# 2-Iodoxybenzoic acid-mediated transformation of halogenated hydrocarbon in the presence of tetraethyl ammonium bromide

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2-Iodoxybenzoic acid (IBX) has been shown to react with alkyl halides in the presence of tetraethyl ammonium bromide to give 2-iodobenzoate esters. Most of the monohalides and dihalides reacted easily with moderate to good yields. The 2-iodobenzoate esters containing other functional groups can offer further synthetic uses. The 2-iodobenzoic acid can be recycled easily and oxidised to IBX again.

**Keywords**: 2-iodoxybenzoic acid, tetrabutylammonium bromide, halogenated hydrocarbon, esters

2-Iodoxybenzoic acid (IBX) is a versatile mild oxidising agent,[1–3] which is widely used in various transformations such as the selective oxidation of alcohols to carbonyl compounds. It is efficient, easily available and stable to moisture and air. Recent reports have shown that IBX can be used for other transformations such as the $\alpha$-functionalisation of ketones[4] and the direct halo-oxygenation of alkenes.[5] Other uses of this reagent in organic synthesis remain to be explored.

Here we report a new use of IBX. It provides a convenient way to synthesise 2-iodobenzoate esters by the reaction of IBX with halogenated hydrocarbon in the presence of TBAB. The iodinated products can be further modified,[6–8] especially the disubstituted ones, to synthesise medium-ring compounds.[6,7] This method is more efficient and practicable than the traditional ones, which usually employed carbonyl chlorides or organolithium reagents.[6,8]

During our work using IBX in combination with TBAB,[9–12] in addition to the predicted products, substitution of one chlorine atom of 1,2-dichloroethane (DCE) by IBX occurred quantitatively. In general, esterification of an organic acid with halogenated hydrocarbon (RX) occurs using PTC[13–15] or in polar aprotic solvents.[16,17] A point of interest was whether or not 2-iodobenzoic acid can react with RX. To our surprise, 2-iodobenzoic acid cannot be esterified in the presence or in the absence of TBAB, nor did IBX react in the absence of TBAB. It is IBX in combination with TBAB that reacts with RX. Further research showed that some other PTCs and other halides can also be used in the reaction.

Most primary halohydrocarbons gave good yields and the bromide has higher reactivity than chloride (Table 1, entries 1, 2, 5 and 8). However, ethyl chloroacetate resulted in a better yield than ethyl bromoacetate, possibly because the chlorine atom has a higher electronegativity (entries 11 and 12). The yield with *n*-pentyl iodide was lower than the bromide analogue, perhaps due to the decomposition of the *n*-pentyl iodide as shown in the red brown colour of the reaction mixture (entries 6 and 7). As previously reported,[4] ketones must have at least two $\alpha$-hydrogen atoms at one carbon atom when undergoing $\alpha$-oxygenation by IBX. However, under our conditions 2-bromopropane (entries 3, 4 and 13) reacted easily in moderate yields. $\alpha$-Phenylethyl bromide reacted in 58% yield with acetopenone as a minor byproduct[18] and another unknown one.[18] Allyl chloride and propargyl bromide were also tolerated and gave moderate yields (entries 9 and 10). However, it seems that this method cannot be applied to sterically hindered halohydrocarbons such as tertiary and cyclic ones. tert-Butyl chloride and chlorocyclohexane did not react when subjected to the conditions. Bromocylohexane gave a product with a minor unknown one which could not be separated with the total yield of 17%.

Interestingly, the formation of mono- or bi-substitution products can be controlled (Table 2) in certain conditions when dihalides were subjected to the reaction. Most of the reactions only gave the monosubstitution product in good to excellent yields (entries 3, 7, 9 and 11). Dichloromethane and dibromomethane gave only disubstituted products (entries 1 and 2), and attempts to get the monosubstitution products failed under various conditions. Monosubstitution of DCE can be obtained quantitatively when the reaction was carried out using DCE as solvent. However, when the disubstituted product was considered as the target, the reaction was sluggish and always gave two products (entry 4). Additionally, the reaction of dibromides gave the disubstituted compound as the sole product using 2.5 equiv.. of IBX/TBAB in one portion (entries 6 and 10). More IBX/TBAB were needed for dichlorides and was added in several portions (entries 8 and 12). Mono- or bi-substitution products obtained can be easily hydrolysed[19,20] to the corresponding alcohol, which provides an efficient and practicable route to prepare alcohol including some that were difficult to synthesise by conventional methods. 2-Iodobenzoic acid can be recovered and oxidised to IBX easily.[21,22] Other polyhalogenated hydrocarbons such as iodoform, tetrabromomethane, trichloroacetaldehyde and 1,1,2,2-tetrachloroethane cannot be employed in this reaction.

