Supplementary Material (ESI) for Organic & Biomolecular Chemistry

High-yielding Synthesis of Nefopam Analogues (Functionalized Benzoxazocines) by Sequential One-pot Cascade Operations

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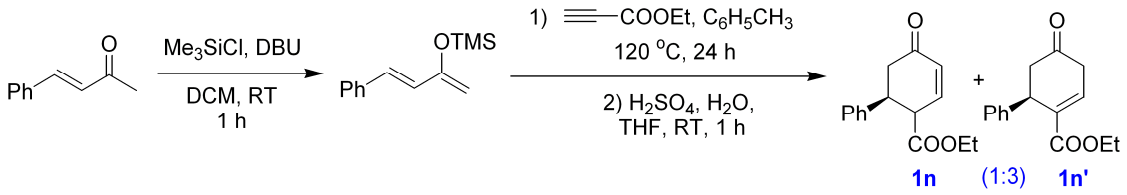
General Methods: The ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively. The chemical shifts are reported in ppm downfield to TMS (δ = 0) for ^{1}H NMR and relative to the central $CDCl_3$ resonance (δ = 77.0) for ^{13}C NMR. *In the ^{13}C NMR spectra, the nature of the carbons (C, CH, CH_2 or CH_3) was determined by recording the DEPT-135 experiment, and is given in parentheses.* The coupling constants *J* are given in Hz. Column chromatography was performed using Acme's silica gel (particle size 0.063-0.200 mm). High-resolution mass spectra were recorded on micromass ESI-TOF MS. GCMS mass spectrometry was performed on Shimadzu GCMS-QP2010 mass spectrometer. IR spectra were recorded on JASCO FT/IR-5300. Elemental analyses were recorded on a Thermo Finnigan Flash EA 1112 analyzer. Mass spectra were recorded on either VG7070H mass spectrometer using EI technique or Shimadzu-LCMS-2010 A mass spectrometer. The X-ray diffraction measurements were carried out at 298 K on an automated Enraf-Nonious MACH 3 diffractometer using graphite monochromated, Mo-Kα (λ = 0.71073 Å) radiation with CAD4 software or the X-ray intensity data were measured at 298 K on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a Mo-Kα fine-focus sealed tube (λ = 0.71073 Å). For thin-layer chromatography (TLC), silica gel plates Merck 60 F254 were used and compounds were visualized by irradiation with UV light and/or by

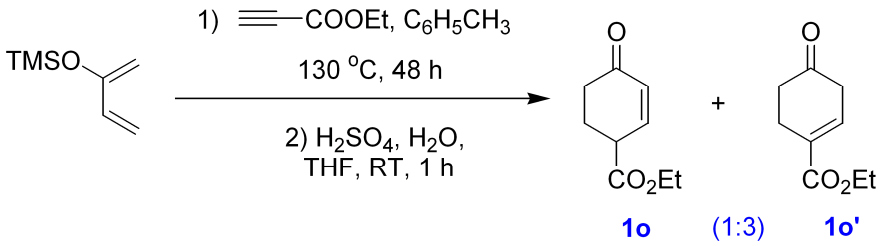
treatment with a solution of *p*-anisaldehyde (23 mL), conc. H_2SO_4 (35 mL), acetic acid (10 mL), and ethanol (900 mL) followed by heating.

Materials: All solvents and commercially available chemicals were used as received. Hagemann's esters **1a-m** was prepared from alkyl acetoacetates and aldehydes with high yields in one-step according to our recent modified method.[1] Hagemann's ester **1n** was prepared from benzylidene acetone with high yield in two-steps according to literature procedures (see Scheme S1).[2] Hagemann's ester **1o** was prepared from trimethyl-(1-methylene-allyloxy)-silane and propynoic acid ethyl ester with high yield in two-steps according to literature procedure (see Scheme S2).[2c]

Scheme S1. Synthesis of Hagemann's ester **1n**



Scheme S2. Synthesis of Hagemann's ester **1o**



General Experimental Procedures for the Synthesis of Highly Functionalized 5,6-Dihyro-2*H*-Benzo[b][1,4]oxazocines: The syntheses of highly functionalized 5,6-dihyro-2*H*-Benzo[b][1,4]oxazocines from corresponding Hagemann's esters involves the following three-steps.

Piperidine/K_2CO_3-Catalyzed Three-Component Enamine Amination/Iso-Aromatization/*O*-Allylation Reactions in One-Pot: In an ordinary glass vial equipped with a magnetic stirring bar, to 1.0 mmol of the Hagemann's esters **1** was added 2.0 mL of solvent, and then the catalyst piperidine **3a** (0.05 mmol, 4.95 μL) was added and the reaction mixture was stirred at 25 °C for the 0.5 h; then 0.5 mmol of nitrosobenzene **2a** was added in one-portion and the reaction mixture was stirred at 25 °C for 1 h. To the reaction mixture, allyl bromide (181.5 mg, 1.5 mmol) and K_2CO_3 (345.5 mg, 2.5 mmol) was added and stirring continued at RT for 24 h. The crude reaction mixture was worked up with aqueous NH_4Cl solution and the aqueous layer was extracted with dichloromethane (2 x 20 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure one-pot products **5** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

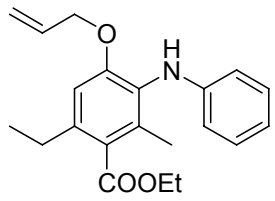
***N*-Allylation:** At 0 °C, to a suspension of sodium hydride (14.4 mg, 0.6 mmol, 3.0 equiv.), in DMF (2 ml, 0.1 M) were added monoene amine **5** (0.2 mmol). After being stirred for 5 min, allyl bromide (48.39 mg, 0.4 mmol, 2.0 equiv.) is added to the reaction mixture at 0 °C, and then the reaction mixture was stirred for 3 to 5 h from 0 °C to RT. The reaction mixture poured into saturated NH_4Cl solution and extracted with DCM (2 x 15 mL). The combined DCM extracts were washed with brine, dried over Na_2SO_4, and evaporated to dryness. Purification of residue by column chromatography (silica gel, mixture of hexane/ethyl acetate) gave **6**.

RCM Reaction: A 10 ml oven-dried round bottom flask equipped with a stir bar was charged with diene amine **6** or enyne amine **10** (0.1 mmol), CH_2Cl_2 (2 ml, 0.05 M) and first generation Grubb's catalyst **3b** (4.11 mg, 0.005 mmol, 5 mol-%). The reaction mixture was stirred under N_2 at room temperature for 8 to 12 h. Solvent CH_2Cl_2 were distilled off at ambient pressure and the RCM products **7** and **12** were purified by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Experimental Procedure for the Cascade Synthesis of Functionalized Heterocycles 12, 13, 14, 18 and 19 via RCM/Diels-Alder Reactions: A 10 ml oven-dried round bottom flask equipped with a stir bar was charged with enyne amine **10** or **16** (0.1 mmol), CH_2Cl_2 (2 ml, 0.05 M) and first generation Grubb's catalyst **3b** (4.11 mg, 0.005 mmol, 5

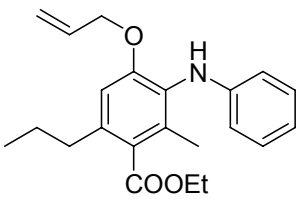
mol-%). The reaction mixture was stirred under N_2 at room temperature for 8 to 12 h. Solvent CH_2Cl_2 were distilled off at ambient pressure and to the crude reaction mixture, *N*-phenylmaleimide (207.8 mg, 0.12 mmol, 1.2 equiv.) or diethyl acetylenedicarboxylate (0.12 mmol, 1.2 equiv) and anhydrous toluene (0.6 ml) were added and heated at 110-120 °C under N_2 in a sealed glass tube for 21 h. The toluene was removed and the residue was purified by column chromatography (silica gel, mixture of hexane/ethyl acetate) to gave **12, 13, 14, 18 and 19** respectively (see Scheme 3).

4-Allyloxy-6-ethyl-2-methyl-3-phenylamino-benzoic acid ethyl ester (5ea): Purified



5ea

by column chromatography using EtOAc/hexane and isolated as a light yellow solid. IR (neat): ν_{max} 3372 (N-*H)*, 2971, 1719 (O-C=O), 1600, 1497, 1281, 1176, 1054, 748 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.16 (2H, t, *J* = 7.6 Hz), 6.78 (1H, t, *J* = 7.2 Hz), 6.65 (1H, s, Ar-*H*), 6.62 (2H, d, *J* = 8.4 Hz), 5.95-5.88 (1H, m, olefinic-*H*), 5.63 (1H, s, N-*H*), 5.26 (1H, dd, *J* = 17.2 Hz, 1.6 Hz, olefinic-*H*), 5.19 (1H, dd, *J* = 10.4 Hz, 1.2 Hz, olefinic-*H*), 4.51 (2H, d, *J* = 5.2 Hz, $OCH_2CH{=}CH_2$), 4.38 (2H, q, *J* = 7.2 Hz, OCH_2CH_3), 2.62 (2H, q, *J* = 7.2 Hz, $ArCH_2CH_3$), 2.13 (3H, s, Ar-CH_3), 1.38 (3H, t, *J* = 7.2 Hz, $ArCH_2CH_3$), 1.23 (3H, t, *J* = 7.2 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 170.0 (C, O-C=O), 153.6 (C), 146.2 (C), 138.3 (C), 132.9 (CH), 132.5 (C), 129.0 (2 x CH), 127.8 (C), 127.6 (C), 119.1 (CH), 117.5 (CH_2, $CH{=}CH_2$), 115.0 (2 x CH), 110.5 (CH), 69.2 (CH_2, $OCH_2CH{=}CH_2$), 61.0 (CH_2, OCH_2CH_3), 27.0 (CH_2, $ArCH_2CH_3$), 15.7 (CH_3, Ar-CH_3), 15.6 (CH_3, $ArCH_2CH_3$), 14.3 (CH_3, OCH_2CH_3); LRMS m/z 339.45 (M^+), calcd $C_{21}H_{25}NO_3$ 339.1834.

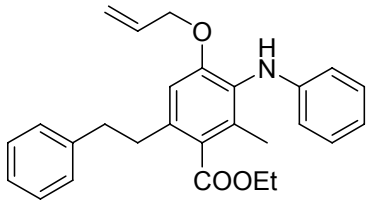


5fa

4-Allyloxy-2-methyl-3-phenylamino-6-propyl-benzoic acid ethyl ester (5fa): Purified by column chromatography using EtOAc/hexane and isolated as a light yellow solid. IR (neat): ν_{max} 3373 (N-*H)*, 2966, 1721 (O-C=O), 1600, 1496, 1464, 1266, 1096, 949, 748 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.18 (2H, t, *J* = 7.6 Hz), 6.80 (1H, t, *J* = 7.2 Hz), 6.64 (1H, s, Ar-*H*), 6.63 (2H, d, *J* = 9.2 Hz), 5.97-5.90

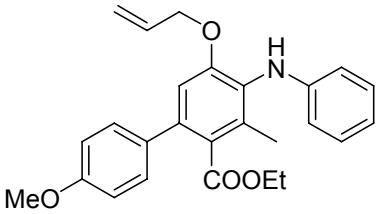
(1H, m, olefinic-*H*), 5.59 (1H, s, N-*H*), 5.27 (1H, d, *J* = 17.6 Hz, olefinic-*H*), 5.21 (1H, d, *J* = 10.8 Hz, olefinic-*H*), 4.51 (2H, d, *J* = 5.2 Hz, OC*H*$_2$CH=CH$_2$), 4.40 (2H, q, *J* = 6.8 Hz, OC*H*$_2$CH$_3$), 2.58 (2H, t, *J* = 7.2 Hz, ArC*H*$_2$CH$_2$CH$_3$), 2.15 (3H, s, Ar-C*H*$_3$), 1.68-1.63 (2H, m, ArCH$_2$C*H*$_2$CH$_3$), 1.40 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$), 0.98 (3H, t, *J* = 7.2 Hz, ArCH$_2$CH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 169.9 (C, O-C=O), 153.4 (C), 146.1 (C), 136.8 (C), 132.8 (CH), 132.4 (C), 128.9 (2 x CH), 128.6 (C), 127.8 (C), 119.0 (CH), 117.4 (CH$_2$, CH=*CH*$_2$), 114.9 (2 x CH), 111.1 (CH), 69.2 (CH$_2$, O*CH*$_2$CH=CH$_2$), 60.9 (CH$_2$, O*CH*$_2$CH$_3$), 36.0 (CH$_2$, ArCH$_2$CH$_2$CH$_3$), 24.6 (CH$_2$, ArCH$_2$CH$_2$CH$_2$CH$_3$), 15.7 (CH$_3$, Ar-*CH*$_3$), 14.2 (CH$_3$, OCH$_2$*CH*$_3$), 14.0 (CH$_3$, ArCH$_2$CH$_2$*CH*$_3$); LRMS m/z 354.00 (M+H$^+$), calcd C$_{22}$H$_{27}$NO$_3$ 353.1991.

4-Allyloxy-2-methyl-6-phenethyl-3-phenylamino-benzoic acid ethyl ester (5ga):



5ga

Purified by column chromatography using EtOAc/hexane and isolated as light yellow oil. IR (neat): ν$_{max}$ 3360 (N-*H*), 2933, 1708 (O-C=O), 1597, 1493, 1263, 1053, 747, 698 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.29 (2H, t, *J* = 7.2 Hz), 7.22-7.16 (5H, m, Ph-*H*), 6.81 (1H, t, *J* = 7.2 Hz), 6.63 (2H, d, *J* = 7.6 Hz), 6.51 (1H, s, Ar-*H*), 5.90-5.85 (1H, m, olefinic-*H*), 5.59 (1H, s, N-*H*), 5.24 (1H, d, *J* = 17.2 Hz, olefinic-*H*), 5.19 (1H, d, *J* = 10.8 Hz, olefinic-*H*), 4.40 (2H, d, *J* = 7.2 Hz, OC*H*$_2$CH=CH$_2$), 4.40 (2H, q, *J* = 7.2 Hz, OC*H*$_2$CH$_3$), 2.94-2.88 (4H, m), 2.16 (3H, s, Ar-C*H*$_3$), 1.40 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 169.3 (C, O-C=O), 153.3 (C), 146.1 (C), 141.6 (C), 135.8 (C), 132.8 (CH), 132.6 (C), 128.9 (2 x CH), 128.5 (2 x CH), 128.4 (2 x CH), 128.3 (C), 128.1 (C), 126.0 (CH), 119.2 (CH), 117.5 (CH$_2$, CH=*CH*$_2$), 115.1 (2 x CH), 111.4 (CH), 69.2 (CH$_2$, O*CH*$_2$CH=CH$_2$), 61.0 (CH$_2$, O*CH*$_2$CH$_3$), 37.8 (CH$_2$), 36.2 (CH$_2$), 15.7 (CH$_3$, Ar-*CH*$_3$), 14.3 (CH$_3$, OCH$_2$*CH*$_3$); LRMS m/z 416.45 (M+H$^+$), calcd for C$_{27}$H$_{29}$NO$_3$ 415.2147.

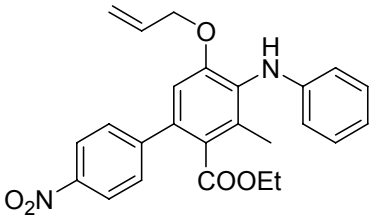


5ia

5-Allyloxy-4'-methoxy-3-methyl-4-phenylamino-biphenyl-2-carboxylic acid ethyl ester (5ia): Purified by column chromatography using EtOAc/hexane and isolated as a light yellow solid. IR (neat): ν$_{max}$ 3054, 1724 (O-C=O), 1608, 1580, 1498, 1263, 1057, 737, 704 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.35 (2H, d, *J* = 8.8 Hz), 7.22 (2H, t, *J* = 7.6 Hz), 6.95 (2H, d, *J*

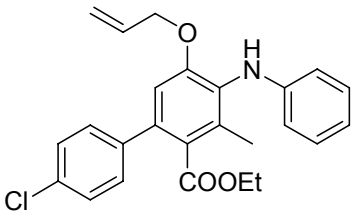
= 8.4 Hz), 6.84 (1H, t, *J* = 7.2 Hz), 6.78 (1H, s, Ar-*H*), 6.71 (2H, d, *J* = 8.4 Hz), 5.98-5.91 (1H, m, olefinic-*H*), 5.74 (1H, s, N-*H*), 5.29 (1H, dd, *J* = 17.2 Hz, 1.6 Hz, olefinic-*H*), 5.23 (1H, dd, *J* = 10.8 Hz, 1.6 Hz, olefinic-*H*), 4.55 (2H, d, *J* = 4.8 Hz, OC*H*$_2$CH=CH$_2$), 4.12 (2H, q, *J* = 7.2 Hz, OC*H*$_2$CH$_3$), 3.85 (CH$_3$, s, OC*H*$_3$), 2.05 (3H, s, Ar-C*H*$_3$), 1.04 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 169.8 (C, O-C=O), 159.0 (C), 153.0 (C), 145.8 (C), 136.7 (C), 133.5 (C), 132.7 (CH), 132.6 (C), 129.4 (2 x CH), 128.9 (C), 128.9 (2 x CH), 127.4 (C), 119.4 (CH), 117.6 (CH$_2$, CH=*CH*$_2$), 115.3 (2 x CH), 113.6 (2 x CH), 111.5 (CH), 69.2 (CH$_2$, O*CH*$_2$CH=CH$_2$), 60.8 (CH$_2$, O*CH*$_2$CH$_3$), 55.3 (CH$_3$, O*CH*$_3$), 15.7 (CH$_3$, Ar-*CH*$_3$), 13.8 (CH$_3$, OCH$_2$C*H*$_3$); LCMS m/z 417.80 (M+H$^+$), calcd for $C_{26}H_{27}NO_4$ 417.1940.

