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Supporting Information

Polymerisable squaramide receptors for anion binding and sensing

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Detailed analytical data

3-ethoxy-4-((4-vinylphenyl)amino)cyclobut-3-ene-1,2-dione (**2**): ^{1}H NMR (400 MHz, DMSO-d_6, δ): 10.76 (br, 1H, NH), 7.42 (m, 2H, Ar H), 7.31 (m, 2H, Ar H), 6.64 (dd, 1H, vinyl CH), 5.73 (dd, 1H, vinyl CH_2), 5.16 (dd, 1H, vinyl CH_2), 4.73 (q, 2H, CH_2), 1.38 (t, 3H, CH_3); ^{13}C NMR (100MHz, DMSO-d_6, δ): 184.2, 169.8, 138.1, 136.4, 133.5, 127.4, 120.1, 114.0, 70.2,16.2. ESI-MS *m/z*: 266.1 $[M+Na]^+$ (100%), 244.1 $[M+H]^+$ (19%); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{14}NO_3$, 244.0974; found, 244.0956.

3,4-bis((4-vinylphenyl)amino)cyclobut-3-ene-1,2-dione (**3**): ^{1}H NMR (400 MHz, DMSO-d_6, δ): 9.89 (br, 2H, NH), 7.44 (m, 8H, Ar H), 6.65 (dd, 2H, vinyl CH), 5.73 (dd, 2H, vinyl CH_2), 5.16 (dd, 2H, vinyl CH_2); ^{13}C NMR (100MHz, DMSO-d_6, δ): 182.1, 165.9, 138.6, 136.4, 132.8, 127.7, 119.1, 113.7. ESI-MS *m/z*: 339.2 $[M+Na]^+$, 317.2 $[M+H]^+$ (39.4%); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{20}H_{17}N_2O_2$, 317.1290; found, 317.1284.

3-(phenylamino)-4-((4-vinylphenyl)amino)cyclobut-3-ene-1,2-dione (**4**): ^{1}H NMR (400 MHz, DMSO-d_6, δ): 9.88 (br, 1H, NH), 9.83 (br, 1H, NH), 7.45 (m, 6H, Ar H), 7.36 (t, 2H, Ar H), 7.04 (t, 1H, Ar H), 6.65 (dd, 1H, vinyl CH), 5.73 (dd, 1H, vinyl CH_2), 5.16 (dd, 1H, vinyl CH_2); ^{13}C NMR (100MHz, DMSO-d_6, δ): 182.1, 166.2, 165.9, 139.0, 138.7, 136.4, 132.8, 130.0, 127.7, 123.9, 119.1, 119.0, 113.6. ESI-MS *m/z*: 289.0 $[M-H]^-$ (100%); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{15}N_2O_2$, 291.1134; found, 291.1131.

3-((3-nitrophenyl)amino)-4-((4-vinylphenyl)amino)cyclobut-3-ene-1,2-dione (**5**): ^{1}H NMR (400 MHz, DMSO-d_6, δ): 10.16 (br, 1H, NH), 9.96 (br, 1H, NH), 8.38 (s, 1H, Ar H), 7.84 (dd, 1H, Ar H), 7.75 (dd, 1H, Ar H), 7.40 (dd, 4H, Ar H), 6.65 (dd, 1H, vinyl CH), 5.73 (dd, 1H, vinyl CH_2), 5.16 (dd, 1H, vinyl CH_2); ^{13}C NMR (100MHz, DMSO-d_6, δ): 182.3, 166.5, 165.6, 162.8, 149.1, 140.5, 138.4, 136.4, 133.1, 131.1, 127.7, 125.0, 119.3, 117.9, 113.8, 113.4. ESI-MS *m/z*: 333.9 $[M-H]^-$ (100%); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{14}N_3O_4$, 336.0984; found, 336.0987.

