Supporting Information

Copper-Catalyzed Asymmetric Allylic C-H Amination of Alkenes using *N*-arylhydroxylamines

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1. General Information

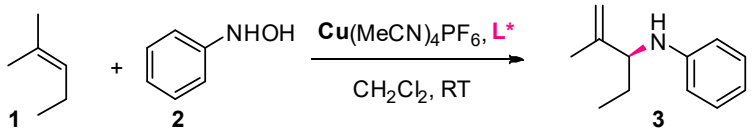
All reactions were performed in an atmosphere of argon using standard Schlenk tube or glovebox techniques. Reagent grade solvents were freshly distilled over appropriate drying reagents and stored over activated (250 °C) 4 Å molecular sieves in a Schlenk flask under argon. All organic substrates were received from commercial sources and were used without further purification. Arylhydroxylamines were prepared by following literature methods.[1] Column chromatography was performed on silica gel (60-120 mesh size), and thin layer chromatography was performed on aluminum plates pre-coated with silica gel 60 F_{254} (0.25 mm). The ^{1}H and ^{13}C NMR spectra were recorded on a Varian 400 MHz and JEOL 400 MHz FT-NMR spectrometers, and the data are reported in parts per million (ppm) relative to TMS, with the residual solvent peak as an internal reference. Multiplicities are reported as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad; coupling constant(s) in Hz. Mass spectra were recorded from Agilent GC-MS (7890A-5975CVL MSD) spectrometer. Enantioselectivity was measured by GC (HP 5890 series II) Astec Chiraldex columns and HPLC (Agilent 1100 series) using and Chiralcel columns respectively. Optical activity was measured on Autopol III polarimeter. High resolution mass spectra (HRMS) were obtained at Louisiana State University.

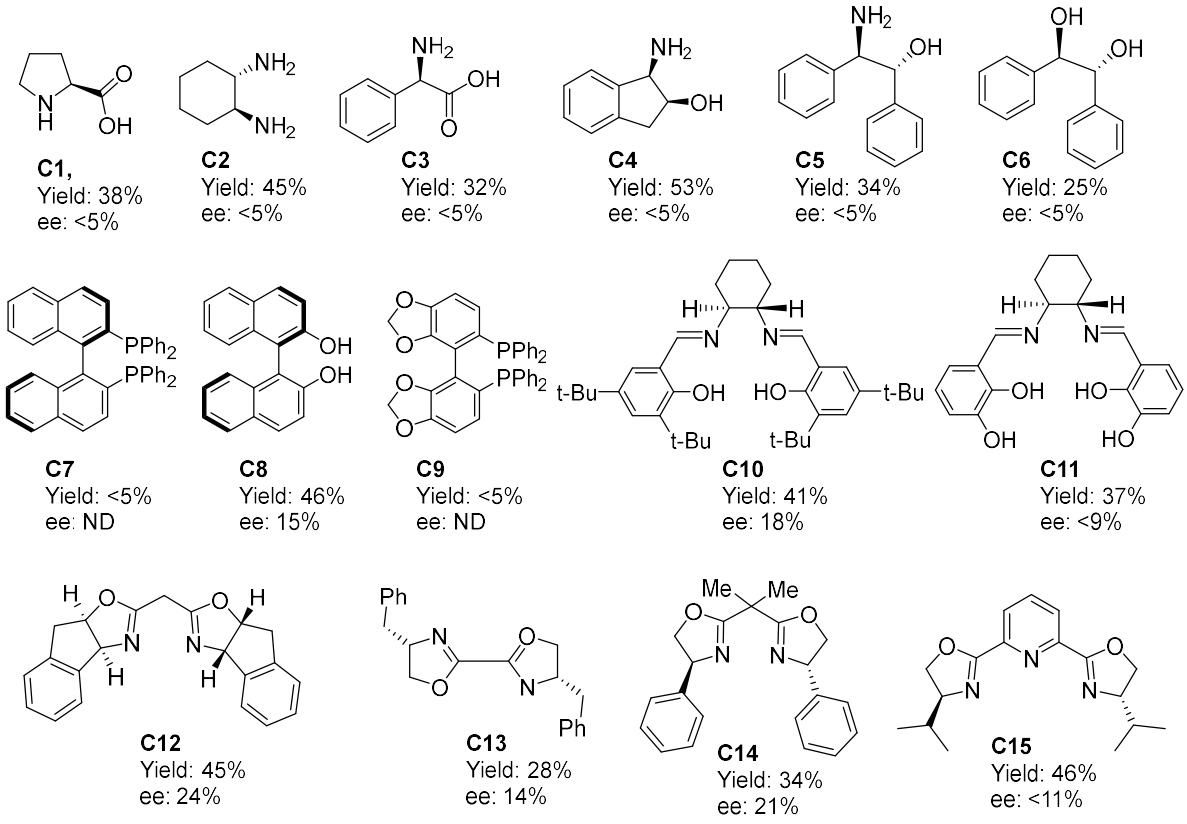
The diffraction data were collected at low temperature on a Nonius Kappa CCD equipped with Mo Kα (λ=0.71073 Å) and a Bruker Kappa Apex II equipped with Cu (λ=1.54178 Å) radiation source diffractometer, a graphite monochromator, and an Oxford Cryostream low-temperature device. Absorption collections were made by the multi-scan method.

2. General Procedure for the Cu-Catalyzed Asymmetric Allylic C-H Amination of Simple Alkenes:

A Schlenk flask was charged with $Cu(MeCN)_4PF_6$ (10 mol %), R-(+)-BINAM (12 mol %) and CH_2Cl_2 (2 mL). The flask was placed in an oil bath preset at 25 °C and stirred for 0.5 h. An alkene (0.5 mmol) was added and then a solution of arylhydroxylamine (1.5 mmol) in CH_2Cl_2 (4 mL) was added slowly with the help of a syringe pump over a period of 4 h under a positive pressure of nitrogen. The reaction was allowed to continue for a further 2-4 h to ensure complete consumption of the arylhydroxylamine. The reaction mixture was filtered through a short celite bed by eluting with CH_2Cl_2 (10 mL), and the filtrate was analyzed by GC-MS. Analytically pure product was isolated by column chromatography on silica gel (230-460 mesh, hexanes/EtOAc). The product was completely characterized by NMR and MS spectroscopic methods and further chiral HPLC is used to measure the enantioselectivity.

3. Chiral ligand screening data toward the catalytic synthesis of chiral *N*-aryl allylamines:

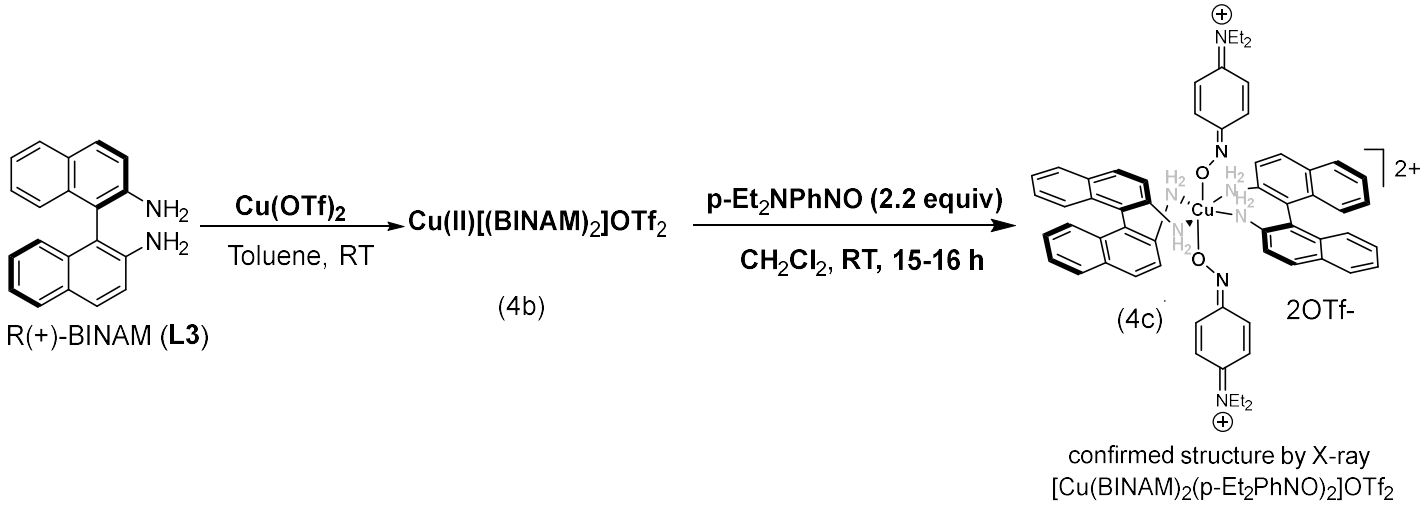




[a] % yields measured by GC-MS [b] %ee measured by chiral GC [c] 1:1.2 metal-Ligand ratio

4. Synthesis, Isolation and Characterization of $Cu^{II}OTf_2$-R(+)BINAM (4b) and $Cu^{II}OTf_2$-R(+)BINAM-pEt2PhNO (4c) complexes:

To the mixture of [$Cu(OTf)_2$] (0.635 g, 1.76 mmol) and R(+)-BINAM ligand (1.0 g, 3.52 mmol), toluene (10 mL) was added and continued stirring at room temperature for 6 hours. Solvent was removed under vacuum and the crude product which was directly re-crystallized from ethylacetate:hexane mixture(5:1) to obtain pure [$Cu(BINAM)_2$]OTf_2 complex **4b** (1.28 g, 78% yield).



Scheme S1. Synthesis of Cu-BINAM-Nitroso complex

The Cu-complex (1.28 g, 1.37 mmol) obtained above was dissolved in dichloromethane (10 mL) and added *N,N*-diethyl-4-nitrosoaniline (0.40 g, 2.2 mmol). The dark brown solution becomes dark green immediately. After stirring overnight (15 h), the dark green solution was filtered, and the solvent was removed on rotavap. The solid residue was triturated with diethyl ether (10 mL x 2). Recrystallization from CH_2Cl_2/hexane at -20 °C provided dark greenish crystals suitable for X-ray diffraction. The crystal structures of **4b** and **4c** are shown in Figure S1 and Figure S2 respectively. The molecular structure of 4b is similar to the one reported earlier with CCDC#677060.[2]

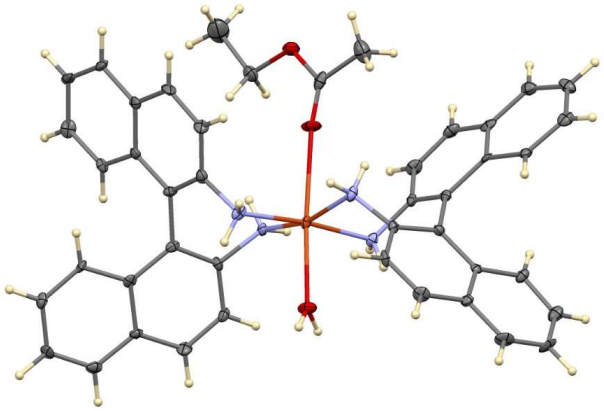


Figure S1. Single crystal X-ray structure of **4b**.

However, molecular structure of **4c** is completely novel and the details of X-ray data and structure determination can be found in the additional supplementary materials document. This crystal structure data has been deposited via the joint CCDC/FIZ Karlsruhe deposition service and the data has been assigned to CCDC#2047831.

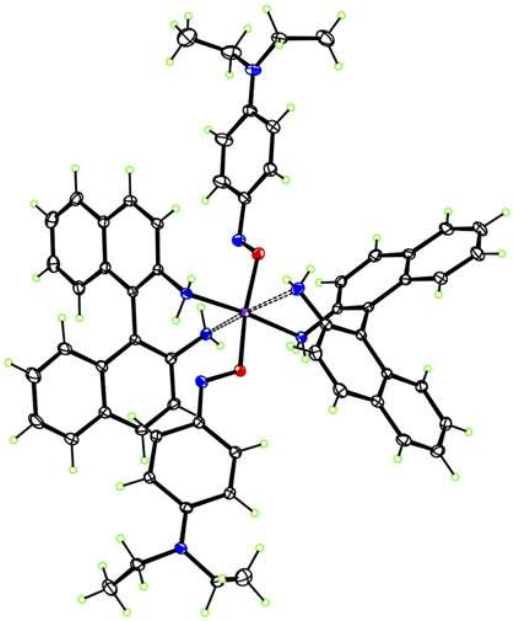
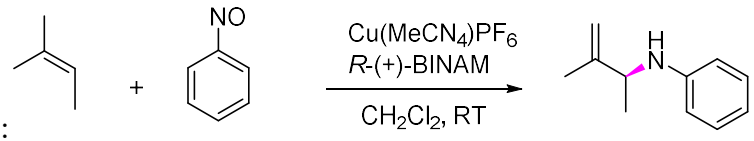


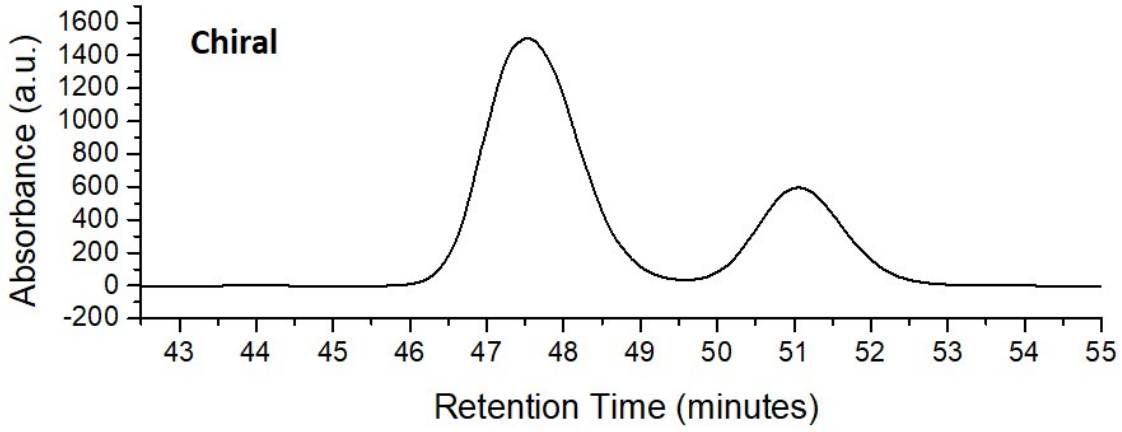
Figure S2. Single crystal X-ray structure of complex **4c**.

5. Control Experiment with Nitrosobenzene:

A dichloromethane (2.0 mL) solution of $Cu(MeCN)_4PF_6$ (19 mg, 10 mol %) and R-(+)-BINAM (28 mg, 20 mol %) was stirred at 25 °C for 0.5 h. 2-methylbut-2-ene (106 mg, 1.5 mmol) was added followed by the slow addition (4 h) of nitrosobenzene (54 mg, 0.5 mmol). The product was isolated by column chromatography and confirmed by both GC-MS and NMR. The racemic product was prepared in the same experimental conditions without the R-(+)-BINAM ligand. As shown below, the HPLC analysis of racemic and chiral products indicates 47% enantioselectivity.

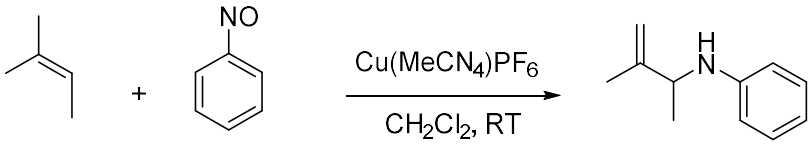
Chiral version:

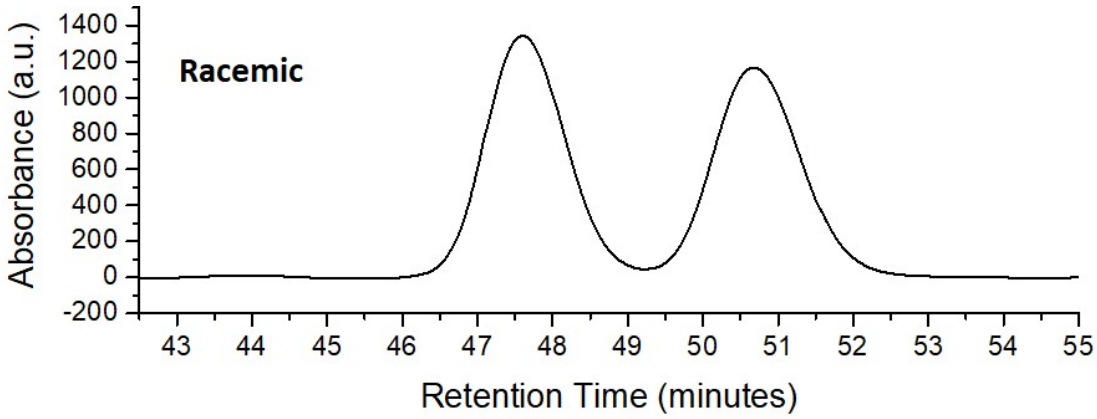




Peak #	RetTime Type [min]	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	47.525 MM	1.4465	1.29890e5	1496.63745	73.6036
2	51.068 MM	1.3431	4.65826e4	578.06775	26.3964
Totals :			1.76473e5	2074.70520	

Racemic version:

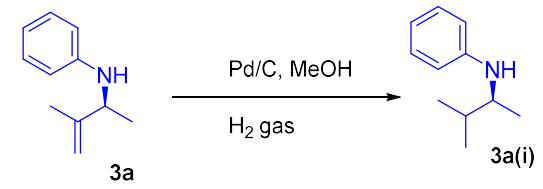




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	47.597	MM	1.2299	9.72091e4	1317.27100	51.2719
2	50.688	MM	1.3548	9.23860e4	1136.51746	48.7281
Totals :				1.89595e5	2453.78845	

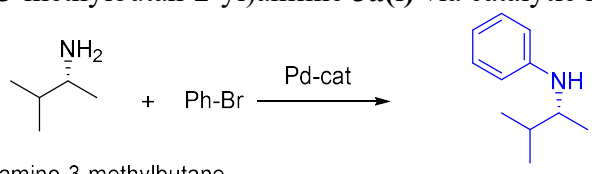
6. Determination of Absolute Configuration:

In order to determine the absolute configuration of major *N*-aryl allylamine enantiomer, we have synthesized chiral *N*-(3-methylbutan-2-yl)anilines **3a(i)** and **3a(ii)** using two alternate approaches (**Scheme S2** and **Scheme S3**) i.e. Pd-catalyzed hydrogenation and Pd-catalyzed *N*-arylation. The catalytic hydrogenation of allyl double bond of **3a** led to *N*-(3-methylbutan-2-yl)aniline **3a(i)**.[3] Alternatively, Buchwald-Hartwig amination (Pd-catalyzed *N*-arylation)[4] of commercially available chiral R(-)-amine produced the corresponding R(-)-*N*-(3-methylbutan-2-yl)aniline **3a(ii)** in good yield. Additionally, for the comparison purpose, we have synthesized racemic *N*-(3-methylbutan-2-yl)aniline **3a(iii)** via catalytic hydrogenation of racemic version of **3a** (**Scheme S4**).

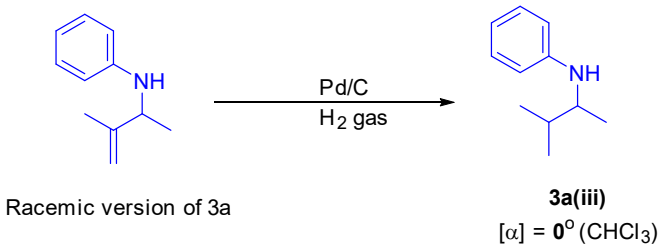


[α] = +11.5° ($CHCl_3$), ee = 53% [α] = +19.9° ($CHCl_3$), ee = 51.4%

Scheme S2. Synthesis of *N*-(3-methylbutan-2-yl)aniline **3a(i)** via catalytic hydrogenation



Scheme S3. Synthesis of *N*-(3-methylbutan-2-yl)aniline **3a(ii)** via Buchwald-Hartwig amination



Scheme S4. Synthesis of racemic *N*-(3-methylbutan-2-yl)aniline **3a(iii)** via catalytic hydrogenation

HPLC analysis and the optical activity data of **3a(iii)**, **3a(i)**, and **3a(ii)** are provided in the Figures **S3**, **S4** and **S5**. The structure of **3a(iii)** was confirmed by GC-MS and ^{1}H-NMR (Figure **S6**) analysis**.** In comparison to the racemic mixture (Figure **S4**), the major enantiomer from the scheme S2 is on the right whereas the major enantiomer from scheme **S3** is on the left. This observation clearly indicates that the absolute configuration of the major enantiomer {**3a(i)**} obtained from Cu-catalyzed asymmetric allylic amination is exactly opposite to the R(-)-*N*-(3-methylbutan-2-yl)aniline **3a(ii)** which confirms the stereochemistry of **3a(i)** as S(+)-*N*-(3-methylbutan-2-yl)aniline. In addition to that, optical activity data comparison of **3a(i)** and **3a(ii)** supports the absolute configuration assignment. Accordingly, we assigned "S" configuration to all the products obtained from our Cu-catalyzed asymmetric allylic amination.

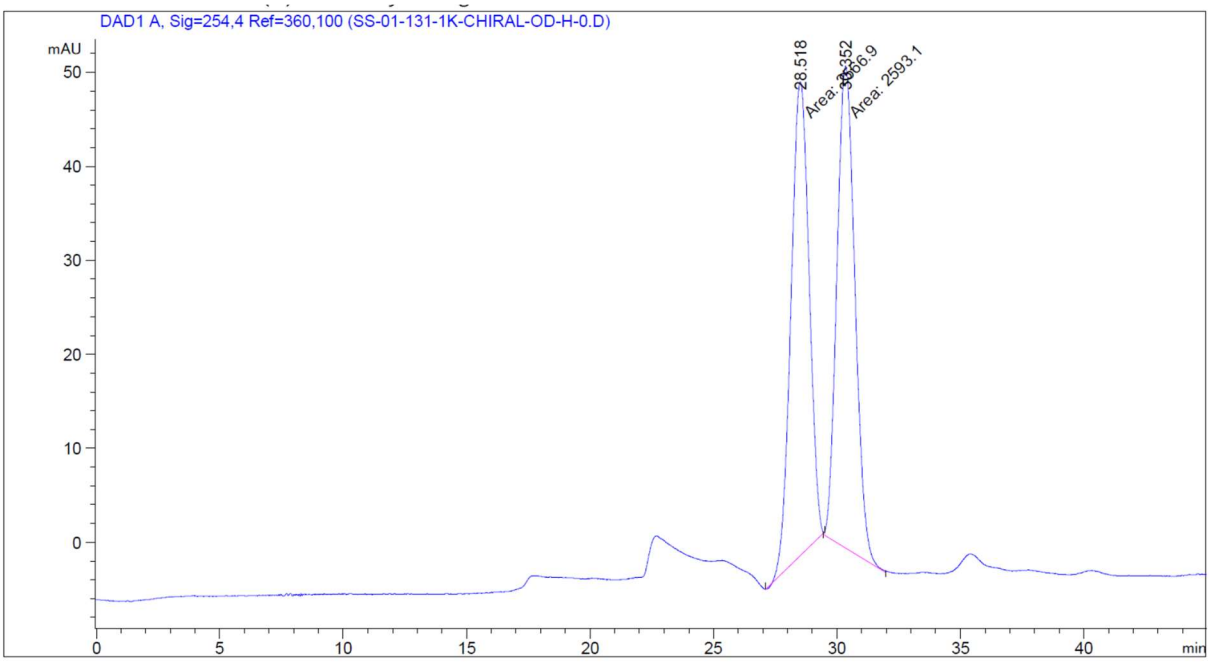


Figure S3. HPLC analysis of racemic *N*-(3-methylbutan-2-yl)aniline **3a(iii)**

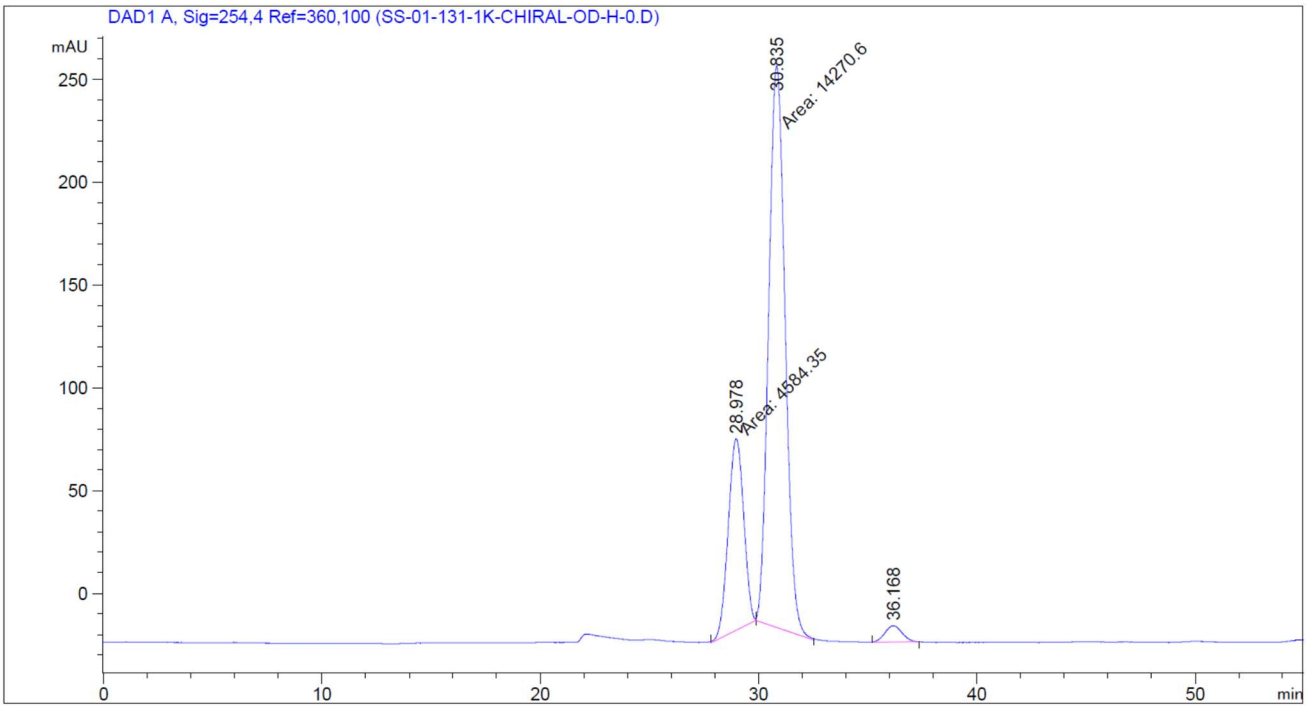


Figure S4. HPLC analysis of chiral *N*-(3-methylbutan-2-yl)aniline **3a(i)**

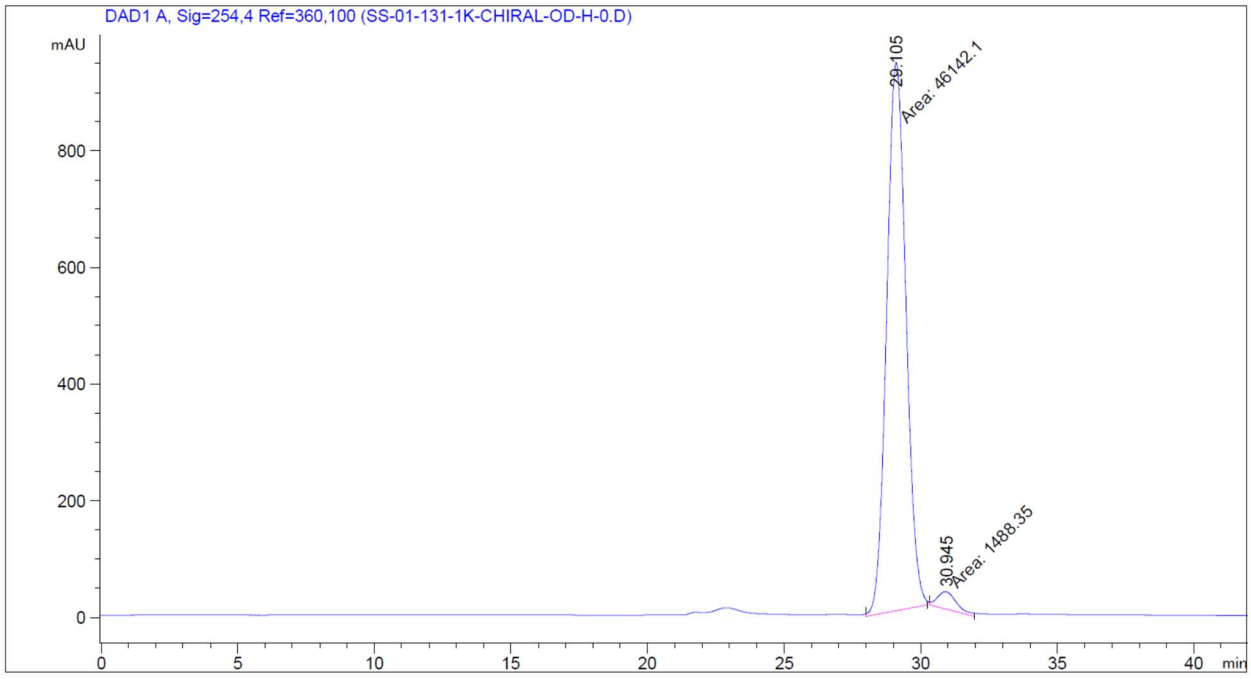


Figure S5. HPLC analysis of chiral *N*-(3-methylbutan-2-yl)aniline **3a(ii)**

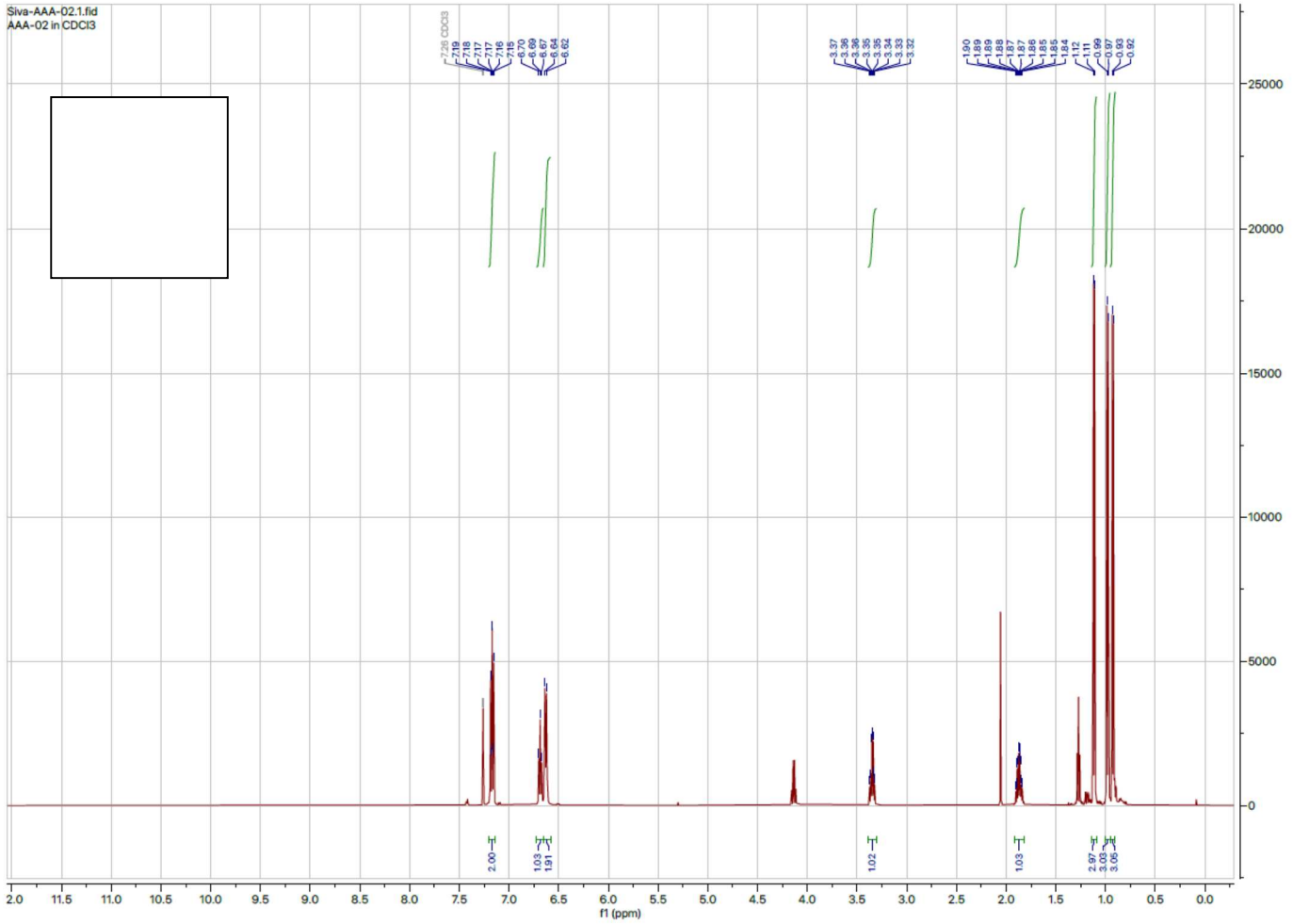
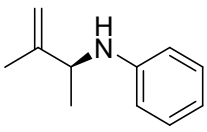


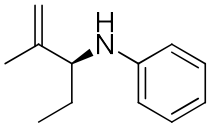
Figure S6. NMR analysis of racemic *N*-(3-methylbutan-2-yl)aniline **3a(iii)**

7. Characterization Data of the Chiral *N*-Aryl Allylamine Products



3a

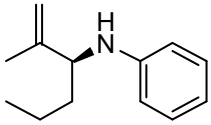
(*S*)-*N*-(3-methylbut-3-en-2-yl)aniline (3a): A dichloromethane (2.0 mL) solution of $Cu(MeCN)_4PF_6$ (19 mg, 10 mol %) and R-(+)-BINAM (28 mg, 20 mol %) was stirred at 25 °C for 0.5 h. 2-methylbut-2-ene (106 mg, 1.5 mmol) was added followed by the slow addition (4 h) of phenylhydroxylamine (55 mg, 0.5 mmol). The product **3a** was isolated by a column chromatography on silica gel (hexanes/EtOAc = 99:1–98:2; TLC: R_f = 0.75 (5% EtOAc in hexanes)). Yield = 47 mg (58%). Data for **3a:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (t, J = 7.8 Hz, 2H), 6.70 (t, J = 7.2 Hz, 1H), 6.61 (d, J = 8.0 Hz, 2H), 4.99 (s, 1H), 4.86 (s, 1H), 3.89 (q, J = 6.8 Hz, 1H), 1.73 (s, 3H), 1.34 (d, J = 6.8 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.0, 129.0, 117.4, 113.5, 110.9, 54.8, 21.1, 18.2 ppm; GC-MS for $C_{11}H_{15}N$, m/z = 161.23 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[5]



3b

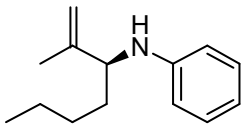
(*S*)-*N*-(2-methylpent-1-en-3-yl)aniline (3b): A dichloromethane (2.0 mL) solution of $Cu(MeCN)_4PF_6$ (19 mg, 10 mol %) and R-(+)-BINAM (28 mg, 20 mol %) was stirred at 25 °C for 0.5 h. 2-methylpent-2-ene (127 mg, 1.5 mmol) was added followed by the slow addition (4 h) of phenylhydroxylamine (55 mg, 0.5 mmol). The product **3b** was isolated by a column

chromatography on silica gel (hexanes/EtOAc = 99:1–98:2; TLC: R_f = 0.75 (5% EtOAc in hexanes)). Yield = 59 mg (67%). Data for **3b:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (t, *J* = 7.2 Hz, 2H), 6.60 (t, *J* = 7.4 Hz, 1H), 6.52 (d, *J* = 8.4 Hz, 2H), 4.90 (s, 1H), 4.85 (s, 1H), 3.64 (bs, 1H), 3.59 (t, *J* = 6.8 Hz, 1H), 1.59 (s, 3H), 1.55 (t, *J* = 7.0 Hz, 2H), 0.89 (t, *J* = 7.4 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.9, 145.6, 129.1, 117.0, 113.3, 112.3, 61.1, 27.3, 17.8, 10.9 ppm; IR (KBr) 3406, 3053, 2964, 2932, 1602, 1505, 1482, 1317, 1260, 1100, 1024, 800, 749, 687 cm-1. GC-MS for $C_{12}H_{17}N$, *m/z* = 175.10 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[6]



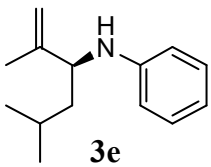
3c

(*S*)-*N*-(2-methylhex-1-en-3-yl)aniline (3c): A dichloromethane (2.0 mL) solution of $Cu(MeCN)_4PF_6$ (19 mg, 10 mol %) and R-(+)-BINAM (28 mg, 20 mol %) was stirred at 25 °C for 0.5 h. 2-methylhex-2-ene (148 mg, 1.5 mmol) was added followed by the slow addition (4 h) of phenylhydroxylamine (55 mg, 0.5 mmol). The product **3c** was isolated by a column chromatography on silica gel (hexanes/EtOAc = 99:1–98:2; TLC: R_f = 0.75 (5% EtOAc in hexanes)). Yield = 58 mg (61%). Data for **3c:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (t, *J* = 7.6 Hz, 2H), 6.67 (t, *J* = 7.2 Hz, 1H), 6.58 (d, *J* = 8.4 Hz, 2H), 4.98 (s, 1H), 4.91 (s, 1H), 3.76 (t, *J* = 6.8 Hz, 1H), 3.70 (bs, 1H), 1.67 (s, 3H), 1.62–1.55 (m, 2H), 1.47–1.36 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.8, 145.8, 129.0, 116.9, 113.1, 112.0, 59.2, 36.6, 19.5, 17.7, 14.0 ppm; GC-MS for $C_{13}H_{19}N$, *m/z* = 189.03 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[7]



3d

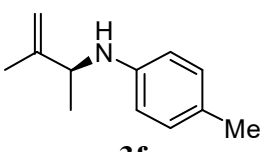
(*S*)-*N*-(2-methylhept-1-en-3-yl)aniline (3d): A dichloromethane (2.0 mL) solution of $Cu(MeCN)_4PF_6$ (19 mg, 10 mol %) and R-(+)-BINAM (28 mg, 20 mol %) was stirred at 25 °C for 0.5 h. 2-methylhept-2-ene (170 mg, 1.5 mmol) was added followed by the slow addition (4 h) of phenylhydroxylamine (55 mg, 0.5 mmol). The product **3d** was isolated by a column chromatography on silica gel (hexanes/EtOAc = 99:1–98:2; TLC: R_f = 0.75 (5% EtOAc in hexanes)). Yield = 60 mg (59%). Data for **3d:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 7.6, 7.2 Hz, 2H), 6.65 (t, *J* = 7.4 Hz, 1H), 6.57 (d, *J* = 7.6 Hz, 2H), 4.95 (s, 1H), 4.89 (s, 1H), 3.72 (t, *J* = 6.8 Hz, 1H), 3.69 (bs, 1H), 1.65 (s, 3H), 1.58 (q, *J* = 3.0 Hz, 2H), 1.37–1.33 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.9, 146.0, 129.1, 117.0, 113.2, 112.0, 59.5, 34.3, 28.6, 22.7, 17.7, 14.1 ppm; IR (KBr): 3410, 3052, 2956, 2929, 2857, 1648, 1601, 1505, 1373, 1317, 1257, 1153, 894, 748, 690 cm^{-1}. GC-MS for $C_{14}H_{21}N$, *m/z* = 203.12 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[6]



3e

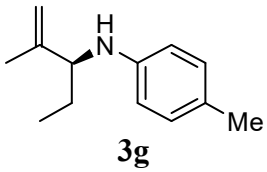
(*S*)-*N*-(2,5-dimethylhex-1-en-3-yl)aniline (3e): A dichloromethane (2.0 mL) solution of $Cu(MeCN)_4PF_6$ (19 mg, 10 mol %) and R-(+)-BINAM (28 mg, 20 mol %) was stirred at 25 °C for 0.5 h. 2,5-dimethylhex-2-ene (170 mg, 1.5 mmol) was added followed by the slow addition (4 h) of phenylhydroxylamine (55 mg, 0.5 mmol). The product **3e** was isolated by a column chromatography on silica gel (hexanes/EtOAc = 99:1–98:2; TLC: R_f = 0.75 (5% EtOAc in hexanes)). Yield = 66 mg (65%). Data for **3e:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (t, *J* = 8.0 Hz, 2H), 6.66 (t, *J* = 7.6 Hz, 1H), 6.57 (d,

J = 7.6 Hz, 2H), 4.98 (s, 1H), 4.88 (s, 1H), 3.81 (t, J = 7.0 Hz, 1H), 3.66 (bs, 1H), 1.78–1.66 (m, 1H), 1.57 (s, 3H), 1.45 (t, J = 6.6 Hz, 2H), 0.95 (d, J = 6.8 Hz, 3H), 0.92 (d, J = 6.8 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.7, 146.1, 129.0, 116.9, 113.1, 111.8, 57.4, 44.0, 24.9, 22.8, 22.5, 17.5 ppm; GC-MS for $C_{14}H_{21}N$, m/z = 203.16 (M^+); HRMS (IT-TOF/ESI) Calcd for $C_{14}H_{22}N$ ($[M+H]^+$) 204.1747, Found 204.1746.



