Naphthalene- and perylenediimides with hydroquinones, catechols, boronic esters and imines in the core

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Supporting Information

1. Materials and methods

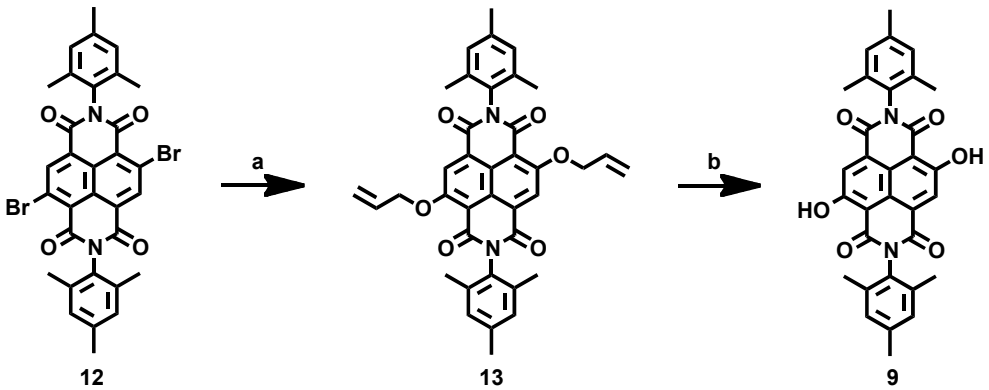
As in ref. S1, Supporting Information. In brief, reagents for synthesis were purchased from Aldrich, Fluka and Acros. All the reactions are performed in N_2 or Ar atmosphere. Unless stated otherwise, column chromatography was carried out on silica gel 60 (Fluka, 40-63 μm). Analytical (TLC) and preparative thin layer chromatography (PTLC) were performed on silica gel 60 (Fluka, 0.2 mm) and silica gel GF (Analtech, 1 mm), respectively. pH values were measured with a Consort C832 pH meter equipped with a VWR glass membrane pH electrode. IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer (ATR, Golden Gate, unless stated) and are reported as wavenumbers ν in cm^{-1} with band intensities indicated as s (strong), m (medium), w (weak). ^{1}H and ^{13}C spectra were recorded (as indicated) either on a Bruker 300 MHz, 400 MHz or 500 MHz spectrometer and are reported as chemical shifts (δ) in ppm relative to TMS (δ = 0). Spin multiplicities are reported as a singlet (s), doublet (d), triplet (t) and quartet (q) with

coupling constants (*J*) given in Hz, or multiplet (m). Broad peaks are marked as br. Proton signals with low deuterium exchange rates (half life ≥ 5 min) are marked "exchangeable". ^{1}H and ^{13}C resonances were assigned with the aid of additional information from 1D & 2D NMR spectra (H,H-COSY, DEPT 135, HSQC and HMBC). Multiplicity of ^{13}C signals are assigned with the aid of DEPT 135, and reported as s (*C*), d (*CH*), t (CH_2) and q (CH_3). ESI-MS were performed on a ESI API 150EX with 2 mM ammonium acetate in methanol as a solvent and are reported as *m/z* (%). Accurate mass determinations using ESI (HR ESI-MS) were performed on a Sciex QSTAR Pulsar or Bruker Daltonics maXis mass spectrometer.

Abbreviations: CAN: Cerium (IV) ammonium nitrate; DMF: N,N-Dimethylformamide; m.s.: Molecular Sieves; $Pd(PPh_3)_4$: Tetrakis(triphenylphosphine)palladium(0); rt: Room temperature; TEMPO: 2,2,6,6-Tetramethylpiperidinooxy; TEOA: Triethanolamine; TFA: Trifluoroacetic acid.

2. Synthesis

2.1. Synthesis of disubstituted cNDIs



Scheme S1. a) Allylalcohol, NaH, CH_2Cl_2, 4 Å m.s., 4 h, rt, 86%; b) $Pd(PPh_3)_4$, phenylsilane, CH_2Cl_2, 4 Å m.s., 10 h, rt, 80%.

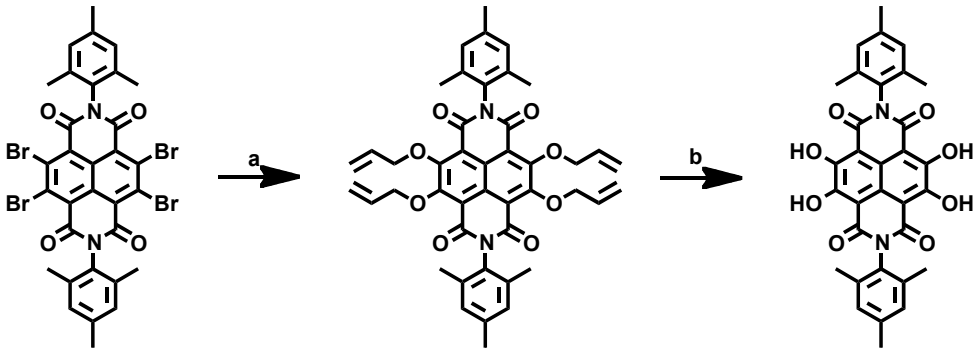
Compound 12. This compound was prepared following the literature procedures (*S1*).