Some derivatives of IBX, such as IBX amides[23] and IBX esters[8,24] (Fig. 1), have been prepared and characterised. Single-crystal X-ray analysis revealed that derivatives of IBX have a pseudobenziodoxole structure due to iodine-oxygen secondary bonding interactions. In comparison to IBX, pseudobenziodoxoles have greater solubility due to a partial disruption of their polymeric nature resulting from the redirection of iodine-oxygen secondary bonding. Bis(2-iodobenzoate) can be accessed easily according to the method above. We prepared **21** from **14** and **22** from **20** (Fig. 1). The most characteristic signals in the $^{13}$C NMR spectra were those of the ipso carbon, **C**–$IO_2$, found at about 151 ppm[23,24] which differ from the corresponding esters (**C**–I, 94 ppm). The single crystals of **21** were grown from DMSO, and were suitable for X-ray analysis (Fig. 2, Table 3). Within the molecule, there was an intramolecular close contact between the I(V) centre and the oxygen atom of the ester group ($I_1$–$O_3$ 2.7172(49) and $I_2$–$O_6$ 2.7417(39) Å) afford the pseudobenziodoxole ring. Strong secondary I···O bonding interactions ($I_2$–$O_1$ 2.7473(40) Å) between neighbouring molecules occurs, forming a polymeric structure. This may be the reason why both of them have a low solubility in most organic solvents, but are soluble in DMSO. The other I(V) centre ($I_1$–$O_{10}$ 2.7702(62) Å) coordinates with oxygen from a DMSO molecule.

In conclusion, the reaction of halogenated hydrocarbons with IBX easily affords 2-iodobenzoate esters in the presence of TBAB in moderate to high yields. This provides a new synthetic application for the hypervalent iodo-compound IBX. Most importantly, the reaction of dihalides under controlled

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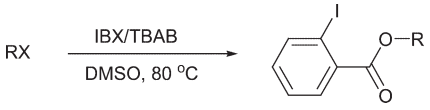
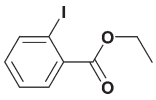
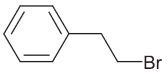
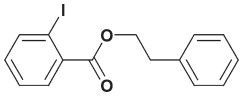
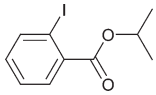
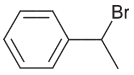
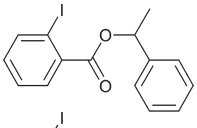
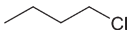
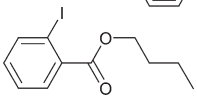
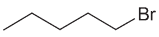
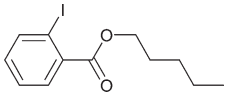
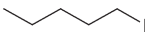
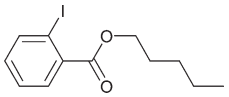
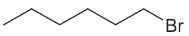
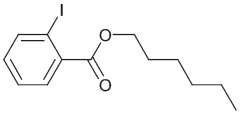
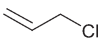
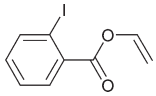
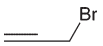
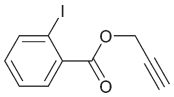
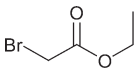
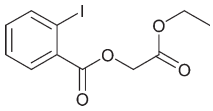
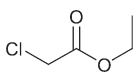
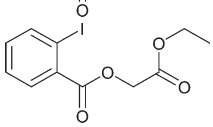
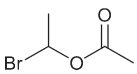
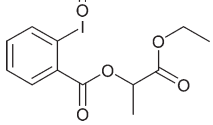
**Table 1** 2-Iodobenzoate esters from IBX with monohalides in the presence of TBAB

