

Synthesis and Self-Association, Absorption, and Fluorescence Properties of Differentially Functionalized Hexakis(*p*-substituted-phenylethynyl)benzenes

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Supporting Information

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- ^1H NMR spectra of **3–13** (page S10–S24)

General. Et_3N was distilled from CaH_2 under an argon atmosphere. The other solvents and all commercially available reagents were used without any purification. ^1H and ^{13}C NMR spectra were recorded at 300 MHz and 75 MHz, respectively. Recycle preparative GPC was performed on a Japan Analytical Industry LC-918 with polystyrene gel columns (JAIGEL 1H and 2H).

TABLE S1. Absorption and Fluorescence Spectral Data of 3^a

compd	solvent	$\lambda_{\text{max}}(\text{abs})$ (nm)	$\log \epsilon$	$\lambda_{\text{cut-off}}$ (nm)	$\lambda_{\text{max}}(\text{em})$ (nm) ^b	Stokes shift (nm)
3a	CHCl ₃	363.8	5.19	416.0	459.0	95.2
3b	CHCl ₃	362.3	5.22	414.3	458.0	95.7
	benzene	361.2	5.21	412.0	454.8	93.6
	1,4-dioxane	359.5	5.24	410.4	454.2	94.7
3d	CHCl ₃	360.2	5.28	409.8	456.0	95.8
	benzene	360.0	5.21	410.2	456.8	96.8
	1,4-dioxane	358.8	5.24	408.0	455.8	97.0
3f	CHCl ₃	364.5	5.19	422.7	466.0	101.5
3g	CHCl ₃	367.6	5.20	426.2	466.8	99.2
3h	CHCl ₃	368.8	5.20	425.6	462.6	93.8
		332.6	5.17			
		316.6	5.16			
	benzene	367.2	5.16	421.6	460.4	93.2
		310.0	4.62			
	1,4-dioxane	364.5	5.19	420.3	460.0	95.5
		308.9	4.65			
3i	CHCl ₃	367.4	5.17	425.2	466.6	99.2
3j	CHCl ₃	364.0	5.16	421.4	466.8	102.8
3l	CHCl ₃	378.3	5.09	458.6	NA	NA
		318.1	4.80			
	benzene	380.6	5.08	443.4	469.6	89.0
		317.6	4.73			
	1,4-dioxane	380.0	5.11	443.2	469.6	89.6
		316.8	4.75			
	CH ₂ Cl ₂	386.2	5.11	456.6	NA	NA
		318.3	4.80			
3m	CHCl ₃	464.0	4.97	558.2	NA	NA
		340.2	4.95			
	hexane	438.8	4.90	538.9	NA	NA
		333.0	4.93			
	benzene	454.2	4.99	531.6	NA	NA
		334.4	4.97			
	1,4-dioxane	453.2	5.01	534.8	NA	NA
		332.4	4.96			
	CH ₂ Cl ₂	465.5	4.99	560.9	NA	NA
		338.2	4.95			
3n	CHCl ₃	433.2	5.01	566.6	NA	NA
		332.0	4.85			
	hexane	424.9	4.97	531.3	NA	NA
		327.7	4.83			
	CH ₂ Cl ₂	439.5	5.00	568.7	NA	NA
		327.0	4.84			

TABLE S1. Absorption and Fluorescence Spectral Data of 3^a (continued)

compd	solvent	$\lambda_{\text{max}}(\text{abs})$ (nm)	$\log \epsilon$	$\lambda_{\text{cut-off}}$ (nm)	$\lambda_{\text{max}}(\text{em})$ (nm) ^b	Stokes shift (nm)
3o	CHCl ₃	428.6	5.08	485.0	504.8	76.2
		319.8	4.89			
	hexane	418.6	5.12	455.8	472.2	53.6
		401.2	5.12		501.8	100.6
		321.0	4.90			
	1,4-dioxane	423.8	5.08	477.0	492.6	68.8
		318.6	4.88			
	CH ₂ Cl ₂	434.2	5.15	496.6	530.8	96.6
		318.8	4.98			
	CH ₃ CN	434.0	5.11	514.6	569.6	135.6
		315.2	5.03			
3p	CHCl ₃	418.6	5.07	508.4	515.1	96.5
	hexane	398.0	5.12	479.2	479.2	81.2
	1,4-dioxane	411.0	5.05	497.4	500.6	89.6
3q	CHCl ₃	448.6	5.02	527.8	555.6	107.0
		329.0	5.00			
	benzene	440.8	5.03	510.1	527.2	86.4
		325.3	4.99			
	1,4-dioxane	440.4	5.05	512.4	541.2	100.8
		323.8	4.99			
	CH ₂ Cl ₂	452.4	5.03	533.2	575.2	122.8
		328.6	5.00			
	CHCl ₃	434.8	5.01	547.0	563.8	129.0
		323.4	4.91			
3r	hexane	415.8	5.07	512.0	508.4	92.6
		316.2	4.90			
	benzene	427.4	5.02	529.6	533.6	106.2
		319.4	4.90			
	1,4-dioxane	426.0	5.04	529.6	540.4	114.4
		317.4	4.92			
	CHCl ₃	480.8	4.92	595.6	NA	NA
		375.2	5.08			
3s	benzene	468.2	4.90	567.2	NA	NA
		370.1	5.01			
	CH ₂ Cl ₂	477.3	4.91	594.1	NA	NA
		372.1	5.04			
	CHCl ₃	436.0	5.04	601.0	NA	NA
		384.8	5.05			
	hexane	422.9	5.02	601.6	NA	NA
		378.8	5.10			
	CH ₂ Cl ₂	437.9	5.10	607.0	NA	NA
		381.1	5.10			

^a Absorption and fluorescence spectra were measured at $[3] = 1.0 \times 10^{-5}$ M and $[3] = 1.0 \times 10^{-6}$ M, respectively, at room temperature. ^b The excitation wavelength is almost the same as $\lambda_{\text{max}}(\text{abs})$ in each case because the excitation spectrum of each **3** almost matched the absorption spectrum.

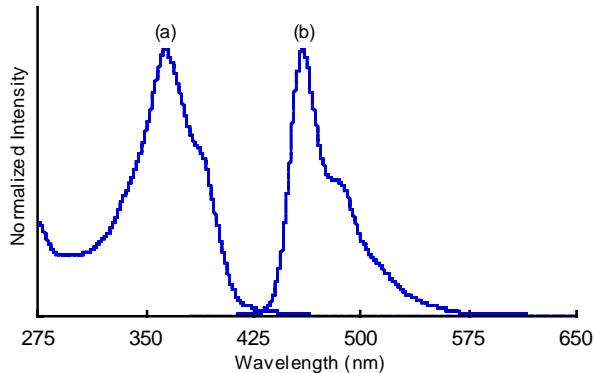


Figure S1. Normalized (a) absorption and (b) fluorescence spectra of **3a** in CHCl_3 .

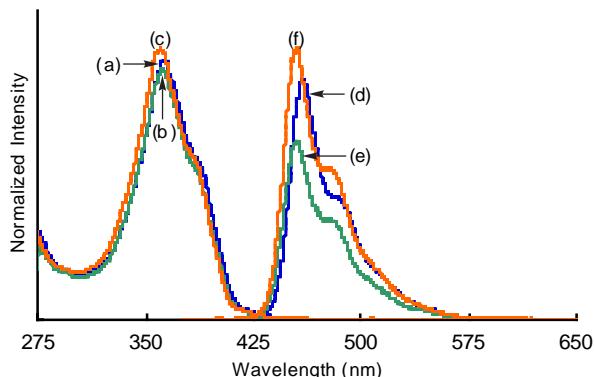


Figure S2. Normalized absorption spectra of **3b** in (a) CHCl_3 , (b) benzene, and (c) 1,4-dioxane. Normalized fluorescence spectra of **3b** in (d) CHCl_3 , (e) benzene, and (f) 1,4-dioxane.

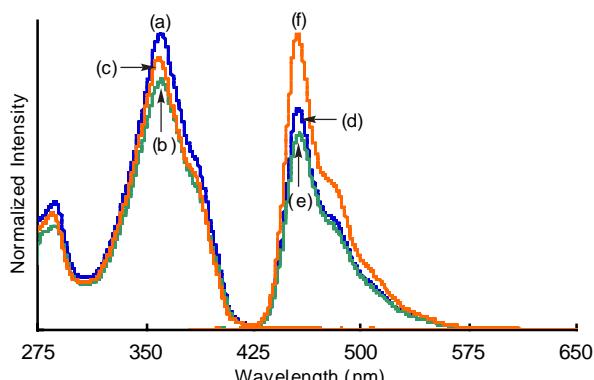


Figure S3. Normalized absorption spectra of **3d** in (a) CHCl_3 , (b) benzene, and (c) 1,4-dioxane. Normalized fluorescence spectra of **3d** in (d) CHCl_3 , (e) benzene, and (f) 1,4-dioxane.

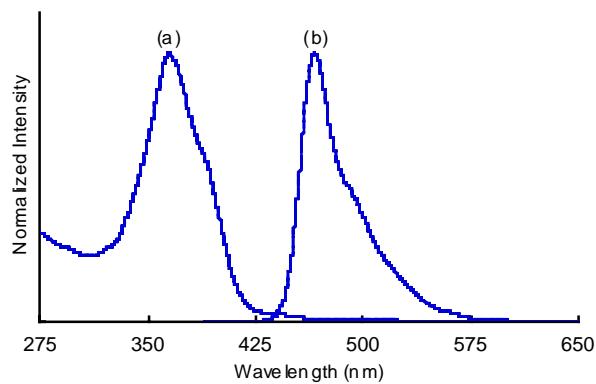


Figure S4. Normalized (a) absorption and (b) fluorescence spectra of **3f** in CHCl_3 .

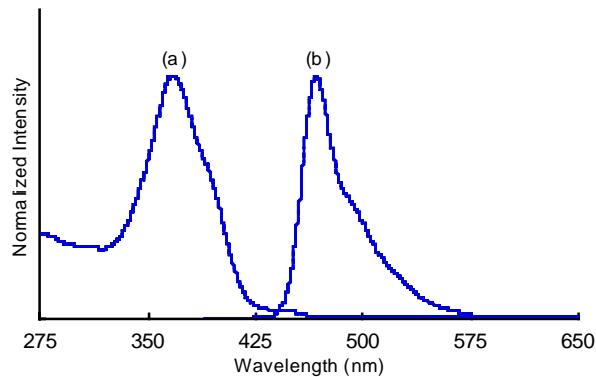


Figure S5. Normalized (a) absorption and (b) fluorescence spectra of **3g** in CHCl_3 .

