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Addition of Silyl Ketene Acetals to Nitrones Catalyzed by Lanthanide Triflates

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Abstract—α-Aryl-*N*-phenyl nitrones reacted with silyl ketene acetals mediated by lanthanum trifloromethanesulfonate (triflate) to afford the addition product in excellent yield under mild conditions. α-Aryl-*N*-*tert*-butyl nitrone reacted with ethyl trimethylsilylacetate to yield the unexpected α,β-unsaturated ester in a 100% *E*-form. A possible mechanism for the process is discussed.

Nitrones offer interesting advantages with respect to imines, hydrazones and other nitrogen derivatives of aldehydes in reactions with nucleophiles. They possess the highest polarized C═N bond and a reactive oxygen atom which can bring about the reaction with allyltrimethylsilane,[1] silyl enol ethers,[2] silyl ketene acetals[3] and vinyl ketene acetals[4] in the presence of a Lewis acid such as TMSOTf or ZnI_2. Recently, it was reported that rare earth metal triflates are excellent water tolerant and reusable catalysts and have unique properties compared to traditional Lewis acids in several important carbon–carbon bond forming reactions.[5] They are extensively used in organic synthetic processes such as aldol condensations,[6] Diels–Alder reactions,[7] Friedel–Crafts acylations,[8] Michael addition,[9] allylation[10] and ring-opening reactions of epoxides[11] and aziridines.[12] We have reported that glyoxylates react smoothly with alkenes in the presence of ytterbium triflate[13] and additionally, a one-pot synthesis of amino phosphonates from aldehydes using ytterbium triflate as catalyst.[14] However, to our knowledge, the reaction of nitrones with silyl ketene acetals catalyzed by lanthanide triflates are still not known. We wish to report here the development of lanthanide triflates as catalysts for the reaction of nitrones and silyl ketene acetals for the first time.

We found that lanthanide triflates acted quite well as reusable catalysts in the reaction of nitrones with silyl ketene acetals. Screening of a series of lanthanide (III) triflates catalysts for the model reaction of α,*N*-diphenyl nitrone with ethyl trimethylsilylacetate revealed that lanthanum triflate is superior to other rare earth metal triflates. We selected lanthanum triflate as catalyst and examined the effect of the solvent on the yield of product in the model reaction. Among the solvents examined, polar solvents such as tetrahydrofuran or dichloromethane are more beneficial to promote the reaction than nonpolar solvents such as toluene. However, acetonitrile is the poorest, contrary to the effect on glyoxylate-ene reaction.[13] Traditional Lewis acids such as $BF_3{\cdot}Et_2O$, $AlCl_3$ and $TiCl_4$ furnish adduct in an extremely low yield (Table 1). Also, lanthanum triflate could be recovered and reused after the reaction was complete. It is noteworthy that the yield of the second run of recycled catalyst was comparable to that of the first run (Entry 6, Table 1).

Table 1. The 1,3-dipolar addition of nitrone **1f** (R^1=Ph) to **2a** (R^2, R^3=H) catalyzed by Lewis acid

Entry	Solvent	Catalyst	*T* (h)	Yield (%)
1	CH_2Cl_2	$Yb(OTf)_3$	10	58
2	THF	$Yb(OTf)_3$	10	53
3	$C_6H_5CH_3$	$Yb(OTf)_3$	10	28
4	CH_3CN	$Yb(OTf)_3$	24	5
5	CH_2Cl_2	$La(OTf)_3$	4	80
6	CH_2Cl_2	$La(OTf)_3$	4	78[a]
7	CH_2Cl_2	$Sc(OTf)_3$	10	14
8	CH_2Cl_2	$Sm(OTf)_3$	10	59
9	CH_2Cl_2	$La(OTf)_3$[b]	10	23
10	CH_2Cl_2	$La(OTf)_3$[c]	10	13
11	CH_2Cl_2	$BF_3{\cdot}Et_2O$	10	21
12	CH_2Cl_2	$AlCl_3$	10	17
13	CH_2Cl_2	$TiCl_4$	10	8
14	CH_2Cl_2	ZnI_2	10	39

[a] Second run with recycled $La(OTf)_3$.
[b] 0.05 equiv.
[c] 0.01 equiv.

