Supporting Information for

Robust R^2_2 (8) Hydrogen Bonded Dimer for Crystal Engineering of Glycoluril Derivatives

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Synthesis of compound 1

The coupling reaction between **4** and 3-ethynylpyridine (**5**) was readily accomplished using $Pd(PPh_3Cl_2)_2$ and CuI as catalysts in the presence of Et_3N in DMF at 100 °C (monitored by TLC), and then the solvent was removed under reduced pressure. The solid residue was purified by flash chromatography (SiO2, $CHCl_3$-MeOH, 50:1) to give **1**, as illustrated in Scheme 2. In order to purify the crude product, about 2 mL ethyl acetate was added and the solution was vibrated by ultrasonic oscillator. At this stage a white solid appeared. Finally, the solvent and the desired solid compound 1 were separated by centrifugation. M.p. 280-283℃. IR (KBr, cm-1): 3221w, 2212w, 1753s, 1710s, 1464m, 1274w, 1027w, 811w, 705w. ^{1}H NMR (600 MHz, cdcl3) δ 8.94 (s, 2H), 8.55 (s, 2H), 7.90 (d, J = 12.6 Hz, 4H), 7.45 (s, 2H), 7.31 (s, 2H), 5.81 (d, J = 16.8 Hz, 2H), 4.37-4.32 (m, 4H), 4.13 (q, J = 7.2 Hz 2H), 1.35 (t, J = 7.2 Hz, 3H), 1.18 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, cdcl3) δ 166.1, 157. 6, 152.5, 148.5, 139.4, 138.5, 131.4, 123.4, 123.1, 92.0, 90.5, 63.2, 63.1, 41.8, 14.1, 13.7. HRMS (ESI): m/z[M+H+] calcd for C32H27N6O6: 591.1980; found: 591.1986.

Synthesis of compound 2

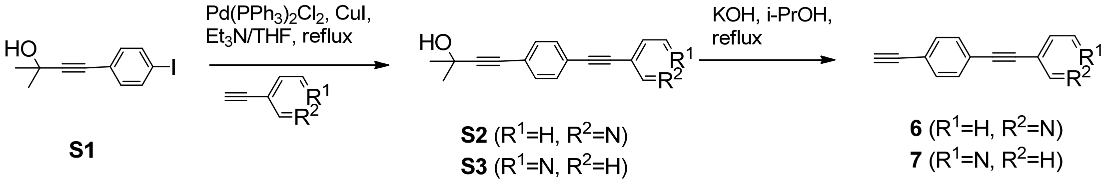
The procedure was similar to **1** except that 3-ethynylpyridine was replaced by 3-((4-ethynylphenyl)ethynyl)pyridine(6). Compound 2 was obtained as a yellow solid. M.p. >300℃; IR (KBr, cm-1): 3396w, 2215w, 1727s, 1511s, 1454m, 1408w, 1140w, 1024w, 838w, 704w. ^{1}H NMR (600 MHz, dmso) δ 8.80 (s, 2H), 8.61(d, J = 7.2 Hz, 2H), 8.02 (d, J = 7.8 Hz, 2H), 7.74 (d, J = 7.8 Hz, 4H), 7.68 (d, J = 7.8 Hz, 4H), 7.55 (s, 2H), 7.49 (t, J = 6.6 Hz, 2H), 5.50 (d, J = 15.6 Hz, 2H), 4.51 (d, J = 16.2 Hz, 2H), 4.28 (q, J = 14.4, 7.2 Hz, 2H), 4.17 (q, J = 14.4, 7.2 Hz, 2H), 1.28 (t, J = 7.2 Hz, 3H), 1.23 (t, J = 7.2 Hz, 3H). HRMS (ESI): m/z[M+H+] calcd for C48H35N6O6: 791.2608; found: 791.2613. Regretfully, carbon signals were not found despite collected more than 12 h due to the poor solubility.

Synthesis of the compound 3

The procedure was similar to **1** except that 3-ethynylpyridine was replaced by 4-((4-ethynylphenyl)ethynyl)pyridine(7)14. Compound 3 was obtained as a yellow solid. M.p. >300℃; IR (KBr, cm-1): 3418w, 3072w, 2218w, 1722s, 1592s, 1453m, 1419w, 1272w, 1032w, 837w, 821w, 704w. ^{1}H NMR (600 MHz, dmso) δ 8.65 (s, 4H), 7.75 (d, J = 7.8 Hz, 4H), 7.71 (d, J = 8.4 Hz, 4H), 7.57 (s, 2H), 7.56 (d, J = 2.4 Hz, 4H), 5.49 (d, J = 16.8 Hz, 2H), 4.52 (d, J = 16.2 Hz, 2H), 4.27 (d, J = 7.2Hz, 2H), 4.17 (d, J = 7.2 Hz, 2H), 1.27 (t, J = 7.2 Hz, 3H), 1.23 (t, J = 7.2 Hz, 3H). HRMS (ESI): m/z[M+H+] calcd for C48H35N6O6: 791.2606; found: 791.2613. Regretfully, carbon signals were not found despite collected more than 12 h due to the poor solubility

Synthesis of compound 6 and 7[1]

Scheme S1 Synthetic route for the preparation of compound **6** and **7**



Experimental

2-methyl-4-(4-(pyridin-3-ylethynyl)phenyl)but-3-yn-2-ol(**S2**)

The iodo compound **S1** (1.00 g, 3.52 mmol), CuI (0.67 g, 0.352 mmol), Pd $(PPh_3)_2Cl_2$ (0.124g, 0.176 mmol), were dissolved in THF (15 mL) and Et_3N (15 mL) under an Ar atmosphere. 3-ethynylpyridine (0.439 g, 4.22 mmol) was added, and the reaction was stirred at 90 ℃ for 5 h. The resulting mixture was diluted with $CHCl_3$ and washed three times with 1 M HCl(aq). The organic extract was dried with Na_2SO_4, filtered and concentrated. Flash chromatography [petroleum ether:EtOAc, 50:1] gave **S2** (0.62 g, 2.87 mmol) as orange-yellow solid: mp 168.0–172.6 ℃, IR (KBr, cm^{-1}): 3240s, 2982m, 2933w, 2218w, 1507m, 1409m, 1271m, 1171s, 968m, 840s, 807w, 702s, 565w. ^{1}H NMR (600 MHz, cdcl$_3$) δ 8.83 (s, 1H), 8.54 (t, J = 7.8 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.43 (d, J =7.8 Hz, 2H), 7.40 (d, J = 7.8 Hz, 2H), 7.31 (m, 1H), 4.39 (s, 1H), 1.63 (s, 6H). ^{13}C NMR (150 MHz, cdcl3) δ 159.2, 152.1, 151.9, 148.2, 138.6, 131.6, 123.2, 121.9, 120.3, 96.9, 92.3, 87.2, 81.3, 65.0. MS (EI) m/z (%)=261(M$^+$, 64), 246(100).

2-methyl-4-(4-(pyridin-4-ylethynyl)phenyl)but-3-yn-2-ol(**S3**)

The iodo compound S1 (1.14 g, 4.01 mmol), CuI (0.76 g, 0.401 mmol), Pd $(PPh_3)_2Cl_2$ (0.141 g, 0.201 mmol), were dissolved in THF (15 mL) and Et_3N (15 mL) under an Ar atmosphere. 3-ethynylpyridine (0.501 g, 4.82 mmol) was added, and the reaction was stirred at 90 ^{o}C for 5 h. The resulting mixture was diluted with $CHCl_3$ and washed three times with 1 M HCl(aq). The organic extract was dried with Na_2SO_4, filtered and concentrated. Flash chromatography [petroleum ether:EtOAc, 50:1] gave **S3** (0.88 g, 3.368 mmol) as orange-yellow solid: mp 179.4–182.6 ℃, IR (KBr, cm^{-1}): 3186s, 2978m, 2931w, 2218w, 1593s, 1409m, 1271m, 1169s, 966m, 843s, 830s, 539w. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 4.4 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 4.4 Hz, 2H), 2.78 (s, 1H), 1.56 (s, 6H). ^{13}C NMR (100 MHz, cdcl$_3$) δ 149.6, 131.7, 131.2, 125.5, 123.7, 121.7, 96.3, 93.5, 88.1, 81.4, 65.4, 31.4. MS (EI) m/z (%)=261(M$^+$, 67), 246(100).

3-((4-ethynylphenyl)ethynyl)pyridine(**6**)

A mixture of 2-methyl-4-(4-(pyridin-3-ylethynyl)phenyl)but-3-yn-2-ol(**S2**) (0.62 g, 2.37 mmol), 0.4 g of KOH and 50 ml of i-BuOH was stirred for 5 h under reflux conditions. The resulting mixture was diluted with $CHCl_3$ and washed with 1 M HCl(aq). The organic extract was dried with Na_2SO_4, filtered and concentrated. Flash chromatography [petroleum ether:EtOAc, 100:1] gave **6** (0.25 g, 1.232 mmol) as orange-yellow solid: mp 126.2–128.4 ℃, IR (KBr, cm^{-1}): 3447w, 3165s, 2093w, 1562w, 1496m, 1408m, 834s, 809m, 705s. ^{1}H NMR (400 MHz, cdcl$_3$) δ 8.77 – 8.760 (m, 1H), 8.55-8.54 (m, 1H), 7.80-7.77 (m, 1H), 7.51 – 7.46 (m, 4H), 7.29 – 7.25 (m, 1H), 3.21 (s, 1H). ^{13}C NMR (100 MHz, cdcl$_3$) δ 152.0, 148.6, 138.2, 131.9, 131.4, 122.9, 122.7, 122.3, 119.9, 91.9, 87.7, 82.9, 79.3. MS (EI) m/z (%)=203(M$^+$, 100), 176(9).

