

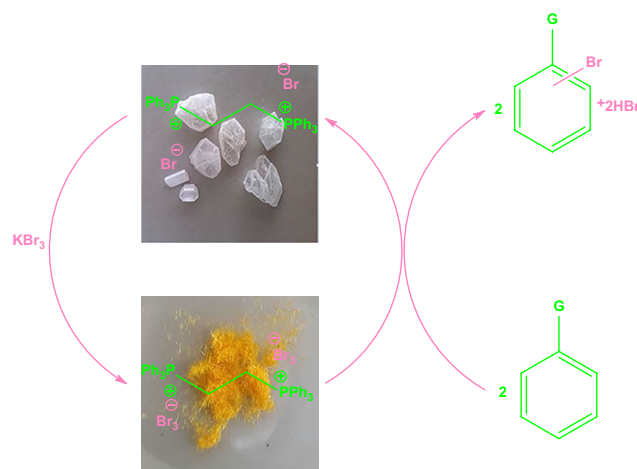
# The synthesis of 1,2-ethanediylbis(triphenylphosphonium) ditribromide as a new brominating agent in the presence of solvents and under solvent-free conditions

Reihaneh Salmasi<sup>1</sup> · Mostafa Gholizadeh<sup>1</sup>  · Alireza Salimi<sup>1</sup> · Jered C. Garrison<sup>2</sup>

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**Abstract** 1,2-Ethanediylbis(triphenylphosphonium) ditribromide was quantitatively prepared and used for the bromination of anilines and phenols in the presence of a mixed solvent system (DCM/MeOH 2:1) and also under solvent-free conditions. This new ionic liquid has advantages over similar brominating agents in terms of short reaction time, simple workup, regioselectivity and high yields. Single-crystal X-ray analysis of title salt revealed that the bistrphenylphosphonium cation is organized around an inversion center located at the center of the  $-\text{CH}_2-\text{CH}_2-$  bridge and the two triphenylphosphine segments are anti with respect to one another. All the tribromide anions adopt a linear geometry with different Br–Br–Br bond angles for each anion.

## Graphical Abstract



**Keywords** Bromination · Regioselectivity · Crystal structure · Nucleophilic substitutions · Solvent-free

## Introduction

In current times, organic ammonium and phosphonium tribromides are becoming a small yet important groups of reagents for organic transformations [1–20]. Because of their ease of formation, mildness, environmental benignity and immense versatility, these reagents have become quite popular and a number of reports are available discussing the importance of these reagents in various types of organic transformations. Also, the bromination of aromatic substrates has received more attention in recent years for the synthesis of biologically active compounds, including natural products and intermediates for agrochemicals. Numerous important biomedical and industrial products,

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✉ Mostafa Gholizadeh  
m\_gholizadeh@um.ac.ir

<sup>1</sup> Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, Mashhad 91775-1436, Islamic Republic of Iran

<sup>2</sup> Department of Pharmaceutical Sciences, University of Nebraska Medical Center, Omaha, NE 985830, USA

such as potent antitumor, antibacterial, antifungal, antiviral and antioxidizing agents, utilize brominated aromatic substrates.

Bromine, the most common brominating reagent, brominates unsaturated compounds via a free radical method [2, 3]. Since treatment of bromine as a brominating reagent is not always easy because of its volatile and toxic character, many attempts to develop a stable solid agent in place of liquid bromine have been made. Among brominating reagents, ionic liquids such as phenyltrimethylammoniumtribromide, cetyltriethylammoniumtribromide, tetrabutylammoniumtribromide, ethyltriphenylphosphoniumtribromide, tridecylmethylphosphoniumtribromide and benzyltriphenylphosphoniumtribromide [1–8] are much more suitable. Because of their following characteristics: thermal stability, non-flammable, non-volatile [9], ease of storage and handling, environmental compatibility as well as experimentally [10], maintenance of desired stoichiometry [11, 12], regioselectivity of products and efficiency usually give good yields and also benchtop reagents.

Relative to ammoniumtribromides that frequently produce poly-brominated aromatic compounds [13],