Keywords: α-aryl-*N*-phenyl nitrone; Lewis acid; lanthanine triflates.
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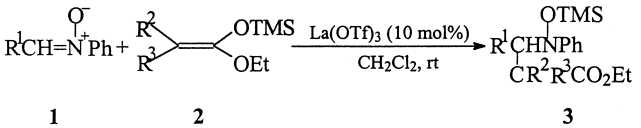


1 2 3 (1)

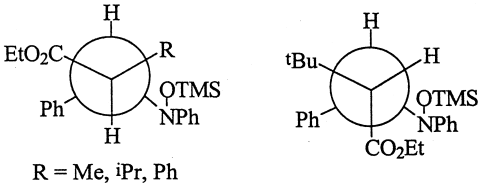
Several examples of the 1,3-polar additions are listed in Table 2. In each case, the reaction proceeded smoothly in the presence of a catalytic amount of lanthanum triflate (10 mol%) under extremely mild conditions to give the corresponding β-amino ester derivatives in very good yields after work-up. We were intrigued that α-(4-hydroxyphenyl)-*N*-phenyl nitrone reacted with ethyl trimethylsilylacetate to give product **3b** in 37% yield while α-(3-pyridyl)-*N*-phenyl nitrone afforded the equivalent product in 87% yield. While many Lewis acids are deactivated or sometimes decomposed by heteroatoms and even when the desired reactions proceed, more than stoichiometric amounts of the Lewis acids are needed because the acids are trapped by the nitrogen and oxygen atoms. α-(3-Pyridyl)-*N*-phenyl nitrone and α-(4-hydroxyphenyl)-*N*-phenyl nitrone are difficult to use with traditional Lewis acids due to coordination of the metal with co-ordinateable atoms which deactivate the catalyst.[15] However, it was found that addition of heteroatom-containing nitrones to ethyl trimethylsilylacetate proceeded smoothly in the presence of a catalytic amount of lanthanum triflate and lanthanide triflates were not deactivated under the reaction conditions. The lower yield of **3b** may be ascribed to the insolubility of **1b** in dichloromethane.

We were interested in extending this sequence to α-alkyl nitrones and silyl ketene acetals. Unfortunately, α-alkyl nitrones such as α-ethyl, α-isopropyl, α-cyclohexyl *N*-phenyl nitrones are very unstable in the presence of lanthanum triflate. Additionally, no products were obtained by three component coupling reactions of alkyl aldehydes, hydroxylamine and ethyl trimethylsilylacetate catalyzed by lanthanum triflate in the presence of MS 4Å. However, the reaction between α-(2-phenylvinyl)-*N*-phenyl nitrone in which the nitrone moiety is stabilized by a conjugated phenylvinyl group and ethyl trimethylsilylacetate proceeded very well while α-(1-propenyl)-*N*-phenyl nitrone is unstable

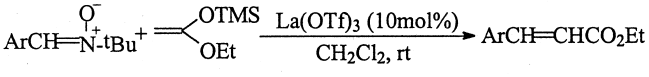
Table 3. The reaction of nitrone **4** with **2a**

Entry	Nitrone **4**(Ar)	*T* (h)	Product	Yield (%)
1	**4a**(4-methoxyphenyl)	8	**5a**	81
2	**4b**(4-methylphenyl)	8	**5b**	87
3	**4c**(phenyl)	8	**5c**	79
4	**4d**(4-chlorophenyl)	8	**5d**	82
5	**4e**(4-nitrophenyl)	8	**5e**	86
6	**4f**(2-nitrophenyl)	8	**5f**	73
7	**4g**(3-nitrophenyl)	8	**5g**	78

under the reaction conditions. The α,*N*-diphenyl nitrone reacted with ketene acetals **2b**, **2d**, **2e**, **2f** to furnish adducts **3l**, **3n**, **3o**, **3p** which have a similar structure. However, the vicinal coupling constants between the α-H and β-H of the carbonyl group are 11.28, 11.08, 12.80 and 7.91 Hz, respectively. According to substituted ethane the corresponding sequence: $J_{gauche}<J_{trans}$, we speculate they have the following conformation (Newman projection):[16]



