Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

In-depth structure–selectivity investigations on asymmetric, copper-catalyzed oxidative biaryl coupling in the presence of 5-*cis*-substituted prolinamines

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1. Synthetic procedures

For general information about apparatus and methods used, the synthesis of **9f** and the procedure for the oxidative biaryl coupling, see article.

Biaryl **1c**,[1] prolinamines **8c**,**e**–**q**,[2] **9a**,[3] **9m**–**o**,[2] and **10b**–**f**,[2] prolinol **12**,[3] and amine $H_2NC(CH_2OBn)_3$[4] were prepared according to literature procedures. Prolinamines **8d** and **10a** are commercially available.

1.1 Prolinamines 8 and 9

1.1.1 General procedure for the mesylation and amination of prolinol 12

MsCl (1.05 equiv) and NEt_3 (1.5 equiv) were added at 0 °C to a solution of the alcohol **12** (1.0 equiv) in anhydrous CH_2Cl_2 (10 mL/mmol **12**)**.** After 1–2 d at r.t., an excess of the amine (4–20 equiv) was added and stirring was continued for 1–4 d. Evaporation of the solvent and column chromatography provided prolinamines **8** and **9**.

1.1.2 (2*S*,5*R*)-2-((*tert*-Butyl(methyl)amino)methyl)-1-methyl-5-phenylpyrrolidine (8a)

According to the general procedure, alcohol **12** (180 mg, 941 µmol) was mesylated and treated with *tert*-butylmethylamine (900 µL, 654 mg, 7.51 mmol) to give, after column chromatography (silica gel, CH_2Cl_2/MeOH, 1:0–9:1) and filtration through a pad of basic alumina (activity I, CH_2Cl_2/MeOH, 9:1), prolinamine **8a** (177 mg, 680 µmol, 72%) as a slightly brownish oil.

R_f 0.27 (CH_2Cl_2/MeOH 9:1). $[\alpha]_D^{22}$ –6.2 (*c* 1.00 in MeOH). IR (ATR) ν_{max}/cm^{-1} 2967w, 2777w, 1452w, 1360w, 1219w, 1190w, 1021w, 964w, 755s, 699vs. ^{1}H NMR δ_H(400 MHz; $CDCl_3$) 1.09 (9 H, s, $C(CH_3)_3$), 1.68 (2 H, m, 3-*H*H, 4-*H*H), 2.05 (2 H, m 3-H*H*, 4-H*H*), 2.21 (3 H, s, 1-CH_3), 2.27 (3 H, s, $NCH_3C(CH_3)_3$), 2.51 (3 H, m, 2-H, 2-CH_2), 3.26 (1 H, dd, *J* = 8.4, 6.6 Hz, 5-H), 7.23 (1 H, m, Ar-H), 7.34 (4 H, m, Ar-H) ppm. ^{13}C NMR δ_C(100 MHz; $CDCl_3$) 26.2 ($C(CH_3)_3$), 29.6 (C-3), 34.1 (C-4), 36.3 ($N(CH_3)C(CH_3)_3$), 39.8 (1-CH_3), 54.2 ($C(CH_3)_3$), 56.8 (2-CH_2), 66.1 (C-2), 72.9 (C-5), 127.0, 127.5, 128.4 (CH-Ar), 144.2 (C_q-Ar) ppm. HRMS (ESI, pos.) *m/z* calcd for $C_{17}H_{29}N_2$ $[M + H]^+$ 261.2325, found 261.2327.

1.1.3 (2*S*,5*R*)-1-Methyl-2-((methyl(phenyl)amino)methyl)-5-phenylpyrrolidine (8b)

According to the general procedure, the alcohol **12** (180 mg, 941 µmol) was mesylated and treated with *N*-methylaniline (2.04 mL, 2.02 g, 18.8 mmol) to give, after column chromatography (silica gel, CH_2Cl_2/MeOH, 1:0–9:1) and filtration through a pad of basic alumina (activity I, CH_2Cl_2/MeOH, 9:1), prolinamine **8b** (174 mg, 620 µmol, 66%) as a brownish oil.

R_f 0.73 (CH_2Cl_2/MeOH 9:1). $[\alpha]_D^{21}$ 25.9 (*c* 0.50 in MeOH). IR (ATR) ν_{max}/cm^{-1} 2945w, 2871w, 2783w, 1598vs, 1504vs, 1450s, 1365s, 1191s, 1033w, 990w, 745vs, 691vs. ^{1}H NMR δ_H (400 MHz; $CDCl_3$) 1.74 (2 H, m, 3-*H*H, 4-*H*H), 2.05 (2 H, m, 3-H*H*, 4-H*H*), 2.28 (3 H, s, 1-CH_3), 2.89 (1 H, m, 2-H), 3.09 (3 H, s, N(CH_3)Ar), 3.35 (2 H, m, 5-H, 2-C*H*H), 3.67 (1 H, dd, *J* = 14.7, 5.2 Hz, 2-CH*H*), 6.73 (1 H, m, Ar-H), 6.81 (2 H, m, Ar-H), 7.28 (3 H, m, Ar-H), 7.36 (2 H, m, Ar-H), 7.41 (2 H, m, Ar-H) ppm. ^{13}C NMR δ_C(100 MHz; $CDCl_3$) 28.7 (C-3), 34.3 (C-4), 39.6 (NCH_3Ar), 40.0 (1-CH_3), 57.8 (2-CH_2), 64.5 (C-2), 72.7 (C-5), 112.1, 116.1, 127.1, 127.4, 128.4, 129.2 (CH-Ar), 144.1, 149.9 (C_q-Ar) ppm. HRMS (ESI, pos.) *m/z* calcd for $C_{19}H_{25}N_2$ $[M + H]^+$ 281.2012, found 281.2014.

1.1.4 (2*S*,5*R*)-2-((Ethylamino)methyl)-1-methyl-5-phenylpyrrolidine (9b)

According to the general procedure, alcohol **12** (150 mg, 784 µmol) was mesylated and treated with aq ethylamine (70%, 1.27 mL, 707 mg, 15.7 mmol) and MeOH (2 mL) to give, after column chromatography (1. silica gel, deactivated with 7.5% aq NH_3 (25%), CH_2Cl_2/MeOH, 1:0–9:1; 2. silica gel, deactivated with 7.5% aq NH_3 (25%), petroleum ether/Et_2O, 1:0–0:1), prolinamine **9b** (106 mg, 488 µmol, 62%) as a brownish oil.

R_f 0.27 (Et_2O, deact. SiO_2). $[\alpha]_D^{21}$ 36.7 (*c* 0.10 in MeOH). IR (ATR) ν_{max}/cm^{-1} 2962w, 2786w, 1452w, 1138w, 1073w, 1040w, 755s, 699vs. ^{1}H NMR δ_H(400 MHz; $CDCl_3$) 1.16 (3 H, t, *J* = 7.1 Hz, NCH_2CH_3), 1.69 (2 H, m, 4-*H*H, NH), 1.82 (1 H, m, 3-*H*H), 1.97 (1 H, m, 3-H*H*), 2.06 (1 H, m, 4-H*H*), 2.16 (3 H, s, 1-CH_3), 2.61 (1 H, m, 2-H), 2.72 (3 H, m, 2-C*H*H, NCH_2CH_3), 2.81 (1 H, dd, *J* = 11.3, 3.6 Hz, 2-CH*H*), 3.28 (1 H, dd, *J* = 9.5, 6.6 Hz, 5-H), 7.23 (1 H, m, Ar-H), 7.32 (4 H, m, Ar-H) ppm. ^{13}C NMR δ_C(100 MHz; $CDCl_3$) 15.4 (NCH_2CH_3), 28.2 (C-3), 34.3 (C-4), 39.5 (1-CH*3*), 44.8 (NCH_2CH_3),

1 X. Li, J. B. Hewgley, C. A. Mulrooney, J. Yang and M. C. Kozlowski, *J. Org. Chem.*, 2003, **68**, 5500.

2 F. Prause, J. Kaldun, B. Arensmeyer, B. Wennemann, B. Fröhlich, D. Scharnagel and M. Breuning, *Synthesis*, 2015, DOI: 10.1055/s-0034-1379457.

3 D. Scharnagel, F. Prause, J. Kaldun, R. G. Haase and M. Breuning, *Chem. Commun.*, 2014, **50**, 6623.

4 M. Segura, F. Sansone, A. Casnati and R. Ungaro, *Synthesis*, 2001, 2105.

53.1 (2-CH_2), 66.0 (C-2), 72.7 (C-5), 127.1, 127.5, 128.4 (Ar-H), 144.0 (C_q-Ar) ppm. HRMS (ESI, pos.) *m/z* calcd for $C_{14}H_{23}N_2$ $[M + H]^+$ 219.1856, found. 219.1854.

1.1.5 (2*S*,5*R*)-1-Methyl-2-((neopentylamino)methyl)-5-phenylpyrrolidine (9c)

According to the general procedure, alcohol **12** (150 mg, 784 µmol) was mesylated and treated with neopentylamine hydrochloride (1.77 g, 14.3 mmol) NEt_3 (2.00 mL, 1.46 g, 14.3 mmol) and MeOH (2 mL) to give, after column chromatography (silica gel, CH_2Cl_2/MeOH, 1:0–9:1) and filtration through a pad of basic alumina (activity I, CH_2Cl_2/MeOH, 9:1), prolinamine **9c** (160 mg, 614 µmol, 78%) as a colorless resin.

R_f 0.51 (CH_2Cl_2/MeOH 9:1). $[\alpha]_D^{22}$ = 38.5 (*c* 0.50 in MeOH). IR (ATR) ν_{max}/cm^{-1} 2949s, 2866w, 2784w, 1454s, 1361w, 1139w, 1040w, 755s, 698vs. ^{1}H NMR δ_H(400 MHz; $CDCl_3$) 0.95 (9 H, s, $C(CH_3)_3$), 1.30 (1 H, br s, NH), 1.68 (1 H, m, 4-*H*H), 1.84 (1 H, m, 3-*H*H), 1.95 (1 H, m, 3-H*H*), 2.05 (1 H, m, 4-H*H*), 2.18 (3 H, s, 1-CH_3), 2.39 (1 H, d, *J* = 11.3 Hz, C*H*HC$(CH_3)_3$), 2.44 (1 H, d, *J* = 11.3 Hz, CH*H*C$(CH_3)_3$), 2.63 (1 H, m, 2-H), 2.72 (1 H, dd, *J* = 11.4, 5.6 Hz, 2-C*H*H), 2.78 (1 H, dd, *J* = 11.4, 4.0 Hz, CH*H*N), 3.30 (1 H, dd, *J* = 9.6, 6.7 Hz, 5-H), 7.23 (1 H, m, Ar-H), 7.33 (4 H, m, Ar-H) ppm. ^{13}C NMR δ_C(100 MHz; $CDCl_3$) 28.0 (C(*C*$H_3)_3$), 28.2 (C-3), 31.9 (*C*$(CH_3)_3$), 34.6 (C-4), 39.6 (1-CH_3), 54.5 (2-CH_2), 63.2 (*C*H_2C$(CH_3)_3$), 66.2 (C-2), 72.7 (C-5), 127.0, 127.4, 128.4 (CH-Ar), 144.3 (C_q-Ar) ppm. HRMS (ESI, pos.) *m/z* calcd for $C_{17}H_{29}N_2$ $[M + H]^+$ 261.2325, found 261.2326.

1.1.6 (2*S*,5*R*)-2-((Isopropylamino)methyl)-1-methyl-5-phenylpyrrolidine (9d)

According to the general procedure, alcohol **12** (150 mg, 784 µmol) was mesylated and treated with isopropylamine (1.34 mL, 926 mg, 15.7 mmol) to give, after column chromatography (1. silica gel, deactivated with 7.5% aq NH_3 (25%), CH_2Cl_2/MeOH, 1:0–9:1; 2. silica gel, deactivated with 7.5% aq NH_3 (25%), petroleum ether/Et_2O, 1:0–0:1), prolinamine **9d** (97.0 mg, 417 µmol, 53%) as a yellow oil.

R_f 0.31 (Et_2O, deact. SiO_2). $[\alpha]_D^{21}$ 15.0 (*c* 0.20 in MeOH). IR (ATR) ν_{max}/cm^{-1} 2962w, 2783w, 1453w, 1378w, 1336w, 1173w, 1139w, 1080w, 1043w, 755s, 698vs. ^{1}H NMR δ_H(400 MHz; $CDCl_3$) 1.09 (3 H, d, *J* = 6.2 Hz, NCH(C*H*$_3)_2$), 1.11 (3 H, d, *J* = 6.2 Hz, NCH(C*H*$_3)_2$), 1.48 (1 H, br s, NH), 1.67 (1 H, m, 4-*H*H), 1.80 (1 H, m, 3-*H*H), 1.97 (1 H, m, 3-H*H*), 2.06 (1 H, m, 4-H*H*), 2.16 (3 H, s, 1-CH_3), 2.59 (1 H, m, 2-H), 2.66 (1 H, dd, *J* = 11.0, 6.4 Hz, 2-C*H*H), 2.83 (2 H, m, CH*H*N, NC*H*$(CH_3)_2$), 3.29 (1 H, dd, *J* = 9.5, 6.7 Hz, 5-H), 7.22 (1 H, m, Ar-H), 7.32 (4 H, m, Ar-H) ppm. ^{13}C NMR δ_C(100 MHz; $CDCl_3$) 23.0 (NCH(*C*$H_3)_2$), 23.3 (NCH(*C*$H_3)_2$), 28.2 (C-3), 34.3 (C-4), 39.4 (1-CH_3), 49.5 (N*C*H$(CH_3)_2$), 51.0 (2-*C*H_2), 66.2 (C-2), 72.6 (C-5), 127.0, 127.4, 128.4 (CH-Ar), 144.1 (C_q-Ar) ppm. HRMS (ESI, pos.) *m/z* calcd for $C_{15}H_{25}N_2$ $[M + H]^+$ 233.2012, found 233.2013.

1.1.7 (2*S*,5*R*)-1-Methyl-2-((pentan-3-ylamino)methyl)-5-phenylpyrrolidine (9e)

According to the general procedure, alcohol **12** (150 mg, 784 µmol) was mesylated and treated with 3-pentylamine (914 µL, 683 mg, 7.84 mmol) to give, after column chromatography (silica gel, Et_2O), prolinamine **9e** (112 mg, 430 µmol, 55%) as a colorless oil.

R_f 0.13 (Et_2O). $[\alpha]_D^{22}$ 29.0 (*c* 0.50 in MeOH). IR (ATR) ν_{max}/cm^{-1} 2958s, 2872w, 2784w, 1453s, 1350w, 1158w, 1082w, 1043w, 754s, 698vs. ^{1}H NMR δ_H(400 MHz; $CDCl_3$) 0.92 (3 H, t, *J* = 7.5 Hz, CH_2CH_3), 0.94 (3 H, t, *J* = 7.5 Hz, CH_2CH_3), 1.46 (5 H, m, CH(CH_2C$H_3)_2$, N*H*), 1.69 (1 H, m, 4-*H*H), 1.86 (1 H, m, 3-*H*H), 1.97 (1 H, m, 3-H*H*), 2.05 (1 H, m, 4-H), 2.16 (3 H, s, 1-CH_3), 2.39 (1 H, quint, *J* = 6.0 Hz, NC*H*$(CH_2CH_3)_2$), 2.60 (1 H, m, 2-H), 2.65 (1 H, dd, *J* = 11.0, 6.1 Hz, 2-C*H*H), 2.79 (1 H, dd, *J* = 11.0, 3.2 Hz, 2-CH*H*), 3.29 (1 H, dd, *J* = 9.6, 6.7 Hz, 5-H), 7.23 (1 H, m, Ar-H), 7.33 (4 H, m, Ar-H) ppm. ^{13}C NMR δ_C(100 MHz; $CDCl_3$) 10.1, 10.3 (CH_2CH_3), 26.2, 26.3 (CH_2CH_3), 28.1 (C-3), 34.4 (C-4), 39.3 (1-CH_3), 50.2 (2-CH_2), 61.1 ((N*C*H$(CH_2CH_3)_2$), 66.4 (C-2), 72.6 (C-5), 127.0, 127.4, 128.4 (CH-Ar), 144.1 (C_q-Ar) ppm. HRMS (ESI, pos.) *m/z* calcd for $C_{17}H_{29}N_2$ $[M + H]^+$ 261.2325, found. 261.2325.

1.1.8 (2*R*,5*S*)-1-Methyl-2-phenyl-5-((((*S*)-1-phenylpropyl)amino)methyl)pyrrolidine (9g)

According to the general procedure, alcohol **12** (150 mg, 784 µmol) was mesylated and treated with (*S*)-1-phenylpropylamine (967 µL, 900 mg, 6.66 mmol) to give, after column chromatography (silica gel, petroleum ether/EtOAc, 1:0–1:1), prolinamine **9g** (157 mg, 509 µmol, 65%) as a colorless oil.

R_f 0.32 (CH_2Cl_2/MeOH 9:1). $[\alpha]_D^{21}$ 19.8 (*c* 0.50 in MeOH). IR (ATR) ν_{max}/cm^{-1} 2958w, 2783w, 1491w, 1451s, 1356w, 1283w, 1193w, 1122w, 1043w, 754s, 698vs. ^{1}H NMR δ_H(400 MHz; $CDCl_3$) 0.85 (3 H, t, *J* = 7.4 Hz, CH_2CH_3), 1.66 (2 H, m, 3-*H*H, C*H*HCH_3), 1.82 (3 H, m, 4-*H*H, CH*H*CH_3, N*H*), 1.96 (1 H, m, 4-H*H*), 2.05 (1 H, m, 3-H*H*), 2.07 (3 H, s, 1-CH_3), 2.54 (2 H, m, 5-H, 5-C*H*H), 2.66 (1 H, dd, *J* = 10.8, 3.1 Hz, 5-CH*H*), 3.26 (1 H, dd, *J* = 9.6, 6.6 Hz, 2-H), 3.52 (1 H, dd, *J* = 7.8, 5.8 Hz, C*H*CH_2CH_3), 7.24 (2 H, m, Ar-H), 7.33 (8 H, m, Ar-H) ppm. ^{13}C NMR δ_C(100 MHz; $CDCl_3$) 11.0 (CH_2CH_3), 28.2 (C-4), 31.1 (CH_2CH_3), 34.5 (C-3), 39.4 (1-CH_3), 50.8 (5-CH_2), 65.4 ($CHCH_2CH_3$), 66.2 (C-5), 72.7 (C-2), 126.9, 127.0, 127.40, 127.43, 128.36, 128.40 (CH-Ar), 144.2, 144.9 (C_q-Ar) ppm. HRMS (ESI, pos.) *m/z* calcd for $C_{21}H_{29}N_2$ $[M + H]^+$ 309.2325, found 309.2327.

1.1.9 (2*S*,5*R*)-2-((((*S*)-3,3-dimethylbutan-2-yl)amino)methyl)-1-methyl-5-phenylpyrrolidine (9h)

According to the general procedure, alcohol **12** (150 mg, 784 µmol) was mesylated and treated with (*S*)-3,3-dimethyl-2-butanylamine (1.19 mL, 900 mg, 8.89 mmol) to give, after column chromatography (silica gel, CH_2Cl_2/MeOH, 100:0–97:3) and filtration through a pad of basic alumina (activity I, CH_2Cl_2/MeOH, 9:1), prolinamine **9h** (111 mg, 404 µmol, 52%) as a colorless oil.

R_f 0.4 (EtOAc). $[\alpha]_D^{21}$ 48.6 (*c* 0.50 in MeOH). IR (ATR) ν_{max}/cm^{-1} 2952w, 2784w, 1452w, 1370w, 1335w, 1203w, 1149w, 1119w, 1041w, 754s, 698vs. ^{1}H NMR δ_H(400 MHz; $CDCl_3$) 0.93 (9 H, s, C(CH_3)$_3$), 0.99 (3 H, d, *J* = 6.4 Hz, CHC*H*$_3$), 1.38 (1 H, br s, NH), 1.66 (1 H, m, 4-*H*H), 1.92 (2 H, m, 3-H$_2$), 2.05 (1 H, m, 4-H*H*), 2.14 (3 H, s, 1-CH_3), 2.27 (1 H, q, *J* = 6.4 Hz, C*H*CH_3), 2.49 (1 H, dd, *J* = 11.0, 6.0 Hz, 2-C*H*H), 2.59 (1 H, m, 2-H), 2.96 (1 H, dd, *J* = 11.0, 2.8 Hz, CH*H*N), 3.29 (1 H, dd, *J* = 9.5, 6.9 Hz, 5-H), 7.23 (1 H, m, Ar-H), 7.32 (4 H, m, Ar-H) ppm. ^{13}C NMR δ_C(100 MHz; $CDCl_3$) 15.3 (CH*C*H$_3$), 26.7 (C(*C*H$_3$)$_3$), 28.1 (C-3), 34.5 (C-4), 34.6 (*C*(CH$_3$)$_3$), 39.1 (1-CH_3), 52.3 (2-CH_2), 64.0 (*C*HCH$_3$), 66.5 (C-2), 72.5 (C-5), 127.0, 127.4, 128.4 (CH-Ar), 144.3 (C$_q$-Ar) ppm. HRMS (ESI, pos.) *m/z* calcd for $C_{18}H_{31}N_2$ $[M + H]^+$ 275.2482, found 275.2481.

