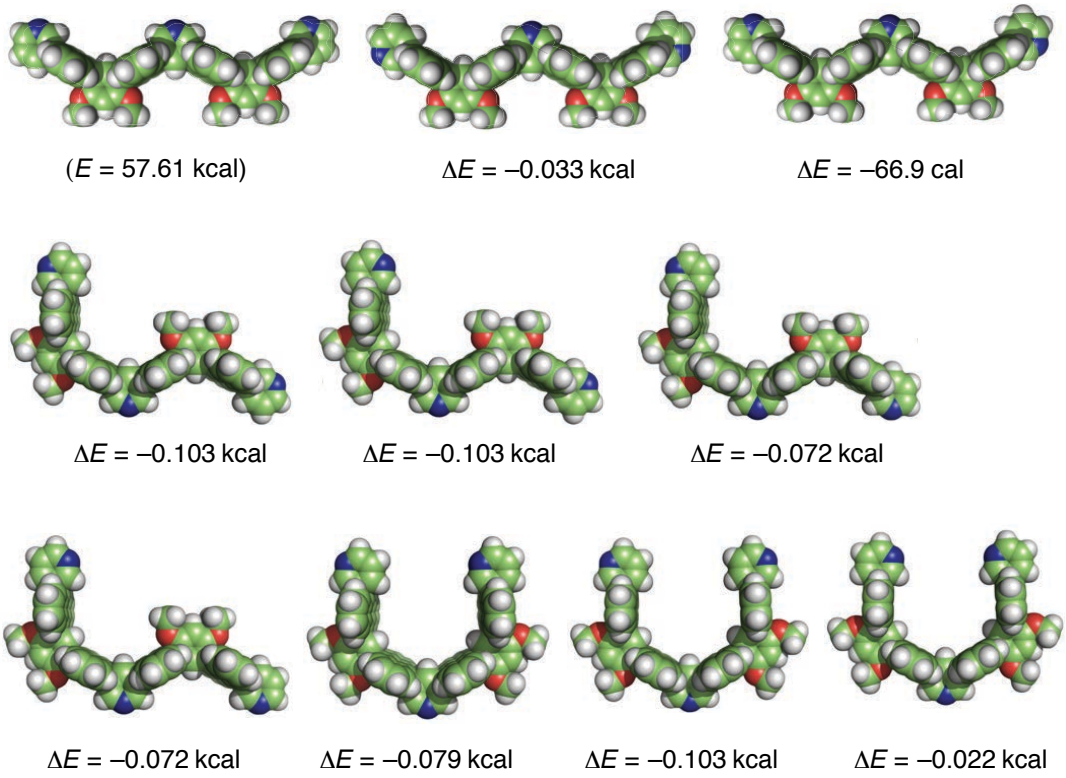
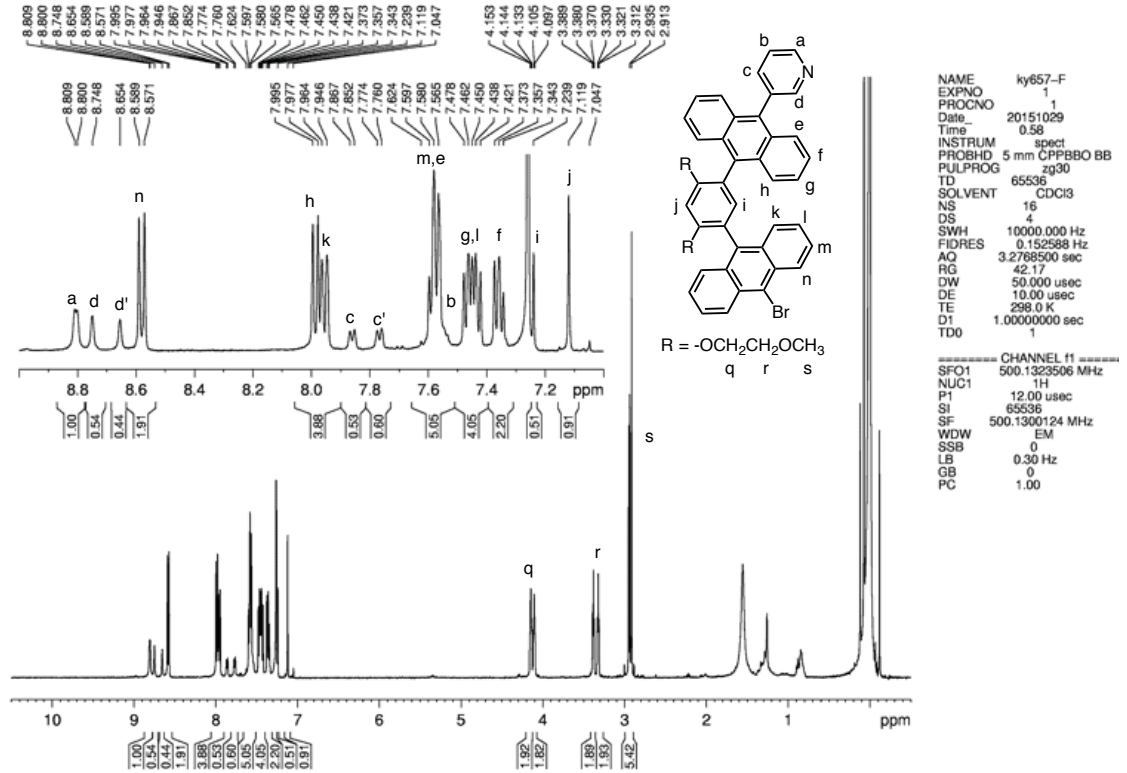
Type of file: PDF
Title of file for HTML: Supplementary Information
Description: Supplementary Figures, Supplementary Table, Supplementary Methods, and Supplementary References.

Type of file: PDF
Title of file for HTML: Peer Review File
Description:

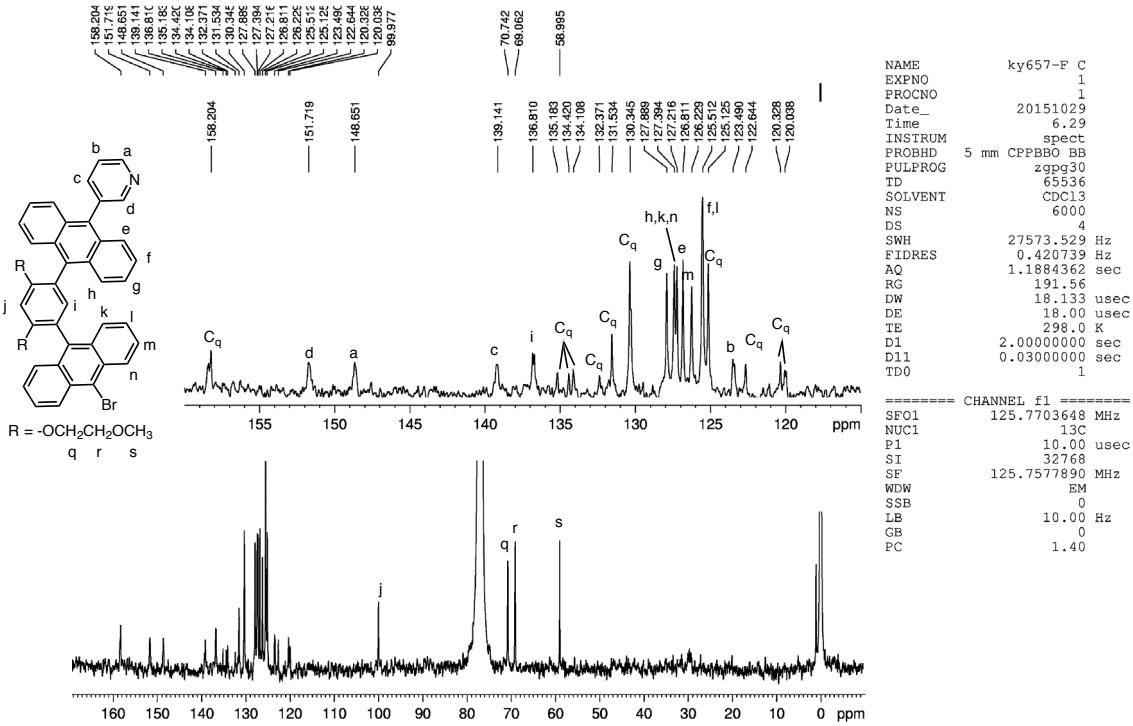
Supplementary Figures



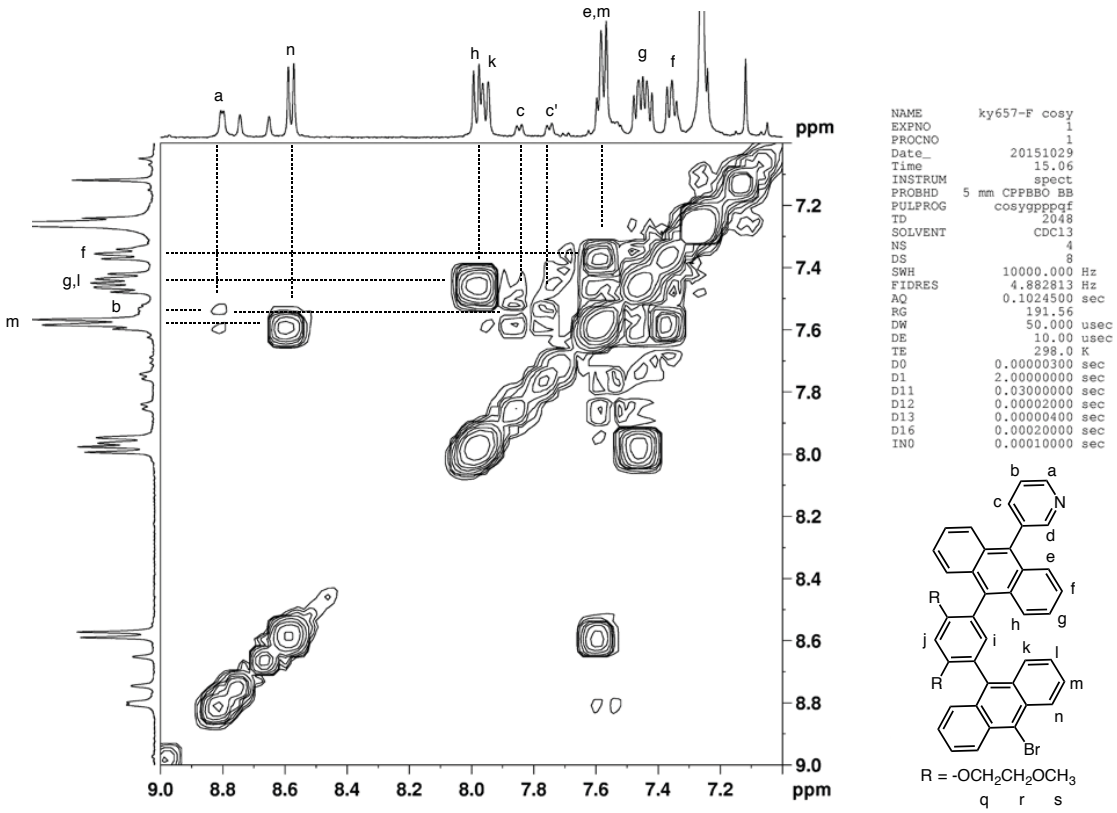
Supplementary Figure 1 | Optimized structures and energies (based on the upper-left structure) of ten stereoisomers of ligand **1** (R = -OCH_3) (PM6 calculations).



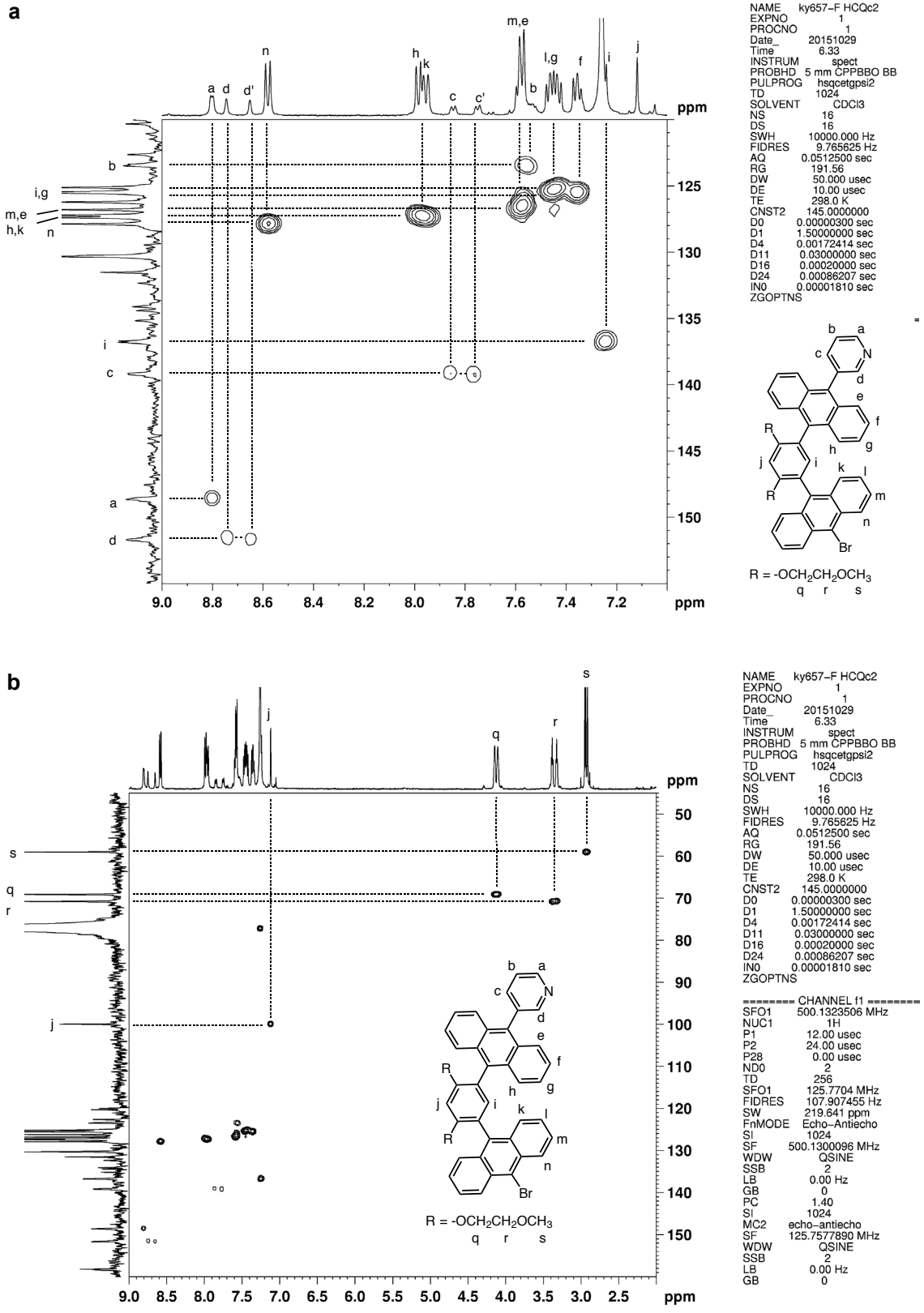
Supplementary Figure 2 | ^{1}H NMR spectrum (500 MHz, $CDCl_3$, room temperature) of **6a**.



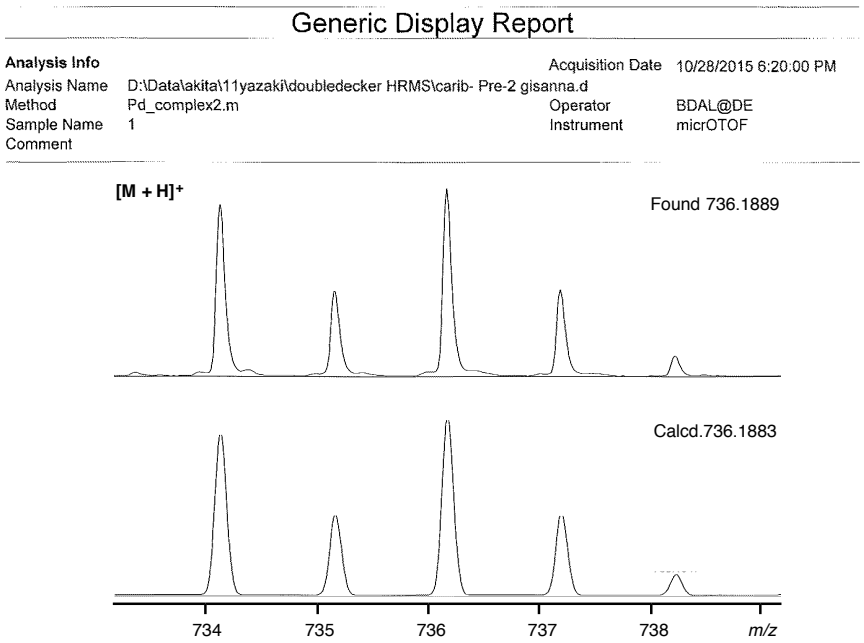
Supplementary Figure 3 | ^{13}C NMR spectrum (125 MHz, $CDCl_3$, room temperature) of **6a**.



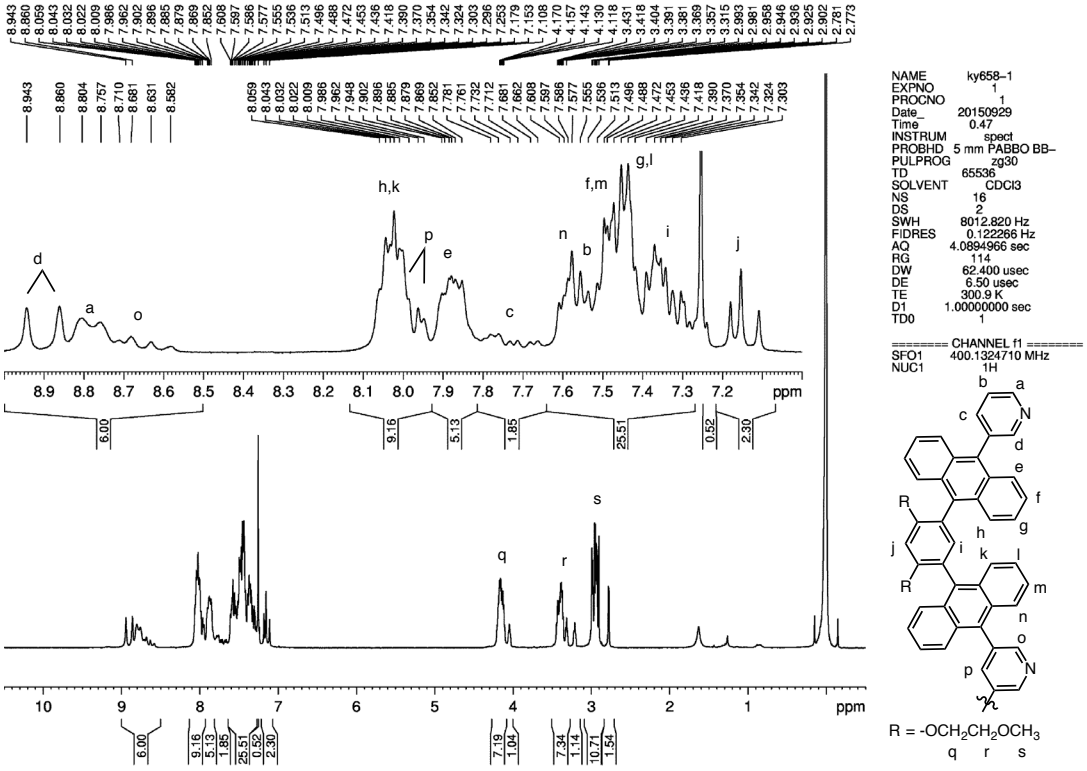
Supplementary Figure 4 | HH COSY spectrum (500 MHz, $CDCl_3$, room temperature) of **6a**.



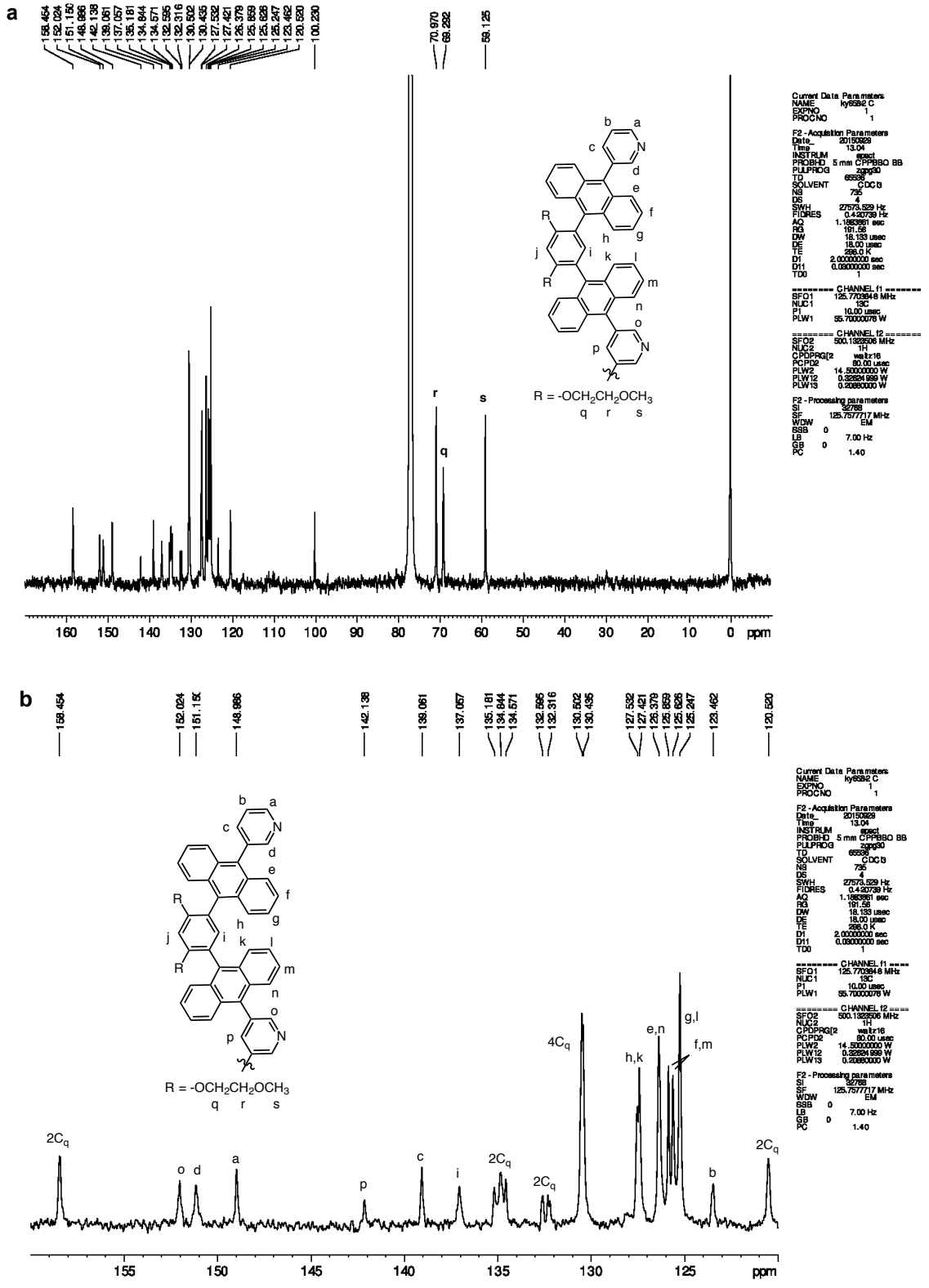
Supplementary Figure 5 | HSQC spectra (500 MHz, $CDCl_3$, room temperature) of **6a**. (a) The aromatic and (b) aliphatic regions.



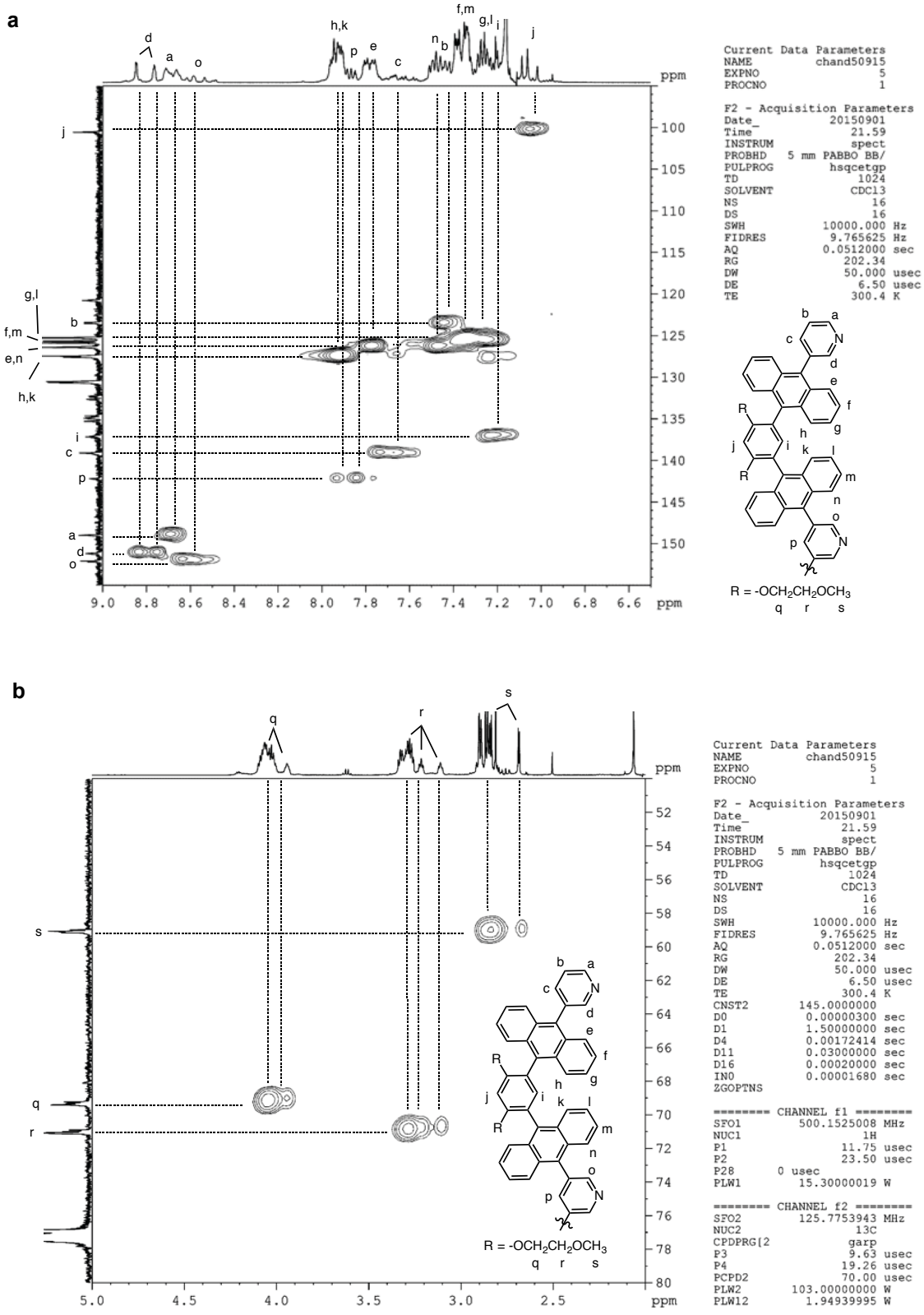
Supplementary Figure 6 | HR MS spectrum (ESI) of **6a**.



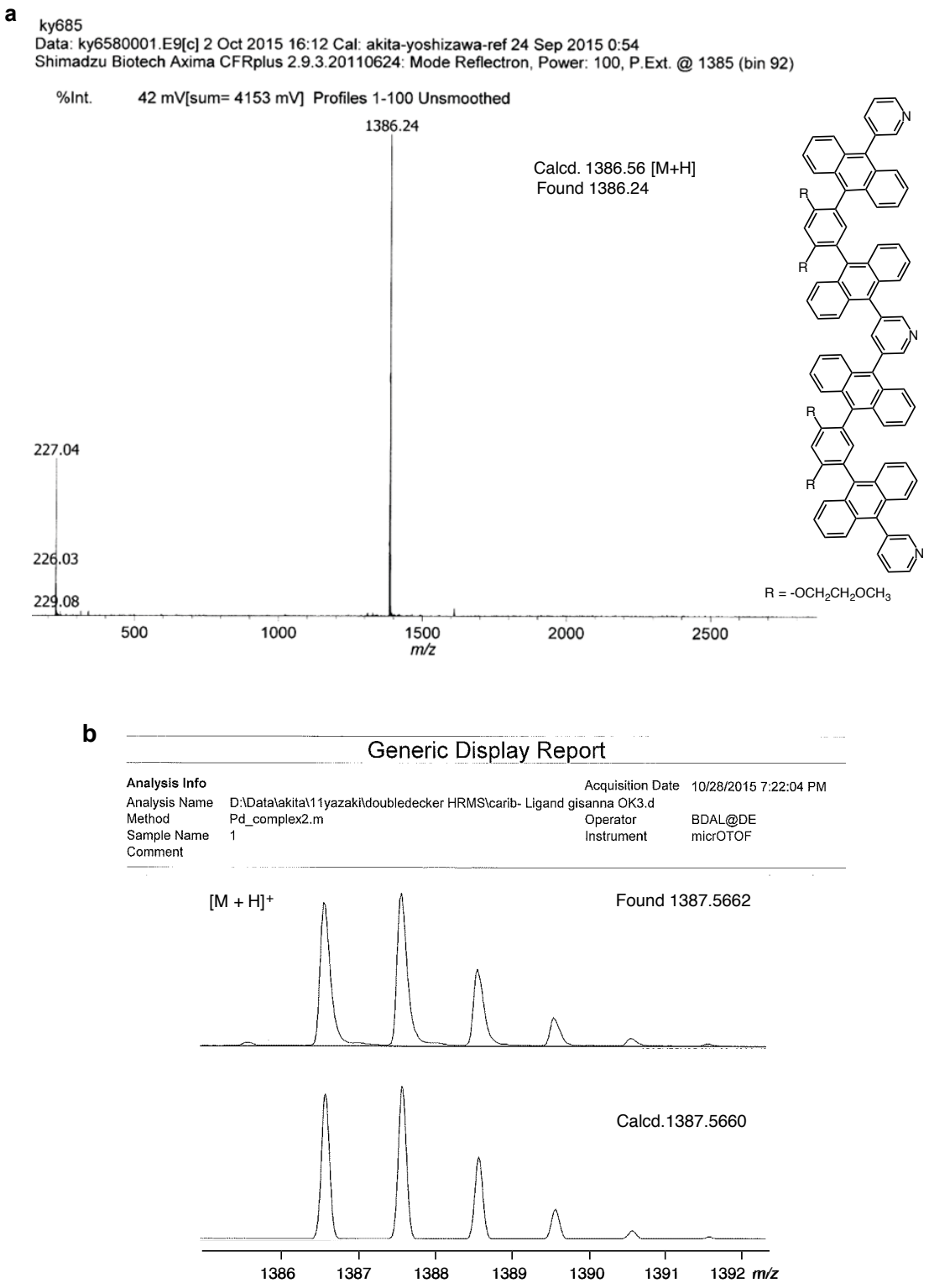
Supplementary Figure 7 | ^{1}H NMR spectrum (500 MHz, $CDCl_3$, room temperature) of **1a**.