R = Me, iPr, Ph

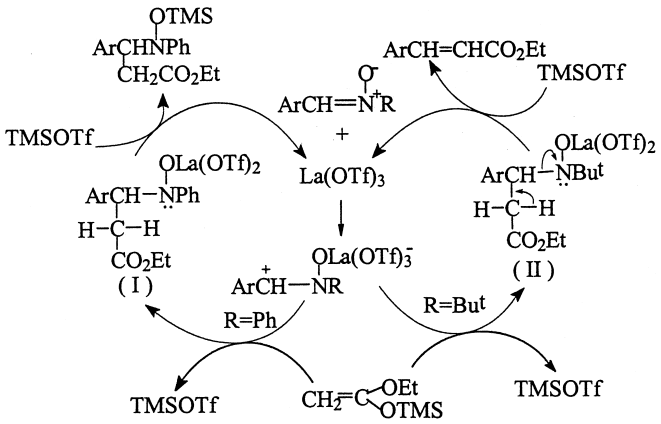


4 2a 5 (2)

Moreover, we further examined the reaction of α-aryl-*N*-*tert*-butyl nitrone with ethyl trimethylsilylacetate catalyzed by lanthanum triflate in dichloromethane as exemplified in Eq. (2). Contrary to our expectation, the reaction furnished α,β-unsaturated esters in a completely *E*-form as in Table 3. Of particular note is the fact that the reaction between the nitrones and ethyl trimethylsilylacetate did not occur without lanthanum triflate and, furthermore, the nitrones did not decompose to yield aldehyde in the presence of catalyst. Therefore, the α,β-unsaturated esters were not the product of aldehydes reacting with ethyl trimethylsilylacetate.

Table 2. The 1,3-dipolar addition of nitrone **1** to **2** catalyzed by $La(OTf)_3$

Entry	Nitrone **1**(**R**)	**2**	*T* (h)	Product	Yield (%)
1	**1a**(4-methoxyphenyl)	**2a**(R^2=R^3=H)	4	**3a**	97
2	**1b**(4-hydroxyphenyl)	**2a**	10	**3b**	37
3	**1c**(4-methylphenyl)	**2a**	4	**3c**	87
4	**1d**(4-chlorophenyl)	**2a**	10	**3d**	98
5	**1e**(4-bromophenyl)	**2a**	10	**3e**	91
6	**1f**(phenyl)	**2a**	4	**3f**	80
7	**1g**(3-pyridyl)	**2a**	10	**3g**	94
8	**1h**(3-nitrophenyl)	**2a**	10	**3h**	75
9	**1i**(2-furfuryl)	**2a**	4	**3i**	78
10	**1j**(4-nitrophenyl)	**2a**	10	**3j**	94
11	**1k**(2-phenylvinyl)	**2a**	10	**3k**	86
12	**1f**	**2b**(R^2=CH_3, R^3=H)	10	**3l**	91
13	**1f**	**2c**(R^2=R^3=CH_3)	10	**3m**	90
14	**1f**	**2d**(R^2=^{i}Pr, R^3=H)	10	**3n**	86
15	**1f**	**2e**(R^2=Ph, R^3=H)	10	**3o**	80
16	**1f**	**2f**(R^2=^{t}Bu, R^3=H)	20	**3p**	68



Scheme 1. A plausible mechanism.

N-Phenyl nitrone and *N-tert*-butyl nitrone reacted with ethyl trimethylsilylacetate to afford β-amino ester derivatives and α,β-unsaturated esters, respectively. This could be accounted for by the mechanism shown in Scheme 1. The N-anion is difficult to leave as a leaving group, although an N-anion would be a better one with an attached phenyl to stabilize it. The intermediate II that has more basic nitrogen after combining with a proton favors elimination compared with the intermediate I. Thus the β-elimination from intermediate II delivers the more stabilized α,β-unsaturated esters, whereas the intermediate I in which nitrogen lone pair electron is stabilized by the phenyl group renders addition product.

In summary, we found that lanthanum triflate is an excellent catalyst for the reaction of *N-tert* butyl nitrone and *N*-phenyl nitrone with silyl ketene acetals under mild conditions which provides α,β-unsaturated esters and β-amino ester derivatives in good to excellent yields. The real advantage of the procedure is the simplicity and robustness of the reaction, the catalyst is stable in water, recoverable and reusable without loss of yield.

Experimental

Solvents used were purified and dried by the standard procedures before use. Lanthanide triflates were prepared by the reported method.[17] Nitrone were generated by the known method.[18] Ethyl trimethylsilylacetate was prepared according to literature procedure.[19] ^{1}H NMR spectra were recorded on VX-300 spectrometer in $CDCl_3$ solution, and chemical shifts are reported in ppm on the δ scale relative to internal tetramethylsilane. IR spectra were measured on a Perkin–Elmer FT-IR spectrophotometer. Mass spectra were obtained on a Finnigan 4021 Mass spectrometer at 70 ev and mass data were tabulated as *m*/*z* values.

