Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Enantioselective Synthesis of α-Aryl Alkylamines by Rh(I)-Catalyzed Additions of Arylboronic Acids to Aliphatic Imines.

Mónica Trincado and Jonathan A. Ellman*
Department of Chemistry, University of California,
Berkeley, California 94720
jellman@berkeley.edu

Table of Contents

General Methods. The arylboronic acids were purchased from Aldrich and were recrystallized from water before use. 3-Acetylphenylboronic acid was purchased from Frontier Scientific, Inc. and was recrystallized from water before use. 3-Phenylpropionaldehyde was purchased from Acros and distilled prior to use. *N*-Diphenylphosphinoyl imines and *N*-tosyl imines were prepared from α–amido sulfone precursors immediately prior to use, according to literature procedures.[1] μ-Dichlorotetraethylene dirhodium(I) was purchased from Strem. Acetylacetonatobis(cyclooctene)rhodium was synthesized from rhodium trichloride (purchased from Strem) according to the literature procedures.[2] All commercially available chiral ligands were purchased from Strem and use without purification. Ligand **2** was synthesized according to the literature procedures.[3] Toluene and 1,4-dioxane were passed through columns of activated alumina under nitrogen pressure and stored over MS 3Å in a nitrogen filled glove box. Triethylamine (NEt_3) was distilled over calcium hydride under an atmosphere of nitrogen immediately prior to use. K_3PO_4 was purchased from Aldrich and dried prior use. PS-DEAM resin (2.72 mmol/g) was purchased from Argonaut Technologies, Inc. Arylboronic acid additions reactions were performed in Kimble 5 mL microvials (Kimble product number 60700-5) equipped with PTFE stir-vanes (Kimble product number 749060-003) and capped with mini-inert seals (Kimble product number 749110-0022) and blue nylon caps (Kimble product number 410119-2015). The reaction solutions in vials were heated in an aluminum heating block (UC machine shop) and the temperature was maintained by an IKA stirrer/hotplate (RCT basic model) with a thermisor controller (ETS-D4).

Flash column chromatography was carried out either with Merck 60 230-240 mesh silica gel, or using a Biotage SP Flash Purification System (Biotage No. SP1-B1A) with Flash+ cartridges (Biotage No. FPK0-1107-16046). Enantiomeric excess determinations were performed on an Agilent 1100 series LC equipped with a Daicel AD or OD column and a multiwavelength detector. ^{1}H and $^{13}C\{^{1}H\}$ NMR chemical shifts are reported in ppm relative to either the residual solvent peak (^{1}H, ^{13}C) or TMS (^{1}H) as an internal standard. IR spectra were recorded as thin films on a Nicolet Avatar 360 FTIR spectrometer equipped with an attenuated total reflectance accessory or as KBr pellets on a Nicolet MAGNA-IR 850 spectrometer, and only partial data are listed. Melting points were determined on a Mel-Temp apparatus and are reported uncorrected. Mass spectrometry (HRMS) was carried out by the University of California at Berkeley Mass Spectrometry Facility.

Typical procedure for optimization screens.

Reactions were set up in a nitrogen filled glove box.

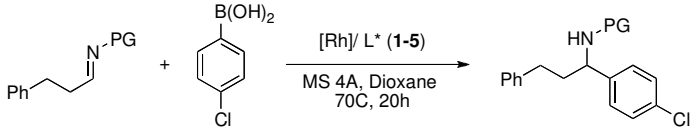
Procedure for entry 1. Imine **6a** (41.8 mg, 0.125 mmol, 1 equiv) was weighed into a vial with a stir-vane. The ligand **1** (3.6 mg, 0.0069 mmol, 0.055 equiv) was added as a solution in 0.25 mL of dioxane followed by a dioxane solution (0.25 mL) of acetylacetonatobis(cyclooctene)rhodium (2.6 mg, 0.0062 mmol, 0.05 equiv). The solution was stirred until it was homogeneous (1 min), and powdered, activated 4Å MS (200 mg) were added. Freshly distilled Et_3N (17 μL, 0.125 mmol, 1 equiv) was added. The vial was capped and heated to 70 ºC in a heating block and a dioxane (0.5 mL) solution of **8a** (39.1 mg, 0.250 mmol, 2 equiv) was then added over 10 h. After 20 h, the reaction mixture was allowed to cool to rt. The mixture was extracted with EtOAc (2 x 5 mL) and

the combined organic layers were dried over Na_2SO_4. The crude material was purified by chromatography (10:1-0:1, Hexane/ EtOAc).

Procedure for entries 2-7 and 12-38, Table 1. To a vial containing a stir-vane, 4-chlorophenylboronic acid (39.1 mg, 0.250 mmol, 2 equiv) and powered 4Å molecular sieves (200 mg) was added a mixture of rhodium and the corresponding ligand (**1**-**5**) in 0.75 mL. The vial was then sealed using a mini-inert seal and a blue nylon cap, and the vial was removed from the glove box. The vial was then placed in a heating block with stirring and heated at 55-70 °C (aluminum block temperature) for 30-90 min. The reaction mixture was allowed to cool to rt and the vial was transferred to the glove box. To the vial was added the *N*-phosphinoyl or *N*-tosyl imine (0.125 mmol, 1 equiv) in 0.25 mL of dioxane. For entries 14-17 and 29-30, NEt_3 (0.25 mmol, 2 equiv) and imine were sequentially added. The vial was then heated at 55 ºC (entries 13-16, 18, 20, 28 and 29) or 70 °C for 20 h. The reaction mixtures were allowed to cool to rt, filtered through a short pad of Celite and washed with CH_2Cl_2. The combined organic layers were washed with brine (1 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The conversion to product was determined by integration relative to 2,6-dimethoxytoluene, which was used as an internal standard. The crude residue was purified by silica gel chromatography or using Biotage flash purification, eluting with EtOAc/hexanes. For the reactions of *N*-phosphinoyl imine **6a**, enantiomeric excesses were determined by chiral HPLC analysis (Chiralpak OD-H, hexanes/EtOH 97/3, 0.9 mL min^{-1}): t_R = 18.8 min (major), t_R = 20.9 min (minor). For the reactions of *N*-tosyl imine **7a**, enantiomeric excesses were determined by chiral HPLC analysis (Chiralpak OD-H, hexanes/*i*-PrOH 80/20, 0.5 mL min^{-1}): t_R = 17.5 min (major), t_R = 32.6 min (minor).

Procedure for entries 7-11 and 39, Table 1. A solution of rhodium precatalyst and ligand **1** in dioxane (0.5 mL) was stirred for 90 min at 70 ºC. Imine **6a** or **7a** (0.125 mmol) in dioxane (0.5 mL), chlorophenylboronic acid (39.1 mg, 0.250 mmol, 2 equiv), powered 4Å molecular sieves (200 mg) and K_3PO_4 were successively added and the resulting mixture was stirred for 20 h at 70 ºC. The reaction was quenched with water and extracted with CH_2Cl_2. The combined organic layers were washed with brine (1 mL). The combined organic layers were washed with brine (1 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The conversion to product was determined by integration relative to 2,6-dimethoxytoluene, which was used as an internal standard.

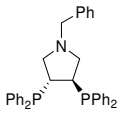
Table 1. Full results of catalyst optimization results.



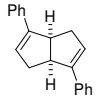
6a: PG = $P(O)Ph_2$
7a: PG = Ts

8a

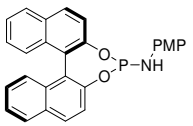
9a: PG = $P(O)Ph_2$
10a: PG = Ts



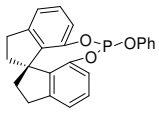
1



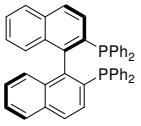
2



3



4



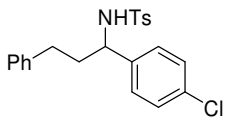
5

entry[a]	Imine	mol % [Rh]	mol% chiral ligand	Additive	Product	Yield (%)[b]	ee (%)[c]
1	6a	5 mol%[Rh(acac)(coe)$_2$]	5.5 mol% **1**	NEt_3 (1 equiv)	9a	17	nd
2	6a	10 mol%[Rh(acac)(coe)$_2$]	11 mol% **1**	--	9a	74	59
3	6a	10 mol%[Rh(acac)(coe)$_2$]	13 mol% **1**	--	9a	70	76
4	6a	10 mol%[Rh(acac)(coe)$_2$]	14 mol% **1**	--	9a	71	86
5	6a	10 mol%[Rh(acac)(coe)$_2$]	15 mol%**1**	--	9a	51	86
6	6a	5 mol% [Rh(acac)(coe)$_2$]	7 mol% **1**	--	9a	65	84
7[d]	6a	5 mol% [Rh(acac)(coe)$_2$]	7 mol% **1**	--	9a	70	90
8[e]	6a	5 mol% [Rh(acac)(coe)$_2$]	7 mol% **1**	--	9a	75	90
9[e]	6a	5 mol% [Rh(acac)(coe)$_2$]	7 mol% **1**	K_3PO_4 (0.5 equiv)	9a	79	94
10[e]	6a	5 mol% [Rh(acac)(coe)$_2$]	7 mol% **1**	K_3PO_4 (1 equiv)	9a	34	--
11[e]	6a	5 mol% [Rh(acac)(coe)$_2$]	7 mol% **1**	K_3PO_4 (0.2 equiv)	9a	89	90
12[d]	6a	3 mol% [Rh(acac)(coe)$_2$]	3.3 mol% **1**		9a	53	81
13[f]	6a	5 mol% [RhCl(C_2H_4)$_2$]$_2$	5.5 mol% **1**	--	9a	44	91
14[f]	6a	5 mol% [RhCl(C_2H_4)$_2$]$_2$	5.5 mol% **1**	NEt_3 (2 equiv)	9a	46	91
15[f]	6a	5 mol% [RhCl(C_2H_4)$_2$]$_2$	5.5 mol% **2**	NEt_3 (2 equiv)	9a	75	-80
16[f]	6a	5 mol% [RhCl(C_2H_4)$_2$]$_2$	7 mol% **2**	NEt_3 (2 equiv)	9a	70	-78
17[g]	6a	5 mol% [RhCl(C_2H_4)$_2$]$_2$	7 mol% **2**	NEt_3 (2 equiv)	9a	69	-60
18[f]	6a	5 mol% [Rh(acac)(coe)$_2$]	5.5 mol% **2**	--	9a	37	-71
19[g]	6a	5 mol% [Rh(acac)(coe)$_2$]	5.5 mol% **2**	--	9a	41	-56
20[f]	6a	5 mol% [Rh(acac)(coe)$_2$]	7 mol% **2**	--	9a	41	-74
21[g]	6a	5 mol% [Rh(acac)(coe)$_2$]	7 mol% **2**	--	9a	45	-60
22	6a	3 mol% [Rh(acac)(coe)$_2$]	7.5 mol% **3**	--	9a	46	6
23	6a	5 mol% [Rh(acac)(coe)$_2$]	14 mol% **3**	--	9a	40	14
24	6a	3 mol% [Rh(acac)(coe)$_2$]	6 mol% **4**	--	9a	36	7
25	6a	5 mol% [Rh(acac)(coe)$_2$]	15 mol% **4**	--	9a	35	10
26	6a	3 mol% [Rh(acac)(coe)$_2$]	3.3 mol% **5**	--	9a	41	70
27	6a	5 mol% [Rh(acac)(coe)$_2$]	7 mol% **5**	--	9a	36	74
28[f]	7a	5 mol% [RhCl(C_2H_4)$_2$]$_2$	5.5 mol% **2**	NEt_3 (2 equiv)	10a	79	-69
29[f]	7a	5 mol% [RhCl(C_2H_4)$_2$]$_2$	7 mol% **2**	NEt_3 (2 equiv)	10a	75	-67
30[g]	7a	5 mol% [Rh(acac)(coe)$_2$]	7 mol% **2**	--	10a	60	-63
31[g]	7a	3 mol% [Rh(acac)(coe)$_2$]	3.3 mol% **2**	--	10a	55	-62
32[g]	7a	3 mol% [Rh(acac)(coe)$_2$]	7.5 mol% **3**	--	10a	85	19
33[g]	7a	5 mol% [Rh(acac)(coe)$_2$]	14 mol% **3**	--	10a	80	23
34[g]	7a	3 mol% [Rh(acac)(coe)$_2$]	6 mol% **4**	--	10a	40	12
35[g]	7a	5 mol% [Rh(acac)(coe)$_2$]	14 mol% **4**	--	10a	37	15
36[g]	7a	3 mol% [Rh(acac)(coe)$_2$]	3.3 mol% **5**	--	10a	75	63
37[g]	7a	5 mol% [Rh(acac)(coe)$_2$]	7 mol% **5**	--	10a	69	68
38[g]	7a	3 mol% [Rh(acac)(coe)$_2$]	3.3 mol% **1**	--	10a	78	93
39[e]	7a	3 mol% [Rh(acac)(coe)$_2$]	3.3 mol% **1**	K_3PO_4 (0.2 equiv)	10a	99	95

[a]The reaction was carried out with 1 equiv of imine and 2 equiv of boronic acid in the presence of the rhodium catalyst and the chiral ligand indicated in dioxane (0.12 M) at 70 ºC. [b]Yields were determined by ^{1}H-NMR, using 2,6-dimethoxytoluene as an internal standard in $CDCl_3$. [c]Enantiomeric excess of the pure product was determined by chiral HPLC. [d]The imine was added to the reaction mixture after 90 min at 70 °C. [e]The boronic acid and imine were added to the reaction mixture after 90 min at 70 °C. [f]The reaction was carried out at 55 °C. [g]The reactions were running at 70 ºC.

Representative procedure for the enantioselective Rh(I)-catalyzed additions of aryboronic acids to *N*-tosyl imines.

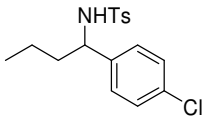
A vial containing a stir-vane, acetylacetonatobis(cyclooctene)rhodium (1.5 mg, 0.00375 mmol, 0.03 equiv) and (*R*)-Deguphos (2.2 mg, 0.00425 mmol, 0.033 equiv) in 0.50 mL of dioxane is sealed using a mini-inert seal and a blue nylon cap, and removed from the glove box. The vial was then placed in a heating block with stirring and heated at 70 °C (aluminium block temperature) for 90 min. The reaction mixture was allowed to cool to rt and the vial was transferred to the glove box. To the vial was added the arylboronic acid **8** (0.250 mmol, 2 equiv) a mixture of *N*-tosyl imine (0.125 mmol, 1 equiv) in 0.50 mL of dioxane, K_3PO_4 (5.3 mg, 0.025, 0.2 equiv) and powered 4Å molecular sieves (200 mg), after transferring back to the heating block, the vial was then heated at 70 °C for 20 h. The reaction mixture was allowed to cool at rt. The reaction was quenched with water and extracted with CH_2Cl_2. The combined organic layers were washed with brine (1 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The crude material was taken up in THF (5 mL) and PS-DEAM resin (200 mg) and placed on a shaker for 10 h. The THF solution was filtered to remove the resin, and the resin was washed with ethyl acetate (4 x 10 mL). The filtrates were combined and concentrated. The conversion to product was determined by integration relative to 2,6-dimethoxytoluene, which was used as an internal standard. The crude residue was purified by flash column chromatography on a Biotage Flash+ cartridge with a gradient of EtOAc in hexanes to provide the tosylamides **10**.



***N*-(1-(4-chlorophenyl)-1-phenylpropyl)-tosylamide (10a).** The general procedure was followed and the product was isolated by flash

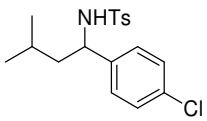
column chromatography on a Biotage Flash+ cartridge with a gradient of 0% to 30% EtOAc in hexanes, affording **10a** as a white solid (47 mg, 94% yield). R_f = 0.47 (Hexane: EtOAc, 3:1). mp 138-140 ºC. 95% ee (Chiralpak OD-H, hexanes/IPA 80/20, 0.5 mL min^{-1}, λ = 230 nm, t_R = 18.5 min (major), t_R = 33.4 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.30-7.11 (m, 7H), 7.06 (dd, *J* = 6.8, 1.6 Hz, 2H), 6.99 (dd, *J* = 8.4, 2.0 Hz, 2H), 5.78-5.75 (m, 1H), 4.30 (q, *J* = 7.6 Hz, 1H), 2.58-2.51 (m, 2H), 2.42 (s, 3H), 2.13-2.10 (m, 1H), 2.09-1.97 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 143.3 , 140.6, 139.1, 137.4, 133.2, 129.4, 128.6, 128.5, 128.4, 128.1, 127.1, 126.1, 57.3, 38.8, 32.0, 21.5. HRMS (ES+) *m/z*: Calcd for $C_{22}H_{22}ClNO_2S$ $[M+Na]^+$ 422.0957; found 422.0965. IR (KBr, cm^{-1}) 3225, 1597, 1431, 1262, 810,683.



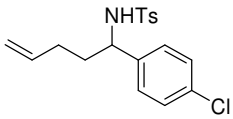
***N*-(1-(4-chlorophenyl)butyl)-tosylamide (10b).** The general procedure was followed and the product was isolated by flash column chromatography on a Biotage Flash+ cartridge with a gradient of 0% to 30% EtOAc in hexanes, affording **10b** as a white solid (37.5 mg, 89% yield). R_f = 0.44 (Hexane: EtOAc, 3:1). mp 125-127 ºC. 93% ee (Chiralpak OD-H, hexanes/IPA 80/20, 0.5 mL min^{-1}, λ = 230 nm, t_R = 11.9 min (major), t_R = 14.6 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 5.31 (d, *J* = 7.6 Hz, 1H), 4.29 (q, *J* = 7.2 Hz, 1H), 2.41(s, 3H), 1.77-1.60 (m, 2H), 1.33-1.13 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 143.2, 139.5, 137.5, 132.9, 129.3, 128.4, 127.9, 126.9, 57.4, 39.5, 21.43, 18.9, 13.5. HRMS (FAB+) *m/z*: Calcd for $C_{17}H_{20}ClNO_2S$ $[MH]^+$ 338.0981; found 338.0977. IR (KBr, cm^{-1}) 3257, 1430, 1317, 1166, 811.



***N*-(1-(4-chlorophenyl)-3-methylbutyl)-tosylamide (10c).** The general procedure was followed and the product was isolated by flash column chromatography on a Biotage Flash+ cartridge with a gradient of 0% to 30% EtOAc in hexanes, affording **10c** as a white solid (42 mg, 96% yield). R_f = 0.53 (Hexane: EtOAc, 3:1). mp 93-95 ºC. 91% ee (Chiralpak OD-H, hexanes/IPA 80/20, 0.5 mL min^{-1}, λ = 230 nm, t_R = 10.3 min (major), t_R = 18.4 min (minor).

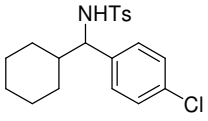
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.8 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.05 (dt, *J* = 8.4, 2.4 Hz, 2H), 6.94 (dt, *J* = 8.4, 2.8 Hz, 2H), 5.70 (d, *J* = 8.0 Hz, 1H), 4.30 (q, *J* = 7.6 Hz, 1H), 2.43 (s, 3H), 1.64-1.51 (m, 1H), 1.50-1.41 (m, 2H), 0.82 (d, *J* = 6.4 Hz, 3H), 0.79 (d, *J* = 6.0 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 143.1, 139.7, 137.5, 132.9, 129.2, 128.3, 127.9, 127.1, 57.4, 46.6, 24.5, 22.3, 22.1, 21.4. HRMS (ES+) *m/z*: Calcd for $C_{18}H_{22}ClNO_2S$ $[M+Na]^+$ 374.0957; found 374.0960. IR (KBr, cm^{-1}) 3260, 1595, 1398, 1087, 374, 679.



***N*-(1-(4-chlorophenyl)pent-4-enyl))-tosylamide (10d).** The general procedure was followed and the product was isolated by flash column chromatography on a Biotage Flash+ cartridge with a gradient of 0% to 20% EtOAc in hexanes, affording **10d** as a white solid (38 mg, 87% yield). R_f = 0.50 (Hexane: EtOAc, 3:1). mp 99-101 ºC. 98% ee (Chiralpak OD-H, hexanes/IPA 80/20, 0.5 mL min^{-1}, λ = 230 nm, t_R = 9.4 min (major), t_R = 11.6 min (minor).

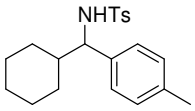
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.10 (dt, *J* = 8.4, 2.8 Hz, 2H), 6.97 (dt, *J* = 8.8, 2.0 Hz, 2H), 5.86 (d, *J* = 8.0 Hz, 1H), 5.75-5.65 (m, 1H), 4.99-4.92 (m, 2H), 4.29 (q, *J* = 5.4 Hz, 1H), 2.41 (s, 3H), 2.03-0.7 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 143.2, 139.3, 137.5, 136.9, 133.9, 129.3, 128.5,

128.1, 127.0, 115.7, 57.2, 36.4, 29.9, 21.4. LRMS (ES+) *m/z*: Calcd for $C_{18}H_{20}ClNO_2S$ $[M+Na]^+$ 372; found 372. IR (KBr, cm^{-1}) 3265, 1442, 1317, 1287, 1166, 1089, 835.



***N*-(1-(4-chlorophenyl)cyclohexylmethyl)-tosylamide (10e).** The general procedure was followed and the product was isolated by flash column chromatography on a Biotage Flash+ cartridge with a gradient of 0% to 30% EtOAc in hexanes, affording **10e** as a white solid (38 mg, 80% yield). R_f = 0.52 (Hexane: EtOAc, 3:1). mp 155-157 ºC. 96% ee (Chiralpak OD-H, hexanes/IPA 85/15, 0.5 mL min^{-1}, λ = 230 nm, t_R = 12.5 min (major), t_R = 19.7 min (minor).

