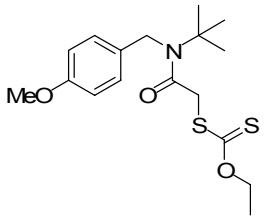
Supplementary Material (ESI) for Chemical Communications

Typical procedure for the synthesis of xanthates.

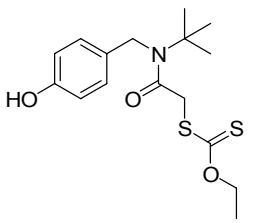
To a solution of the substituted benzaldehyde (1.0 mmol) in methanol (5 mL) and molecular sieves (4A, 100 mg), *t*-butilamine (1.0 mmol) was added at room temperature. After 2 h $NaBH_4$ (2.5 mmol) was added at 0 ºC and stirred for 1 h at the same temperature. The reaction mixture was filtered over a celite pad and the solvent was evaporated. The resulting residue was dissolved in EtOAc (5 mL) and washed with water (2 x 5 mL), dried over Na_2SO_4 and concentrated under reduced pressure to afford the corresponding secondary amine, which was used to the next reaction without further purification.

To a solution of the crude amine in dichloromethane (5 mL) and triethylamine (1.0 mmol), acid chloride (1.0 mmol) was added at 0 ºC. After 2 h the solvent was evaporated and the resulting residue was dissolved in EtOAc (5 mL) and washed with water (2 x 5 mL), dried over Na_2SO_4 and concentrated in vacuo to afford the corresponding chloride, which was used to the next reaction without further purification.

O-ethylxanthic acid, potassium salt (1.5 mmol) was added to a solution of crude chloride in methanol (5 mL). After the reaction was completed, the mixture was filtered and the solvent was evaporated. The resulting residue was dissolved in EtOAc (5 mL) and washed with water (2 x 5 mL), dried over Na_2SO_4 and concentrated in vacuo. The resulting yellowish solid was purified by column chromatography on silica gel (hexane/EtOAc).

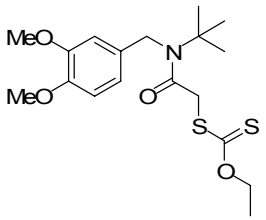


S-(N-(4-methoxybenzyl)-N-tert-butylcarbamoyl)methyl O-ethyl carbonodithioate (5a). White solid (80%). R_f = 0.44 (Hexane/EtOAc 8:2); IR (neat, cm^{-1}): C=O 1648; ^1H NMR (300 MHz, $CDCl_3$) δ 7.18 (d, 2H, *J*= 8.7 Hz), 6.93 (d, 2H, *J*= 8.7 Hz), 4.66 (s, 2H), 4.61 (q, 2H, *J*= 7.0 Hz), 4.06 (s, 2H), 3.81 (s, 3H), 1.44 (s, 9H), 1.37 (t, 3H, *J*= 7.0 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 214.2 (CS), 167.5 (C=O), 158.8, 130.4, 126.7, 114.3, 70.2, 58.7, 55.3, 48.7, 42.4, 28.6, 13.7. EI-MS m/z (%) 356 (M + H^+, 25); HRMS (FAB^+) *m/z* calcd for $C_{17}H_{26}N_1O_3S_2$ $(M + H)^+$ 356.1354, found 356.1347.

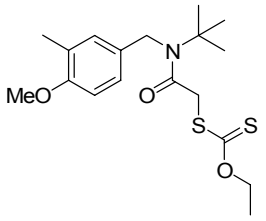


S-(N-(4-hydroxybenzyl)-N-tert-butylcarbamoyl)methyl O-ethyl carbonodithioate 5b. White solid (77%). R_f = 0.15 (Hexane/EtOAc 8:2); IR (neat, cm^{-1}): C=O 1663; ^1H NMR

