N-Iodosuccinimide: A Highly Effective Regioselective Reagent for Iodoesterification of Alkenes

by **Aleti R. Reddy**[a]), **Payare L. Sangwan***[a]), **Praveen K. Chinthakindi**[a]), **Saleem Farooq**[a]), **Vidavalur Siddaiah**[b]), and **Surrinder Koul***[a])

[a]) Bioorganic Chemistry Division, CSIR-Indian Institute of Integrative Medicine, Canal Road, Jammu Tawi 180 001, India (phone: +91-191-2569021 (direct), EPABX +91-191-2569000-09 ext. 371, 236, 210; fax: +91-191-2569333; e-mail: skoul@iiim.ac.in, plsangwan@iiim.ac.in)

[b]) Department of Organic Chemistry, Food, Drugs and Water, Andhra University, Visakhapatnam 530 003, India

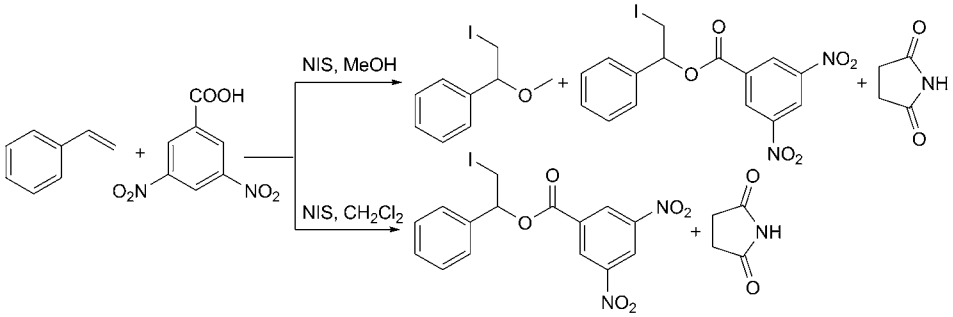
A rapid, convenient, and efficient method has been achieved for regioselective iodoesterification of alkenes with aliphatic and aromatic acids, and protected amino acids in the presence of *N*-iodosuccinimide (NIS) in nearly quantitative yields. Optically enriched iodohydrins have been achieved by $LiAlH_4$ (LAH) reduction of diastereoisomeric iodo esters.

Introduction. – Stereo- and regioselective 1,2 additions across alkene C=C bonds constitute an important area of research in organic chemistry [1], and there are several methodologies available in the literature. These include the formation of vicinal halohydrins [2], halo ethers [3], through transition metal-catalyzed addition of an O-nucleophile- halogen atom to the alkenes, regioselective bromofluorination of alkenes [4], and other methods [5][6]. *N*-Iodosuccinimide (NIS) like NBS [7] is one of the versatile reagents used for regioselective vicinal halohydrin [8], haloether [9], and halosulfonate [10] formation from alkenes. Many other applications of NIS include the direct iodination of aromatic rings [11], iodination of OH group [12], and activation of thioglycosides in glycosylation [13]. The use of NIS for the preparation of iodo esters from alkenes is very limited, as there are only few reports are available in the literature [14–17]. Regarding the importance of functionalization of alkenes, especially haloesterification due to their applications in various important transformations [8–10], a detailed study of NIS-mediated iodoesterification of different alkenes and acids is highly desired.

In this direction, an attempt has been made to carry out a detailed study of the application of NIS for a broad spectrum of iodoesterification of styrene and aliphatic alkenes with aliphatic and aromatic acids, and protected amino acids. The methodology is advantageous, as the products are obtained in high yields, and the reaction by-product (succinimide) is easily convertible to NIS [18]. The β-iodo ester products are important, as these can be transformed to other functional groups [19], including optically active β-iodohydrins (through biocatalytic [20] or other approaches); the latter are important moieties for the preparation of bioactive molecules [21–23].

Results and Discussion. – For iodoesterification, a reaction of styrene with 3,5-dinitrobenzoic acid (DNBA; 1 equiv.) was carried out in MeOH in the presence of NIS (1.2 equiv.), and a mixture of β-iodo ester and iodo ether in a 70 : 30 ratio was obtained (*Scheme 1*). The formation of iodo ether is attributed due to the participation of the solvent (MeOH) [9]. Since the reaction in MeOH afforded iodo ether as by-product, use of other solvents was also attempted. With the same reactants, a panel of seven solvents *viz.* THF, DME, $CHCl_3$, CH_2Cl_2, toluene, DMF, and H_2O were tried, and the reactions were carried out at 20–22°.

Scheme 1. *Synthesis of β-Iodo Esters and Iodo Ethers from Alkenes*



The reaction in H_2O resulted in the formation of iodohydrin as the second major reaction product (> 30% yield). Best results in terms of high yield (> 95%), single-product formation, and minimum reaction time were achieved with CH_2Cl_2 as the solvent. When the reaction of styrene (1 equiv.), DNBA acid (1 equiv.), and NIS (1.2 equiv.) in CH_2Cl_2 was run at low temperature (0–2°), products in lower yields (78%) were obtained. The reactions at elevated temperatures (> 40°) afforded complex mixtures, and very low yields of the products were obtained. With other solvents, longer reaction times (1–2 h) and low yields were observed (*Table 1*). The results of this study are compiled in *Table 1*.

Table 1. *Effects of Different Solvents on the Reaction of Styrene with 3,5-Dinitrobenzoic Acid in the Presence of NIS*

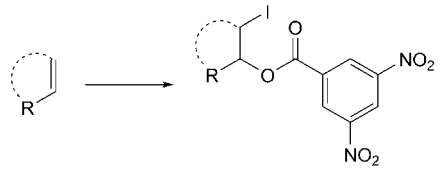
Entry	Solvent	Time [h]	Temp. [°]	Conversion [%]	Yield[a]) [%]
1	H_2O	5	20–22	99	42[b])
2	MeOH	2	20–22	99	61
3	DME	4	20–22	86	86
4	MeCN	1	20–22	81	81
5	$CHCl_3$	1	20–22	90	90
6	CH_2Cl_2	0.25	20–22	99	99
7	CH_2Cl_2	1	0–2	78	78
8	CH_2Cl_2	0.5	> 40	92	65
9	DMF	4	20–22	48	48
10	THF	3	20–22	54	54

[a]) Yield of isolated racemic ester formed from styrene (1 equiv.), 3,5-dinitrobenzoic acid (1 equiv.), and NIS (1.2 equiv.). [b]) Mixture of iodo ester and iodohydrin (70 : 30).

The regioselective iodoesterification methodology was further extended to other alkenes (*Table 2*, *Entries 2–9*) to evaluate the feasibility of the reaction. Thus, cyclic alkenes such as 1,2-dihydronaphthalene, cyclohexene, dihydropyran (*Entries 3*, *4*, and *6*, resp.) when subjected to reaction with DNBA and NIS in CH_2Cl_2 at 20–22°, afforded *s-trans*-esters in excellent yields (92–99%), without the formation of any other regioisomer. However, the reactions with *n*-alkenes such as hex-1-ene (**8**) and oct-1-ene (**9**) gave mixtures of two products (*Entries 8* and *9*). Substrate **8** furnished **8a** as major product (74%) and **8b** as the minor compound (24%). Substrate **9** furnished **9a** and **9b** in an 80:16 ratio. The compounds were characterized by spectral analyses.

The products obtained in most of the cases were fairly pure and did not require any further purification. Interestingly, in all the reactions, the completion of the reaction was marked by the appearance of a pink color from colorless at the start of the reaction. The haloesterification also worked well for tri-*O*-acetyl-D-glucal (*Table 2*, *Entry 7*) with formation of a mixture of diastereoisomers (96:4, based on NMR) in excellent yield. The products, 2-deoxy-2-iodo-glucopyranosyl-type esters, are used as glucosyl donors in carbohydrate chemistry [24].