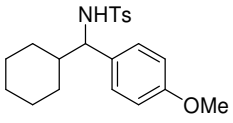
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.08-7.05 (m, 4H), 6.85 (dd, *J* = 8.0, 2.0 Hz, 2H), 4.92 (d, *J* = 8.0 Hz, 1H), 4.02 (t, *J* = 8.0 Hz, 1H), 2.36 (s, 3H), 1.88-1.72 (m, 2H), 1.61-1.50 (m, 3H), 1.28-0.83 (m, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 143.9, 143.0, 137.3, 129.1, 128.8, 126.9, 125.3, 124.8, 63.1, 43.4, 29.6, 29.4, 26.0, 25.7, 21.2. HRMS (ES+) *m/z*: Calcd for $C_{20}H_{24}ClNO_2S$ $[M+Na]^+$ 400.1114; found 400.1123. IR (KBr, cm^{-1}) 3220, 1317, 1287, 685, 667.



***N*-(1-(4-methylphenyl) (cyclohexyl)methyl)-tosylamide (10f).** The general procedure was followed and the product was isolated by flash column chromatography on a Biotage Flash+ cartridge with a gradient of 0% to 30% EtOAc in hexanes, affording **10f** as a white solid (32 mg, 71% yield). R_f = 0.51 (Hexane: EtOAc, 3:1). mp 149-151 ºC. 96% ee (Chiralpak OD-H, hexanes/IPA 80/20, 0.5 mL min^{-1}, λ = 230 nm, t_R = 10.0 min (major), t_R = 15.3 min (minor)).

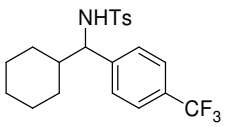
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (dd, *J* = 8.4, 2.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.0 Hz, 2H), 5.75 (d, *J* = 8.8 Hz, 1H), 4.02 (t, *J* = 8.4 Hz, 1H), 2.46 (s, 3H), 2.36 (s, 3H), 2.02 (m, 1H), 1.75 (m, 1H), 1.63-1.45 (m, 3H),

1.33 (m, 1H), 1.21-0.82 (m, 5H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 142.5, 137.7, 136.9, 136.4, 129.0, 128.6, 127.0, 126.9, 63.3, 43.6, 29.7, 29.5, 26.2, 25.9, 21.4, 21.0. HRMS (ES+) *m/z*: Calcd for $C_{21}H_{27}NO_2S$ $[M+Na]^+$ 380.1660; found 380.1667. IR (KBr, cm^{-1}) 3220, 1317, 1287, 685, 667.



***N*-(1-(4-methoxyphenyl) (cyclohexyl)methyl)-tosylamide (10g).** The general procedure was followed and the product was isolated by flash column chromatography on a Biotage Flash+ cartridge with a gradient of 0% to 30% EtOAc in hexanes, affording **10g** as a white solid (34.5 mg, 74% yield). R_f = 0.39 (Hexane: EtOAc, 3:1). mp 156-158 ºC. 90% ee (Chiralpak OD-H, hexanes/IPA 80/20, 0.5 mL min^{-1}, λ = 230 nm, t_R = 11.4 min (major), t_R = 18.5 min (minor)).

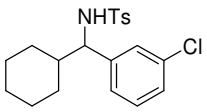
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 7.6 Hz, 2H), 6.86 (dd, *J* = 8.8, 2.0 Hz, 2H), 6.66 (dd, *J* = 8.4, 2.0 Hz, 2H), 5.10 (d, *J* = 8.4 Hz, 1H), 4.00 (t, *J* = 8.0 Hz, 1H), 3.77 (s, 3H), 2.37 (s, 3H), 1.97 (m, 1H), 1.75 (m, 1H), 1.63-1.44 (m, 3H), 1.32 (d, *J* = 13.2 Hz, 1H), 1.20-0.79 (m, 5H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 158.7, 142.6, 137.8, 132.1, 129.1, 128.1, 127.1, 113.5, 63.0, 55.2, 43.8, 29.7, 29.6, 26.2, 25.9, 21.4. LRMS (ES+) *m/z*: Calcd for $C_{21}H_{27}NO_3S$ $[M+Na]^+$ 396; found 396. IR (KBr, cm^{-1}) 3261, 1496, 1317, 1270, 1089, 705.



***N*-(1-(4-trifluoromethylphenyl) (cyclohexyl)methyl)-tosylamide (10h).** The general procedure was followed and the product was isolated by flash column chromatography on a Biotage Flash+ cartridge with a gradient of 0% to 30% EtOAc in hexanes, affording **10h** as a white solid (46 mg, 89% yield). R_f = 0.50 (Hexane: EtOAc, 3:1). mp 152-154 ºC. 91% ee (Chiralpak

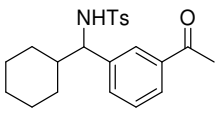
OD-H, hexanes/IPA 80/20, 0.5 mL min^{-1}, λ = 230 nm, t_R = 9.7 min (major), t_R = 19.7 min (minor)).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.10 (d, *J* = 8.8 Hz, 1H), 4.14 (t, *J* = 8.4 Hz, 1H), 2.33 (s, 3H), 2.01 (m, 1H), 1.74 (m, 1H), 1.61-1.56 (m, 3H), 1.27 (d, *J* = 13.6 Hz, 1H), 1.18-0.81 (m, 5H). For the $^{13}C\{^1H\}$ NMR spectrum see page S28. HRMS (ES+) *m/z*: Calcd for $C_{21}H_{24}NO_2F_3S$ $[M+Na]^+$ 434.1378; found 434.1389. IR (KBr, cm^{-1}) 3278, 1443, 1321, 1164, 808.



***N*-(1-(3-chlorophenyl) (cyclohexyl)methyl)-tosylamide (10i).** The general procedure was followed and the product was isolated by flash column chromatography on a Biotage Flash+ cartridge with a gradient of 0% to 30% EtOAc in hexanes, affording **10i** as a white solid (35.5 mg, 75% yield). R_f = 0.48 (Hexane: EtOAc, 3:1). mp 111-113 ºC. 90% ee (Chiralpak OD-H, hexanes/IPA 80/20, 0.5 mL min^{-1}, λ = 230 nm, t_R = 14.8 min (major), t_R = 18.1 min (minor)).

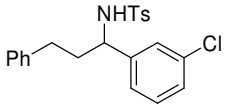
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.11-7.08 (m, 4H), 6.92-6.90 (m, 1H), 6.80 (s, 1H), 5.39 (d, *J* = 8.4 Hz, 1H), 4.02 (t, *J* = 8.0 Hz, 1H), 2.37 (s, 3H), 1.97 (m, 1H), 1.76 (m, 1H), 1.68-1.55 (m, 3H), 1.30 (m, 1H), 1.17-0.87 (m, 5H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 143.1, 141.9, 137.3, 133.9, 129.4, 129.2, 127.3, 127.0, 126.9, 125.2, 63.0, 43.4, 29.7, 29.3, 26.0, 25.8, 21.4. HRMS (ES+) *m/z*: Calcd for $C_{20}H_{24}ClNO_2S$ $[M+Na]^+$ 400.1114; found 400.1120. IR (KBr, cm^{-1}) 3271, 1442, 1287, 722, 667.



***N*-(1-(3-acetylphenyl) (cyclohexyl)methyl)-tosylamide (10j).** The general procedure was followed and the product was isolated by flash

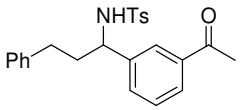
column chromatography on a Biotage Flash+ cartridge with a gradient of 0% to 40% EtOAc in hexanes, affording **10j** as a white solid (39 mg, 81% yield). R_f = 0.27 (Hexane: EtOAc, 3:1). mp 137-139 ºC. 89% ee (Chiralpak OD-H, hexanes/IPA 80/20, 0.5 mL min^{-1}, λ = 230 nm, t_R = 15.4 min (major), t_R = 25.5 min (minor)).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75-7.71 (m, 1H), 7.49 (m, 3H), 7.31-7.25 (m, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 5.76 (d, *J* = 8.4 Hz, 1H), 4.14 (t, *J* = 8.0 Hz, 1H), 2.52 (s, 3H), 2.32 (s, 3H), 1.97 (m, 1H), 1.74 (m, 1H), 1.62-1.50 (m, 3H), 1.28 (m, 1H), 1.18-0.89 (m, 5H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 197.9, 142.9, 140.6, 137.6, 136.8, 132.0, 129.2, 128.4, 127.0, 126.97, 126.92, 63.2, 43.6, 29.7, 29.3, 26.6, 26.1, 25.8, 21.4. HRMS (ES+) *m/z*: Calcd for $C_{22}H_{27}ClNO_3S$ $[M+Na]^+$ 408.1609; found 408.1618. IR (KBr, cm^{-1}) 3270, 1690, 1440, 1316, 1168, 813, 685.



***N*-(1-(3-chlorophenyl)-1-phenylpropyl)-tosylamide (10k).** The general procedure was followed and the product was isolated by flash column chromatography on a Biotage Flash+ cartridge with a gradient of 0% to 30% EtOAc in hexanes, affording **10k** as a colorless oil (37 mg, 74% yield). R_f = 0.41 (Hexane: EtOAc, 3:1). 93% ee (Chiralpak OD-H, hexanes/IPA 85/25, 0.5 mL min^{-1}, λ = 230 nm, t_R = 19.1 min (major), t_R = 34.3 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 8.4 Hz, 2H), 7.27-7.04 (m, 9H), 6.95 (t, *J* = 4.0 Hz, 1H),), 6.86 (s, 1H), 5.43 (d, *J* = 8.0 Hz, 1H), 4.26 (q, *J* = 7.6 Hz, 1H), 2.59-2.43 (m, 2H), 2.37 (s, 3H), 2.10-1.67 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 143.3, 142.5, 140.5, 137.2, 134.2, 129.8, 129.3, 128.4, 128.3, 127.5, 127.0, 126.9, 126.1, 124.7, 57.3, 38.8, 32.0, 21.4. HRMS (ES+) *m/z*: Calcd for $C_{22}H_{22}ClNO_2S$ $[M+Na]^+$ 422.0957; found 422.0968. IR (KBr, cm^{-1}) 3235, 1435, 1136, 1090, 805, 710.



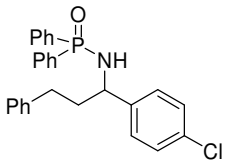
***N*-(1-(3-acetylphenyl)-1-phenylpropyl)-tosylamide (10l).** The general procedure was followed and the product was isolated by flash column chromatography on a Biotage Flash+ cartridge with a gradient of 0% to 40% EtOAc in hexanes, affording **10l** as a white solid (41mg, 80% yield). R_f = 0.22 (Hexane: EtOAc, 3:1). mp 108-110 ºC. 90% ee (Chiralpak OD-H, hexanes/IPA 75/25, 0.5 mL min^{-1}, λ = 230 nm, t_R = 16.8 min (major), t_R = 30.8 min (minor)).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (dt, *J* = 8.8, 1.6 Hz, 1H), 7.58 (s, 1H), 7.51 (d, *J* = 8.0 Hz, 2H),), 7.31-7.15 (m, 5H), 7.06-7.30 (m, 4H), 5.97 (d, *J* = 8.0 Hz, 1H), 4.37 (q, *J* = 7.6 Hz, 1H), 2.63-2.52 (m, 2H), 2.50 (s, 3H), 2.31 (s, 3H), 2.17-1.94 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 197.9, 143.1, 141.5, 140.6, 137.6, 137.1, 131.6, 129.4, 128.8, 128.5, 128.4, 127.4, 127.0, 126.5, 126.1, 57.7, 39.0, 32.1, 26.6. 21.4. HRMS (ES+) *m/z*: Calcd for $C_{24}H_{25}NO_3S$ $[M+Na]^+$ 430.1453; found 430.1460. IR (KBr, cm^{-1}) 3255, 1685, 1431, 1160, 809, 70870.

Representative procedure for the enantioselective Rh(I)-catalyzed additions of aryboronic acids to *N*-phosphinoyl imines.

A vial containing a stir-vane, acetylacetonatobis(cyclooctene)rhodium (2.6 mg, 0.0062 mmol, 0.05 equiv) and (*R,R*)-Deguphos (4.6 mg, 0.00875 mmol, 0.07 equiv) in 0.50 mL of dioxane is sealed using a mini-inert seal and a blue nylon cap, and removed from the glove box. The vial was then placed in a heating block with stirring and heated at 70 °C (aluminium block temperature) for 90 min. The reaction mixture was allowed to cool to rt and the vial was transferred to the glove box. To the vial was added the arylboronic acid **8** (0.250 mmol, 2 equiv) a mixture of *N*-phosphinoyl imine (0.125 mmol, 1 equiv) in 0.50

mL of dioxane, K_3PO_4 (5.3 mg, 0.025, 0.2 equiv) and powered 4Å molecular sieves (200 mg), after transferring back to the heating block, the vial was then heated at 70 °C for 20 h. The reaction mixture was allowed to cool at rt. The reaction was quenched with water and extracted with CH_2Cl_2. The combined organic layers were washed with brine (1 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The crude material was taken up in THF (5 mL) and PS-DEAM resin (200 mg) and placed on a shaker for 10 h. The THF solution was filtered to remove the resin, and the resin was washed with ethyl acetate (4 x 10 mL). The filtrates were combined and concentrated. The conversion to product was determined by integration relative to 2,6-dimethoxytoluene, which was used as an internal standard. The crude residue was purified by flash column chromatography on a Biotage Flash+ cartridge with a gradient of EtOAc in hexanes to provide the phosphoramides **9**.

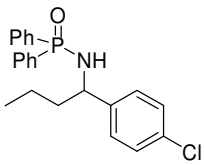


***N*-(1-(4-chlorophenyl)-1-phenylpropyl)-diphenylphosphoramide (9a).** Procedure for the reaction performed on 5 mmol scale (entry 7, Table 1). A solution of Rh(acac)(coe)$_2$ (105.6 mg, 0.25 mmol, 0.05 equiv) and (*R*)-Deguphos (185.4 mg, 0.35 mmol, 0.07 equiv, mmol in dioxane (20 mL) was prepared in a glovebox and then was stirred for 90 min at 70 ºC. Imine **6a** (1.67 g, 5 mmol, 1 equiv) in dioxane (20 mL), 4-chorophenylboronic acid (1.56 g, 10 mmol, 2 equiv), powered 4Å molecular sieves (8 g) and K_3PO_4 (212 mg, 1 mmol, 0.2 equiv) were successively added and the resulting mixture was stirred for 20 h at 70 ºC. The reaction mixture was diluted with water and extracted with CH_2Cl_2.The crude material was taken up in THF (200 mL) and PS-DEAM resin (13.8 g, 1.58 mmol/g) and shaken for 16 h. The

THF solution was filtered and the resin was washed with ethyl acetate (5x). The product was isolated by flash column chromatography on a Biotage Flash+ cartridge with a gradient of 10% to 95% EtOAc in hexanes, affording **9a** as a white solid (2.05 g, 92% yield). R_f = 0.62 (Hexane: EtOAc, 1:10). mp 192-194 ºC. 90% ee (Chiralpak OD-H, hexanes/EtOH 97/3, 0.9 mL min^{-1}, λ = 230 nm, t_R = 18.8 min (major), t_R = 20.9 min (minor)).

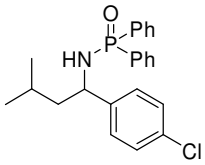
The resulting resin was treated with a 90:5:5 THF/water/acetic acid mixture (150 mL) for 12 h. The liquid phase was drained and the resin rinsed with the above cleavage mixture (1x) and THF (3x). The combined filtrates were concentrated and dried to afford 670 mg of 4-chlorophenylboronic acid (43%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89-7.84 (m, 2H), 7.77-7.72 (m, 2H), 7.55-7.10 (m, 15H), 4.22 (q, *J* = 7.2 Hz, 1H), 3.31 (dd, *J* = 9.6, 6.0 Hz, 1H), 2.62-2.52 (m, 2H), 2.35-2.29 (m, 1H), 2.15-2.12 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 142.14, 142.10, 141.1, 133.5, 132.9, 132.5, 132.4, 131.9, 131.8, 128.7, 128.6, 128.5, 128.49, 128.41, 128.3, 128.0, 125.9, 54.9, 40.8, 32.3. ^{31}P (162 MHz, $CDCl_3$): δ 9.6. HRMS (FAB+) *m/z*: Calcd for $C_{27}H_{25}ClNOP$ $[MH]^+$ 446.1441; found 446.1438. IR (KBr, cm^{-1}) 2930, 1491, 1436, 1178, 1124, 1014, 827, 750, 697.



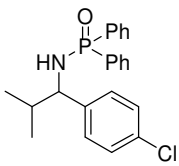
***N*-(1-(4-chlorophenyl)butyl)-diphenylphosphoramide (9b).** The general procedure was followed and the product was isolated by flash column chromatography on a Biotage Flash+ cartridge with a gradient of 10% to 95% EtOAc in hexanes, affording **9b** as a white solid (43 mg, 89% yield). R_f = 0.50 (Hexane: EtOAc, 1:10). mp 155-157 ºC. 86% ee (Chiralpak OD-H, hexanes/EtOH 97/3, 0.8 mL min^{-1}, λ = 230 nm, t_R = 14.4 min (major), t_R = 18.5 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88-7.85 (m, 2H), 7.77-7.72 (m, 2H), 7.53-7.14 (m, 6H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.16 (q, *J* = 7.6 Hz, 1H), 3.37 (dd, *J* = 9.2, 6.0 Hz, 1H), 1.98-1.71 (m, 2H), 1.31-1.16 (m, 2H), 0.85 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 142.6, 133.6, 132.7, 132.6, 132.5, 131.9, 131.8, 128.6, 128.5, 128.4, 128.3, 127.9, 55.0, 41.8, 19.4, 13.8. ^{31}P (162 MHz, $CDCl_3$): δ 9.9. HRMS (FAB+) *m/z*: Calcd for $C_{22}H_{23}ClNOP$ $[MH]^+$ 384.1284; found 384.1284. IR (KBr, cm^{-1}) 3214, 1491, 1435, 1181, 1125, 1014, 819, 745, 692.



***N*-(1-(4-chlorophenyl)-3-methylbutyl)-diphenylphosphoramide (9c).** The general procedure was followed and the product was isolated by flash column chromatography on a Biotage Flash+ cartridge with a gradient of 10% to 95% EtOAc in hexanes, affording **9c** as a colorless oil (40 mg, 80% yield). R_f = 0.51 (Hexane: EtOAc, 1:10). 81% ee (Chiralpak OD-H, hexanes/EtOH 97/3, 0.9 mL min^{-1}, λ = 230 nm, t_R = 9.6 min (major), t_R = 15.4 min (minor).

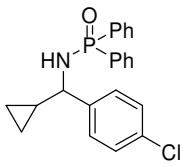
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86-7.82 (m, 2H), 7.73-7.71 (m, 2H), 7.49-7.27 (m, 6H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 4.16 (t, *J* = 8.4 Hz, 1H), 3.20-3.16 (m, 1H), 1.79-1.74 (m, 1H), 1.64-1.51 (m, 1H), 1.50-1.47 (m, 1H), 0.83 (d, *J* = 6.4 Hz, 3H), 0.80 (d, *J* = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 142.7, 133.5, 132.6, 132.5, 132.4, 131.9, 128.65, 128.60, 128.5, 128.4, 128.2, 127.9, 53.4, 49.2, 24.9, 22.7, 22.1. HRMS (ES+) *m/z*: Calcd for $C_{23}H_{25}ClNOP$ $[M+Na]^+$ 420.1260; found 420.1269. IR (KBr, cm^{-1}) 3020, 1455, 1180, 1123, 1014, 750, 697.



***N*-(1-(4-chlorophenyl)-2-methylpropyl))-diphenylphosphoramide (9d).** The general procedure was followed and the product was isolated by flash column chromatography on a Biotage Flash+ cartridge with a

gradient of 10% to 95% EtOAc in hexanes, affording **9d** as a white solid (36 mg, 75% yield). R_f = 0.53 (Hexane: EtOAc, 1:10). mp 170-172 ºC. 84% ee (Chiralpak AD-H, hexanes/IPA 90/10, 1.0 mL min^{-1}, λ = 222 nm, t_R = 17.6 min (minor) t_R = 20.7 min (major).

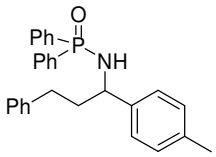
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85-7.77 (m, 2H), 7.68-7.61 (m, 2H), 7.47-7.25 (m, 6H), 7.20 (d, *J* = 11.2 Hz, 2H), 6.97 (d, *J* = 11.2 Hz, 2H), 3.88-3.85 (m, 1H), 3.35-3.25 (m, 1H), 1.97-1.95 (m, 1H), 0.99 (d, *J* = 8.8 Hz, 3H), 0.79 (d, *J* = 9.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 141.6, 134.1, 133.6, 132.8, 132.6, 132.5, 132.2, 131.94, 131.86, 131.8, 131.7, 128.7, 128.6, 128.4, 128.2, 128.1, 60.9, 35.6, 19.32, 19.29. HRMS (FAB+) *m/z*: Calcd for $C_{22}H_{23}ClNOP$ $[MH]^+$ 384.1284; found 384.1283. IR (KBr, cm^{-1}) 2955, 1436, 1185, 1123, 1014, 693.



