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Amide Phosphonium Salt Catalyzed Enantioselective Mannich Addition of Isoxazole-based Nucleophiles to β,γ-Alkynyl-α-ketimino Esters

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Preparation of β,γ-alkynyl-α-imino ester 1

These substrates were prepared according to literature procedure. ^[1-2] **1a**, **1b**, **1c**, **1d**, **1e**, **1f**, **1g** and **1j** are Known compounds. New compounds **1h**, **1i**, **1k**, **1l**, **1m**, **1n** and **1o** were prepared according to literature procedures. Fluorinated alkynyl ketimine **1p** was prepared according to literature procedure. ^[3]

Ethyl-(*E***)-2-(((benzyloxy)carbonyl)imino)-4-phenylbut-3-ynoate (1b):** Light yellow oil, 2.4 g, 82% yield, ¹H NMR (400 MHz, CDCl₃) δ 7.46 – 7.41 (m, 3H), 7.38 – 7.33 (m, 4H), 7.33 – 7.27 (m, 3H), 5.35 (s, 2H), 4.42 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 161.2, 160.9, 146.1, 135.0, 133.1, 131.2, 128.7, 119.6, 102.7, 81.2, 69.0, 63.5, 14.1; HRMS (ESI) m/z: [M + Na]⁺ calcd for (C₂₀H₁₇NNaO₄)⁺ 358.1050, found 358.1056.



Ethyl-(*E***)-2-(((benzyloxy)carbonyl)imino)-4-(4-fluorophenyl)but-3-ynoate (1c):** White solid, 1.2 g, 73% yield, ¹H NMR (400 MHz, CDCl₃) δ 7.46 – 7.37 (m, 2H), 7.34 – 7.26 (m, 5H), 7.07 – 6.98 (m, 2H), 5.34 (s, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.3 (d, *J* = 254.5 Hz), 161.2, 160.8, 146.0, 135.5 (d, *J* = 9.0 Hz), 135.1, 128.8, 128.7, 116.2 (d, *J* = 22.4 Hz), 115.8, 101.6, 81.1, 69.0, 63.6, 14.1; HRMS (ESI) m/z: [M + Na]⁺ calcd for (C₂₀H₁₆FNNaO₄)⁺ 376.0956, found 376.0963.



Ethyl-(*E***)-2-(((benzyloxy)carbonyl)imino)-4-(4-chlorophenyl)but-3-ynoate (1d):** White solid, 0.9 g, 70% yield, ¹H NMR (400 MHz, CDCl₃) δ 7.44 – 7.39 (m, 2H), 7.34 – 7.27 (m, 5H), 7.24 – 7.15 (m, 2H), 5.34 (s, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H).; ¹³C NMR (100 MHz, CDCl₃) δ 161.1, 160.8, 145.9, 137.7, 135.0, 134.3, 129.1, 128.8, 128.7, 118.0, 101.2, 81.8, 69.0, 63.6, 14.1; HRMS (ESI) m/z: [M + Na]⁺ calcd for (C₂₀H₁₆ClNNaO₄)⁺ 392.0660, found 392.0656.



Ethyl-(*E***)-2-(((benzyloxy)carbonyl)imino)-4-(4-bromophenyl)but-3-ynoate (1e): yellow solid, 1.4 g, 74% yield, ¹H NMR (400 MHz, CDCl₃) δ 7.46 (d,** *J* **= 8.0 Hz, 2H), 7.43 – 7.39 (m, 2H), 7.33 – 7.26 (m, 3H), 7.13 (d,** *J* **= 8.0 Hz, 2H), 5.33 (s, 2H), 4.40 (q,** *J* **= 7.1 Hz, 2H), 1.39 (t,** *J* **= 7.1 Hz, 3H), 1.39 (t,** *J* **= 7.1 Hz, 3H), 1.39 (t, J = 7.1**

3H); ¹³C NMR (100 MHz, CDCl₃) δ 161.1, 160.7, 145.9, 135.0, 134.3, 132.1, 128.7, 126.1, 118.5, 101.2, 81.9, 69.0, 63.6, 14.1; HRMS (ESI) m/z: [M + H]⁺ calcd for (C₂₀H₁₇BrNO₄)⁺ 414.0335, found 414.0349.



