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Effective Synthesis of Optically Active Trifluoromethyldiazirinyl Homophenylalanine and Aroylalanine Derivatives with the Friedel-Crafts Reaction in Triflic Acid

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The Friedel-Crafts reaction with 3-(3-methoxyphenyl)-3-(trifluoromethyl)-3*H*-diazirine and optically active *N*-TFA-Asp(Cl)-OMe in triflic acid afforded homophenylalanine derivatives without any loss of the optical purity.

Key words: diazirine; photoaffinity labeling; Friedel-Crafts reaction; triflic acid

Photoaffinity labeling is a useful biochemical method in investigations of structural and functional relationships between small biologically active compounds and biomolecules such as enzymes, RNA, and DNA.[1)] Various compounds, such as phenyldiazirine, arylazide and benzophenone have been developed as photophores. This is ideal, because we can provide photolabeling groups with minimum structural alteration. It has also been established that the (3-trifluoromethyl)phenyldiazirinyl function can be selectively activated without damaging peptides and proteins by irradiating at 350 nm.[2)] But this usually requires manipulation steps to introduce photophores into the target molecules, and also independent construction of the (3-trifluoromethyl)phenyldiazirinyl groups. These limitations encouraged us to establish an effective protocol to provide the (3-trifluoromethyl)phenyldiazirinyl photophore.[3)] It is considered that amino acid derivatives carrying a photolabeling group would become a powerful tool in investigations of biologically active peptides, and for studying their metabolic pathways.

We focused on developing the (3-trifluoromethyl)diazirinyl photophore into homophenylalanine (hPhe), since interesting biological behavior has been discovered by replacing a phenylalanine with hPhe in biological peptides[4,5)] and has also been reported as a starting material for pharmaceutical products such as benazepril and enarapril, both of which inhibit the angiotensin converting enzyme (ACE).[6,7)] The efficient synthesis of photoactivatable optically pure hPhe is important for this. Although several synthetic protocols for optically active hPhe have been reported by various method including enzymatic resolution,[8)] Suzuki-coupling,[9)] diastereoselective Michael addition[10)] and catalytic asymmetric hydrogenation,[11)] these required special reagents or precursors. It might not be sutable to apply those for the preparation of diazirinylated hPhe, because some conditions might reduce the diazirine function. In this paper, we report an effective method for providing optically active diazirinyl hPhe featuring the Friedel-Crafts (F-C) reaction with 3-(3-methoxyphenyl)-3-(trifluoromethyl)-3*H*-diazirin **1**[12)] and the β-acid chloride of aspartic acid **2**[13)] as the key step.

Results and Discussion

We chose the β-acid chloride form of *N*-trifluoromethyl (*S*)-aspartic acid α-methyl ester **2** as the electrophilic precursor. When we first attempted the reaction between **1** and **2** at room temperature, employing aluminium chloride as the activator, however, the desired reaction did not proceed and both **1** and **2** were recovered in CH_2Cl_2 or CH_3NO_2. (Fig. 1, Runs 1 and 2) The reflux conditions led the decomposition of **2**. (Fig. 1, Runs 3 and 4) Although the F–C reaction between *N*-aspartic anhydride derivatives and aromatics have been reported,[14–19)] the aromatics had to be in excess amounts as the solvents. It would be preferable if we could use stoichiometric amounts of aromatics in the process by taking account of both the operational feasibility and economic matters. The reaction did not proceed by employing titanium chloride, which has been effective for formylation,[20)] as the activator in CH_2Cl_2 or under neat conditions. (Fig. 1, Runs 5 and 6) It was found that the desired reaction proceeded smoothly at 0 °C to give adducts **3** and **4** in an over 87% yield by employing a stoichiometric amount of **1** when trifluoromethanesulfonic acid (TfOH) was employed as the solvent. The suspension at the initial stage became a clear solution upon the start of the reaction. Regioisomers **3** and **4** were readily separated by silica gel column chromatography. The NOESY spectrum of major product **3** gave the correlation signals between $C_{2'}$ OCH_3 and $C_{3'}$ H, which disclosed the substitution pattern. In the case of minor product **4**, NOESY correlation was obtained between $C_{4'}$ OCH_3 and both $C_{3'}$ and $C_{5'}$ H. (*R*)-**2** was also reacted with **1** under the same condition to