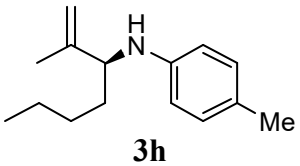
3f

(*S*)-4-methyl-*N*-(3-methylbut-3-en-2-yl)aniline (3f): A dichloromethane (2.0 mL) solution of $Cu(MeCN)_4PF_6$ (17 mg, 10 mol %) and R-(+)-BINAM (25 mg, 20 mol %) was stirred at 25 °C for 0.5 h. 2-methylbut-2-ene (94 mg, 1.5 mmol) was added followed by the slow addition (4 h) of *N*-(*p*-tolyl)hydroxylamine (55 mg, 0.5 mmol). The product **3f** was isolated by a column chromatography on silica gel (hexanes/EtOAc = 99:1–98:2; TLC: R_f = 0.7 (5% EtOAc in hexanes)). Yield = 43 mg (55%). Data for **3f:** ^1H NMR (400 MHz, $CDCl_3$) δ 6.99 (d, J = 8.4 Hz, 2H), 6.53 (d, J = 8.4 Hz, 2H), 5.01 (s, 1H), 4.87 (s, 1H), 3.89 (q, J = 6.8 Hz, 1H), 3.61 (bs, 1H), 2.26 (s, 3H), 1.74 (s, 3H), 1.34 (d, J = 6.8 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.4, 145.2, 129.5, 126.1, 113.3, 110.5, 54.7, 21.2, 20.3, 18.1 ppm; GC-MS for $C_{14}H_{17}N$, m/z = 175.13 (M^+); HRMS (IT-TOF/ESI) Calcd for $C_{14}H_{18}N$ ($[M+H]^+$) 176.1434, Found 176.1431.



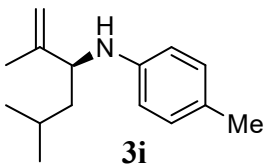
3g

(*S*)-4-methyl-*N*-(2-methylpent-1-en-3-yl)aniline (3g): A dichloromethane (2.0 mL) solution of $Cu(MeCN)_4PF_6$ (17 mg, 10 mol %) and R-(+)-BINAM (25 mg, 20 mol %) was stirred at 25 °C for 0.5 h. 2-methylpent-2-ene (113 mg, 1.5 mmol) was added followed by the slow addition (4 h) of *N*-(*p*-tolyl)hydroxylamine (55 mg, 0.5 mmol). The product **3g** was isolated by a column chromatography on silica gel (hexanes/EtOAc = 99:1–98:2; TLC: R_f = 0.7 (5% EtOAc in hexanes)). Yield = 49 mg (58%). Data for **3g:** ^1H NMR (400 MHz, $CDCl_3$) δ 6.98 (d, J = 8.0 Hz, 2H), 6.54 (d, J = 8.4 Hz, 2H), 4.98 (s, 1H), 4.93 (s, 1H), 3.66 (t, J = 6.8 Hz, 1H), 3.61 (bs, 1H), 2.25 (s, 3H), 1.68 (s, 3H), 1.63 (q, J = 7.4 Hz, 2H), 0.98 (t, J = 7.4 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.5, 145.4, 129.5, 126.0, 113.3, 112.2, 61.2, 27.1, 20.3, 17.6, 10.8 ppm; GC-MS for $C_{13}H_{19}N$, m/z = 189.15 (M^+); HRMS (IT-TOF/ESI) Calcd for $C_{13}H_{20}N$ ($[M+H]^+$) 190.1590, Found 190.1589.



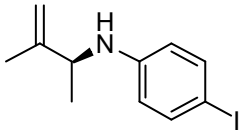
3h

(*S*)-4-methyl-*N*-(2-methylhept-1-en-3-yl)aniline (3h): A dichloromethane (2.0 mL) solution of $Cu(MeCN)_4PF_6$ (17 mg, 10 mol %) and R-(+)-BINAM (25 mg, 20 mol %) was stirred at 25 °C for 0.5 h. 2-methylhept-2-ene (150 mg, 1.5 mmol) was added followed by the slow addition (4 h) of *N*-(*p*-tolyl)hydroxylamine (55 mg, 0.5 mmol). The product **3h** was isolated by a column chromatography on silica gel (hexanes/EtOAc = 99:1–98:2; TLC: R_f = 0.75 (5% EtOAc in hexanes)). Yield = 59 mg (62%). Data for **3h:** ^1H NMR (400 MHz, $CDCl_3$) δ 6.87 (d, J = 8.8 Hz, 2H), 6.42 (d, J = 8.4 Hz, 2H), 4.86 (s, 1H), 4.80 (s, 1H), 3.61 (t, J = 6.8 Hz, 1H), 3.49 (bs, 1H), 2.13 (s, 3H), 1.56 (s, 3H), 1.48 (p, J = 3.4 Hz, 2H), 1.28–1.25 (m, 4H), 0.82 (t, J = 7.0 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 146.2, 145.7, 129.7, 126.2, 113.5, 112.0, 59.9, 34.3, 28.7, 22.8, 20.5, 17.8, 14.2 ppm; GC-MS for $C_{15}H_{23}N$, m/z = 217.18 (M^+); HRMS (IT-TOF/ESI) Calcd for $C_{15}H_{24}N$ ($[M+H]^+$) 218.1903, Found 218.1905.



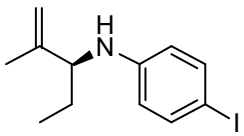
3i

(*S*)-*N*-(2,5-dimethylhex-1-en-3-yl)-4-methylaniline (3i): A dichloromethane (2.0 mL) solution of $Cu(MeCN)_4PF_6$ (17 mg, 10 mol %) and R-(+)-BINAM (25 mg, 20 mol %) was stirred at 25 °C for 0.5 h. 2,5-dimethylhex-2-ene (150 mg, 1.5 mmol) was added followed by the slow addition (4 h) of *N*-(*p*-tolyl)hydroxylamine (55 mg, 0.5 mmol). The product **3i** was isolated by a column chromatography on silica gel (hexanes/EtOAc = 99:1–98:2; TLC: R_f = 0.7 (5% EtOAc in hexanes)). Yield = 63 mg (65%). Data for **3i:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (d, *J* = 8.4 Hz, 2H), 6.53 (d, *J* = 8.4, 2H), 4.99 (s, 1H), 4.90 (s, 1H), 3.81 (t, *J* = 7.2 Hz, 1H), 3.56 (bs, 1H), 2.25 (s, 3H), 1.78–1.72 (m, 1H), 1.68 (s, 3H), 1.46 (t, *J* = 7.0 Hz, 2H), 0.98 (d, *J* = 6.4 Hz, 3H), 0.95 (d, *J* = 6.4 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 146.2, 145.4, 129.5, 126.0, 113.3, 111.7, 57.7, 44.0, 24.9, 22.8, 22.5, 20.3, 17.5 ppm; GC-MS for $C_{15}H_{23}N$, *m/z* = 217.18 (M^+); HRMS (IT-TOF/ESI) Calcd for $C_{15}H_{24}N$ ($[M+H]^+$) 218.1903, Found 218.1903.



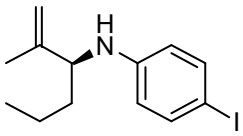
3j

(*S*)-4-iodo-*N*-(3-methylbut-3-en-2-yl)aniline (3j): A dichloromethane (2.0 mL) solution of $Cu(MeCN)_4PF_6$ (9 mg, 10 mol %) and R-(+)-BINAM (13 mg, 20 mol %) was stirred at 25 °C for 0.5 h. 2-methylbut-2-ene (49 mg, 1.5 mmol) was added followed by the slow addition (4 h) of *N*-(4-iodophenyl)hydroxylamine (55 mg, 0.5 mmol). The product **3j** was isolated by a column chromatography on silica gel (hexanes/EtOAc = 99:1–98:2; TLC: R_f = 0.75 (5% EtOAc in hexanes)). Yield = 53mg (76%). Data for **3j:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.4 Hz, 2H), 6.34 (d, *J* = 8.8 Hz, 2H), 4.95 (s, 1H), 4.85 (s, 1H), 3.82 (t, *J* = 6.6 Hz, 1H), 3.76 (bs, 1H), 1.69 (s, 3H), 1.32 (d, *J* = 6.4 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.0, 146.7, 137.6, 115.4, 110.9, 77.6, 54.4, 21.1, 18.0 ppm; GC-MS for $C_{11}H_{14}IN$, *m/z* = 287.01 (M^+); HRMS (IT-TOF/ESI) Calcd for $C_{11}H_{15}IN$ ($[M+H]^+$) 288.0244, Found 288.0243.



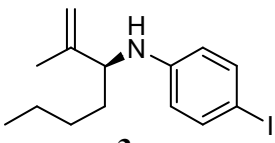
3k

(*S*)-4-iodo-*N*-(2-methylpent-1-en-3-yl)aniline (3k): A dichloromethane (2.0 mL) solution of $Cu(MeCN)_4PF_6$ (9 mg, 10 mol %) and R-(+)-BINAM (13 mg, 20 mol %) was stirred at 25 °C for 0.5 h. 2-methylpent-2-ene (59 mg, 1.5 mmol) was added followed by the slow addition (4 h) of *N*-(4-iodophenyl)hydroxylamine (55 mg, 0.5 mmol). The product **3k** was isolated by a column chromatography on silica gel (hexanes/EtOAc = 99:1–98:2; TLC: R_f = 0.75 (5% EtOAc in hexanes)). Yield = 60 mg (86%). Data for **3k:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.4 Hz, 2H), 6.36 (d, *J* = 8.4 Hz, 2H), 4.93 (s, 1H), 4.92 (s, 1H), 3.75 (bs, 1H), 3.60 (t, *J* = 6.6 Hz, 1H), 1.63 (s, 3H), 1.62–1.58 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.2, 144.7, 137.5, 115.4, 112.6, 77.4, 60.9, 27.0, 17.6, 10.7 ppm; GC-MS for $C_{12}H_{16}IN$, *m/z* = 301.03 (M^+); HRMS (IT-TOF/ESI) Calcd for $C_{12}H_{17}IN$ ($[M+H]^+$) 302.0400, Found 302.0398.



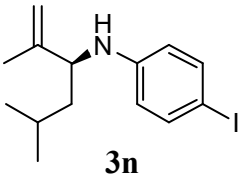
3l

(*S*)-4-iodo-*N*-(2-methylhex-1-en-3-yl)aniline (3l): A dichloromethane (2.0 mL) solution of $Cu(MeCN)_4PF_6$ (9 mg, 10 mol %) and R-(+)-BINAM (13 mg, 20 mol %) was stirred at 25 °C for 0.5 h. 2-methylhex-2-ene (69 mg, 1.5 mmol) was added followed by the slow addition (4 h) of *N*-(4-iodophenyl)hydroxylamine (55 mg, 0.5 mmol). The product **3l** was isolated by a column chromatography on silica gel (hexanes/EtOAc = 99:1–98:2; TLC: R_f = 0.75 (5% EtOAc in hexanes)). Yield = 58 mg (78%). Data for **3l:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.8 Hz, 2H), 6.36 (d, *J* = 8.8 Hz, 2H), 4.93 (s, 1H), 4.89 (s, 1H), 3.74 (bs, 1H), 3.69 (t, *J* = 6.8 Hz, 1H), 1.63 (s, 3H), 1.60–1.52 (m, 2H), 1.44–1.33 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.2, 145.2, 137.6, 115.4, 112.3, 77.4, 59.1, 36.5, 19.4, 17.6, 13.9 ppm; GC-MS for $C_{13}H_{18}IN$, *m/z* = 315.04 (M^+); HRMS (IT-TOF/ESI) Calcd for $C_{13}H_{19}IN$ ($[M+H]^+$) 316.0557, Found 316.0555.



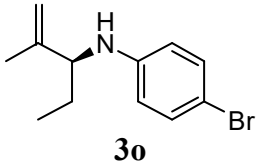
3m

(*S*)-4-iodo-*N*-(2-methylhept-1-en-3-yl)aniline (3m): A dichloromethane (2.0 mL) solution of $Cu(MeCN)_4PF_6$ (9 mg, 10 mol %) and R-(+)-BINAM (13 mg, 20 mol %) was stirred at 25 °C for 0.5 h. 2-methylhept-2-ene (79 mg, 1.5 mmol) was added followed by the slow addition (4 h) of *N*-(4-iodophenyl)hydroxylamine (55 mg, 0.5 mmol). The product **3m** was isolated by a column chromatography on silica gel (hexanes/EtOAc = 99:1–98:2; TLC: R_f = 0.75 (5% EtOAc in hexanes)). Yield = 62 mg (81%). Data for **3m:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.8 Hz, 2H), 6.35 (d, *J* = 8.8 Hz, 2H), 4.93 (s, 1H), 4.90 (s, 1H), 3.74 (bs, 1H), 3.67 (t, *J* = 6.8 Hz, 1H), 1.63 (s, 3H), 1.60–1.54 (m, 2H), 1.35–1.33 (m, 4H), 0.91 (t, *J* = 6.8 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.2, 145.2, 137.5, 115.4, 112.3, 77.4, 59.3, 34.0, 28.4, 22.5, 17.6, 14.0 ppm; GC-MS for $C_{14}H_{20}IN$, *m/z* = 329.06 (M^+); HRMS (IT-TOF/ESI) Calcd for $C_{14}H_{21}IN$ ($[M+H]^+$) 330.0713, Found 330.0710.



3n

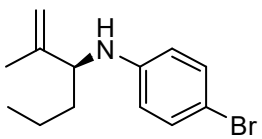
(*S*)-*N*-(2,5-dimethylhex-1-en-3-yl)-4-iodoaniline (3n): A dichloromethane (2.0 mL) solution of $Cu(MeCN)_4PF_6$ (9 mg, 10 mol %) and R-(+)-BINAM (13 mg, 20 mol %) was stirred at 25 °C for 0.5 h. 2,5-dimethylhex-2-ene (79 mg, 1.5 mmol) was added followed by the slow addition (4 h) of *N*-(4-iodophenyl)hydroxylamine (55 mg, 0.5 mmol). The product **3n** was isolated by a column chromatography on silica gel (hexanes/EtOAc = 99:1–98:2; TLC: R_f = 0.75 (5% EtOAc in hexanes)). Yield = 56 mg (73%). Data for **3n:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.8 Hz, 2H), 6.36 (d, *J* = 8.8 Hz, 2H), 4.94 (s, 1H), 4.88 (s, 1H), 3.75 (t, *J* = 7.2 Hz, 1H), 3.71 (bs, 1H), 1.74–1.67 (m, 1H), 1.63 (s, 3H), 1.46–1.41 (m, 2H), 0.94 (d, *J* = 6.4 Hz, 3H), 0.92 (d, *J* = 6.4 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.2, 145.5, 137.6, 115.4, 112.1, 77.4, 57.4, 43.8, 24.8, 22.8, 22.4, 17.5 ppm; GC-MS for $C_{14}H_{20}IN$, *m/z* = 329.06 (M^+); HRMS (IT-TOF/ESI) Calcd for $C_{14}H_{21}IN$ ($[M+H]^+$) 330.0713, Found 330.0710.



3o

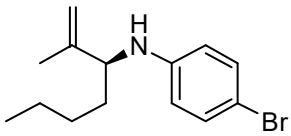
(*S*)-4-bromo-*N*-(2-methylpent-1-en-3-yl)aniline (3o): A dichloromethane (2.0 mL) solution of $Cu(MeCN)_4PF_6$ (11 mg, 10 mol %) and R-(+)-BINAM (17 mg, 20 mol %) was stirred at 25 °C for 0.5 h. 2-methylpent-2-ene (74 mg, 1.5 mmol) was added followed by the slow addition (4 h) of *N*-(4-bromophenyl)hydroxylamine (55 mg, 0.5 mmol). The

product **3o** was isolated by a column chromatography on silica gel (hexanes/EtOAc = 99:1–98:2; TLC: R_f = 0.75 (5% EtOAc in hexanes)). Yield = 58 mg (79%). Data for **3o:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.4 Hz, 2H), 6.46 (d, *J* = 8.4 Hz, 2H), 4.94 (s, 1H), 4.93 (s, 1H), 3.74 (bs, 1H), 3.60 (t, *J* = 6.6 Hz, 1H), 1.64 (s, 3H), 1.62–1.58 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 146.7, 144.8, 131.7, 114.8, 112.6, 108.5, 61.0, 27.0, 17.6, 10.7 ppm; GC-MS for $C_{12}H_{16}BrN$, *m/z* = 253.04 (M^+); HRMS (IT-TOF/ESI) Calcd for $C_{12}H_{17}BrN$ ($[M+H]^+$) 254.0539, Found 254.0537.



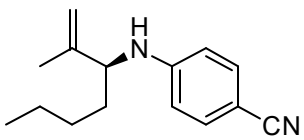
3p

(*S*)-4-bromo-*N*-(2-methylhex-1-en-3-yl)aniline (3p): A dichloromethane (2.0 mL) solution of $Cu(MeCN)_4PF_6$ (11 mg, 10 mol %) and R-(+)-BINAM (17 mg, 20 mol %) was stirred at 25 °C for 0.5 h. 2-methylhex-2-ene (86 mg, 1.5 mmol) was added followed by the slow addition (4 h) of *N*-(4-bromophenyl)hydroxylamine (55 mg, 0.5 mmol). The product **3p** was isolated by a column chromatography on silica gel (hexanes/EtOAc = 99:1–98:2; TLC: R_f = 0.75 (5% EtOAc in hexanes)). Yield = 55 mg (71%). Data for **3p:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.8 Hz, 2H), 6.45 (d, *J* = 8.4 Hz, 2H), 4.94 (s, 1H), 4.90 (s, 1H), 3.72 (bs, 1H), 3.69 (t, *J* = 6.8 Hz 1H), 1.64 (s, 3H), 1.60–1.52 (m, 2H), 1.45–1.32 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 146.7, 145.3, 131.7, 114.7, 112.3, 108.4, 59.3, 36.5, 19.4, 17.5, 13.9 ppm; GC-MS for $C_{13}H_{18}BrN$, *m/z* = 267.06 (M^+); HRMS (IT-TOF/ESI) Calcd for $C_{13}H_{19}BrN$ ($[M+H]^+$) 268.0695, Found 268.0693.



3q

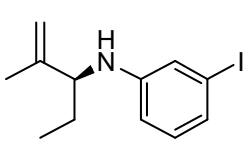
(*S*)-4-bromo-*N*-(2-methylhept-1-en-3-yl)aniline (3q): A dichloromethane (2.0 mL) solution of $Cu(MeCN)_4PF_6$ (11 mg, 10 mol %) and R-(+)-BINAM (17 mg, 20 mol %) was stirred at 25 °C for 0.5 h. 2-methylhept-2-ene (98 mg, 1.5 mmol) was added followed by the slow addition (4 h) of *N*-(4-bromophenyl)hydroxylamine (55 mg, 0.5 mmol). The product **3q** was isolated by a column chromatography on silica gel (hexanes/EtOAc = 99:1–98:2; TLC: R_f = 0.75 (5% EtOAc in hexanes)). Yield = 56 mg (68%). Data for **3q:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.4 Hz, 2H), 6.45 (d, *J* = 8.8 Hz, 2H), 4.94 (s, 1H), 4.90 (s, 1H), 3.73 (bs, 1H), 3.67 (t, *J* = 6.8 Hz, 1H), 1.64 (s, 3H), 1.60–1.54 (m, 2H), 1.36–1.34 (m, 4H), 0.92 (t, *J* = 6.6 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 146.6, 145.2, 131.7, 114.7, 112.4, 108.4, 59.5, 34.0, 28.4, 22.5, 17.6, 14.0 ppm; GC-MS for $C_{14}H_{20}BrN$, *m/z* = 281.07 (M^+); HRMS (IT-TOF/ESI) Calcd for $C_{14}H_{21}BrN$ ($[M+H]^+$) 282.0852, Found 282.0848.



3r

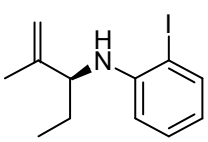
(*S*)-4-((2-methylhept-1-en-3-yl)amino)benzonitrile (3r): A dichloromethane (2.0 mL) solution of $Cu(MeCN)_4PF_6$ (11 mg, 10 mol %) and R-(+)-BINAM (17 mg, 20 mol %) was stirred at 25 °C for 0.5 h. 2-methylhept-2-ene (137 mg, 1.5 mmol) was added followed by the slow addition (4 h) of *N*-(4-cyanophenyl)hydroxylamine (55 mg, 0.5 mmol). The product **3r** was isolated by a column chromatography on silica gel (hexanes/EtOAc = 99:1–98:2; TLC: R_f = 0.75 (5% EtOAc in hexanes)). Yield = 33 mg (35%). Data for **3r:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.4 Hz, 2H), 6.53 (d, *J* = 8.8 Hz, 2H), 4.94 (s, 1H), 4.92 (s, 1H), 4.33 (bs, 1H), 3.74 (q, *J* = 6.8 Hz, 1H), 1.65 (s, 3H), 1.62–1.55 (m, 2H), 1.39–1.33 (m, 4H), 0.91 (t, *J* = 6.8 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz,

$CDCl_3$) δ 150.8, 144.4, 133.4, 120.6, 112.7, 98.1, 59.0, 33.7, 28.2, 22.4, 17.6, 13.9 ppm; GC-MS for $C_{15}H_{20}N_2$, *m/z* = 228.16 (M^+); HRMS (IT-TOF/ESI) Calcd for $C_{15}H_{21}N_2$ ($[M+H]^+$) 229.1699, Found 229.1700.



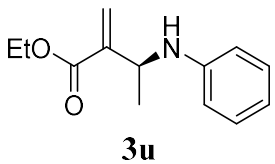
3s

(*S*)-3-iodo-*N*-(2-methylpent-1-en-3-yl)aniline (3s): A dichloromethane (2.0 mL) solution of $Cu(MeCN)_4PF_6$ (9 mg, 10 mol %) and R-(+)-BINAM (13 mg, 20 mol %) was stirred at 25 °C for 0.5 h. 2-methylpent-2-ene (59 mg, 1.5 mmol) was added followed by the slow addition (4 h) of *N*-(3-iodophenyl)hydroxylamine (55 mg, 0.5 mmol). The product **3s** was isolated by a column chromatography on silica gel (hexanes/EtOAc = 99:1–98:2; TLC: R_f = 0.75 (5% EtOAc in hexanes)). Yield = 57 mg (82%). Data for **3s:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (d, *J* = 7.6 Hz, 1H), 6.93 (s, 1H), 6.84 (t, *J* = 8.0, 1H), 6.52 (d, *J* = 8.0 Hz, 1H), 4.96 (s, 1H), 4.94 (s, 1H), 3.73 (bs, 1H), 3.61 (t, *J* = 6.3 Hz 1H), 1.65 (s, 3H), 1.62–1.57 (m, 2H), 0.95 (t, *J* = 7.6 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 148.9, 144.7, 130.5, 125.7, 121.8, 112.6, 112.3, 95.1, 60.8, 27.0, 17.6, 10.7 ppm; GC-MS for $C_{12}H_{16}IN$, *m/z* = 301.03 (M^+); HRMS (IT-TOF/ESI) Calcd for $C_{12}H_{17}IN$ ($[M+H]^+$) 302.0400, Found 302.0401.



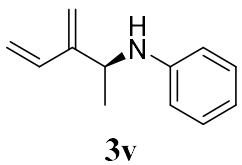
3t

(*S*)-2-iodo-*N*-(2-methylpent-1-en-3-yl)aniline (3t): A dichloromethane (2.0 mL) solution of $Cu(MeCN)_4PF_6$ (9 mg, 10 mol %) and R-(+)-BINAM (13 mg, 20 mol %) was stirred at 25 °C for 0.5 h. 2-methylpent-2-ene (59 mg, 1.5 mmol) was added followed by the slow addition (4 h) of *N*-(2-iodophenyl)hydroxylamine (55 mg, 0.5 mmol). The product **3t** was isolated by a column chromatography on silica gel (hexanes/EtOAc = 99:1–98:2; TLC: R_f = 0.75 (5% EtOAc in hexanes)). Yield = 48 mg (68%). Data for **3t:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 1H), 7.18 (t, *J* = 7.6, 1H), 6.55 (d, *J* = 8.4 Hz, 1H), 6.44 (t, *J* = 7.6, 1H), 4.99 (s, 1H), 4.96 (s, 1H), 4.31 (bs, 1H), 3.73 (q, *J* = 6.6 Hz 1H), 1.78–1.72 (m, 2H), 1.70 (s, 3H), 1.04 (t, *J* = 7.4 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 146.5, 144.7, 138.8, 129.1, 118.3, 112.5, 111.7, 85.5, 61.4, 27.1, 17.7, 10.8 ppm; GC-MS for $C_{12}H_{16}IN$, *m/z* = 301.03 (M^+); HRMS (IT-TOF/ESI) Calcd for $C_{12}H_{17}IN$ ($[M+H]^+$) 302.0400, Found 302.0399.



3u

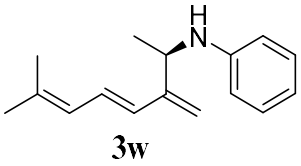
(*S*)-ethyl 2-methylene-3-(phenylamino)butanoate (3u): A dichloromethane (2.0 mL) solution of $Cu(MeCN)_4PF_6$ (19 mg, 10 mol %) and R-(+)-BINAM (28 mg, 20 mol %) was stirred at 25 °C for 0.5 h. Ethyl tiglate (194 mg, 1.5 mmol) was added followed by the slow addition (4 h) of phenylhydroxylamine (55 mg, 0.5 mmol). The product **5a** was isolated by a column chromatography on silica gel (hexanes/EtOAc = 98:2–96:6; TLC: R_f = 0.45 (5% EtOAc in hexanes)). Yield = 60 mg (54%). GC-MS for $C_{13}H_{17}NO_2$, *m/z* = 219.16 (M^+). For ^{1}H NMR and $^{13}C\{^1H\}$ NMR please check the reference 8.



3v

(*S*)-*N*-(3-methylenepent-4-en-2-yl)aniline (3v): A dichloromethane (2.0 mL) solution of $Cu(MeCN)_4PF_6$ (19 mg, 10 mol %) and R-(+)-BINAM (28 mg, 20 mol %) was stirred at 25 °C for 0.5 h. (*E*)-3-methylpenta-1,3-diene (124 mg, 1.5 mmol) was added followed by the slow addition (4 h) of phenylhydroxylamine (55 mg, 0.5 mmol). The product **5b** was isolated by a column chromatography on silica gel (hexanes/EtOAc = 99:1–98:2; TLC: R_f = 0.7 (5% EtOAc in hexanes)).

Yield = 42 mg (48%). GC-MS for $C_{12}H_{15}N$, *m/z* = 173.12 (M^+). For ^1H NMR and $^{13}C\{^1H\}$ NMR please check the reference 9.



3w

***N*-((*S*,4*Z*,6*E*)-2,6-dimethylocta-1,4,6-trien-3-yl)aniline (3w):** A dichloromethane (2.0 mL) solution of $Cu(MeCN)_4PF_6$ (19 mg, 10 mol %) and R-(+)-BINAM (28 mg, 20 mol %) was stirred at 25 °C for 0.5 h. 2,6-dimethylocta-2,4,6-triene (206 mg, 1.5 mmol) was added followed by the slow addition (4 h) of phenylhydroxylamine (55 mg, 0.5 mmol). The product **5c** was isolated by a column chromatography on silica gel (hexanes/EtOAc = 99:1–98:2; TLC: R_f = 0.65 (5% EtOAc in hexanes)). Yield = 67 mg (58%). GC-MS for $C_{16}H_{21}N$, *m/z* = 227.16 (M^+). For ^1H NMR and $^{13}C\{^1H\}$ NMR please check the reference 9.

8. References

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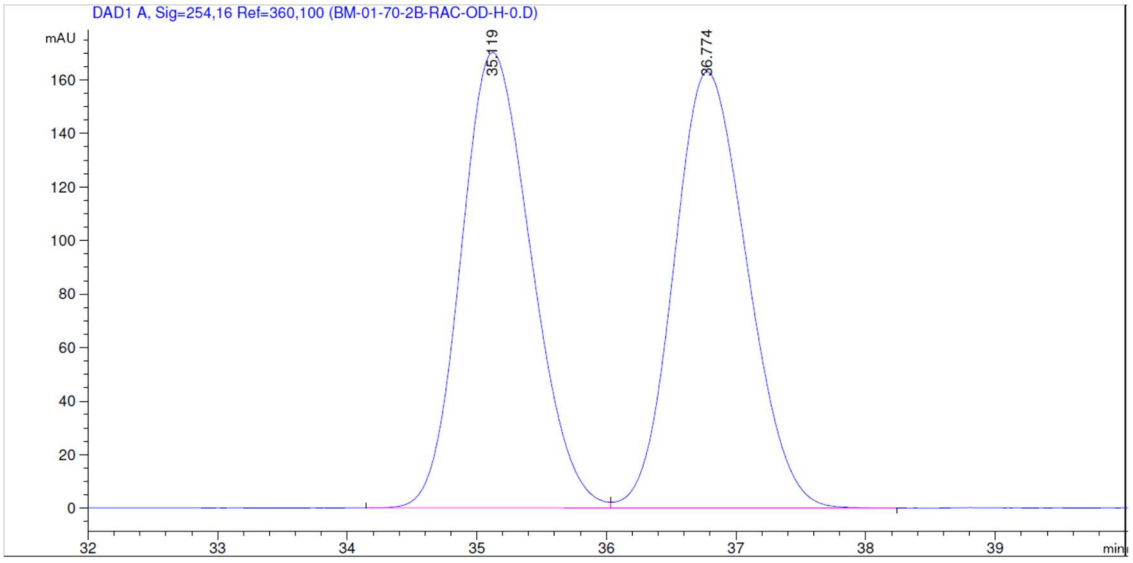
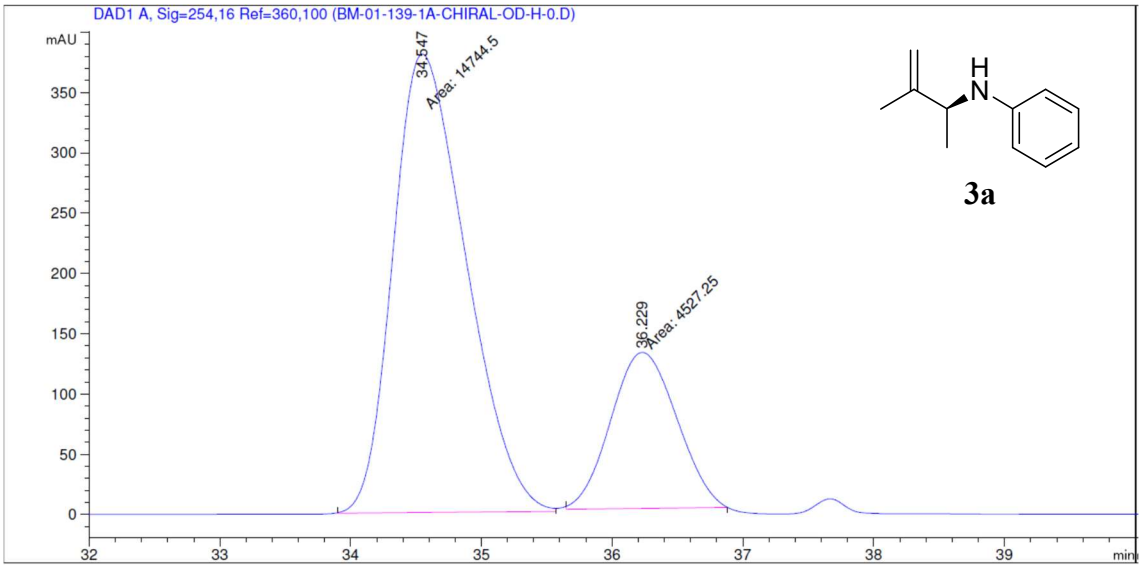
9. HPLC chromatograms of the racemic and chiral *N*-aryl allylamines

Racemic: *N*-(2-methylbut-1-en-3-yl)aniline (3a)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.119	BV	0.5867	6401.06689	170.21545	49.9772
2	36.774	VB	0.6184	6406.90771	163.05145	50.0228
Totals :				1.28080e4	333.26691	

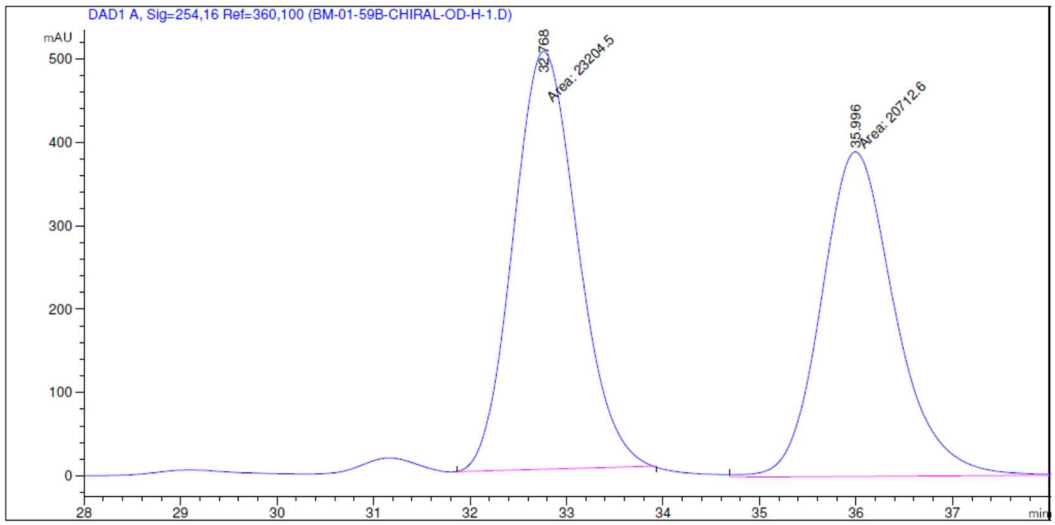
Chiral: *N*-(2-methylbut-1-en-3-yl)aniline (3a) (53% *ee*)



Signal 1: DAD1 A, Sig=254,16 Ref=360,100

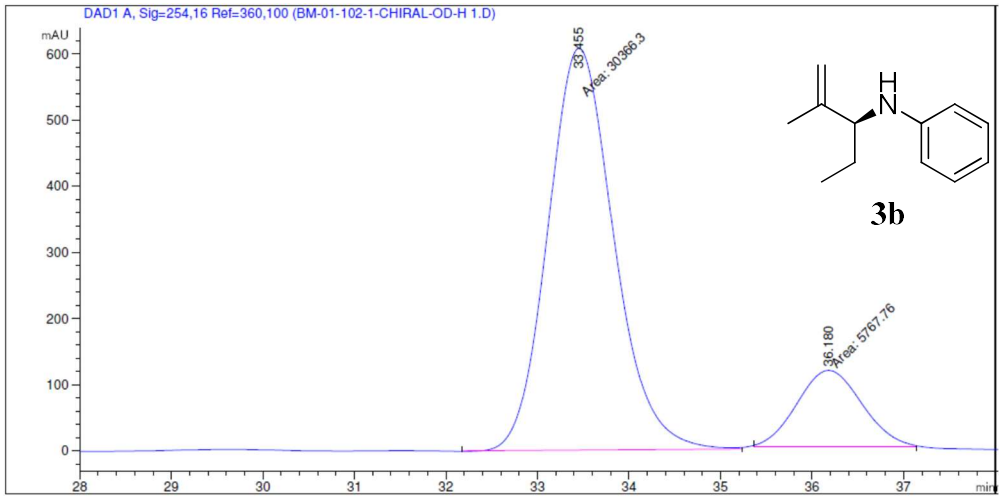
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.547	MM	0.6463	1.47445e4	380.24365	76.5083
2	36.229	MP	0.5832	4527.24854	129.37712	23.4917
Totals :				1.92717e4	509.62077	

Racemic: *N*-(2-methylpent-1-en-3-yl)aniline (3b)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.768	MM	0.7716	2.32045e4	501.19479	52.8371
2	35.996	MM	0.8866	2.07126e4	389.35547	47.1629
Totals :				4.39171e4	890.55026	

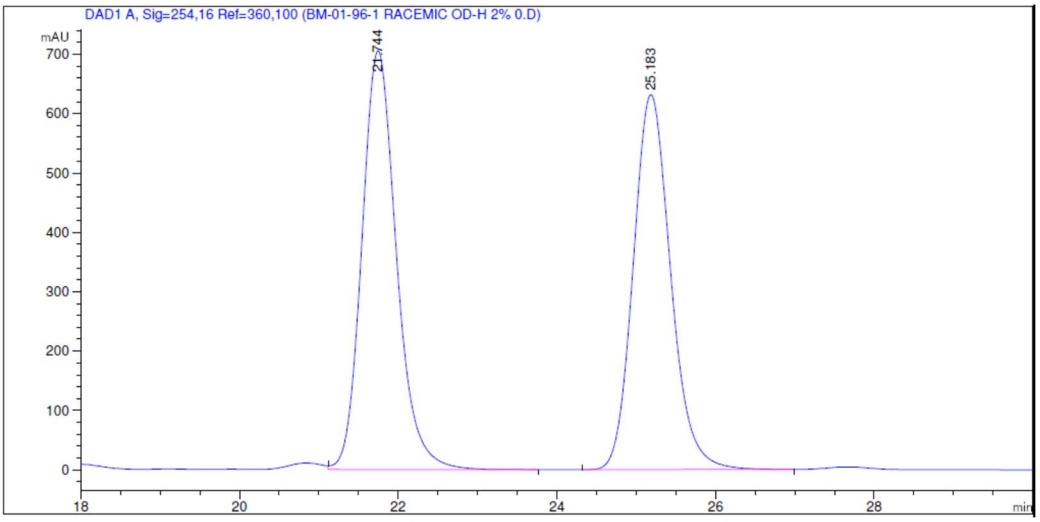
Chiral: (*S*)-*N*-(2-methylpent-1-en-3-yl)aniline (3b) (69% *ee*)



Signal 1: DAD1 A, Sig=254,16 Ref=360,100

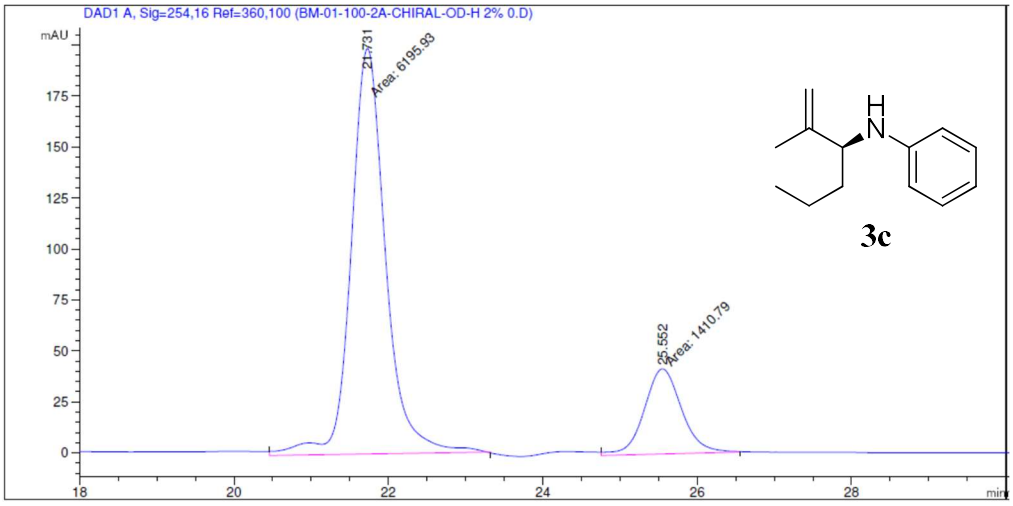
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.455	PP	0.8282	3.01115e4	605.94995	84.2692
2	36.181	MM	0.8176	5621.00049	114.57680	15.7308
Totals :				3.57325e4	720.52675	