Compound 13. To a solution of **12** (73 mg, 0.11 mmol) in dry CH_2Cl_2 (4 ml) with 4 Å molecular sieves, AllylONa (330 µl of 1.0 M solution of NaH in allylalcohol) was added. The mixture was stirred at rt for 4 h. CH_2Cl_2 (20 ml) was added and the organic layer was washed with brine (1 x 25 ml), H_2O (2 x 25 ml), dried over Na_2SO_4 and concentrated *in vacuo*. Purification by PTLC (CH_2Cl_2/Petroleum ether 10:1) afforded **13** (59 mg, 86%) as a yellow solid. Mp: >220 ºC; R_f (CH_2Cl_2): 0.3; IR (neat): 2921 (w), 2257 (w), 1738 (s), 1700 (m), 1664 (s), 1575 (s), 1480 (w), 1438 (s), 1409 (m), 1361 (s), 1290 (m), 1222 (s), 1090 (m), 990 (m), 910 (s), 837 (s), 764 (m), 727 (s), 645 (m), 529 (s); ^{1}H NMR (400 MHz, $CDCl_3$): 8.57 (s, 2H), 7.04 (s, 4H), 6.13 (ddt, ^3J (H,H) = 17.2, 10.5, 5.1 Hz, 2H), 5.68 (dq, ^3J (H,H) = 17.2 Hz, ^2J (H,H) = 1.5 Hz, ^4J (H,H) = 1.5 Hz, 2H), 5.38 (dq, ^3J (H,H) = 10.5 Hz, ^2J (H,H) = 1.5 Hz, ^4J (H,H) = 1.5 Hz, 2H), 4.99 (dt, ^3J (H,H) = 5.1 Hz, ^4J (H,H) = 1.5 Hz, 4H), 2.36 (s, 6H), 2.10 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): 162.1 (s), 160.6 (s), 160.3 (s), 139.1 (s), 135.2 (s), 131.5 (d), 131.1 (s), 129.7 (d), 127.8 (s), 124.9 (s), 120.8 (d), 119.6 (t), 111.9 (s), 71.2 (t), 21.4 (q), 18.1 (q); MS (ESI, CH_2Cl_2): 615 (95, $[M + H]^+$), 573 (100, $[M – Allyl]^+$), 533 (33, $[M – (2 x Allyl)]^+$); HRMS (ESI, CH_2Cl_2): Calculated for $C_{38}H_{35}O_6N_2^+$: 615.2489, found: 615.2491.

Compound 9. To a solution of **13** (46 mg, 0.07 mmol) and $Pd(PPh_3)_4$ (5 mg, 4.0 µmol) in dry CH_2Cl_2 (3 ml) with 4 Å molecular sieves, phenylsilane (65 µl, 0.52 mmol) was added. The solution was stirred at rt for 10 h. The solvent was removed *in vacuo* and the residue was purified by PTLC (CH_2Cl_2/Petroleum ether 10:1) to afford **9** (32 mg, 80%) as a yellow solid. Mp: >220 ºC; R_f (CH_2Cl_2): 0.2; IR (neat): 3458 (w), 2970 (m), 1738 (s), 1637 (m), 1580 (m), 1440 (m), 1413 (m), 1365 (s), 1278 (w), 1217 (s), 1010 (w), 800 (m), 527 (m); ^{1}H NMR (400 MHz, $CDCl_3$):

12.26 (s, 2H), 8.43 (s, 2H), 7.09 (s, 4H), 2.38 (s, 6H), 2.11 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): 168.0 (s), 162.4 (s), 161.6 (s), 139.8 (s), 135.2 (s), 129.9 (d), 129.6 (s), 127.8 (s), 125.4 (d), 122.7 (s), 106.9 (s), 21.4 (q), 18.0 (q); MS (ESI, CH_2Cl_2): 533 (100, $[M - H]^-$); HRMS (ESI, CH_2Cl_2): Calculated for $C_{32}H_{27}N_2O_6^+$: 535.1863, found: 535.1863.

2.2 Synthesis of tetrasubstituted cNDIs



Scheme S2. a) Allylalcohol, NaH, CH_2Cl_2, 4 Å m.s., 12 h, rt, 88%; b) $Pd(PPh_3)_4$, phenylsilane, CH_2Cl_2, 4 Å m.s., 16 h, rt, 35%.

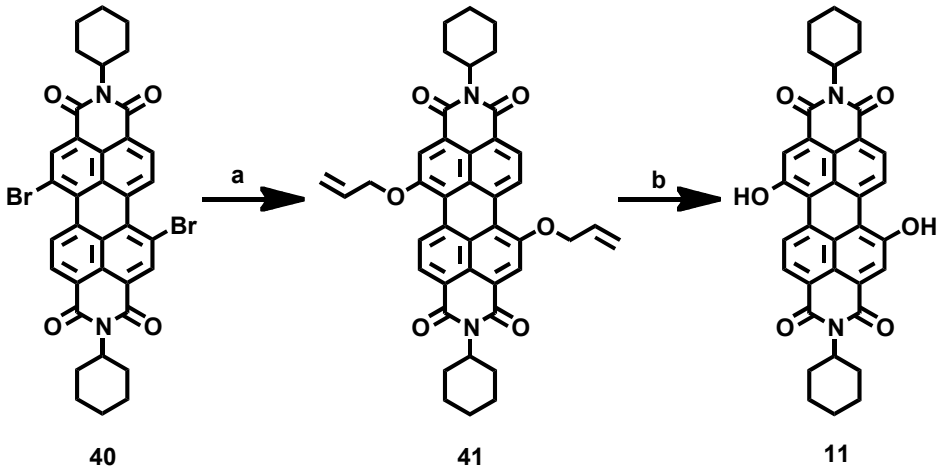
Compound 38. This compound was prepared following previously reported procedures (*S1*).