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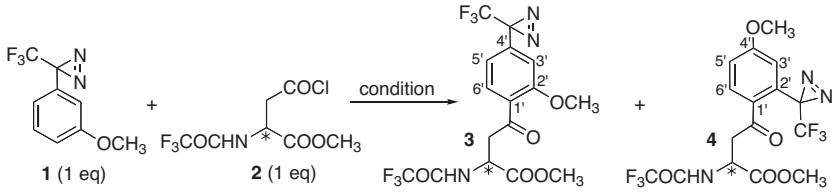


Entry	Catalyst	Solvent	Temperature	Time (h)	Yield
1	$AlCl_3$	CH_2Cl_2	rt	12h	0[a]
2	$AlCl_3$	CH_3NO_2	rt	12h	0[a]
3	$AlCl_3$	CH_2Cl_2	reflux	12h	0[b]
4	$AlCl_3$	CH_3NO_2	reflux	12h	0[b]
5	$TiCl_4$	CH_2Cl_2	50°C	3h	0[b]
6	$TiCl_4$		0°C	2h	0[a]
7	TfOH		0°C	2h	(*S*)−71 (**3**), 28 (**4**) (*R*)−68 (**3**), 19 (**4**)
8	TfOH		50°C	2h	0[b]

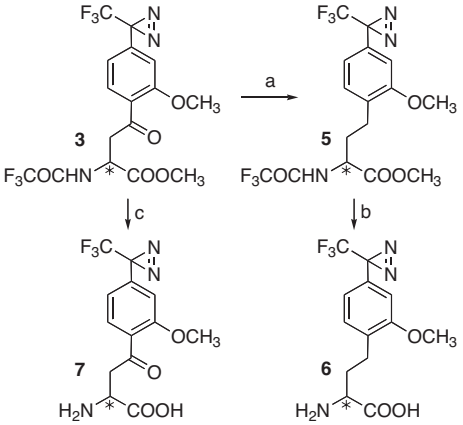
[a] no reaction occurred, [b] the starting material **1** was decomposed.

Fig. 1. Friedel-Crafts Reaction with Diazirinyl Compound **1** and Optically Pure Aspartic Acid Derivative **2**.

afford (*R*)-**3** and **4** in good yields. (Fig. 1, Run 7) A higher temperature afforded a complex mixture because of the decomposition of **1** and **2**. (Fig. 1, Run 8) These results are consistent with the report that the diazirinyl *N-N* double bond was easily decomposed in the presence of a Lewis acid over 25 °C.[21] Unfortunately, 3-phenyl-3-(3-trifluoromethyl)-3*H*-diazirine, which has no activating methoxy substituent on the benzene ring, did not react with (*S*)- or (*R*)-**2** in TfOH at 0 °C. A higher temperature decomposed the diazirinyl ring. We have already reported that 3-phenyl-3-(3-trifluoromethyl)-3*H*-diazirine easily reacted with the dichloromethyl methyl ether to give a formylation product in TfOH.[22] These results indicated that the reactivity of both the acyl donor and acyl acceptor also played a critical role. Furthermore, the trifluoromethyldiazirinyl moiety acted slightly as an electron-withdrawing group for the nucleophilic substitution of aromatic compounds.[23]

With adducts **3** and **4** in hand, the newly introduced carbonyl group was then reduced to a hPhe derivative. It has already been reported that the diazirinyl *N-N* double bond was labiel under H_2–Pd/C conditions.[24] We found that selective reduction of benzylic carbonyl to methylene could be performed with the triethylsilane/TFA system to give **5** in a good yield.[25] No decomposition of the diazirinyl ring occured during the reduction. Finally, deprotection of (*S*)- and (*R*)-**5** was performed under an alkaline condition to afford diazirinyl hPhe **6** in a good yield (90%). However, the conditions decomposed the product to result in a complex mixture when aroyl derivative **3** was employed. Deprotection of **3** could be achieved by treating with 6 N HCl in acetic acid at 80 °C, affording **7** (Scheme 1).

