SUPPORTING INFORMATION

Asymmetric Syntheses of Three-Membered Heterocycles Using Chiral Amide-Based Ammonium Ylides

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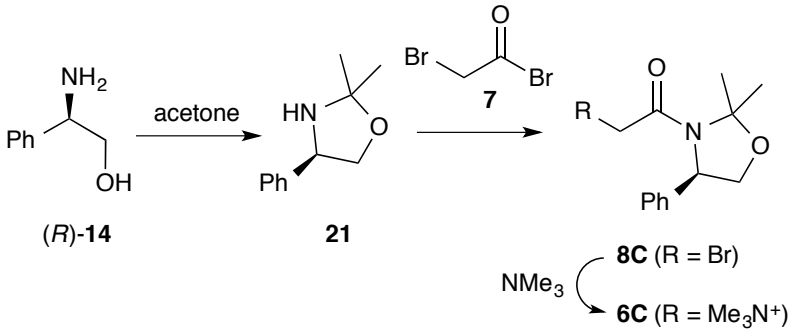
1. General Information:

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 III 300 MHz spectrometer, a Bruker Avance DRX 500 MHz, and on a Bruker Avance III 700 MHz spectrometer with TCI cryoprobe. All NMR spectra were referenced on the solvent peak. High resolution mass spectra were obtained using a Thermo Fisher Scientific LTQ Orbitrap XL with an Ion Max API Source. All analyses were made in the positive ionisation mode. IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer with ATR unit. All chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. All reactions were performed under an Ar-atmosphere. CH_2Cl_2 was distilled over P_2O_5 and stored under Ar (it was not necessary to dry CH_2Cl_2 prior to every experiment and usually this quality could be used successfully in these reactions over the course of 3-4 weeks after distillation). Column chromatography was carried out using silica gel and heptanes/EtOAc or CH_2Cl_2/MeOH (different ratios) as the eluent. Flushing the column with Et_3N (1% in heptanes) prior to use was found beneficial in some cases. Starting imines[1] were prepared according to literature procedures. Single-crystal structure analyses were carried out on a Bruker Smart X2S diffractometer operating with Mo-K_α radiation (λ= 0.71073 Å). Geometry optimization has been performed using the Jaguar 8.0 pseudospectral program package using the well established B3LYP hybrid density functional with the D3 dispersion correction and the standard split valence polarized 6-31G* basis as implemented in Jaguar. All the optimization calculations were carried out using the Poisson-Boltzmann polarizable continuum method as incorporated in Jaguar, and parameters for CH_2Cl_2. Energies were obtained by single point energy calculations at the B3LYP-D3/6-311+G**(CH_2Cl_2) level. The correct nature of each stationary point has been checked by performing frequency calculations at the B3LYP/6-31G*(CH_2Cl_2) level of theory. Thermal and entropic contributions to free energy (at 298.15 K) and zero-point energy have been obtained from these frequency calculations. We have made a systematic attempt to locate all possible local minima, with the data presented referring to the lowest energy form.

[1] (a) L. Huang and W. D. Wulff, *J. Am. Chem. Soc.* 2011, **133**, 8892-8895; (b) T. Regiani, V. G. Santos, M. N. Godói, B. G. Vaz, M. N. Eberlin and F. Coelho, *Chem. Commun.* 2011, **47**, 6593-6595; (c) K. Yoshida, N. Akashi and A. Yanagisawa, *Tetrahedron: Asymmetry* 2011, **22**, 1225-1230.

2. Synthesis of Ammonium Amide 6C.



Step 1: (*R*)-**14** (3.00 g, 21.9 mmol) was dissolved in 50 mL acetone and 3.2 g anhydrous $MgSO_4$ were added and the reaction mixture was stirred for 3 h at 20 °C. After filtration and evaporation to dryness the product **21** was obtained in 95% (3.68 g, 20.7 mmol) and used without further purification. The ^{1}H-NMR-spectrum is in full accordance to literature.[2] ^{1}H-NMR (300 MHz, δ, $CDCl_3$, 298 K): 1.45 (s, 3H), 1.52 (s, 3H), 2.04 (b, 1H), 3.71 (t, 1H, J = 7.8 Hz), 4.29 (t, 1H, J = 7.8 Hz), 4.54 (t, 1H, J = 7.8 Hz), 7.26 - 7.41 (m, 5H, Ar-H) ppm.

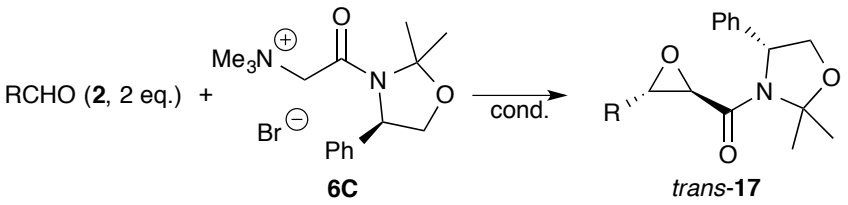
Step 2: Compound **21** (3.68 g, 20.7 mmol, 1 eq.) was dissolved in 25 mL CH_2Cl_2 and 83 mL aqueous saturated Na_2CO_3 solution were added. Then bromide **7** (2.9 mL, 21.7 mmol, 1.05 eq.) was added and the mixture was vigorously stirred for 4 h. After addition of aqueous saturated $NaHCO_3$ the aqueous layer was separated and washed three times with 20 mL CH_2Cl_2. The combined organic phases were dried over anhydrous $MgSO_4$, filtrated and the solvent removed under reduced pressure. The product was purified by column chromatography (silica gel, heptanes:EtOAc = 5:1) to give **8C** (2.57 g, 8.6 mmol, 41 % yield) as a light-brown solid. The ^{1}H-NMR-spectrum was in accordance to literature.[3] ^{1}H-NMR (300 MHz, δ, $CDCl_3$, 298 K): 1.64 (s, 3H), 1.87 (s, 3H), 3.45 (d, 1H, J = 11.0 Hz), 3.52 (d, 1H, J = 11.0 Hz), 3.94 (dd, 1H, J_1 = 9.0 Hz, J_2 = 2.7 Hz), 4.41 (dd, 1H, J_1 = 9.0 Hz, J_2 = 6.5 Hz), 5.07 (dd, 1H, J_1 = 6.5 Hz, J_2 = 2.7 Hz), 7.25 - 7.45 (m, 5H) ppm.

Step 3: Compound **8C** (2.57 g, 8.6 mmol) was dissolved in THF (26 mL) and NMe_3 (2.50 mL, 20.4 mmol, 1.2 eq., 33 % solution in EtOH) was added. After stirring for 24 h at r.t. the solvent was removed with vacuum distillation. The crude product (purity >90%) was purified by column chromatography (heptanes → CH_2Cl_2:MeOH = 5:1) to give the ammonium salt **6C** in 90% yield (2.90 g, 8.1 mmol) as a white hygroscopic foam. $[\alpha]_D^{22}$ (c = 0.6, DCM) = -92; ^{1}H-NMR (700 MHz, δ, $CDCl_3$, 298 K): 1.65 (s, 3H), 1.86 (s, 3H), 2.98 (d, 1H, J = 16.3 Hz), 3.44 (s, 9H), 3.91 (dd, 1H, J_1 = 9.2 Hz, J_2 = 1.7 Hz), 4.46 (dd, 1H, J_1 =

[2] S. Kanemasa and K. Onimura, *Tetrahedron* 1992, **48**, 8631-8644.
[3] R. J. R. Lumby, P. M. Joensuu and H. W. Lam, *Tetrahedron* 2008, **64**, 7729-7740.

9.2 Hz, J_2 = 6.5 Hz), 5.83 (dd, 1H, J_1 = 6.5 Hz, J_2 = 1.7 Hz), 6.07 (d, 1H, J = 16.3 Hz), 7.28 - 7.51 (m, 5H) ppm; ^{13}C NMR (176 MHz, δ, $CDCl_3$, 298 K): 23.5, 25.5, 54.7, 60.1, 64.8, 71.8, 97.5, 126.8, 128.5, 129.5, 140.5, 161.0 ppm; IR (film): $\tilde{\nu}$ = 3011, 2987, 2937, 2882, 1654, 1434, 1412, 1378, 1351, 1237, 1204, 1133, 1064, 1048, 923, 896, 843, 703, 664, 604, 579, 563, 517, 501 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{16}H_{25}N_2O_2^+$: 277.1910 $[M]^+$; found: 277.1904.

3. Syntheses of Epoxides Using Amide 6C:



General Procedure: Ammonium salt **6C** was dissolved in the appropriate solvent (20 mL/mmol ammonium salt) and Cs_2CO_3 (20 eq.) was added to the reaction mixture. After 5 min the aldehyde (2 eq) was added and the suspension was stirred for the indicated time at the given temperature. The reaction was quenched with water and extracted with toluene. The organic phase was washed with brine and dried with anhydrous Na_2SO_4, filtrated and the solvent was removed under reduced pressure. The epoxide was purified by column chromatography (silica gel, heptanes:EtOAc = 7:3).

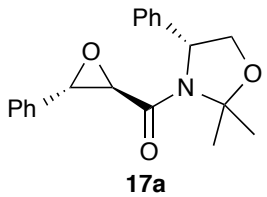
Cond. A: *i*-PrOH, 24 h, 25 °C

Cond. B: toluene, 24 h, 60 °C

Cond. C: toluene, 72 h, 25 °C

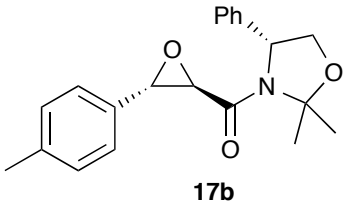
Cond. D: toluene, 24 h, 25 °C

***trans*-epoxide 17a.** Obtained in 78% (1 mmol scale) as a white solid after column chromatography (Cond. A). M.p.: 174 - 177 °C; $[\alpha]_D^{22}$ (c = 1.4, DCM) = -178; ^{1}H NMR (700 MHz, δ, $CDCl_3$, 298 K): 1.72 (s, 3H), 1.88 (s, 3H), 3.22 (d, 1H, J = 1.8 Hz), 3.68 (d, 1H, J = 1.8 Hz), 3.90 (dd, 1H, J_1 = 9.2 Hz, J_2 = 4.2 Hz), 4.41 (dd, 1H, J_1 = 9.2 Hz, J_2 = 6.6 Hz), 5.10 (dd, 1H, J_1 = 6.6 Hz, J_2 = 4.2 Hz), 6.78 (m, 2H), 7. 00 - 7.20 (m, 8H) ppm; ^{13}C NMR (176 MHz, δ, $CDCl_3$, 298 K): 24.3, 25.1, 58.4, 58.9, 61.5, 72.1, 97.3, 125.9, 126.1, 128.4,



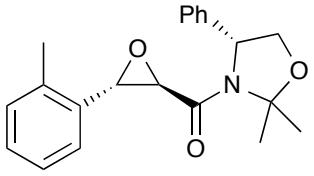
128.5, 128.7, 129.4, 135.3, 140.6, 164.2 ppm; IR (film): $\tilde{\nu}$ = 3032, 2989, 2933, 2873, 1658, 1458, 1437, 1387, 1363, 1252, 1205, 1081, 1066, 894, 849, 772, 749, 695, 660, 596, 552, 513 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{20}H_{21}NO_3$: 324.1594 $[M + H]^+$; found: 324.1595.

***trans*-epoxide 17b.** Obtained in 80% (0.28 mmol scale) as a white solid after column chromatography (Cond. A). M.p.: 139 - 141 °C; $[\alpha]_D^{22}$ (c = 0.6, DCM) = -161; ^{1}H NMR (300 MHz, δ, $CDCl_3$, 298 K): 1.71 (s, 3H), 1.88 (s, 3H), 2.28 (s, 3H), 3.22 (d, 1H, *J* = 1.5 Hz), 3.68 (d, 1H, *J* = 1.5 Hz), 3.90 (dd, 1H, J_1 = 9.0 Hz, J_2 = 4.0 Hz), 4.40 (dd, 1H, J_1 = 9.0 Hz, J_2 = 6.8 Hz), 5.11 (dd, 1H, J_1 = 6.8 Hz, J_2 =4.0 Hz), 6.67 (d, 2H, *J* = 8.1 Hz), 6.95 (m, 2H), 7.10 - 7.21 (m, 5H) ppm; ^{13}C NMR (75 MHz, δ, $CDCl_3$, 298 K): 21.5, 24.3, 25.2, 58.4, 58.6, 61.0, 72.3, 97.7, 125.9, 126.1, 128.3, 129.0, 129.4, 132.3, 138.5, 140.7, 164.5 ppm; IR (film): $\tilde{\nu}$ = 2981, 2934, 2865, 2873, 1619, 1444, 1415, 1378, 1361, 1321, 1305, 1289, 1255, 1205, 1168, 1141, 1076, 1064, 1056, 891, 849, 830, 796, 772, 697, 683, 664, 603, 553, 522, 513, 492 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{21}H_{23}NO_3$: 338.1751 $[M + H]^+$; found: 338.1757.



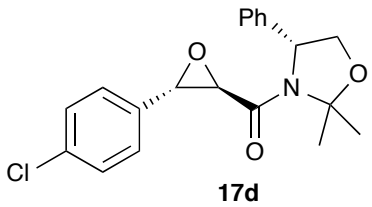
17b

***trans*-epoxide 17c.** Obtained in 79% (0.15 mmol scale) as a colourless residue after column chromatography (Cond. A). M.p.: 94 - 97 °C; $[\alpha]_D^{22}$ (c = 1.0, DCM) = -32; ^{1}H NMR (300 MHz, δ, $CDCl_3$, 298 K): 1.71 (s, 3H), 1.91 (s, 3H), 2.08 (s, 3H), 3.21 (d, 1H, *J* = 1.4 Hz), 3.95 (dd, 1H, J_1 = 9.0 Hz, J_2 = 3.3 Hz), 3.98 (d, 1H, *J* = 1.4 Hz), 4.43 (dd, 1H, J_1 = 9.0 Hz, J_2 = 6.2 Hz), 5.16 (dd, 1H, J_1 = 6.2 Hz, J_2 =3.3 Hz), 6.60 (d, 1H, *J* = 7.9 Hz), 6.97 - 7.00 (m, 2H), 7.06 - 7.25 (m, 6H) ppm; ^{13}C NMR (75 MHz, δ, $CDCl_3$, 298 K): 19.0, 24.0, 25.4, 56.7, 57.5, 61.4, 72.0, 97.3, 124.4, 126.0, 126.3, 128.3, 128.4, 129.5, 130.1, 133.7, 137.1, 141.2, 164.9 ppm; IR (film): $\tilde{\nu}$ = 3026, 2936, 1646, 1436, 1389, 1376, 1364, 1316, 1239, 1064, 1043, 892, 843, 765, 706, 655, 609, 587, 564, 523 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{21}H_{23}NO_3$: 338.1751 $[M + H]^+$; found: 338.1756.



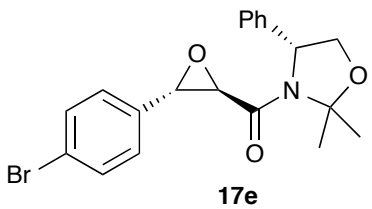
17c

***trans*-epoxide 17d.** Obtained in 75% (0.3 mmol scale) as a colourless residue after column chromatography (Cond. A). M.p.: 133 - 136 °C; $[\alpha]_D^{22}$ (c = 1.8, DCM) = -119; ^{1}H NMR (300 MHz, δ, $CDCl_3$, 298 K): 1.70 (s, 3H), 1.87 (s, 3H), 3.17 (d, 1H, J = 1.4 Hz), 3.62 (d, 1H, J = 1.4 Hz), 3.85 (dd, 1H, J_1 = 9.2 Hz, J_2 = 4.2 Hz), 4.40 (dd, 1H, J_1 = 9.2 Hz, J_2 = 6.8 Hz), 5.08 (dd, 1H, J_1 = 6.8 Hz, J_2 = 4.2 Hz), 6.70 (d, 2H, J = 8.3 Hz), 7.05 - 7.16 (m, 7H) ppm; ^{13}C NMR (75 MHz, δ, $CDCl_3$, 298 K): 24.4, 25.1, 57.6, 58.8, 62.3, 72.2, 97.3, 126.1, 127.2, 128.5, 128.6, 129.5, 133.9, 134.6, 140.6, 164.2 ppm; IR (film): $\tilde{\nu}$ = 2981, 2937, 2863, 2384, 2349, 2307, 1657, 1600, 1495, 1445, 1412, 1377, 1362, 1247, 1320, 1303, 1255, 1205, 1166, 1141, 1077, 1064, 1013, 891, 848, 833, 791, 770, 758, 731, 699, 665, 655, 553 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{20}H_{20}ClNO_3$: 358.1204 $[M + H]^+$; found: 358.1209.



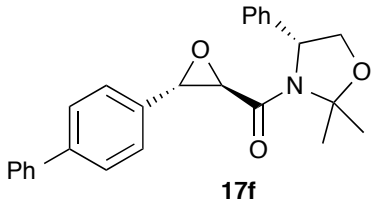
17d

***trans*-epoxide 17e.** Obtained in 85% (0.6 mmol scale) as a slightly yellowish solid after column chromatography (Cond. A). M.p.: 258 - 260 °C; $[\alpha]_D^{22}$ (c = 0.5, DCM) = -75; ^{1}H NMR (300 MHz, δ, $CDCl_3$, 298 K): 1.70 (s, 3H), 1.88 (s, 3H), 3.17 (d, 1H, J = 1.3 Hz), 3.61 (d, 1H, J = 1.3 Hz), 3.88 (dd, 1H, J_1 = 9.1 Hz, J_2 = 4.2 Hz), 4.41 (dd, 1H, J_1 = 9.1 Hz, J_2 = 6.8 Hz), 5.08 (dd, 1H, J_1 = 6.8 Hz, J_2 = 4.2 Hz), 6.63 (d, 2H, J = 7.8 Hz), 7.05 - 7.31 (m, 7H) ppm; ^{13}C NMR (75 MHz, δ, $CDCl_3$, 298 K): 24.3, 25.1, 57.6, 58.8, 61.4, 72.2, 97.4, 122.6, 126.1, 127.5, 128.6, 129.5, 131.5, 134.4, 140.7, 164.2 ppm; IR (film): $\tilde{\nu}$ = 2982, 2934, 2862, 2655, 1594, 1489, 1444, 1408, 1377, 1360, 1319, 1253, 1205, 1166, 1139, 1066, 1010, 971, 935, 889, 845, 831, 804, 789, 768, 757, 723, 699, 664, 638, 562, 553 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{20}H_{20}BrNO_3$: 402.0699 $[M + H]^+$; found: 402.0702.



17e

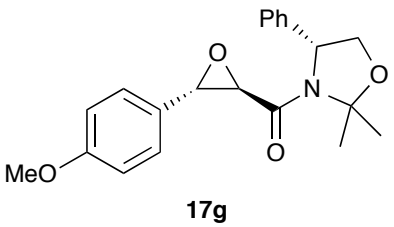
***trans*-epoxide 17f.** Obtained in 89% (0.25 mmol scale) as a white solid after column chromatography (Cond. A). M.p.: 140 - 143 °C; $[\alpha]_D^{22}$ (c = 0.6, DCM) = -11; ^{1}H NMR (700 MHz, δ, $CDCl_3$, 298 K): 1.72 (s, 3H), 1.90 (s, 3H), 3.26 (d, 1H, J = 1.8 Hz), 3.72 (d, 1H, J = 1.8 Hz), 3.90 (dd, 1H, J_1 = 9.2 Hz, J_2 = 4.2 Hz), 4.42 (dd, 1H, J_1 = 9.2 Hz, J_2 = 6.9 Hz), 5.12 (dd, 1H, J_1 = 6.9 Hz, J_2 = 4.2 Hz), 6.84 - 6.68 (m, 2H), 7.05 - 7.82 (m, 12H) ppm; ^{13}C NMR (176 MHz, δ, $CDCl_3$, 298 K): 24.6, 25.3, 58.3, 58.9, 61.5, 72.2, 97.2, 126.2, 126.3, 127.1, 127.3, 127.8, 128.5, 129.2, 129.5, 134.8, 140.6, 140.9, 141.7, 164.5



17f

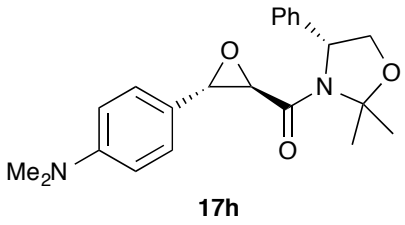
ppm; IR (film): $\tilde{\nu}$ = 3029, 2970, 2928, 2876, 1656, 1442, 1411, 1377, 1362, 1324, 1253, 1201, 1136, 1066, 893, 851, 772, 759, 743, 696, 662, 563, 549, 515 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{26}H_{25}NO_3$: 400.1907 $[M + H]^+$; found: 400.1907.

***trans*-epoxide 17g.** Obtained in 73% (0.5 mmol scale) as a yellowish residue after column chromatography (Cond. A, compound **17g** partially decomposes during silica gel column chromatography). $[\alpha]_D^{22}$ (c = 1.0, DCM) = -132; ^{1}H NMR (300 MHz, δ, $CDCl_3$, 298 K): 1.71 (s, 3H), 1.87 (s, 3H), 3.22 (d, 1H, *J* = 1.4 Hz), 3.62 (d, 1H, *J* = 1.4 Hz), 3.82 (s, 3H), 3.88 (dd, 1H, J_1 = 9.1 Hz, J_2 = 4.0 Hz), 4.39 (dd, 1H, J_1 = 9.1 Hz, J_2 = 6.8 Hz), 5.10 (dd, 1H, J_1 = 6.8 Hz, J_2 = 4.0 Hz), 6.62 - 6.74 (m, 4H), 7.02 - 7.20 (m, 5H) ppm; ^{13}C NMR (75 MHz, δ, $CDCl_3$, 298 K): 24.3, 25.3, 56.0, 58.0, 58.2, 61.2, 71.6, 97.2, 114.1, 126.1, 127.1, 127.2, 128.4, 129.6, 140.7, 160.1, 164.8 ppm; IR (film): $\tilde{\nu}$ = 2976, 2935, 2862, 2838, 1655, 1612, 1515, 1442, 1420, 1386, 1377, 1362, 1322, 1247, 1205, 1175, 1138, 1079, 1064, 1032, 892, 848, 833, 800, 772, 754, 698, 680, 661, 570, 552, 514 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{21}H_{23}NO_4$: 354.1700 $[M + H]^+$; found: 354.1707.



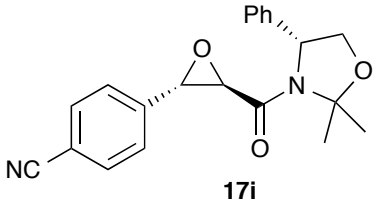
17g

***trans*-epoxide 17h.** Obtained in 60% (0.4 mmol scale) crude yield (Cond. B, compound **17h** fully decomposes during silica gel column chromatography). ^{1}H NMR (700 MHz, δ, $CDCl_3$, 298 K): 1.69 (s, 3H), 1.87 (s, 3H), 2.89 (s, 6H), 3.26 (d, 1H, *J* = 1.9 Hz), 3.63 (d, 1H, *J* = 1.9 Hz), 3.90 (dd, 1H, J_1 = 9.0 Hz, J_2 = 3.8 Hz), 4.40 (dd, 1H, J_1 = 9.0 Hz, J_2 = 6.9 Hz), 5.10 (dd, 1H, J_1 = 6.9 Hz, J_2 = 3.8 Hz), 6.48 (m, 2H), 6.65 (m, 2H), 7.05 - 7.36 (m, 5H) ppm; ^{13}C NMR (75 MHz, δ, $CDCl_3$, 298 K): 24.3, 24.9, 40.8, 58.4, 58.7, 61.2, 72.3, 97.3, 112.4, 125.5, 126.2, 126.4, 127.8, 129.4, 140.8, 150.1, 165.4 ppm; HRMS (ESI): *m/z* calcd for $C_{22}H_{26}N_2O_3$: 367.2016 $[M + H]^+$; found: 367.2019.



