Electronic Supplementary Information

Hydrogen Bonding Promoted Simple and Clean Photo-Induced Reduction of C–X Bond with Isopropanol

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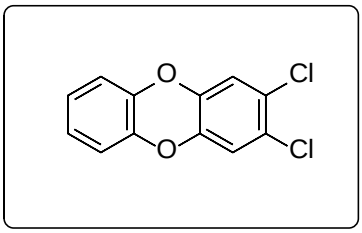
Ⅰ. General methods

All reagents and solvents were purchased from commercial sources (Adamas-beta, TCI, Alfa and Ark) and used without further purification unless otherwise stated. NMR spectra were recorded on Bruker AV300, Bruker AV400 spectrometer and the chemical shifts were reported in parts per million (δ) relative to internal standard TMS (0 ppm) in $CDCl_3$. All reactions were monitored by thin-layer chromatography (TLC). Column chromatography was performed on silica gel (200-300 mesh) and visualized with ultraviolet light. Ethyl acetate and petroleum ether were used as eluents. GC-MS analyses were performed with a Thermo TRACE 1300 ISQ LT spectrometer. All solvents were purified and dried by standard techniques.

Ⅱ. Synthesis of the dibenzo[b,e][1,4]dioxin substrates [1,2]

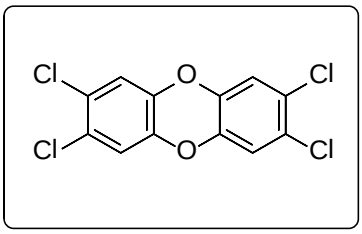
4,5-Dichlorocatechol: To an ice-cooled solution (maintained under nitrogen) of catechol (3.75 g, 32.5 mmol) in anhydrous ether (15 mL) was added, dropwise, with stirring over a period of 120 min, sulphuryl chloride (5.8 mL, 72 mmol), which was distilled under nitrogen before use. The solution was allowed to warm to room temperature and was concentrated under nitrogen. The crystalline precipitate that formed on standing was collected to afford 4,5-dichlorocatechol.

2,3-Dichlorodibenzo[b,e][1,4]dioxin and 2,3,7,8-tetrachlorodibenzo[b,e]-[1,4]dioxin: Condensation of catechol (10 mmol) or 4,5-dichlorocatechol (10 mmol) with 1,2,4-trichloro-5-nitrobenzene (5 mmol) in dimethyl sulfoxide (30 mL) in the presence of anhydrous potassium carbonate (22 mmol) was performed at 130 °C for 24 h. After the reaction the mixture was extracted with EtOAc/H_2O. The combined organic solvent was washed with brine, dried with Na_2SO_4, and then concentrated under reduced pressure to produce the product.



2,3-Dichlorodibenzo[b,e][1,4]dioxin

^{1}H NMR ($CDCl_3$, 600 MHz) δ: 6.94 (s, 2H), 6.92 (dd, *J* = 6.0, 3.6 Hz, 2H), 6.84 (dd, *J* = 6.0, 3.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 151 MHz) δ: 141.2 (2C) 126.4, 124.4 117.7, 116.5; ^{1}H NMR data are consistent with the literature. [3]



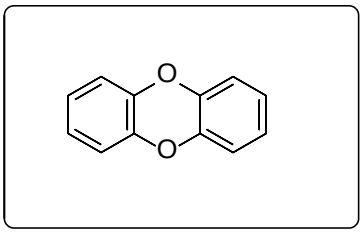
2,3,7,8-Tetrachlorodibenzo[b,e][1,4]dioxin

^{1}H NMR ($CDCl_3$, 600 MHz) δ: 6.97 (s, 4H). ^{13}C NMR ($CDCl_3$, 151 MHz) δ: 140.3, 127.3, 118.0; ^{1}H NMR data are consistent with the literature.[4]

Ⅲ. General procedure for the reduction of C–X bond

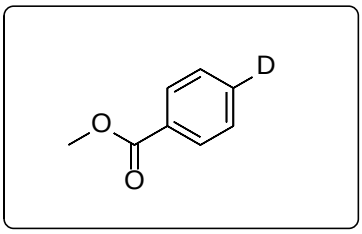
A 15 mL quartz tube was charged with a magnetic stir-bar, halogenated hydrocarbons (0.2 mmol) and isopropanol (1.5 mL). Then the tube was placed in a UV reactor at room temperature and the mixture was stirred for 12, 24 or 36 h. The, 10 mL of water was added to quench the reaction, and the mixture was extracted with EtOAc (5 mL ×4). The combined organic solvent was washed with brine, dried with Na_2SO_4, and then concentrated under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with petroleum ether : EtOAc (300:1-5:1) to afford the products.

Due to their poor solubility, when using 2,3-dichlorodibenzo[b,e][1,4]dioxin (0.03 mmol) and 2,3,7,8-tetrachlorodibenzo[b,e][1,4]dioxin (0.025 mmol) as raw materials, isopropanol (1.5 mL) and DMF (1 mL) were used as mixture solvent.