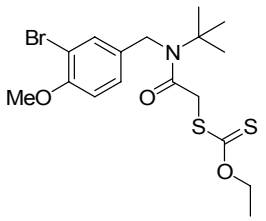
(300 MHz, $CDCl_3$) δ 7.15 (d, 2H, *J*= 8.8 Hz), 6.87 (d, 2H, *J*= 8.8 Hz), 4.65 (s, 2H), 4.58 (q, 2H, *J*= 7.0 Hz), 4.06 (s, 2H), 1.44 (s, 9H), 1.37 (t, 3H, *J*= 7.0 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 213.3 (CS), 166.9 (C=O), 156.0, 128.3, 126.3, 115.4, 69.6, 58.1, 48.2, 41.7, 28.0, 13.2. EI-MS m/z (%) 341 (M^+, 25); HRMS (FAB^+) *m/z* calcd for $C_{16}H_{24}N_1O_3S_2$ $(M + H)^+$ 342.1198, found 342.1198.



S-(N-(3,4-dimethoxybenzyl)-N-tert-butylcarbamoyl)methyl O-ethyl carbonodithioate 7a. White solid (82%). R_f = 0.18 (Hexane/EtOAc 8:2); IR (neat, cm^{-1}): C=O 1651; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.85 (m, 3H), 4.67 (s, 2H), 4.58 (q, 2H, *J*= 7.0 Hz), 4.08 (s, 2H), 3.89 (s, 3H), 3.88 (s, 3H), 1.41 (s, 9H), 1.38 (t, 3H, *J*= 7.0 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 214.1 (CS), 167.5 (C=O), 149.5, 148.3, 131.1, 117.6, 111.7, 70.1, 58.6, 55.9, 55.9, 48.8, 42.3, 28.5, 13.6. EI-MS m/z (%) 385 (M^+, 25); HRMS (FAB^+) *m/z* calcd for $C_{18}H_{28}N_1O_4S_2$ $(M + H)^+$ 386.1460, found 386.1454.

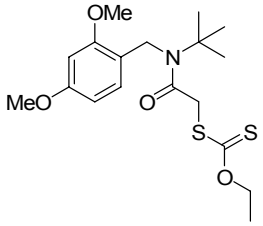


S-(N-(4-methoxy-3-methylbenzyl)-N-tert-butylcarbamoyl)methyl O-ethyl carbonodithioate 7b. White solid (70%). R_f = 0.52 (Hexane/EtOAc 8:2); IR (neat, cm^{-1}): C=O 1648; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (m, 2H), 6.82 (d, 1H, *J*= 8.4 Hz), 4.63 (s, 2H), 4.58 (q, 2H, *J*= 7.2 Hz), 4.07 (s, 2H), 3.82 (s, 3H), 2.22 (s, 3H), 1.44 (s, 9H), 1.35 (t, 3H, *J*= 7.2 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 214.1 (CS), 167.5 (C=O), 157.0, 130.0, 128.0, 127.3, 123.9, 110.2, 70.1, 58.7, 55.4, 48.7, 42.4, 28.6, 16.2, 13.6; EI-MS m/z (%) 369 (M^+, 25).

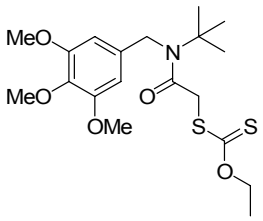


S-(N-(3-bromo-4-methoxybenzyl)-N-tert-butylcarbamoyl)methyl O-ethyl carbonodithioate 7c. White solid (75%). R_f = 0.25 (Hexane/EtAOc, 3:7); IR (neat, cm^{-1}):

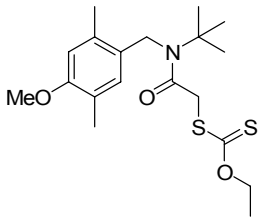
C=O 1669, 1643; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (d, 1H, *J*= 2.4 Hz), 7.21 (dd, 1H, *J*= 8.3, 2.1 Hz), 6.92 (d, 1H, *J*= 8.4 Hz), 4.65 (s, 2H), 4.60 (q, 2H, *J*= 7.2 Hz), 4.04 (s, 2H), 3.90 (s, 3H), 1.44 (s, 9H), 1.41 (t, 3H, *J*= 7.2 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 214.1 (CS), 167.5 (C=O), 155.1, 132.1, 130.6, 125.6, 112.3, 112.2, 70.4, 58.9, 56.3, 48.1, 42.3, 28.6, 13.8; EI-MS m/z (%) 433 (M^+, 25) HRMS (FAB^+) *m/z* calcd for $C_{17}H_{24}BrNO_3S_2$ $(M + H)^+$ 434.0459, found 434.0449.



