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The Highly Selective Formation of Biaryls by the Cyclization of Arylethynes Catalyzed by Vanadyl Phtalocyanine

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General procedures.

Chromatographic purifications were performed on silica gel (35-70 mesh, Merck) columns. Thin-layer chromatography was carried out using Merck Kiesegel 60-F254 plates. ^{1}H NMR spectra were recorded as $CDCl_3$ solutions on a Bruker AM 400 instrument using tetramethylsilane (TMS) as an internal standard. GC-MS spectra were obtained with a VG-Quattro spectrometer equipped with a 30 m Supelco SPB-5 capillary column.

GC separation conditions. The products yield and the isomeric ratios for all the reactions were determined by GC analyses performed on a Focus Thermo instrument equipped with a 15 m Restek MTX-5 capillary column and a FID detector. Chemical yields were determined by adding a suitable internal standard (dodecane or tetradecane) to the reaction mixture at the end of each experiment and were reproducible within ±2% for multiple experiments.

The starting compounds were commercially available and used without further purification unless otherwise reported. 2-Ethynylnaphthalene and 2, 6-dimethoxy-1-ethynylbenzene were obtained as reported in the literature.[17]

The characterization of the reaction products was reported in previous papers[5]while in the case of 4-fluoro-ethynylbenzene and 2, 6-dimethoxy-ethynylbenzene, the analytical data are reported below.

Determination of the kinetic isotope effect k_H/k_D. Equimolar amounts of ethynylbenzene and ethynylbenzene-d_1 (9.8 mmol) were placed in two different round-bottom flasks and 3 mg of **1**(1.7×10^{-3} mmol) were added in each reaction.Dodecane (1.2 mmol) was added as an internal standard and the flasks were stirred under nitrogen in the same oil bath at 160ºC for 12 hours. The reaction mixtures were analyzed by GC, integrating and correcting the peak area of the starting compounds for the response of the FID detector.

All the elemental analyses gave satisfactory results and are reported below.

Analytical data

2, 6-dimethoxy-1-ethynylbenzene: The compound was purified on a silica gel column eluting with a mixture of hexane/diethyl ether 70:30. Yield 55%. m.p. 99-100ºC; ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.28(t, 1H, J=8.6 Hz), 6.56(d, 2H, J=8.6 Hz), 3.91(s, 6 H); EI MS: m/z(%) 162(100). Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.05; H, 6.21; Found C, 73.96; H, 6.25.

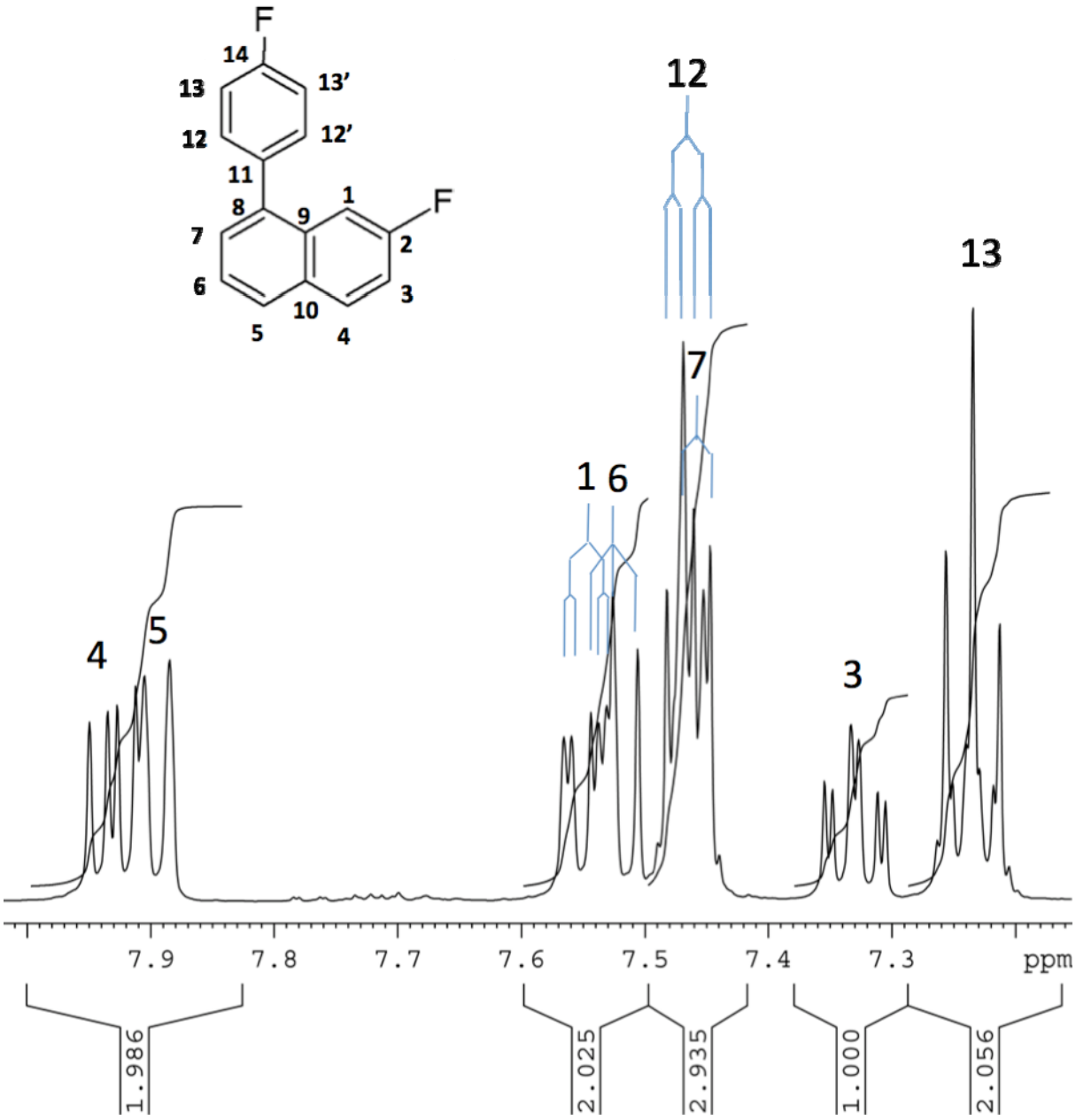
7-fluoro-1-(4'-fluorophenyl)naphthalene: The compound was purified on a silica gel column eluting with a mixture of hexane/diethyl ether 98:2. Yield 68%. m.p. 50-52ºC; ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.93(dd, 1H, J_H=9.2; J_F=5.1 Hz), 7.90(d, 1H, J=8.2 Hz), 7.55(dd, 1 H, J_H=2.4; J_F=8.7 Hz), 7.53(m, 1H), 7.46(m, 1H), 7.45(m, 1H), 7.33(dt, 2 H, J_H=9.2; J_F=3.5 Hz), 7.23(dt, 2 H, J_H=9.1; J_F=8.2 Hz),; EI MS: m/z(%) 240(100). Anal. Calcd for $C_{16}H_{10}F_2$: C, 79.98; H, 4.19; Found C, 80.06; H, 4.25.