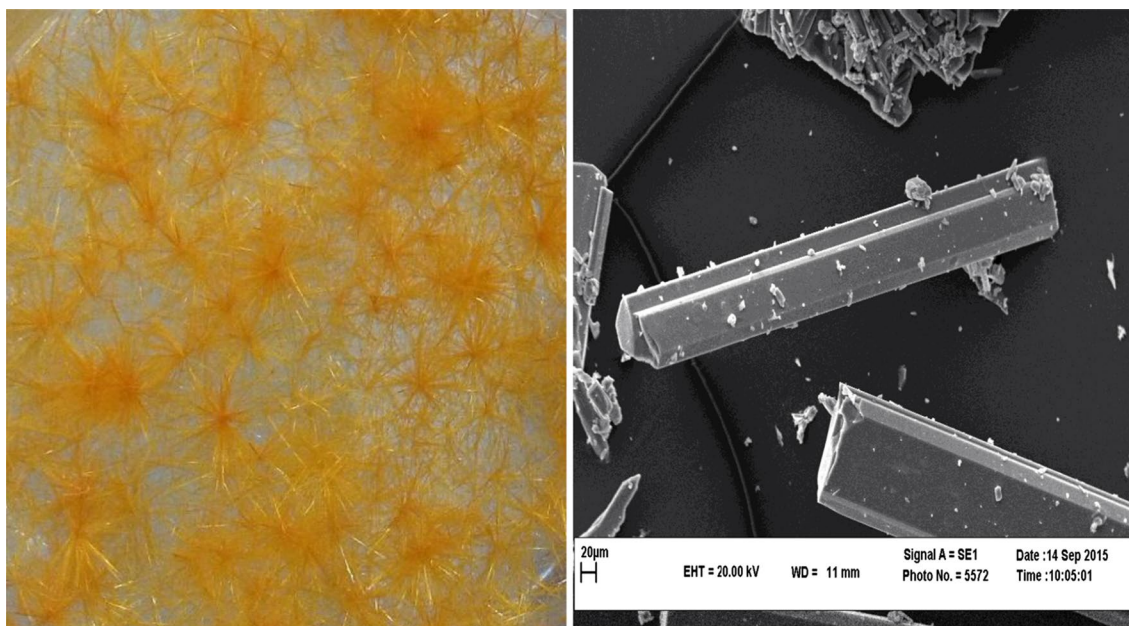
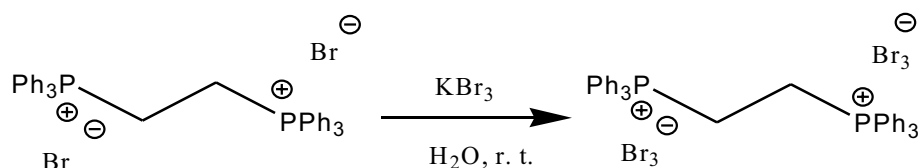
phosphoniumtribromides possess a more mild reactivity in the brominating of organic compounds [14–17]. To date, numerous substrates have been brominated by phosphoniumtribromides [18]. It would be extremely useful to develop further synthetic protocols for the synthesis of organic tribromide reagents [19, 20].

Herein, we have synthesized a novel brominating agent as 1,2-ethanediylbis(triphenylphosphonium) ditribromide (**1**). This reagent has higher bromine content per molecule, regioselectivity and the bromination efficiency. In addition, we have demonstrated that the spent reagent can be recovered and easily recycled five times.

## Results and discussion

The reagent 1,2-ethanediylbis(triphenylphosphonium) dibromide (**2**) [21] as white crystal was treated with molecular bromine (Scheme 1). The yellow precipitate of (**1**) was filtered (98 % yield, m.p.: 223–225 °C) and recrystallized in chloroform to obtain suitable single crystals which are shown in Fig. 1. It is stable for several months at room

**Scheme 1** Processes for the preparation of 1,2-ethanediylbis-(triphenylphosphonium) ditribromide (**1**) in water and under ambient temperature



**Fig. 1** Image of needle single crystals (*left*) and scanning electron micrograph (SEM) (*right*) of 1,2-ethanediylbis(triphenylphosphonium) ditribromide (**1**)

temperature without loss of its activity, and it has been characterized by spectral and analytical data (see supporting information).

Single-crystal X-ray analysis of (**1**) revealed that the asymmetric unit of  $C_{38}H_{34}P_2^{2+}2Br_3^-$  salt contains two bistriphenylphosphonium cations and four tribromide anions (Table 1; Fig. 2). The geometry of dications (bond lengths and angles) is general and comparable with our previously reported periodate salt [22].