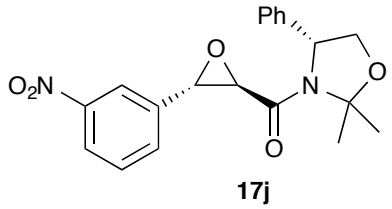
17h

***trans*-epoxide 17i.** Obtained in 62% (0.45 mmol scale) as a slightly yellowish residue after column chromatography (Cond. C). M.p.: 85 - 88 °C; $[\alpha]_D^{22}$ (c = 0.5, DCM) = -113; ^{1}H NMR (300 MHz, δ, $CDCl_3$, 298 K): 1.71 (s, 3H), 1.88 (s, 3H), 3.16 (d, 1H, J = 1.7 Hz), 3.69 (d, 1H, J = 1.7 Hz), 3.87 (dd, 1H, J_1 = 9.3 Hz, J_2 = 4.4 Hz), 4.42 (dd, 1H, J_1 = 9.3 Hz, J_2 = 6.8 Hz), 5.07 (dd, 1H, J_1 = 6.8 Hz, J_2 = 4.4 Hz), 6.97 (m, 2H), 7.11 (m, 5H), 7.44 (m, 2H) ppm; ^{13}C NMR (75 MHz, δ, $CDCl_3$, 298 K): 24.4, 25.2, 57.5, 59.0, 61.5, 72.2, 97.5, 112.7, 119.0, 126.1, 126.4, 128.6, 129.5, 132.2, 140.6, 140.8, 165.6 ppm; IR (film): $\tilde{\nu}$ = 3093, 3046, 2857, 2744, 2229, 1702, 1658, 1607, 1571, 1416, 1383, 1361, 1309, 1295, 1251, 1201, 1171, 1139, 1071, 1016, 893, 828, 772, 736, 705, 643, 562, 545 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{21}H_{20}N_2O_3$: 349.1547 $[M + H]^+$; found: 349.1552.



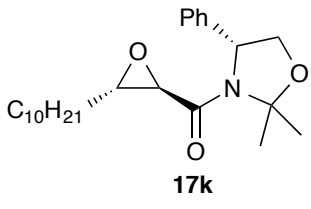
17i

***trans*-epoxide 17j.** Obtained in 68% (0.5 mmol scale) as a yellow solid after column chromatography (Cond. C). M.p.: 117 - 120 °C; $[\alpha]_D^{22}$ (c = 0.4, DCM) = -183; ^{1}H NMR (300 MHz, δ, $CDCl_3$, 298 K): 1.72 (s, 3H), 1.89 (s, 3H), 3.20 (d, 1H, J = 1.8 Hz), 3.72 (d, 1H, J = 1.8 Hz), 3.87 (dd, 1H, J_1 = 9.2 Hz, J_2 = 4.6 Hz), 4.42 (dd, 1H, J_1 = 9.2 Hz, J_2 = 6.8 Hz), 5.07 (dd, 1H, J_1 = 6.8 Hz, J_2 = 4.6 Hz), 6.96 - 7.17 (m, 6H), 7.35 (m, 1H), 7.58 (m, 1H), 8.10 (m, 1H) ppm; ^{13}C NMR (75 MHz, δ, $CDCl_3$, 298 K): 24.5, 25.1, 57.1, 59.1, 61.6, 72.3, 97.5, 121.0, 123.6, 126.1, 128.5, 129.5, 129.6, 131.5, 137.7, 140.2, 148.3, 163.5 ppm; IR (film): $\tilde{\nu}$ = 2986, 2934, 2877, 1659, 1651, 1528, 1454, 1433, 1378, 1349, 1305, 1252, 1203, 1167, 1138, 1064, 889, 847, 802, 775, 735, 700, 677, 610, 565, 552, 515 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{20}H_{20}N_2O_5$: 369.1445 $[M + H]^+$; found: 369.1449.



17j

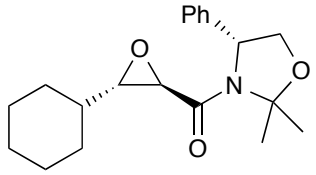
***trans*-epoxide 17k.** Obtained in 42% (0.4 mmol scale) as a colourless hygroscopic residue after column chromatography (Cond. D). $[\alpha]_D^{22}$ (c = 0.5, DCM) = -68; ^{1}H NMR (300 MHz, δ, $CDCl_3$, 298 K): 0.81 - 1.36 (m, 21H), 1.67 (s, 3H), 1.85 (s, 3H), 2.83 (dt, 1H, J_1 = 5.6 Hz, J_2 = 2.1 Hz), 2.93 (d, 1H, J = 2.1 Hz), 3.91 (dd, 1H, J_1 = 9.1 Hz, J_2 = 3.9 Hz), 4.42 (dd, 1H, J_1 = 9.1 Hz, J_2 = 6.8 Hz), 5.15 (dd, 1H, J_1 = 6.8 Hz, J_2 = 3.9 Hz), 7.24 - 7.32 (m, 5H) ppm; ^{13}C NMR (75 MHz, δ, $CDCl_3$, 298 K): 14.5, 23.0, 24.1, 25.2, 25.5, 29.5, 29.6, 29.8 (2x), 29.9, 31.1, 32.2, 54.5, 59.2, 61.4, 71.8, 97.5, 126.3, 128.5, 129.6, 141.5, 165.8



17k

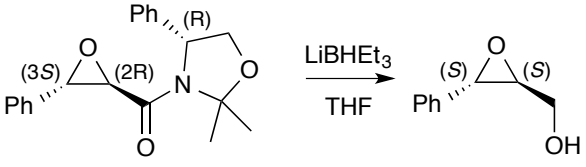
ppm; IR (film): $\tilde{\nu}$ = 2923, 2853, 1657, 1450, 1399, 1376, 1363, 1253, 1204, 1169, 1140, 1067, 904, 848, 758, 700, 664, 518 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{24}H_{37}NO_3$: 388.2846 $[M + H]^+$; found: 388.2847.

***trans*-epoxide 17l.** Obtained in 39% (0.5 mmol scale) as a colourless residue after column chromatography (Cond. D). M.p.: 63 - 65 °C; $[\alpha]_D^{22}$ (c = 0.6, DCM) = -76; ^{1}H NMR (300 MHz, δ, $CDCl_3$, 298 K): 0.46 - 1.63 (m, 11H), 1.66 (s, 3H), 1.86 (s, 3H), 2.76 (dd, 1H, J_1 = 5.5 Hz, J_2 = 1.9 Hz), 3.04 (d, 1H, J = 1.9 Hz), 3.91 (dd, 1H, J_1 = 9.1 Hz, J_2 = 3.3 Hz), 4.42 (dd, 1H, J_1 = 9.1 Hz, J_2 = 6.4 Hz), 5.16 (dd, 1H, J_1 = 6.4 Hz, J_2 = 3.3 Hz), 7.25 - 7.42 (m, 5H) ppm; ^{13}C NMR (75 MHz, δ, $CDCl_3$, 298 K): 24.0, 25.2, 25.7, 25.8, 26.3, 28.3, 28.8, 38.9, 52.3, 61.6, 63.3, 71.9, 97.3, 126.3, 128.5, 129.4, 141.9, 166.1 ppm; IR (film): $\tilde{\nu}$ = 2984, 2926, 2850, 1644, 1444, 1395, 1374, 1362, 1339, 1314, 1283, 1247, 1235, 1205, 1164, 1132, 1064, 974, 900, 885, 844, 772, 703, 660, 578, 564, 514 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{20}H_{27}NO_3$: 320.2064 $[M + H]^+$; found: 320.2070.



17l

4. Reduction of Epoxide 17a:



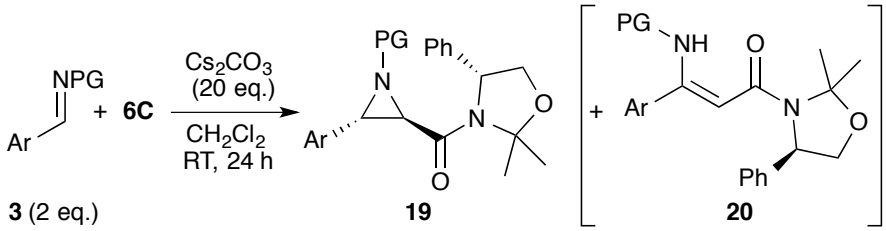
17a **18**

In analogy to literature,[4] **17a** (130 mg, 0.4 mmol) was dissolved in 5 mL THF. Then $LiBHEt_3$ (1.0 mL, 1 mmol, 1 M THF, 2.5 eq.) was added to the mixture and stirred for 35 min. The reaction was quenched with aqueous NH_4Cl solution followed by the extraction with Et_2O and brine. The organic phase was dried with anhydrous Na_2SO_4, filtrated, and the solvent removed under reduced pressure. Epoxyalcohol **18** (32 mg, 0.21 mmol) was obtained after column chromatography (silica gel, heptanes: EtOAc = 8:2 → 1:1) as a colourless oil in 53% non-optimized yield. Analytical data are in accordance to literature.[5] $[\alpha]_D^{20}$ (c = 1.0, DCM) = -57; ^{1}H-NMR (300 MHz, δ, $CDCl_3$, 298 K): 1.80 (br, 1H), 3.10 (m, 1H), 3.76 (dd, 1H, J_1 =

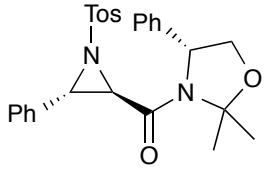
[4] F. Sarabia, C. Vivar-Garcia, M. Garcia-Castro and J. Martin-Ortiz, *J. Org. Chem.* 2011, **76**, 3139-3150.
[5] a) S. K., Cherian and P. Kumar, *Tetrahedron: Asymmetry*. 2007, **18**, 982-987; b) F. Sarabia, S. Chammaa, M. Garica-Castro and F. Martin-Galvez, *Chem. Commun.*, 2009, 5763-5765; c) P. G. Gordillo, D. M. Aparicio, M. Flores, A. Mendoza, L. Orea, J. R. Juarez, G. Huelgas, D. Gnecco and J. L. Teran, *Eur. J. Org. Chem.,* 2013, 5561-5565.

12.7 Hz, J_2 = 3.9 Hz), 3.93 (d, 1H, J = 1.8 Hz), 3.98 (dd, 1H, J_1 = 12.7 Hz, J_2 = 2.2 Hz), 7.20 - 7.42 (m, 5H) ppm.

5. Syntheses of Aziridines Using Amide 6C:

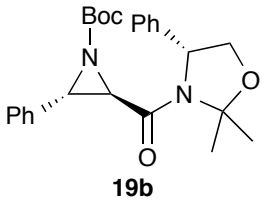


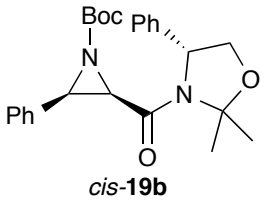
General procedure for the preparation of aziridines: A mixture of **6C** (0.4 mmol), aldimine **3** (2 eq.), and 20 equivalents of solid Cs_2CO_3 in CH_2Cl_2 (8 mL) was vigorously stirred for 24 h at room temperature. CH_2Cl_2 and brine were added and the phases separated. The aqueous layer was extracted twice with CH_2Cl_2, the combined organic layers were extracted with brine and the aqueous layer was re-extracted twice with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtrated, evaporated, and dried *in vacuo*. Column chromatography (silica gel, heptanes/EtOAc = 20:1 – 2:1) gave the aziridines 1**9** in the reported yields. In most cases the minor *cis*-isomers and the olefins **20** could not be obtained in pure form.

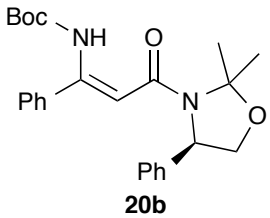


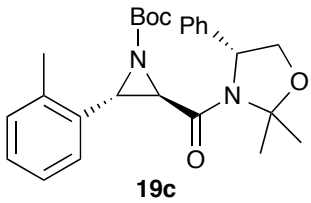
19a

***trans*-N-tosyl aziridine 19a.** Obtained in 39% as a colourless oil after column chromatography (crude NMR yield 70%). $[\alpha]_D^{23}$ (c = 1.2, DCM) = -78; ^{1}H NMR (300 MHz, δ, $CDCl_3$, 298 K): 1.76 (s, 3H), 1.95 (s, 3H), 2.42 (s, 3H), 3.21 (d, 1H, J = 4.1 Hz), 4.03 (dd, 1H, J = 8.9, 1.6 Hz), 4.44 (d, 1H, J = 4.1 Hz), 4.53 (dd, 1H, J = 8.9, 6.3 Hz), 5.56 (dd, 1H, J = 6.3, 1.6 Hz), 6.85 – 6.93 (m, 2H), 7.21 – 7.48 (m, 10H), 7.77 – 7.85 (m, 2H) ppm; ^{13}C NMR (75 MHz, δ, $CDCl_3$, 298 K): 21.6, 22.3, 25.4, 47.1, 49.5, 61.2, 71.5, 96.9, 126.2, 126.9, 127.6, 128.1, 128.3, 128.4, 129.2, 129.7, 132.9, 136.5, 141.3, 144.6, 161.4 ppm; IR (film): $\tilde{\nu}$ = 2970, 1662, 1432, 1378, 1329, 1238, 1204, 1159, 1085, 1063, 929, 812, 756, 695, 579 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{27}H_{28}N_2O_4S$: 477.1843 $[M + H]^+$; found: 477.1834.

***trans*-N-Boc aziridine 19b.** Obtained in 62% as a colourless residue. M.p.: 136 - 139 °C; 
19b
$[\alpha]_D^{23}$ (c = 1.6, DCM) = -110; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 1.48 (s, 9H), 1.73 (s, 3H), 1.89 (s, 3H), 2.87 (d, 1H, *J* = 2.5 Hz), 3.69 (d, 1H, *J* = 2.5 Hz), 3.96 (dd, 1H, *J* = 9.1, 3.5 Hz), 4.47 (dd, 1H, *J* = 9.1, 6.8 Hz), 5.28 (dd, 1H, *J* = 6.8, 3.5 Hz), 6.88 (d, 2H, *J* = 6.9 Hz), 7.19 – 7.28 (m, 8H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 23.8, 25.0, 28.0, 44.5, 44.8, 61.5, 71.6, 81.7, 96.8, 125.7, 126.5, 127.7, 128.0, 128.1, 129.1, 135.3, 140.9, 159.2, 163.7 ppm; IR (film): $\tilde{\nu}$ = 3009, 2984, 2935, 2868, 1715, 1652, 1433, 1395, 1364, 1333, 1253, 1223, 1204, 1074, 1053, 819, 755, 746, 705, 691, 635 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{25}H_{30}N_2O_4$: 423.2278 $[M + H]^+$; found: 423.2287.

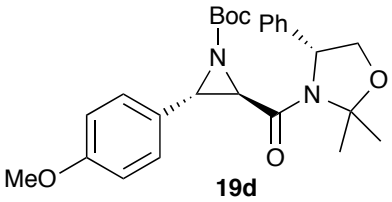
***cis*-N-Boc aziridine 19b.** Obtained in trace amounts and lower purity during the isolation of 
cis-**19b**
trans-**19b**. ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): 1.41 (s, 9H), 1.46 (s, 3H), 1.54 (s, 3H), 3.27 (d, 1H, *J* = 6.8 Hz), 3.33 (d, 1H, *J* = 6.8 Hz), 3.87 (dd, 1H, *J* = 8.9, 2.4 Hz), 4.29 (dd, 1H, *J* = 8.9, 6.5 Hz), 5.29 (dd, 1H, *J* = 6.5, 2.4 Hz), 7.02 – 7.09 (m, 2H), 7.18 – 7.25 (m, 4H), 7.34 – 7.40 (m, 4H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 22.9, 25.1, 27.8, 44.5, 45.6, 60.8, 71.6, 82.1, 96.8, 126.4, 127.6, 127.8, 127.9, 128.0, 129.0, 132.9, 141.7, 161.0, 162.1 ppm; HRMS (ESI): *m/z* calcd for $C_{25}H_{30}N_2O_4$: 423.2278 $[M + H]^+$; found: 423.2282.

Olefine 20b. Obtained in minor amounts during the isolation of *trans*-**19b**. ^{1}H NMR (700 
20b
MHz, δ, $CDCl_3$, 298 K): 1.34 (s, 9H), 1.72 (s, 3H), 1.91 (s, 3H), 3.91 (dd, 1H, *J* = 8.9, 3.2 Hz), 4.37 (dd, 1H, *J* = 8.9, 6.7 Hz), 4.86 (s, 1H), 4.91 (dd, 1H, *J* = 6.7, 3.2 Hz), 6.97 (d, 2H, *J* = 7.3 Hz), 7.21 (t, 2H, *J* = 7.8 Hz), 7.27 - 7.34 (m, 4H), 7.36 – 7.41 (m, 2H), 10.84 (s, 1H) ppm; ^{13}C NMR (176 MHz, δ, $CDCl_3$, 298 K): 23.9, 25.8, 28.2, 61.9, 71.6, 80.9, 96.4, 101.6, 126.3, 127.2, 127.8, 128.1, 129.1, 129.2, 137.3, 141.4, 152.2, 152.9, 166.1 ppm; HRMS (ESI): *m/z* calcd for $C_{25}H_{30}N_2O_4$: 423.2278 $[M + H]^+$; found: 423.2284.

***trans*-N-Boc aziridine 19c.** Obtained in 63% as a mixture of *trans* and *cis*-aziridine (7.5:1). 
19c
$[\alpha]_D^{23}$ (c = 2.6, DCM) = -99; ^{1}H NMR (500 MHz, δ, $CDCl_3$, 298 K): *major-trans*: 1.46 (s, 9H), 1.74 (s, 3H), 1.92 (s, 3H), 2.21 (s, 3H), 2.94 (d, 1H, *J* = 2.2 Hz), 3.86 (d, 1H, *J* = 2.2 Hz), 4.00 (dd, 1H, *J* = 8.9, 2.1 Hz), 4.49 (dd, 1H, *J* = 8.9, 6.8 Hz), 5.31 (dd, 1H,

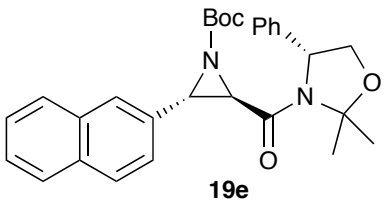
J = 6.8, 2.1 Hz), 6.53 (d, 1H, J = 7.5 Hz), 6.90 – 6.95 (m, 1H), 7.00 – 7.10 (m, 1H), 7.12 – 7.40 (m, 6H) ppm; ^{13}C NMR (125 MHz, δ, $CDCl_3$, 298 K): 18.9, 23.5, 25.2, 27.9, 43.2, 43.4, 61.4, 71.5, 81.7, 96.8, 125.6, 125.8, 125.9, 127.7, 128.0, 129.2, 129.7, 133.4, 137.4, 141.5, 159.5, 163.9 ppm; IR (film): $\bar{\nu}$ = 2979, 2934, 1725, 1652, 1429, 1390, 1365, 1328, 1305, 1284, 1249, 1205, 1151, 1083, 1069, 1050, 814, 765, 753, 703 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{26}H_{32}N_2O_4$: 437.2435 $[M + H]^+$; found: 437.2433.

***trans*-N-Boc aziridine 19d.** Obtained in 57% after neutral alumina column chromatography (**19d** is relatively unstable and quickly decomposed at higher temperature or under more acidic conditions). $[\alpha]_D^{23}$ (c = 1.5, DCM) = -96; ^{1}H NMR (300 MHz, δ, $CDCl_3$, 298 K): 1.37 (s, 9H), 1.64 (s, 3H), 1.79 (s, 3H), 2.76 (d, 1H, J = 2.6 Hz), 3.56 (d, 1H, J = 2.6 Hz), 3.67 (s, 3H), 3.87 (dd, 1H, J = 8.9, 3.4 Hz), 4.37 (dd, 1H, J = 8.9, 6.7 Hz), 5.19 (dd, 1H, J = 6.7, 3.4 Hz), 6.58 (d, 2H, J = 8.6 Hz), 6.69 (d, 2H, J = 8.6 Hz), 7.05 – 7.18 (m, 5H) ppm; ^{13}C NMR (75 MHz, δ, $CDCl_3$, 298 K): 23.8, 25.0, 27.9, 44.2, 44.6, 52.2, 61.5, 81.6, 96.8, 113.5, 125.8, 127.4, 127.7, 128.0, 129.1, 141.0, 159.2, 159.3, 163.9 ppm; IR (film): $\bar{\nu}$ = 2933, 1713, 1651, 1518, 1420, 1398, 1365, 1289, 1155, 1080, 1064, 1033, 815, 752, 703, 619 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{26}H_{32}N_2O_5$: 453.2384 $[M + H]^+$; found: 453.2383.



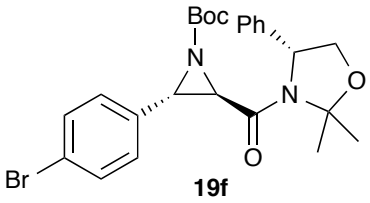
19d

***trans*-N-Boc aziridine 19e.** Obtained in 58% as a colourless hygroscopic residue (containing some co-eluting starting imine-based impurities). $[\alpha]_D^{23}$ (c = 0.2, DCM) = -93; ^{1}H NMR (300 MHz, δ, $CDCl_3$, 298 K): 1.49 (s, 9H), 1.75 (s, 3H), 1.91 (s, 3H), 2.97 (d, 1H, J = 2.6 Hz), 3.84 (d, 1H, J = 2.6 Hz), 3.96 (dd, 1H, J = 9.0, 3.6 Hz), 4.47 (dd, 1H, J = 9.0, 6.8 Hz), 5.29 (dd, 1H, J = 6.8, 3.6 Hz), 6.96 – 7.03 (m, 2H), 7.11 – 7.25 (m, 3H), 7.32 (s, 1H), 7.41 – 7.79 (m, 6H) ppm; ^{13}C NMR (75 MHz, δ, $CDCl_3$, 298 K): 23.9, 25.0, 28.0, 44.7, 44.9, 61.5, 71.6, 81.8, 96.8, 124.0, 125.7, 125.8, 125.9, 126.1, 127.6, 127.7, 127.8, 128.0, 128.1, 129.1, 132.9, 133.0, 140.9, 159.3, 164.0 ppm; IR (film): $\bar{\nu}$ = 2970, 2929, 1725, 1651, 1435, 1324, 1249, 1148, 1050, 815, 753, 702 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{32}N_2O_4$: 473.2435 $[M + H]^+$; found: 473.2429.