Compound 39. To a solution of **38** (46 mg, 0.05 mmol) in dry CH_2Cl_2 (3ml) with 4 Å molecular sieves, AllylONa (340 µl of 1.0 M solution of NaH in allylalcohol) was added. The mixture was stirred at rt for 12 h. CH_2Cl_2 (20 ml) was added and the organic layer was washed with brine (1 x 25 ml), H_2O (2 x 25 ml), dried over Na_2SO_4 and concentrated *in vacuo*. Purification by PTLC (CH_2Cl_2/petroleum ether 3:2) afforded **39** (36 mg, 88%) as a yellow solid. Mp: >220 ºC; R_f (CH_2Cl_2): 0.5; IR (neat): 2920 (w), 1710 (s), 1675 (s), 1557 (m), 1408 (s), 1352 (m), 1317 (w), 1286 (m), 1198 (s), 1042 (m), 949 (s), 829 (s), 717 (s), 532 (s); ^{1}H NMR (400 MHz,

$CDCl_3$): 7.05 (s, 4H), 6.21 (ddt, ^3J (H,H) = 17.1, 10.4, 6.4 Hz, 4H), 5.38 (dq, ^3J (H,H) = 17.1 Hz, ^2J (H,H) = 1.3 Hz, ^4J (H,H) = 1.3 Hz, 4H), 5.24 (dd, ^3J (H,H) = 10.4 Hz, ^2J (H,H) = 1.3 Hz, 4H), 4.76 (br. d, ^3J (H,H) = 6.4 Hz, 8H), 2.36 (s, 6H), 2.11 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): 160.2 (s), 158.6 (s), 139.1 (s), 135.2 (s), 133.5 (d), 131.1 (s), 129.8 (d), 123.3 (s), 119.8 (t), 119.3 (s), 76.6 (t), 21.5 (q), 18.2 (q); MS (ESI, CH_2Cl_2): 726 (92, $[M + H]^+$), 686 (65, $[M – Allyl]^+$), 644 (100, $[M – (2 \times Allyl)]^+$), 604 (44, $[M – (3 \times Allyl)]^+$); HRMS (ESI, CH_2Cl_2): Calculated for $C_{44}H_{43}O_8N_2^+$: 727.3013, found: 727.3000.

Compound 10. To a solution of **39** (11 mg, 0.01 mmol) and $Pd(PPh_3)_4$ (1 mg, 0.7 μmol) in CH_2Cl_2 (2 ml) with 4 Å molecular sieves, phenylsilane (26 μl, 0.21 mmol) was added. The solution was stirred at rt for 16 h. The solvent was removed *in vacuo* and the residue was purified by PTLC (DCM/MeOH/TFA 97:2:1) to afford **10** (3 mg, 35%) as a yellow-orange solid. Mp: >220 ºC; R_f (CH_2Cl_2/MeOH/TFA 97:2:1): 0.3; IR (neat): 2920 (w), 1738 (s), 1636 (m), 1576 (m), 1457 (s), 1365 (s), 1296 (m), 1203 (s), 1098 (m), 881 (m), 832 (s), 796 (s), 744 (s), 606 (m), 543 (m); ^{1}H NMR (400 MHz, $CDCl_3$): 12.46 (s, 4H), 7.12 (s, 4H), 2.40 (s, 6H), 2.13 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): 167.6 (s), 154.6 (s), 140.3 (s), 135.2 (s), 130.0 (d), 128.5 (s), 114.3 (s), 106.7 (s), 21.4 (q), 17.8 (q); MS (ESI, CH_2Cl_2): 565 (100, $[M - H]^-$).

2.3. Synthesis of disubstituted cPDIs



Scheme S3. a) Allylalcohol, NaH, DMF, 1 h, 100°C, 55%; b) $Pd(PPh_3)_4$, phenylsilane, CH_2Cl_2, 1 h, rt, 65%.

Compound 40. This compound was prepared following the literature procedures (*S2)*.

Compound 41. To a solution of **40** (100 mg, 0.14 mmol) in dry DMF (10 ml), AllylONa (300 µl of 2.5 M solution of NaH in allylalcohol) was added at rt. The mixture was refluxed to 100°C for 1 h. The solution was allowed to cool down to rt and 30 ml of H_2O were added. The resulting suspension was diluted with CH_2Cl_2. The organic layer was washed with brine (2 x 100 ml), H_2O (1 x 100 ml), dried over Na_2SO_4 and concentrated *in vacuo*. Silica gel column chromatography (CH_2Cl_2) of the residue gave **40** (53 mg, 55%) as a dark red powder. Mp: > 220 °C; R_f (CH_2Cl_2): 0.3; IR (neat): 2924 (w), 2854 (w), 1692 (s), 1649 (s), 1596 (s), 1411 (w), 1332 (s), 1271 (s); ^{1}H NMR (500 MHz, $CDCl_3$): 9.61 (d, ^3J (H,H) = 8.4 Hz, 2H), 8.57 (d, ^3J (H,H) = 8.4 Hz, 2H), 8.27 (s, 2H), 6.26 (ddt, ^3J (H,H) = 17.1, 10.6, 5.3 Hz, 2H), 5.62 (dd, ^3J (H,H) = 17.1 Hz, ^2J (H,H) = 1.1 Hz, 2H), 5.48 (dd, ^3J (H,H) = 10.5 Hz, ^2J (H,H) = 1.1 Hz, 2H), 5.15-4.99 (m, 6H), 2.63-2.55 (m, 4H), 1.95-1.92 (m, 4H), 1.88-1.65 (m, 6H), 1.51-1.32 (m, 6H); ^{13}C NMR (125

MHz, $CDCl_3$): 164.0 (s), 163.9 (s), 156.3 (s), 133.7 (s), 132.0 (d), 129.3 (d), 128.8 (d), 123.9 (s), 123.9 (s), 122.0 (s), 121.8 (s), 119.4 (t), 118.0 (d), 70.9 (t), 54.0 (d), 29.7 (t), 29.1 (t), 26.6 (t), 25.5 (t); MS (ESI, CH_2Cl_2): 667 (100, $[M + H]^+$); HRMS (ESI, CH_2Cl_2): Calculated for $C_{42}H_{39}N_6O_6N_2^+$: 667.28026, found: 667.27953.

