Electronic Supplementary Information

for

Diastereoselective synthesis of propargylic N-hydroxylamines via NHC-copper(I) halide-catalyzed reaction of terminal alkynes with chiral nitrones on water

Łukasz Woźniak, Olga Krajewska-Staszewska and Michał Michalak

Institute of Organic Chemistry, Polish Academy of Sciences

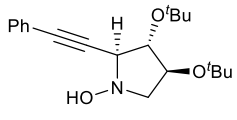
Kasprzaka 44/52, 01-224 Warsaw, Poland

General remarks

NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 solutions (unless indicated otherwise); chemical shifts are quoted on the δ scale, ppm, with the solvent signal as the internal standard ($CHCl_3$, ^{1}H NMR 7.26 ppm; $CDCl_3$, ^{13}C NMR 77.00 ppm, DMSO-d_6 2.50 ppm, ^{13}C NMR 39.40 ppm). High resolution mass spectra (HRMS) were taken using EI technique or electrospray ionisation (ESI). Column chromatography was performed on Merck silica gel 60, 230-400 mesh. TLC was performed on aluminum sheets, Merck 60F 254. Anhydrous solvents were obtained by distillation over $CaCl_2$ (CH_2Cl_2) or Na/benzophenone (THF, hexane).

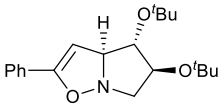
Air-sensitive reactions were performed in flame-dried glassware under argon. Organic extracts were dried and solvents were evaporated in a rotary evaporator. Reagents were used as they were purchased unless otherwise indicated. Phenylacetylene (**2a**), 1-ethynyl-4-fluorobenzene (**2b**), 1-ethynyl-4-methoxybenzene (**2c**), 1-ethynyl-2-methoxybenzene (**2d**), 4-ethynyl-*N*,*N*-dimethylaniline (**2e**) and 3-ethynylthiophene (**2f**) were commercially available from Aldrich. 1-Ethynyl-4-nitrobenzene (**2h**)[1] and benzyl but-3-yn-1yl ether (**8**)[2] were prepared followed by literature procedures. $[IMes]_2CuPF_6$ were commercially available from Aldrich and used as received. SIMesCuCl,[3] SIMesCuBr,[4] IMesCuCl,[3] IMesCuBr,[5] SIPrCuCl,[3] SIPrCuBr,[6] SIPrCuI,[6] IPrCuCl,[3] IPrCuBr,[6] IPrCuI,[6] $[ICy]_2CuPF_6$,[7] and $[IPr]_2CuPF_6$[8] were prepared followed by literature procedure. Nitrones **1a**,[9] **1b**,[10] **1c**[11] and **1d**[12] were prepared followed by literature procedures.

General procedure for synthesis of propargylic *N*-hydroxylamine: To a solution (or suspension) of nitrone (1 eq.) in degassed water (0.2 M), acetylene (1.2 eq.), copper catalyst (5 mol%) and Et_3N or TMG (*N*,*N*,*N*',*N*'-tetramethylguanidine, 1.0 eq.) were added at rt as follows. The biphasic mixture was stirred for indicated time. Then reaction mixture was diluted with EtOAc (15 mL per 1 mmol of used nitrone), and the aqueous phase was separated and extracted with two additional portions of EtOAc. The combined extracts were washed with brine, dried over Na_2SO_4 and evaporated. The residue was chromatographed on silica (silica : crude reaction mixture = 30 : 1 w/w) using an appropriate eluting system to afford product.

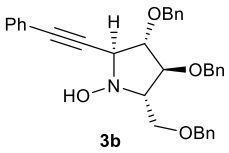


3a

(2*S*,3*S*,4*S*)-3,4-di-*tert*-Butoxy-2-(phenylethynyl)pyrrolidin-1-ol (3a) was obtained according to general procedure using nitrone **1a** (229. 3 mg, 1.0 mmol), phenylacetylene (130 μL, 1.2 mmol), Et_3N (130 μL, 1.0 mmol) and SIPrCuI (29.1 mg, 0.05 mmol, 5 mol%). The crude product was chromatographed (10 g of silica, 15% EtOAc/*n*-hexanes) to give a colourless oil (318.7 mg, 96%). $[\alpha]_D^{25}$ = 39.4 (c 1.2, $CHCl_3$); IR (film): 3373, 2975, 2933, 2871, 1599 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): 7.47-7.40 (m, 2H), 7.32-7.27 (m, 3H), 4.06 (dd, *J* = 6.0, 5.6 Hz, 1H), 3.99-3.95 (m, 1H), 3.73 (br s, 1H), 3.23-3.17 (m, 2H), 1.26 (s, 9H), 1.18 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): 131.7, 128.2, 128.1, 123.0, 86.9, 85.5, 82.8, 77.2, 77.0, 76.8, 76.0, 74.6, 74.0, 66.4, 62.9, 28.8, 28.5; HRMS (ESI) *m/z* calcd for $C_{20}H_{29}NO_3Na$ $[M+Na]^+$ 354.2040; found 354.2023. To further confirm the structure of **3a**, propargylic N-hydroxylamine was transformed to respective dihydroisoxazole by gold-catalyzed cyclization[13] (see below).

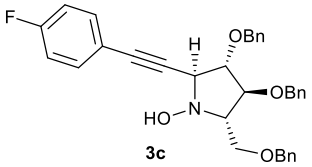


(1*S*,2*S*,7a*S*)-1,2-Di-*tert*-butoxy-6-phenyl-2,3,5,7a-tetrahydro-1H-pyrrolizine To a solution of propargylic N-hydroxylamine 3a (149.2 mg, 0.45 mmol) in DCM (4.5 mL), $AuCl_4{\cdot}2H_2O$ (9.1 mg, 0.023 mmol, 5 mol%) and DMAP (16.5 mg, 30 mol%, 0.135 mmol) were added sequantialy and the reaction mixture was heated under reflux for 2h under atmosphere of argon. Then solvent was evaporated and the residue was chromatographed on silica (20% Et2O/n-pentane) to give a light-yellow oil (118.5 mg, 79%). $[\alpha]_D^{25}$ = 59.7 (c 1.2, $CHCl_3$); IR (film): 3438, 2974, 1685, 1651 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): 7.51-7.46 (m, 2H), 7.34-7.27 (m, 3H), 5.26 (d, *J* = 1.8 Hz, 1H), 4.10-4.07 (m, 1H), 4.42-4.39 (m, 1H), 3.95-3.90 (m, 1H), 3.89 (dd, *J* = 5.9, 4.1 Hz, 1H), 3.62 (dd, *J* = 9.7, 5.6 Hz, 1H), 3.06 (dd, *J* = 9.4, 9.7 Hz, 1H), 1.21 (s, 9H), 1.16 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): 152.8, 129.0, 128.8, 128.3, 125.6, 94.4, 80.9, 76.3, 74.0, 73.8, 61.1, 28.1, 28.5; HRMS (ESI) *m/z* calcd for $C_{20}H_{30}NO_3$ $[M+H]^+$ 332.2220; found 322.2217.



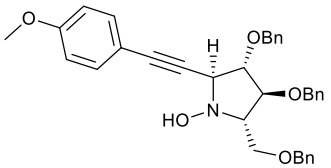
(2*S*,3*S*,4*S*,5*S*)-3,4-Bis(benzyloxy)-2-[(benzyloxy)methyl]-5-(phenylethynyl)pyrrolidin-1-ol (3b) was obtained according to general procedure using nitrone (**1b**) (208.8 mg, 0.5 mmol), phenylacetylene (**2a**) (66 μL, 0.6 mmol), Et_3N (70 μL, 0.5 mmol) and SIPrCuI (14.5 mg, 0.025

mmol). The crude product was chromatographed on silica (15% EtOAc/*n*-hexanes) to give a colourless oil (244.5 mg, 94%). $[\alpha]_D^{25}$ = -26.2 (c 1.2, $CHCl_3$); IR (film): 3370, 3031, 2865, 1953 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6): 8.30 (s, 1H), 7.42-7.24 (m, 20H), 4.67-4.47 (m, 6H), 4.29 (d, *J* = 4.3 Hz, 1H), 4.10-4.07 (m, 1H), 3.92 (dd, *J* = 5.8, 2.2 Hz, 1H), 3.70 (dd, *J* = 10.2, 3.7 Hz, 1H), 3.65 (dd, *J* = 10.2, 5.1 Hz, 1H), 3.30-3.26 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): 138.9, 138.6, 138.2, 131.8, 129.1, 128.9, 128.7, 128.6, 128.6, 128.3, 128.1, 128.0, 127.9, 127.9, 127.8, 122.9, 87.5, 86.4, 86.0, 83.3, 79.6, 72.9, 71.4, 71.0, 69.5, 68.4, 62.0; HRMS (ESI) *m/z* calcd for $C_{34}H_{33}NO_4Na$ $[M+Na]^+$ 542.2302; found 542.2282.



3c

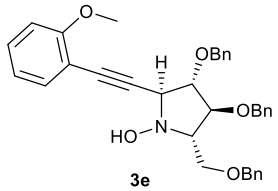
(2*S*,3*S*,4*S*,5*S*)-3,4-bis(benzyloxy)-2-[(benzyloxy)methyl]-5-[(4-fluorophenyl) ethynyl]pyrrolidin-1-ol (3c) was obtained according to general procedure I using nitrone **1b** (208.8 mg, 0.5 mmol), 1-ethynyl-4-fluorobenzene (**2b**) (69 μL, 0.6 mmol, 1.2 eq.), Et_3N (70 μL, 0.5 mmol, 1.0 eq.) and SIPrCuI (14.5 mg, 0.025 mmol, 5 mol%). The crude product was chromatographed on silica (DCM) to give a colourless oil (263.9 mg, 98%). $[\alpha]_D^{25}$ = -27.0 (c 0.7, $CHCl_3$); IR (film): 3371, 3064, 3031, 2923, 2865, 1600, 1506 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6): 8.32 (s, 1H), 7.48-7.44 (m, 2H), 7.38-7.26 (m, 15H), 7.24-7.18 (m, 2H), 4.67-4.47 (m, 6H), 4.29 (br s, 1H), 4.11-4.08 (m, 1H), 3.95-3.91 (m, 1H), 3.73-3.69 (m, 1H), 3.68-3.64 (m, 1H), 3.31-3.27 (m, 1H); ^{13}C NMR (150 MHz, DMSO-d_6): 162.2 (d, J_{CF} = 247.2 Hz), 138.9, 138.6, 138.2, 134.1 (d, J_{CF} = 8.5 Hz), 128.7, 128.6, 128.3, 128.1, 127.9, 127.9, 127.8, 119.4 (d, J_{CF} = 3.0 Hz), 116.3 (d, J_{CF} = 22.1 Hz), 87.3, 86.4, 85.0, 83.3, 79.6, 71.4, 71.1, 69.5, 68.4, 62.0; ^{19}F NMR (470 MHz, $CDCl_3$): -110.7. HRMS (ESI) *m/z* calcd for $C_{34}H_{32}FNO_4Na$ $[M+Na]^+$ 560.2208; found 560.2188.



3d

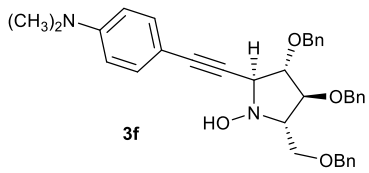
(2*S*,3*S*,4*S*,5*S*)-3,4-bis(benzyloxy)-2-[(benzyloxy)methyl]-5-[(4-methoxyphenyl)ethynyl]pyrrolidin-1-ol (3d) was obtained according to general procedure

using nitrone **1b** (208.8 mg, 0.5 mmol), 1-ethynyl-4-methoxybenzene (**2c**) (78 μL, 0.6 mmol), Et_3N (70 μL, 0.5 mmol) and SIPrCuI (14.5 mg, 0.025 mmol). The crude product was chromatographed on silica (2% Et_2O/DCM) to give a colourless oil (266.5 mg, 97%). $[\alpha]_D^{25}$ = -28.8 (c 1.0, CH_3Cl); IR (film): 3392, 2923, 2222, 1606, 1510 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): 8.26 (s, 1H), 7.38-7.24 (m, 17H), 6.96-6.90 (m, 2H), 4.64 (d, *J* = 12Hz, 1H), 4.59-4.46 (m, 5H), 4.26 (d, *J* = 2.4 Hz, 1H), 4.10-4.05 (m, 1H), 3.91 (dd, *J* = 5.4, 2.4 Hz, 1H), 3.77 (s, 3H), 3.70 (dd, *J* = 10.2, 3.6 Hz, 1H), 3.65 (dd, *J* = 10.2, 4.8 Hz, 1H), 3.30-3.25 (m, 1H); ^{13}C NMR (150 MHz, DMSO) δ 159.7, 138.9, 138.6, 138.3, 133.3, 128.7, 128.6, 128.3, 128.0, 127.9, 127.9, 127.8, 115.0, 114.6, 86.5, 85.9, 85.8, 83.3, 79.6, 72.9, 71.3, 71.0, 69.4, 68.4, 62.1, 55.6; HRMS (ESI) *m/z* calcd for $C_{35}H_{35}NO_5Na$ $[M+Na]^+$ 572.2407; found: 572.2398.



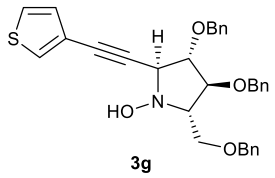
3e

(2*S*,3*S*,4*S*,5*S*)-3,4-bis(benzyloxy)-2-[(benzyloxy)methyl]-5-[(2-methoxyphenyl)ethynyl]pyrrolidin-1-ol (3e) was obtained according to general procedure I using nitrone **1b** (104.4 mg, 0.25 mmol), 1-etynyl-2-methoxybenzene (**2d**) (39 μL, 0.30 mmol), Et_3N (35 μL, 0.25 mmol) and SIPrCuI (7.6 mg, 0.013 mmol, 5 mol%). The crude product was chromatographed on silica (35% Et_2O/*n*-pentane) to give a colourless oil (126.5 mg, 92%). $[\alpha]_D^{25}$ = -41.8 (c 1.0, $CHCl_3$); IR (film): 3352, 3062, 3030, 2919, 2866, 1596, 1576, 1494, 1454 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6): 8.22 (s, 1H), 7.35-7.21 (m, 17H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.91-6.86 (m, 1H), 4.65-4.43 (m, 6H), 4.25 (d, *J* = 3.0 Hz, 1H), 4.08-4.04 (m, 1H), 3.89 (dd, *J* = 6.0, 2.4 Hz, 1H), 3.75 (s, 3H), 3.67 (dd, *J* = 10.2, 3.8 Hz, 1H), 3.62 (dd, *J* = 10.2, 5.1 Hz, 1H), 3.35-3.29 (m, 1H); ^{13}C NMR (150 MHz, DMSO-d_6): 160.2, 138.9, 138.6, 138.3, 133.7, 130.4, 128.7, 128.6, 128.6, 128.4, 128.1, 128.0, 127.9, 127.8, 120.8, 112.0, 111.8, 91.2, 86.5, 83.4, 72.9, 71.4, 71.0, 69.4, 68.4, 62.3, 56.0; HRMS (ESI) *m/z* calcd for $C_{35}H_{35}NO_5Na$ $[M+Na]^+$ 572.2407; found: 572.2431.



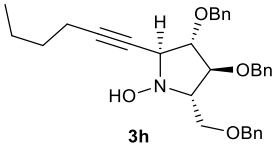
3f

(2*S*,3*S*,4*S*,5*S*)-3,4-Bis(benzyloxy)-2-[(benzyloxy)methyl]-5-{[4-(dimethylamino)phenyl]ethynyl}cpyrrolidin-1-ol (3f) was obtained according to general procedure I using nitrone **1b** (208.8 mg, 0.5 mmol), 4-ethynyl-*N*,*N*-dimethylaniline (**2e**) (87.1 mg, 0.6 mmol), Et_3N (70 μL, 0.5 mmol) and SIPrCuI (14.5 mg, 0.025 mmol, 5 mol%). The crude product was chromatographed on silica (1% Et_3N in 40% Et_2O/*n*-hexanes to 50% Et_2O/hexanes) to give colourless oil (206.7 mg, 73%). $[\alpha]_D^{25}$ = -40.0 (c 0.9, $CHCl_3$); IR (film): 3222, 3062, 3030, 2863, 2217, 1609, 1522 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6): 8.18 (s, 1H), 7.33-7.24 (m, 15H), 7.20-7.17 (m, 2H), 6.65-6.61 (m, 2H), 4.63-4.44 (m, 6H), 4.21 (d, *J* = 2.8 Hz, 1H), 4.04-4.01 (m, 1H), 3.87 (dd, *J* = 5.8, 2.2 Hz, 1H), 3.67 (dd, *J* = 10.3, 3.7 Hz, 1H), 3.61 (dd, *J* = 10.3, 5.1 Hz, 1H), 3.26-3.22 (m, 1H), 2.89 (s, 6H); ^{13}C NMR (150 MHz, DMSO-d_6): 150.3, 132.8, 128.7, 128.6, 128.6, 128.3, 128.0, 127.9, 127.9, 127.8, 112.2, 109.4, 87.0, 86.6, 84.7, 83.3, 72.9, 71.3, 71.0, 69.4, 68.4, 62.2. HRMS (ESI) *m/z* calcd for $C_{36}H_{38}N_2O_4Na$ $[M+Na]^+$ 585.2724; found: 585.2736.



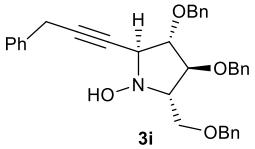
3g

(2*S*,3*S*,4*S*,5*S*)-3,4-Bis(benzyloxy)-2-[(benzyloxy)methyl]-5-(thiophen-3-ylethynyl)pyrrolidin-1-ol (3g) was synthesized according to general procedure using nitrone **1b** (104.4 mg, 0.25 mmol), 3-ethynylthiophene (**2f**) (33 μL, 0.30 mmol), Et_3N (35 μL, 0.25 mmol) and SIPrCuI (7.6 mg, 0.013 mmol). The crude product was chromatographed on silica (40% Et_2O/*n*-pentane) to give a colourless oil (111.8 mg, 85%). $[\alpha]_D^{25}$ = -13.9 (c 2.0, DCM); IR (film): 3373, 2924, 2856, 2221, 1598, 1490, 1454 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6): 8.26 (s, 1H), 7.70-7.67 (m, 1H), 7.57-7.54 (m, 1H), 7.35-7.21 (m, 15H), 7.11-7.07 (m, 1H), 4.63-4.44 (m, 6H), 2.24 (d, *J* = 2.5 Hz, 1H), 4.06-4.02 (m, 1H), 3.88 (dd, *J* = 5.8, 2.1 Hz, 1H), 3.67 (dd, *J* = 10.2, 3.7 Hz, 1H), 3.62 (dd, *J* = 10.2, 5.0 Hz, 1H), 3.26-3.20 (m, 1H); ^{13}C NMR (150 MHz, DMSO-d_6): 138.9, 138.6, 138.2, 130.1, 129.9, 128.7, 128.6, 128.3, 128.1, 127.9, 127.9, 127.8, 127.1, 121.8, 86.8, 86.4, 83.2, 81.4, 72.9, 71.4, 71.1, 69.4, 68.4, 62.1. HRMS (ESI) *m/z* calcd for $C_{32}H_{31}SNO_4Na$ $[M+Na]^+$ 548.1866; found 548.1882.



3h

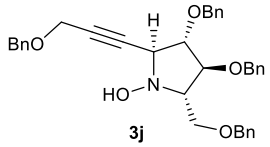
(2*S*,3*S*,4*S*,5*S*)-3,4-bis(Benzyloxy)-2-[(benzyloxy)methyl]-5-(hex-1-yn-1-yl)pyrrolidin-1-ol (3h) was obtained according to modified general procedure using nitrone **1b** (208.8 mg, 0.5 mmol), hex-1-yn (**2i**) (230 μL, 2.0 mmol, 4.0 eq), TMG (63 μL, 0.5 mmol, 1.0 eq) and SIPrCuI (14.5 mg, 0.025 mmol, 5 mol%). The crude product was chromatographed on silica (15% Et_2O/*n*-hexanes) to give a colourless oil (204.3 mg, 82%). $[\alpha]_D^{25}$ = -5.2 (c 1.4, $CHCl_3$); IR (film): 3377, 3063, 3030, 2955, 2930, 2869, 1496, 1454 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6): 8.05 (s, 1H), 7.35-7.20 (m, 15H), 4.58-4.42 (m, 6H), 3.98 (d, *J* = 1.8 Hz, 1H), 3.91-3.88 (m, 1H), 3.81 (dd, *J* = 6.0, 2.0 Hz, 1H), 3.64 (dd, *J* = 10.2, 3.7 Hz, 1H), 3.58 (dd, *J* = 10.2, 5.1 Hz, 1H), 3.19-3.14 (m, 1H), 2.20-2.14 (m, 2H), 1.42-1.31 (m, 4H), 0.82 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, DMSO-d_6): 139.0, 138.7, 138.3, 128.7, 128.6, 128.6, 128.3, 128.0, 128.0, 127.9, 127.8, 86.7, 86.4, 83.3, 77.6, 72.9, 71.2, 71.1, 69.1, 68.4, 61.7, 30.8, 21.7, 18.3, 13.9; HRMS (ESI) *m/z* calcd. for $C_{32}H_{37}NO_4Na$ $[M+Na]^+$ 522.2615; found: 522.2613.



3i

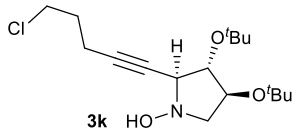
(2*S*,3*S*,4*S*,5*S*)-3,4-bis(benzyloxy)-2-[(benzyloxy)methyl]-5-(3-phenylprop-1-yn-1-yl)pyrrolidin-1-ol (3i) was obtained according to general procedure I using nitrone **1b** (104.4 mg, 0.25 mmol), prop-2-yn-1-ylbenzene (**2j**) (37 μL, 0.30 mmol), TMG (31 μL, 0.25 mmol) and SIPrCuI (7.6 mg, 0.013 mmol). The crude product was chromatographed on silica (35% Et_2O/*n*-pentane) to give a colourless oil (106.0 mg, 79%). $[\alpha]_D^{25}$ = 1.9 (c 1.2, $CHCl_3$); dr >95:5 based on HPLC (40% MTBE/hexanes; 1 mL/min., IA column, DAD detector, 244 nm): major peak 12.8 min (purity >95% based on HPLC); IR (film): 3376, 3062, 3030, 2922, 2865, 1549, 1453 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6): 8.16 (s, 1H), 7.37-7.16 (m, 20H), 4.59-4.43 (m, 6H), 4.08 (d, *J* = 1.9 Hz, 1H), 3.98-3.96 (m, 1H), 3.84 (dd, *J* = 6.0, 1.9 Hz, 1H), 3.68 (s, 2H), 3.65 (dd, *J* = 10.3, 3.1 Hz, 1H), 3.60 (dd, *J* = 10.3, 5.0 Hz, 1H), 3.24-3.19 (m, 1H); ^{13}C NMR (150 MHz, DMSO-d_6): 138.9, 138.6, 138.2, 137.2, 128.7, 128.7, 128.6, 128.6, 128.3, 128.2, 128.0, 127.9, 127.9, 127.8, 126.8,

86.5, 84.2, 83.4, 79.7, 72.9, 71.2, 71.1, 69.3, 68.4, 61.7, 24.7; HRMS (ESI) *m/z* calcd for $C_{35}H_{35}NO_4Na$ $[M+Na]^+$ 556.2458; found 556.2456.



3j

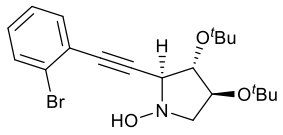
(2*S*,3*S*,4*S*,5*S*)-3,4-bis(benzyloxy)-2-[(benzyloxy)methyl]-5-[3-(benzyloxy)prop-1-yn-1-yl]pyrrolidin-1-ol (3j) was obtained according to general procedure using nitrone **1b** (104.4 mg, 0.25 mmol), ((prop-2-yn-1-yloxy)methyl)benzene (**2k**) (43.9 mg, 0.30 mmol, 1.2 eq.), TMG (31 μL, 0.25 mmol, 1.0 eq.) and SIPrCuI (7.6 mg, 0.013 mmol, 5 mol%). The crude product was chromatographed on silica (40% Et_2O/*n*-pentane) to give a colourless oil (86.8 mg, 62%). $[\alpha]_D^{25}$ = -4.2 (c 0.9, DCM); dr >95:5 based on HPLC (40% MTBE/hexanes; 1 mL/min., IA column, DAD detector): major peak 19.4 min (purity >95% based on HPLC, DAD detector 206 nm); IR (film): 3380, 3062, 3030, 2864, 1496, 1454 cm^{-1}; ^1H NMR (600 MHz, benzene-d_6): 7.29-7.18 (m, 7H), 7.14-6.98 (m, 13H), 6.94 (br s, 1H), 4.51-4.47 (m, 3H), 4.46-4.34 (m, 4H), 4.30-4.21 (m, 3H), 4.16 (dd, *J* = 6.0, 2.4 Hz, 1H), 4.00 (d, *J* = 1.9 Hz, 2H), 3.78-3.70 (m, 2H), 3.66 (dd, *J* = 9.6, 3.6 Hz, 1H); ^{13}C NMR (150 MHz, benzene-d_6): 138.4, 138.4, 138.0, 138.0, 128.2, 128.2, 128.1, 128.0, 127.8, 127.6, 127.4, 127.3, 127.3, 86.8, 83.3, 83.1, 82.7, 73.0, 71.7, 71.0, 69.6, 67.9, 62.2, 57.2. HRMS (ESI) *m/z* calcd for $C_{36}H_{37}NO_5Na$ $[M+Na]^+$ 586.2564; found 586.2581.



3k

(2*S*,3*S*,4*S*)-3,4-di-*tert*-butoxy-2-(5-chloropent-1-yn-1yl)pyrrolidin-1-ol (3k) was obtained according to general procedure (procedure A) using nitrone **1a** (229.0 mg, 1.0 mmol), 5-chloro-pen-1-yne (**2l**) (127 μL, 1.2 mmol), TMG (126 μL, 1.0 mmol, 1.0 mmol) and SIPrCuI (29.0 mg, 0.05 mmol, 5 mol%). The crude product was chromatographed on silica (30% Et_2O/*n*-pentane) to give a colourless oil (208.9 mg, 63%). $[\alpha]_D^{25}$ = 54.1 (c 0.6, CH_3Cl); IR (film): 3381, 2975, 2934, 2871cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6): 8.13 (s, 1H), 3.81-3.76 (m, 1H), 3.74-3.69 (m, 3H), 3.17 (br s, 1H), 2.88 (br d, *J* = 4.6 Hz, 2H), 2.35 (t, *J* = 6.6 Hz, 1H), 2.35 (t, *J* = 6.6 Hz, 1H), 1.90-1.83 (m, 2H), 1.16 (s, 9H), 1.10 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): 82.9, 75.8, 73.9, 73.6, 65.6, 63.6, 44.5, 31.6, 29.1, 28.7, 25.6, 23.9, 16.1; HRMS (ESI) *m/z* calcd for $C_{17}H_{30}NO_3ClNa$ [M+Na]+ 354.1812; found 354.1816.

Procedure B To a soultion of alane [prepared by heating trimethylaluminum (0.2 mL, 2.09 mmol); alkyne **2a** (221 µL mg, 2.09 mmol) and Et_3N (29 µL, 10 mol%, 0.01 mmol) at 60 °C for 6h in hexanes (3 mL), as previously described[14]] in anhydrous hexane (4 mL), a solution of nitrone (114.7 mg, 0.5 mmol) in anhydrous THF (8 mL) was added dropwise at rt, and stirred at this temperature for 16 h. Then reaction mixture was quenched with sat. solution of Rochelle salt (10 mL) and extracted with DCM (3 x 10 mL). The combined organic extracts were dried over Na_2SO_4 and evaporated. The residue was chromatographed on silica (40% Et_2O/*n*-pentane) to give colourless oil (142.6 mg, 85%). Dr 87:13 based on ^{1}H NMR: major isomer 3.33 ppm(t), minor isomer 3.48 ppm (t).

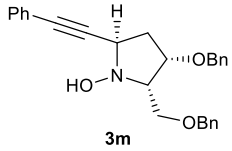


3l

(2*S*,3*S*,4*S*)-2-[(2-Bromophenyl)ethynyl]-3,4-di-*tert*-butoxypyrrolidin-1-ol (3l) was obtained according to general procedure (procedure A) using nitrone **1a** (917.3 mg, 4.0 mmol), 1-ethynyl-2-bromobenzene (**2m**) (869.0 mg, 4.8 mmol), Et_3N (0.56 mL, 4.0 mmol) and SIPrCuI (46.5 mg, 0.08 mmol, 2 mol%). The crude product was chromatographed on silica (35% Et_2O/*n*-pentane) to give a light-yellow oil (1.51 g, 92%). $[\alpha]_D^{25}$ = 36.7 (c 1.1, CH_3Cl); dr >95:5 based on HPLC (40% MTBE/hexanes; 1 mL/min., IA column, DAD detector, 204 nm): major peak 6.6 min., minor peak 7.7 min (purity >95% based on HPLC); IR (film): 3369, 2975, 2933, 2871, 1471cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6): 8.32 (br s, 1H), 7.70-7.67 (m, 1H), 7.55-7.52 (m, 1H), 7.41-7.37 (m, 1H), 7.32-7.28 (m, 1H), 3.93-3.86 (m, 2H), 3.51 (br d, *J* = 4.2 Hz, 1H), 3.02-2.95 (m, 2H), 1.20 (s, 9H), 1.12 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): 134.1, 132.9, 130.6, 128.2, 124.9, 124.8, 94.1, 82.9, 79.6, 76.0, 74.2, 73.8, 66.3, 63.7, 29.1, 28.7. HRMS (ESI) *m/z* calcd for $C_{20}H_{28}NO_3BrNa$ $[M+Na]^+$: 432.1145; found: 432.1128.

Procedure B To a soultion of alane [prepared by heating trimethylaluminum (0.2 mL, 2.09 mmol); alkyne (377.6 mg, 2.08 mmol) and Et_3N (29 µL, 10 mol%, 0.01 mmol) at 60 °C for 6h in hexane (3 mL), as previously described[14]] in anhydrous hexanes (4 mL), a solution of nitrone (114.7 mg, 0.5 mmol) in anhydrous THF (8 mL) was added dropwise at rt, and stirred at this temperature for 10 h (TLC analysis indicated presence of two product R_f = 0.40 and 0.36, 40% Et_2O/*n*-pentane). Then reaction mixture was quenched with sat. solution of Rochelle salt (10 mL) and extracted with DCM (3 x 10 mL). The combined organic extracts were dried over

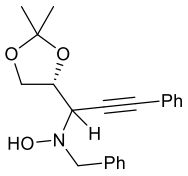
Na_2SO_4 and evaporated. The residue was chromatographed on silica (35% Et_2O/*n*-pentane) to give light yellow oil (159.6 mg, 78%). Dr 88:12 based on HPLC (40% MTBE/hexanes; 1 mL/min., IA column, DAD detector, 204 nm): major peak 6.6 min. (Purity 94% based on HPLC).



3m

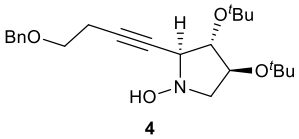
(2*S*,3*S*,5*R*)-3-(benzyloxy)-2-[(benzyloxy)methyl]-5-(phenylethynyl)pyrrolidin-1-ol (3m) was obtained according to general procedure (procedure A) using nitrone **1d** (155.7 mg, 0.5 mmol), phenylacetylene (**2a**) (61.3 mg, 0.6 mmol), Et_3N (70 µL, 0.5 mmol) and SIPrCuI (12.2 mg, 0.025 mmol, 5 mol%). The crude product was chromatographed on silica (35% Et_2O/*n*-pentane) to give a light-yellow oil (195.2 mg, 94%). $[\alpha]_D^{25}$ = 48.8 (c 1.3, CH_3Cl); dr >95:5 based on HPLC (40% MTBE/hexanes; 1 mL/min., IA column, DAD detector, 244 nm): major peak 29.0 min., minor peak 34.5 min. (purity >95% based on HPLC) IR (film): 3364, 3031, 2866, 2229 1490 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): 7.44-7.39 (m, 2H), 7.36-7.25 (m, 13H), 5.15 (br s, 1H), 4.62-4.46 (m, 5H), 4.34-4.28 (m, 1H), 3.96 (dd, *J* = 9.3, 7.3 Hz, 1H), 3.84 (dd, *J* = 9.3, 5.5 Hz, 1H), 3.54-3.48 (m, 1H), 2.44 (ddd, *J* = 13.3, 7.7, 2.6 Hz, 1H), 2.27-2.18 (m, 1H); ^{13}C NMR (151 MHz, cdcl$_3$) δ 138.2, 138.2, 131.8, 128.4, 128.3, 128.2, 127.8, 127.6, 127.5, 127.4, 125.6, 122.5, 86.6, 86.2, 75.6, 73.6, 71.1, 68.1, 67.9, 57.4, 36.9.; HRMS (ESI) *m/z* calcd for $C_{27}H_{27}NO_3Na$ $[M+Na]^+$ 436.1883; found 436.1862.

Procdure B: To a solution of alkynylalane [prepared by heating trimethylaluminum (0.2 mL, 2.09 mmol); alkyne **2a** (229.1 µL, 2.09 mmol) and Et_3N (29 µL, 10 mol%, 0.01 mmol) at 60 °C for 6h in hexane (3 mL), as previously described[14]] in hexane (3 mL), the solution of nitrone **1d** (155.7 mg, 0.5 mmol) in anhydrous THF (10 mL) was added dropwise at rt, and stirred for 16h at this temp. Then reaction mixture was quenched with sat. solution of NH_4Cl (20 mL) and extracted with DCM (3 x 15 mL). The combined organic extracts were dried over Na_2SO_4 and evaporated. The residue was chromatographed on silica (35% Et_2O/*n*-pentane) to give a colourless oil (157.1 mg, 76%). dr >95:5 based on HPLC (40% MTBE/hexanes; 1 mL/min., IA column, DAD detector, 244 nm): major peak 29.0 min., minor peak 34.5 min. (purity >95% based on HPLC).



3n

3-[benzyl(hydroxy)amino]-3,4,5-trideoxy-1,2-*O*-(1-methylethylidene)-5-phenyl-D-*erythro*-pent-4-ynitol (3n) was obtained according to general procedure using nitrone **1c** (188.2 mg, 0.80 mmol), phenylacetylene (**2a**) (105 μL, 0.96 mmol), Et_3N (112 μL, 0.80 mmol, 1.0 eq.) and SIPrCuI (23.2 mg, 0.04 mmol, 5 mol%). The crude product was chromatographed on silica (40% Et_2O/*n*-pentane) to give a colourless oil (255.1 mg, 95%). $[\alpha]_D^{25}$ = 55.8 (c 1.0, $CHCl_3$); IR (film): 3403, 3061, 3031, 2986, 2933, 2886, 1598, 1491, 1455 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6): 8.06 (s, 1H), 7.49-7.48 (m, 2H), 7.40-7.28 (m, 7H), 7.26-7.21 (m, 1H), 4.32-4.27 (m, 1H), 4.09 (dd, *J* = 8.6, 6.3 Hz, 1H), 4.03-3.98 (m, 3H), 3.89 (d, *J* = 13.1 Hz, 1H), 1.33 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6): 138.4, 131.9, 129.7, 129.1, 129.0, 128.5, 127.5, 122.9, 108.6, 87.2, 85.2, 76.7, 67.1, 62.1, 62.0, 26.9, 26.3; HRMS (ESI) *m/z* calcd. for $C_{21}H_{24}NO_3$ $[M+H]^+$ 338.1751; found 338.1757.



4

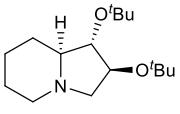
(2*S*,3*S*,4*S*)-2-[4-(2-benzyloxy)but-1-yn-1yl]-3,4-di-*tert*-butoxypyrrolidin-1-ol (4) Procedure A To a suspension of nitrone **1a** (458.6 mg, 2.0 mmol) in degassed water (10 mL), alcohol **8** (640.9 mg, 4.0 mmol), SIPrCuI (116.2 mg, 10 mol%, 0.2 mmol), and TMG (0.25 mL, 2.0 mmol) were added as follow and stirred for 16 h at 50 °C (temp. oil bath). Then reaction mixture was extracted with Et_2O (3 x 10 mL). The combined extracts were washed with brine (1 x 20 mL), dried over Na_2SO_4 and the solvent was evaporated. The residue was chromatographed on silica (50 g, 45% Et_2O/*n*-pentane) to give a yellow oil (514.5 mg, 66%). $[\alpha]_D^{25}$ = 28.7 (c 2.1, CH_3Cl); IR (film): 3381, 2975, 1455 cm^{-1}; dr 89:11 (based on ^1H NMR, major diasteromer 3.51 ppm (t), 3.59 ppm (t); ^1H NMR (500 MHz, DMSO-d_6): 8.14 (s, 1H), 7.38-7.26 (m, 5H), 4.50 (s, 2H), 3.82-3.77 (m, 1H), 3.73 (dd, *J* = 6.5, 3.5 Hz, 1H), 3.51 (t, *J* = 6.8 Hz, 2H), 3.20-3.12 (m, 1H), 2.92-2.85 (m, 2H), 2.48 (dd, *J* = 6.5, 1.9 Hz, 1H), 1.14 (s, 9H), 1.10 (s, 9H); ^{13}C NMR (125 MHz, DMSO-d_6): 138.8, 128.6, 127.9, 127.8, 82.9, 75.8, 73.9, 73.7, 72.2, 68.4, 65.7, 29.1, 28.7, 20.0; HRMS (ESI) *m/z* calcd for $C_{23}H_{35}NO_4Na$ $[M+Na]^+$ 412.2458; found 412.2464.

Table 1. Optimization of the addtion of alcohol **8** to nitrone **1a**

Alcohol **8** (eq.)	SIPrCuI (mol%)	Base	Temp. (°C), time (16h)	Yield (%)
1	5	Et_3N	rt	11
1	10	Et_3N	rt	18
1	10	TMG	rt	27
2	10	TMG	65	39
2	10	TMG	50	66

Procedure B To a solution of alkyne **8** (240.0 mg, 1.5 mmol, 3.0 eq.) in THF (10 mL), cooled to -40 °C, a solution of *n*-BuLi (0.6 mL, 1.5 mmol) was added dropwise within 5 min. and stirred for 30 min. at this temp. Then solution of nitrone **1a** (114.7 mg, 0.5 mmol) in anhydrous THF (5 mL) was added dropwise. After 1h, cooling bath was removed and the reaction mixture was allowed to warm to rt. Then reaction was quenched with sat. solution of NH_4Cl (20 mL), and extracted with Et_2O (3 x 10 mL). The combined organic extracts were washed with brine (1 x 20 mL), dried over Na_2SO_4, and evaporated to give a light-yellow oil (176.1 mg, 90%, dr >95:5 based ^1H NMR).

Procedure C To a solution of alkynylalane [prepared by heating trimethylaluminum (0.2 mL, 2.09 mmol); alkyne **8** (302.2 mg, 1.88 mmol) and Et_3N (29 µL, 10 mol%, 0.01 mmol) at 60 °C for 6h in hexane (3 mL), as previously described[14]], the solution of nitrone **1a** (114.7 mg, 0.5 mmol) in anhydrous THF (10 mL) was added dropwise at rt, and stirred for 6h at this temp. Then reaction mixture was quenched with sat. solution of NH_4Cl (20 mL) and extracted with DCM (3 x 10 mL). The combined organic extracts were dried over Na_2SO_4 and evaporated. The residue was chromatographed on silica (40% Et_2O/*n*-pentane) to give a colourless oil (57.2 mg, 29% dr >92:8 based ^1H NMR).



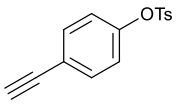
6

(1*S*,2*S*,8a*S*)-1,2-di-*tert*-Butoxyoctahydroindolizine (6)

A solution of propargylic N-hydroxyl amine **4** (109.9 mg, 0.28 mmol) in MeOH (20 mL) and $Pd(OH)_2$/C (39.3 mg, 20% Degussa type) was stirred under hydrogen (50 bar) for 16h at rt. Then reaction mixture was filtered through a small pad of celite, washed with MeOH, and

evaporated. The crude aminoalcohol **5** (74.3 mg) was used in the next step without further purification.

