Electronic Supplementary Material (ESI) for Organic and Biomolecular Chemistry

SUPPORTING INFORMATION

Identification of the best-suited leaving group for the diastereoselective synthesis of glycidic amides from stabilised ammonium ylides and aldehydes

Richard Herchl,[a] Martin Stiftinger,[b] and Mario Waser[*a]

a) Institute of Organic Chemistry, Johannes Kepler University Linz, Altenbergerstraße 69, 4040 Linz, Austria. Fax: +43 732 2468 8747; Tel: +43 732 2468 8748;

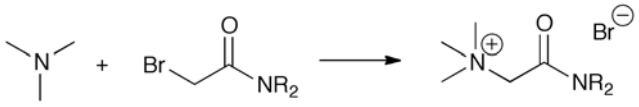
b) Institute of Analytical Chemistry, Johannes Kepler University Linz, Altenbergerstraße 69, 4040 Linz, Austria.

E-mail: Mario.waser@jku.at

1. General Information:

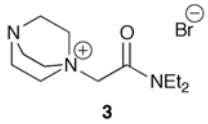
Melting points were measured on a Kofler melting point microscope (Reichert, Vienna). ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker Avance DRX 500 MHz spectrometer using a TXI cryoprobe with z-gradient coil and on a Bruker Avance DPX 200 MHz spectrometer. Typical resolutions and chemical shift precisions were +/- 0.5 Hz for ^{1}H and +/- 0.8 Hz for ^{13}C. All NMR spectra were referenced on the solvent peak. High resolution mass spectra were obtained using an Agilent 6520 Q-TOF mass spectrometer with an ESI source and an Agilent G1607A coaxial sprayer. All analyses were made in the positive ionisation mode. Purine (exact mass for $[M+H]^+$ = 121.050873) and 1,2,3,4,5,6-hexakis(2,2,3,3-tetrafluoropropoxy)-1,3,5,2,4,6-triazatriphosphinane (exact mass for $[M+H]^+$ = 922.009798) were used for internal mass calibration. IR spectra were recorded on a Shimadzu IR Affinity-1 fourier transform infrared spectrometer. All chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. All reactions were performed under an Ar-atmosphere.

2. Syntheses of Ammonium Salts:



General Procedure: One equivalent of tertiary amine was added to a solution of one equivalent of the α-bromo amide in THF (10 mL / g amide) and stirred for 24 h at room temperature. The resulting solid was filtered off, washed 3 times with EtOAc, and dried in vacuo to give the product in sufficient purity for the epoxide formation reaction.

Ammonium Salt 3. Prepared from DABCO and 2-bromo-*N*,*N*-diethylacetamide[1] (4.06 g, 20.9 mmol) in 73% (4.65 g, 15.2 mmol). White solid. M.p.: 190-193 °C; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 1.13 (t, *J* = 7.5 Hz, 3H), 1.22 (t, *J* = 7.5 Hz, 3H), 3.22 (t, *J* = 7.3 Hz, 6H), 3.34 (q, *J* = 7.5 Hz, 2H), 3.48 (q, *J* = 7.5 Hz, 2H), 4.07 (t, *J* = 7.3 Hz, 6H), 4.73 (s, 2H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 12.8 (CH_3-), 14.4 (CH_3-), 41.0 (-CH_2-), 42.1 (-CH_2-), 45.4 (-NCH_2-), 53.0 (-NCH_2-) 61.2 (-CH_2CO-), 162.2 (-CO-) ppm; IR (film): $\tilde{\nu}$ = 3532, 3406, 2972, 2941, 2893, 1632, 1489, 1479, 1470, 1431, 1397, 1368, 1310, 1265, 1215, 1109, 1072, 1053, 961, 893, 839 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{12}H_{24}N_3O^+$: 226.1919 [M^+]; found: 226.1922.



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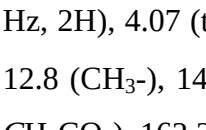
Ammonium Salt 4. Prepared from quinuclidine (0.58 g, 5.2 mmol) and 2-bromo-*N*,*N*-diethylacetamide (1.01 g, 5.2 mmol) in 96% (1.13 g, 5 mmol) as a white to slightly yellow solid. M.p.: decomp > 230 °C; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 0.91 (t, *J* = 7.5 Hz, 3H), 1.06 (t, *J* = 7.5 Hz, 3H), 1.80 (m, 6H), 2.02 (m, 1H), 3.11 (q, *J* = 7.5 Hz, 2H), 3.23 (q, *J* = 7.5 Hz, 2H), 3.96 (m, 6H), 4.60 (s, 2H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 12.8 (CH_3-), 14.4 (CH_3-), 19.5 (-CH-), 24.0 (-CH_2-), 40.9 (-CH_2-), 42.1 (-CH_2-), 55.2 (-CH_2-), 61.3 (-CH_2CO-), 162.5 (-CO-) ppm; IR (film): $\tilde{\nu}$ = 3404, 2938, 2880, 1643, 1458, 1431, 1406, 1383, 1356, 1267, 1215, 1153, 1107, 1045, 978, 939, 889, 837, 747 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{13}H_{25}N_2O^+$: 225.1967 [M^+]; found: 225.1970.



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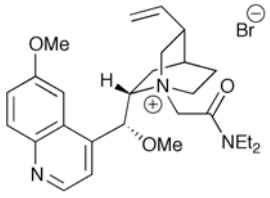
Ammonium Salt 5. Prepared from O-methyl protected quinine[2] (166 mg, 0.49 mmol) and 2-bromo-*N*,*N*-diethylacetamide (95 mg, 0.49 mmol) in 95% (210 mg, 0.46 mmol) after column chromatography ($CHCl_3$: MeOH = 9 : 1) as a slightly yellow highly viscous oil. $[\alpha]_D^{20}$ (c = 1.21, $CHCl_3$) = -115.2°; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 1.08 (m, 1H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.82 (m, 1H), 2.05 - 2.19 (m, 3H), 2.82 (m, 1H), 3.40 (s, 3H), 3.41 - 3.47 (m, 2H), 3.52 - 3.55 (m, 1H), 3.91 (m, 1H), 4.09 (s, 3H), 4.22 (m, 1H), 4.37 - 4.48 (m, 3H), 4.83 (m, 1H), 5.01 (m, 2H), 5.25 (m, 2H), 5.54 (m, 1H), 6.16 (m, 1H), 7.43 (m, 3H), 8.05 (d, *J* = 4.5 Hz, 1H), 8.80 (d, *J* = 8.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 13.1, 14.6, 22.9, 25.6, 26.3, 37.4, 41.2, 42.5, 56.5, 57.3,



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[1] T. Hama, X. Liu, D. A. Culkin and J. F. Hartwig, *J. Am. Chem. Soc.*, 2003, **125**, 11176-11177.
[2] C. D. Papageorgiou, M. A. Cubillo de Dios, S. V. Ley and M. J. Gaunt, *Angew. Chem. Int. Ed.*, 2004, **43**, 4641-4644.

57.5, 58.5, 59.7, 62.4, 77.7, 100.6, 116.6, 119.0, 123.1, 126.7, 131.9, 137.0, 138.3, 144.8, 147.0, 159.1, 164.0 ppm; IR (film): $\tilde{\nu}$ = 3402, 2972, 2936, 1637, 1618, 1589, 1508, 1474, 1458, 1435, 1404, 1385, 1358, 1302, 1292, 1271, 1240, 1227, 1180, 1140, 1088, 1028, 982, 908, 891, 867, 835 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{27}H_{38}N_3O_3^+$: 452.2913 [M^+]; found: 452.2905.

Ammonium Salt 7. Prepared from Me_3N (33% in EtOH) and 2-bromo-*N*,*N*-diethylacetamide (8.92 g, 45.9 mmol) in 88% (10.27 g, 40.5 mmol) as a white solid. M.p.: 186-188 °C; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 1.14 (t, *J* = 7.3 Hz, 3H), 1.27 (t, *J* = 7.3 Hz, 3H), 3.36 (q, *J* = 7.3 Hz, 2H), 3.47 (q, *J* = 7.3 Hz, 2H), 3.63 (s, 9H), 5.00 (s, 2H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 12.9 (CH_3-), 14.5 (CH_3-), 41.0 (-CH_2-), 42.0 (-CH_2-), 54.7 (-$N^+(CH_3)_3$), 63.2 (-*C*H_2CO-), 162.4 (-CO-) ppm; IR (film): $\tilde{\nu}$ = 3003, 2978, 2945, 1639, 1483, 1467, 1446, 1433, 1384, 1357, 1278, 1238, 1215, 1139, 1097, 1078, 1022, 975, 954, 927, 894 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_9H_{21}N_2O^+$: 173.1654 [M^+]; found: 173.1651.

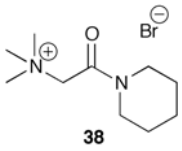
Ammonium Salt 34. Prepared from Me_3N (33% in EtOH) and 2-bromo-*N*,*N*-dibenzylacetamide[3] (1.37 g, 4.31 mmol) in 75% (1.22 g, 3.23 mmol) as a white solid. M.p.: 212-216 °C; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 3.47 (s, 9H), 4.64 (s, 2H), 4.79 (s, 2H), 5.03 (s, 2H), 7.17-7.35 (m, 10H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 49.7 (-CH_2-Ar), 50.4 (-CH_2-Ar), 54.7 (-$N^+(CH_3)_3$), 63.5 (-*C*H_2CO-), 127.0 (Ar-C), 128.0 (Ar-C), 128.1 (Ar-C), 128.2 (Ar-C), 129.0 (Ar-C), 129.3 (Ar-C), 135.4 (Ar-C_{quat}), 135.7 (Ar-C_{quat}), 164.2 (-CO-) ppm; IR (film): $\tilde{\nu}$ = 3410, 3030, 2937, 1645, 1492, 1448, 1431, 1408, 1359, 1215, 1083, 972, 921, 759, 707, 696, 624 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{19}H_{25}N_2O^+$: 297.1961 [M^+]; found: 297.1960.