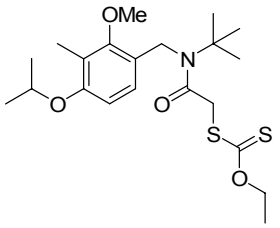
S-(N-(2,4-dimethoxybenzyl)-N-tert-butylcarbamoyl)methyl O-ethyl carbonodithioate 9. White solid: (81%). R_f = 0.42 (Hexane/EtOAc, 8:2); IR (neat, cm^{-1}): C=O 1649; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 (d, 1H, *J*= 8.2 Hz), 6.53 (m, 2H), 4.61 (q, 2H, *J*= 7.0 Hz), 4.57 (s, 2H), 4.02 (s, 2H), 3.83 (s, 3H), 3.81 (s, 3H), 1.44 (s, 9H), 1.37 (t, 3H, *J*= 7.0 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 214.1 (CS), 167.7 (C=O), 160.0, 156.9, 126.9, 118.9, 103.9, 98.5, 70.1, 58.4, 55.3, 55.2, 44.1, 42.0, 28.3, 13.7; EI-MS m/z (%) 385 (M^+, 15); HRMS (FAB^+) *m/z* calcd for $C_{18}H_{28}N_1O_4S_2$ $(M + H)^+$ 386.1460, found 386.1461.



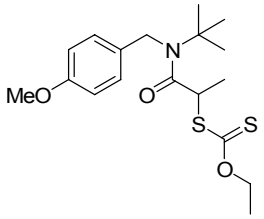
S-(N-(3,4,5-trimethoxybenzyl)-N-tert-butylcarbamoyl)methyl O-ethyl carbonodithioate 11. White solid (79%). R_f = 0.23 (Hexane/EtOAc, 8:2); IR (neat, cm^{-1}): C=O 1651; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.48 (s, 2H), 4.67 (s, 2H), 4.62 (q, 2H, *J*= 7.0 Hz), 4.07 (s, 2H), 3.86 (s, 6H), 3.85 (s, 3H), 1.48 (s, 9H), 1.38 (t, 3H, *J*= 7.0 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 214.2 (CS), 167.6 (C=O), 153.8, 134.3, 102.7, 70.3, 60.8, 58.8, 56.2, 49.3, 42.3, 28.6, 13.7; EI-MS m/z (%) 415 (M^+, 25); HRMS (FAB^+) *m/z* calcd for $C_{19}H_{30}N_1O_5S_2$ $(M + H)^+$ 416.1565, found 416.1564.



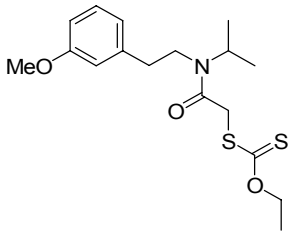
S-(N-(4-methoxy-2,5-dimethylbenzyl)-N-tert-butylcarbamoyl)methyl O-ethyl carbonodithioate 13. White solid (77%). R_f = 0.59 (Hexane/EtOAc, 8:2); IR (neat, cm^{-1}): C=O 1649; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.04 (s, 1H), 6.65 (s, 1H), 4.58 (q, 2H, *J*= 7.5 Hz), 4.53 (s, 2H), 4.00 (s, 2H), 3.82 (s, 3H), 2.26 (s, 3H), 2.19 (s, 3H), 1.46 (s, 9H), 1.37 (t, 3H, *J*= 7.2 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 214.3 (CS), 167.7 (C=O), 156.5, 132.2, 127.5, 127.4, 124.3, 112.5, 70.2, 58.6, 55.4, 46.6, 42.0, 28.8, 19.0, 16.0, 13.7. EI-MS m/z (%) 326 (M + H^+, 45); HRMS (FAB^+) *m/z* calcd for $C_{15}H_{20}N_1O_3S_2$ $(M + H)^+$ 326.0885, found 326.0882.



