Supplemental materials

Synthesis and characterization

Chemicals: Phenol (99%) **(1a)** and phenol-$^{13}C_6$ (99ATM% ^{13}C) **(1b)** were purchased from Sigma Aldrich (St. Louis, MO, USA), 4-bromo-2-fluorophenol (99%) **(1c)**, 3-fluorophenol (98%) **(1f)** and 4-fluorophenol (99%) **(1g),** 1,4-dibromobenzene (99%) **(2a),** bromobenzene (99%) **(2b),** copper-(I)-bromide (98%), magnesium sulfate and $CDCl_3$ (99.8%) with TMS (0.03 %) from Acros (Morris Plains, NJ, USA), 1-fluorophenol (97%) **(1d)** from Maybridge (Morris Plains, NJ, USA) and 4-bromo-3-fluorophenol (97%) **(1e)** from Matrix Scientific (Columbia, SC, USA). Copper powder (mesh size 99,9%), potassium hydroxide (*p.a.*), methanol (*p.a.*), *n*-hexane (95%), acetonitrile, silica gel 60 Å C:C 40-63 µm were purchased from Fisher Chemical (Pittsburgh, PA, USA).

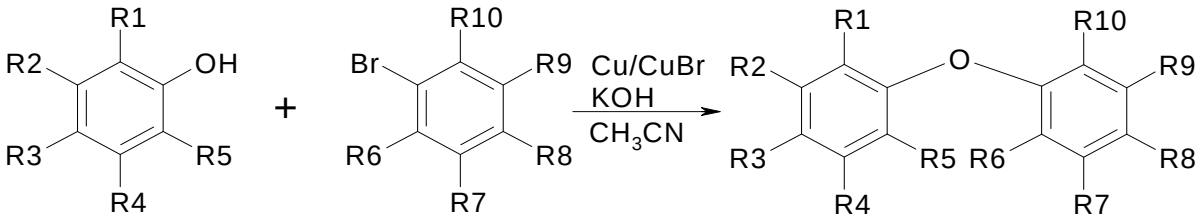
Synthesis: PBDE 3, $^{13}C_6$-isotopic labeled PBDE 3 ($^{13}C_6$-PBDE 3) and F-PBDEs 3, *i.e.* 2-fluoro-4-bromodiphenyl ether (3-2F), 2´-fluoro-4-bromodiphenyl ether (3-2´F), 3-fluoro-4-bromodiphenyl ether (3-3F), 3´-fluoro-4-bromodiphenyl ether (3-3´F) and 4´-fluoro-4-bromodiphenyl ether (3-4´F), were synthesized by nucleophilic substitution of bromobenzenes and by phenols. *General procedure:* A mixture of a phenol **(1a-g)** (10 mmol), potassium hydroxide (0.56 g, 10 mmol), bromobenzene **(2a,b)** (12 mmol), copper bromide (1.44 g, 10 mmol) and copper powder (0.64 g, 10 mmol) was heated under refluxing at 130°C for 2 h in acetonitrile. For the reaction equation and yields, see Fig. S1.

Synthesis monitoring and clean-up procedure: The reactions were monitored and the purity of all compounds was determined by gas chromatography (GC) and thin layer chromatography (TLC). A GC (Varian 3800 Palo Alto, CA, USA) equipped with a flame ionization detector (FID) was used. Separation was performed on a CP-sil 5CB column (Chrompack, Darmstadt, Germany) 20 m x 0.25 mm ID., 0.25 µm film thickness. Nitrogen

was used as carrier gas. The column temperature was programmed from 50 °C to 250 °C at 5 °C/min and hold for ten minutes. For TLC ALUGRAM SIL G/UV_{254}, (Machery-Nagel, Düren, Germany) was used as stationary and *n*-hexane as mobile phase. After the reaction was completed the mixture was suspended in diethyl ether and the solution filtered of the employed magnesium sulfate. The solution was evaporated under reduced pressure and the crude product purified by column chromatography on a silica gel column with *n*-hexane as mobile phase. Impurities formed by bromination were removed under reduced pressure using a kuegelrohr distillation. Flash chromatography was the method of choice for the purification processes. Silica gel was used as stationary and *n*-hexane as mobile phase. For 1 g of crude product ca. 300 g silica gel was used. All F-PBDEs 3 and PBDEs 3 were re-crystallized from methanol.