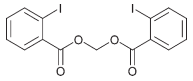
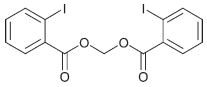
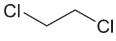
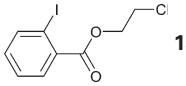
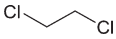
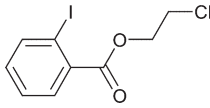
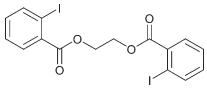
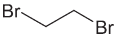
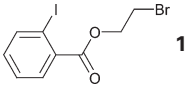
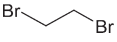
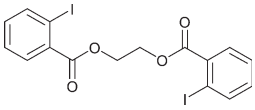



| Entry | RX | Time/h | Product | Yield/%[a] |
|---|---|---|---|---|
| |  | 0.25 |  **1** | 86 |
| |  | 0.25 |  **2** | 82 |
| |  | 0.25 |  **3** | 73 |
| |  | 0.5 |  **4** | 73[b] |
| |  | 1 |  **5** | 43 |
| |  | |  **6** | 90 |
| |  | 0.25 |  **6** | 54 |
| |  | 0.25 |  **7** | 87 |
| |  | 0.25 |  **8** | 67 |
| |  | 0.25 |  **9** | 70 |
| |  | 0.25 |  **10** | 59 |
| |  | 0.25 |  **10** | 83 |
| |  | 0.25 |  **11** | 71 |

[a] Isolated yield.
[b] 2.0 equiv. of IBX/TBAB was used.

conditions can lead to the corresponding monosubstitution products or disubstitution ones which can be modified further for other useful applications. Ethylene bis(2-iodobenzoate) and 1,4-butanyl bis(2-iodobenzoate) were further converted to bis(2-iodoxybenzoate esters) **21** and **22**. The single-crystal X-ray analysis of **21** showed a pseudobenziodoxole structure. The secondary I···O bonding interactions between neighboring molecules occurs to give a polymeric structure which may account for their low solubility in most organic solvents.

**Table 2** 2-iodobenzoate esters from IBX with dihalides in the presence of TBAB

| Entry | $RX_2$ | Time /h | Product | Yield/%[a] |
|---|---|---|---|---|
| |  | 0.5 |  **12** | 37 |
| |  | 0.5 |  **12** | 9 |
| |  | 5 |  **13** | 76[b] |
| |  | 3 |  **13** + | 14/75[c] |
| | | |  **14** | |
| |  | 1 |  **15** | 47[d] |
| |  | 1 |  **14** | 91[e] |
| |  | 1 |  16 | 72[f] |
| |  | 1.3 |  **17** | 96[g] |
| |  | 0.5 |  **18** + | 80/3[f] |
| | | |  **17** | |
| |  | 0.5 |  **17** | 88[e] |
| |  | 2 |  **19** | 85[f] |
| |  | 2 |  **20** | 100[h] |

[a] Isolated yield.
[b] 40 equiv. of DCE was used.
[c] IBX/TBAB 11 equiv., added in seven portions at t=0 (2 equiv.), 40 min (2 equiv.), 70 min (2 equiv.), 90 min (1 equiv.), 105 min (1 equiv.), 135 min (1 equiv.), 150 min (2 equiv.) and then stirred for another 30 min.
[d] RX2/IBX/TBAB=15/1/1.
[e] IBX/TBAB 2.5 equiv. with the concentration of IBX 1.25 M.
[f] RX2/IBX/TBAB=10/1/1.
[g] IBX/TBAB 6 equiv., added in four portions at t=0 (2 equiv.), 30 min (1 equiv.), 50 min (2 equiv.), 90 min (1 equiv.), and then stirred for another 30 min.
[h] IBX/TBAB 6.5 equiv., added in four portions at t=0 (2 equiv.), 30 min (1 equiv.), 50 min (2 equiv.), 90 min (1.5 equiv.), and then stirred for another 30 min.