Dibenzo[b,e][1,4]dioxin

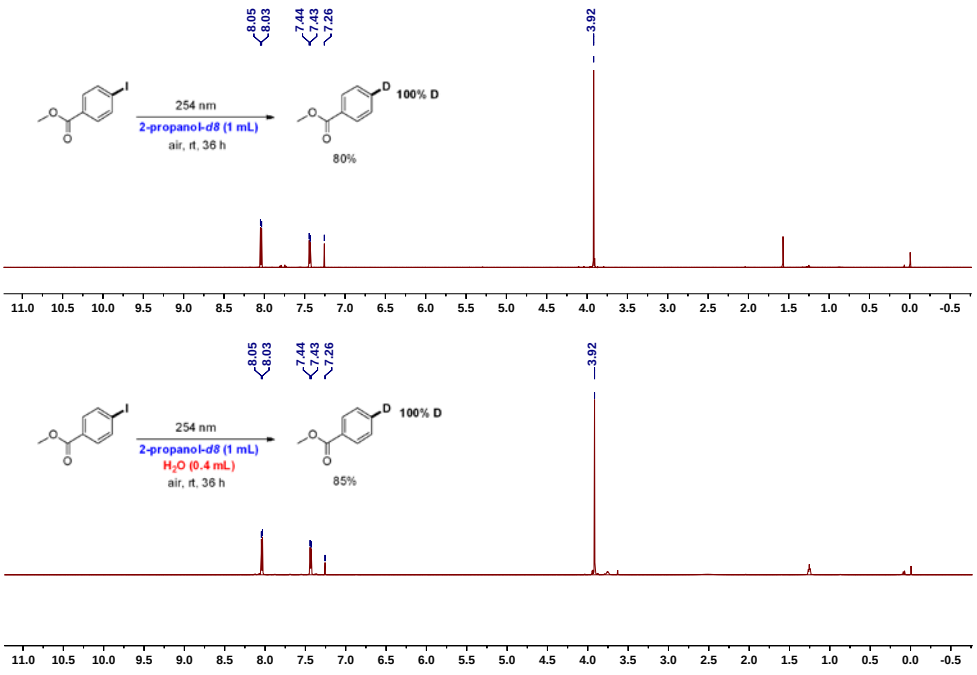
^{1}H NMR ($CDCl_3$, 600 MHz) δ: 6.91 – 6.87 (m, 4H), 6.86 – 6.82 (m, 4H). ^{13}C NMR ($CDCl_3$, 151 MHz) δ: 142.2, 123.8, 116.3; ^{1}H NMR data are consistent with the literature.[4]



Methyl 4-*d*-benzoate

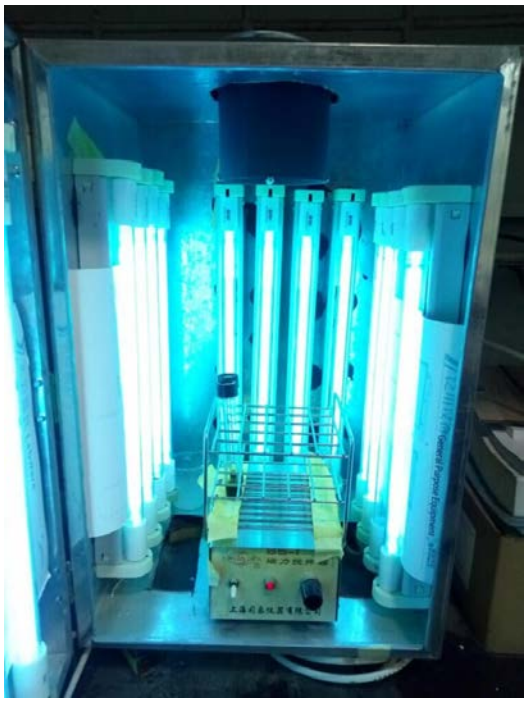
^{1}H NMR ($CDCl_3$, 600 MHz) δ: 8.04 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 3.92 (s, 3H). ^{13}C NMR ($CDCl_3$, 151 MHz) δ: 167.1, 132.6 (t, *J* = 24.2 Hz), 130.2, 129.6, 128.2, 52.1. ^{1}H and ^{13}C NMR data are consistent with the literature [5].

Ⅳ Deuterium experiments



Ⅴ Photo reactor

The photo reactor was made in-house. We used a small metal box and fixed a certain number (16 lamps, each lamp is 6 W) of UV lamps around it. A small fan was installed on top to keep the temperature inside the box at r.t. A magnetic stirrer was placed inside the box. The quartz reaction tube was placed on a metal test tube rack during the reaction.



Ⅵ. Computational details

All the calculations were carried out with Gaussian 09 software package.[6] Geometry optimizations were carried out at M06-2X[7]/6-31+G(d,p)/IEFPCM[8](2-propanol) level of theory. Vibrational frequencies were also calculated for all stationary points to verify them as energy minima or transition states. Intrinsic reaction coordinate (IRC)[9] calculations were carried out as well to confirm whether the transition states were connected with expected reactants and products. The optimized geometries and molecular surface electrostatic potentials were displayed using CYLview (version 1.0b)[10] and Gaussview 5[11], respectively. Spin density calculations and interpretations were performed using Multiwfn 3.5.[12] The intermolecular hydrogen bonds were analyzed by quantum theory of atoms in molecules (QTAIM)[13] theory using AIMAll (version 08.11.06)[14] program.

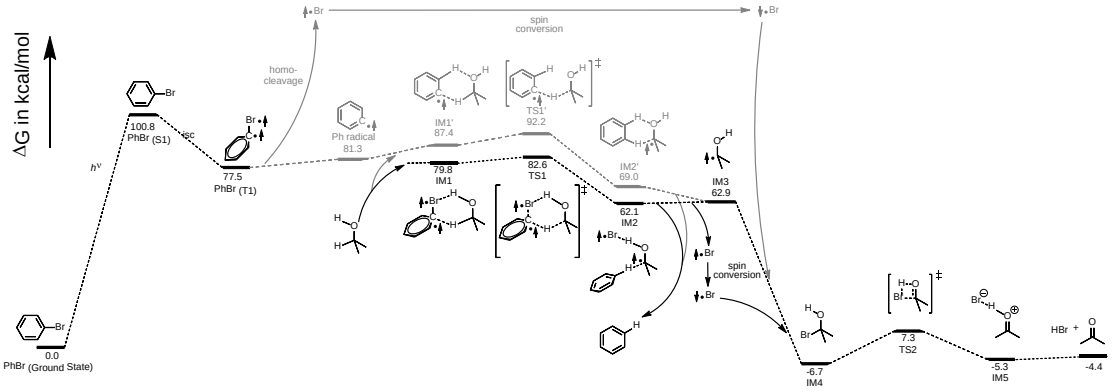


Fig. S1 Reaction mechanism and potential energy surface of **black pathway** and **grey pathway**. Some non-covalent intermolecular interactions are omitted.

