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SUPPORTING INFORMATION

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Title: Synthesis of Chiral (Indol-2-yl)methanamines and Insight into the Stereochemistry Protecting Effects of the 9-Phenyl-9-fluorenyl Protecting Group

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Table of Contents

Additional information, figures and schemes

Quenching experiment of 12:

12 (100 mol-%) was stirred together with *s*-BuLi (200 mol-%) at -30°C for 1h. Reaction quenched with MeOD.

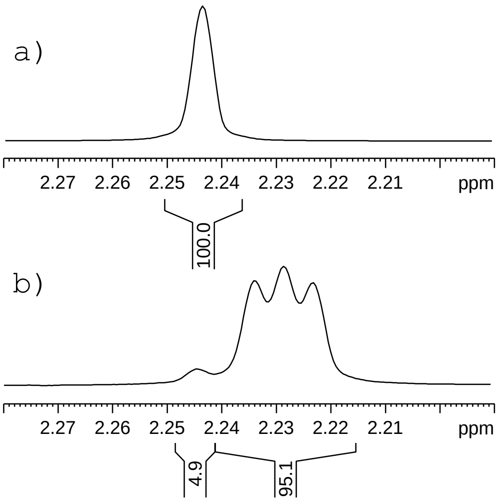
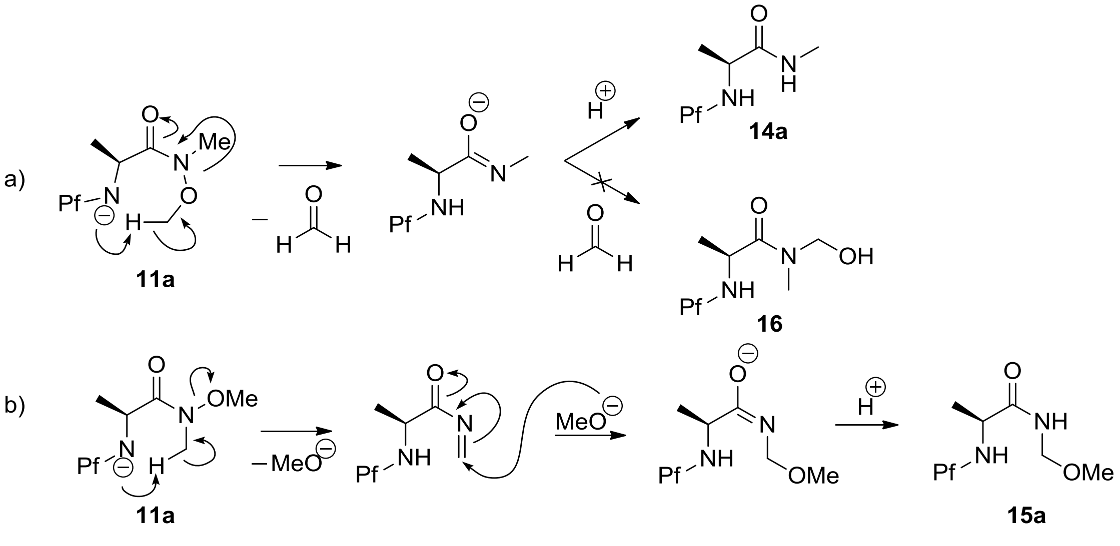
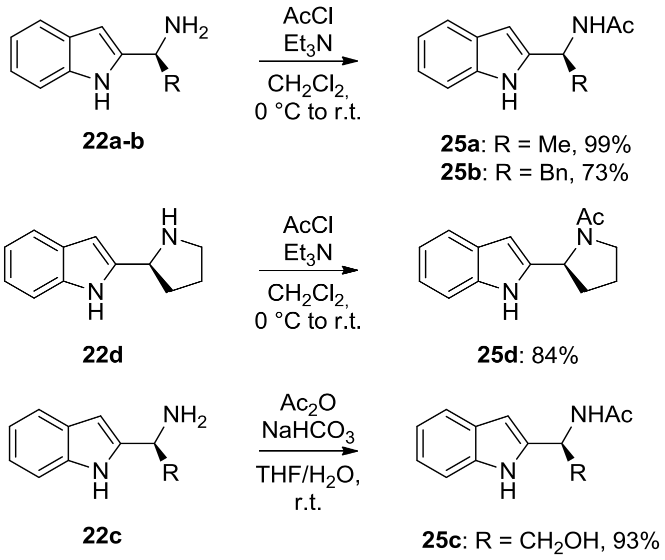


Figure S1. Benzylic protons of 12; b) Benzylic protons of 12 after deuterium labeling.

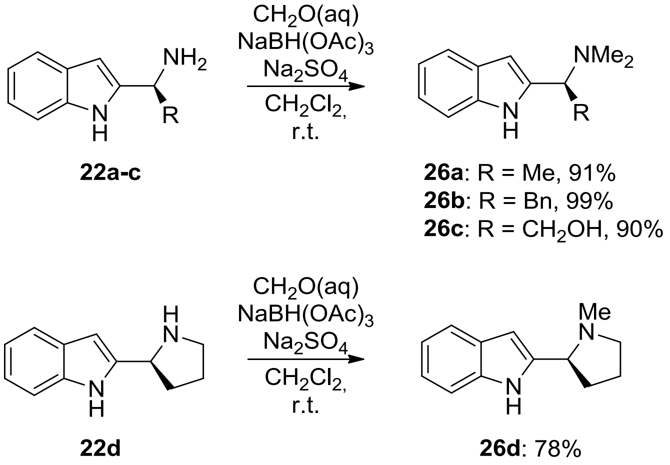
Suggested decomposition mechanism of Weinreb amide 11a:



Scheme S1. a) Proposed mechanism for the decomposition of Weinreb amide 11a into amide 14a. b) Proposed mechanism for the decomposition of Weinreb amide 11a into *N,O* acetal 15a.



Scheme S2. Acylation of 2-indolyl methanamines 22a-d.

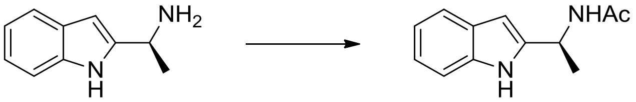


Scheme S3. Reductive amination of 2-indolyl methanamines 22a-d.

Figure S2. Chemical shifts of the α-hydrogens in amino esters 10a and *N*-benzyl-L-alanine methyl ester

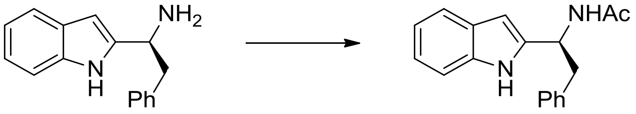
Experimental details

(*S*)-N-(1-(1H-indol-2-yl)ethyl)acetamide (25a)



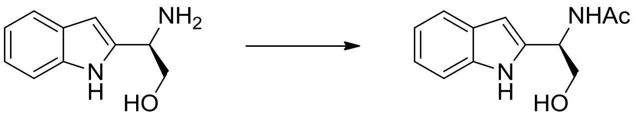
Compound **22a** (160 mg, 1 mmol, 100 mol-%) was dissolved in CH_2Cl_2 (2.5 mL). Et_3N (0.17 mL, 1.2 mmol, 120 mol-%) was added. The solution was cooled down to 0 °C and AcCl (0.09 mL, 1.2 mmol, 120 mol-%) was added dropwise. The solution was stirred at 0 °C for 15 min and at rt for 2 h. The reaction mixture was washed with citric acid (10 mL, 5 w-%) and the aqueous phase was extracted with CH_2Cl_2 (2 x 10 mL) Combined organic layers were dried over Na_2SO_4 and filtered. The solvents were evaporated to give **25a**: yield 99% (202 mg); R_f 0.27 (CH_2Cl_2:MeOH, 9:1, visualized by UV or by ninhydrin staining); yellow solid; mp 119-121 °C; Chiral HPLC analysis (Chiralpak IB, 98:2 Hexane:EtOH, 1 mL/min, retention times: (*S*)-enantiomer = 53.9 min, (*R*)-enantiomer = 59.3 min), (*S*) = 99 % *ee*, (*R*) = 97 % *ee*; $[\alpha]_D$ (*S*) -222.2 (*c* 0.62 in CH_2Cl_2), (*R*) +211.1 (*c* 0.69 in CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 9.17 (br s, 1H), 7.53 (m, 1H), 7.29 (m, 1 H), 7.14 (ddd, *J* = 8.0, 7.2, 1.3 Hz, 1H), 7.05 (ddd, *J* = 8.0, 6.8, 1.1 Hz, 1H), 6.30 (m, 1H), 6.06 (br d, *J* = 7.4 Hz, 1H), 5.22 (dq, *J* = 7.3, 7.1 Hz, 1H), 1.95 (s, 3H), 1.59 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 141.1, 135.9, 127.4, 121.9, 120.2, 119.6, 111.0, 98.0, 42.9, 23.1, 18.1; IR (film) ν 3386, 3272, 3081, 3057, 2978, 2932, 1643, 1541, 1457, 1301, 1165, 790, 738 cm^{-1}; HRMS-ESI calculated for $C_{12}H_{15}N_2O$ [M + H] 203.1184, found 203.1181.

(*S*)-N-(1-(1H-indol-2-yl)-2-phenylethyl)acetamide (25b)



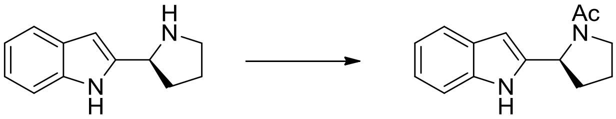
Compound **25b** was prepared with the same procedure as compound **25a**; obtained after silica gel chromatography (Hex:EtOAc, 1:1): yield 73% (134 mg); R_f 0.49 (CH_2Cl_2:MeOH, 9:1; visualized by UV or by ninhydrin staining); pale yellow solid; mp 178-180 °C dec.; $[\alpha]_D$ -120.5 (*c* 1.1 in MeOH); ^1H NMR (400 MHz, CD_3CN) δ 9.32 (br s, 1H), 7.48 (m, 1H), 7.35 (m, 1H), 7.18 - 7.30 (m, 5H), 7.09 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.01 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H), 6.80 (m, 1H), 6.32 (m, 1 H), 5.33 (m, 1H), 3.30 (dd, *J* = 13.9, 6.2 Hz, 1H), 3.12 (dd, *J* = 13.9, 8.8 Hz, 1H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ 172.6, 140.6, 139.4, 137.9, 130.3, 129.6, 129.2, 127.5, 122.2, 120.9, 120.1, 111.9, 99.7, 50.5, 41.8, 22.5; IR (film) ν 3389, 3273, 3088, 3058, 2926, 1632, 1455, 1288, 789, 750, 699 cm^{-1}; HRMS-ESI calculated for $C_{18}H_{18}N_2NaO$ [M + Na] 301.1317, found 301.1315.

(*R*)-N-(2-hydroxy-1-(1H-indol-2-yl)ethyl)acetamide (25c)



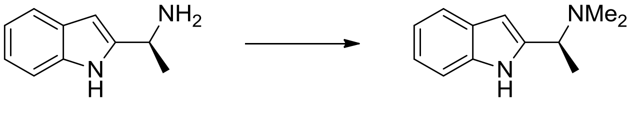
Compound **22c** (88 mg, 0.5 mmol, 100 mol-%) was dissolved in THF (1 mL) and aqueous sat. $NaHCO_3$ (3 mL) was added. Acetic anhydride (0.14 mL, 1.5 mmol, 300 mol-%) was added dropwise and the reaction mixture was stirred for 18 h. The reaction mixture was diluted with EtOAc (5 mL) and the organic phase was washed with H_2O (5 mL). The combined aqueous phases were extracted with EtOAc (2 x 10 mL). Combined organic phases were dried over Na_2SO_4 and filtered. The solvents were evaporated to give a white solid. The crude product was purified by silica gel column chromatography (CH_2Cl_2:MeOH, 93:7) to give **25c**: yield 93% (101 mg); R_f 0.41 (CH_2Cl_2:MeOH, 9:1; visualized by UV or by ninhydrin staining); white solid; mp 138-139 °C; $[\alpha]_D$ -130.6 (*c* 1.0 in CH_2Cl_2); ^1H NMR (400 MHz, CD_3OD) δ 7.45 (m, 1H), 7.31 (m, 1H), 7.04 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 6.95 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 6.34 (m, 1H), 5.22 (app t, *J* = 5.9 Hz, 1H), 3.93 (dd, *J* = 11.2, 5.3 Hz, 1H), 3.84 (dd, *J* = 11.2, 6.6 Hz, 1H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ 173.2, 138.4, 137.9, 129.6, 122.2, 120.9, 120.1, 111.9, 100.0, 64.9, 51.2, 22.7; IR (film) ν 3379, 3279, 3083, 3058, 2928, 2879, 1639, 1541, 1456, 1291, 1041, 794, 787 cm^{-1}; HRMS-ESI calculated for $C_{12}H_{15}N_2O_2$ [M + H] 219.1134, found 219.1136.

(*S*)-1-(2-(1H-indol-2-yl)pyrrolidin-1-yl)ethanone (25d)



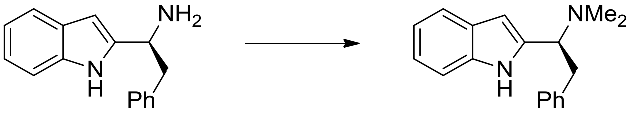
Compound **25d** was prepared using the same procedure as for compound **25a** to give **25d** after silica gel chromatography (Hex:EtOAc, 1:9): yield 84% (56 mg); R_f 0.31 (Hex:EtOAc, 1:9; visualized by UV); light yellow solid; mp 138-140 °C; $[\alpha]_D$ -111.4 (*c* 2.0 in CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$, major rotamer at 25 °C) δ 9.76 (br s, 1H), 7.53 (m, 1H), 7.31 (m, 1H), 7.13 (m, 1H), 7.04 (m, 1H), 6.29 (m, 1H), 5.45 (br m, 1H), 3.50 (m, 2H), 2.55 (m, 1H), 2.12 - 2.34 (m, 3H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, major rotamer at 25 °C) δ 171.2, 140.1, 136.1, 127.2, 121.8, 120.1, 119.4, 111.1, 97.3, 53.8, 48.1, 28.5, 25.2, 22.7; IR (film) ν 3245, 2975, 2877, 1624, 1548, 1418, 1341, 1303, 758, 728 cm^{-1}; HRMS-ESI calculated for $C_{14}H_{17}N_2O$ [M + H] 229.1341; found 229.1351. Variable ^1H NMR (400 MHz, DMSO-d_6) can be found in the supporting information.

(*S*)-1-(1H-indol-2-yl)-N,N-dimethylethanamine (26a)



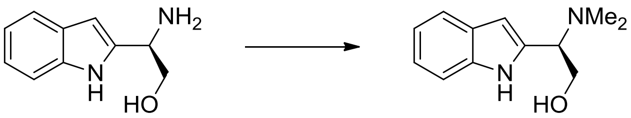
Compound **22a** (80 mg, 0.5 mmol, 100 mol-%) was dissolved in CH_2Cl_2 (12 mL) and CH_2O (0.18 mL, 2 mmol, aq. 37 w-%, 400 mol-%), anhydrous Na_2SO_4 (400 mg, 2.82 mmol, 564 mol-%) and $NaBH(OAc)_3$ (1.00 g, 5 mmol, 1000 mol -%) were added. The reaction was stirred at rt for 18 h and quenched with sat. $NaHCO_3$ (aq., 10 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic layers were dried over Na_2SO_4 and filtered. The solvents were evaporated to give a pale yellow solid. The crude product was purified by silica gel column chromatography (CH_2Cl_2:MeOH, 9:1) to give **26a**: yield 90% (99 mg); R_f 0.26 (CH_2Cl_2:MeOH, 9:1; visualized by UV or by ninhydrin staining); pale yellow solid; mp 46-48 °C; [α]$_D$ -1.7 (*c* 1.2 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (br s, 1H), 7.55 (m, 1H), 7.32 (m, 1 H), 7.13 (ddd, *J* = 8.0, 7.0, 1.3 Hz, 1H), 7.06 (ddd, *J* = 7.8, 7.2, 1.1 Hz, 1H), 6.31 (m, 1H), 3.82 (q, *J* = 6.8 Hz, 1H), 2.26 (s, 6H), 1.41 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 135.9, 128.2, 121.4, 120.1, 119.4, 110.8, 99.8, 58.1, 41.3, 13.0; IR (film) ν 3402, 3236 3081, 3056, 2975, 1455, 1301, 1081, 790, 730 cm^{-1}; HRMS-ESI calculated for $C_{12}H_{17}N_2$ [M + H] 189.1392, found 189.1388.

(*S*)-1-(1H-indol-2-yl)-N,N-dimethyl-2-phenylethanamine (26b)



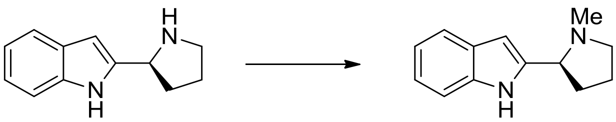
Compound **26b** was prepared with the same method as compound **26a**. The crude product was purified by silica gel column chromatography (EtOAc): yield 99% (130 mg); R$_f$ 0.32 (EtOAc, visualized by UV or by ninhydrin staining); brown oil; [α]$_D$ -123.7 (*c* 0.8 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (br s, 1H), 7.50 (m, 1H), 7.30 (m, 1H), 7.03 - 7.22 (m, 7H), 6.22 (m, 1H), 3.87 (dd, *J* = 9.3, 4.4 Hz, 1H), 3.27 (dd, *J* = 13.7, 4.4 Hz, 1H), 3.06 (dd, *J* = 13.7, 9.3 Hz, 1H), 2.33 ppm (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 138.4, 135.8, 129.0, 128.3, 128.2, 126.1, 121.4, 120.2, 119.4, 110.7, 101.7, 65.6, 42.2, 36.2; IR (film) ν 3410, 3239, 3083, 3059, 2933, 2861, 2824, 2781, 1495, 1032, 1019, 787, 749, 699 cm^{-1}; HRMS-ESI calculated for $C_{18}H_{21}N_2$ [M + H] 265.1705, found 265.1707.

(*R*)-2-(dimethylamino)-2-(1H-indol-2-yl)ethanol (26c)



Compound **26c** was prepared with the same method as compound **26a**. The crude product was purified by flash column chromatography (CH_2Cl_2:MeOH, 3:1): yield 93% (95 mg); R$_f$ 0.43 (CH_2Cl_2:MeOH, 3:1; visualized by UV or by ninhydrin staining); white solid; mp 90-93 °C; [α]$_D$ -100.1 (*c* 0.8 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (br s, 1H), 7.57 (app d, *J* = 7.9 Hz, 1H), 7.33 (app d, *J* = 8.1 Hz, 1H), 7.16 (ddd, *J* = 8.4, 6.7, 1.3 Hz, 1H), 7.09 (ddd, *J* = 7.7, 7.0, 0.9 Hz, 1 H), 6.35 (m, 1H), 3.94 (dd, *J* = 11.0, 5.1 Hz, 1H), 3.87 (dd, *J* = 11.2, 6.0 Hz, 1H), 3.66 (br s, 1H), 3.63 (app t, *J* = 5.5 Hz, 1H), 2.29 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.0, 135.2, 127.8, 121.9, 120.3, 119.8, 111.0, 102.1, 64.5, 61.6, 42.5; IR (film) ν 3398, 3276, 3082, 3055, 2946, 2871, 2830, 2785, 1456, 1290, 1032, 791, 746 cm^{-1}; HRMS-ESI calculated for $C_{12}H_{17}N_2O$ [M + H] 205.1341, found 205.1334.

(*S*)-2-(1-methylpyrrolidin-2-yl)-1H-indole (26d)

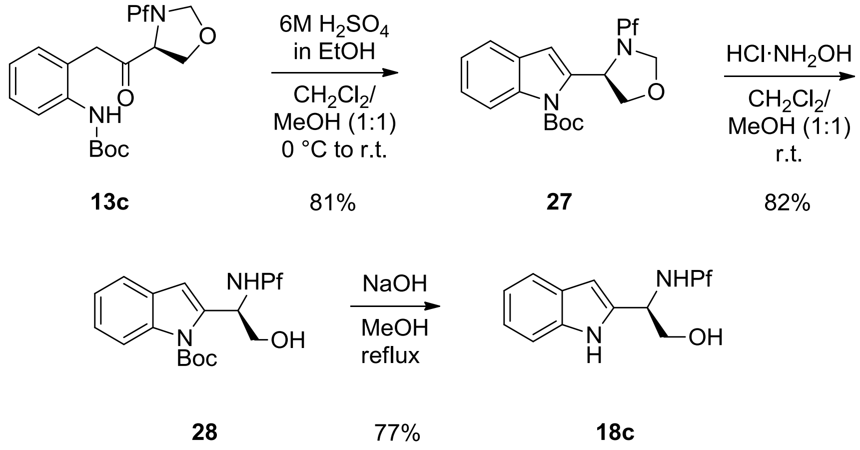


Compound **26d** was prepared with the same method as compound **26a**. The crude product was purified by silica gel column chromatography (CH_2Cl_2:MeOH, 96:4 and then 94:6): yield 78% (57 mg); R$_f$ 0.38

(CH_2Cl_2:MeOH, 9:1; visualized by UV); oil; $[\alpha]_D$ -129.0 (*c* 1.45 in CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 8.63 (br, 1H), 7.54 (m, 1H), 7.34 (m, 1H), 7.14 (ddd, J = 8.0, 7.2, 1.3 Hz, 1H), 7.07 (ddd, J = 7.9, 7.1, 1.1 Hz, 1H), 6.38 (m, 1H), 3.46 (app t, J = 8.05 Hz, 1H), 3.27 (m, 1H), 2.38 (m, 1H), 2.28 (s, 3H), 2.21 (m, 1H), 1.82 – 2.04 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 136.0, 128.4, 121.5, 120.0, 119.5, 110.9, 100.9, 64.8, 56.6, 40.4, 33.2, 22.6; IR (film) ν 3397, 3242, 2943, 2780, 1456, 1286, 1115, 1040, 749, 736 cm^{-1}; HRMS-ESI calculated for $C_{13}H_{17}N_2$ [M + H] 201.1392, found 201.1387.

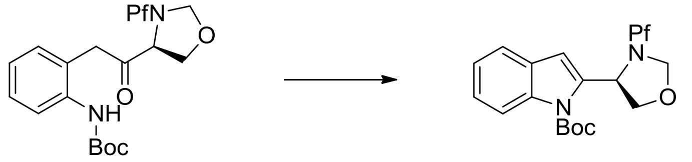
Stepwise approach to 18c

In addition to the telescoped reaction to indole **18c,** a stepwise approach is presented below:



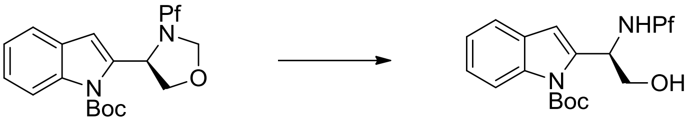
Scheme S4. Stepwise synthesis of 18c

(*R*)-tert-butyl 2-(3-(9-phenyl-9H-fluoren-9-yl)oxazolidin-4-yl)-1H-indole-1-carboxylate (27)



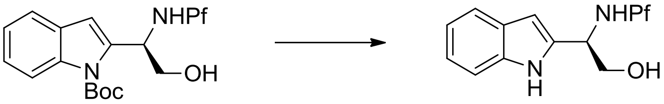
Compound **13c** (274 mg, 0.5 mmol, 100 mol-%) was dissolved in CH_2Cl_2 (2.5 mL) and MeOH (2.5 mL). The solution was cooled to 0 °C. H_2SO_4 (0.84 mL, 5 mmol, 6M in EtOH, 1000 mol-%) was added dropwise. The reaction was stirred for 1 h at 0 °C then taken to rt and stirred an additional 1.5 h. The reaction was poured into sat $NaHCO_3$ (aq., 15 mL) WARNING! GAS EVOLUTION! The reaction mixture was extracted with CH_2Cl_2 (3 x 15 mL). The combined organic phases were dried over Na_2SO_4, filtered and the solvents were removed by evaporation. Silica gel chromatography (Hex:EtOAc, 93:7) afforded **27**: yield 81% (215 mg); R_f 0.68 (Hex:EtOAc, 3:1; visulized by UV); white powder; mp 185-187 °C dec.; $[\alpha]_D$ +6.0 (*c* 0.61 in CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (m, 1H), 7.71 (m, 1H), 7.68 (m, 1H), 7.54 – 7.61 (m, 4H), 7.17 – 7.48 (m, 9H), 7.12 (s, 1H), 7.03 (m, 1H), 5.13 (d, J = 6.8 Hz, 1H), 4.93 (d, J = 6.8 Hz, 1H), 4.34 (ddd, J = 7.3, 3.8, 0.9 Hz, 1H), 3.62 (app. t, J = 7.6 Hz, 1H), 3.45 (dd, J = 7.8, 3.9 Hz, 1H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 149.2, 147.4, 144.3, 143.1, 141.7, 138.8, 137.4, 129.1, 128.8, 128.5, 128.2, 128.1, 127.9, 127.4, 127.1, 126.9, 125.5, 123.6, 122.8, 120.2, 119.6, 119.4, 115.5, 107.0, 84.7, 83.9, 77.6, 72.8, 58.9, 27.8; IR (film) ν 3061, 2978, 2871, 1730, 1451, 1328, 1157, 1116, 1089, 730, 699 cm^{-1}; HRMS-ESI calculated for $C_{35}H_{33}N_2O_3$ [M + H] 529.2491, found 529.2491.

(*R*)-tert-butyl 2-(2-hydroxy-1-((9-phenyl-9H-fluoren-9-yl)amino)ethyl)-1H-indole-1-carboxylate (28)



To a solution of **27** (75 mg, 0.14 mmol, 100 mol-%) in CH_2Cl_2 (3 mL) and MeOH (3 mL) was added hydroxylamine·HCl (49 mg, 0.71 mmol, 500 mol-%) at rt. The reaction mixture was stirred for 96 h after which the solvents were evaporated and the solid residue partitioned between CH_2Cl_2 (10 mL) and citric acid (10 mL, 5w-%). The phases were separated and the organic phase was washed once with citric acid (10 mL, 5w-%). The combined aqueous phases were back extracted with CH_2Cl_2 (10 mL) and subsequently discarded. The combined organic phases were dried over Na_2SO_4, filtered and the solvent removed by evaporation. Silica gel chromatography (Hex:EtOAc, 4:1) gave **28**: yield 83% (60 mg); R_f 0.42 (Hex:EtOAc, 3:1; visulized by UV); white foam; $[\alpha]_D$ -204.0 (*c* 0.47 in CH_2Cl_2); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.85 (m, 2H), 7.69 (m, 1H), 6.98 – 7.55 (m, 13H), 6.85 (m, 1H), 6.55 (m, 1H), 4.71 (br m, 1H), 3.86 (br m, 1H), 3.68 (br s, 1H), 3.32 (br m, 1H), 1.24 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 150.7, 149.7, 149.0, 146.0, 145.5, 141.1, 139.7, 136.8, 129.2, 128.6, 128.2, 127.9, 127.4, 126.8, 126.6, 126.3, 125.7, 123.4, 122.8, 120.3, 120.1, 115.3, 109.4, 83.7, 73.7, 65.4, 53.6, 27.7; IR (film) ν 3441, 3331, 2977, 2930, 1728, 1452, 1327, 1157, 1031, 731, 699 cm^{-1}; HRMS-ESI calculated for $C_{34}H_{33}N_2O_3$ [M + H] 517.2491, found 517.2499. Additional information: Compound suffers from rotamerism. The ^{1}H peak at δ 3.32 is overlapping with the residual water from the DMSO-d_6. The presence of a peak at that particular chemical shift was made evident by a 2D ^{1}H^{1}H-COSY experiment that can be found later in the supporting information. ^{1}H NMR at varying temperatures can also be found in the supporting information.

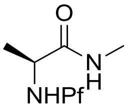
(*R*)-2-(1H-indol-2-yl)-2-((9-phenyl-9H-fluoren-9-yl)amino)ethanol (18c)



28 (120 mg, 0.25 mmol, 100 mol-%) was dissolved in MeOH (4 mL). NaOH (0.25 mL, 1.25 mmol, 5 M in H_2O, 500 mol-%) was added and the solution was refluxed for 0.5 h. The solution was taken to rt and acidified with HCl (aq., 1 M) and extracted with CH_2Cl_2 (2 x 10 mL). The combined organic phases were washed with NaOH (10 mL, aq., 1 M) dried over Na_2SO_4 filtered and the solvents were evaporated to give **18c**: yield 77% (80 mg). The analytical data of the compound received via this stepwise procedure was identical to that reported in this article.

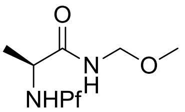
Analytical data of miscellaneous products

(*S*)-N-methyl-2-((9-phenyl-9H-fluoren-9-yl)amino)propanamide (14a)



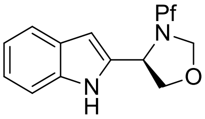
R_f 0.17 (Hex:EtOAc, 1:1; visulized by UV); colorless solid; mp 149-153 °C; $[\alpha]_D$ +112.3 (*c* 0.84 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (m, 1H), 7.64 (m, 1H), 7.12 – 7.40 (m, 11H), 7.07 (br m, 1H), 2.62 (d, J = 4.9 Hz, 3H), 2.54 (q, J = 7.1 Hz, 1H), 1.08 (d, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 149.3, 148.1, 144.1, 141.1, 140.1, 128.6, 128.5, 128.1, 127.5, 127.4, 126.0, 125.5, 124.4, 120.2, 120.2, 73.1, 52.8, 25.7, 21.5; IR (film) ν 3369, 3294, 3061, 2969, 1651, 1530, 1447, 1154, 732, 699 cm^{-1}; HRMS-ESI calculated for $C_{23}H_{23}N_2O$ [M + H] 343.1810, found 343.1804.

(*S*)-N-(methoxymethyl)-2-((9-phenyl-9H-fluoren-9-yl)amino)propanamide (15a)



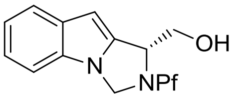
R_f 0.32 (Hex:EtOAc, 1:1; visulized by UV); colorless sticky solid; $[\alpha]_D$ +111.9 (*c* 0.67 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (br t, J = 6.7 Hz, 1H), 7.72 (m, 1H), 7.65 (m, 1H), 7.12 – 7.43 (m, 11H), 4.58 (dd, J = 11.2, 7.1 Hz, 1H), 4.57 (dd, J = 11.3, 7.2 Hz, 1H), 3.20 (s, 3H), 2.60 (q, J = 7.1 Hz, 1H), 2.45 (br s, 1H), 1.12 (d, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 149.1, 147.9, 144.0, 141.2, 140.1, 128.7, 128.7, 128.5, 128.1, 127.8, 127.5, 126.0, 125.5, 124.4, 120.3, 120.2, 73.2, 71.1, 56.1, 52.7, 21.5; IR (film) ν 3299, 3061, 2978, 2931, 1667, 1506, 1447, 1125, 1065, 731, 698 cm^{-1}; HRMS-ESI calculated for $C_{24}H_{25}N_2O_2$ [M + H] 373.1916, found 373.1915. Additional information: 2D NMR spectra (^{1}H^{1}H-COSY, ^{1}H^{13}C-HSQC and ^{1}H^{13}C-HMBC CIGAR) can be found later in the supporting information.

(*R*)-4-(1H-indol-2-yl)-3-(9-phenyl-9H-fluoren-9-yl)oxazolidine (19)



R_f: 0.58 (Hex:EtOAc, 3:1; visulized by UV); beige solid; mp 182-187 dec.; $[\alpha]_D$ +13.1 (*c* 0.58 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (br s, 1H), 7.75 (m, 1H), 7.65 (m, 2H), 7.02 – 7.51 (m, 14H), 6.05 (m, 1H), 5.08 (d, J = 6.6 Hz, 1H), 4.81 (d, J = 6.6 Hz, 1H), 3.90 (dd, J = 7.2, 4.1 Hz, 1H), 3.79 (dd, J = 7.2, 4.1 Hz, 1H), 3.50 (app t, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 146.8, 143.6, 141.6, 140.0, 139.2, 135.6, 129.0, 128.6, 128.5, 128.1, 127.9, 127.5, 127.0, 127.0, 125.3, 121.5, 120.2, 120.0, 119.7, 119.6, 110.6, 99.2, 84.3, 77.1, 71.0, 56.3; IR (film) ν 3434, 3058, 2869, 1487, 1450, 1289, 1158, 1016, 734, 701 cm^{-1}; HRMS-ESI calculated for $C_{30}H_{25}N_2O$[M + H] 429.1967, found 429.1952.

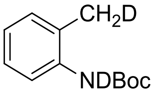
(*R*)-(2-(9-phenyl-9H-fluoren-9-yl)-2,3-dihydro-1H-imidazo[1,5-a]indol-1-yl)methanol (20)



R$_f$ 0.30 (Hex:EtOAc, 3:1; visulized by UV); pale orange foam; $[\alpha]_D$ -508.3 (*c* 0.12 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (m, 1H), 7.65 (m, 1H), 7.45 – 7.59 (m, 4H), 7.02 – 7.35 (m, 10H), 6.90 (m, 1H), 5.91 (s, 1H), 5.33 (m, 1H), 5.31 (m, 1H), 3.80 (app t, J = 5.5 Hz, 1H), 3.54 (ddd, J = 11.0, 7.2, 5.2 Hz, 1H), 3.35 (app dt, J = 11.0, 6.0 Hz), 6.76 (app t, J = 6.76 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 145.8, 143.4, 142.8, 141.2, 139.3, 133.7, 131.1, 128.9, 128.8, 128.1, 128.0, 127.8, 127.0, 125.4, 125.0, 120.8, 120.7, 120.1, 119.9, 119.5, 109.5, 92.0, 77.9, 64.8, 64.8, 60.0; IR (film) ν 3563, 3426, 3056, 2933, 2873, 1422, 1222, 1032, 1008, 731, 702 cm^{-1}; HRMS-ESI calculated for $C_{30}H_{25}N_2O$ [M + H] 429.1967, found 429.1954. Additional information: 2D NMR spectra (^{1}H^{1}H-COSY, ^{1}H^{13}C-HSQC and ^{1}H^{13}C-HMBC CIGAR) can be found later in the supporting information.

Analytical data

***tert*-butyl *o*-tolylcarbamate-d$_2$ (12-d$_2$)**



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (br d, J = 7.5 Hz, 1H), 7.19 (m, 1H), 7.14 (m, 1H), 6.99 (m, 1H), 2.23 (t, J = 2.2 Hz, 2H), 1.53 (s, 9H). Additional information: The ^{1}H spectra of the deuterated compound **12** is in all respects identical to the non deuterated counterpart with the exception for the disappearance of the N-H carbamate proton (δ 6.25) and the disappearance of the benzylic singlet (δ 2.24) with the appearance of a triplet (δ 2.23). ^{1}H spectrum and an overlay of the two compounds can be found later in the supporting information.

Computational data

Table S1. Molecular mechanics conformational search on 10a, showing data for the 5 lowest energy conformations[a]

Entry	Force Field	Conformer	Dihedral angle[b] [°]	Energy[c] [kJ/mol]	Population distribution[d] [%]
1	MM2*	1	-177	0	84.5
		2	2	5.0	11.3
		3	-150	8.9	2.3
		4	32	12.3	0.6
		5	119	13.8	0.3
2	MM3*	1	179	0	87.4
		2	13	7.1	5.0
		3	38	8.1	3.4
		4	170	10.2	1.4
		5	26	10.2	1.4
3	MMFF[e]	1	-155	0	92.7
		2	-148	8.6	2.8
		3	34	9.3	2.2
		4	27	9.8	1.8
		5	-167	13.1	0.5
4	OPLS-2005	1	10	0	35.4
		2	-139	0.4	29.8
		3	-155	2.6	12.4
		4	-143	3.1	10.1
		5	16	6.3	2.8
5	OPLS-2005 (QM-refined)	1	-162	0	69.6
		2	-151	4.5	11.2
		3	19	4.7	10.5
		4	35	5.6	7.4
		5	16	12.0	0.5

[a] Calculations performed in gas phase using MacroModel 10.0, without any constraints; electrostatic treatment was set to constant dielectric. [b] Dihedral angle between H(4)-C(3)-C(2)-O(1). [c] Relative potential energy. [d] Determined as the Boltzmann distribution at $T = 298.15$ K. [e] MMFFs gave the same result.

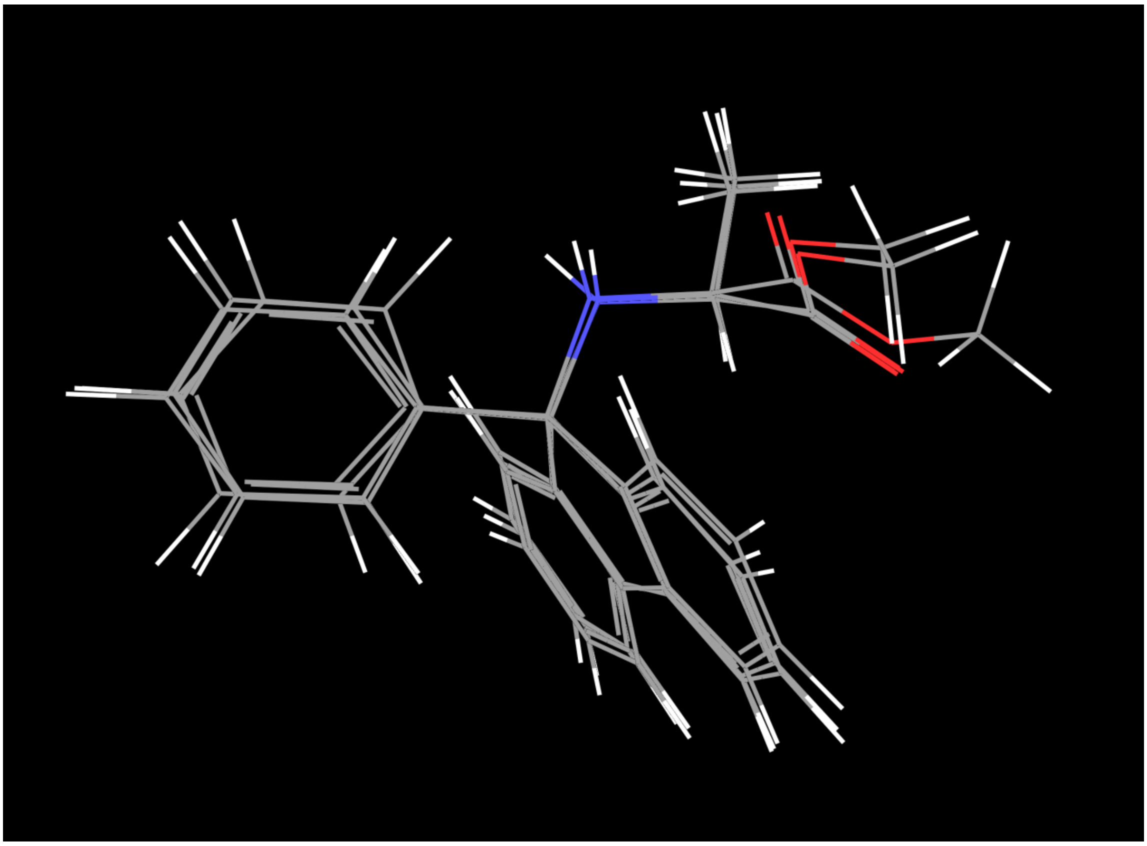


Figure S3. Conformers 1, 3 and 5 from QM refined conformational search calculations of 10a

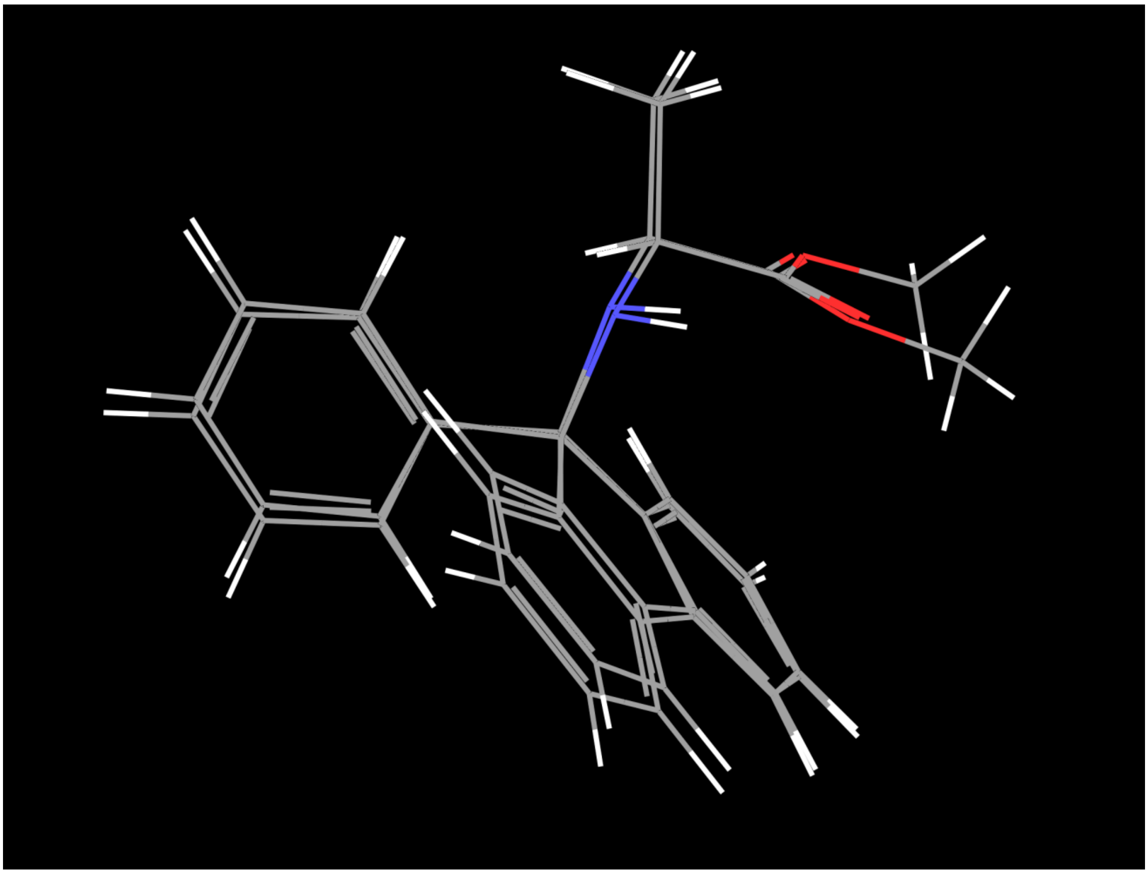


Figure S4. Conformers 2 and 4 from QM refined conformational search calculations of 10a

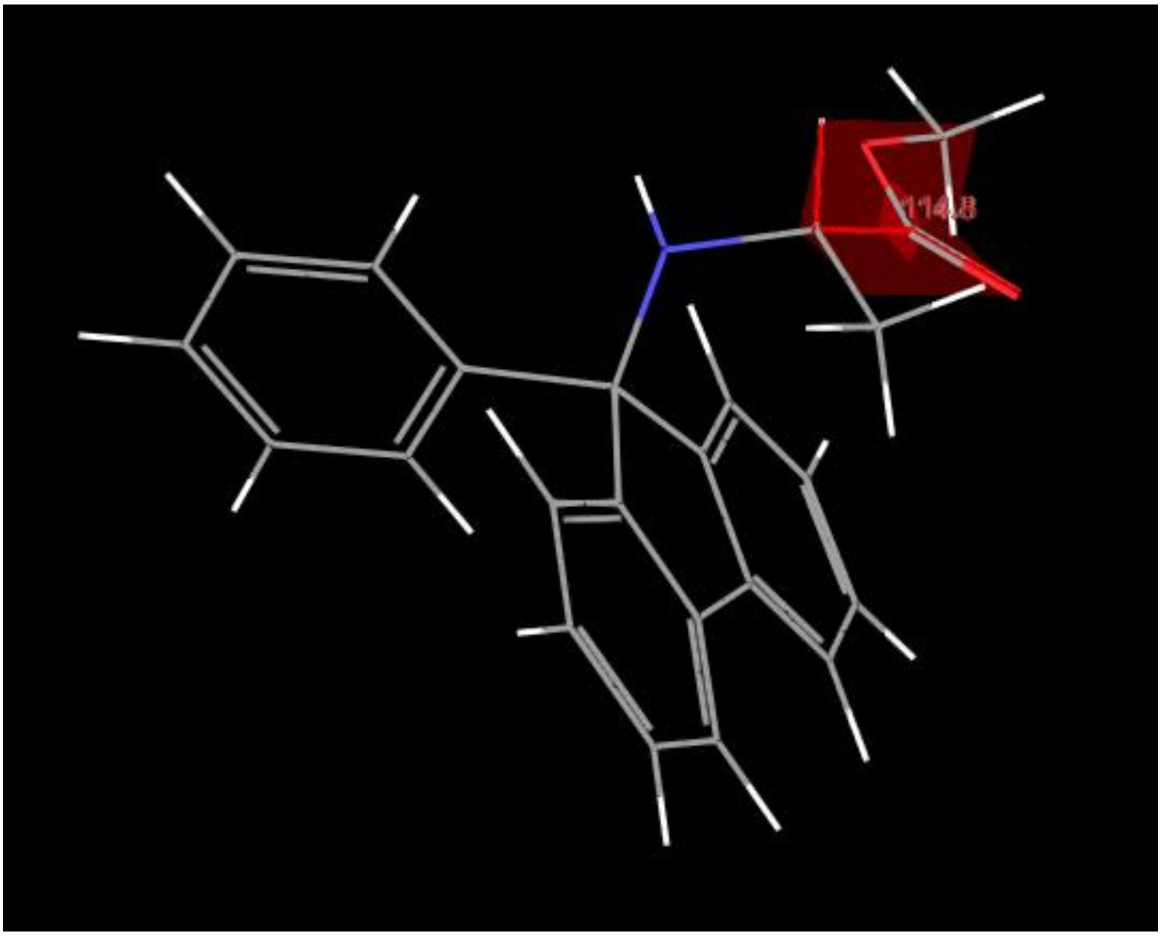


Figure S5. Higher energy conformer (conformer 6) of 10a were deprotonation of the α-hydrogen is likely to occur. Relative energy difference between lowest energy conformer (entry 5, conformer 1, SI Table 1), 17.8 kJ/mol. Dihedral angle between H(4) and C(7): -178°

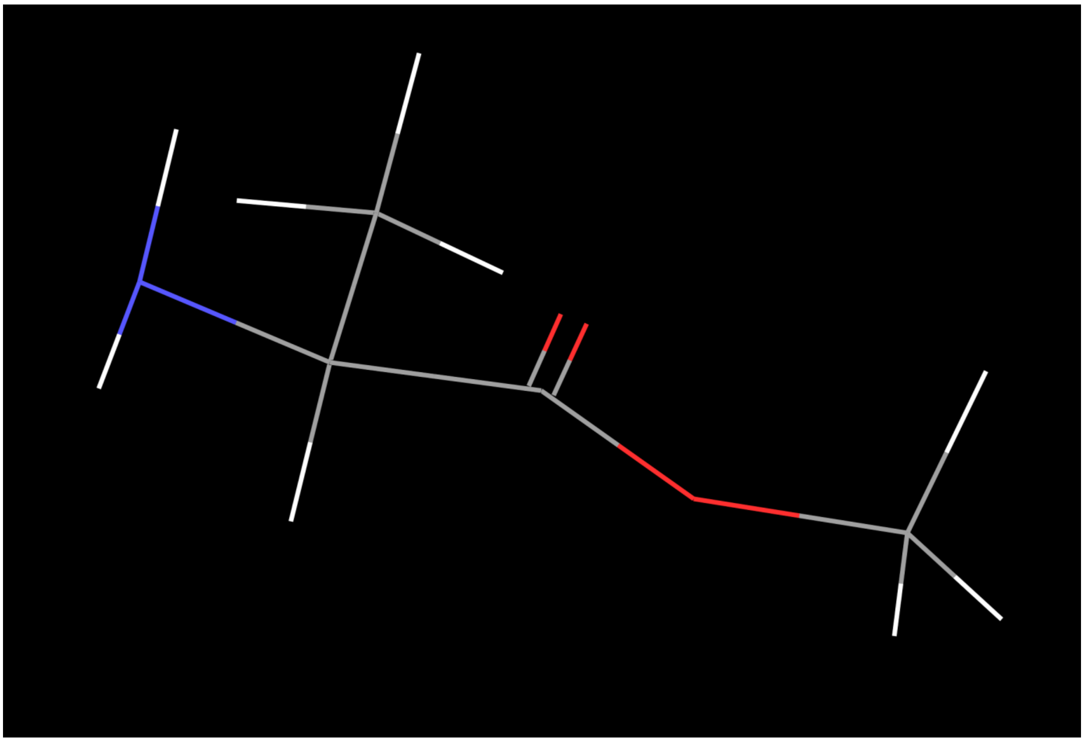


Figure S6. Lowest energy conformer of 9a

Table S2. Coordinate scan of 9a (free base), rotation around the α-hydrogen and the C-O carbonyl double bond

Dihedral Angle	E (Hartree)	ΔE (Hartree)	ΔE kJ/mol
-180	-363,061001	0,001535	4,03
-170	-363,061456	0,001080	2,84
-160	-363,061945	0,000591	1,55
-150	-363,062320	0,000216	0,57
-140	-363,062515	0,000021	0,06
-130	-363,062536	0,000000	0,00
-120	-363,062415	0,000121	0,32
-110	-363,062182	0,000354	0,93
-100	-363,061841	0,000695	1,82
-90	-363,061340	0,001196	3,14
-80	-363,060701	0,001835	4,82
-70	-363,060061	0,002475	6,50
-60	-363,059534	0,003002	7,88
-50	-363,059231	0,003305	8,68
-40	-363,059201	0,003335	8,76
-30	-363,059383	0,003153	8,28
-20	-363,059637	0,002899	7,61
-10	-363,059860	0,002676	7,03
0	-363,060020	0,002516	6,61
10	-363,060135	0,002401	6,30
20	-363,060210	0,002326	6,11
30	-363,060235	0,002301	6,04
40	-363,060278	0,002258	5,93
50	-363,060310	0,002226	5,84
60	-363,060311	0,002225	5,84
70	-363,060303	0,002233	5,86
80	-363,060258	0,002278	5,98
90	-363,060206	0,002330	6,12
100	-363,060167	0,002369	6,22
110	-363,060160	0,002376	6,24
120	-363,060218	0,002318	6,09
130	-363,060317	0,002219	5,83
140	-363,060394	0,002142	5,62
150	-363,060486	0,002050	5,38
160	-363,060577	0,001959	5,14
170	-363,060717	0,001819	4,78
180	-363,061001	0,001535	4,03

Table S3. Coordinate scan of 10a, rotation around the α-hydrogen and the C-O carbonyl double bond

Dihedral Angle	E (Hartree)	ΔE (Hartree)	ΔE kJ/mol
-180	-1094,340593	0,001784	4,68
-170	-1094,341367	0,001010	2,65
-160	-1094,341863	0,000514	1,35
-150	-1094,342197	0,000180	0,47
-140	-1094,342377	0,000000	0,00
-130	-1094,342196	0,000181	0,48
-120	-1094,341858	0,000519	1,36
-110	-1094,341322	0,001055	2,77
-100	-1094,340614	0,001763	4,63
-90	-1094,339701	0,002676	7,03
-80	-1094,338523	0,003854	10,12
-70	-1094,337122	0,005255	13,80
-60	-1094,335731	0,006646	17,45
-50	-1094,334377	0,008000	21,00
-40	-1094,332163	0,010214	26,82
-30	-1094,334278	0,008099	21,26
-20	-1094,336079	0,006298	16,54
-10	-1094,337490	0,004887	12,83
0	-1094,338455	0,003922	10,30
10	-1094,339074	0,003303	8,67
20	-1094,339308	0,003069	8,06
30	-1094,339196	0,003181	8,35
40	-1094,338900	0,003477	9,13
50	-1094,338485	0,003892	10,22
60	-1094,337935	0,004442	11,66
70	-1094,337544	0,004833	12,69
80	-1094,337269	0,005108	13,41
90	-1094,336988	0,005389	14,15
100	-1094,336609	0,005768	15,14
110	-1094,336226	0,006151	16,15
120	-1094,335545	0,006832	17,94
130	-1094,334829	0,007548	19,82
140	-1094,334738	0,007639	20,06
150	-1094,336303	0,006074	15,95
160	-1094,337999	0,004378	11,49
170	-1094,339482	0,002895	7,60
180	-1094,340593	0,001784	4,68

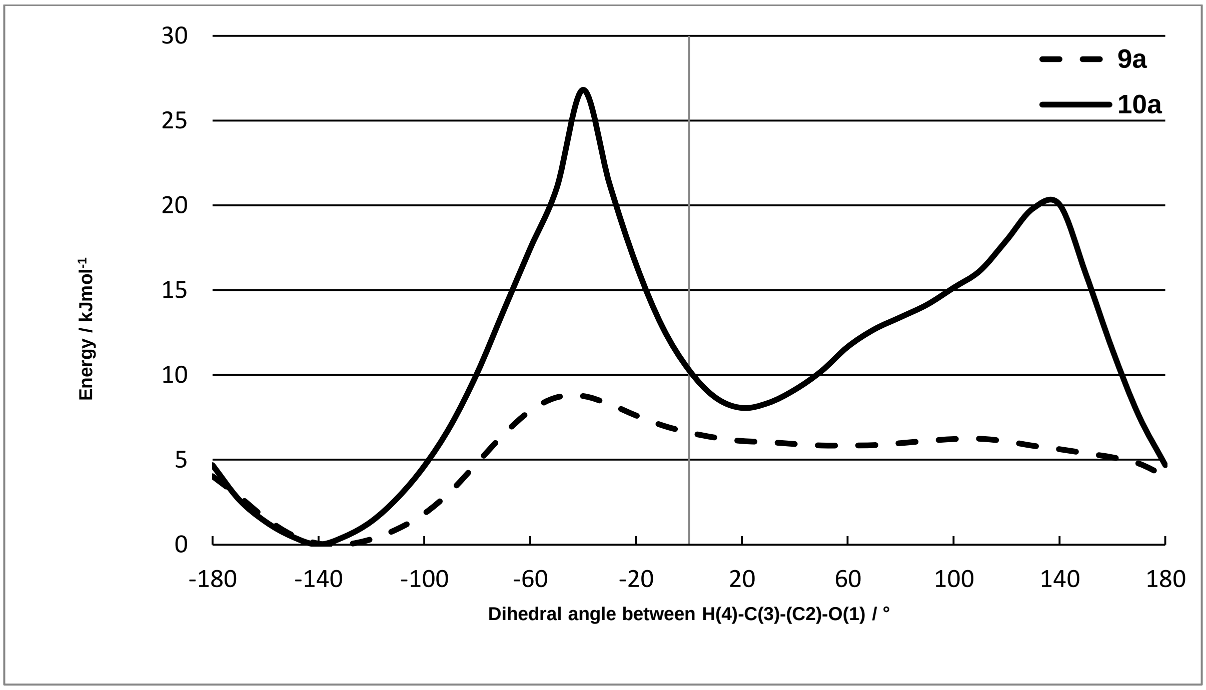


Figure S7. Coordinate scan of 9a and 10a, rotation around the C(2)-C(3) bond in 10° increments. Calculations performed in gas phase with Jaguar 8.0; theory: DFT(B3LYP) with the basis set 6-31G**. Energy: relative total electronic energy.