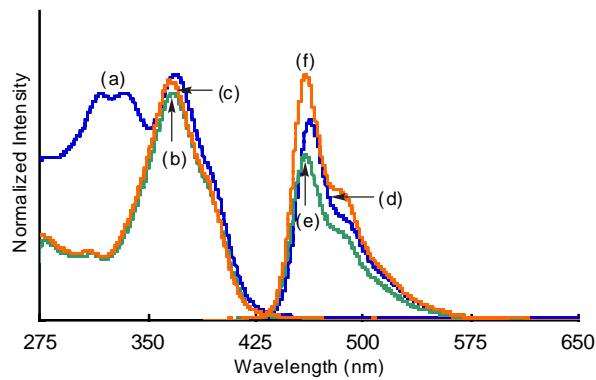


Figure S6. Normalized absorption spectra of **3h** in (a) CHCl_3 , (b) benzene, and (c) 1,4-dioxane. Normalized fluorescence spectra of **3h** in (d) CHCl_3 , (e) benzene, and (f) 1,4-dioxane.

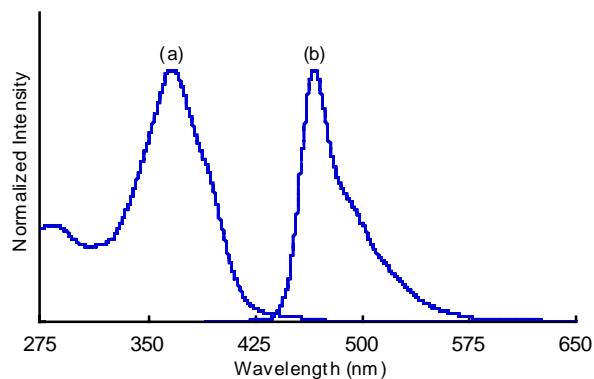


Figure S7. Normalized (a) absorption and (b) fluorescence spectra of **3i** in CHCl_3 .

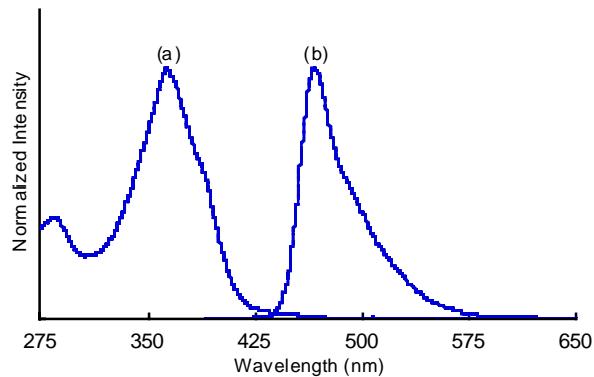


Figure S8. Normalized (a) absorption and (b) fluorescence spectra of **3j** in CHCl_3 .

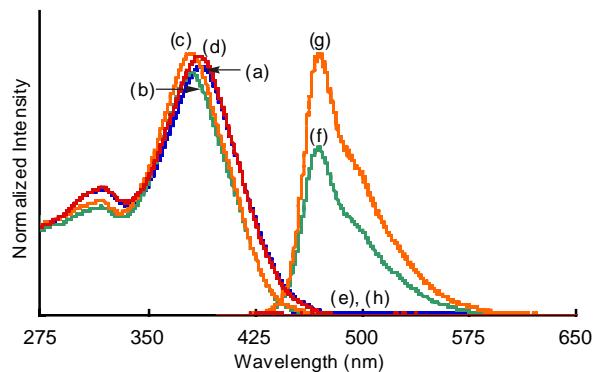


Figure S9. Normalized absorption spectra of **3l** in (a) CHCl_3 , (b) benzene, (c) 1,4-dioxane, and (d) CH_2Cl_2 . Normalized fluorescence spectra of **3l** in (e) CHCl_3 , (f) benzene, (g) 1,4-dioxane, and (h) CH_2Cl_2 .

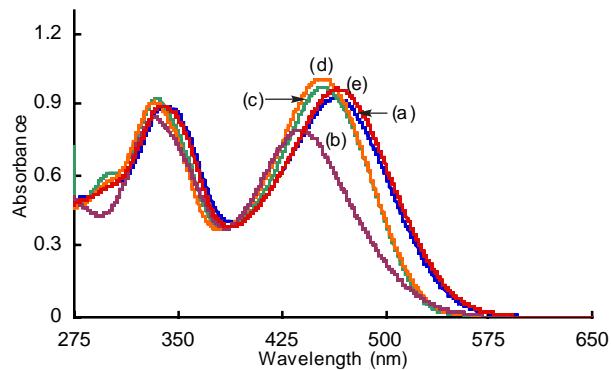


Figure S10. Absorption spectra of **3m** in (a) CHCl₃, (b) hexane, (c) benzene, (d) 1,4-dioxane, and (e) CH₂Cl₂.

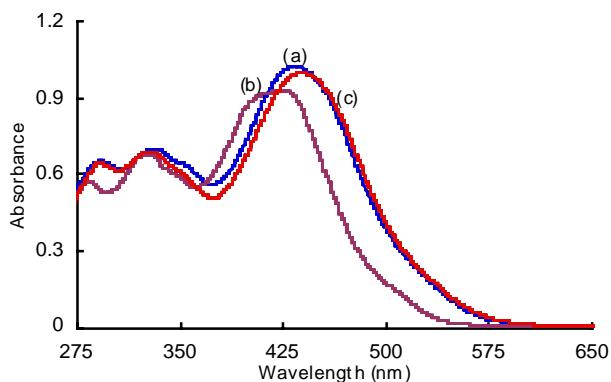


Figure S11. Absorption spectra of **3n** in (a) CHCl₃, (b) hexane, and (c) CH₂Cl₂.

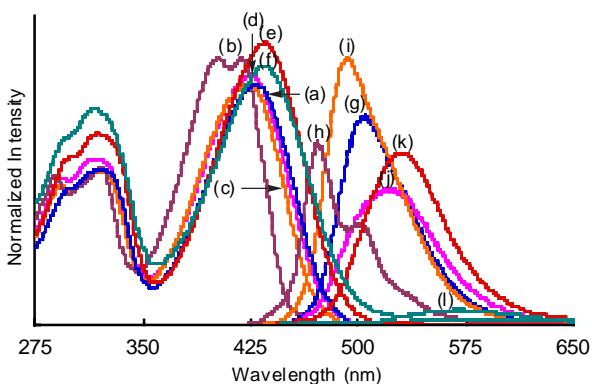


Figure S12. Normalized absorption spectra of **3o** in (a) CHCl₃, (b) hexane, (c) 1,4-dioxane, (d) EtOAc, (e) CH₂Cl₂, and (f) CH₃CN. Normalized fluorescence spectra of **3o** in (g) CHCl₃, (h) hexane, (i) 1,4-dioxane, (j) EtOAc, (k) CH₂Cl₂, and (l) CH₃CN.

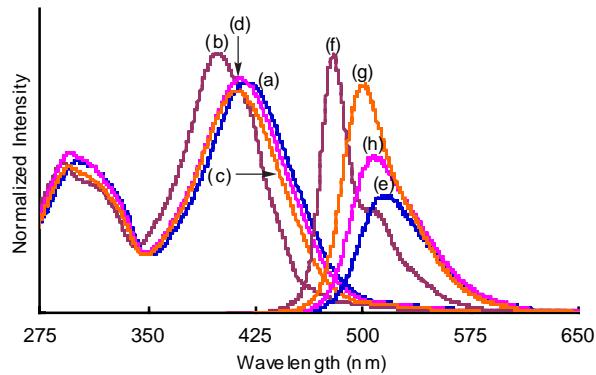


Figure S13. Normalized absorption spectra of **3p** in (a) CHCl₃, (b) hexane, (c) 1,4-dioxane, and (d) EtOAc. Normalized fluorescence spectra of **3p** in (e) CHCl₃, (f) hexane, (g) 1,4-dioxane, and (h) EtOAc.

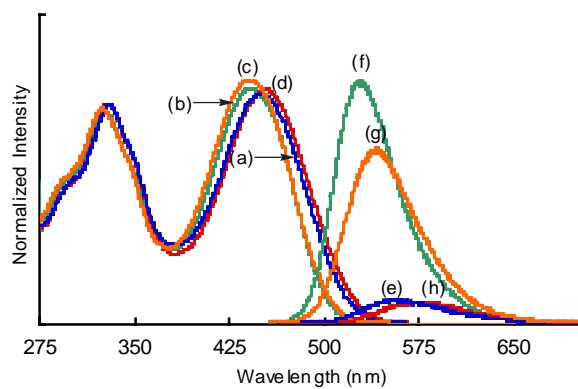


Figure S14. Normalized absorption spectra of **3q** in (a) CHCl₃, (b) benzene, (c) 1,4-dioxane, and (d) CH₂Cl₂. Normalized fluorescence spectra of **3q** in (e) CHCl₃, (f) benzene, (g) 1,4-dioxane, and (h) CH₂Cl₂.

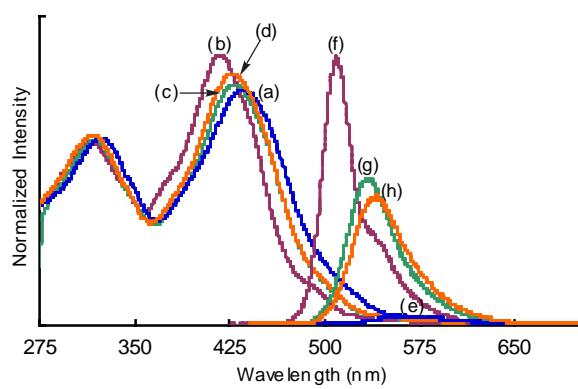


Figure S15. Normalized absorption spectra of **3r** in (a) CHCl₃, (b) hexane, (c) benzene, and (d) 1,4-dioxane. Normalized fluorescence spectra of **3r** in (e) CHCl₃, (f) hexane, (g) benzene, and (h) 1,4-dioxane.

