Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information (ESI):

Regioselectivity Control of Radiation-Induced Reaction: Electron Beam-Induced Fries Rearrangement of Sulfonamide within β-Cyclodextrin Inclusion Complex

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Experimental

Materials and Measurements. Benzenesulfonanilide (BSA) and phenyl *p*-toluenesulfonate (PTS) were purified by recrystallization from MeOH/H_2O. *p*-Toluenesulfonanilide (TSA) was prepared from *p*-toluenesulfonyl chloride and aniline following the previously reported procedure.[S1] Organic solvents were purified by standard procedures. All the other chemicals were purchased from TCI and used directly unless otherwise noted.

NMR spectra were recorded using a JEOL GSX270W NMR (^{1}H, 270 MHz; ^{13}C, 67.8 MHz) spectrometer. X-ray diffraction (XRD) patterns were measured using a Rigaku CN2013 diffractometer. Gas chromatography (GC) measurement carried out with a Shimadzu GC-1700AF equipped with FID by using a J&W Scientific DB-1 capillary column. GC-MS analysis was performed with a Shimadzu GCMS-QP5000.

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Characterization Data of EB-Fries Rearrangement Products.

2-Aminophenyl phenyl sulfone (*o*-Fries product from BSA): ^{1}H NMR ($CDCl_3$, TMS) δ 7.92 (d, *J* = 8 Hz, 2H, ArH), 7.83 (d, *J* = 8 Hz, 1H, ArH), 7.57-7.44 (m, 3H, ArH), 7.27 (t, *J* = 8 Hz, 1H, ArH), 6.77 (t, *J* = 8 Hz, 1H, ArH), 6.64 (d, *J* = 8 Hz, 1H, ArH), 4.96 (br, 2H, $-NH_2$). ^{13}C NMR ($CDCl_3$, TMS) δ 146.3, 141.8, 135.0, 133.1, 129.9, 129.0, 126.8, 121.8, 117.8, 117.7. MS (EI) *m/z* 233 (M^+), 168, 92, 80, 65, 51.

4-Aminophenyl phenyl sulfone (*p*-Fries product from BSA): ^{1}H NMR (Acetone-d_6, TMS) δ 7.91-7.88 (m, 2H, ArH), 7.64 (d, *J* = 8 Hz, 2H, ArH), 7.57-7.51 (m, 3H, ArH), 6.75 (d, *J* = 8 Hz, 2H, ArH), 5.52 (br, 2H, $-NH_2$). ^{13}C NMR (Acetone-d_6, TMS) δ 154.2, 145.0, 133.2, 130.6, 130.0, 128.5, 127.7, 114.3. MS (EI) *m/z* 233 (M^+), 140, 108, 92, 80, 65, 51.

2-Aminophenyl 4-tolyl sulfone (*o*-Fries product from TSA): ^{1}H NMR ($CDCl_3$, TMS) δ 7.84-7.79 (m, 3H, ArH), 7.28-7.25 (m, 3H, ArH), 6.77 (t, *J* = 8 Hz, 1H, ArH), 6.63 (d, *J* = 8 Hz, 1H, ArH), 5.10 (br, 2H, $-NH_2$), 2.38 (s, 3H, $-CH_3$). ^{13}C NMR ($CDCl_3$, TMS) δ 146.1, 144.0, 138.8, 134.8, 129.8, 129.7, 126.9, 122.3, 117.8, 117.5, 21.6. MS (EI) *m/z* 247 (M^+), 182, 167, 139, 91, 80, 65.

4-Aminophenyl 4-tolyl sulfone (*p*-Fries product from TSA): ^{1}H NMR ($CDCl_3$, TMS) δ 7.77 (d, *J* = 8 Hz, 2H, ArH), 7.68 (d, *J* = 8 Hz, 2H, ArH), 7.25 (d, *J* = 8 Hz, 2H, ArH), 6.64 (d, *J* = 8 Hz, 2H, ArH), 4.06 (br, 2H, $-NH_2$), 2.37 (s, 3H, $-CH_3$). ^{13}C NMR ($CDCl_3$, TMS) δ 150.9, 143.3, 140.0, 129.9, 129.7, 127.1, 114.2, 21.5. MS (EI) *m/z* 247 (M^+), 140, 108, 92, 80, 65.

