Supporting Information

Discovery of an Iridacycle Catalyst with Improved Reactivity and Enantioselectivity in the Hydrogenation of Dialkyl Ketimines

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General Information

Working Techniques:

All chemicals were purchased from Acros Organics, Sigma-Aldrich, Fluka, Merck Molecula or Strem Chemicals and used as received, unless otherwise noted. Anhydrous solvents were obtained in sure-seal bottles from Aldrich or Fluka, collected from a purification column system (PureSolv, Innovative Technology Inc.) or purified using standard methods (distillation of potassium/benzophenone or CaH_2). Air sensitive reactions were carried out in an atmosphere of purified nitrogen by using a glovebox and/or standard Schlenk techniques under argon.
Column chromatographic purifications were performed on Merck silica gel 60 (particle size 40-63 nm). The eluents were of technical grade and distilled prior to use. The hydrogenation experiments were prepared under purified nitrogen in a glove box (MBraun Labmaster 130) and the dichloromethane was purchased from Aldrich (≥ 99.5%, over molecular sieves).

Analytical Methods:

Melting Points (**m.p.**): Melting points were determined on a Büchi 535 and Büchi 545 apparatus. The Büchi 545 apparaturs was calibrated with benzoic acid.

Thin Layer Chromatography (**TLC**): TLC plates were obtained from Machrey-Nagel (Polygram SIL/UV254, 0.2 mm silica with fluorescence indicator). UV light (254 nm) or or stain solutions ($KMnO_4$, $Ce(SO_4)_2$, Ninhydrine) were used to visualize the respective compounds.

NMR-Spectrocopy (**NMR**): NMR spectra were measured either on a Bruker Avance 400 (^{1}H: 400 MHz, ^{13}C: 100.6 MHz) or a Bruker Avance 500 (^{1}H: 500 MHz, ^{13}C: 125.8 MHz) spectrometer. The chemical shifts (δ) are given in ppm. The chemical shift δ values were corrected to the signal of the signals of the deuterated solvents: 7.26 ppm (^{1}H-NMR) and 77.16 ppm (^{13}C{^{1}H}-NMR) for $CDCl_3$; 5.32 ppm (^{1}H-NMR) and 53.5 ppm (^{13}C{^{1}H}-NMR) for CD_2Cl_2. ^{31}P{^{1}H}-NMR spectra are calibrated relative to 85% phosphoric acid (δ = 0 ppm) and ^{19}F-NMR spectra relative to $CFCl_3$ (δ = 0 ppm) as external standards. ^{13}C and ^{31}P spectra were recorded ^{1}H-decoupled. The assignment of ^{1}H and ^{13}C signals was accomplished, when needed by two-dimensional correlation experiments (COSY and HSQC). Multiplets are assigned as: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), sex (sextet), sept (septet) and m (multiplet). Broad signals are assigned with: br (broad).

Infrared Spectroscopy (**IR**): Infrared spectra were collected on a Shimadzu FTIR-8400S spectrometer. The compounds were measured as pure substance via Specac ATR attachment. The absorption bands are given in wave numbers (ν [cm^{-1}]). The peak intensity is described by: s (strong), m (medium), w (weak).

Mass Spectroscopy (**MS**): Mass spectra were measured by Dr. H. Nadig (Departement of Chemistry, University of Basel) on a VG70-250 spectrometer (electron ionization (EI)) or on a MAR 312 spectrometer (fast atom bombardement (FAB)). FAB was performed with 3-nitrobenzyl alcohol (NBA)) as matrix. The signals are given in mass-to-charge ratios (m/z). The fragments and relative intensities are given in brackets.

Optical Rotations ($[\alpha]_D^{20}$): Optical rotations were measured on a Perkin Elmer Polarimeter 341 (in a cuvette (l = 1 dm)) at 20 °C at 589 nm. The concentration (c) is given in g/100 mL.

Elemental Analysis (EA): Elemental analyses were measured by Mr. W. Kirsch (department of Chemistry, University of Basel) and by M. Schneider (Microanalytical Laboratory of the Department of Organic Chemistry at the ETH Zurich) on a Leco CHN-900 (C-, H-, N-detection). The data are indicated in mass percent.

High Resolution Mass Spectrometry (**HRMS**) Performed by Dr. H. Nadig (Departement of Chemistry, University of Basel) on a Bruker maXis 4G and by the Laboratory of Mass Spectroscopy of the Department of Organic Chemistry at the ETH Zurich on a Bruker Daltonics maXis (UHR-TOF) and Bruker solariX 94 ESI/MALDI-FT-ICR spectrometer.

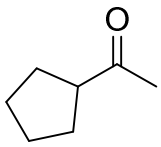
High Performance Liquid Chromatography (**HPLC**): HPLC analyses were performed on Shimadzu systems with SLC-10A/SIL-20AHT system controller, CTO-10AC/AS column oven, LC10-AD/20-AD pump system, DGU-14A/20AD3 degasser and SPD-M10A/M20A diode array- or UV/VIS detector. Chiral columns Chiracel AD-H, AS-H, OB-H, OD-H, OJ or OJ-H (0.46 x 250 mm) from Daicel Chemical Industries were used.

Gas Chromatography (GC) : Gas chromatograms were recorded on Carlo Erba HRGC Mega2 Series 800 (HRGS Mega2), on CarboErga GC8000Top and on Shimadzu GC-2010 plus instruments, Separations on achiral phases were performed on a Restek Rtx-1701 (30 m x 0.25 mm x 0.25 µmol) or a Macherey-Nagel Optima 5-Amin (0.25 mm x 0.25 µm x 30 m) column. Separations of enantiomers were achieved on a *Chiraldex γ*-cyclodextrin TFA G-TA (30 m x 0.25 mm x 0.12 µm) or a *Brechbühler β*-cyclodextrin DEtTButSil (SE54), (0.25 mm x 0.25 µm x 25 m) column.

Gas Chromatography / Mass Spectroscopy (GC-MS) : GC-MS analysis was performed on open-source 5890 Series II (GC-columns : Macherey-Nagel OPTIMA1 Me2Si, 25 m x 0.2 mm, 0.35 um, 20 psi, split ca. 20 :1, carrier gas : 1 mL/min heliem, 5971 series mass selective detector (EI) ; Macherey-Nagel Optima5 5% PhMeSi, 25 m 0.2 mm, 0.35 um, 20 psi, split ca 20 :1, carrier gas : 1 mL/min helium, 5970A series mass selective detector (EI)) and Shimadzu GC 2010 plus with GCMS-QP2010 SE mass detectors. The signals are given in mass-to-charge ratios (*m*/*z*) with the relative intensity in brackets.

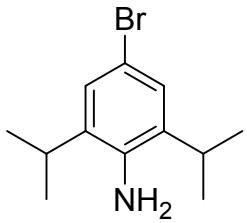
Synthetic Procedures

1-Cyclopentylethanone (15)[1]



Into a 25 mL two-necked round-bottom flask was placed a magnetic stirrer, the flask was closed with a stopper, and dried with a Bunsen burner while evacuating. After cooling to room temperature, the flask was purged with argon three times and cyclopentanoic acid (1 g, 8.85 mmol, 1.0 eq.) was added and dissolved in dry diethylether (8 mL). The reaction mixture was cooled to -78 °C with the aid of a dry ice / acetone bath and a solution of MeLi (1.6 M, 12.5 mL, 20.11 mmol, 2.3 eq.) was added dropwise via syringe over a period of 15 minutes. The reaction was allowed to warm to room temperature while stirring overnight. After quenching with saturated NH_4Cl solution (8 mL) the mixture turned clear and layers were separated. The organic layer was washed with water (10 mL= and the aequeous layer washed with ether (10 mL). The combined organic phases were dried over $MgSO_4$, filtered and solvents removed under reduced pressure to afford 0.5 g (4.4 mmol, 50%) of **15** as a clear oil.
$C_7H_{12}O$ (112.17 g/mol):
^{1}H-NMR (400 MHz, $CDCl_3$, δ/ppm) δ 2.94 – 2.78 (m, 1H, C*H*), 2.16 (s, 3H, CH_3), 1.88 – 1.45 (m, 10H, CH_2). **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 211.44 (*C*=O), 52.40 (*C*H), 28.95 (CH_2CH_2CH), 28.86 (CH_2CH_2CH), 26.10 (CH_3). **GC-MS:** (Rtx-5MS, 100.2/10.270/10): t_R = 3.3 min, *m/z* = 113 ($[M+1]^+$).

4-Bromo-2,6-diisopropylaniline (16)[2]



In a 500 mL round-bottom flask was placed 2,6-diisopropylaniline (6 mL, technical, ~90%, ~30 mmol) and dissolved in CH_2Cl_2 (250 mL). Tetrabutylammonium tribromide (15.4 g, 32 mmol) was added in one go. The reaction was stirred for 30 minutes before the solvent was removed under reduced pressure. The residue was redissolved in diethyl ether (250 mL), washed with NaOH (0.5 M, 150 mL), water (2 x 150 mL), dried over $MgSO_4$, filtered and solvents removed under reduced pressure to afford 7.6 g (29.7 mmol, 98%) of **16** as a yellow oil.
$C_{12}H_{18}BrN$ (256.18 g/mol):
^{1}H-NMR (400 MHz, $CDCl_3$, δ/ppm) δ 7.11 (s, 2H, CH_{Ar}), 3.70 (s, 2H, NH_2), 2.95 – 2.81 (m, 2H, $CH(CH_3)_2$), 1.25 (d, *J* = 6.8 Hz, 12H, CH_3).

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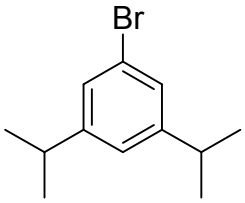
[1] M. Hanack , K. A. Fuchs , C. J. Collins, *J. Am. Chem. Soc.* **1983**, *105*, 4008-4017
[2] V. Diemer, H. Chaumeil, A. Defoin, A. Fort, A. Boeglin, C. Carré, *Eur. J. Org. Chem.* **2006**, 2727-2738

1-Bromo-3,5-diisopropylbenzene (17)[2]

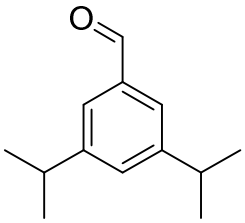


In a 500 mL round-bottom flask was placed **16** (7.6 g, 29.7 mmol, 1.0 eq.) and suspended in HCl (2 M, 70 mL). The reaction mixture was cooled to -5 °C and sodium nitrite (5.12 g, 74 mmol, 1.05 eq) was added portionwise. After addition the reaction was stirred for 30 minutes before H_3PO_4 (50% in water, 35 mL, 300 mmol, 4.0 eq.) was added. The mixture was stirred at 4 °C overnight. Ether (100 mL) was added and layers were separated. The aeqeuous layer was washed with ether (2 x 100 mL) and the combined organic layers were dried over $MgSO_4$, filtered and solvents removed under reduced pressure. Purification by distillation (115 °C, 0.15 mbar) afforded 4.0 g (16.6 mmol, 56%) of **17** as a yellow oil.

$C_{12}H_{17}Br$ (241.17 g/mol):

b.p.: 115°C at 0.1 torr; **^{1}H-NMR** (400 MHz, $CDCl_3$, δ/ppm) δ 7.18 (d, J = 1.5 Hz, 2H, CH_{Ar}CBrCH_{Ar}), 6.98 (s, 1H, CH_{Ar}), 2.92 – 2.77 (m, 2H, CH(CH_3)$_2$), 1.23 (d, J = 6.9 Hz, 12H, CH_3).

