SUPPORTING INFORMATION

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DOUBLE-BRØNSTED ACIDIC DEEP EUTECTIC SOLVENTS AND THEIR APPLICATIONS AS SOLVENTS AND CATALYSTS IN CHEMICAL TRANSFORMATIONS

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INDEX

Figure S1: Theoretical Melting curves of the molecules analyzed. ChCl = Choline chloride, TMG = trimethylglycine, L-histidine, glycine, L-proline, +CSA = (+)-camphorsulfonic acid, CA•H_2O = citric acid monohydrate, urea, pTSA •H_2O = p-toluensulphonic acid monohydrate, OA•H_2O = oxalic acid dihydrate, GA= glycolic acid, PAA = phenylacetic acid, thymol, L-menthol, Gly = glycerol, acetic acid, LA = DL-lactic acid, EG = ethylene glycol, 1,2-PD = 1,2-propanediol.

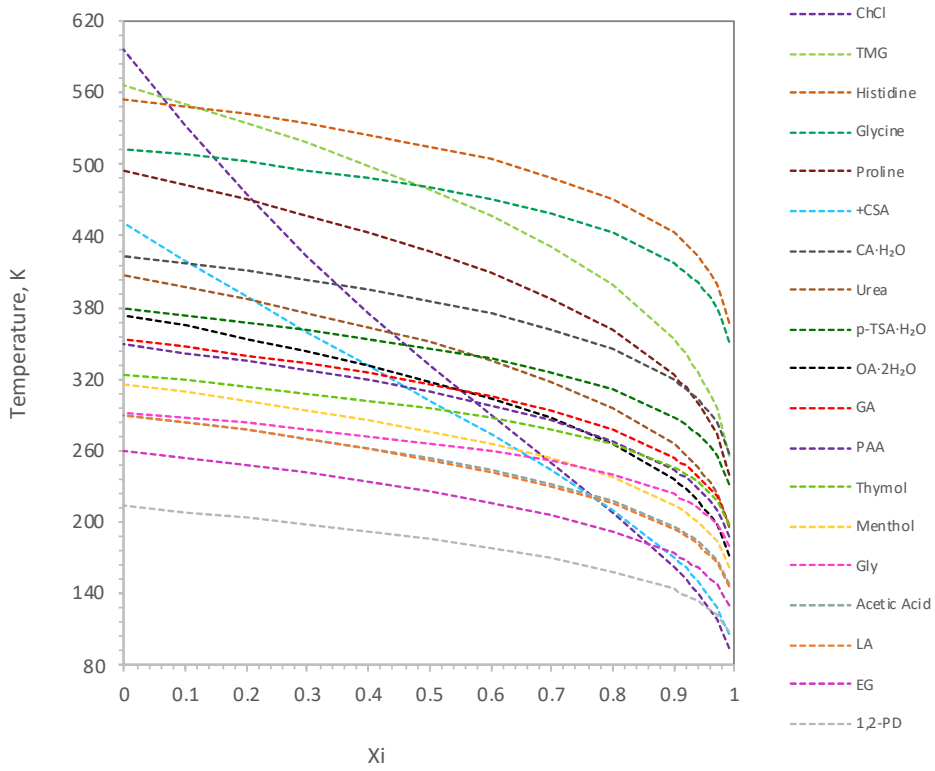
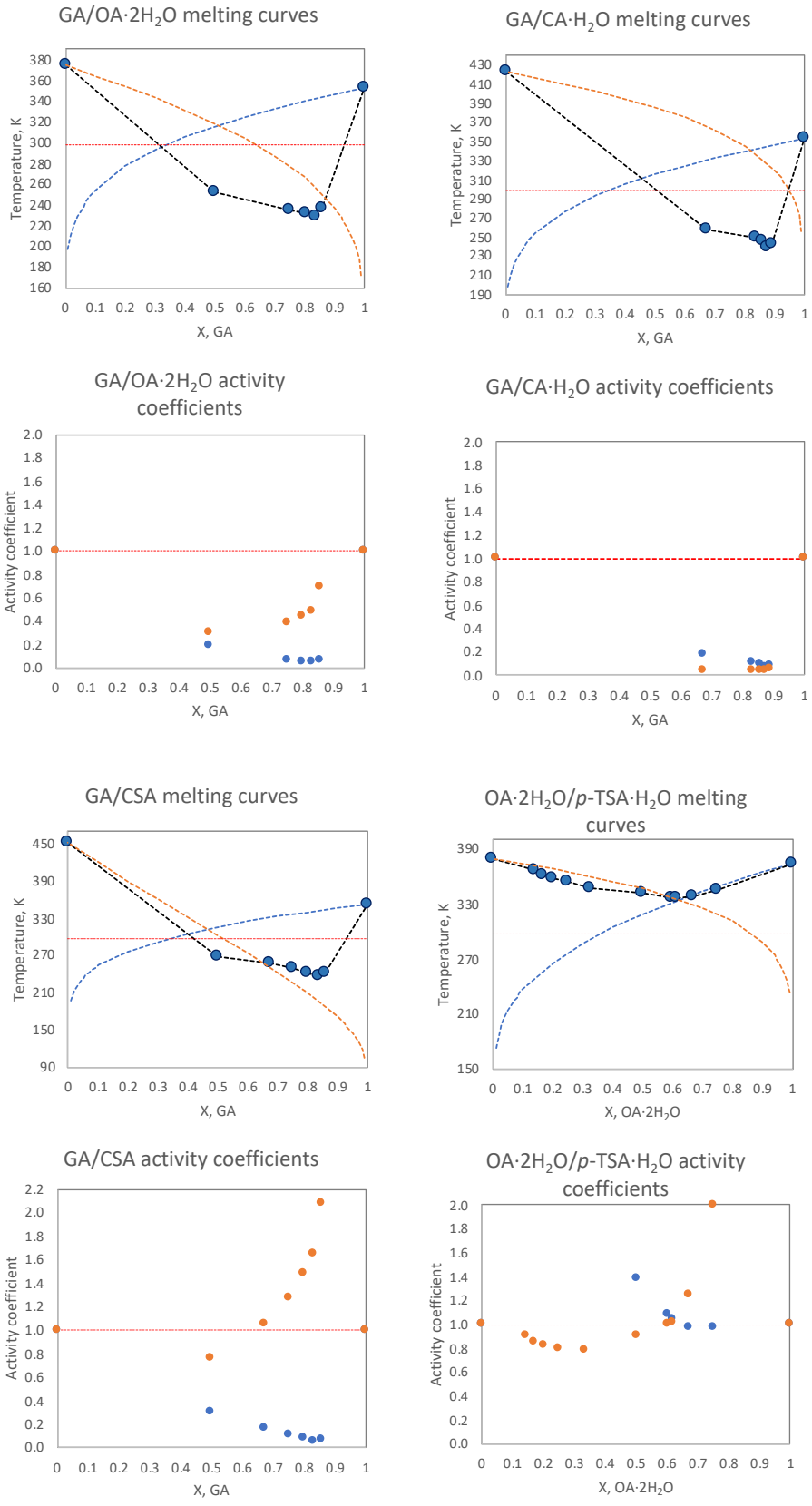
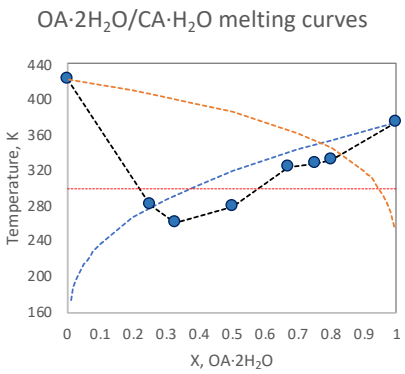
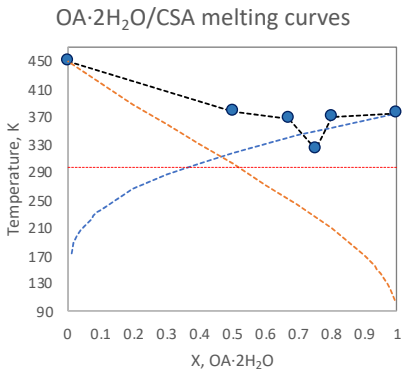
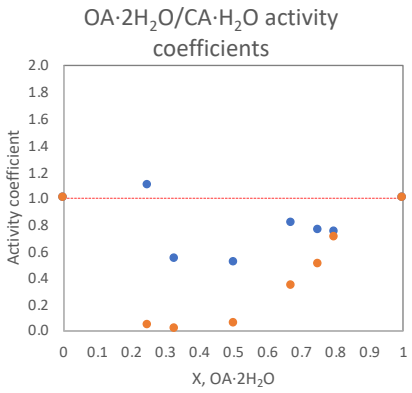


