Supporting information

Transamination at the crossroad of the one-pot synthesis of N-substituted quinonediimines and C-substituted benzobisimidazoles

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1. General Informations

All reagents were used as received. ^{1}H Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker Avance 250 Ultrashield or on a JEOL ECS400 NMR spectrometer Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) using the residual protonated solvent as an internal standard (For proton: $CDCl_3$, 7.26 ppm; DMSO-d_6, 2.50 ppm; Acetone-d_6, 2.05 ppm. For ^{13}C: $CDCl_3$, 77.0 ppm; DMSO-d_6, 39.4 ppm; Acetone-d_6, 30.8 ppm). High Resolution Mass Spectrometry (HRMS-ESI) and Mass Spectrometry (ESI-MS) analyses were performed on a QStar Elite (Applied Biosystems SCIEX) spectrometer or on a SYNAPT G2 HDMS (Waters) spectrometer. These two instruments are equipped with an electrospray ionization source. Elemental analyses were determined with a Thermo Finnigan EA 1112. UV-vis absorption spectra were measured with a Varian Cary 50. Fluorescence spectra were measured with a Varian Cary Eclipse fluorescence spectrophotometer. The intensity data of the X-ray-quality crystals were collected on a Bruker–Nonius KappaCCD diffractometer using MoKα radiation (λ = 0.71073 Å). Fourier Transform Infrared (FTIR) spectrum was measured with a Bruker VERTEX 70 spectrometer in the Attenuated Total Reflection (ATR) mode using a Pike MIRacle™ ATR accessory.

Although compounds **3a**[S1] and **3d**[S2] are reported in the literature, their NMR spectra have not been published to the best of our knowledge. The ^{13}C NMR spectra compounds **1a-j** could not be recording in solution owing to drastic problems of relaxation for the sp^2 carbons of this class of molecules.

2. Organic synthesis

General procedure for the synthesis tetrasubstituted 2,5-diamino-1,4-benzoquinonediimine 1:

To a suspension of 1,2,4,5-tetraaminobenzene tetrahydrochloride TAB·4HCl (m = 59 mg, 0.20 mmol, 1 equiv.) in MeOH (v = 2.5 mL, concentration A = 0.8 M; or v = 2.0 mL, concentration B = 1.0 M; or v = 1.7 mL, concentration C = 1.2 M; or v = 1.4 mL, concentration D = 1.4 M), was added the primary amine (2.0 mmol, 10 equiv.). The mixture was stirred overnight at room temperature. The resulting precipitate was filtered off, washed with water (and/or other solvents) and dried under vacuum.

***N*^{1},*N*^{2},*N*^{4},*N*^{5}-tetramethyl-2,5-diamino-1,4-benzoquinonediimine 1a:**

A solution of methylamine in water (40% v/v) and TAB·4HCl at concentration A were used as reagent to afford the desired product (m = 8 mg, 22% yield) as an orange powder. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 6.14 (br s, 2H, N*H*), 5.21 (s, 2H, C*H*), 3.05 (s, 12H, CH_3). HRMS (ESI-TOF): m/z $[M+H]^+$ for $C_{10}H_{17}N_4^+$, calcd. 193.1448, found 193.1448, error < 1 ppm.

***N*^{1},*N*^{2},*N*^{4},*N*^{5}-tetrapropyl-2,5-diamino-1,4-benzoquinonediimine 1b:**

A solution of *n*-propylamine and TAB·4HCl at concentration C were used as reagent and the obtained precipitate was isolated by filtration, washed with water, Et_2O and dried under vacuum affording the desired product as a yellow solid (m = 54 mg, 88% yield). ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 6.34 (br s, 2H, N*H*), 5.22 (s, 2H, C*H*), 3.19 (br s, 8H, NCH_2), 1.70 (sext, $^3J_{HH}$ = 7.2 Hz, 8H, CH_2CH$_3$), 1.00 (t, $^3J_{HH}$ = 7.4 Hz, 12H, CH_3). MS-ESI: m/z $[M+H]^+$ for $C_{18}H_{33}N_4^+$, calcd. 305.3, found 305.3. Elementary analysis: for $C_{18}H_{32}N_4 \cdot 0.2H_2O$, calcd. C 70.17, H 10.60, N 18.19; found C 69.98, H 10.31, N 18.58.

***N*^{1},*N*^{2},*N*^{4},*N*^{5}-tetrabutyl-2,5-diamino-1,4-benzoquinonediimine 1c:**

A solution of *n*-butylamine and TAB·4HCl at concentration D were used as reagent and the obtained precipitate was isolated by filtration, washed with water, Et_2O and dried under vacuum affording the desired product as a yellow solid (m = 43 mg, 59% yield). ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 6.32 (br s, 2H, N*H*), 5.22 (s, 2H, C*H*), 3.22 (br s, 8H, NCH_2), 1.67 (quint, $^3J_{HH}$ = 7.2 Hz, 8H, NCH$_2$CH_2), 1.43 (sext, $^3J_{HH}$ = 7.3 Hz, 8H, CH_2CH$_3$), 0.96 (t, $^3J_{HH}$ = 7.3 Hz, 12H, CH$_2$CH_3). MS-ESI: m/z $[M+H]^+$ for $C_{22}H_{41}N_4^+$ calcd. 361.3, found 361.3. Elementary analysis: for $C_{22}H_{40}N_4$, calcd. C 73.28, H 11.18, N 15.54, found C 72.90, H 11.36 N, 15.59.

***N*^{1},*N*^{2},*N*^{4},*N*^{5}-tetraoctyl-2,5-diamino-1,4-benzoquinonediimine 1d:**

A solution of 1-octylamine and TAB·4HCl at concentration C were used as reagent and the obtained precipitate was isolated by filtration, washed with water and dried under vacuum affording the desired product as a yellow solid (m = 78 mg, 67% yield). ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 6.30 (br s, 2H, N*H*), 5.21 (s, 2H, C*H*), 3.21 (br s, 8H, NCH_2), 1.70-1.61 (m, 8H, CH_2), 1.40-1.20 (m, 40H, CH_2), 0.89 (t, $^3J_{HH}$ = 6.6 Hz, 12H, CH_3). MS-ESI: m/z $[M+H]^+$ for $C_{38}H_{73}N_4^+$, calcd. 585.6, found 585.6. Elementary analysis: for $C_{38}H_{72}N_4$, calcd. C 78.02, H 12.41, N 9.58, found C 77.57, H 12.26 N 9.78.

***N*^{1},*N*^{2},*N*^{4},*N*^{5}-tetrakis (1,3-dihydroxypropan-2-yl)-2,5-diamino-1,4-benzoquinonediimine 1e:**

A solution of serinol and TAB·4HCl at concentration A were used as reagent to afford a solution which was evaporated under vacuum. The resulting crude compound was taken up with water and the obtained precipitate was dried under vacuum to afford the desired product as a brown solid (m = 11 mg, 12% yield). ^{1}H NMR (250 MHz, DMSO-d_6): δ (ppm) = 6.63 (br s, 2H, N*H*), 5.50 (s, 2H, C*H-quinone*), 4.59 (brs, 8H, O*H*), 3.56-3.39 (m, 20H, C*H*(CH_2)$_2$). HRMS (ESI-TOF): m/z $[M+H]^+$ for $C_{18}H_{33}N_4O_8^+$, calcd. 433.2293, found 433.2295, error < 1 ppm.

***N*^{1},*N*^{2},*N*^{4},*N*^{5}-tetrakis (6-hydrohexyl)-2,5-diamino-1,4-benzoquinonediimine 1f:**

A solution of 6-amino-1-hexanol and TAB·4HCl at concentration A were used as reagent. Water was added to the resulting red mixture at the end of the reaction and the obtained precipitate was filtered off and dried under vacuum to afford the desired product as a yellow solid (m = 24 mg, 22 % yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 6.47 (br s, 2H, N*H*), 5.21 (s, 2H, C*H*), 4.33(br t, $^3J_{HH}$ = 5.0 Hz, 4H, O*H*), 3.38 (q, $^3J_{HH}$ = 5.8 Hz, 8H, NCH_2), 3.19 (br s, 8H, CH_2OH), 1.61-1.53 (m, 8H, CH_2), 1.46-1.38 (m, 8H, CH_2), 1.37-1.28 (m, 16H, CH_2). HRMS (ESI-TOF): m/z $[M+H]^+$ for $C_{30}H_{57}N_4O_4^+$, calcd. 537.4374, found 537.4378, error < 2 ppm.

***N*^{1},*N*^{2},*N*^{4},*N*^{5}-tetrakis (3-butenyl)-2,5-diamino-1,4-benzoquinonediimine 1g:**

A solution of 3-butenylamine and TAB·4HCl at concentration B were used as reagent and the obtained precipitate was isolated by filtration, washed with water and dried under vacuum affording the desired product as an orange solid (m = 20 mg, 28% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.40 (br s, 2H, N*H*), 5.96-5.79 (m, 4H, C*H*=CH_2), 5.20 (s, 2H, C*H-quinone*), 5.13 (dm, $^3J_{HH}$ = 17.3 Hz, 4H, CH=C$H_{2\text{-}trans}$), 5.07 (dm, $^3J_{HH}$ = 10.1 Hz, 4H, CH=C$H_{2\text{-}cis}$), 3.29 (br s, 8H, NCH_2), 2.45 (q, $^3J_{HH}$ = 6.6 Hz , 8H, CH_2-CH=CH_2). HRMS (ESI-TOF): m/z $[M+H]^+$ for $C_{22}H_{33}N_4^+$, calcd. 353.2700, found 353.2698, error < 1 ppm.