The enantiopurity of compounds **6** and **7** was determined by chiral HPLC (Chirobiotic T, Astec)[26] which revealed this as >98% ee, proving no racemization during the synthesis (Fig. 2).



Scheme 1. Synthesis of the Optically Pure Diazirinyl Homophenylalanine Derivatives.

Reagents and conditions: (a) triethylsilane, trifluoroacetic acid, (*S*)-76%, (*R*)-80%; (b) NaOH, MeOH, (*S*)-91%, (*R*)-90%; (c) 6 N HCl, acetic acid, 80 °C, (*S*)-94%, (*R*)-88%.

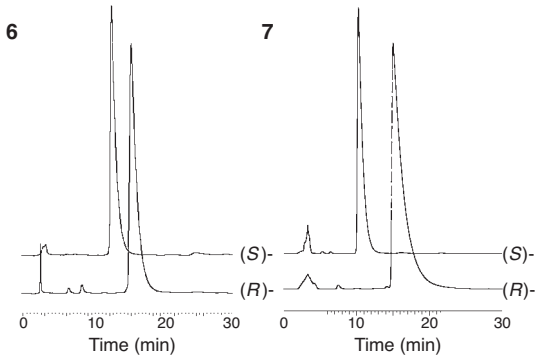


Fig. 2. Chiral HPLC Chromatogram of Synthetic Diazirinyl (*S*)- or (*R*)-**6** and (*S*)- or (*R*)-**7**.

Condition: Chirobiotic T (Astec) 4.6 × 250 mm, eluted with 10% EtOH–H_2O; flow rate of 1.0 ml/min; UV detection at 210 nm.

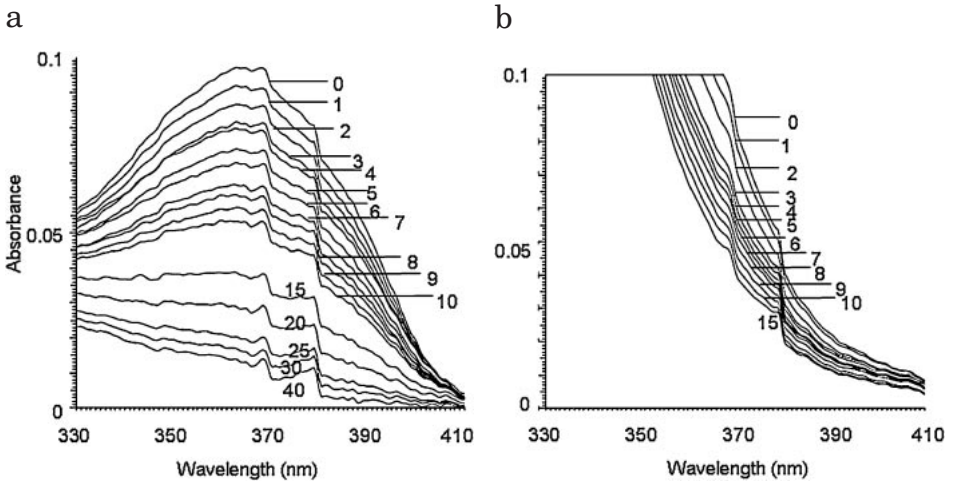


Fig. 3. Photolysis of 0.5 mM of (*S*)-**6** (a) and (*S*)-**7** (b) in Methanol with 15 W Black Light. The photolysis reaction mixture, at the times (in min), is indicated by the numbers.