Table 2. *Regioselective Iodoesterfication of Alkenes with 3,5-Dinitrobenzoic Acid in the Presence of NIS*[a])



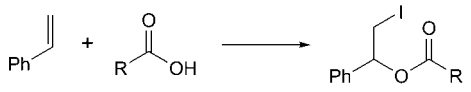
1 – 9 **1a – 9a**

Entry	Reactant	Product	Yield[b]) [%]
1	Styrene (**1**)	**1a**	99
2	1*H*-Indene (**2**)	**2a**	98
3	1,2-Dihydronaphthalene (**3**)	**3a**	96
4	Cyclohexene (**4**)	**4a**	97
5	Cyclopentene (**5**)	**5a**	94
6	3,4-Dihydro-2*H*-pyran (**6**)	**6a**	99
7	(2*R*,3*S*,4*R*)-2-[(Acetyloxy)methyl]-3,4-dihydro-2*H*-pyran-3,4-diyl diacetate (**7**)	**7a**	92[c])
8	Hex-1-ene (**8**)	1-(Iodomethyl)pentyl 3,5-dinitrobenzoate (**8a**)	74
		2-Iodohexyl 3,5-dinitrobenzoate (**8b**)	(24)[d])
9	Oct-1-ene (**9**)	1-(Iodomethyl)hepthyl 3,5-dinitrobenzoate (**9a**)	80
		2-Iodooctyl 3,5-dinitrobenzoate (**9b**)	(16)[d])

[a]) Temp., 20–22°, time, 25–30 min; CH_2Cl_2 as solvent. [b]) Yields of isolated products. All compounds are racemic. [c]) The major optically active product. [d]) Yields of minor regioisomer given in paranthesis.

The methodology was further extended to other acids, and involved the reaction of styrene with different aromatic and aliphatic acids in the presence of NIS, and all the reactions proceeded very well and were complete in *ca.* 15 min to afford the desired products (single product in each case) in 94–99% yields (*Table 3*).

Table 3. *Regioselective Esterification of Styrene with Aromatic and Aliphatic Acids*



10 – 23 **10a – 23a**

Entry	R	Product	Yield[a]) [%]
10	Ph	**10a**	98
11	4-F–C_6H_4	**11a**	96
12	2-HO–C_6H_4	**12a**	95
13	3,4,5-$(AcO)_3$–C_6H_2	**13a**	94
14	Pyridin-4-yl	**14a**	96
15	4-AcS–C_6H_4	**15a**	96
16	2-AcNH–C_6H_4	**16a**	99
17	H	**17a**	97
18	$PhCH_2$	**18a**	99
19	(1*R*)-1-Bromoethyl	**19a**	99[b])
20	(1*S*)-1-(6-Methoxynaphthalen-2-yl)ethyl	**20a**	94[c])
21	$AcO(Ph)_2C$	**21a**	99
22	(*R*)-Hydroxy(phenyl)methyl	**22a**	98[d])
23	Cyclopropyl	**23a**	98

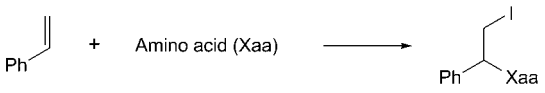
[a]) Yield of isolated products. Reactions performed in the presence of styrene (1 equiv.), acids (1 equiv.), NIS (1.2 equiv.), and CH_2Cl_2 (3 ml); time, 15 min; temp., 20–22°. [b]) Diastereoisomer mixture (55 : 45). [c]) Diastereoisomer mixture (53 : 47). [d]) Diastereoisomer mixture 55 : 45.

With optically active (*R*)-2-bromopropanoic acid (*Entry 19*), diastereoselectivity of the reaction was poor, and two diastereoisomers in a 55 : 45 ratio were obtained. The mixture could not be separated by usual column chromatography or by preparative thin layer chromatography. However, the isomers were resolved by HPLC using *Chiralcel ADH* chiral column. The reaction of (*S*)-naproxen (=(+)-(*S*)-2-(6-methoxynaphthalen-2-yl)propanoic acid) also afforded a mixture of diastereoisomers (53 : 47). The feasibility of the reaction, when tested with acids bearing additional functional groups in the form of OH, SH, and an NH_2 group such as gallic acid, 4-sulfanylbenzoic acid, and anthranilic acid, did not prove successful and no reaction product was obtained. When 2-hydroxy-2,2-diphenylacetic acid, salicylic acid, and (*R*)-mandelic acid (*Entries 21* (deacetylated), *12*, and *22*, resp.), were reacted with styrene, the reactions were successful with salicylic acid (a single product **12a**; *Entry 12*) and mandelic acid (product **23a**, as a mixture of diastereoisomers, dr 55 : 45; *Entry 23*; based on ^{1}H-NMR) in high yields. The reaction failed with 2-hydroxy-2,2-diphenylacetic acid, possibly due to the absence of H-bond formation between OH with COOH. These results indicated the possible deterrent effects of the free OH, SH, or NH_2 groups on the reaction, as the

reactions of the *O*-, *N*-, and *S*-protected derivatives (including substrate **21**) with the alkenes resulted in successful formation of the desired products in high yields (*Entries 13*, *15*, *16*, and *21*).

It was also attempted to carry out the reaction of styrene with α-amino acids, but *N*-unprotected amino acids (*Table 4*, *Entries 29* and *30*) failed to afford any product for the same reasons as mentioned above for unprotected acids. However, *N*-protected amino acids such as *N*-Boc- or *N*-Fmoc-glycine, gave exclusively single products (established by spectral studies) in $>97\%$ yields (*Entries 24–28*). Reaction of *N*-protected amino acids such as (*S*)-phenylalanine, (*S*)-leucine, and (*S*)-proline with styrene resulted to afford, in poor diastereoselectivity, mixtures of two diastereoisomers in $>97\%$ yields with best de value of 26% (dr 63:37) observed for (*S*)-*N*-Boc-phenylalanine. This mixture was separated on neutral alumina column by using 4% CH_2Cl_2 in toluene as eluent and also resolved on chiral HPLC (*ADH* chiral column; flow rate, 0.8 ml/min; mobile phase, 20% ^{i}PrOH in hexane, at 254-nm wavelength; UV detector; *Fig.*, *a–c*). Attempts to deprotect with commercial lipases and esterases (through hydrolysis of the ester bond) were unsuccessful. Therefore, the deprotection of the amino acid diastereoisomers was carried out with $LiAlH_4$ (LAH) (*Scheme 2*) [25]. With LAH, the major isomer (t_R 12.38 min; *Fig.*, *b*) afforded iodohydrin $[\alpha]_D = -35.2$ ($c = 1$, $CHCl_3$), which is similar to that reported in [26] (-36.3 ($c = 1$, $CHCl_3$)) with (*R*)-configuration and optical purity of $>96\%$ (confirmed by HPLC using *ODH* chiral column; flow rate, 1 ml/min; mobile phase 10% i-PrOH in hexane; at 254-nm wavelength; UV detector). The minor product (*Fig.*, *c*) of hydrolysis gave halohydrin with (*S*)-configuration with an optical purity of $>94\%$. The reduction product *N*-Boc amino alcohol had a optical purity of $>98\%$ (ee determined based on comparison of $[\alpha]_D$ with the literature value ($[\alpha]_D = 26.20$) [27]. The by-product, a protected amino alcohol, is a very useful chiral synthon used in peptide chemistry. The results of the above experiments are compiled in *Table 4*.

Table 4. *Regioselective Iodoesterification of Styrene with Protected Amino Acids*



24 – 30 **24a – 30a**

Entry	Reactant	Product	Yield[a]) [%]
24	Boc-Gly-OH	**24a**	98
25	Fmoc-Gly-OH	**25a**	97
26	Fmoc-Leu-OH	**26a** (dr $\geq$ 53:47)	99
27	Boc-Phe-OH	**27a** (dr $\geq$ 63:37)	99
28	Boc-Pro-OH	**28a** (dr $\geq$ 54:46)	97
29	Fmoc-Tyr-OH	No reaction	–
30	Fmoc-Lys-OH	No reaction	–

[a]) Yield of isolated Product. Reaction in the presence of styrene (1 equiv.), *N*-protected amino acids (1 equiv.), NIS (1.2 equiv.), and CH_2Cl_2 (3 ml); time, 15 min; temp., 20–22°.