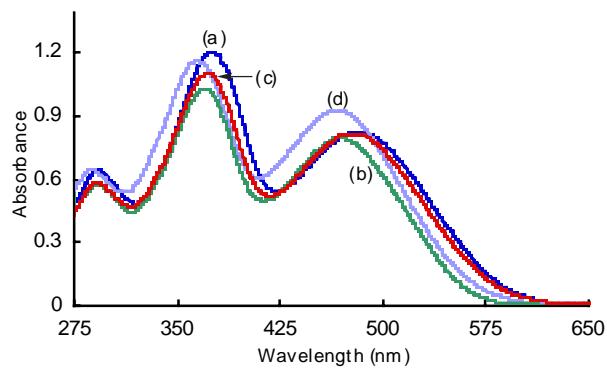


Figure S16. Absorption spectra of **3s** in (a) CHCl_3 , (b) benzene, (c) CH_2Cl_2 , and (d) THF.

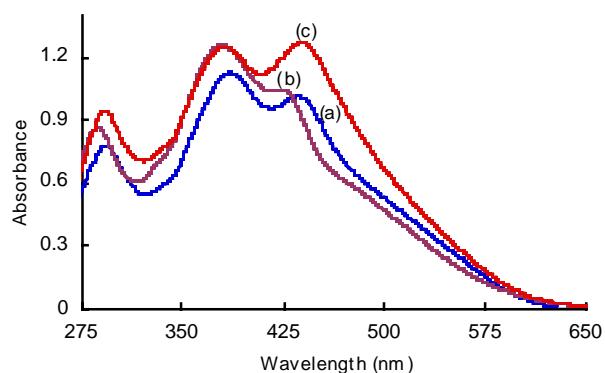
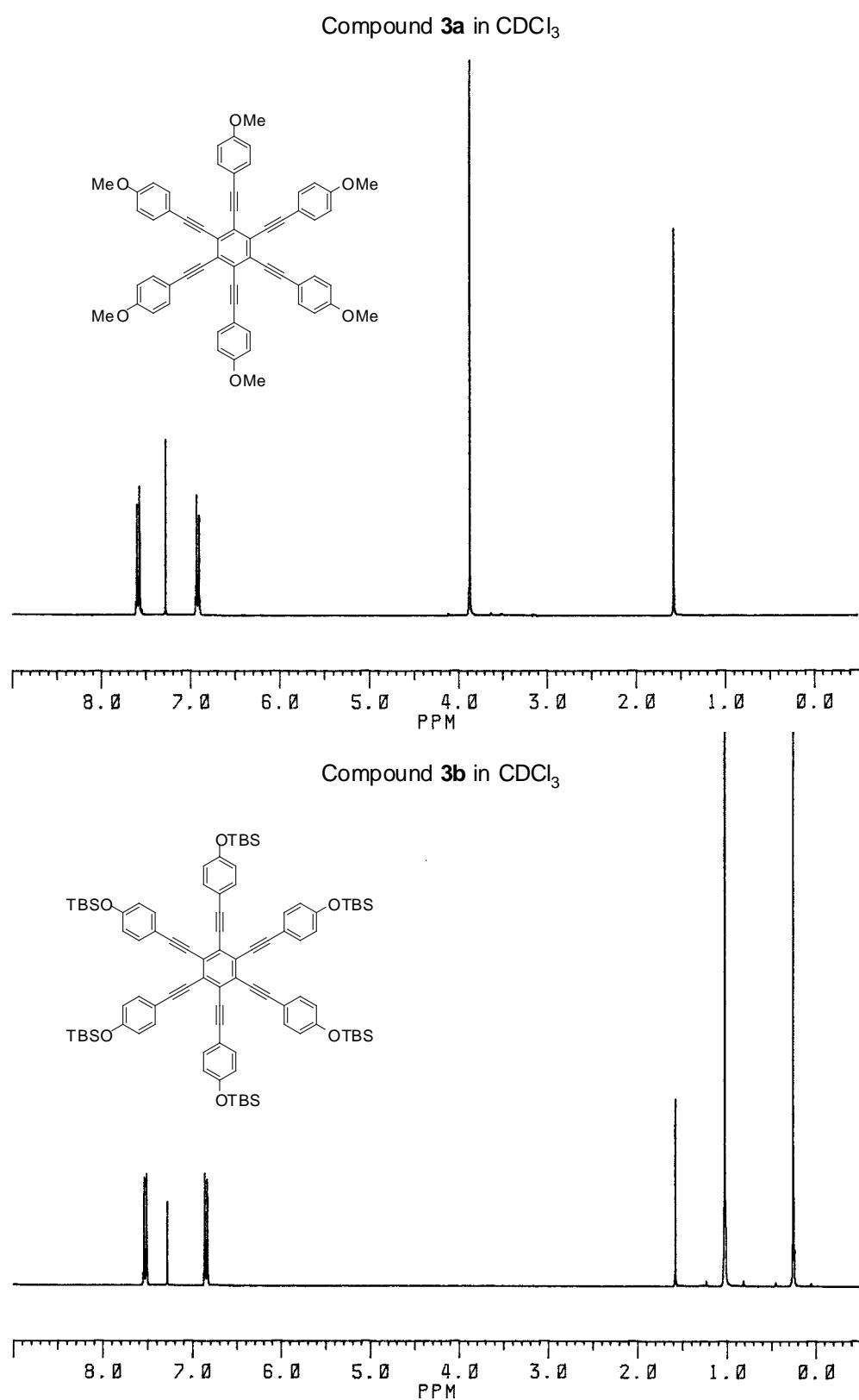
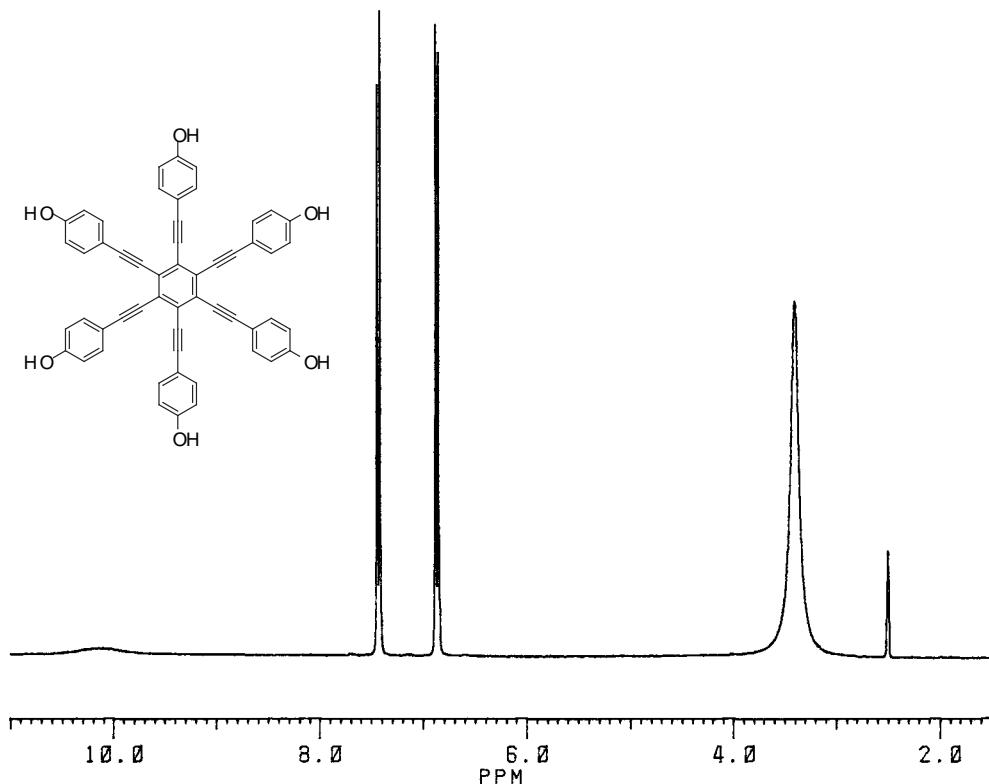


Figure S17. Absorption spectra of **3t** in (a) CHCl_3 , (b) hexane, and (c) CH_2Cl_2 .

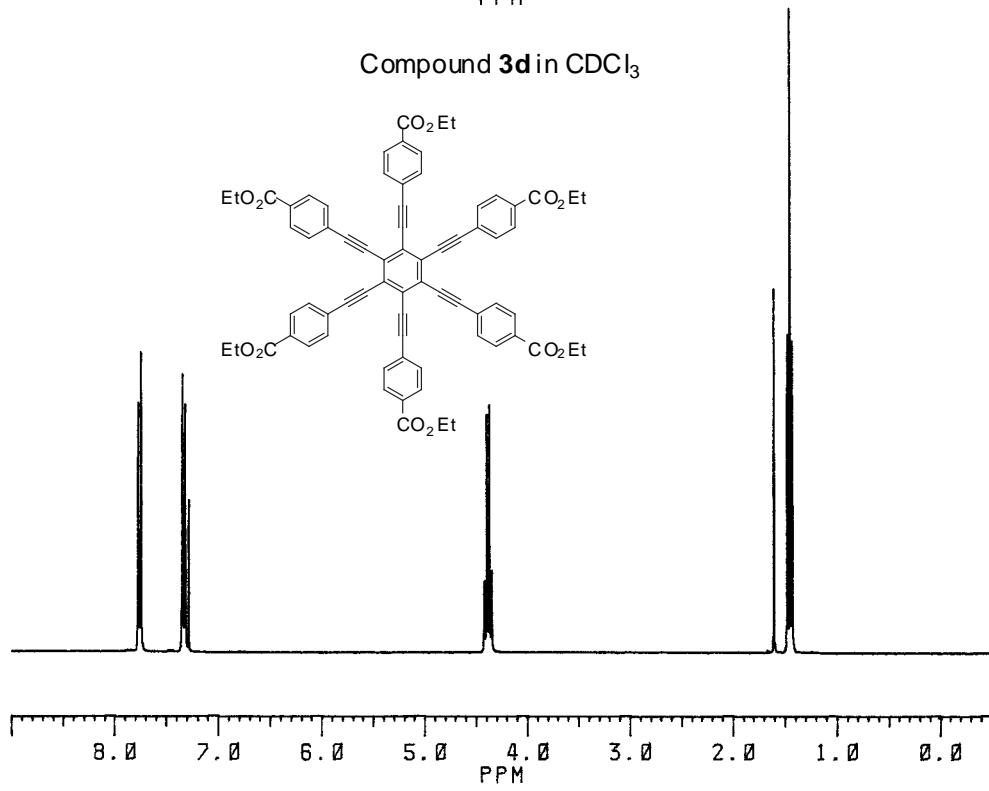
¹H NMR Spectra of 3–13.