The photolysis properties of the diazirinyl compounds were examined under black light (15 W). We have already demonstrated that the concentration of the diazirinyl compound had to be set to less than 1 mM to minimize isomerization to the diazo compound.[27] The maximum absorption at 360 nm for **6** and **7** was decreased by increasing irradiation time (Fig. 3). The half-life of **6** and **7** was determined to be 8.5 and 3.2 min, respectively, based on the intensity at 360 nm. We concluded the values were appropriate for photoaffinity labeling.

We developed in these studies an effective synthesis of photoreactive and enantiomerically pure hPhe and 2-methoxybenzoylalanine from the 3-(3-methoxyphenyl)-3-(trifluoromethyl)-3*H*-diazirin and (*S*)- and (*R*)-aspartic acid derivative as an effective photolabeling probe without racemization. The key F–C reaction proceeded by employing trifluoromethanesulfonic acid as the solvent. The subsequent silane promoted reduction to enable transformation of the benzylic carbonyl to methylene. The results will contribute to studies on the structure-activity relationship for the side chain of aromatic α-amino acids.

Experimental

General methods. Optical rotation values were measured by a Jasco DIP-370 polarimeter, and IR spectra were measured by a Jasco FTIR-4100 instrument. ^{1}H-, ^{13}C- and ^{19}F-NMR spectra were measured by a Jeol ECA 500 spectrometer. In the ^{1}H-NMR spectra, the chemical shifts are expressed in ppm downfield from the signal for tetramethylsilane that was used as an internal standard. Splitting patterns are designated as s (singlet), d (doublet), t (triplet), and m (multiplet). In the ^{13}C-NMR spectra, the ^{13}C chemical shifts of the solvents were used as the internal standards ($^{13}CDCl_3$, 77.0 ppm; and $^{13}CD_3OD$, 49.5 ppm). In the ^{19}F-NMR spectra, the chemical shifts are reported as default values without correction. MS data were obtained with a Hitachi NanoFrontier LD mass spectrometer. Chiral HPLC was performed with Chirobiotic T (Astec), 4.6 × 250 mm, eluted with 10% EtOH–H_2O; flow rate, 1.0 ml/min; UV detection at 210 nm.

*(*S*)-Methyl 4-(2-methoxy-4-(3-(trifluoromethyl)-3*H*-diazirin-3-yl) phenyl)-4-oxo-2-(2,2,2-trifluoroacetamido)butanoate ((*S*)-3) and (*S*)-methyl 4-(4-methoxy-2-(3-(trifluoromethyl)-3*H*-diazirin-3-yl)phenyl)-4-oxo-2-(2,2,2-trifluoroacetamido)butanoate ((*S*)-4).* Compounds **1**[12] (24.7 mg, 0.11 mmol) and (*S*)-**2**[13] (29.0 mg, 0.11 mmol) were dissolved in TfOH (0.25 ml, 2.9 mmol) at 0 °C. The yellow reaction mixture was stirred for two hours at the same temperature, then poured into cold water and AcOEt (30:30 ml). The organic layer successively was washed with aqueous 1 M HCl, saturated $NaHCO_3$, 1 N HCl and saturated NaCl, then dried over $MgSO_4$, and filtered. The filtrate was concentrated, and the residue was subjected to silica chromatography (AcOEt:n-hexane = 1:5) to afford pure (*S*)-**3** (34.4 mg, 71%) and (*S*)-**4** (13.6 mg, 28%) as a pale yellow oil.