Ethyl-(*E*)-2-(((benzyloxy)carbonyl)imino)-4-(4-methoxyphenyl)but-3-ynoate(1f): Light yellow liquid, 1.5 g, 67% yield, ¹H NMR (400 MHz, CDCl₃) δ 7.45 – 7.41 (m, 2H), 7.36 – 7.27 (m, 5H), 6.84 (d, *J* = 8.4 Hz, 2H), 5.35 (s, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 1.39 (d, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 162.1, 161.4, 161.1, 146.2, 135.2, 135.2, 128.7, 128.7, 128.5, 114.4, 111.5, 104.1, 81.4, 68.9, 63.4, 55.6, 14.1; HRMS (ESI) m/z: [M + Na]⁺ calcd for (C₂₁H₁₉NNaO₅)⁺ 388.1155, found 388.1160.



Ethyl-(*E***)-2-(((benzyloxy)carbonyl)imino)-4-(p-tolyl)but-3-ynoate (1g):** Light yellow liquid, 1.3 g, 70% yield, ¹H NMR (400 MHz, CDCl₃) δ 7.47 – 7.38 (m, 2H), 7.33 – 7.23 (m, 5H), 7.28 – 7.22 (m, 2H), 7.15 (d, *J* = 7.3 Hz, 2H), 5.35 (s, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 1.40 (d, *J* = 7.1 Hz, 3H).; ¹³C NMR (100 MHz, CDCl₃) δ 161.3, 161.0, 146.2, 142.1, 135.1, 133.2, 129.5, 128.7, 116.6, 103.5, 81.2, 69.0, 63.5, 21.9, 14.1; HRMS (ESI) m/z: [M + Na]⁺ calcd for (C₂₁H₁₉NNaO₄)⁺ 372.1206, found 372.1210.



Ethyl-(*E***)-2-(((benzyloxy)carbonyl)imino)-4-(4-(tert-butyl)phenyl)but-3-ynoate (1h):** White solid, 2 g, 73% yield, ¹H NMR (400 MHz, CDCl₃) δ 7.46 – 7.40 (m, 2H), 7.39 – 7.35 (m, 2H), 7.35 – 7.27 (m, 5H), 5.35 (s, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.40 (d, *J* = 7.1 Hz, 3H), 1.33 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 161.3, 161.0, 155.1, 146.3, 135.1, 133.0, 128.7, 128.7, 128.5, 125.8, 116.6, 103.4, 81.1, 69.0, 63.5, 35.2, 31.2, 31.1, 14.1; HRMS (ESI) m/z: [M + Na]⁺ calcd for (C₂₄H₂₅NNaO₄)⁺ 414.1676, found 414.1682.



Ethyl-(*E*)-2-(((benzyloxy)carbonyl)imino)-4-(2-chlorophenyl)but-3-ynoate (1i): Light yellow liquid, 1.2 g, 65% yield, ¹H NMR (400 MHz, CDCl₃) δ 7.45 – 7.38 (m, 4H), 7.37 – 7.28 (m, 4H),

7.25 – 7.21 (m, 1H), 5.34 (s, 2H), 4.42 (q, J = 7.1 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H).; ¹³C NMR (100 MHz, CDCl₃) δ 161.0, 160.6, 145.8, 137.5, 134.9, 132.3, 129.7, 128.8, 128.7, 126.8, 120.0, 98.4, 85.1, 69.2, 63.6, 14.1; HRMS (ESI) m/z: [M + Na]⁺ calcd for (C₂₀H₁₆ClNNaO₄)⁺ 392.0660, found 392.0656.