To a solution of crude aminoalcohol **5** (74.3 mg) in a mixture of anhydrous CCl_4 (2.4 mL) and DCM (2.4 mL), Et_3N (70 μL) and plymer-supported PPh_3 (306 mg, 0.49 mmol, 1.6 mmol/g, 200-400 mesh) were added and vigorously shaken under atmosphere of argon for 24h at rt. Then reaction mixture was filtered through Schott funnel (porosity G3) and the residual resin was successively washed with DCM (2 × 4 mL), MeOH (2 × 4 mL), DCM (2 × 4 mL) and MeOH (2 × 4 mL). Then solvents were evaporated and the crude product was chromatographed on silica (50% Et_2O/ hexanes) to give a colourless oil (49.4 mg, 75% after two steps). $[\alpha]_D^{25}$ = 42.0 (c 0.54, CH_3Cl) lit.[15] $[\alpha]_D^{25}$ = 42.8 (c 0.48, CH_3Cl); IR (film): 2975, 2934, 1648 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): 3.78-3.73 (m, 1H), 3.60 (dd, *J* = 8.4, 4.2 Hz, 1H), 2.95-2.84 (m, 2H), 2.54-2.33 (m, 1H), 1.93-1.81 (m, 2H), 1.79-1.45 (m, 6H), 1.17 (s, 9H), 1.14 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): 83.7, 76.8, 73.7, 73.5, 67.0, 62.1, 53.6, 29.2, 29.0, 28.7, 28.5, 24.8, 24.1; HRMS (ESI) *m/z* calcd for $C_{16}H_{31}NO_2Na$ $[M+Na]^+$ 292.2247; found 292.2253. The ^1H NMR, ^{13}C NMR and optical rotation were in agreement with those reported.[15]

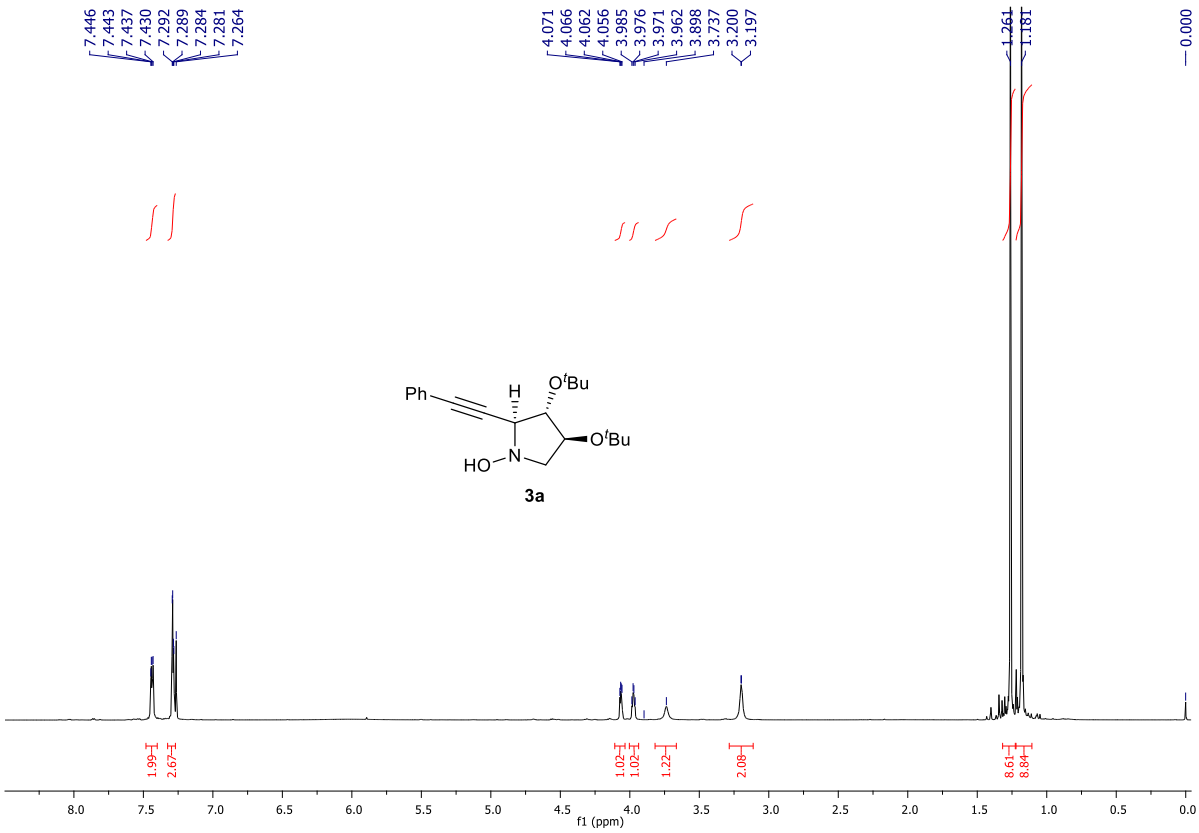


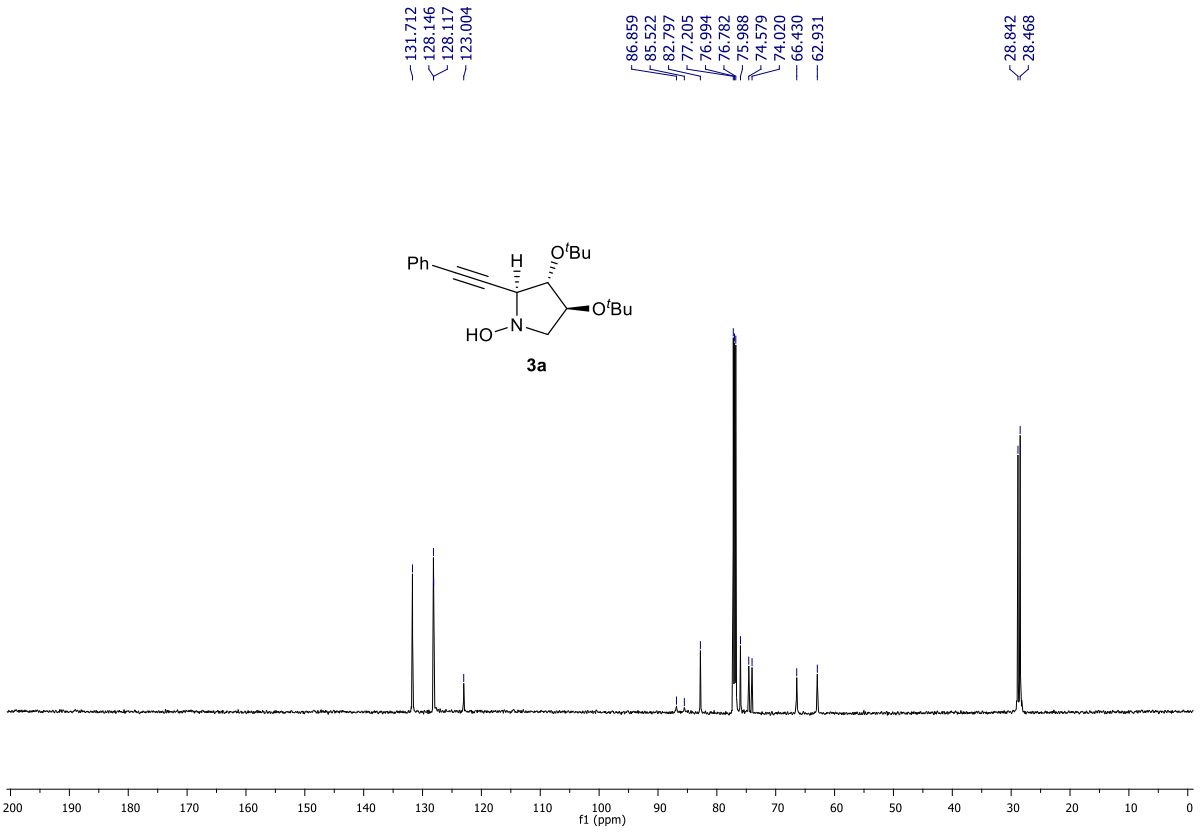
2h

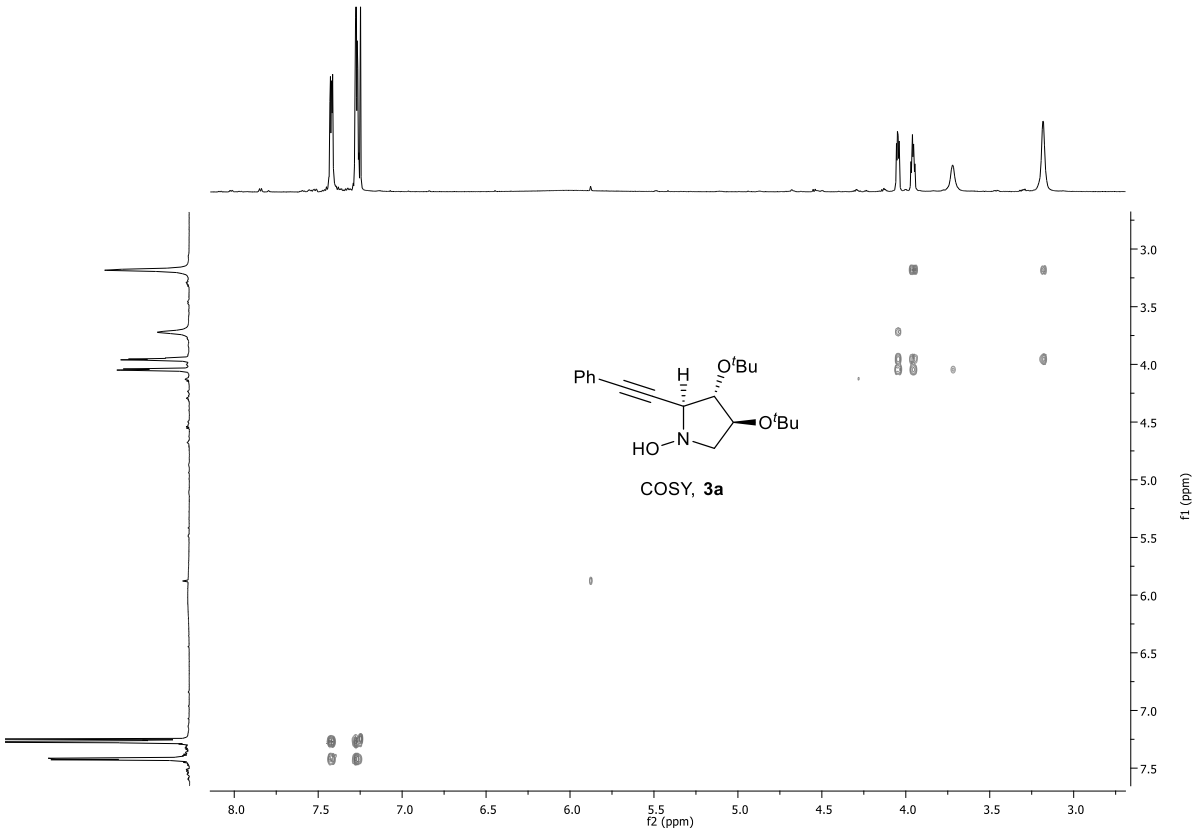
4-Ethynylphenyl 4-methylbenzenesulfonate (**2h**) To a suspension of K_2CO_3 (2.21 g, 16.0 mmol, 2.0 eq) in anhydrous MeOH (30 mL), cooled to 0 °C, tosyl-protected 4-hydroxybenzaldehyde (2.21 mmol, 8.0 mmol) was added. Next, Bestmann-Ohira reagent (1.68 g, 9.6 mmol, 1.2 mmol) was added dropwise by means of syringe, and the reaction mixture was stirred for 16h at rt. Then reaction mixture was diluted with Rochelle salt sat. solution (30 mL) and water (50 mL). After 15 min. of stirring, the aqueous phase was separated and extracted with EtOAc (3 x 30 mL). The combined organic extracts were washed with brine (2 x 30 mL), dried over MgSO4, and evaporated. The residue was chromatographed on silica (5% EtOAc/*n*-hexanes) to give alkyne **2h** as a white solid (1.38 g, 62%). 7.71-7.76 (m, 2H), 7.42-7.37 (m, 2H), 7.33-7.28 (m, 2H), 7.02-6.80 (m, 2H), 3.09 (s, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 149.6, 145.6, 133.4, 132.0, 129.8, 128.5, 122.5, 121.1, 82.2, 78.3, 21.7.

References:

1. B. P. Machin and B. L. Pagenkopf, *Synlett*, 2011, 2799.
2. I. N. Michaelides, B. Darses and D. J. Dixon, *Org. Lett.*, 2011, **13**, 664.
3. O. Santoro, A. Collado, A. M. Z. Slawin, S. P. Nolan and C. S. J. Cazin, *Chem. Commun.*, 2013, **49**, 10483.
4. S. Díez-González, A. Correa, L. Cavallo and S. P. Nolan, *Chem. – Eur. J.*, 2006, **12**, 7558.
5. J. Broggi, S. Díez-González, J. L. Petersen, S. Berteina-Raboin, S. P. Nolan and L. A. Agrofoglio, *Synthesis*, 2008, 141.
6. S. Diez-Gonzalez, E. C. Escudero-Adan, J. Benet-Buchholz, E. D. Stevens, A. M. Z. Slawin and S. P. Nolan, *Dalton Trans.*, 2010, **39**, 7595.
7. S. Díez-González and S. P. Nolan, *Angew. Chem. Int. Ed.*, 2008, **47**, 8881.
8. S. Díez-González, N. M. Scott and S. P. Nolan, *Organometallics*, 2006, **25**, 2355.
9. S. Cicchi, I. Hold and A. Brandi, *J. Org. Chem.*, 1993, **58**, 5274.
10. W.-B. Wang, M.-H. Huang, Y.-X. Li, P.-X. Rui, X.-G. Hu, W. Zhang, J.-K. Su, Z.-L. Zhang, J.-S. Zhu, W.-H. Xu, X.-Q. Xie, Y.-M. Jia and C.-Y. Yu, *Synlett*, 2010, 488.
11. S. Stecko, M. Michalak, M. Stodulski, Ł. Mucha, K. Parda, B. Furman and M. Chmielewski, *Synthesis*, 2012, **44**, 2695.
12. M. Maciejko, S. Stecko, O. Staszewska-Krajewska, M. Jurczak, B. Furman and M. Chmielewski, *Synthesis*, 2012, **44**, 2825.
13. O. Debleds, C. D. Zotto, E. Vrancken, J.-M. Campagne and P. Retailleau, *Adv. Synth. Catal.*, 2009, **351**, 1991.
14. C. Pillard, V. Desvergnes and S. Py, *Tetrahedron Lett.*, 2007, **48**, 6209.
15. A. Goti, F. Cardona and A. Brandi, *Synlett*, 1996, 761.

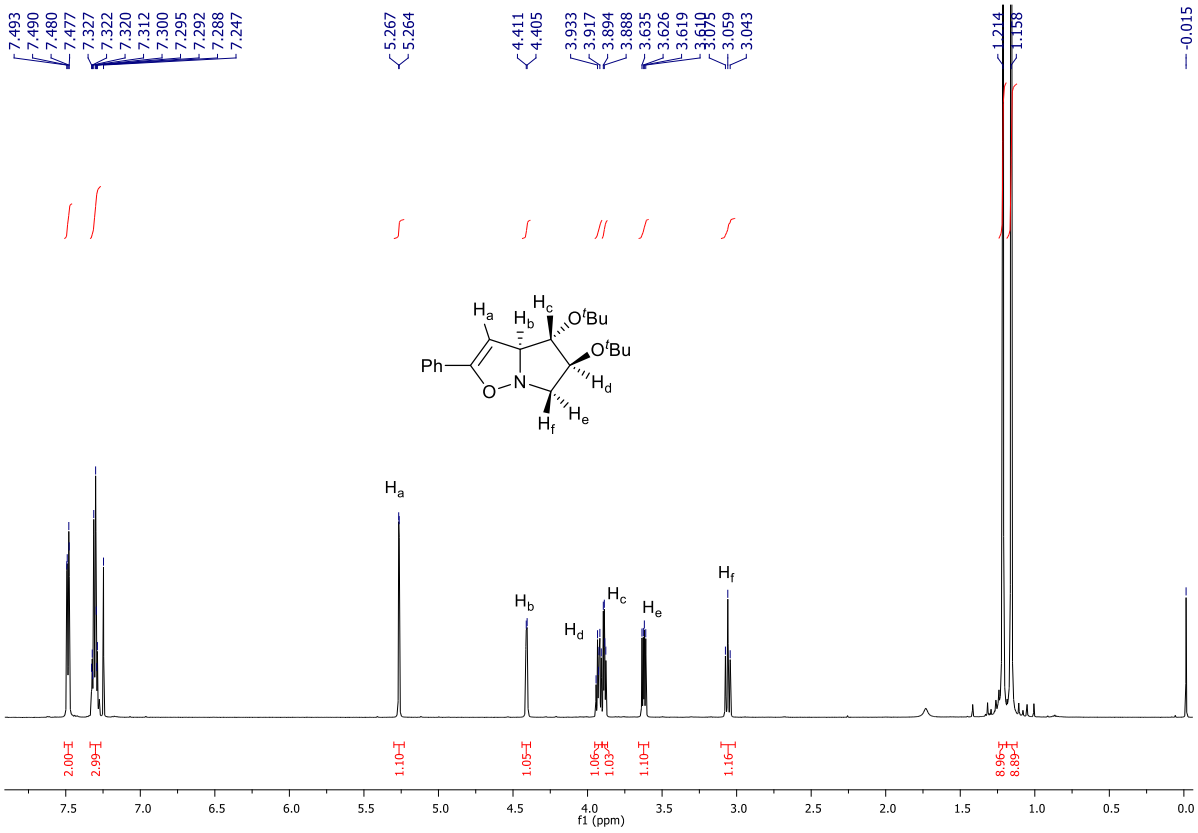

7.446
7.443
7.437
7.430
7.292
7.289
7.284
7.281
7.264
4.071
4.066
4.062
4.056
3.985
3.976
3.971
3.962
3.898
3.737
3.200
3.197
1.261
1.181
0.000
Ph
H
O^{t}Bu
O^{t}Bu
HO
N
3a
1.99
2.67
1.02
1.02
1.22
2.08
8.61
8.84
f1 (ppm)

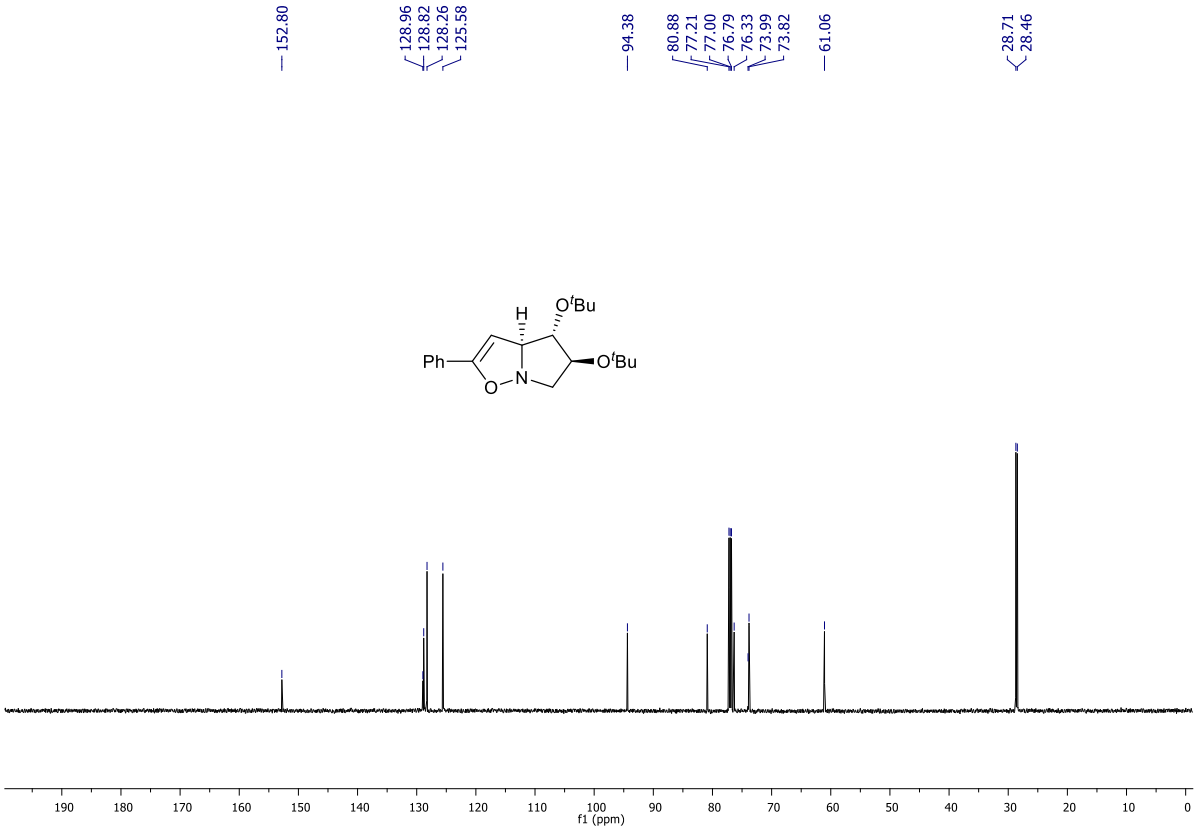

131.712
128.146
128.117
123.004
86.859
85.522
82.797
77.205
76.994
76.782
75.988
74.579
74.020
66.430
62.931
28.842
28.468
Ph
H
O^{t}Bu
O^{t}Bu
HO
N
3a
f1 (ppm)

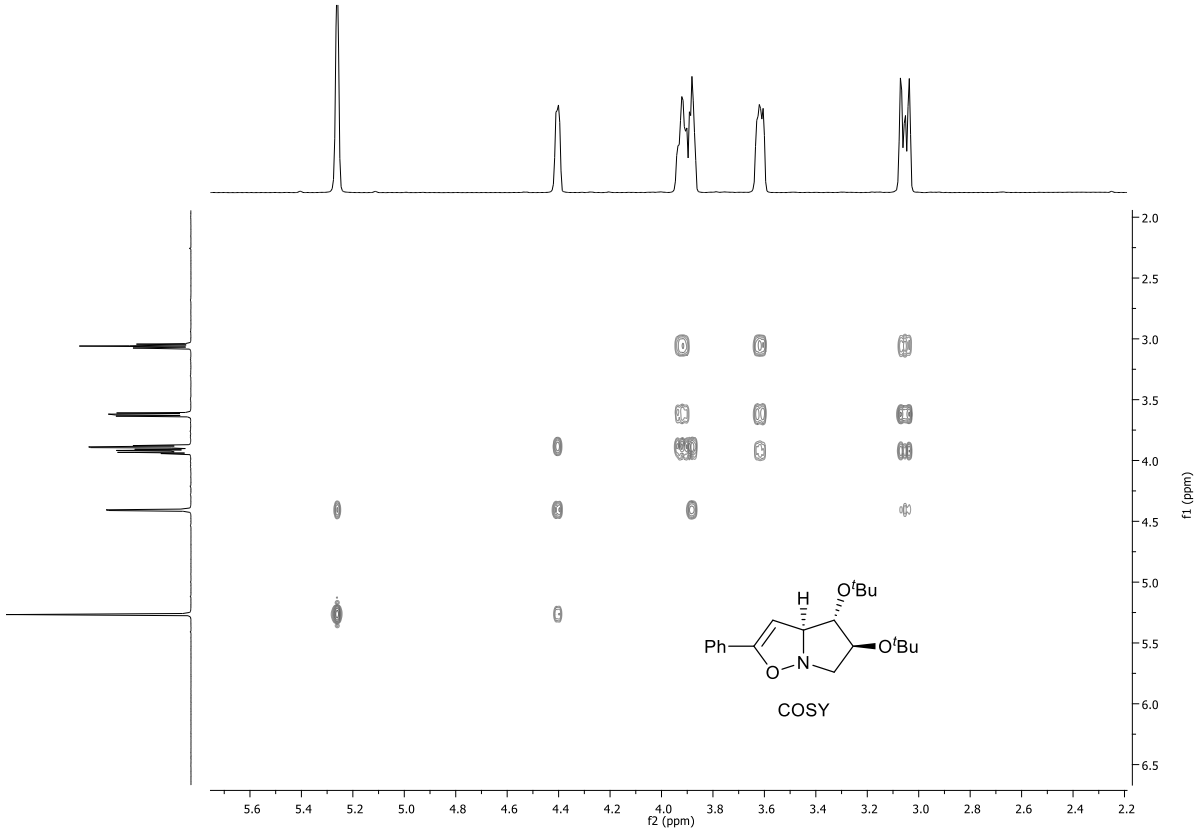


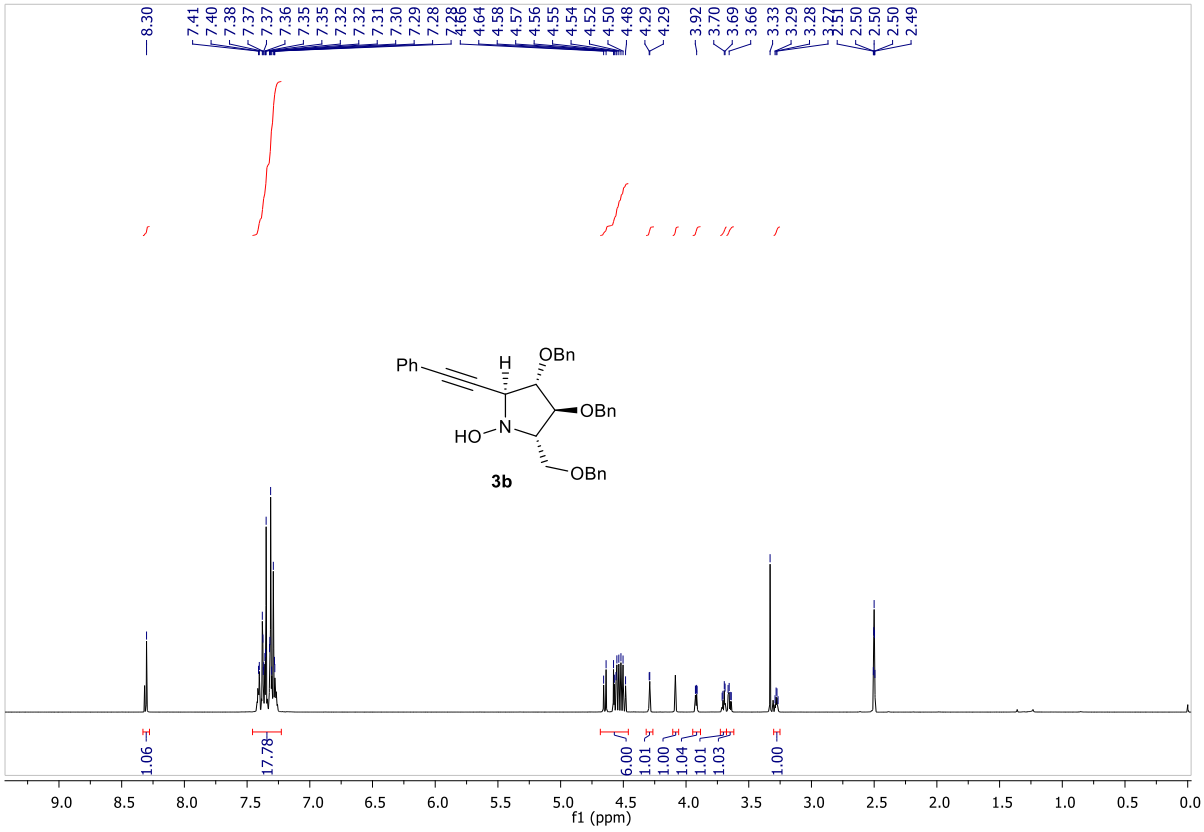
COSY, **3a**

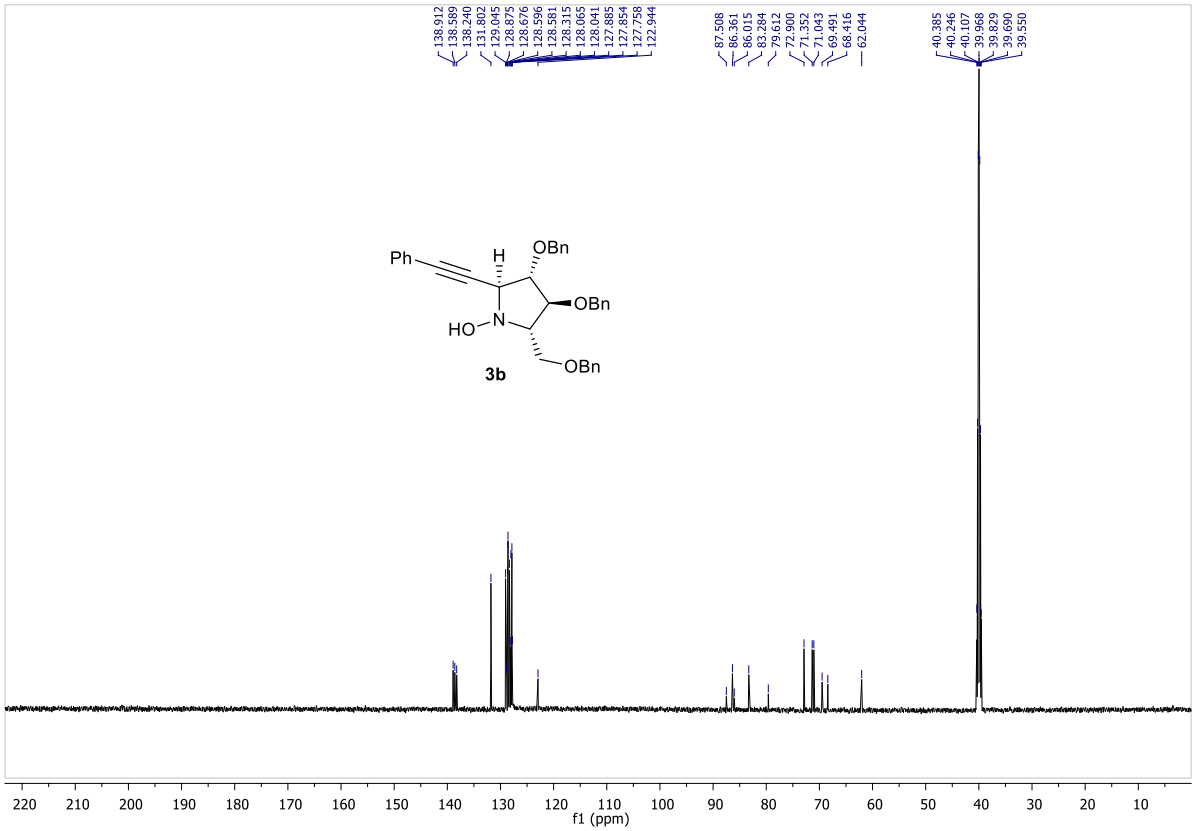
HSQC, **3a**

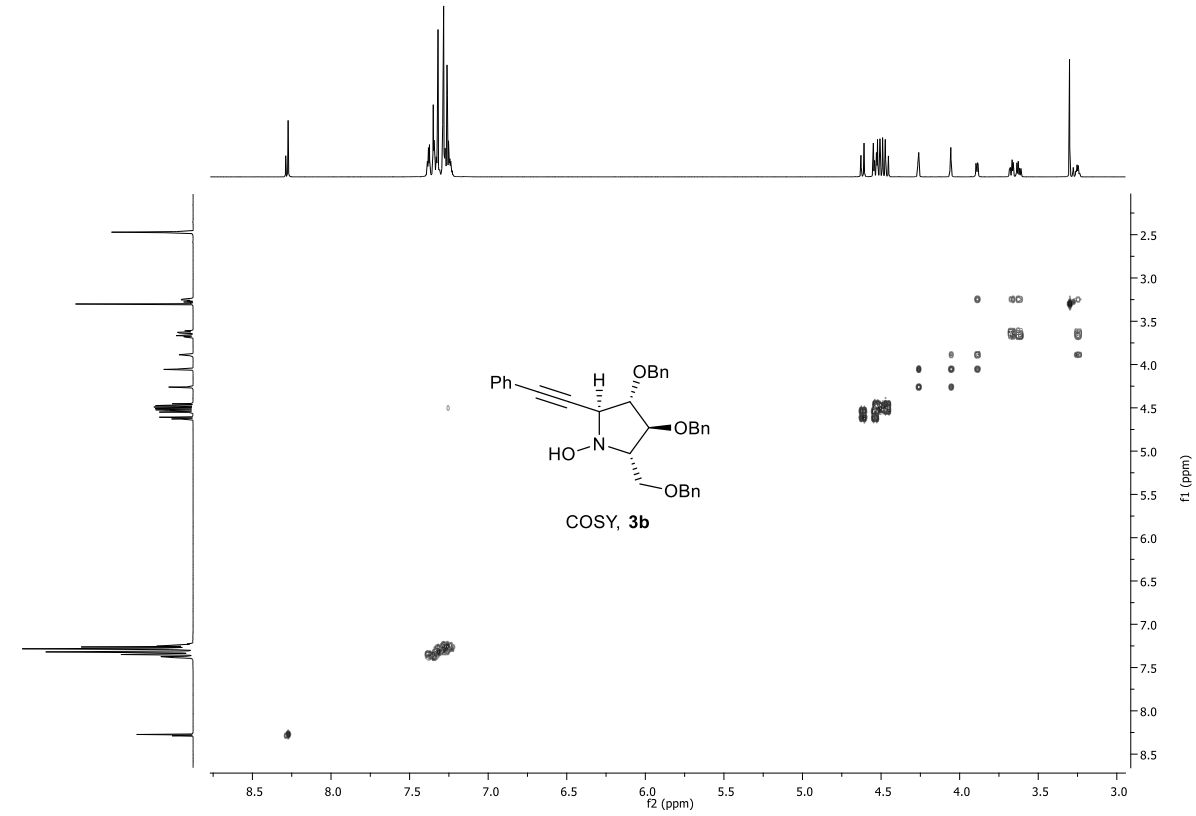

7.493
7.490
7.480
7.477
7.327
7.322
7.320
7.312
7.300
7.295
7.292
7.288
7.247
5.267
5.264
4.411
4.405
3.933
3.917
3.894
3.888
3.635
3.626
3.619
3.610
3.059
3.043
1.214
1.158
-0.015
Ha
Hb
Hc
OtBu
OtBu
Hd
He
Hf
Ph
O
N
2.00
2.99
1.10
1.05
1.06
1.03
1.10
1.16
8.96
8.89
f1 (ppm)

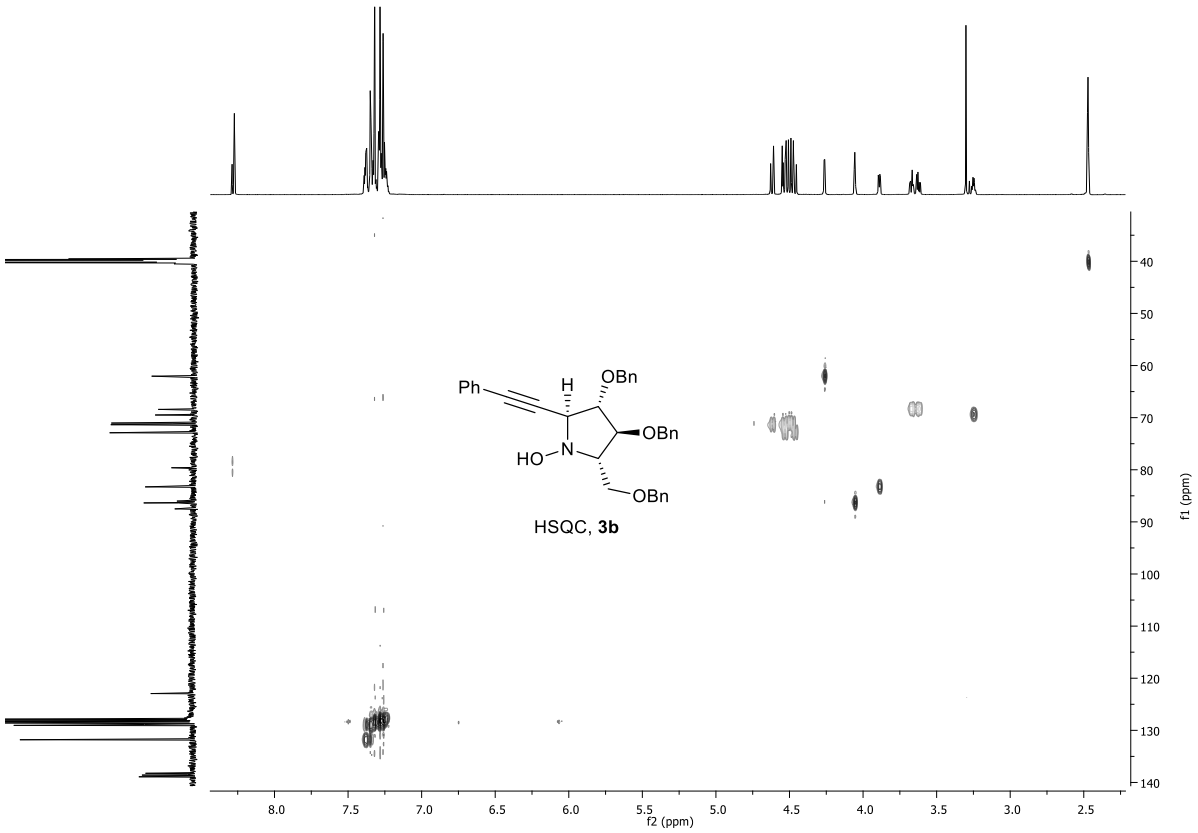

152.80
128.96
128.82
128.26
125.58
94.38
80.88
77.21
77.00
76.79
76.33
73.99
73.82
61.06
28.71
28.46
H
OtBu
Ph
OtBu
O
N
f1 (ppm)


H
O^{t}Bu
Ph
O^{t}Bu
O
N
COSY
f2 (ppm)
f1 (ppm)


Ph
H
OBn
OBn
HO
N
OBn
3b
f1 (ppm)

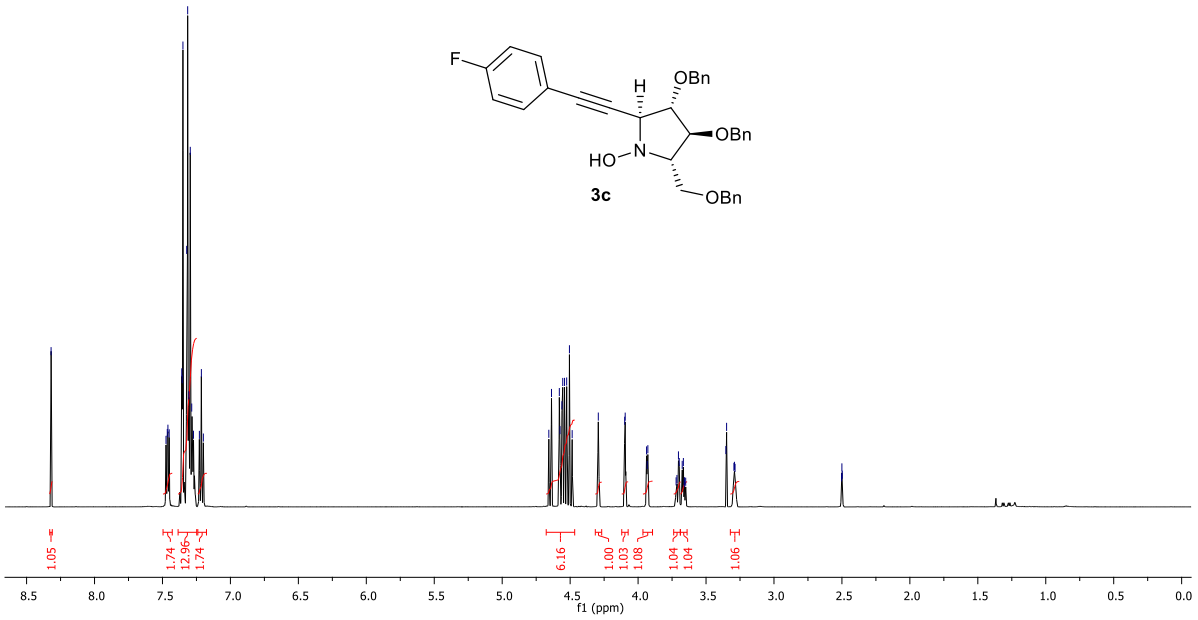

138.912
138.589
138.240
131.802
129.045
128.875
128.676
128.596
128.581
128.315
128.065
128.041
127.885
127.854
127.758
122.944
87.508
86.361
86.015
83.284
79.612
72.900
71.352
71.043
69.491
68.416
62.044
40.385
40.246
40.107
39.968
39.829
39.690
39.550
Ph
H
OBn
OBn
HO
N
OBn
3b
f1 (ppm)