General procedure

To a solution of lanthanum trifluoromethanesulfonate (59 mg, 0.1 mmol) in dichloromethane (2 ml) was added successively α,*N*-diphenyl nitrone (197 mg, 1 mmol) and ethyl trimethylsilylacetate (168 mg, 1.05 mmol). The mixture was stirred for 4 h at room temperature. Water was added to the reaction mixture, the layers separated and the mixture was extracted again with water. After evaporation of water, lanthanum trifluoromethanesulfonate was recovered. The organic layer was dried over sodium sulfate and the crude product was purified by silica gel column chromatography to afford the desired adduct **3f** (286 mg, 80% yield).

Ethyl *N*-phenyl-*N*-trimethylsilyloxy-amino-3-(4-methoxyphenyl)-propionate (3a). Yellow oil; ^{1}H NMR δ: 7.29–6.84 (m, 9H), 4.83 (dd, *J*=6.5, 8.3 Hz, 1H), 4.08 (q, *J*=7.1 Hz, 2H), 3.86 (s, 3H), 3.10 (dd, *J*=6.5, 15.6 Hz, 1H), 2.92 (dd, *J*=8.3, 15.6 Hz, 1H), 1.21 (t, *J*=7.1 Hz, 3H), 0.01 (s, 9H). MS: *m*/*z*, 387 (M^+, 0.9), 300 (12.3), 298 (14.6), 207 (100.0), 165 (38.4), 135 (6.1), 73 (4.7). IR: ν (neat), 2960, 2905, 1737, 1613, 1596, 1515, 1488, 1372, 1304, 1251, 924, 699 cm^{-1}. Anal. Calcd For $C_{21}H_{29}NO_4Si$: C, 65.08, H, 7.54, N, 3.61; found: C, 64.81, H, 7.78, N, 3.54.

Ethyl *N*-phenyl-*N*-trimethylsilyloxy-amino-3-(4-hydroxyphenyl)-propionate (3b). Yellow oil; ^{1}H NMR δ: 7.34–6.74 (m, 9H), 5.30 (s, broad, 1H), 4.80 (dd, *J*=6.4, 8.5 Hz, 1H), 4.08 (q, *J*=7.1 Hz, 2H), 3.09 (dd, *J*=6.4, 15.6 Hz, 1H), 2.98 (dd, *J*=8.5, 15.6 Hz, 1H), 1.21 (t, *J*=7.1 Hz, 3H), 0.01 (s, 9H). MS: *m*/*z*, 373 (M^+, 29.5), 286 (45.2), 284 (67.2), 265 (100.0), 193 (18.7), 181 (31.1), 151 (48.4), 73 (28.2). IR: ν (neat), 3402, 2960, 1878, 1702, 1610, 1596, 1514, 1484, 1448, 1254, 1030, 758 cm^{-1}. Anal. Calcd For $C_{20}H_{27}NO_4Si$: C, 64.31, H, 7.29, N, 3.75; found: C, 64.61, H, 7.48, N, 3.72.

Ethyl *N*-phenyl-*N*-trimethylsilyloxy-amino-3-(4-methylphenyl)-propionate (3c). Yellow oil; ^{1}H NMR δ: 7.34–7.07 (m, 9H), 4.86 (dd, *J*=6.7, 8.1 Hz, 1H), 4.09 (q, *J*=7.1 Hz, 2H), 3.12 (dd, *J*=6.7, 15.7 Hz, 1H), 2.98 (dd, *J*=8.1, 15.7 Hz, 1H), 2.39 (s, 3H), 1.22 (t, *J*=7.1 Hz, 3H), 0.00 (s, 9H). MS: *m*/*z*, 370 (M^+-1, 2.5), 284 (4.9), 194 (12.7), 191 (32.0), 181 (14.0), 149 (100.0), 119 (25.4), 105 (10.2), 73 (16.9). IR: ν (neat), 2960, 1732, 1594, 1510, 1484, 1448, 1254, 1032, 928, 882, 764, 702 cm^{-1}. Anal. Calcd For $C_{21}H_{29}NO_3Si$: C, 67.88, H, 7.87, N, 3.77; found: C, 67.74, H, 7.80, N, 3.80.