**Table 1** Structural data and refinement for title compound

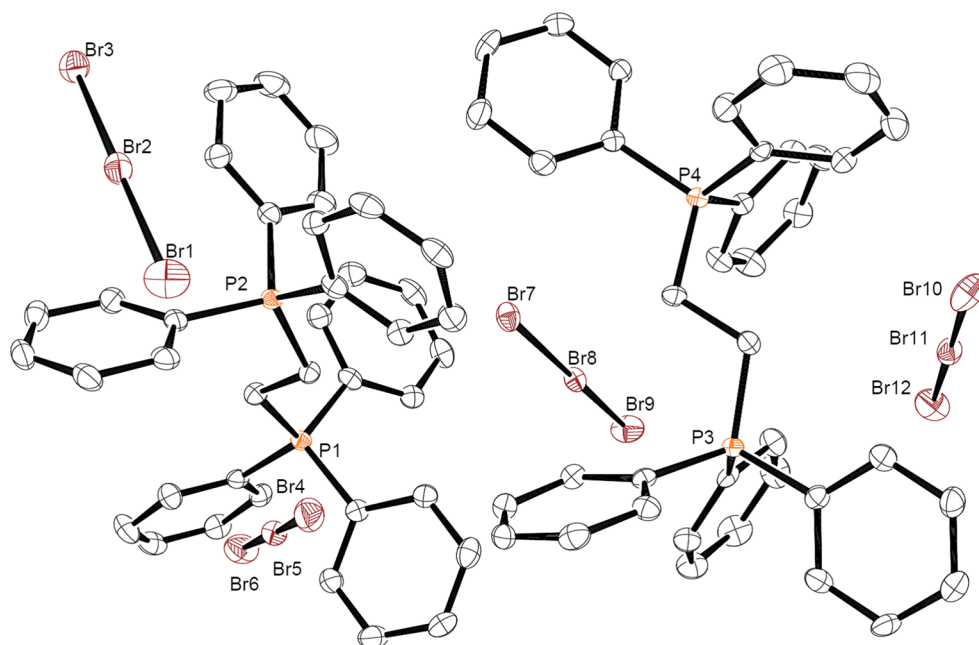
Chemical formula	$C_{38}H_{34}Br_6P_2$
$M_r$	1032.06
Crystal system, space group	Triclinic, $P_1^-$
Temperature (K)	100
$a, b, c$ (Å)	12.3584(3), 15.9950(3), 19.8876(4)
$\alpha, \beta, \gamma$ (°)	102.570(2), 100.138(2), 90.770(2)
$V$ (Å <sup>3</sup> )	3771.61(14)
$Z$	4
Radiation type	CuK $\alpha$
$\mu$ (mm <sup>-1</sup> )	8.696
Crystal size (mm)	0.15 × 0.10 × 0.02
Diffractometer	Xcalibur, Onyx, Ultra
Absorption correction	Multi-scan
$T_{min}, T_{max}$	0.481, 1.000
No. of measured, unique	61,807, 15,449
GOOF	1.066
$R_1(I > 2\sigma(I))$	0.0376
$wR_2(I > 2\sigma(I))$	0.1007

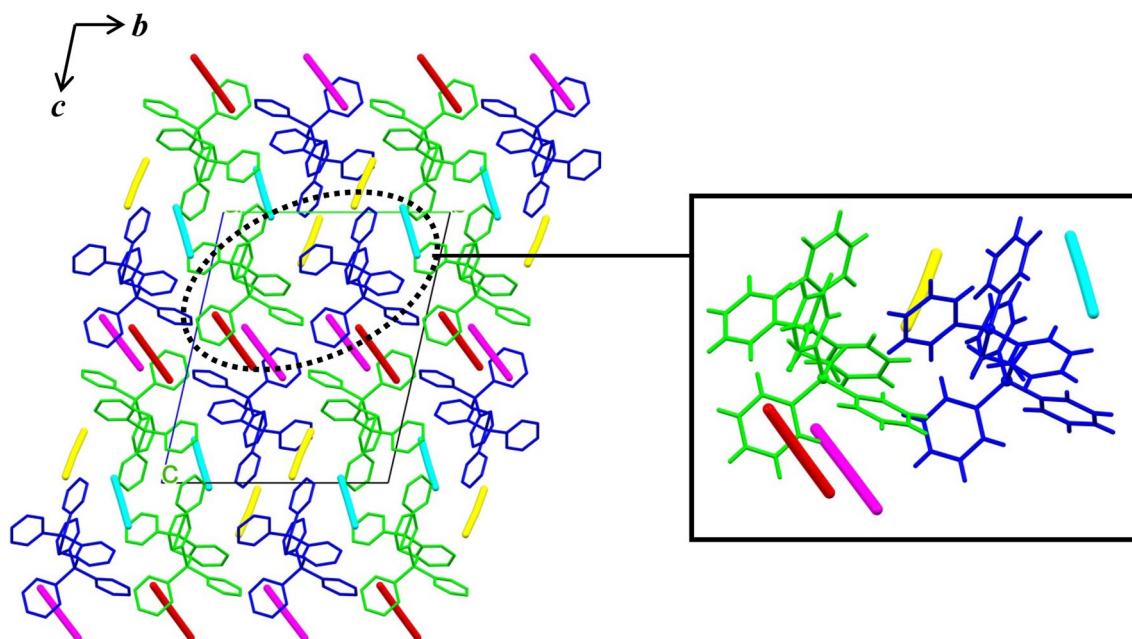
The bistriphenylphosphonium cations lie in general positions and the phosphorous atoms exhibit a slightly distorted tetrahedral geometry. The bond angles around the P atoms are in the range of 107.6(2)–113(3)° for  $P_1$ , 108.7(2)–112.4(3)° for  $P_2$ , 106.6(3)–112.6(2)° for  $P_3$  and 107.2(3)–111.5(2)° for  $P_4$ . The torsion angles of  $P-C_{ethyl}-C_{ethyl}-P$  for dications are 162.8(3)° (for dications with  $P_1$  and  $P_2$  atoms) and  $-161.8(3)^\circ$  (for dications with  $P_3$  and  $P_4$  atoms). The difference of phenyl ring arrangement in the  $-PPh_3$  moieties of dications could be presented by the maximum deviation of phosphorous atom from the phenyl ring planes which are 0.188 Å (from the phenyl ring with  $C_1$  atom) and 0.223 Å (from the phenyl ring with  $C_{71}$  atom).

