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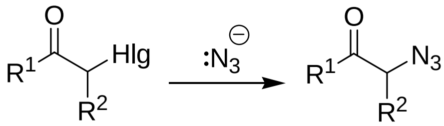
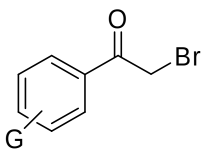
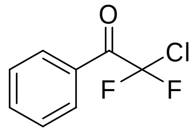
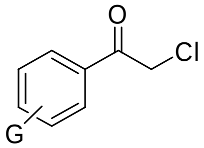
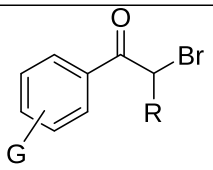
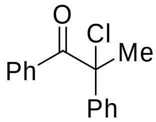
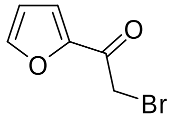
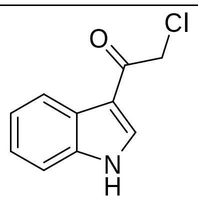
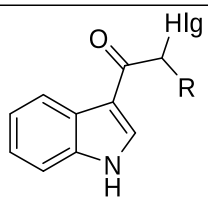
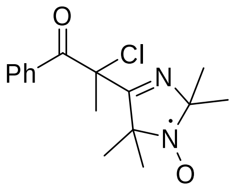
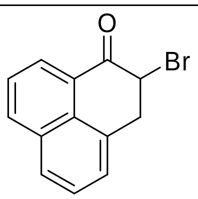
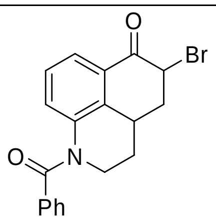
Supporting Information

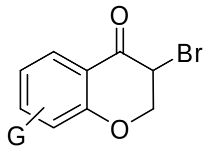
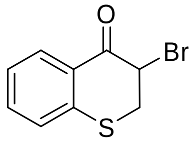
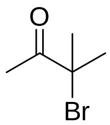
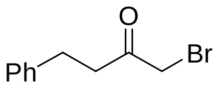
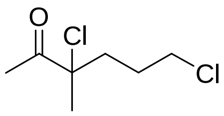
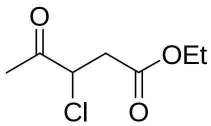
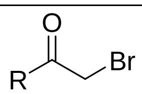
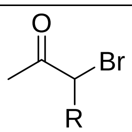
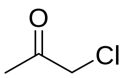
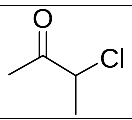
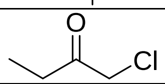
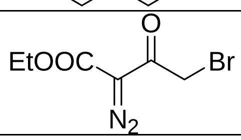
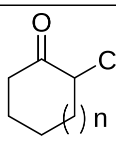
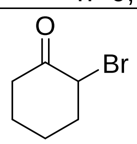
The numbering of the references corresponds to that used in the main text.

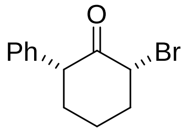
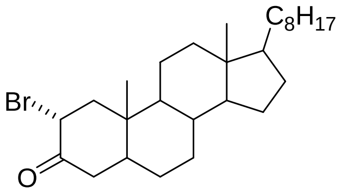
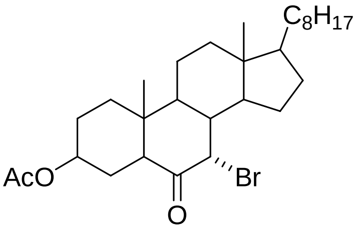
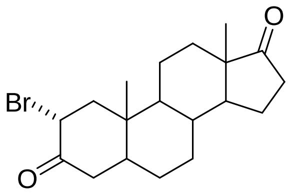
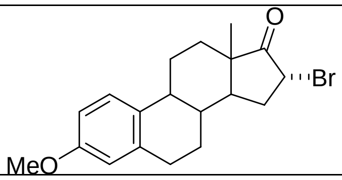
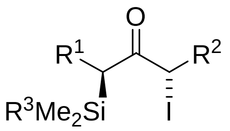
Table 1. Synthesis of α-azido ketones by nucleophilic substitution of α-halo ketones