4-((4-ethynylphenyl)ethynyl)pyridine(**7**)

A mixture of 2-methyl-4-(4-(pyridin-4-ylethynyl)phenyl)but-3-yn-2-ol(**S3**) (0.88 g, 3.368 mmol), 0.4 g of KOH and 50 ml of i-BuOH was stirred for 5 h under reflux conditions. The resulting mixture was diluted with $CHCl_3$ and washed with 1 M HCl(aq). The organic extract was dried with Na_2SO_4, filtered and concentrated. Flash chromatography [petroleum ether:EtOAc, 100:1] gave **9** (0.45 g, 2.22 mmol) as orange-yellow solid: mp 159.3–161.6 ℃, IR (KBr, cm^{-1}): 3446w, 3142s, 2166m, 1561s, 1500m, 1405m, 839m, 821s, 539m. ^{1}H NMR (400 MHz, cdcl$_3$) δ 8.61 (s , 2H), 7.50 (s, 4H), 7.39 (d, *J* = 2.0 Hz, 2H), 3.21 (s, 1H). ^{13}C NMR (100 MHz, cdcl$_3$) δ 149.7, 132.2, 131.7, 131.2, 125.5, 122.4, 93.3, 88.4, 83.0,79.5. MS (EI) m/z (%) = 203(M$^+$, 100), 176(10).

(1) (a) Eirik Glimsdal, Marcus Carlsson, Tomas Kindahl, Mikael Lindgren, Cesar Lopes, and Bertil Eliasson *J. Phys. Chem. A* **2010**, 114, 3431–3442.(b) Polyansky, D. E.; Danilov, E. O.; Voskresensky, S. V.; Rodgers, M. A. J.; Neckers. D. C. *J. Phys. Chem. A* **2006**, 110, 4969-4978.

Comment S1: Details of the refinements of complexes **1**a-d, **2**a, and **3**a-b.

For **1**a, In the refinement, all the C-bounded hydrogen atoms were postitioned geometrically with the C-H distances of methyl, metylene, aromatic being 0.98, 0.99 and 0.95 Å, respectively and these thermal factors of hydrogen atoms were set with U_{iso}(H)=1.5U_{eq}(methyl C) and U_{iso}(H)=1.2U_{eq}(methylene and aromatic C). The N-bounded hydrogen atoms were located from the difference frourier electron maps and the N-H distances were refined freely and U_{iso}(H)=1.2U_{eq}(N). Hydrogen atoms attached to methanol oxygen atoms were also located from the difference frourier electron map with the O-H distance refined freely and U_{iso}(H)=1.5U_{eq}(O).

For **1**b, In the refinement, the ethanol solvent moleculer (C34-C34-O7) was found to be disordered over two sites. The commands DFIX and EADP were used in the refinement to restrain some distances (eg. C33-O7=2.45(1) Å and C34-O7=1.45(1) Å) and thermal factors. The final most satisfactory occupancies for the O7, O7’-involved ethanol were 0.85:0.15 for the major and minor components, respectively. All the C-bounded hydrogen atoms were postitioned geometrically with the C-H distances of methyl, metylene, aromatic being 0.98, 0.99 and 0.95 Å, respectively and these thermal factors of hydrogen atoms were set with U_{iso}(H)=1.5U_{eq}(methyl C) and U_{iso}(H)=1.2U_{eq}(methylene and aromatic C). The N-H distances were restrained to be 0.96 Å and U_{iso}(H)=1.2U_{eq}(N). Hydrogen atoms attached to ethanol oxygen atoms were positioned best matching their hydrogen-bond enviroment with O-H=0.84 Å and U_{iso}(H)=1.5U_{eq}(O).

For **1**c, In the refinement, one of the ethoxy groups (C31-C32) was found to be disordered. The commands DFIX, and EADP were used in the refinement to restrain some distances (eg. C32-C32=1.51(1) Å and C31-O6=1.45(1) Å) and thermal factors. The final most satisfactory occupancies for the C31-, C31’-involved ethoxy were 0.80:0.20 for the major and minor components. The water solvent molecule was also disordered with the final occupancies of 0.78:0.22 for the major and minor components. All the C- and N-bounded hydrogen atoms were positioned geometrically with the C-H distances of methyl, metylene, aromatic being 0.96, 0.97 and 0.93 Å, respectively and these thermal factors of hydrogen atoms were set with U_{iso}(H)=1.5U_{eq}(methyl C) and U_{iso}(H)=1.2U_{eq}(methylene and aromatic C). The N-H distances were restrained to be 0.88 Å and U_{iso}(H)=1.2U_{eq}(N). Hydrogen atoms attached to water oxygen atoms were positioned best matching their hydrogen-bond enviroment with O-H=0.82 Å and U_{iso}(H)=1.5U_{eq}(O).

For **1**d, In the refinement,all the C-bounded hydrogen atoms were postitioned geometrically with the C-H distances of methyl, metylene, aromatic being 0.96, 0.97 and 0.93 Å, respectively and these thermal factors of hydrogen atoms were set with U_{iso}(H)=1.5U_{eq}(methyl C) and U_{iso}(H)=1.2U_{eq}(methylene and aromatic C). The N-H distances were restrained to be 0.88 Å and U_{iso}(H)=1.2U_{eq}(N).

For **2**a, In the refinement, one of the ethoxy groups (C47-C48) was found to be disordered. Diffraction data was collected at 123 K and no commands were used in the refinement. The final most satisfactory occupancies for the C47-, C47'-involved ethoxy were 0.73:0.27 for the major and minor components. One of three methanol molecules(O7) was disordered and the final occupancies of 0.69:0.31 for the major and minor components. All the C- and N-bounded hydrogen atoms were positioned geometrically with the C-H distances of methyl, metylene, aromatic being 0.98, 0.99 and 0.95 Å, respectively and these thermal factors of hydrogen atoms were set with $U_{iso}(H)=1.5U_{eq}$(methyl C) and $U_{iso}(H)=1.2U_{eq}$(methylene and aromatic C). The N-H distances were restrained to be 0.88 Å and $U_{iso}(H)=1.2U_{eq}(N)$. Hydrogen atoms attached to methanol oxygen atoms were positioned best matching their hydrogen-bond enviroment with O-H=0.84 Å and $U_{iso}(H)=1.5U_{eq}(O)$.

For **3**a, In the refinement, one of the pyridyl ring (C32-C36-N5) was found to be disordered. The crystal was cracking easily at a low temperature, despite we tried 150，200，and 250 K. The commands AFIX, ISOR and EADP were used in the refinement to restrain some distances (eg. AFIX 66) and thermal factors. The final most satisfactory occupancies for the C47-, C47'-involved ethoxy were 0.78:0.22 for the major and minor components. All the C- and N-bounded hydrogen atoms were positioned geometrically with the C-H distances of methyl, metylene, aromatic being 0.96, 0.97 and 0.93 Å, respectively and these thermal factors of hydrogen atoms were set with $U_{iso}(H)=1.5U_{eq}$(methyl C) and $U_{iso}(H)=1.2U_{eq}$(methylene and aromatic C). The N-H distances were restrained to be 0.86 Å and $U_{iso}(H)=1.2U_{eq}(N)$. Hydrogen atoms attached to water oxygen atoms were positioned best matching their hydrogen-bond enviroment with O-H=0.82 Å and $U_{iso}(H)=1.5U_{eq}(O)$.

For **3**b, In the refinement, one of the ethoxy groups (C47-C48) was found to be disordered. The commands DFIX, and EADP were used in the refinement to restrain some distances (eg. C47-C48=1.51(1) Å and C47-O6=1.42(1) Å) and thermal factors. The final most satisfactory occupancies for the C47-, C47'-involved ethoxy were 0.73:0.27 for the major and minor components. All the C- and N-bounded hydrogen atoms were positioned geometrically with the C-H distances of methyl, metylene, aromatic being 0.98, 0.99 and 0.95 Å, respectively and these thermal factors of hydrogen atoms were set with $U_{iso}(H)=1.5U_{eq}$(methyl C) and $U_{iso}(H)=1.2U_{eq}$(methylene and aromatic C). The N-H distances were restrained to be 0.88 Å and $U_{iso}(H)=1.2U_{eq}(N)$.

Table S1. Crystallographic Data and Structure Refinement Details for Compounds **1**−**3** Solvates

empirical formula	**1**-1MeOH (**1**a)	**1**-1EtOH (**1**b)	**1**-1H_2O (**1**c)	**1**-1DMSO (**1**d)	**2**-3MeOH (**2**a)	**3**-2H_2O (**3**a)	**3**-1DMF (**3**b)
CCDC deposition number	951239	951240	951241	951242	951243	951244	951245
formula	$C_{33}H_{30}N_6O_7$	$C_{35}H_{32}N_6O_7$	$C_{32}H_{28}N_6O_7$	$C_{34}H_{32}N_6O_7S$	$C_{51}H_{46}N_6O_9$	$C_{48}H_{38}N_6O_8$	$C_{51}H_{41}N_7O_7$
formula weight	622.63	636.66	608.60	668.72	886.94	826.84	863.91
crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic
space group	P-1	P-1	P-1	P-1	P-1	P-1	P2(1)/n