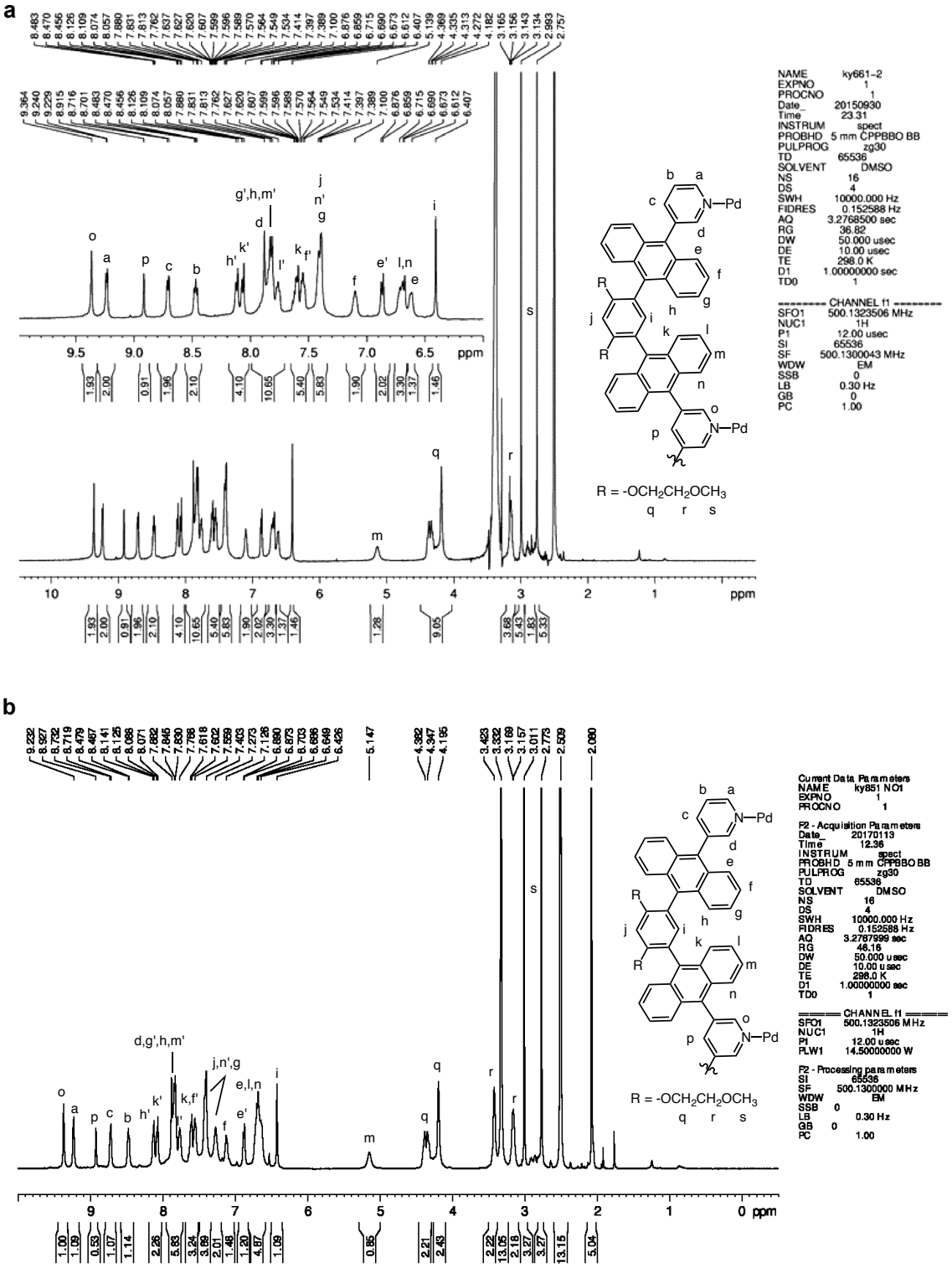
Supplementary Figure 8 | ^{13}C NMR spectra (125 MHz, $CDCl_3$, room temperature) of **1a**. (a) The aromatic and aliphatic and (b) aromatic regions.



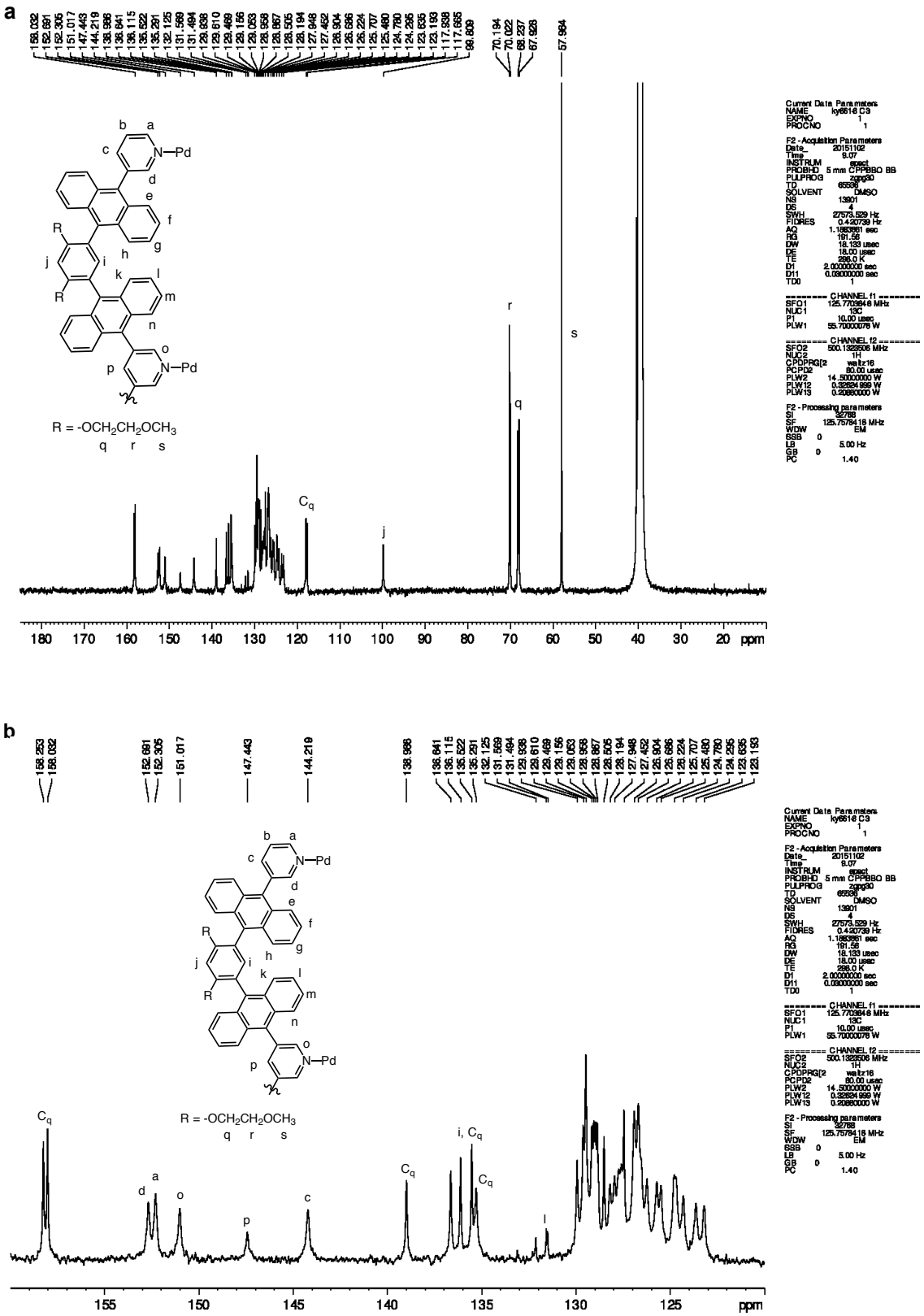
Supplementary Figure 9 | HSQC spectra (500 MHz, $CDCl_3$, room temperature) of **1a**. (a) The aromatic and (b) aliphatic regions.



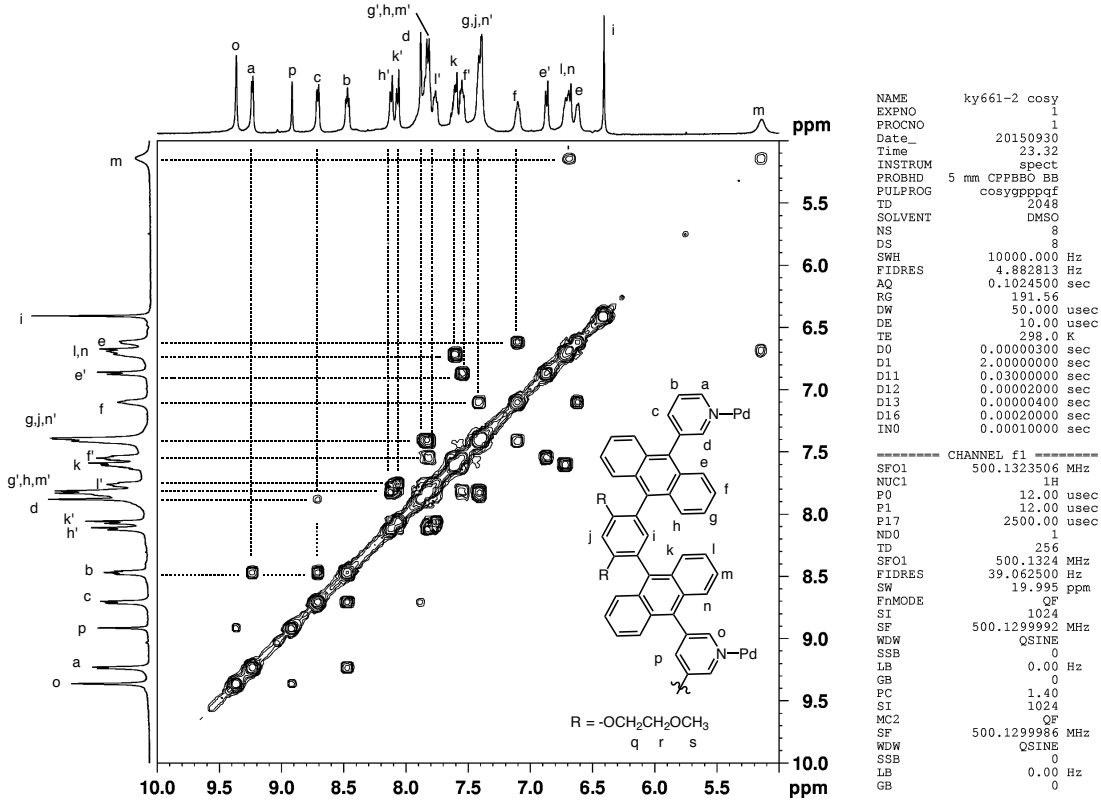
Supplementary Figure 10 | (a) MALDI-TOF MS (dithranol) and (b) HR MS (ESI) spectra of **1a**.



Supplementary Figure 11 | ^{1}H NMR spectra (500 MHz, DMSO-d_6, room temperature) of (a) **2a** and (b) **2a'**.



Supplementary Figure 12 | ^{13}C NMR spectra (125 MHz, DMSO-d_6, room temperature) of **2a**. (a) The aromatic and aliphatic and (b) aromatic regions.



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D11	0.03000000 sec
D12	0.00002000 sec
D13	0.00000400 sec
D16	0.00020000 sec
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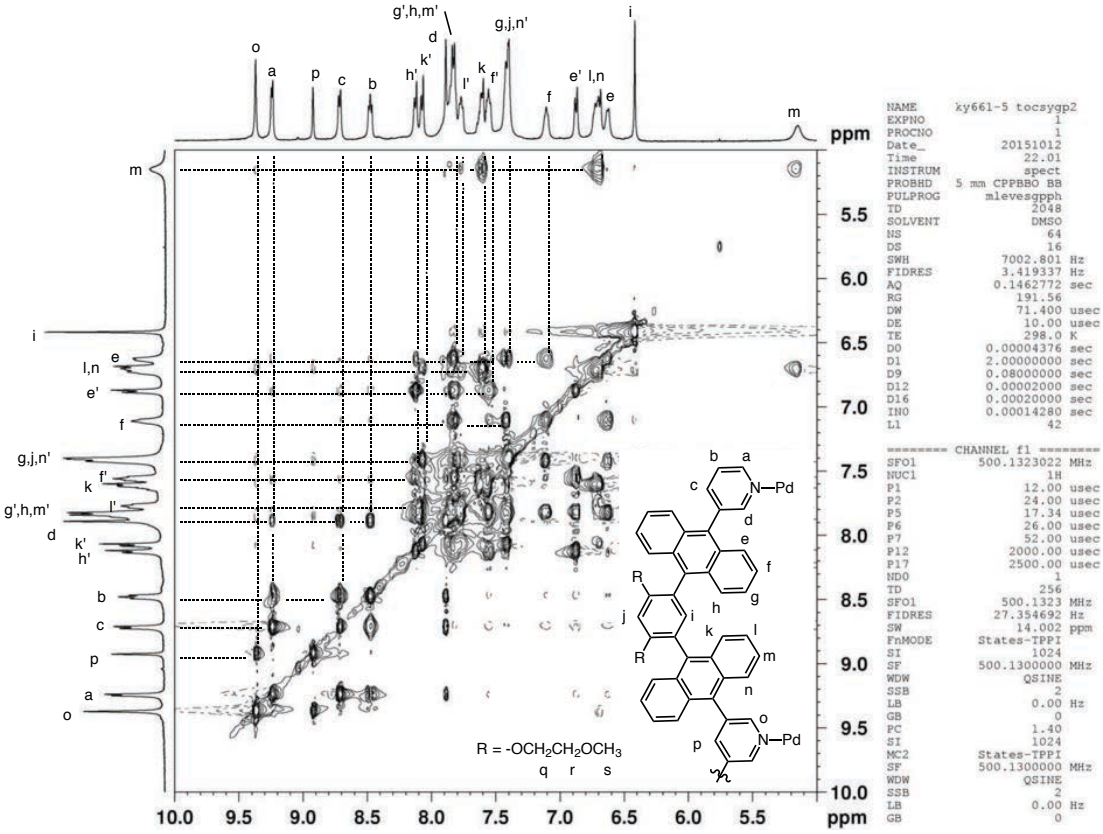
Supplementary Figure 13 | HH COSY spectrum (500 MHz, DMSO-d_6, room temperature) of **2a**.



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P7	52.00 usec
P12	2000.00 usec
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GB	0
PC	1.40
SI	1024
MC2	States-TPPI
SF	500.1300000 MHz
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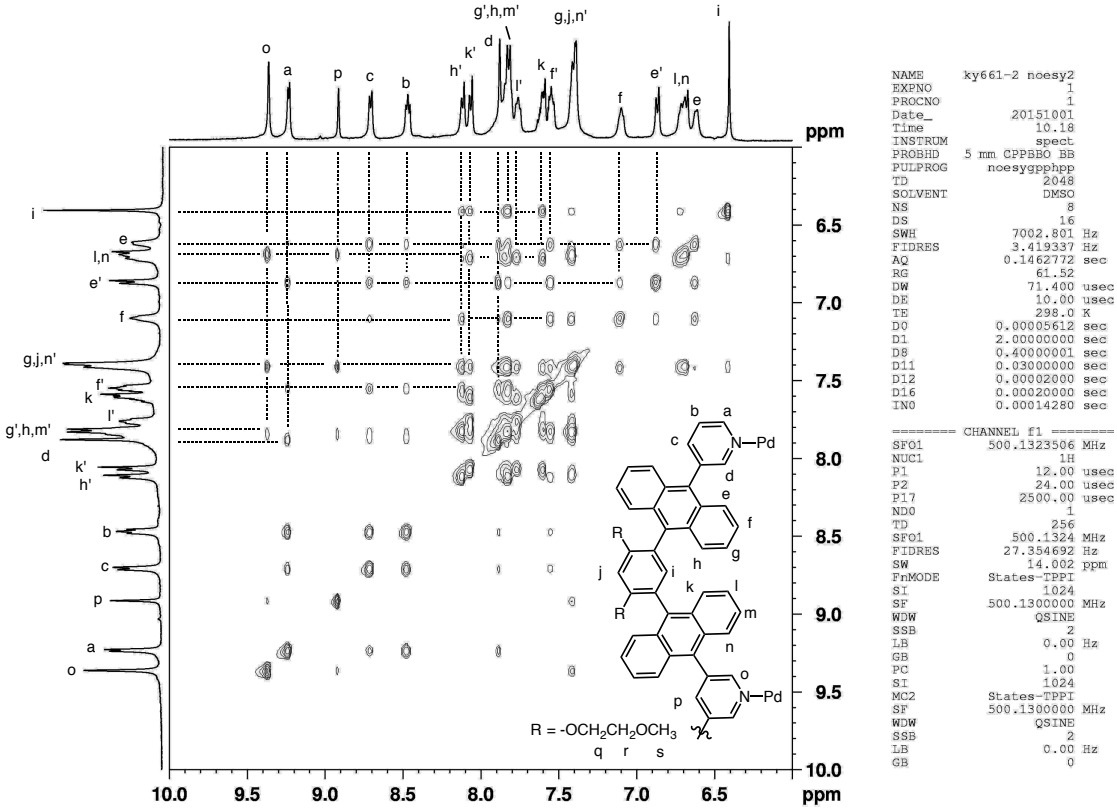
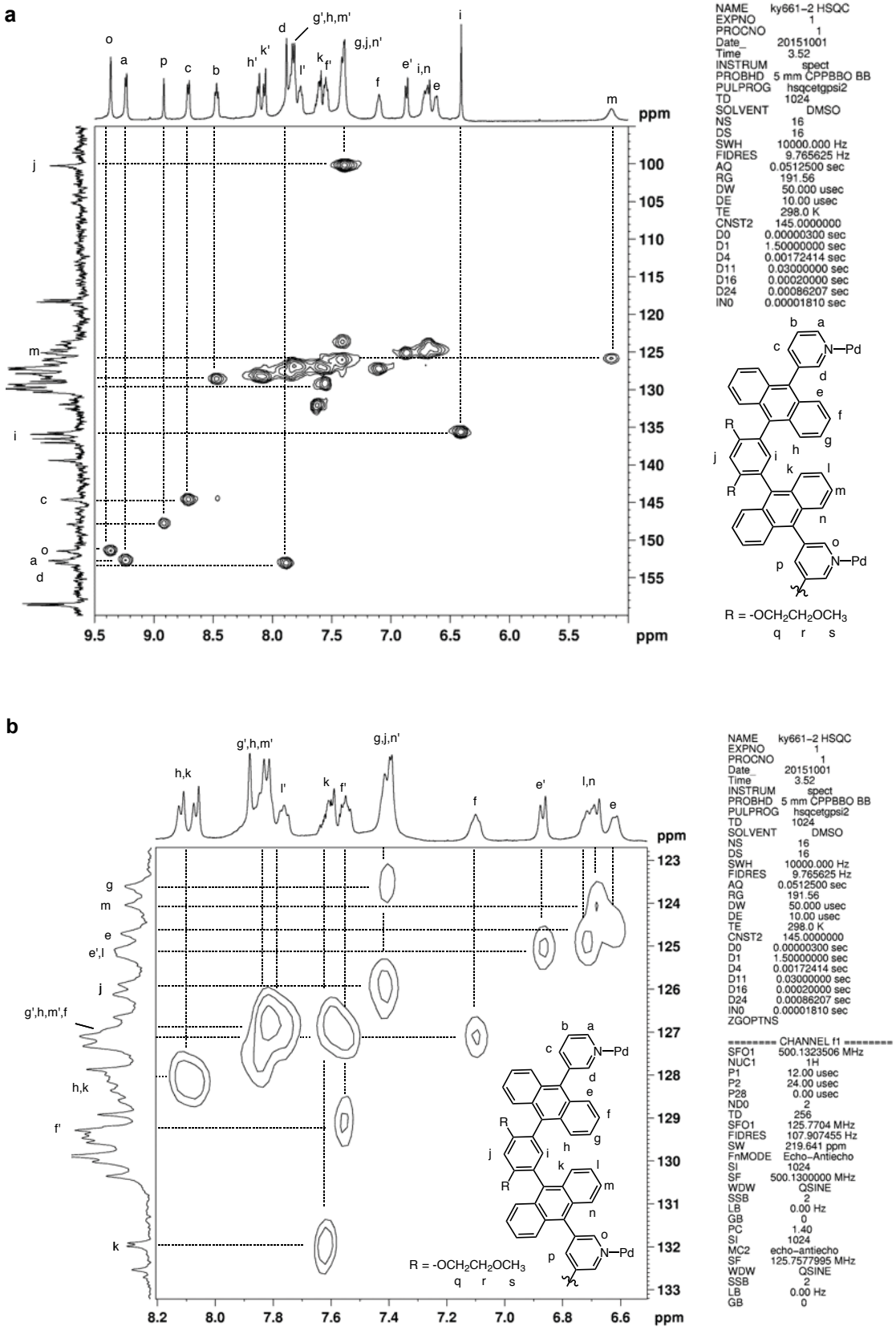
Supplementary Figure 14 | HH TOCSY spectrum (500 MHz, DMSO-d_6, room temperature) of **2a**.



Supplementary Figure 15 | NOESY spectrum (500 MHz, DMSO-d_6, room temperature) of **2a**.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p
c
b
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k'
d
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l'
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f'
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e
i
m
ppm
j
m
i
c
o
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d
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D24 0.00086207 sec
IN0 0.00001810 sec
b a
c
N—Pd
d
e
f
R
g
h
j
i
k
l
R
m
n
o
p
N—Pd
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q r s
b
a
g',h,m'
g,j,n'
h,k
l'
k
f'
f
e'
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ppm
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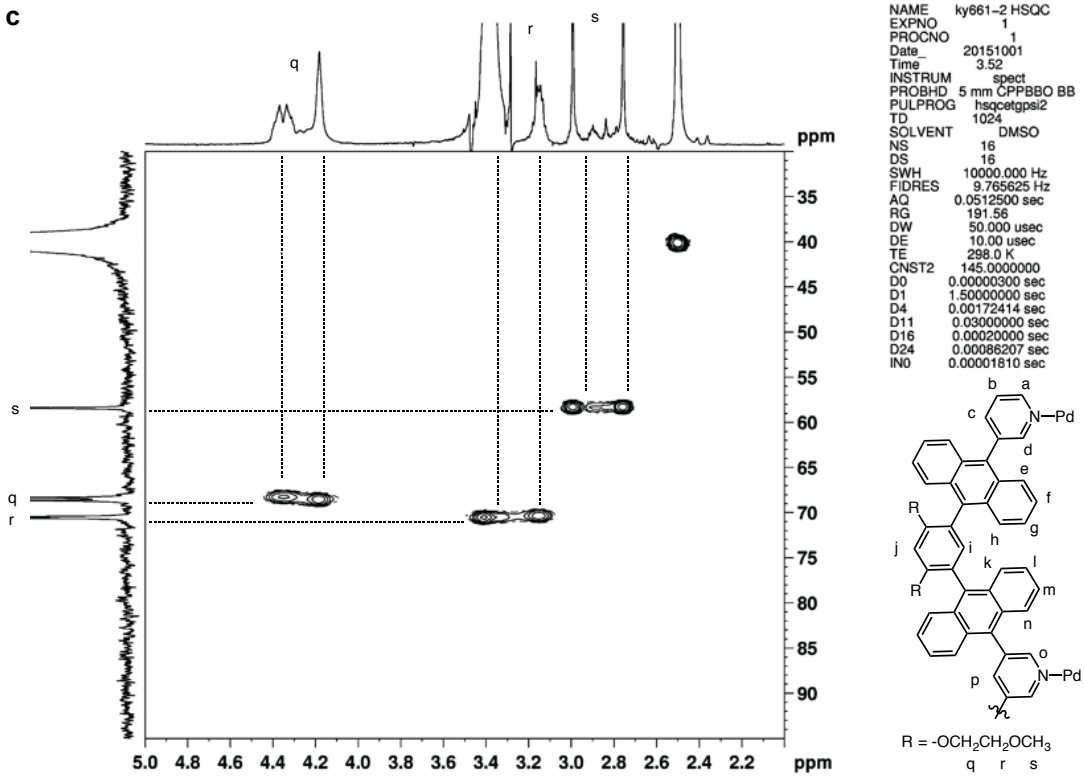
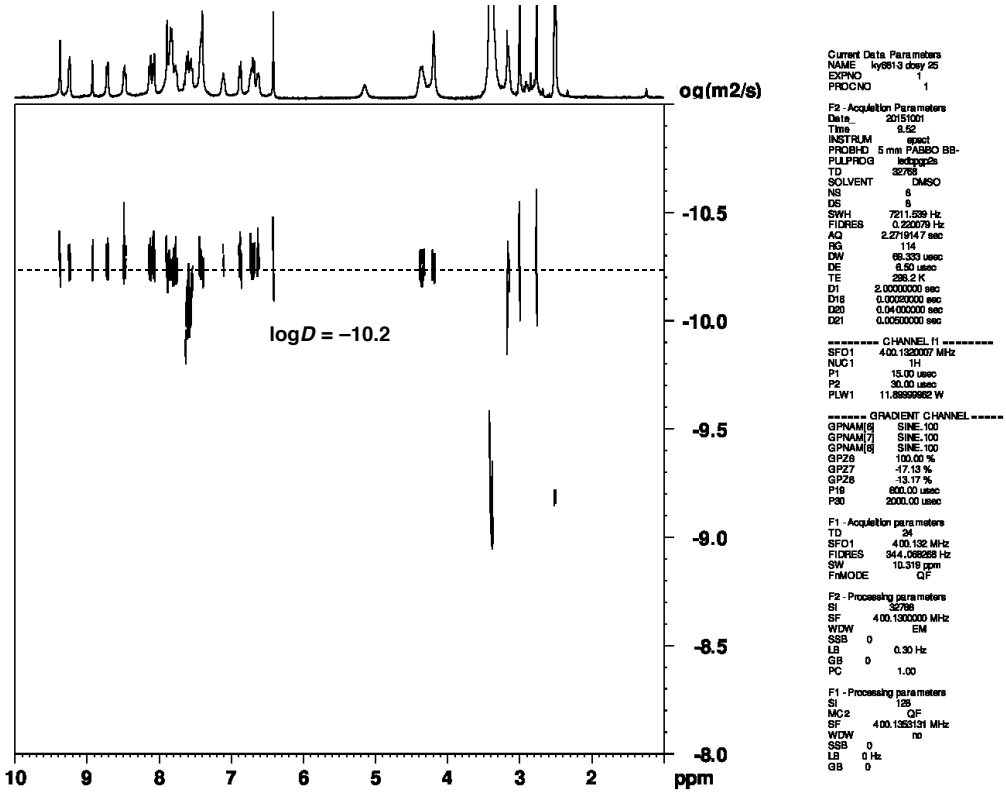
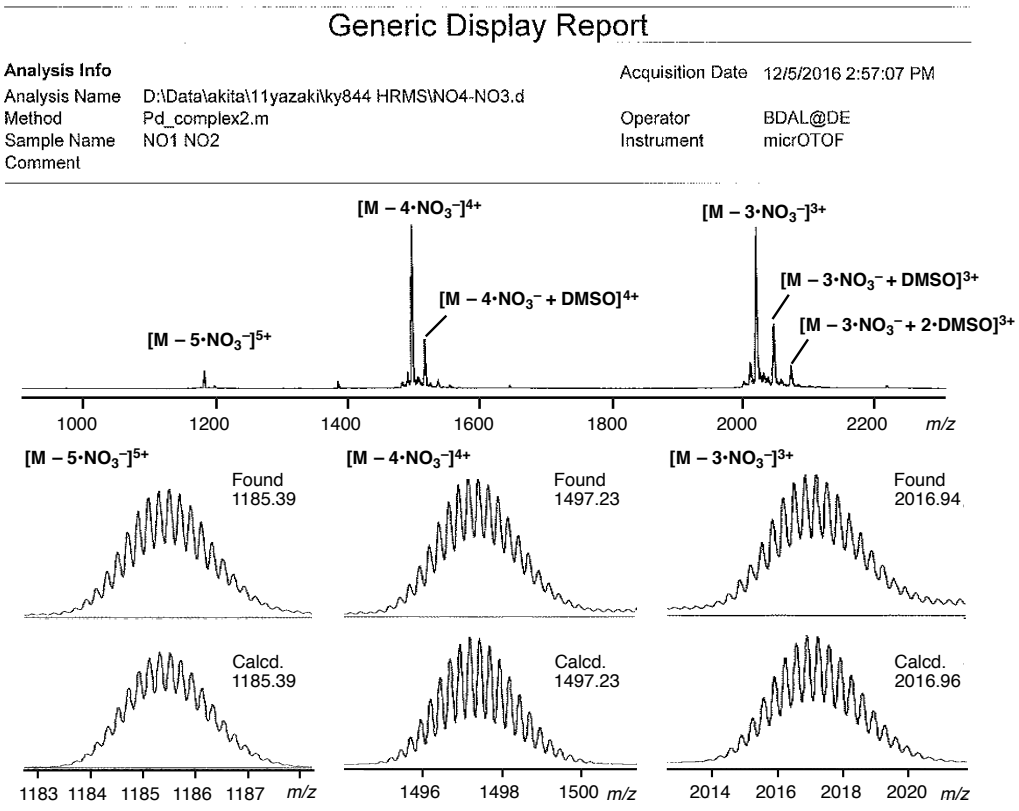


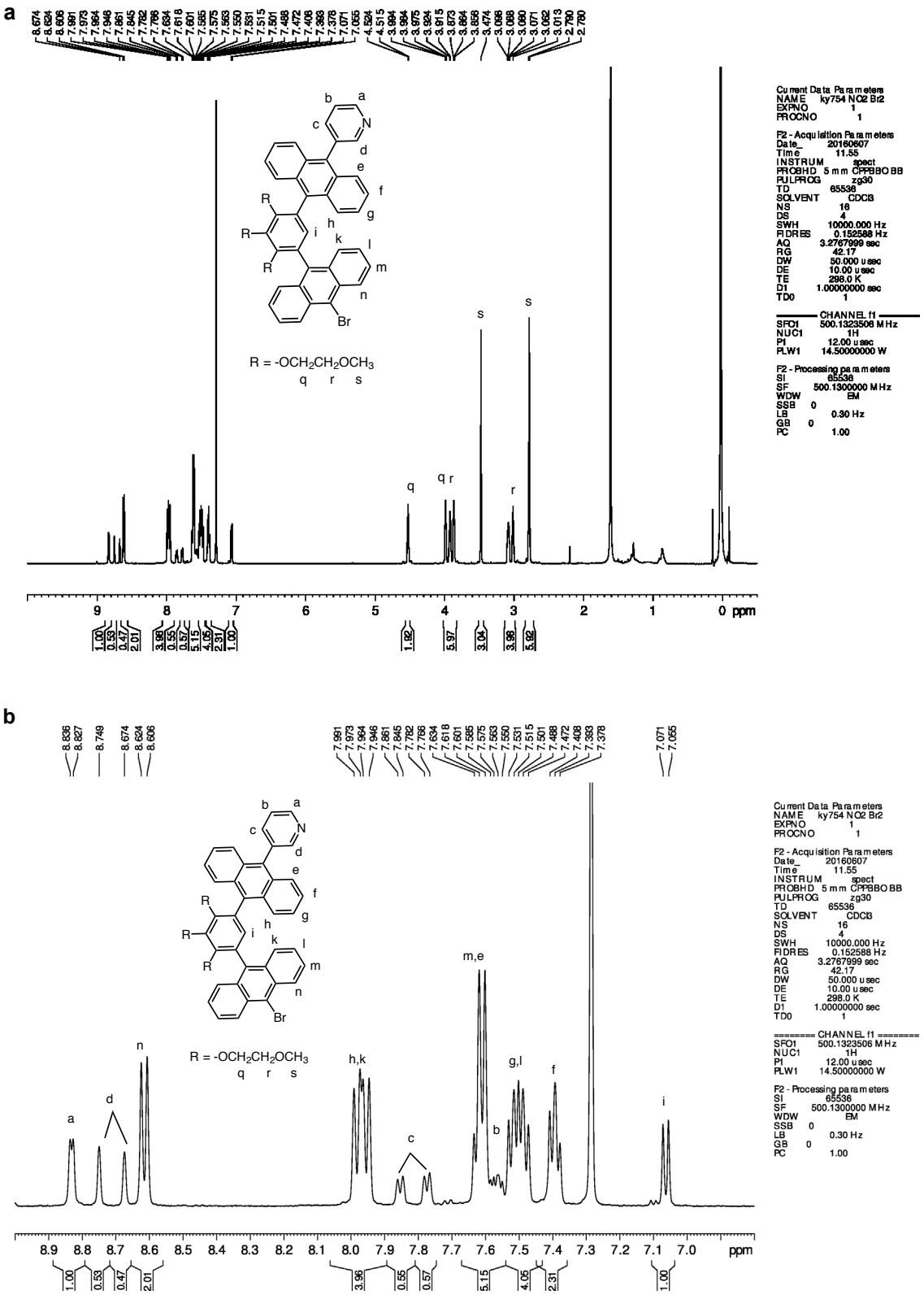
Supplementary Figure 16 | HSQC spectra (500 MHz, DMSO-d_6, room temperature) of **2a**. (a,b) The aromatic and (c) aliphatic regions.