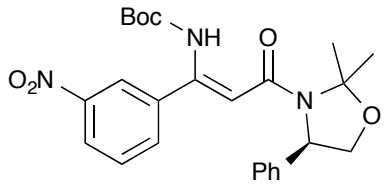
19e

***trans*-N-Boc aziridine 19f.** Obtained in 32% as a colourless solid (Olefine **20f** could not be isolated in pure form due to co-elution of different impurities and starting imine decomposition products). M.p.: 149 - 151 °C; $[\alpha]_D^{23}$ (c = 1.1, DCM) = -99; ^{1}H NMR (700 MHz, δ, $CDCl_3$, 298 K): 1.46 (s, 9H), 1.70 (s, 3H), 1.85 (s, 3H), 2.75 (d, 1H, *J* = 2.5 Hz), 3.56 (d, 1H, *J* = 2.5 Hz), 3.92 (dd, 1H, *J* = 9.1, 3.8 Hz), 4.43 (dd, 1H, *J* = 9.1, 6.8 Hz), 5.21 (dd, 1H, *J* = 6.8, 3.8 Hz), 6.70 (d, 2H, *J* = 8.3 Hz), 7.10 – 7.14 (m, 1H), 7.18 – 7.23 (m, 6H) ppm; ^{13}C NMR (176 MHz, δ, $CDCl_3$, 298 K): 24.1, 25.0, 28.1, 43.9, 45.3, 61.8, 71.8, 82.1, 97.0, 121.8, 125.9, 127.8, 128.2, 128.3, 129.4, 131.3, 131.8, 134.8, 140.9, 159.2, 163.5 ppm; IR (film): $\tilde{\nu}$ = 2981, 2970, 1717, 1654, 1438, 1412, 1387, 1365, 1295, 1250, 1155, 1073, 1012, 873, 850, 806, 729, 705, 656 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{25}H_{29}BrN_2O_4$: 501.1383 $[M + H]^+$; found: 501.1376.



19f

Olefine 20g. Obtained in around 50% containing some co-eluting impurities that could not be separated. ^{1}H NMR (300 MHz, δ, $CDCl_3$, 298 K): 1.38 (s, 9H), 1.76 (s, 3H), 1.94 (s, 3H), 3.96 (dd, 1H, *J* = 9.0, 3.7 Hz), 4.42 (dd, 1H, *J* = 9.0, 6.7 Hz), 4.93 (s, 1H), 4.94 (dd, 1H, *J* = 6.7, 3.7 Hz), 7.30 – 7.48 (m, 7H), 7.75 – 7.82 (m, 1H), 8.13 – 8.21 (m, 1H), 10.92 (s, 1H) ppm; ^{13}C NMR (75 MHz, δ, $CDCl_3$, 298 K): 23.9, 25.4, 28.0, 61.9, 71.4, 81.5, 96.3, 102.9, 121.9, 123.7, 126.1, 128.3, 128.5, 129.3, 133.1, 138.7, 140.8, 147.8, 149.8, 152.0, 165.3 ppm; IR (film): $\tilde{\nu}$ = 2979, 2934, 2874, 1731, 1614, 1529, 1487, 1390, 1348, 1247, 1224, 1203, 1147, 1069, 1049, 836, 806, 735, 700, 666 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{25}H_{29}N_3O_6$: 468.2129 $[M + H]^+$; found: 468.2124.



20g

6. DFT Calculations:

Energies and geometries

All geometries (cartesian coordinates in Å) were obtained after geometry optimization at the B3LYP-d3/6-31G*(CH_2Cl_2) level of theory. Energies (in a.u.) were obtained after single point calculations at the indicated level of theory.

Frequency calculations have been carried out at the B3LYP/6-31G*(CH_2Cl_2) level of theory in order to check the correct nature of the point on the potential energy surface and to obtain the thermal and entropic contributions to free energy (at 298.15 K) and zero-point energies.

(*Z*)-Ylide^{Re}

E(B3LYP-d3/6-31G*(CH_2Cl_2)) = -884.058884

E(B3LYP-d3/6-311+G**(CH_2Cl_2)) = -884.304324

G_{tot}(B3LYP-d3/6-31G*(CH_2Cl_2)) = -883.721283

C	2.40502	7.82372	13.76974
H	1.77337	7.50810	12.94133
O	-0.41306	6.11546	18.13832
N	1.85360	6.11952	17.69753
C	3.29982	8.88515	13.60265
C	2.31899	7.16503	14.99629
H	1.62297	6.34286	15.13577
C	3.12165	7.55918	16.07391
C	3.10860	6.79372	17.38563
H	3.42559	7.46666	18.20151
C	4.01016	8.62623	15.90261
H	4.63657	8.94224	16.73615
C	4.10282	9.28486	14.67336
H	4.80204	10.10947	14.5527
C	2.13022	4.80624	18.34157
O	3.57135	4.71168	18.33590
C	4.06211	5.58796	17.33152
C	1.53025	3.66774	17.51384
H	1.75470	2.69646	17.97142
H	1.93980	3.68652	16.49774
H	0.44830	3.80875	17.45726
C	1.71126	4.74211	19.80941
H	2.14404	5.58989	20.35099
H	2.08278	3.81157	20.25348
H	0.62468	4.78087	19.89369
C	0.72954	8.20050	18.08835
C	0.64512	6.81169	17.98597
N	-0.52235	9.01278	18.13940
H	1.57756	8.77940	17.76344
H	-1.50090	7.65998	19.42303
H	-0.64718	8.99605	20.25204
H	-2.20873	9.31975	19.42245
C	-1.28847	8.72784	19.41109
C	-1.41970	8.74133	16.95151
H	-1.66189	7.67928	16.96874
H	-2.32276	9.35494	17.02399
H	-0.85876	8.98831	16.04957
C	-0.14370	10.46694	18.13012
H	-1.04620	11.07501	18.22422
H	0.53232	10.65337	18.96785
H	0.36108	10.69252	17.18832

H	5.10019	5.84597	17.56208
H	4.02331	5.12212	16.33485
H	3.36953	9.39659	12.64492

(*Z*)-Ylide^{Si}

E(B3LYP-d3/6-31G*(CH_2Cl_2)) = -884.054861

E(B3LYP-d3/6-311+G**(CH_2Cl_2)) = -884.301148

G_{tot}(B3LYP-d3/6-31G*(CH_2Cl_2)) = -883.718214

C	2.98382	7.91794	13.74858
H	2.48525	7.63943	12.82166
O	0.86283	7.93826	18.69050
N	1.77007	6.13769	17.45347
C	3.91177	8.96438	13.75665
C	2.69371	7.22756	14.92688
H	1.96831	6.41895	14.93450
C	3.32342	7.57183	16.13001
C	3.08835	6.76633	17.39455
H	3.26797	7.40432	18.27259
C	4.24422	8.62699	16.13156
H	4.73410	8.90797	17.06300
C	4.54123	9.31769	14.95335
H	5.26249	10.13278	14.96970
C	1.89965	4.81895	18.13812
O	3.31732	4.66306	18.37028
C	3.99437	5.52938	17.46639
C	1.41376	3.69770	17.21197
H	1.55438	2.71609	17.68087
H	1.96816	3.72439	16.26759
H	0.35013	3.83586	16.99017
C	1.22322	4.75415	19.50683
H	1.54966	5.59520	20.12381
H	1.48930	3.81403	20.00194
H	0.13641	4.79977	19.39391
C	-0.50314	6.68263	17.19292
C	0.67010	7.01365	17.84312
N	-1.76903	7.42368	17.46759
H	-0.55218	6.01614	16.34698
H	-0.79450	9.27951	17.69117
H	-1.39663	8.94434	16.03968
H	-2.55628	9.41523	17.33126
C	-1.62440	8.88643	17.10507
C	-2.14648	7.31487	18.92705
H	-1.30788	7.70039	19.50555
H	-3.05542	7.89522	19.11330
H	-2.31189	6.25957	19.15086
C	-2.87134	6.82367	16.64149
H	-3.80366	7.35496	16.84943
H	-2.61256	6.92051	15.58388
H	-2.96835	5.76756	16.90337
H	4.99232	5.74015	17.86209
H	4.09551	5.07033	16.47035
H	4.14052	9.50162	12.83822

(*E*)-Ylide^{Re}

E(B3LYP-d3/6-31G*(CH_2Cl_2)) = -884.036428

E(B3LYP-d3/6-311+G**(CH_2Cl_2)) = -884.282907

G_{tot}(B3LYP-d3/6-31G*(CH_2Cl_2)) = -883.695308

C	4.84926	6.66759	14.07569
H	5.56417	5.96809	13.64578
O	0.97095	7.10096	19.43915
N	1.76417	6.15252	17.40489

C	4.42430	7.77579	13.33568
C	4.36726	6.45441	15.36882
H	4.71560	5.59782	15.93769
C	3.44510	7.34134	15.94790
C	2.88779	7.14400	17.35050
H	2.50738	8.10118	17.71160
C	3.04295	8.45861	15.20202
H	2.35103	9.17412	15.64419
C	3.52074	8.67485	13.90596
H	3.19364	9.54988	13.34634
C	2.38640	4.84789	17.82410
O	3.76675	5.15035	18.16162
C	3.88474	6.55887	18.35513
C	2.45850	3.85101	16.65849
H	3.20282	3.08052	16.88753
H	2.74739	4.35597	15.73327
H	1.49684	3.35160	16.50474
C	1.71272	4.19597	19.03491
H	1.78996	4.84073	19.90986
H	2.20511	3.23826	19.23718
H	0.65363	4.00820	18.82975
C	-0.61105	6.67514	17.78958
C	0.68445	6.67250	18.28363
H	3.58829	6.84301	19.37231
H	4.92740	6.83943	18.17369
H	4.80185	7.94078	12.32827
H	-1.38896	7.10637	18.40433
N	-1.07082	6.45793	16.38033
C	-0.44519	7.45265	15.42740
H	0.62979	7.28103	15.43251
H	-0.85301	7.30639	14.42223
H	-0.67186	8.45623	15.79030
C	-0.78164	5.06888	15.87275
H	0.29667	4.95853	15.84012
H	-1.22001	4.35196	16.56929
H	-1.21174	4.95072	14.87379
C	-2.56578	6.65471	16.35152
H	-2.92292	6.49429	15.33199
H	-3.02302	5.93503	17.03268
H	-2.79188	7.67352	16.67235

(*E*)-Ylide^{Si}

E(B3LYP-d3/6-31G*(CH_2Cl_2)) = -884.033835

E(B3LYP-d3/6-311+G**(CH_2Cl_2)) = -884.282209

G_{tot}(B3LYP-d3/6-31G*(CH_2Cl_2)) = -883.695300

C	2.00779	8.24398	14.44598
H	1.15368	8.21149	13.77245
O	-0.24058	5.90651	17.69680
N	2.04936	5.81307	18.09589
C	3.06408	9.12294	14.19204
C	2.03621	7.40440	15.56257
H	1.20408	6.73627	15.76352
C	3.12611	7.43633	16.44126
C	3.26082	6.48244	17.61811
H	3.75595	7.02761	18.43455
C	4.17575	8.33200	16.18888
H	5.02444	8.37117	16.87186
C	4.15049	9.16708	15.07027
H	4.97617	9.85147	14.88533
C	2.16790	4.35342	17.87396
O	3.59368	4.15734	17.93009

C	4.17183	5.27039	17.26040
C	1.63973	3.86791	16.51441
H	1.87191	2.80393	16.38629
H	2.09686	4.42646	15.69180
H	0.56239	4.02816	16.47012
C	1.55368	3.56778	19.02588
H	2.00447	3.88574	19.97098
H	1.72930	2.49512	18.88810
H	0.47665	3.75107	19.05703
C	0.59717	7.56206	19.07324
C	0.76348	6.42561	18.28112
H	5.19871	5.39561	17.61596
H	4.19798	5.11680	16.17298
H	3.03939	9.77265	13.31972
H	-0.38134	8.02096	19.06624
N	1.47926	8.16807	20.11931
C	2.38507	9.24684	19.55858
H	3.03250	8.81079	18.80395
H	1.75058	10.00233	19.09247
H	2.98202	9.69031	20.36244
C	2.28991	7.14082	20.87289
H	2.88215	6.56201	20.17116
H	2.93011	7.65244	21.59643
H	1.59080	6.47382	21.37952
C	0.57878	8.83944	21.13306
H	1.19473	9.29258	21.91455
H	-0.00608	9.60919	20.62471
H	-0.08626	8.08343	21.55343

7. X-Ray Crystallography:

Single-crystal structure analyses were carried out on a Bruker Smart X2S diffractometer operating with Mo-K_α radiation (λ= 0.71073 Å). Further crystallographic and refinement data can be found in Table 1. The structures were solved by direct methods (SHELXS-97)[6] and refined by full-matrix least squares on F^2 (SHELXL-97).[7] The H atoms were calculated geometrically, and a riding model was applied in the refinement process. The Flack parameter for the crystal structure of **17a** is 0.7(13) and hence not suitable for the determination of the absolute configuration. Therefore, the configurations of the three stereogenic carbon atoms were deduced from the known *R*-configuration of the starting material **6C**. The presence of the bromine atom permitted the determination of the absolute configuration of **19f** by refining the Flack parameter [0.002(13)]. The determined configuration is in agreement with the absolute configuration of stereogenic center of the starting material **6**C. The oxygen atoms of the oxazolidine rings of both compounds were found to be disordered over two positions

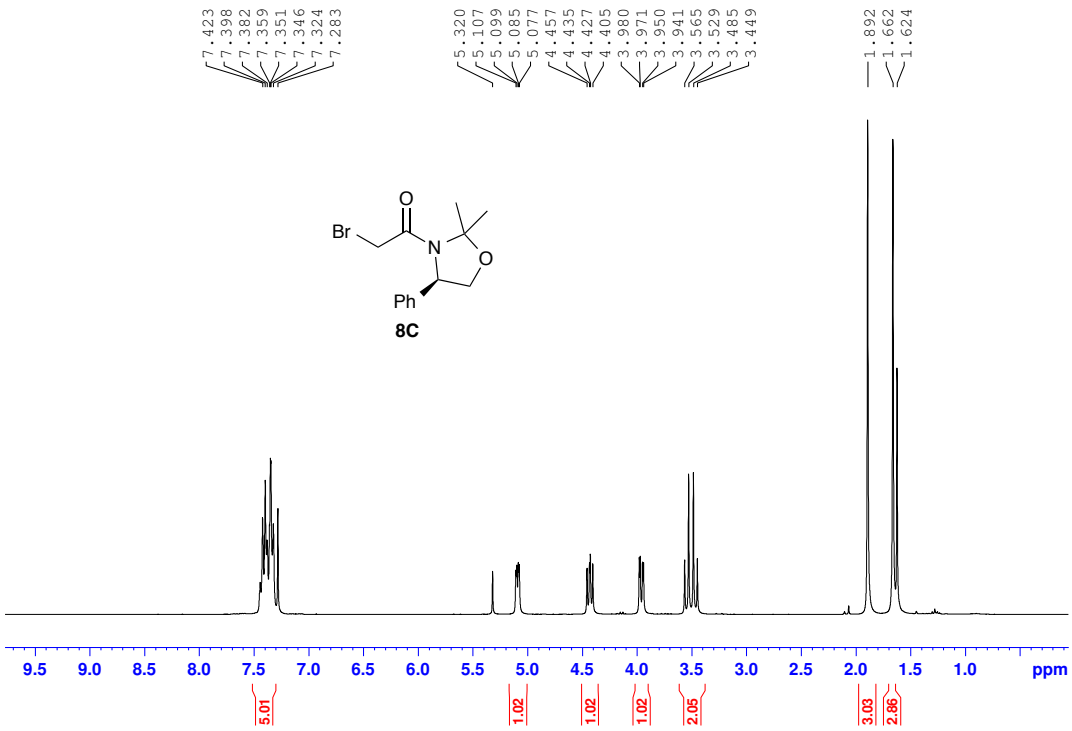
[6] (a) G. M. Sheldrick, *SHELXS-97, Program for the Solution of Crystal Structures*, Göttingen, Germany, 1997. See also: G. M. Sheldrick, *Acta Crystallographica*, 1990, **A46**, 467-473.
[7] (a) G. M. Sheldrick, *SHELXL-97, Program for crystal structure refinement*, Göttingen, Germany, 1997. See also: G. M. Sheldrick, *Acta Crystallographica*, 2008, **A64**, 112-122.

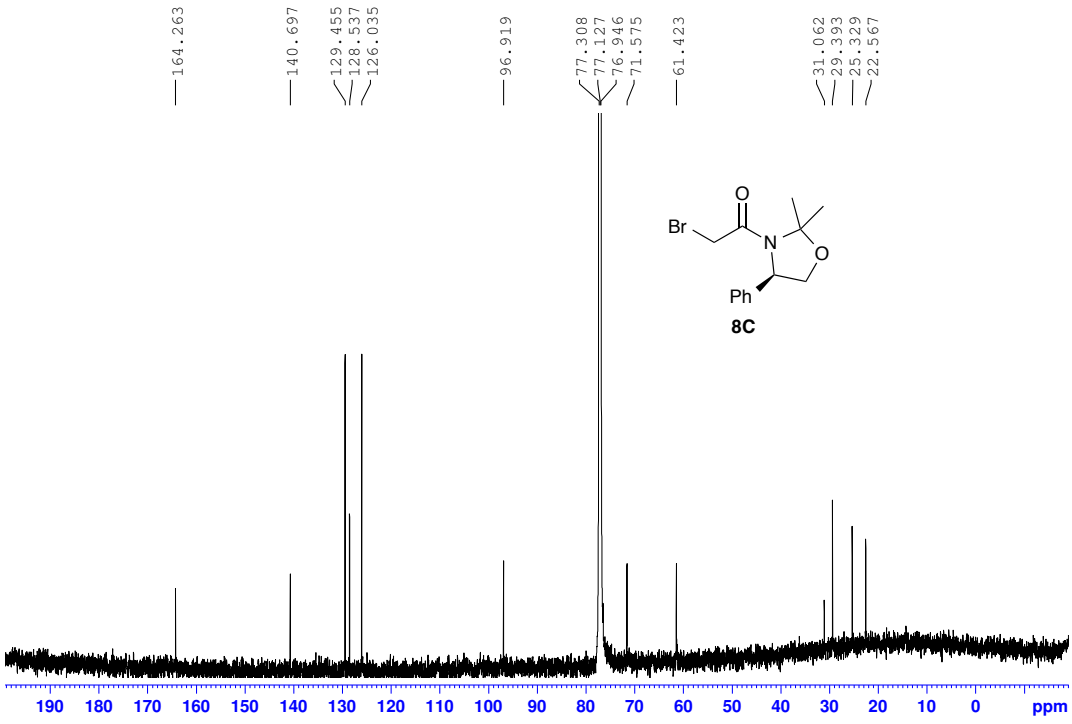
(refined occupancy 55:45 for **17a** and 65:35 for **19f**). CCDC 1023711 contains the supplementary crystallographic data for compound **17a**. CCDC 1030561 contains the supplementary crystallographic data for compound **19f**. These data can be obtained free of charge from The Cambrige Crystallographic Data Centre at www.ccdc.cam.ac.uk.

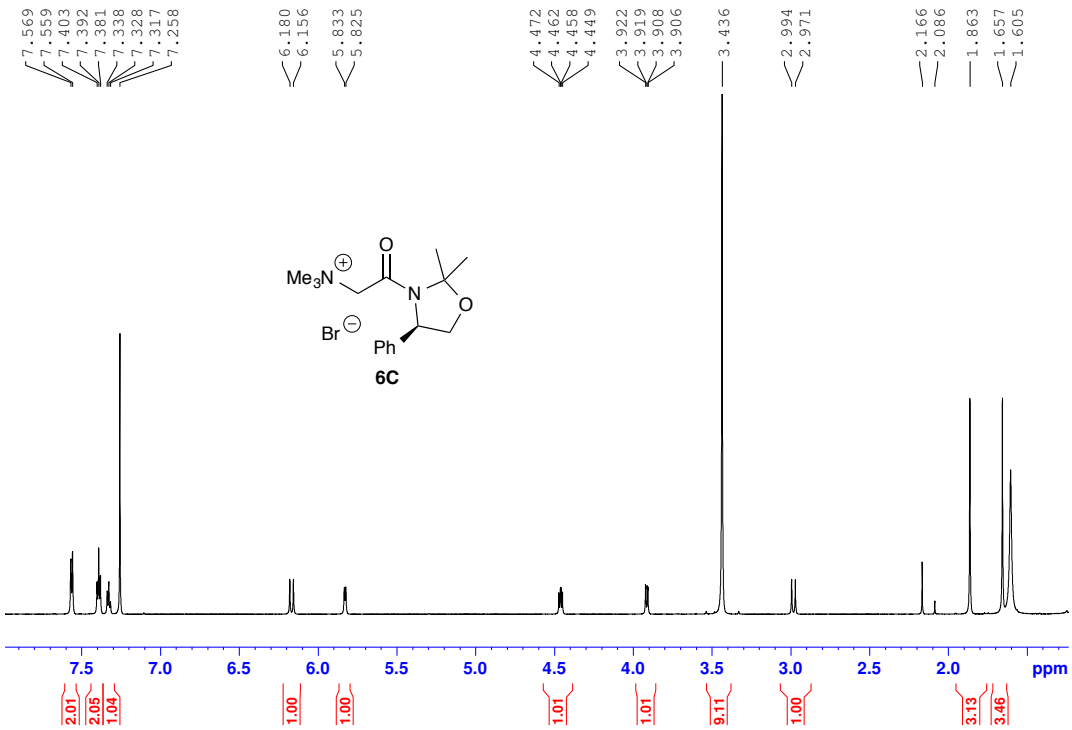
Table 1: Crystal Data and Data Collection and Structure Refinement Details for Compounds **17a** and **19f**.