Compound 11. To a solution of **41** (100 mg, 0.15 mmol) and $Pd(PPh_3)_4$ (6 mg, 5 μmol) in CH_2Cl_2 (40 ml), phenylsilane (50 μl, 0,40 mmol) was added. The solution was stirred at rt for 1 h. The solvent was removed *in vacuo* and the crude solid was washed with petroleum ether (12 x 10 ml) and diethyl ether (12 x 10 ml). The solid was dried overnight *in vacuo* to gave **11** (70 mg, 79%) as a dark violet powder. Mp: > 220 °C; IR (neat): 3271 (w), 2925 (w), 2854 (w), 1688 (s), 1641 (s), 1582 (s), 1029 (w); ^{1}H NMR (500 MHz, DMSO-d_6): 12.39 (br. s, 2H), 9.63 (d, ^3J (H,H) = 8.4 Hz, 2H), 8.33 (d, ^3J (H,H) = 8.4 Hz, 2H), 8.28 (s, 2H), 4.89 (tt, ^3J (H,H) = 12.3, 3.7 Hz, 2H), 2.44-2.36 (m, 4H), 1.88-1.85 (m, 4H), 1.74-1.69 (m, 6H), 1.43-1.32 (m, 3H), 1.27-1.22 (m, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): 163.3 (s), 163.0 (s), 133.7 (s), 131.5 (s), 128.8 (q), 128.7 (q), 128.4 (q), 127.7 (d), 127.3 (d), 122.9 (q), 122.5 (q), 122.1 (d), 120.8 (q), 117.9 (s), 52.8 (d), 28.6 (t), 26.1 (t), 25.2 (t); MS (ESI, CH_2Cl_2/MeOH 1:1): 585 (100, $[M - H]^-$).

3. Absorption spectroscopy

pH Profiles. UV-Vis spectra were recorded on a JASCO V-650 spectrophotometer equipped with a stirrer and a temperature controller (25 ºC) or on a Cary 50 spectrophotometer.

To a solution of **9** in DMSO (2 ml, 0.04 mM), water (0.5 ml, 1 mM TEOA pH 7.0) was added. Subsequently, aliquots (10 μl) of NaOH (0.05 M) and HCl (0.04 M) were added. After each addition, the solution was stirred for 2 minutes at rt before measuring the pH by direct insertion of the electrode in the solution. Finally, at stable pH, an absorption spectrum was recorded after

every addition of acid or base (Fig. 2). The same procedure was applied for the titration of **10** in DMSO (2 ml, 0.04 mM) and **11** in DMSO (2 ml, 0.06 mM) with the same addition of buffer solution (0.5 ml, 1 mM TEOA pH 7.0) (Figs. S1, S2).

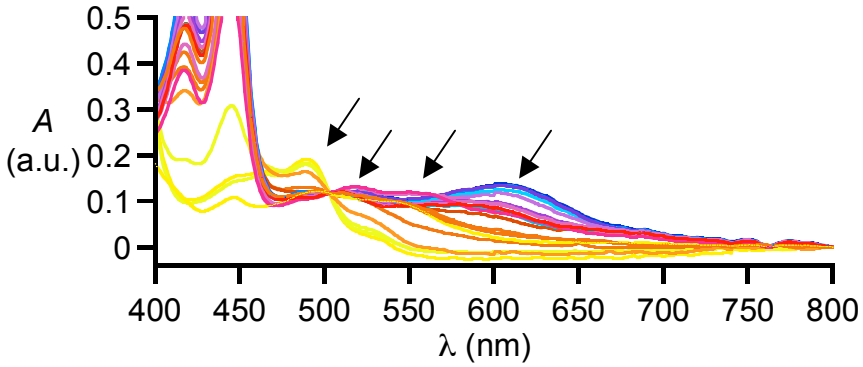


Figure S1. Changes in absorption spectra of **10** with increasing pH. Arrows indicate maxima associated with **10**, **17**, **18**, and **19** (Fig. 5).

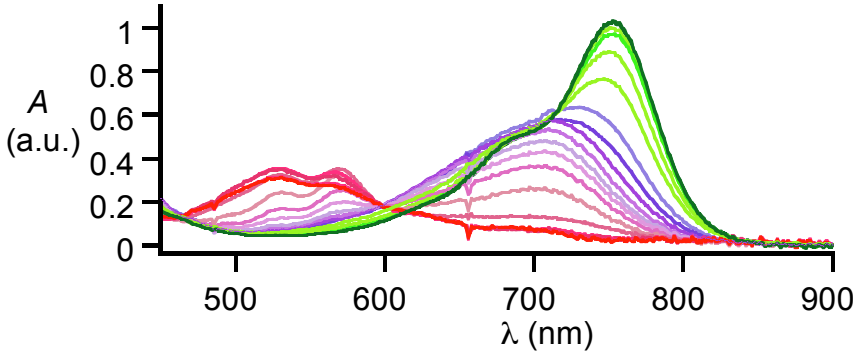


Figure S2. Changes in absorption spectra of **11** with increasing pH.

The absorption maxima (λ_{max}) for each spectra of **9**, **10** and **11** were plotted in function of the measured pH (Fig. 4) and the pK_a values were determined by fitting the plots to the Hill equation (S1)

$$\lambda = \lambda_{AHm} + (\lambda_{AH(m-1)} - \lambda_{AHm}) / [1 + (pK_a/pH)^n] \quad \text{(S1)}$$

where λ is the λ_{max} of the sample, λ_{AHm} and $\lambda_{AH(m-1)}$ are the absorbance wavelength of the species involved in the deprotonation equilibrium, *n* is the Hill coefficient. The results are summarized in Table 1.

The recorded UV-Vis spectra from the titration and the corresponding pH values were imported in HypSpec software (S3) for the pK_a analysis of the compounds **9** and **11**. The processing of these data gave the spectra (Figure S3) for the compound **9** and the relative pK_a at 7.2 ± 0.1 and 11.5 ± 0.1. For the compound **11** (Figure S4), the shape of the fully protonated species was affected by partial precipitation of the compound during the titration at acidic pH. The extrapolated pK_a for **11** were at 8.0 ± 0.1 and 10.6 ± 0.1. All the pK_a obtained by HypSpec were in reasonable agreement with the values calculated from the titration. For the compound **10**, the analysis with HypSpec was not possible because of the large overlap of the spectra of the different species.