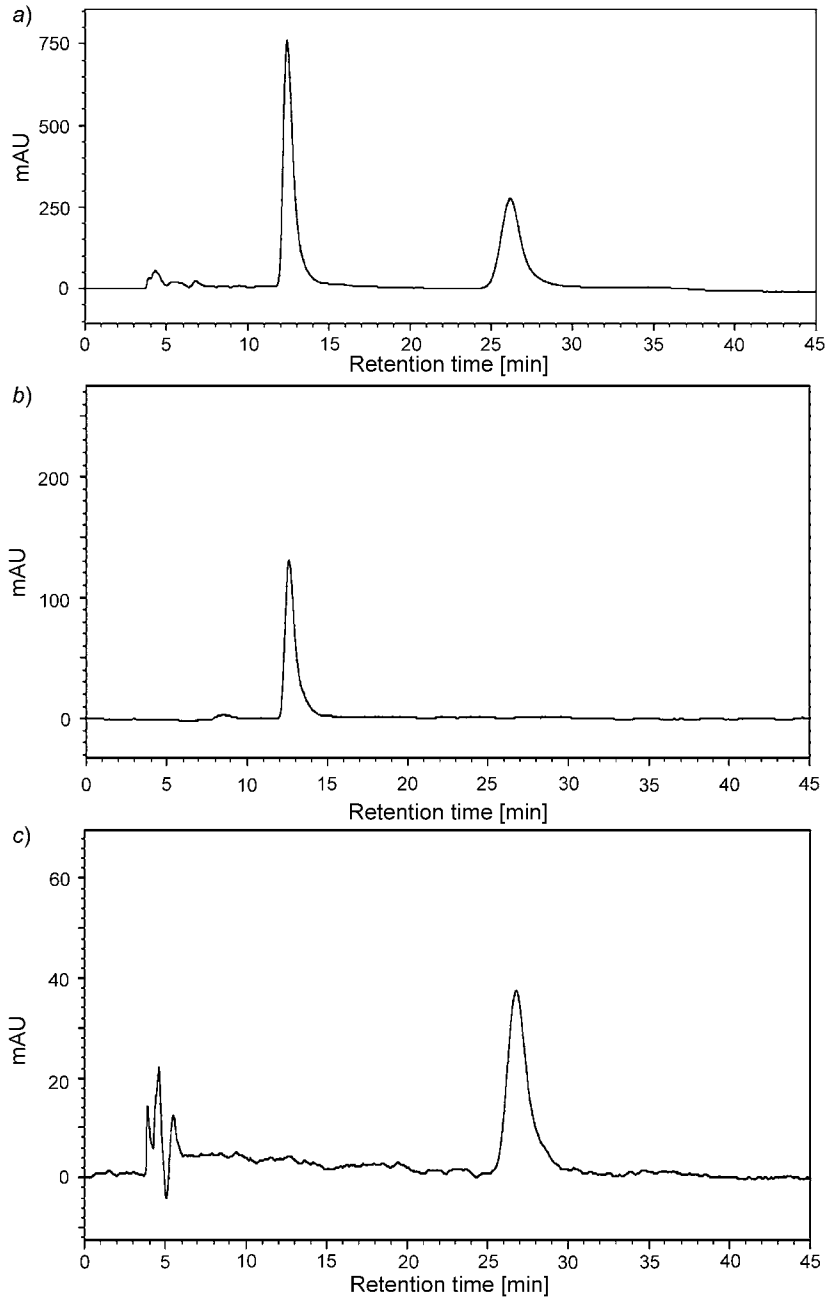
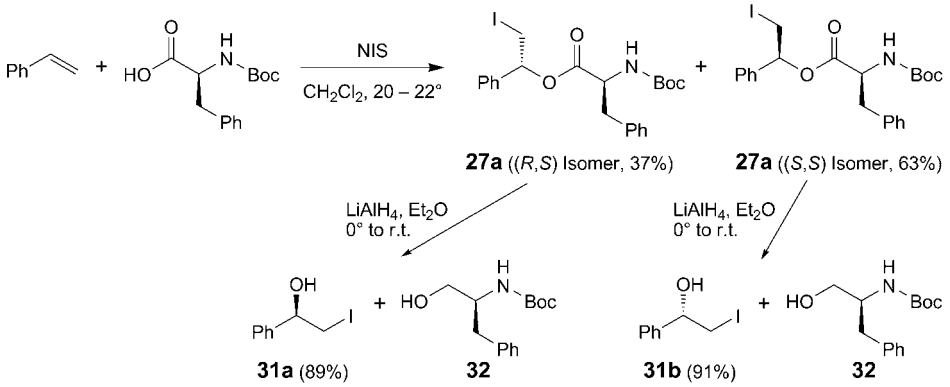


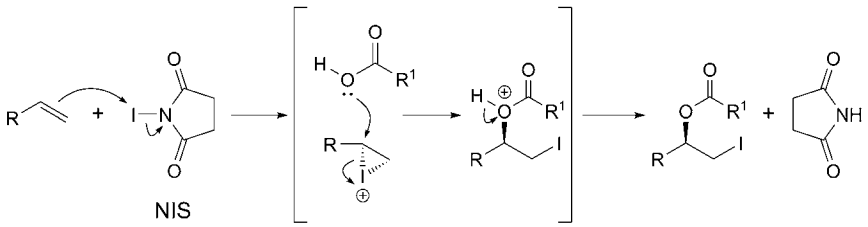
Fig. 1. *Resolution of diastereoisomers by chiral HPLC. a*) Reaction product **27a** ((*R*,*S*),(*S*,*S*)-isomer), *b*) Compound **27a** ((*S*,*S*)-isomer), and *c*) Compound **27a** ((*R*,*S*)-isomer).

Scheme 2. *Optical Purity and Absolute Configuration of Iodo Esters through Resolution of Diastereoisomers*



For the regioselective iodoesterification of alkenes, a plausible mechanism has been proposed in *Scheme 3*. The mechanism involves the iodonium intermediate formation facilitated by NIS, followed by the attack of the acid to form unstable oxonium intermediate, which is rearranged to give the desired product, namely s-*trans*-iodo ester.

Scheme 3. *Proposed Reaction Mechanism*



Conclusions. – In summary, an efficient methodology has been developed for the regioselective iodoesterification of several alkenes using different acids including aliphatic and aromatic acids, and protected amino acids, bearing functional groups, such as SH, OH, NH, in presence of *N*-iodosuccinimide as catalyst. The method offers the advantage of easy handling of the reactants and products, short reaction times, high yields, good regioselectivities, and least formation of other regioisomers.

Experimental Part

General. All reagents were purchased from *Sigma-Aldrich*, India and used without further purification. All the solvents used in reactions were distilled and dried prior to use. All reactions were monitored by TLC on 0.25-mm silica-gel *60* F_{254} plates coated on alumina sheet (*E. Merck*). Enantiomeric excess (ee [%]) was determined by using chiral HPLC on *ODH* chiral columns. M.p.: *Büchi B-542* apparatus by an open-capillary method; uncorrected. Optical rotations: *Perkin-Elmer 241*

polarimeter at 25° using sodium D light. IR Spectra: *Perkin-Elmer* FT-IR spectrometer, as KBr pellet or neat sample. ^{1}H- and ^{13}C-NMR spectra: *Bruker Avance* instruments at 200, 400, and 500 MHz using $CDCl_3$ as solvent with TMS as internal standard. MS: *Jeol MSD-300* instrument. Elemental analysis: *Elementar Vario EL-III*.

General Procedures for Iodoesterification of Alkenes. All the iodo esters, **1a**–**28a**, were prepared by the addition of *N*-iodosuccinimide (NIS; 1.2 mmol) to a CH_2Cl_2 soln. (3 ml) of an alkene (1 mmol) and an acid (1 mmol) at 20–22°, and the mixture was stirred for 15 min. After the completion of the reaction (monitored by TLC), the mixture was worked up by adding 10% $Na_2S_2O_3$ (5 ml), H_2O (10 ml), and CH_2Cl_2 (10 ml). The org. layer was separated, and the aq. phase was extracted with CH_2Cl_2 (10 ml), and the extraction process was repeated twice. The combined org. layers were dried (Na_2SO_4), and the solvent was evaporated. The product obtained was subjected to CC wherever required using 60–120 SiO_2 and AcOEt/hexane 1:6 as eluent to furnish products in the overall yields of 92–99%. Physical and spectroscopic data of the synthesized compounds, **1a**–**28a**, are given below.

2-Iodo-1-phenylethyl 3,5-Dinitrobenzoate (**1a**). White solid. M.p. 131.5°. IR (neat): 1725, 1627, 1544, 1460, 1344, 1267, 1160, 1076, 999, 921, 811. ^{1}H-NMR (200 MHz): 3.59–3.78 (*m*, 2 H); 6.20 (*dd*, *J* = 8.5, 13.5, 1 H); 7.39–7.42 (*m*, 5 H); 9.21 (*s*, 2 H); 9.26 (*s*, 1 H). ^{13}C-NMR (125 MHz): 6.6; 78.0; 122.7; 126.4 (2 CH); 129.0 (2 CH); 129.4; 129.6 (2 CH); 133.4; 137.2; 148.7; 161.4. MS: 442.07 (M^+).