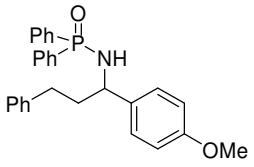
***N*-(1-(4-chlorophenyl)-2-methylpropyl))-diphenylphosphoramide (9e).** The general procedure was followed and the product was isolated by flash column chromatography on a Biotage Flash+ cartridge with a gradient of 10% to 95% EtOAc in hexanes, affording **9e** as a white solid (38 mg, 79% yield). R_f = 0.55 (Hexane: EtOAc, 1:10). mp 149-151 ºC. 95% ee (Chiralpak AD-H, hexanes/IPA 90/10, 1.0 mL min^{-1}, λ = 210 nm, t_R = 19.5 min (minor), t_R = 21.6 min (major).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95-7.89 (m, 2H), 7.78-7.74 (m, 2H), 7.55-7.23 (m, 10H), 3.68 (c, *J* = 9.6 Hz, 1H), 3.42 (t, *J* = 5.6 Hz, 1H), 1.25-1.20 (m, 1H), 0.60-0.47 (m, 2H), 0.41 (sext, *J* = 4.8 Hz, 1H), 0.25 (sext, *J* = 4.8 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 141.9, 132.8, 132.4, 132.3, 132.2, 132.1, 132.0, 131.9, 131.8, 128.6, 128.5, 128.4, 128.3, 61.5, 19.4, 5.3, 3.9. HRMS (FAB+) *m/z*: Calcd for $C_{22}H_{21}ClNOP$ $[MH]^+$

382.1127; found 382.1118. IR (KBr, cm^{-1}) 3203, 1491, 1436, 1183, 1124, 1014, 748, 692.

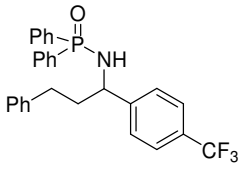


***N*-(1-(4-tolyl)-1-phenylpropyl)-diphenylphosphoramide (9f).** The general procedure was followed and the product was isolated by flash column chromatography on a Biotage Flash+ cartridge with a gradient of 10% to 95% EtOAc in hexanes, affording **9f** as a white solid (38 mg, 71% yield). R_f = 0.65 (Hexane: EtOAc, 1:10). mp 165-167 ºC. 91% ee (Chiralpak OD-H, hexanes/EtOH 97/3, 1.0 mL min^{-1}, λ = 210 nm, t_R = 9.7 min (major), t_R = 19.7 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88-7.82 (m, 2H), 7.80-7.77 (m, 2H), 7.52-7.09 (m, 15H), 4.19 (m, 1H), 3.42 (td, *J* = 9.6, 6.8 Hz, 1H), 2.59-2.47 (m, 2H), 2.39 (s, 3H), 2.40-2.32 (m, 1H), 2.18-2.06 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 141.9, 140.5, 140.4, 136.9, 133.9, 132.6, 132.5, 131.9, 131.8, 131.7, 131.4, 129.3, 128.5, 128.43, 128.38, 128.30, 126.4, 125.8, 55.3, 41.0, 32.4, 21.1. LRMS (FAB+) *m/z*: Calcd for $C_{28}H_{28}ClNOP$ $[MH]^+$ 426.1987; found 426.1981. IR (KBr, cm^{-1}) 3143, 1437, 1193, 1109, 1068, 723, 695.



***N*-(1-(4-methoxyphenyl)-1-phenylpropyl)-diphenylphosphoramide (9g).** The general procedure was followed and the product was isolated by flash column chromatography on a Biotage Flash+ cartridge with a gradient of 10% to 95% EtOAc in hexanes, affording **9g** as a white solid (37.5 mg, 68% yield). R_f = 0.58 (Hexane: EtOAc, 1:10). mp 180-182 ºC. 86% ee (Chiralpak OD-H, hexanes/EtOH 97/3, 0.9 mL min^{-1}, λ = 210 nm, t_R = 20.0 min (major), t_R = 22.5. min (minor).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90-7.86 (dd, *J* = 12.0, 7.2 Hz, 2H), 7.81-7.76 (dd, *J* = 12.0, 7.2 Hz, 2H), 7.54-7.16 (m, 11H), 7.13 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 4.21-4.15. (m, 1H), 3.85 (s, 3H), 3.29-3.25 (m, 1H), 2.62-2.46 (m, 2H),), 2.39-2.32 (m, 1H), 2.20-2.02 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.7, 141.5, 135.62, 135.56, 132.7, 132.6, 132.5, 131.9, 131.8, 131.7, 131.4, 128.6, 128.44, 128.37, 128.32, 128.26, 127.7, 125.8, 55.3, 55.0, 40.9, 32.4. LRMS (ES+) *m/z*: Calcd for $C_{28}H_{28}NO_2P$ $[M+Na]^+$ 464; found 464. IR (KBr, cm^{-1}) 3209, 1512, 1437, 1247, 183, 1030, 830, 750, 697.



***N*-(1-(4-trifluoromethylphenyl)-1-phenylpropyl)-diphenylphosphoramide (9h).** The general procedure was followed and the product was isolated by flash column chromatography on a Biotage Flash+ cartridge with a gradient of 10% to 95% EtOAc in hexanes, affording **9h** as a white solid (51 mg, 85% yield). R_f = 0.67 (Hexane: EtOAc, 1:10). mp 190-192 ºC. 82% ee (Chiralpak OD-H, hexanes/EtOH 97/3, 0.9 mL min^{-1}, λ = 230 nm, t_R = 16.9 min (major), t_R = 19.6 min (minor)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90-7.84 (m, 2H), 7.74-7.72 (m, 2H), 7.56-7.10 (m, 13H), 7.11 (d, *J* = 7.2Hz, 2H), 4.45-4.25. (m, 1H), 3.55 (dd, *J* = 10.0, 6.4Hz, 1H), 2.66-2.62 (m, 1H), 2.57-2.54 (m, 1H), 2.34-2.30 (m, 1H), 2.18-2.12 (m, 1H). For the ^{13}C{^{1}H} NMR spectrum see page 40. HRMS (FAB+) *m/z*: Calcd for $C_{28}H_{25}NOF_3P$ $[MH]^+$ 480.1704; found 480.1704. IR (KBr, cm^{-1}) 3187, 1512, 1438, 1327, 1180, 1122, 1018, 752, 698.

References

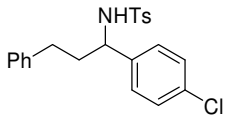
(1) For the synthesis of *N*-Tosyl aldimines: Chemla, F.; Hebbe, V; Normant, J. F.: *Synthesis* **2000**, *1*, 75. For the synthesis of *N*-Dpp imines: Yamaguchi, A.; Matsunaga, S.; Shibasaki, M. *Tetrahedron Lett.* **2006**, *47*, 3985.

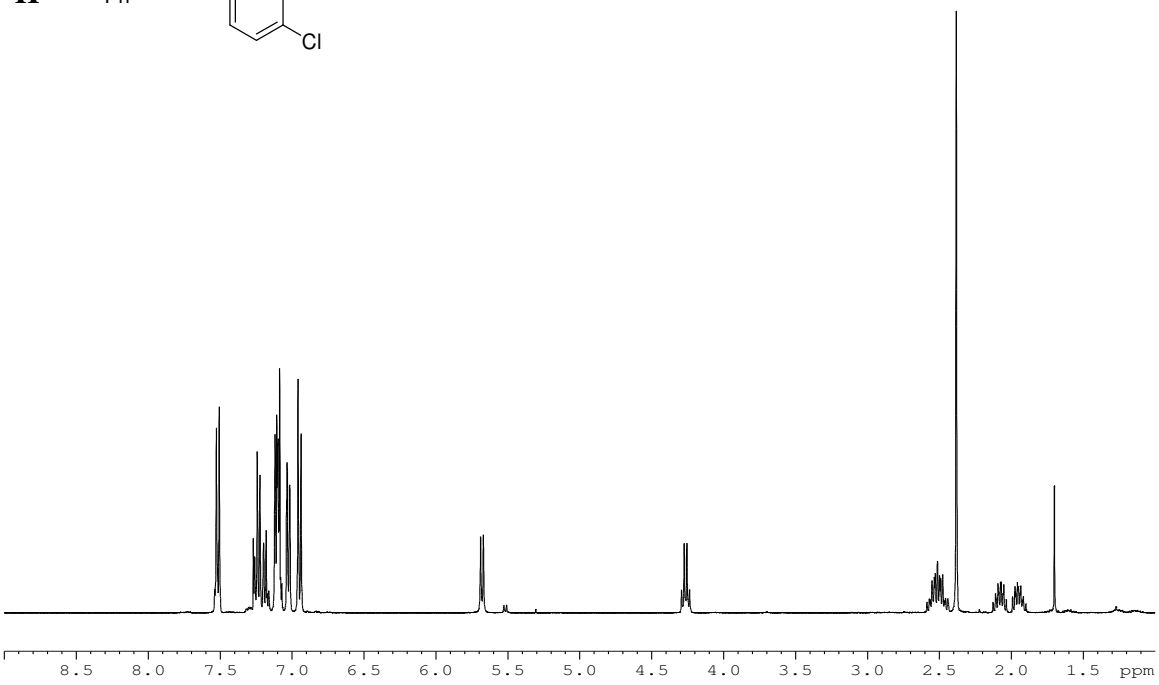
(2) Burke, J. M.; Coapes, R. B.; Goeta, A. E.; Howard, J. A.; Marder, T. B.; Robins E. G.; Westcott, S. A. *J. Organometallic Chem*. **2002**, *649*, 199.

(3) (a) Henry, P. M.; Davies, M.; Ferguson, G.; Philips, S.; Restivo, R. *Chem. Commun.* **1974**, 112. (b) Lemke, K.; Ballschuh, S.; Kunath, A.; Theil, F. *Tetrahedron: Asymmetry* **1997**, *8*, 2051. (c) Wang, Z. Q.; Feng, C. G.; Xu, M. H.; Lin, G. Q. *J. Am. Chem. Soc.* **2007**, *129*, 5336.