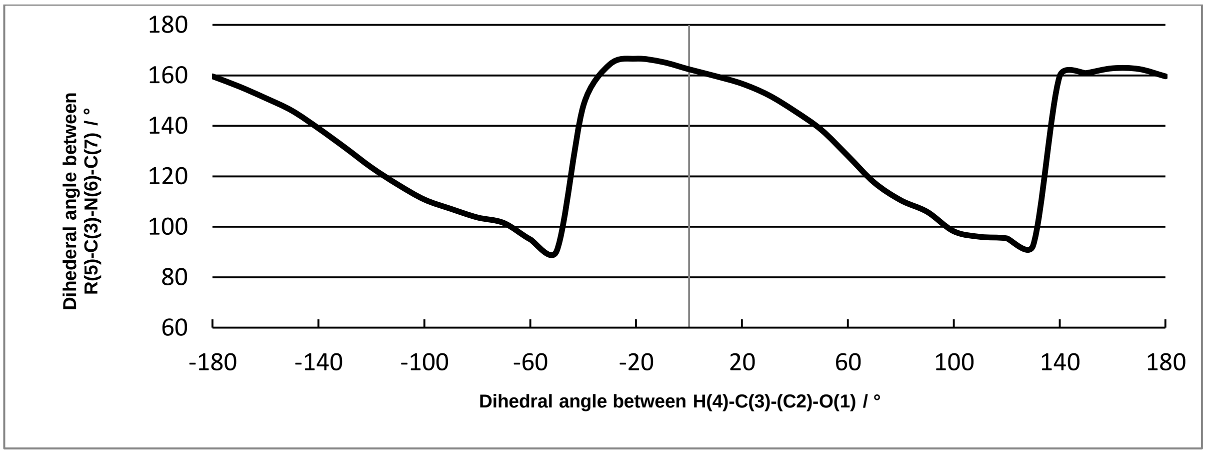


Figure S8. Dihedral angle between R(5)-C(3)-N(6)-C(7) during the rotation of the C(2)-C(3) bond of 10a.

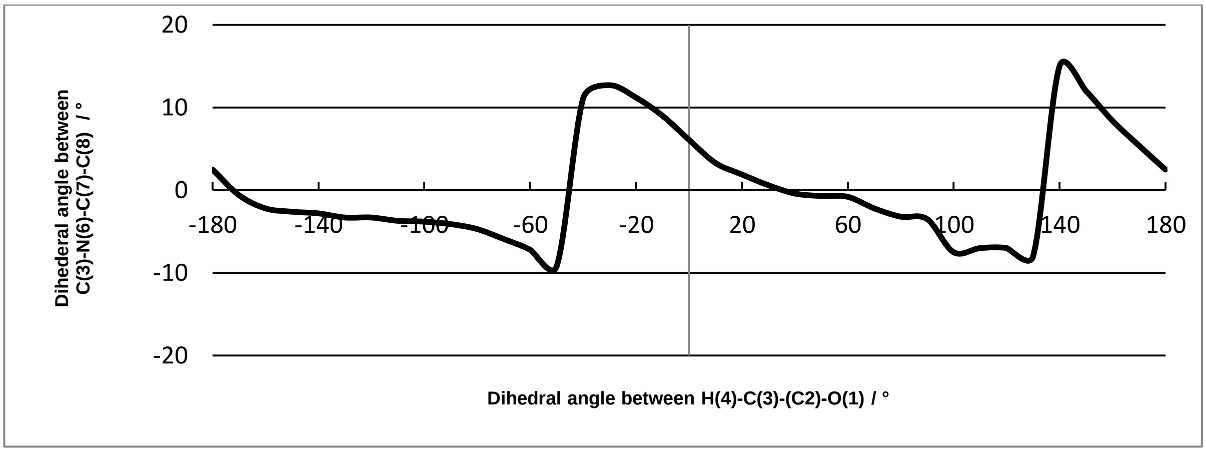


Figure S9. Dihedral angle between C(3)-N(6)-C(7)-C(8), during the rotation of the C(2)-C(3) bond of 10a.

Cartesian coordinates for compound 10a conformer 1

Total electronic energy: E = -1093.918254; Number of Imaginary frequencies: 0

C	-3.21560	-0.14150	-1.48890
C	-3.04050	1.32810	-1.12210
O	-4.07820	-0.77420	-0.68730
C	-4.29400	-2.15570	-0.99040
O	-2.66710	-0.66640	-2.43210
C	-3.93140	2.15980	-2.04750
N	-1.65270	1.75440	-1.25670
C	-0.80380	1.49160	-0.08680
C	-0.91090	0.07160	0.48270
C	-1.38740	0.09360	1.80140
C	-1.61260	1.49750	2.19460
C	-1.29540	2.31880	1.10520
C	-2.06950	2.05250	3.38760
C	-2.20920	3.43840	3.46800
C	-1.90190	4.25300	2.37490
C	-1.44070	3.69510	1.17980
C	-0.60920	-1.12990	-0.14330
C	-0.79970	-2.32030	0.56350
C	-1.27900	-2.29950	1.87610
C	-1.57520	-1.09170	2.50870
C	0.63910	1.87850	-0.41910
C	1.70830	1.31120	0.28260
C	3.01670	1.71110	0.02600
C	3.27830	2.68300	-0.93820
C	2.21930	3.25540	-1.63730
C	0.90720	2.86050	-1.37760
H	-3.35880	1.46670	-0.08480
H	-4.70550	-2.26260	-1.99630
H	-4.99770	-2.51490	-0.24190
H	-3.34890	-2.69930	-0.92560
H	-3.59700	2.04990	-3.08330
H	-4.97610	1.84210	-1.98000
H	-3.85530	3.21130	-1.76360
H	-1.25100	1.30750	-2.08190
H	-2.31590	1.42400	4.23820
H	-2.56210	3.88960	4.38990
H	-2.02010	5.32870	2.45820
H	-1.19610	4.31980	0.32510
H	-0.24240	-1.14630	-1.16620
H	-0.57010	-3.26970	0.08960
H	-1.41820	-3.23420	2.41050
H	-1.94240	-1.08060	3.53070
H	1.51760	0.55130	1.03450
H	3.83370	1.25870	0.57930
H	4.29910	2.99080	-1.14170
H	2.41100	4.01530	-2.38860
H	0.08330	3.31660	-1.91610

Cartesian coordinates for compound 10a conformer 2

Total electronic energy: E = -1093.916531; Number of Imaginary frequencies: 0

C	-3.67290	1.33580	-1.20600
C	-2.30980	1.19840	-1.87860
O	-4.23760	2.52860	-1.44250
C	-5.52080	2.72080	-0.83970
O	-4.21190	0.45130	-0.58410
C	-2.54550	0.71200	-3.31330
N	-1.45010	0.26120	-1.17450
C	-0.70820	0.78770	-0.01420
C	-0.25170	-0.42560	0.79610
C	-0.87000	-0.45380	2.05270
C	-1.70510	0.75310	2.18950
C	-1.57510	1.52010	1.02170
C	-2.48900	1.19630	3.25070
C	-3.13310	2.42930	3.13850
C	-2.97100	3.21310	1.99480
C	-2.17970	2.76710	0.93140
C	0.61020	-1.43470	0.39680
C	0.85850	-2.48640	1.28310
C	0.24690	-2.51770	2.53850
C	-0.62380	-1.50210	2.93550
C	0.48230	1.62590	-0.48060
C	0.99100	1.49590	-1.77460
C	2.11470	2.22260	-2.16950
C	2.74830	3.07970	-1.27420
C	2.25190	3.20620	0.02310
C	1.12650	2.48730	0.41500
H	-1.82780	2.18110	-1.90640
H	-5.43550	2.62420	0.24560
H	-5.83070	3.72650	-1.11800
H	-6.22980	1.97870	-1.21200
H	-2.99500	-0.28550	-3.29780
H	-3.21070	1.39040	-3.85410
H	-1.58990	0.65240	-3.83830
H	-2.01210	-0.53430	-0.87510
H	-2.59030	0.60270	4.15450
H	-3.74830	2.79180	3.95600
H	-3.45170	4.18490	1.93490
H	-2.03650	3.39990	0.05940
H	1.08350	-1.39980	-0.58060
H	1.53540	-3.28480	0.99630
H	0.45380	-3.34170	3.21410
H	-1.09610	-1.53220	3.91300
H	0.50230	0.81570	-2.46450
H	2.49530	2.11430	-3.18070
H	3.62250	3.64440	-1.58240
H	2.74070	3.86780	0.73130
H	0.74520	2.59250	1.42710

Cartesian coordinates for compound 10a conformer 3

Total electronic energy: E = -1093.916473; Number of Imaginary frequencies: 0

C	-3.44690	-0.17780	-1.02830
C	-3.08900	1.30440	-1.09310
O	-2.81310	-0.87890	-1.98900
C	-3.10630	-2.27660	-2.01380
O	-4.24920	-0.66840	-0.27220
C	-3.87820	1.93780	-2.24200
N	-1.67070	1.59240	-1.26420
C	-0.83230	1.45010	-0.06660
C	-0.96890	0.10490	0.65590
C	-1.47820	0.27890	1.95020
C	-1.67880	1.72180	2.18380
C	-1.31450	2.41410	1.02180
C	-2.14490	2.41250	3.29970
C	-2.24370	3.80270	3.23010
C	-1.88630	4.48840	2.06620
C	-1.41700	3.79420	0.94790
C	-0.66150	-1.16140	0.17910
C	-0.88800	-2.26450	1.00640
C	-1.41020	-2.09220	2.29090
C	-1.70560	-0.81860	2.77660
C	0.61820	1.77040	-0.43540
C	0.90910	2.62280	-1.50470
C	2.22930	2.96290	-1.79930
C	3.27400	2.46460	-1.02600
C	2.98980	1.62250	0.04790
C	1.67350	1.27720	0.34000
H	-3.42120	1.73330	-0.14370
H	-2.49120	-2.69570	-2.80870
H	-2.85770	-2.72580	-1.04910
H	-4.16670	-2.43610	-2.22010
H	-3.72200	3.01830	-2.22840
H	-3.52950	1.54570	-3.20220
H	-4.94670	1.72690	-2.14510
H	-1.29280	1.02040	-2.01860
H	-2.43000	1.88470	4.20500
H	-2.60350	4.35880	4.09000
H	-1.97140	5.56990	2.03360
H	-1.13360	4.31840	0.03930
H	-0.25210	-1.29220	-0.82010
H	-0.65270	-3.26340	0.65150
H	-1.58400	-2.96000	2.91910
H	-2.10530	-0.69070	3.77810
H	0.09580	3.02280	-2.10100
H	2.43850	3.62300	-2.63550
H	4.30090	2.73020	-1.25600
H	3.79540	1.22970	0.66040
H	1.46450	0.61950	1.17840

Cartesian coordinates for compound 10a conformer 4

Total electronic energy: E = -1093.916138; Number of Imaginary frequencies: 0

C	-3.63990	1.72500	-1.29200
C	-2.28610	1.44540	-1.94490
O	-4.09520	0.67070	-0.60080
C	-5.32050	0.88250	0.10470
O	-4.26010	2.75310	-1.42980
C	-2.55180	1.00420	-3.38890
N	-1.46140	0.45360	-1.27510
C	-0.72860	0.87640	-0.06980
C	-0.30820	-0.40400	0.65310
C	-0.92760	-0.50410	1.90530
C	-1.73220	0.71100	2.12620
C	-1.58800	1.55090	1.01080
C	-2.49890	1.10290	3.21980
C	-3.11440	2.35570	3.19170
C	-2.94590	3.20540	2.09740
C	-2.16890	2.81190	1.00270
C	0.52730	-1.40500	0.18360
C	0.74700	-2.52280	0.99310
C	0.13440	-2.62610	2.24420
C	-0.70910	-1.61780	2.71260
C	0.48900	1.71880	-0.45450
C	1.01660	1.67160	-1.74650
C	2.16460	2.39610	-2.06880
C	2.80360	3.16780	-1.10250
C	2.28770	3.21130	0.19250
C	1.13830	2.49510	0.51240
H	-1.75090	2.40130	-1.95810
H	-5.18780	1.69040	0.82890
H	-5.53510	-0.05620	0.61200
H	-6.12010	1.14360	-0.59130
H	-3.06050	0.03490	-3.39850
H	-3.17650	1.73480	-3.90810
H	-1.60180	0.89880	-3.91690
H	-2.02080	-0.36680	-1.05720
H	-2.60550	0.45620	4.08580
H	-3.71450	2.67980	4.03620
H	-3.41460	4.18430	2.09590
H	-2.02390	3.49400	0.16910
H	1.00350	-1.31320	-0.78880
H	1.40320	-3.31640	0.65010
H	0.31990	-3.50030	2.86030
H	-1.18080	-1.70300	3.68710
H	0.52270	1.05840	-2.49340
H	2.55940	2.35370	-3.07940
H	3.69640	3.73120	-1.35450
H	2.77980	3.80660	0.95530
H	0.74230	2.53610	1.52350

Cartesian coordinates for compound 10a conformer 5

Total electronic energy: E = -1093.913674; Number of Imaginary frequencies: 0

C	-3.39460	-0.16840	-1.08940
C	-3.09780	1.32730	-1.03680
O	-2.78640	-0.78470	-2.11240
C	-3.05290	-2.18340	-2.21270
O	-4.16230	-0.72350	-0.33900
C	-3.91560	2.01170	-2.13390
N	-1.68390	1.62190	-1.22950
C	-0.84810	1.55890	-0.02390
C	-0.95940	0.17750	0.62730
C	-1.46970	0.27410	1.92850
C	-1.71670	1.69720	2.23050
C	-1.34710	2.45700	1.11260
C	-2.21730	2.31760	3.37290
C	-2.34460	3.70730	3.37760
C	-1.97890	4.46330	2.26100
C	-1.47560	3.83800	1.11660
C	-0.62010	-1.05020	0.07930
C	-0.81290	-2.19910	0.85030
C	-1.33260	-2.10810	2.14420
C	-1.66230	-0.87090	2.69720
C	0.60430	1.84890	-0.40370
C	1.50780	2.32170	0.55490
C	2.84520	2.52570	0.22750
C	3.30000	2.26290	-1.06420
C	2.40780	1.78750	-2.02120
C	1.06820	1.57670	-1.69380
H	-3.46970	1.65400	-0.05530
H	-2.46580	-2.53710	-3.05900
H	-2.75100	-2.68700	-1.29090
H	-4.11800	-2.35830	-2.38030
H	-3.54590	1.71220	-3.11860
H	-4.97100	1.74080	-2.05280
H	-3.83470	3.09860	-2.03530
H	-1.57640	2.53820	-1.65900
H	-2.50480	1.73610	4.24360
H	-2.73150	4.20790	4.25950
H	-2.08150	5.54340	2.28610
H	-1.17510	4.42680	0.25260
H	-0.22320	-1.10920	-0.93070
H	-0.55380	-3.17190	0.44340
H	-1.47880	-3.01200	2.72690
H	-2.06380	-0.80720	3.70410
H	1.16290	2.53050	1.56360
H	3.53270	2.89360	0.98280
H	4.34190	2.42700	-1.32080
H	2.75260	1.57560	-3.02870
H	0.37380	1.19450	-2.43460

Cartesian coordinates for compound 10a conformer 6

Total electronic energy: E = -1093.911474; Number of Imaginary frequencies: 0

C	-3.91560	1.32770	-0.85780
C	-2.83920	0.52240	-1.59620
O	-3.86840	2.62630	-1.21910
C	-4.85850	3.46120	-0.61740
O	-4.75040	0.88300	-0.10920
C	-2.95740	-0.95480	-1.24610
N	-1.48610	1.08260	-1.51070
C	-0.74720	1.06250	-0.23920
C	-0.34780	-0.36000	0.16790
C	-0.82480	-0.66850	1.44800
C	-1.57810	0.49210	1.95840
C	-1.53300	1.51060	0.99610
C	-2.23850	0.68930	3.16870
C	-2.84170	1.92400	3.40700
C	-2.77140	2.94800	2.45940
C	-2.10960	2.74790	1.24570
C	0.39140	-1.27690	-0.56080
C	0.64240	-2.53020	0.00350
C	0.16300	-2.84510	1.27780
C	-0.57340	-1.91560	2.01370
C	0.53590	1.88650	-0.42130
C	1.17210	2.46690	0.68200
C	2.37330	3.15370	0.52910
C	2.95940	3.27420	-0.72980
C	2.33690	2.69370	-1.83130
C	1.13680	1.99970	-1.67920
H	-3.10490	0.63750	-2.65580
H	-5.85730	3.14100	-0.92200
H	-4.78390	3.40580	0.47110
H	-4.65300	4.47020	-0.97210
H	-2.87520	-1.13030	-0.17270
H	-3.93860	-1.31620	-1.56150
H	-2.18050	-1.52220	-1.76190
H	-1.51650	2.04150	-1.85050
H	-2.27960	-0.09630	3.91700
H	-3.36270	2.09570	4.34350
H	-3.22960	3.90910	2.67310
H	-2.04150	3.54710	0.51140
H	0.75760	-1.02440	-1.55230
H	1.21630	-3.26650	-0.55030
H	0.36860	-3.82340	1.70080
H	-0.94410	-2.16550	3.00350
H	0.72720	2.38110	1.66880
H	2.85030	3.59780	1.39720
H	3.89350	3.81370	-0.84940
H	2.78650	2.77530	-2.81620
H	0.66560	1.53520	-2.53890

Cartesian coordinates for compound 9a lowest energy conformer

Total electronic energy: E = -362.912493; Number of Imaginary frequencies: 0

C	-1.16470	1.16020	-0.42460
C	-2.60420	0.74540	-0.12870
O	-0.60940	1.80190	0.61580
C	0.74910	2.20980	0.43300
O	-0.57620	0.93610	-1.45600
C	-2.60710	-0.34140	0.94940
N	-3.31760	0.28180	-1.30240
H	-3.11570	1.63070	0.26590
H	1.03480	2.70870	1.35710
H	0.82690	2.89230	-0.41560
H	1.38320	1.34010	0.25010
H	-3.63910	-0.61680	1.17360
H	-2.08400	-1.23320	0.58710
H	-2.11480	0.00510	1.86000
H	-3.33120	1.00350	-2.01730
H	-2.82090	-0.50700	-1.71050

Crystal Structure Determinations

The single-crystal X-ray diffraction studies were carried out on a Bruker-Nonius Kappa-CCD diffractometer at 123(2) K using MoKα radiation (λ = 0.71073 Å) (**18b**, **10a**, **11a**, **23**, **10b**, **11b**, **10d**, **11d**), or a Bruker D8 Venture at 123(2) K , using CuKα radiation (λ = 1.54178 Å) (**24**). Direct Methods (SHELXS-97 [a)]) were used for structure solution and refinement was carried out using SHELXL-97 or SHELXL-2013/SHELXL-2014 [a)] (full-matrix least-squares on F^2). Hydrogen atoms were localized by difference electron density determination and refined using a riding model (H(N), H(O) free).

Semi-absorption corrections were applied for **18b**, **23**, **10b**, **11b**, **10d** and **11d**, a numerical absorption correction was applied for **24**. An extinction correction was applied for **10a**.

The absolute configuration of **18b**, **10a**, **11a**, **23**, **10b**, **11b**, **10d**, **11d** could not be determined reliably by refinement of Flack's x-parameter, [b)] Parsons x-parameter [c)] nor Hofft's y-parameter, [d)] using the effects of anomalous scattering. For all structures the enantiomer (absolute configuration) has been assigned by reference to an unchanging chiral centre in the synthetic procedure. In **24** the absolute configuration could be determined using the effects of anomalous scattering and in addition the enantiomer (absolute configuration) has been assigned by reference to an unchanging chiral centre in the synthetic procedure.

Crystallographic data (excluding structure factors) for the structures reported in this work have been deposited to the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1036698 (**18b**), CCDC-1036699 (**10a**), CCDC-1036700 (**11a**), CCDC-1036701 (**23**), CCDC-1036702 (**24**), CCDC-1036703 (**10b**), CCDC-1036704 (**11b**), CCDC-1036705 (**10d**), and CCDC-1036706 (**11d**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge DB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk).

a) G. M. Sheldrick, *Acta Crystallogr.* 2008, A64, 112-122.

b) H. D. Flack, *Acta Crystallogr.* 1983, A39, 876-881.

c) S. Parsons, H. D. Flack Flack, *Acta Crystallogr.* 2004, A60, s61.

d) R. W. W. Hooft, L. H. Straver, A. L. Spek, *J. Appl. Cryst.* 2008, 41, 96-103.

Crystal structure compound: 18b

Crystals where obtained by recrystallization from EtOAc/Hexane.

18b: colourless crystals, $C_{35}H_{28}N_2$, *M* = 476.59, crystal size 0.50 x 0.40 x 0.30 mm, *T* = 123(2) K, monoclinic, space group $P2_1$ (No. 4), *a* = 9.440(1) Å, *b* = 9.371(1) Å, *c* = 14.258(2) Å, *β* = 92.03(1)°, *V* = 1260.5(3) $Å^3$, *Z* = 2, *ρ*(calc) = 1.256 Mg m^{-3}, *F*(000) = 504, *μ* = 0.073 mm^{-1}, 17877 reflections ($2\theta_{max}$ = 55°), 5769 unique [R_{int} = 0.024], 340 parameters, 3 restraints, *R*1 (for 5509 *I* > 2σ(*I*)) = 0.030, *wR2 (all data)* = 0.076, S = 1.04, largest diff. peak and hole 0.227 and -0.173 e $Å^{-3}$, Parsons x = -0.1(6), y = 0.9(8).

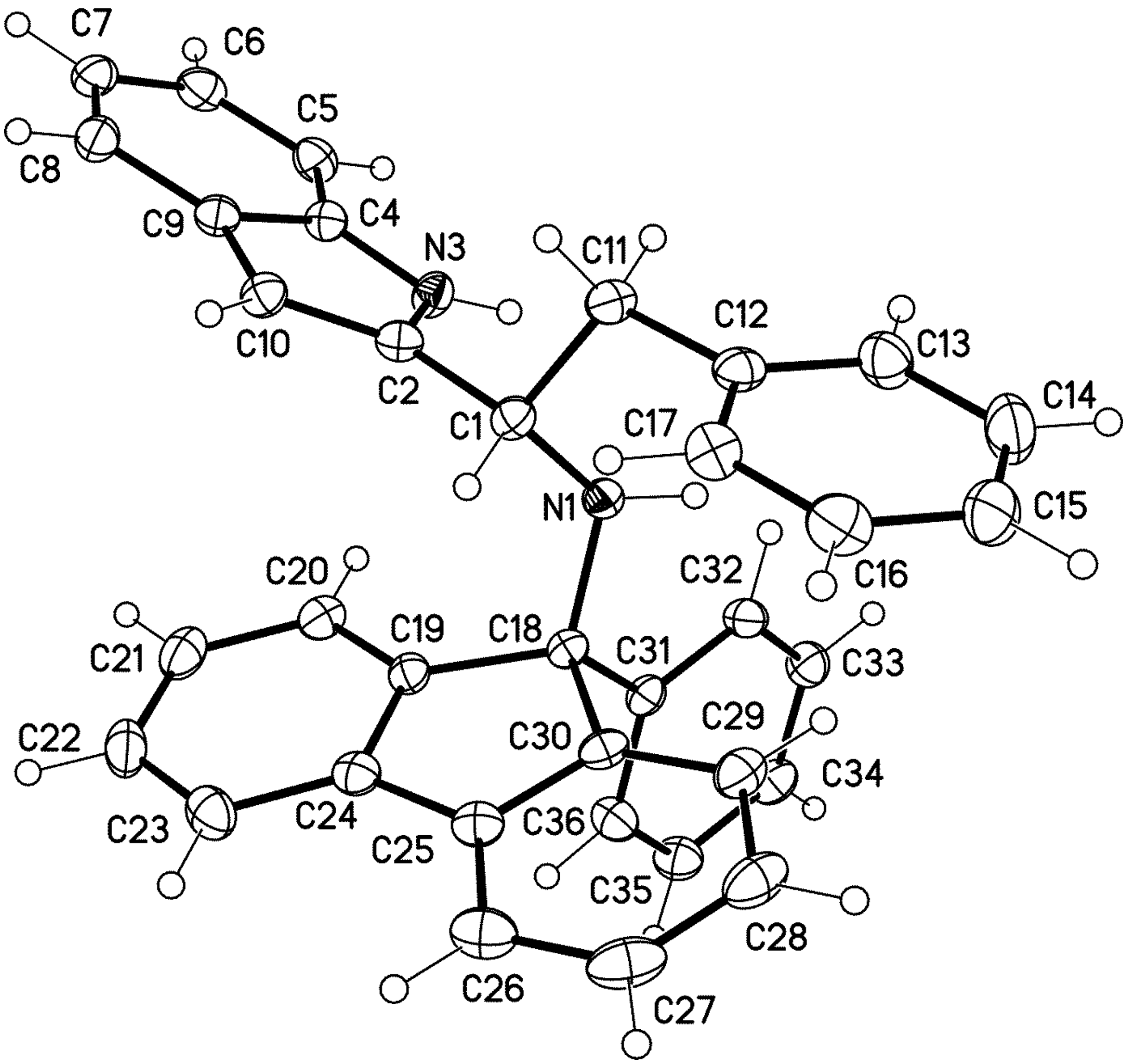


Fig. S1-Xray. Molecular structure of **18b** (displacement parameters are drawn at 50% probability level).

Crystal structure compound: 10a

Crystals where obtained through recrystallization from MeOH

10a: colourless crystals, $C_{23}H_{21}NO_2$, M = 343.41, crystal size 0.50 x 0.25 x 0.15 mm, T = 123(2) K, orthorhombic, space group $P2_12_12_1$ (No.19), a = 8.9475(7) Å, b = 10.3246(4) Å, c = 18.946(2) Å, V = 1750.3(2) $Å^3$, Z = 4, ρ(calc) = 1.303 Mg m^{-3}, F(000) = 728, μ = 0.083 mm^{-1}, 15610 reflections ($2\theta_{max}$ = 55°), 4015 unique [R_{int} = 0.023], 240 parameters, 1 restraint, $R1$ (for 3826 $I > 2\sigma(I)$) = 0.031, *wR2 (all data)* = 0.080, S = 1.06, largest diff. peak and hole 0.228 and -0.150 e $Å^{-3}$, Flack's x = -0.4(10), y = -0.1(4).

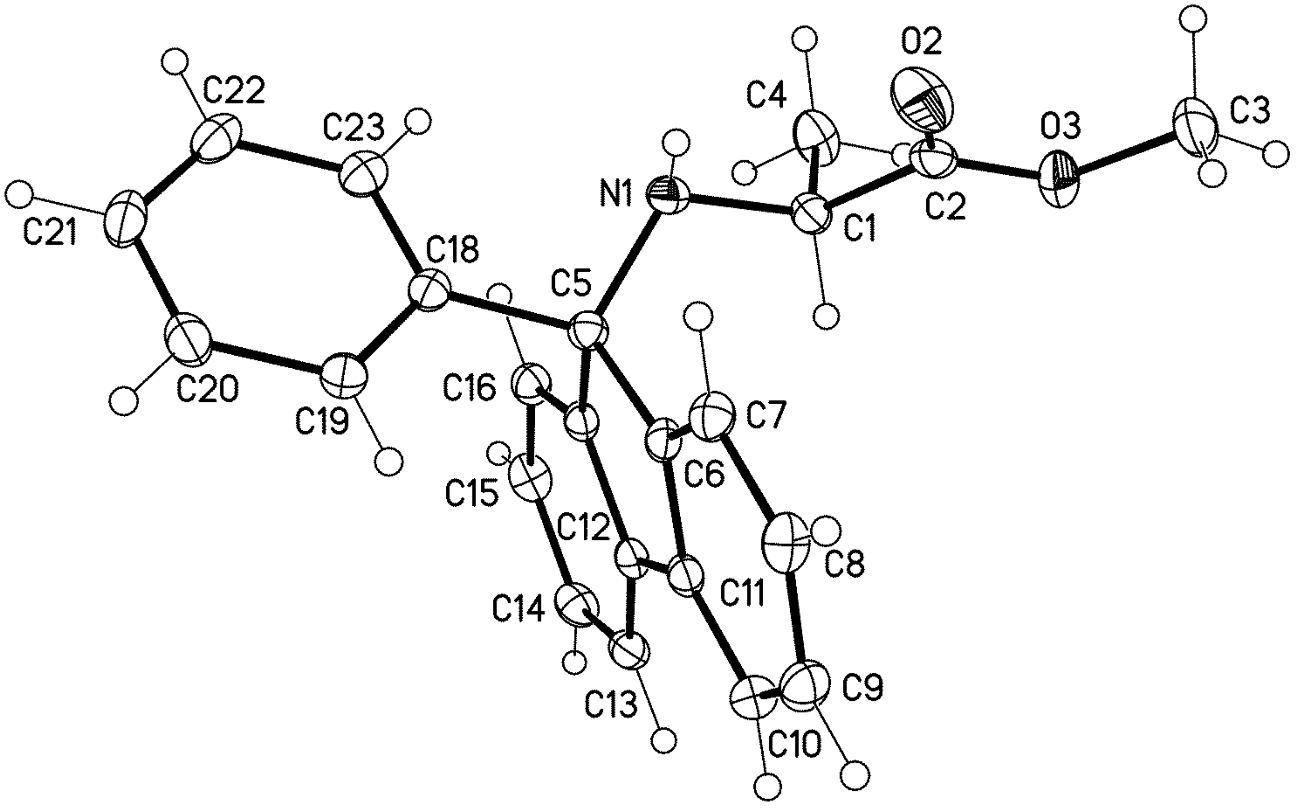


Fig. S2-Xray. Molecular structure of **10a** (displacement parameters are drawn at 50% probability level).

Crystal structure compound: 11a

Crystals where obtained by vapor diffusion using a binary solvent system EtOAc/Hexane.

11a: colourless crystals, $C_{23}H_{24}N_2O_2$, M = 372.45, crystal size 0.60 x 0.30 x 0.10 mm, T = 123(2) K, orthorhombic, space group $P2_12_12_1$ (No.19), a = 10.274(1) Å, b = 13.700(1) Å, c = 14.397(1) Å, V = 2026.4(3) $Å^3$, Z = 4, ρ(calc) = 1.221 Mg m^{-3}, F(000) = 792, μ = 0.078 mm^{-1}, 23936 reflections ($2\theta_{max}$ = 55°), 4643 unique [R_{int} = 0.035], 258 parameters, 1 restraint, $R1$ (for 4218 $I > 2\sigma(I)$) = 0.037, *wR2 (all data)* = 0.085, S = 1.09, largest diff. peak and hole 0.267 and -0.204 e $Å^{-3}$, Flack's x = -0.2(10), y = 0.1(5).

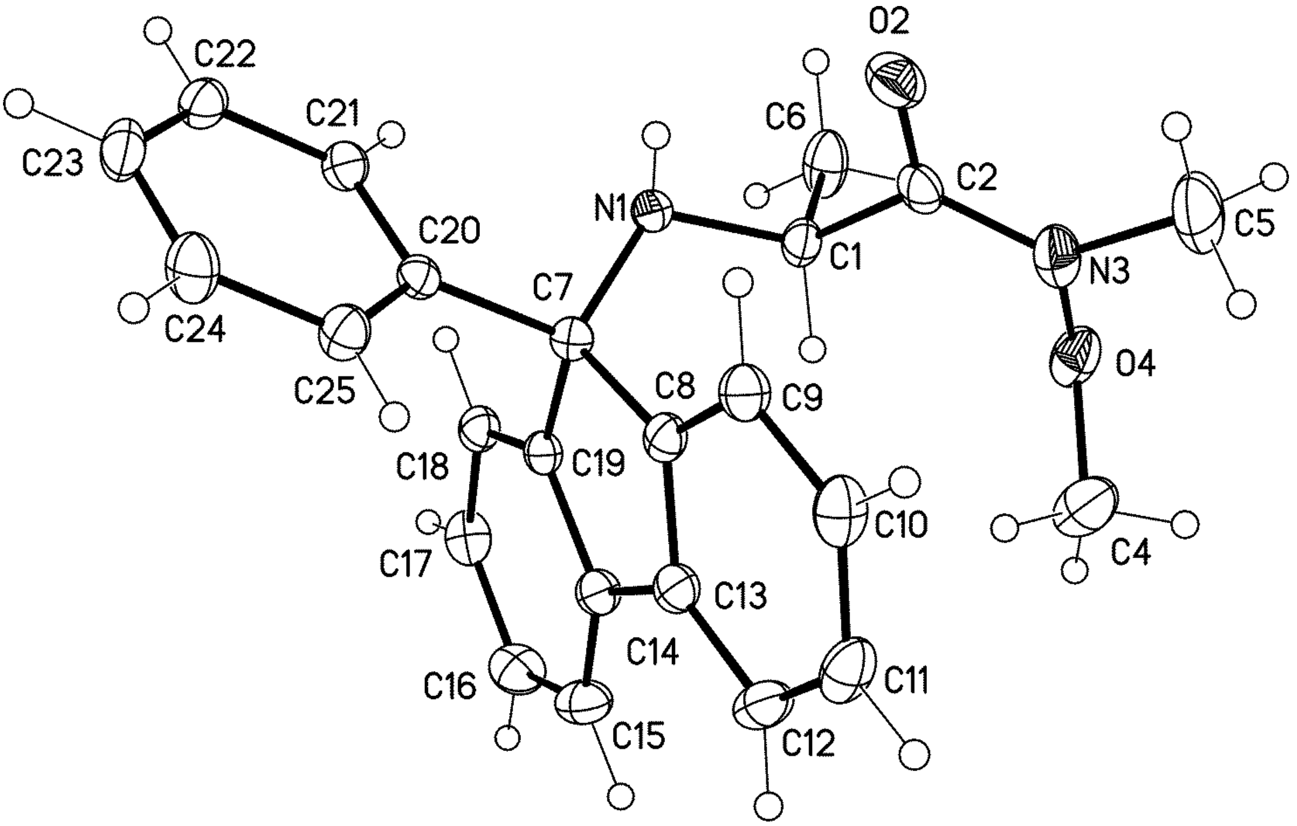


Fig. S3-Xray. Molecular structure of **11a** (displacement parameters are drawn at 50% probability level).

Crystal structure compound: 23

Four crystalographically independent molecules (2 acids, 2 betaine form, see Fig. S5-8). Clathrate with EtOAc.

Crystals where obtained by vapor diffusion using a binary solvent system EtOAc/Hexane.

23: colourless crystals, $C_{35}H_{28}NO_2$ – ¼ ($C_4H_8O_2$), *M* = 351.41, crystal size 0.30 x 0.20 x 0.15 mm, *T* = 123(2) K, triclinic, space group P1 (No. 1), *a* = 11.326(2) Å, *b* = 12.672(2) Å, *c* = 13.312(3) Å, *α* = 83.08(2)°, *β* = 89.82(2)°, *γ* = 79.33(2)°, *V* = 1863.5(6) Å^3, *Z* = 4, *ρ*(calc) = 1.253 Mg m^{-3}, *F*(000) = 744, *μ* = 0.081 mm^{-1}, 18930 reflections ($2\theta_{max}$ = 50°), 12061 unique [R_{int} = 0.041], 950 parameters, 11 restraints, *R*1 (for 9114 *I* > 2σ(*I*)) = 0.067, *wR2 (all data)* = 0.173, S = 1.02, largest diff. peak and hole 0.619 and -0.542 e Å^{-3} (in clathrat EtOAc), Parsons x = 0.1(10), y = 0.4(10).

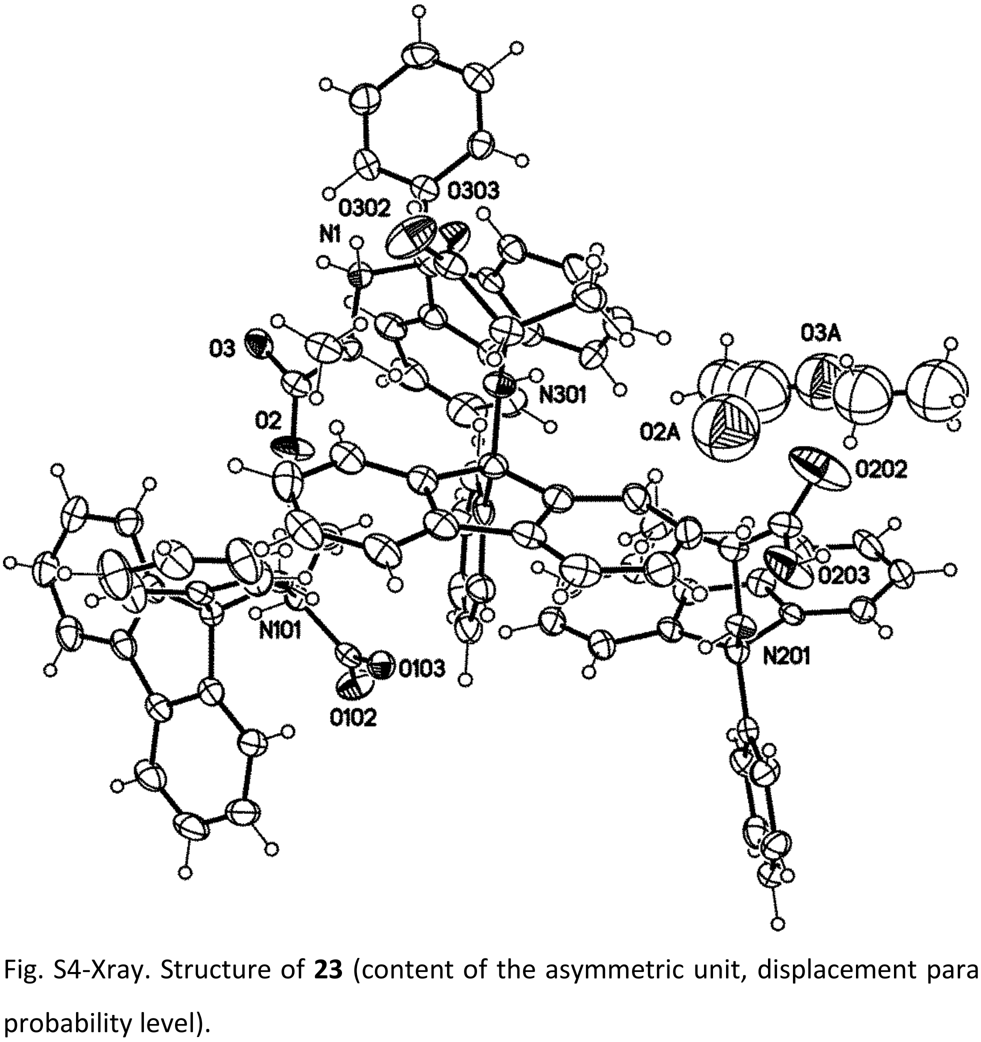


Fig. S4-Xray. Structure of **23** (content of the asymmetric unit, displacement parameters are drawn at 50% probability level).

Structure 1

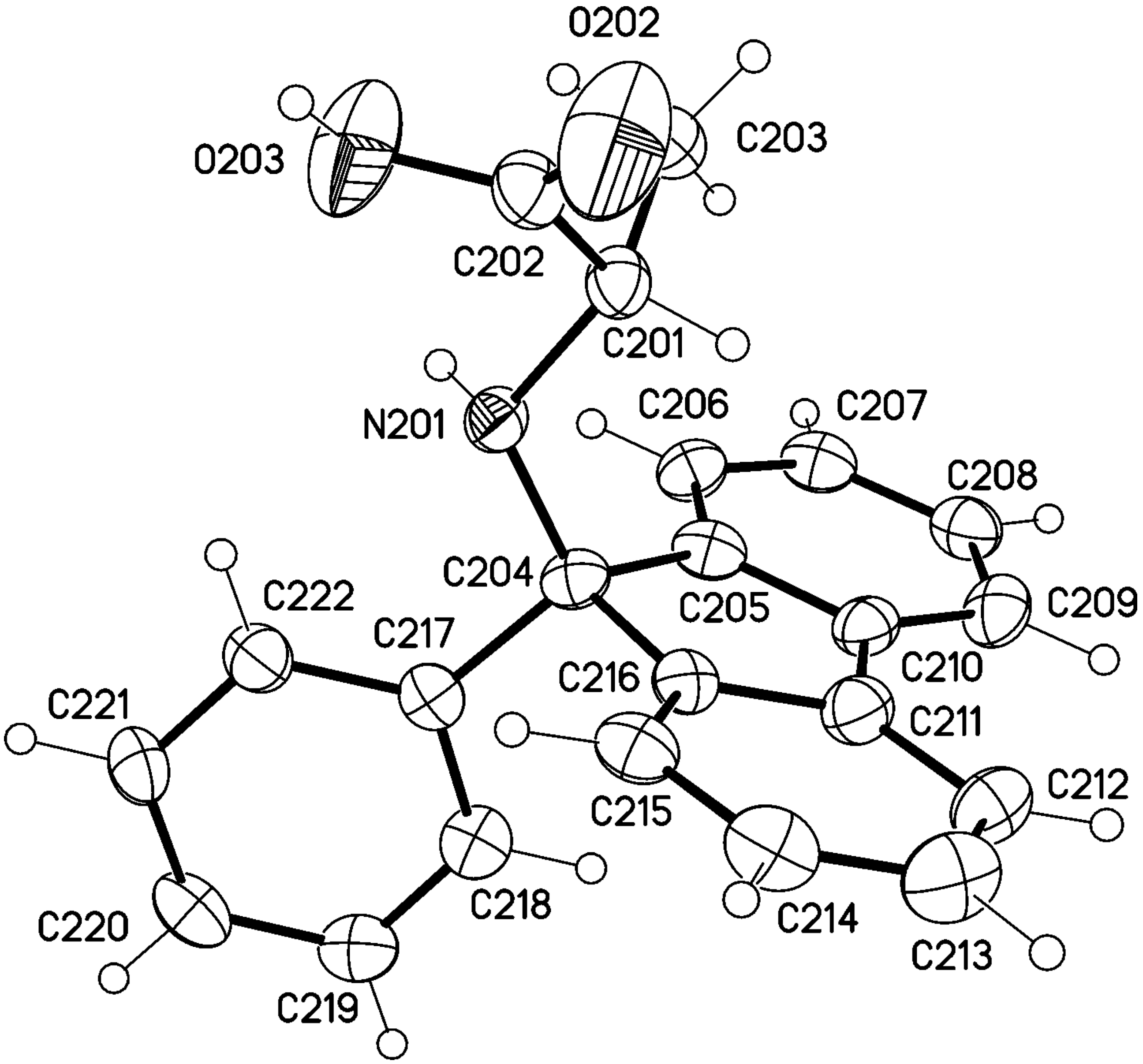


Fig. S5-Xray. Structure 1 of **23** (displacement parameters are drawn at 50% probability level).

Structure 2

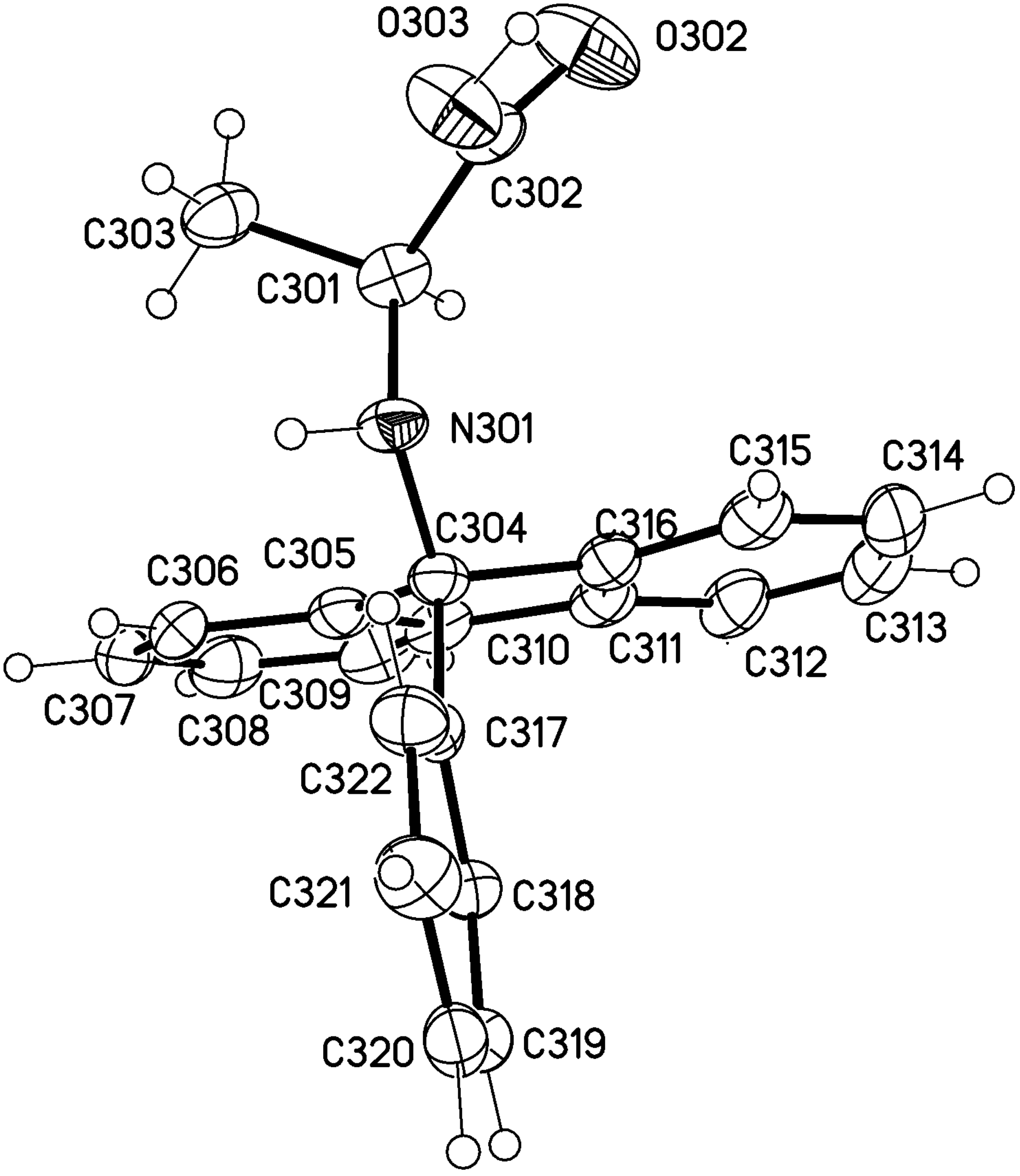


Fig. S6-Xray. Structure 2 of **23** (displacement parameters are drawn at 50% probability level).

Structure 3

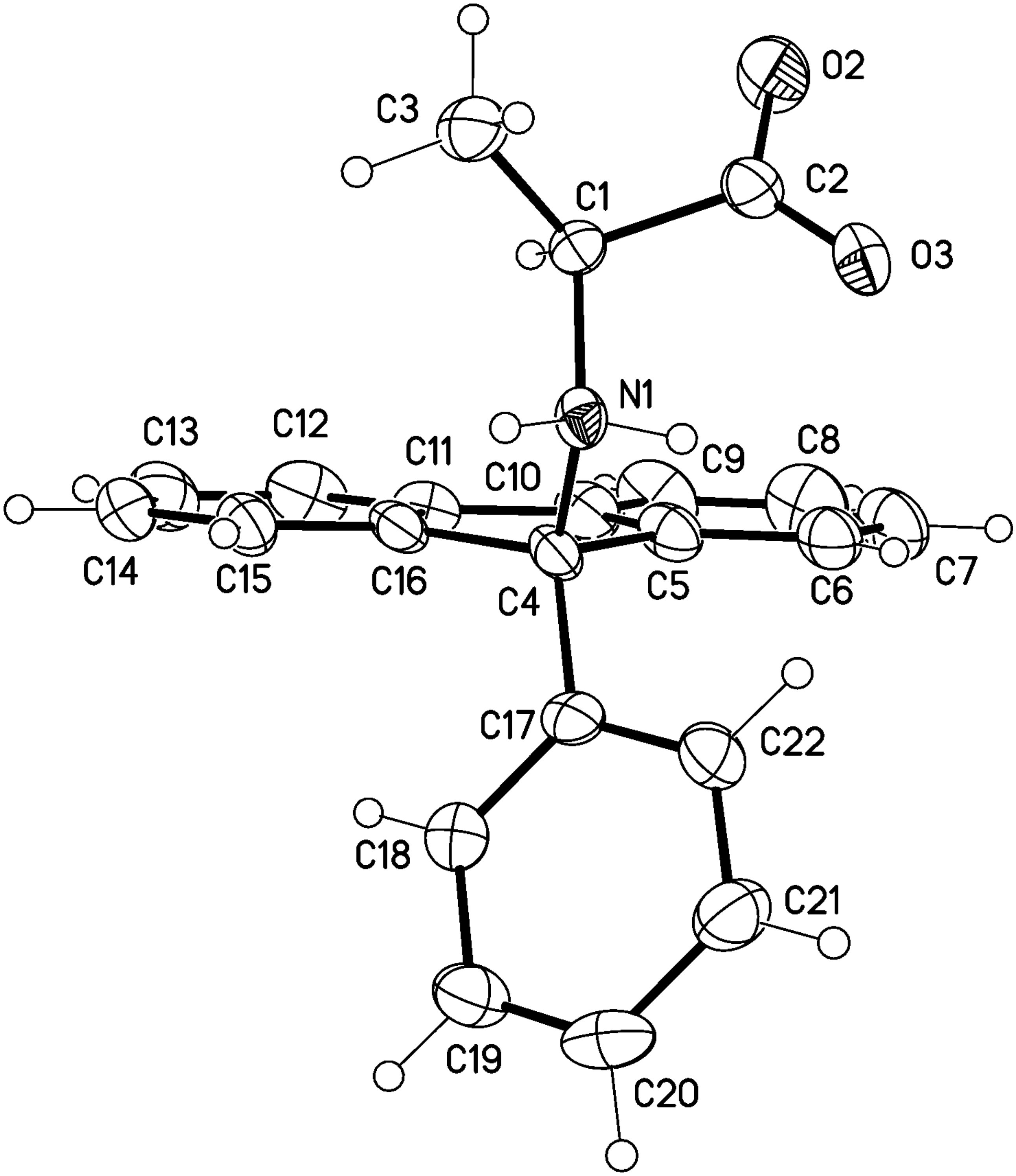


Fig. S7-Xray. Structure 3 of **23** (displacement parameters are drawn at 50% probability level).

Structure 4

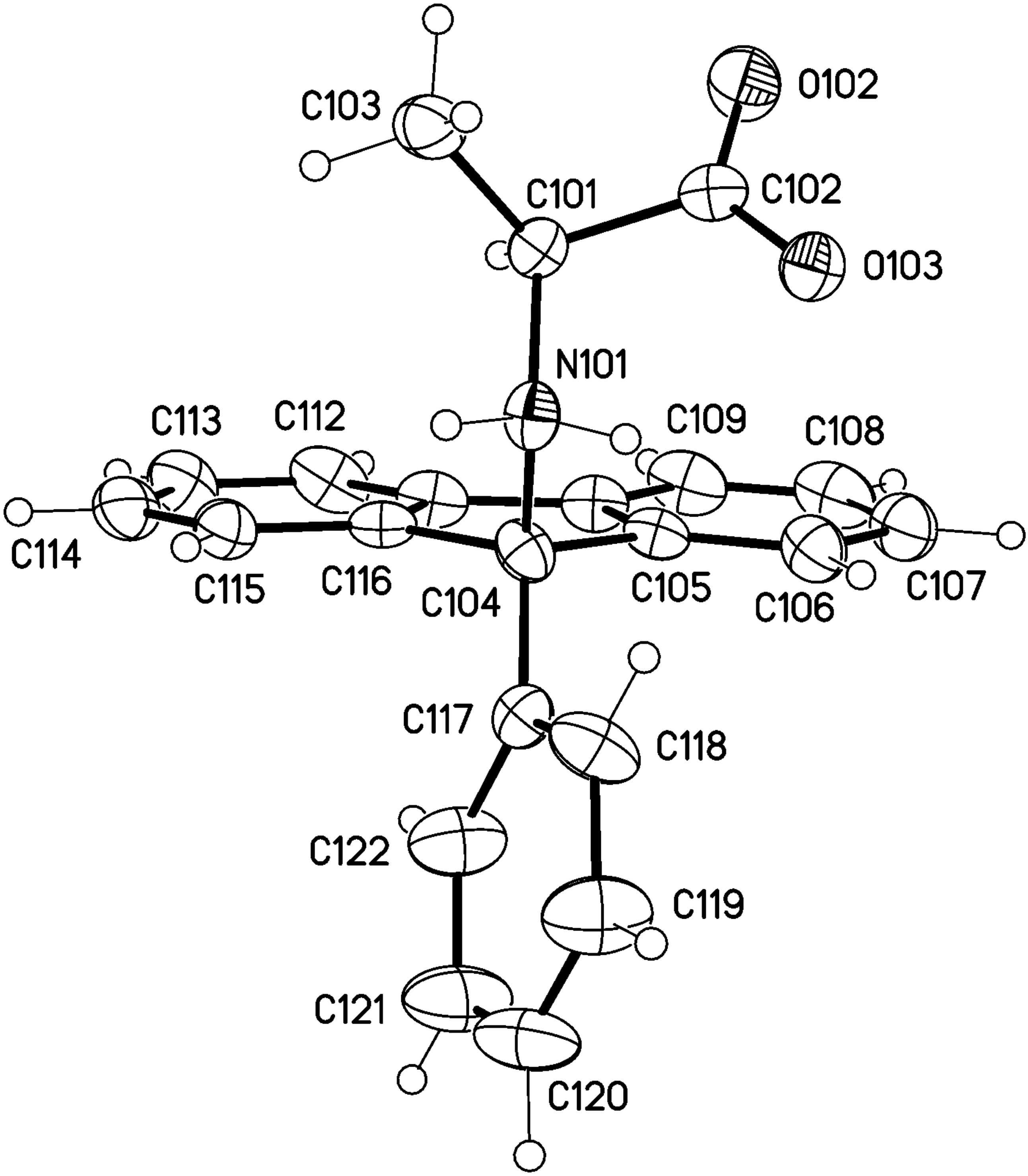


Fig. S8-Xray. Structure 4 of **23** (displacement parameters are drawn at 50% probability level).

Crystal structure compound: 24

Crystals where obtained by evaporation of a solution of **24** in hexane/EtOAc (9:1).

24: colourless crystals, $C_{23}H_{21}NO$, *M* = 327.41, crystal size 0.28 x 0.24 x 0.08 mm, *T* = 123(2) K, orthorhombic, space group $P2_12_12_1$ (No.19), *a* = 8.3323(2) Å, *b* = 13.3896(4) Å, *c* = 15.6658(4) Å, *V* = 1747.77(8) Å^3, *Z* = 4, *ρ*(calc) = 1.244 Mg m^{-3}, *F*(000) = 696, *μ* = 0.586 mm^{-1}, 10908 reflections ($2\theta_{max}$ = 140°), 3274 unique [R_{int} = 0.023], 230 parameters, 1 restraint, *R*1 (for 3141 *I* > 2σ(*I*)) = 0.027, *wR2 (all data)* = 0.067, S = 1.06, largest diff. peak and hole 0.122 and -0.123 e Å^{-3}, Parsons x = -0.08(9), y = -0.07(10).