Ethyl-(*E*)-2-(((benzyloxy)carbonyl)imino)-4-(naphthalen-1-yl)but-3-ynoate (1j): White solid, 2.1 g, 80% yield, ¹H NMR (400 MHz, CDCl₃) δ 8.30 (d, *J* = 7.6 Hz, 1H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.60 (ddd, *J* = 16.7, 10.9, 3.9 Hz, 3H), 7.51 – 7.31 (m, 4H), 7.26 – 7.21 (m, 2H), 5.40 (s, 2H), 4.48 (q, *J* = 7.1 Hz, 2H), 1.47 (t, *J* = 7.1 Hz, 3H).; ¹³C NMR (100 MHz, CDCl₃) δ 161.5, 160.9, 146.2, 135.0, 133.7, 133.6, 133.1, 132.2, 128.7, 128.0, 127.1, 125.8, 125.2, 117.2, 101.3, 86.0, 69.2, 63.6, 14.2; HRMS (ESI) m/z: [M + Na]⁺ calcd for (C₂₄H₁₉NNaO₄)⁺ 408.1206, found 408.1202.



Ethyl-(*E***)-2-(((benzyloxy)carbonyl)imino)-4-cyclopropylbut-3-ynoate (1k)**: Light yellow liquid, 0.8 g, 76% yield, ¹H NMR (400 MHz, CDCl₃) δ 1H NMR (400 MHz,) δ 7.40 (d, J = 6.9 Hz, 2H), 7.36 – 7.32 (m, 3H), 5.27 (s, 2H), 4.33 (q, J = 6.8 Hz, 2H), 1.36 – 1.32 (m, 4H), 0.97 – 0.92 (m, 2H), 0.82 – 0.72 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 161.4, 161.0, 135.1, 128.8, 128.7, 128.6, 128.5, 128.4, 128.2, 127.6, 110.8, 69.4, 68.8, 68.7, 66.9, 63.3, 45.2, 14.1, 13.9, 10.4, 10.1; HRMS (ESI) m/z: [M + Na]⁺ calcd for (C₁₇H₁₇NNaO₄)⁺ 322.1050, found 322.1055.



Ethyl-(*E*)-2-(((benzyloxy)carbonyl)imino)-4-(triisopropylsilyl)but-3-ynoate (11): Light yellow liquid, 2.3 g, 86% yield, ¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.32 (m, 5H), 5.26 (s, 2H), 4.35 (q, J= 7.1 Hz, 2H), 1.35 (d, J= 7.1 Hz, 3H), 1.08 (s, 21H); ¹³C NMR (100 MHz, CDCl₃) δ 161.0, 160.4, 145.7, 134.7, 128.7, 128.7, 109.0, 96.7, 69.2, 63.4, 18.5, 14.0, 11.0; HRMS (ESI) m/z: [M + Na]⁺ calcd for (C₂₃H₃₃NNaO₄Si)⁺ 438.2071, found 438.2064.

Cbz CO₂Me 1m

Light yellow liquid, 1.1 g, 70% yield, ¹H NMR (400 MHz, CDCl₃) δ 7.46 – 7.40 (m, 3H), 7.38 – 7.33 (m, 4H), 7.30 (s, 3H), 5.36 (s, 2H), 3.96 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 161.3, 161.1, 145.8, 135.0, 133.1, 131.3, 128.7, 128.7, 120.5, 119.6, 102.8, 81.1, 69.0, 54.0; HRMS (ESI-TOF) m/z: [M + Na]⁺ calcd for (C₁₉H₁₅NNaO₄)⁺ 344.0893, found 344.0899.

Light yellow liquid , 1.6g, 79% yield, ¹H NMR (400 MHz, CDCl₃) δ 7.45 – 7.40 (m, 3H), 7.37 – 7.33 (m, 4H), 7.32 – 7.27 (m, 3H), 5.35 (s, 2H), 5.27 – 5.18 (m, 1H), 1.39 (d, *J* = 6.2 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 161.1, 159.9, 146.2, 134.9, 133.1, 130.9, 128.7, 119.6, 102.3, 80.9, 71.4, 68.4, 21.7; HRMS (ESI-TOF) m/z: [M + Na]+ calcd for (C₂₁H₁₉NNaO₄)⁺ 372.1206, found 372.1215.