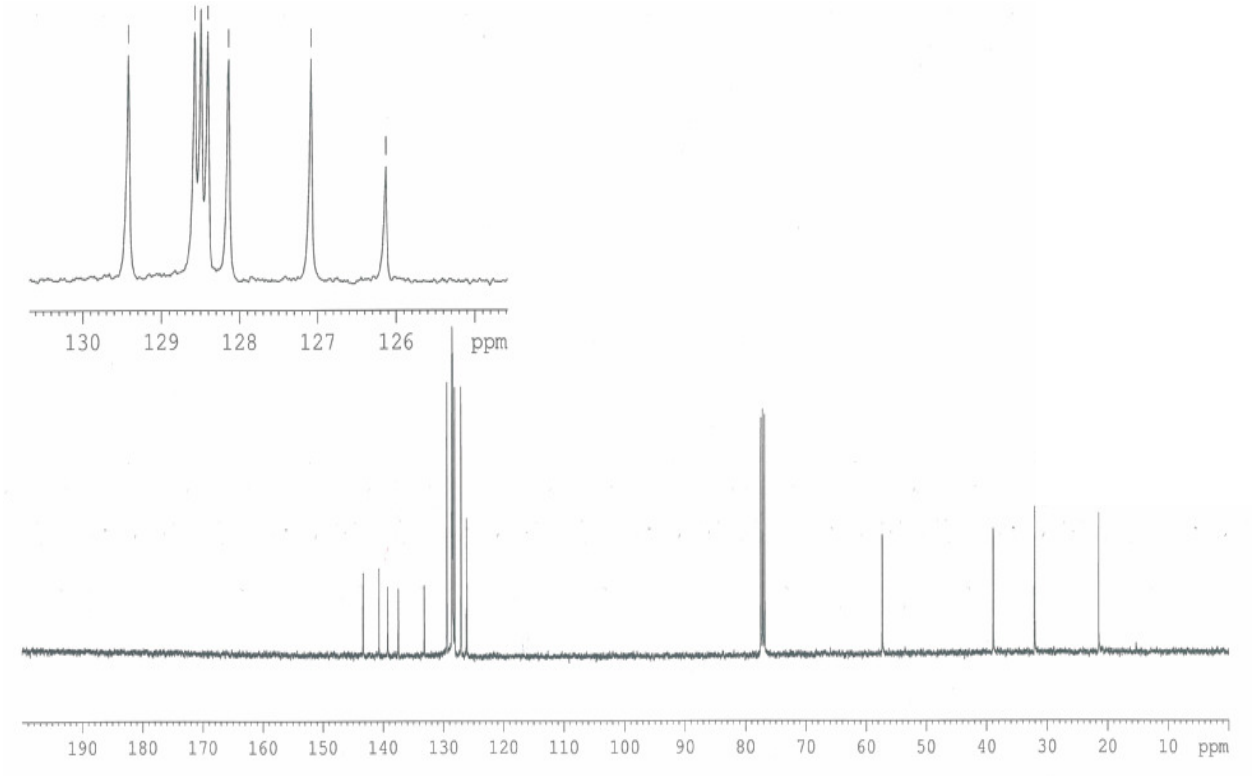
10a

^{1}H


NHTs
Ph
Cl

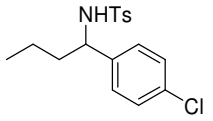

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm

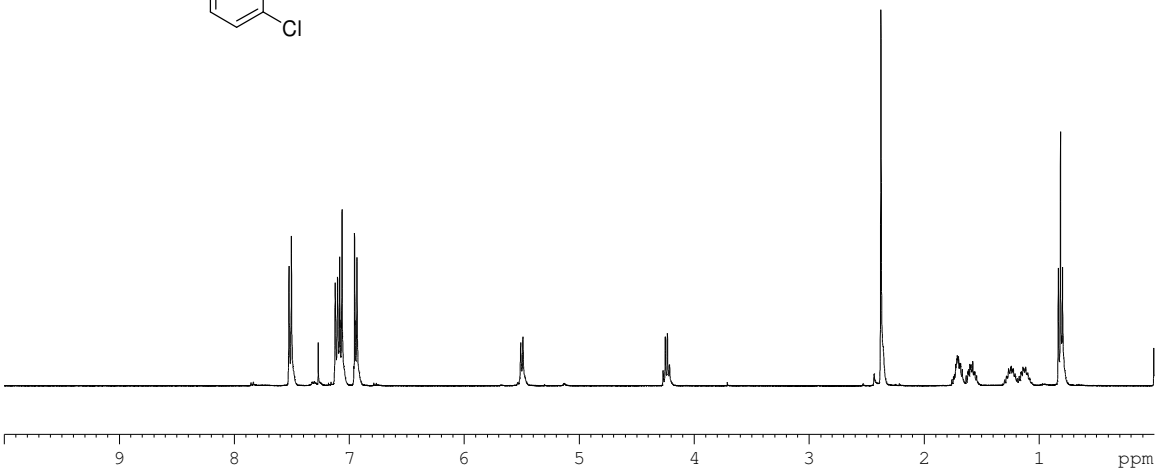
^{13}C


130 129 128 127 126 ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

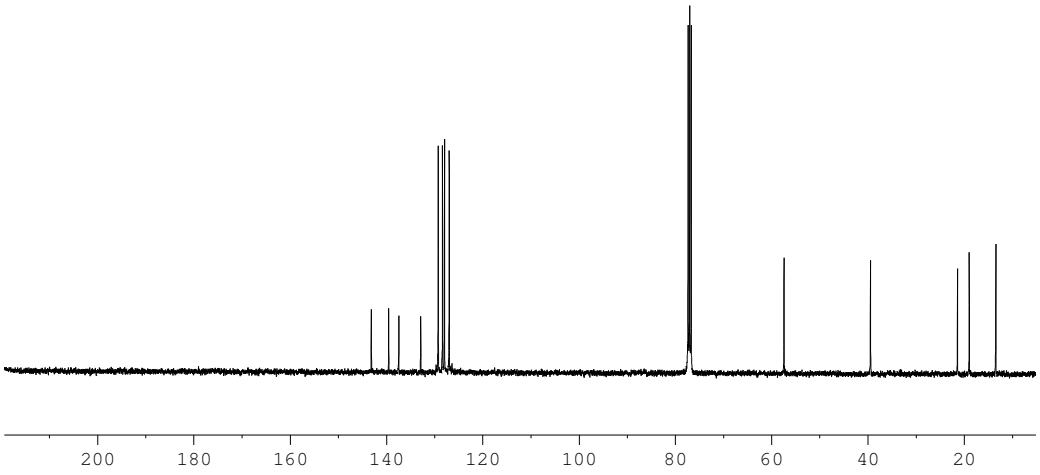
10b

^{1}H



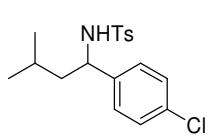


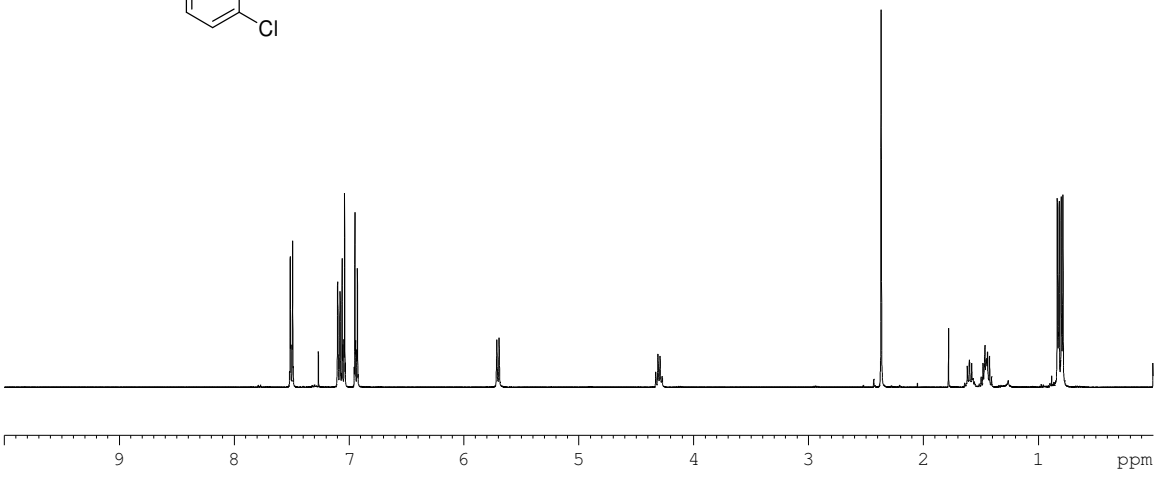
^{13}C



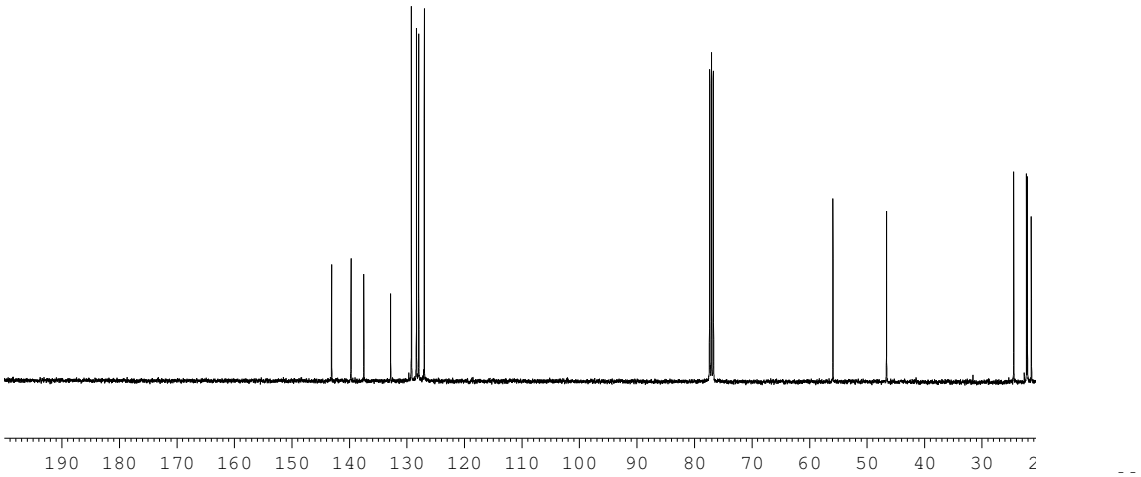
10c

^{1}H


NHTs
Cl

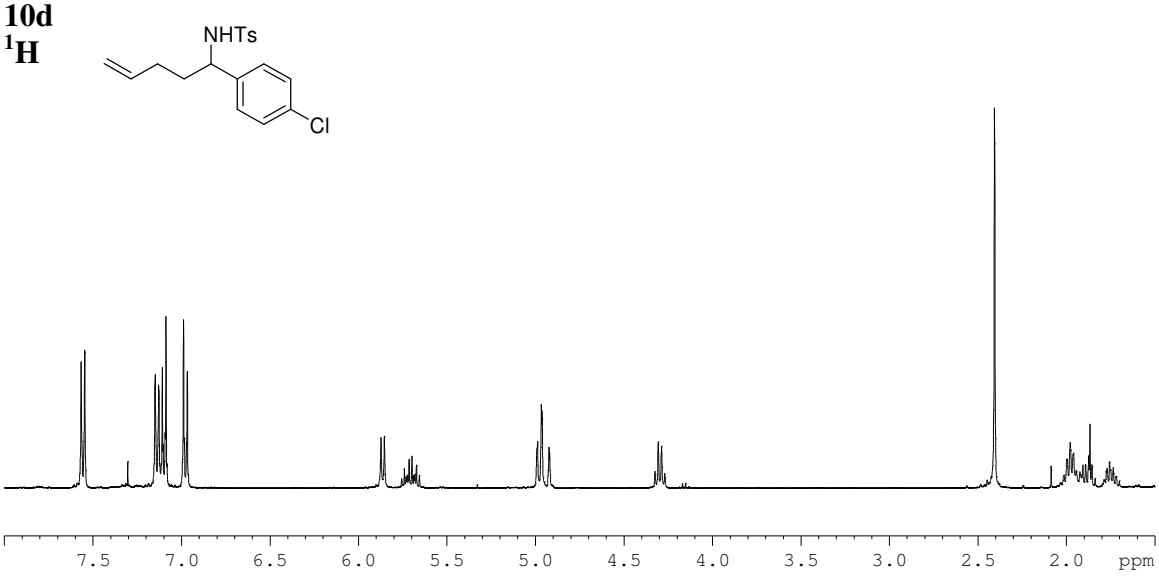

9
8
7
6
5
4
3
2
1
ppm

^{13}C

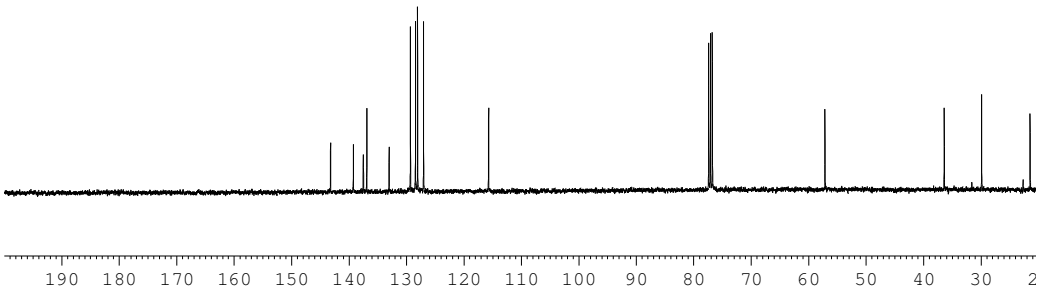

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30

10d

^{1}H

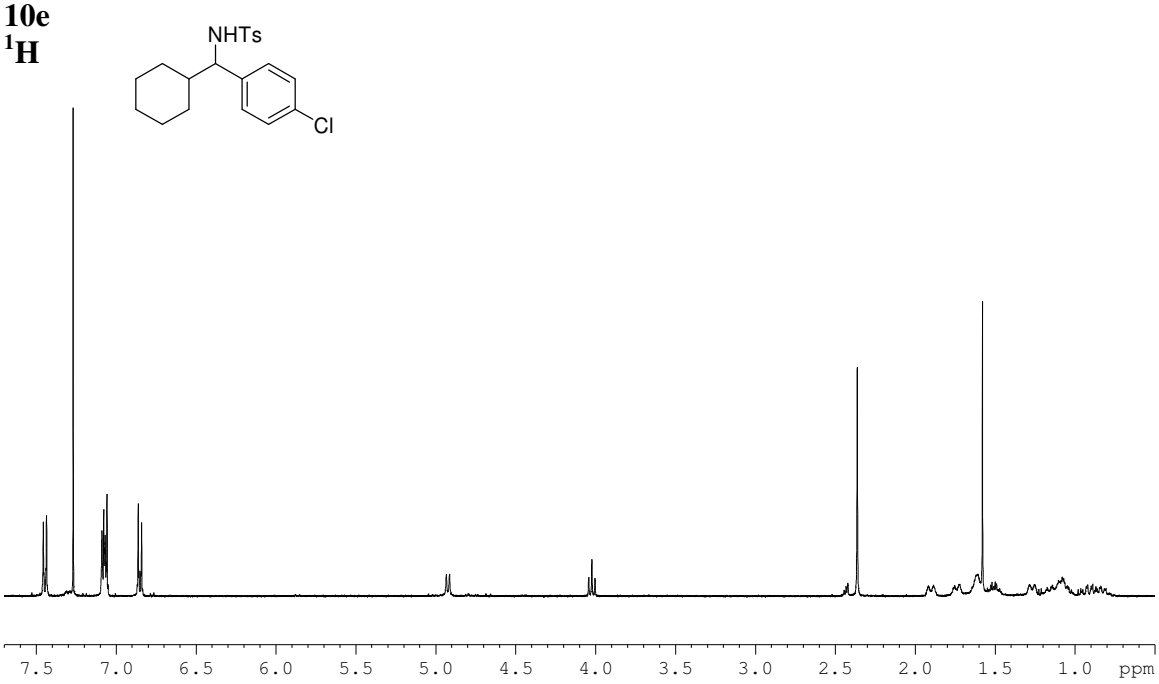

NHTs
Cl
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm

^{13}C

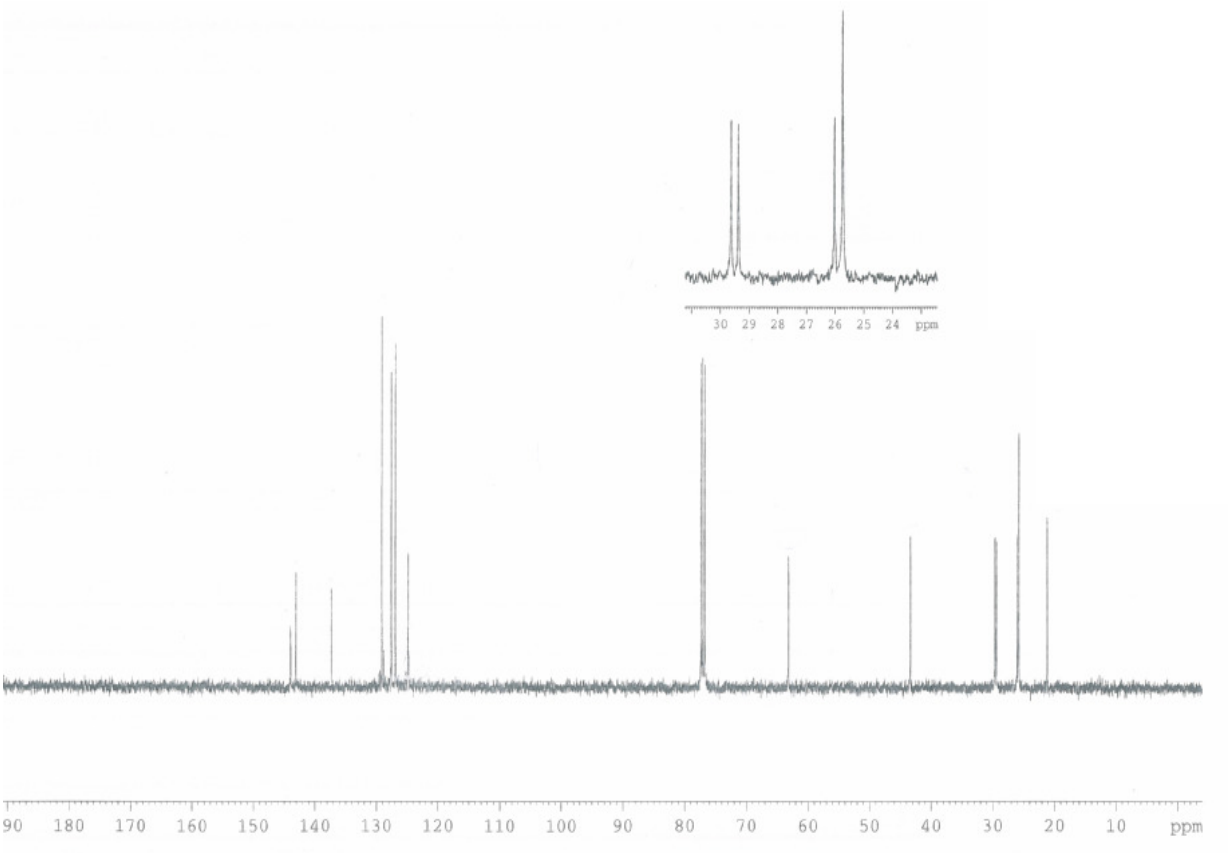

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
2

10e

^{1}H

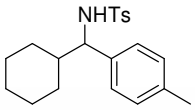

NHTs
Cl
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm

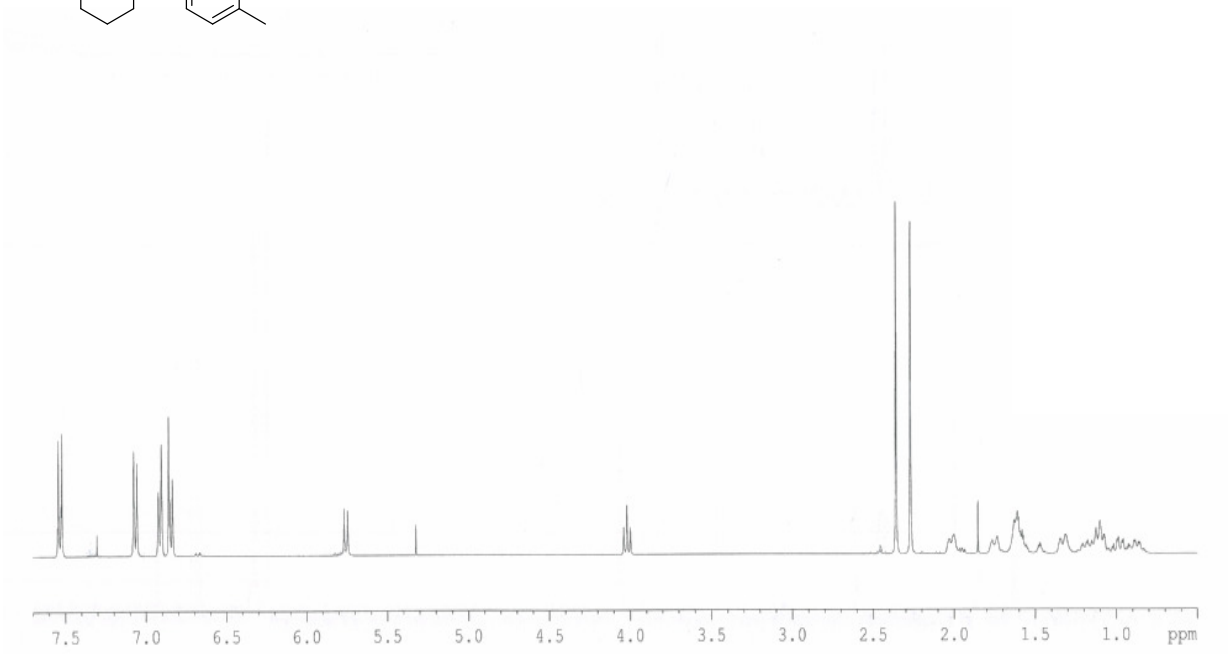
^{13}C


30 29 28 27 26 25 24 ppm
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

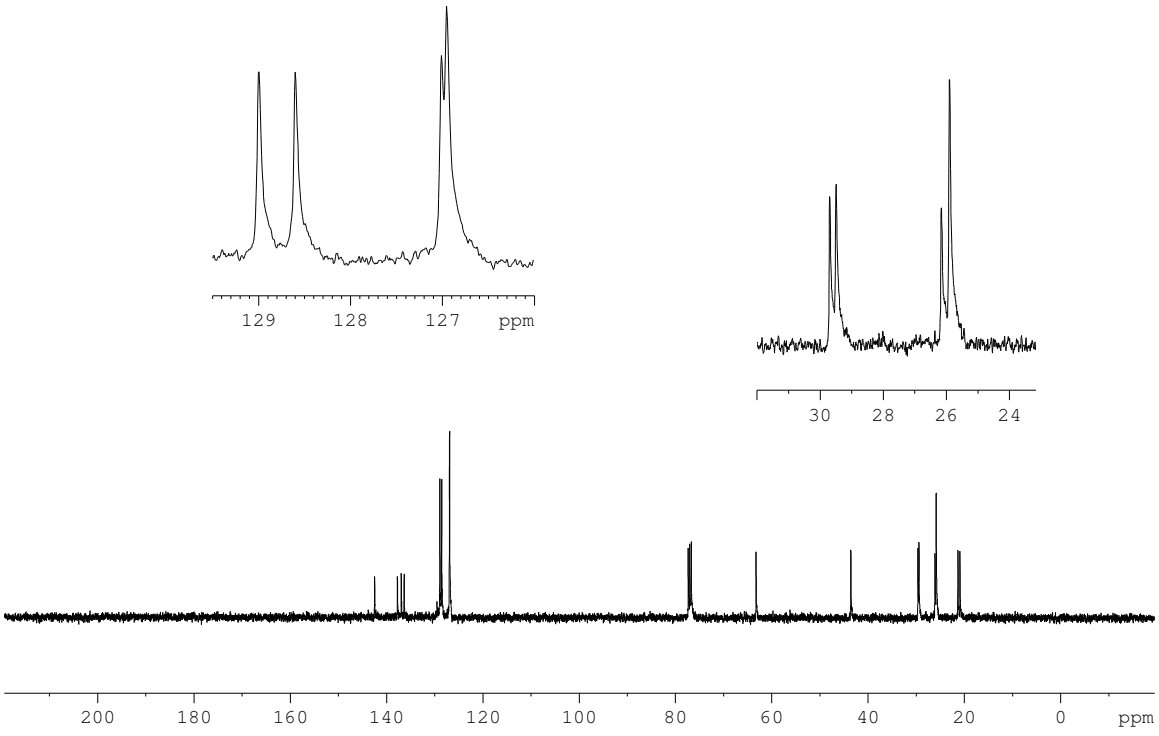
10f

^{1}H


NHTs

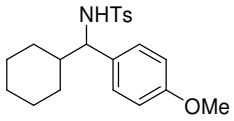

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

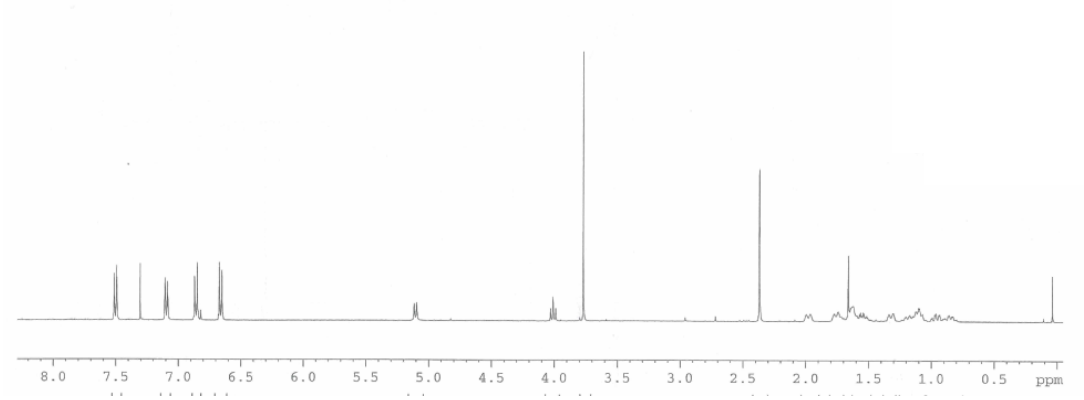
^{13}C


129
128
127
ppm
30
28
26
24
200
180
160
140
120
100
80
60
40
20
0
ppm

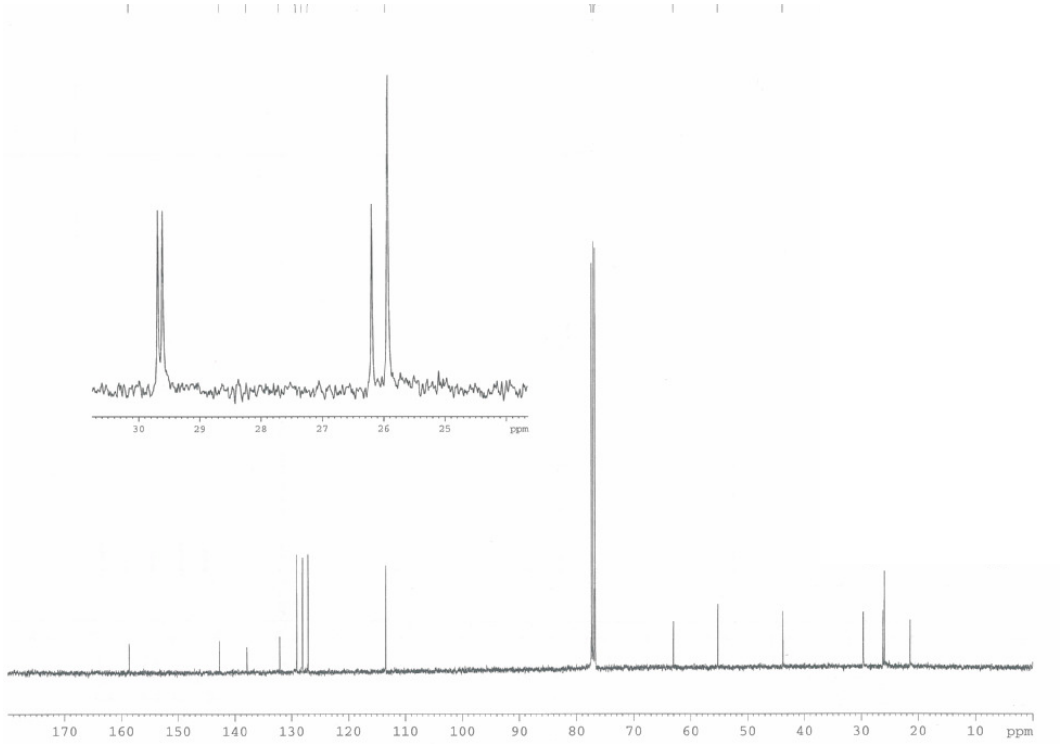
10g

^{1}H


NHTs
OMe

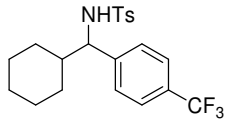