Substrate	Azide source	Conditions	Yield	Ref.
	n.d.	n.d.	73 %	15
	NaN_3	DMSO/RT	85-95 %[a]	16
	NaN_3	DMSO/RT	47-72 %	17
	NaN_3	DMSO/RT	86-97 %	18
	NaN_3	DMF/0ºC	n.d.	19
	NaN_3	DMF/RT	~100 %	20
	NaN_3	DMF/0 ºC	55 %	21
	NaN_3	DMF/0-10 ºC	n.d.	22
	NaN_3	DMF/AcOH/0ºC	80-82 %	23
	NaN_3	Me_2CO/RT	100 %[a]	24
	NaN_3	Me_2CO/RT	99 %	25
	NaN_3	Me_2CO/RT	81-94 %	26
	NaN_3	Me_2CO-H_2O/Δ	83 %	27
	NaN_3	Me_2CO-H_2O/50 ºC	87 %[a]	28,29
	NaN_3	Me_2CO-H_2O	72 %[b]	30
	NaN_3	Me_2CO-H_2O/50 ºC	88-100 %	31-33
	NaN_3	Me_2CO-H_2O/ β-CD/RT	99 %	34
	NaN_3	Me_2CO-H_2O/RT	76-92 %	35
	TBAA	Me_2CO-H_2O/ 0-25 ºC	n.d.	36
	PSAA	n.d.	n.d.	37
	NaN_3	EtOH-AcOH-H_2O/ 30 ºC	76-93 %	38
	NaN_3	EtOH-H_2O/0 ºC	83-95 %	27
	NaN_3	MeOH-H_2O/0 ºC	n.d.	39
	NaN_3	EtOH-Me_2CO-H_2O	79 %[b]	40
	NaN_3	H_2O/Δ	65 %	27
	NaN_3	[bmim][PF_6]H_2O/RT	95-98 %	41
	NaN_3	[emim][BF_4]/RT	88-89 %	42
	PSAA (Amberlite-400)	CH_2Cl_2/RT	100 %	43
	PSAA (Amberlite IRA 900)	CH_2Cl_2/30 ºC	68-95 %	44
	NaN_3	PhMe/Aliquat 336 /55 ºC	41-87 %	45

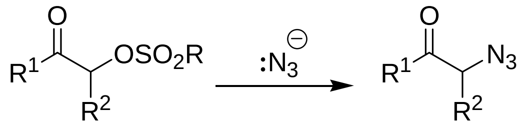
Substrate	Azide source	Conditions	Yield	Ref.
	NaN_3	DMSO/100 ºC	81 %	46
	NaN_3	DMF/RT	n.d.	47
	NaN_3	KI/Me_2CO/RT	85 %	48
	NaN_3	KI/Me_2CO	83 %[b]	49
	NaN_3	Me_2CO/RT	95 %	50
	NaN_3	Me_2CO-H_2O/RT	76-78 %	51
 R = alkyl	NaN_3	DMSO/RT	80-98 %	18
	NaN_3	DMSO	95 %[b]	52
	NaN_3	DMF/RT	86-96 %	53
	NaN_3	THF-H_2O/RT	n.d.[a]	54
	NaN_3	MeOH/0 ºC	95 %	55
	NaN_3	MeOH-AcOH/Δ	n.d.	56
	NaN_3	DMSO/RT	86 %	18
	NaN_3	Me_2CO-H_2O/Δ	100 %	57
 R= H, Me, Et Hlg=Cl, Br	NaN_3	DMSO/RT	73-90 %	58
	NaN_3	DMSO/RT	n.d.	59
	NaN_3	DMF/AcOH/10 ºC	81 %	60
	NaN_3	DMF/AcOH	92 %[b]	61