*2,3-Dihydro-2-iodo-1*H*-inden-1-yl 3,5-Dinitrobenzoate* (**2a**). White solid. M.p. 128.3°. IR (neat): 3031, 2924, 1734, 1628, 1543, 1456, 1415, 1344, 1271, 1212, 1076, 1052, 1002, 950, 920, 823, 764, 720, 700. ^{1}H-NMR (200 MHz): 3.44 (*dd*, *J* = 4.3, 17.2, 1 H); 3.90 (*dd*, *J* = 6.7, 17.2, 1 H); 4.70 (*m*, 1 H); 6.73 (*d*, *J* = 3.3, 1 H); 7.32–7.51 (*m*, 4 H); 9.13 (*s*, 2 H); 9.24 (*s*, 1 H). ^{13}C-NMR (125 MHz): 22.8; 43.5; 88.3; 122.7; 125.1; 126.0; 127.9; 129.6 (2 CH); 130.4; 133.3; 137.3; 142.4; 148.7 (2 C); 162.0. MS: 454.98 (M^+).

1,2,3,4-Tetrahydro-2-iodonaphthalen-1-yl 3,5-Dinitrobenzoate (**3a**). White solid. M.p. 155.6°. IR (neat): 1776, 1710, 1627, 1599, 1544, 1490, 1457, 1430, 1344, 1266, 919, 811, 750, 724, 642. ^{1}H-NMR (200 MHz): 2.34 (*m*, 2 H); 3.03 (*m*, 2 H); 4.75 (*m*, 1 H); 6.57 (*d*, *J* = 4.52, 1 H); 7.23–7.35 (*s*, 4 H); 9.13 (*s*, 2 H); 9.23 (*s*, 1 H). ^{13}C-NMR (100 MHz): 26.2; 28.0; 29.1; 77.6; 122.6; 126.9; 129.3; 129.5; 129.6 (2 CH); 130.0; 130.3; 133.6; 136.2; 148.7 (2 C); 161.77. MS: 491.08 ($[M + Na]^+$).

2-Iodocyclohexyl 3,5-Dinitrobenzoate (**4a**). White solid. M.p. 116.4°. IR (neat): 2938, 1731, 1627, 1544, 1456, 1344, 1274, 1168, 1076, 1008, 920, 857, 799, 769, 723. ^{1}H-NMR (200 MHz): 1.43–1.62 (*m*, 4 H); 1.95–2.04 (*m*, 1 H); 2.10–2.28 (*m*, 2 H); 2.55–2.60 (*m*, 1 H); 4.20–4.32 (*m*, 1 H); 5.21–5.23 (*m*, 1 H); 9.20 (*s*, 2 H); 9.25 (*s*, 1 H). ^{13}C-NMR (125 MHz): 23.8, 27.3, 30.5, 32.0, 38.2, 79.8, 122.6, 129.6 (2 CH), 133.9, 148.7 (2 C), 161.5. MS: 443.07 ($[M + Na]^+$).

2-Iodocyclopentyl 3,5-Dinitrobenzoate (**5a**). White solid. M.p. 110.7°. IR (neat): 2921, 1730, 1617, 1544, 1465, 1324, 1244, 1148, 1016, 1009, 910, 857, 790, 769, 713. ^{1}H-NMR (200 MHz): 1.93–2.05 (*m*, 3 H); 2.14–2.21 (*m*, 1 H); 2.39–2.50 (*m*, 2 H); 4.37 (*m*, 1 H); 5.67 (*m*, 1 H); 9.12 (*s*, 2 H); 9.24 (*s*, 1 H). ^{13}C-NMR (100 MHz): 22.7; 26.6; 29.7; 36.5; 86.6; 122.6; 129.4; 133.6 (2 CH); 148.7 (2 C); 161.7. MS: 429.05 ($[M + Na]^+$).

*Tetrahydro-3-iodo-2*H*-pyran-2-yl 3,5-Dinitrobenzoate* (**6a**). White solid. M.p. 122.5°. IR (neat): 2925, 1771, 1627, 1545, 1460, 1345, 1270, 1214, 1069, 1022, 922, 868, 757, 725, 698. ^{1}H-NMR (200 MHz): 1.77–1.92 (*m*, 2 H); 2.20–2.27 (*m*, 1 H); 2.46–2.49 (*m*, 1 H); 3.88–3.94 (*m*, 1 H); 4.09–4.15 (*m*, 1 H); 4.29–4.36 (*m*, 1 H); 6.21 (*d*, *J* = 5.97, 1 H); 9.18 (*s*, 2 H); 9.28 (*s*, 1 H). ^{13}C-NMR (100 MHz): 24.7; 25.2; 32.6; 65.7; 97.8; 122.9; 129.6 (2 CH); 133.2; 148.8 (2 C); 160.8. MS: 444.6 ($[M + Na]^+$).

*(2*S*,3*R*,4*S*,5*R*,6*R*)-4,5-Bis(acetyloxy)-6-[(acetyloxy)methyl]tetrahydro-3-iodo-2*H*-pyran-2-yl 3,5-Dinitrobenzoate* (**7a**). White solid. M.p. 178.9°. IR (neat): 3476, 3099, 3024, 1753, 1629, 1366, 1345, 1267, 1235, 1160, 1042, 751, 729. ^{1}H-NMR (400 MHz): 2.05 (*s*, 3 H); 2.08 (*s*, 3 H); 2.14 (*s*, 3 H); 4.01 (*dd*, *J* = 4.4, 9.2, 1 H); 4.14 (*dd*, *J* = 9.6, 9.6, 1 H); 4.24 (*dd*, *J* = 9.6, 9.6, 1 H); 4.36 (*dd*, *J* = 8.9, 9.6, 1 H); 5.11 (*t*, *J* = 9.6, 8.9, 1 H); 5.44 (*dd*, *J* = 8.9, 8.9, 1 H); 6.17 (*d*, *J* = 9.6, 1 H); 9.21 (*s*, 2 H); 9.30 (*s*, 1 H). ^{13}C-NMR (125 MHz): 20.6 (2 Me); 20.7; 24.9; 61.3; 68.3; 73.4; 74.8; 95.6; 123.3; 129.9 (2 CH); 132.2; 148.8 (2 C); 160.5; 169.4; 169.5; 170.5. MS: 632.7 ($[M + Na]^+$).

1-(Iodomethyl)pentyl 3,5-Dinitrobenzoate (**8a**). Major product. Colorless liquid. IR (neat): 2925, 1731, 1627, 1545, 1459, 1344, 1274, 1163, 1075, 921, 723. ^{1}H-NMR (200 MHz): 0.94 (*t*, *J* = 6.53, 3 H); 1.37–1.41 (*m*, 4 H); 1.85 (*m*, 2 H); 3.38–3.58 (*m*, 2 H); 5.07 (*m*, 1 H); 9.19 (*s*, 2 H); 9.26 (*s*, 1 H). ^{13}C-NMR

(125 MHz): 7.1; 13.9; 22.4; 27.3; 34.0; 75.4; 122.6; 129.58; 129.63; 133.8; 148.8 (2 C); 161.8. MS: 421 ($[M + Na]^+$).

2-Iodohexyl 3,5-Dinitrobenzoate (**8b**). Minor product. Colorless liquid. IR (neat): 2924, 1731, 1626, 1544, 1458, 1345, 1275, 1164, 1076, 922, 724. ^{1}H-NMR (500 MHz): 0.95 (*t*, *J* = 7.2, 3 H); 1.36 – 1.48 (*m*, 4 H); 1.85 – 1.91 (*m*, 4 H); 4.34 – 4.36 (*m*, 1 H); 4.60 – 4.70 (*m*, 2 H); 9.20 (*s*, 2 H); 9.26 (*s*, 1 H). ^{13}C-NMR (125 MHz): 13.8; 21.9; 29.5; 31.4; 36.2; 71.1; 122.6; 129.4; 129.5; 133.5; 148.8 (2 C); 161.9. MS: 421 ($[M + Na]^+$).