1.1.10 (2*R*,5*S*)-1-Methyl-2-phenyl-5-((((*R*)-1-phenylethyl)amino)methyl)pyrrolidine (9i)

According to the general procedure, alcohol **12** (180 mg, 941 µmol) was mesylated and treated with (*R*)-1-phenylethylamine (2.40 mL, 2.28 g, 18.8 mmol) to give, after column chromatography (1. silica gel, CH_2Cl_2/MeOH, 100:0–97:3, 2. silica gel, petroleum ether/EtOAc, 1:0–2:1) and filtration through a pad of basic alumina (activity I, CH_2Cl_2/MeOH, 9:1), prolinamine **9i** (173 mg, 588 µmol, 62%) as an orange solid.

R_f 0.47 (EtOAc). Mp 52–55 °C. $[\alpha]_D^{21}$ 60.5 (*c* 1.00 in MeOH). IR (ATR) ν_{max}/cm^{-1} 2960w, 2841w, 2784w, 1490w, 1447s, 1341w, 1199s, 1128w, 1083s, 1041w, 755vs, 698vs. ^{1}H-NMR δ_H(400 MHz; $CDCl_3$) 1.43 (3 H, d, *J* = 6.6 Hz, CHC*H*$_3$), 1.74 (2 H, m, 3-*H*H, NH), 1.95 (2 H, m, 4-H$_2$), 2.08 (1 H, m, 3-H*H*), 2.16 (3 H, s, 1-CH_3), 2.59 (2 H, m, 5-C*H*H, 5-H), 2.67 (1 H, m, 5-CH*H*), 3.31 (1 H, dd, *J* = 9.8, 6.7 Hz, 2-H), 3.85 (1 H, q, *J* = 6.6 Hz, C*H*CH_3), 7.27 (2 H, m, Ar-H), 7.38 (8 H, m, Ar-H) ppm. ^{13}C NMR δ_C(100 MHz, $CDCl_3$) 25.1 (CH*C*H$_3$), 27.8 (C-4), 34.6 (C-3), 39.4 (1-CH_3), 50.7 (5-CH_2), 59.0 (*C*HCH$_3$), 66.1 (C-5), 72.7 (C-2), 126.78, 126.81, 127.0, 127.4, 128.38, 128.41 (CH-Ar), 144.2, 146.4 (C$_q$-Ar) ppm. HRMS (ESI, pos.) *m/z* calcd for $C_{20}H_{27}N_2$ $[M + H]^+$ 295.2169, found 295.2167.

1.1.11 (2*S*,5*R*)-2-((*tert*-Butylamino)methyl)-1-methyl-5-phenylpyrrolidine (9j)

According to the general procedure, alcohol **12** (150 mg, 784 µmol) was mesylated and treated with *tert*-butylamine (1.65 mL, 1.15 g, 15.7 mmol) to give, after column chromatography (silica gel, deactivated with 7.5% aq NH_3 (25%), CH_2Cl_2/MeOH, 1:0–9:1), prolinamine **9j** (125 mg, 507 µmol, 65%) as a yellow oil.

R_f 0.35 (CH_2Cl_2/MeOH 9:1). $[\alpha]_D^{21}$ 16.6 (*c* 0.20 in MeOH). IR (ATR) ν_{max}/cm^{-1} 2961s, 2836w, 2782w, 1452w, 1360s, 1230s, 1085w, 1027w, 755s, 698vs. ^{1}H-NMR δ_H(400 MHz; $CDCl_3$) 1.15 (9 H, s, C(CH_3)$_3$), 1.25 (1 H, br s, NH), 1.69 (1 H, m, 4-*H*H), 1.78 (1 H, m, 3-*H*H), 1.98 (1 H, m, 3-H*H*), 2.06 (1 H, m, 4-H*H*), 2.17 (3 H, s, 1-CH_3), 2.57 (1 H, m, 2-H), 2.65 (1 H, dd, *J* = 10.6, 6.7 Hz, 2-C*H*H), 2.78 (1 H, dd, *J* = 10.6, 3.6 Hz, 2-CH*H*), 3.29 (1 H, dd, *J* = 9.4, 6.6 Hz, 5-H), 7.23 (1 H, m, Ar-H), 7.33 (4 H, m, Ar-H) ppm. ^{13}C NMR δ_C(100 MHz; $CDCl_3$) 28.3 (C-3), 29.2 (C(*C*H$_3$)$_2$), 34.3 (C-4), 39.5 (1-CH_3), 46.2 (2-CH_2), 50.1 (*C*(CH$_3$)$_2$), 66.5 (C-2), 72.6 (C-5), 127.0, 127.4, 128.4 (CH-Ar), 144.1 (C$_q$-Ar) ppm. HRMS (ESI, pos.) *m/z* calcd for $C_{16}H_{27}N_2$ $[M + H]^+$ 247.2169, found 247.2170.

1.1.12 (2*S*,5*R*)-2-(((1,3-bis(benzyloxy)-2-((benzyloxy)methyl)propan-2-yl)amino)methyl)-1-methyl-5-phenylpyrrolidine (9k)

According to the general procedure, alcohol **12** (200 mg, 1.05 mol) was mesylated and treated with 1,3-bis(benzyloxy)-2-((benzyloxy)methyl)propan-2-amine (1.64 g, 4.20 mmol) to give, after column chromatography (1. silica gel, CH_2Cl_2/MeOH, 100:0–95:5, 2. silica gel, petroleum ether/EtOAc/MeOH/NH_3 (aq, 25%), 400:600:9:1 prolinamine **9k** (279 mg, 494 µmol, 47 %) as a colorless oil.

R_f 0.66 (petroleum ether/EtOAc/MeOH/aq NH_3 (25%), 400:600:9:1). $[\alpha]_D^{28}$ 28.6 (*c* 1.0 MeOH). IR (ATR) ν_{max}/cm^{-1} 2855w, 1452w, 1363w, 1204w, 1090s, 1074s, 1027w, 733s, 695vs. ^{1}H-NMR δ_H(300 MHz; $CDCl_3$) 1.63-1.90 (2 H, m, 3-*H*H, 4-*H*H), 1.91-2.15 (3 H, m, 3-H*H*, 4-H*H*, NH), 2.18 (3 H, s, 1-CH_3), 2.63 (1 H, m, 2-H), 2.77 (1 H, dd, *J* = 10.3, 6.9 Hz, 2-C*H*H), 2.90 (1 H, dd, *J* = 10.4, 3.4 Hz, 2-CH*H*), 3.32 (1 H, dd, *J* = 9.5, 6.5 Hz, 5-H), 3.58 (3 H, d, *J* = 9.2 Hz, C(C*H*HO)$_3$), 3.62 (3 H, d, *J* = 9.2 Hz, C(CH*H*O)$_3$), 4.59 (6 H, s, CH_2Ar), 7.23-7.46 (20 H, m, Ar-H) ppm. ^{13}C NMR δ_C(75 MHz; $CDCl_3$) 28.1 (C-3), 34.4 (C-4), 39.4 (1-CH_3), 45.6 (2-CH_2), 59.4 (*C*(CH$_2$)$_3$), 66.5 (C-2), 70.3 (C(*C*H$_2$)$_3$), 72.5 (C-5), 73.4 (CH_2Ar), 126.9, 127.41, 127.44, 127.5, 128.3 (Ar-H), 138.8, 144.1 (C$_q$-Ar) ppm. HRMS (ESI, pos.) *m/z* calcd for $C_{37}H_{45}N_2O_3$ $[M + H]^+$ 565.3425, found 565.3421.

1.1.13 (2*R*,5*S*)-1-Methyl-2-phenyl-5-((phenylamino)methyl)pyrrolidine (9l)

According to the general procedure, alcohol **12** (150 mg, 784 µmol) was mesylated and treated with aniline (1.43 mL, 1.46 g, 15.7 mmol) to give, after column chromatography (1. silica gel, deactivated with 7.5% aq NH_3 (25%), petroleum ether/EtOAc, 1:0–3:1; 2. silica gel, deactivated with 7.5% aq NH_3 (25%), petroleum ether/Et_2O, 1:0–11:1) and filtration through a pad of basic alumina (activity I, CH_2Cl_2/MeOH, 9:1), prolinamine **9l** (152 mg, 570 µmol, 73%) as a colorless oil.

R_f 0.77 (petroleum ether/EtOAc 3:1, deact. SiO_2). $[\alpha]_D^{21}$ 23.9 (*c* 0.20 in MeOH). IR (ATR) ν_{max}/cm^{-1} 3376br, 2947w, 2839w, 2788w, 1602vs, 1504vs, 1428s, 1315s, 1086w, 1045w, 938w, 746vs, 690vs. ^{1}H NMR δ_H(400 MHz; $CDCl_3$) 1.75 (1 H, m, 3-*H*H), 1.99 (2 H, m, 4-H_2), 2.14 (1 H, m, 3-H*H*), 2.20 (3 H, s, 1-CH_3), 2.82 (1 H, m, 5-H), 3.24 (1 H, dd, *J* = 11.7, 4.7 Hz, 5-C*H*H), 3.32 (1 H, dd, *J* = 11.8, 2.5 Hz, 5-CH*H*), 3.39 (1 H, dd, *J* = 9.6, 6.9 Hz, 2-H), 4.40 (1 H, br s, NH), 6.73 (3 H, m, Ar-H), 7.24 (2 H, m, Ar-H), 7.30 (1 H, m, Ar-H), 7.40 (4 H, m, Ar-H) ppm. ^{13}C NMR δ_C(100 MHz, $CDCl_3$) 26.5 (C-4), 33.3 (C-3), 37.7 (1-CH_3), 44.1 (5-CH_2), 63.9 (C-5), 71.4 (C-2), 112.0, 116.1, 126.2, 126.4, 127.5, 128.4 (CH-Ar), 142.7, 148.2 (C_q-Ar) ppm. HRMS (ESI, pos.) *m/z* calcd for $C_{18}H_{23}N_2$ $[M + H]^+$ 267.1856, found 267.1855.

1.2 Naphthol esters 1

1.2.1 Isopropyl 3-hydroxy-2-naphthoate (1b)[5]

A suspension of 3-hydroxy-2-naphthoic acid (480 mg, 2.55 mmol) in anhydrous benzene (10 mL) and anhydrous DMF (20 µL) was treated dropwise with $SOCl_2$ (556 µL, 910 mg, 7.65 mmol) and stirred for 3 h at 40 °C. The solvent was removed under reduced pressure and the resulting orange solid was suspended in *i*PrOH (15 mL). The solvent was removed after 18 h at 60 °C and sat. aq Na_2CO_3 (20 mL) was slowly added. The mixture was extracted with CH_2Cl_2 (3 × 20 mL) and the combined organic layers were dried over $MgSO_4$. Removal of the solvent and column chromatography (silica gel, petroleum ether/EtOAc, 19:1) delivered the ester **1b** (438 mg, 1.90 mmol, 75%) as a yellow solid.

R_f 0.71 (petroleum ether/Et_2O 5:1). Mp 67–68 °C. IR (ATR) ν_{max}/cm^{-1} 3252br, 2974w, 1678s, 1304s, 1277vs, 1207vs, 1142vs, 1101vs, 1065vs, 788s, 739s, 689s. ^{1}H NMR δ_H(500 MHz; $CDCl_3$) 1.46 (6 H, d, *J* = 6.3 Hz, CH(C*H*$_3$)$_2$), 5.37 (1 H, sept, *J* = 6.3 Hz, C*H*(CH$_3$)$_2$), 7.32 (2 H, m, 4-H, 7-H), 7.49 (1 H, m, 6-H), 7.68 (1 H, d, *J* = 8.3 Hz, 5-H), 7.81 (1 H, d, *J* = 8.2 Hz, 8-H), 8.48 (1 H, s, 1-H), 10.65 (1 H, s, OH) ppm. ^{13}C NMR δ_C(125 MHz, $CDCl_3$) 22.0 (CH(*C*H$_3$)$_2$), 69.8 (*C*H(CH$_3$)$_2$), 111.7 (C-4), 114.8 (C-2), 124.0 (C-7), 126.4 (C-5), 127.1 (C-8a), 129.1 (C-6), 129.3 (C-8), 132.4 (C-1), 137.9 (C-4a), 156.6 (C-3), 169.6 (CO_2) ppm. HRMS (ESI, pos.) *m/z* calcd for $C_{14}H_{14}O_3Na$ $[M + Na]^+$ 253.0835, found 253.0828.

1.2.2 *tert*-Butyl 3-hydroxy-2-naphthoate (1d)[6]

A solution of 3-hydroxy-2-naphthoic acid (3.00 g, 15.9 mmol) and 1,1'-carbonyldiimidazole (2.58 g, 15.9 mmol) in anhydrous DMF (16 mL) was stirred at 50 °C for 1 h. DBU (2.38 mL, 2.42 g, 15.9 mmol) and *t*BuOH (2.98 mL, 2.36 g, 31.8 mmol) were added and stirring was continued for 16 h at 50 °C. Et_2O (100 mL) and sat. aq $NaHCO_3$ (100 mL) were added and the layers were separated. The aqueous layer was extracted with Et_2O (100 mL) and the combined organic layers were dried over $MgSO_4$. Removal of the solvent and column chromatography (silica gel, petroleum ether/CH_2Cl_2, 2:1) delivered the ester **1d** (2.04 g, 11.8 mmol, 74%) as a yellow solid.
The spectroscopic data of **1d** were consistent with those reported in literature.[6]

1.3 Binaphthols 2

1.3.1 Preparation of homochiral (*M*)-2a by trituration

Scalemic (*M*)-**2a** (62% ee, 740 mg, 1.84 mmol) was suspended in EtOAc (11 mL) and ultra-sonificated for 2 min. Filtration afforded crystalline material of (*M*)-**2a** with low enantiopurity (414 mg, 1.03 mmol, 56%, 35% ee) and, from the mother liquor, highly enantioenriched material of (*M*)-**2a** (326 mg, 810 µmol, 44%, 96% ee).

1.3.2 Diisopropyl (*M*)-2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylate [(*M*)-2b (75% ee)][5]

This compound was obtained in the oxidative coupling of **1b** in the presence of CuCl•**9f** (see Table 6, entry 6).

Yellow solid. R_f 0.38 (petroleum ether/Et_2O 5:1). Mp 205–207 °C. $[\alpha]_D^{29}$ 111.5 (*c* 1.00 in CH_2Cl_2). IR (ATR) ν_{max}/cm^{-1} 3200br, 2982w, 1667s, 1338w, 1281vs, 1215s, 1104vs, 1072s, 915w, 795s, 737s. ^{1}H NMR δ_H(500 MHz; $CDCl_3$) 1.47 (6 H, d, *J* = 6.3 Hz, CH(C*H*$_3$)$_2$), 1.49 (6 H, d, *J* = 6.3 Hz, CH(C*H*$_3$)$_2$), 5.38 (2 H, sept, *J* = 6.3 Hz, C*H*(CH$_3$)$_2$), 7.15 (2 H, m, 5-H), 7.34 (4 H, m, 6-H, 7-H), 7.93 (2 H, m, 8-H), 8.67 (2 H, s, 1-H), 10.93 (2 H, s, OH) ppm. ^{13}C NMR δ_C(125 MHz, $CDCl_3$) 22.1 (CH(*C*H$_3$)$_2$), 69.9 (*C*H(CH$_3$)$_2$), 114.8 (C-2), 117.0 (C-4), 124.0 (C-7), 124.8 (C-5), 127.3 (C-8a), 129.4 (C-6), 129.9

5 Compounds **1b** and **2b** are known, but not fully characterized: (a) A. Caselli, G. B. Giovenzana, G. Palmisano, M. Sisti and T. Pilati, *Tetrahedron: Asymmetry*, 2003, **14**, 1451; (b) S. K. Alamsetti, E. Poonguzhali, D. Ganapathy and G. Sekar, *Adv. Synth. Catal.*, 2013, **355**, 2803.

6 For a different approach to **1d**, see: M. Noji, T. Ohno, K. Fuji, N. Futaba, H. Tajima and K. Ishii, *J. Org. Chem.*, 2003, **68**, 9340.

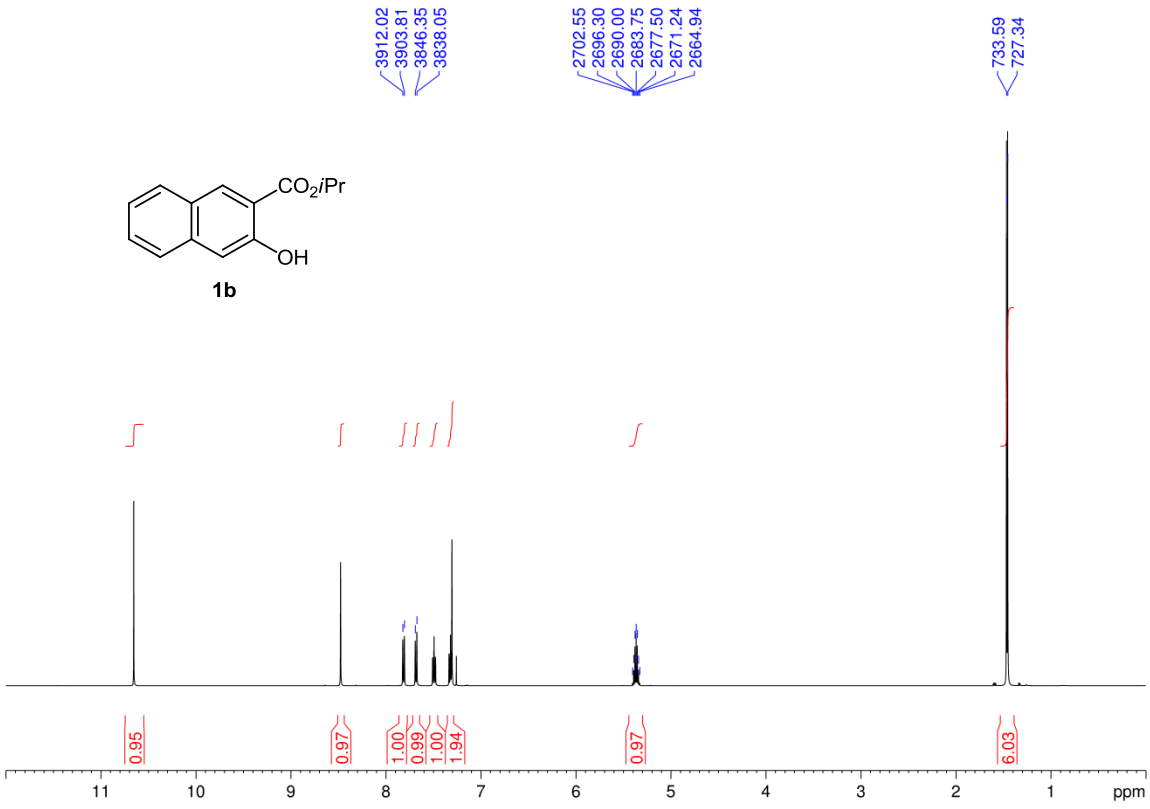
(C-8), 132.8 (C-1), 137.2 (C-4a), 154.3 (C-3), 169.8 (CO_2) ppm. HRMS (ESI, pos.) *m/z* calcd for $C_{28}H_{26}O_6Na$ $[M + Na]^+$ 481.1622, found 481.1613.