5-Allyloxy-3-methyl-4'-nitro-4-phenylamino-biphenyl-2-carboxylic acid ethyl ester (5ja): Purified by column chromatography using EtOAc/hexane and isolated as a light yellow solid. IR (neat): ν$_{max}$ 3387 (N-*H*), 2976, 1727 (O-C=O), 1598, 1515, 1473, 1258, 1056, 743, 702 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.26 (2H, d, *J* = 8.8 Hz), 7.57 (2H, d, *J* = 8.8 Hz), 7.23 (2H, t, *J* = 7.6 Hz), 6.88 (1H, t, *J* = 7.2 Hz), 6.79 (1H, s, Ar-*H*), 6.73 (2H, d, *J* = 8.4 Hz), 6.02-5.92 (1H, m, olefinic-*H*), 5.88 (1H, s, N-*H*), 5.31 (1H, d, *J* = 17.6 Hz, olefinic-*H*), 5.26 (1H, d, *J* = 10.8 Hz, olefinic-*H*), 4.59 (2H, d, *J* = 5.2 Hz, OC*H*$_2$CH=CH$_2$), 4.09 (2H, q, *J* = 7.2 Hz, OC*H*$_2$CH$_3$), 2.22 (3H, s, Ar-C*H*$_3$), 1.03 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 169.1 (C, O-C=O), 153.0 (C), 148.0 (C), 147.0 (C), 145.2 (C), 134.4 (C), 132.8 (C), 132.4 (CH), 130.8 (C), 129.2 (2 x CH), 129.1 (2 x CH), 127.4 (C), 123.5 (2 x CH), 120.0 (CH), 118.0 (CH$_2$, CH=*CH*$_2$), 115.8 (2 x CH), 111.2 (CH), 69.5 (CH$_2$, O*CH*$_2$CH=CH$_2$), 61.2 (CH$_2$, O*CH*$_2$CH$_3$), 16.2 (CH$_3$, Ar-*CH*$_3$), 13.8 (CH$_3$, OCH$_2$C*H*$_3$); LCMS m/z 433.35 (M+H$^+$), calcd for $C_{25}H_{24}N_2O_5$ 432.1685.



5ja

5-Allyloxy-4'-chloro-3-methyl-4-phenylamino-biphenyl-2-carboxylic acid ethyl ester (5ka): Purified by column chromatography using EtOAc/hexane and isolated as a light yellow solid. IR (neat): ν$_{max}$ 3352 (N-*H*), 2985, 1705 (O-C=O), 1601, 1494, 1277, 1059, 745 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.38 (2H, d, *J* = 8.4



5ka

Hz), 7.34 (2H, d, *J* = 8.4 Hz), 7.22 (2H, t, *J* = 7.6 Hz), 6.86 (1H, t, *J* = 7.2 Hz), 6.76 (1H, s, Ar-*H*), 6.72 (2H, d, *J* = 8.4 Hz), 5.99-5.92 (1H, m, olefinic-*H*), 5.78 (1H, s, N-*H*), 5.29 (1H, d, *J* = 17.6 Hz, olefinic-*H*), 5.24 (1H, d, *J* = 10.4 Hz, olefinic-*H*), 4.56 (2H, d, *J* = 5.2 Hz, OC*H*$_2$CH=CH$_2$), 4.09 (2H, q, *J* = 7.2 Hz, OC*H*$_2$CH$_3$), 2.22 (3H, s, Ar-C*H*$_3$), 1.03 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 169.4 (C, O-C=O), 153.0 (C), 145.5 (C), 139.6 (C), 135.6 (C), 133.4 (C), 132.7 (C), 132.6 (CH), 129.7 (C), 129.6 (2 x CH), 129.0 (2 x CH), 128.4 (2 x CH), 127.4 (C), 119.6 (CH), 117.8 (CH$_2$, CH=*CH*$_2$), 115.5 (2 x CH), 111.3 (CH), 69.3 (CH$_2$, O*CH*$_2$CH=CH$_2$), 61.0 (CH$_2$, O*CH*$_2$CH$_3$), 15.9 (CH$_3$, Ar-*CH*$_3$), 13.7 (CH$_3$, OCH$_2$C*H*$_3$); LCMS m/z 420.90 (M$^+$), calcd for $C_{25}H_{24}ClNO_3$ 421.1445.

4-Allyloxy-6-benzo[1,3]dioxol-5-yl-2-methyl-3-phenylamino-benzoic acid ethyl ester (5la): Purified by column chromatography using EtOAc/hexane and isolated as a liquid. IR (neat): ν$_{max}$ 3316 (N-*H*), 2982, 1713 (O-C=O), 1599, 1494, 1236, 1039, 754, 661 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.21 (2H, t, *J* = 7.6 Hz), 6.90 (1H, d, *J* = 1.2 Hz), 6.86 (3H, m), 6.75 (1H, s), 6.70 (2H, d, *J* = 7.6 Hz), 5.99 (2H, s, OC*H*$_2$O), 5.98-5.91 (1H, m, olefinic-*H*), 5.74 (1H, s, N-*H*), 5.28 (1H, dd, *J* = 16.8 Hz, 1.2 Hz, olefinic-*H*), 5.22 (1H, dd, *J* = 10.4 Hz, 1.2 Hz, olefinic-*H*), 4.55 (2H, d, *J* = 5.2 Hz, OC*H*$_2$CH=CH$_2$), 4.13 (2H, q, *J* = 7.2 Hz, OC*H*$_2$CH$_3$), 2.19 (3H, s, Ar-C*H*$_3$), 1.09 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 169.7 (C, O-C=O), 152.9 (C), 147.5 (C) 146.9 (C), 145.7 (C), 136.5 (C), 135.0 (C), 132.6 (CH), 132.5 (C), 129.2 (C), 129.0 (2 x CH), 127.5 (C), 121.8 (CH), 119.5 (CH), 117.7 (CH$_2$, CH=*CH*$_2$), 115.4 (2 x CH), 111.4 (CH), 108.9 (CH), 108.1 (CH), 101.2 (CH$_2$, O*CH*$_2$O), 69.3 (CH$_2$, O*CH*$_2$CH=CH$_2$), 60.9 (CH$_2$, O*CH*$_2$CH$_3$), 15.8 (CH$_3$, Ar-*CH*$_3$), 13.9 (CH$_3$, OCH$_2$*CH*$_3$); LCMS m/z 430.50 (M-H$^+$), calcd for $C_{26}H_{25}NO_5$ 431.1733.

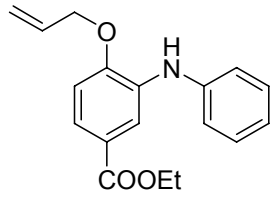
5la

4-Allyloxy-6-furan-2-yl-2-methyl-3-phenylamino-benzoic acid ethyl ester (5ma): Purified by column chromatography using EtOAc/hexane and isolated as a light yellow solid. IR (neat): ν$_{max}$ 3387 (N-*H*), 3054, 1723 (O-C=O), 1599, 1497, 1265, 1057, 737, 703 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.47 (1H, d, *J* = 1.6 Hz), 7.21 (2H, t, *J* =

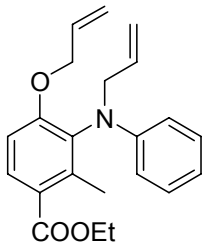
5ma

7.6 Hz), 7.08 (1H, s, Ar-*H*), 6.85 (1H, t, *J* = 7.2 Hz), 6.69 (2H, d, *J* = 8.4 Hz), 6.52 (1H, d, *J* = 3.2 Hz), 6.47 (1H, dd, *J* = 3.2 Hz, 2.0 Hz), 6.02-5.92 (1H, m, olefinic-*H*), 5.79 (1H, s, N-*H*), 5.31 (1H, d, *J* = 17.6 Hz, olefinic-*H*), 5.24 (1H, d, *J* = 10.4 Hz, olefinic-*H*), 4.59 (2H, d, *J* = 4.8 Hz, OC*H*$_2$CH=CH$_2$), 4.35 (2H, q, *J* = 7.2 Hz, OC*H*$_2$CH$_3$), 2.16 (3H, s, Ar-C*H*$_3$), 1.30 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 169.8 (C, O-C=O), 152.8 (C), 152.2 (C), 145.4 (C), 142.2 (CH), 132.6 (CH), 132.0 (C), 129.9 (C), 129.0 (2 x CH), 125.5 (C), 124.6 (C), 119.7 (CH), 117.8 (CH$_2$, CH=*CH*$_2$), 115.7 (2 x CH), 111.6 (CH), 108.3 (CH), 107.0 (CH), 69.4 (CH$_2$, O*CH*$_2$CH=CH$_2$), 61.3 (CH$_2$, O*CH*$_2$CH$_3$), 15.6 (CH$_3$, Ar-*CH*$_3$), 14.1 (CH$_3$, OCH$_2$C*H*$_3$); LCMS m/z 378.10 (M+H$^+$), calcd for $C_{23}H_{23}NO_4$ 377.1627.

4-Allyloxy-3-phenylamino-benzoic acid ethyl ester (5oa): Purified by column chromatography using EtOAc/hexane and isolated as light yellow liquid. IR (neat): ν$_{max}$ 3387 (N-*H*), 1701 (O-C=O), 1673, 1592, 1247, 1020, 761, 664 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.97 (1H, d, *J* = 2.0 Hz), 7.56 (1H, dd, *J* = 8.4 Hz, 2.0 Hz), 7.32 (2H, t, *J* = 7.2 Hz), 7.19 (2H, d, *J* = 7.6 Hz), 6.99 (1H, t, *J* = 7.2 Hz), 6.88 (1H, d, *J* = 8.4 Hz), 6.20 (1H, s, N-*H*), 6.12-6.04 (1H, m, olefinic-*H*), 5.43 (1H, dd, *J* = 17.2 Hz, 1.2 Hz, olefinic-*H*), 5.34 (1H, dd, *J* = 10.8 Hz, 1.2 Hz, olefinic-*H*), 4.67 (2H, d, *J* = 4.8 Hz, OC*H*$_2$CH=CH$_2$), 4.32 (2H, q, *J* = 7.2 Hz, OC*H*$_2$CH$_3$), 1.36 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 166.6 (C, O-C=O), 150.5 (C), 142.0 (C), 133.1 (C), 132.5 (CH), 129.4 (2 x CH), 123.3 (C), 121.9 (CH), 121.8 (CH), 119.0 (2 x CH), 118.4 (CH$_2$, CH=*CH*$_2$), 115.0 (CH), 110.8 (CH), 69.5 (CH$_2$, O*CH*$_2$CH=CH$_2$), 60.6 (CH$_2$, O*CH*$_2$CH$_3$), 14.4 (CH$_3$, OCH$_2$C*H*$_3$); LRMS m/z 298.05 (M+H$^+$), calcd for $C_{18}H_{19}NO_3$ 297.1365.



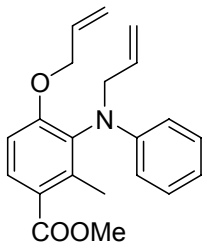
5oa



6aa

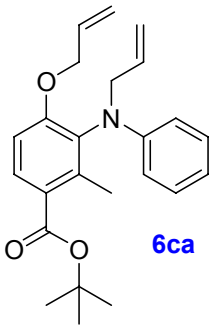
4-Allyloxy-3-(allyl-phenyl-amino)-2-methyl-benzoic acid ethyl ester (6aa): Purified by column chromatography using EtOAc/hexane and isolated as a light yellow liquid. IR (neat): ν$_{max}$ 3084, 2980, 1714 (O-C=O), 1599, 1500, 1161, 1068, 748, 692 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.93 (1H, d, *J* = 8.8 Hz), 7.17 (2H, t, *J* = 7.6 Hz), 6.85 (1H, d, *J* = 8.8 Hz), 6.72 (1H, t, *J* = 7.2 Hz), 6.52 (2H, d, *J* = 8.0 Hz), 6.04-5.97 (1H,

m, olefinic-*H*), 5.88-5.81 (1H, m, olefinic-*H*), 5.30-5.12 (4H, m, olefinic-*H*), 4.52 (2H, d, *J* = 4.8 Hz, OC*H*$_2$CH=CH$_2$), 4.38 (2H, q, *J* = 7.2 Hz, OC*H*$_2$CH$_3$), 4.18 (2H, dABq, *J* = 18.0, 5.6 Hz, NC*H*$_2$CH=CH$_2$), 2.45 (3H, s, Ar-C*H*$_3$), 1.42 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.4 (C, O-C=O), 159.0 (C), 148.2 (C), 142.4 (C), 135.2 (CH), 134.4 (C), 132.4 (CH), 130.7 (CH), 128.8 (2 x CH), 123.8 (C), 117.7 (CH$_2$, CH=*CH*$_2$), 116.8 (CH), 116.6 (CH$_2$, CH=*CH*$_2$), 112.4 (2 x CH), 110.0 (CH), 68.7 (CH$_2$, O*CH*$_2$CH=CH$_2$), 60.5 (CH$_2$, O*CH*$_2$CH$_3$), 54.4 (CH$_2$, N*CH*$_2$CH=CH$_2$), 15.9 (CH$_3$, Ar-*CH*$_3$), 14.3 (CH$_3$, OCH$_2$*CH*$_3$); GCMS m/z 351.25 (M^+), calcd for $C_{22}H_{25}NO_3$ 351.4388.



6ba

4-Allyloxy-3-(allyl-phenyl-amino)-2-methyl-benzoic acid methyl ester (6ba): Purified by column chromatography using EtOAc/hexane and isolated as a light yellow liquid. IR (neat): ν_{max} 1718 (O-C=O), 1597, 1499, 1267, 1064, 749 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.87 (1H, d, *J* = 8.4 Hz), 7.13 (2H, t, *J* = 8.0 Hz), 6.81 (1H, d, *J* = 8.8 Hz), 6.68 (1H, t, *J* = 7.6 Hz), 6.48 (2H, d, *J* = 8.0 Hz), 6.00-5.94 (1H, m, olefinic-*H*), 5.86-5.78 (1H, m, olefinic-*H*), 5.26-5.08 (4H, m, olefinic-*H*), 4.49 (2H, d, *J* = 4.4 Hz, OC*H*$_2$CH=CH$_2$), 4.12 (2H, dABq, *J* = 17.2, 5.6 Hz, NC*H*$_2$CH=CH$_2$), 3.88 (CH$_3$, s, OC*H*$_3$), 2.44 (3H, s, Ar-C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.8 (C, O-C=O), 159.2 (C), 148.2 (C), 142.6 (C), 135.2 (CH), 134.4 (C), 132.4 (CH), 130.9 (CH), 128.8 (2 x CH), 123.4 (C), 117.7 (CH$_2$, CH=*CH*$_2$), 116.8 (CH), 116.6 (CH$_2$, CH=*CH*$_2$), 112.3 (2 x CH), 110.0 (CH), 68.7 (CH$_2$, O*CH*$_2$CH=CH$_2$), 54.4 (CH$_2$, N*CH*$_2$CH=CH$_2$), 51.7 (CH$_3$, O*CH*$_3$), 15.9 (CH$_3$, Ar-*CH*$_3$); LCMS m/z 337.35 (M^+), calcd for $C_{21}H_{23}NO_3$ 337.1678.

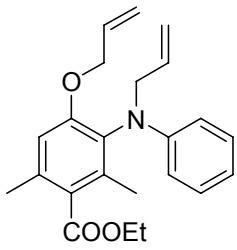


6ca

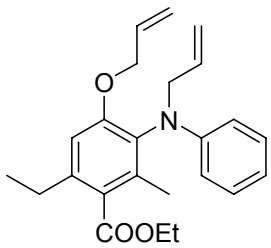
4-Allyloxy-3-(allyl-phenyl-amino)-2-methyl-benzoic acid *tert*-butyl ester (6ca): Purified by column chromatography using EtOAc/hexane and isolated as a light yellow liquid. IR (neat): ν_{max} 2977, 1709 (O-C=O), 1595, 1500, 1248, 1066, 747 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.81 (1H, d, *J* = 8.4 Hz), 7.13 (2H, t, *J* = 7.6 Hz), 6.80 (1H, d, *J* = 8.8 Hz), 6.68 (1H, t, *J* = 7.2 Hz), 6.49 (2H, d, *J* = 8.4 Hz), 6.04-5.94 (1H, m, olefinic-*H*), 5.85-5.78 (1H, m, olefinic-*H*), 5.27-5.09 (4H, m, olefinic-*H*), 4.48 (2H, d, *J* = 4.8 Hz, OC*H*$_2$CH=CH$_2$), 4.15 (2H, dABq, *J* = 17.2, 5.6 Hz,

NC*H*$_2$CH=CH$_2$), 2.41 (3H, s, Ar-C*H*$_3$), 1.60 (9H, s, C(C*H*$_3$)$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.0 (C, O-C=O), 158.7 (C), 148.2 (C), 141.7 (C), 135.3 (CH), 134.4 (C), 132.5 (CH), 130.5 (CH), 128.8 (2 x CH), 125.6 (C), 117.1 (CH_2, CH=*CH*$_2$), 116.7 (CH), 116.5 (CH_2, CH=*CH*$_2$), 112.3 (2 x CH), 109.9 (CH), 80.8 (C, *C*(CH$_3$)$_3$), 68.7 (CH_2, O*CH*$_2$CH=CH$_2$), 54.5 (CH_2, N*CH*$_2$CH=CH$_2$), 28.3 (3 x CH_3, C(*CH*$_3$)$_3$), 16.0 (CH_3, Ar-*CH*$_3$); LCMS m/z 379.60 ($M+H^+$), calcd $C_{24}H_{29}NO_3$ 379.2147.

4-Allyloxy-3-(allyl-phenyl-amino)-2,6-dimethyl-benzoic acid ethyl ester (6da): Purified by column chromatography using EtOAc/hexane and isolated as a solid. IR (neat): ν_{max} 2976, 1722 (O-C=O), 1601, 1500, 1271, 1186, 748 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.15 (2H, t, *J* = 7.2 Hz), 6.69 (1H, t, *J* = 7.2 Hz), 6.66 (1H, s, Ar-*H*), 6.53 (2H, d, *J* = 8.4 Hz), 6.03-5.96 (1H, m, olefinic-*H*), 5.87-5.80 (1H, m, olefinic-*H*), 5.30-5.12 (4H, m, olefinic-*H*), 4.45 (2H, d, *J* = 4.4 Hz, OC*H*$_2$CH=CH$_2$), 4.41 (2H, q, *J* = 7.2 Hz, OC*H*$_2$CH$_3$), 4.20 (2H, dABq, *J* = 16.0, 5.2 Hz, NC*H*$_2$CH=CH$_2$), 2.37 (3H, s, Ar-C*H*$_3$), 2.17 (3H, s, Ar-C*H*$_3$), 1.41 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 169.8 (C, O-C=O), 156.5 (C), 148.3 (C), 136.8 (C), 135.5 (CH), 134.8 (C), 132.8 (CH), 131.8 (C), 128.8 (2 x CH), 127.8 (C), 116.9 (CH_2, CH=*CH*$_2$), 116.6 (CH), 116.4 (CH_2, CH=*CH*$_2$), 112.9 (CH), 112.4 (2 x CH), 68.8 (CH_2, O*CH*$_2$CH=CH$_2$), 60.9 (CH_2, O*CH*$_2$CH$_3$), 54.6 (CH_2, N*CH*$_2$CH=CH$_2$), 20.2 (CH_3, Ar-*CH*$_3$), 15.5 (CH_3, Ar-*CH*$_3$), 14.3 (CH_3, OCH$_2$*CH*$_3$); GCMS m/z 365.15 (M^+), calcd $C_{23}H_{27}NO_3$ 365.4654.