1, 3, 5-(4'-fluorophenyl)benzene: The compound was purified on a silica gel column eluting with a mixture of hexane/diethyl ether 95:5. Yield 75%. m.p. 229-230ºC;^{1}H NMR(400 MHz, $CDCl_3$), 7.68(s, 3 H,), 7.65(dd, 12 H, J_H=6.4 Hz); EI MS; m/z(%) 360(100). Anal. Calcd for $C_{24}H_{15}F_3$: C, 79.98; H, 4.19; Found C, 80.10; H, 4.05.

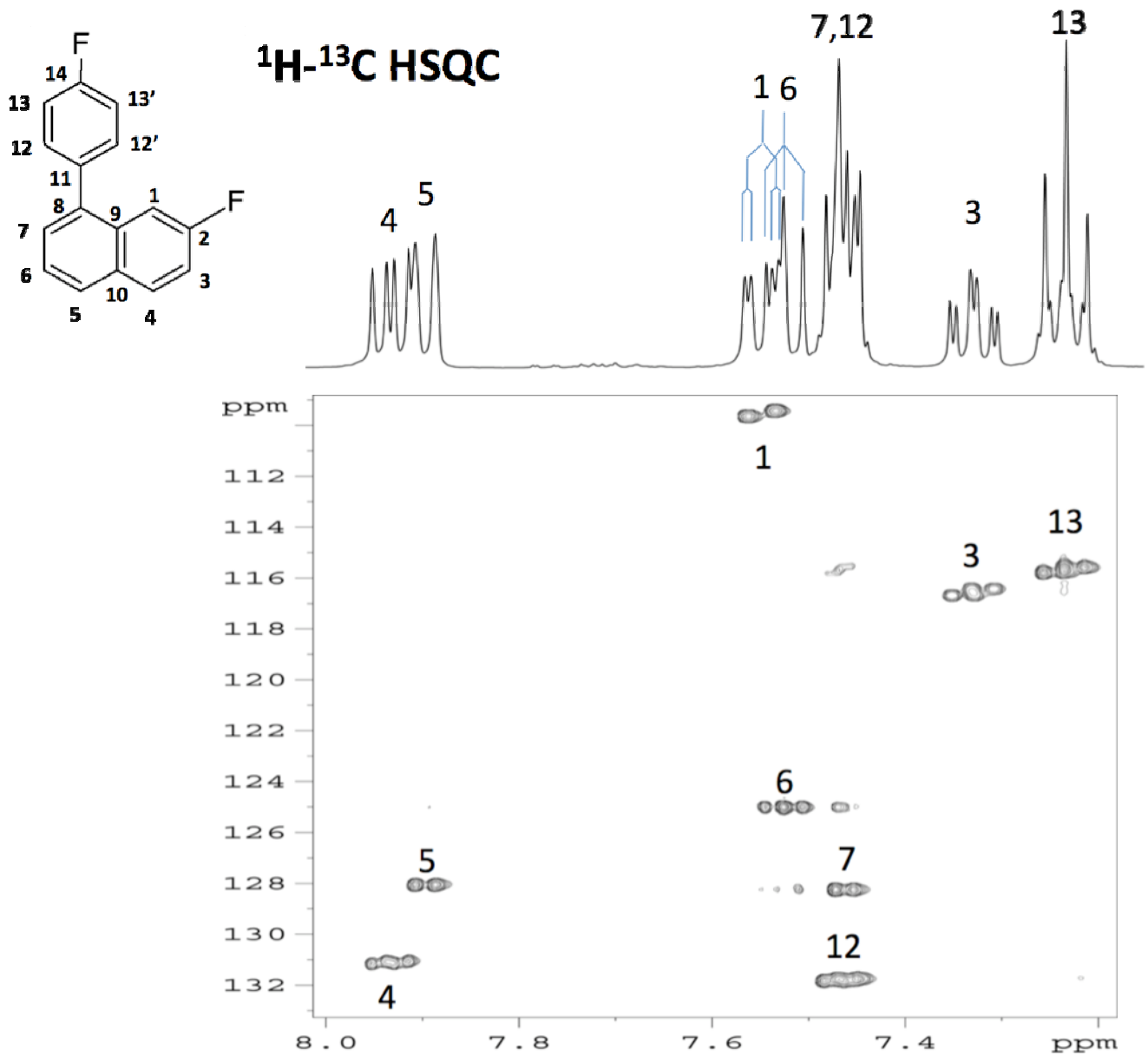
1, 2, 4-(4'-fluorophenyl)benzene: The compound was purified on a silica gel column eluting with a mixture of hexane/diethyl ether 95:5. Yield 68%. m.p. 136-137ºC; ^{1}H NMR(400 MHz, $CDCl_3$) 7.63(m, 2 H), 7.58(m, 2 H), 7.47(d, 1 H, J_H=8 Hz), 7.12(m, 6 H), 6.92(m, 4 H); EI MS: m/z(%) 360(100). Anal. Calcd for $C_{24}H_{15}F_3$: C, 79.98; H, 4.19; Found C, 79.86; H, 4.25.