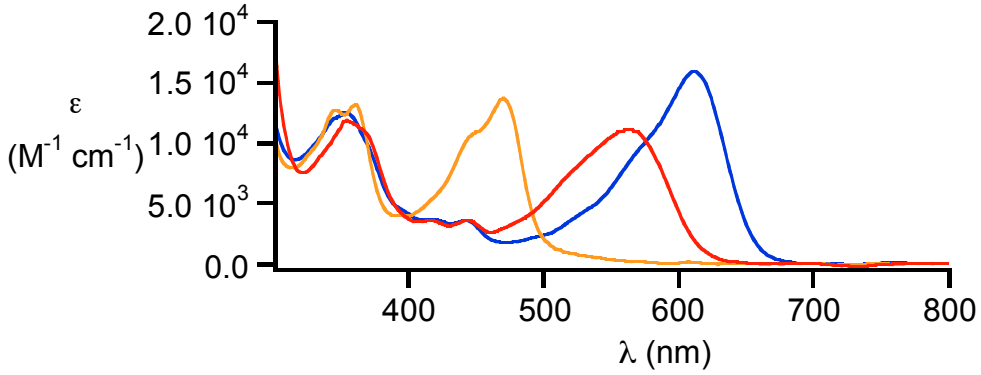


Figure S3. HypSpec spectra of **9**, **14** and **15** in 4:1 DMSO/H_2O (calculated from original data in Fig. 2).

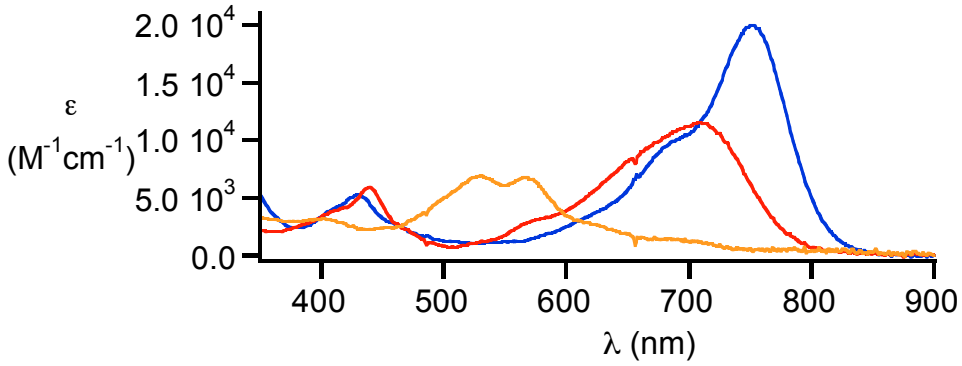


Figure S4. HypSpec elaborated spectra of titration of **11**, **20** and **21** in 4:1 DMSO/H_2O (calculated from original data in Fig. S2).

Solvatochromism. 8 vials were filled with a solution of **9** in CH_2Cl_2 (20 μl, 0.18 mM) and the solvent was removed *in vacuo* overnight. Then each vials was filled with one of the solvent (2 ml) reported in the Table S1. The solutions were stirred for 2 minutes at rt before measuring the UV-Vis Spectra.

Table S1. Solvents investigated with relative Lewis basicity and polarity function data.

Solvent	Lewis Basicity ($kJmol^{-1}$)	Dielectric Constant (ε) [a]	Polarity Function $f(\varepsilon)$ [b]
Dichloromethane	10.00	9.08	0.72924
Acetonitrile	60.39	36.60	0.92228
Dioxane	74.09	2.30	0.30233
Ethyl Acetate	75.55	6.02	0.62594
Acetone	76.03	20.70	0.86784
Tetrahydrofuran	90.40	7.52	0.68487
Dimethylsulfoxide	105.34	47.20	0.94902
Dimethylformamide	110.49	38.30	0.92556

[a] According to the Sigma-Aldrich catalogue. [b] $f(\varepsilon) = (\varepsilon - 1) / (\varepsilon + 2)$.

The λ_{max} (nm) of each sample was converted in wavenumber (cm^{-1}) and finally plotted in function of the Lewis basicity or the polarity function $f(\varepsilon)$ (Figure 7). The same procedure was applied for the investigation with **10** dissolved in CH_2Cl_2 (20 µl, 0.17 mM) and **11** dissolved in CH_2Cl_2/MeOH (1:1, 20 µl, 0.03 mM).

DMF sensing. 150 ml of commercial available DMF were distilled at 165-170°C. 20 consecutive fractions (5 ml) were collected and cooled down in a water bath. At rt, a solution of **9** in CH_2Cl_2 (200 µl, 0.38 mM) was added to each fraction (2.5 ml) and, after 2 minutes stirring, the spectra were measured (Fig. 8). The ratio (F) between the absorption at 538 and 610 nm of **9** is directly related with the basicity of the different fractions. This parameter was plotted in function of the fraction number (Fig. 8b).

Boronic acid esters. To a solution of **10** (0.80 mg, 1.4 µmol) in 4:1 DMSO/H_2O (2 ml, 1mM TRIS pH 8), phenylboronic acid (7.0 mM in DMSO, 10 or 20 µl portions) was added at rt and the solution was stirred for 2 minutes. Then the pH was checked by direct insertion of the electrode in the solution and the spectrum was measured. The same procedure was applied for the titration of **9** (0.75 mg, 1.4 µmol) and **11** (0.20 mg, 0.3 µmol) in the same solvent system.