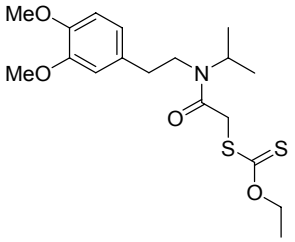
S-(N-(4-isopropoxy-2-methoxy-3-methylbenzyl)-N-tert-butylcarbamoyl)methyl O-ethyl carbonodithioate 15. White solid (74%). R_f = 0.39 (Hexane/EtOAc, 8:2); IR (neat, cm^{-1}): C=O 1650; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.04 (d, 1H, *J*= 8.4 Hz), 7.01 (d, 1H, *J*= 8.4 Hz), 4.69 (s, 2H), 4.60 (q, 2H, *J*= 7.9 Hz), 4.50 (hpt, 1H, *J*= 6.0 Hz), 4.05 (s, 2H), 3.74 (s, 3H), 2.15 (s, 3H), 1.45 (s, 9H), 1.36 (t, 3H, *J*= 7.9 Hz), 1.35 (d, 6H, *J*= 6.1 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 214.1 (CS), 167.6 (C=O), 156.5, 155.9, 123.6, 122.9, 121.1, 108.8, 70.4, 70.1, 60.1, 58.6, 44.3, 42.2, 28.4, 22.2, 13.7, 9.2; EI-MS m/z (%) 427 (M^+, 15); HRMS (FAB^+) *m/z* calcd for $C_{21}H_{34}N_1O_4S_2$ (M^+) 427.1929, found 427.1925.



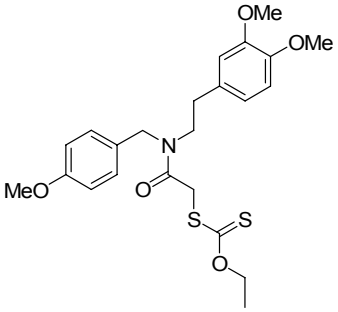
S-1-(N-(4-methoxybenzyl)-N-tert-butylcarbamoyl)ethyl O-ethyl carbonodithioate 17. Rotamers mix. White solid (75%). R_f = 0.52 (Hexane/EtOAc, 8:2); IR (neat, cm^{-1}): C=O 1640; EI-MS m/z (%) 369 (M^+, 35); HRMS (FAB^+) *m/z* calcd for $C_{18}H_{28}N_1O_3S_2$ $(M + H)^+$ 370.1511, found 370.1506.



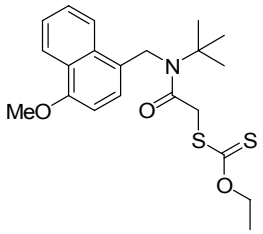
S-(N-(3-methoxyphenethyl)-N-isopropylcarbamoyl)methyl O-ethyl carbonodithioate 19a. Rotamers mix. White solid (82%). R_f = 0.24 (Hexane/EtOAc, 2:8); IR (cm^{-1}): C=O 1641; EI-MS m/z (%) 355 (M^+, 35); HRMS (FAB^+) *m/z* calcd for $C_{17}H_{26}N_1O_3S_2$ $(M + H)^+$ 356.1354, found 356.1351.



S-(N-(3,4-dimethoxyphenethyl)-N-isopropylcarbamoyl)methyl O-ethyl carbonodithioate 19b. Rotamers mix. White solid (81%). R_f = 0.41 (Hexane/EtOAc, 8:2); IR (neat, cm^{-1}): C=O 1641; EI-MS m/z (%) 385 (M^+, 15); HRMS (FAB^+) *m/z* calcd for $C_{18}H_{28}N_1O_4S_2$ $(M + H)^+$ 386.1460, found 386.1468.



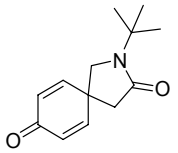
S-(N-(3,4-dimethoxyphenethyl)-N-(4-methoxybenzyl)carbamoyl)methyl O-ethyl carbonodithioate 21. Rotamers mix. White solid (85%). R_f = 0.18 (Hexane/EtOAc, 8:2); IR (neat, cm^{-1}): C=O 1643; EI-MS m/z (%) 363 (M^+, 35); HRMS (FAB^+) *m/z* calcd for $C_{23}H_{30}N_1O_5S_2$ $(M + H)^+$ 364.1565, found 364.1571.