6da

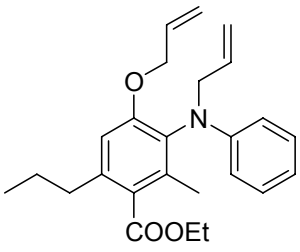


6ea

4-Allyloxy-3-(allyl-phenyl-amino)-6-ethyl-2-methyl-benzoic acid ethyl ester (6ea): Purified by column chromatography using EtOAc/hexane and isolated as a solid. IR (neat): ν_{max} 2975, 1720 (O-C=O), 1598, 1500, 1424, 1240, 1040, 743, 693 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.13 (2H, t, *J* = 8.0 Hz), 6.68 (1H, t, *J* = 8.0 Hz), 6.67 (1H, s, Ar-*H*), 6.51 (2H, d, *J* = 8.4 Hz), 6.02-5.95 (1H, m, olefinic-*H*), 5.85-5.78 (1H, m, olefinic-*H*), 5.28-5.11 (4H, m, olefinic-*H*), 4.45 (2H, d, *J* = 4.0 Hz, OC*H*$_2$CH=CH$_2$), 4.39 (2H, q, *J* = 7.2 Hz, OC*H*$_2$CH$_3$), 4.18 (2H, dABq, *J* = 16.4, 5.2 Hz, NC*H*$_2$CH=CH$_2$), 2.65 (2H, q, *J* = 7.6 Hz, ArC*H*$_2$CH$_3$), 2.14 (3H, s, Ar-C*H*$_3$), 1.39

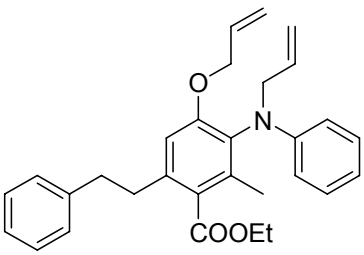
(3H, t, *J* = 7.2 Hz, OCH_2CH_3), 1.26 (3H, t, *J* = 7.2 Hz, $ArCH_2CH_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 169.9 (C, O-C=O), 156.6 (C), 148.3 (C), 140.8 (C), 136.5 (C), 135.5 (CH), 132.8 (CH), 131.9 (C), 128.8 (2 x CH), 127.4 (C), 116.9 (CH_2, CH=CH_2), 116.6 (CH), 116.3 (CH_2, CH=CH_2), 112.4 (2 x CH), 111.4 (CH), 68.8 (CH_2, $OCH_2CH=CH_2$), 61.0 (CH_2, OCH_2CH_3), 54.6 (CH_2, $NCH_2CH=CH_2$), 27.1 (CH_2, $ArCH_2CH_3$), 15.6 (CH_3, Ar-CH_3), 15.4 (CH_3, $ArCH_2CH_3$), 14.2 (CH_3, OCH_2CH_3); LCMS m/z 379.60 ($M+H^+$), calcd $C_{24}H_{29}NO_3$ 379.2147.

4-Allyloxy-3-(allyl-phenyl-amino)-2-methyl-6-propyl-benzoic acid ethyl ester (6fa): Purified by column chromatography using EtOAc/hexane and isolated as a solid. IR (neat): ν_{max} 2964, 1722 (O-C=O), 1597, 1500, 1460, 1272, 1045, 747, 691 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.13 (2H, t, *J* = 7.2 Hz), 6.67 (1H, t, *J* = 7.6 Hz), 6.65 (1H, s, Ar-*H*), 6.50 (2H, d, *J* = 8.4 Hz), 6.01-5.95 (1H, m, olefinic-*H*), 5.85-5.78 (1H, m, olefinic-*H*), 5.29-5.10 (4H, m, olefinic-*H*), 4.44 (2H, d, *J* = 2.4 Hz, $OCH_2CH=CH_2$), 4.39 (2H, q, *J* = 7.2 Hz, OCH_2CH_3), 4.14 (2H, dABq, *J* = 16.4, 5.2 Hz, $NCH_2CH=CH_2$), 2.59 (2H, dt, *J* = 7.6, 3.2 Hz, $ArCH_2CH_2CH_3$), 2.13 (3H, s, Ar-CH_3), 1.66 (2H, sextet, *J* = 7.6 Hz, $ArCH_2CH_2CH_3$), 1.39 (3H, t, *J* = 7.2 Hz, OCH_2CH_3), 0.98 (3H, t, *J* = 7.2 Hz, $ArCH_2CH_2CH_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 169.9 (C, O-C=O), 156.4 (C), 148.3 (C), 139.4 (C), 136.5 (C), 135.6 (CH), 132.8 (CH), 131.9 (C), 128.8 (2 x CH), 127.7 (C), 116.9 (CH_2, CH=CH_2), 116.6 (CH), 116.3 (CH_2, CH=CH_2), 112.4 (2 x CH), 112.0 (CH), 68.8 (CH_2, $OCH_2CH=CH_2$), 60.9 (CH_2, OCH_2CH_3), 54.6 (CH_2, $NCH_2CH=CH_2$), 36.2 (CH_2, $ArCH_2CH_2CH_3$), 24.5 (CH_2, $ArCH_2CH_2CH_3$), 15.4 (CH_3, Ar-CH_3), 14.3 (CH_3, OCH_2CH_3), 14.1 (CH_3, $ArCH_2CH_2CH_3$); LCMS m/z 393.85 ($M+H^+$), calcd $C_{25}H_{31}NO_3$ 393.2304.



6fa

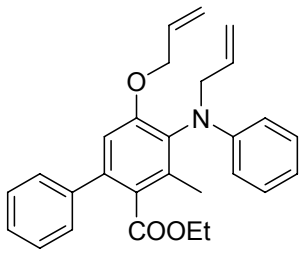
4-Allyloxy-3-(allyl-phenyl-amino)-2-methyl-6-phenethyl-benzoic acid ethyl ester (6ga): Purified by column chromatography using EtOAc/hexane and isolated as a yellow oil. IR (neat): ν_{max} 2979, 1722 (O-C=O), 1597, 1497, 1454, 1268, 1047, 748, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.30 (2H, t, *J* = 7.2 Hz), 7.22 (1H, t, *J* = 8.0 Hz), 7.19



6ga

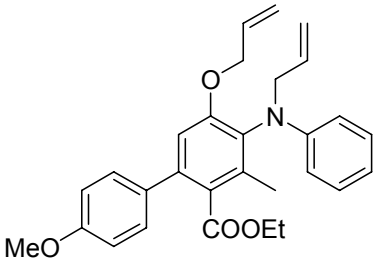
(2H, d, *J* = 8.4 Hz), 7.14 (2H, t, *J* = 7.2 Hz), 6.86 (1H, t, *J* = 7.2 Hz), 6.52 (1H, s, Ar-*H*), 6.51 (2H, d, *J* = 8.4 Hz), 5.99-5.94 (1H, m, olefinic-*H*), 5.78-5.74 (1H, m, olefinic-*H*), 5.26 (1H, dd, *J* = 17.2, 1.2 Hz, olefinic-*H*), 5.16-5.08 (3H, m, olefinic-*H*), 4.40 (2H, q, *J* = 7.2 Hz, OC*H*$_2$CH$_3$), 4.34 (2H, dd, *J* = 3.2, 1.0 Hz, OC*H*$_2$CH=CH$_2$), 4.14 (2H, dABq, *J* = 18.0, 5.6 Hz, NC*H*$_2$CH=CH$_2$), 2.93-2.90 (4H, m, PhC*H*$_2$C*H*$_2$Ar), 2.16 (3H, s, Ar-C*H*$_3$), 1.39 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 169.8 (C, O-C=O), 156.5 (C), 148.3 (C), 141.5 (C), 138.4 (C), 136.8 (C), 135.5 (CH), 132.8 (CH), 132.2 (C), 128.8 (2 x CH), 128.5 (2 x CH), 128.4 (2 x CH), 127.7 (C), 126.0 (CH), 116.9 (CH$_2$, CH=*CH*$_2$), 116.7 (CH), 116.4 (CH$_2$, CH=*CH*$_2$), 112.46 (2 x CH), 112.4 (CH), 68.8 (CH$_2$, O*CH*$_2$CH=CH$_2$), 61.1 (CH$_2$, O*CH*$_2$CH$_3$), 54.5 (CH$_2$, N*CH*$_2$CH=CH$_2$), 37.7 (CH$_2$, PhCH$_2$*C*H$_2$Ar), 36.3 (CH$_2$, Ph*C*H$_2$CH$_2$Ar), 15.5 (CH$_3$, Ar-*CH*$_3$), 14.3 (CH$_3$, OCH$_2$*CH*$_3$); LCMS m/z 454.00 (M-H$^+$), calcd $C_{30}H_{33}NO_3$ 455.2460.

5-Allyloxy-4-(allyl-phenyl-amino)-3-methyl-biphenyl-2-carboxylic acid ethyl ester (6ha): Purified by column chromatography using EtOAc/hexane and isolated as a light yellow solid. IR (neat): ν_{max} 3061, 2924, 1724 (O-C=O), 1599, 1500, 1093, 748, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.43-7.28 (5H, m, Ph-*H*), 7.19 (2H, t, *J* = 7.6 Hz), 6.83 (1H, s, Ar-*H*), 6.74 (1H, t, *J* = 7.2 Hz), 6.60 (2H, d, *J* = 7.6 Hz), 6.08-6.00 (1H, m, olefinic-*H*), 5.88-5.81 (1H, m, olefinic-*H*), 5.38-5.14 (4H, m, olefinic-*H*), 4.50 (2H, br s, OC*H*$_2$CH=CH$_2$), 4.26 (2H, dABq, *J* = 16.0, 5.2 Hz, NC*H*$_2$CH=CH$_2$), 4.08 (2H, q, *J* = 7.2 Hz, OC*H*$_2$CH$_3$), 2.27 (3H, s, Ar-C*H*$_3$), 0.97 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 169.5 (C, O-C=O), 156.4 (C), 148.1 (C), 141.0 (C), 139.9 (C), 137.5 (C), 135.4 (CH), 133.3 (C), 132.6 (CH), 128.9 (2 x CH), 128.24 (2 x CH), 128.2 (2 x CH), 127.4 (CH), 127.2 (C), 117.1 (CH$_2$, CH=*CH*$_2$), 116.8 (CH), 116.5 (CH$_2$, CH=*CH*$_2$), 112.5 (CH), 112.4 (2 x CH), 68.9 (CH$_2$, O*CH*$_2$CH=CH$_2$), 60.9 (CH$_2$, O*CH*$_2$CH$_3$), 54.6 (CH$_2$, N*CH*$_2$CH=CH$_2$), 15.5 (CH$_3$, Ar-*CH*$_3$), 13.6 (CH$_3$, OCH$_2$*CH*$_3$); GCMS m/z 427.20 (M$^+$), calcd $C_{28}H_{29}NO_3$ 427.5348.



6ha

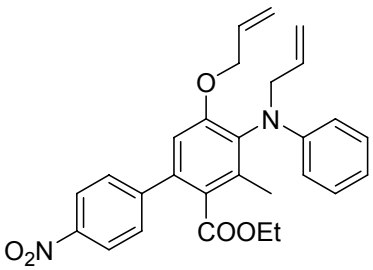
5-Allyloxy-4-(allyl-phenyl-amino)-4'-methoxy-3-methyl-biphenyl-2-carboxylic acid ethyl ester (6ia):



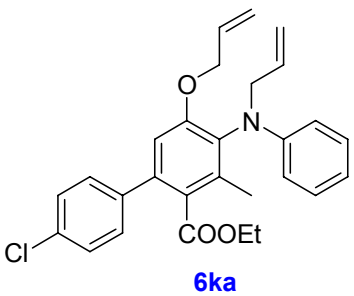
6ia

Purified by column chromatography using EtOAc/hexane and isolated as a liquid. IR (neat): ν_{max} 2979, 1721 (O-C=O), 1600, 1500, 1246, 1037, 745 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.34 (2H, d, *J* = 8.4 Hz), 7.16 (2H, t, *J* = 7.6 Hz), 6.94 (2H, d, *J* = 8.4 Hz), 6.77 (1H, s, Ar-*H*), 6.70 (1H, t, *J* = 7.2 Hz), 6.57 (2H, d, *J* = 8.0 Hz), 6.02-6.00 (1H, m, olefinic-*H*), 5.82-5.80 (1H, m, olefinic-*H*), 5.29 (1H, d, *J* = 17.2 Hz, olefinic-*H*), 5.19-5.11 (3H, m, olefinic-*H*), 4.47 (2H, d, *J* = 4.8 Hz, $OCH_2CH=CH_2$), 4.18 (2H, dABq, *J* = 18.0, 5.2 Hz, $NCH_2CH=CH_2$), 4.08 (2H, q, *J* = 7.2 Hz, OCH_2CH_3), 3.84 (CH_3, s, OCH_3), 2.21 (3H, s, Ar-CH_3), 1.03 (3H, t, *J* = 7.2 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 169.7 (C, O-C=O), 159.2 (C), 156.4 (C), 148.2 (C), 139.4 (C), 137.2 (C), 135.4 (CH), 133.4 (C), 133.0 (C), 132.6 (CH), 129.3 (2 x CH), 128.8 (2 x CH), 127.3 (C), 117.1 (CH_2, $CH=CH_2$), 116.8 (CH), 116.5 (CH_2, $CH=CH_2$), 113.7 (2 x CH), 112.6 (CH), 112.5 (2 x CH), 68.8 (CH_2, $OCH_2CH=CH_2$), 60.9 (CH_2, OCH_2CH_3), 55.3 (CH_3, OCH_3), 54.6 (CH_2, $NCH_2CH=CH_2$), 15.4 (CH_3, Ar-CH_3), 13.8 (CH_3, OCH_2CH_3); LCMS m/z 457.0 (M^+), calcd $C_{29}H_{31}NO_4$ 457.2253.

5-Allyloxy-4-(allyl-phenyl-amino)-3-methyl-4'-nitro-biphenyl-2-carboxylic acid ethyl ester (6ja): Purified by column chromatography using EtOAc/hexane and isolated as a light yellow solid. IR (neat): ν_{max} 1722 (O-C=O), 1597, 1519, 1500, 1243, 1068 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.28 (2H, d, *J* = 8.4 Hz), 7.58 (2H, d, *J* = 8.8 Hz), 7.18 (2H, t, *J* = 7.6 Hz), 6.77 (1H, s, Ar-*H*), 6.73 (1H, t, *J* = 7.2 Hz), 6.57 (2H, d, *J* = 8.4 Hz), 6.04-5.98 (1H, m, olefinic-*H*), 5.86-5.79 (1H, m, olefinic-*H*), 5.30 (1H, dd, *J* = 17.2, 1.6 Hz, olefinic-*H*), 5.19 (1H, dd, *J* = 15.2, 1.2 Hz, olefinic-*H*), 5.16 (2H, dd, *J* = 10.4, 1.2 Hz, olefinic-*H*), 4.50 (2H, d, *J* = 4.8 Hz, $OCH_2CH=CH_2$), 4.20 (2H, dABq, *J* = 17.2, 5.6 Hz, $NCH_2CH=CH_2$), 4.08 (2H, q, *J* = 7.2 Hz, OCH_2CH_3), 2.25 (3H, s, Ar-CH_3), 1.02 (3H, t, *J* = 6.4 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 168.9 (C, O-C=O), 156.8 (C), 147.9 (C), 147.8 (C), 147.3 (C), 138.3 (C), 137.5 (C), 135.2 (CH), 134.5 (C), 132.3 (CH), 129.2 (2 x CH), 129.0 (2 x CH), 127.1 (C), 123.5 (2 x CH), 117.5 (CH_2, $CH=CH_2$), 117.2 (CH), 116.8 (CH_2, $CH=CH_2$), 112.7 (2 x CH), 112.3 (CH), 69.0 (CH_2,



6ja

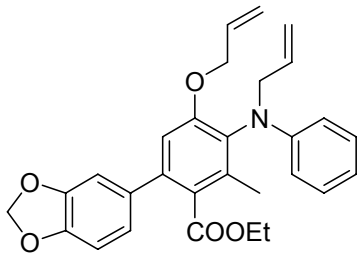


6ka

O*CH*$_2$CH=CH$_2$), 61.2 (CH$_2$, O*CH*$_2$CH$_3$), 54.5 (CH$_2$, N*CH*$_2$CH=CH$_2$), 15.6 (CH$_3$, Ar-*CH*$_3$), 13.8 (CH$_3$, OCH$_2$*CH*$_3$); LCMS m/z 471.00 (M-H$^+$), calcd $C_{28}H_{28}N_2O_5$ 472.1998.

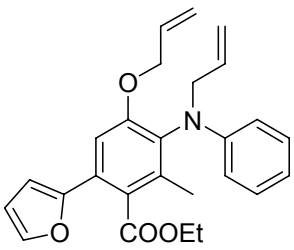
5-Allyloxy-4-(allyl-phenyl-amino)-4'-chloro-3-methyl-biphenyl-2-carboxylic acid ethyl ester (6ka): Purified by column chromatography using EtOAc/hexane and isolated as a light yellow solid. IR (neat): ν_{max} 2980, 1722 (O-C=O), 1598, 1498, 1249, 1070, 741 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.39 (2H, d, *J* = 8.4 Hz), 7.35 (2H, d, *J* = 8.4 Hz), 7.17 (2H, t, *J* = 8.0 Hz), 6.75 (1H, s, Ar-*H*), 6.72 (1H, t, *J* = 7.6 Hz), 6.57 (2H, d, *J* = 8.4 Hz), 6.05-5.98 (1H, m, olefinic-*H*), 5.85-5.78 (1H, m, olefinic-*H*), 5.30 (1H, d, *J* = 17.2 Hz, olefinic-*H*), 5.18 (1H, d, *J* = 17.2 Hz, olefinic-*H*), 5.14 (2H, br d, *J* = 10.4 Hz, olefinic-*H*), 4.48 (2H, d, *J* = 4.4 Hz, O*CH*$_2$CH=CH$_2$), 4.22 (2H, dABq, *J* = 16.4, 5.6 Hz, N*CH*$_2$CH=CH$_2$), 4.08 (2H, q, *J* = 7.2 Hz, O*CH*$_2$CH$_3$), 2.24 (3H, s, Ar-C*H*$_3$), 1.03 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 169.3 (C, O-C=O), 156.5 (C), 148.0 (C), 139.4 (C), 138.5 (C), 137.7 (C), 135.3 (CH), 133.64 (C), 133.61 (C), 132.5 (CH), 129.6 (2 x CH), 128.9 (2 x CH), 128.4 (2 x CH), 127.2 (C), 117.2 (CH$_2$, CH=*CH*$_2$), 116.9 (CH), 116.6 (CH$_2$, CH=*CH*$_2$), 112.4 (2 x CH), 112.4 (CH), 68.9 (CH$_2$, O*CH*$_2$CH=CH$_2$), 61.0 (CH$_2$, O*CH*$_2$CH$_3$), 54.5 (CH$_2$, N*CH*$_2$CH=CH$_2$), 15.4 (CH$_3$, Ar-*CH*$_3$), 13.7 (CH$_3$, OCH$_2$*CH*$_3$); LCMS m/z 461.10 (M$^+$), calcd $C_{28}H_{28}ClNO_3$ 461.1758.