Ammonium Salt 36. Prepared from *N*-benzyl-2-bromoacetamide[4] (3.07 g, 13.44 mmol) in 91% (3.52 g, 12.26 mmol) as a white solid. M.p.: 177-179 °C; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 3.39 (s, 9H), 4.43 (d, *J* = 6.4 Hz, 2H), 4.73 (s, 2H), 7.24 (m, 1H), 7.31 (m, 2H), 7.36 (m, 2H) ppm, 9.23 (t, *J* = 6.4 Hz, 1H); ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 43.6 (-CH_2-Ar), 54.9 (-$N^+(CH_3)_3$), 65.2 (-*C*H_2CO-),

[3] P. M. P. Gois and C. A. M. Afonso, *Eur. J. Org. Chem.*, 2003, 3798-3810.
[4] A. M. R. Smith, H. S. Rzepa, A. J. P. White, D. Billen and K. K. (M.) Hii, *J. Org. Chem.*, 2010, **75**, 3085.

127.7 (Ar-C), 128.1 (Ar-C), 128.8 (Ar-C), 137.5 (Ar-C_{quat}), 162.8 (-CO-) ppm; IR (film): $\bar{\nu}$ = 3380, 3190, 3043, 3012, 2914, 1680, 1550, 1473, 1454, 1414, 1396, 1263, 1230, 1066, 1029, 996, 906, 736, 696 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{12}H_{19}N_2O^+$: 207.1492 [M^+]; found: 350.1492.

Ammonium Salt 38. Prepared from Me_3N (33% in EtOH) and 2-bromo-1-(piperidin-1-yl)ethanone[5] (1.11 g, 5.4 mmol) in 71% (1.02 g, 3.84 mmol). Hygroscopic white to off-white solid. M.p.: 223-226 °C; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 1.56-1.68 (m, 6H), 3.46 (m, 4H), 3.60 (s, 9H), 5.11 (s, 2H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 24.1 (-CH_2-), 25.4 (-CH_2-), 26.4 (-CH_2-), 43.0 (-CON-*C*H_2-), 46.4 (-CON-*C*H_2-), 54.7 (-$N^+(CH_3)_3$), 63.6 (-*C*H_2CO-), 161.3 (-CO-) ppm; IR (film): $\bar{\nu}$ = 2935, 2897, 1637, 1469, 1448, 1381, 1251, 1226, 1143, 1018, 979, 950, 931, 914 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{10}H_{21}N_2O^+$: 185.1648 [M^+]; found: 185.1644.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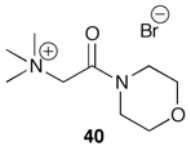
Ammonium Salt 40. Prepared from Me_3N (33% in EtOH) and 2-bromo-1-(morpholin-4-yl)ethanone[6] (0.87 g, 4.2 mmol) in 75% (0.84 g, 3.16 mmol). Hygroscopic white to grey solid. M.p.: 171-175 °C; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 3.57 (m, 2H), 3.60 (s, 9H), 3.63 (m, 2H), 3.69 (m, 2H), 3.77 (m, 2H), 5.26 (s, 2H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 42.0 (-CH_2-), 45.7 (-CH_2-), 54.8 (-$N^+(CH_3)_3$), 63.5 (-CH_2-), 66.4 (-CH_2-), 66.6 (-CH_2-), 162.0 (-CO-) ppm; IR (film): $\bar{\nu}$ = 3388, 2970, 2920, 2868, 1649, 1490, 1465, 1446, 1273, 1255, 1232, 1112, 987, 929, 611, 599 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_9H_{19}N_2O_2^+$: 187.1441 [M^+]; found: 187.1444.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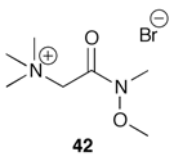
Ammonium Salt 42. Prepared from Me_3N (33% in EtOH) and 2-bromo-*N*-methoxy-*N*-methylacetamide[7] (481 mg, 2.64 mmol) in 79% (505 mg, 2.10 mmol) as a very hygroscopic residue; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 3.22 (s, 3H), 3.71 (s, 9H), 3.94 (s, 3H), 5.14 (s, 2H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 31.8 (-CH_3), 54.0 (-$N^+(CH_3)_3$), 62.4 (-OCH_3), 62.6 (-CH_2-), 164.1 (-CO-) ppm; IR (film): $\bar{\nu}$ = 3383, 2972, 2947, 1670, 1489, 1473, 1458, 1398, 1201, 1182, 1008, 964, 925, 910, 636 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_7H_{17}N_2O_2^+$: 161.1285 [M^+]; found: 161.1285.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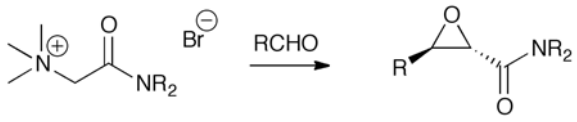
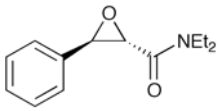
[5] B. C. Gorske, B. L. Bastian, G. D. Geske, and H. E. Blackwell, *J. Am. Chem. Soc.*, 2007, **129**, 8928-8929.
[6] A. Kaori, N. Shigeo, and T. Yuko, *Tetrahedron Lett.*, 2009, **50**, 5689-5691.
[7] A. K. Ghosh, S. Banerjee, S. Sinha, S. B. Kang, and B. Zajc, *J. Org. Chem.*, 2009, **74**, 3689-3697.

3. Syntheses of Glycidic Amides:



General procedure for the preparation of epoxides under biphasic conditions (using 2 equiv. of aldehyde): A vigorously stirred solution of ammonium salt (1 mmol) in CH_2Cl_2 (10 mL) was cooled to 0 °C, followed by addition of 50% NaOH (5 mL). After 5 min the aldehyde (2 mmol) was added in one portion. The biphasic mixture was warmed to 25 °C over 1 h and vigorously stirred for 23 h. After extraction with EtOAc the organic layer was washed with brine, dried over Na_2SO_4 and evaporated to dryness. Column chromatography (silica gel, heptanes/EtOAc = 7:3) gave the glycidic amides in the reported yields.

***trans*-*N*,*N*-diethyl-3-phenyloxirane-2-carboxamide (2).** Obtained in 92% as a white to yellow solid. Analytical data are in full accordance with those reported in literature.[8] M.p.: 85-88 °C; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 1.16 (t, *J* = 7.3 Hz, 3H), 1.20 (t, *J* = 7.3 Hz, 3H), 3.40-3.51 (m, 4H), 3.58 (d, *J* = 1.4 Hz, 1H), 4.09 (d, *J* = 1.4 Hz, 1H), 7.32-7.39 (m, 5H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 13.1, 15.0, 41.0, 41.6, 57.3, 57.7, 125.8, 128.6, 128.7, 135.9, 165.8 ppm; IR (film): $\tilde{\nu}$ = 2972, 2933, 2873, 1643, 1487, 1450, 1409, 1365, 1271, 1217, 1145, 1095, 1076, 893, 754, 698, 617 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{13}H_{17}NO_2$: 220.1332 $[M+H]^+$; found: 220.1329.



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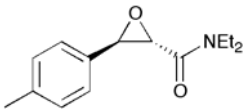
***trans*-*N*,*N*-diethyl-3-(*p*-tolyl)oxirane-2-carboxamide (9).** Obtained in 95% as a white to yellow solid. Analytical data are in full accordance with those reported in literature.[8] M.p.: 72-75 °C; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 1.15 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H), 2.34 (s, 3H), 3.38-3.49 (m, 4H), 3.57 (d, *J* = 1.7 Hz, 1H), 4.03 (d, *J* = 1.7 Hz, 1H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 13.0, 15.0, 21.3, 40.9, 41.5, 57.2, 57.7, 125.7, 129.4, 132.8, 138.7, 165.9 ppm; IR (film): $\tilde{\nu}$ = 2970, 2933, 2870, 1643, 1469, 1421, 1375, 1271, 1217, 1145, 1099, 1070, 891, 806, 765 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{14}H_{19}NO_2$: 234.1489 $[M+H]^+$; found: 234.1492.



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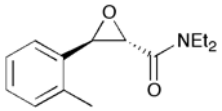
[8] Y.-G. Zhou, X.-L. Hou, L.-X. Dai, L.-J. Xia and M.-H. Tang, *J. Chem. Soc., Perkin Trans. 1*, 1999, 77-80.

***trans*-*N*,*N*-diethyl-3-(*o*-tolyl)oxirane-2-carboxamide (11).** Obtained in 90% as an off-white solid matching the reported data.[9] M.p.: 79-83 °C; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 1.15 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.3 Hz, 3H), 2.39 (s, 3H), 3.35-3.49 (m, 4H), 3.47 (d, *J* = 2.2 Hz, 1H), 4.21 (d, *J* = 2.2 Hz, 1H), 7.12-7.24 (m, 4H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 13.1, 15.1, 19.0, 41.0, 41.6, 56.0, 56.4, 124.3, 126.3, 128.3, 130.2, 134.3, 136.4, 166.0 ppm; IR (film): $\bar{\nu}$ = 2974, 2933, 1653, 1483, 1463, 1381, 1363, 1263, 1219, 1143, 1097, 902, 754, 609 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{14}H_{19}NO_2$: 234.1489 $[M+H]^+$; found: 234.1484.