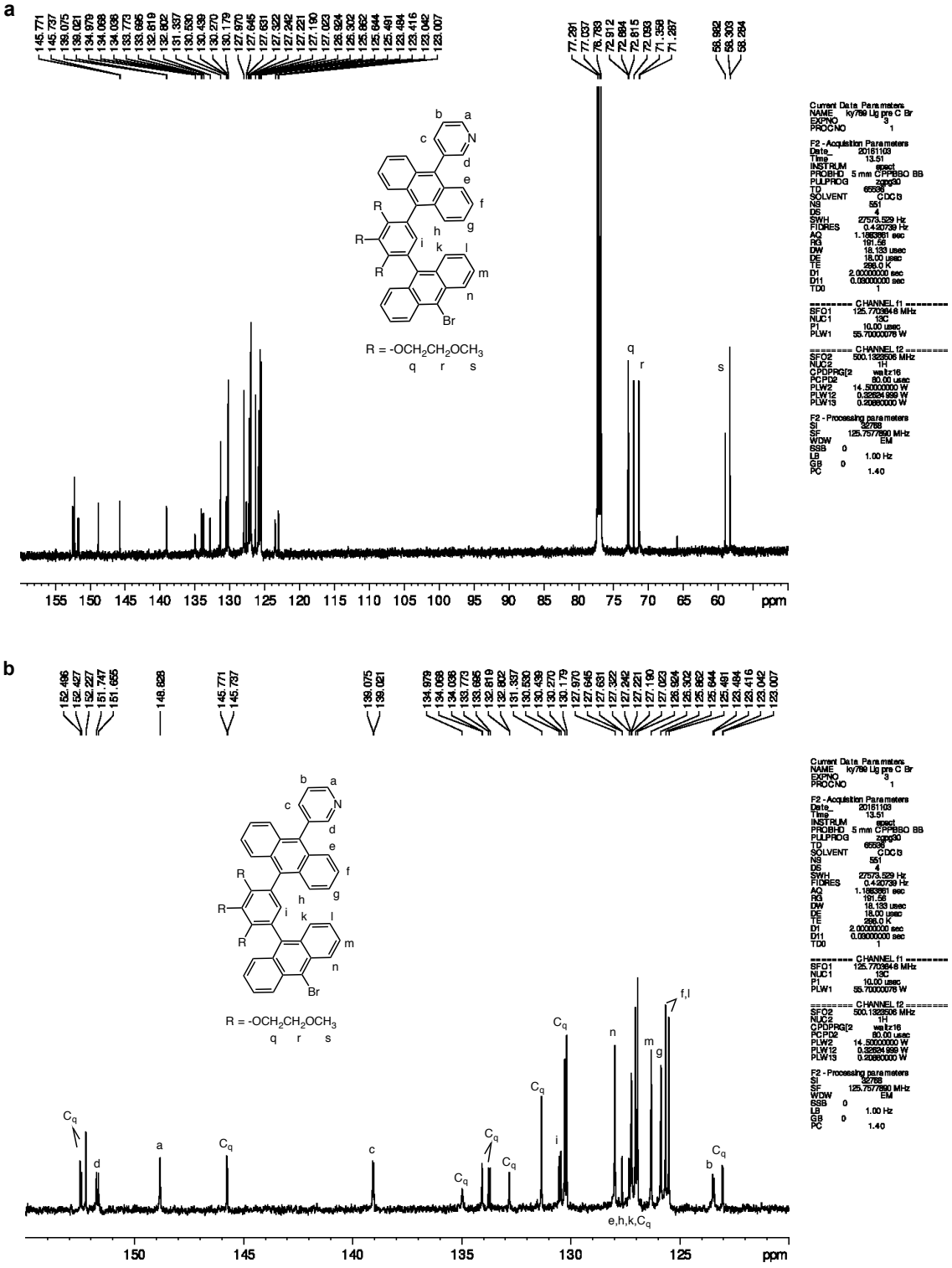
Supplementary Figure 17 | DOSY NMR (500 MHz, DMSO-d_6, 298 K) of **2a**.



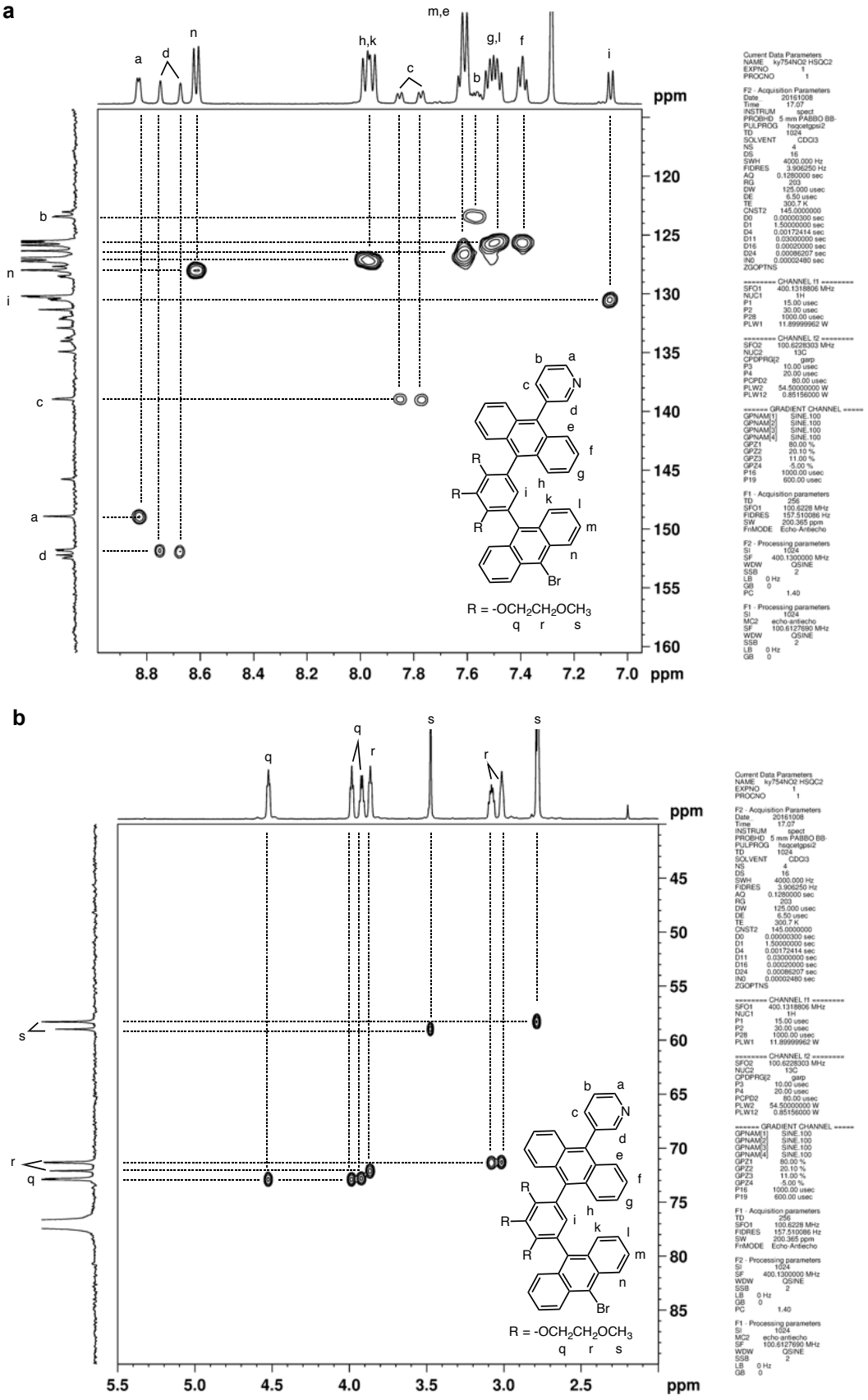
Supplementary Figure 18 | ESI-TOF MS spectrum (CH_3OH) of **2a**.



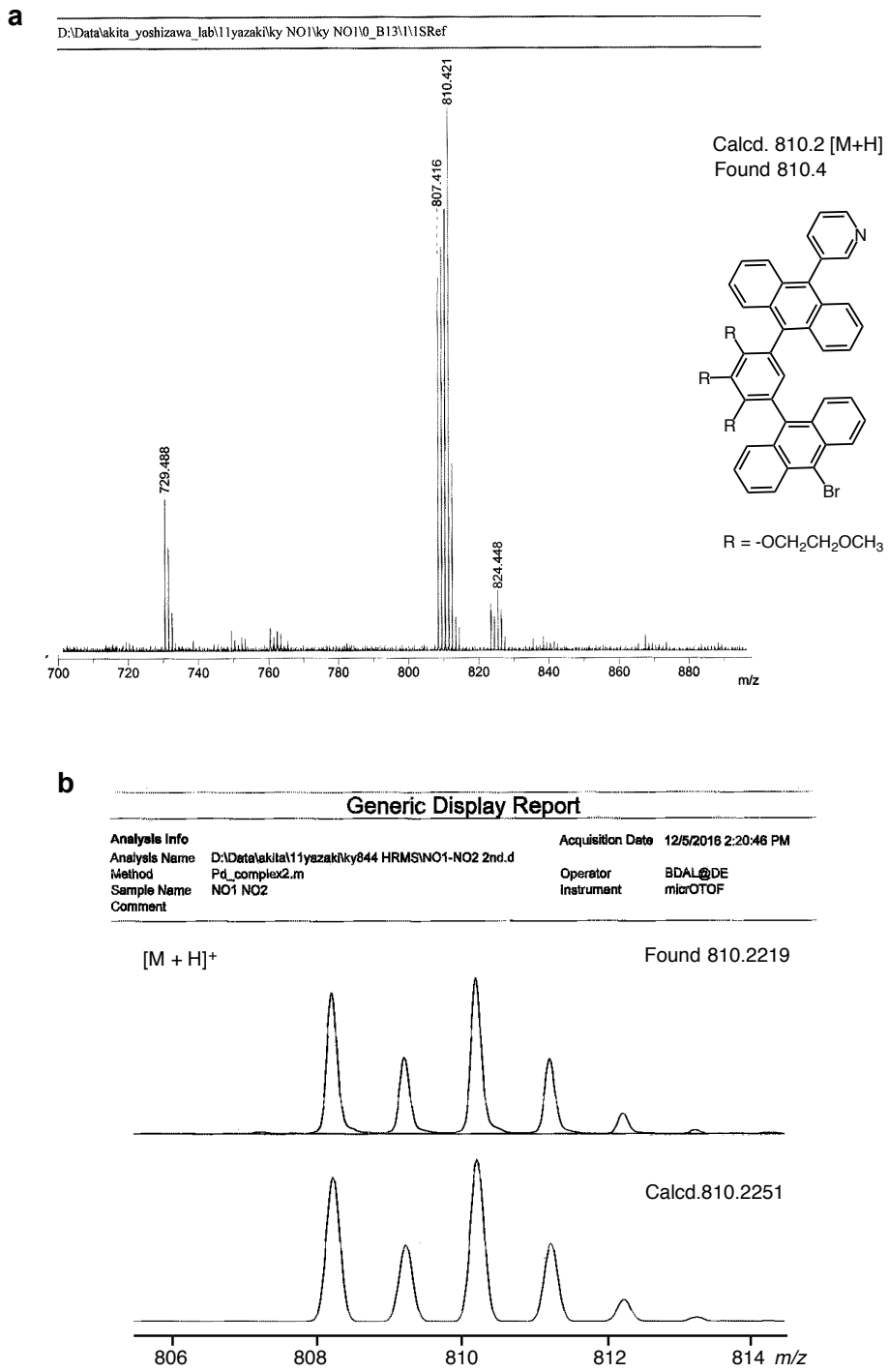
Supplementary Figure 19 | ^{1}H NMR spectra (500 MHz, $CDCl_3$, room temperature) of **6b**. (a) The aromatic and aliphatic and (b) aromatic regions.



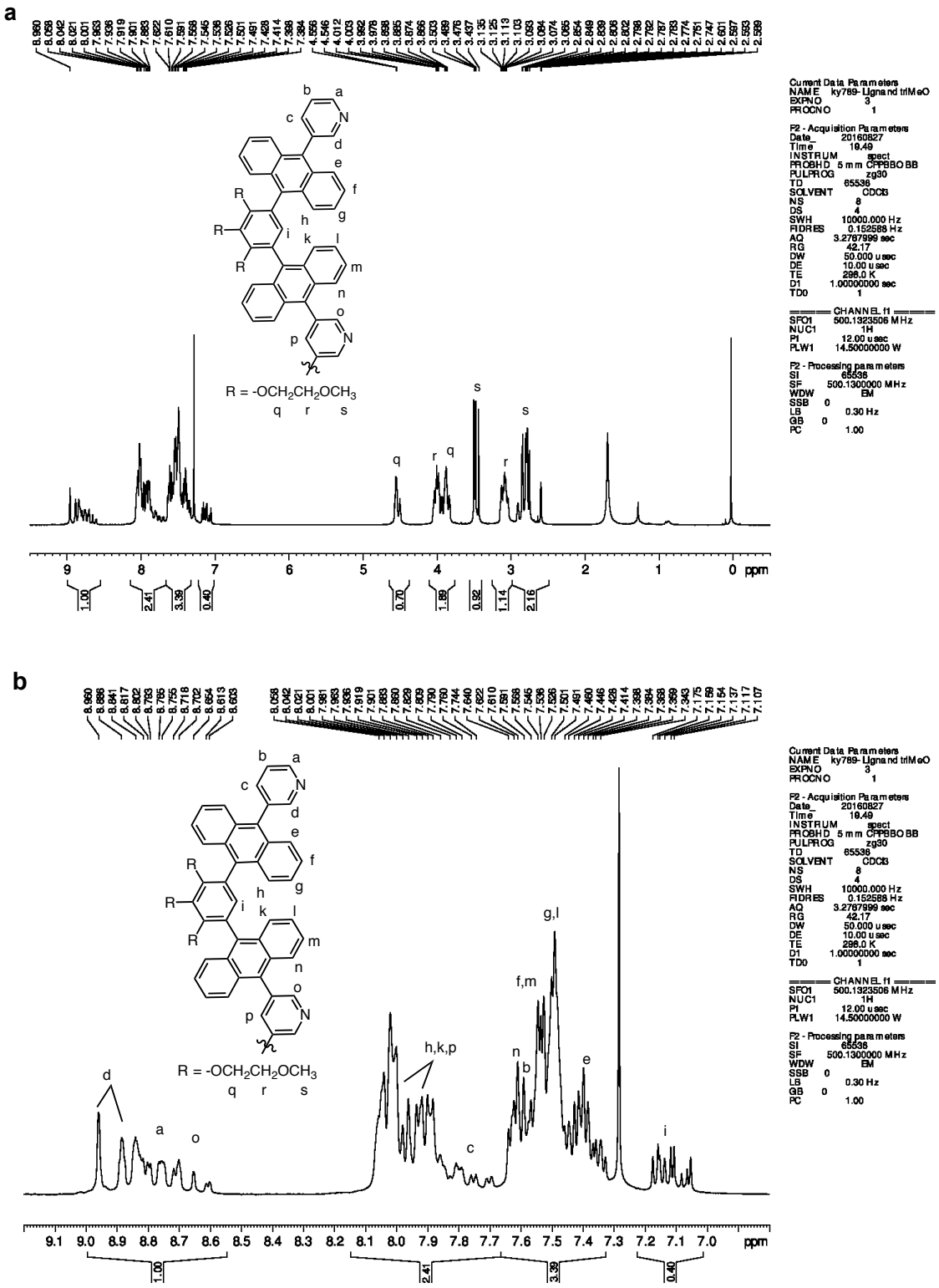
Supplementary Figure 20 | ^{13}C NMR spectra (125 MHz, $CDCl_3$, room temperature) of **6b**. (a) The aromatic and aliphatic and (b) aromatic regions.



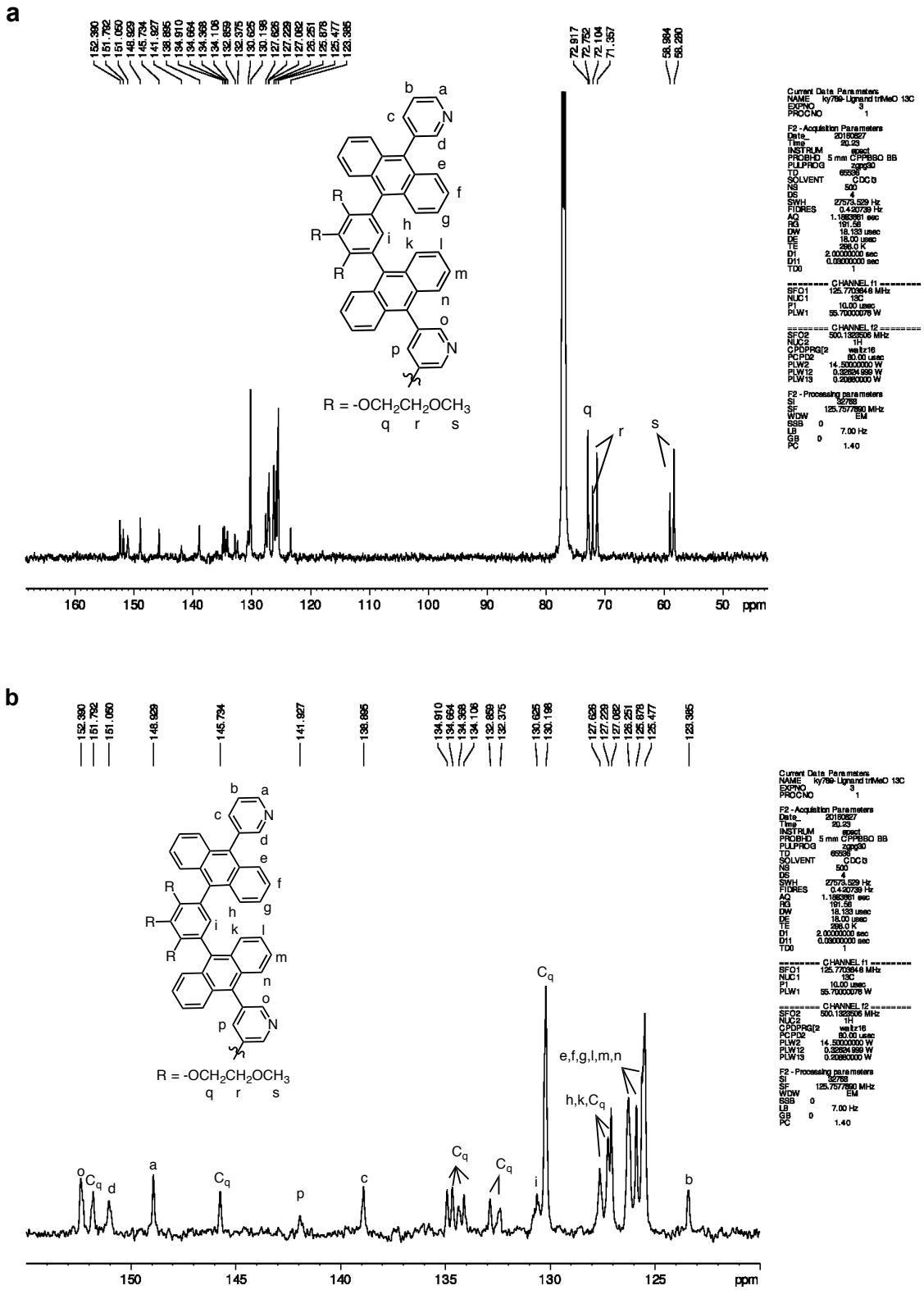
Supplementary Figure 21 | HSQC spectra (500 MHz, $CDCl_3$, room temperature) of **6b**. (a) The aromatic and (b) aliphatic regions.



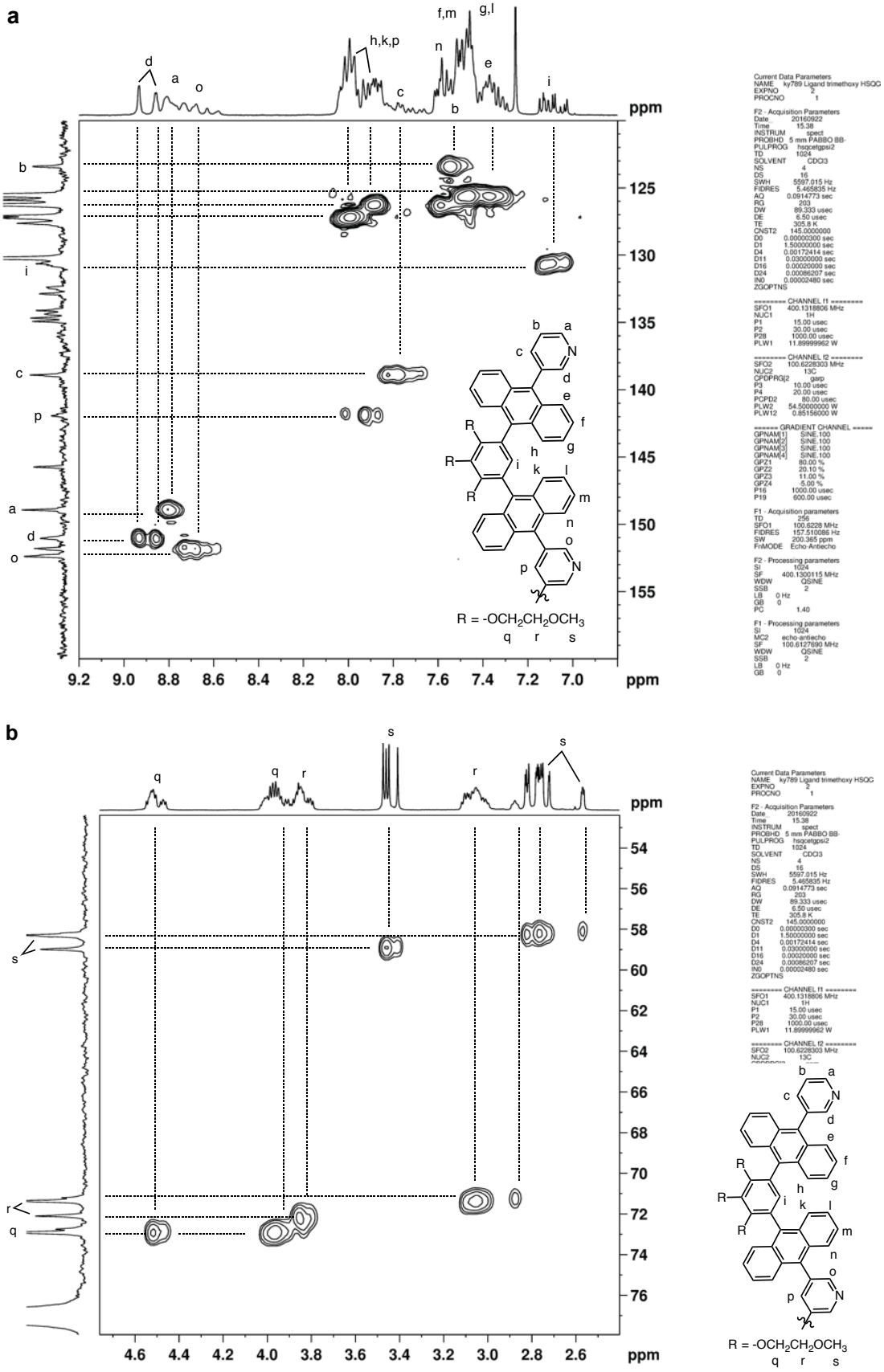
Supplementary Figure 22 | (a) MALDI-TOF MS (dithranol) and (b) HR MS (ESI) spectra of **6b**.



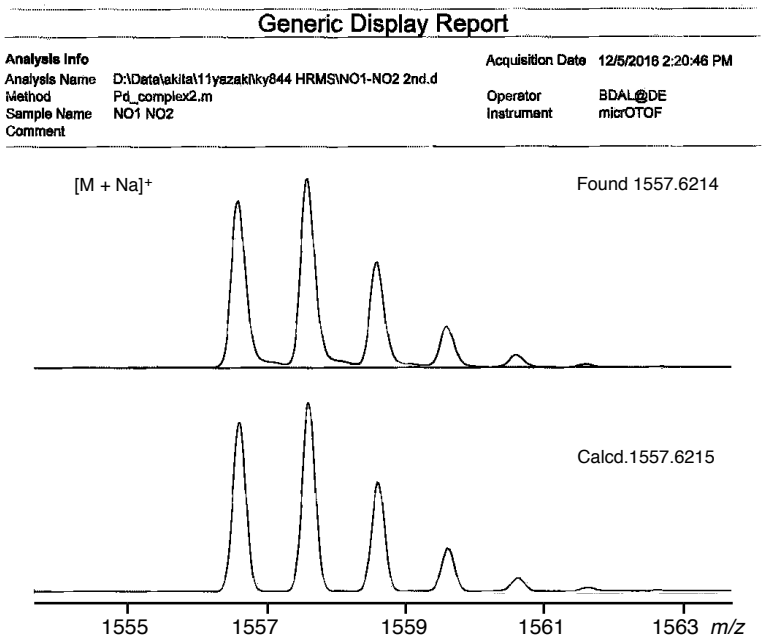
Supplementary Figure 23 | ^{1}H NMR spectra (500 MHz, $CDCl_3$, room temperature) of **1b**. (a) The aromatic and aliphatic and (b) aromatic regions.



Supplementary Figure 24 | ^{13}C NMR spectra (125 MHz, $CDCl_3$, room temperature) of **1b**. (a) The aromatic and aliphatic and (b) aromatic regions.