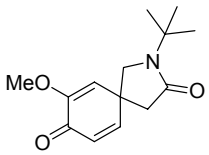
S-(*N*-*tert*-butyl-*N*-((1-methoxynaphthalen-4-yl)methyl)carbamoyl)methyl *O*-ethyl carbonodithioate **23**. White solid (65%). R_f = 0.43 (Hexane/EtOAc, 8:2); IR (neat, cm^{-1}): C=O 1649; ^1H NMR (300 MHz, $CDCl_3$) δ 8.37 (1H), 7.87 (d, 1H, *J*= 7.5 Hz), 7.56 (m, 2H), 7.41 (d, 1H, *J*= 7.8 Hz), 6.84 (d, 1H, *J*= 7.8 Hz), 5.07 (d, 2H, *J*= 0.9 Hz), 4.51 (q, 2H, *J*= 6.9 Hz), 4.01 (s, 2H), 4.00 (s, 3H), 1.51 (s, 9H), 1.28 (t, 3H, *J*= 7.8 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 213.9 (CS), 167.9 (C=O), 155.0, 126.9, 125.3, 125.0, 123.1, 123.1, 121.5, 103.1, 70.2, 58.7, 55.5, 46.6, 41.6, 28.4, 13.6; EI-MS m/z (%) 405 (M^+, 35); HRMS (FAB^+) *m/z* calcd for $C_{21}H_{28}N_1O_3S_2$ (M^+) 405.1511, found 405.1503.

Typical Procedure for Radical spirocyclisation.

A solution of the corresponding xanthate (1.0 mmol) in 1,2-dichloroethane (5 mL) was heated at reflux and 10% mol lauryl peroxide (1.2-1.5 mmol) was then added every 1 h until complete consumption of the xanthate was observed (Indication by TLC). The solvent was removed under reduced pressure and the residue purified by chromatography on a silica gel column (hexane/EtOAc) to furnish the desire product.

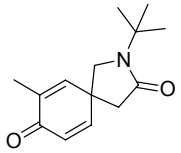


Azaespiro [4.5]decano derivative 6. White solid (85%). R_f = 0.27 (Hexane/EtOAc 3:7); IR (neat, cm^{-1}): C=O 1676, 1628; ^1H NMR (300 MHz, $CDCl_3$) δ 6.96 (d, 2H, *J*= 10.2 Hz), 6.34 (d, 2H, *J*= 10.2 Hz), 4.49 (s, 2H), 2.54 (s, 2H), 1.43 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 185.0 (C=O), 171.6 (C=O), 150.1, 129.3, 54.6, 53.0, 42.6, 40.8, 27.6; EI-MS m/z (%) 219 (M^+, 65); HRMS (FAB+) *m/z* calcd for $C_{13}H_{18}N_1O_2$ $(M + H)^+$ 220.1338, found 220.1337.

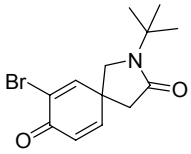


Azaespiro [4.5]decano derivative 8a. White solid (75%). R_f = 0.26 (Hexane/EtOAc 4:6); IR (cm^{-1}): C=O 1671, 1642; ^1H NMR (300 MHz, $CDCl_3$) δ 6.99 (dd, 1H, *J*= 9.9, 2.4 Hz), 6.36 (d, 1H, *J*= 9.6 Hz), 5.84 (d, 1H, *J*= 2.7 Hz), 3.69 (s, 3H), 3.52 (s, 2H), 2.57 (s, 2H),

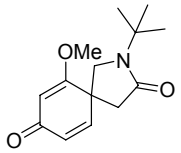
1.44 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 180.2 (C=O), 171.9 (C=O), 151.6, 128.5, 117.2, 54.9, 54.5, 64.1, 43.6, 41.6, 27.6; EI-MS m/z (%) 249 (M^+, 35); HRMS (FAB^+) *m/z* calcd for $C_{14}H_{20}N_1O_3$ $(M + H)^+$ 250.1443, found 250.1447.