Light yellow liquid, 0.7g, 68% yield, ¹H NMR (400 MHz, CDCl₃) δ 7.49 – 7.37 (m, 4H), 7.36 – 7.26 (m, 6H), 5.33 (s, 2H), 1.56 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 161.5, 160.1, 147.4, 135.1, 133.8, 133.0, 131.1, 128.9, 128.7, 128.7, 119.8, 102.1, 84.8, 81.4, 80.5, 68.9, 53.6, 27.9; HRMS (ESI-TOF) m/z: [M + Na]⁺ calcd for (C₂₂H₂₁NNaO₄)⁺ 386.1363, found 386.1370.

Preparation of Preparation of nitroisoxazole 2

These substrates were prepared according to literature procedure.^[4] All of the nitroisoxazole substrates employed in the current study are known compounds.

References:

- (a) I. Mizota, Y. Matsuda, S. Kamimura, H. Tanaka and M. Shimizu, *Org. Lett.*, **2013**, *15*, 4206;
 (b) M. Guo, D. Li and Z. Zhang, *J. Org. Chem.*, **2003**, *68*, 10172.
- (a) M. Hatano, H. Okamoto, T. Kawakami, K. Toh, H. Nakatsuji, A. Sakakura, and K. Ishihara, *Chem Sci.* 2018, *9*, 6361; (b) J. X. Yang, Z. Wang, Z. Y He, G. F. Li, L. Hong, W. S. Sun, and R. Wang, *Angew.Chem. Int.Ed.* 2020, *59*,642; (c) K. Ogura, T. Takehara, T. Suzuki, S. Nakamura, *Adv. Synth. Catal.* 2021, *363*, 4544.
- 3. B. M. Trost, C.-I. J. Hung, M. J. Scharf, Angew. Chem. Int. Ed. 2018, 57, 11408
- 4. X. Xia, Q. Zhu, J. Wang, J. Chen, W. Cao, B. Zhu, X. Wu, J. Org. Chem. 2018, 83, 14617

¹H NMR, ¹³C NMR and HPLC spectra of isolated compounds



f1 (ppm)





IDA OI	DR CHT 20-Hill				
Peak#	Ret. Time	Height	Area	Area%	
1	6.254	351671	4488186	49.711	
2	7.694	251721	4540355	50.289	
Total		603392	9028541	100.000	



PDA Ch	PDA Chi 254nm					
Peak#	Ret. Time	Height	Area	Area%		
1	6.361	1305918	14927206	19.569		
2	7.706	2761163	61354573	80.431		
Total		4067081	76281779	100.000		







Peak#	Ret. Time	Height	Area	Area%
1	20.764	92538	3710297	53.266
2	23.470	22797	3255315	46.734
Total		115334	6965612	100.000



FDA CI	DA CITI 254IIII				
Peak#	Ret. Time	Height	Area	Area%	
1	20.471	10038	384636	1.473	
2	22.353	229062	25724569	98.527	
Total		239099	26109205	100.000	







Peak#	Ret. Time	Height	Area	Area%	
1	26.093	13805	904714	49.830	
2	42.689	10565	910904	50.170	
Total		24370	1815617	100.000	



PDA Ch1 254nm					
Peak#	Ret. Time	Height	Area	Area%	
1	25.674	132408	8615887	97.869	
2	42.365	1884	187618	2.131	
Total		134292	8803505	100.000	







Peak#	Ret. Time	Height	Area	Area%
1	29.849	193817	10498686	49.364
2	36.210	176107	10769201	50.636
Total		369924	21267887	100.000



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Peak#	Ret. Time	Height	Area		
1	29.594	136111	7352629		
2	36.241	18443	1123352		
Total		154555	8475981		

Area% 86.747 13.253 100.000







<Peak table>
PDA Ch1 254nm
Pack#UBat Time

	Peak#	Ret. Time	Height	Area	Area%
	1	31.994	73159	4212877	49.897
	2	39.238	64145	4230330	50.103
	Total		137303	8443207	100.000
L	Total	l	101000	0110201	100.00



PDA Ch	PDA Ch1 254nm					
Peak#	Ret. Time	Height	Area	Area%		
1	31.696	134263	7863810	87.000		
2	38.941	17866	1175093	13.000		
Total		152129	9038904	100.000		