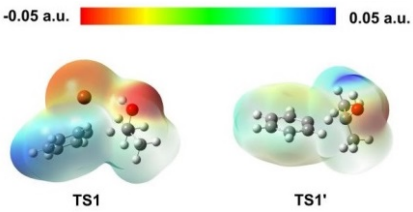


Fig. S2 Molecular surface electrostatic potential of TS1 and TS1', ranging from -0.05 a.u. to 0.05 a.u. The blue and red regions represent for positive and negative charges, respectively.

Table S1. Interaction type, distance (*d*, in Å), electronic kinetic energy density (G, in a.u.), E(hydrogen bond) (in kcal/mol), and sum of E(hydrogen bond) (E(total), in kcal/mol) of **IM1**, **IM1'**, **TS1**, **TS1'**, **IM2** and **IM2'**. The forming and breaking bonds in transition states are not considered here.

	interaction type	*d*/Å	G (a.u.)	E(hydrogen bond) = -0.429*G*627.51 (kcal/mol)	E(total) (kcal/mol)
IM1	O-H...Br	2.54	0.0095	-2.5	-5.5
	C-H...Br	2.62	0.0061	-1.6	
	C-H...Br	2.74	0.0054	-1.4	
IM1'	C-H...radical	2.75	0.0046	-1.2	-3.9
	C-H...radical	2.89	0.0034	-0.9	
	C-H...O	2.59	0.0066	-1.8	
TS1	O-H...Br	2.59	0.0094	-2.5	-3.4
	C-H...Br	3.19	0.0035	-0.9	
TS1'	/	/	/	0.0	0.0
IM2	O-H...Br	2.51	0.0100	-2.7	-5.7
	C-H...Br	3.00	0.0045	-1.2	
	C-H...radical	2.46	0.0076	-2.0	
	radical...π	2.55	0.0220	/	
IM2'	C-H...O	2.55	0.0069	-1.8	-2.9
	C-H...radical	2.82	0.0042	-1.1	

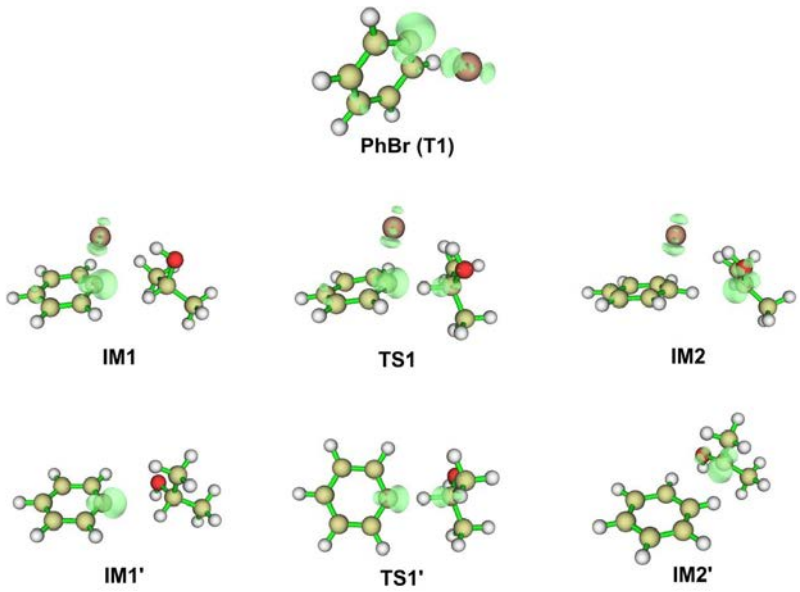


Fig. S3 Spin density of **PhBr (T1)**, **IM1**, **TS1**, **IM2**, **IM1'**, **TS1'** and **IM2'** using the wavefunctions obtaind from Gaussian 09. Isovalues are set to 0.025 a.u.

Table S2. Dipole moments of **IM1**, **TS1**, **IM2**, **IM1'**, **TS1'** and **IM2'** calculated at M06-2X/6-31+G(d,p)/IEFPCM(2-propanol) level of theory.

Structure	Dipole Moment /Debye	Structure	Dipole Moment /Debye
IM1	9.0805	**IM1'**	2.0416
TS1	6.9465	**TS1'**	1.9533
IM2	5.7155	**IM2'**	2.0724