Azaespiro [4.5]decano derivative 8b. White solid (83%). R_f = 0.42 (Hexane/EtOAc 3:7); IR (neat, cm^{-1}): C=O 1685, 1642; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.93 (dd, 1H, *J*= 9.9, 3 Hz), 6.70 (sex, 1H, *J*= 1.2 Hz), 6.32 (d, 1H, *J*= 9.9 Hz), 3.46 (d, 2H, *J*= 0.9 Hz), 2.50 (s, 3H), 1.92 (d, 3H, *J*= 1.5 Hz), 1.43 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 185.7 (C=O), 171.7 (C=O), 149.8, 145.5, 135.9, 128.8, 54.6, 53.3, 42.8, 40.9, 27.7, 15.9; EI-MS m/z (%) 233 (M^+, 45); HRMS (FAB^+) *m/z* calcd for $C_{14}H_{19}NO_2$ $(M + H)^+$ 234.1494, found 234.1493.

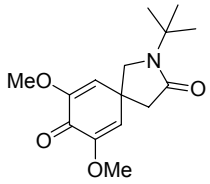


Azaespiro [4.5]decano derivative 8c. White solid (75%). R_f = 0.27 (Hexane/EtOAc 3:7); IR (neat, cm^{-1}): C=O 1692, 1661; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, 1H, *J*= 2.7 Hz), 6.99 (dd, 1H, *J*= 9.9, 2.7 Hz), 6.44 (d, 1H, *J*= 9.9 Hz), 2.36 (dd, 2H, *J*= 10.2, 4.1 Hz), 2.31 (dd, 2H, *J*= 16.2, 2.7 Hz), 1.44 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 177.9 (C=O), 171.0 (C=O), 150.1, 150.0, 127.8, 125.6, 54.9, 52.5, 44.1, 42.1, 27.7; EI-MS m/z (%) 297 (M^+, 100); HRMS (FAB^+) *m/z* calcd for $C_{13}H_{16}BrNO_2$ $(M + H)^+$ 298.0443, found 298.0443.

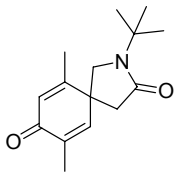


Azaespiro [4.5]decano derivative 10a. White solid (85%). R_f = 0.30 (Hexane/EtOAc 4:6); IR (neat, cm^{-1}): C=O 1686, 1661; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.76 (d, 1H, *J*= 9.6 Hz), 6.22 (dd, 1H, *J*= 10.2, 1.8 Hz), 5.64 (d, 1H, *J*= 1.2 Hz), 3.79 (s, 3H), 3.77 (d, 1H, *J*= 9.9 Hz), 3.37 (d, 1H, *J*= 9.9 Hz), 2.90 (d, 1H, *J*= 16.2 Hz), 2.41 (d, 1H, *J*= 16.8 Hz), 1.43 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 187.0 (C=O), 174.6 (C=O), 171.4, 146.7, 127.1, 103.0, 55.9, 54.6, 52.9, 41.8, 41.7, 27.5; EI-MS m/z (%) 249 (M^+, 95); HRMS (FAB^+) *m/z* calcd for $C_{14}H_{20}N_1O_3$ $(M + H)^+$ 250.1443, found 250.1437.

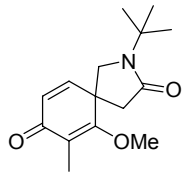
Supplementary Material (ESI) for Chemical Communications



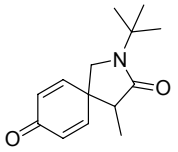
Azaespiro [4.5]decano derivative 12. White solid (70%). R_f = 0.16 (Hexane/EtOAc 3:7); IR (neat, cm^{-1}): C=O 1687, 1670; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.87 (s, 2H), 3.69 (s, 6H), 3.52 (s, 2H), 2.58 (s, 2H), 1.45 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 175.8 (C=O), 172.3 (C=O), 151.2, 117.6, 109.1, 55.5, 55.3, 54.6, 44.9, 39.4, 27.8; EI-MS m/z (%) 279 (M^+, 45); HRMS (FAB^+) *m/z* calcd for $C_{15}H_{22}N_1O_4$ $(M + H)^+$ 280.1549, found 280.1551.



