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Quinuclidine *N*-oxide (QNO) (1)
A magnetically stirred solution of quinuclidine (3g, 27mmol) in Et_2O (50ml) was cooled to -78°C. O_3 was passed through the solution for 3 hours (during which time a precipitate formed), before purging with N_2 for 5 minutes. The mixture was allowed to warm to ambient temperature before removing the Et_2O *in vacuo* affording QNO (3.26g, 95%) as a white solid to be used immediately or stored over P_2O_5 in a vacuum desiccator.

Lithiation of QNO
A suspension of QNO (0.5g, 3.94mmol) in THF (50ml) was subject to ultrasonic irradiation for 10 minutes before cooling to -78°C and adding a 1.3M solution of ^{t}BuLi in hexane (3.33ml, 4.33mmol). The mixture was stirred at -78°C for an additional 30 minutes after which time a deep orange colour forms. Use of such a solution of Li-QNO is described in the following procedures.

Methyl 2-(nitromethyl)-3-phenylpropanoate (4)
A suspension of QNO (0.95g, 7.5mmol) in dry THF (50ml) was subject to ultrasonic radiation for 10 minutes under an atmosphere of N_2. The resulting suspension was magnetically stirred and cooled to -78°C before adding a 1.3M solution of ^{t}BuLi in hexane (2.31ml, 3.0mmol). The solution was stirred for a further 30 minutes before adding methyl 3-nitroproponate (2) (0.2g, 1.5mmol) in THF (2ml) and stirring at -78°C for a further 30 minutes. Benzyl bromide (0.37ml, 3.15mmol) was then added drop-wise and the resultant mixture allowed to warm to ambient temperature. Acetic acid (1ml) was added followed by water (10ml) and the phases were separated. The aqueous phase was re-extracted with Et_2O (3 x 15ml). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated to a yellow oil which was purified by flash column chromatography (loading and eluting with 40% ethyl acetate 60% hexane) to give afford the title product as a colourless oil (0.33g, 99%).
^{1}H NMR (400MHz, $CDCl_3$) δ 7.33-7.28 (3H, m, aromatic); 7.16-7.09 (2H, m, aromatic) 4.67 (1H, dd, 1 of $C\underline{H}_2NO_2$ *J*=9.0); 4.42 (1H, dd, 1 of $C\underline{H}_2NO_2$ *J*=4.5); 3.74 (3H, s, $OC\underline{H}_3$); 3.43 (1H, m, $C\underline{H}CO_2CH_3$); 3.10 (1H, dd, 1 of $C\underline{H}_2Ph$ *J*=6.0); 2.79 (1H, dd, 1 of $C\underline{H}_2Ph$ *J*=9.0). ^{13}C NMR (100MHz, $CDCl_3$) δ 172.5, 136.4, 129.0, 128.8, 127.4, 74.0, 52.5, 45.0, 35.1. IR (neat) 3076, 3056, 3023, 2955, 1739, 1550, 1494, 1435, 1376, 1245, 1200, 1172, 1099, 1075, 1040, 968, 843, 743cm^{-1}. Acc. Mass (CI+NH_3) calculated 241.11884, found 241.11860.

(*Z*)-1-(Hex-3-enyl)benzene (6)
QNO (1.94g, 15.3mmol) in THF (100ml) was lithiated under the described conditions above with 1.3M ^{t}BuLi (2.38ml, 3.09mmol). The mixture was allowed to warm to -5°C before adding *via* a cannula to a suspension of the phosphonium salt (4) (1.41g, 3.07mmol) in THF (15ml) at -5°C. The resultant bright orange ylide suspension was allowed to warm to ambient temperature and stir for 2 hours before adding propionaldehyde (0.23ml, 3.26mmol) and allowing the mixture to stir overnight. Saturated ammonium chloride (10ml) and water (50ml) were added and the phases separated. The aqueous phase was re-extracted with Et_2O (3 x 50ml) and the combined organics washed with water (50ml) and brine (50ml) before drying ($MgSO_4$), filtering and removing the solvents *in vacuo*. The crude solid was suspended in Et_2O and