The absorption maxima (λ_{max}) for each spectra of **9**, **10** and **11** were plotted in function of the concentration in the solution of the phenylboronic acid (Fig. 9) and the K_D values were determined by fitting the plots to the Hill equation (S2)

$$\lambda = \lambda_0 + (\lambda_1 - \lambda_0) / [1 + (K_D/c_{\text{phenylboronic acid}})^n] \qquad \text{(S2)}$$

where λ is the λ_{max} of the sample, λ_0 and λ_1 are the absorbance wavelength of the species involved in the esterification equilibrium, n is the Hill coefficient.

The pH profiles for **22** (2 ml, 0.02 mM, 4:1 DMSO/H_2O) (Fig. 10b) and **23** (2 ml, 0.07 mM, 4:1 DMSO/H_2O) (Figure S5) were measured and analyzed as described for **9**, **10**, **11**, using eq S1.

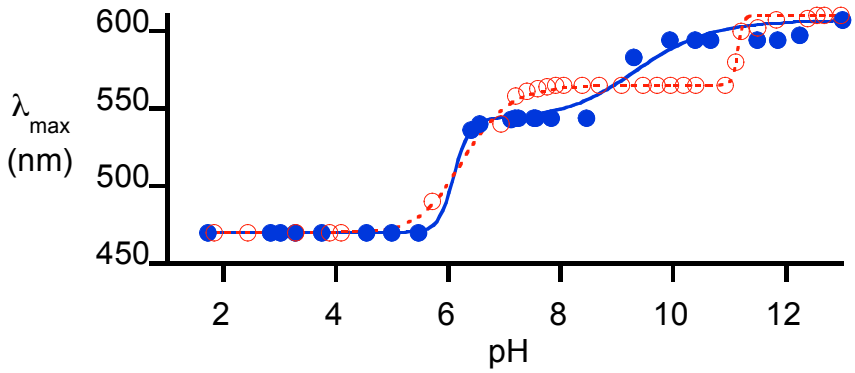


Figure S5. Absorption maxima of **23** (●) and **9** (○) as a function of pH.

Iminoquinones. To a solution of **9** (5.0 mg, 9 μmol) in dry acetonitrile (4 ml), CAN (1.2 mg, 2 μmol) and TEMPO (0.7 mg, 4 μmol) were added at rt. The mixture was refluxed to 100 °C in O_2 atmosphere. The reaction was followed by UV-Vis measurements of aliquots (200 μl) of the boiling mixture quenched with a solution of aniline (0.5 ml, 5.5 mmol) in 4:1 DMSO/H_2O (2.5 ml, 1 mM TEOA pH 7). Constant intensity and shape of the peak at 638 nm suggested that the reaction was completed after 2 h. The red shifted absorption at 638 nm, compared with the absorption of **9** at the same pH, was consistent with the formation of iminoquinone **26** (Fig. 11a). The pH titration as described for **9**-**11**, using eq S1 (Fig. 11b). The result was consistent with the formation of iminium **32** (Fig. 11a).

The same procedure with different amines was applied for the formation of the iminoquinones **27**-**31** and the corresponding iminium species **33**-**37** (Fig. 11b).

4. Fluorescence spectroscopy

The fluorescence and the excitation spectra were measured on a Cary Eclipse fluorimeter or on Jobin Yvon FluoroLog 3 to cover the spectral region up to 950 nm and were corrected for the wavelength-dependent sensitivity of the detection. Rhodamine 6g (S4) and IR-140 (S5) were used as standards to determine the fluorescence quantum yield. Time-resolved fluorescence measurements were performed using the time-correlated single photon counting (TCSPC) setup as in ref. S6. Excitation was carried out with <90 ps pulses generated with a laser diode at 395 nm (PicoQuant model LDH-PC-400B) and fluorescence was detected at magic angle. The full width at half-maximum (FWHM) of the instrument response function (IRF) was around 200 ps.