3-((3,5-bis(trifluoromethyl)phenyl)amino)-4-((4-vinylphenyl)amino)cyclobut-3-ene-1,2-dione (**6**): ^{1}H NMR (400 MHz, DMSO-d_6, δ): 10.27 (s, 1H, NH), 10.03 (s, 1H, NH), 8.00 (s, 2H, Ar H), 7.67 (s, 1H, Ar H), 7.75 (dd, 1H, Ar H), 7.40 (dd, 4H, Ar H), 6.65 (dd, 1H, vinyl CH), 5.73 (dd, 1H, vinyl CH_2), 5.17 (dd, 1H, vinyl CH_2); ^{13}C NMR (100MHz, DMSO-d_6, δ): 183.3, 182.6, 166.8, 165.3, 162.8, 141.2, 138.3, 136.4, 133.2, 131.8 (q), 129.4, 128.7, 127.7, 125.0, 122.3, 119.4, 119.2, 116.0, 113.8. ESI-MS *m/z*: 424.9 $[M-H]^-$ (100%); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{20}H_{13}N_2O_2F_6$, 427.0881; found, 427.0886.

3-(benzylamino)-4-((4-vinylphenyl)amino)cyclobut-3-ene-1,2-dione (**7**): ^{1}H NMR (400 MHz, DMSO-d_6, δ): 9.66 (br, 1H, NH), 7.97 (br, 1H, NH), 7.10-7.50 (m, 9H, Ar H), 6.64 (dd, 1H, vinyl CH), 5.69 (dd, 1H, vinyl CH_2), 5.12 (dd, 1H, vinyl CH_2), 4.78 (s, 2H, CH_2); ^{13}C NMR (100MHz, DMSO-d_6, δ): 184.6, 180.9, 169.4, 164.0, 139.1, 139.0, 136.5, 132.2, 129.3, 128.2, 128.1, 127.7, 118.6, 116.0, 113.3. 47.8. ESI-MS *m/z*: 303.0 $[M-H]^-$ (100%); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{19}H_{17}N_2O_2$, 305.1290; found, 305.1288.

3-((3,5-bis(trifluoromethyl)benzyl)amino)-4-((4-vinylphenyl)amino)cyclobut-3-ene-1,2-dione (**8**): ^{1}H NMR (400 MHz, DMSO-d_6, δ): 9.78 (br, 1H, NH), 8.09 (s, 2H, Ar H), 8.02 (s, 1H, Ar H), 8.00 (br, 1H, NH), 7.34-7.45 (dd, 4H, Ar H), 6.64 (dd, 1H, vinyl CH), 5.69 (dd, 1H, vinyl CH_2), 5.12 (dd, 1H, vinyl CH_2), 4.97 (s, 2H, CH_2); ^{13}C NMR (100MHz, DMSO-d_6, δ): 184.6, 181.3, 169.4, 164.5, 142.7, 139.0, 136.5, 132.3, 131.0 (q), 129.2, 127.7, 125.2, 122.5, 121.8, 118.8, 113.3. 46.7. ESI-MS *m/z*: 439.9 $[M-H]^-$ (100%); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{21}H_{15}N_2O_2F_6$, 441.1038; found, 441.1030.