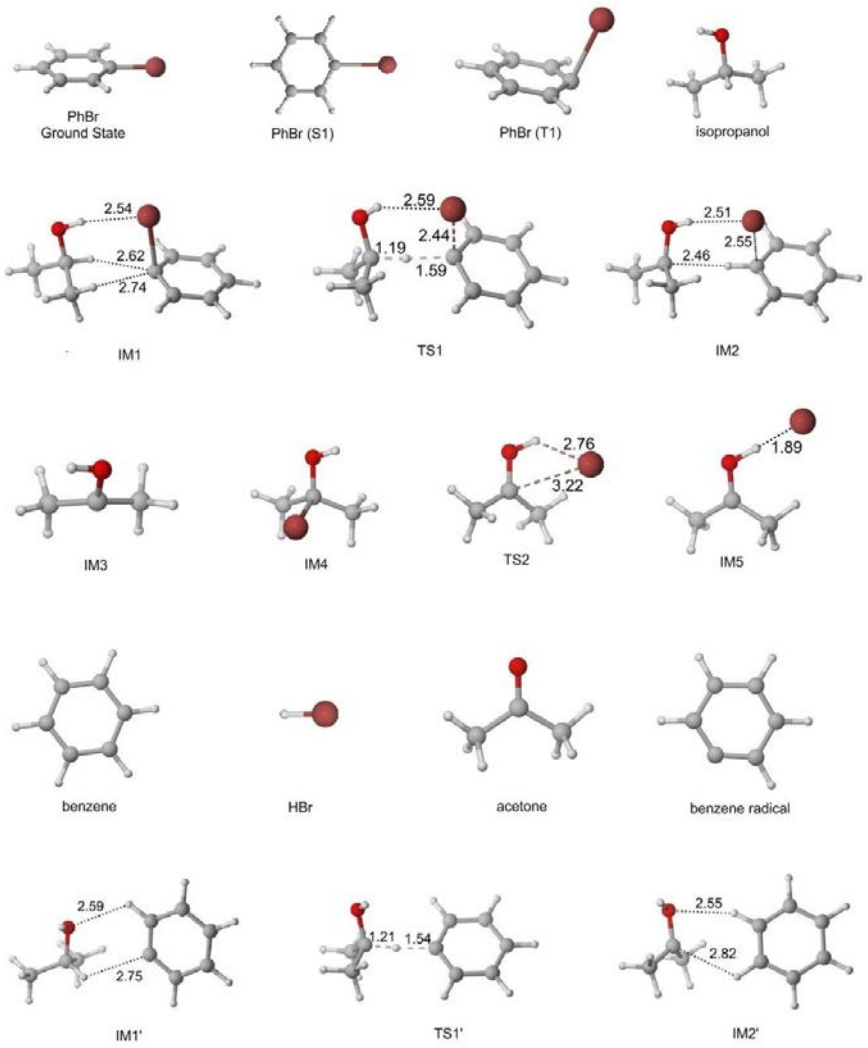


Fig. S4 Optimized structures of reactants, intermediates, transition states and products. Distances are in Å, interactions are in dots and breaking/forming bonds in transition states are in dashed bonds.

Cartesian Coordinate

PhBr (Ground State)

C	-2.16689300	-1.20507400	0.00005900
C	-0.77274100	-1.21400600	0.00006600
C	-0.09335000	-0.00001700	0.00008700
C	-0.77273500	1.21400300	0.00006400
C	-2.16686500	1.20509100	0.00006100
C	-2.86775900	0.00000400	0.00007400
H	-2.70287400	-2.14883900	0.00004300
H	-0.22412800	-2.14948300	0.00003000
H	-0.22407700	2.14945300	0.00002700
H	-2.70286000	2.14884700	0.00004500
H	-3.95256700	0.00002800	0.00007000
Br	1.79567300	0.00000000	-0.00007700

PhBr (S1)

C	2.41904800	-1.22806000	0.00002700
C	1.03363400	-1.23307800	0.00000800
C	0.35583000	0.00000400	-0.00000800
C	1.03364200	1.23308200	-0.00000800
C	2.41905600	1.22805500	-0.00002200
C	3.10582700	-0.00000400	0.00000300
H	2.97917100	-2.15790100	0.00003400
H	0.47431700	-2.16551800	0.00004300
H	0.47433100	2.16552600	-0.00004000
H	2.97918400	2.15789300	-0.00002300
H	4.19140200	-0.00000800	0.00000700
Br	-2.09430400	0.00000000	0.00000000

PhBr (T1)

C	-1.91601400	1.22574400	-0.25492400
C	-0.93347300	1.24169400	0.72192100
C	-0.37288300	0.00210100	1.08816600
C	-0.93024300	-1.23962700	0.72400900
C	-1.91295900	-1.22798000	-0.25283100
C	-2.39448700	-0.00221100	-0.74307400
H	-2.33384800	2.15626500	-0.62432300
H	-0.55863300	2.16937100	1.14192700
H	-0.55301900	-2.16557800	1.14569400
H	-2.32841700	-2.16024000	-0.62050800
H	-3.17863900	-0.00387200	-1.49354700
Br	1.70608300	0.00016400	-0.20711000

IM1

C	2.61086700	-1.07650700	-1.34294300
C	1.23774200	-0.92500500	-1.24928900
C	0.69782700	-0.71276200	0.03546400
C	1.43402800	-0.88262800	1.22507100
C	2.80554300	-1.02950800	1.10535500
C	3.38527900	-1.13087500	-0.17123200
H	3.08430100	-1.18542100	-2.31271200
H	0.60285000	-0.90933700	-2.12965400
H	0.94781500	-0.83616500	2.19466200
H	3.42724300	-1.10025200	1.99136500
H	4.45781600	-1.27453700	-0.25375800
Br	0.39126000	1.71869000	0.00636200
C	-3.86617100	-1.40303800	-0.64286000
C	-2.63978100	-0.65937300	-0.14521500
H	-1.77945700	-0.91373000	-0.78397100
H	-4.07406900	-1.15016700	-1.68587200
H	-3.71661900	-2.48374000	-0.56782100
H	-4.73640600	-1.12905300	-0.03724300
C	-2.30315400	-1.00989500	1.29964900
H	-1.48352300	-0.38409100	1.66829700
H	-3.17631700	-0.84239000	1.93928800
H	-2.00069400	-2.05910800	1.38487500
O	-2.91613700	0.73441600	-0.27527400
H	-2.09102400	1.21606400	-0.11193300

TS1

imaginary frequency = -382.89 cm^{-1}

C	2.60266500	-1.08897200	-1.17477100
C	1.24501700	-0.84337200	-1.27150000
C	0.51590800	-0.60407000	-0.08125600
C	1.10327600	-0.78919600	1.19557000
C	2.46058500	-1.04910900	1.27351600
C	3.20536200	-1.19318600	0.09247900
H	3.20037400	-1.22806800	-2.06982700
H	0.74977300	-0.78142800	-2.23639000
H	0.49866900	-0.68567300	2.09254500
H	2.94536400	-1.15722900	2.23806100
H	4.26809000	-1.40416600	0.15681400
Br	0.23892600	1.82457900	-0.03327000
C	-2.82456400	-2.05338000	-0.52526700
C	-2.24394500	-0.74857600	-0.03043900
H	-1.06069300	-0.81136200	-0.11129200
H	-2.54204500	-2.23033900	-1.56611900

H	-2.46847700	-2.88589400	0.08658900
H	-3.91851300	-2.01868600	-0.46173000
C	-2.53393700	-0.44632600	1.42898400
H	-2.05318700	0.48826400	1.73656300
H	-3.61527200	-0.34778100	1.57900400
H	-2.16549800	-1.25448200	2.06805000
O	-2.65284900	0.28343900	-0.89184100
H	-2.16041000	1.08620200	-0.65700100