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

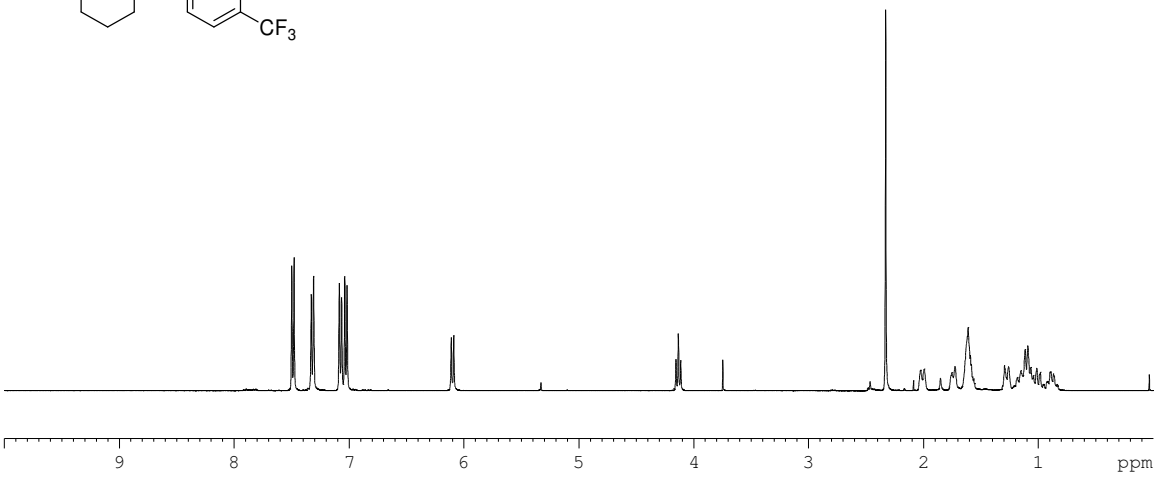
^{13}C


30
29
28
27
26
25
ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

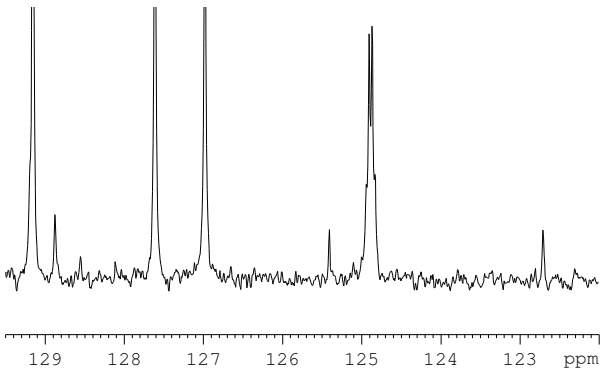
10h

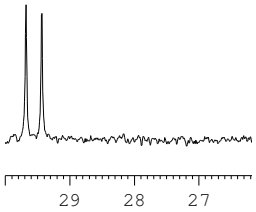
^{1}H

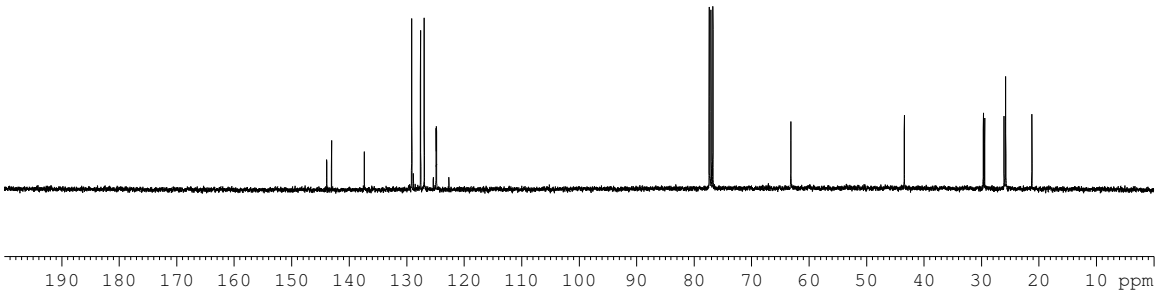

NHTs
CF3


9
8
7
6
5
4
3
2
1
ppm

^{13}C

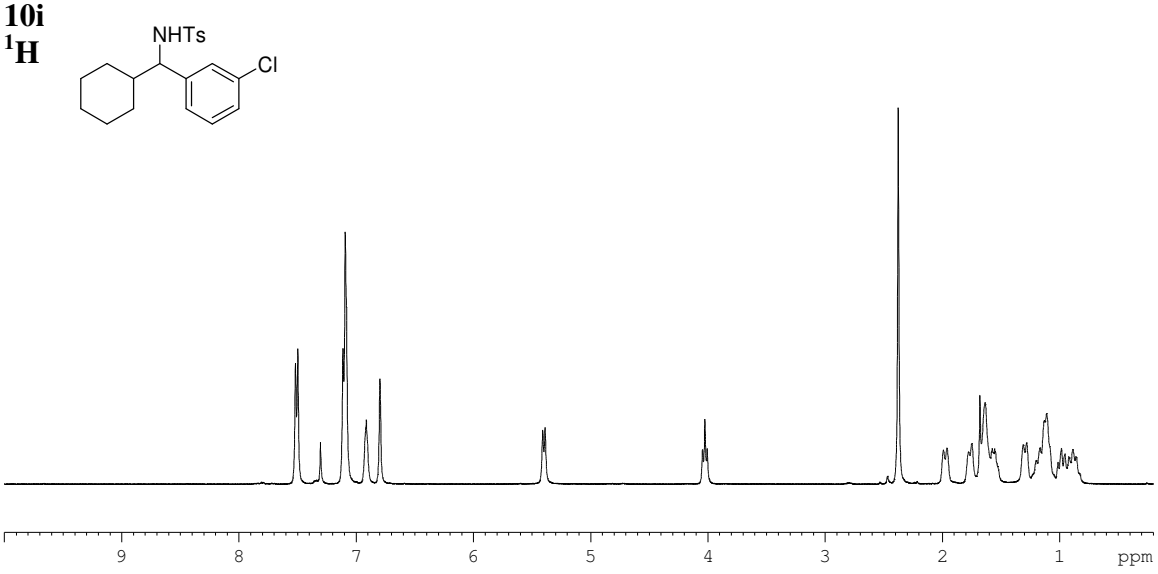

129
128
127
126
125
124
123
ppm


29
28
27

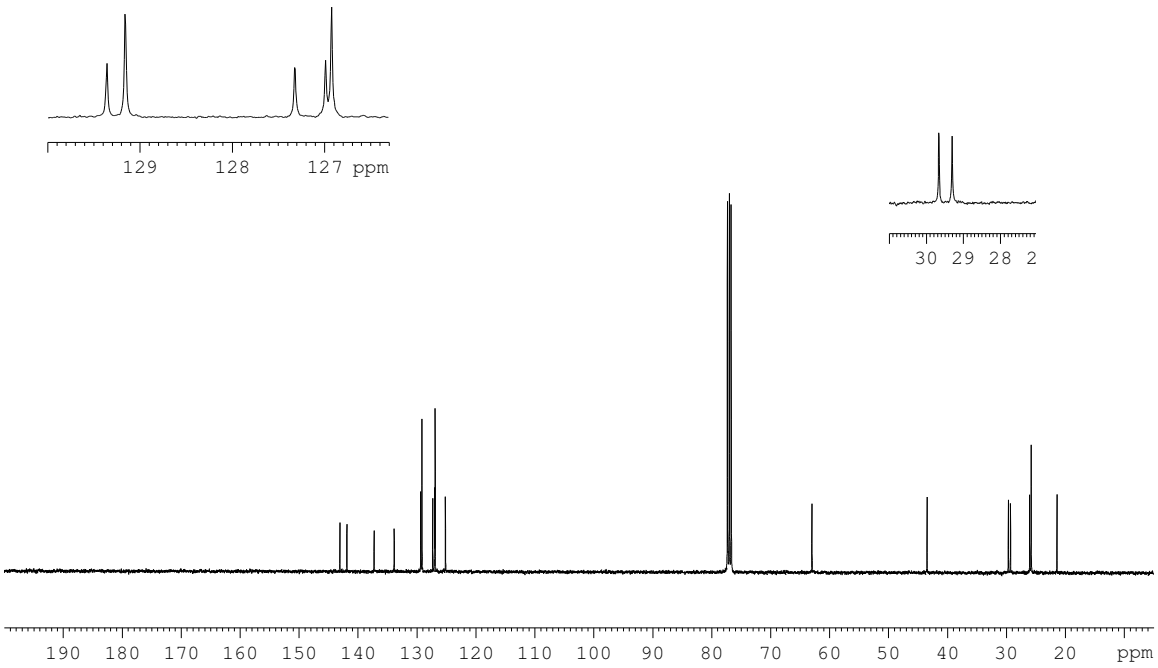

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

10i

^{1}H

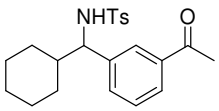

NHTs
Cl
9
8
7
6
5
4
3
2
1
ppm

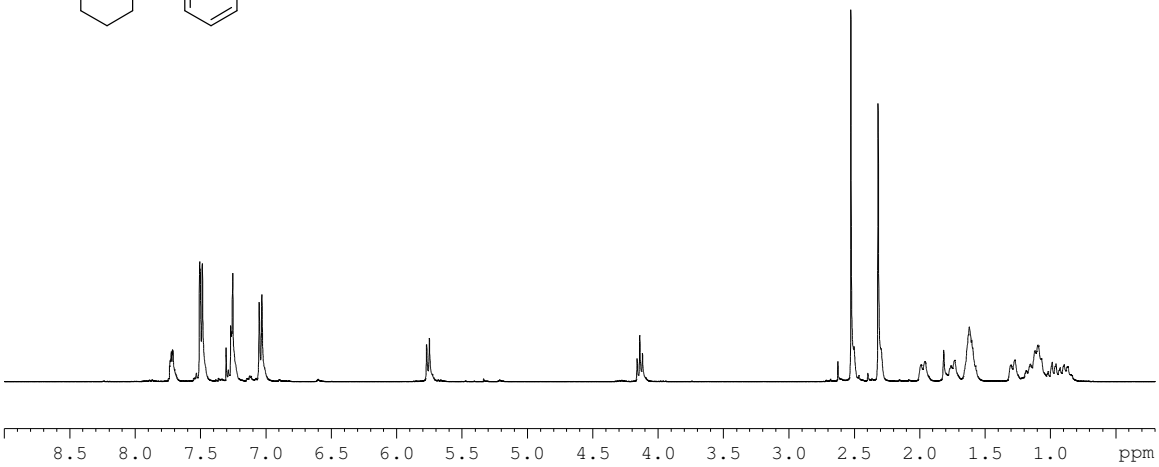
^{13}C


129
128
127 ppm
30 29 28 2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

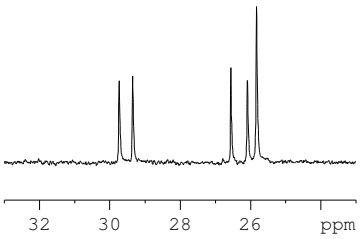
10j

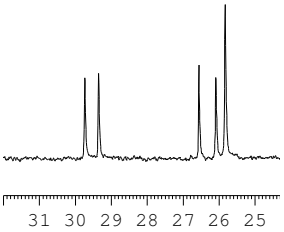
^{1}H

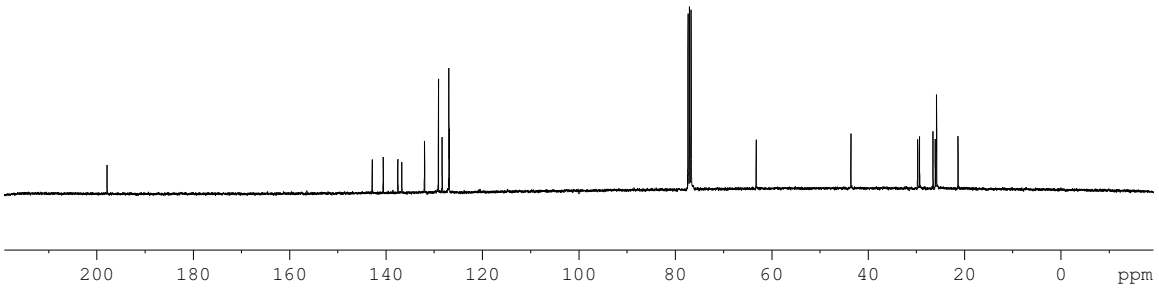

NHTs
O


8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm

^{13}C

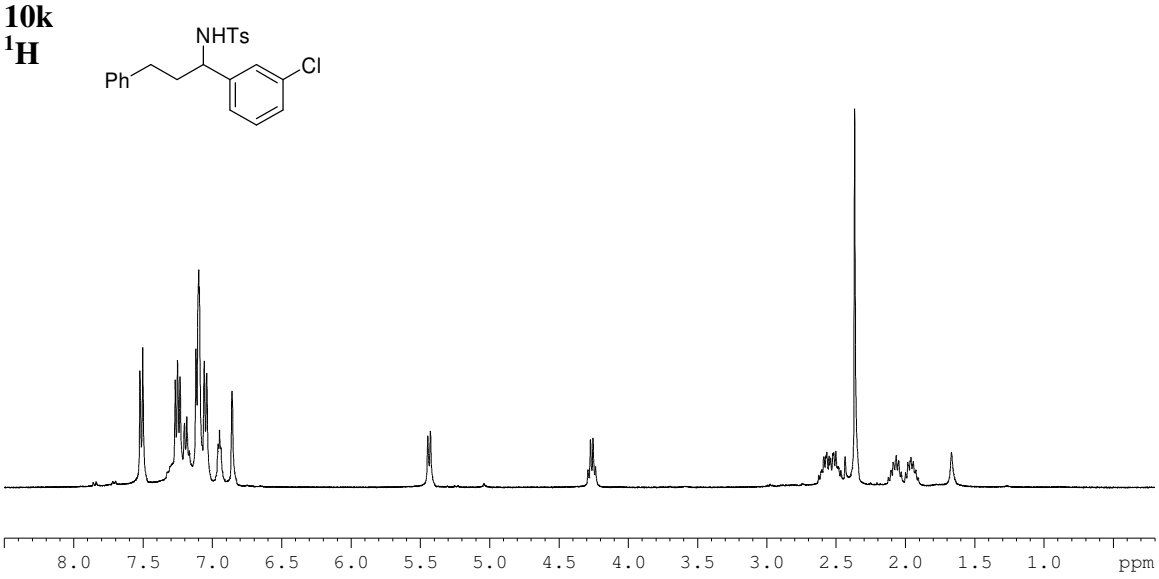

32 30 28 26 ppm


31 30 29 28 27 26 25

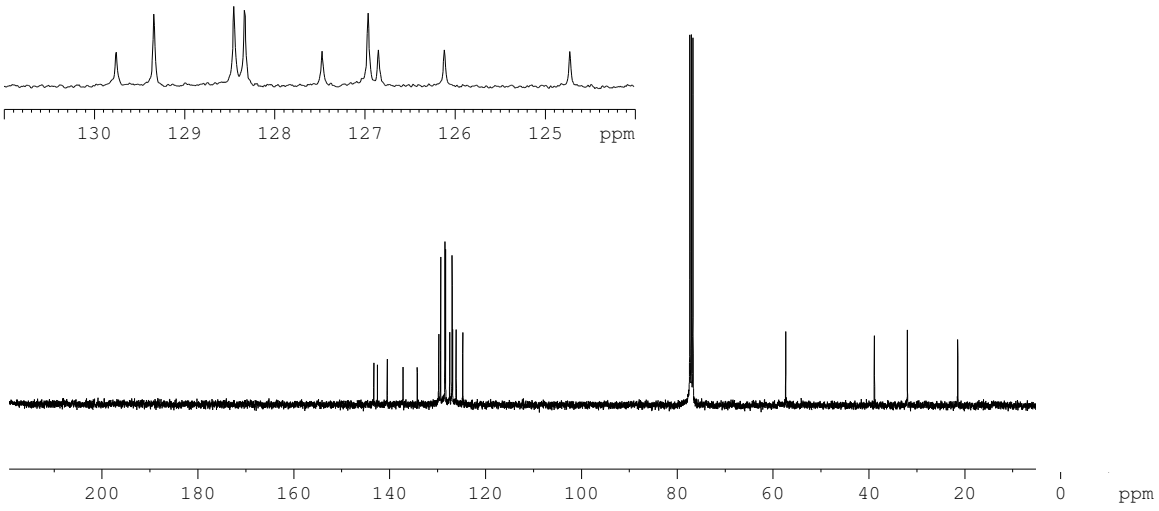

200 180 160 140 120 100 80 60 40 20 0 ppm

10k

^{1}H

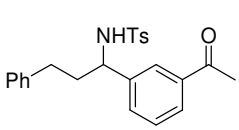

NHTs
Cl
Ph
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm

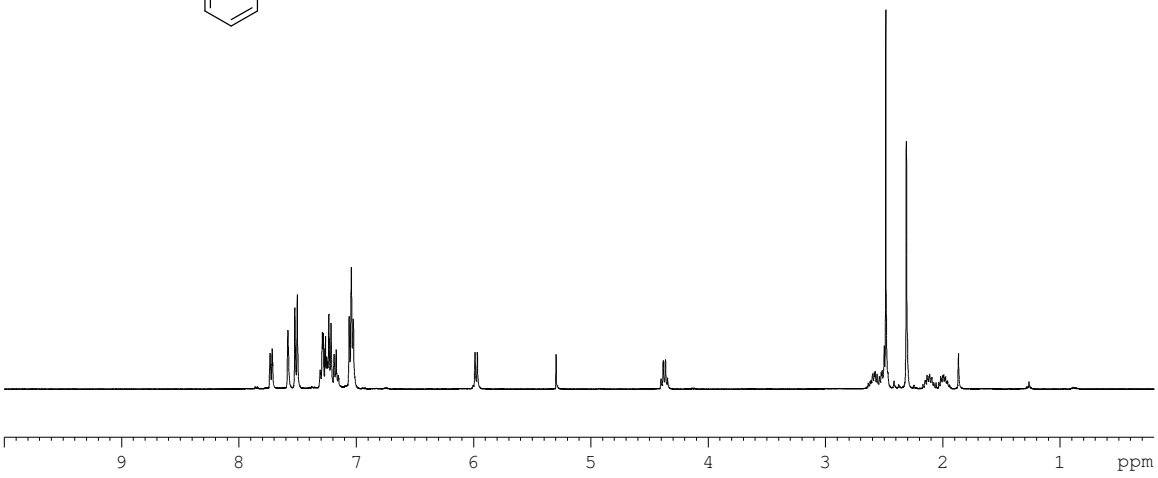
^{13}C


130 129 128 127 126 125 ppm
200 180 160 140 120 100 80 60 40 20 0 ppm

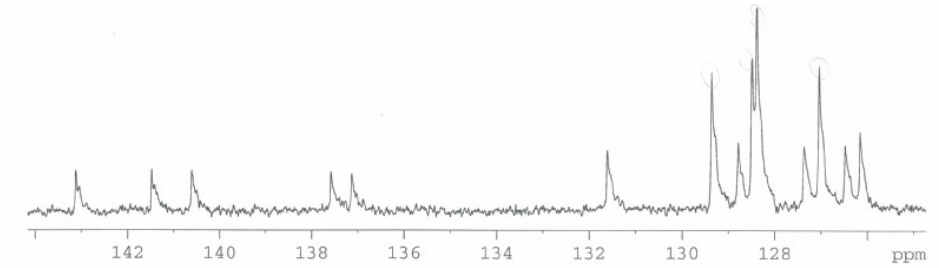
10l

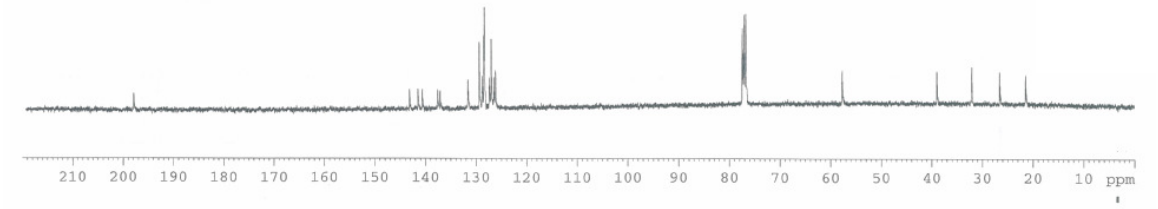
^{1}H


NHTs
O
Ph


9
8
7
6
5
4
3
2
1
ppm

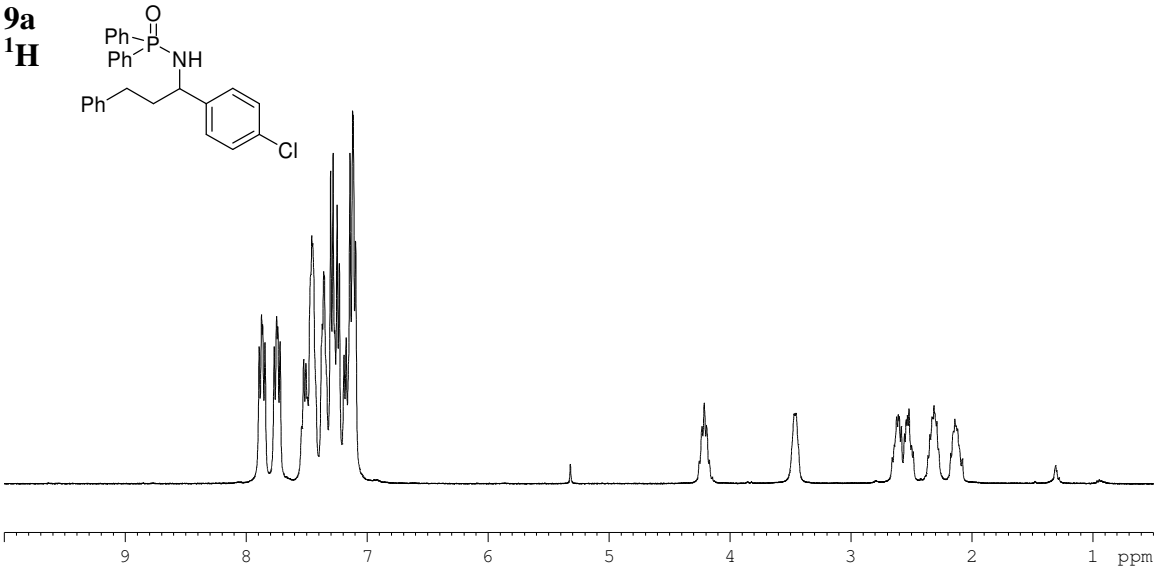
^{13}C