Crystal Data	**17a**	**19f**
Empirical formula	$C_{20}H_{21}NO_3$	$C_{25}H_{29}BrN_2O_4$
Formula weight	323.38	501.41
Crystal size (mm)	0.87 × 0.48 × 0.42	0.67 × 0.41 × 0.30
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a (Å)	7.4058(6)	7.880(2)
b (Å)	12.3833(12)	12.465(3)
c (Å)	18.9412(18)	25.404(4)
V (Å^3)	1737.1(3)	2495.2(9)
D_{calcd} (g cm^{-1})	1.237	1.335
Z	4	4
μ (mm^{-1})	0.08	1.68
T (K)	233	300
θ range (°)	2.7 – 25.1	2.3 – 23.3
No. of reflections measured	19092	17475
No. of independent reflections	3073	3589
Parameters refined/restraints	230/0	304/0
R_{int}	0.053	0.079
Absorption correction	multi scan	multi scan
T_{min}, T_{max}	0.93, 0.97	0.44, 0.63
Largest diff. peak and hole (e Å^{-3})	0.15 / -0.16	0.20 / -0.30
Flack parameter	0.7(13)	0.002(13)
Final R indices [$I \geq 2\sigma(I)$]	$R_1 = 0.035$	$R_1 = 0.047$
	$wR_2 = 0.098$	$wR_2 = 0.108$
CCDC no.	1023711	1030561

8. Copies of selected NMR spectra:



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4.458
4.449
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3.919
3.908
3.906
3.436
2.994
2.971
2.166
2.086
1.863
1.657
1.605
Me3N
Br
O
N
O
Ph
6C
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
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1.01
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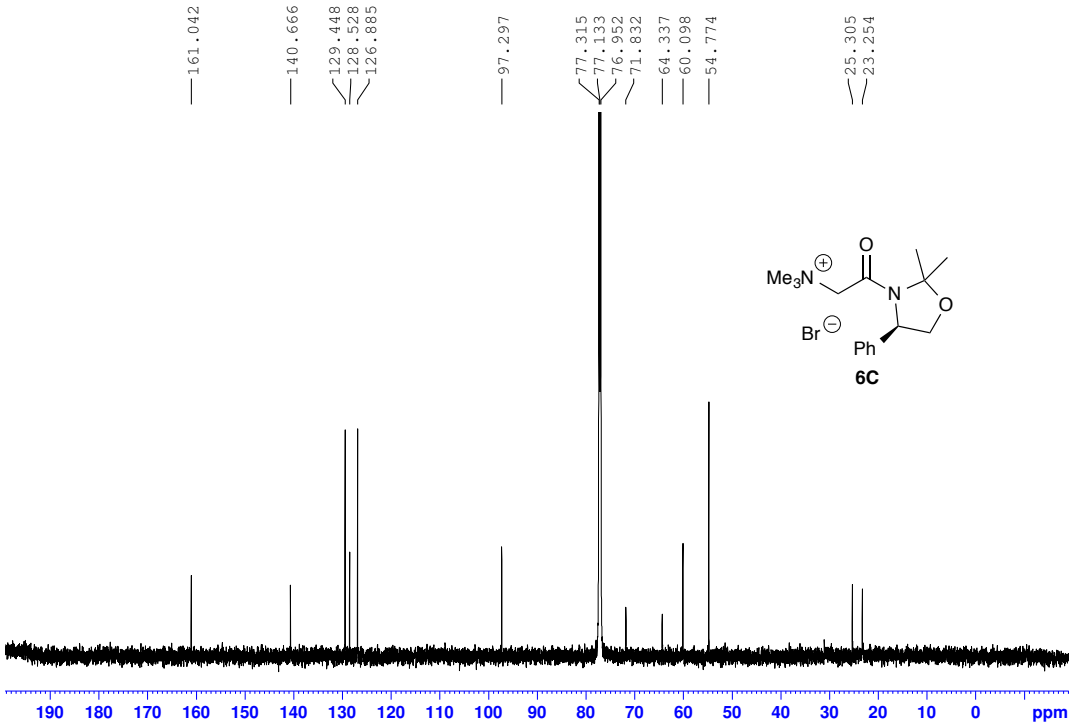
3.46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25.305
23.254
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Br
O
N
O
Ph
6C
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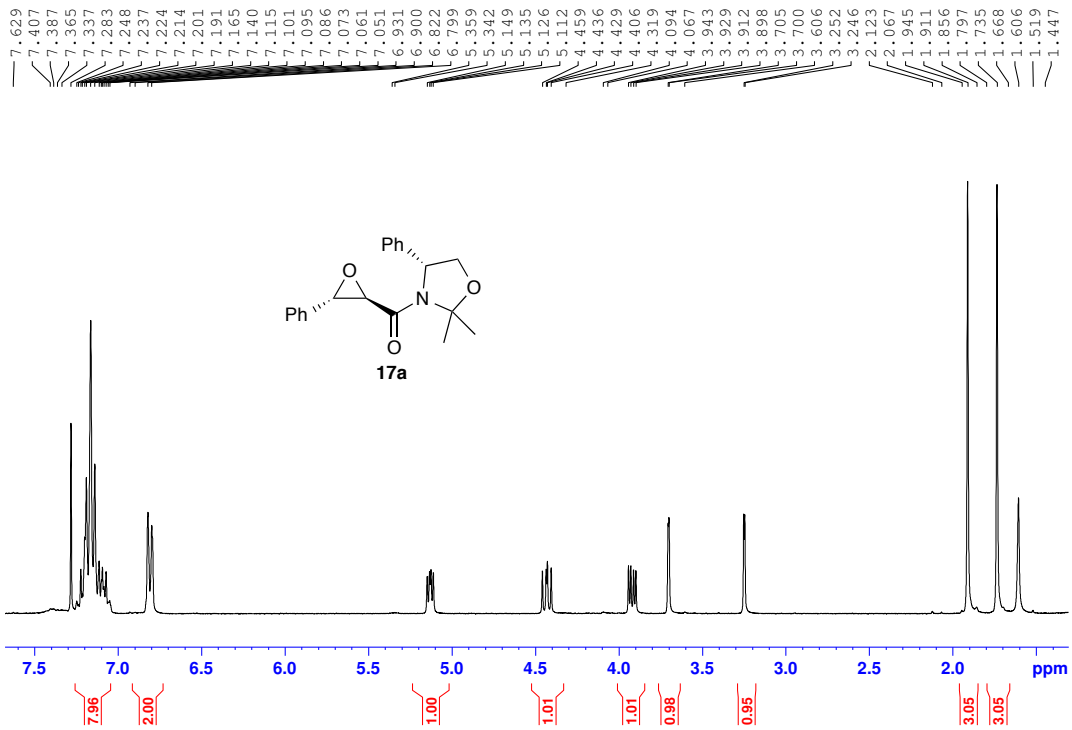
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Ph
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Ph
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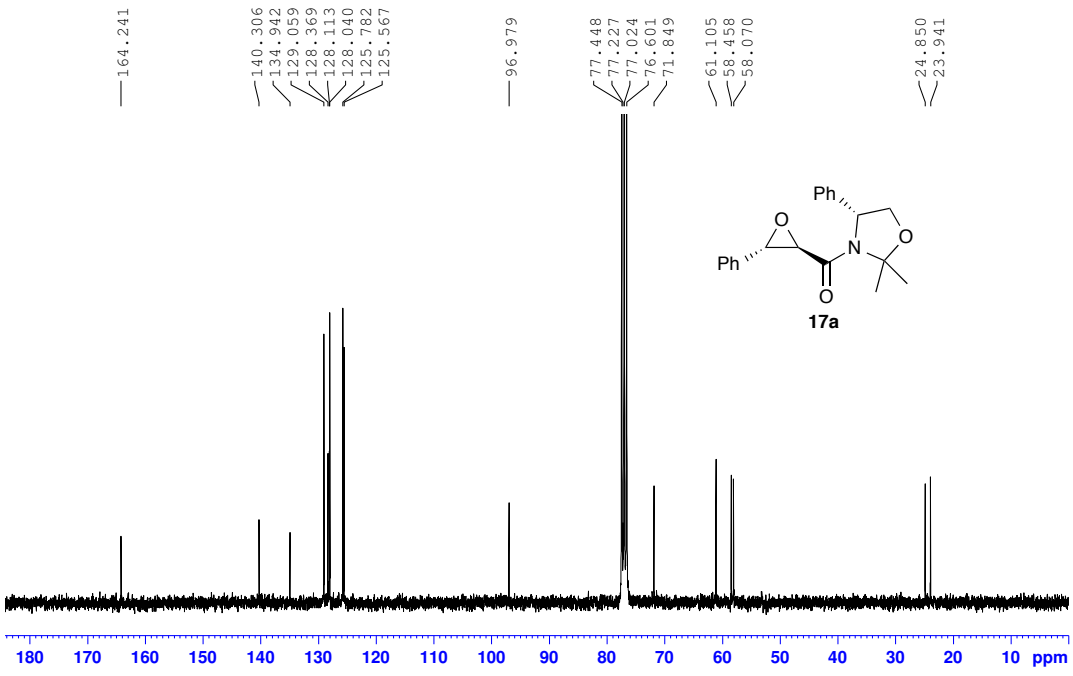
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Ph
O
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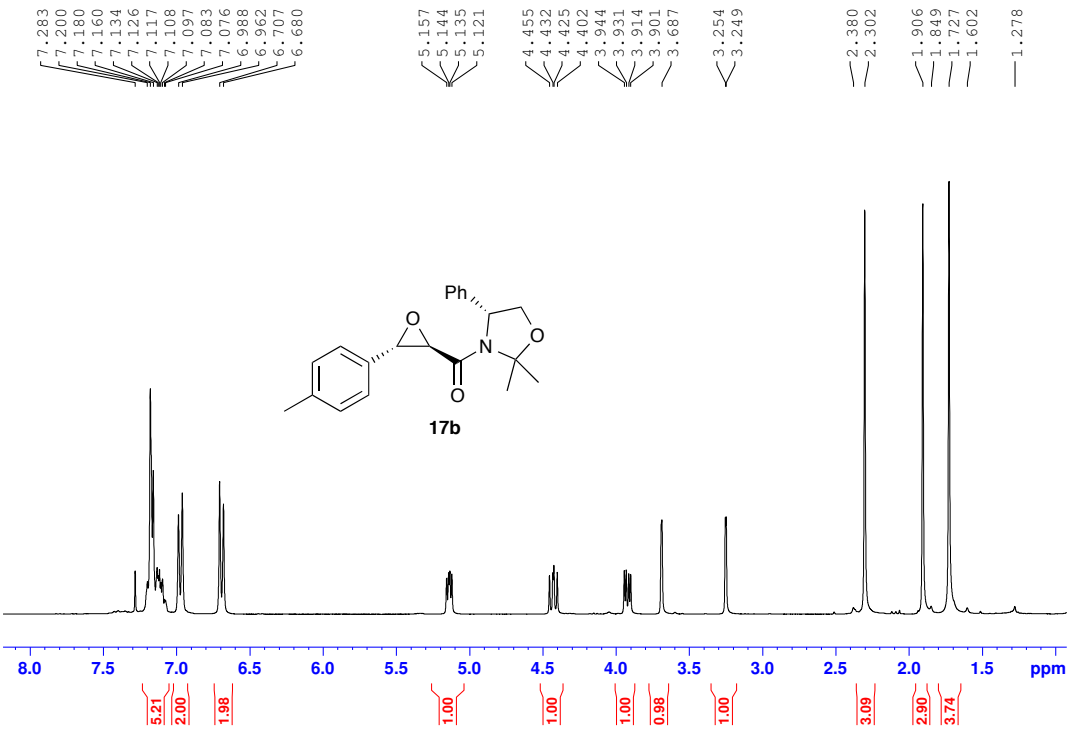
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4.425
4.402
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3.931
3.914
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3.249
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2.302
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Ph
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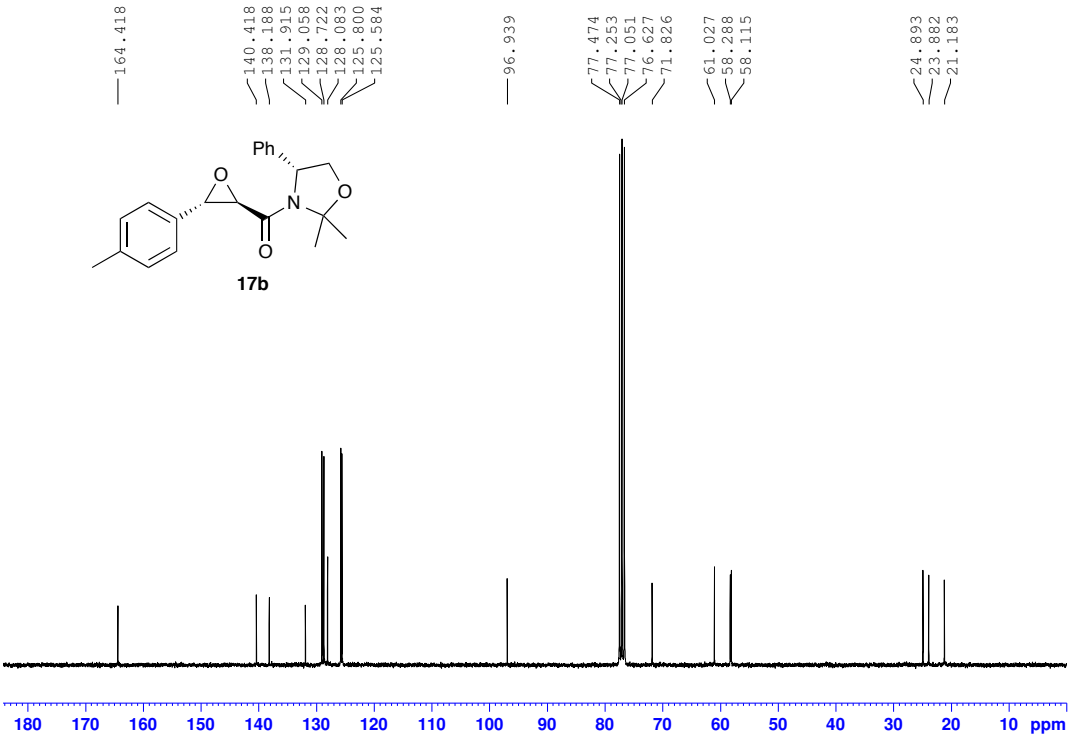
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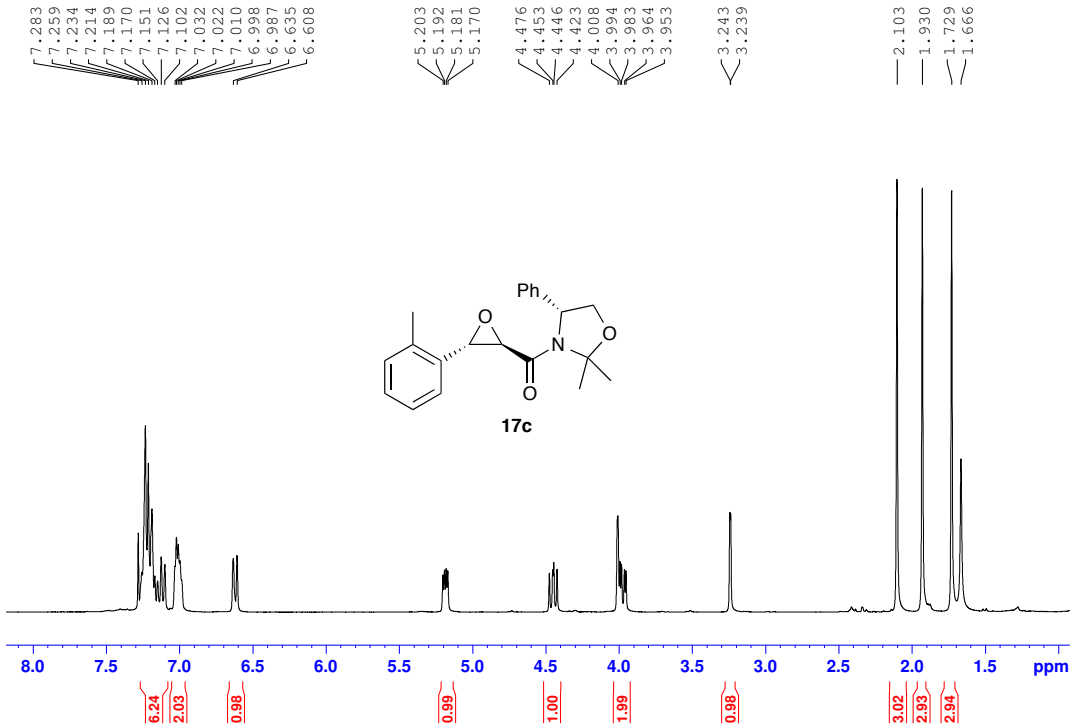
ppm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7.126
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7.022
7.010
6.998
6.987
6.635
6.608
5.203
5.192
5.181
5.170
4.476
4.453
4.446
4.423
4.008
3.994
3.983
3.964
3.953
3.243
3.239
2.103
1.930
1.729
1.666
Ph
O
N
O
O
17c
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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ppm
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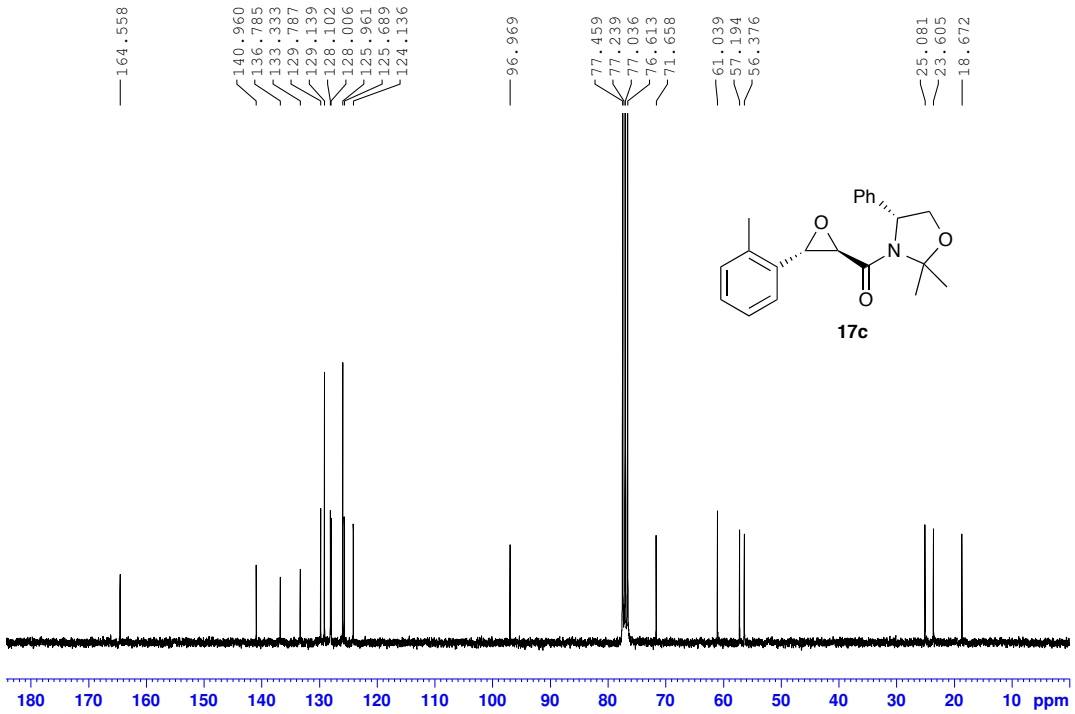
0.99
1.00
1.99
0.98
3.02
2.93
2.94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128.006
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77.459
77.239
77.036
76.613
71.658
61.039
57.194
56.376
25.081
23.605
18.672
Ph
O
N
O
O
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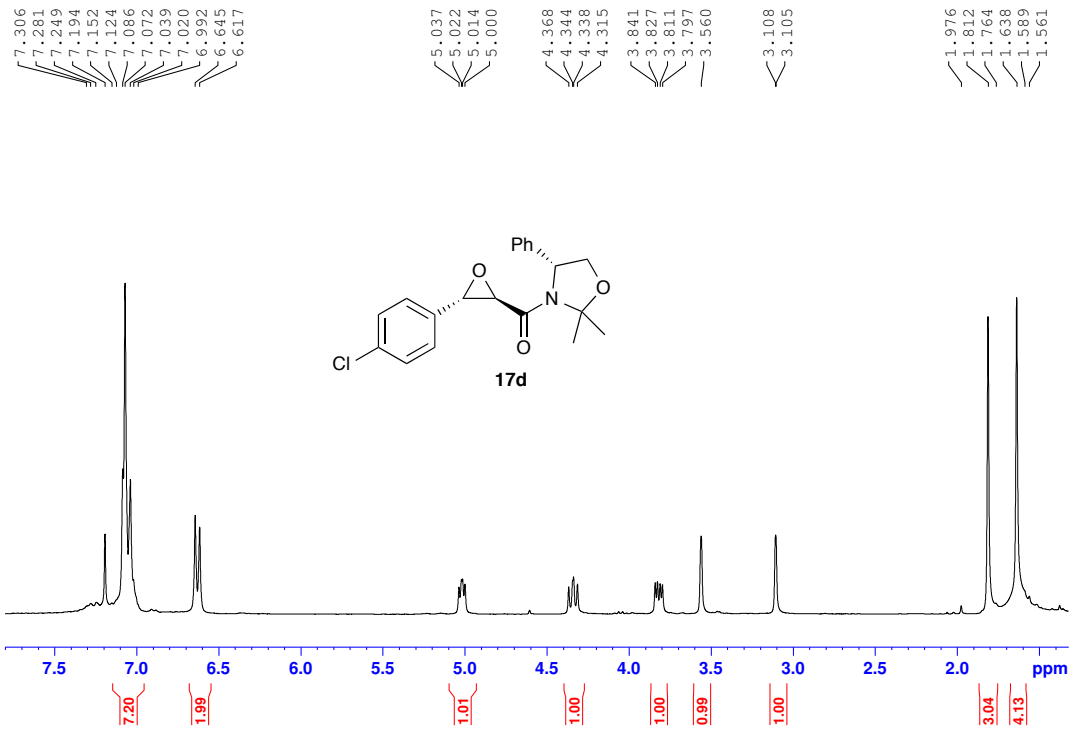
10
ppm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5.037
5.022
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5.000
4.368
4.344
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3.841
3.827
3.811
3.797
3.560
3.108
3.105
1.976
1.812
1.764
1.638
1.589
1.561
Ph
O
N
O
O
Cl
17d
7.5
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5.0
4.5
4.0
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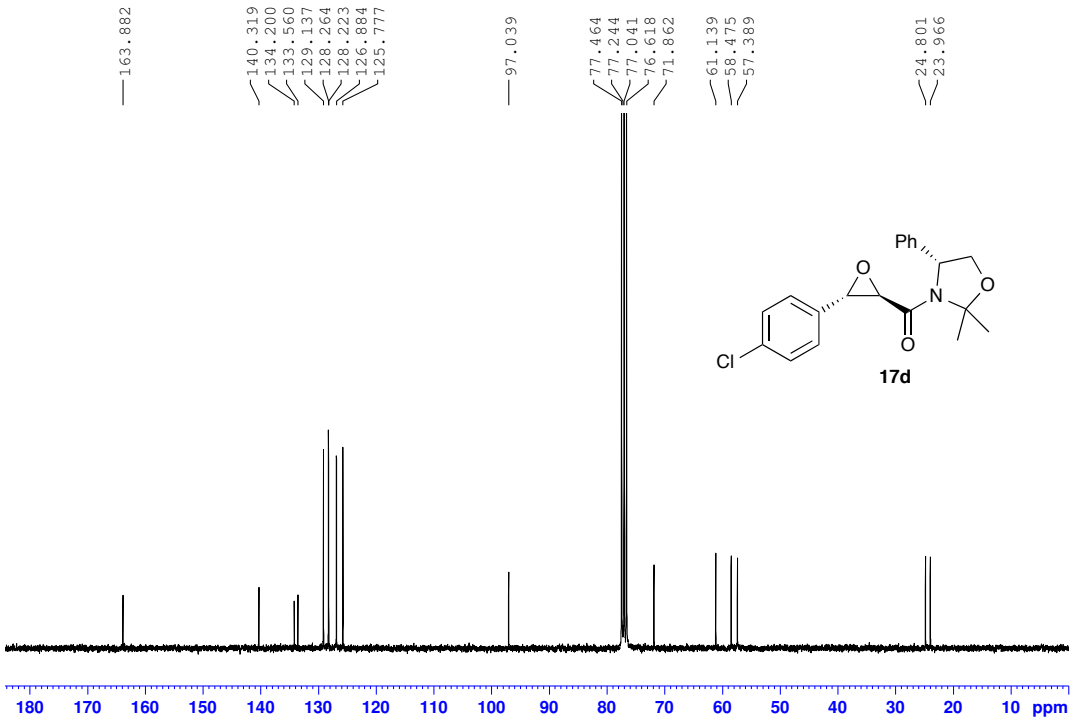
4.13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58.475
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O
N
O
O
Cl
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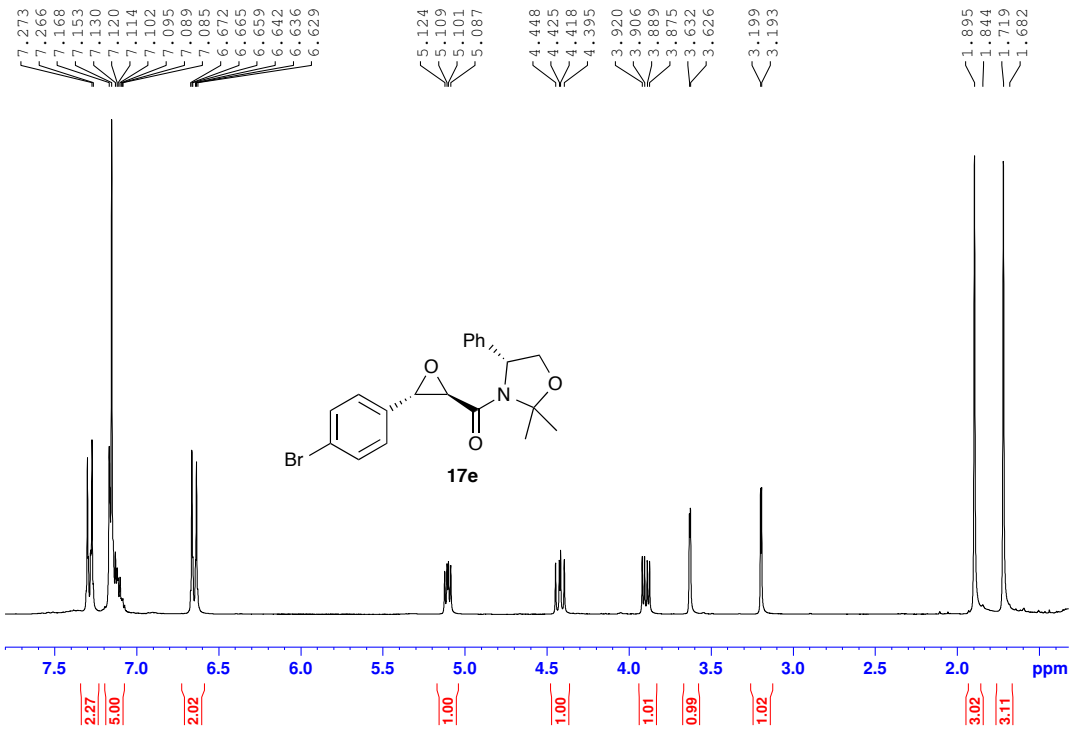
10
ppm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6.659
6.642
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6.629
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3.906
3.889
3.875
3.632
3.626
3.199
3.193
1.895
1.844
1.719
1.682
Ph
O
N
O
O
Br
17e
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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1.01
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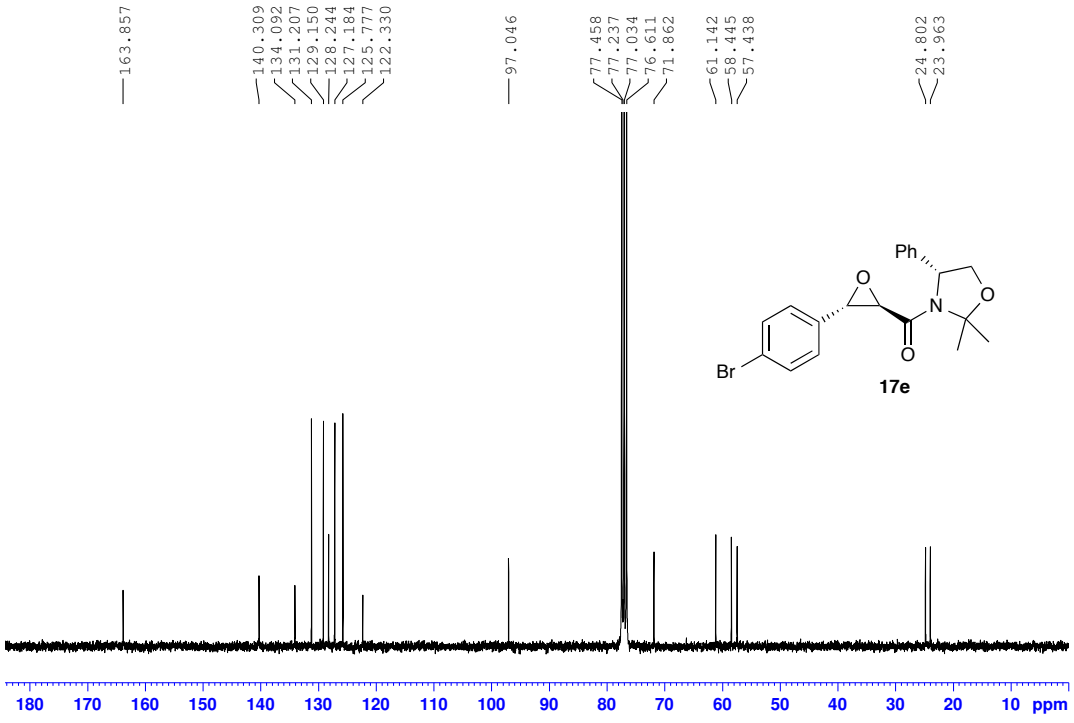
3.11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77.237
77.034
76.611
71.862
61.142
58.445
57.438
24.802
23.963
Ph
O
N
O
O
Br
17e
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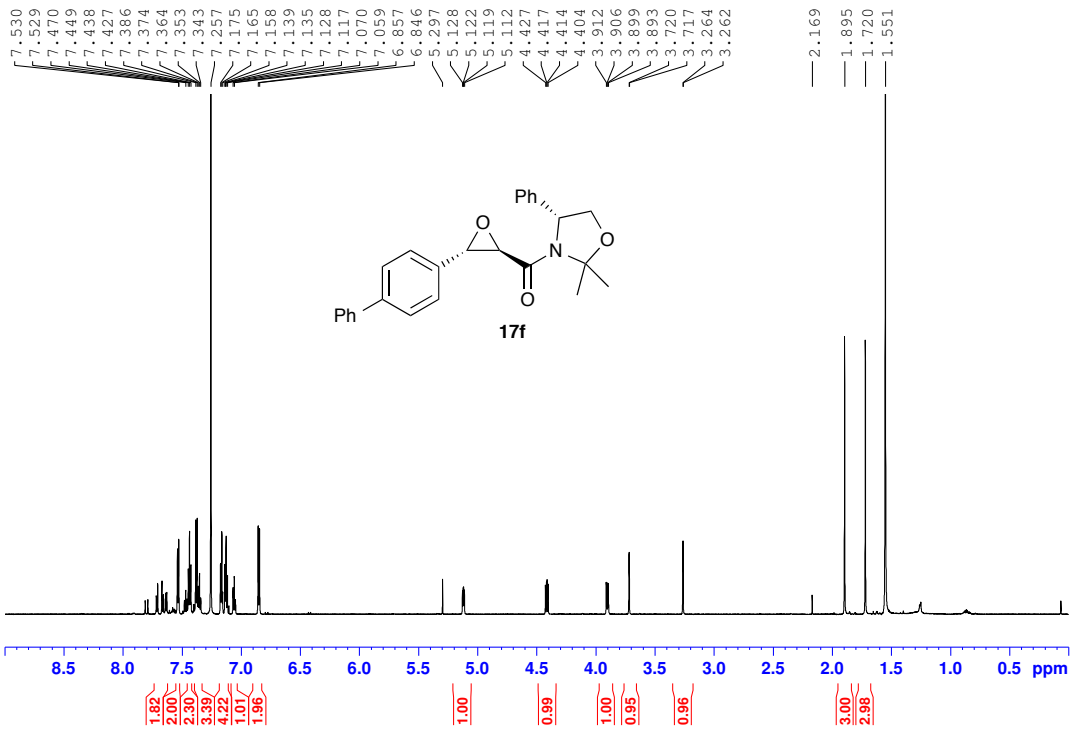
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.175
7.165
7.158
7.139
7.135
7.128
7.117
7.070
7.059
6.857
6.846
5.297
5.128
5.122
5.119
5.112
4.427
4.417
4.414
4.404
3.912
3.906
3.899
3.893
3.720
3.717
3.264
3.262
2.169
1.895
1.720
1.551
Ph
O
N
O
O
Ph
17f
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
1.82
2.00
2.30
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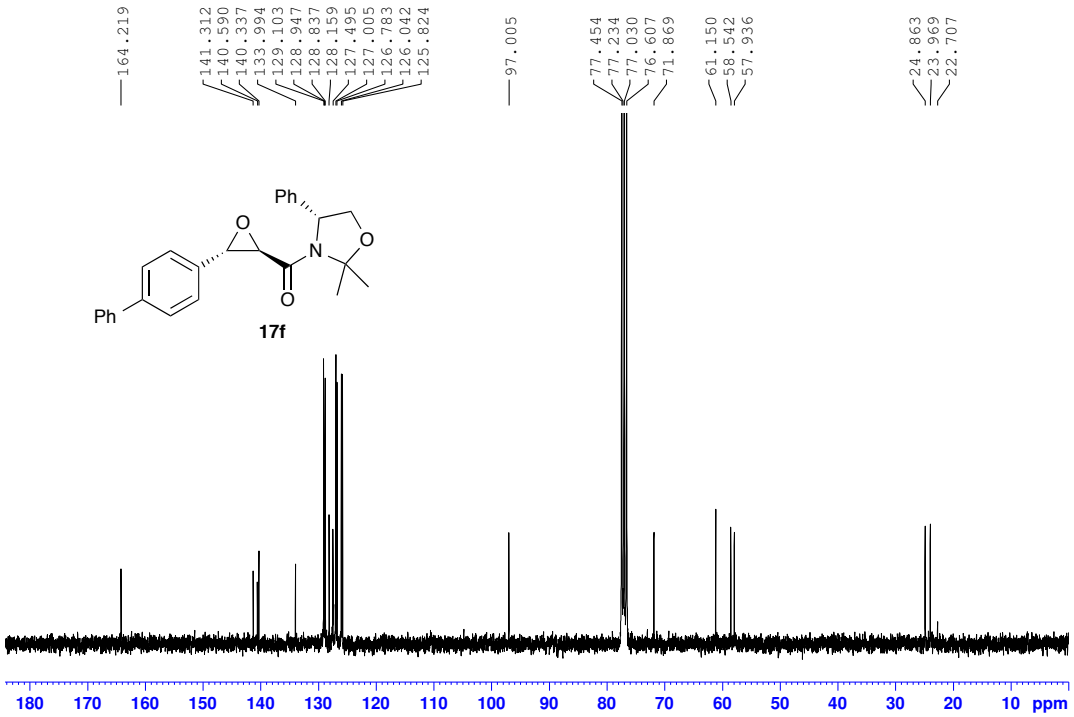
4.22
1.01
1.96
1.00
0.99
1.00
0.95
0.96
3.00
2.98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128.837
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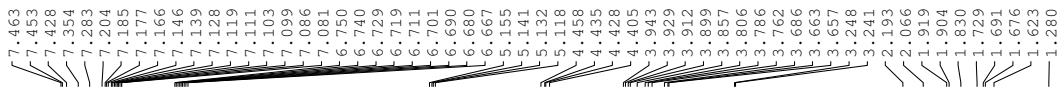
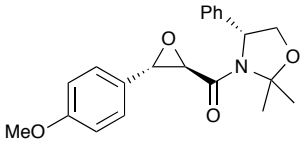
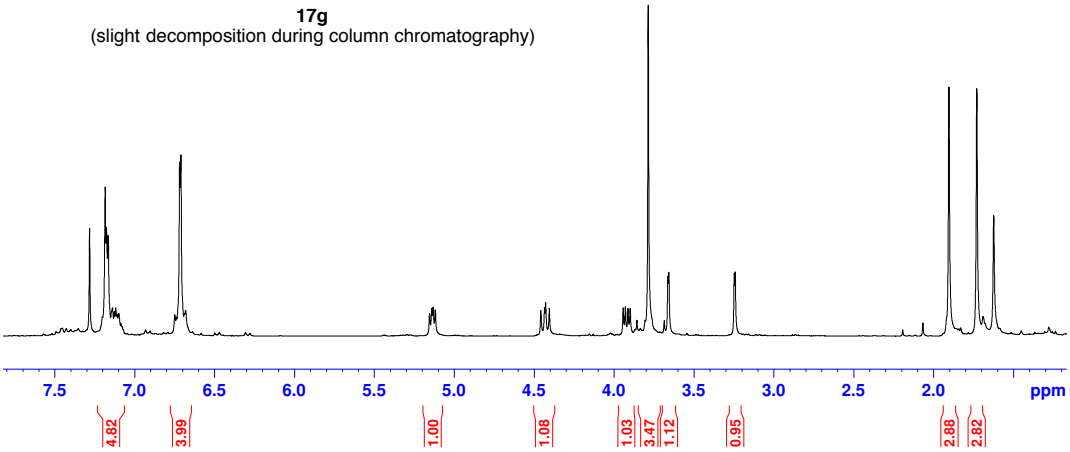
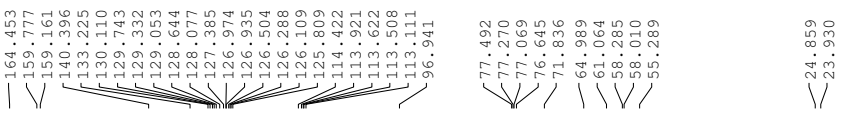
127.495
127.005
126.783
126.042
125.824
97.005
77.454
77.234
77.030
76.607
71.869
61.150
58.542
57.936
24.863
23.969
22.707
Ph
O
N
O
O
Ph
17f
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