(*S*)-**3**: $[\alpha]_D$ +77° (c 1.0, $CHCl_3$); IR (film) cm^{-1}: 3330, 1720, 1675, 1610; ^{1}H-NMR ($CDCl_3$) δ: 7.79 (1H, d, J = 8.0 Hz), 7.54 (1H, brd, J = 8.0 Hz), 6.80 (1H, d, J = 8.0 Hz), 6.66 (1H, s), 4.89–4.86 (1H, m), 3.91 (3H, s), 3.78 (1H, dd, J = 19.2, 4.3 Hz), 3.73 (3H, s), 3.57 (1H, dd, J = 18.9, 4.0 Hz); ^{13}C-NMR ($CDCl_3$) δ: 197.34, 170.12, 159.47, 156.91 (q, $^2J_{CF}$ = 37.6 Hz), 136.06, 131.46, 126.42, 121.77 (q, $^1J_{CF}$ = 274.7 Hz), 118.80, 115.63 (q, $^1J_{CF}$ = 287.9 Hz), 109.63, 55.85, 53.15, 48.92, 45.29, 28.45 (q, $^2J_{CF}$ = 40.4 Hz); ^{19}F-NMR ($CDCl_3$) δ: −63.18, −74.34; ESI-MS m/z: 442 $(M+H)^+$; ESI-HRMS: calcd. for $C_{16}H_{14}F_6N_4O_5$ $(M+H)^+$, 442.0832; found, m/z 442.0826.

(*S*)-**4**: $[\alpha]_D$ +57° (c 1.0, $CHCl_3$); IR (film) cm^{-1}: 3330, 1725, 1690, 1610; ^{1}H-NMR ($CDCl_3$) δ: 7.82 (1H, d, J = 8.6 Hz), 7.63 (1H, brd, J = 7.4 Hz), 7.19 (1H, s), 7.02 (1H, d, J = 8.6 Hz), 4.97–4.94 (1H, m), 3.91 (3H, s), 3.86–3.82 (4H, m), 3.56 (1H, dd, J = 18.3, 3.4 Hz); ^{13}C-NMR ($CDCl_3$) δ: 196.22, 169.70, 163.71, 157.05 (q, $^2J_{CF}$ = 38.0 Hz), 132.51, 130.09, 129.53, 121.62 (q, $^1J_{CF}$ = 275.1 Hz), 117.60, 115.56 (q, $^1J_{CF}$ = 287.5 Hz), 115.20, 55.87, 53.25, 48.71, 40.81, 29.22 (q, $^2J_{CF}$ = 40.0 Hz); ^{19}F-NMR ($CDCl_3$) δ: −66.75, −72.86; ESI-MS m/z: 442 $(M+H)^+$; ESI-HRMS: calcd. for $C_{16}H_{14}F_6N_4O_5$ $(M+H)^+$, 442.0832; found, m/z 442.0828.

*(*R*)-Methyl 4-(2-methoxy-4-(3-(trifluoromethyl)-3*H*-diazirin-3-yl) phenyl)-4-oxo-2-(2,2,2-trifluoroacetamido)butanoate ((*R*)-3) and (*R*)-methyl 4-(4-methoxy-2-(3-(trifluoromethyl)-3*H*-diazirin-3-yl)phenyl)-4-oxo-2-(2,2,2-trifluoroacetamido)butanoate ((*R*)-4).* The same treatment of **1** (24.7 mg, 0.11 mmol) and (*R*)-**2** (29.0 mg, 0.11 mmol) as that just described gave (*R*)-**3** (33.0 mg, 68%) and (*R*)-**4** (9.2 mg, 19%) as yellow oil. The ^{1}H-, ^{13}C-NMR and IR data for these samples were identical with these recorded for (*S*)-**3** and **4**.