142
140
138
136
134
132
130
128
ppm

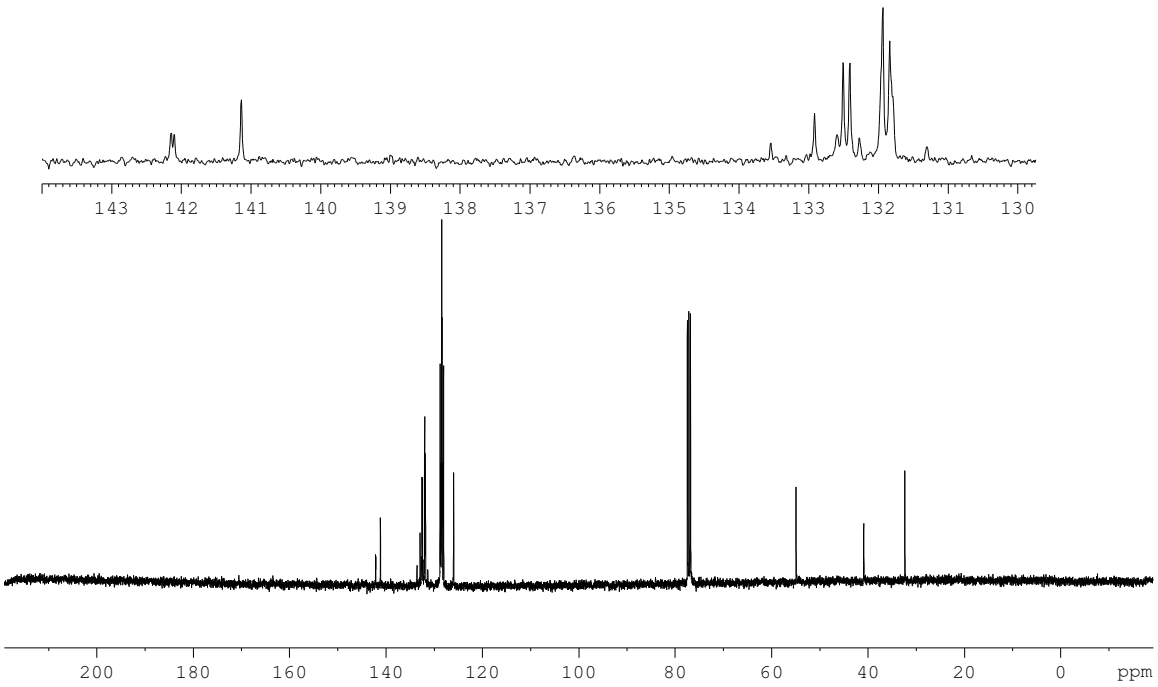

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

9a

^{1}H

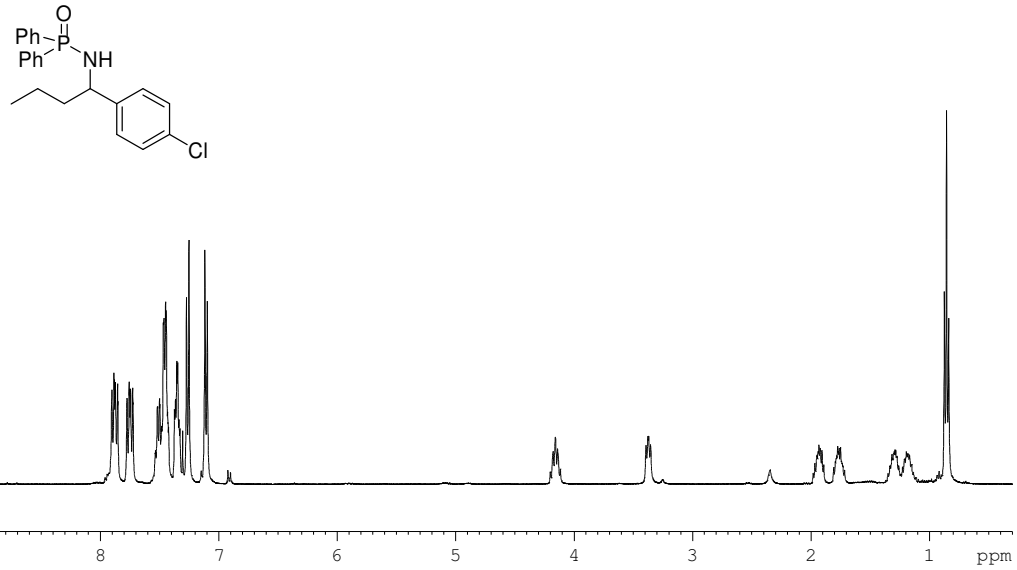

O
Ph
Ph
P
NH
Ph
Cl
9
8
7
6
5
4
3
2
1
ppm

^{13}C

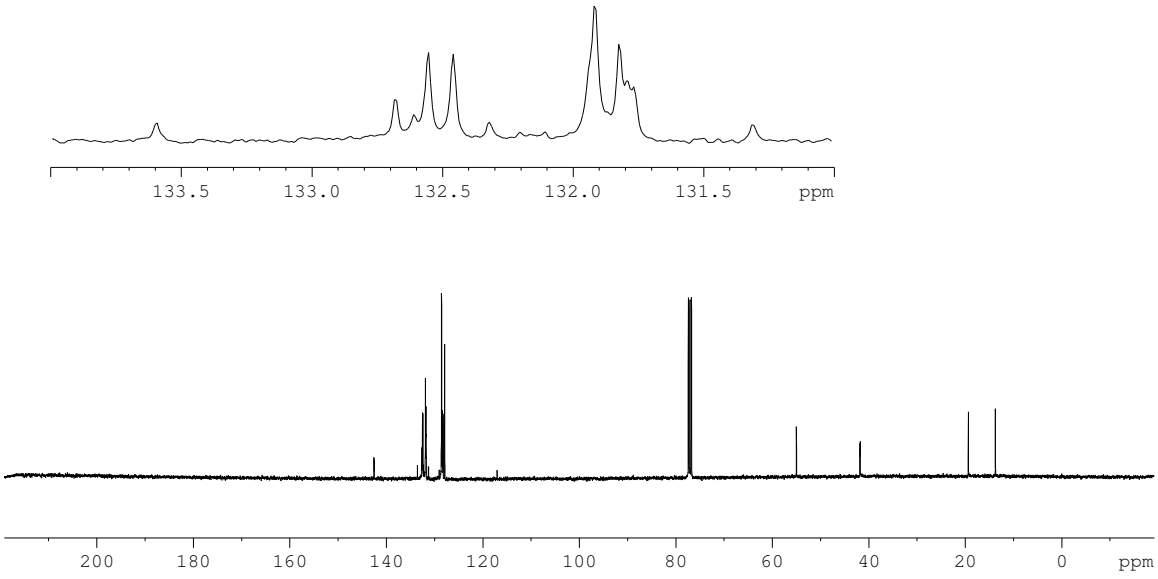

143
142
141
140
139
138
137
136
135
134
133
132
131
130
200
180
160
140
120
100
80
60
40
20
0
ppm

9b

^{1}H

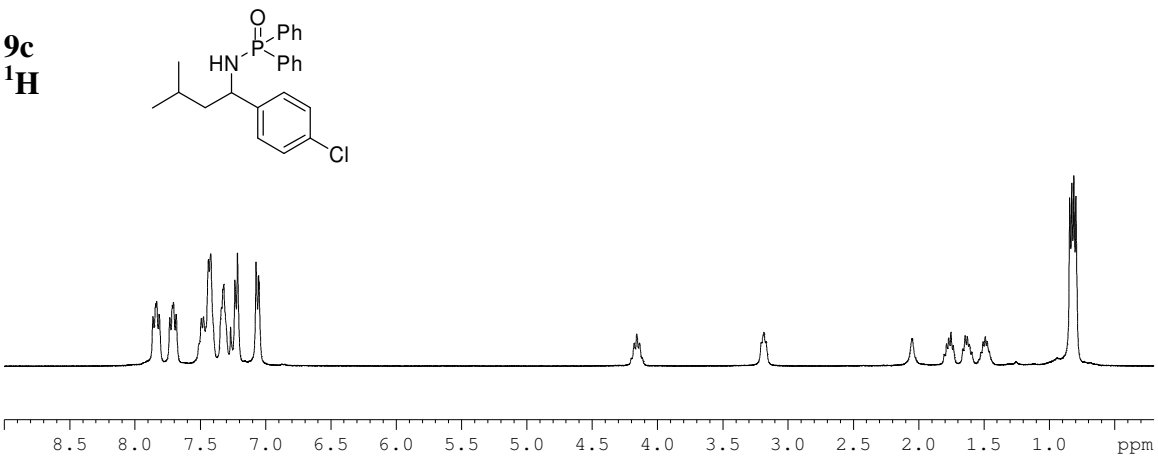

O
Ph
Ph
P
NH
Cl
9
8
7
6
5
4
3
2
1
ppm

^{13}C

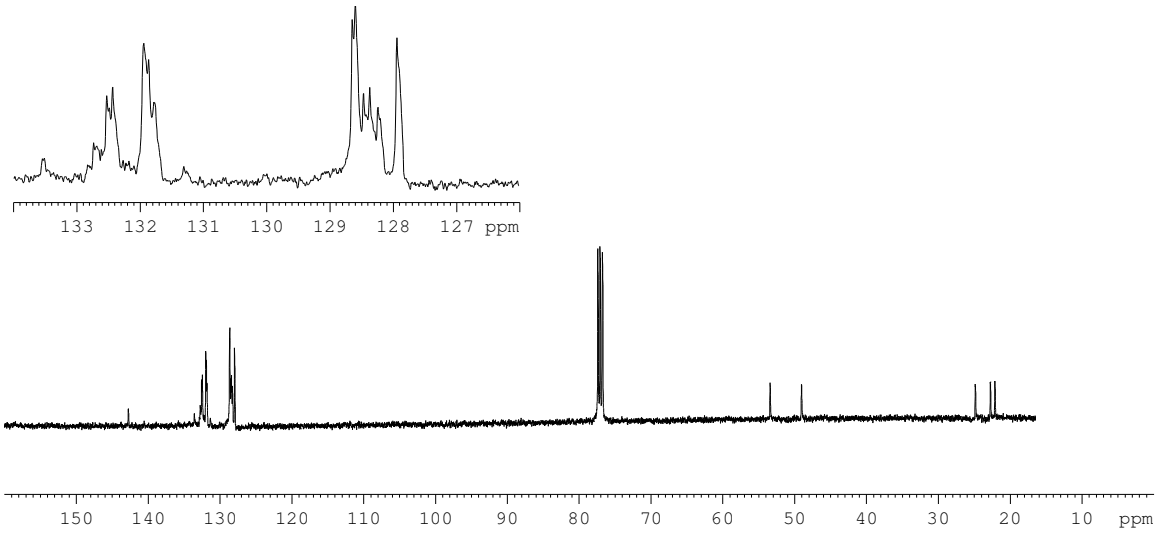

133.5
133.0
132.5
132.0
131.5
ppm
200
180
160
140
120
100
80
60
40
20
0
ppm

9c

^{1}H

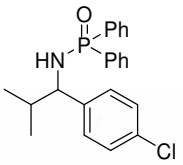

O
Ph
P
HN
Ph
Cl
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm

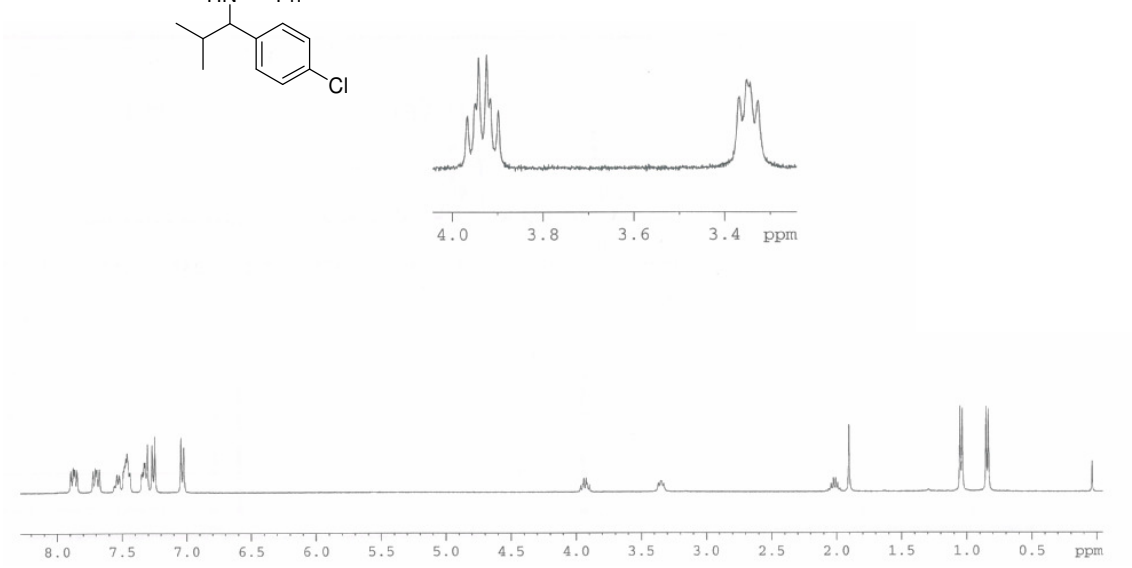
^{13}C


133 132 131 130 129 128 127 ppm
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

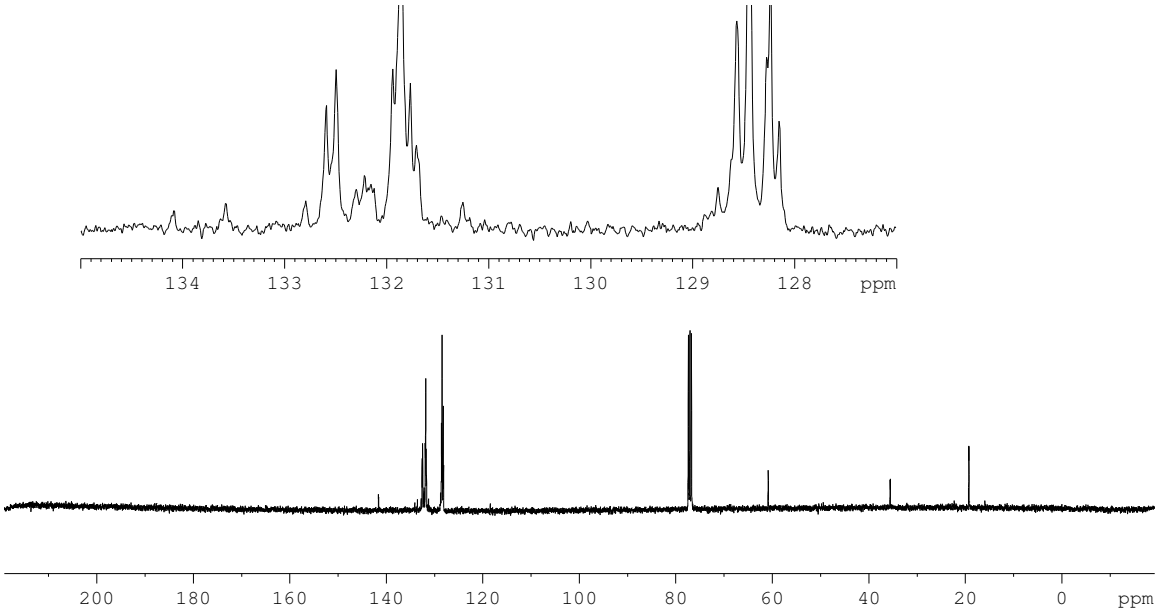
9d

^{1}H


O
Ph
HN
P
Ph
Cl

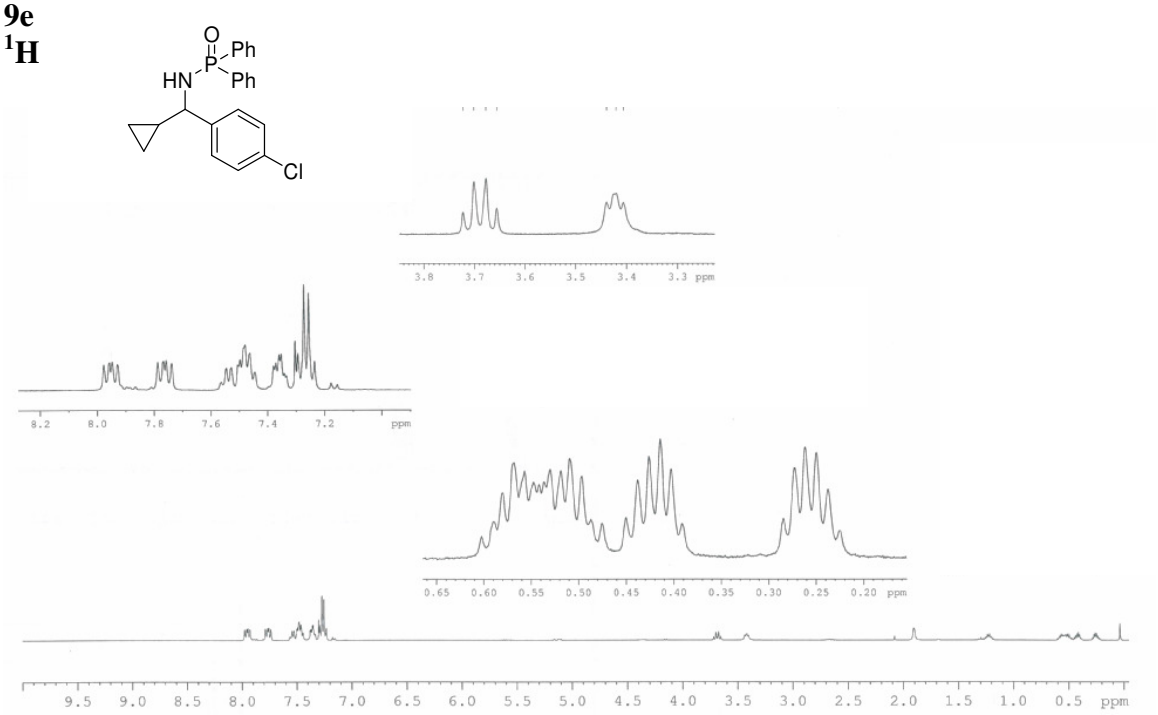

4.0
3.8
3.6
3.4
ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

^{13}C

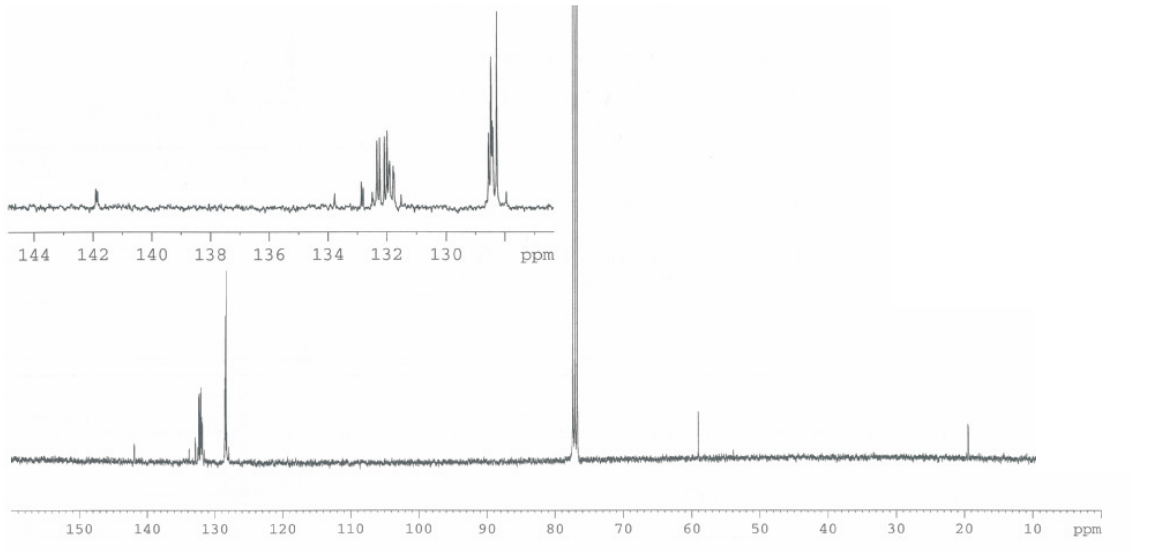

134
133
132
131
130
129
128
ppm
200
180
160
140
120
100
80
60
40
20
0
ppm

9e

^{1}H

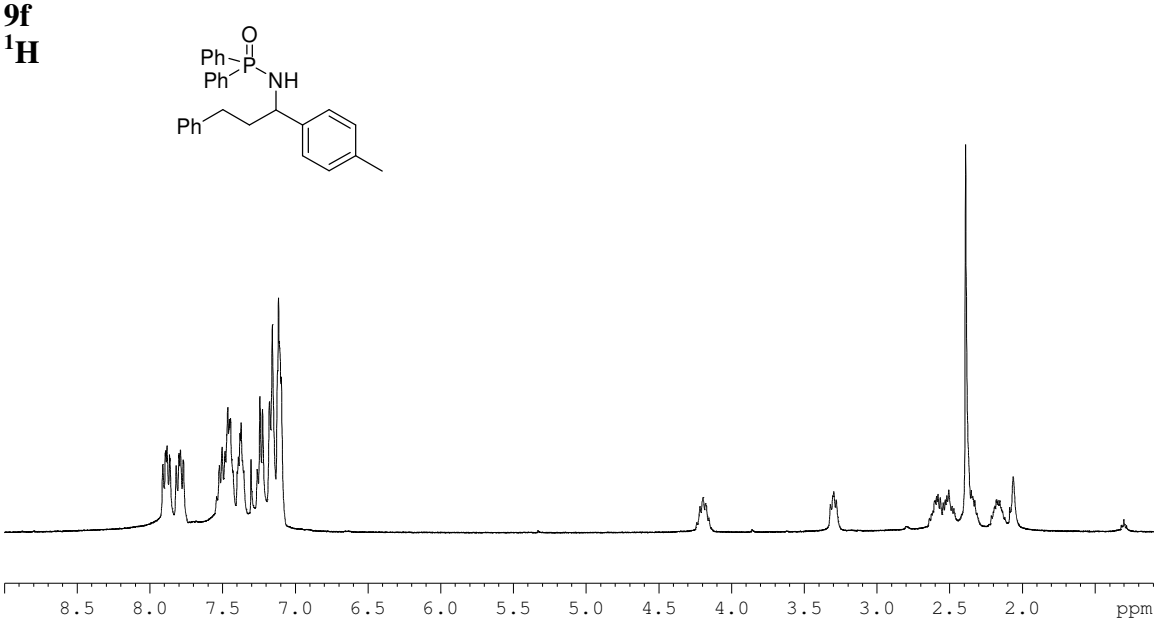

O
Ph
P
Ph
HN
Cl
3.8 3.7 3.6 3.5 3.4 3.3 ppm
8.2 8.0 7.8 7.6 7.4 7.2 ppm
0.65 0.60 0.55 0.50 0.45 0.40 0.35 0.30 0.25 0.20 ppm
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

^{13}C

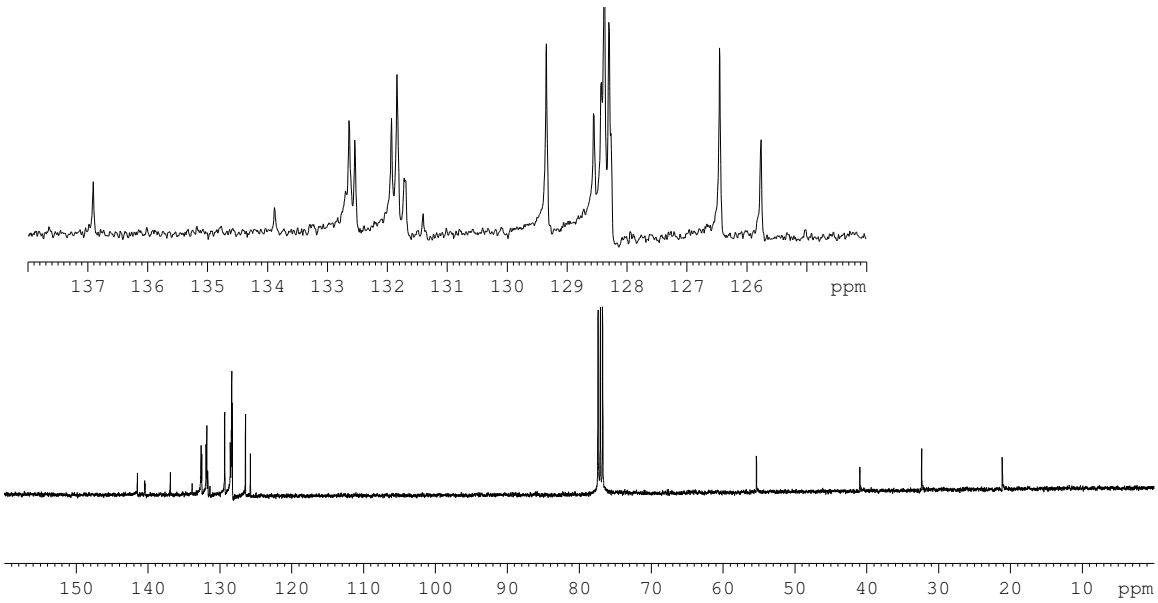

144 142 140 138 136 134 132 130 ppm
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