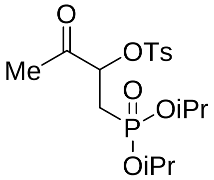
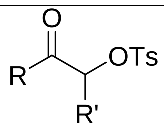
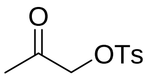
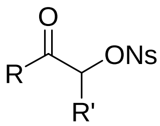
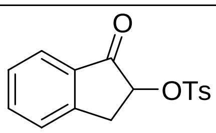
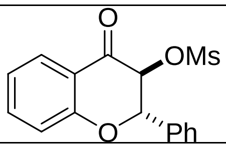
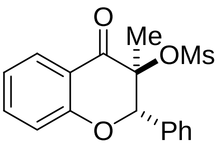
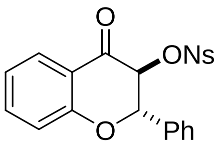
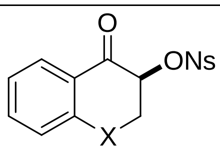
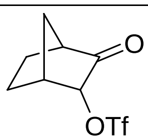
Substrate	**Azide source**	**Conditions**	**Yield**	**Ref.**
	NaN_3	DMSO	n.d.	62
	NaN_3	Me_2CO/ 18-crown-6/RT	73-95 %	26
	NaN_3	Me_2CO/ 18-crown-6/RT	26 %	26
	NaN_3	MeOH-H_2O/Δ	n.d.[a]	63
	NaN_3	EtOH-AcOH-H_2O/ 0 ºC	93 %	38
	NaN_3	DMSO/RT	95 %[a]	16
	NaN_3	DMSO/RT	89 %[a]	64
	NaN_3	Me_2CO/Δ	92 %[c]	65
 R= branched alkyl	NaN_3	EtOH-AcOH-H_2O/ 0 ºC	100 %[a]	66
 R= Bn, Ph	NaN_3	MeOH/0 ºC	90-95 %[a]	67
	NaN_3	NMP	65 %[b]	68
	NaN_3	EtOH-AcOH-H_2O/ 0 ºC	85 %	38
	NaN_3	H_2O-AcOH (few drops)/RT	87 %	13
	NaN_3	Me_2CO/RT	75 %	69
	NaN_3	H_2O-AcOH (few drops)/RT	n.d.	70
	NaN_3	H_2O-AcOH (few drops)/RT	n.d.	70
	NaN_3	Me_2CO-H_2O/ 0 ºC-RT	95 %	71
 n=0, 1, 2	KN_3	DMSO/RT	60-85 %	72,73
	NaN_3	MeOH/0 ºC	48-67 %	74
	NaN_3	DMSO/RT	n.d.[a]	75
	NaN_3	DMSO	n.d.[b]	62

Substrate	**Azide source**	**Conditions**	**Yield**	**Ref.**
	NaN_3	DMSO	n.d.[b]	62
	NaN_3	NMP	51 %[b,d]	76
	NaN_3	NMP-AcOH/RT	65 %	68,77
	NaN_3	NMP-AcOH/RT	96 %	77
	NaN_3	DMSO/H_2SO_4 (cat.)/ 60 °C	70 %	68
 and related systems	TMGA	MeCN/RT	83-92 %	78
	TMGA	$MeNO_2$/RT	95 %	79
	NaN_3	DMF-AcOH/RT	88 %	77
 R^1-R^3 = alkyl, benzyl	NaN_3	DMSO/RT	41-83 %[f]	80

n.d.: no data given
[a] Used in the subsequent transformation step without any purification
[b] Temperature not specified
[c] > 5 % β elimination product
[d] Overall yield of bromination and substitution steps
[e] From 2α-iodocholestananone
[f] d.e. ≥ 90 %, e.e. ≥ 95%

Table 2. Synthesis of α-azido ketones by nucleophilic substitution of α-sulfonyloxy ketones



Substrate	Azide source	Conditions	Yield	Ref.
	TBAA	THF/-10 ºC	98 %	81
 R = Ar, $CH=CH_2$ R' = H R = Ph, Et R' = Me	NaN_3	$CHCl_3$/pillared clay/90-100 ºC	88-97 %	82,83
	NaN_3	EtOH-AcOH-H_2O/0 ºC	49 %	66
 R= alkyl, allyl, Ph	NaN_3	Me_2CO/RT	68-96 %	84
	NaN_3	$CHCl_3$/pillared clay/RT	86-96 %	83
	NaN_3	DMF/RT	10 %[a]	85
	NaN_3	DMF/RT	67 %	86
	NaN_3	Me_2CO/18-crown-6/RT	50 %	26
 X= bond, CH_2, O, S	NaN_3	Me_2CO/RT	68-96 %	84
	NaN_3	MeOH/Δ	(69)[b]	87

[a] Reaction quenched at low conversion
[b] Not isolated in pure form, major (75 %) product of a ≥7 component mixture (GC analysis) obtained by vacuum distillation.