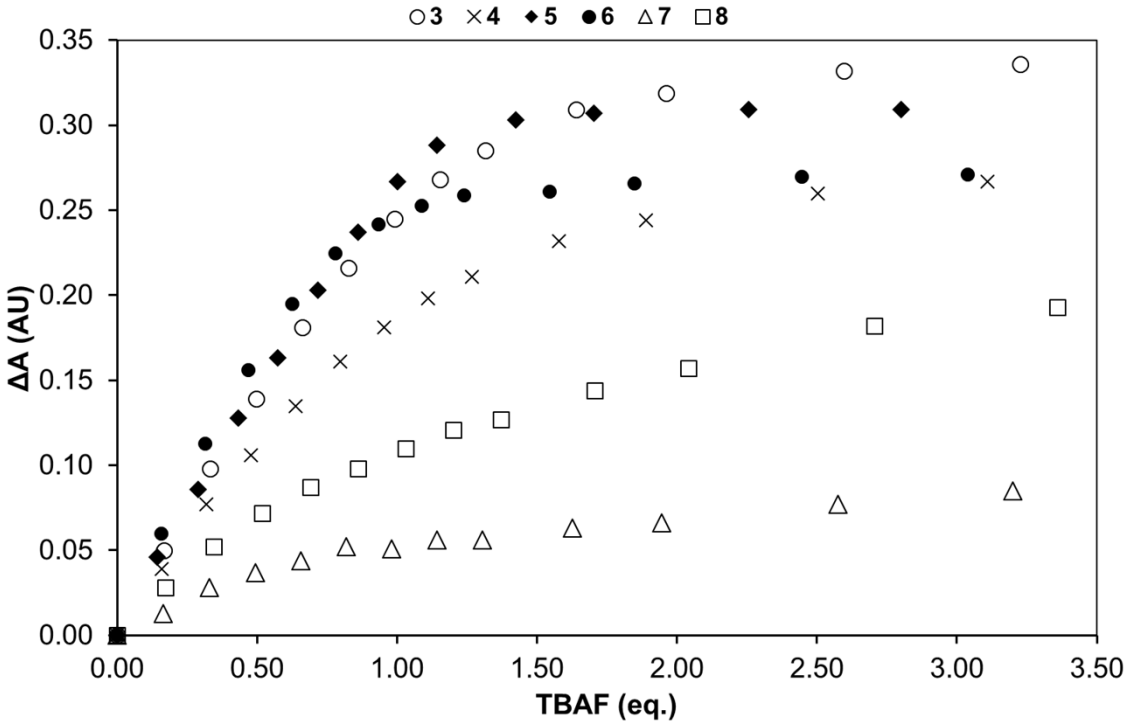


Figure S1. Overlay of binding isotherms obtained by UV-Vis titration of the synthesised receptors (1.0×10^{-5} mol L^{-1}) and TBAF, in DMSO. Plotted results correspond to absorbance values at 397 nm.

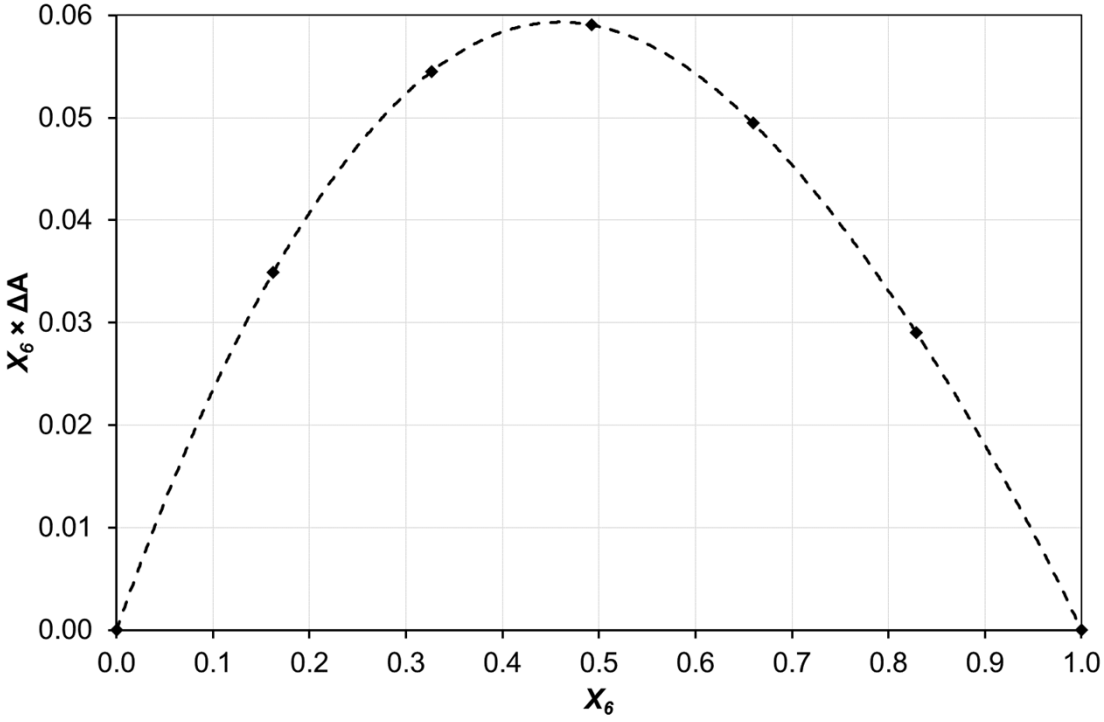


Figure S2. Job plot for the association of squaramide monomer **6** and TBAF.