All of the tribromide anions adopt a linear geometry with Br–Br–Br angles of 178.6(2)°, 179.4(3)°, 176.4(3)° and 177.9(2)° for  $Br_{1-3}$ ,  $Br_{4-6}$ ,  $Br_{7-9}$  and  $Br_{10-12}$  anions, respectively. The bond lengths of Br–Br for two anions ( $Br_{1-3}$ ,  $Br_{4-6}$ ) are the same, while these distances within  $Br_{7-9}$  and  $Br_{10-12}$  anions are dissimilar with the differences of 0.022, 0.001, 0.198 and 0.182 Å for anions, respectively.

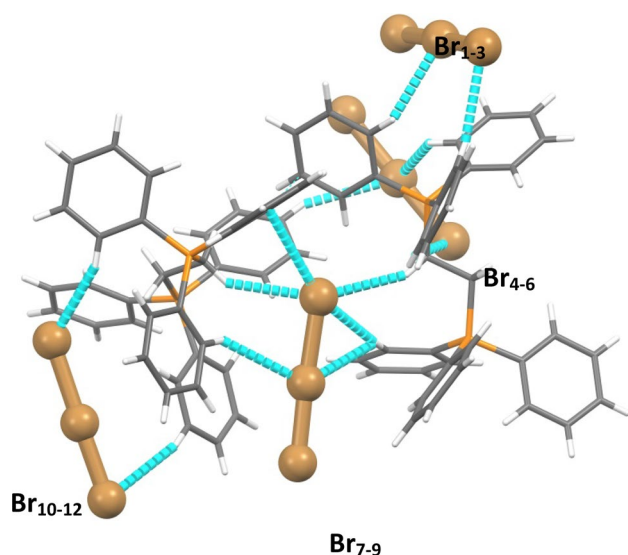
In the crystal packing, the bistriphenylphosphonium dications and ditribromide anions are linked together by several C–H...Br non-classical hydrogen bonds with H...Br distances ranging from 2.873 to 3.023 Å for  $Br_{1-3}$ , from 2.830 to 3.047 Å for  $Br_{4-6}$ , from 2.791 to 2.989 Å for  $Br_{7-9}$  and from 2.805 to 3.534 Å for  $Br_{10-12}$  anions (Figs. 3, 4). In fact, besides the common hydrogen bonds involving oxygen and nitrogen atoms, halogens can also be involved as C–H...X ( $X=Cl, Br, I$ ) weak interactions which can play a crucial

**Fig. 2** Asymmetric unit of the title salt, with atom labels and 50 % probability displacement ellipsoids for non-H atoms. The hydrogen atoms and atom labels of carbon atoms were not shown for clarity





**Fig. 3** A representation of the crystal packing of title compound along *a*-axis (left), the asymmetric unit with different colors of tribromide anions (red, pink, yellow and cyan colors) and phosphonium cations (green and blue) which are shown by symmetry equivalences (right)



**Fig. 4** C–H...Br interactions between tribromide anions and phosphonium cations

role in the stabilization of supramolecular assemblies [23]. The  $\text{Br}_{7-9}$  anion is involved in the  $\text{Br}\dots\text{Br}$  centrosymmetry interaction with the  $\text{Br}_9\dots\text{Br}_9$  distance of 3.487(2) Å. The cation moieties are also interacting through C–H... $\pi$  interactions with each other.

We studied the brominating properties of title compound for anilines and phenols in the presence a mixed solvent (DCM/MeOH 2:1) and under solvent-free conditions. The

proposed probably mechanism for bromination of aniline and phenol under solvent-free conditions might be as outlined in Scheme 2. This mechanism depicts (1) in a rapid equilibrium with the dibromide moiety and bromine under solvent-free conditions.

Furthermore, a plausible mechanism of brominating agent for aniline and phenol in the presence of the mixed solvent system (DCM/MeOH, 2:1) might be outlined in Scheme 3.

