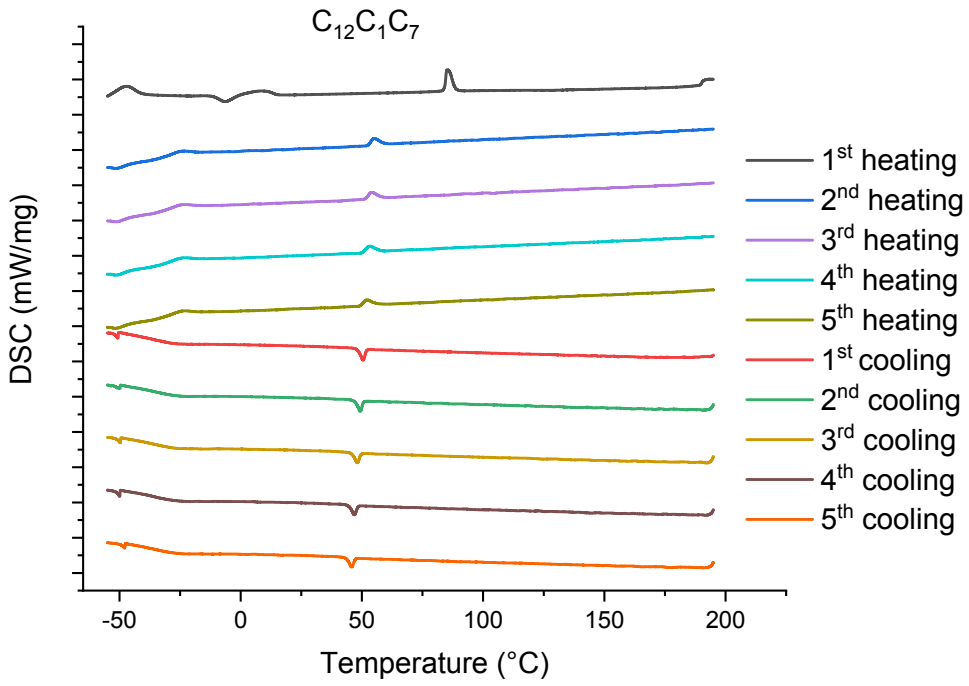

Figure S61: DSC traces of compound **$C_{12}C_1C_7$** (5 °C/min)

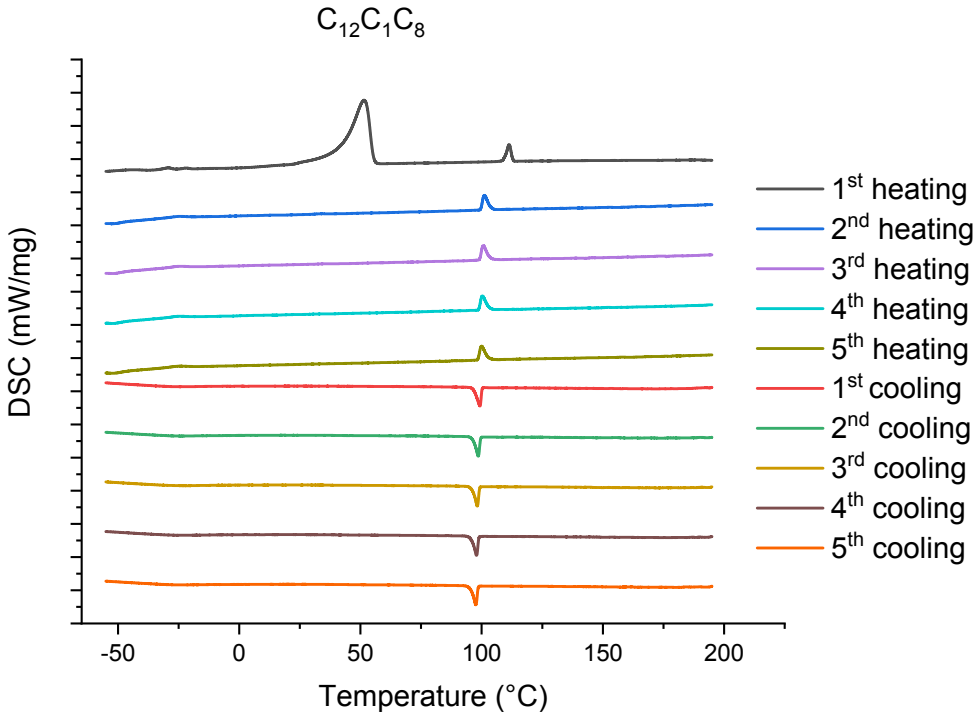

Figure S62: DSC traces of compound **$C_{12}C_1C_8$** (5 °C/min)

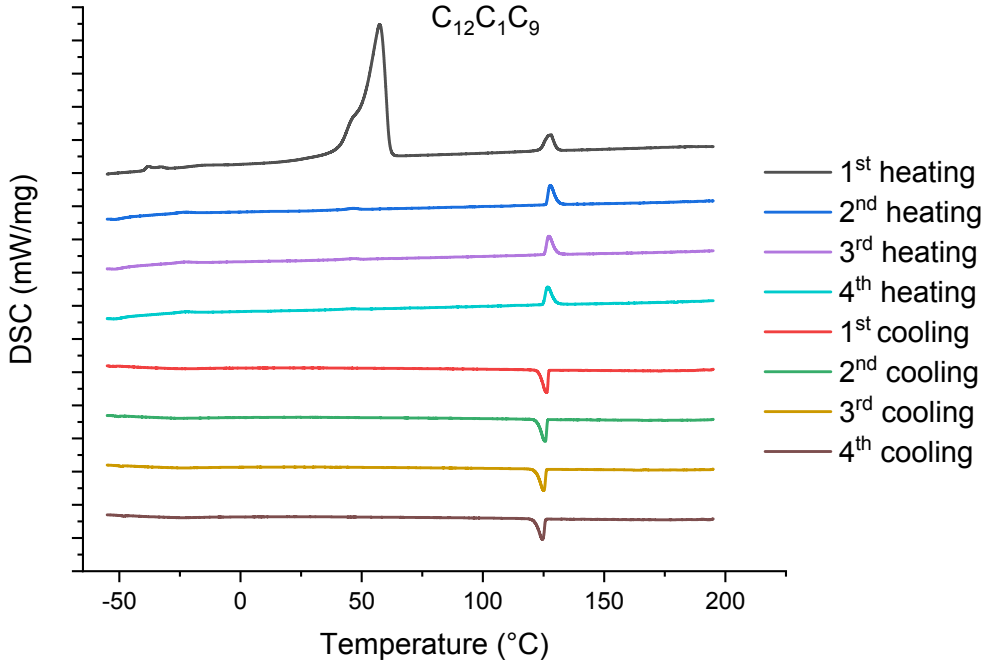

Figure S63: DSC traces of compound **$C_{12}C_1C_9$** (5 °C/min)

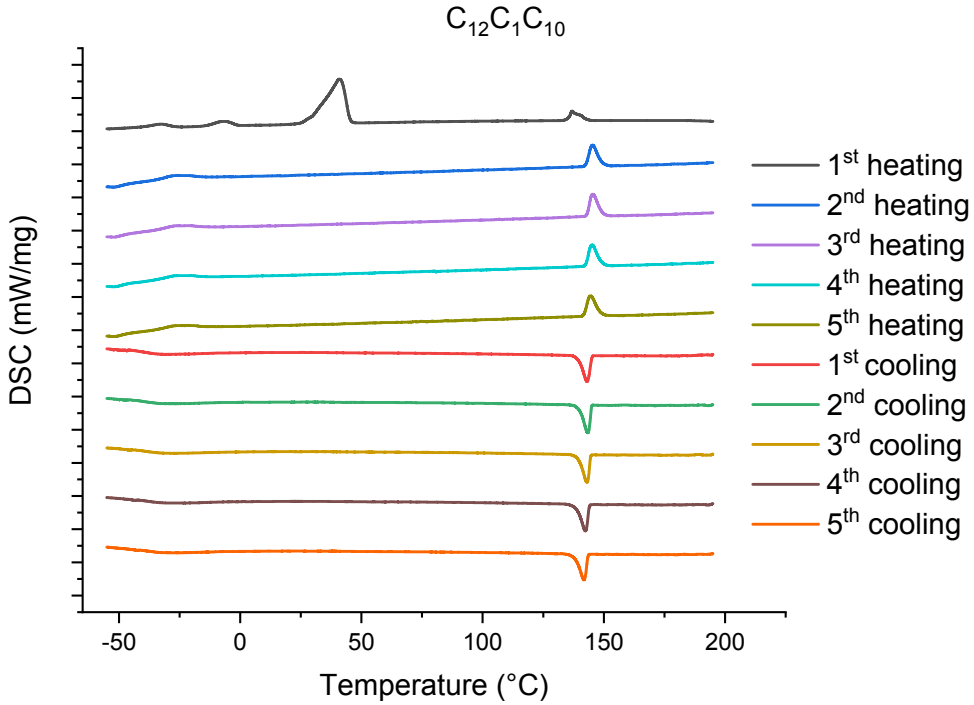

Figure S64: DSC traces of compound **$C_{12}C_1C_{10}$** (5 °C/min)

