Tetrahedron Letters 57 (2016) 1794–1797

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Synthesis, structure, and reaction of chiral 2-azidoimidazolinium salts: (7a*S*)-3-azido-5,6,7,7a-tetrahydro-2-[(1*R*)-1-phenylethyl]-1*H*-pyrrolo[1,2-*c*]imidazolium hexafluorophosphate and 2-azido-1,3-bis[(*S*)-1-phenylethyl]imidazolinium hexafluorophosphate

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ARTICLE INFO

Article history:
Received 16 January 2016
Revised 8 March 2016
Accepted 11 March 2016
Available online 11 March 2016

Keywords:
Chiral compounds
Azides
Imidazolinium salts
Migratory amidation

ABSTRACT

Two chiral 2-azidoimidazolinium salts [(7a*S*)-3-azido-5,6,7,7a-tetrahydro-2-[(1*R*)-1-phenylethyl]-1*H*-pyrrolo[1,2-*c*]imidazolium hexafluorophosphate (**2**) and 2-azido-1,3-bis[(*S*)-1-phenylethyl]imidazolinium hexafluorophosphate (**3**)] were synthesized, and their structures were determined by X-ray single crystal structural analysis. Migratory amidation reaction of enol silyl ether with **3** proceeded, but good diastereoselectivity was not observed in the reaction.

We have recently developed various synthetic methods using 2-azido-1,3-dimethylimidazolinium salts with nucleophilic compounds. For example, 2-azido-1,3-dimethylimidazolinium chloride (ADMC **1a**) and its corresponding hexafluorophosphate (ADMP **1b**) were observed to be efficient diazo-transfer reagents (Fig. 1).[1] ADMC **1a** was prepared by the reaction of 2-chloro-1,3-dimethylimidazolinium chloride (DMC) and sodium azide. ADMP **1b** was isolated as a thermally stable crystal with a low explosibility.[2b] ADMC **1a** and ADMP **1b** reacted with 1,3-dicarbonyl compounds under mild basic conditions to give 2-diazo-1,3-dicarbonyl compounds in high yields; these products were easily isolated because the reaction byproducts are highly soluble in water.[2] Naphthols reacted with ADMC **1a** in the presence of Et_3N to give the corresponding diazonaphthoquinones in good to high yields.[3] Furthermore, ADMP **1b** shows efficient diazo-transfer ability to primary amines even without the aid of a metal catalyst such as Cu(II).[4] 2-Azidoimidazolinium salts **1** also show azide-transfer ability to oxygen nucleophiles.[5] In addition, migratory amidation proceeded when ADMP **1b** was treated with a benzyl aryl ketone or enol silyl ether of an aryl ketone, giving α-aryl amide (Scheme 1).[6] These reactions were initiated by the attack of a nucleophile at an azide moiety in **1**. We hypothesized that if an efficient asymmetric environment could be constructed around the azide group in the 2-azidoimidazolinium salt, the salt would be a new asymmetric reagent for the introduction of a nitrogen functional group. However, the synthesis of optically active chiral 2-azido-1,3-dialkylimidazolinium salts has not been previously reported. Recently, Ishikawa developed efficient chiral cyclic guanidine possessing an imidazoline structure.[7,8] Inspired by the results, we examined the synthesis of chiral 2-azido-1,3-dialkylimidazolinium salts and successfully prepared (7a*S*)-3-azido-5,6,7,7a-tetrahydro-2-[(1*R*)-1-phenylethyl]-1*H*-pyrrolo[1,2-*c*]imidazolium hexafluorophosphate (**2**) and 2-azido-1,3-bis[(*S*)-1-phenylethyl]imidazolinium hexafluorophosphate (**3**) (Fig. 1). Although a fine X-ray structure of 2-azido-1,3-dialkylimidazolinium salt has not been reported,[9] we determined the unambiguous structures of **2** and **3** by single-crystal X-ray diffraction, with good *R* factors. In this Letter, we report the synthesis, structure, and reaction of optically active chiral 2-azido-1,3-dialkylimidazolinium salts **2** and **3** in detail.

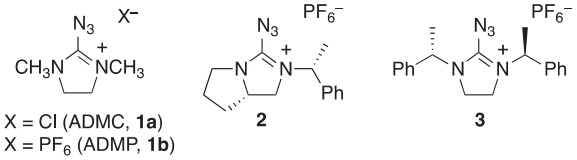

Figure 1. 2-Azido-1,3-dialkylimidazolinium salts **1**–**3**.