(*R*)-**3**, $[\alpha]_D$ −76° (c 1.0, $CHCl_3$); (*R*)-**4**, $[\alpha]_D$ −58° (c 1.0, $CHCl_3$)

*(*S*)-Methyl 4-(2-methoxy-4-(3-(trifluoromethyl)-3*H*-diazirin-3-yl) phenyl)-2-(2,2,2-trifluoroacetamido)butanoate ((*S*)-5).* To a solution of (*S*)-**3** (169 mg, 0.38 mmol) in TFA (1.5 ml, 20 mmol), Et_3SiH (0.30 ml, 1.9 mmol) was added dropwise. The reaction mixture was stirred for two hours and then partitioned with AcOEt (80 ml). The organic layer was successively washed with saturated $NaHCO_3$, 1 N HCl and saturated NaCl, then dried over $MgSO_4$ and filtered. After the filtrate had been concentrated, the residue was subjected to silica chromatography (AcOEt:n-hexane = 1:10) to afford a colorless amorphous mass (115 mg, 76%).

$[\alpha]_D$ +65° (c 1.0, $CHCl_3$); IR (film) cm^{-1}: 3320, 1720, 1610; ^{1}H-NMR ($CDCl_3$) δ: 7.11 (1H, d, $J = 7.4$ Hz), 7.04 (1H, d, $J = 7.4$ Hz), 6.74 (1H, brd, $J = 6.9$ Hz), 6.57 (1H, s), 4.64–4.62 (1H, m), 3.81 (1H, s), 3.68 (1H, s), 2.64 (2H, t, $J = 7.7$ Hz), 2.25–2.22 (1H, m), 2.10–2.03 (1H, m); ^{13}C-NMR ($CDCl_3$) δ: 171.00, 157.40, 156.74 (q, $^2J_{CF} = 37.2$ Hz), 130.41, 130.21, 128.69, 122.07 (q, $^1J_{CF} = 274.3$ Hz), 118.90, 115.63 (q, $^1J_{CF} = 287.5$ Hz), 108.12, 55.24, 52.65, 52.18, 31.03, 28.37 (q, $^2J_{CF} = 40.0$ Hz), 25.32; ^{19}F-NMR ($CDCl_3$) δ: −66.54, −75.28. ESI-MS m/z: 400 $(M - N_2 + H)^+$; ESI-HRMS: calcd. for $C_{16}H_{16}F_6NO_4$ $(M - N_2 + H)^+$, 400.0978; found, m/z 400.0989.

*(*R*)-Methyl 4-(2-methoxy-4-(3-(trifluoromethyl)-3*H*-diazirin-3-yl) phenyl)-2-(2,2,2-trifluoroacetamido)butanoate ((*R*)-5).* The same treatment of (*R*)-**3** (168 mg, 0.38 mmol) as that just described gave (*R*)-**5** (121 mg, 80%) as yellow oil. The ^{1}H-, ^{13}C-NMR and IR data for these samples were identical to these recorded for (*S*)-**5**.

$[\alpha]_D$ −65° (c 1.0, $CHCl_3$).

*(*S*)-2-Amino-4-(2-methoxy-4-(3-(trifluoromethyl)-3*H*-diazirin-3-yl) phenyl)butanoic acid ((*S*)-6).* To a solution of (*S*)-**4** (26.4 mg, 60 µmol) in MeOH (6.0 ml), 1 N NaOH (0.50 ml) was added at room temperature. After stirring for 1 h, silica gel (2 g) was added. The resulting mixture was then evaporated. The residue was subjected to silica chromatography (CH_2Cl_2:MeOH:H_2O:acetic acid = 10:2:0.25:0.05) to afford a colorless solid (17.3 mg, 91%).

$[\alpha]_D$ −15° (c 2.0, MeOH); IR (film) cm^{-1}: 2950, 1680; ^{1}H-NMR (CD_3OD) δ: 7.22 (1H, d, $J = 7.4$ Hz), 6.79 (1H, d, $J = 7.4$ Hz), 6.68 (1H, s), 4.33 (1H, q, $J = 4.8$ Hz), 3.82 (3H, s), 2.73 (2H, t, $J = 7.4$ Hz), 2.27–2.18 (1H, m), 2.07–2.01 (1H, m); ^{13}C-NMR (CD_3OD) δ: 173.82, 159.24, 132.56, 131.76, 129.42, 123.65 (q, $^1J_{CF} = 273.5$ Hz), 119.90, 109.14, 55.92, 53.69, 31.64, 29.57 (q, $^2J_{CF} = 40.4$ Hz), 27.44; ^{19}F-NMR (CD_3OD) δ: −66.38; ESI-MS m/z: 318 $(M + H)^+$; ESI-HRMS: calcd. for $C_{13}H_{15}F_3N_3O_3$ $(M + H)^+$, 318.1060; found, m/z 318.1067; chiral HPLC $t_R = 13.2$ min.