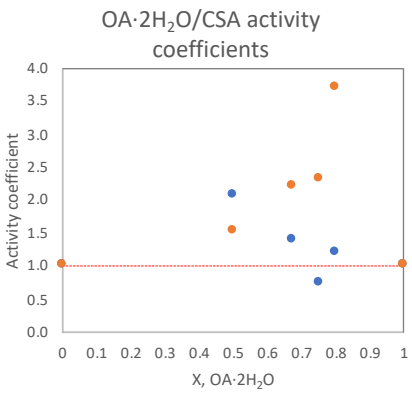
Figure S2: Experimental melting points / theoretical melting curves comparison and activity coefficients of the mixtures of the molecules analyzed. +CSA = (+)-camphorsulfonic acid, CA•H_2O = citric acid monohydrate, pTSA •H_2O = p-toluensulphonic acid monohydrate, OA•H_2O = oxalic acid dihydrate, GA= glycolic acid, PAA = phenylacetic acid, acetic acid, LA = DL-lactic acid.

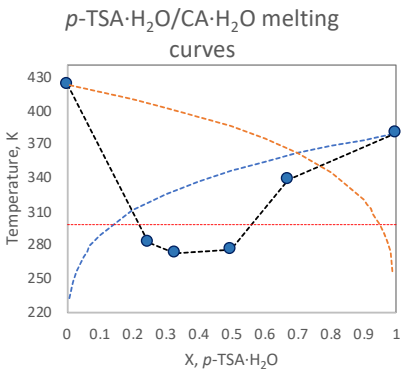


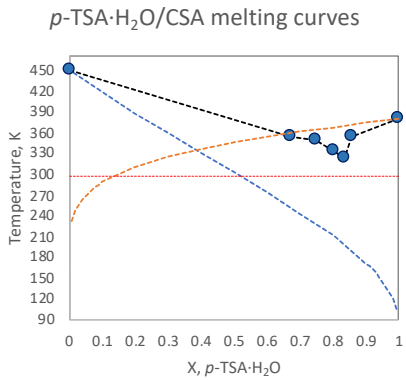

OA·2H2O/CA·H2O melting curves
Temperature, K
X, OA·2H2O


OA·2H2O/CSA melting curves
Temperature, K
X, OA·2H2O


OA·2H2O/CA·H2O activity coefficients
Activity coefficient
X, OA·2H2O


OA·2H2O/CSA activity coefficients
Activity coefficient
X, OA·2H2O


p-TSA·H2O/CA·H2O melting curves
Temperature, K
X, p-TSA·H2O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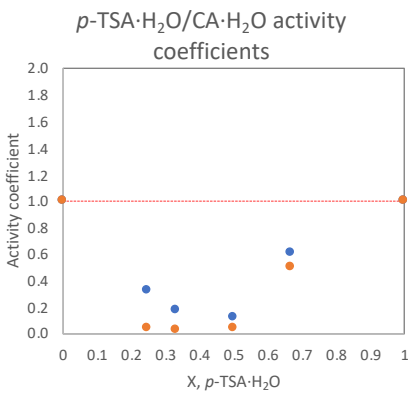
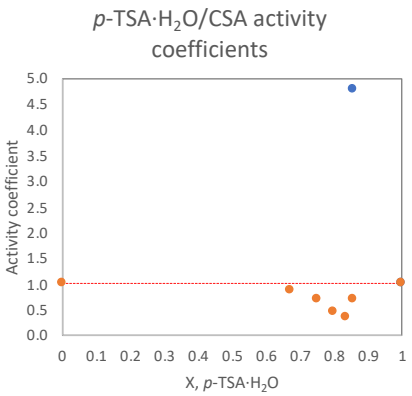
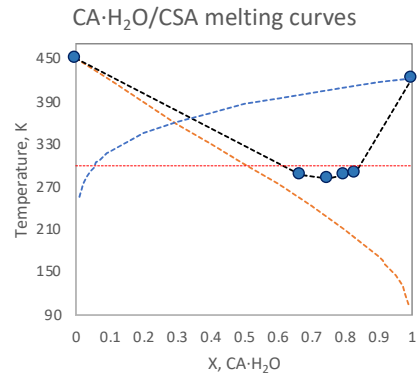
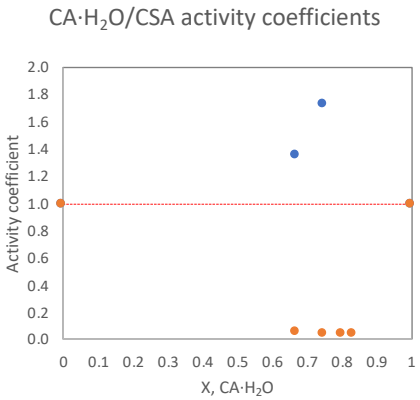
Temperature, K
X, p-TSA·H2O