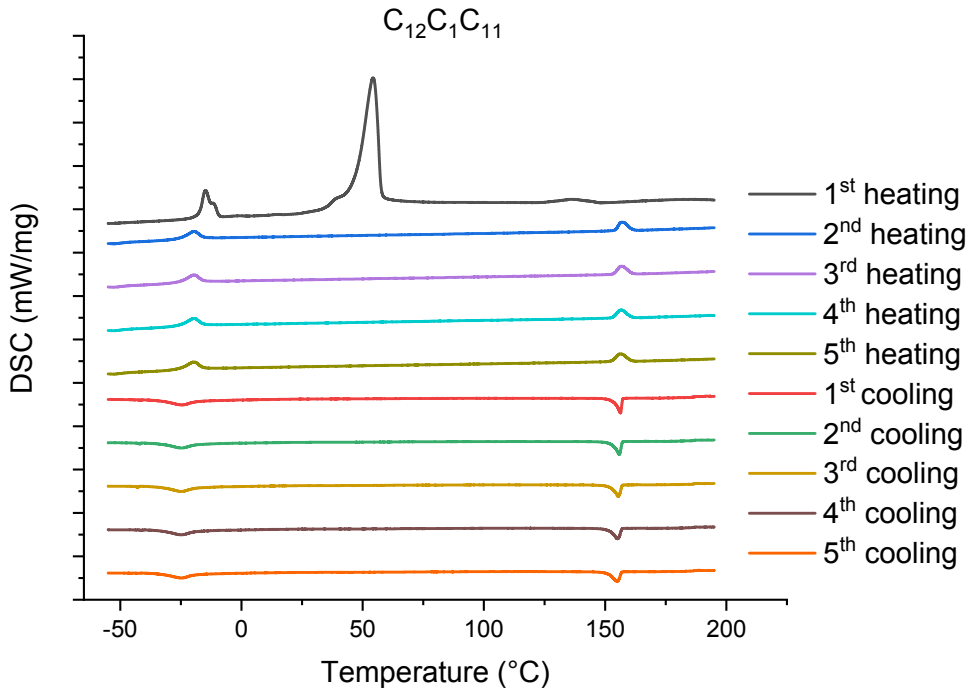

Figure S65: DSC traces of compound **$C_{12}C_1C_{11}$** (5 °C/min)

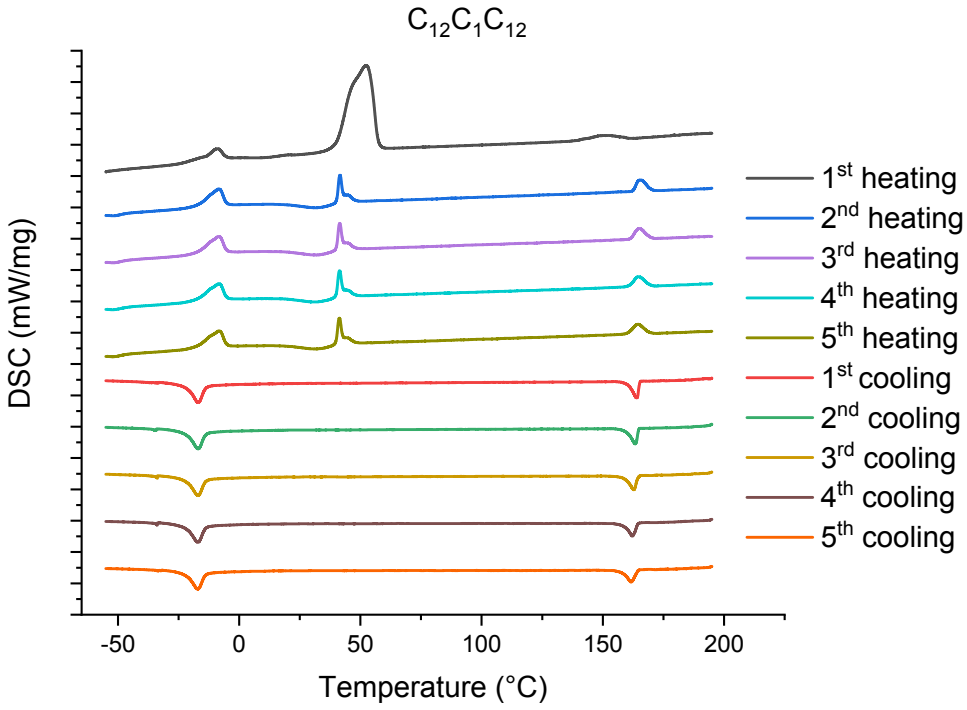

Figure S66: DSC traces of compound **$C_{12}C_1C_{12}$** (5 °C/min)

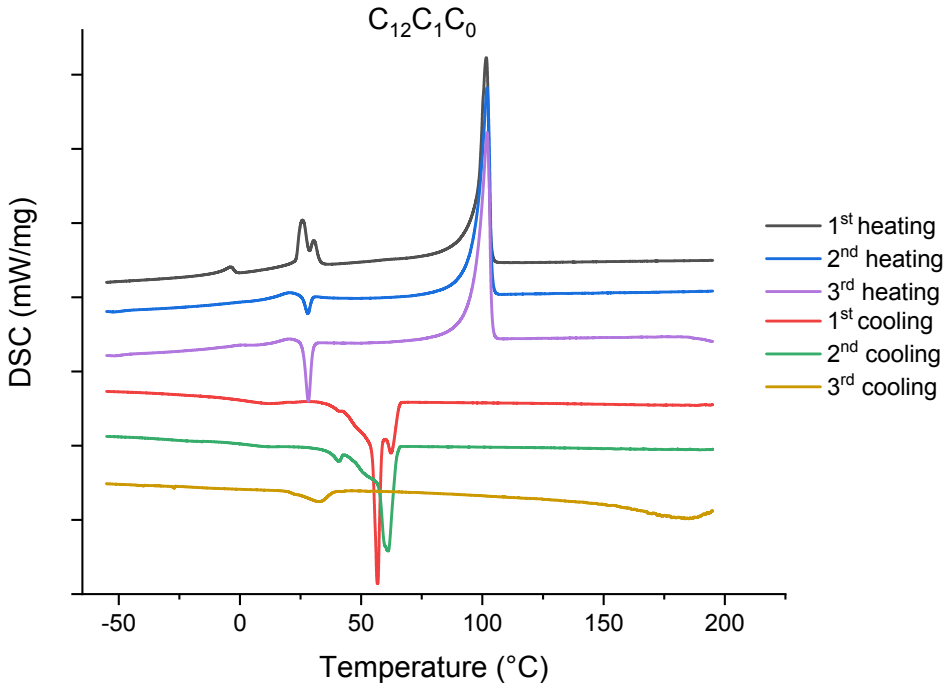

Figure S67: DSC traces of compound **$C_{12}C_1C_0$** (5 °C/min)

Table S3: Phase transition temperatures (and associated enthalpies in J/g) for compounds **$C_{12}C_1C_0$** to **$C_{12}C_1C_{12}$**.

$C_{12}C_1C_0$	1st run Cr —(-10.1 °C (2.15))→ Cr' ⇄ (22.3 °C (7.02) / 41.7 °C (-0.2)) Cr'' ⇄ (28.8 °C (2.77) / 59.7 °C (-71.66)) Cr''' ⇄ (84.0 °C (53.55) / 67.0 °C (-12.65)) L_{Iso} 2nd run Cr' —(24.7 °C (-3.56))→ Cr ⇄ (85.3 °C (97.67) / 67.3 °C (-61.70)) L_{Iso} Cr ⇄ (43.1 °C (-2.05)) Cr''
$C_{12}C_1C_1$	1st heating Cr —(53.1°C (26.33))→ Cr' ⇄ (67.2 °C (22.99)) Cr'' —(77.4 °C (68.29))→ SmA —(148.2 °C (2.70))→ L_{Iso} 2nd run Cr' —(27.7 °C (-21.22))→ Cr ⇄ (81.9 °C (75.83) / 36.2 °C (-54.18)) SmA ⇄ (120.0 °C (0.89) / 120.0 °C (-0.93)) L_{Iso}

$C_{12}C_1C_2$	1st run Cr —(-13.6 °C (2.42))→ Cr' —(63.1 °C (31.41))→ L_{Iso} 2nd run Tg —(-29.7 °C)→ Cr' —(10.5 °C (0.62))→ SmA —(65.0 °C (0.25))→ L_{Iso} Tg ←(-27.6 °C)— Cr' ←(-3.4 °C (0.48))— SmA ←— L_{Iso}
$C_{12}C_1C_3$	1st run Cr —(28.9 °C (74.96))→ L_{Iso} 2nd run Tg —(-30.7 °C)→ L_{Iso} Tg ←(-35.5 °C)— L_{Iso}
$C_{12}C_1C_4$	1st run Cr —(34.6 °C (72.83))→ L_{Iso} 2nd run Tg —(-27.2 °C)→ L_{Iso} —(8.2 °C (-45.7))→ Cr —(35.3 °C (48.2))→ L_{Iso} Tg ←(-33.7 °C)— L_{Iso}
$C_{12}C_1C_5$	1st run SmA —(-30.1 °C (-19.87))→ Cr —(4.8 °C (34.76))→ SmA —(51.7 °C (4.02))→ L_{Iso} 2nd run Tg —(-27.1 °C)→ L_{Iso} Tg ←(-37.9 °C)— L_{Iso}
$C_{12}C_1C_6$	1st run Cr —(-13.1 °C (6.11))→ Cr' —(38.9 °C (71.7))→ L_{Iso} 2nd run Tg —(-30.5 °C)→ L_{Iso} Tg ←(-33.0 °C)— L_{Iso}

$C_{12}C_1C_7$	1st run SmA —(-12.6 °C (-6.43))→ Cr —(-1.0 °C (5.44))→ SmC —(82.3 °C (4.36))→ L_{Iso} 2nd run Tg —(-28.6 °C)→ / ←(-33.7 °C)— SmC —(52.6 °C (1.85))→ / ←(52.2 °C (-1.56))— L_{Iso}
$C_{12}C_1C_8$	1st run Cr —(22.3 °C (37.0))→ SmC —(106.4 °C (2.66))→ L_{Iso} 2nd run Tg —(-36.0 °C)→ / ←(-39.8 °C)— SmC —(98.6 °C (2.79))→ / ←(100.9 °C (-2.69))— L_{Iso}
$C_{12}C_1C_9$	1st run Cr —(33.6 °C (20.28))→ SmC —(122.9 °C (1.26))→ L_{Iso} 2nd run Tg —(-32.8 °C)→ / ←(-33.3 °C)— SmC —(129.1 °C (4.23))→ / ←(127.7 °C (-4.21))— L_{Iso}
$C_{12}C_1C_{10}$	1st run Cr —(-41.2 °C (1.44))→ Cr' —(-16.4° C (2.33))→ Cr'' —(22.4 °C (29.32))→ SmC —(132.9 °C (3.15))→ L_{Iso} 2nd run Tg —(-31.0 °C)→ / ←(-33.9 °C)— SmC —(140.7 °C (6.66))→ / ←(145.7 °C (-6.59))— L_{Iso}
$C_{12}C_1C_{11}$	1st run Cr —(-19.4 °C (7.09))→ Cr' —(33.2 °C (51.55))→ SmA —(127.6 °C (2.37))→ L_{Iso}