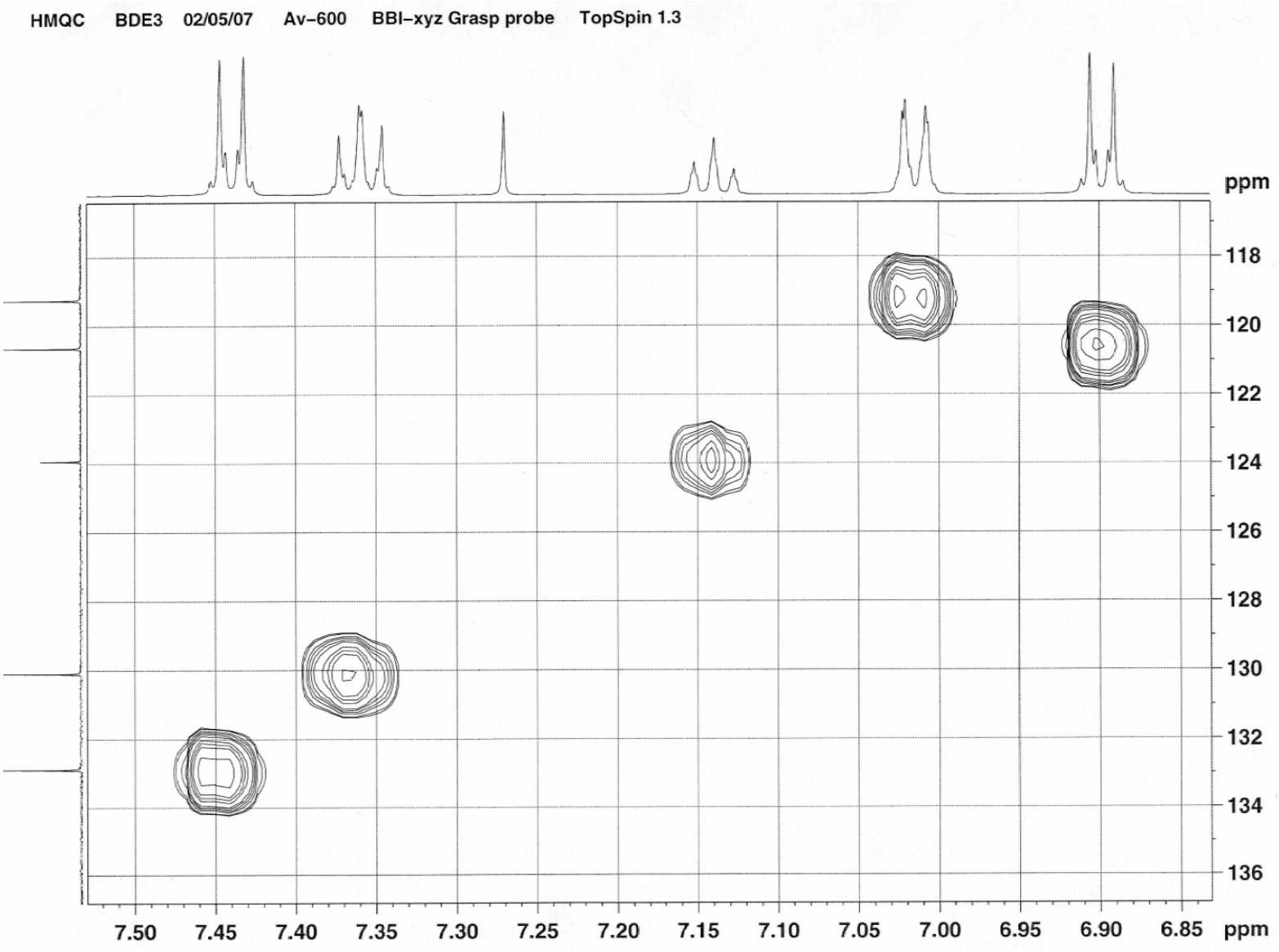
GC- MS characterization

Analysis of F-PBDEs and PBDEs were carried out on a Agilent Technologies 6890N Network GC-system (Agilent, Palo Alto, CA, USA) GC with Agilent Technologies 5975 inert MS detection and autosampler (Agilent). Briefly, 1 μl was injected splitless, 1 ug absolute. The injection temperature was set to 275 °C. Separation was performed on a CP-Sil 8 capillary column (50 m × 0.25 mm I.D., 0.25 μm film thickness). Helium was used as the carrier gas at a flow of 1.2 mL/min. The split was opened after 2 min. The column temperature for the CP Sil-8 was programmed from 45^{o}C to 245^{o}C with 20^{o}C/min. The final temperature was held for ten minutes. Detection was based on EI-MS-mode in the full scan mode (m/z 50-500). Hydrogen was used as reagent gas at a flow of 3 mL/min. The ion source temperature was 230^{o}C. A list of the main ions is given in the supplement materials.



PBDE/F-PBDE					starting materials	
no.	**BZ/BZL-no.**	**Substitution pattern**	**Yield[%]**	**Purity [%]**	**phenol**	**bromobenzene**
(3a)	PBDE 3	R1-7,9,10=H; R8=Br	59	99.5	**(1a)** R1-5=H	**(2a)** R6,7,9,10=H; R8=Br
(3b)	$^{13}C_6$-PBDE 3	R1-7,R9R10=H; R8=Br	60	99.5	**(1b)** R1-5=H (^{13}C)	**(2a)** R6,7,9,10=H; R8=Br
(3c)	F-PBDE 3-2F	R1=F; R2,4-10=H; R3=Br	54	99.9	**(1c)** R1=F; R2,4,5=H; R3=Br	**(2b)** R6-10=H
(3d)	F-PBDE 3-2´F	R1=F; R2-7,9,10=H; R8=Br	59	99.5	**(1d)** R1=F; R2-5=H	**(2a)** R6,7,9,10=H; R8=Br
(3e)	F-PBDE 3-3F	R1,4-10=H; R2=F; R3=Br	55	99.9	**(1e)** R1,4,5=H; R2=F; R3=Br	**(2b)** R6-10=H
(3f)	F-PBDE 3-3´F	R1,3-7,9,10=H; R2=F; R8=Br	60	99.2	**(1f)** R1,3-5=H; R2=F	**(2a)** R6,7,9,10=H; R8=Br
(3g)	F-PBDE 3-4´F	R1,2,4-7,9,10=H; R3=F; R8=Br	58	99.9	**(1g)** R1,2,4,5=H; R3=F	**(2a)** R6,7,9,10=H; R8=Br