***N*^{1},*N*^{2},*N*^{4},*N*^{5}-tetrakis (1-phenylethyl)-2,5-diamino-1,4-benzoquinonediimine 1h:**

A solution of (±)-1-phenylethylamine and TAB·4HCl at concentration B were used as reagent and the obtained precipitate was filtered off, washed with water and dried under vacuum to afford the desired product as a yellow solid (m = 60 mg, 54% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 7.47-6.98 (m, 20H, Ar*H*), 6.74 (br m, 2H, N*H*), 5.26 (s, 1H, C*H-quinone*), 5.19-5.10 (m, 1H, C*H-quinone*), 4.66-4.26 (br m, 4H, C*H*CH_3), 1.61-0.91 (m, 12H, C*H*$_3$). The number of NMR signals is more important than expected because of the presence of different isomers in solution. HRMS (ESI-TOF): m/z $[M+H]^+$ for $C_{38}H_{41}N_4^+$, calcd. 553.3326, found 553.3325, error < 1 ppm.

***N*^{1},*N*^{2},*N*^{4},*N*^{5}-tetrakis (3-morpholinopropyl)-2,5-diamino-1,4-benzoquinonediimine 1i:**

A solution of 3-morpholinopropylamine and TAB·4HCl at concentration C were used as reagent and EtOH was replaced by iPrOH. The obtained precipitate was filtered off, washed with water and dried under vacuum to afford the desired product as a yellow solid (m = 27 mg, 21% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.93 (br s, 2H, N*H*) 5.23 (s, 2H, C*H*), 3.73 (t, $^3J_{HH}$ = 4.6 Hz, 16H, C*H*$_2$O), 3.31 (br s, 8H, N(H)C*H*$_2$), 2.44 (m, 24H, C*H*$_2$), 1.92 (quint, $^3J_{HH}$ = 6.9 Hz, 8H, NCH$_2$C*H*$_2$). HRMS (ESI-TOF): m/z $[M+H]^+$ for $C_{34}H_{61}N_8O_4^+$, calcd. 645.4810, found 645.4811, error < 1 ppm.

***N*^{1},*N*^{2},*N*^{4},*N*^{5}-tetrakis (cyclohexyl)-2,5-diamino-1,4-benzoquinonediimine 1j:**

A solution of cyclohexylamine and TAB·4HCl at concentration A were used as reagent and the obtained precipitate was filtered off, washed with MeOH and dried under vacuum to afford the desired product as a yellow solid (m = 34 mg, 36% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.40 (br s, 2H, N*H*), 5.26 (s, 2H, C*H-quinone*), 3.41-3.22 (m, 4H, NC*H*), 1.95-1.69 (m, 16H, C*H*$_2$), 1.67-1.59 (m, 4H, C*H*$_2$), 1.45-1.21 (m, 20H, C*H*$_2$). HRMS (ESI-TOF): m/z $[M+H]^+$ for $C_{30}H_{49}N_4^+$, calcd. 465.3952, found 465.3953, error < 1 ppm.

General procedure for the synthesis of 2,6-disubstituted benzo[1,2-d:4,5-d']bisimidazoles 3a, 3c and 3d (route a):

To a suspension of 1,2,4,5-tetraaminobenzene tetrahydrochloride TAB·4HCl (m = 59 mg, 0.20 mmol, 1 equiv.) in MeOH (v = 2.5 mL, concentration A = 0.8 M; or v = 2.0 mL, concentration B = 1.0 M; or v = 1.7 mL, concentration C = 1.2 M; or v = 1.4 mL, concentration D = 1.4 M), was added the primary amine (2.0 mmol, 10 equiv.). The mixture was stirred overnight at room temperature. The resulting precipitate was filtered off, washed with water (and/or other solvents) and dried under vacuum.

2,6-diphenylbenzo[1,2-d:4,5-d']bisimidazole 3a:

A solution of benzylamine and TAB·4HCl at concentration A were used as reagent and the obtained precipitate was filtered off, washed with water and dried under vacuum to afford the desired product as a yellow solid (m = 53 mg, 85% yield). ^{1}H NMR (250 MHz, DMSO-d_6): δ (ppm) = 12.72 (br s, 2H, N*H*), 8.24-8.15 (m, 4H, Ph*H*), 7.71 (br s, 2H, Ar*H*), 7.61-7.44 (m, 6H, Ph*H*). No ^{13}C NMR spectrum of 3a could be recorded owing to its poor solubility. HRMS (ESI-TOF): m/z $[M+H]^+$ for $C_{20}H_{15}N_4^+$, calcd. 311.1291, found 311.1290, error < 1 ppm.

2,6-bis(3,4,5-trimethoxyphenyl) benzo[1,2-d:4,5-d']bisimidazole 3b:

3,4,5-Trimethoxybenzylamine (v = 0.13 mL, 0.80 mmol, 5 equiv.) was added to a solution of TAB·4HCl (m = 45 mg, 0.16 mmol) in MeOH (v = 2.5 mL, concentration = 0.6 M). The mixture was stirred for overnight at room temperature. The resulting yellowish precipitate was isolated by filtration, washed with water dried under vacuum to afford the desired product (m = 62 mg, 63%). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.70 (br s, 2H, N*H*), 7.88 (br s, 1H, *I* = 0.5, Ar*H-isomer B*), 7.71 (s, 2H, *I* = 1, Ar*H-isomer A*), 7.58-7.52 (m, 4H, Ph*H*), 7.50 (br s, 1H, *I* = 0.5, Ar*H-isomer B*), 3.92 (s, 12H, CH_3), 3.74 (s, 6H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 153.1, 151.6, 151.2, 141.5, 141.0, 138.6, 132.9, 132.4, 125.7, 106.6, 103.5, 98.4, 90.7, 60.1, 55.9. MS-ESI: m/z $[M+H]^+$ for $C_{26}H_{27}N_4O_6^+$, calcd, 491.2, found 491.2. The number of NMR signals is more important than expected because of the presence of two conformers or tautomers in solution at room temperature. Elementary analysis: for $C_{26}H_{26}N_4O_6 \cdot 0.5H_2O$, calcd. C 62.52, H 5.45, N 11.22, found C 62.52, H 5.15, N 10.97.

2,6-di(3-pyridyl) benzo[1,2-d:4,5-d']bisimidazole 3c:

A solution of 3-picolylamine and TAB·4HCl at concentration A were used as reagent and the obtained precipitate was filtered off, washed with water and dried under vacuum to afford the desired product as a brown solid (m = 56 mg, 89% yield) as a brown powder. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 13.01 (br s, 2H, N*H*), 9.38 (s, 2H, Py*H*), 8.68 (dd, $^{3}J_{HH}$ = 4.8 Hz, $^{4}J_{HH}$ = 1.2 Hz, 2H, Py*H*), 8.52 (dm, $^{3}J_{HH}$ = 8.0 Hz, 2H, Py*H*), 7.79 (br s, 2H, Ar*H*), 7.60 (dd, $^{3}J_{HH}$ = 8.0 Hz, $^{3}J_{HH}$ = 4.8 Hz, 2H, Py*H*). No ^{13}C NMR spectrum of **3c** could be recorded owing to its poor solubility. MS-ESI: m/z $[M+H]^+$ for $C_{18}H_{13}N_6^+$, calcd. 313.1, found 313.1. Elementary analysis: for $C_{18}H_{13}N_6 \cdot 1.5H_2O$, calcd. C 63.71, H 4.46, N 24.76, found C 63.50, H 3.90 N 24.76.

***N*^{1},*N*^{5}-di(2-pyridylmethylene)-1,2,4,5-tetraaminobenzene 6d:**

2-Picolylamine (v = 0.14 mL, 1.3 mmol, 10 equiv.) was added to a solution of TAB·4HCl (m = 38 mg, 0.13 mmol, 1 equiv.) in H_2O (v = 1.5 mL). The mixture was stirred for 4 hrs at room temperature. The resulting red precipitate was filtered off, washed with water and dried under vacuum to afford the

desired product (m = 23 mg, 70 µmol, 54% yield). ^{1}H NMR (250 MHz, DMSO-d_6): δ (ppm) = 8.72 (s, 2H, N=C*H*), 8.63 (dm, $^{3}J_{HH}$ = 4.9 Hz, 2H, Py*H*), 8.29 (d, $^{3}J_{HH}$ = 7.9 Hz, 2H, Py*H*), 7.85 (td, $^{3}J_{HH}$ = 7.7 Hz, $^{4}J_{HH}$ = 1.3 Hz, 2H, Py*H*), 7.60 (s, 1H, Ph*H*), 7.60 (ddd, $^{3}J_{HH}$ = 7.3 Hz, $^{3}J_{HH}$ = 4.9 Hz, $^{4}J_{HH}$ = 0.9 Hz, 2H, Py*H*), 6.09 (s, 1H, Ph*H*), 5.66 (br s, 4H, NH_2). No ^{13}C NMR spectrum of **3d** could be recorded owing to its low stability. HRMS (ESI-TOF): m/z $[M+H]^+$ for $C_{18}H_{17}N_6^+$,calcd. 317.1509, found 317.1508, error $<$ 1 ppm,

2,6-di(2-pyridyl) benzo[1,2-d:4,5-d']bisimidazole 3d:

Route a "One-pot": Following the general synthesis protocol, a solution of 2-picolylamine and TAB·4HCl at concentration C were used. the resulting yellowdish precipitate was filtered off, washed with MeOH and dried under vacuum to afford the desired product as a white solid (m = 25 mg, 40% yield).