a (Å)	9.224(1)	9.240(4)	9.0028(7)	10.593(4)	8.9810(9)	9.118(3)	8.6103(13)
b (Å)	12.231(2)	12.251(5)	12.188(9)	13.595(5)	12.498(1)	12.291(4)	31.467(5)
c (Å)	14.169(2)	14.291(6)	14.278(1)	13.825(5)	20.847(2)	20.327(6)	16.826(3)
α (deg)	85.858(2)	85.662(7)	82.971(1)	116.453(5)	84.296(2)	82.842(6)	90.00
β (deg)	73.698(2)	74.595(6)	76.802(1)	102.398(7)	78.149(2)	79.340(6)	103.106(3)
γ (deg)	75.367(2)	75.064(6)	76.409(1)	100.412(6)	76.410(2)	75.048(5)	90.00
Z	2	2	2	2	2	2	4
V(Å^3)	1484.6(4)	1506.9(11)	1478.7(2)	1651.7(9)	2222.7(4)	2155.8(11)	4440.1(12)
Dcalcd(g cm^{-3})	1.393	1.403	1.367	1.345	1.325	1.274	1.292
μ (Mo Kα) (mm^{-1})	0.100	0.100	0.099	0.156	0.092	0.088	0.088
F(000)	652	668	636	700	932	864	1808
temp (K)	123(2)	200(2)	200(2)	298(2)	123(2)	298(2)	123(2)
θ min−max (deg)	2.28，27.00	1.48，19.02	1.47，25.65	2.07, 25.02	1.91, 26.00	2.05, 25.01	1.79, 20.69
tot., unique data	10384，6341	5277，2355	28628，5508	12427, 5802	14382, 8594	19927, 7557	17708, 4554
R(int)	0.0539	0.0387	0.0288	0.0803	0.0226	0.0626	0.0530
obsd data [I > 2σ(I)]	5084	1809	4341	3221	7314	5071	3469
Nref, Npar	6341,428	2355,438	5508,438	5802,425	8594, 644	7557, 574	4554, 598
R1,wR2 (all data)	0.0787 , 0.1530	0.0900, 0.2249	0.0817 , 0.1732	0.1355, 0.2385	0.0796, 0.1626	0.1649, 0.2539	0.0687, 0.1528
S	1.058	1.084	1.071	0.997	1.104	1.167	1.056
min and max resd dens (e Å^{-3})	-0.242，0.387	-0.307，0.348	-0.433，0.675	-0.452, 0.771	-0.476, 0.318	-0.378, 0.336	-0.644, 0.299

Table S2. geometrical parameters of **1**a-d, **2**a, **3**a-b solvates

solvates	torsion angles		dihedral angles		dihedral angles	
	atoms	angle	mean plane	angle	mean plane	angle
1-1MeOH (**1**a)	C4-C6-C7-C8	118	R1(C1-C5-N1)-R2(C8-C13)	24.33	R1(C1-C5-N1)- R3(C16-C20-N2)	49
	C11-C14-C15-C16	46	R3(C16-C20-N2)-R2(C8-C13)	25.93		
1-1EtOH (**1**b)	C4-C6-C7-C8	-55	R1(C1-C5-N1)-R2(C8-C13)	26.53	R1(C1-C5-N1)- R3(C16-C20-N2)	48
	C11-C14-C15-C16	-126	R3(C16-C20-N2)-R2(C8-C13)	23.39		
1-1H$_2$O (**1**c)	C4-C6-C7-C8	-153	R1(C1-C5-N1)-R2(C8-C13)	25.41	R1(C1-C5-N1)- R3(C16-C20-N2)	38
	C11-C14-C15-C16	-77	R3(C16-C20-N2)-R2(C8-C13)	13.9		
1-1DMSO (**1**d)	C4-C6-C7-C8	42	R1(C1-C5-N1)-R2(C8-C13)	32.81	R1(C1-C5-N1)- R3(C16-C20-N2)	30
	C11-C14-C15-C16	99	R3(C16-C20-N2)- R2(C8-C13)	3.61		
2-3MeOH (**2**a)	C4-C6-C7-C8	-71	R1(C1-C5-N1)-R3(16-C21)	18.50	R1(C1-C5-N1)- R2(C8-C13)	6
	C11-C14-C15-C16	-125	R2(C8-C13) -R3(16-C21)	13.77	R4(C24-C29) - R5(C32-C36-N2)	5.
	C19-C22-C23-C24	132	R4(C24-C29) -R3(16-C21)	37.70	R1(C1-C5-N1)- R5(C32-C36-N2)	61
	C27-C30-C31-C32	-68	R5(C32-C36-N2)-R3(16-C21)	42.88	R2(C8-C13)-R4(C24-C29)	51
3-2H$_2$O (**3**a)	C3-C6-C7-C8	37	R1(C1-C5-N6)-R3(16-C21)	45.28	R1(C1-C5-N6)- R2(C8-C13)	11
	C11-C14-C15-C16	-142	R2(C8-C13) -R3(16-C21)	33.50	R4(C24-C29) - R5(C32-C36-N5)	6
	C19-C22-C23-C24	36	R4(C24-C29) -R3(16-C21)	8.54	R1(C1-C5-N6)- R5(C32-C36-N5)	51
	C27-C30-C31-C32	143	R5(C32-C36-N5)-R3(16-C21)	7.05	R2(C8-C13)-R4(C24-C29)	36

3-1DMF (**3**b)	C4-C6-C7-C8	122	R1(C1-C5-N1)-R3(16-C21)	8.96	R1(C1-C5-N1)- R2(C8-C13)	27
	C11-C14-C15-C16	-16	R2(C8-C13) -R3(16-C21)	20.22	R4(C24-C29) - R5(C32-C36-N2)	7
	C19-C22-C23-C24	-40	R4(C24-C29) -R3(16-C21)	12.74	R1(C1-C5-N1)- R5(C32-C36-N2)	12
	C27-C30-C31-C32	-31	R5(C32-C36-N2)-R3(16-C21)	20.07	R2(C8-C13)-R4(C24-C29)	32

Table S3. weak hydrogen bond of **1-3** solvates

	D-H · · · A	d(H...A)	d(D · · · A)	∠(D-H • • • A)
1·MeOH[a]	C(1)-H(1) · · · O(1)^{i}	2.39	3.236(3)	148
	C(18)-H(18) · · · O(1)^{ii}	2.51	3.392(3)	154
1·EtOH[b]	C(1)-H(1) · · · O(1)^{i}	2.47	3.314(1)	148
	C(18)-H(18) · · · O(1)^{ii}	2.54	3.406(1)	151
1·H_2O[c]	C(1)-H(1) · · · O(1)^{i}	2.60	3.249(3)	126
	C(18)-H(18) · · · O(1)^{ii}	2.58	3.473(4)	157
1·DMSO[d]	C(18)-H(18) · · · O(2)^{i}	2.50	3.343（5）	151
2·MeOH[e]	C(2)-H(2) · · · O(1)^{i}	2.54	3.402(3)	151
	C(35)-H(35) · · · O(1)^{ii}	2.37	3.190(3)	144
3-H_2O[f]	C(35)-H(35) · · · O(1)^{i}	2.53	3.381(7)	153
3-DMF[g]	C(1)-H(1) · · · O(2)^{i}	2.54	3.278(5)	134

[a]Symmetry codes: (i) x, y, -1+z; (ii) 1-x, -y, 1-z. (□) x, y, 1+z; [b]Symmetry codes: (i) x, y, 1+z; (ii) 1-x, 1-y, -z; [c]Symmetry codes: (i) x, y, 1+z; (ii) -x, 1-y, 1-z; [d]Symmetry codes: (i) 1-x,2-y,2-z; [e]Symmetry codes: (i) 3-x, -y, 1-z; (ii) -1+x, y, 1+z; [f]Symmetry codes: (i) -x,2-y,2-z ; (□) 1-x,1-y,1-z; [g]Symmetry codes: (i) -x,1-y,-z ; (□) x, y, -1+z.

Table S4. C-H---π and π---π interactions

C-H---π Interactions				
	C-H→R(j)	H---R (Å)	∠C-H---R (°)	C---R (Å)
1·MeOH[a]	C(22)-H(22A)→R(C8-13)^{i}	2.65	140	3.472(2)
1·EtOH[b]	C(22)-H(22B)→R(C8-13)^{i}	2.66	140	3.478(8)
1·H_2O[c]	C(22)-H(22B)→R(C8-13)^{i}	2.66	140	3.478(8)
2·MeOH[d]	C(38)-H(38B)→R(C16-21)^{i}	2.79	138	3.586(3)
2·H_2O[e]	C(38)-H(38A)→R(C16-21)^{i}	2.74	139	3.528 (5)
π---π Interactions				
	R(i) → R(j)	∠R(i) ---R(j) (°)	R(i) ---R(j) (Å)	
1·DMSO[f]	R(N1-C16-C20) → R(C8-13)^{i}	3.60	3.670(3)	

[a]Symmetry codes: (□) 1-x, -y, -z; [b]Symmetry codes: (□) 1-x, 1-y, -z; [c]Symmetry codes: (□) -x, 1-y, 2-z; [d]Symmetry codes: (□) 2-X,-Y,2-Z; [e]Symmetry codes: (□) 1-X,2-Y,1-Z; [f]Symmetry codes: (i) 1-x,2-y,2-z.

Packing arrangements of 1b

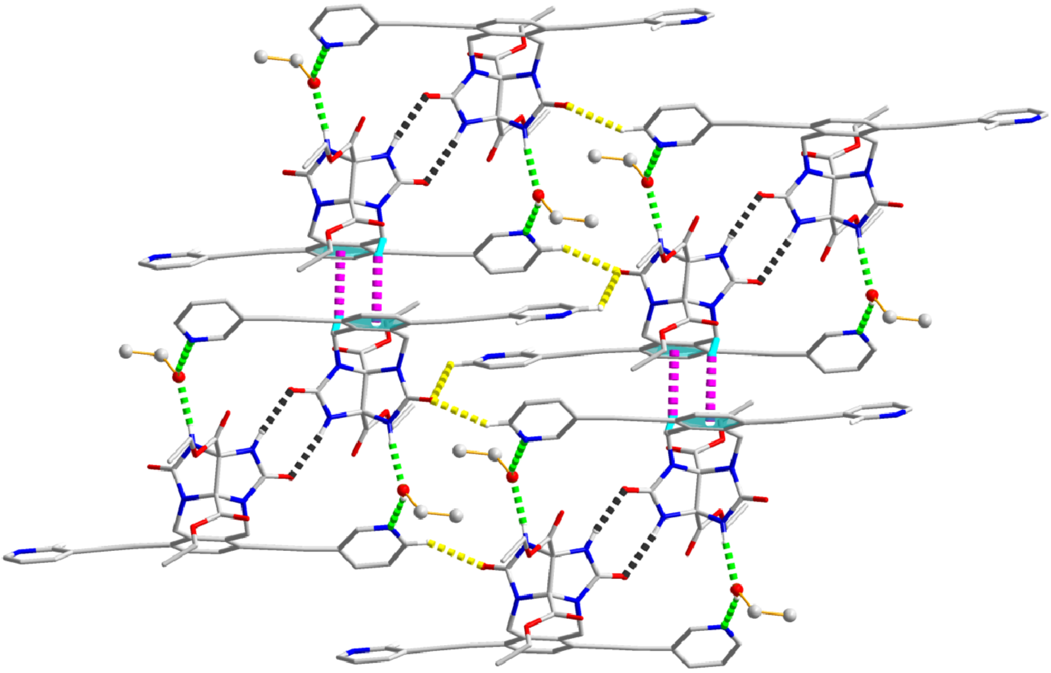


Figure S1 Packing of solvates **1**b, showing the formation of two-dimensional layer in EtOH. Hydrogen bonds are drawn as dashed lines.