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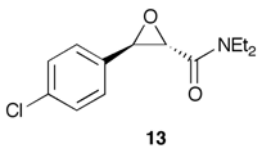
***trans*-3-(4-chlorophenyl)-*N*,*N*-diethyloxirane-2-carboxamide (13).** Obtained in 90% as a colourless oil. Analytical data are in full accordance with those reported in literature.[8] ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 1.16 (t, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H), 3.38-3.48 (m, 4H), 3.53 (d, *J* = 1.3 Hz, 1H), 4.07 (d, *J* = 1.3 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 12.5, 14.5, 40.5, 41.1, 56.5, 56.7, 126.5, 128.4, 133.9, 134.1, 164.9 ppm; IR (film): $\bar{\nu}$ = 2970, 2933, 1645, 1483, 1465, 1417, 1271, 1217, 1085, 1012, 894, 808 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{13}H_{16}ClNO_2$: 276.0762 $[M+Na]^+$; found: 276.0762.



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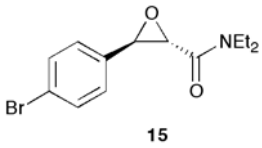
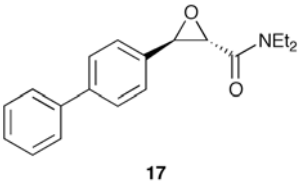
***trans*-3-(4-bromophenyl)-*N*,*N*-diethyloxirane-2-carboxamide (15).** Obtained in 97% as a a colourless oil. Analytical data are in full accordance with those reported in literature.[10] M.p.: 101-104 °C; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 1.11 (t, *J* = 7.3 Hz, 3H), 1.16 (t, *J* = 7.3 Hz, 3H), 3.31-3.45 (m, 4H), 3.51 (s, 1H), 4.00 (s, 1H), 7.15 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 13.1, 15.1, 41.1, 41.7, 57.1, 57.3, 122.7, 127.5, 131.9, 135.0, 165.4 ppm; IR (film): $\bar{\nu}$ = 2968, 2931, 1645, 1481, 1465, 1446, 1417, 1305, 1271, 1217, 1145, 1097, 1066, 1008, 947, 894, 873, 829, 806, 729 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{13}H_{16}BrNO_2$: 298.0437 $[M+H]^+$; found: 298.0439.



15

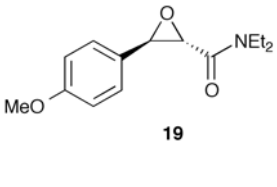
[9] C. C. Tung, A. J. Speziale, and H. W. Frazier, *J. Org. Chem.*, 1963, **28**, 1514-1521.
[10] R. Imashiro, T. Yamanaka, and M. Seki, *Tetrahedron: Asymmetry*, 1999, **10**, 2845-2851.

***trans*-3-([1,1'-biphenyl]-4-yl)-*N*,*N*-diethyloxirane-2-carboxamide (17).** Obtained in 93% as a colourless oil which solidifies in the freezer. Analytical data are in accordance with those reported in literature.[8] M.p.: 104-107 °C; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 1.18 (t, *J* = 6.9 Hz, 3H), 1.22 (t, *J* = 7.0 Hz, 3H), 3.39-3.51 (m, 4H), 3.65 (d, *J* = 2.3 Hz, 1H), 4.14 (d, *J* = 2.3 Hz, 1H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.59 (m, 4H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 13.2, 15.1, 41.1, 41.7, 57.4, 57.6, 126.4, 127.2, 127.5, 127.7, 129.0, 134.9, 140.6, 141.8, 165.8 ppm; IR (film): $\tilde{\nu}$ = 3032, 2976, 2933, 2361, 1653, 1485, 1463, 1263, 1219, 1144, 1076, 898, 842, 814, 763, 729, 698 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{19}H_{21}NO_2$: 296.1645 $[M+H]^+$; found: 296.1643.



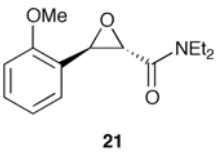
17

***trans*-*N*,*N*-diethyl-3-(4-methoxyphenyl)oxirane-2-carboxamide (19).** Obtained in 83% as a colourless oil. Analytical data are in full accordance with those reported in literature.[11] ^{1}H NMR (200 MHz, δ, $CDCl_3$, 298 K): 1.11-1.23 (m, 6H), 3.37-3.52 (m, 4H), 3.58 (d, *J* = 1.8 Hz, 1H), 3.80 (s, 3H), 4.02 (d, *J* = 1.8 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 2H) ppm; ^{13}C NMR (50 MHz, δ, $CDCl_3$, 298 K): 12.6, 14.8, 40.8, 41.4, 55.2, 57.0, 57.5, 114.1, 127.0, 127.7, 160.0, 165.8 ppm; IR (film): $\tilde{\nu}$ = 2972, 2931, 1641, 1612, 1510, 1483, 1467, 1276, 1244, 1220, 1166, 1029, 900, 835, 813 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{14}H_{19}NO_3$: 272.1257 $[M+Na]^+$; found: 272.1251.



19

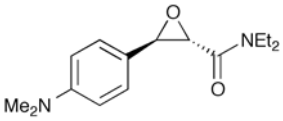
***trans*-*N*,*N*-diethyl-3-(2-methoxyphenyl)oxirane-2-carboxamide (21).** Obtained in 98% as a bright yellow solid. M.p.: 79-83 °C; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 1.13 (t, *J* = 7.2 Hz, 3H), 1.17 (t, *J* = 7.2 Hz, 3H), 3.29-3.53 (m, 4H), 3.46 (d, *J* = 1.1 Hz, 1H), 3.80 (s, 3H), 4.31 (d, *J* = 1.1 Hz, 1H), 6.85 (d, *J* = 7.9 Hz, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.26 (t, *J* = 7.9 Hz, 1H), ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 13.1, 14.7, 40.8, 41.4, 53.9, 55.4, 56.7, 110.3, 120.8, 124.5, 125.5, 129.5, 158.1, 166.1 ppm; IR (film): $\tilde{\nu}$ = 2978, 1649, 1602, 1494, 1481, 1465, 1440, 1382, 1288, 1253, 1234, 1219, 1141, 1099, 1018, 894, 877, 815, 754 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{14}H_{19}NO_3$: 272.1257 $[M+Na]^+$; found: 272.1260.



21

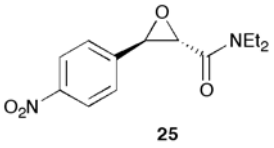
[11] R. Imashiro and M. Seki, *J. Org. Chem.*, 2004, **69**, 4216-4226.

***trans*-*N*,*N*-diethyl-3-(4-dimethylaminophenyl)oxirane-2-carboxamide (23).** ^{1}H NMR of the crude product showed less than 5% of **23** besides unreacted starting material **22**. ^{1}H NMR and HRMS of the crude product were consistent with formation of the *trans*-epoxide: ^{1}H NMR (200 MHz, δ, $CDCl_3$, 298 K): 1.18 (m, 6H), 2.89 (s, 6 H), 3.37 (m, 4H), 3.58 (d, *J* = 1.7 Hz, 1H), 3.92 (d, *J* = 1.7 Hz, 1H), 6.61 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 2H) ppm; HRMS (ESI): *m/z* calcd for $C_{15}H_{22}N_2O_2$: 263.1754 $[M+Na]^+$; found: 263.1756.



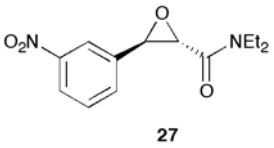
23

***trans*-*N*,*N*-diethyl-3-(4-nitrophenyl)oxirane-2-carboxamide (25).** Obtained in 17% besides the corresponding Cannizzaro disproportionation products which were removed by column chromatography. Analytical data are in accordance with those reported in literature.[8] ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 1.16 (t, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H), 3.38-3.52 (m, 4H), 3.58 (s, 1H), 4.23 (s, 1H), 7.50 (d, *J* = 8.8 Hz, 2H), 8.23 (d, *J* = 8.8 Hz, 2H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 13.0, 15.2, 41.3, 41.8, 56.7, 57.6, 124.1, 126.6, 143.3, 148.2, 164.9 ppm; IR (film): $\tilde{\nu}$ = 2978, 2935, 1647, 1602, 1517, 1342, 1263, 1217, 1143, 1107, 856, 842, 615 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{13}H_{16}N_2O_4$: 287.1002 $[M+Na]^+$; found: 287.1002.



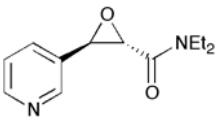
25

***trans*-*N*,*N*-diethyl-3-(3-nitrophenyl)oxirane-2-carboxamide (27).** Obtained in 12% besides the corresponding Cannizzaro disproportionation products which were removed by column chromatography. Analytical data are in accordance with those reported in literature.[9] M.p.: 105-108 °C; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 1.18 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H), 3.40-3.52 (m, 4H), 3.60 (s, 1H), 4.24 (d, *J* = 1.3 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 7.1 Hz, 1H), 8.19 (m, 2H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 13.1, 15.2, 41.2, 41.8, 56.6, 57.4, 120.7, 123.7, 129.9, 132.0, 138.4, 148.7, 164.9 ppm; IR (film): $\tilde{\nu}$ = 2976, 2933, 2872, 1631, 1529, 1473, 1458, 1384, 1298, 1265, 1215, 1115, 1095, 1078, 954, 877, 846, 812, 729, 684 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{13}H_{16}N_2O_4$: 287.1002 $[M+Na]^+$; found: 287.1002.