4-Allyloxy-3-(allyl-phenyl-amino)-6-benzo[1,3]dioxol-5-yl-2-methyl-benzoic acid ethyl ester (6la): Purified by column chromatography using EtOAc/hexane and isolated as a liquid. IR (neat): ν_{max} 2981, 1721 (O-C=O), 1597, 1498, 1477, 1239, 1040, 744 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.15 (2H, t, *J* = 7.6 Hz), 6.90-6.82 (3H, m), 6.75 (1H, s, Ar-*H*), 6.69 (1H, t, *J* = 7.2 Hz), 6.55 (2H, d, *J* = 8.0 Hz), 6.04-5.97 (1H, m, olefinic-*H*), 5.99 (2H, s, O*CH*$_2$O), 5.84-5.77 (1H, m, olefinic-*H*), 5.30 (1H, dd, *J* = 17.2, 1.6 Hz, olefinic-*H*), 5.17 (1H, dd, *J* = 17.2, 1.2 Hz, olefinic-*H*), 5.12-5.11 (2H, m, olefinic-*H*), 4.46 (2H, d, *J* = 4.4 Hz, O*CH*$_2$CH=CH$_2$), 4.19 (2H, dABq, *J* = 17.2, 5.6 Hz, N*CH*$_2$CH=CH$_2$), 4.12 (2H, q, *J* = 7.2 Hz, O*CH*$_2$CH$_3$), 2.21 (3H, s, Ar-C*H*$_3$), 1.09 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 169.6 (C, O-C=O), 156.4 (C), 148.2 (C), 147.6 (C), 147.2 (C), 139.3 (C), 137.3 (C), 135.4 (CH), 134.9 (C), 133.2 (C), 132.6 (CH), 128.9 (2 x CH), 127.4 (C), 121.8 (CH), 117.2 (CH$_2$, CH=*CH*$_2$), 116.9 (CH),



6la

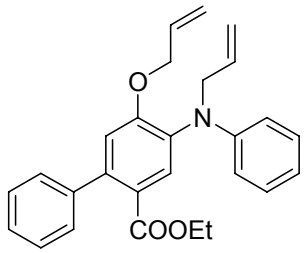
116.5 (CH_2, CH=*CH_2*), 112.6 (2 x CH), 112.59 (CH), 108.9 (CH), 108.2 (CH), 101.2 (CH_2, O*CH_2*O), 68.9 (CH_2, O*CH_2*CH=CH_2), 61.0 (CH_2, O*CH_2*CH_3), 54.6 (CH_2, N*CH_2*CH=CH_2), 15.5 (CH_3, Ar-*CH_3*), 13.9 (CH_3, OCH$_2$*CH_3*); LCMS m/z 472.50 ($M+H^+$), calcd $C_{29}H_{29}NO_5$ 471.2046.



6ma

4-Allyloxy-3-(allyl-phenyl-amino)-6-furan-2-yl-2-methyl-benzoic acid ethyl ester (6ma): Purified by column chromatography using EtOAc/hexane and isolated as a light yellow solid. IR (neat): ν_{max} 2982, 1725 (O-C=O), 1597, 1498, 1468, 1267, 1069, 746 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.47 (1H, s, Ar-*H*), 7.14 (2H, t, *J* = 8.0 Hz), 7.07 (1H, s, Ar-*H*), 6.69 (1H, t, *J* = 7.6 Hz), 6.55-6.52 (3H, m), 6.47-6.46 (1H, m), 6.03-5.97 (1H, m, olefinic-*H*), 5.87-5.76 (1H, m, olefinic-*H*), 5.26 (1H, dd, *J* = 17.2, 1.2 Hz, olefinic-*H*), 5.19 (1H, d, *J* = 17.2 Hz, olefinic-*H*), 5.14 (1H, dd, *J* = 10.0, 1.2 Hz, olefinic-*H*), 5.12 (1H, dd, *J* = 10.0, 1.2 Hz, olefinic-*H*), 4.50 (2H, d, *J* = 3.2 Hz, O*CH_2*CH=CH_2), 4.34 (2H, q, *J* = 7.2 Hz, O*CH_2*CH_3), 4.16 (2H, dABq, *J* = 18.0, 5.6 Hz, N*CH_2*CH=CH_2), 2.17 (3H, s, Ar-C*H_3*), 1.29 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H_3*); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 169.7 (C, O-C=O), 156.5 (C), 151.2 (C) 148.0 (C), 142.5 (CH), 137.3 (C), 135.2 (CH), 133.6 (C), 132.5 (CH), 128.9 (2 x CH), 127.4 (C), 125.4 (C), 117.2 (CH_2, CH=*CH_2*), 116.9 (CH), 116.6 (CH_2, CH=*CH_2*), 112.6 (2 x CH), 111.7 (CH), 109.3 (CH), 107.7 (CH), 68.9 (CH_2, O*CH_2*CH=CH_2), 61.4 (CH_2, O*CH_2*CH_3), 54.4 (CH_2, N*CH_2*CH=CH_2), 15.2 (CH_3, Ar-*CH_3*), 14.1 (CH_3, OCH$_2$*CH_3*); LCMS m/z 418.00 ($M+H^+$), calcd $C_{26}H_{27}NO_4$ 417.1940.

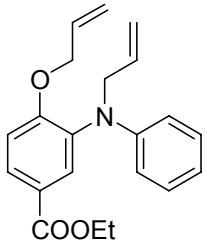
5-Allyloxy-4-(allyl-phenyl-amino)-biphenyl-2-carboxylic acid ethyl ester (6na):



6na

Purified by column chromatography using EtOAc/hexane and isolated as a light yellow solid. IR (neat): ν_{max} 3061, 3026, 2982, 1714 (O-C=O), 1645, 1599, 1554, 1107, 1022, 746, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.85 (1H, s, Ar-*H*), 7.46-7.36 (5H, m, Ph-*H*), 7.19 (2H, t, *J* = 7.2 Hz), 6.91 (1H, s, Ar-*H*), 6.77 (1H, t, *J* = 7.2 Hz), 6.73 (2H, d, *J* = 8.4 Hz), 6.04-5.97 (1H, m, olefinic-*H*), 5.89-5.81 (1H, m, olefinic-*H*), 5.39 (1H, br d, *J* = 17.2 Hz, olefinic-*H*), 5.20 (1H, br d, *J* = 10.4 Hz, olefinic-*H*), 5.17-5.15 (2H, m), 4.56 (2H, br d, *J* = 4.8 Hz, O*CH_2*CH=CH_2), 4.35 (2H, br d, *J* = 4.8 Hz, N*CH_2*CH=CH_2), 4.09 (2H, q, *J* = 7.2 Hz,

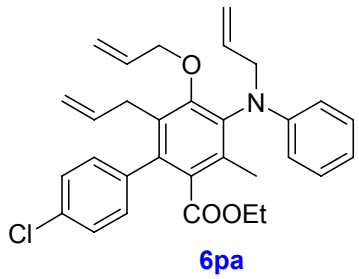
OC*H*$_2$CH$_3$), 1.02 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 167.6 (C, O-C=O), 156.8 (C), 148.3 (C), 142.2 (C), 141.6 (C), 134.8 (CH), 134.5 (C), 132.3 (CH), 131.9 (CH), 128.7 (2 x CH), 128.4 (2 x CH), 127.9 (2 x CH), 127.2 (CH), 123.7 (C), 117.8 (CH), 117.4 (CH$_2$, CH=*CH*$_2$), 116.3 (CH$_2$, CH=*CH*$_2$), 116.0 (CH), 114.3 (2 x CH), 69.0 (CH$_2$, O*CH*$_2$CH=CH$_2$), 60.7 (CH$_2$, O*CH*$_2$CH$_3$), 54.5 (CH$_2$, N*CH*$_2$CH=CH$_2$), 13.7 (CH$_3$, OCH$_2$*CH*$_3$); GCMS m/z 413.10 (M$^+$), calcd $C_{27}H_{27}NO_3$ 413.5082.



6oa

4-Allyloxy-3-(allyl-phenyl-amino)-benzoic acid ethyl ester (6oa): Purified by column chromatography using EtOAc/hexane and isolated as a light yellow liquid. IR (neat): ν$_{max}$ 2980, 1711 (O-C=O), 1599, 1539, 1499, 1237, 1021, 747, 693 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.97-7.93 (2H, m), 7.15 (2H, t, *J* = 7.6 Hz), 6.99 (1H, d, *J* = 8.8 Hz), 6.74 (1H, t, *J* = 7.2 Hz), 6.64 (2H, d, *J* = 8.0 Hz), 6.04-5.98 (1H, m, olefinic-*H*), 5.90-5.80 (1H, m, olefinic-*H*), 5.35-5.14 (4H, m, olefinic-*H*), 4.56 (2H, br d, *J* = 4.8 Hz, OC*H*$_2$CH=CH$_2$), 4.35 (2H, q, *J* = 7.2 Hz, OC*H*$_2$CH$_3$), 4.31 (2H, br d, *J* = 12 Hz, NC*H*$_2$CH=CH$_2$), 1.38 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 166.1 (C, O-C=O), 158.8 (C), 148.4 (C), 135.3 (C), 134.74 (CH), 132.3 (CH), 131.7 (CH), 128.9 (CH), 128.7 (2 x CH), 123.8 (C), 117.6 (CH), 117.4 (CH$_2$, CH=*CH*$_2$), 116.3 (CH$_2$, CH=*CH*$_2$), 113.9 (2 x CH), 113.6 (CH), 68.9 (CH$_2$, O*CH*$_2$CH=CH$_2$), 60.8 (CH$_2$, O*CH*$_2$CH$_3$), 54.4 (CH$_2$, N*CH*$_2$CH=CH$_2$), 14.4 (CH$_3$, OCH$_2$*CH*$_3$); LCMS m/z 338.00 (M+H$^+$), calcd $C_{21}H_{23}NO_3$ 337.1678.

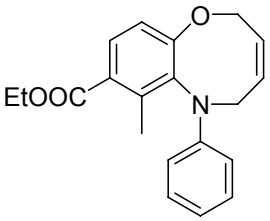
6-Allyl-5-allyloxy-4-(allyl-phenyl-amino)-4'-chloro-3-methyl-biphenyl-2-carboxylic acid ethyl ester (6pa): Purified by column chromatography using EtOAc/hexane and isolated as a light yellow solid. IR (neat): ν$_{max}$ 2979, 1726 (O-C=O), 1598, 1497, 1442, 1206, 1122, 1090, 919 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.35-7.33 (2H, m), 7.24-7.19 (4H, m), 6.74 (1H, t, *J* = 7.2 Hz), 6.62 (2H, d, *J* = 8.0 Hz), 6.03-5.96 (1H, m, olefinic-*H*), 5.91-5.83 (1H, m, olefinic-*H*), 5.80-5.74 (1H, m, olefinic-*H*), 5.28 (1H, d, *J* = 17.2 Hz, olefinic-*H*), 5.20-5.10 (3H, m, olefinic-*H*), 4.90 (1H, dd, *J* = 8.4, 1.6 Hz, olefinic-*H*), 4.70 (1H, dd, *J* = 8.8, 1.6 Hz, olefinic-*H*), 4.32-4.19 (3H, m,



6pa

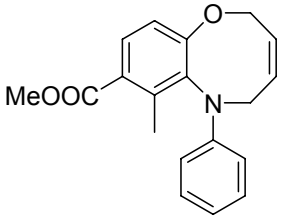
OC*H*$_2$CH=CH$_2$, NC*H*$_2$CH=CH$_2$), 4.08-4.03 (1H, m, NC*H*$_2$CH=CH$_2$), 3.93 (2H, q, *J* = 7.2 Hz, OC*H*$_2$CH$_3$), 3.20 (2H, d, *J* = 5.6 Hz, ArC*H*$_2$CH=CH$_2$), 2.03 (3H, s, Ar-C*H*$_3$), 0.96 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 169.0 (C, O-C=O), 155.9 (C), 147.6 (C), 137.7 (C), 137.6 (C), 136.9 (C), 136.8 (CH), 134.9 (CH), 134.2 (C), 133.7 (CH), 133.5 (C), 132.2 (C), 131.2 (C), 131.1 (CH), 130.9 (CH), 129.3 (3 x CH), 127.9 (CH), 127.8 (CH), 117.2 (CH), 117.2 (CH$_2$, CH=*CH*$_2$), 117.1 (CH$_2$, CH=*CH*$_2$), 115.2 (CH$_2$, CH=*CH*$_2$), 112.6 (CH), 74.1 (CH$_2$, O*CH*$_2$CH=*CH*$_2$), 60.9 (CH$_2$, O*CH*$_2$CH$_3$), 54.5 (CH$_2$, N*CH*$_2$CH=*CH*$_2$), 32.0 (CH$_2$, Ar*CH*$_2$CH=CH$_2$), 15.7 (CH$_3$, Ar-*CH*$_3$), 13.7 (CH$_3$, OCH$_2$C*H*$_3$); LCMS m/z 501.20 (M$^+$), calcd $C_{31}H_{32}ClNO_3$ 501.2071.

7-Methyl-6-phenyl-5,6-dihydro-2H-benzo[b][1,4]oxazocine-8-carboxylic acid ethyl ester (7aa): Purified by column chromatography using EtOAc/hexane and isolated as a light yellow liquid. IR (neat): ν$_{max}$ 3030, 2978, 1712 (O-C=O), 1597, 1500, 1105, 1022, 746, 692 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.79 (1H, d, *J* = 8.8 Hz), 7.20 (2H, t, *J* = 7.6 Hz), 6.92 (1H, d, *J* = 8.8 Hz), 6.75 (1H, t, *J* = 7.2 Hz), 6.48 (2H, d, *J* = 8.4 Hz), 6.00 (1H, br d, *J* = 10.4 Hz, olefinic-*H*), 5.85-5.81 (1H, m, olefinic-*H*), 4.67 (2H, m, OC*H*$_2$CH=CH), 4.31 (2H, q, *J* = 7.2 Hz, OC*H*$_2$CH$_3$), 4.30 (1H, m, NC*H*$_2$), 3.97 (1H, m, NC*H*$_2$), 2.32 (3H, s, Ar-C*H*$_3$), 1.38 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 167.4 (C, O-C=O), 159.2 (C), 147.2 (C), 142.5 (C), 132.7 (CH), 132.1 (C), 130.2 (CH), 129.4 (CH), 129.4 (2 x CH), 125.8 (CH), 124.6 (C), 118.4 (CH), 117.6 (CH), 112.4 (CH), 65.4 (CH$_2$, O*CH*$_2$), 60.6 (CH$_2$, O*CH*$_2$CH$_3$), 50.1 (CH$_2$, N*CH*$_2$), 15.3 (CH$_3$, Ar-*CH*$_3$), 14.4 (CH$_3$, OCH$_2$*CH*$_3$); GCMS m/z 323.20 (M$^+$), calcd $C_{20}H_{21}NO_3$ 323.3857; Anal. calcd for $C_{20}H_{21}NO_3$ (323.38): C, 74.28; H, 6.55; N, 4.33. Found: C, 74.314; H, 6.549; N, 4.348%.



7aa

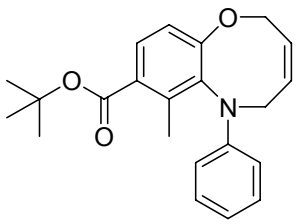
7-Methyl-6-phenyl-5,6-dihydro-2H-benzo[b][1,4]oxazocine-8-carboxylic acid methyl ester (7ba): Purified by column chromatography using EtOAc/hexane and isolated as a light yellow liquid. IR (neat): ν$_{max}$ 2949, 1719 (O-C=O), 1595, 1500, 1436, 1236, 1022, 741 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.79 (1H, d, *J* = 8.8 Hz), 7.20 (2H, t, *J* = 7.6 Hz), 6.92 (1H, d, *J* = 8.8 Hz), 6.75 (1H, t, *J* = 7.2 Hz), 6.48



7ba

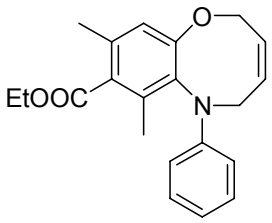
(2H, d, *J* = 8.0 Hz), 6.00 (1H, br d, *J* = 10.8 Hz, olefinic-*H*), 5.84-5.81 (1H, m, olefinic-*H*), 4.67 (2H, m, OC*H*$_2$CH=CH), 4.37 (1H, m, NC*H*$_2$), 3.97 (1H, m, NC*H*$_2$), 3.86 (3H, s, OC*H*$_3$), 2.32 (3H, s, Ar-C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.8 (C, O-C=O), 159.3 (C), 147.2 (C), 142.7 (C), 132.7 (CH), 132.1 (C), 130.2 (CH), 129.4 (CH), 129.4 (2 x CH), 125.8 (CH), 124.2 (C), 118.4 (CH), 117.6 (CH), 112.4 (CH), 65.4 (CH_2, O*CH*$_2$), 51.8 (CH_3, O*CH*$_3$), 50.1 (CH_2, N*CH*$_2$), 15.3 (CH_3, Ar-*CH*$_3$); LCMS m/z 309.85 (M+H$^+$), calcd $C_{19}H_{19}NO_3$ 309.1365; Anal. calcd for $C_{19}H_{19}NO_3$ (309.13): C, 73.77; H, 6.19; N, 4.53. Found: C, 73.65; H, 6.22; N, 4.62%.