Racemic: *N*-(2-methylhex-1-en-3-yl)aniline (3c)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.744	VB	0.4643	2.12969e4	705.29095	50.7663
2	25.183	BB	0.5056	2.06540e4	631.52881	49.2337
Totals :				4.19509e4	1336.81976	

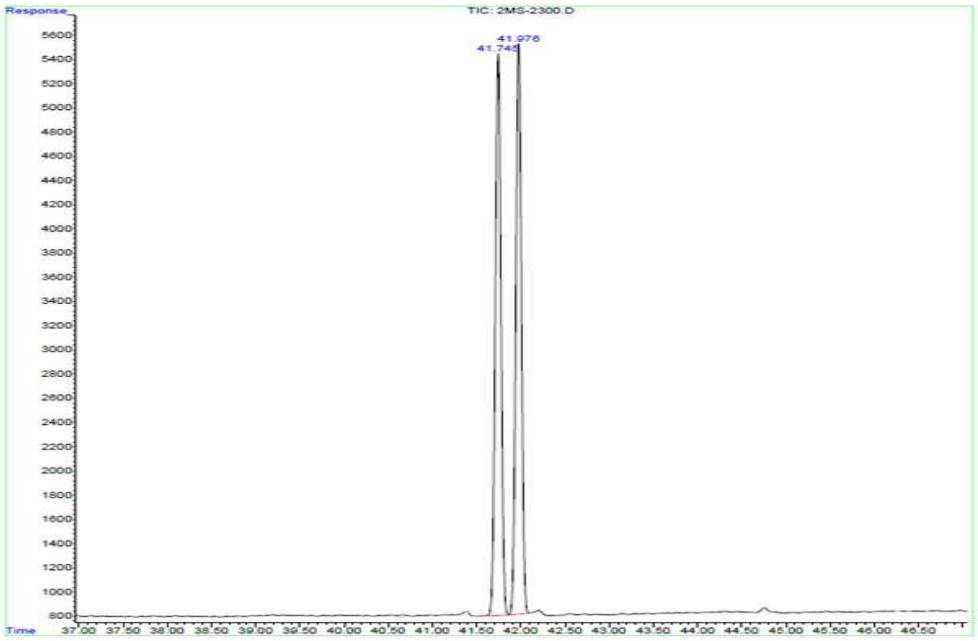
Chiral: (*S*)-*N*-(2-methylhex-1-en-3-yl)aniline (3c) (63% *ee*)



Signal 1: DAD1 A, Sig=254,16 Ref=360,100

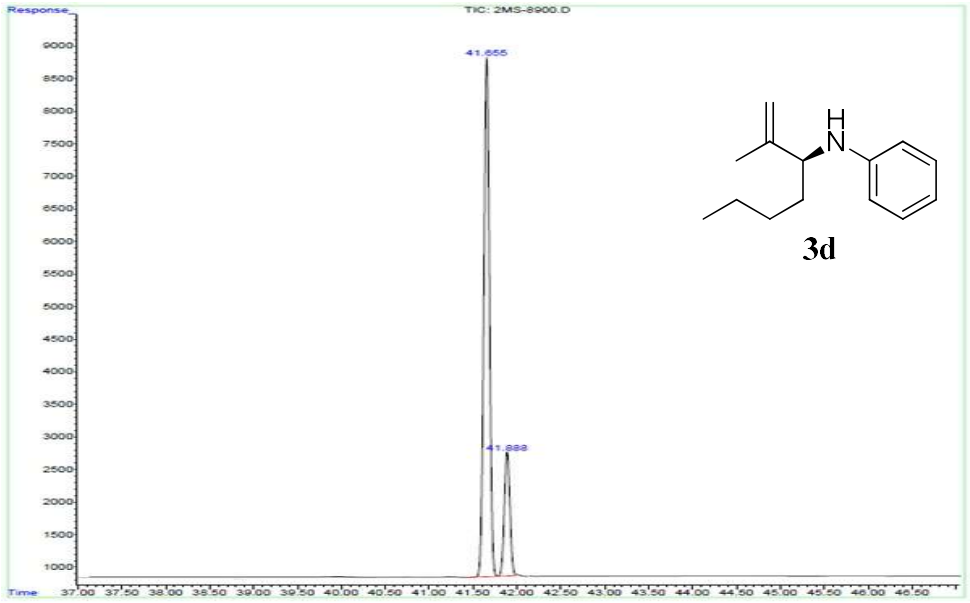
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.731	MM	0.5193	6195.93115	198.85376	81.4534
2	25.552	MM	0.5633	1410.78638	41.74030	18.5466
Totals :				7606.71753	240.59406	

Racemic: *N*-(2-methylhept-1-en-3-yl)aniline (3d):



R.T. min	Start min	End min	peak height	peak area
41.745	41.579	41.863	4646	208838
41.976	41.863	42.091	4705	207263

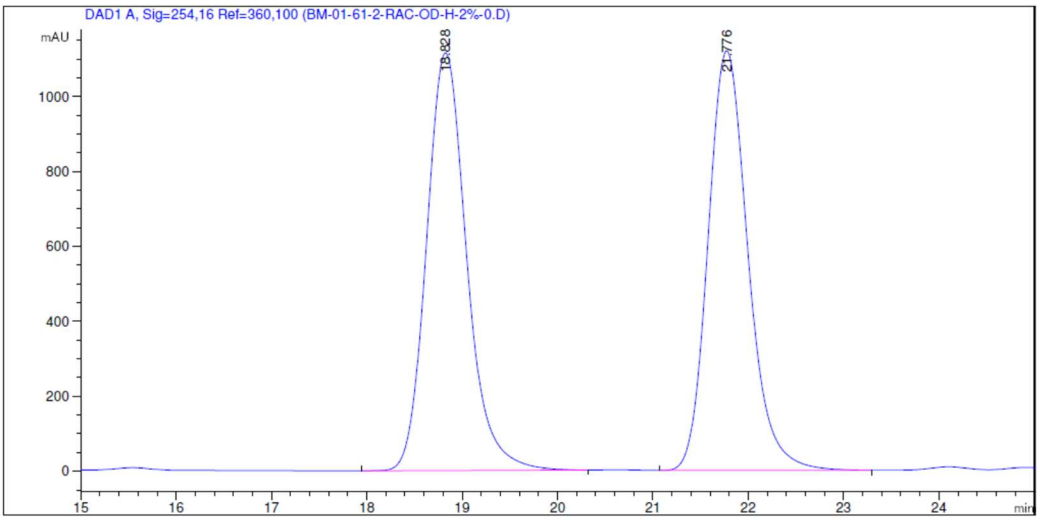
Chiral: (*S*)-*N*-(2-methylhept-1-en-3-yl)aniline (3d): (61% *ee*)



3d

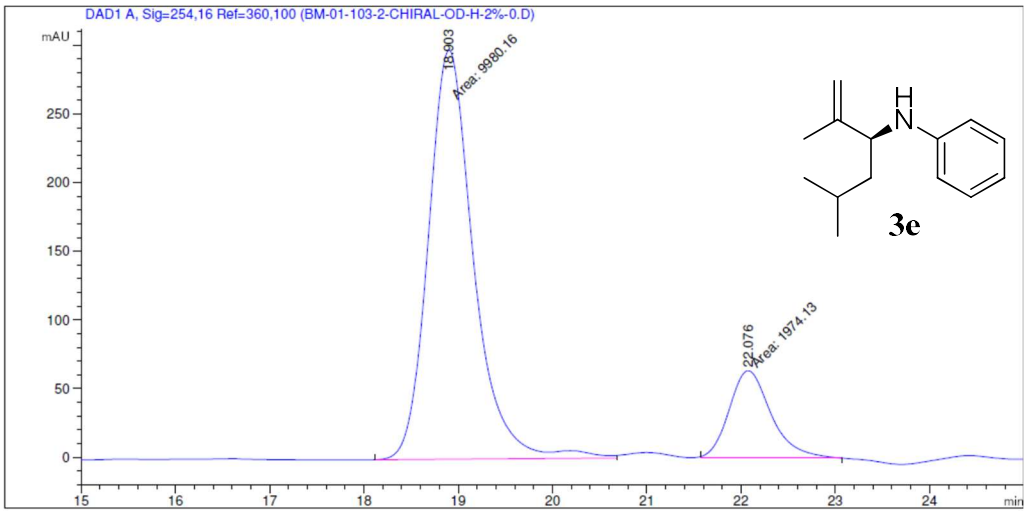
R.T. min	Start min	End min	peak height	peak area
41.655	41.440	41.779	7940	355289
41.888	41.779	42.019	1903	84839

Racemic: *N*-(2,5-dimethylhex-1-en-3-yl)aniline (3e)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.828	BB	0.4511	3.25697e4	1114.03784	50.0332
2	21.776	BB	0.4511	3.25265e4	1118.96033	49.9668
Totals :				6.50962e4	2232.99817	

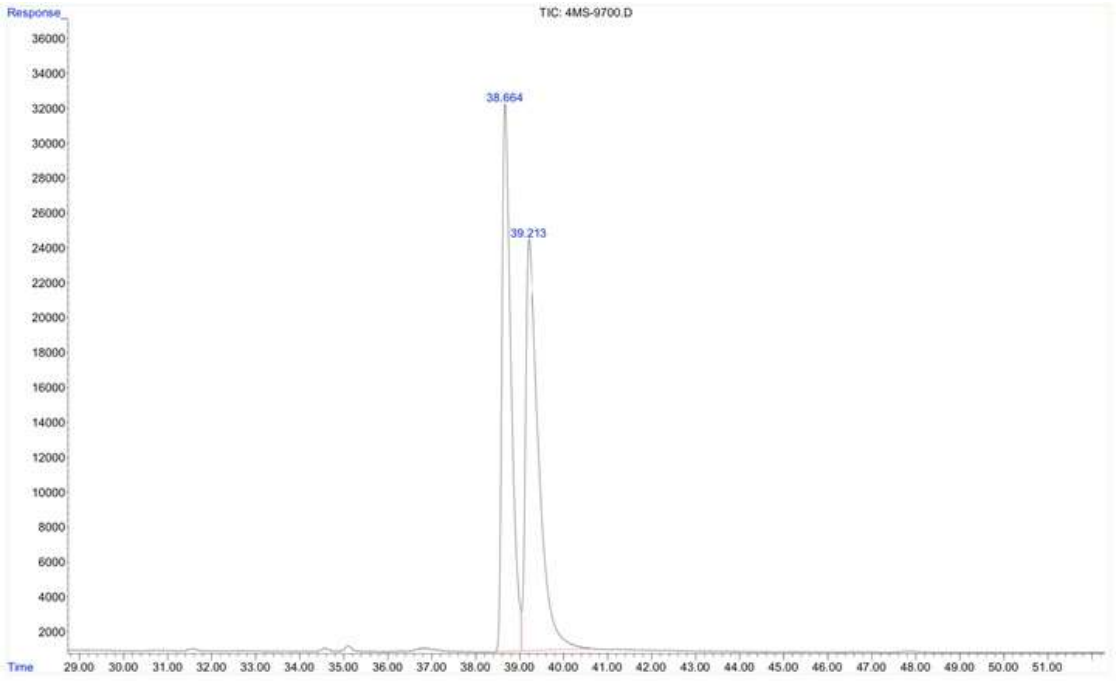
Chiral: (*S*)-*N*-(2,5-dimethylhex-1-en-3-yl)aniline (3e) (67% *ee*)



Signal 1: DAD1 A, Sig=254,16 Ref=360,100

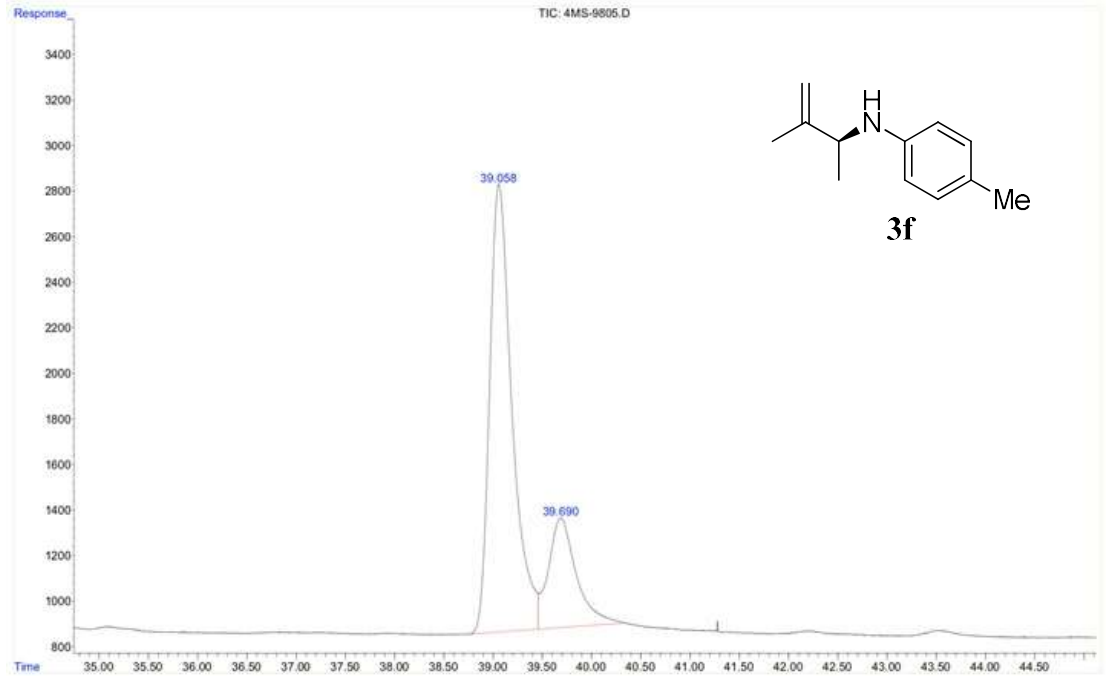
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.903	PM	0.5581	9980.16113	298.02954	83.4860
2	22.076	MP	0.5166	1974.12744	63.69362	16.5140
Totals :				1.19543e4	361.72316	

Racemic: 4-methyl-*N*-(2-methylbut-1-en-3-yl)aniline (3f)



Ret Time	Type	Width	Area	Start Time	End Time
38.664	BV	0.210	4484345	38.356	39.031
39.213	VB	0.290	4938940	39.031	40.632

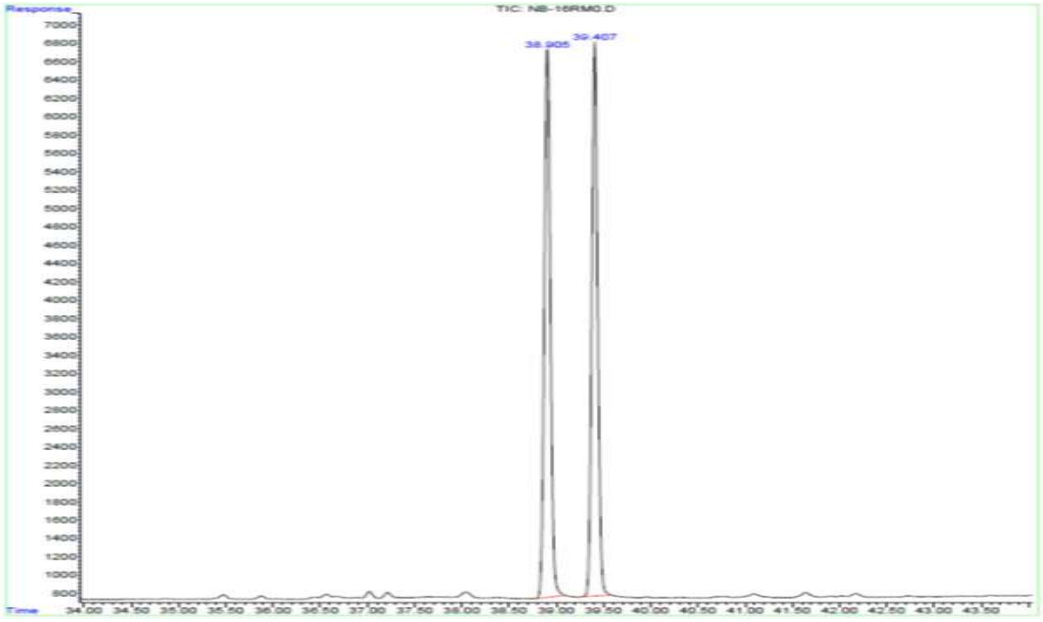
Chiral: 4-methyl-*N*-(2-methylbut-1-en-3-yl)aniline (3f) (53% ee)



3f

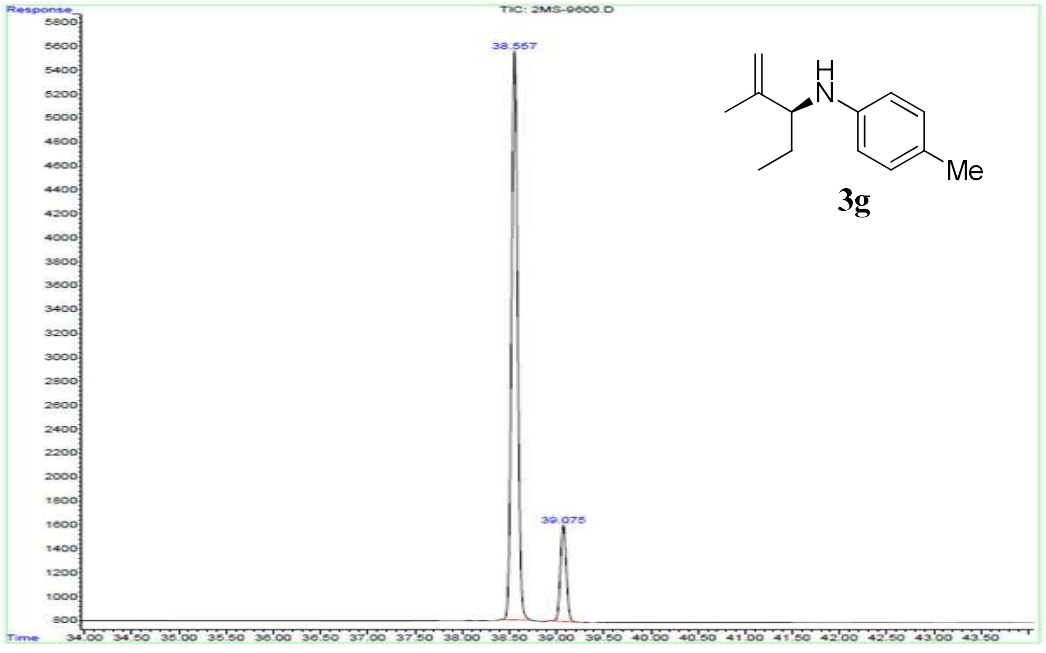
Ret Time	Type	Width	Area	Start Time	End Time
39.058	BV	0.237	310754	38.723	39.458
39.690	VB	0.291	95390	39.458	40.340

Racemic: 4-methyl-*N*-(2-methylpent-1-en-3-yl)aniline (3g)



R.T. min	Start min	End min	peak height	peak area
38.905	38.775	39.092	5972	270719
39.407	39.259	39.582	6017	260605

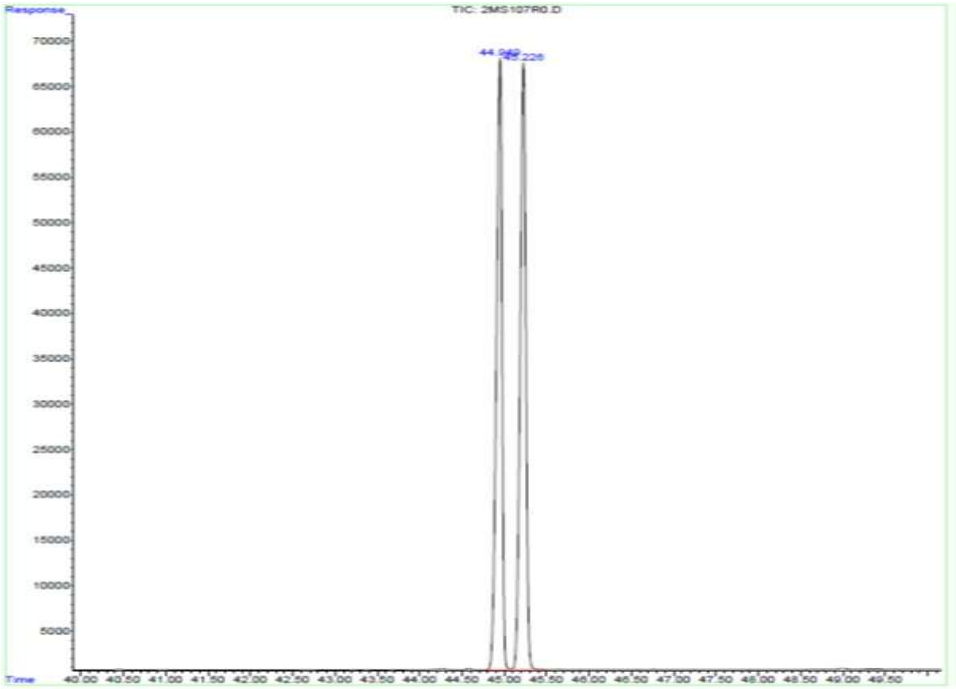
Chiral: (*S*)-4-methyl-*N*-(2-methylpent-1-en-3-yl)aniline (3g): (72% *ee*)



3g

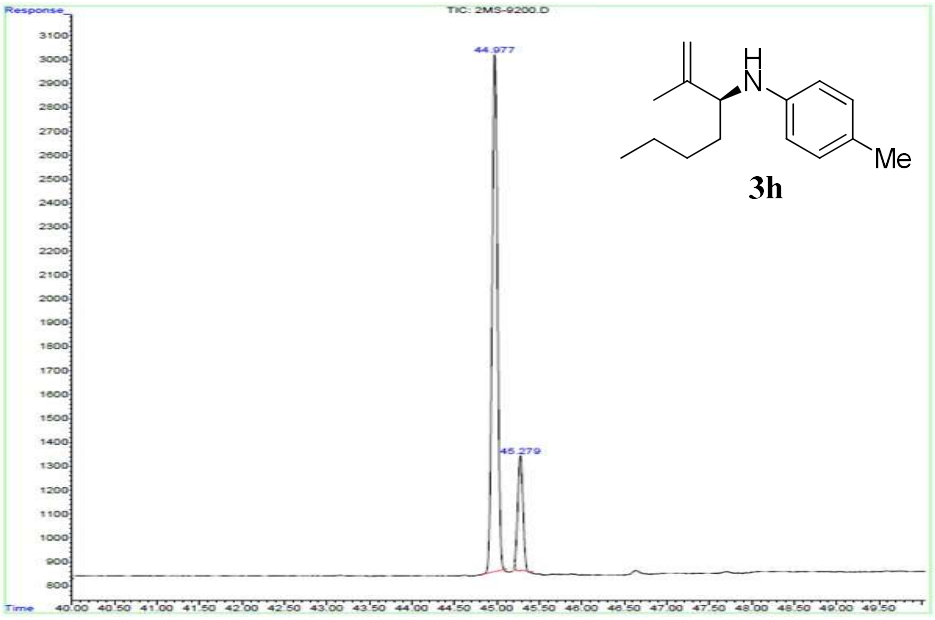
R.T. min	Start min	End min	peak height	peak area
38.557	38.410	38.730	4752	212764
39.075	38.925	39.198	807	35243

Racemic: 4-methyl-*N*-(2-methylhept-1-en-3-yl)aniline (3h)



R.T. min	Start min	End min	peak height	peak area
44.949	44.780	45.080	67237	3108182
45.226	45.080	45.487	66827	3120968

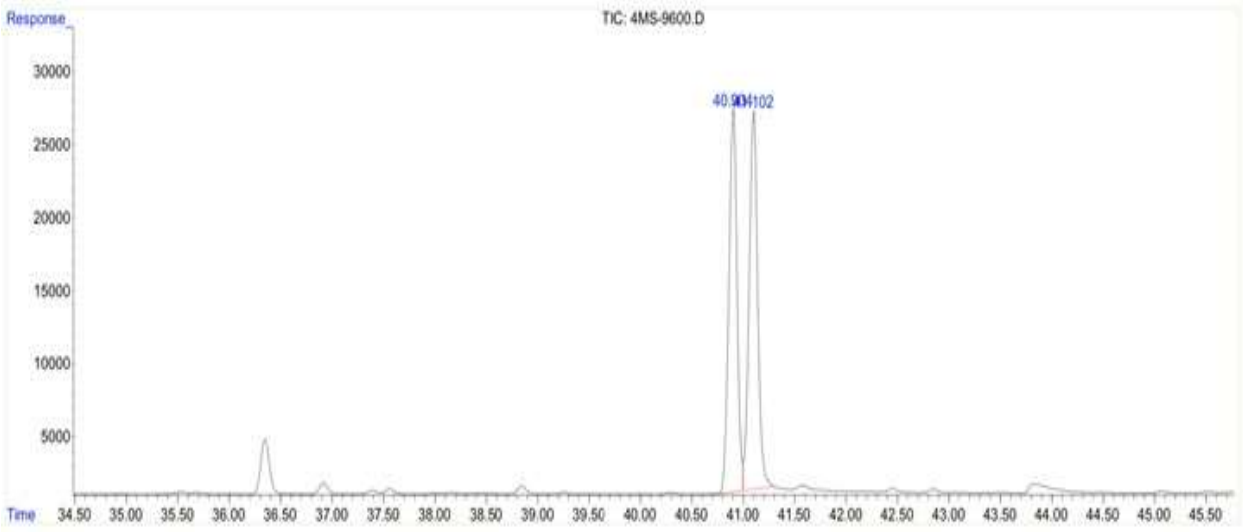
Chiral: (*S*)-4-methyl-*N*-(2-methylhept-1-en-3-yl)aniline (3h): (66% *ee*)



3h

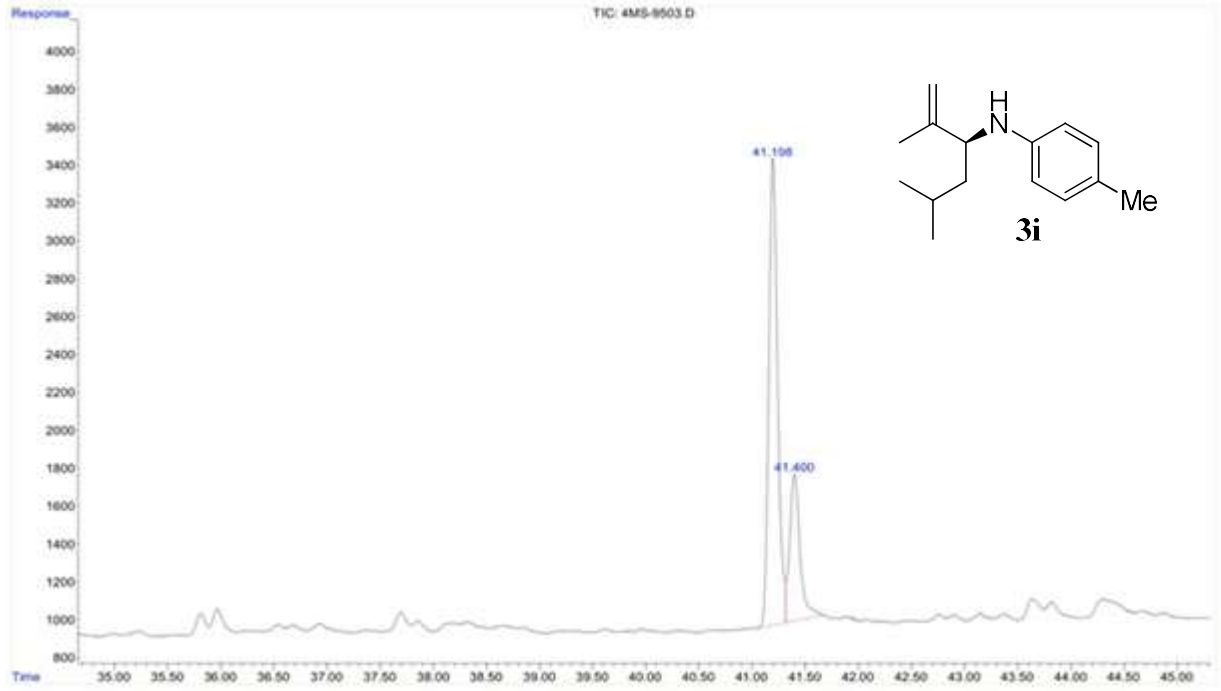
R.T. min	Start min	End min	peak height	peak area
44.977	44.834	45.093	2161	96305
45.279	45.154	45.399	473	20106

Racemic: 4-methyl-*N*-(2,5-dimethylhex-1-en-3-yl)aniline (3i)



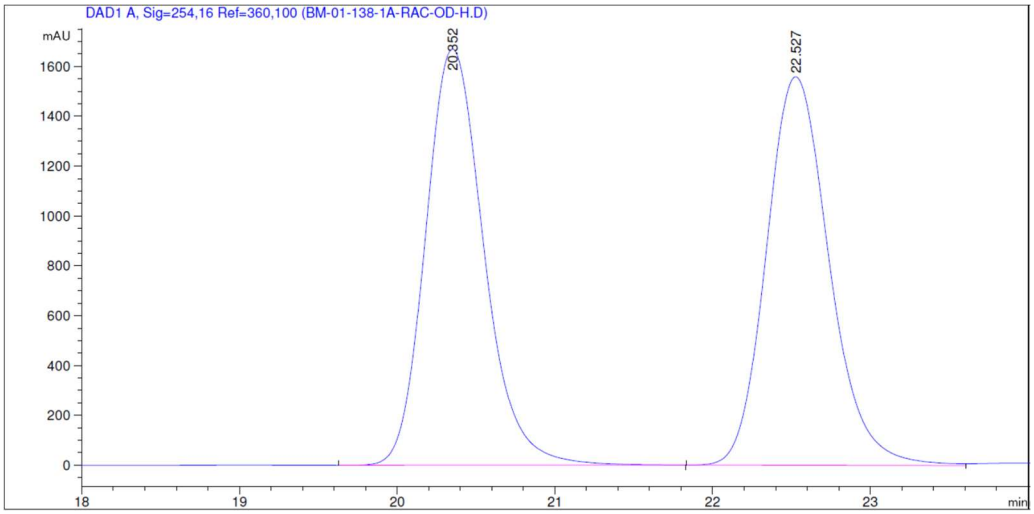
Ret Time	Type	Width	Area	Start Time	End Time
40.904	BV	0.086	1444689	40.738	40.998
41.102	VB	0.090	1502621	40.998	41.306

Chiral: (*S*)-4-methyl-*N*-(2,5-dimethylhex-1-en-3-yl)aniline (3i) (46% *ee*)



Ret Time	Type	Width	Area	Start Time	End Time
41.198	BV	0.090	141964	41.053	41.317
41.400	VB	0.103	52515	41.317	41.665

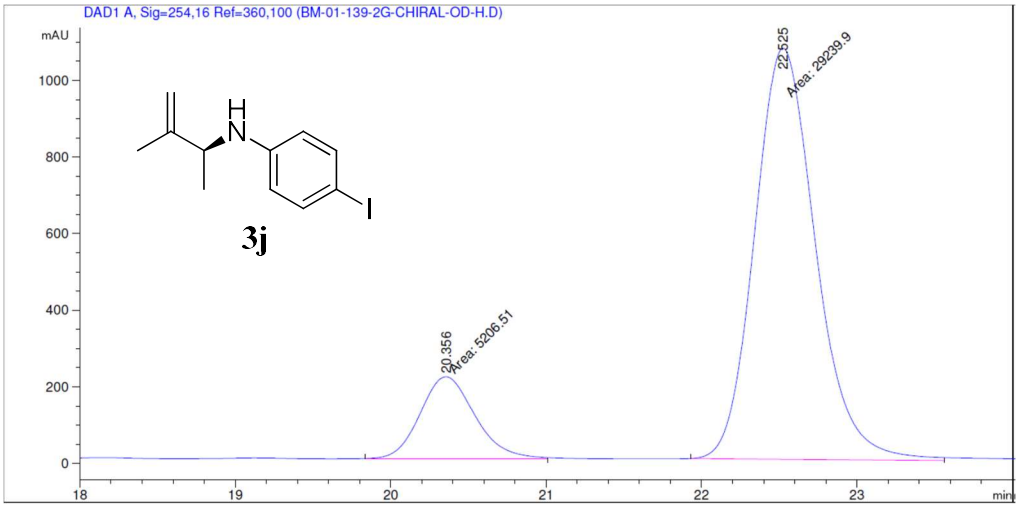
Racemic: 4-iodo-*N*-(3-methylbut-3-en-2-yl)aniline (3j)



Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.352	BB	0.3976	4.28942e4	1670.16455	49.8265
2	22.527	BV	0.4272	4.31929e4	1559.32898	50.1735
Totals :				8.60870e4	3229.49353	

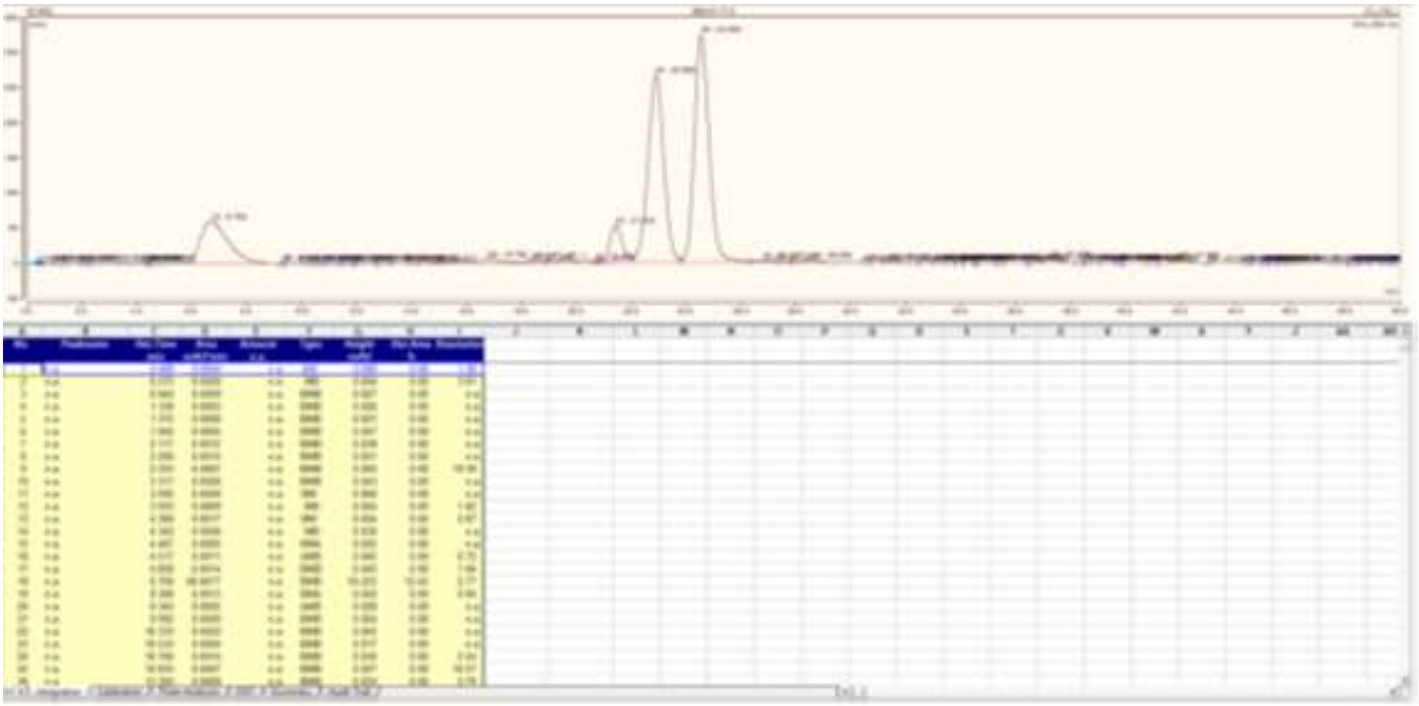
Chiral: (*S*)-4-iodo-*N*-(3-methylbut-3-en-2-yl)aniline (3j) (70% *ee*)



Signal 1: DAD1 A, Sig=254,16 Ref=360,100

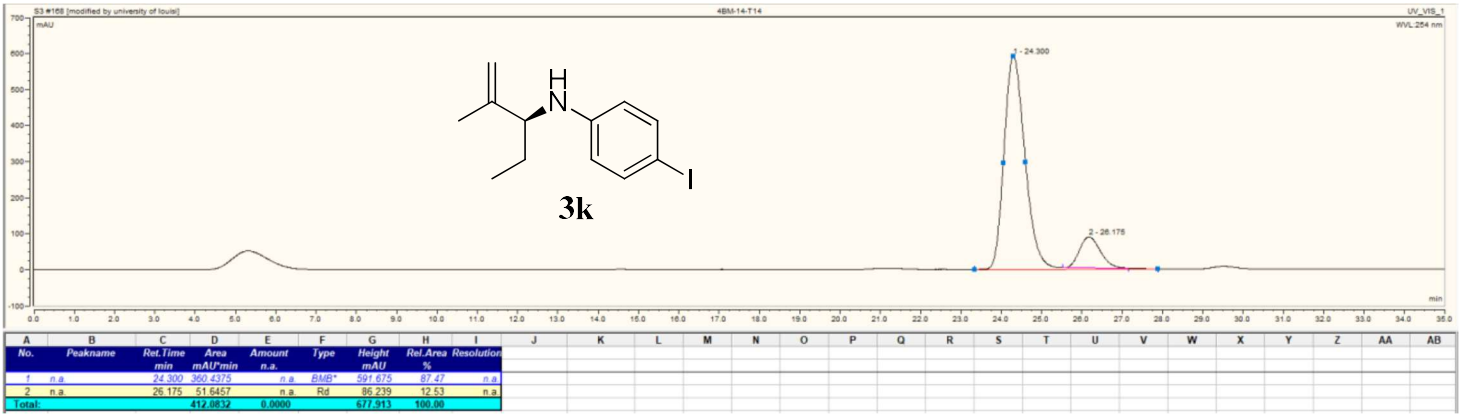
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.356	PM	0.4066	5206.51123	213.43393	15.1148
2	22.525	PM	0.4539	2.92399e4	1073.54565	84.8852
Totals :				3.44464e4	1286.97958	

Racemic: 4-iodo-*N*-(2-methylpent-1-en-3-yl)aniline (3k)



tr_1-22.90, tr_2-24.55

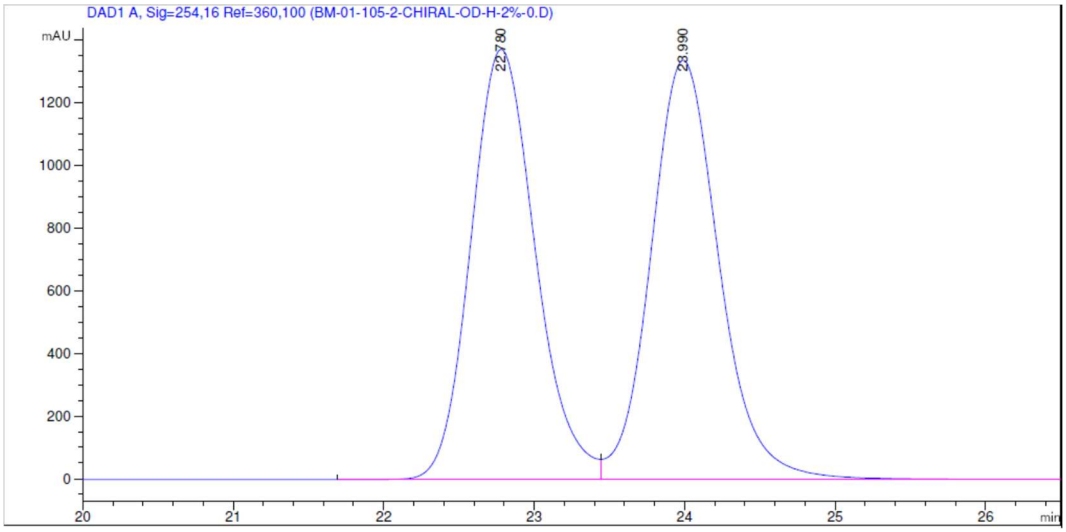
Chiral: (*S*)-4-iodo-*N*-(2-methylpent-1-en-3-yl)aniline (3k) (79% *ee*)



No.	Peakname	Ret.Time min	Area mAU*min	Amount n.a.	Type	Height mAU	Rel.Area %	Resolution
1	n.a.	24.300	360.4375	n.a.	BMB*	591.675	87.47	n.a.
2	n.a.	26.175	51.6457	n.a.	Rd	86.239	12.53	n.a.
Total:			412.0832	0.0000		677.913	100.00	