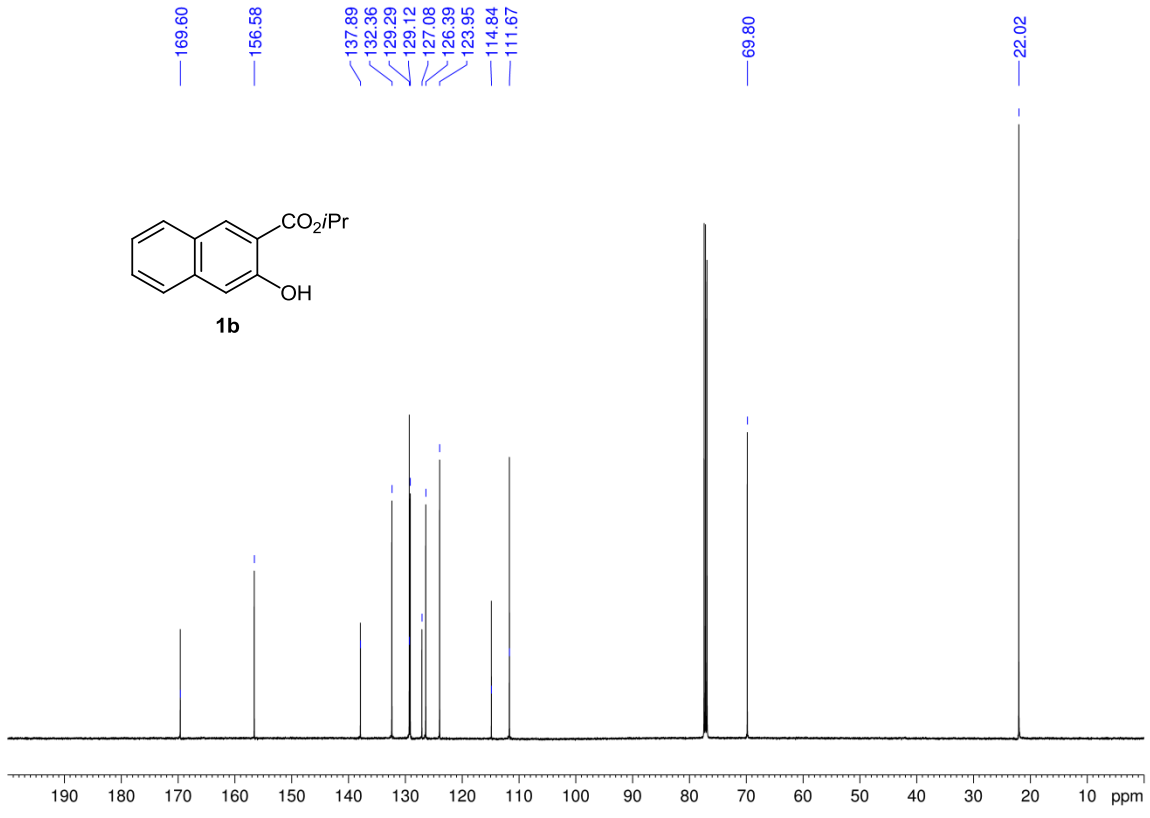
1.3.3 Transesterification of (*M*)-2b to (*M*)-2a

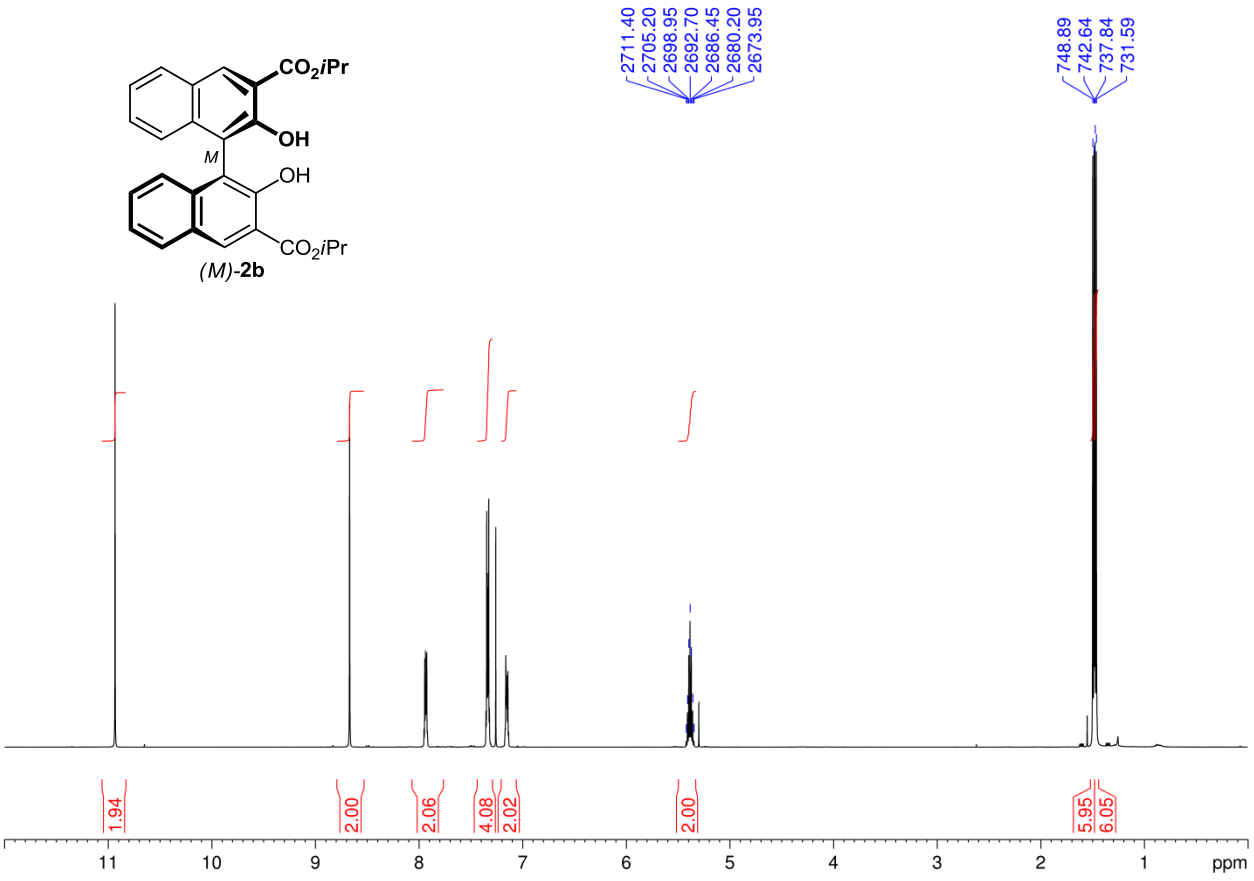
LiOMe (0.1 M in MeOH, 665 µL, 66.5 µmol) was added to a solution of (*M*)-**2c** (61 mg, 133 µmol, 69% ee, obtained in the oxidative coupling of **1b** in the presence of CuCl•**9c**, see Table 6, entry 2) in anhydrous MeOH (6 mL) and anhydrous CH_2Cl_2 (5 mL). LiOMe (0.1 M in MeOH, 133 µL, 13.3 µmol) was added after 2 d at r.t. and stirring was continued for 1 d. Sat. aq NH_4Cl (2 mL) was added and the layers separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL) and the combined organic layers were dried over $MgSO_4$. Removal of the solvent and column chromatography (silica gel, petroleum ether/CH_2Cl_2, 1:2/0:1) delivered the binol (*M*)-**2a** (50 mg, 124 µmol, 93%, 68% ee) as a yellow solid.

2. Copies of ^{1}H and ^{13}C NMR spectra

The ^{1}H and ^{13}C NMR spectra of all new compounds are listed in numerical order.