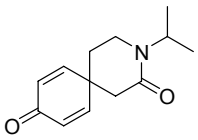
Azaespiro [4.5]decano derivative 14. White solid (55%). R_f = 0.27 (Hexane/EtOAc 3:7); IR (neat, cm^{-1}): C=O 1673, 1636; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.67 (d, 1H, *J*= 1.2 Hz), 6.12 (d, 1H, *J*= 1.2 Hz), 3.52 (d, 1H, *J*= 10.8 Hz), 3.47 (d, 1H, *J*= 10.8 Hz), 2.53 (d, 1H, *J*= 17.4 Hz), 2.52 (d, 1H, *J*= 17.4 Hz), 2.03 (d, 1H, *J*= 1.2 Hz), 1.90 (d, 3H, *J*= 1.2 Hz), 1.44 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 186.1 (C=O), 172.2 (C=O), 158.8, 147.3, 134.3, 127.9, 54.7, 52.9, 42.0, 41.9, 27.6, 19.1, 15.4; EI-MS m/z (%) 247 (M^+, 55); HRMS (FAB^+) *m/z* calcd for $C_{15}H_{21}NO_2$ $(M + H)^+$ 248.1651, found 248.1644.



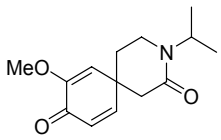
Azaespiro [4.5]decano derivative 16. White solid (74%). R_f = 0.47 (Hexane/EtOAc 3:7); IR (neat, cm^{-1}): C=O 1650, 1602; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.78 (d, 1H, *J*= 9.6 Hz), 6.26 (d, 1H, *J*= 9.9 Hz), 3.97 (s, 3H), 3.76 (d, 1H, *J*= 9.6 Hz), 3.31 (d, 1H, *J*= 10.2 Hz), 2.88 (d, 1H, *J*= 16.2 Hz), 2.36 (d, 1H, *J*= 16.5 Hz), 1.92 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 188.2 (C=O), 171.5 (C=O), 170.5, 146.9, 126.8, 120.1, 61.7, 54.6, 52.2, 43.2, 41.0, 27.6, 9.8; EI-MS m/z (%) 263 (M^+, 45); HRMS (FAB^+) *m/z* calcd for $C_{15}H_{22}N_1O_3$ $(M + H)^+$ 264.1600, found 264.1590.



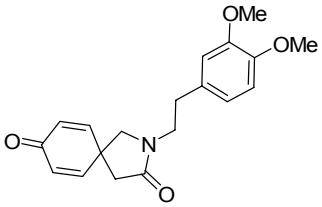
Azaespiro [4.5]decano derivative 18. White solid (68%). R_f = 0.32 (Hexane/EtOAc 3:7); IR (neat, cm^{-1}): C=O 1688, 1667; ^1H NMR (300 MHz, $CDCl_3$) δ 6.89 (dd, 2H, *J*= 10.2, 2.7 Hz), 6.41 (d, 2H, *J*= 10.2 Hz), 3.54 (d, 1H, *J*= 10.2 Hz), 3.34 (d, 1H, *J*= 9.9 Hz), 2.68 (q, 1H, *J*= 7.2 Hz), 1.43 (s, 9H), 0.95 (d, 2H, *J*= 7.5 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 185.4 (C=O), 173.9 (C=O), 150.1, 147.9, 131.4, 130.5, 54.5, 51.1, 47.3, 46.3, 27.6, 9.7; EI-MS m/z (%) 233 (M^+, 45); HRMS (FAB$^+$) *m/z* calcd for $C_{14}H_{19}NO_2$ $(M + H)^+$ 234.1494, found 234.1492.



