Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Ruthenium catalyzed regioselective coupling of terminal alkynes, amine and carbon dioxide leading to anti-Markovnikov adducts

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1. Experimental

All chemicals and reagents were purchased from firms of repute with their highest purity available and were used without further purification. [RuCl2(p-cymene)]2 precursor and phosphine ligands were purchased from Sigma-Aldrich. The reaction mixture was analyzed by GC (Perkin-Elmer, Clarus 400) equipped with a flame ionization detector (FID) and a capillary column (Elite-1, 30 m × 0.32 mm × 0.25 μm). The crude product was purified by column chromatography on silica gel (eluting with 80:20 petroleum ether/ethyl acetate) to afford the product.

General procedure for synthesis of vinyl carbamate from CO_2

In a typical experimental procedure, the alkynes (2 mmol), secondary amine (4 mmol), $[RuCl_2(p\text{-cymene})]_2$ (1 mol %), DPPE (1 mol %) and ACN (10 ml) were charged into a 100 ml stainless steel autoclave with a mechanical stirrer at room temperature. The autoclave was flushed with carbon dioxide and reaction mixture was then pressurized to 5 MPa of CO_2 pressure; the reactor was heated to 80 ^oC and stirred for 24 h at 600 rpm. After completion of reaction, the reactor was cooled to room temperature and the remaining carbon dioxide was carefully vented and then the reactor was opened. The crude product which was then purified by column chromatography on silica gel (100–200 mesh size), with petroleum ether/ethyl acetate (PE–EtOAc, 80:20) as eluent to afford a pure product. The products were further characterized by GCMS analysis, ^1H NMR and ^{13}C NMR spectra (Varian 300 MHz NMR Spectrometer) using TMS as internal standard. GCMS analysis was done on Shimadzu-QP2010 mass spectrometer (Shimadzu GC-MS QP 2010) (Rtx-17, 30 m x 25 mm ID, film thickness 0.25 mm df) (column flow 2 mL min-1, 80 ^oC to 240 ^oC at 10 ^oC min-1. rise).

2. Spectral Data of Products[1-3]

i. (*Z*)-*β*-*[(diethylcarbamoyl)oxy]styrene*

^1H NMR (300 MHz, $CDCl_3$, 25 ^oC, TMS) spectrum: δ = 7.54 (d, J = 7.2 Hz, 1H), 7.27-7.34 (m, 5H), 5.6 (d, J = 7.2, 1H), 3.40 (q, J =7.2, 4H), 1.26 (t, J=7.2, 6H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ= 152.8, 135.6, 135.1, 128.6, 128.3, 126.8, 126.0, 109.5, 42.4, 17.8; **GCMS** (70 eV, EI) *m/z* (%): 219 (15) (M^+), 131 (5), 120 (10), 100 (100), 91 (20), 72 (70), 44 (20).

ii. (Z)-4-methylstyryl diethylcarbamate

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.43 (d, J = 7.2, 1H), 7.11-7.25 (m, 4H), 5.57 (d, J = 7.2, 1H), 3.40 (q, J = 7.2, 4H), 2.32 (s, 3H), 1.27 (t, J = 7.2, 6H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ= 152.9, 135.0, 131.8, 129.0, 128.5, 125.8, 109.4, 42.3, 21.2, 14.14; **GCMS** (70 eV, EI) *m/z* (%) :233 (10) (M^+), 100 (100), 72 (65.0), 44 (24.5).

iii. (Z)-styryl benzyl(methyl)carbamate

^{1}H NMR (300 MHz, $CDCl_3$,) spectrum: δ = 7.6 (d, J = 7.5 Hz, 1H), 7.17-7.36 (m, 10 H), 5.68 (t, J = 7.5, 1H), 4.65 (s, 1H), 4.59 (s, 1H), 3.04 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ= 153.8, 135.6, 135.5, 128.8, 128.6, 128.4, 128.3, 128.0, 127.7, 127.6, 127.4, 109.9, 53.0, 35.0; **GCMS** (70 eV, EI) *m/z* (%) : 267 (3.8) (M^+), 148 (17.2), 91 (100), 65 (10.0), 56 (15).

iv. (Z)-styryl diallylcarbamate

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.51 (d, J = 7.2, 1H), 7.23-7.33 (m, 5H), 5.81-5.86 (m, 2H), 5.64 (d, J = 7.2, 1H), 5.17-5.23(m, 4H), 3.96-4.01 (m, 4H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ= 153.0, 135.5, 134.4, 132.8, 128.8, 128.3, 126.9, 117.95, 110.0, 49.6; **GCMS** (70 eV, EI) *m/z* (%): 243 (86) (M^+), 124 (86.2), 91 (35.0), 81 (17.4), 41 (100.0).

v. (Z)-β-[(dibutylcarbamoyl)oxy]styrene

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.53 (d, J = 7.2, 1H), 7.20-7.34 (m, 5H), 5.60 (d, J = 7.2 Hz, 1H), 3.34 (q, J = 7.2, 4H), 1.55 (m, 4H), 1.25-1.38 (m, 8H), 0.91-0.97 (m, 6H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ= 153.0, 135.5, 134.6, 128.5, 128.2, 126.7, 109.2, 47.8, 30.11, 20.1, 13.9; **GCMS** (70 eV, EI) *m/z* (%): 275 (10) (M^+), 156 (45), 120 (10), 100 (25), 91 (17), 57 (100), 41 (20).

vi. (Z)-styryl pyrrolidine-1-carboxylate

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.56 (d, J = 7.5, 1H), 7.20-7.35 (m, 5 H), 5.60 (d, J = 7.5, 1H), 3.57 (t, J = 6.6, 2H), 3.47 (t, J = 6.6, 2 H), 1.85-1.98 (m, 4H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ= 151.7, 135.4, 134.6, 128.7, 128.3, 126.8, 109.3, 46.1, 25.7; **GCMS** (70 eV, EI) *m/z* (%) :217 (10.4) (M^+), 98 (100), 56 (23.0).

