





Synthesis and characterization of tetraphenylammonium salts

Hikaru Fujita ^{1✉}, Ozora Sasamoto ¹, Shiori Kobayashi¹, Masanori Kitamura ^{1,2} & Munetaka Kunishima ^{1✉}

The phenyl (Ph) group is a representative substituent in the field of organic chemistry as benzene (the parent molecule) is of fundamental importance. Simple Ph-substituted compounds of common chemical elements are well known. However, extensive structural characterization of tetraphenylammonium (Ph_4N^+) salts has not been reported. Herein, the synthesis of Ph_4N^+ salts and their characterization data including the ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra and the single-crystal X-ray structure have been presented. An intermolecular radical coupling reaction between an aryl radical and a triarylammonium radical cation was conducted to synthesize the target moieties. The Ph_4N^+ salts described herein are the simplest tetraarylammonium (Ar_4N^+) salts known. The results reported herein can potentially help access the otherwise inaccessible non-bridged Ar_4N^+ salts, a new class of rigid and sterically hindered organic cations.

¹ Faculty of Pharmaceutical Sciences, Institute of Medical, Pharmaceutical, and Health Sciences, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan. ² Present address: Faculty of Pharmaceutical Sciences, Matsuyama University, 4-2, Bunkyo-cho, Matsuyama 790-8578, Japan.

✉ email: hfujita@staff.kanazawa-u.ac.jp; kunisima@p.kanazawa-u.ac.jp

The elements in groups 13 (B and Al), 14 (C and Si), and 15 (N and P) typically form tetrahedral ions or molecules of the general formula $R_4Z^{0\pm 1}$, when four identical substituents (R_4) are attached to the central element (Z). The charge on the atom Z depends on the group to which it belongs: -1 , 0 , and $+1$ for groups 13, 14, and 15, respectively. Compounds of type $R_4Z^{0\pm 1}$, bearing simple R substituents, are of special importance and considered benchmark compounds. The structural features, physical properties, and chemical reactivities of the other derivatives belonging to this class of compounds were compared with those of the benchmark compounds for a deeper understanding of the compound characteristics. Therefore, for a long time, organic chemists have focused on synthesizing such $R_4Z^{0\pm 1}$ compounds bearing simple R substituents. The compounds of the general formula $R_4Z^{0\pm 1}$ ($R = \text{Ph}$ (Ph_4B^- , Ph_4Al^- , Ph_4C , Ph_4Si , and Ph_4P^+ ; Fig. 1))^{1–6} are known since long. Ph_4Si was identified more than 130 years ago. The fundamental properties of these $\text{Ph}_4Z^{0\pm 1}$ compounds have been studied extensively over a long period of time. The results serve as references during the study of the corresponding tetraaryl-substituted compounds ($\text{Ar}_4Z^{0\pm 1}$). Quantum chemical calculations have been conducted for Ph_4N^+ . However, the experimental properties of this simple organic cation remain largely unknown. Though several researchers have reported the application prospects of the Ph_4N^+ salts (Supplementary Table 1), the synthetic route followed, and the compound characteristics have not been reported.

It has been reported that the pentatritiated tetraphenylammonium salts (**1**; Fig. 2a) can be formed following the nuclear-chemical method via the tritium β -decay of hexatritiated benzene (C_6T_6)^{8,9}. The isomorphous co-crystallization data and the radioactivity-based yields have been documented. However, the detailed synthetic procedure and data from experiments conducted for structure identification have not been reported. Bridged Ar_4N^+ salts are structurally similar to the Ph_4N^+ salts. In 1963, Nesmeyanov synthesized the (*N,N*-diphenyl)carbazolium salts (**2**; Fig. 2b) as the first examples of this class of compounds¹⁰. The key reaction step affording **2** from precursor **3** was the intramolecular *N*-arylation of triarylamine. The step proceeded via the decomposition of the spatially proximal

aryldiazonium moiety. This process resulted in the formation of a 5-membered ring containing a nitrogen atom bearing four aromatic rings. Following the success of the method, a similar cyclization strategy was followed for the synthesis of various (*N,N*-diaryl)carbazolium salts^{11–16} (such as **4** and **5**; Fig. 2c), and sulfide- or amide-bridged Ar_4N^+ salts (**6**¹⁷ and **7**¹⁸, respectively). Recently, the quaternary ammonium structure of **2** was confirmed using the single-crystal X-ray diffraction technique^{13,16}. However, none of these bridged Ar_4N^+ salts could be converted to Ph_4N^+ salts, as there is a dearth of efficient methods that can be used to remove the bridge moieties¹⁷.

Ar_4N^+ is a promising organic cation that can be used for developing surfactants, supporting electrolytes, phase-transfer catalysts, and anion-exchange membranes¹³. Also, it is potentially useful for industrial and biological studies. The wide application range of the cation can be attributed to the high chemical stability^{14,15} and unique rigid structure of the organic cation. Although the bridged Ar_4N^+ cations represented by **2** have been studied and characterized, non-bridged Ar_4N^+ cations have not been explored because of synthetic limitations.

Herein, we report a synthetic strategy for the preparation of Ph_4N^+ salts. To the best of our knowledge, this is the first report where the results of structural characteristics of the cation have been reported.

Results and discussion

Synthetic strategy. The direct *N*-phenylation of triphenylamine (**8**; Fig. 3a) using a Ph cation (or its synthetic equivalent) to form Ph_4N^+ is difficult because **8** is weakly nucleophilic (indicated by the low pK_{aH} value (-3.91)¹⁹ recorded during *N*-protonation). Ph_4N^+ salts could not be obtained by reacting **8** with a phenyldiazonium unit¹⁰. The *N*-phenylation of **8** using diphenyliodonium²⁰ or the in-situ-generated benzyne²¹ unit was

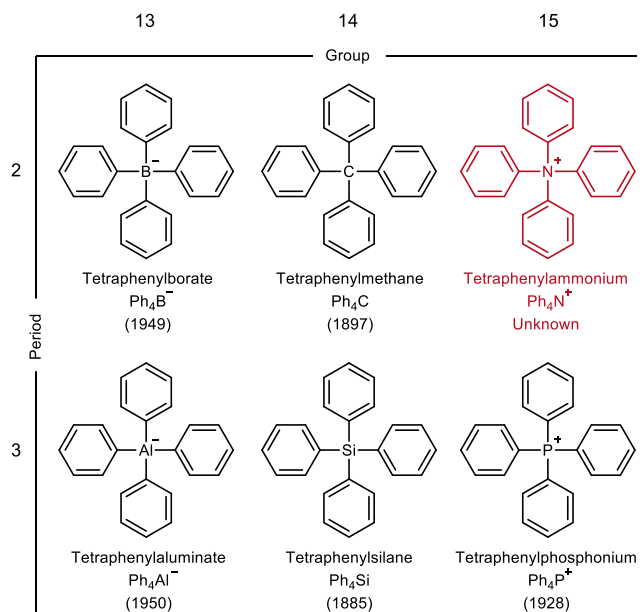


Fig. 1 Structures of Ph_4 -substituted elements belonging to the groups 13–15, $\text{Ph}_4Z^{0\pm 1}$. The number in the parentheses indicates the year of synthesis (reported in the literature).