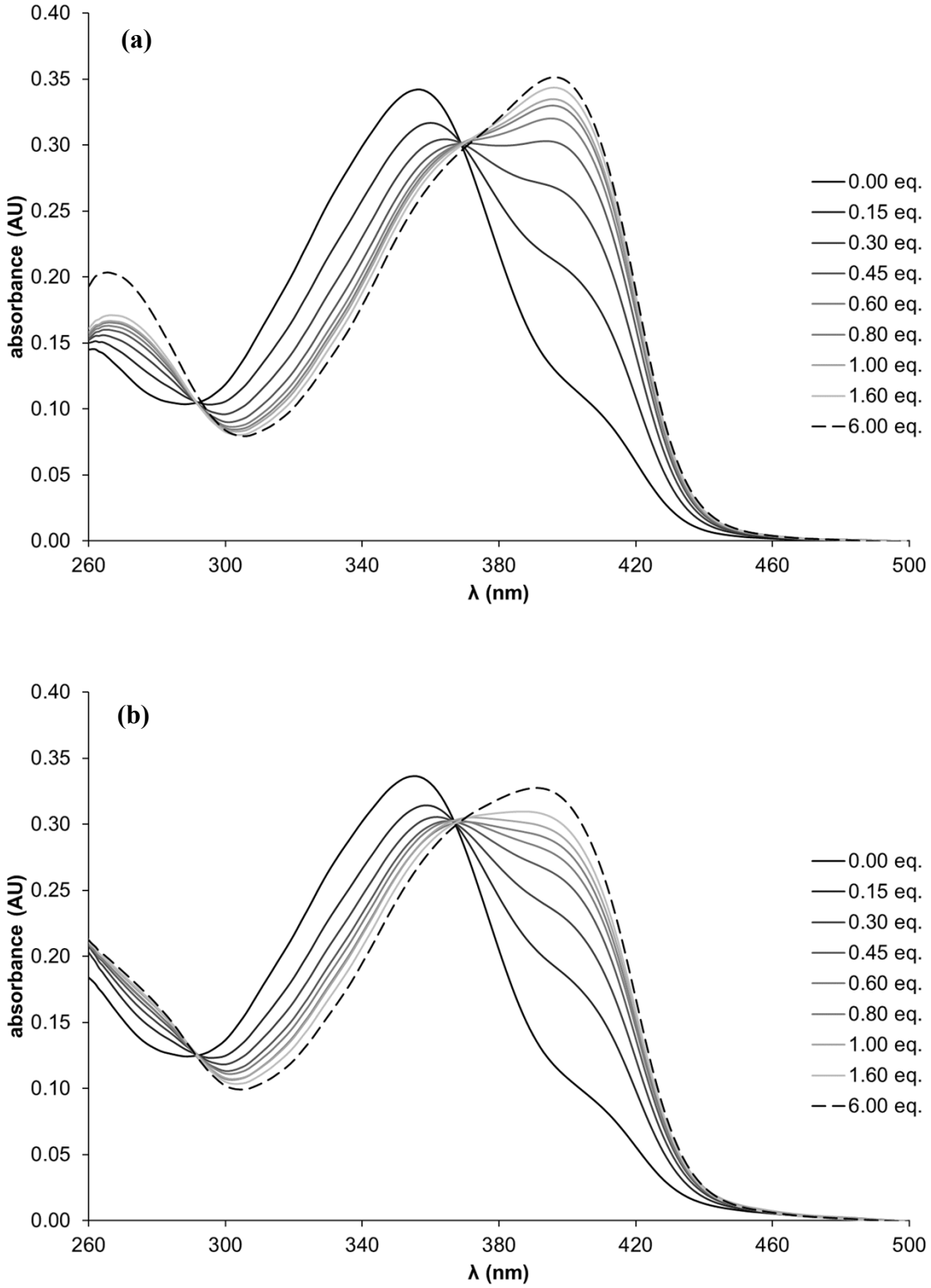
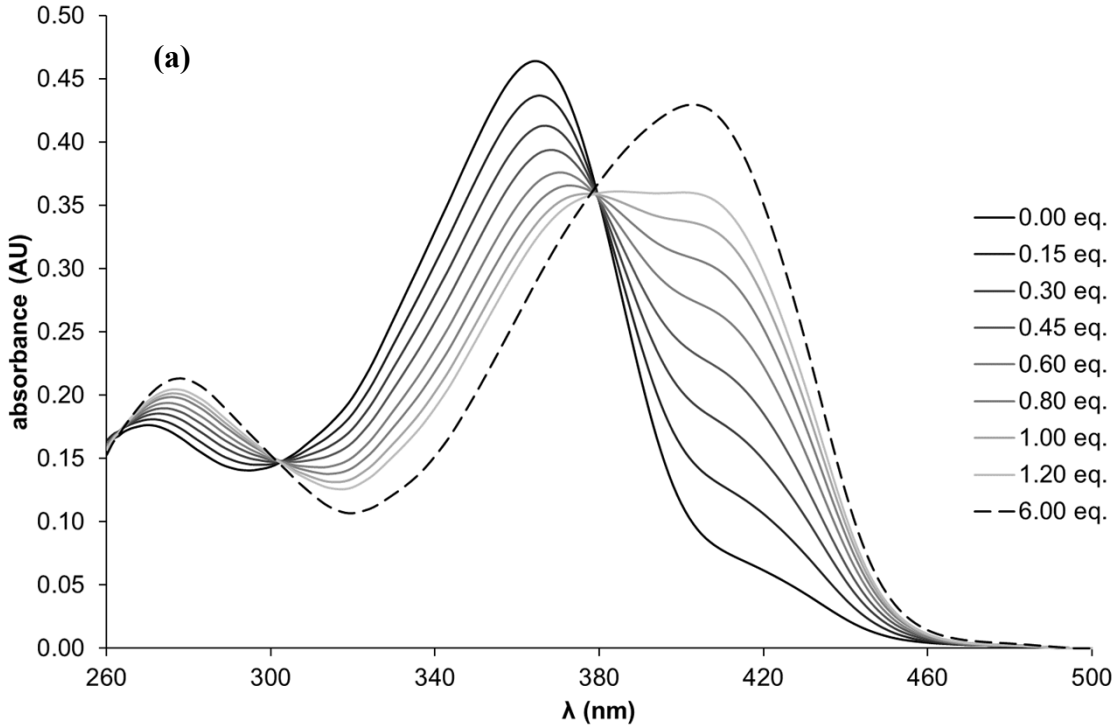