1, 2, 4-(2', 6'-dimethoxypheyl)benzene: The compound was purified on a silica gel column eluting with a mixture of hexane/diethyl ether 70:30. Yield 60%. m.p. 204-205ºC; ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.39(m, 2H), 7.28(s, 1H), 7.23(d, 1 H, J=12.2 Hz), 7.09(m, 2H), 6.68(s, 1 H), 6.65 (s, 1 H), 6.43(d, 2 H, J=5.6 Hz), 6.41(d, 2 H, J=5.6 Hz), 3.78(s, 6 H) , 3.56(s, 6 H), 3.54(s, 6 H); EI MS: m/z(%) 486(100). Anal. Calcd for $C_{30}H_{30}O_6$: C, 74.05; H, 6.21; Found C, 74.10; H, 6.05.

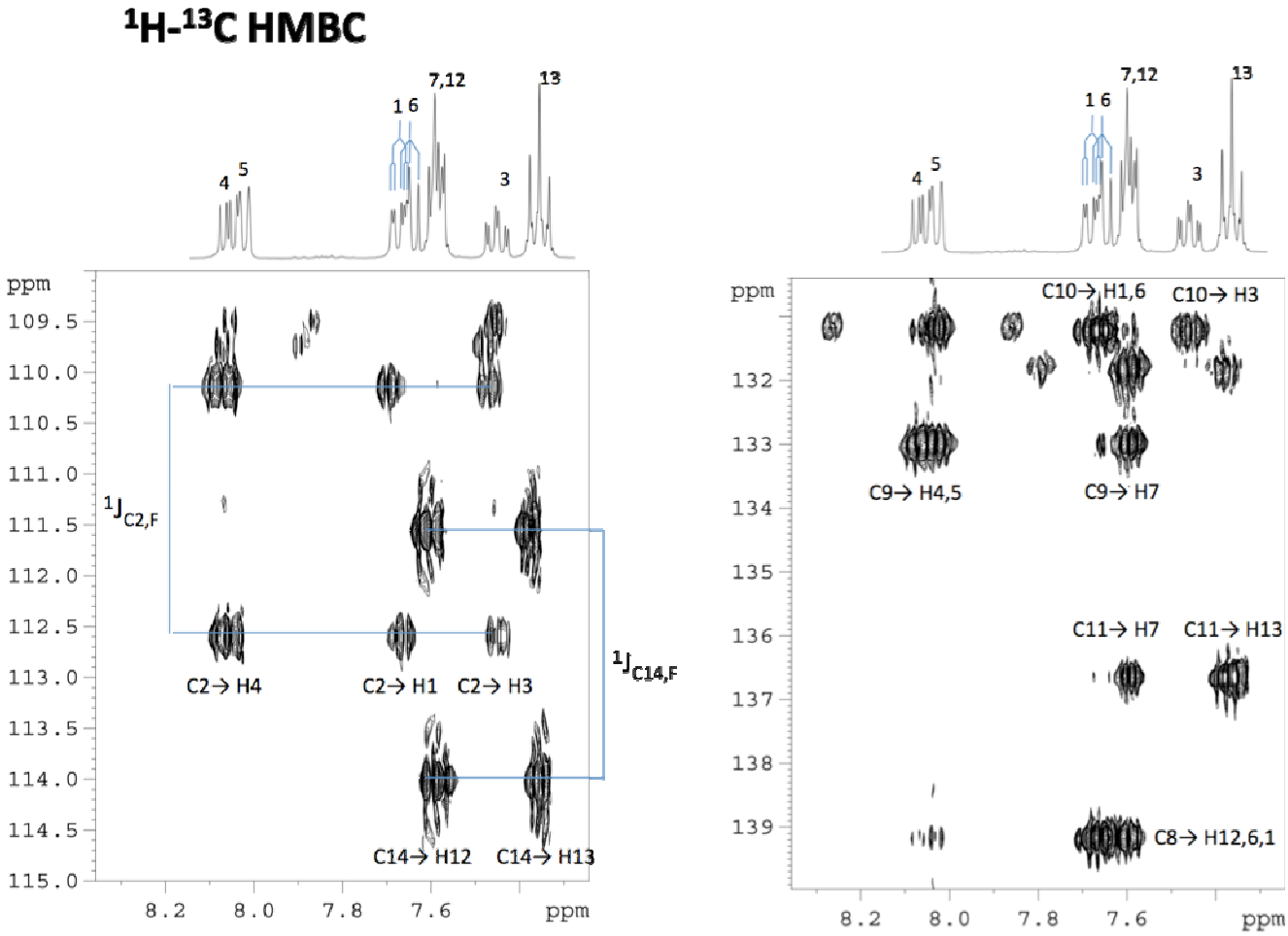
1, 3, 5-(2', 6'-dimethoxypheyl)benzene: The compound was purified on a silica gel column eluting with a mixture of hexane/diethyl ether 70:30. Yield 50%. m.p. 234-235ºC; ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.41(s, 3H), 7.26(d, 3 H, J=14.2 Hz), 6.67(d, 6H, J=14.2 Hz), 3.75(s, 18 H); EI MS: m/z(%) 486(100). EI MS: m/z(%) 486(100). Anal. Calcd for $C_{30}H_{30}O_6$: C, 74.05; H, 6.21; Found C, 74.16; H, 6.25.



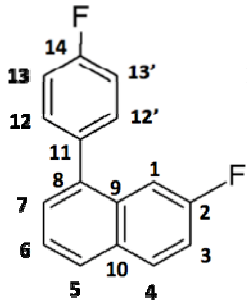
S1: ^{1}H spectrum of 7-fluoro-1-(4'-fluoro)phenyl naphthalene