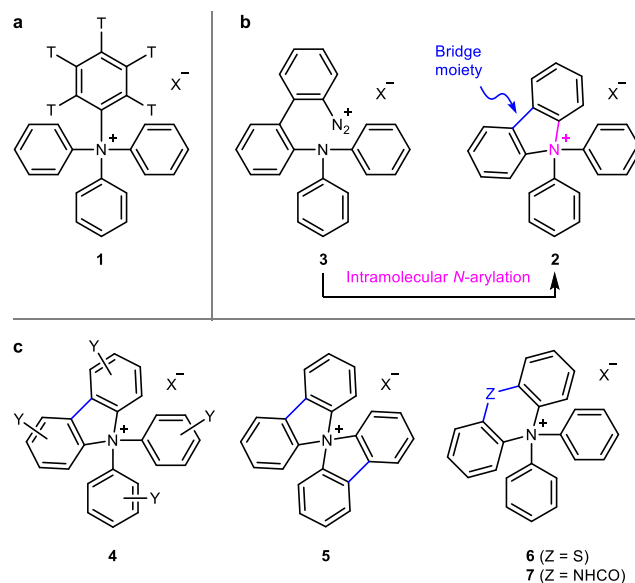


Fig. 2 Ar_4N^+ salts reported in the literature. Counter anions are depicted in the general form X. **a** Pentatritiated Ph_4N^+ salts (**1**) reported without proper structural data. **b** Synthesis of (*N,N*-diphenyl)carbazolium salts (**2**) from precursor **3** following the process of intramolecular *N*-arylation. The bridge moiety indicated in blue must be removed to obtain the Ph_4N^+ salts. **c** Other bridged Ar_4N^+ salts such as (*N,N*-diphenyl)carbazolium salts (**4**) bearing various substituents Y on the aryl groups, spirocarbazolium salts (**5**), sulfide-bridged Ar_4N^+ salts (**6**), and amide-bridged Ar_4N^+ salts (**7**) prepared following the intramolecular *N*-arylation strategy. The bridge moieties are indicated in blue.

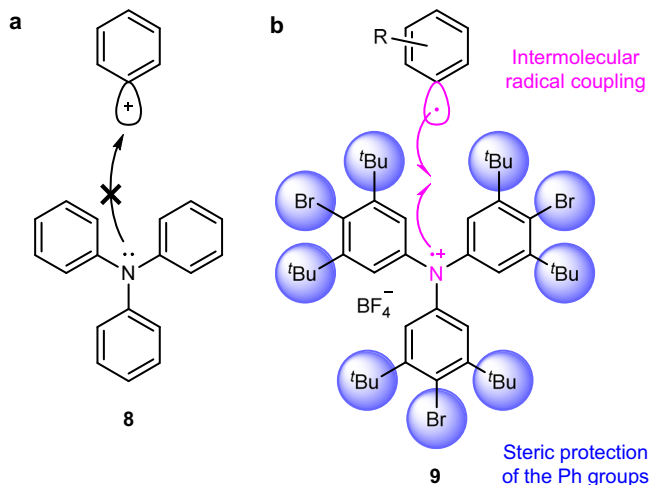


Fig. 3 Synthetic strategy followed for the construction of a non-bridged Ar_4N^+ structure. **a** Direct *N*-phenylation of **8** with a Ph cation is difficult as the N atom is a weak nucleophile. **b** Intermolecular radical coupling reaction between an aryl radical and the triarylammonium salt **9** bearing bulky protecting groups that exert steric hindrance and block the reactions at the Ph groups.

also unsuccessful. We designed the triarylammonium salt (**9**; Fig. 3b) as a novel precursor that could be used for the synthesis of Ph_4N^+ to address the problem of low reactivity of **8**. In general, triarylamines can be oxidized to form the corresponding radical cations (referred to as triarylammoniumyls) that exhibit high reactivity. Triphenylammoniumyl easily dimerizes via the para positions of the Ph groups following the process of intermolecular radical coupling to afford tetraphenylbenzidine²². The results obtained from quantum chemical calculations revealed that the singly occupied molecular orbital of triphenylammoniumyl was spread over all the Ph rings and the central nitrogen atom²³. Therefore, we expected that the intermolecular radical coupling reaction involving a triphenylammoniumyl unit and an aryl radical occurs via the nitrogen atom if the Ph group is hindered by steric protection. The tert-butyl and bromo groups were selected as the bulky protecting groups of **9** at the meta- and para-positions, respectively. These groups can exert a large extent of steric hindrance and can be removed at the later stages of the synthetic procedure.

Synthesis. The starting material used for the synthesis of the target was tris[(3,5-di-tert-butyl)phenyl]amine (**10**; Fig. 4), which was prepared over three steps starting from benzene: Friedel–Crafts reaction, dealkylative bromination, and palladium-catalyzed amination^{24,25}. The para-brominated compound **11** was formed in 81% yield when **10** was treated with *N*-bromosuccinimide (NBS). The triarylamine **11** was then activated to form the triarylammoniumyl salt **9** following the one-electron oxidation process using AgBF_4 ²⁶. It was isolated as a monohydrate in 93% yield. Similar to other triarylammoniumyl salts²², **9** was a blue solid. The color could be attributed to the absorption over the visible region ($\lambda_{\text{max}} = 797 \text{ nm}$ in *o*-dichlorobenzene). Following this, we investigated the key intermolecular radical coupling reactions. Bis(3,5-di-tert-butyl)benzoyl peroxide (**13**) was used as the starting material for the in situ generation of the (3,5-di-tert-butyl)phenyl radical (**12**). The formation of the radical proceeded via the process of O–O homolysis, which was followed by the process of decarboxylation²⁷. A mixture of **9** and **13** was heated to 120 °C in *o*-dichlorobenzene in the presence of (2,6-di-tert-butyl)pyridine (**14**; used as a base) until the