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http://dx.doi.org/10.1016/j.tetlet.2016.03.036
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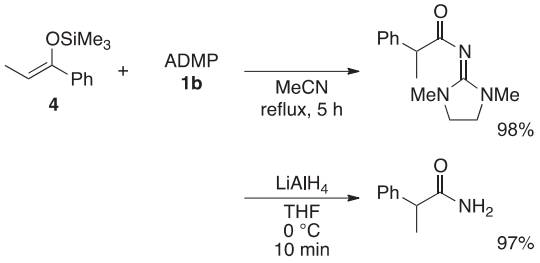
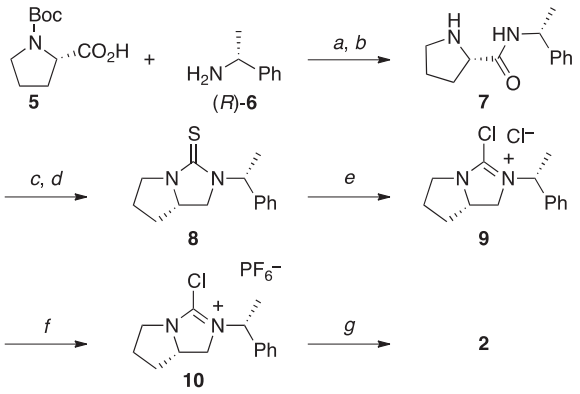


Scheme 1. Migratory amidation with ADMP **1b**.



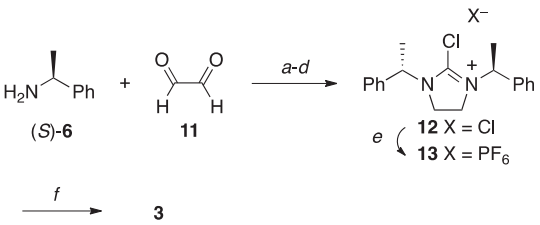
Scheme 2. Synthesis of chiral bicyclic 2-azido-1,3-dialkylimidazolinium salt **2**. (a) DCC (1.1 equiv), DMAP (1.1 equiv), CH_2Cl_2, rt, 26 h (93%); (b) 3 M HCl aq., MeOH, 50 °C, 8 h (83%); (c) $LiAlH_4$ (4.5 equiv), THF, 60 °C, 7 h; (d) thiocarbonyl imidazole (1.1 equiv), *o*-dichlorobenzene, reflux, 6 h (2 steps, 62%); (e) $(COCl)_2$ (1.4 equiv), toluene, 70 °C, 5 h; (f) KPF_6 (1.3 equiv), CH_3CN, rt, 0.5 h (2 steps, 75%); (g) NaN_3 (2.0 equiv), CH_3CN, 0 °C, 1 h (52%).

Bicyclic 2-azido-1,3-dialkylimidazolinium salt **2** was synthesized as shown in Scheme 2. First, bicyclic thiourea **8** was synthesized from *N*-Boc-L-proline **5** and (*R*)-1-phenylethylamine (**6**) in four steps using a procedure similar to that of Ishikawa (Scheme 2).[8b] Thiourea **8**[10] was converted into chloroimidazolinium chloride **9** by treatment with oxalyl chloride, and **9** was subsequently transformed to azidoimidazolinium salt **2** by anion exchange with KPF_6 and successive azide introduction with sodium azide.[11]

Moreover, C_2-symmetric azidoimidazolinium salt **3** was synthesized via known chloroimidazolinium chloride **12**[8b] prepared from (*S*)-1-phenylethylamine (**6**) and oxalaldehyde **11** (Scheme 3).[12]

Single crystals of **2** and **3** were obtained by recrystallization from a mixed solvent of hexane and ethyl acetate, and we successfully determined their X-ray structures (Figs. 2 and 3, Table 1).[13]

In Table 2, bond lengths and bond angles of azide moieties in several azides are shown as a reference.[14] The N(1)–N(2) and



Scheme 3. Synthesis of C_2-symmetric chiral 2-azido-1,3-dialkylimidazolinium salt **3**. (a) Cat. AcOH, CH_2Cl_2, rt, 24 h (76%); (b) $NaBH_4$ (5.0 equiv), MeOH, rt, 27 h (88%); (c) $CSCl_2$ (1.5 equiv), Et_3N (2.0 equiv), CH_2Cl_2, rt, 5 h (47%); (d) $(COCl)_2$ (1.8 equiv), toluene, 70 °C, 26 h (92%); (e) KPF_6 (1.8 equiv), CH_3CN, rt, 1 h (97%); (f) NaN_3 (1.7 equiv), CH_3CN, 0 °C, 1 h (84%).