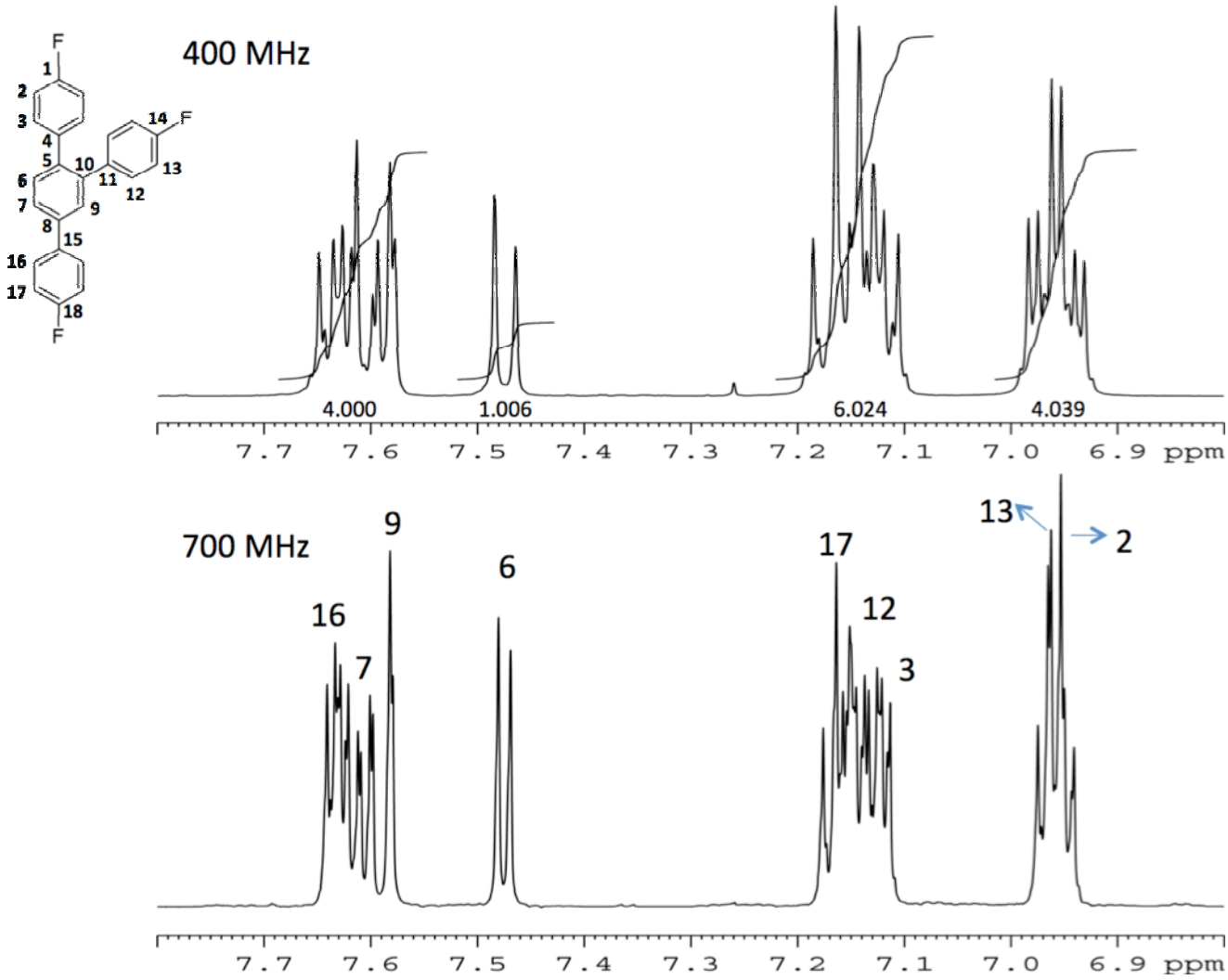
S2: ^{1}H-^{13}C HSQC spectrum of 7-fluoro-1-(4'-fluoro)phenyl naphthalene



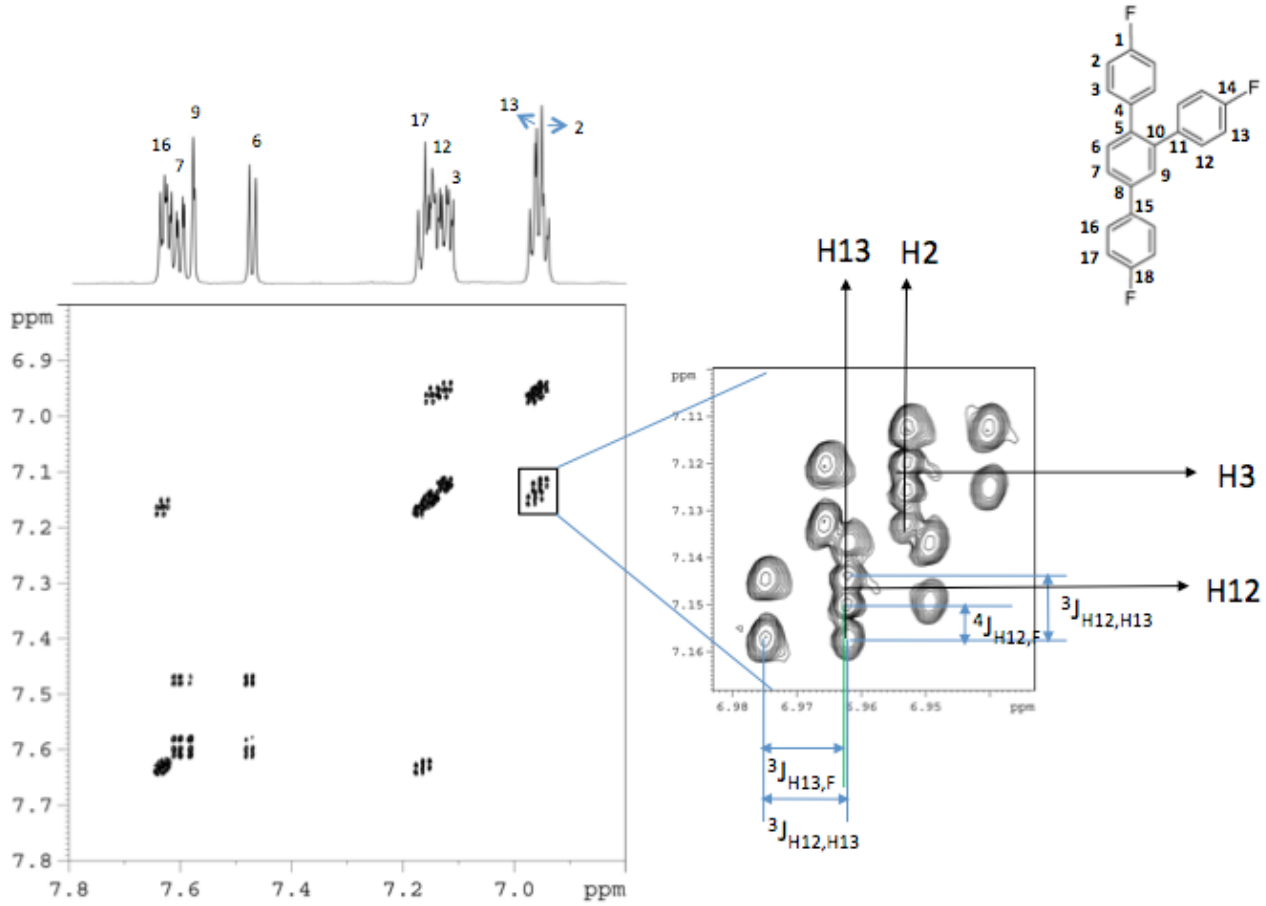
S3: ^{1}H-^{13}C spectra of 7-fluoro-1-(4'-fluoro)phenyl naphthalene