3,5-Di-isopropylbenzaldehyde (18)[2]

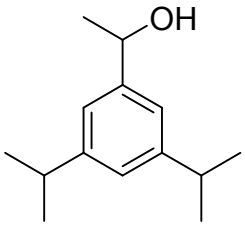


In a 100 mL three-necked round-bottom flask equipped with a magnetic stirrer, argon inlet, thermometer and a stopper was placed **17** (4.0 g, 16.6 mmol, 1.0 eq.) and cooled to -78 °C with the aid of a dry ice / acetone bath. *n*-BuLi (1.6 M, 18.26 mmol, 1.1 eq.) was added dropwise via syringe and the resultant suspension was stirred for 20 minutes at -78 °C. Then DMF (1.33 g, 18.26 mmol, 1.1 eq.) was added dropwise via syringe, the mixture stirred for 10 minutes being allowed to warm to -10 °C. The reaction was quenched with water (12 mL) at -10 °C and the mixture warmed to room temperature. Layers were separated and the aeqeuous layer washed with ether (100 mL). Organic layers were combined and solvents removed under reduced pressure. The residue was purified by flash chromatography (SiO_2, 18 x 4.5 cm, cyclohexane/EtOAc 20:1) to afford 2.05 g (10.77 mmol, 65%) of **18** as a clear oil.

$C_{13}H_{18}O$ (190.28 g/mol):

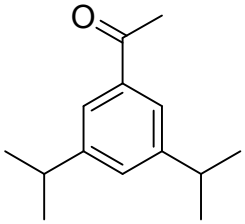
R_f (SiO_2, *n*-pentane/AcOEt 10:1, UV, $Ce(SO_4)_2$) = 0.63; **^{1}H-NMR** (400 MHz, $CDCl_3$, δ/ppm) δ 9.99 (s, 1H, CHO), 7.57 (d, J = 1.7 Hz, 2H, CH_{Ar}CHOCH_{Ar}), 7.35 (s, 1H, CH_{Ar}), 3.04 – 2.90 (m, 2H, CH(CH_3)$_2$), 1.29 (dd, J = 6.9, 1.8 Hz, 12H, CH_3).

1-(3,5-Di-isopropylphenyl)ethanol (19)



In a 100 mL three-necked round-bottom flask equipped with a magnetic stirrer, argon inlet and a stopper was placed **18** (2.05 g, 10.77 mmol, 1.0 eq.) and dissolved in dry diethyl ether (40 mL). The solution was cooled to 0 °C and MeMgBr (3.0 M, 16.2 mmol, 1.5 eq.) was added dropwise via syringe. The reaction mixture was stirred at 0 °C for 15 minutes before being allowed to warm to room temperature and stirred for 2 hours. The mixture was cooled to 0 °C again and quenched with sat. NH_4Cl (40 mL) and water (20 mL). After warming to room temperature, layers were separated and the aq. layer was extracted with EtOAc (3 x 60 mL). The combined organic layers were dried over $MgSO_4$, filtered and solvents removed under reduced pressure. The residue was purified via flash chromatography (SiO_2, 15 x 3 cm, cyclohexane/EtOAc 5:1) to afford 1.89 g (9.16 mmol, 85%) of **19** as an orange viscous oil.
$C_{14}H_{22}O$ (206.32 g/mol):
^{1}H-NMR (400 MHz, $CDCl_3$, δ/ppm) δ 7.06 (d, J = 1.6 Hz, 2H, CH_{Ar}), 7.01 (d, J = 1.6 Hz, 1H, CH_{Ar}), 4.87 (qd, J = 6.4, 3.6 Hz, 1H, CH(OH)), 2.90 (hept, J = 6.9 Hz, 2H, CH(CH_3)$_2$), 1.51 (d, J = 6.4 Hz, 3H, CH_3CHOH), 1.26 (d, J = 6.9 Hz, 12H, CH(CH_3)$_2$). **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 149.30 (*C*CH(CH$_3$)$_2$), 145.89 (*C*CH(OH)), 124.12 (*C*H$_{Ar}$CCH(CH$_3$)$_2$), 121.10 (*C*H$_{Ar}$CCH(CH$_3$)$_2$CCH(OH)), 70.98 (*C*H(OH)), 34.40 (*C*H(CH$_3$)$_2$), 25.22 (C=O*C*H$_3$), 24.24 (CH(*C*H$_3$)$_2$); **IR** (neat, ATR) ν/cm^{-1} = 3340 (m_{br}), 2961 (s), 2929 (m), 2887 (m), 2868 (m), 1603 (w), 1467 (m), 1459 (m), 1450 (m), 1382 (w), 1363 (m), 1176 (w), 1112 (w), 1073 (w), 1020 (w), 873 (w), 716 (m); **GC-MS**: (Rtx-5MS, 100.2/10.270/10): t_R = 11.8 min, m/z = 206 ([M]$^+$).

1-(3,5-Di-isopropylphenyl)ethanone (20)[3]



In a 100 mL round-bottom flask was placed **19** (1.0 g, 4.5 mmol, 1.0 eq.) and dissolved in CH_2Cl_2 (50 mL). Dess-Martin Periodane (2.7 g, 6.37 mmol, 1.4 eq.) was added in one portion and the resultant mixture stirred for one hour at room temperature. The reaction mixture was poured into a solution of pentane/EtOAc (4:1, 80 mL) and a white precipitate was formed. The suspension was filtered over a frit (SiO_2) and a yellow solution was obtained. The fritt was rinsed with more pentane/EtOAc (4:1, 100 mL) and solvents were removed under reduced pressure. The residue was purified by flash chromatography (SiO_2, 18 x 3 cm, cyclohexane/EtOAc 20:1) to afford 1.0 g (4.31 mmol, 96%) of **20** as an orange oil.
$C_{14}H_{20}O$ (204.31 g/mol):
^{1}H-NMR (400 MHz, $CDCl_3$, δ/ppm) δ 7.64 (d, J = 1.7 Hz, 2H, CH_{Ar}), 7.29 (t, J = 1.6 Hz, 1H, CH_{Ar}), 3.03 – 2.86 (m, 2H, CH(CH$_3$)$_2$), 2.60 (s, 3H, CH_3C=O), 1.28 (d, J = 6.9 Hz, 12H, CH(CH_3)$_2$). **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 198.83 (*C*=O), 149.46 (*C*CH(CH$_3$)$_2$), 137.59 (*C*C=O), 129.93 (CH_{Ar}), 124.07 (2 CH_{Ar}), 34.32 (*C*H(CH$_3$)$_2$), 26.92 (C=O*C*H$_3$), 24.12 (CH(*C*H$_3$)$_2$).

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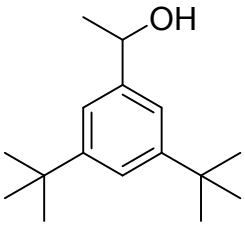
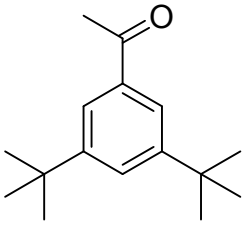
[3] N. Yoneda, T. Fukuhara, Y. Takahashi, A. Suzuki, *Chem. Lett.* **1979**, 1003-1006

1-(3,5-Di-tert-butylphenyl)ethanol (21)[4]



In a 100 mL three-necked round-bottom flask equipped with a magnetic stirrer, argon inlet and a stopper was placed 3,5-di-tertbutylbenzaldehyde (1.0 g, 4.5 mmol, 1.0 eq.) and dissolved in dry diethyl ether (18 mL). The solution was cooled to 0 °C and MeMgBr (3.0 M, 6.82 mmol, 1.5 eq.) was added dropwise via syringe. The reaction mixture was stirred at 0 °C for 15 minutes before being allowed to warm to room temperature and stirred for 2 hours. The mixture was cooled to 0°C again and quenched with sat. NH_4Cl (40 mL) and water (20 mL). After warming to room temperature, layers were separated and the aq. layer was extracted with EtOAc (3 x 60 mL). The combined organic layers were dried over $MgSO_4$, filtered and solvents removed under reduced pressure to afford 1.05 g (4.47 mmol, 96%) of **21** as a white solid.
$C_{16}H_{26}O$ (234.38 g/mol):
^{1}H-NMR (400 MHz, $CDCl_3$, δ/ppm) δ 7.36 (t, *J* = 1.8 Hz, 1H, C*H*$_{Ar}$), 7.23 (d, *J* = 1.7 Hz, 2H, C*H*$_{Ar}$), 4.90 (q, *J* = 6.4 H, 1H, C*H*OH), 1.77 (s_{br}, 1H, O*H*), 1.52 (d, *J* = 6.5 Hz, 3H, C*H*$_3$), 1.34 (s, 18H, C(C*H*$_3$)$_3$).

1-(3,5-Di-tert-butylphenyl)ethanone (22)[5]



In a 100 mL round-bottom flask was placed **21** (1.05 g, 4.47 mmol, 1.0 eq.) and dissolved in CH_2Cl_2 (50 mL). Dess-Martin Periodane (2.5 g, 5.9 mmol, 1.32 eq.) was added in one portion and the resultant mixture stirred for one hour at room temperature. The reaction mixture was poured into a solution of pentane/EtOAc (4:1, 80 mL) and a white precipitate was formed. The suspension was filtered over a fritt (SiO_2) and a yellow solution was obtained. The frit was rinsed with more pentane/EtOAc (4:1, 100 mL) and solvents were removed under reduced pressure. The residue was purified by flash chromatography (SiO_2, 18 x 3 cm, cyclohexane/EtOAc 20:1) to afford 1.0 g (4.31 mmol, 96%) of **22** as a clear oil.
$C_{16}H_{24}O$ (232.36 g/mol):
^{1}H-NMR (400 MHz, $CDCl_3$, δ/ppm) δ 7.81 (d, *J* = 1.8 Hz, 2H, C*H*$_{Ar}$), 7.65 (t, *J* = 1.8 Hz, 1H, C*H*$_{Ar}$), 2.62 (s, 3H, C=OC*H*$_3$), 1.36 (s, 18H, C(C*H*$_3$)$_3$); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 199.04 (*C*=O), 151.36 (*C*$_{Ar}$C(CH$_3$)$_3$), 137.04 (*C*$_{Ar}$C=O), 127.50 (1 *C*H$_{Ar}$), 122.66 (2 *C*H$_{Ar}$), 35.13 (*C*(CH$_3$)$_3$), 31.54 (C(*C*H$_3$)$_3$), 27.07 (C=O*C*H$_3$).