7-Methyl-6-phenyl-5,6-dihydro-2H-benzo[b][1,4]oxazocine-8-carboxylic acid *tert*-butyl ester (7ca): Purified by column chromatography using EtOAc/hexane and isolated as a light yellow liquid. IR (neat): ν_{max} 2975, 1709 (O-C=O), 1595, 1499, 1240, 1061, 744, 688 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.71 (1H, d, *J* = 8.8 Hz), 7.20 (2H, t, *J* = 7.6 Hz), 6.91 (1H, d, *J* = 8.8 Hz), 6.75 (1H, t, *J* = 7.2 Hz), 6.49 (2H, d, *J* = 8.0 Hz), 6.00-5.97 (1H, m, olefinic-*H*), 5.85-5.78 (1H, m, olefinic-*H*), 4.66 (2H, m, OC*H*$_2$CH=CH), 4.36 (1H, m, NC*H*$_2$), 3.98 (1H, m, NC*H*$_2$), 2.29 (3H, s, Ar-C*H*$_3$), 1.58 (9H, s, C(C*H*$_3$)$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 166.9 (C, O-C=O), 158.7 (C), 147.3 (C), 141.7 (C), 132.7 (CH), 132.0 (C), 130.1 (CH), 129.38 (CH), 129.4 (2 x CH), 126.5 (C), 125.9 (CH), 118.2 (CH), 117.5 (CH), 112.4 (CH), 80.9 (C), 65.4 (CH_2, O*CH*$_2$), 50.0 (CH_2, N*CH*$_2$), 28.3 (3 x CH_3, C(*CH*$_3$)$_3$), 15.3 (CH_3, Ar-*CH*$_3$); LCMS m/z 351.95 (M+H$^+$), calcd $C_{22}H_{25}NO_3$ 351.1834; Anal. calcd for $C_{22}H_{25}NO_3$ (351.18): C, 75.19; H, 7.17; N, 3.99. Found: C, 75.25; H, 7.20; N, 4.05%.



7ca

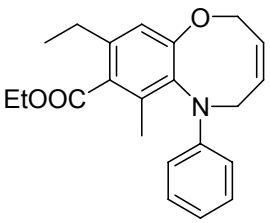
7,9-Dimethyl-6-phenyl-5,6-dihydro-2H-benzo[b][1,4]oxazocine-8-carboxylic acid ethyl ester (7da): Purified by column chromatography using EtOAc/hexane and isolated as a solid. IR (neat): ν_{max} 2926, 1724 (O-C=O), 1599, 1500, 1180, 1103, 748, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.22 (2H, t, *J* = 8.0 Hz), 6.78 (1H, s, Ar-*H*), 6.75 (1H, t, *J* = 7.2 Hz), 6.53 (2H, d, *J* = 8.0 Hz), 6.00 (1H, br d, *J* = 10.8 Hz, olefinic-*H*), 5.84-5.81 (1H, m, olefinic-*H*), 4.58 (2H, m, OC*H*$_2$CH=CH), 4.40 (2H, q, *J* = 7.2 Hz, OC*H*$_2$CH$_3$), 4.40-4.35 (1H, m, NC*H*$_2$), 3.98 (1H, m, NC*H*$_2$), 2.31 (3H, s, Ar-



7da

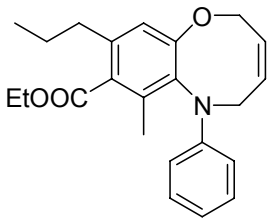
C*H*$_3$), 2.04 (3H, s, Ar-C*H*$_3$), 1.40 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 169.7 (C, O-C=O), 156.4 (C), 147.2 (C), 136.5 (C), 134.7 (C), 132.5 (CH), 129.4 (C), 129.3 (CH), 129.3 (2 x CH), 128.9 (C), 126.1 (CH), 120.3 (CH), 117.4 (CH), 112.4 (CH), 65.3 (CH$_2$, O*CH*$_2$), 60.9 (CH$_2$, O*CH*$_2$CH$_3$), 49.8 (CH$_2$, N*CH*$_2$), 19.5 (CH$_3$, Ar-*CH*$_3$), 14.9 (CH$_3$, Ar-*CH*$_3$), 14.3 (CH$_3$, OCH$_2$*CH*$_3$); GCMS m/z 337.20 (M$^+$), calcd $C_{21}H_{23}NO_3$ 337.4123; Anal. calcd for $C_{21}H_{23}NO_3$ (337.41): C, 74.75; H, 6.87; N, 4.15. Found: C, 74.727; H, 6.852; N, 4.273%.

9-Ethyl-7-methyl-6-phenyl-5,6-dihydro-2H-benzo[b][1,4]oxazocine-8-carboxylic acid ethyl ester (7ea): Purified by column chromatography using EtOAc/hexane and isolated as a solid. IR (neat): ν$_{max}$ 2975, 1716 (O-C=O), 1598, 1563, 1501, 1249, 1057, 746 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.20 (2H, t, *J* = 7.2 Hz), 6.80 (1H, s, Ar-*H*), 6.74 (1H, t, *J* = 7.2 Hz), 6.52 (2H, d, *J* = 8.4 Hz), 6.00-5.96 (1H, m, olefinic-*H*), 5.83-5.79 (1H, m, olefinic-*H*), 4.68 (2H, m, OC*H*$_2$CH=CH), 4.38 (2H, q, *J* = 7.2 Hz, OC*H*$_2$CH$_3$), 4.38-4.35 (1H, m, NC*H*$_2$), 3.98 (1H, m, NC*H*$_2$), 2.62 (2H, q, *J* = 7.6 Hz, ArC*H*$_2$CH$_3$), 2.02 (3H, s, Ar-C*H*$_3$), 1.38 (3H, t, *J* = 7.2 Hz, ArCH$_2$C*H*$_3$), 1.24 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 169.8 (C, O-C=O), 156.6 (C), 147.2 (C), 140.7 (C), 136.2 (C), 132.4 (CH), 129.4 (C), 129.33 (CH), 129.3 (2 x CH), 128.5 (C), 126.1 (CH), 118.6 (CH), 117.4 (CH), 112.5 (CH), 65.4 (CH$_2$, O*CH*$_2$), 61.0 (CH$_2$, O*CH*$_2$CH$_3$), 49.8 (CH$_2$, N*CH*$_2$), 26.4 (CH$_2$, Ar*CH*$_2$CH$_3$), 15.2 (CH$_3$, Ar-*CH*$_3$), 14.9 (CH$_3$, ArCH$_2$*C*H$_3$), 14.2 (CH$_3$, OCH$_2$*CH*$_3$); LCMS m/z 351.95 (M+H$^+$), calcd $C_{22}H_{25}NO_3$ 351.1834; Anal. calcd for $C_{22}H_{25}NO_3$ (351.18): C, 75.19; H, 7.17; N, 3.99. Found: C, 75.25; H, 7.22; N, 4.12%.



7ea

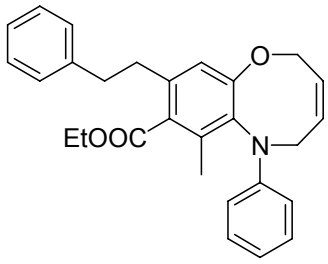
7-Methyl-6-phenyl-9-propyl-5,6-dihydro-2H-benzo[b][1,4]oxazocine-8-carboxylic acid ethyl ester (7fa): Purified by column chromatography using EtOAc/hexane and isolated as a solid. IR (neat): ν$_{max}$ 2961, 1721 (O-C=O), 1598, 1564, 1500, 1182, 1103, 747 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.19 (2H, t, *J* = 8.0 Hz), 6.77 (1H, s, Ar-*H*), 6.73 (1H, t, *J* = 7.2 Hz), 6.50 (2H, d, *J* = 8.0 Hz), 5.97 (1H, br d, *J* = 10.8 Hz, olefinic-*H*), 5.83-5.77 (1H, m, olefinic-*H*), 4.54 (2H, m, OC*H*$_2$CH=CH), 4.37 (2H, q,



7fa

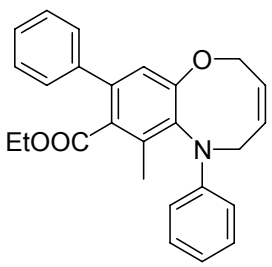
J = 7.2 Hz, OC*H*$_2$CH$_3$), 4.37-4.35 (1H, m, NC*H*$_2$), 3.98 (1H, m, NC*H*$_2$), 2.53 (2H, t, *J* = 7.6 Hz, ArC*H*$_2$CH$_2$CH$_3$), 2.01 (3H, s, Ar-C*H*$_3$), 1.63 (2H, sextet, *J* = 7.6 Hz, ArCH$_2$C*H*$_2$CH$_3$), 1.37 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$), 0.96 (3H, t, *J* = 7.2 Hz, ArCH$_2$CH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 169.8 (C, O-C=O), 156.4 (C), 147.2 (C), 139.2 (C), 136.2 (C), 132.4 (CH), 129.5 (C), 129.33 (CH), 129.3 (2 x CH), 128.8 (C), 126.2 (CH), 119.4 (CH), 117.4 (CH), 112.5 (CH), 65.4 (CH$_2$, O*CH*$_2$), 61.0 (CH$_2$, O*CH*$_2$CH$_3$), 49.8 (CH$_2$, N*CH*$_2$), 35.5 (CH$_2$, Ar*C*H$_2$CH$_2$CH$_3$), 24.1 (CH$_2$, ArCH$_2$*CH*$_2$CH$_3$), 14.9 (CH$_3$, Ar-*CH*$_3$), 14.2 (CH$_3$, OCH$_2$*CH*$_3$), 14.1 (CH$_3$, ArCH$_2$CH$_2$*C*H$_3$); LCMS m/z 365.50 (M$^+$), calcd $C_{23}H_{27}NO_3$ 365.1991; Anal. calcd for $C_{23}H_{27}NO_3$ (365.19): C, 75.59; H, 7.45; N, 3.83. Found: C, 75.62; H, 7.49; N, 3.88%.

7-Methyl-9-phenethyl-6-phenyl-5,6-dihydro-2H-benzo[b][1,4]oxazocine-8-carboxylic acid ethyl ester (7ga): Purified by column chromatography using EtOAc/hexane and isolated as a liquid. IR (neat): ν$_{max}$ 3028, 1722 (O-C=O), 1598, 1562, 1498, 1248, 1054, 748, 696 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.31 (2H, t, *J* = 8.0 Hz), 7.23-7.19 (5H, m, Ph-*H*), 6.82 (1H, s, Ar-*H*), 6.75 (1H, t, *J* = 7.2 Hz), 6.53 (2H, d, *J* = 8.0 Hz), 5.99 (1H, br d, *J* = 10.8 Hz, olefinic-*H*), 5.83-5.80 (1H, m, olefinic-*H*), 4.74 (2H, m, OC*H*$_2$CH=CH), 4.39 (2H, q, *J* = 7.2 Hz, OC*H*$_2$CH$_3$), 4.40-4.35 (1H, m, NC*H*$_2$), 3.98 (1H, m, NC*H*$_2$), 2.94-2.84 (4H, m, PhC*H*$_2$C*H*$_2$Ar), 2.04 (3H, s, Ar-C*H*$_3$), 1.38 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 169.8 (C, O-C=O), 156.6 (C), 147.2 (C), 141.7 (C), 138.5 (C), 136.5 (C), 132.4 (CH), 129.8 (C), 129.37 (CH), 129.4 (2 x CH), 128.7 (C), 128.4 (2 x CH), 128.3 (2 x CH), 126.2 (CH), 126.0 (CH), 119.5 (CH), 117.5 (CH), 112.5 (CH), 65.5 (CH$_2$, O*CH*$_2$), 61.2 (CH$_2$, O*CH*$_2$CH$_3$), 49.7 (CH$_2$, N*CH*$_2$), 37.6 (CH$_2$), 35.8 (CH$_2$), 15.0 (CH$_3$, Ar-*CH*$_3$), 14.3 (CH$_3$, OCH$_2$*CH*$_3$); LCMS m/z 428.00 (M+H$^+$), calcd $C_{28}H_{29}NO_3$ 427.2147; Anal. calcd for $C_{28}H_{29}NO_3$ (427.21): C, 78.66; H, 6.84; N, 3.28. Found: C, 78.71; H, 6.88; N, 3.32%.



7ga

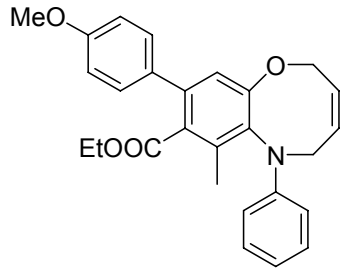
7-Methyl-6,9-diphenyl-5,6-dihydro-2H-benzo[b][1,4]oxazocine-8-carboxylic acid ethyl ester (7ha): Purified by column chromatography using EtOAc/hexane and isolated as a light yellow solid. IR (neat): ν$_{max}$



7ha

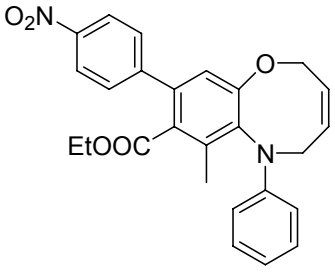
3034, 2976, 1722 (O-C=O), 1599, 1500, 1197, 1062, 748, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.38-7.32 (5H, m, Ph-*H*), 7.23 (2H, t, *J* = 7.6 Hz), 6.95 (1H, s, Ar-*H*), 6.77 (1H, t, *J* = 7.2 Hz), 6.58 (2H, d, *J* = 8.0 Hz), 6.04-6.00 (1H, m, olefinic-*H*), 5.84-5.81 (1H, m, olefinic-*H*), 4.49 (2H, m, OCH_2), 4.02 (2H, q, *J* = 7.2 Hz, OCH_2CH_3), 4.02 (1H, m, NCH_2), 3.65 (1H, m, NCH_2), 2.11 (3H, s, Ar-CH_3), 0.93 (3H, t, *J* = 7.2 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 169.5 (C, O-C=O), 156.6 (C), 147.0 (C), 140.5 (C), 139.7 (C), 137.2 (C), 132.3 (CH), 131.1 (C), 129.4 (2 x CH), 128.2 (C), 128.2 (2 x CH), 128.16 (2 x CH), 128.1 (CH), 127.4 (CH), 126.3 (CH), 120.1 (CH), 117.7 (CH), 112.7 (CH), 65.8 (CH_2, OCH_2), 60.9 (CH_2, OCH_2CH_3), 49.7 (CH_2, NCH_2), 15.1 (CH_3, Ar-CH_3), 13.6 (CH_3, OCH_2CH_3); GCMS m/z 399.20 (M^+), calcd $C_{26}H_{25}NO_3$ 399.4816; Anal. calcd for $C_{26}H_{25}NO_3$ (399.48): C, 78.17; H, 6.31; N, 3.51. Found: C, 78.31; H, 6.302; N, 3.56%.

9-(4-Methoxy-phenyl)-7-methyl-6-phenyl-5,6-dihydro-2H-benzo[b][1,4]oxazocine-8-carboxylic acid ethyl ester (7ia): Purified by column chromatography using EtOAc/hexane and isolated as a light yellow oil. IR (neat): ν_{max} 3058, 1722 (O-C=O), 1601, 1551, 1499, 1465, 1247, 1029, 737, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.31 (2H, d, *J* = 8.4 Hz), 7.23 (2H, t, *J* = 8.4 Hz), 6.93 (2H, d, *J* = 8.4 Hz), 6.92 (1H, s, Ar-*H*), 6.76 (1H, t, *J* = 7.2 Hz), 6.58 (2H, d, *J* = 8.0 Hz), 6.03-6.00 (1H, m, olefinic-*H*), 5.87-5.79 (1H, m, olefinic-*H*), 4.54-4.47 (3H, m, OCH_2, NCH_2), 4.07 (2H, q, *J* = 7.2 Hz, OCH_2CH_3), 4.10-4.05 (1H, m, NCH_2), 3.84 (3H, s, OCH_3), 2.10 (3H, s, Ar-CH_3), 1.01 (3H, t, *J* = 7.2 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 169.7 (C, O-C=O), 159.1 (C), 156.5 (C), 147.0 (C), 139.2 (C), 136.9 (C), 132.9 (C), 132.3 (CH), 130.8 (C), 129.4 (2 x CH), 129.3 (CH), 129.29 (2 x CH), 128.3 (C), 126.3 (CH), 120.0 (CH), 117.6 (CH), 113.7 (2 x CH), 112.6 (CH), 65.7 (CH_2, OCH_2), 60.9 (CH_2, OCH_2CH_3), 55.3 (CH_3, OCH_3), 49.7 (CH_2, NCH_2), 15.0 (CH_3, Ar-CH_3), 13.8 (CH_3, OCH_2CH_3); LCMS m/z 430.00 ($M+H^+$), calcd $C_{27}H_{27}NO_4$ 429.1940; Anal. calcd for $C_{27}H_{27}NO_4$ (429.19): C, 75.50; H, 6.34; N, 3.26. Found: C, 75.58; H, 6.32; N, 3.32%.



7ia

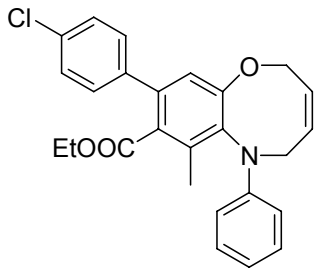
7-Methyl-9-(4-nitro-phenyl)-6-phenyl-5,6-dihydro-2H-benzo[b][1,4]oxazocine-8-carboxylic acid ethyl ester



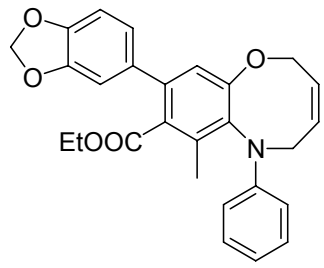
7ja

(7ja): Purified by column chromatography using EtOAc/hexane and isolated as a light yellow solid. IR (neat): ν_{max} 2978, 1721 (O-C=O), 1597, 1552, 1498, 1265, 1061, 733, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.26 (2H, d, *J* = 8.8 Hz), 7.55 (2H, d, *J* = 8.8 Hz), 7.25 (2H, t, *J* = 8.4 Hz), 6.94 (1H, s, Ar-*H*), 6.79 (1H, t, *J* = 7.2 Hz), 6.58 (2H, d, *J* = 8.0 Hz), 6.05-6.02 (1H, m, olefinic-*H*), 5.86-5.83 (1H, m, olefinic-*H*), 4.51 (3H, m, O*CH*$_2$, N*CH*$_2$), 4.06 (2H, q, *J* = 7.2 Hz, O*CH*$_2$CH$_3$), 4.10-4.02 (1H, m, N*CH*$_2$), 2.13 (3H, s, Ar-C*H*$_3$), 1.00 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 168.8 (C, O-C=O), 157.0 (C), 147.3 (C), 147.2 (C), 146.7 (C), 138.1 (C), 137.3 (C), 132.4 (C), 132.4 (CH), 129.5 (2 x CH), 129.13 (CH), 129.1 (2 x CH), 127.9 (C), 126.2 (CH), 123.5 (2 x CH), 120.1 (CH), 118.0 (CH), 112.7 (CH), 66.0 (CH_2, O*CH*$_2$), 61.2 (CH_2, O*CH*$_2$CH$_3$), 49.7 (CH_2, N*CH*$_2$), 15.2 (CH_3, Ar-*CH*$_3$), 13.7 (CH_3, OCH$_2$*CH*$_3$); LCMS m/z 443.00 ($M-H^+$), calcd $C_{26}H_{24}N_2O_5$ 444.1685; Anal. calcd for $C_{26}H_{24}N_2O_5$ (444.16): C, 70.26; H, 5.44; N, 6.30. Found: C, 70.15; H, 5.47; N, 6.41%.