Ph
H
OBn
OBn
HO
N
OBn
COSY, 3b
f2 (ppm)
f1 (ppm)

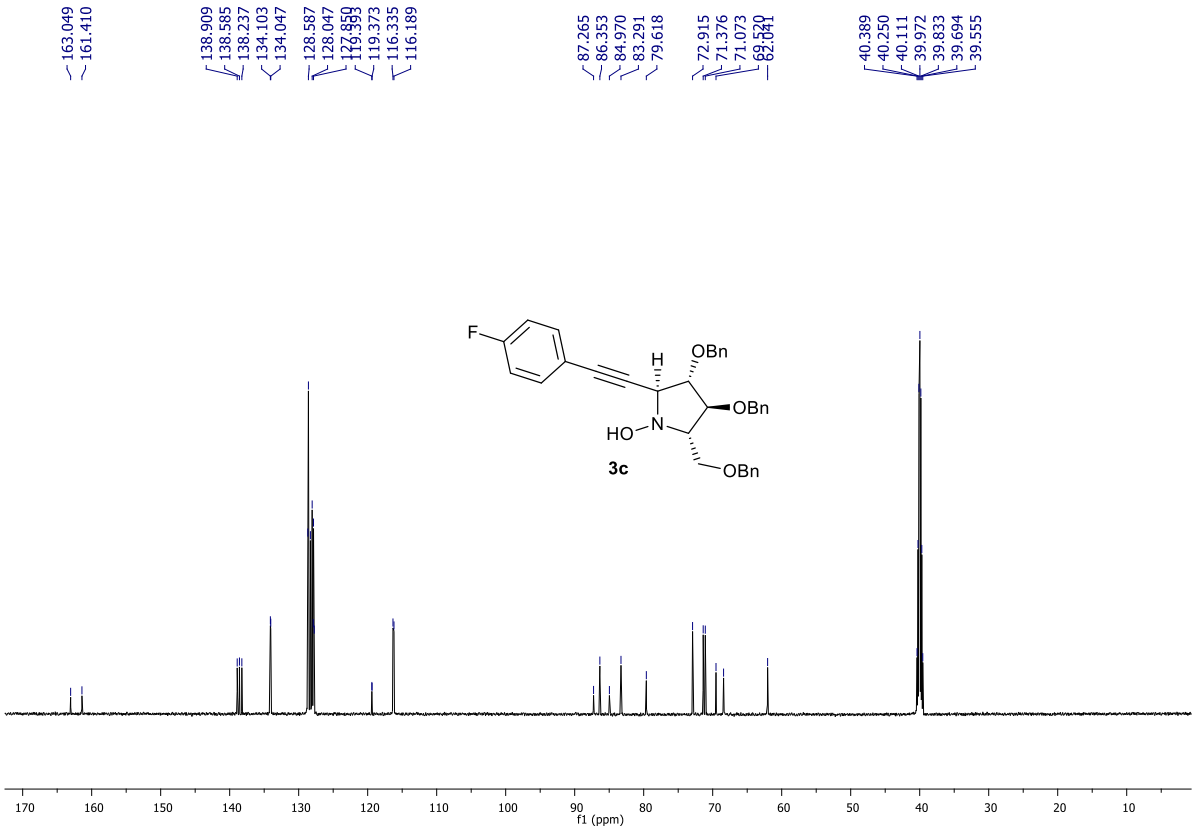

Ph
H
OBn
OBn
HO
N
OBn
f2 (ppm)
f1 (ppm)

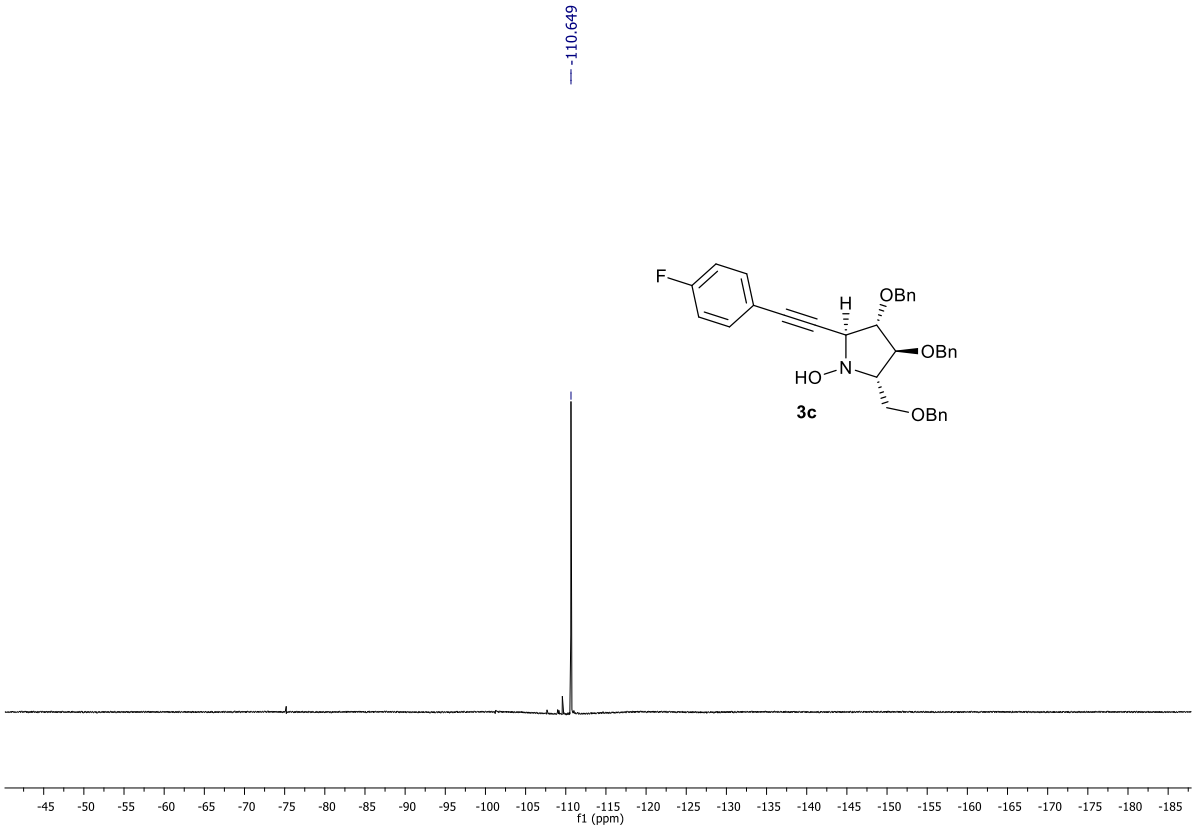
HSQC, **3b**

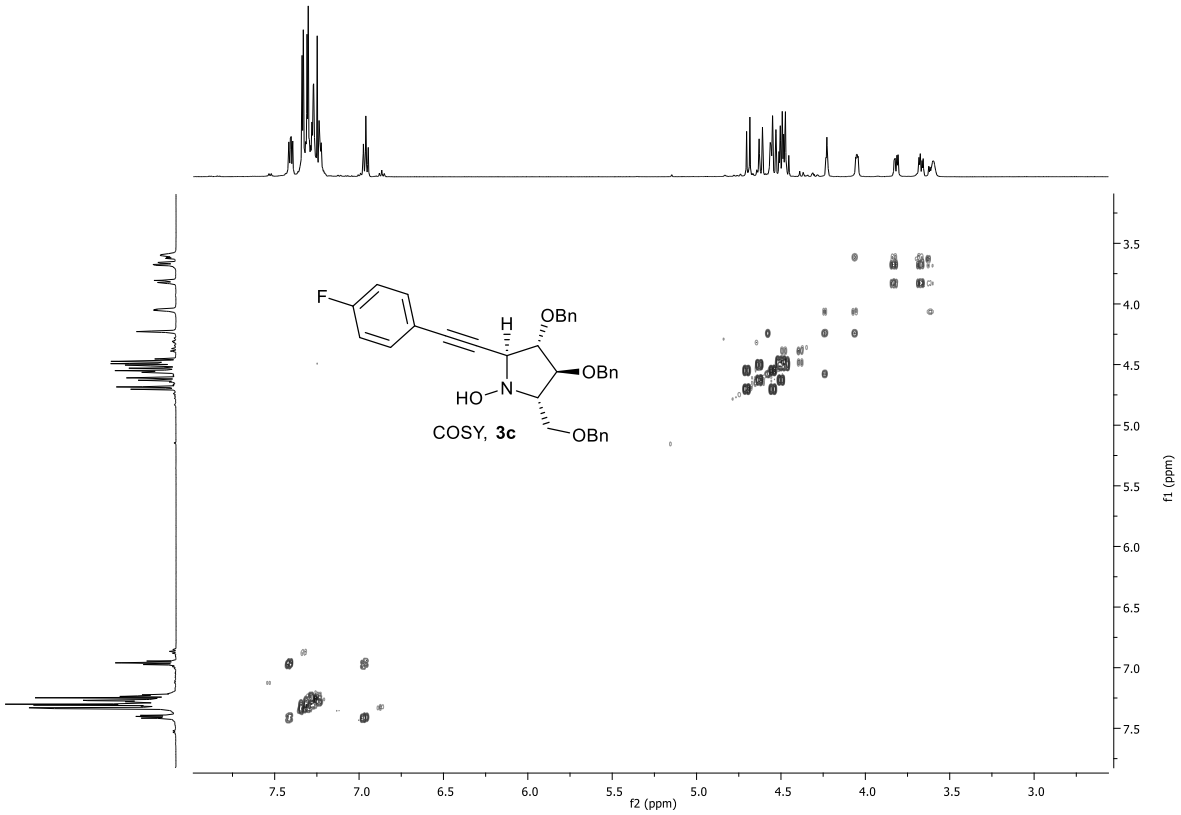

8.320
7.474
7.465
7.460
7.451
7.358
7.355
7.349
7.322
7.315
7.306
7.295
7.285
7.272
7.228
7.214
7.199
4.657
4.637
4.580
4.575
4.560
4.555
4.541
4.526
4.505
4.485
4.293
4.099
4.095
3.938
3.928
3.703
3.667
3.354
3.349
3.295
3.291
3.286
2.503
2.500
2.497

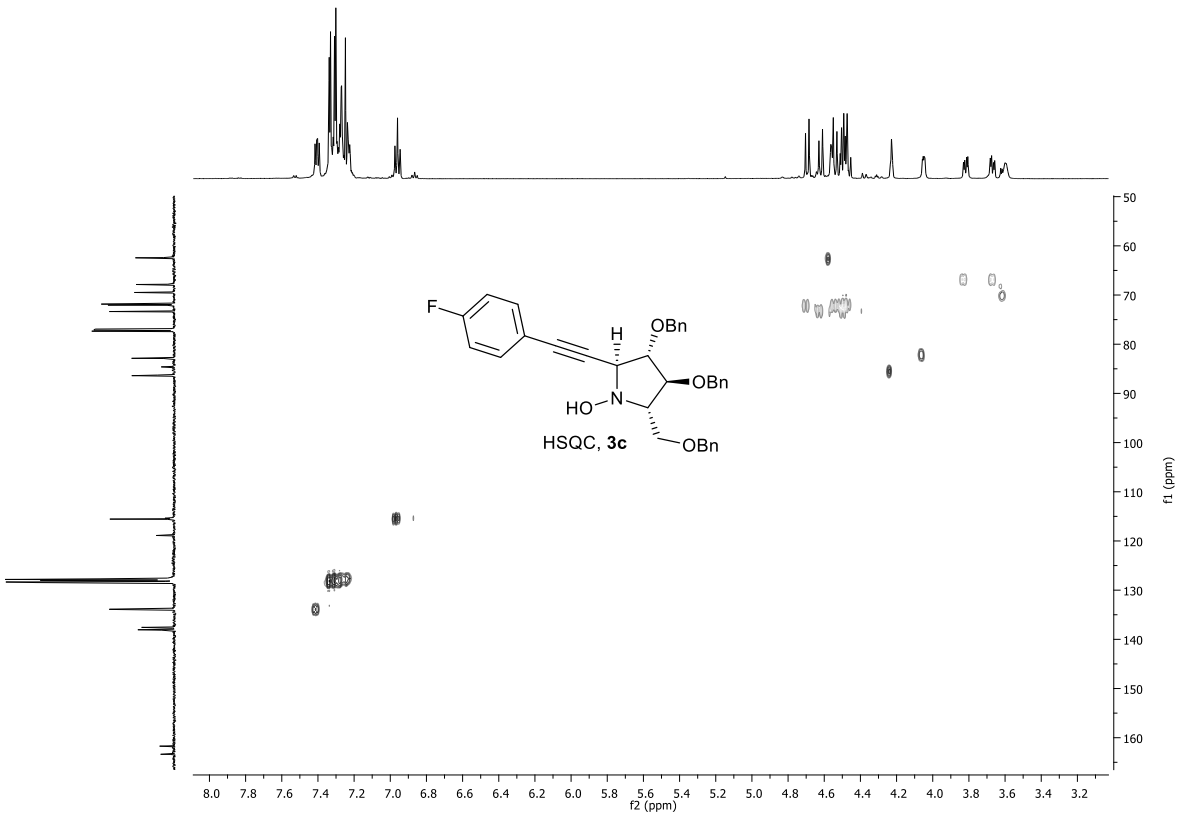

F
H
OBn
OBn
HO
N
OBn
1.05
1.74
12.96
1.74
6.16
1.00
1.03
1.08
1.04
1.04
1.06
f1 (ppm)

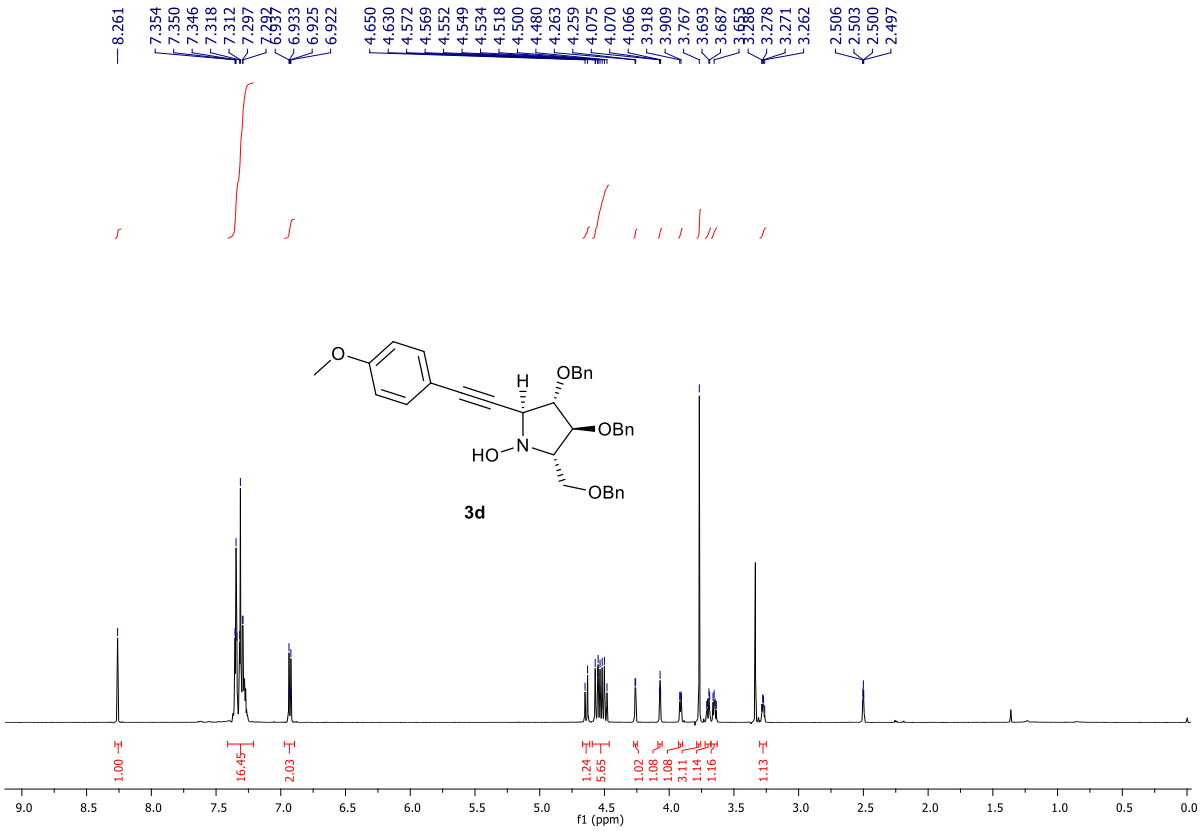
3c

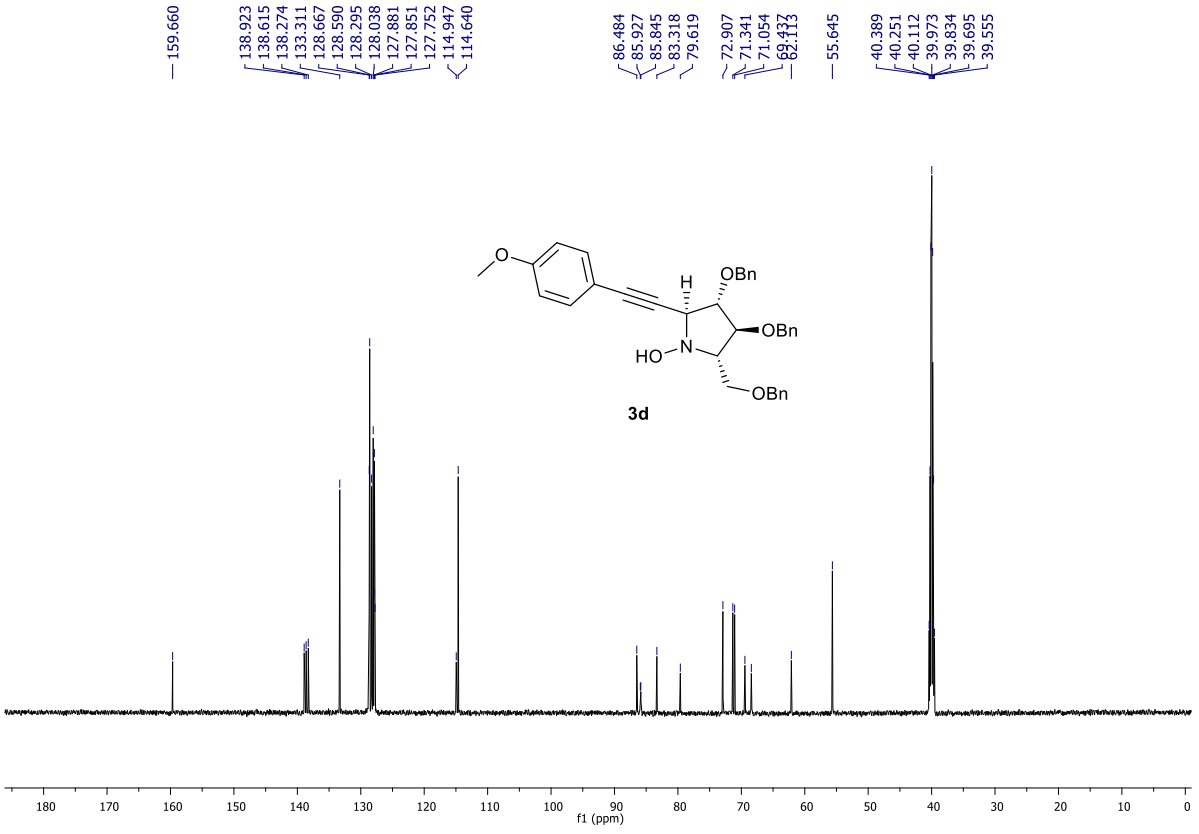

163.049
161.410
138.909
138.585
138.237
134.103
134.047
128.587
128.047
127.850
119.393
119.373
116.335
116.189
87.265
86.353
84.970
83.291
79.618
72.915
71.376
71.073
62.041
40.389
40.250
40.111
39.972
39.833
39.694
39.555
F
H
OBn
OBn
HO
N
OBn
3c
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

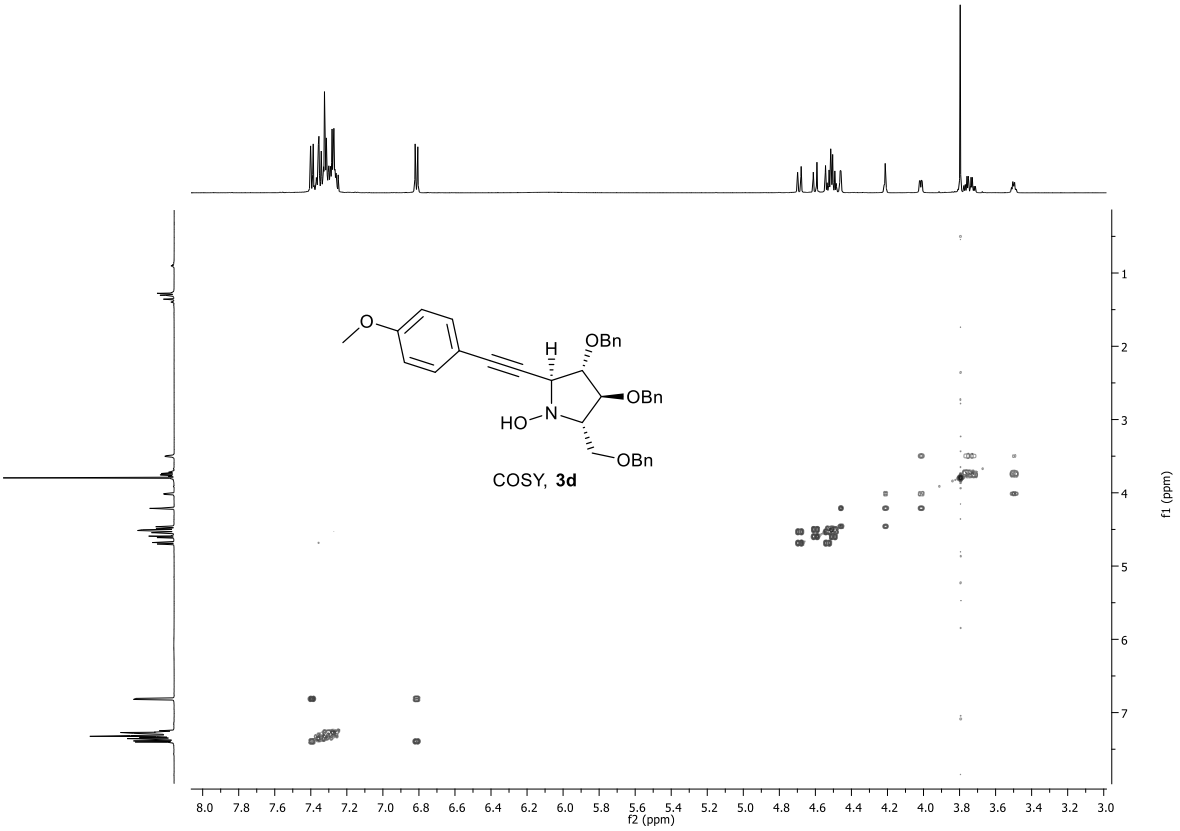

-110.649
F
H
OBn
OBn
HO
N
OBn
3c
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
-180
-185
f1 (ppm)


F
H
OBn
OBn
HO
N
OBn
COSY, 3c
f2 (ppm)
f1 (ppm)

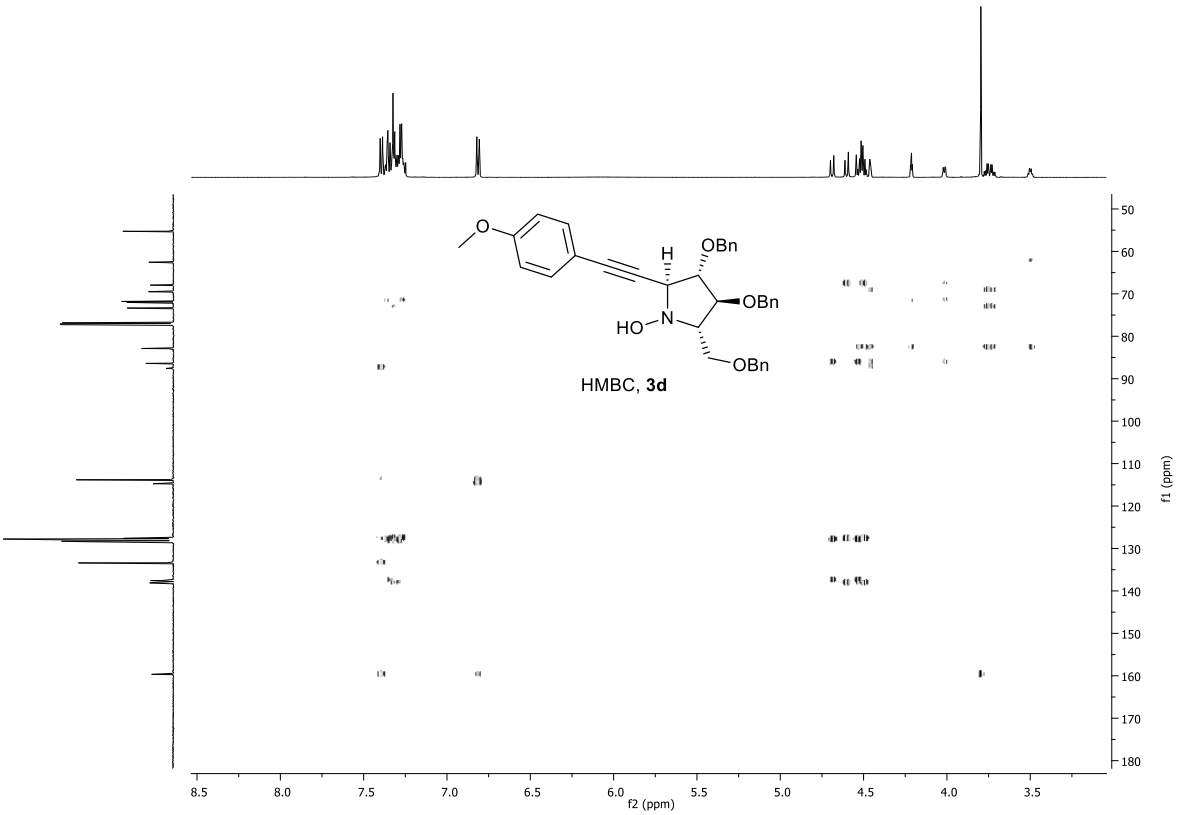

F
H
OBn
OBn
HO
N
OBn
HSQC, 3c
f2 (ppm)
f1 (ppm)


8.261
7.354
7.350
7.346
7.318
7.312
7.297
7.292
6.933
6.925
6.922
4.650
4.630
4.572
4.569
4.552
4.549
4.534
4.518
4.500
4.480
4.263
4.259
4.075
4.070
4.066
3.918
3.909
3.767
3.693
3.687
3.653
3.286
3.278
3.271
3.262
2.506
2.503
2.500
2.497
O
H
OBn
OBn
HO
N
OBn
3d
1.00
16.45
2.03
1.24
5.65
1.02
1.08
1.08
3.11
1.14
1.16
1.13
f1 (ppm)

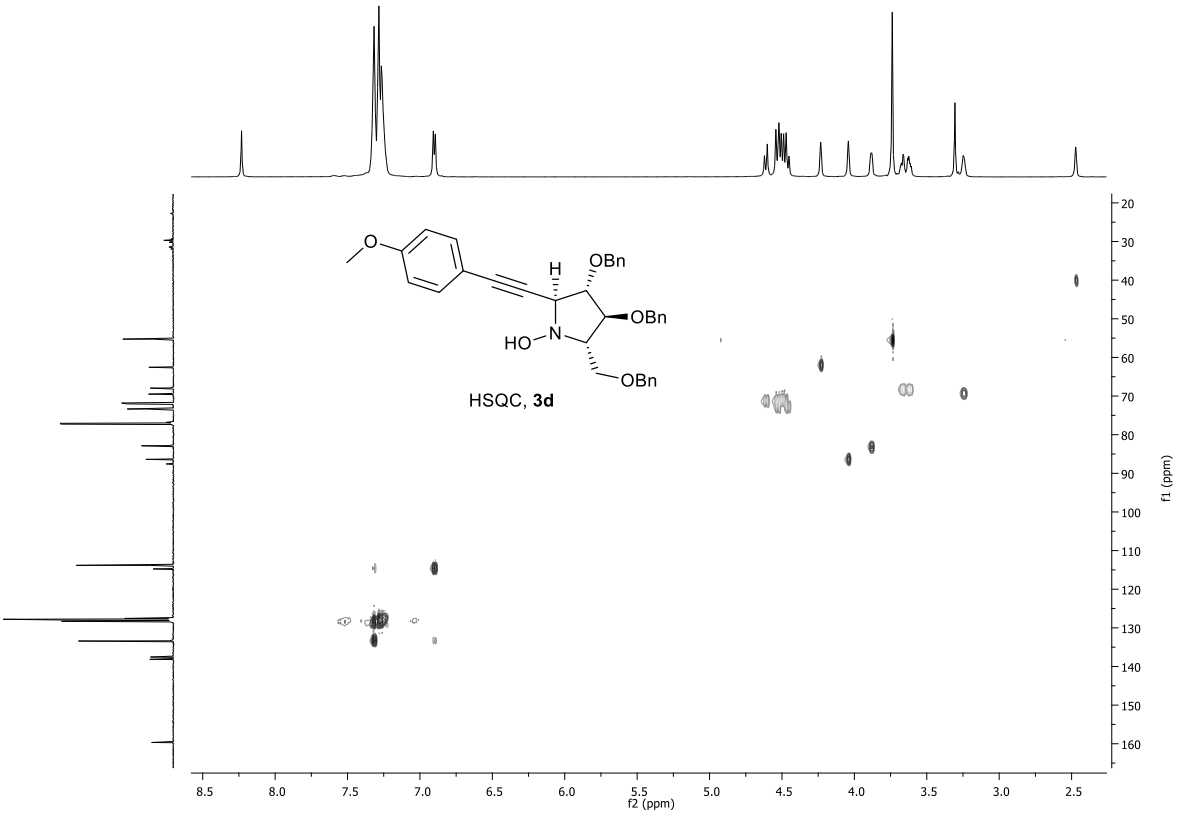

159.660
138.923
138.615
138.274
133.311
128.667
128.590
128.295
128.038
127.881
127.851
127.752
114.947
114.640
86.484
85.927
85.845
83.318
79.619
72.907
71.341
71.054
69.437
62.113
55.645
40.389
40.251
40.112
39.973
39.834
39.695
39.555
O
H
OBn
OBn
HO
N
OBn
3d
f1 (ppm)