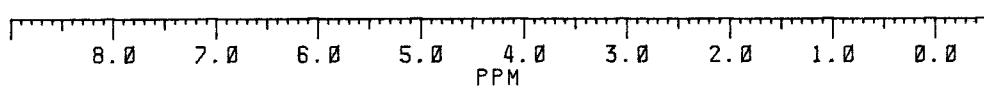
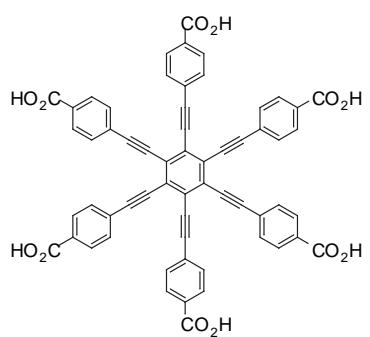
Compound **3c** in DMSO-*d*₆



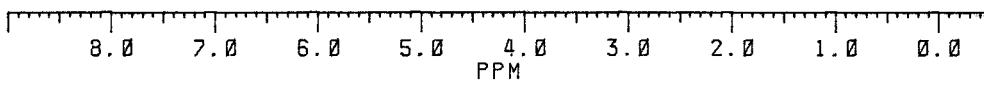
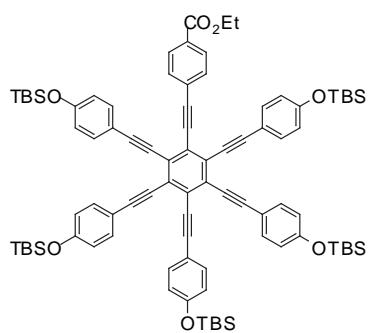
Compound **3d** in CDCl₃



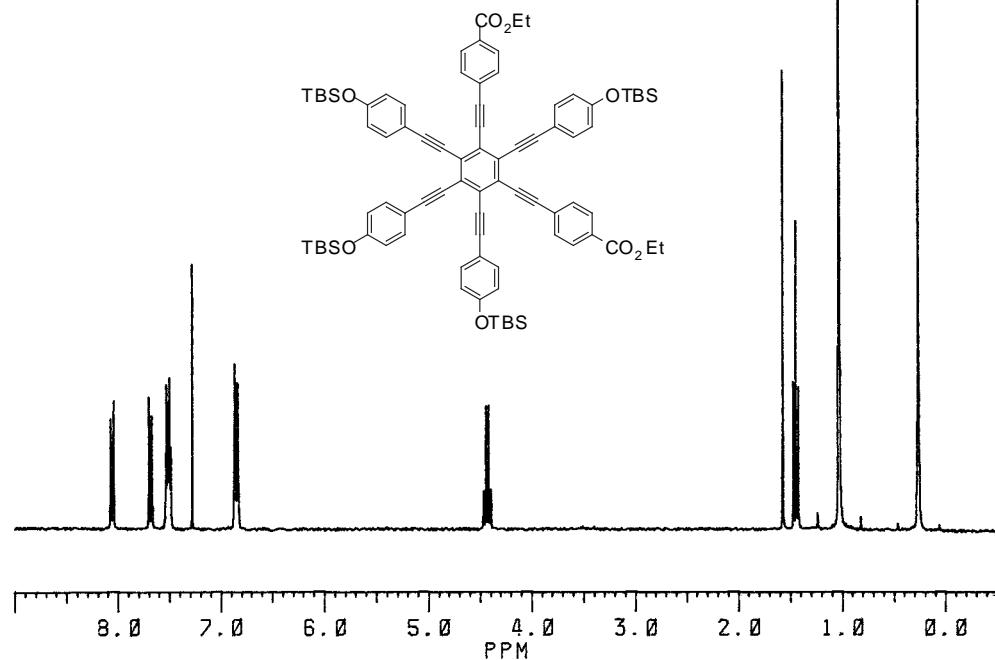
Compound **3e** in DMSO-*d*₆



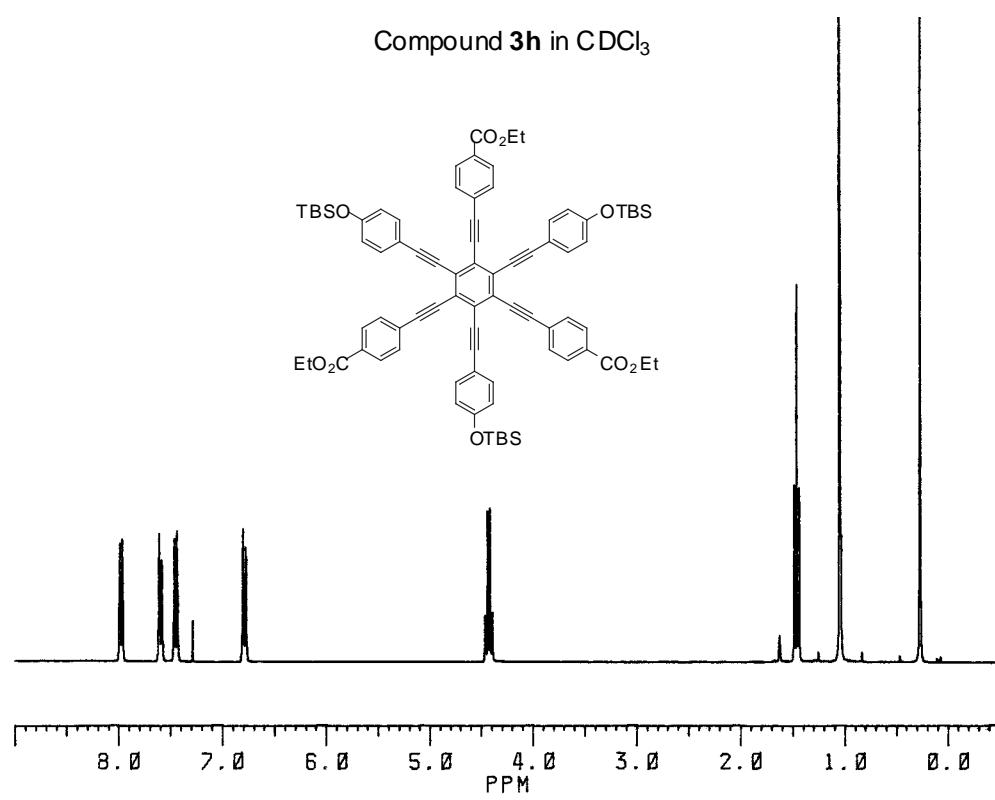
Compound **3f** in CDCl₃



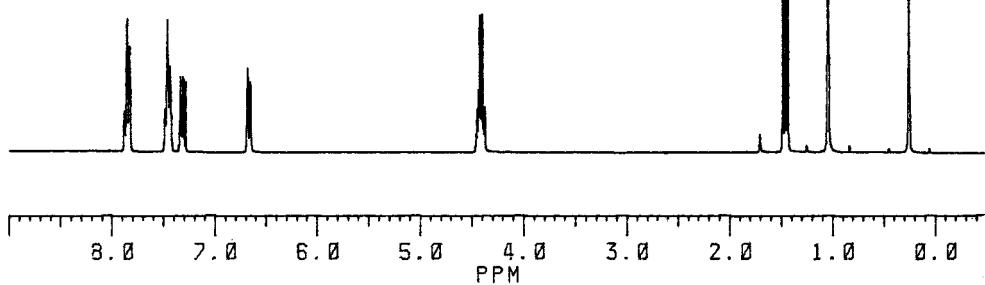
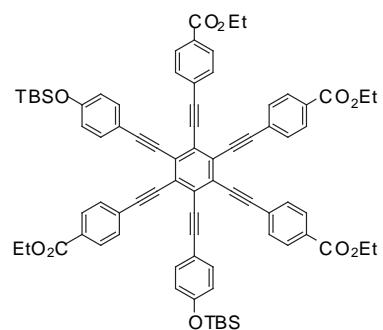
Compound **3g** in CDCl_3



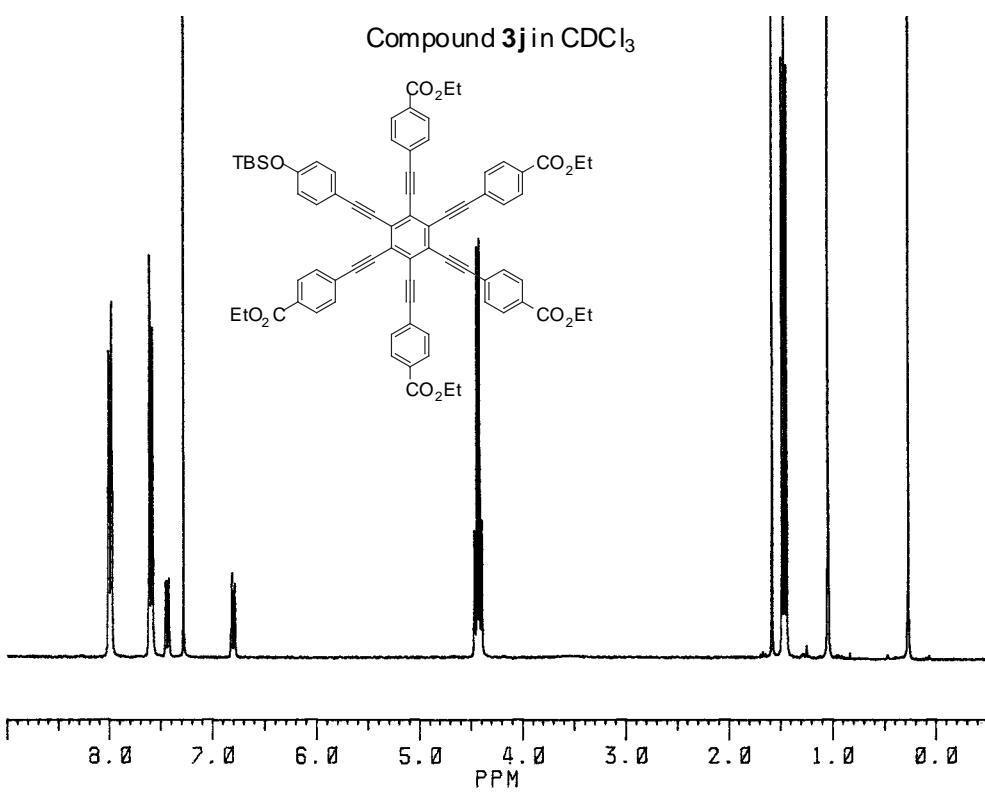
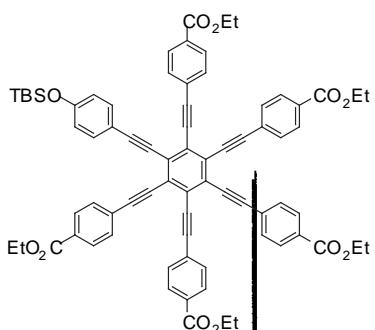
Compound **3h** in CDCl_3