Fig. S1: Synthesis of the PBDE 3, $^{13}C_6$-PBDE 3 and F-PBDEs 3 **(3a-g)** by nucleophilic substitution of bromobenzenes **(2a-b)** and phenols **(1a-g)**. For details, see Experimental section.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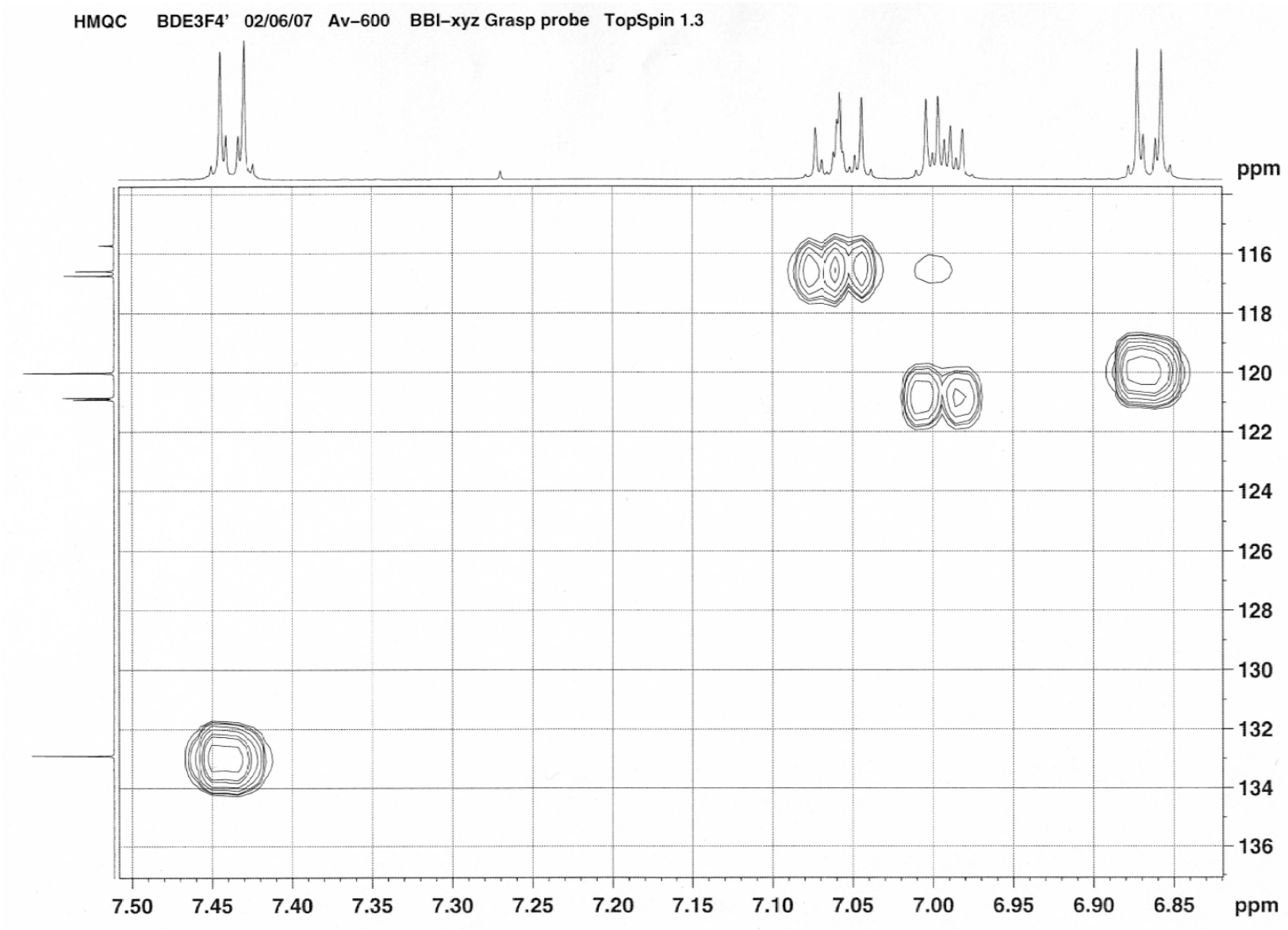
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118
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128
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7.50
7.45
7.40
7.35
7.30
7.25
7.20
7.15
7.10
7.05
7.00
6.95
6.90
6.85
ppm