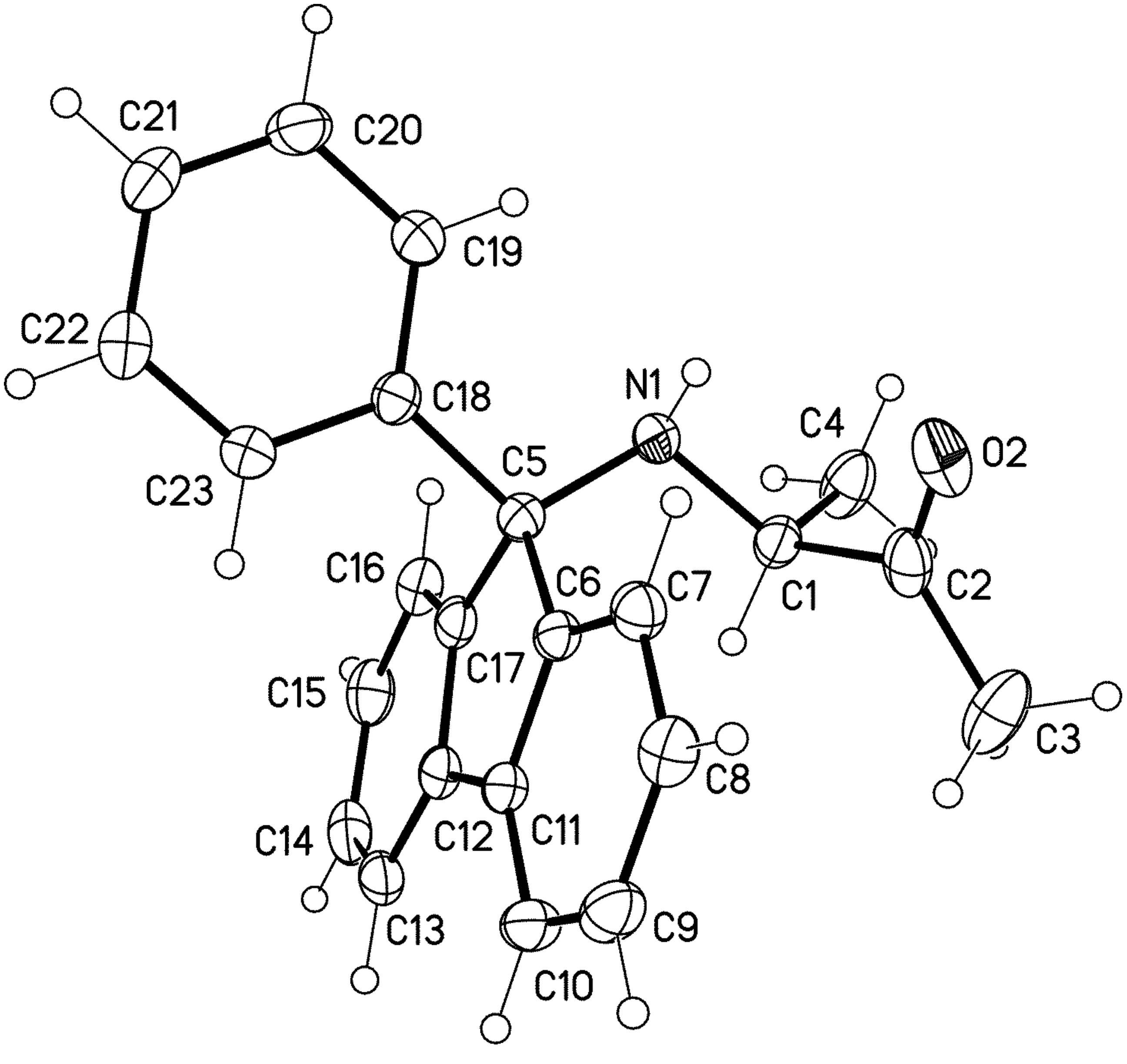


Fig. S9-Xray. Molecular structure of **24** (displacement parameters are drawn at 50% probability level).

Crystal structure compound: 10b

Crystals where obtained by vapor diffusion using a binary solvent system EtOAc/Hexane.

10b: colourless crystals, $C_{29}H_{25}NO_2$, M = 419.50, crystal size 0.50 x 0.30 x 0.20 mm, T = 123(2) K, orthorhombic, space group $P2_12_12_1$ (No.19), a = 7.850(1) Å, b = 15.332(2) Å, c = 18.525(2) Å, V = 2196.7(5) Å^3, Z = 4, ρ(calc) = 1.268 Mg m^{-3}, F(000) = 888, μ = 0.079 mm^{-1}, 39952 reflections ($2\theta_{max}$ = 55°), 5049 unique [R_{int} = 0.038], 293 parameters, 1 restraint, $R1$ (for 4787 $I > 2\sigma(I)$) = 0.030, *wR2 (all data)* = 0.074, S = 1.07, largest diff. peak and hole 0.239 and -0.218 e Å^{-3}, Parsons x = 0.5(3), y = 0.6(3).

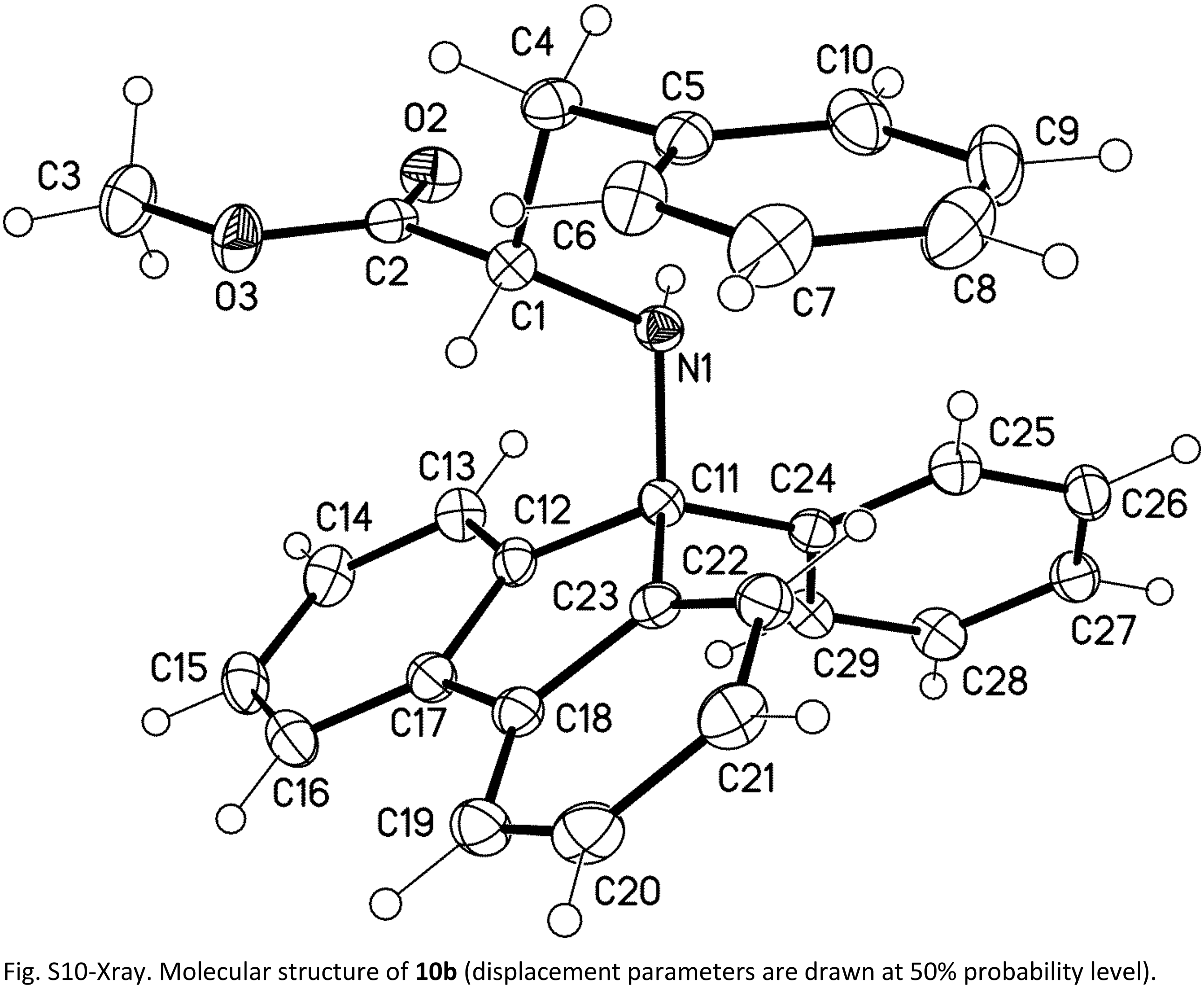


Fig. S10-Xray. Molecular structure of **10b** (displacement parameters are drawn at 50% probability level).

Crystal structure compound: 11b

Two crystalographically independent molecules.

Crystals where obtained by vapor diffusion using a binary solvent system EtOAc/Hexane.

11b: colourless crystals, $C_{30}H_{28}N_2O_2$, M = 448.54, crystal size 0.50 x 0.30 x 0.20 mm, T = 123(2) K, monoclinic, space group $P2_1$ (No. 4), a = 10.964(2) Å, b = 14.605(1) Å, c = 15.874(2) Å, β = 103.65(2)°, V = 2470.1(6) $Å^3$, Z = 4, ρ(calc) = 1.206 Mg m^{-3}, F(000) = 952, μ = 0.076 mm^{-1}, 28363 reflections ($2\theta_{max}$ = 55°), 11178 unique [R_{int} = 0.026], 623 parameters, 3 restraints, $R1$ (for 9839 $I > 2\sigma(I)$) = 0.035, *wR2 (all data)* = 0.079, S = 1.03, largest diff. peak and hole 0.217 and -0.191 e $Å^{-3}$, Parsons x = -0.4(3), y = -0.4(3).

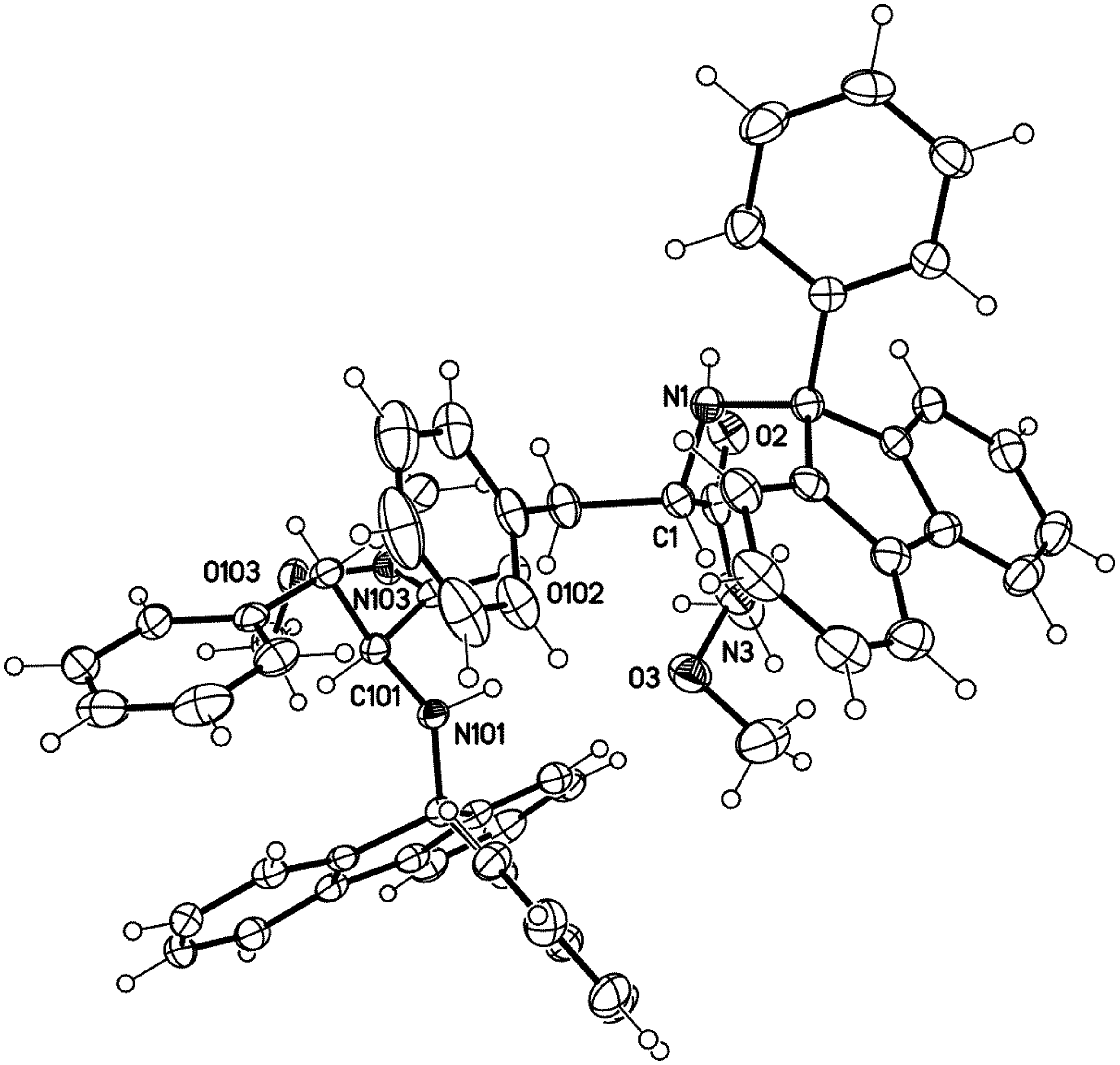


Fig. S11-Xray. Molecular structure of **11b** (both crystallographic independent molecules, displacement parameters are drawn at 50% probability level).

Structure 1

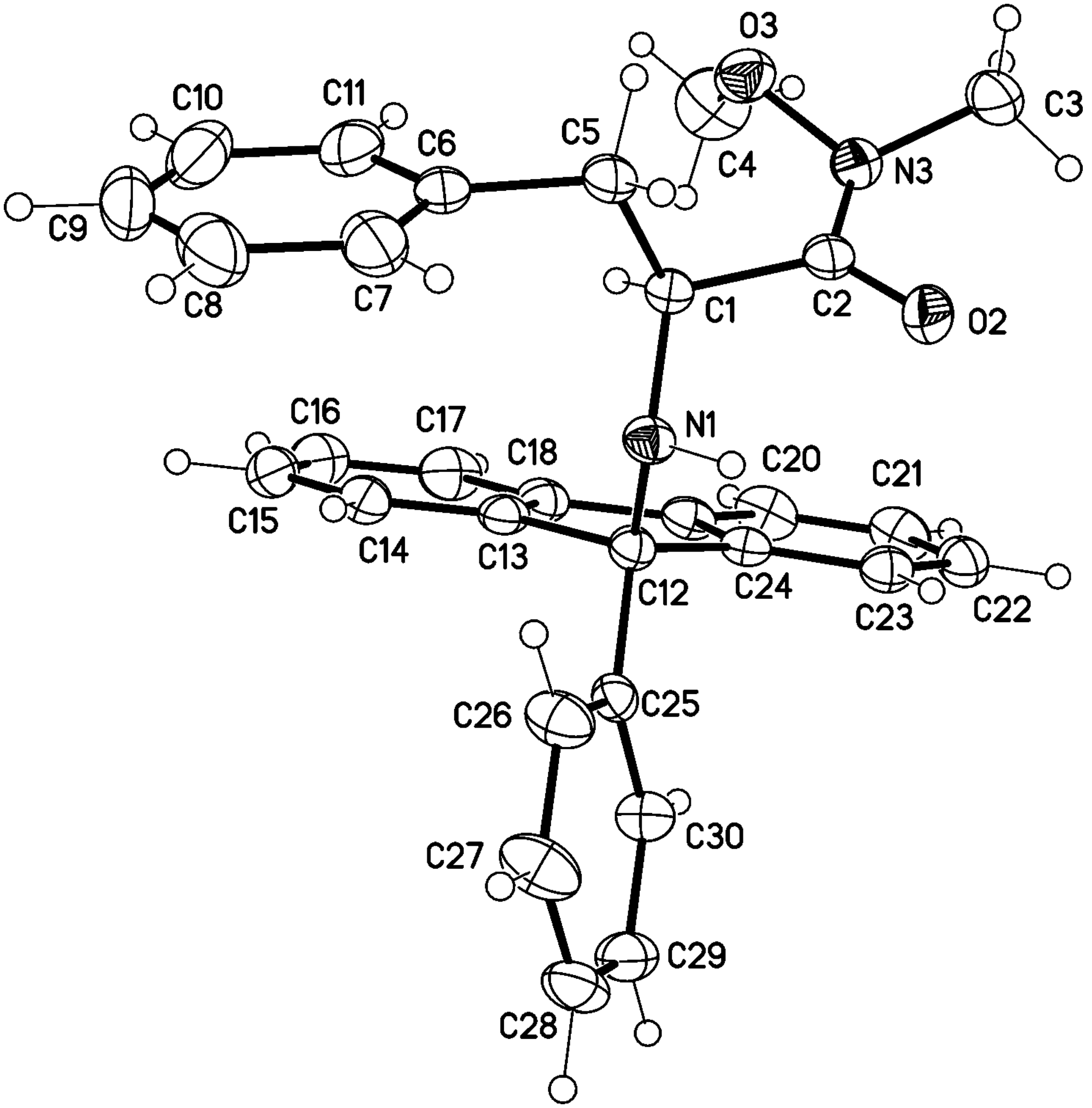


Fig. S12-Xray. Molecule 1 of **11b** (displacement parameters are drawn at 50% probability level).

Structure 2

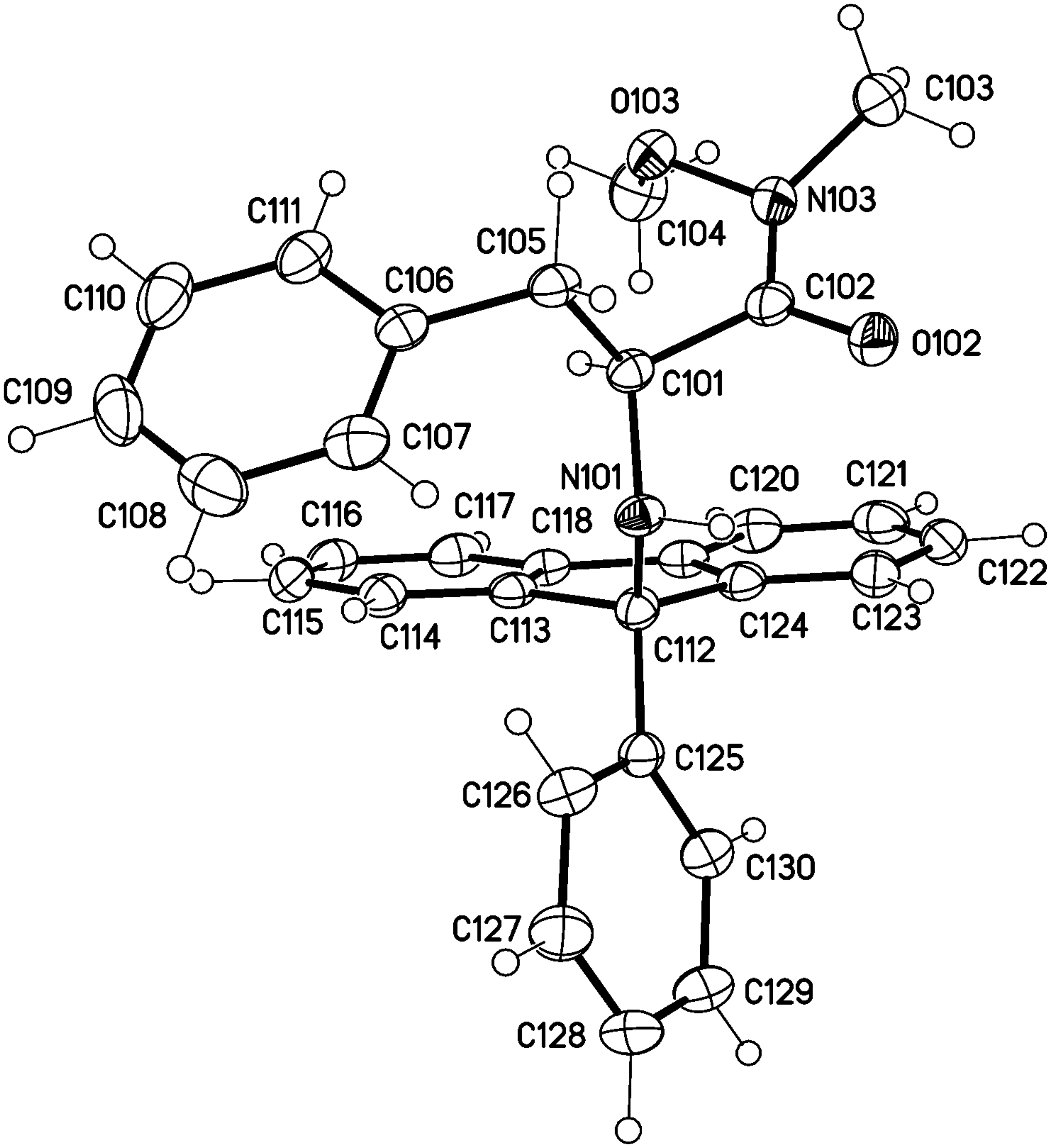


Fig. S13-Xray. Molecule 2 of **11b** (displacement parameters are drawn at 50% probability level).

Crystal structure compound: 10d

Crystals where obtained by vapor diffusion using a binary solvent system EtOAc/Hexane.

10d: colourless crystals, $C_{25}H_{23}NO_2$, M = 369.44, crystal size 0.60 x 0.50 x 0.40 mm, T = 123(2) K, orthorhombic, space group $P2_12_12_1$ (No.19), a = 9.401(1) Å, b = 12.101(2) Å, c = 17.148(3) Å, V = 1950.8(5) Å^3, Z = 4, ρ(calc) = 1.258 Mg m^{-3}, F(000) = 784, μ = 0.079 mm^{-1}, 24656 reflections ($2\theta_{max}$ = 55°), 4465 unique [R_{int} = 0.020], 254 parameters, $R1$ (for 4219 $I > 2\sigma(I)$) = 0.030, *wR2 (all data)* = 0.075, S = 1.06, largest diff. peak and hole 0.224 and -0.150 e Å^{-3}, Parsons x = -0.2(2), y = -0.2(2).

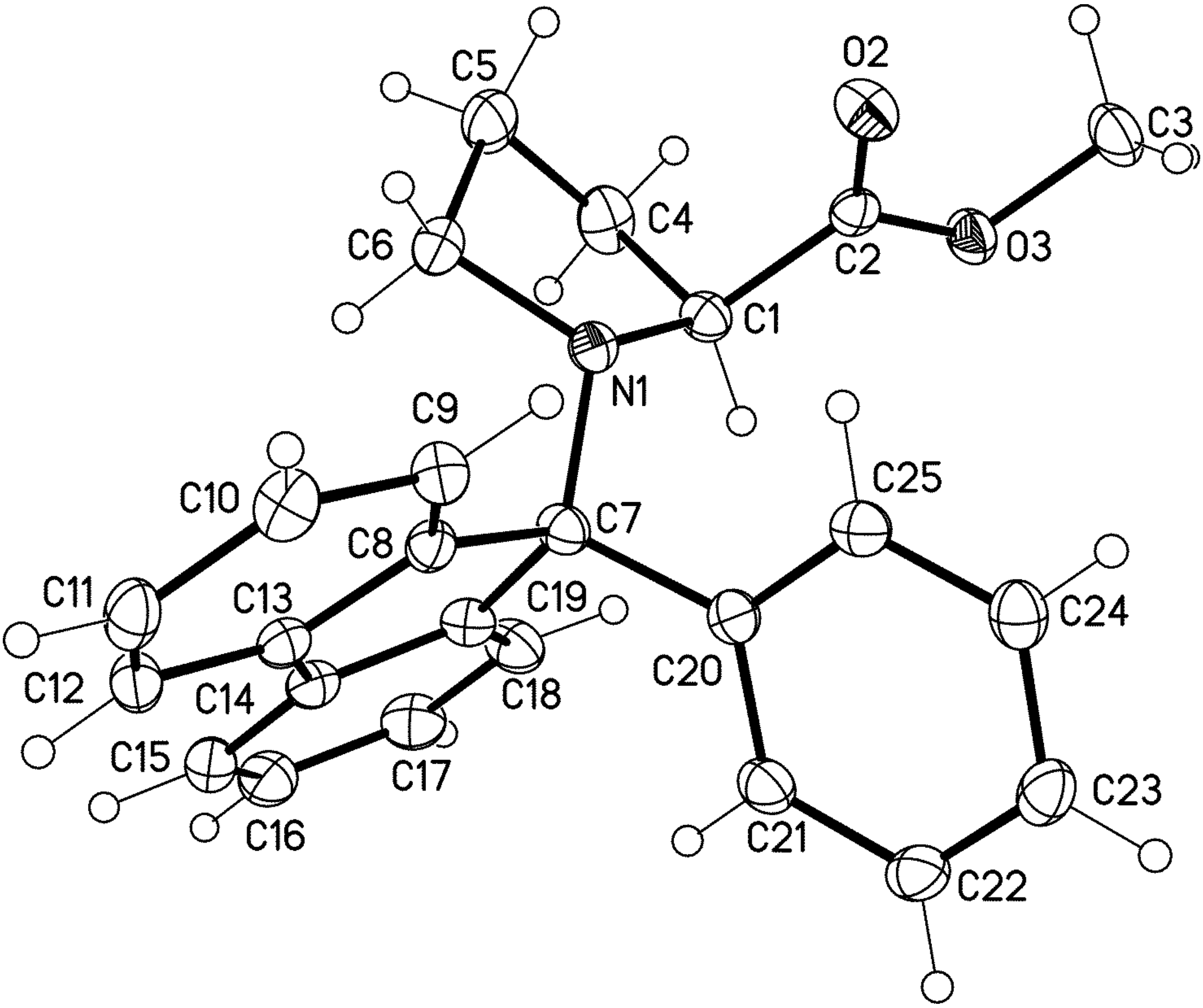


Fig. S14-Xray. Molecular structure of **10d** (displacement parameters are drawn at 50% probability level).

Crystal structure compound: 11d

Crystals where obtained by vapor diffusion using a binary solvent system EtOAc/Hexane.

11d: colourless crystals, $C_{26}H_{26}N_2O_2$, M = 398.49, crystal size 0.50 x 0.30 x 0.12 mm, T = 123(2) K, orthorhombic, space group $P2_12_12_1$ (No.19), a = 10.165(2) Å, b = 13.758(2) Å, c = 14.815(1) Å, V = 2071.9(5) Å^3, Z = 4, ρ(calc) = 1.277 Mg m^{-3}, F(000) = 848, μ = 0.081 mm^{-1}, 25754 reflections ($2\theta_{max}$ = 55°), 4761 unique [R_{int} = 0.031], 273 parameters, $R1$ (for 4255 $I > 2\sigma(I)$) = 0.037, *wR2 (all data)* = 0.083, S = 1.07, largest diff. peak and hole 0.223 and -0.165 e Å^{-3}, Parsons x = -0.3(3), y = 0.1(4).

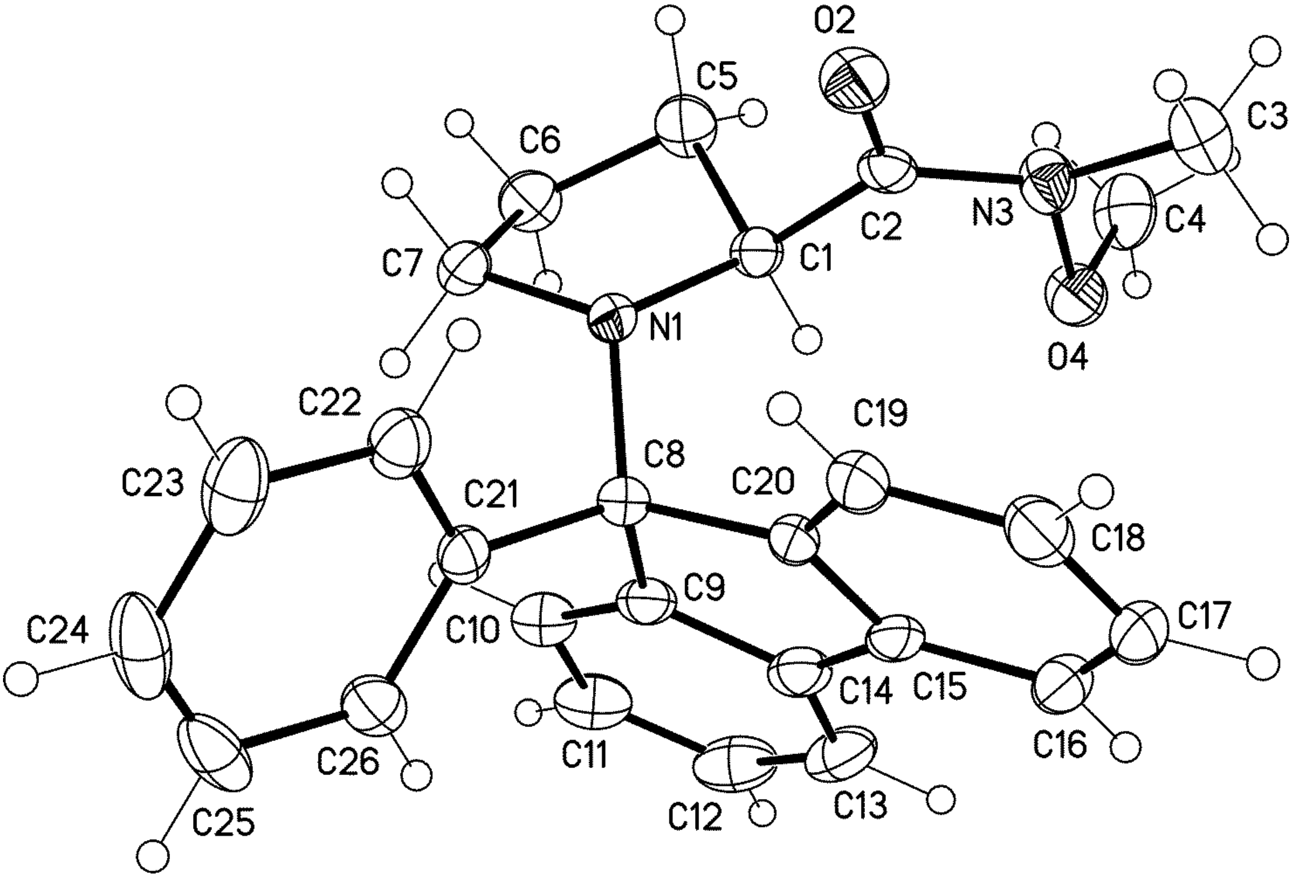


Fig. S15-Xray. Molecular structure of **11d** (displacement parameters are drawn at 50% probability level).

General information regarding HPLC data collection

The data was collected using a Waters M-45 pump connected to a Waters 2487 Dual λ absorbance detector. The detector was run in dual wavelength mode. Solvents used were of HPLC grade and filtered through a Millipore filter (45 μm) prior to use. The sample preparation consisted of dissolving approximately 1 mg of analyte in 2 mL of the designated eluent and filtering the sample through a Millipore filter (45 μm). Columns used were purchased from Daicel (Chiral Technologies Europe). All analysis was done under isocratic eluent conditions. The eluent flow was set to 1 mL/min. The samples were injected manually with a Rheodyne injector equipped with a 10 μL sample loop. The compounds below described as racemic (labeled with the prefix (*Rac*)) are in fact scalemic mixtures of pure enantiomers prepared from both the L and the D enantiomer of the corresponding amino acid, hence the integration of these mixtures do not give rise to a perfect 1:1 ratio of the two enantiomers.

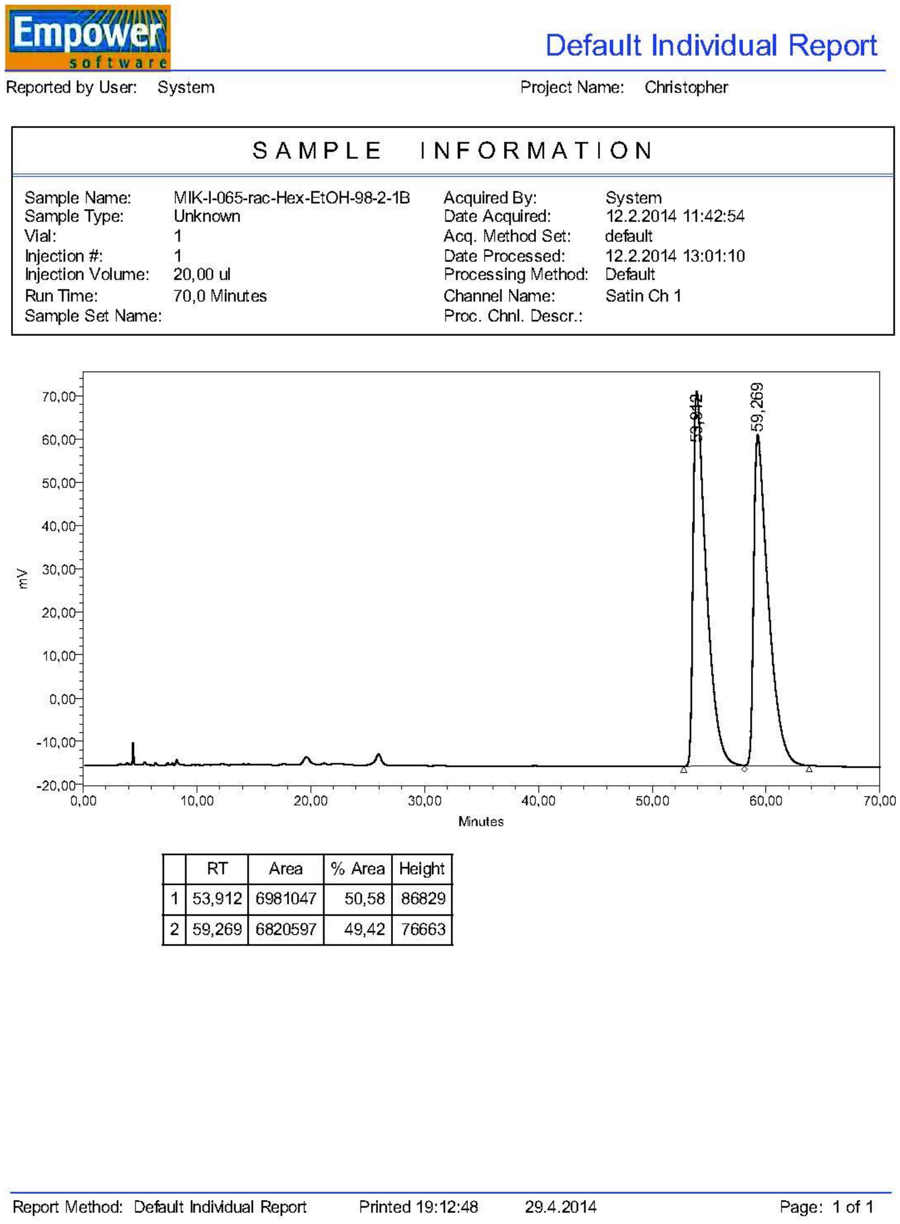
HPLC: (*Rac*)-25a

Column: Chiralpak IB; Dimensions: 250 x 4.6 mm; Particle size: 5 µm

Eluent: Hex: EtOH; 98:2 (isocratic conditions)

Detector: λ = 254 nm

Retention times: (*S*)-**25a** = 53.9 min; (*R*)-**25a** = 59.3 min



Default Individual Report

Reported by User: System
Project Name: Christopher

SAMPLE INFORMATION

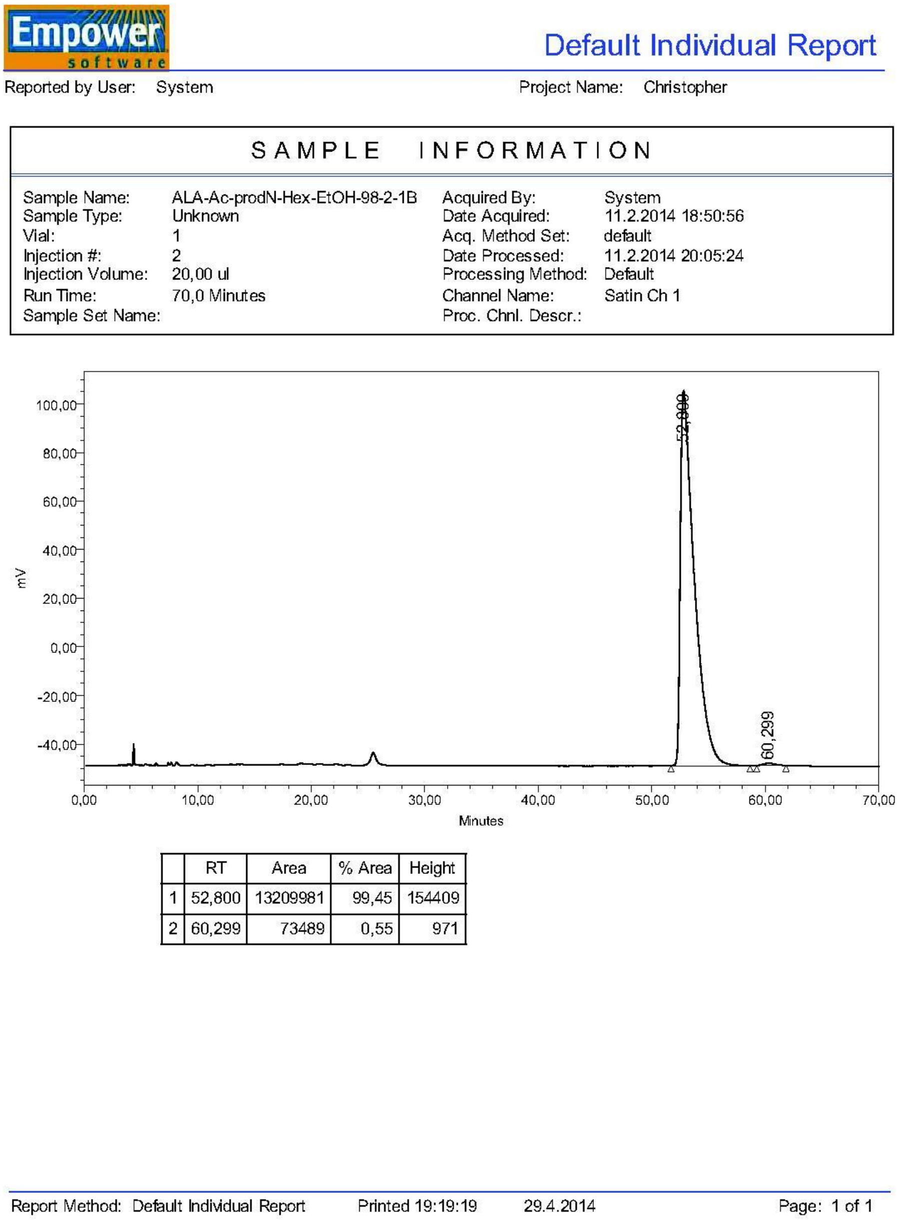
Sample Name:	MIK-I-065-rac-Hex-EtOH-98-2-1B	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	12.2.2014 11:42:54
Vial:	1	Acq. Method Set:	default
Injection #:	1	Date Processed:	12.2.2014 13:01:10
Injection Volume:	20,00 ul	Processing Method:	Default
Run Time:	70,0 Minutes	Channel Name:	Satin Ch 1
Sample Set Name:		Proc. Chnl. Descr.:	

	RT	Area	% Area	Height
1	53,912	6981047	50,58	86829
2	59,269	6820597	49,42	76663

Report Method: Default Individual Report Printed 19:12:48 29.4.2014 Page: 1 of 1

HPLC: (*S*)-25a

ee = 99%



Default Individual Report

Reported by User: System
Project Name: Christopher

SAMPLE INFORMATION

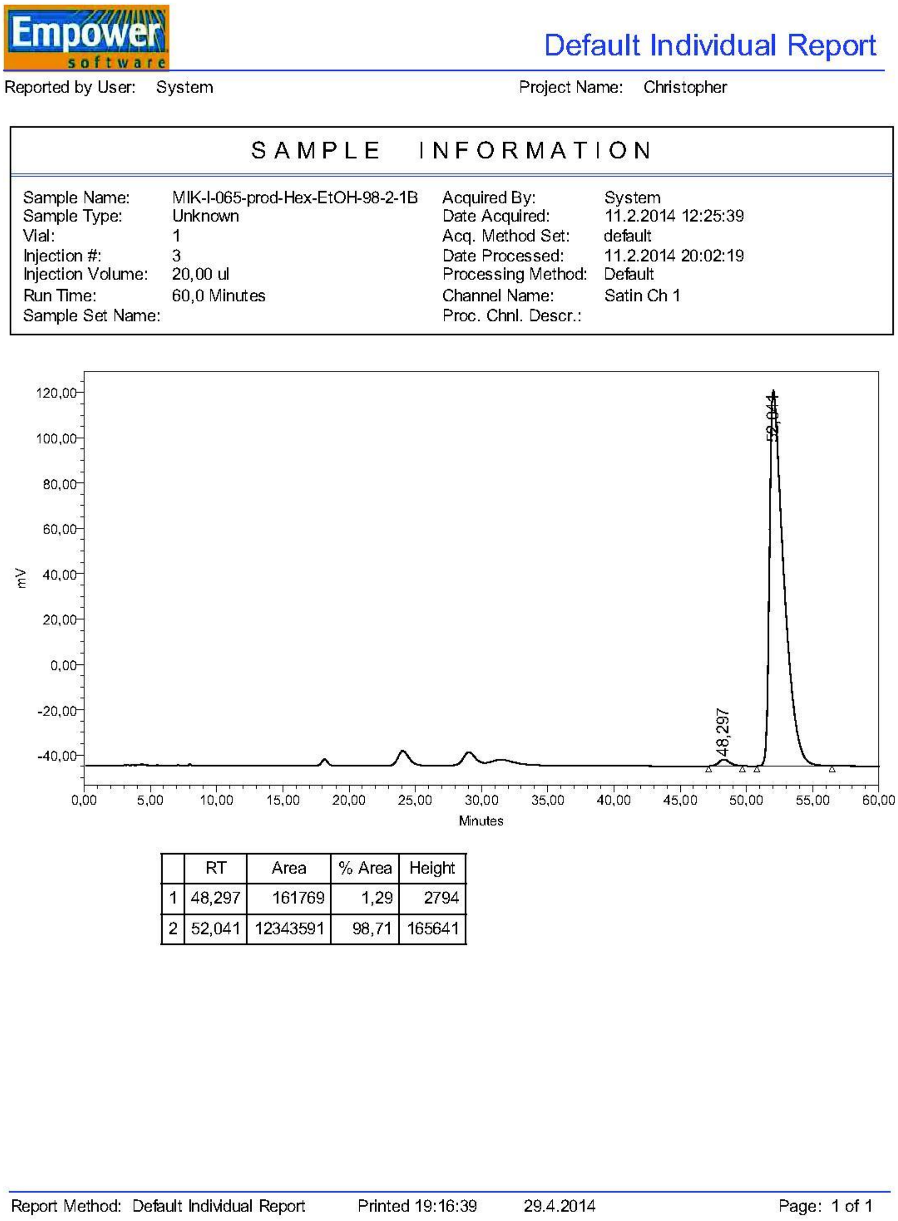
Sample Name: ALA-Ac-prodN-Hex-EtOH-98-2-1B
Sample Type: Unknown
Vial: 1
Injection #: 2
Injection Volume: 20,00 ul
Run Time: 70,0 Minutes
Sample Set Name:
Acquired By: System
Date Acquired: 11.2.2014 18:50:56
Acq. Method Set: default
Date Processed: 11.2.2014 20:05:24
Processing Method: Default
Channel Name: Satin Ch 1
Proc. Chnl. Descr.:

	RT	Area	% Area	Height
1	52,800	13209981	99,45	154409
2	60,299	73489	0,55	971

Report Method: Default Individual Report Printed 19:19:19 29.4.2014 Page: 1 of 1

HPLC: (*R*)-25a

ee = 97%



Default Individual Report

Reported by User: System

Project Name: Christopher

SAMPLE INFORMATION

Sample Name:	MIK-I-065-prod-Hex-EtOH-98-2-1B	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	11.2.2014 12:25:39
Vial:	1	Acq. Method Set:	default
Injection #:	3	Date Processed:	11.2.2014 20:02:19
Injection Volume:	20,00 ul	Processing Method:	Default
Run Time:	60,0 Minutes	Channel Name:	Satin Ch 1
Sample Set Name:		Proc. Chnl. Descr.:	

	RT	Area	% Area	Height
1	48,297	161769	1,29	2794
2	52,041	12343591	98,71	165641

Report Method: Default Individual Report Printed 19:16:39 29.4.2014 Page: 1 of 1

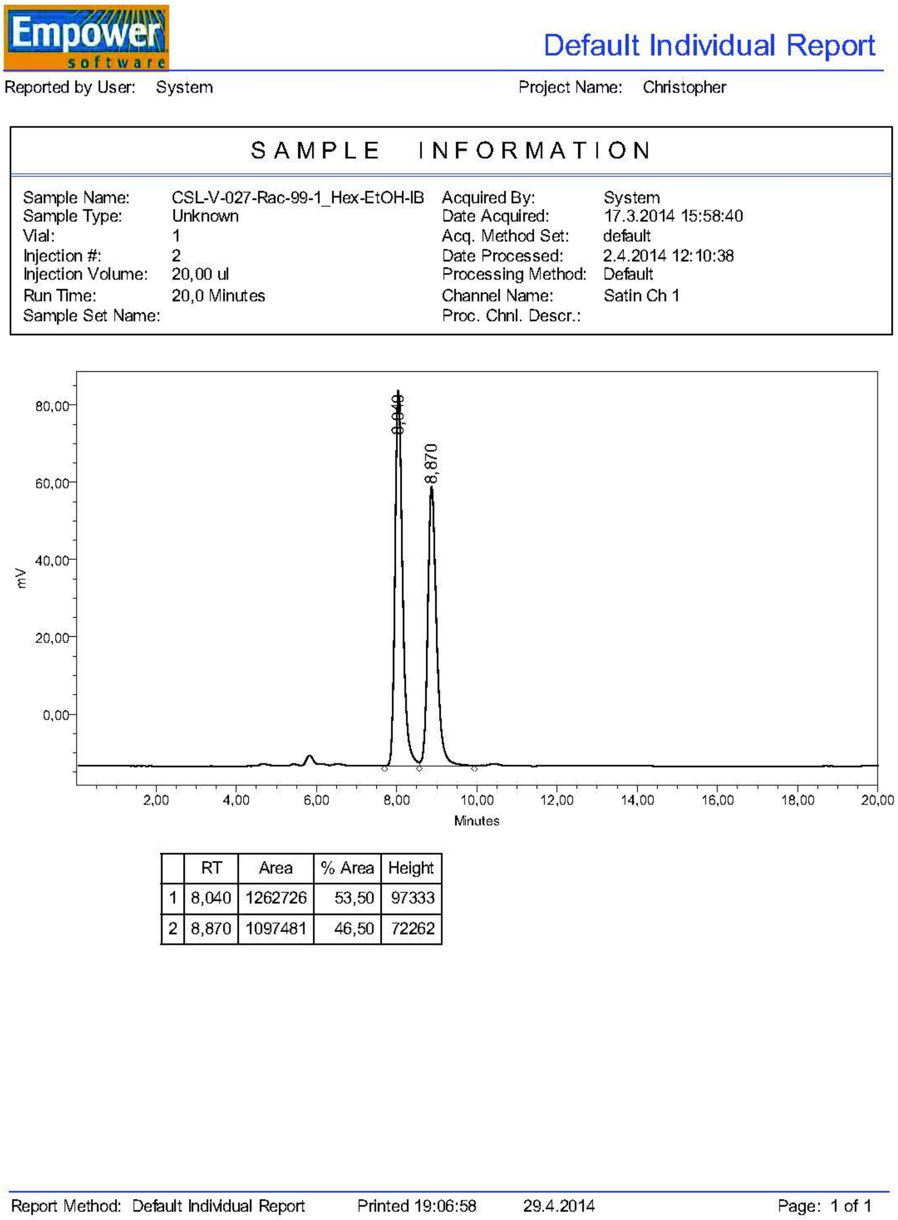
HPLC: (*Rac*)-13b

Column: Chiralpak IB; Dimensions: 250 x 4.6 mm; Particle size: 5 µm

Eluent: Hex:EtOH; 99:1 (isocratic conditions)

Detector: λ = 254 nm

Retention times: (*R*)-**13b** = 8.0 min; (*S*)-**13b** = 8.9 min



Empower software

Default Individual Report

Reported by User: System   Project Name: Christopher

SAMPLE INFORMATION

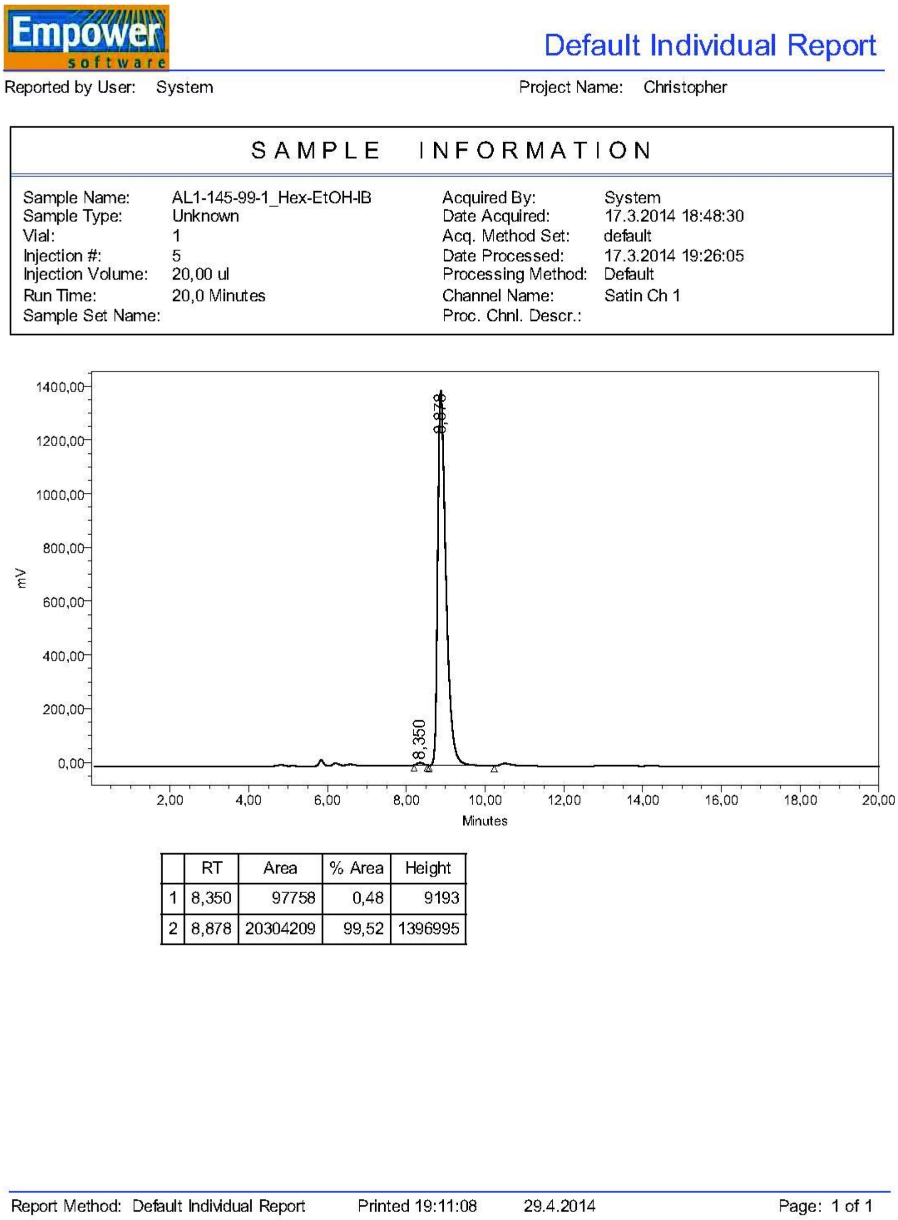
Sample Name:	CSL-V-027-Rac-99-1_Hex-EtOH-IB	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	17.3.2014 15:58:40
Vial:	1	Acq. Method Set:	default
Injection #:	2	Date Processed:	2.4.2014 12:10:38
Injection Volume:	20,00 ul	Processing Method:	Default
Run Time:	20,0 Minutes	Channel Name:	Satin Ch 1
Sample Set Name:		Proc. Chnl. Descr.:	

	RT	Area	% Area	Height
1	8,040	1262726	53,50	97333
2	8,870	1097481	46,50	72262

Report Method: Default Individual Report   Printed 19:06:58   29.4.2014   Page: 1 of 1

HPLC: (*S*)-13b

ee = 99%



Empower software

Default Individual Report

Reported by User: System

Project Name: Christopher

SAMPLE INFORMATION

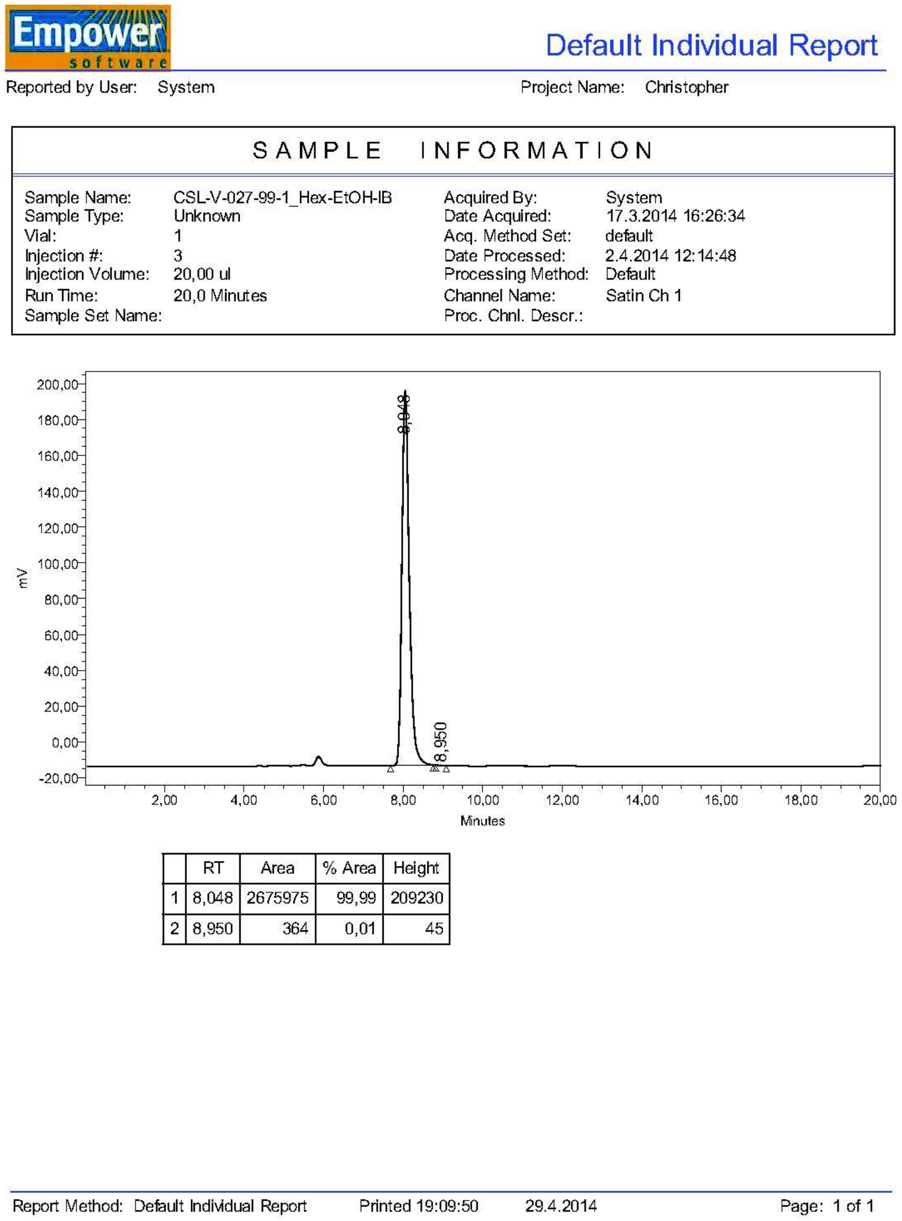
Sample Name:	AL1-145-99-1_Hex-EtOH-IB	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	17.3.2014 18:48:30
Vial:	1	Acq. Method Set:	default
Injection #:	5	Date Processed:	17.3.2014 19:26:05
Injection Volume:	20,00 ul	Processing Method:	Default
Run Time:	20,0 Minutes	Channel Name:	Satin Ch 1
Sample Set Name:		Proc. Chnl. Descr.:	