	2nd run Cr ⇄ (-27.4 °C (2.52) / -18.4 °C (-2.87)) SmA ⇄ (152.8 °C (2.10) / 158.4 °C (-2.12)) L_{Iso}
$C_{12}C_1C_{12}$	1st run Cr —(-24.0 °C (3.58))→ Cr' —(37.9 °C (72.31))→ SmA —(140.3 °C (4.03))→ L_{Iso} 2nd run Cr —(-18.5 °C (8.64))→ Cr' —(39.2 °C (6.25))→ SmA —(161.5 °C (4.13))→ L_{Iso} Cr' ← (-11.8 °C (-9.38)) SmA ← (165.9 °C (-4.16)) L_{Iso}

VII. Small Angle X-Ray Scattering (SAXS)

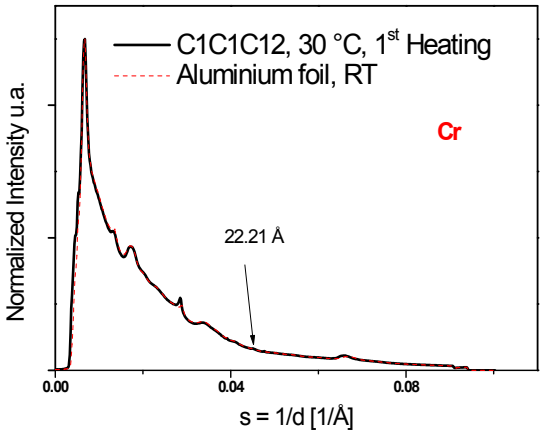

Figure S68: SAXS for compound $\mathbf{C_{12}C_1C_1}$ at 30 °C

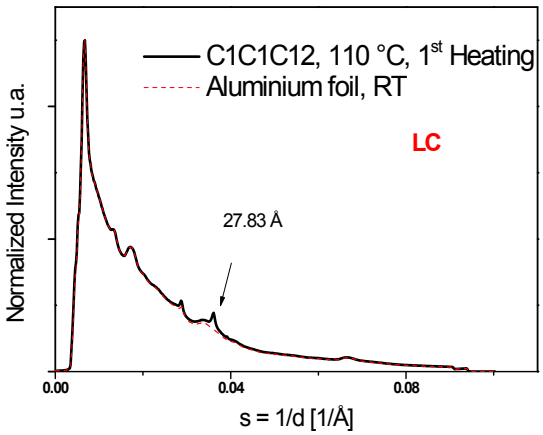

Figure S69: SAXS for compound $\mathbf{C_{12}C_1C_1}$ at 110 °C

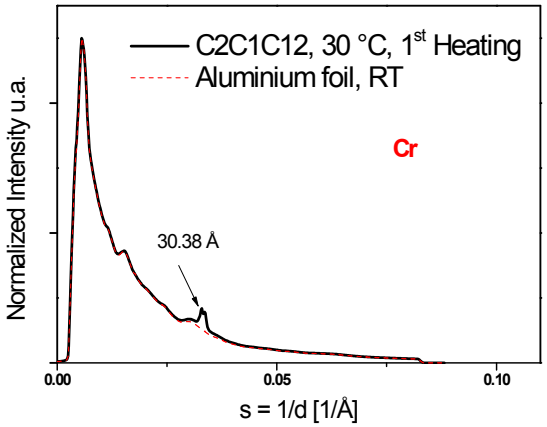

Figure S70: SAXS for compound $\mathbf{C_{12}C_1C_2}$ at 30 °C

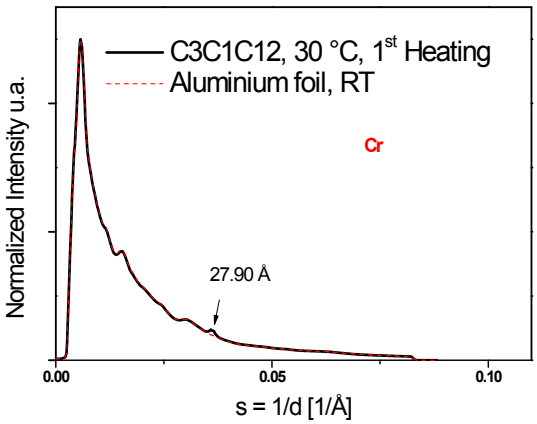

Figure S71: SAXS for compound $\mathbf{C_{12}C_1C_3}$ at 30 °C

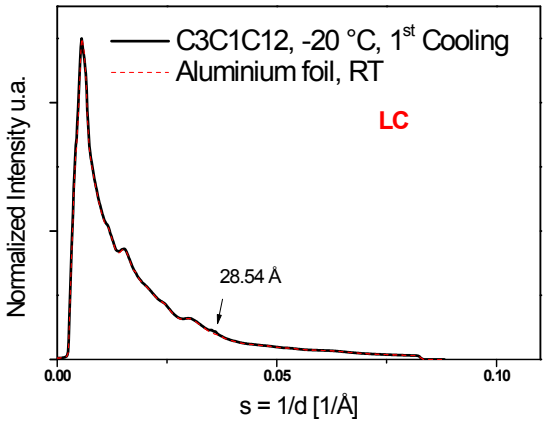

Figure S72: SAXS for compound $\mathbf{C_{12}C_1C_3}$ at -20 °C

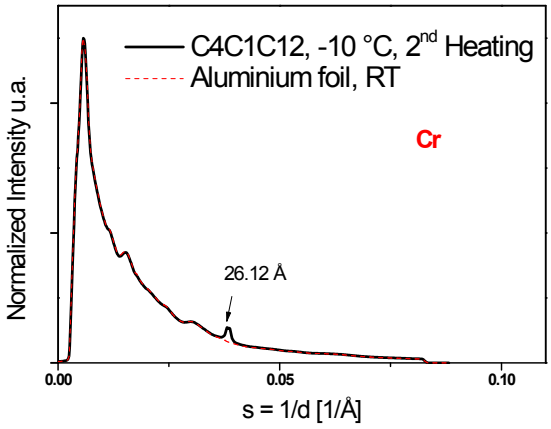

Figure S73: SAXS for compound $\mathbf{C_{12}C_1C_4}$ at -10 °C

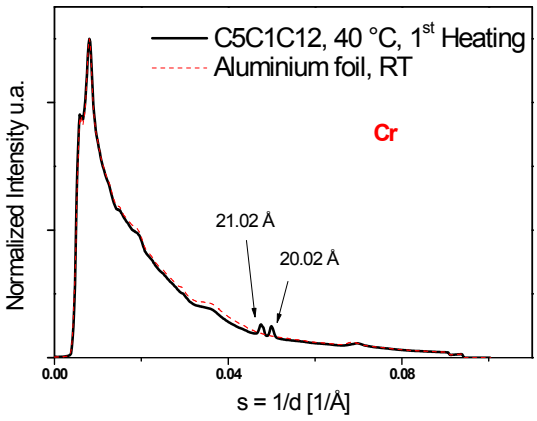

Figure S74: SAXS for compound $\mathbf{C_{12}C_1C_5}$ at 40 °C

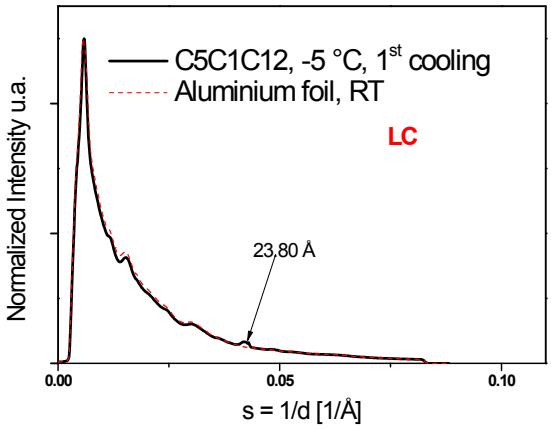

Figure S75: SAXS for compound $\mathbf{C_{12}C_1C_5}$ at -5 °C