1-(Iodomethyl)hepthyl 3,5-Dinitrobenzoate (**9a**). Colorless liquid. IR (neat): 2925, 1732, 1627, 1597, 1548, 1461, 1419, 1345, 1274, 1161, 1131, 1076, 998, 966, 922, 824, 770, 724, 646. ^{1}H-NMR (200 MHz): 0.95 (*t*, *J* = 6.0, 3 H); 1.25 – 2.37 (*m*, 10 H); 3.50 (*dd*, *J* = 5.8, 11.0, 2 H); 5.14 (*m*, 1 H); 9.19 (*s*, 2 H); 9.23 (*s*, 1 H). ^{13}C-NMR (125 MHz): 7.1; 14.0; 22.5; 25.1; 28.9; 31.6; 34.2; 75.4; 122.6; 129.6 (2 CH); 133.7; 148.7 (2 C); 161.8. MS: 452.22 ($[M + 2]^+$).

2-Iodo-1-phenylethyl Benzoate (**10a**). White solid. M.p. 128.3°. IR (neat): 2923, 1725, 1603, 1506, 1454, 1153, 1107, 1089, 763, 698. ^{1}H-NMR (500 MHz): 3.57 – 3.65 (*m*, 2 H); 6.09 (*dd*, *J* = 5.2, 12.9, 1 H); 7.35 – 7.39 (*m*, 3 H); 7.42 – 7.48 (*m*, 4 H); 7.55 – 7.58 (*m*, 1 H); 8.13 (*d*, *J* = 8.47, 2 H). ^{13}C-NMR (100 MHz): 8.0; 75.4; 126.4 (2 CH); 128.4 (2 CH); 128.6 (2 CH); 129.5; 129.6; 129.7 (2 CH); 133.2; 138.4; 165.1. MS: 354.8 ($[M + 2]^+$).

2-Iodo-1-phenylethyl 4-Fluorobenzoate (**11a**). Oil. IR (neat): 1725, 1603, 1506, 1356, 1265, 1178, 1153, 1107, 910, 853, 763. ^{1}H-NMR (200 MHz): 3.53 – 3.68 (*dd*, *J* = 5.6, 10.8, 2 H); 6.05 (*dd*, *J* = 5.7, 12.8, 1 H); 7.11 (*d*, *J* = 8.7, 1 H); 7.13 (*d*, *J* = 8.4, 1 H); 7.34 – 7.42 (*m*, 5 H); 8.13 (*d*, *J* = 8.7, 1 H); 8.15 (*d*, *J* = 8.6, 1 H). ^{13}C-NMR (100 MHz): 7.9; 75.7; 115.6; 115.8; 126.0; 126.3; 128.8; 128.78; 128.82; 132.4; 132.5; 138.4; 164.3; 164.7; 167.2. MS: 393.11 ($[M + Na]^+$).

2-Iodo-1-phenylethyl 2-Hydroxybenzoate (**12a**). White gummy liquid. IR (neat): 2922, 1676, 1612, 1585, 1463, 1411, 1293, 1247, 1208, 1156, 1133, 1086, 1030, 794, 698, 670. ^{1}H-NMR (200 MHz): 3.54 – 3.64 (*m*, 2 H); 6.10 (*dd*, *J* = 5.5, 12.9, 1 H); 6.91 – 7.00 (*m*, 2 H); 7.41 – 7.53 (*m*, 6 H); 8.04 (*dd*, *J* = 1.16, 8.0, 1 H); 10.52 (*m*, 1 H). ^{13}C-NMR (100 MHz): 7.3; 76.1; 112.0; 117.7; 119.3; 125.9 (2 CH); 126.5; 128.8 (2 CH); 130.0; 136.1; 138.1; 161.5; 167.6. MS: 352.3 (M^+).

2-Iodo-1-phenylethyl 3,4,5-Tris(acetyloxy)benzoate (**13a**). White solid. M.p. 140.6°. IR (neat): 2939, 1781, 1726, 1427, 1370, 1325, 1242, 1053, 945, 851, 700. ^{1}H-NMR (200 MHz): 2.31 (br. *s*, 9 H); 3.51 – 3.61 (*m*, 2 H); 6.06 (*dd*, *J* = 5.5, 13.2, 1 H); 7.37 (br. *s*, 5 H); 7.86 (*s*, 2 H). ^{13}C-NMR (100 MHz): 7.3; 20.2 (2 Me); 20.6; 76.4; 122.5 (2 CH); 126.3 (2 CH); 128.0; 128.9 (2 CH); 129.0; 138.0; 143.5; 163.2; 166.4; 167.6. MS: 548.8 ($[M + Na]^+$).

2-Iodo-1-phenylethyl Pyridine-4-carboxylate (**14a**). White gummy mass. IR (neat): 3063, 1716, 1591, 1494, 1477, 1453, 1120, 1328, 1275, 1180, 1110, 1041, 1024, 1001, 945, 828, 739, 698, 642, 580. ^{1}H-NMR (200 MHz): 3.52 – 3.61 (*m*, 2 H); 6.16 (*dd*, *J* = 5.4, 7.5, 1 H); 7.27 – 7.52 (*m*, 5 H); 8.38 (*d*, *J* = 6.2, 1 H); 8.82 (*d*, *J* = 6.3, 1 H); 9.32 (br. *s*, 2 H). ^{13}C-NMR (125 MHz): 7.7; 76.3; 123.6; 125.9; 127.3; 127.4; 128.7; 128.9; 129.1; 137.6; 137.9; 150.8; 153.5; 164.0. MS: 354.75 ($[M + 1]^+$).

2-Iodo-1-phenylethyl 4-(Acetylsulfanyl)benzoate (**15a**). White solid. M.p. 110.3°. IR (neat): 3063, 3062, 1731, 1595, 1566, 1494, 1454, 1415, 1397, 1353, 1261, 1210, 1179, 1102, 1053, 1516, 1002, 949, 944, 759, 729, 666, 644, 614, 582. ^{1}H-NMR (200 MHz): 2.46 (*s*, 3 H); 3.54 – 3.63 (*m*, 2 H); 6.09 (*dd*, *J* = 6.7, 13.0, 1 H); 7.39 (*s*, 5 H); 7.52 (*d*, *J* = 7.8, 2 H); 8.15 (*d*, *J* = 7.8, 2 H). ^{13}C-NMR (100 MHz): 7.8; 30.4; 75.8; 126.3 (2 CH); 128.6 (2 CH); 128.8; 130.1 (2 CH); 130.5; 134.0; 134.1 (2 CH); 138.3; 164.4; 192.4. MS: 448.8 ($[M + Na]^+$).

2-Iodo-1-phenylethyl 2-(Acetylamino)benzoate (**16a**). Yellow semisolid. IR (neat): 2924, 1689, 1588, 1525, 1447, 1364, 1296, 1257, 1164, 1140, 1083, 1049, 1003, 951, 756, 700, 651, 581, 554. ^{1}H-NMR (500 MHz): 2.18 (*s*, 3 H); 3.56 – 3.64 (*m*, 2 H); 6.06 (*dd*, *J* = 6.7, 13.0, 1 H); 7.15 (*dd*, *J* = 1.0, 8.2, 1 H); 7.36 – 7.39 (*m*, 5 H); 7.56 (*dd*, *J* = 8.1, 1.6, 1 H); 8.23 (*dd*, *J* = 8.0, 1.6, 1 H); 8.70 (*d*, *J* = 8.4, 1 H). ^{13}C-NMR (125 MHz): 8.2; 26.3; 77.0; 115.0; 121.1; 123.3; 126.9 (2 CH); 129.7 (2 CH); 129.8; 131.7; 135.9; 138.9; 142.6; 167.7; 169.8. MS: 431.7 ($[M + Na]^+$).

2-Iodo-1-phenylethyl Formate (**17a**). Colorless semisolid. IR (neat): 2924, 1725, 1604, 1494, 1453, 1414, 1296, 1051, 1023, 936, 761, 699, 644, 575, 539. ^{1}H-NMR (200 MHz): 3.38 – 3.53 (*m*, 2 H); 5.97 (*dd*, *J* = 6.3, 13.2, 1 H); 7.33 (br. *s*, 5 H); 8.08 (*s*, 1 H). ^{13}C-NMR (125 MHz): 7.8; 75.0; 126.4 (2 CH); 128.5 (2 CH); 128.8; 138.0; 159.8. MS: 276.6 (M^+).