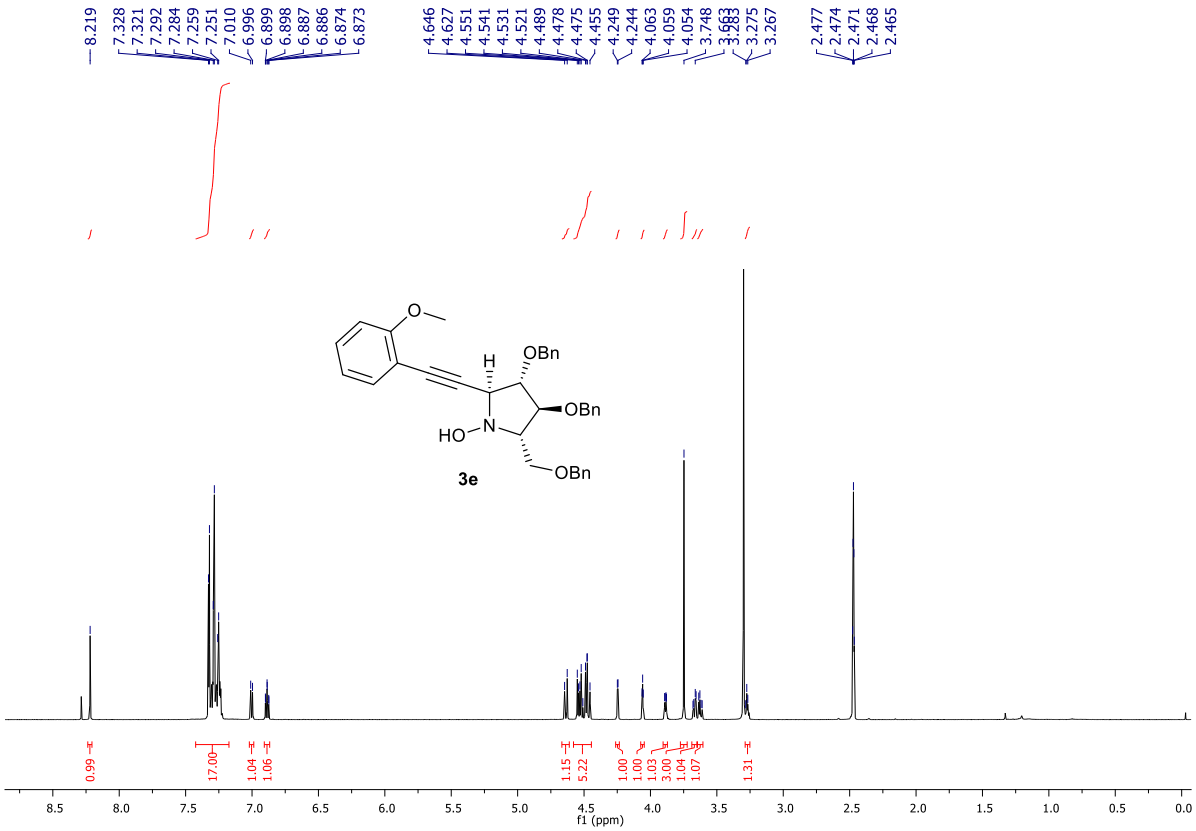


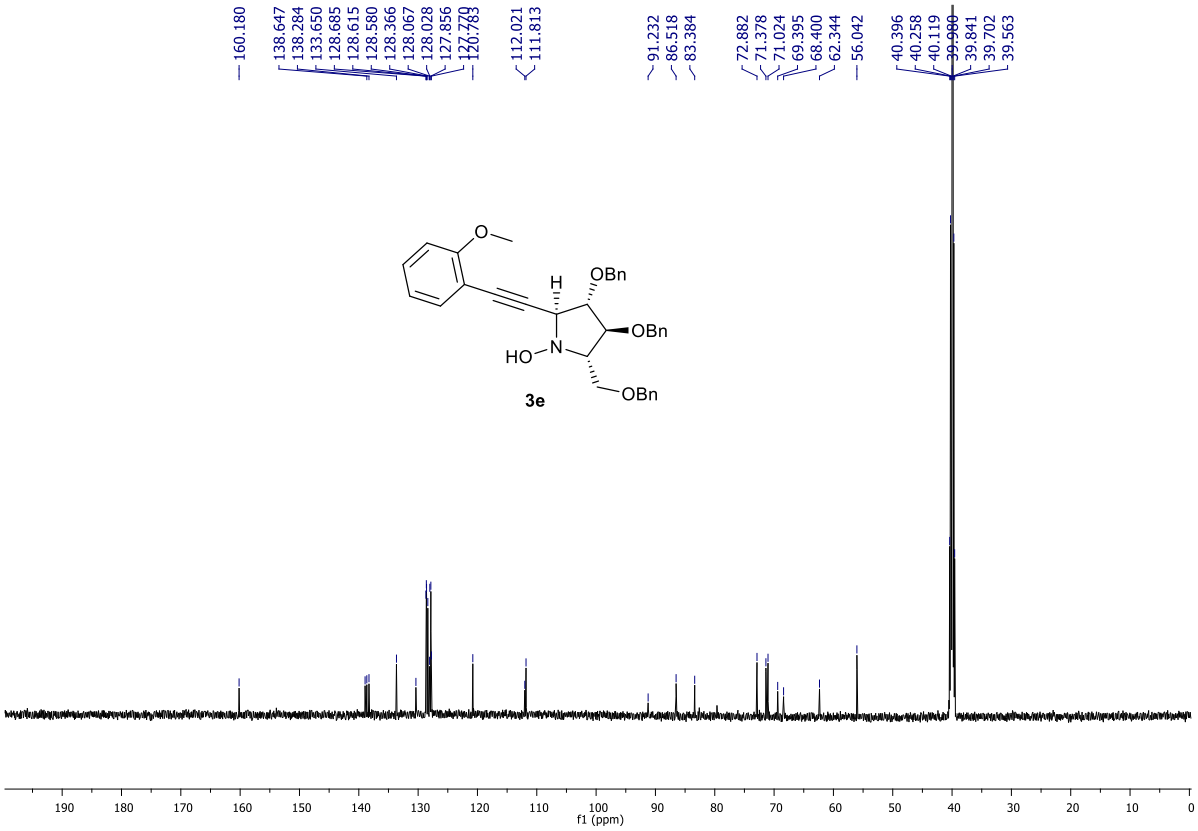
COSY, **3d**

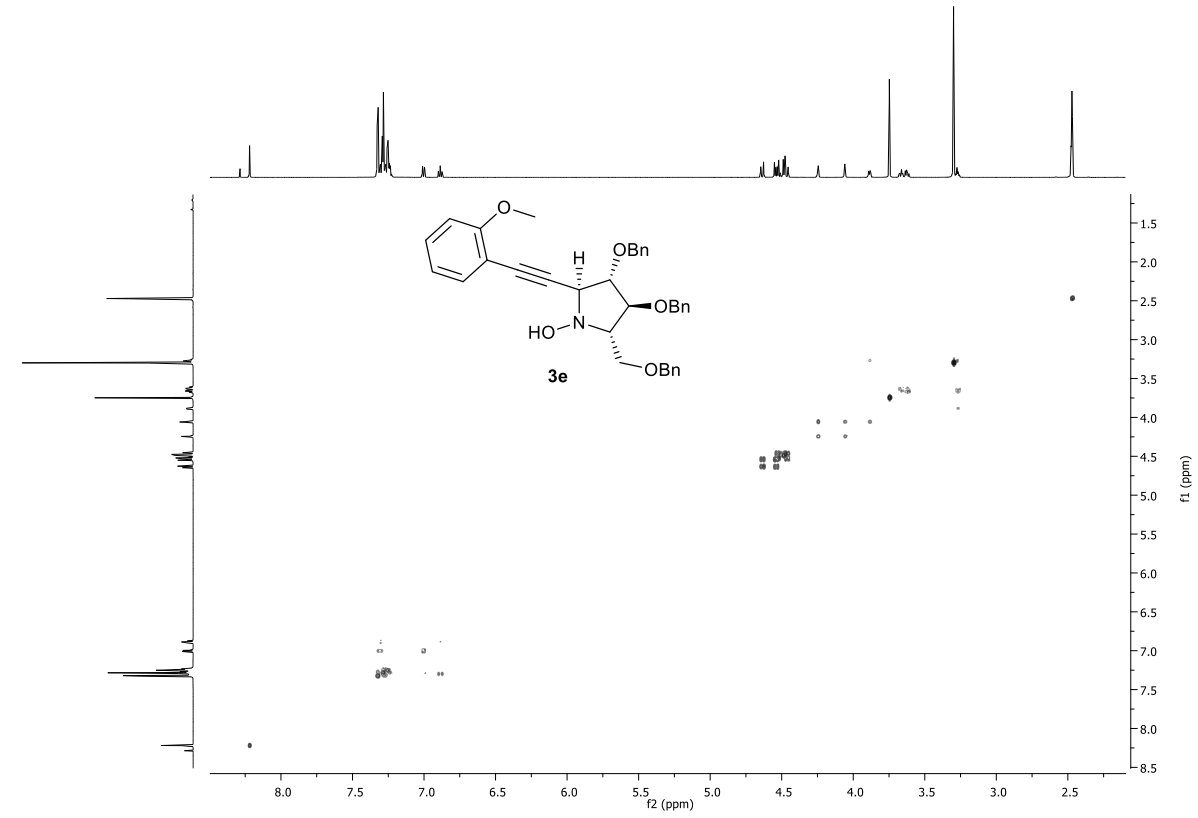


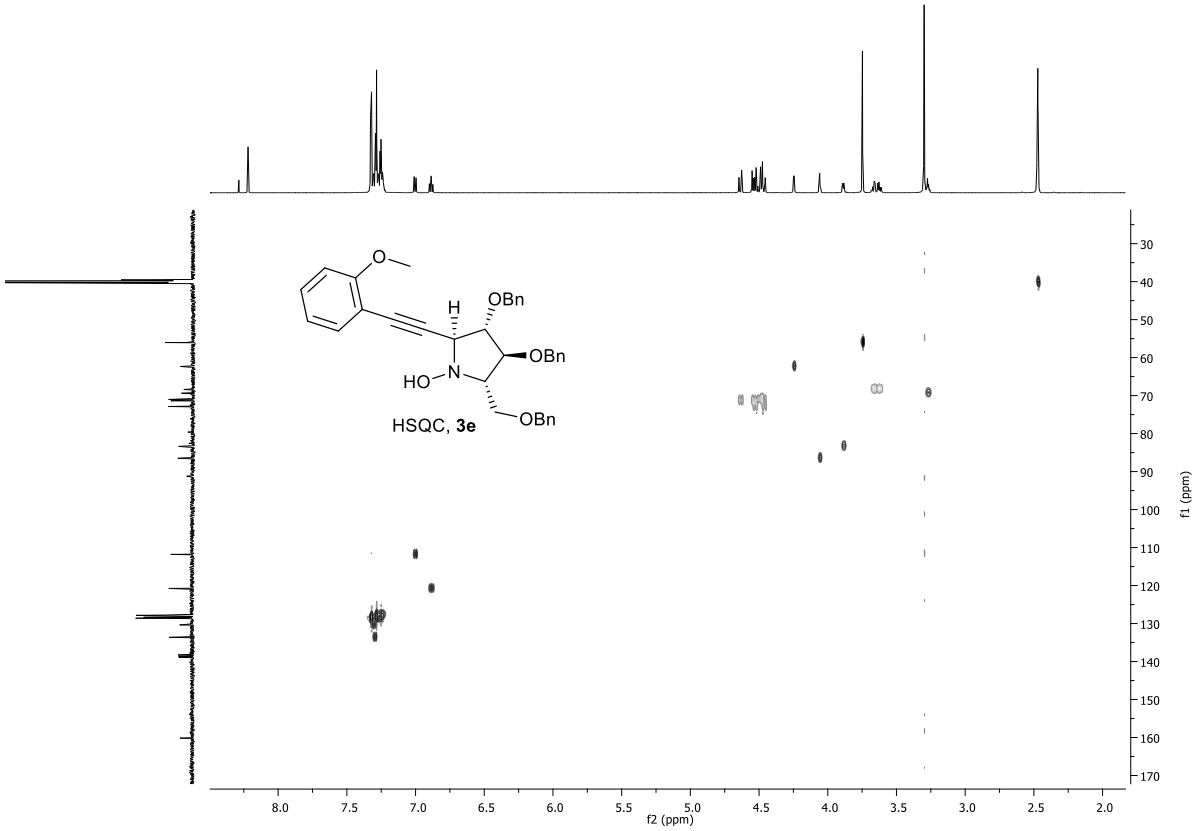
HMBC, **3d**

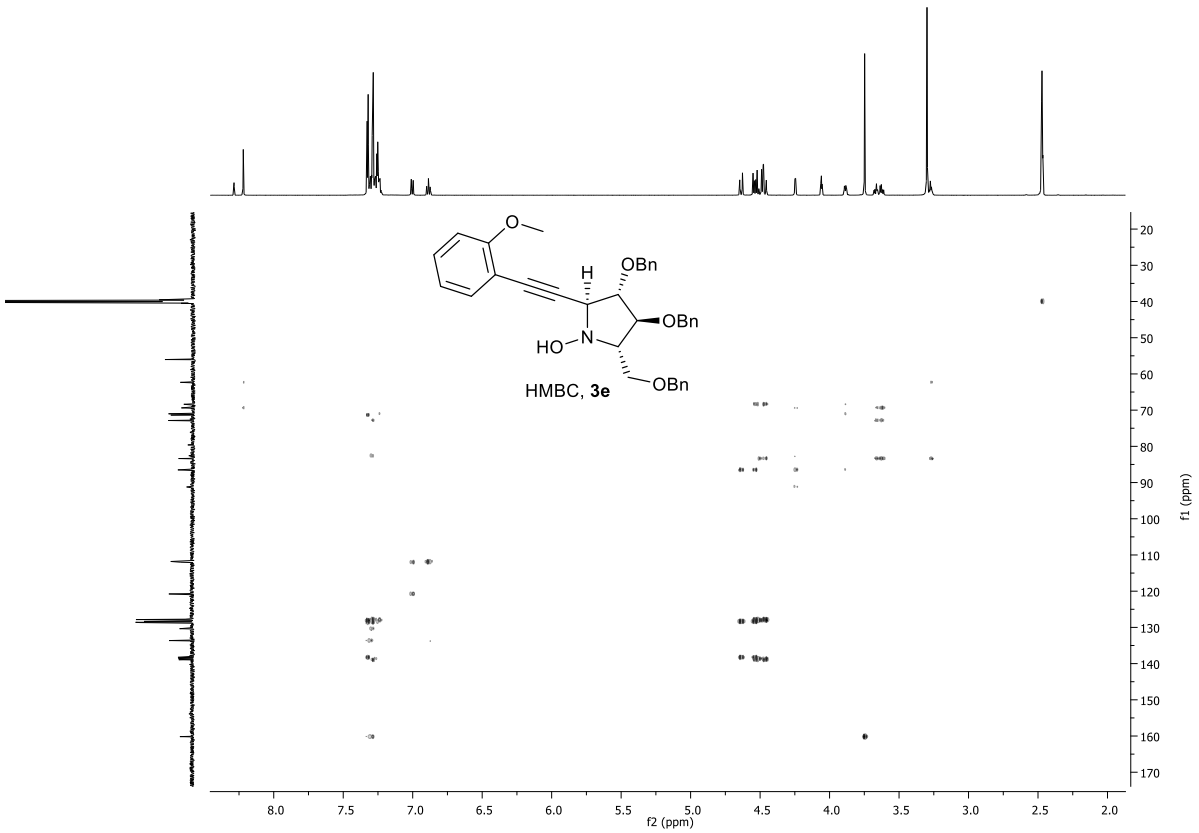

HSQC, 3d
f2 (ppm)
f1 (ppm)

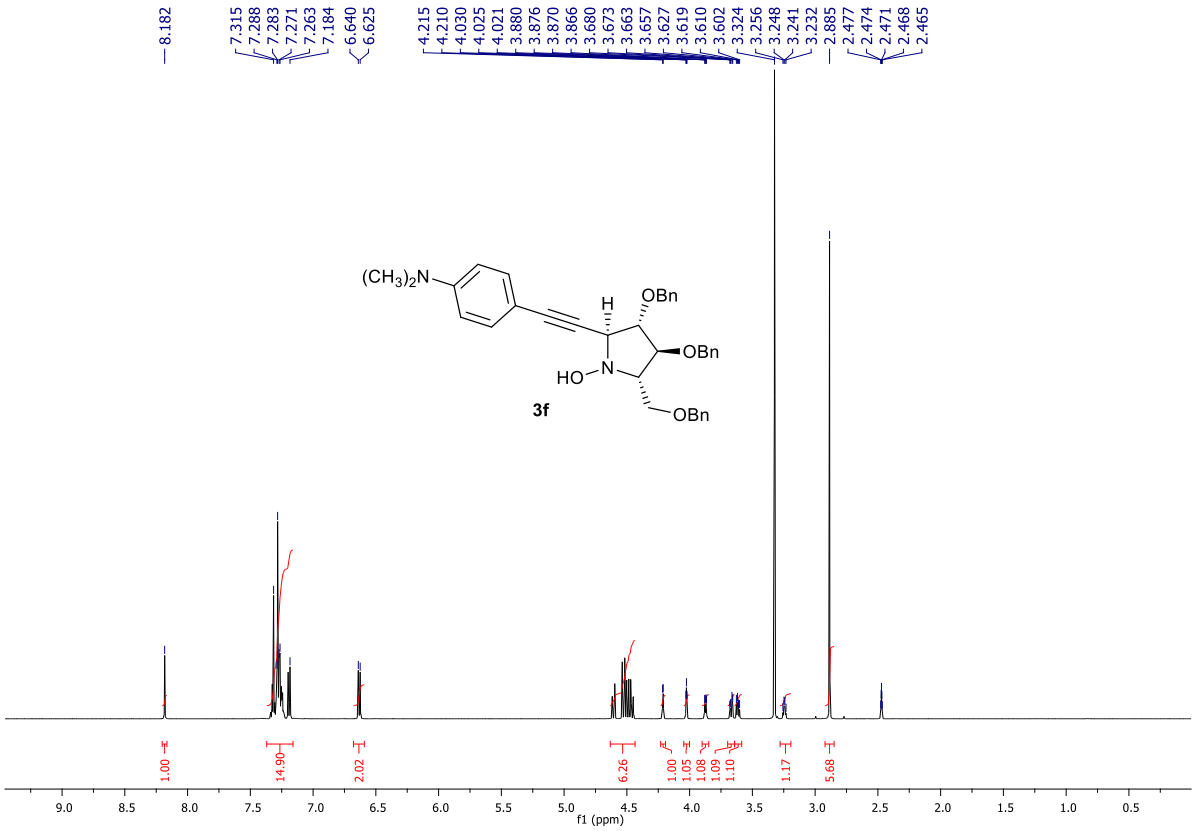

8.219
7.328
7.321
7.292
7.284
7.259
7.251
7.010
6.996
6.899
6.898
6.887
6.886
6.874
6.873
4.646
4.627
4.551
4.541
4.531
4.521
4.489
4.478
4.475
4.455
4.249
4.244
4.063
4.059
4.054
3.748
3.663
3.283
3.275
3.267
2.477
2.474
2.471
2.468
2.465
3e
f1 (ppm)

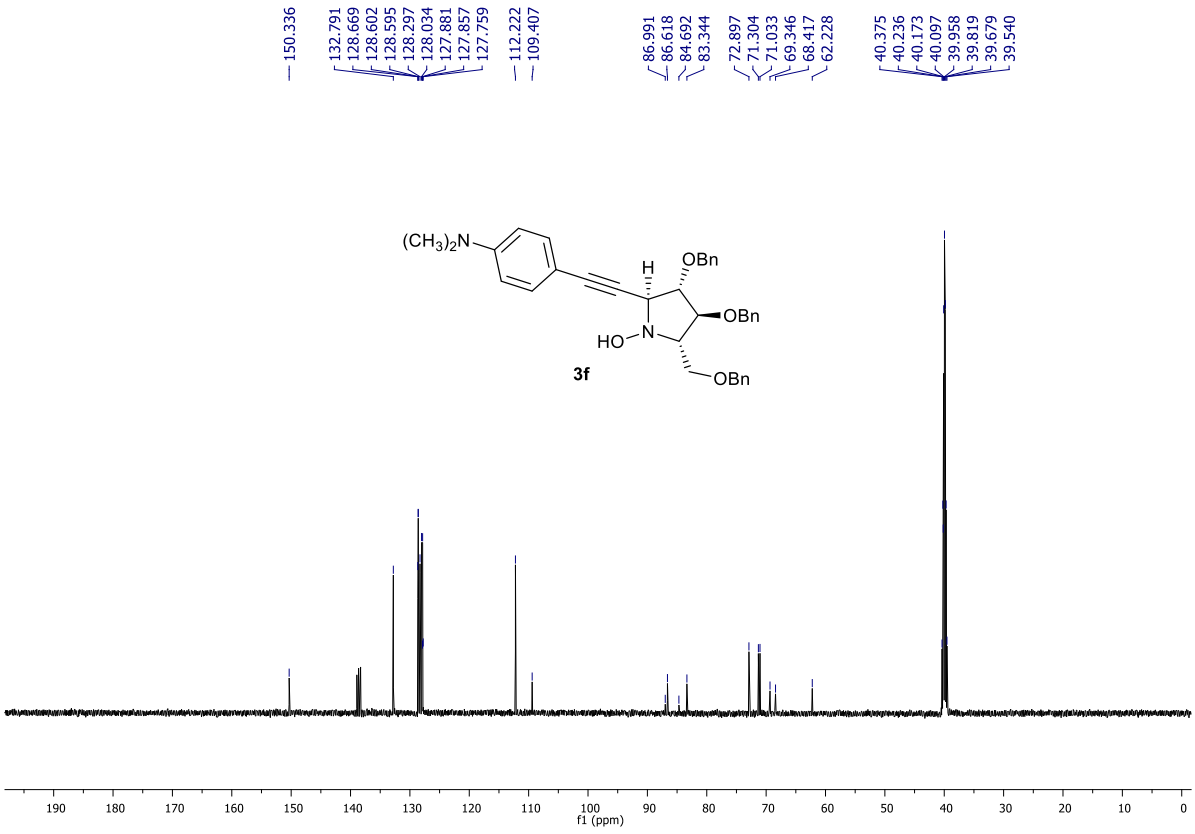

160.180
138.647
138.284
133.650
128.685
128.615
128.580
128.366
128.067
128.028
127.856
127.770
120.783
112.021
111.813
91.232
86.518
83.384
72.882
71.378
71.024
69.395
68.400
62.344
56.042
40.396
40.258
40.119
39.980
39.841
39.702
39.563
O
H
OBn
OBn
HO
N
OBn
3e
f1 (ppm)

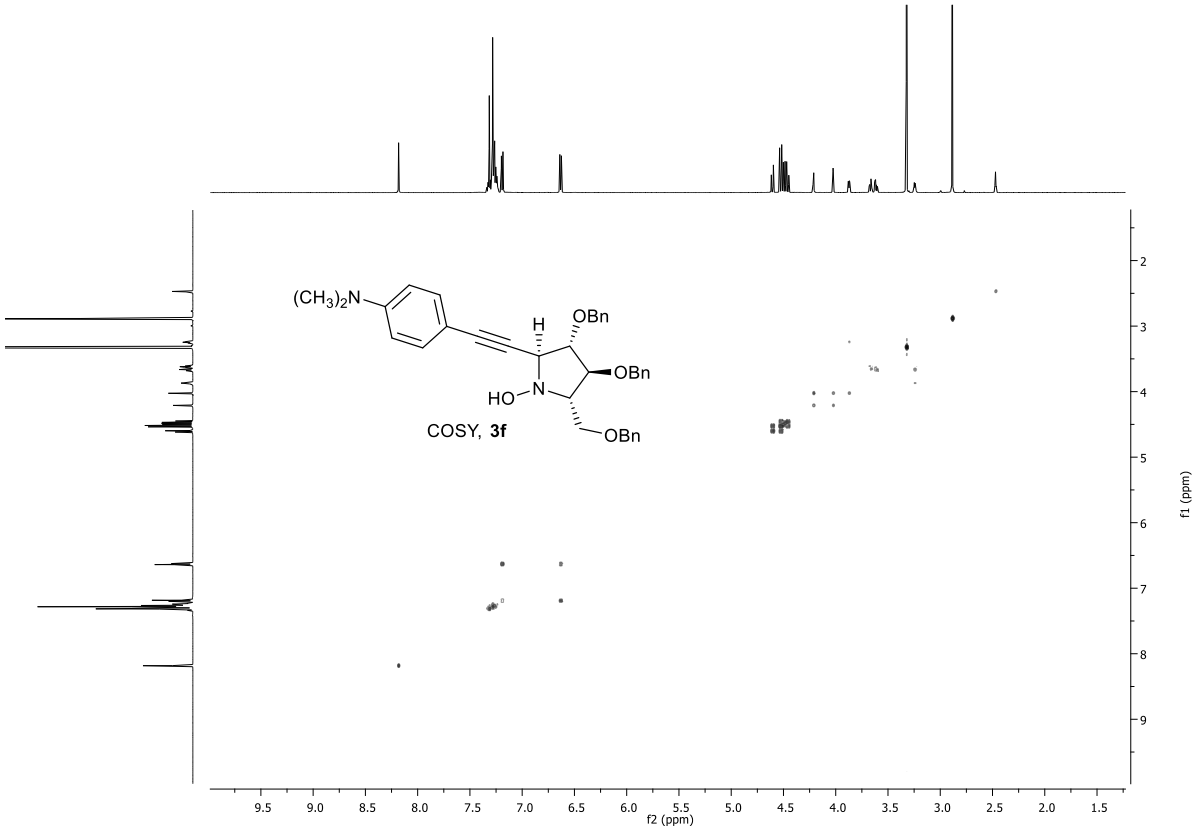

O
H
OBn
OBn
HO
N
OBn
3e
f1 (ppm)
f2 (ppm)

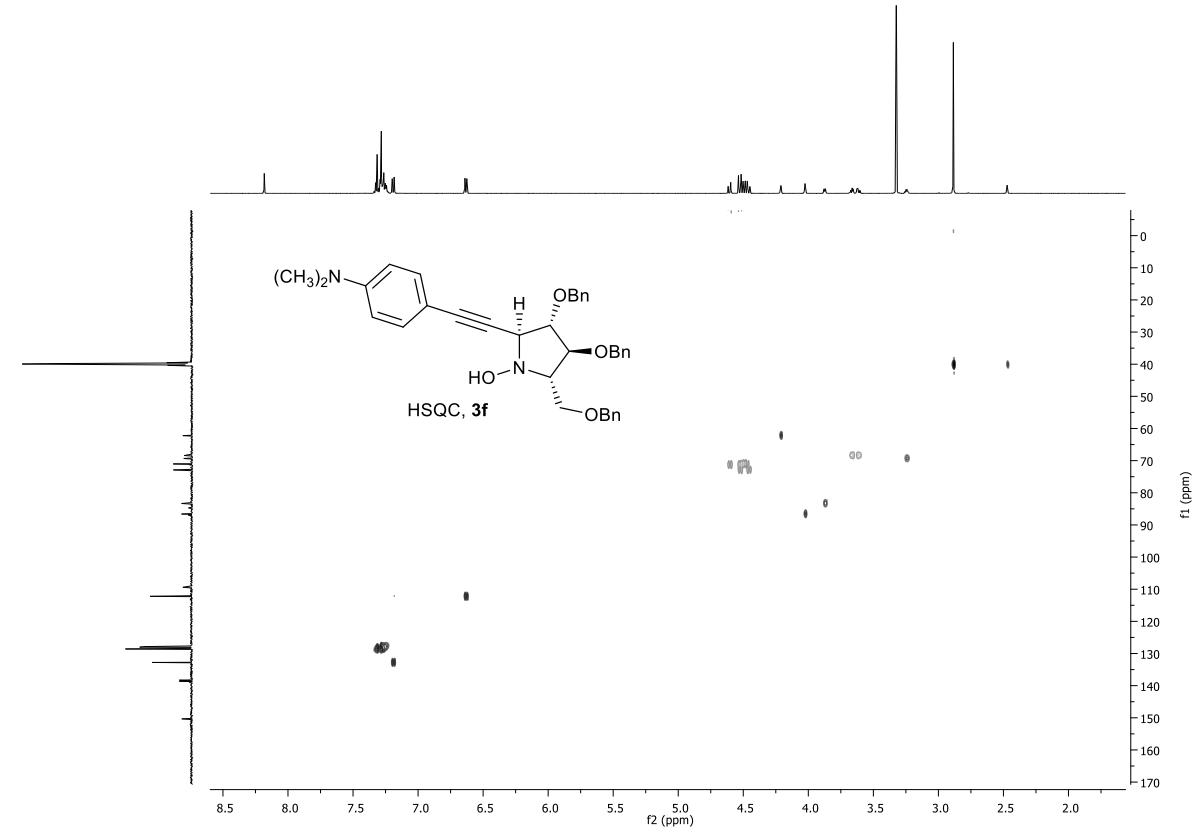

O
H
OBn
OBn
HO
N
OBn
HSQC, 3e
f2 (ppm)
f1 (ppm)

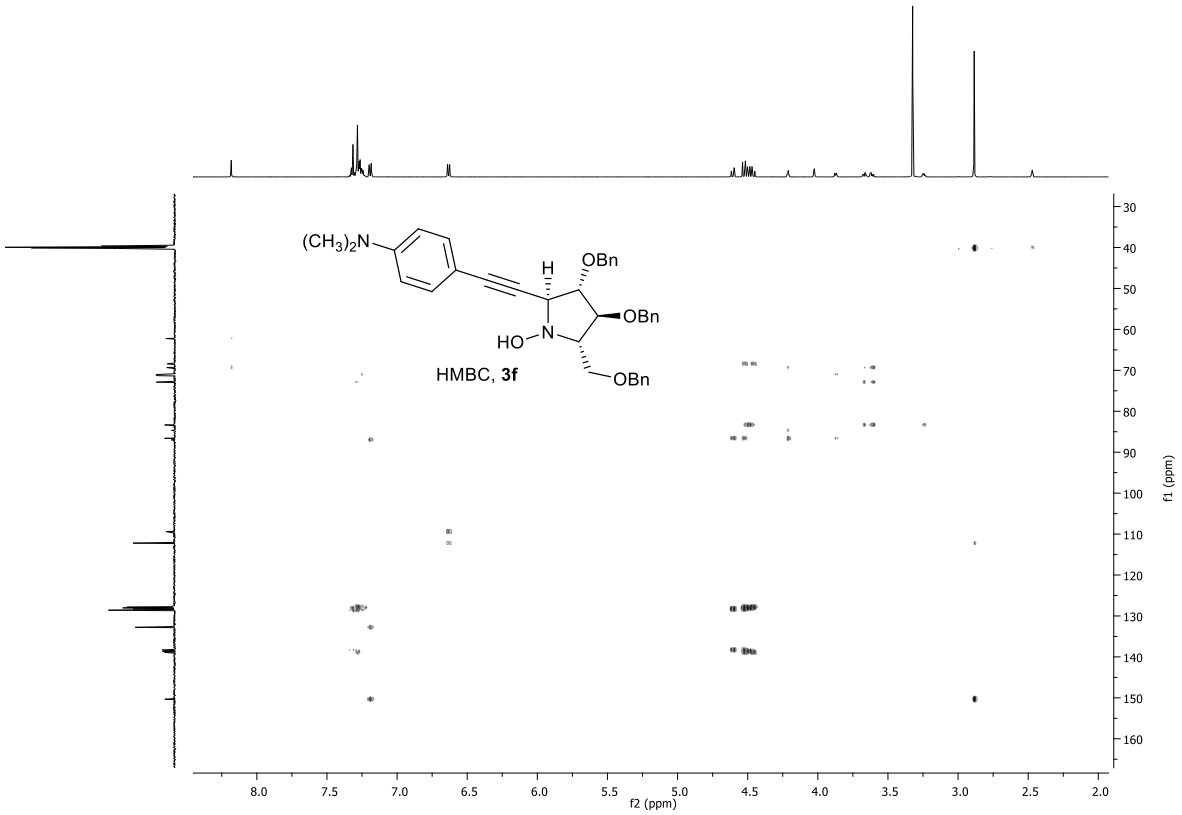

O
H
OBn
OBn
HO
N
OBn
HMBC, 3e
f2 (ppm)
f1 (ppm)

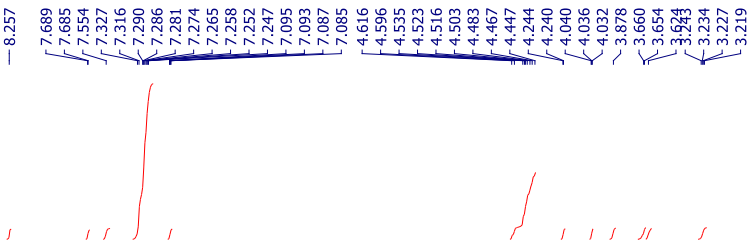

8.182
7.315
7.288
7.283
7.271
7.263
7.184
6.640
6.625
4.215
4.210
4.030
4.025
4.021
3.880
3.876
3.870
3.866
3.680
3.673
3.663
3.657
3.627
3.619
3.610
3.602
3.324
3.256
3.248
3.241
3.232
2.885
2.477
2.474
2.471
2.468
2.465
(CH3)2N
H
OBn
OBn
HO
N
OBn
3f
1.00
14.90
2.02
6.26
1.00
1.05
1.08
1.09
1.10
1.17
5.68
f1 (ppm)

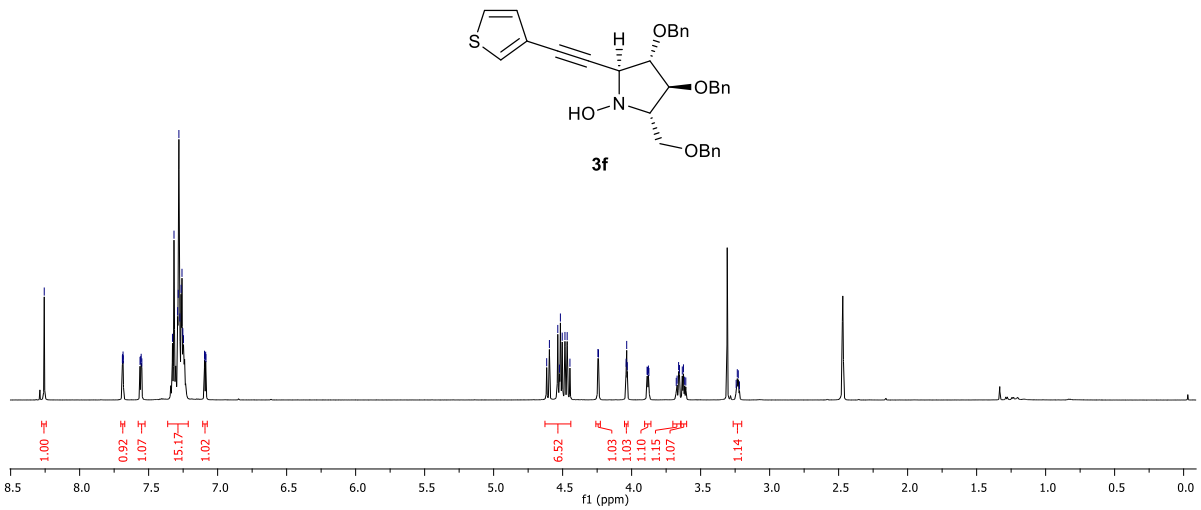

150.336
132.791
128.669
128.602
128.595
128.297
128.034
127.881
127.857
127.759
112.222
109.407
86.991
86.618
84.692
83.344
72.897
71.304
71.033
69.346
68.417
62.228
40.375
40.236
40.173
40.097
39.958
39.819
39.679
39.540
(CH3)2N
H
OBn
OBn
HO
N
OBn
3f
f1 (ppm)

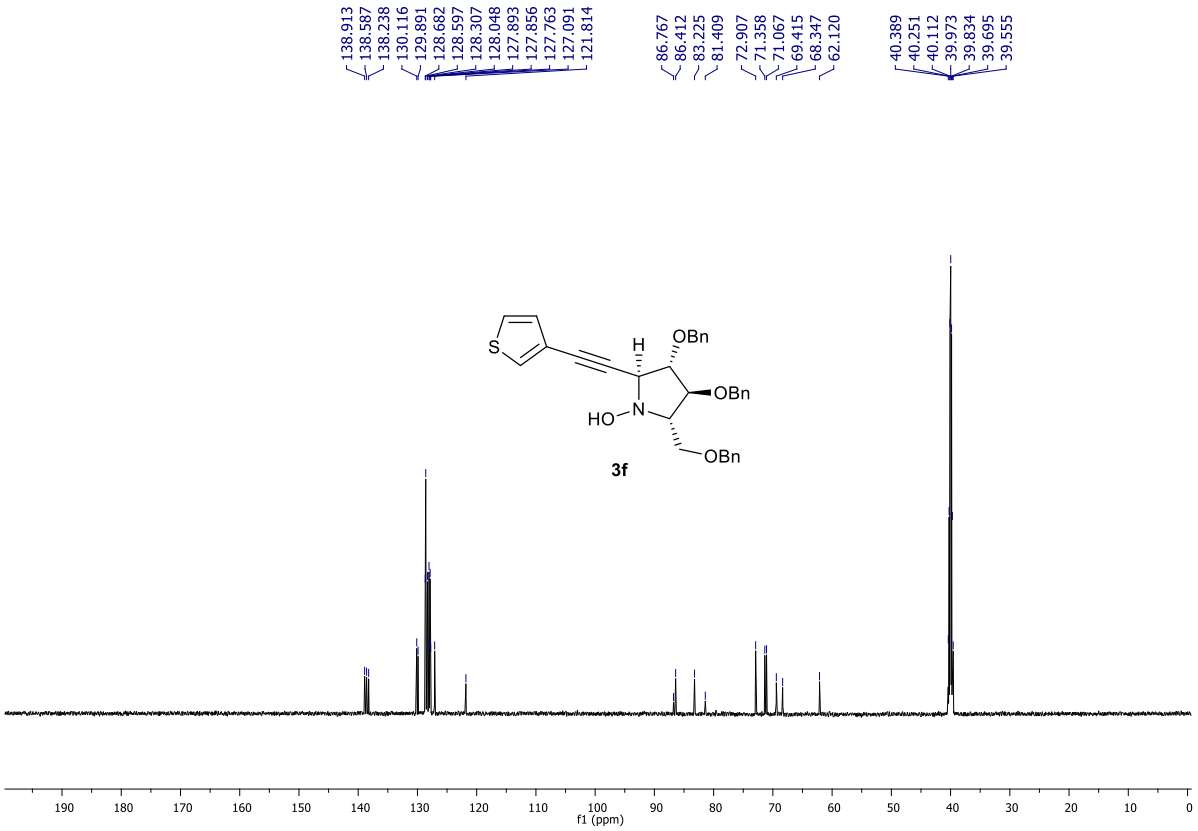

(CH3)2N
H
OBn
OBn
HO
N
OBn
COSY, 3f
f2 (ppm)
f1 (ppm)

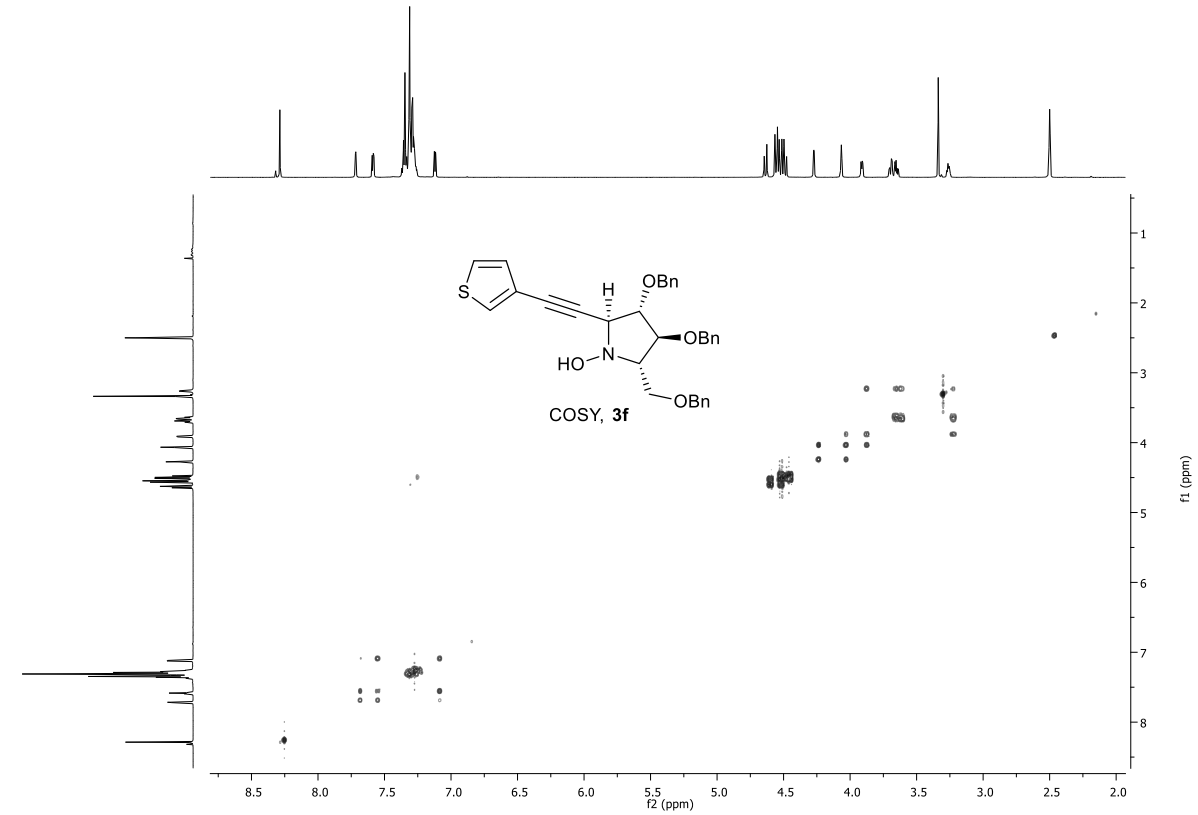

(CH3)2N
H
OBn
OBn
HO
N
OBn
HSQC, 3f
f2 (ppm)
f1 (ppm)

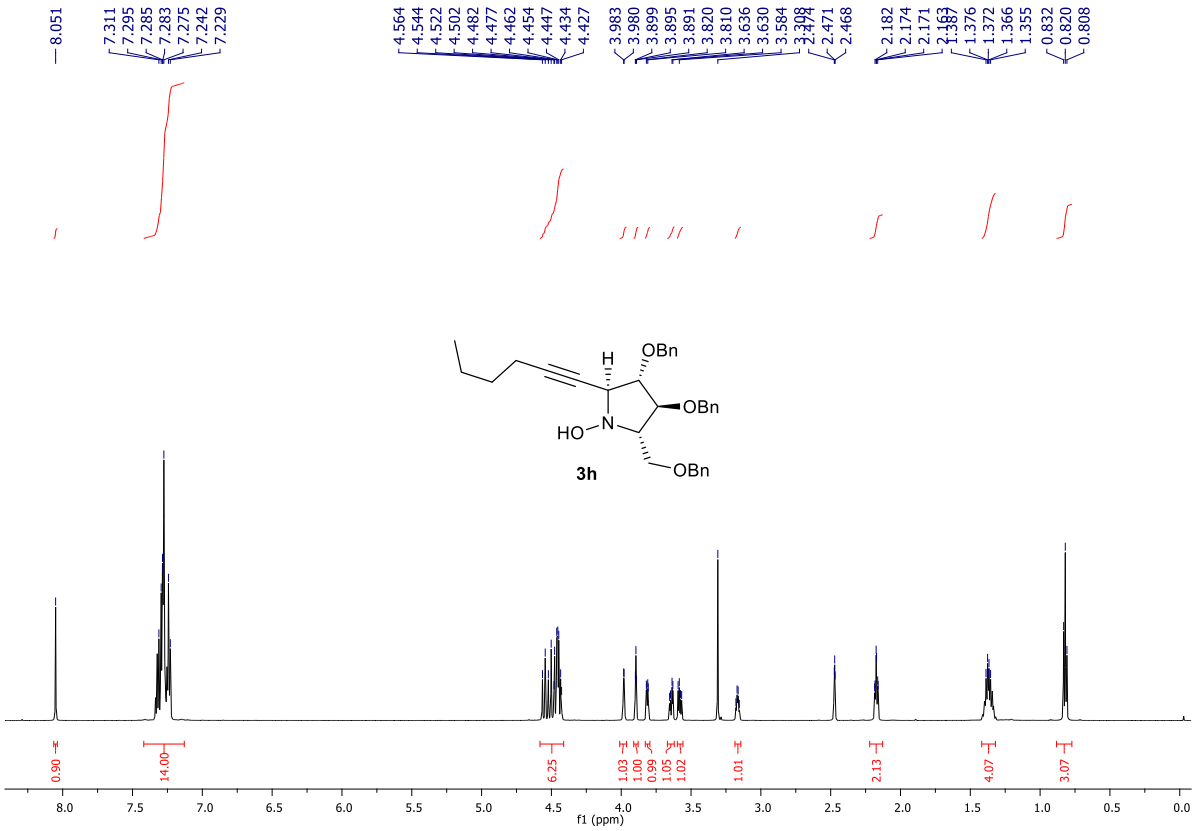

(CH3)2N
H
OBn
OBn
HO
N
OBn
HMBC, 3f
f2 (ppm)
f1 (ppm)

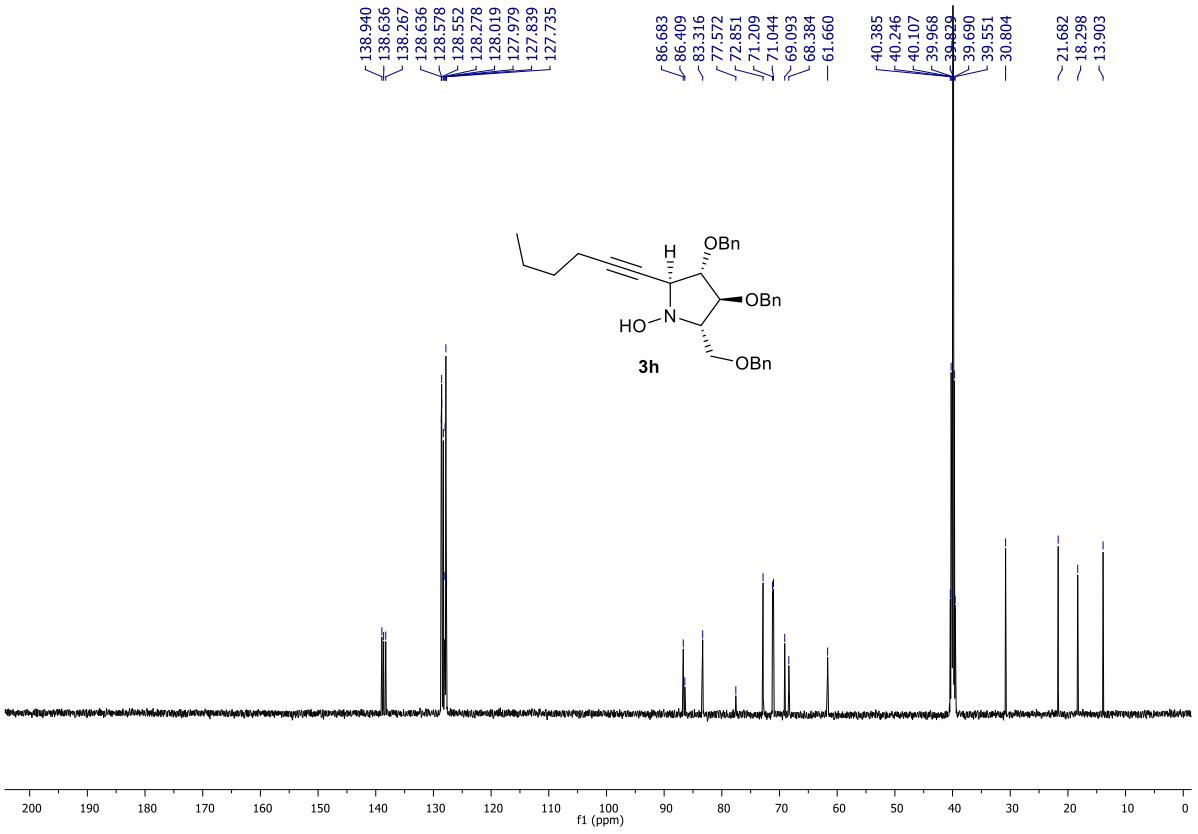

8.257
7.689
7.685
7.554
7.327
7.316
7.290
7.286
7.281
7.274
7.265
7.258
7.252
7.247
7.095
7.093
7.087
7.085
4.616
4.596
4.535
4.523
4.516
4.503
4.483
4.467
4.447
4.244
4.240
4.040
4.036
4.032
3.878
3.660
3.654
3.234
3.227
3.219