characteristic blue color of **9** disappeared. The reaction conditions were selected from the results of the screening experiments (vide infra). The desired Ar_4N^+ salt **15** was successfully formed in a low yield (0.1%), which was then isolated using the normal-phase ion-pair chromatography technique²⁸. Under these conditions, 4 g of **9** could be converted to 5 mg of **15**. The byproducts formed during the reaction were triarylamine **11** (11%), solvent adduct **16** (4% based on **13**), and sterically congested triarylamines **17** (7%) and **18** (8%) possessing ortho-[(3,5-di-tert-butyl)benzoyl]oxy and ortho-(3,5-di-tert-butyl)phenyl groups, respectively. The structures of **17** and **18** were determined using the single-crystal X-ray diffraction technique (Supplementary Tables 2 and 3, respectively). The formation of **17** and **18** indicated that the extent of steric protection provided by the meta-tert-butyl groups in **9** was not sufficient to efficiently inhibit the occurrence of the ortho-substitution reactions at the Ph rings. Supplementary Table 4 shows the process of reaction condition screening for the intermolecular radical coupling reaction conducted on a small scale using **9** (80–100 mg). When the reaction was conducted in *o*-dichlorobenzene in the presence of **14** (entry 1), the yield of the desired ammonium salt **15** was 0.12% (determined by ¹H NMR spectroscopic analysis). Although the same yield (0.12%, entry 2) of **15** was obtained when the reaction was carried out in the absence of **14**, it was difficult to purify the product under these conditions as various byproducts were also formed during the process. The use of other solvents in combination with **14** afforded lower (entries 3–10) or undetectable (entries 11–14) yields of **15**, and a complex mixture of compounds which could not be purified or analyzed (entries 16–21). Thus, the reaction conditions presented in entry 1 were used to synthesize **15** from **9** (4 g). We also attempted the intermolecular radical coupling reaction involving **13** and tris[(3,5-di-tert-butyl)phenyl]ammoniumyl BF_4^- (**19**; devoid of the *p*-bromo groups). The latter was prepared following the one-electron oxidation of **10**. However, the desired product tetrakis[(3,5-di-tert-butyl)phenyl]ammonium BF_4^- (**20**) could not be isolated as the reaction yielded a complex mixture. Therefore, the removal of all the bromo groups in **15** was carried out following the process of bromine–lithium exchange using ⁿBuLi at –78 °C. The resulting product was protonated with (2,6-di-tert-butyl)pyridinium BF_4^- salt (**21**), affording **20** in 90% yield. Since we selected diacyl peroxide **13** as the precursor of aryl radical **12** to introduce the (3,5-di-tert-butyl)phenyl group in **9**, the ammonium nitrogen of **20** was connected to four identical aryl groups. The counter anion of **20** was exchanged to prepare the corresponding $\text{B}(\text{C}_6\text{F}_5)_4^-$ salt (**22**), the structure of which was confirmed using the single-crystal X-ray diffraction technique (Supplementary Table 5). The final step toward the formation of Ph_4N^+ involved the dealkylation of the tert-butyl groups present on the aromatic rings of **20**. All the eight tert-butyl groups could be successfully removed when **20** was heated at 150 °C over a period of 14 h in a solvent amount of trifluoromethanesulfonic acid (TfOH)²⁹. The reaction afforded $\text{Ph}_4\text{N}^+ \text{BF}_4^-$ (**23**) in 59% yield. This result indicates the high stability of Ph_4N^+ under extremely harsh acidic conditions. Following the process of counter anion exchange, the BF_4^- salt (**23**) was converted to the $\text{B}(\text{C}_6\text{F}_5)_4^-$ salt (**24**; yield: 81%; white solid). The purity of the counter anion was confirmed using the ¹⁹F NMR spectroscopy technique.

¹H and ¹³C NMR spectra. The ¹H NMR signals corresponding to **24** (spectra recorded in $(\text{CD}_3)_2\text{CO}$) appeared at approximately 7.89, 7.69, and 7.65 ppm. The signal corresponded to the ortho, meta, and para-protons present in the Ph ring, respectively. The ¹³C NMR signals corresponding to **24** (spectra recorded in $(\text{CD}_3)_2\text{CO}$) appeared at 149.7 (ipso), in the range of 131.4–131.2

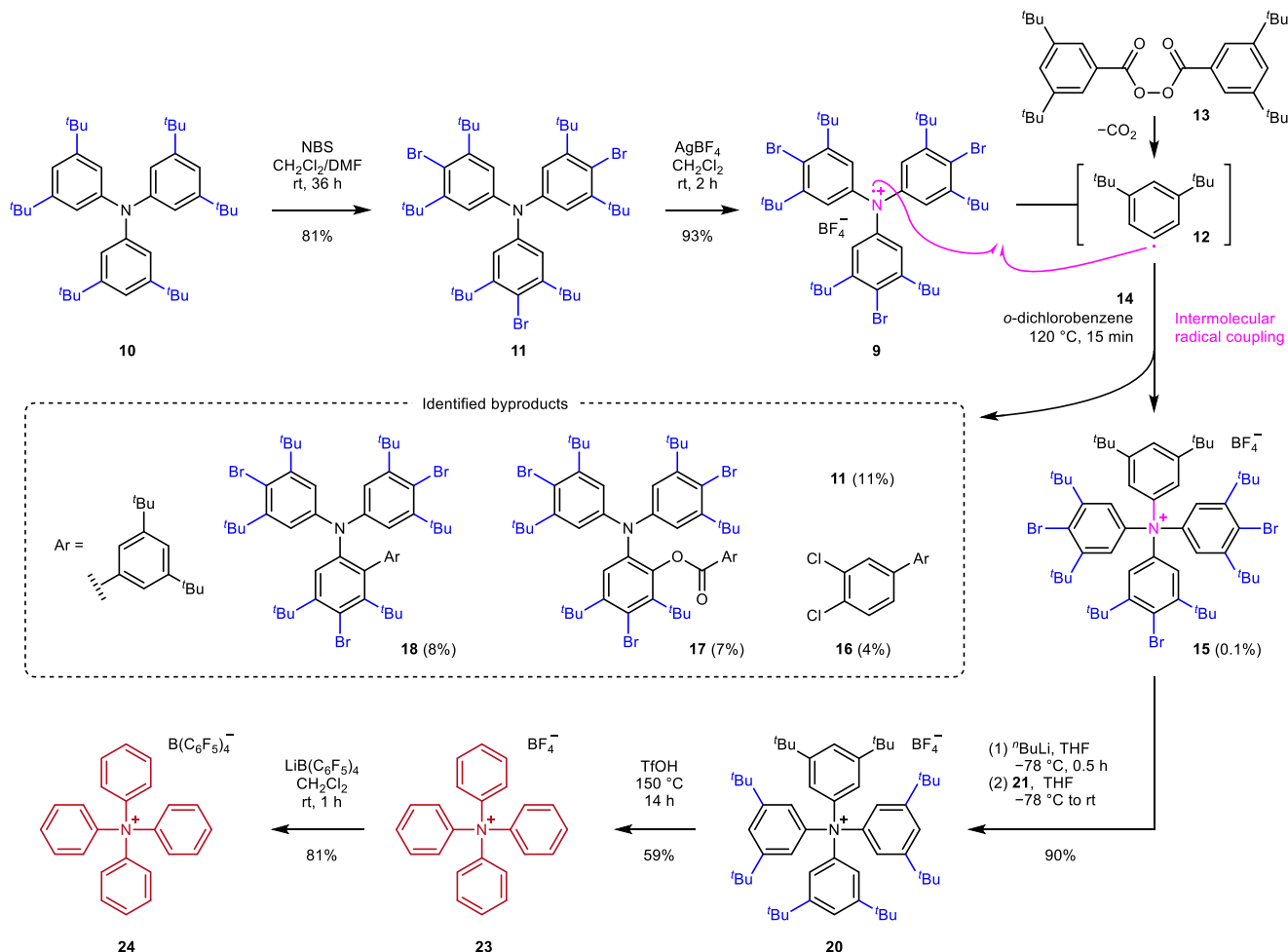


Fig. 4 Synthetic scheme for the formation of the Ph_4N^+ salts **23 and **24**.** Triarylammonium salt **9** was prepared from **10** over 2 steps. The intermolecular radical coupling reaction between **9** and aryl radical **12**, formed in situ following the thermolysis of the diacyl peroxide **13**, yielded the Ar_4N^+ salt (**15**) along with various byproducts (**11**, **16**, **17**, and **18**). Removal of the bromo and tert-butyl groups in **15** afforded **23**, whose counter anion was exchanged to obtain **24**.