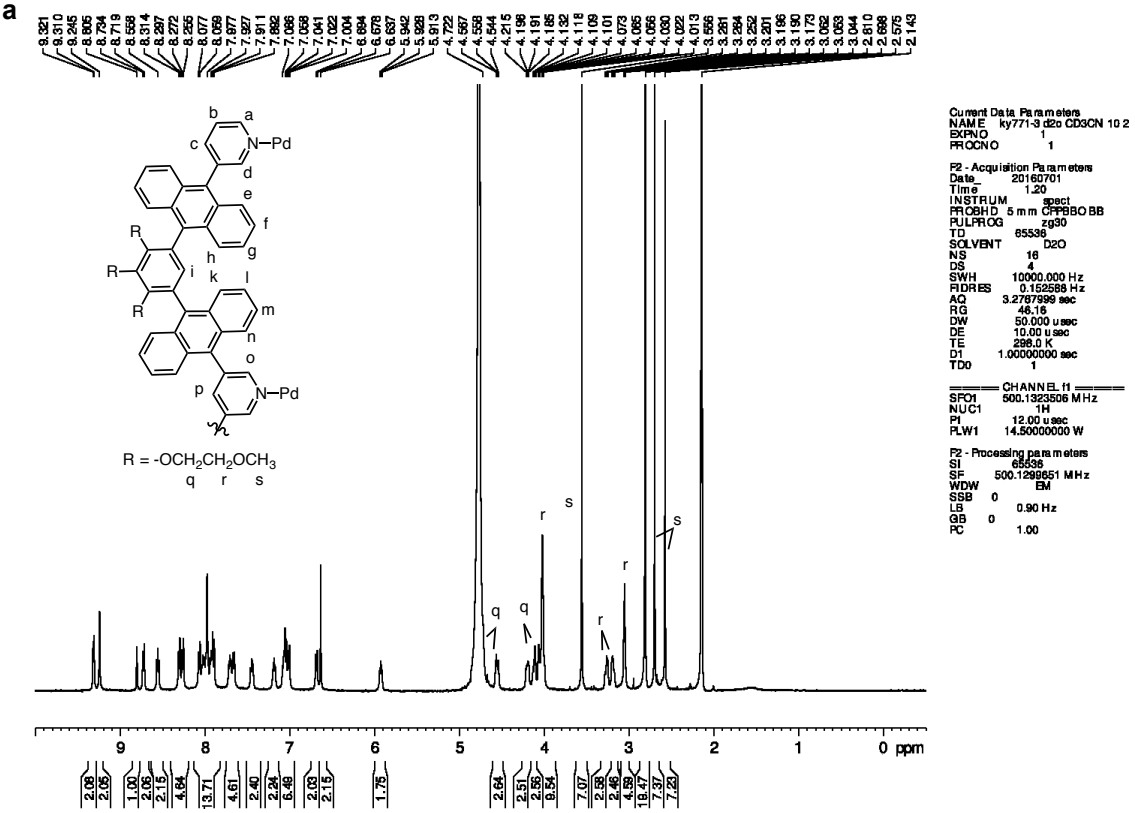


Supplementary Figure 25 | HSQC spectra (500 MHz, $CDCl_3$, room temperature) of **1b**. (a) The aromatic and (b) aliphatic regions.



Supplementary Figure 26 | HR MS spectrum (ESI) of **1b**.

a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PROCNO 1
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TE 298.0 K
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NUC1 1H
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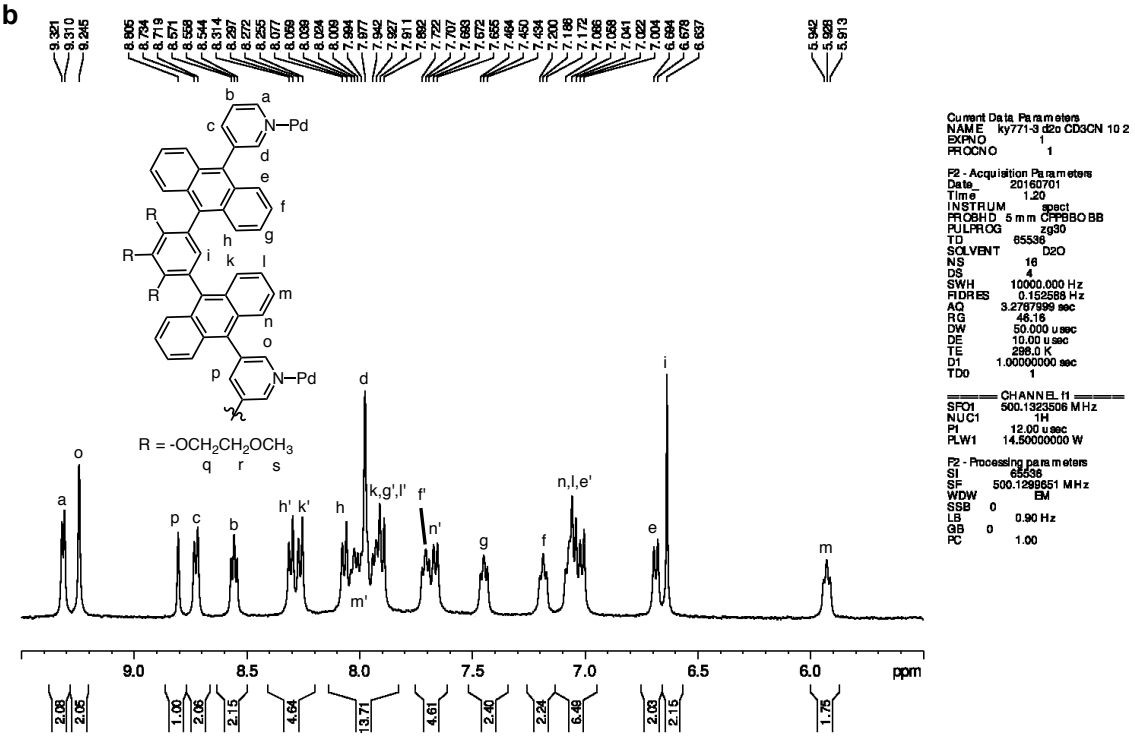
b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RG 46.16
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
CHANNEL f1
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NUC1 1H
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PC 1.00
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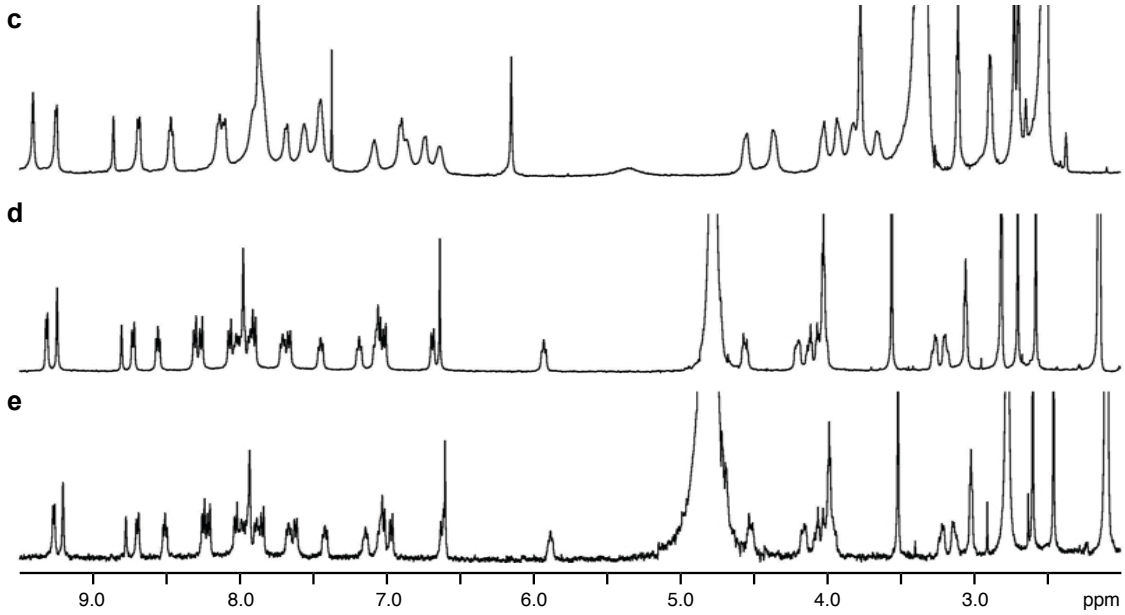
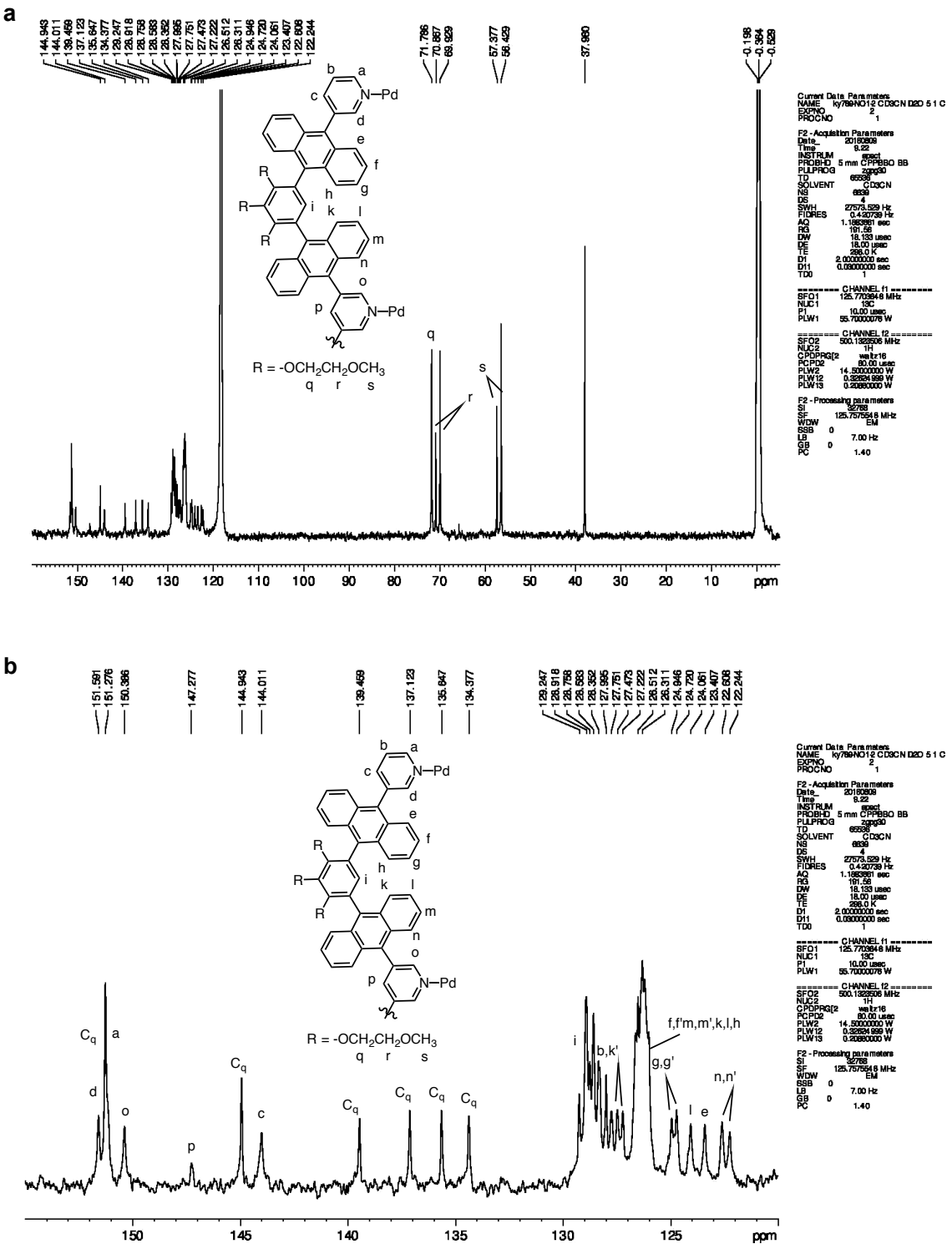
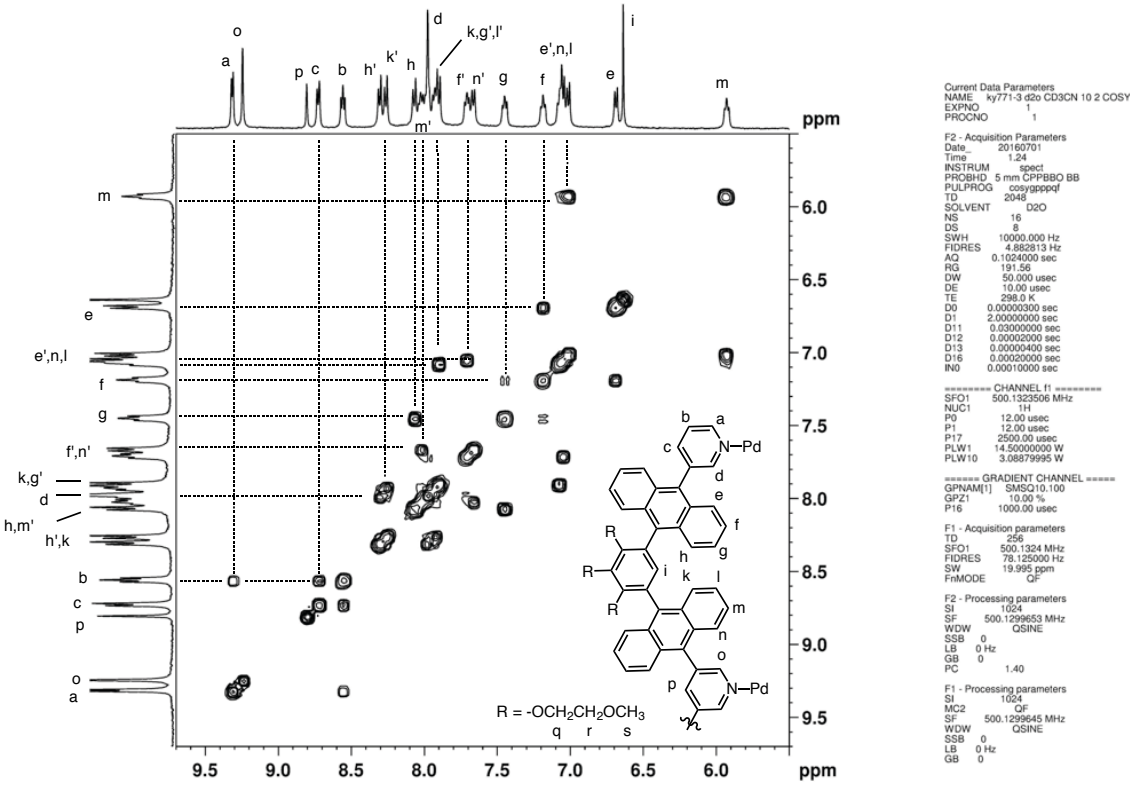


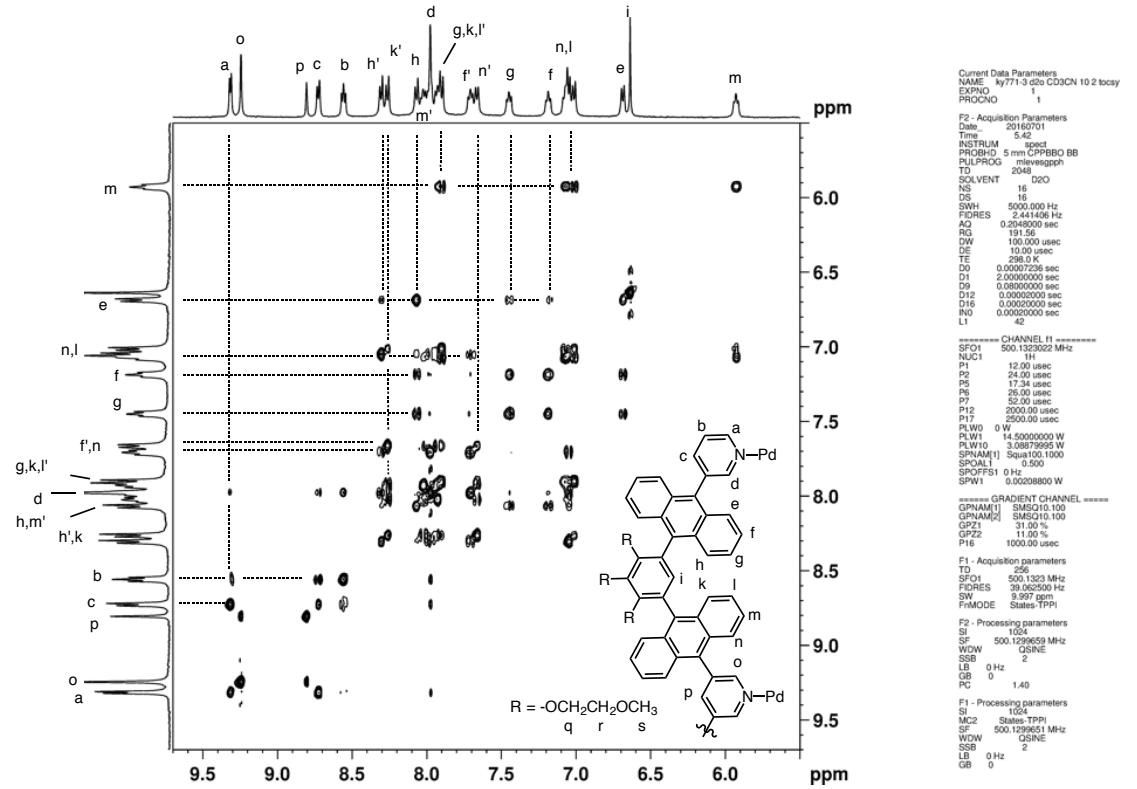
Supplementary Figure 27 | ^{1}H NMR spectra (500 MHz, D_2O:CD_3CN = 5:1, room temperature) of **2b**. (a) The aromatic and aliphatic and (b) aromatic regions. ^{1}H NMR spectra (500 MHz, room temperature) of **2b** in (c) DMSO-d_6, (d) D_2O:CD_3CN = 5:1, and (e) D_2O:CD_3CN = 100:1.



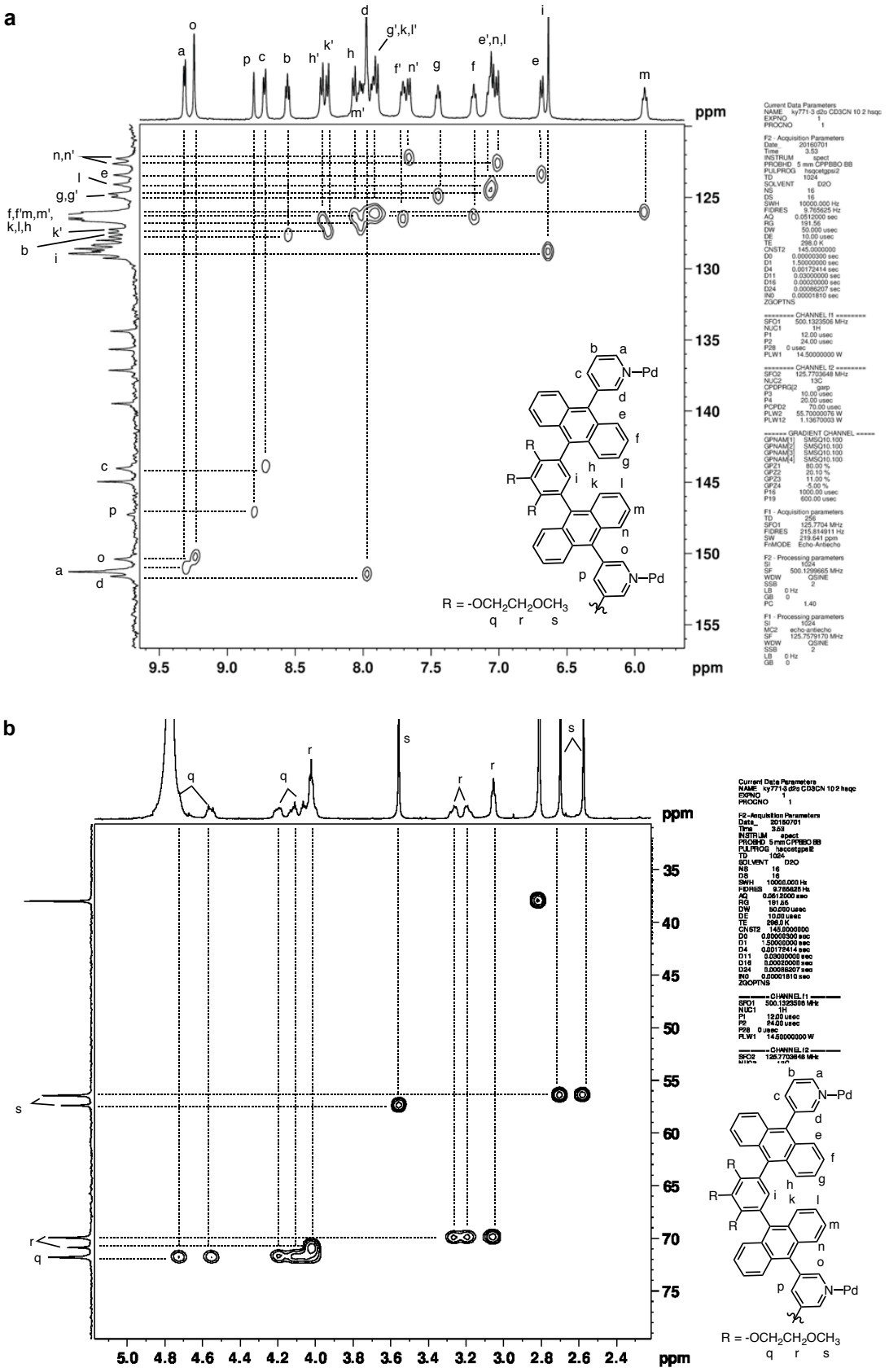
Supplementary Figure 28 | ^{13}C NMR spectra (125 MHz, D_2O:CD_3CN = 5:1, room temperature) of **2b**. (a) The aromatic and aliphatic and (b) aromatic regions.



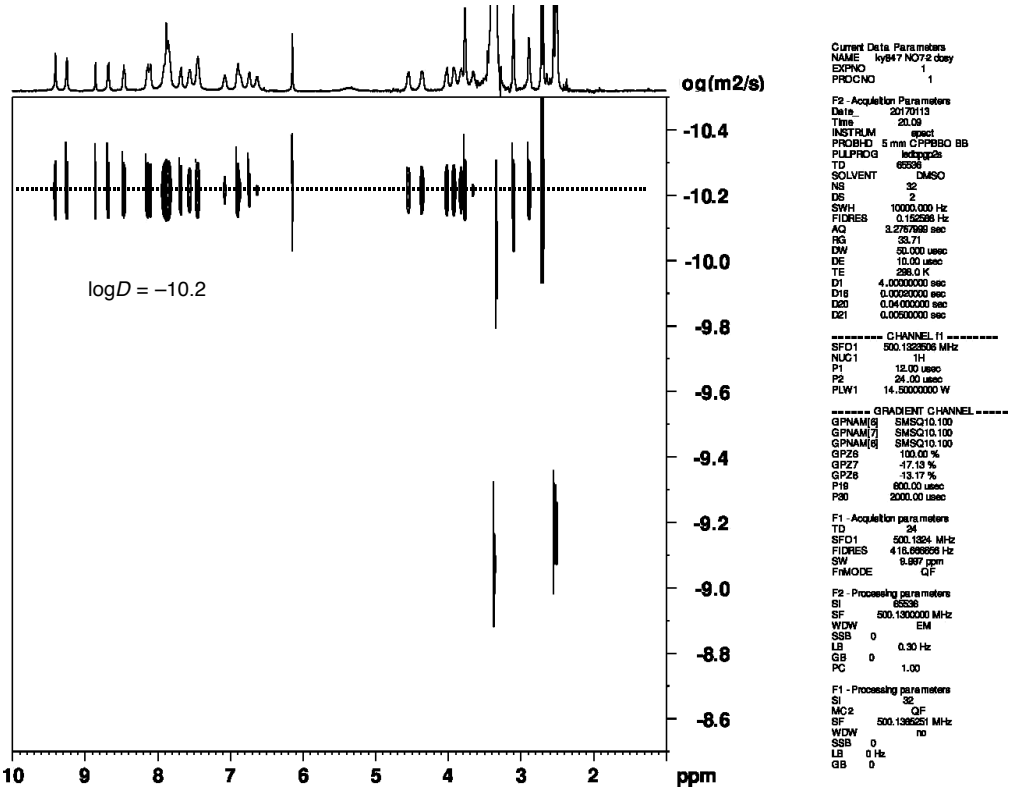
Supplementary Figure 29 | HH COSY spectrum (500 MHz, D_2O:CD_3CN = 5:1, room temperature) of **2b**.



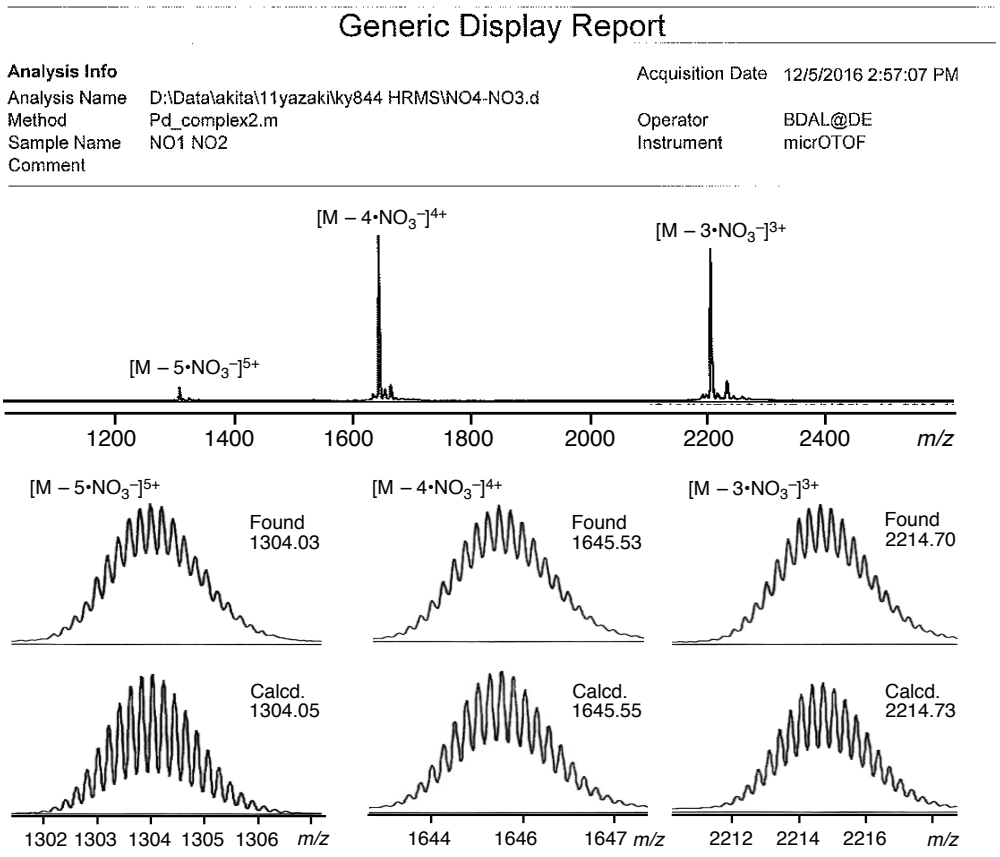
Supplementary Figure 30 | HH TOCSY spectrum (500 MHz, D_2O:CD_3CN = 5:1, room temperature) of **2b**.



Supplementary Figure 31 | HSQC spectra (500 MHz, D_2O:CD_3CN = 5:1, room temperature) of **2b**. (a) The aromatic and (b) aliphatic regions.

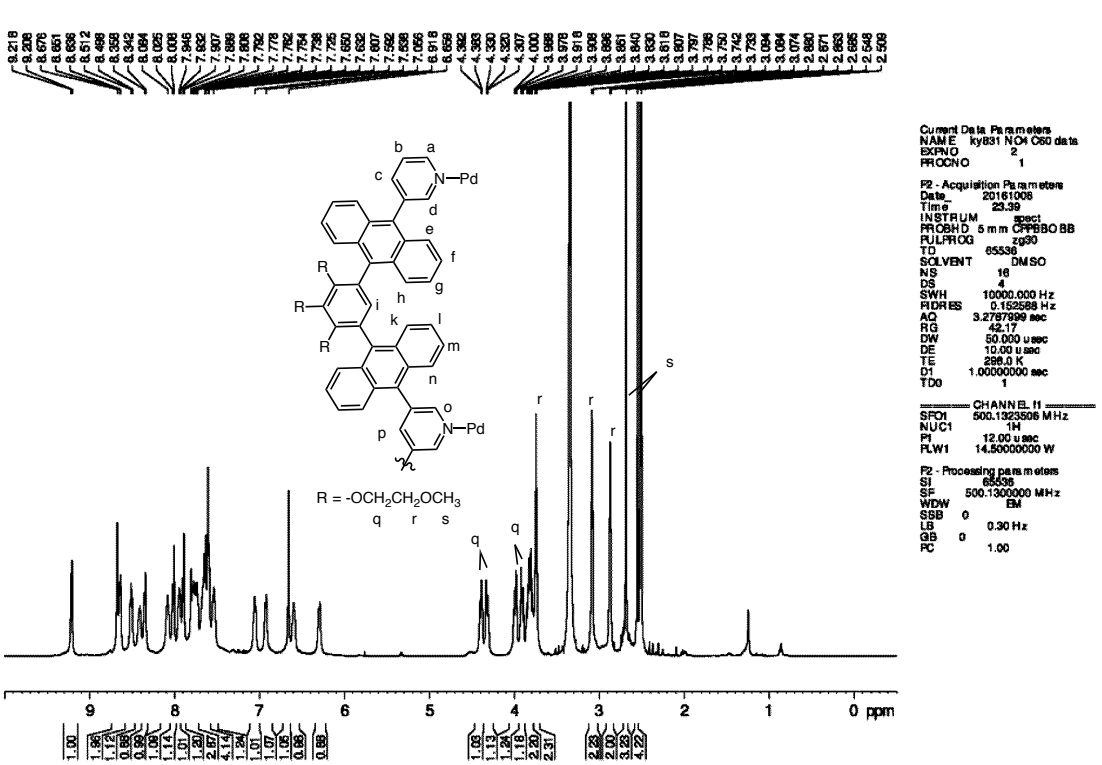


Supplementary Figure 32 | DOSY NMR spectrum (500 MHz, DMSO-d_6, 298 K) of **2b**.