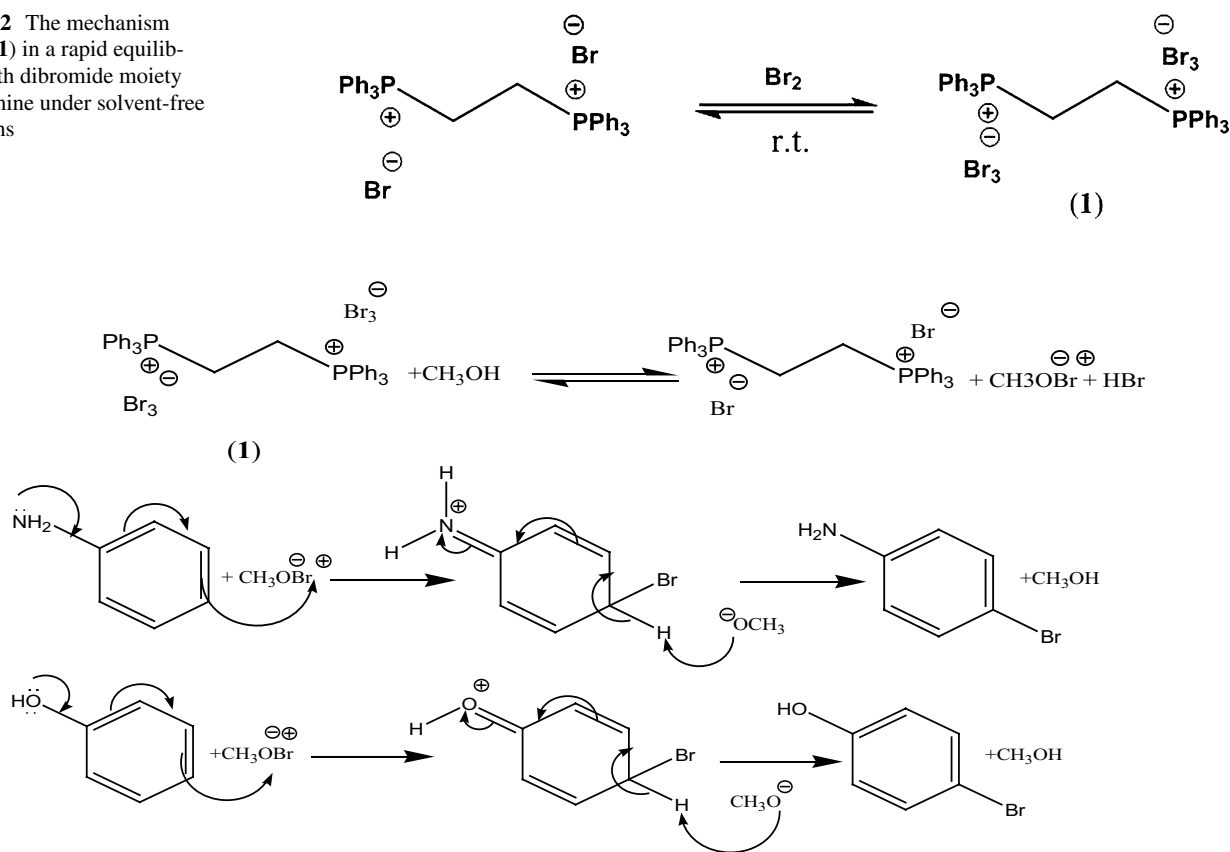
This brominating agent (1) is easily and cheaply prepared by treatment with bromine in high yield. It is completely soluble in DMF, DMSO and acetonitrile while insoluble in ethyl acetate, *n*-hexane and carbon tetrachloride. It is noteworthy that bromination of organic compounds are usually affected by using equimolar ratios of bromine or tribromide (1) with the substrate. Tribromides are more suitable than the liquid bromine because of their crystalline nature, hence ease of storage, transport and maintenance of desired stoichiometry.

One more advantages of (1) in comparison with the bromine and similar brominating agents are much less hygroscopicity at the benchtop and also its stability at room temperature. The bromine content of the reagent in CHNS spectra and the calculated results are in good agreement.

In order to find the optimum condition for the bromination of variety anilines and phenols with (1), we have chosen 4-chloroaniline as a model substrate. We have accomplished the bromination in the presence of different solvents such as mixture of dichloromethane and methanol, dichloromethane, chloroform, ethyl acetate, acetonitrile, *n*-hexane and



**Scheme 2** The mechanism depicts (1) in a rapid equilibrium with dibromide moiety and bromine under solvent-free conditions



**Scheme 3** The proposed mechanism of bromating agent for aniline in the presence of mixed solvents

**Table 2** Optimizing bromination of 4-chloroaniline using (1)

Entries	Solvent	Molar ratio brominating agent:substrate	Reaction time (min)	Yield (%) <sup>a</sup>
1	DCM/MeOH 2:1	1:1	<5 min	98
2	DCM/MeOH 2:1	0.75:1	<5 min	80
3	DCM/MeOH 2:1	0.5:1	<5 min	60
4	DCM/MeOH 2:1	0.25:1	<5 min	35
5	DCM	1:1	15	80
6	CH <sub>3</sub> COOCH <sub>2</sub> CH <sub>3</sub>	1:1	15	N.R.
7	CHCl <sub>3</sub>	1:1	15	60
8	CH <sub>3</sub> CN	1:1	15	60
9	CCl <sub>4</sub>	1:1	15	N.R.
10	<i>n</i> -Hexane	1:1	15	N.R.

1:1 molar ratio of substrate to brominating agent at room temperature of solvents


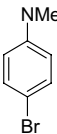
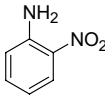
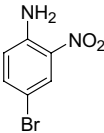
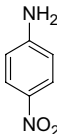
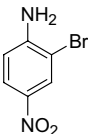
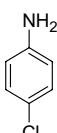
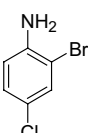
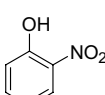
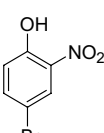
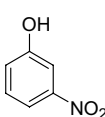
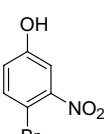
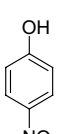
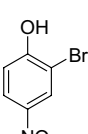
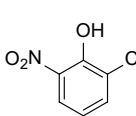
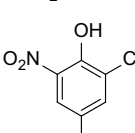
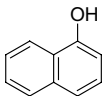
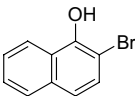
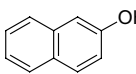
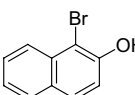
<sup>a</sup> Yields refer to isolated products

also carbon tetrachloride at room temperature and with different molar ratio of brominating agents. The experimental results show that mixture of solvents (DCM/MeOH, 2:1) and 1:1 molar ratio of substrate to brominating agent is the best choice for this purpose. The results are shown in Table 2.