Packing arrangements of 1c

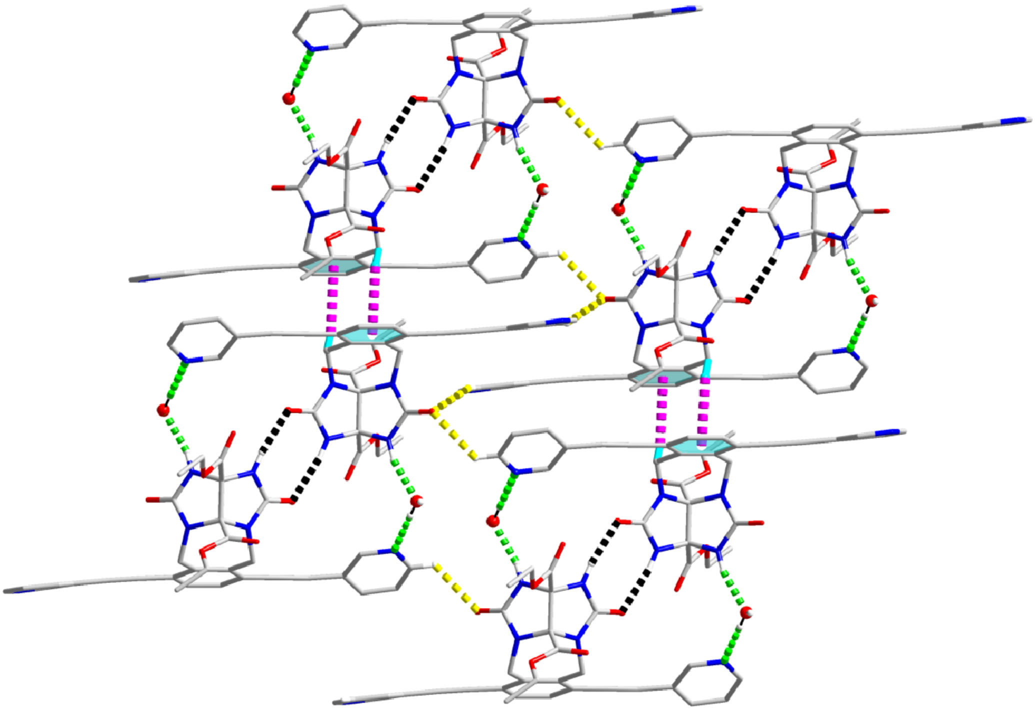


Figure S2 Packing of solvates **1**c, showing the formation of two-dimensional layer in H_2O. Hydrogen bonds are drawn as dashed lines.