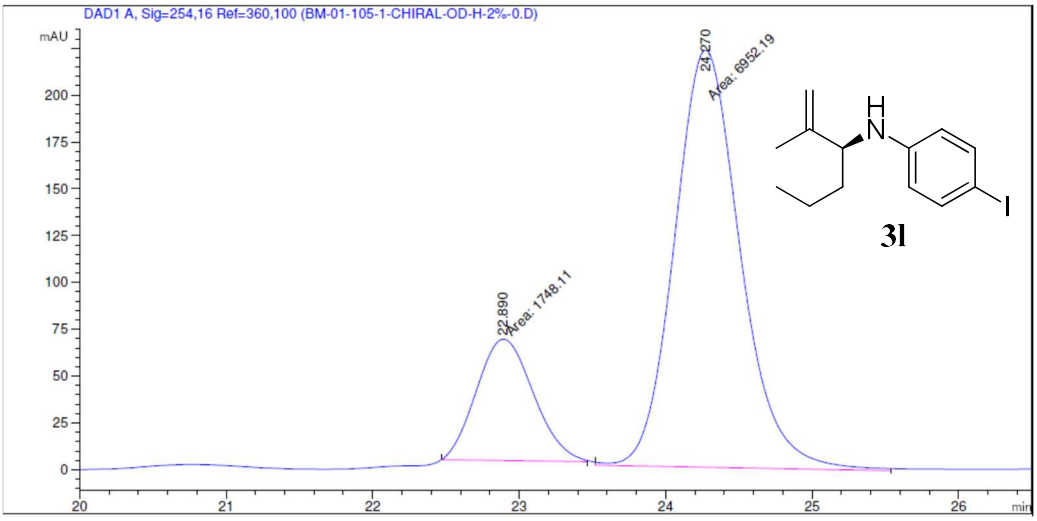
tr_1-23.15, tr_2-25.50

Racemic: 4-iodo-*N*-(2-methylhex-1-en-3-yl)aniline (3l)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.780	BV	0.4631	4.08410e4	1372.93347	49.2277
2	23.990	VB	0.4851	4.21225e4	1338.57227	50.7723
Totals :				8.29635e4	2711.50574	

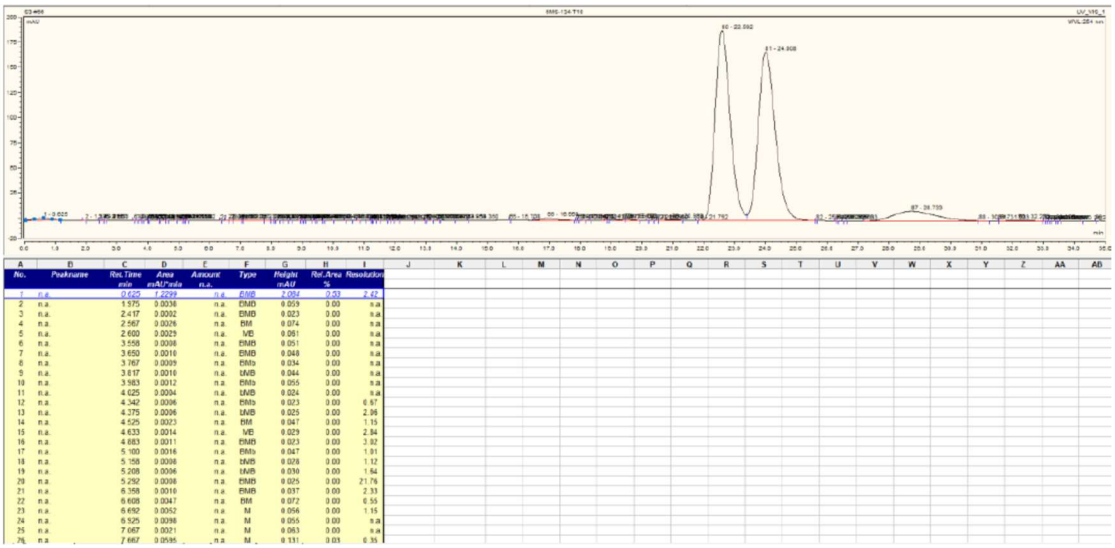
Chiral: (*S*)-4-iodo-*N*-(2-methylhex-1-en-3-yl)aniline (3l) (60% *ee*)



Signal 1: DAD1 A, Sig=254,16 Ref=360,100

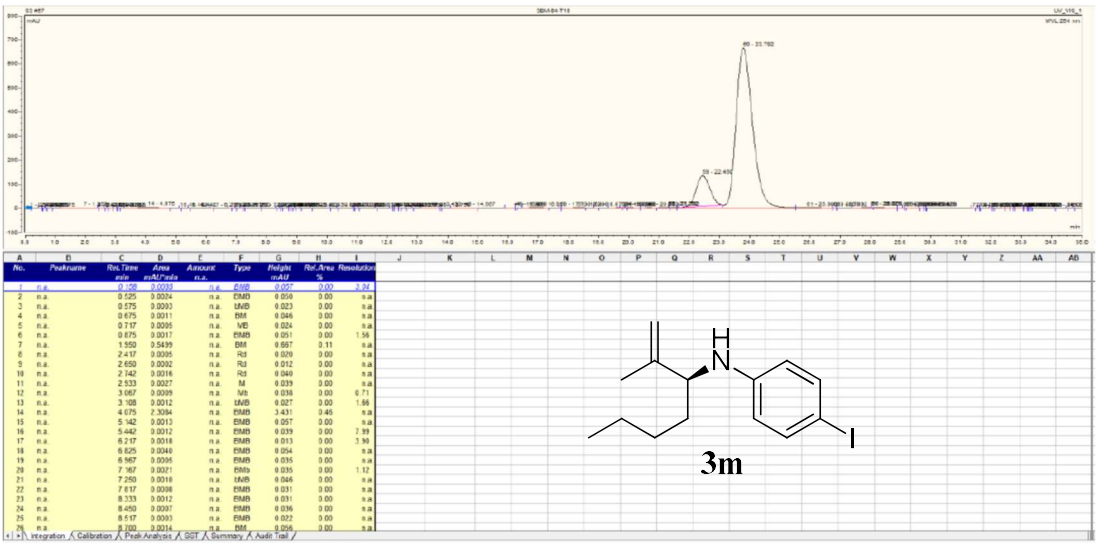
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.890	MM	0.4493	1748.11011	64.84074	20.0925
2	24.270	MM	0.5202	6952.18652	222.72963	79.9075
Totals :				8700.29663	287.57037	

Racemic: 4-iodo-*N*-(2-methylhept-1-en-3-yl)aniline (3m)



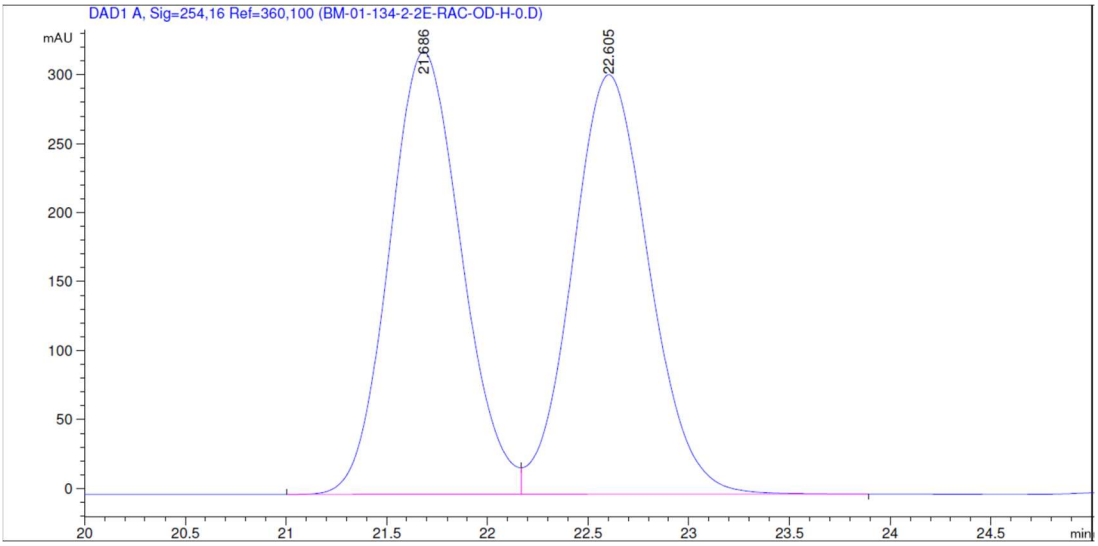
tr_1-22.59, tr_2-24.01

Chiral: (*S*)-4-iodo-*N*-(2-methylhept-1-en-3-yl)aniline (3m) (73% *ee*)



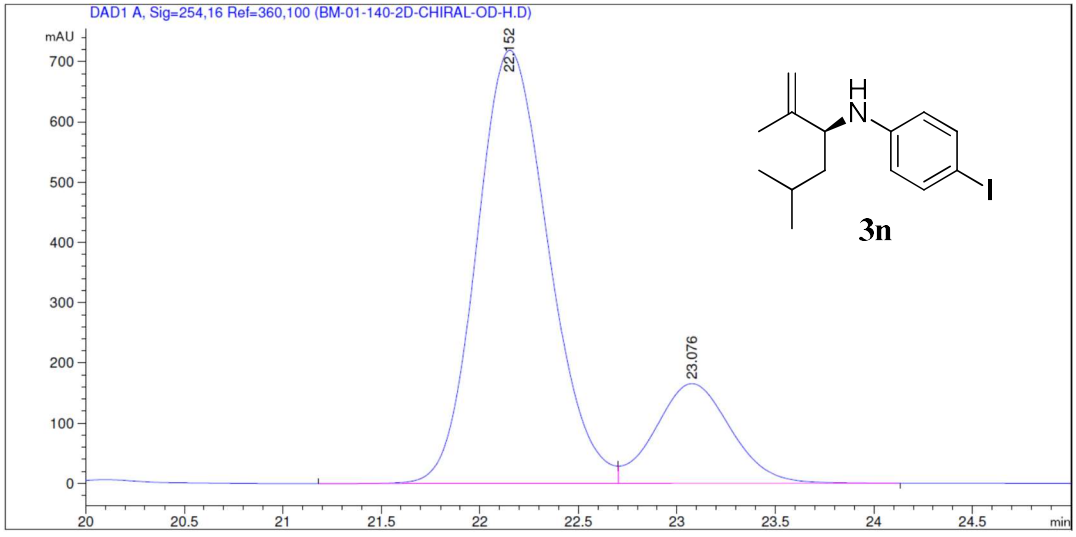
tr_1-22.45, tr_2-23.8

Racemic: *N*-(2,5-dimethylhex-1-en-3-yl)-4-iodoaniline (3n)



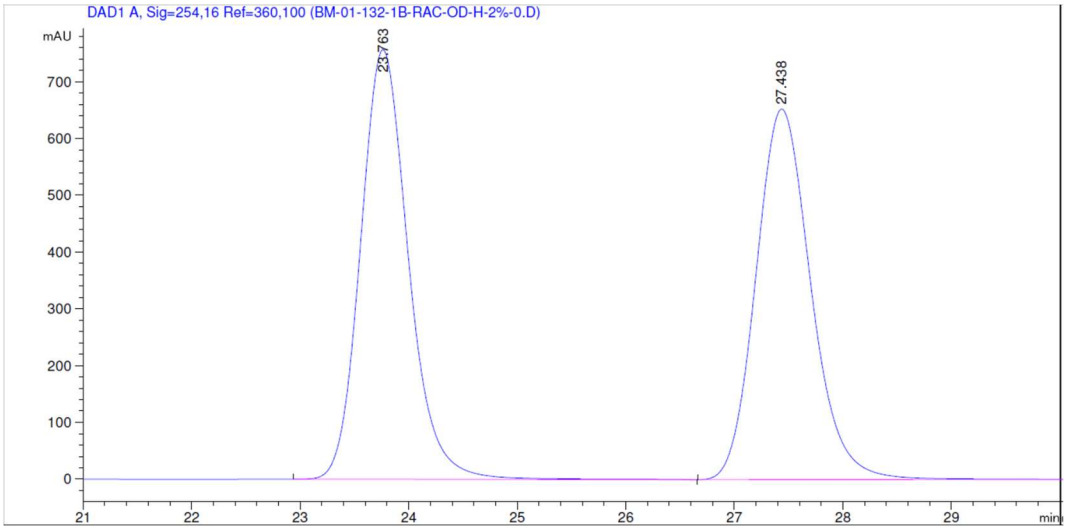
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.686	BV	0.3882	7981.36572	320.84698	49.7284
2	22.605	VB	0.4134	8068.55908	304.20215	50.2716
Totals :				1.60499e4	625.04913	

Chiral: (*S*)-*N*-(2,5-dimethylhex-1-en-3-yl)-4-iodoaniline (3n) (61% *ee*)



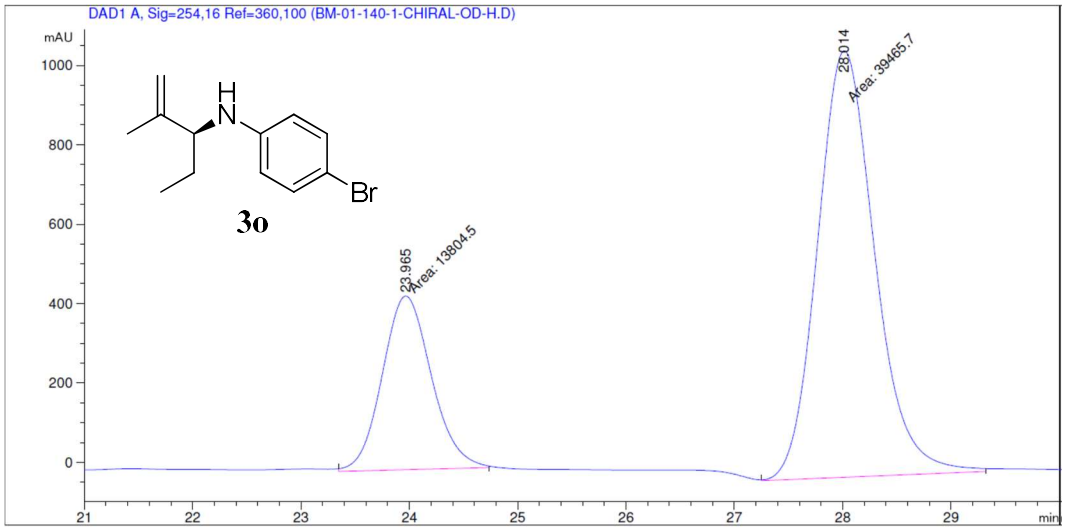
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.152	BV	0.3951	1.81897e4	719.21979	80.5138
2	23.076	VB	0.4103	4402.32813	165.50386	19.4862
Totals :				2.25920e4	884.72365	

Racemic: 4-bromo-*N*-(2-methylpent-1-en-3-yl)aniline (3o)



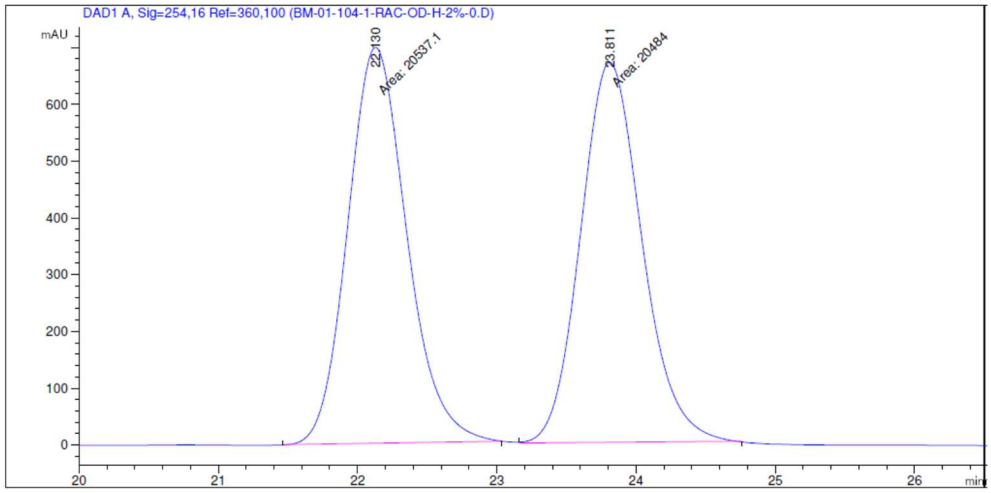
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.763	BB	0.4734	2.31897e4	756.89630	50.3111
2	27.438	BB	0.5472	2.29029e4	653.03748	49.6889
Totals :				4.60926e4	1409.93378	

Chiral: (*S*)-4-bromo-*N*-(2-methylpent-1-en-3-yl)aniline (3o) (48% *ee*)



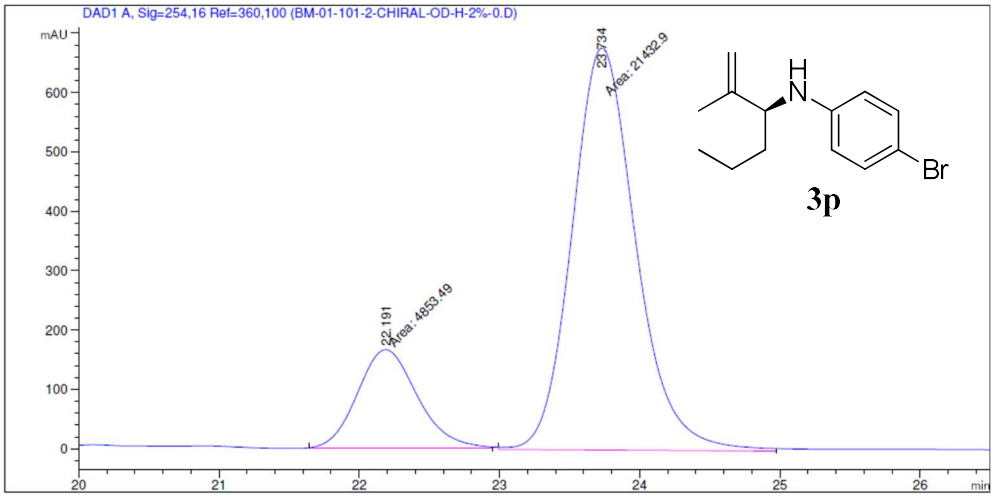
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.965	MM	0.5259	1.38045e4	437.45798	25.9141
2	28.014	MM	0.6123	3.94657e4	1074.28857	74.0859
Totals :				5.32701e4	1511.74655	

Racemic: 4-bromo-*N*-(2-methylhex-1-en-3-yl)aniline (3p)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.130	MM	0.4908	2.05371e4	697.40369	50.0646
2	23.811	MM	0.5100	2.04840e4	669.34784	49.9354
Totals :				4.10211e4	1366.75153	

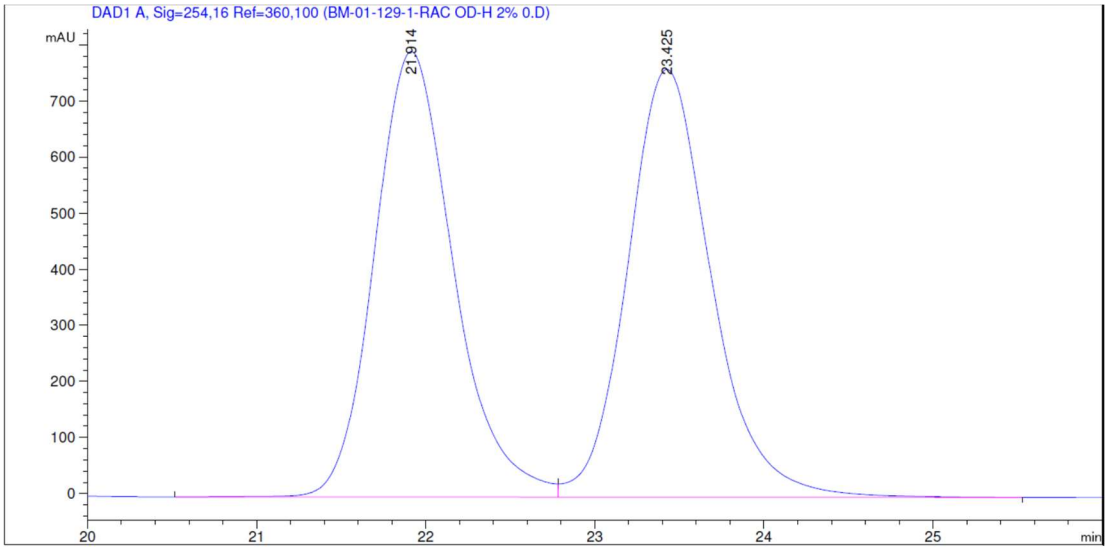
Chiral: (*S*)-4-bromo-*N*-(2-methylhex-1-en-3-yl)aniline (3p) (63% *ee*)



Signal 1: DAD1 A, Sig=254,16 Ref=360,100

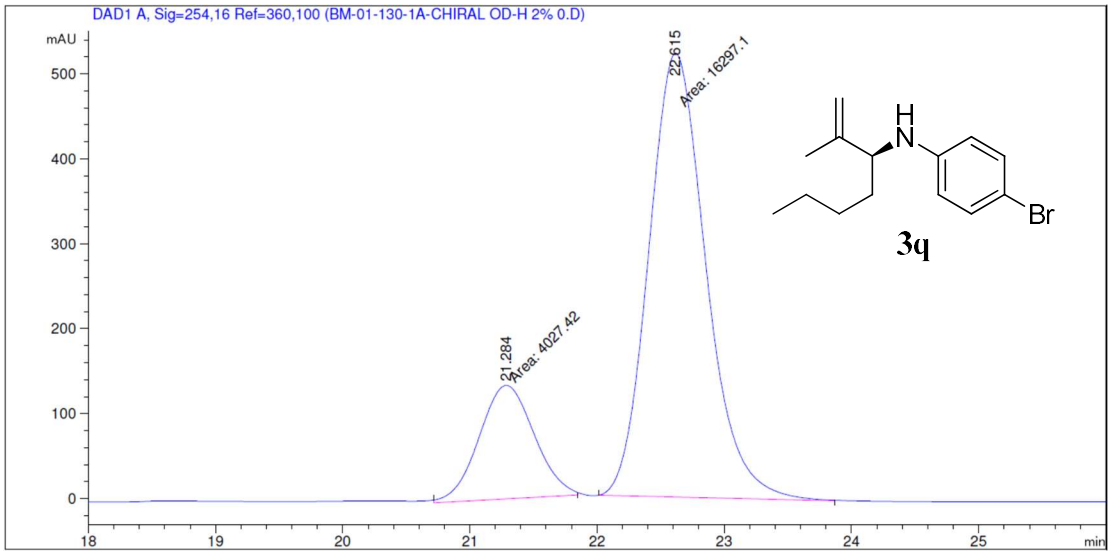
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.191	MM	0.4904	4853.48682	164.95062	18.4639
2	23.734	MM	0.5273	2.14329e4	677.49182	81.5361
Totals :				2.62864e4	842.44244	

Racemic: 4-bromo-*N*-(2-methylhept-1-en-3-yl)aniline (3q)



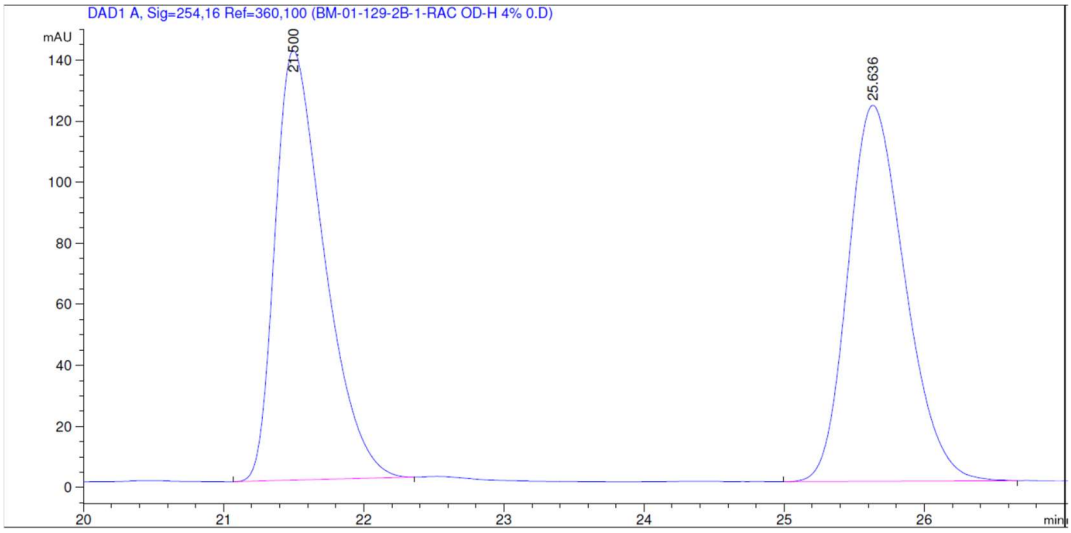
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.914	BV	0.5113	2.58309e4	794.48883	49.5655
2	23.425	VB	0.5200	2.62838e4	762.81140	50.4345
Totals :				5.21147e4	1557.30023	

Chiral: (*S*)-4-bromo-*N*-(2-methylhept-1-en-3-yl)aniline (3q) (60% *ee*)



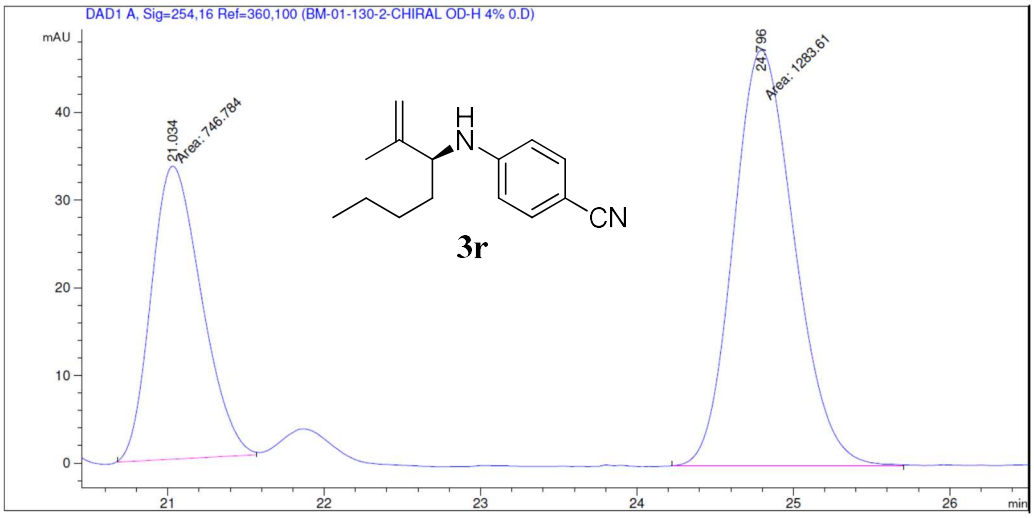
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.284	MM	0.5019	4027.42285	133.72746	19.8155
2	22.615	PM	0.5199	1.62971e4	522.41565	80.1845
Totals :				2.03246e4	656.14311	

Racemic: 4-((2-methylhept-1-en-3-yl)amino)benzonitrile (3r)



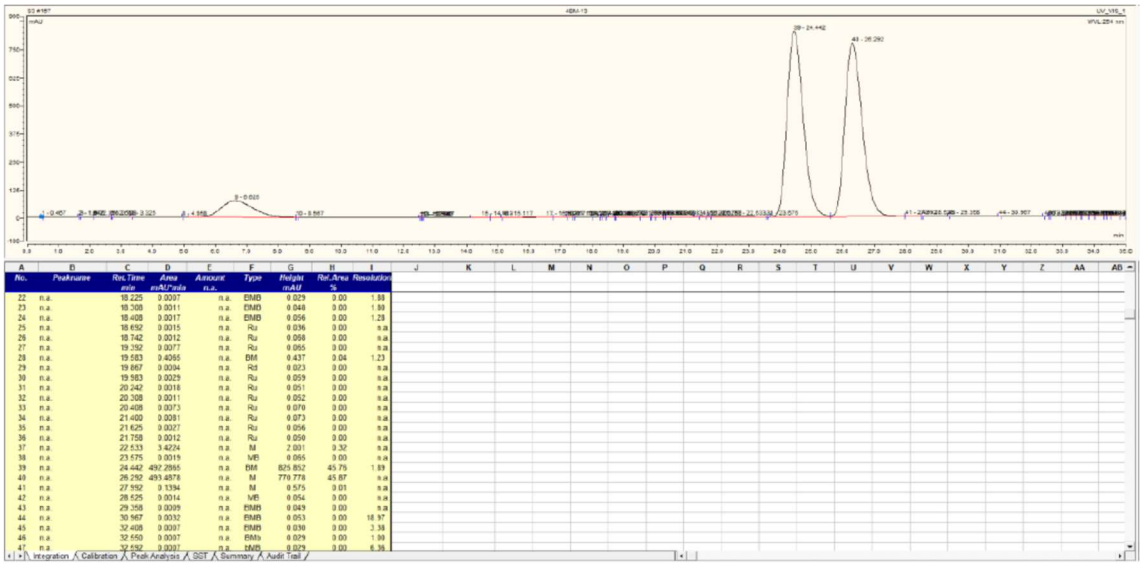
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.500	BB	0.3728	3436.03882	140.74513	49.6385
2	25.636	BB	0.4361	3486.09033	123.21353	50.3615
Totals :				6922.12915	263.95866	

Chiral: (*S*)-4-((2-methylhept-1-en-3-yl)amino)benzonitrile (3r) (26% *ee*)



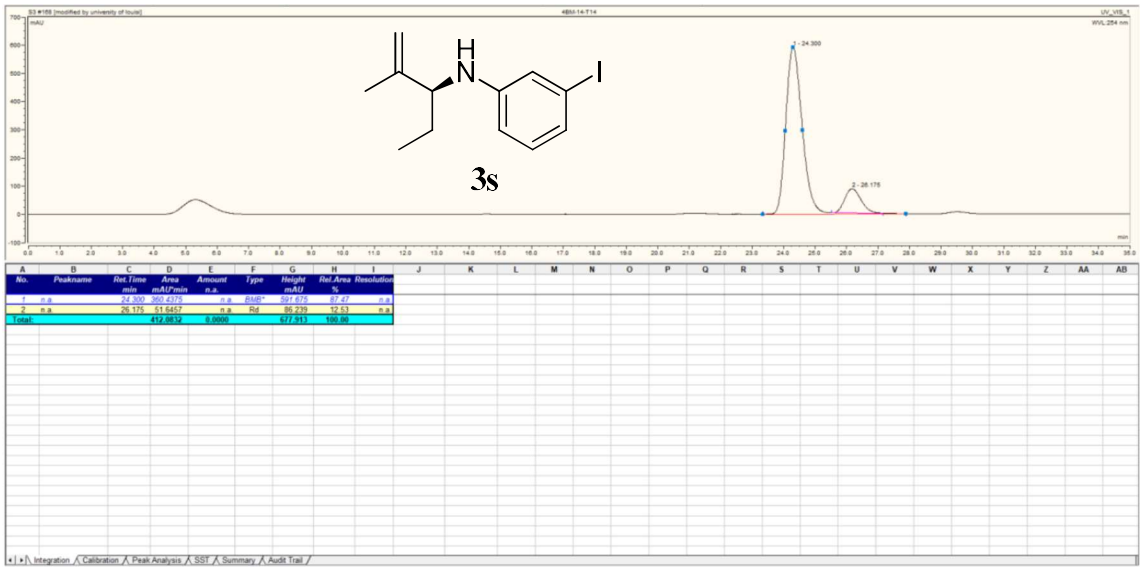
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.034	PM	0.3724	746.78448	33.41962	36.7802
2	24.796	PM	0.4516	1283.61487	47.37314	63.2198
Totals :				2030.39935	80.79276	

Racemic: 3-iodo-*N*-(2-methylpent-1-en-3-yl)aniline (3s)



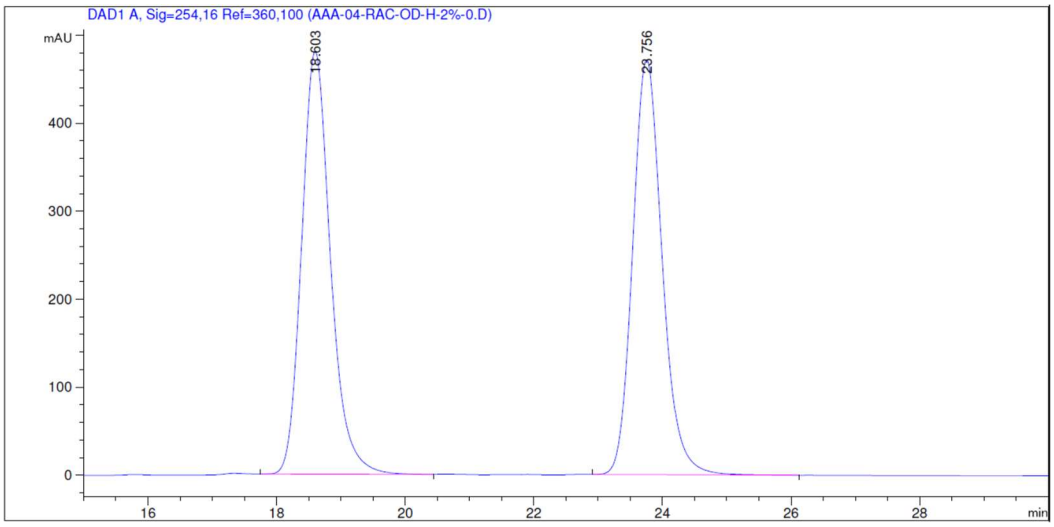
(tr_1-24.44, tr_2-26.29)

Chiral: (*S*)-3-iodo-*N*-(2-methylpent-1-en-3-yl)aniline (3s) (75% *ee*)



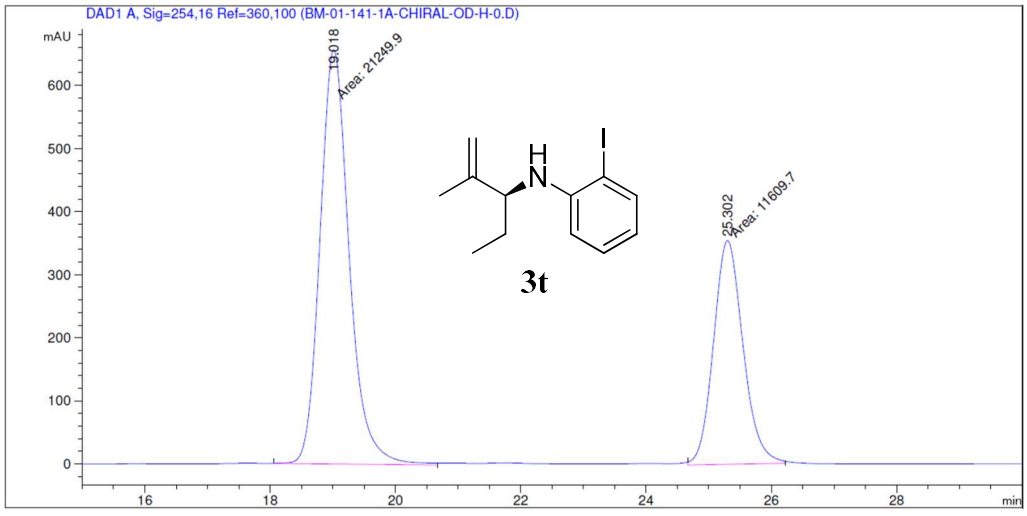
(tr_1-24.30, tr_2-26.18)

Racemic: 2-iodo-*N*-(2-methylpent-1-en-3-yl)aniline (3t)



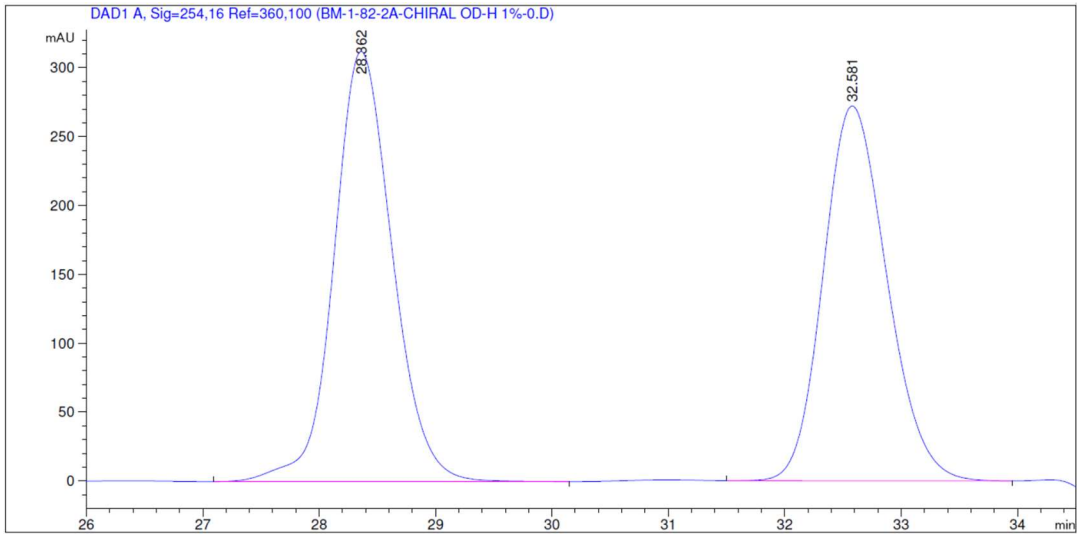
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.603	BB	0.4773	1.49611e4	480.44565	49.9420
2	23.756	BB	0.4909	1.49958e4	471.74524	50.0580
Totals :				2.99569e4	952.19089	

Chiral: (*S*)-2-iodo-*N*-(2-methylpent-1-en-3-yl)aniline (3t) (29% ee)



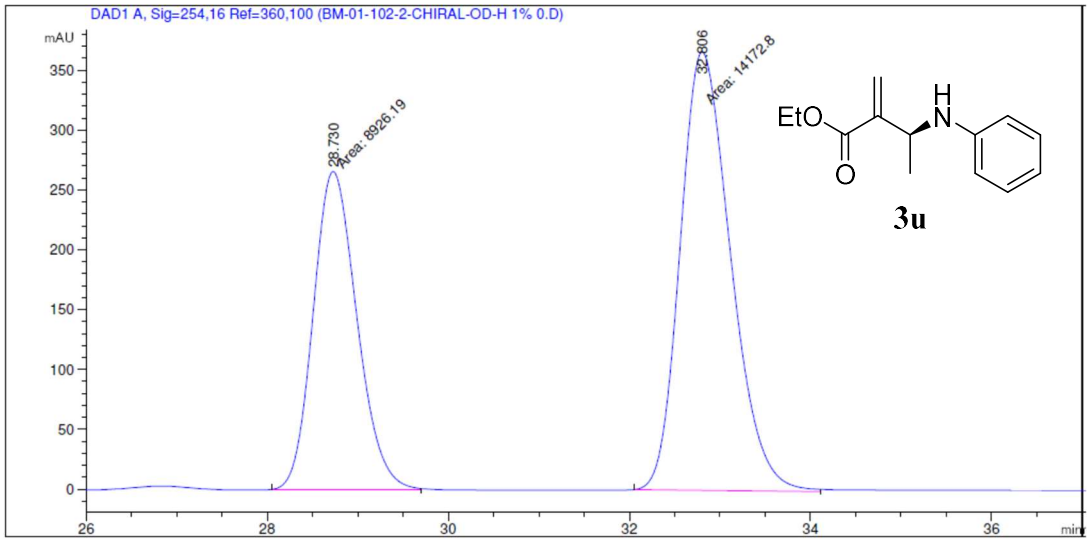
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.018	PM	0.5393	2.12499e4	656.67297	64.6688
2	25.302	MM	0.5457	1.16097e4	354.56409	35.3312
Totals :				3.28596e4	1011.23706	

Racemic: Ethyl 2-methylene-3-(phenylamino)butanoate (3u)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.362	BB	0.5366	1.08856e4	312.35538	51.2626
2	32.581	BB	0.5936	1.03493e4	272.20889	48.7374
Totals :				2.12349e4	584.56427	

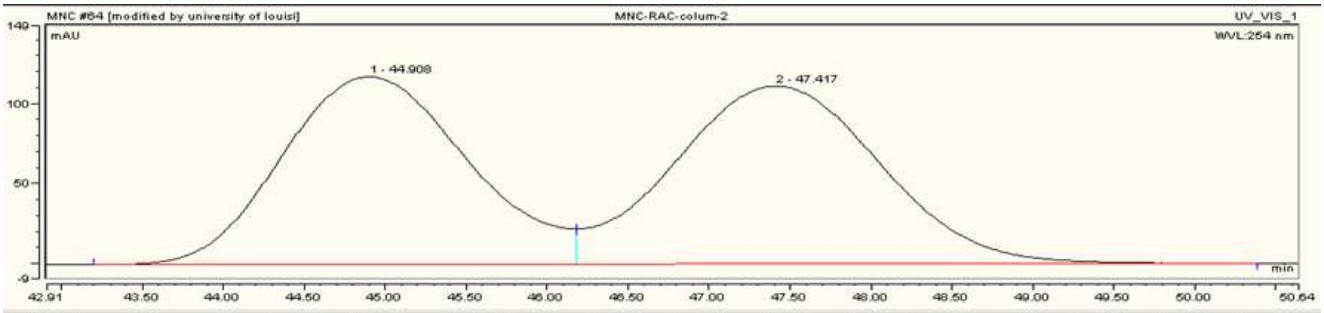
Chiral: (*S*)-ethyl 2-methylene-3-(phenylamino)butanoate (3u) (23% *ee*)



Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.730	MM	0.5598	8926.19336	265.74686	38.6433
2	32.806	PM	0.6451	1.41728e4	366.14670	61.3567
Totals :				2.30990e4	631.89355	

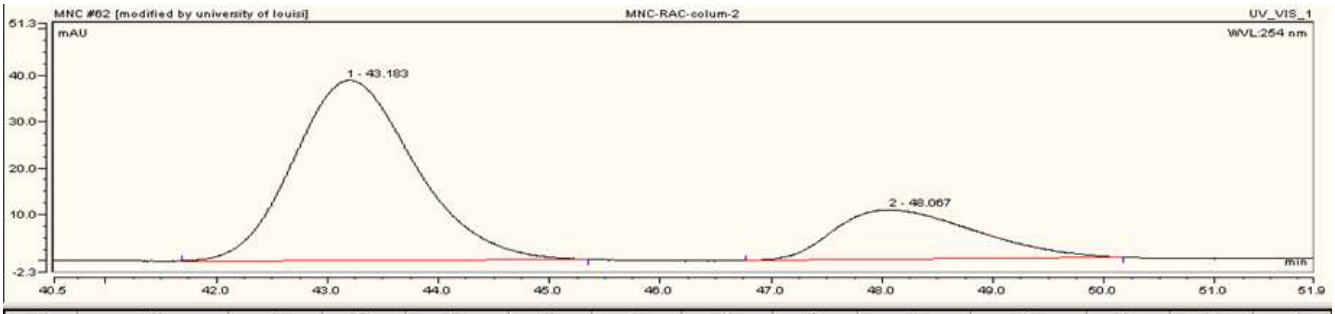
Racemic: Ethyl 2-methylene-3-(phenylamino)butanoate (3u)



No.	Peakname	Ret.Time min	Area mAU*min	Amount	Type	Height mAU	Rel.Area %	Resolution
1	n.a.	44.908	156.1257	n.a.	BM	117.233	48.62	1.11
2	n.a.	47.417	165.0079	n.a.	MB	111.210	51.38	n.a.
Total:			321.1336	0.0000		228.443	100.00	

RAC (OD-H column) 0.3 ml flow rate and 99.3% hexane 0.7% IPA, RT = 44 and 48 run time 80 min.