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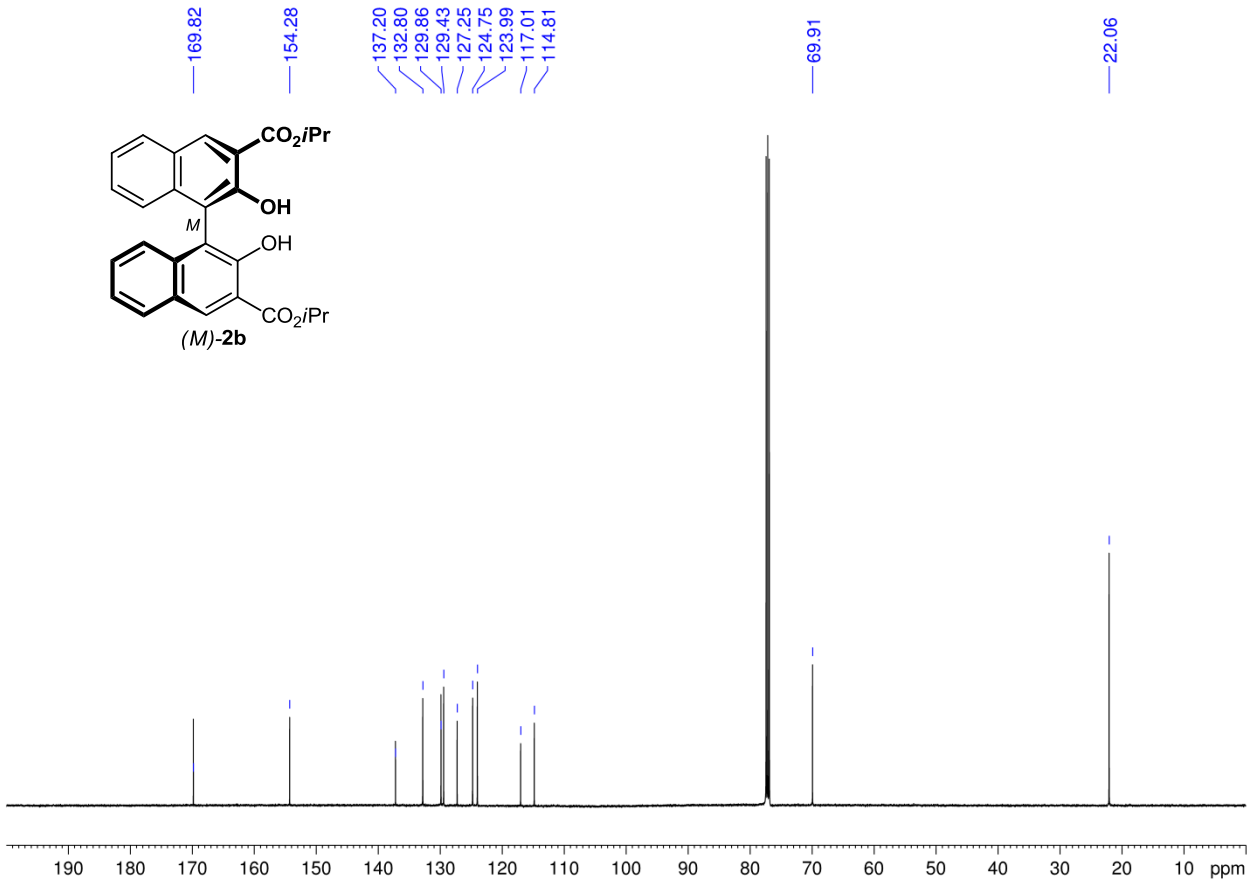
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OH
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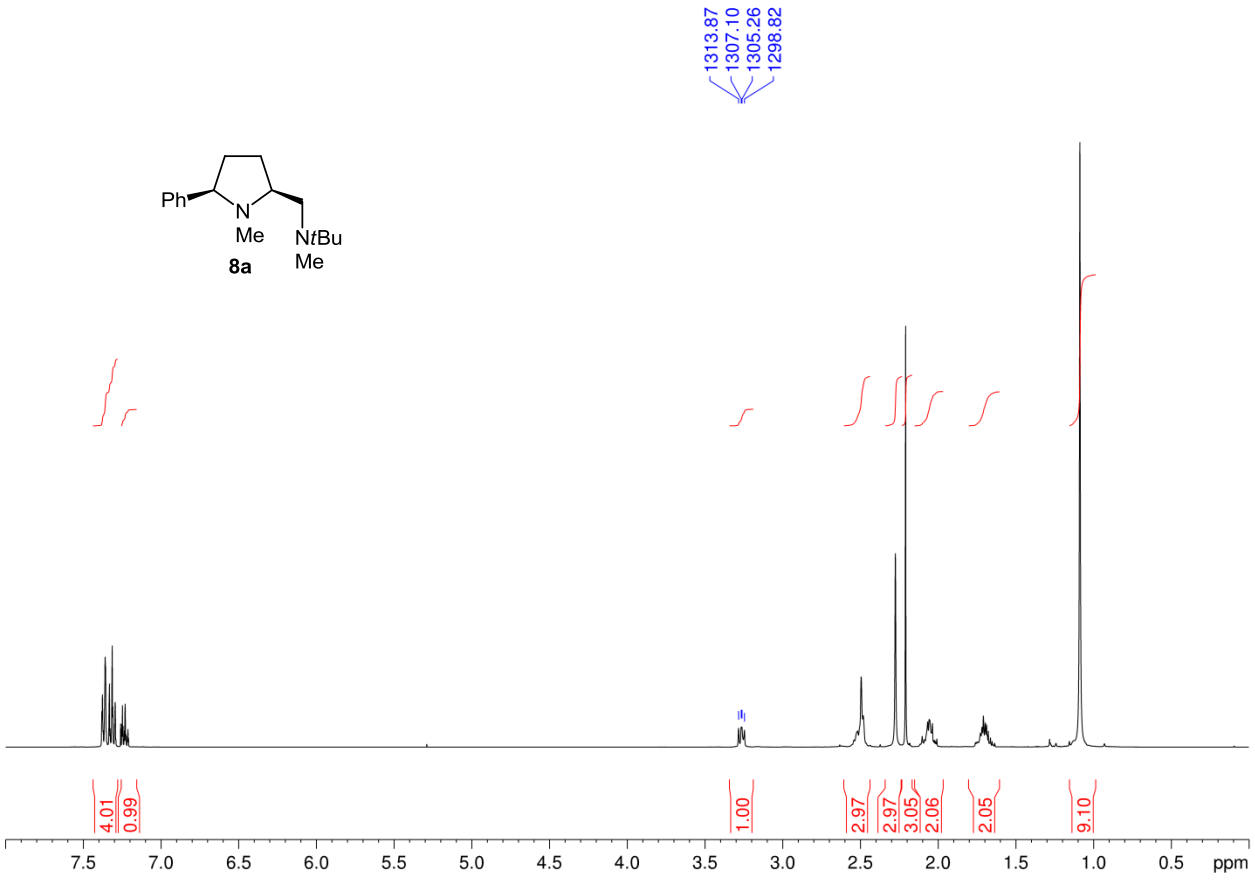
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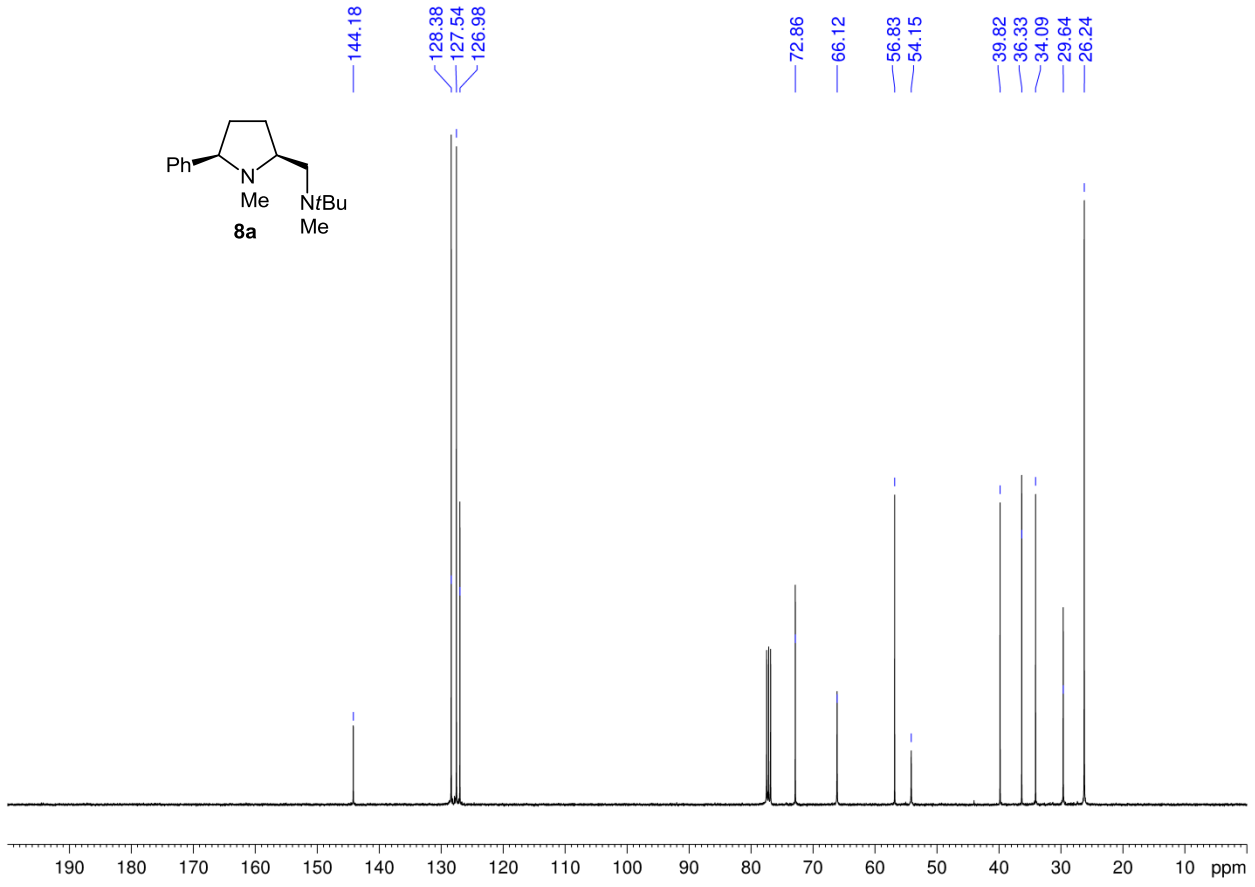
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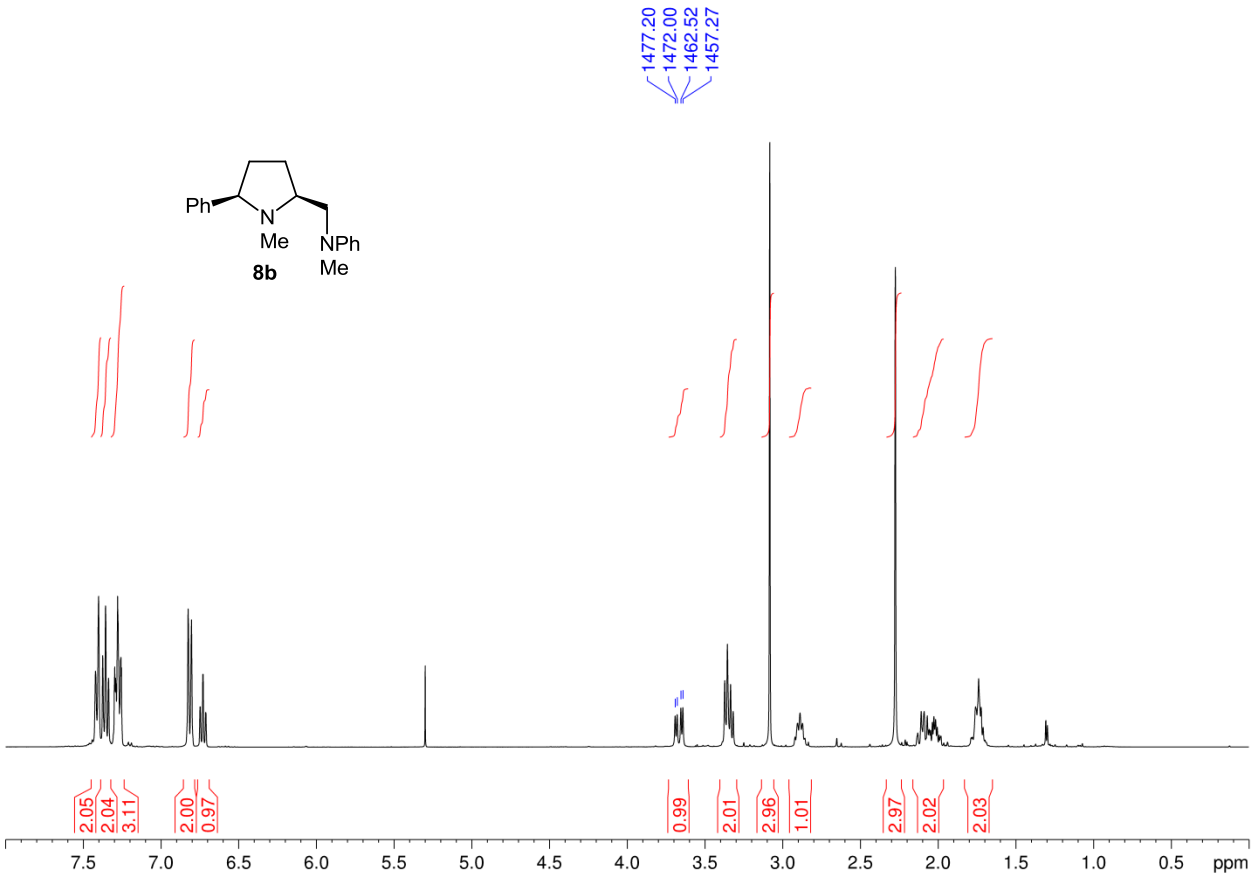
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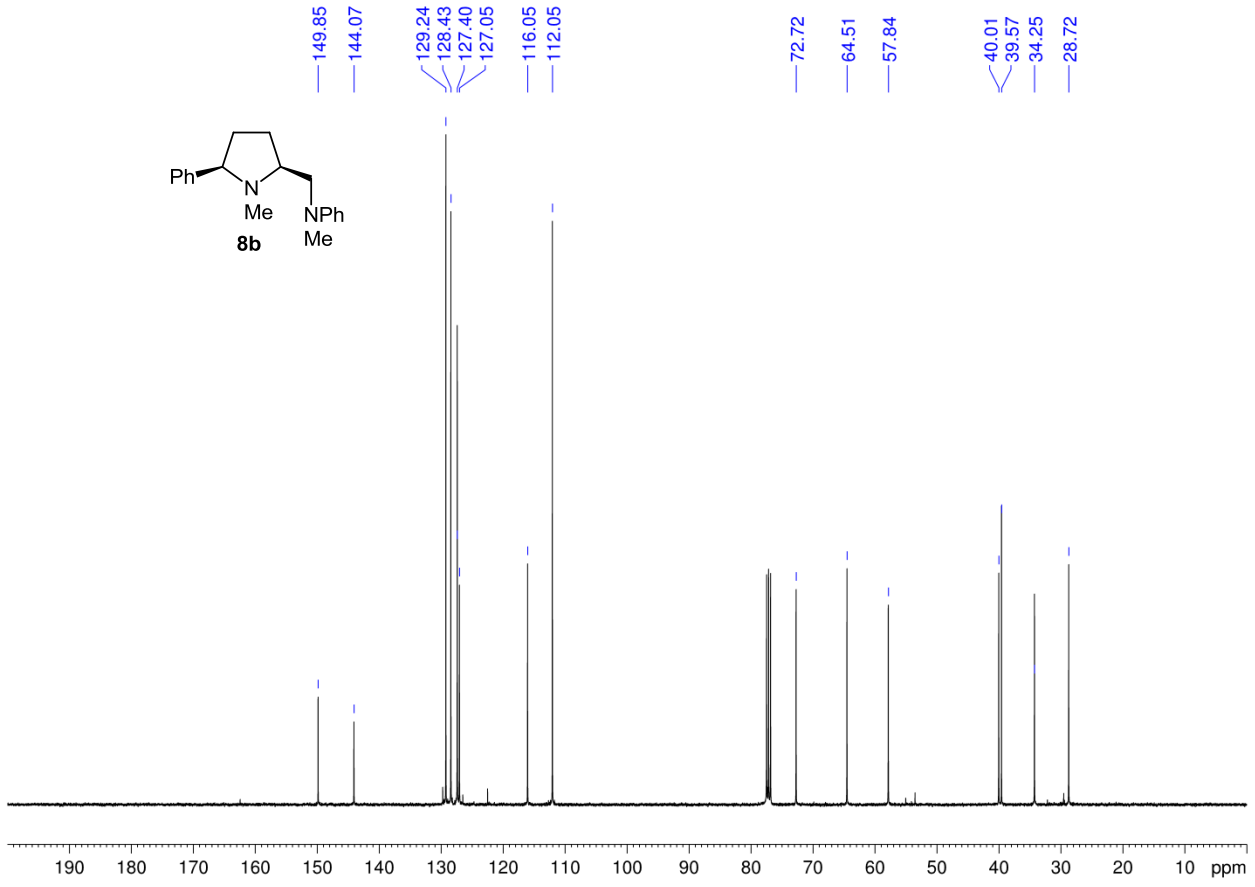
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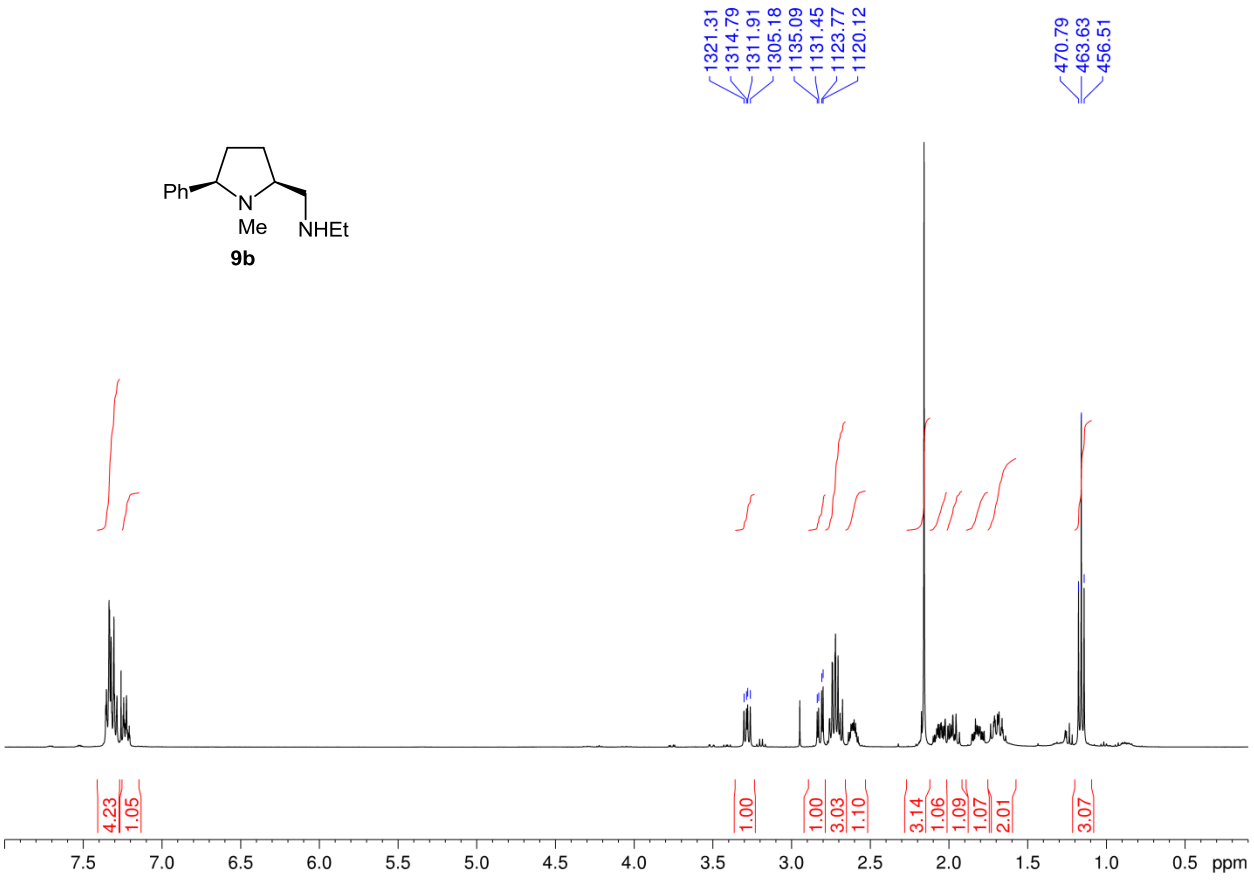
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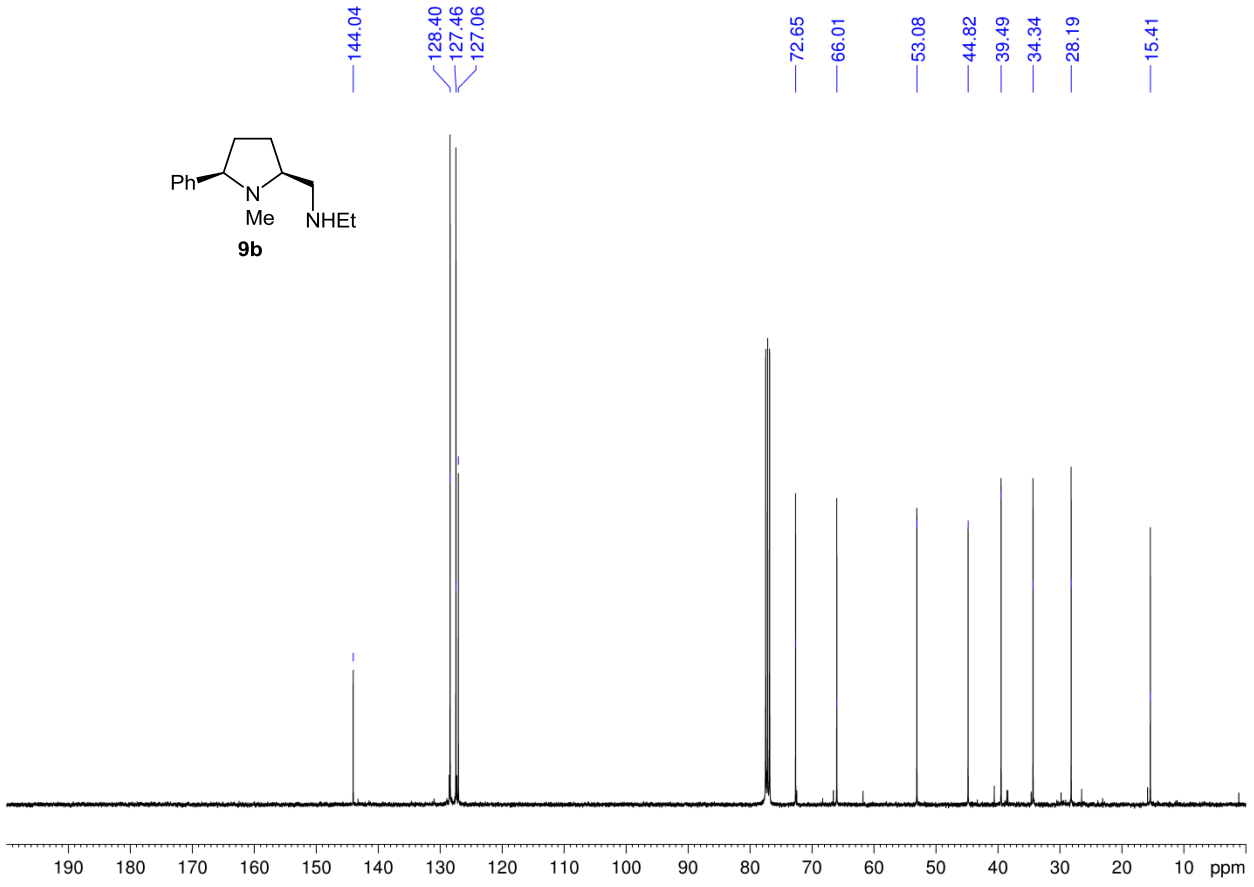
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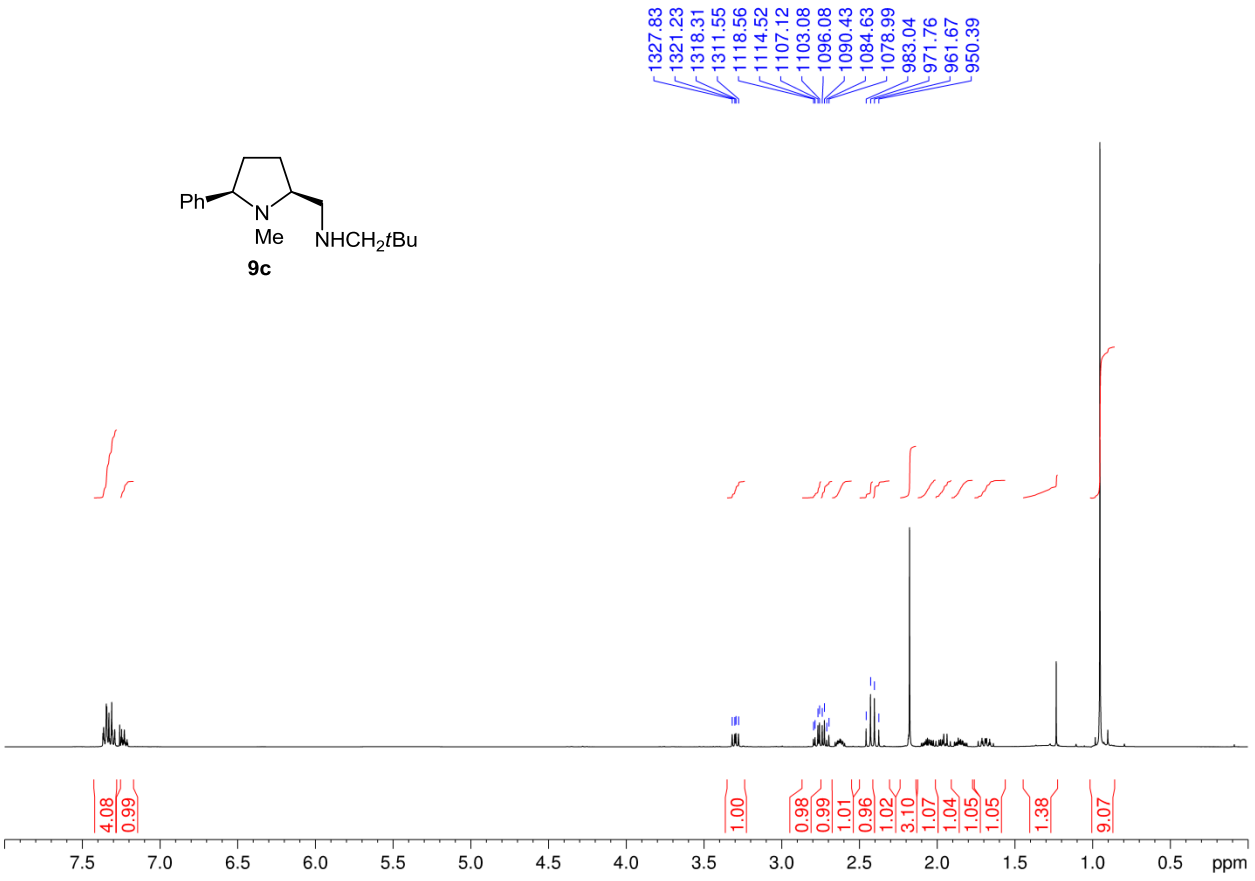
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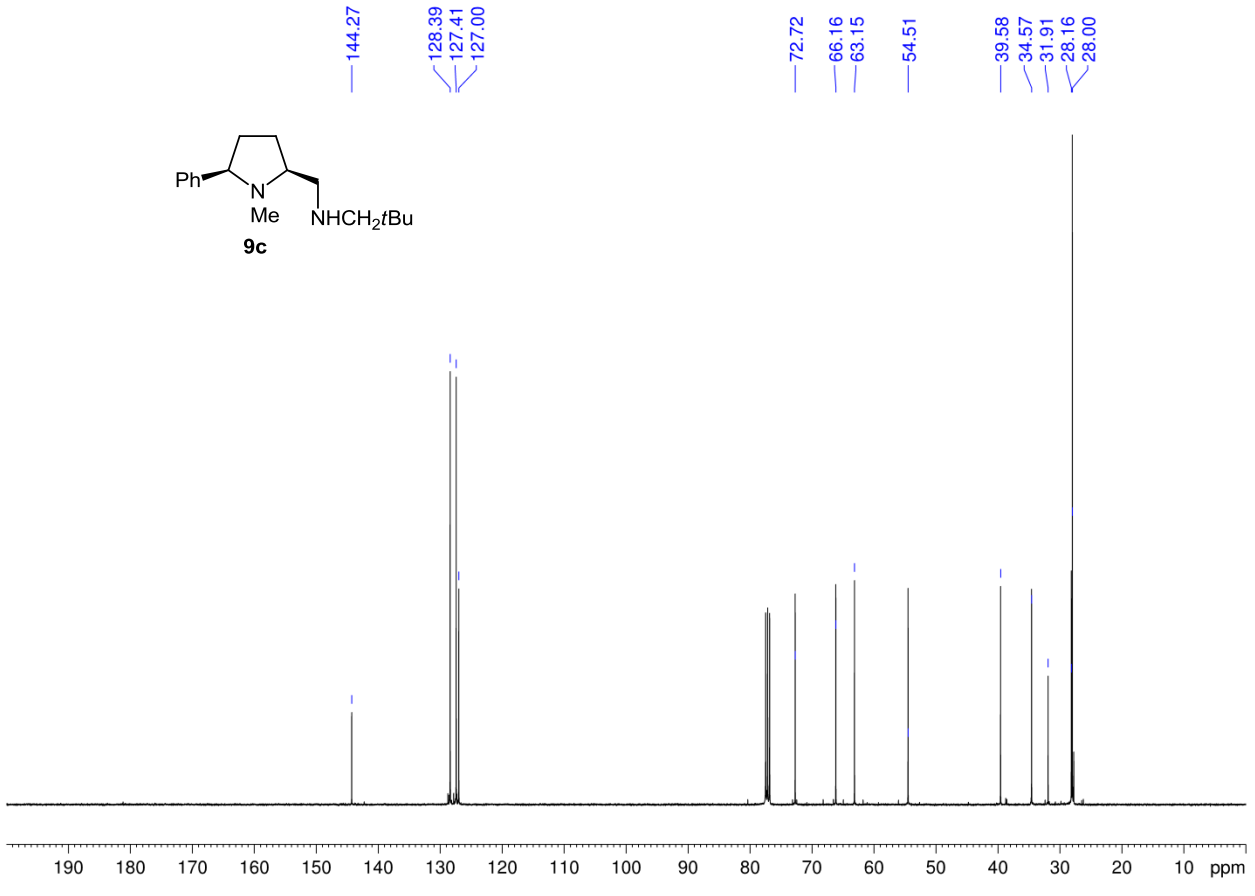
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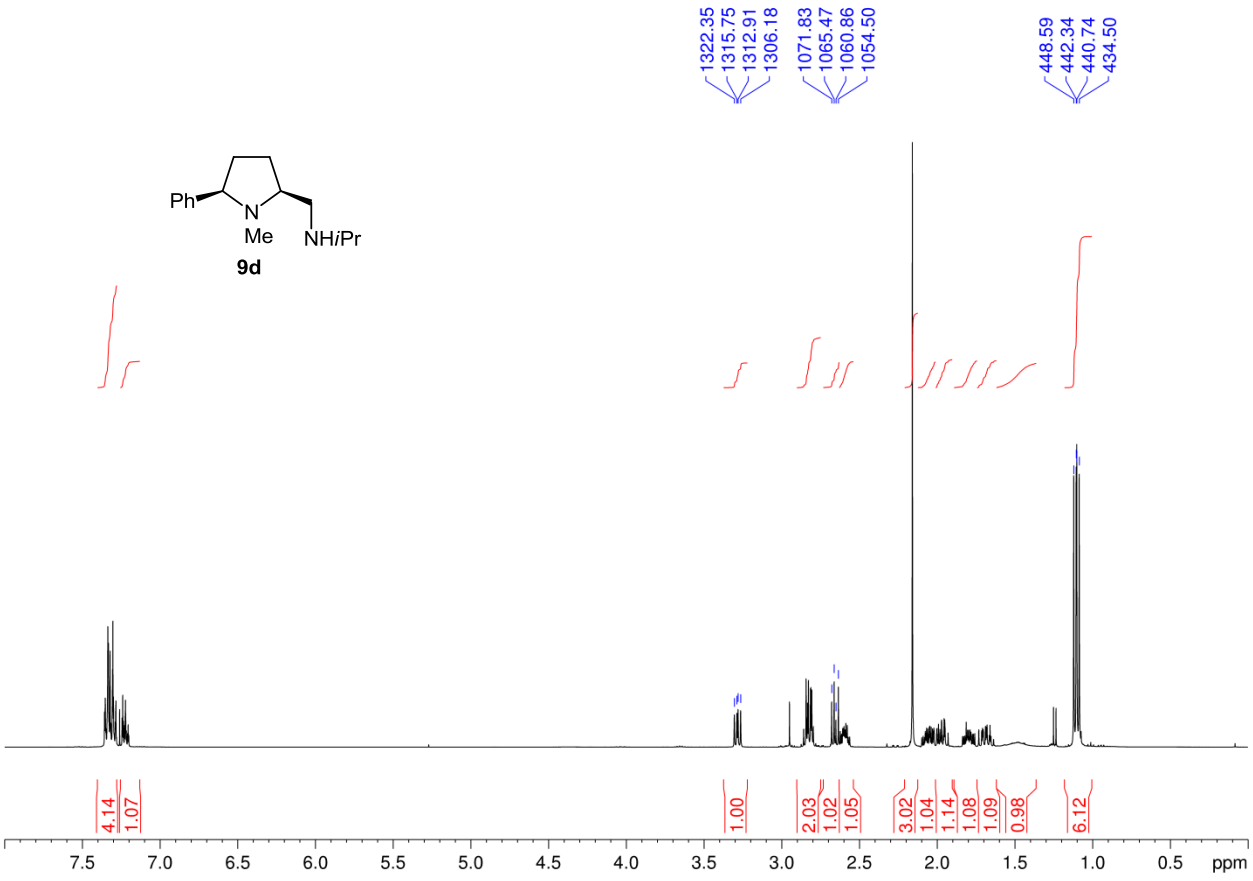
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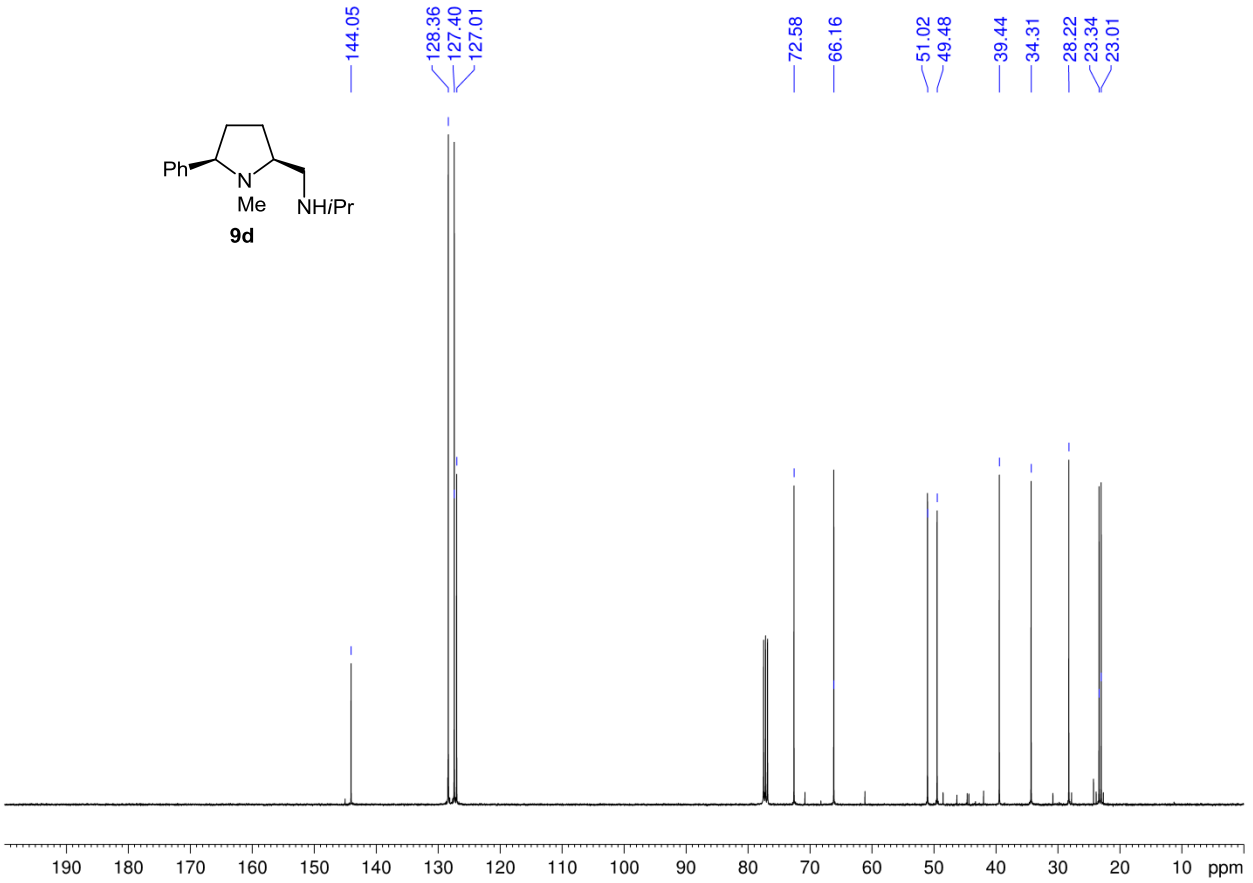
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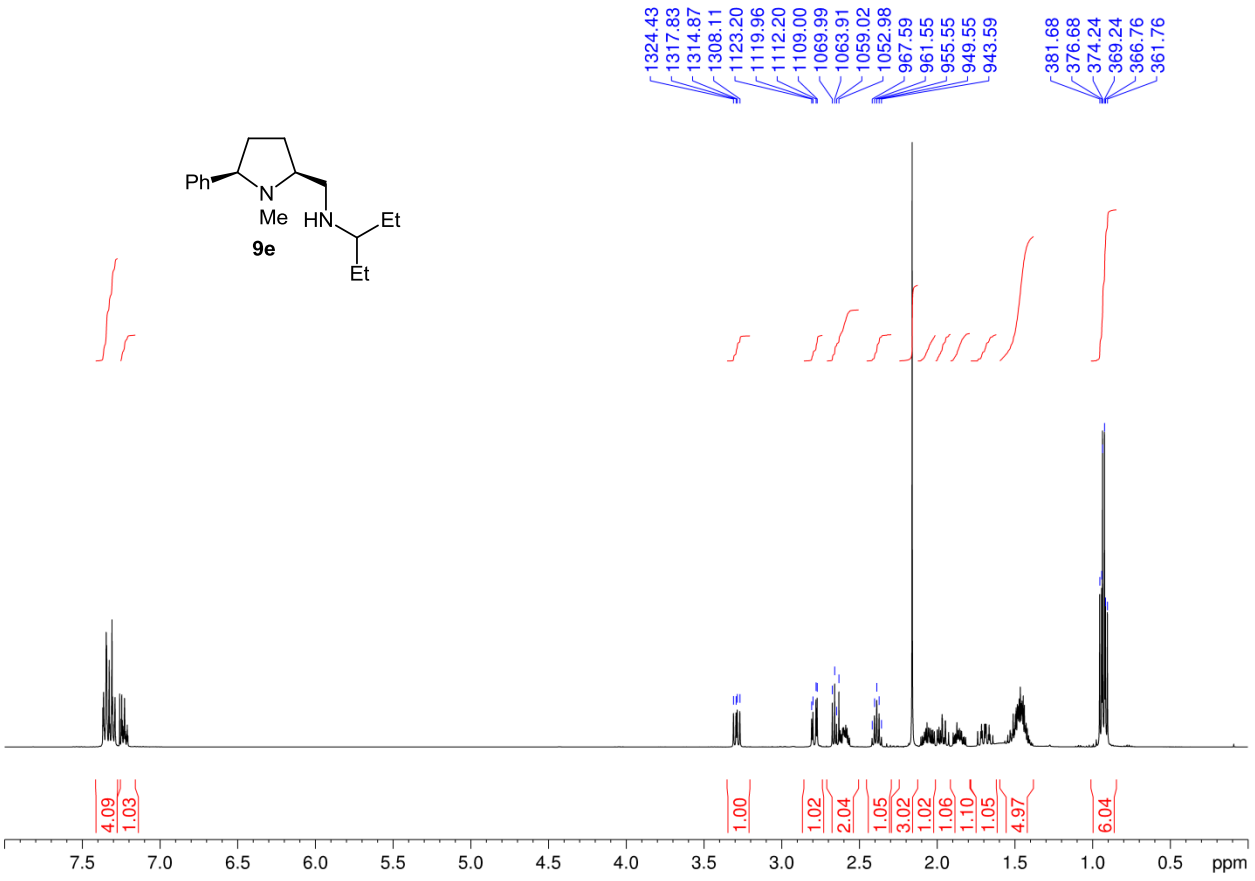
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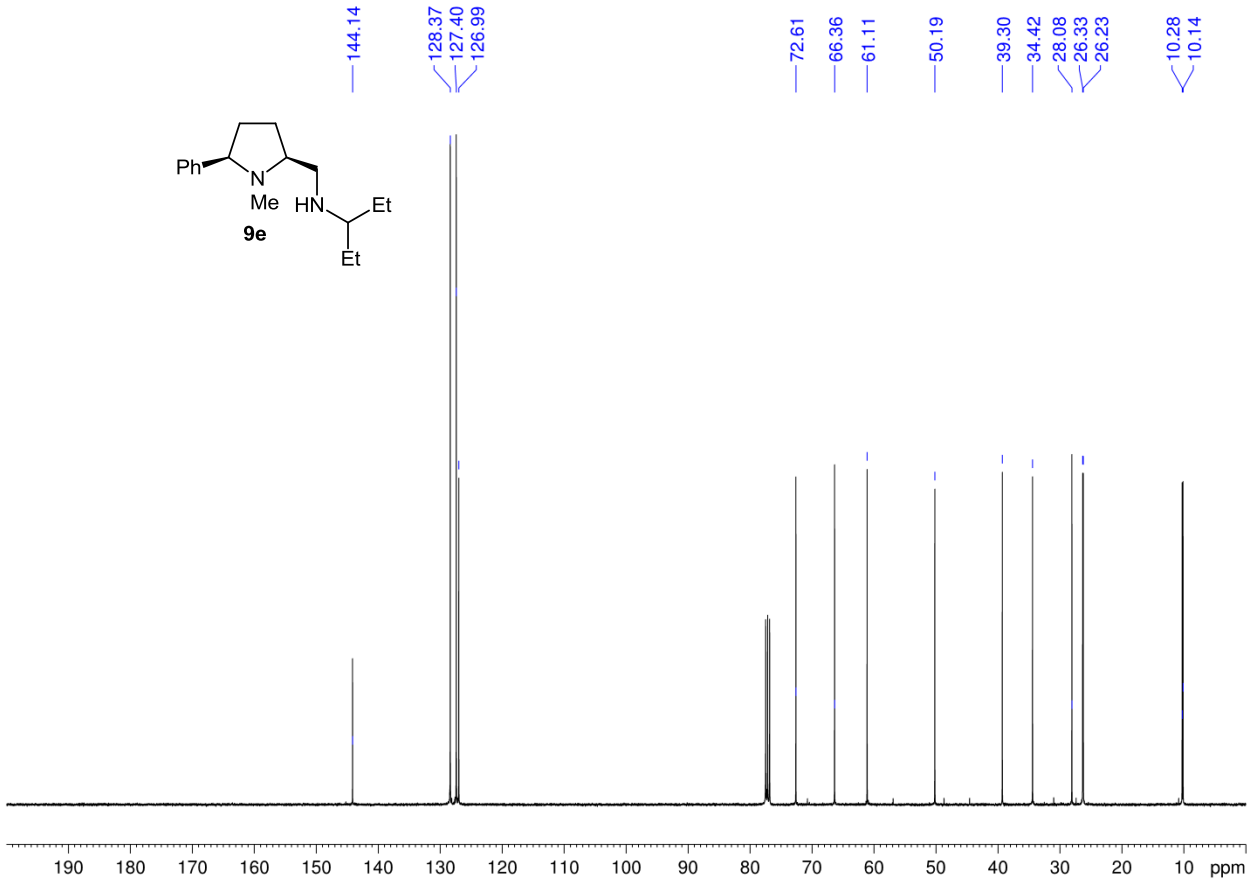
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28.08
26.33
26.23
10.28
10.14
Ph
N
Me
HN
Et
Et
9e
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150
140
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110
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70
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30
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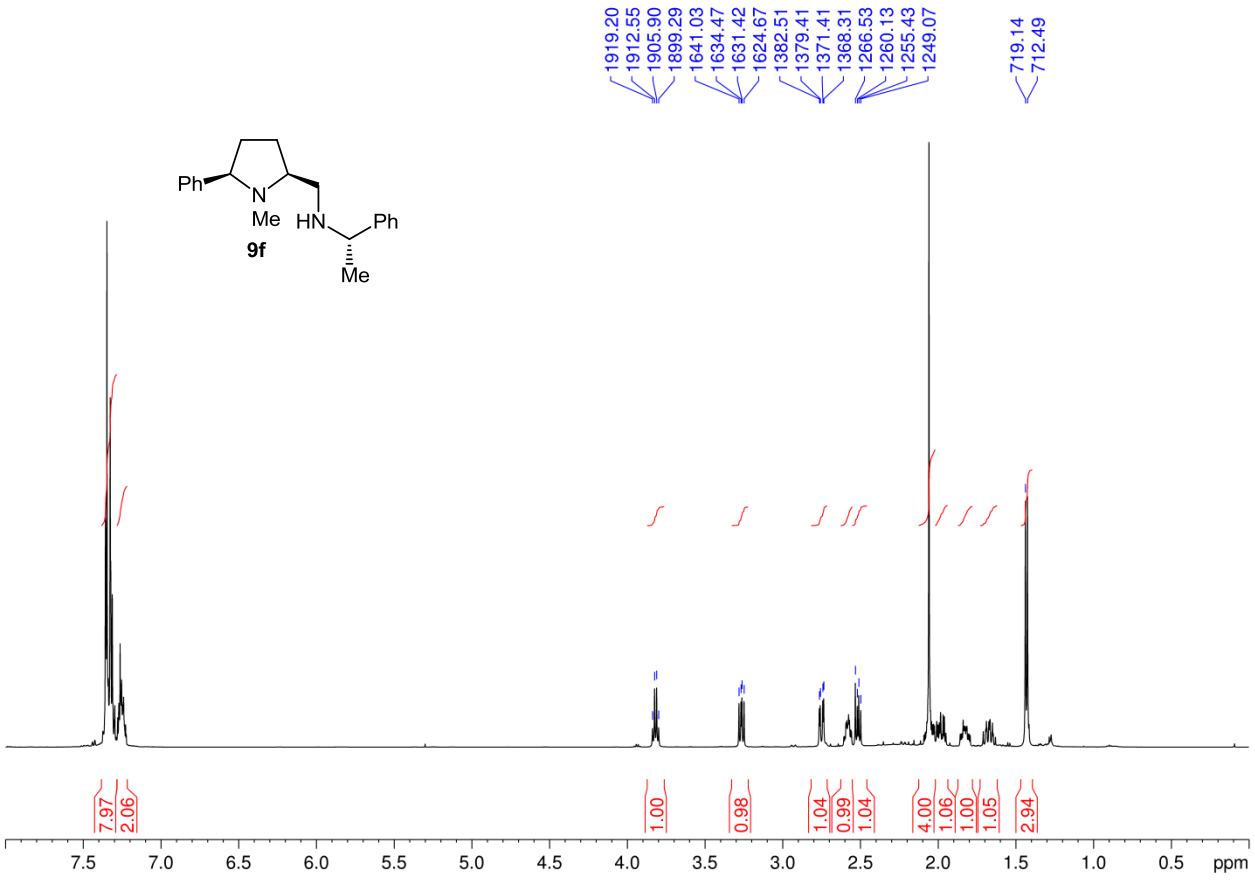
10
ppm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1371.41
1368.31
1266.53
1260.13
1255.43
1249.07
719.14
712.49
Ph
N
Me
HN
Ph
Me
9f
7.97
2.06
1.00
0.98
1.04
0.99
1.04
4.00
1.06
1.00
1.05
2.94
7.5
7.0
6.5
6.0
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4.5
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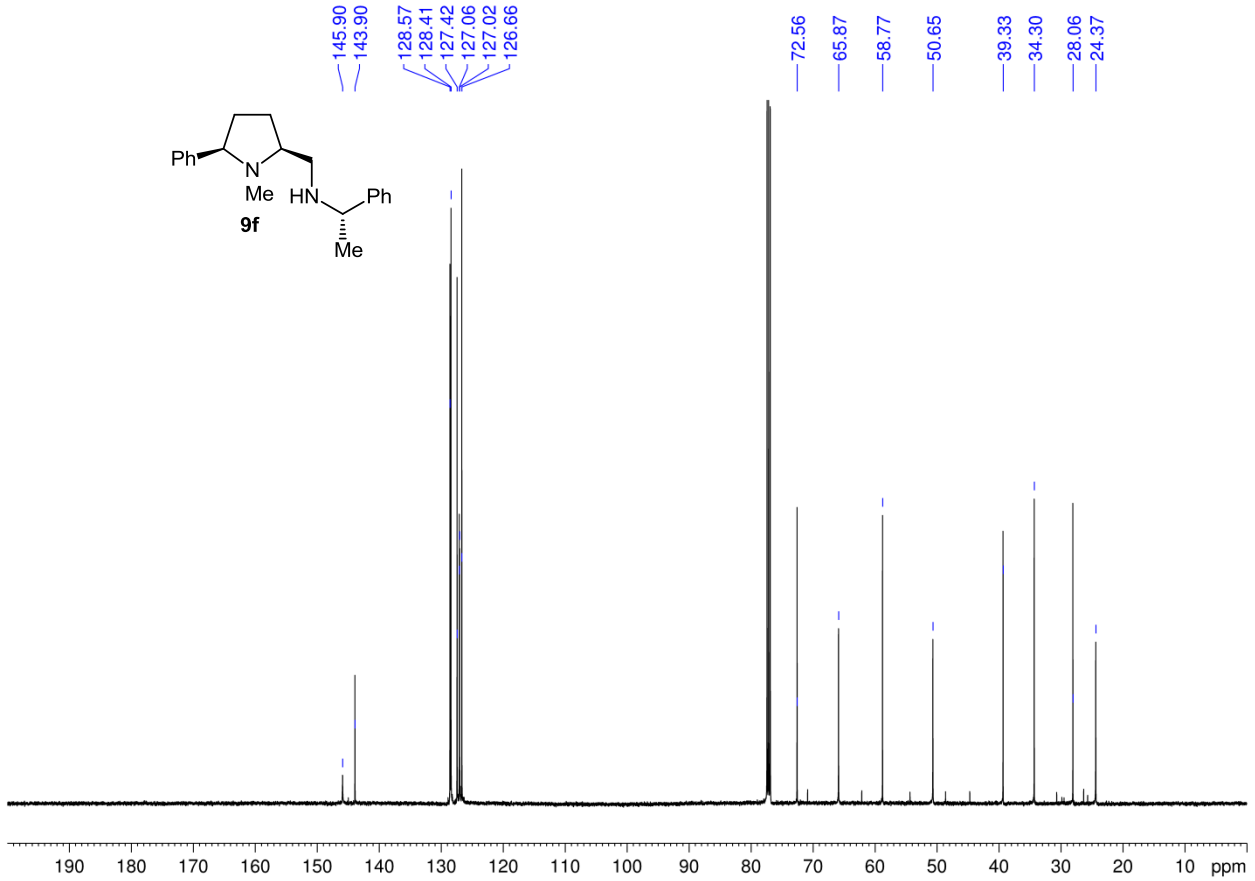
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127.06
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126.66
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58.77
50.65
39.33
34.30
28.06
24.37
Ph
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Me