Vii. (Z)-β-[(Piperidinocarbamoyl)oxy

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.51 (d, J = 7.5, 1H), 7.23-7.35 (m, 5H), 5.61 (d, J = 7.5,

1H), 3.51-3.58 (m, 4H), 1.25-1.34 (m, 6H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$): δ= 152.2, 135.7, 134.6, 128.6, 128.3, 126.8, 109.7, 45.2, 25.4, 24.3; **GCMS** (70 eV, EI) *m/z* (%):231 (10) (M^+), 186 (5), 120 (7), 112 (100), 91 (15), 69 (65), 56 (15), 41 (30).

viii. (Z)-4-(trifluoromethyl)styryl diethylcarbamate

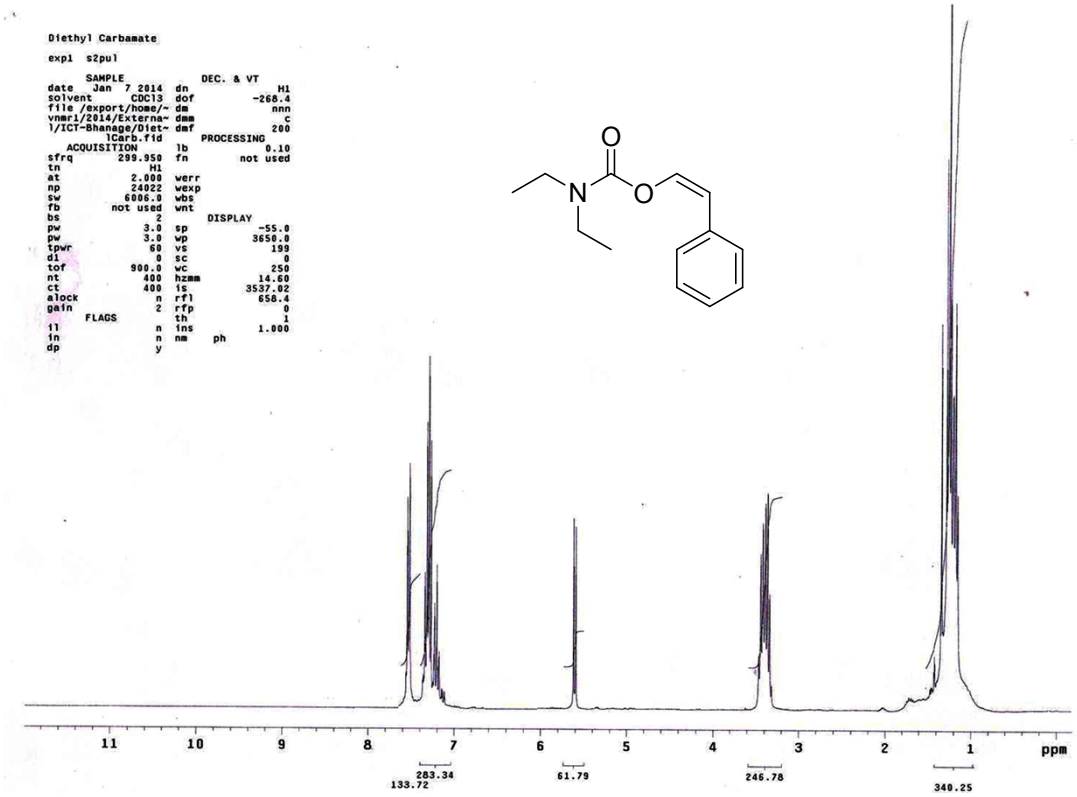
GCMS (70 eV, EI) *m/z* (%) :287 (1.8) (M^+), 100 (100), 72 (60.0), 44 (41.5).