9f

^{1}H

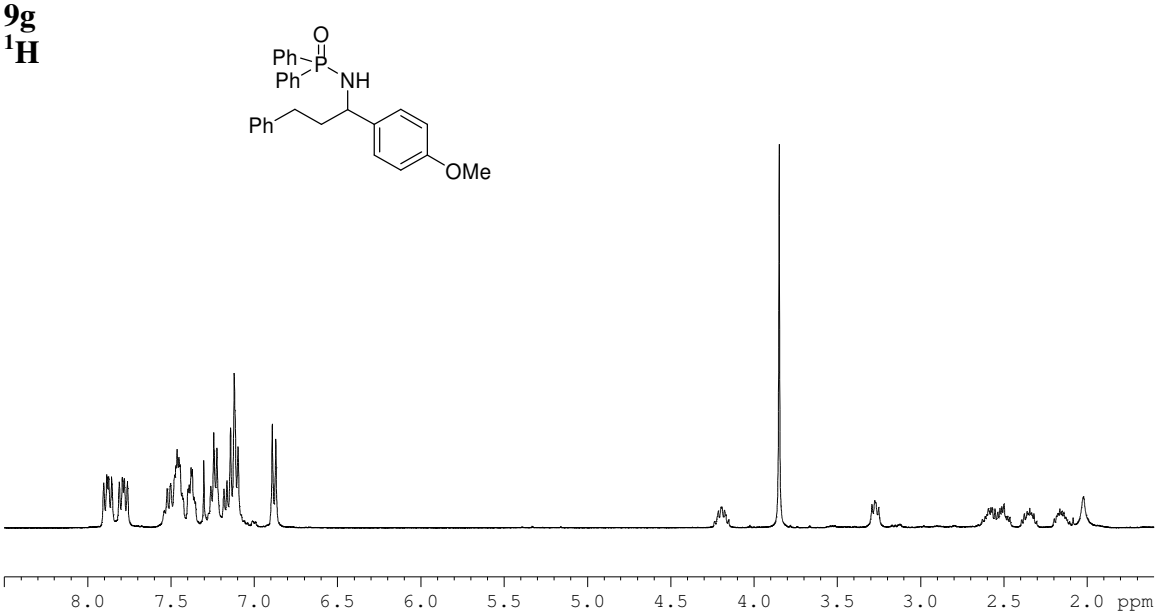

O
Ph
Ph
P
NH
Ph
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 ppm

^{13}C

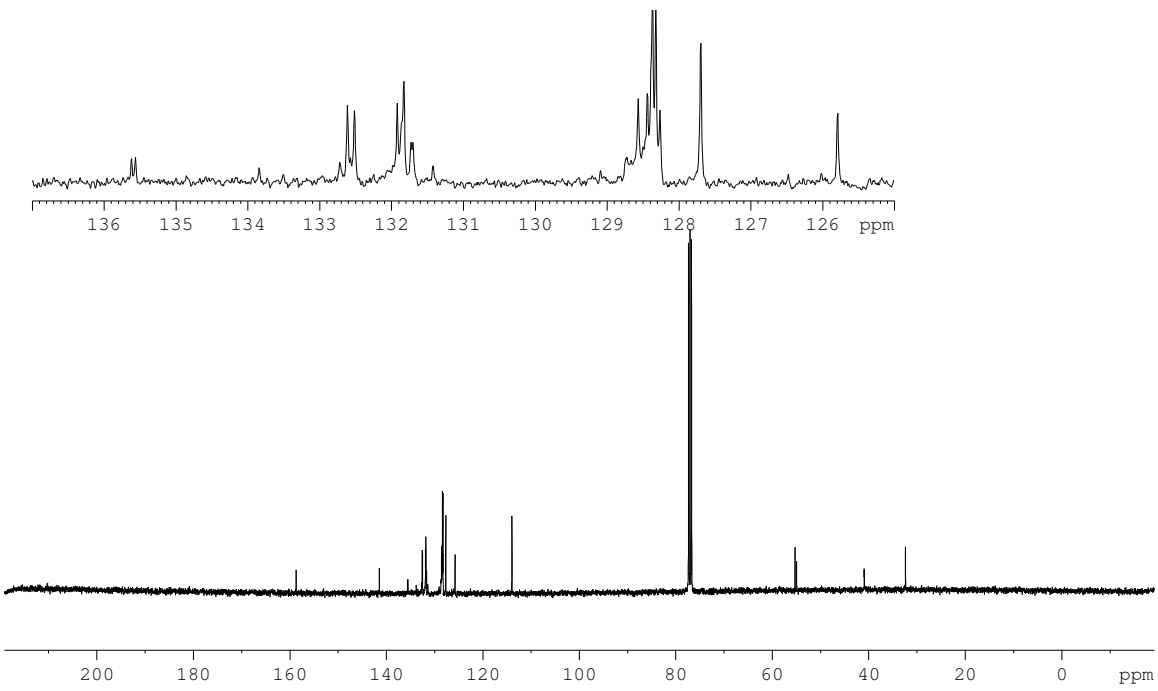

137 136 135 134 133 132 131 130 129 128 127 126 ppm
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

9g

^{1}H

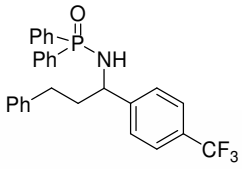

O
Ph
P
Ph
NH
Ph
OMe
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm

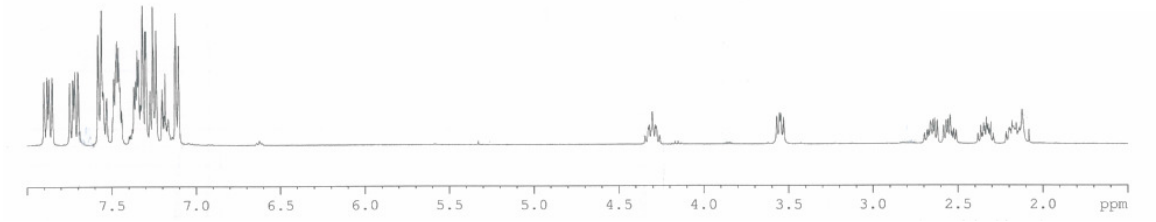
^{13}C


136
135
134
133
132
131
130
129
128
127
126
ppm
200
180
160
140
120
100
80
60
40
20
0
ppm

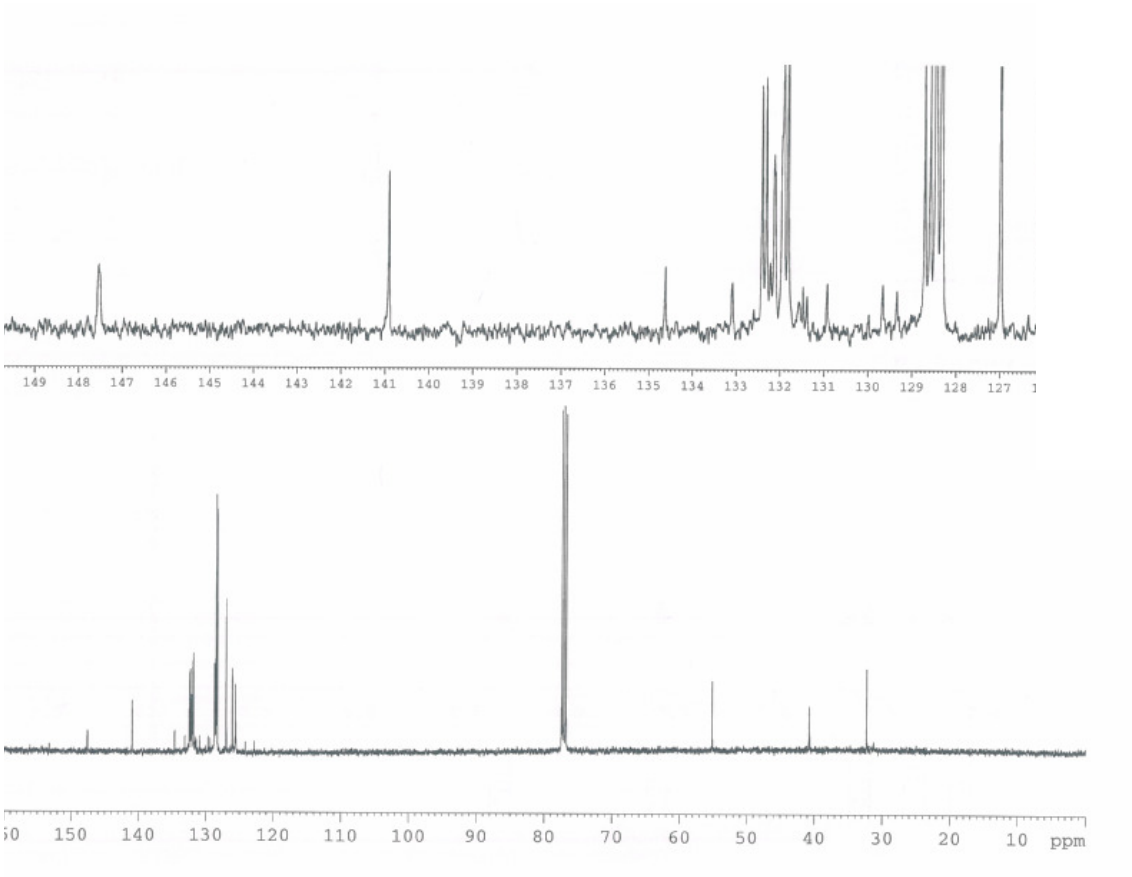
9h

^{1}H

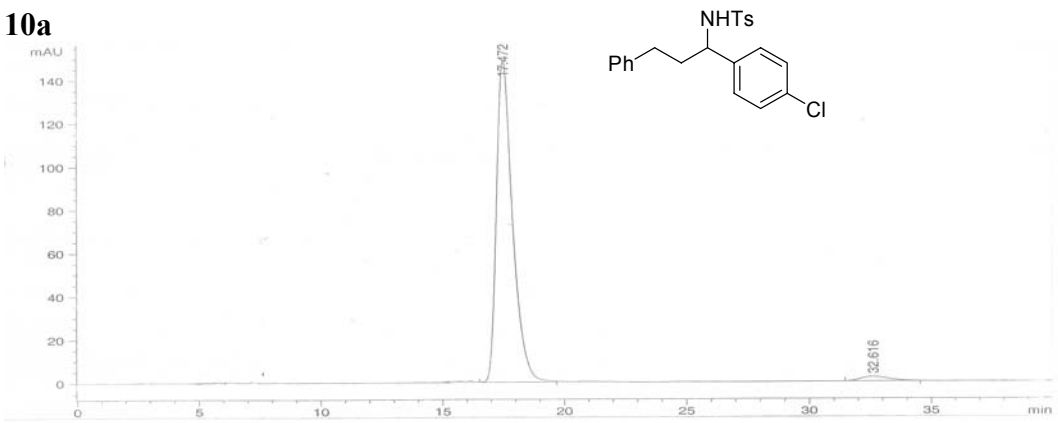

O
Ph
Ph
P
NH
Ph
CF3


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm

^{13}C


149 148 147 146 145 144 143 142 141 140 139 138 137 136 135 134 133 132 131 130 129 128 127
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

10a



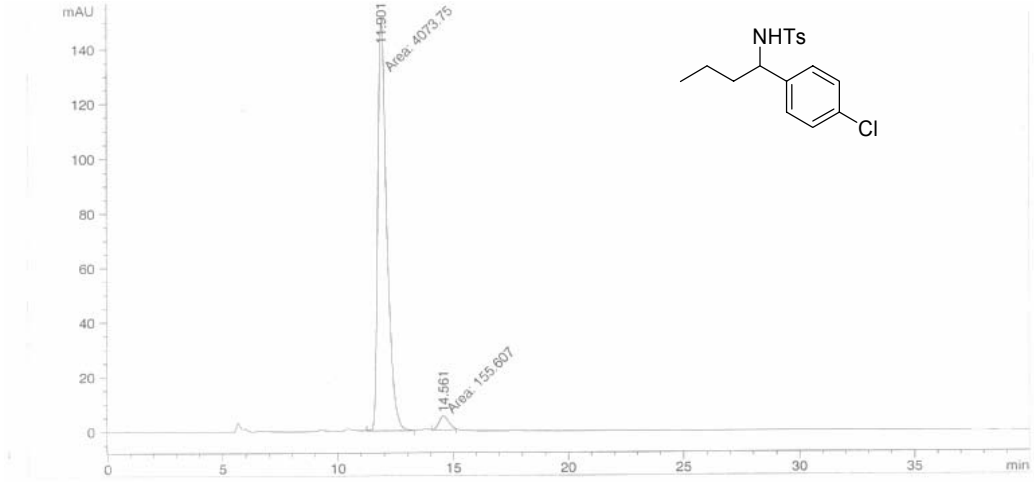
Area Percent Report

orted By : Signal
ultiplier : 1.0000
ilution : 1.0000
se Multiplier & Dilution Factor with ISTDs

ignal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.472	VB	0.6858	6822.37158	149.10960	97.4633
2	32.616	BB	1.0907	177.56927	2.09965	2.5367
Totals :				6999.94086	151.20926	

10b



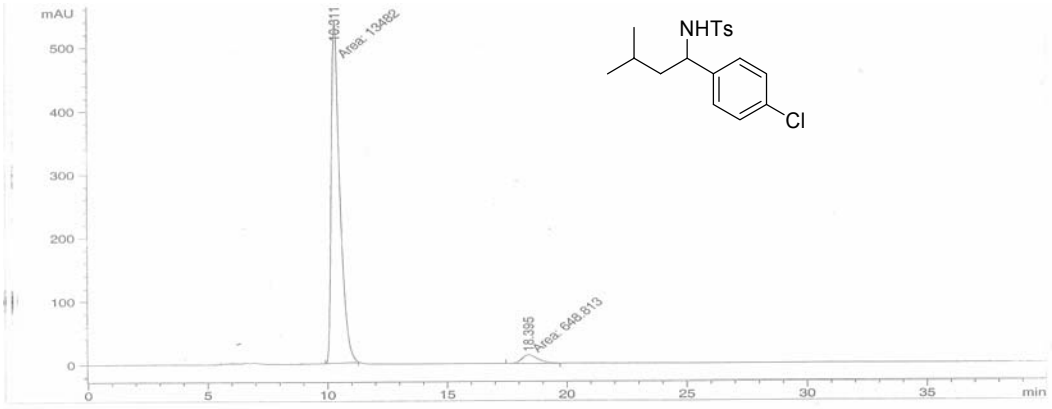
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: MWD1 D, Sig=230,16 Ref=360,100

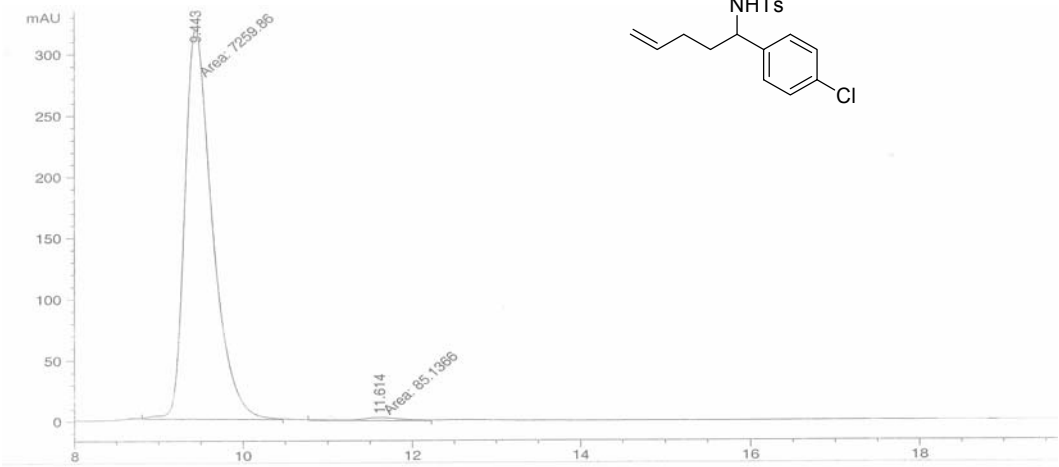
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.901	MM	0.4535	4073.75195	149.70436	96.3208
2	14.561	MM	0.5077	155.60712	5.10840	3.6792
Totals :				4229.35907	154.81276	

10c



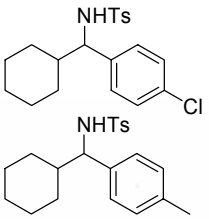

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area      Height      Area
  #   [min]       [min]   [mAU*s]      [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.311 MM    0.4190 1.34820e4   536.21442  95.4085
   2  18.395 MM    0.7953  648.81342   13.59645   4.5915

Totals :                  1.41308e4   549.81087
```

10d



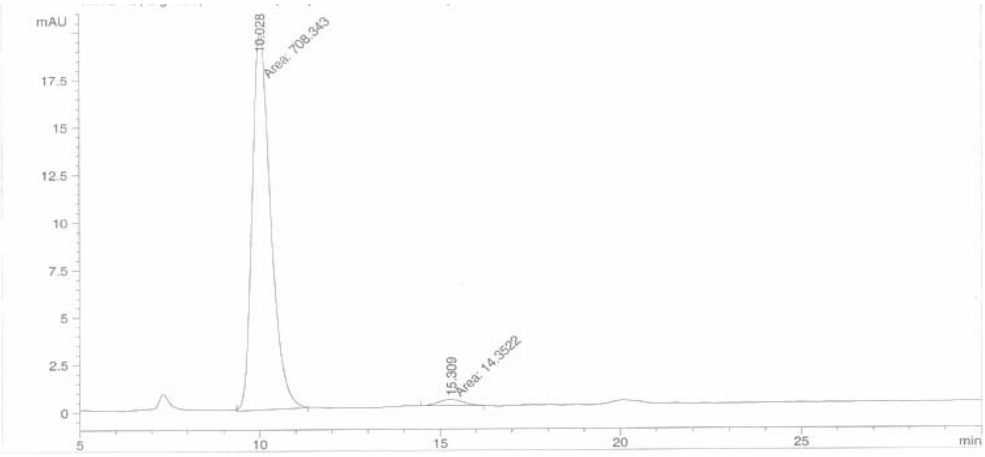

```
==========================================================================
                        Area Percent Report
==========================================================================

orted By              :      Signal
ultiplier             :      1.0000
ilution               :      1.0000
se Multiplier & Dilution Factor with ISTDs


ignal 1: MWD1 C, Sig=210,8 Ref=360,100

eak RetTime Type  Width     Area      Height      Area
  #   [min]       [min]   [mAU*s]      [mAU]       %
---|-------|----|-------|----------|----------|--------|
  1   9.443 MM    0.3802 7259.85596  318.25342  98.8409
  2  11.614 MM    0.5685   85.13660    2.49602   1.1591

otals :                   7344.99256  320.74944
```

10e



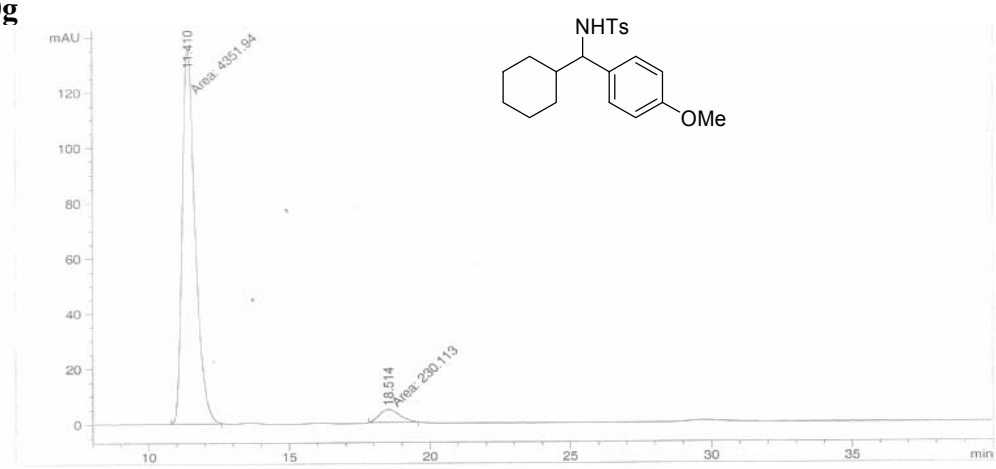

```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area      Height      Area
  #   [min]        [min]    [mAU*s]    [mAU]       %
----|-------|----|--------|----------|----------|--------|
   1  12.543 MM     0.7555 1243.84570   27.44007  97.9206
   2  19.743 MM     1.0421   26.41413 4.22433e-1   2.0794