HN
Ph
Me
9f
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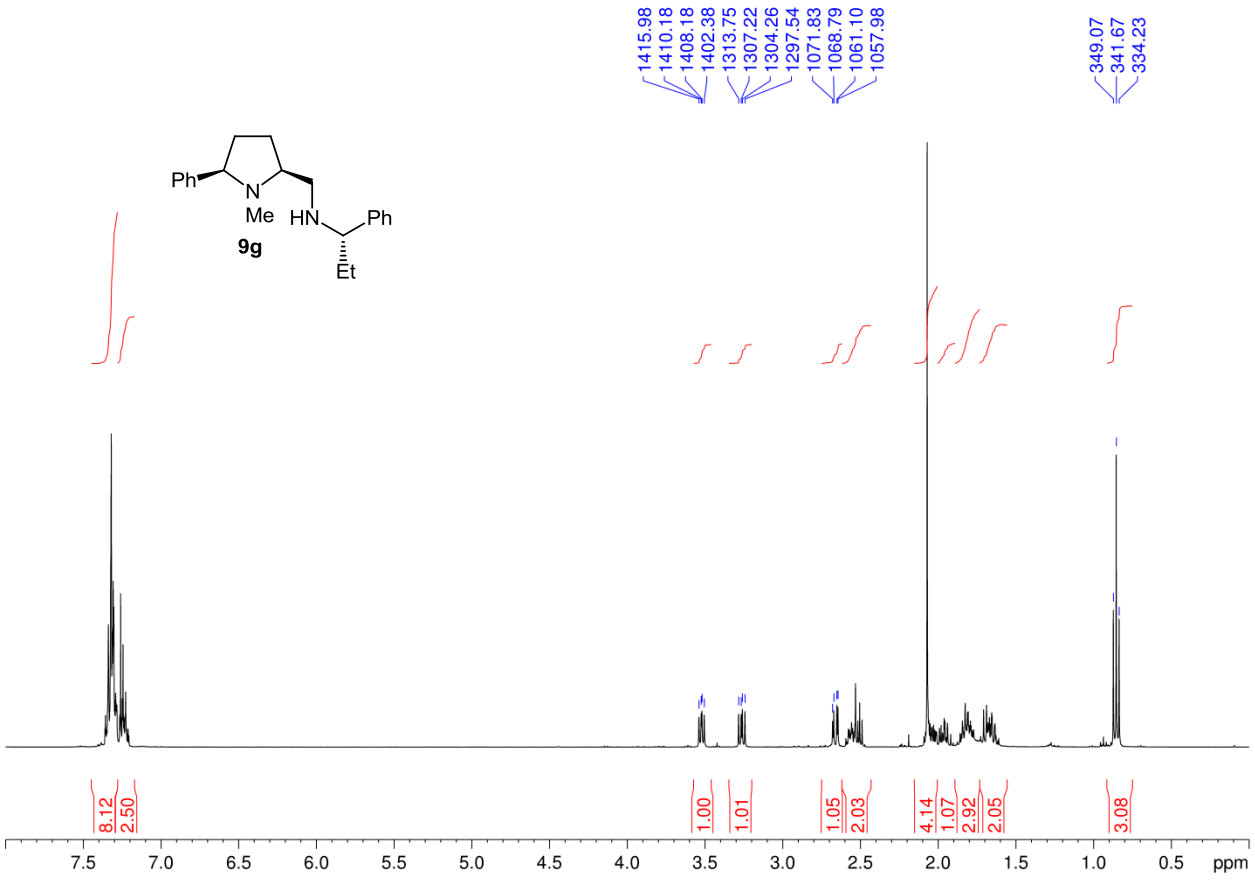
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1402.38
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1304.26
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1061.10
1057.98
349.07
341.67
334.23
Ph
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Me
HN
Ph
Et
9g
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2.50
1.00
1.01
1.05
2.03
4.14
1.07
2.92
2.05
3.08
7.5
7.0
6.5
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1.0
0.5
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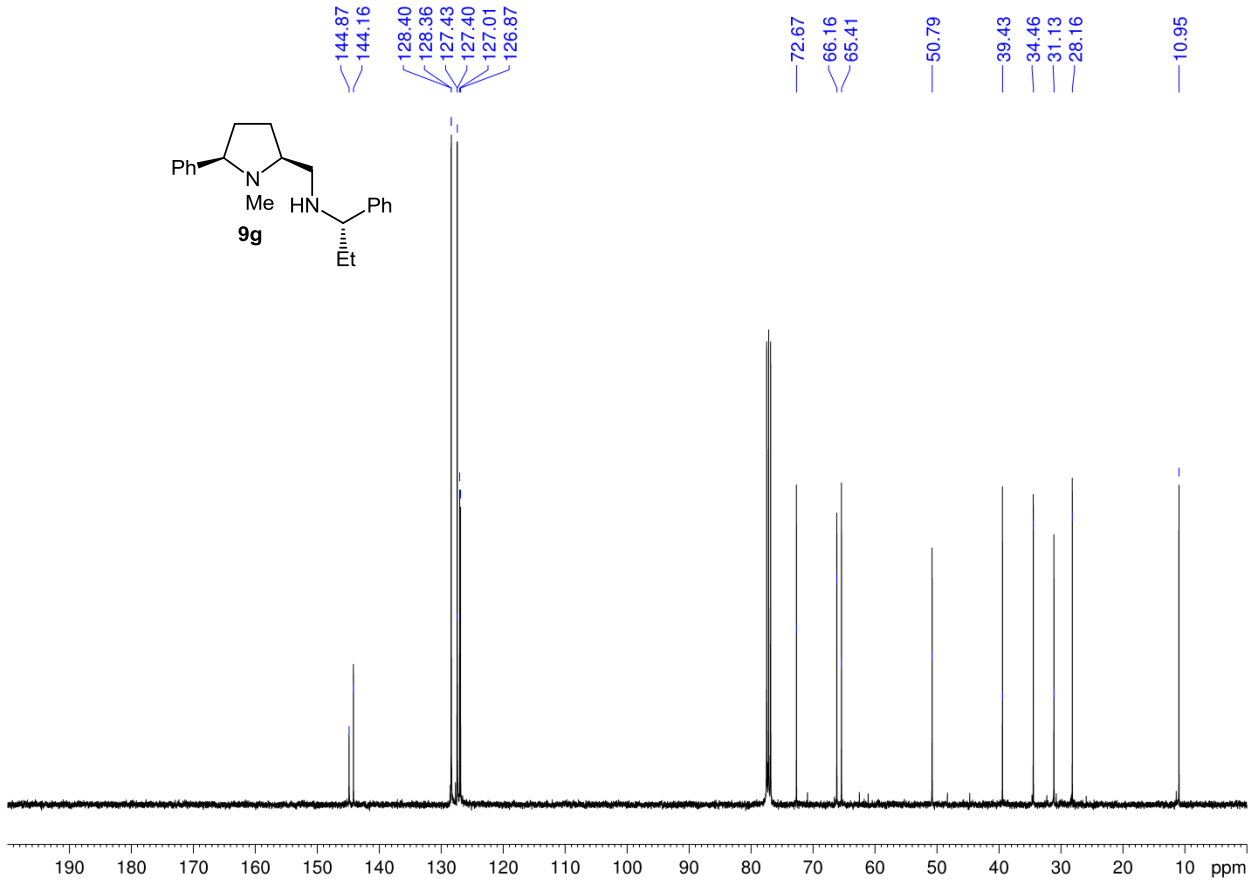
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126.87
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66.16
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39.43
34.46
31.13
28.16
10.95
Ph
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Me
HN
Ph
Et
9g
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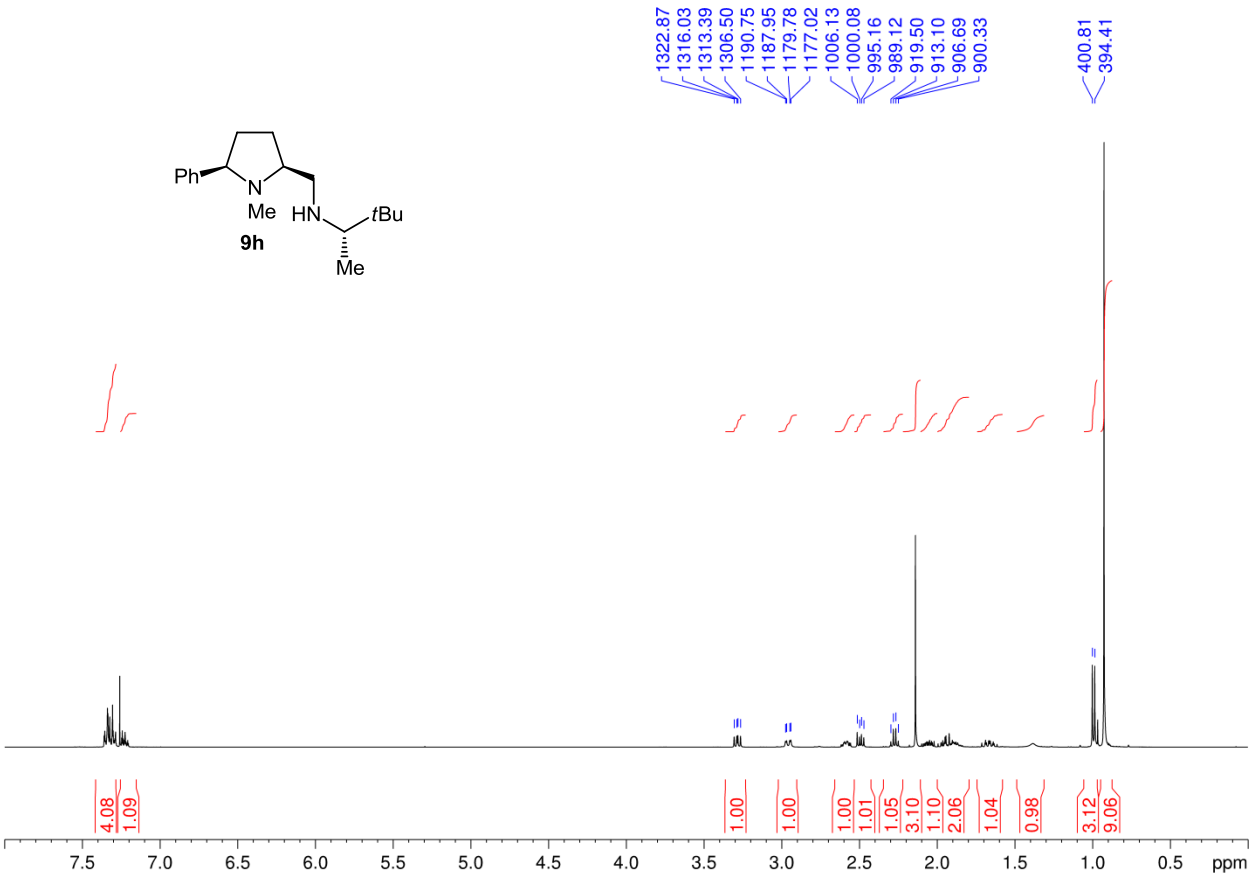
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1006.13
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989.12
919.50
913.10
906.69
900.33
400.81
394.41
Ph
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Me
HN
tBu
Me
9h
4.08
1.09
1.00
1.00
1.00
1.01
1.05
3.10
1.10
2.06
1.04
0.98
3.12
9.06
7.5
7.0
6.5
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2.0
1.5
1.0
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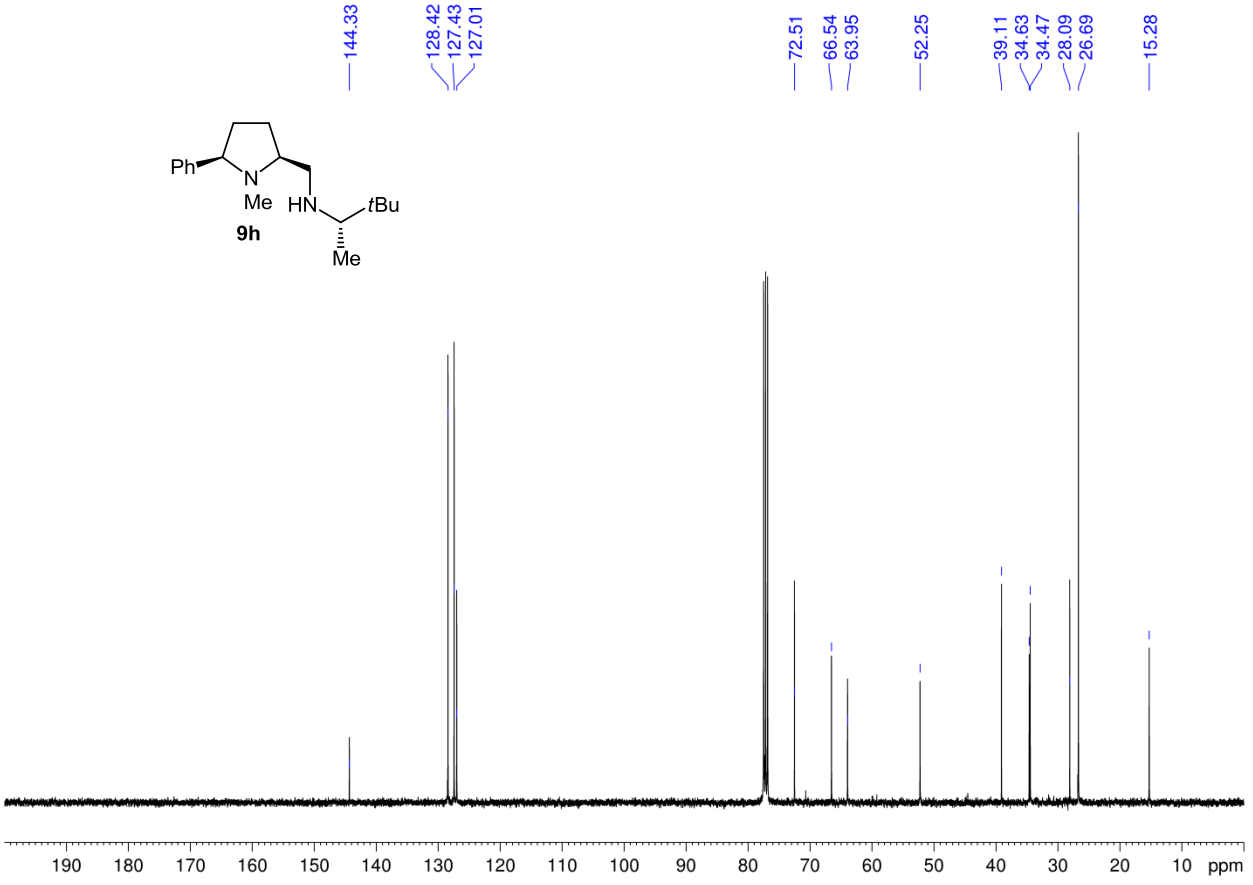
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34.47
28.09
26.69
15.28
Ph
N
Me
HN
tBu
Me
9h
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30
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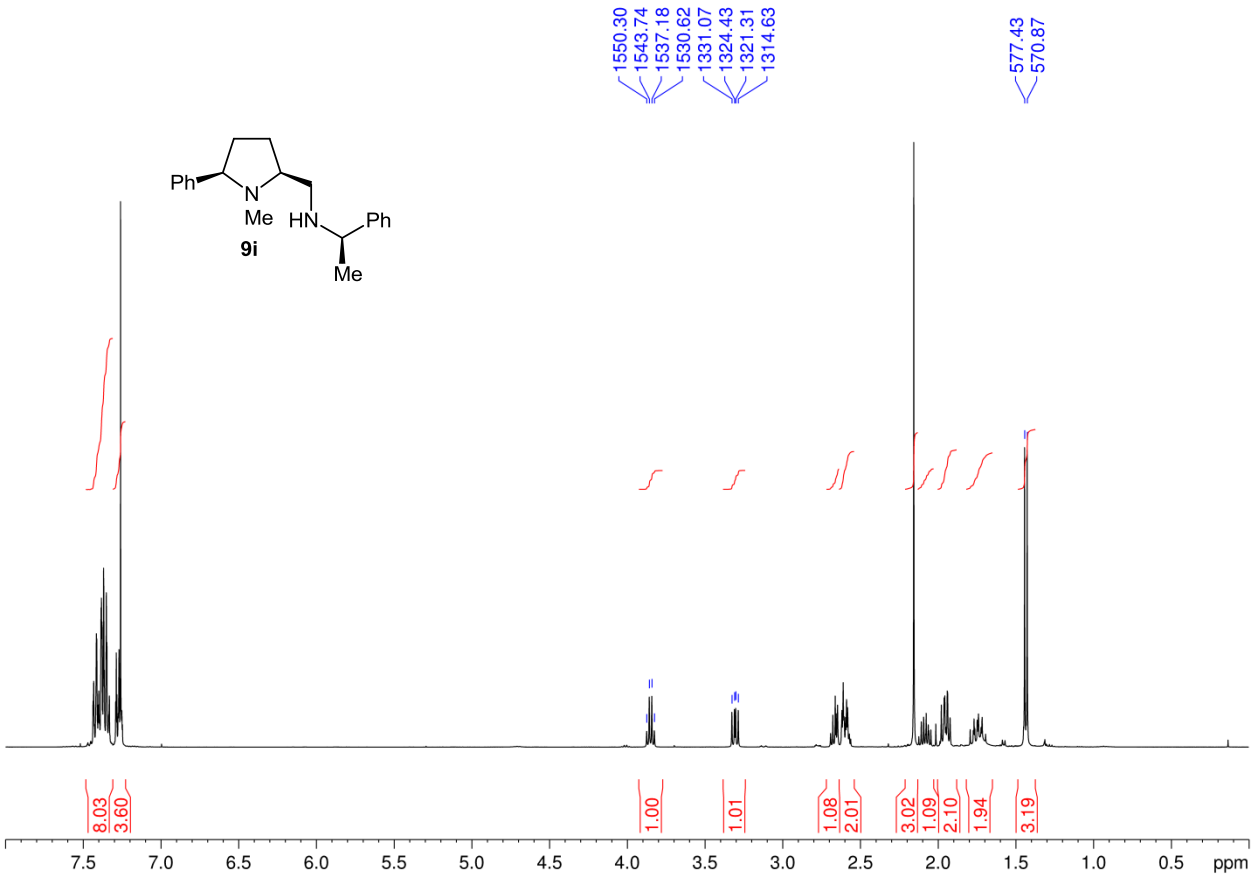
ppm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1331.07
1324.43
1321.31
1314.63
577.43
570.87
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Me
HN
Ph
Me
9i
8.03
3.60
1.00
1.01
1.08
2.01
3.02
1.09
2.10
1.94
3.19
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6.5
6.0
5.5
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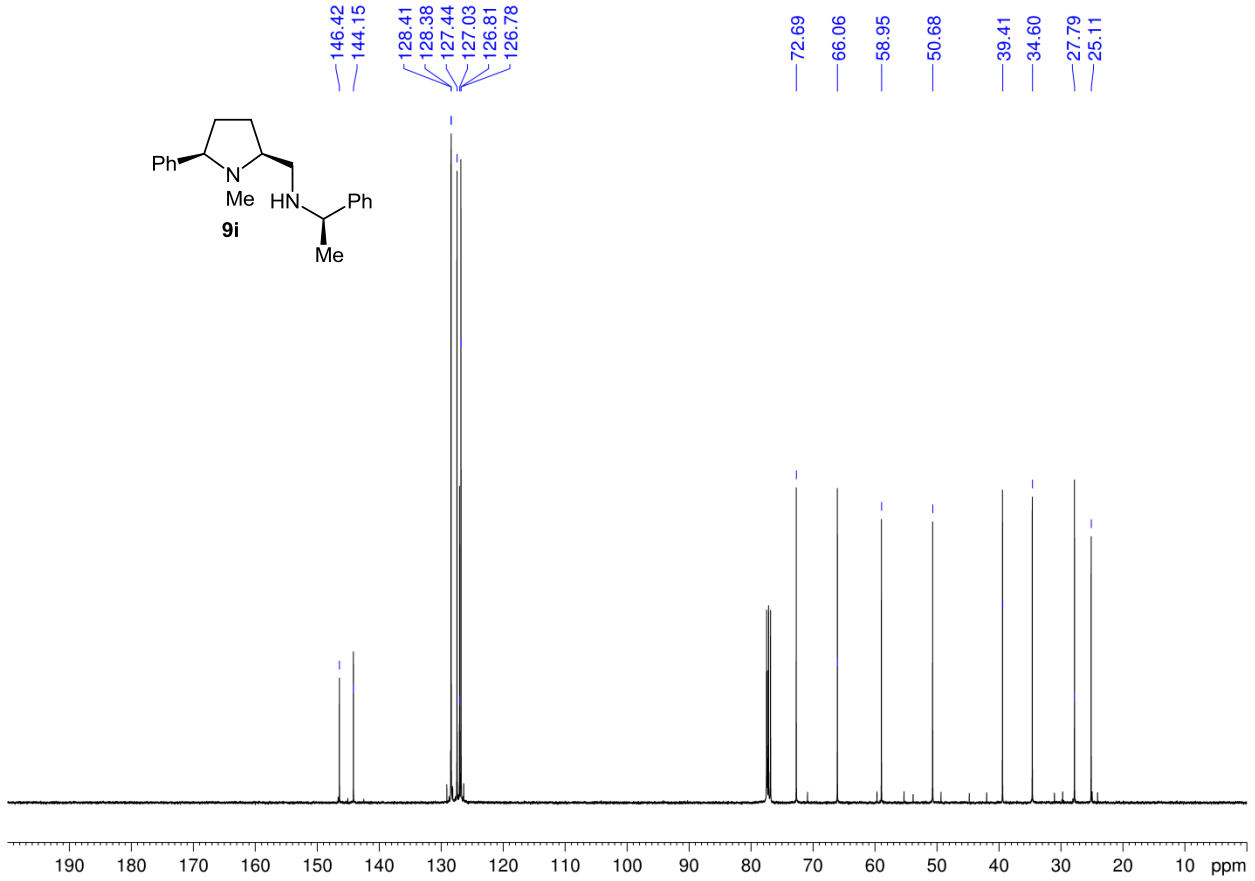
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm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34.60
27.79
25.11
Ph
N
Me
HN
Ph
Me
9i
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180