Ethyl *N*-phenyl-*N*-trimethylsilyloxy-amino-3-(4-chlorophenyl)-propionate (3d). Yellow oil; ^{1}H NMR δ: 7.34–

7.08 (m, 9H), 4.82 (dd, *J*=6.6, 8.3 Hz, 1H), 4.09 (q, *J*=7.2 Hz, 2H), 3.11 (dd, *J*=6.6, 15.8 Hz, 1H), 2.96 (dd, *J*=8.3, 15.8 Hz, 1H), 1.21 (t, *J*=7.2 Hz, 3H), 0.00 (s, 9H). MS: *m*/*z*, 390 (M^+-1, 1.6), 303 (6.2), 213 (15.5), 181 (33.5), 169 (100.0), 139 (29.0), 73 (63.9). IR: ν (neat), 2962, 1732, 1594, 1486, 1254, 1032, 930, 770, 702 cm^{-1}. Anal. Calcd For $C_{20}H_{26}ClNO_3Si$: C, 61.28, H, 6.69, N, 3.57; found: C, 61.27, H, 6.74, N, 3.62.

Ethyl *N*-phenyl-*N*-trimethylsilyloxy-amino-3-(4-bromophenyl)-propionate (3e). Yellow oil; ^1H NMR δ: 7.46–7.08 (m, 9H), 4.81 (dd, *J*=6.6, 8.3 Hz, 1H), 4.09 (q, *J*=7.1 Hz, 2H), 3.11 (dd, *J*=6.6, 15.8 Hz, 1H), 2.96 (dd, *J*=8.3, 15.8 Hz, 1H), 1.21 (t, *J*=7.1 Hz, 3H), 0.01 (s, 9H). MS: *m*/*z*, 437 (M^++2, 41.6), 435 (M^+, 38.7), 349 (63.6), 347 (100.0), 215 (76.5), 213 (77.5). IR: ν (neat), 2960, 1732, 1594, 1450, 1374, 1076, 928, 768, 724 cm^{-1}. Anal. Calcd For $C_{20}H_{26}BrNO_3Si$: C, 55.04, H, 6.00, N, 3.20; found: C, 55.28, H, 5.90, N, 3.39.

Ethyl *N*-phenyl-*N*-trimethylsilyloxy-amino-3-phenylpropionate (3f). Yellow oil; ^1H NMR δ: 7.34–7.07 (m, 10H), 4.88 (dd, *J*=6.7, 8.0 Hz, 1H), 4.07 (q, *J*=7.1 Hz, 2H), 3.12 (dd, *J*=8.0, 15.8 Hz, 1H), 3.01 (dd, *J*=8.0, 15.8 Hz, 1H), 1.20 (t, *J*=7.1 Hz, 3H), 0.01 (s, 9H). MS: *m*/*z*, 357 (M^+, 7.8), 342 (4.5), 287 (21.2), 286 (100.0), 268 (11.8), 257 (18.6), 239 (15.8). IR: ν (neat), 3034, 2961, 1737, 1596, 1454, 1251, 1029, 765, 698 cm^{-1}. Anal. Calcd For $C_{20}H_{27}NO_3Si$: C, 67.19, H, 7.61, N, 3.92; found: C, 67.20, H, 7.69, N, 4.01.

Ethyl *N*-phenyl-*N*-trimethylsilyloxy-amino-3-(3-pyridyl)-propionate (3g). Yellow oil; ^1H NMR δ: 8.56–7.03 (m, 9H), 4.86 (dd, *J*=6.6, 8.2 Hz, 1H), 4.09 (q, *J*=7.1 Hz, 2H), 3.17 (dd, *J*=6.6, 15.9 Hz, 1H), 3.01 (dd, *J*=8.2, 15.9 Hz, 1H), 1.21 (t, *J*=7.1 Hz, 3H), 0.09 (s, 9H). MS: *m*/*z*, 358 (M^+, 3.5), 357 (M^+-1, 6.3), 271 (19.7), 250 (41.0), 181 (47.1), 180 (100.0), 136 (31.8), 73 (86.6). IR: ν (neat), 2960, 1732, 1594, 1484, 1032, 880, 796, 662 cm^{-1}. Anal. Calcd For $C_{19}H_{26}N_2O_3Si$: C, 63.65, H, 7.31, N, 7.81; found: C, 63.50, H, 7.32, N, 7.58.