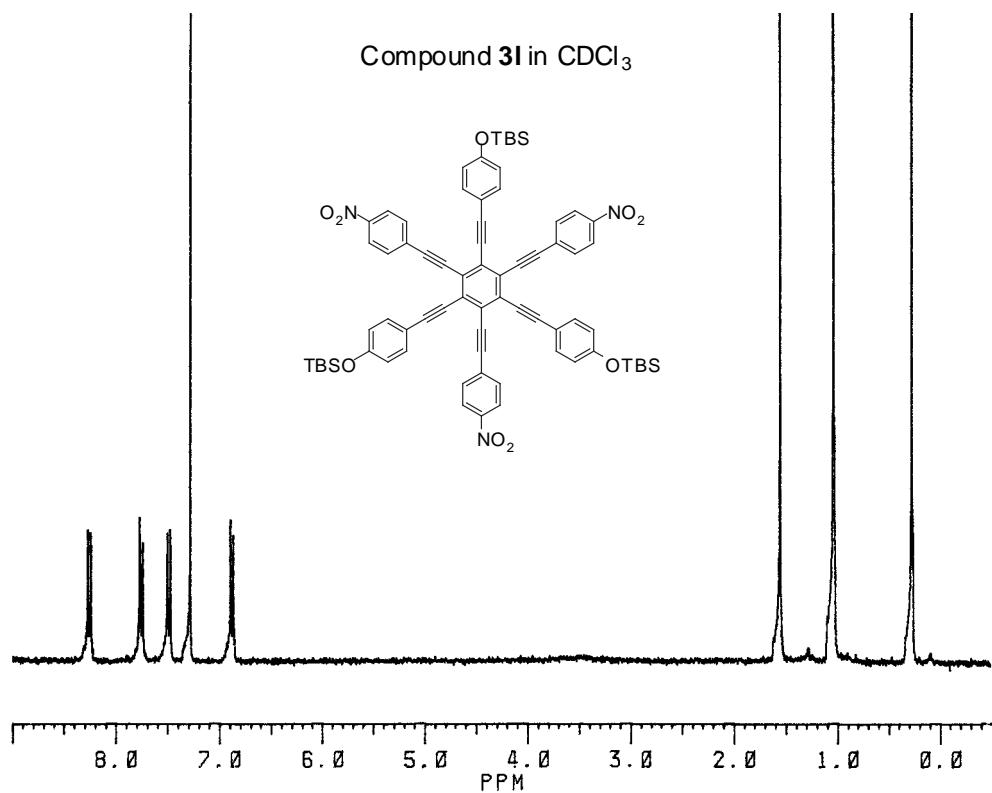
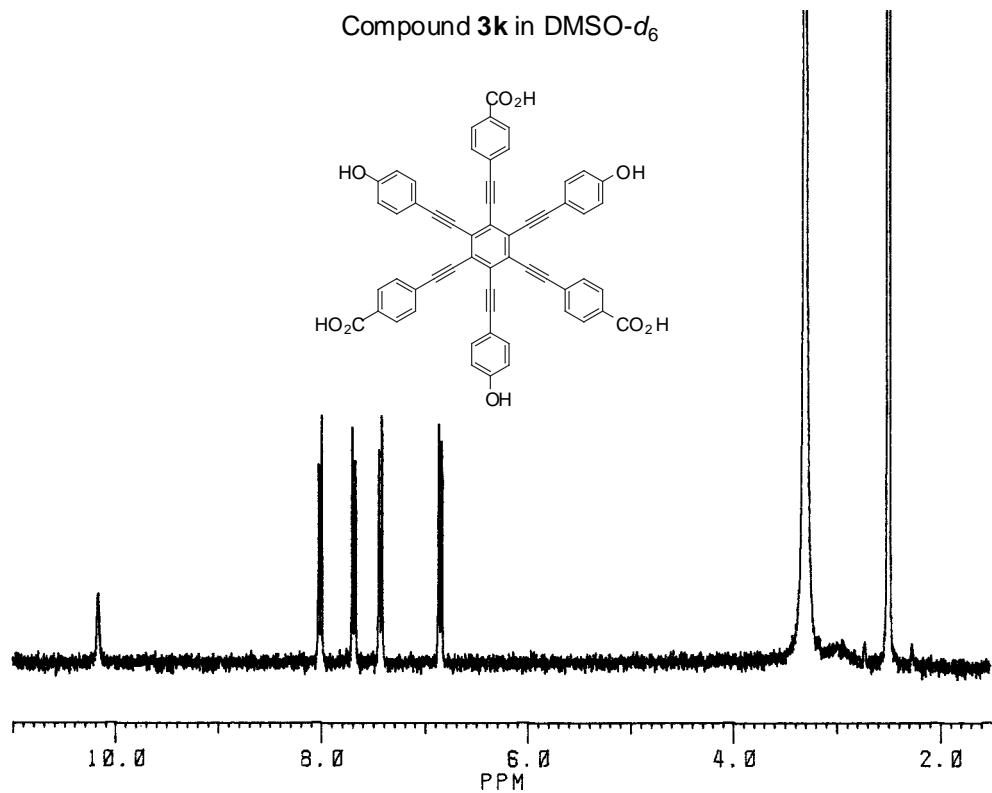


Compound **3i** in CDCl_3

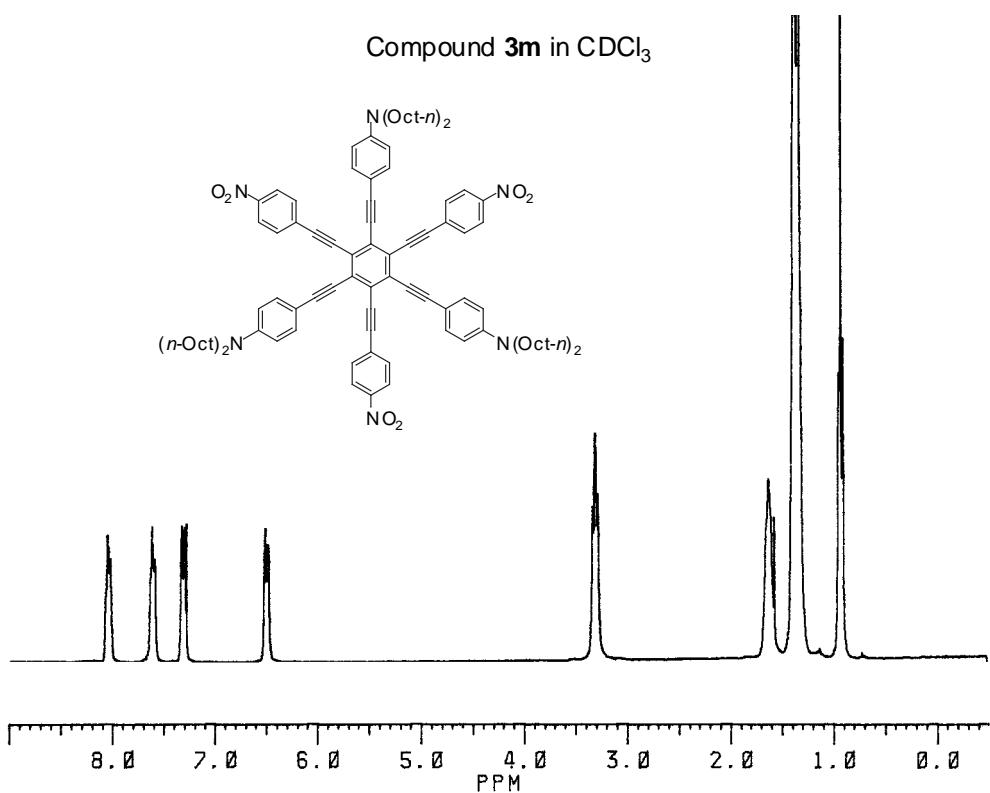
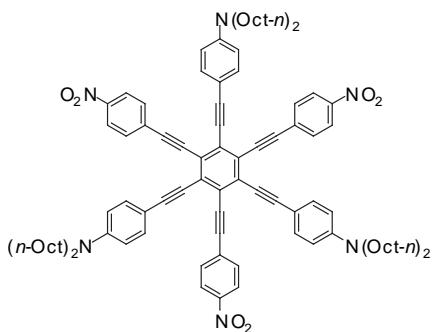