	RT	Area	% Area	Height
1	8,350	97758	0,48	9193
2	8,878	20304209	99,52	1396995

Report Method: Default Individual Report Printed 19:11:08 29.4.2014 Page: 1 of 1

HPLC: (*R*)-13b

ee = > 99%



Default Individual Report

Reported by User: System

Project Name: Christopher

SAMPLE INFORMATION

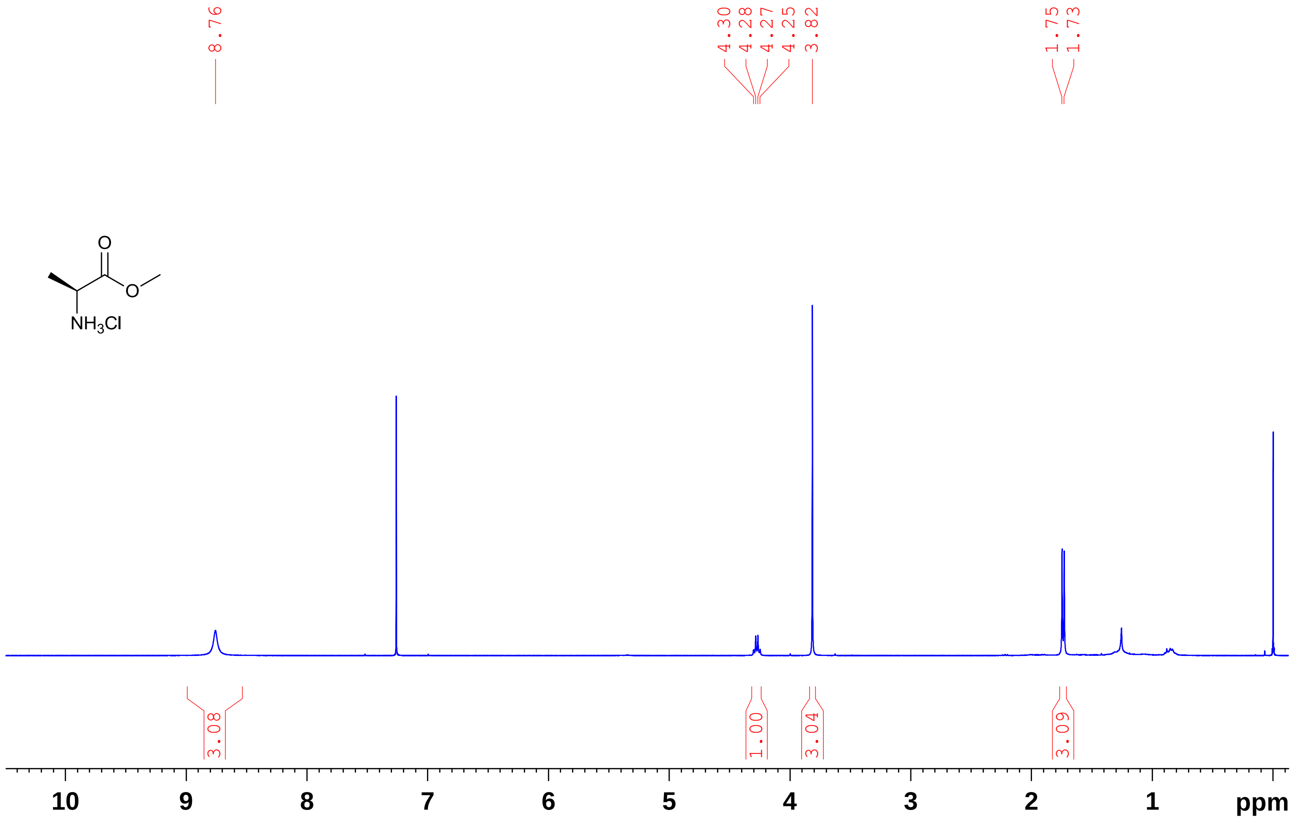
Sample Name: CSL-V-027-99-1_Hex-EtOH-IB
Sample Type: Unknown
Vial: 1
Injection #: 3
Injection Volume: 20,00 ul
Run Time: 20,0 Minutes
Sample Set Name:

Acquired By: System
Date Acquired: 17.3.2014 16:26:34
Acq. Method Set: default
Date Processed: 2.4.2014 12:14:48
Processing Method: Default
Channel Name: Satin Ch 1
Proc. Chnl. Descr.:

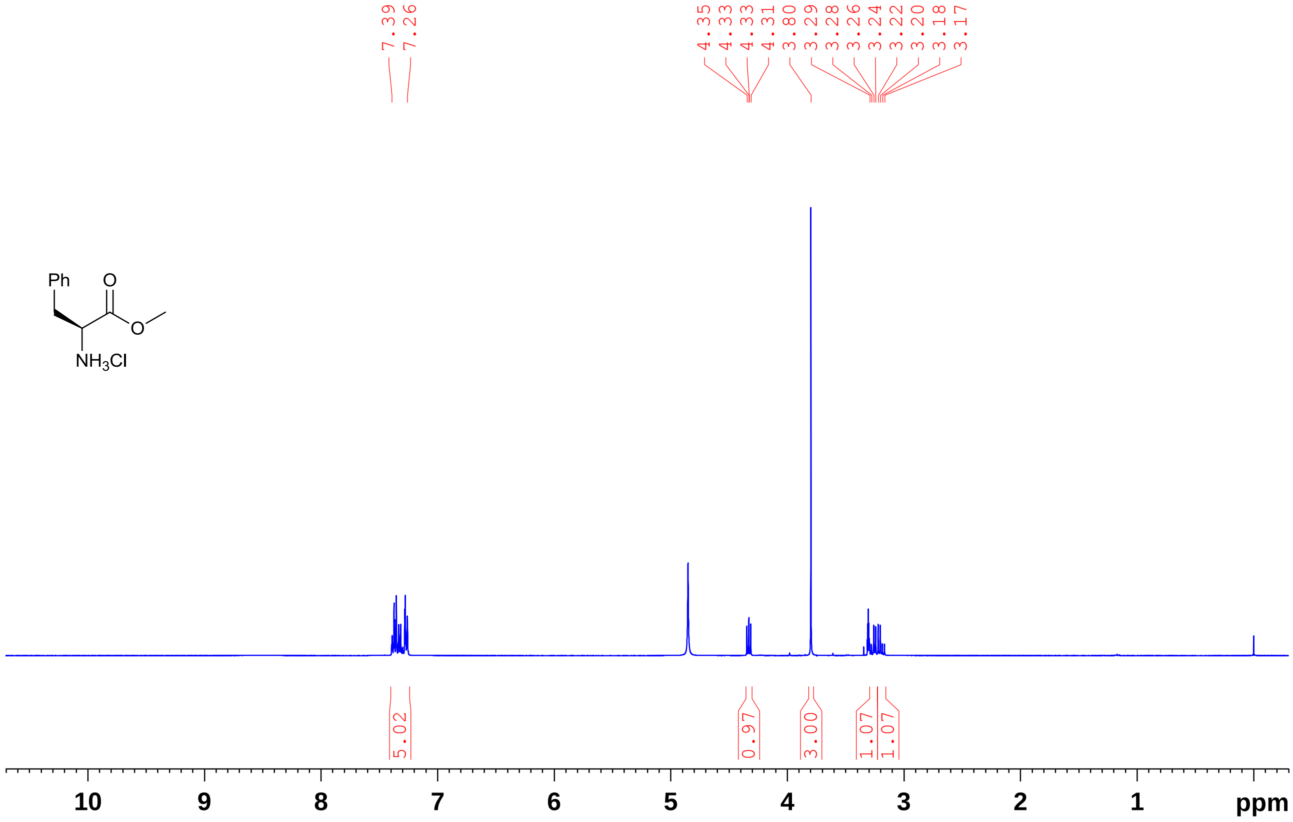
	RT	Area	% Area	Height
1	8,048	2675975	99,99	209230
2	8,950	364	0,01	45

Report Method: Default Individual Report   Printed 19:09:50   29.4.2014   Page: 1 of 1

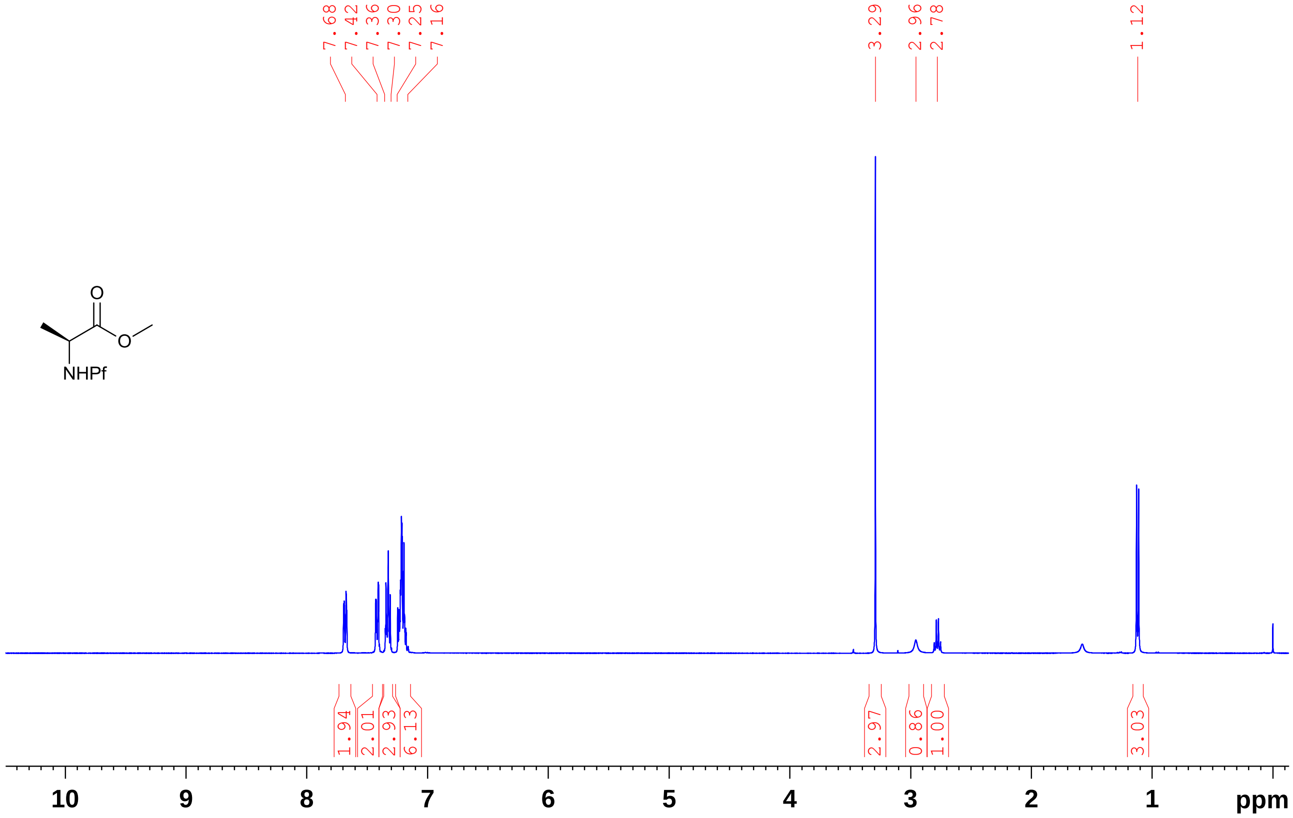
NMR ^{1}H: 9a



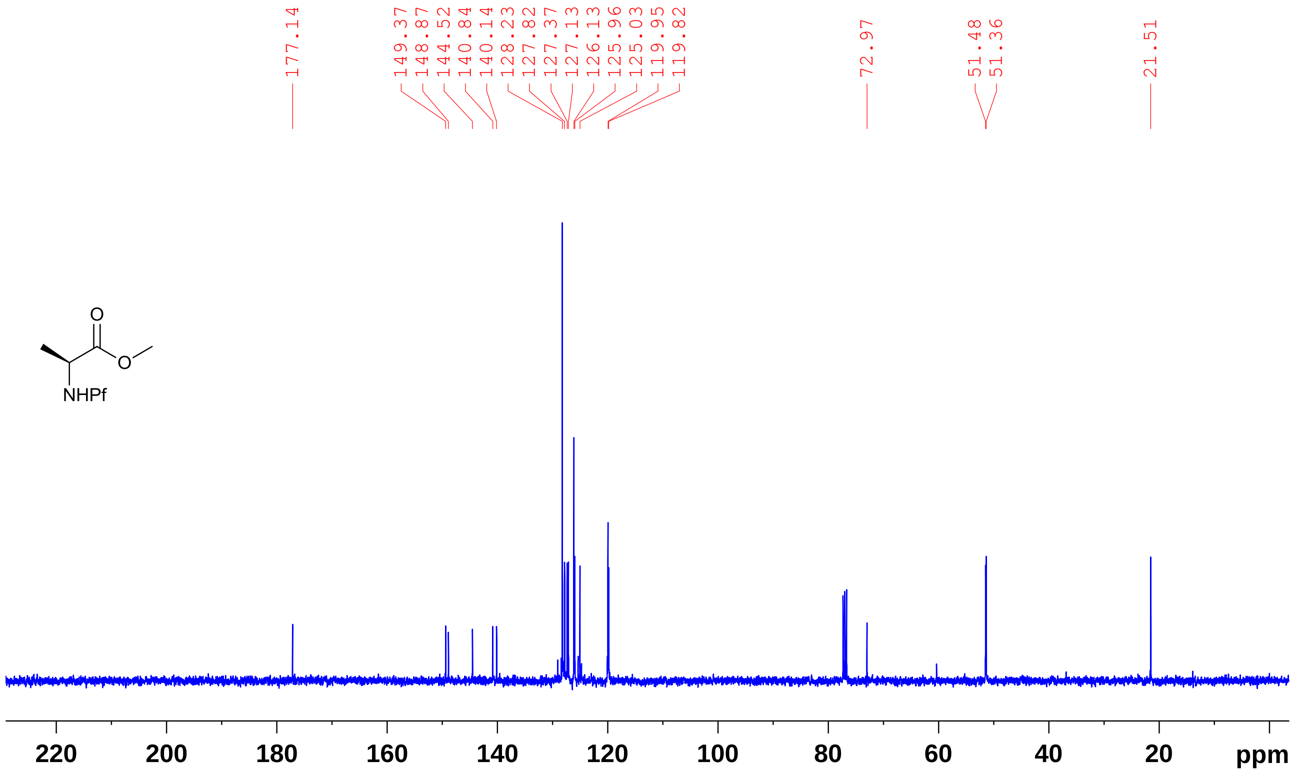
NMR ^{1}H: 9b



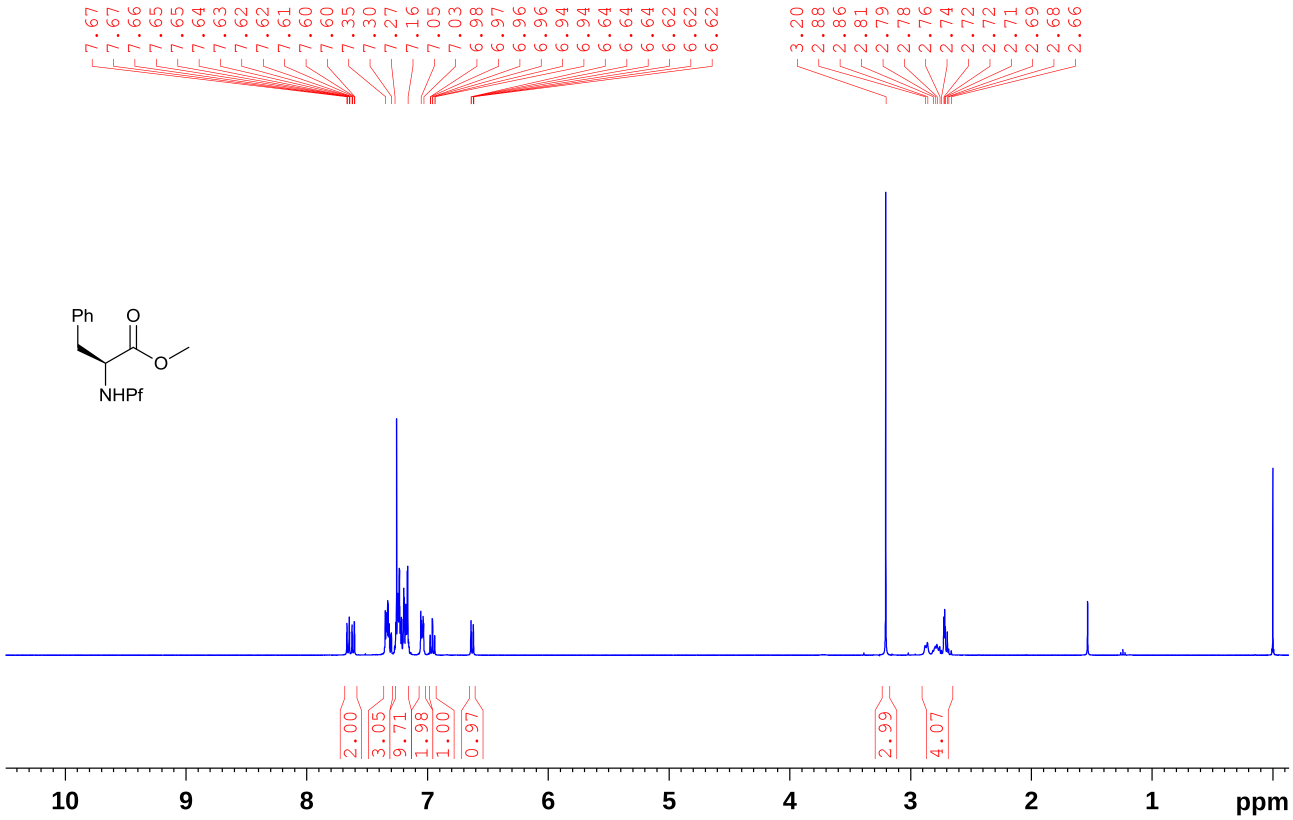
NMR ^{1}H: 10a



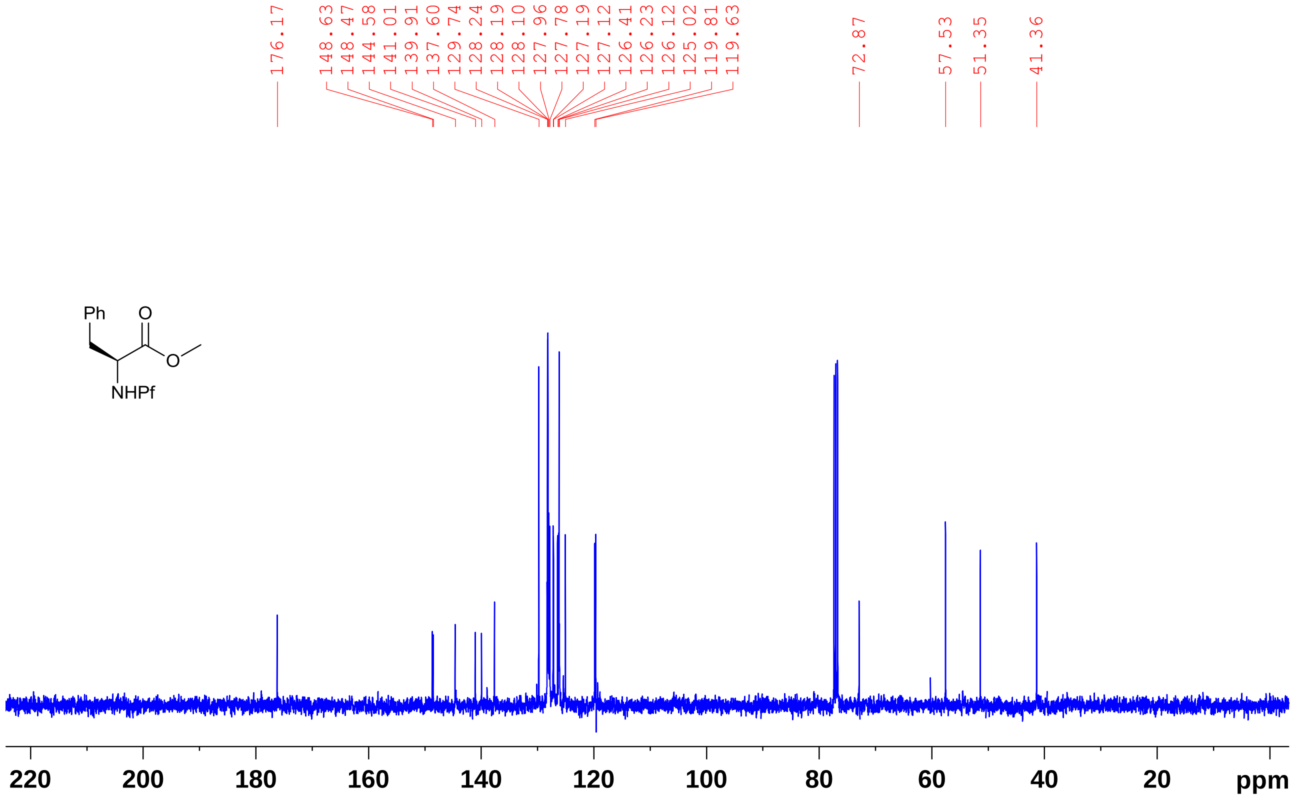
NMR ^{13}C: 10a



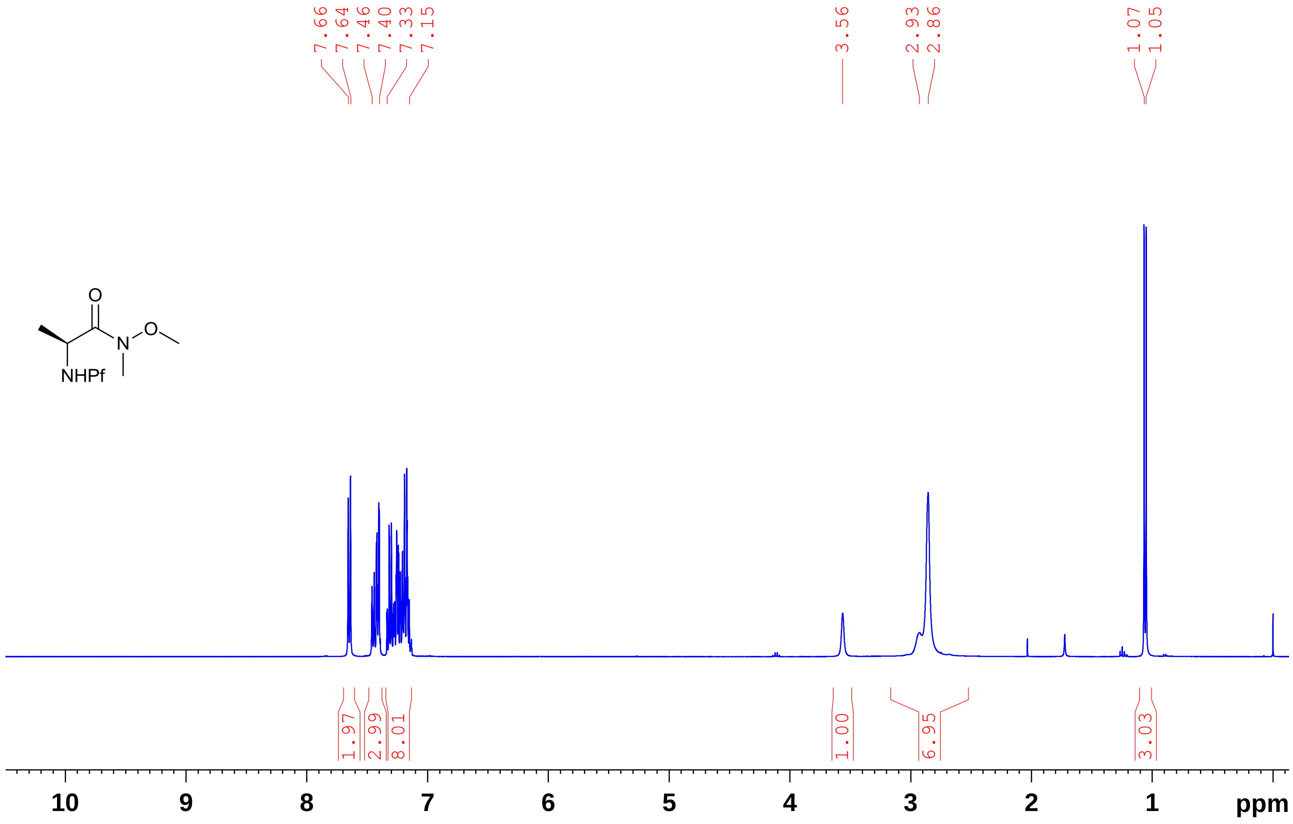
NMR ^{1}H: 10b



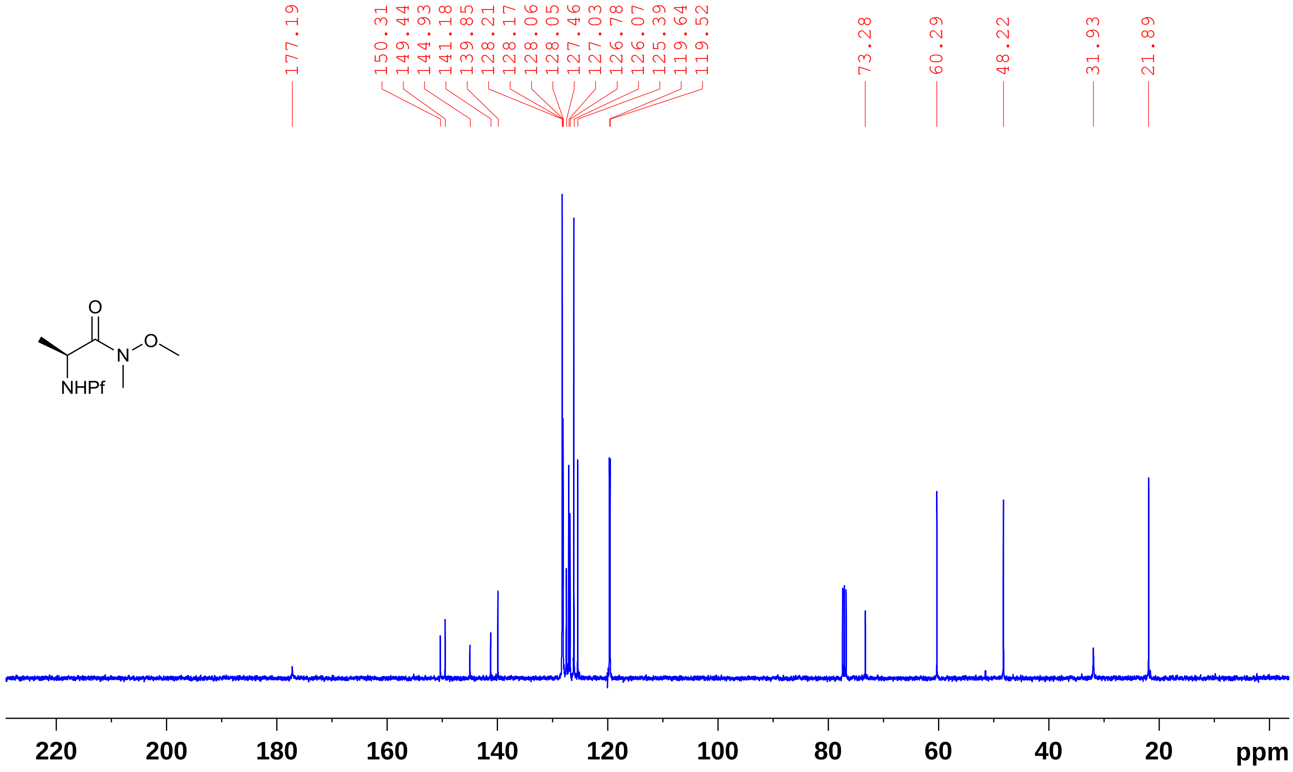
NMR ^{13}C: 10b



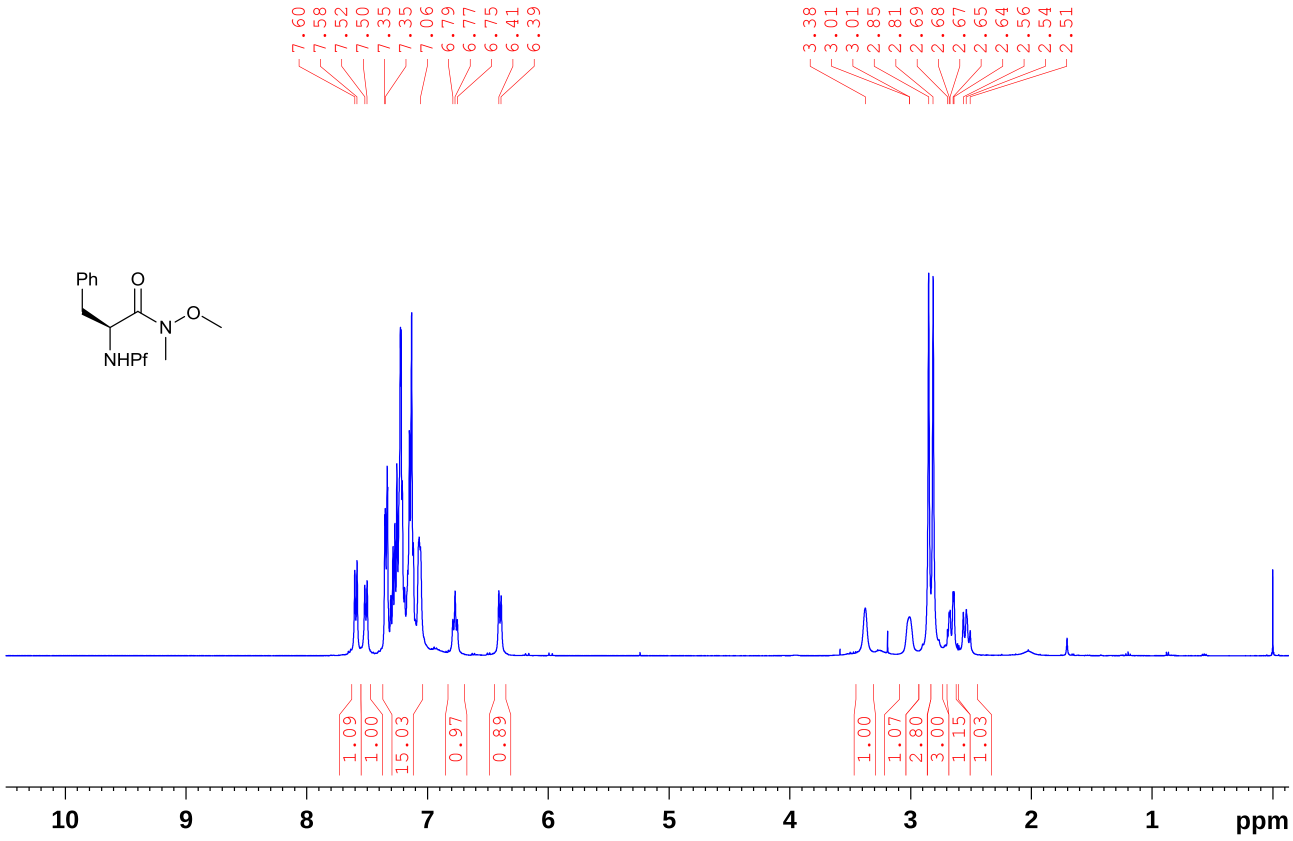
NMR ^{1}H: 11a



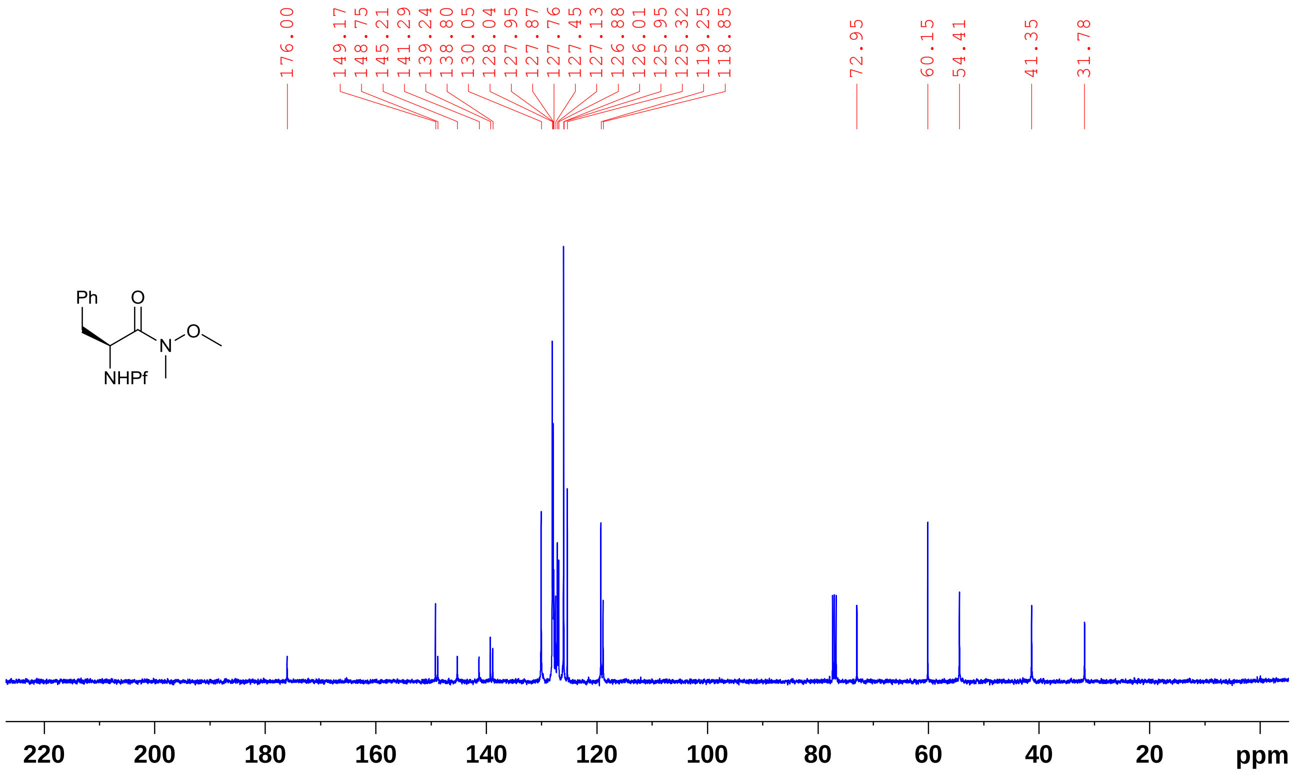
NMR ^{13}C: 11a



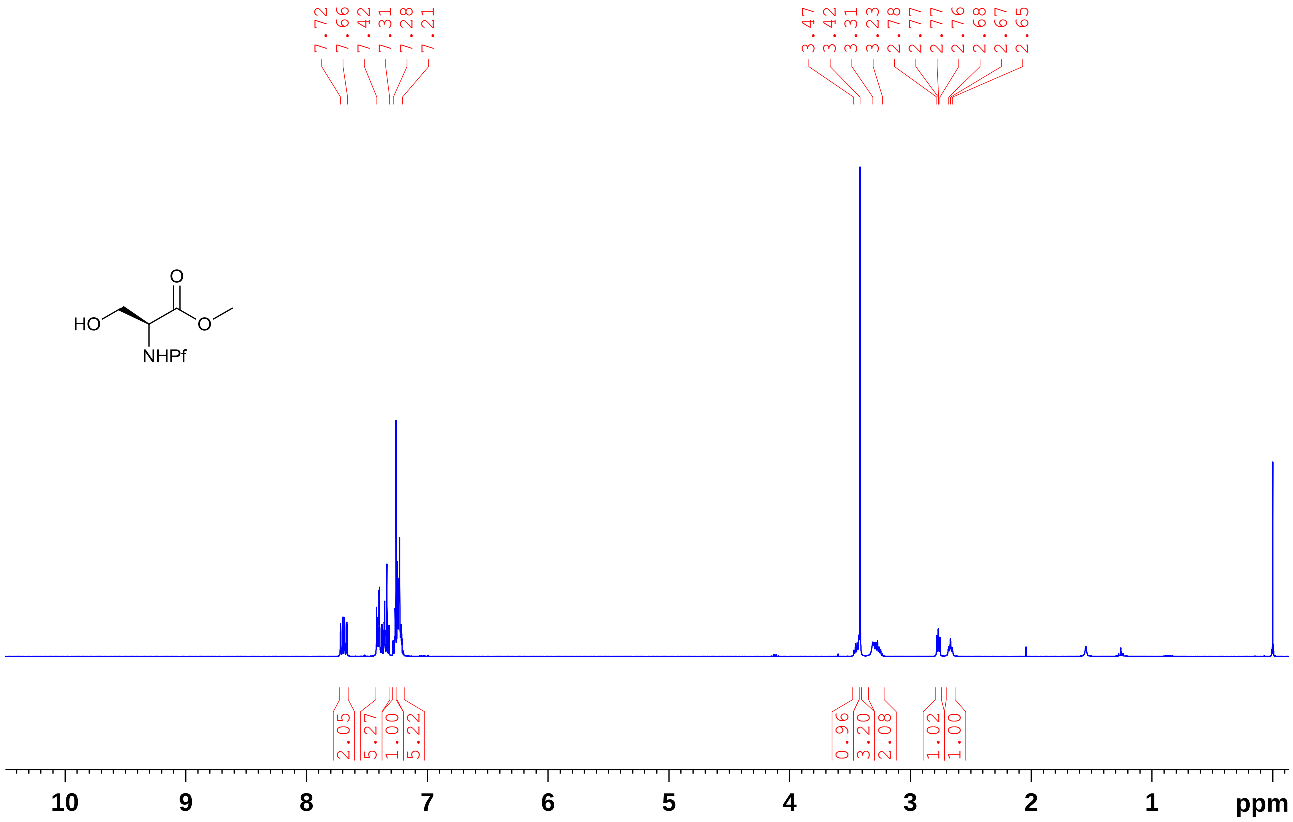
NMR ^{1}H: 11b



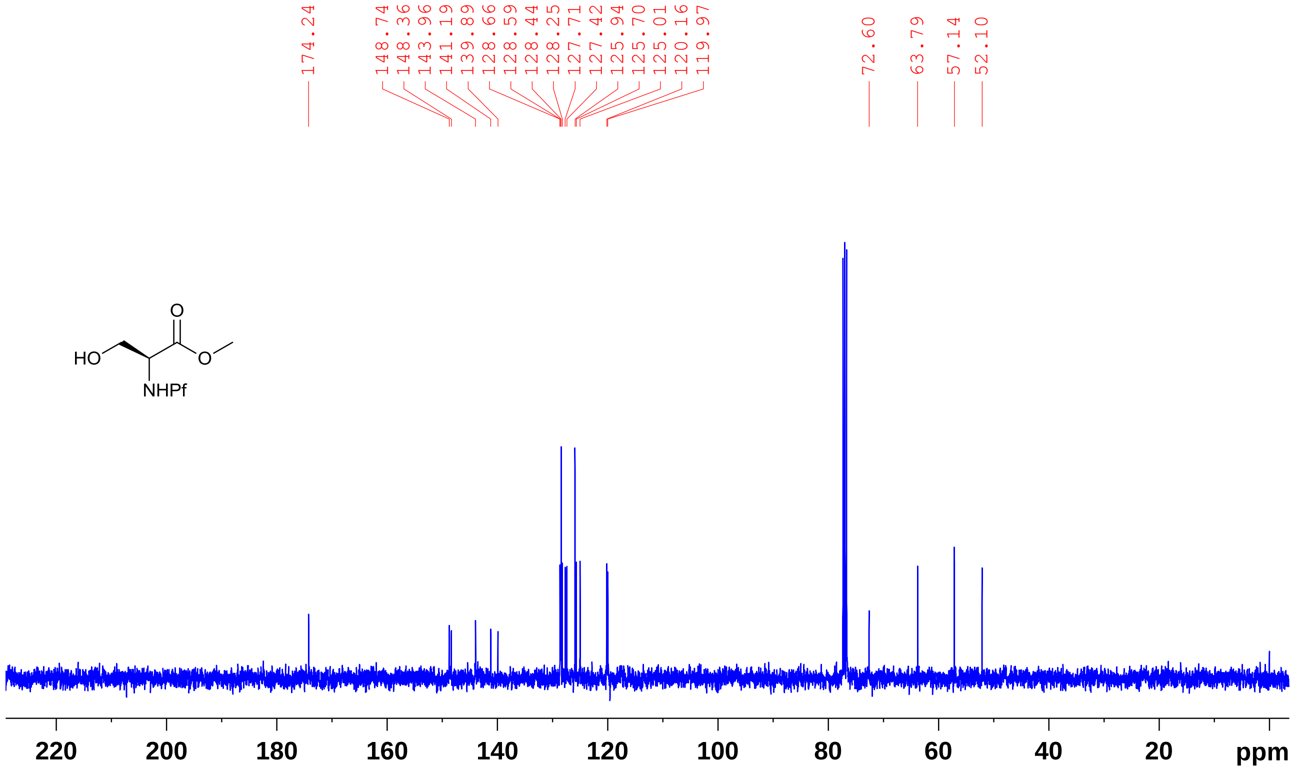
NMR ^{13}C: 11b



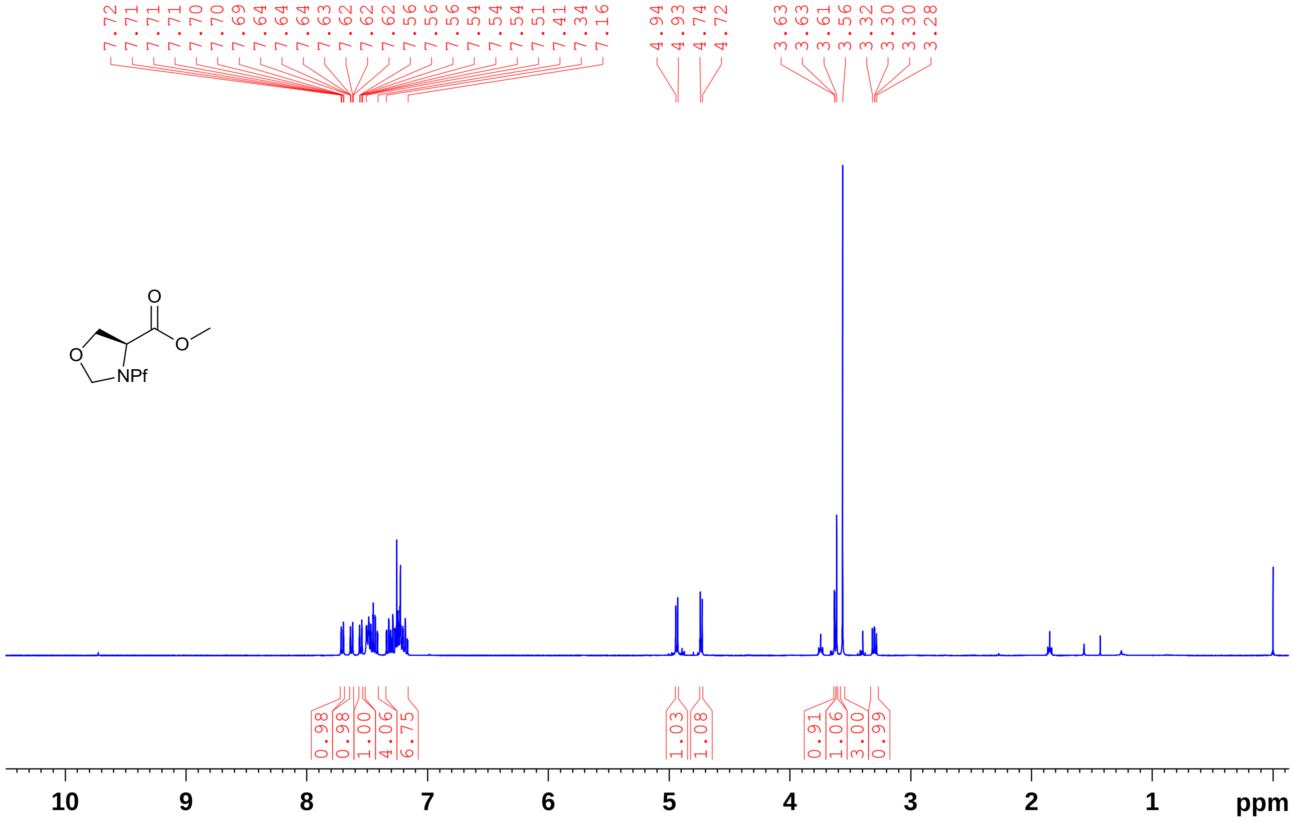
NMR ^{1}H: Intermediate in the synthesis of 10c



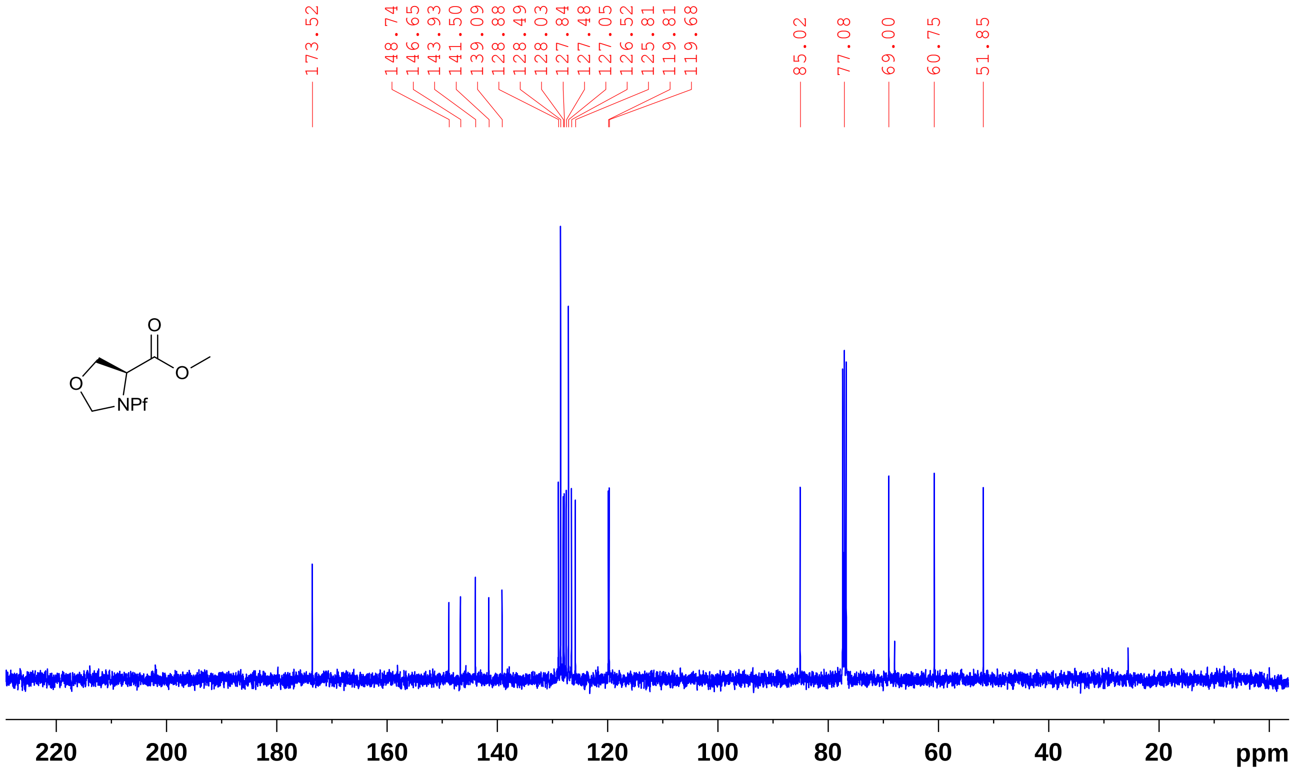
NMR ^{13}C: Intermediate in the synthesis of 10c