(para and meta), and at 126.8 (ortho) ppm. The signals were assigned to the corresponding carbon atoms using the HMQC technique. The ^1H and ^{13}C NMR signals corresponding to **24** appeared downfield compared to the signals corresponding to **8** (Fig. 5a, b). The downfield shift can be attributed to the strong inductive effect exerted by the ammonium nitrogen in **24** and the loss of the resonance effect of the lone pair of electrons on nitrogen present in **8** following *N*-quaternization. The signals corresponding to the meta and para protons present in **24** (at ~ 7.69 and ~ 7.65 ppm, respectively) appeared at up-field compared to the signals corresponding to Ph_4P^+ $\text{B}(\text{C}_6\text{F}_5)_4^-$ (**25**; ~ 7.88 and ~ 8.02 ppm for meta and para protons, respectively). The up-field shift may be attributed to the strong anisotropic effects observed in Ph_4N^+ . The generation of the strong anisotropic effects can be attributed to the fact that Ph_4N^+ is smaller than Ph_4P^+ . Similarly, we observed that the signals corresponding to the meta and para protons in Ph_4C ($(\text{CD}_3)_2\text{CO}$; at ~ 7.29 and ~ 7.21 ppm, respectively) appeared up-field compared to the signals corresponding to Ph_4Si (meta and para protons appear at ~ 7.44 and ~ 7.48 ppm, respectively; Supplementary Fig. 1)³¹.

Single-crystal X-ray structure analysis. The single-crystal X-ray diffraction technique was used to analyze the structure of **24**. Analysis of the results proved the quaternary ammonium structure of **24** (Fig. 5c, top view). The counter anion $\text{B}(\text{C}_6\text{F}_5)_4^-$ was

omitted for clarity (Supplementary Table 6). The Ph_4N^+ structure exhibited S_4 -like symmetry and not D_{2d} -like symmetry. The result agreed well with the theoretically predicted result³². The $\text{N}-\text{C}(\text{sp}^2)$ bond length in **24** (present between the Ph_4N^+ nitrogen unit and the sp^2 carbon atom) in the Ph group was 1.529 ± 0.003 Å (Fig. 5c, side view). This bond is longer than the $\text{N}-\text{C}(\text{sp}^2)$ bonds in $(\text{CH}_3)_3\text{PhN}^+$, $(\text{CH}_3)_2\text{Ph}_2\text{N}^+$, $(\text{CH}_3)_3\text{Ph}_3\text{N}^+$, and *N,N*-diphenylcarbazolium, which were 1.50³³, 1.51²¹, 1.52²¹, and 1.51–1.52¹⁶ Å, respectively (data from Cambridge Crystallographic Data Center (CCDC) deposition numbers of 291166, 1433867, 1433868, and 1890475, respectively). The long $\text{N}-\text{C}(\text{sp}^2)$ bond in Ph_4N^+ indicates the presence of an unusually hindered environment around the ammonium nitrogen atom. The lengths of the bonds formed between the central atom and the sp^2 carbons in Ph_4C , Ph_4B^- , Ph_4P^+ , Ph_4Si , and Ph_4Al^- were 1.56³⁴, 1.64–1.66³⁵, 1.79³⁶, 1.88³⁷, and 2.00–2.03³⁸ Å, respectively. Thus, Ph_4N^+ is characterized by the most sterically congested environment among these $\text{Ph}_4\text{Z}^{0\pm 1}$, reflecting the difficulty faced during synthesis. The $\text{C}-\text{N}$ bond length of Ph_4N^+ (1.529 Å) was ca. 8% longer than that of **8** (1.419 Å)³⁹, whereas the $\text{C}-\text{P}$ bond length of Ph_4P^+ (1.792 Å) was ca. 2% shorter than that of Ph_3P (1.828 Å)³⁹. The shortest distance between the ortho-hydrogen in the Ph unit and the ipso carbon in the adjacent Ph group in Ph_4N^+ was 2.46 Å (Fig. 5c, side view). The Van der Waals radii for hydrogen (1.00 Å) and carbon (1.77 Å) indicate that steric repulsion is generated⁴⁰. The