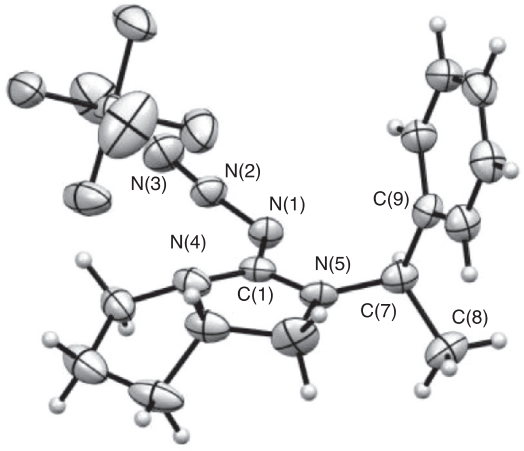


Figure 2. ORTEP of **2**. Thermal ellipsoids set at 50%. Crystal data of **2**: $C_{14}H_{18}F_6N_5P$, M = 401.29, orthorhombic, a = 8.457 (2), b = 10.074 (3), c = 20.740 (6) Å, V = 1766.9 (8) Å^3, T = 123 K, space group $P2_12_12_1$, Z = 4, 19,639 reflections measured, 3201 unique (R_{int} = 0.045), which were used in all calculations. $R[F^2 > 2\sigma(F^2)]$ = 0.045, $wR(F^2)$ = 0.115.

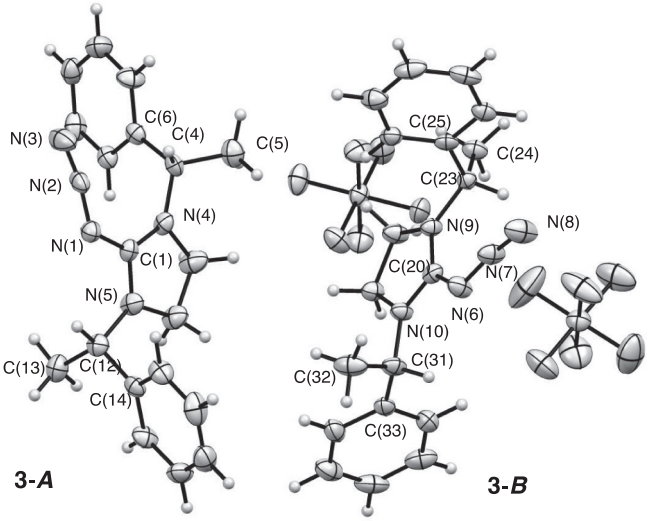


Figure 3. ORTEP of **3**. Thermal ellipsoids set at 50%. Crystal data of **3**: $C_{19}H_{22}F_6N_5P$, M = 465.38, monoclinic, a = 6.961 (3), b = 21.148 (7), c = 14.194 (6) Å, V = 2087.4 (13) Å^3, T = 123 K, space group $P2_1$, Z = 4, 26,019 reflections measured, 7397 unique (R_{int} = 0.060), which were used in all calculations. $R[F^2 > 2\sigma(F^2)]$ = 0.054, $wR(F^2)$ = 0.107.

N(2)–N(3) bond lengths of sulfonylazides are 1.24–1.28 Å, 1.11–1.13 Å, respectively (Runs 1–5). The difference between N(1)–N(2) and N(2)–N(3) bond lengths is 0.12–0.17 Å. In contrast, the difference between N(1)–N(2) and N(2)–N(3) bond lengths of alkyl azides is smaller (0.05–0.08 Å) than those of sulfonylazides.