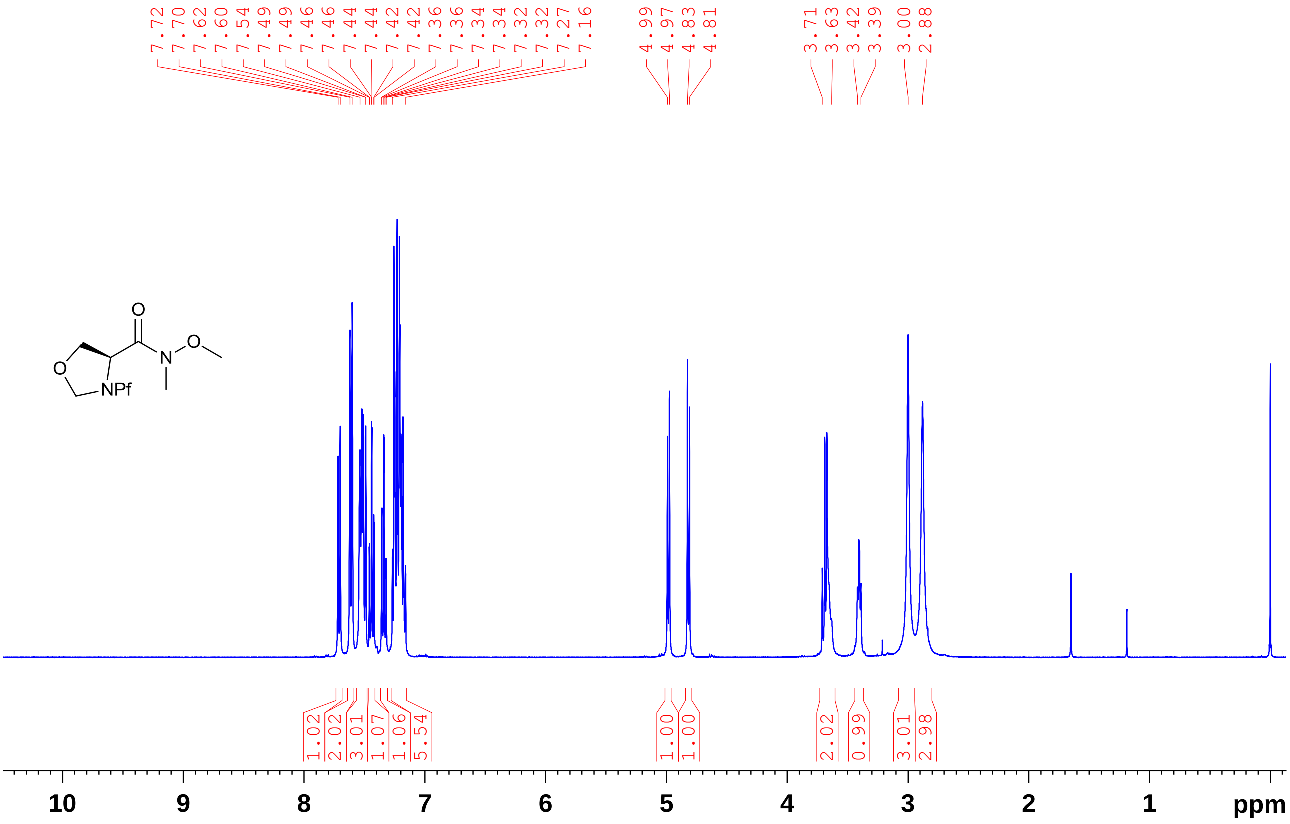
NMR ^{1}H: 10c



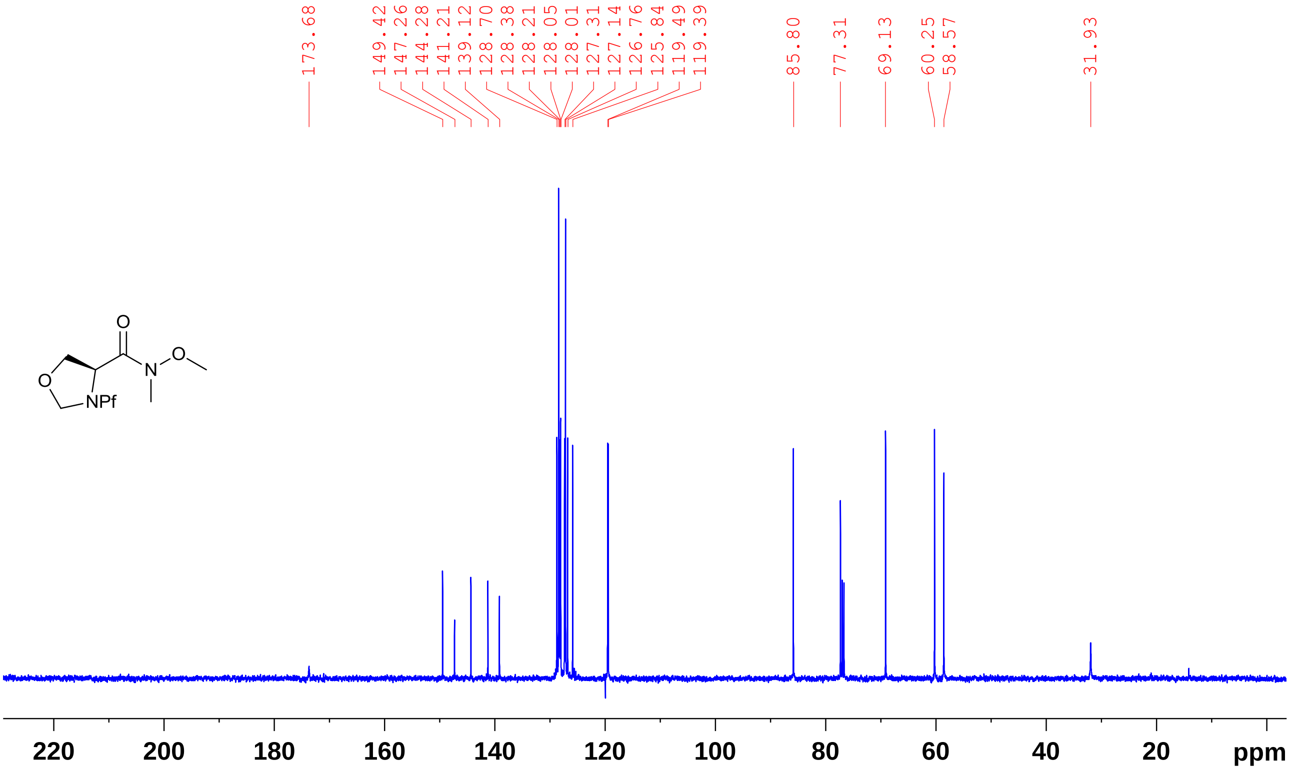
NMR ^{13}C: 10c



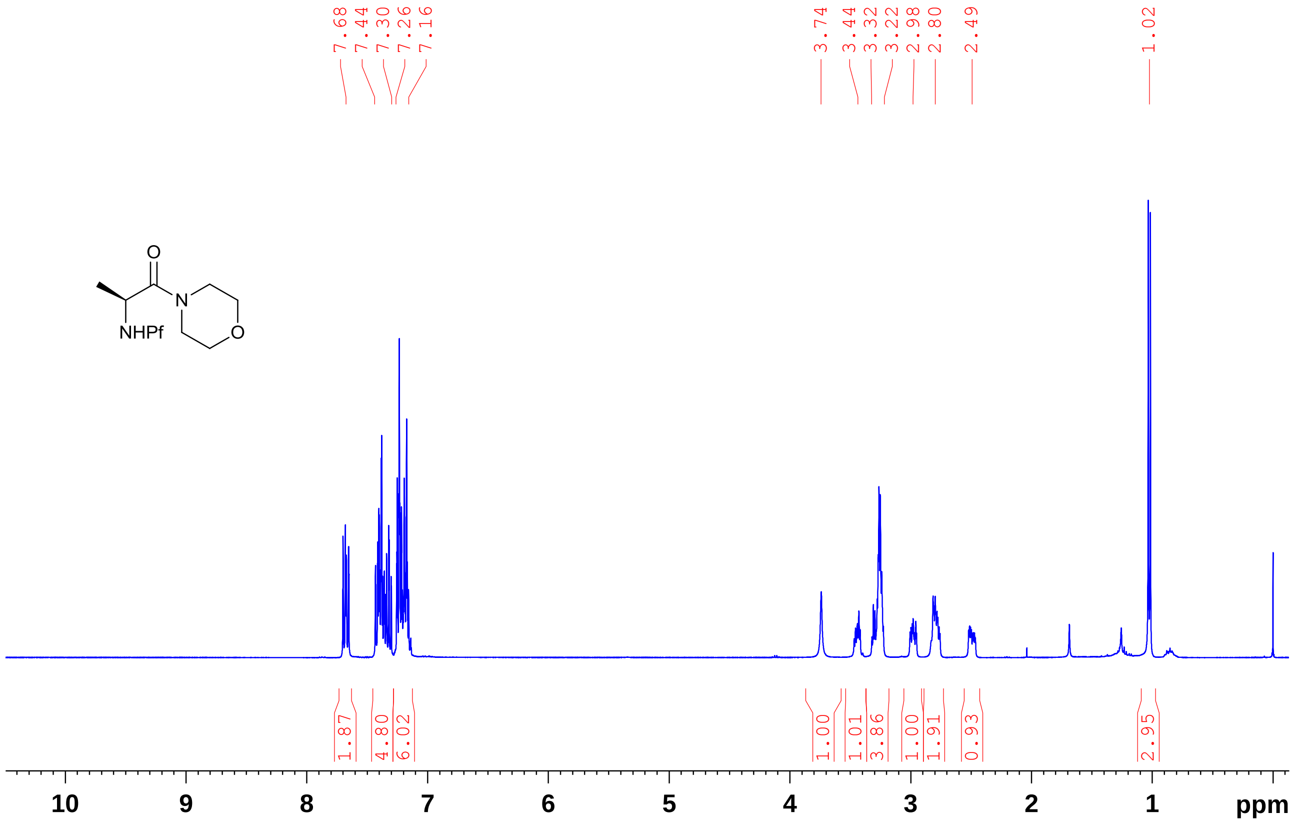
NMR ^{1}H: 11c



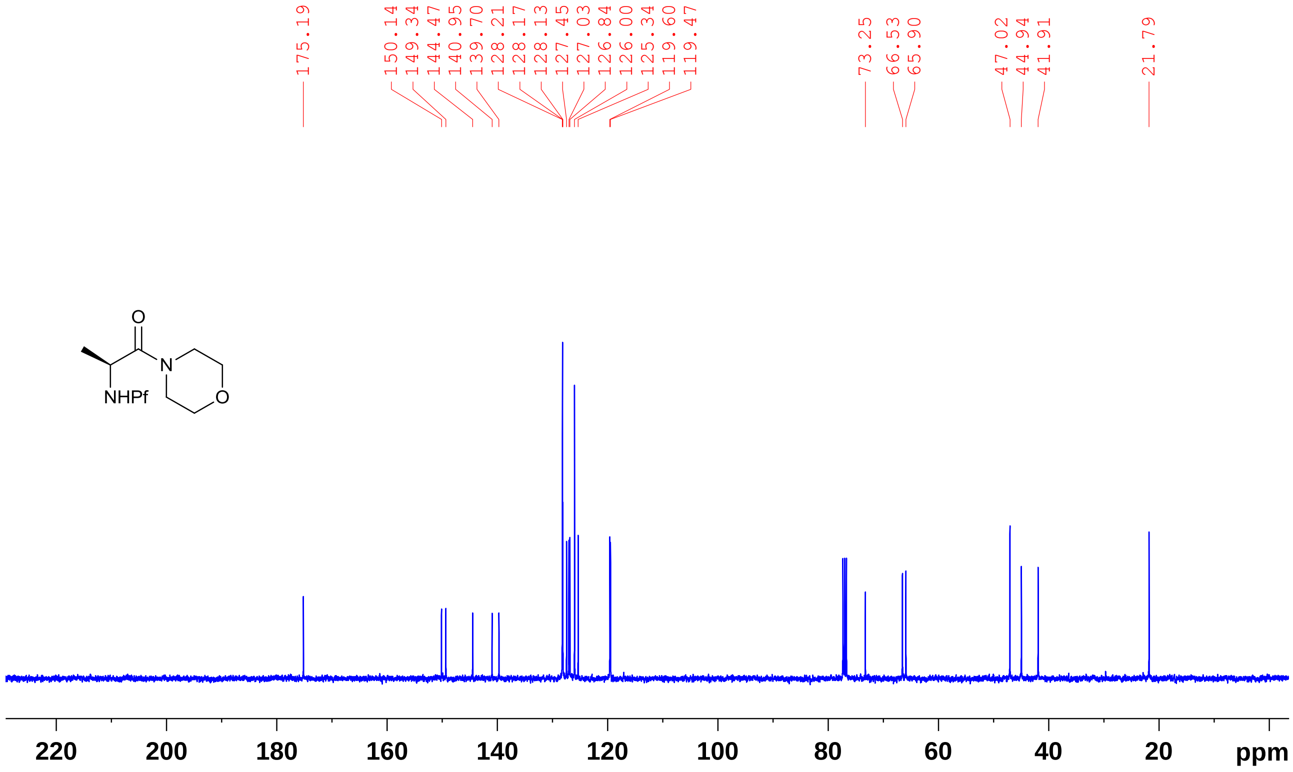
NMR ^{13}C: 11c



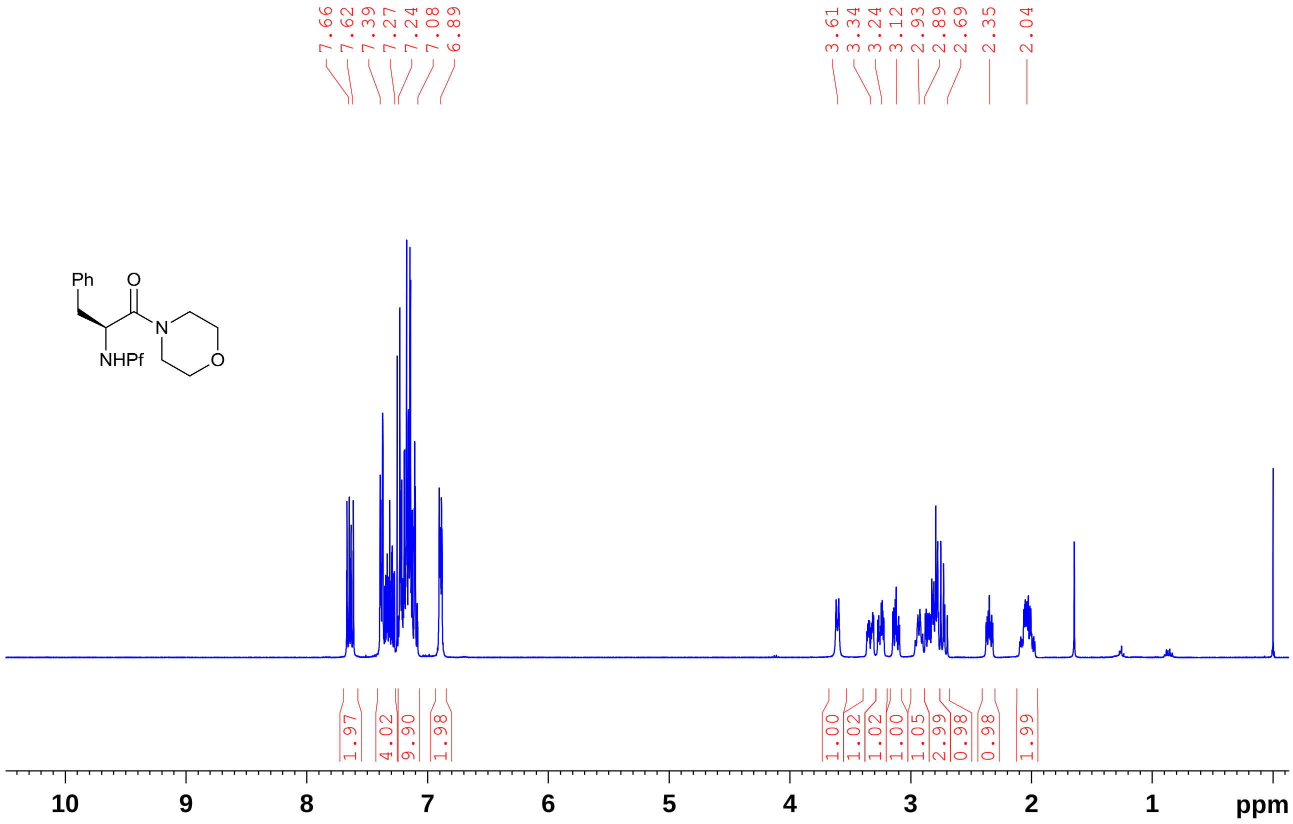
NMR ^{1}H: 17a



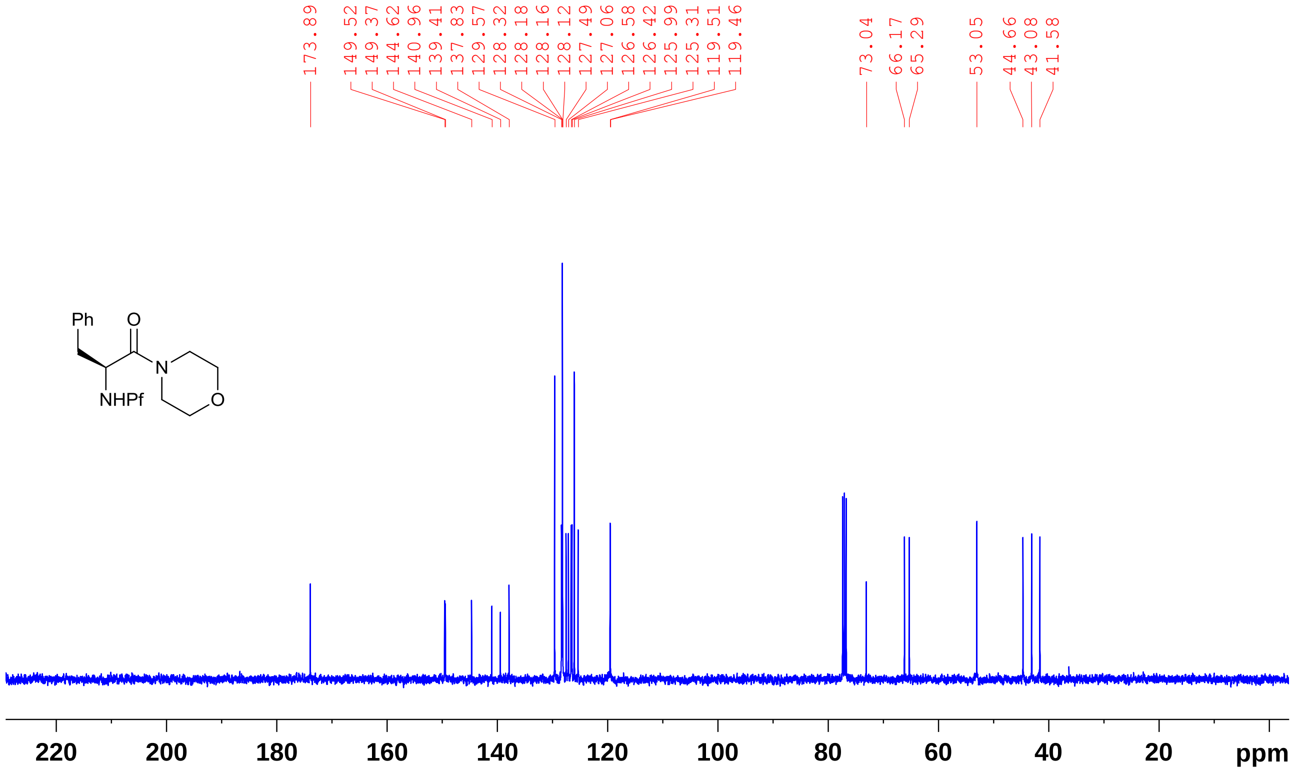
NMR ^{13}C: 17a



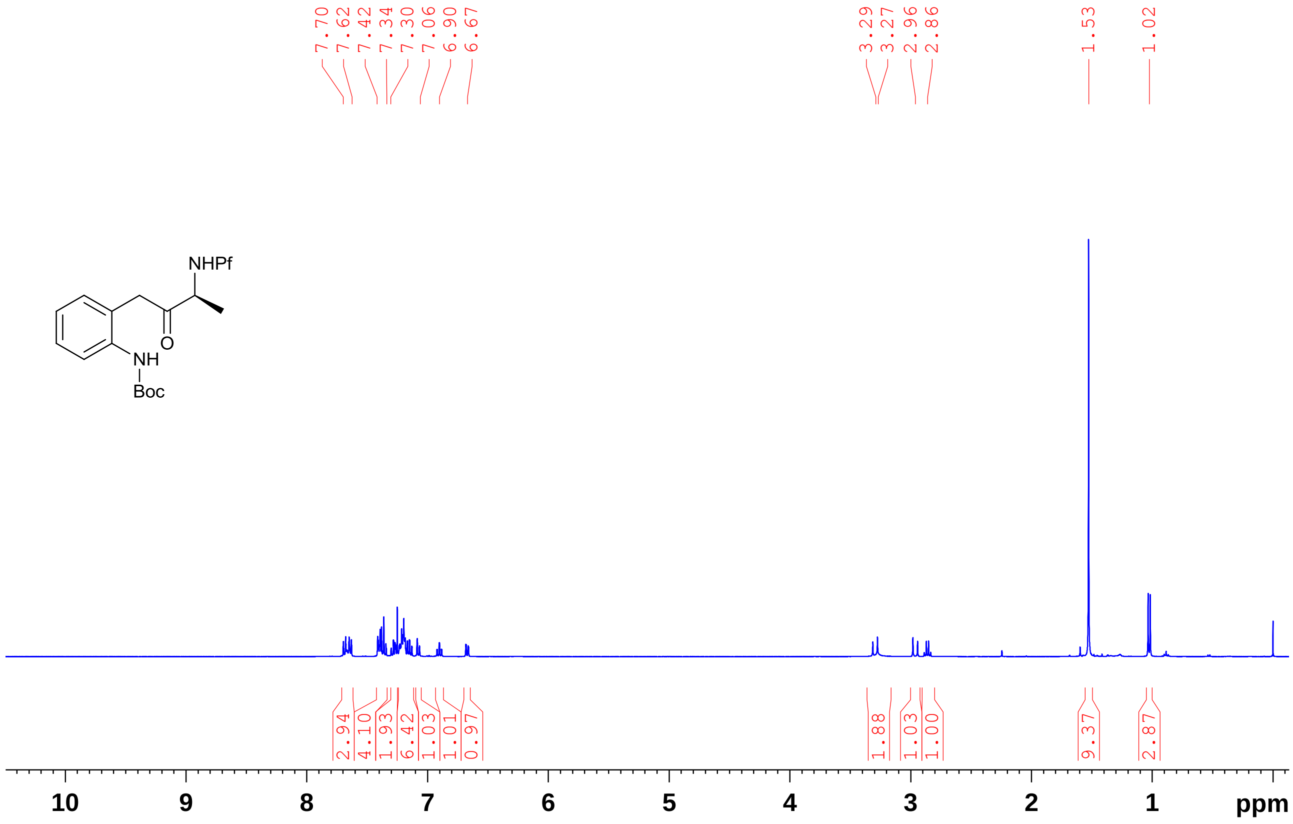
NMR ^{1}H: 17b



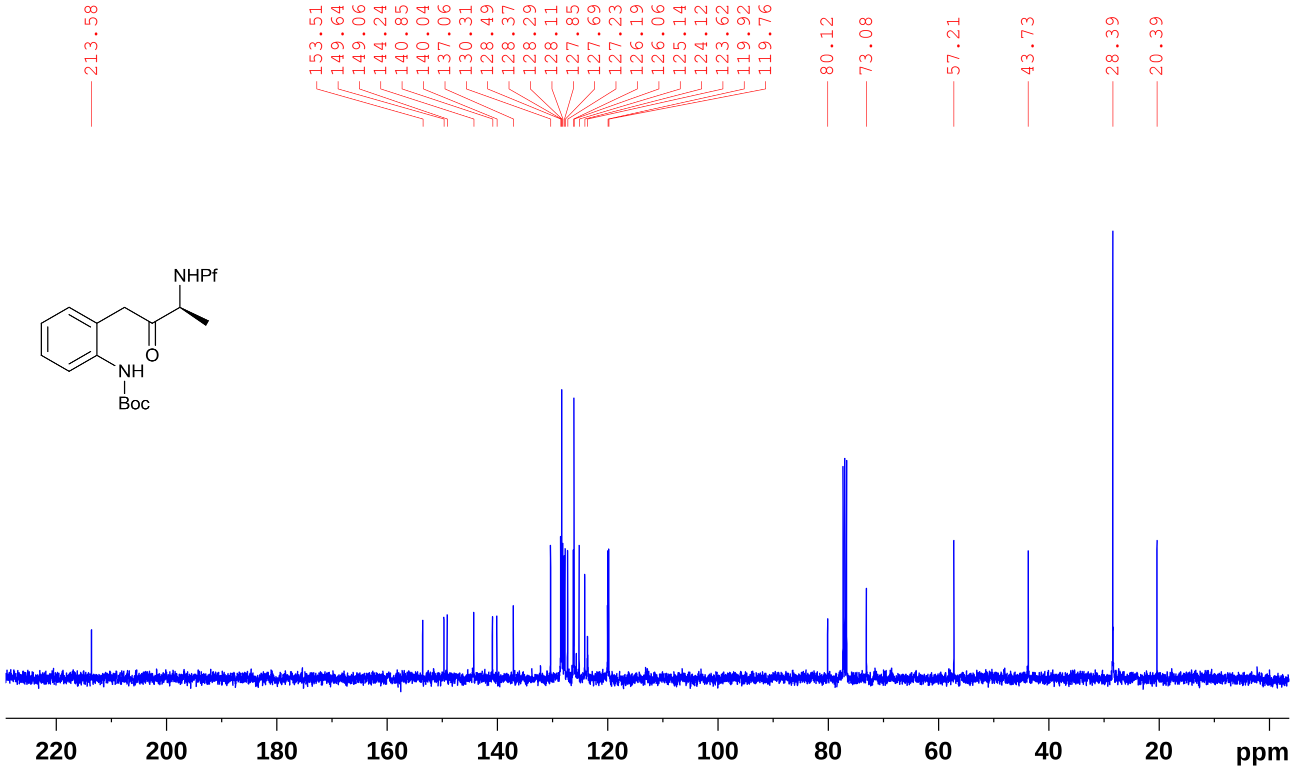
NMR ^{13}C: 17b



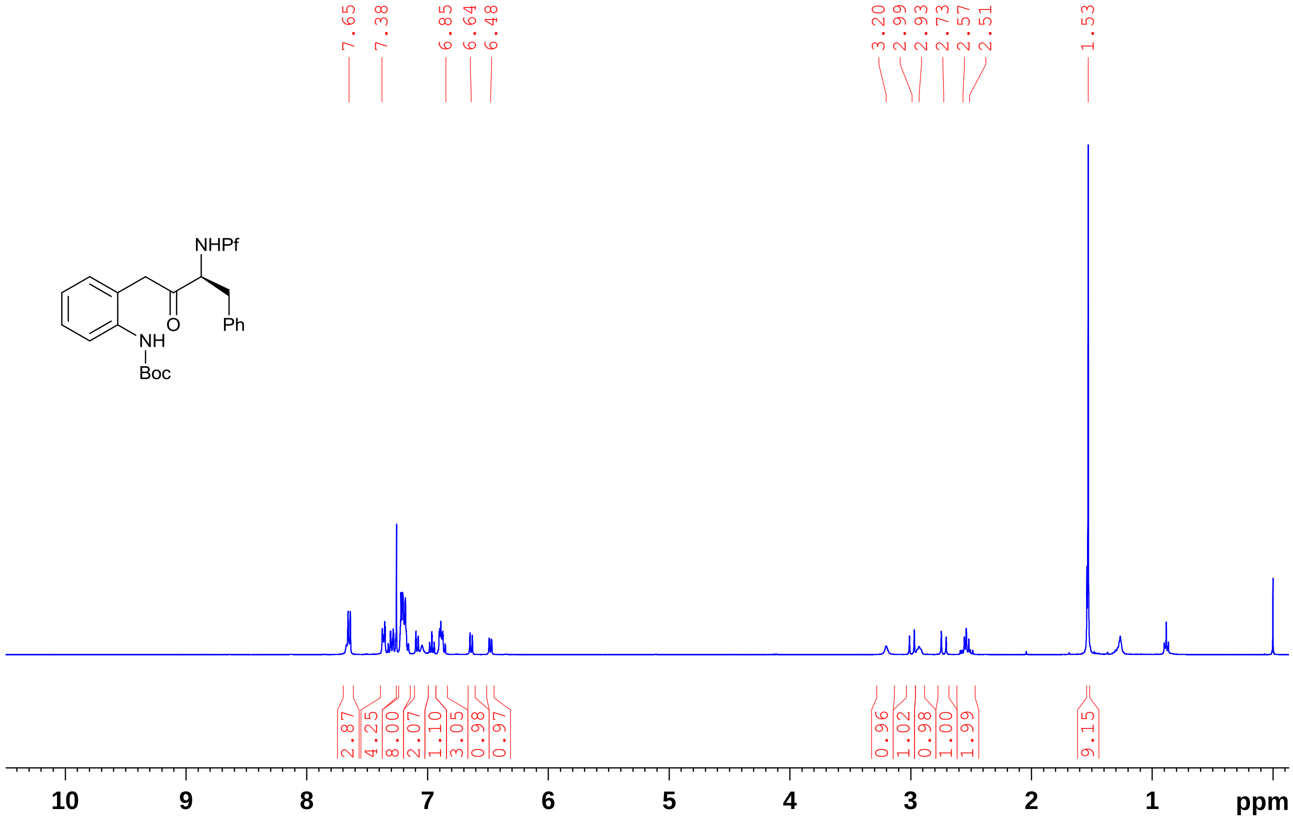
NMR ^{1}H: 13a



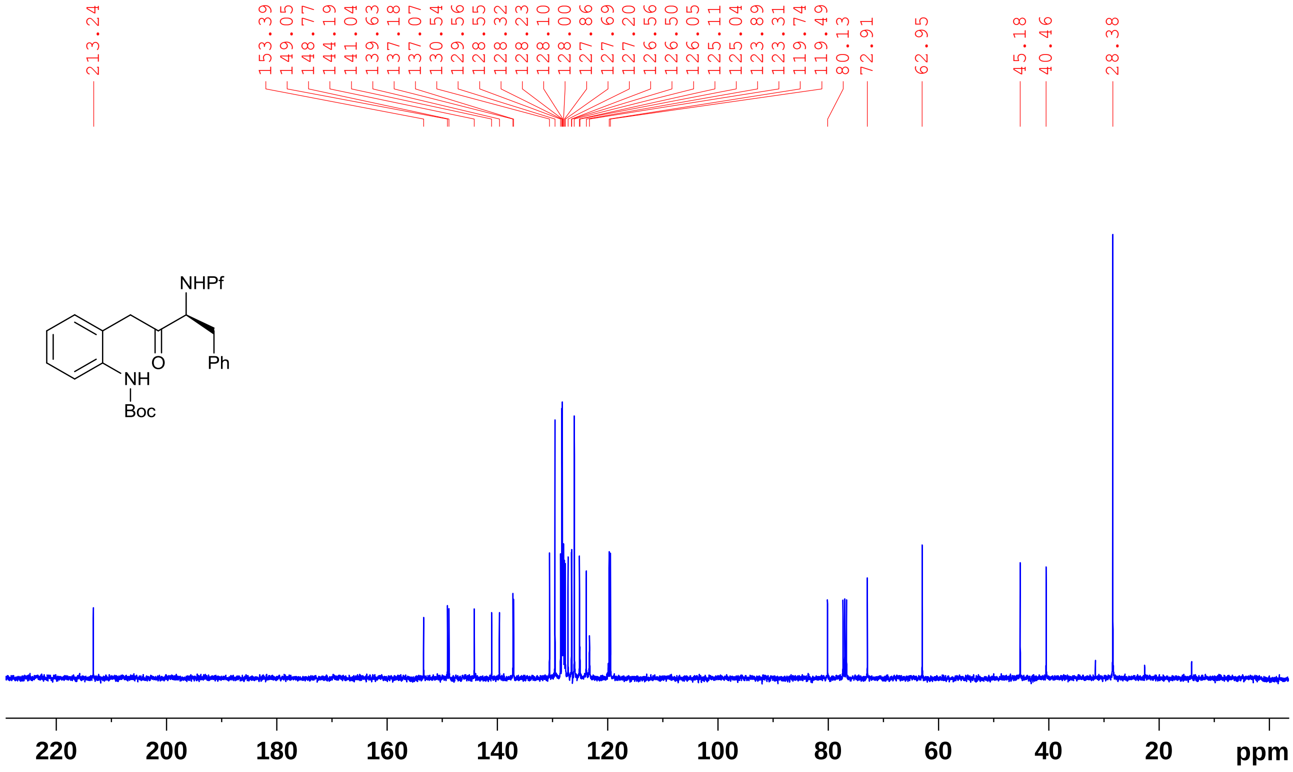
NMR ^{13}C: 13a



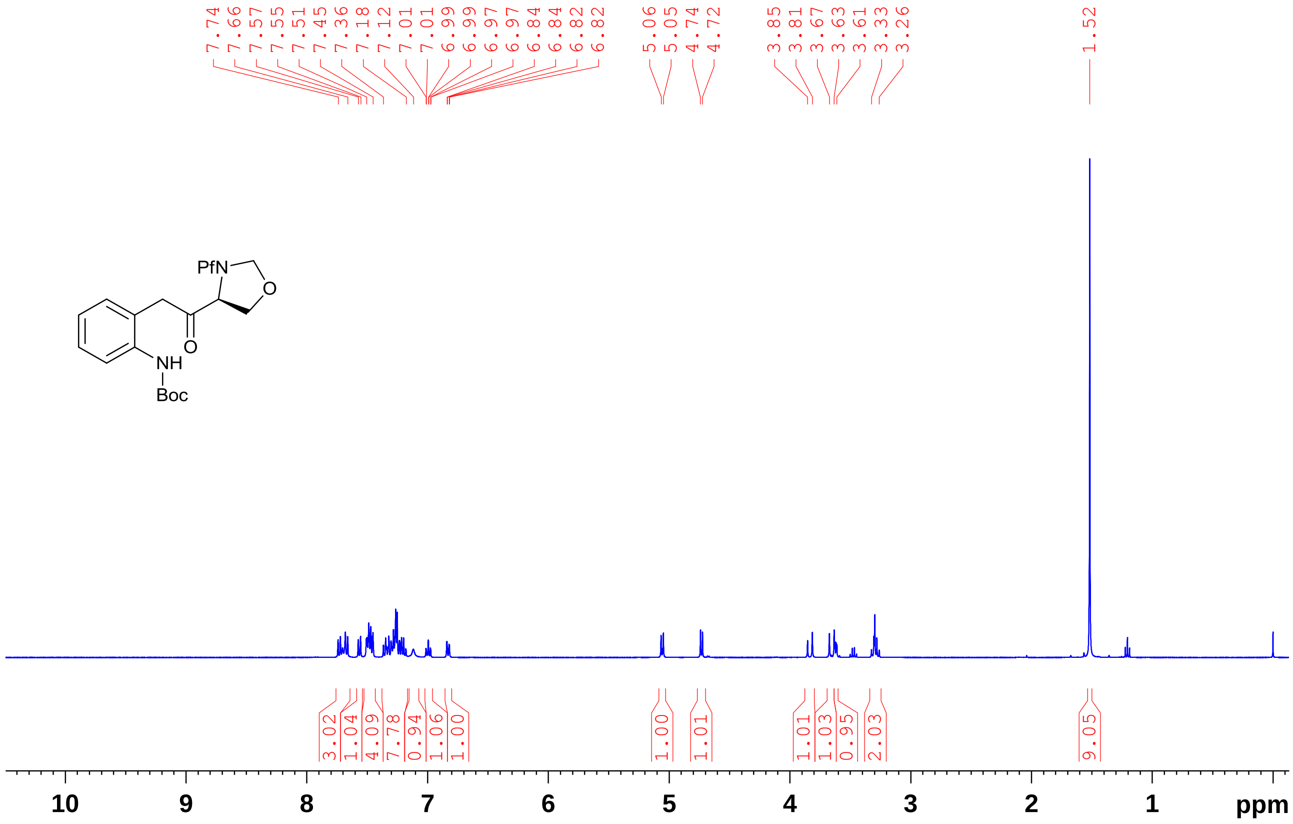
NMR ^{1}H: 13b



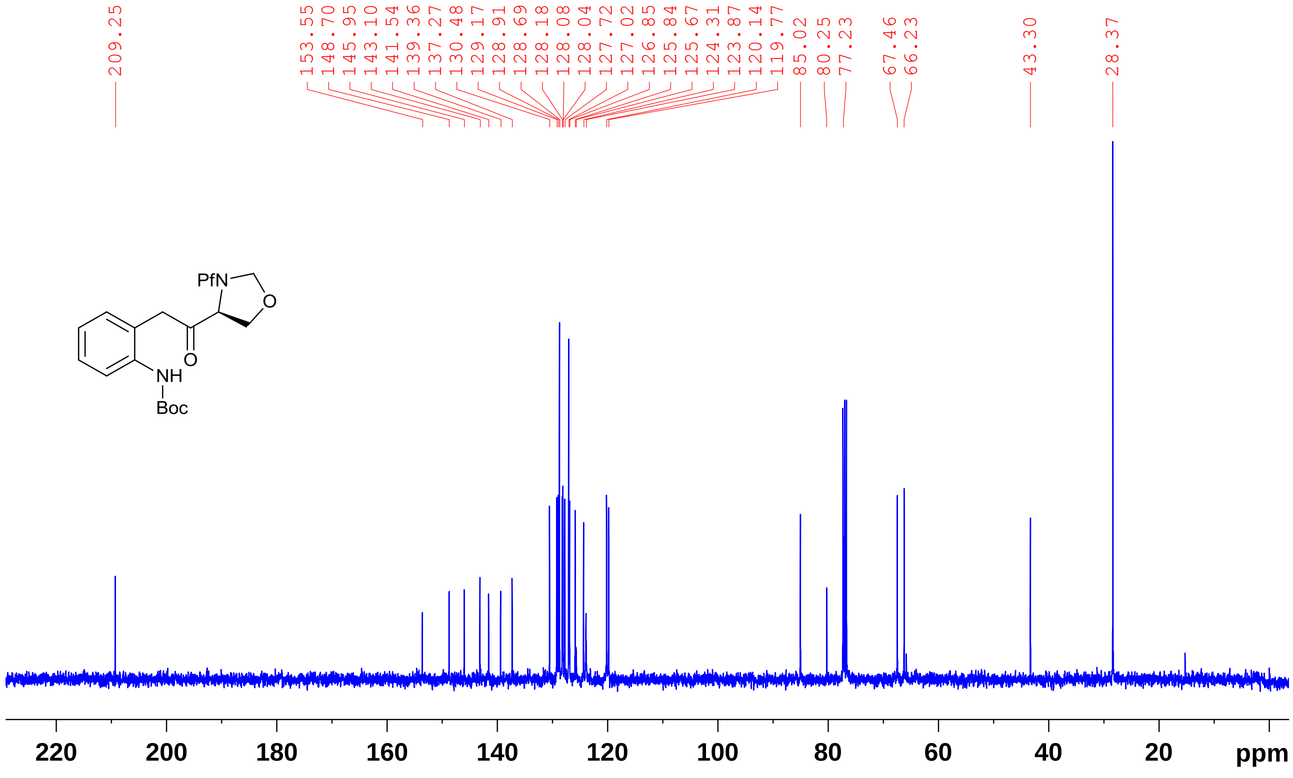
NMR ^{13}C: 13b



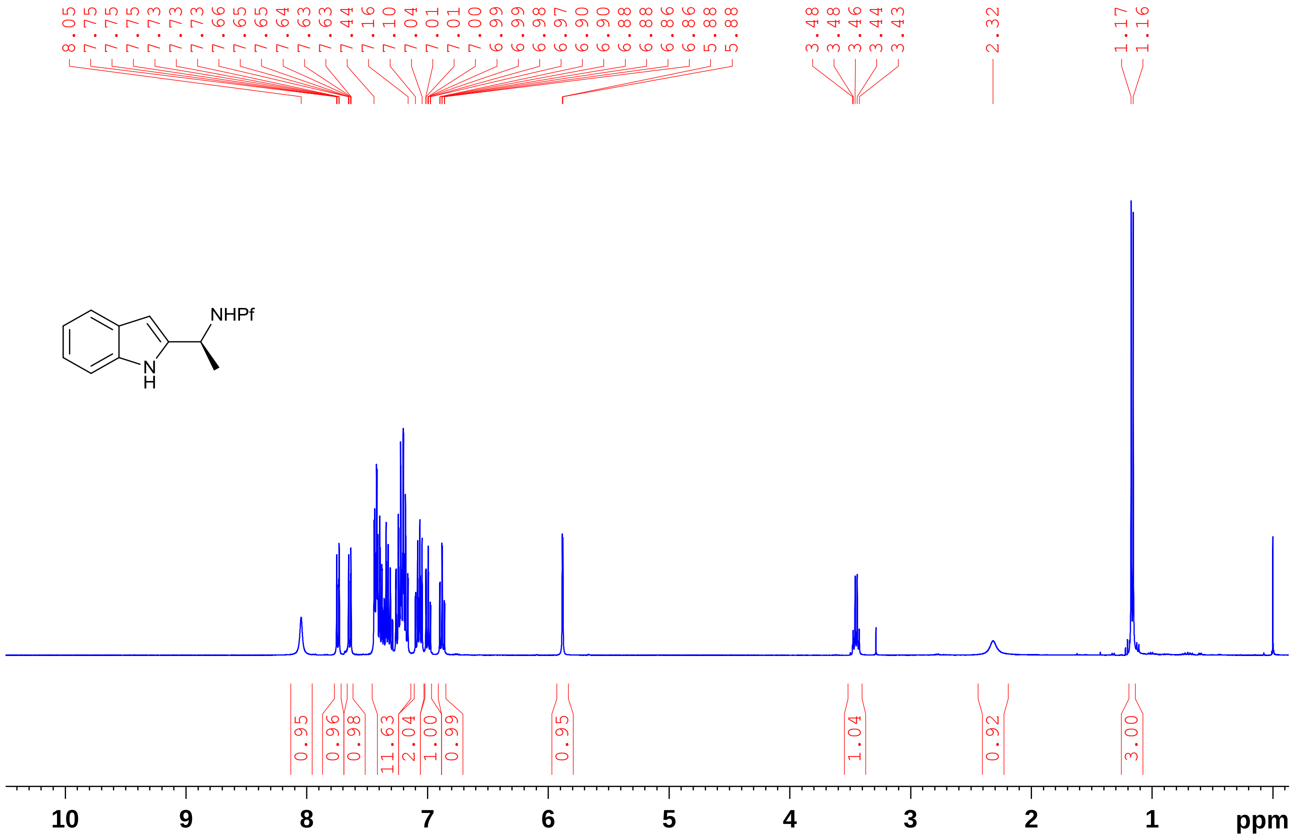
NMR ^{1}H: 13c



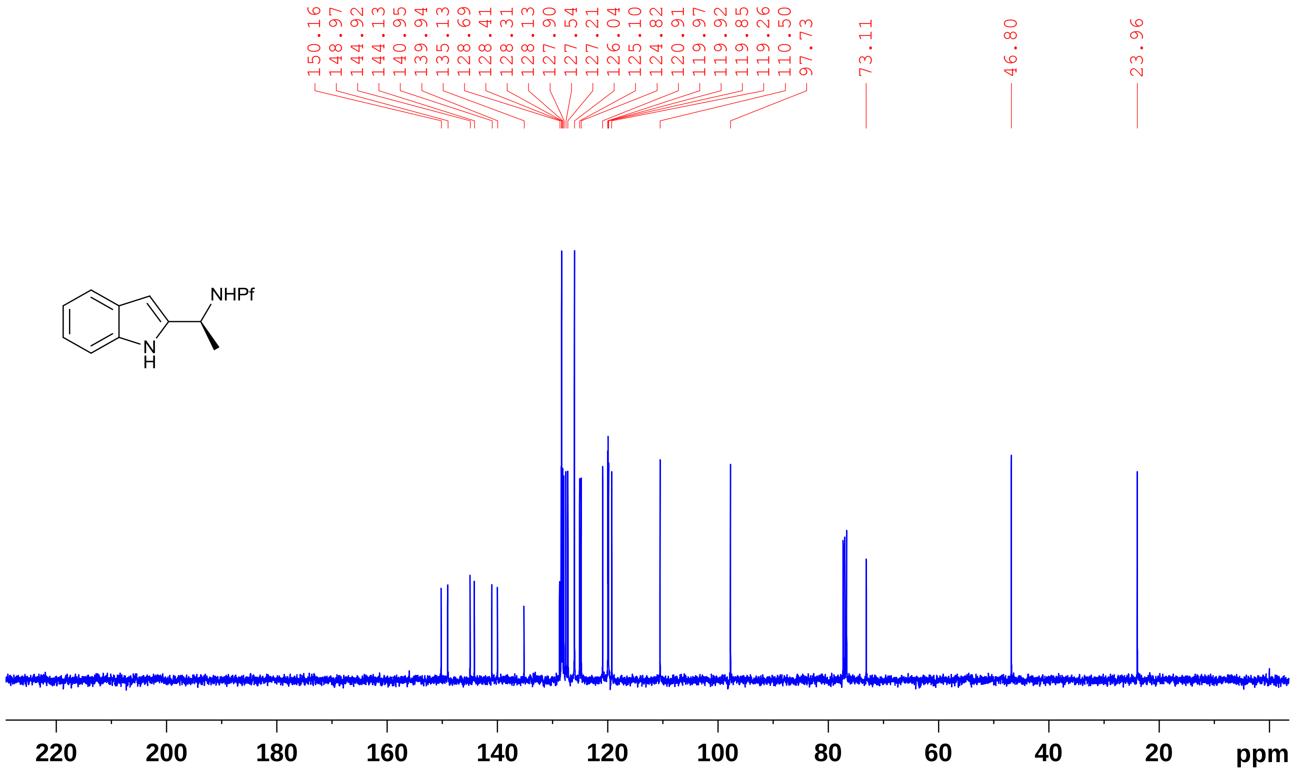
NMR ^{13}C: 13c



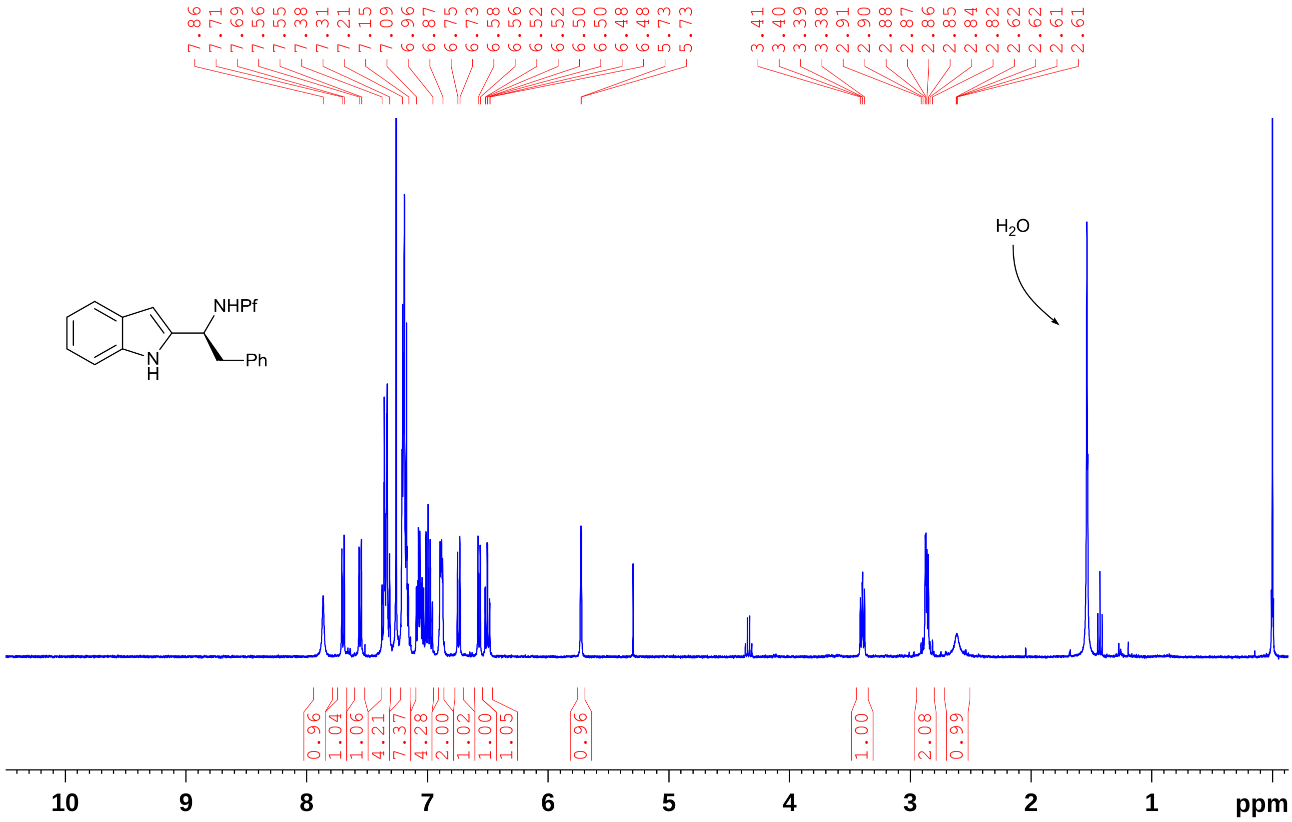
NMR ^{1}H: 18a



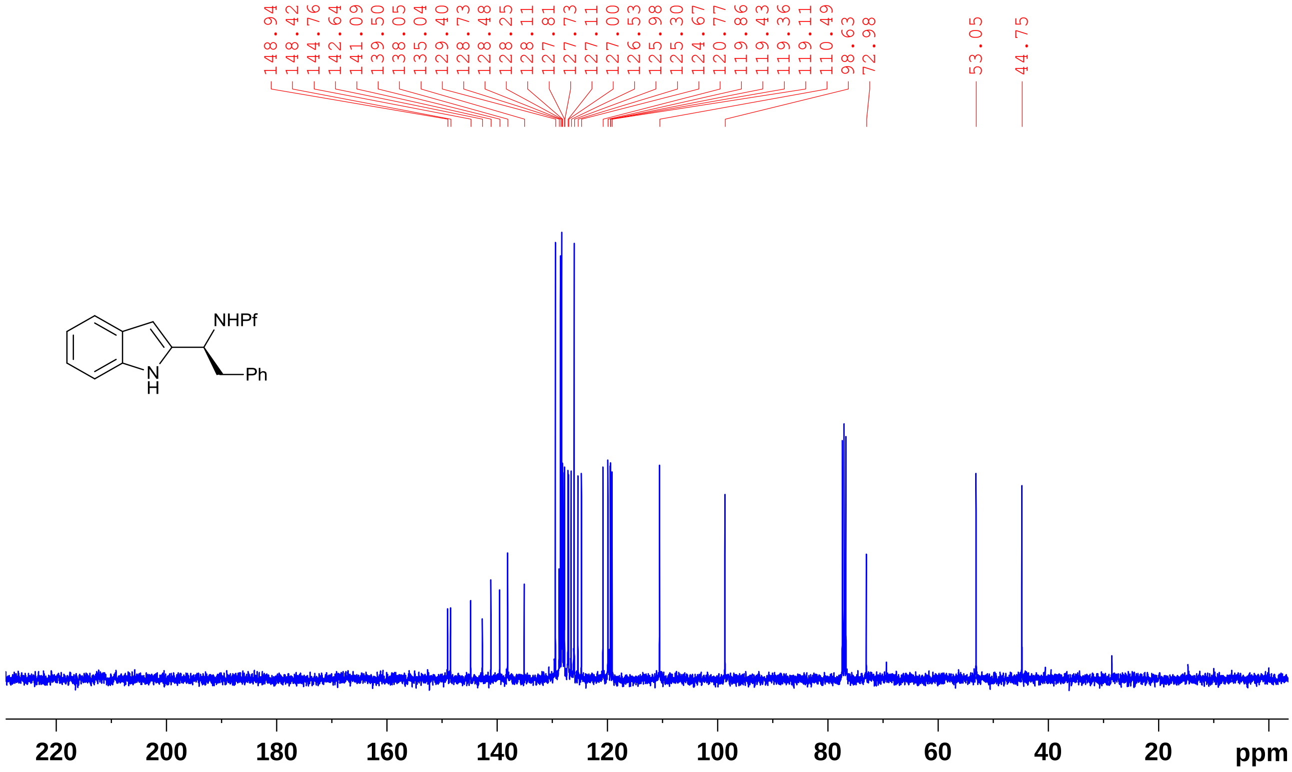
NMR ^{13}C: 18a



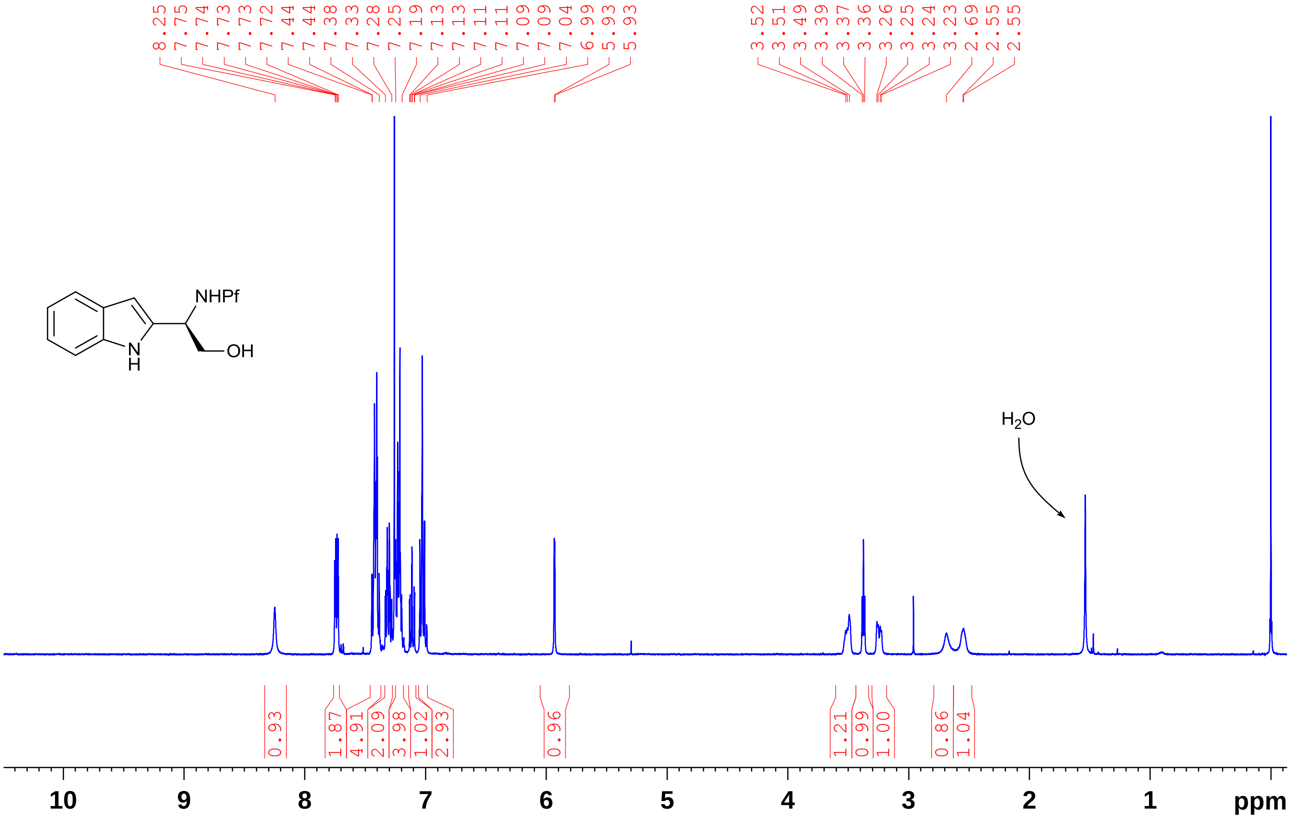
NMR ^{1}H: 18b



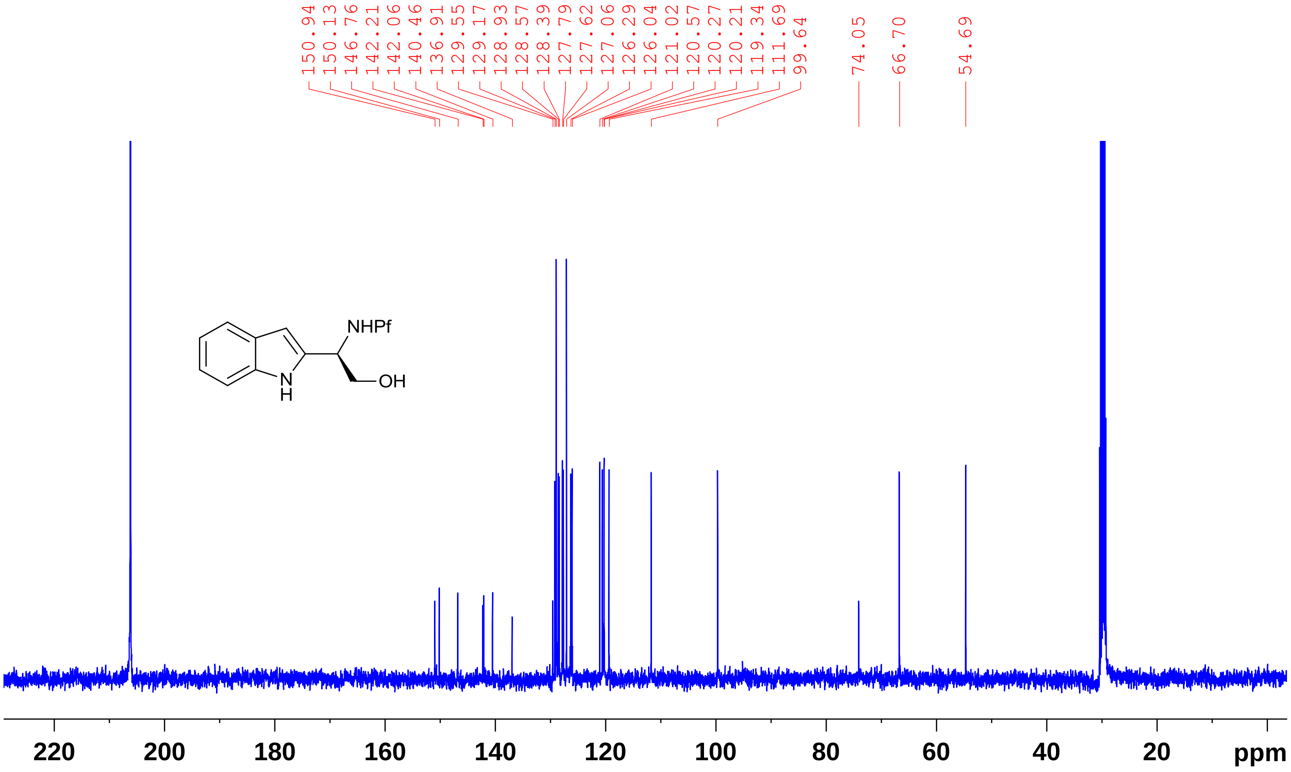
NMR ^{13}C: 18b



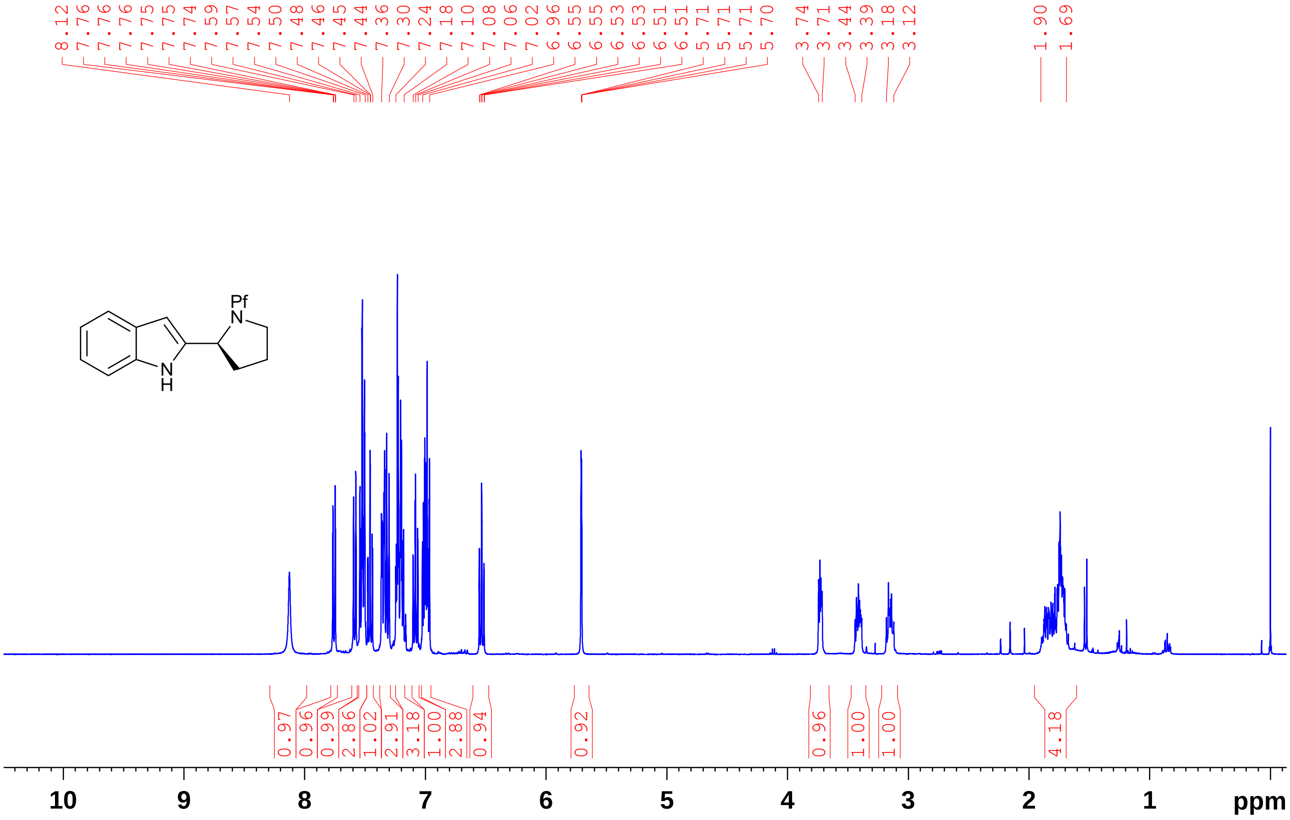
NMR ^{1}H: 18c