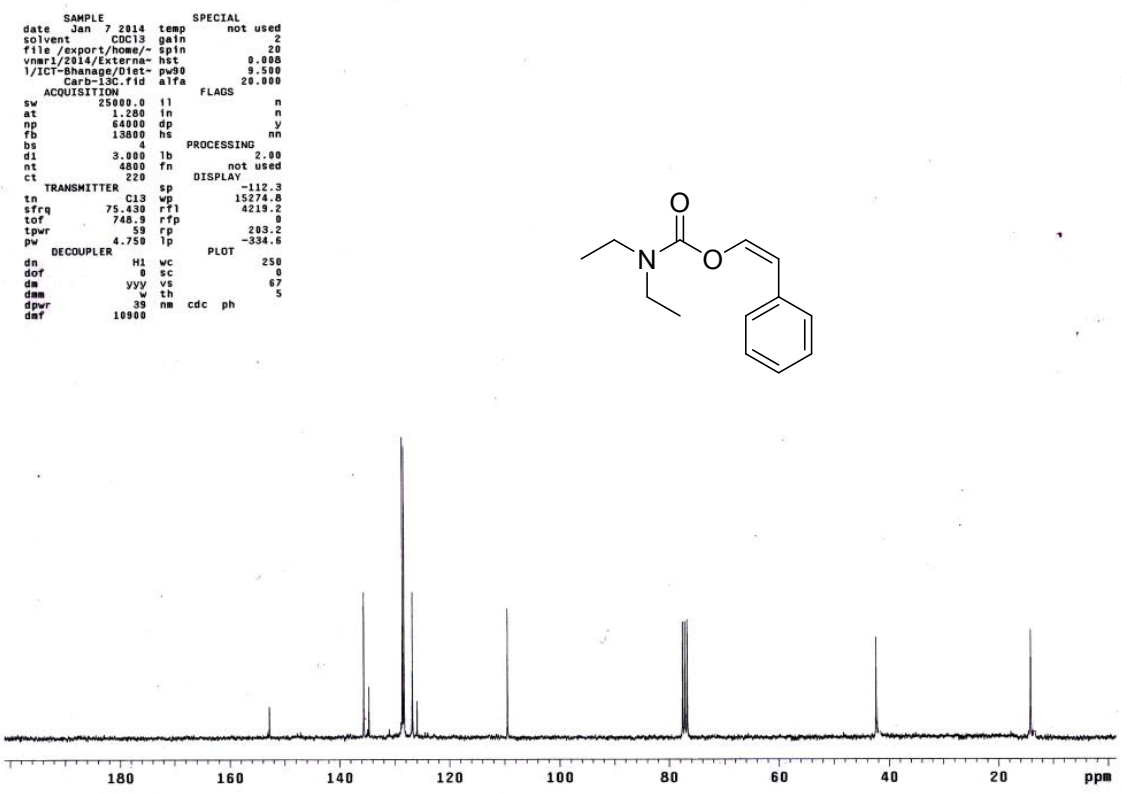
ix. (Z)-styryl piperidine-1-carboxylate

GCMS (70 eV, EI) *m/z* (%) :231 (8.2) (M^+), 112 (100), 91 (10.6), 69 (70.0), 57(10).

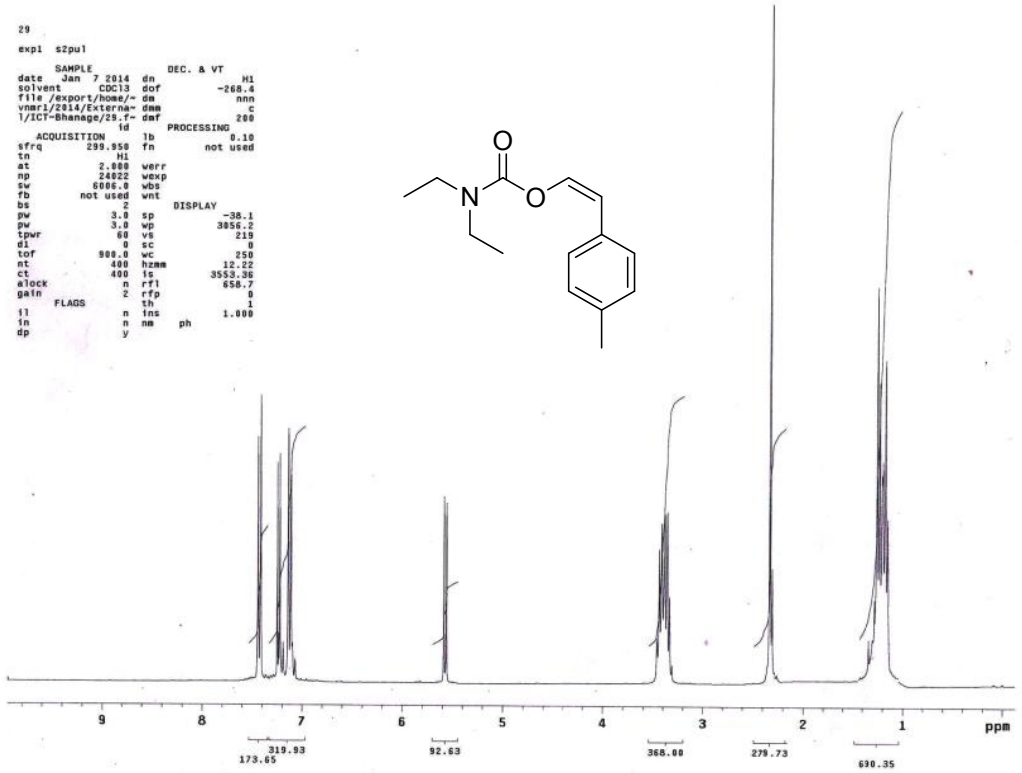
3. ^{1}H and ^{13}C NMR spectra of selected compounds