2-Iodo-1-phenylethyl 2-Phenylacetate (**18a**). Brown liquid. IR (neat): 2923, 1741, 1647, 1602, 1495, 1454, 1414, 1339, 1298, 1247, 1137, 1053. ^{1}H-NMR (200 MHz): 3.43 (*d*, *J* = 6.5, 2 H); 3.65 (*s*, 2 H); 5.86 (*t*, *J* = 6.5, 1 H); 7.22 – 7.39 (*m*, 10 H). ^{13}C-NMR (125 MHz): 7.8; 41.2; 75.2; 125.9 (2 CH); 127.0; 128.46 (2 CH); 128.48 (2 CH); 128.52; 129.5 (2 CH); 133.4; 138.1; 170.01. MS: 388.8 ([*M* + Na]$^+$).

*2-Iodo-1-phenylethyl (2*R*)-2-Bromopropanoate* (**19a**; major diastereoisomer 55 : 45). Oil. IR (neat): 3031, 2975, 1741, 1584, 1447, 1415, 1374, 1259, 1215, 1150, 1094, 1056, 986, 842, 758, 698, 647, 576. ^{1}H-NMR (200 MHz): 1.86 (*d*, *J* = 6.95, 3 H); 3.41 – 3.53 (*m*, 2 H); 4.44 (*q*, *J* = 6.9, 1 H); 5.89 (*t*, *J* = 5.5, 1 H); 7.36 (br. *s*, 5 H). ^{13}C-NMR (125 MHz): 7.4; 22.0; 40.4; 76.6; 126.1 (2 CH); 128.9 (2 CH); 129.1; 137.8; 168.8. MS: 384.4 ([*M* + 1]$^+$).

*2-Iodo-1-phenylethyl (2*S*)-2-(6-Methoxynaphthalen-2-yl)propanoate* (**20a**). White solid. M.p. 137.3°. IR (neat): 2827, 1706, 1630, 1601, 1500, 1456, 1376, 1254, 1216, 1178, 1135, 926, 889, 852, 804, 756, 700. ^{1}H-NMR (500 MHz): 1.50 (*d*, *J* = 7.1, 3 H); 3.23 – 3.30 (*m*, 2 H); 3.80 (*s*, 3 H); 3.86 (*q*, *J* = 7.1, 1 H); 5.75 (*t*, *J* = 5.5, 1 H); 6.95 – 7.02 (*m*, 4 H); 7.03 – 7.05 (*m*, 4 H); 7.51 – 7.61 (*m*, 3 H). ^{13}C-NMR (125 MHz): 7.5; 18.4; 45.5; 55.4; 75.5; 105.6; 119.0; 126.2; 126.4; 126.6 (2 C); 126.6; 127.2; 128.7 (2 C); 129.0; 129.4; 133.8; 135.3; 138.5; 157.7; 173.2. MS: 482.9 ([*M* + Na]$^+$).

2-Iodo-1-phenylethyl 2-(Acetyloxy)-2,2-diphenylacetate (**21a**). Oil. IR (neat): 2924, 1746, 1714, 1590, 1493, 1449, 1419, 1367, 1237, 1117, 1082, 1032, 1001, 730, 698, 555. ^{1}H-NMR (200 MHz): 2.19 (*s*, 3 H); 3.45 (*d*, *J* = 5.8, 2 H); 5.81 (*t*, *J* = 5.8, 1 H); 6.94 – 6.98 (*m*, 2 H); 7.17 – 7.36 (*m*, 9 H); 7.42 – 7.54 (*m*, 4 H). ^{13}C-NMR (125 MHz): 7.2; 21.5; 76.6; 84.1; 125.7 (2 C); 127.5 (2 C); 127.6 (2 C); 127.8 (2 C); 127.9 (2 C); 128.0; 128.1; 128.3 (2 C); 128.4; 137.7; 139.2; 139.5; 167.7; 169.3. MS: 522.7 ([*M* + Na]$^+$).

*2-Iodo-1-phenylethyl (2*R*)-2-Hydroxy-2-phenylacetate* (**22a**). Pale-yellow oil. IR (neat): 3394, 2938, 1776, 1704, 1503, 1436, 1492, 1365, 1231, 1127, 1021, 1011, 745, 697, 545. ^{1}H-NMR (400 MHz): 3.42 – 3.47 (*m*, 1 H); 3.48 – 3.57 (*m*, 1 H); 5.89 (*dd*, *J* = 8.4, 1 H); 6.90 (*s*, 1 H); 7.24 – 7.42 (*m*, 8 H); 7.15 – 7.22 (*m*, 1 H); 7.51 (*m*, 1 H). ^{13}C-NMR (100 MHz): 6.4; 72.8; 76.2; 125.4; 126.0; 126.6 (2 CH); 128.1; 128.1 (2 CH); 128.2 (2 CH); 128.3; 137.2; 137.3; 171.8. MS: 404.90 ([*M* + Na]$^+$).

2-Iodo-1-phenylethyl Cyclopropanecarboxylate (**23a**). Pale-yellow oil. IR (neat): 1776, 1713, 1492, 1451, 1174, 854, 821, 758. ^{1}H-NMR (200 MHz): 0.86 – 0.93 (*m*, 2 H); 1.02 – 1.08 (*m*, 2 H); 1.65 – 1.72 (*m*, 1 H); 3.46 (*d*, *J* = 6.5, 2 H); 5.86 (*t*, *J* = 6.5, 1 H); 7.30 (br. *s*, 5 H). ^{13}C-NMR (100 MHz): 8.2; 8.8 (2 CH_2); 12.8; 74.8; 126.2 (2 CH); 128.1 (2 CH); 128.2; 138.4; 173.6. MS: 315.9 (M^+).

2-Iodo-1-phenylethyl N-*[(*tert-*Butoxycarbonyl)glycinate* (**24a**). Yellow gummy mass. IR (neat): 2924, 1752, 1512, 1453, 1368, 1286, 1249, 1161, 961, 860, 759, 699, 639, 589. ^{1}H-NMR (200 MHz): 1.43 (*s*, 9 H); 3.40 – 3.50 (*m*, 2 H); 3.96 – 4.03 (*m*, 2 H); 5.93 (*t*, *J* = 5.9, 1 H); 7.35 – 7.39 (*m*, 5 H). ^{13}C-NMR (100 MHz): 7.3; 27.9 (3 Me); 42.3; 75.9; 79.8; 125.9 (2 CH); 128.4 (2 CH); 128.4; 137.7; 155.6; 169.2. MS: 427.9 ([*M* + Na]$^+$).

2-Iodo-1-phenylethyl N-*{[(9*H*-Fluoren-9-yl)methoxy]carbonyl}glycinate* (**25a**). Yellow gummy mass. IR (neat): 2925, 1723, 1519, 1449, 1409, 1377, 1191, 1052, 1002, 946, 757, 699. ^{1}H-NMR (200 MHz): 3.46 (*d*, *J* = 7.1, 2 H); 4.07 – 4.13 (*m*, 2 H); 4.26 (*t*, *J* = 6.7, 1 H); 4.40 (*d*, *J* = 7.0, 2 H); 5.95 (*t*, *J* = 5.8, 1 H); 7.20 – 7.76 (*m*, 9 H); 7.59 (*d*, *J* = 7.2, 2 H); 7.73 (*d*, *J* = 7.2, 2 H). ^{13}C-NMR (100 MHz): 7.1; 42.8; 47.0; 67.2; 76.4; 112.0 (2 CH); 125.0 (2 CH); 126.4 (2 CH); 127.0 (2 CH); 127.7 (2 CH); 128.8 (2 CH); 129.0; 137.7; 141.2 (2 C); 143.7 (2 C); 156.2; 168.9. MS: 549.9 ([*M* + Na]$^+$).