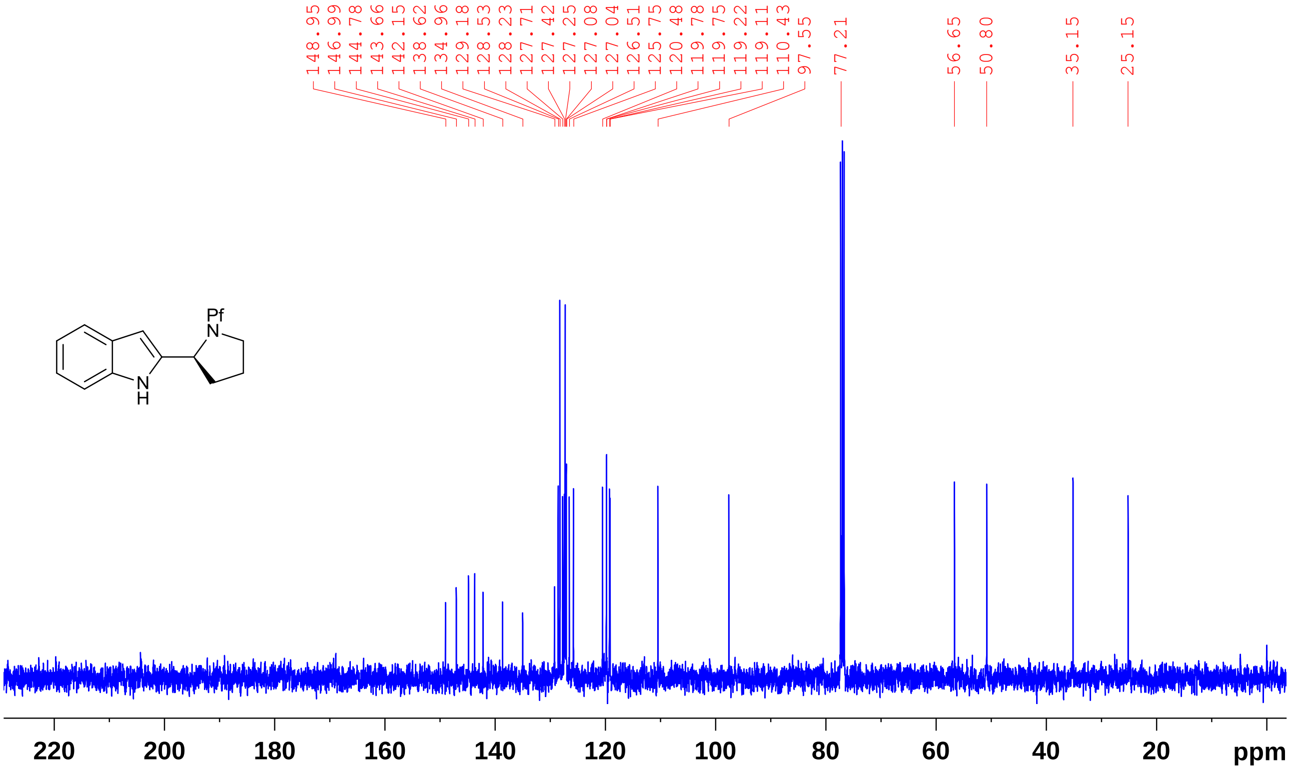
NMR ^{13}C: 18c



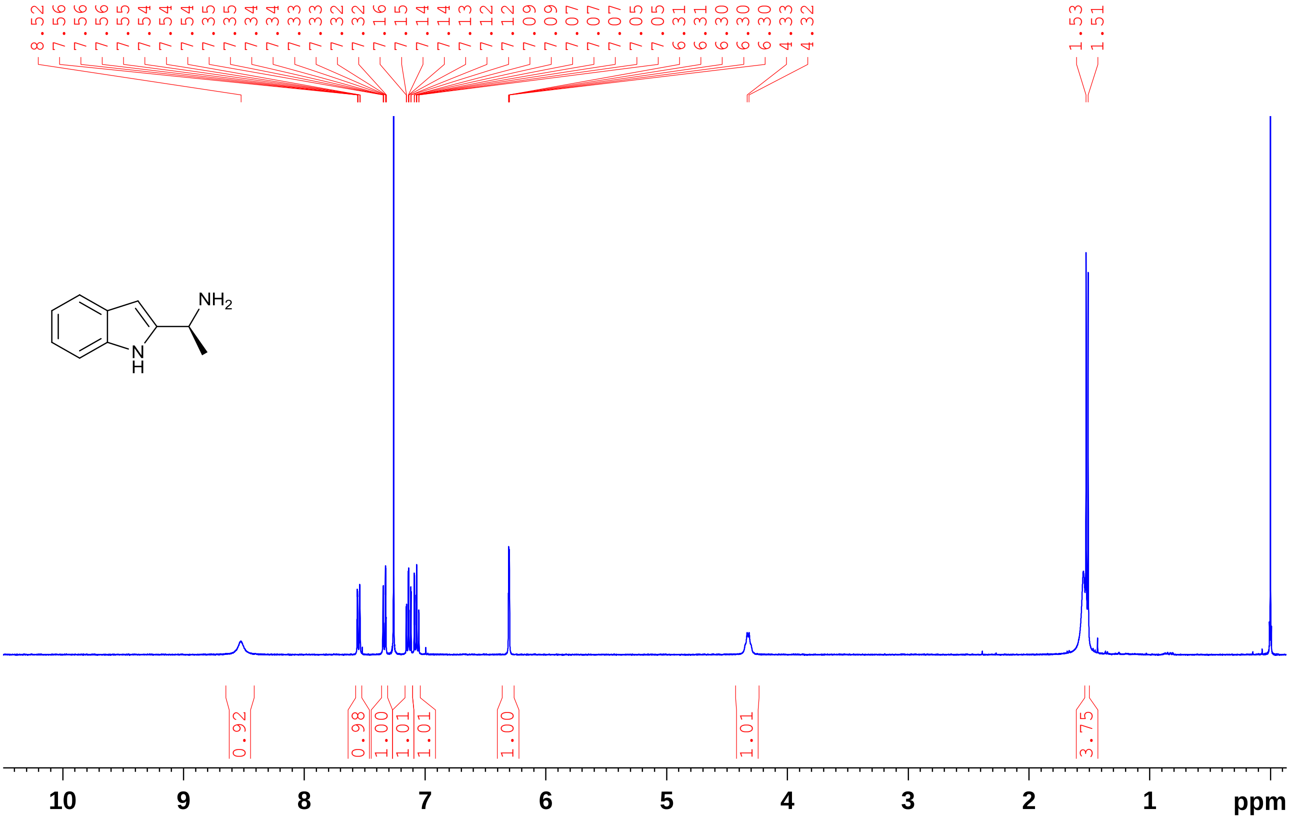
NMR ^{1}H: 18d



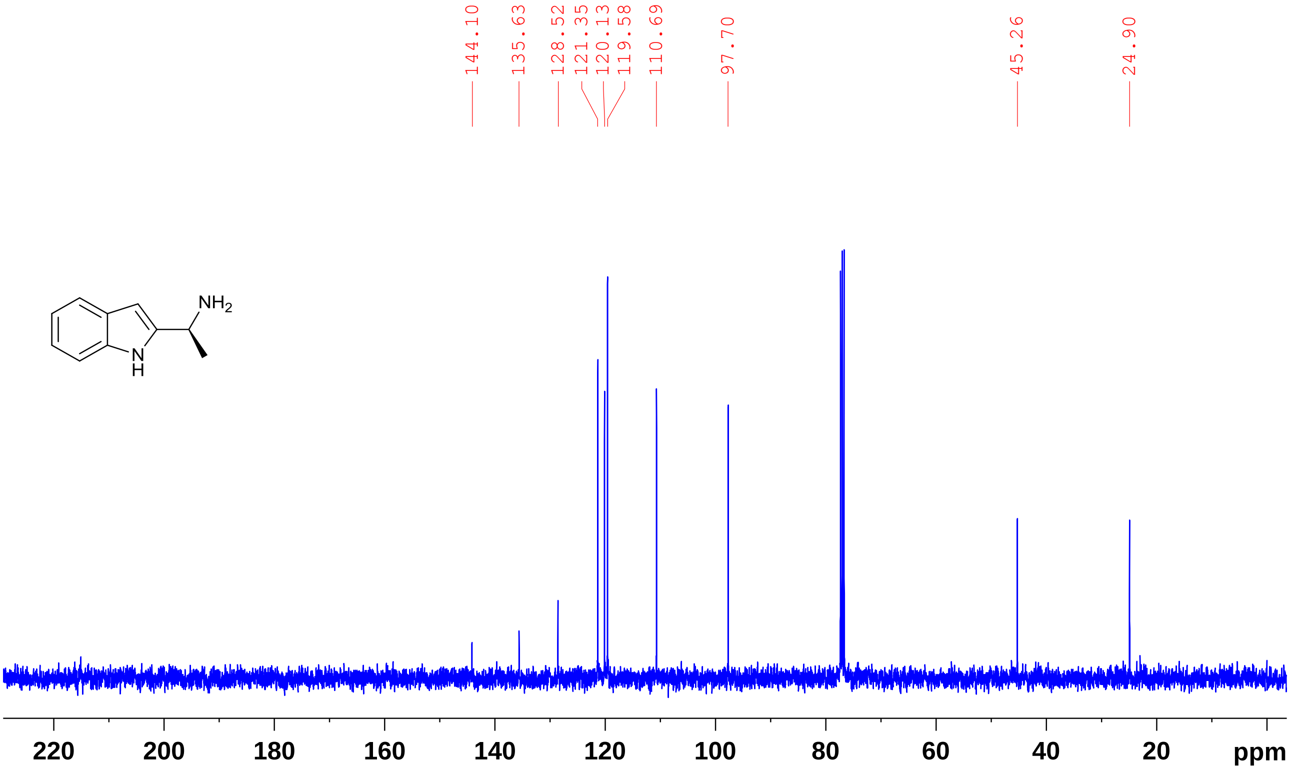
NMR ^{13}C: 18d



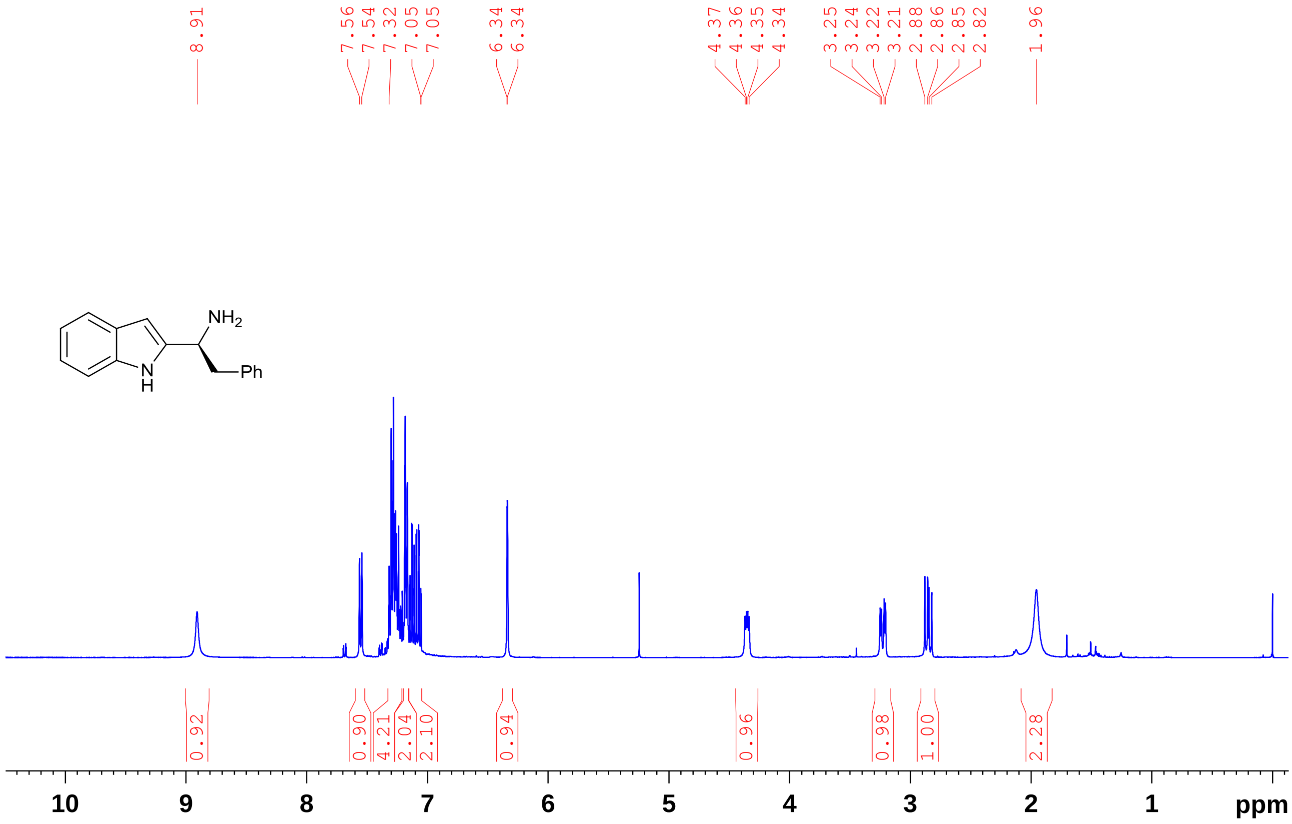
NMR ^{1}H: 22a



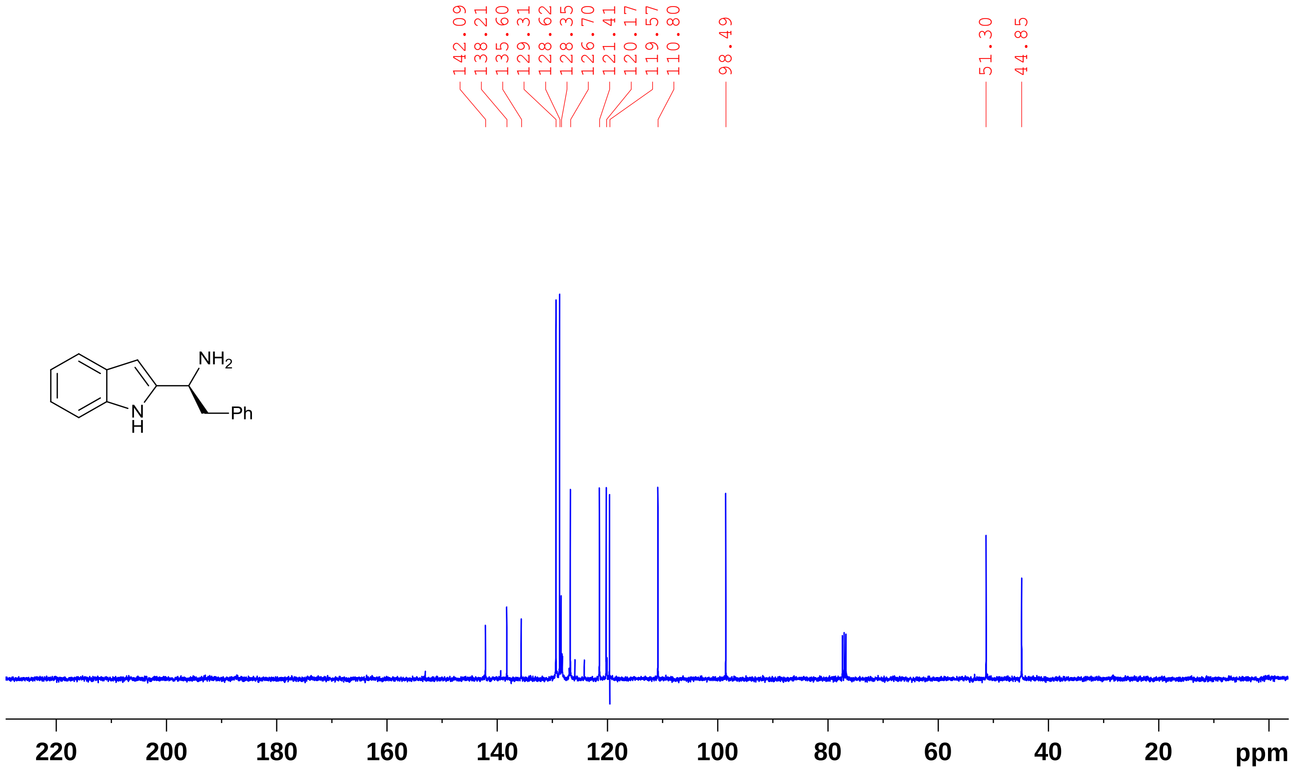
NMR ^{13}C: 22a



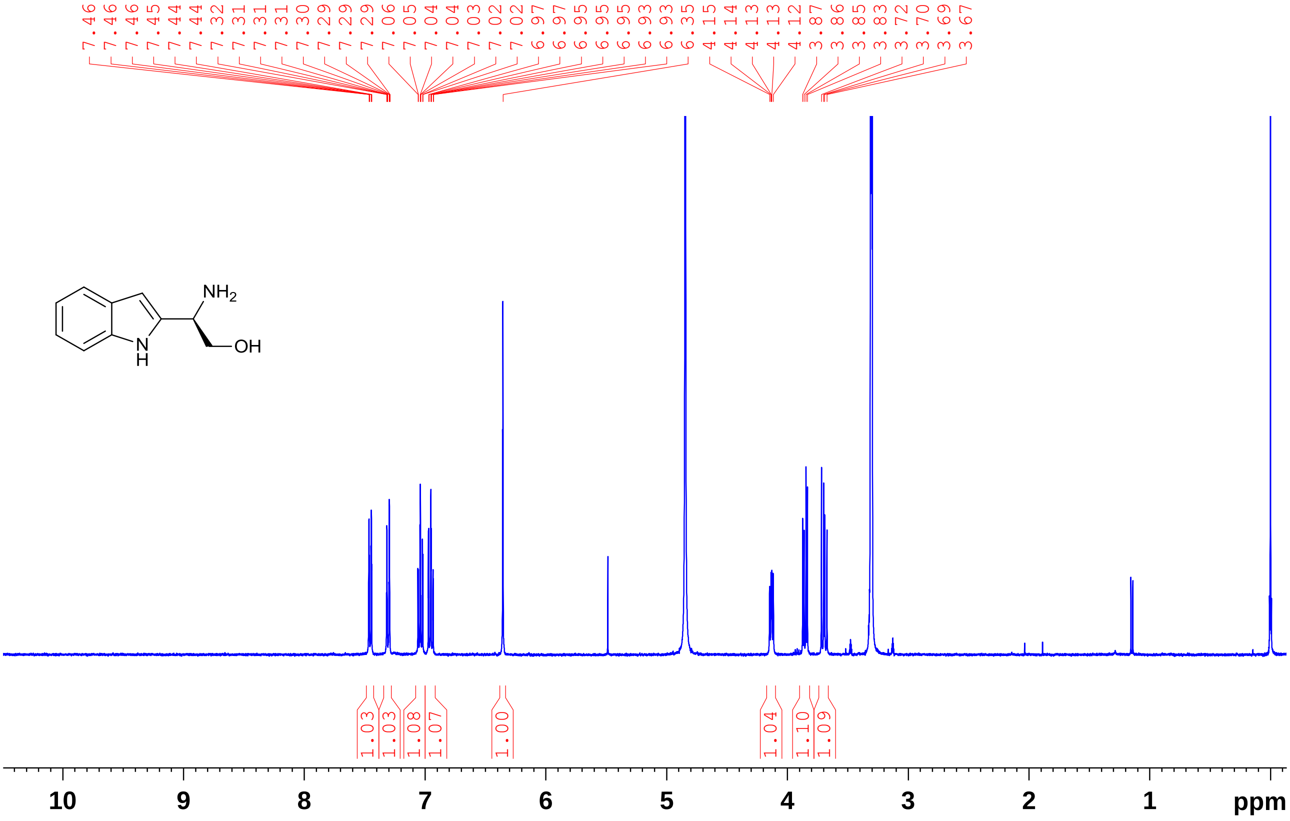
NMR ^{1}H: 22b



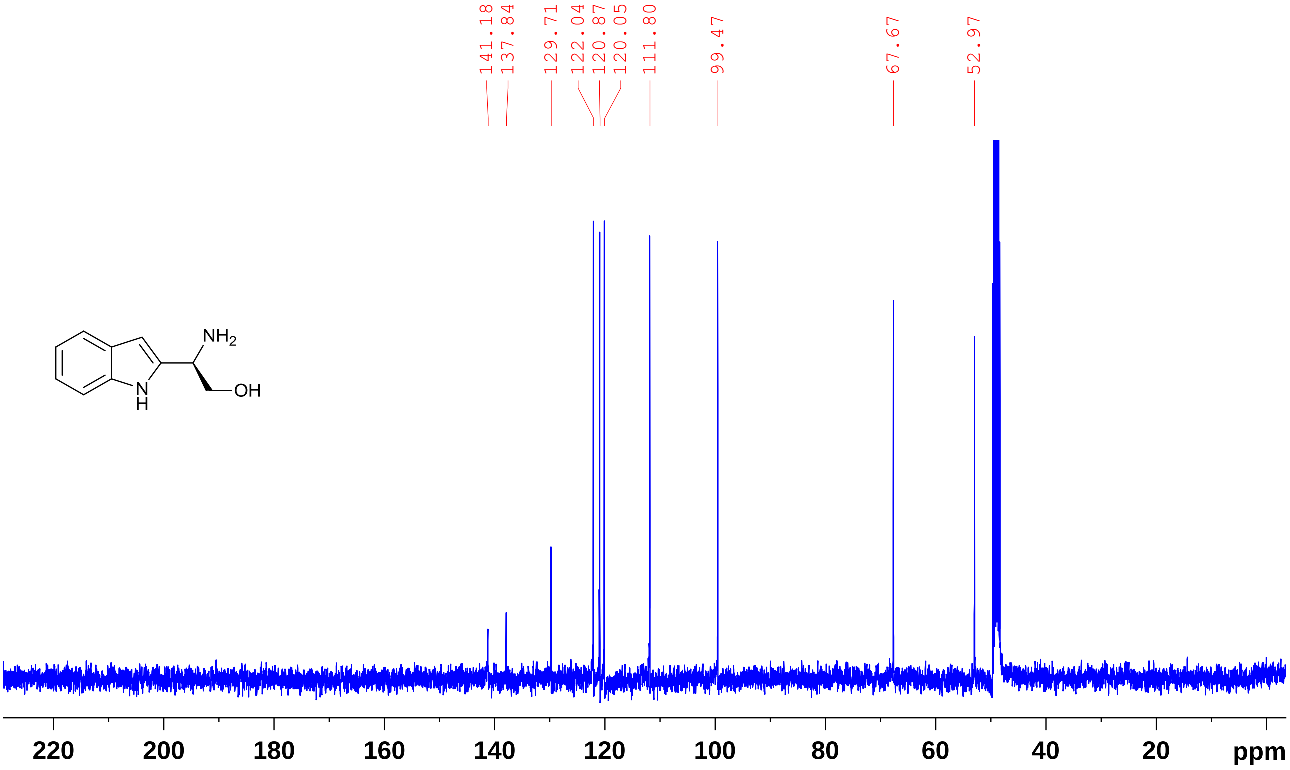
NMR ^{13}C: 22b



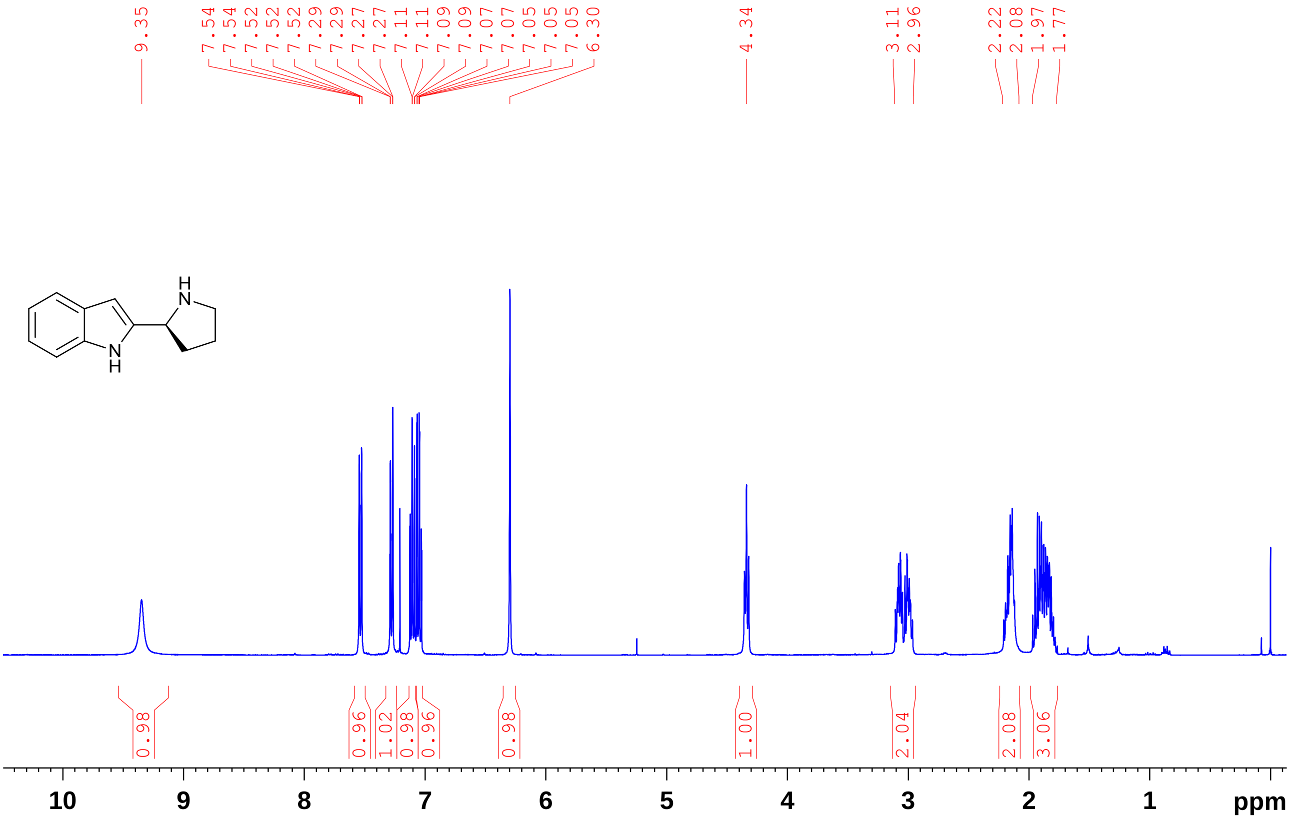
NMR ^{1}H: 22c



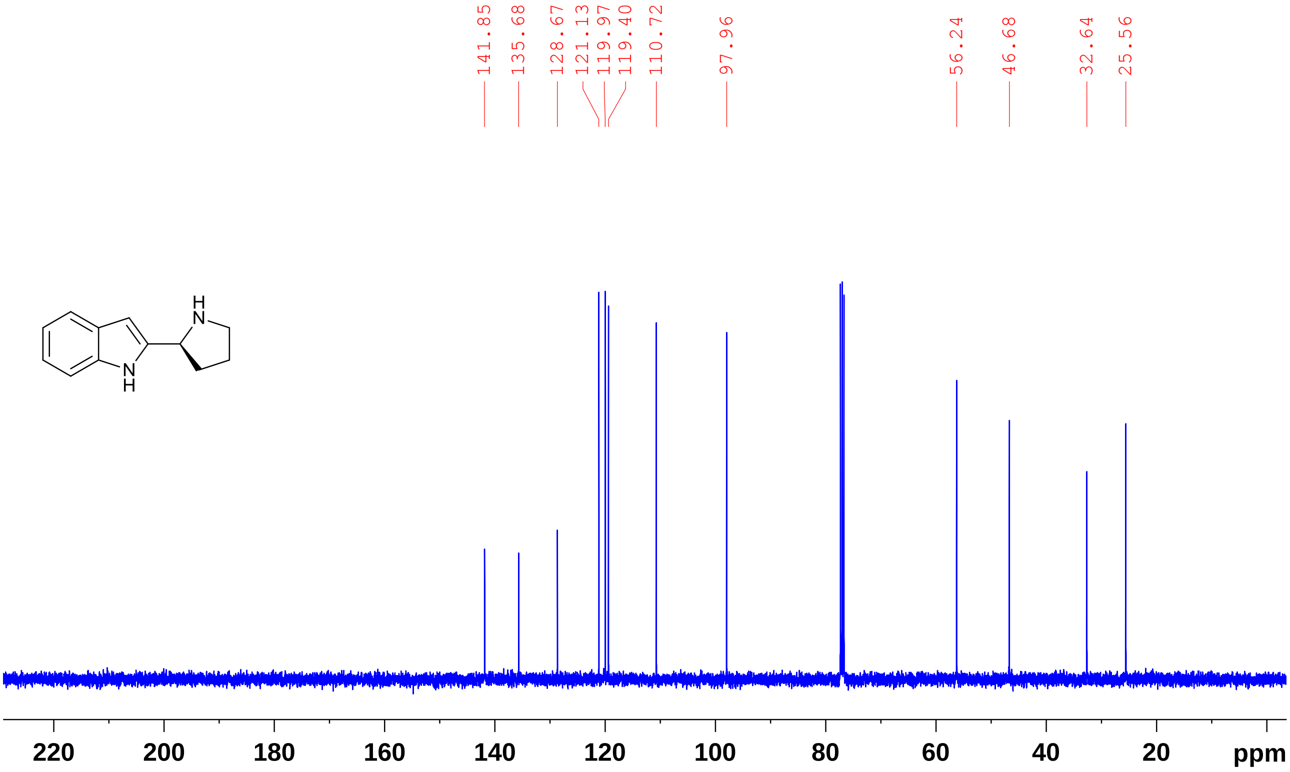
NMR ^{1}H: 22c



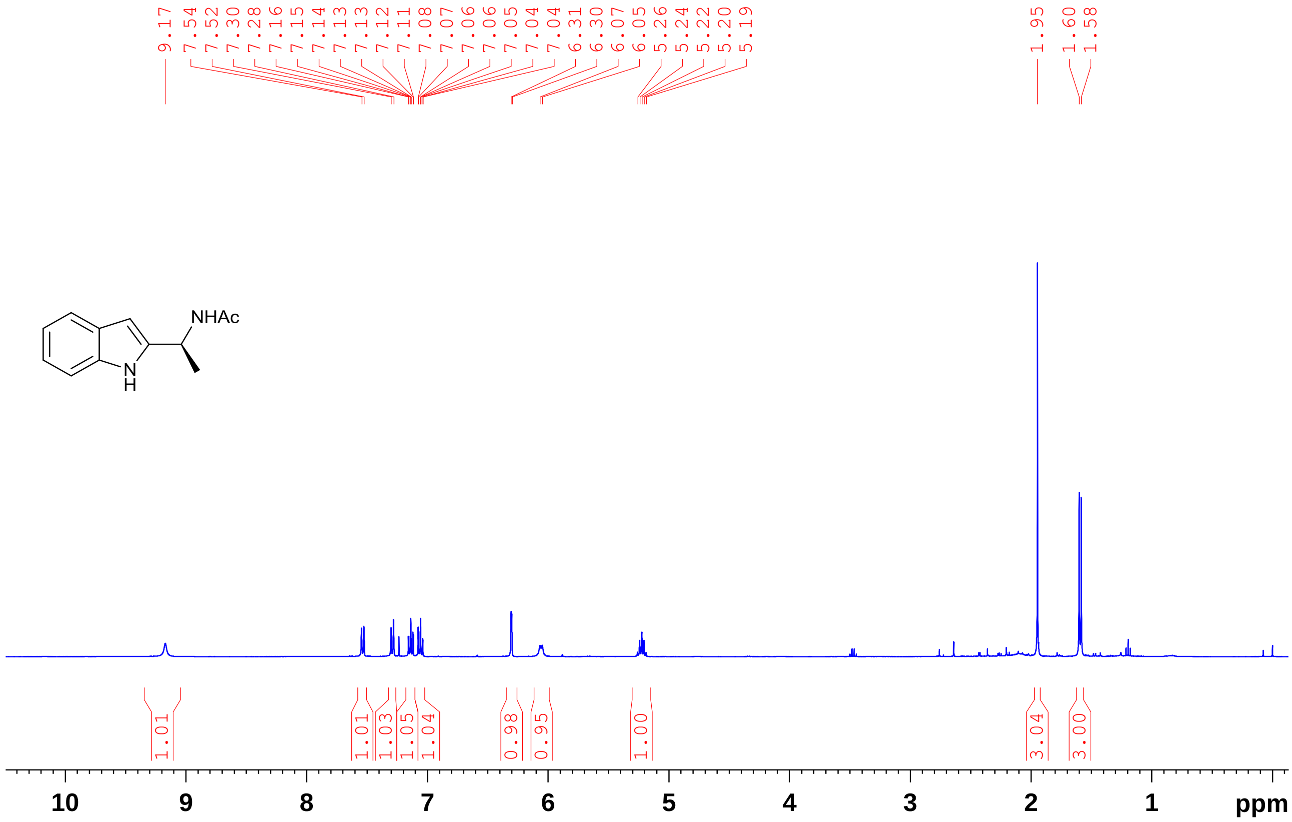
NMR ^{1}H: 22d



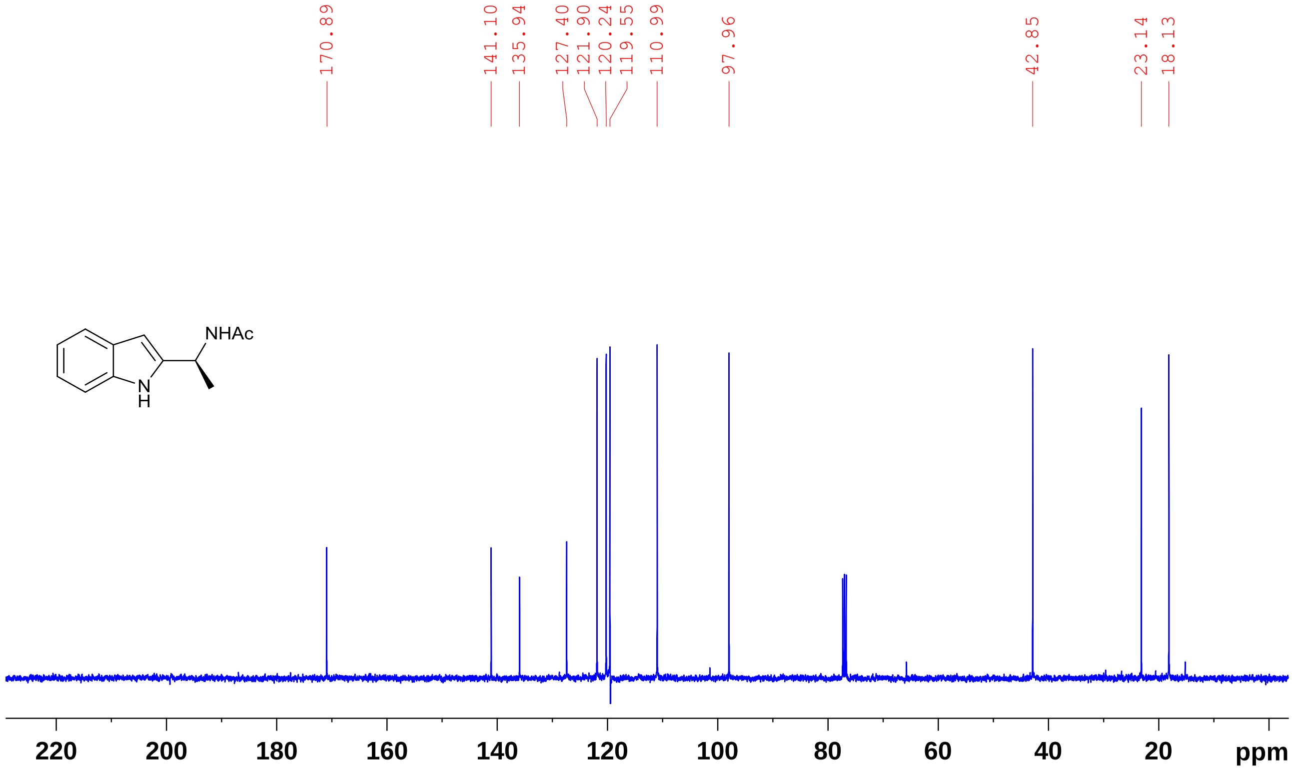
NMR ^{13}C: 22d



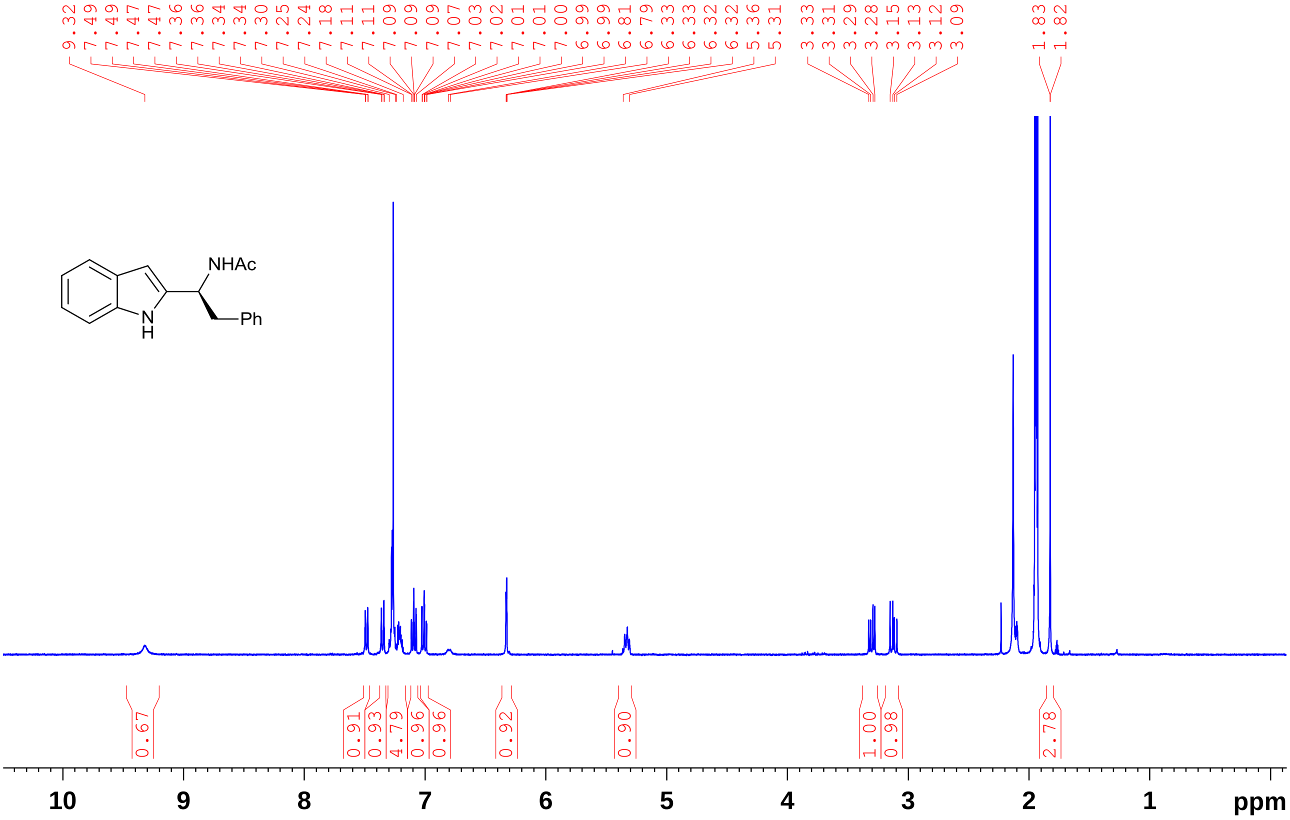
NMR ^{1}H: 25a



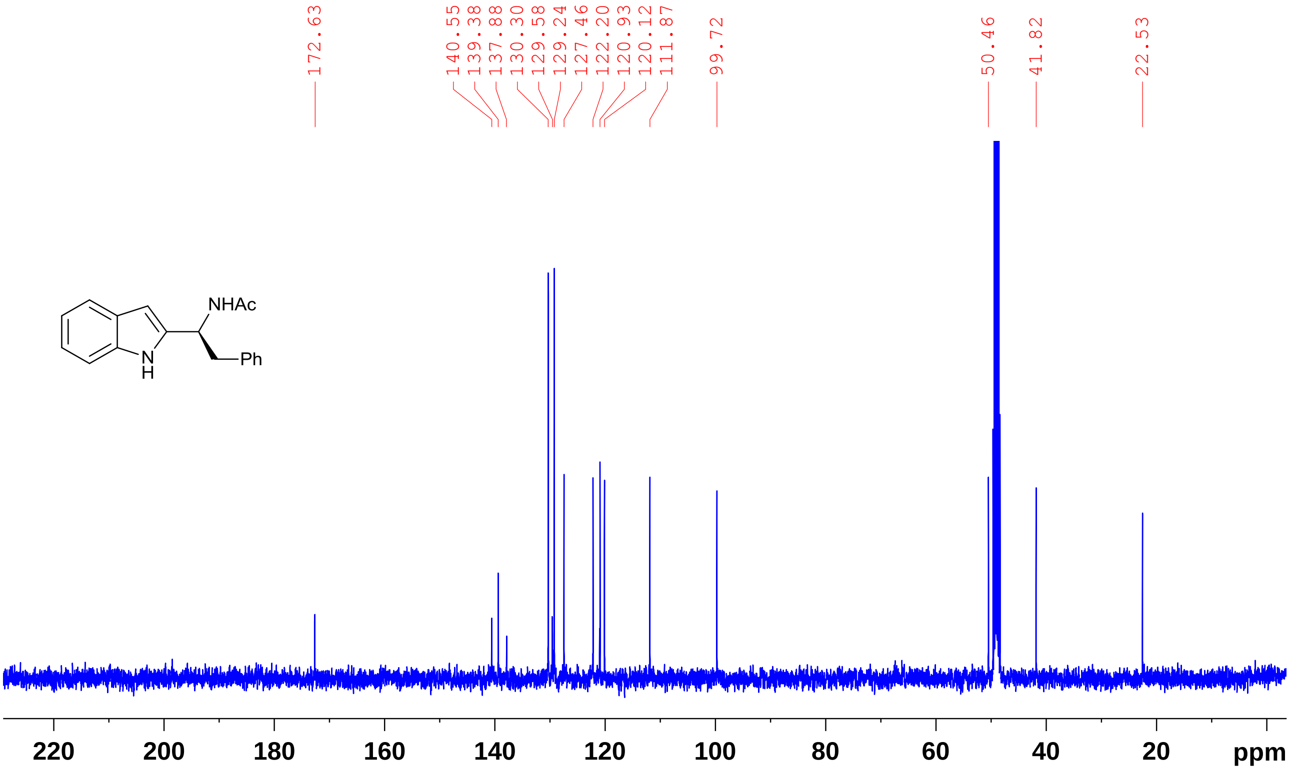
NMR ^{13}C: 25a



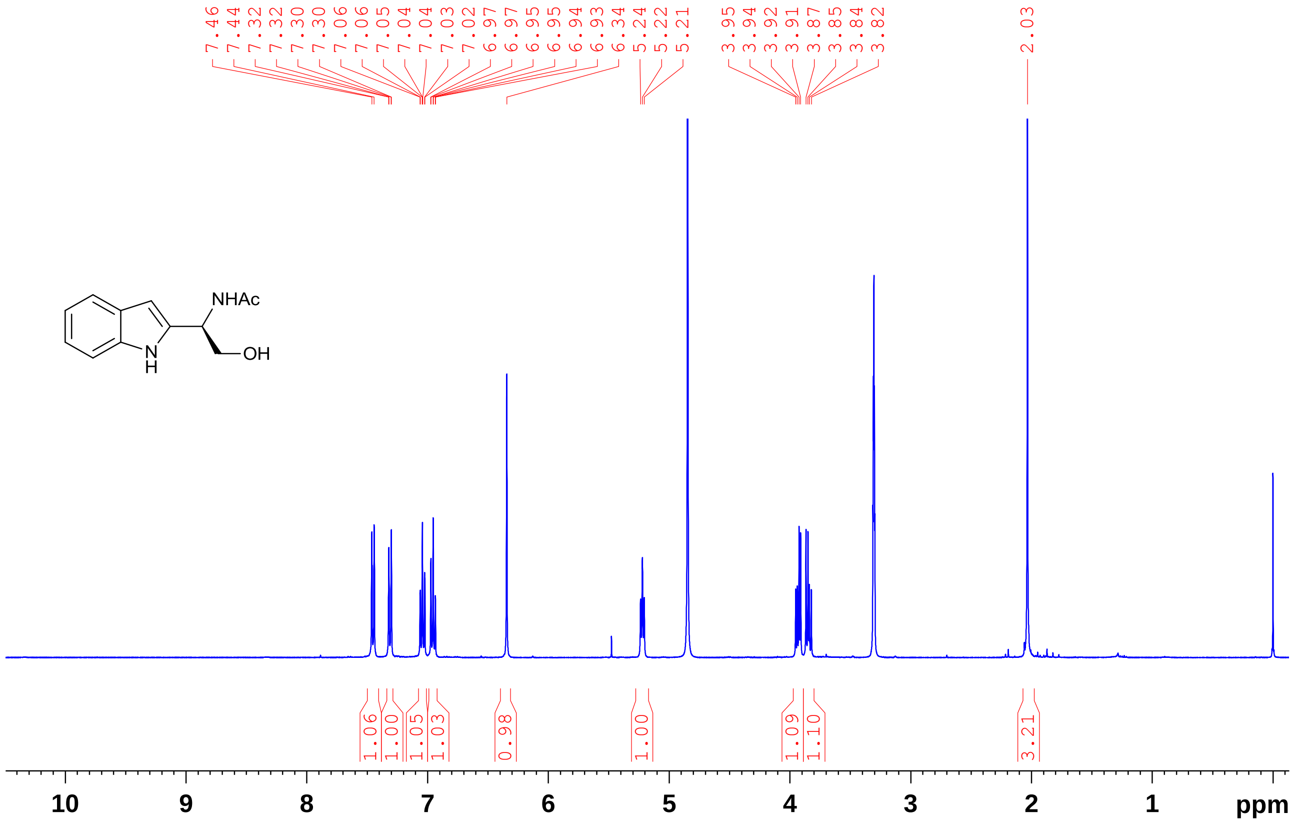
NMR ^{1}H: 25b



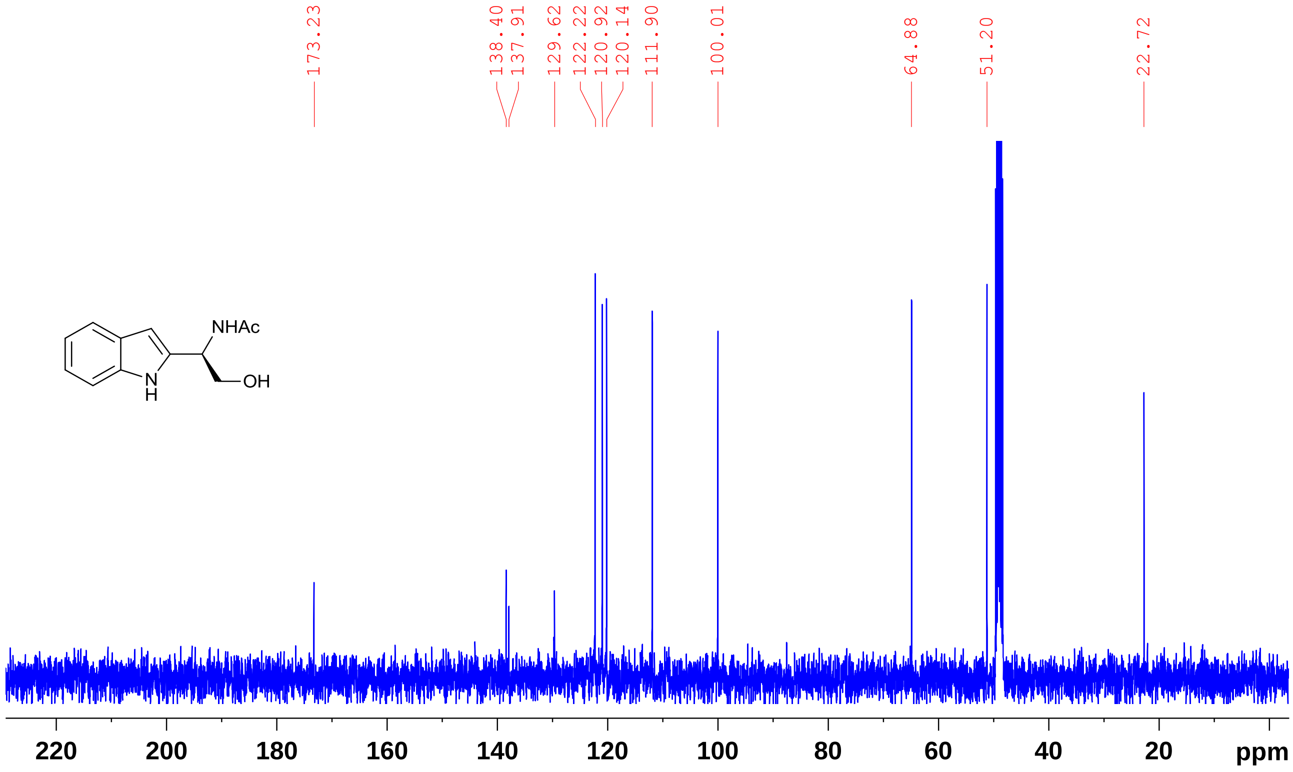
NMR ^{13}C: 25b



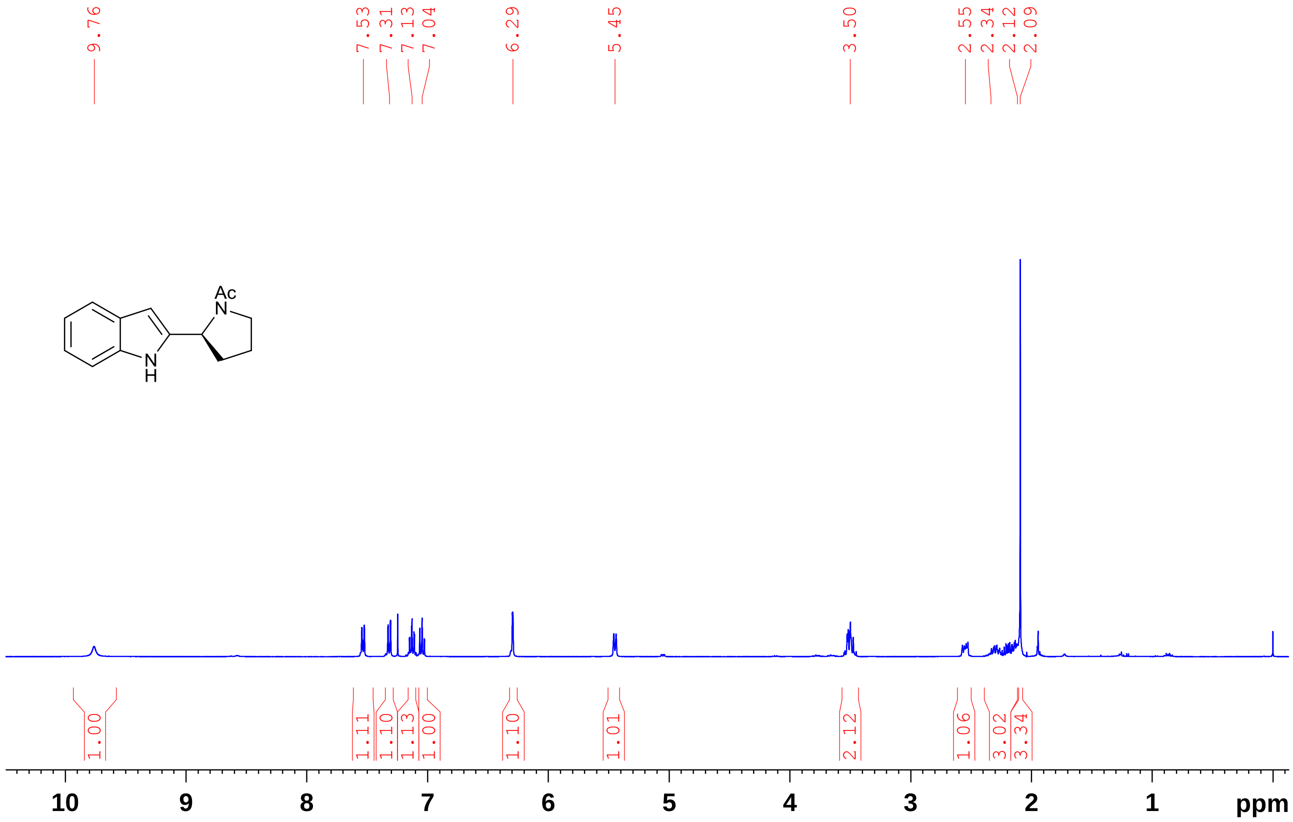
NMR ^{1}H: 25c



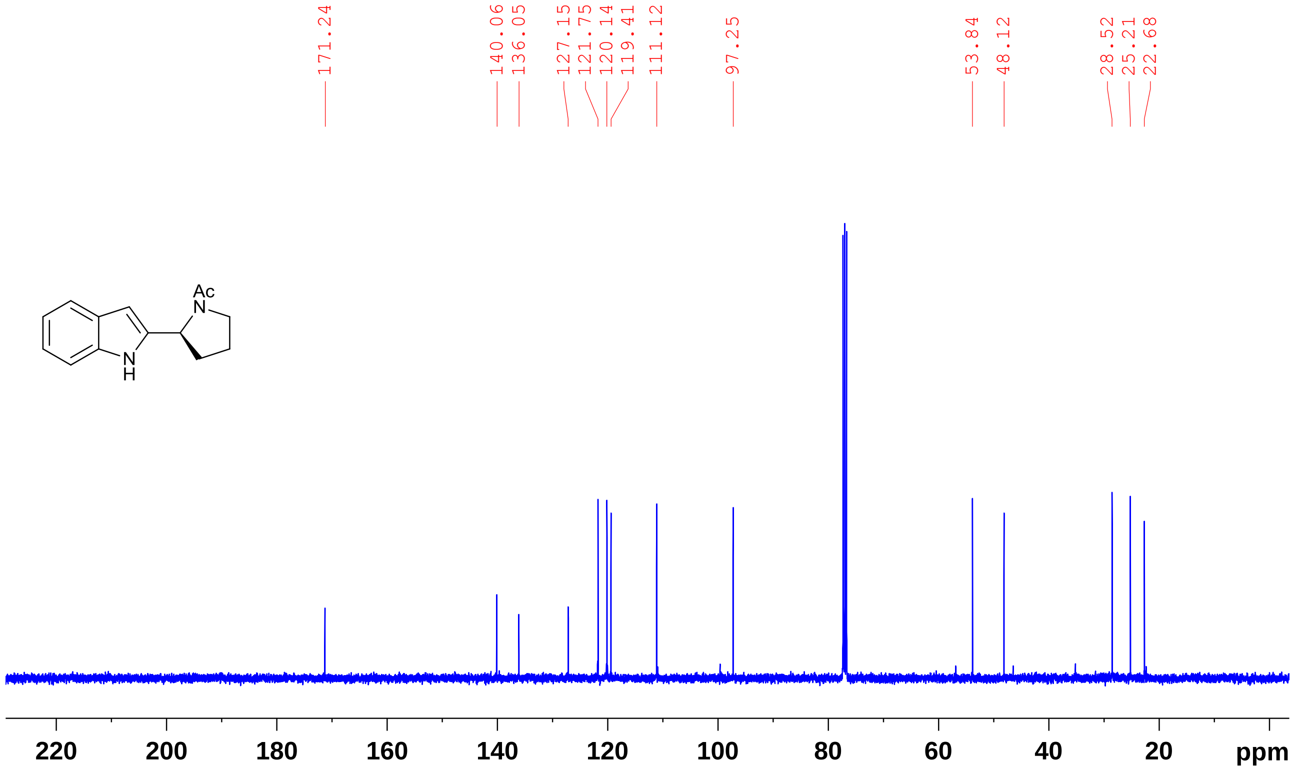
NMR ^{13}C: 25c



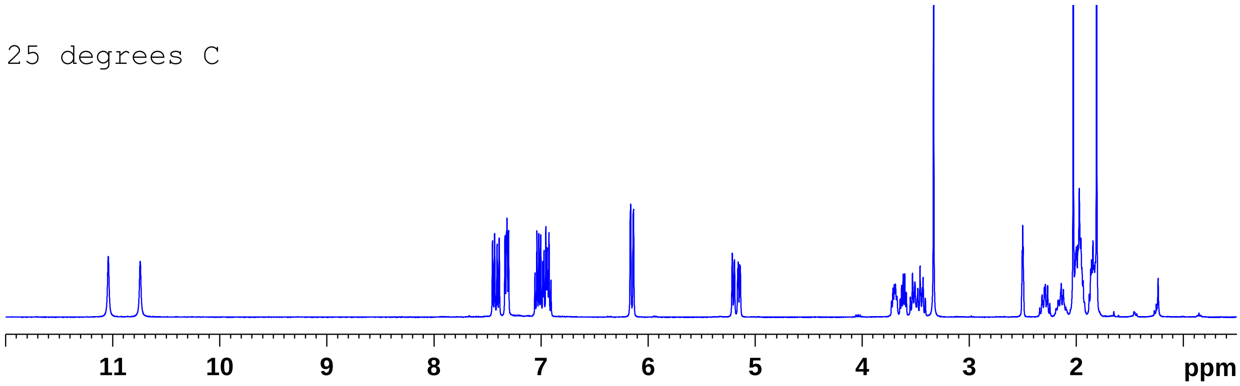
NMR ^{1}H: 25d

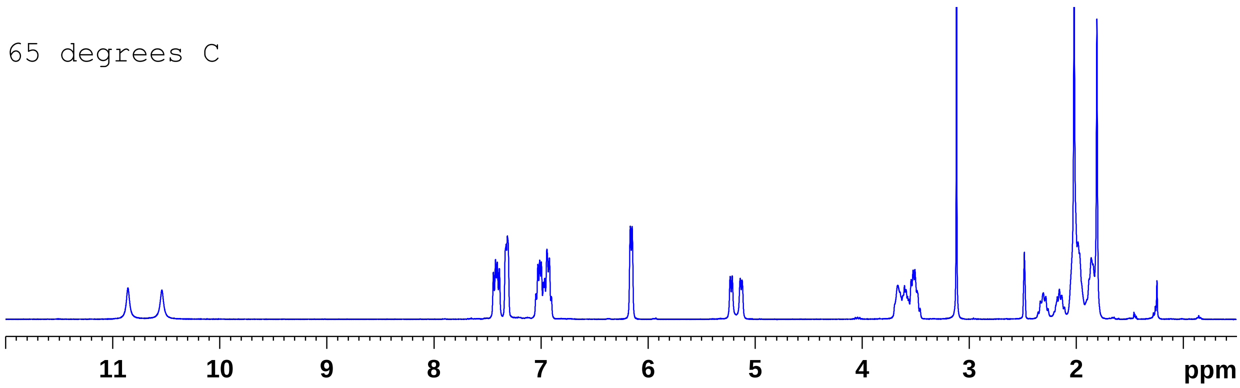