9-(4-Chloro-phenyl)-7-methyl-6-phenyl-5,6-dihydro-2H-benzo[b][1,4]oxazocine-8-carboxylic acid ethyl ester (7ka): Purified by column chromatography using EtOAc/hexane and isolated as a light yellow solid. IR (neat): ν_{max} 2980, 1724 (O-C=O), 1596, 1550, 1494, 1269, 1063, 744 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.36-7.29 (4H, m, Ph-*H*), 7.25-7.20 (2H, m), 6.91 (1H, s, Ar-*H*), 6.78 (1H, t, *J* = 7.2 Hz), 6.57 (2H, d, *J* = 8.0 Hz), 6.04-6.00 (1H, m, olefinic-*H*), 5.85-5.82 (1H, m, olefinic-*H*), 4.49 (3H, m, O*CH*$_2$, N*CH*$_2$), 4.06 (2H, q, *J* = 7.2 Hz, O*CH*$_2$CH$_3$), 4.08-4.05 (1H, m, N*CH*$_2$), 2.10 (3H, s, Ar-C*H*$_3$), 1.01 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 169.3 (C, O-C=O), 156.7 (C), 146.9 (C), 138.9 (C), 138.3 (C), 137.5 (C), 133.6 (C), 132.4 (CH), 131.4 (C), 129.5 (2 x CH), 129.4 (CH), 129.4 (2 x CH), 128.2 (2 x CH), 128.1 (C), 126.2 (CH), 120.1 (CH), 117.8 (CH), 112.7 (CH), 65.8 (CH_2, O*CH*$_2$), 61.1 (CH_2, O*CH*$_2$CH$_3$), 49.7 (CH_2, N*CH*$_2$), 15.1 (CH_3, Ar-*CH*$_3$), 13.7 (CH_3, OCH$_2$*CH*$_3$); LCMS m/z 434.25 ($M+H^+$), calcd $C_{26}H_{24}ClNO_3$ 433.1445; Anal. calcd for $C_{26}H_{24}ClNO_3$ (433.14): C, 71.97; H, 5.57; N, 3.23. Found: C, 72.11; H, 5.53; N, 3.28%.



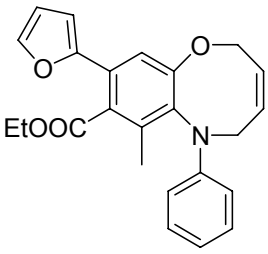
7ka



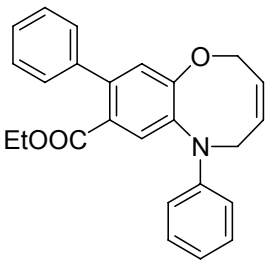
7la

9-Benzo[1,3]dioxol-5-yl-7-methyl-6-phenyl-5,6-dihydro-2H-benzo[b][1,4]oxazocine-8-carboxylic acid ethyl ester (7la): Purified by column chromatography using EtOAc/hexane and isolated as a light yellow solid. IR (neat): ν_{max} 2908, 1714 (O-C=O), 1596, 1550, 1500, 1471, 1239, 1030, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.23 (2H, t, *J* = 7.6 Hz), 6.91 (1H, s, Ar-*H*), 6.89 (1H, d, *J* = 1.6 Hz), 6.88-6.81 (2H, m), 6.77 (1H, t, *J* = 7.2 Hz), 6.57 (2H, d, *J* = 8.0 Hz), 6.04-5.98 (1H, m, olefinic-*H*), 5.98 (2H, s, O*CH*$_2$O), 5.84-5.81 (1H, m, olefinic-*H*), 4.68-4.49 (3H, m, O*CH*$_2$, N*CH*$_2$), 4.11 (2H, q, *J* = 7.2 Hz, O*CH*$_2$CH$_3$), 4.10-4.05 (1H, m, N*CH*$_2$), 2.09 (3H, s, Ar-C*H*$_3$), 1.08 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 169.6 (C, O-C=O), 156.6 (C), 147.5 (C), 147.1 (C), 147.0 (C), 139.3 (C), 137.0 (C), 134.4 (C), 132.3 (CH), 131.0 (C), 129.4 (2 x CH), 129.4 (CH), 128.3 (C), 126.3 (CH), 121.8 (CH), 120.1 (CH), 117.7 (CH), 112.7 (CH), 108.9 (CH), 108.1 (CH), 101.1 (CH$_2$, O*CH*$_2$O), 65.8 (CH$_2$, O*CH*$_2$), 61.0 (CH$_2$, O*CH*$_2$CH$_3$), 49.7 (CH$_2$, N*CH*$_2$), 15.1 (CH$_3$, Ar-*CH*$_3$), 13.9 (CH$_3$, OCH$_2$*CH*$_3$); LCMS m/z 442.70 ($M-H^+$), calcd $C_{27}H_{25}NO_5$ 443.1733; Anal. calcd for $C_{27}H_{25}NO_5$ (443.17): C, 73.12; H, 5.68; N, 3.16. Found: C, 73.22; H, 5.63; N, 3.12%.

9-Furan-2-yl-7-methyl-6-phenyl-5,6-dihydro-2H-benzo[b][1,4]oxazocine-8-arboxylic acid ethyl ester (7ma): Purified by column chromatography using EtOAc/hexane and isolated as a liquid. IR (neat): ν_{max} 2920, 1726 (O-C=O), 1599, 1498, 1270, 1063, 745, 694 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.45 (1H, s), 7.21 (2H, t, *J* = 8.4 Hz), 7.21 (1H, s), 6.76 (1H, t, *J* = 7.6 Hz), 6.55 (2H, d, *J* = 8.4 Hz), 6.55 (1H, s, Ar-*H*), 6.46-6.44 (1H, m), 6.02-5.99 (1H, m, olefinic-*H*), 5.84-5.80 (1H, m, olefinic-*H*), 4.48 (3H, m, O*CH*$_2$, N*CH*$_2$), 4.33 (2H, q, *J* = 7.2 Hz, O*CH*$_2$CH$_3$), 4.33-4.30 (1H, m, N*CH*$_2$), 2.05 (3H, s, Ar-C*H*$_3$), 1.28 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 169.7 (C, O-C=O), 156.7 (C), 151.8 (C), 146.8 (C), 142.5 (CH), 136.9 (C), 132.2 (CH), 131.8 (C), 129.4 (2 x CH), 129.38 (CH), 127.3 (C), 126.4 (CH), 126.0 (C), 117.8 (CH), 117.1 (CH), 112.8 (CH), 111.6 (CH), 107.6 (CH), 66.1 (CH$_2$, O*CH*$_2$), 61.4 (CH$_2$, O*CH*$_2$CH$_3$), 49.5 (CH$_2$, N*CH*$_2$), 14.8 (CH$_3$, Ar-*CH*$_3$), 14.1



7ma

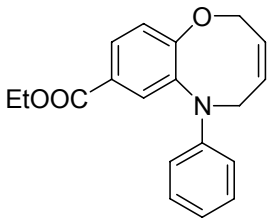


7na

(CH_3, OCH_2CH_3); LCMS m/z 389.16 (M^+), calcd $C_{24}H_{23}NO_4$ 389.1627; Anal. calcd for $C_{24}H_{23}NO_4$ (389.16): C, 74.02; H, 5.95; N, 3.60. Found: C, 74.15; H, 5.98; N, 3.68%.

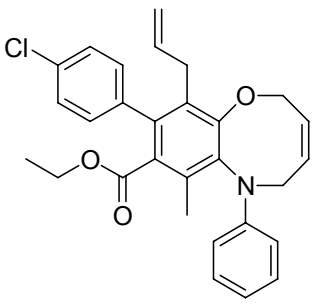
6,9-Diphenyl-5,6-dihydro-2H-benzo[b][1,4]oxazocine-8-carboxylic acid ethyl ester (7na): Purified by column chromatography using EtOAc/hexane and isolated as a light yellow solid. IR (neat): ν_{max} 3030, 2959, 2926, 1714 (O-C=O), 1597, 1545, 1500, 1105, 746, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.77 (1H, s, Ar-*H*), 7.43-7.34 (5H, m, Ph-*H*), 7.27 (2H, t, *J* = 7.2 Hz), 7.07 (1H, s, Ar-*H*), 6.84 (1H, t, *J* = 7.2 Hz), 6.79 (2H, d, *J* = 8.0 Hz), 6.07-6.04 (1H, m, olefinic-*H*), 5.89-5.84 (1H, m, olefinic-*H*), 4.62 (2H, d, *J* = 6.4 Hz, OCH_2), 4.42 (2H, d, *J* = 2.0 Hz, NCH_2), 4.07 (2H, q, *J* = 7.2 Hz, OCH_2CH_3), 1.01 (3H, t, *J* = 7.2 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.6 (C, O-C=O), 157.7 (C), 147.4 (C), 141.9 (C), 141.0 (C), 133.1 (CH), 133.0 (C), 132.1 (CH), 129.3 (2 x CH), 128.3 (2 x CH), 127.9 (2 x CH), 127.2 (CH), 126.6 (CH), 125.1 (C), 123.9 (CH), 118.4 (CH), 113.9 (2 x CH), 66.9 (CH_2, OCH_2), 60.7 (CH_2, OCH_2CH_3), 50.1 (CH_2, NCH_2), 13.7 (CH_3, OCH_2CH_3); GCMS m/z 385.05 (M^+), calcd $C_{25}H_{23}NO_3$ 385.4551; Anal. calcd for $C_{25}H_{23}NO_3$ (385.45): C, 77.90; H, 6.01; N, 3.63. Found: C, 77.937; H, 6.059; N, 3.709%.

6-Phenyl-5,6-dihydro-2H-benzo[b][1,4]oxazocine-8-carboxylic acid ethyl ester (7oa):



7oa

Purified by column chromatography using EtOAc/hexane and isolated as a light yellow liquid. IR (neat): ν_{max} 2982, 1711 (O-C=O), 1598, 1540, 1243, 1024, 745, 691 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.91 (1H, d, *J* = 2.4 Hz), 7.85 (1H, dd, *J* = 8.8, 2.4 Hz), 7.22 (2H, t, *J* = 7.6 Hz), 7.10 (1H, d, *J* = 8.8 Hz), 6.79 (1H, t, *J* = 7.2 Hz), 6.69 (2H, d, *J* = 8.8 Hz), 6.04-6.00 (1H, m, olefinic-*H*), 5.86-5.80 (1H, m, olefinic-*H*), 4.58 (2H, d, *J* = 6.4 Hz, OCH_2CH=CH), 4.37 (2H, d, *J* = 1.6 Hz, NCH_2), 4.35 (2H, q, *J* = 7.2 Hz, OCH_2CH_3), 1.35 (3H, t, *J* = 7.2 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 165.9 (C, O-C=O), 159.8 (C), 147.4 (C), 133.8 (C), 133.0 (CH), 132.3 (CH), 129.3 (2 x CH), 128.6 (CH), 126.3 (CH), 124.9 (C), 121.5 (CH), 118.1 (CH), 113.5 (2 x CH), 66.6 (CH_2, OCH_2), 60.8 (CH_2, OCH_2CH_3), 50.1 (CH_2, NCH_2), 14.3 (CH_3, OCH_2CH_3); LCMS m/z 309.85 ($M+H^+$), calcd $C_{19}H_{19}NO_3$ 309.1365; Anal. calcd for $C_{19}H_{19}NO_3$

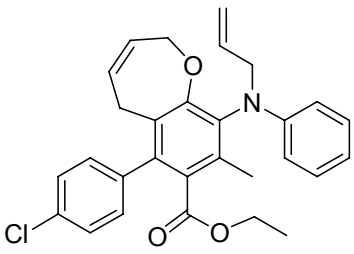


7pa

(309.13): C, 73.77; H, 6.19; N, 4.53. Found: C, 73.81; H, 6.22; N, 4.62%.

10-Allyl-9-(4-chloro-phenyl)-7-methyl-6-phenyl-5,6-dihydro-2H-benzo[b][1,4]oxazocine-8-carboxylic acid ethyl ester (7pa): Purified by column chromatography using EtOAc/hexane and isolated as a light yellow solid. IR (neat): ν_{max} 2974, 1720 (O-C=O), 1598, 1497, 1271, 1087, 738 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.34 (2H, d, *J* = 7.6 Hz), 7.28-7.18 (4H, m), 6.77 (1H, t, *J* = 7.2 Hz), 6.59 (2H, d, *J* = 7.2 Hz), 6.06-6.02 (1H, m, olefinic-*H*), 5.83-5.77 (2H, m, olefinic-*H*), 4.90 (1H, dd, *J* = 10.4, 1.2 Hz, olefinic-*H*), 4.73 (1H, dd, *J* = 17.2, 1.2 Hz, olefinic-*H*), 4.66 (1H, br s, NCH_2), 4.45-4.44 (2H, m, OCH_2), 4.06-4.02 (1H, m, NCH_2), 3.93 (2H, q, *J* = 7.2 Hz, OCH_2CH$_3$), 3.15 (2H, m, ArCH_2CH=CH$_2$), 2.02 (3H, s, Ar-CH_3), 0.94 (3H, t, *J* = 7.2 Hz, OCH$_2$CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 169.2 (C, O-C=O), 155.5 (C), 146.7 (C), 137.3 (C), 137.0 (C), 136.9 (CH), 133.4 (C), 133.2 (C), 132.6 (C), 131.9 (CH), 130.9 (2 x CH), 129.6 (C), 129.2 (3 x CH), 128.3 (C), 127.9 (2 x CH), 126.9 (CH), 117.7 (CH), 114.7 (CH$_2$), 113.0 (CH), 66.9 (CH$_2$, O*CH$_2$*), 60.9 (CH$_2$, O*CH$_2$*CH$_3$), 48.9 (CH$_2$, N*CH$_2$*), 32.3 (CH$_2$), 15.1 (CH$_3$, Ar-*CH$_3$*), 13.7 (CH$_3$, OCH$_2$*CH$_3$*); LCMS m/z 473.17 (M^+), calcd $C_{29}H_{28}ClNO_3$ 473.1758; Anal. calcd for $C_{29}H_{28}ClNO_3$ (473.17): C, 73.48; H, 5.95; N, 2.96. Found: C, 73.43; H, 5.98; N, 2.92%.

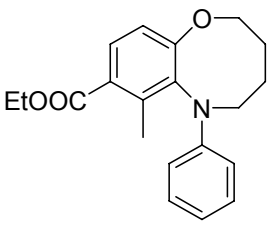
9-(Allyl-phenyl-amino)-6-(4-chloro-phenyl)-8-methyl-2,5-dihydro-benzo[b]oxepine-7-carboxylic acid ethyl ester (7'pa): Purified by column chromatography using EtOAc/hexane and isolated as a light yellow solid. IR (neat): ν_{max} 1723 (O-C=O), 1599, 1497, 1247, 1087, 733 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40 (2H, t, *J* = 8.0 Hz), 7.28-7.18 (4H, m), 6.75 (1H, t, *J* = 7.6 Hz), 6.62 (2H, d, *J* = 8.0 Hz), 6.09-6.00 (1H, m, olefinic-*H*), 5.69-5.63 (1H, m, olefinic-*H*), 5.37-5.29 (2H, m, olefinic-*H*), 5.23-5.19 (1H, m), 4.49-4.43 (1H, m), 4.33 (1H, dd, *J* = 16.4, 5.6 Hz), 4.20-4.06 (2H, m), 4.00 (2H, q, *J* = 7.2 Hz, OCH_2CH$_3$), 3.54 (1H, br d, *J* = 16.0 Hz), 2.90 (1H, dd, *J* = 15.6, 8.0 Hz), 2.18 (3H, s, Ar-CH_3), 1.03 (3H, t, *J* = 7.2 Hz, OCH$_2$CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 169.1 (C, O-C=O), 157.2 (C), 148.3 (C), 138.7 (C), 136.9



7'pa

(C), 135.6 (C), 135.5 (C), 135.35 (CH), 135.3 (C), 134.1 (C), 133.6 (C), 130.9 (2 x CH), 129.0 (CH), 129.0 (2 x CH), 128.2 (CH), 127.7 (CH), 125.0 (CH), 117.2 (CH), 116.7 (CH_2), 112.9 (2 x CH), 70.7 (CH_2, O*C*H_2), 61.0 (CH_2, O*C*$H_2$$CH_3$), 55.0 ($CH_2$, N*C*$H_2$), 27.1 ($CH_2$), 15.3 ($CH_3$, Ar-*C*$H_3$), 13.7 ($CH_3$, OCH_2*C*H_3); LCMS m/z 473.10 (M^+), calcd $C_{29}H_{28}ClNO_3$ 473.1758; Anal. calcd for $C_{29}H_{28}ClNO_3$ (473.17): C, 73.48; H, 5.95; N, 2.96. Found: C, 73.55; H, 5.91; N, 3.05%.