Supplementary Figure 33 | ESI-TOF MS spectrum (CH_3OH) of **2b**.

a


R = -OCH2CH2OCH3
q r s
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EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
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Time 23.39
INSTRUM spect
PROBHD 5 mm CPPBBO BB
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 4
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 42.17
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
CHANNEL f1
SFO1 500.1323506 MHz
NUC1 1H
P1 12.00 usec
PLW1 14.50000000 W
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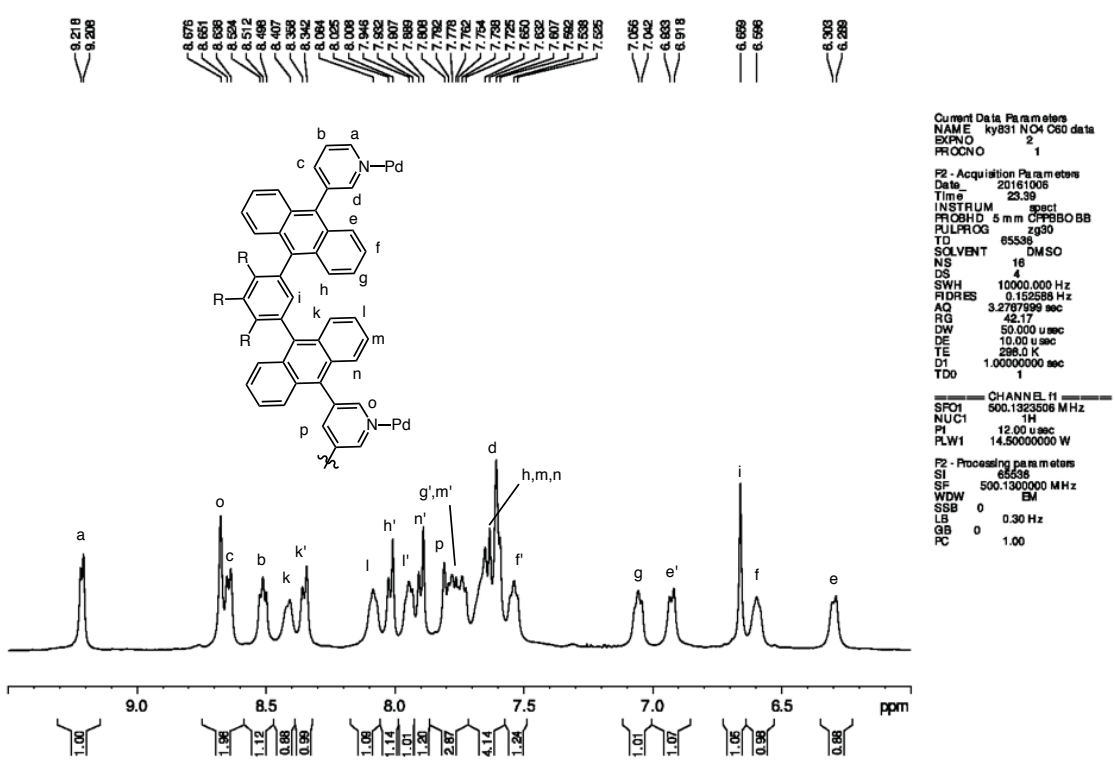
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
ppm

b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NAME ky831 NO4 C60 data
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20161006
Time 23.39
INSTRUM spect
PROBHD 5 mm CPPBBO BB
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 4
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 42.17
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
CHANNEL f1
SFO1 500.1323506 MHz
NUC1 1H
P1 12.00 usec
PLW1 14.50000000 W
F2 - Processing parameters
SI 65536
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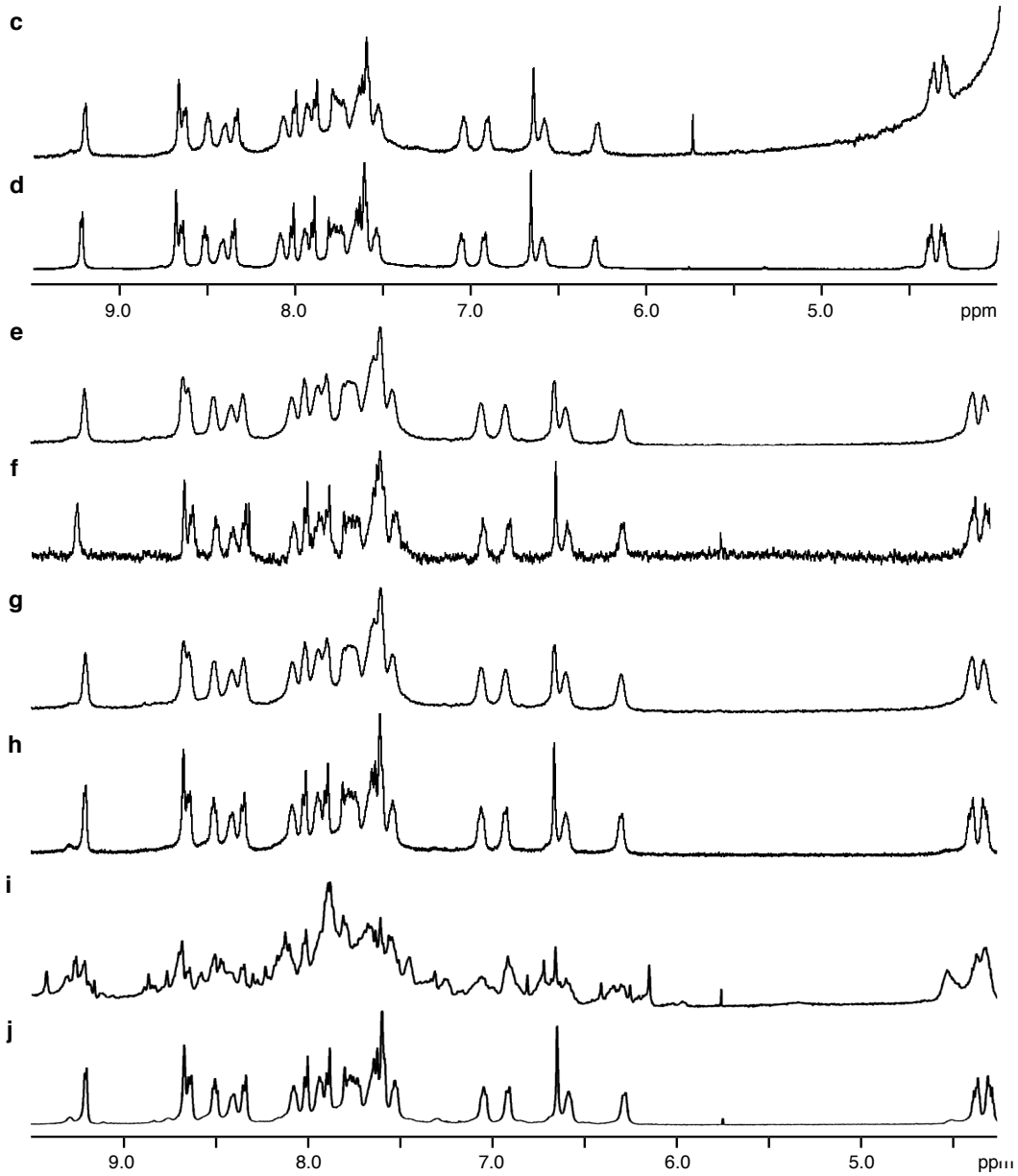
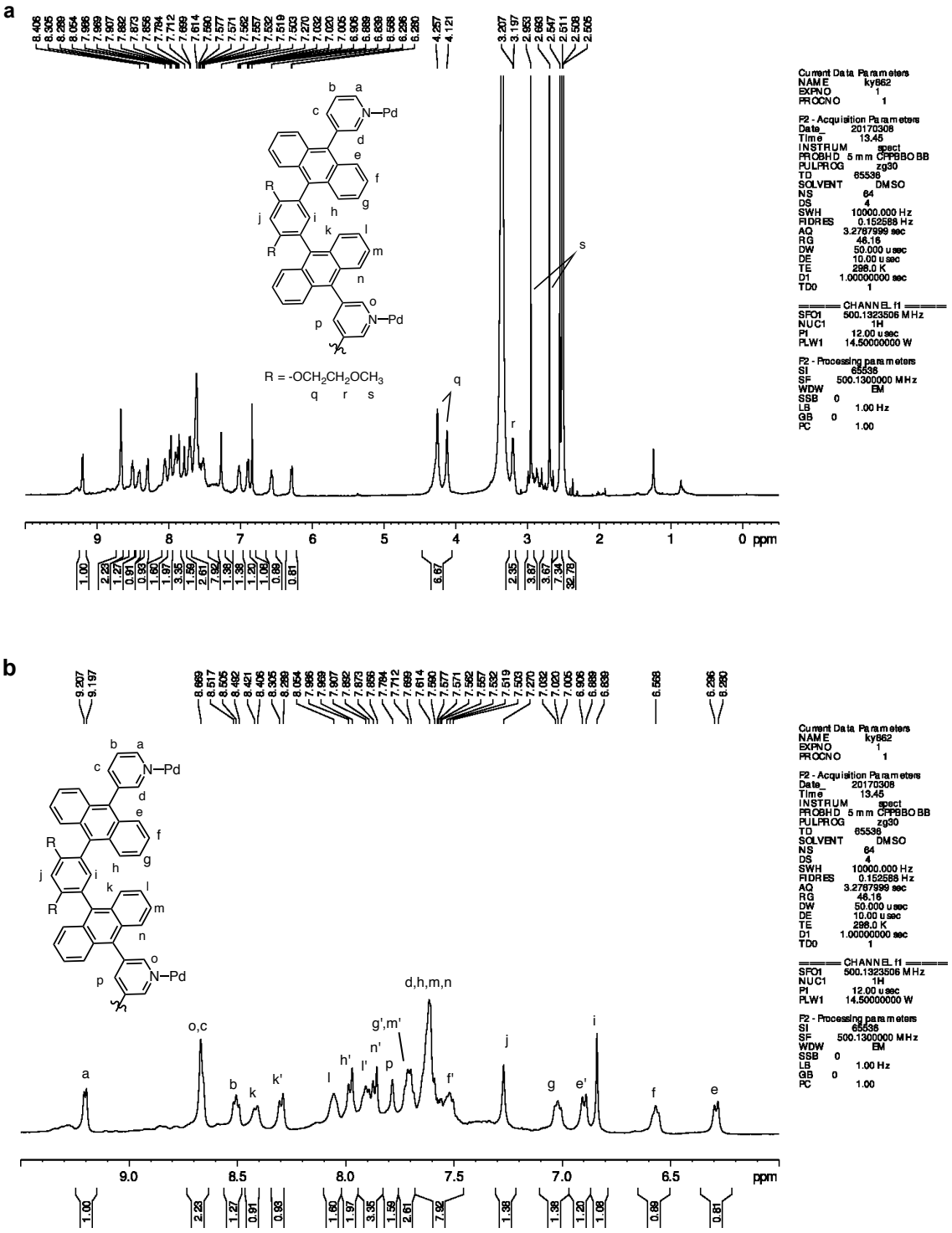
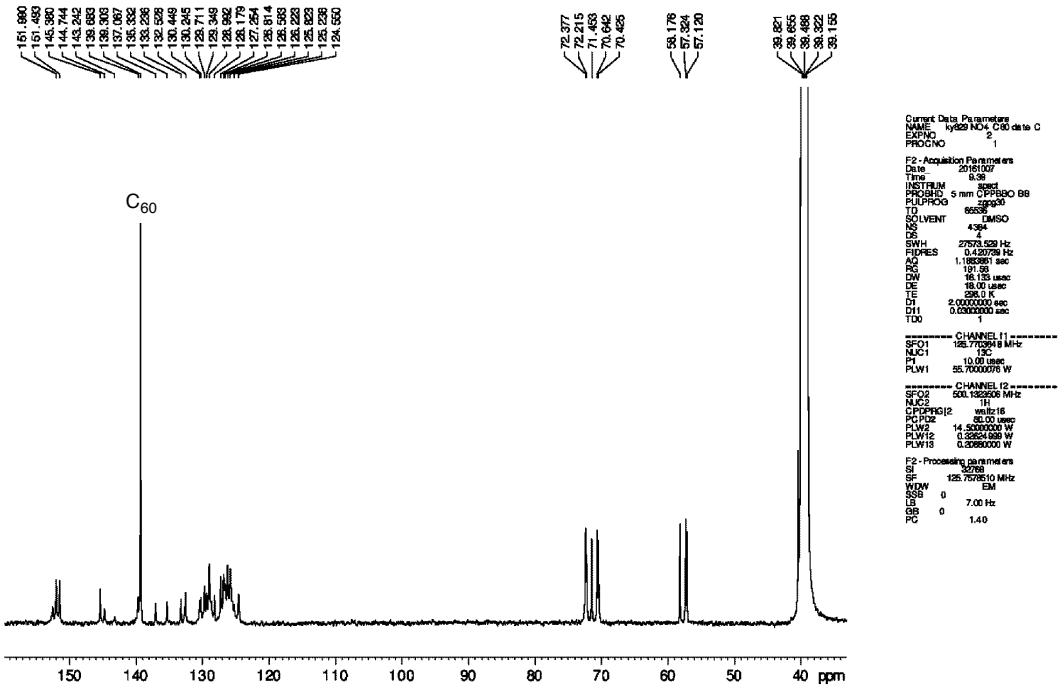
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
h,m,n
g',m'
ppm



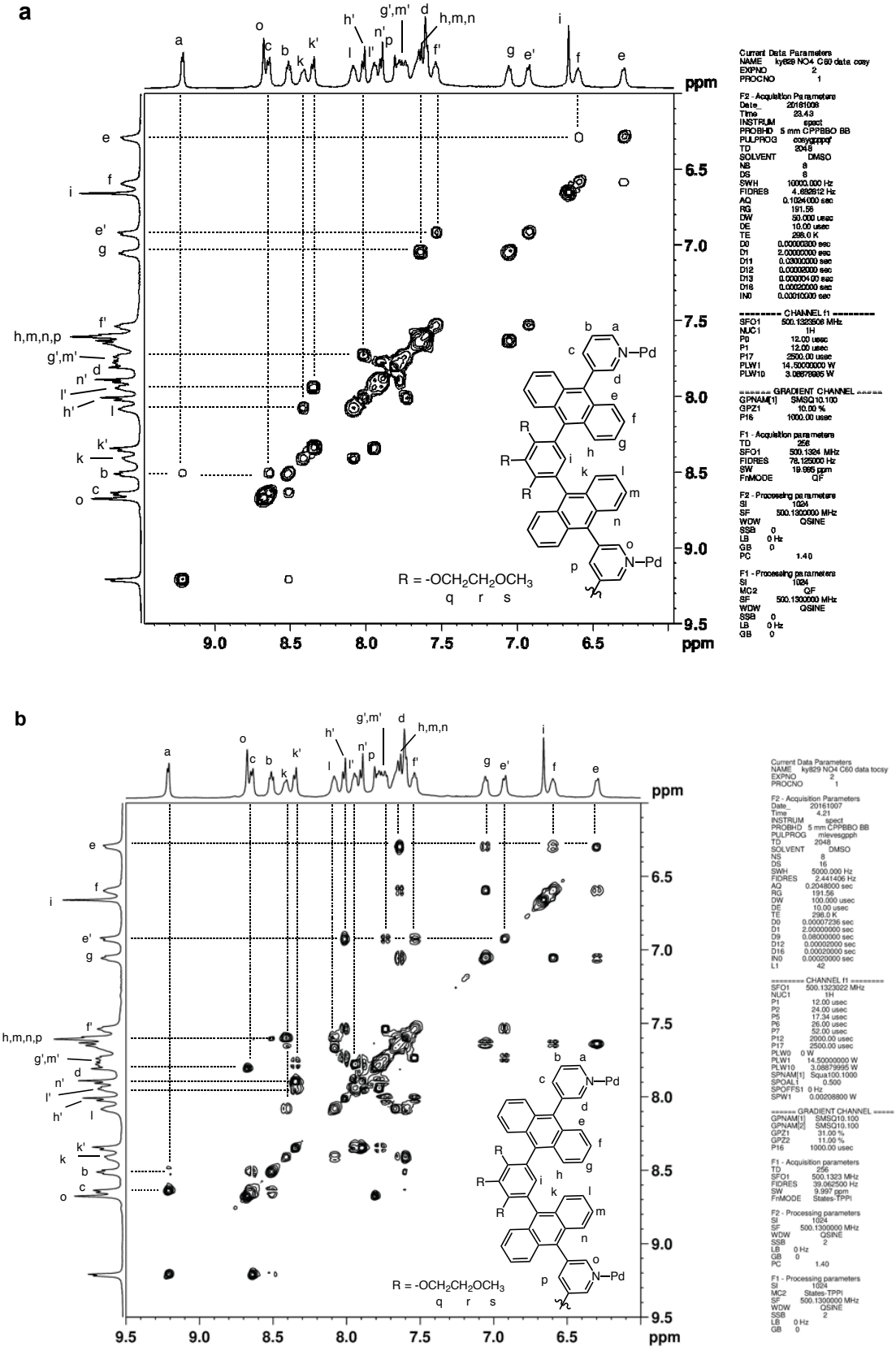
Supplementary Figure 34 | ^{1}H NMR spectra (500 MHz, DMSO-d_6, room temperature) of $(C_{60})_2$@**3b**. (a) The aromatic and aliphatic and (b) aromatic regions. The ^{1}H NMR spectra of $(C_{60})_2$@**3b** obtained by (c) the route 1 and (d) the route 2. Concentration-dependent ^{1}H NMR spectra of $(C_{60})_2$@**3b** in (e) 0.36 mM and (f) 5.0 μM and time-dependent ^{1}H NMR spectra of $(C_{60})_2$@**3b** after (g) 10 min and (h) 5 d at room temperature. ^{1}H NMR spectra of a mixture of **2b** and C_{60} after (i) 6 h at 70 ºC and (j) 3 h at 110 ºC.



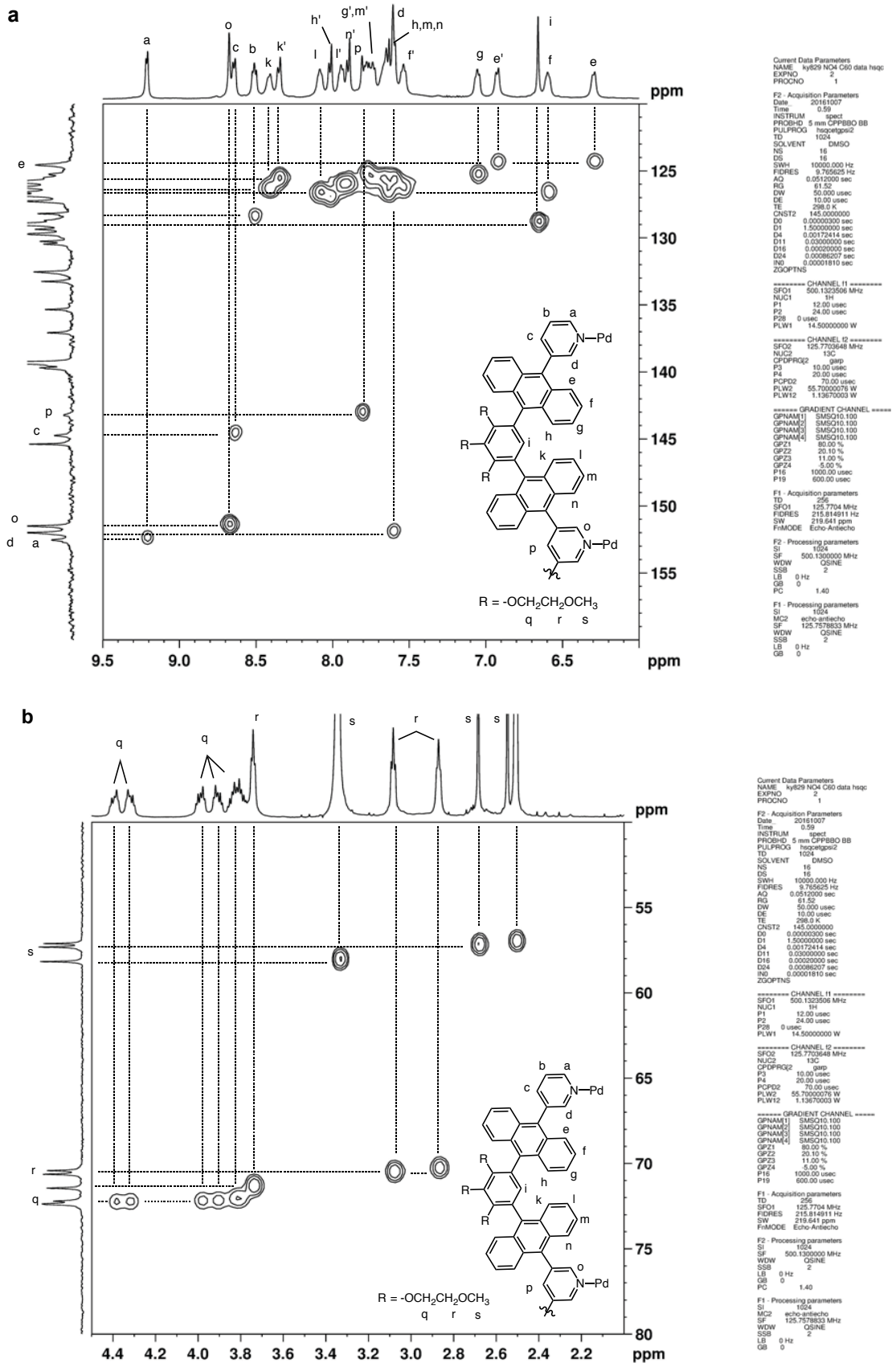
Supplementary Figure 35 | ^{1}H NMR spectra (500 MHz, DMSO-d_6, room temperature) of $(C_{60})_2$@**3a**. (a) The aromatic and aliphatic and (b) aromatic regions.



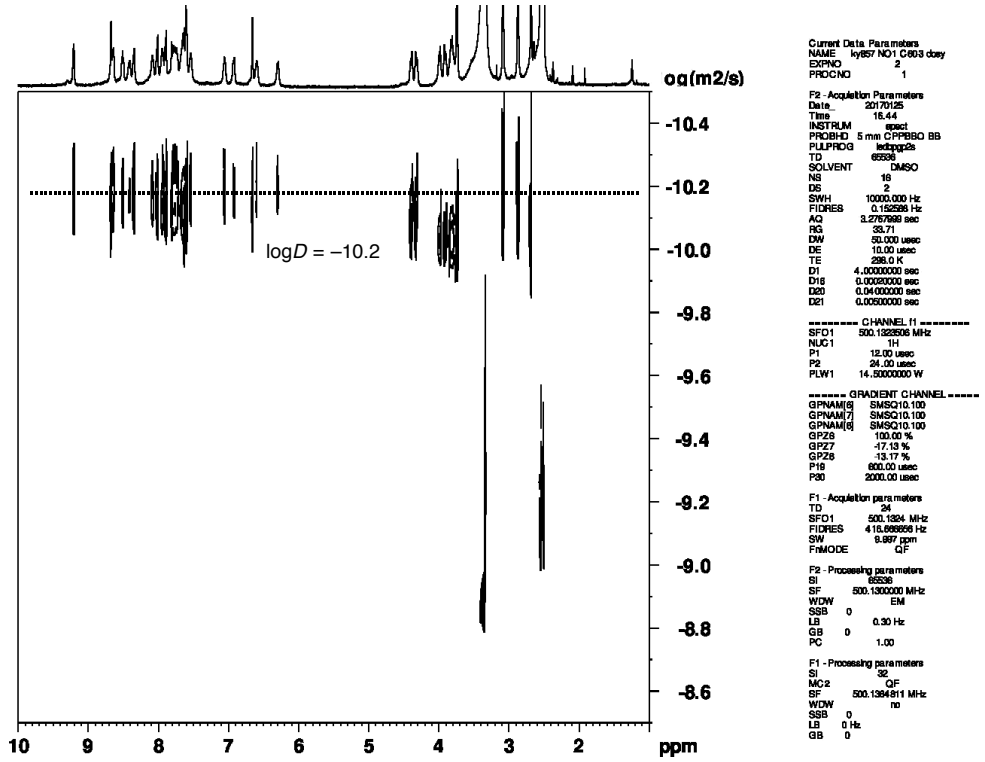
Supplementary Figure 36 | ^{13}C NMR spectrum (125 MHz, DMSO-d_6, room temperature) of $(C_{60})_2$@**3b**.



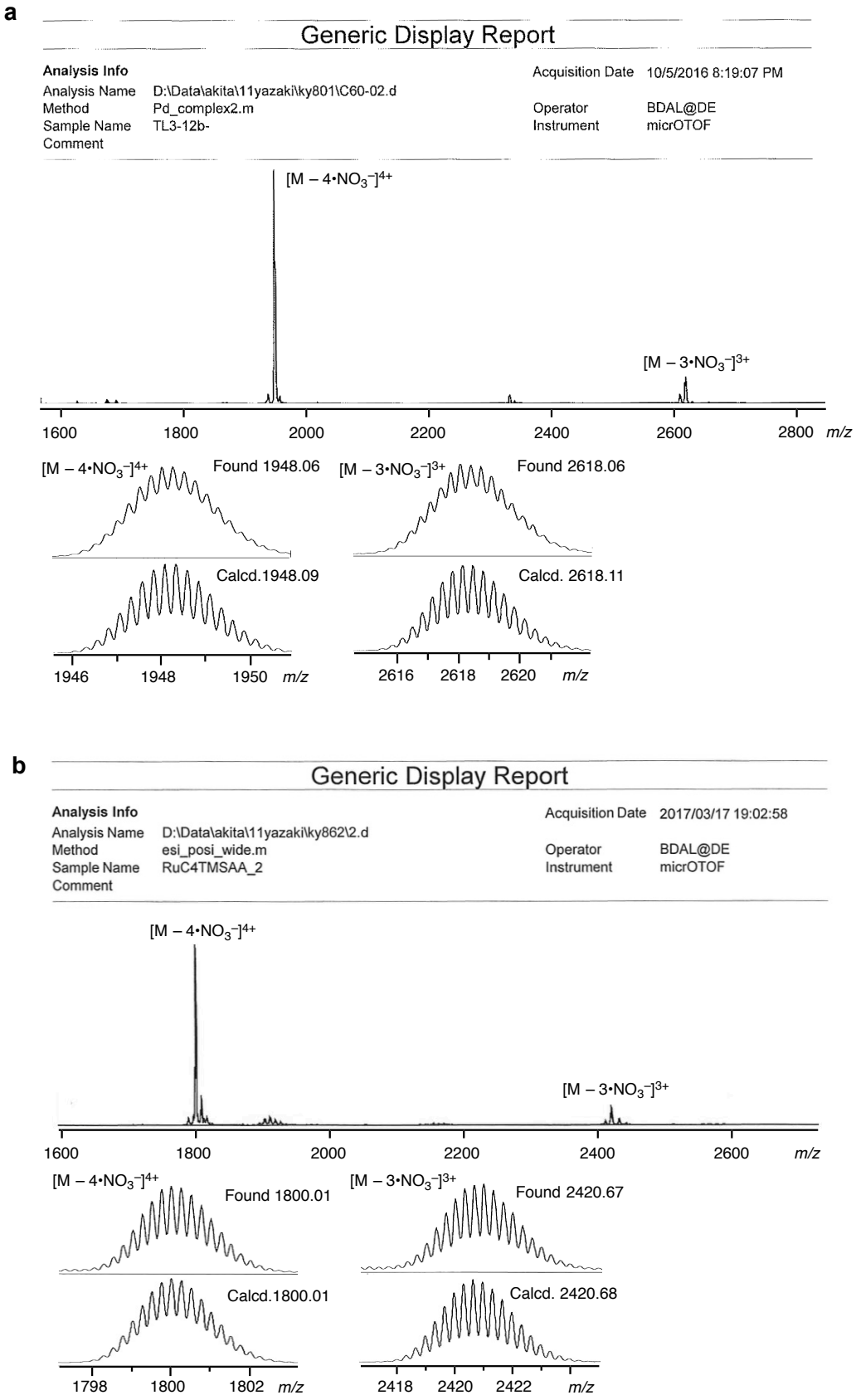
Supplementary Figure 37 | (a) HH COSY and (b) HH TOCSY spectra (500 MHz, DMSO-d_6, room temperature) of $(C_{60})_2$@**3b**.