p-TSA·H2O/CA·H2O activity coefficients
Activity coefficient
X, p-TSA·H2O


p-TSA·H2O/CSA activity coefficients
Activity coefficient
X, p-TSA·H2O


CA·H2O/CSA melting curves
Temperature, K
450
390
330
270
210
150
90
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1
X, CA·H2O


CA·H2O/CSA activity coefficients
Activity coefficient
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1
X, CA·H2O

S1: Claisen-Schmidt reaction detailed synthetic procedures and NMR data

1-phenyl-3-(p-tolyl)prop-2-en-1-one 3a. Synthesized from acetophenone **1a** (24 mg, 0.2 mmol) and 4-methylbenzaldehyde **2a** (29 mg, 0.24 mmol). Reaction time 3h. Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 98:2 $\rightarrow$ 95:5) yielded **3a** (40 mg, 90%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): 8.04 – 8.00 (m, 2H), 7.80 (d, J = 15.7, 1H), 7.59 – 7.47 (m, 5H), 7.49 (d, J = 15.7, 1H), 7.26 – 7.22 (m, 2H), 2.40 (s, 3H) ppm. Spectral data are in good agreement with literature values [1].

3-(4-fluorophenyl)-1-phenylprop-2-en-1-one 3b. Synthesized from acetophenone **1a** (24 mg, 0.2 mmol) and 4-fluorobenzaldehyde **2b** (30 mg, 0.24 mmol). Reaction time 2h. Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 95:5) yielded **3b** (43 mg, 95%) as a pale-yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): 8.03 − 8.01 (m, 2H), 7.78 (d, J = 16.0 Hz, 1H), 7.66 − 7.58 (m, 3H), 7.53 − 7.44 (m, 3H), 7.11 (t, J = 8.0 Hz, 2 H) ppm. Spectral data are in good agreement with literature values[1].

3-(3-chlorophenyl)-1-phenylprop-2-en-1-one 3c. Synthesized from acetophenone **1a** (24 mg, 0.2 mmol) and 3-chlorobenzaldehyde **2c** (34 mg, 0.24 mmol). Reaction time 3h. Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 9:1) yielded **3c** (37 mg, 76%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): 8.01 (t, J = 1.9 Hz, 1H), 7.92 (dt, J = 7.7, 1.4 Hz, 1H), 7.85 (d, J = 15.7 Hz, 1H), 7.71 – 7.64 (m, 2H), 7.58 (dt, J = 8.2, 1.4 Hz, 1H), 7.50 (d, J = 9.1 Hz, 1H), 7.46 (ddd, J = 5.6, 4.0, 1.7 Hz, 4H) ppm. Spectral data are in good agreement with literature values[2].

3-(2-bromophenyl)-1-phenylprop-2-en-1-one 3d. Synthesized from acetophenone **1a** (24 mg, 0.2 mmol) and 2-bromobenzaldehyde **2d** (44 mg, 0.24 mmol). Reaction time 2h. Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 98:2) yielded **3d** (57 mg, 99%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.69 – 7.66 (m, 1H), 7.61 – 7.56 (m, 2H), 7.49 – 7.41 (m, 6H), 7.36 (ddd, J = 7.9, 6.5, 2.7 Hz, 1H), 7.13 (d, J = 16.1 Hz, 1H) ppm. Spectral data are in good agreement with literature values[2].