2-Hydroxyphenyl 4-tolyl sulfone (*o*-Fries product from PTS): ^{1}H NMR (Acetone-d_6, TMS) δ 9.46 (s, 1H, -OH), 7.91-7.88 (m, 3H, ArH), 7.50 (t, *J* = 8 Hz, 1H, ArH), 7.40 (d, *J* = 8 Hz, 2H, ArH), 7.05 (t, *J* = 8 Hz, 1H, ArH), 6.99 (d, *J* = 8 Hz, 1H, ArH), 2.40 (s, 3H, $-CH_3$). ^{13}C NMR (Acetone-d_6, TMS) δ 156.4, 145.2, 140.1, 136.5, 130.5, 130.0, 128.6, 127.2, 120.9, 118.9, 21.4. MS (EI) *m/z* 248 (M^+), 181, 108, 92, 77, 65, 51.

4-Hydroxyphenyl 4-tolyl sulfone (*p*-Fries product from PTS): ^{1}H NMR (Acetone-d_6, TMS) δ 9.53 (s, 1H, -OH), 7.81 (d, *J* = 8 Hz, 4H, ArH), 7.38 (d, *J* = 8 Hz, 2H, ArH), 6.99 (d, *J* = 8 Hz, 2H, ArH), 2.38 (s, 3H, $-CH_3$). ^{13}C NMR ($CDCl_3$, TMS) δ 162.7, 144.6, 141.2, 133.7, 130.8, 130.7, 128.1, 116.8, 21.4. MS (EI) *m/z* 248 (M^+), 141, 108, 92, 77, 65, 51.

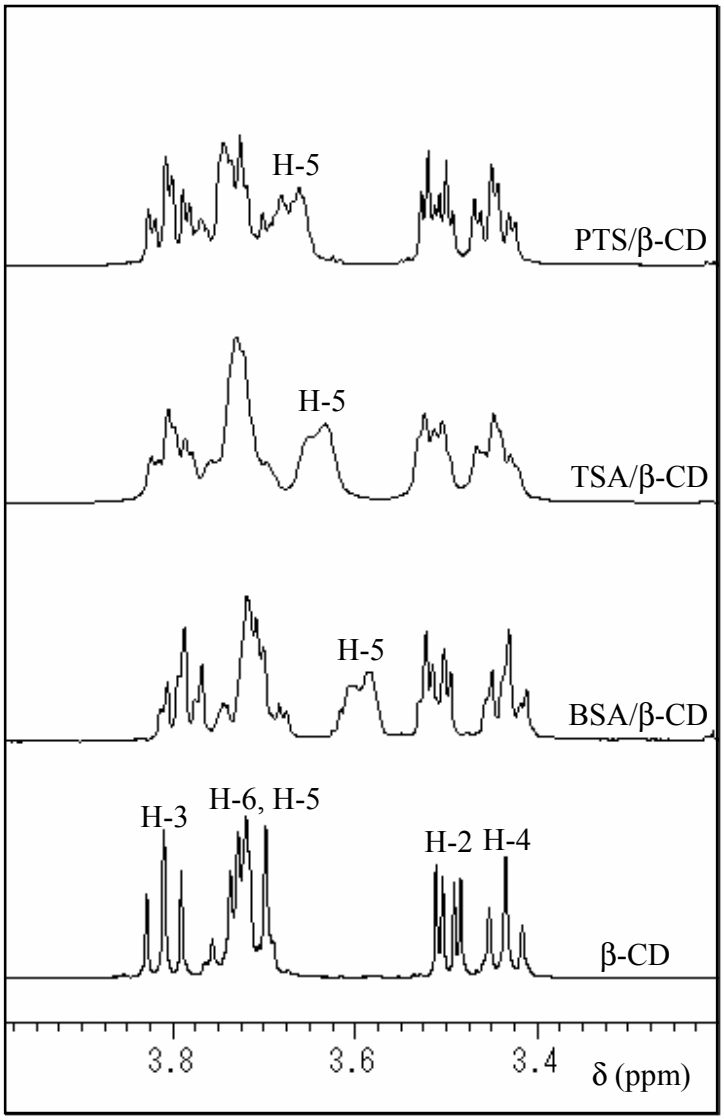


Fig. S1 ^{1}H NMR spectra of β-CD moieties in the inclusion complexes.