Compound **2** crystallized in the orthorhombic space group $P2_12_12_1$.[13] The azide group of **2** is bent, with an N(1)–N(2)–N(3) angle of 171.7(3)°. The N(1)–N(2) and N(2)–N(3) bond lengths of **2** are 1.267(3) and 1.116(4) Å, respectively, and the difference of between N(1)–N(2) and N(2)–N(3) bond lengths was 0.15 Å. These data are more similar to those of sulfonyl azides than to those of alkyl azides. The dihedral N(2)–N(1)–C(1)–N(4) angle is 19.9(4)°, indicating that the azide group is less twisted with reference to the imidazoline ring plane (<30°) than that of ADMP, in which the corresponding dihedral angle is −39.85° (computational calculation; B3LYP/6-31G**).[4b] The chiral 1-phenylethyl group (–CH(CH_3)Ph) in **2** is opposite to the azide group, and the

Table 1
Selected geometric parameters for **2** and **3** (distances in Å, angles in degrees)

2	**3-*A***	**3-*B***
N(1)–N(2) 1.267(3)	N(1)–N(2) 1,265(5)	N(6)–N(7) 1.248(5)
N(2)–N(3) 1.116(4)	N(2)–N(3) 1.121(5)	N(7)–N(8) 1.116(5)
C(1)–N(1) 1.372(4)	C(1)–N(1) 1.385(5)	C(20)–N(6) 1.369(5)
C(1)–N(4) 1.327(4)	C(1)–N(4) 1.317(5)	C(20)–N(9) 1.325(5)
C(1)–N(5) 1.319(4)	C(1)–N(5) 1.328(5)	C(20)–N(10) 1.322(5)
N(1)–N(2)–N(3) 171.7(3)	N(1)–N(2)–N(3) 168.6(4)	N(6)–N(7)–N(8) 168.9(4)
N(2)–N(1)–C(1)–N(4) 19.9(4)	N(2)–N(1)–C(1)–N(4) 14.0(6)	N(7)–N(6)–C(20)–N(9) −4.6(6)
N(2)–N(1)–C(1)–N(5) −160.7(2)	N(2)–N(1)–C(1)–N(5) −167.0(3)	N(7)–N(6)–C(20)–N(10) 177.4(3)
C(1)–N(5)–C(7)–C(9) 95.6(3)	C(1)–N(5)–C(12)–C(14) −128.7(4)	C(20)–N(10)–C(31)–C(33) −148.3(3)
	C(1)–N(4)–C(4)–C(6) −85.7(4)	C(20)–N(9)–C(23)–C(25) −85.0

Table 2
Bond lengths of azide moieties in several azides, as determined by X-ray analysis and computational methods (distances in Å, angles in degrees)

Run	Azide	Method[a]	N(1)–N(2)	N(2)–N(3)	N(1)–N(2)–N(3)
1	**14**[b]	X-ray	1.244(3)	1.125(3)	173.8(2)
2	**14**[b]	X-ray	1.251(3)	1.129(3)	173.5(3)
3	**15**[c]	X-ray	1.2781(16)	1.1103(16)	172.43(13)
4	**16**[d]	X-ray	1.273(3)	1.121(3)	174.2(3)
5	**17**[e]	X-ray	1.258(3)	1.116(4)	173.0(3)
6	**17**[e]	X-ray	1.178(3)	1.133(3)	172.8(3)
7	**18**[f]	Calc	1.237	1.156	172.7
8	**1b**[g,h]	Calc	1.251	1.129	168.86

[a] X-ray: X-ray single crystal structure. Calc: computational calculation.
[b] Data are quoted from Ref. 14b Two crystallographically independent molecules are observed in the unit, as shown in Runs 1 and 2.
[c] The data are quoted from Ref. 14f.
[d] The data are quoted from Ref. 14c.
[e] The data are quoted from Ref. 14d Data for the sulfonyl azide component of **14** and the alkyl azide component of **14** are shown in Run 5 and Run 6, respectively.
[f] Optimized by calculation (MP2/6-311G). The data are quoted from Ref. 15.
[g] Optimized by calculation (B3LYP/6-31G**). The data are quoted from Ref. 4b.
[h] Dihedral angles N(4)–C–N(1)–N(2) and N(5)–C–N(1)–N(2) are −39.85° and 149.60°, respectively.

C(7)–C(9) bond between the phenyl group and chiral center C(7) places almost perpendicular to the imidazoline ring plane (95.6 (3)° for the dihedral C(1)–N(5)–C(7)–C(9) angle). The bond length of C(1)–N(1) (1.372(4) Å) is the longest among the C–N bond connected to C(1) (1.327(4) Å for C(1)–N(4), 1.319(4) Å for C(1)–N(5)). These data suggest that the structure of **2** is similar to azidoimidazolinium **I** (**Ia** and **Ib**), not to guanidinodiazonium **II** (Fig. 4).