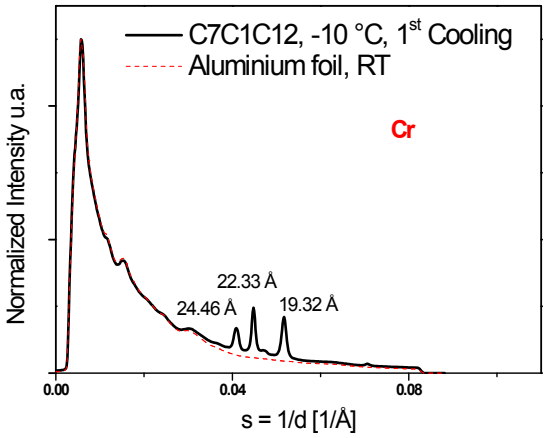

Figure S76: SAXS for compound $\mathbf{C_{12}C_1C_7}$ at -10 °C

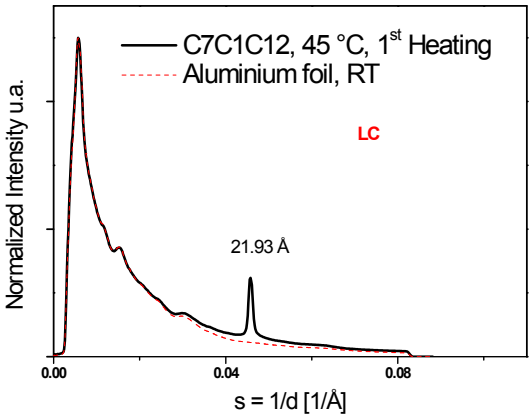

Figure S77: SAXS for compound $\mathbf{C_{12}C_1C_7}$ at 45 °C

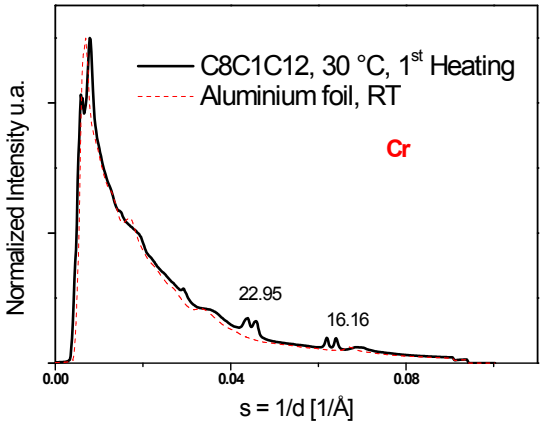

Figure S78: SAXS for compound $\mathbf{C_{12}C_1C_8}$ at 30 °C

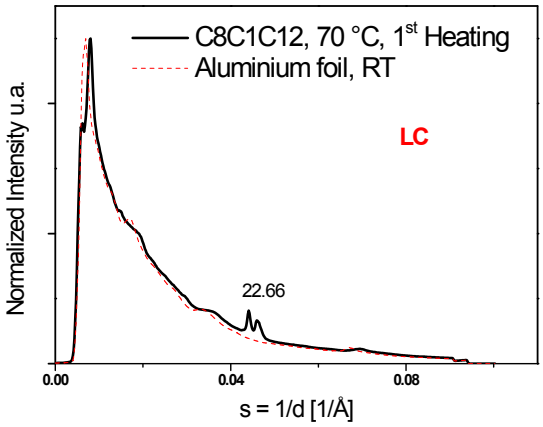

Figure S79: SAXS for compound $\mathbf{C_{12}C_1C_2}$ at 70 °C

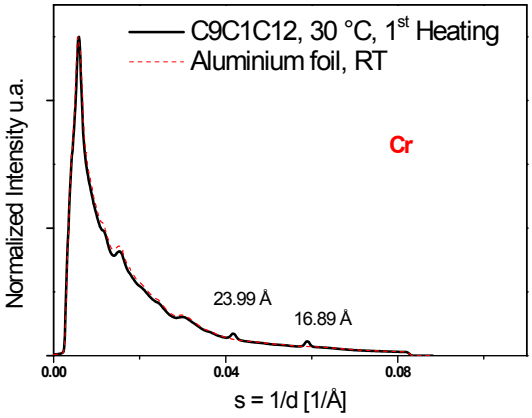

Figure S80: SAXS for compound $\mathbf{C_{12}C_1C_9}$ at 30 °C

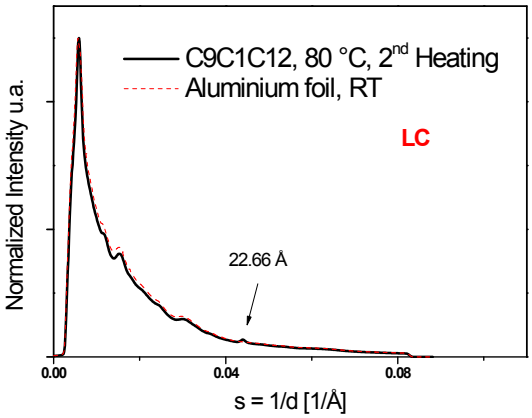

Figure S81: SAXS for compound $\mathbf{C_{12}C_1C_9}$ at 80 °C

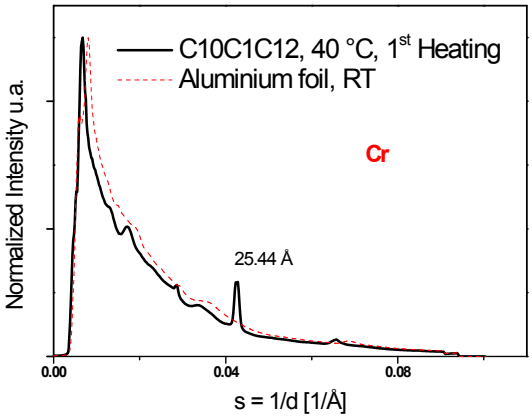

Figure S82: SAXS for compound $\mathbf{C_{12}C_1C_{10}}$ at 40 °C

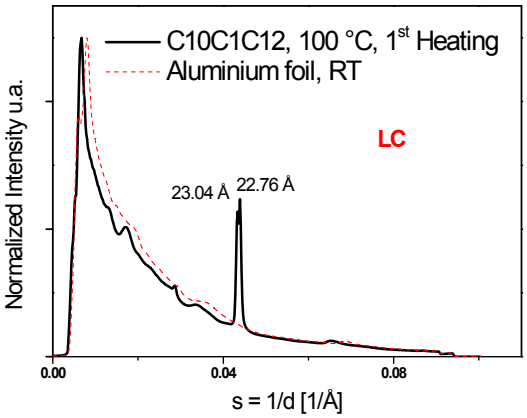

Figure S83: SAXS for compound $\mathbf{C_{12}C_1C_{10}}$ at 100 °C

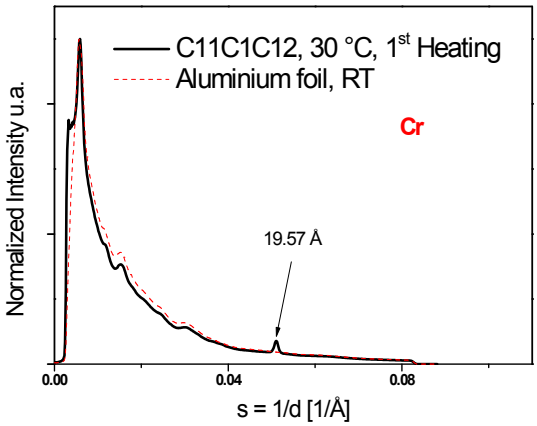

Figure S84: SAXS for compound $\mathbf{C_{12}C_1C_{11}}$ at 30 °C

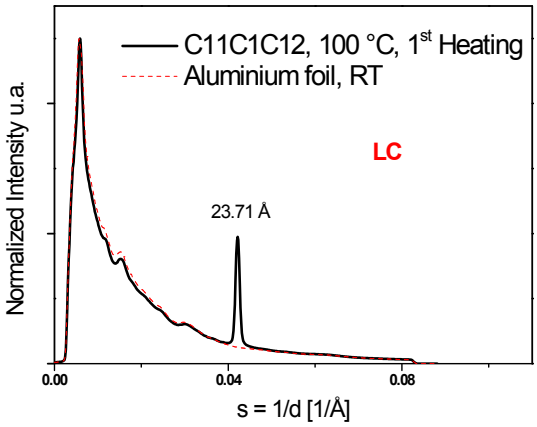

Figure S85: SAXS for compound $\mathbf{C_{12}C_1C_{11}}$ at 100 °C

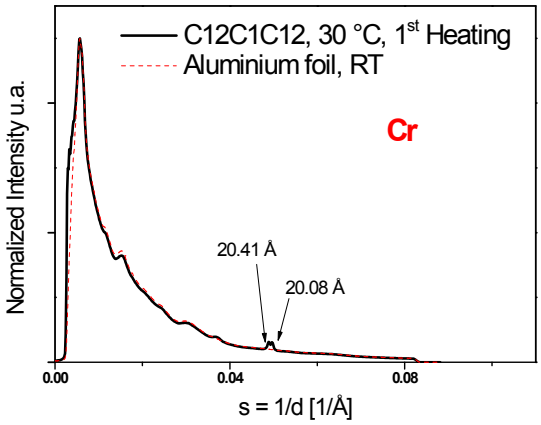

Figure S86: SAXS for compound $\mathbf{C_{12}C_1C_{12}}$ at 30 °C

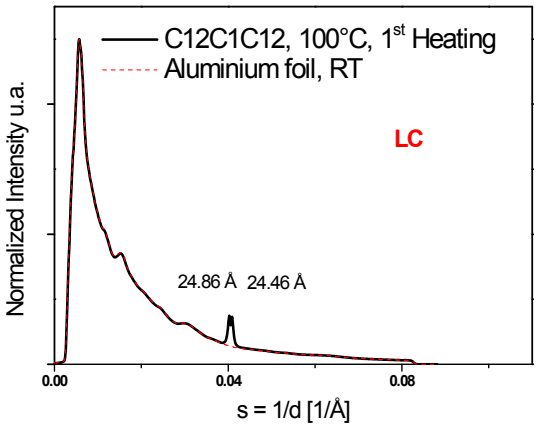