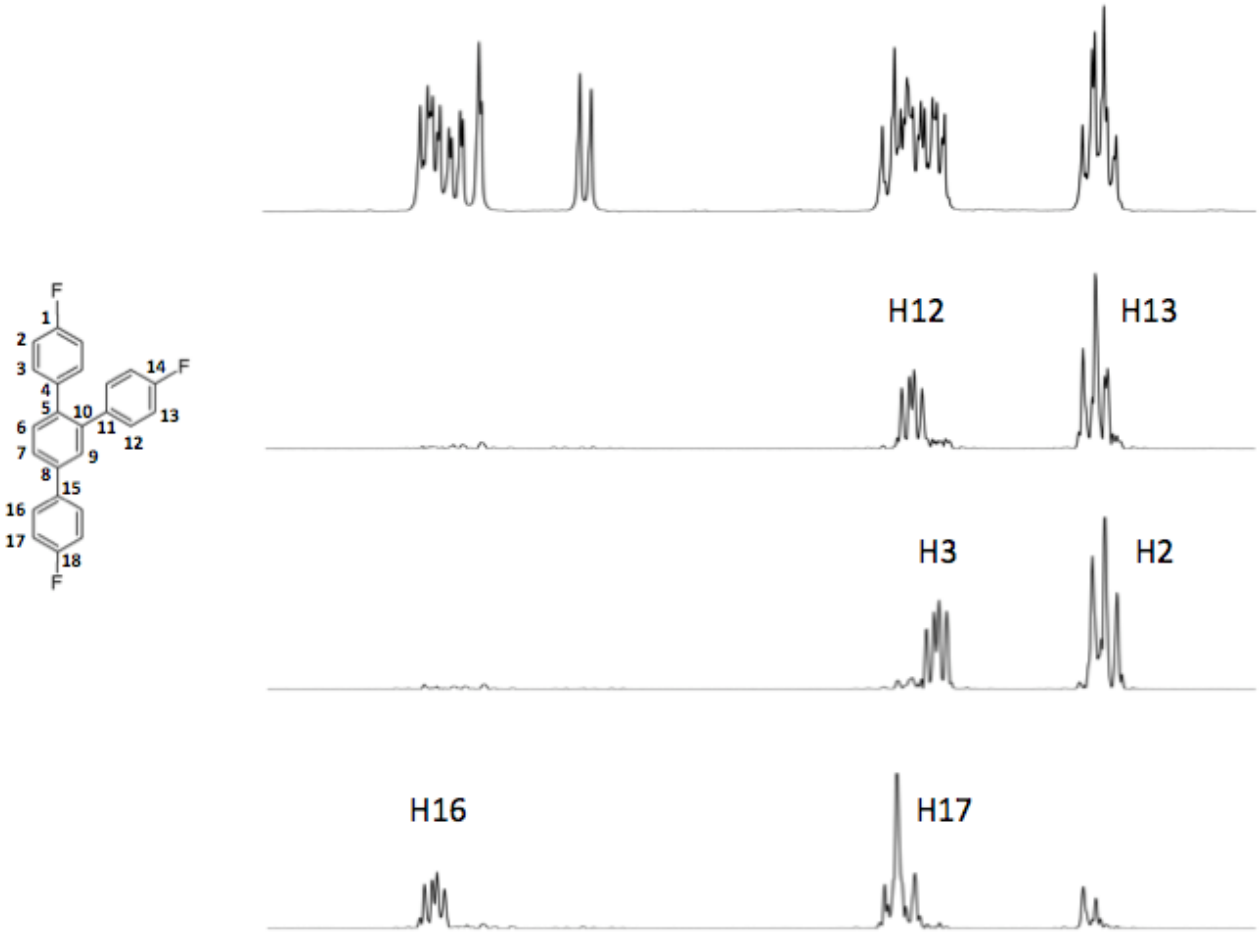
C-1	109.5	23.0(1-F)	H-1	7.55	2.4 (1-3); 8.7 (1-F)
C-2	112.0	-245.5(2-F)			
C-3	116.5	26.6(3-F)	H-3	7.33	9.2(3-4); 8.5(3-F)
C-4	131.1	8.9(4-F)	H-4	7.93	5.1(4-F)
C-5	128.0		H-5	7.90	8.2(5-6)
C-6	125.0		H-6	7.53	7.4(6-7)
C-7	128.2		H-7	7.46	
C-8	139.7				
C-9	133.7				
C-10	131.9				
C-11	137.1				
C-12	131.7	7.9(12-F)	H-12	7.46	9.1(12-13);5.1(12-F)
C-13	115.7	23.1(13-F)	H-13	7.23	8.2(13-F)
C-14	113.4	-247.9(14-F)			