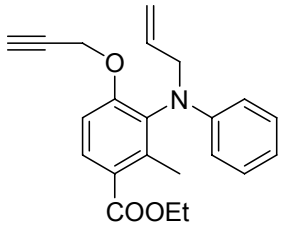
7-Methyl-6-phenyl-3,4, 5,6-tetrahydro-2H-benzo[b][1,4]oxazocine-8-carboxylic acid ethyl ester (8aa): Purified by column chromatography using EtOAc/hexane and isolated as a light yellow liquid. IR (neat): ν_{max} 2933, 1712 (O-C=O), 1595, 1499, 1278, 1050, 747 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.85 (1H, d, *J* = 8.4 Hz), 7.17 (2H, t, *J* = 8.4 Hz), 7.01 (1H, d, *J* = 8.8 Hz), 6.68 (1H, t, *J* = 7.2 Hz), 6.47 (2H, d, *J* = 8.0 Hz), 4.35 (2H, q, *J* = 7.2 Hz, O*C*$H_2$$CH_3$), 4.29-4.13 (3H, m), 3.1 (1H, m), 2.33 (3H, s, Ar-*C*H_3), 2.08 (1H, m), 1.74-1.60 (3H, m), 1.39 (3H, t, *J* = 7.2 Hz, OCH_2*C*H_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.5 (C, O-C=O), 159.9 (C), 147.8 (C), 142.2 (C), 136.7 (C), 130.6 (CH), 129.31 (CH), 129.3 (2 x CH), 126.6 (C), 119.4 (CH), 116.7 (CH), 112.2 (CH), 72.9 (CH_2, O*C*H_2), 60.7 (CH_2, O*C*$H_2$$CH_3$), 50.2 ($CH_2$, N*C*$H_2$), 28.7 ($CH_2$), 23.7 ($CH_2$), 15.2 ($CH_3$, Ar-*C*$H_3$), 14.3 ($CH_3$, OCH_2*C*H_3); LCMS m/z 325.55 (M^+), calcd $C_{20}H_{23}NO_3$ 325.1678; Anal. calcd for $C_{20}H_{23}NO_3$ (325.16): C, 73.82; H, 7.12; N, 4.30. Found: C, 73.78; H, 7.16; N, 4.36%.



8aa

3-Phenylamino-4-prop-2-ynyloxy-benzoic acid ethyl ester (9oa): Purified by column chromatography using EtOAc/hexane and isolated as a light yellow liquid. IR (neat): ν_{max} 3297 (N-*H*), 3294 (C≡C-H), 1709 (O-C=O), 1594, 1572, 1495, 1245, 1022, 753, 694 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.00 (1H, d, *J* = 2.0 Hz), 7.59 (1H, dd, *J* = 8.8, 2.4 Hz), 7.30 (2H, t, *J* = 7.6 Hz), 7.18 (2H, d, *J* = 8.8 Hz), 7.02-6.98 (2H, m), 6.19 (1H, s, N-*H*), 4.81 (2H, d, *J* = 2.4 Hz, O*C*H_2C≡CH), 4.33 (2H, q, *J* = 7.2 Hz, O*C*$H_2$$CH_3$), 2.59 (1H, t, *J* = 2.4 Hz, OCH_2C≡C*H*), 1.36 (3H, t, *J* = 7.2 Hz, OCH_2*C*H_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 166.5 (C, O-C=O), 149.5 (C), 141.8 (C), 133.4 (C), 129.5 (2 x CH), 124.1 (C),

9oa

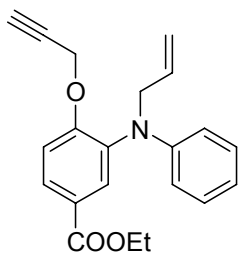


10aa

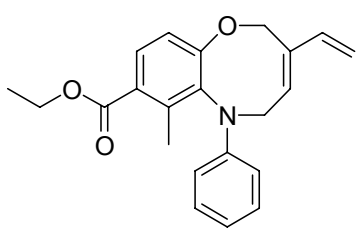
121.9 (CH), 121.7 (CH), 119.1 (2 x CH), 115.3 (CH), 111.3 (CH), 77.8 (C, *C*≡CH), 76.4 (CH, C≡*CH*), 60.8 (CH_2, O*CH*$_2$$CH_3$), 56.4 ($CH_2$, O*CH*$_2$C≡CH), 14.4 ($CH_3$, OCH$_2$*CH*$_3$); LRMS m/z 296.00 ($M^+$), calcd $C_{18}H_{17}NO_3$ 296.1208.

3-(Allyl-phenyl-amino)-2-methyl-4-prop-2-ynyloxy-benzoic acid ethyl ester (10aa): Purified by column chromatography using EtOAc/hexane and isolated as a light yellow liquid. IR (neat): ν_{max} 3290 (C≡C-H), 2980, 1712 (O-C=O), 1599, 1500, 1168, 1068, 746, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.93 (1H, d, *J* = 8.4 Hz), 7.15 (2H, t, *J* = 7.2 Hz), 6.99 (1H, d, *J* = 8.8 Hz), 6.70 (1H, t, *J* = 7.2 Hz), 6.48 (2H, d, *J* = 8.4 Hz), 6.02-5.95 (1H, m, olefinic-*H*), 5.27 (1H, dd, *J* = 17.2, 1.6 Hz, olefinic-*H*), 5.12 (1H, dd, *J* = 10.4, 1.6 Hz, olefinic-*H*), 4.72 (2H, dABq, *J* = 16.4, 2.8 Hz, OC*H*$_2$C≡CH), 4.35 (2H, q, *J* = 6.8 Hz, OC*H*$_2$$CH_3$), 4.18 (2H, dABq, *J* = 16.0, 5.6 Hz, NC*H*$_2$CH=CH_2), 2.46 (1H, t, *J* = 2.4 Hz, OCH$_2$C≡C*H*), 2.42 (3H, s, Ar-C*H*$_3$), 1.39 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.4 (C, O-C=O), 158.0 (C), 147.9 (C), 142.5 (C), 135.0 (CH), 134.5 (C), 130.6 (CH), 128.9 (2 x CH), 124.6 (C), 116.9 (CH), 116.8 (CH_2), 112.3 (2 x CH), 110.4 (CH), 77.9 (C, *C*≡CH), 75.9 (CH, C≡*CH*), 60.7 (CH_2, O*CH*$_2$$CH_3$), 55.8 ($CH_2$, O*CH*$_2$C≡CH), 54.5 ($CH_2$, N*CH*$_2$CH=$CH_2$), 15.9 ($CH_3$, Ar-*CH*$_3$), 14.4 ($CH_3$, OCH$_2$*CH*$_3$); GCMS m/z 349.25 ($M^+$), calcd $C_{22}H_{23}NO_3$ 349.1678.

3-(Allyl-phenyl-amino)-4-prop-2-ynyloxy-benzoic acid ethyl ester (**10oa**): Purified by column chromatography using EtOAc/hexane and isolated as a solid. IR (neat): ν_{max} 3289 (C≡C-H), 1712 (O-C=O), 1590, 1517, 1438, 1180, 1030, 743, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.98-7.94 (2H, m), 7.17-7.12 (3H, m), 6.74 (1H, t, *J* = 8.0 Hz), 6.62 (2H, d, *J* = 8.4 Hz), 6.05-5.98 (1H, m, olefinic-*H*), 5.35-5.25 (1H, m, olefinic-*H*), 5.16 (1H, dd, *J* = 10.4, 1.6 Hz, olefinic-*H*), 4.70 (2H, d, *J* = 2.4 Hz, OC*H*$_2$C≡CH), 4.34 (2H, q, *J* = 7.2 Hz, OCH$_2$$CH_3$), 4.24 (2H, d, *J* = 5.2 Hz, NC*H*$_2$CH=CH_2), 2.47 (1H, t, *J* = 2.0 Hz, OCH$_2$C≡C*H*), 1.36 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 165.9 (C, O-C=O), 157.7 (C), 148.1 (C), 135.6 (C), 134.5 (CH), 131.9 (CH), 128.8 (3 x CH), 124.6 (C), 117.6 (CH), 116.4 (CH_2), 113.9 (2 x CH), 113.7 (CH), 77.7 (C), 76.06 (CH), 60.8 (CH_2, O*CH*$_2$$CH_3$), 56.1 ($CH_2$, O*CH*$_2$C≡CH), 54.3 ($CH_2$,



10oa

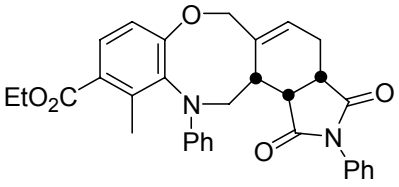


11aa

N*CH*$_2$), 14.3 (CH_3, OCH_2*CH*$_3$); LCMS m/z 336.35 ($M+H^+$), calcd $C_{21}H_{21}NO_3$ 335.1521.

7-Methyl-6-phenyl-3-vinyl-5,6-dihydro-2H-benzo[b][1,4]oxazocine-8-carboxylic acid ethyl ester (11aa): Purified by column chromatography using EtOAc/hexane and isolated as a solid. IR (neat): ν_{max} 2980, 2932, 1714 (O-C=O), 1597, 1500, 1103, 1049, 748, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.79 (1H, d, *J* = 8.8 Hz), 7.20 (2H, t, *J* = 7.2 Hz), 6.93 (1H, d, *J* = 8.8 Hz), 6.76 (1H, t, *J* = 7.2 Hz), 6.50 (2H, d, *J* = 8.0 Hz), 6.32 (1H, dd, *J* = 17.6, 11.2 Hz, olefinic-*H*), 5.95 (1H, t, *J* = 4.0 Hz, olefinic-*H*), 5.28 (1H, br d, *J* = 17.6 Hz, olefinic-*H*), 5.02 (1H, br d, *J* = 10.8 Hz, olefinic-*H*), 4.78-4.77 (3H, m), 4.33 (2H, q, *J* = 7.2 Hz, OC*H*$_2$CH$_3$), 4.10 (1H, m), 2.29 (3H, s, Ar-C*H*$_3$), 1.38 (3H, t, *J* = 7.2 Hz, OCH_2C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.4 (C, O-C=O), 159.1 (C), 147.0 (C), 142.2 (C), 137.6 (CH), 135.9 (C), 132.6 (C), 131.9 (CH), 130.3 (CH), 129.41 (CH), 129.4 (2 x CH), 125.1 (C), 118.4 (CH), 117.7 (CH), 112.5 (CH), 112.3 (CH_2), 64.7 (CH_2, O*CH*$_2$), 60.6 (CH_2, O*CH*$_2$CH$_3$), 48.9 (CH_2, N*CH*$_2$), 15.3 (CH_3, Ar-*CH*$_3$), 14.3 (CH_3, OCH_2*CH*$_3$); GCMS m/z 349.20 (M^+), calcd $C_{22}H_{23}NO_3$ 349.1678; Anal. calcd for $C_{22}H_{23}NO_3$ (349.16): C, 75.62; H, 6.63; N, 4.01. Found: C, 75.773; H, 6.629; N, 4.024%.

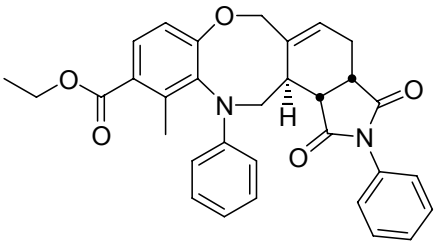
***endo*-Ethyl-11-methyl-1,3-dioxo-2,12-diphenyl-1,2,3,3a,4,6,12,13,13a,13b-decahydrobenzo[2,3][1,4]oxazocino[6,7-e]isoindole-10-carboxylate (12aa):** Purified by column chromatography using EtOAc/hexane and isolated as a solid. IR (neat): ν_{max} 3061, 2924, 1776 (C=O), 1705 (O-C=O), 1601, 1496, 1105, 1037, 748, 694 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.84 (1H, d, *J* = 8.4 Hz), 7.49 (2H, t, *J* = 7.6 Hz, *P*h-*H*), 7.41 (1H, t, *J* = 7.6 Hz, *P*h-*H*), 7.32 (2H, d, *J* = 7.6 Hz), 7.19 (2H, t, *J* = 8.0 Hz), 7.05 (1H, d, *J* = 8.4 Hz), 6.73 (1H, t, *J* = 7.2 Hz), 6.54 (2H, d, *J* = 7.6 Hz), 5.73 (1H, t, *J* = 5.2 Hz, olefinic-*H*), 4.64 (1H, d, *J* = 12.4 Hz), 4.35 (2H, q, *J* = 7.2 Hz, OC*H*$_2$CH$_3$), 4.35-4.27 (2H, m), 3.65-3.61 (1H, m), 3.38-3.32 (3H, m), 2.56-2.50 (1H, m), 2.39-2.35 (1H, m), 2.29 (3H, s, Ar-C*H*$_3$), 1.38 (3H, t, *J* = 7.2 Hz, OCH_2C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 178.3 (C=O), 176.9 (C=O), 167.3 (C, O-C=O), 159.8 (C), 146.4 (C), 141.0 (C), 139.2 (C), 139.1 (C), 131.6 (C), 130.5 (CH), 129.5 (2 x CH), 129.2 (2 x CH), 128.8 (CH), 127.9 (C), 127.8 (CH), 126.3 (3 x CH), 120.4 (CH), 117.5 (CH), 112.3 (CH), 78.5 (CH_2, O*CH*$_2$), 60.9 (CH_2,



endo-12aa

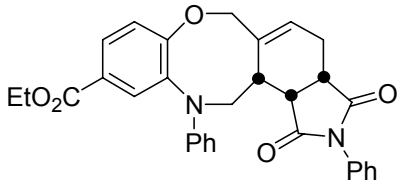
O*CH*$_2$CH$_3$), 48.7 (CH$_2$, N*CH*$_2$), 42.7 (CH), 38.9 (CH), 34.5 (CH), 23.1 (CH$_2$), 15.6 (CH$_3$, Ar-*CH*$_3$), 14.3 (CH$_3$, OCH$_2$*CH*$_3$); GCMS m/z 522.10 (M$^+$), calcd $C_{32}H_{30}N_2O_5$ 522.2155.

***exo*-Ethyl-11-methyl-1,3-dioxo-2,12-diphenyl-1,2,3,3a,4,6,12,13,13a,13b-decahydrobenzo[2,3][1,4]oxazocino[6,7-e]isoindole-10-carboxylate (13aa):** Purified by column chromatography using EtOAc/hexane and isolated as a solid. IR (neat): ν_{max} 3061, 2924, 1705 (O-C=O), 1601, 1496, 1105, 1037, 748, 694 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.88 (1H, d, *J* = 8.4 Hz), 7.45 (2H, t, *J* = 7.2 Hz), 7.40-7.36 (1H,m), 7.22 (2H, d, *J* = 8.0 Hz), 7.21 (2H, t, *J* = 8.0 Hz), 7.05 (1H, d, *J* = 8.4 Hz), 6.74 (1H, t, *J* = 7.6 Hz), 6.50 (2H, d, *J* = 8.0 Hz), 5.62 (1H, dd, *J* = 6.8, 2.0 Hz, olefinic-*H*), 4.58 (1H, d, *J* = 12.0 Hz), 4.37 (2H, q, *J* = 7.2 Hz, OC*H*$_2$CH$_3$), 4.28-4.22 (2H, m), 3.74 (1H, d, *J* = 11.2 Hz), 3.29-3.18 (3H, m), 2.66-2.59 (1H, m), 2.52-2.47 (1H, m), 2.40 (3H, s, Ar-C*H*$_3$), 1.38 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$, DEPT-135) δ 178.5 (C=O), 177.5 (C=O), 167.3 (C, O-C=O), 159.7 (C), 146.7 (C), 141.4 (C), 139.6 (C), 138.6 (C), 131.8 (C), 131.0 (CH), 129.5 (2 x CH), 129.1 (2 x CH), 128.7 (CH), 128.1 (C), 127.5 (CH), 126.2 (3 x CH), 120.7 (CH), 117.5 (CH), 111.9 (CH), 79.6 (CH$_2$, O*CH*$_2$), 60.9 (CH$_2$, O*CH*$_2$CH$_3$), 53.1 (CH$_2$, N*CH*$_2$), 43.8 (CH), 38.1 (CH), 35.7 (CH), 23.8 (CH$_2$), 15.2 (CH$_3$, Ar-*CH*$_3$), 14.3 (CH$_3$, OCH$_2$*CH*$_3$); GCMS m/z 522.10 (M$^+$), calcd $C_{32}H_{30}N_2O_5$ 522.2155.



13aa

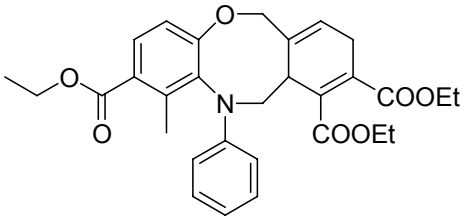
***endo*-Ethyl-1,3-dioxo-2,12-diphenyl-1,2,3,3a,4,6,12,13,13a,13b-decahydrobenzo[2,3][1,4]oxazocino[6,7-e]isoindole-10-carboxylate (12oa):** Purified by column chromatography using EtOAc/hexane and isolated as a solid. IR (neat): ν_{max} 1709 (O-C=O), 1597, 1498, 1265, 1107, 736, 700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.92 (1H, d, *J* = 2.0 Hz), 7.74 (1H, dd, *J* = 8.4, 2.4 Hz), 7.46 (2H, t, *J* = 7.6 Hz), 7.38 (1H, t, *J* = 7.6 Hz), 7.28-7.24 (4H, m), 7.11 (1H, d, *J* = 8.4 Hz), 6.92 (2H, d, *J* = 8.0 Hz), 6.85 (1H, t, *J* = 7.2 Hz), 5.85 (1H, m, olefinic-*H*), 4.58 (2H, m, OC*H*$_2$), 4.41 (1H, dd, *J* = 15.6, 4.4 Hz), 4.35-4.21 (3H, m, OC*H*$_2$CH$_3$, NC*H*$_2$), 3.35-3.30 (2H, m), 3.20-3.17 (1H, m), 2.78-2.72 (1H, m), 2.22-2.18 (1H, m), 1.35 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$, DEPT-135) δ



endo-**12oa**

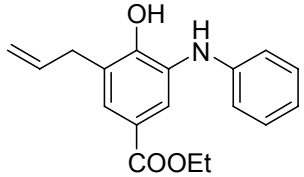
178.4 (C=O), 176.5 (C=O), 166.0 (C, O-C=O), 158.8 (C), 144.99 (C), 138.92 (C), 138.6 (C), 131.8 (C), 129.6 (2 x CH), 129.3 (2 x CH), 128.9 (CH), 128.7 (CH), 126.7 (CH), 126.5 (3 x CH), 126.4 (CH), 126.0 (C), 122.5 (CH), 119.3 (CH), 115.7 (CH), 75.8 (CH_2, O*CH₂*), 60.9 (CH_2, O*CH₂*CH_3), 48.5 (CH_2, N*CH₂*), 42.3 (CH), 40.0 (CH), 33.6 (CH), 24.2 (CH_2), 14.3 (CH_3, OCH_2*CH₃*); LCMS m/z 507.00 ($M-H^+$), calcd $C_{31}H_{28}N_2O_5$ 508.1998; Anal. calcd for $C_{31}H_{28}N_2O_5$ (508.19): C, 73.21; H, 5.55; N, 5.51. Found: C, 73.28; H, 5.57; N, 5.56%.