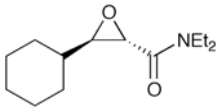
27

***trans*-*N*,*N*-diethyl-3-(pyridin-3-yl)oxirane-2-carboxamide (29).** ^{1}H NMR of the crude product showed less than 10% of **29** and the corresponding Cannizzaro disproportionation products. ^{1}H NMR signals of the *trans*-fused oxirane ring are in accordance with literature.[8]



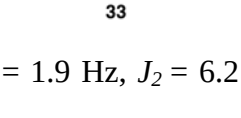
29

***trans*-*N*,*N*-diethyl-3-(cyclohexyl)oxirane-2-carboxamide (33).** Obtained in 54% as a colourless oil. Analytical data are in accordance with those reported in literature.[8] ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 1.10 (t, J = 7.3 Hz, 3H), 1.22 (t, J = 7.2 Hz, 3H), 1.12-1.35 (m, 6H), 1.59-1.87 (m, 5H), 2.92 (dd, J_1 = 1.9 Hz, J_2 = 6.2 Hz,1H) 3.28-3.48 (m, 5H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 13.1, 15.0, 25.5, 25.7, 26.2, 29.1, 29.6, 39.8, 40.8, 41.5, 52.5, 62.3, 166.9 ppm; IR (film): $\tilde{\nu}$ = 2970, 2924, 2852, 1649, 1462, 1450, 1423, 1381, 1263, 1220, 1145, 1097, 1074, 904, 592, 551 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{13}H_{23}NO_2$: 226.1802 $[M+H]^+$; found: 226.1802.



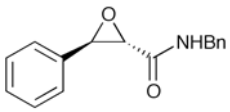
33

***trans*-*N*,*N*-dibenzyl-3-phenyloxirane-2-carboxamide (35).** Obtained in 74% as a white to yellow solid. Analytical data are in full accordance with those reported in literature.[12] M.p.: 118-121 °C; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 3.70 (d, J = 1.2 Hz, 1H), 4.14 (d, J = 1.2 Hz, 1H), 4.55 (s, 2H), 4.69 (d, J = 4.8 Hz, 2H), 7.15-7.41 (m, 15H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 48.8, 49.4, 57.5, 58.2, 125.8, 126.7, 127.8, 128.0, 128.4, 128.6, 128.7, 128.8, 129.2, 135.4, 135.9, 136.5, 167.3 ppm; IR (film): $\tilde{\nu}$ = 3030, 2918, 1645, 1469, 1448, 1255, 1217, 1192, 1078, 1028, 862, 752, 696 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{23}H_{21}NO_2$: 344.1645 $[M+H]^+$; found: 344.1644.



35

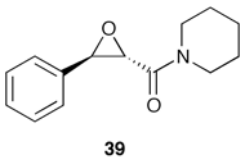
***trans*-*N*-benzyl-3-phenyloxirane-2-carboxamide (37).** Obtained in 49% as a white solid. Analytical data are in full accordance with those reported in literature.[13] M.p.: 121-125 °C; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 3.58 (d, J = 1.2 Hz, 1H), 3.90 (d, J = 1.2 Hz, 1H), 4.49 (m, 2H), 6.57 (bs, 1H), 7.26-7.36 (m, 10H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 43.0, 59.1, 59.2, 125.9, 127.8, 127.9, 128.8, 128.9, 129.2, 134.9, 137.6, 167.4 ppm; IR (film): $\tilde{\nu}$ = 3233, 3062, 3030, 2926, 1654, 1543, 1492, 1454, 1425, 1352, 1251, 1232, 1080, 1026, 885, 756, 740, 692 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{16}H_{15}NO_2$: 276.0995 $[M+Na]^+$; found: 276.0997.



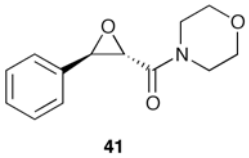
37

[12] O. Meth-Cohn, C. Moore, and H. C. Taljaard, *J. Chem. Soc., Perkin Trans. 1*, 1988, 2663-2674.
[13] T. Nemoto, T. Ohshima and M. Shibasaki, *J. Am. Chem. Soc.*, 2001, **123**, 9474.

***trans*-(3-phenyloxiran-2-yl)(piperidin-1-yl)methanone (39).** Obtained in 93% as a yellowish oil. Analytical data are in full accordance with those reported in literature.[14] ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 1.57-1.67 (m, 6H), 3.46-3.65 (m, 4H), 3.61 (d, *J* = 1.9 Hz, 1H), 4.05 (d, *J* = 1.9 Hz, 1H), 7.26-7.38 (m, 5H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 24.5, 25.5, 26.6, 43.4, 46.1, 57.6, 57.7, 125.7, 128.7, 128.8, 135.9, 164.9 ppm; IR (film): $\bar{\nu}$ = 2941, 2902, 2852, 1643, 1473, 1440, 1413, 1259, 1251, 1228, 1130, 1016, 902, 841, 804, 744, 690 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{14}H_{17}NO_2$: 232.1332 $[M+H]^+$; found: 232.1330.