IM2

C	2.87865600	-0.87691600	-1.22158200
C	1.50354900	-0.78730100	-1.34646600
C	0.68378900	-0.84745300	-0.19015400
C	1.27452000	-1.08346200	1.07769700
C	2.65039600	-1.17210600	1.19127400
C	3.45037900	-1.06160300	0.04501700
H	3.51382500	-0.81239600	-2.09828700
H	1.03986000	-0.64993900	-2.31770600
H	0.63749000	-1.17249300	1.95214400
H	3.11142700	-1.33202800	2.15982100
H	4.52996100	-1.12459700	0.13939000
Br	0.36198300	1.67228200	0.07763100
C	-3.88575300	-1.56431000	-0.55005200
C	-2.81885100	-0.64071500	-0.06981700
H	-0.39278400	-0.95247500	-0.30548000
H	-3.78210600	-1.75636700	-1.62184100
H	-3.83965000	-2.51683900	-0.01636000
H	-4.88786400	-1.13537900	-0.38321600
C	-2.62910100	-0.42343700	1.39897600
H	-1.72297300	0.15578600	1.60886700
H	-3.47942100	0.12952400	1.83262400
H	-2.55413500	-1.38141000	1.92081400
O	-2.68749600	0.46470000	-0.88218200
H	-1.98857900	1.04497100	-0.53974200

IM3

C	-1.36347100	-0.52423700	0.02929400
C	-0.00860300	0.03145200	-0.24698900
H	-2.14215000	0.11967800	-0.38964200
H	-1.46479900	-1.52259700	-0.40318300
H	-1.54893100	-0.60840000	1.11337100
C	1.21086000	-0.78483800	0.03471800
H	2.11024800	-0.32871600	-0.39368200
H	1.37872400	-0.89428200	1.11957900

H	1.10640300	-1.78699800	-0.38795700
O	0.06870800	1.37548700	0.06039600
H	0.97812300	1.68315600	-0.04379100

IM1’

C	2.57573100	-1.28685600	0.13912400
C	1.21721500	-0.94851600	0.19983500
C	0.90304700	0.38233300	0.02730700
C	1.80738400	1.39773200	-0.19762400
C	3.16052700	1.03517600	-0.25425900
C	3.53726600	-0.29888600	-0.08679600
H	2.87936000	-2.32177900	0.26865200
H	0.44560600	-1.69267100	0.37030500
H	1.49856600	2.43070200	-0.32630800
H	3.91490000	1.79691800	-0.42853700
H	4.58723900	-0.57041700	-0.13187900
C	-2.43892200	0.65114300	1.26544500
C	-2.46079400	0.12858900	-0.15929500
H	-1.71836200	0.68245100	-0.75371900
H	-1.44675400	0.51565000	1.70551800
H	-2.68819300	1.71571300	1.28635000
H	-3.17053200	0.10900500	1.87418100
C	-3.83217300	0.26915200	-0.80613700
H	-3.82937400	-0.13515200	-1.82364800
H	-4.58146300	-0.27189000	-0.21878100
H	-4.12476000	1.32209200	-0.86098000
O	-2.06703600	-1.24430800	-0.09242900
H	-2.04563300	-1.60535800	-0.98732000

TS1’

imaginary frequency = -932.92 cm^{-1}

C	2.60514800	-1.22830500	-0.06779100
C	1.20689500	-1.16330500	-0.05666600
C	0.60834900	0.08407100	0.01977100
C	1.32974000	1.26563300	0.08621100
C	2.72783800	1.18790000	0.07339100
C	3.35962700	-0.05497000	-0.00300500
H	3.10237200	-2.19247100	-0.12816700
H	0.61063000	-2.07129800	-0.10762300
H	0.83263800	2.23059300	0.14706900
H	3.32056200	2.09715200	0.12259200
H	4.44384700	-0.10925700	-0.01244700
C	-2.55201600	-0.63398400	1.29437400
C	-2.13391600	-0.01207000	-0.01699000
H	-0.92763700	0.09311500	0.02276100

H	-2.09334600	-1.61968400	1.41284100
H	-2.24166900	-0.00095600	2.12976900
H	-3.64188800	-0.74957200	1.32913900
C	-2.67936200	1.37987400	-0.26371400
H	-2.30793700	1.78409500	-1.21135600
H	-3.77508000	1.35694900	-0.30028300
H	-2.37061300	2.05588900	0.53874300
O	-2.44395400	-0.91463500	-1.05406100
H	-2.23405700	-0.50653800	-1.90403600

IM2’

C	2.09736900	-1.36696300	-0.04831200
C	0.90489500	-0.64216900	-0.08680400
C	0.93913100	0.75347000	-0.09286000
C	2.16351300	1.42271800	-0.06188200
C	3.35518100	0.69690900	-0.02376100
C	3.32199200	-0.69835300	-0.01676300
H	2.07216900	-2.45259700	-0.04314200
H	-0.05117700	-1.15834200	-0.11448300
H	2.18957400	2.50830900	-0.06744000
H	4.30769000	1.21784600	0.00071400
H	4.24877300	-1.26345800	0.01290200
C	-2.36458700	0.24165900	1.46440100
C	-2.48216300	-0.01400500	0.00124600
H	0.00754200	1.31281600	-0.12327200
H	-1.59624200	-0.39793800	1.91050600
H	-2.09976600	1.28542000	1.65177700
H	-3.31386200	0.03687200	1.98676900
C	-3.25904700	0.91139500	-0.87651500
H	-3.06214300	0.71921800	-1.93716100
H	-4.34492500	0.80484600	-0.71471400
H	-2.99178500	1.95009100	-0.66650500
O	-2.58360400	-1.36236800	-0.27852300
H	-2.75472700	-1.49210300	-1.22025800

IM4

Br	-2.82338800	0.21000700	-2.40431100
C	-3.31492100	-0.43989800	0.33568800
C	-2.13693100	0.03980600	-0.47939700
H	-3.64892000	-1.41936200	-0.01026900
H	-2.99626900	-0.51888600	1.38028400
H	-4.13791800	0.27182200	0.26323800
C	-1.65391700	1.42284600	-0.09582000
H	-1.29768400	1.38328500	0.93907000