2-Iodo-1-phenylethyl N-*{[(9*H*-Fluoren-9-yl)methoxy]carbonyl}-*L*-leucinate* (**26a**). Yellow gummy mass. IR (neat): 2956, 1722, 1516, 1449, 1410, 1329, 1252, 1193, 1165, 1121, 1048, 951, 758, 740, 679. ^{1}H-NMR (200 MHz): 0.96 (*d*, *J* = 5.8, 3 H); 0.99 (*d*, *J* = 5.8, 3 H); 1.21 – 1.86 (*m*, 3 H); 3.49 (*d*, *J* = 6.8, 2 H); 4.22 (*t*, *J* = 6.7, 1 H); 4.37 – 4.49 (*m*, 3 H); 5.14 – 5.17 (*m*, 1 H); 5.85 – 5.93 (*m*, 1 H); 7.25 – 7.42 (*m*, 9 H); 7.59 (*d*, *J* = 6.9, 2 H); 7.75 (*d*, *J* = 6.9, 2 H). ^{13}C-NMR (100 MHz): 7.2; 21.7; 22.8; 24.6; 41.2; 47.1; 52.6; 66.9; 76.4; 119.9 (2 CH); 125.0 (2 CH); 125.7; 126.1 (2 CH); 127.6 (2 CH); 128.1 (2 CH); 128.8 (2 CH); 137.7; 141.2 (2 C); 143.8 (2 C); 155.9; 171.9. MS: 606.0 ([*M* + Na]$^+$).

2-Iodo-1-phenylethyl N-*[(*tert-*Butoxy)carbonyl]-*L*-phenylalaninate* (**27a**; mixture of two diastereoisomers 55 : 45). Yellow gummy mass. IR (neat): 3030, 2976, 1746, 1714, 1585, 1496, 1454, 1414, 1390, 1366, 1249, 1165, 1079, 1055, 1028, 859, 753, 699. ^{1}H-NMR (200 MHz): 1.41 (*s*, 9 H); 3.02 – 3.15 (*m*, 2 H); 3.38 – 3.42 (*m*, 2 H); 4.66 – 4.69 (*m*, 1 H); 4.91 (*m*, 1 H); 5.85 – 5.94 (*m*, 1 H); 6.90 (*m*, 1 H); 7.16 – 7.80 (*m*, 9 H). ^{13}C-NMR (100 MHz): 7.0; 28.4 (3 Me); 38.0; 54.4; 76.5; 79.9; 126.9; 127.0 (2 C); 128.5 (2 C); 128.8 (2 C); 129.4 (2 C); 129.6; 135.7; 137.9; 155.1; 170.9. MS: 517.75 ([*M* + Na]$^+$).

2-Iodo-1-phenylethyl N-*[(*tert-*Butoxy)carbonyl]*-L-*phenylalaninate* (**27a**; (*S*,*S*)-isomer, major diastereoisomer). Yellow gummy mass. IR (neat): 3030, 2976, 1746, 1714, 1585, 1496, 1454, 1414, 1390, 1366, 1249, 1165, 1079, 1055, 1028, 859, 753, 699. ^{1}H-NMR (200 MHz*):* 1.31 (*s*, 9 H); 3.02–3.15 (*m*, 2 H); 3.30–3.42 (*m*, 2 H); 4.51–4.63 (*m*, 1 H); 4.85–4.89 (*m*, 1 H); 5.75–5.82 (*m*, 1 H); 7.12–7.30 (*m*, 10 H). ^{13}C-NMR (100 MHz): 7.0; 28.3 (3 Me); 38.5; 54.4; 76.3; 79.9; 126.4; 127.0 (2 C); 128.6 (2 C); 128.7 (2 C); 129.3 (2 C); 129.5; 136.0; 137.8; 154.9; 170.9. MS: 517.81 ($[M + Na]^+$).

2-Iodo-1-phenylethyl N-*[(*tert-*Butoxy)carbonyl]*-L-*phenylalaninate* (**27a**; (*R*,*S*)-isomer, minor diastereoisomer). Yellow gummy liquid. IR (neat): 3030, 2976, 1746, 1714, 1585, 1496, 1454, 1414, 1390, 1366, 1249, 1165, 1079, 1055, 1028, 859, 753, 699. ^{1}H-NMR (200 MHz): 1.41 (*s*, 9 H); 3.03–3.15 (*m*, 2 H); 3.40–3.57 (*m*, 2 H); 4.66–4.69 (*m*, 1 H); 4.91 (*m*, 1 H); 5.87–5.94 (*m*, 1 H); 6.91 (*m*, 1 H); 7.16–7.90 (*m*, 9 H). ^{13}C-NMR (100 MHz): 6.7; 28.3 (3 Me); 38.0; 54.3; 76.5; 80.0; 126.9; 127.0 (2 C); 128.5 (2 C); 128.8 (2 C); 129.3 (2 C); 129.5; 135.6; 137.6; 155.0; 170.7. MS: 517.78 ($[M + Na]^+$).

*1-(*tert-*Butyl) 2-(2-Iodo-1-phenylethyl) (2*S*)-Pyrrolidine-1,2-dicarboxylate* (**28a**). White solid. M.p. 107.1°. IR (neat): 2976, 1748, 1698, 1478, 1454, 1397, 1293, 1254, 1067, 957, 851, 821, 770, 700. ^{1}H-NMR (200 MHz): 1.46 (*s*, 9 H); 1.90–1.99 (*m*, 2 H); 2.20–2.30 (*m*, 2 H); 3.42 (*m*, 4 H); 4.31–4.44 (*m*, 1 H); 5.83–5.96 (*m*, 1 H); 7.27–7.35 (*m*, 5 H). ^{13}C-NMR (100 MHz): 7.2; 23.5; 28.1; 28.3; 28.5; 30.9; 46.4; 59.1; 75.6; 80.2; 126.4 (2 CH); 128.6 (2 CH); 128.9; 138.1; 153.9; 171.8. MS: 467.9 ($[M + Na]^+$).

General Procedures for the Preparation Iodohydrins. A soln. of **27a** (1 mmol) in 50 ml of anh. Et_2O was cooled to 0° and treated with Et_2O soln. of $LiAlH_4$ (2 mmol). The ice-bath was removed, and the mixture was allowed to attain r.t. (*ca.* 20°) and then stirred for 2.5 h. The reaction was monitored by TLC. The excess of reducing agent was quenched by the sequential addition of AcOEt (15 ml) and H_2O (15 ml). The org. layer was separated, washed with brine soln., and then dried (Na_2SO_4). The residue after evaporation amounted to 0.12 g of the desired product, which was purified.

*(1*R*)-2-Iodo-1-phenylethanol* (**31a**). Yield: 89%. Oil. $[\alpha]_D^{25} = -35.5$ ($c = 1$, $CHCl_3$; [26]: $[\alpha]_D^{25} = +36.3$ ($c = 1$, $CHCl_3$). Optical purity < 96%. IR (neat): 3392, 3085, 2956, 1608, 1498, 1454, 1263, 1062, 1001, 967, 767, 752. ^{1}H-NMR (200 MHz): 2.47 (*s*, 1 H); 3.41 (*dd*, $J = 8.7$, 10.2, 1 H); 3.51 (*dd*, $J = 3.7$, 8.7, 1 H); 4.87 (*dd*, $J = 3.7$, 8.8, 1 H); 7.38 (br. *s*, 5 H). ^{13}C-NMR (100 MHz): 14.9; 74.2; 125.8; 128.3 (2 CH); 128.6 (2 CH); 141.6. MS: 271.9 ($[M + Na]^+$).

*(1*S*)-2-Iodo-1-phenylethanol* (**31b**). Yield: 91%. Oil. NMR and IR spectra of the compound were identical to those of its (*R*)-enantiomer. $[\alpha]_D^{25} = +35.1$ ($c = 1$, $CHCl_3$); [26]: $[\alpha]_D^{25} = -36.3$ ($c = 1$, $CHCl_3$). Optical purity < 94%.

tert-*Butyl [(2*S*)-1-Hydroxy-3-phenylpropan-2-yl]carbamate* (**32**). White solid. $[\alpha]_D^{25} = -26.5$ ($c = 1$, $CHCl_3$); [27]: $[\alpha]_D^{25} = -27.0$ ($c = 1$, $CHCl_3$)). IR (neat): 1685. ^{1}H-NMR (200 MHz): 1.91 (*s*, 9 H); 2.66 (*m*, 1 H), 2.83 (*d*, $J = 7.0$, 2 H); 3.55–3.67 (*m*, 2 H); 3.86 (*m*, 1 H); 4.82 (*m*, 1 H); 7.19–7.34 (*m*, 5 H). ^{13}C-NMR (100 MHz): 28.3 (3 Me); 37.5; 53.7; 64.4; 79.7; 126.5; 128.6 (2 CH); 129.3 (2 CH); 137.8; 156.2. MS: 274.2 ($[M + Na]^+$).