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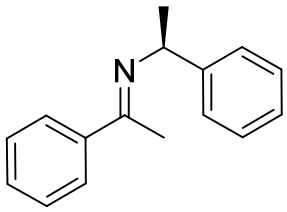
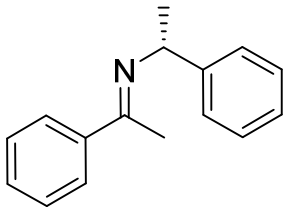
[4] D. C. Ebner, J. T. Bagdanoff, E. M. Ferreira, R. M. McFadden, D. D. Caspi, R. M. Trend, B. M. Stoltz, *Chem. Eur. J.* **2009**, *15*, 12978-12992
[5] L. Zhang, A. M. Nadzan, R. A. Heyman, D. L. Love, D. E. Mais, G. Croston, W. W. Lamph, M. F. Boehm, *J. Med. Chem.* **1996**, 39, 2659-2663

(*S*)-1-phenyl-*N*-(1-phenylethylidene)ethanamine ((*S*)-23)[6]



By general method acetophenone (1.96 g, 16.32 mmol, 1.2 eq.) and (*S*)-1-phenylethanamine (1.65 g, 13.6 mmol, 1.0 eq.) were dissolved in dry benzene (20 mL). Purification by Kugelrohr distillation (135 °C at 0.15 mbar) afforded (*S*)-**23** (1.92 g, 8.6 mmol, 63 %) as a clear oil.
$C_{16}H_{17}N$ (223.31 g/mol):
b.p.: 135 °C (0.15 mbar); 10:1 *E*/*Z* mixture, major: **^{1}H-NMR** (500 MHz, $CDCl_3$) δ: 7.84 (m, 2H, $CH_{Ar}C_{Ar}C$=N), 7.47 (d, *J* = 7.8 Hz, 2H, $CH_{Ar}CH_{Ar}C_{Ar}C$=N), 7.39 (m, 3H, $CH_{Ar}C_{Ar}CH(CH_3)$ and $CH_{Ar}CH_{Ar}CH_{Ar}C_{Ar}C$=N), 7.33 (t, *J* = 7.5 Hz, 2H, $CH_{Ar}CH_{Ar}C_{Ar}CH(CH_3)$), 7.23 (t, *J* = 7.7 Hz, 1H, $CH_{Ar}CH_{Ar}CH_{Ar}C_{Ar}CH(CH_3)$N), 4.84 (q, *J* = 6.5 Hz, 1H, $C_{Ar}CH(CH_3)$N=C), 2.27 (s, 3H, C=NCH_3), 1.54 (d, *J* = 6.5 Hz, 3H, CH(CH_3)); **^{13}C{^{1}H}-NMR** (126 MHz, $CDCl_3$) δ 163.68 (*C*=N), 146.37 ($C_{Ar}CH(CH_3)$N), 141.68 ($C_{Ar}C$=N), 129.56 ($CH_{Ar}CH_{Ar}CH_{Ar}C_{Ar}C$=N), 128.51 ($CH_{Ar}CH_{Ar}C_{Ar}CH(CH_3)$N), 128.33 ($CH_{Ar}CH_{Ar}C_{Ar}C$=N), 126.95 ($CH_{Ar}C_{Ar}C$=N), 126.82 ($CH_{Ar}C_{Ar}CH(CH_3)$N), 126.67 ($CH_{Ar}CH_{Ar}CH_{Ar}C_{Ar}CH(CH_3)$N), 60.00 ($CH(CH_3)$N), 25.25 (CH($CH_3$)N), 15.78 (C=N$CH_3$); **Optical Rotation**: $[\alpha]_D^{20}$ = +92.5 (c 0.75 in $CHCl_3$, 0.75% EtOH) (Lit. +97.7 (c 1.8 in CCl_4)).

(*R*)-1-phenyl-*N*-(1-phenylethylidene)ethanamine ((*R*)-23)[6]



By general method acetophenone (0.98 g, 8.16 mmol, 1.2 eq.) and (*R*)-1-phenylethanamine (0.824 g, 6.8 mmol, 1.0 eq.) were dissolved in dry benzene (10 mL). Purification by Kugelrohr distillation (135 °C at 0.15 mbar) afforded (*R*)-**23** (0.925 g, 4.14 mmol, 61 %) as a clear oil.
$C_{16}H_{17}N$ (223.31 g/mol):
^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.84 (m, 2H, $CH_{Ar}C_{Ar}C$=N), 7.47 (d, *J* = 7.8 Hz, 2H, $CH_{Ar}CH_{Ar}C_{Ar}C$=N), 7.39 (m, 3H, $CH_{Ar}C_{Ar}CH(CH_3)$ and $CH_{Ar}CH_{Ar}CH_{Ar}C_{Ar}C$=N), 7.33 (t, *J* = 7.5 Hz, 2H, $CH_{Ar}CH_{Ar}C_{Ar}CH(CH_3)$N), 7.23 (t, *J* = 7.7 Hz, 1H, $CH_{Ar}CH_{Ar}CH_{Ar}C_{Ar}CH(CH_3)$), 4.84 (q, *J* = 6.5 Hz, 1H, $C_{Ar}CH(CH_3)$N=C), 2.27 (s, 3H, C=NCH_3), 1.54 (d, *J* = 6.5 Hz, 3H, CH(CH_3)); **Optical Rotation**: $[\alpha]_D^{20}$ = -94.0 (c 0.75 in $CHCl_3$, 0.75% EtOH) (Lit. -97.7 (c 1.8 in CCl_4)).

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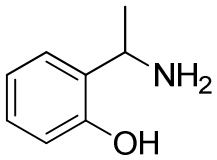
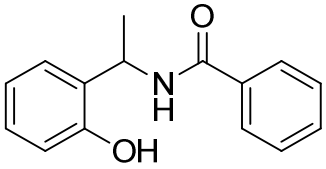
[6] E. Rogalska , C. Belzecki, *J. Org. Chem.* **1984**, *49*, 1397-1402

2-(1-aminoethyl)phenol (24)[7]



In a 500 mL three-neck round bottom flask equipped with a magnetic stirrer and a reflux condenser was inserted 2-methoxybenzonitrile (4.50 g, 33.8 mmol, 1.0 eq), CuBr (98.0 mg, 0.683 mmol, 0.02 eq) and dissolved in dry THF (75 mL). A solution of MeMgCl in THF (3M, 21.4 mL, 4.81 g MeMgCl, 64.3 mmol, 1.9 eq) was added and the resultant mixture heated to reflux for 16 hours. A short reaction control via TLC depicted all the starting material had not been consumed and therefore again a solution of MeMgCl in THF (3M, 5.00 mL, 1.12 g, 15.0 mmol, 0.4 eq; total 5.93 g MeMgCl) was added and refluxing continued for further 5 hours. Afterwards the reaction mixture was allowed to cool to room temperature. A mechanical stirrer, a ammonia condensation vessel and washing bottles were mounted and the mixture cooled to -78 °C. Subsequently ammonia (approx. 200 mL) was condensed into the reaction mixture. Lithium (1.19 g, 169 mmol, 5.0 eq) was added in small pieces until the reaction mixture turned blue. The cooling bath was removed and the reaction mixture was allowed to warm up overnight while stirring and evaporating all ammonia. *tert*-Butylmethylether (MTBE) was added to the mixture, cooled to 0 °C and titrated with concentrated HCl to pH 8. The organic layer was separated, the aequeous layer salted out and extracted with MTBE (3 x 100 mL). The combined organic layers were washed with brine (100 mL), 0.5 M HCl (3 x 150 mL) and the acidic aequeous phase extracted with MTBE (3 x 50 mL). The acidic aequeous layer was set to pH 11 with 10% NaOH (10%), salted out and extracted with MTBE (3 x 50 mL). The combined organic layers were dried over $MgSO_4$, solvents removed under reduced pressure and the residue was purified via distillation (60-65 °C at 0.08 mbar). **24** was obtained as a greenish oil (1.03 g, 7.5 mmol, 22%). The product contained 1-(2-Methoxyphenyl)ethanamine as an impurity (0.265 g, 1.8 mmol, 4%).
$C_8H_{11}NO$ (137.18 g/mol):
b.p.: 65°C (0.08 mbar); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.15 (td, ^3J = 7.9 Hz, ^4J = 1.7 Hz, 1H, $CH_{Ar}CH_{Ar}C_{Ar}CH(NH_2)$); 6.97 (dd, ^3J = 7.5 Hz, ^4J = 1.5 Hz, 1H, $CH_{Ar}C_{Ar}(OH)$); 6.84 (dd, ^3J = 8.1 Hz, ^4J = 0.9 Hz, 1H, $CH_{Ar}C_{Ar}CH(NH_2)$); 6.78 (td, ^3J = 7.4 Hz, ^4J = 1.1 Hz, 1H, $CH_{Ar}CH_{Ar}C_{Ar}(OH)$); 4.33 (q, J = 6.6 Hz, 1H, $CH(NH_2)(CH_3)$); 3.85 (s, 2H, NH_2); 1.48 (d, J = 6.7 Hz, 3H, CH_3); **^{13}C{^{1}H}-NMR** (126 MHz, $CDCl_3$) δ 157.76 ($C_{Ar}(OH)$, 128.59 ($C_{Ar}CH$); 128.23 (CH_{Ar}); 127.31 (CH_{Ar}); 119.13 (CH_{Ar}); 117.35 (CH_{Ar}); 51.87 ($CH(NH_2)(CH_3)$); 24.01 (CH_3).

***N*-(1-(2-hydroxyphenyl)ethyl)benzamide (25)**

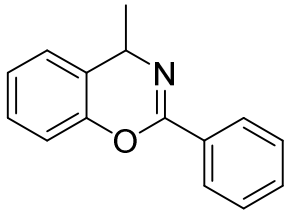


In a 25 mL two-neck round bottom flash equipped with a magnetic stirrer and a septum was placed crude **24** (1.295 g, 9.3 mmol, 1.24 eq), dissolved in CH_2Cl_2 (10 mL) and cooled to 0 °C. Benzoylchloride (1.05 g, 7.50 mmol, 1.0 eq) and triethylamine (0.833 g, 8.25 mmol, 1.1 eq) were added via syringe pump over a period of 5 minutes. After another 10 minutes the cooling bath was removed and the reaction mixture allowed to warm to room temperature while stirring overnight. Solvents were removed at the rotavap and the crude was purified *via* elution chromatography (7 cm x 4 cm, SiO_2, EtOAc) to give **25** as a yellow oil. The product contained N-(1-(2-Methoxy-phenyl)ethyl)benzamide as an impurity of about 25%. Thus, the crude product was transferred to an

[7] E. Peter Kündig, C. Botuha, G. Lemercier, P. Romanens, L. Saudan, S. Thibault, *Helv.Chim. Acta* **2004**, *87*, 561-579

25 mL oven-dried argon-purged two-neck round bottom flask, dissolved in 5 mL CH_2Cl_2 and cooled to -78 °C. A solution of BBr_3 (1M in CH_2Cl_2) was added dropwise via syringe and the resultant mixture stirred for 15 minutes. The cooling bath was removed and reaction mixture allowed to warm to room temperature overnight. 10% NaOH (10 mL) were added dropwise and the resultant mixture stirred for 10 minutes. Layers were separated and the aeqeous layer was acidified with 1M HCl (25 mL), set to pH 8 via addition of saturated $NaHCO_3$ solution and extracted with CH_2Cl_2 (2 x 25 mL). The combined organic layers were dried over $MgSO_4$, solvents removed under reduced pressure and **25** obtained as a yellow oil (1.54 g, 6.4 mmol, 85%). Enantiomers were separated by semipreparative HPLC. **25** was dissolved in a mixture of heptane/2-propanol (9:1) to a concentration of 0.3g mL^{-1}. Daicel Chiralcel OD (2 cm x 25 cm), *n*-hexane : 2-propanol (90:10), 6 mL min^{-1}, 40 °C, 0.25 mL injection volume, t_R = 41.0 min (*S*)-(+), t_R = 49.0 min (*R*)-(-)
$C_{15}H_{15}NO_2$ (241.29 g/mol):
m.p.: 131-133 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 9.23 (s, 1H, $C_{Ar}(OH)$), 7.75 (m, 2H, $CH_{Ar}C_{Ar}C$=O), 7.51 (m, 1H, $CH_{Ar}CH_{Ar}CH_{Ar}C_{Ar}C$=O), 7.43 (m, 2H, $CH_{Ar}CH_{Ar}C_{Ar}C$=O), 7.28 (dd, ^3J = 7.7, ^4J = 1.7 Hz, 1H, $CH_{Ar}C_{Ar}CHNH$), 7.20 (ddd, ^3J = 8.1, 7.3, ^4J = 1.7 Hz, 1H, $CH_{Ar}CH_{Ar}C_{Ar}(OH)$), 6.97 (dd, ^3J = 8.1, ^4J = 1.3 Hz, 1H, $CH_{Ar}C_{Ar}(OH)$), 6.90 (td, ^3J = 7.5, ^4J = 1.3 Hz, 1H, $CH_{Ar}CH_{Ar}C_{Ar}CHNH$), 6.53 (d, ^3J = 8.5 Hz, 1H, N*H*), 5.51 (dq, ^3J = 8.6, 7.1 Hz, 1H, C*H*NH), 1.73 (d, ^3J = 7.0 Hz, 3H, CH_3); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 168.73 (*C*=O); 155.47 ($C_{Ar}(OH)$); 133.12 ($C_{Ar}C$=O); 132.31 ($CH_{Ar}CH_{Ar}CH_{Ar}C_{Ar}C$=O); 129.48 ($CH_{Ar}CH_{Ar}C_{Ar}(OH)$); 128.82 ($CH_{Ar}CH_{Ar}C_{Ar}C$=O); 128.57 ($C_{Ar}CHNH$); 127.26 ($CH_{Ar}C_{Ar}C$=O); 125.91 ($CH_{Ar}C_{Ar}CHNH$); 120.39 ($CH_{Ar}CH_{Ar}C_{Ar}CHNH$); 118.60 ($CH_{Ar}C_{Ar}(OH)$); 43.64 (*C*HNH); 19.79 (CH_3); **IR** (neat, ATR) ν/cm^{-1} = 3350 (m), 3065 (w), 2932 (w), 2733 (w), 2677 (w), 2620 (w), 1623 (m), 1602 (m), 1568 (w), 1538 (s), 1488 (s), 1409 (m), 1349 (m), 1277 (m), 1232 (s), 1188 (m), 1132 (m), 1102 (m), 1019 (m), 928 (w), 872 (w), 838 (m), 765 (s), 705 (s), 696 (s); **MS** (EI, 70 eV): 241.1 (45.8%, $[M]^+$). 226.1 (11%, $[M\text{-}CH_3]^+$); **HRMS**: calculated: 241.1098; found: 241.1102; **EA**: calculated: C: 74.67, H: 6.27, N: 5.81; found: C: 74.39, H: 6.45, N: 5.67; **Optical Rotation** (*R*)-isomer: : $[\alpha]_D^{20}$ = -26.5 (c 0.75 in $CHCl_3$, 0.75% EtOH); **Optical Rotation** (*S*)-isomer: $[\alpha]_D^{20}$ = +24.8 (c 0.75 in $CHCl_3$, 0.75% EtOH).