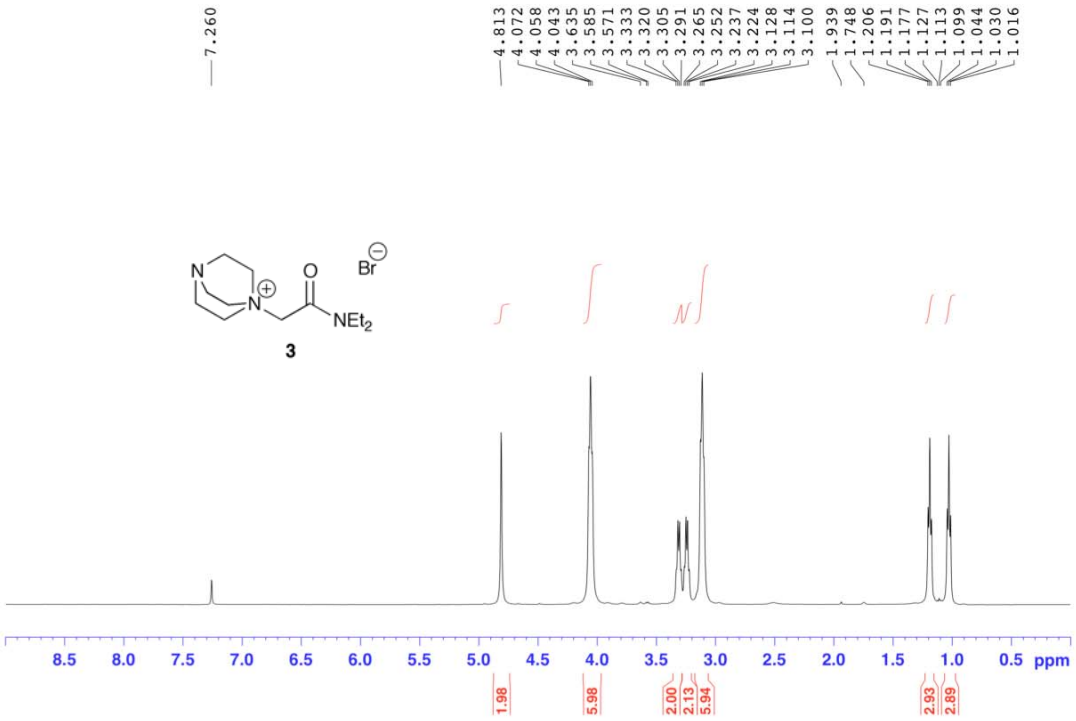

39

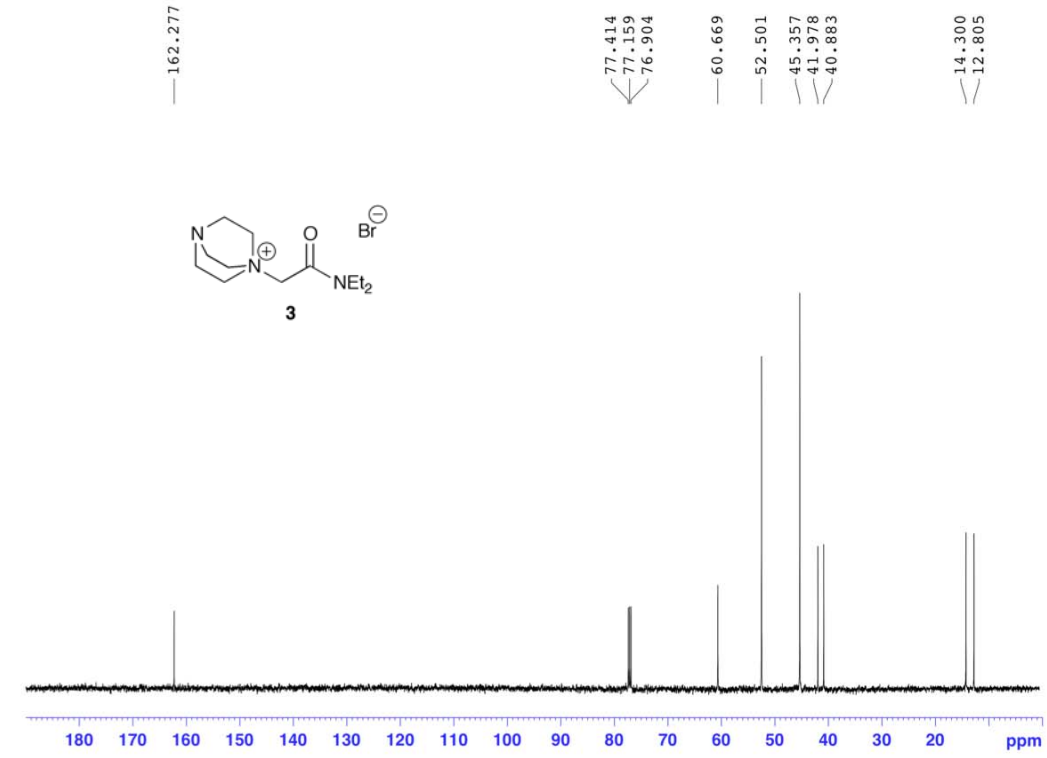
***trans*-morpholino-3-phenyloxiran-2-yl)methanone (41).** Obtained in 86% as a colourless oil. ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 3.56 (m, 1H), 3.62 (d, *J* = 2.0 Hz, 1H), 3.62-3.70 (m, 7H), 4.06 (d, *J* = 2.0 Hz, 1H), 7.27-7.37 (m, 5H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 42.5, 45.5, 57.4, 57.8, 66.7, 66.8, 125.8, 128.8, 129.0, 135.5, 165.3 ppm; IR (film): $\bar{\nu}$ = 2964, 2914, 2900, 2858, 1654, 1467, 1445, 1273, 1240, 1192, 1114, 1068, 1041, 970, 912, 856, 754, 731, 700, 600 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{13}H_{15}NO_3$: 234.1125 $[M+H]^+$; found: 234.1126.

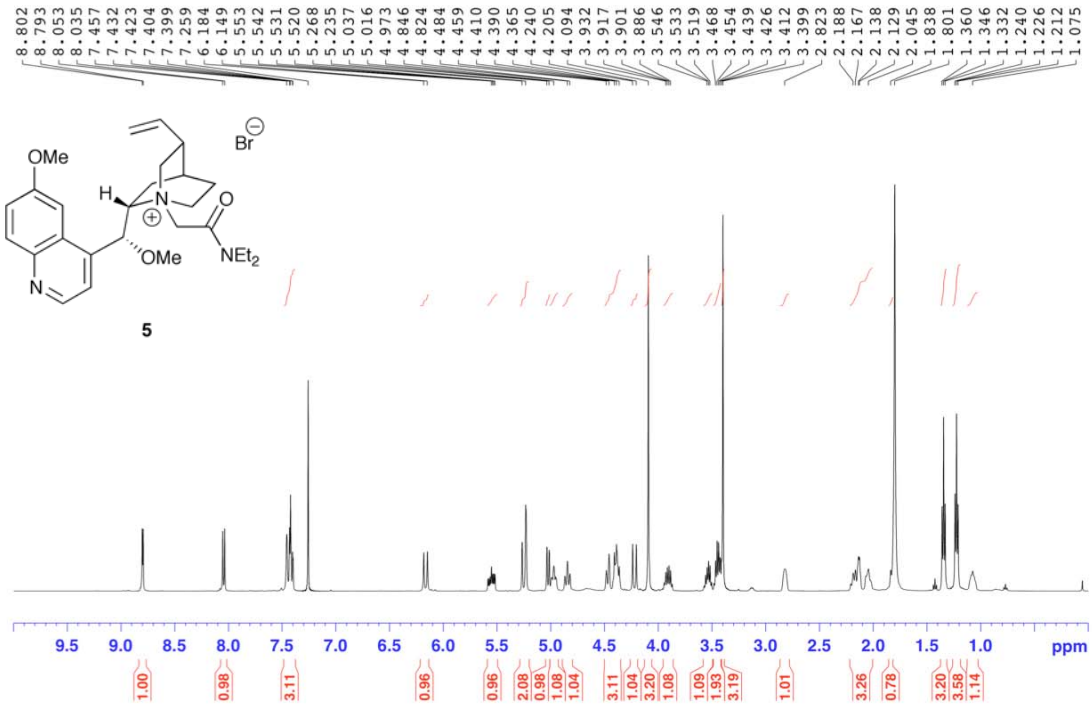

41

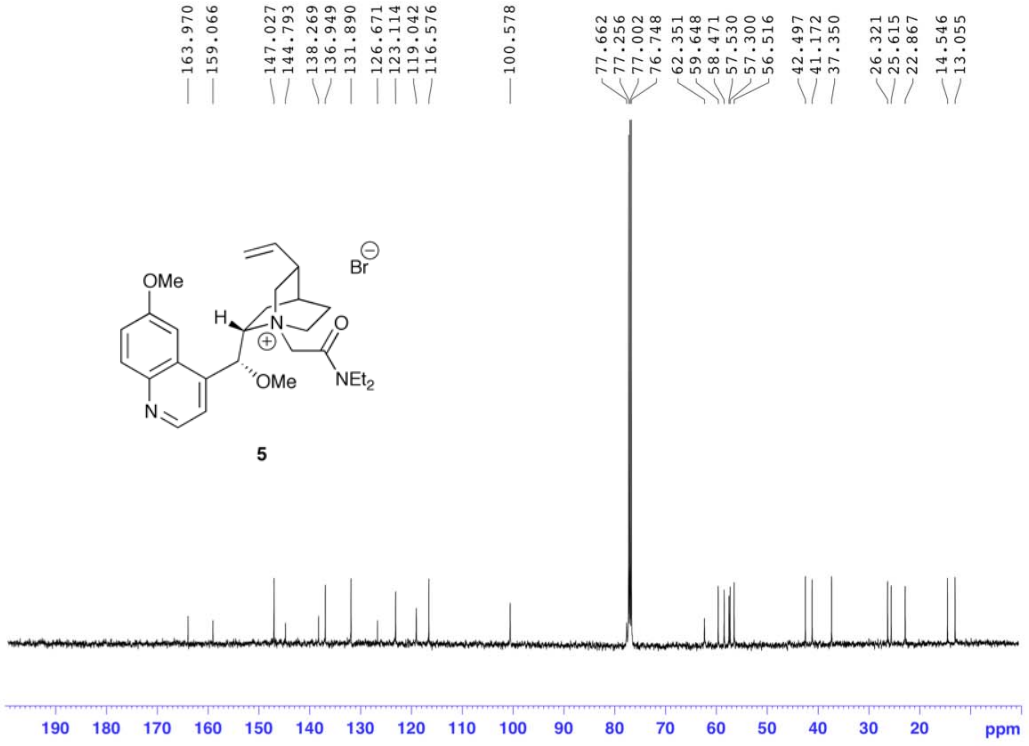
[14] T. Satoh, T. Shimura, and K. Sakai, *Heterocycles*, 2003, **59**, 137-147.

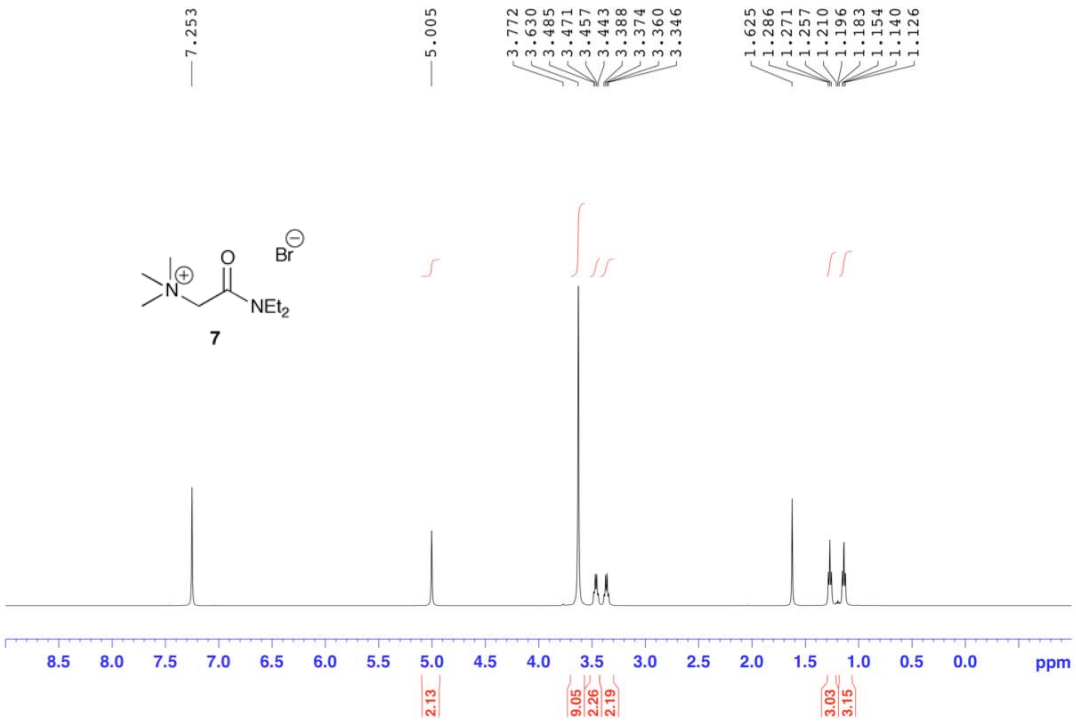
4. NMR Spectra of Ammonium Salts:

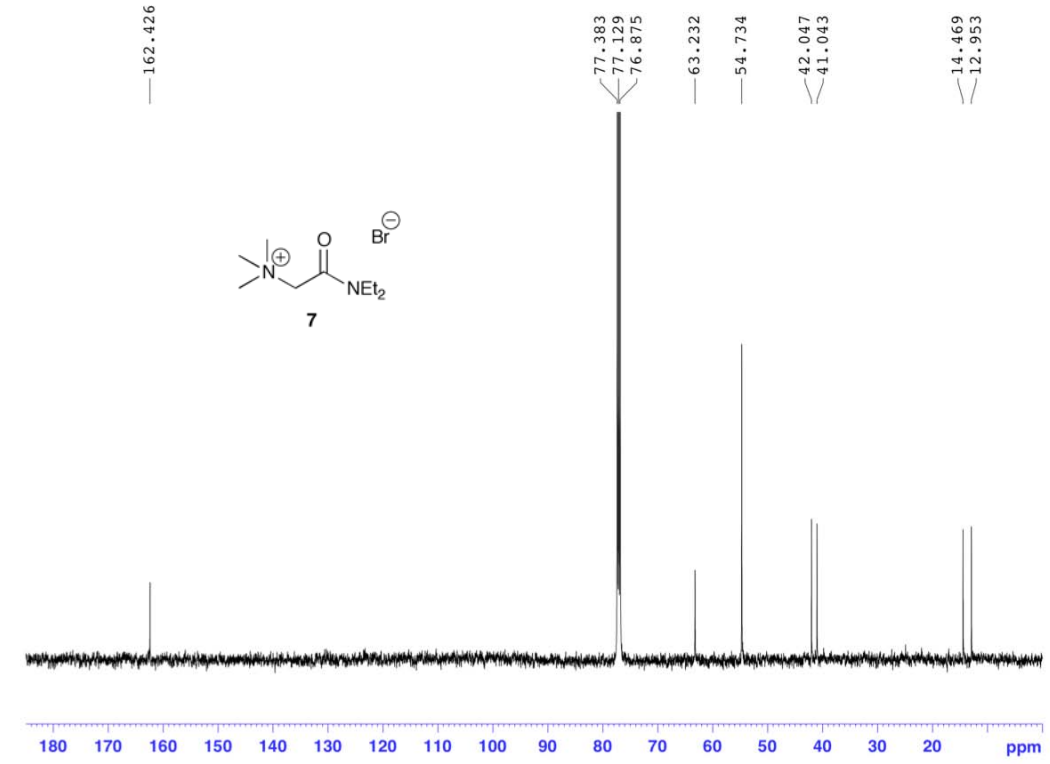


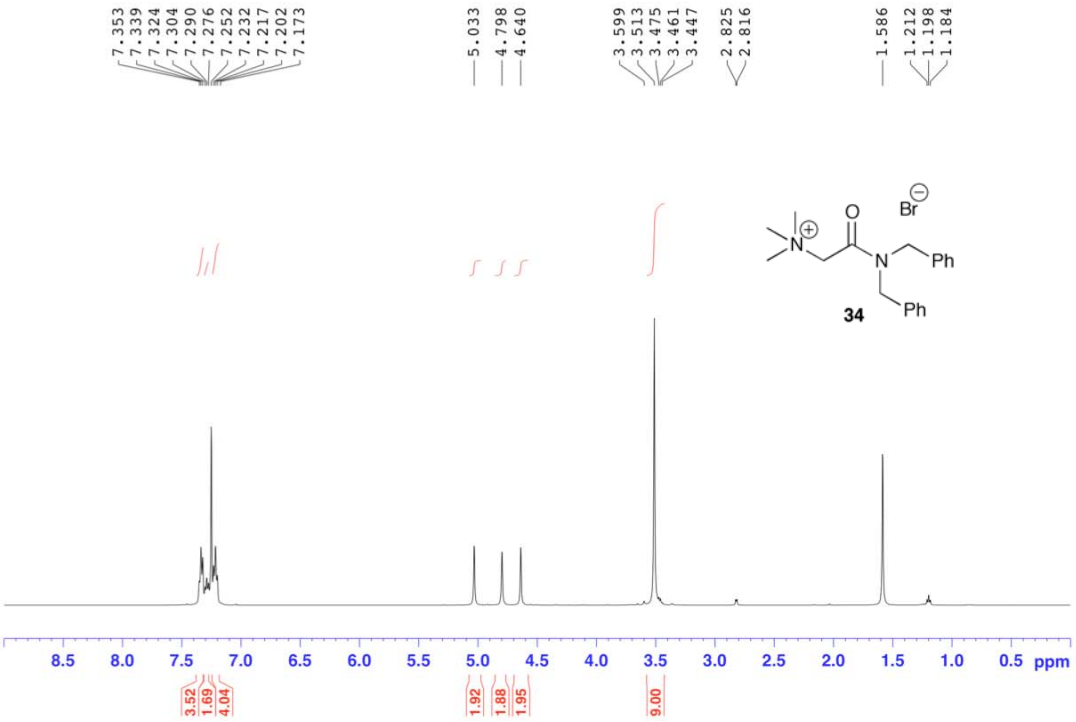


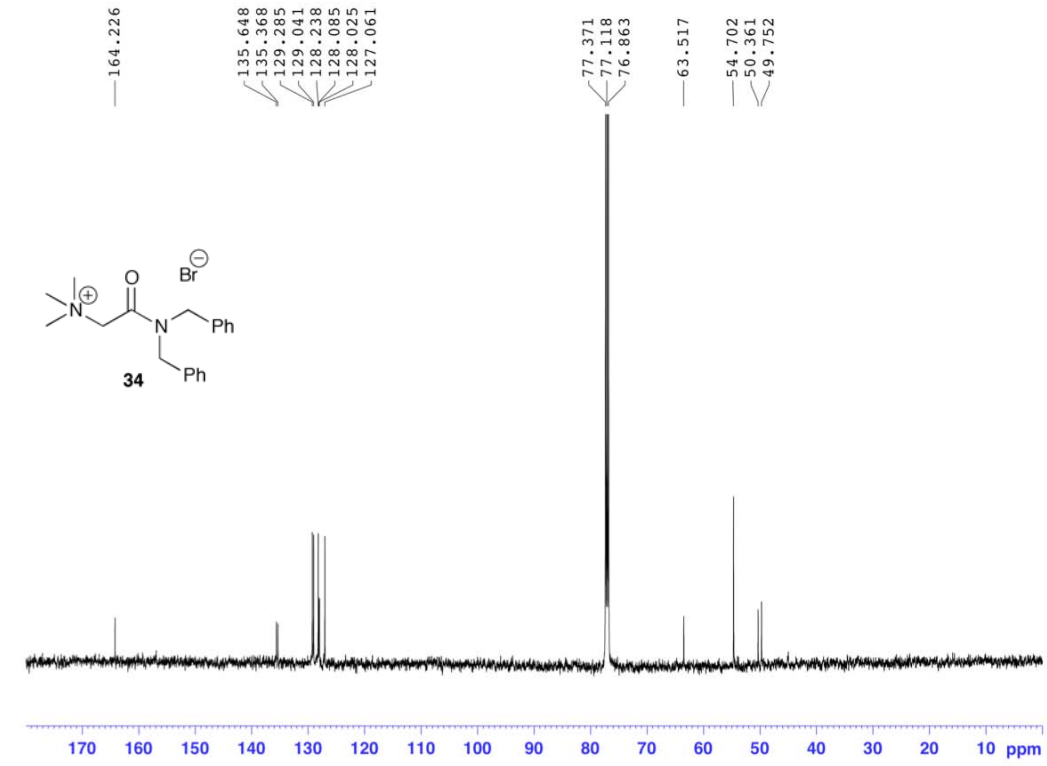


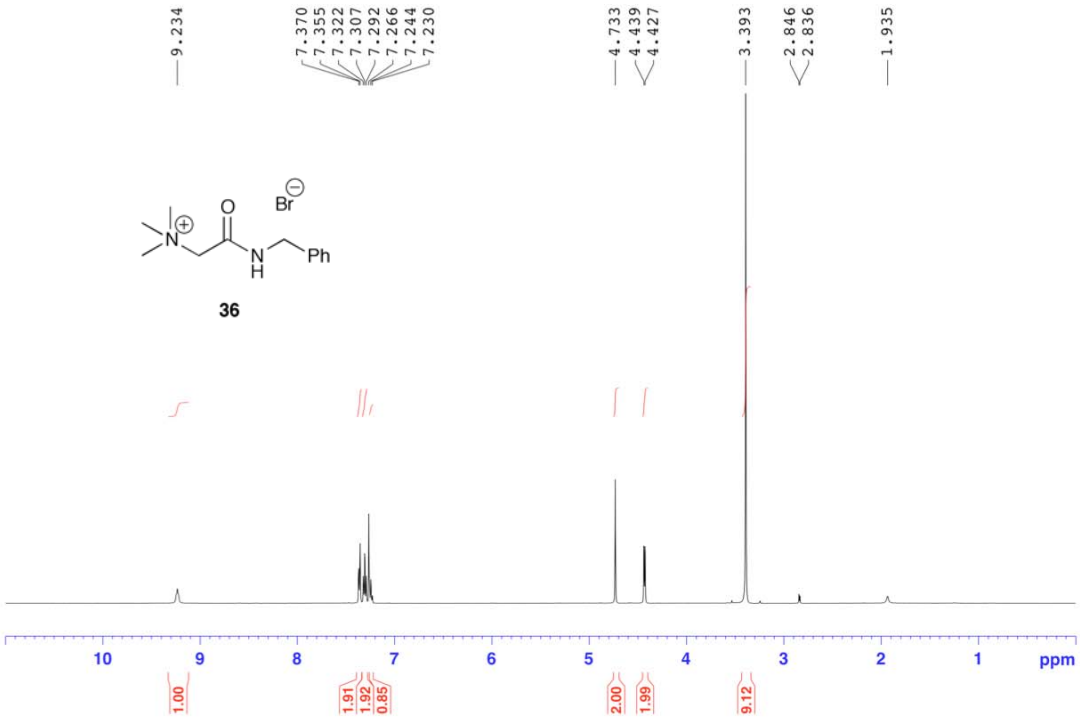


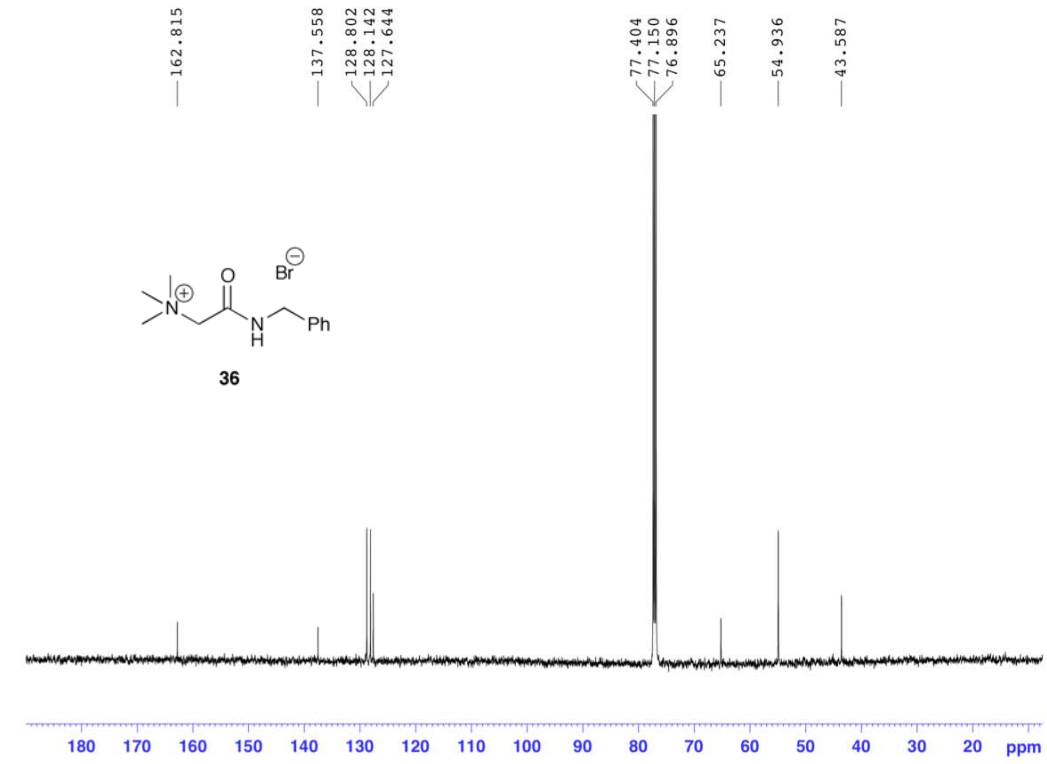


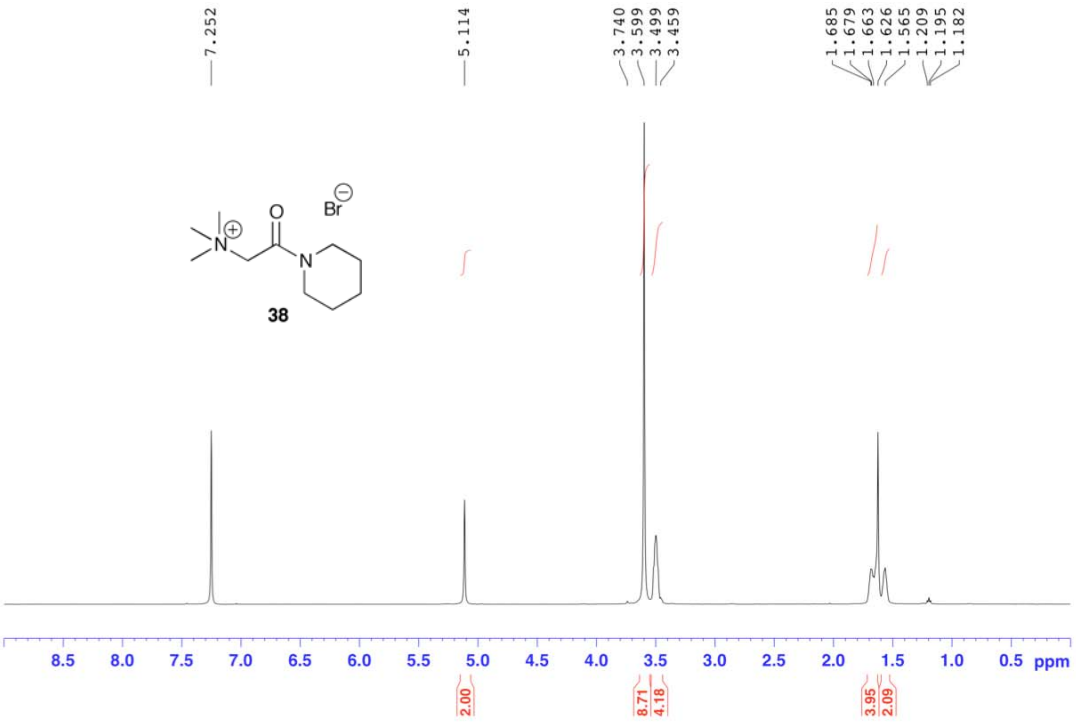