Compound **3** crystallized in the monoclinic space group $P2_1$, with two crystallographically independent molecules **3-*A*** and **3-*B*** in the unit.[13] The bending angles of N(1)–N(2)–N(3) and N(6)–N(7)–N(8) are 168.6(4)° and 168.9(4)°, respectively, which are slightly smaller than that of **2** and those of various sulfonyl azides. The difference in the bond lengths between two kinds of N–N bonds in the azide group (N(terminal)–N(center) and N(center)–N(inside)) are similar to that of **2** and the azide group in sulfonyl azides (1.265(5) Å for N(1)–N(2), 1.121(5) Å for N(2)–N(3), 1.248(5) Å for N(6)–N(7), and 1.116(5) Å for N(7)–N(8)). The dihedral angles for N(2)–N(1)–C(1)–N(4) and N(7)–N(6)–C(20)–N(9) are 14.0(6)°, and −4.6(6)°, respectively, and the azide groups are located nearly in the imidazoline ring plane. With respect to the conformation of chiral 1-phenylethylgroups (–CH(CH$_3$)Ph) in **3**, the most bulky phenyl groups are located almost perpendicular to the imidazoline ring, and the next-bulkiest groups (i.e., methyl groups) are located opposite to the azide group. The smallest groups (i.e., hydrogens) are located near the azide group. The tendencies of the lengths of the C–N bonds connecting the azide and imidazoline ring (C(1)–N(1) 1.385(5) Å and C(20)–N(6) 1.369 (5) Å) and the C–N bonds in the imidazoline ring (C(1)–N(4) 1.317(5) Å, C(1)–N(5) 1.328(5) Å, C(20)–N(9) 1.325(5) Å, and C(20)–N(10) 1.322(5) Å) are similar to the corresponding tendencies observed in **2**, which suggests that the structure of **3** is not like the guanidinodiazonium resonance form **II** but is rather like the azidoimidazolinium resonance form **I** in the solid state.

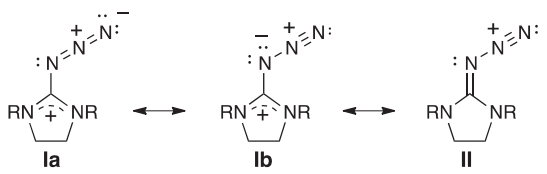
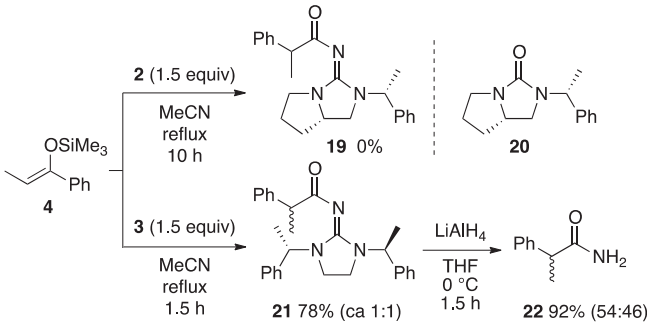


Figure 4. Resonance structure of 2-azido-1,3-dialkylimidazolinium salt.



Scheme 4. Reaction of enol silyl ether **4** with chiral azidoimidazolinium salts **2** and **3**.

To examine the efficiency of **2** and **3** as chiral reagents, we attempted migratory amidation reactions with enol silyl ether **4**. In the reaction of bicyclic **2**, the desired migratory amidation product **19** was not obtained; the formation of bicyclic formation urea **20** was observed after quenching with water (Scheme 4). The reaction of C_2-symmetric **3** and **4** proceeded to give desired product **21** in 78% yield, which was converted to α-aryl amide **22** in 92% yield. However, diastereoselectivity was not observed in the reaction of **3** and **4** (ca. 1:1 by ^{1}H NMR) and the enantiomer ratio of **22** was 54:46, as determined by chiral HPLC analysis.[16] As previously mentioned, the X-ray analysis of **3** shows that the smallest substituent, hydrogen, on the chiral center is placed near the azide group in the solid state, which suggests that the asymmetric environment around the azide group in **3** is not well constructed, which would explain why the reaction of **3** and **4** afforded low diastereoselectivity.