1-phenyl-3-(pyridin-4-yl)prop-2-en-1-one 3e. Synthesized from acetophenone **1a** (24 mg, 0.2 mmol) and isonicotinaldehyde **2e** (27 mg, 0.24 mmol). Reaction time 3h. Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 9:1) yielded **3e** (24 mg, 56%) as a white solid. ^{1}H-NMR

(300 MHz, $CDCl_3$): 8.64 (d, J = 4.5 Hz, 2H), 7.98 − 7.95 (2H, m), 7.63 (d, J = 1.8 Hz, 2H), 7.56 − 7.41 (5H, m) ppm. Spectral data are in good agreement with literature values[3].

1-phenyl-3-(thiophen-2-yl)prop-2-en-1-one 3f. Synthesized from acetophenone **1a** (24 mg, 0.2 mmol) thiophene-2-carbaldehyde **2f** (26 mg, 0.24 mmol). Reaction time 2h. Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 4:1 $\rightarrow$ 1:1) yielded **3f** (20 mg, 48%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.94 − 7.92 (m, 2H), 7.87 (d, J = 16.0 Hz, 1H), 7.52 −7.48 (m, 1H), 7.44 − 7.41 (m, 2H), 7.34 (d, J = 4.0 Hz, 1H), 7.29 − 7.18 (m, 2H), 7.02 − 7.00 (m, 1H) ppm. Spectral data are in good agreement with literature values[1].

1-(4-fluorophenyl)-3-(p-tolyl)prop-2-en-1-one 3g. Synthesized from 1-(4-fluorophenyl)ethan-1-one **1f** (28 mg, 0.2 mmol) and 4-methylbenzaldehyde **2a** (29 mg, 0.24 mmol). Reaction time 3h. Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 98:2) yielded **3g** (37 mg, 77%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.99 − 7.89 (m, 2H), 7.70 (d, J = 15.6 Hz, 1H), 7.44 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 15.6 Hz, 1H), 7.22 − 6.99 (m, 4H), 2.29 (s, 3H) ppm. Spectral data are in good agreement with literature values[4].

1-(4-chlorophenyl)-3-(p-tolyl)prop-2-en-1-one 3h. Synthesized from 1-(4-chlorophenyl)ethan-1-one **1c** (31 mg, 0.2 mmol) and 4-methylbenzaldehyde **2a** (29 mg, 0.24 mmol). Reaction time 1h. Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 98:2 $\rightarrow$ 95:5) yielded **3h** (51 mg, 99%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.84 (d, J = 8.0 Hz, 2H), 7.68 (d, J = 16.0 Hz, 1H), 7.42 (d, J = 8.0 Hz, 2H), 7.35 − 7.30 (m, 3H), 7.10 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 16.0 Hz, 1H), 2.27 (s, 3H) ppm. Spectral data are in good agreement with literature values[4].

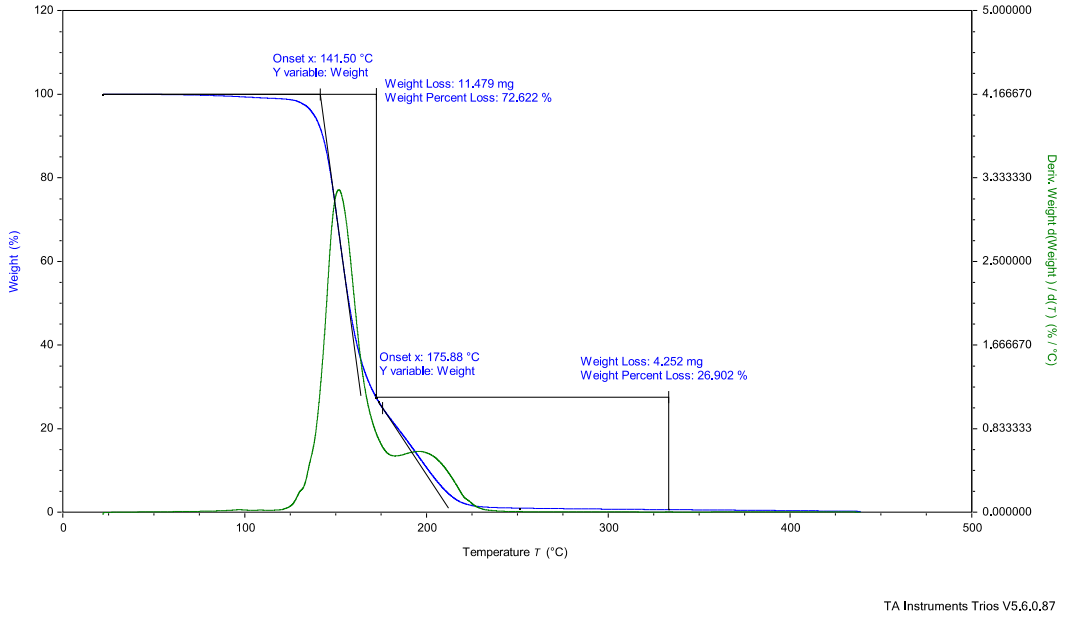
S2: Synthesis of indoles detailed synthetic procedures and NMR data