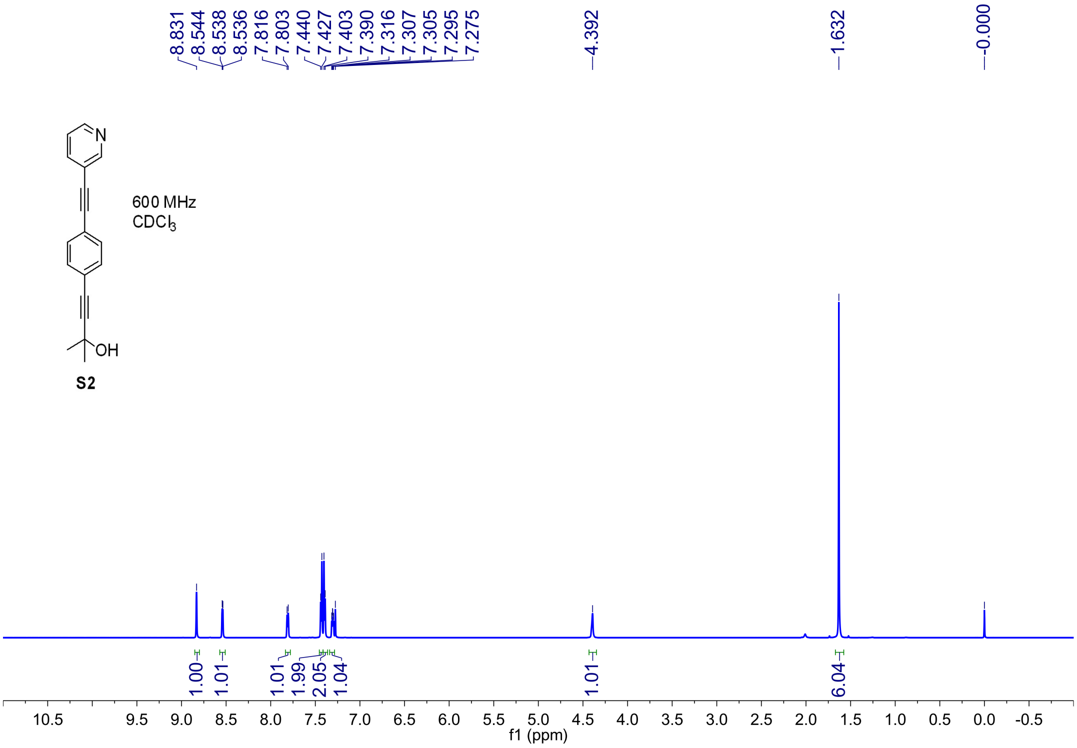


Figure S3 ^{1}H NMR spectrum of compound **S2**

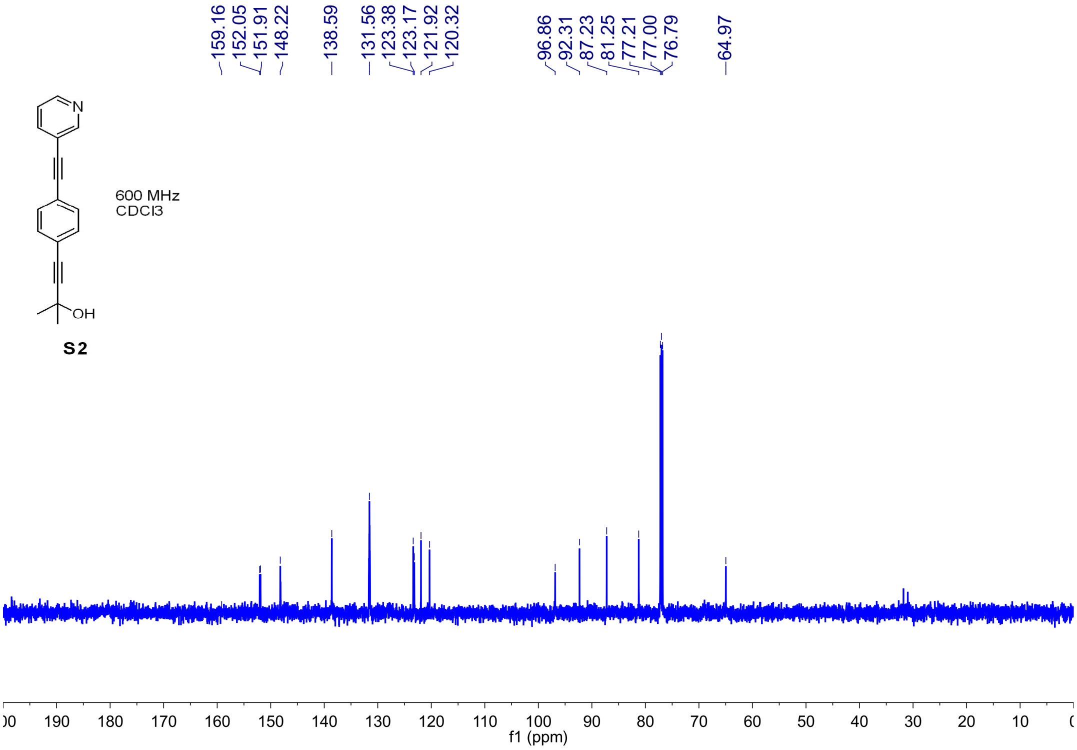


Figure S4 ^{13}C NMR spectrum of compound **S2**

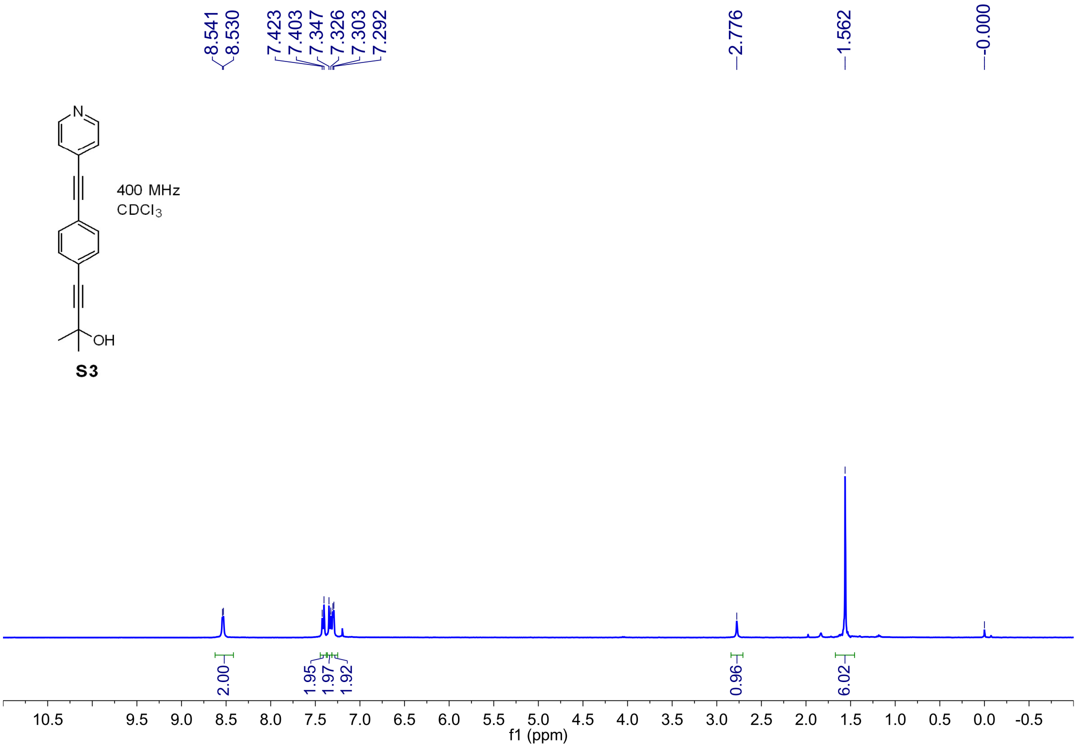


Figure S5 ^{1}H NMR spectrum of compound **S3**

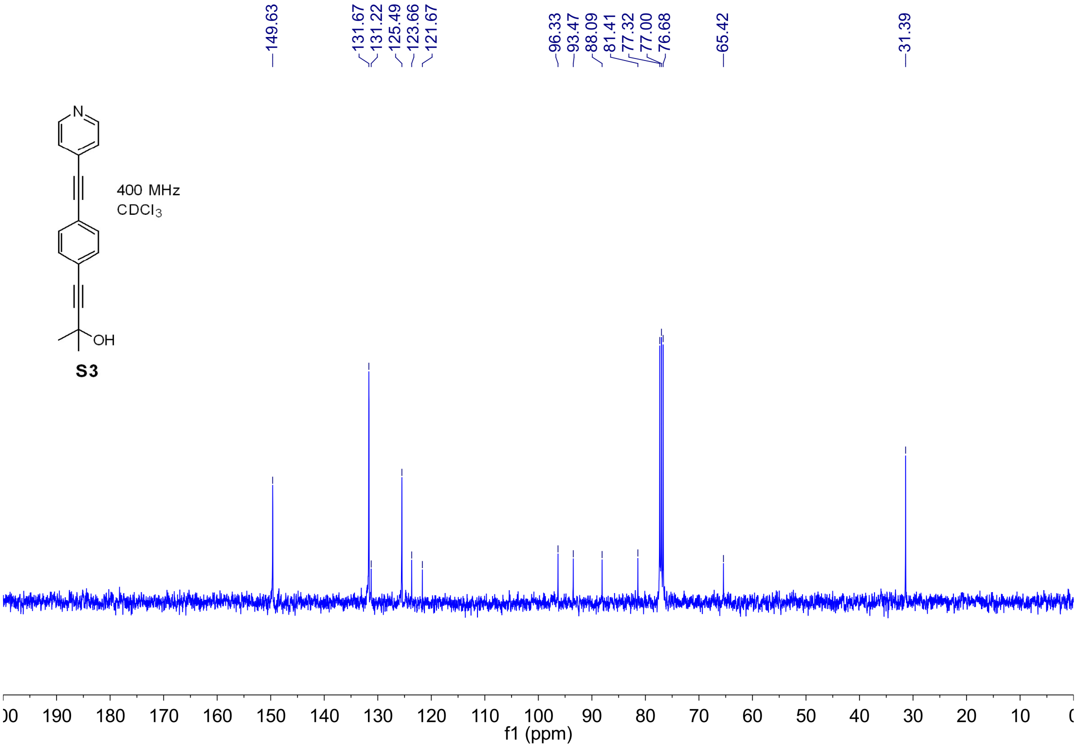


Figure S6 ^{13}C NMR spectrum of compound **S3**

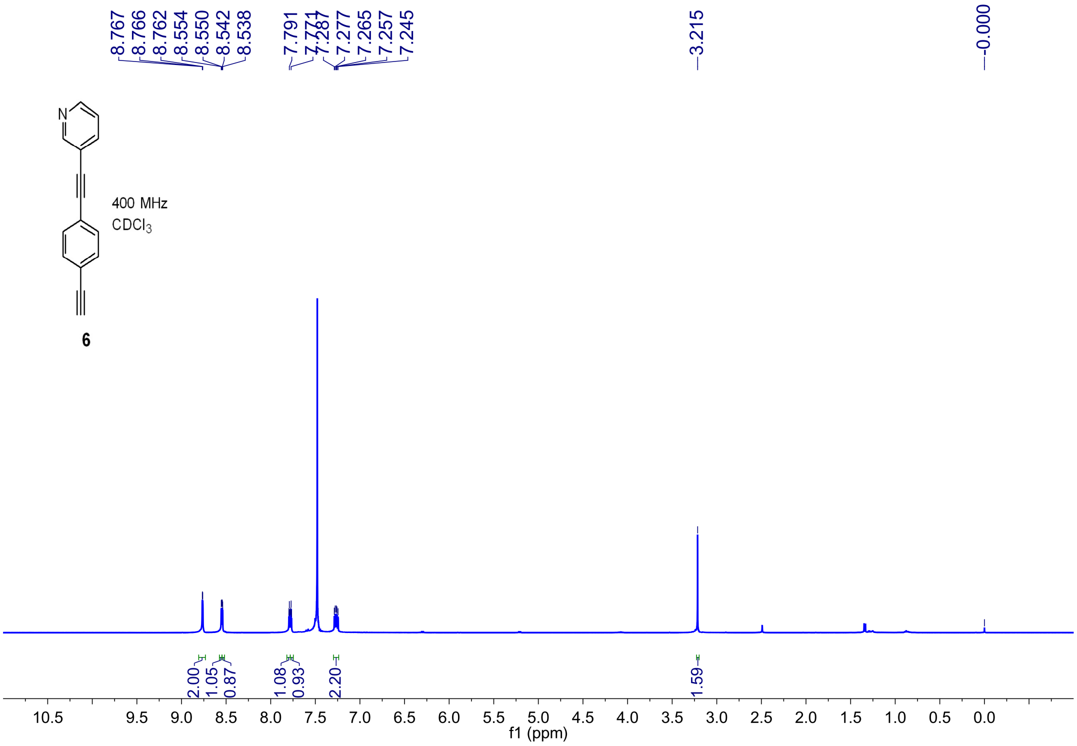


Figure S7 ^{1}H NMR spectrum of compound **6**

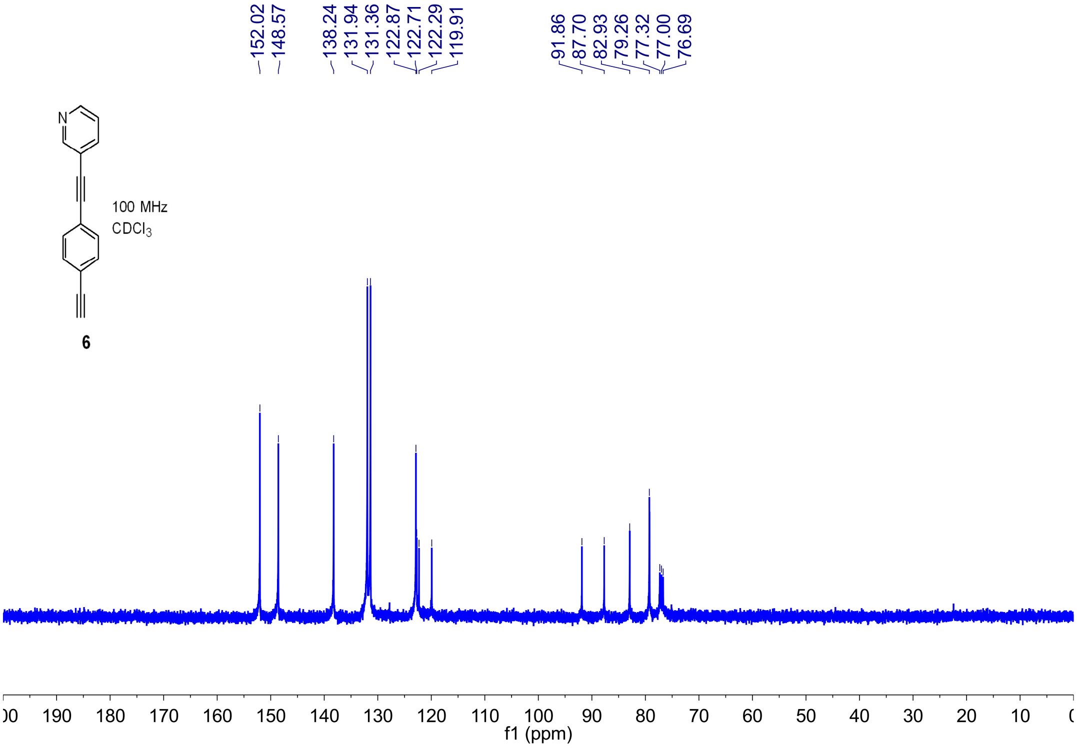


Figure S8 ^{13}C NMR spectrum of compound **6**

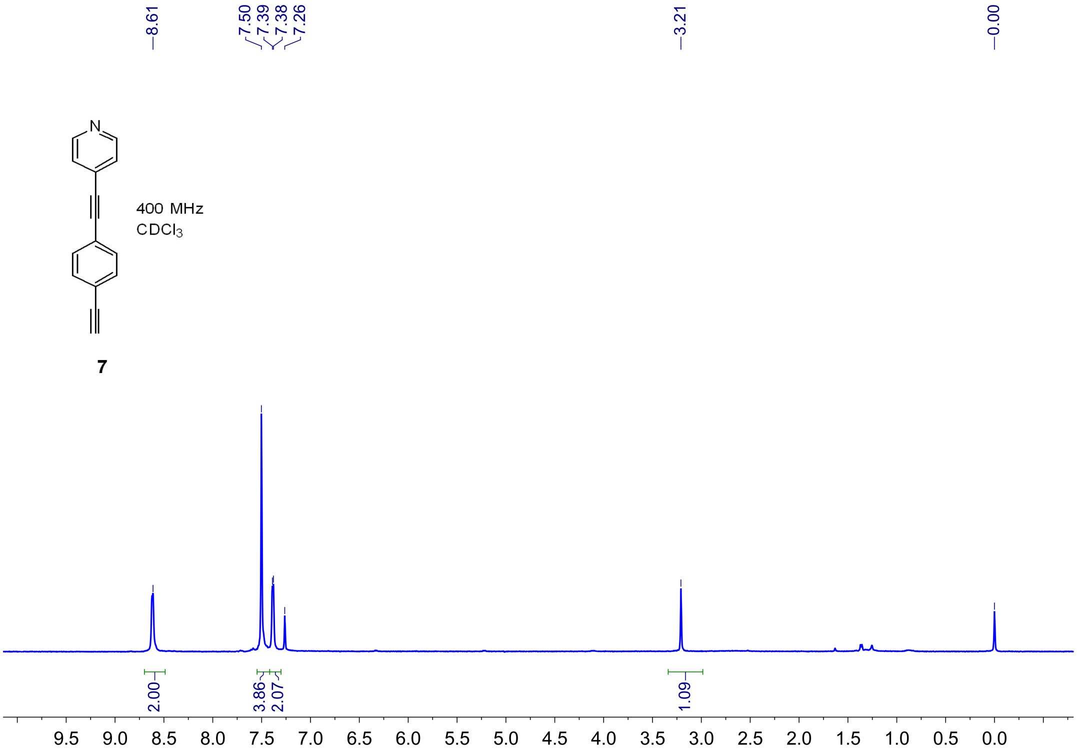


Figure S9 ^{1}H NMR spectrum of compound **7**

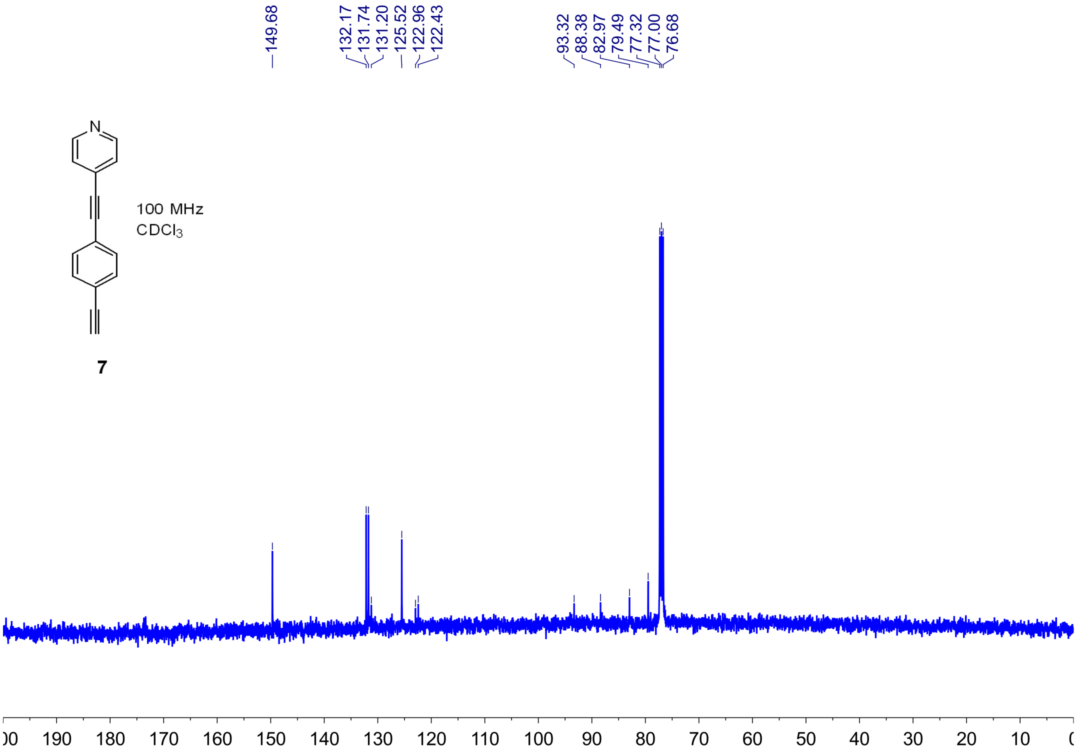


Figure S10 ^{13}C NMR spectrum of compound **7**