Ethyl *N*-phenyl-*N*-trimethylsilyloxy-amino-3-(3-nitrophenyl)-propionate (3h). Yellow oil; ^1H NMR δ: 8.21–7.08 (m, 9H), 4.94 (dd, *J*=6.5, 8.3 Hz, 1H), 4.10 (q, *J*=7.1 Hz, 2H), 3.18 (dd, *J*=6.5, 16.1 Hz, 1H), 3.07 (dd, *J*=8.3, 16.1 Hz, 1H), 1.22 (t, *J*=7.1 Hz, 3H), 0.00 (s, 9H). MS: *m*/*z*, 401 (M^+-1, 4.5), 315 (18.8), 294 (36.5), 225 (14.1), 181 (18.9), 190 (97.0), 176 (19.6), 73 (100.0). IR: ν (neat), 3074, 2962, 1728, 1595, 1484, 1380, 1354, 1318, 1106, 1032, 880, 848, 808, 776, 704, 642 cm^{-1}. Anal. Calcd For $C_{20}H_{26}N_2O_5Si$: C, 59.68, H, 6.51, N, 6.96; found: C, 59.79, H, 6.53, N, 6.88.

Ethyl *N*-phenyl-*N*-trimethylsilyloxy-amino-3-(2-furyl)-propionate (3i). Yellow oil; ^1H NMR δ: 7.44 (dd, *J*=0.7, 1.8 Hz, 1H), 7.35–7.30 (m, 2H), 7.19–7.08 (m, 3H), 6.38 (dd, *J*=1.8, 3.2 Hz, 1H), 6.23 (d, *J*=3.2 Hz, 1H), 4.98 (t, *J*=7.3 Hz, 1H), 4.11 (q, *J*=7.1 Hz, 2H), 2.99 (d, *J*=7.3 Hz, 2H), 1.24 (t, *J*=7.1 Hz, 3H), 0.01 (s, 9H). MS: *m*/*z*, 347 (M^+, 5.3), 260 (17.0), 181 (12.6), 167 (100.0), 125 (37.4), 95 (32.1). IR: ν (neat), 2962, 2904, 1738, 1597, 1488, 1252, 1158, 879, 845 cm^{-1}. Anal. Calcd For $C_{18}H_{25}NO_4Si$: C, 62.21, H, 7.25, N, 4.03; found; C, 62.16, H, 7.48, N, 4.00.

Ethyl *N*-phenyl-*N*-trimethylsilyloxy-amino-3-(4-nitrophenyl)-propionate (3j). Yellow oil; ^1H NMR δ: 8.20–7.08 (m, 9H), 4.94 (dd, *J*=6.5, 8.4 Hz, 1H), 4.11 (q, *J*=7.1 Hz, 2H), 3.19 (dd, *J*=6.5, 16.1 Hz, 1H), 3.04 (dd, *J*=8.4, 16.1 Hz, 1H), 1.23 (t, *J*=7.1 Hz, 3H), 0.01 (s, 9H). MS: *m*/*z* 402 (M^+, 1.0), 401 (3.6), 315 (16.3), 294 (41.9), 180 (100.0), 73 (74.0). IR: ν (neat), 3030, 2961, 2904, 1737, 1596, 1525, 1488, 1348, 1252, 1206, 856, 847 cm^{-1}. Anal. Calcd For $C_{20}H_{26}N_2O_5Si$: C, 59.68, H, 6.51, N, 6.96; found: C, 59.67, H, 6.62, N, 6.92.

Ethyl 3-(*N*-phenyl-*N*-trimethylsilyloxy-amino)-5-phenyl-4-pentenoate (3k). Yellow oil; ^1H NMR δ: 7.22–7.11 (m, 9H), 6.95–6.93 (m, 1H), 6.27 (d, *J*=16.4 Hz, 1H), 6.20 (d, *J*=16.4 Hz, 1H), 4.28 (dd, *J*=6.2, 13.8 Hz, 1H), 4.01 (q, *J*=7.1 Hz, 2H), 2.77 (dd, *J*=6.0, 15.2 Hz, 1H), 2.56 (dd, *J*=8.2, 15.2 Hz, 1H), 1.12 (t, *J*=7.1 Hz, 3H), 0.01 (s, 9H). MS: *m*/*z*, 383 (M^+, 0.5), 296 (7.1), 203 (33.9), 157 (41.7), 129 (100.0), 115 (29.1), 77 (39.6). IR: ν (neat), 3030, 2960, 2877, 1732, 1598, 1480, 1250, 1020, 885, 850 cm^{-1}. Anal. Calcd For $C_{22}H_{29}NO_3Si$: C, 68.89, H, 7.62, N, 3.65; found: C, 68.86, H, 7.64, N, 3.29.