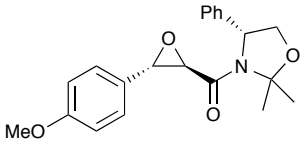




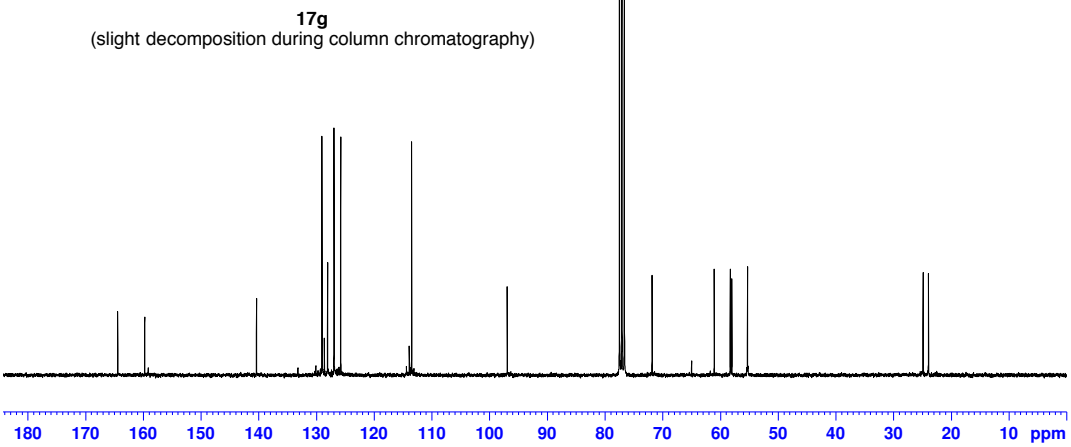
17g
(slight decomposition during column chromatography)

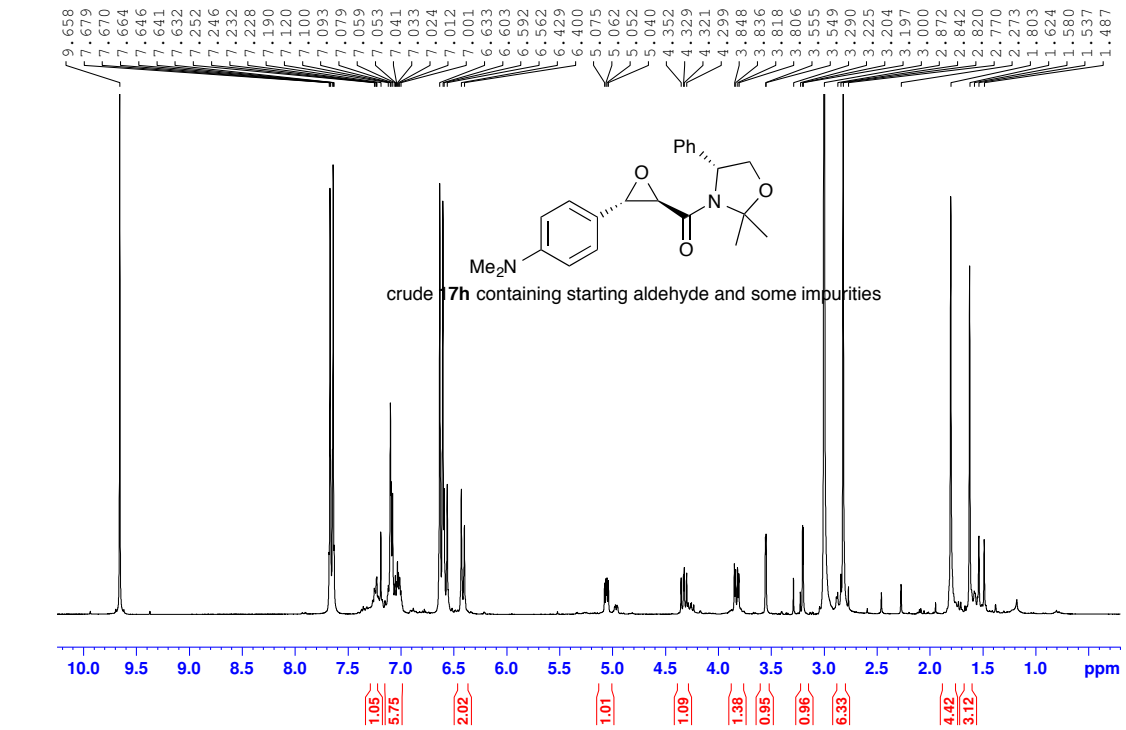




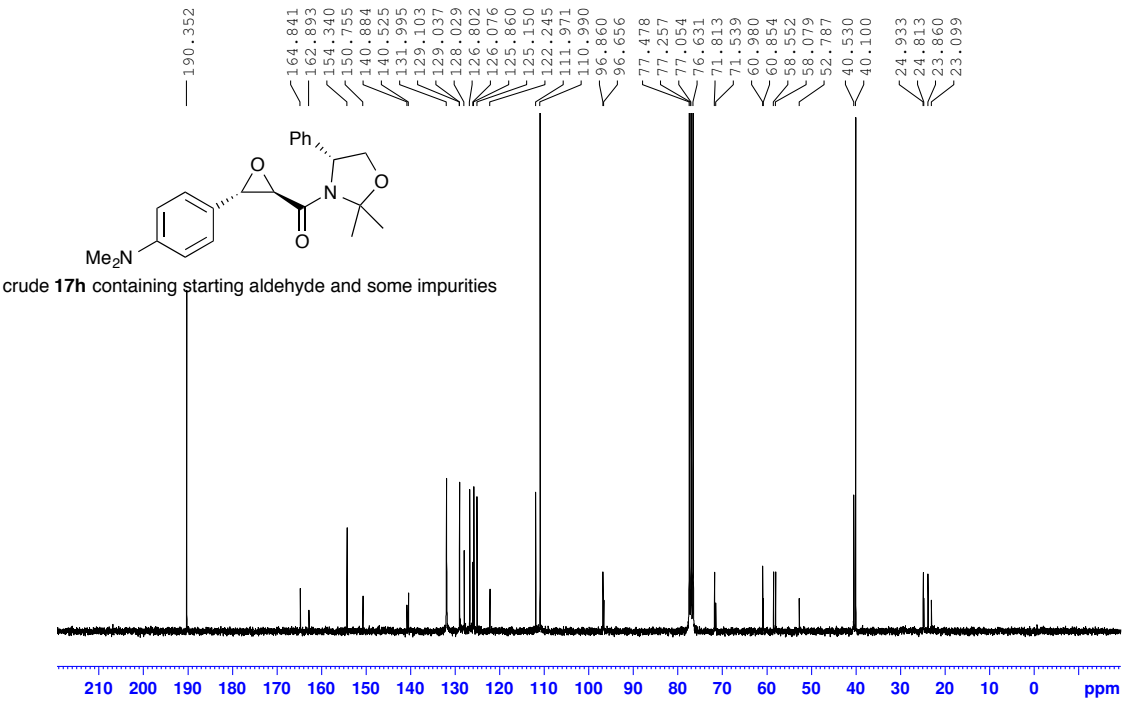


17g
(slight decomposition during column chromatography)