Figure S87: SAXS for compound $\mathbf{C_{12}C_1C_{12}}$ at 100 °C

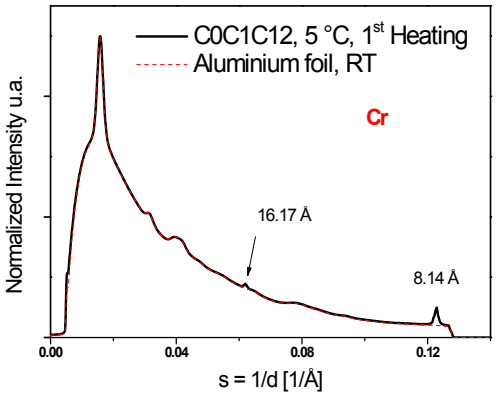

Figure S88: SAXS for compound $\mathbf{C_{12}C_1C_0}$ at 5 °C

VIII. Polarizing optical microscopy images

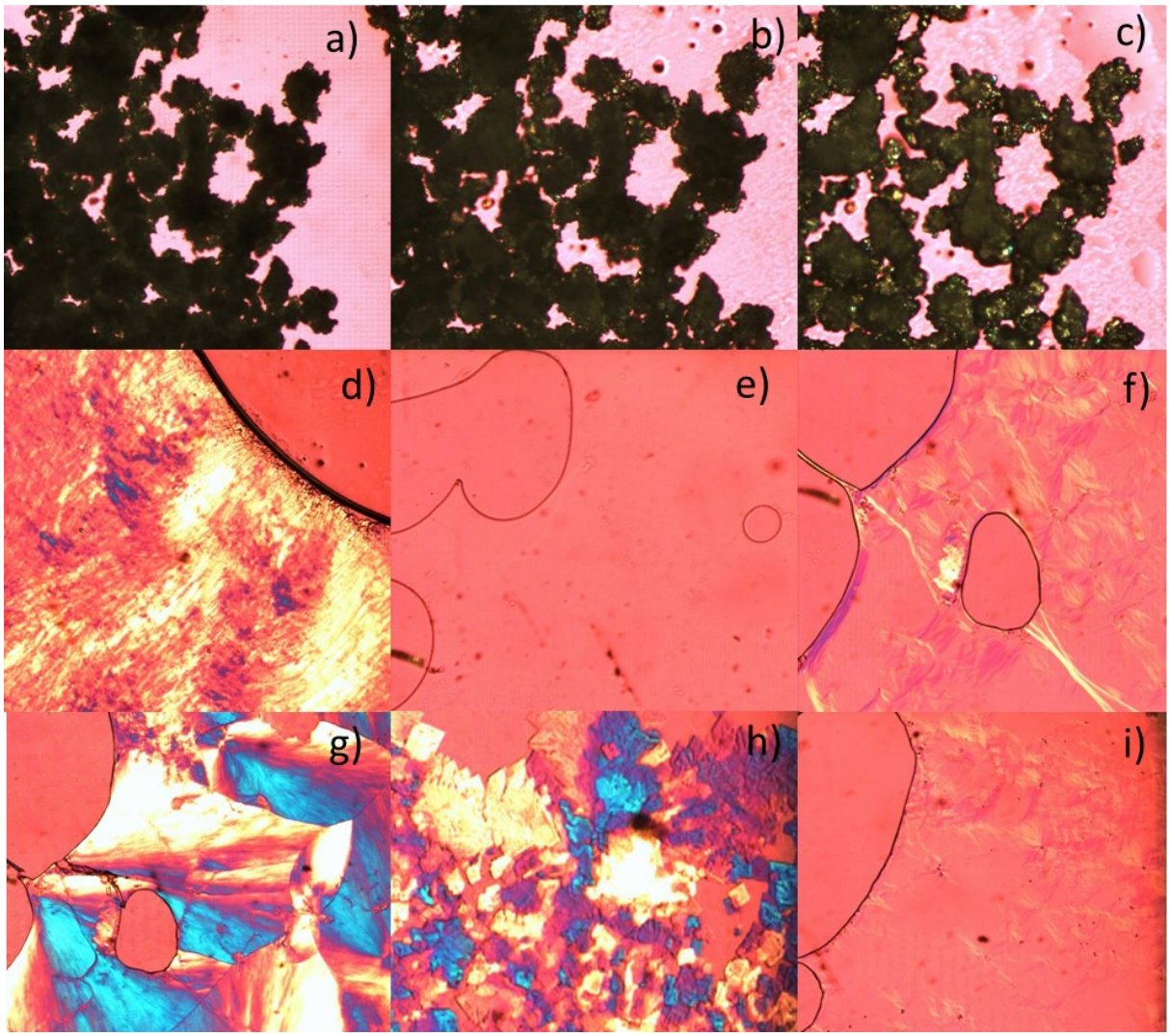

Figure S89: Polarizing optical microscopy images of $\mathbf{C_{12}C_1C_1}$: a) Cr at 40 °C (1st heating); b) Cr' at 65 °C (1st heating); c) Cr" at 75 °C (1st heating); d) SmA at 100 °C (1st heating): e) Liso at 160°C (1st heating); f) SmA at 100 °C (1st cooling); g) Cr' at 20 °C (1st cooling); h) Cr at 50 °C (2nd heating); i) SmA at 100 °C (2nd heating)

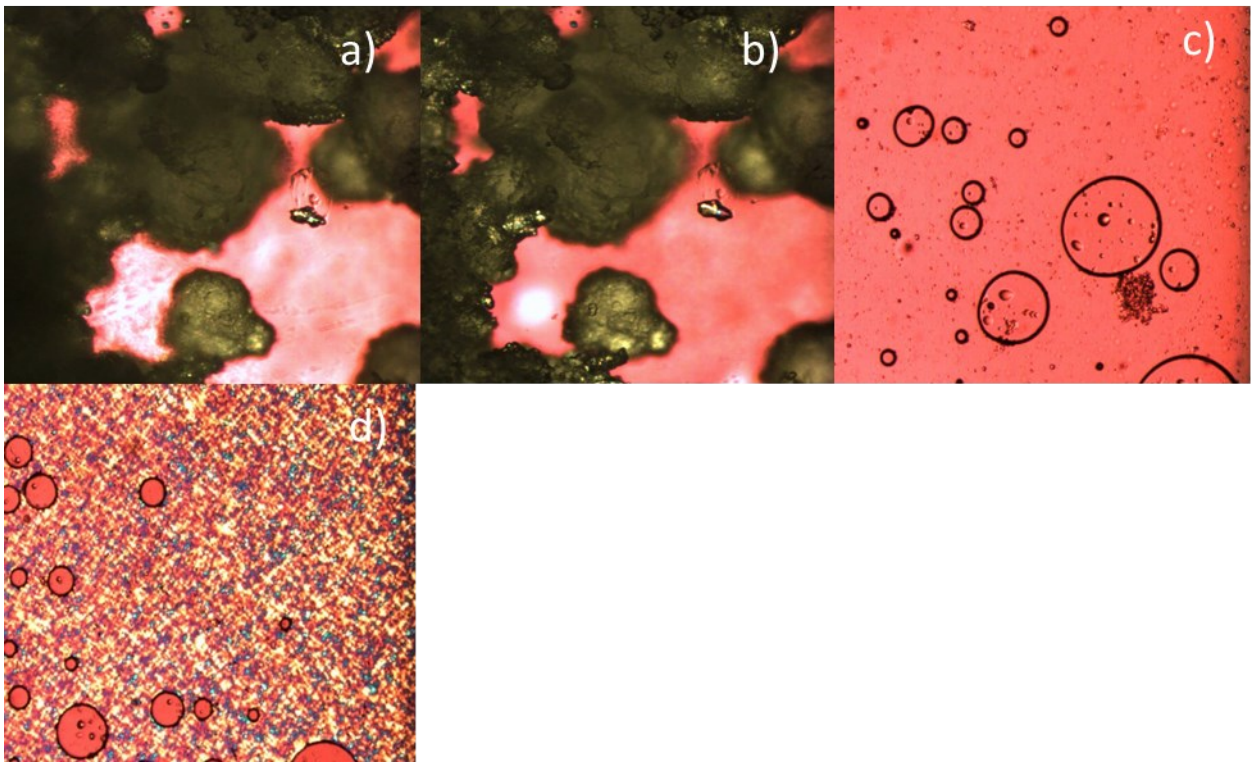

Figure S90: Polarizing optical microscopy images of **$C_{12}C_1C_2$**: a) Cr at -20 °C (1st heating); b) Cr' at 0 °C (1st heating); c) L_{iso} at 80 °C (1st heating); d) Sm at -10 °C (1st cooling)

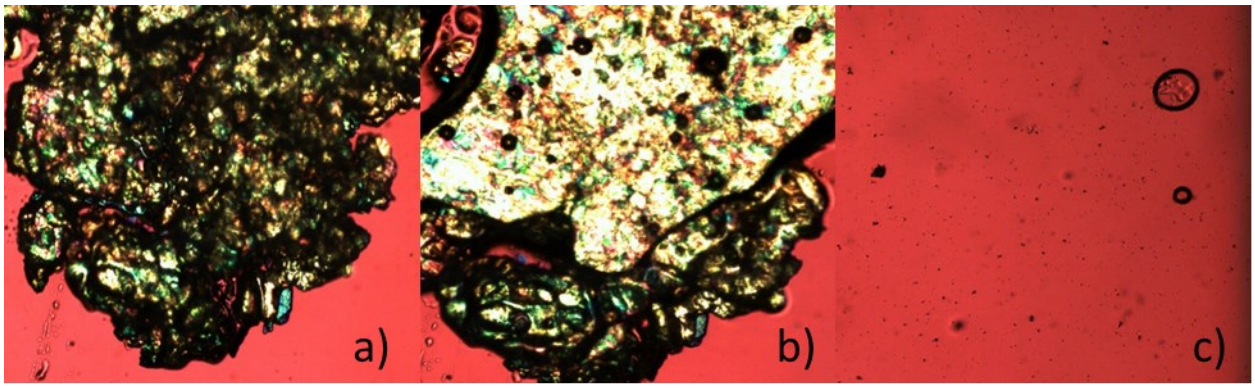

Figure S91: Polarizing optical microscopy images of **$C_{12}C_1C_3$**: a) Cr at 0 °C (1st heating); b) Cr→SmA at 25 °C (1st heating); c) L_{iso} at 60 °C (1st heating)

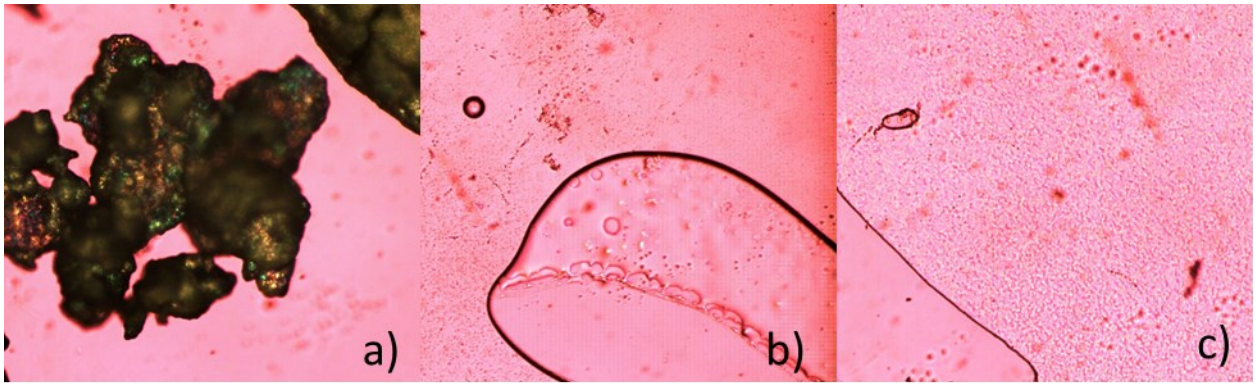

Figure S92: Polarizing optical microscopy images of $\mathbf{C_{12}C_1C_4}$: a) Cr at 30 °C (1st heating); b) L_{iso} at 60 °C (1st heating); c) Cr at 20 °C (2nd heating)