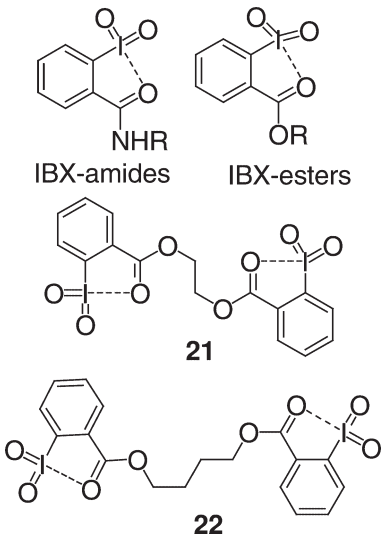



**Fig. 1** Derivatives of IBX.

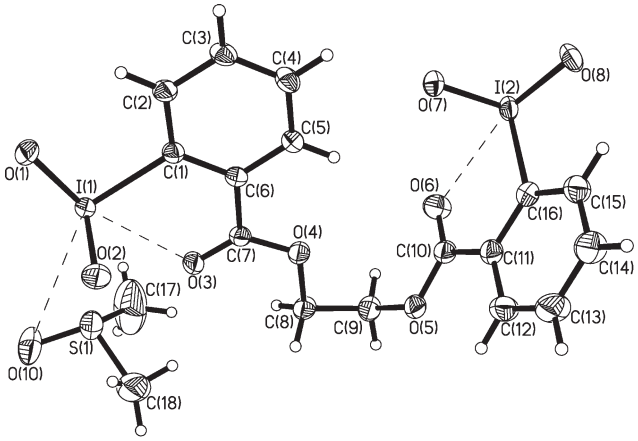



**Fig. 2** X-ray crystal structure of **21**.

**Table 3** Details of X-ray crystal structure determination of ethane-1,2-diyl bis(2-iodoxybenzoate esters) DMSO solvate (**21**)[a] CCDC-842863

| | |
|---|---|
| Formula | $C_{18}H_{18}I_2O_9S$ |
| Molecular weight | 664.20 |
| Crystal system, space group | Triclinic, P -1 |
| Unit cell dimensions | $a$ = 8.385(5) Å, $b$ = 12.554(7) Å, $c$ = 13.003(6) Å<br>α = 61.31(3)°, β = 71.80(4)°, γ = 73.44(4)° |
| Volume, crystal size | 1125.6(10) Å$^3$, 0.22×0.16×0.11mm$^3$ |
| Wavelength | 0.71073 Å |
| Temperature | 294K |
| Z, Density (calcd) | 2, 2.060 g cm$^{-3}$ |
| Absorption coefficient | 2.944 mm$^{-1}$ |
| θ range for data collection | 3.13–27.48 |
| F(000) | 676 |
| Index ranges | $-10\leq h\leq 10$, $-16\leq k\leq 16$, $-16\leq l\leq 16$ |
| Reflections collected /unique | 11582/5087 [$R_{(int)}$=0.0506] |
| Data/restraints/parameters | 5087/3/291 |
| Goodness of fit on $F^2$ | 1.023 |
| Final R indices [I>2σ(I)] | $R^1$=0.0379, $wR^2$=0.0960 |
| R indices (all data) | $R^1$=0.0433, $wR^2$=0.0999 |
| Largest diff. peak and hole | 1.779 e, –0.986.Å$^3$ |

[a]There is a disordered water molecule in the crystal which was omitted from the formula of compound **21**.

## Experimental

IR spectra were recorded on Bruker ALPHA FT-IR spectrometer. Melting points were observed on RY-2 Melting Point Tester and are uncorrected. $^1$HNMR (400 MHz) and $^{13}$CNMR (100 MHz) were determined on a Bruker Avance III 400MHz spectrometer with $CDCl_3$ or $(CD_3)_2SO$ as the solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts were reported in units (ppm). All coupling constants ($J$ values) were reported in Hz. HRMS was performed on a Bruker Daltonic Inc, Autoflex TOF/TOFIII (ESI). Preparative TLC (20×20 cm) was performed on Silica $Gel_{60}F_{254}$. The IBX that was used was prepared according to the literature.[22]

*Synthesis of compounds* **1**–**11** *(Table 1); general procedure*

*n*-$C_5H_{11}Br$ (75.5 mg, 0.5 mmol), IBX (175 mg, 0.625 mmol), TBAB (202 mg, 0.625 mmol) were added to DMSO (0.5 mL) successively. The mixture was stirred for 15 min at 80 °C, then cooled to rt, ethyl acetate (10 mL) was added to the solution, and washed with brine (10 mL). The organic layer was dried over $MgSO_4$ and evaporated *in vacuo*. The crude product was purified by preparative TLC (eluent: PE–EtOAc, 6:1) to give compound **6**.