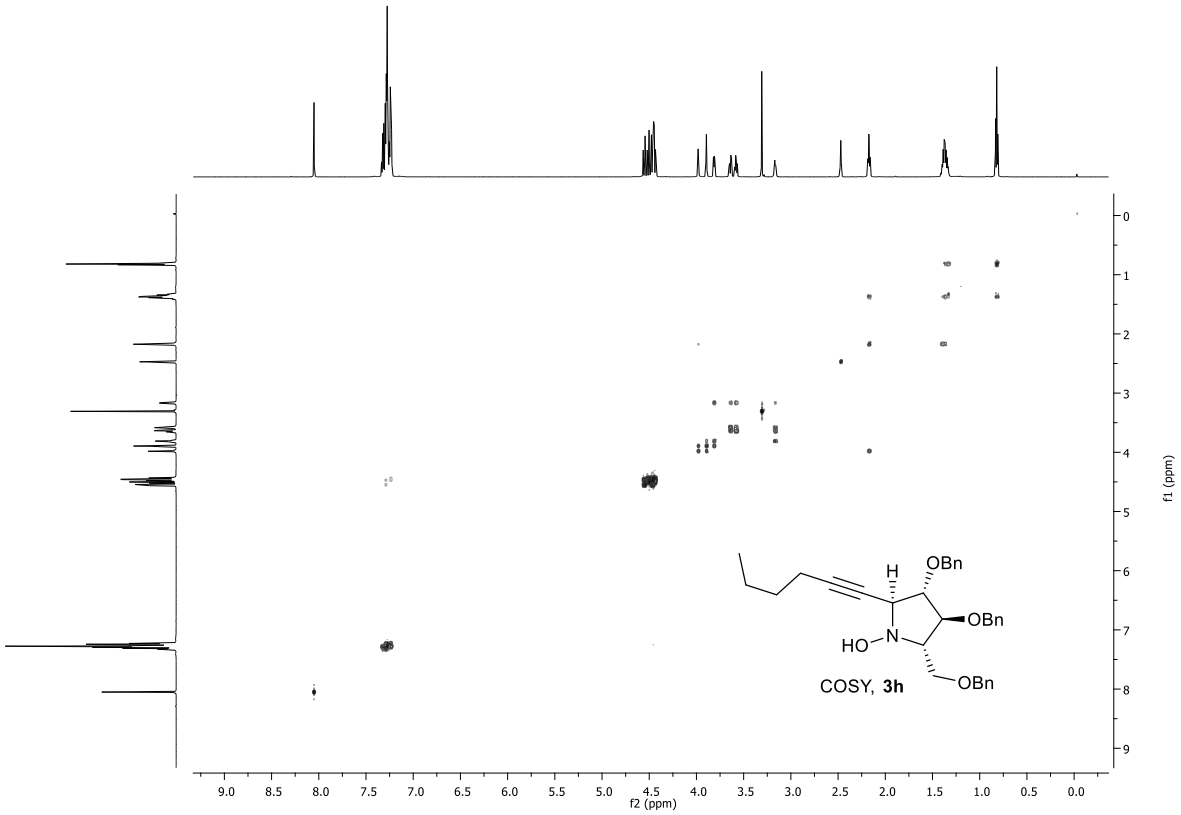

S
H
OBn
OBn
HO
N
OBn
3f
1.00
0.92
1.07
15.17
1.02
6.52
1.03
1.03
1.10
1.15
1.07
1.14
f1 (ppm)

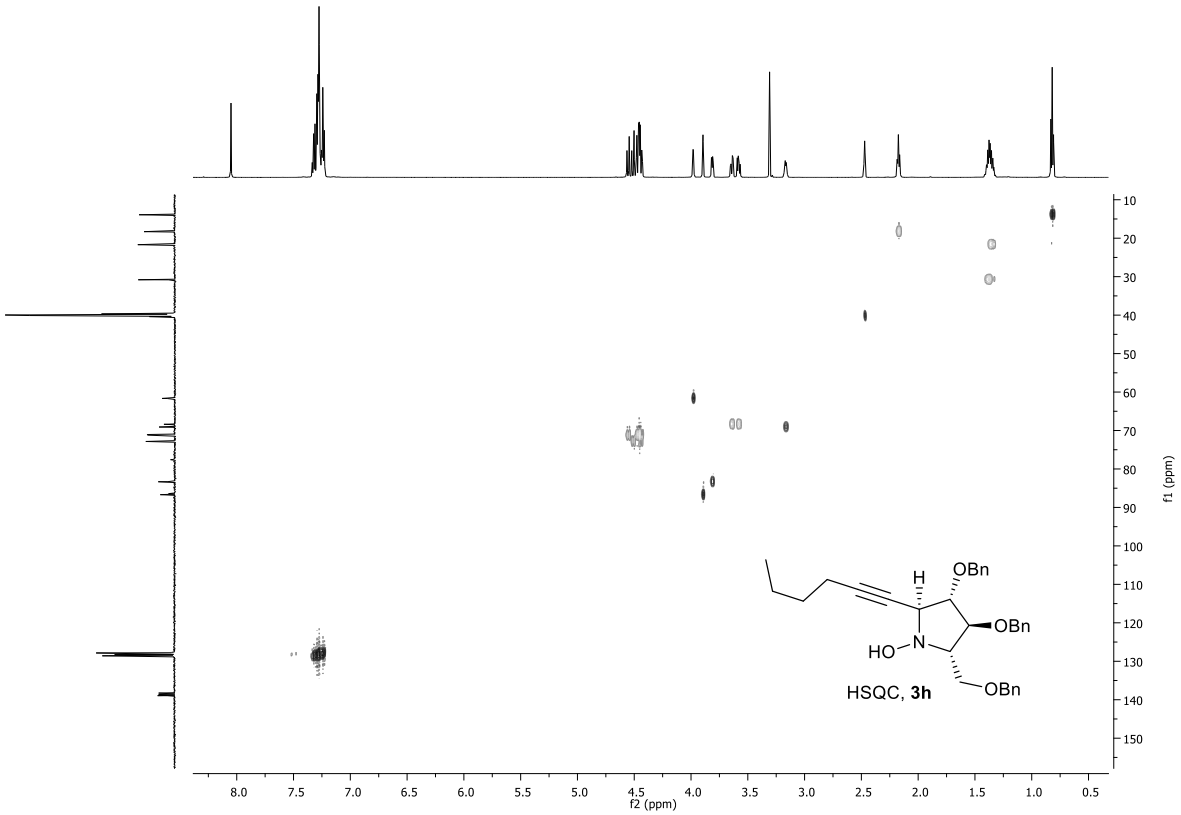

138.913
138.587
138.238
130.116
129.891
128.682
128.597
128.307
128.048
127.893
127.856
127.763
127.091
121.814
86.767
86.412
83.225
81.409
72.907
71.358
71.067
69.415
68.347
62.120
40.389
40.251
40.112
39.973
39.834
39.695
39.555
S
H
OBn
OBn
HO
N
OBn
3f
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

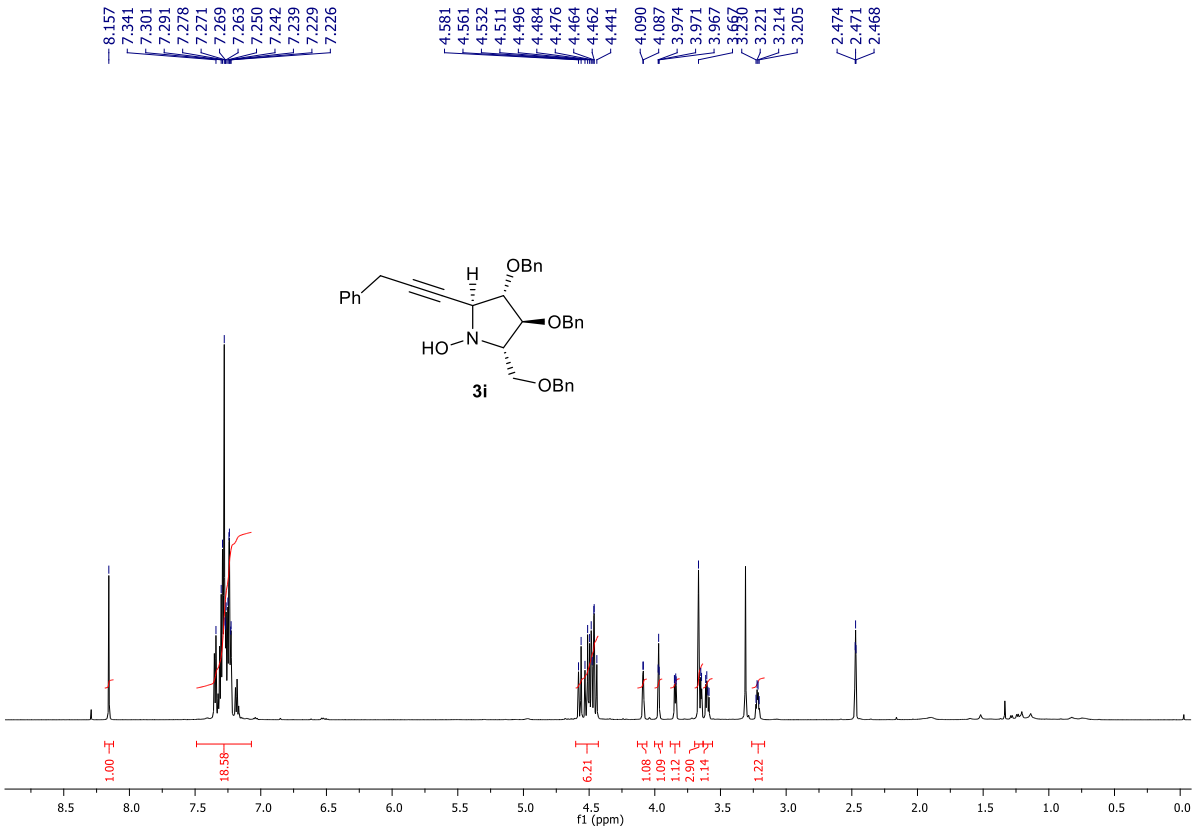

S
H
OBn
OBn
HO
N
OBn
COSY, 3f
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f2 (ppm)
1
2
3
4
5
6
7
8
f1 (ppm)

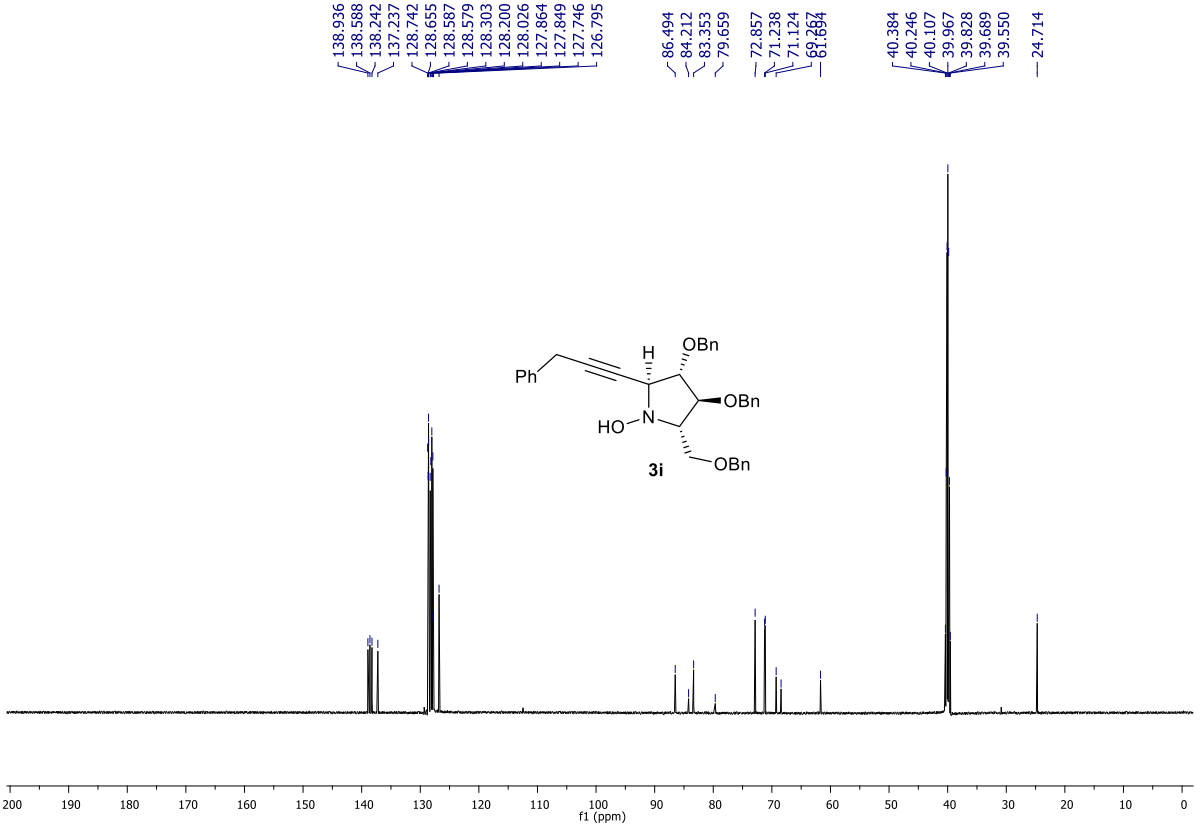

8.051
7.311
7.295
7.285
7.283
7.275
7.242
7.229
4.564
4.544
4.522
4.502
4.482
4.477
4.462
4.454
4.447
4.434
4.427
3.983
3.980
3.899
3.895
3.891
3.820
3.810
3.636
3.630
3.584
2.471
2.468
2.182
2.174
2.171
1.376
1.372
1.366
1.355
0.832
0.820
0.808
OBn
H
OBn
HO
N
OBn
3h
0.90
14.00
6.25
1.03
1.00
0.99
1.05
1.02
1.01
2.13
4.07
3.07
f1 (ppm)

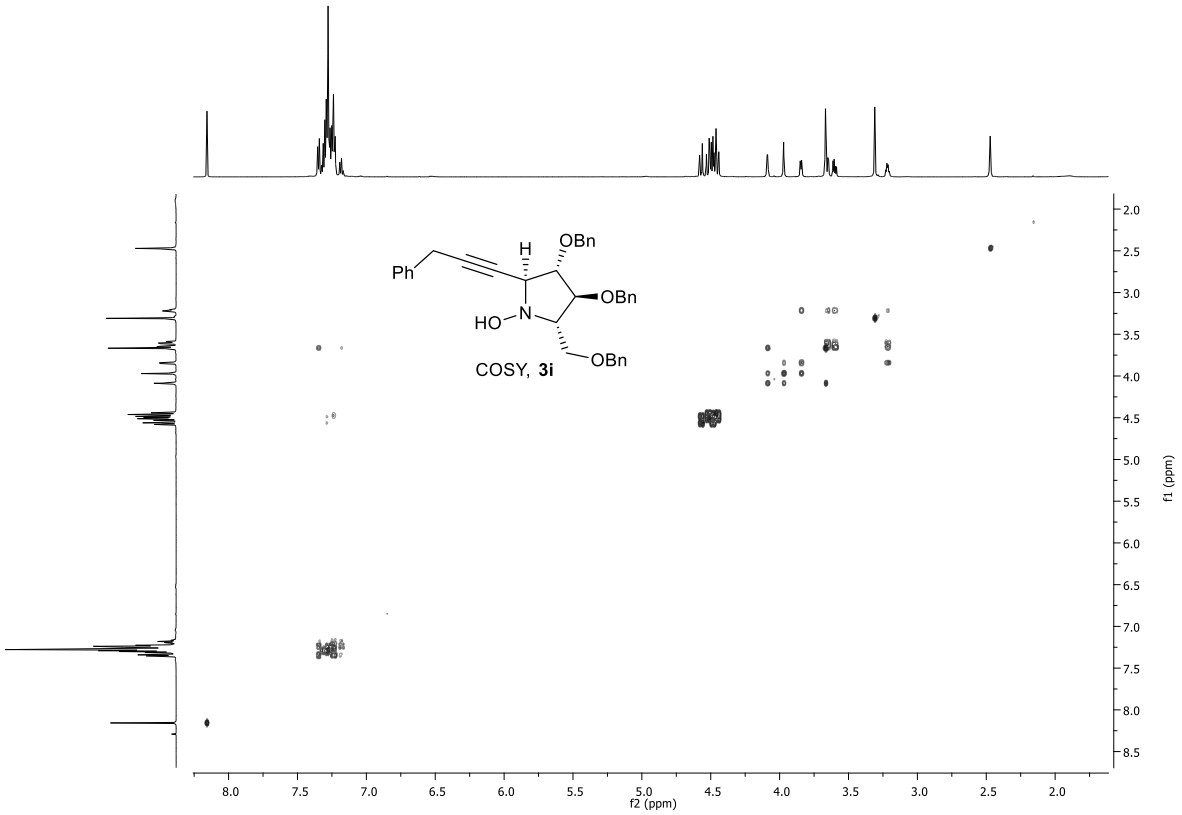

138.940
138.636
138.267
128.636
128.578
128.552
128.278
128.019
127.979
127.839
127.735
86.683
86.409
83.316
77.572
72.851
71.209
71.044
69.093
68.384
61.660
40.385
40.246
40.107
39.968
39.829
39.690
39.551
30.804
21.682
18.298
13.903
OBn
H
OBn
HO
N
OBn
3h
f1 (ppm)

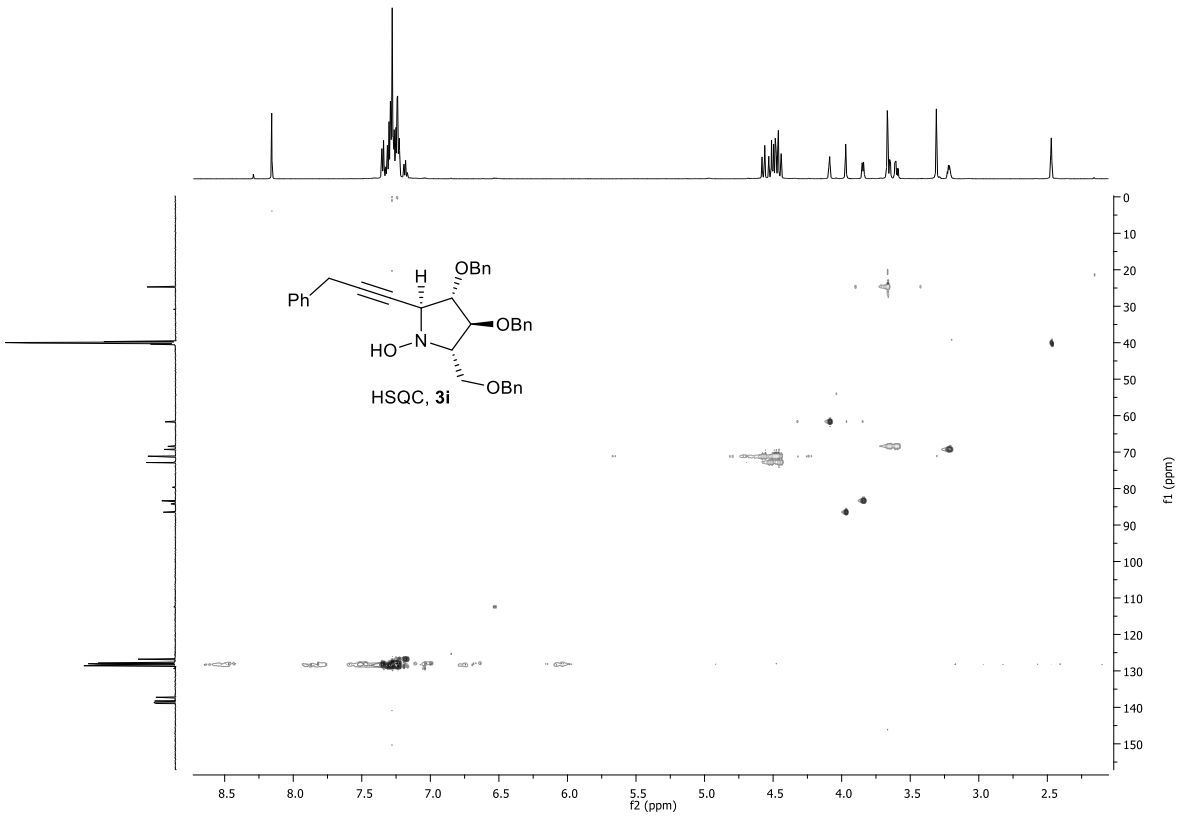

f2 (ppm)
f1 (ppm)
OBn
H
OBn
HO
N
OBn
COSY, 3h

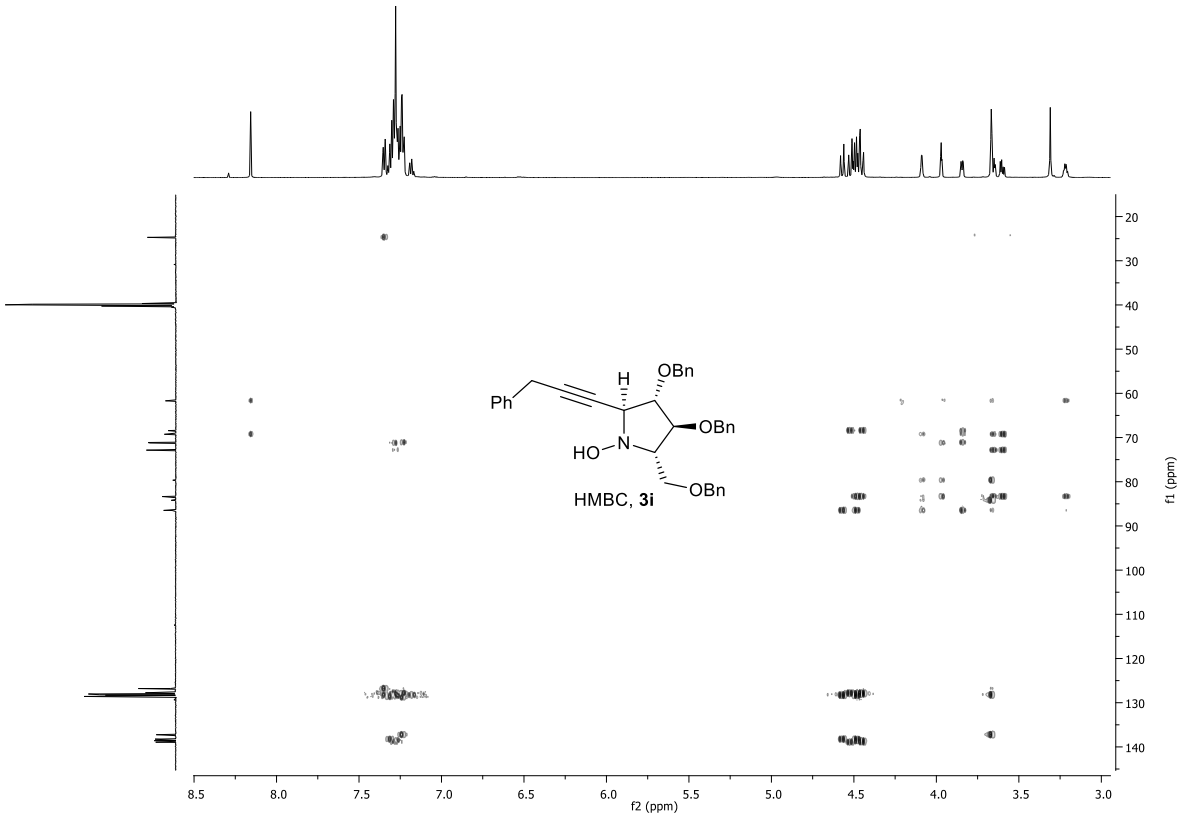

f2 (ppm)
f1 (ppm)
OBn
H
OBn
HO
N
OBn
HSQC, 3h

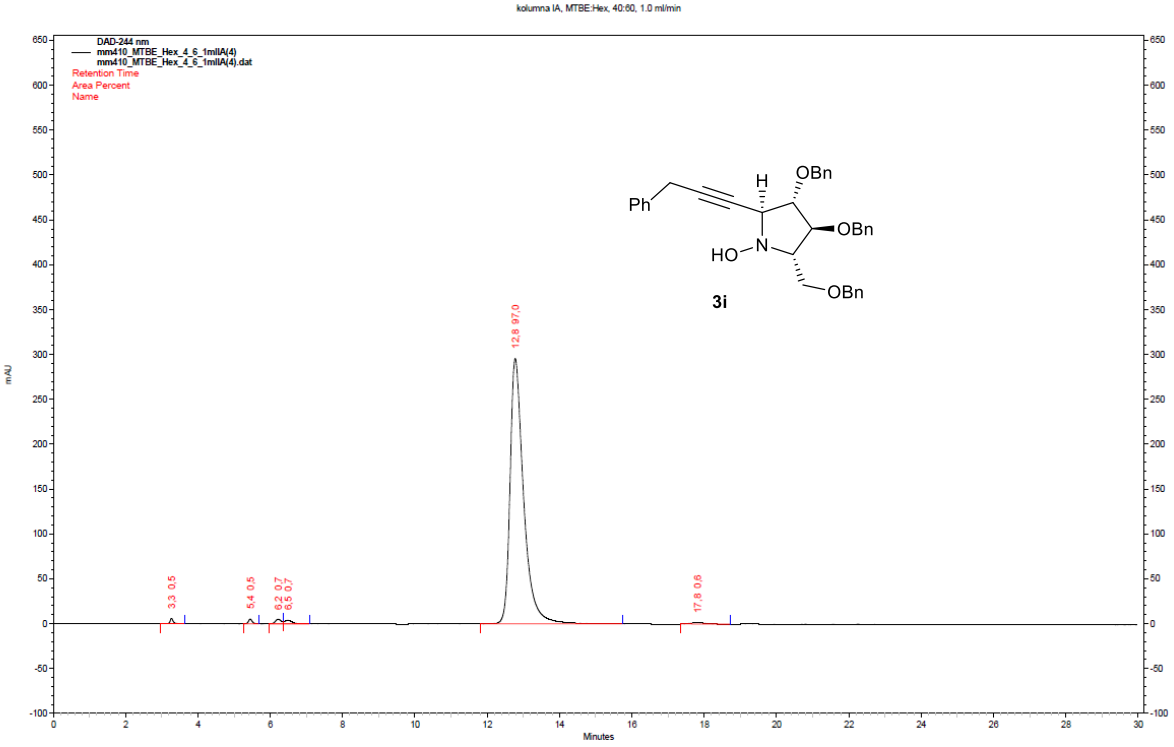

8.157
7.341
7.301
7.291
7.278
7.271
7.269
7.263
7.250
7.242
7.239
7.229
7.226
4.581
4.561
4.532
4.511
4.496
4.484
4.476
4.464
4.462
4.441
4.090
4.087
3.974
3.971
3.967
3.230
3.221
3.214
3.205
2.474
2.471
2.468
Ph
H
OBn
OBn
HO
N
OBn
3i
1.00
18.58
6.21
1.08
1.09
1.12
2.90
1.14
1.22
f1 (ppm)

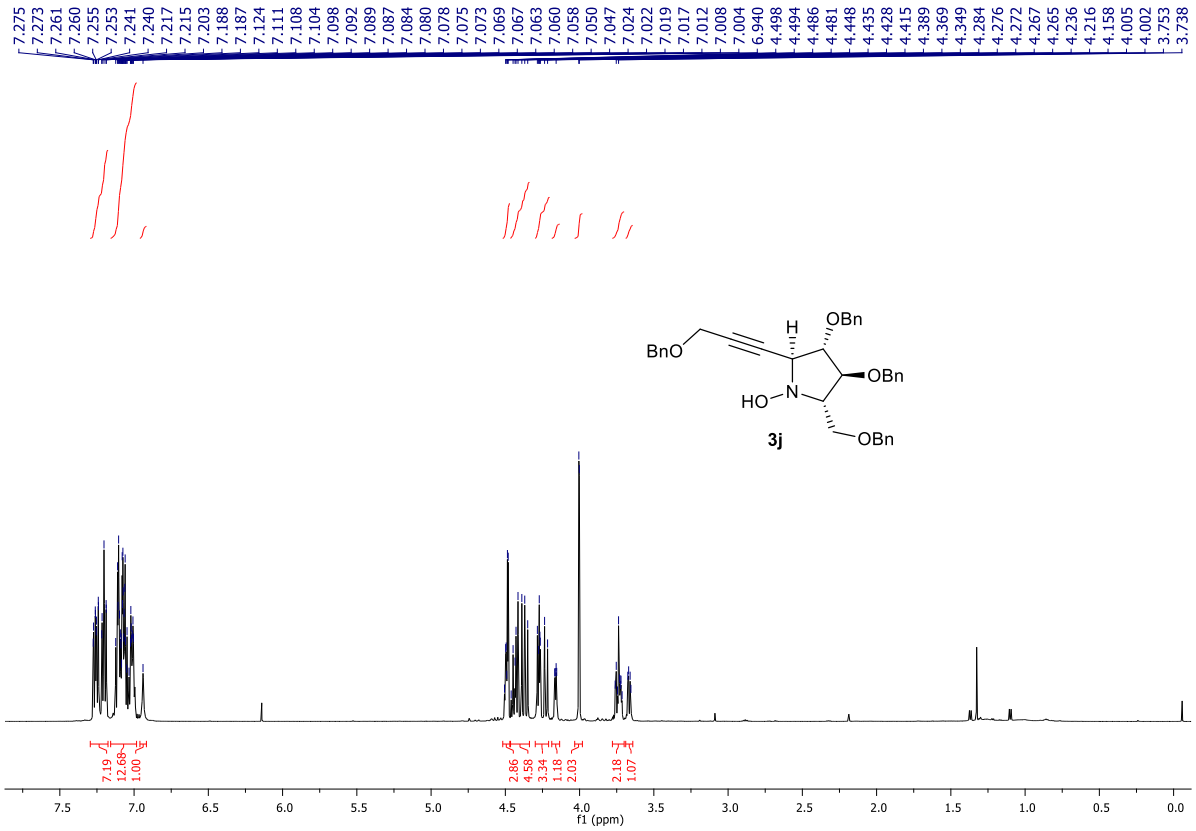

138.936
138.588
138.242
137.237
128.742
128.655
128.587
128.579
128.303
128.200
128.026
127.864
127.849
127.746
126.795
86.494
84.212
83.353
79.659
72.857
71.238
71.124
69.267
61.694
40.384
40.246
40.107
39.967
39.828
39.689
39.550
24.714
Ph
H
OBn
OBn
HO
N
OBn
3i
f1 (ppm)

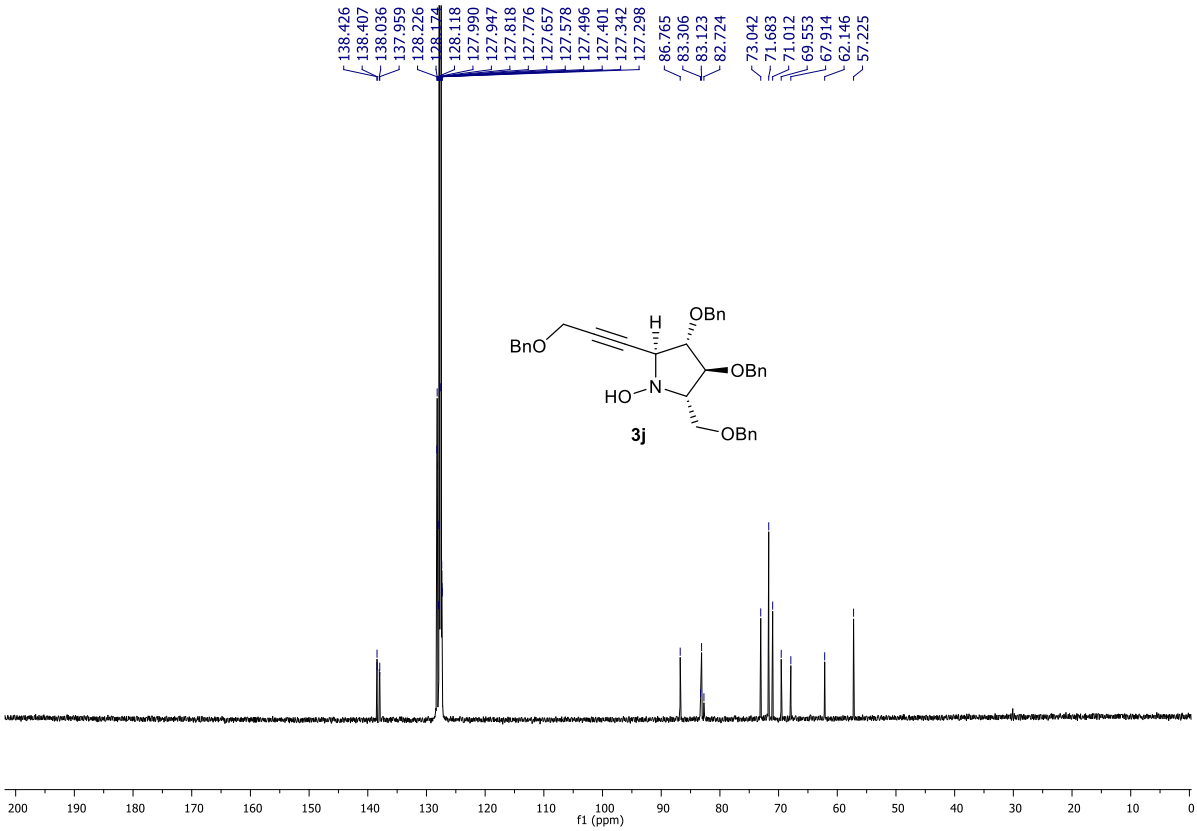

Ph
H
OBn
OBn
HO
N
OBn
COSY, 3i
f2 (ppm)
f1 (ppm)

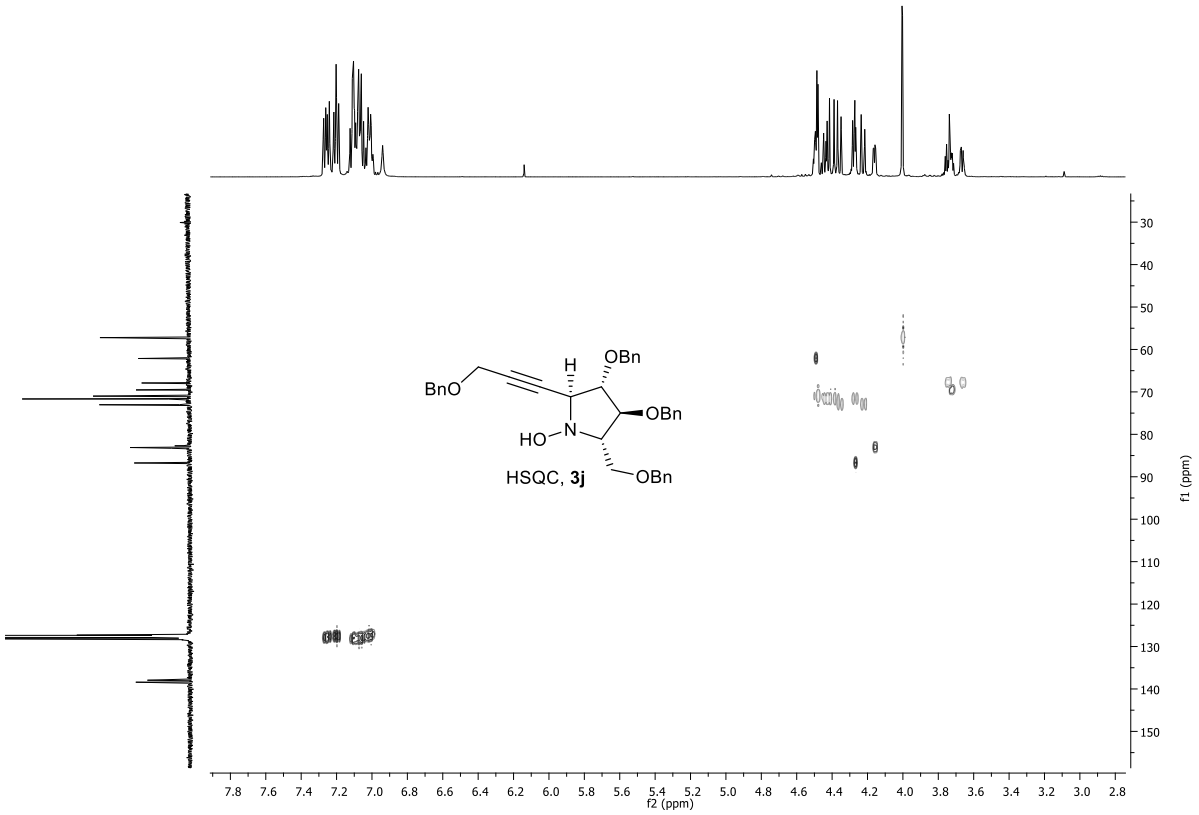

Ph
H
OBn
OBn
HO
N
OBn
HSQC, 3i
f2 (ppm)
f1 (ppm)

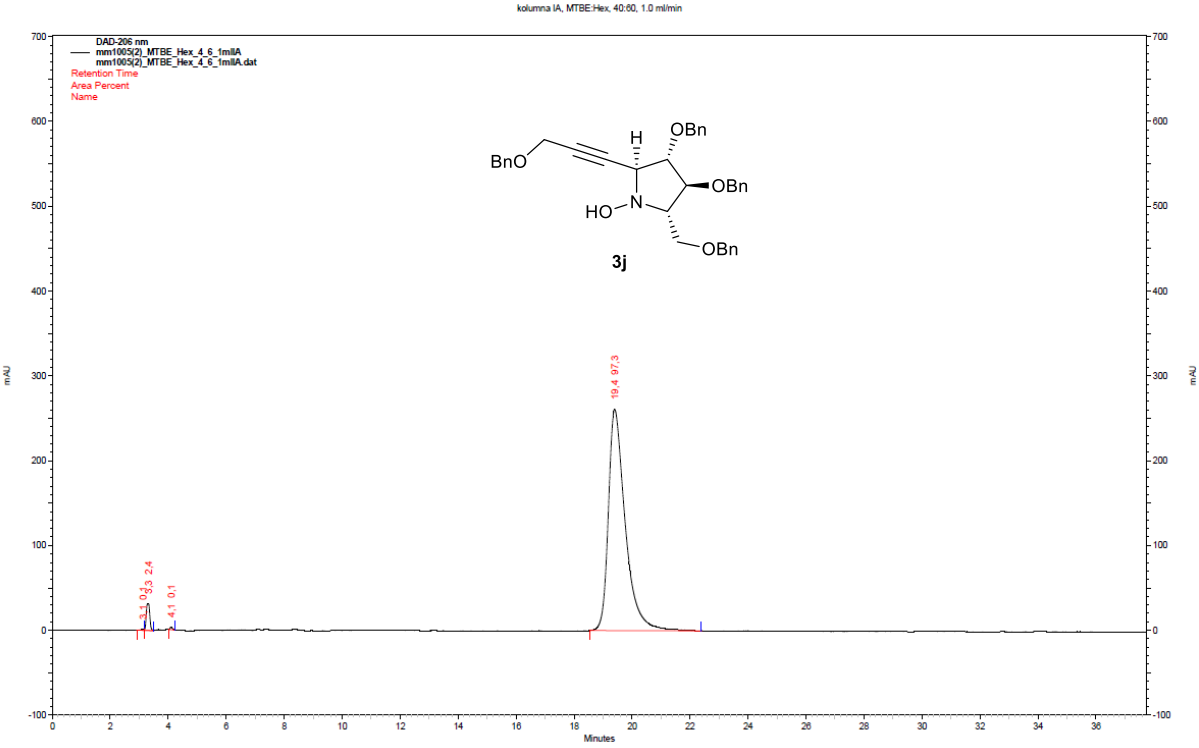

Ph
H
OBn
OBn
HO
N
OBn
HMBC, 3i
f2 (ppm)
f1 (ppm)