Route b: 6d (m = 17 mg, 50.6 µmol) was dissolved in EtOH (96%， v = 40 mL). The solution was stirring in air for 3 days and the solvent was then removed under reduced pressure. The resulting crude product was taken up with EtOH (v = 3 mL), sonicated, collected by filtration, and dried under vacuum to afford the desired as a pale white powder (m = 13 mg, 83% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.92 (br s, 2H, N*H*), 8.74 (d, $^{3}J_{HH}$ = 4.4 Hz, 2H, Py*H*), 8.35 (d, $^{3}J_{HH}$ = 7.9 Hz, 2H, Py*H*), 8.00 (td, $^{3}J_{HH}$ = 7.7 Hz, $^{4}J_{HH}$ = 1.6 Hz, 2H, Py*H*), 7.96 (br s, 1H, *I* = 0.5, Ph*H-isomer B*), 7.74 (br s, 2H, *I* = 1, Ph*H-isomer A*), 7.60 (br s, 1H, *I* = 0.5, Ph*H-isomer B*), 7.52 (ddd, $^{3}J_{HH}$ = 7.4 Hz, $^{3}J_{HH}$ = 4.9 Hz, $^{4}J_{HH}$ = 0.9 Hz, 2H, Py*H*). The number of NMR signals is more important than expected because of the presence of two conformers or tautomers in solution at room temperature. No ^{13}C NMR spectrum of **3d** could be recorded owing to its poor solubility. MS-ESI: m/z $[M+H]^+$ for $C_{18}H_{12}N_6^+$ calcd. 312.1, found 313.1.

3. NMR spectra

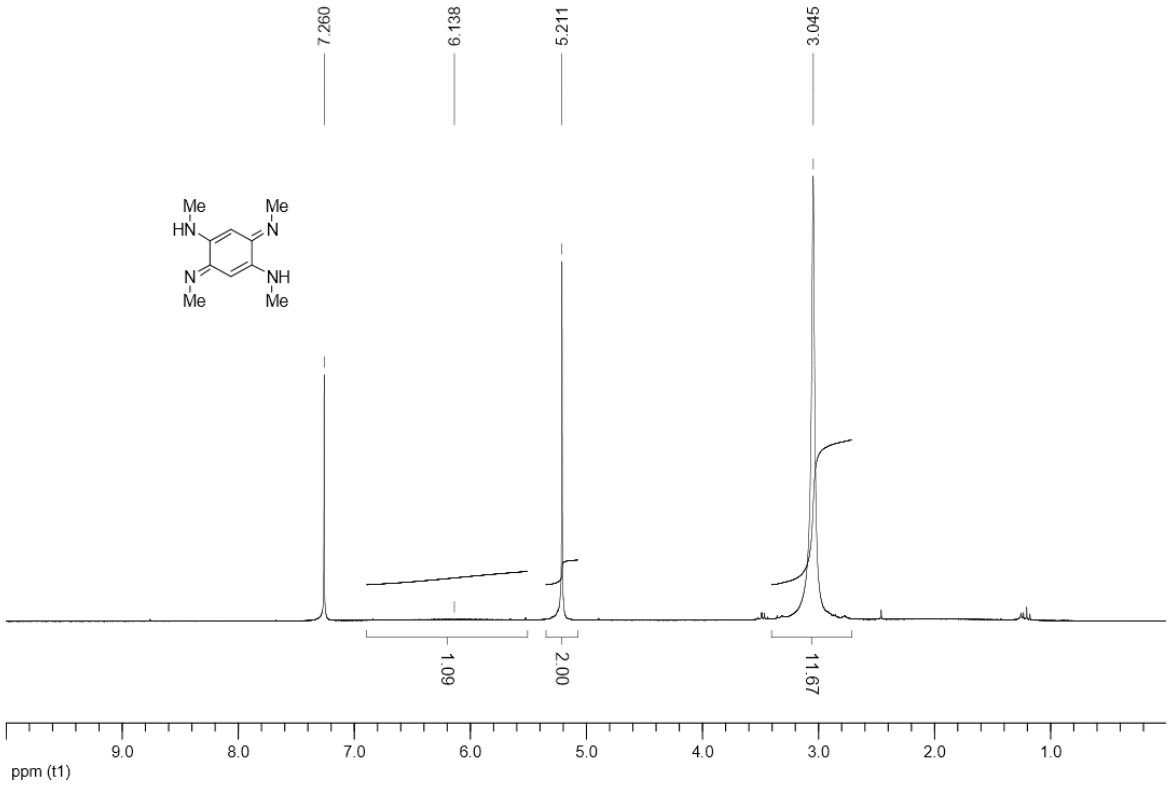

Figure S1: ^{1}H NMR spectrum of **1a** in $CDCl_3$ (250 MHz)

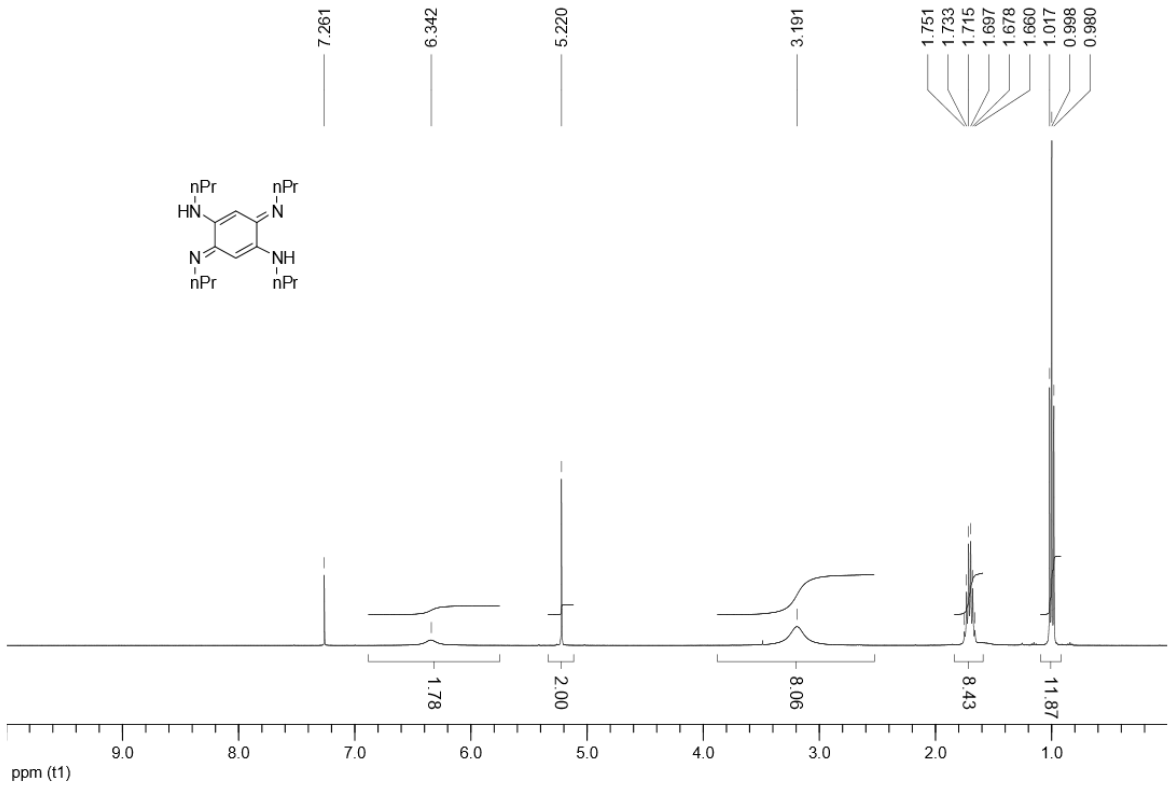

Figure S2: ^{1}H NMR spectrum of **1b** in $CDCl_3$ (400 MHz)