References

15 S. D. Higgins and C. B. Thomas, *J. Chem. Soc., Perkin Trans 1* 1983, 1483-1488.

16 J. Ackrell, J. M. Muchowski, E. Galeazzi and A. Guzman, *J. Org. Chem.* 1986, **51**, 3374-3376.

17 J. M. Holub, K. O'Tool-Colin, A. Getzel, A. Argenti, M. A. Evans, D. C. Smith, G. A. Dalglish, A. Rifat, S. L. Wilson, B. M. Taylor, U. Miott, J. Glersaye, K. S. Lam, B. J. McCranor, J. D. Berkowitz, R-B. Miller, J. R. Lukens, K. Krumpe, J. T. Gupton and B. S. Burnham, *Molecules* 2004, **9**, 135-157.

18 H. Takeuchi, S. Yanagida, T. Ozaki, S. Hagiwara and S. Eguchi, *J. Org. Chem.* 1989, **54**, 431-434.

19 V. J. Majo and P. T. Perumal, *J. Org. Chem.* 1998, **63**, 7136-7142.

20 V. J. Majo and P. T. Perumal, *Tetrahedron Lett.* 1997, **38**, 6889-6892.

21 N. De Meyer, A. Haemers, L. Mishra, H. K. Pandey, L. A. C. Pieters, D. A. Vanden Berghe and A. J. Vlietnick, *J. Med. Chem.* 1991, **34**, 736-746.

22 D. Knittel, H. Hemetsberger and H. Weidmann, *Monatsh. Chem.* 1970, **101**, 157-160.

23 P. N. D. Singh, S. M. Mandel, R. M. Robinson, Z. Zhu, R. Franz, B. S. Ault and A. D. Gudmundsdottir, *J. Org. Chem.* 2003, **68**, 7951-7960.

24 R. Zhao, B.-C. Chen, M. S. Bednarz, B. Wang, A. P. Skoumbourdis, J. E. Sundeen, T. C. M. Dhar, E. J. Iwanowicz, B. Balasubramanian and J. C. Barrish, *ARKIVOC* 2007, **xii**, 36-42.

25 M. Pulici, F. Quartieri and E. R. Felder, *J. Comb. Chem.* 2005, **7**, 463-473.

26 T. Patonay, É. Juhász-Tóth and A. Bényei, *Eur. J. Org. Chem*. 2002, 285-295.

27 H. Bretschneider and H. Hörmann, *Monatsh. Chem.* 1953, **84**, 1021-1032.

28 T. G. M. Dhar, J. Guo, Z. Shen, W. J. Pitts, H. H. Gu, B.-C. Chen, R. Zhao, M. S. Bednarz and E. J. Iwanowicz, *Org. Lett.* 2002, **4**, 2091-2093.

29 T. G. M. Dhar, Z. Shen, J. Guo, C. Liu, S. H. Watterson, H. H. Gu, W. J. Pitts, C. A. Fleener, K. A. Rouleau, N. Z. Sherbina, K. W. McIntyre, M. R. Witmer, J. A. Tredup, B.-C. Chen, R. Zhao, M. S. Bednarz, D. L. Cheney, J. F. MacMaster, L. M. Miller, K. K. Berry, T. W. Harper, J. C. Barrish, D. L. Hollenbaugh and E. J. Iwanowicz, *J. Med. Chem.* 2002, **45**, 2127-2130.

30 R. K. Hunnur, P. R. Latthe and B. V. Badami, *J. Chem. Res.* 2005, 592-594.

31 E. J. Iwanowicz, S. H. Watterson, J. Guo, W. J. Pitts, T. G. M. Dhar, Z. Shen, P. Chen, H. H. Gu, C. A. Fleener, K. A. Rouleau, D. L. Cheney, R. M. Townsend and D. L. Hollenbaugh, *Bioorg. Med. Chem. Lett.* 2003, **13**, 2059-2063.

32 T. G. M. Dhar, Z. Shen, H. H. Gu, P. Chen, D. Norris, S. H. Watterson, S. K. Ballentine, C. A. Fleener, K. A. Rouleau, J. C. Barrish, R. Townsend, D. L. Hollenbaugh and E. J. Iwanowicz, *Bioorg. Med. Chem. Lett.* 2003, **13**, 3557-3560.

33 X. Ouyang, E. L. Piatnitski, V. Pattaropong, X. Chen, H. Y. He, A. S. Kiselyov, A. Velankar, J. Kawakami, M. Labelle, L. Smith, J. Lohman, S. P. Lee, A. Malikzay, J. Fleming, J. Gerlak, Y. Wang, R. L. Rosler, K. Zhou, S. Mitelman, M. Camara, D. Surguladze, J. F. Doody and M. C. Tuma, *Bioorg. Med. Chem. Lett*. 2006, **16**, 1191-1196.