Peak#	Ret. Time	Height	Area	Area%
1	24.973	44337	1959135	50.029
2	30.000	39314	1956882	49.971
Total		83652	3916017	100.000



PDA Ch1 254nm					
Peak# Ret. Time		Height	Area	Area%	
1	24.806	122443	5501662	84. 521	
2	29.869	20351	1007574	15.479	
Total		142795	6509235	100.000	





Peak#	Ret. Time	Height	Area	Area%
1	26. 292	8158	385988	49.822
2	28.858	8245	388740	50.178
Total		16403	774728	100.000



Peak#	Ret. Time	Height	Area	Area%
1	26.098	26499	1281726	87.326
2	28.687	3867	186022	12.674
Total		30365	1467748	100.000





0-20 30 40 10 Ó

50 min

<Peak table> PDA Ch1 254nm
 PbA cfil 20mm

 Peak# Ret. Time

 1
 41.064

 2
 46.787
 Height Area% Area 89.292 10.708 12179693 146194 19261 1460576 13640270 100.000 Total 165455







Peak#	Ret. Time	Height	Area	Area%
1	29.001	183837	9634658	49.927
2	35.058	168512	9662693	50.073
Total		352349	19297351	100.000



PDA Ch1 254nm					
Peak#	Ret. Time	Height	Area	Area%	
1	28.175	719152	39389245	90.658	
2	34.317	71351	4059005	9.342	
Total		790503	43448250	100.000	







Peak#	Ret. Time	Height	Area	Area%
1	25.585	12921	949904	49.595
2	41.739	11332	965416	50.405
Total		24254	1915320	100.000



PDA Ch1 254nm					
Peak#	Ret. Time	Height	Area	Area%	
1	25.073	78177	5514603	84.848	
2	41.061	11277	984810	15.152	
Total		89454	6499413	100.000	







PDA Ch	DA CHI 254HM					
Peak#	Ret. Time	Height	Area	Area%		
1	26.795	146222	11061848	82.974		
2	55.371	19583	2269885	17.026		
Total		165805	13331733	100.000		





Peak#	Ret. Time	ime Height	Area	Area%	
1	42.168	155689	11757966	85.392	
2	48.335	24555	2011415	14.608	
Total		180244	13769381	100.000	







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PDA Ch1 254nm					
Peak#	Ret. Time	Height	Area	Area%	
1	25.115	92712	3999205	49.981	
2	33.483	70755	4002208	50.019	
Total		163468	8001413	100.000	



1	PDA Ch	1 254nm			
	Peak#	Ret. Time	Height	Area	Area%
	1	24.983	308748	12700586	94.744
	2	33.458	13631	704609	5.256
	Total		322378	13405194	100.000







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PDA (Ch1	254_{1}	nm	
Deels	# D.	*	т.;	~

Peak#	Ret. Time	Height	Area	Area%
1	26.804	63902	3006509	50.025
2	35.937	49484	3003561	49.975
Total		113386	6010070	100.000



Peak#	Ret. Time	Height	Area	Area%
1	26.904	679352	30761042	85.234
2	36. 194	93139	5329081	14.766
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1	28.857	843629	41548996	85.389
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2	56.016	17890	1694976	49.887
Total		43915	3397610	100.000



PDA Ch	1 254nm			
Peak#	Ret. Time	Height	Area	Area%
1	37.921	96699	5938305	95.885
2	55.976	3107	254850	4.115
Total		99806	6193156	100.000







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PDA Ch	1 254nm			
Peak#	Ret. Time	Height	Area	Area%
1	25.179	114616	4656823	50.013
2	30.859	95699	4654384	49.987
Total		210315	9311207	100.000



Peak#	Ret. Time	Height	Area	Area%
1	26.335	222633	11910508	91.503
2	32.195	17384	1106025	8.497
Total		240016	13016533	100.000







Peak#	Ret. Time	Height	Area	Area%
1	18.961	52294	2536744	50.923
2	22.209	44040	2444759	49.077
Total		96334	4981503	100.000