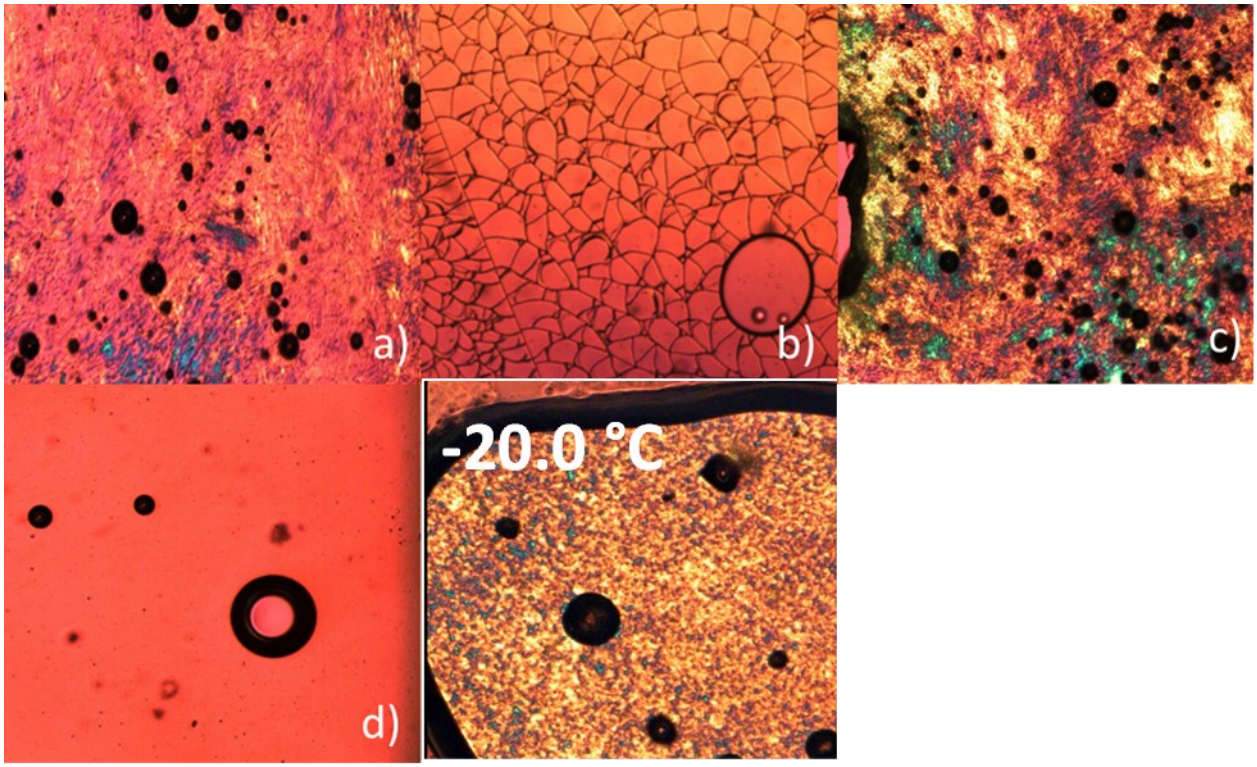

Figure S93: Polarizing optical microscopy images of $\mathbf{C_{12}C_1C_5}$: a) SmA at -45 °C (1st heating); b) Cr at 5 °C (1st heating); c) SmA at 30 °C (1st heating); d) L_{iso} at 70 °C (1st heating), SmA at -20°C

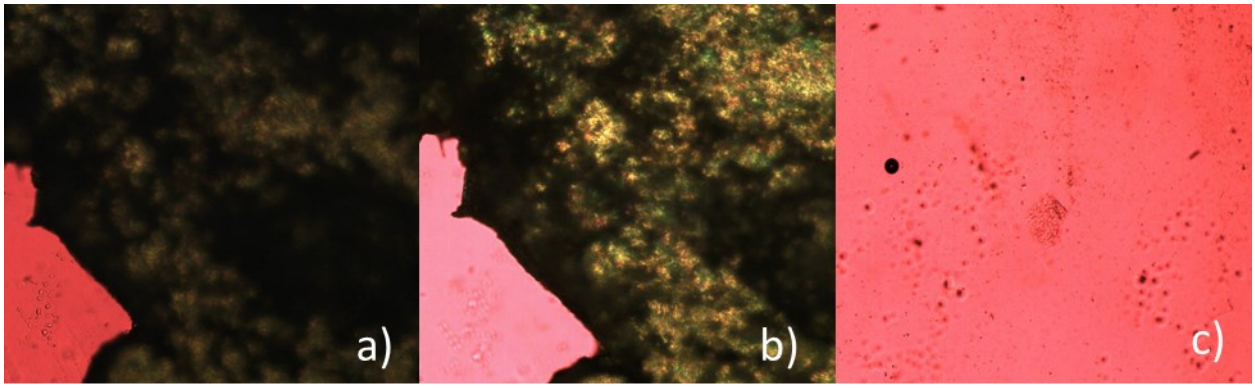

Figure S94: Polarizing optical microscopy images of **$C_{12}C_1C_6$**: a) Cr at -20 °C (1st heating); b) Cr' at 0 °C (1st heating); c) L_{iso} at 60 °C (1st heating)

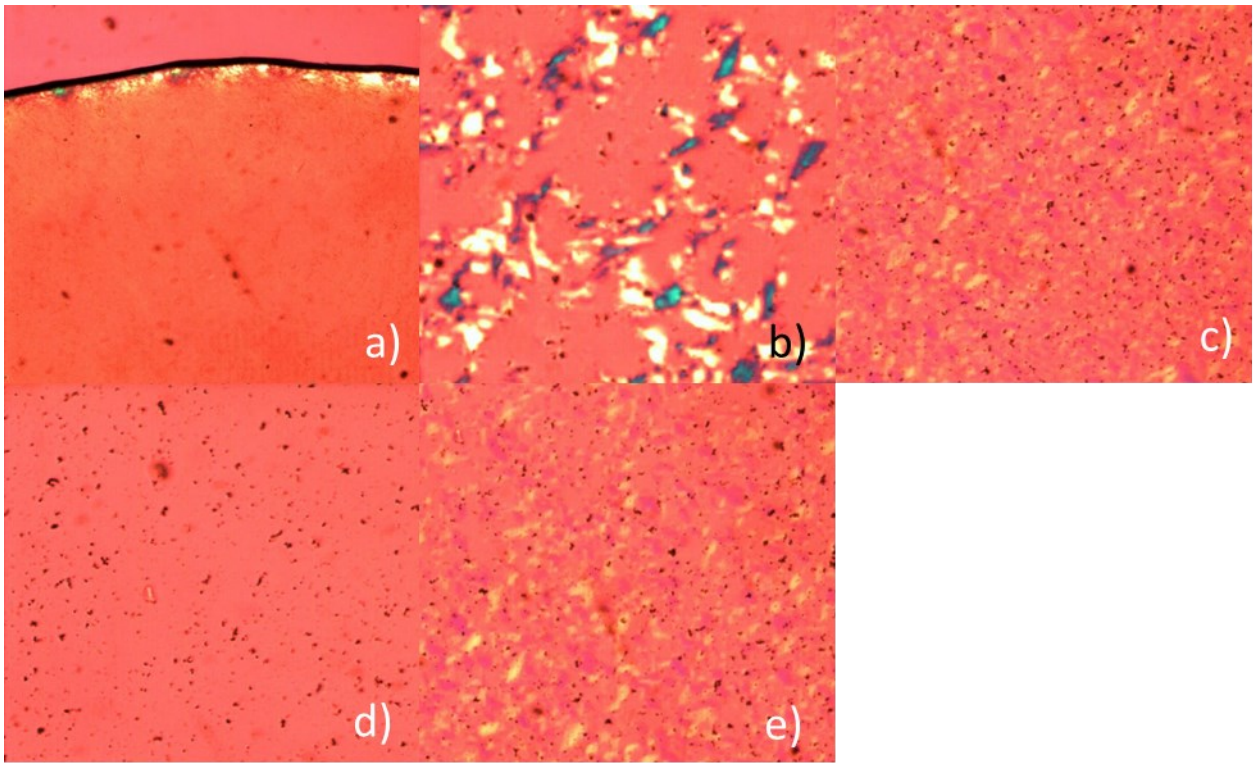

Figure S95: Polarizing optical microscopy images of **$C_{12}C_1C_7$**: a) SmC at -20 °C (1st heating); b) Cr at -2 °C (1st heating); c) SmC at 20 °C (1st heating); d) L_{iso} at 95 °C (1st heating); e) SmC at 40 °C (1st cooling)