Compound **3j** in CDCl_3

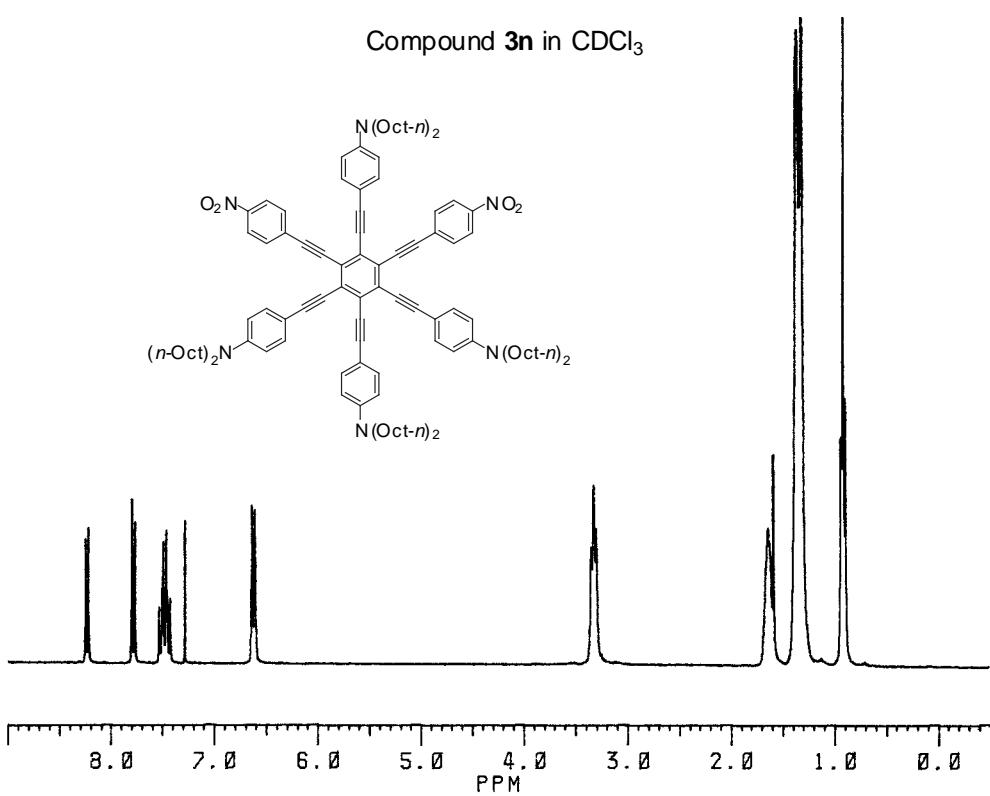
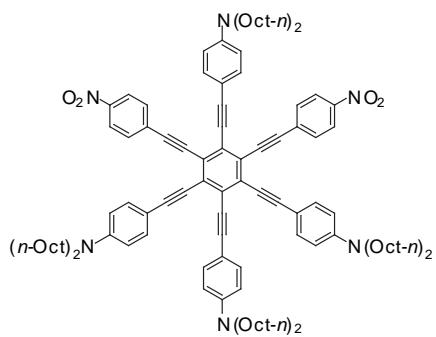