FDA CI	1 20411			
Peak#	Ret. Time	Height	Area	Area%
1	19.314	294401	14001732	87.910
2	22.800	33283	1925664	12.090
Total		327684	15927396	100.000







I DA OL	1 20 mm			
Peak#	Ret. Time	Height	Area	Area%
1	28.427	186069	10608470	50.078
2	33. 330	162563	10575578	49.922
Total		348632	21184048	100.000



PDA Ch	PDA Ch1 254nm				
Peak#	Ret. Time	Height	Area	Area%	
1	28.416	328332	19077195	81.002	
2	33.465	68428	4474346	18.998	
Total		396761	23551541	100.000	





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		0 = 4
PUA	L n l	2 54 nm
1 0 11	UIII.	201111

PDA CHI 254hm					
Peak#	Ret. Time	Height	Area	Area%	
1	46.936	22395	2283253	50.286	
2	55.166	17657	2257256	49.714	
Total		40052	4540508	100.000	



PDA Ch	1 254nm			
Peak#	Ret. Time	Height	Area	Area%
1	47.282	2619	253730	15.089
2	55.086	11132	1427843	84.911
Total		13751	1681573	100.000









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PDA Ch1 254nm					
Height	Area	Area%			
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36671	1519189	47.612			
81993	3190793	100.000			
	Height 45322 36671 81993	Height Area 45322 1671604 36671 1519189 81993 3190793			



PDA Ch	PDA Ch1 254nm					
Peak#	Ret. Time	Height	Area	Area%		
1	19.422	201966	7721636	86.605		
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PDA Ch	1 254nm			
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1	7.252	316464	4703503	49.999
2	8.338	272844	4703708	50.001
Total		589307	9407211	100.000



PDA Ch	1 254nm			
Peak#	Ret. Time	Height	Area	Area%
1	7.196	219243	3334428	85.912
2	8.306	31230	546791	14.088
Total		250473	3881219	100.000







Peak#	Ret. Time	Height	Area	Area%
1	24. 991	68034	3964778	49.708
2	30. 377	59459	4011402	50.292
Total		127494	7976180	100.000



PDA CHI 254HM					
Peak#	Ret. Time	Height	Area	Area%	
1	24.944	426702	24963984	85.487	
2	30.469	62512	4238173	14.513	
Total		489215	29202158	100.000	







i Dii Oli						
Peak#	Ret. Time	Height	Area	Area%		
1	43.903	15095	1488388	49.249		
2	54.905	15861	1533801	50.751		
Total		30957	3022189	100.000		



PDA Chi 254nm					
Peak#	Ret. Time	Height	Area	Area%	
1	43. 582	110173	10445294	86.092	
2	54.901	17645	1687474	13.908	
Total		127819	12132768	100.000	







Peak#	Ret. Time	Height	Area	Area%
1	21.385	43835	2331217	49.761
2	26.000	39572	2353641	50.239
Total		83408	4684858	100.000



PDA CI	1 234mm			
Peak#	Ret. Time	Height	Area	Area%
1	21.121	423504	21942707	86.484
2	26.018	56457	3429321	13.516
Total		479961	25372028	100.000







Peak#	Ret. Time	Height	Area	Area%
1	30.186	115858	8442854	48.945
2	38. 512	100324	8806763	51.055
Total		216182	17249617	100.000



PDA CI	DA CHI 254hili					
Peak#	Ret. Time	Height	Area	Area%		
1	29.973	61778	4701722	82.130		
2	38.383	11644	1022995	17.870		
Total		73422	5724717	100.000		
Total		13444	0724717	100.000		







Peak#	Ret. Time	Height	Area	Area%
1	8.662	125038	4896151	51.968
2	10.959	77334	4525348	48.032
Total		202373	9421499	100.000



PDA Ch1 254nm					
Peak#	Ret. Time	Height	Area	Area%	
1	8. 999	77597	2886112	16.845	
2	11.633	248346	14246829	83.155	
Total		325943	17132942	100.000	