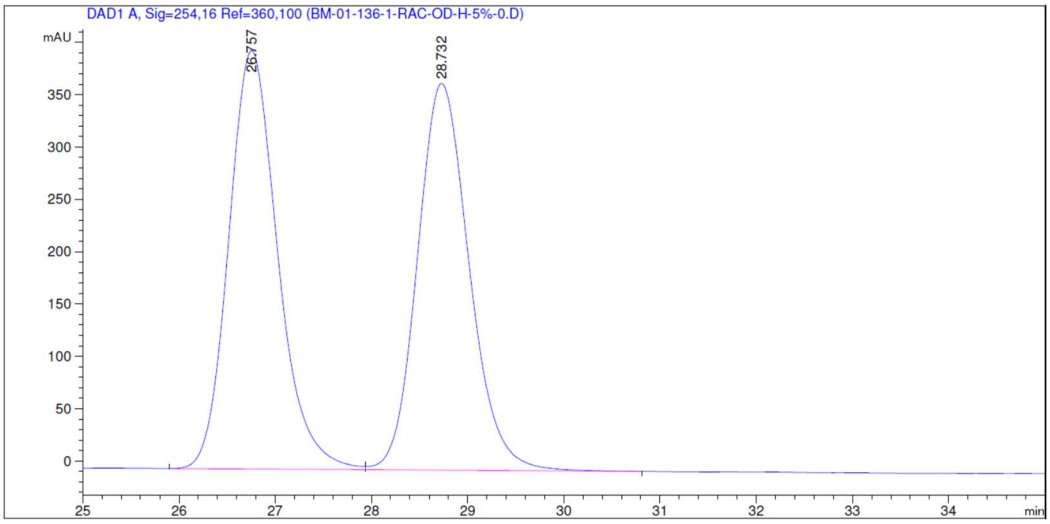
Chiral: (*S*)-ethyl 2-methylene-3-(phenylamino)butanoate (3u) (51% *ee*)



No.	Peakname	Ret.Time min	Area mAU*min	Amount	Type	Height mAU	Rel.Area %	Resolution
1	n.a.	43.183	49.1514	n.a.	BMB	38.822	75.68	2.22
2	n.a.	48.067	15.7984	n.a.	BMB	10.651	24.32	n.a.
Total:			64.9498	0.0000		49.473	100.00	

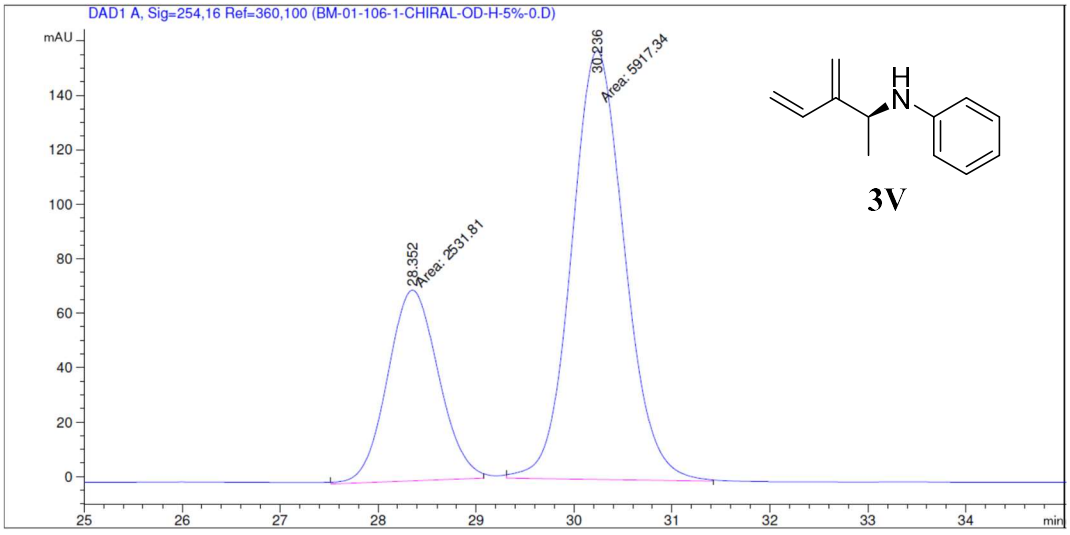
(OD-H column) 0.3 ml flow rate and 99.3% hexane 0.7% IPA, RT = 43 and 48 run time 80 min.

Racemic: *N*-(3-methylenepent-4-en-2-yl)aniline (3v)



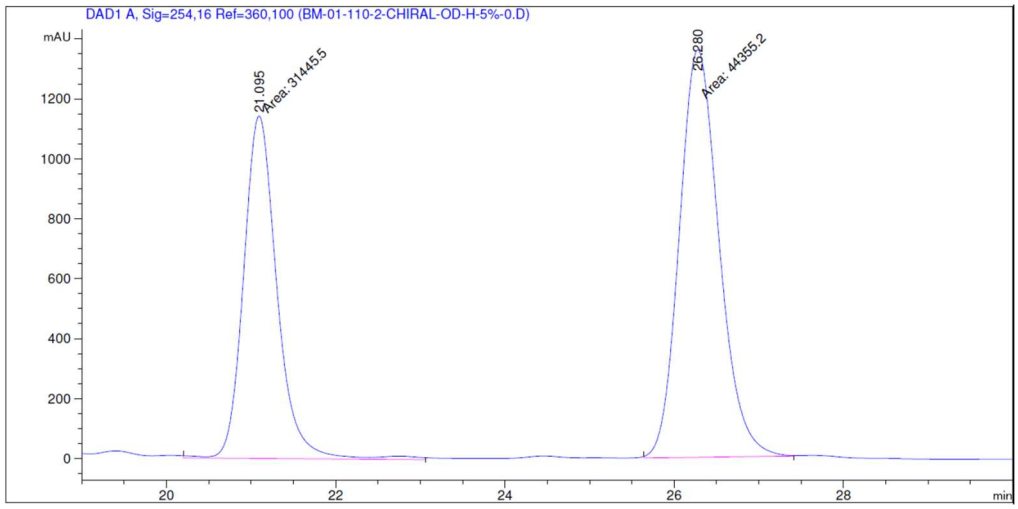
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.757	BV	0.5463	1.41309e4	399.82385	50.5862
2	28.732	VB	0.5759	1.38034e4	369.47177	49.4138
Totals :				2.79343e4	769.29562	

Chiral: (*S*)-*N*-(3-methylenepent-4-en-2-yl)aniline (3v) (40% *ee*)



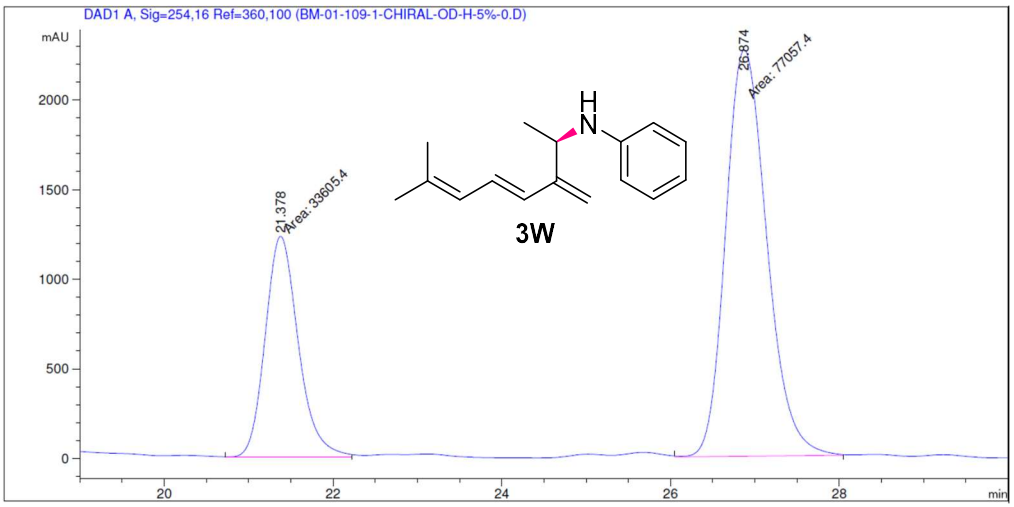
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.352	MM	0.6029	2531.80664	69.99104	29.9652
2	30.236	MM	0.6267	5917.33887	157.37259	70.0348
Totals :				8449.14551	227.36362	

Racemic: (S,E)-N-(7-methyl-3-methyleneocta-4,6-dien-2-yl)aniline (3w)



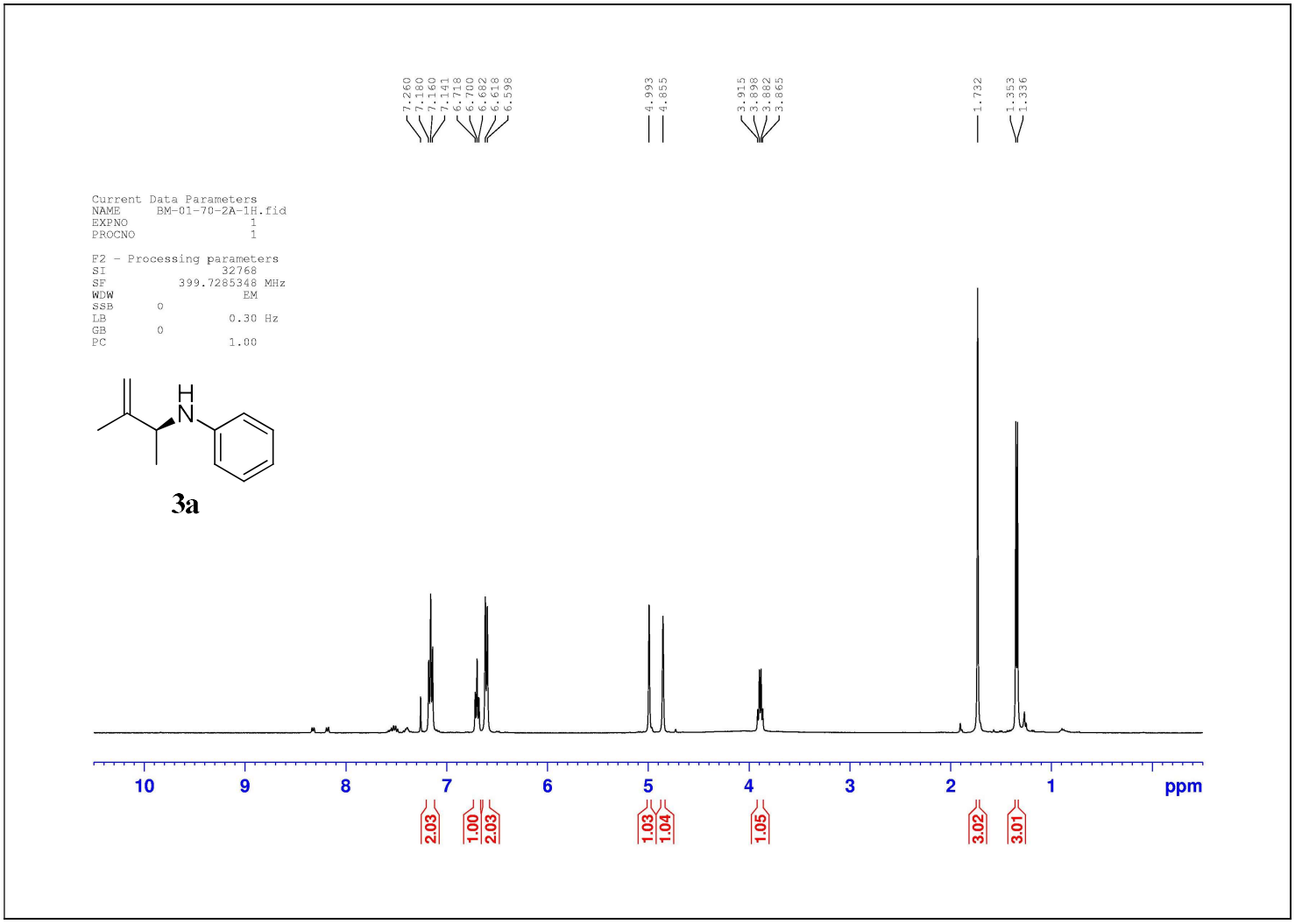
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.095	MM	0.4585	3.14455e4	1142.96802	41.4845
2	26.280	MM	0.5436	4.43552e4	1359.90491	58.5155
Totals :				7.58008e4	2502.87292	

Chiral: (S,E)-N-(7-methyl-3-methyleneocta-4,6-dien-2-yl)aniline (3w) (39% *ee*)

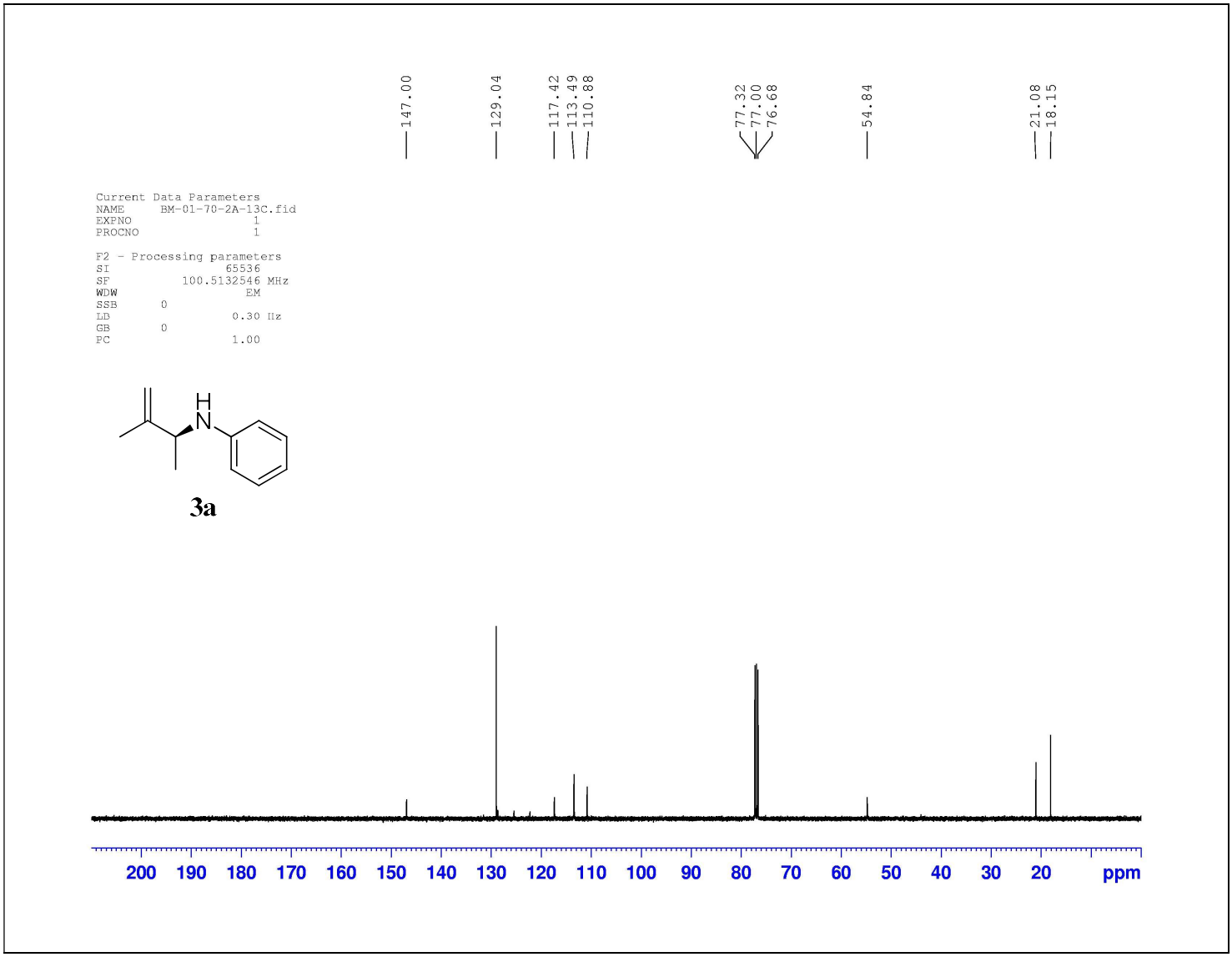


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.378	MM	0.4549	3.36054e4	1231.21655	30.3674
2	26.874	MM	0.5666	7.70574e4	2266.49707	69.6326
Totals :				1.10663e5	3497.71362	

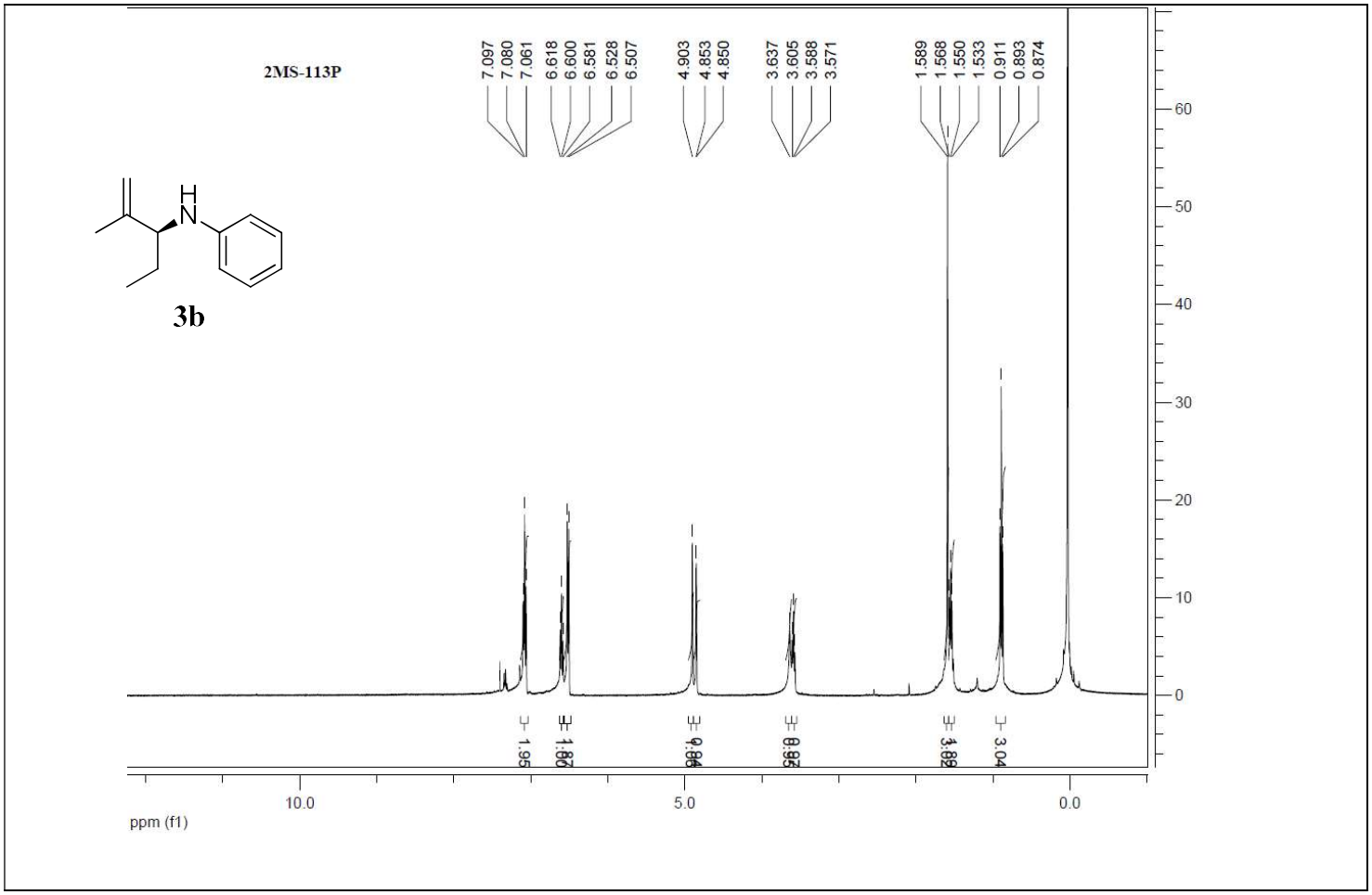
10. ^{1}H and ^{13}C NMR Spectra of the Products



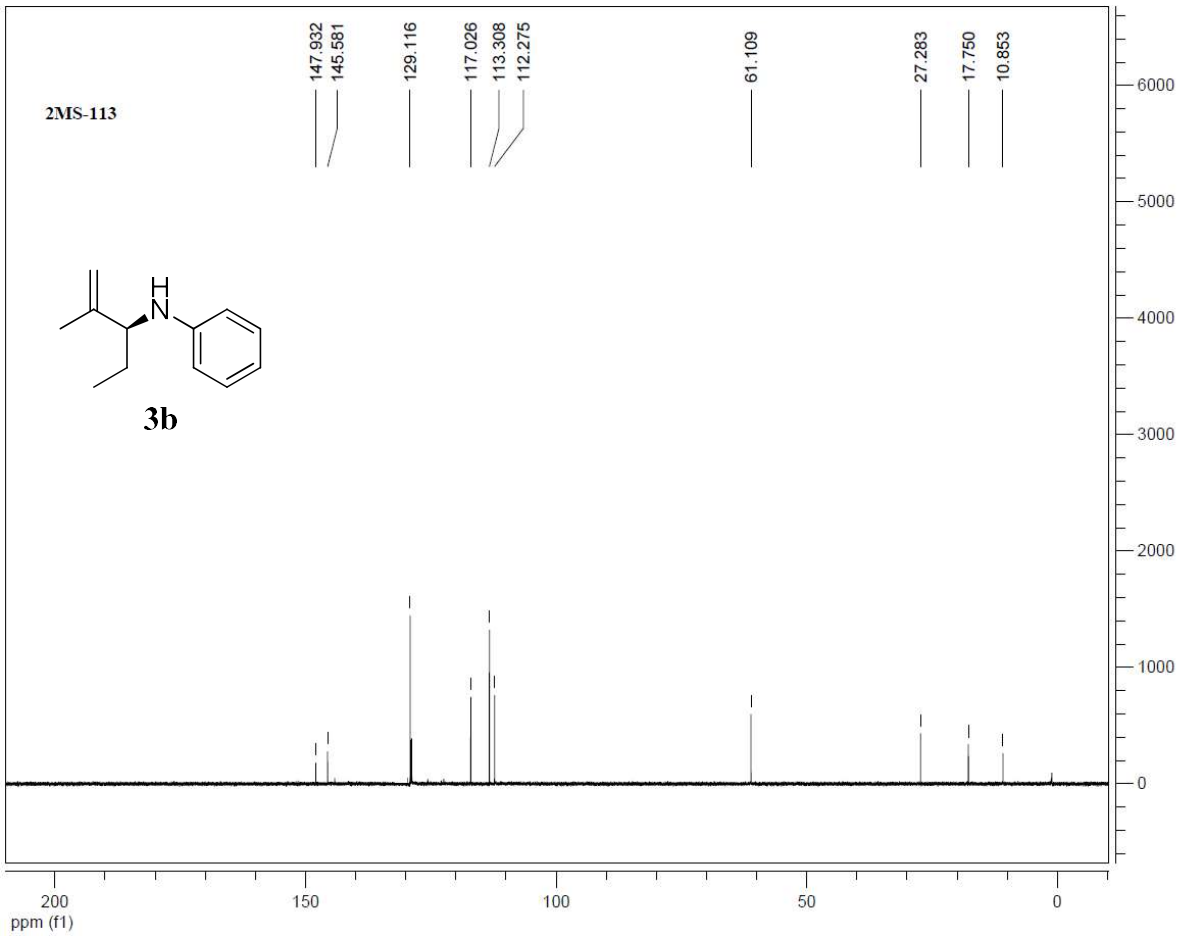
^{1}H Spectra of **3a** in $CDCl_3$.



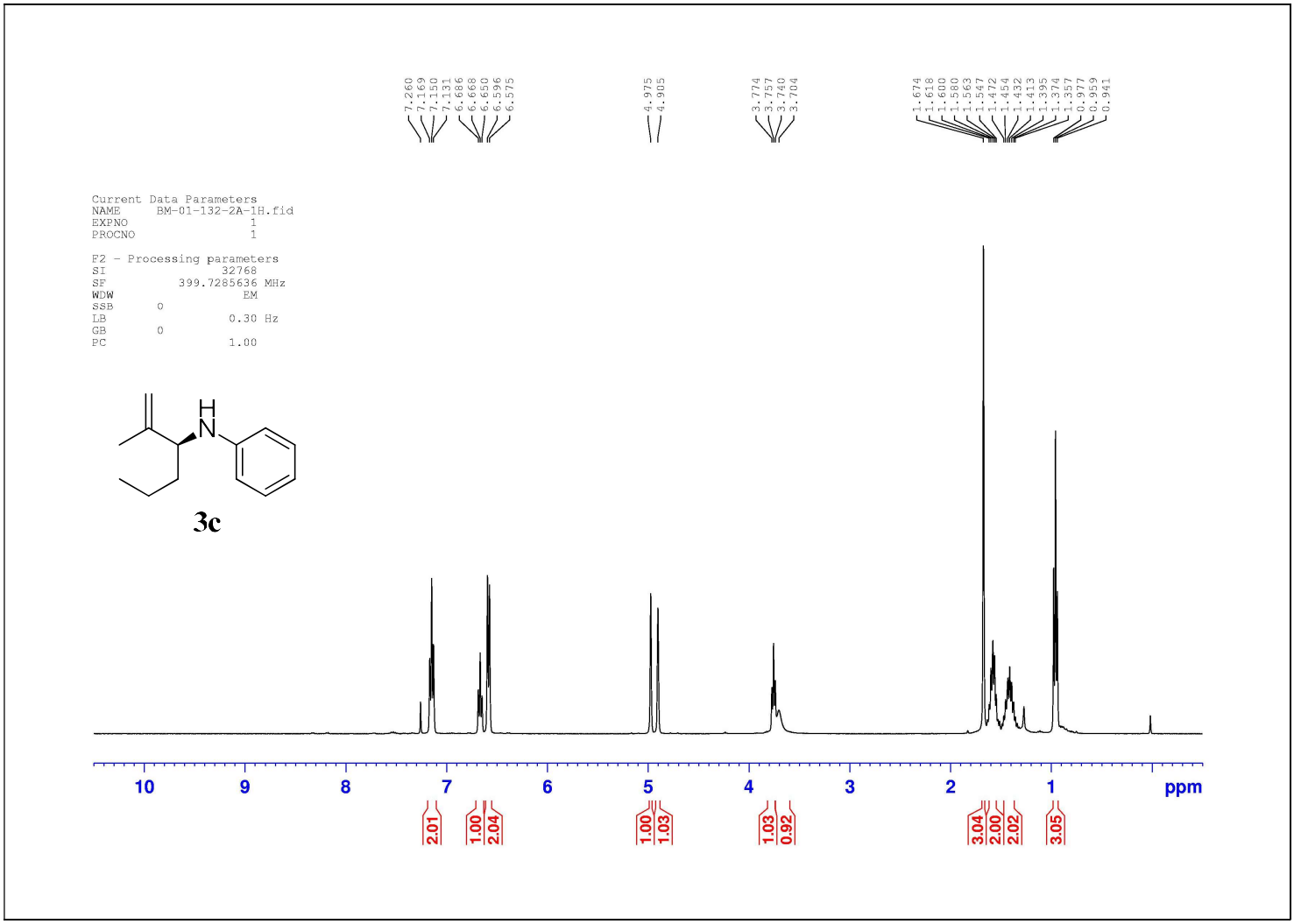
^{13}C NMR Spectra of **3a** in $CDCl_3$.



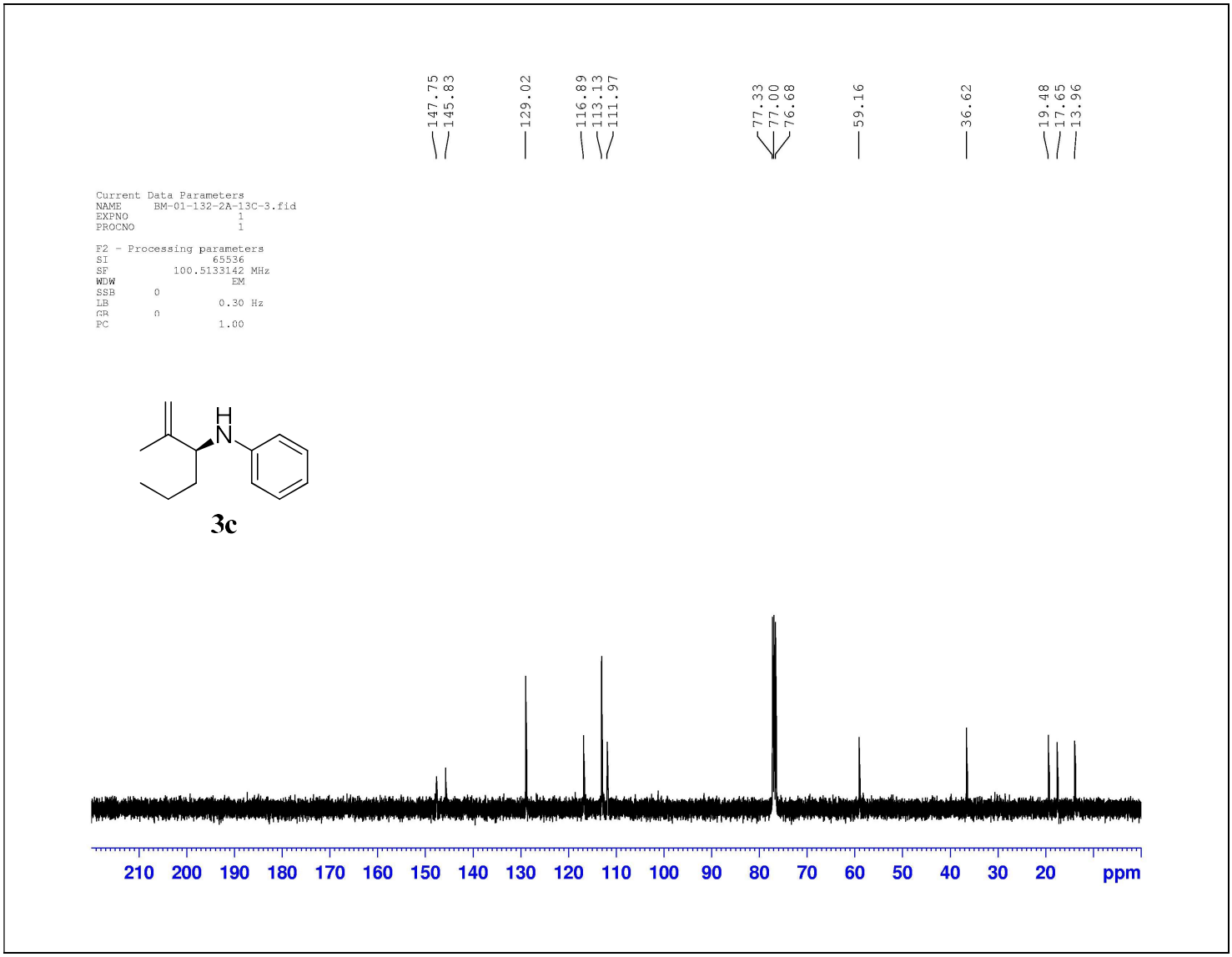
^{1}H Spectra of **3b** in $CDCl_3$.



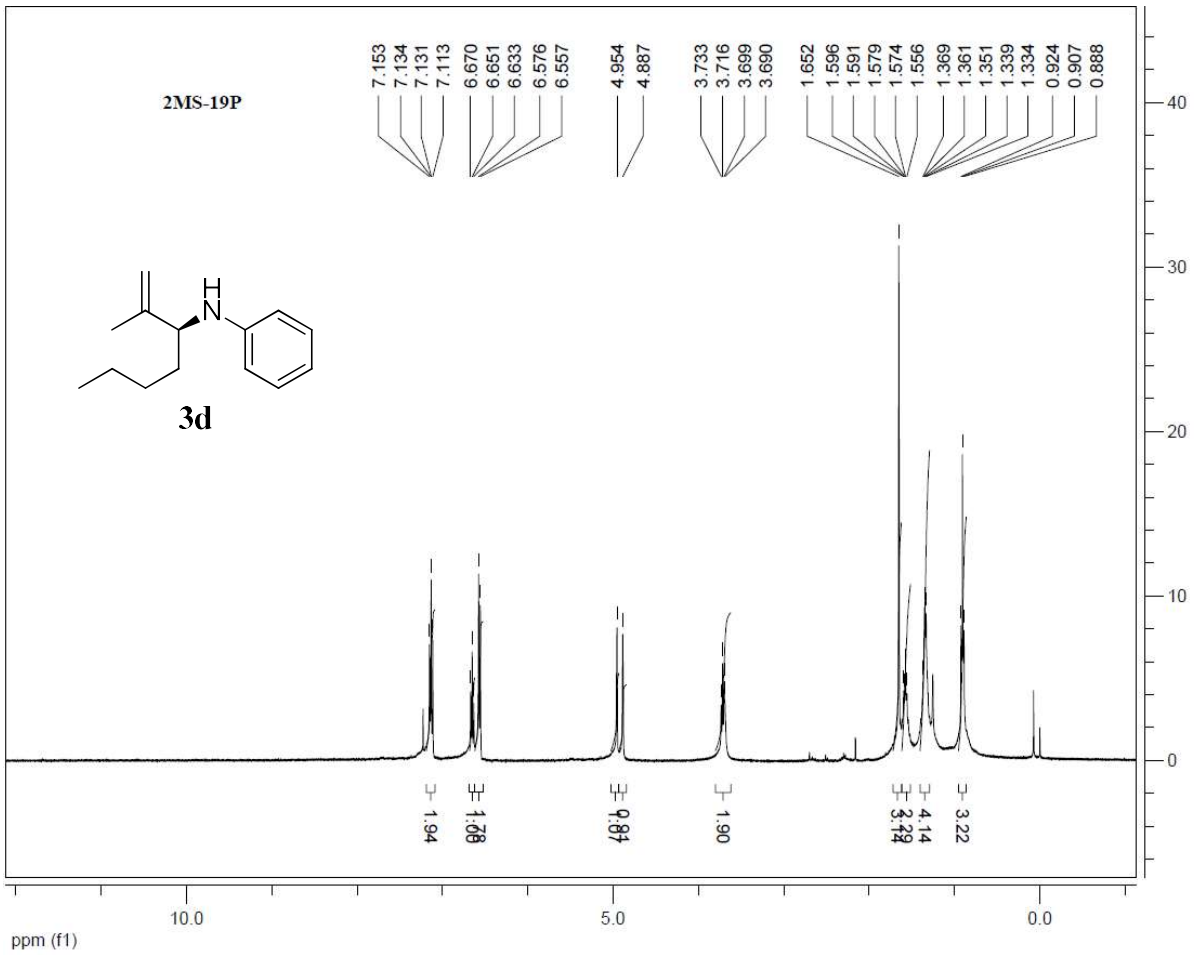
^{13}C NMR Spectra of **3b** in $CDCl_3$.



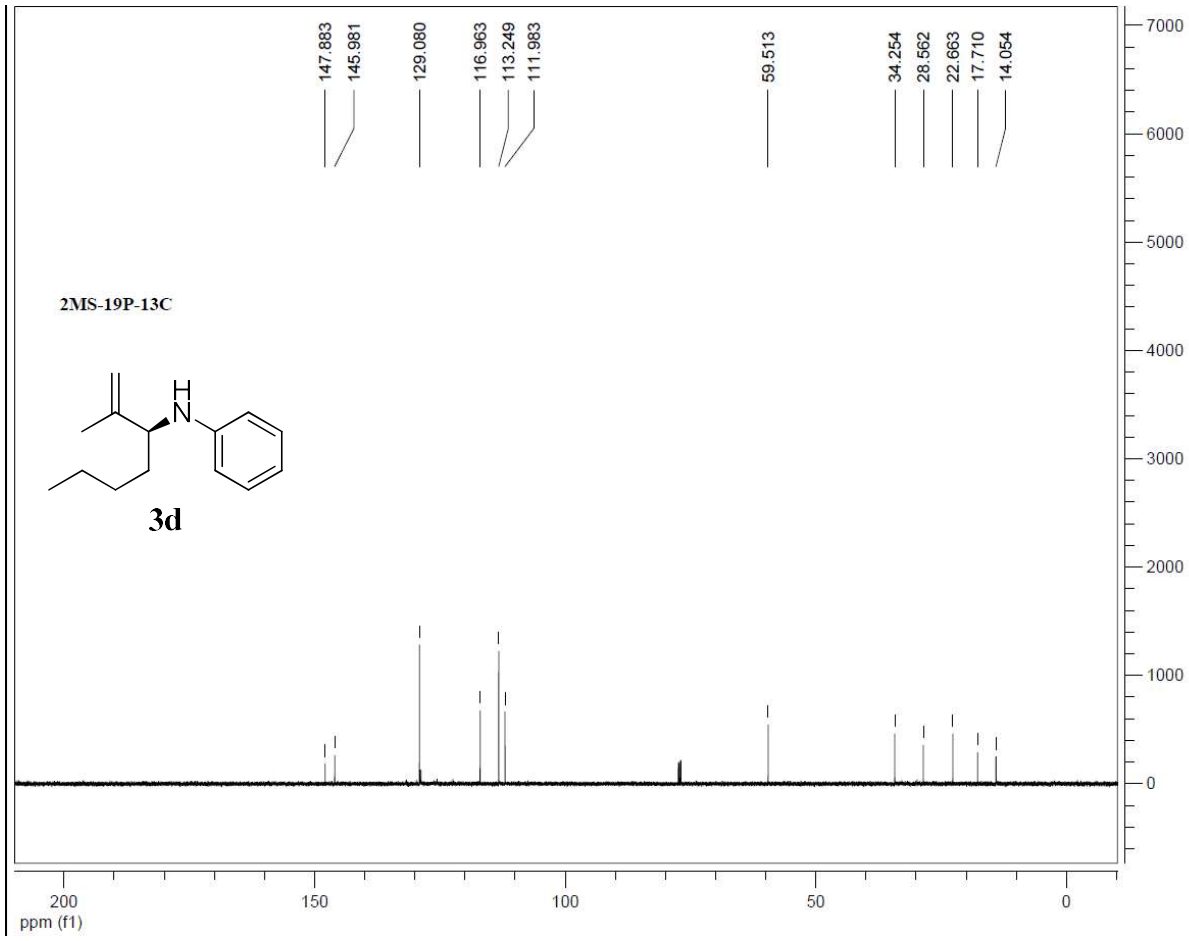
^{1}H Spectra of **3c** in $CDCl_3$.