Supplementary Data. Copies of selected ^{1}H- and ^{13}C-NMR spectra associated with this article are available from the authors upon request.

We thank Dr. *Ram Vishwakarma*, Director of IIIM, Jammu, for his keen interest and encouragement. The authors (*A. R. R.*, *P. K. C.*, and *S. F.*) thank UGC-CSIR for providing SRF fellowship.

REFERENCES

[1] S. Adimurthy, S. Ghosh, P. U. Patoliya, G. Ramachandraiah, M. Agrawal, M. R. Gandhi, S. C. Upadhyay, P. K. Ghosh, B. C. Ranu, *Green Chem.* **2008**, *10*, 232; M. Jeganmohan, M. Shanmugasundaram, K. J. Chang, C. H. Cheng, *Chem. Commun.* **2002**, 2552; B. C. Ranu, R. Chakraborty, M. Saha, *Tetrahedron Lett.* **1993**, *34*, 4659.

[2] S. D. Stamatov, J. Stawinski, *Eur. J. Org. Chem.* **2008**, 2635; T. Moriuchi, M. Yamaguchi, K. Kikushima, T. Hirao, *Tetrahedron Lett.* **2007**, *48*, 2667.

[3] V. A. Mahajan, P. D. Shinde, A. S. Gajare, M. Karthikeyan, R. D. Wakharkar, *Green Chem.* **2002**, *4*, 325.

[4] M. Lubke, R. Skupin, G. Haufe, *J. Fluorine Chem.* **2000**, *102*, 125.

[5] J.-F. Wei, L.-H. Zhang, Z.-G. Chen, X.-Y. Shi, J.-J. Cao, *Org. Biomol. Chem.* **2009**, *7*, 3280; V. Nair, T. G. George, V. Sheeba, A. Augustine, L. Balagopal, L. G. Nair, *Synlett* **2000**, 1597; G. Li, H.-X. Wei, S. H. Kim, *Org. Lett.* **2000**, *2*, 2249; M. Curini, F. Epifano, M. C. Marcotullio, O. Rosati, *Tetrahedron Lett.* **2002**, *43*, 1201; M. Smietana, V. Gouverneur, C. Mioskowski, *Tetrahedron Lett.* **2000**, *41*, 193.
[6] I. Carrera, M. C. Brovetto, G. Seoane, *Tetrahedron* **2007**, *63*, 4095; A. Kirschning, C. Plumeier, L. Rose, *Chem. Commun.***1998**, 33; I. Saikia, K. K. Rajbongshi, P. Phukan, *Tetrahedron Lett.* **2012**, *53*, 758; M. K. Agarwal, S. Adimurthy, B. Ganguly, P. K. Ghosh, *Tetrahedron* **2009**, *65*, 2791; A. K. Yadav, B. K. Singh, N. Singh, R. P. Tripathi, *Tetrahedron Lett.* **2007**, *48*, 6628.
[7] S. M. Ahmad, D. C. Braddock, G. Cansell, S. A. Hermitage, J. M. Redmond, A. J. P. White, *Tetrahedron Lett.* **2007**, *48*, 5948; S. J. Zhi, H. Sun, C. Lin, G. Q. Zhang, G. G. Li, Y. Pan, *Science China Chem.* **2010**, *53*, 140; X.-L. Wu, G.-W. Wang, *Tetrahedron* **2009**, *65*, 8802; T. M. Shaikh, P. U. Karabal, G. Suryavanshi, A. Sudalai, *Tetrahedron Lett.* **2009**, *50*, 2815; S. Hajra, M. Bhowmick, D. Sinha, *J. Org. Chem.* **2006**, *71*, 9237.
[8] J. S. Yadav, B. V. S. Reddy, G. Baishya, S. J. Harshavardhan, C. J. Chary, M. K. Gupta, *Tetrahedron Lett.* **2005**, *46*, 3569.
[9] B. Das, K. Venkateshwarlu, K. Damodar, K. Suneel, *J. Mol. Catal. A* **2007**, *269*, 17.
[10] R. R. Wolff, V. Basava, R. M. Giuliano, W. J. Boyko, J. H. Schauble, *Can. J. Chem.* **2006**, *84*, 667; V. Basava, B. Flores, M. Giovine, T. Licisyn, K. Walck, W. Boyko, R. Giuliano, *J. Carbohydr. Chem.* **2008**, *27*, 389.
[11] G. A. Olah, Q. Wang, G. Sandford, G. K. S. Prakash, *J. Org. Chem*. **1993**, *58*, 3194; P. Bovonsombat, G. J. Angara, E. McNelis, *Synlett* **1992**, *2*, 131.
[12] A. K. Bose, B. Lal, *Tetrahedron Lett.* **1973**, *14*, 3937.
[13] T. Kajimoto, Y. Ishioka, T. Katoh, M. Node, *J. Carbohydr. Chem.* **2007**, *26*, 469; T. Kajimoto, Y. Ishioka, T. Katoh, M. Node, *Bioorg. Med. Chem. Lett.* **2006**, *16*, 5736.
[14] G. Haaima, R. T. Weavers, *Tetrahedron Lett*. **1988**, *29*, 1085.
[15] M. Adinolfi, M. Parrilli, G. Barone, G. Laonigro, L. Mangoni, *Tetrahedron Lett.* **1976**, *40*, 3661.
[16] J. Bange, A. F. Haugan, J. R. Knight, J. Sweeney, *J. Chem. Soc., Perkin Trans. 1* **1998**, 1039; J. B. Sweeney, J. R. Knight, S. Thobhani, *Tetrahedron Lett.* **2006**, *62*, 11565.
[17] Y. D. Vankar, G. Kumaravel, *Tetrahedron Lett.* **1984**, *25*, 233.
[18] W. R. Benson, E. T. McBee, L. Rand, *Org. Synth.* **1973**, *Coll. Vol. 5*, 663.
[19] T.-Y. Luh, M.-K. Leung, K.-T. Wong, *Chem. Rev.* **2000**, *100*, 3187; Y. Ju, R. S. Varma, *Green Chem.* **2004**, *6*, 219; Y. Guindon, B. Guerin, C. Chabot, W. Ogilvie, *J. Am. Chem. Soc.* **1996**, *118*, 12528; H. Adkins, K. Folkers, *J. Am. Chem. Soc.* **1931**, *53*, 1095.
[20] D. Bianchi, P. Moraschini, A. Bosetti, P. Cesti, *Tetrahedron: Asymmetry* **1994**, *5*, 1917; G. Reddipalli, M. Venkataiah, N. W. Fadnavis, *Tetrahedron: Asymmetry* **2010**, *21*, 320.
[21] C. Martin, L. Papazian, G. Perrin, P. Saux, F. Gouin, *Chest* **1993**, *103*, 1826; B. Machhia, A. Balsamo, M. C. Breschi, A. Lapucci, A. Lucacchini, F. Macchia, C. Manera, A. Martinelli, C. Martini, E. Martinotti, S. Nencettit, *J. Med. Chem.* **1992**, *35*, 1009.
[22] S. Lu, B. Herbert, G. Haufe, K. W. Laue, W. L. Padgett, O. Oshunleti, J. W. Daly, K. L. Kirk, *J. Med. Chem.* **2000**, *43*, 1611.
[23] F. M. McMillan, J. Archbold, M. J. McLeish, J. M. Caine, K. R. Criscione, G. L. Grunewald, J. L. Martin, *J. Med. Chem.* **2004**, *47*, 37; K. E. Furse, T. P. Lybrand, *J. Med. Chem.* **2003**, *46*, 4450.
[24] W. R. Roush, C. E. Bennett, *J. Am. Chem. Soc.* **1999**, *121*, 3541.
[25] B. T. O'Neill, D. Yohannes, M. W. Bundesmann, E. P. Arnold, *Org. Lett.* **2000**, *2*, 4201.
[26] L. C. Fardelone, J. A. R. Rodrigues, P. J. S. Moran, *Arkivoc* **2003**, *x*, 410; L. M. Aleixo, M. Carvalho, P. J. S. Moran, J. A. R. Rodrigues, *Bioorg. Med. Chem. Lett.* **1993**, *3*, 1637.
[27] A. Sarkar, S. R. Roy, N. Parikh, A. K. Chakraborti, *J. Org. Chem*. **2011**, *76*, 7132.

Received July 21, 2012