5. Supplementary figures

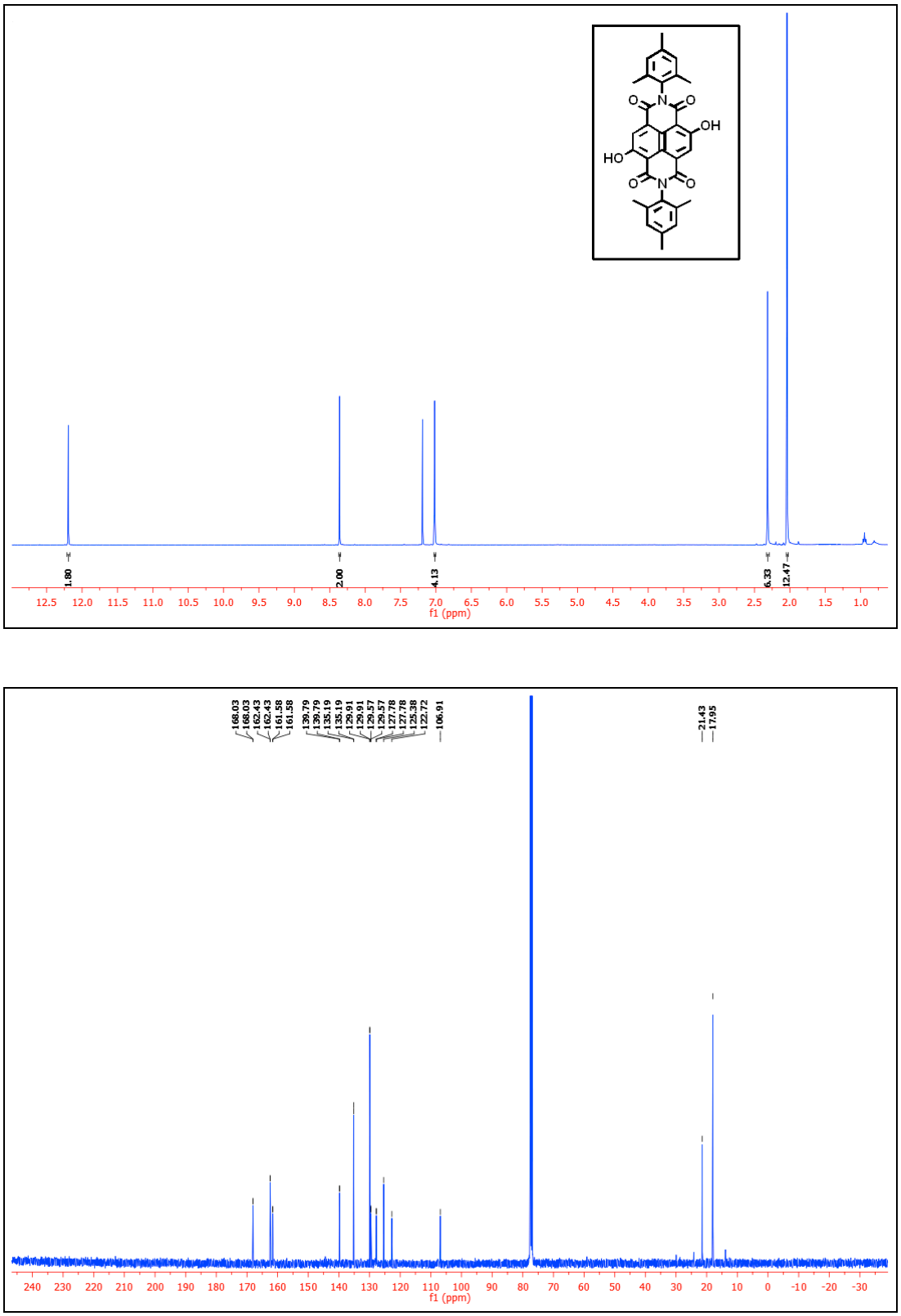
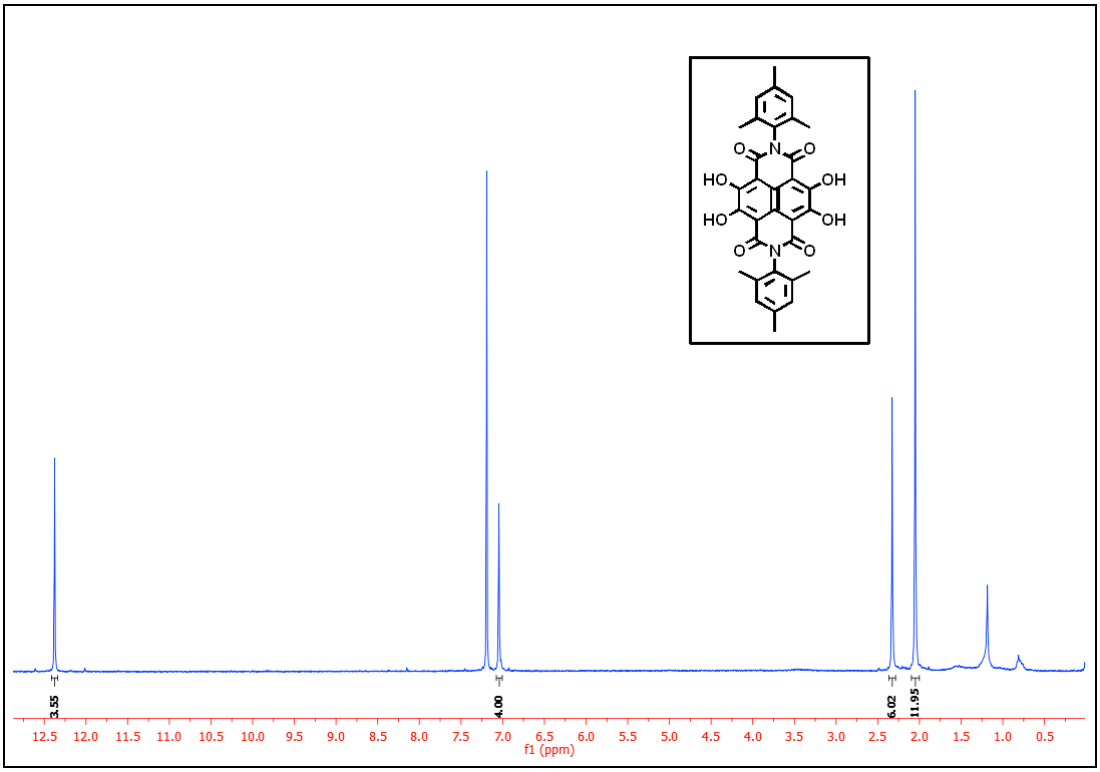


Figure S6. ^{1}H (top) and ^{13}C (bottom) NMR spectra of target molecule **9** in $CDCl_3$.



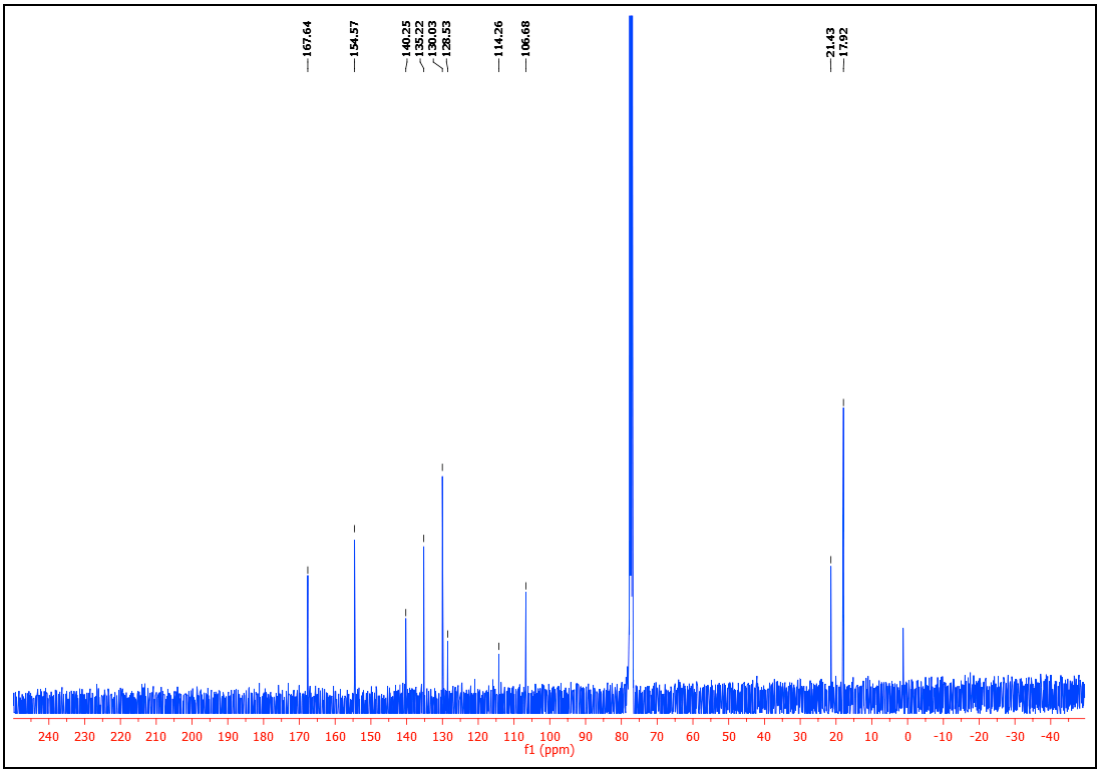


Figure S7. ^{1}H (top) and ^{13}C (bottom) NMR spectra of target molecule **10** in $CDCl_3$.

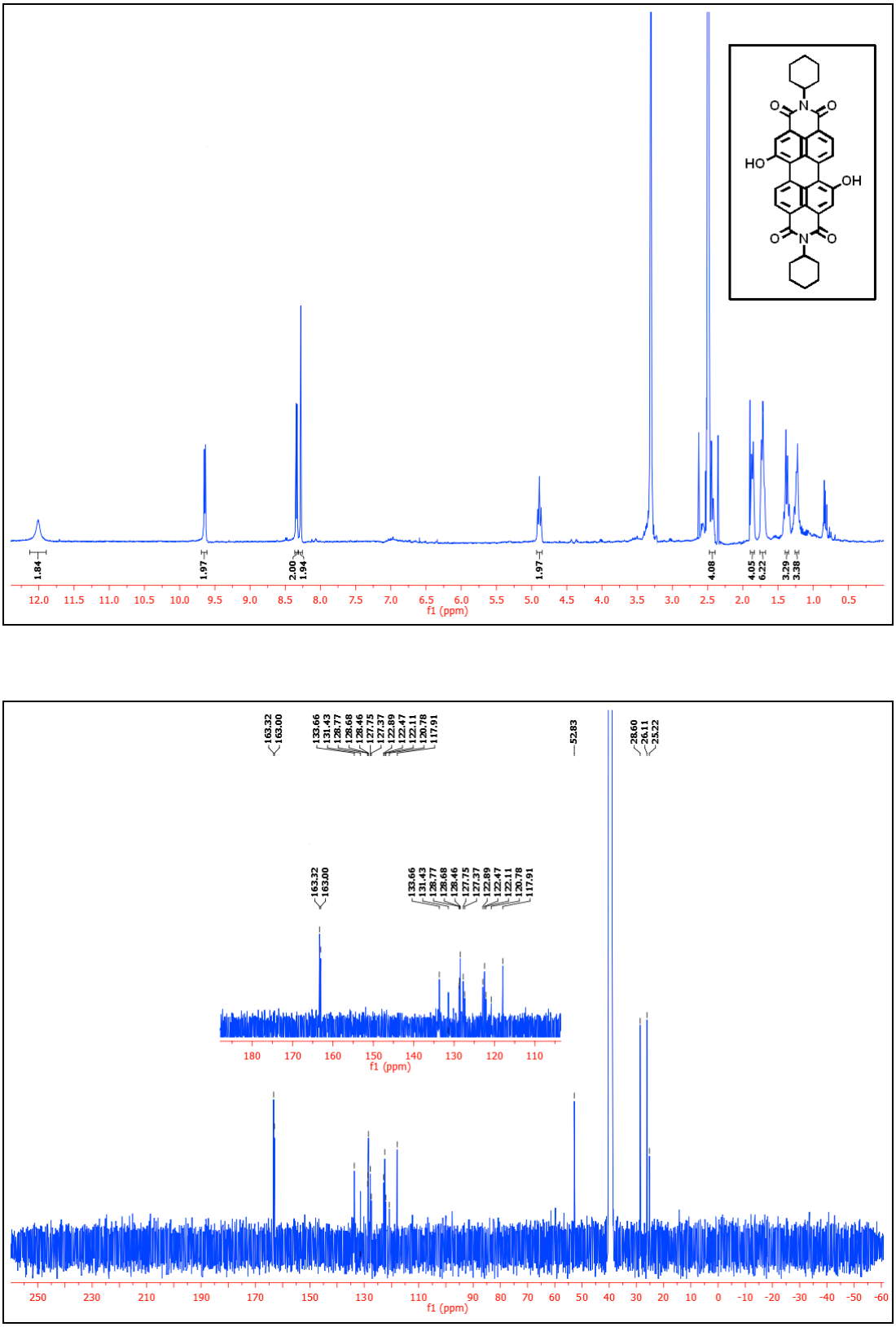


Figure S8. ^{1}H (top) and ^{13}C (bottom) NMR spectra of target molecule **11** in DMSO-d_6.

6. References

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