In conclusion, we synthesized the chiral 2-azidoimidazolinium salts **2** and **3** and characterized their structure by X-ray single-crystal structural analysis. The X-ray analysis results suggested that the structures of **2** and **3** are not like the resonance form of guanidinodiazonium but rather like azidoimidazolinium resonance form in the solid state. We are continuing to develop a new chiral

azidoimidazolinium salt with a shielded azide group for the enantioselective introduction of nitrogen functional groups.

Acknowledgments

This work was supported by JSPS KAKENHI Grant Number 26410054.

Supplementary data

Supplementary data (experimental procedure and physical data for **20**, **21**, and **22**. ^{1}H and ^{13}C NMR spectra of **2**, **3**, **8**, **10**, **13**, **20**, **21**, and **22**) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2016.03.036.

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9. Although we previously showed single-crystal X-ray structure of ADMP **1b**, the R factor was large for discussing the structure.[4b]
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11. *Preparation of* **2**. To a solution of amide **7**[10] (6.10 g, 28.0 mmol) in THF (140 mL), $LiAlH_4$ (4.82 g, 127 mmol) was added at 0 °C. After stirring the mixture for 7 h at 60 °C, the reaction was quenched by adding water at 0 °C and the resulting mixture was passed through Celite pad. The filtrate extracted with CH_2Cl_2 three times, and washed with brine, and then dried over anhydrous Na_2SO_4. The solvent was removed in vacuo to afford crude diamine (6.05 g). The crude compound was dissolved in *o*-dichlorobenzene (140 mL), and thiocarbonyl imidazole (5.60 g, 31.5 mmol) was added. After stirring the mixture for 6 h at reflux (185 °C), the solvent was removed in vacuo to afford crude compounds, which were purified by column chromatography (SiO_2; hexane/EtOAc = 4:1), and then recrystallization (hexane/EtOAc) to give pure **8** (4.25 g, 17.3 mmol) in 62% yield (2 steps). Spectral data for **8**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.26 (m, 5H), 6.10 (q, 1H, J = 7.1 Hz), 4.19–4.09 (m, 1H), 3.82–3.75 (m, 1H), 3.42–3.24 (m, 3H), 2.07–1.82 (m, 3H), 1.56 (d, 3H, J = 7.1 Hz), 1.42–1.24 (m, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$, (δ = 77.0) δ 185.3, 139.6, 128.6, 127.6, 127.1, 59.4, 53.6, 48.1, 46.6, 30.9, 24.7, 15.3; IR (KBr): 2972, 1653, 1490, 1436, 1385, 1293, 701; HRMS (FAB^+) Found; m/z, 247.1274. Calcd for $C_{14}H_{19}N_2S$: $(M+H)^+$ 247.1269; mp 120–122 °C; $[\alpha]_D^{23}$ +52.3 (c 0.992, $CHCl_3$); colorless crystal. To a solution of **8** (3.31 g, 13.5 mmol) in toluene (60 mL), oxalyl chloride (1.6 mL, 18.8 mmol) was added at 0 °C. After stirring the mixture for 5 h at 70 °C, volatile materials were removed in vacuo to give crude **9**. The crude **9** was diluted with MeCN (50 mL), and potassium hexafluorophosphate (3.12 g, 17.0 mmol) was added to the solution. After stirring the mixture for 30 min at room temperature, the mixture was passed through Celite pad. The filtrate was concentrated in vacuo to afford crude compound, which was purified by recrystallization (hexane/EtOAc) to give the pure **10** (3.97 g, 10.1 mmol) in 75% yield (2 steps). Spectral data for **10**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45–7.40 (m, 3H), 7.39–7.30 (m, 2H), 5.31 (q, 1H, J = 7.0 Hz), 4.41–4.39 (m, 1H), 4.13–4.11 (m, 1H), 3.94–3.89 (m, 2H), 3.58–3.53 (m. 1H), 2.42–2.35 (m, 1H), 2.30–2.22 (m, 1H), 2.19–2.02 (m, 2H), 1.76 (dd, 3H, J = 7.0, 2.1 Hz); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 156.0, 136.8, 