H	-0.83631200	1.75184200	-0.74198100
H	-2.47029400	2.14268100	-0.16681500
O	-1.15292800	-0.91897200	-0.45420200
H	-0.33288700	-0.56810600	-0.83017100

TS2

imaginary frequency = -112.83 cm^{-1}

Br	1.56650100	-0.06115100	-0.10234100
C	-2.37058300	-0.82940900	-0.77505800
C	-1.63632200	0.03245000	0.16280400
H	-2.75362600	-1.72153200	-0.28148100
H	-3.15073900	-0.27566800	-1.29769300
H	-1.62033700	-1.13489700	-1.51958000
C	-1.44673100	1.47027000	-0.09535100
H	-2.43222400	1.93090100	0.06342700
H	-0.70754000	1.92491200	0.56065000
H	-1.18157300	1.62201000	-1.14353400
O	-1.21582300	-0.53106100	1.22059900
H	-0.53311600	0.00318300	1.68099300

IM5

Br	1.82010700	-0.02812600	0.00597800
C	-3.29428700	-0.47804800	0.02255100
C	-1.88306300	-0.03484400	-0.00640800
H	-3.38136700	-1.53286500	-0.23157200
H	-3.66657700	-0.31297100	1.04112000
H	-3.89636000	0.14647300	-0.64144300
C	-1.54299700	1.40804000	-0.00457700
H	-0.49979600	1.58131800	0.25631800
H	-1.72390100	1.77620900	-1.02256800
H	-2.22329700	1.94786800	0.65709200
O	-1.00049000	-0.92649700	-0.03895000
H	0.01355600	-0.58053200	-0.02596800

HBr

Br	0.00000000	0.00000000	0.03933400
H	0.00000000	0.00000000	-1.37668800

acetone

C	0.00000000	0.17934800	0.00000700
O	0.00000300	1.39793300	-0.00000300
C	-1.28455600	-0.61178400	0.00268000
H	-1.25170000	-1.38996900	0.77061200
H	-2.13714500	0.04722700	0.16679600

H	-1.39274300	-1.11631300	-0.96336000
C	1.28455300	-0.61179100	-0.00268400
H	1.39275600	-1.11626800	0.96338100
H	1.25169500	-1.39000300	-0.77058600
H	2.13713300	0.04722300	-0.16683200