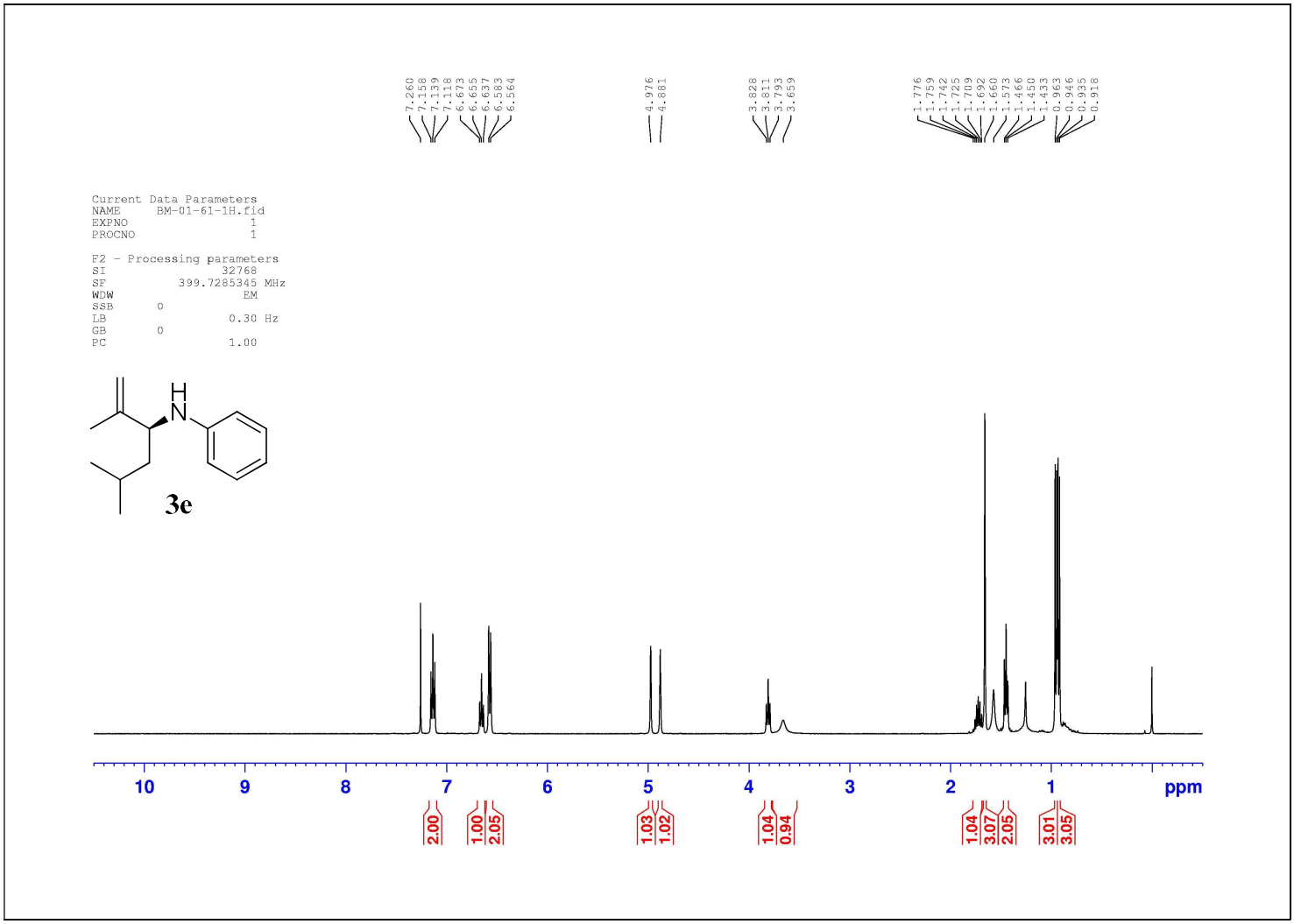
^{13}C NMR Spectra of **3c** in $CDCl_3$.



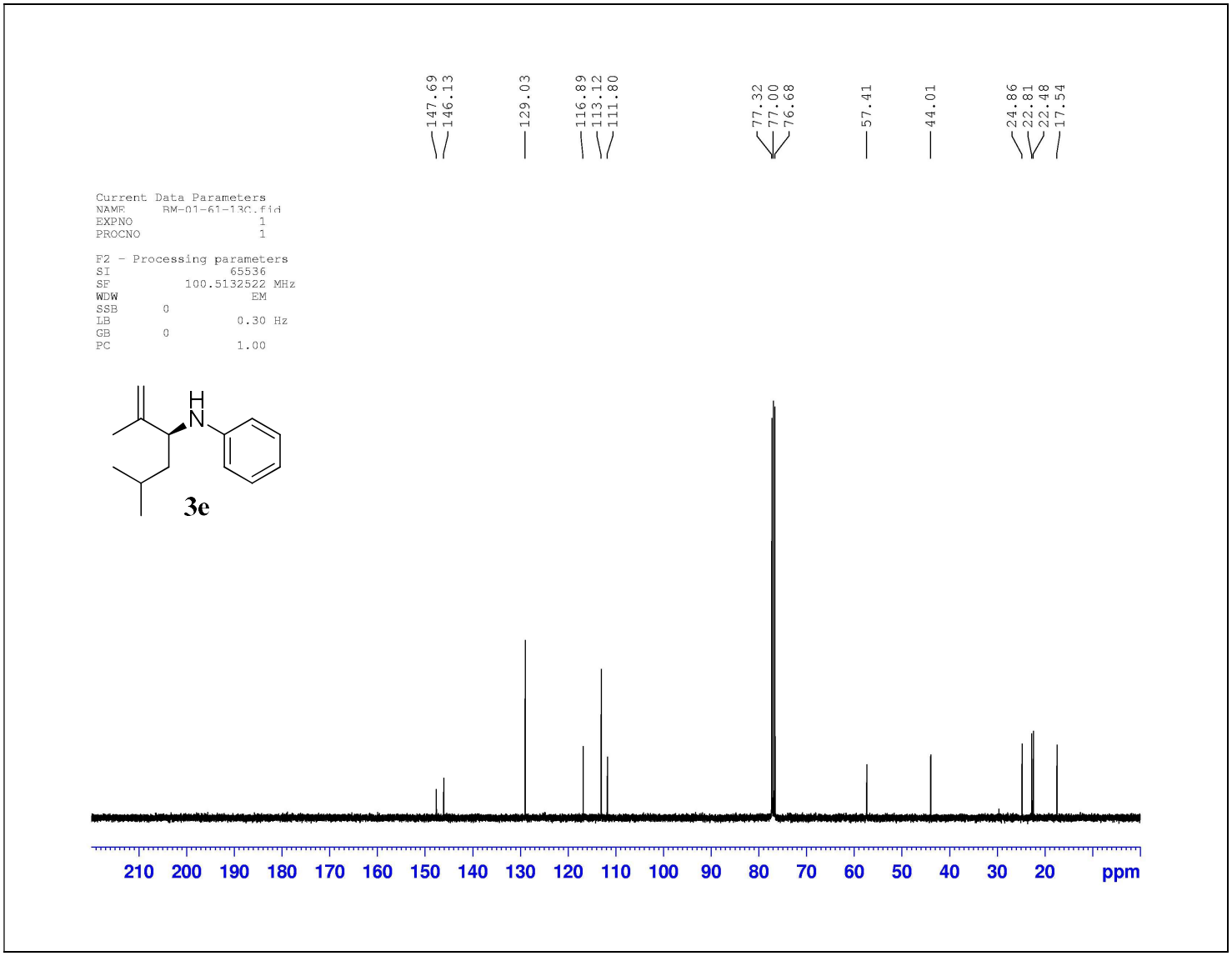
^{1}H Spectra of **3d** in $CDCl_3$.



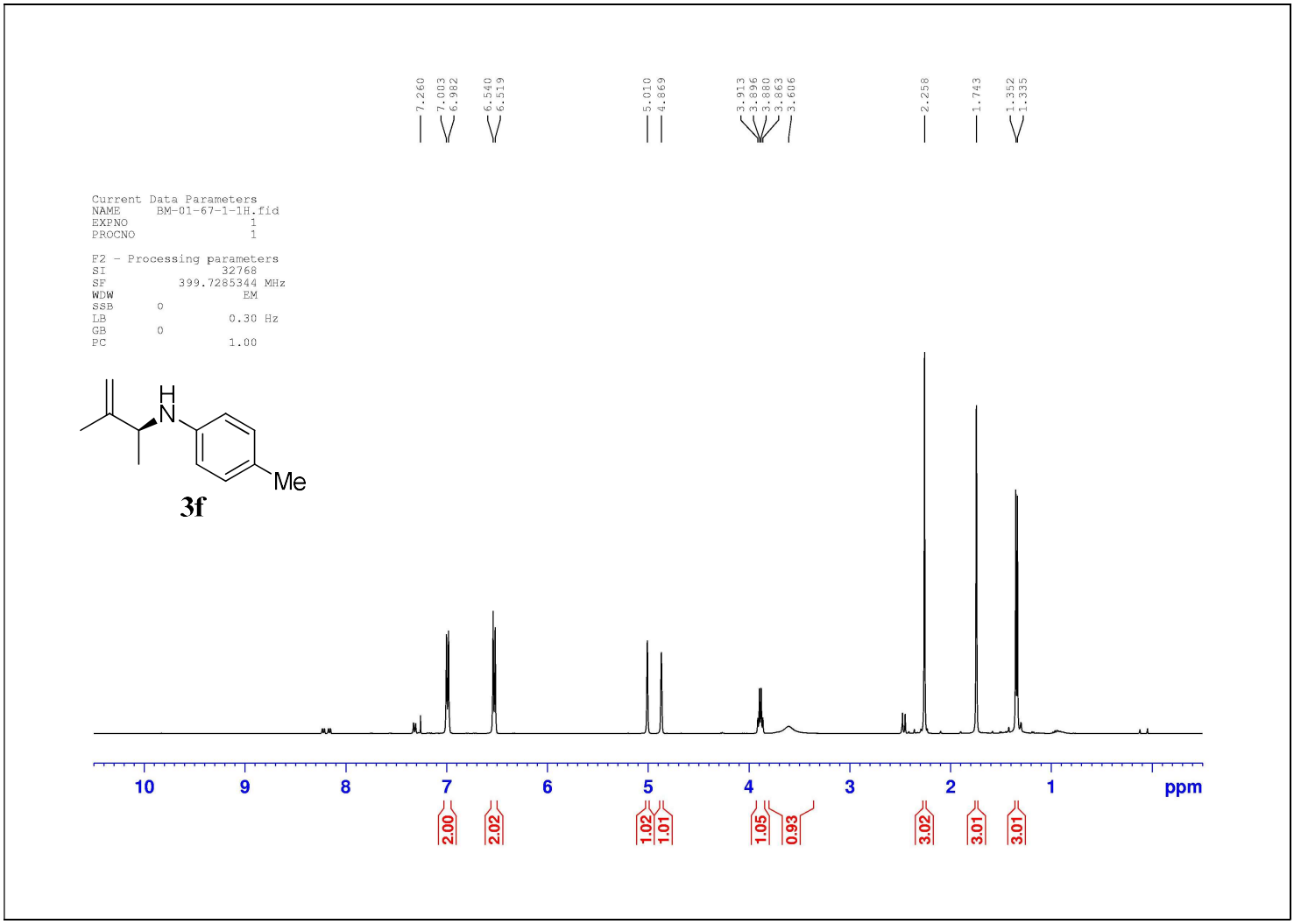
^{13}C NMR Spectra of **3d** in $CDCl_3$.



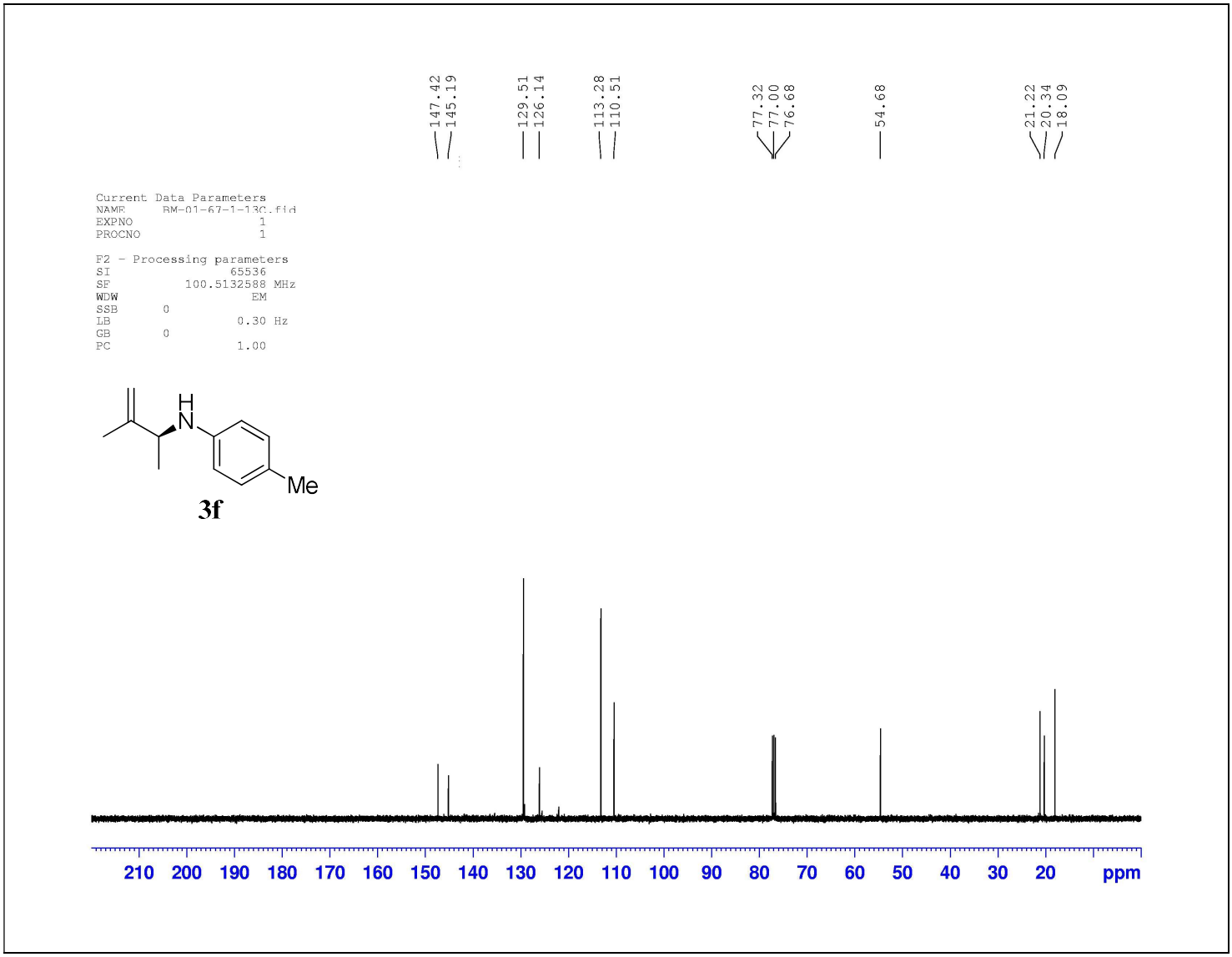
^{1}H Spectra of **3e** in $CDCl_3$.



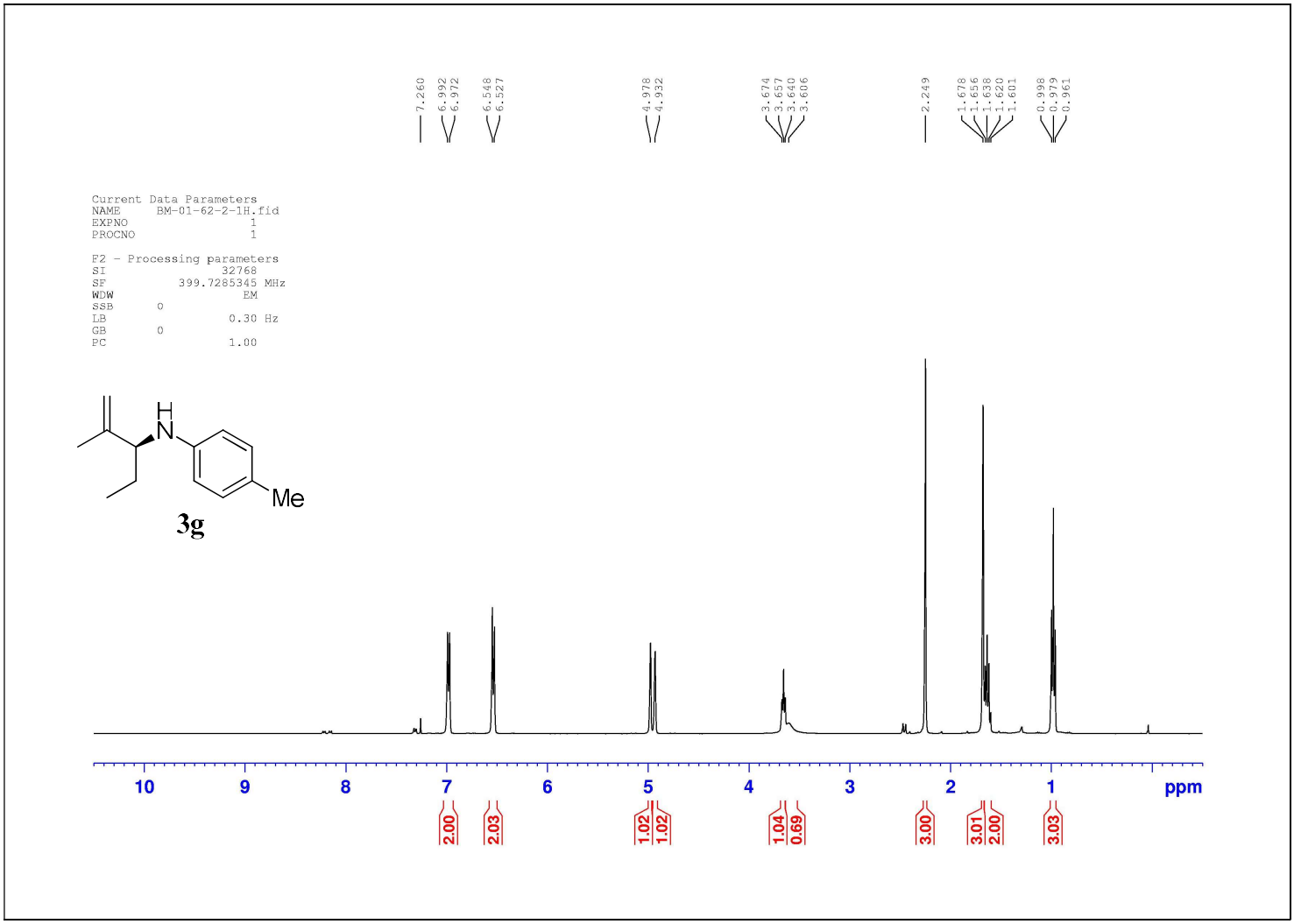
^{13}C NMR Spectra of **3e** in $CDCl_3$.



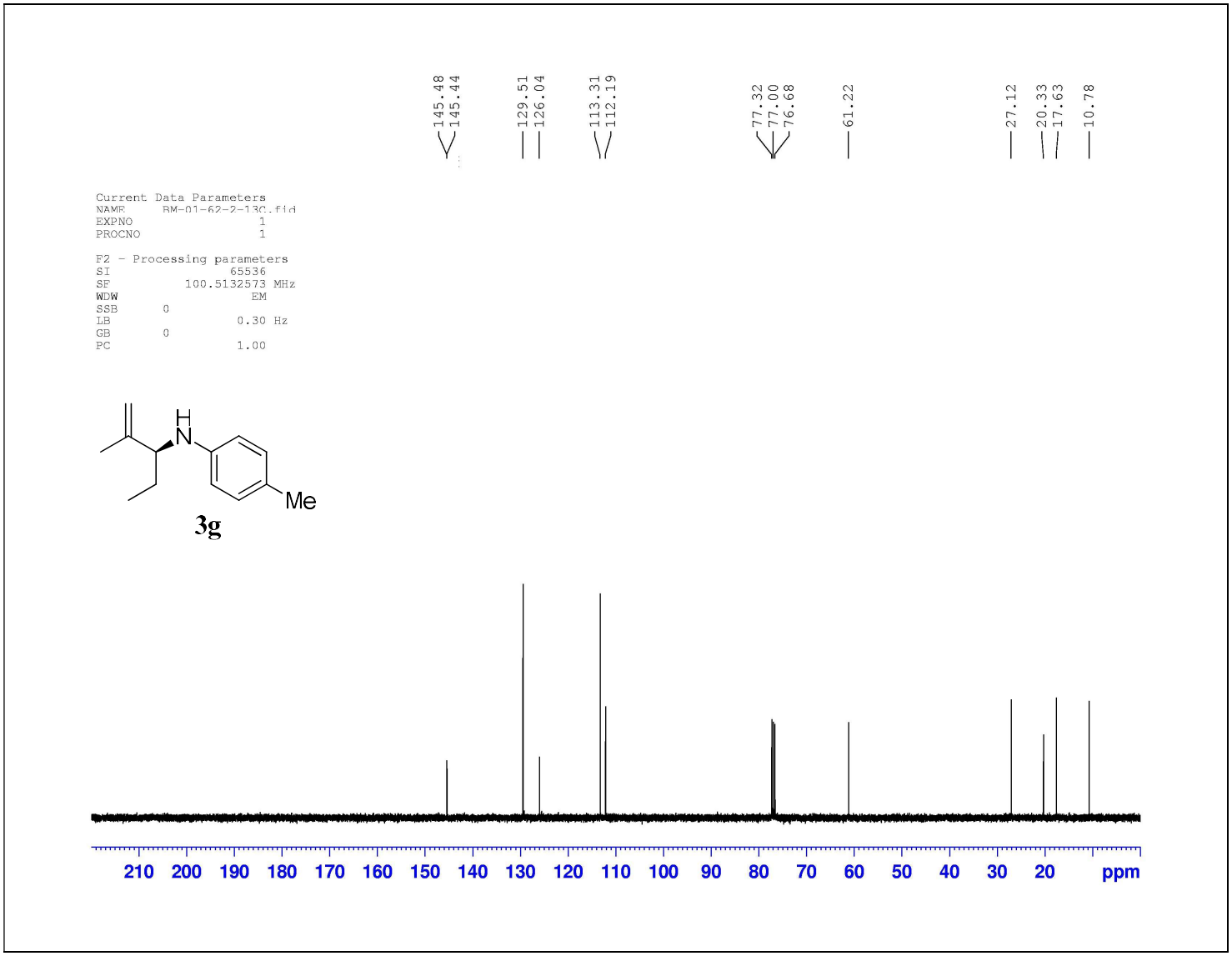
^{1}H Spectra of **3f** in $CDCl_3$.



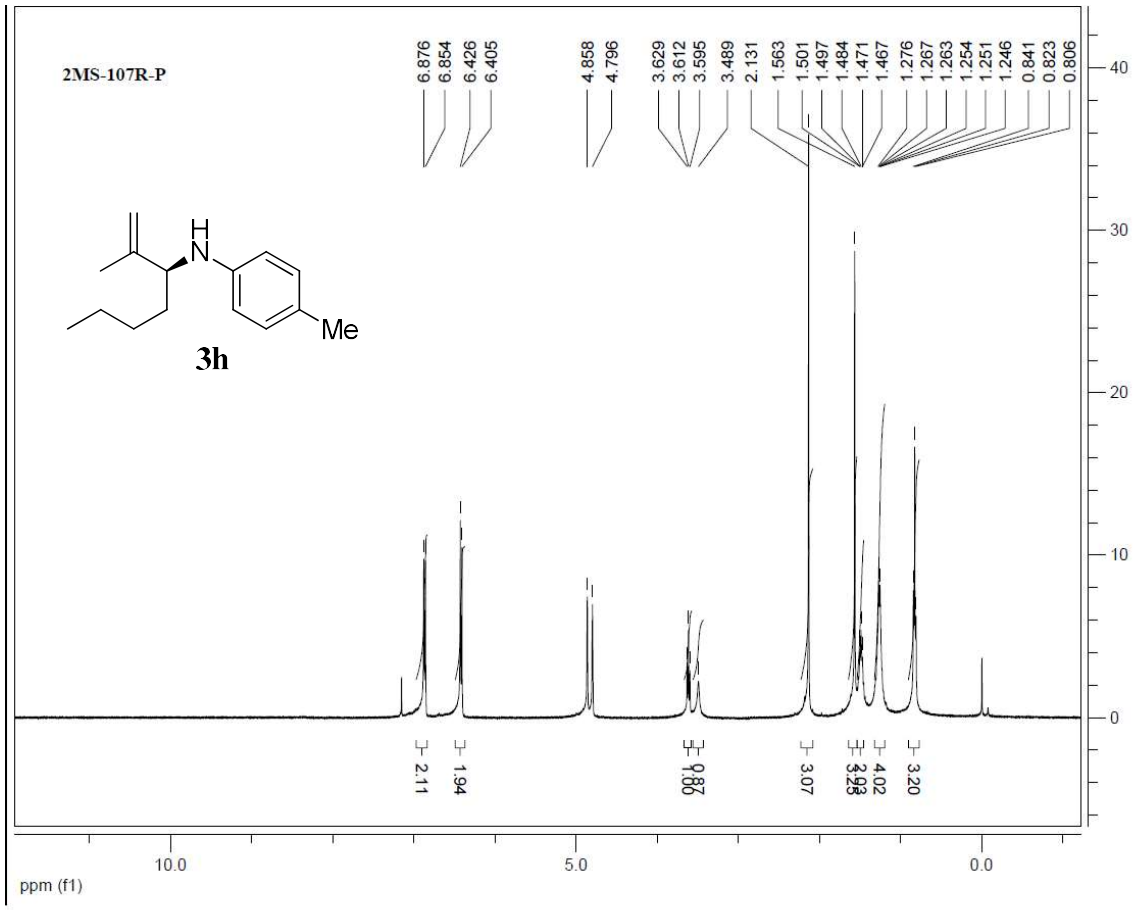
^{13}C NMR Spectra of **3f** in $CDCl_3$.



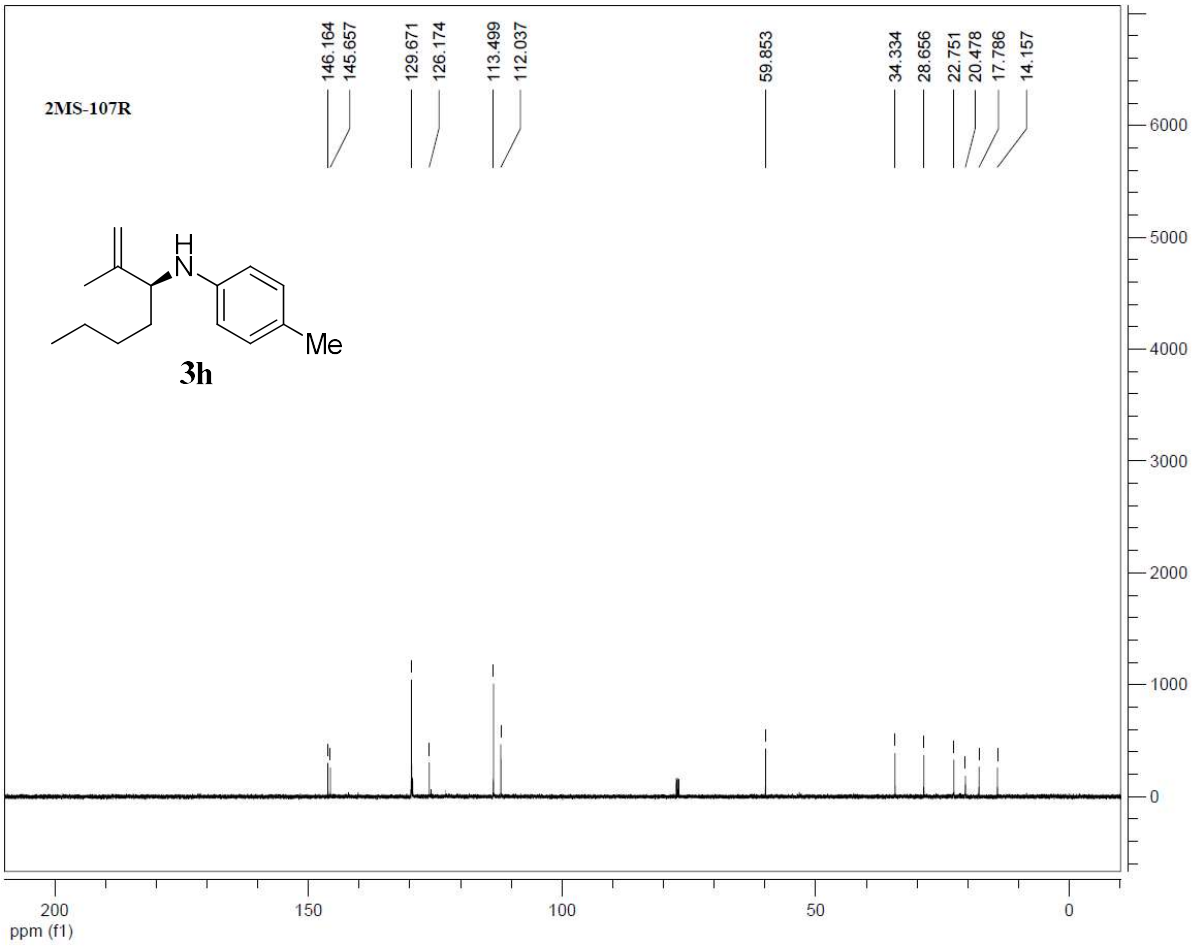
^{1}H Spectra of **3g** in $CDCl_3$.



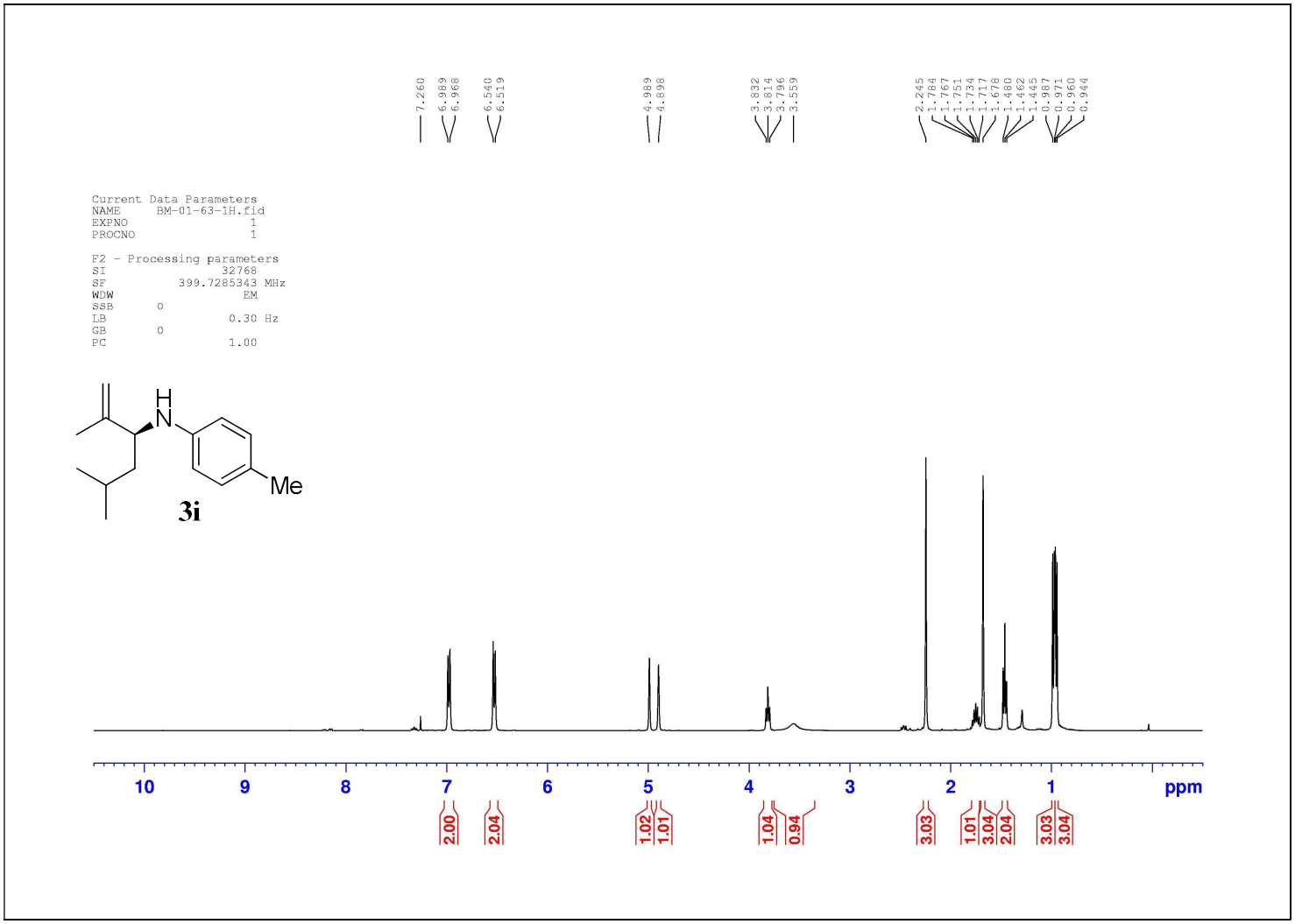
^{13}C NMR Spectra of **3g** in $CDCl_3$.



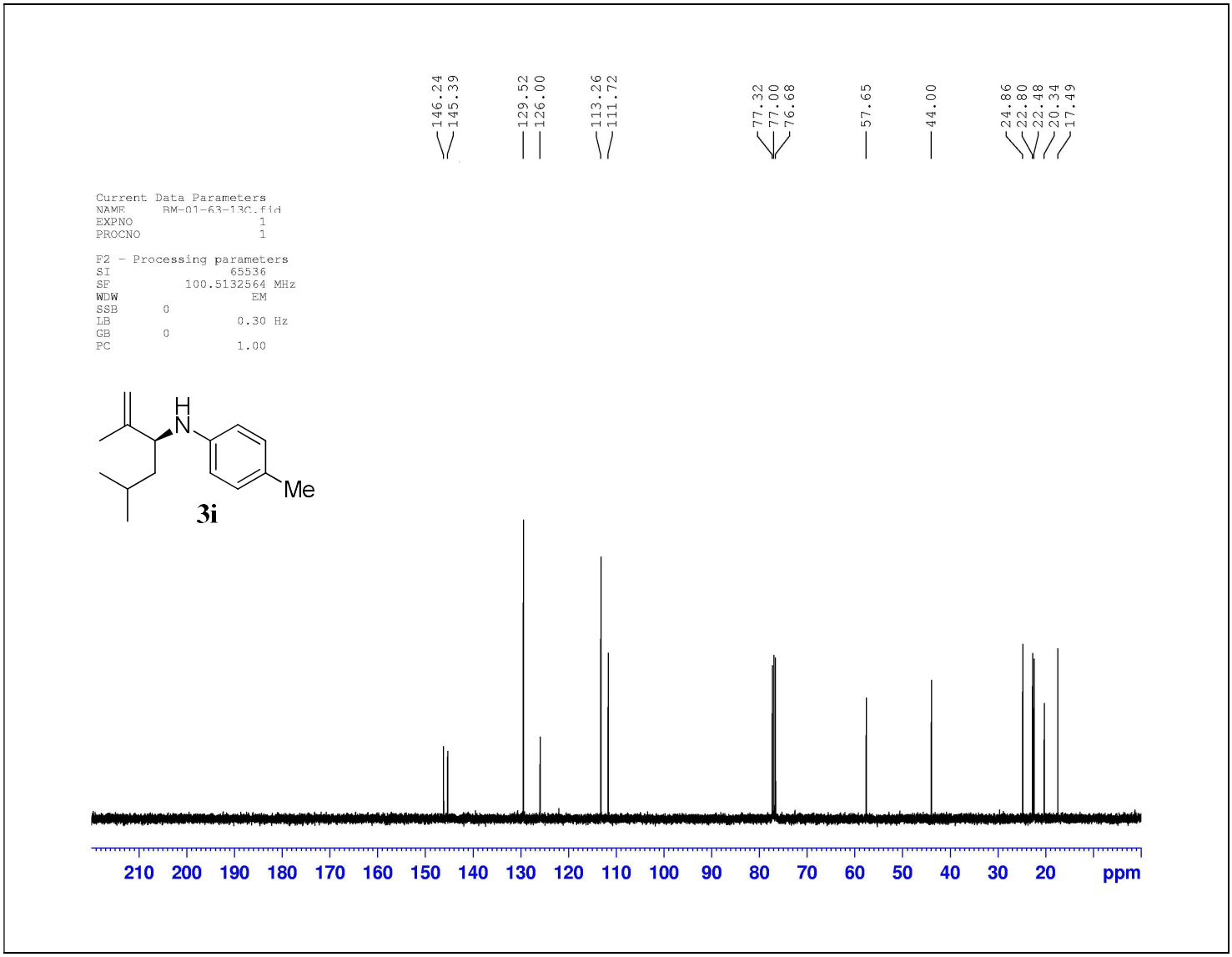
^{1}H Spectra of **3h** in $CDCl_3$.



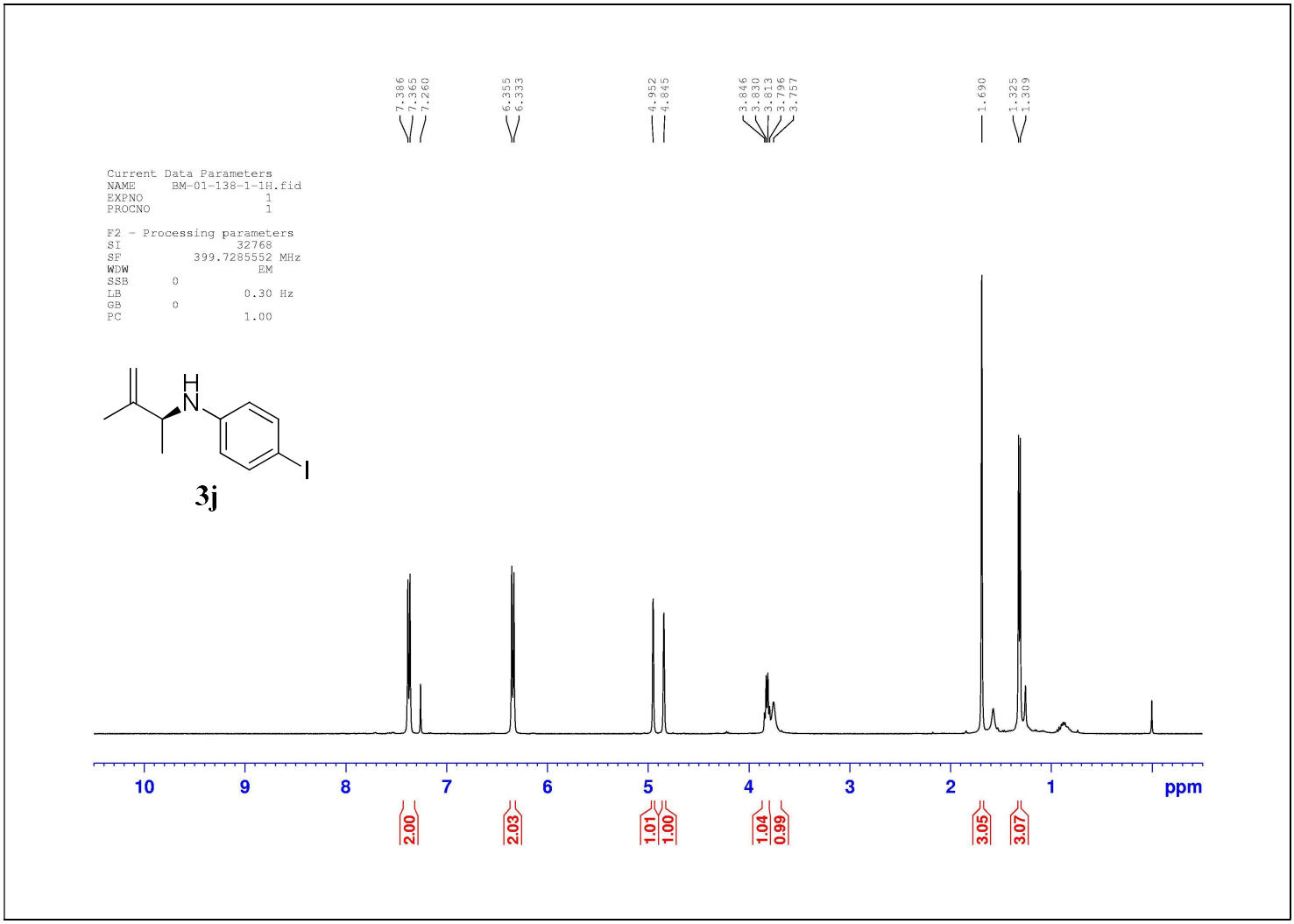
^{13}C NMR Spectra of **3h** in $CDCl_3$.



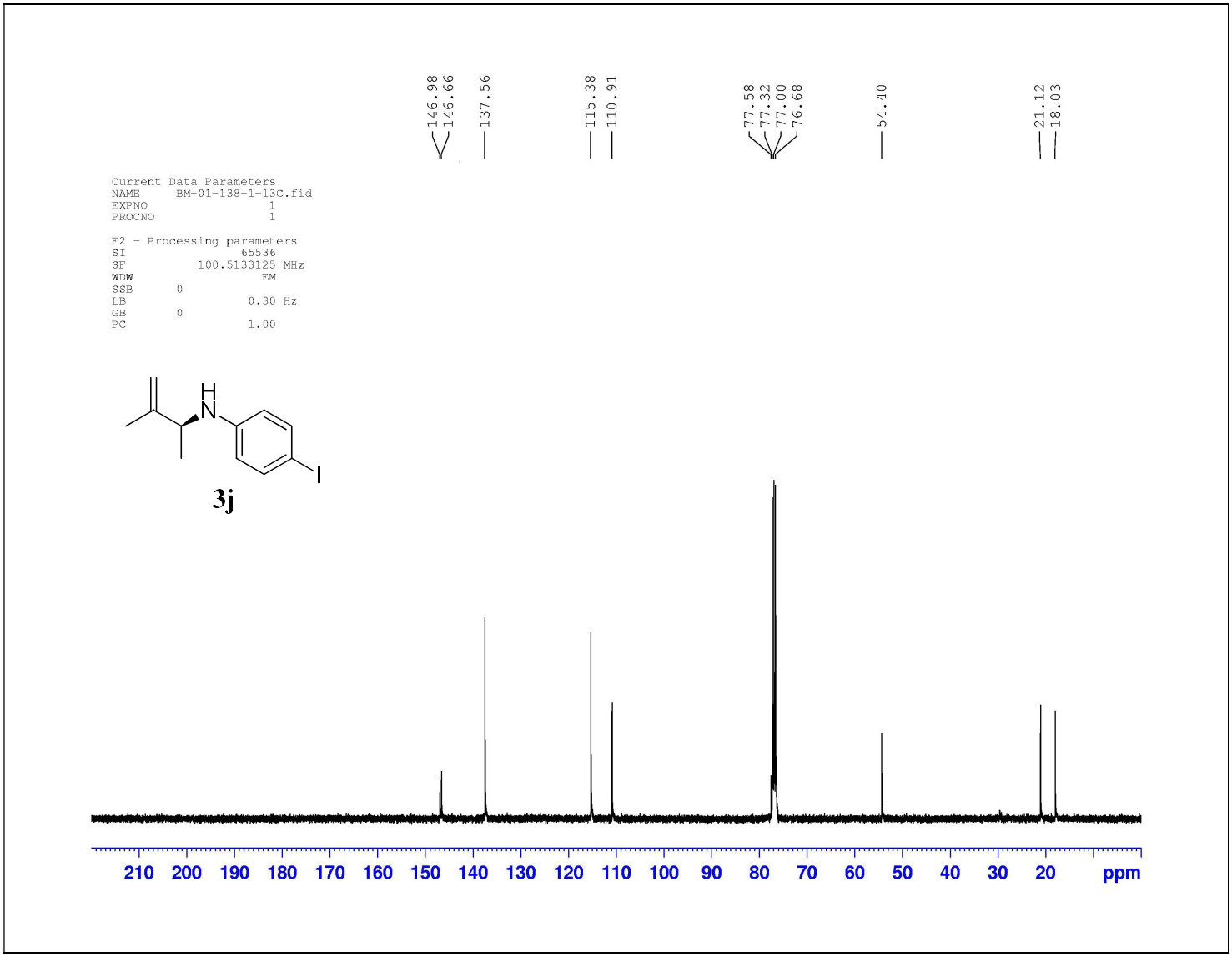
^{1}H Spectra of **3i** in $CDCl_3$.



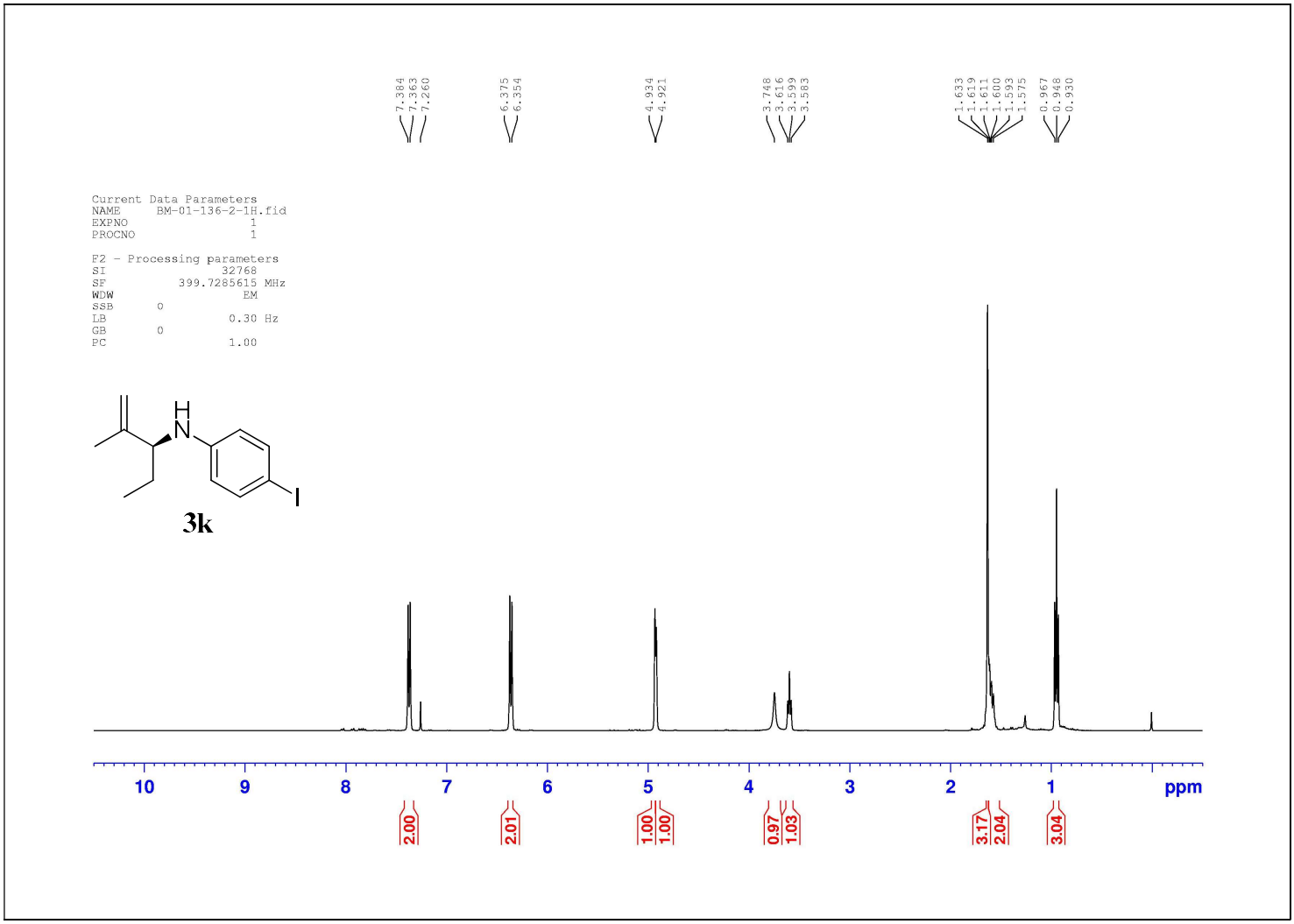
^{13}C NMR Spectra of **3i** in $CDCl_3$.



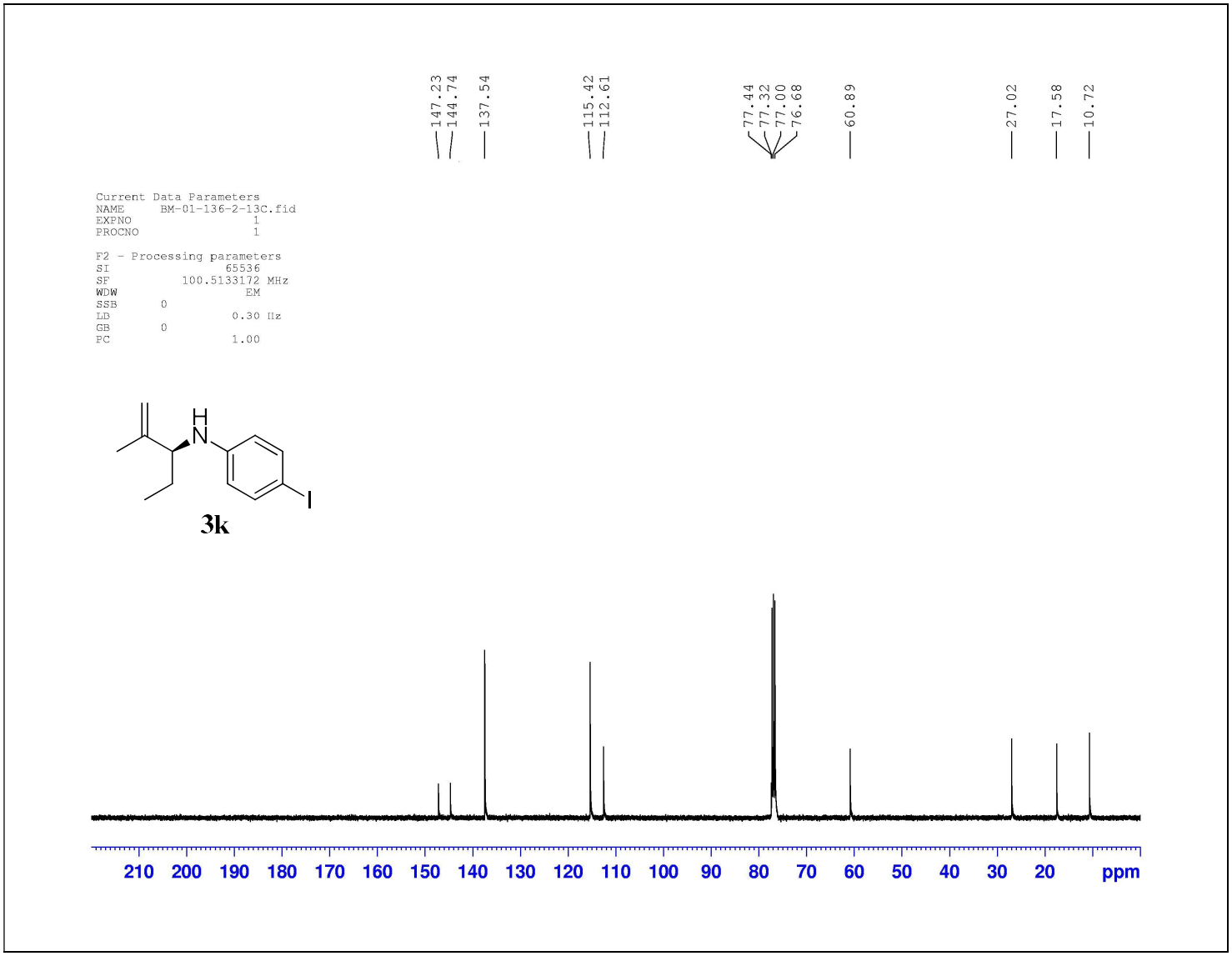
^{1}H Spectra of **3j** in $CDCl_3$.



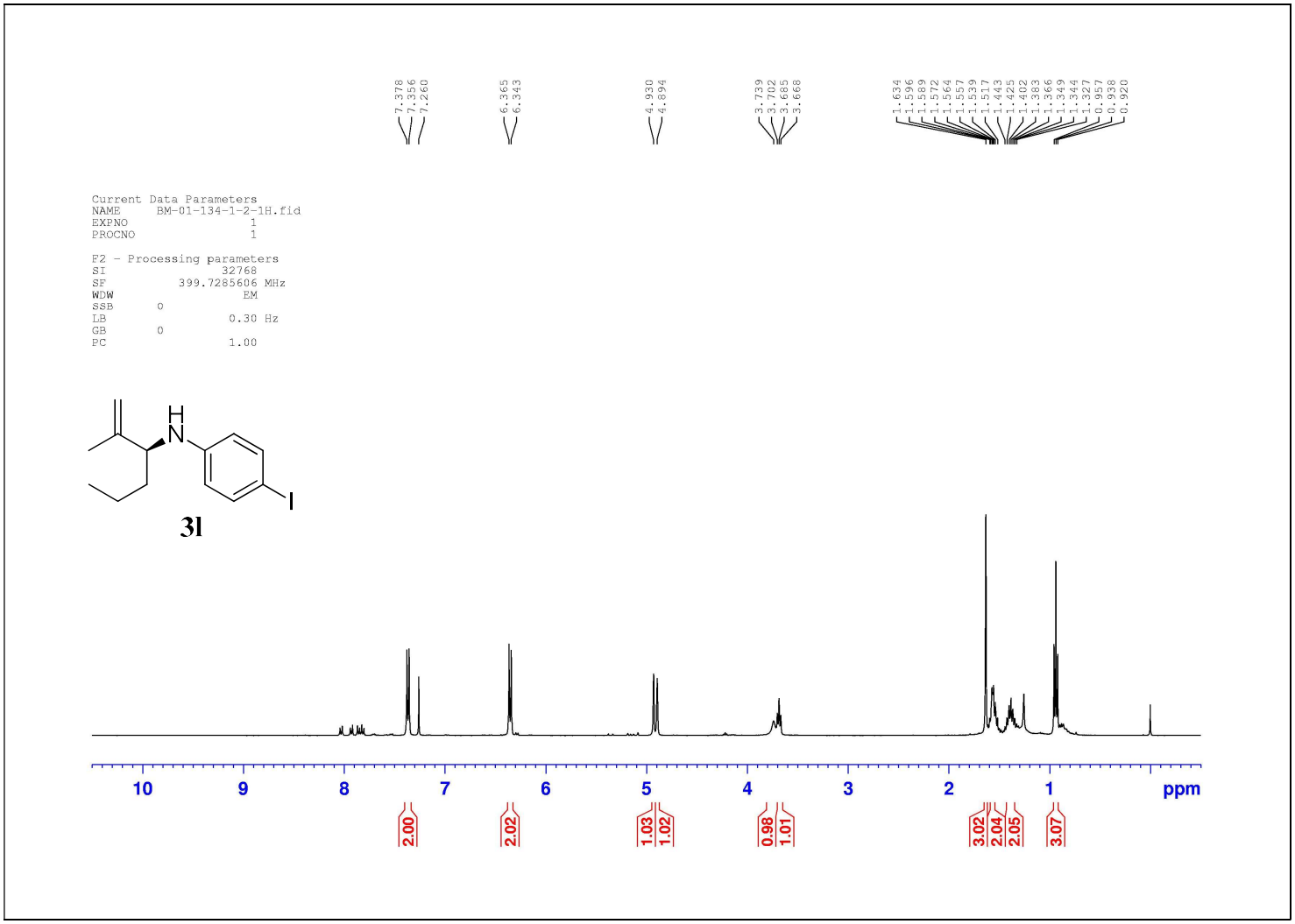
^{13}C NMR Spectra of **3j** in $CDCl_3$.



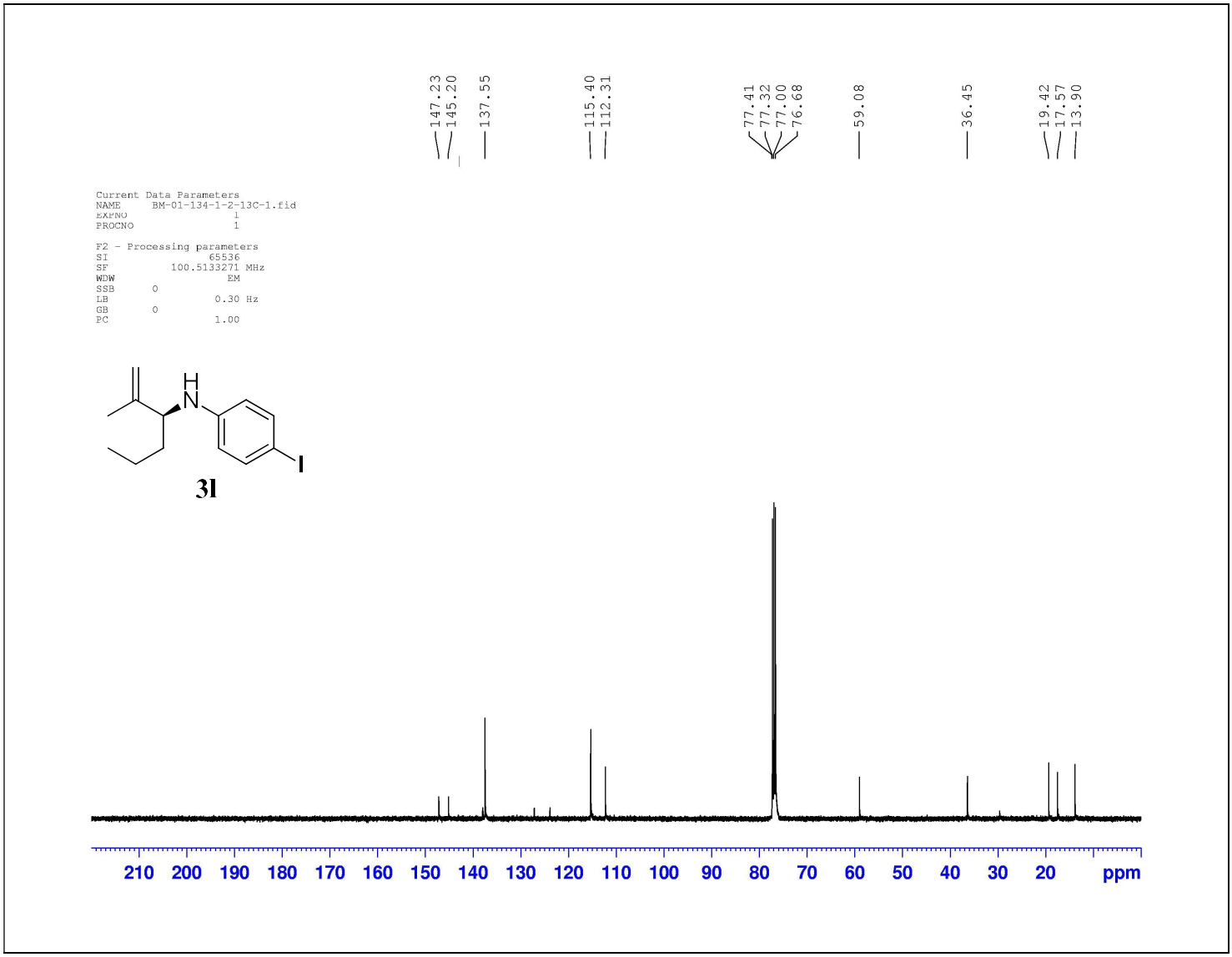
^{1}H Spectra of **3k** in $CDCl_3$.



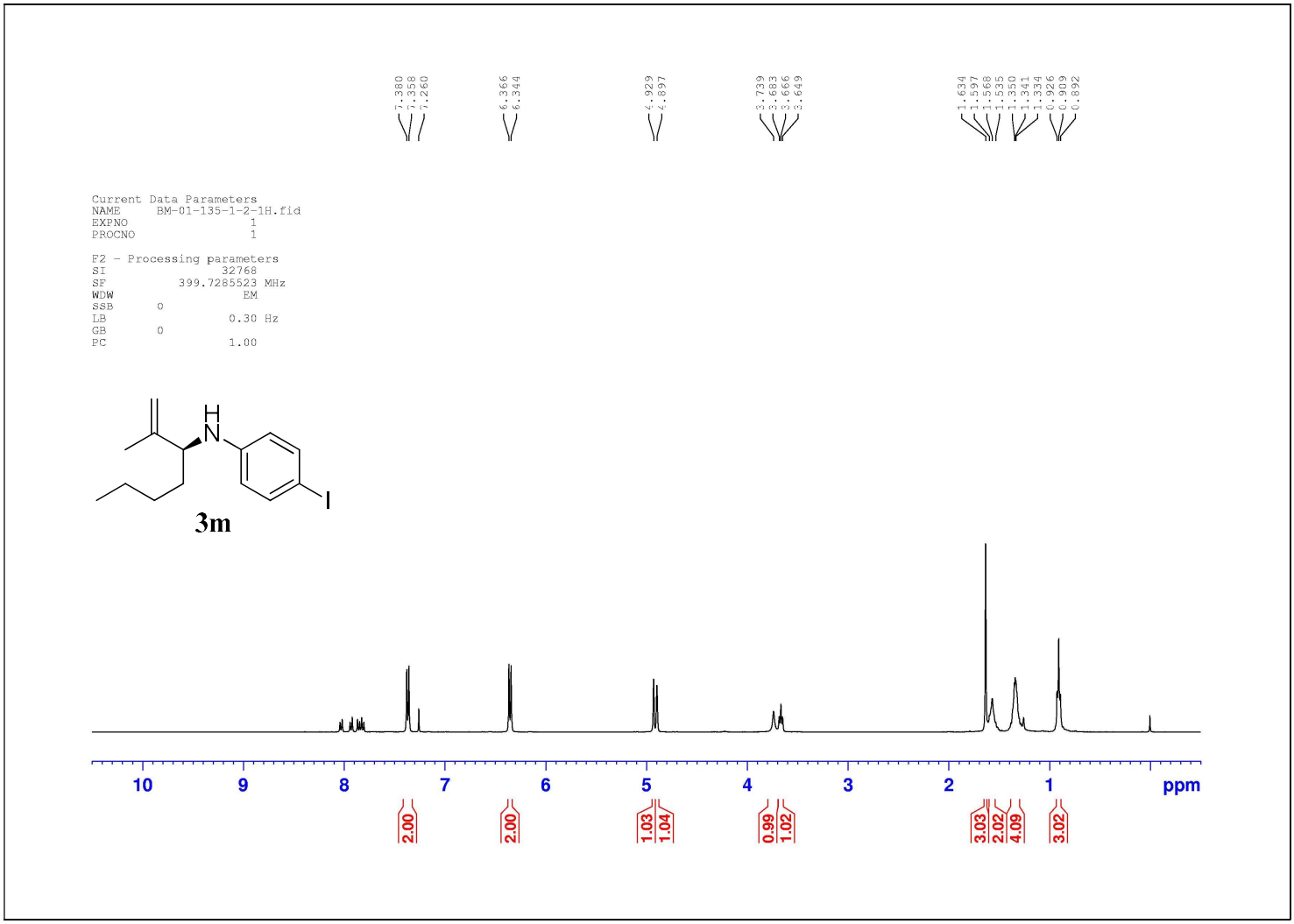
^{13}C NMR Spectra of **3k** in $CDCl_3$.



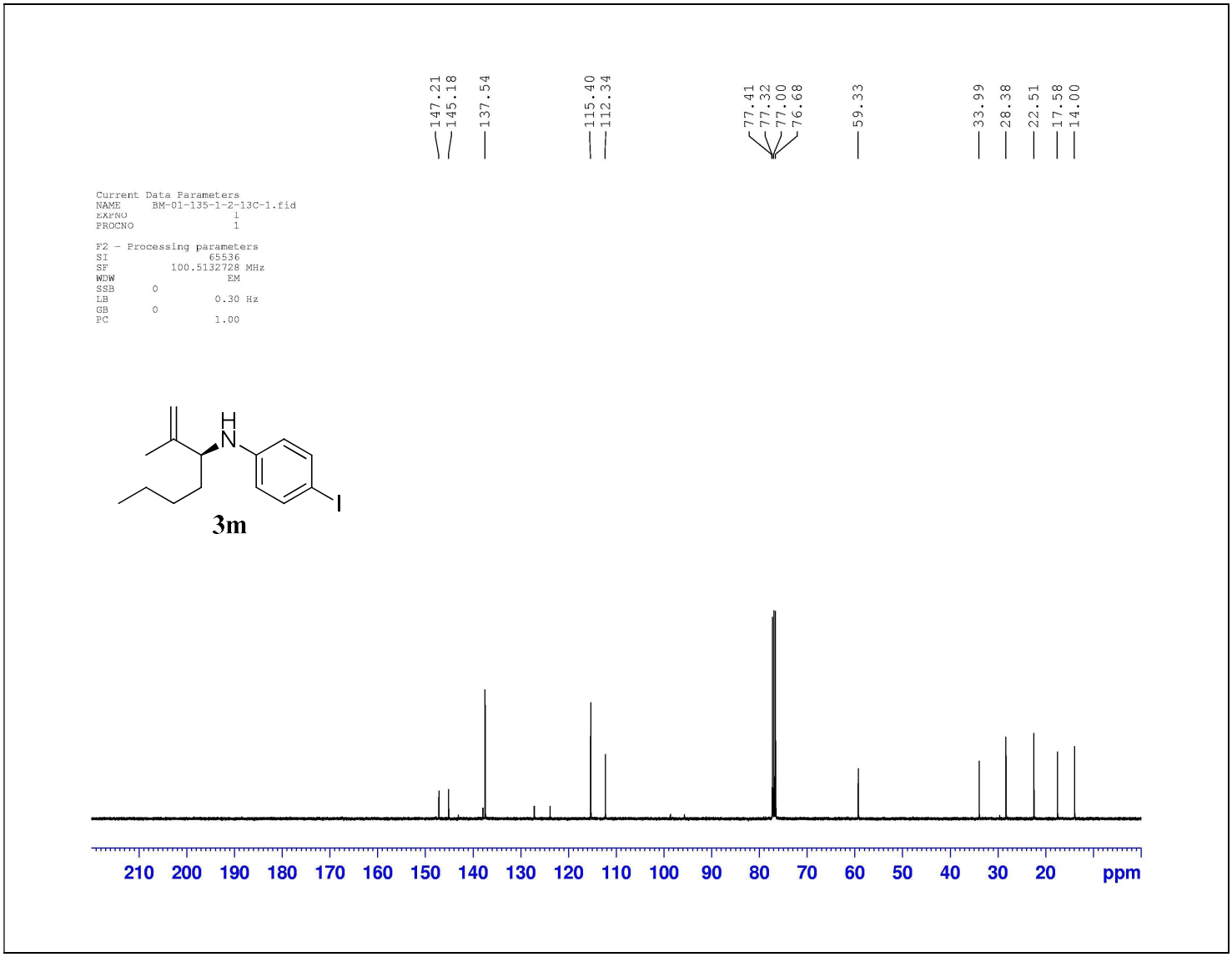
^{1}H Spectra of **3l** in $CDCl_3$.



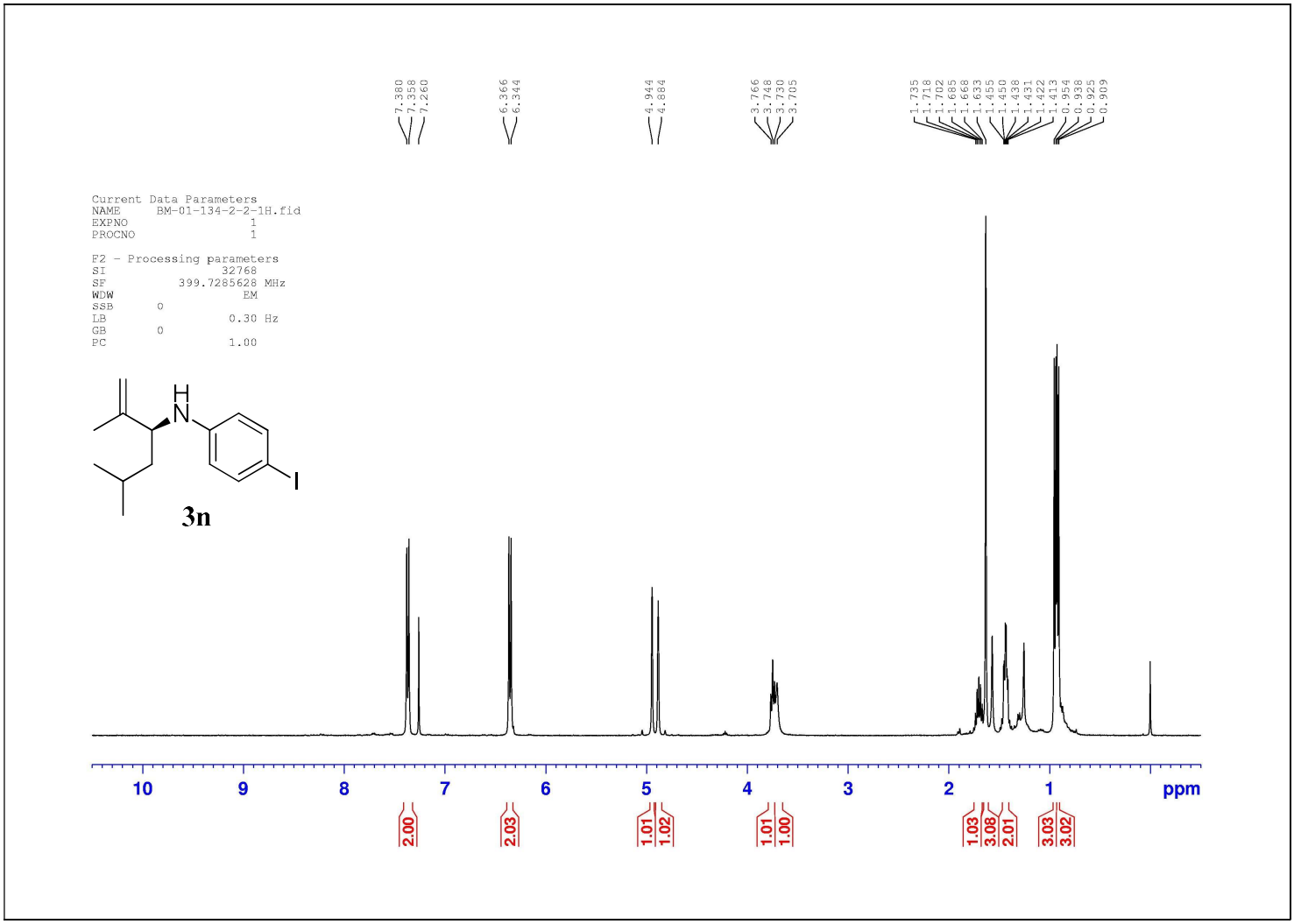
^{13}C NMR Spectra of **3l** in $CDCl_3$.



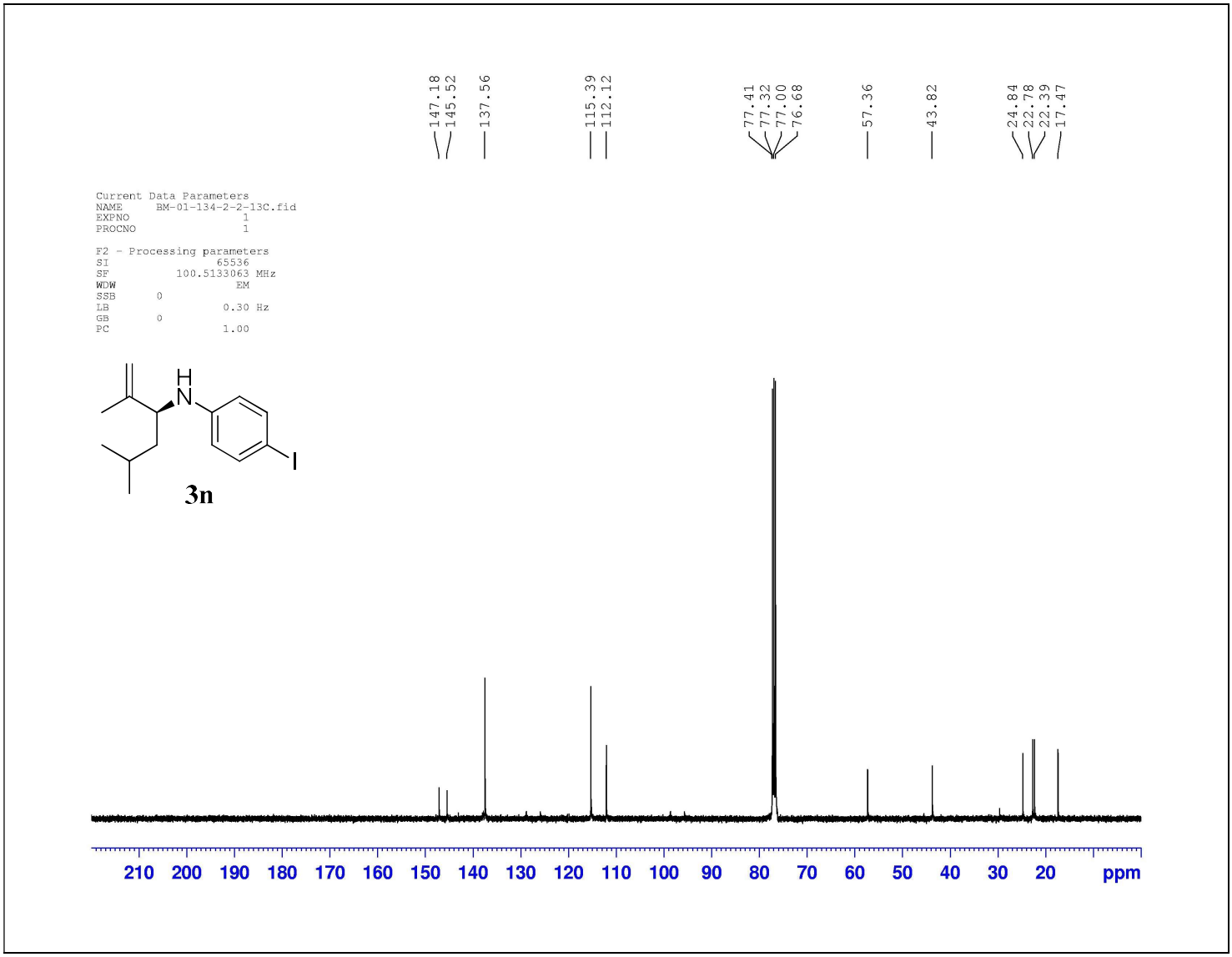
^{1}H Spectra of **3m** in $CDCl_3$.



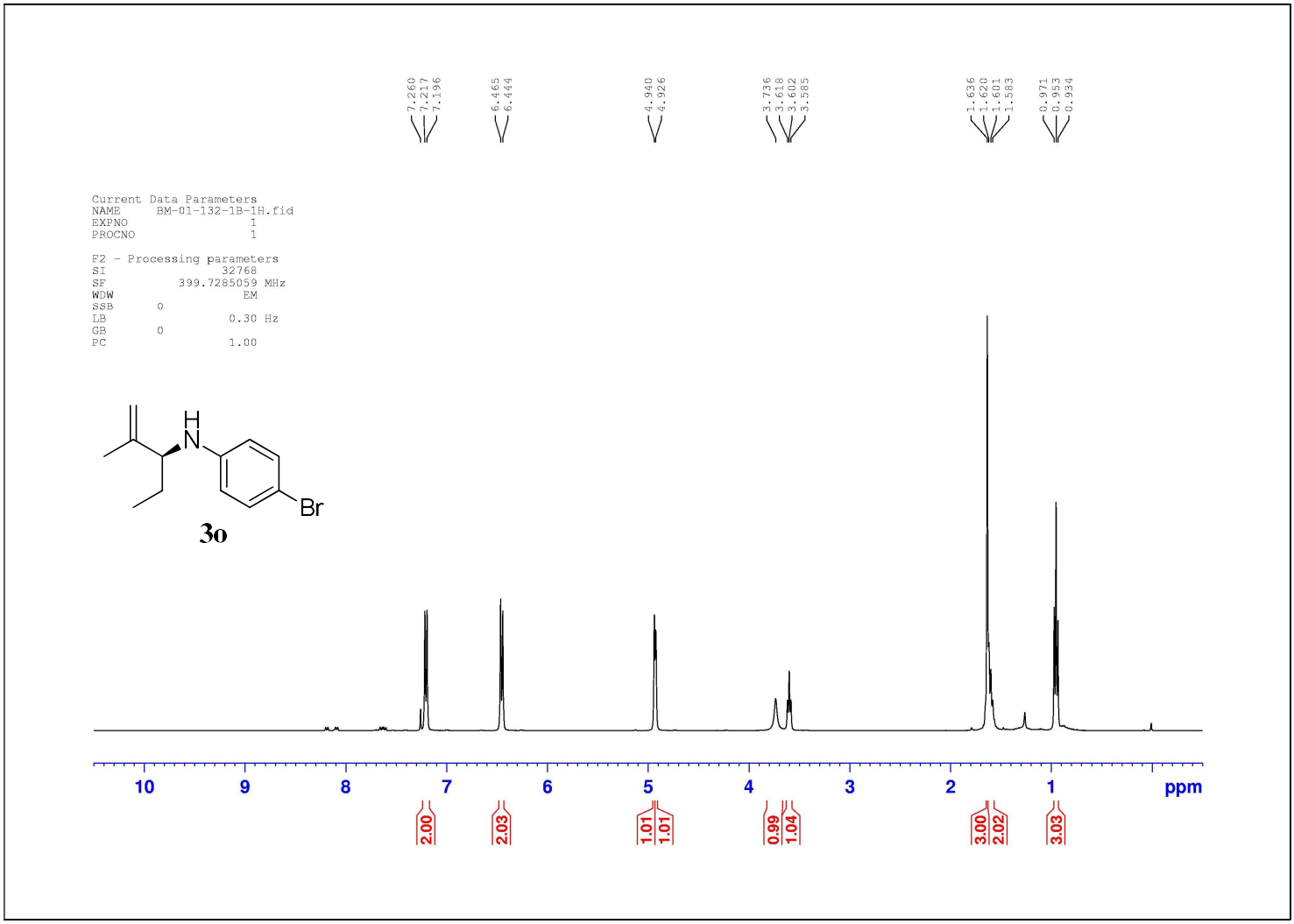
^{13}C NMR Spectra of **3m** in $CDCl_3$.