*(*R*)-2-Amino-4-(2-methoxy-4-(3-(trifluoromethyl)-3*H*-diazirin-3-yl) phenyl)butanoic acid ((*R*)-6).* The same treatment of (*R*)-**4** (26.0 mg, 60 µmol) as that just described gave (*R*)-**6** (16.8 mg, 90%) as yellow oil. The ^{1}H-, ^{13}C-NMR and IR data for these samples were identical to these recorded for (*S*)-**6**.

$[\alpha]_D$ +15° (c 2.0, MeOH); chiral HPLC $t_R = 17.0$ min

*(*S*)-2-Amino-4-(2-methoxy-4-(3-(trifluoromethyl)-3*H*-diazirin-3-yl) phenyl)-4-oxobutanoic acid ((*S*)-7).* To a stirred solution of (*S*)-**3** (31.6 mg, 72 µmol) in acetic acid (12 ml), concentrated HCl (12 ml) was added. The reaction mixture was stirred for 12 h at 50 °C and then concentrated. The residue was subjected to silica chromatography (CH_2Cl_2:MeOH:H_2O:acetic acid = 10:2:0.25:0.05) to afford a colorless solid (22.3 mg, 94%).

$[\alpha]_D$ −14° (c 2.0, MeOH); IR (film) cm^{-1}: 2940, 1670, 1610; ^{1}H-NMR (CD_3OD) δ: 7.87 (1H, d, $J = 8.0$ Hz), 6.95 (1H, d, $J = 8.6$ Hz), 6.81 (1H, s), 3.99–3.97 (4H, m), 3.72 (1H, d, $J = 19.5$ Hz), 3.55 (1H, d, $J = 19.5$ Hz); ^{13}C-NMR (CD_3OD) δ: 199.11, 179.04, 160.88, 136.24, 132.52, 128.79, 123.34 (q, $^1J_{CF} = 273.9$ Hz), 119.74, 111.08, 56.54, 51.84, 29.54 (q, $^2J_{CF} = 40.4$ Hz), 23.2; ^{19}F-NMR (CD_3OD) δ: −66.83; ESI-MS m/z: 332 $(M + H)^+$; ESI-HRMS: calcd. for $C_{13}H_{13}F_3N_3O_4$ $(M + H)^+$, 332.0853; found, m/z 332.0866; chiral HPLC $t_R = 10.2$ min.

*(*R*)-2-Amino-4-(2-methoxy-4-(3-(trifluoromethyl)-3*H*-diazirin-3-yl) phenyl)-4-oxobutanoic acid ((*R*)-7).* The same treatment of (*R*)-**4** (31.8 mg, 72 µmol) as that just described gave (*R*)-**7** (21.0 mg, 88%) as yellow oil. The ^{1}H-, ^{13}C-NMR and IR data for these samples were identical to these recorded for (*S*)-**6**.

$[\alpha]_D$ +14° (c 2.0, MeOH); chiral HPLC $t_R = 15.0$ min

Photolysis of the diazirinyl compounds in methanol. A methanolic solution of (*S*)-**6** or **7** (0.5 mM) was placed in a quartz cuvette. After replacing the inner atmosphere with nitrogen, photolysis was carried out with 15 W black-light (UVP, San Gabriel, California, USA) at a distance 2 cm from the surface of light source.

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