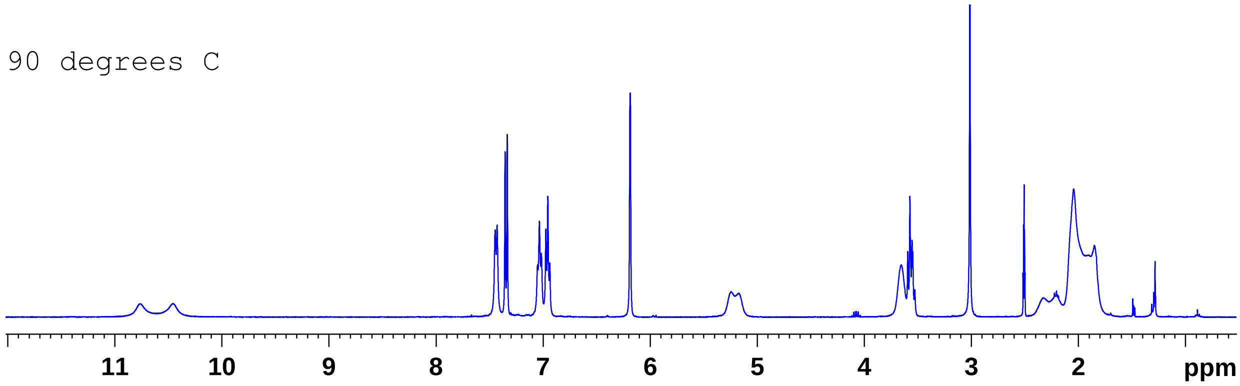
NMR ^{13}C: 25d

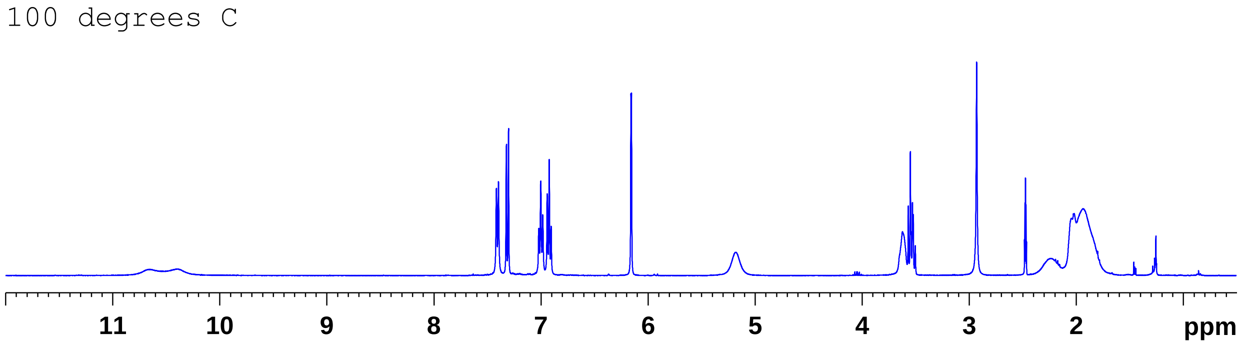


NMR ^{1}H: 25d variable temperature experiment in DMSO-d_6

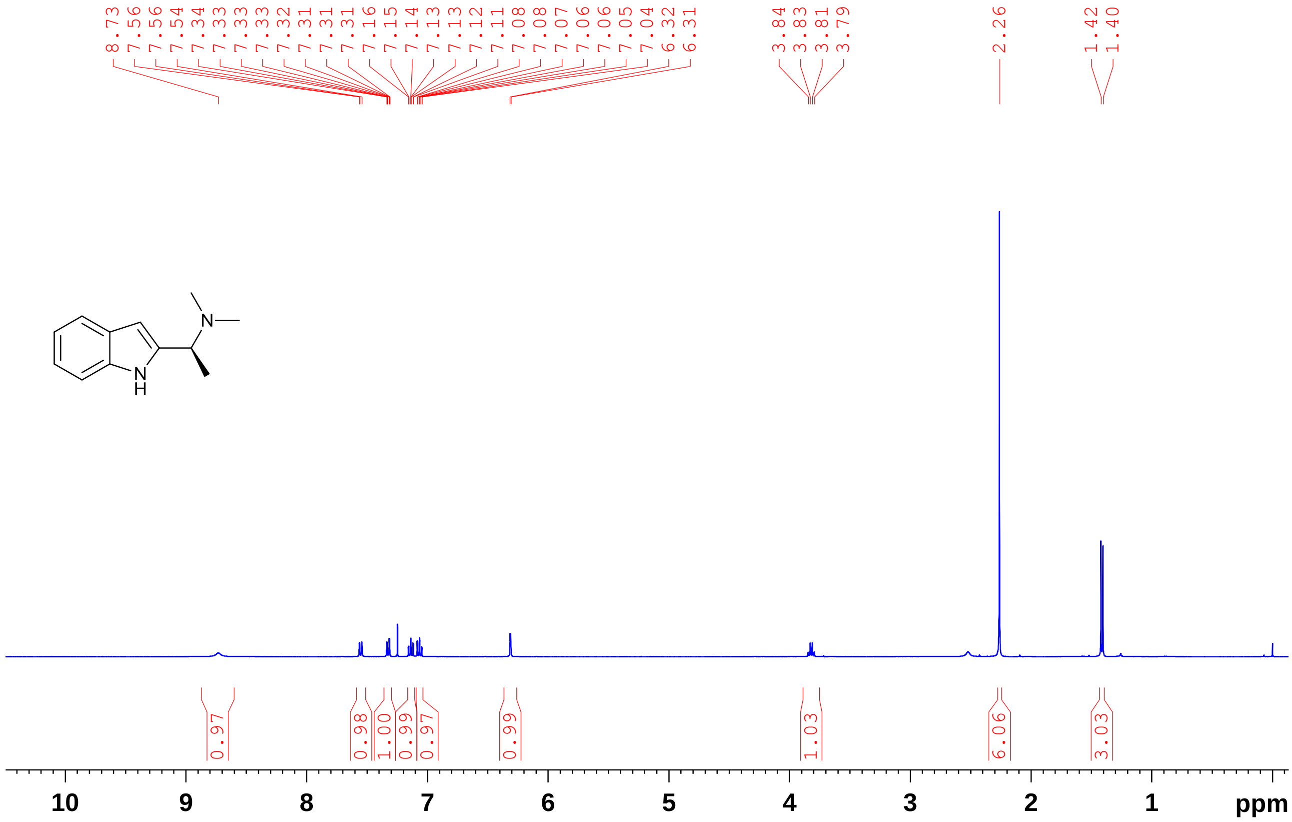




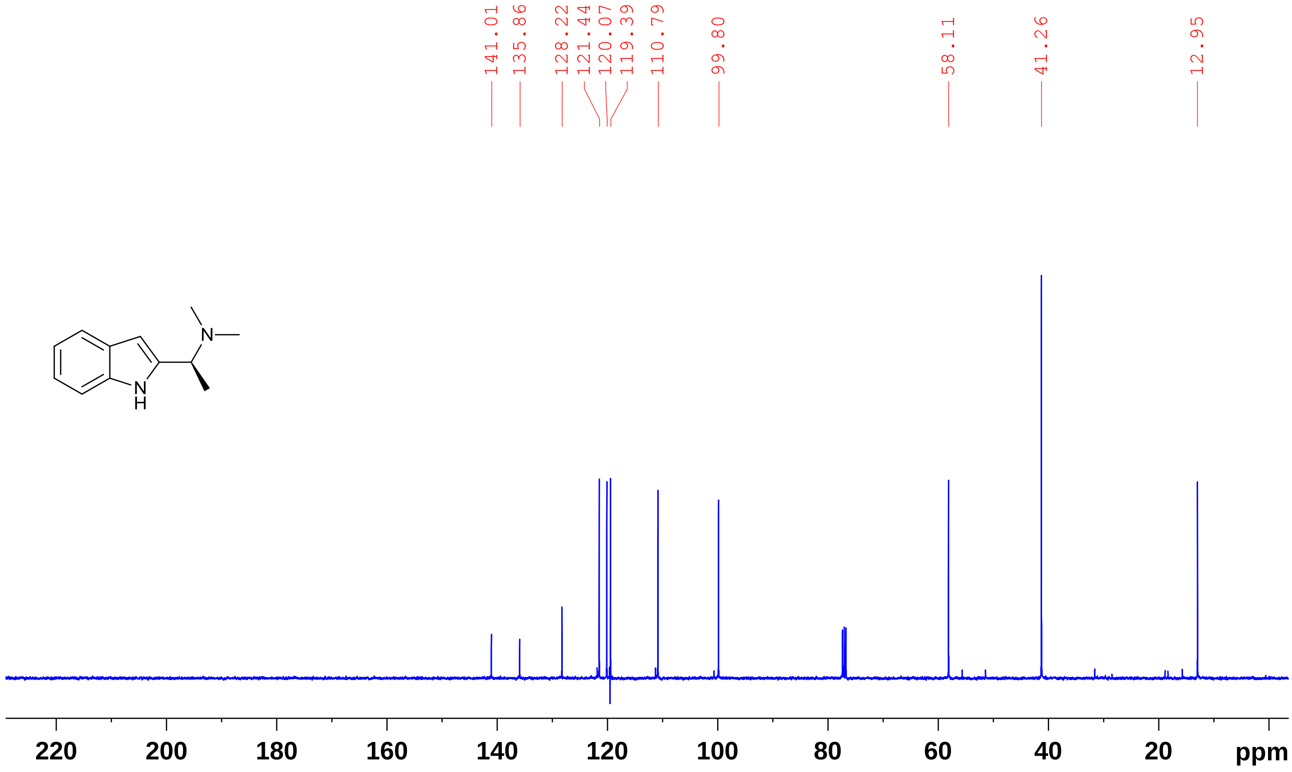




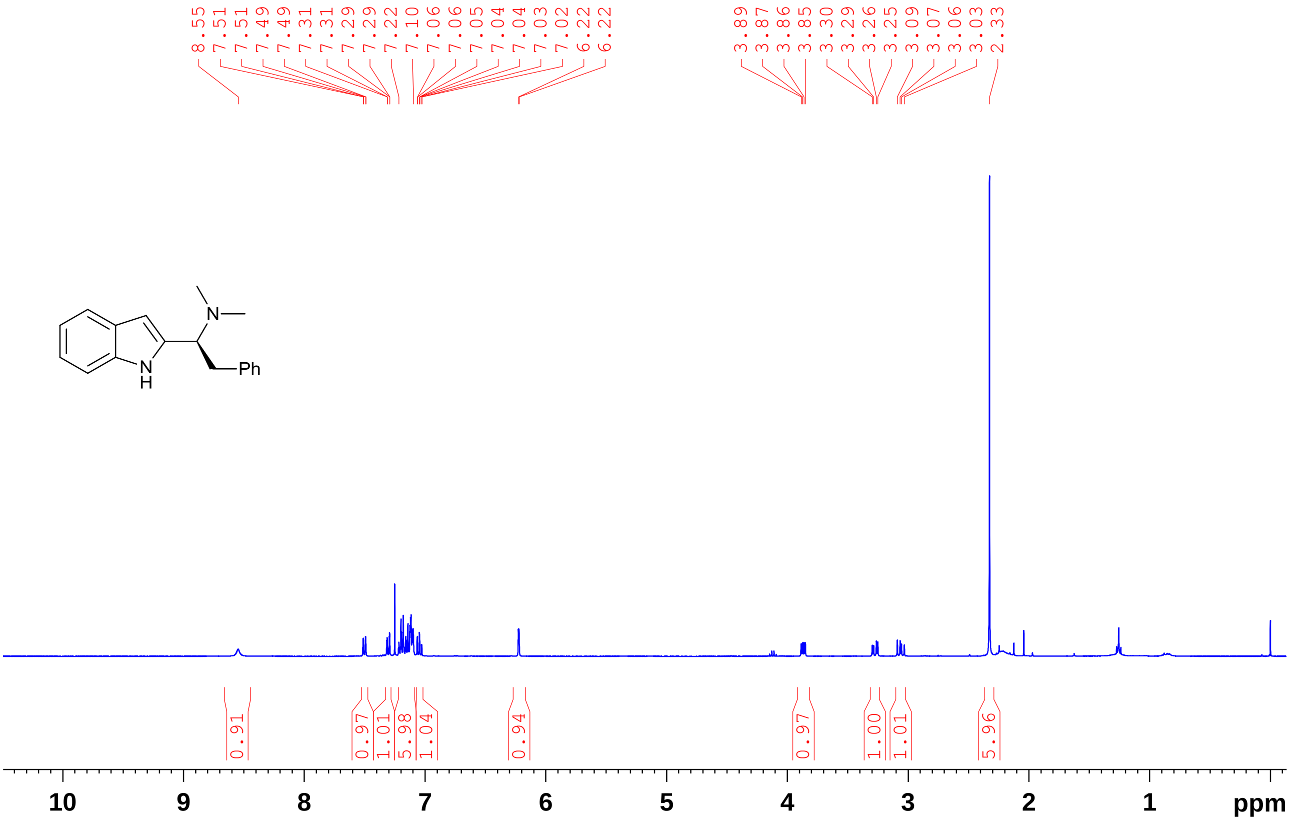
NMR ^{1}H: 26a



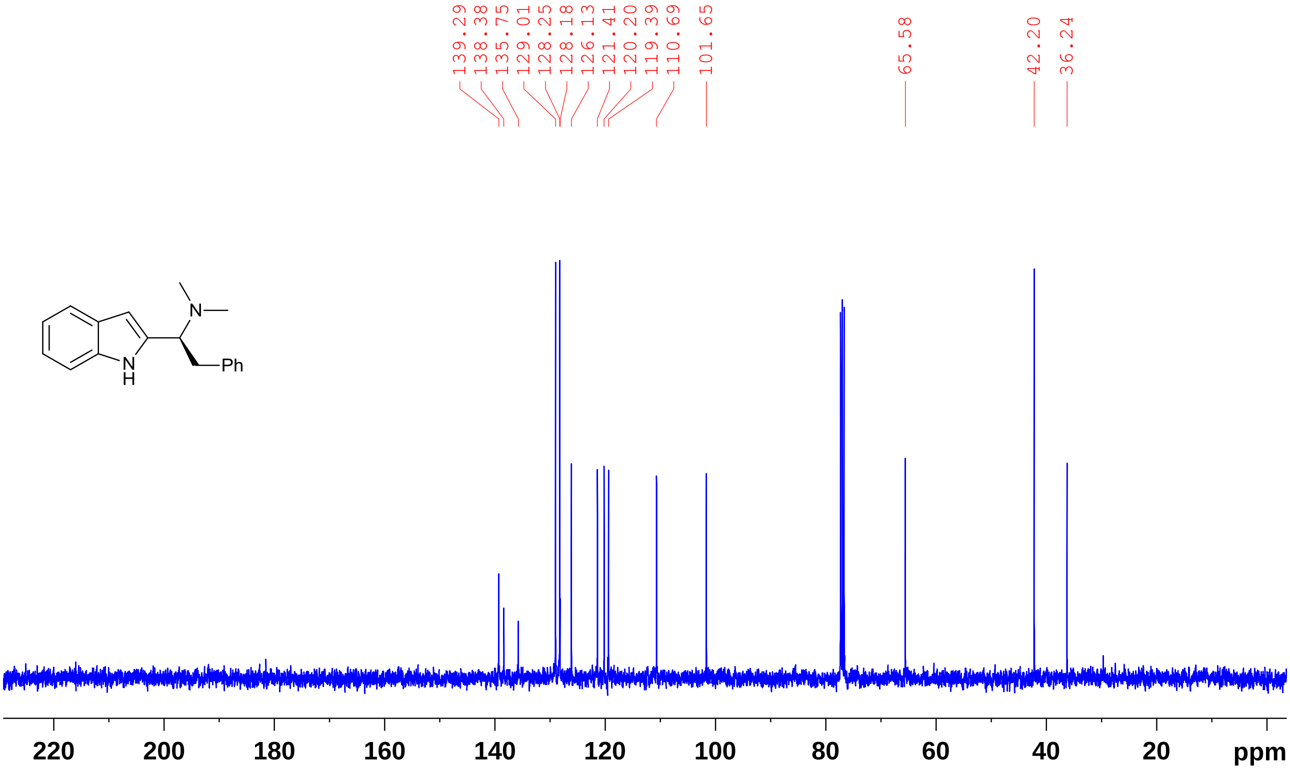
NMR ^{13}C: 26a



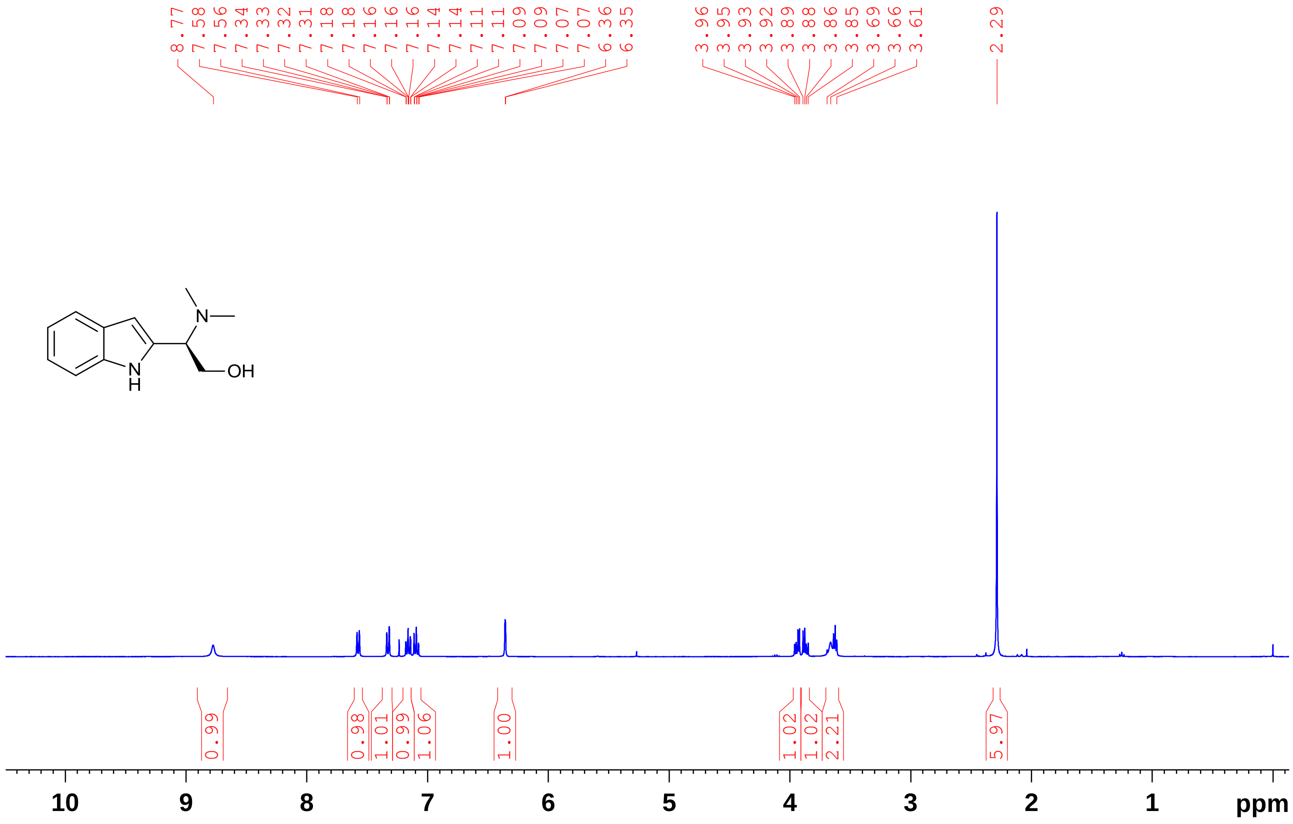
NMR ^{1}H: 26b



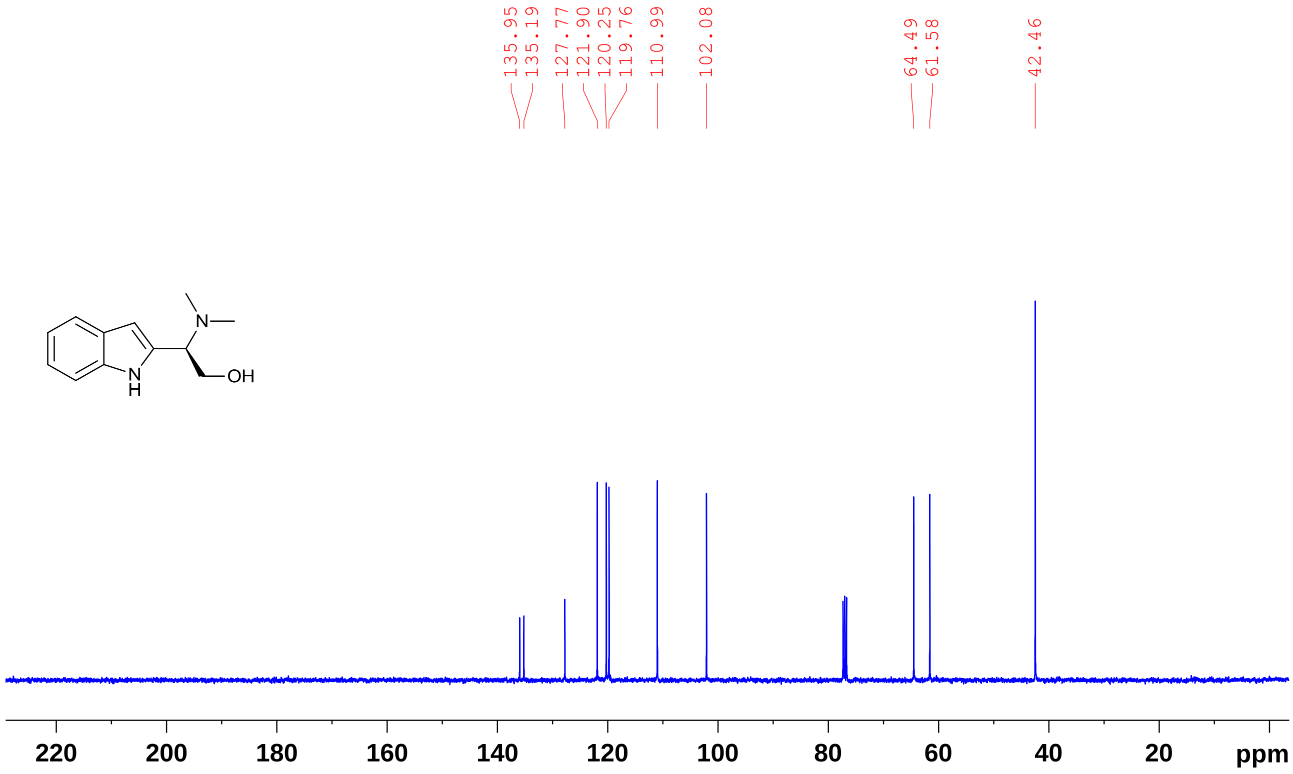
NMR ^{13}C: 26b



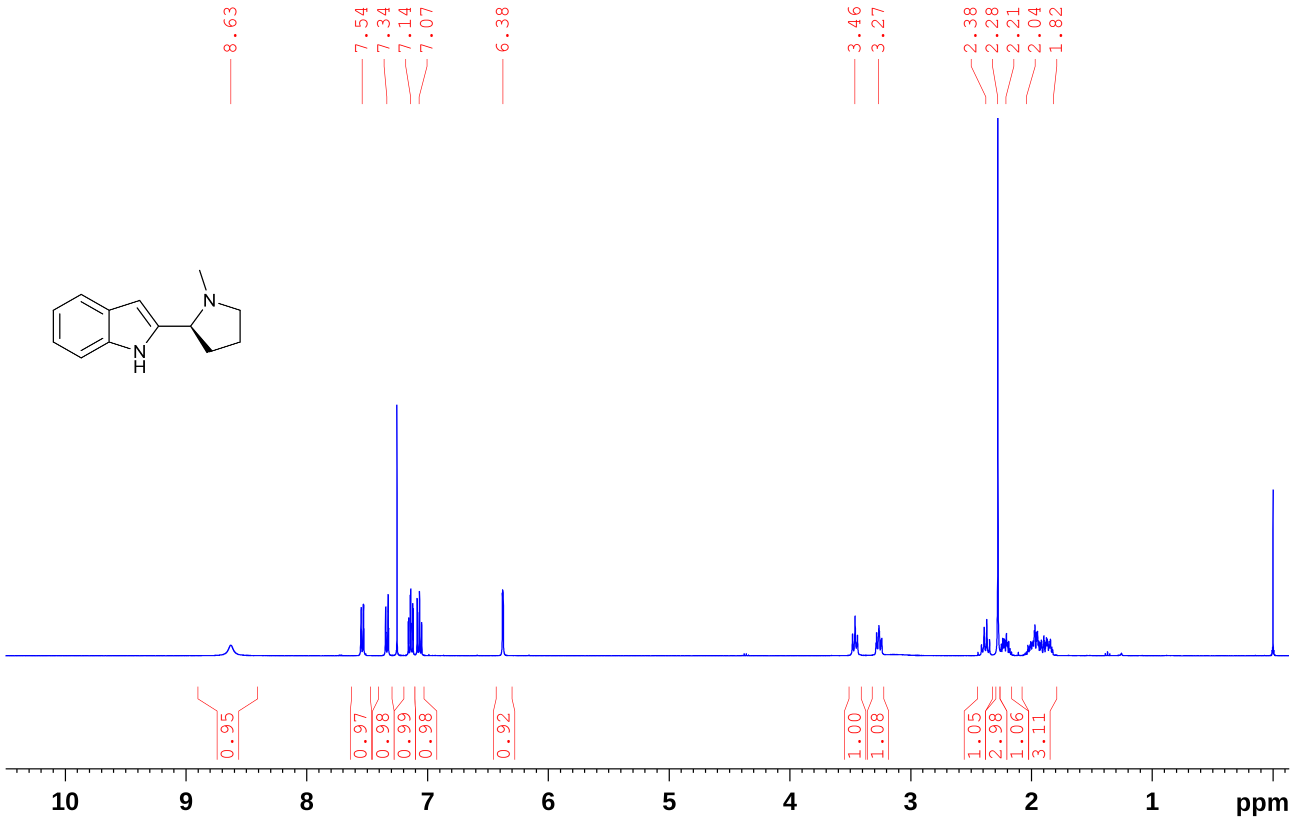
NMR ^{1}H: 26c



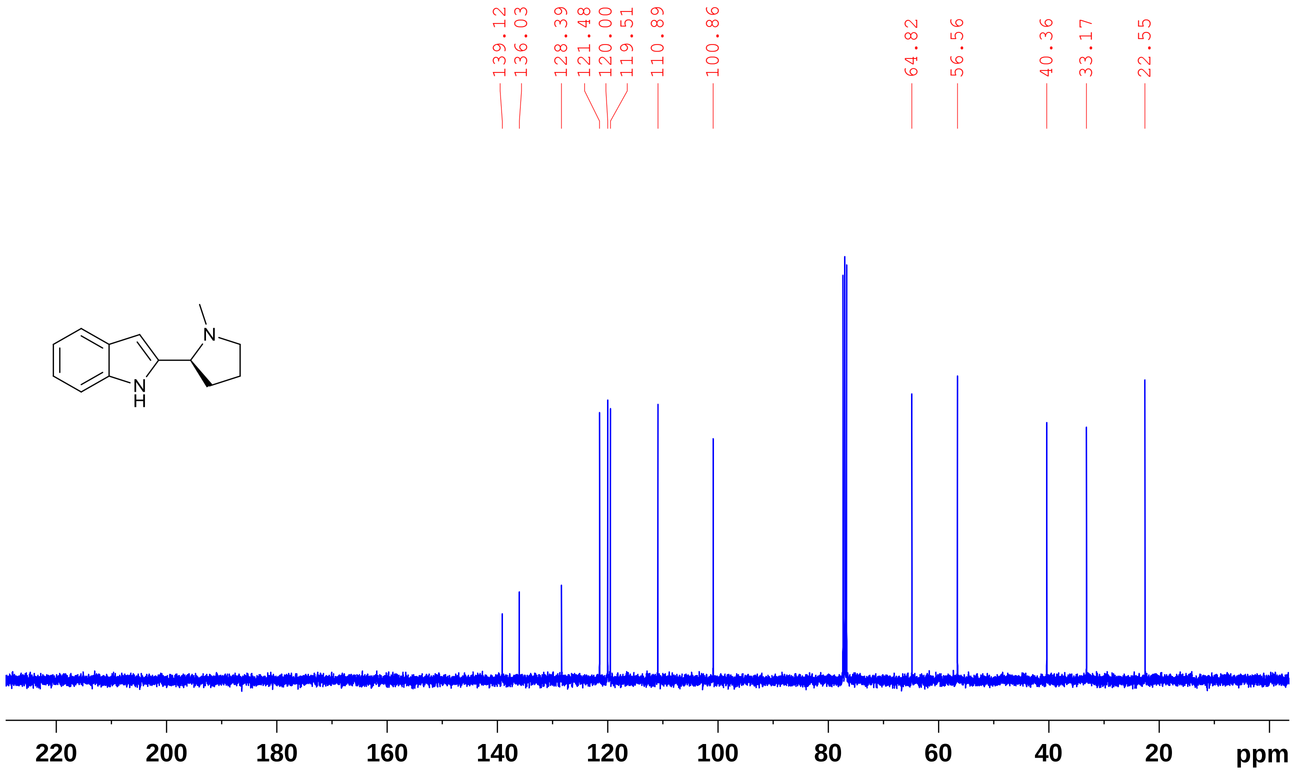
NMR ^{13}C: 26c



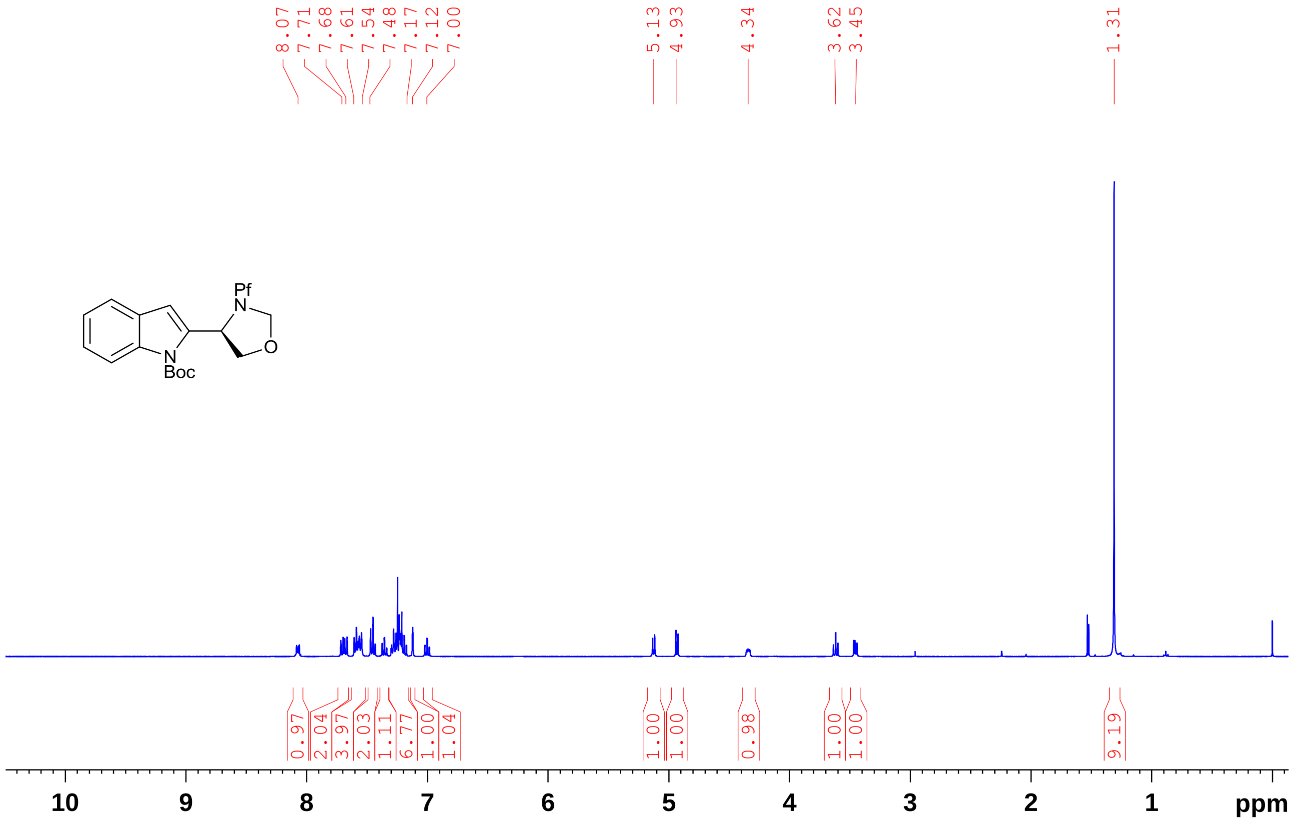
NMR ^{1}H: 26d



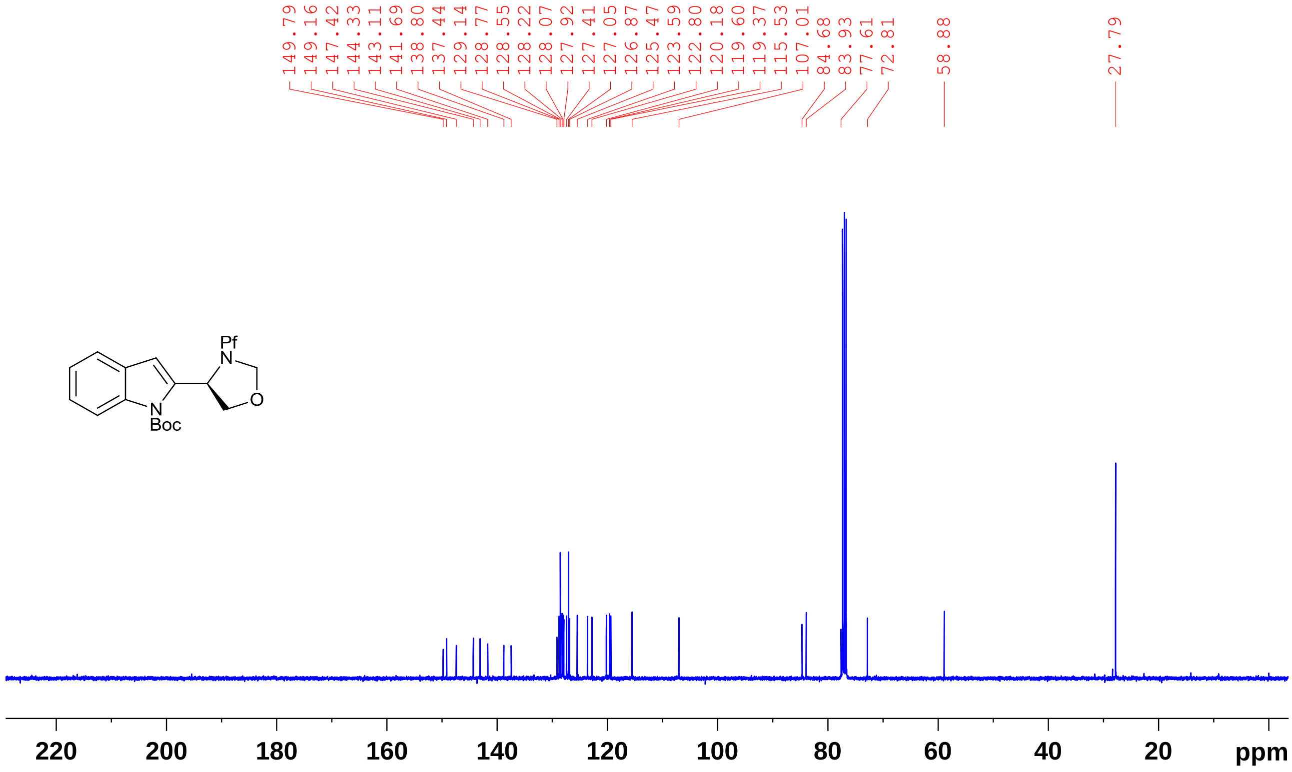
NMR ^{13}C: 26d



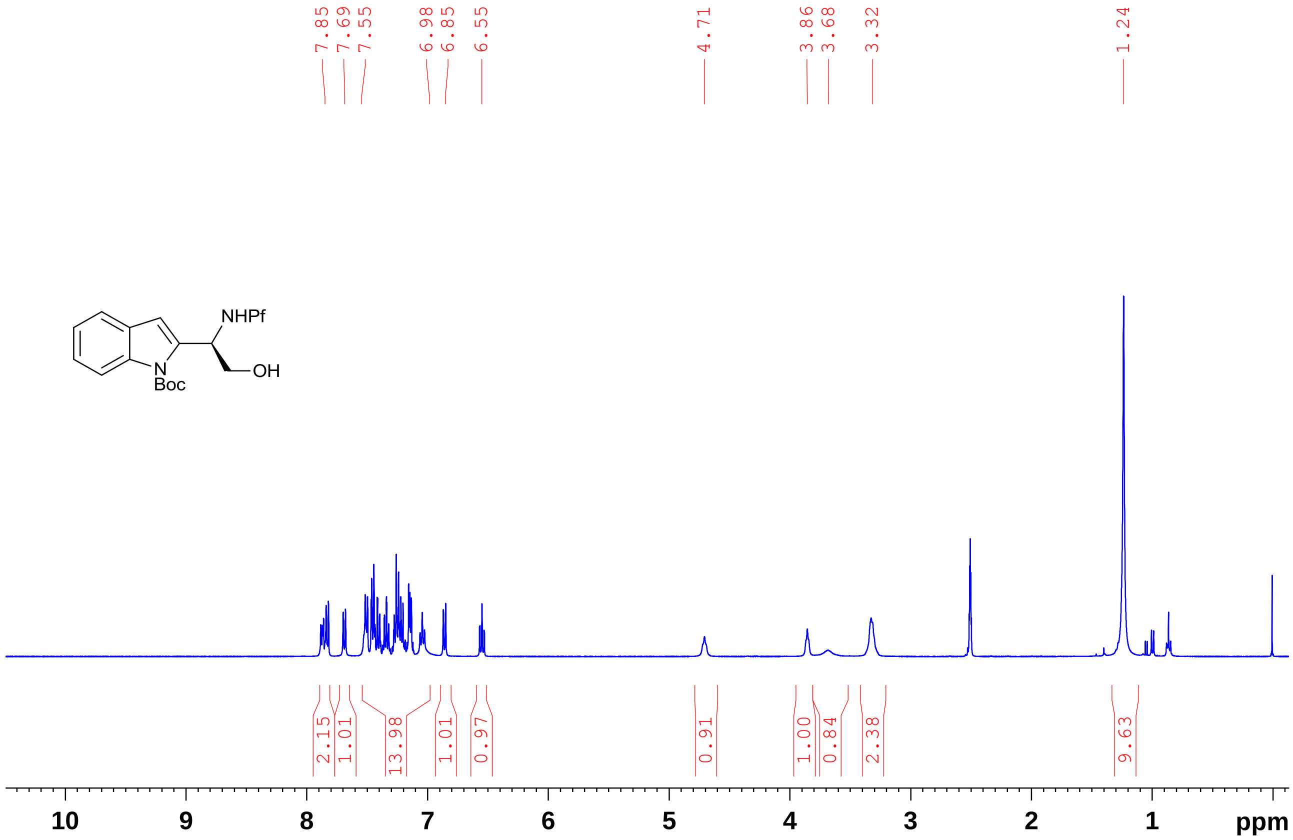
NMR ¹H: 27



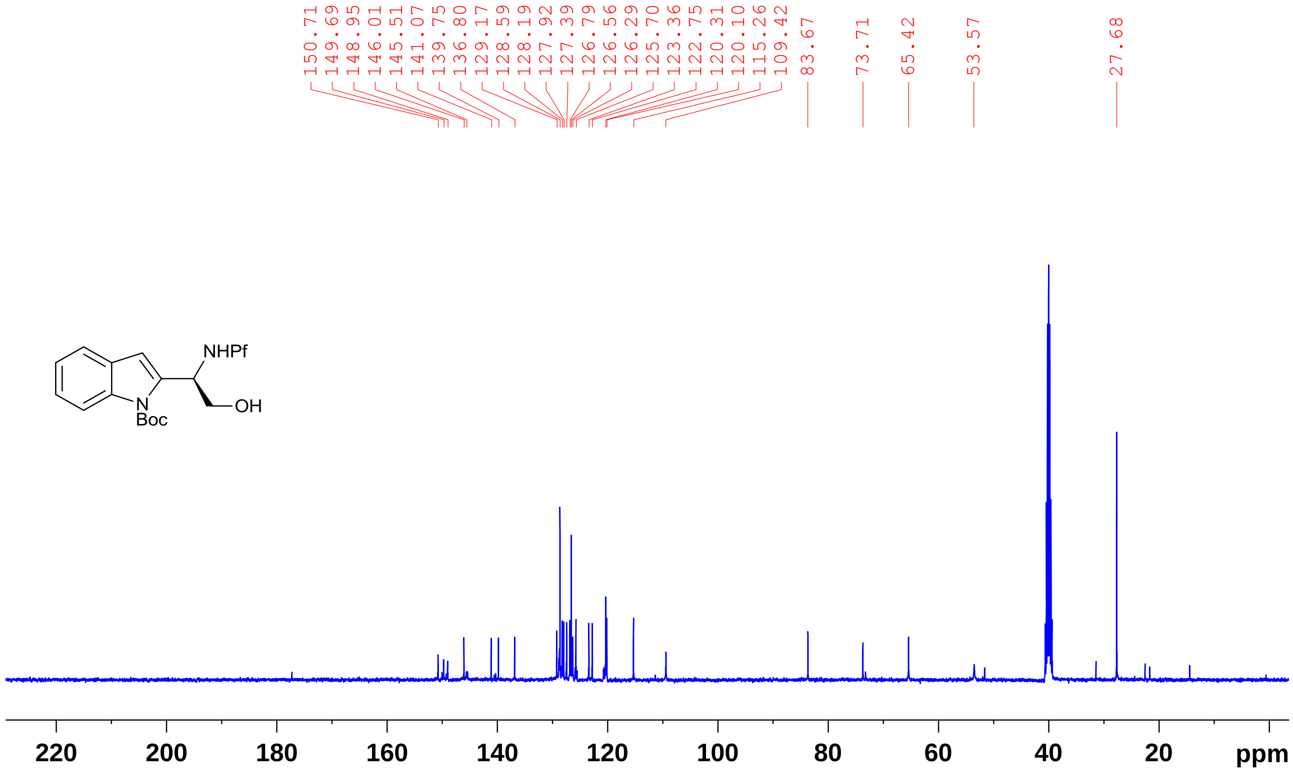
NMR ¹³C: 27



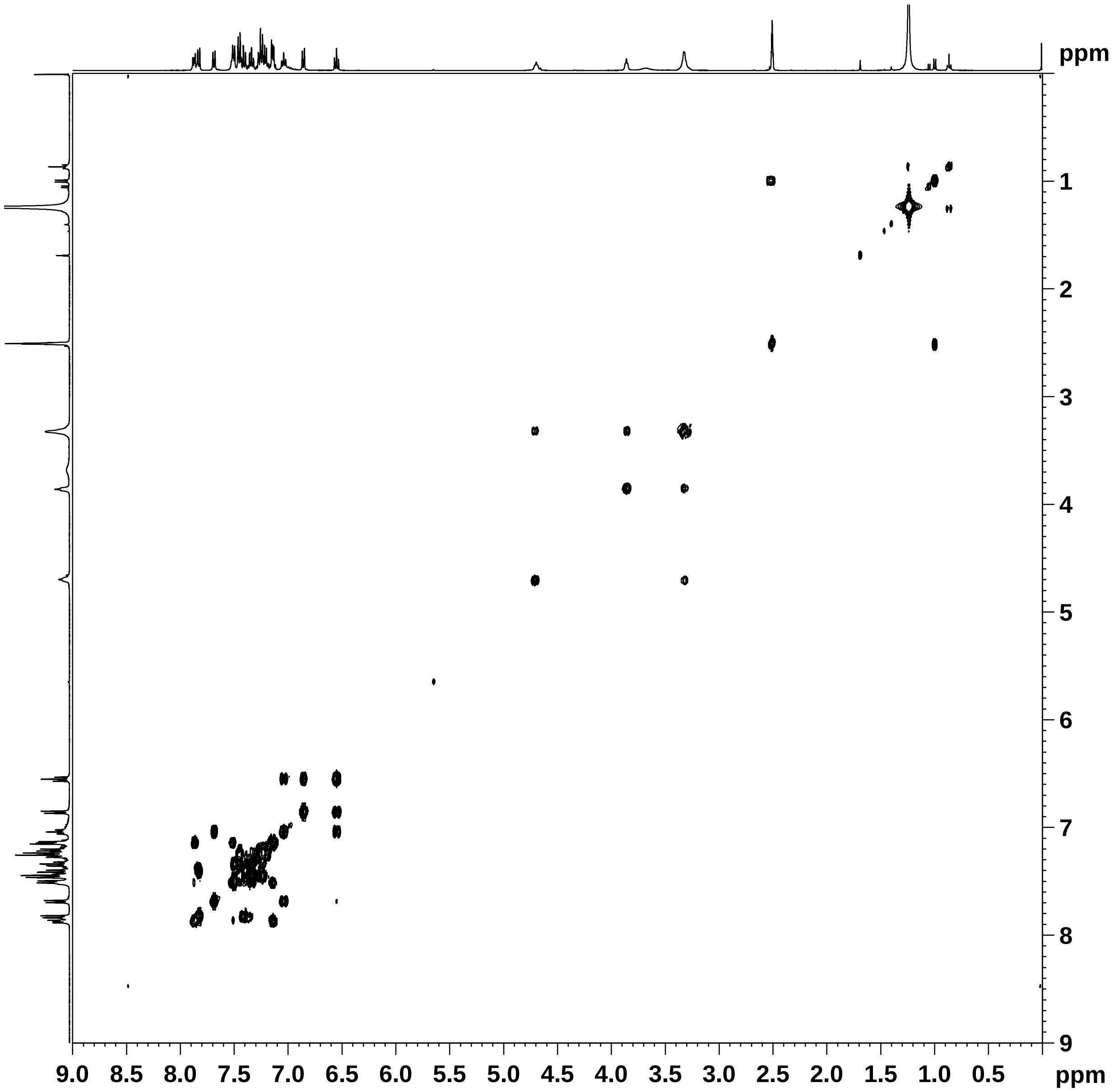
NMR ^{1}H: 28



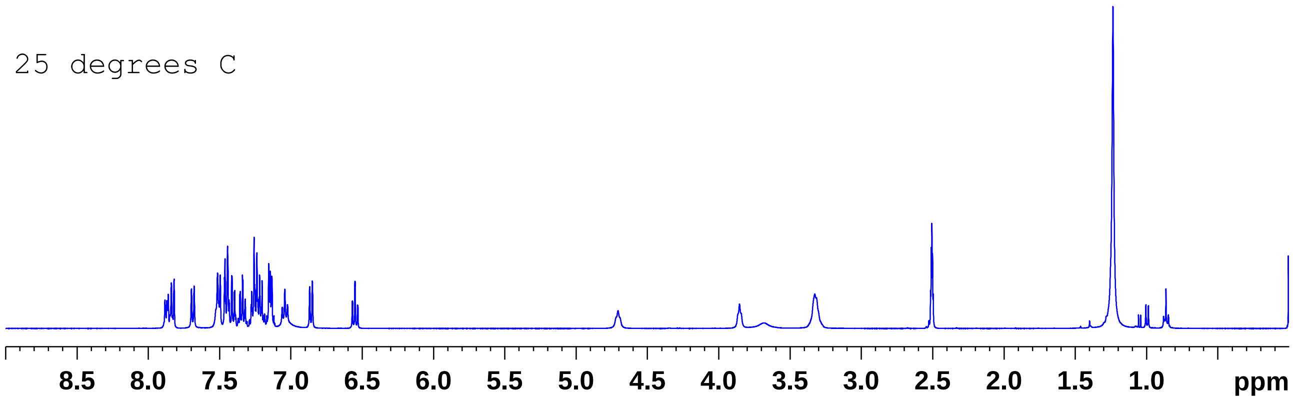
NMR ^{13}C: 28



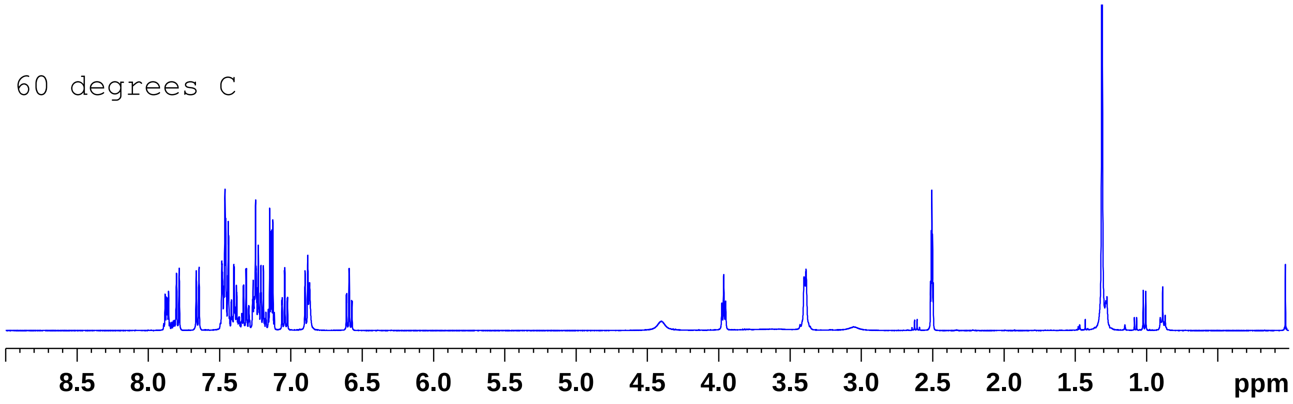
NMR 2D ^{1}H^{1}H COSY: 28



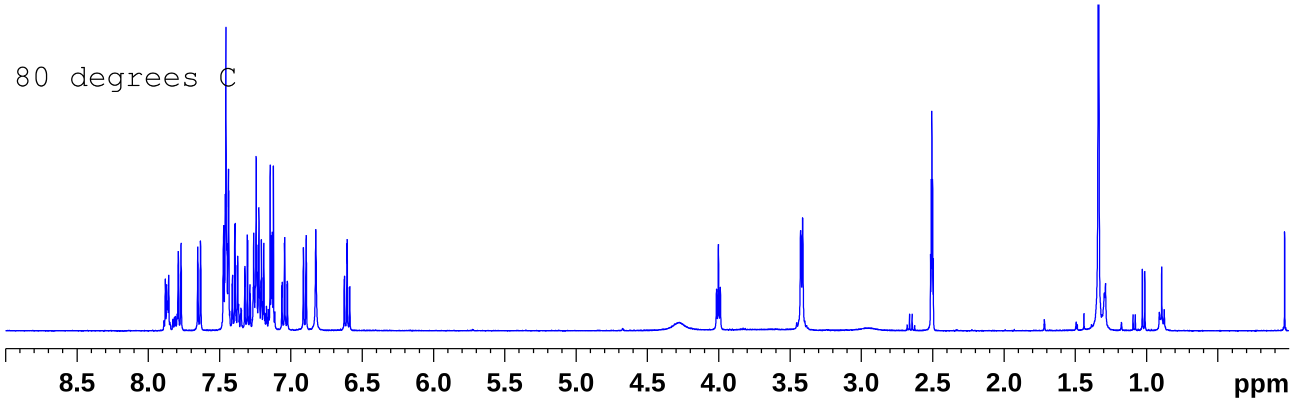
NMR ^{1}H: 28 variable temperature experiment in DMSO-d_6