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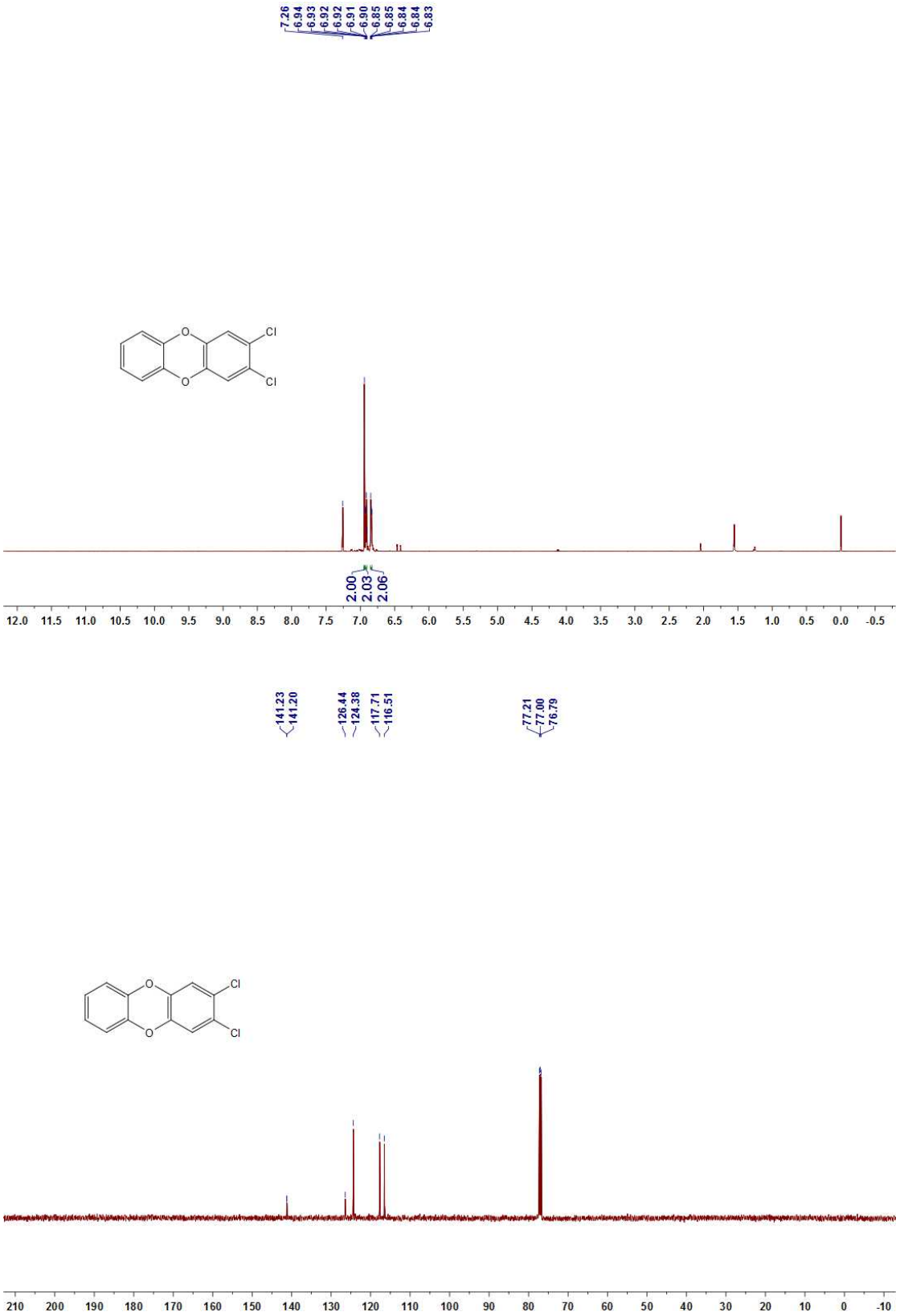
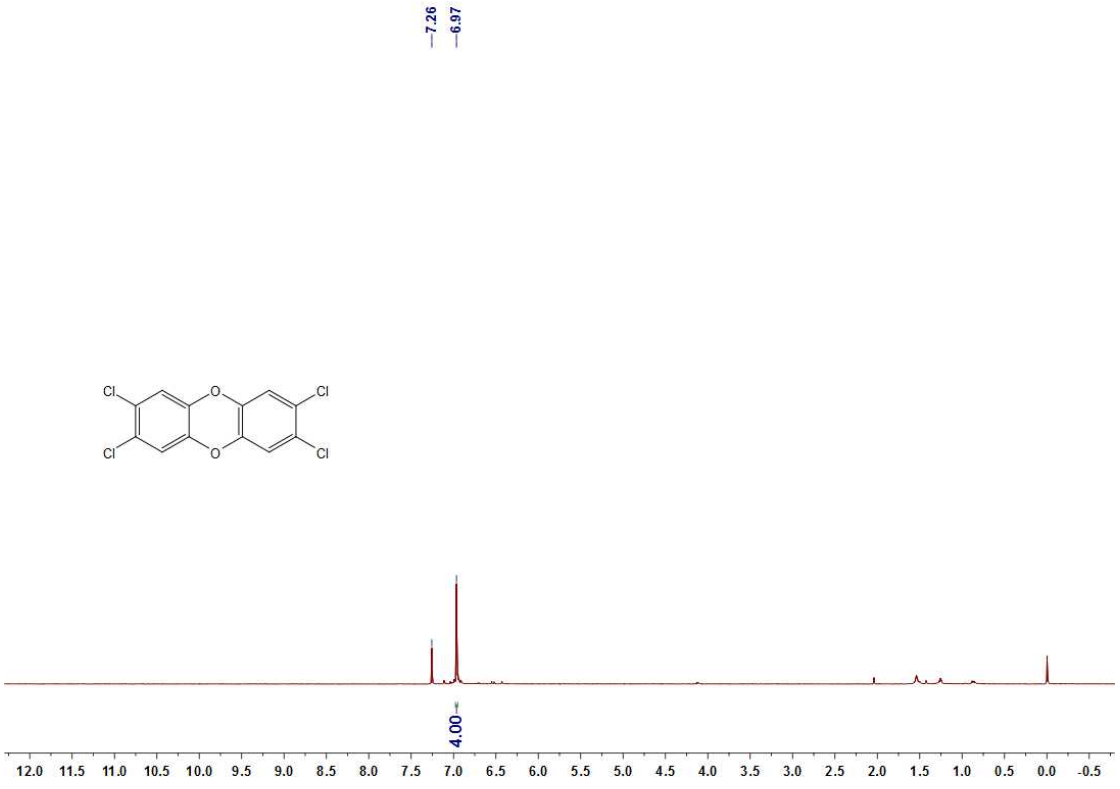
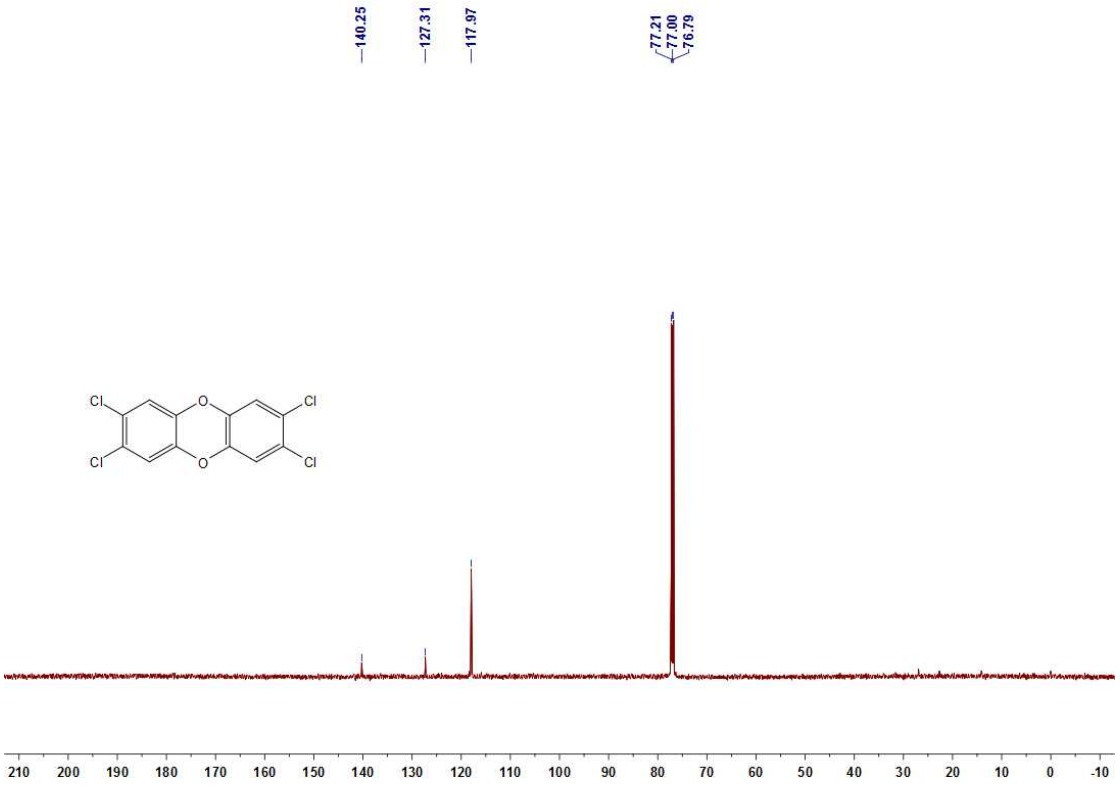
Ⅷ. Copies of ^{1}H NMR and ^{13}C NMR