In the following, various anilines and phenols were monobrominated with complete regioselectivity in the

presence of solvents and under solvent-free conditions at room temperature in high yields and the results are summarized in Table 3. In an aromatic electrophilic substitution reaction, para-orientation is favored ortho-orientation due to stereoelectronic effects. Substitution of the aromatic ring with *N,N*-dimethylaniline gave exclusively its para-derivative. When two *o,p*-directing groups are present in

**Table 3** Bromination of various aromatics using (1) under different conditions at room temperature

Entries	Substrate	Product <sup>a</sup>	Yield <sup>b</sup> (%) (Time)		b.p. or m.p. (°C) (References)	
			DCM/MeOH 2:1	Solvent-free	Found	Reported
1			98 (<5 min)	95 (2 min)	53	52–54 [24]
2			98 (<5 min)	92 (5 min)	109–112	110–113 [24]
3			92 (<5 min)	90 (10 min)	105	104–105 [25]
4			90 (<5 min)	87 (10 min)	64–66	64–68 [24]
5			95 (<5 min)	90 (5 min)	89–93	90–94 [24]
6			85 (<5 min)	80 (10 min)	143–144	144–145 [25]
7			90 (<5 min)	85 (10 min)	112–114	111–115 [24]
8			95 (<5 min)	90 (5 min)	113	114 [25]
9			90 (<5 min)	90 (10 min)	43–45	44–46 [26]
10			90 (<5 min)	90 (10 min)	79–81	78–81 [24]

Entries	Substrate	Product <sup>a</sup>	Yield <sup>b</sup> (%) (Time)		b.p. or m.p. (°C) (References)	
			DCM/MeOH 2:1	Solvent-free	Found	Reported
11			N.R.	N.R.	–	–
12			90 (<5 min)	90 (10 min)	112–114	113–115 [24]

<sup>a</sup> Reactions were monitored by TLC

<sup>b</sup> Yields refer to isolated products

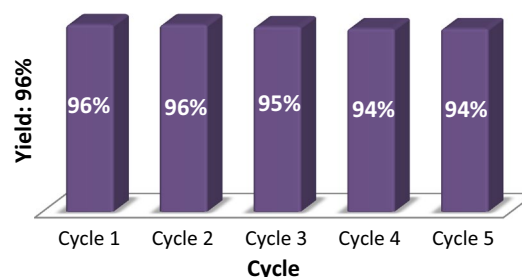
an aromatic ring, substituents having higher *o,p*-directing power influence the incoming bromo group to its para-position and if the para-position is blocked then to its ortho-position as shown for related brominated substrates (Entries 1–5). As expected in the presence of both a meta substituent and *o,p*-directing substituents in the same aromatic ring, the *o,p*-directing groups control the incoming bromo group to its para-position and if the para-position is blocked, the bromination takes place in the ortho- of the *o,p*-directing groups as demonstrated for *p*-nitro aniline (Entry 6).

Regioselective bromination has been demonstrated with anilines bearing various combinations of functional groups. Phenolic substrates bearing *o*-nitro and *o*-chloro and also 3,5 dimethyl groups survived under the described conditions giving corresponding *p*-bromo products, respectively (Entries 8, 12). The fused ring phenolic compound such as  $\alpha$ -naphthol afforded the expected 2-bromo- $\alpha$ -naphthol (Entry 9). The  $\beta$ -naphthol as the same as of  $\alpha$ -naphthol was to produce of 1-bromo- $\beta$ -naphthol (Entry 10). The benzoin was remained unchanged (Entry 11).

We have also conducted these bromination reactions under solvent-free conditions. Under these conditions compared to the presence of mixed solvents, bromination of anilines and phenols occurred on much more longer time (Table 3). All reactions produced better yields in comparison with conventional conditions.

#### Regeneration of ionic liquid under mixture of solvent conditions

After the addition of ether into the reaction mixture, the solid precipitate dissolved in water and filtered off. The water soluble ionic liquid dibromide was recovered by evaporation of the aqueous solution. The recovered ionic liquid dibromide was dried at 100 °C for 12 h and treated with molecular  $\text{KBr}_3$  and reused for the subsequent reaction without loss of activity.



**Fig. 5** Reusability of ionic liquid 1,2-ethanediylbis(triphenylphosphonium) ditribromide (**1**) in the bromination of 4-chloroaniline

The effectiveness of ionic liquid, their recyclability and regeneration processes were observed for the bromination of 4-chloroaniline found be effective up to five cycles in the presence of mixture of solvent (DCM/MeOH 2:1) (Fig. 5).