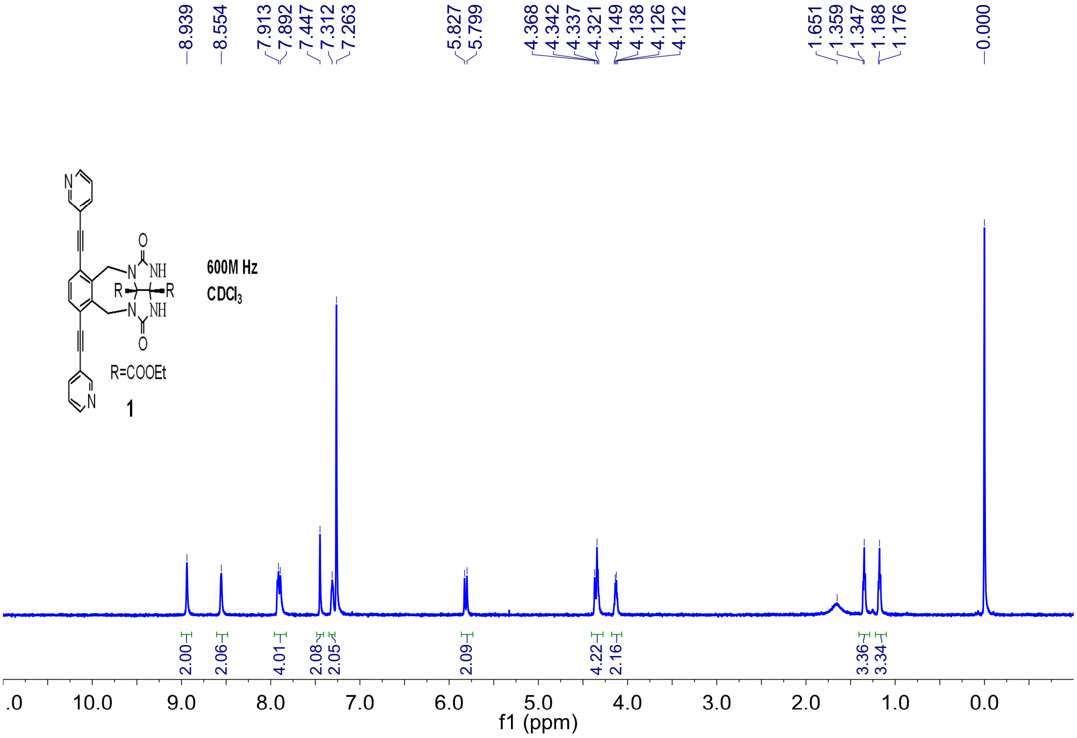


Figure S11 ^{1}HNMR spectrum of compound **1**

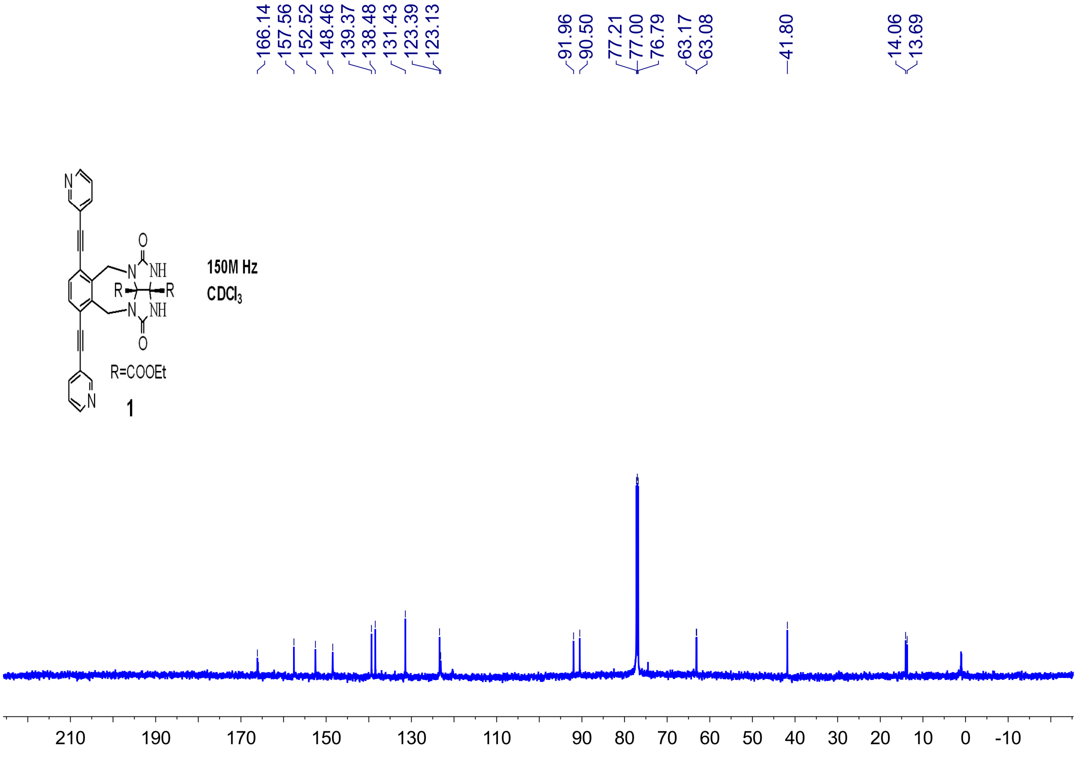
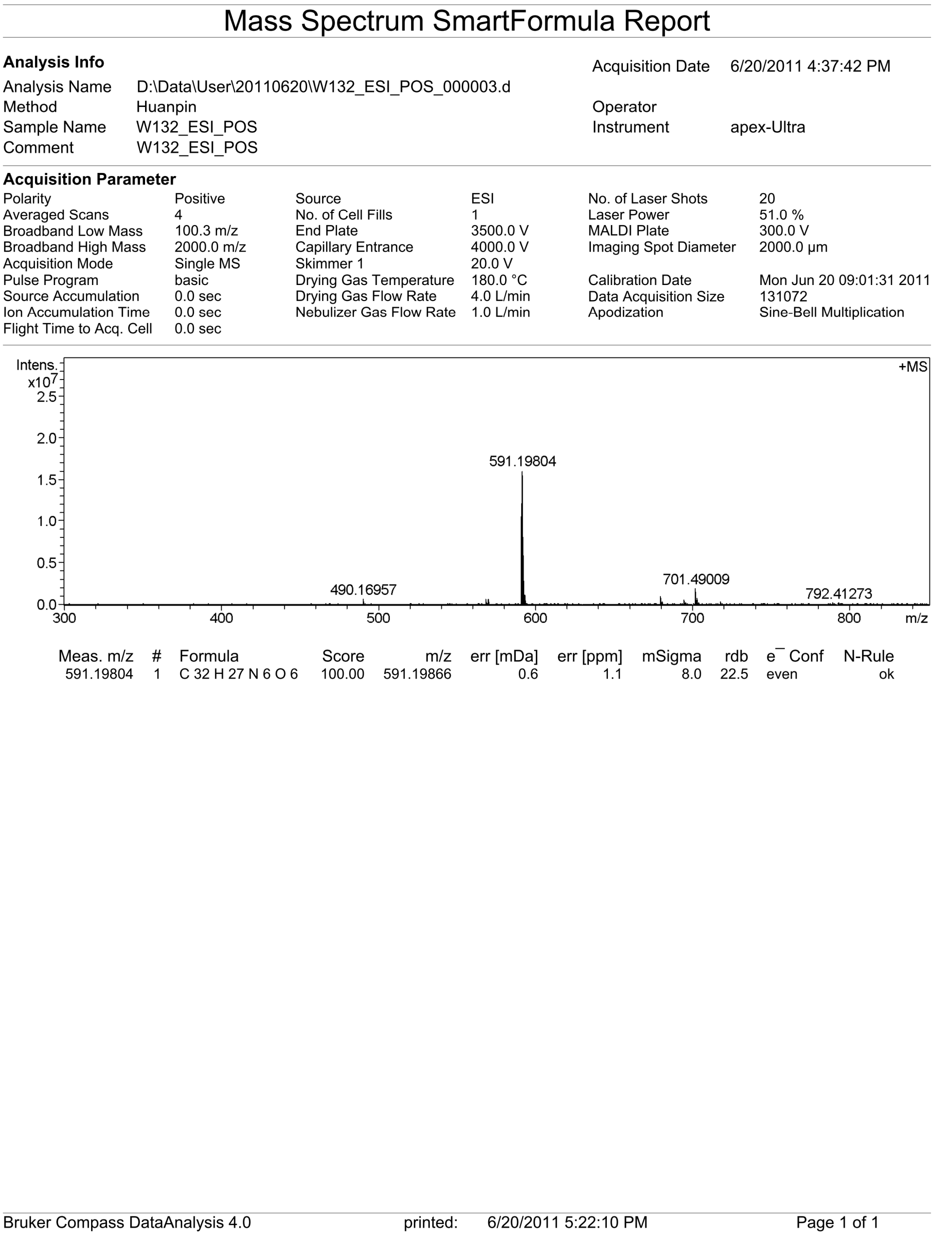


Figure S12 ^{13}C NMR spectrum of compound **1**



Mass Spectrum SmartFormula Report

Analysis Info

		Acquisition Date	6/20/2011 4:37:42 PM
Analysis Name	D:\Data\User\20110620\W132_ESI_POS_000003.d		
Method	Huanpin	Operator	
Sample Name	W132_ESI_POS	Instrument	apex-Ultra
Comment	W132_ESI_POS		

Acquisition Parameter

Polarity	Positive	Source	ESI	No. of Laser Shots	20
Averaged Scans	4	No. of Cell Fills	1	Laser Power	51.0 %
Broadband Low Mass	100.3 m/z	End Plate	3500.0 V	MALDI Plate	300.0 V