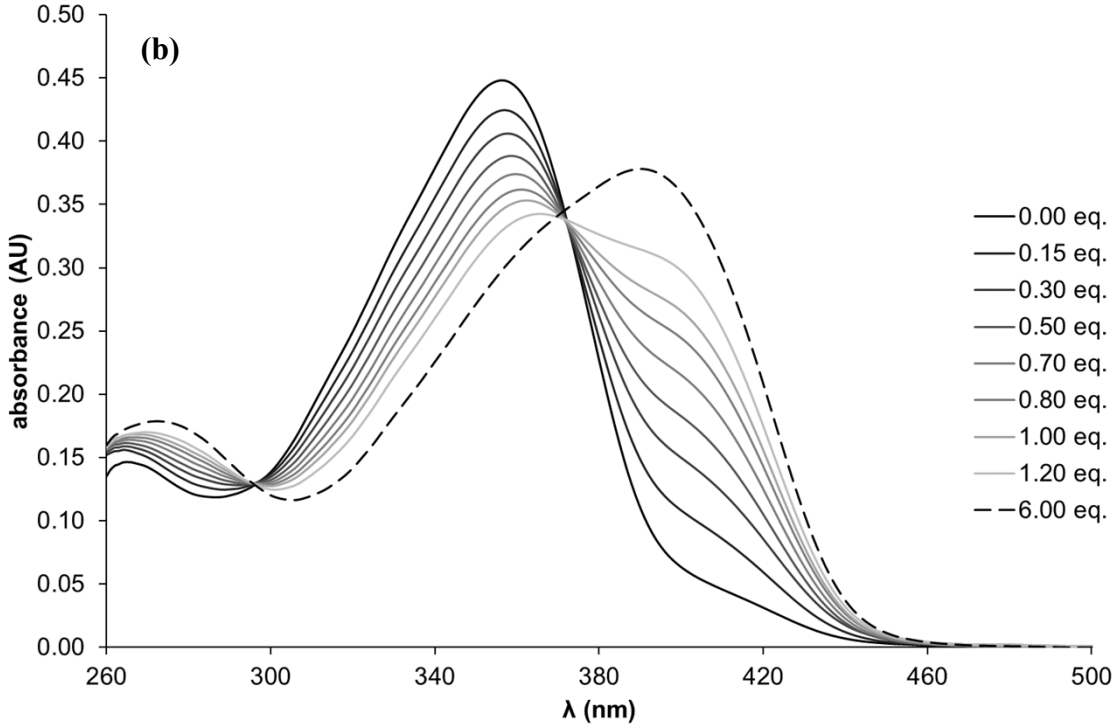