Triethyl-1-methyl-12-phenyl-8,10a,11,12-tetrahydro-6H-dibenzo[b,f][1,4]oxazocine-2,9,10-tricarboxylate (14aa): Purified by column chromatography using EtOAc/hexane and isolated as a solid. IR (neat): ν_{max} 2985, 1721 (O-C=O), 1597, 1502, 1480, 1263, 1071, 737, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.89 (1H, d, *J* = 8.4 Hz), 7.18 (2H, t, *J* = 8.0 Hz), 7.08 (1H, d, *J* = 8.4 Hz), 6.72 (1H, t, *J* = 7.2 Hz), 6.57 (2H, d, *J* = 7.6 Hz), 5.61-5.60 (1H, m, olefinic-*H*), 4.67 (1H, br d, *J* = 12.0 Hz), 4.50-4.33 (6H, m), 4.24 (2H, q, *J* = 7.2 Hz, O*CH₂*CH_3), 3.93-3.91 (1H, m), 2.97-2.75 (3H, m), 2.36 (3H, s, Ar-C*H₃*), 1.45 (3H, t, *J* = 7.2 Hz, OCH_2*CH₃*), 1.40 (3H, t, *J* = 7.2 Hz, OCH_2*CH₃*), 1.31 (3H, t, *J* = 7.2 Hz, OCH_2*CH₃*); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.6 (C, O-C=O), 167.3 (C, O-C=O), 167.0 (C, O-C=O), 159.8 (C), 147.1 (C), 141.2 (C), 139.1 (C), 136.9 (C), 136.5 (C), 134.4 (C), 131.1 (CH), 129.3 (2 x CH), 127.9 (C), 125.6 (CH), 120.3 (CH), 117.1 (CH), 111.5 (2 x CH), 79.1 (CH_2, O*CH₂*), 61.7 (CH_2, O*CH₂*CH_3), 61.4 (CH_2, O*CH₂*CH_3), 60.9 (CH_2, O*CH₂*CH_3), 54.7 (CH_2, N*CH₂*), 38.1 (CH), 28.9 (CH_2), 14.9 (CH_3, Ar-*CH₃*), 14.3 (CH_3, OCH_2*CH₃*), 14.1 (CH_3, OCH_2*CH₃*), 13.9 (CH_3, OCH_2*CH₃*); LCMS m/z 520.00 ($M+H^+$), calcd $C_{30}H_{33}NO_7$ 519.2257; Anal. calcd for $C_{30}H_{33}NO_7$ (519.22): C, 69.35; H, 6.40; N, 2.70. Found: C, 69.28; H, 6.45; N, 2.78%.



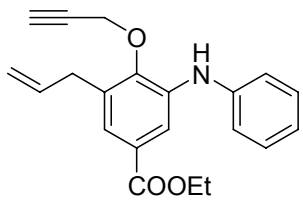
14aa

3-Allyl-4-hydroxy-5-phenylamino-benzoic acid ethyl ester (15oa): Purified by column chromatography using EtOAc/hexane and isolated as a light yellow liquid. IR (neat): ν_{max} 3371 (O-H & N-*H)*, 1685 (O-C=O), 1677, 1598, 1517, 1219, 1026, 745, 697 cm^{-1}; ^1H NMR



15oa

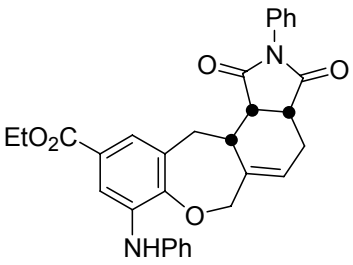
($CDCl_3$) δ 7.80 (1H, d, *J* = 1.6 Hz), 7.70 (1H, s, Ar-*H*), 7.23 (2H, t, *J* = 8.0 Hz), 6.91 (1H, t, *J* = 7.2 Hz), 6.78 (2H, d, *J* = 8.0 Hz), 6.43 (1H, s, O-*H*), 6.08-6.03 (1H, m, olefinic-*H*), 5.31 (1H, s, N-*H*), 5.19-5.15 (2H, m, olefinic-*H*), 4.31 (2H, q, *J* = 7.2 Hz, OCH_2CH_3), 3.48 (2H, d, *J* = 6.0 Hz, $CH_2CH{=}CH_2$), 1.35 (3H, t, *J* = 7.2 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 166.3 (C, O-C=O), 153.4 (C), 145.1 (C), 135.8 (CH), 129.5 (2 x CH), 129.0 (C), 128.5 (CH), 125.9 (C), 124.3 (CH), 122.8 (C), 120.8 (CH), 116.6 (CH_2, $CH{=}CH_2$), 116.1 (2 x CH), 60.7 (CH_2, OCH_2CH_3), 34.6 (CH_2, $CH_2CH{=}CH_2$), 14.3 (CH_3, OCH_2CH_3); LCMS m/z 298.05 ($M+H^+$), calcd $C_{18}H_{19}NO_3$ 297.1365.



16oa

3-Allyl-5-phenylamino-4-prop-2-ynyloxy-benzoic acid ethyl ester (16oa): Purified by column chromatography using EtOAc/hexane and isolated as a light yellow liquid. IR (neat): ν_{max} 3389 (C≡C-H & N-*H)*, 1712 (O-C=O), 1590, 1517, 1256, 1030, 743, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.87 (1H, d, *J* = 2.4 Hz), 7.45 (1H, d, *J* = 2.0 Hz), 7.32 (2H, t, *J* = 8.4 Hz), 7.13 (2H, dd, *J* = 7.6 Hz, 2.0 Hz), 7.00 (1H, t, *J* = 7.2 Hz), 6.19 (1H, s, N-*H*), 6.04-5.99 (1H, m, olefinic-*H*), 5.14-5.10 (2H, m, olefinic-*H*), 4.60 (2H, d, *J* = 2.4 Hz, $OCH_2C{\equiv}CH$), 4.33 (2H, q, *J* = 7.2 Hz, OCH_2CH_3), 3.50 (2H, d, *J* = 2.4 Hz, $ArCH_2CH{=}CH_2$), 2.54 (1H, t, *J* = 2.4 Hz, $OCH_2C{\equiv}CH$), 1.35 (3H, t, *J* = 7.2 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 166.4 (C, O-C=O), 149.1 (C), 142.0 (C), 137.2 (C), 136.4 (CH), 133.8 (C), 129.5 (2 x CH), 127.2 (C), 123.2 (CH), 121.8 (CH), 118.7 (2 x CH), 116.5 (CH_2, $CH{=}CH_2$), 115.5 (CH), 78.7 (C, *C*≡CH), 76.1 (CH, C≡*CH*), 60.9 (CH_2, $OCH_2C{\equiv}CH$), 60.5 (CH_2, OCH_2CH_3), 34.3 (CH_2, $ArCH_2CH{=}CH_2$), 14.3 (CH_3, OCH_2CH_3); LCMS m/z 336.55 ($M+H^+$), calcd $C_{21}H_{21}NO_3$ 335.1521.

***endo*-Ethyl-8-anilino-1,3-dioxo-2-phenyl-2,3,3a,4,6,12,12a,12b-octahydro-1*H*-benzo[6,7]oxepino[4,3-e]isoindole-10-carboxylate (18oa):** Purified by column chromatography using EtOAc/hexane and isolated as a solid. IR (neat): ν_{max} 1709 (O-C=O), 1586 1496, 1470, 1035, 736, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.82 (1H, d, *J* = 1.2 Hz), 7.46 (2H, t, *J* = 7.6 Hz), 7.39 (1H, t, *J* = 7.6 Hz), 7.36 (1H, d, *J* = 1.2 Hz), 7.29 (2H, t, *J* = 8.4 Hz), 7.20 (2H,



***endo*-18oa**

d, *J* = 8.0 Hz), 7.15 (2H, d, *J* = 8.0 Hz), 6.98 (1H, t, *J* = 7.6 Hz), 6.17-6.16 (2H, m, ArPhN*H* and olefinic-*H*), 5.25 (1H, d, *J* = 12.4 Hz), 4.54 (1H, d, *J* = 12.4 Hz), 4.31 (2H, q, *J* = 7.2 Hz, OC*H*$_2$CH$_3$), 4.25 (1H, d, *J* = 14.8 Hz), 3.43-3.35 (2H, m), 3.02-2.88 (3H, m), 2.35-2.31 (1H, m), 1.35 (3H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 178.3 (C=O), 176.5 (C=O), 166.5 (C, O-C=O), 148.1 (C), 142.0 (C), 139.8 (C), 133.9 (C), 131.7 (C), 129.4 (2 x CH), 129.1 (2 x CH), 128.7 (CH), 127.3 (CH), 126.3 (2 x CH), 124.7 (C), 124.6 (CH), 122.9 (C), 121.7 (CH), 119.1 (2 x CH), 113.8 (CH), 70.4 (CH_2, O*CH*$_2$), 60.6 (CH_2, O*CH*$_2$CH$_3$), 44.5 (CH), 40.2 (CH), 38.9 (CH), 33.9 (CH_2), 24.9 (CH_2), 14.4 (CH_3, OCH$_2$*CH*$_3$); LCMS m/z 509.05 ($M+H^+$), calcd $C_{31}H_{28}N_2O_5$ 508.1998; Anal. calcd for $C_{31}H_{28}N_2O_5$ (508.19): C, 73.21; H, 5.55; N, 5.51. Found: C, 73.35; H, 5.52; N, 5.58%.

References:

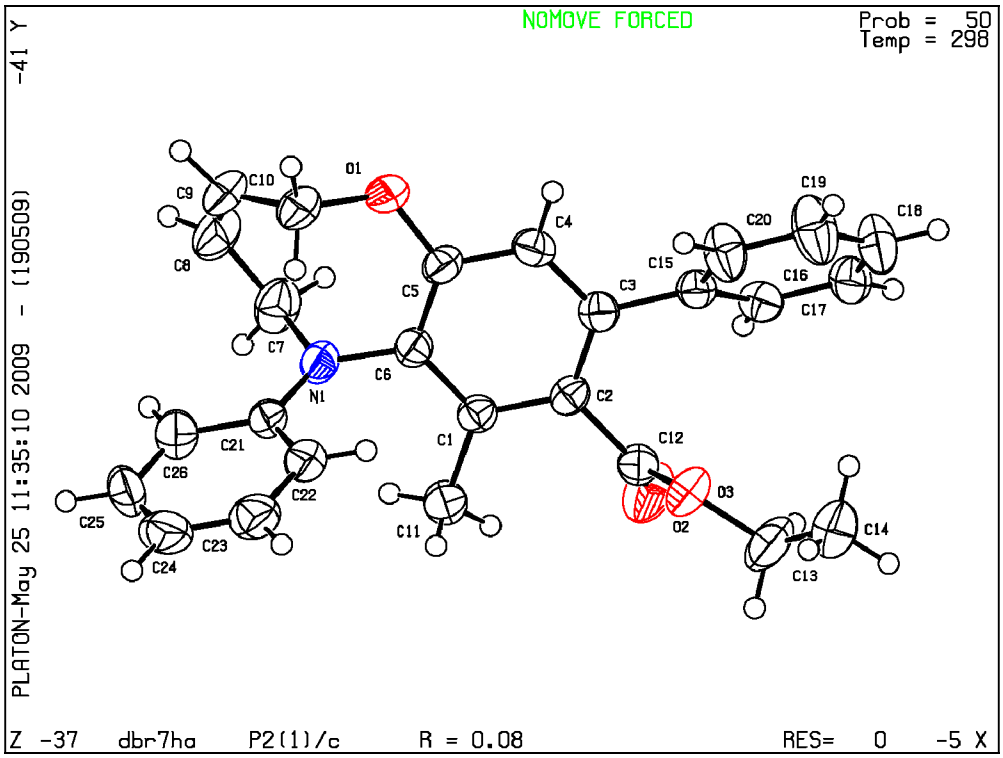
1. (a) Ramachary, D. B.; Ramakumar, K.; Narayana, V. V. *J. Org. Chem.* **2007**, *72*, 1458-1463; (b) Ramachary, D. B.; Narayana, V. V.; Ramakumar, K. *Eur. J. Org. Chem.* **2008**, 3907–3911.
2. (a) Taniguchi, Y.; Inanaga, J.; Yamaguchi, M. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3229-3230. (b) Yamamoto, Y.; Nunokawa, K.; Ohno, M.; Eguchi, S. *Synthesis* **1996**, 949-953. (c) Ackland, D. J.; Pinhey, J. T. *J. Chem. Soc. Perkin Trans 1* **1987**, 2689-2694.

Check CIF/PLATON report
Data block: DBR-7ha

```
Bond precision:      C-C = 0.0043 A              Wavelength=0.71073
Cell:        a=14.2321(13)  b=13.8619(13)  c=11.2976(11)
             alpha=90       beta=105.460(2) gamma=90
Temperature: 298 K
                    Calculated                      Reported
Volume              2148.2(4)                       2148.2(4)
Space group         P 21/c                          P2(1)/c
Hall group          -P 2ybc                         ?
Moiety formula      C26 H25 N O3                    ?
Sum formula         C26 H25 N O3                    C26 H25 N O3
Mr                  399.47                          399.47
Dx,g cm-3           1.235                           1.235
Z                   4                               4
Mu (mm-1)           0.080                           0.080
F000                848.0                           848.0
F000'               848.38
h,k,lmax            17,17,13                        17,17,13
Nref                4246                            4240
Tmin,Tmax           0.990,0.995                     0.969,0.995
Tmin'               0.969
Correction method= MULTI-SCAN
Data completeness= 0.999       Theta(max)= 26.050
R(reflections)= 0.0784( 3108)     wR2(reflections)= 0.1655( 4240)
S = 1.121             Npar= 273
```

PLATON version of 19/05/2009; check.def file version of 13/05/2009

Data block DBR-7ha - ellipsoid plot

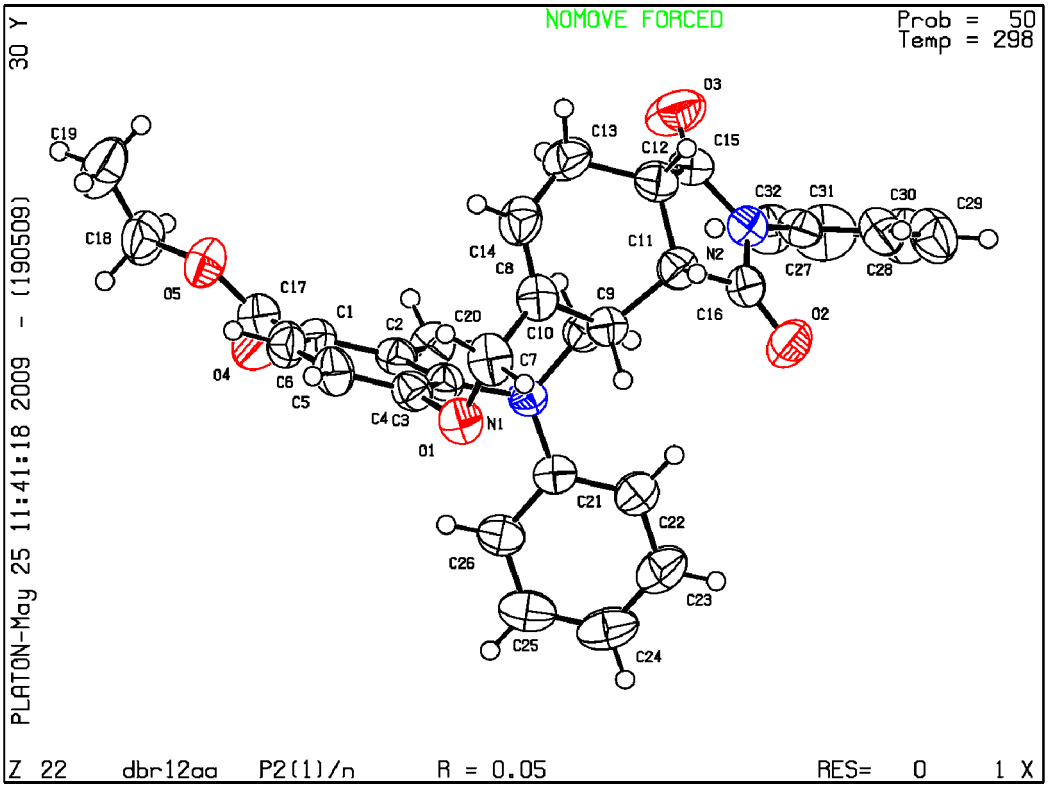

NOMOVE FORCED
Prob = 50
Temp = 298
-41 Y
PLATON-May 25 11:35:10 2009 - (190509)
O1
C10
C9
C8
C7
N1
C6
C5
C4
C3
C15
C20
C19
C18
C16
C17
C2
C1
C12
O3
O2
C14
C13
C11
C21
C26
C22
C25
C23
C24
Z -37 dbr7ha P2(1)/c R = 0.08 RES= 0 -5 X

Check CIF/PLATON report
Data block: DBR-12aa

```
Bond precision:     C-C = 0.0028 A              Wavelength=0.71073
Cell:       a=12.9791(7)   b=15.0018(8)   c=13.9935(8)
            alpha=90       beta=91.827(1) gamma=90
Temperature:298 K
                  Calculated                    Reported
Volume            2723.3(3)                     2723.3(3)
Space group       P 21/n                        P2(1)/n
Hall group        -P 2yn                        ?
Moiety formula    C32 H30 N2 O5                 ?
Sum formula       C32 H30 N2 O5                 C32 H30 N2 O5
Mr                522.58                        522.58
Dx,g cm-3         1.275                         1.275
Z                 4                             4
Mu (mm-1)         0.086                         0.086
F000              1104.0                        1104.0
F000'             1104.52
h,k,lmax          16,18,17                      15,18,17
Nref              5382                          5359
Tmin,Tmax         0.970,0.983                   0.970,0.983
Tmin'             0.970
Correction method= MULTI-SCAN
Data completeness= 0.996       Theta(max)= 26.050
R(reflections)= 0.0473( 3670)     wR2(reflections)= 0.1228( 5359)
S = 1.021            Npar= 354
```

PLATON version of 19/05/2009; check.def file version of 13/05/2009

Data block DBR-12aa - ellipsoid plot


NOMOVE FORCED
Prob = 50
Temp = 298
30 Y
PLATON-May 25 11:41:18 2009 - (190509)
Z 22 dbr12aa P2(1)/n R = 0.05 RES= 0 1 X
O3
C19
C13
C12
C15
C32
C31
C30
C29
C18
C14
C8
C11
N2
C27
C28
O5
C17
C1
C2
C20
C10
C9
C16
O2
O4
C6
C7
C5
C4
C3
N1
O1
C21
C22
C26
C23
C25
C24