Broadband High Mass	2000.0 m/z	Capillary Entrance	4000.0 V	Imaging Spot Diameter	2000.0 µm
Acquisition Mode	Single MS	Skimmer 1	20.0 V		
Pulse Program	basic	Drying Gas Temperature	180.0 °C	Calibration Date	Mon Jun 20 09:01:31 2011
Source Accumulation	0.0 sec	Drying Gas Flow Rate	4.0 L/min	Data Acquisition Size	131072
Ion Accumulation Time	0.0 sec	Nebulizer Gas Flow Rate	1.0 L/min	Apodization	Sine-Bell Multiplication
Flight Time to Acq. Cell	0.0 sec				

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
591.19804	1	C 32 H 27 N 6 O 6	100.00	591.19866	0.6	1.1	8.0	22.5	even	ok

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Figure S13 HRMS spectrum of compound **1**

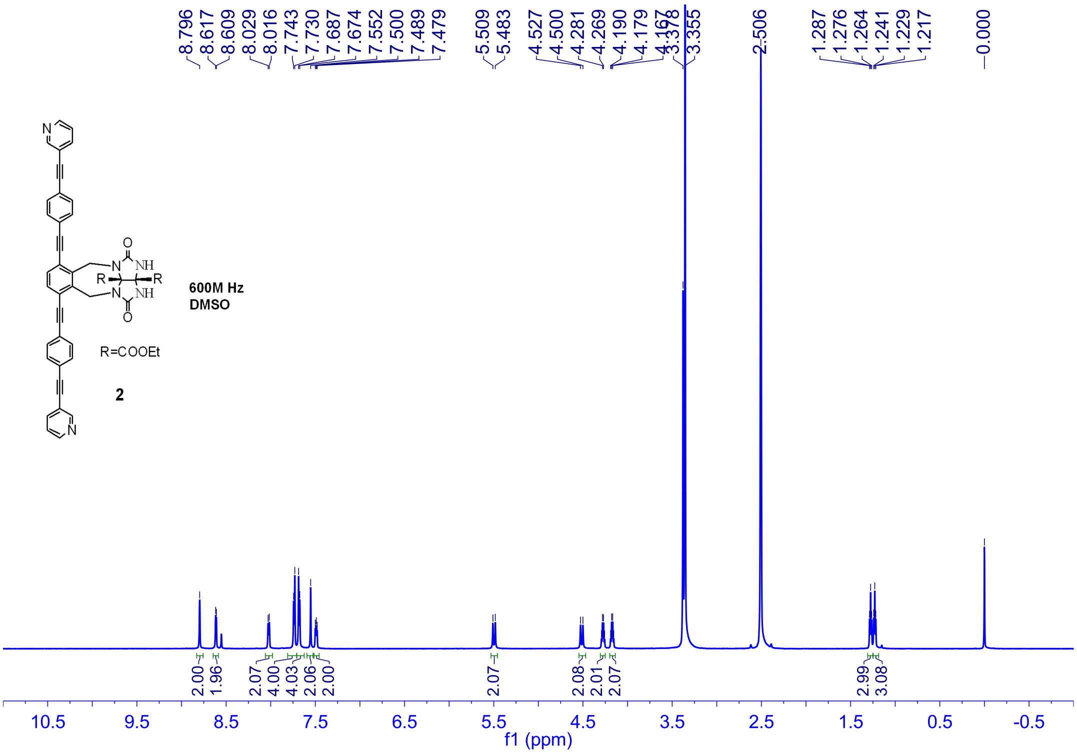
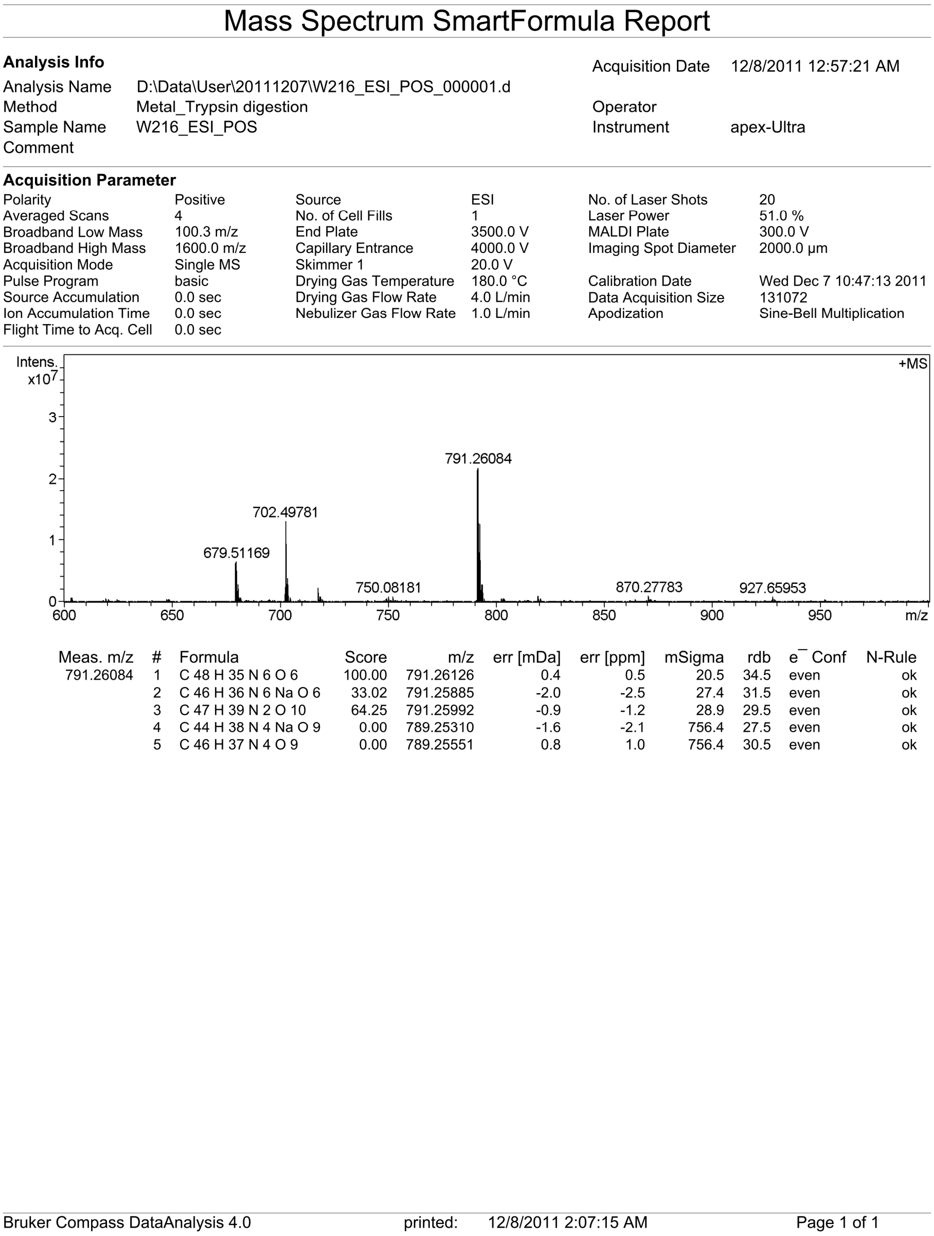