^{1}H and ^{13}C NMR spectra of **2,3-dichlorodibenzo[b,e][1,4]dioxin**

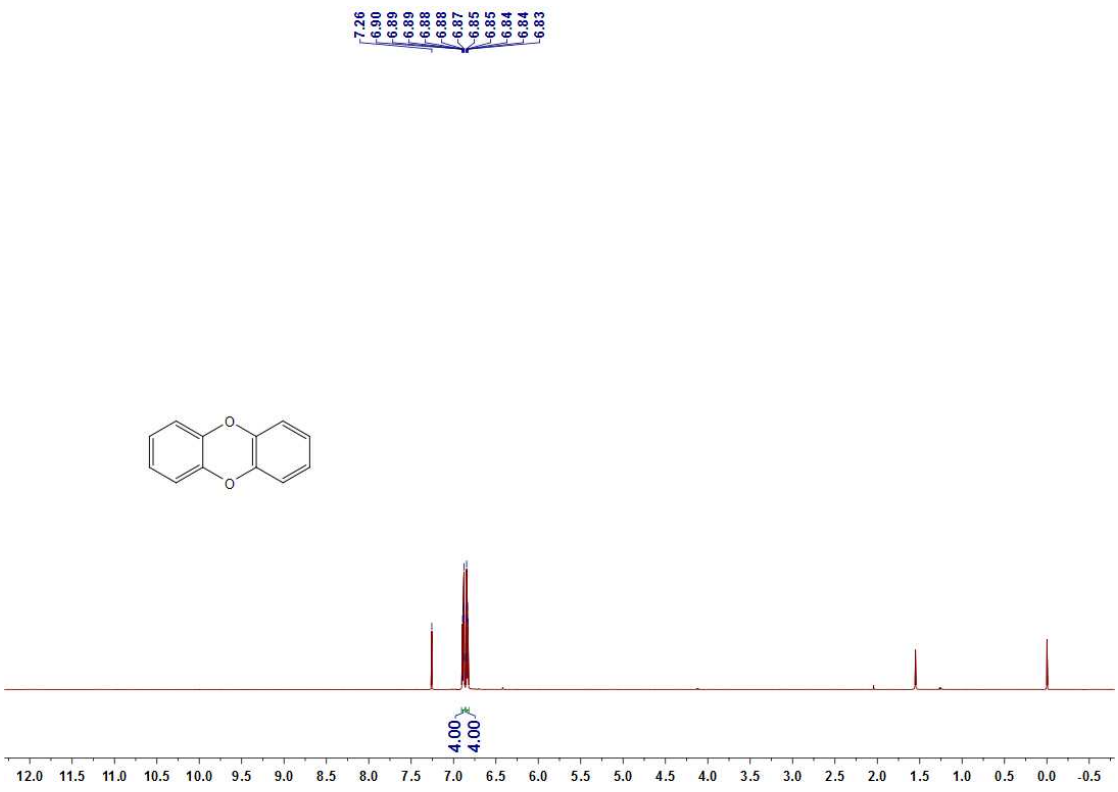


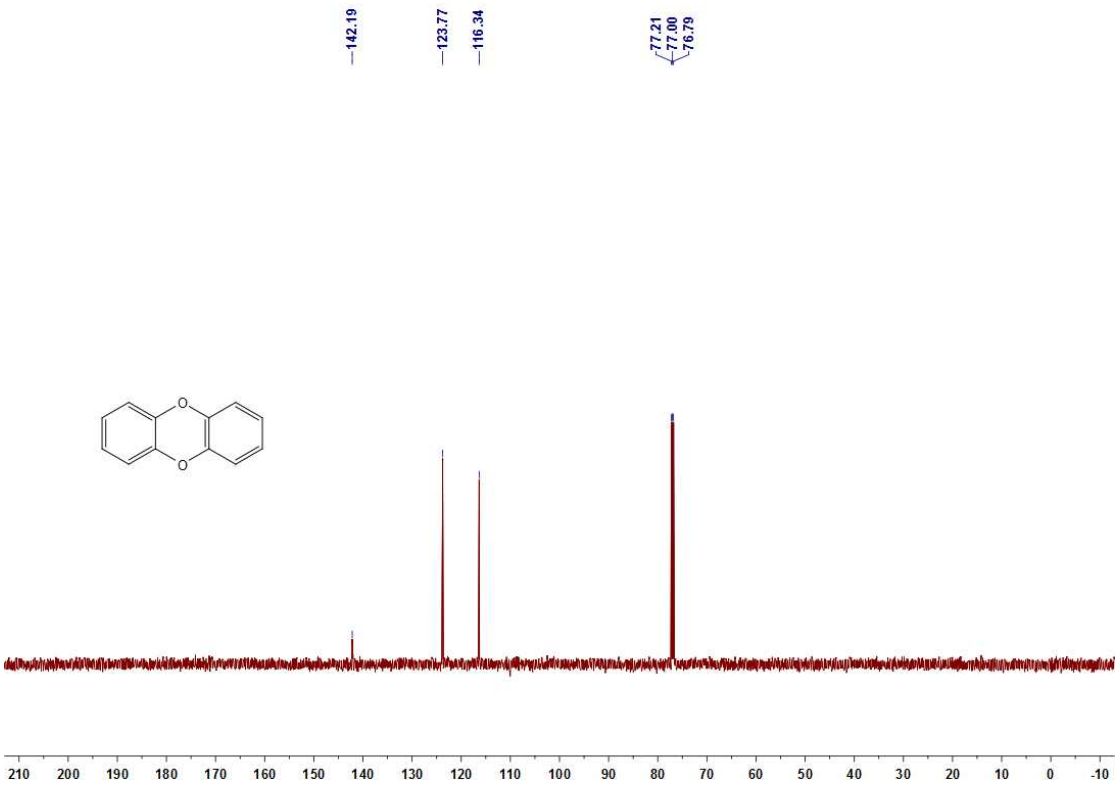
^{1}H and ^{13}C NMR spectra of **2,3,7,8-tetrachlorodibenzo[b,e][1,4]dioxin**





^{1}H and ^{13}C NMR spectra of **dibenzo[b,e][1,4]dioxin**





^{1}H and ^{13}C NMR spectra of **methyl 4-d-benzoate**