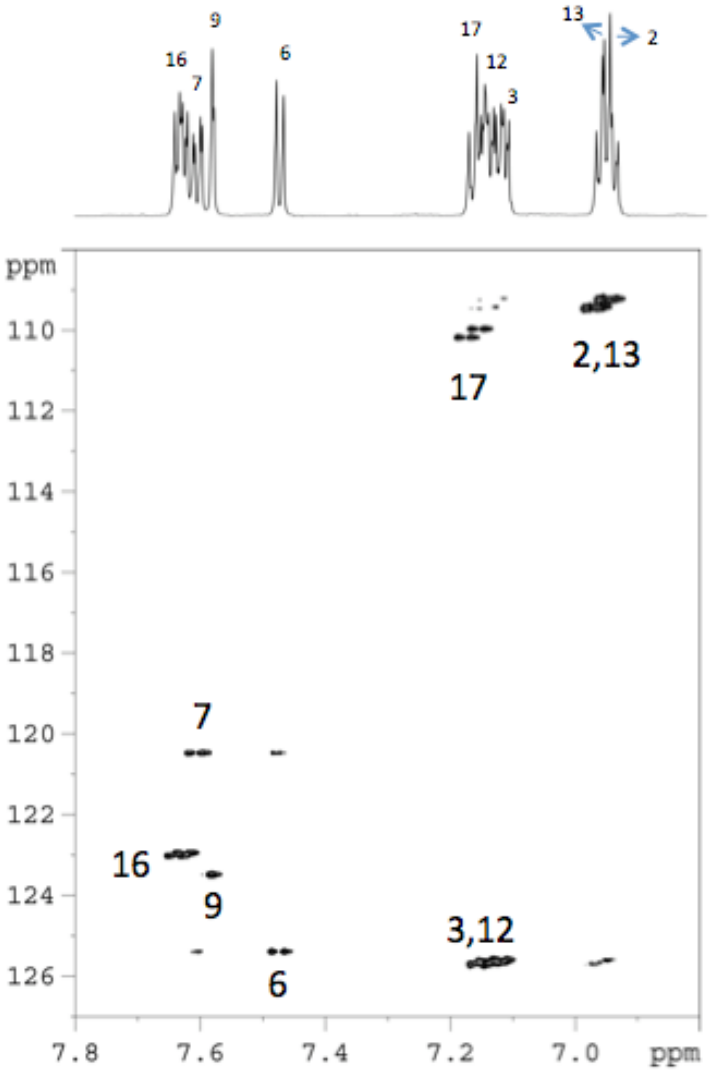
S4: ^{1}H spectra of 1,2,4-(4'-fluoro)triphenylbenzene at different field



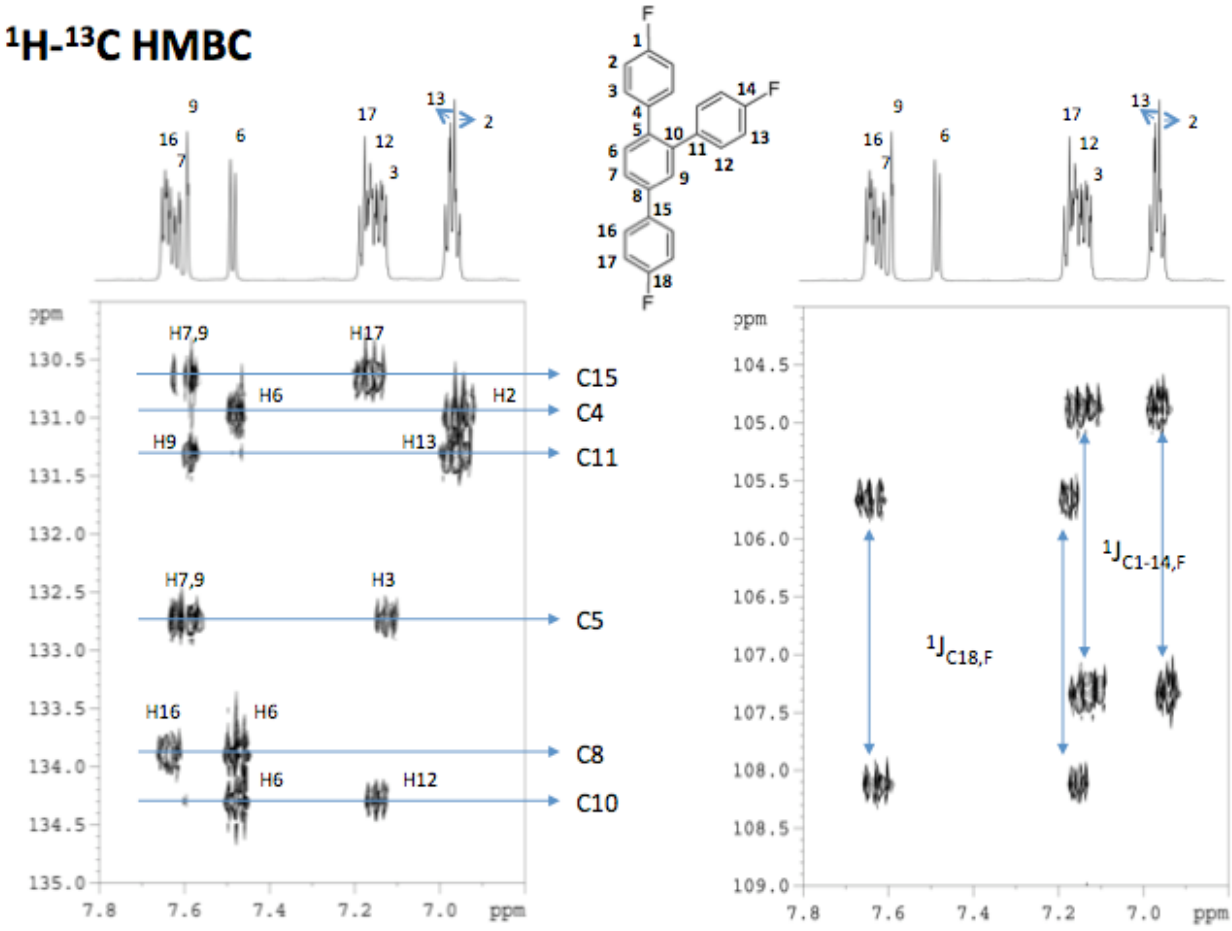
S5: ^{1}H-COSY spectrum of 1,2,4-(4'-fluoro)triphenylbenzene