*Ethyl 2-iodobenzoate ester* (**1**): Oil,[8] IR (KBr): $\nu_{max}$ = 2981, 1725, 1582, 1289, 1250, 1101, 1014, 741 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, $J$ = 7.9 Hz, 1H),7.75 (d, $J$ = 7.7 Hz, 1H), 7.35 (t, $J$ = 7.6 Hz, 1H), 7.09 (t, $J$ = 7.7 Hz, 1H), 4.36 (q, $J$ = 7.1 Hz, 2H), 1.37 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.55, 141.20, 135.49, 132.50, 130.81, 127.89, 94.00, 61.69, 14.27.

*2-Phenylethyl 2-iodobenzoate ester* (**2**): Oil,[25] IR (KBr): $\nu_{max}$ = 2981, 1722, 1247, 1130, 741 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, $J$ = 7.9 Hz, 1H), 7.77 (d, $J$ = 7.7 Hz, 1H), 7.48–7.22 (m, 6H), 7.16 (t, $J$ = 7.4 Hz, 1H), 4.61 (t, $J$ = 7.0 Hz, 2H), 3.15 (t, $J$ = 7.0 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.43, 141.36, 137.68, 135.17, 132.67, 130.99, 129.05, 128.65, 127.95, 126.74, 94.21, 66.14, 35.10.

*Isopropyl 2-iodobenzoate ester* (**3**): Oil,[8] IR (KBr): $\nu_{max}$ = 2981, 1722, 1289, 1101, 742 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, $J$ = 7.9 Hz, 1H), 7.73 (d, $J$ = 7.7 Hz, 1H), 7.36 (t, $J$ = 7.6 Hz, 1H), 7.10 (t, $J$ = 7.6 Hz, 1H), 5.32–5.19 (m, 1H),1.38 (d, $J$ = 6.3 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.22, 141.12, 136.03, 132.33, 130.66, 127.87, 93.80, 69.54, 21.88.

*1-Phenylethyl 2-iodobenzoate ester* (**4**): Oil,[26] IR (KBr): $\nu_{max}$ = 1727, 1250, 742 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, $J$ = 7.9, 0.7 Hz, 1H), 7.84 (dd, $J$ = 7.8, 1.4 Hz, 1H), 7.50 (d, $J$ = 7.2 Hz, 2H), 7.41 (ddd, $J$ = 7.6, 5.5, 2.4 Hz, 3H), 7.21–7.13 (m, 1H), 6.19 (q, $J$ = 6.6 Hz, 1H), 1.74 (d, $J$ = 6.6 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.79, 141.32, 141.21, 135.43, 132.56, 130.96, 128.59, 128.09, 127.91, 126.36, 94.05, 74.09, 22.2.

*Butyl 2-iodobenzoate ester* (**5**): Oil[27], IR (KBr): $\nu_{max}$ = 2960, 1726, 1254, 739 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, $J$ = 7.8 Hz, 1H), 7.77 (dd, $J$ = 7.7, 1.2 Hz, 1H), 7.38 (t, $J$ = 7.3 Hz, 1H), 7.13 (td, $J$ = 7.8, 1.3 Hz, 1H), 4.33 (t, $J$ = 6.6 Hz, 2H), 1.84–1.63 (m, 2H), 1.55–1.34 (m, 2H), 0.97 (t, $J$ = 7.4 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.67, 141.25, 135.60, 132.47, 130.83, 127.88, 93.96, 65.57, 30.64, 19.31, 13.75.

*Pentyl 2-iodobenzoate ester* (**6**): Oil, IR (KBr): $\nu_{max}$ = 2956, 1727, 1268, 742 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, $J$ = 7.9 Hz, 1H), 7.78 (dd, $J$ = 7.7, 1.1 Hz, 1H), 7.39 (t, $J$ = 7.5 Hz, 1H), 7.13 (td, $J$ = 7.8, 1.2 Hz, 1H), 4.33 (t, $J$ = 6.7 Hz, 2H),1.83–1.69 (m, 2H), 1.50–1.31 (m, 4H), 0.93 (t, $J$ = 7.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.43, 141.18, 135.49, 132.46, 130.80, 127.85, 94.02, 65.74, 28.29, 28.18, 22.34, 14.05. HRMS (ESI) Calcd for $[C_{12}H_{15}IO_2+Na]^+$: 341.0014. Found: 341.0017.