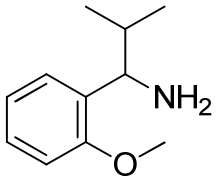
4-Methyl-2-phenyl-4H-benzo[e][1,3]oxazine (26)



In a 10 mL 2-neck round bottom flask was placed (*R*)-**25** (61.3 mg, 0.254 mmol, 1.0 eq.), dissolved in CH_2Cl_2 (2 mL) and cooled to -40 °C. $POCl_3$ (0.63 mL of a 0.4M solution, 0.254 mmol, 1.0 eq.) was added and the reaction mixture stirred for 30 minutes. Then pyridine (125 uL, 120 mg, 1.524 mmol, 6.0 eq) was added and stirring continued for 15 minutes. Afterwards the cooling bath was removed and the mixture allowed to warm to room temperature while stirring overnight. Reaction was quenched with 1M NaOH (2.5 mL), extracted with diethylether (2 x 5 mL) and solvents removed under reduced pressure. Purification *via* flash chromatography (SiO_2, 18 x 2.5 cm, 7 mL frctns, cyclohexane/EtOAc 10:1, frctns 12-14) gave (*R*)-**26** as a clear oil (1.3 mg, 0.0058 mmol, 2%). With the identical procedure, (*S*)-**25** (58.9 mg, 0.244 mmol, 1.0 eq.) gave (*S*)-**26** (3.3 mg, 0.015 mmol, 6%) as a clear oil.
$C_{15}H_{13}NO$ (223.27 g/mol):
^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.10 (m, 2H, $CH_{Ar}C_{Ar}C$=N), 7.47 (m, 3H, $CH_{Ar}CH_{Ar}C_{Ar}C$=N and $CH_{Ar}CH_{Ar}CH_{Ar}C_{Ar}C$=N), 7.23 (m, 1H, $CH_{Ar}CH_{Ar}C_{Ar}$-O), 7.14 (m, 2H, $CH_{Ar}C_{Ar}CH(CH_3)N$ and

$CH_{Ar}CH_{Ar}C_{Ar}CH(CH_3)N$), 7.04 (d, J = 8.0 Hz, 1H, $CH_{Ar}C_{Ar}$-O), 4.83 (q, J = 6.9 Hz, 1H, $CH(CH_3)N$), 1.58 (d, J = 6.9 Hz, 3H, $CH(CH_3)N$); **$^{13}C\{^1H\}$-NMR** (101 MHz, $CDCl_3$) δ 151.72 (O-C=N), 148.97 (C_{Ar}-O), 132.55 (C_{Ar}C=N), 131.05 ($CH_{Ar}CH_{Ar}CH_{Ar}C_{Ar}C$=N), 128.36 ($CH_{Ar}CH_{Ar}C_{Ar}C$=N), 128.04 ($CH_{Ar}CH_{Ar}C_{Ar}$-O), 127.55 ($CH_{Ar}C_{Ar}C$=N), 126.12 ($CH_{Ar}C_{Ar}CH(CH_3)N$), 124.89 ($CH_{Ar}CH_{Ar}C_{Ar}CH(CH_3)N$), 115.62 ($CH_{Ar}C_{Ar}$-O), 50.16 ($CH(CH_3)N$), 25.51 ($CH_3$); **IR** (neat, ATR) ν/$cm^{-1}$ = 3059 (w), 2964 (m), 2925 (m), 2854 (w), 1670 (s), 1585 (w), 1488 (m), 1462 (w), 1449 (m), 1347 (m), 1289 (w), 1248 (m), 1226 (s), 1198 (m), 1112 (m), 1055 (m), 1023 (m); **HRMS**: calculated: 223.0992; found: 223.0986; **Optical Rotation** (*R*)-isomer: $[\alpha]_D^{20}$ = -8.6 (c 0.13 in $CHCl_3$, 0.75% EtOH); **Optical Rotation** (*S*)-isomer: $[\alpha]_D^{20}$ = +10.3 (c 0.165 in $CHCl_3$, 0.75% EtOH).

1-(2-methoxyphenyl)-2-methylpropan-1-amine (27)[8]



In a 500 mL three-neck round bottom flask equipped with a magnetic stirrer and a reflux condenser was inserted 2-methoxybenzonitrile (4.50 g, 33.8 mmol, 1.0 eq), CuBr (98.0 mg, 0.683 mmol, 0.02 eq) and dissolved in dry THF (75 mL). A solution of isopropyl magnesium chloride in THF (2 M, 32 mL, 6.61 g ^{i}PrMgCl, 64.27 mmol, 1.9 eq) was added and the resultant mixture heated to reflux for 16 hours. Afterwards the reaction mixture was allowed to cool to room temperature. A mechanical stirrer, a ammonia condensation vessel and washing bottles were mounted and the mixture cooled to -78 °C. Subsequently ammonia (approx. 200 mL) was condensed into the reaction mixture. Lithium (735 mg, 105 mmol, 3.1 eq) was added in small pieces until the reaction mixture turned blue. The cooling bath was removed and the reaction mixture was allowed to warm up overnight while stirring and evaporating all ammonia. *Tert*-butylmethylether (MTBE) was added to the mixture, cooled to 0 °C and titrated with concentrated HCl to pH 8. The organic layer was separated and the aeqeuous layer salted out and extracted with MTBE (3 x 100 mL). The combined organic layers were washed with brine (100 mL), 0.5 M HCl (3 x 150 mL) and the acidic aeqeuous phase extracted with MTBE (3 x 50 mL). The acidic aeqeuous layer was set to pH 11 with 10% NaOH (10%), salted out and extracted with MTBE (3 x 50 mL). The combined organic layers were dried over anhydrous $MgSO_4$, solvents removed at the rotavap and the residue was purified *via* distillation (63 °C at 0.08 mbar) to afford **27** (5.21 g, 29 mmol, 86%) as a yellow oil.
$C_{11}H_{17}NO$ (179.26 g/mol):
b.p.: 65 °C at 0.08 mbar; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.24 (m, 1H, $CH_{Ar}C_{Ar}CH(NH_2)$), 7.19 (m, 1H, $CH_{Ar}CH_{Ar}C_{Ar}CH(NH_2)$), 6.93 (t, J = 7.5, 1H, $CH_{Ar}CH_{Ar}C_{Ar}(OCH_3)$), 6.85 (d, J = 8.2 Hz, 1H, $CH_{Ar}C_{Ar}(OCH_3)$), 3.88 (d, J = 7.6 Hz, 1H, $CH(NH_2)$), 3.82 (s, 3H, OCH_3), 1.97 (m, 1H, $CH(CH_3)_2$), 1.50 (s, 2H, NH_2), 0.99 (d, J = 6.7 Hz, 3H, $CH(CH_3)_2$), 0.79 (d, J = 6.8 Hz, 3H, $CH(CH_3)_2$).

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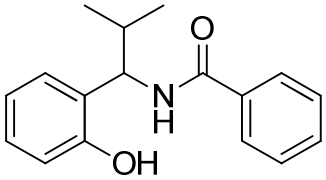
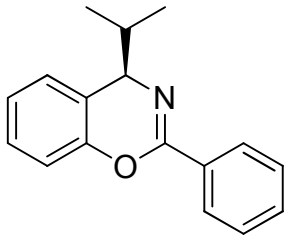
[8] F. J. Weiberth, S. S. Hall, *J. Org. Chem.* **1986**, *51*, 5338-5341