Figure S3. UV-Vis spectra collected during the titration of receptor **6** (1.0×10^{-5} mol L^{-1}) with (a) TBAOBz and (b) TBAP, in DMSO.


(a)
absorbance (AU)
λ (nm)
0.00 eq.
0.15 eq.
0.30 eq.
0.45 eq.
0.60 eq.
0.80 eq.
1.00 eq.
1.20 eq.
6.00 eq.


(b)
absorbance (AU)
λ (nm)
0.00 eq.
0.15 eq.
0.30 eq.
0.50 eq.
0.70 eq.
0.80 eq.
1.00 eq.
1.20 eq.
6.00 eq.

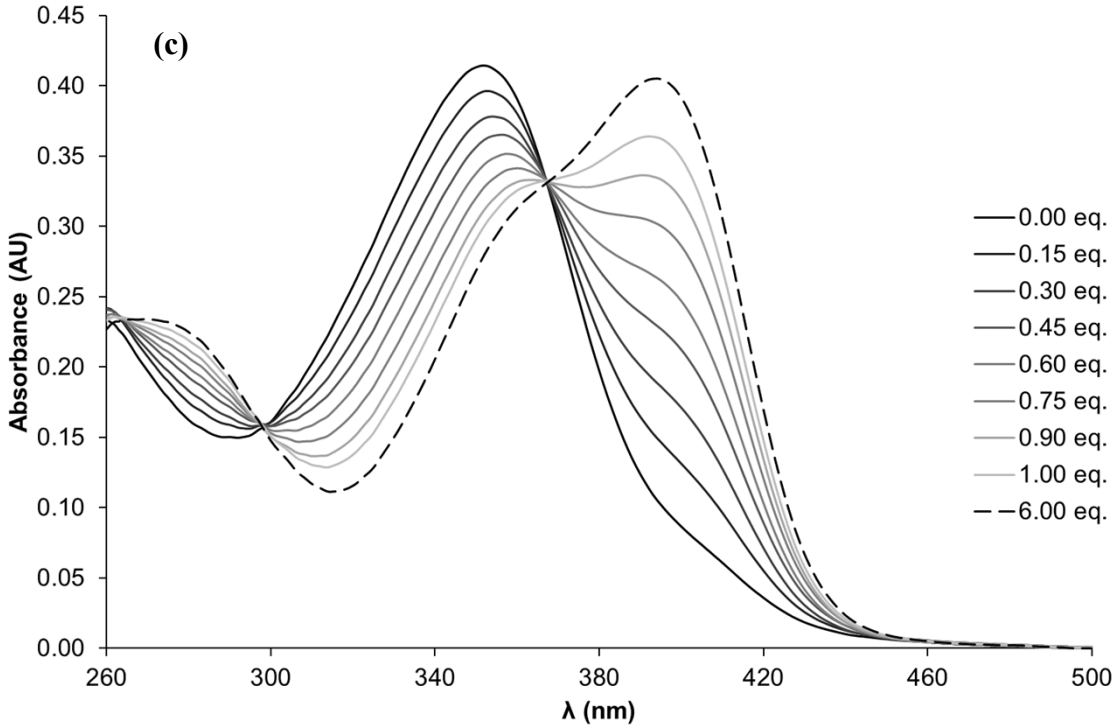


Figure S4. UV-Vis spectra collected during the titration of (a) receptor **3** (1.0×10^{-5} mol L^{-1}) with TBAF, (b) receptor **4** with TBAF anc (c) receptor **5** with TBAF, in DMSO.