2-phenyl-1H-indole 4. Synthesized from 4-methyl-N-(2-(phenylethynyl)phenyl)benzenesulfonamide **4** (0.2 mmol, 70 mg) in GA/pTSA/H_2O, at 80 °C for 24h. Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 95:5) yielded **5** as a white solid (see Table 4 to confront yields). ^{1}H NMR (400 MHz, $CDCl_3$): 8.29 (s, 1H), 7.65 – 7.62 (m, 3H), 7.43 (t, J = 7.5 Hz, 2H), 7.38 (d, J = 7.5 Hz, 1H), 7.31 (t, J = 7.5 Hz, 1H), 7.19 (t, J = 7.5 Hz, 1H), 7.12 (t, J = 7.5 Hz, 1H), 6.82 (s, 1H) ppm. Spectral data are in good agreement with literature values[4].

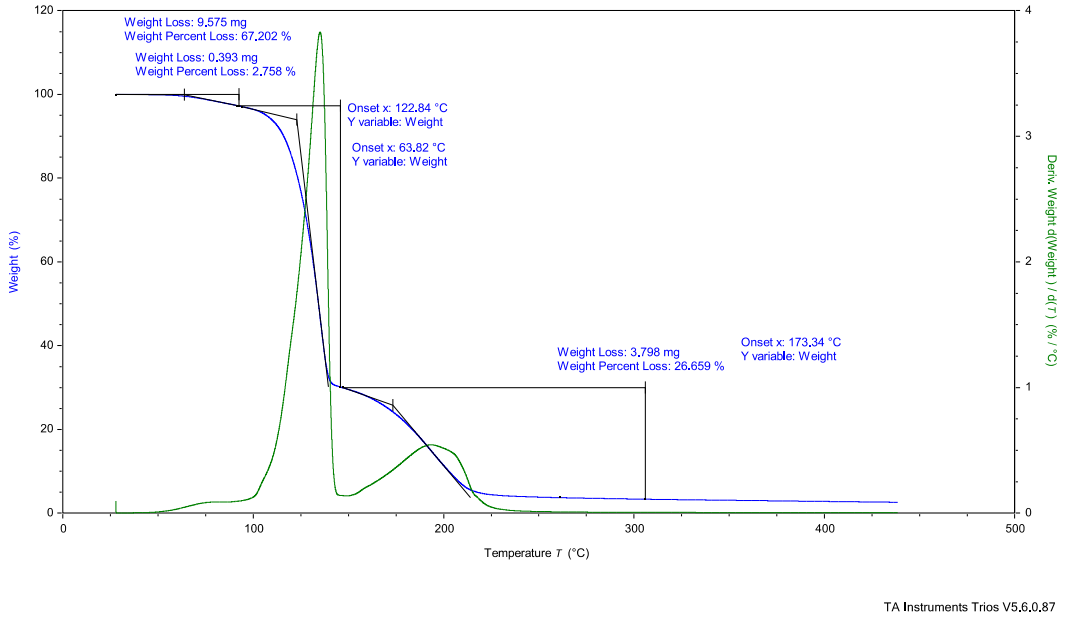
2-phenyl-1-tosyl-1H-indole 6. Synthesized from 4-methyl-N-(2-(phenylethynyl)phenyl) benzenesulfonamide **4** (0.2 mmol, 70 mg) in GA/+CSA/H_2O, at 80 °C for 24h. Purification of crude by column chromatography (SiO_2, Hex/EtOAc 95:5) yielded **6** (27%, 14 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): 8.29 (d, J = 8.6 Hz, 1H), 7.49-7.47 (m, 2H), 7.45 – 7.38 (m, 4H), 7.34-7.31 (m, 1H), 7.25 – 7.18 (m, 3H), 7.02 (d, J = 8.3 Hz, 2H), 6.52 (s, 1H), 2.26 (s, 3H) ppm. Spectral data are in good agreement with literature values[5].