Ethyl 3-(*N*-phenyl-*N*-trimethylsilyloxy-amino)-2-methyl-3-phenyl-propionate (3l). Yellow oil; ^1H NMR δ: 7.14–7.03 (m, 5H), 6.91–6.85 (m, 5H), 4.44 (d, *J*=11.3 Hz, 1H), 4.21 (dq, *J*=3.7, 7.2 Hz, 2H), 3.22 (dq, *J*=7.1, 11.3 Hz, 1H), 1.31 (t, *J*=7.2 Hz, 3H), 0.85 (d, *J*=7.1 Hz, 3H), 0.00 (s, 9H). MS: *m*/*z*, 371 (M^+, 11.0), 270 (100.0), 180 (30.8), 135 (69.4), 119 (20.9), 91 (27.9). IR: ν (neat), 3031, 2960, 1729, 1593, 1484, 1452, 1379, 1251, 1051, 961, 702 cm^{-1}. Anal. Calcd For $C_{21}H_{29}NO_3Si$: C, 67.89, H, 7.87, N, 3.77; found: C, 68.14, H, 8.01, N, 3.79.

Ethyl 3-(*N*-phenyl-*N*-trimethylsilyloxy-amino)-2,2-dimethyl-3-phenyl-propionate (3m). Yellow oil; ^1H NMR δ: 7.32–6.96 (m, 10H), 4.68 (s, 1H), 4.29–4.12 (m, 2H), 1.49 (s, 3H), 1.39 (t, *J*=7.1 Hz, 3H), 0.90 (s, 3H), 0.00 (s, 9H). MS: *m*/*z*, 386 (M^++1, 0.4), 370 (1.6), 340 (0.6), 296 (9.7), 270 (100.0), 180 (17.3). IR: ν (neat), 3030, 2977, 1729, 1594, 1484, 1387, 1252, 983, 768 cm^{-1}. Anal. Calcd For $C_{22}H_{31}NO_3Si$: C, 68.54, H, 8.10, N, 3.63; found: C, 68.29, H, 7.89, N, 3.62.

Ethyl 3-(*N*-phenyl-*N*-trimethylsilyloxy-amino)-2-(1′-methylethyl)-3-phenyl-propionate (3n). Yellow oil; ^1H NMR δ: 7.59–7.08 (m, 10H), 4.64 (d, *J*=11.1 Hz, 1H), 3.86 (q, *J*=7.0 Hz, 2H), 3.24 (dd, *J*=3.7, 11.1 Hz, 1H), 2.30–2.10 (m, 1H), 1.37 (t, *J*=6.9 Hz, 3H), 1.24 (d, *J*=7.0 Hz, 3H), 1.10 (d, *J*=7.0 Hz, 3H), 0.19 (s, 9H). MS: *m*/*z*, 399 (M^+, 7.6), 384 (0.8), 354 (2.2), 310 (14.4), 270 (100.0), 180 (45.2), 145 (75.3). IR: ν (neat), 3030, 2962, 1770, 1730, 1596, 1491, 1374, 1261, 1186, 1033, 758, 702 cm^{-1}. Anal. Calcd For $C_{23}H_{33}NO_3Si$: C, 69.13, H, 8.32, N, 3.51; found: C, 69.14, H, 8.47, N, 3.63.

Ethyl 3-(*N*-phenyl-*N*-trimethylsilyloxy-amino)-2-phenyl-3-phenyl-propionate (3o). Yellow oil; ^1H NMR δ: 7.68–6.99 (m, 15H), 5.33 (d, *J*=12.8 Hz, 1H), 4.68 (d, *J*=12.8 Hz, 1H), 4.36 (m, 2H), 1.48 (t, *J*=7.1 Hz, 3H),

0.34 (s, 9H). MS: *m*/*z*, 434 (M^++1, 0.5), 344 (3.7), 298 (0.5), 270 (100.0), 181 (15.5), 180 (21.8), 91 (18.2). IR: ν (neat), 3029, 2958, 1730, 1593, 1484, 1452, 1306, 1253, 1157, 1029, 848, 700 cm^{-1}. Anal. Calcd For $C_{26}H_{31}NO_3Si$: C, 72.02, H, 7.21, N, 3.23; found: C, 72.24, H, 7.42, N, 3.40.