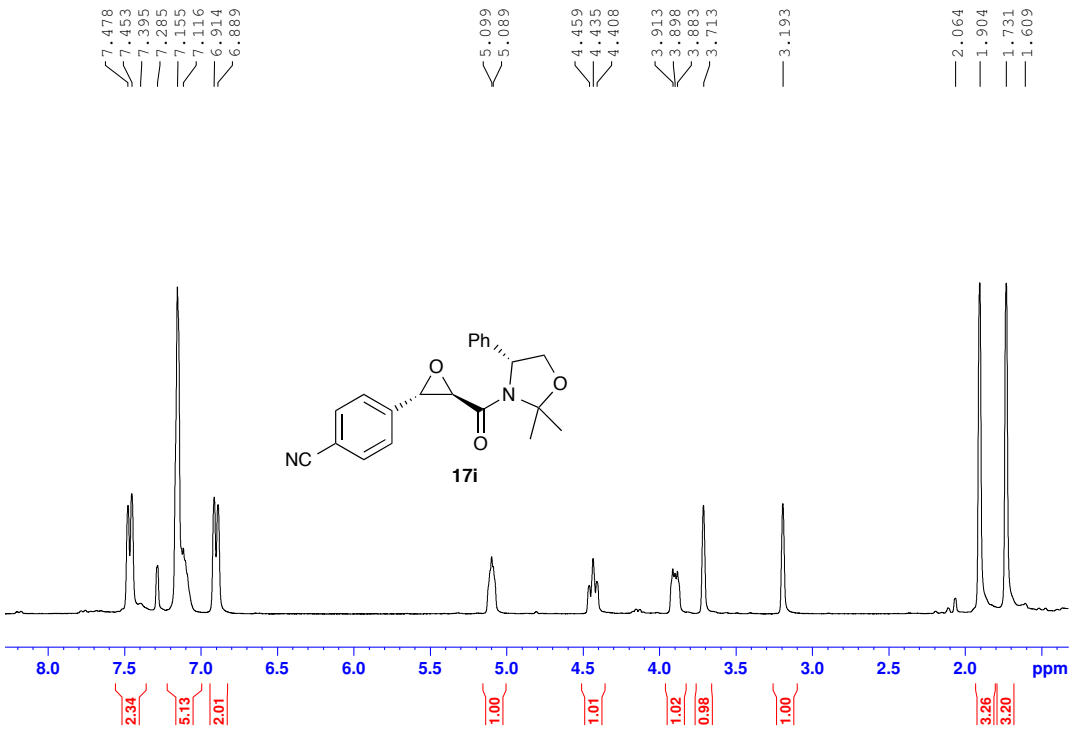




crude **17h** containing starting aldehyde and some impurities



crude **17h** containing starting aldehyde and some impurities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6.889
5.099
5.089
4.459
4.435
4.408
3.913
3.898
3.883
3.713
3.193
2.064
1.904
1.731
1.609
Ph
O
N
O
O
NC
17i
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
ppm
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5.13
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1.00
1.01
1.02
0.98
1.00
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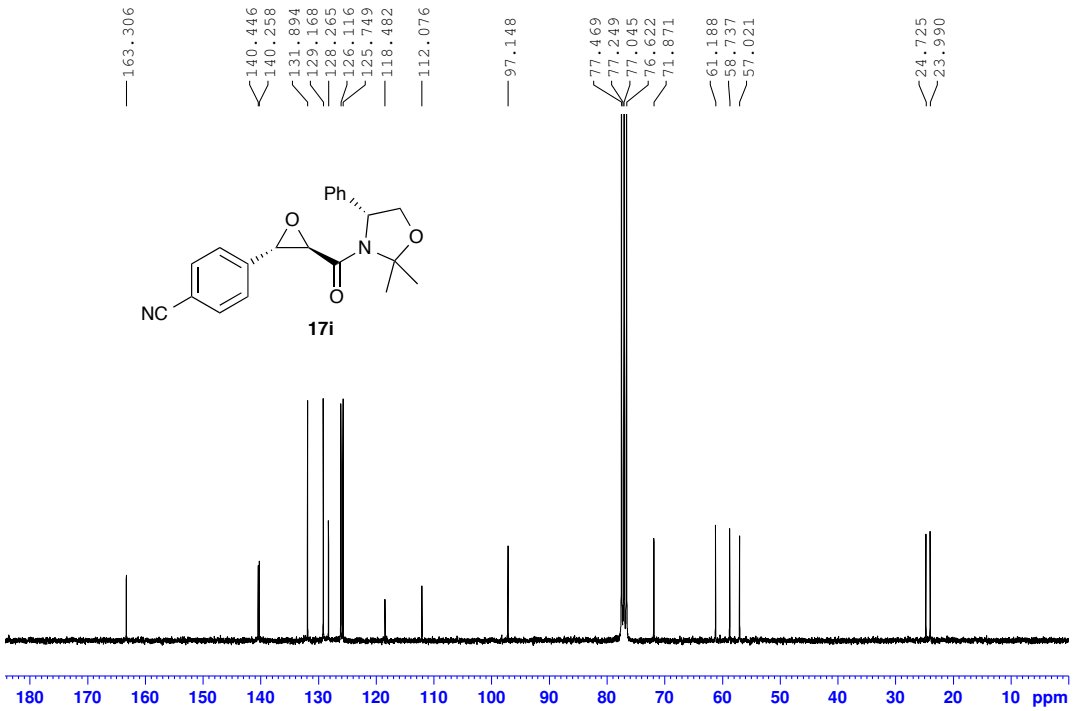
3.20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125.749
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77.469
77.249
77.045
76.622
71.871
61.188
58.737
57.021
24.725
23.990
Ph
O
N
O
O
NC
17i
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150
140
130
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110
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70
60
50
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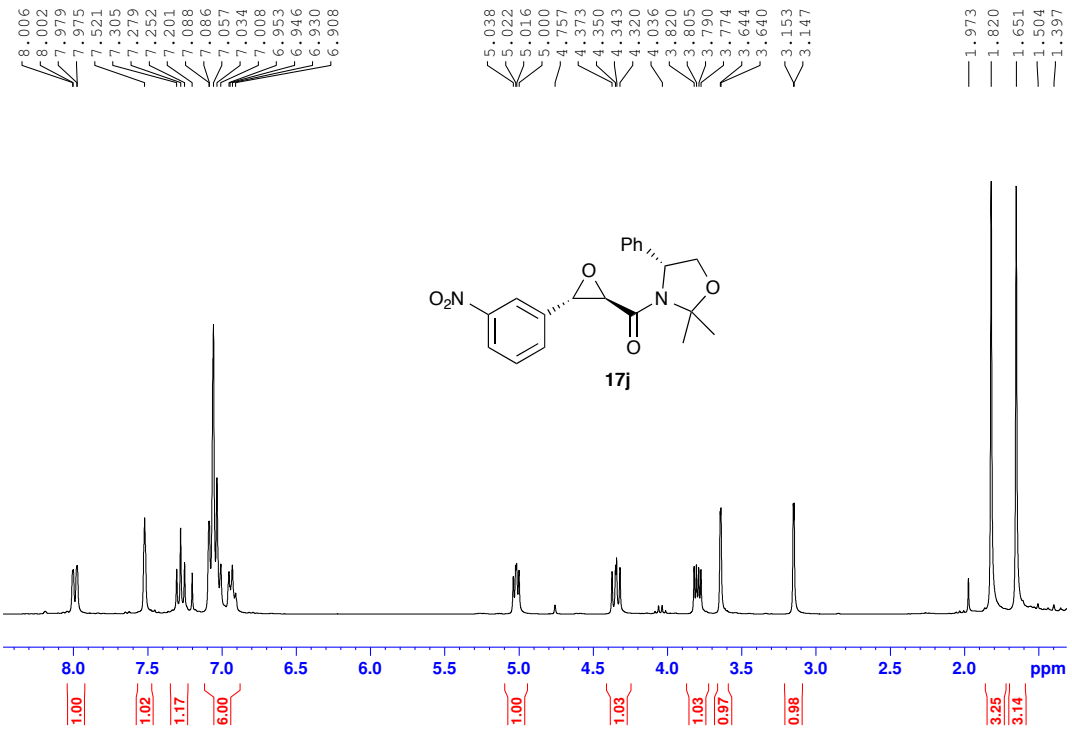
30
20
10
ppm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7.034
7.008
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6.946
6.930
6.908
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5.022
5.016
5.000
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4.350
4.343
4.320
4.036
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3.805
3.790
3.774
3.644
3.640
3.153
3.147
1.973
1.820
1.651
1.504
1.397
Ph
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N
O
O2N
O
17j
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7.0
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5.5
5.0
4.5
4.0
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3.0
2.5
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1.00
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1.03
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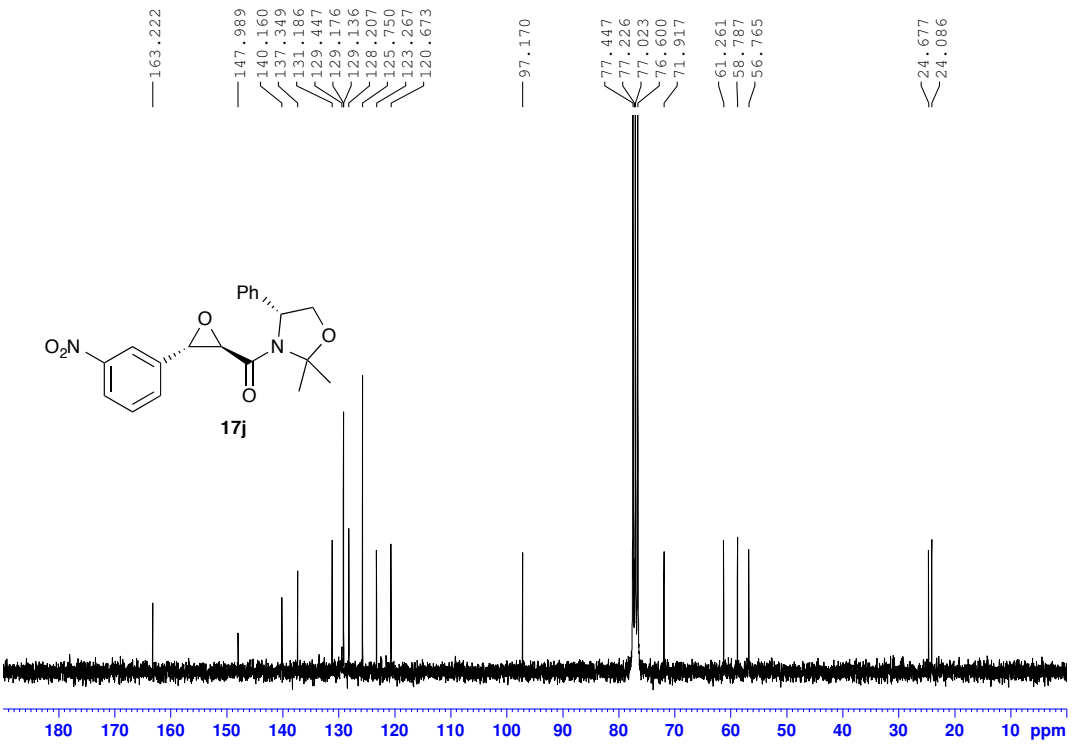
3.14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129.176
129.136
128.207
125.750
123.267
120.673
97.170
77.447
77.226
77.023
76.600
71.917
61.261
58.787
56.765
24.677
24.086
Ph
O
N
O
O2N
O
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150
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120
110
100
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70
60
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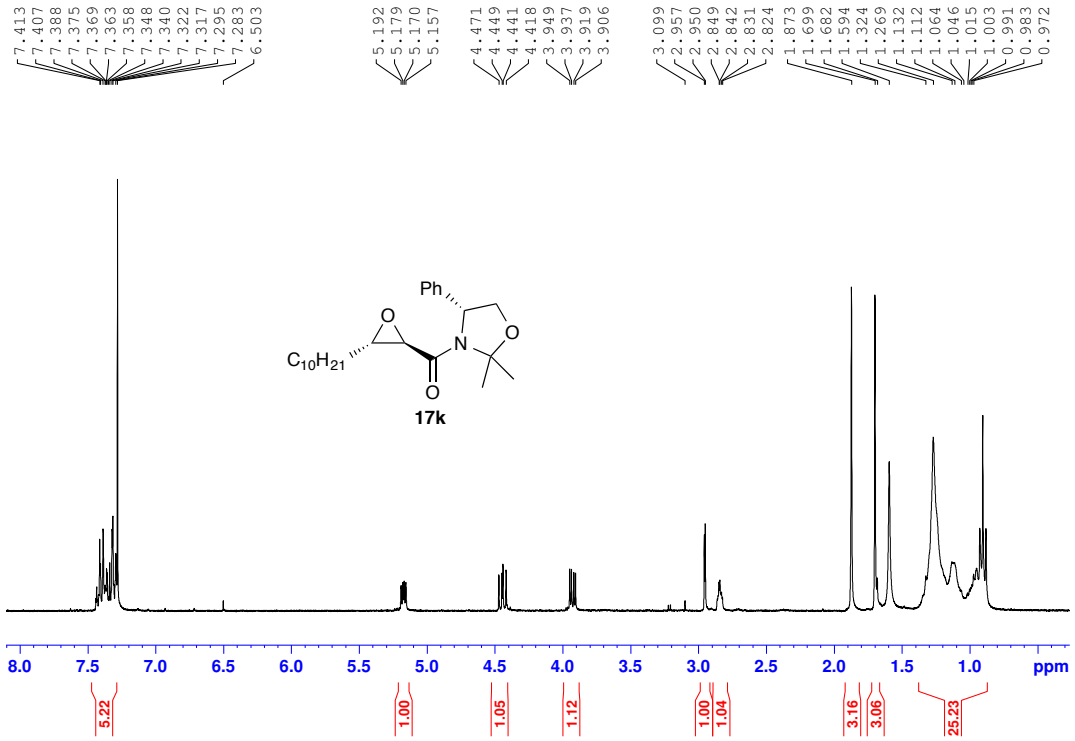
10
ppm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5.179
5.170
5.157
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4.449
4.441
4.418
3.949
3.937
3.919
3.906
3.099
2.957
2.950
2.849
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2.831
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1.269
1.132
1.112
1.064
1.046
1.015
1.003
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0.983
0.972
Ph
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N
O
C10H21
O
17k
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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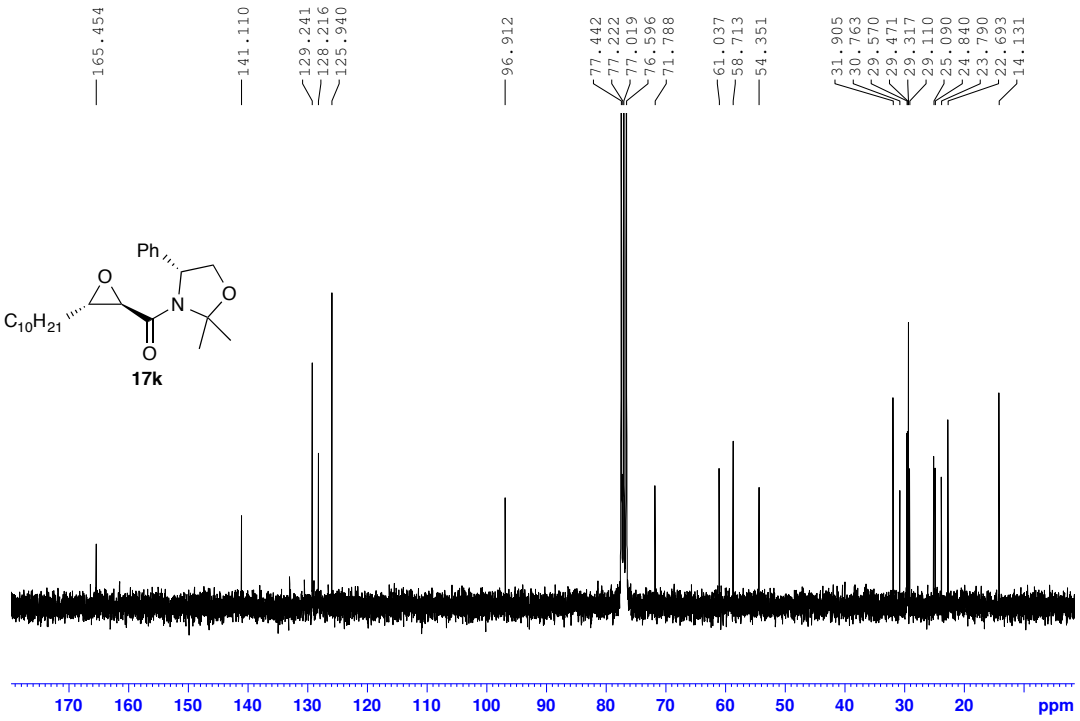
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58.713
54.351
31.905
30.763
29.570
29.471
29.317
29.110
25.090
24.840
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Ph
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N
O
C10H21
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80
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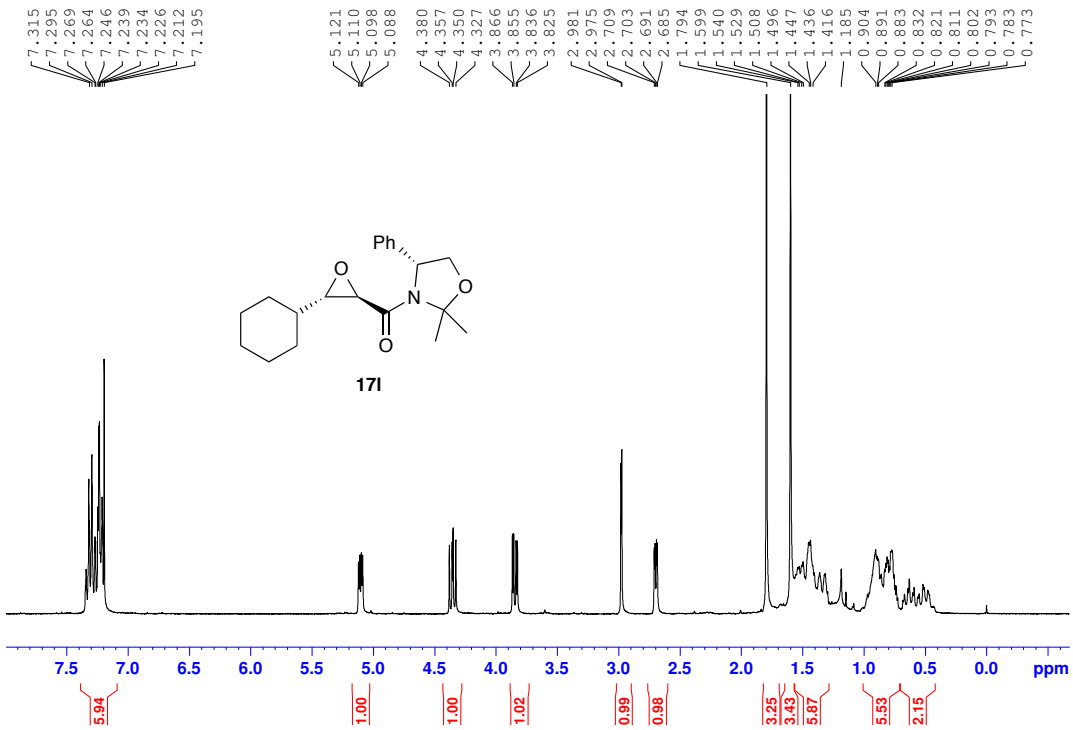
ppm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3.836
3.825
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2.975
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1.599
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1.447
1.436
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1.185
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0.891
0.883
0.832
0.821
0.811
0.802
0.793
0.783
0.773
Ph
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N
O
O
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6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
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1.5
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0.5
0.0
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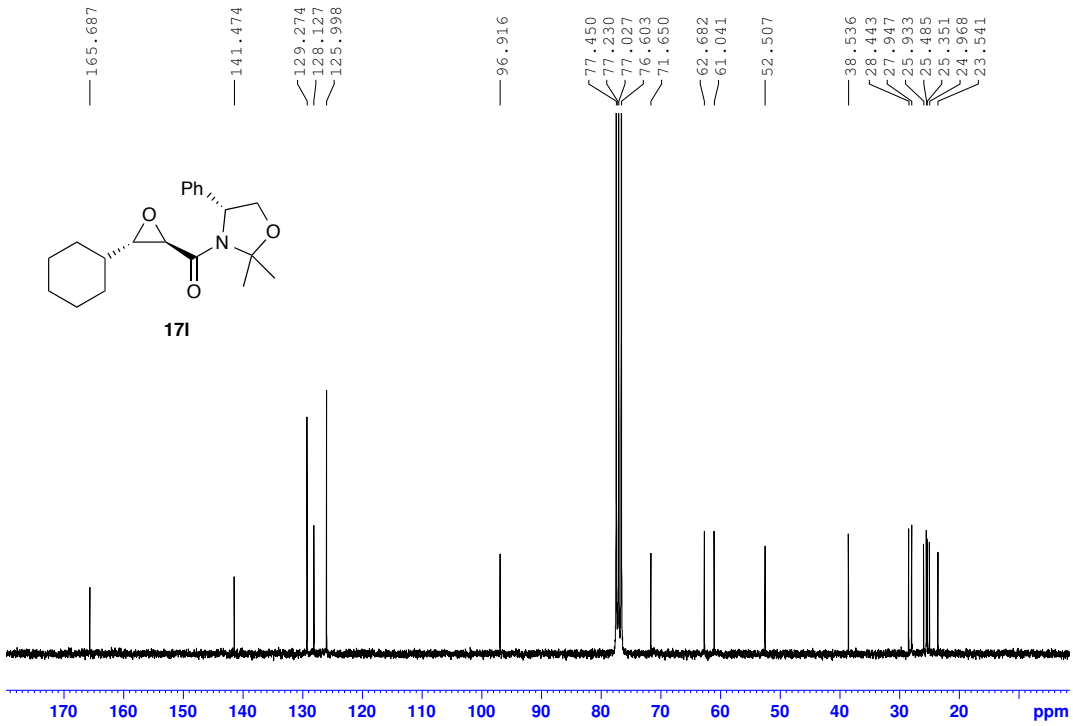
17l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61.041
52.507
38.536
28.443
27.947
25.933
25.485
25.351
24.968
23.541
Ph
O
N
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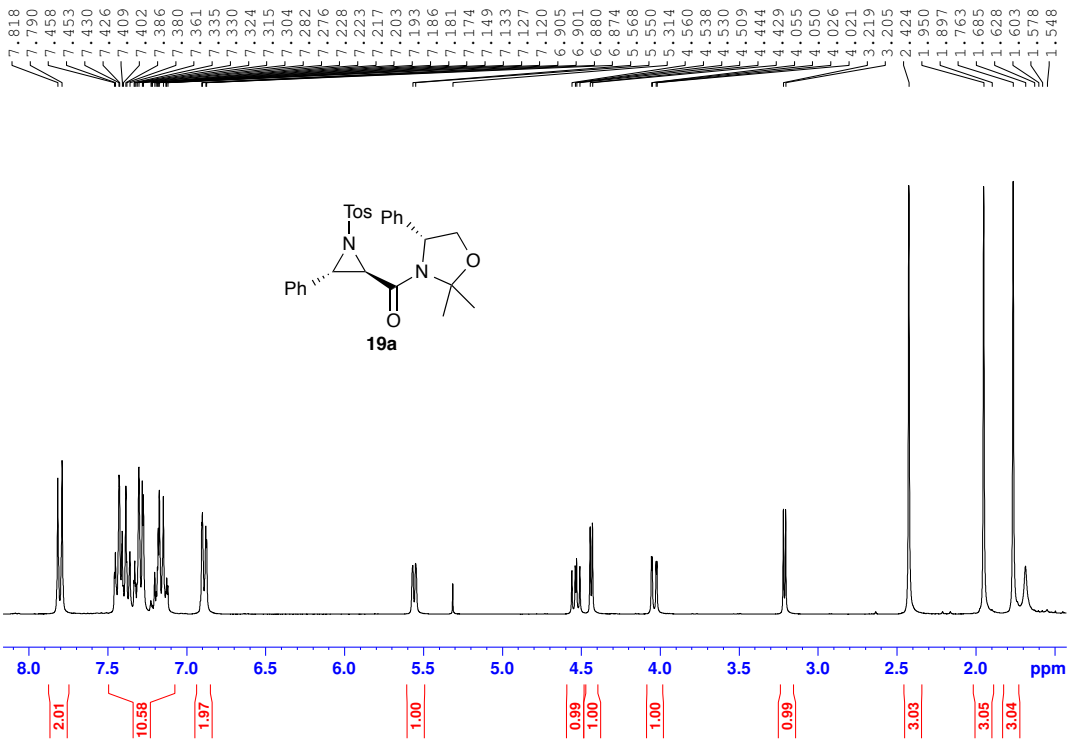
20
ppm