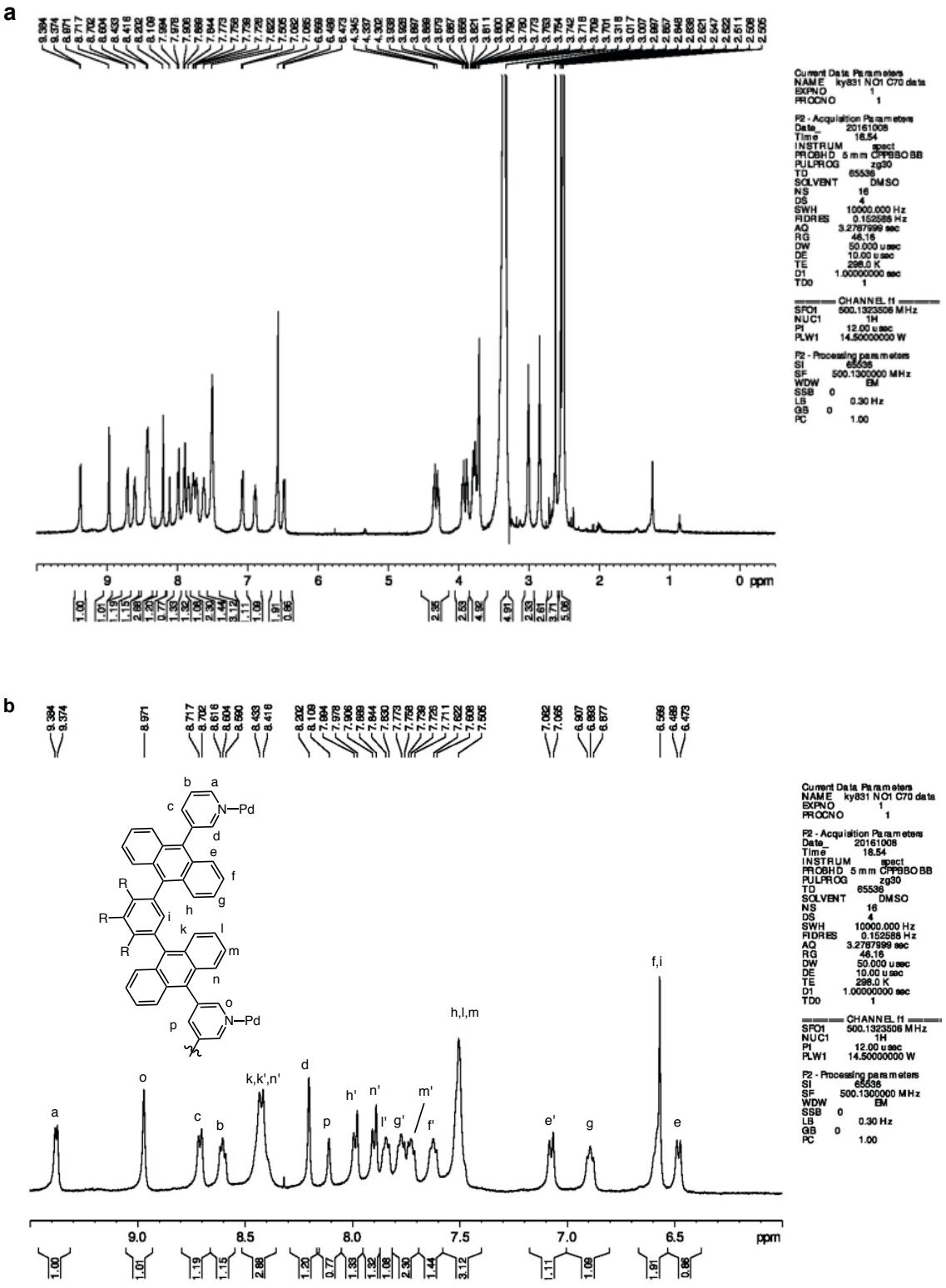
Supplementary Figure 38 | HSQC spectra (500 MHz, DMSO-d_6, room temperature) of $(C_{60})_2$@**3b**. (a) The aromatic and (b) aliphatic regions.



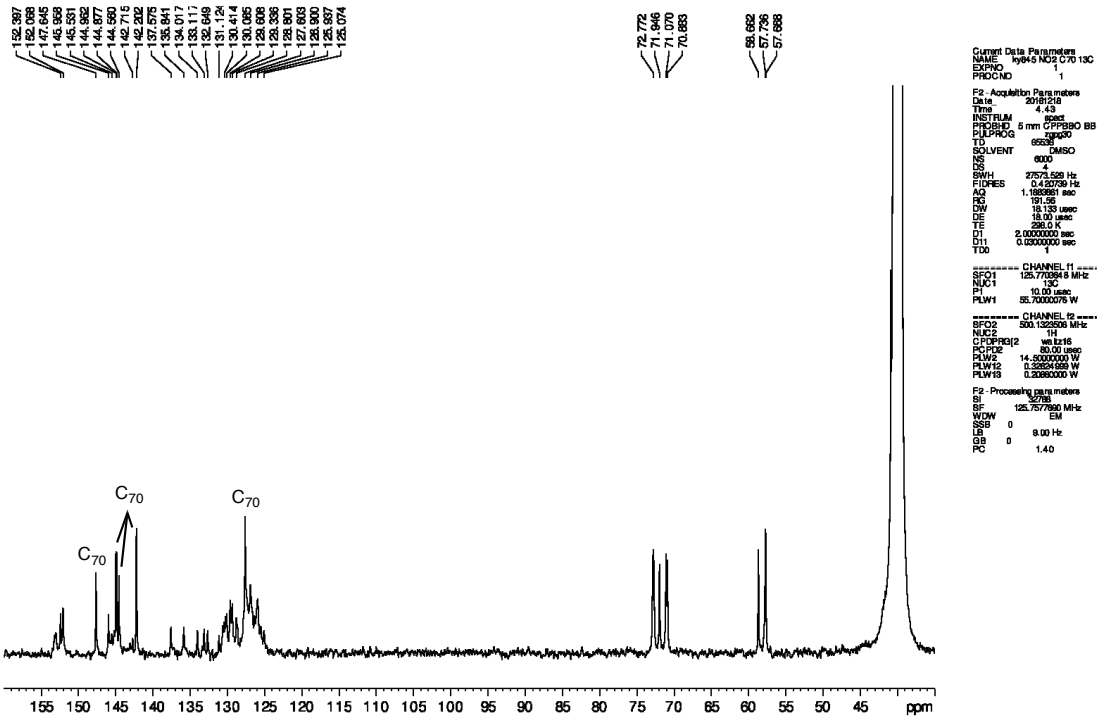
Supplementary Figure 39 | DOSY NMR spectrum (500 MHz, DMSO-d_6, 298 K) of $(C_{60})_2$@**3b**.



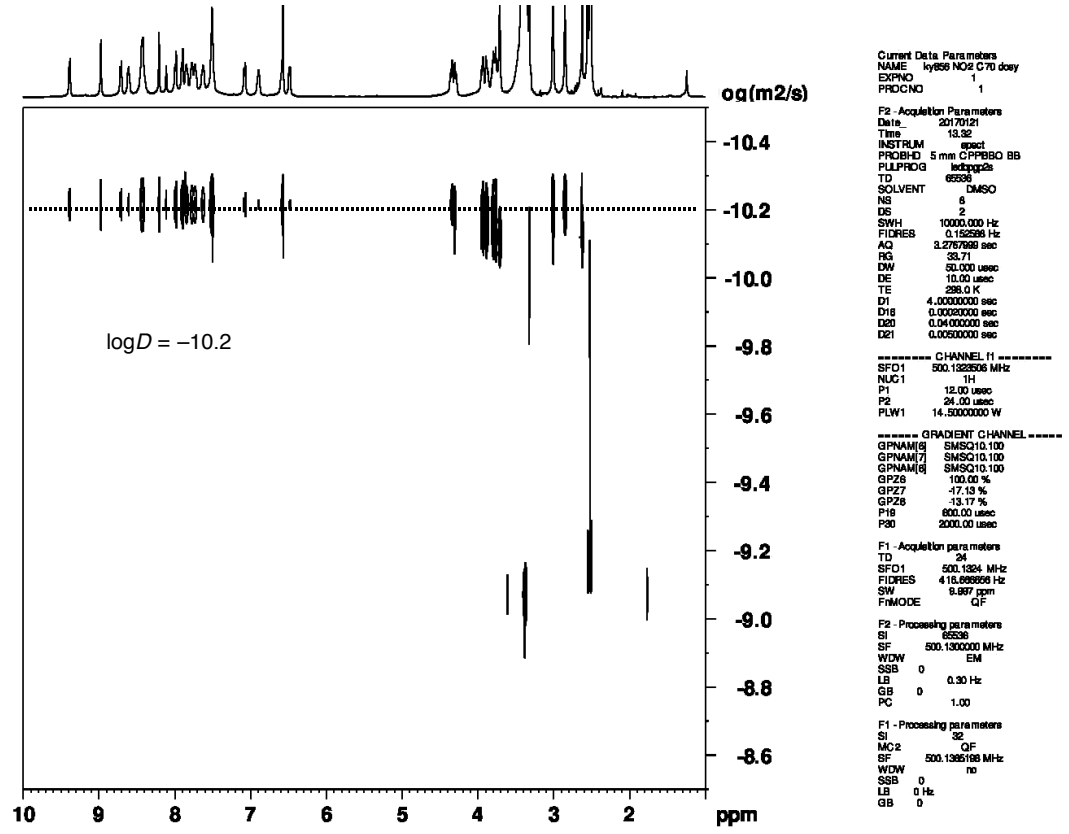
Supplementary Figure 40 | ESI-TOF MS spectra (CH_3CN) of (a) $(C_{60})_2$@**3b** and (b) $(C_{60})_2$@**3a**.



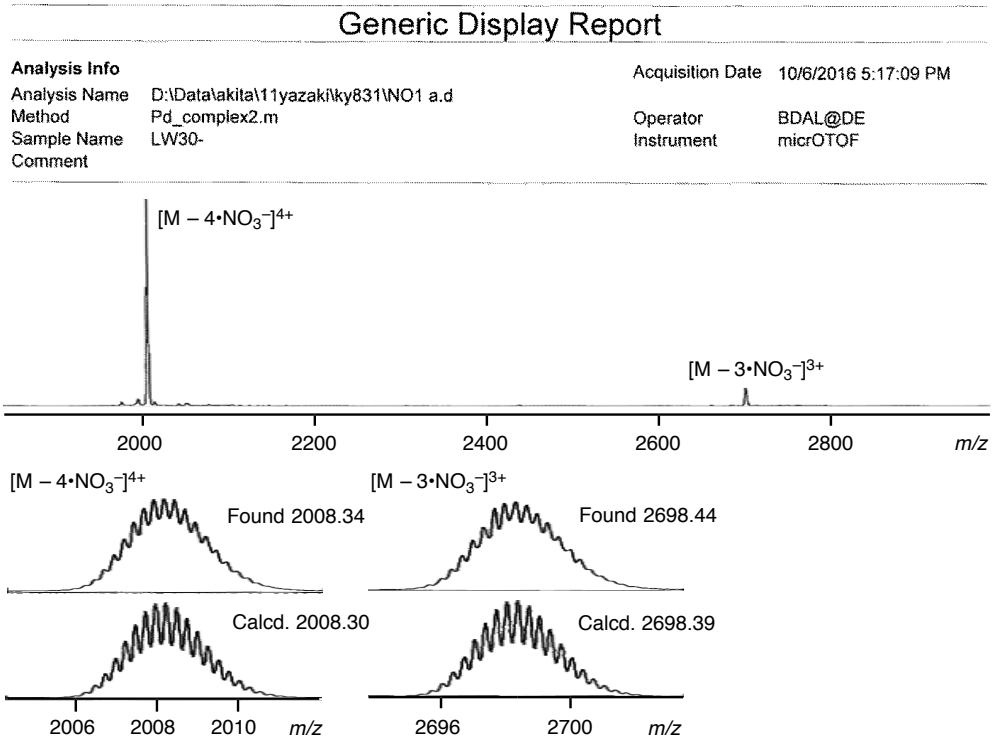
Supplementary Figure 41 | ^{1}H NMR spectra (500 MHz, DMSO-d_6, room temperature) of $(C_{70})_2$@**3b**. (a) The aromatic and aliphatic and (b) aromatic regions.



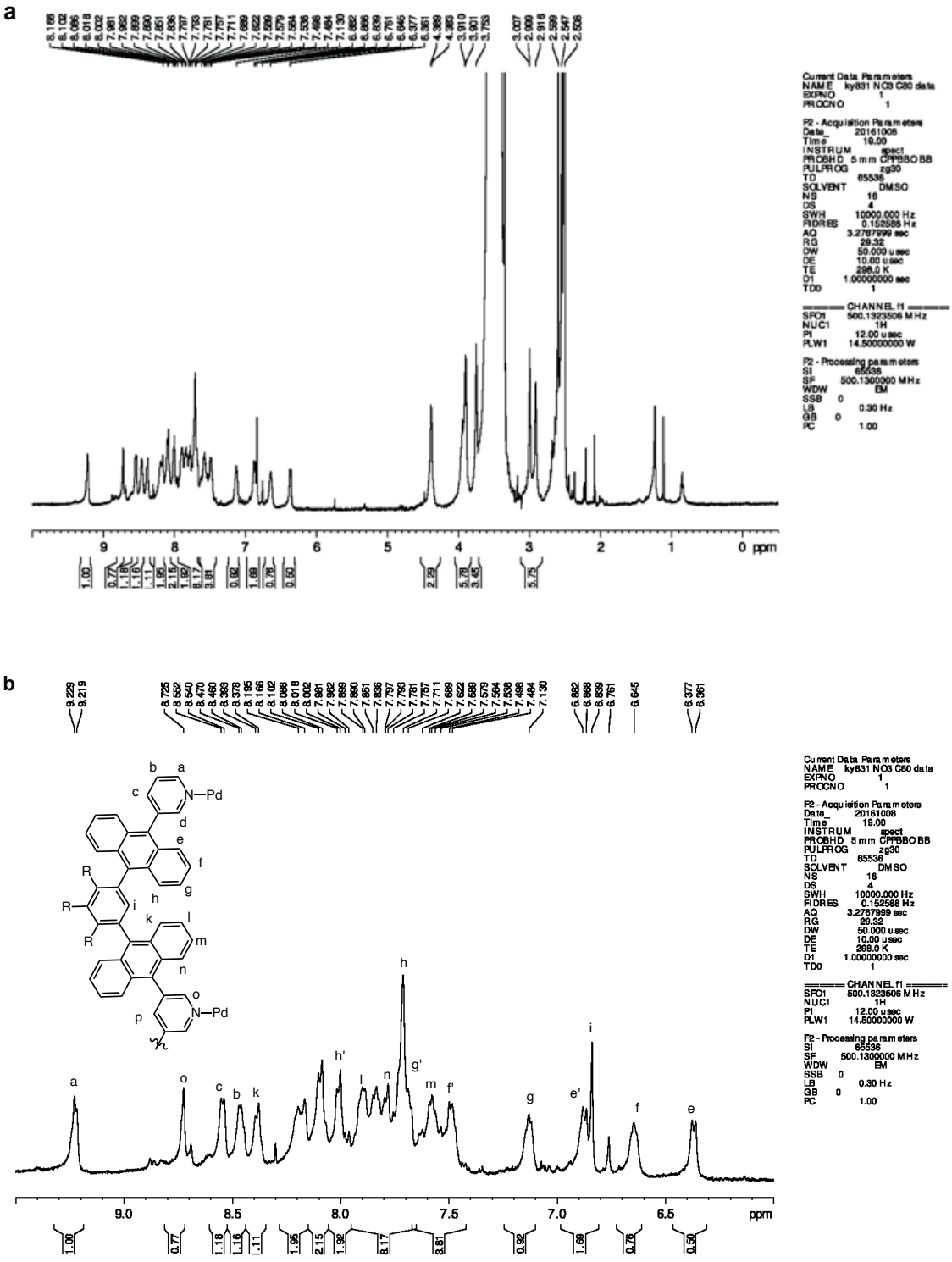
Supplementary Figure 42 | ^{13}C NMR spectrum (125 MHz, DMSO-d_6, room temperature) of $(C_{70})_2$@**3b**.



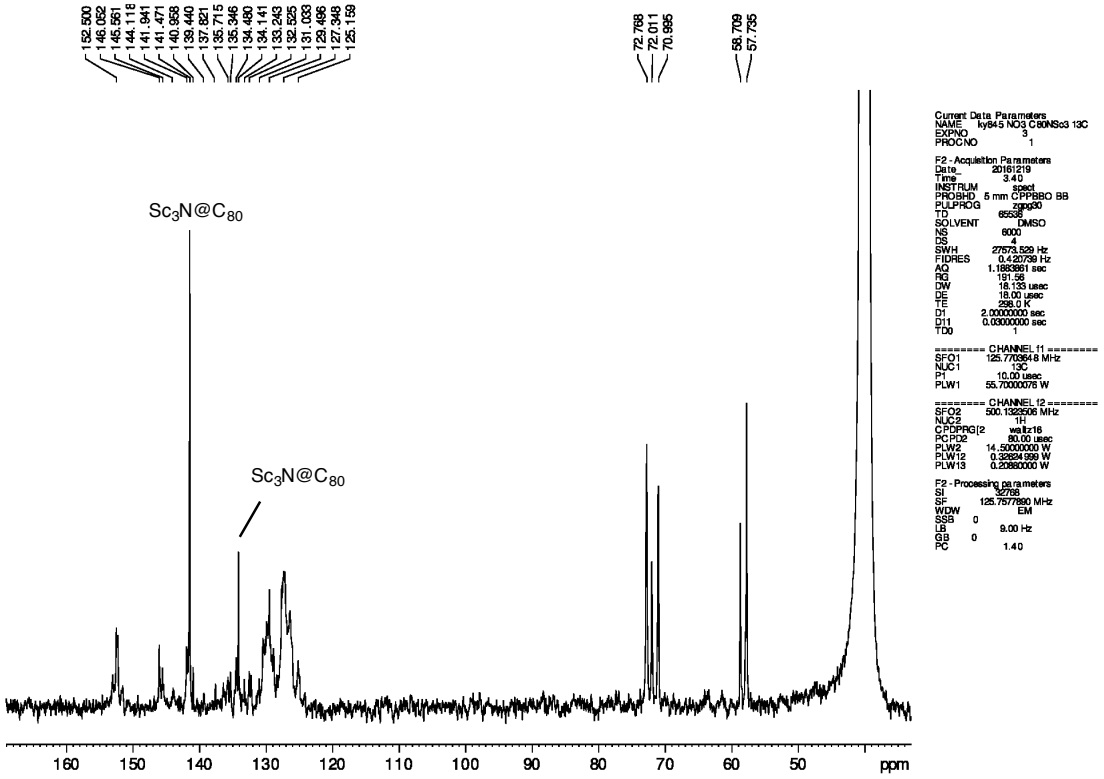
Supplementary Figure 43 | DOSY NMR spectrum (500 MHz, DMSO-d_6, 298 K) of $(C_{70})_2$@**3b**.



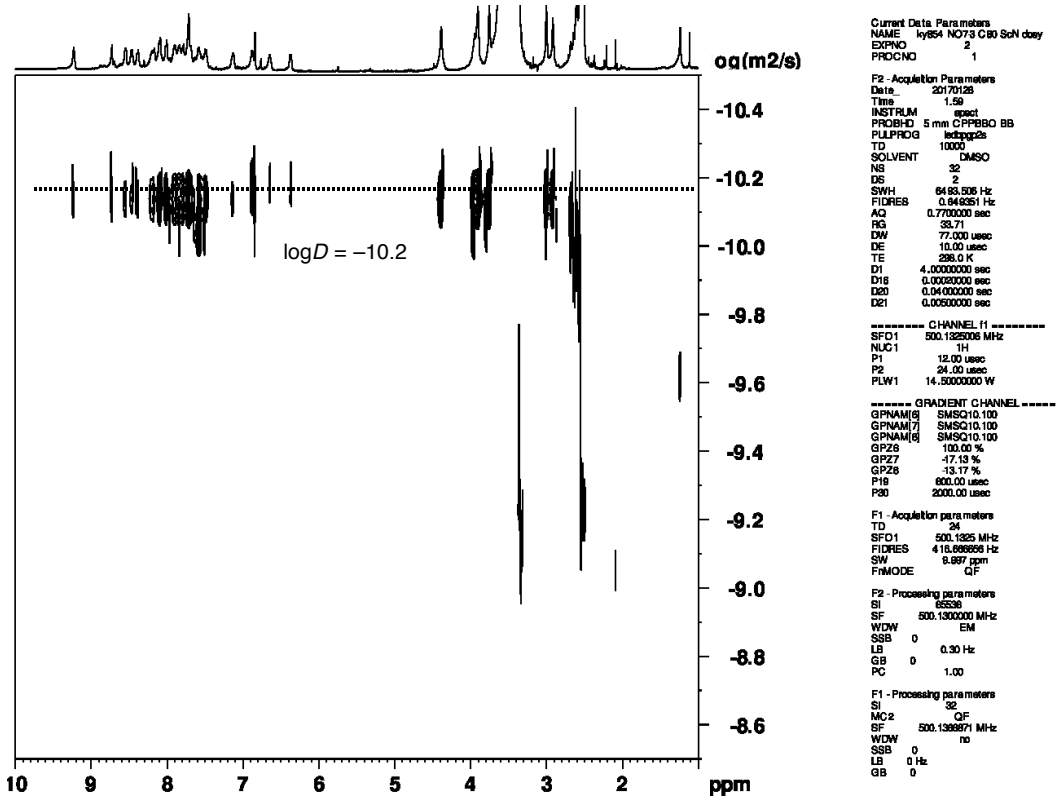
Supplementary Figure 44 | ESI-TOF MS spectrum (CH_3CN) of $(C_{70})_2$@**3b**.



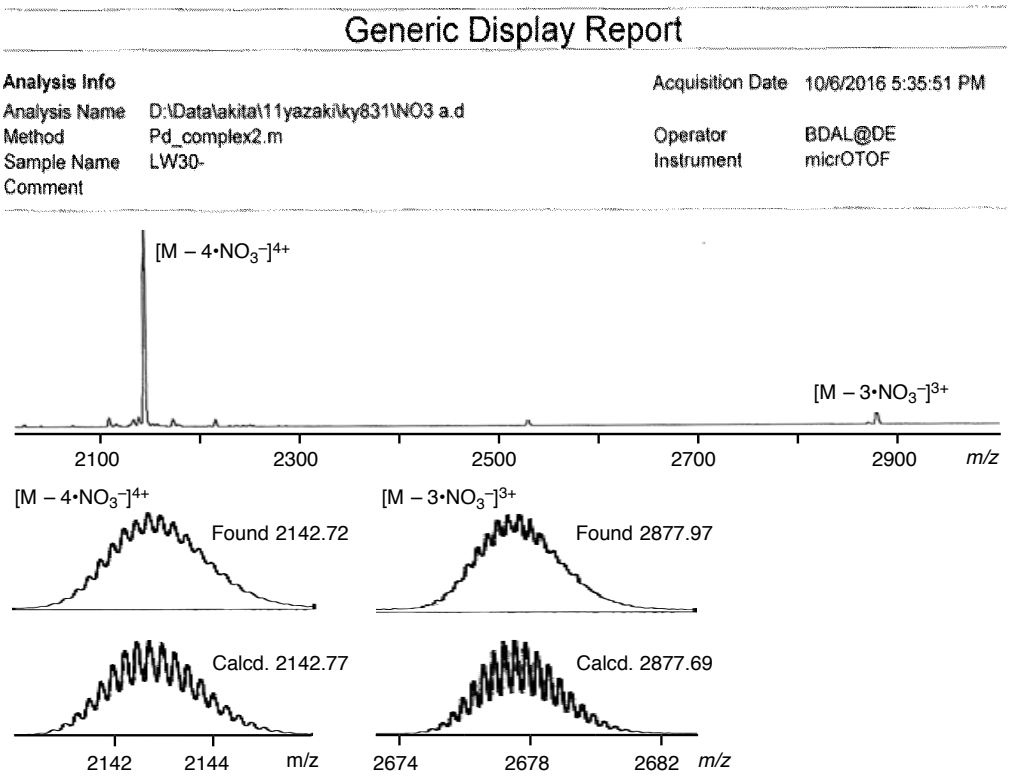
Supplementary Figure 45 | ^{1}H NMR spectra (500 MHz, DMSO-d_6, room temperature) of $(Sc_3N@C_{80})_2$@**3b**. (a) The aromatic and aliphatic and (b) aromatic regions.



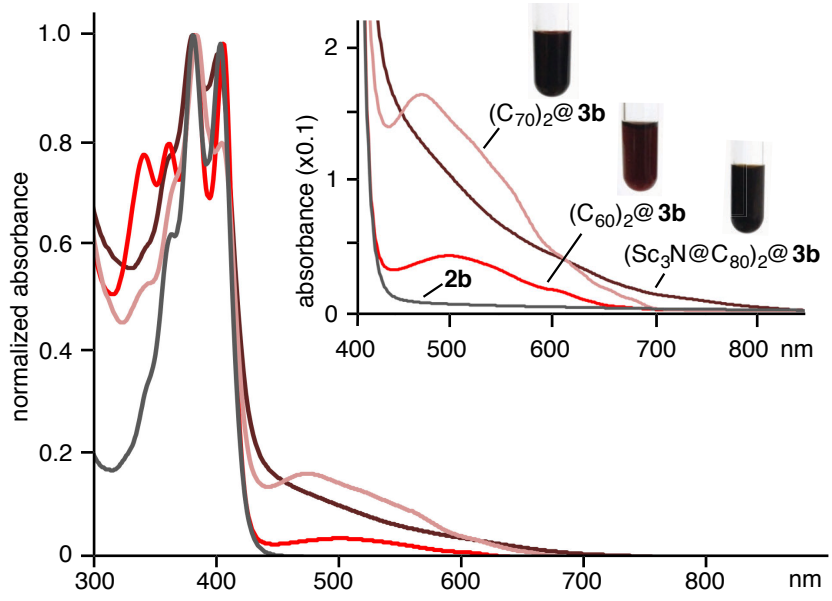
Supplementary Figure 46 | ^{13}C NMR spectrum (125 MHz, DMSO-d_6, room temperature) of $(Sc_3N@C_{80})_2$@**3b**.



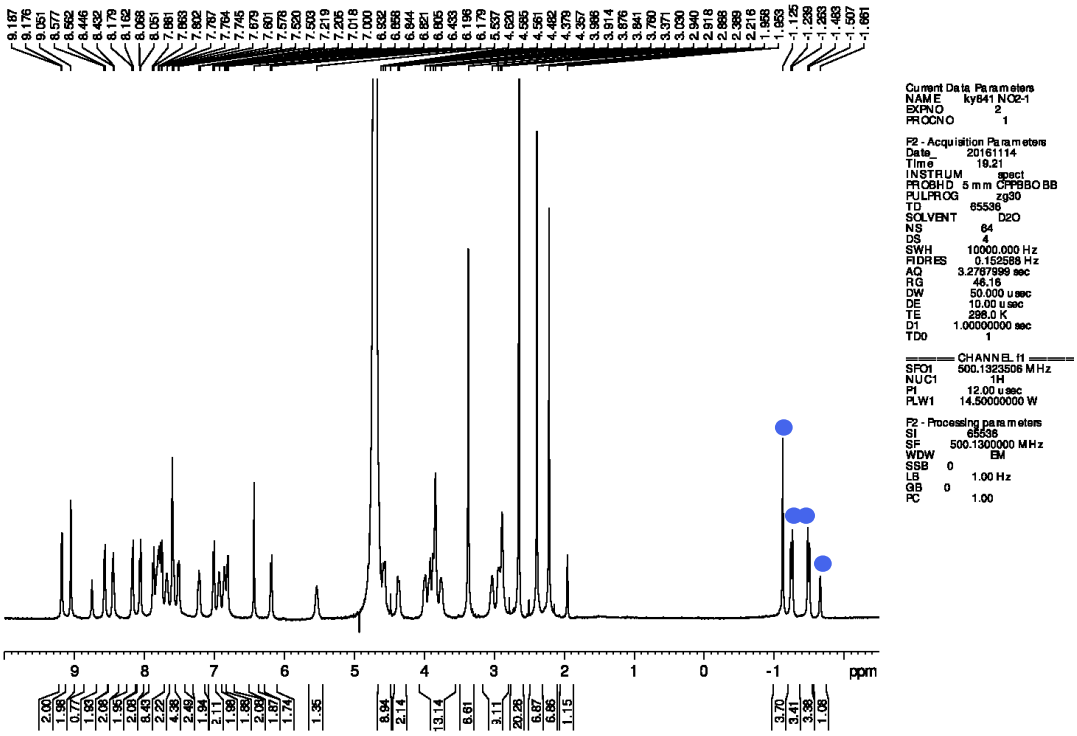
Supplementary Figure 47 | DOSY NMR spectrum (500 MHz, DMSO-d_6, 298 K) of $(Sc_3N@C_{80})_2$@**3b**.



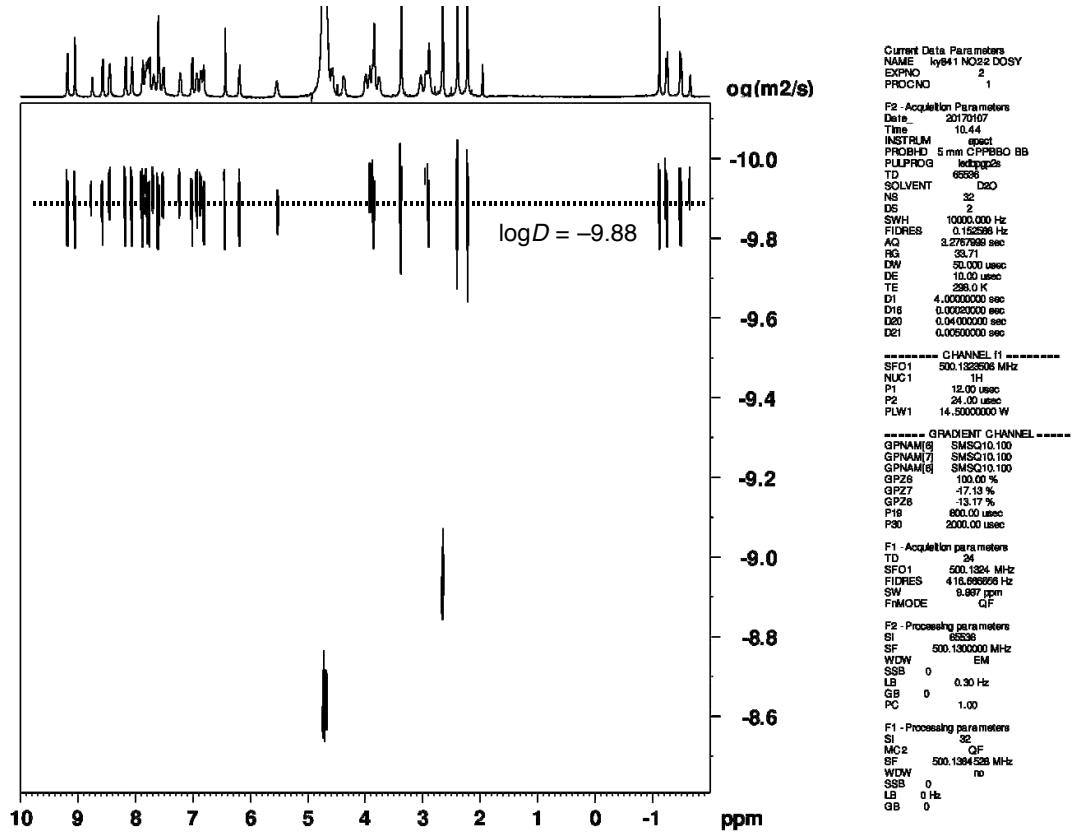
Supplementary Figure 48 | ESI-TOF MS spectrum (CH_3CN) of $(Sc_3N@C_{80})_2$@**3b**.