***N*-(1-(2-hydroxyphenyl)-2-methylpropyl)benzamide (28)**

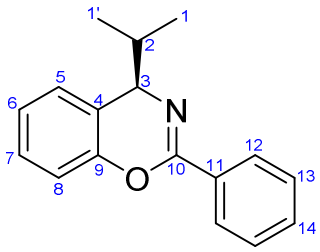


In a 25 mL round-bottom flask was placed **27** (1.0 g, 5.59 mmol, 1.0 eq.) and cooled to 0 °C. Benzoyl chloride (782 mg, 5.59 mmol, 1.0 eq.) and triethylamine (621 mg, 6.15 mmol, 1.1 eq.) were added dropwise and the reaction mixture was stirred at room temperature for 24 hours. Elution chromatography (SiO_2, EtOAc) and removal of solvents under reduced pressure afforded *N*-(1-(2-methoxyphenyl)-2-methylpropyl)benzamide (1.52 g, 5.36 mmol, 96 %) which was dissolved in dry dichloromethane (12 mL) and cooled to -78 °C. Boron tribromide (1.0 M in CH_2Cl_2, 16.1 mmol, 3.0 eq.) was added dropwise, the cooling bath removed and the reaction mixture allowed to warm up to room temperature while stirring overnight. It was then cooled to 0 °C and quenched by addition NaOH (10% w/w, 30 mL). After seizure of gas evolution layers were separated and the aeqeous layer acidified with concentrated HCl (8 mL). It was then basified to pH of 8 by addition of $NaHCO_3$ (150 mL) and extracted with CH_2Cl_2 (2 x 25 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and solvents removed under reduced pressure. The residue was dried *in vacuo* to afford **28** (1.2 g, 4.46 mmol, 83 %) as a white solid. Enantiomers were separated via semipreparative HPLC (Daicel Chiralcel AD (2 cm x 25 cm), *n*-hexane : 2-propanol (90:10), 6 mL min^{-1}, 25 °C, 0.4 mL injection volume, t_R = 43.0 min (+), t_R = 52.0 min (-), **28** was dissolved in a mixture of heptane/2-propanol (9:1) to a concentration of 0.3g mL^{-1}.
$C_{17}H_{19}NO_2$ (269.34 g/mol):
m.p.: 138 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 8.56 (s, 1H, O*H*), 7.75 (m, 2H, CH_{Ar}C$_{Ar}$C=O), 7.48 (m, 1H, CH_{Ar}CH$_{Ar}$CH$_{Ar}$C$_{Ar}$C=O), 7.39 (m, 2H, CH_{Ar}CH$_{Ar}$CH$_{Ar}$C$_{Ar}$C=O), 7.17 (dd, J = 7.6, 1.6 Hz, 1H, CH_{Ar}C$_{Ar}$CHNH), 7.14 (m, 1H, CH_{Ar}CH$_{Ar}$C$_{Ar}$(OH)), 7.02 (d, *J* = 9.1 Hz, 1H, NH), 6.94 (dd, *J* = 8.1, 1.2 Hz, 1H, CH_{Ar}C$_{Ar}$(OH)), 6.87 (td, *J* = 7.5, 1.2 Hz, 1H, CH_{Ar}CH$_{Ar}$C$_{Ar}$CHNH), 4.91 (dd, *J* = 10.3, 9.1 Hz, 1H, C*H*NH), 2.43 (dhept, *J* = 10.3, 6.6 Hz, 1H, C*H*(CH$_3$)$_2$), 1.18 (d, *J* = 6.6 Hz, 3H, CH_3), 0.87 (d, *J* = 6.6 Hz, 3H, CH_3); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 168.46 (*C*=O), 155.22 (*C*$_{Ar}$(OH)), 133.87 (*C*$_{Ar}$C=O), 131.96 (*C*H$_{Ar}$CH$_{Ar}$CH$_{Ar}$C$_{Ar}$C=O), 128.85 (*C*H$_{Ar}$CH$_{Ar}$C$_{Ar}$(OH)), 128.75 (*C*H$_{Ar}$CH$_{Ar}$C$_{Ar}$C=O), 128.14 (*C*H$_{Ar}$C$_{Ar}$CHNH), 127.44 (*C*$_{Ar}$CHNH), 127.19 (*C*H$_{Ar}$C$_{Ar}$C=O), 120.54 (*C*H$_{Ar}$CH$_{Ar}$C$_{Ar}$CHNH), 118.02 (*C*H$_{Ar}$C$_{Ar}$(OH)), 56.86 (*C*HNH), 31.32 (*C*H(CH$_3$)$_2$), 20.61 (*C*H$_3$), 20.51 (*C*H$_3$); **IR** (neat, ATR) ν/cm^{-1} = 3401 (m), 3155 (w), 3103 (w), 3076 (w), 2955 (w), 2870 (w), 1633 (s), 1603 (s), 1576 (m), 1487 (m), 1453 (s), 1380 (m), 1311 (m), 1259 (m), 1252 (m), 1188 (m), 1130 (m), 1116 (s), 1104 (w), 1040 (m), 930 (m), 857 (m), 756 (s), 704 (s), 685 (s); **MS** (EI, 70 eV): 269.1 (3.4%, $[M]^+$). 226.1 (49%, $[M\text{-}C_3H_7]^+$); **HRMS**: calculated: 269.1411; found: 269.1413; **EA**: calculated: C, 75.81; H, 7.11; N, 5.20; found: C, 74.60 H, 7.13; N, 5.13; **Optical Rotation** (*R*)-isomer: : $[\alpha]_D^{20}$ = -24.3 (c 0.75 in $CHCl_3$, 0.75% EtOH); **Optical Rotation** (*S*)-isomer: $[\alpha]_D^{20}$ = + 25.7 (c 0.75 in $CHCl_3$, 0.75% EtOH).

4-Isopropyl-2-phenyl-4H-benzo[e][1,3]oxazine (29)

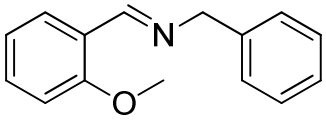


In a 10 mL Schlenk vial was placed (*R*)-**28** (100 mg, 0.37 mmol, 1.0 eq.) and dissolved in CH_2Cl_2 (1 mL). The solution was cooled to -40 °C with the aid of a cryostat. Then a solution of $POCl_3$ (0.4 M in CH_2Cl_2, 1 mL, 0.4 mmol, 1.08 eq.) was added dropwise. The reaction mixture was stirred at -40 °C for 2 hours. Pyridine (176 mg, 2.23 mmol, 6.0 eq.) was added dropwise and stirring continued for one hour. The cryostat was removed and the reaction mixture allowed to warm to room temperature while stirring overnight. It was then cooled to 0 °C and quenched with NaOH solution (1 M, 5 mL, 5 mmol). After ether extraction (3 x 25 mL) the combined organic layers were dried over $MgSO_4$, filtered and solvents removed under reduced pressure. The residue was purified by flash chromatography to afford (*R*)-**28** (39 mg, 0.155 mmol, 42%) as an off-white oil.
Identical to the procedure above, (*S*)-**28** (538 mg, 2.0 mmol, 1.0 eq.) , a solution of $POCl_3$ (306 mg, 2.0 mmol, 1.0 eq.) and pyridine (949 mg, 12 mmol, 6.0 eq.) gave (*S*)-**29** (114 mg, 0.45 mmol, 23%) as a clear oil.
$C_{17}H_{17}NO$ (251.32 g/mol):



^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.10 (m, 2H, H12), 7.46 (m, 3H, H13 and H14), 7.25 (td, *J* = 7.7, 1.8 Hz, 1H, H7), 7.14 (td, *J* = 7.4, 1.2 Hz, 1H, H6), 7.09 (dd, *J* = 7.5, 1.7 Hz, 1H, H5), 7.04 (dd, *J* = 8.1, 1.0 Hz, 1H, H8), 4.67 (d, *J* = 3.9 Hz, 1H, H3), 2.14 (m, 1H, H2), 1.09 (d, *J* = 6.8 Hz, 3H, H1), 0.86 (d, *J* = 6.8 Hz, 3H, H1'); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 152.10 (C10), 149.90 (C9), 132.53 (C11), 131.04 (C14), 128.36 (C13), 127.96 (C7), 127.62 (C12), 126.80 (C5), 124.56 (C6), 122.50 (C4), 115.39 (C8), 60.06 (C3), 36.56 (C2), 18.93 (C1), 17.20 (C1'); **IR** (neat, ATR) ν/cm^{-1} = 3066 (w), 3044 (w), 2959 (m), 2928 (w), 2871 (w), 1675 (s), 1586 (w), 1486 (m), 1458 (m), 1355 (m), 1291 (m), 1243 (m), 1224 (s), 1194 (m), 1063 (m), 1028 (w); **HRMS**: calculated: 251.1305; found: 251.1308; **EA**: calc. C, 81.24; H, 6.82; N, 5.57; O, 6.37; found: C, 80.91; H, 7.48; N, 5.20; **Optical Rotation** (*R*)-isomer: : $[\alpha]_D^{20}$ = -44.4 (c 1.65 in $CHCl_3$, 0.75% EtOH); **Optical Rotation** (*S*)-isomer: $[\alpha]_D^{20}$ = + 20.4 (c 0.75 in $CHCl_3$, 0.75% EtOH).

***N*-(2-methoxybenzylidene)-1-phenylmethanamine (30)**[9]

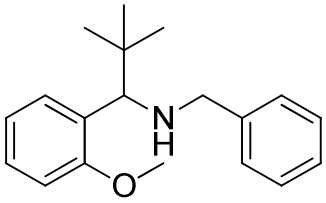


A 50 mL two-necked round-bottom flask equipped with a stirring bar and a Schlenk bridge was set under argon atmosphere and charged with 4 Å molecular sieves (4.00 g). Benzylamine (8.0 mL, 73.4 mmol, 1.0 eq) was added and dissolved in CH_2Cl_2 (19 mL). To the stirred mixture was added a solution of 2-methoxybenzaldehyde (10.0 g, 73.4 mmol, 1.0 eq) in CH_2Cl_2 (4.3 mL) and stirring continued for three hours.The reaction mixture was filtered through a pad of celite and the solvent was removed under reduced pressure. Distillation (0.09-0.10 mbar, 136-138 °C) of the filtrate gave **30** (14.5 g, 64.4 mmol, 88%) as a colourless oil.

[9] G. Bernardinelli, D. Fernandez, R. Gosmini, P. Meier, A. Ripa, P. Schüpfer, B. Treptow, E. P. Kündig, *Chirality* **2000**, *12*, 529-539

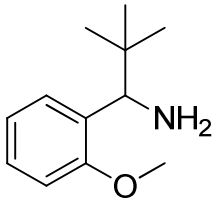
$C_{15}H_{15}NO$ (225.29 g/mol):
b.p.: 136-138 °C at 0.09-0.10 mbar; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.85 (s, 1H, C*H*=N), 8.01 (dd, ^3J = 7.7 Hz, ^4J = 1.6 Hz, 1H, $CH_{Ar}C_{Ar}CH$=N), 7.39 (m, 1H, $CH_{Ar}CH_{Ar}C_{Ar}(OCH_3)$), 7.33 (m, 4H, $CH_{Ar}CH_2$ and $CH_{Ar}CH_{Ar}CH_2$), 7.24 (m, 1H, $CH_{Ar}CH_{Ar}CH_{Ar}CH_2$), 6.98 (t, ^3J = 7.5 Hz, 1H, $CH_{Ar}C_{Ar}(OCH_3)$), 6.92 (d, J = 8.3 Hz, 1H, $CH_{Ar}CH_{Ar}C_{Ar}CH$=N), 4.82 (s, 2H, CH_2), 3.88 (s, 3H, OCH_3); **GC-MS** (EI, 70 eV, PhMeSi, 100.2/10.270/10): t_R = 16.9 min, m/z = 224 ($[M-H]^+$).

_N_-benzyl-1-(2-methoxyphenyl)-2,2-dimethylpropan-1-amine (31)[9]



A 250 mL two-necked round-bottom flask equipped with a stirring bar and a Schlenk bridge was set under argon atmosphere and charged with *tert*-BuLi (22 mL of a 1.7 M solution in pentane, 37.8 mmol, 1.7 eq). The solution was cooled to -30 °C and via a cooling trap the solvent was removed *in vacuo*. The resulting colourless solid was cooled to -78 °C and THF (22 mL) was added slowly resulting in a yellow suspension. Afterwards a solution of **30** (5.00 g, 22.2 mmol, 1.0 eq) in THF (11 mL) was added over a period of two hours using a syringe pump and causing the mixture to turn purple. After three hours h the mixture was allowed to warm to 0 °C and stirring was continued overnight. A saturated aqueous solution of NH_4Cl (11 mL) was added and the mixture turned yellow. Layers were separated, the aqueous layer was extracted with Et_2O (2 x 20 mL), the combined organic layers were dried over Na_2SO_4 and solvent was removed under reduced pressure. Distillation (0.06-0.08 mbar, 131-142 °C) of the residue gave **31** (4.82 g, 17.0 mmol, 77%) as a yellow oil.
$C_{19}H_{25}NO$ (283.41 g/mol):
b.p.: 131-142 °C at 0.06-0.08 mbar; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, J = 7.3 Hz, 1H, $CH_{Ar}C_{Ar}CHNH$), 7.18 (m, 4H, $CH_{Ar}C_{Ar}CH_2$ and $CH_{Ar}CH_{Ar}C_{Ar}CH_2$), 7.21 (m, 2H, $CH_{Ar}CH_{Ar}C_{Ar}CHNH$ and $CH_{Ar}CH_{Ar}CH_{Ar}C_{Ar}CH_2$), 6.97 (t, J = 7.2 Hz, 1H, $CH_{Ar}CH_{Ar}C_{Ar}(OCH_3)$), 6.87 (d, J = 8.1 Hz, 1H, $CH_{Ar}C_{Ar}(OCH_3)$), 4.06 (s, 1H, C*H*NH), 3.77 (s, 3H, OCH_3), 3.55 (d, J = 13.2 Hz, 1H, CH_2), 3.39 (d, J = 13.2 Hz, 1H, CH_2), 0.89 (s, 9H, $C(CH_3)_3$).

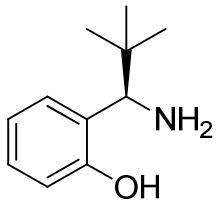
1-(2-methoxyphenyl)-2,2-dimethylpropan-1-amine (32)[9]



A 50 mL round-bottom flask equipped with a stirring bar and an argon tube was charged with Pd/C (Degussa type 101 NE/W, 0.343 g), **31** (4.82 g, 17.0 mmol, 1.0 eq) and EtOH (15 mL). The mixture was degassed performing three "freeze-pump-thaw" cycles purging with hydrogen each time. Afterwards the mixture was heated to 60 °C and stirred for 26 hours under ambient hydrogen pressure. After cooling to room temperature the mixture was filtered through a pad of celite and the solvent was removed under reduced pressure. Distillation (0.06-0.08 mbar, 82-85 °C) of the residue gave **32** (2.93 g, 15.2 mmol, 89%). Enantiomers were separated by recrystallisation. A 25 mL round-bottom flask equipped with a stirring bar and a reflux condenser was charged with **32** (2.93 g, 15.2 mmol, 1.0 eq), (*S*)-mandelic acid (2.31 g, 15.2 mmol, 1.0 eq) and AcOEt (4.5 mL). The mixture was heated to reflux until all the solid was dissolved and the stirring bar was removed from

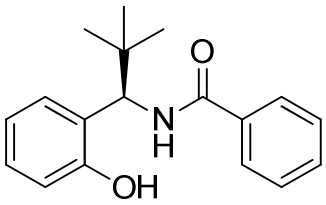
the hot solution. After 22 hours the mother liquor was decanted and the remaining crystals were washed with Et_2O and *n*-pentane and dried *in vacuo*. Afterwards the obtained (*R*,*S*)-salt was recrystallized twice as follows. A 50 mL round-bottom flask with a stirring bar was charged with the (*R*,*S*)-salt (1.95 g, 5.64 mmol), AcOEt (14.5 mL) and EtOH (1.16 mL). The mixture was heated until all salt dissolved and the stirring bar was removed. After 40 hours the mother liquor was decanted and the precipitated crystals were washed with Et_2O and *n*-pentane and dried in vacuo. A diastereomeric excess >96% was detected by ^{1}H-NMR. The enantiomerically enriched (*R*,*S*)-salt (0.980 g, 2.84 mmol) was put into a separating funnel and 10% aqueous NaOH (10 mL) was added. Extraction of this mixture with AcOEt (3 x 25 mL), drying over Na_2SO_4 and evaporation of the solvent gave (*R*)-**32** (0.544 g, 2.81 mmol, 37%) as a colourless oil. The mother liquors from the preceeding recrystallisations were combined in a separating funnel, diluted with TBME (40 mL) and washed with 10% aqueous NaOH (2 x 20 mL). The combined aqeuos layers were extracted with TBME (3 x 40 mL). The combined organic layers were dried over Na_2SO_4 and evaporation of the solvent gave already partially enantiomerically enriched (*S*)-**32** (2.37 g, 12.3 mmol). A 50 mL round-bottom flask was charged with partially enantiomerically enriched (*S*)-**32**, (*R*)-mandelic acid (1.86 g, 12.3 mmol), AcOEt (26.3 mL) and EtOH (0.7 mL) and the mixture was heated until all solid dissolved. After 20 hours the mother liquor was decanted and the crystals were washed with Et_2O and *n*-pentane. This recrystallisation procedure was repeated once. A diastereomeric excess >96% was detected by ^{1}H-NMR. The free amine was obtained from the (*S*,*R*)-salt (0.727 g, 2.11 mmol) by addition of 10% aqueous NaOH and subsequent extraction with AcOEt as described above to afford (*S*)-**32** (0.381 g, 1.97 mmol, 26%) as a colourless oil.
$C_{12}H_{19}NO$ (193.29 g/mol):
b.p.: 82-85 °C at 0.06-0.08 mbar; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 7.34 (m_{br}, 1H, $CH_{Ar}C_{Ar}CHNH_2$), 7.19 (t, *J* = 7.8 Hz, 1H, $CH_{Ar}CH_{Ar}C_{Ar}CHNH_2$), 6.93 (t, *J* = 7.4 Hz, 1H, $CH_{Ar}CH_{Ar}C_{Ar}(OCH_3)$), 6.84 (d, *J* = 8.2 Hz, 1H, $CH_{Ar}C_{Ar}(OCH_3)$), 4.26 (s, 1H, $CHNH_2$), 3.79 (s, 3H, OCH_3), 1.52 (s_{br}, 2H, NH_2), 0.91 (s, 9H, $C(CH_3)_3$); **GC-MS** (EI, 70 eV, PhMeSi, 100.2/10.270/10): t_R = 10.3 min, *m/z* = 136 ($[M-(C(CH_3)_3)]^+$). **Optical Rotation** (*R*)-isomer: : $[\alpha]_D^{20}$ = +37.0 (c 2.02 in EtOH); **Optical Rotation** (*S*)-isomer: $[\alpha]_D^{20}$ = -37.1 (c 2.02 in EtOH).

(*R*)-(-)-2-(1-amino-2,2-dimethylpropyl)phenol (33)[9]



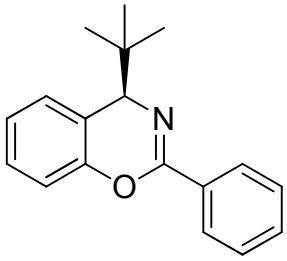
In a 25 mL two-necked round-bottom flask equipped with a stirring bar and a Schlenk bridge (*R*)-**32** (0.537 g, 2.78 mmol, 1.0 eq) was dissolved in CH_2Cl_2 (4.7 mL) and cooled to -78 °C. BBr_3 (7.5 mL of a 1 M solution in CH_2Cl_2) was added dropwise and the mixture was stirred overnight. The reaction mixture was poured on a saturated aqueous solution of $NaHCO_3$ (20 mL) and ice. Additional $NaHCO_3$ solution was added until a pH at 9 was observed. Phase separation, extraction with CH_2Cl_2 (3 x 30 mL), drying over Na_2SO_4 and evaporation of the solvent gave crude (*R*)-**33** (511 mg, 2.78 mmol, 99%) as a brown solid.
$C_{11}H_{17}NO$ (179.26 g/mol):
^{1}H-NMR (250 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.3 Hz, 1H, $CH_{Ar}CH_{Ar}C_{Ar}CH(NH_2)$), 6.90 (d, *J* = 7.1 Hz, 1H, $CH_{Ar}C_{Ar}CH(NH_2)$), 6.81 (d, *J* = 8.0 Hz, 1H, $CH_{Ar}C_{Ar}(OH)$), 6.74 (t, *J* = 7.2 Hz, 1H, $CH_{Ar}CH_{Ar}C_{Ar}(OH)$), 3.87 (s, 1H, $CH(NH_2)$), 0.96 (s, 9H, $C(CH_3)_3$); **Optical Rotation** (*R*)-isomer: : $[\alpha]_D^{20}$ = -37.6 (c 2.06 in $CDCl_3$, 0.75% EtOH).

(*R*)-(-)N-(1-(2-hydroxyphenyl)-2,2-dimethylpropyl)benzamide (34)[10]

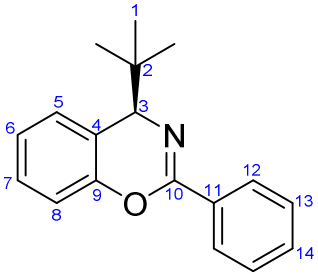


In a 25 mL two-necked round-bottom flask equipped with a stirring bar and a Schlenk bridge a solution of crude (*R*)-**33** (0.470 g, 2.62 mmol, 1.0 eq) in CH_2Cl_2 (7.5 mL) was cooled to 0 °C and benzoyl chloride (0.33 mL, 2,88 mmol, 1.1 eq) and triethylamine (0.44 mL, 3.15 mmol, 1.2 eq) were added. The cooling bath was removed after 5 min. and the mixture was stirred at room temperature for 18 hours. Elution of the reaction mixture with AcOEt through a short silica gel column gave (*R*)-**34** (435 mg, 1.54 mmol, 59%) as a grey solid.
$C_{18}H_{21}NO_2$ (283.36 g/mol):
m.p.: 151-152 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 7.2 Hz, 1H, N*H*), 7.80 (d, *J* = 6.9 Hz, 2H, CH_{Ar}C$_{Ar}$C=O), 7.52 (t, *J* = 7.7 Hz, 1H, CH_{Ar}CH$_{Ar}$CH$_{Ar}$C$_{Ar}$C=O), 7.40 (t, *J* = 7.7 Hz, 2H, CH_{Ar}CH$_{Ar}$C$_{Ar}$C=O), 7.13 (t, *J* = 7.3 Hz, 1H, CH_{Ar}CH$_{Ar}$C$_{Ar}$(OH)), 6.89 (t, *J* = 7.5 Hz, 1H, CH_{Ar}CH$_{Ar}$C$_{Ar}$CHNH), 6.78 (d, *J* = 8.1 Hz, 1H, CH_{Ar}C$_{Ar}$(OH)), 5.25 (d, *J* = 9.9 Hz, 1H, C*H*NH), 1.06 (s, 9H, C(C*H*$_3$)$_3$); **IR** (neat, ATR) ν/cm^{-1} = 3395 (m), 3236 (w), 3185 (w), 2961 (m), 2866 (w), 1639 (s), 1625 (s), 1600 (m), 1531 (s), 1487 (m), 1453 (s), 1356 (m), 1245 (m), 1208 (m), 1174 (m), 1110 (m), 1063 (m), 1024 (m), 838 (m), 751 (s), 704 (s), 691 (s); **MS** (EI, 70 eV): 283.1 (1.4%, $[M]^+$). 226.1 (100%, $[M\text{-}C_4H_9]^+$); **Optical Rotation** (*R*)-isomer: : $[\alpha]_D^{20}$ = -114.0 (c 3.26 in EtOH).

(*R*)-(-)-4-(tert-butyl)-2-phenyl-4H-benzo[e][1,3]oxazine (35)[10]



In a 10 mL Schlenk vial was placed (*R*)-**34** (75 mg, 0.265 mmol, 1.0 eq.) and dissolved in CH_2Cl_2 (2.6 mL). The solution was cooled to -40 °C with the aid of a cryostat. Then a solution of $POCl_3$ (40 mg, 0.265 mmol, 1.0 eq.) was added dropwise. The reaction mixture was stirred at -40 °C for 30 minutes. Pyridine (126 mg, 1.59 mmol, 6.0 eq.) was added dropwise and stirring continued for one hour. The cryostat was removed and the reaction mixture allowed to warm to room temperature while stirring overnight. It was then cooled to 0 °C and quenched with NaOH solution (1 M, 5 mL, 5 mmol). After ether extraction (3 x 25 mL) the combined organic layers were dried over $MgSO_4$, filtered and solvents removed under reduced pressure. The residue was purified by flash chromatography (SiO_2, cyclohexane/EtOAc 20:1, 20x2 cm, 7 mL fractions) to afford (*R*)-**35** (20 mg, 0.073 mmol, 28%) as a clear oil.
$C_{18}H_{19}NO$ (265.35 g/mol):



^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.13 (m, 2H, H12), 7.50 (m, 1H, H14) 7.47 (m, 2H, H13), 7.30 (m, 1H, H7), 7.16 (m, 1H, H6), 7.13 (m, 1H, H5), 7.08 (d, *J* = 7.9 Hz, 1H, H8), 4.46 (s, 1H, H3), 0.99 (s, 9H, H1); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 152.32 (C10), 150.39 (C9), 132.37 (C11), 131.12 (C14), 128.68 (C5), 128.40 (C13), 128.02 (C7), 127.79 (C12), 123.96 (C6), 121.61 (C4), 115.50 (C8), 64.71 (C3), 38.88 (C2),

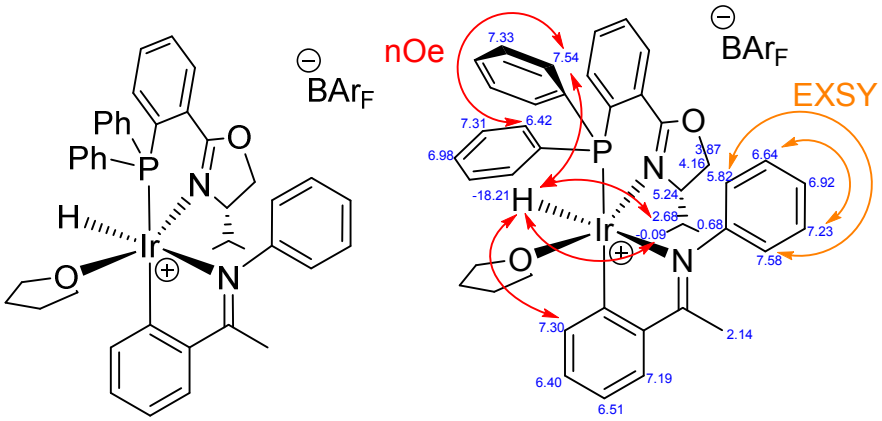
[10] E. P. Kündig, P. Meier, *Helv. Chim. Acta* **1999**, *82*, 1360-1370

26.18 C(1); **IR** (neat, ATR) ν/cm^{-1} = 3058 (w), 3032 (w), 2950 (m), 2930 (w), 2905 (m), 1667 (s), 1583 (w), 1494 (m), 1486 (m), 1477 (m), 1458 (m), 1449 (m), 1391 (w), 1363 (m), 1348 (s), 1287 (w), 1244 (s), 1221 (s), 1193 (s), 1177 (m), 1091 (s), 1066 (s), 1023 (m); **HRMS**: calculated: 265.1462; found: 265.1464; **Optical Rotation** (*R*)-isomer: : $[\alpha]_D^{20}$ = -11.0 (c 1.1 in $CHCl_3$, 0.75% EtOH).

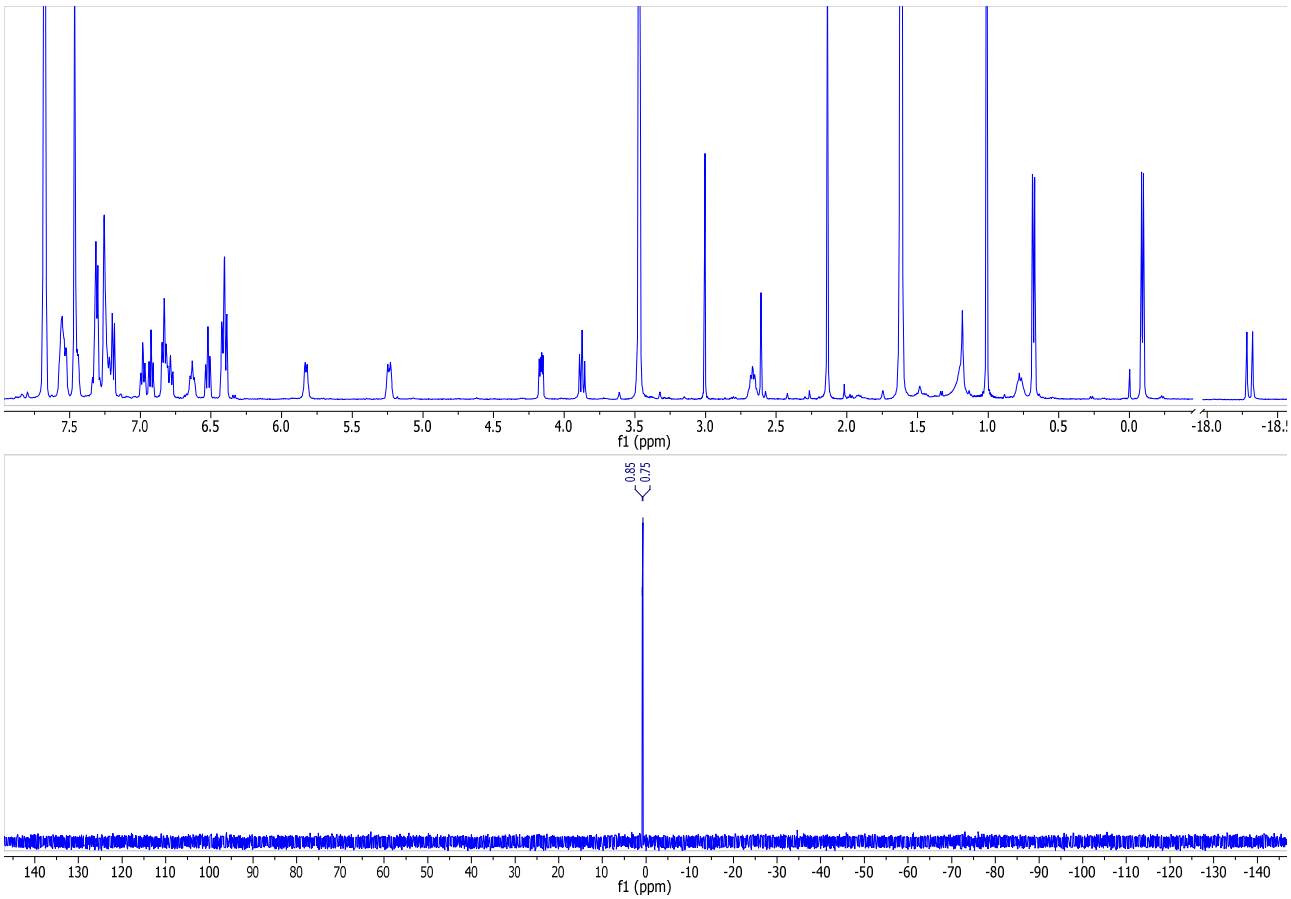
Synthesis of Complexes

General method:
An 8 mL oven-dried glass vial was equipped with a magnetic stirrer and closed with a septum. It was evacuated while cooling to room temperature and purged with argon three times. [Ir(L)(COD)]BArF and the corresponding imine were placed into the vial and the vial was closed again. After evacuation and purging with hydrogen gas via balloon three times, freshly distilled dry THF (2 mL) was added and the reaction mixture was stirred at room temperature for 4 hours. A distinct colour change from red/orange to bright yellow was observed in all cases. The solvent was evaporated via a N_2 stream and LiCl (100 mg) and SiO_2 (100 mg) were added and suspended in EtOAc (2 mL). The vial was closed again and stirred overnight at room temperature. The solvent was evaporated via a N_2 stream and the residue was suspended in Pentane/TBME (1:1) and eluted on SiO_2 (2.5 x 20 cm) where the yellow band was collected. The solvent was removed under reduced pressure and the residue triturated with pentane to give a yellow solid.

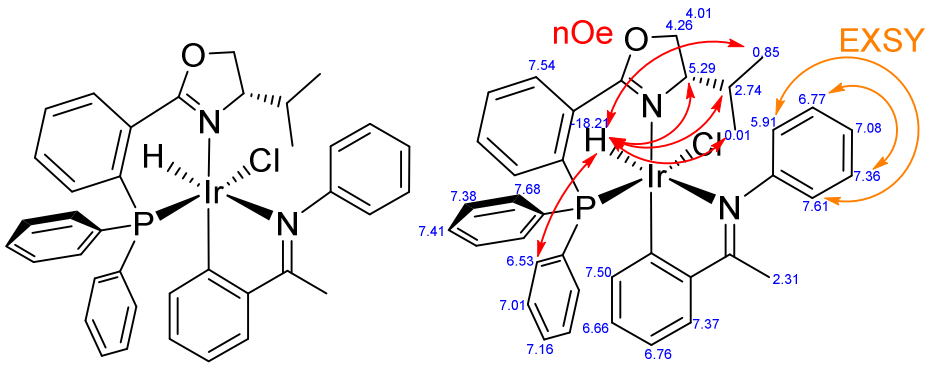
[Ir((*S*)-^{i}Pr-PHOX)(I1)(H)(THF)]BAr$_F$ (2)



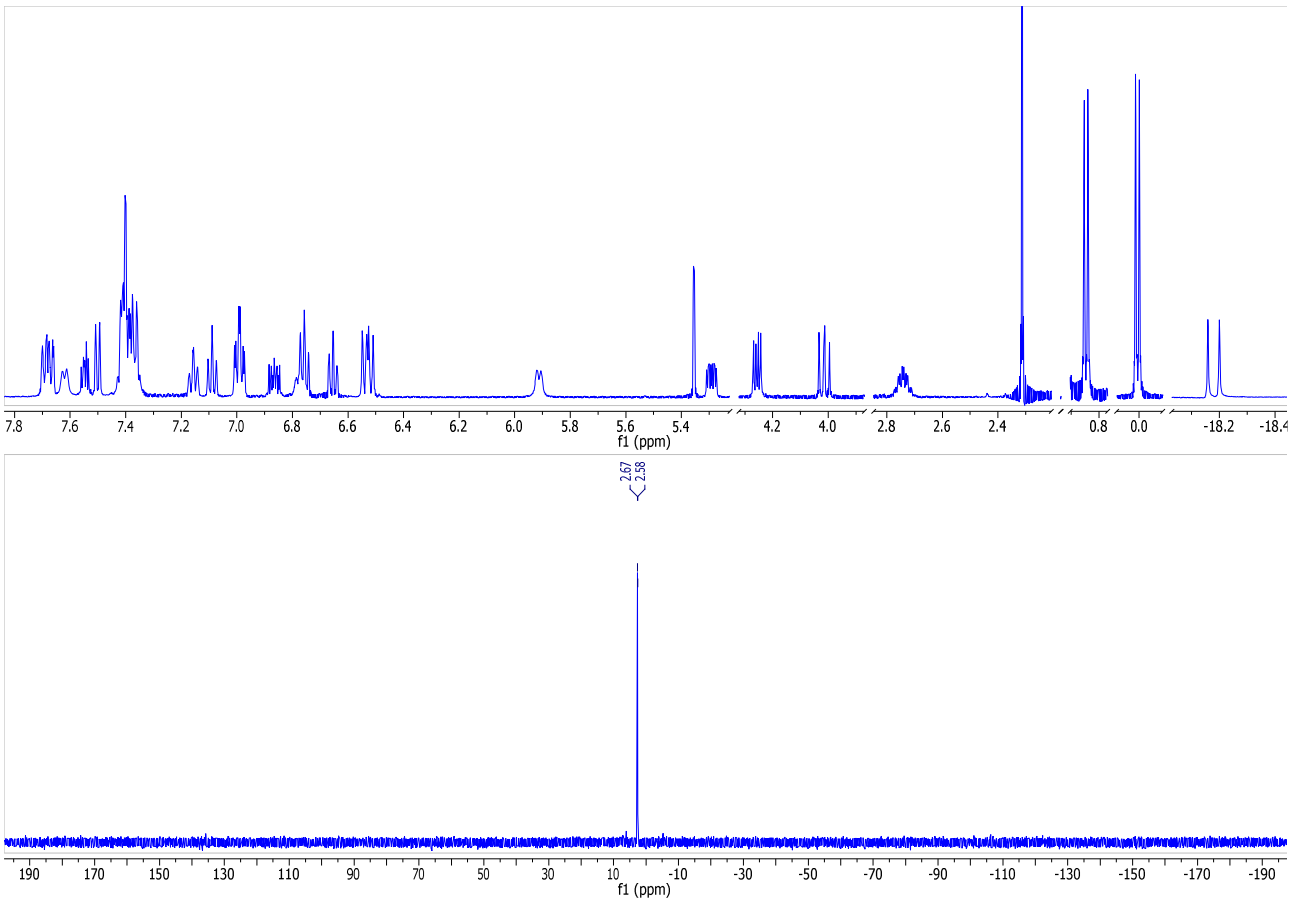
In the glove box, **3** (10 mg, 0.0126 mmol, 1.0 eq.) and NaBArF (11.1 mg, 0.0126 mmol, 1.0 eq.) were added to a young's NMR tube and dissolved in THF-d_8 at room temperature.The mixture was shaken until it turned homogenous and NMR spectra were recorded.
$C_{74}H_{57}BF_{24}IrN_2O_2P$ (M_W = 1696.34 g/mol):
^{1}H-NMR (500 MHz, THF) δ 7.68 (s, 8H), 7.59 – 7.50 (m, 3H), 7.46 (s, 4H), 7.44 (d, *J* = 2.9 Hz, 1H), 7.35 – 7.28 (m, 3H), 7.24 (d, *J* = 18.7 Hz, 4H), 7.19 (d, *J* = 7.9 Hz, 1H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.83 (t, *J* = 7.1 Hz, 2H), 6.81 – 6.76 (m, 1H), 6.64 (d, *J* = 7.3 Hz, 1H), 6.52 (t, *J* = 7.4 Hz, 1H), 6.41 (t, *J* = 9.0 Hz, 3H), 5.83 (d, *J* = 7.2 Hz, 1H), 5.30 – 5.17 (m, 1H), 4.16 (dd, *J* = 8.6, 4.5 Hz, 1H), 3.87 (t, *J* = 9.4 Hz, 1H), 2.72 – 2.63 (m, 1H), 2.14 (s, 3H), 0.68 (d, *J* = 7.1 Hz, 3H), -0.09 (d, *J* = 6.9 Hz, 3H), -18.30 (d, *J* = 20.7 Hz, 1H); **^{31}P{^{1}H}-NMR** (202 MHz, THF) δ 0.80 (d, *J* = 19.8 Hz).