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150
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120
110
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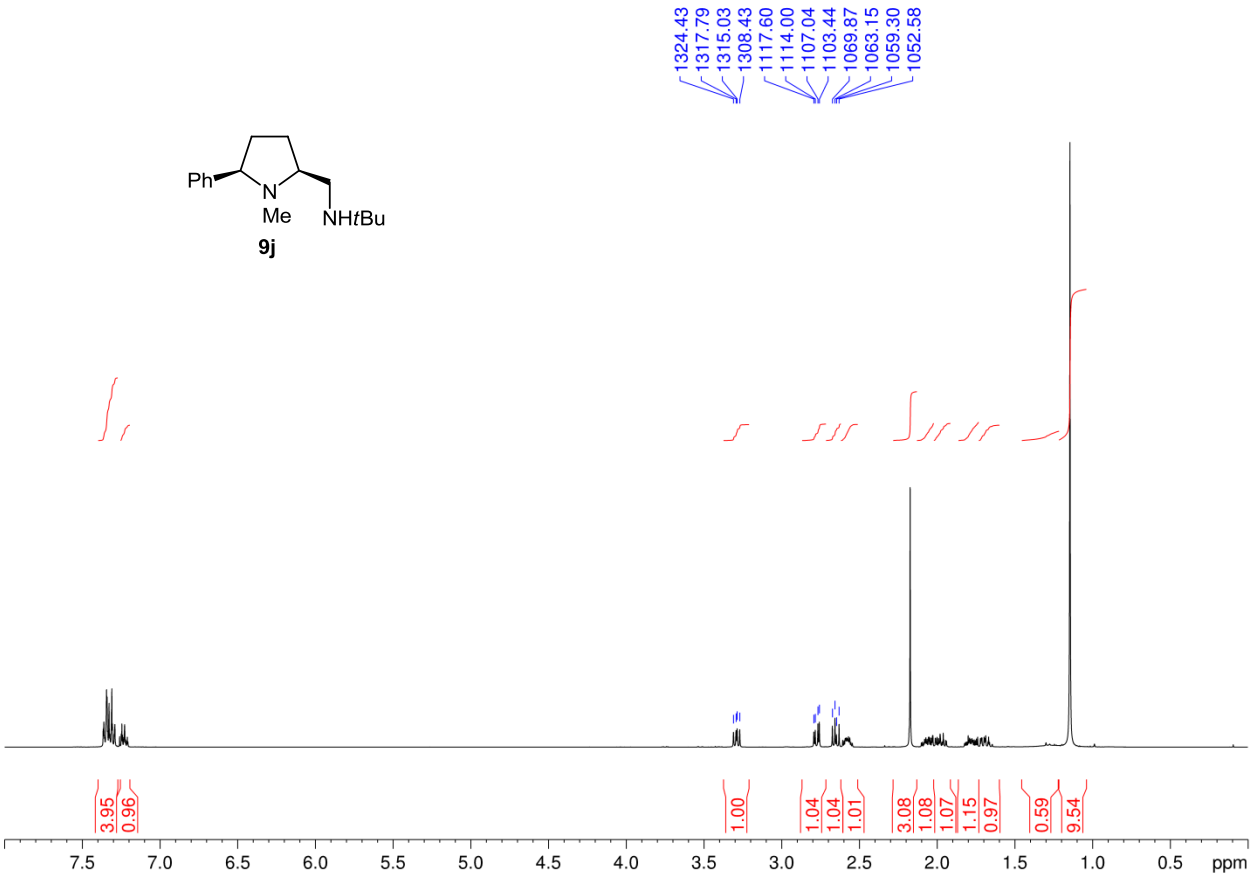
70
60
50
40
30
20
10
ppm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1308.43
1117.60
1114.00
1107.04
1103.44
1069.87
1063.15
1059.30
1052.58
Ph
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Me
NHtBu
9j
3.95
0.96
1.00
1.04
1.04
1.01
3.08
1.08
1.07
1.15
0.97
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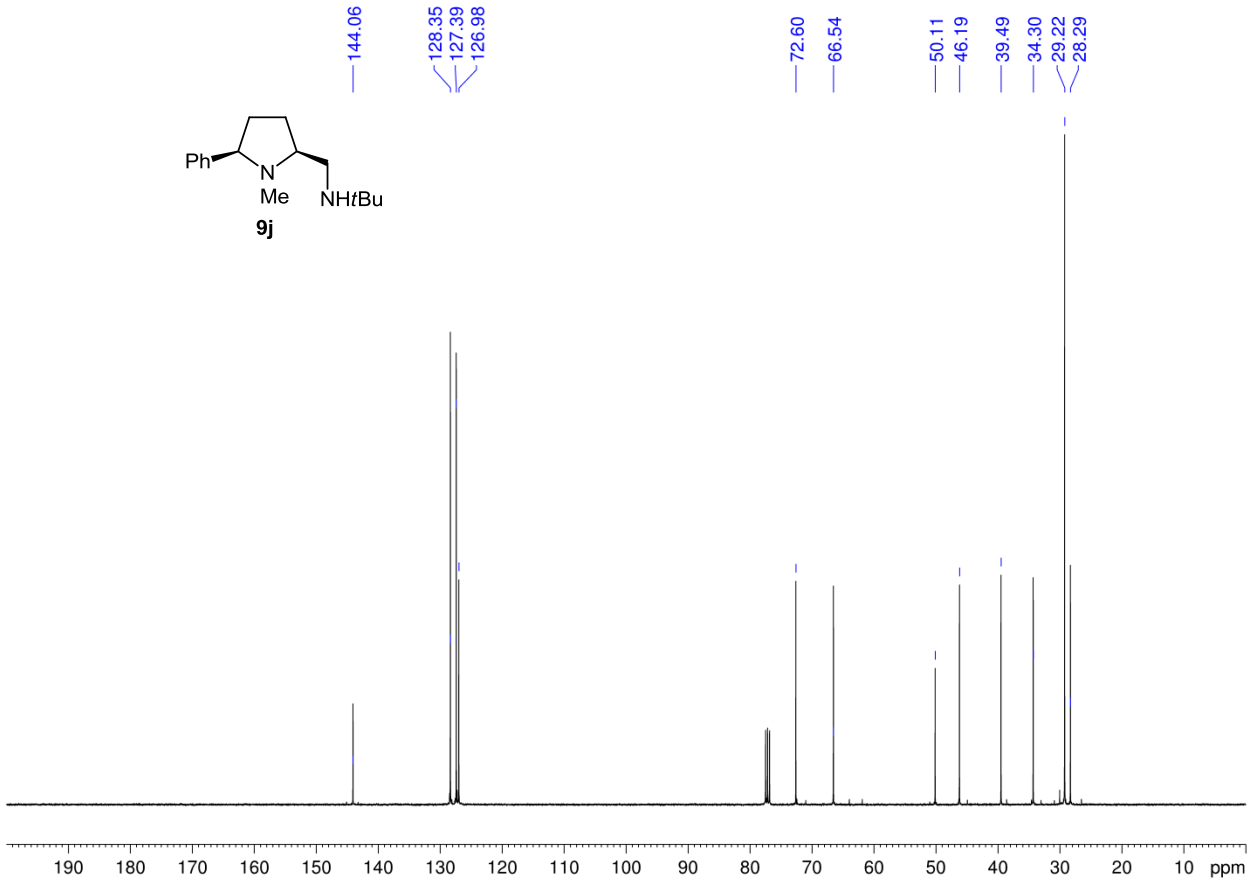
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm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29.22
28.29
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NHtBu
9j
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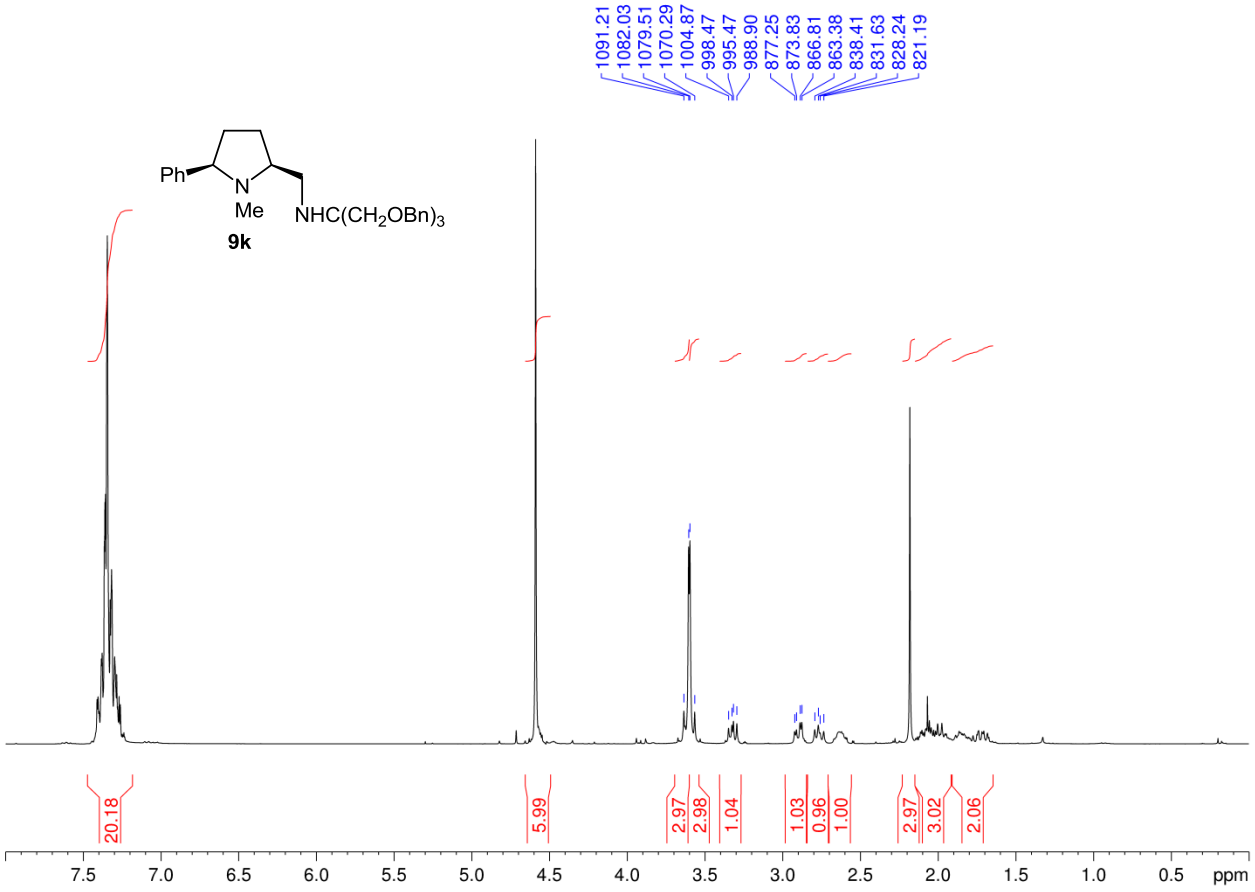
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1070.29
1004.87
998.47
995.47
988.90
877.25
873.83
866.81
863.38
838.41
831.63
828.24
821.19
Ph
N
Me
NHC(CH2OBn)3
9k
20.18
5.99
2.97
2.98
1.04
1.03
0.96
1.00
2.97
3.02
2.06
7.5
7.0
6.5
6.0
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4.5
4.0
3.5
3.0
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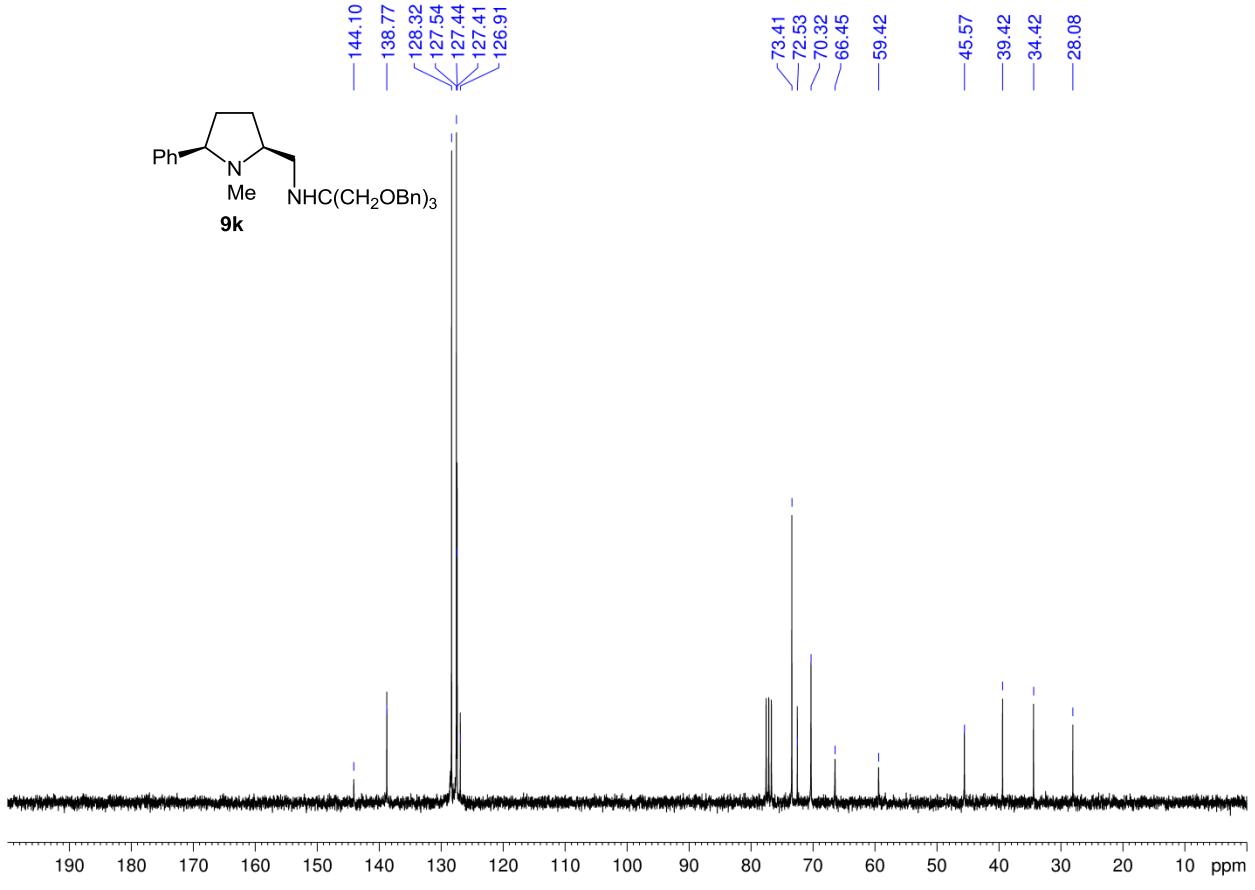
2.0
1.5
1.0
0.5
ppm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126.91
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39.42
34.42
28.08
Ph
N
Me
NHC(CH2OBn)3
9k
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150
140
130
120
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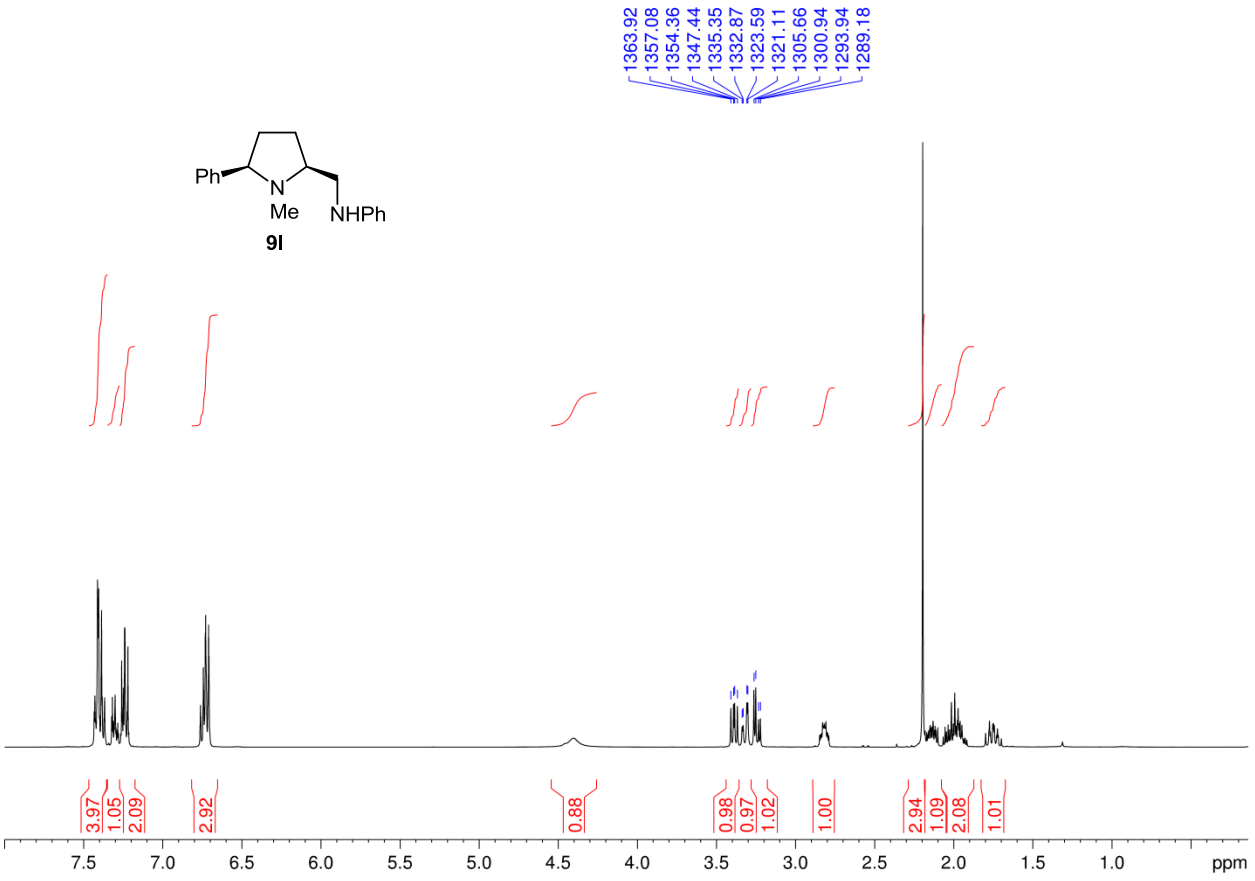
70
60
50
40
30
20
10
ppm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1354.36
1347.44
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1323.59
1321.11
1305.66
1300.94
1293.94
1289.18
Ph
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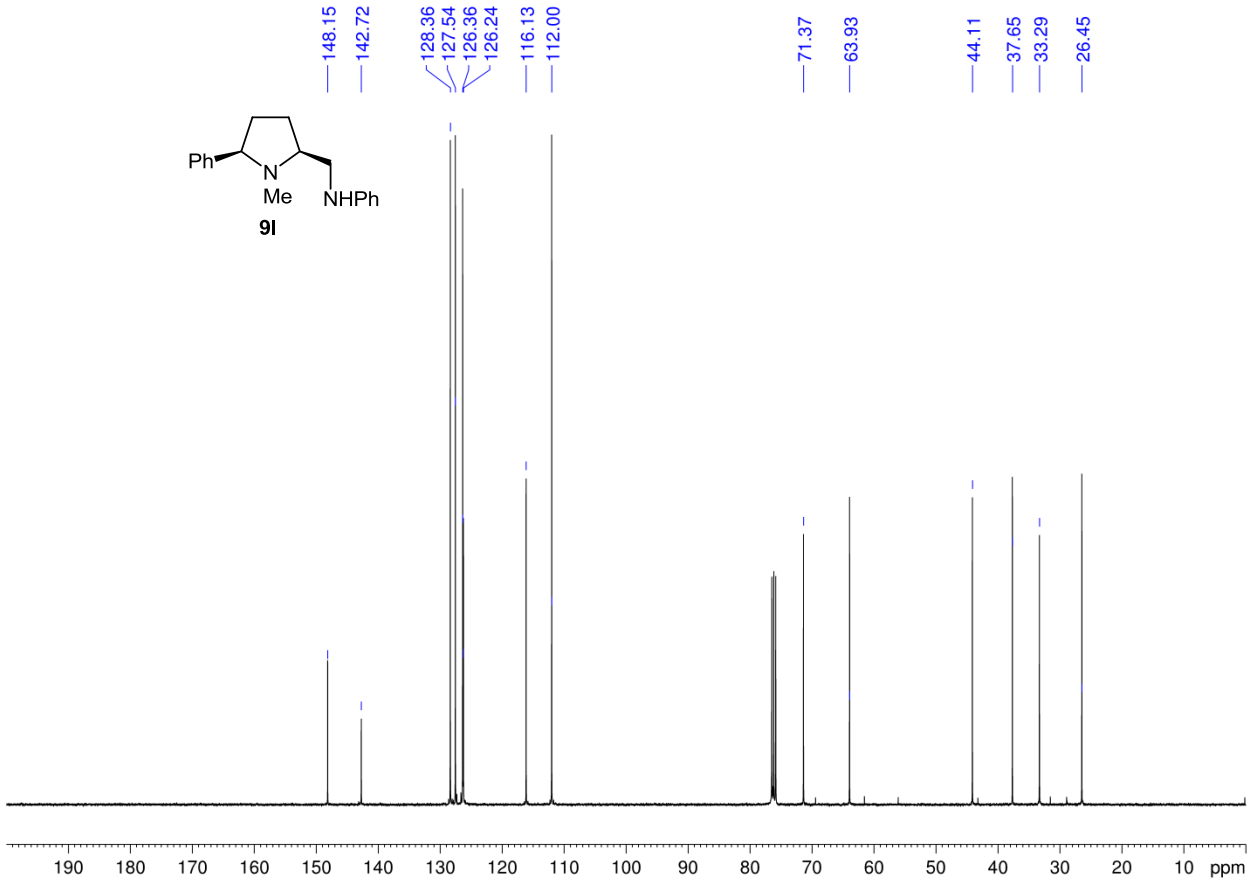
Me
NHPh
9l
3.97
1.05
2.09
2.92
0.88
0.98
0.97
1.02
1.00
2.94
1.09
2.08
1.01
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm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127.54
126.36
126.24
116.13
112.00
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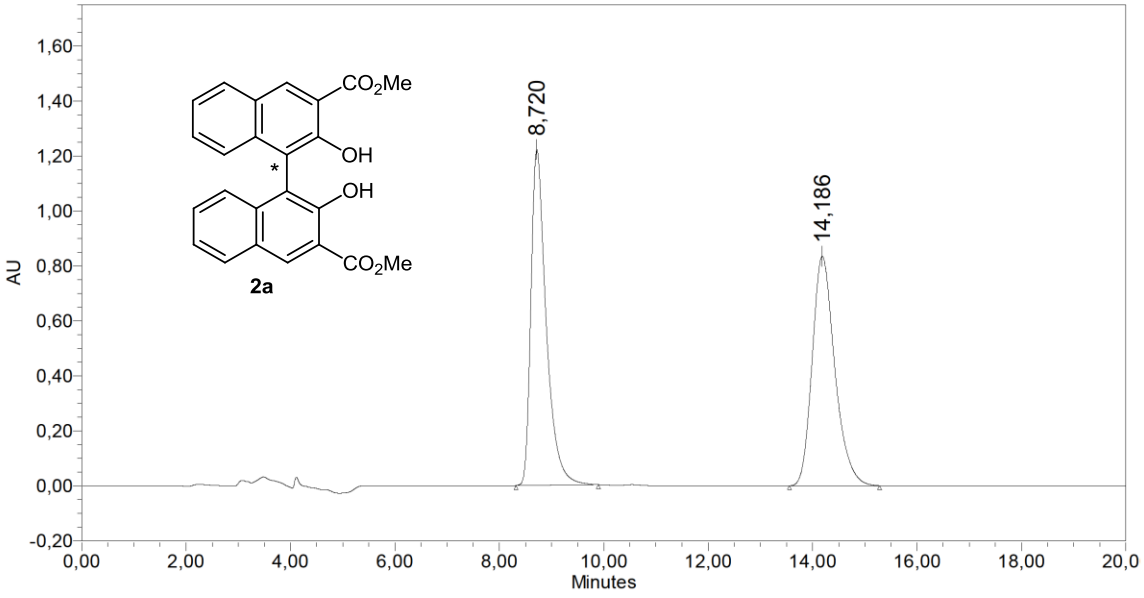
63.93
44.11
37.65
33.29
26.45
Ph
N
Me
NHPh
9l
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