^{1}H, ^{13}C and ^{19}F NMR and MS characterization

4-bromodiphenyl ether (PBDE 3): **^{1}H NMR ($CDCl_3$):** *δ 7.43* (H-3/5, 2H, *m*, ^{3}J=9.0Hz), *δ 7.35* (H3´/5´, 2H, *m*, ^{3}J=8.4Hz, ^{3}J=7.4Hz), *δ 7.13* (H4´, 1H, *tt*, ^{3}J=7.4Hz, ^{4}J=1.1Hz), *δ 7.00* (H2´/6´, 2H, *m*), *δ 6.89* (H2/6, 2H, *m*, ^{3}J=9.00); **MS (*m/z*)**: $[M+1]^{+\cdot}$ *249* (14 %), *251* (13 %), $[M]^{+\cdot}$ *248* (100 %), *250* (97 %) , $[M-1]^{+\cdot}$ *247* (2 %), *249* (14 %), $[M-C_2H_3]^{+\cdot}$ *221* (1 %), *223* (1 %), $[M-C_2H_4]^{+\cdot}$ *220* (3 %), *222* (3 %), $[M-C_6H_4]^{+\cdot}$ *172* (3 %), *174* (3 %), $[M-Br]^{+\cdot}$ *169* (8 %), $[M-HBr]^{+\cdot}$ *168* (12 %), $[M-CH_2Br]^{+\cdot}$ *155* (3 %), $[M-C_2Br]^{+\cdot}$ *145* (8 %), $[M-C_2HBr]^{+\cdot}$ *144* (1 %), $[M-C_2H_2Br]^{+\cdot}$ *143* (8 %), $[M-C_2H_3Br]^{+\cdot}$ *142* (8 %), $[M-C_2H_4Br]^{+\cdot}$ *141* (66 %), $[M-C_2H_5Br]^{+\cdot}$ *140* (3 %), $[M-C_2H_6Br]^{+\cdot}$ *139* (12 %), $[M]^{++}$ *124* (1 %), *125* (1 %), $[C_8H_7O]^{+\cdot}$ *119* (3 %), $[C_8H_5O]^{+\cdot}$ *117* (3 %), $[C_9H_7]^{+\cdot}$ *115* (28 %), $[C_6H_6O]^{+\cdot}$ *94* (3 %), $[C_6H_6]^{+\cdot}$ *78* (4 %), $[C_6H_5]^{+\cdot}$ *77* (57 %), $[C_6H_4]^{+\cdot}$ *76* (14 %), $[C_6H_3]^{+\cdot}$ *75* (14 %), $[C_4H_6O]^{+\cdot}$ *70* (6 %).

2-fluoro-4-bromodiphenyl ether (3-2F): **^{1}H NMR ($CDCl_3$)**: *δ 7.37* (H3, 1H, *dd*, $^{3}J_{H,F}$=10.0Hz, $^{4}J_{H,H}$=2.4Hz), *δ 7.35* (H-3´/5´, 2H, *m*, ^{3}J=8.4Hz, ^{3}J=7.4Hz), *δ 7.24* (H5, 1H, *ddd*, $^{3}J_{H,H}$=8.4Hz, $^{4}J_{H,H}$=2.2 Hz, $^{5}J_{H,F}$=1.5Hz) *δ 7.13* (H4´, 1H, *tt*, ^{3}J=7.4Hz, ^{4}J=1.0Hz), *δ 6.99* (H2´/6´, 2H, *m*), *δ 6.94* (H6, 1H, *dd* , $^{3}J_{H,H}$=8.4Hz, $^{3}J_{H,F}$=8.4Hz). **^{19}F NMR ($CDCl_3$):** *δ -128.05* (*ddd*, $^{3}J_{F,H2}$=10.0, $^{4}J_{F,H6}$=8.4, $^{5}J_{F,H5}$=1.5). **MS (*m/z*) :** $[M+1]^{+\cdot}$ *267* (13 %), *269* (12 %), $[M]^{+\cdot}$ *266* (100 %), *268* (97 %) , $[M-1]^{+\cdot}$ *265* (2 %), *267* (13 %), $[M-F]^{+\cdot}$ *247* (1 %), *249* (1 %), $[M-HF]^{+\cdot}$ *246* (2 %), *248* (2 %), $[M-C_2H_3]^{+\cdot}$ *239* (3 %), *241* (1 %), $[M-C_2H_4]^{+\cdot}$ *238* (11 %), *240* (11 %), $[M-C_2H_5]^{+\cdot}$ *237* (1 %), *239* (3 %),$[M-C_2H_4F]^{+\cdot}$ *219* (1 %), *221* (1 %), $[M-C_6H_4]^{+\cdot}$ *190* (2 %), *192* (2 %), $[M-C_6H_5]^{+\cdot}$ *189* (3 %), *191* (3 %), $[M-Br]^{+\cdot}$ *187* (3 %), $[M-HBr]^{+\cdot}$ *186* (5 %), $[M-C_6H_5O]^{+\cdot}$ *173* (1 %), *175* (1 %), $[M-C_2Br]^{+\cdot}$ *163* (6 %), $[M-C_2HBr]^{+\cdot}$ *162* (1 %), $[M-C_2H_2Br]^{+\cdot}$ *161* (7 %), $[M-C_2H_3Br]^{+\cdot}$ *160* (6 %), $[M-C_2H_4Br]^{+\cdot}$ *159* (49 %), $[M-C_2H_5Br]^{+\cdot}$ *158* (2 %), $[M-C_2H_6Br]^{+\cdot}$ *157* (7 %), $[C_8H_8FO]^{+\cdot}$ *139* (8 %), $[C_9H_6F]^{+\cdot}$ *133* (14 %),