34 M. S. Reddy, M. Nareder and K. Rama Rao, *Tetrahedron* 2007, **63**, 331-336.

35 S. H. Kim, J. U. Jeong, D. O. Choi and K. J. Lee, *Bull. Korean Chem. Soc.* 1993, **14**, 11-12.

36 F. Navas, M. J. Bishop, D. T. Garrison, S. J. Hodson, J. D. Speake, E. C. Bigham, D. H. Drewry, D. L. Saussy, J. H. Liacos, P. E. Irving and M. J. Gobel, *Bioorg. Med. Chem. Lett.* 2002, **12**, 575-579.

37 P. Molina, P. M. Fresneda, P. Almendros, *Heterocycles* 1993, **36**, 2255-2258.

38 J. H. Boyer and D. Straw, *J. Am. Chem. Soc*. 1952, **74**, 4506-4508.

39 B. Batanero, J. Escudero and F. Barba, *Synthesis* 1999, 1809-1813.

40 E. Zbiral and J. Stroh, *Liebigs Ann. Chem.* 1969, **727**, 231-233.

41 N. M. T. Lourenco and C. A. M. Afonso, *Tetrahedron* 2003, **59**, 789-794.

42 Y. X. Li, W. L. Bao and Z. M. Wang, *Chinese Chem. Lett.* 2003, ***14***, 239-242.

43 A. Hassner and M. Stern, *Angew. Chem*., *Int. Ed. Engl.* 1986, **25**, 478-479.

44 E. C. S. Brenelli, J. A. Brenelli and R. C. L. Pinto, *Tetrahedron Lett.* 2005, **46**, 4531-4533.

45 L. Widler, J. Green, M. Missbach, M. Susa and E. Altmann, *Bioorg. Med. Chem. Lett.* 2001, **11**, 849-852.

46 T. G. Archibald and K. Baum, *J. Org. Chem.* 1990, **55**, 3562-3565.

47 L. C. Fardelone, J. A. R. Rodrigues and P. J. S. Moran, *J. Mol. Cat. B* 2006, **39**, 9-12.

48 U. Schmidt and J. Wild, *Liebigs Ann. Chem.* 1985, 1882-1894.

49 U. Schmidt, A. Lieberknecht, H. Grisser and H. Boekens, *Liebigs Ann. Chem.* 1985, 785-793.

50 K. M. Peese and D. Y. Gin, *J. Am. Chem. Soc.* 2006, **128**, 8734-8735.

51 S. W. You, M. K. Kim and K.-J. Lee, *Bull. Korean Chem. Soc.* 2000, **21**, 797-800.

52 P. J. S. Moran, J. A. R. Rodrigues, I. Joekes, E. C. S. Brenelli and R. A. Leite, *Biocatalysis* 1994, **9**, 321-328.

53 U. Ghosh, D. Ganessunker, V. J. Sattigeri, K. E. Carlson, D. J. Mortensen, B. S. Katzenellenbogen and J. A. Katzenellenbogen, *Bioorg. Med. Chem.* 2003, **11**, 629-657.

54 Y.-F. Zhu, R. S. Struthers, P. J. Connors, Y. Gao, T. D. Gross and J. Saunders, *Bioorg. Med. Chem. Lett.* 2002, **12**, 399-402.

55 P. Besse, H. Veschambre, M. Dickman and R. Chenevert, *J. Org. Chem.* 1994, **59**, 8288-8291.

56 J. H. Boyer, and D. Straw, *J. Am. Chem. Soc.* 1953, **75**, 1642-1644.

57 C. J. Moody and J. G. Ward, *J. Chem. Soc., Perkin Trans. 1* 1984, 2903-2909.

58 J. Bergman, J.-E. Bäckvall and J.-O. Lindström, *Tetrahedron*, 1973, **29**, 971-976.

59 V. A. Reznikov, G. I. Roshchupkina,T. V. Ribalova and Y. V. Gatilov, *Russ. Chem. Bull., Int. Ed.* 2001, **50**, 874-881.