3. Copies of HPLC spectra

The HPLC spectra of binaphthol esters **2a**–**2d** are listed in numerical order.

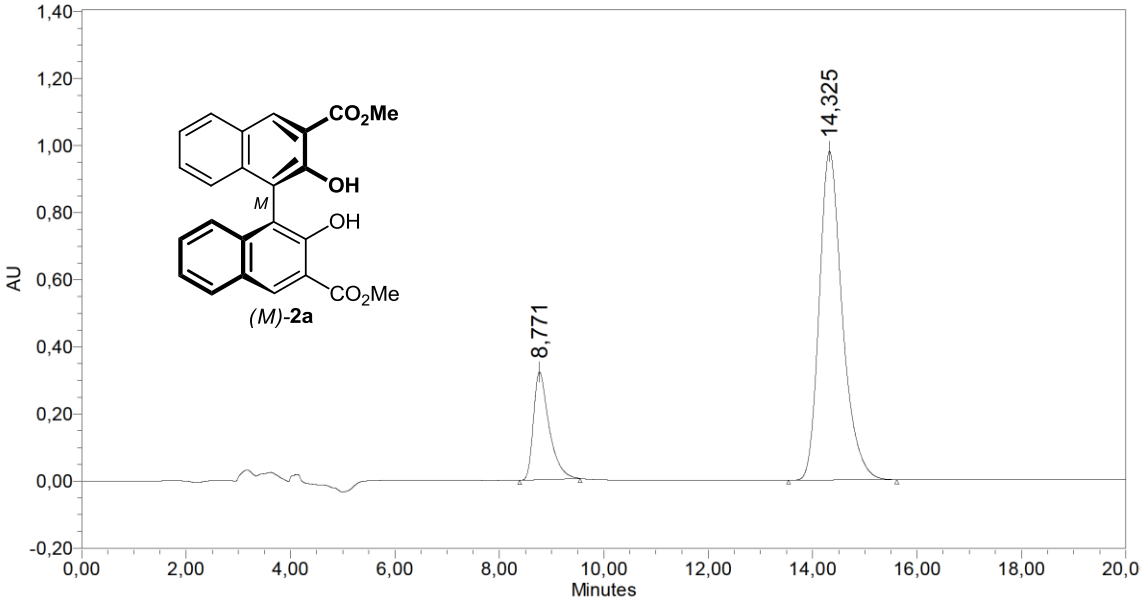
2a (racemic sample):

HPLC conditions: Chiralpak AD-H, *n*-hexane/*i*PrOH 80:20, 1.0 mL/min, 254 nm.