129.6, 129.4, 126.6, 62.7, 57.8, 50.2, 47.2, 30.1, 25.4, 16.2; IR (KBr): 3462, 1653, 1559, 1497, 1457, 1276, 1111, 834, 703, 557; HRMS (FAB^+) Found; m/z, 249.1164. Calcd for $C_{14}H_{18}^{35}ClN_2$: $(M-PF_6)^+$ 249.1159; $[\alpha]_D^{23}$ −97.0 (c 1.02, MeOH); mp 124–126 °C; white solid. To a solution of **10** (2.64 g, 6.70 mmol) in MeCN (20 mL), sodium azido (516 mg, 7.94 mmol) was added. After stirring the mixture for 1 h at 0 °C, the mixture was passed through Cerite pad. The filtrate was concentrated in vacuo to afford crude compounds, which were purified by recrystallization (hexane/EtOAc) to give **2** (1.41 g, 3.51 mmol) in 52% yield. Spectral data for **2**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45–7.36 (m, 3H), 7.32–7.30 (m, 2H), 5.31 (q, 1H, J = 7.1 Hz), 4.44–4.40 (m, 1H), 4.11 (q, 1H, J = 7.1 Hz), 3.94–387 (m, 2H), 3.57–3.53 (m, 1H), 2.40–2.37 (m, 1H), 2.29–2.27 (m, 1H), 2.14–2.09 (m, 2H), 1.63 (d, 3H, J = 7.1 Hz); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 156.1, 136.8, 129.6, 129.4, 126.6, 62.8, 57.8, 50.2, 47.2, 30.2, 25.4, 16.3; mp 171–173 °C; $[\alpha]_D^{23}$ −78.3 (c 0.996, MeOH); Anal. Calcd for $C_{14}H_{18}F_6N_5P$: C, 41.90; H, 4.52; N, 17.45. Found: C, 42.00; H; 4.49, N; 17.35; white solid.
12. *Preparation of* **3**. To a solution **12**[8b] (3.13 g, 8.99 mmol) in MeCN (50 mL), potassium hexafluorophosphate (2.53 g, 13.6 mmol) was added at room temperature under argon. After stirring the mixture for 1 h, the mixture was passed through Celite pad. The filtrate was concentrated in vacuo to afford crude compounds, which were purified by recrystallization (EtOAc/acetone) to give **13** (3.88 g, 8.46 mmol) in 97% yield. Spectral data for **13**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45–7.44 (m, 8H), 7.40–7.38 (m, 2H), 5.34 (q, 2H, J = 7.1 Hz), 4.39–4.34 (m, 2H), 4.01–3.96 (m, 2H), 1.80 (d, 6H, J = 7.0 Hz); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 153.5, 136.2, 129.5, 129.3, 127.2, 57.5, 45.2, 17.7; IR (KBr) 2982, 2084, 1653, 1455, 1359, 1294, 1204, 1138, 1028, 839, 709, 557; HRMS (FAB^+) Found; m/z, 313.1461. Calcd for $C_{19}H_{22}^{35}ClN_2$: $(M-PF_6)^+$ 313.1472; mp 210–214 °C; $[\alpha]_D^{23}$ −13.6 (c 0.987, acetone). To a solution of **13** (1.10 g, 2.41 mmol) in MeCN (12 mL), sodium azide (236 mg, 3.63 mmol) was added at 0 °C under argon. After stirring the mixture for 1 h, the mixture was passed through Celite pad. The filtrate was concentrated in vacuo to afford crude compounds, which were purified by recrystallization (hexane/EtOAc) to give **3** (809 mg, 2.02 mmol) in 84% yield. Spectral data for **3**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47–7.43 (m, 4H), 7.40–7.35 (m, 6H), 5.25 (q, 2H, J = 5.4 Hz), 3.86–3.81 (m, 2H), 3.62–3.58 (m, 2H), 1.70 (d, 6H, J = 7.0 Hz); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 153.7, 137.0, 129.5, 129.2, 126.6, 55.5, 43.2, 18.0; IR (KBr) δ 2906, 2345, 2166, 1538, 835, 556 cm^{-1}; Anal. Calcd for $C_{19}H_{22}F_6N_5P$: C, 49.04; H, 4.76; N, 15.05. Found: C, 49.11; H; 4.72, N; 14.95; HRMS (FAB^+) Found; m/z, 320.1867. Calcd for $C_{19}H_{22}N_5$: $(M-PF_6)^+$ 320.1875; mp 171–173 °C; $[\alpha]_D^{23}$ −7.44 (c 1.07, acetone), yellow crystal.
13. Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.Uk). CCDC 1416637 contains the supplementary crystallographic data for **2**. CCDC 1416639 contains the supplementary crystallographic data for **3**.
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16. The enantiomeric ratio was determined by HPLC analysis using a chiral column (DAICEL CHIRALCEL OD-H, hexane/*i*-PrOH = 9:1).