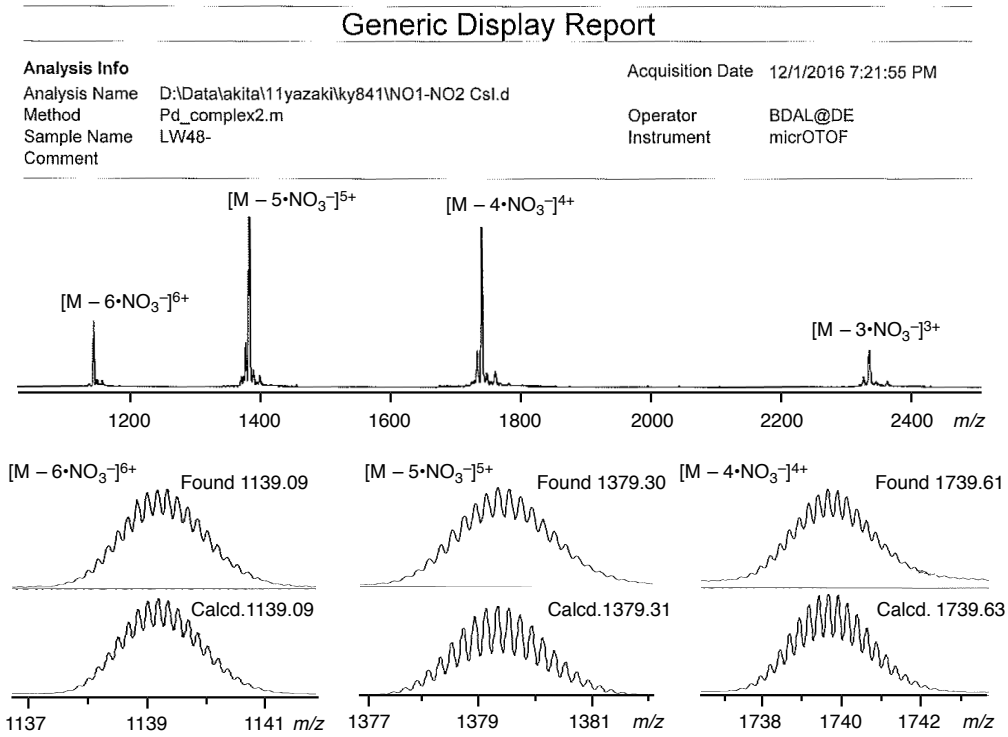
Supplementary Figure 49 | Normalized UV-visible spectra (~0.3 mM, DMSO, room temperature) and photographs of $(C_{60})_2$@**3b**, $(C_{70})_2$@**3b**, and $(Sc_3N@C_{80})_2$@**3b**.



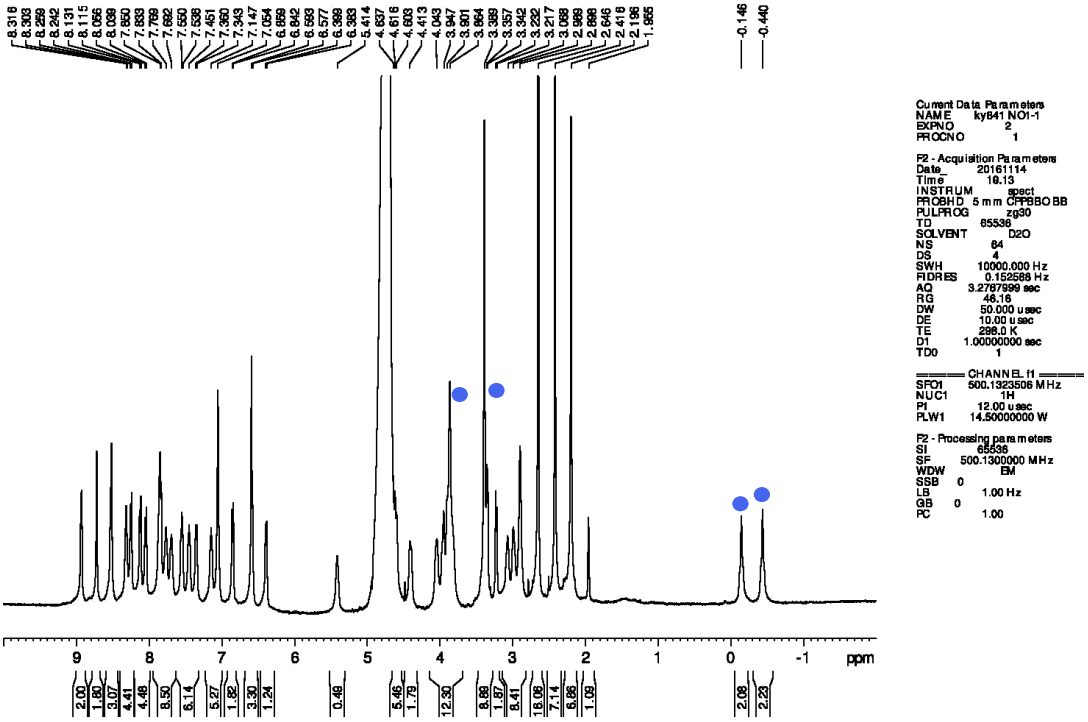
Supplementary Figure 50 | ^{1}H NMR spectrum (500 MHz, D_2O:CD_3CN = 100:1, room temperature) of (**4a**/**4a**)@**2b**.



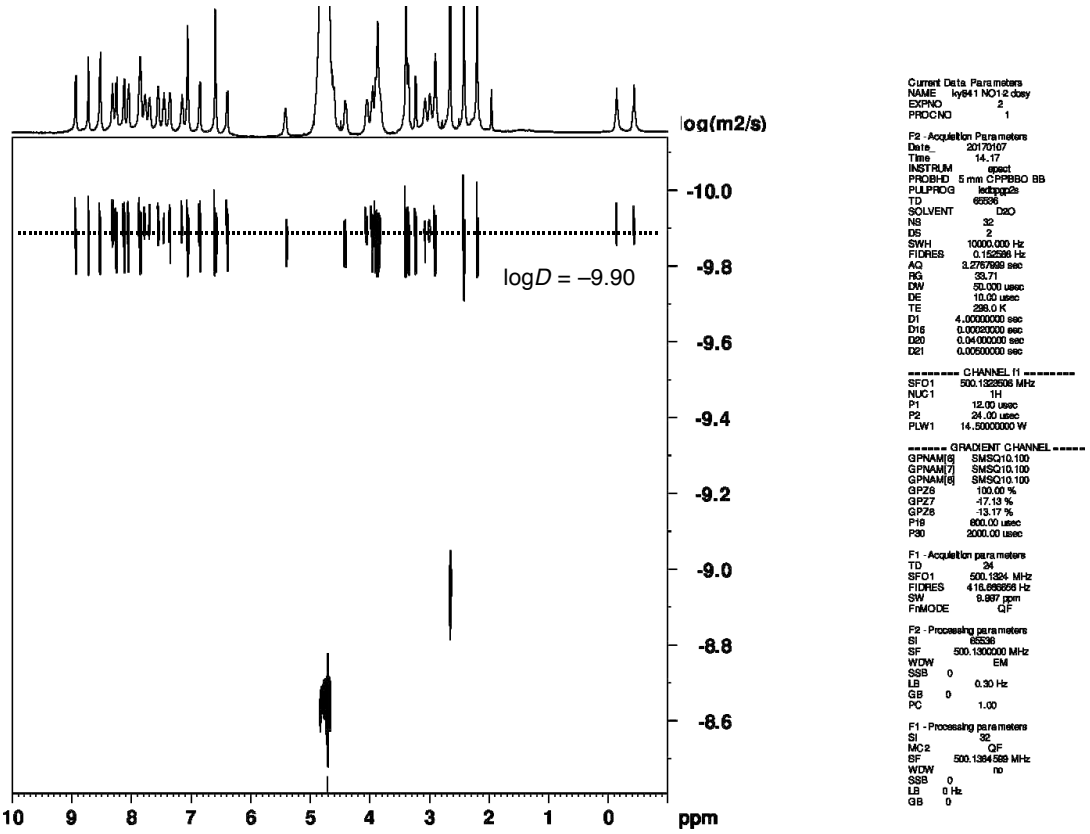
Supplementary Figure 51 | DOSY NMR spectrum (500 MHz, D_2O:CD_3CN = 100:1, 298 K) of (**4a**/**4a**)@**2b**.



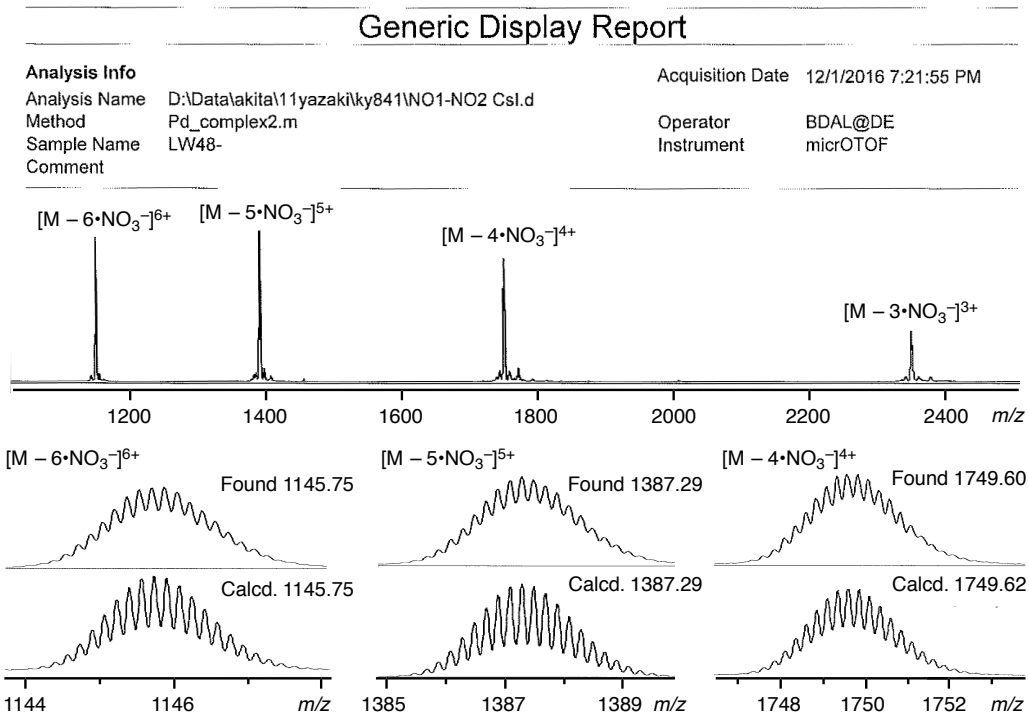
Supplementary Figure 52 | ESI-TOF MS spectrum (H_2O:CH_3CN = 100:1) of (**4a**/**4a**)@**2b**.



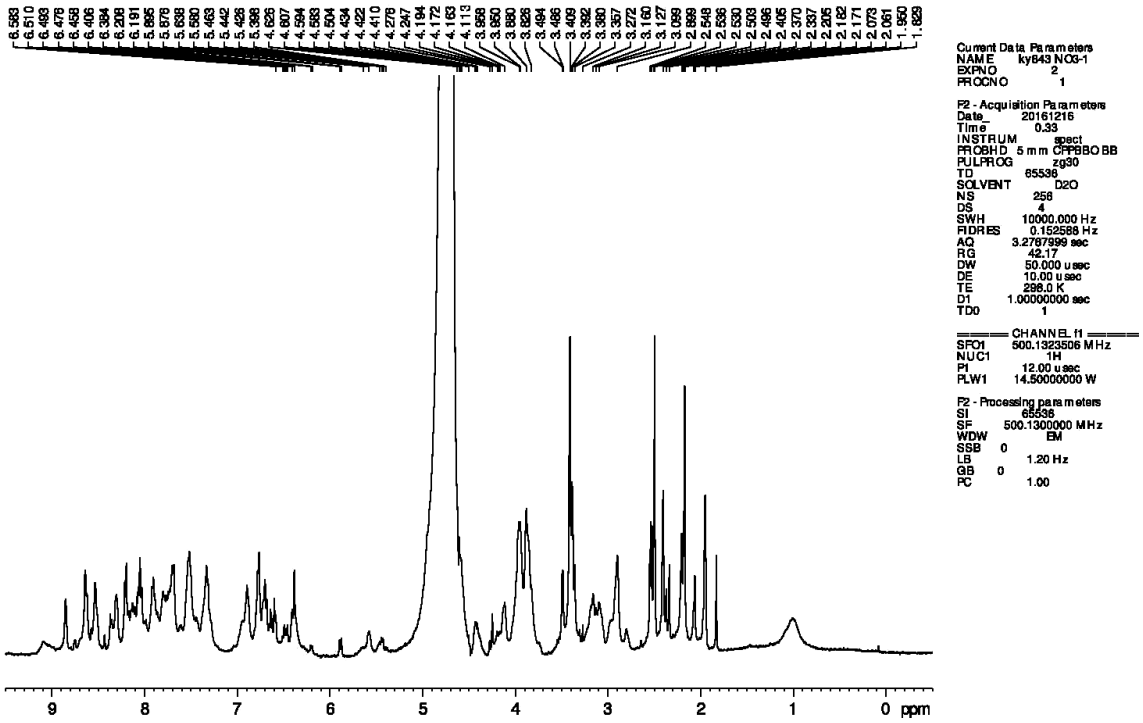
Supplementary Figure 53 | ^{1}H NMR spectrum (500 MHz, D_2O:CD_3CN = 100:1, room temperature) of (**4c**/**4c**)@**2b**.



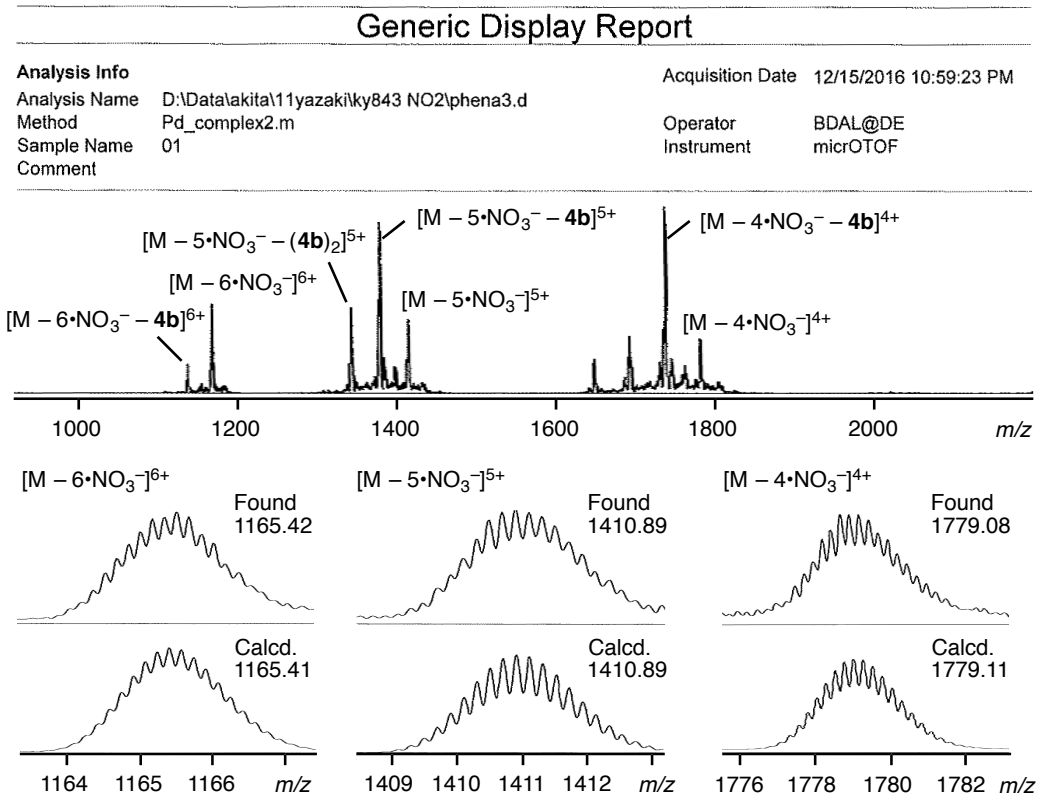
Supplementary Figure 54 | DOSY NMR spectrum (500 MHz, D_2O:CD_3CN = 100:1, 298 K) of (**4c**/**4c**)@**2b**.



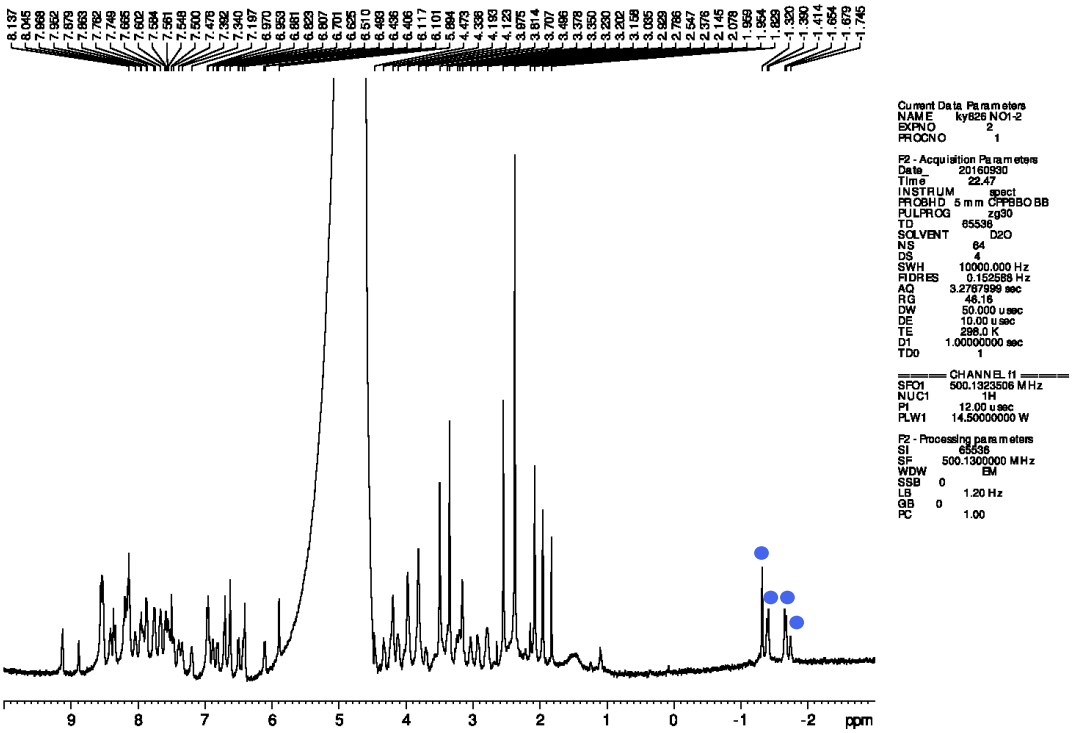
Supplementary Figure 55 | ESI-TOF MS spectrum (H_2O:CH_3CN = 100:1) of (**4c**/**4c**)@**2b**.



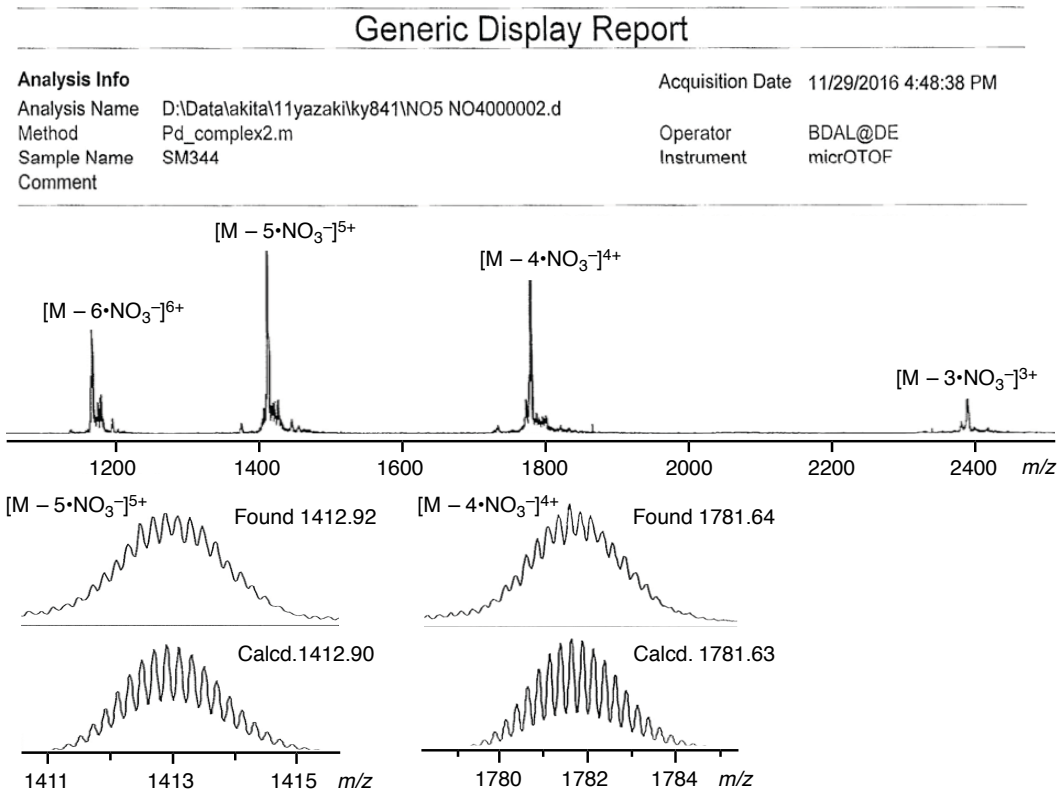
Supplementary Figure 56 | ^{1}H NMR spectrum (500 MHz, D_2O:CD_3CN = 100:1, room temperature) of (**4b**/(**4b**)$_2$)@**2b**.



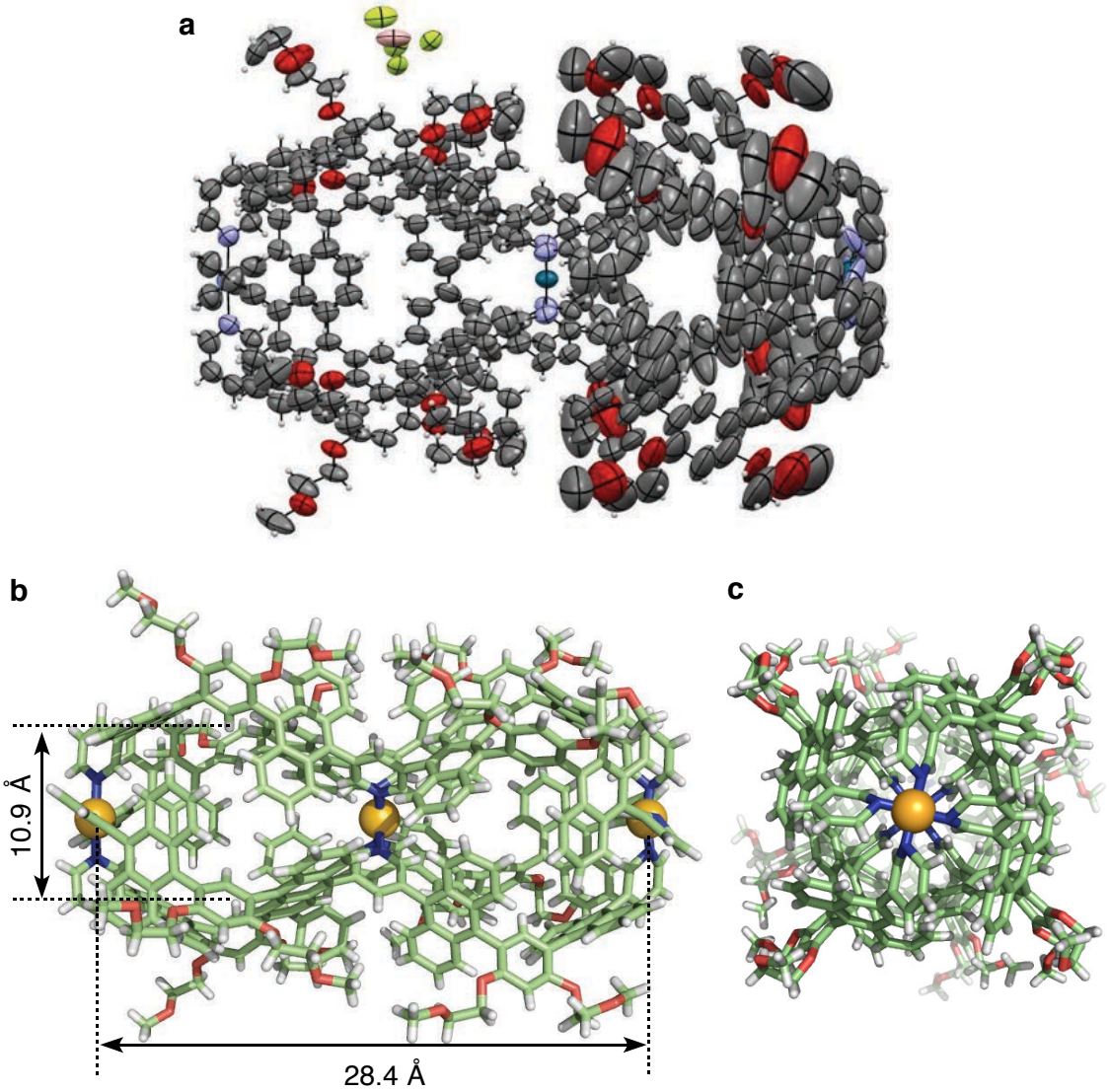
Supplementary Figure 57 | ESI-TOF MS spectrum (H_2O:CH_3CN = 100:1) of (**4b**/(**4b**)$_2$)@**2b**.



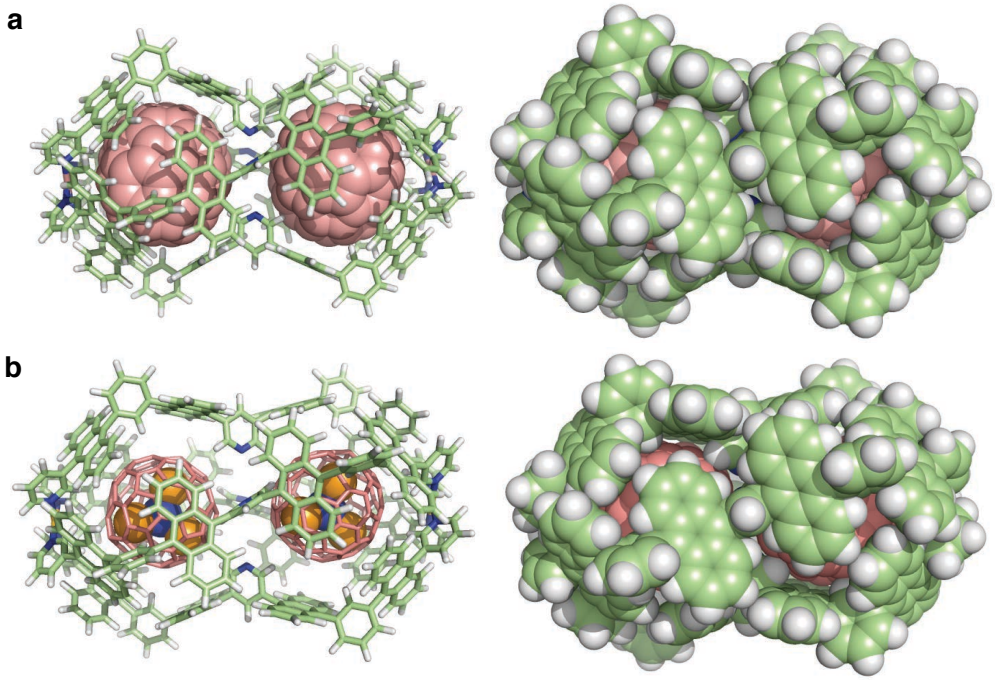
Supplementary Figure 58 | ^{1}H NMR spectrum (500 MHz, D_2O:CD_3CN = 100:1, room temperature) of (**4a**/(**4b**)$_2$)@**2b**.



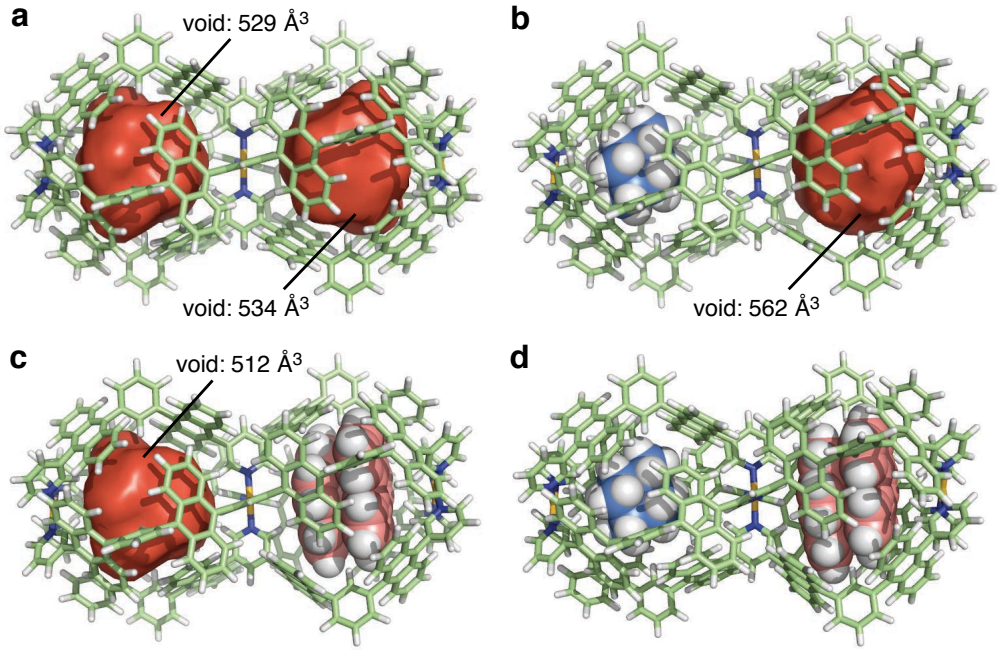
Supplementary Figure 59 | ESI-TOF MS spectrum (H_2O:CH_3CN = 100:1) of (**4a**/(**4b**)$_2$)@**2b**.