Ethyl 3-(*N*-phenyl-*N*-trimethylsilyloxy-amino)-2-(1′,1′-dimethylethyl)-3-phenyl-propionate (3p). Yellow oil; ^1H NMR δ: 7.02–6.78 (m, 10H), 4.37 (d, *J*=7.9 Hz, 1H), 3.60 (dq, *J*=7.2, 10.8 Hz, 2H), 3.20 (d, *J*=7.9 Hz, 1H), 1.15 (s, 9H), 0.82 (t, *J*=7.2 Hz, 3H), 0.10 (s, 9H). MS: *m*/*z*, 414 (M^++1, 6.3), 398 (1.9), 324 (26.6), 270 (100.0), 268 (41.8), 180 (17.1), 177 (37.4), 131 (21.5). IR: ν (neat), 3027, 2958, 1729, 1594, 1451, 1398, 1206, 1143, 1098, 878, 847, 701 cm^{-1}. Anal. Calcd For $C_{24}H_{35}NO_3Si$: C, 69.69, H, 8.53, N, 3.39; found: C, 69.71, H, 8.84, N, 3.32.

Ethyl 3-(4-methoxyphenyl)-2-propenate (5a).[20] ^1H NMR δ: 7.64 (d, *J*=15.9 Hz, 2H), 7.46 (d, *J*=14.0 Hz, 2H), 6.88 (d, *J*=14.0 Hz, 1H), 6.30 (d, *J*=15.9 Hz, 1H), 4.24 (d, *J*=7.1 Hz, 2H), 3.82 (s, 3H), 1.32 (t, *J*=7.1 Hz, 3H).

Ethyl 3-(4-methylphenyl)-2-propenate (5b).[20] ^1H NMR δ: 7.54 (d, *J*=16.0 Hz, 1H), 7.30 (d, *J*=8.1 Hz, 2H), 7.06 (d, *J*=8.1 Hz, 2H), 6.27 (d, *J*=16.0 Hz, 1H), 3.97 (q, *J*=7.1 Hz, 2H), 2.24 (s, 3H), 1.11 (t, *J*=7.1 Hz, 3H).

Ethyl 3-phenyl-2-propenate (5c).[20] ^1H NMR δ: 7.56 (d, *J*=16.0 Hz, 1H), 7.41~7.24 (m, 5H), 6.31 (d, *J*=16.0 Hz, 1H), 3.96 (q, *J*=7.1 Hz, 2H), 1.11 (t, *J*=7.1 Hz, 3H).

Ethyl 3-(4-chlorophenyl)-2-propenate (5d).[20] ^1H NMR δ: 7.51 (d, *J*=16.0 Hz, 1H), 7.35–7.22 (m, 4H), 6.28 (d, *J*=16.0 Hz, 1H), 3.97 (q, *J*=7.1 Hz, 3H), 1.12 (t, *J*=7.1 Hz, 3H).

Ethyl 3-(4-nitrophenyl)-2-propenate (5e).[20] ^1H NMR δ: 8.19–8.15 (m, 2H), 7.64 (d, *J*=16.0 Hz, 1H), 7.62–7.59 (m, 2H), 6.48 (d, *J*=16.0 Hz, 1H), 4.22 (q, *J*=7.1 Hz, 2H), 1.28 (t, *J*=7.1 Hz, 3H).

Ethyl 3-(2-nitrophenyl)-2-propenate (5f).[20] ^1H NMR δ: 7.85 (d, *J*=15.7 Hz, 1H), 7.80–7.20 (m, 4H), 6.27 (d, *J*=15.7 Hz, 1H), 4.17 (q, *J*=7.1 Hz, 2H), 1.22 (t, *J*=7.1 Hz, 3H).

Ethyl 3-(3-nitrophenyl)-2-propenate (5g).[20] ^1H NMR δ: 8.30 (t, *J*=1.7 Hz, 1H), 8.15 (dd, *J*=1.2, 8.2 Hz, 1H), 7.75 (d, *J*=7.7 Hz, 1H), 7.64 (d, *J*=16.1 Hz, 1H), 7.51 (t, *J*=8.0 Hz, 1H), 6.49 (d, *J*=16.1 Hz, 1H), 4.22 (q, *J*=7.1 Hz, 2H), 1.28 (t, *J*=7.1 Hz, 3H).

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