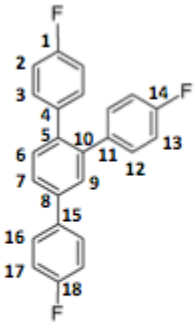
S6: ^{1}H-COSY traces spectrum of 1,2,4-(4'-fluoro)triphenylbenzene



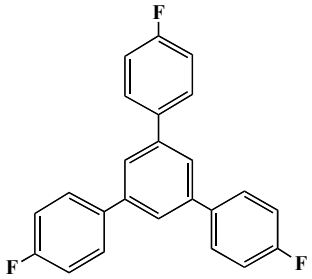
S7:^{1}H-^{13}C HSQC spectra of 1,2,4-tris(4’-fluorophenyl)benzene

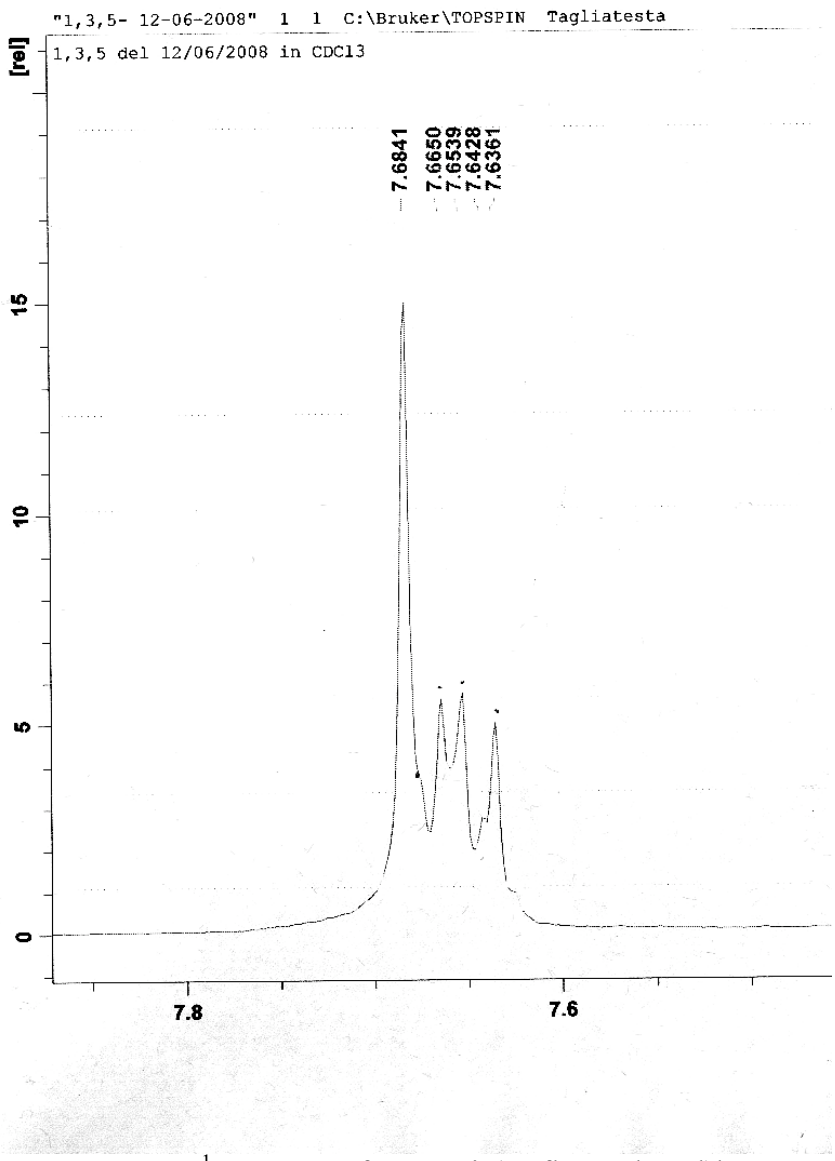


S8: ^{1}H-^{13}C HMBC spectra of 1,2,4-tris(4'-fluorophenyl)benzene

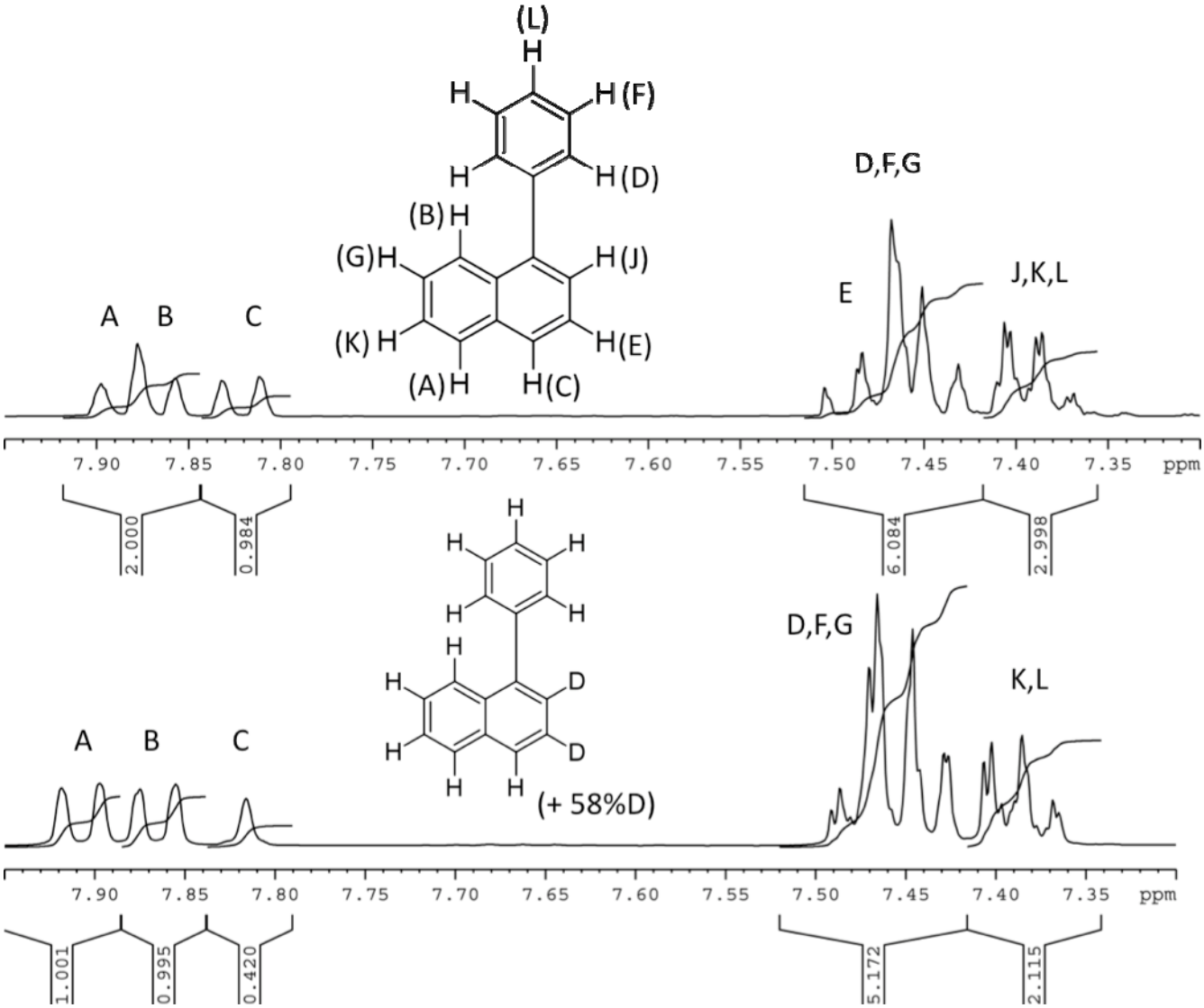


C-1	106.1	-245.5(C1-F)			
C-2	109.2	20.5(C2-F)	H-2	6.95	8.8(2-3), 8.9(2-F)
C-3	125.4	7.5(C3-F)	H-3	7.12	5.2(3-F)
C-4	131.0				
C-5	132.8				
C-6	125.4		H-6	7.47	8.0(6-7), ~1(6-9)
C-7	120.5		H-7	7.61	2.4(7-9)
C-8	133.9				
C-9	123.5		H-9	7.58	
C-10	134.3				
C-11	131.4				
C-12	125.5	7.5(C12-F)	H-12	7.15	8.8(12-13), 5.4(12-F)