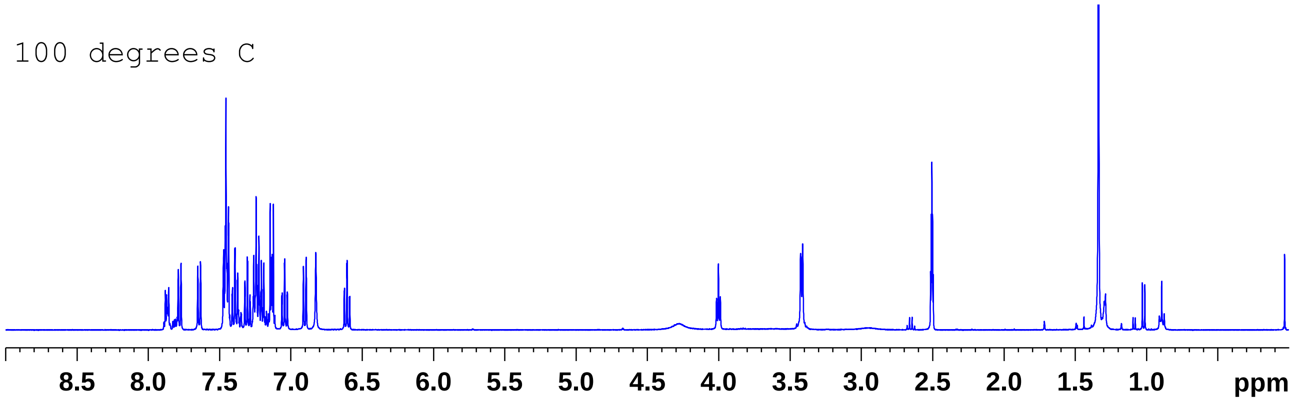
25 degrees C



60 degrees C

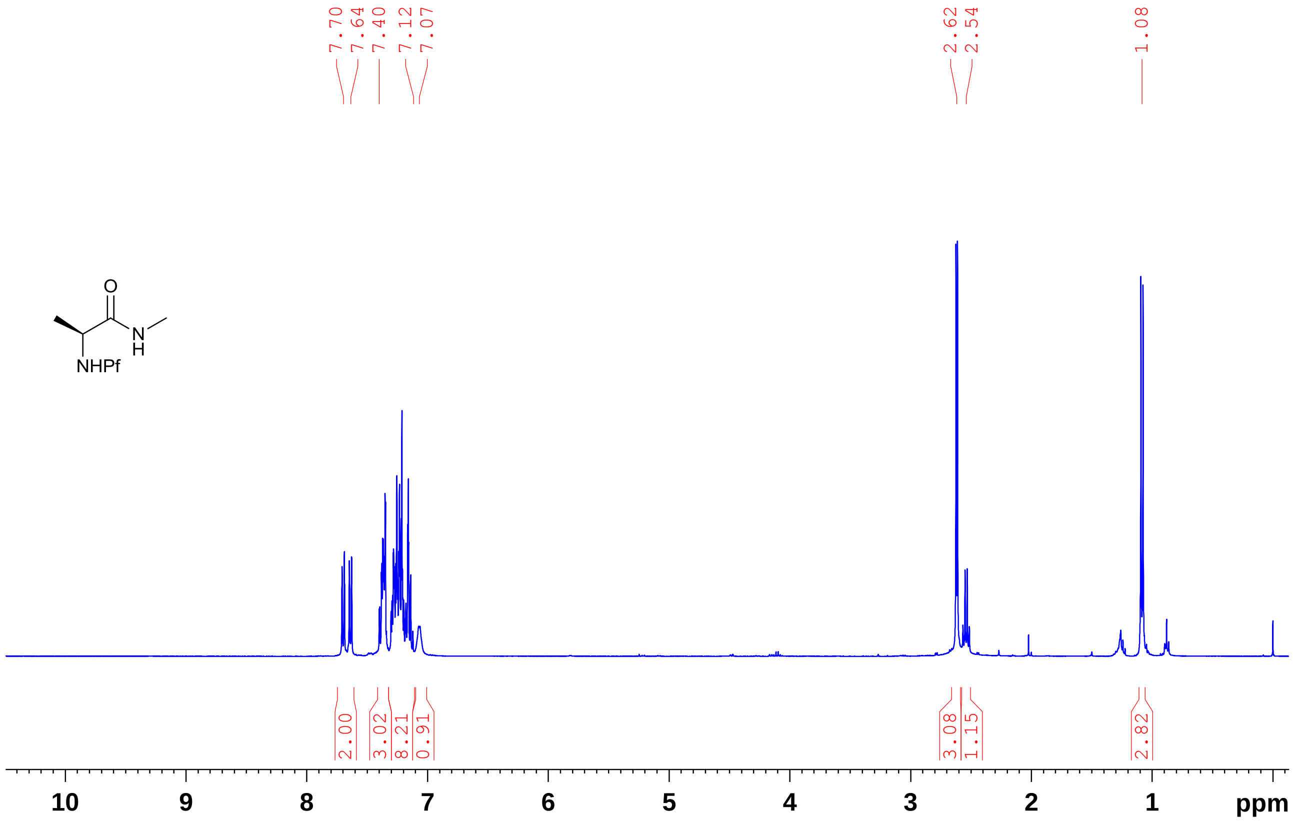


80 degrees C

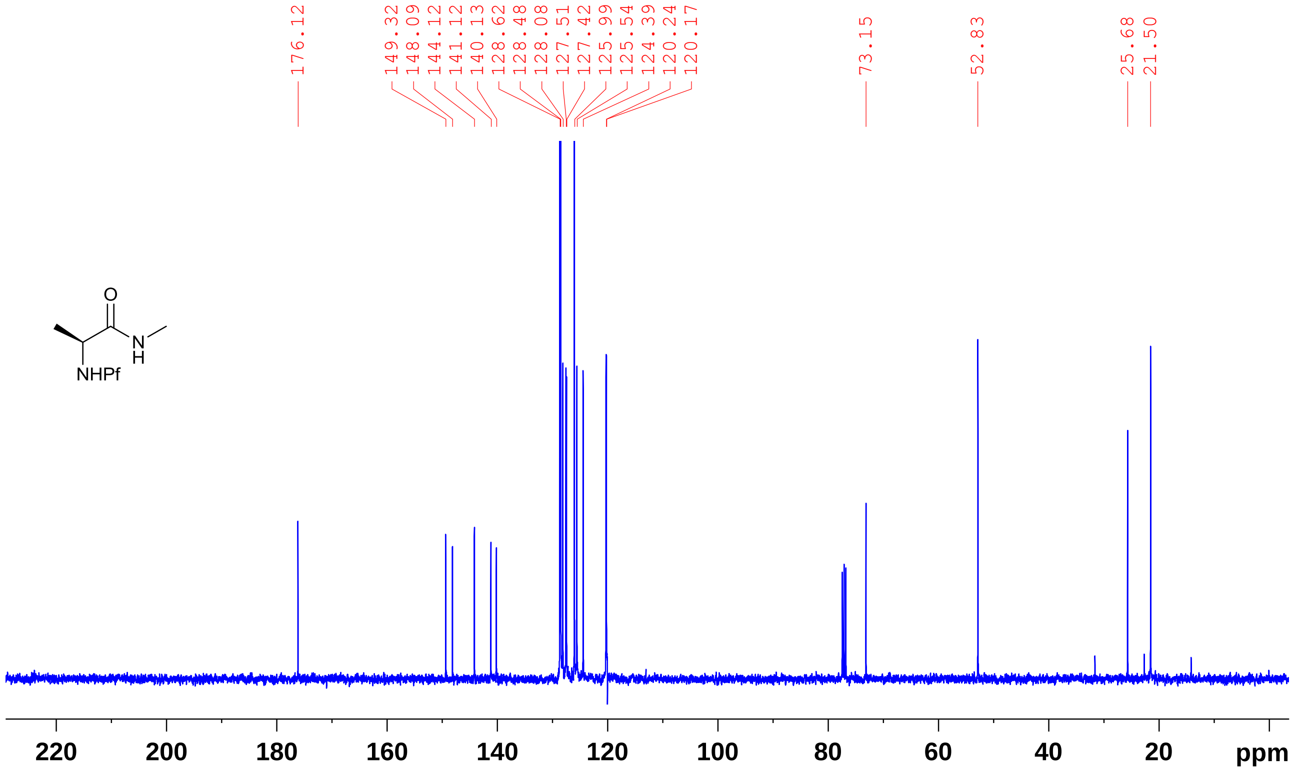


100 degrees C

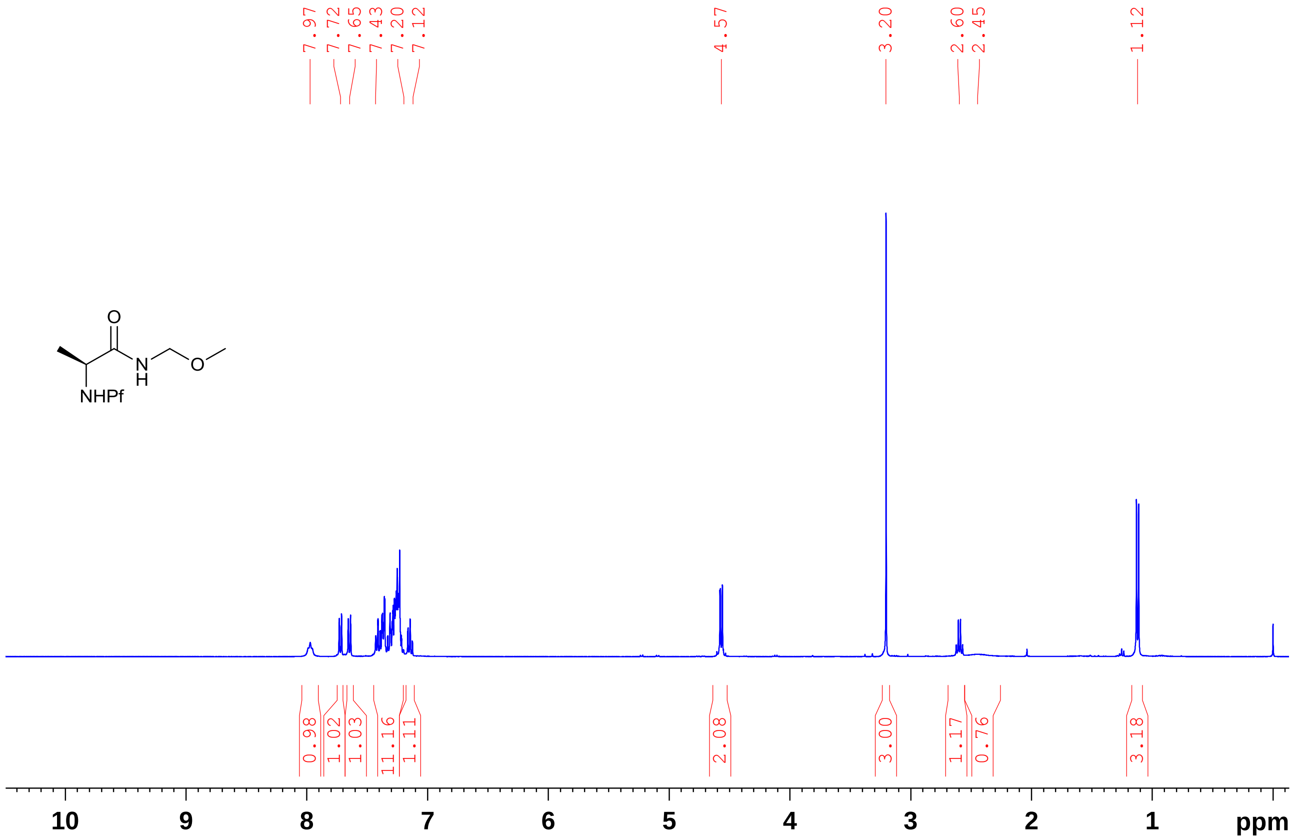
NMR ^{1}H: 14a



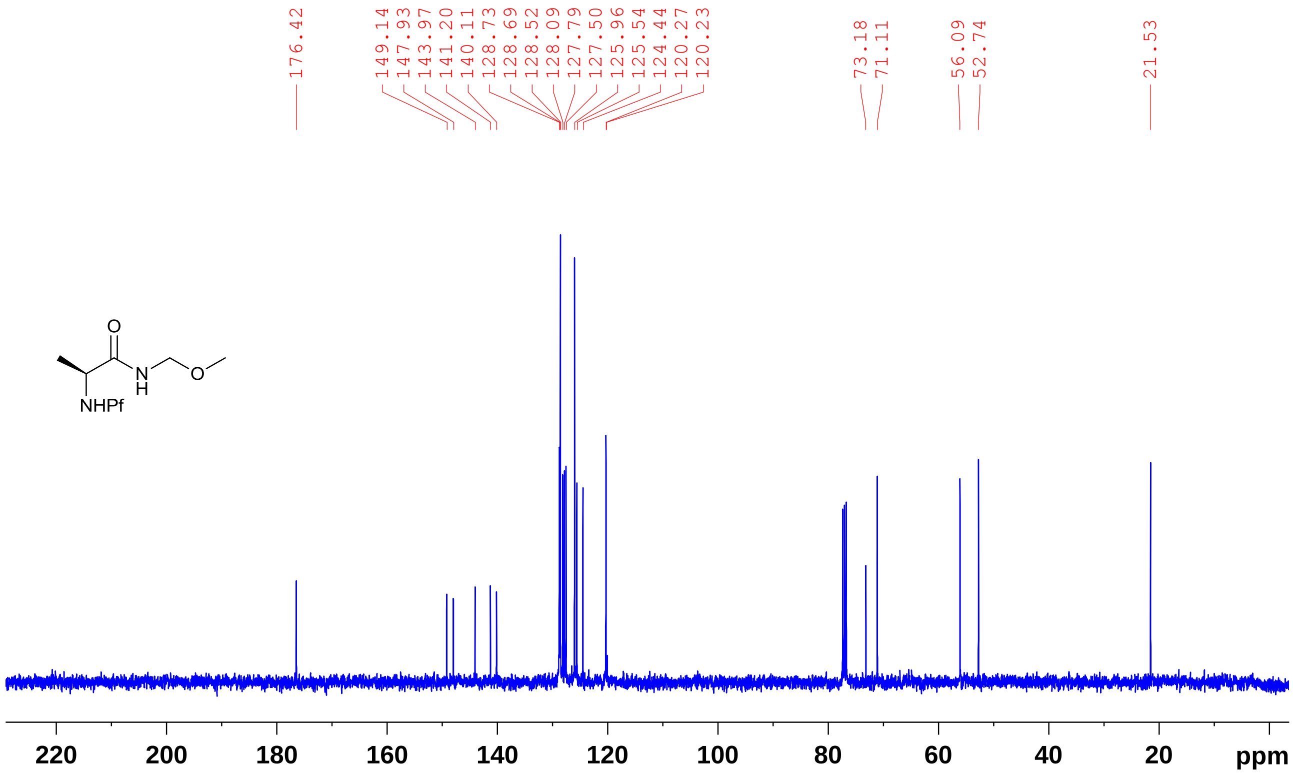
NMR ^{13}C: 14a



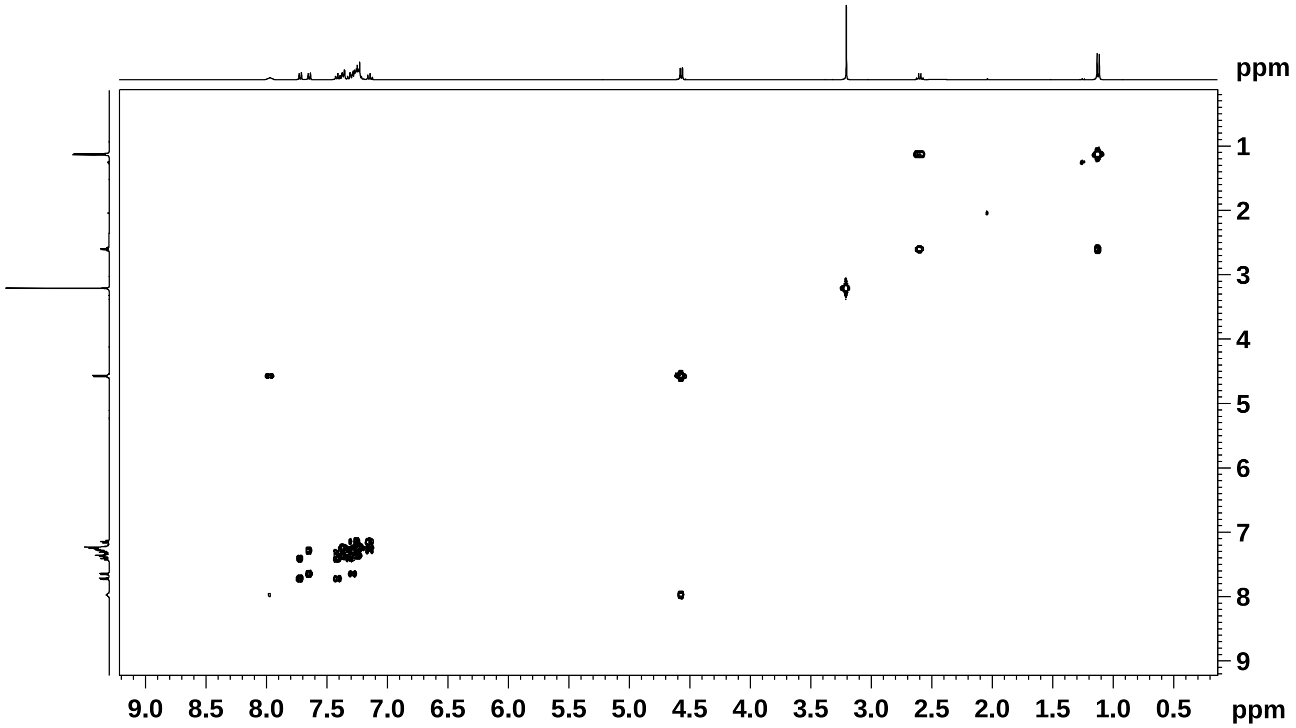
NMR ^{1}H: 15a



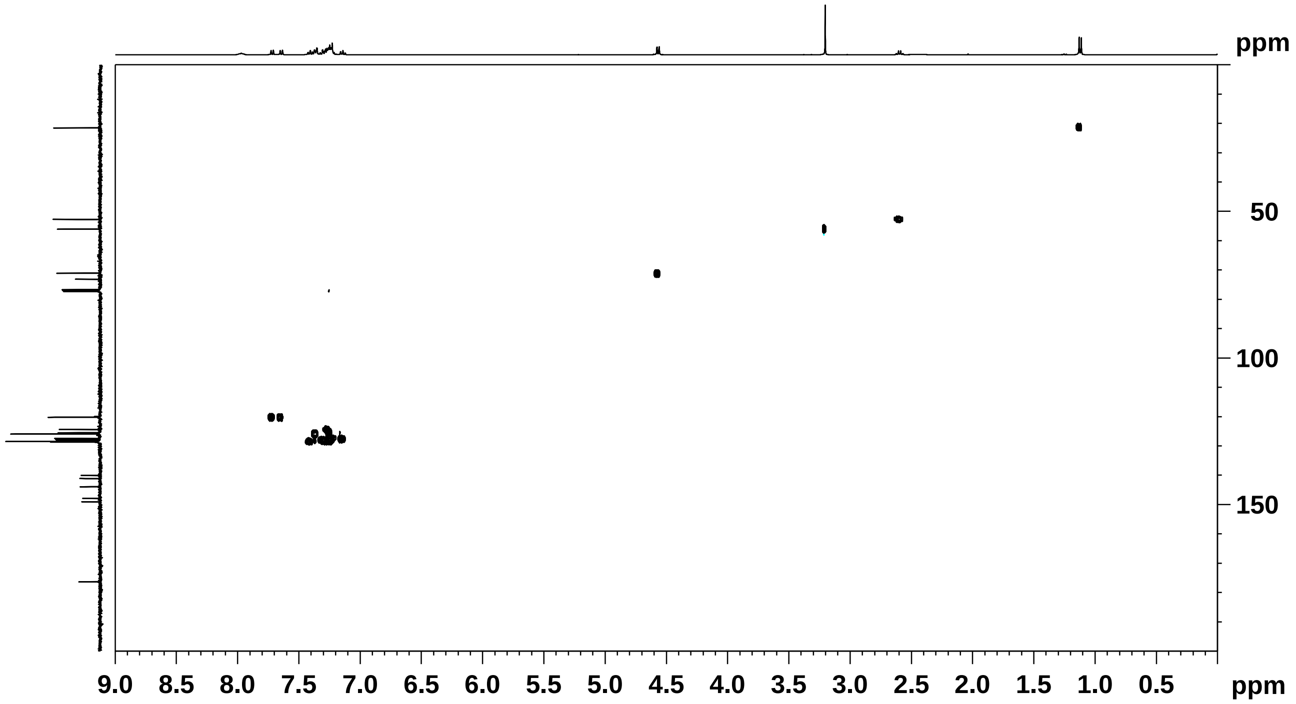
NMR ^{13}C: 15a



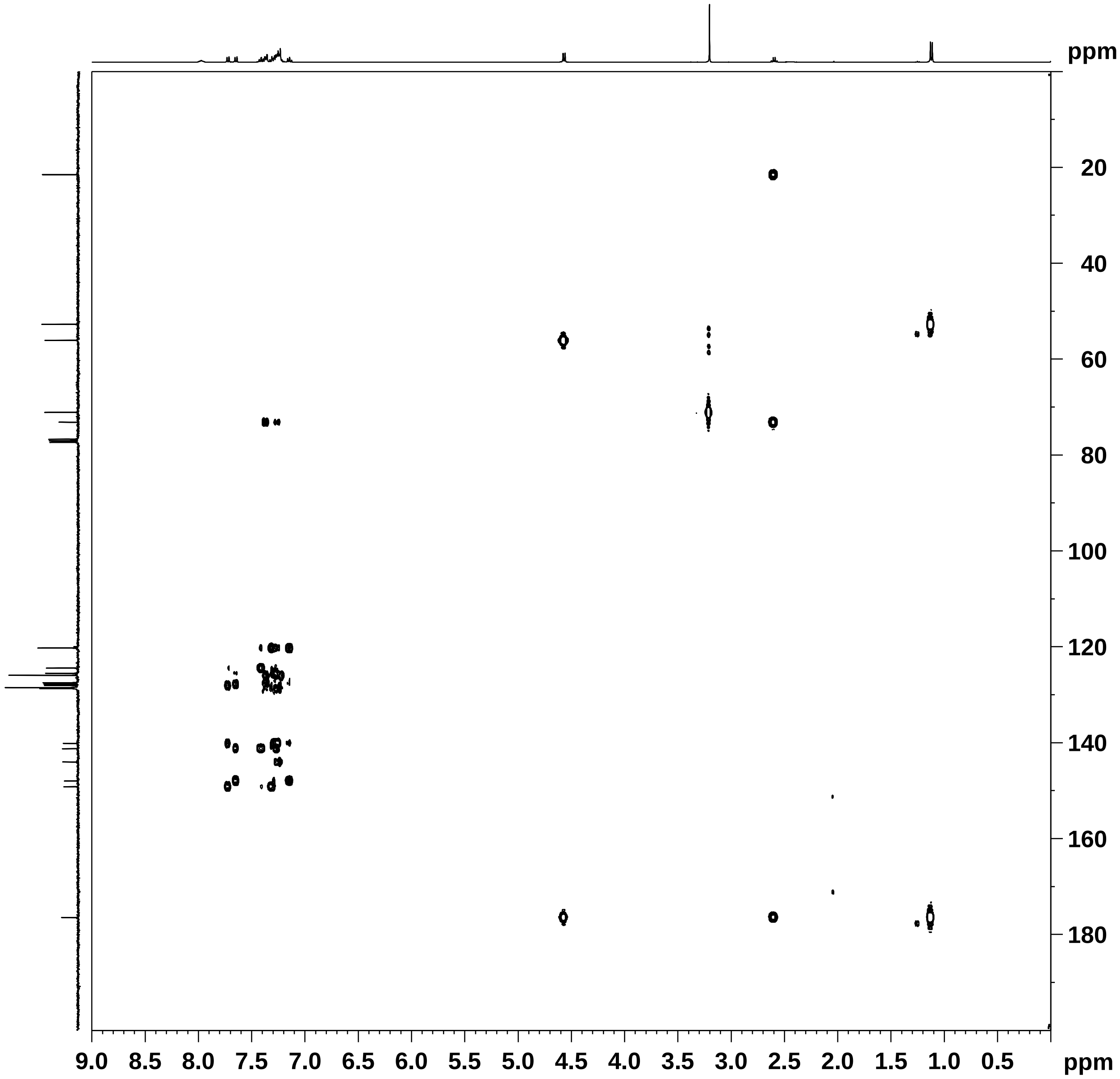
NMR 2D $^1H^1H$ COSY: 15a



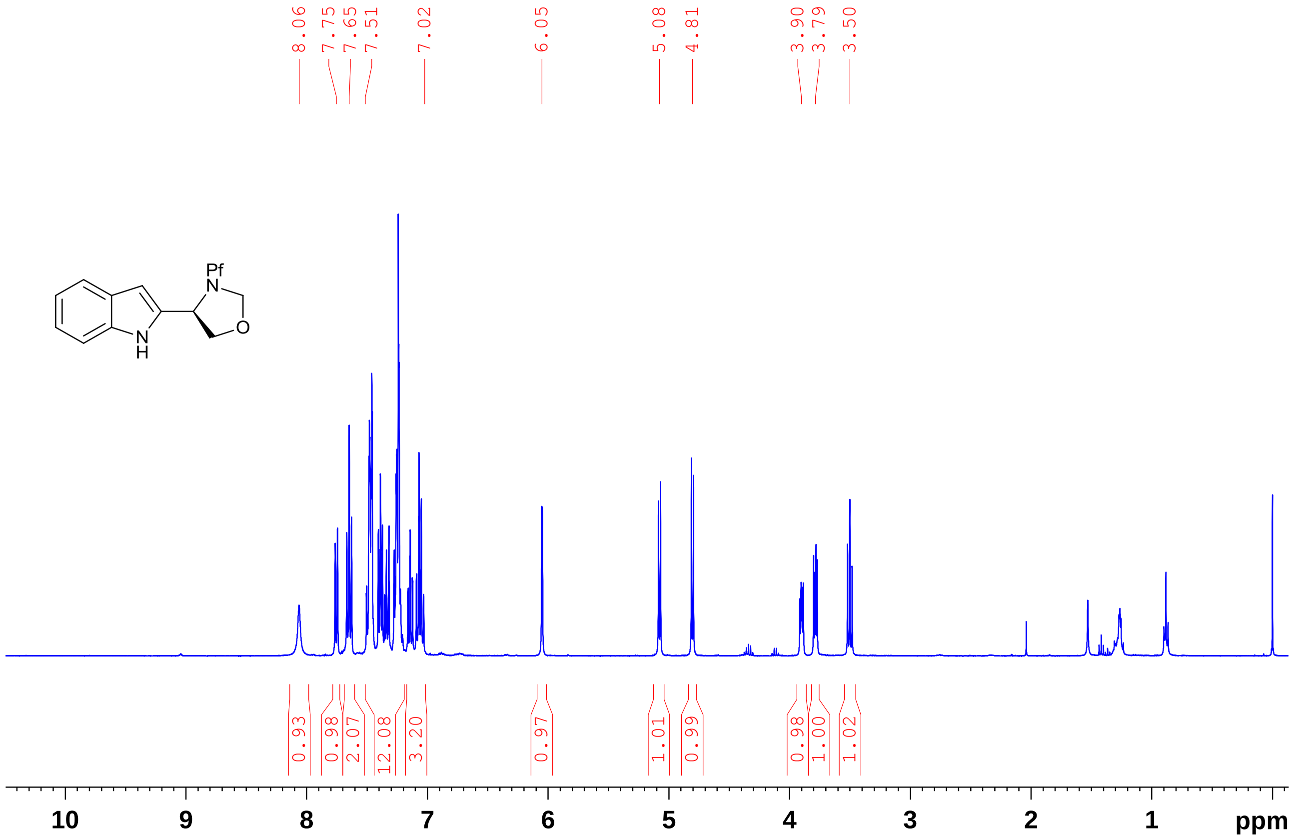
NMR 2D $^1H^{13}C$ HSQC: 15a



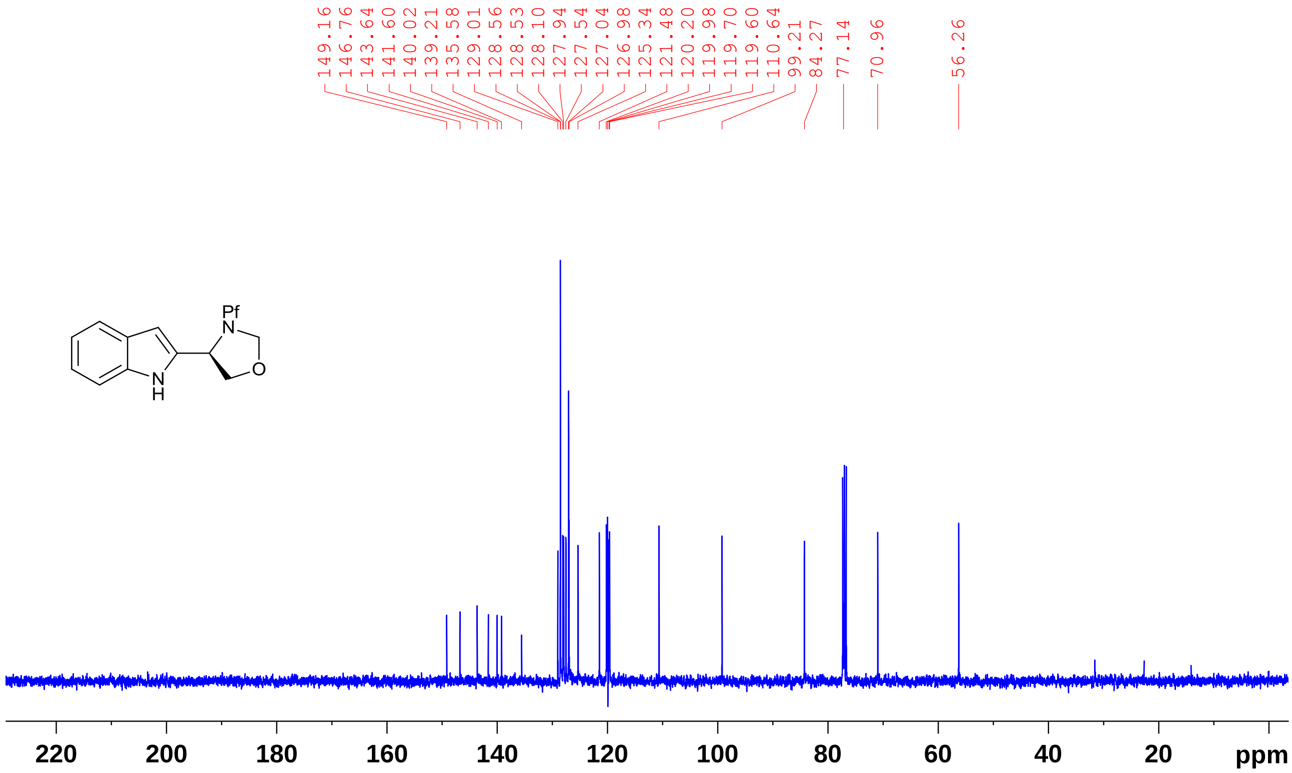
NMR 2D $^1H^{13}C$ HMBC CIGAR: 15a



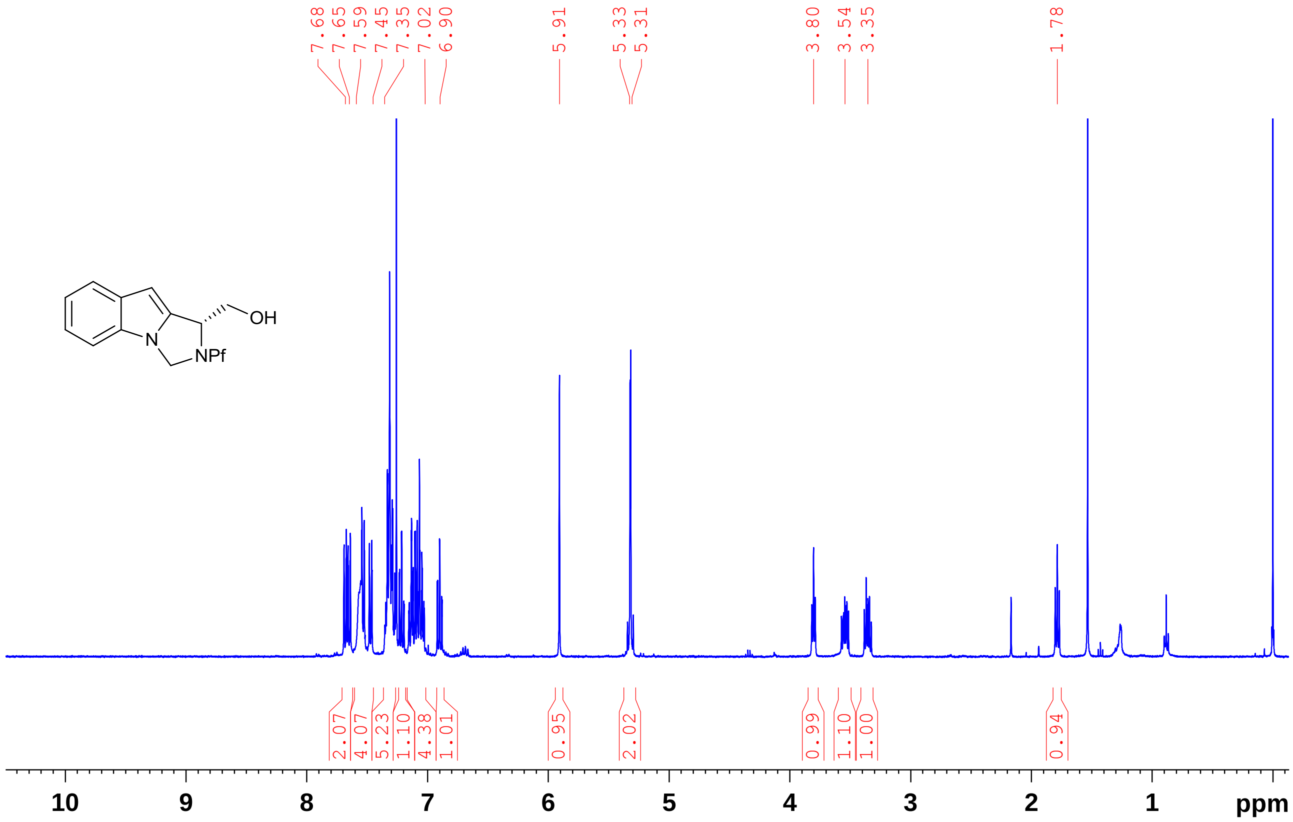
NMR ^{1}H: 21



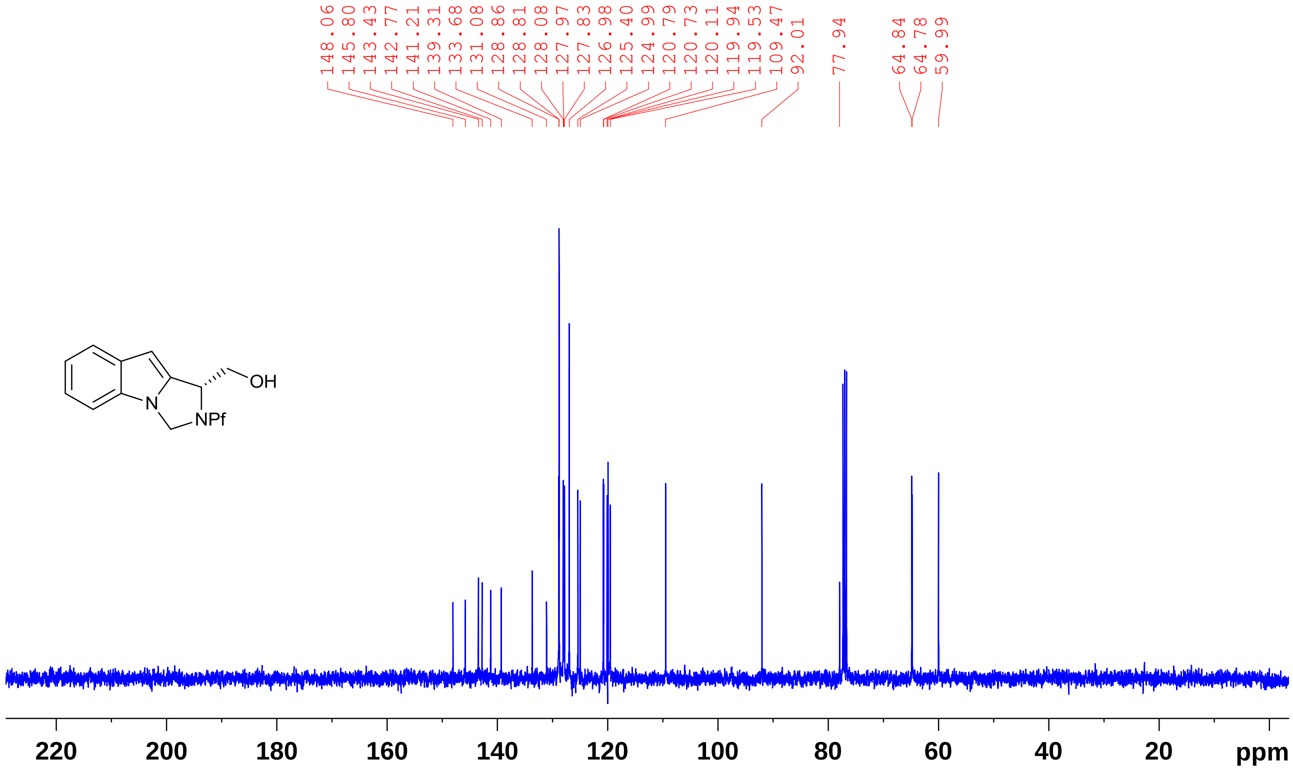
NMR ^{13}C: 21



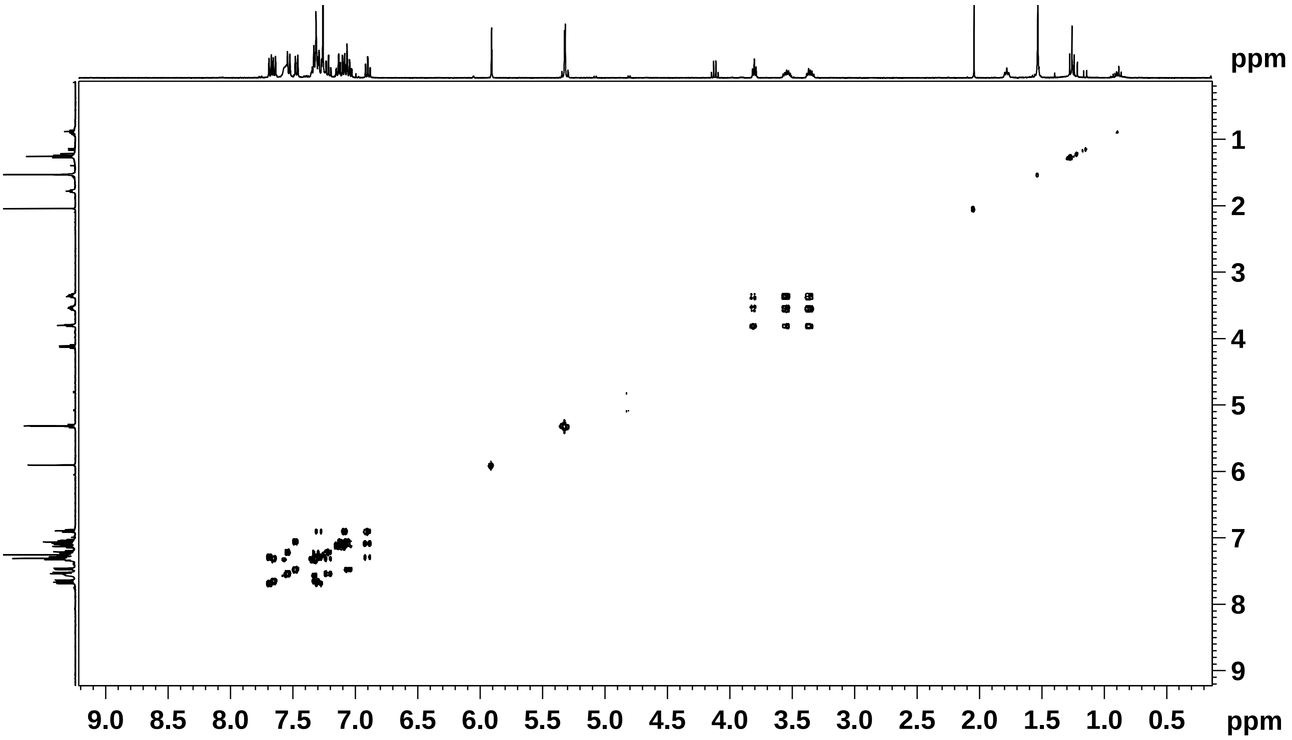
NMR ^{1}H: 20



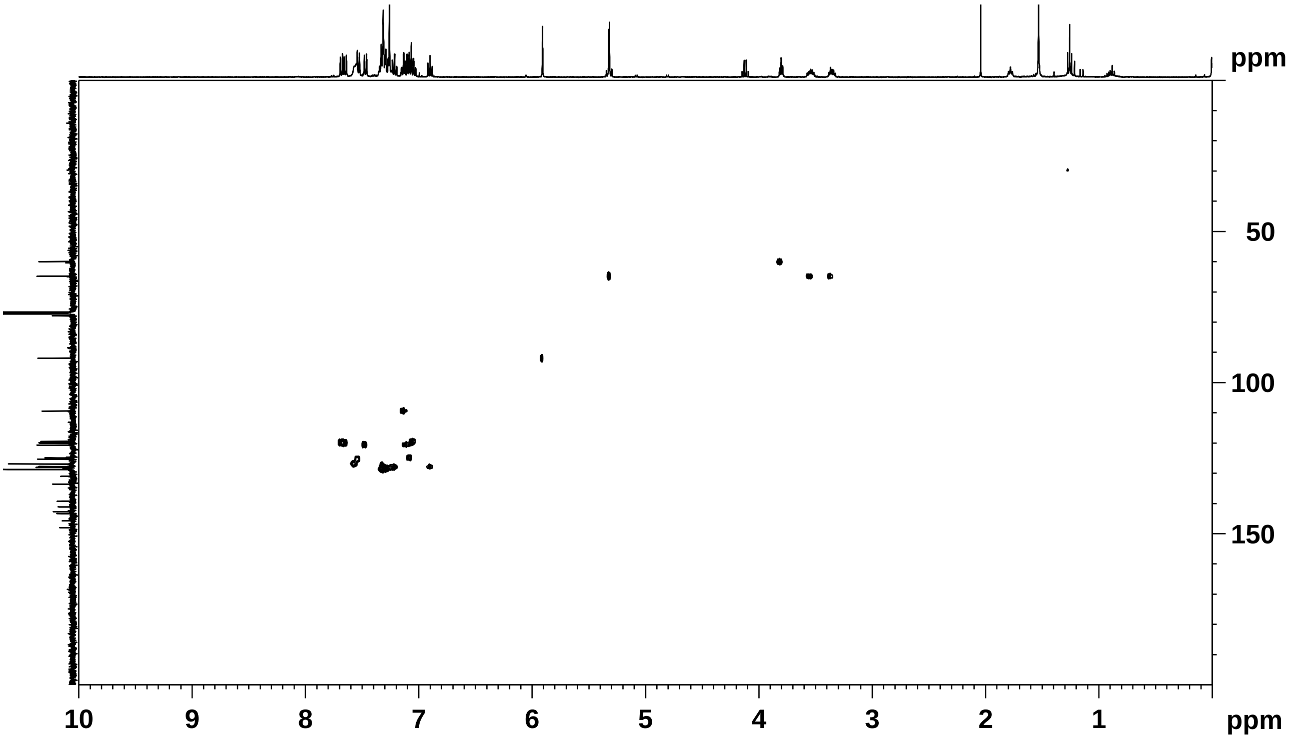
NMR ^{13}C: 20



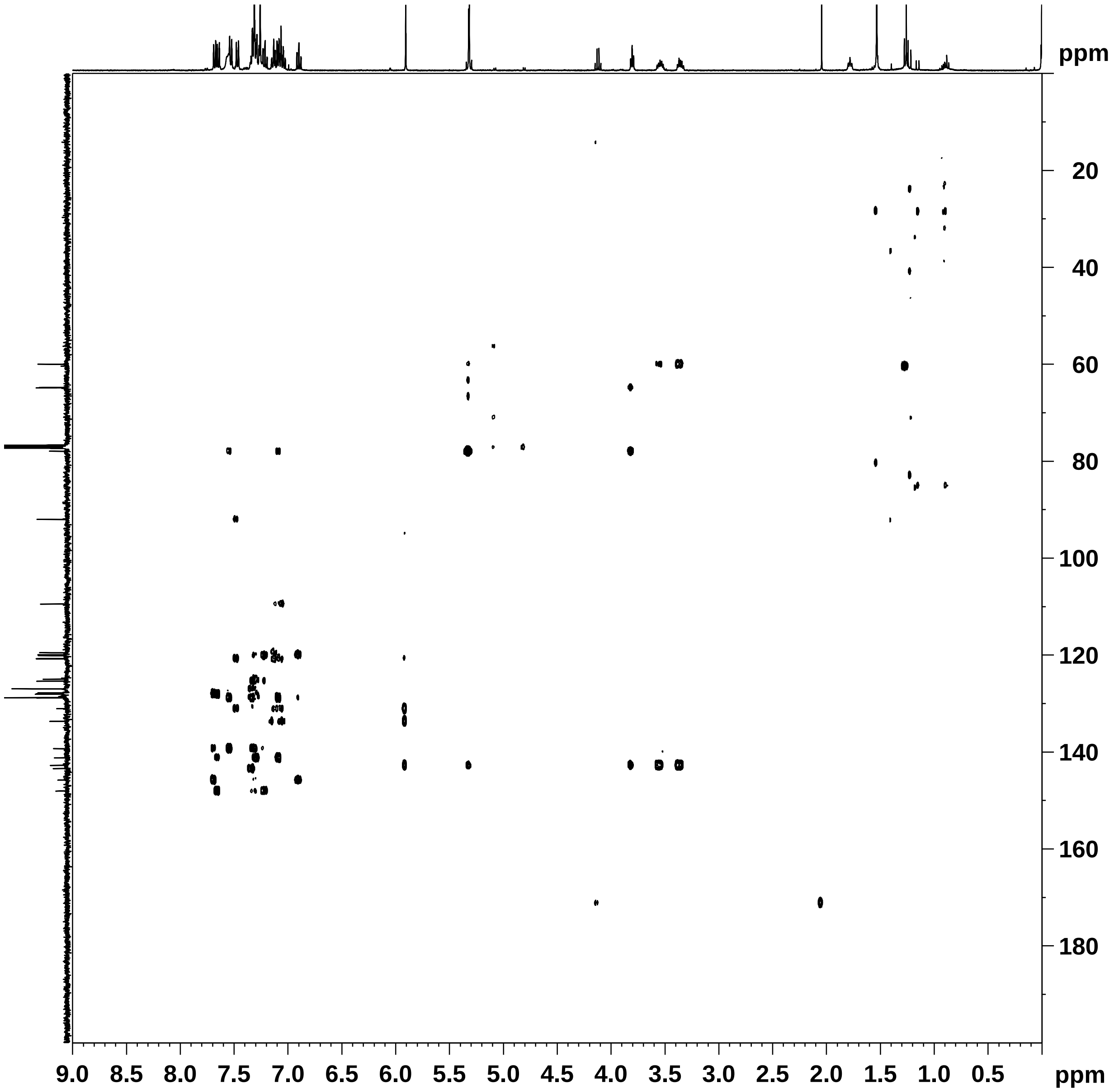
NMR 2D $^1H^1H$ COSY: 20



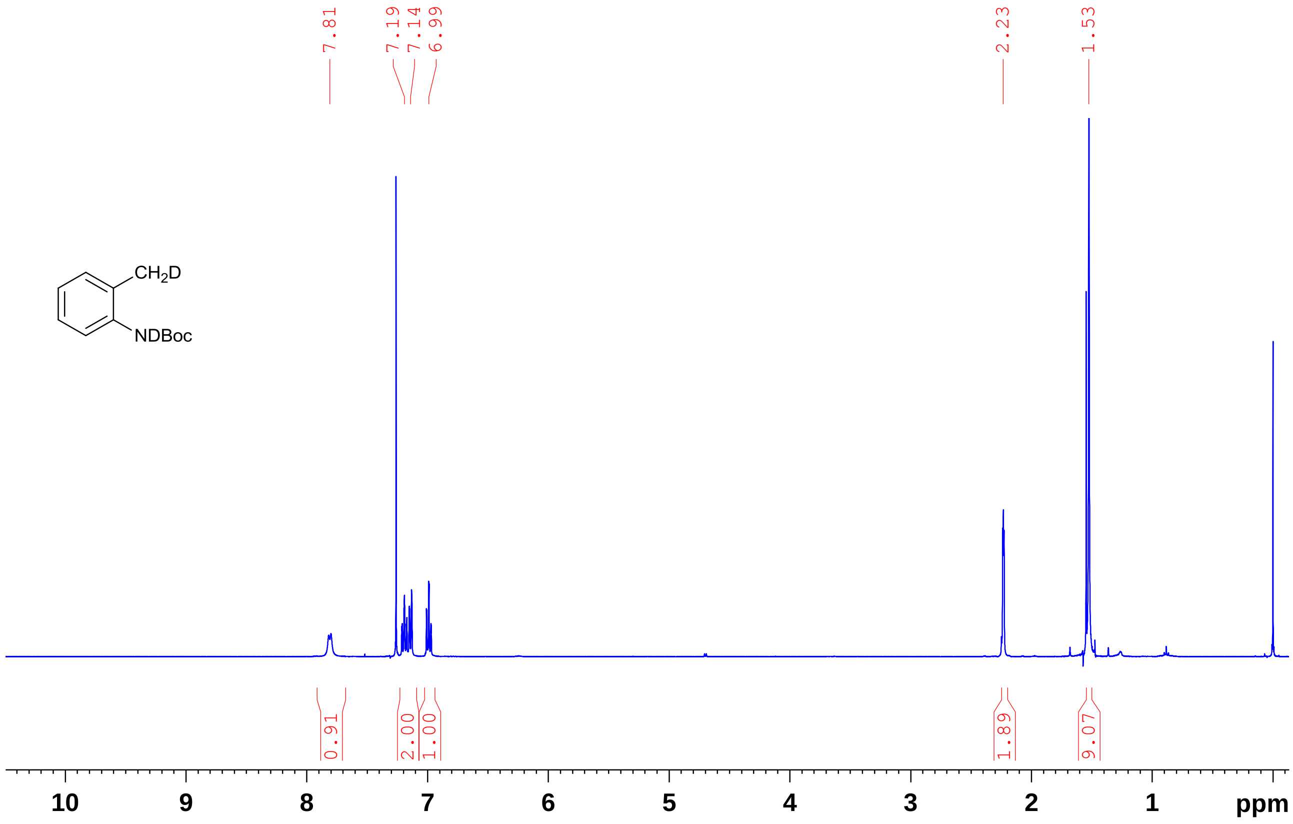
NMR 2D $^1H^{13}C$ HSQC: 20



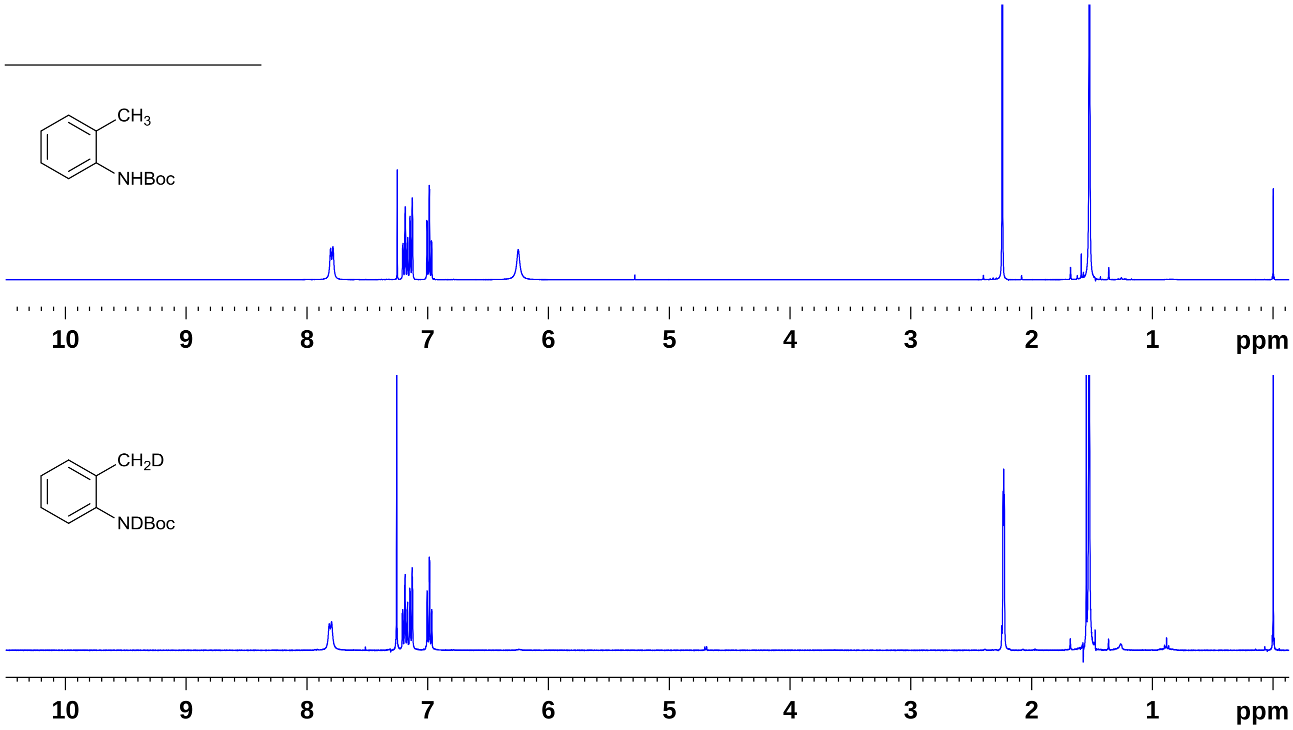
NMR 2D $^{1}H^{13}C$ HMBC CIGAR: 20



NMR ^{1}H: 12-d$_2$

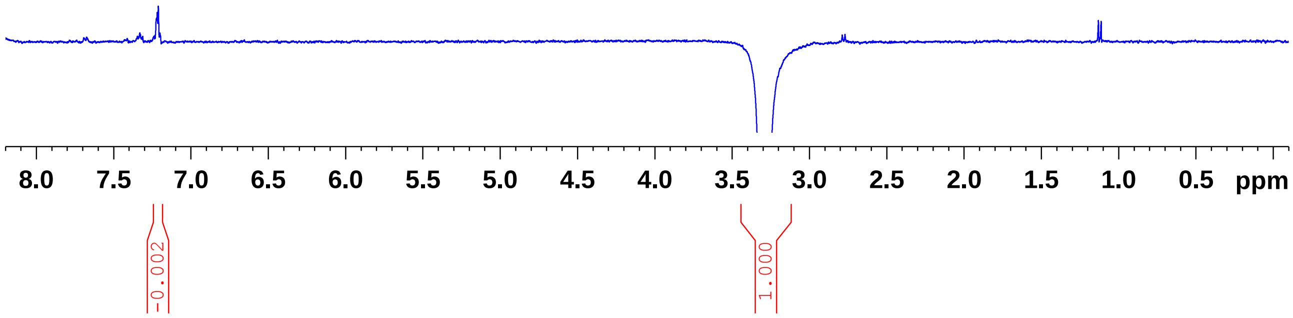


NMR ^{1}H: comparisons between 12 and 12-d$_2$

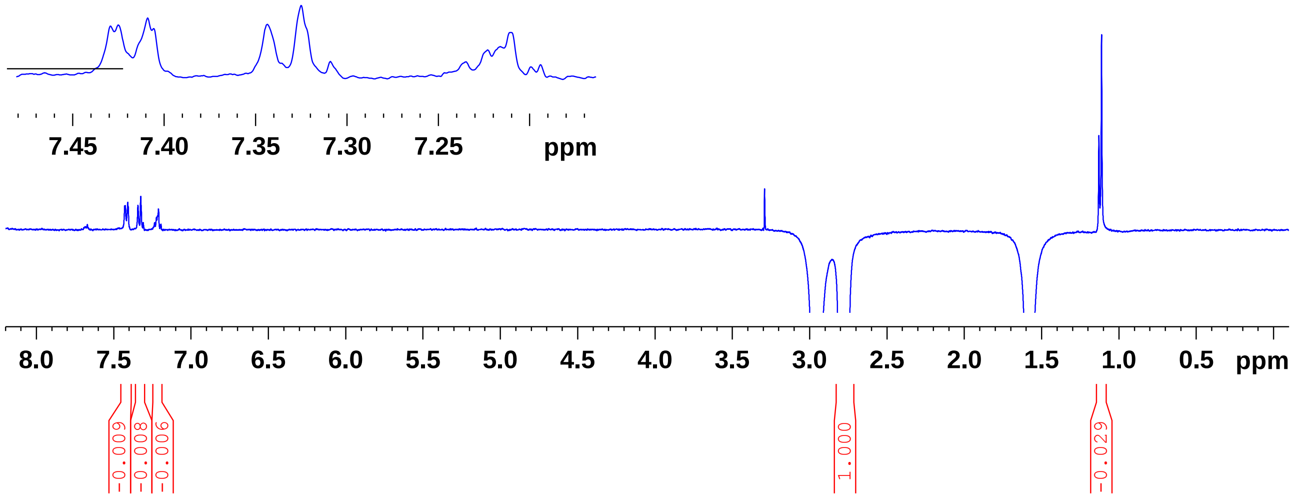


NMR 1D-CSSF-NOESY 10a

Selected Peak: δ 3.29 ppm



Selected Peak: δ 2.78 ppm



Selected Peak: δ 1.12 ppm