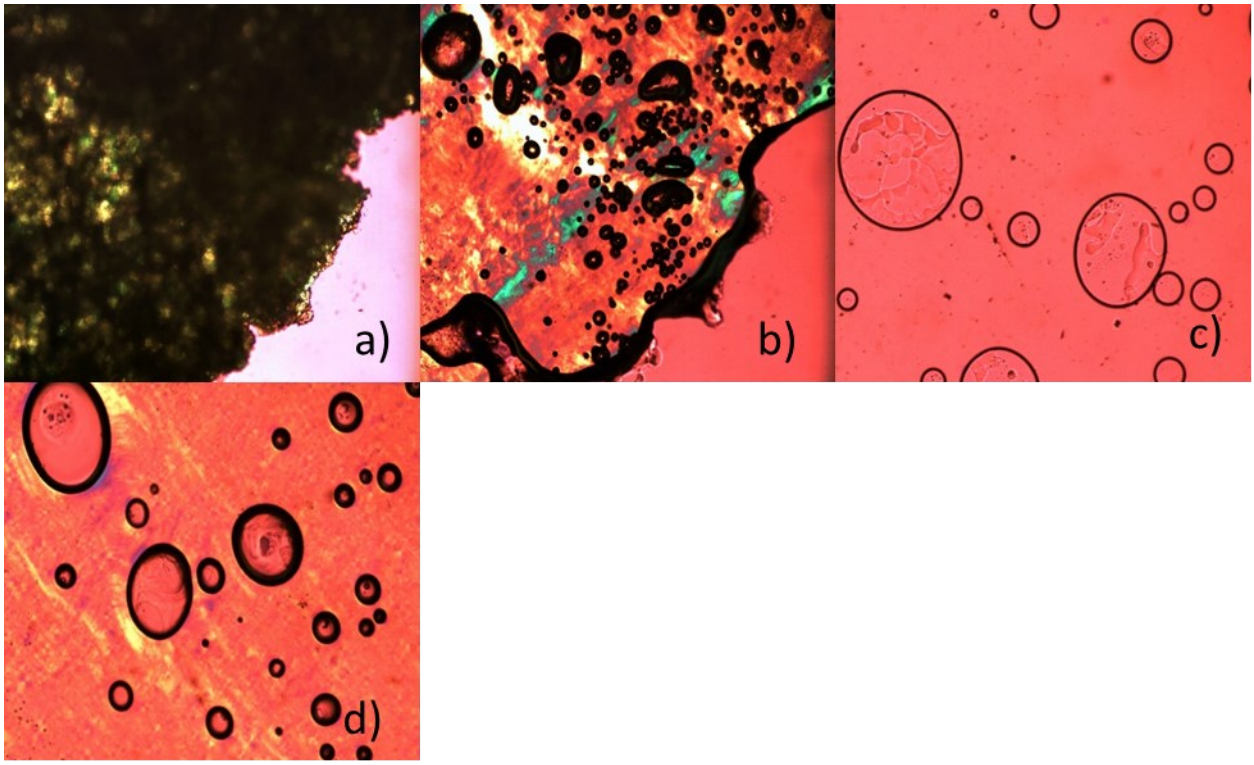

Figure S96: Polarizing optical microscopy images of **$C_{12}C_1C_8$**: a) Cr at 20°C (1st heating); b) SmC at 60°C (1st heating); c) L_{iso} at 120°C (1st heating); d) SmC at 85°C (1st cooling)

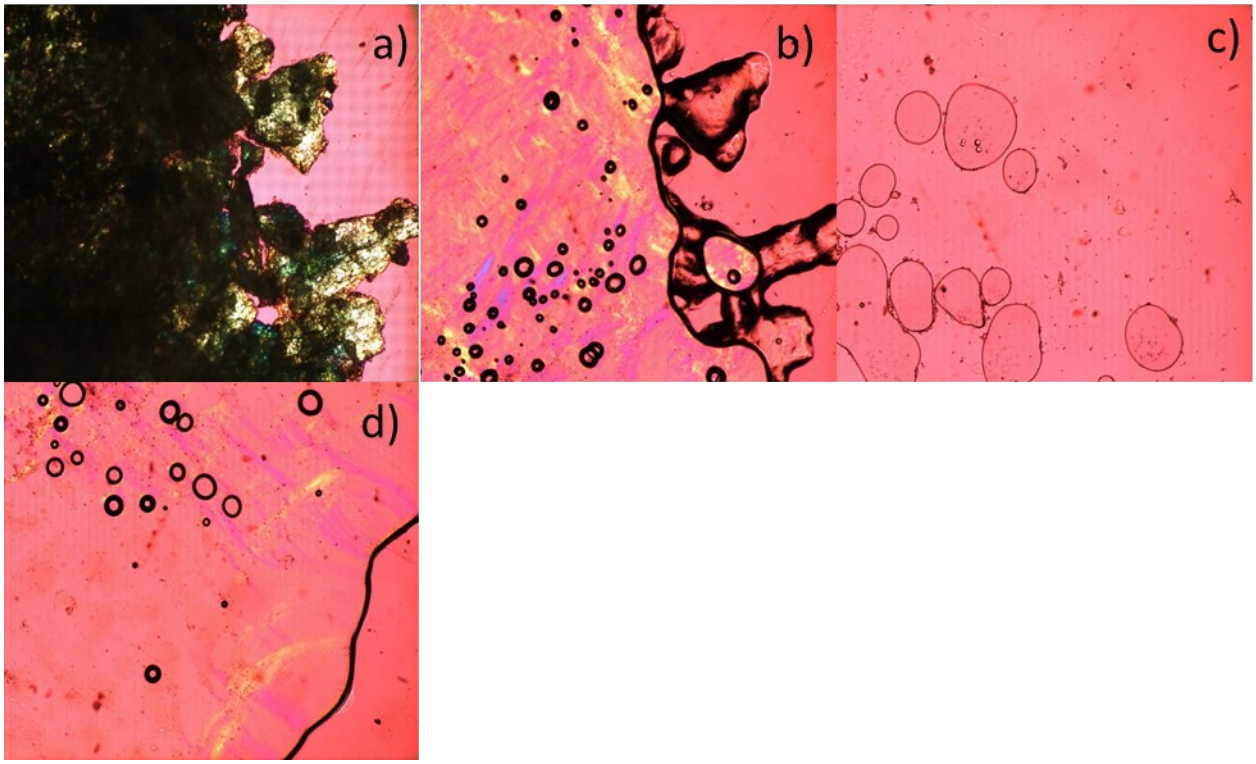

Figure S97: Polarizing optical microscopy images of **$C_{12}C_1C_9$**: a) Cr at 20 °C (1st heating); b) SmC at 70 °C (1st heating); c) L_{iso} at 135 °C (1st heating); d) SmC at 115 °C (1st cooling)

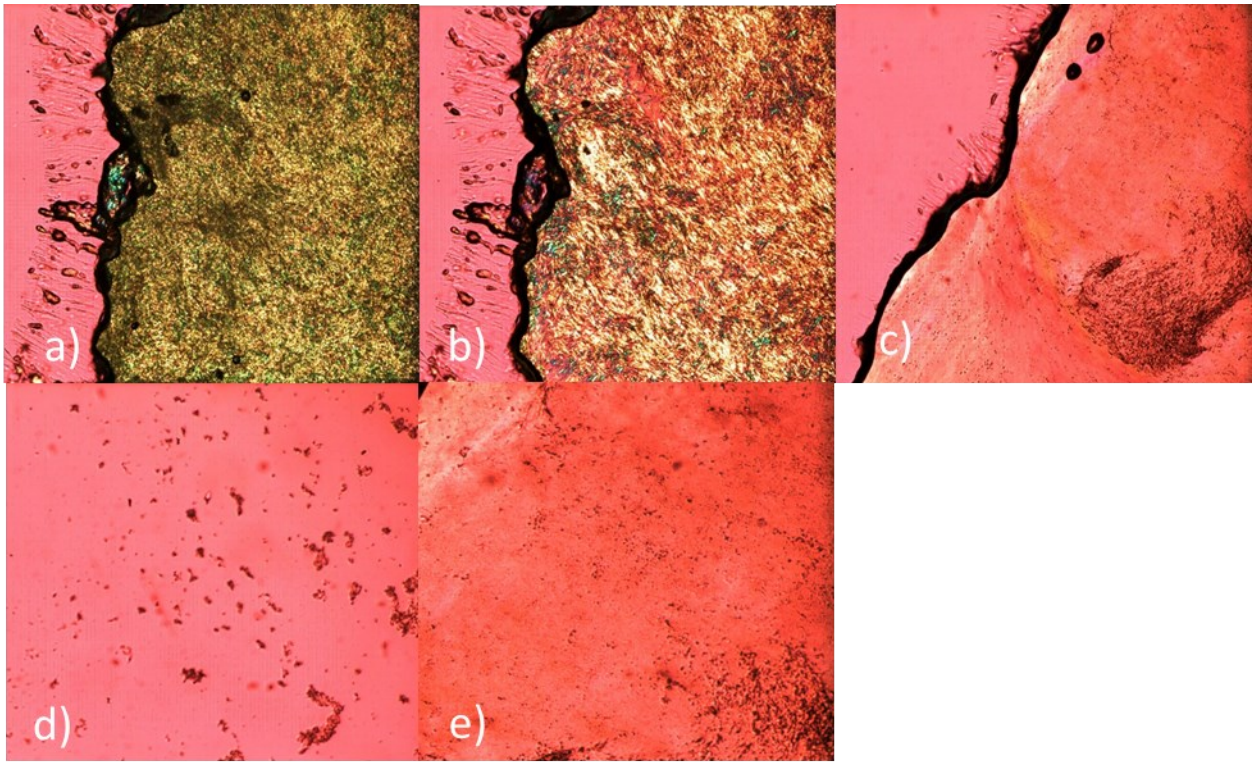

Figure S98: Polarizing optical microscopy images of **$C_{12}C_1C_{10}$**: a) Cr at -45 °C (1st heating); b) Cr' at -22 °C (1st heating); c) SmC at 90 °C (1st heating); d) L_{iso} at 155 °C (1st heating); e) SmC at 135 °C (1st cooling)