C-13	109.2	20.5(C13-F)	H-13	6.96	8.7(13-F)
C-14	106.1	-245.5(C14-F)			
C-15	130.7				
C-16	123.0	7.8(C16-F)	H-16	7.63	8.8(16-17), 5.3(16-F)
C-17	110.1	20.3(C17-F)	H-17	7.16	8.5(17-F)
C-18	106.9	-244.0(C18-F)			

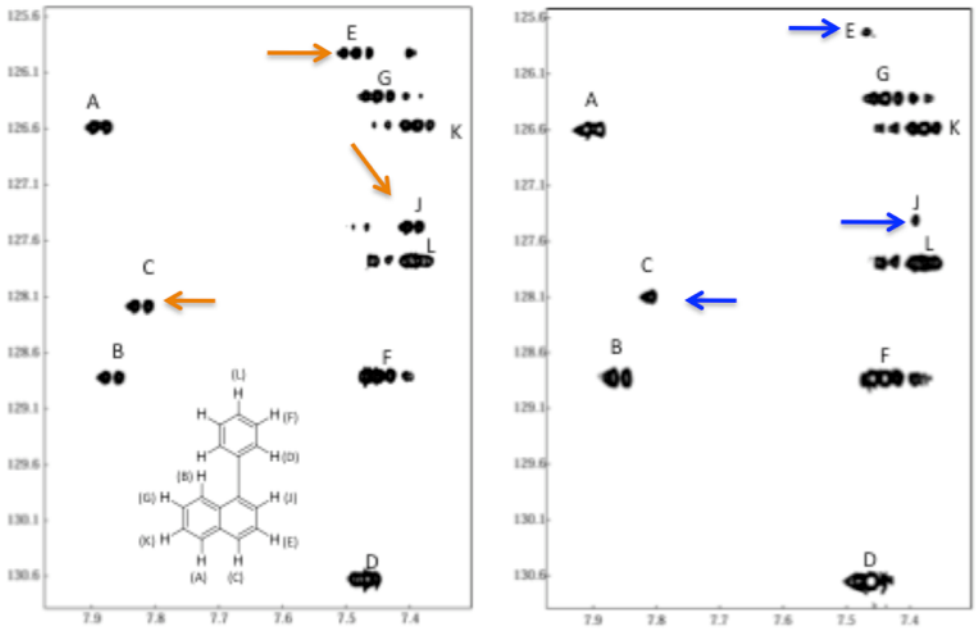




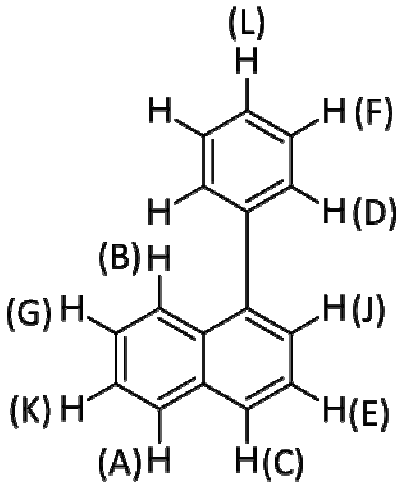
S9: ^{1}H spectra of 1,3,5-tris(4’-fluorophenyl)benzene



S10: ^{1}H spectra of 1-phenylnaphthalene with and without deuterium incorporation



S11: HSQC spectra of 1-phenylnaphthalene with and without deuterium incorporation



Proton	Integral H	Integral D
A	1.01	1.05
B	1.06	1.00
C	1.04	0.42
D	1.96	2.11
E	0.96	0.05
F	1.97	2.00
G	1.03	0.97
J	1.00	0.07
K	0.99	1.00
L	0.98	0.96