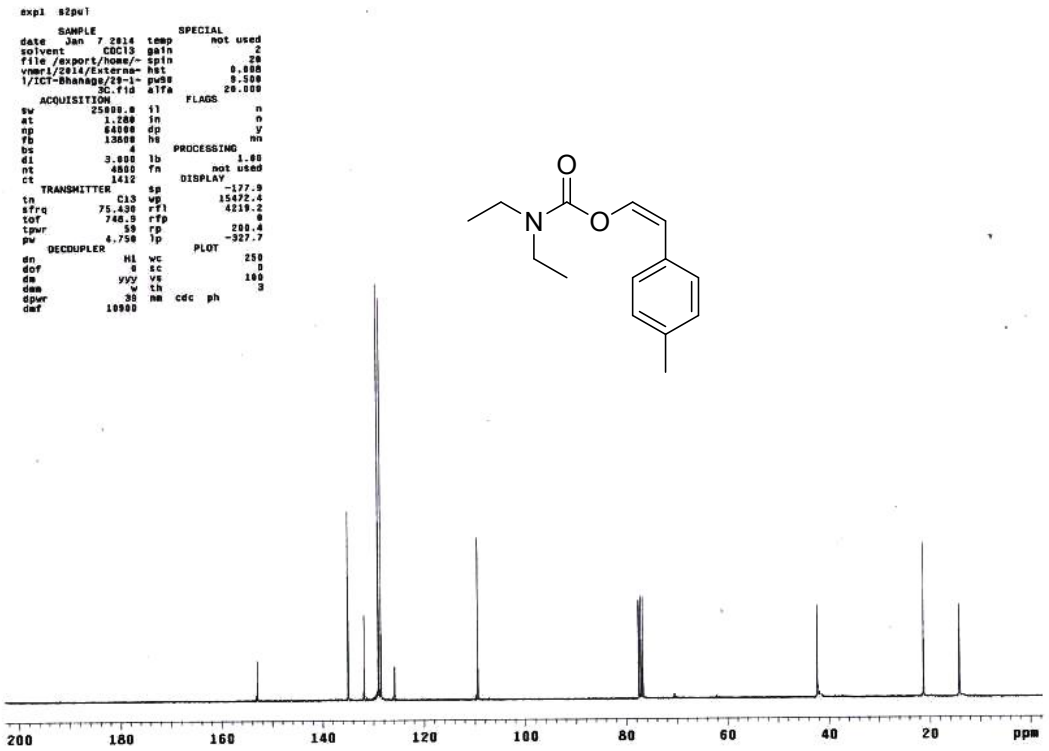
(Z)-β-[(diethylcarbamoyl)oxy]styrene



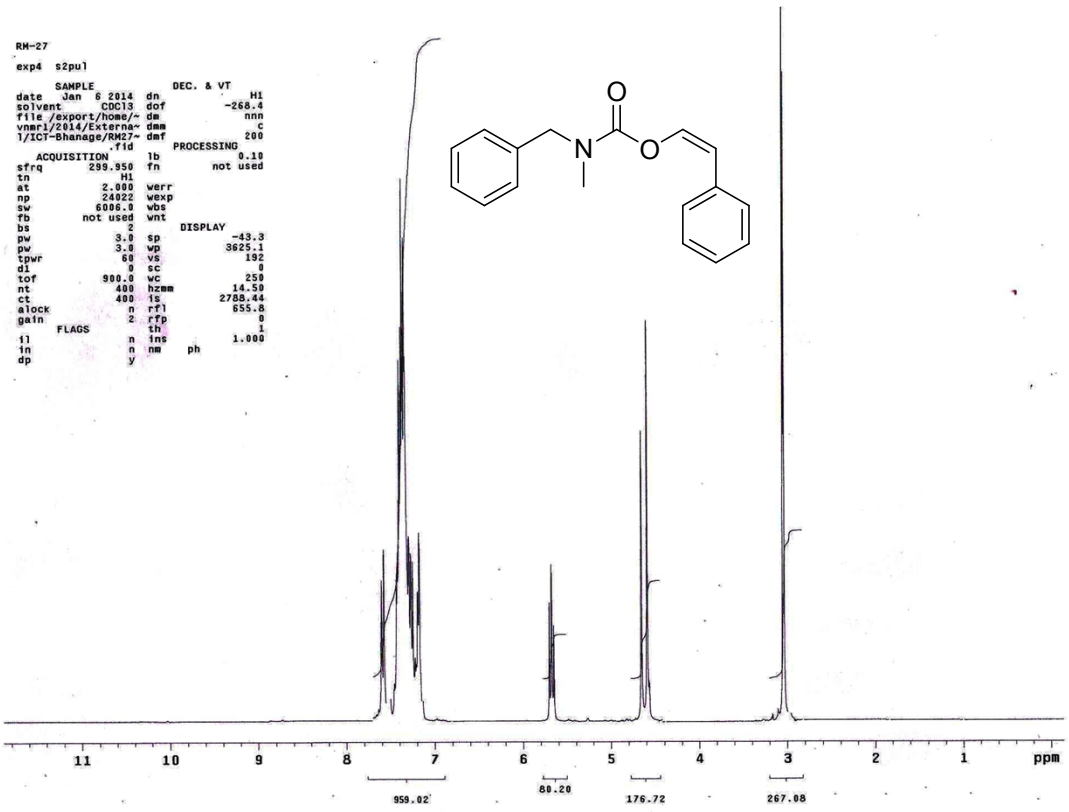


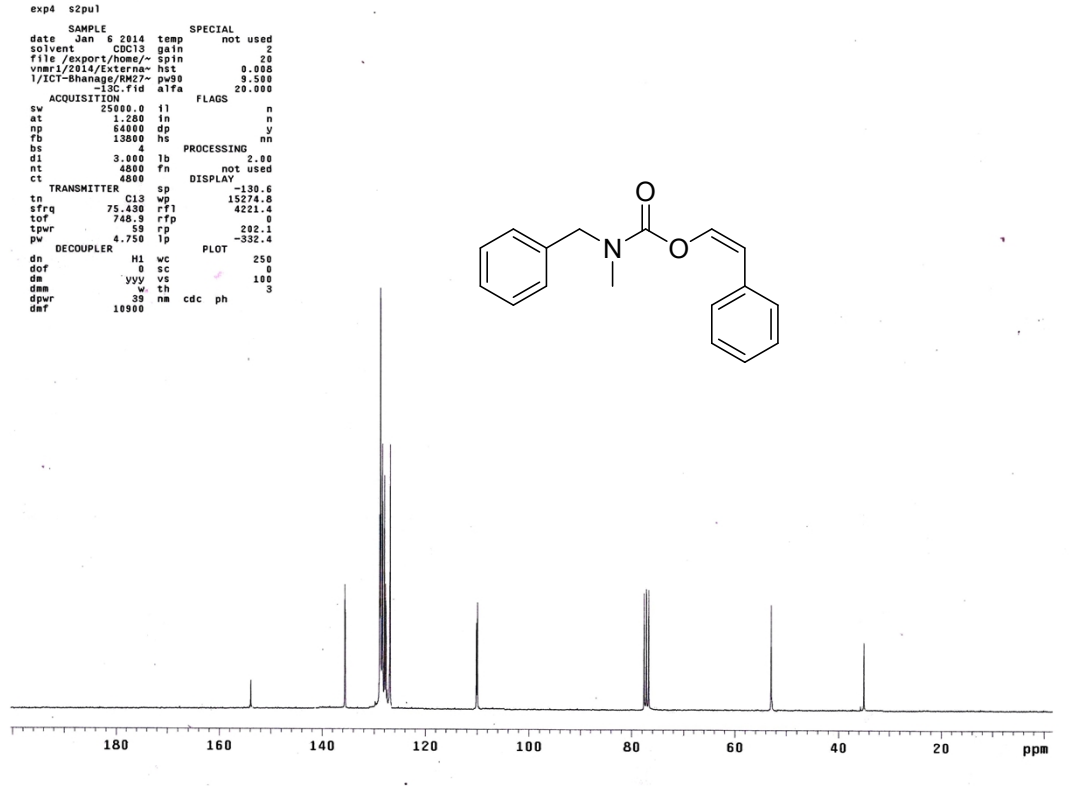