Peak#	Ret. Time	Height	Area	Area%
1	38.101	26106	2271682	49.999
2	44. 405	23495	2271753	50.001
Total		49601	4543435	100.000



IDA OI					
Peak#	Ret. Time	Height	Area	Area%	
1	37.569	50930	4418331	86.364	
2	44.140	7333	697602	13.636	
Total		58263	5115933	100.000	









<Peak table> PDA Ch1 254nm

Peak#	Ret. Time	Height	Area	Area%
1	9.243	33320	618324	50.030
2	10.196	31720	617572	49.970
Total		65040	1235895	100.000



ł	PDA CHI 254hili				
	Peak#	Ret. Time	Height	Area	Area%
	1	9.207	646697	12396592	87.631
	2	10.181	86501	1749697	12.369
	Total		733198	14146289	100.000







Peak#	Ret. Time	Height	Area	Area%
1	9.630	3964133	89750260	49.369
2	11.091	3641473	92045428	50.631
Total		7605606	181795688	100.000



FDA CI	-DA CITI 254IIII					
Peak#	Ret. Time	Height	Area	Area%		
1	9.740	970245	19084562	87.555		
2	11.310	125987	2712659	12.445		
Total		1096232	21797221	100.000		







PDA Ch1 254nm

Peak#	Ret. Time	Height	Area	Area%
1	12.020	2641783	59485338	50.493
2	14.532	1978158	58322633	49.507
Total		4619941	117807972	100.000



PDA CHI 254HIII				
Peak#	Ret. Time	Height	Area	Area%
1	11.949	2170280	52798384	87.621
2	14.600	265207	7459140	12.379
Total		2435487	60257524	100.000







<Peak table> PDA Ch1 254nm

Peak#	Ret. Time	Height	Area	Area%
1	29.535	78922	3986040	50.395
2	36.699	64184	3923582	49.605
tota	1	143106	7909622	100.000



Peak#	Ret. Time	Height	Area	Area%
1	29.424	347178	18427080	84.365
2	36.690	54115	3414941	15. 635
tota	1	401293	21842021	100.000





<Peak table> PDA Ch1 254nm

PDA Chi 254nm				
Peak#	Ret. Time	Height	Area	Area%
1	14.136	330757	8977411	50.453
2	16.132	132241	8816367	49.547
tota	1	462998	17793778	100.000



PDA Ch1 254nm				
Peak#	Ret. Time	Height	Area	Area%
1	14.174	166183	4450173	17.484
2	15.952	355186	21002547	82.516
tota	1	521369	25452720	100.000






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PDA	Ch1	254nm

Peak#	Ret. Time	Height	Area	Area%
1	23.917	50565	2402672	53.415
2	27.457	19757	2095459	46.585
tota	1	70322	4498131	100.000



<Peak table>

PDA Chl 254nm						
Peak#	Ret. Time	Height	Area	Area%		
1	23.906	33801	1587956	14.158		
2	26.866	102119	9628281	85.842		
tota	1	135920	11216237	100.000		









<Peak table> PDA Ch1 254nm

Peak#	Ret. Time	Height	Area	Area%
1	22.820	60116	2333860	50.295
2	27.753	49770	2306443	49.705
Total		109886	4640302	100.000



<Peak table> PDA Ch1 254nm

PDA Chi 254nm					
Peak#	Ret. Time	Height	Area	Area%	
1	22.780	151904	5979825	98.538	
2	27.757	2063	88695	1.462	
Total		153967	6068521	100.000	





PDA Chi 254hm					
Peak#	Ret. Time	Height	Area	Area%	
1	33. 491	33497	1830468	49.980	
2	36.054	31301	1831902	50.020	
Total		64798	3662370	100.000	



<Peak table> PDA Ch1 254nm

Peak#	Ret. Time	Height	Area	Area%
1	33.369	89374	4983095	84.080
2	35.983	15835	943508	15.920
Total		105209	5926603	100.000





¹H NMR, ¹³C NMR spectra of β,γ-Alkynyl-α-ketimino Esters































Cbz~NH CO2Me

Ő 'n= -NO₂

Ph

-3.96