*Hexyl 2-iodobenzoate ester* (**7**): Oil,[28] IR (KBr): $\nu_{max}$ = 2956, 1729, 1289, 1134, 741 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, $J$ = 7.9 Hz, 1H), 7.76 (d, $J$ = 7.7 Hz, 1H), 7.37 (t, $J$ = 7.6 Hz, 1H), 7.11 (t, $J$ = 7.6 Hz, 1H), 4.31 (t, $J$ = 6.7 Hz, 2H), 1.81–1.70 (m, 2H), 1.50–1.37 (m, 2H), 1.37–1.26 (m, 4H), 0.88 (t, $J$ = 6.5 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.62, 141.24, 135.60, 132.46, 130.82, 127.87, 93.98, 65.86, 31.45, 28.58, 25.73, 22.56, 14.05.

*Allyl 2-iodobenzoate ester* (**8**): Oil,[29] IR (KBr): $\nu_{max}$ = 3079, 2944, 1728, 1249, 1129, 1013, 741 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, $J$ = 7.9 Hz, 1H), 7.80 (dd, $J$ = 7.7, 1.0 Hz, 1H), 7.37 (t, $J$ = 7.4 Hz, 1H), 7.12 (td, $J$ = 7.9, 1.1 Hz, 1H), 6.03 (dq, $J$ = 11.0, 5.7 Hz, 1H), 5.42 (dd, $J$ = 17.2, 0.9 Hz, 1H), 5.29 (d, $J$ = 10.4 Hz, 1H), 4.82 (d, $J$ = 5.7 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.10, 141.35, 135.04, 132.69, 131.82, 130.99, 127.93, 118.89, 94.19, 66.23.

*Prop-2-ynyl 2-iodobenzoate ester* (**9**): Oil, IR (KBr): $\nu_{max}$ = 3294, 2129, 1732, 1246, 1096, 740 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.9 Hz, 1H), 7.84 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.40 (dd, *J* = 11.1, 4.1 Hz, 1H), 7.15 (td, *J* = 7.9, 1.5 Hz, 1H), 4.93 (d, *J* = 2.4 Hz, 2H), 2.56 (t, *J* = 2.4 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.44, 141.51, 133.99, 133.06, 131.29, 127.98, 94.41, 77.34, 75.54 52.98. HRMS (ESI) Calcd for $[C_{10}H_7IO_2+Na]^+$: 308.9388. Found: 308.9385.

*Ethoxycarbonylmethyl 2-iodobenzoate ester* (**10**): Oil,[30] IR (KBr): $\nu_{max}$ = 2963, 1739, 1211, 1013, 744 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.9 Hz, 1H), 7.91 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.14 (td, *J* = 7.8, 1.3 Hz, 1H), 4.82 (s, 2H),4.23 (q, *J* = 7.1 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 167.45, 165.58, 141.48, 133.81, 133.15, 131.53, 127.99, 94.45, 61.57, 61.47, 14.17).

*1-Ethoxycarbonyl-ethyl 2-iodobenzoate ester*, (**11**): Solid, m.p. 42–44 °C, IR (KBr): $\nu_{max}$ = 2966, 1735, 1250, 1100, 744 cm$^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.9 Hz, 1H), 7.92 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.17 (td, *J* = 7.8, 1.5 Hz, 1H), 5.34 (q, *J* = 7.1 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.63 (d, *J* = 7.1 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H).$^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.44, 165.73, 141.36, 134.30, 132.94, 131.40, 127.95, 94.22, 69.74, 61.52, 16.96, 14.15. HRMS (ESI) Calcd for $[C_{12}H_{13}IO_4+Na]^+$: 370.9756. Found: 370.9755.