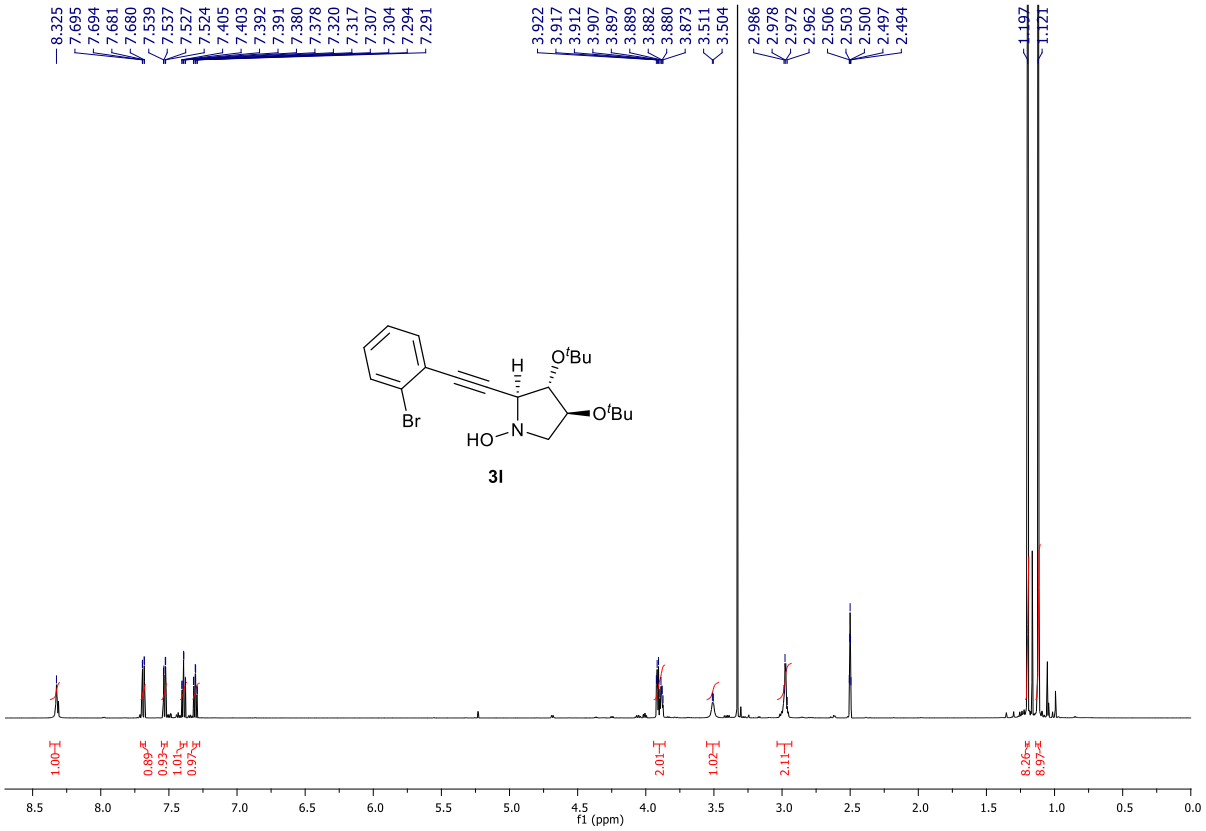

kolumna IA, MTBE:Hex, 40:60, 1.0 ml/min
DAD-244 nm
mm410_MTBE_Hex_4_6_1mlIA(4)
mm410_MTBE_Hex_4_6_1mlIA(4).dat
Retention Time
Area Percent
Name
Ph
H
OBn
OBn
HO
N
OBn
3i
12,8 97,0
3,3 0,5
5,4 0,5
6,2 0,7
6,5 0,7
17,8 0,6
mAU
Minutes

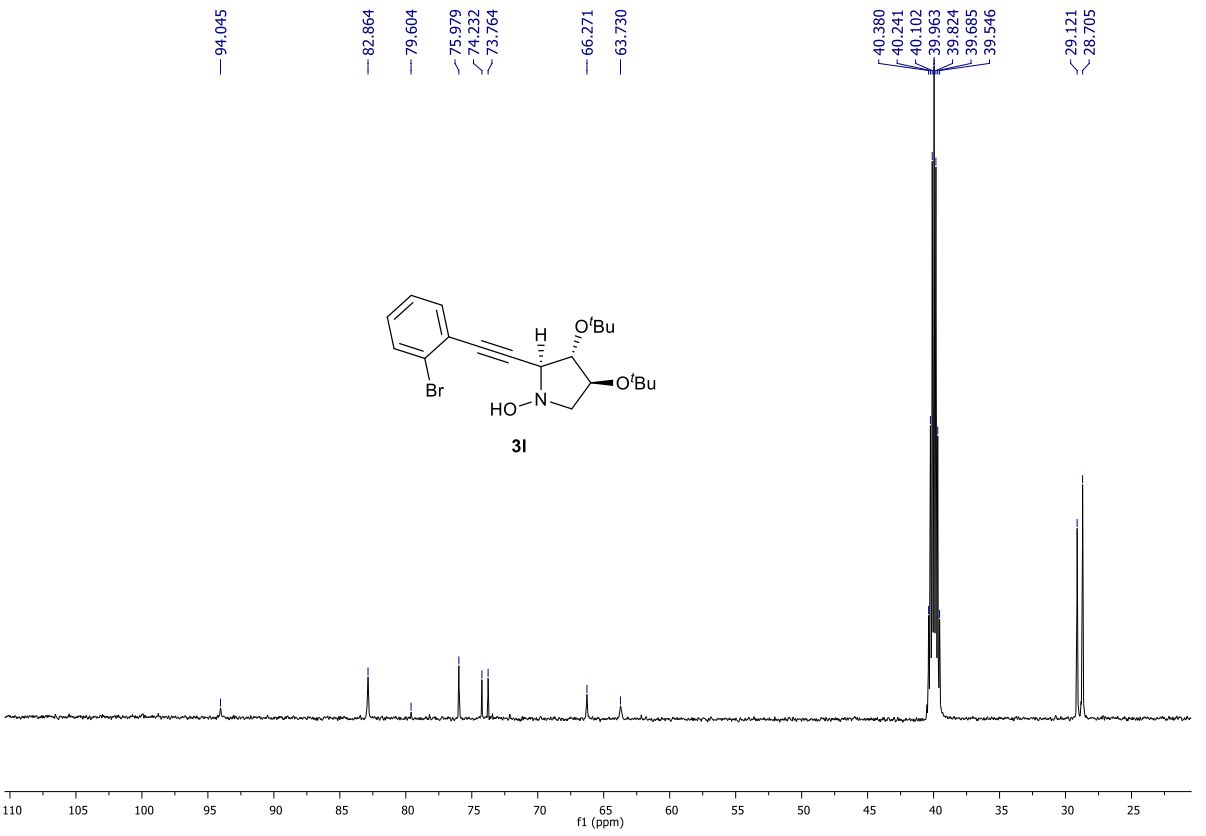

7.275
7.273
7.261
7.260
7.255
7.253
7.241
7.240
7.217
7.215
7.203
7.188
7.187
7.124
7.111
7.108
7.104
7.098
7.092
7.089
7.087
7.084
7.080
7.078
7.075
7.073
7.069
7.067
7.063
7.060
7.058
7.050
7.047
7.024
7.022
7.019
7.017
7.012
7.008
7.004
6.940
4.498
4.494
4.486
4.481
4.448
4.435
4.428
4.415
4.389
4.369
4.349
4.284
4.276
4.272
4.267
4.265
4.236
4.216
4.158
4.005
4.002
3.753
3.738
BnO
H
OBn
OBn
HO
N
OBn
3j
7.19
12.68
1.00
2.86
4.58
3.34
1.18
2.03
2.18
1.07
f1 (ppm)

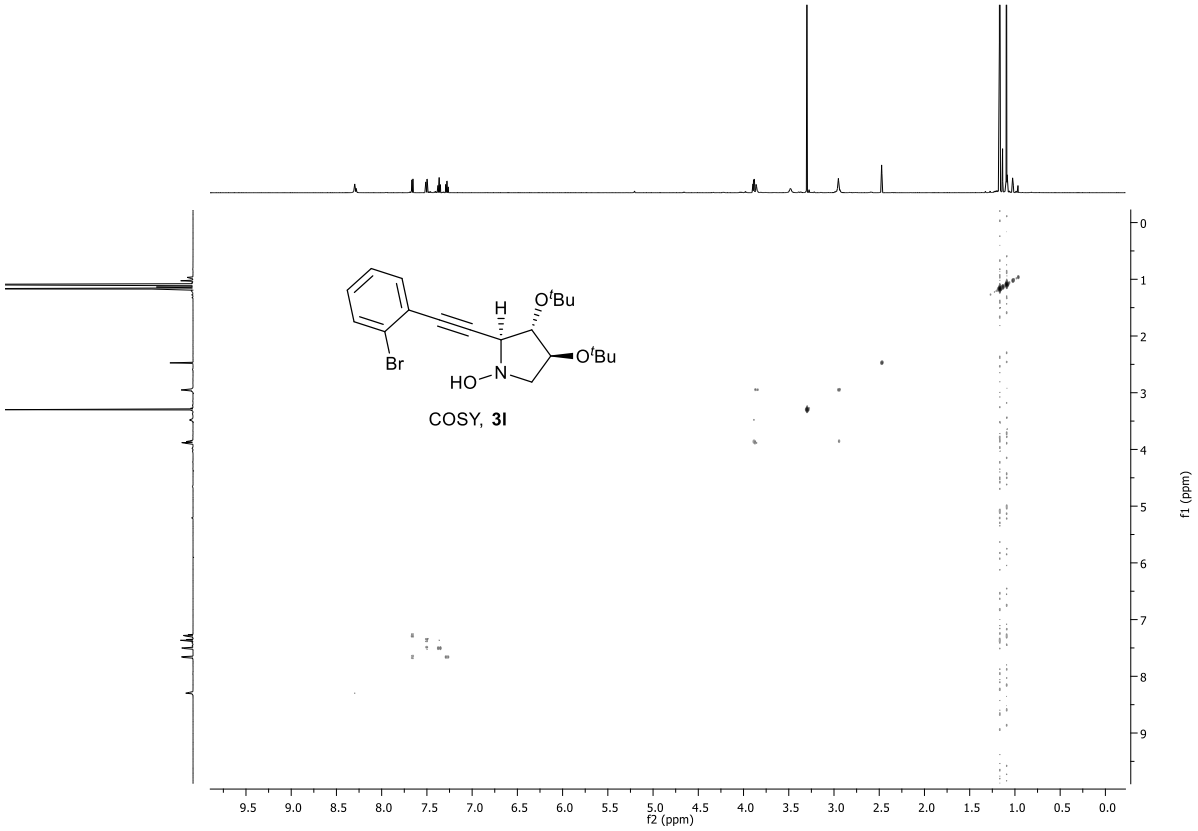

138.426
138.407
138.036
137.959
128.226
128.174
128.118
127.990
127.947
127.818
127.776
127.657
127.578
127.496
127.401
127.342
127.298
86.765
83.306
83.123
82.724
73.042
71.683
71.012
69.553
67.914
62.146
57.225
BnO
H
OBn
OBn
HO
N
OBn
3j
f1 (ppm)


BnO
H
OBn
OBn
HO
N
OBn
HSQC, 3j
f1 (ppm)
f2 (ppm)

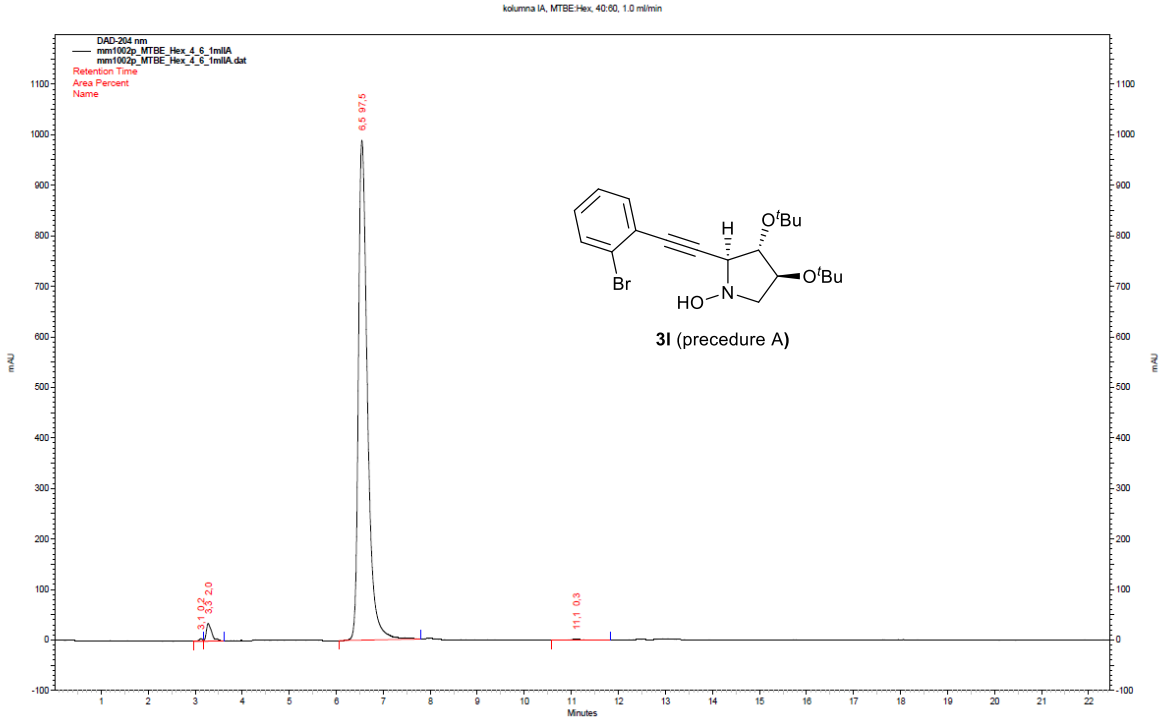

kolumna IA, MTBE:Hex, 40:60, 1.0 ml/min
DAD-206 nm
mm1005(2)_MTBE_Hex_4_6_1mlIA
mm1005(2)_MTBE_Hex_4_6_1mlIA.dat
Retention Time
Area Percent
Name
BnO
H
OBn
OBn
HO
N
OBn
3j
19,4 97,3
3,1 0,1
3,3 2,4
4,1 0,1
mAU
Minutes


8.325
7.695
7.694
7.681
7.680
7.539
7.537
7.527
7.524
7.405
7.403
7.392
7.391
7.380
7.378
7.320
7.317
7.307
7.304
7.294
7.291
3.922
3.917
3.912
3.907
3.897
3.889
3.882
3.880
3.873
3.511
3.504
2.986
2.978
2.972
2.962
2.506
2.503
2.500
2.497
2.494
1.197
1.121
Br
H
O^{t}Bu
O^{t}Bu
HO
N
3l
1.00
0.89
0.93
1.01
0.97
2.01
1.02
2.11
8.26
8.97
f1 (ppm)

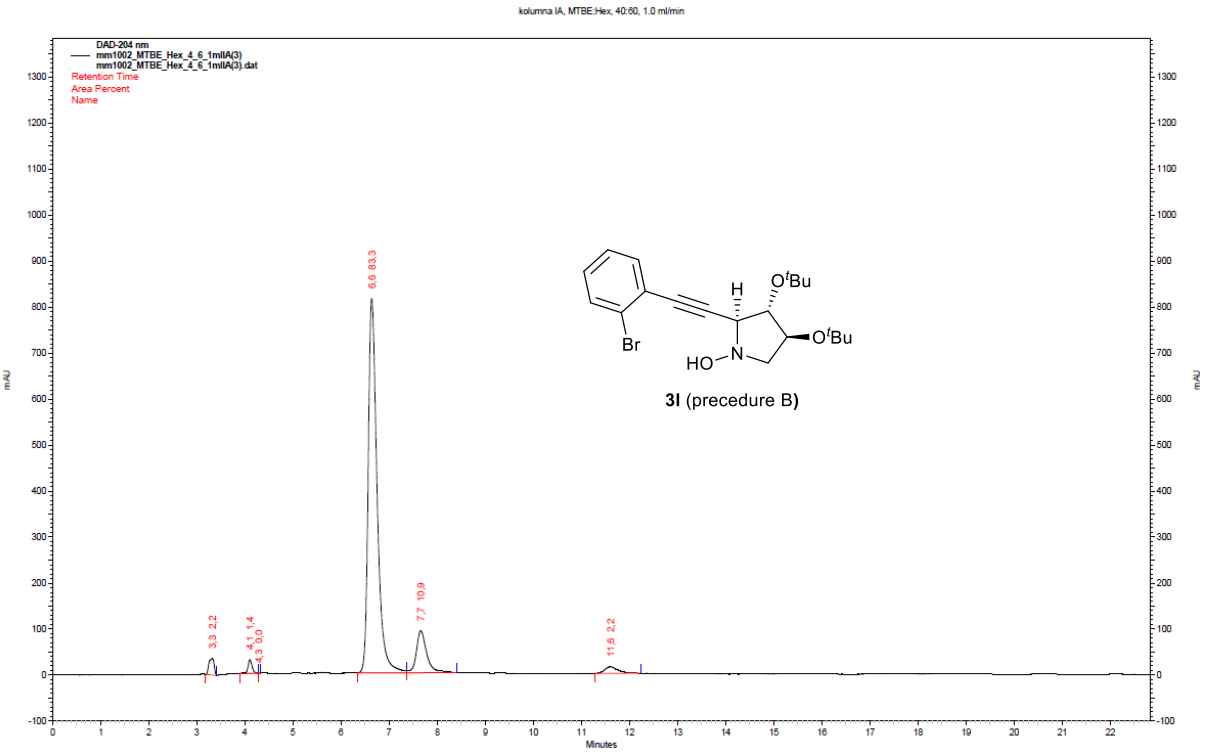

94.045
82.864
79.604
75.979
74.232
73.764
66.271
63.730
40.380
40.241
40.102
39.963
39.824
39.685
39.546
29.121
28.705
Br
H
O^{t}Bu
O^{t}Bu
HO
N
3l
f1 (ppm)



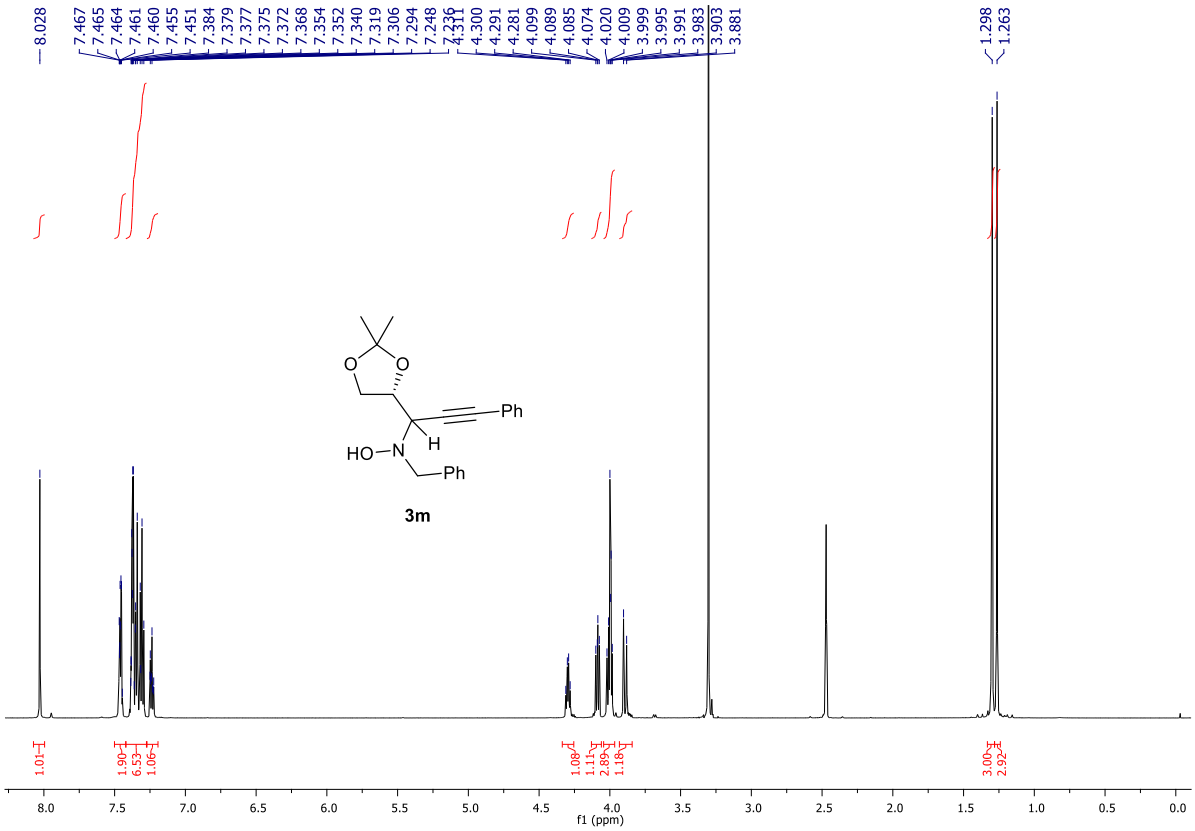
COSY, **3l**



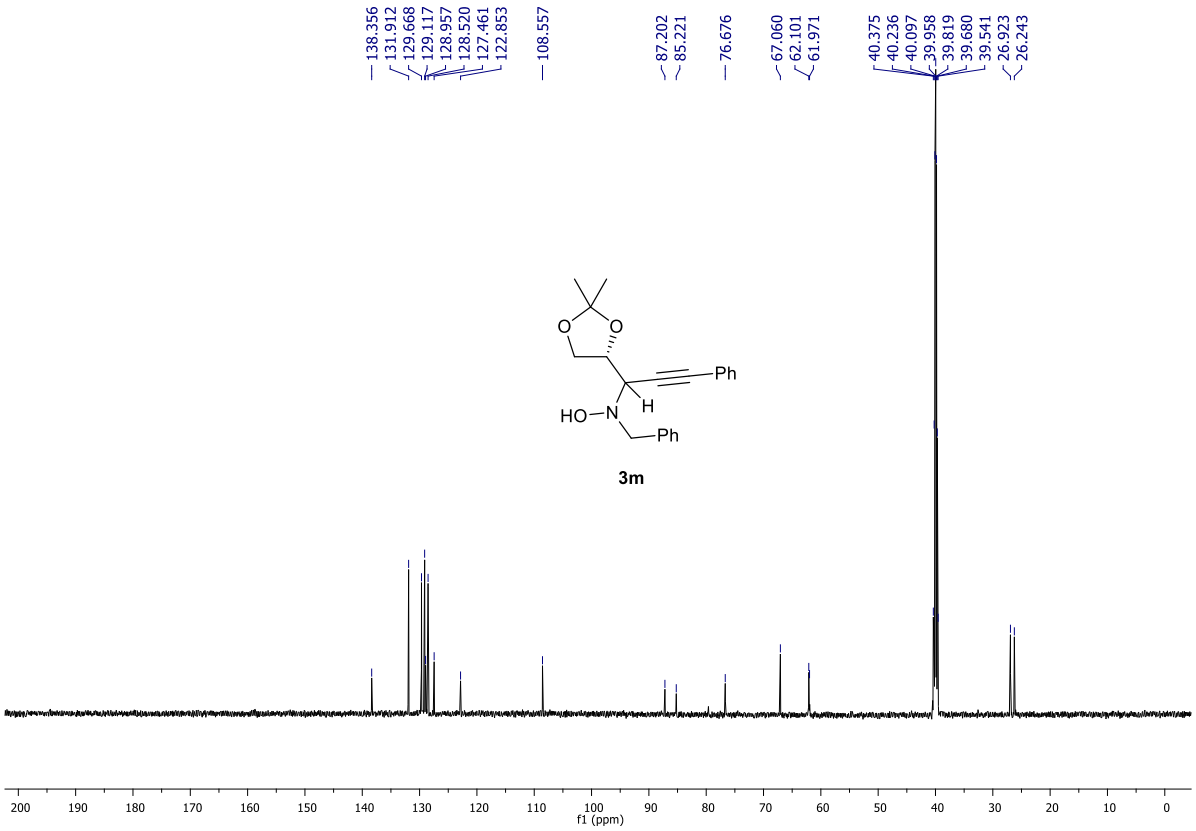
3l (precedure A)



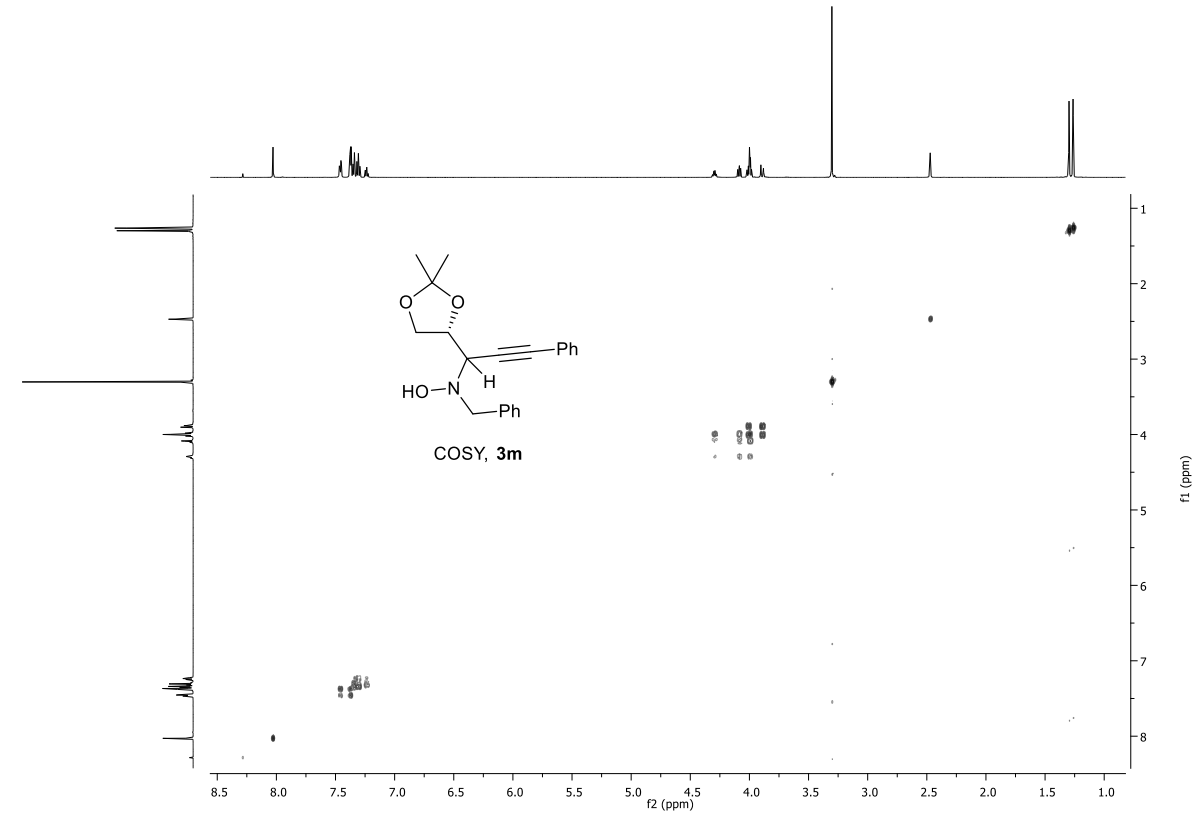
3l (precedure B)



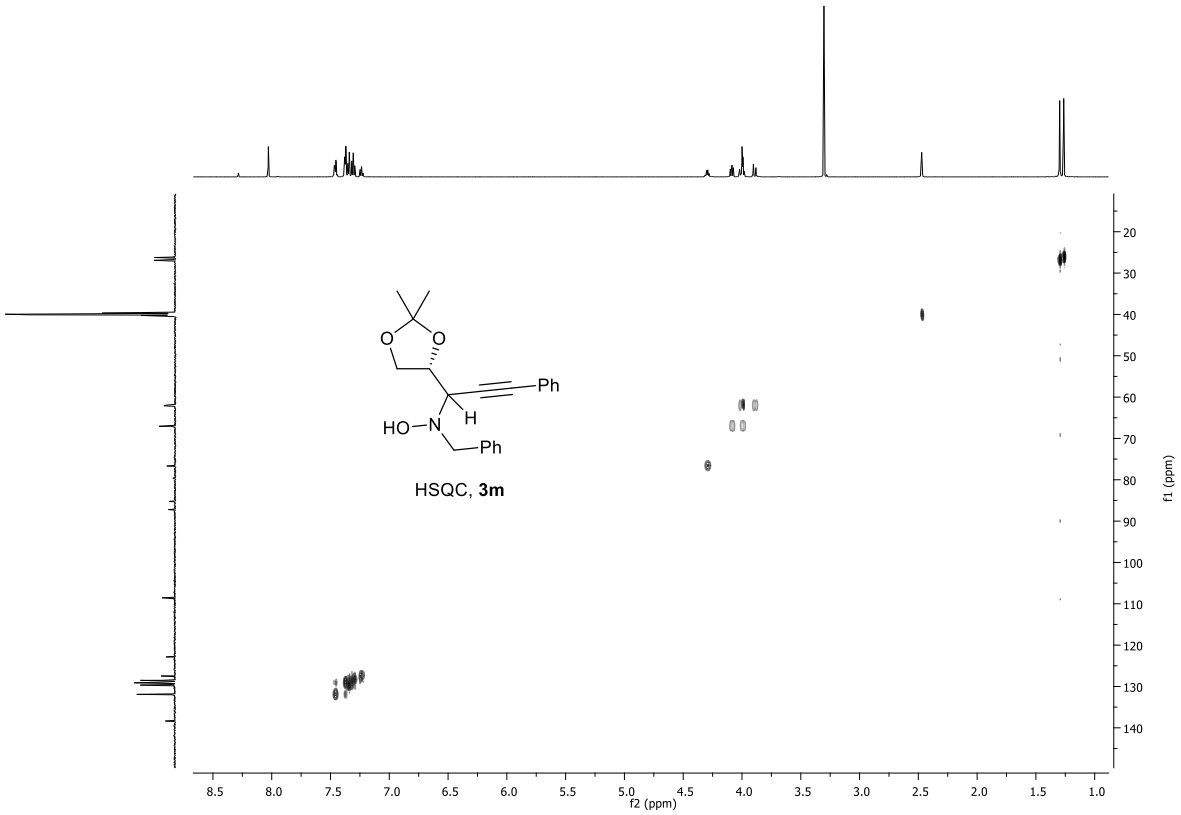
3m

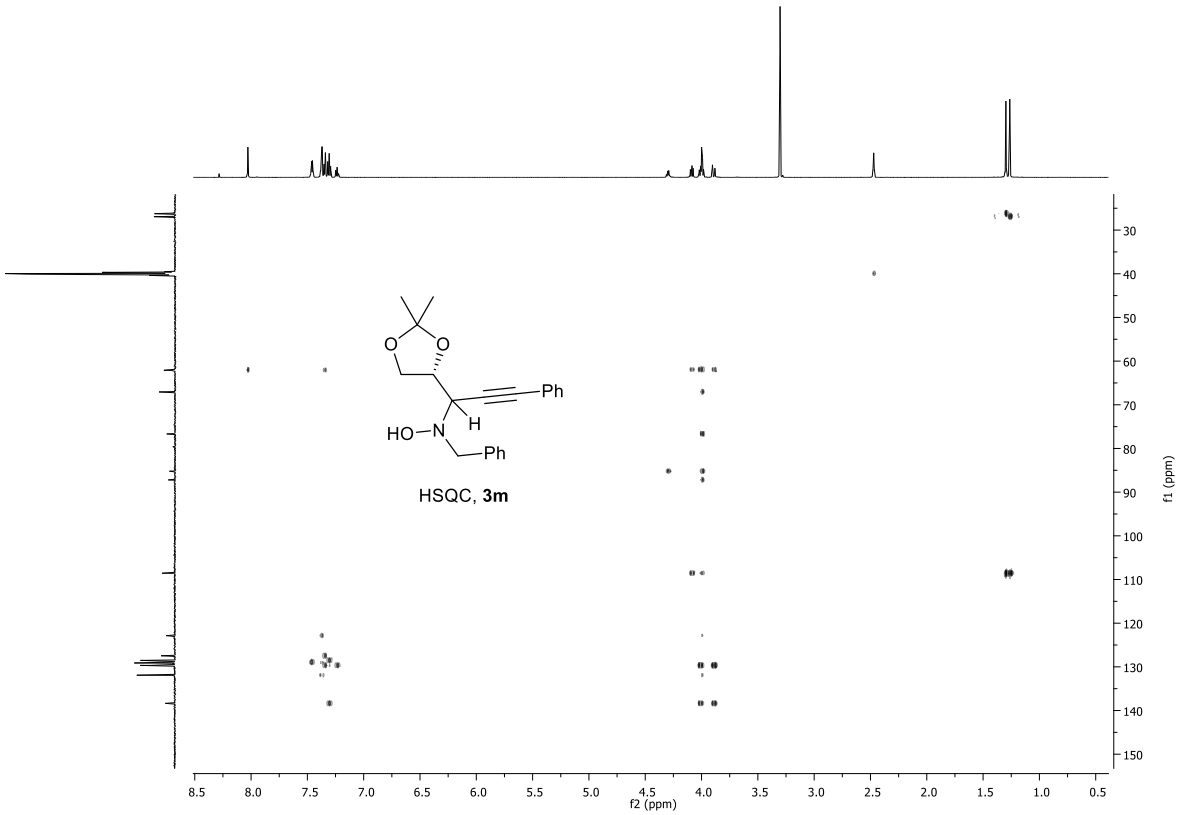

138.356
131.912
129.668
129.117
128.957
128.520
127.461
122.853
108.557
87.202
85.221
76.676
67.060
62.101
61.971
40.375
40.236
40.097
39.958
39.819
39.680
39.541
26.923
26.243
Ph
HO
N
H
Ph
f1 (ppm)

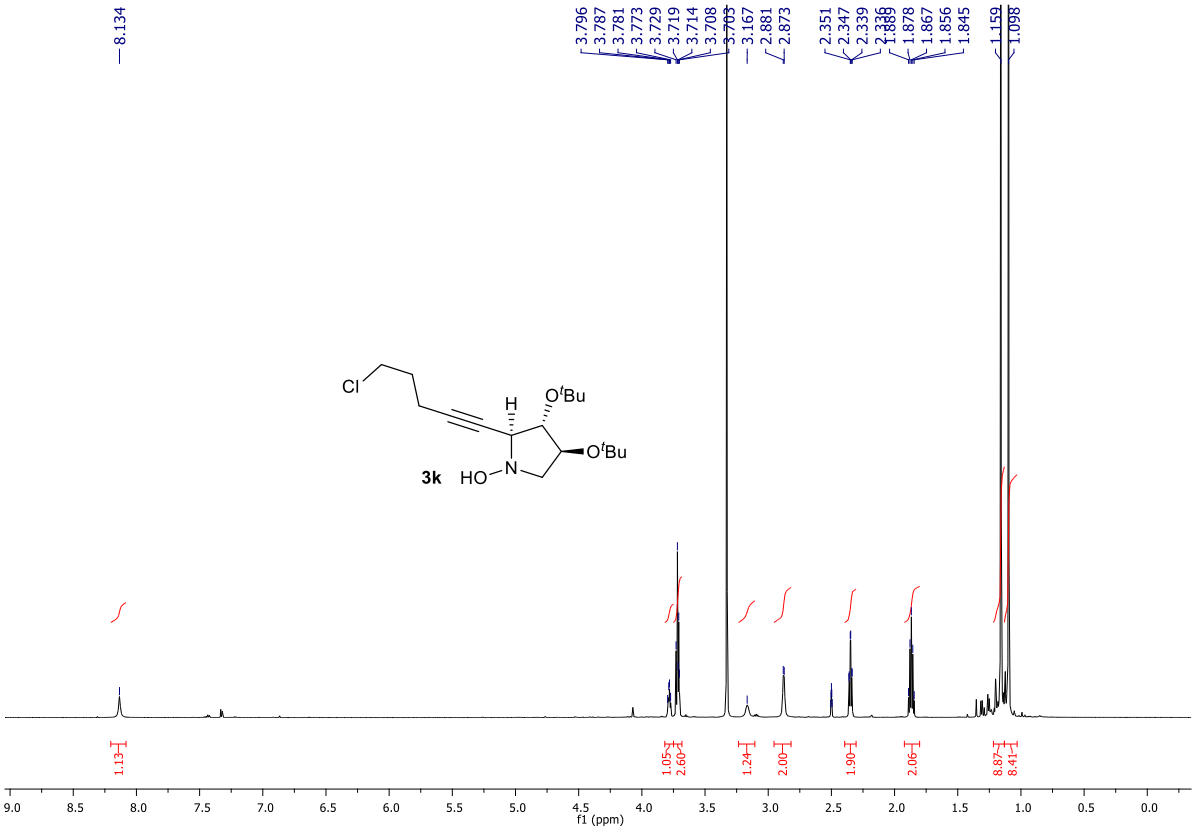
3m

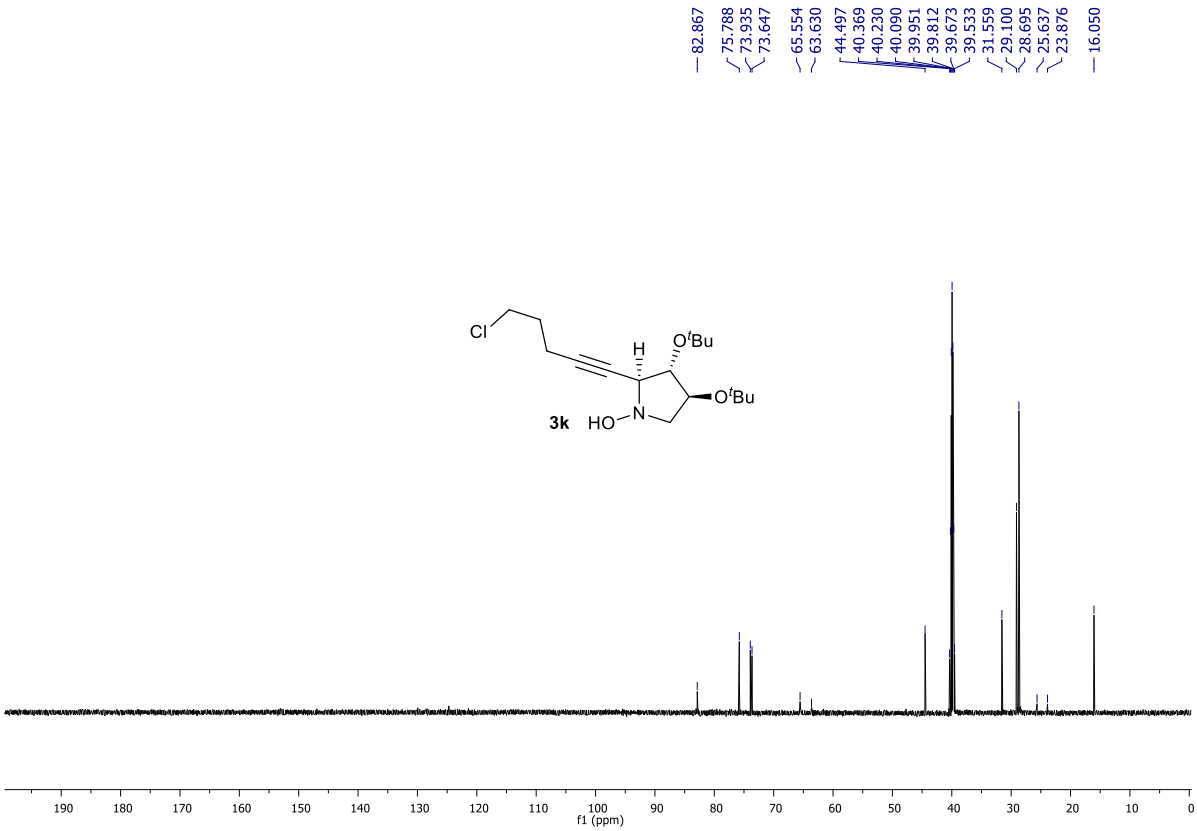

Ph
HO
N
H
Ph
f2 (ppm)
f1 (ppm)