Totals :                   1270.25983   27.86250
```

10f



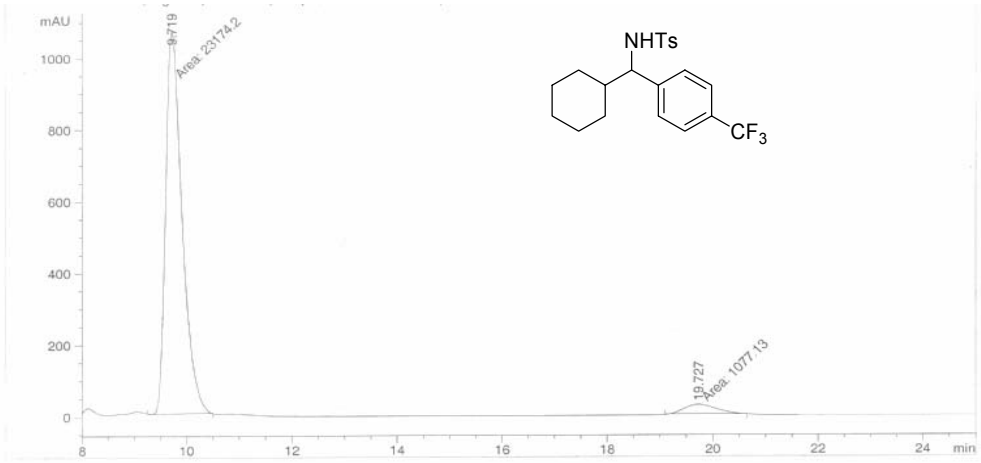

```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area      Height      Area
  #   [min]        [min]    [mAU*s]    [mAU]       %
----|-------|----|--------|----------|----------|--------|
   1  10.028 MM     0.5939  708.34302   19.87876  98.0141
   2  15.309 MM     0.7491   14.35216 3.19314e-1   1.9859

Totals :                   722.69518   20.19807
```

10g



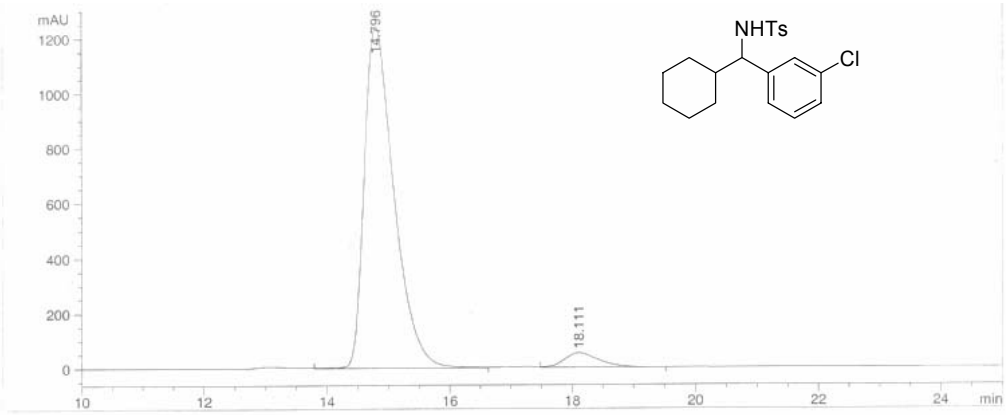

```
=====================================================================
                    Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.410 MM    0.5345 4351.93994  135.70813  94.9779
   2  18.514 MM    0.8305  230.11317    4.61798   5.0221

Totals :                  4582.05312  140.32611
```

10h



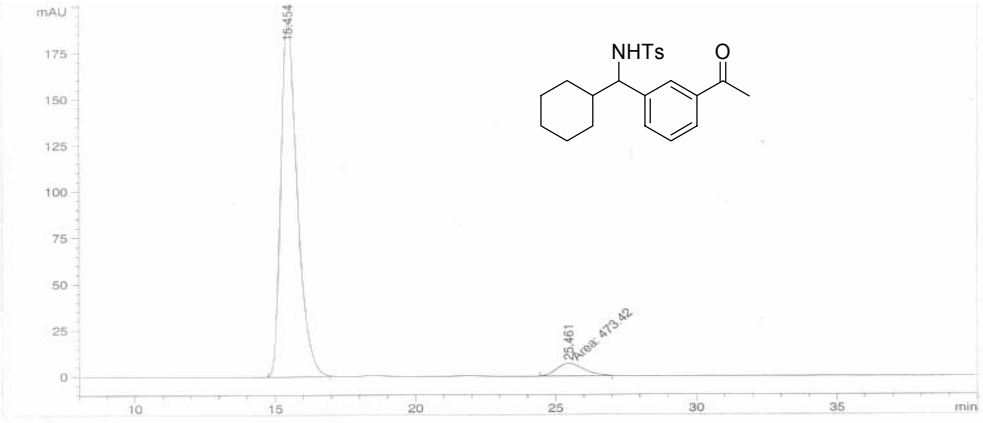

```
=====================================================================
                    Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.719 MM    0.3629 2.31742e4  1064.24548  95.5585
   2  19.727 MM    0.6791 1077.13159   26.43612   4.4415

Totals :                  2.42514e4  1090.68160
```

10i



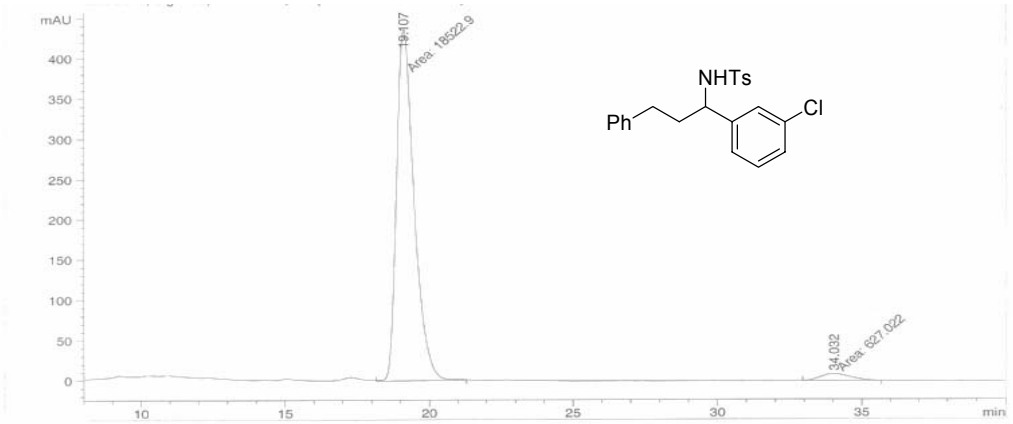

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]      %
----|-------|----|-------|----------|----------|--------|
   1  14.796 VV    0.5078 4.16516e4  1240.37769  95.1222
   2  18.111 VB    0.6038 2135.85352   53.26540   4.8778

Totals :                  4.37874e4  1293.64309
```

10j



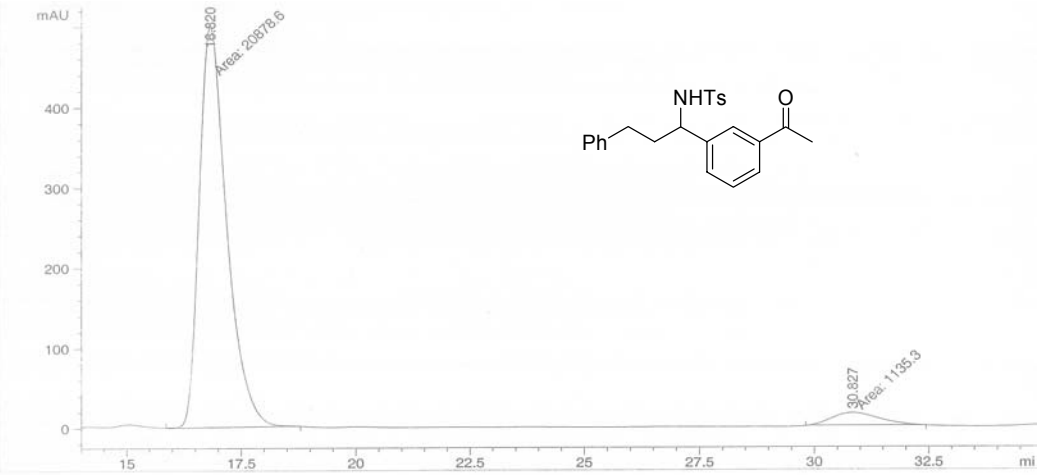

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]      %
----|-------|----|-------|----------|----------|--------|
   1  15.454 BB    0.6214 7857.95117  192.03940  94.3176
   2  25.461 MM    1.1332  473.41977    6.96293   5.6824

Totals :                  8331.37094  199.00233
```

10k



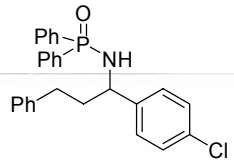

```
=====================================================================
                    Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  19.107 MM    0.7078 1.85229e4   436.17819  96.7257
   2  34.032 MM    1.2384  627.02234    8.43858   3.2743

Totals :                  1.91499e4   444.61677
```

10l




```
=====================================================================
                    Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.820 MM    0.6968 2.08786e4   499.36090  94.8428
   2  30.827 MM    1.1962 1135.29797   15.81770   5.1572

Totals :                  2.20139e4   515.17860
```

9a



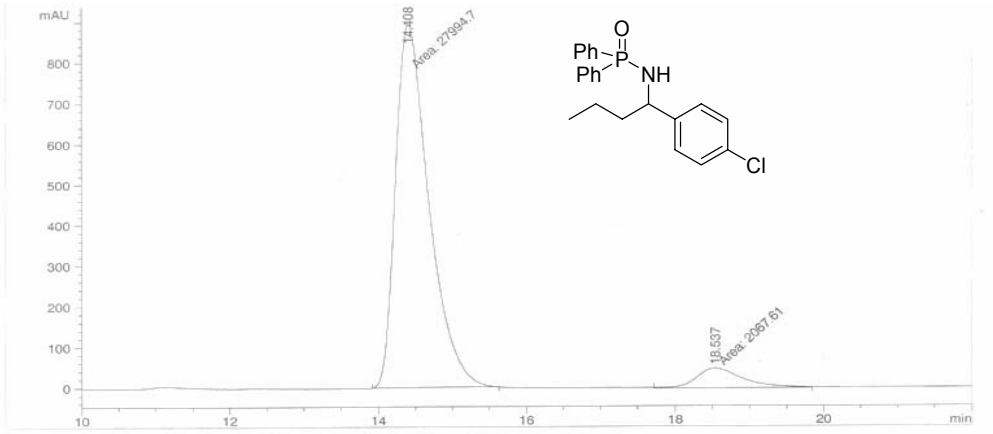
Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.850	MF	0.9137	4382.16016	79.93278	94.7905
2	20.928	FM	1.2464	240.83580	3.22050	5.2095
Totals :				4622.99596	83.15328	

Signal 2: MWD1 B, Sig=254,16 Ref=360,100

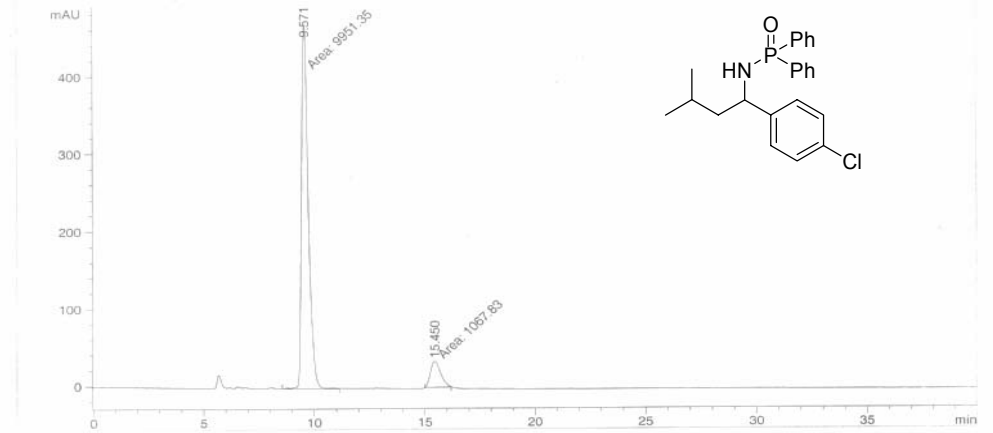
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.854	MM	0.8968	294.16290	5.46691	94.8482
2	21.001	MM	0.9286	15.97789	2.86766e-1	5.1518
Totals :				310.14080	5.75367	

9b



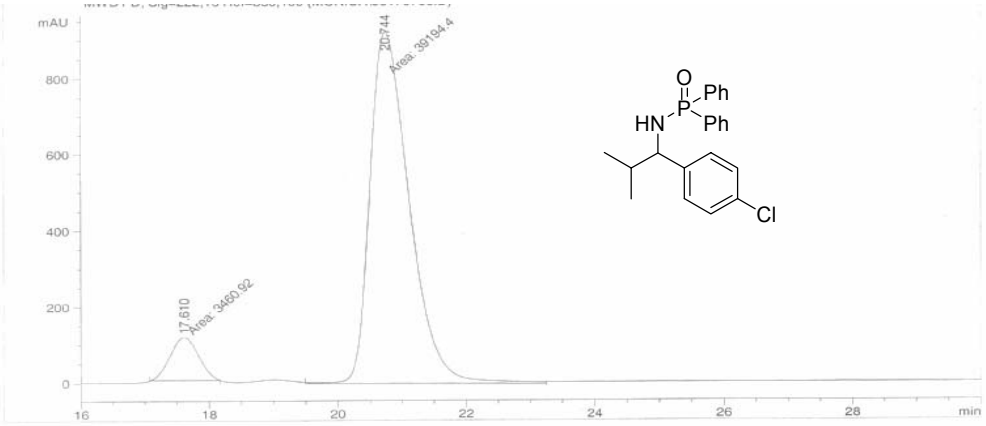

```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area      Height      Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  14.408 MM    0.5226 2.79947e4   892.86774  93.1222
   2  18.537 MM    0.7076 2067.61182   48.70267   6.8778

Totals :                  3.00623e4   941.57040
```

9c



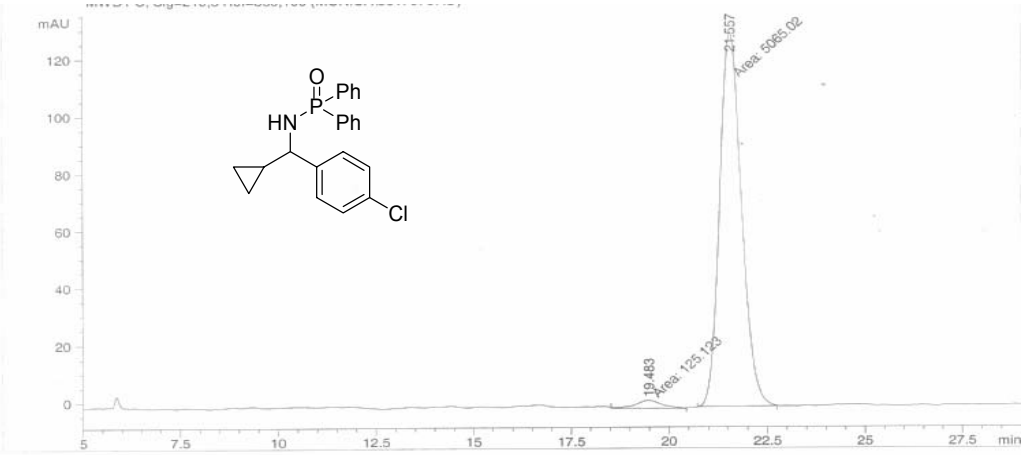

```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area      Height      Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.571 MM    0.3525 9951.35352  470.49469  90.3094
   2  15.450 MM    0.5330 1067.82703   33.39040   9.6906

Totals :                  1.10192e4   503.88509
```

9d



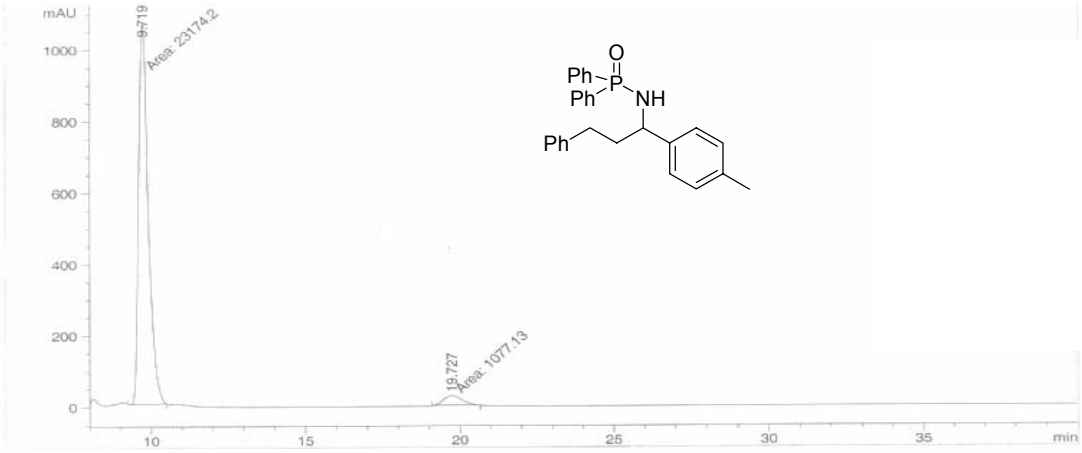

```
=====================================================================
                    Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 D, Sig=222,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]   [mAU*s]      [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.610 MM    0.5099 3460.92041  113.13480   8.1137
   2  20.744 MM    0.7076 3.91944e4   923.11694  91.8863

Totals :                  4.26554e4  1036.25174
```

9e



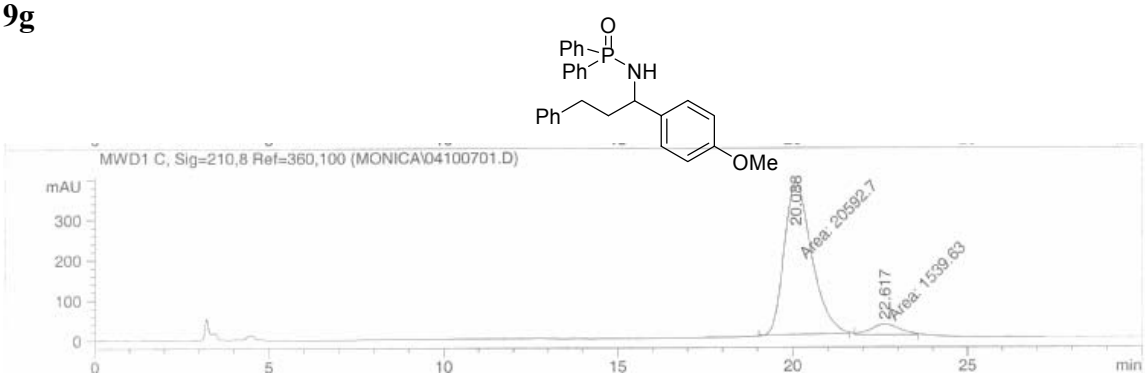

```
=====================================================================
                    Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]   [mAU*s]      [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  19.483 MM    0.7622  125.12321    2.73602   2.4108
   2  21.557 MM    0.6444 5065.02148  131.00134  97.5892

Totals :                  5190.14470  133.73736
```

9f



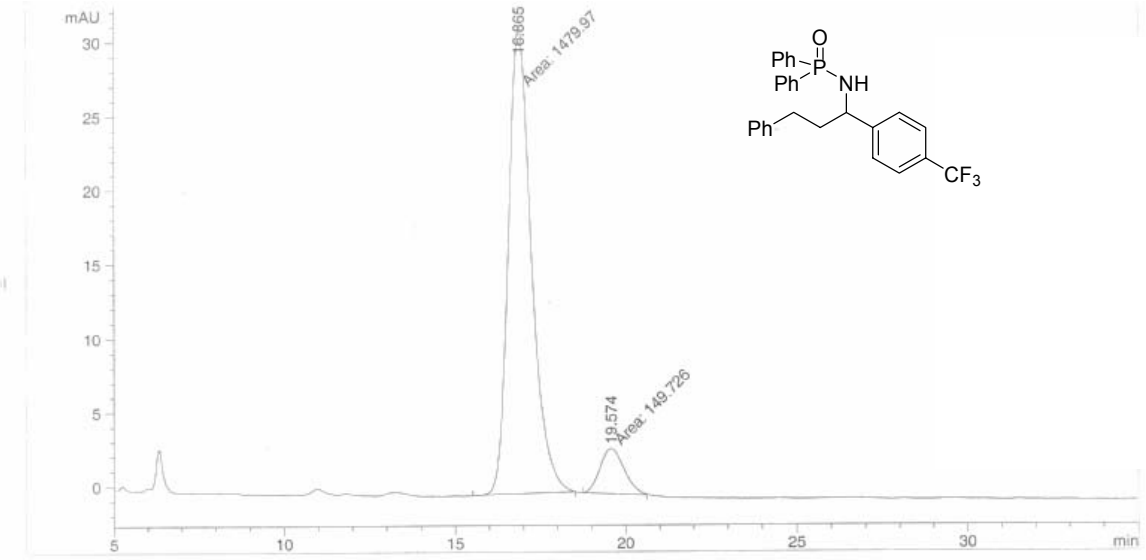

```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]      %
----|-------|----|-------|----------|----------|--------|
   1   9.719 MM    0.3629 2.31742e4  1064.24548  95.5585
   2  19.727 MM    0.6791 1077.13159   26.43612   4.4415

Totals :                  2.42514e4  1090.68160
```

9g




```
Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]      %
----|-------|----|-------|----------|----------|--------|
   1  20.088 MM    0.9089 2.05927e4   377.60992  93.0435
   2  22.617 MM    0.9724 1539.63428   26.38808   6.9565

Totals :                  2.21323e4   403.99801
```

9h




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.865 MM    0.7873 1479.97034   31.32814  90.8126
   2  19.574 MM    0.8181  149.72626    3.05014   9.1874

Totals :                  1629.69659   34.37828
```