triphenylphosphine oxide removed by filtration. The filtrate was concentrated *in vacuo* and purified by flash column chromatography (loading and eluting in hexane) affording alkene 5 as a colourless oil (0.32g, 65%).
^{1}H NMR (400MHz, $CDCl_3$) δ 7.14-7.33 (5H, m, aromatics); 5.35-5.43 (2H, m, $CH_2C\underline{H}C\underline{H}CH_2$); 2.60 (2H, t, $PhC\underline{H}_2CH_2$ *J*=7.7Hz); 2.30-2.39 (2H, m, $PhCH_2C\underline{H}_2$); 1.93-2.04 (2H, m, $CHC\underline{H}_2CH_3$); 0.92 (3H, t, $C\underline{H}_3$ J=6.88Hz).). ^{13}C NMR (100MHz, $CDCl_3$) δ 142.12, 132.63, 132.29, 128.47, 128.26, 125.76, 36.14, 29.10, 20.56, 14.22. IR (neat) 3085, 3060, 3030, 3004, 2959, 2930, 2874, 2855, 1601, 1494, 1453, 1400, 1360,1329,1302, 1260, 1073, 1028, 965, 900, 870,803, 769cm^{-1}.

Non-4-yn-2-ol (8)
A suspension of QNO (3.86g, 30.39mmol) in dry THF (100ml) was lithiated with a 1.57M solution of ^{t}BuLi in hexane (3.87ml, 6.08mmol) under identical conditions to those described above. The solution was warmed to 0°C before adding 1-hexyne (0.5g, 6.08mmol) in THF (5ml) and allowing to warm to ambient temperature. At this point the reaction mixture was cooled to -78°C before adding propylene oxide (0.44ml, 6.26mmol) and allowing the mixture to warm to ambient temperature and stir for a further 2 hours. 10% acetic acid (30ml) was added and the phases separated before re-extracting the aqueous phase with Et_2O (2 x 50ml). The organics were combined and washed with water (50ml), saturated $NaHCO_3$ (50ml) and brine (50ml) before drying ($MgSO_4$) filtering and concentrating *in vacuo* to a colourless liquid (0.46g, 55%).
^{1}H NMR (400MHz, $CDCl_3$) δ 0.82 (3H, t, $C\underline{H}_3CH_2$); 1.23 (3H, d, $C\underline{H}_3CH(OH)CH_2$); 1.33-1.58 (4H, m, $CH_3C\underline{H}_2C\underline{H}_2$); 1.85-1.99 (1H, bs, O<u>H</u>); 2.12 (2H, q, $CH_2C\underline{H}_2CC$); 2.20-2.39 (2H, m, $CCC\underline{H}_2CH(OH)CH_3$); 3.85-3.9 (1H, m C<u>H</u>OH).
^{13}C NMR (100MHz, $CDCl_3$) δ 13.91, 18.76, 22.30, 22.54, 29.82, 30.04, 31.14, 31.46, 66.93. IR (neat) 3359, 2958, 2872, 1458, 1430, 1376, 1355, 1327, 1115, 1085, 940cm^{-1}.