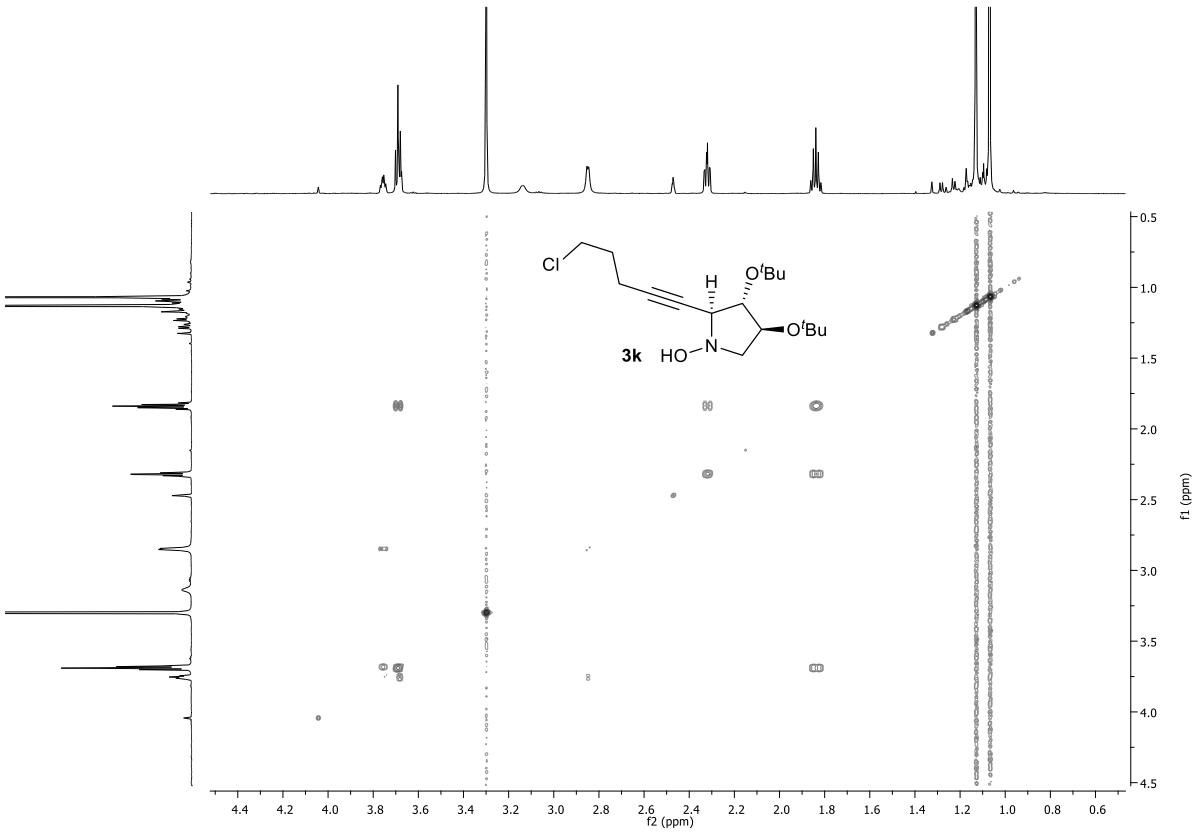
COSY, **3m**

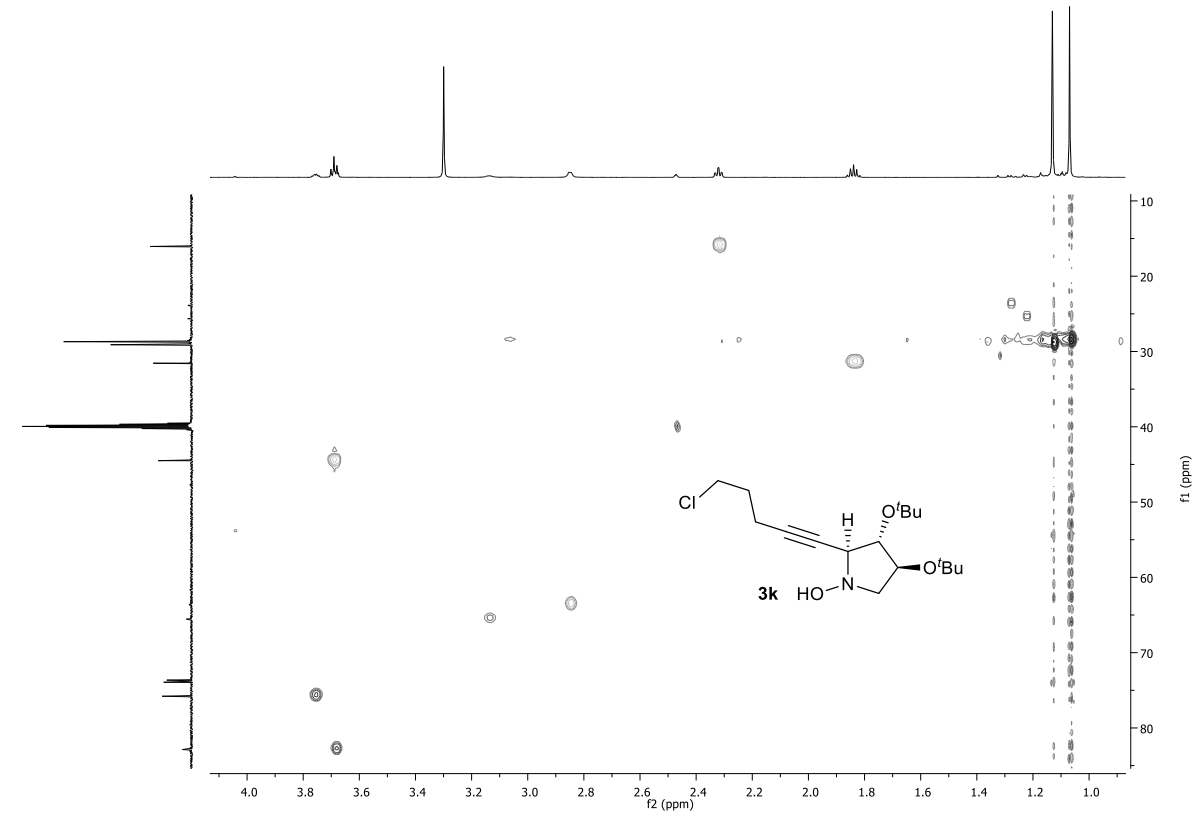

HSQC, **3m**
f2 (ppm)
f1 (ppm)

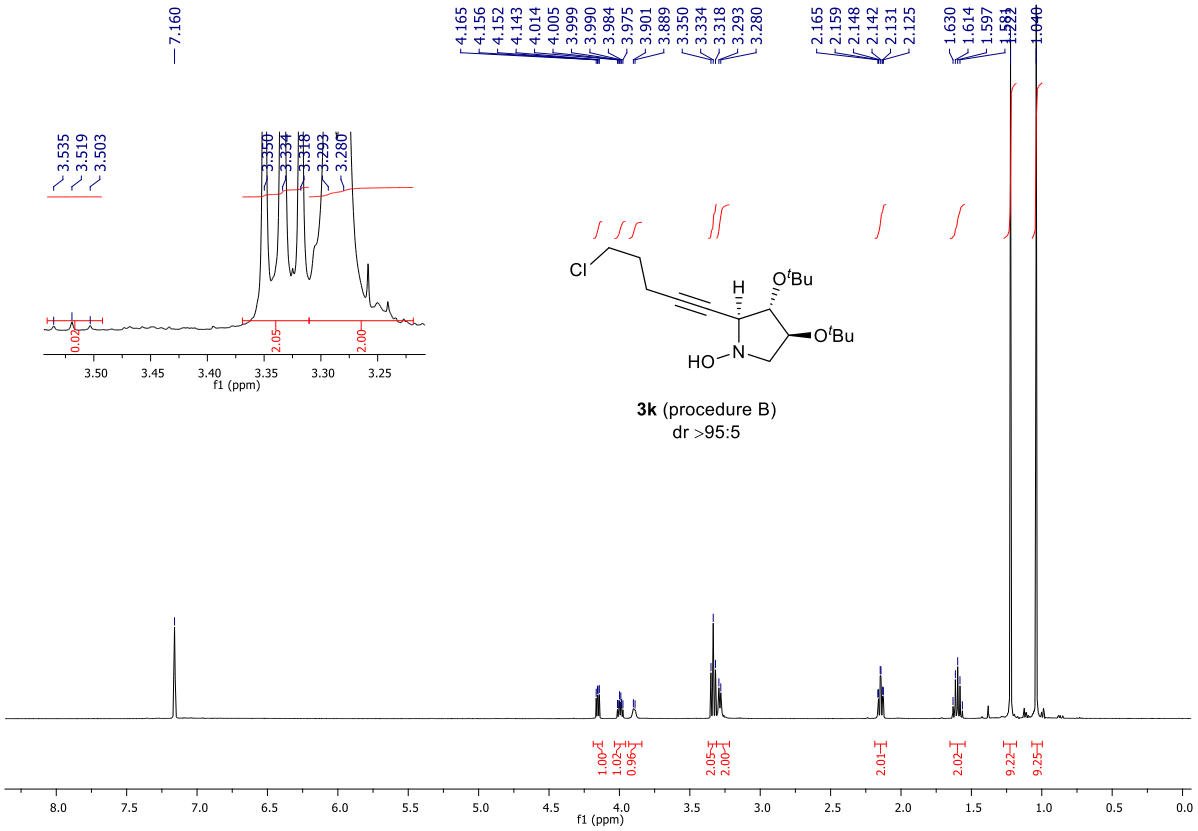

HSQC, **3m**
f2 (ppm)
f1 (ppm)


8.134
3.796
3.787
3.781
3.773
3.729
3.719
3.714
3.708
3.703
3.167
2.881
2.873
2.351
2.347
2.339
2.336
1.889
1.878
1.867
1.856
1.845
1.159
1.098
Cl
H
O^{t}Bu
O^{t}Bu
N
HO
3k
1.13
1.05
2.60
1.24
2.00
1.90
2.06
8.87
8.41
f1 (ppm)

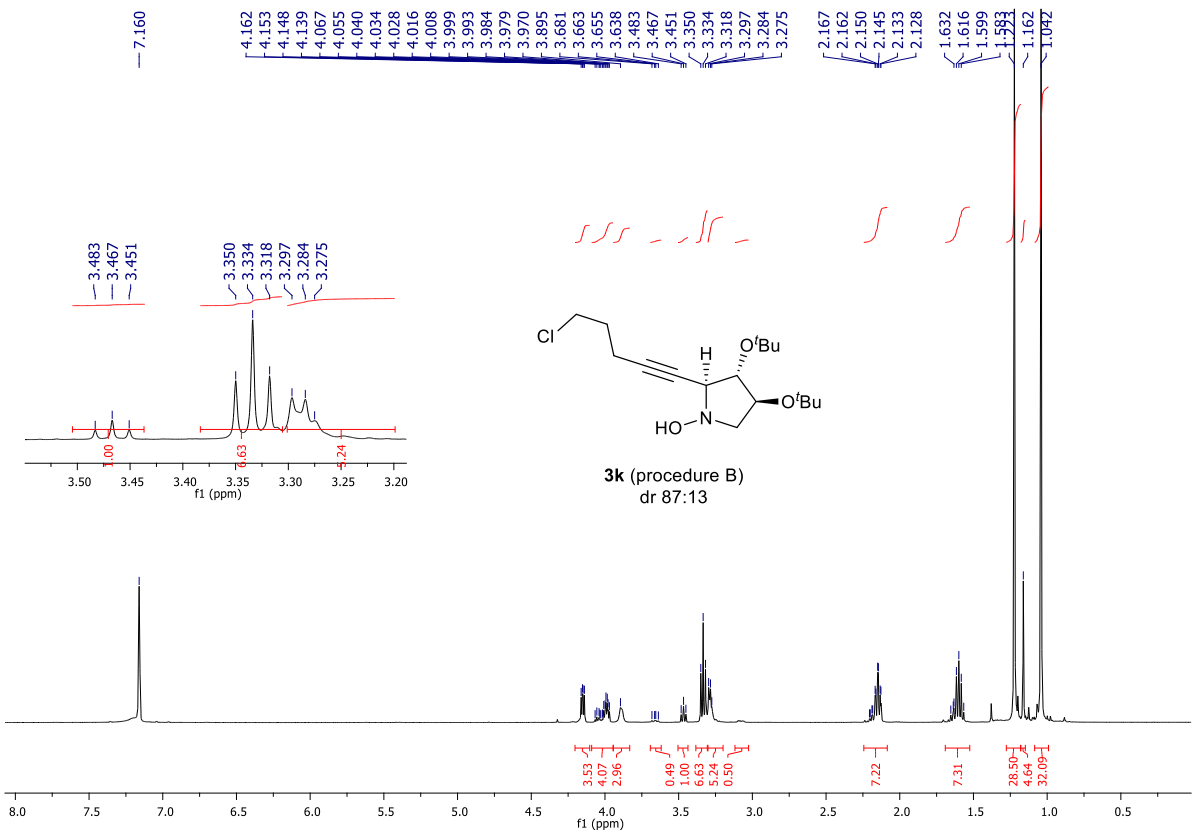

82.867
75.788
73.935
73.647
65.554
63.630
44.497
40.369
40.230
40.090
39.951
39.812
39.673
39.533
31.559
29.100
28.695
25.637
23.876
16.050
Cl
H
O^{t}Bu
O^{t}Bu
N
HO
3k
f1 (ppm)


Cl
H
O^{t}Bu
O^{t}Bu
3k
HO
N
f1 (ppm)
f2 (ppm)

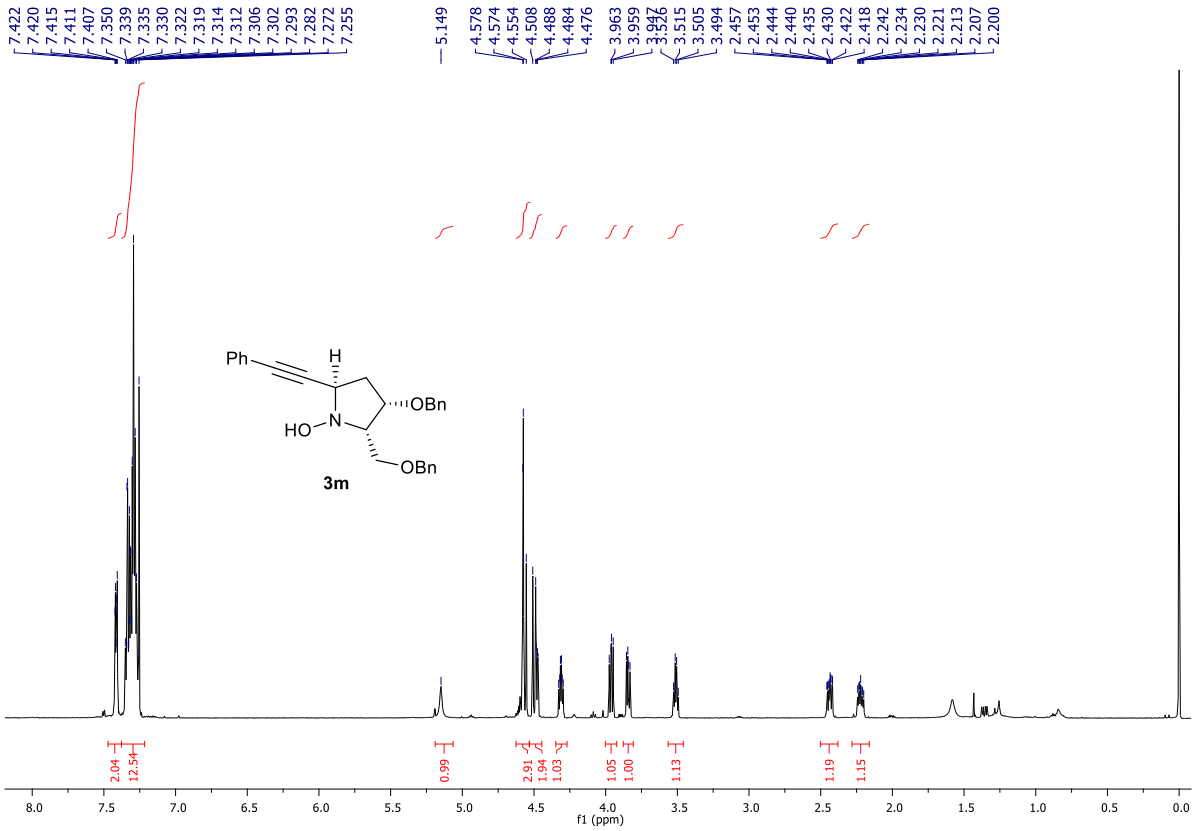

Cl
H
O^{t}Bu
O^{t}Bu
3k
HO
N
f1 (ppm)
f2 (ppm)

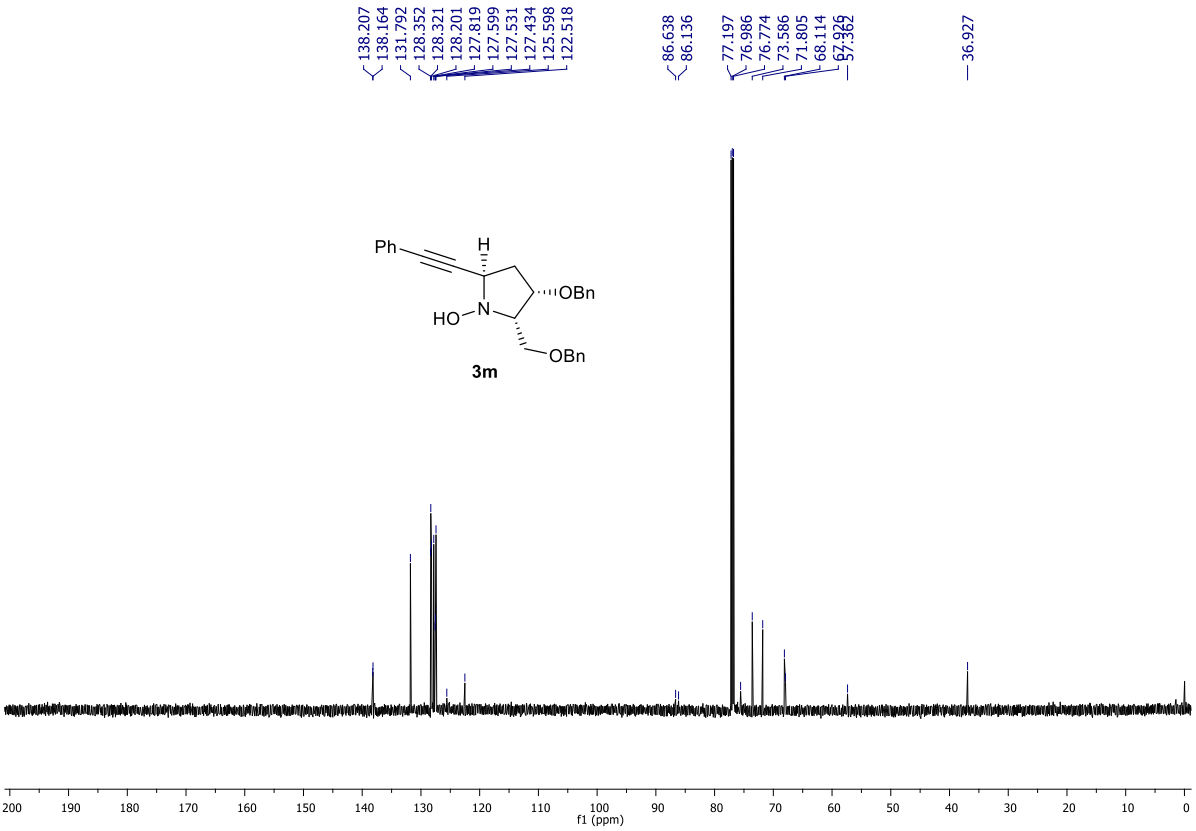


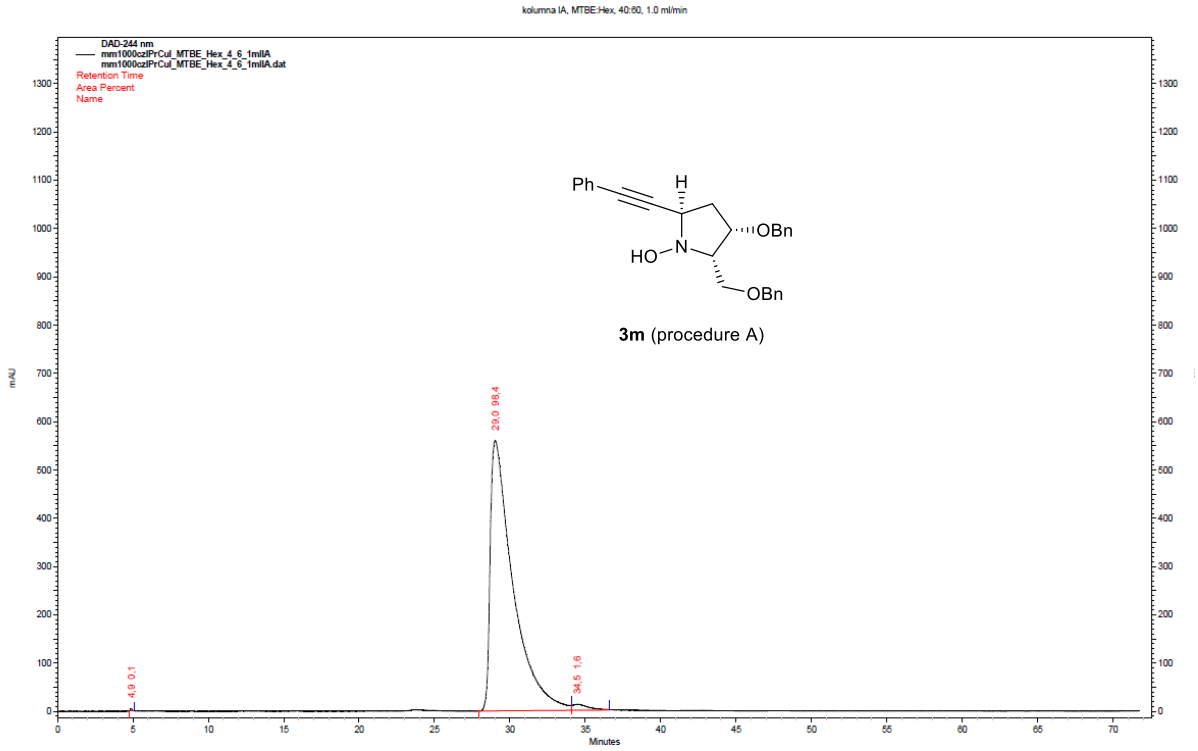
3k (procedure B)
dr >95:5

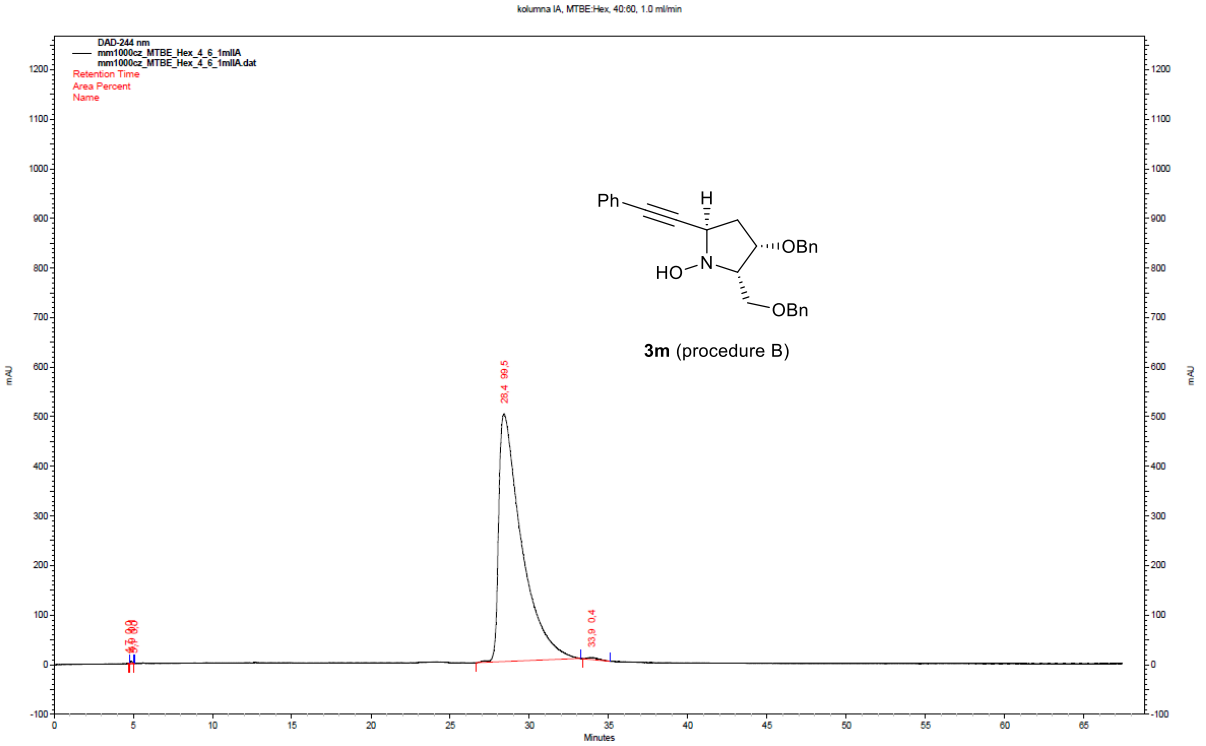


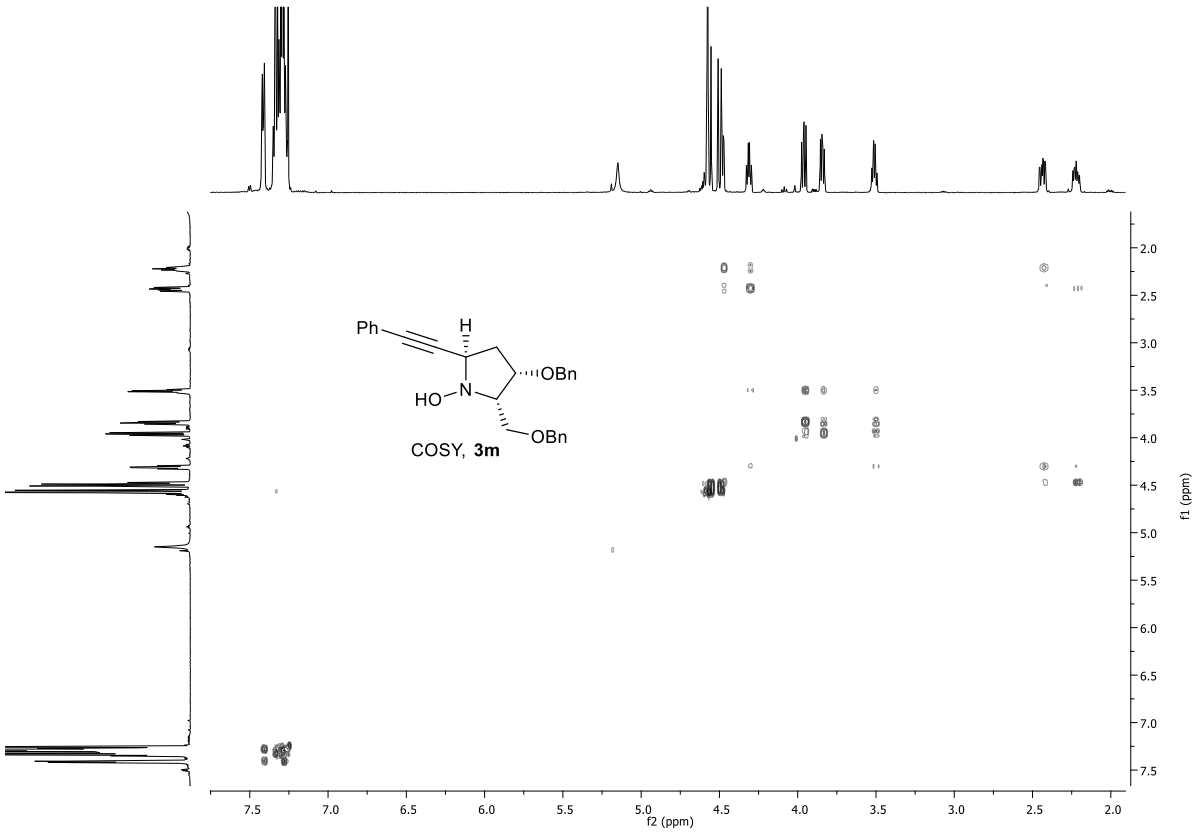
3k (procedure B)
dr 87:13

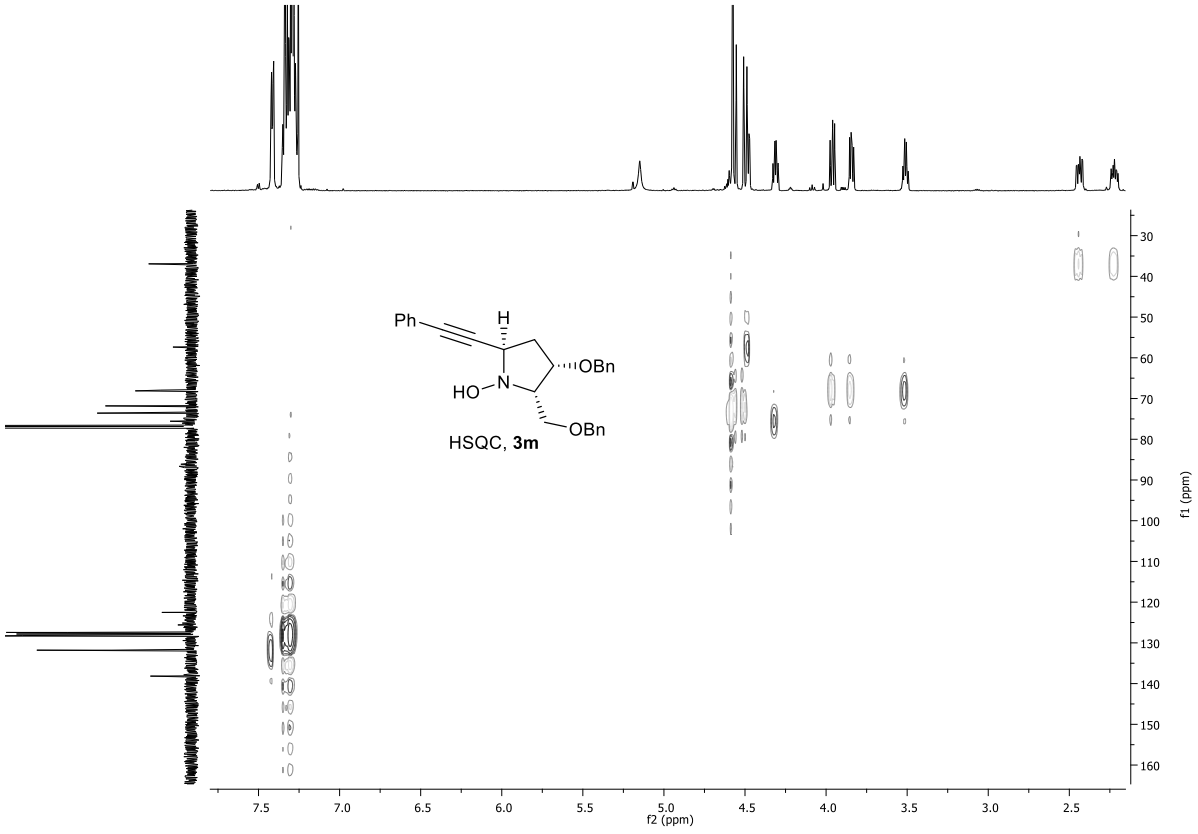

7.422
7.420
7.415
7.411
7.407
7.350
7.339
7.335
7.330
7.322
7.319
7.314
7.312
7.306
7.302
7.293
7.282
7.272
7.255
5.149
4.578
4.574
4.554
4.508
4.488
4.484
4.476
3.963
3.959
3.947
3.526
3.515
3.505
3.494
2.457
2.453
2.444
2.440
2.435
2.430
2.422
2.418
2.242
2.234
2.230
2.221
2.213
2.207
2.200
Ph
H
OBn
HO
N
OBn
3m
2.04
12.54
0.99
2.91
1.94
1.03
1.05
1.00
1.13
1.19
1.15
f1 (ppm)

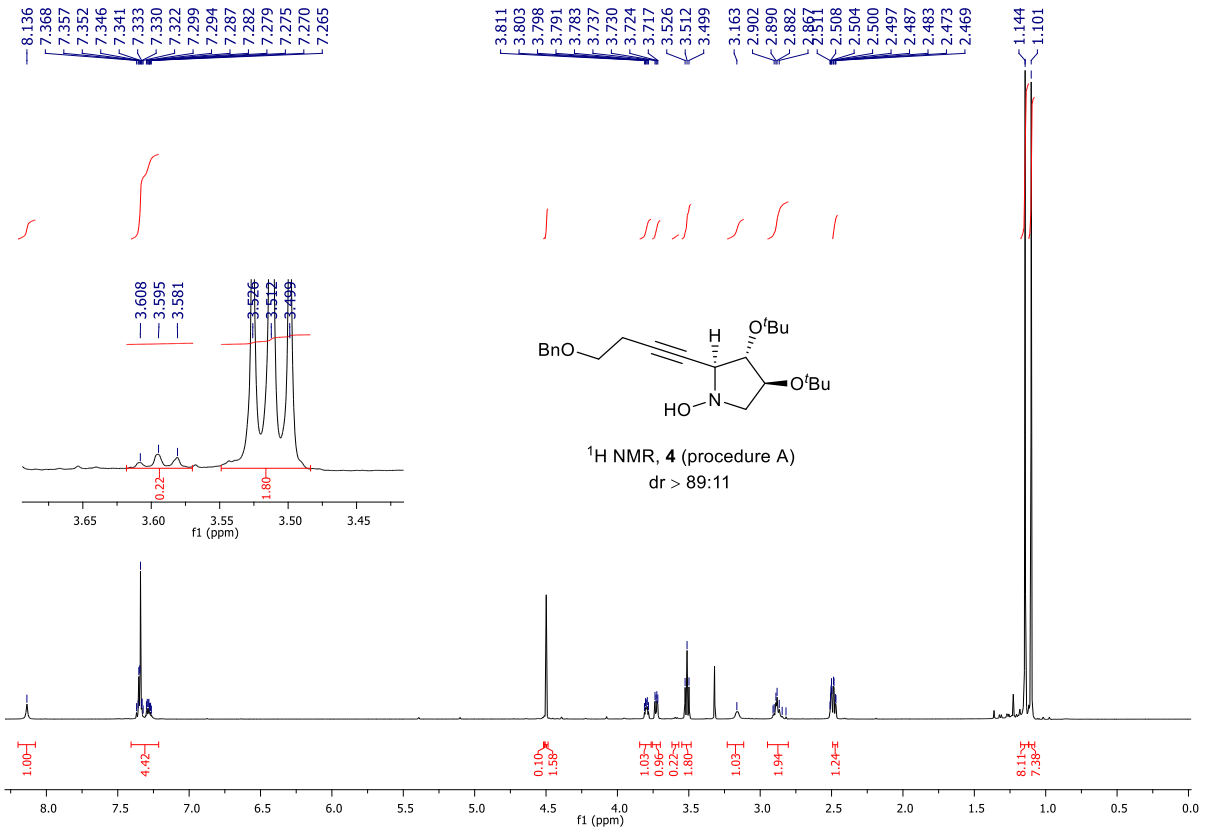

138.207
138.164
131.792
128.352
128.321
128.201
127.819
127.599
127.531
127.434
125.598
122.518
86.638
86.136
77.197
76.986
76.774
73.586
71.805
68.114
67.926
57.362
36.927
Ph
H
OBn
HO
N
OBn
3m
f1 (ppm)

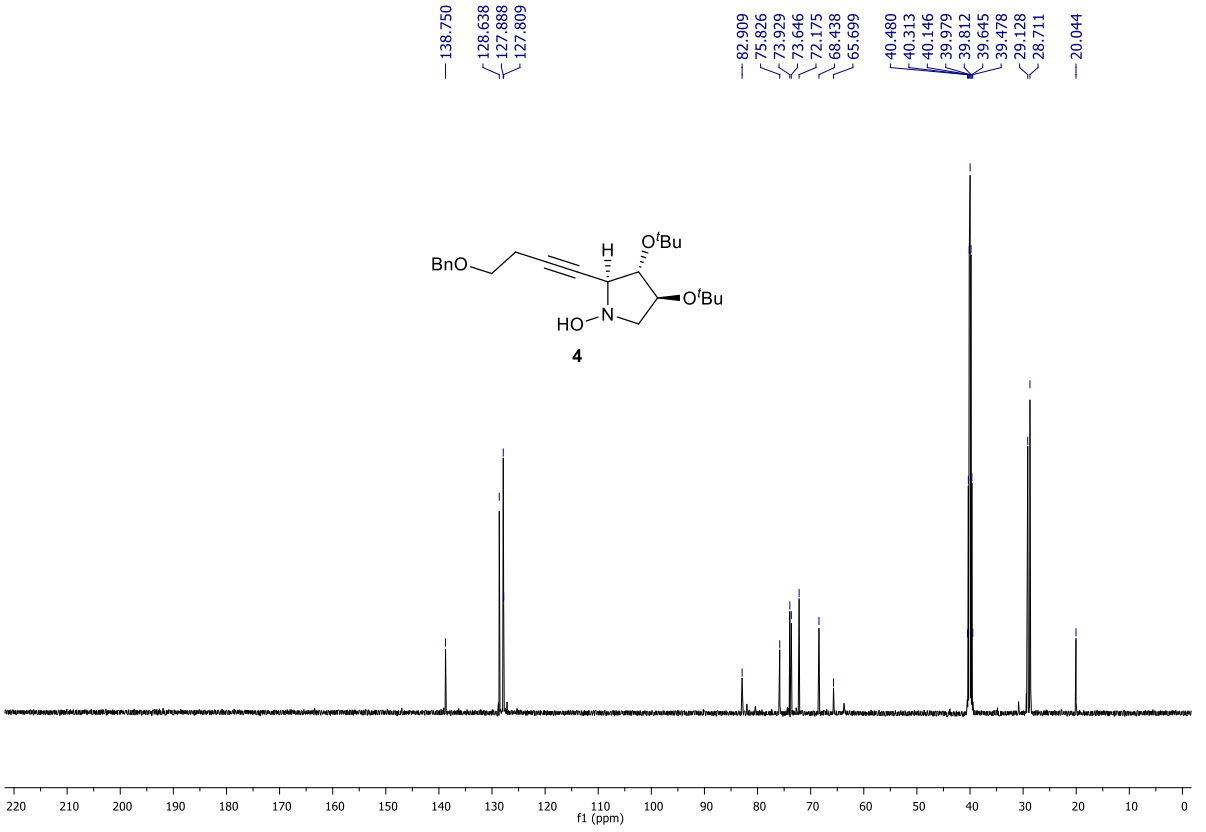

kolumna IA, MTBE:Hex, 40:60, 1.0 ml/min
DAD-244 nm
mm1000czIPrCul_MTBE_Hex_4_6_1mlIA
mm1000czIPrCul_MTBE_Hex_4_6_1mlIA.dat
Retention Time
Area Percent
Name
Ph
H
OBn
HO
N
OBn
3m (procedure A)
29.0 98.4
4.9 0.1
34.5 1.6
mAU
Minutes