(Z)-4-methylstyryl diethylcarbamate





(Z)-styryl benzyl(methyl)carbamate





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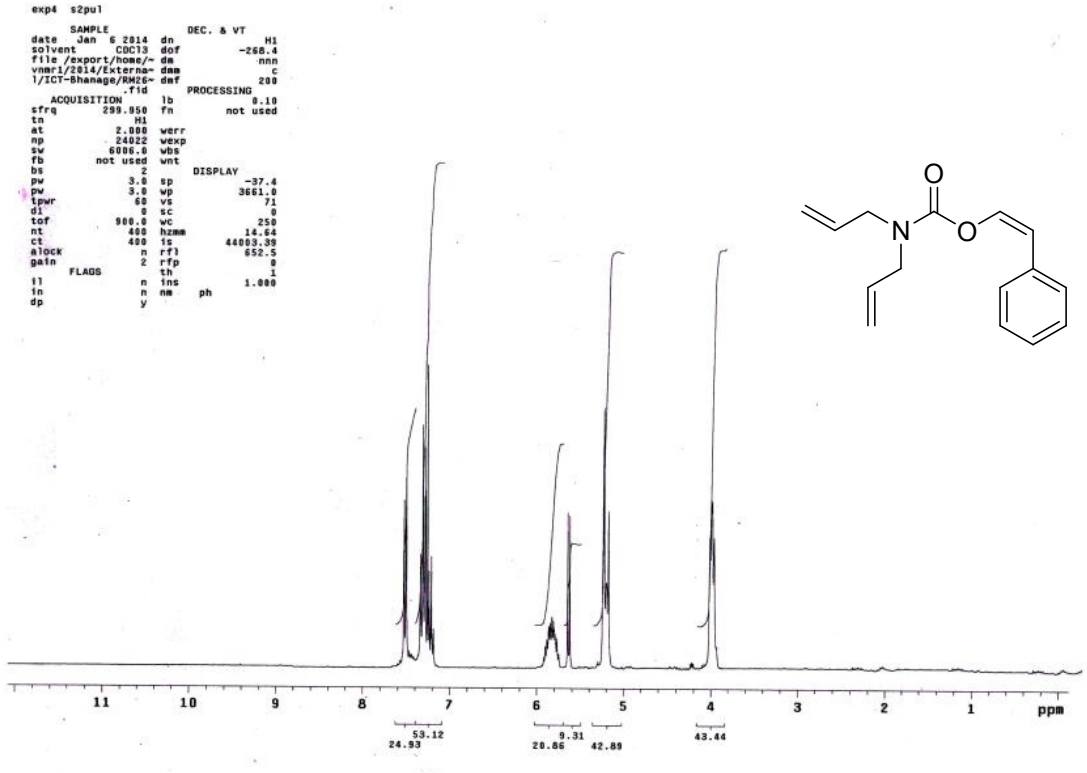
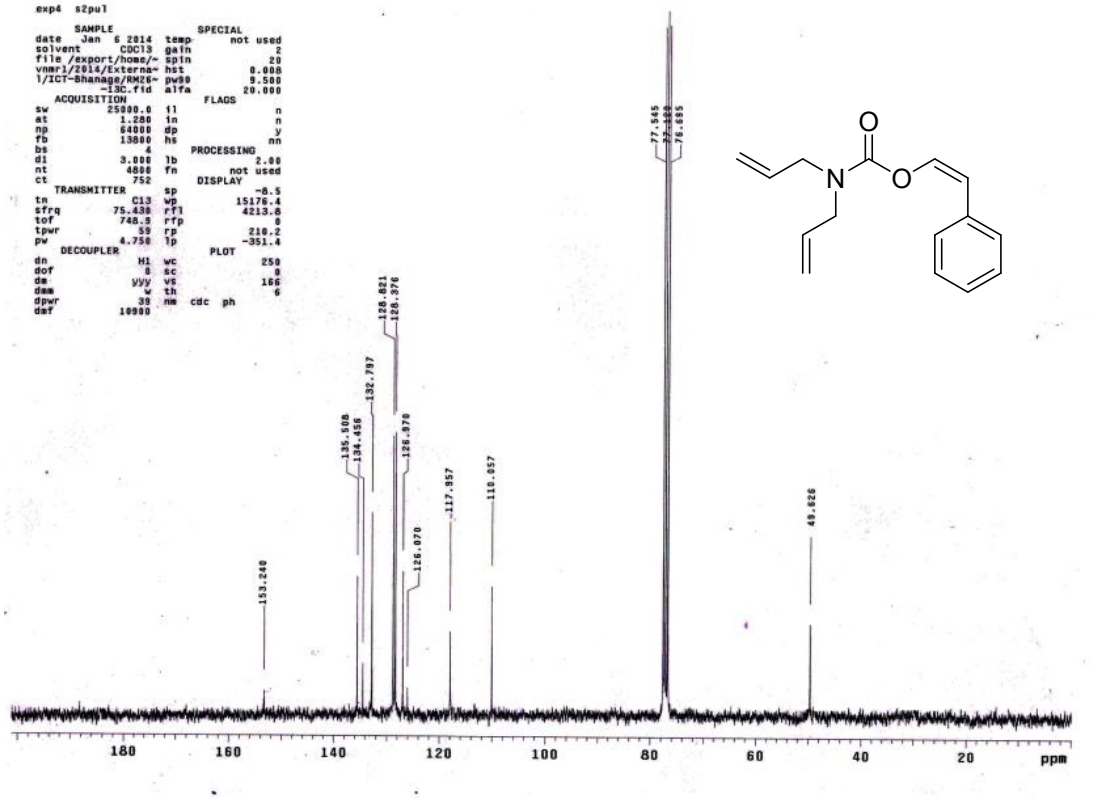
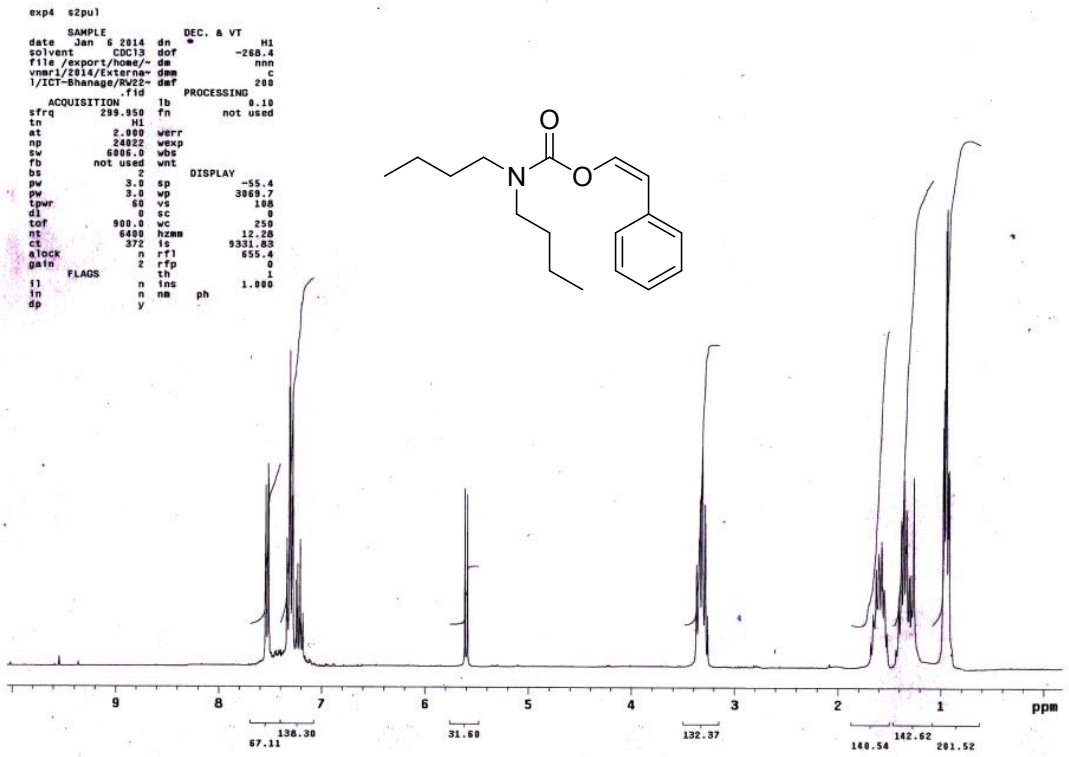
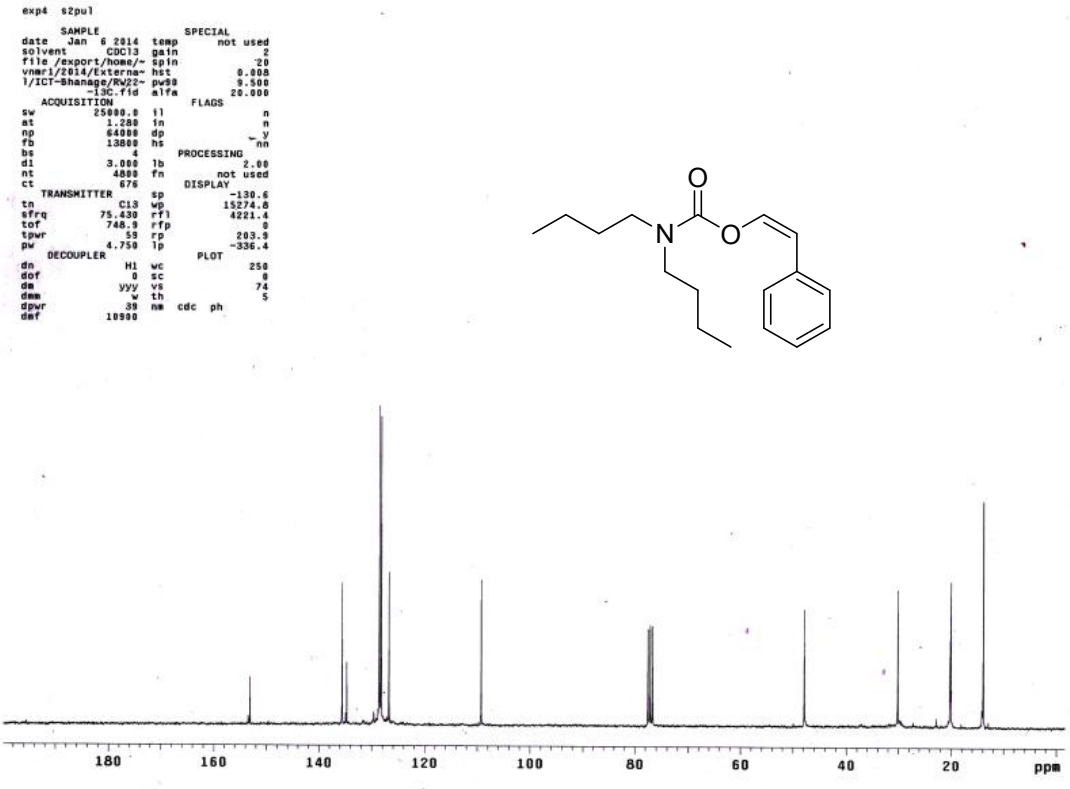