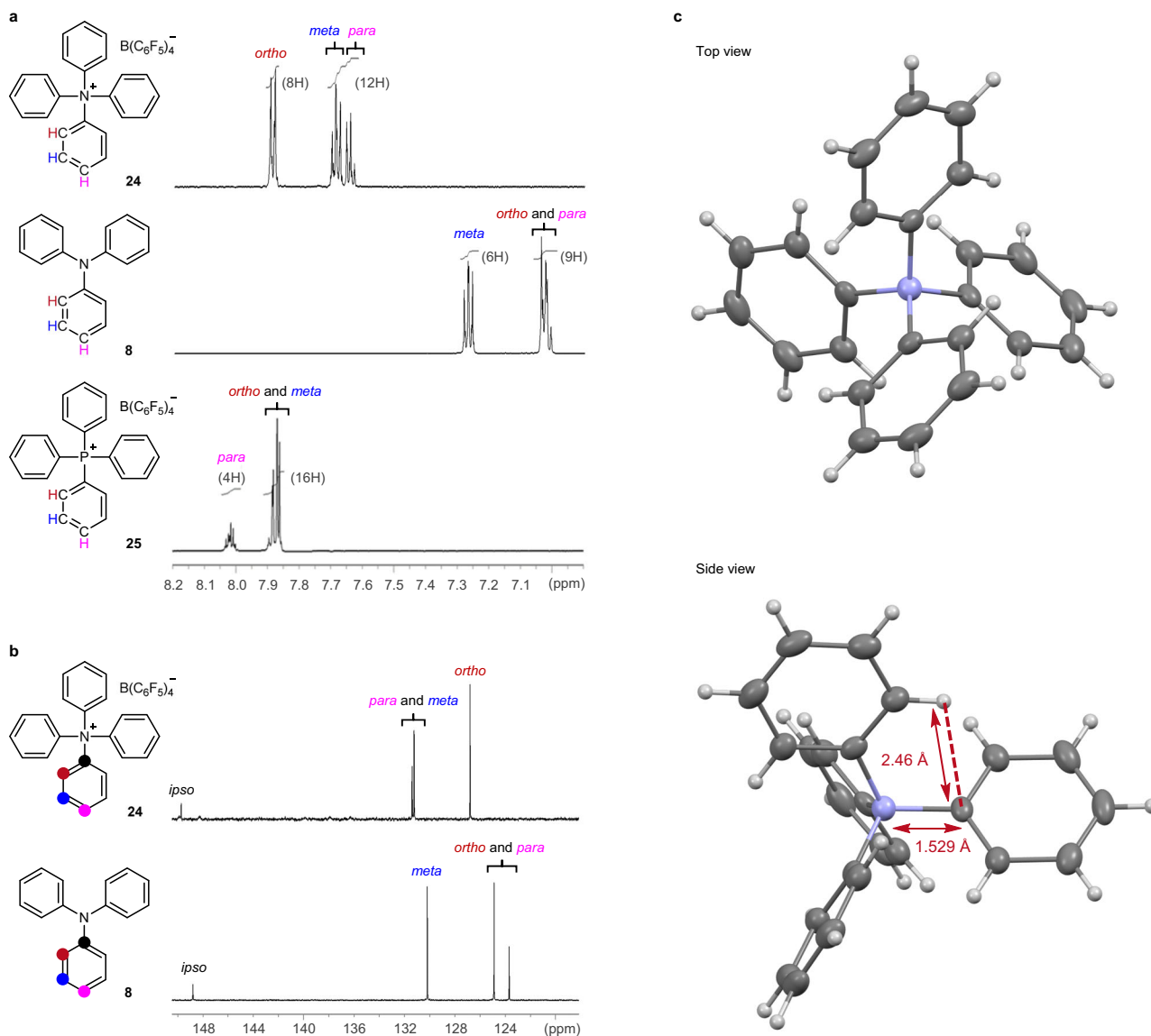


Fig. 5 Structural characterization of Ph_4N^+ . **a** Comparison of the ^1H NMR spectral profiles (600 MHz, $(\text{CD}_3)_2\text{CO}$) recorded for **24**, **8**, and **25**. The number of protons is presented in the parentheses. **b** Comparison of the ^{13}C NMR spectral profiles (150 MHz, $(\text{CD}_3)_2\text{CO}$) recorded for **24** and **8**. **c** Single-crystal X-ray structure of **24**. All ellipsoids are contoured at the 50% probability level. The counter anion was omitted for clarity.

corresponding H–C distances in Ph_4C , Ph_4B^- , and Ph_4P^+ were 2.54³⁴, 2.59³⁵, and 2.76³⁶ Å, respectively, indicating that the extent of steric repulsion observed in these cases was lower than that observed in Ph_4N^+ . The N–C(sp^2) bond length in octa-tert-butylated Ph_4N^+ salt **22** was in the range of 1.53–1.54 Å and the H–C distance was 2.48 Å. These values are slightly higher than the corresponding values recorded for **24**. This suggested the generation of steric and electronic effects in the presence of the meta-tert-butyl groups in **22** present in the ammonium structure.

Initial evaluation of alkaline stability. Alkaline stability of Ph_4N^+ salt **23** was compared with that of *N,N*-diphenylcarbazolium PF_6^- salt **2-PF₆** by heating their solutions in $\text{CD}_3\text{OD}/\text{D}_2\text{O}$ (3:1, containing 5 M KOH) to 80 °C. The ^1H NMR monitoring revealed that **23** was gradually decomposed over 5 days (Supplementary Fig. 2) whereas **2-PF₆** almost completely disappeared in 24 h (Supplementary Fig. 4). Therefore, **23** exhibited higher alkaline stability than **2-PF₆**. The rapid decrease of the signal assigned to the ortho-protons of **23** suggested that H/D exchange occurred during this

experiment¹⁴. Octa-tert-butylated Ph_4N^+ salt **20** exhibited excellent alkaline stability. No apparent spectral change of **20** was observed under the same conditions for 30 days (Supplementary Fig. 5). The alkaline stability of **20** can be compared with that of sterically hindered imidazolium salts⁴¹, which were also inert under similar alkaline conditions.

In conclusion, we have synthesized Ph_4N^+ salts which are structurally simple non-bridged Ar_4N^+ salts. The ^1H and ^{13}C NMR spectra of the Ph_4N^+ salts have been presented. The single-crystal X-ray structure analysis revealed the long N–C bond present in this organic cation. The Ph_4N^+ salts described herein are essential benchmarks for non-bridged Ar_4N^+ salts. We have confirmed that the non-bridged Ar_4N^+ salts we prepared are highly stable under basic conditions. Our findings will encourage further synthetic study of this new class of organic cations which are attractive for diverse applications. The concept of the radical coupling reaction (between a triarylammoniumyl and an aryl radical) reported herein can potentially be applied to the synthesis of various non-bridged Ar_4N^+ salts. Further studies need to be conducted to achieve higher product yields.

Methods

Synthesis of tris[(4-bromo-3,5-di-tert-butyl)phenyl]amine (11). Triarylamine 10 (5.0 g, 8.6 mmol) and NBS (5.0 g, 28 mmol) were added to a mixture of CH₂Cl₂/DMF (1:1, 42.0 ml) at room temperature. After 68 h, the reaction mixture was quenched with saturated aqueous Na₂S₂O₃ (30 ml) and then extracted with CHCl₃ (200 ml). The organic layer was washed with brine, dried (Na₂SO₄), and filtrated. The filtrate was concentrated under reduced pressure. The crude product was recrystallized from CHCl₃/MeOH to afford a white solid (5.7 g, 81%). Mp: 246–247 °C; TLC (hexane): RF = 0.50; ¹H NMR (600 MHz, CDCl₃): δ 7.11 (s, 6H), 1.48 (s, 54H); ¹³C NMR (150 MHz, CDCl₃): δ 150.0, 144.9, 121.8, 117.8, 38.4, 31.0; HRMS (ESI-TOF, *m/z*): [M]⁺ calcd for C₄₂H₆₀Br₃N, 815.2276; found, 815.2278.

Synthesis of tris[(4-bromo-3,5-di-tert-butyl)phenyl]ammonium tetrafluoroborate monohydrate (9). A mixture of triarylamine 11 (1.000 g, 1.22 mmol) and AgBF₄ (260 mg, 1.34 mmol) in CH₂Cl₂ (12.5 ml) was stirred for 2 h at room temperature. The reaction mixture was then filtrated. The filtrate was concentrated under reduced pressure. The residue was washed with hexane to afford a blue solid (1.044 mg, 93%). Mp: 166 °C (decomp.); UV/vis: λ_{max} 797 nm (in *o*-dichlorobenzene); HRMS (ESI-TOF, *m/z*): [M – BF₄ – H₂O]⁺ calcd for C₄₂H₆₀Br₃N, 815.2276; found, 815.2262; analysis (% calcd, % found for C₄₂H₆₂Br₃F₄NO): C (54.63, 54.37), H (6.77, 6.48), N (1.52, 1.58).