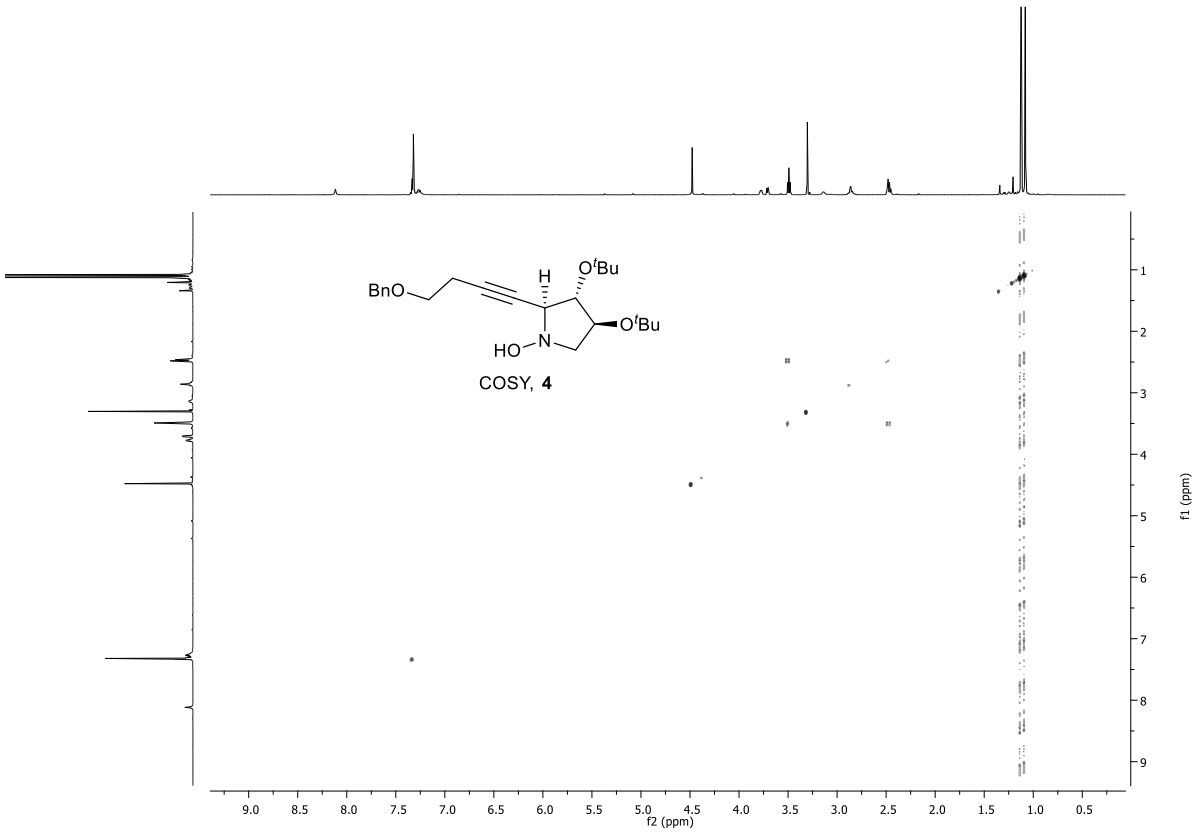

kolumna IA, MTBE:Hex, 40:60, 1.0 ml/min
DAD-244 nm
mm1000cz_MTBE_Hex_4_6_1mlIA
mm1000cz_MTBE_Hex_4_6_1mlIA.dat
Retention Time
Area Percent
Name
Ph
H
OBn
HO
N
OBn
3m (procedure B)
28.4 99.5
33.9 0.4
mAU
Minutes

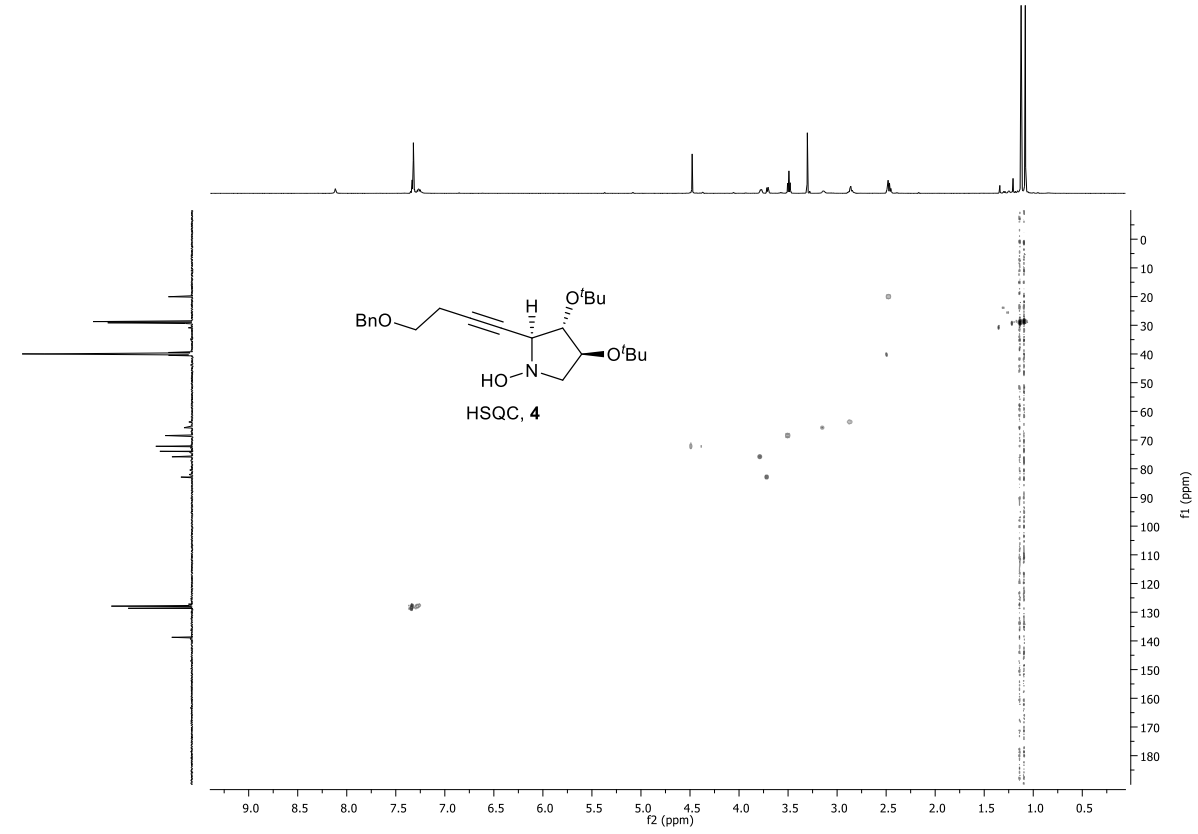

Ph
H
OBn
HO
N
OBn
COSY, 3m
f2 (ppm)
f1 (ppm)

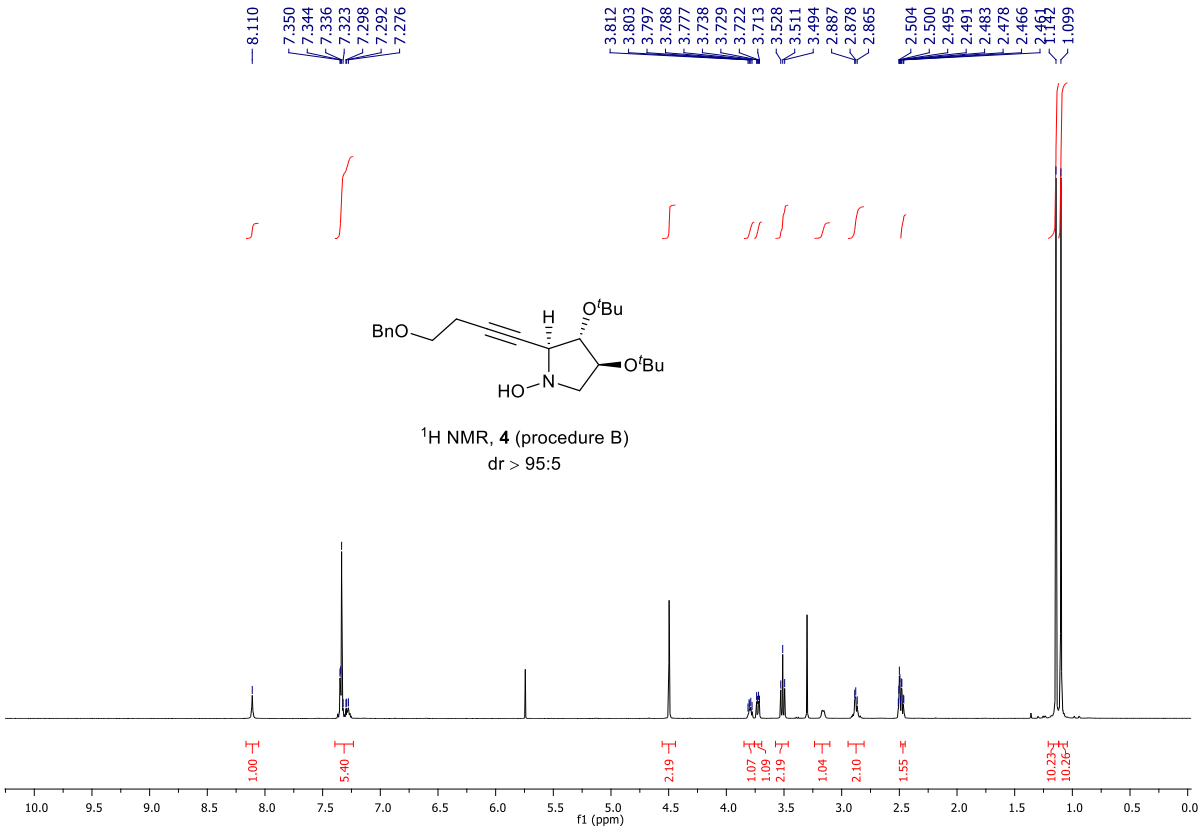

Ph
H
OBn
HO
N
OBn
HSQC, 3m
f2 (ppm)
f1 (ppm)


8.136
7.368
7.357
7.352
7.346
7.341
7.333
7.330
7.322
7.299
7.294
7.287
7.282
7.279
7.275
7.270
7.265
3.811
3.803
3.798
3.791
3.783
3.737
3.730
3.724
3.717
3.526
3.512
3.499
3.163
2.902
2.890
2.882
2.867
2.511
2.508
2.504
2.500
2.497
2.487
2.483
2.473
2.469
1.144
1.101
3.608
3.595
3.581
3.526
3.512
3.499
0.22
1.80
3.65
3.60
3.55
3.50
3.45
f1 (ppm)
BnO
H
O^{t}Bu
O^{t}Bu
HO
N
^{1}H NMR, **4** (procedure A)
dr > 89:11
1.00
4.42
0.10
1.58
1.03
0.96
0.22
1.80
1.03
1.94
1.24
8.11
7.38
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
0.0
f1 (ppm)

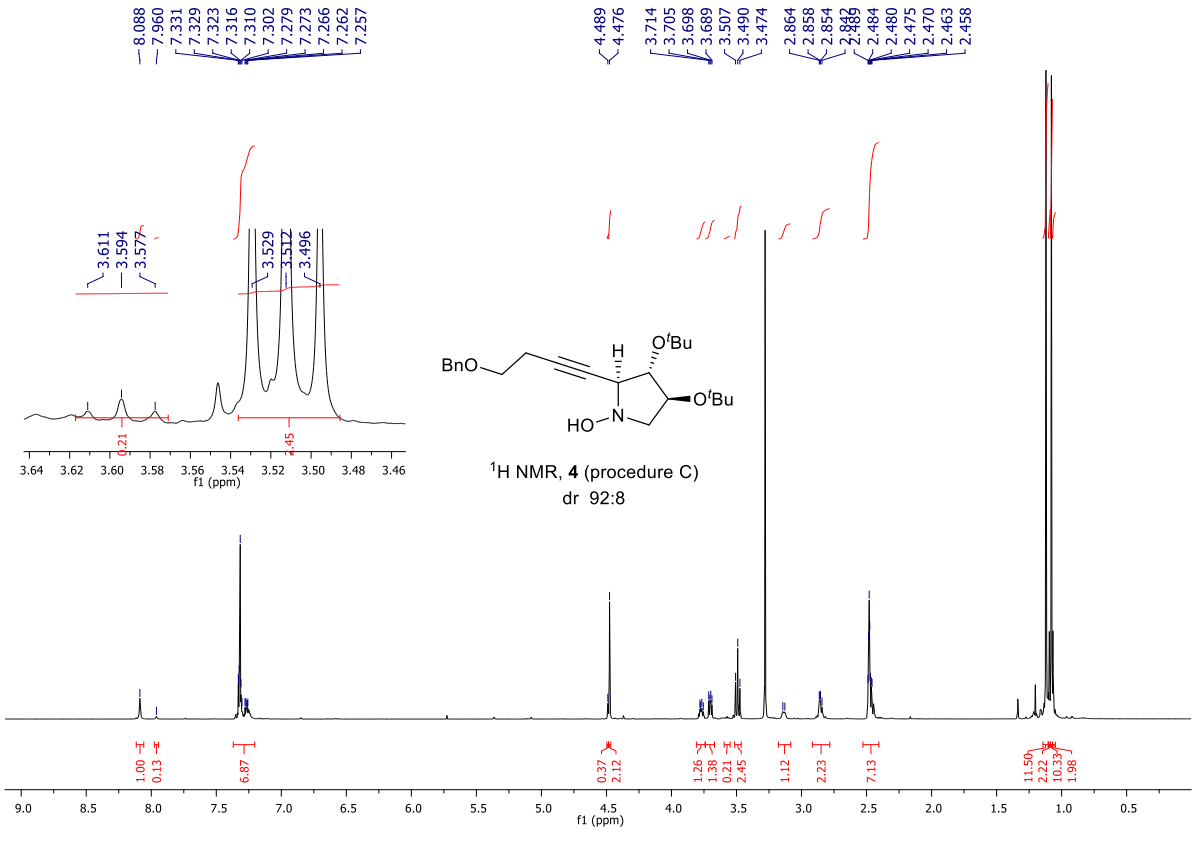

138.750
128.638
127.888
127.809
82.909
75.826
73.929
73.646
72.175
68.438
65.699
40.480
40.313
40.146
39.979
39.812
39.645
39.478
29.128
28.711
20.044
BnO
H
O^{t}Bu
O^{t}Bu
HO
N
4
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


BnO
H
O^{t}Bu
O^{t}Bu
HO
N
COSY, 4
f2 (ppm)
f1 (ppm)

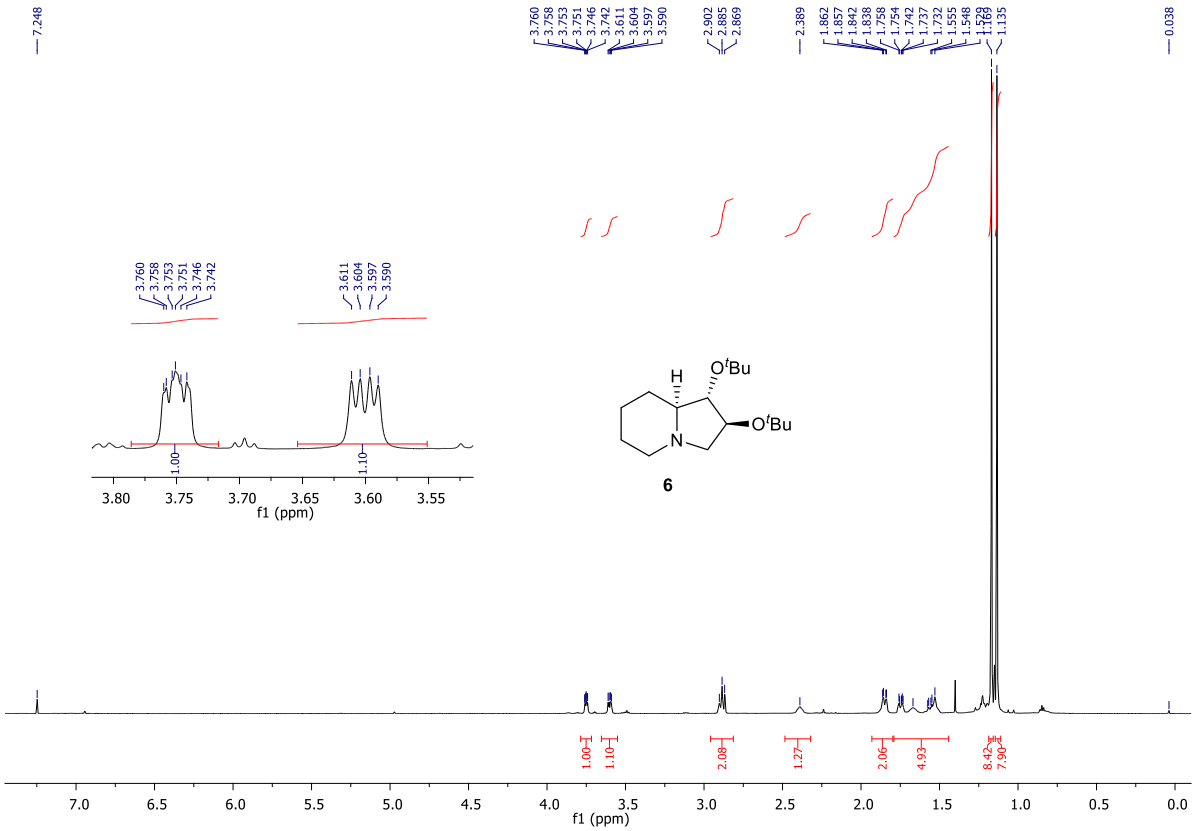

BnO
H
O^{t}Bu
O^{t}Bu
HO
N
HSQC, 4
f2 (ppm)
f1 (ppm)

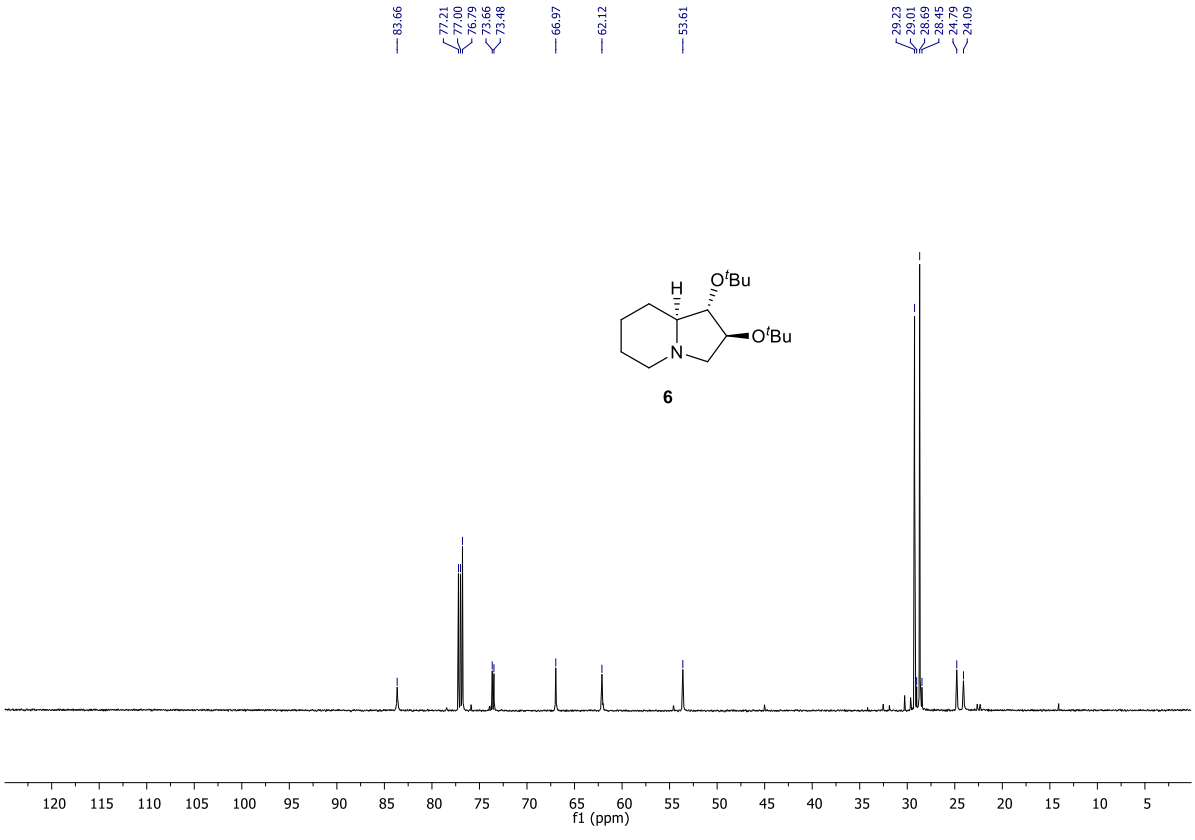


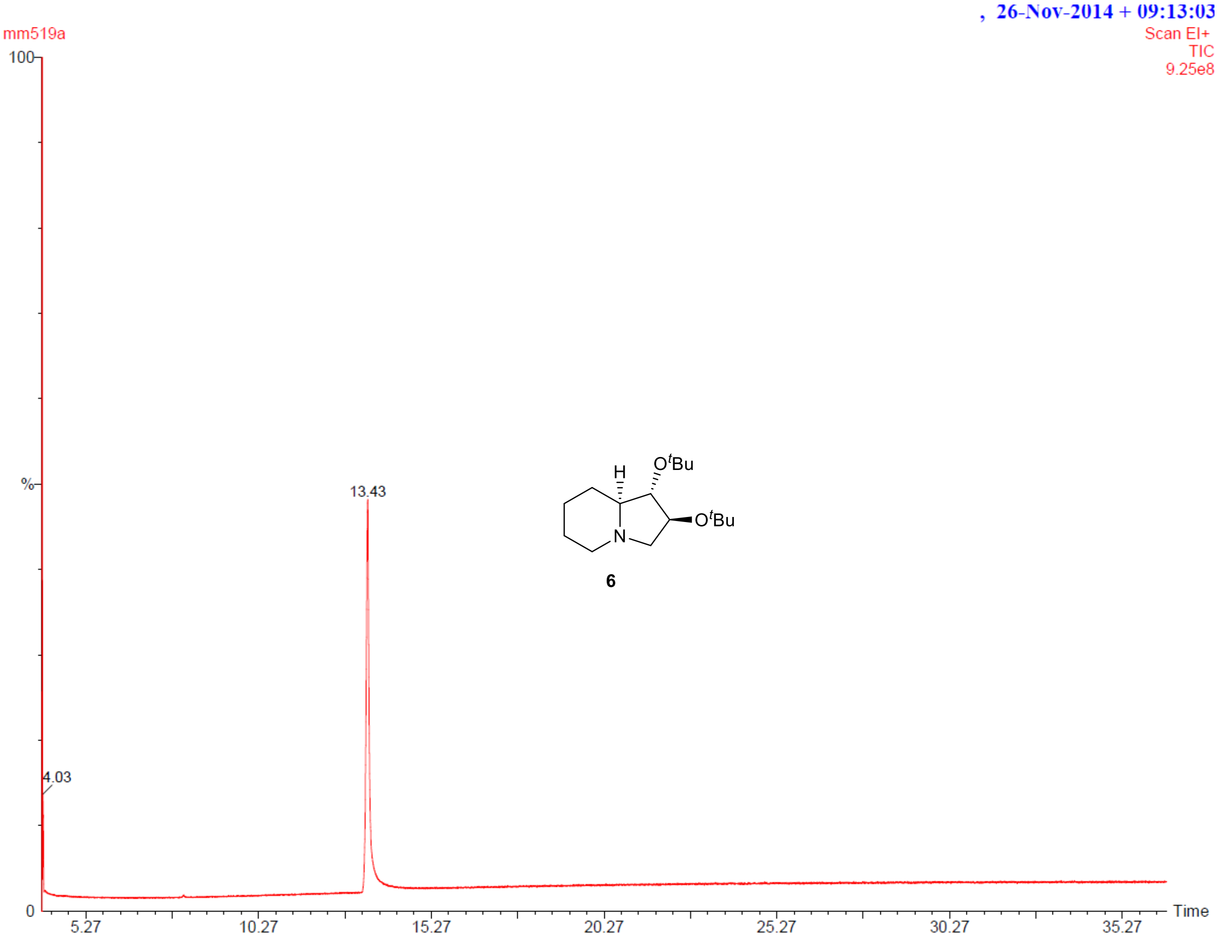
^{1}H NMR, **4** (procedure B)
dr > 95:5

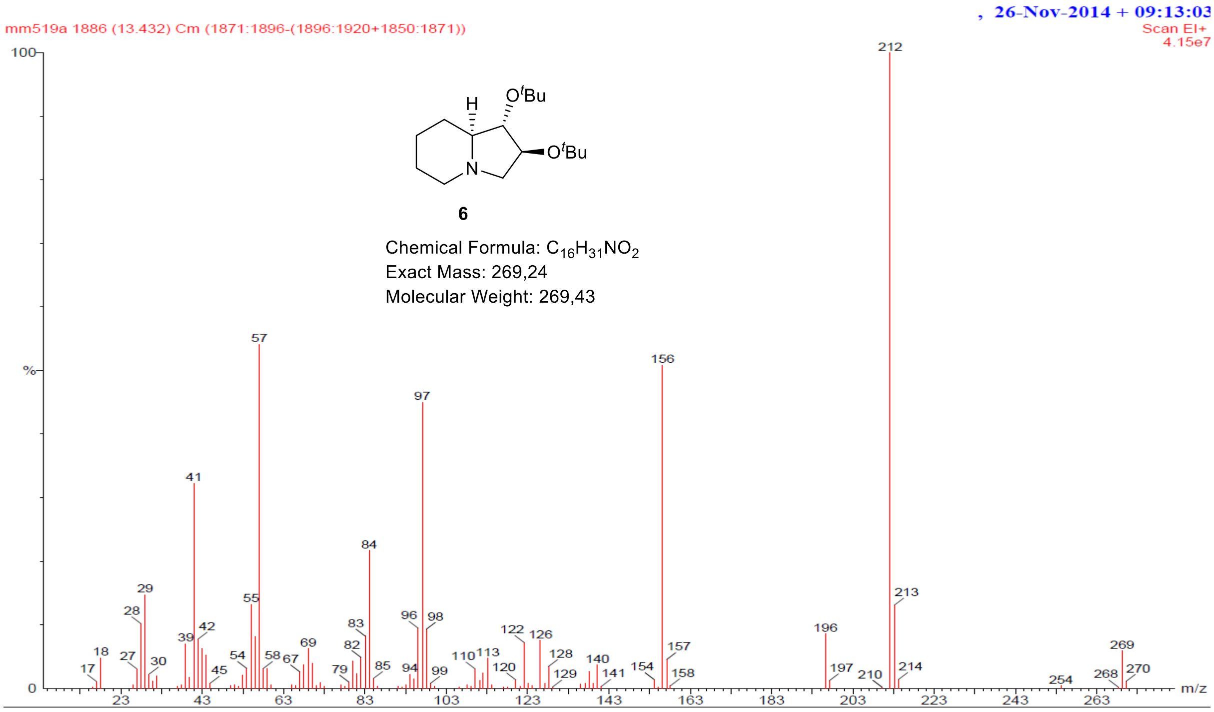


^{1}H NMR, **4** (procedure C)
dr 92:8


7.248
3.760
3.758
3.753
3.751
3.746
3.742
3.611
3.604
3.597
3.590
2.902
2.885
2.869
2.389
1.862
1.857
1.842
1.838
1.758
1.754
1.742
1.737
1.732
1.555
1.548
1.529
1.169
1.135
0.038
1.00
1.10
2.08
1.27
2.06
4.93
8.42
7.90
f1 (ppm)
O^tBu
H
N
O^tBu
6


83.66
77.21
77.00
76.79
73.66
73.48
66.97
62.12
53.61
29.23
29.01
28.69
28.45
24.79
24.09
f1 (ppm)
O^tBu
H
N
O^tBu
6


mm519a
, 26-Nov-2014 + 09:13:03
Scan EI+
TIC
9.25e8
100
%
0
13.43
4.03
H
O^{t}Bu
O^{t}Bu
N
6
5.27
10.27
15.27
20.27
25.27
30.27
35.27
Time

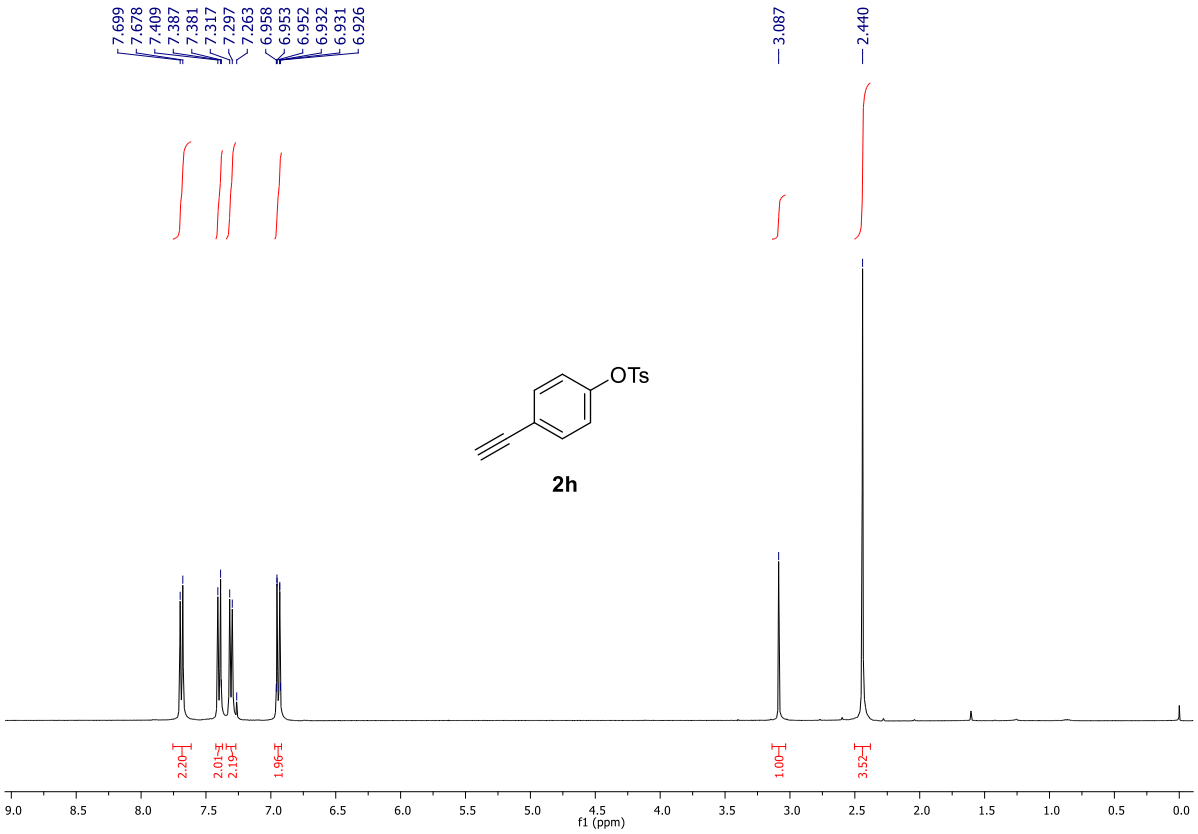

mm519a 1886 (13.432) Cm (1871:1896-(1896:1920+1850:1871))
, 26-Nov-2014 + 09:13:03
Scan EI+
4.15e7
100
%
0
H
O^{t}Bu
O^{t}Bu
N
6
Chemical Formula: $C_{16}H_{31}NO_2$
Exact Mass: 269,24
Molecular Weight: 269,43
212
57
156
97
41
84
29
28
55
213
83
96
98
42
39
122
126
196
269
m/z

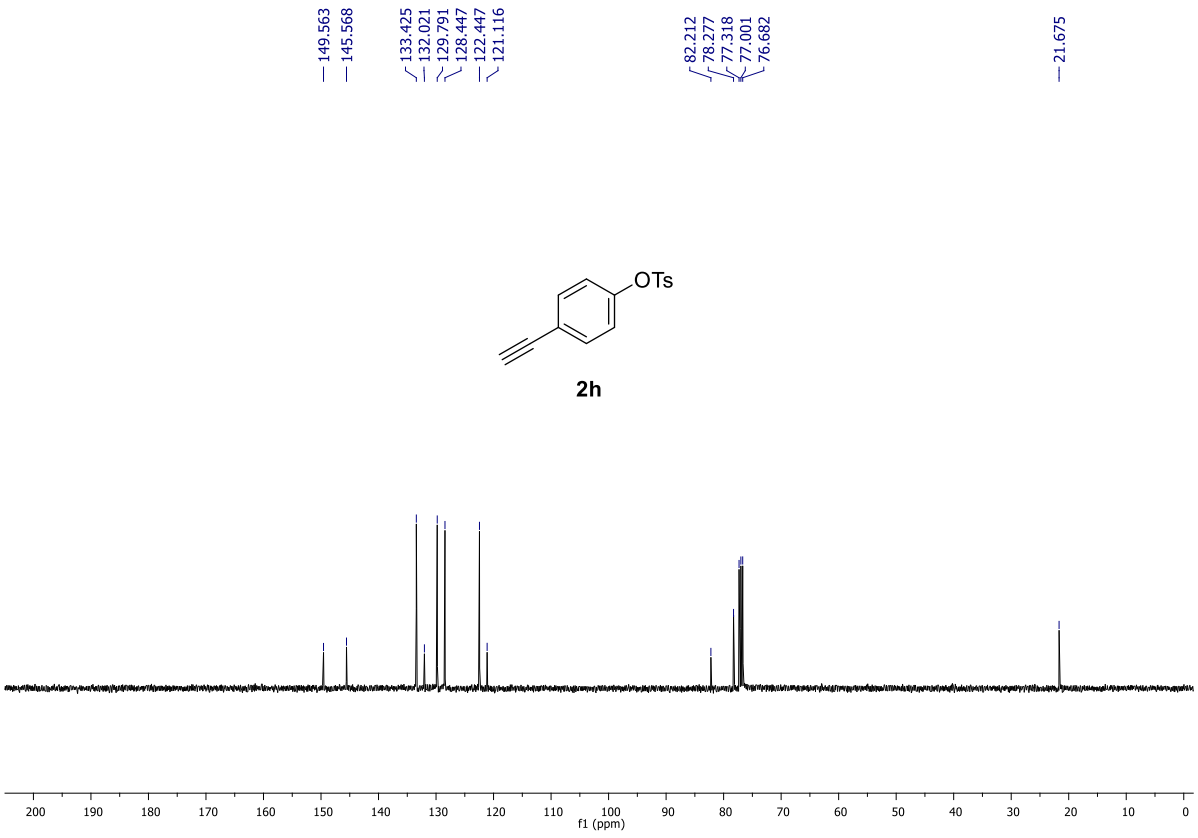
Spectrum Report

Data file: C:\TurboMass\KRZSIEK.PRO\Data\mm519a 26-Nov-2014 09:13:03
Scan: 1886 (13.432)
Process: Cm (1874:1896-(1897:1915+1856:1872))
Function: Scan (15:400) EI+
Description:

Printed: Wed Nov 26 10:00:21 2014

No	Mass	Inten	%BPI	%TIC	No	Mass	Inten	%BPI	%TIC
1:	16	7.78e4	0.18	0.03	54:	95	6.25e5	1.42	0.25
2:	17	4.73e5	1.07	0.19	55:	96	4.16e6	9.44	1.69
3:	18	2.25e6	5.11	0.91	56:	97	1.98e7	45.08	8.07
4:	26	2.29e5	0.52	0.09	57:	98	4.05e6	9.20	1.65
5:	27	1.35e6	3.06	0.55	58:	99	3.18e5	0.72	0.13
6:	28	4.71e6	10.71	1.92	59:	100	1.45e5	0.33	0.06
7:	29	6.47e6	14.71	2.63	60:	106	6.49e4	0.15	0.03
8:	30	9.81e5	2.23	0.40	61:	108	2.24e5	0.51	0.09
9:	31	4.88e5	1.11	0.20	62:	109	1.46e5	0.33	0.06
10:	32	8.87e5	2.02	0.36	63:	110	1.32e6	3.01	0.54
11:	37	1.38e5	0.31	0.06	64:	111	5.32e5	1.21	0.22
12:	38	2.62e5	0.60	0.11	65:	112	1.06e6	2.42	0.43
13:	39	3.10e6	7.05	1.26	66:	113	2.09e6	4.75	0.85
14:	40	7.46e5	1.70	0.30	67:	114	2.36e5	0.54	0.10
15:	41	1.43e7	32.45	5.81	68:	117	4.81e4	0.11	0.02
16:	42	3.40e6	7.73	1.38	69:	118	8.78e4	0.20	0.04
17:	43	2.75e6	6.24	1.12	70:	120	5.83e5	1.32	0.24
18:	44	2.31e6	5.25	0.94	71:	121	1.15e5	0.26	0.05
19:	45	3.35e5	0.76	0.14	72:	122	3.14e6	7.13	1.28
20:	50	2.00e5	0.45	0.08	73:	123	3.20e5	0.73	0.13
21:	51	2.30e5	0.52	0.09	74:	124	1.58e5	0.36	0.06
22:	52	1.26e5	0.29	0.05	75:	126	3.31e6	7.52	1.35
23:	53	8.83e5	2.01	0.36	76:	127	3.38e5	0.77	0.14
24:	54	1.36e6	3.10	0.55	77:	128	1.51e6	3.44	0.62
25:	55	5.83e6	13.24	2.37	78:	129	6.89e4	0.16	0.03
26:	56	3.63e6	8.24	1.47	79:	136	3.13e5	0.71	0.13
27:	57	2.38e7	54.06	9.67	80:	137	3.79e5	0.86	0.15
28:	58	1.35e6	3.08	0.55	81:	138	1.18e6	2.67	0.48
29:	59	1.37e6	3.12	0.56	82:	139	3.29e5	0.75	0.13
30:	60	2.15e5	0.49	0.09	83:	140	1.62e6	3.67	0.66
31:	65	2.46e5	0.56	0.10	84:	141	1.19e5	0.27	0.05
32:	66	1.66e5	0.38	0.07	85:	154	5.91e5	1.34	0.24
33:	67	1.10e6	2.49	0.45	86:	155	8.78e4	0.20	0.04
34:	68	1.62e6	3.67	0.66	87:	156	2.25e7	51.13	9.15
35:	69	2.72e6	6.17	1.10	88:	157	1.96e6	4.46	0.80
36:	70	1.70e6	3.85	0.69	89:	158	1.54e5	0.35	0.06
37:	71	1.88e5	0.43	0.08	90:	193	4.51e4	0.10	0.02
38:	72	3.92e5	0.89	0.16	91:	196	3.76e6	8.55	1.53
39:	73	1.21e5	0.28	0.05	92:	197	5.12e5	1.16	0.21
40:	77	2.41e5	0.55	0.10	93:	210	5.59e4	0.13	0.02
41:	78	1.60e5	0.36	0.07	94:	212	4.40e7	100.00	17.89
42:	79	4.29e5	0.98	0.17	95:	213	5.70e6	12.95	2.32
43:	80	1.89e6	4.29	0.77	96:	214	5.73e5	1.30	0.23
44:	81	1.00e6	2.28	0.41	97:	254	1.64e5	0.37	0.07
45:	82	2.13e6	4.84	0.87	98:	268	8.17e4	0.19	0.03
46:	83	3.60e6	8.17	1.46	99:	269	2.60e6	5.91	1.06
47:	84	9.57e6	21.75	3.89	100:	270	4.61e5	1.05	0.19
48:	85	6.49e5	1.47	0.26					
49:	86	1.04e5	0.24	0.04					
50:	91	1.45e5	0.33	0.06					
51:	92	4.86e4	0.11	0.02					
52:	93	2.51e5	0.57	0.10					
53:	94	9.68e5	2.20	0.39					


7.699
7.678
7.409
7.387
7.381
7.317
7.297
7.263
6.958
6.953
6.952
6.932
6.931
6.926
3.087
2.440
OTs
2h
2.20
2.01
2.19
1.96
1.00
3.52
f1 (ppm)


149.563
145.568
133.425
132.021
129.791
128.447
122.447
121.116
82.212
78.277
77.318
77.001
76.682
21.675
OTs
2h
f1 (ppm)