Figure S4: Thermogravimetric analyses (TGA) of the DESs with the curve's derivative

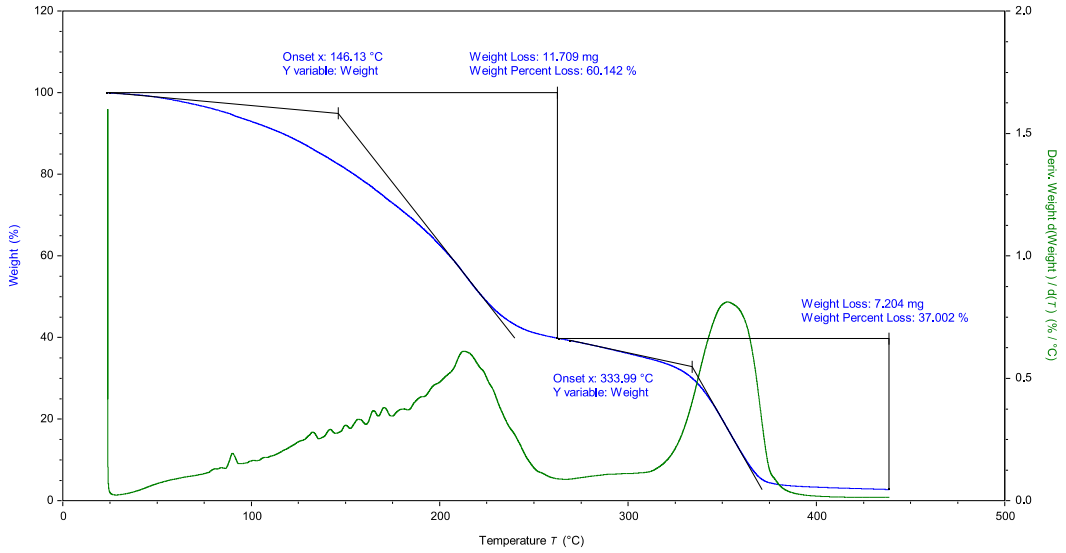
- CA·H_2O/+CSA



pTSA·H_2O/CA·H_2O



GA/+CSA/H_2O



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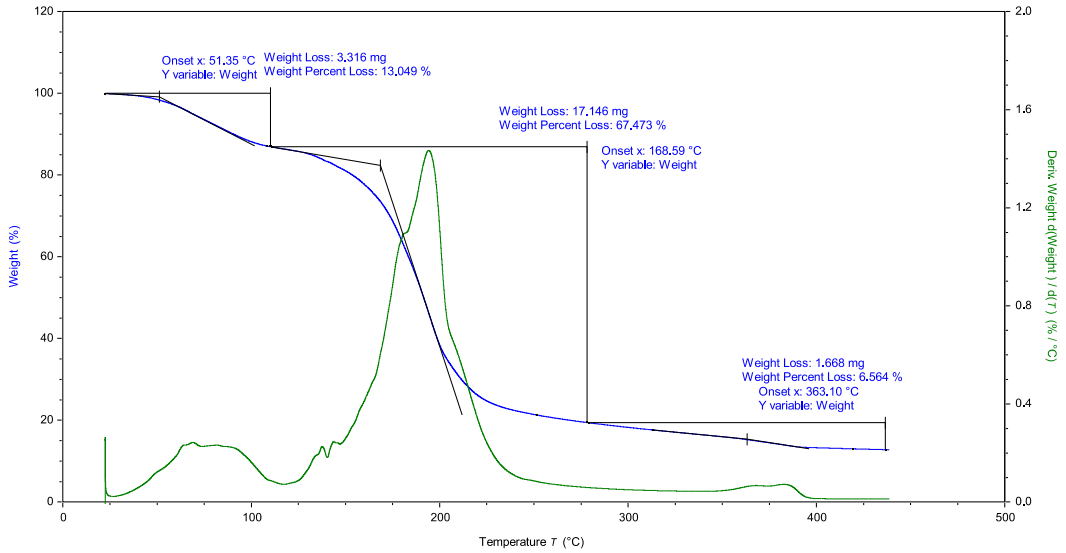
GA/pTSA/H_2O



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