Synthesis of tris[(4-bromo-3,5-di-tert-butyl)phenyl][(3,5-di-tert-butyl)phenyl]ammonium tetrafluoroborate (15). A mixture of triarylaminium salt 9 (1.000 g, 1.08 mmol), diacyl peroxide 13 (1.550 g, 3.321 mmol), and pyridine 14 (250 μl, 1.11 mmol) in *o*-dichlorobenzene (8.5 ml) was heated to 120 °C for 15 min. Then, the reaction mixture was cooled to room temperature and filtered (CHCl₃, 20 ml). This reaction procedure was repeated another three times to obtain a set of four filtrate solutions. The combined filtrate solution was passed through NaBF₄-treated silica gel to afford Fraction A (CHCl₃ as an eluent, 350 ml) followed by Fraction B (CHCl₃/MeOH = 90:10 as an eluent, 400 ml). Concentration of Fractions A and B under reduced pressure afforded Residues A and B, respectively. Residue B was purified by ion-pair column chromatography (NaBF₄-treated silica gel, CHCl₃/MeOH = 95:5) followed by preparative thin layer ion-pair chromatography [NaBF₄-treated silica gel TLC plate, 0.50 mm thick, three times (CHCl₃/MeOH = 90:10, hexane/EtOAc = 30:70, and hexane/EtOAc = 40:60 for the first, the second, and the third chromatography, respectively)] to afford 15 as an off-white solid (4.97 mg, 0.11%). TLC (NaBF₄-treated silica gel, CHCl₃/MeOH = 90:10): RF = 0.40; ¹H NMR (600 MHz, CDCl₃): δ 7.60 (t, *J* = 1.5 Hz, 1H), 7.47 (s, 6H), 7.23 (d, *J* = 1.5 Hz, 2H), 1.48 (s, 54H), 1.28 (s, 18H); ¹³C NMR (600 MHz, CD₃OD): δ 7.78 (t, *J* = 1.4 Hz, 1H), 7.47 (s, 6H), 7.28 (d, *J* = 1.4 Hz, 2H), 1.48 (s, 54H), 1.28 (s, 18H); ¹³C NMR (150 MHz, CDCl₃): δ 154.6, 152.9, 147.9, 146.3, 127.5, 124.8, 122.7, 119.3, 39.3, 35.9, 31.3, 30.6; ¹⁹F NMR (376 MHz, CDCl₃): δ –154.4; HRMS (ESI-TOF, *m/z*): [M – BF₄]⁺ calcd for C₅₆H₈₁Br₃N, 1004.3919; found, 1004.3898.

Partial purification of Residue A by column chromatography (silica gel, hexane/CHCl₃ = 100:0 to 90:10 to 80:20) afforded Fraction A1 (containing compounds 11, 16, and 18) and Fraction A2 (containing compound 17). Further purification of Fraction A1 using recycling preparative HPLC afforded 11 (404 mg, 11%), 16 (348 mg, 3.9% based on 13), and 18 (366 mg, 8.4%). Further purification of Fraction A2 (silica gel, hexane/CHCl₃ = 90:10) followed by recrystallization (hexane/CHCl₃) afforded 17 (312 mg, 6.9%).

Synthesis of tris[(3,5-di-tert-butyl)phenyl]ammonium tetrafluoroborate dihydrate (19). A mixture of triarylamine 10 (150 mg, 0.26 mmol) and AgBF₄ (60 mg, 0.31 mmol) in CH₂Cl₂ (2.5 ml) was stirred for 1.5 h at room temperature. The reaction mixture was then filtrated. The filtrate was concentrated under reduced pressure. The residue was washed with hexane to afford a blue solid (155 mg, 85%). Mp: 170 °C (decomp.); UV/vis: λ_{max} 353 nm (in *o*-dichlorobenzene); HRMS (ESI-TOF, *m/z*): [M – BF₄ – 2H₂O]⁺ calcd for C₄₂H₆₃N, 581.4961; found, 581.4973; analysis (% calcd, % found for C₄₂H₆₇BF₄NO₂): C (71.57, 71.14), H (9.58, 9.18), N (1.99, 1.91).

Synthesis of tetrakis[(3,5-di-tert-butyl)phenyl]ammonium tetrafluoroborate (20). ⁿBuLi solution in hexane (1.56 M, 110 μl, 172 μmol) was added to a solution of Ar₄N⁺ salt 15 (5.8 mg, 5.3 μmol) in THF (1.7 ml) at –78 °C. After 25 min, the reaction mixture was quenched by adding 21 (47.0 mg, 168 μmol) under N₂ flow. After 5 min, the reaction mixture was allowed to warm to room temperature and concentrated under reduced pressure. The residue was suspended in CH₂Cl₂ (10 ml). The resulting suspension was filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by ion-pair column chromatography (NaBF₄-treated silica gel, CHCl₃/MeOH = 100:0 to 90:10) followed by preparative thin layer ion-pair chromatography (NaBF₄-treated silica gel TLC plate, 0.50 mm thick, CHCl₃/MeOH = 90:10) to afford an off-white solid (4.1 mg, 90%). TLC (NaBF₄-treated silica gel, CHCl₃/MeOH = 90:10): RF = 0.35; ¹H NMR (600 MHz, CDCl₃): δ 7.53–7.51 (m, 4H), 7.33–7.30 (m, 8H), 1.25 (s, 72H); ¹H NMR (600 MHz, CD₃OD): δ 7.67 (t, *J* = 1.6 Hz, 4H), 7.42 (d, *J* = 1.6 Hz, 8H), 1.26 (s, 72H); ¹³C NMR (100 MHz, CDCl₃): δ 153.9, 148.5, 124.2, 119.7, 35.7, 31.3; ¹⁹F

NMR (565 MHz, CDCl₃): δ –154.6; HRMS (ESI-TOF, *m/z*): [M – BF₄]⁺ calcd for C₅₆H₈₄N, 770.6604; found, 770.6587.

Synthesis of tetrakis[(3,5-di-tert-butyl)phenyl]ammonium tetrakis(pentafluorophenyl)borate (22). A solution of Ar₄N⁺ salt 20 (1.47 mg, 1.7 μmol) and LiB(C₆F₅)₄-Et₂O (4.2 mg, 5.6 μmol as a 1:1 complex) in CH₂Cl₂ (500 μl) was stirred for 25 min at room temperature. The reaction mixture was directly purified by column chromatography (diol-functionalized silica gel, CH₂Cl₂) to afford an off-white solid (2.19 mg, 88%). TLC (CHCl₃/acetone = 80:20): RF = 0.17; ¹H NMR (600 MHz, CDCl₃): δ 7.52 (t, *J* = 1.4 Hz, 4H), 7.29 (d, *J* = 1.4 Hz, 8H), 1.22 (s, 72H); ¹³C NMR (150 MHz, CDCl₃): δ 153.9, 148.4, 124.2, 119.8, 35.6, 31.2; ¹⁹F NMR (565 MHz, CDCl₃): δ –132.5, –163.5, –167.0; HRMS (ESI-TOF, *m/z*): [M – B(C₆F₅)₄]⁺ calcd for C₅₆H₈₄N, 770.6604; found, 770.6589. Suitable crystals for X-ray analysis were obtained by recrystallization (acetone/MeOH).