17l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7.223
7.217
7.203
7.193
7.186
7.181
7.174
7.149
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7.127
7.120
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4.560
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4.509
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4.429
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Tos
Ph
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Ph
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O
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7.0
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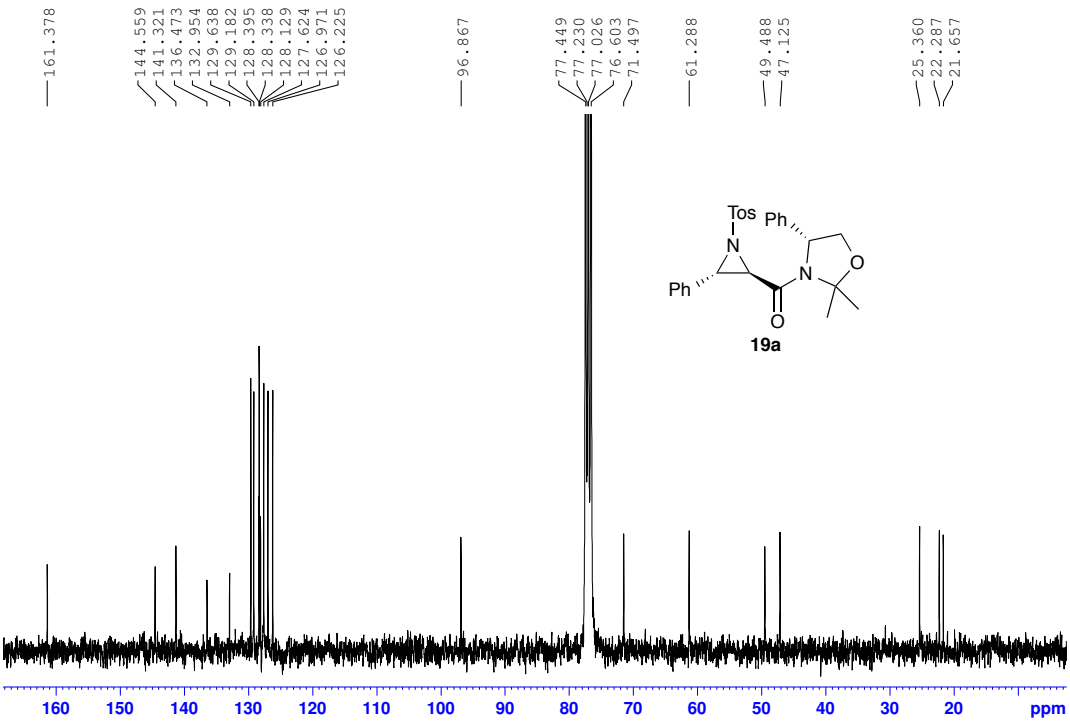
3.04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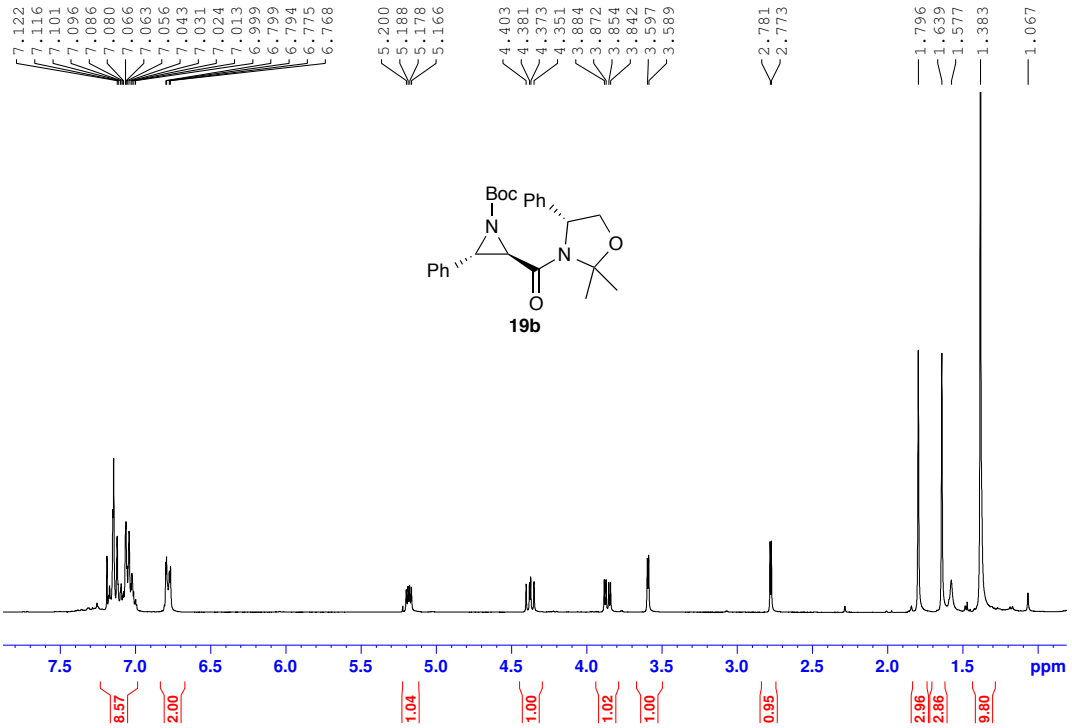
129.182
128.395
128.338
128.129
127.624
126.971
126.225
96.867
77.449
77.230
77.026
76.603
71.497
61.288
49.488
47.125
25.360
22.287
21.657
Tos
Ph
N
Ph
N
O
O
19a
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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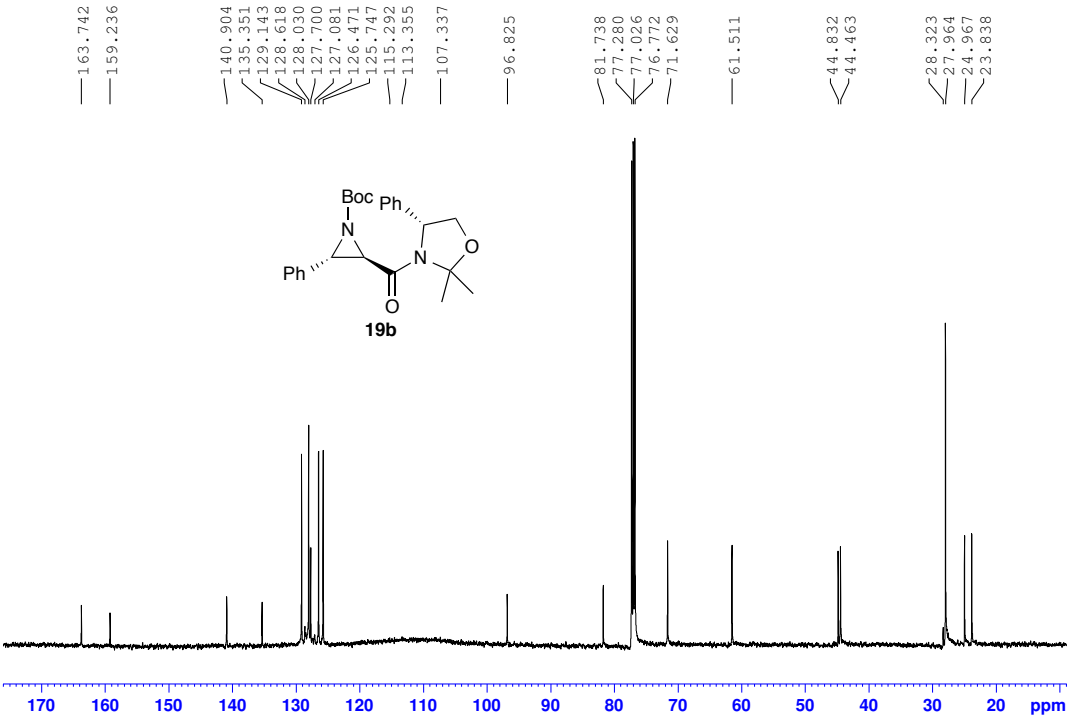
7.116
7.101
7.096
7.086
7.080
7.066
7.063
7.056
7.043
7.031
7.024
7.013
6.999
6.799
6.794
6.775
6.768
5.200
5.188
5.178
5.166
4.403
4.381
4.373
4.351
3.884
3.872
3.854
3.842
3.597
3.589
2.781
2.773
1.796
1.639
1.577
1.383
1.067
Boc
Ph
N
Ph
N
O
O
19b
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
8.57
2.00
1.04
1.00
1.02
1.00
0.95
2.96
2.86
9.80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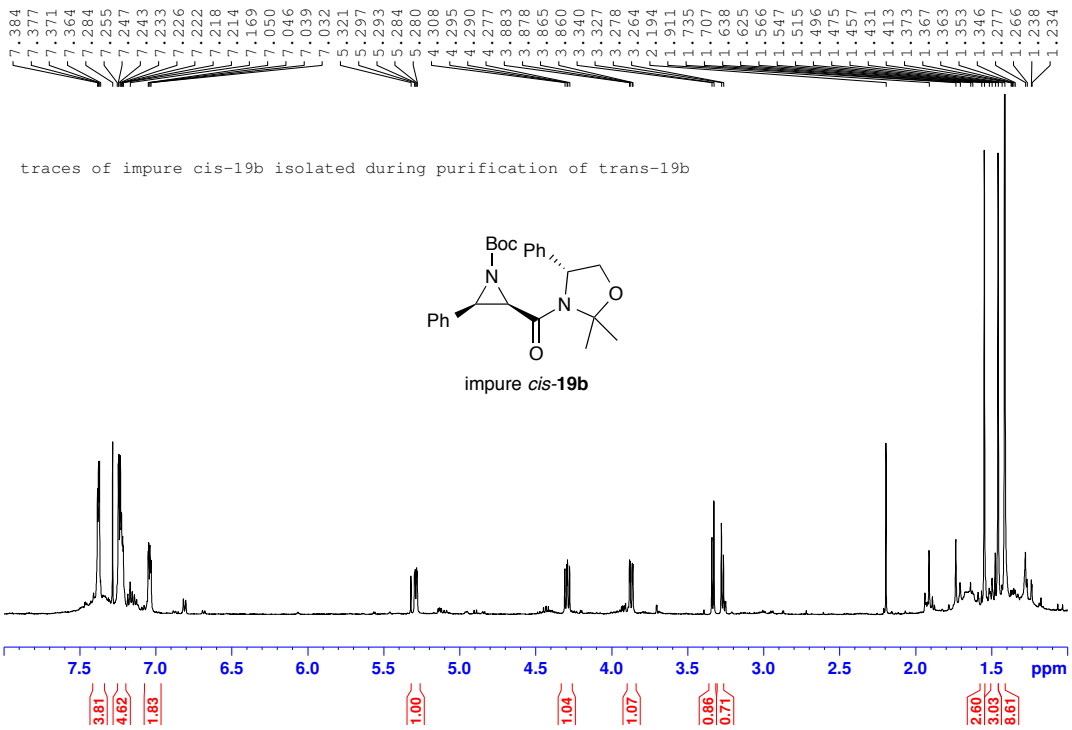
159.236
140.904
135.351
129.143
128.618
128.030
127.700
127.081
126.471
125.747
115.292
113.355
107.337
96.825
81.738
77.280
77.026
76.772
71.629
61.511
44.832
44.463
28.323
27.964
24.967
23.838
Boc
Ph
N
Ph
N
O
O
19b
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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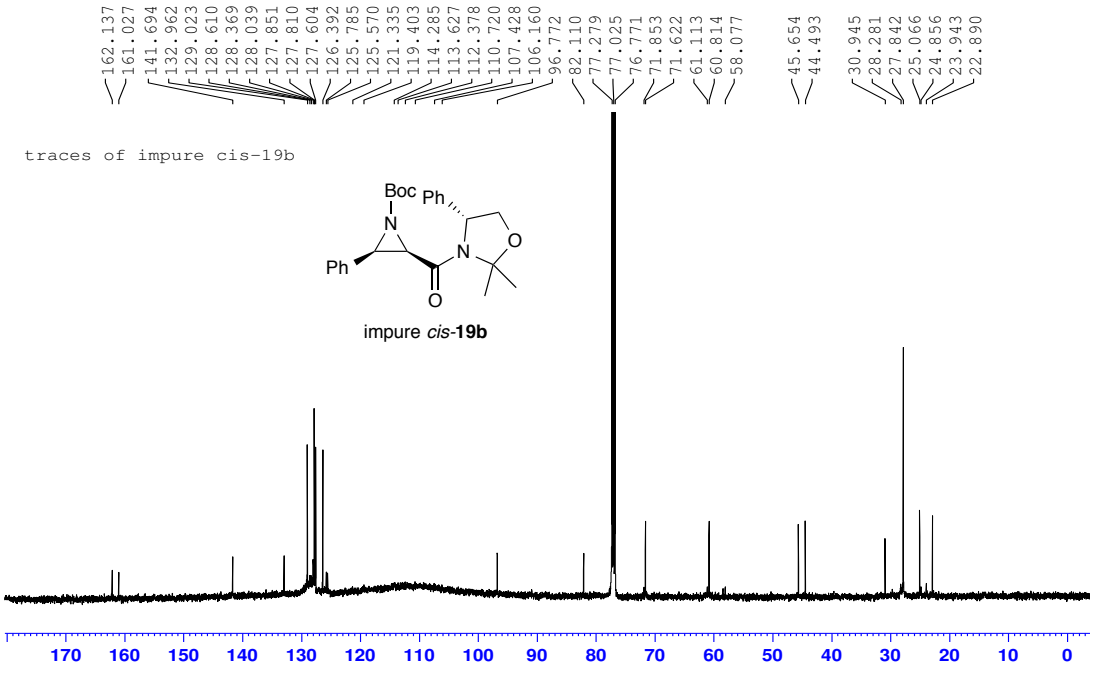
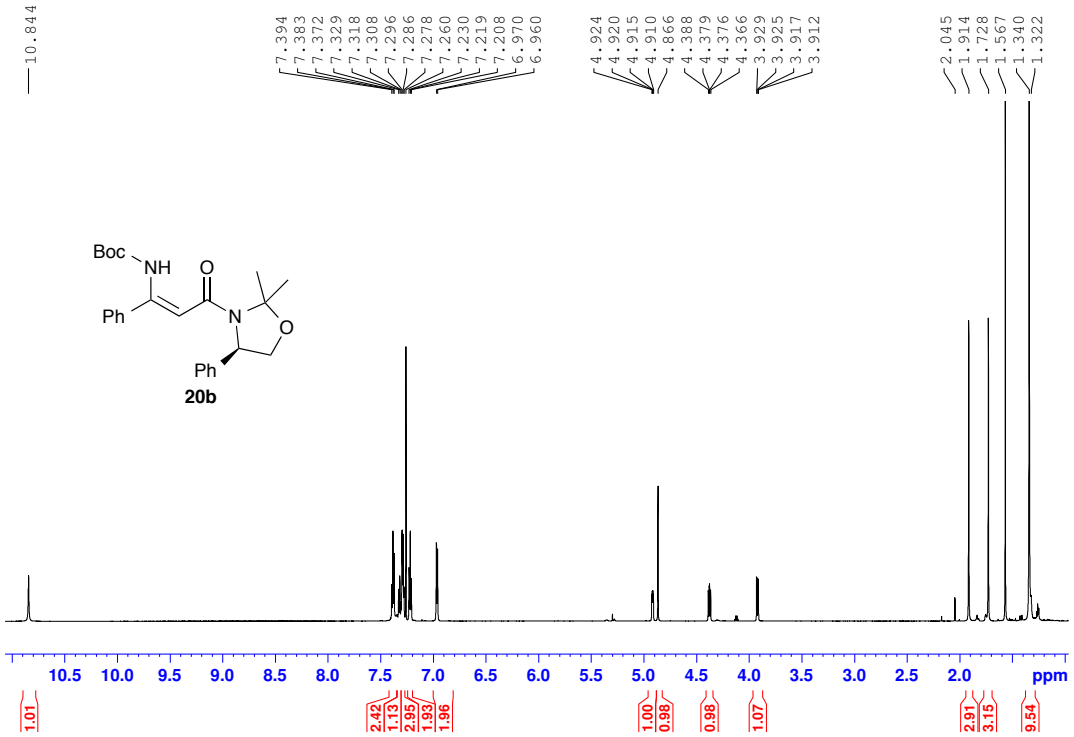
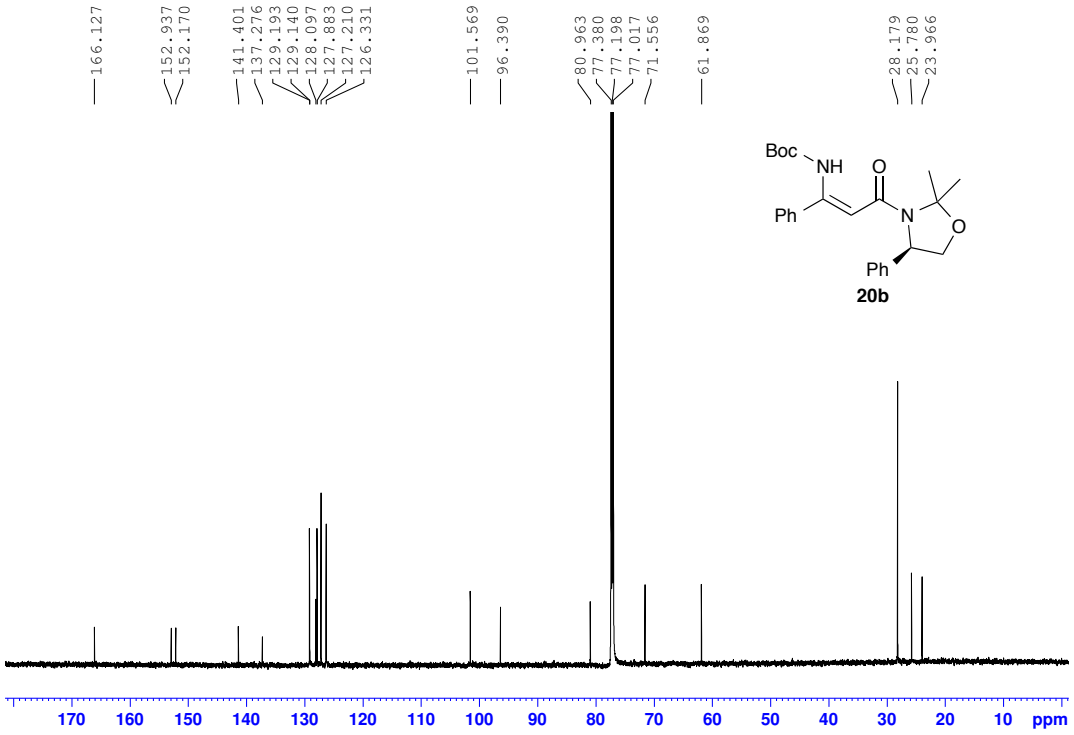
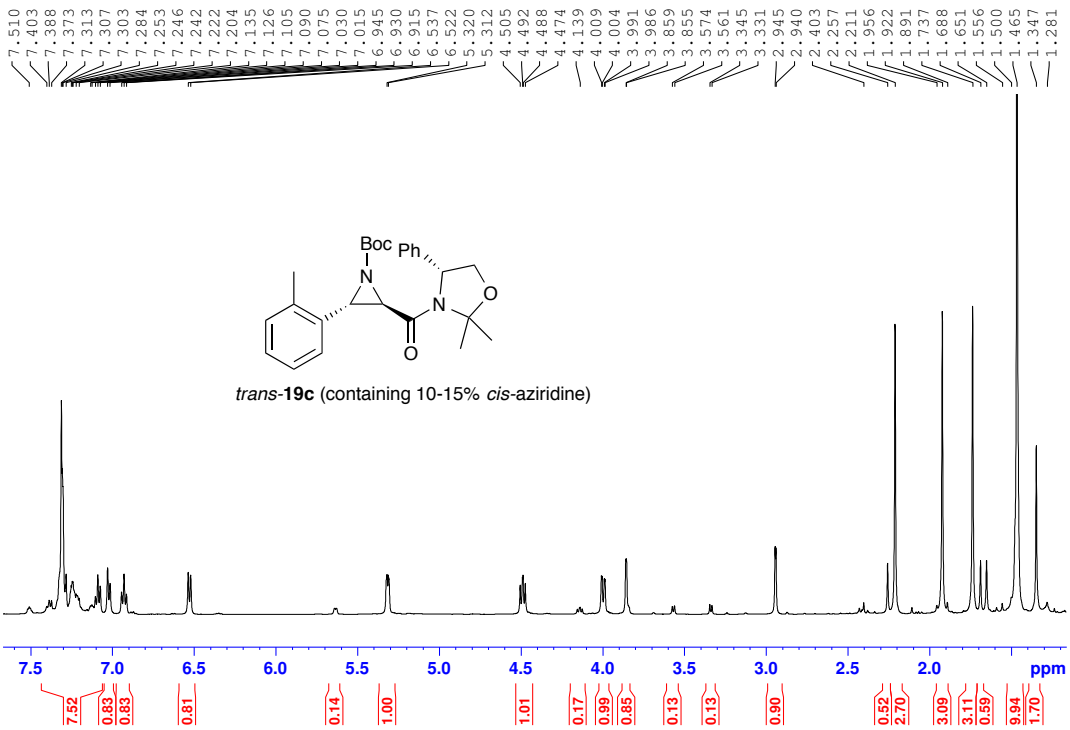
7.377
7.371
7.364
7.284
7.255
7.247
7.243
7.233
7.226
7.222
7.218
7.214
7.169
7.050
7.046
7.039
7.032
5.321
5.297
5.293
5.284
5.280
4.308
4.295
4.290
4.277
3.883
3.878
3.865
3.860
3.340
3.327
3.278
3.264
2.194
1.911
1.735
1.707
1.638
1.625
1.566
1.547
1.515
1.496
1.475
1.457
1.431
1.413
1.373
1.367
1.363
1.353
1.346
1.277
1.266
1.238
1.234
traces of impure cis-19b isolated during purification of trans-19b
Boc
Ph
N
Ph
N
O
O
impure cis-19b
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
ppm
3.81
4.62
1.83
1.00
1.04
1.07
0.86
0.71
2.60
3.03
8.61

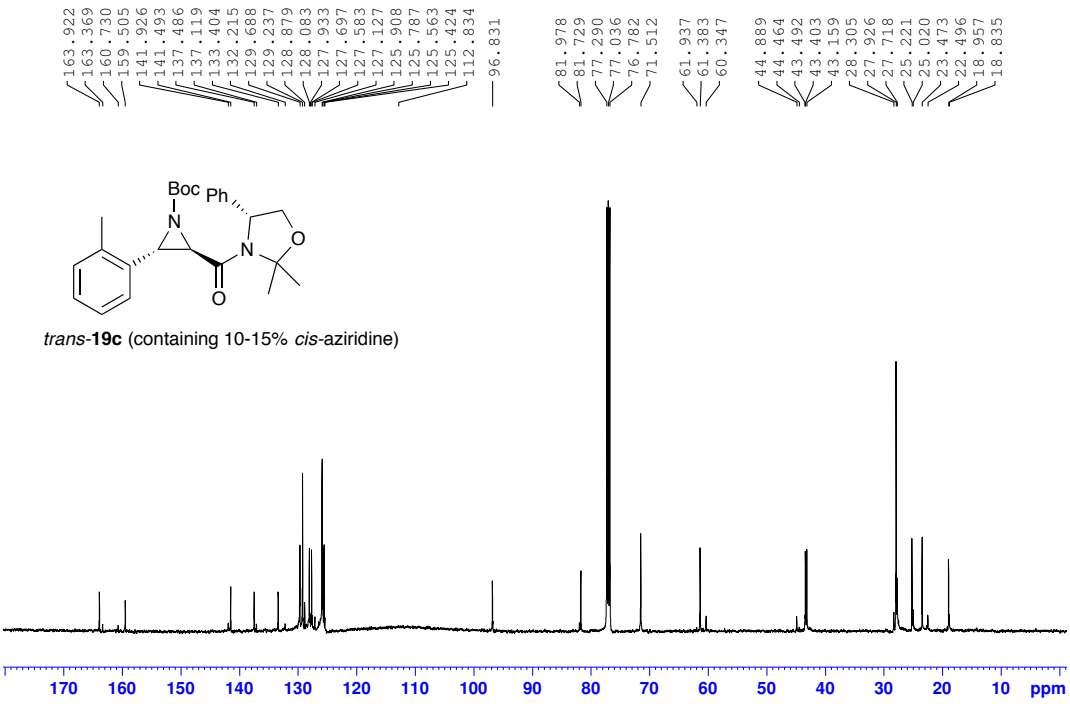

162.137
161.027
141.694
132.962
129.023
128.610
128.369
128.039
127.851
127.810
127.604
126.392
125.785
125.570
121.335
119.403
114.285
113.627
112.378
110.720
107.428
106.160
96.772
82.110
77.279
77.025
76.771
71.853
71.622
61.113
60.814
58.077
45.654
44.493
30.945
28.281
27.842
25.066
24.856
23.943
22.890
traces of impure cis-19b
Boc
Ph
N
Ph
N
O
O
impure cis-19b
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