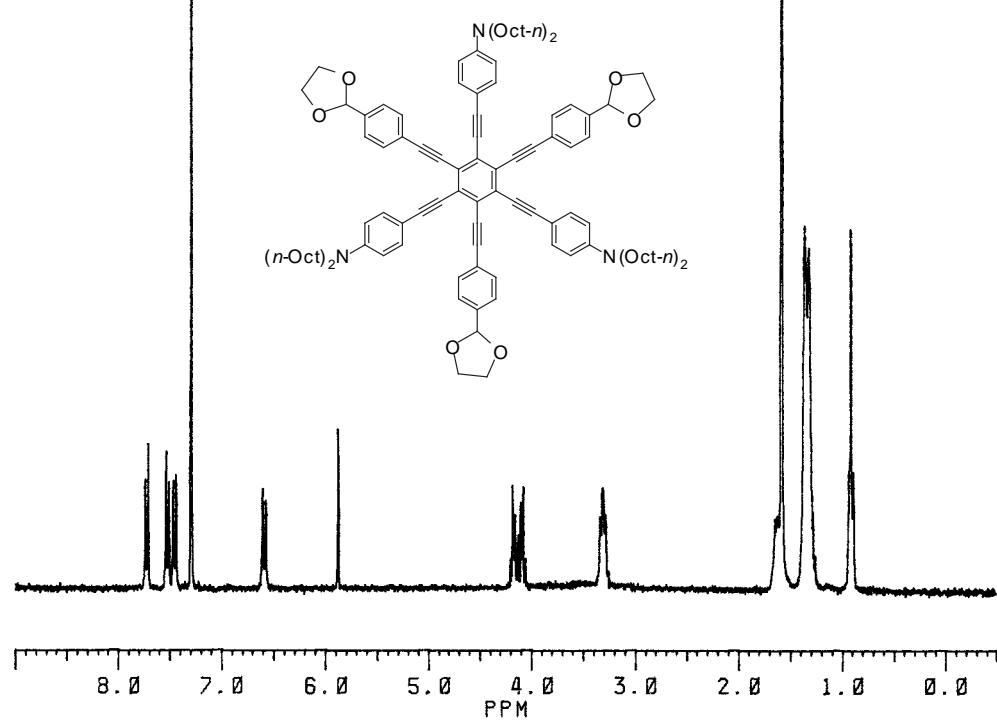
Compound **3m** in CDCl_3



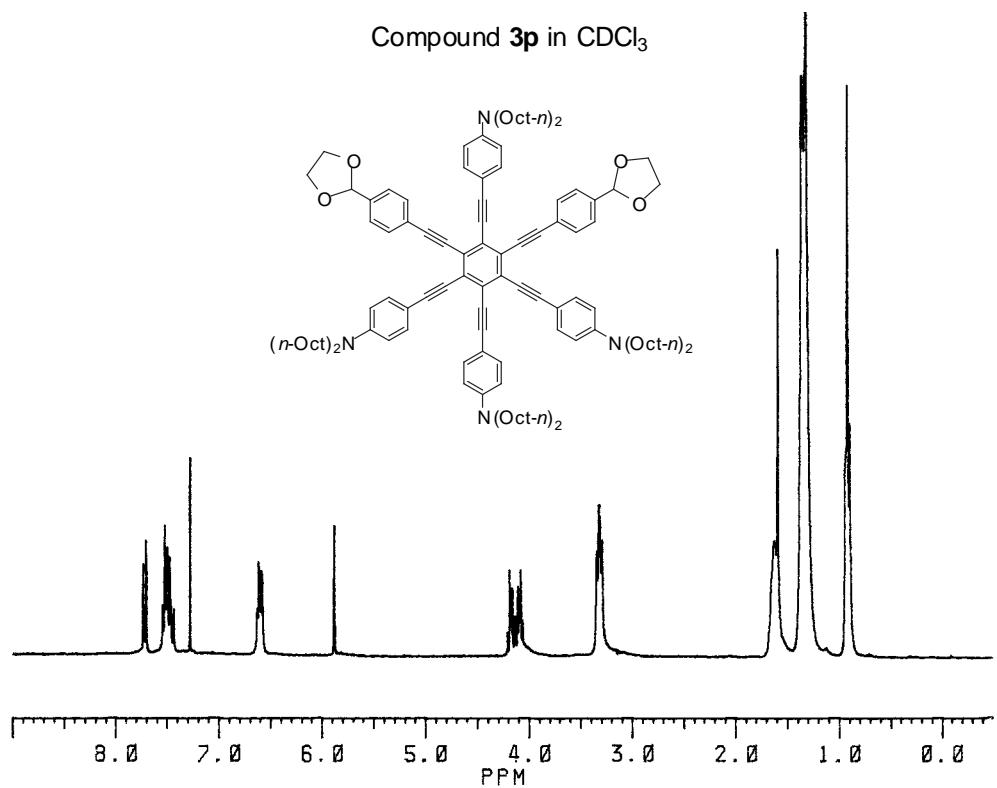
Compound **3n** in CDCl_3



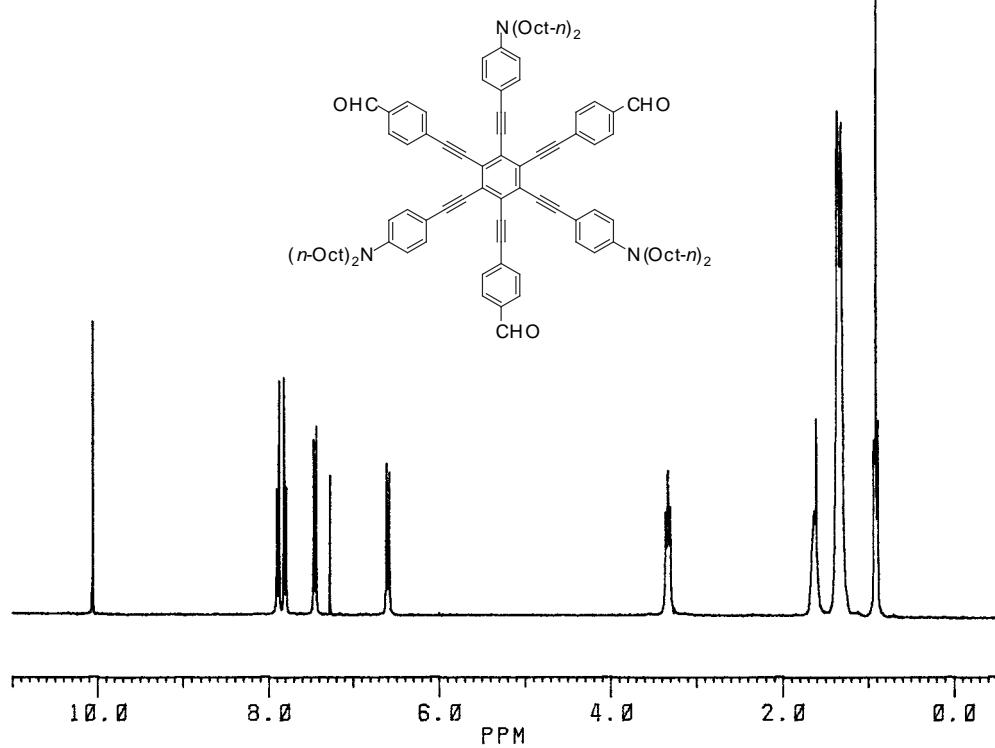
Compound **3o** in CDCl_3



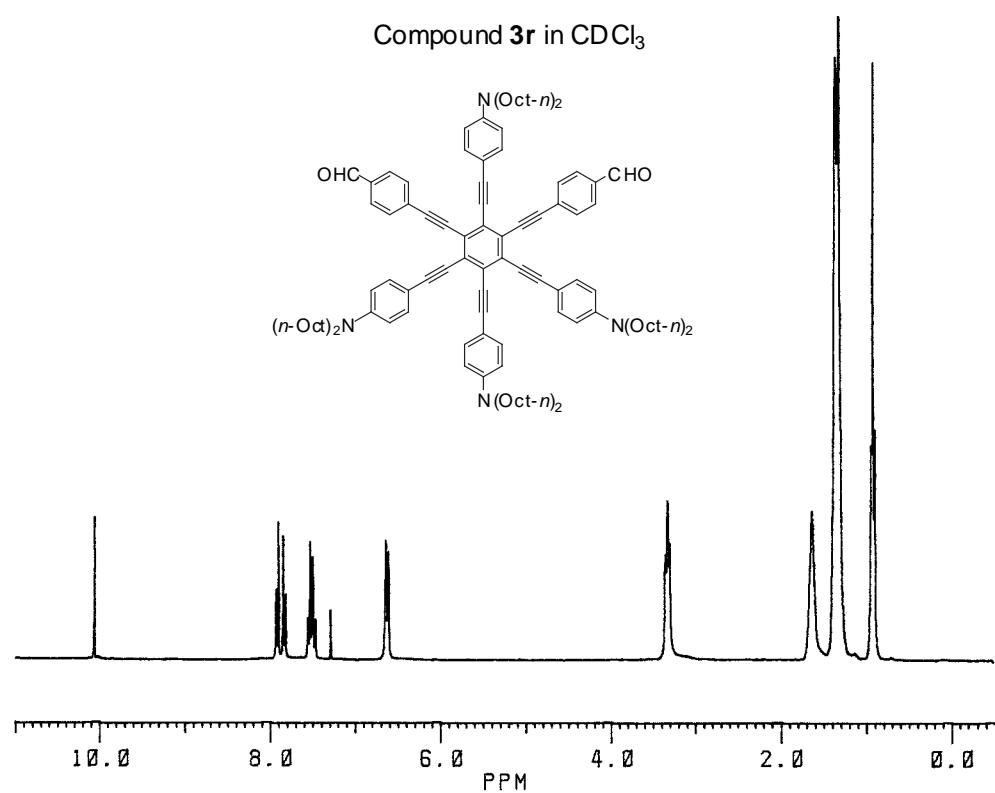
Compound **3p** in CDCl_3



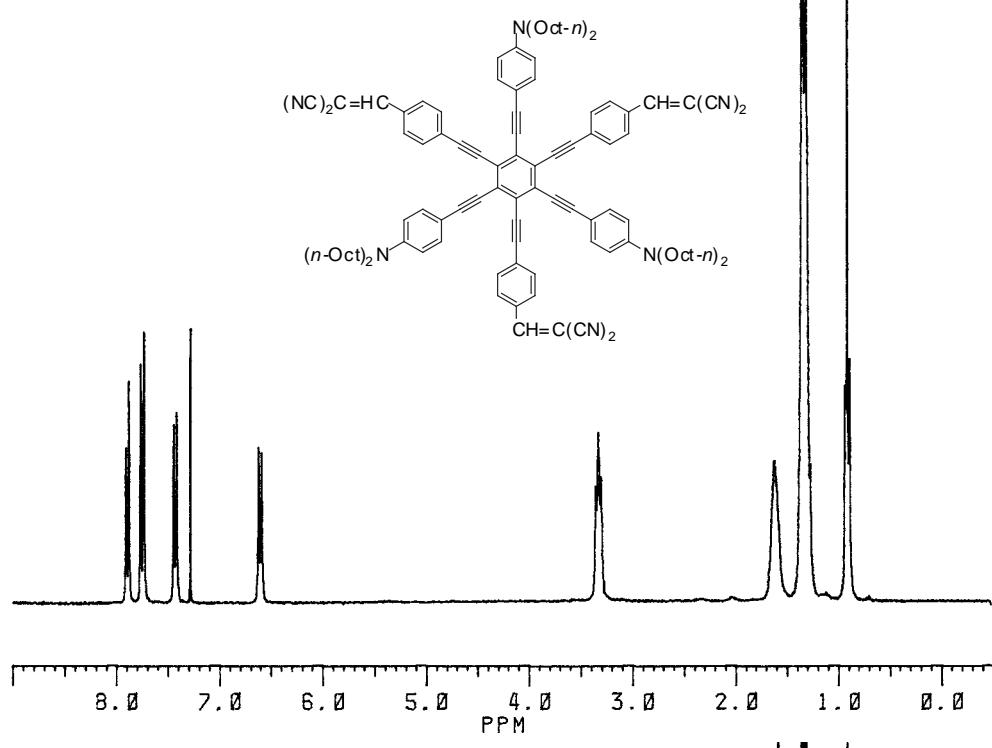
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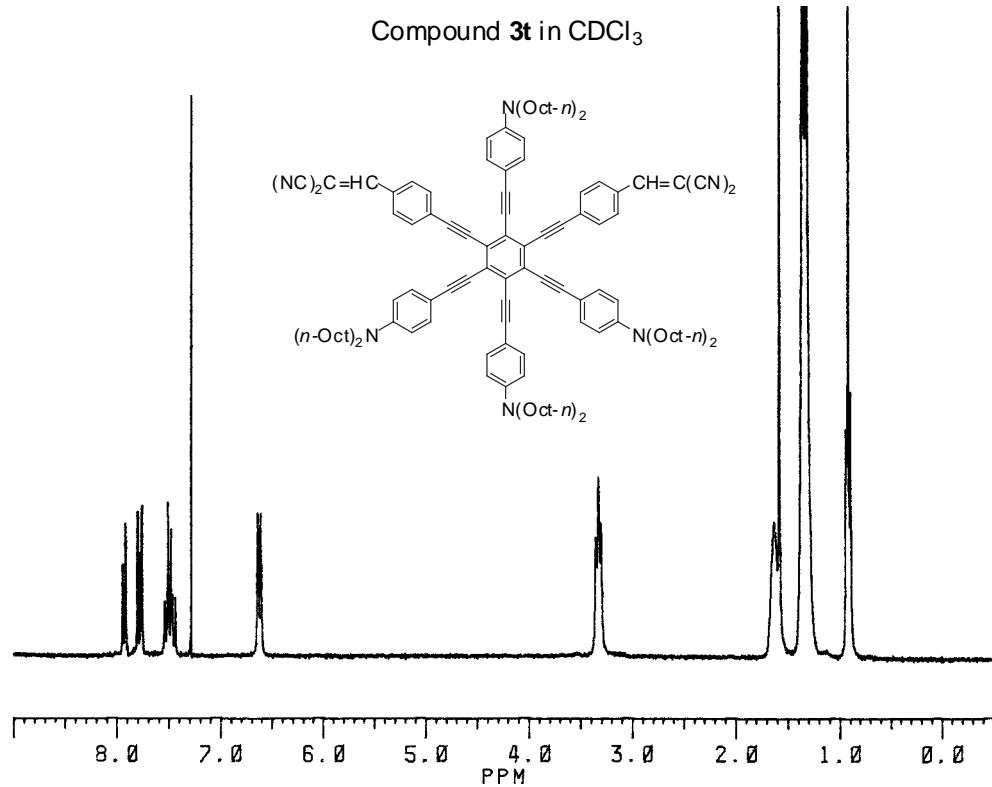
Compound **3r** in CDCl_3



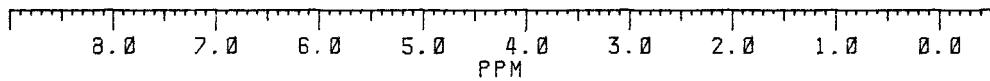
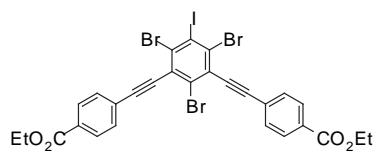
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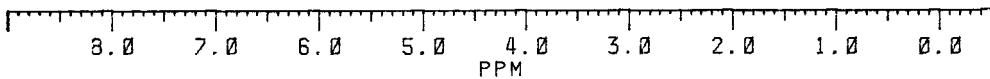
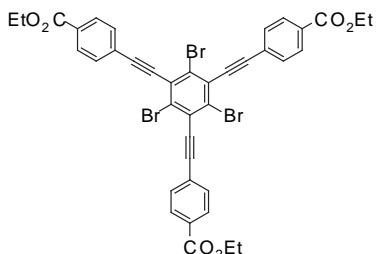
Compound **3t** in CDCl_3



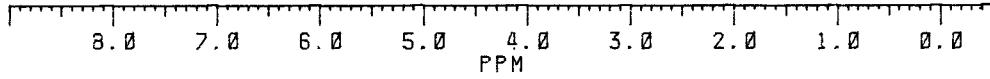
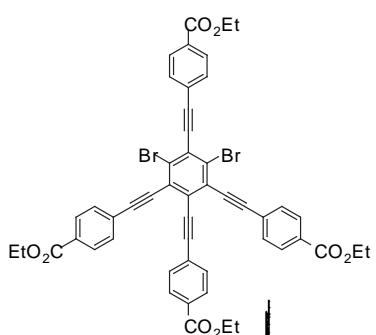
Compound 4 in CDCl_3



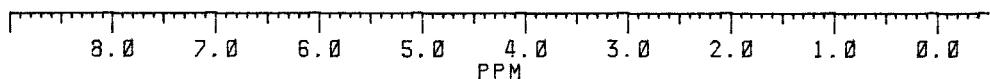
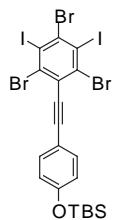
Compound 5 in CDCl_3



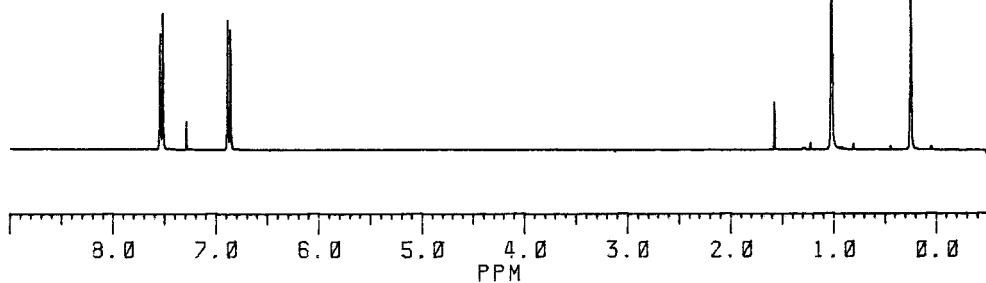
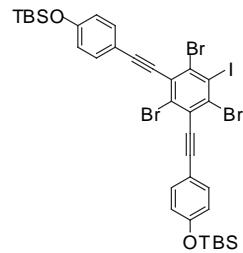
Compound **6** in CDCl_3