$[M]^{++}$ *133* (14 %), $[C_6H_6O]^{+\cdot}$ *94* (10 %), $[C_6H_6]^{+\cdot}$ *78* (4 %), $[C_6H_5]^{+\cdot}$ *77* (62 %), $[C_6H_4]^{+\cdot}$ *76* (3 %), $[C_6H_3]^{+\cdot}$ *75* (3 %), $[C_4H_6O]^{+\cdot}$ *70* (6 %).

2´-fluoro-4-bromodiphenyl ether (3-2´F): **^{1}H NMR ($CDCl_3$):** *δ 7.43* (H-3/5, 2H, *m*, ^3J=9.0Hz), *δ 7.22-7.12* (H3´,4´,5´, 3H, *m*, ^3J=8.3Hz, ^4J=6.7Hz), *δ 7.09* (H6´, 1H, *ddd*, ^3J=7.8Hz, $^4J_{F,H}$=7.8Hz, $^4J_{H,H}$=2.0Hz), *δ 6.87* (H2/6, 2H, *m*, ^3J=9.00). **^{19}F NMR ($CDCl_3$):** *δ -130.68* (*m*) non-symmetrically. **MS (m/z):** $[M+1]^{+\cdot}$ *267* (13 %), *269* (12 %), $[M]^{+\cdot}$ *266* (100 %), *268* (98 %), $[M-1]^{+\cdot}$ *267* (13 %), $[M-F]^{+\cdot}$ *247* (>1%), *249* (>1 %), $[M-HF]^{+\cdot}$ *246* (2 %), *248* (2 %), $[M-C_2H_4]^{+\cdot}$ *238* (2 %), *240* (2 %), $[M-C_2H_5]^{+\cdot}$ *237* (>1 %), *239* (>1 %), $[M-C_2H_4F]^{+\cdot}$ *219* (>1 %), *221* (>1 %), $[M-Br]^{+\cdot}$ *187* (5 %), $[M-HBr]^{+\cdot}$ *186* (7 %), $[M-C_6H_3F]^{+\cdot}$ *172* (1 %), *174* (1 %), $[M-C_6H_4F]^{+\cdot}$ *171* (2 %), *173* (2 %), $[M-C_2H_2Br]^{+\cdot}$ *161* (1 %), $[M-C_2H_3Br]^{+\cdot}$ *160* (9 %), $[M-C_2H_4Br]^{+\cdot}$ *159* (78 %), $[M-C_2H_5Br]^{+\cdot}$ *158* (3 %), $[M-C_2H_6Br]^{+\cdot}$ *157* (18 %), $[M-C_6H_4OF]^{+\cdot}$ *155* (11 %), *157* (18 %), $[C_8H_8FO]^{+\cdot}$ *139* (8 %), $[C_9H_6F]^{+\cdot}$ *133* (24 %), $[M]^{++\cdot}$ *133* (24 %), $[C_8H_7O]^{+\cdot}$ *119* (3 %), $[C_8H_5O]^{+\cdot}$ *117* (3 %), $[C_6H_5F]^{+\cdot}$ 96 (1 %), $[C_6H_4F]^{+\cdot}$ 95 (8 %), $[C_6H_6O]^{+\cdot}$ *94* (12 %), $[C_6H_5]^{+\cdot}$ *77* (2 %), $[C_6H_4]^{+\cdot}$ *76* (21 %), $[C_6H_3]^{+\cdot}$ *75* (36 %).

3-fluoro-4-bromodiphenyl ether (3-3F): **^{1}H NMR ($CDCl_3$):** *δ 7.45* (H5, 1H, *dd*, $^3J_{H,H}$=8.0Hz, $^4J_{H,F}$=8.7Hz), *δ 7.38* (H-3´/5´, 2H, *m*, ^3J=8.4Hz, ^3J=7.4Hz), *δ 7.17* (H4´, 1H, *tt*, ^3J=7.4Hz, ^4J=1.1Hz), *δ 7.03* (H2´/6´, 2H, *m*), *δ 6.76* (H2, 1H, *dd*, $^3J_{H,F}$=9.8Hz, $^4J_{H,H}$ =2.7Hz,) *δ 6.69* (H6, 1H, *ddd*, $^3J_{H,H}$=8.7Hz, $^4J_{H,H}$=2.7 Hz$^5J_{H,F}$=1.1Hz). **^{19}F NMR ($CDCl_3$):** *δ -104.64* (*ddd*, $^3J_{F,H2}$=9.8, $^4J_{F,H5}$=8.7, $^5J_{F,H6}$=1.1). **MS (*m/z*):** $[M+1]^{+\cdot}$ *267* (15 %), *269* (12 %), $[M]^{+\cdot}$ *266* (100 %), *268* (96 %) , $[M-1]^{+\cdot}$ *265* (2 %), *267* (15 %), $[M-C_2H_3]^{+\cdot}$ *239* (2 %), *241* (1 %), $[M-C_2H_4]^{+\cdot}$ *238* (4 %), *240* (4 %), $[M-C_2H_5]^{+\cdot}$ *237* (1 %), *239* (2 %), $[M-C_6H_4]^{+\cdot}$ *190* (2 %), *192* (2 %), $[M-C_6H_5]^{+\cdot}$ *189* (1 %), *191* (1 %), $[M-Br]^{+\cdot}$ *187* (6 %), $[M-HBr]^{+\cdot}$ *186* (12 %), [M-