Figure S14 ^{1}HNMR spectrum of compound **2**



Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\User\20111207\W216_ESI_POS_000001.d	Acquisition Date	12/8/2011 12:57:21 AM
Method	Metal_Trypsin digestion	Operator	
Sample Name	W216_ESI_POS	Instrument	apex-Ultra
Comment			

Acquisition Parameter

Polarity	Positive	Source	ESI	No. of Laser Shots	20
Averaged Scans	4	No. of Cell Fills	1	Laser Power	51.0 %
Broadband Low Mass	100.3 m/z	End Plate	3500.0 V	MALDI Plate	300.0 V
Broadband High Mass	1600.0 m/z	Capillary Entrance	4000.0 V	Imaging Spot Diameter	2000.0 µm
Acquisition Mode	Single MS	Skimmer 1	20.0 V		
Pulse Program	basic	Drying Gas Temperature	180.0 °C	Calibration Date	Wed Dec 7 10:47:13 2011
Source Accumulation	0.0 sec	Drying Gas Flow Rate	4.0 L/min	Data Acquisition Size	131072
Ion Accumulation Time	0.0 sec	Nebulizer Gas Flow Rate	1.0 L/min	Apodization	Sine-Bell Multiplication
Flight Time to Acq. Cell	0.0 sec				

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
791.26084	1	C 48 H 35 N 6 O 6	100.00	791.26126	0.4	0.5	20.5	34.5	even	ok
	2	C 46 H 36 N 6 Na O 6	33.02	791.25885	-2.0	-2.5	27.4	31.5	even	ok
	3	C 47 H 39 N 2 O 10	64.25	791.25992	-0.9	-1.2	28.9	29.5	even	ok
	4	C 44 H 38 N 4 Na O 9	0.00	789.25310	-1.6	-2.1	756.4	27.5	even	ok
	5	C 46 H 37 N 4 O 9	0.00	789.25551	0.8	1.0	756.4	30.5	even	ok

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Figure S15 HRMS spectrum of compound **2**

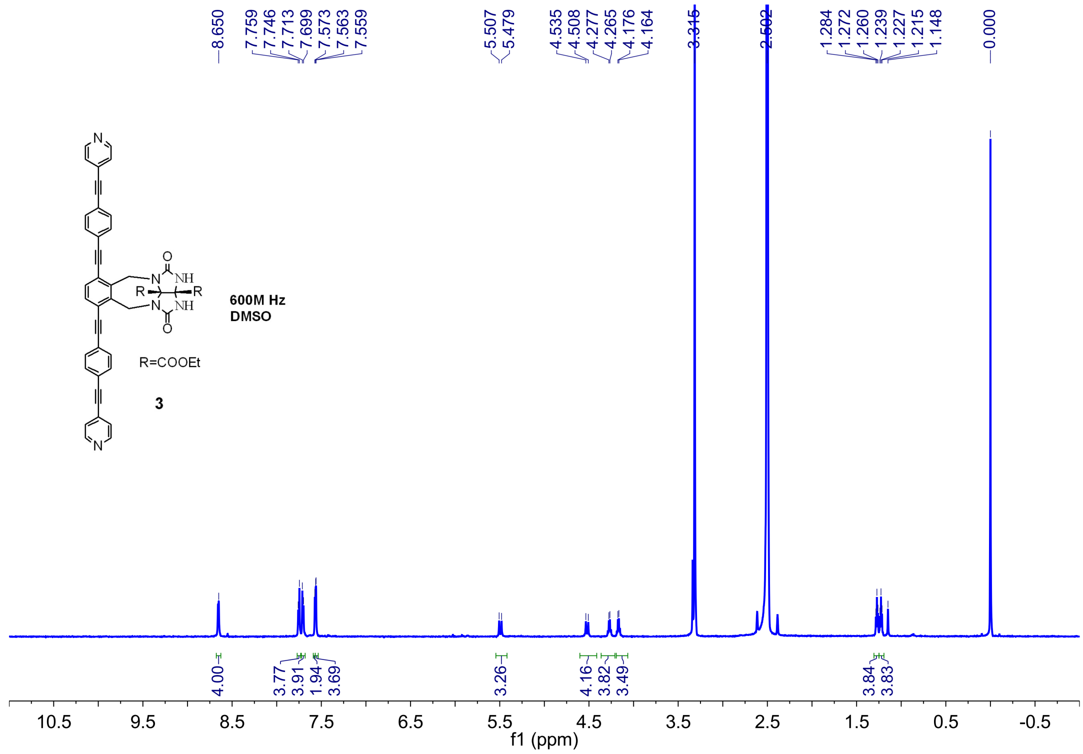


Figure S16 ^{1}HNMR spectrum of compound **3**

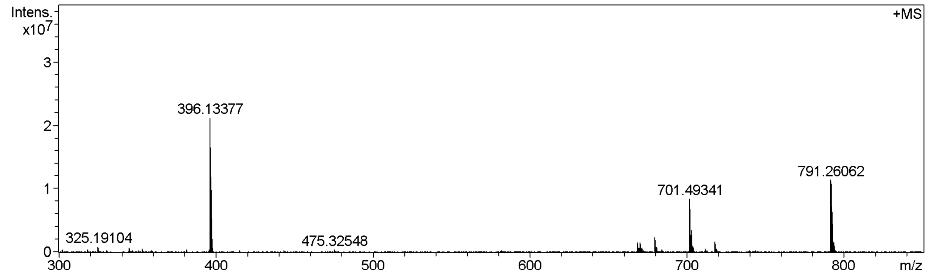
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\User\20110620\W162_ESI_POS_000002.d	Acquisition Date	6/20/2011 4:31:48 PM
Method	Huanpin	Operator	
Sample Name	W162_ESI_POS	Instrument	apex-Ultra
Comment	W162_ESI_POS		

Acquisition Parameter

Polarity	Positive	Source	ESI	No. of Laser Shots	20
Averaged Scans	2	No. of Cell Fills	1	Laser Power	51.0 %
Broadband Low Mass	100.3 m/z	End Plate	3500.0 V	MALDI Plate	300.0 V
Broadband High Mass	2000.0 m/z	Capillary Entrance	4000.0 V	Imaging Spot Diameter	2000.0 µm
Acquisition Mode	Single MS	Skimmer 1	20.0 V		
Pulse Program	basic	Drying Gas Temperature	180.0 °C	Calibration Date	Mon Jun 20 09:01:31 2011
Source Accumulation	0.0 sec	Drying Gas Flow Rate	4.0 L/min	Data Acquisition Size	131072
Ion Accumulation Time	0.0 sec	Nebulizer Gas Flow Rate	1.0 L/min	Apodization	Sine-Bell Multiplication
Flight Time to Acq. Cell	0.0 sec				



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
791.26062	1	C 48 H 35 N 6 O 6	100.00	791.26126	0.6	0.8	10.9	34.5	even	ok

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Figure S17 HRMS spectrum of compound **3**