*Synthesis of compounds* **12**–**20** *(Table 2); general procedure*

*(1) Mono-substitution products*

1, 4-Dichlorobutane (158.8 mg, 1.25 mmol, 10 equiv.), IBX (35 mg, 0.125 mmol, 1 equiv.), TBAB (40 mg, 0.125 mmol, 1 equiv.) were added to DMSO (1 mL) in succession. The mixture was stirred for 1 h at 80 °C, then cooled to rt. Ethyl acetate (10 mL) was added to the solution and this was washed with brine (10 mL). The organic layer was dried over $MgSO_4$ and evaporated *in vacuo*. The crude product was purified by preparative TLC (eluent: PE/EtOAc, 6:1) to give **19**.

*(2) Bi-substitution products*

1,4-Dichlorobutane (137.2 mg, 0.29 mmol, 1 equiv.), IBX/TBAB (2 equiv.) were added to DMSO (2 mL) in succession, and heated to 80 °C, then another 4.5 equiv. was added in three portions at t=30 min (1 equiv.), 50 min (2 equiv.), 90 min (1.5 equiv.). The mixture was stirred for another 30 min, then cooled to rt. Ethyl acetate (10 mL) was added to the solution, and this was washed with brine (10 mL). The organic layer was dried over $MgSO_4$ and evaporated *in vacuo*. The crude product was purified by preparative TLC (eluent: PE/EtOAc, 6:1) to give **20**.

*Methane-1,1-diyl bis(2-iodobenzoate)* (**12**): Solid, m.p.72–74 °C, IR (KBr): $\nu_{max}$ = 1745, 1234, 1036, 736 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.9 Hz, 2H), 7.93 (d, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 2H), 6.24 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 164.71, 141.77, 133.44, 133.18, 131.75, 128.04, 94.75, 80.48. HRMS (ESI) Calcd for $[C_{15}H_{10}I_2O_4+Na]^+$: 530.8566. Found: 530.8568.

*2-Chloroethyl 2-iodobenzoate* (**13**): Oil, IR (KBr): $\nu_{max}$ = 1730, 1247, 742 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.8 Hz, 1H), 7.88 (d, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 4.60 (t, *J* = 5.4 Hz, 2H),3.84 (t, *J* = 5.4 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.64, 141.34, 134.25, 133.04, 131.22, 128.07, 94.46, 65.09, 41.87. HRMS (ESI) Calcd for $[C_9H_8ClIO_2+Na]^+$: 332.9155. Found: 332.9158.

*2-Bromoethyl 2-iodobenzoate* (**15**): Oil, IR (KBr): $\nu_{max}$ = 1730, 1249, 742 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.9 Hz, 1H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 4.63 (t, *J* = 6.1 Hz, 2H), 3.64 (t, *J* = 6.1 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.80, 141.48, 134.27, 133.02, 131.30, 128.04, 94.35, 64.82, 28.58. HRMS (ESI) Calcd for $[C_9H_8{}^{79}BrIO_2+Na]^+$: 376.8650. Found: 376.8646.

*Ethane-1,2-diyl bis(2-iodobenzoate)* (**14**): Solid, m.p. 58–59 °C (lit.[6,31]. 58–59 °C)IR (KBr): $\nu_{max}$ = 1723, 1242, 734 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.9 Hz, 2H), 7.83 (d, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.11 (dd, *J* = 11.3, 3.9 Hz, 2H), 4.68 (s, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.10, 141.42, 134.52, 132.93, 131.30, 128.02, 94.33, 63.15.

*3-Chloropropyl 2-iodobenzoate* (**16**): Oil, IR (KBr): $\nu_{max}$ = 2962, 1729, 1289, 1131, 742 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.9 Hz, 1H),7.78 (d, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 4.50 (t, *J* = 6.0 Hz, 2H), 3.72 (t, *J* = 6.4 Hz, 2H), 2.25 (p, *J* = 6.2 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.43, 141.31, 132.68, 130.92, 127.94, 93.88, 62.42, 41.31, 31.57. HRMS (ESI) Calcd for $[C_{10}H_{10}ClIO_2+Na]^+$: 346.9312. Found: 346.9316.

*3-Bromopropyl 2-iodobenzoate* (**18**): Oil, IR (KBr): $\nu_{max}$ = 2961, 1730, 1289, 1130, 743 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.9 Hz, 1H), 7.77 (d, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 4.48 (t, *J* = 5.8 Hz, 2H), 3.57 (t, *J* = 6.3 Hz, 2H), 2.37–2.28 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.41, 141.31, 135.21, 132.74, 130.96, 127.97, 93.96, 63.41, 31.64, 29.58. HRMS (ESI) Calcd for $[C_{10}H_{10}{}^{79}BrIO_2+Na]^+$: 390.8807. Found: 390.8799.