Synthesis of tetraphenylammonium tetrafluoroborate (23). A solution of Ar₄N⁺ salt 20 (3.92 mg, 4.6 μmol) in TfOH (2.0 ml) was heated to 150 °C for 14 h, and then cooled to room temperature. The reaction mixture was concentrated under reduced pressure, and the residue was dissolved in H₂O (6 ml). The solution was neutralized with aqueous NaOH (0.5 M), saturated with NaBF₄ (~3 g), and extracted with CHCl₃ (10 × 5 ml). The organic layer was dried (Na₂SO₄) and filtrated. The filtrate was concentrated under reduced pressure. Preparative thin layer ion-pair chromatography (NaBF₄-treated silica gel TLC plate, 0.5 mm thick, CHCl₃/MeOH = 90:10) afforded an off-white solid (1.10 mg, 59%). TLC (NaBF₄-treated silica gel, CHCl₃/MeOH = 95:5): RF = 0.45; ¹H NMR (600 MHz, CD₃OD): δ 7.76–7.70 (m, 8H), 7.65–7.55 (m, 12H); ¹³C NMR (150 MHz, CD₃OD): δ 150.0, 131.6, 131.4, 127.0; ¹⁹F NMR (565 MHz, CDCl₃): δ –153.8; IR: 2958, 2920, 2851, 1733, 1477, 1452, 1259, 1091, 1043, 1022, 996, 799, 757, 692, 631, 491, 431, 412 cm^{–1}; HRMS (ESI-TOF, *m/z*): [M – BF₄]⁺ calcd for C₂₄H₂₀N, 322.1596; found, 322.1602.

Synthesis of tetraphenylammonium tetrakis(pentafluorophenyl)borate (24). A solution of Ar₄N⁺ salt 23 (1.10 mg, 2.7 μmol) and LiB(C₆F₅)₄-Et₂O (4.1 mg, 5.4 μmol as a 1:1 complex) in CH₂Cl₂ (500 μl) was stirred for 1 h at room temperature. The reaction mixture was directly purified by column chromatography (diol-functionalized silica gel, CH₂Cl₂) to afford a white solid (2.17 mg, 81%). TLC (diol-functionalized silica gel, CHCl₃): RF = 0.31; ¹H NMR [600 MHz, (CD₃)₂CO]: δ 7.91–7.87 (m, 8H), 7.72–7.67 (m, 8H), 7.67–7.62 (m, 4H); ¹³C NMR [150 MHz, (CD₃)₂CO]: δ 149.7, 131.4, 131.2, 126.8; ¹⁹F NMR (565 MHz, CDCl₃): δ –132.4, –163.1, –166.8; IR: 2955, 2917, 2850, 1712, 1643, 1513, 1462, 1275, 1086, 979, 775, 756, 746, 692, 661, 418 cm^{–1}; HRMS (ESI-TOF, *m/z*): [M – B(C₆F₅)₄]⁺ calcd for C₂₄H₂₀N, 332.1596; found, 332.1606. Suitable crystals for X-ray analysis were obtained by recrystallization (acetone/MeOH).

Data availability

The data supporting the findings of this study are available within the article and its Supplementary Information file. CCDC 2117248, 2117243, 2117249, and 2117251 contain the supplementary crystallographic data for compounds 17, 18, 22, and 24, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Received: 26 November 2021; Accepted: 20 April 2022;

Published online: 09 May 2022

References

- Wittig, G., Keicher, G., Rückert, A. & Raff, P. Über bor-alkalimetall-organische komplexverbindungen. *Justus Liebig's Ann. Chem.* **563**, 110–126 (1949).
- Wittig, G. & Bub, O. Über komplexbildung mit triphenyl-aluminium. *Justus Liebig's Ann. Chem.* **566**, 113–129 (1950).
- Gomberg, M. Tetraphenylmethan. *Ber. Dtsch. Chem. Ges.* **30**, 2043–2047 (1897).
- Polis, A. Ueber aromatische siliciumverbindungen. *Ber. Dtsch. Chem. Ges.* **18**, 1540–1544 (1885).
- Dodonow, J. & Medox, H. Zur kenntnis der grignardschen reaktion: uber die darstellung von tetraphenyl-phosphoniumsalzen. *Ber. dtsh. Chem. Ges. A/B* **61**, 907–911 (1928).
- Kolitorowa, J. H. O działaniu bromku fenylomagnezowego na pięciochlorek fosforu. *Rocz. Chem.* **575**, 568–575 (1928).
- Giesecking, R. L. et al. Nonlinear optical properties of X(C₆H₅)₄ (X = B[–], C, N⁺, P⁺): A new class of molecules with a negative third-order polarizability. *J. Am. Chem. Soc.* **137**, 9635–9642 (2015).
- Nefedov, V. D., Toropova, M. A., Shchepina, N. E., Avrorin, V. V. & Zhuravlev, V. E. Application of a nuclear chemical method for the synthesis of unknown organic onium compounds. *Sov. Radiochem. (Engl. Transl. Radiokhimiya)* **25**, 336–338 (1983).