60 S. V. D'Andrea, A. Ghosh, W. Wang, J. P. Freeman and J. Szmuszkovicz, *J. Org. Chem.* 1991, **56**, 2680-2684.

61 Okide, G. B. *Tetrahedron* 1993, **49**, 9517-9524.

62 L. Benati, R. Leardini, M. Minozzi, D. Nanni, P. Spagnolo, S. Strazzari, G. Zanardi and G. Calestani, *Tetrahedron* 2002, **58**, 3485-3492.

63 S. S. Al-Hassan, R. J. Cameron, A. W. C. Curran, W. J. S. Lyall, S. H. Nicholson, D. R. Robinson, A. Stuart, C. J. Suckling, I. Stirling, H. C. S. Wood, *J. Chem. Soc., Perkin Trans 1* 1985, 1645-1659.

64 W. Aelterman, N. de Kimpe, V. Tyvorskii, O. Kulinkovich, *J. Org. Chem.* 2001, **66**, 53-58.

65 S. Mangelinckx, P. Van Vooren, D. De Clerk, F. Fülöp, N. De Kimpe, *ARKIVOC* 2006, **iii**, 202-209.

66 J. S. Dickschat, . Reichenbach, I. Wagner-Döbler and S. Schulz, S. *Eur. J. Org. Chem.* 2005, 4141-4153.

67 P. Besse, H. Veschambre, R. Chenevert and M. Dickman, *Tetrahedron: Asymmetry* 1994, **5**, 1727-1744.

68 A. Wolloch and E. Zbiral, *Tetrahedron* 1976, **32**, 1289-1292.

69 J. Hannedouche, P. Peach, D. J. Cross, J. A. Kenny, I. Mann, I. Houson, L. Campbell, T. Walsgrove and M. Wills, *Tetrahedron* 2006, **62**, 5549.

70 M. O. Forster and H. E. Fierz, *J. Chem. Soc.* 1908, 669-678.

71 A. Padwa, M. M. Sá, and M. D. Weingarten, *Tetrahedron*, 1997, **53**, 2371-2386.

72 K. M. Ermolaev, *Zh. Org. Khim.* 1972, **8**, 1828-1831, *Chem. Abstr.* 1973, **78**, 29291s.

73 K. M. Ermolaev, V. I. Maimind, *Zh. Org. Khim.* 1969, **5**, 1218-1221, *Chem. Abstr.* 1969, **71**, 101374w.

74 F. Effenberger, T. Beisswenger, and R. Az, *Chem. Ber.* 1985, **118**, 4869-4876.

75 O. E. Edwards and K. K. Purushothaman, *Can. J. Chem.* 1964, **42**, 712-716.

76 S. C. Smith and C. H. Heathcock, *J. Org. Chem.* 1992, **57**,6379-6380.

77 B. Schönecker and K. Ponsold, *J. Prakt. Chem.* 1971, **313**, 817-824.

78 C. Li, T.-L. Shih, J. U. Jeong, A. Arasappan and P. L. Fuchs, *Tetrahedron Lett.* 1994, **35**, 2645-2646.

79 J. U. Jeong, C. Guo and P. L. Fuchs, P. L. *J. Am. Chem. Soc.* 1999, **121**, 2071-2084.

80 D. Enders and D. Klein, *Synlett* 1999, 719-720.

81 G. Penz and E. Zbiral, *Chem. Ber.* 1985, **118**, 4131-4143.

82 R. S. Varma and D. Kumar, *Catal. Lett.* 1998, **53**, 225-227.

83 R. S. Varma, K. P. Naicker and D. Kumar, *J. Mol. Catal. A: Chem.* 1999, **149**, 153-160.

84 T. Patonay and R. V. Hoffman, *J. Org. Chem.* 1994, **59**, 2902-2905.

85 (a) T. Patonay, M. Rákosi, G. Litkei, T. Mester, R. Bognár, in *Flavonoids and Bioflavonoids, Current Research Trends,* ed. L. Farkas, M. Gábor, F. Kállay, Akadémiai Kiadó, Budapest – Elsevier, Amsterdam, 1977, 227-234; (b) T. Patonay, M. Rákosi, G. Litkei, R. Bognár, R. *Liebigs Ann. Chem.* 1979, 161-173.

86 T. Patonay, E. Patonay-Péli, G. Litkei, L. Szilágyi, G. Batta, Z. Dinya, *J. Heterocycl. Chem.* 1988, **25**, 343-347.

87 X. Creary and A. J. Rollin, *J. Org. Chem.* 1979, **44**, 1798-1806.