$C_6H_5O]^{+\cdot}$ *173* (1 %), *175* (1 %), $[M\text{-}C_2Br]^{+\cdot}$ *163* (4 %), $[M\text{-}C_2HBr]^{+\cdot}$ *162* (1 %), $[M\text{-}C_2H_2Br]^{+\cdot}$ *161* (5 %), $[M\text{-}C_2H_3Br]^{+\cdot}$ *160* (7 %), $[M\text{-}C_2H_4Br]^{+\cdot}$ *159* (55 %), $[M\text{-}C_2H_5Br]^{+\cdot}$ *158* (2 %), $[M\text{-}C_2H_6Br]^{+\cdot}$ *157* (8 %), $[C_8H_8FO]^{+\cdot}$ *139* (6 %), $[C_9H_6F]^{+\cdot}$ *133* (16 %), $[M]^{++}$ *133* (16 %), $[C_6H_6O]^{+\cdot}$ *94* (17 %), $[C_6H_6]^{+\cdot}$ *78* (4 %), $[C_6H_5]^{+\cdot}$ *77* (56 %), $[C_6H_4]^{+\cdot}$ *76* (2 %), $[C_6H_3]^{+\cdot}$ *75* (3 %), $[C_4H_6O]^{+\cdot}$ *70* (6 %).

3´-fluoro-4-bromodiphenyl ether (3-3´F): **^{1}H NMR ($CDCl_3$):** δ *7.48* (H-3/5, 2H, *m*, ^3J=9.0Hz), δ *7.30* (H5´, 1H, *ddd*, ^3J=8.3Hz, ^4J=6.7Hz), δ *6.94* (H2/6, 2H, *m*, ^3J=9.00), δ *6.84* (H4´, 1H, *dddd*, $^3J_{H;H}$=$^3J_{H;F}$ =8.3Hz, $^4J_{H,H}$=2.4Hz,), δ *6.79* (H6´, 1H, *dd*, ^3J=8.3Hz,) δ *6.72* (H2´, 1H, *ddd*, $^3J_{F,H}$=10.0Hz, $^4J_{H,H}$=2.4Hz). **^{19}F NMR ($CDCl_3$):** δ *-110,84* (*ddd*, $^3J_{F,H2´}$=10.0, $^3J_{F,H4´}$=8.3, $^4J_{F,H5´}$=6.6). **MS (*m/z*):** $[M+1]^{+\cdot}$ *267* (13 %), *269* (12 %), $[M]^{+\cdot}$ *266* (100 %), *268* (95 %) , $[M\text{-}1]^{+\cdot}$ *267* (13 %), $[M\text{-}HF]^{+\cdot}$ *246* (>1 %), *248* (>1 %), $[M\text{-}C_2H_3]^{+\cdot}$ *239* (2 %), *241* (1 %), $[M\text{-}C_2H_4]^{+\cdot}$ *238* (5 %), *240* (5 %), $[M\text{-}C_2H_5]^{+\cdot}$ *237* (1 %), *239* (2 %), $[M\text{-}C_2H_4F]^{+\cdot}$ *219* (1 %), *221* (1 %), $[M\text{-}Br]^{+\cdot}$ *187* (6 %), $[M\text{-}HBr]^{+\cdot}$ *186* (10 %), $[M\text{-}C_6H_3F]^{+\cdot}$ *172* (3 %), *174* (3 %), $[M\text{-}C_6H_4F]^{+\cdot}$ *171* (1 %), *173* (1 %), $[M\text{-}C_2H_2Br]^{+\cdot}$ *161* (1 %), $[M\text{-}C_2H_3Br]^{+\cdot}$ *160* (7 %), $[M\text{-}C_2H_4Br]^{+\cdot}$ *159* (56 %), $[M\text{-}C_2H_5Br]^{+\cdot}$ *158* (2 %), $[M\text{-}C_2H_6Br]^{+\cdot}$ *157* (12 %), $[M\text{-}C_6H_4OF]^{+\cdot}$ *155* (5 %), *157* (12 %), $[C_8H_8FO]^{+\cdot}$ *139* (5 %), $[C_9H_6F]^{+\cdot}$ *133* (16 %), $[M]^{++}$ *133* (16 %), $[C_8H_7O]^{+\cdot}$ *119* (2 %), $[C_8H_5O]^{+\cdot}$ *117* (2 %), $[C_6H_5F]^{+\cdot}$ 96 (1 %), $[C_6H_4F]^{+\cdot}$ 95 (10 %), $[C_6H_6O]^{+\cdot}$ *94* (6 %), $[C_6H_5]^{+\cdot}$ *77* (1 %), $[C_6H_4]^{+\cdot}$ *76* (8 %), $[C_6H_3]^{+\cdot}$ *75* (18 %).

4´-fluoro-4-bromodiphenyl ether (3-4´F): **^{1}H NMR ($CDCl_3$):** δ 7.41 (H-3/5, 2H, *dt*, ^3J=9.0Hz), δ 7.07-6.93 (H2´,3´,5´,6´, 4H, *m*), δ 6.83 (H2/6, 2H, *dt*, ^3J=9.00). **^{19}F NMR ($CDCl_3$):** δ -104.64 (*dddd*, 2H $^3J_{F,H3´/5´}$=8.0, $^4J_{F,H2´/6´}$=4.6). **MS (*m/z*):** $[M+1]^{+\cdot}$ *267* (13 %), *269* (11 %), $[M]^{+\cdot}$ *266* (100 %), *268* (95 %) , $[M\text{-}1]^{+\cdot}$ *267* (13 %) $[M\text{-}C_2H_3]^{+\cdot}$ *239* (1 %), *241*

(>1 %), $[M\text{-}C_2H_4]^{+\cdot}$ *238* (1 %), *240* (1 %), $[M\text{-}C_2H_5]^{+\cdot}$ *237* (1 %), *239* (1 $[M\text{-}Br]^{+\cdot}$ *187* (4 %), $[M\text{-}HBr]^{+\cdot}$ *186* (6 %), $[M\text{-}C_6H_3F]^{+\cdot}$ *172* (2 %), *174* (2 %), $[M\text{-}C_6H_4F]^{+\cdot}$ *171* (1 %), *173* (1 %), $[M\text{-}C_2H_2Br]^{+\cdot}$ *161* (>1 %), $[M\text{-}C_2H_3Br]^{+\cdot}$ *160* (6 %), $[M\text{-}C_2H_4Br]^{+\cdot}$ *159* (53 %), $[M\text{-}C_2H_5Br]^{+\cdot}$ *158* (3 %), $[M\text{-}C_2H_6Br]^{+\cdot}$ *157* (12 %), $[M\text{-}C_6H_4OF]^{+\cdot}$ *155* (6 %), *157* (12 %), $[C_8H_8FO]^{+\cdot}$ *139* (4 %), $[C_9H_6F]^{+\cdot}$ *133* (16 %), $[M]^{++}$ *133* (16 %), $[C_8H_7O]^{+\cdot}$ *119* (2 %), $[C_8H_5O]^{+\cdot}$ *117* (2 %), $[C_6H_5F]^{+\cdot}$ 96 (1 %), $[C_6H_4F]^{+\cdot}$ 95 (8 %), $[C_6H_6O]^{+\cdot}$ *94* (7 %), $[C_6H_5]^{+\cdot}$ *77* (1 %), $[C_6H_4]^{+\cdot}$ *76* (10 %), $[C_6H_3]^{+\cdot}$ *75* (18 %).

4-bromodiphenyl ether $^{13}C_6$ (PBDE 3): **^{1}H NMR ($CDCl_3$):** *δ 7.43* (H-3/5, 2H, *m*, ^3J=9.0Hz), *δ 7.35* (H3´/5´, 2H, *m*, ^3J=8.4Hz, ^3J=7.4Hz), *δ 7.13* (H4´, 1H, *tt*, ^3J=7.4Hz, ^4J=1.1Hz), *δ 7.00* (H2´/6´, 2H, *m*), *δ 6.89* (H2/6, 2H, *m*, ^3J=9.00); **MS (*m/z*)**: $[M+1]^{+\cdot}$ *255* (14 %), *257* (13 %), $[M]^{+\cdot}$ *254* (100 %), *256* (97 %) , $[M-1]^{+\cdot}$ *253* (2 %), *255* (14 %), $[M\text{-}C_2H_3]^{+\cdot}$ *221* (1 %), *223* (1 %), $[M\text{-}C_2H_4]^{+\cdot}$ *220* (3 %), *222* (3 %), $[M\text{-}Br]^{+\cdot}$ *175* (7 %), $[M\text{-}HBr]^{+\cdot}$ 174 (14 %), $[M\text{-}C_6H_4]^{+\cdot}$ *172* (3 %), *174* (14 %), $[M\text{-}C_6H_5]^{+\cdot}$ *171* (1 %), *173* (1 %), $[M\text{-}^xC_2H_yBr]^{+\cdot}$ *148* (1 %), *147* (24 %), *146* (25 %), *145* (12 %), *144* (5 %), *143* (5 %), (x=13,12.5,12;y=1-6), $[M\text{-}CH_2Br]^{+\cdot}$ *155* (2 %), $[M\text{-}C_2Br]^{+\cdot}$ *145* (8 %), $[M\text{-}C_2HBr]^{+\cdot}$ *144* (1 %), $[M\text{-}C_2H_2Br]^{+\cdot}$ *143* (8 %), $[M\text{-}C_2H_3Br]^{+\cdot}$ *142* (8 %), $[M\text{-}C_2H_4Br]^{+\cdot}$ *141* (66 %), $[M\text{-}C_2H_5Br]^{+\cdot}$ *140* (3 %), $[M\text{-}C_2H_6Br]^{+\cdot}$ *139* (12 %), $[M]^{++}$ *127* (1 %), *128* (1 %), $[C_8H_7O]^{+\cdot}$ *119* (3 %), $[C_8H_5O]^{+\cdot}$ *117* (3 %), $[C_9H_7]^{+\cdot}$ *115* (28 %), $[^{13}C_6H_6O]^{+\cdot}$ 100 (2 %), $[C_6H_4O]^{+\cdot}$ *92* (2 %), $[^{13}C_6H_5]^{+\cdot}$ 83 (31 %), $[^{13}C_6H_4]^{+\cdot}$ 82 (3 %), $[^{13}C_6H_3]^{+\cdot}$ 81 (2 %), $[C_6H_5]^{+\cdot}$ *77* (2 %), $[C_6H_4]^{+\cdot}$ *76* (8 %), $[C_6H_3]^{+\cdot}$ *75* (8 %).

References of for Table 4

None (X_{1-4} = H)

ATOWAH
BEQYOL
CEJJKX
CEJKEI
DILDOR
EMOFER
ENANUC
EYADUD
FANYAU
FANYEZ
FANYID
FANYOJ
FEFPEM
FEFPEMOI
MIRNAC
MISVEP
NOTHIM
NESGUN
NIBFIN
NPHOPN
PBRPHEO1
SUCVER
SUSCIS
SUSNID
TAPMED
TAPMIH
TAMPON
TAPMUT
FIMQIC
FUDQIE
FUDQOK
FUDQHQ
FUHTIH
FUQBOI
FUQBOIO1
ICAKOM
IXOGAD
IXOGADOI
JAKPIV
JAKPOB
JAKPUH
JAQDAH
JAQDAHO1
JEJWIE
JEJWIEO1

KOWVEX
QIKHOH
RAFFIO
RAFFIO1
TAPNAA
TAPNEE
TAPNII
TAPNOX
TAPNUU
TAPPAC
TAPPET
TAPPIK
TAPPOQ
TAPPUW
TAPQAD
TAPQEH
TAPQIL
TAPQOR
TAPQUX
TAPRAE
TAPREI
TAPRIM
TAPROS
TAPRUY
TAPSAF
TUBQUC
TUBREN
VALZAN
XALTIN
YADDEM
YADDOW
YAFMEY
YUSKUS
YUSKUSO1
LENNAU
YEYTIG

X_1 = F, $X_{2\text{-}4}$ = H
ADEMEC
IDUCIU
IDUJEX
IDUKRU
JOJVAF
MEFSIA
XAVLUC
LENKAR
PELZIQ
PELZOW

VEMCEW

$X_{1,2}$ = F, $X_{3,4}$ = H
UGEHUJ
DILDOR
DILDIL
ASIKOC

$X_{1,3}$ = F, $X_{2,4}$ = H
none

X_{1-3} = F, X_4 = H
none

X_{1-4} = F
ELAQIR
ELAQOX
ELARAK
ELAREO
IBOMOB
IBOMUH
IBONAO
IBONES
IBONIW
IBONOC
NAXDAS
RIBTAX
RIBTEB
RIBTIF
RIBTUR
RIBVAZ
RIBVED
RIBVIH
RIBVON
RUBVUT
WONYIH
WONYON
WONYUT

X_1 = Cl, X_{2-4} = H
BAJYOA
FIPXIL
GAWQAX
IZEMIJO1
QANMOI
RAFXND
UDANOD
XEHQIL

YEBGOD
YEBUGUH
YEBHAO
DELNOY
SESQOX

$X_{1,2}$ = Cl, $X_{3,4}$ = H
CMNPCB

$X_{1,3}$ = Cl, $X_{2,4}$ = H
GICLUZ
KRJES
YEBHOC

X_{1-3} = Cl, X_4 = H
none

X_{1-4} = Cl
none

X_1 =Br, X_{2-4} = H
DATDEI
PUYZUE
SUCVOB

$X_{1,2}$ = Br, $X_{3,4}$ = H
EDATIM
FACWOW
HOHWUE
WOYWOW

$X_{1,3}$ = Br, $X_{2,4}$ = H
IZAPAA
SUCVIV
TOQBAC

X_{1-3} = Br, X_4 = H
none

X_{1-4} = Br
COCDED
COCDEDO1

X_1 = methyl, X_{2-4} = H
DATDAE
LAVSEH
DEXTUW
GEQDOW

$X_{1,2}$ = methyl, $X_{3,4}$ = H
FETXOS
HUFNAX
MXMTRE

$X_{1,3}$ = methyl, $X_{2,4}$ = H
QAMNUN

X_{1-3} = methyl, X_4 = H
none

X_{1-4} = methyl
none