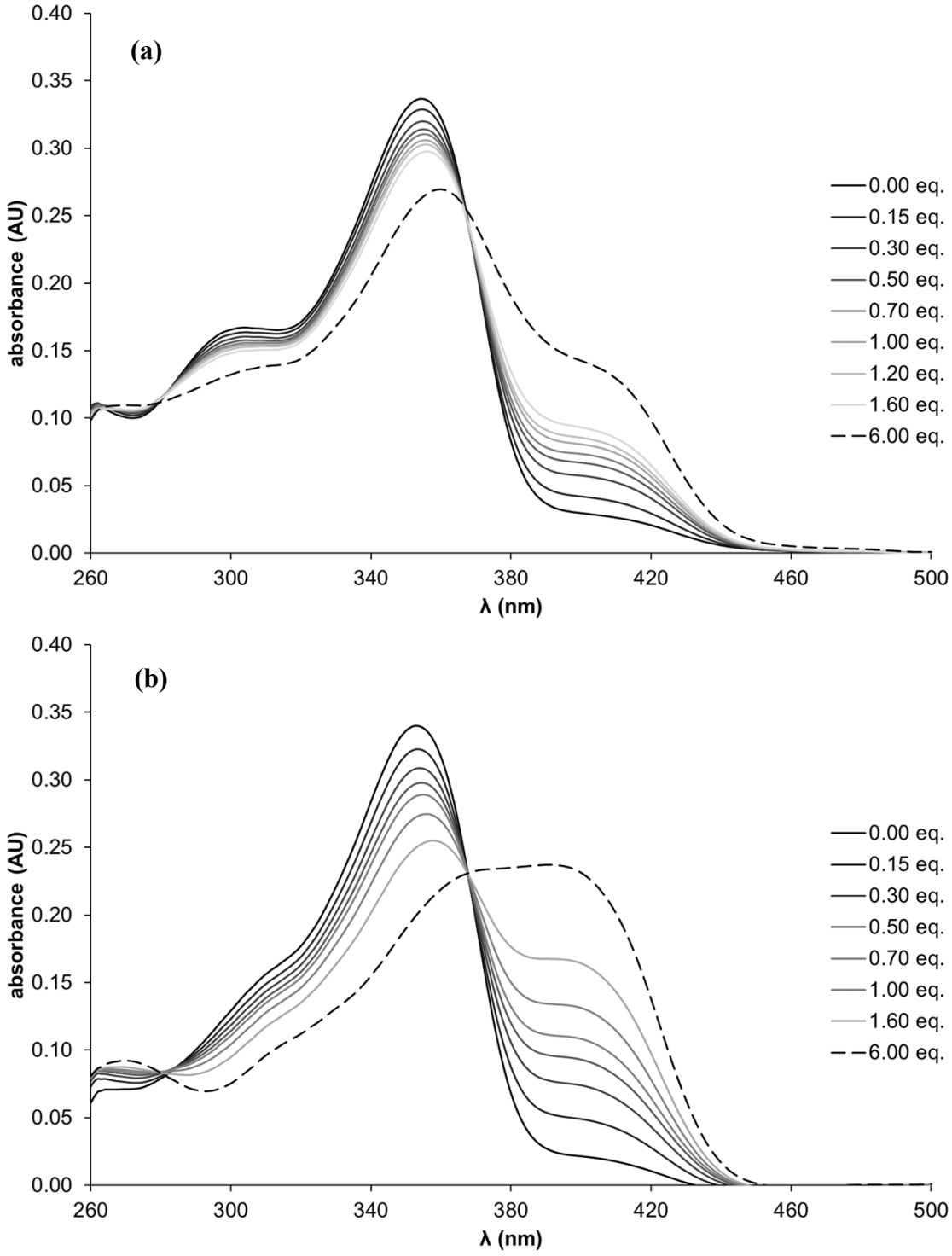


Figure S5. UV-Vis spectra collected during the titration of (a) receptor **7** (1.0×10^{-5} mol L^{-1}) with TBAF and (b) receptor **8** with TBAF, in DMSO.