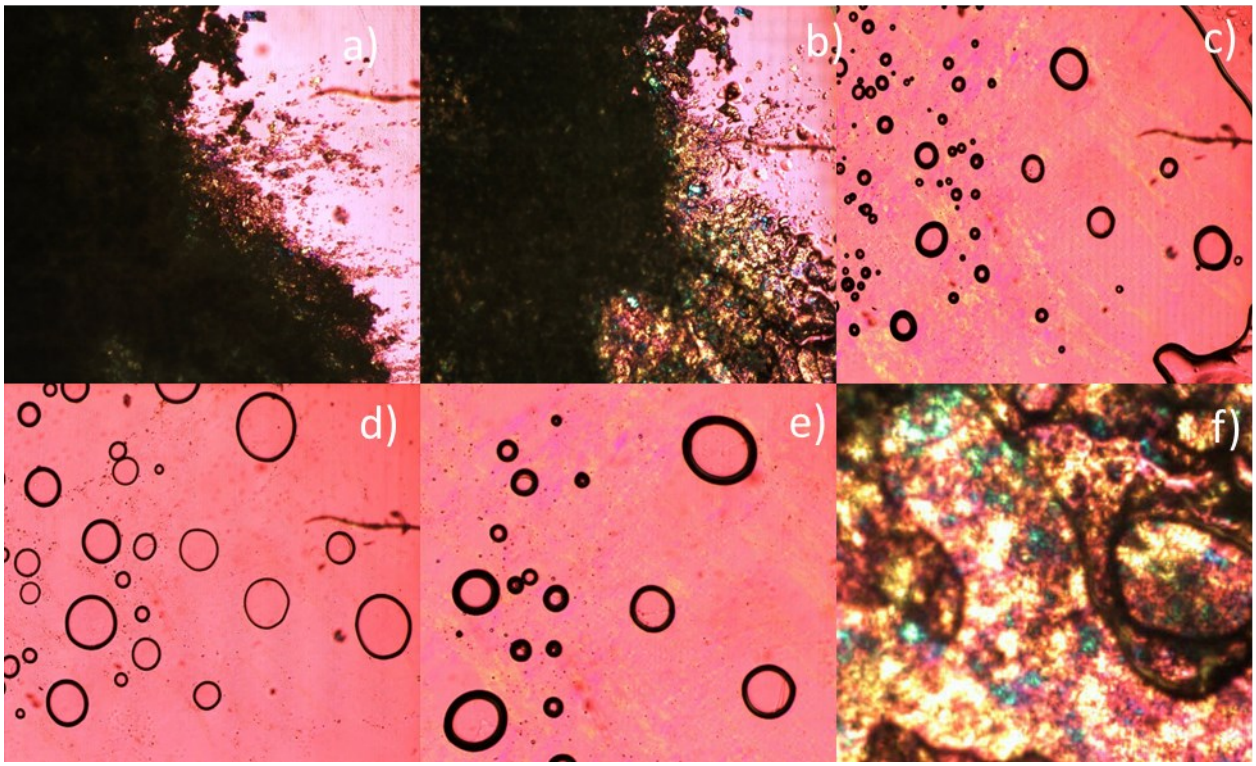

Figure S99: Polarizing optical microscopy images of **$C_{12}C_1C_{11}$**: a) Cr at -30 °C (1st heating); b) Cr' at 10 °C (1st heating); c) SmC at 80 °C (1st heating); d) L_{iso} at 165 °C (1st heating); e) SmC at 145 °C (1st cooling); f) Cr' at -35 °C (1st cooling)

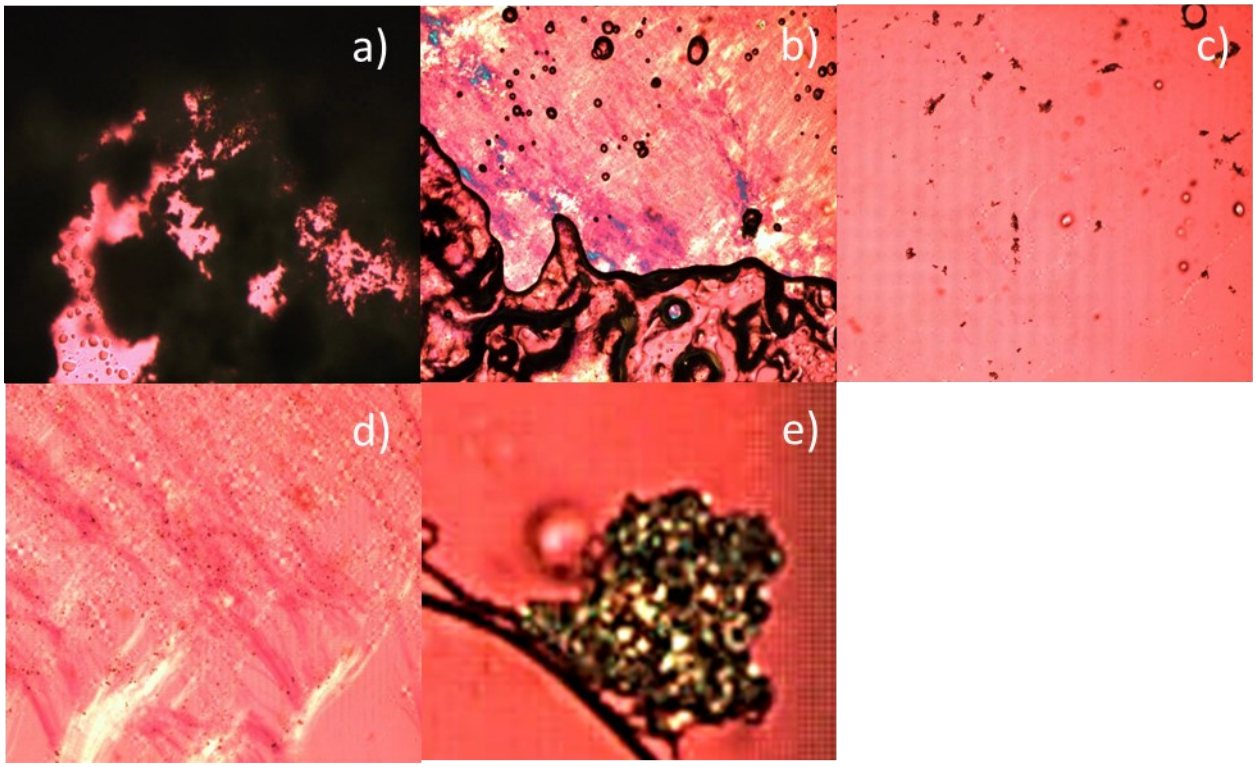

Figure S100: Polarizing optical microscopy images of $\mathbf{C_{12}C_1C_{12}}$: a) Cr at -20 °C (1st heating); b) SmC at 70 °C (1st heating); c) L_{iso} at 175 °C (1st heating); d) SmC at 150 °C (1st cooling); e) Cr' at 10 °C (2nd heating)

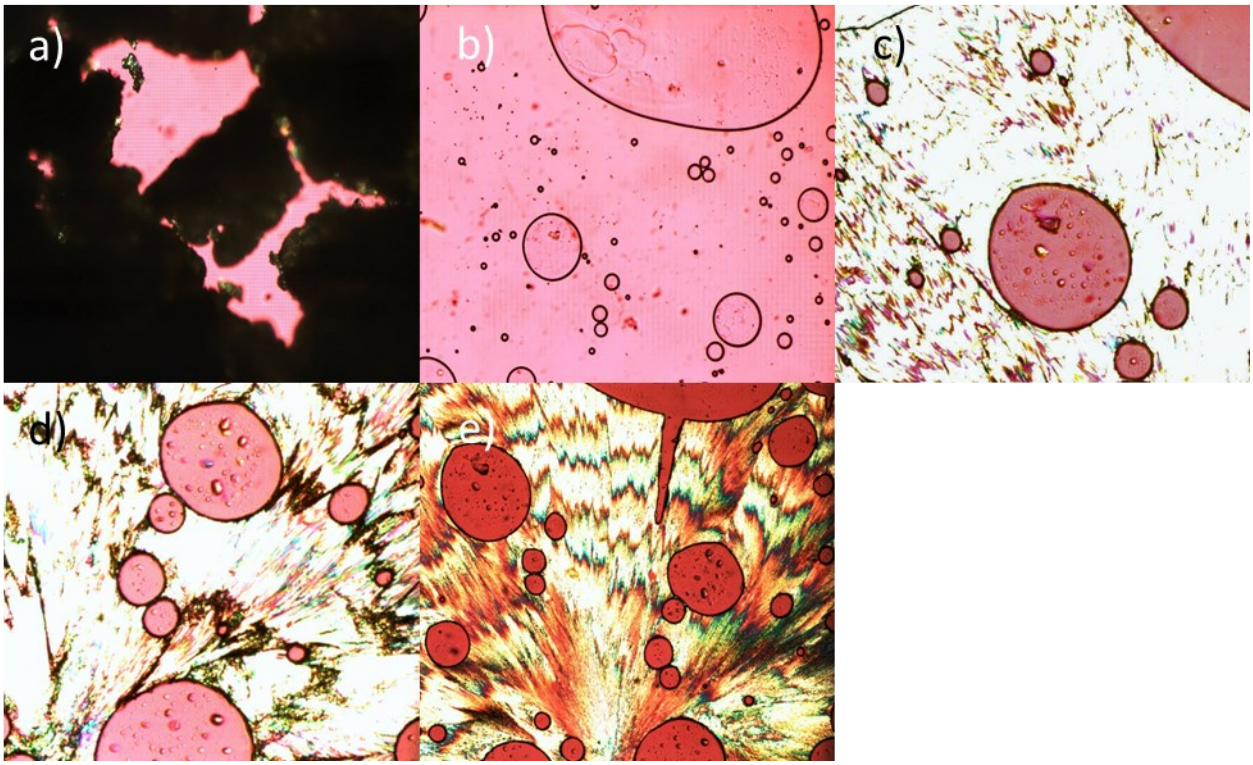

Figure S101: Polarizing optical microscopy images of $\mathbf{C_{12}C_1C_0}$: a) Cr at -15 °C (1st heating); b) L_{iso} at 110 °C (1st heating); c) Cr" at 52 °C (3rd cooling); d) Cr''' at 64 °C (3rd cooling); e) Cr' at 35 °C (3rd heating)

IX. References

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