*Propane-1,3-diyl bis(2-iodobenzoate)* (**17**): Oil,[6] IR (KBr): $\nu_{max}$ = 2963, 1731, 1291, 1132, 743 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.9 Hz, 2H),7.76 (d, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H),7.11 (t, *J* = 7.3 Hz, 2H), 4.51 (t, *J* = 6.1 Hz, 4H),2.26 (p, *J* = 6.1 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.43, 141.29, 135.09, 132.73, 131.00, 127.97, 94.10, 62.46, 27.93.

*4-Chlorobutyl 2-iodobenzoate* (**19**): Oil, IR (KBr): $\nu_{max}$ = 2957, 1725, 1251, 743 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.9 Hz, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 4.39 (s, 2H), 3.62 (s, 2H), 1.97 (s, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.54, 141.30, 135.30, 132.66, 130.88, 127.95, 94.00, 64.83, 44.51, 29.27, 26.07. HRMS (ESI) Calcd for $[C_{11}H_{12}ClIO_2+Na]^+$: 360.9468. Found: 360.9466.

*Butane-1,4-diyl bis(2-iodobenzoate)* (**20**): Solid, m.p. 59–60 °C (lit.[6,31]. 59–60 °C), IR (KBr): $\nu_{max}$ = 1720, 1242, 735 cm$^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.9 Hz, 2H), 7.81 (dd, *J* = 7.7, 1.1 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.23–7.11 (m, 2H), 4.44 (s, 4H), 2.00 (s, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.58, 141.30, 135.35, 132.62, 130.90, 127.94, 94.00, 65.14, 25.50.

*Synthesis of bis(2-iodoxybenzoate esters)*[8]*; typical procedure*

Dichloromethane (20 mL) was added to a vigorously stirred suspension of ethylene bis(2-iodobenzoate) (5 mmol) and sodium hypochlorite solution (5% NaOCl, 30mL), and then acetic acid (10 mL) was added dropwise over 10 min at room temperature. The resulting mixture was stirred overnight. The DCM was evaporated in a vacuum and acetone (50 mL) was added to precipitate the product, which was then filtered and washed with DCM (2×20 mL), acetone (2×20 mL), dried under vacuum to give analytically pure form as white solids **21**; yield: 1.8 g (63%).

*Ethane-1,2-diyl bis(2-iodoxybenzoate esters)* (**21**): Solid, m.p. 165 °C dec, IR (KBr): $\nu_{max}$ = 1687, 1380, 783, 748 cm$^{-1}$; $^1$H NMR (400 MHz, DMSO) δ 8.27 (d, *J* = 7.5 Hz, 2H), 8.16 (d, *J* = 7.3 Hz, 2H), 8.04 (t, *J* = 7.1 Hz, 2H), 7.76 (t, *J* = 7.1 Hz, 2H), 4.82 (s, 4H); $^{13}$C NMR (100 MHz, DMSO) δ 167.29, 151.13, 135.39, 132.52, 131.05, 126.09, 123.63, 64.94. HRMS (ESI) Calcd for $[C_{16}H_{12}I_2O_8+Na]^+$: 608.8519. Found: 608.8502.

*Butane-1,4-diyl bis(2-iodoxybenzoate esters)* (**22**): Solid, m.p. 206–207 °C dec, IR (KBr): $\nu_{max}$ = 1672, 1300, 770 cm$^{-1}$; $^1$H NMR (400 MHz, DMSO) δ 8.27 (d, *J* = 7.7 Hz, 2H), 8.13 (d, *J* = 7.4 Hz, 2H), 8.04 (t, *J* = 7.4 Hz, 2H), 7.77 (t, *J* = 7.3 Hz, 2H), 4.51 (s, 4H), 1.96 (s, 4H); $^{13}$C NMR (100 MHz, DMSO) δ 167.41, 151.01, 135.21, 132.44, 130.66, 126.49, 123.64, 66.82, 25.14. HRMS (ESI) Calcd for $[C_{18}H_{16}I_2O_8+Na]^+$: 636.8832. Found: 636.8817.

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