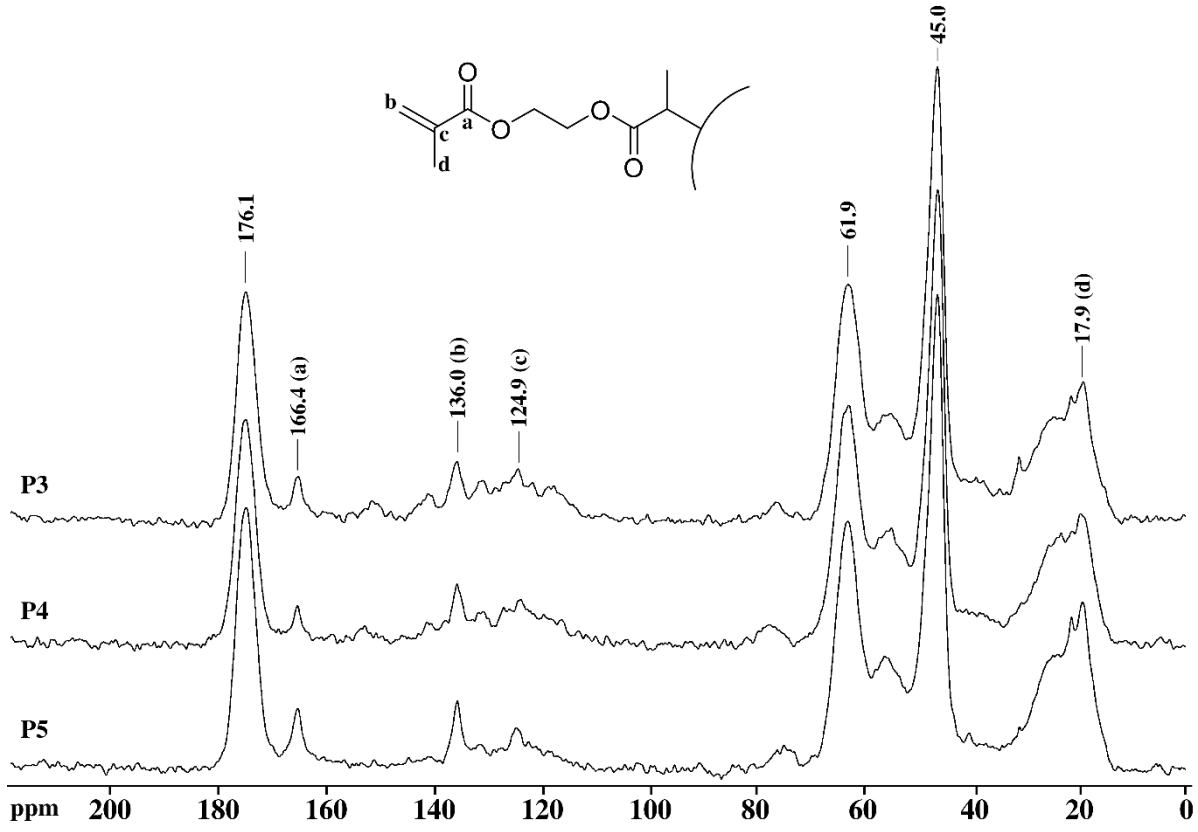


Figure S6. ^{13}C CP-MAS solid state NMR spectra (100 MHz) of polymers **P3**, **P4** and **P5** (3.2 mm SiN_3 rotors, spin rate 10 kHz, contact time 2 ms). Selected peaks are assigned to EDMA and signals (a), (b), (c) and (d) correspond to mono-reacted cross-linker units.