3-Allyl-tetrahydropyran-2-one (10)
QNO (0.45g, 3.58mmol) in THF (25ml) was lithiated with a 1.3M solution of ^{t}BuLi in hexane (2.75ml, 3.58mmol) under the previously described conditions. A 1M solution of δ-valerolactone (9) (0.67ml, 3.58mmol) in THF (3.6ml) was added over 1 hour keeping the temperature at -78°C. The resulting mixture was allowed to stir for a further 20 minutes before allyl bromide (0.37ml, 4.3mmol) in THF (2ml) was added drop-wise. The reaction mixture was then warmed to -30°C and stirred for an additional 2 hours. Saturated ammonium chloride (3ml) and water (20ml) were added and the mixture allowed to warm to ambient temperature. The phases were separated and the aqueous phase was re-extracted with DCM (3 x 25ml). The combined organic solutions were combined, dried (Na_2SO_4), filtered and the solvents were removed *in vacuo* to afford a yellow oil purified by flash column chromatography (compound pre-adsorbed onto silica using DCM, column eluted with 5% EtOAc, 95% hexane) yielding the product as a colourless oil (0.45g, 89%).
^{1}H NMR (400MHz, $CDCl_3$) δ 5.8-5.9 (1H, m, $CH_2C\underline{H}CH_2$); 5.05-5.1 (2H, m, $CH_2CHC\underline{H}_2$); 4.25-4.31 (2H, m, $OC\underline{H}_2CH_2$); 2.65-2.73 (1H, m, 1 of $C\underline{H}_2CHCH_2$); 2.55-2.6 (1H, m, $C(O)C\underline{H}CH_2$); 2.3-2.35 (1H, m, 1 of $C\underline{H}_2CHCH_2$); 2.05-2.11 (1H, m, 1 of $C(O)CHC\underline{H}_2$); 1.90-1.95 (2H, m, $OCH_2C\underline{H}_2$); 1.55 (1H, m, 1 of $C(O)CHC\underline{H}_2$). ^{13}C NMR

(100MHz, $CDCl_3$) δ 174.17, 135.55, 117.84, 68.90, 39.79, 35.91, 24.60, 22.41. IR (neat) 3457, 3082, 2943, 2354, 2310, 1724,1481, 1459, 1442, 1390, 1351, 1255, 1153, 1085, 999, 963, 915, 780, 654cm^{-1}. Acc. Mass (CI+NH_3)$(M+H)^+$ calculated 141.09155, found 141.09166.

(*S*)-3-[1,3] Dithian-2-yl-5-isopropenyl-2-methylcyclohexanone (14)

QNO (0.5g, 4.33mmol) in THF (10ml) was subject to ultrasonic radiation for 10 minutes, cooled to –78°C before adding 1.25M ^{t}BuLi in hexane (0.70ml, 0.88mmol). The mixture was stirred for 30mins at this temperature before adding 1,3-dithiane (0.104g, 0.87mmol) in THF (2ml). The mixture was allowed to warm to room temperature before cooling back down to –78°C and adding carvone (0.135g, 0.9006mmol). The mixture was allowed to warm to room temperature and stir overnight. Saturated aqueous ammonium chloride (5ml) and water (10ml) were added. The mixture was partitioned between Et_2O (10ml) and H_2O (10ml). The aqueous phase was re-extracted with more Et_2O and the organics combined and dried over $MgSO_4$, filtered before concentrating *in vacuo* to give a yellow oil. This was purified by flash column chromatography (gradient elution, hexane to 10% EtOAc in hexane), yielding the title product as a yellow oil (0.22g, 93%).

^{1}H NMR (400MHz $CDCl_3$) δ 1.18 (3H, d, CH(C$\underline{H}_3$)CO), 1.40 (3H, s, CC$\underline{H}_3$), 1.41-2.68 (8H, m, 6 cyclohexane H's and C$\underline{H}_2$CH_2S), 2.75-2.88 (4H, m, 2 x SC$\underline{H}_2$), 3.95 (1H, d, SC$\underline{H}$S), 4.60-4.68 (2H, m, C$\underline{H}_2$CCH_3). ^{13}C NMR (100MHz $CDCl_3$) δ 21.16, 21.97, 26.06, 27.85, 30.66, 30.87, 40.77, 40.96, 41.67, 42.35, 51.80, 55.11, 112.37, 146.78. IR (neat) 3083, 2971, 2923, 2888, 1707, 1642, 1450, 1434, 1368, 1328, 1247, 1207, 1142, 1110, 1058, 960, 898, 802cm^{-1}. m/z (CI+NH_3) $(M+H)^+$ calculated 271.11902, found 271.11974.