10.844
7.394
7.383
7.372
7.329
7.318
7.308
7.296
7.286
7.278
7.260
7.230
7.219
7.208
6.970
6.960
4.924
4.920
4.915
4.910
4.866
4.388
4.379
4.376
4.366
3.929
3.925
3.917
3.912
2.045
1.914
1.728
1.567
1.340
1.322
Boc
NH
O
Ph
N
O
Ph
20b
10.5 10.0 9.5 9.0 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 ppm
1.01
2.42
1.13
2.95
1.93
1.96
1.00
0.98
0.98
1.07
2.91
3.15
9.54

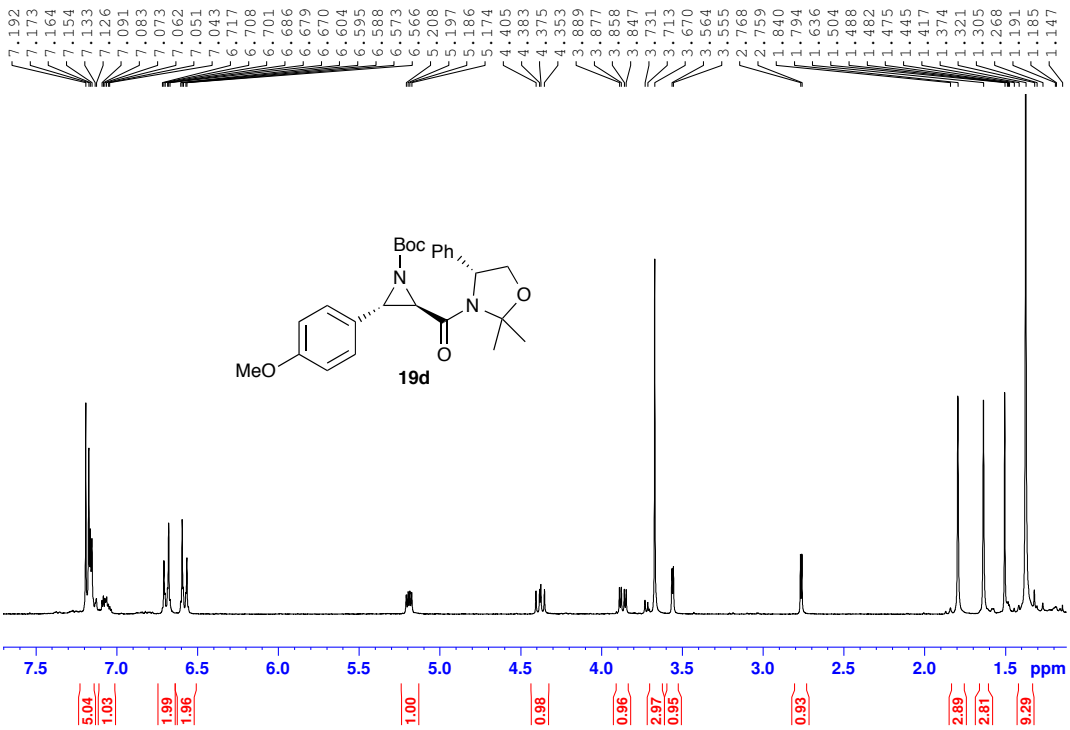

166.127
152.937
152.170
141.401
137.276
129.193
129.140
128.097
127.883
127.210
126.331
101.569
96.390
80.963
77.380
77.198
77.017
71.556
61.869
28.179
25.780
23.966
Boc
NH
O
Ph
N
O
Ph
20b
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

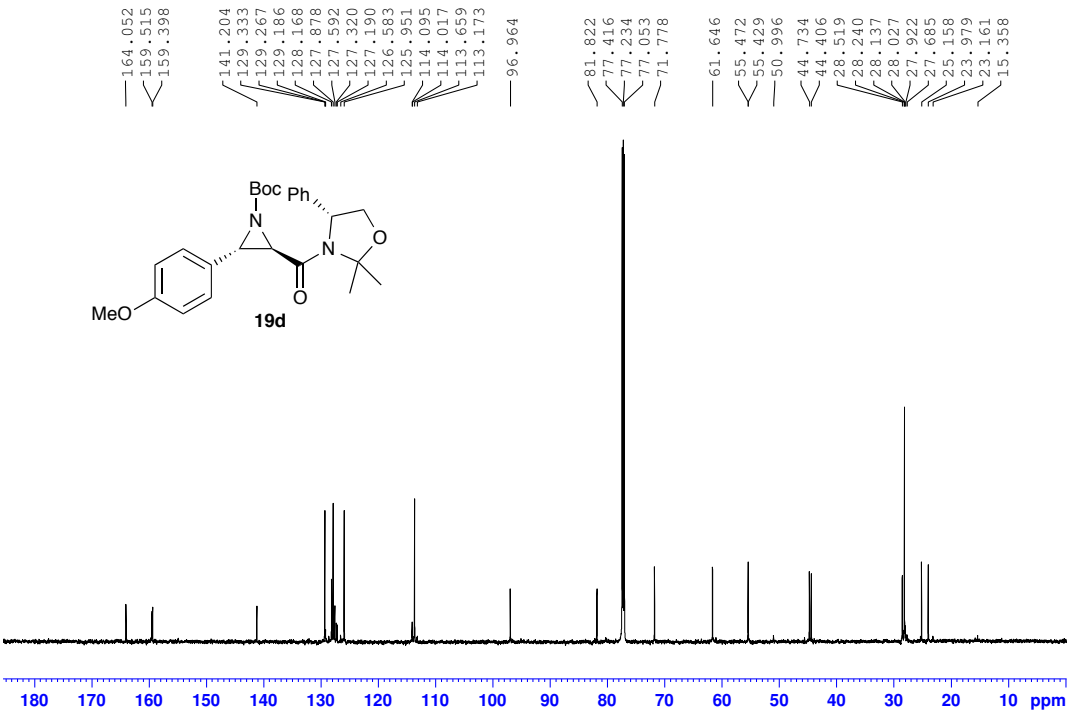


trans-**19c** (containing 10-15% *cis*-aziridine)



trans-**19c** (containing 10-15% *cis*-aziridine)


7.192
7.173
7.164
7.154
7.133
7.126
7.091
7.083
7.073
7.062
7.051
7.043
6.717
6.708
6.701
6.686
6.679
6.670
6.604
6.595
6.588
6.573
6.566
5.208
5.197
5.186
5.174
4.405
4.383
4.375
4.353
3.889
3.877
3.858
3.847
3.731
3.713
3.670
3.564
3.555
2.768
2.759
1.840
1.794
1.636
1.504
1.488
1.482
1.475
1.445
1.417
1.374
1.321
1.305
1.268
1.191
1.185
1.147
Boc
Ph
N
N
O
O
MeO
19d
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
ppm
5.04
1.03
1.99
1.96
1.00
0.98
0.96
2.97
0.95
0.93
2.89
2.81
9.29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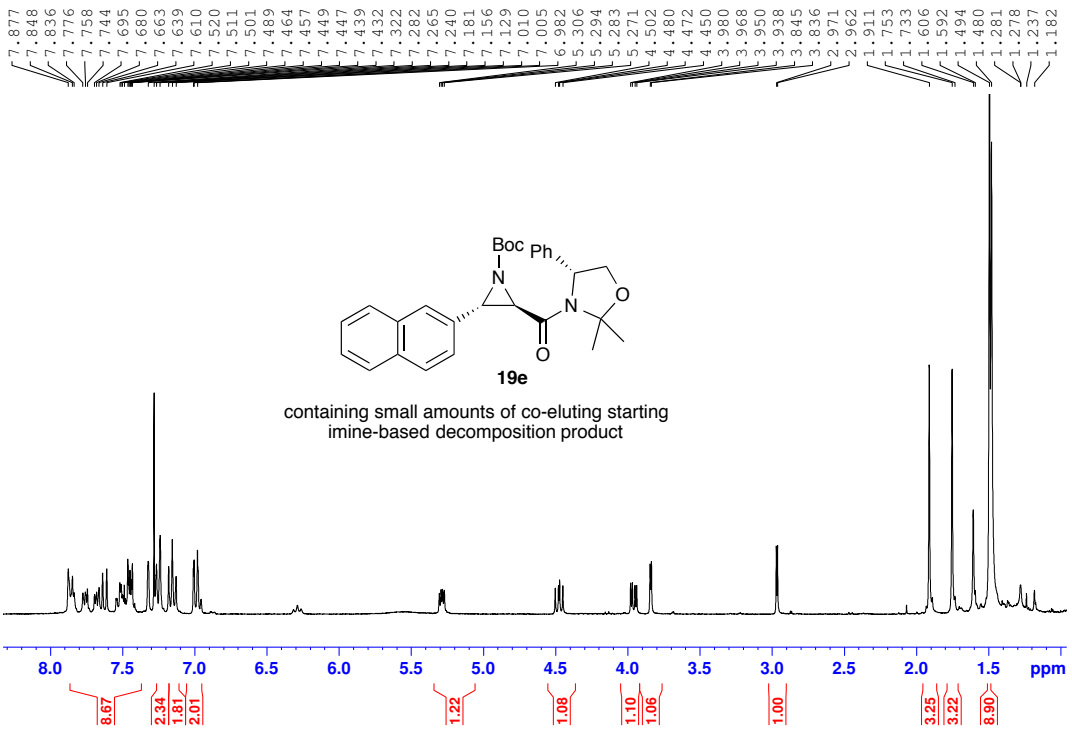
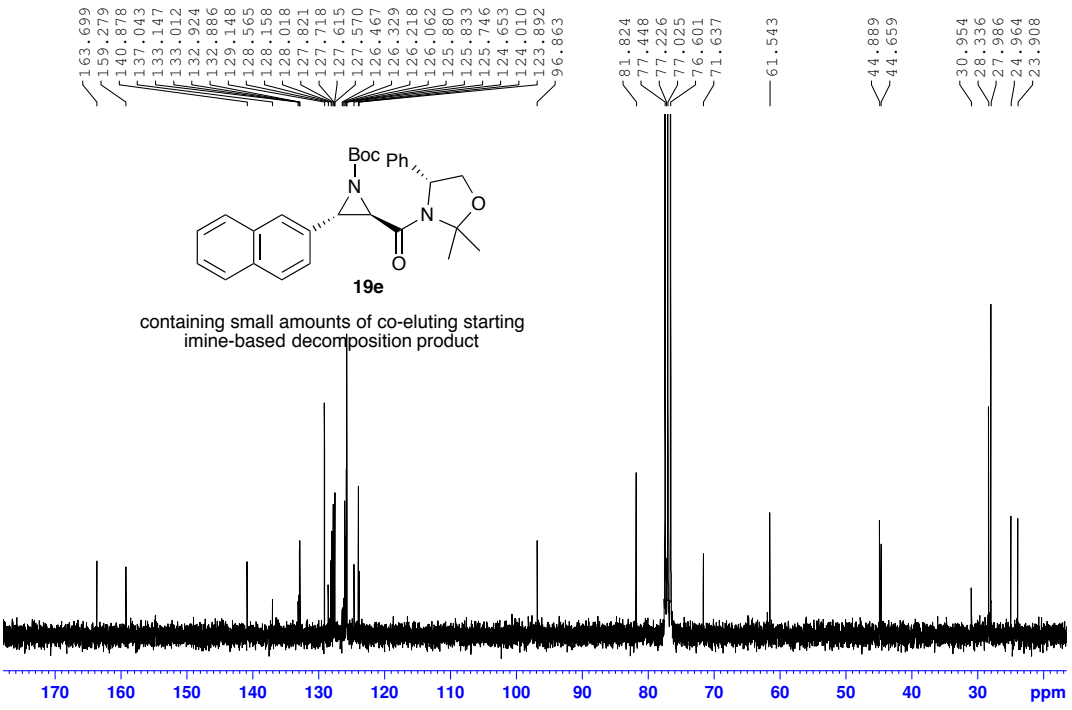
159.515
159.398
141.204
129.333
129.267
129.186
128.168
127.878
127.592
127.320
127.190
126.583
125.951
114.095
114.017
113.659
113.173
96.964
81.822
77.416
77.234
77.053
71.778
61.646
55.472
55.429
50.996
44.734
44.406
28.519
28.240
28.137
28.027
27.922
27.685
25.158
23.979
23.161
15.358
Boc
Ph
N
N
O
O
MeO
19d
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



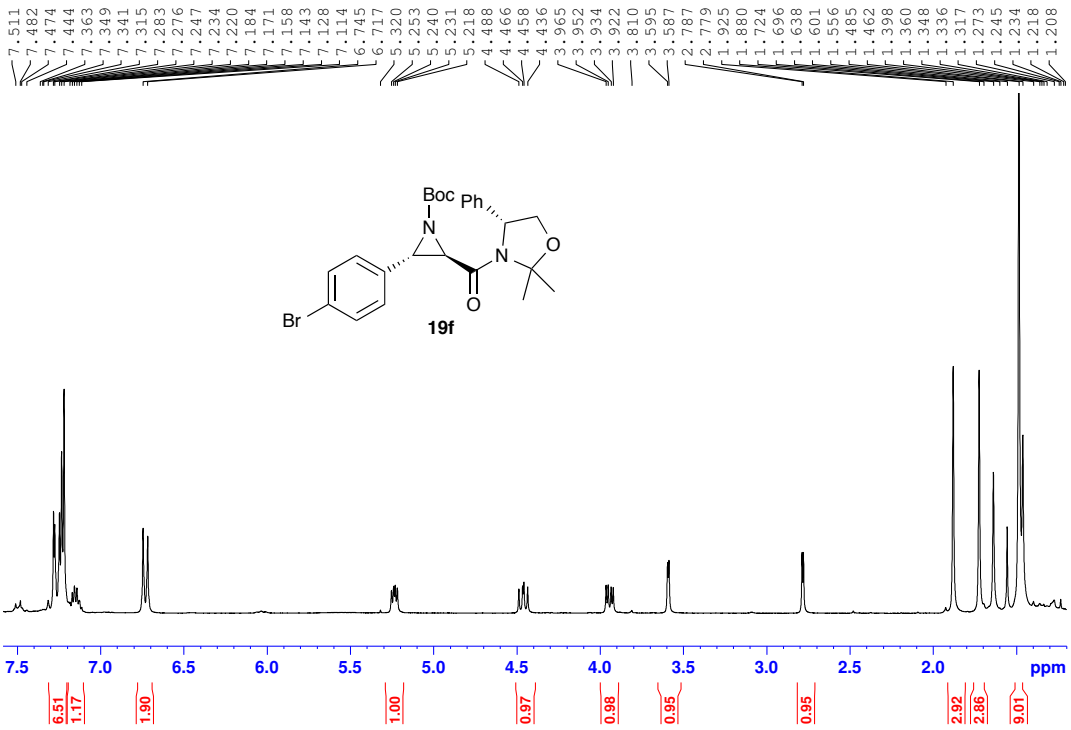
19e

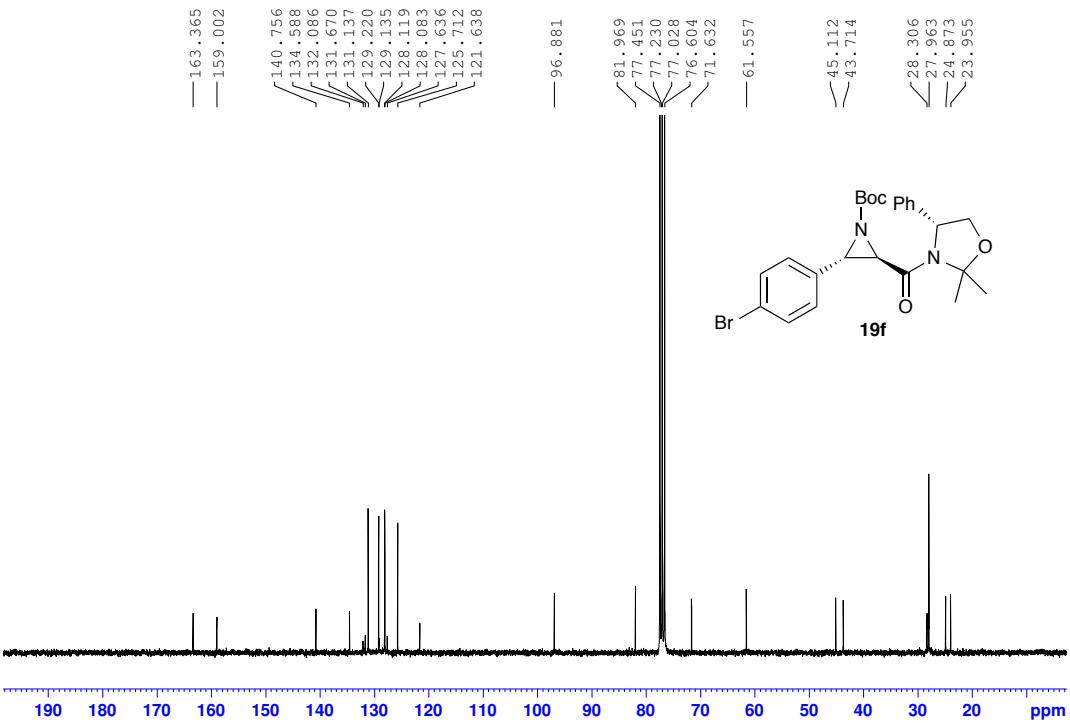
containing small amounts of co-eluting starting imine-based decomposition product



19e

containing small amounts of co-eluting starting imine-based decomposition product


7.511
7.482
7.474
7.444
7.363
7.349
7.341
7.315
7.283
7.276
7.247
7.234
7.220
7.184
7.171
7.158
7.143
7.128
7.114
6.745
6.717
5.320
5.253
5.240
5.231
5.218
4.488
4.466
4.458
4.436
3.965
3.952
3.934
3.922
3.810
3.595
3.587
2.787
2.779
1.925
1.880
1.724
1.696
1.638
1.601
1.556
1.485
1.462
1.398
1.360
1.348
1.336
1.317
1.273
1.245
1.234
1.218
1.208
Boc
Ph
N
N
O
O
Br
19f
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
6.51
1.17
1.90
1.00
0.97
0.98
0.95
0.95
2.92
2.86
9.01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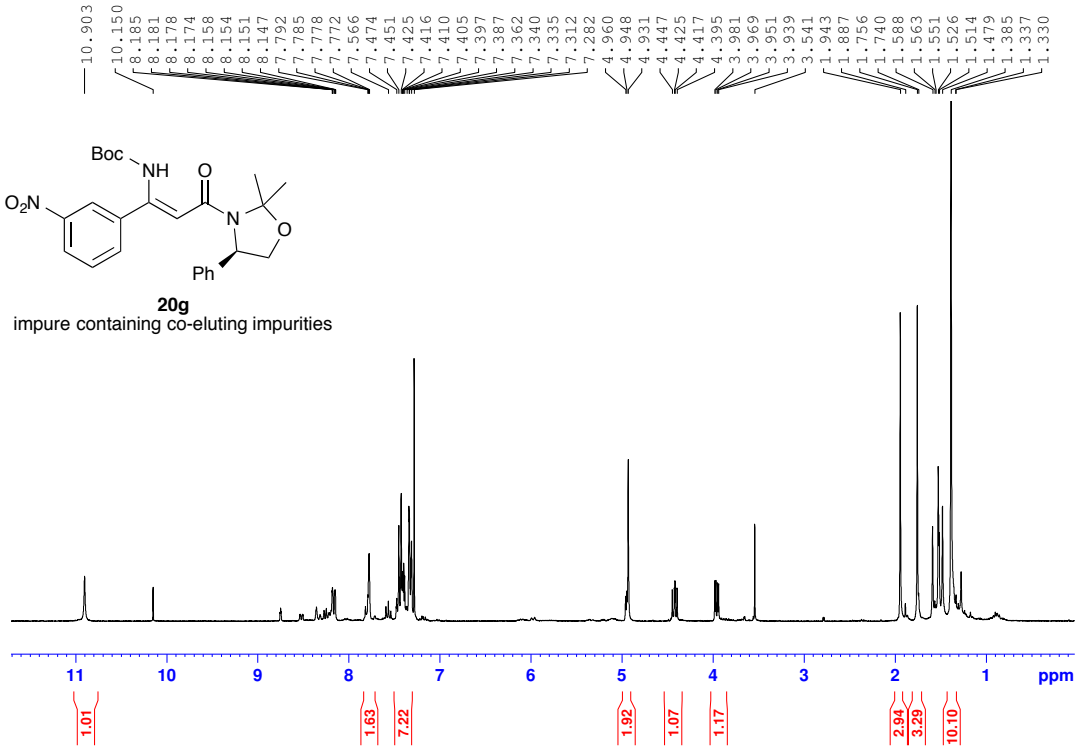
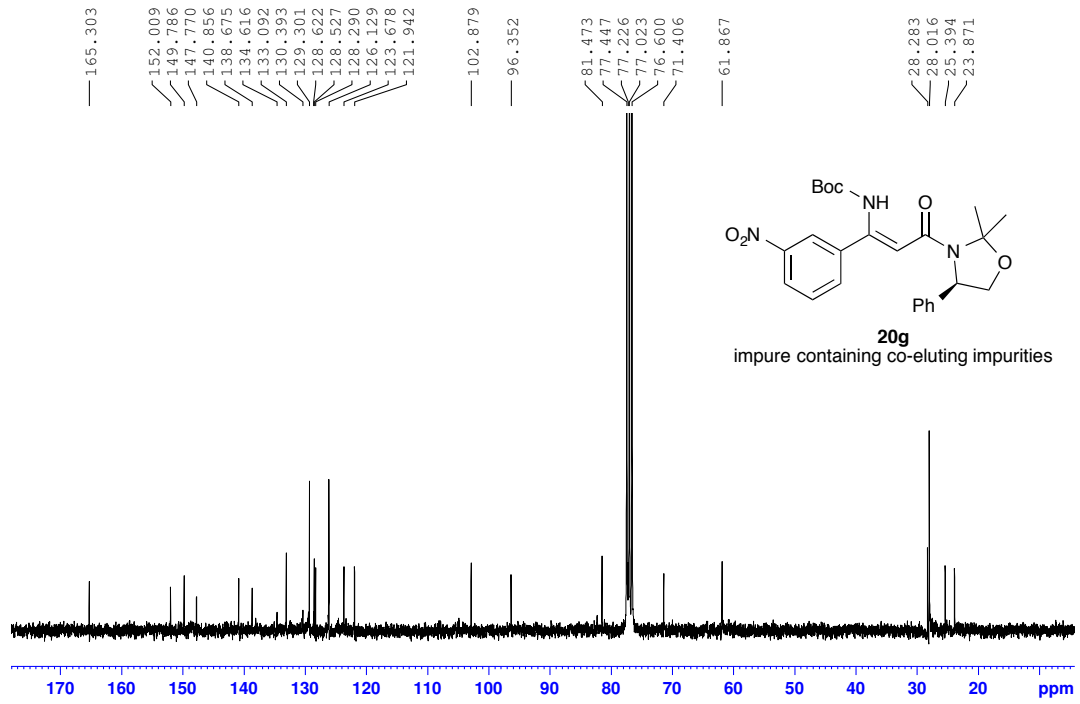
134.588
132.086
131.670
131.137
129.220
129.135
128.119
128.083
127.636
125.712
121.638
96.881
81.969
77.451
77.230
77.028
76.604
71.632
61.557
45.112
43.714
28.306
27.963
24.873
23.955
Boc
Ph
N
N
O
O
Br
19f
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



20g
impure containing co-eluting impurities



20g
impure containing co-eluting impurities