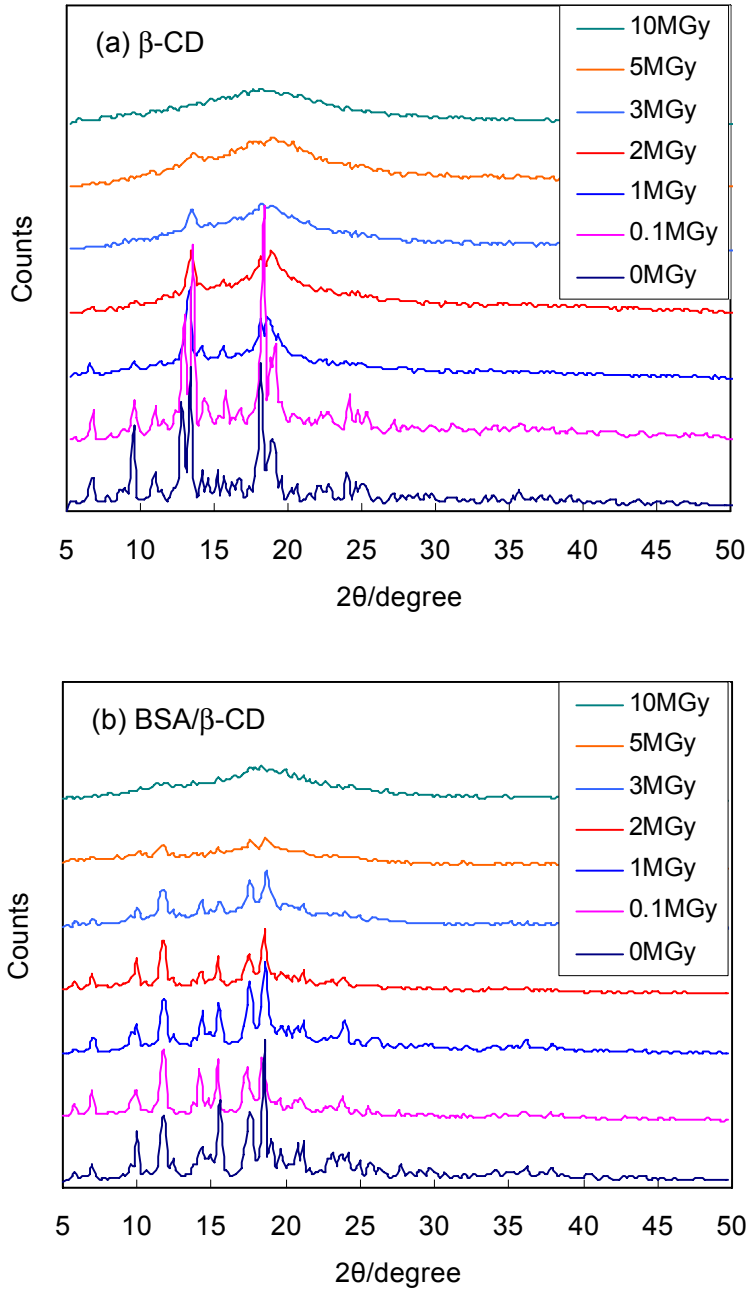
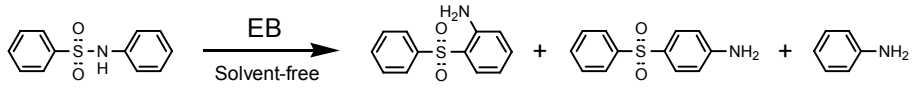


Fig. S2 Change in X-ray diffraction patterns during EB irradiation: (a) β-CD and (b) BSA/β-CD inclusion complex.

Table S1 Product distribution upon the EB-Fries rearrangement of BSA within β-CD inclusion complex[a]



Entry	EB dose[b] (MGy)	Conv.[c] (%)	EB-products[c] (%)			*ortho*:*para*	Proportion of amines (%)
			o-Fries	*p*-Fries	Aniline		
1	0.1	7.8	N.D.[d]	N.D.[d]	35.8	-	36
2	1	46	12.9	20.9	36.2	1 : 1.6	70
3	2	64	16.5	27.5	41.8	1 : 1.7	86
4	3	83	11.7	19.7	26.0	1 : 1.7	57
5	5	93	7.7	13.0	12.9	1 : 1.7	34
6	10	97	6.1	9.5	6.0	1 : 1.6	22

[a] Determined by GC. [b] Absorbed EB dose. [c] Calculated on the consumed BSA.
[d] Not detected.

Reference

(S1) M. Neeman, A. Modiano, *J. Org. Chem.*, 1956, **21**, 667.