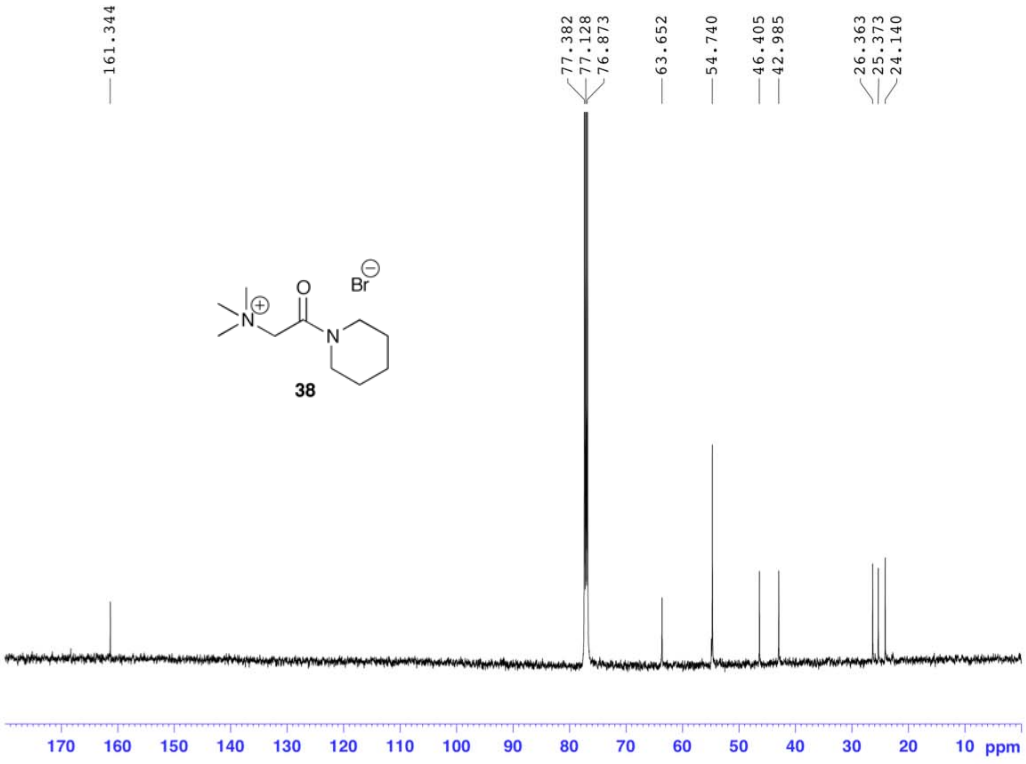


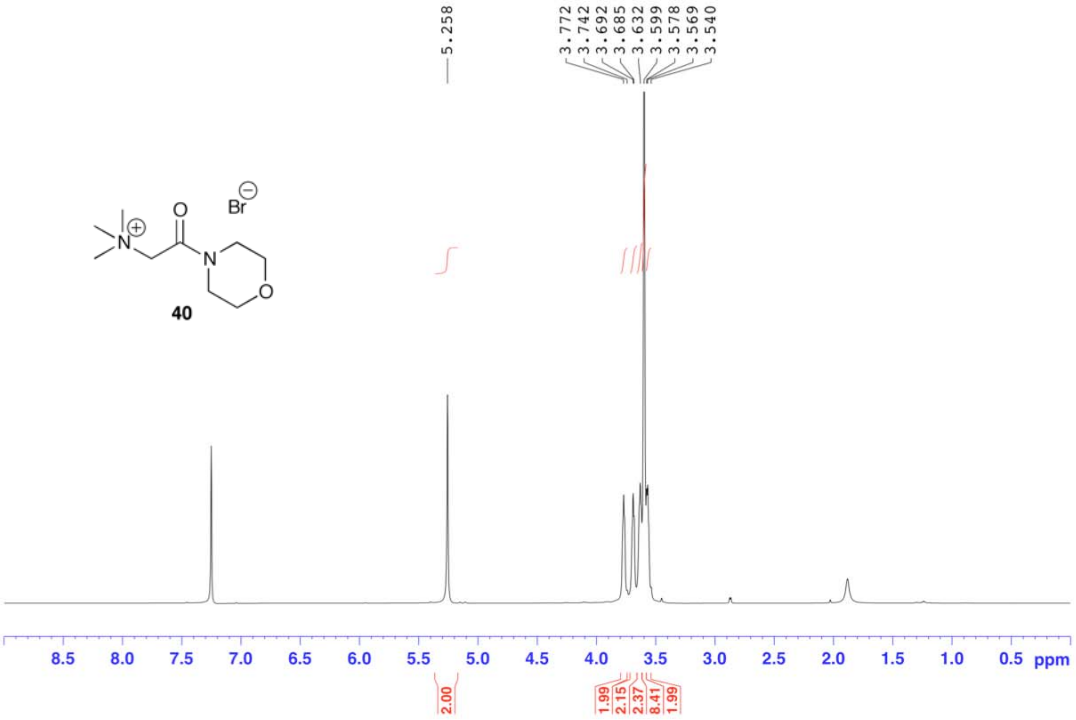


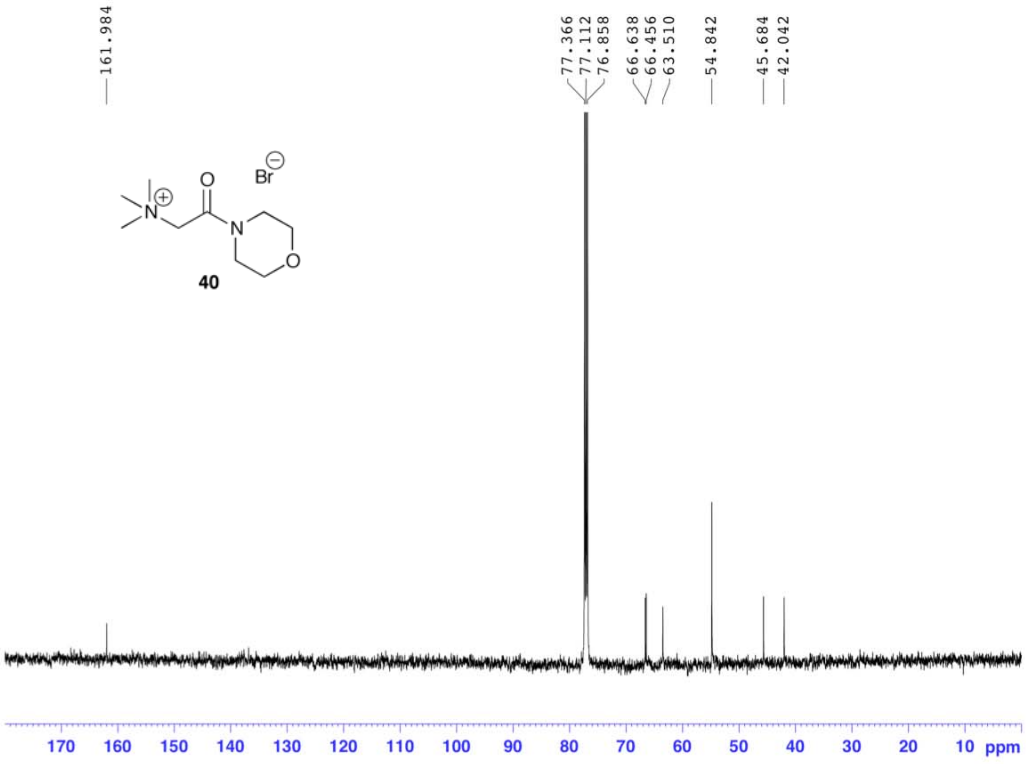


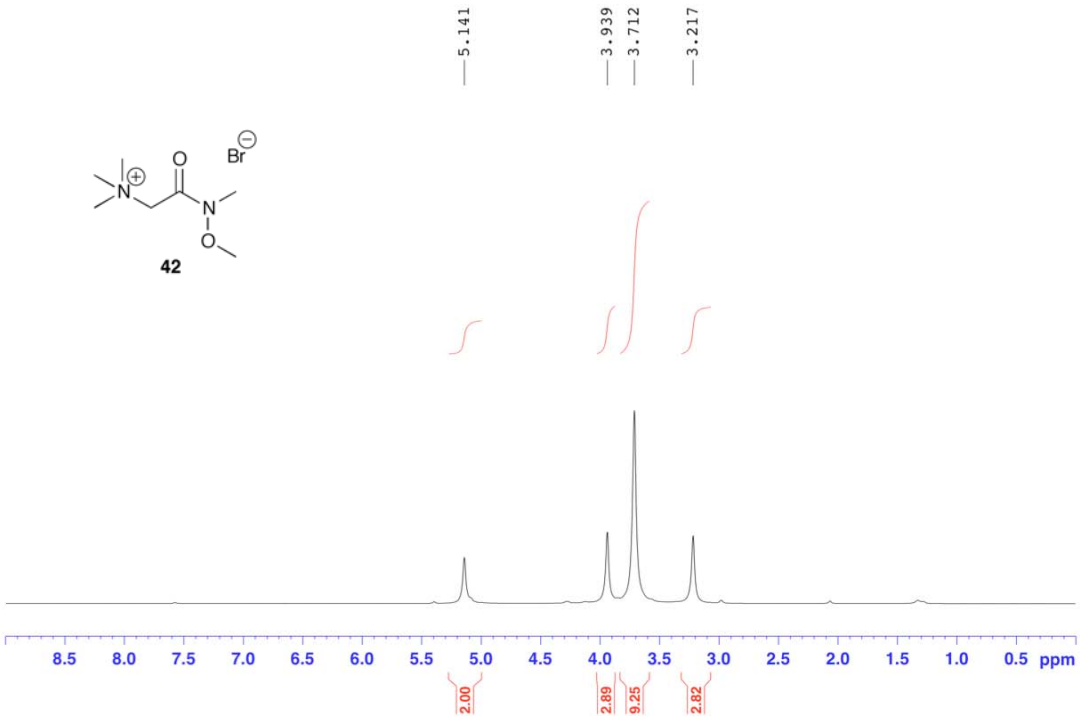


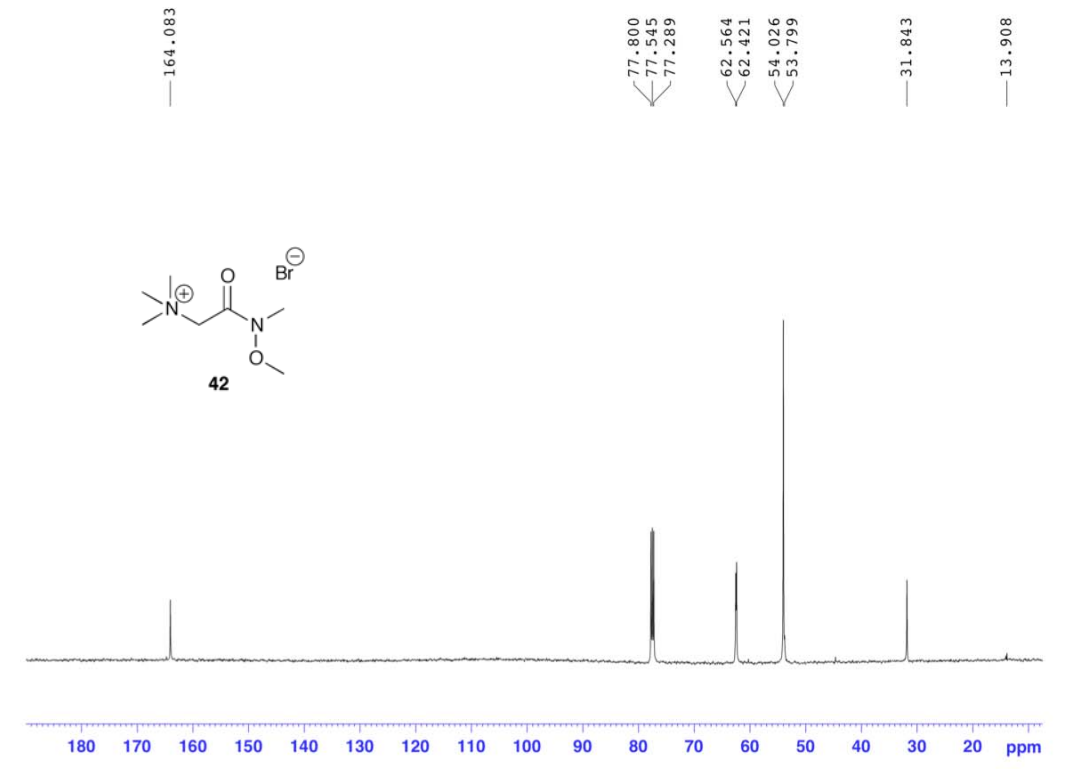





5.258
3.772
3.742
3.692
3.685
3.632
3.599
3.578
3.569
3.540
Br
O
N
O
40
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
1.99
2.15
2.37
8.41
1.99


161.984
77.366
77.112
76.858
66.638
66.456
63.510
54.842
45.684
42.042
Br
O
N
O
40
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm





5. Representative NMR Spectra of *trans*-Glycidic Amides: