column chromatography (hexane to CH_2Cl_2/hexane 1/9) to yield 3,3'-(5-(bromomethyl)-1,3-phenylene)bis(3-(trifluoromethyl)-3*H*-diazirine) **11** (139 mg, 52%) as a colorless oil.

^{1}H-NMR (270 MHz, $CDCl_3$) δ: 7.28 (2H, s), 6.91 (1H, s), 4.42 (2H, s). ^{13}C-NMR (68 MHz, $CDCl_3$) δ: 140.0, 131.0, 128.3, 124.3, 121.7 (q, *J* = 280.5 Hz), 30.8, 28.1 (q, *J* = 39.1 Hz). ^{19}F-NMR (470 MHz, $CDCl_3$) δ: -65.1. MS was not detected. The starting material was able to be recovered (66.8 mg, 31%).

tert-Butyl 3-(3,5-bis(3-(trifluoromethyl)-3H-diazirin-3-yl)phenyl)-2-(diphenylmethyleneamino)propanoate ***12***

tert-Butylglycinate benzophenone imine (78.5 mg, 0.266 mmol) and *O*-allyl-*N*-9-anthracenylmethylcinchonidium bromide (21.9 mg, 36.2 mmol) were dissolved in CH_2Cl_2 (3 mL). 3,3'-(5-(Bromomethyl)-1,3-phenylene)bis(3-(trifluoromethyl)-3*H*-diazirine) **11** (93.5 mg, 0.241 mmol) was added to the mixture and was cooled at –78 °C. To the solution was slowly added BTPP (81.8 mL, 0.362 mmol) followed by stirring for an additional 12 h. After removal of the solvent, the residue was purified by column chromatography (AcOEt/hexane 1:7) to yield *tert*-butyl 3-(3,5-bis(3-(trifluoromethyl)-3*H*-diazirin-3-yl)phenyl)-2-(diphenylmethyleneamino)propanoate **12** (116 mg, 80%) as a colorless oil.

^{1}H-NMR (270 MHz, $CDCl_3$) δ: 7.62-7.29 (8H, m), 6.99 (2H, s), 6.85 (1H, s), 6.61 (2H, d, *J* = 6.9 Hz), 4.07 (1H, t, *J* = 6.6 Hz), 3.19 (2H, d, *J* = 6.3 Hz), 1.45 (9H, s). ^{13}C-NMR (68 MHz, $CDCl_3$) δ: 171.1, 169.9, 140.8, 138.8, 136.0, 128.6, 128.2, 127.9, 127.2, 122.5, 121.7 (q, *J* = 274.9 Hz), 81.6, 66.8, 39.2, 28.0 (q, *J* = 40.8 Hz), 27.9. ^{19}F-NMR (470 MHz, $CDCl_3$) δ: -65.1. HRMS-ESI (*m*/*z*) $[M + H]^+$ calcd for $C_{30}H_{26}F_6N_5O_2$ 602.1991, found 602.1984.

2-Amino-3-(3,5-bis(3-(trifluoromethyl)-3H-diazirin-3-yl)phenyl)propanoic acid ***13***

tert-Butyl 3-(3,5-bis(3-(trifluoromethyl)-3*H*-diazirin-3-yl)phenyl-2-(diphenylmethyleneamino)propanoate **12** (116 mg, 0.192 mmol) was dissolved in TFA (3 mL) at 0 °C. The mixture was stirred for 12 h at room temperature. TFA was evaporated and the residue was purified by column chromatography (CH_2Cl_2 to AcOEt/MeOH/H_2O 4/1/1) to yield 2-amino-3-(3,5-bis(3-(trifluoromethyl)-3*H*-diazirin-3-yl)phenyl)propanoic acid **13** (88.4 mg, 93%) as a colorless amorphous mass.

^{1}H-NMR (270 MHz, CD_3OD) δ: 7.28 (2H, s), 7.16 (1H, s), 3.87 (1H, s), 3.34 (1H, dd, *J* = 7.3, 3.6 Hz), 3.11 (1H, dd, *J* = 13.8, 7.6 Hz). ^{13}C-NMR (68 MHz, CD_3OD) δ: 176.4, 140.5, 131.7, 130.3, 124.8, 123.3 (q, *J* = 274.3 Hz), 56.7, 37.6, 29.3 (q, *J* = 40.8 Hz). ^{19}F-NMR (470 MHz, CD_3OD) δ: -66.9. HRMS-ESI (*m*/*z*) $[M + H]^+$ calcd for $C_{13}H_{10}F_6N_5O_2$ 382.0739, found 382.0714.

*Photolysis of compound **13** in H_2O*

1 mM of a solution of bis-diazirinyl-Phe **13** in H_2O was placed in a quartz cuvette. Photolysis was carried out with a 100 W black light at a distance of 1 cm from the surface of the light source.

Spectra were measured after each minute, and then the half-life was calculated from the decrements of the absorbance around 360 nm.

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REFERENCES

1. (a) J. Brunner, *Annu. Rev. Biochem.*, 1993, **62**, 483; (b) F. Kotzyba-Hilbert, I. Kapfer, and M. Goeldner, *Angew. Chem., Int. Ed. Engl*, 1995, **34**, 1296; (c) G. Dorman and G. D. Prestwich, *Trends Biotechnol.*, 2000, **18**, 64; (d) M. Hashimoto and Y. Hatanaka, *Eur. J. Org. Chem.*, 2008, 2513; (e) E. Smith and I. Collins, *Future Med. Chem.*, 2015, **7**, 159; (f) D. P. Murale, S. S. Hong, M. M. Haque, and J.-S. Lee, *Proteome Sci.*, 2016, **15**, 14; (g) Y. Hatanaka and M. Hashimoto, in Photoaffinity Labeling for Structural Probing within Protein; Springer Japan: Tokyo, 2017.
2. (a) Y. Hatanaka, *Chem. Pharm. Bull.*, 2015, **63**, 1; (b) M. Hashimoto, *Reference Module in Chemistry, Molecular Sciences and Chemical Engineering*, Diaziridines and Diazirines, 2019, 1; (c) Z. P. Tachrim, L. Wang, Y. Murai, and M. Hashimoto, *Molecules*, 2021, **26**, 4496.
3. G. W. J. Fleet, R. R. Porter, and J. R. Knowles, *Nature*, 1969, **224**, 511.
4. R. E. Galardy, L. C. Craig, and M. P. Printz, *Nat. New Biol.*, 1973, **242**, 127.
5. A. Herner, J. Marjanovic, T. M. Lewandowski, V. Marin, V. M. Patterson, L. Miesbauer, D. Ready, J. Williams, A. Vasudevan, and Q. Lin, *J. Am. Chem. Soc.*, 2016, **138**, 14609.
6. J. Brunner, H. Senn, and F. M. Richards, *J. Biol. Chem.*, 1980, **255**, 3313.
7. Y. Hatanaka, M. Hashimoto, H. Nakayama, and Y. Kanaoka, *Chem. Pharm. Bull.*, 1994, **42**, 826.
8. M. L. Lepage, C. Simhadri, C. Liu, M. Takaffoli, L. Bi, B. Crawford, A. S. Milani, and J. E. Wulff, *Science*, 2019, **366**, 875.
9. A. Blencowe, C. Blencowe, K. Cosstick, and W. Hayes, *React. Funct. Polym.*, 2008, **68**, 868.

10. (a) Y. Murai, K. Masuda, Y. Sakihama, Y. Hashidoko, Y. Hatanaka, and M. Hashimoto, *J. Org. Chem.*, 2012, **77**, 8581; (b) Y. Murai, K. Masuda, Y. Ogasawara, L. Wang, Y. Hashidoko, Y. Hatanaka, S. Iwata, T. Kobayashi, and M. Hashimoto, *Eur. J. Org. Chem.*, 2013, 2428.
11. J. E. Horne, M. Walko, A. N. Calabrese, M. A. Levenstein, D. J. Brockwell, N. Kapur, A. J. Wilson, and S. E. Radford, *Angew. Chem. Int. Ed.*, 2018, **57**, 16688.
12. (a) E. J. Corey, F. Xu, and M. C. Noe, *J. Am. Chem. Soc.*, 1997, **119**, 12414; (b) M. J. O'Donnell, *Acc. Chem. Res.*, 2004, **37**, 506.
13. T. C. Cook, M. B. Andrus, and D. H. Ess, *Org. Lett.*, 2012, **14**, 5836.
14. (a) K. Fang, M. Hashimoto, S. Jockusch, N. J. Turro, and K. Nakanishi, *J. Am. Chem. Soc.*, 1998, **120**, 8543; (b) M. Daghish, L. Hennig, M. Findeisen, S. Giesa, F. Schumer, H. Hennig, A. G. Beck-Sickinger, and P. Welzel, *Angew. Chem. Int. Ed.*, 2002, **41**, 2293; (c) M. Hashimoto and Y. Hatanaka, *Anal. Biochem.*, 2006, **348**, 154.
15. H. Nakashima, M. Hashimoto, Y. Sadakane, T. Tomohiro, and Y. Hatanaka, *J. Am. Chem. Soc.*, 2006, **128**, 15092.
16. E. Tullberg and T. Frejd, *Synth. Commun.*, 2007, **37**, 237.
17. B. Raju and G. S. Krishna Rao, *Synthesis*, 1987, 197.