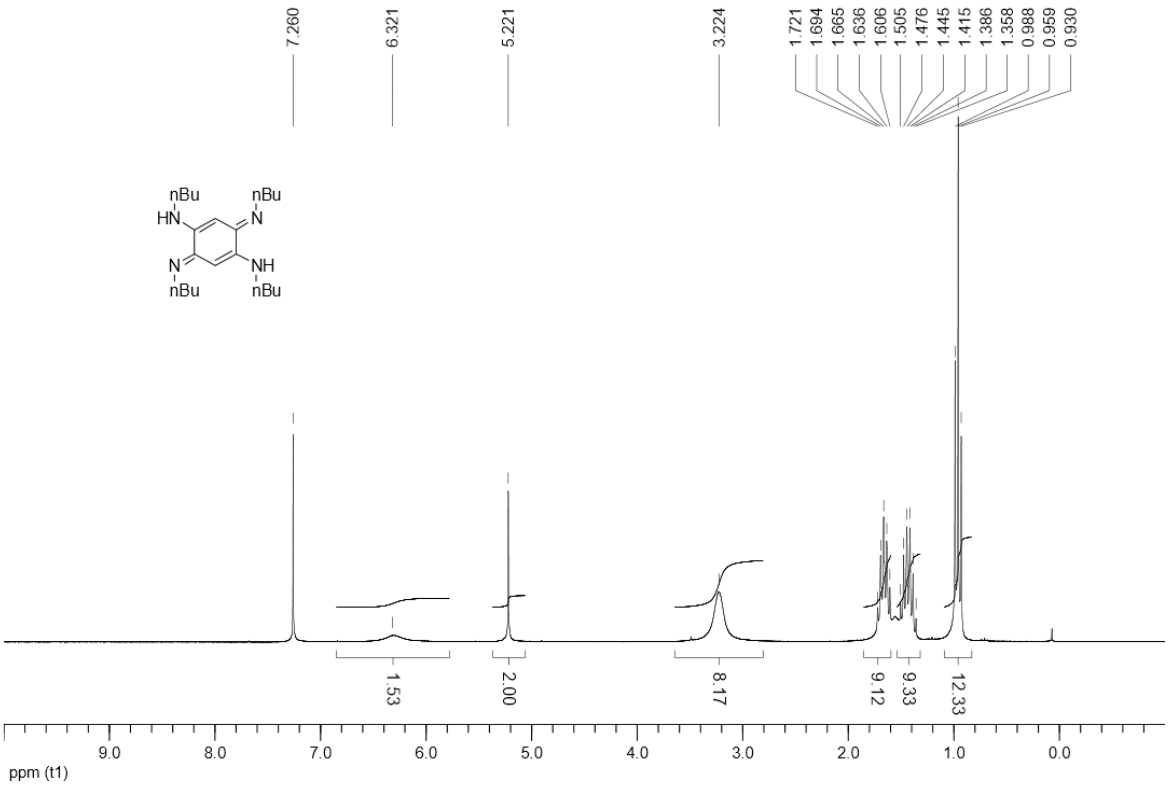

Figure S3: ^{1}H NMR spectrum of **1c** in $CDCl_3$ (250 MHz)

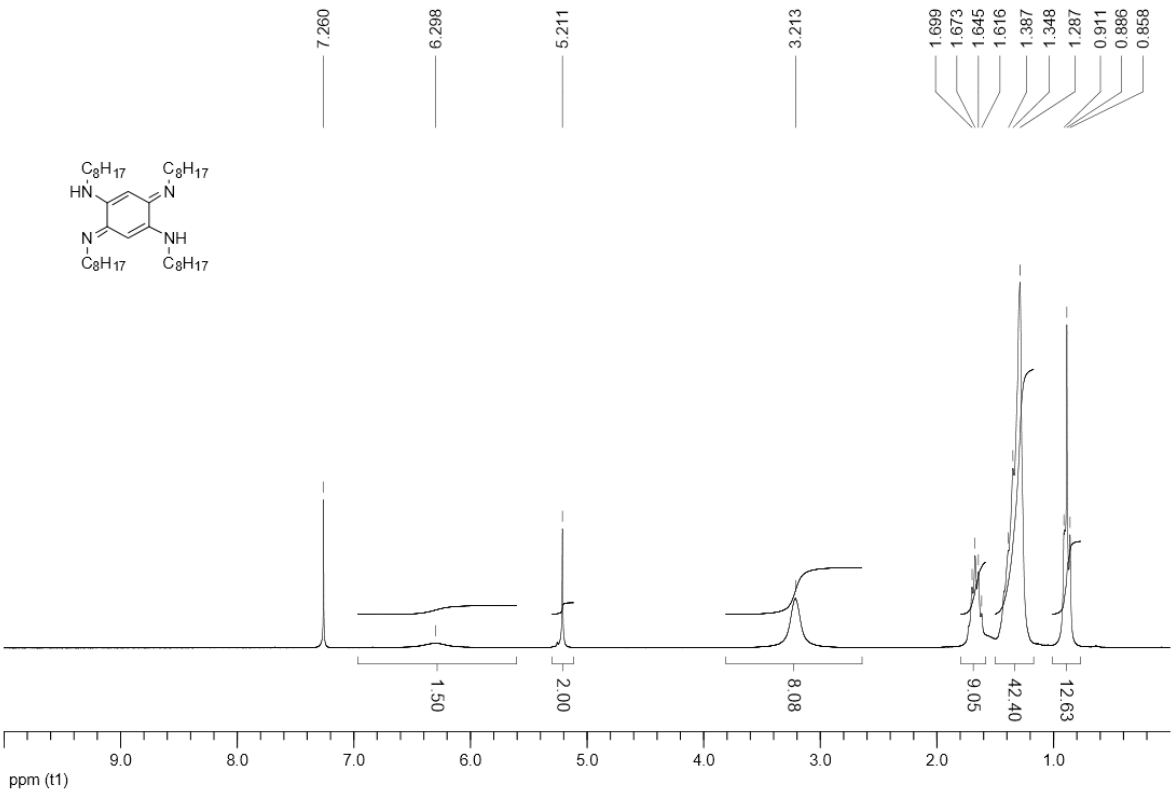

Figure S4: ^{1}H NMR spectrum of **1d** in $CDCl_3$ (250 MHz)

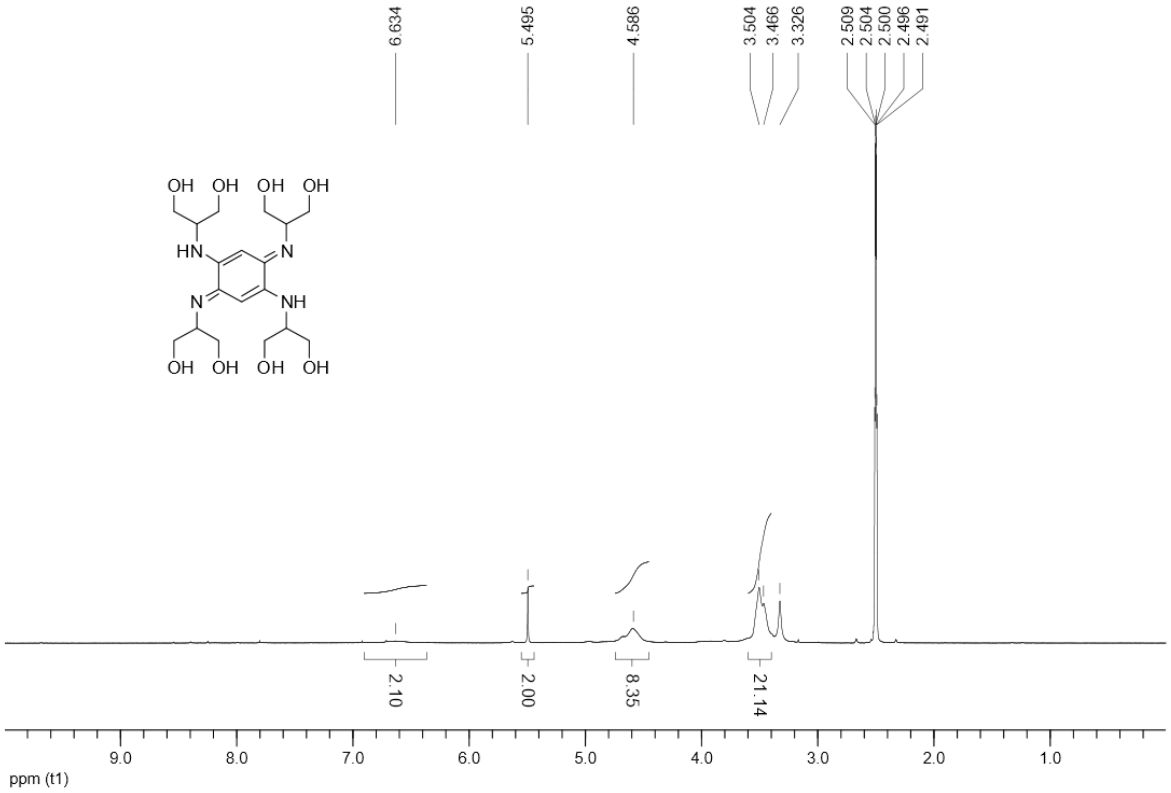

Figure S5: ^{1}H NMR spectrum of **1e** in DMSO-d_6 (400 MHz)

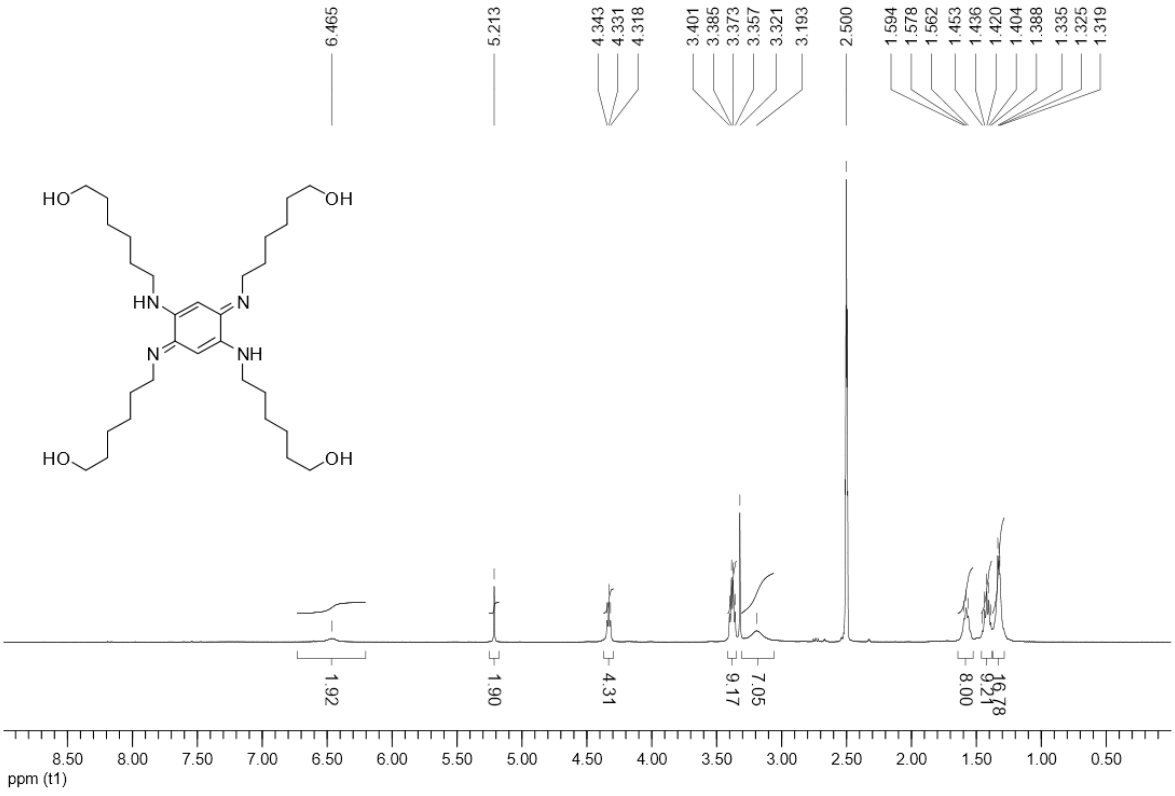

Figure S6: ^{1}H NMR spectrum of **1f** in DMSO-d_6 (400 MHz)

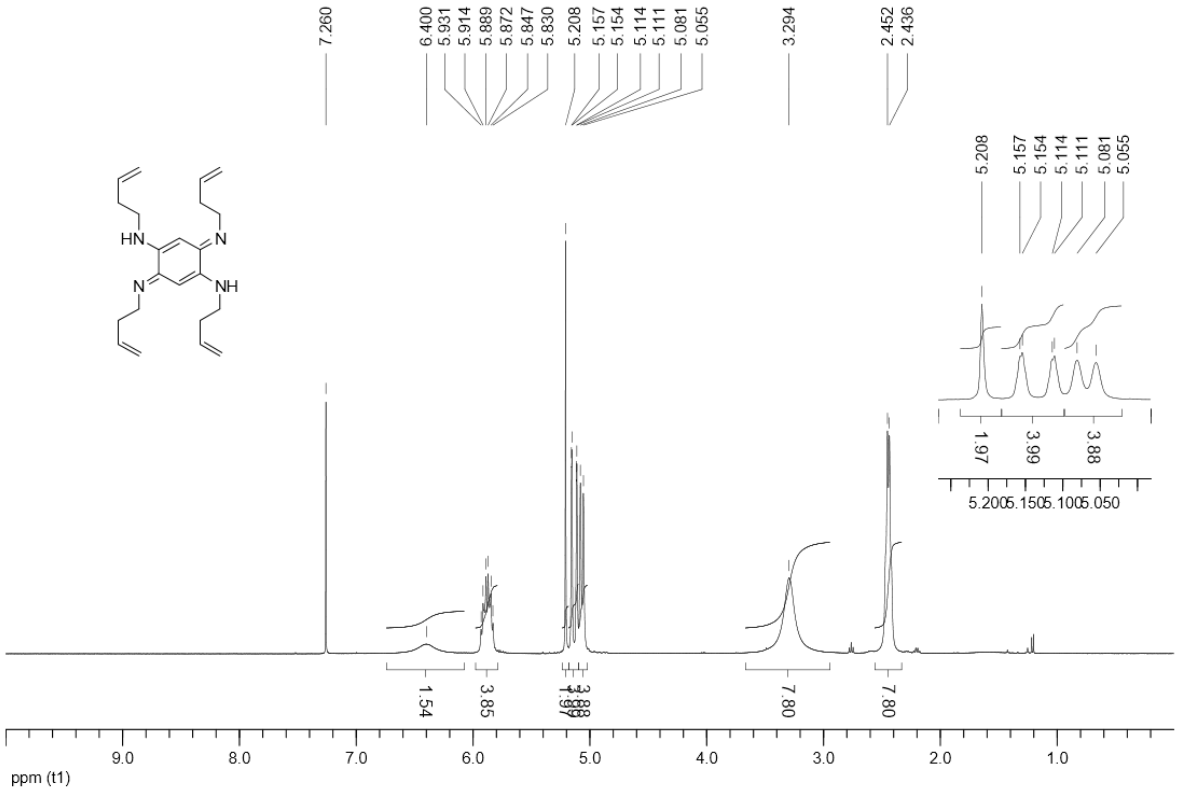

Figure S7: ^{1}H NMR spectrum of **1g** in $CDCl_3$ (400 MHz)

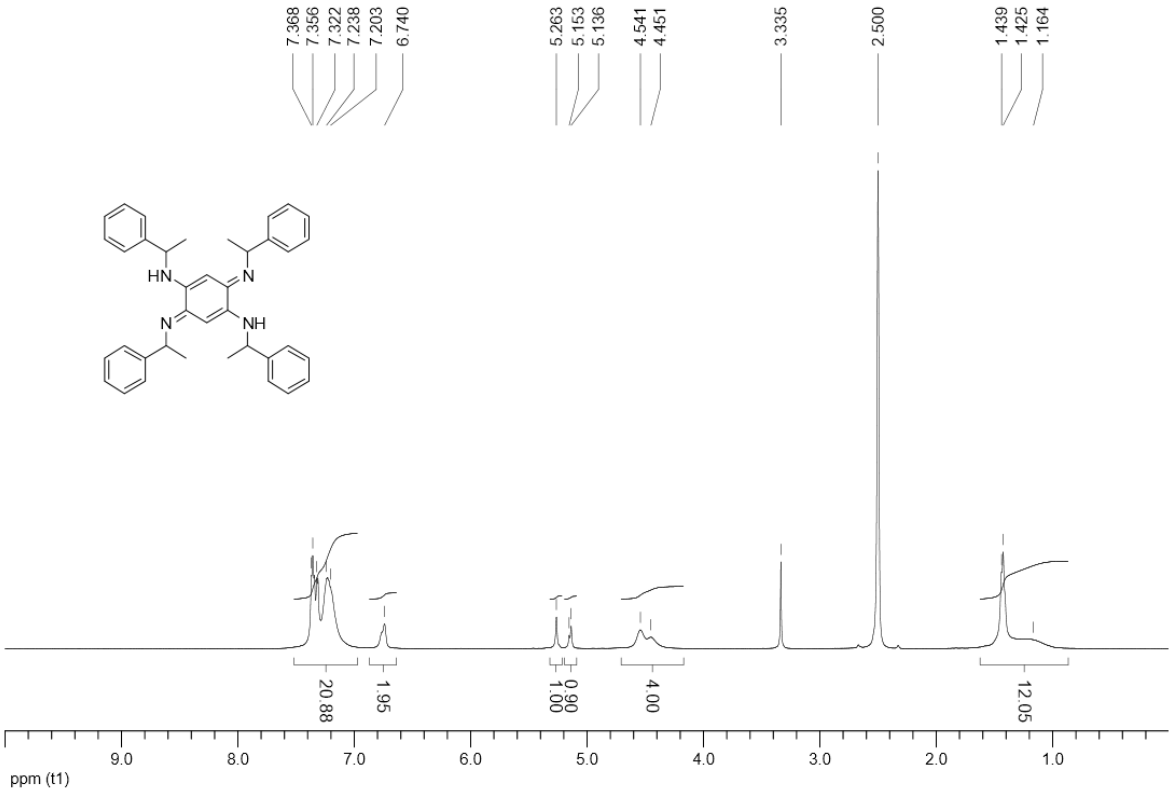

Figure S8: ^{1}H NMR spectrum of **1h** in DMSO-d_6 (400 MHz)

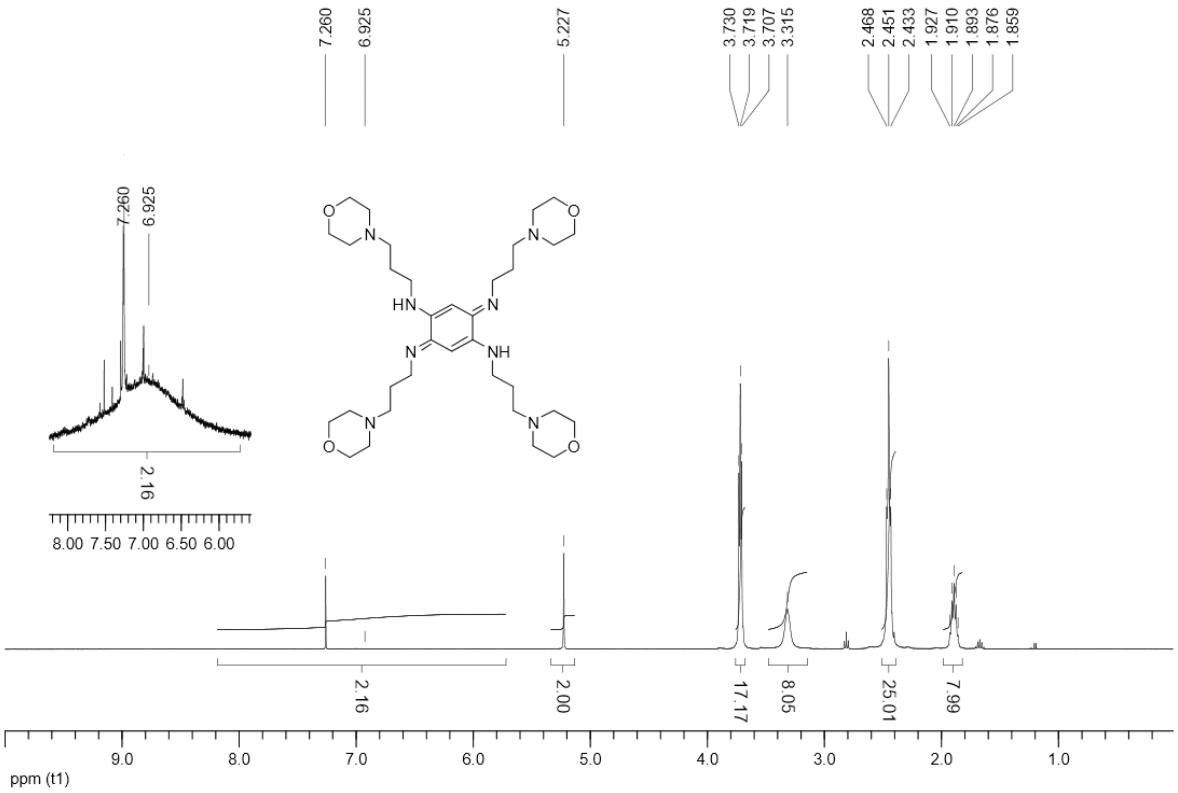

Figure S9: ^{1}H NMR spectrum of **1i** in $CDCl_3$ (400 MHz)

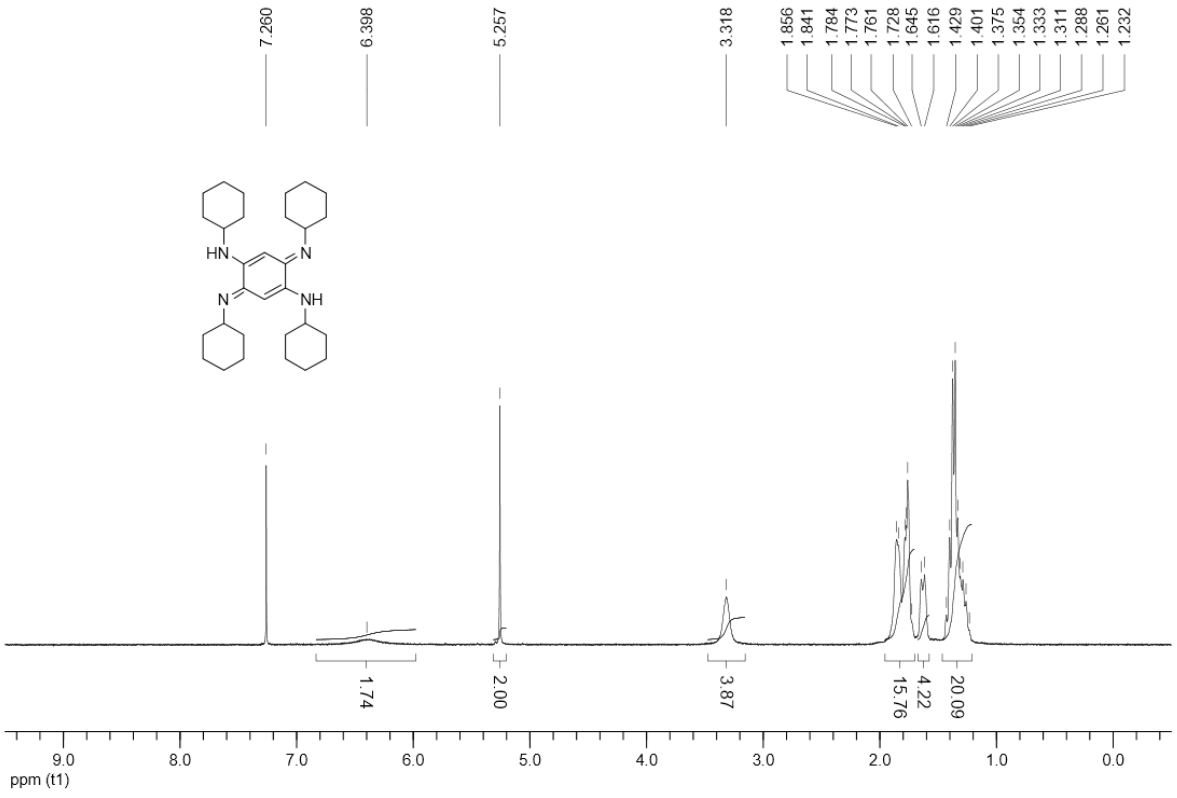

Figure S10: ^{1}H NMR spectrum of **1j** in $CDCl_3$ (400 MHz)

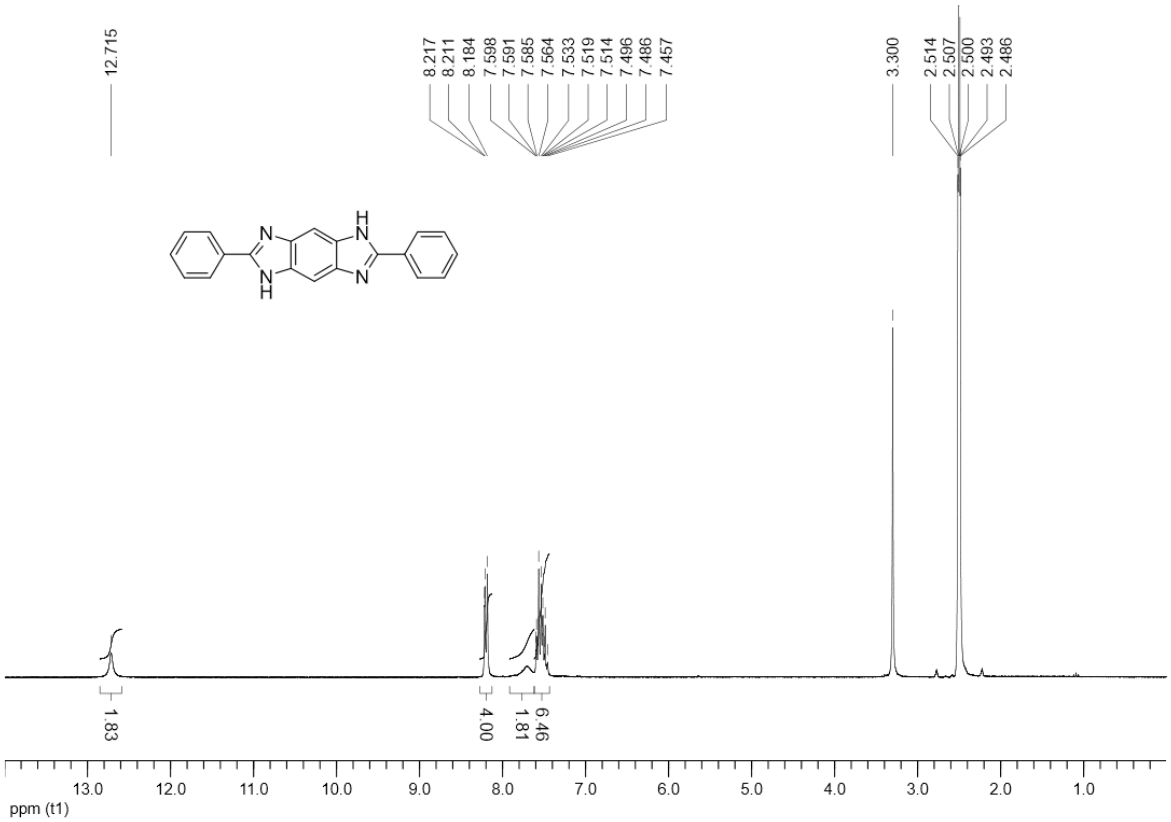

Figure S11: ^{1}H NMR spectrum of **3a** in $CDCl_3$ (400 MHz)

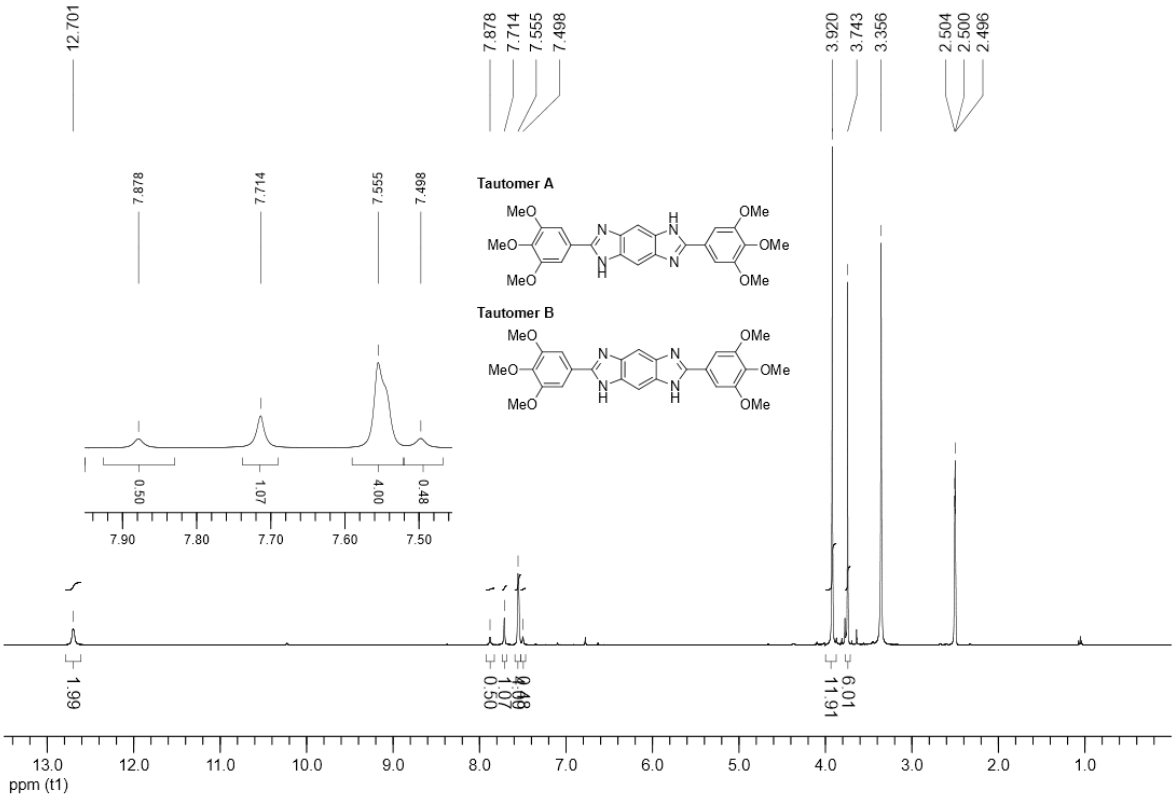

Figure S12: ^{1}H NMR spectrum of **3b** in $CDCl_3$ (400 MHz)

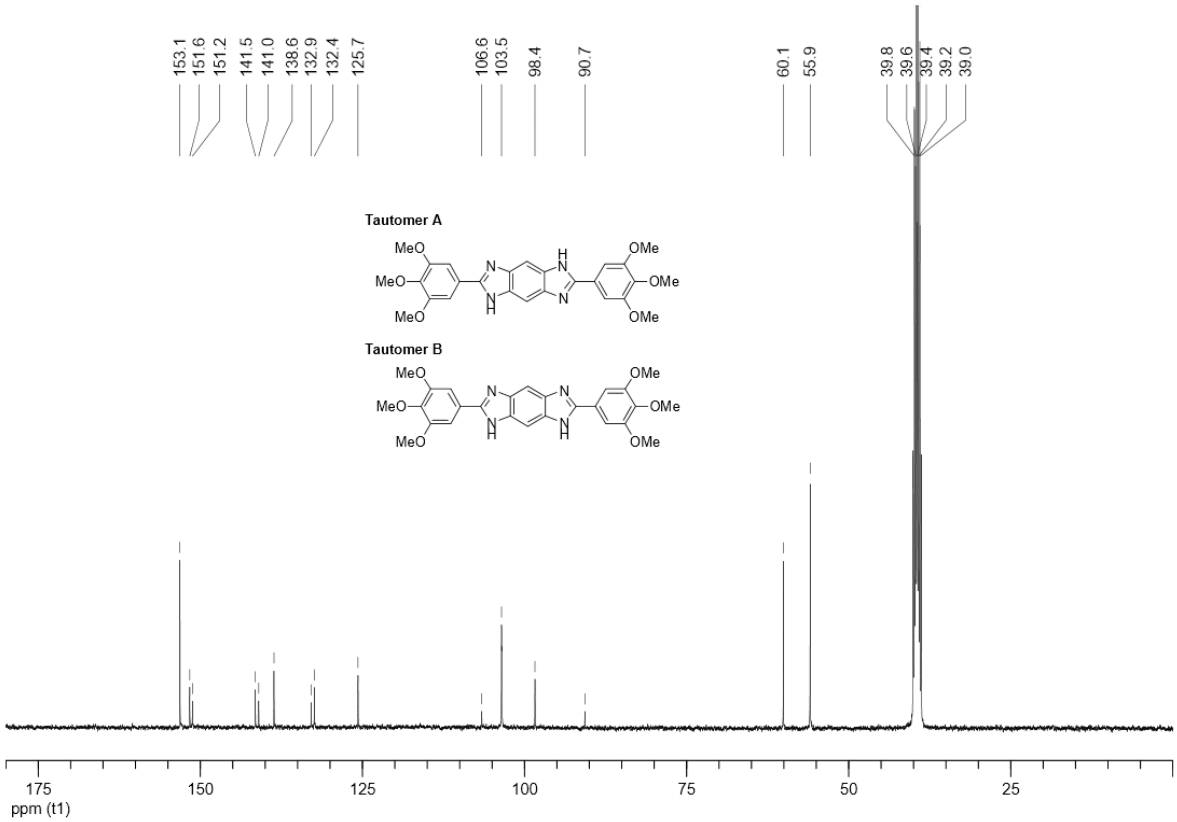

Figure S13: ^{13}C NMR spectrum of **3b** in $CDCl_3$ (100 MHz)

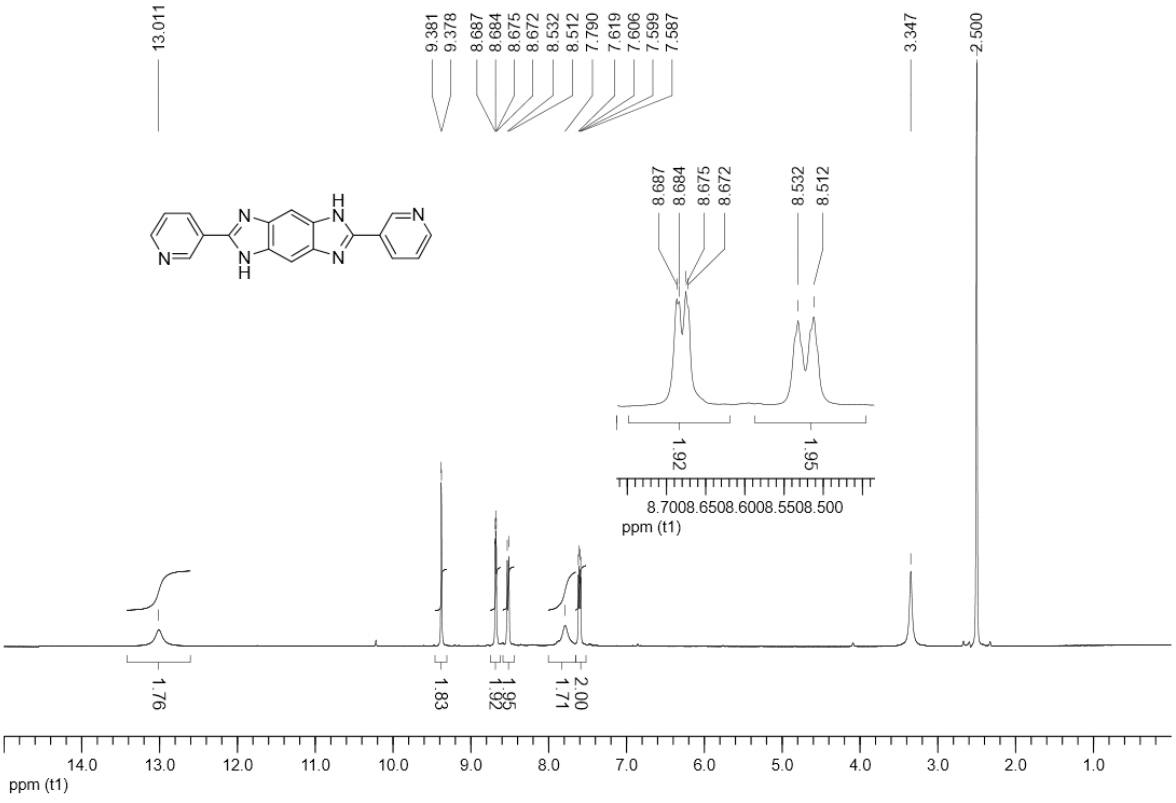

Figure S14: ^{1}H NMR spectrum of **3c** in DMSO-d_6 (400 MHz)