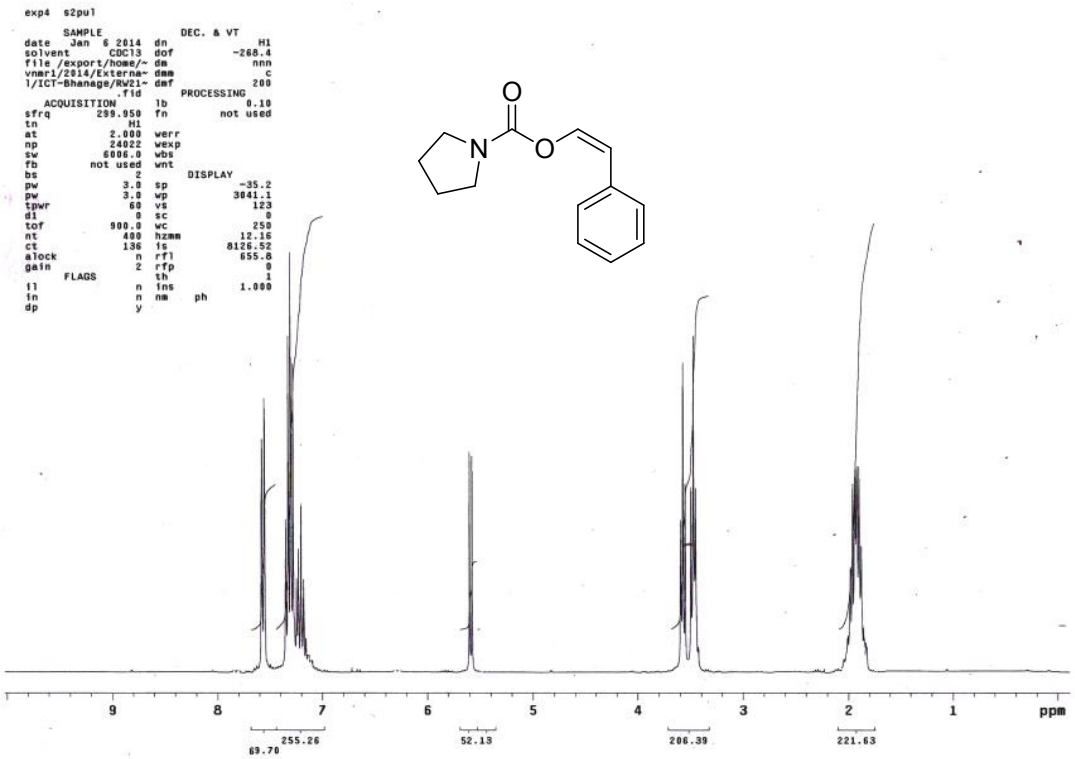


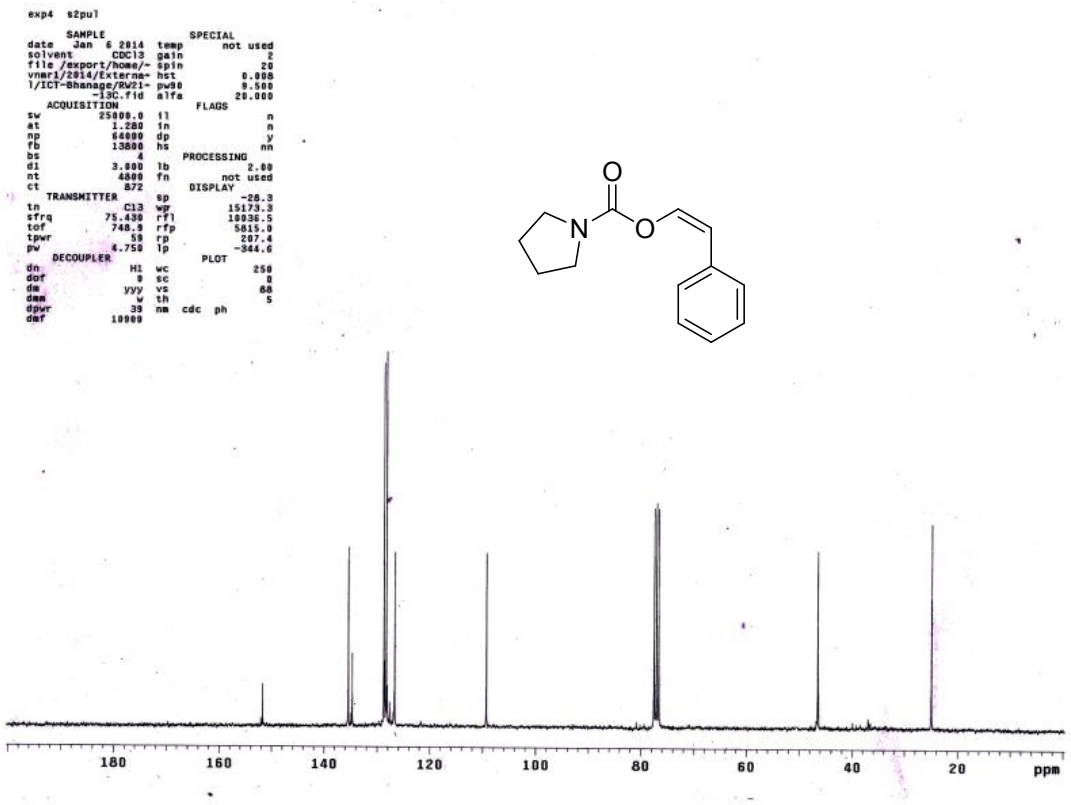
(Z)-styryl dibutylcarbamate



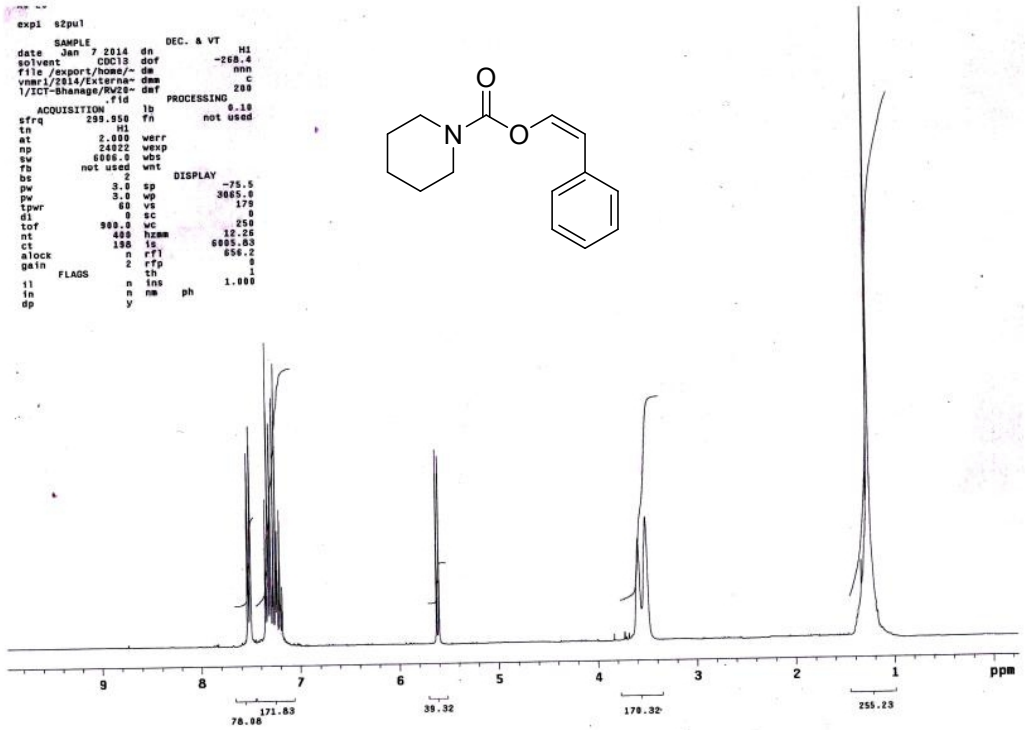


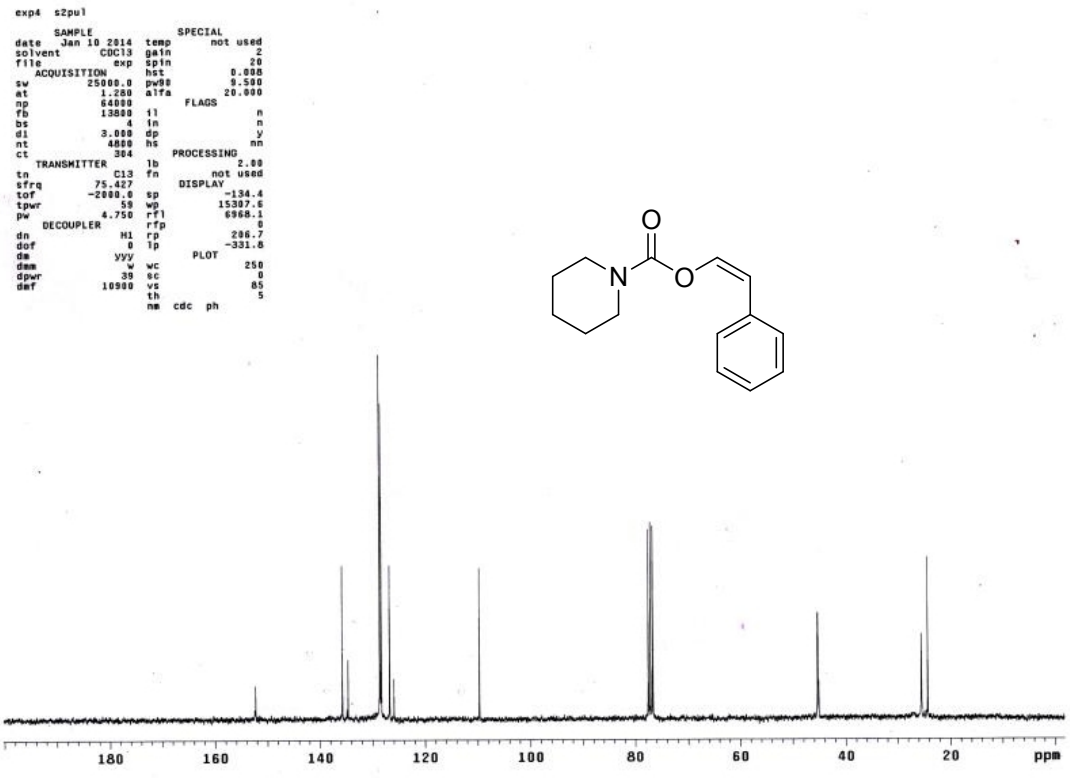
(Z)-styryl pyrrolidine-1-carboxylate





(Z)-styryl piperidine-1-carboxylate





3. References

1] Y. P. Patil, P. J. Tambade, N. S. Nandurkar and B. M. Bhanage, *Cata. Comm*., 2008, **9**, 2068.

2] K. Melis, P. Samulkiewicz, J. Rynkowski and F. Verpoort, *Tetrahedron Lett.,* 2002, **43**, 2713–2716.

3] M. S. Brookhart, J. R. Tucker and G. R. Husk, *J. Am. Chem. Soc*., 1983, **105**, 258.