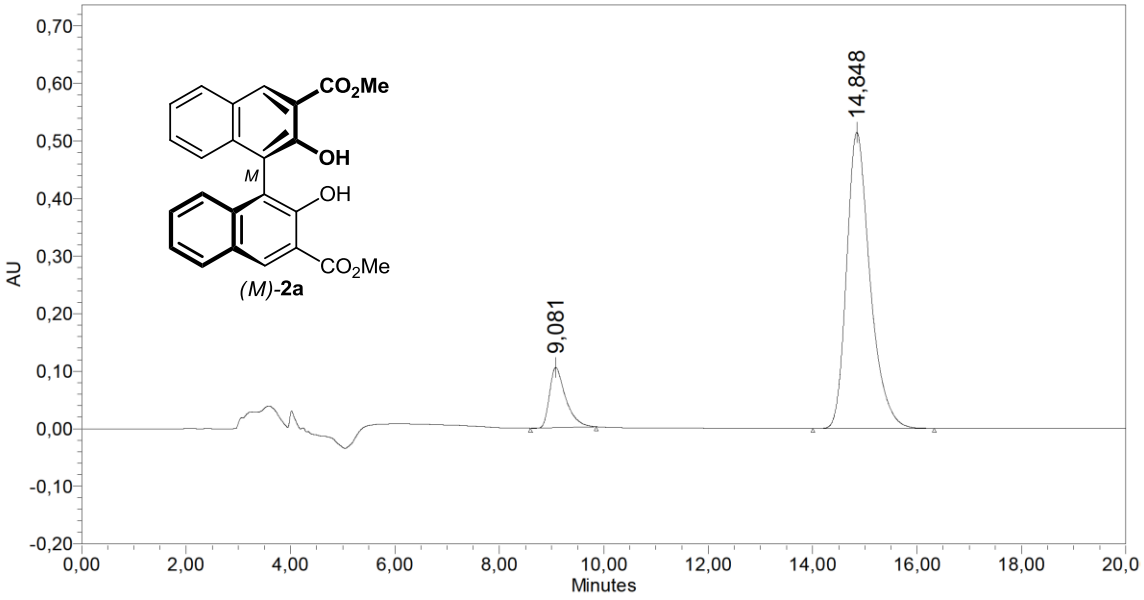
	Ret. Time	Start (min)	End (min)	Height	% Height	Area	% Area
1	8,72	8,33	9,90	1222414	59,44	24738536	49,64
2	14,19	13,56	15,28	834282	40,56	25092940	50,36

(*M*)-**2a** (64% ee, see Table 2, entry 19):



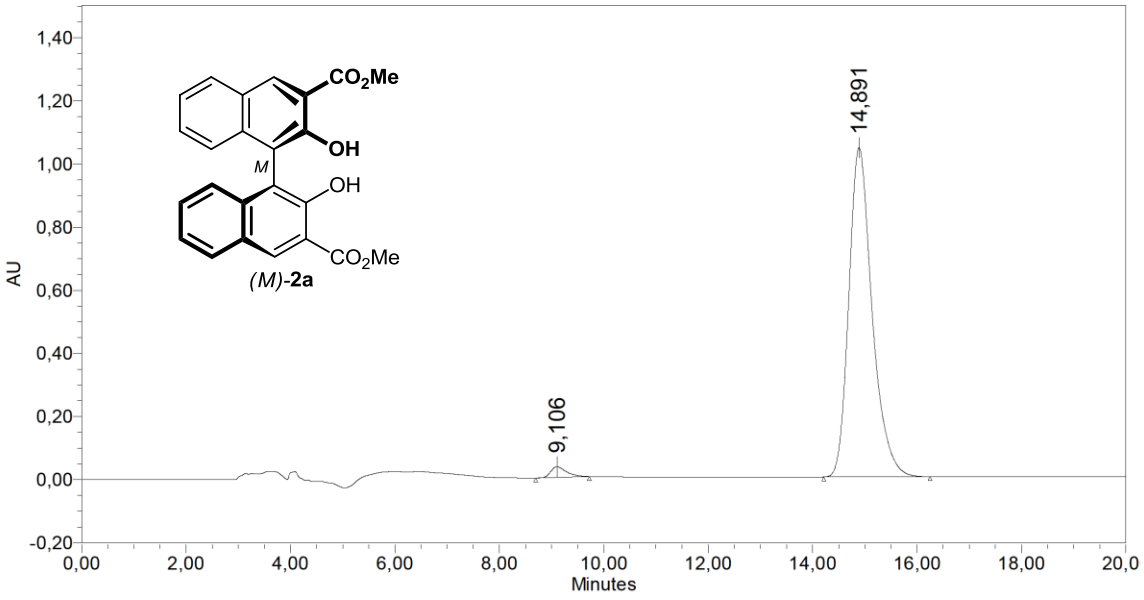
	Ret. Time	Start (min)	End (min)	Height	% Height	Area	% Area
1	8,77	8,39	9,55	321613	24,72	6667356	18,20
2	14,32	13,54	15,62	979449	75,28	29975097	81,80

(*M*)-**2a** (75% ee, see Table 2, entry 16):



	Ret. Time	Start (min)	End (min)	Height	% Height	Area	% Area
1	9,08	8,60	9,86	104838	16,91	2245076	12,27
2	14,85	14,01	16,33	514984	83,09	16056029	87,73

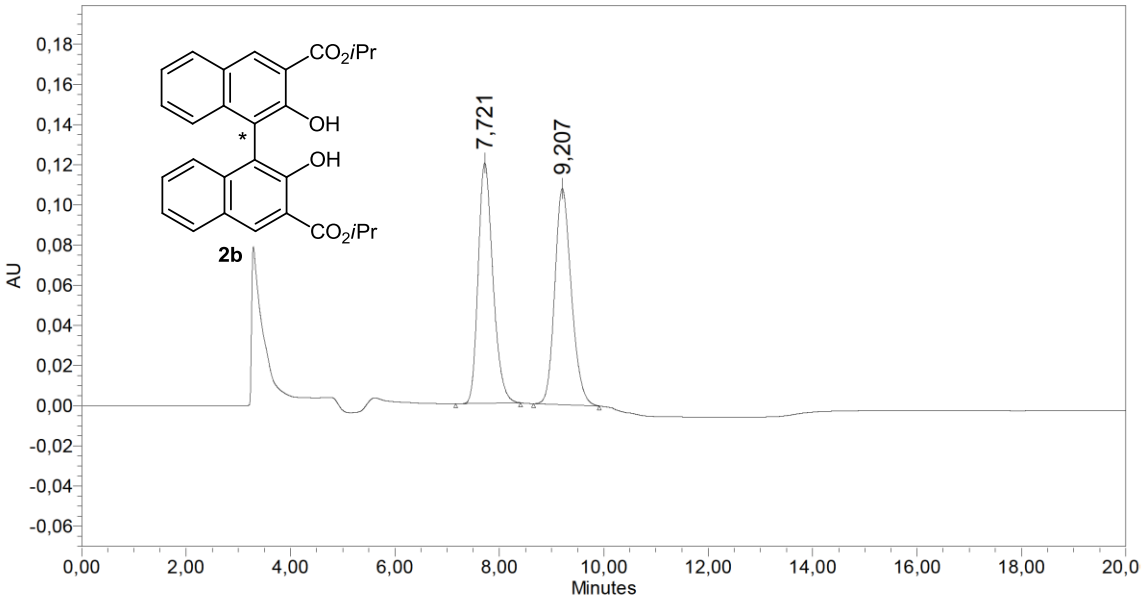
(*M*)-**2a** (96% ee, see Table 2, entry 1):



	Ret. Time	Start (min)	End (min)	Height	% Height	Area	% Area
1	9,11	8,70	9,73	34162	3,17	712273	2,16
2	14,89	14,22	16,25	1042945	96,83	32296852	97,84

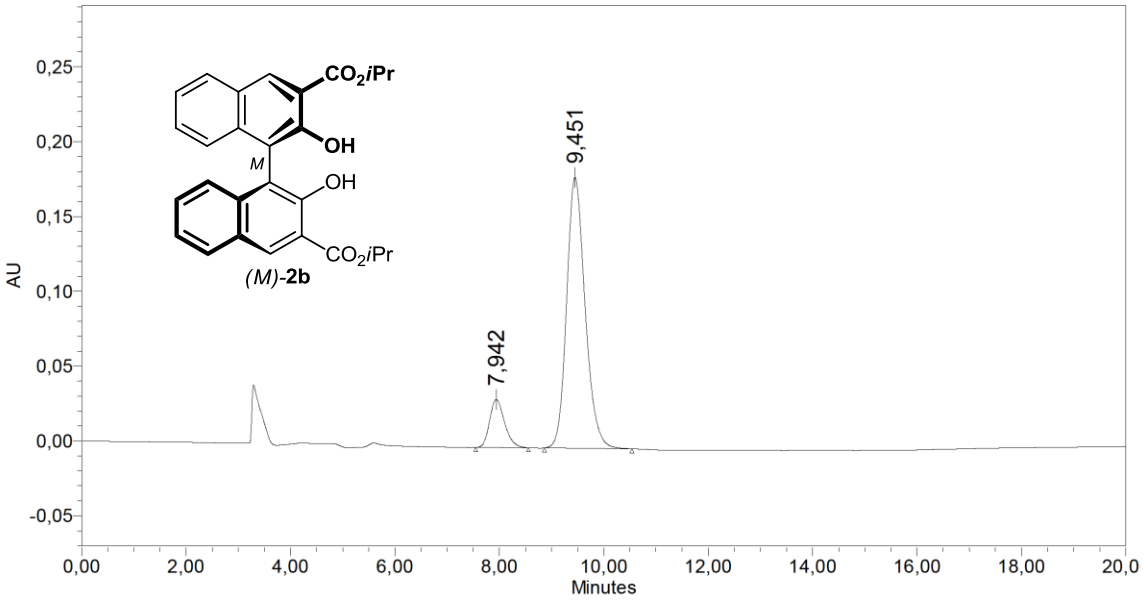
2b (racemic sample):

HPLC conditions: Chiralpak AD-H, *n*-hexane/*i*PrOH 98:02, 1.0 mL/min, 254 nm:



	Ret. Time	Start (min)	End (min)	Height	% Height	Area	% Area
1	7,72	7,17	8,41	119771	52,65	2345536	49,68
2	9,21	8,66	9,92	107728	47,35	2376075	50,32

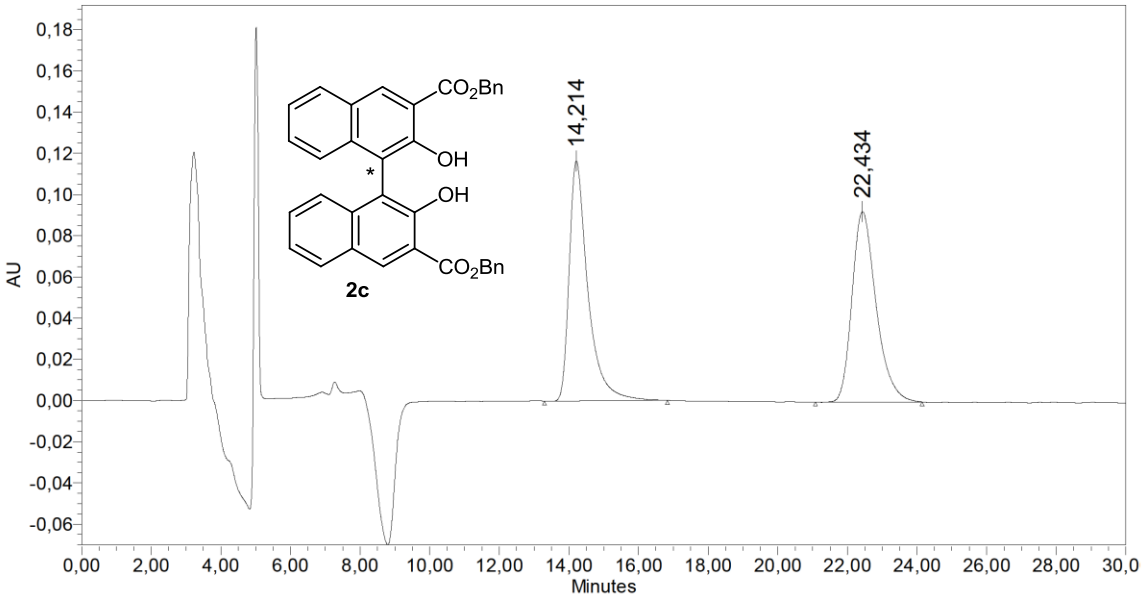
(*M*)-**2b** (75% ee, see Table 6, entry 6):



	Ret. Time	Start (min)	End (min)	Height	% Height	Area	% Area
1	7,94	7,55	8,56	32123	15,08	635393	12,53
2	9,45	8,87	10,54	180955	84,92	4435080	87,47

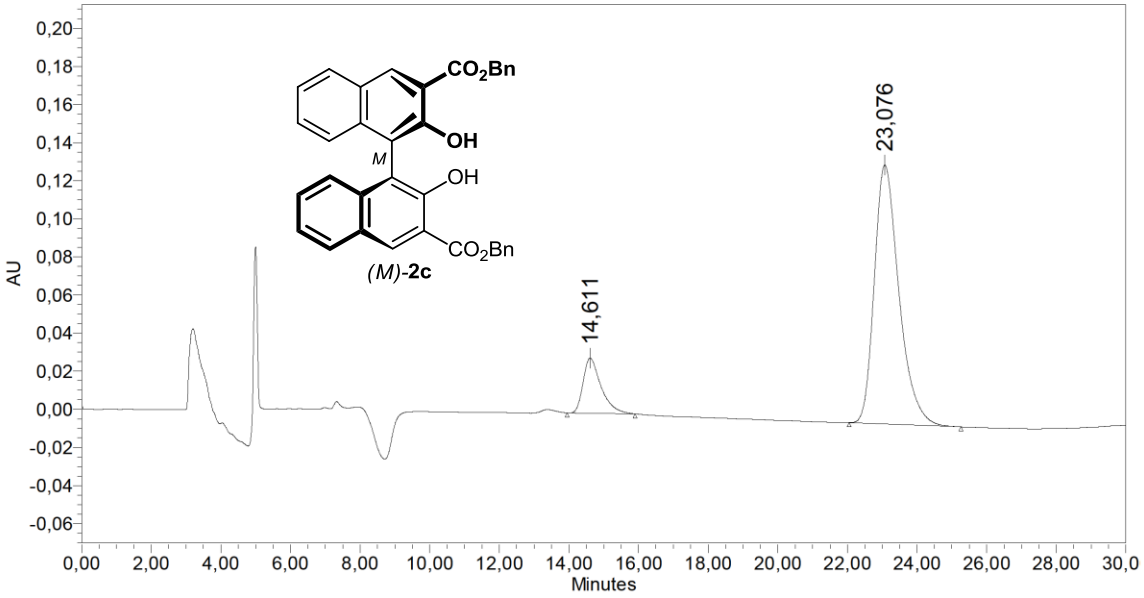
2c (racemic sample):

HPLC conditions: Chiralpak AD-H, *n*-hexane/*i*PrOH 90:10, 1.0 mL/min, 254 nm:



	Ret. Time	Start (min)	End (min)	Height	% Height	Area	% Area
1	14,21	13,30	16,83	116514	55,77	4335003	49,44
2	22,43	21,08	24,15	92415	44,23	4433449	50,56

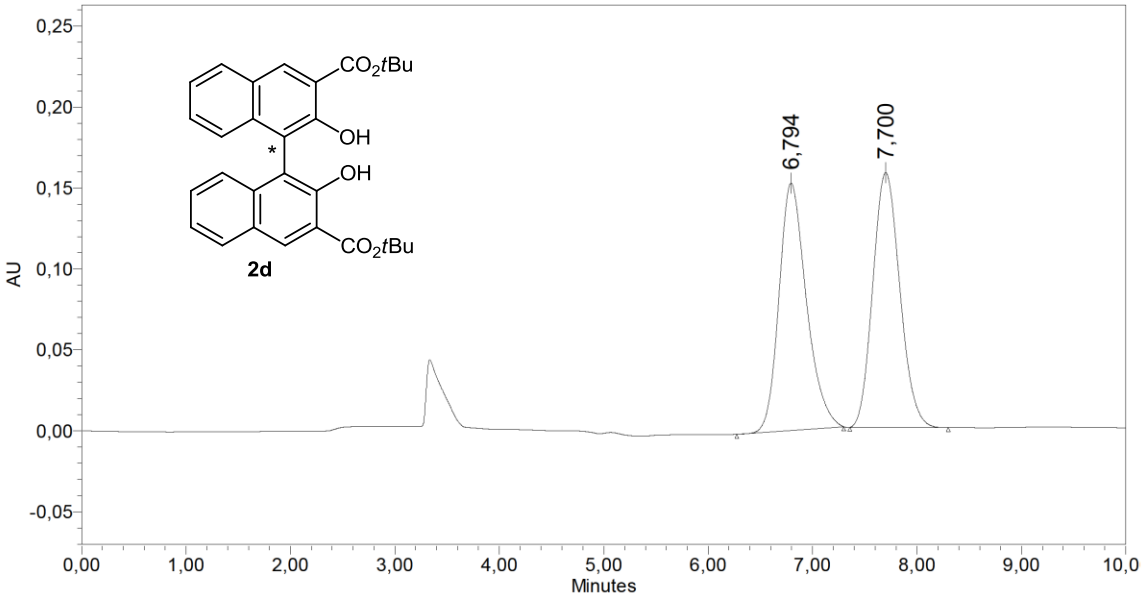
(*M*)-**2c** (73% ee, see Table 6, entry 3):



	Ret. Time	Start (min)	End (min)	Height	% Height	Area	% Area
1	14,61	13,95	15,90	28958	17,56	1031877	13,39
2	23,08	22,05	25,27	135948	82,44	6673526	86,61

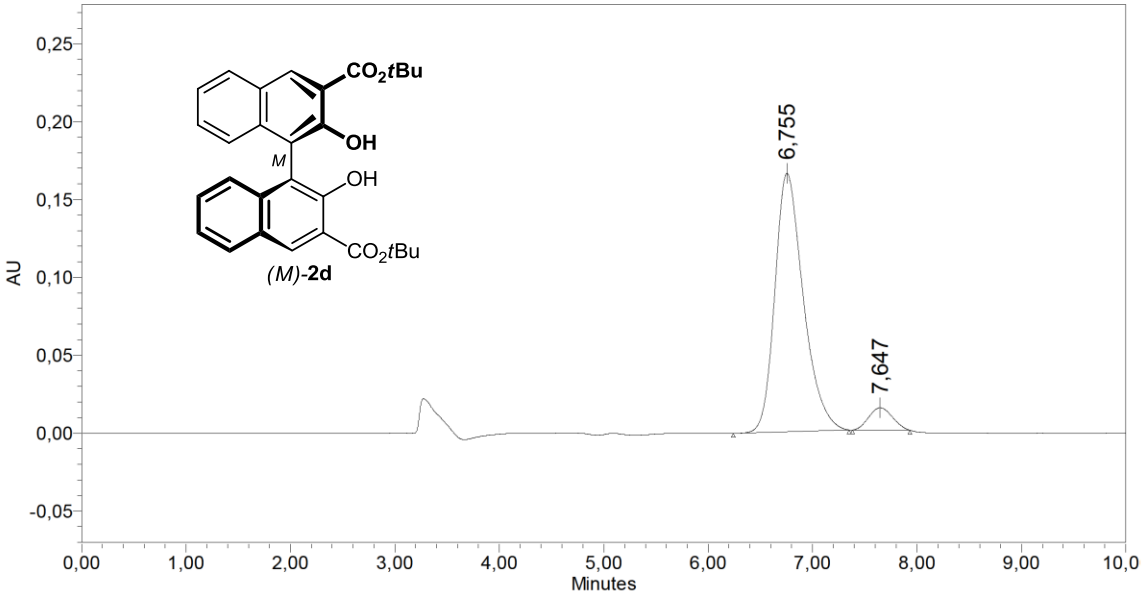
2d (racemic sample):

HPLC conditions: Chiralpak AD-H, *n*-hexane/*i*PrOH 98:02, 1.0 mL/min, 254 nm:



	Ret. Time	Start (min)	End (min)	Height	% Height	Area	% Area
1	6,79	6,28	7,30	152769	49,25	2781976	49,62
2	7,70	7,36	8,30	157444	50,75	2824828	50,38

(*M*)-**2d** (87% ee, see Table 6, entry 9):



	Ret. Time	Start (min)	End (min)	Height	% Height	Area	% Area
1	6,76	6,24	7,35	165996	92,04	3139680	93,28
2	7,65	7,38	7,93	14360	7,96	226201	6,72