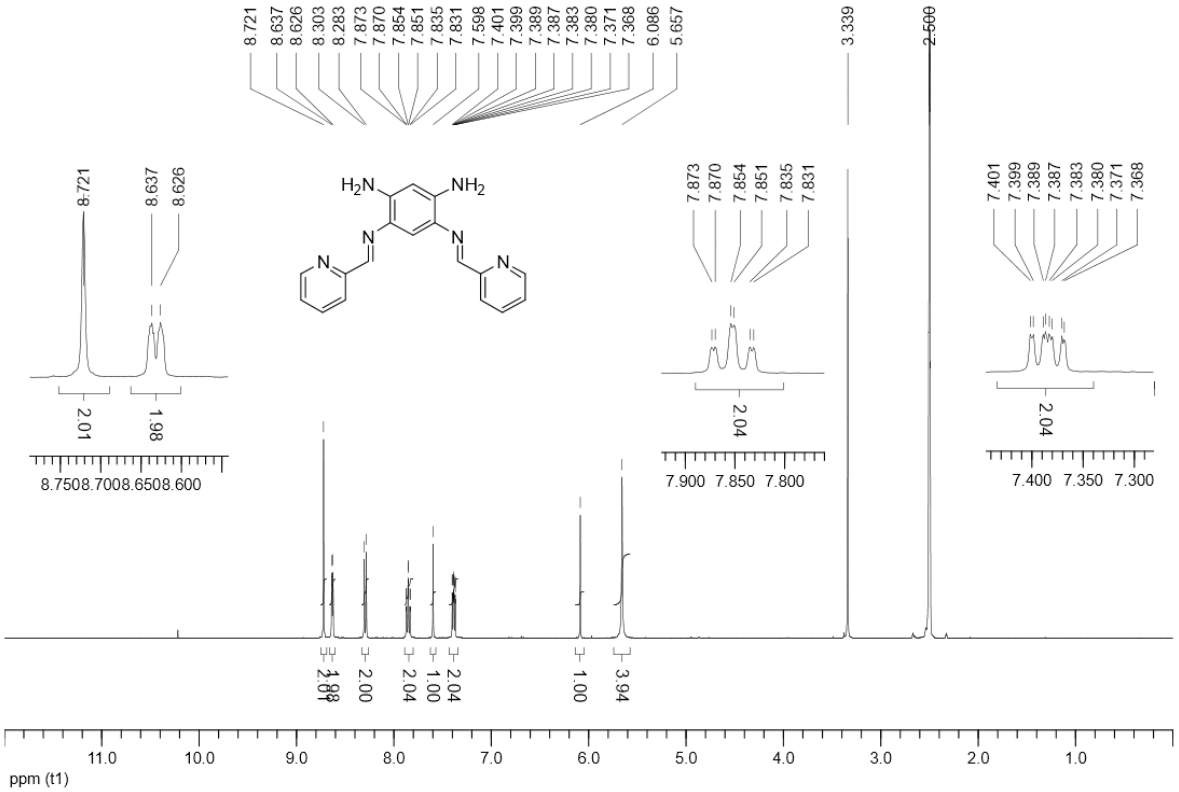

Figure S15: ^{1}H NMR spectrum of **6d** in DMSO-d_6 (400 MHz)

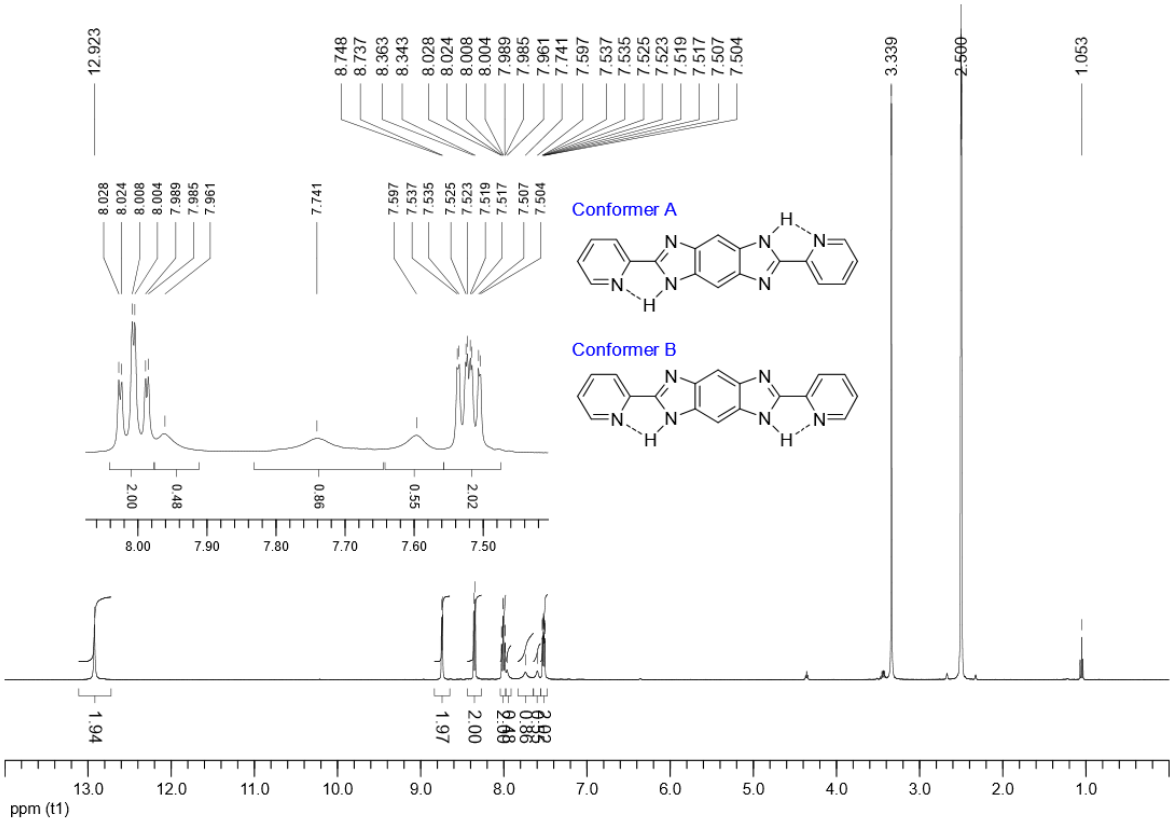

Figure S16: ^{1}H NMR spectrum of **3d** in $CDCl_3$ (400 MHz)

4. Emission studies

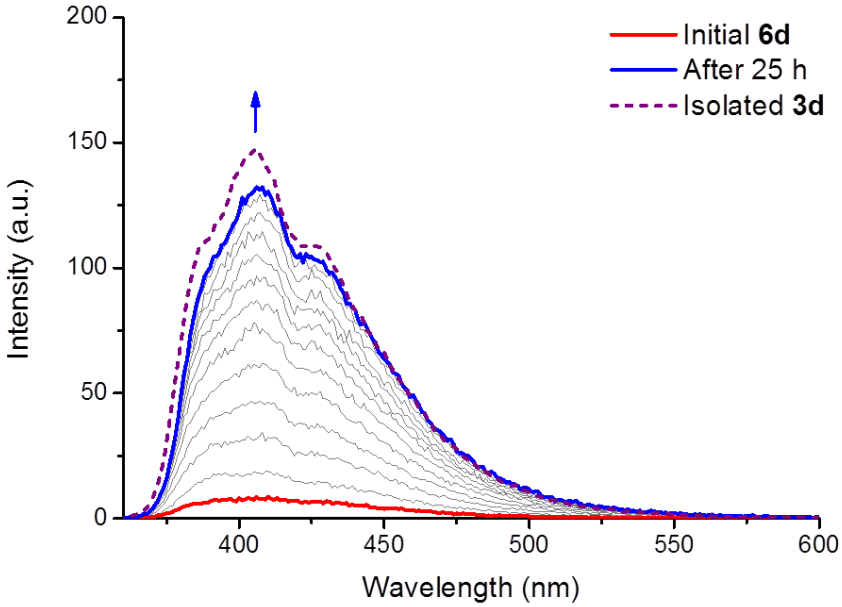

Figure S17: The kinetic evolution of **6d** followed by emission spectrophotometric, and the emission of isolated **3d**, both in EtOH, excited @354 nm.

5. References

S1 a) J. M. Bonnier, M. Gelus, *Rev. Inst. Fr. Pet. Ann. Combust. Liq.* **1967**, *22*, 1008. b) D. W. Tomlin, A. V. Fratini, M. Hunsaker and W. W. Adams *Polymer*, **2000**, *41*, 9003.

S2 T. Ohno, K. Nozaki, M. Haga, *Inorg. Chem.* **1992**, *31*, 4256.