9. Shchepina, N. et al. Ion-molecular reactions of free phenylium ions, generated by tritium β -decay with group V–VII elements. *Tetrahedron Lett.* **41**, 5303–5306 (2000).
10. Nesmeyanov, A. N., Tolstaya, T. P. & Grib, A. V. Diphenyl-*o,o'*-diphenyleneammonium salts. *Dokl. Akad. Nauk SSSR* **153**, 608–611 (1963).
11. Hellwinkel, D. & Seifert, H. 2,2'-Biphenyleneammonium salts. *Chem. Commun.* 1683–1684 (1968).
12. Hellwinkel, D. & Seifert, H. Ringschlussreaktionen von 2'-heterosubstituierten biphenyl-2-diazonium-Salzen zu (spiro)cyclischen tetraarylammonium-salzen und Tribenz[*b,d,f*]azepinen. *Chem. Ber.* **105**, 880–906 (1972).
13. Aharonovich, S., Gjineci, N., Dekel, D. & Diesendruck, C. An effective synthesis of *N,N*-diphenyl carbazolium salts. *Synlett* **29**, 1314–1318 (2018).
14. Gjineci, N., Aharonovich, S., Willdorf-Cohen, S., Dekel, D. R. & Diesendruck, C. E. The reaction mechanism between tetraarylammonium salts and hydroxide. *Eur. J. Org. Chem.* **2020**, 3161–3168 (2020).
15. Gjineci, N., Aharonovich, S., Dekel, D. R. & Diesendruck, C. E. Increasing the alkaline stability of *N,N*-diaryl carbazolium salts using substituent electronic effects. *ACS Appl. Mater. Interfaces* **12**, 49617–49625 (2020).
16. Lu, M. et al. Peraryl-X-onium ions of nitrogen and oxygen. *Org. Chem. Front.* **6**, 2640–2646 (2019).
17. Nesmeyanov, A. N., Tolstaya, T. P., Grib, A. V. & Kirgizbaeva, S. R. Соли *N,N*-дифенилфентиазиния и *N,S*-дифенилфентиазиния. *Dokl. Akad. Nauk SSSR* **174**, 856–859 (1967).
18. Nesmeyanov, A. N., Tolstaya, T. P., Grib, A. V. & Kazanova, K. A. Synthesis of 4,4-diphenyl-7-oxodibenzodihydro-1,4-diazepinium salts. *Bull. Acad. Sci. USSR Div. Chem. Sci.* **22**, 1052–1056 (1973).
19. Hoefnagel, A. J., Hoefnagel, M. A. & Wepster, B. M. Substituent effects. 8. Basic strength of azatriptycene, triphenylamine, and some related amines. *J. Org. Chem.* **46**, 4209–4211 (1981).
20. Makarova, L. G. & Nesmeyanov, A. N. Распад и образование ониевых солей и синтез элементоорганических соединений через ониевые соединения. Сообщение I. Два типа лифенилиониевых солей. *Izv. Akad. Nauk SSSR, Ser. Khim.* 617–626 (1945).
21. Hirsch, M., Dhara, S. & Diesendruck, C. E. *N*-Arylation of tertiary amines under mild conditions. *Org. Lett.* **18**, 980–983 (2016).
22. Creason, S. C., Wheeler, J. & Nelson, R. F. Electrochemical and spectroscopic studies of cation radicals. I. Coupling rates of 4-substituted triphenylammonium ions. *J. Org. Chem.* **37**, 4440–4446 (1972).
23. Munshi, M. U., Berden, G., Martens, J. & Oomens, J. Gas-phase vibrational spectroscopy of triphenylamine: the effect of charge on structure and spectra. *Phys. Chem. Chem. Phys.* **19**, 19881–19889 (2017).
24. Dressler, J. J., Miller, S. A., Meeuwssen, B. T., Riel, A. M. S. & Dahl, B. J. Synthesis of dilactone bridged terphenyls with crankshaft architectures. *Tetrahedron* **71**, 283–292 (2015).
25. Bedford, R. B. & Betham, M. Hydroxylamine *O*-benzyl ether as an ammonia equivalent in the catalytic amination of aryl halides. *Tetrahedron Lett.* **48**, 8947–8950 (2007).
26. Barton, D. H. R., Haynes, R. K., Leclerc, G., Magnus, P. D. & Menzies, I. D. New reactions of triplet oxygen which avoid the spin barrier. *J. Chem. Soc. Perkin Trans. 1*, 2055–2065 (1975).
27. Kawamura, S., Mukherjee, S. & Sodeoka, M. Recent advances in reactions using diacyl peroxides as sources of *O*- and *C*-functional groups. *Org. Biomol. Chem.* **19**, 2096–2109 (2021).
28. Urban, N. D., Schenkel, M. R., Robertson, L. A., Noble, R. D. & Gin, D. L. Modified normal-phase ion-pair chromatographic methods for the facile separation and purification of imidazolium-based ionic compounds. *Tetrahedron Lett.* **53**, 3456–3458 (2012).
29. Lou, Y. et al. Copper-catalyzed enantioselective 1,6-boration of *para*-quinone methides and efficient transformation of *gem*-diarylmethine boronates to triarylmethanes. *Angew. Chem. Int. Ed.* **54**, 12134–12138 (2015).
30. Nakajima, M., Miyamoto, K., Hirano, K. & Uchiyama, M. Diaryl- λ^3 -chloranes: Versatile synthesis and unique reactivity as aryl cation equivalent. *J. Am. Chem. Soc.* **141**, 6499–6503 (2019).
31. Preston, P. N., Sutcliffe, L. H. & Taylor, B. NMR investigation of tetraphenyl-, vinyltriphenyl-, azidotriphenyl- and dihalodiphenyl-derivatives of fourth main group elements. *Spectrochim. Acta Part A Mol. Spectrosc.* **28**, 197–210 (1972).
32. Knop, O., Rankin, K. N., Cameron, T. S. & Boyd, R. J. Crystal chemistry of tetraradial species. Part 10. Tilting at windmills: conformations of the tetraphenyl species $ZPh_4^{0, \pm 1}$ ($Z = B, C, N$). *Can. J. Chem.* **80**, 1351–1366 (2002).
33. Herber, R. H. et al. Synthesis, structure, electrochemistry, and metal-atom dynamics of cyclopentadienyl ferracarboranes. *Eur. J. Inorg. Chem.* **2006**, 1786–1795 (2006).
34. Anthony, A., et al. CCDC 117573: Experimental Crystal Structure Determination. <https://doi.org/10.5517/cc3ybp1> (1999).
35. B. Wilde & F. Olbrich. CCDC 233223: Experimental Crystal Structure Determination. <https://doi.org/10.5517/cc7tpb1> (2004).
36. Fronczek, F. R. CCDC 1491203: Experimental Crystal Structure Determination. *CSD Commun.* <https://doi.org/10.5517/ccdc.csd.c1m1qbbq> (2016).
37. Meyer-Wegner, F. & Bolte, M. CCDC 825254: Experimental Crystal Structure Determination. <https://doi.org/10.5517/ccwpr3d> (2011).
38. Langer, J. et al. Organic heterobimetallic complexes of the alkaline earth metals ($Ae = Ca, Sr, Ba$) with tetrahedral metallate anions of three-valent metals ($M = B, Al, Ga, and V$). *N. J. Chem.* **34**, 1667–1677 (2010). CCDC 765645.
39. Sobolev, A. N., Belsky, V. K., Romm, I. P., Chernikova, N. Y. & Guryanova, E. N. Structural investigation of the triaryl derivatives of the Group V elements. IX. Structure of triphenylamine, $C_{18}H_{15}N$. *Acta Crystallogr. Sect. C. Cryst. Struct. Commun.* **41**, 967–971 (1985).
40. Bondi, A. van der Waals vol umes and radii. *J. Phys. Chem.* **68**, 441–451 (1964).
41. Hugar, K. M., Kostalik, H. A. & Coates, G. W. Imidazolium cations with exceptional alkaline stability: a systematic study of structure-stability relationships. *J. Am. Chem. Soc.* **137**, 8730–8737 (2015).

Acknowledgements

This work was partially supported by JSPS KAKENHI, Grant Nos. 21K15222 and 21H02603, and JST SPRING, Grant Number JPMJSP2135.

Author contributions

M.Kunishima supervised the project; H.F., O.S., M.Kitamura, and M.Kunishima designed the synthetic strategy; H.F. wrote the original draft with contributions from O.S.; H.F. and M.Kunishima reviewed and edited the paper; O.S. performed experiments with contributions from S.K.; H.F., O.S., M.Kitamura, and M.Kunishima analyzed the obtained data.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at <https://doi.org/10.1038/s41467-022-30282-y>.

Correspondence and requests for materials should be addressed to Hikaru Fujita or Munetaka Kunishima.

Peer review information *Nature Communications* thanks Charles Diesendruck, Patric Jannasch, and the other, anonymous, reviewer for their contribution to the peer review of this work.

Reprints and permission information is available at <http://www.nature.com/reprints>

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>.

© The Author(s) 2022