#### Conclusion

In conclusion, we have shown that (**1**) is an efficient brominating agent, easy storage, benchtop and transport reagent for the bromination of anilines and phenols. The bromination reactions in the presence of mixed solvent systems have occurred faster than the reactions under solvent-free conditions. Furthermore, the reactions in the presence of mixed solvent systems were produced excellent yields. The side products of bromination reactions were not observed at all.

#### Experimental

All the phenols and anilines and triphenyl phosphine also 1,2-dibromo ethane were purchased from Fluka and Merck Co. The reactions were monitored by TLC using silica gel plates. The products were identified by comparison

with their  $^1\text{H}$  NMR,  $^{31}\text{P}$  NMR, IR and GC spectra and physical data with those of authentic samples.

$^1\text{H}$  NMR spectra were measured by the Bruker AC 300 MHz spectrometer with  $\text{DMSO-}d_6$  as solvent. IR spectra were recorded by the Shimadzu FT-IR 8440S spectrophotometer.

GC spectra were recorded by a Shimadzu 17a-GC spectrophotometer. Elemental analysis was performed on a LECO 250 instrument.

#### Preparation of 1,2-Ethanedylbis(triphenylphosphonium) ditribromide ( $\text{C}_{38}\text{H}_{34}\text{Br}_6$ )(1)

Bromine (3.072 g, 19.2 mmol) was added dropwise to a solution of KBr (2.28 g, 19.2 mmol) in water (36 ml) in a 50-ml beaker with stirring at room temperature. After 1 h the bromine layer disappeared and  $\text{KBr}_3$  was produced. The  $\text{KBr}_3$  solution was adjoined dropwise to a solution of 1,2-ethanedylbis(triphenylphosphonium) dibromide (2) (6.84 g, 9.6 mmol) in water (300 ml) was added. After stirring the mixture for 30 min, it was filtered and washed with water ( $3 \times 20$  ml). Finally the filtered cake was dried and recrystallized in  $\text{CHCl}_3$  as yellow crystals 9.71 g (98 %). m.p.: 223–225 °C;  $^1\text{H}$  NMR, (300 MHz, DMSO):  $\delta = 4$  (s,  $\text{CH}_2$ ), 7.75, 7.95 (m, aromatic hydrogens) ppm;  $^{31}\text{P}$  NMR (300 MHz, DMSO):  $\delta = 136.2, 134.9, 131.1, 119, 16$  ppm; IR(KBr)  $\bar{\nu} = 481(\text{w}), 523(\text{m}), 684(\text{s}), 734(\text{s}), 1106(\text{s}), 1434(\text{s}), 1480\text{--}1582(\text{m}), 2900(\text{w}), 3051(\text{w}) \text{ cm}^{-1}$ .

#### Determination of $\text{Br}_2$ in 1,2-Ethanedylbis(triphenylphosphonium) ditribromide ( $\text{C}_{38}\text{H}_{34}\text{Br}_6$ )(1)

At first, the reagent (1) was dissolved in DMSO; then, it has determined the amount of molecular bromine in 1, 2-ethanedylbis(triphenylphosphonium) ditribromide by the titration through  $\text{AgNO}_3$ .

#### General procedure for bromination of anilines or phenols in the presence of mixture solvents

To a mixture of anilines or phenols (0.7 mmol) the brominating agent (1) (0.72 g, 0.7 mmol) in dichloromethane (30 ml)-methanol (15 ml) was added. The reaction mixture was stirred at room temperature until decolorization of the orange solution took place. The progress of the reaction was monitored by TLC (eluent: *n*-hexane/ethyl acetate, 7:3). After completion of the reaction, the solvent was evaporated and diethyl ether (10 ml) was added to the residue. The supernatant was decanted and the insoluble residue was washed by ether ( $3 \times 10$  ml). The combined ether extracts were dried on magnesium sulfate and also

evaporated under vacuum to afford monobromo anilines or monobromo phenols which was purified by flash column chromatography over silica gel (*n*-hexane/ethyl acetate, 7:3).

#### General procedure for bromination of anilines or phenols under solvent-free conditions

To a mixture of anilines or phenols (0.7 mmol), the brominating agent (1) (0.72 g, 0.7 mmol) under solvent-free conditions was added. The reaction mixture was stirred at room temperature until disappearance of the starting material (monitored by TLC; eluent: *n*-hexane/ethyl acetate, 7:3).

After complete reaction, water was added into the reaction mixture to quench it. The resulting reaction mixture was extracted with diethyl ether, separated from the organic layer, dried over sodium sulfate and purified by flash column chromatography over silica gel (*n*-hexane/ethyl acetate, 7:3).

The products were identified by comparison with their  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and physical data with those of authentic samples. For examples we have reported some  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR of products as followed:

**4-bromo-*N,N*-dimethyl aniline**  $^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.3(\text{d}, 2\text{H}, \text{ArH}), 6.6(\text{d}, 2\text{H}, \text{ArH}), 3(\text{s}, 6\text{H}, \text{Me})$  ppm.