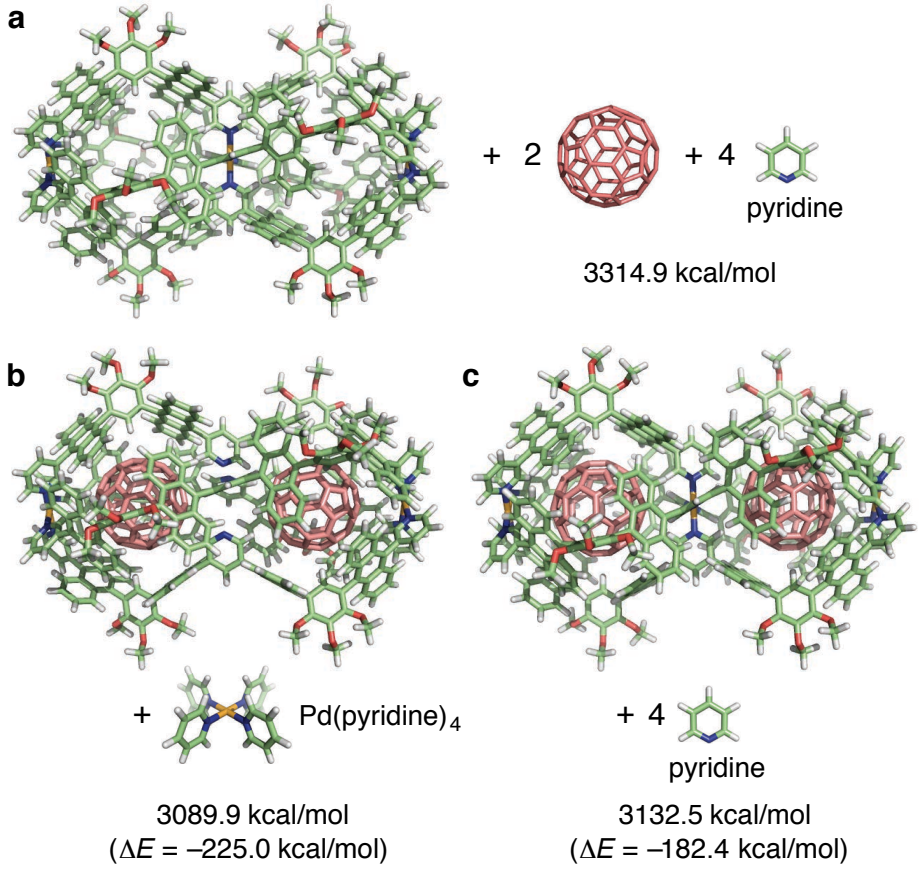
Supplementary Figure 60 | (a) ORTEP drawing of double capsule **2a'**. Ball-and-stick representation of (b) the side and (c) top views of **2a'**. The counterions are omitted for clarity.



Supplementary Figure 61 | Optimized structures of (a) $(C_{70})_2$@**3b** (R = -H) and (b) $(Sc_3N@C_{80})_2$@**3b** (R = -H) by molecular force-field calculation.



Supplementary Figure 62 | Optimized structures and calculated voids of (a) **2b** (R = -H), (b) (**4a**/void)@**2b** (R = -H), (c) (void/(**4b**)$_2$)@**2b** (R = -H), and (d) ((**4a**/(**4b**)$_2$)@**2b** (R = -H) by molecular force-field calculation.



Supplementary Figure 63 | Calculated total energies of (a) **2b** (R = -OCH_3), two fullerenes, two DMSO, and four pyridines, and (b) $(C_{60})_2$@**3b** (R = -OCH_3) and Pd(pyridine)$_4$, and (c) $(C_{60})_2$@**2b** (R = -OCH_3) and four pyridines by molecular force-field calculation.

Supplementary Table

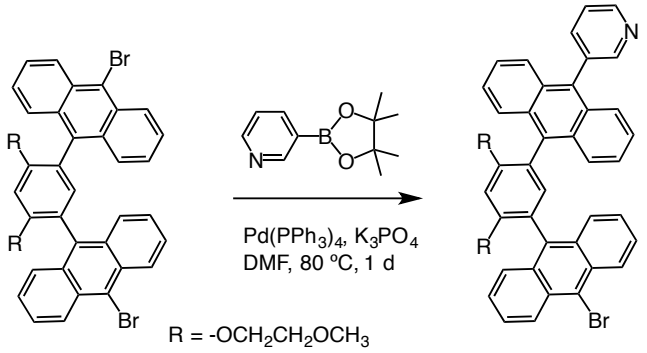
Supplementary Table 1 | Crystal data and structure refinement for **2a'**.

Identification code	KY781	
Empirical formula	C380 H300 B1 F4 N12 O32 Pd3	
Formula weight	5952.61	
Temperature	93 K	
Wavelength	1.54187 Å	
Crystal system	tetragonal	
Space group	P4/ncc	
Unit cell dimensions	a = 26.5390(8) Å	α = 90°
	b = 26.5390(8) Å	β = 90°
	c = 71.806(7) Å	γ = 90°
Volume	50574(5) $Å^3$	
Z	4	
Density (calculated)	0.782 Mg/m^3	
Absorption coefficient	1.216 mm^{-1}	
F(000)	12396.0	
Crystal size	0.189 × 0.184 × 0.047 mm^3	
Theta range for data collection	7.55 to 149.276°.	
Index ranges	-33 <=h<=31, -29<=k<=32, -73<=l<=89	
Reflections collected	152900	
Independent reflections	25558 [R(int) = 0.0690]	
Completeness to theta = 67.687°	98.5 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.944 and 0.678	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	25558 / 370 / 1024	
Goodness-of-fit on F^2	1.204	
Final R indices [I>2sigma(I)]	R_1 = 0.1060, wR_2 = 0.3412	
R indices (all data)	R_1 = 0.1548, wR_2 = 0.3855	
Largest diff. peak and hole	0.79 and -1.67 e.$Å^{-3}$	

The supplementary crystallographic data of **2a'** (CCDC 529139) can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data_request/cif. Disordered solvent molecules and counterions were removed by SQUEEZE program and the result was attached to the CIF file[1-6].

Supplementary Methods

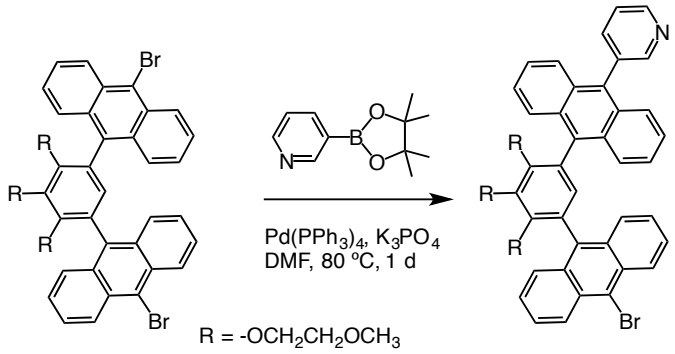
Synthesis of compound 6a



Compound **5a** (2.084 g, 2.829 mmol), 3-pyridineboronic acid pinacol ester (0.614 g, 2.96 mmol), K_3PO_4 (2.673 g, 12.59 mmol), and $Pd(PPh_3)_4$ (124 mg, 0.108 mmol) were added to a 300 mL glass flask filled with N_2. Dry DMF (50 mL) was added to the flask and then the mixture was stirred at 80 ºC for 1 d. The resultant solution was concentrated under reduced pressure. After addition of water, the crude product was extracted with $CHCl_3$. The obtained organic layer was dried over $MgSO_4$, filtrated, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, ethyl acetate : hexane : $CHCl_3$ = 1 : 1 : 1) to afford compound **6a** as a yellow powder (0.819 g, 1.12 mmol, 39%) (see Supplementary Figs 2-6).

^{1}H NMR (500 MHz, $CDCl_3$, room temperature): δ 8.80 (d, J = 5.0 Hz, 1H), 8.74 (s, 0.5H), 8.65 (s, 0.5H), 8.58 (d, J = 9.0 Hz, 2H), 7.99 (d, J = 8.5 Hz, 2H), 7.96 (d, J = 9.0 Hz, 2H), 7.86 (d, J = 7.5 Hz, 0.5H), 7.77 (d, J = 7.0 Hz, 0.5H), 7.62-7.57 (m, 5H), 7.48-7.42 (m, 4H), 7.35 (dd, J = 9.5, 9.5 Hz, 2H), 7.24 (s, 1H), 7.12 (s, 1H), 4.14 (t, J = 5.0 Hz, 2H), 4.17-4.09 (m, 2H), 3.38 (t, J = 5.0 Hz, 2H), 3.32 (t, J = 5.0 Hz, 2H), 2.94 (s, 6H), 2.91 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, room temperature): δ 158.2 (C_q), 151.7 (CH), 148.7 (CH), 139.1 (CH), 136.8 (CH), 135.2 (C_q), 134.4 (C_q), 134.1 (C_q), 132.4 (C_q), 131.5 (C_q), 130.4 (2 × C_q), 127.9 (CH), 127.4 (CH), 127.2 (CH), 126.8 (CH), 126.2 (CH), 125.5 (2 × CH), 125.1 (2 × C_q), 123.5 (CH), 122.6 (C_q), 120.3 (C_q), 120.0 (C_q), 100.0 (CH), 70.7 (CH_2), 69.1 (CH_2), 59.0 (CH_3). FT-IR (KBr, cm^{-1}): 2925, 2879, 2817, 1604, 1506, 1451, 1439, 1376, 1360, 1335, 1303, 1265, 1192, 1162, 1128, 1105, 1058, 1025, 769, 758, 718, 686, 608. HR MS (ESI, CH_3OH): m/z Calcd. for $C_{45}H_{36}NO_4Br$: 736.1883, Found 736.1889 $[M + H]^+$.

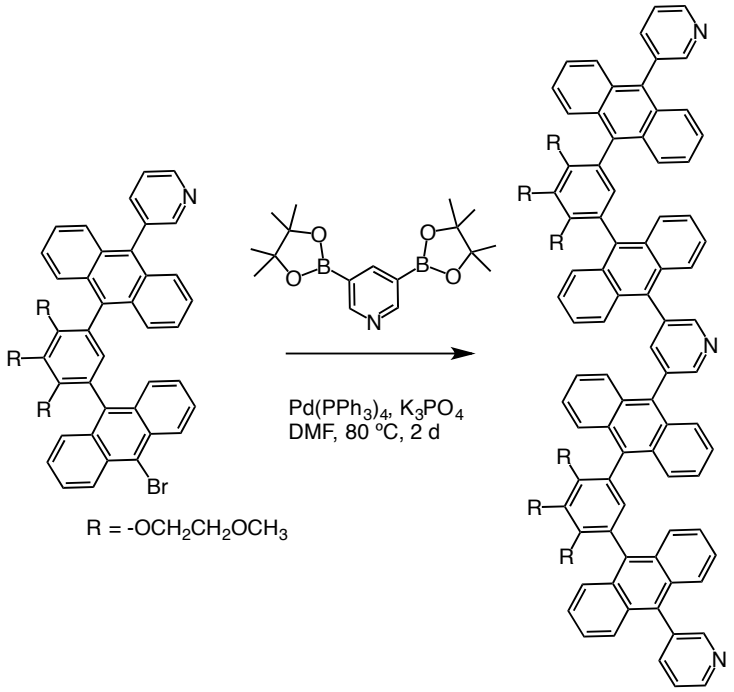
Synthesis of compound 6b



Compound **5b** (2.847 g, 2.945 mmol), 3-pyridineboronic acid pinacol ester (0.5957 g, 2.904 mmol), K_3PO_4 (2.415 g, 11.38 mmol), and $Pd(PPh_3)_4$ (100.2 mg, 0.8675 mmol) were added to a 300 mL glass flask filled with N_2. Dry DMF (50 mL) was added to the flask and then the mixture was stirred at 80 ºC for 1 d. The resultant solution was concentrated under reduced pressure and then washed by water. The crude product was purified by column chromatography (silica gel, ethyl acetate : hexane = 1 : 1) to give compound **6b** and its debrominated compound. A mixture of the resultant powder and DBH was stirred in CH_2Cl_2 (20 mL) for 1 night. The resultant solution was washed with water to give **6b** as yellow powder (0.7843 g, 0.979 mmol, 33%) (see Supplementary Figs 19-22).

^{1}H NMR (500 MHz, $CDCl_3$, room temperature): δ 8.83 (d, J = 4.5 Hz, 1H), 8.75 (s, 0.5H), 8.67 (s, 0.5H), 8.62 (d, J = 9.0 Hz, 2H), 7.97 (m, 4H), 7.85 (d, J = 8.0 Hz, 0.5H), 7.77 (d, J = 8.0 Hz, 0.5H), 7.63-7.55 (m, 5.0H), 7.53-7.49 (m, 4.0H), 7.39 (dd, J = 7.5, 7.5 Hz, 2H), 7.07 (s, 0.5H), 7.06 (s, 0.5H), 4.52-4.51 (m, 2H), 3.98 (t, J = 4.5 Hz, 2H), 3.92 (br, 2H), 3.86 (t, J = 4.0 Hz, 2H), 3.47 (s, 3H), 3.09-3.06 (m, 2H), 3.01 (br, 2H), 2.79-2.78 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, room temperature): δ 152.5 (C_q), 152.4 (C_q), 152.2 (C_q), 151.7 (CH), 151.7 (CH), 148.8 (CH), 145.8 (C_q), 145.7 (C_q), 139.1 (CH), 139.0 (CH), 135.0 (C_q), 134.1 (C_q), 134.0 (C_q), 133.8 (C_q), 133.7 (C_q), 132.8 (C_q), 131.3 (C_q), 130.5 (CH), 130.4 (CH), 130.3 (C_q), 130.2 (C_q), 128.0 (CH), 127.6 (C_q), 127.3 (CH), 127.2 (CH), 127.0 (CH), 126.9 (CH), 126.3 (CH), 125.9 (CH), 125.6 (CH), 125.5 (CH), 123.5 (CH), 123.4 (CH), 123.0 (C_q), 72.9 (CH_2), 72.8 (CH_2), 72.1 (CH_2), 71.4 (CH_2), 71.3 (CH_2), 59.0 (CH_2), 58.3 (CH_3). FT-IR (KBr, cm^{-1}): 2979, 2925, 2881, 2818, 1464, 1438, 1416, 1389, 1348, 1256, 1130, 1106, 1070, 1026, 926, 909, 759. MALDI-TOF MS (dithranol): m/z Calcd. for $C_{48}H_{42}NO_6$: 810.23, Found 810.42 $[M + H]^+$. HR MS (ESI): m/z Calcd. for $C_{48}H_{42}NO_6$: 810.2251, Found 810.2219 $[M + H]^+$.

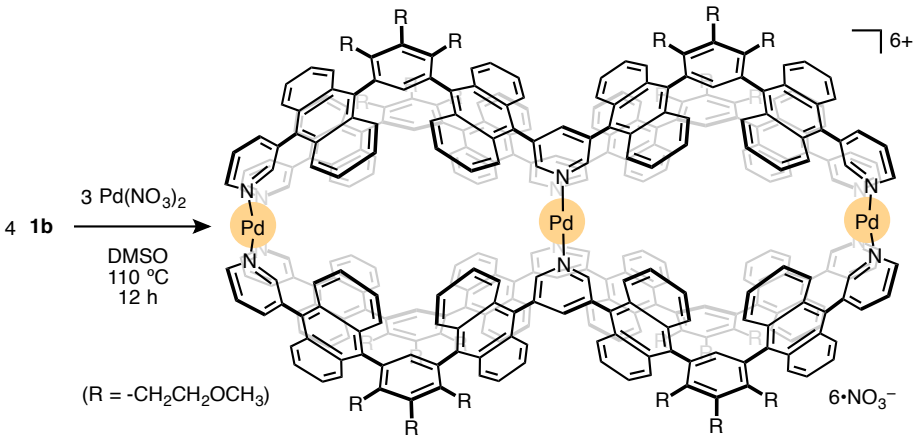
Synthesis of W-shaped ligand 1b



Compound **6b** (1.3568 g, 1.6775 mmol), 3,5-pyridinediboronic acid bis(pinacol) ester (194.6 mg, 0.58 mmol), K_3PO_4 (1.04 g, 4.9 mmol), and $Pd(PPh_3)_4$ (90.5 mg, 78.0 μmol) were added to a 300 mL glass flask filled with N_2. Dry DMF (100 mL) was added to the flask and then the mixture was stirred at 80 ºC for 2 d. After addition of water (200 mL), the precipitation was collected by the filtration. The crude product was purified by gel permeation chromatography to afford ligand **1b** as a yellow powder (345.1 mg, 0.2248 mmol, 39%) (see Supplementary Figs 23-26).

^{1}H NMR (500 MHz, $CDCl_3$, room temperature): δ 8.96-8.60 (m, 6H), 8.06-7.34 (m, 37H), 7.16-7.08 (m, 2H), 4.56-4.54 (m, 4H), 4.01-3.87 (m, 12H), 3.50-3.44 (m, 6H), 3.14-3.07 (m, 8H), 2.86-2.56 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, room temperature): δ 152.4 (CH), 151.8 (C_q), 151.1 (CH), 148.9 (CH), 145.7 (C_q), 141.9 (CH), 138.9 (CH), 134.9 (C_q), 134.7 (C_q), 134.4(C_q), 134.1 (C_q), 132.8 (C_q), 132.4 (C_q), 130.6 (CH), 130.20 (C_q), 127.6 (CH), 127.2 (CH), 127.1 (CH), 126.3 (CH), 125.9 (CH), 125.5 (CH), 123.4 (CH, C_q), 72.9 (CH_2), 72.7 (CH_2), 72.1 (CH_2), 71.4 (CH_2), 59.0 (CH_3), 58.2 (CH_3). FT-IR (KBr, cm^{-1}): 2926, 2877, 2814, 1440, 1415, 1394, 1375, 1356, 1245, 1196, 1129,1104, 1068, 1025, 927, 767, 718, 650. HR MS (ESI, CH_2Cl_2:CH_3OH): *m/z* Calcd. 1557.6215, Found 1557.6214 $[M + Na]^+$.

Formation of double capsule 2b



W-shaped ligand **1b** (91.8 mg, 59.8 μmol), a DMSO-d_6 solution (50 mM) of $Pd(NO_3)_2$ (0.93 mL, 46.4 μmol), which prepared *in situ* from $PdCl_2(DMSO)_2$ and $AgNO_3$, and DMSO-d_6 (4 mL) were added to a glass test tube and then the mixture was stirred at 110 ºC for 12 h. The quantitative formation of double capsule **2b** was confirmed by NMR and MS analyses (see Supplementary Figs 27-33).

^{1}H NMR (500 MHz, D_2O:CD_3CN = 5:1, room temperature): δ 9.32 (d, J = 5.5 Hz, 2H), 9.25 (s, 2H), 8.81 (s, 2H), 8.73 (d, J = 5.5 Hz, 2H), 8.56 (dd, J = 5.5, 5.5 Hz, 2H), 8.31 (d, J = 6.8 Hz, 2H), 8.26 (d, J = 8.5 Hz, 2H), 8.07 (d, J = 9.0 Hz, 2H), 8.04-7.89 (m, 10H), 7.70 (dd, J = 7.5, 7.0 Hz, 2H), 7.66 (d, J = 8.5 Hz, 2H), 7.45 (dd, J = 8.0, 7.0 Hz, 2H), 7.19 (dd, J = 7.0, 7.0 Hz, 2H), 7.09-7.00 (m, 6H), 6.69 (d, J = 8.0 Hz, 2H), 6.64 (s, 2H), 5.92 (dd, J = 8.5, 7.5 Hz, 2H), 4.72 (br, 2H), 4.57-4.54 (m, 2H), 4.21-4.19 (m, 2H), 4.13-4.01 (m, 10H), 3.55 (s, 6H), 3.28-3.25 (m, 2H), 3.20-3.17 (m, 2H), 3.06-3.04 (m, 4H), 2.70 (s, 6H), 2.57 (s, 6H). ^{13}C NMR (120 MHz, D_2O:CD_3CN = 5:1, room temperature): δ 151.6 (CH), 151.3 (CH, C_q), 150.4 (CH), 147.3 (CH), 144.9 (C_q), 144.0 (CH), 139.5 (C_q), 137.1 (C_q), 135.6 (C_q), 134.4 (C_q), 129.2 (CH), 128.9 (C_q), 128.8 (C_q), 128.6 (C_q), 128.4 (C_q), 128.0 (C_q), 127.7 (C_q), 127.4 (CH), 127.2 (CH), 126.5 (CH), 126.3 (CH), 124.9 (CH), 124.7 (CH), 124.0 (CH), 123.4 (CH), 122.6 (CH), 122.2 (CH), 71.8 (CH_2), 70.9 (CH_2), 69.9 (CH_2), 57.4 (CH_3), 56.4 (CH_3). DOSY NMR (500 MHz, DMSO-d_6, 298 K): D = 6.31 × 10^{-11} m^2 s^{-1}. FT-IR (KBr, cm^{-1}): 3060, 2931, 2884, 2816, 1442, 1417, 1378, 1228, 1195, 1105, 1065, 1030, 944, 925, 886, 848, 829, 772, 707, 671, 643, 616. ESI-TOF MS (CH_3CN): m/z 1304.0 [**2b** – 5•NO_3^-]$^{5+}$, 1645.5 [**2b** – 4•NO_3^-]$^{4+}$, 2214.7 [**2b** – 3•NO_3^-]$^{3+}$.

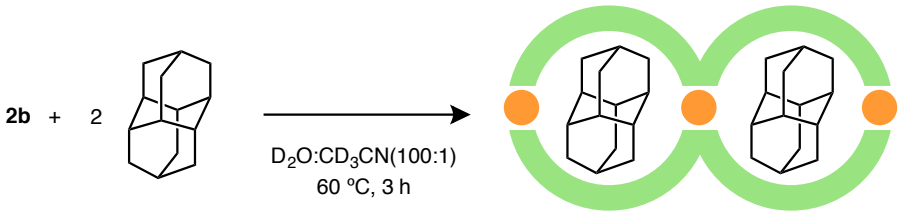
Formation of $(C_{60})_2$@3a, $(C_{70})_2$@3b, and $(Sc_3N@C_{80})_2$@3b

$(C_{60})_2$@3a. ^{1}H NMR (500 MHz, DMSO, room temperature): δ 9.18 (d, J = 5.0 Hz, 2H), 8.67 (br, 4H), 8.51 (dd, J = 9.0, 5.0 Hz, 2H), 8.42 (d, J = 9.0 Hz, 2H), 8.30 (d, J = 8.0 Hz, 2H), 8.05 (br, 2H), 7.98 (d, J = 8.5 Hz, 2H), 7.91-7.86 (m, 4H), 7.78 (s, 1H), 7.71-7.69 (m, 4H), 7.61-7.50 (m, 10H), 7.20 (s, 2H), 7.02 (dd, J = 7.5, 6.0 Hz, 2H), 6.90 (d, J = 8.5 Hz, 2H), 6.84 (s, 2H), 6.57 (br, 2H), 6.29 (d, J = 8.0 Hz, 2H), 4.26 (br, 4H), 4.12 (br, 4H), 3.35 (br, 4H), 3.20 (br, 4H), 2.95 (s, 6H), 2.69 (s, 6H). ESI-TOF MS (CH_3CN) of $(C_{60})_2$@**3a**: m/z 1800.0 $[(C_{60})_2$@**3a** – 4•$NO_3^-]^{4+}$, 2420.7 $[(C_{60})_2$@**3a** – 3•$NO_3^-]^{3+}$.

$(C_{70})_2$@3b. ^{1}H NMR (500 MHz, DMSO, room temperature): δ 9.38 (d, J = 5.0 Hz, 2H), 8.97 (s, 2H), 8.71 (d, J = 7.5 Hz, 2H), 8.60 (dd, J = 7.5, 5.0 Hz, 2H), 8.43-8.41 (m, 2H), 8.20 (s, 2H), 8.12 (s, 2H), 7.99 (d, J = 8.0 Hz, 2H), 7.90 (d, J = 8.5 Hz, 2H), 7.84 (br, 2H), 7.77 (br, 2H), 7.73 (dd, J = 8.5, 6.5 Hz, 2H), 7.62 (br, 2H), 7.51 (br, 6H), 7.07 (d, J = 8.0 Hz, 2H), 6.89 (dd, J = 8.0, 7.0 Hz, 2H), 6.57 (br, 4H), 6.46 (d, J = 8.0 Hz, 2H), 4.36-4.28 (m, 4H), 3.96-3.86 (m, 4H), 3.82-3.74 (m, 4H), 3.71 (t, J = 4.0 Hz, 4H), 3.32 (s, 6H), 3.01 (t, J = 5.0 Hz, 4H), 2.85 (t, J = 4.5 Hz, 4H), 2.62 (s, 6H), 2.55 (s, 6H). ESI-TOF MS (CH_3CN) of $(C_{70})_2$@**3b**: m/z 2008.3 $[(C_{70})_2$@**3b** – 4•$NO_3^-]^{4+}$, 2698.4 $[(C_{70})_2$@**3b** – 3•$NO_3^-]^{3+}$.

$(Sc_3N@C_{80})_2$@3b. ^{1}H NMR (500 MHz, DMSO, room temperature): δ 9.22 (d, J = 5.0 Hz, 2H), 8.73 (s, 2H), 8.55 (d, J = 6.0 Hz, 2H), 8.46 (br, 2H), 8.39 (d, J = 6.0 Hz, 2H), 8.20 (br, 2H), 8.16 (br, 2H), 8.10 (d, J = 7.0 Hz, 2H), 8.01 (d, J = 8.0 Hz, 2H), 7.89 (br, 3H), 7.84 (br, 2H), 7.79(br, 2H), 7.76 (br, 4H), 7.58 (br, 4H), 7.49 (d, J = 6.0 Hz, 2H), 7.13 (br, 2H), 6.88 (d, J = 7.0 Hz, 2H), 6.76 (s, 2H), 6.65 (br, 2H), 6.37 (d, J = 8.0 Hz, 2H), 4.39 (br, 4H), 3.95-3.90 (m, 8H), 3.75 (br, 4H), 3.35 (s, 6H), 3.00 (br, 4H), 2.92 (br, 4H), 2.60 (s, 6H), 2.55 (s, 6H). ESI-TOF MS (CH_3CN) of $(Sc_3N@C_{80})_2$@**3b**: m/z 2142.8 $[(Sc_3N@C_{80})_2$@**3b** – 4•$NO_3^-]^{4+}$, 2877.7 $[(Sc_3N@C_{80})_2$@**3b** – 3•$NO_3^-]^{3+}$.

Encapsulation of diamantane (4a) by 2b

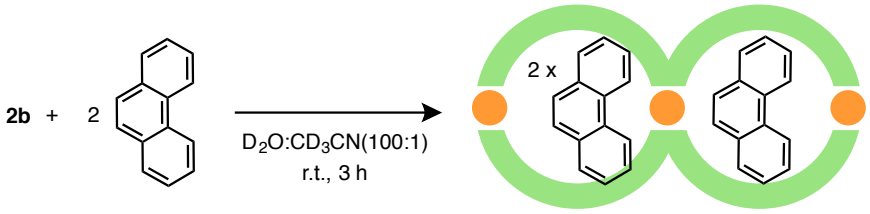


Diamantane (**4a**; 0.8 mg, 4.0 μmol) was added to a 100:1 D_2O:CD_3CN solution (0.6 mL) of double capsule **2b** (1.5 mg, 0.22 μmol) and the mixture was stirred at 60 °C for 3 h. The quantitative formation of a (**4a**/**4a**)@**2b** complex was confirmed by NMR and ESI-TOF MS analyses (see Supplementary Figs 50-52). Similarly, two molecules of *p*-cyclophane (**4c**) were quantitatively encapsulated within **2b** to give a (**4c**/**4c**)@**2b** complex (see Supplementary Figs 53-55).

(4a/4a)@2b. DOSY NMR (500 MHz, D_2O:CD_3CN = 100:1, 298 K): D = 1.32 × 10^{-10} m^2 s^{-1}. ESI-TOF MS (H_2O:CH_3CN = 100:1): m/z 1139.1 [(**4a**/**4a**)@**2b** – 6•NO_3^-]$^{6+}$, 1379.3 [(**4a**/**4a**)@**2b** – 5•NO_3^-]$^{5+}$, 1739.6 [(**4a**/**4a**)@**2b** – 4•NO_3^-]$^{4+}$, 2340.1 [(**4a**/**4a**)@**2b** – 3•NO_3^-]$^{3+}$.

(4c/4c)@2b. DOSY NMR (500 MHz, D_2O:CD_3CN = 100:1, 298 K): D = 1.26 × 10^{-10} m^2 s^{-1}. ESI-TOF MS (H_2O:CH_3CN = 100:1): m/z 1145.8 [(**4c**/**4c**)@**2b** – 6•NO_3^-]$^{6+}$, 1387.3 [(**4c**/**4c**)@**2b** – 5•NO_3^-]$^{5+}$, 1749.6 [(**4c**/**4c**)@**2b** – 4•NO_3^-]$^{4+}$, 2353.5 [(**4c**/**4c**)@**2b** – 3•NO_3^-]$^{3+}$.

Encapsulation of phenanthrene (4b) by 2b



Phenanthrene (**4b**; 0.8 mg, 4.4 μmol) was added to a 100:1 D_2O:CD_3CN solution (0.6 mL) of double capsule **2b** (1.5 mg, 0.22 μmol) and the mixture was stirred at room temperature for 3 h. The formation of a (**4b**/(**4b**)$_2$)@**2b** complex was confirmed by NMR and ESI-TOF MS analyses (see Supplementary Figs 56-57).

ESI-TOF MS (H_2O:CH_3CN = 100:1): m/z 1165.4 [(**4b**/(**4b**)$_2$)@**2b** – 6•NO_3^-]$^{6+}$, 1410.9 [(**4b**/(**4b**)$_2$)@**2b** – 5•NO_3^-]$^{5+}$, 1779.1 [(**4b**/(**4b**)$_2$)@**2b** – 4•NO_3^-]$^{4+}$.

Supplementary References

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