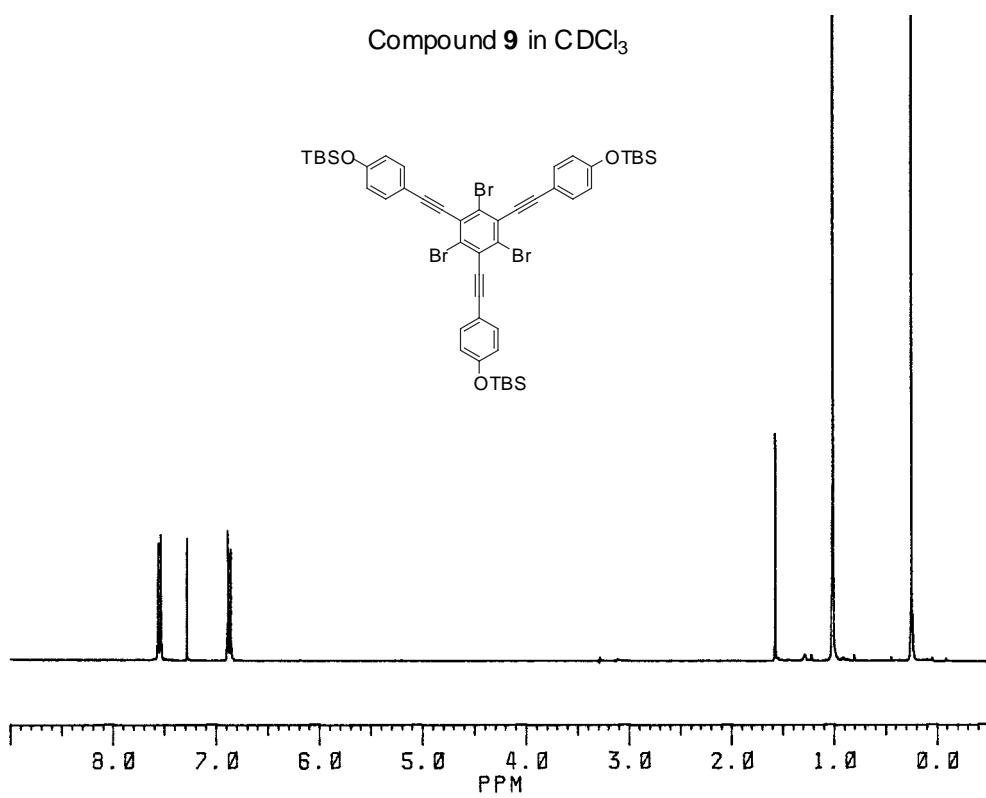
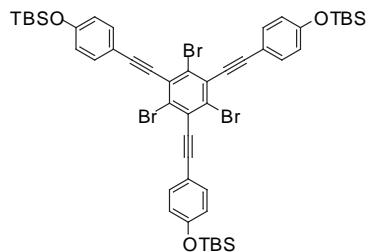
Compound **7** in CDCl_3



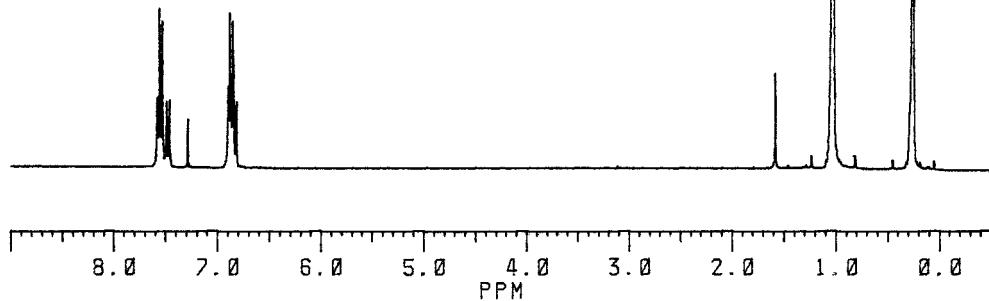
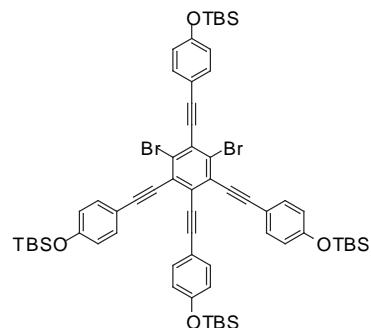
Compound **8** in CDCl_3



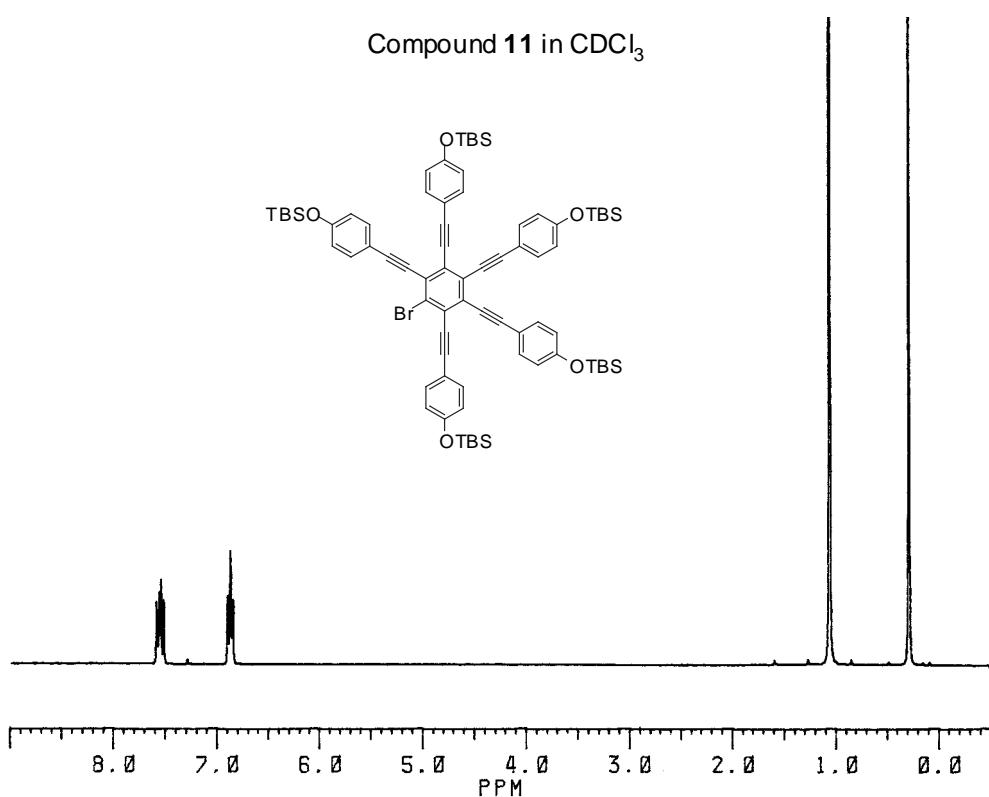
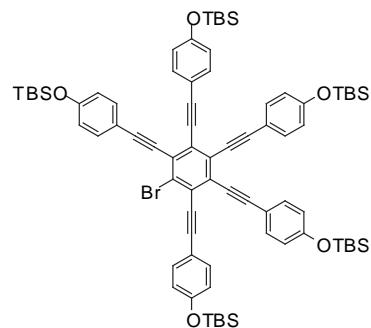
Compound **9** in CDCl_3



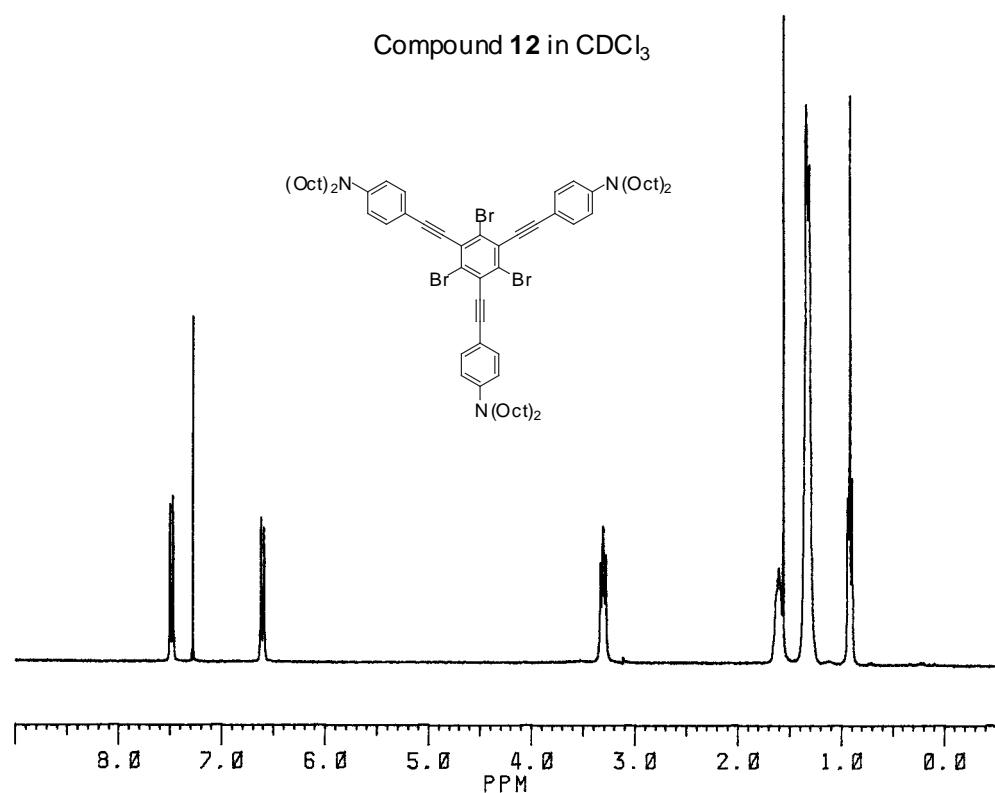
Compound **10** in CDCl_3



Compound **11** in CDCl_3



Compound **12** in CDCl_3



Compound **13** in CDCl_3