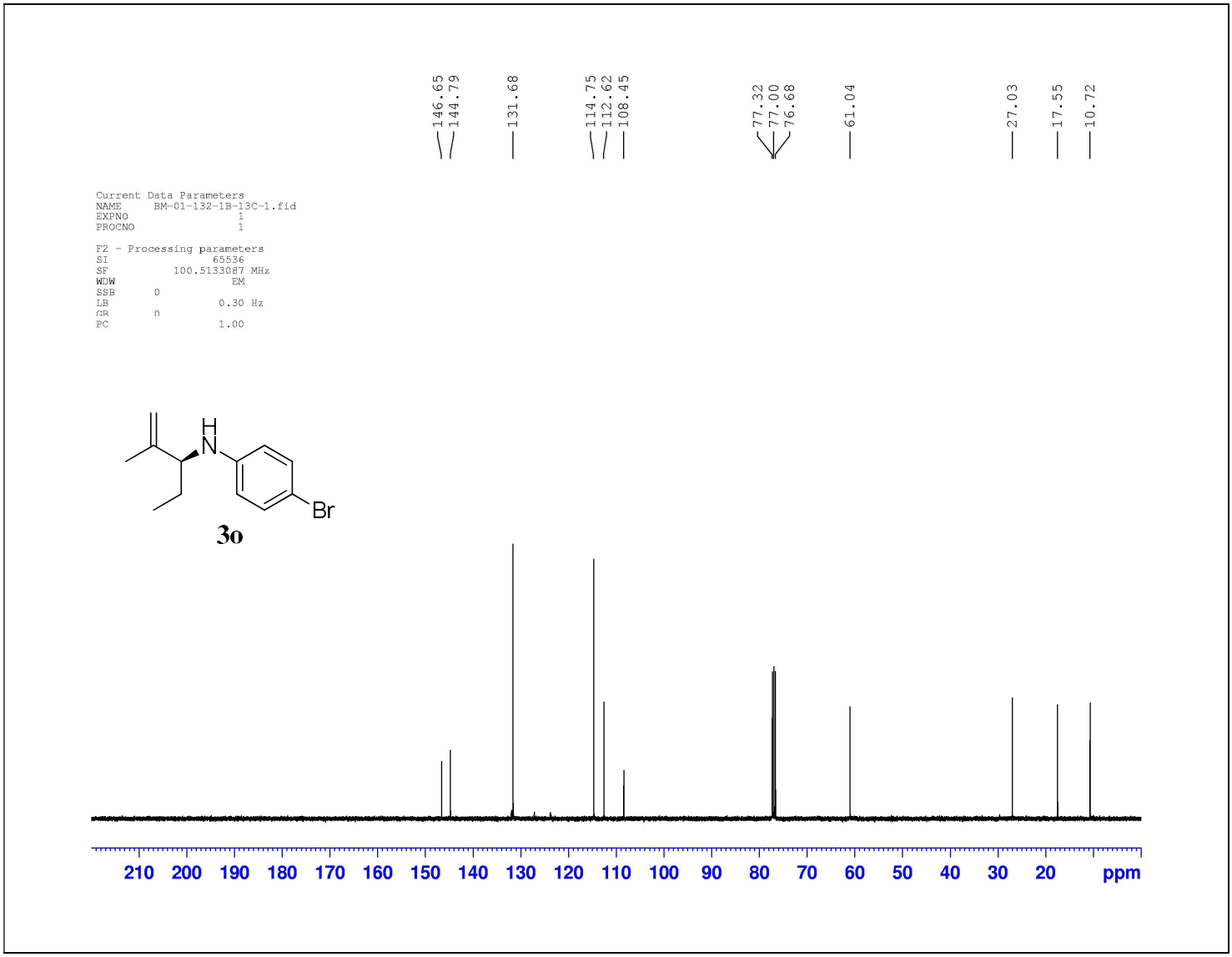
^{1}H Spectra of **3n** in $CDCl_3$.



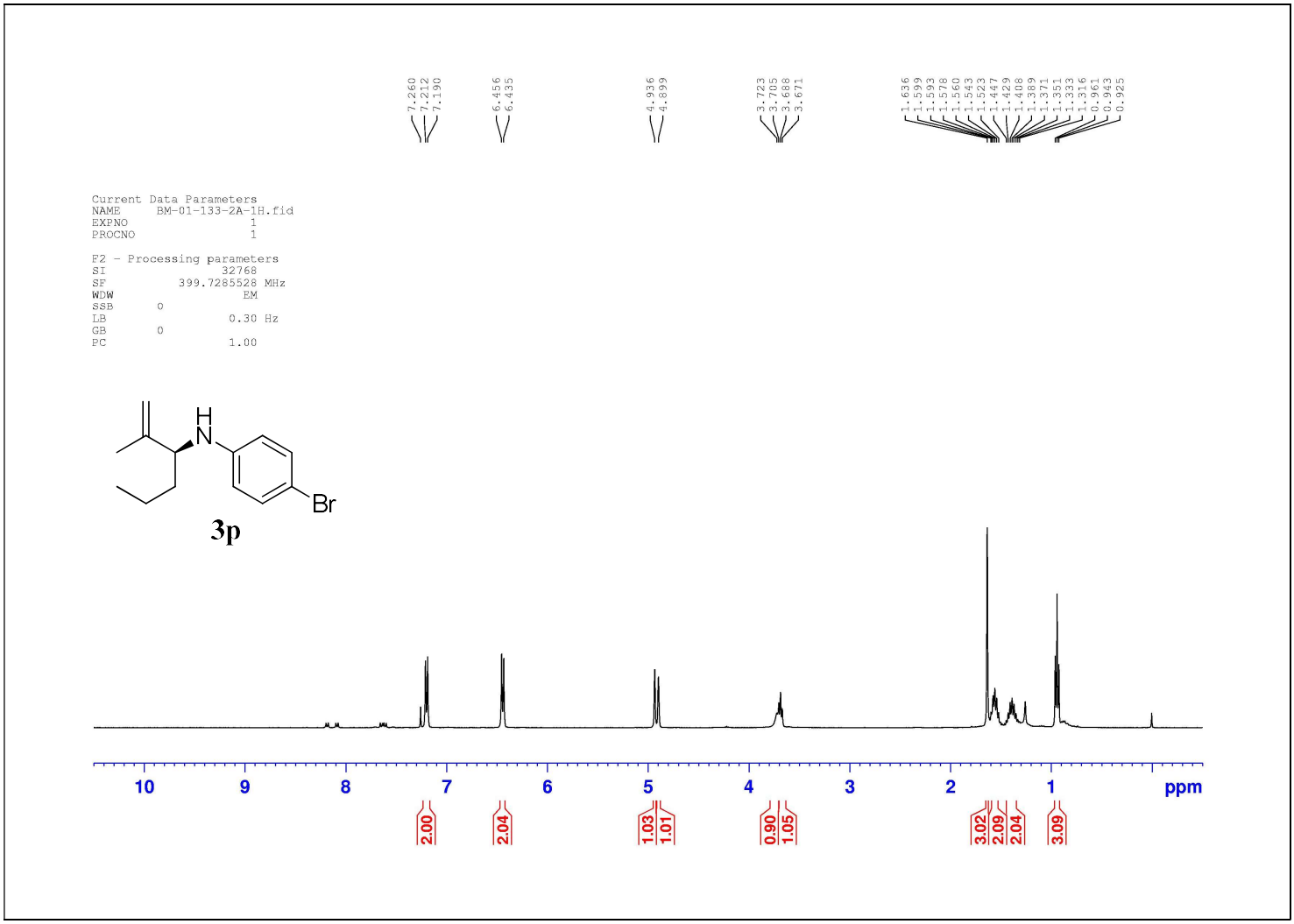
^{13}C NMR Spectra of **3n** in $CDCl_3$.



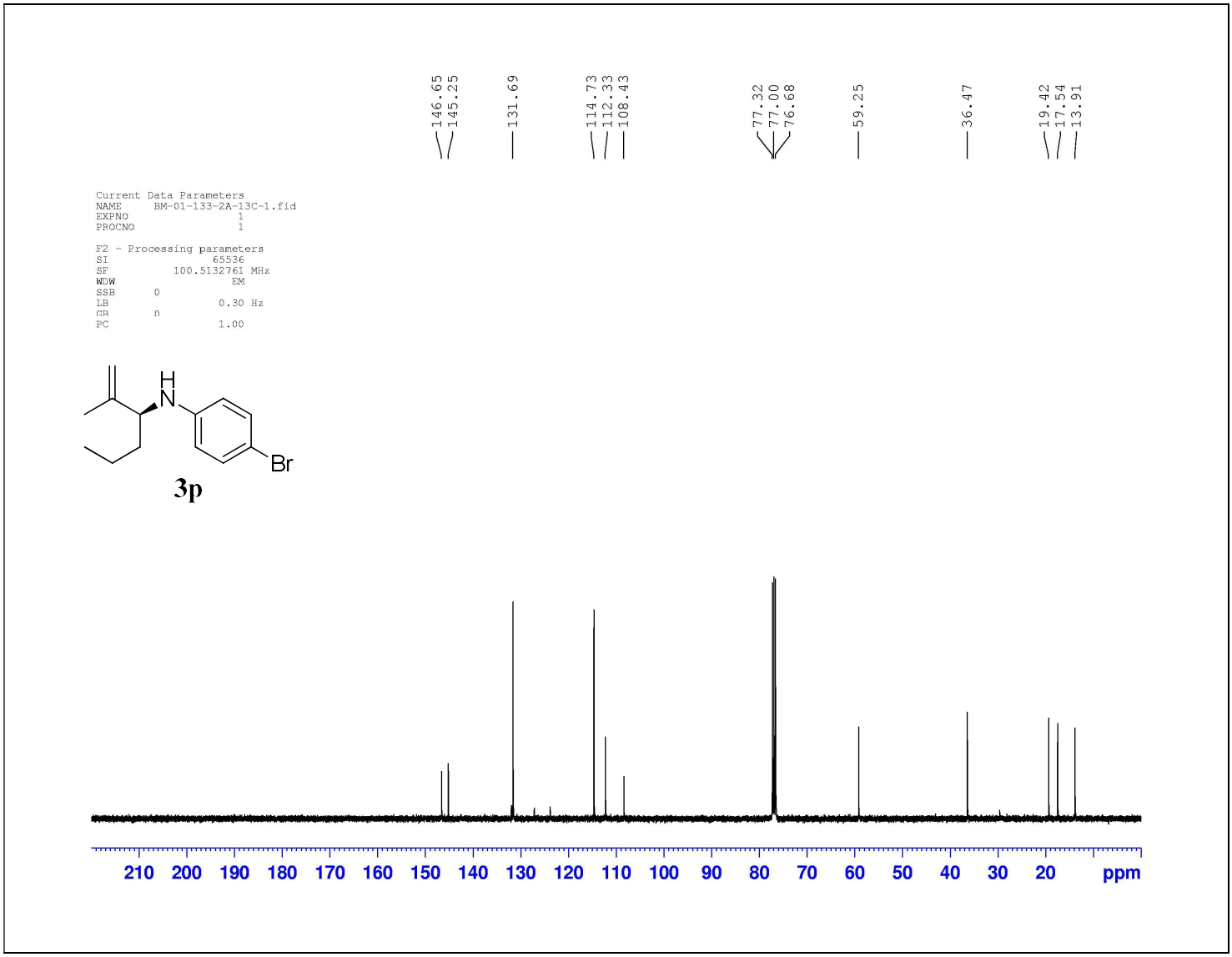
^{1}H Spectra of **3o** in $CDCl_3$.



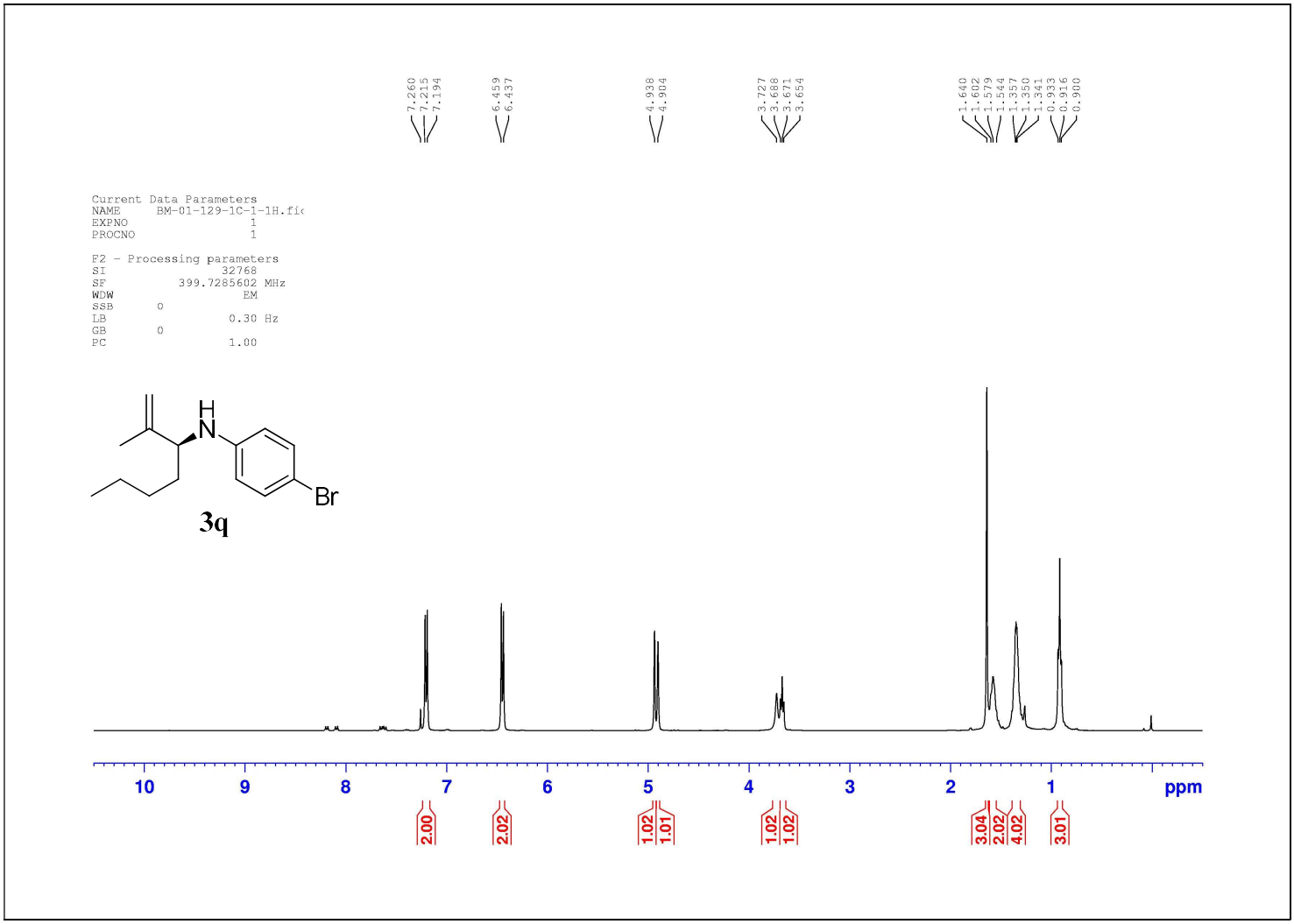
^{13}C NMR Spectra of **3o** in $CDCl_3$.



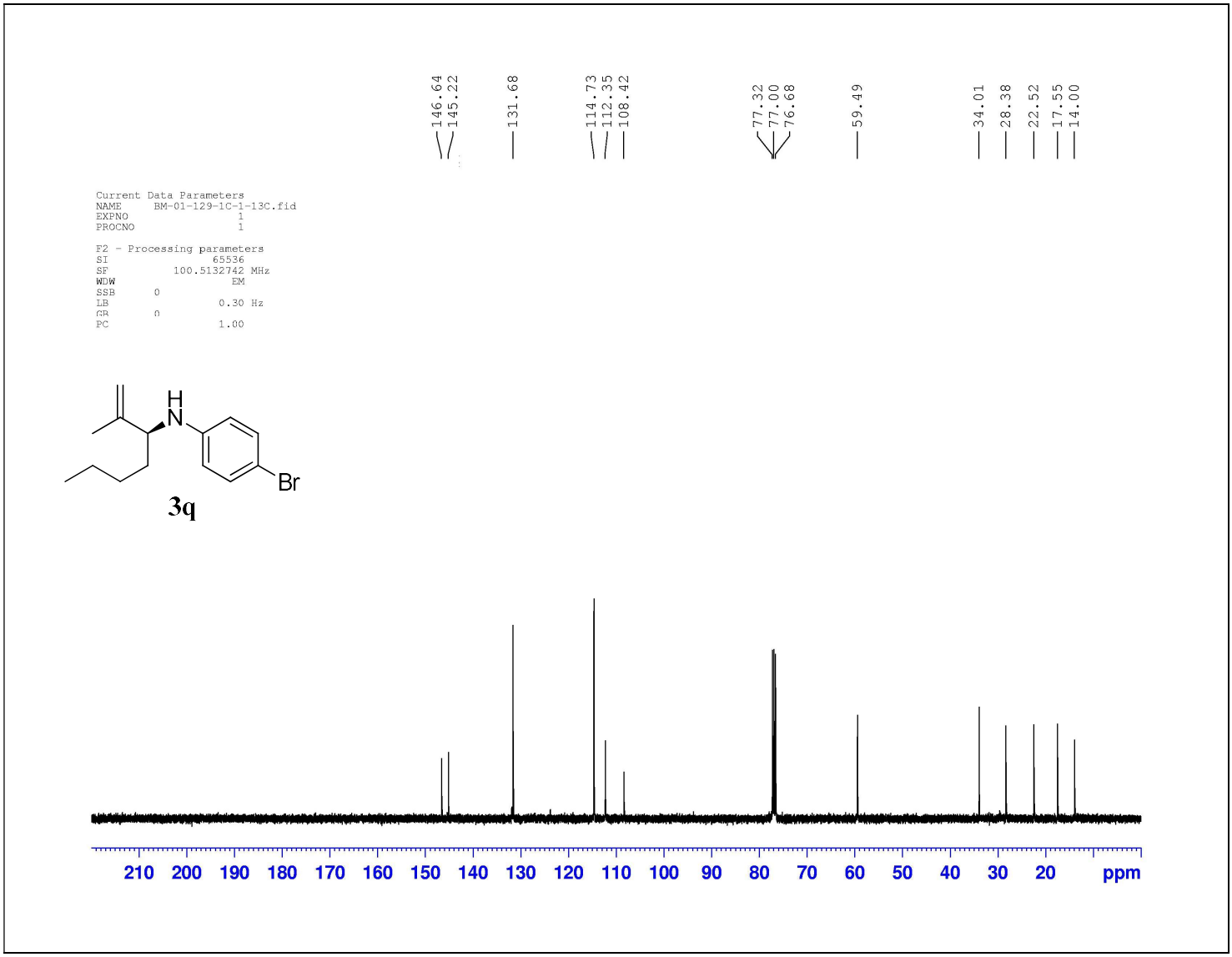
^{1}H Spectra of **3p** in $CDCl_3$.



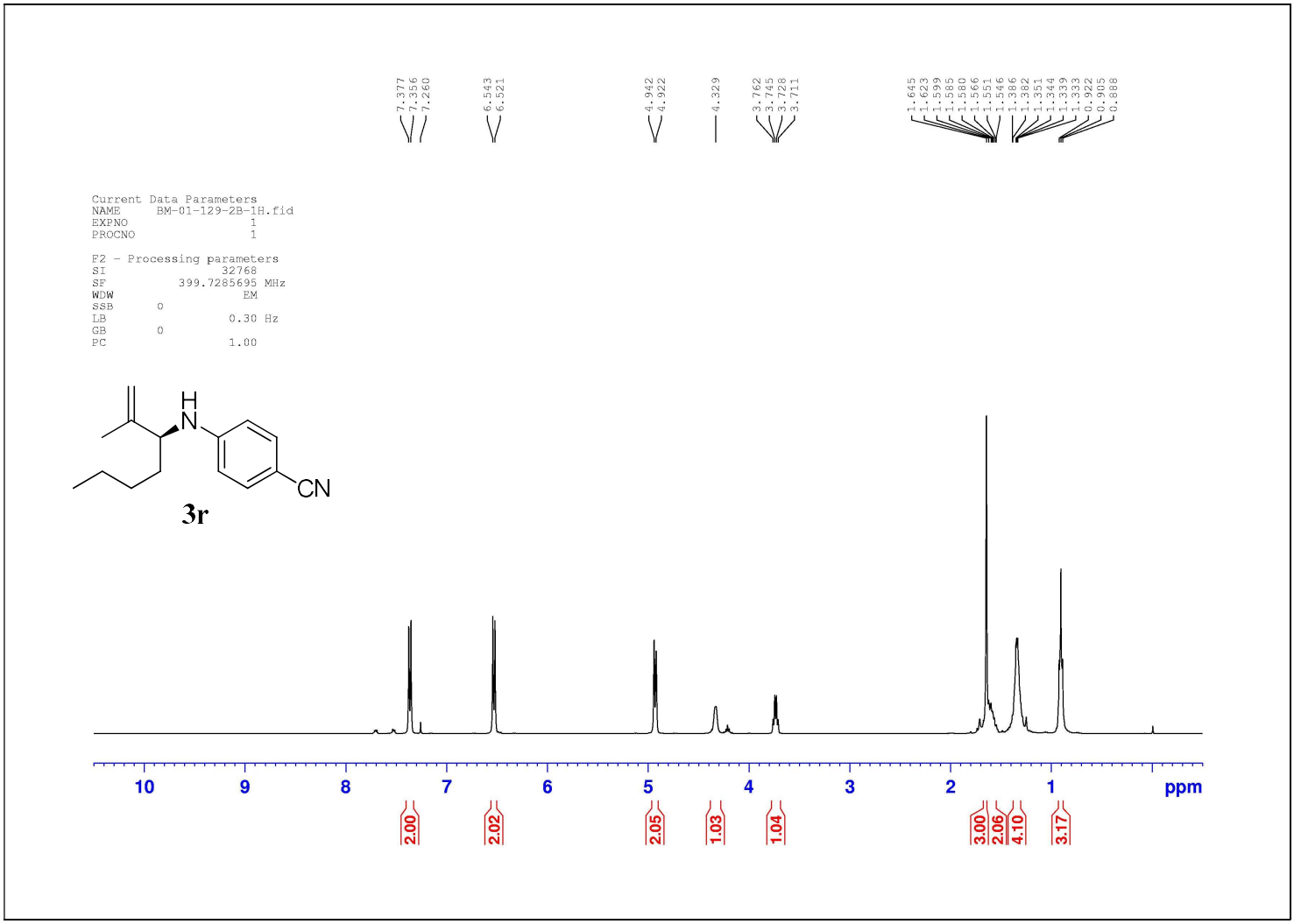
^{13}C NMR Spectra of **3p** in $CDCl_3$.



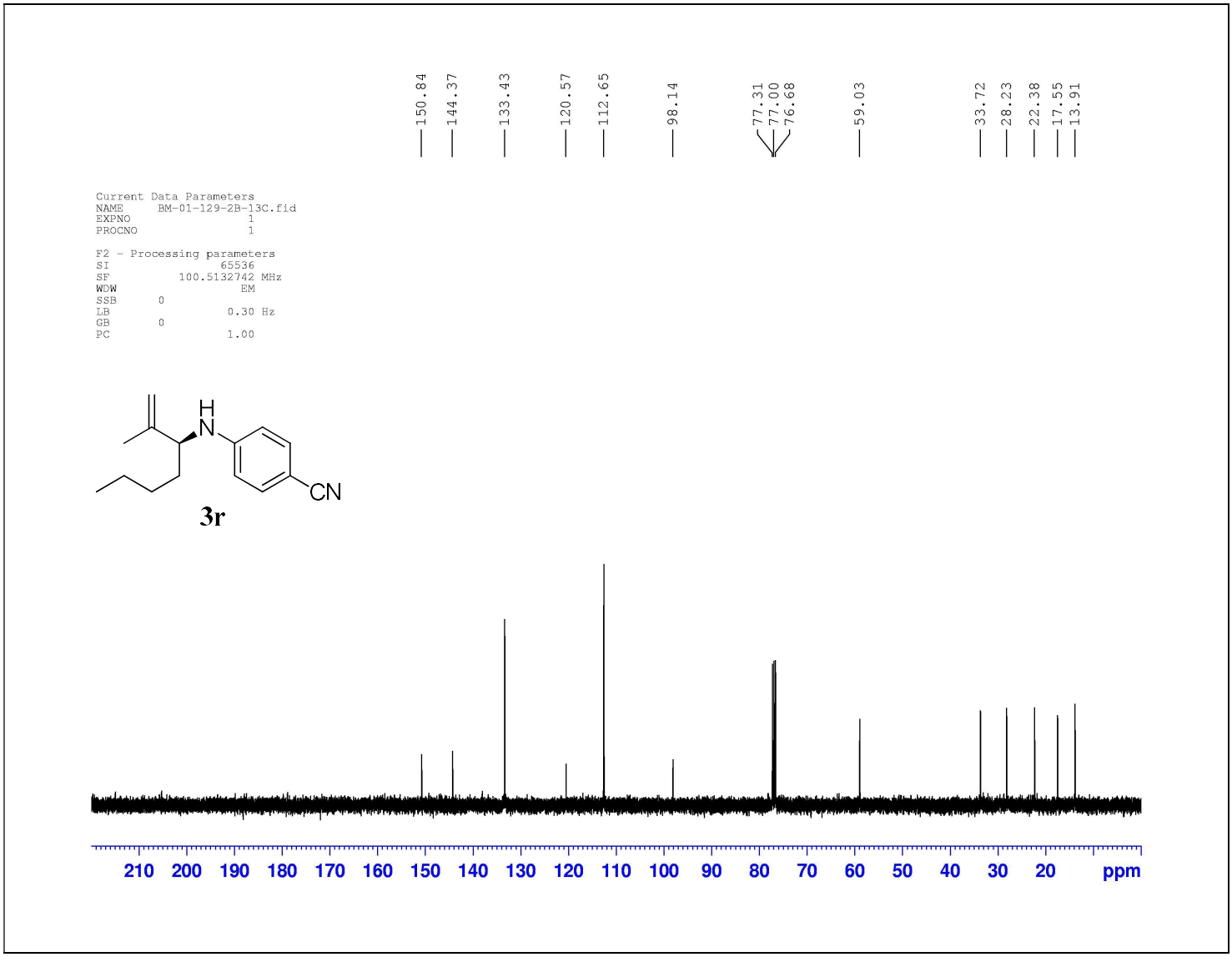
^{1}H Spectra of **3q** in $CDCl_3$.



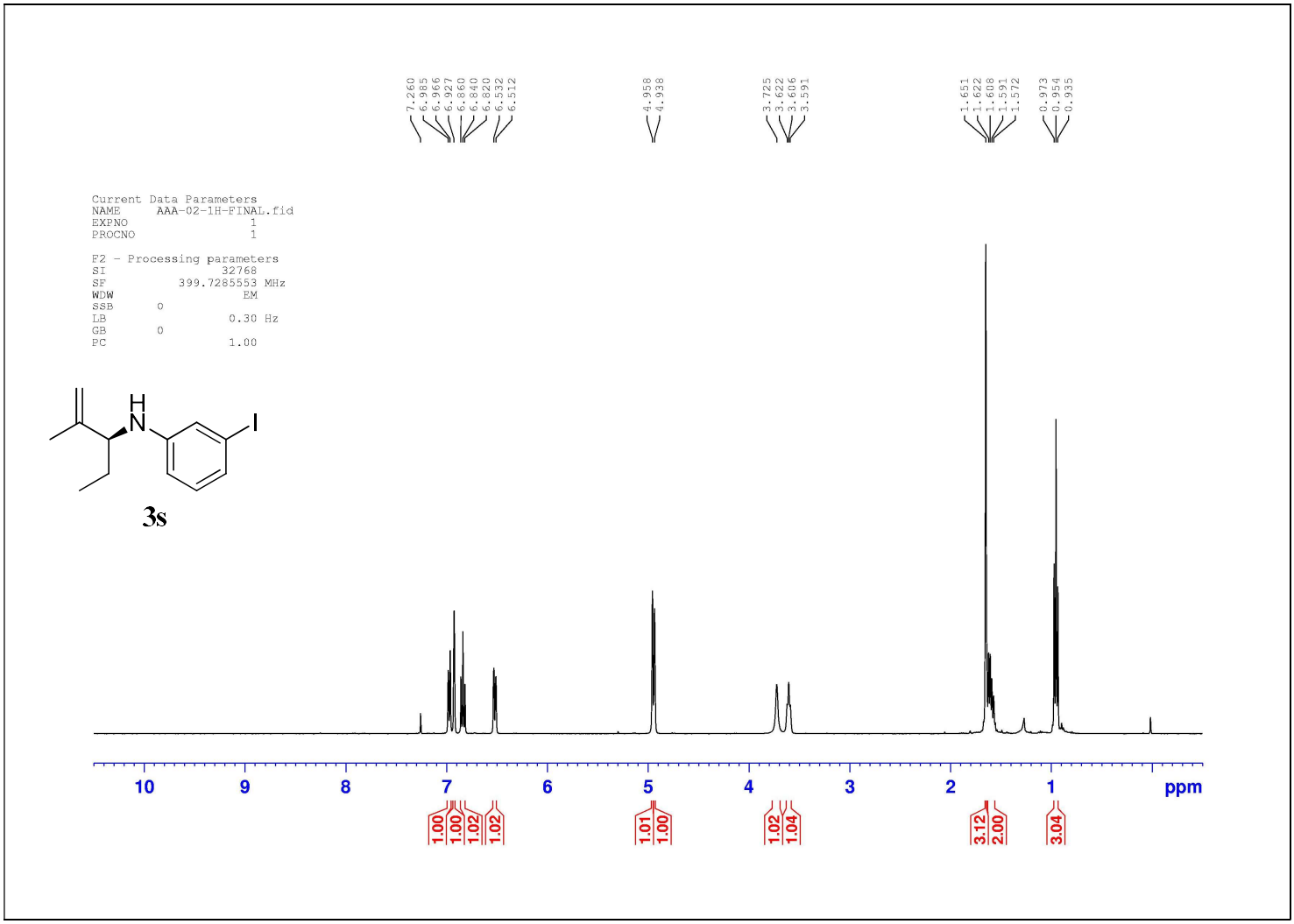
^{13}C NMR Spectra of **3q** in $CDCl_3$.



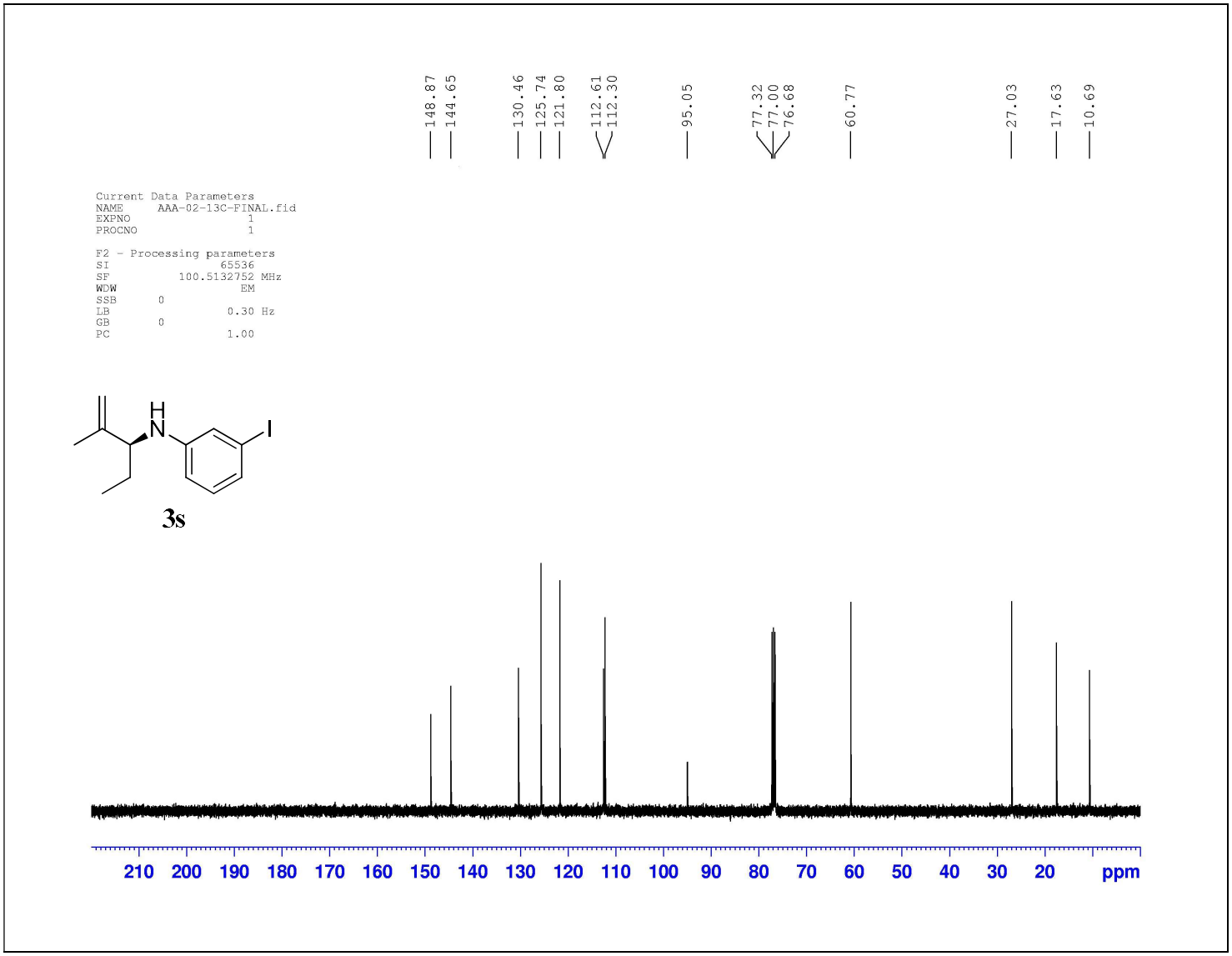
^{1}H Spectra of **3r** in $CDCl_3$.



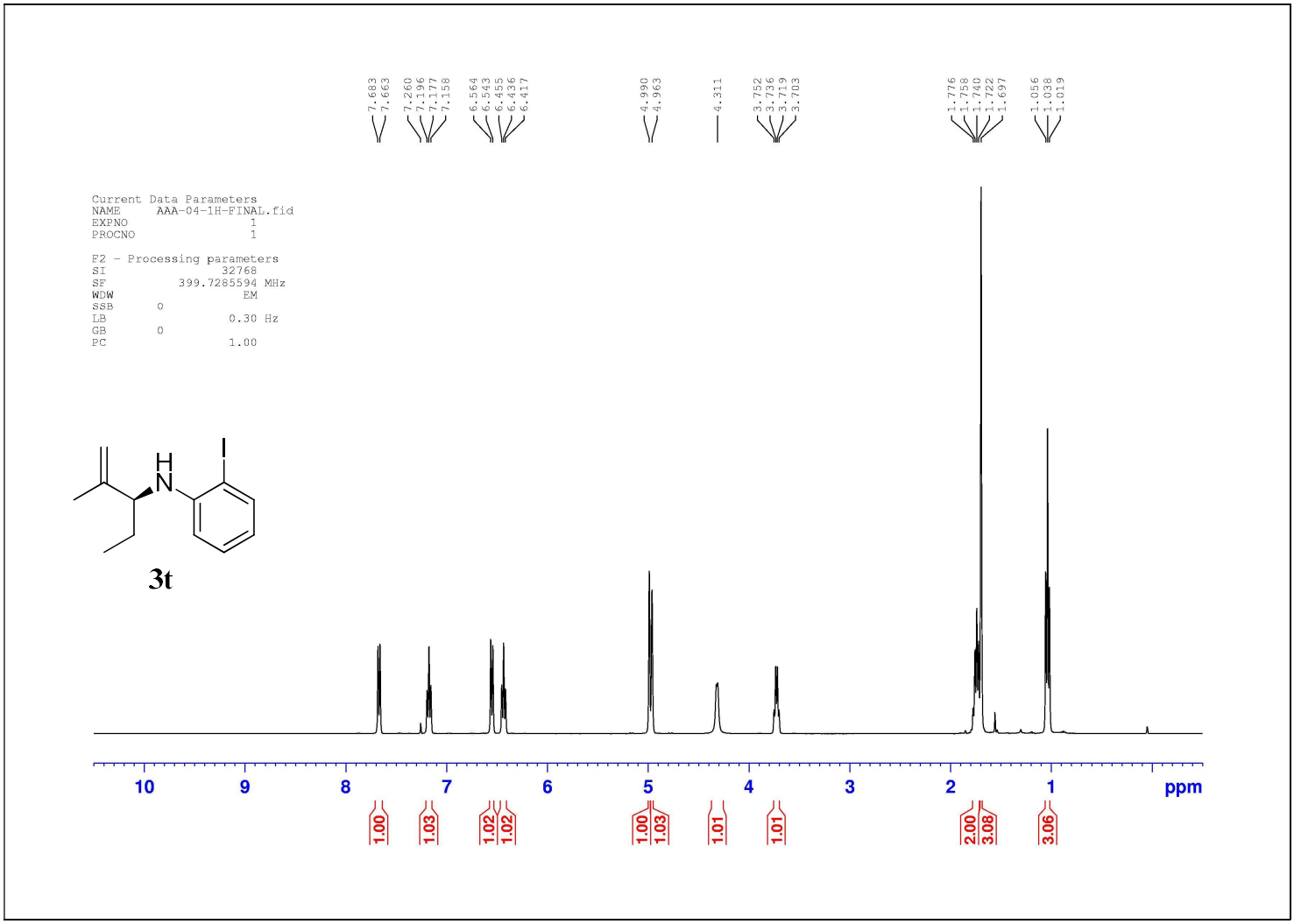
^{13}C NMR Spectra of **3r** in $CDCl_3$.



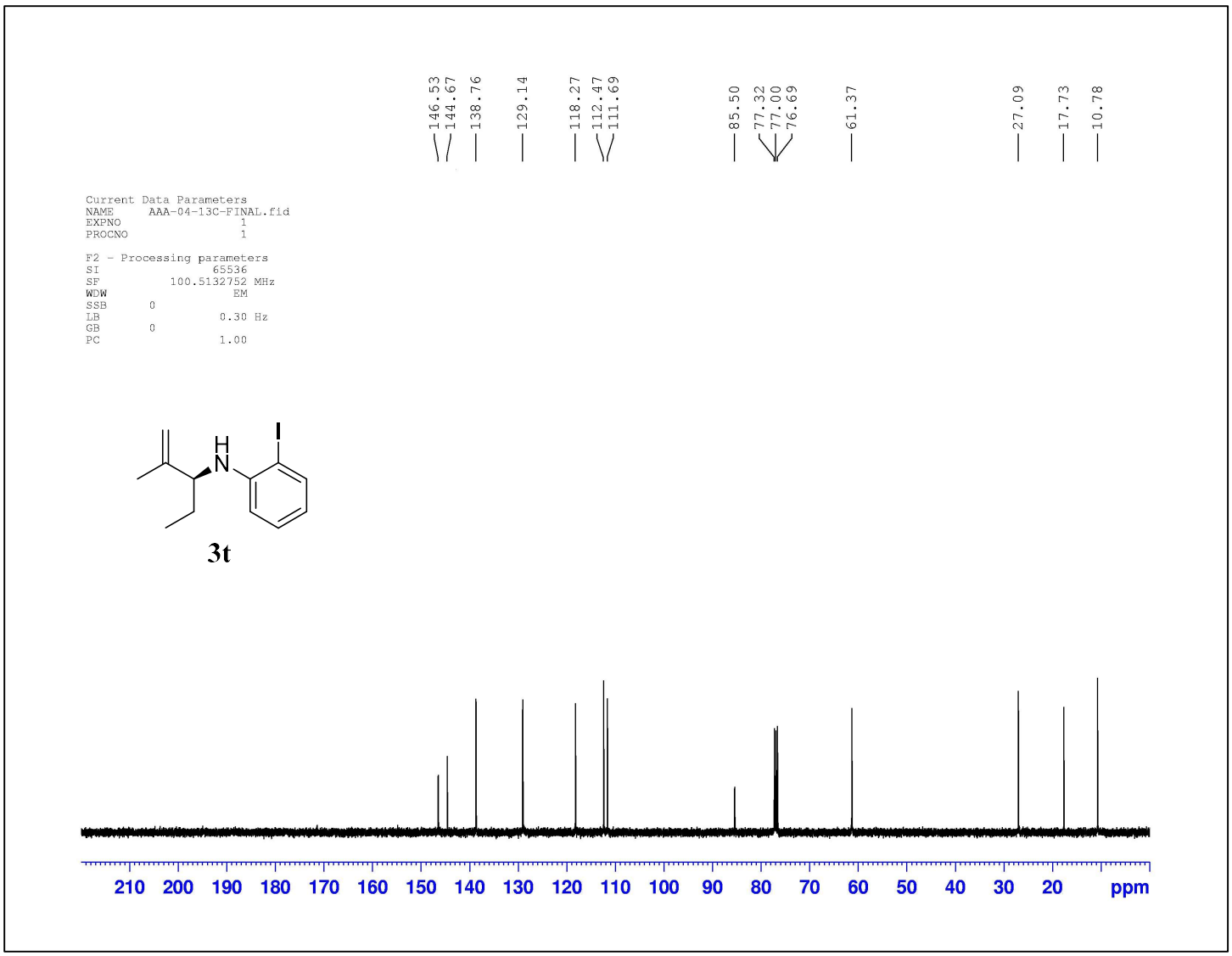
^{1}H Spectra of **3s** in $CDCl_3$.



^{13}C NMR Spectra of **3s** in $CDCl_3$.



^{1}H Spectra of **3t** in $CDCl_3$.



^{13}C NMR Spectra of **3t** in $CDCl_3$.