Azaespiro [4.5]decano derivative 20a. White solid (65%). R_f = 0.48 (Hexane/EtOAc 3:7); IR (neat, cm^{-1}): C=O 1665, 1627;. ^1H NMR (300 MHz, $CDCl_3$) δ 6.85 (d, 2H, *J*= 10.2 Hz), 6.33 (d, 2H, *J*= 10.2 Hz), 4.97 (hpt, 1H, *j*= 6.9 Hz), 3.39 (t, 2H, *J*= 6.3 Hz), 2.44 (s, 2H), 1.95 (t, 2H, *J*= 6.6 Hz), 1.19 (d, 6H, *J*= 6.9 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 185.1 (C=O), 165.8 (C=O), 150.9, 129.5, 44.6, 40.6, 39.2, 37.4, 32.5, 19.2; EI-MS m/z (%) 219 (M^+, 97); HRMS (FAB$^+$) *m/z* calcd for $C_{13}H_{17}NO_2$ $(M + H)^+$ 220.1338, found 220.1333.

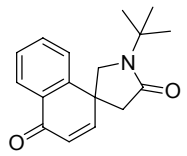


Azaespiro [4.5]decano derivative 20b. White solid (57%). R_f = 0.39 (Hexane/EtOAc 3:7); IR (neat, cm^{-1}): C=O 1669, 1636; ^1H NMR (300 MHz, $CDCl_3$) δ 6.87 (dd, 1H, *J*= 9.9, 2.7 Hz), 6.37 (d, 1H, *J*= 9.9 Hz), 5.70 (d, 1H, *J*= 2.7 Hz), 4.98 (hpt, 1H, 3.67 (s, 3H), 3.40 (t, 2H, *J*=6.6 Hz), 2.48 (d, 1H, *J*=17.4 Hz), 2.47 (d, 1H, *J*= 17.4 Hz), 1.98 (m, 2H), 1.21 (dd, 6H, *J*= 1.5 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 180.3 (C=O), 166.1 (C=O), 151.6, 151.3, 128.8, 117.6, 54.8, 44.2, 41.8, 39.6, 37.8, 33.4, 19.1; EI-MS m/z (%) 249 (M^+, 97); HRMS (FAB$^+$) *m/z* calcd for $C_{14}H_{19}NO_3$ $(M + H)^+$ 250.1443, found 250.1447.



Azaespiro [4.5]decano derivative 22. White solid (65%). R_f = 0.37 (Hexane/EtOAc 3:7); IR (neat, cm^{-1}): C=O 1687, 1666; ^1H NMR (300 MHz, $CDCl_3$) δ 6.75 (m, 3H), 6.72 (d, 2H, *J*= 9.9 Hz), 6.26 (d, 2H, *J*= 10.2 Hz), 3.87 (s, 3H), 3.86 (s, 3H), 3.63 (t, 2H, *J*= 7.2 Hz), 3.28 (s, 2H), 2.85 (t, 2H, *J*= 7.0 Hz), 2.50 (s, 2H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 184.8 (C=O), 171.4 (C=O), 149.9, 149.1, 147.9, 130.3, 129.1, 120.6, 111.6, 111.2, 55.9,

54.5, 43.4, 41.2, 40.9, 33.0; EI-MS m/z (%) 327 (M^+, 35); HRMS (FAB^+) *m/z* calcd for $C_{19}H_{21}N_1O_3$ (M^+) 327.1471, found 327.1474.



Azaespiro [4.5]decano derivative 24. White solid (65%). R_f = 0.51 (Hexane/EtOAc 4:6); IR (neat, cm^{-1}): C=O. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (dd, 1H, *J*= 8.1, 1.5 Hz), 7.67 (m, 2H), 7.49 (m, 1H), 7.05 (d, 1H, *J*= 9.9 Hz), 6.49 (d, 1H, *J*= 9.9 Hz), 3.76 (d, 1H, *J*= 10.2 Hz), 3.70 (d, 1H, *J*= 10.2 Hz), 2.88 (d, 1H, *J*= 16.8 Hz), 2.79 (d, 1H, *J*= 16.8 Hz), 1.47 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 184.0 (C=O), 172.1 (C=O), 151.3, 146.4, 133.5, 130.9, 127.8, 127.7, 127.0, 125.5, 57.5, 54.8, 46.4, 39.6, 27.6; HRMS (FAB^+) *m/z* calcd for $C_{17}H_{19}NO_2$ $(M + H)^+$ 270.1499, found 270.1494.