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 149.5, 132, 114, 108, 40$  ppm.

**4-bromo-2-nitro aniline**  $^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.24(\text{d}, 1\text{H}, \text{ArH}), 7.42(\text{d}, 1\text{H}, \text{ArH}), 6.74(\text{d}, 1\text{H}, \text{ArH}), 6.12(\text{brs}, 2\text{H}, \text{NH}_2)$  ppm.

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 143, 139, 127, 120, 108$  ppm.

**2-bromo-4-nitro aniline**  $^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.4(\text{d}, 1\text{H}, \text{ArH}), 8(\text{dd}, 1\text{H}, \text{ArH}), 6.71(\text{d}, 1\text{H}, \text{ArH}), 5(\text{brs}, 2\text{H}, \text{NH}_2)$  ppm.

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 150, 138.5, 129.3, 124.5, 113.5, 107$  ppm.

**2-bromo-4-chloro aniline**  $^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.4(\text{d}, 1\text{H}, \text{ArH}), 7.1(\text{dd}, 1\text{H}, \text{ArH}), 6.65(\text{d}, 1\text{H}, \text{ArH}), 4.1(\text{brs}, 2\text{H}, \text{NH}_2)$  ppm.

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 144.8, 131, 128.5, 123.5, 120, 115.4$  ppm.



**4-bromo-2-nitro phenol**  $^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 10.5(\text{brs}, 1\text{H}, \text{OH}), 8.25(\text{d}, 1\text{H}, \text{ArH}), 7.7(\text{dd}, 1\text{H}, \text{ArH}), 7.1(\text{d}, 1\text{H}, \text{ArH})$  ppm.

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 153.5, 140, 134, 126.8, 121.2, 111$  ppm.

**4-bromo-3-nitro phenol**  $^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 9.7(\text{brs}, 1\text{H}, \text{OH}), 7.5(\text{d}, 1\text{H}, \text{ArH}), 7.35(\text{d}, 1\text{H}, \text{ArH}), 6.95(\text{dd}, 1\text{H}, \text{ArH})$  ppm.

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 157.5, 150, 135.1, 121.2, 113, 102.5$  ppm.

**2-bromo-4-nitro phenol**  $^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.45(\text{d}, 1\text{H}, \text{ArH}), 8.1(\text{dd}, 1\text{H}, \text{ArH}), 7.1(\text{d}, 1\text{H}, \text{ArH}), 6.2(\text{brs}, 1\text{H}, \text{OH})$  ppm.

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 159.5, 140.5, 126, 125, 119, 111.8$  ppm.

**4-bromo-2-chloro-6-nitro phenol**  $^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 10.4(\text{s}, 1\text{H}, \text{OH}), 8.22(\text{d}, 1\text{H}, \text{ArH}), 7.85(\text{d}, 1\text{H}, \text{ArH})$  ppm.

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 150.1, 140, 134.5, 126, 126.1, 114.9$  ppm.

**2-bromo-1-naphthol**  $^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.25(\text{d}, 1\text{H}, \text{ArH}), 8.2(\text{d}, 1\text{H}, \text{ArH}), 7.65(\text{m}, 3\text{H}, \text{ArH}), 6.75(\text{d}, 1\text{H}, \text{ArH}), 5.45(\text{brs}, 1\text{H}, \text{OH})$  ppm.

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 150.12, 132.8, 129.4, 128.3, 127.2, 127.1, 126, 122, 113.5, 109$  ppm.

**1-bromo-2-naphthol**  $^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.01(\text{d}, 1\text{H}, \text{ArH}), 7.7(\text{d}, 2\text{H}, \text{ArH}), 7.58(\text{t}, 1\text{H}, \text{ArH}), 7.45(\text{t}, 1\text{H}, \text{ArH}), 7.25(\text{t}, 1\text{H}, \text{ArH}), 5.5(\text{brs}, 1\text{H}, \text{OH})$  ppm.

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 152, 132, 130, 129, 128, 127, 125, 124, 117, 113$  ppm.

**4-bromo-3,5-dimethyl phenol**  $^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 6.5(\text{s}, 2\text{H}, \text{ArH}), 5(\text{brs}, 1\text{H}, \text{OH}), 2.35(\text{s}, 6\text{H}, \text{Me})$  ppm.

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 151.2, 131.2, 125.5, 112.2, 16$  ppm.

### X-ray crystallography

X-ray data for title compound were collected on Oxford Diffraction Excalibur PX Ultra. The structures was solved

by direct methods [27] and subsequent different Fourier maps and then refined on  $F^2$  by a full-matrix least-square procedure using anisotropic displacement parameters. The structures were checked for higher symmetry with the help of the program PLATON [28]. For all compounds, the non-H atoms were refined anisotropically and H atoms were placed in the ideal positions. The structural resolution procedure was made using Win GX crystallographic software package [29]. A summary of crystallographic data and structural refinement is given in Table 1.

CCDC-1453108 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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