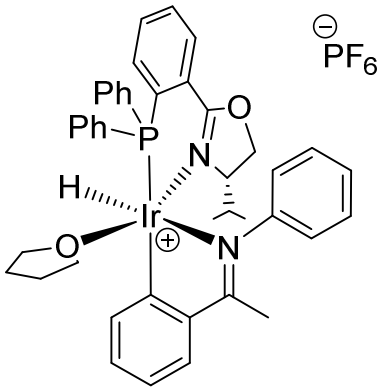
[Ir((*S*)-^{i}Pr-PHOX)(I1)(H)(Cl)] (3)



By general method [Ir(((*S*)-^{i}Pr-PHOX)(COD)]BArF (100 mg, 0.065 mmol, 1.0 eq.) and **I1** (25.3 mg, 0.13 mmol, 2.0 eq.) afforded 24 mg (0.03 mmol, 46%) of **3** as a yellow solid.
$C_{38}H_{37}ClIrN_2OP$ (796.36 g/mol):
^{1}H-NMR (400 MHz, CD_2Cl_2) δ 7.70 – 7.61 (m, 2H), 7.59 (d, J = 7.5 Hz, 1H), 7.55 – 7.49 (m, 1H), 7.47 (d, J = 7.4 Hz, 1H), 7.36 (m, 6H), 7.12 (t, J = 7.2 Hz, 1H), 7.05 (t, J = 7.4 Hz, 1H), 6.96 (td, J = 8.0, 2.4 Hz, 2H), 6.86 – 6.80 (m, 1H), 6.72 (m, 2H), 6.62 (t, J = 7.1 Hz, 1H), 6.49 (dd, J = 11.3, 7.8 Hz, 2H), 5.88 (d, J = 7.2 Hz, 1H), 5.26 (ddd, J = 10.0, 4.2, 3.1 Hz, 1H), 4.22 (dd, J = 8.8, 4.5 Hz, 1H), 4.02 – 3.94 (m, 1H), 2.76 – 2.66 (m, 1H), 2.28 (s, 3H), 0.81 (d, J = 7.1 Hz, 3H), -0.03 (d, J = 6.8 Hz, 3H), -18.21 (d, J = 20.7 Hz, 1H); **^{31}P{^{1}H}-NMR** (162 MHz, CD_2Cl_2) δ 2.63 (d, J = 14.5 Hz).

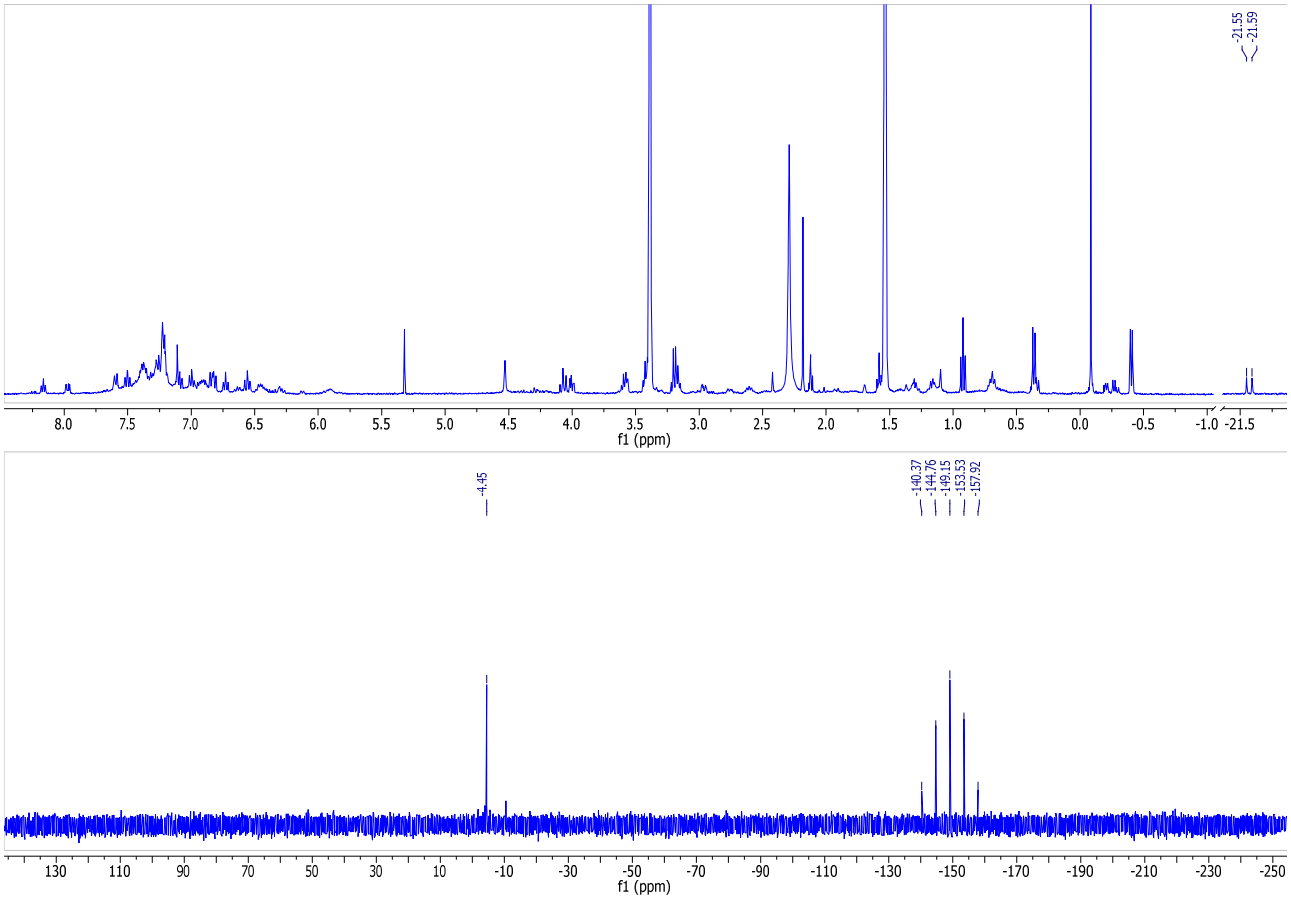


[Ir((*S*)-^{i}Pr-PHOX)(I1)(H)(THF)]PF_6 (5)

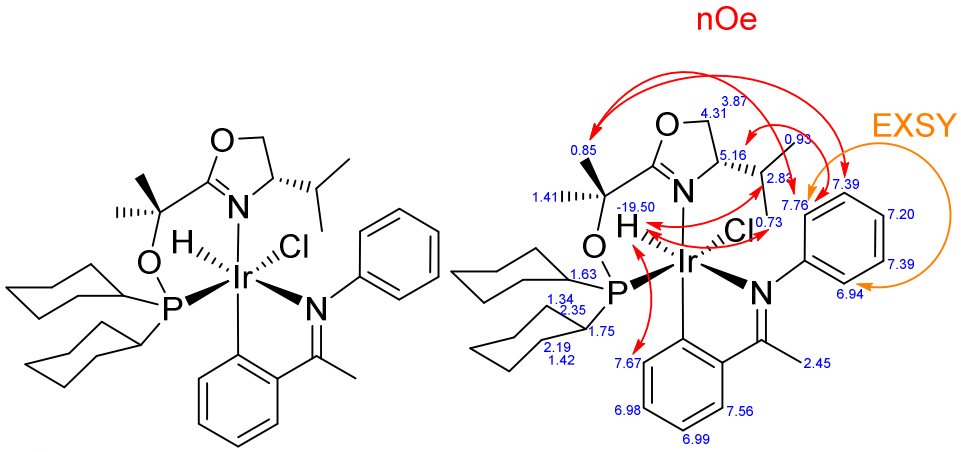


In the glove box, [Ir((*S*)-^{i}Pr-PHOX)(COD)]PF_6 (100 mg, 0.122 mmol, 1.0 eq.) and **I1** (47 mg, 0.241 mmol, 2.0 eq.) was weighed into a schlenk tube and dissolved in dry THF (3 mL). The tube was brought outside of the box and cooled to 0°C. The stopper was replaced with a septum and a long cannula was passed trough into the solution. Hydrogen gas was bubbled through the stirring solution for 90 minutes at 0°C. The needle was pulled out and the resultant orange solution was degassed by freezing the solution in liquid nitrogen and evacuating while warming up in total three times. The solution was layered with dry pentane (5 mL) and placed in the freezer overnight. The solution was carefully decanted and the precipitate was rinsed with pentane (5 mL) and dried in vacuo to give **5** as a yellow amorphous solid. NMR‘s were recorded at this stage. X-Ray quality crystals were obtained by redissolving the precipitate in THF and slow diffusion of diethyl ether into the solution. A total of three crystallisation cycles was required to obtain X-Ray quality crystals.

$C_{42}H_{45}F_6IrN_2O_2P_2$ (977.97 g/mol):
^{1}H-NMR (500 MHz, CD_2Cl_2) δ -21.57 (d, J = 17.0 Hz, 1H); **^{31}P{^{1}H}-NMR** (202 MHz, CD_2Cl_2) δ -4.45 (s), -149.15 (m, PF_6).

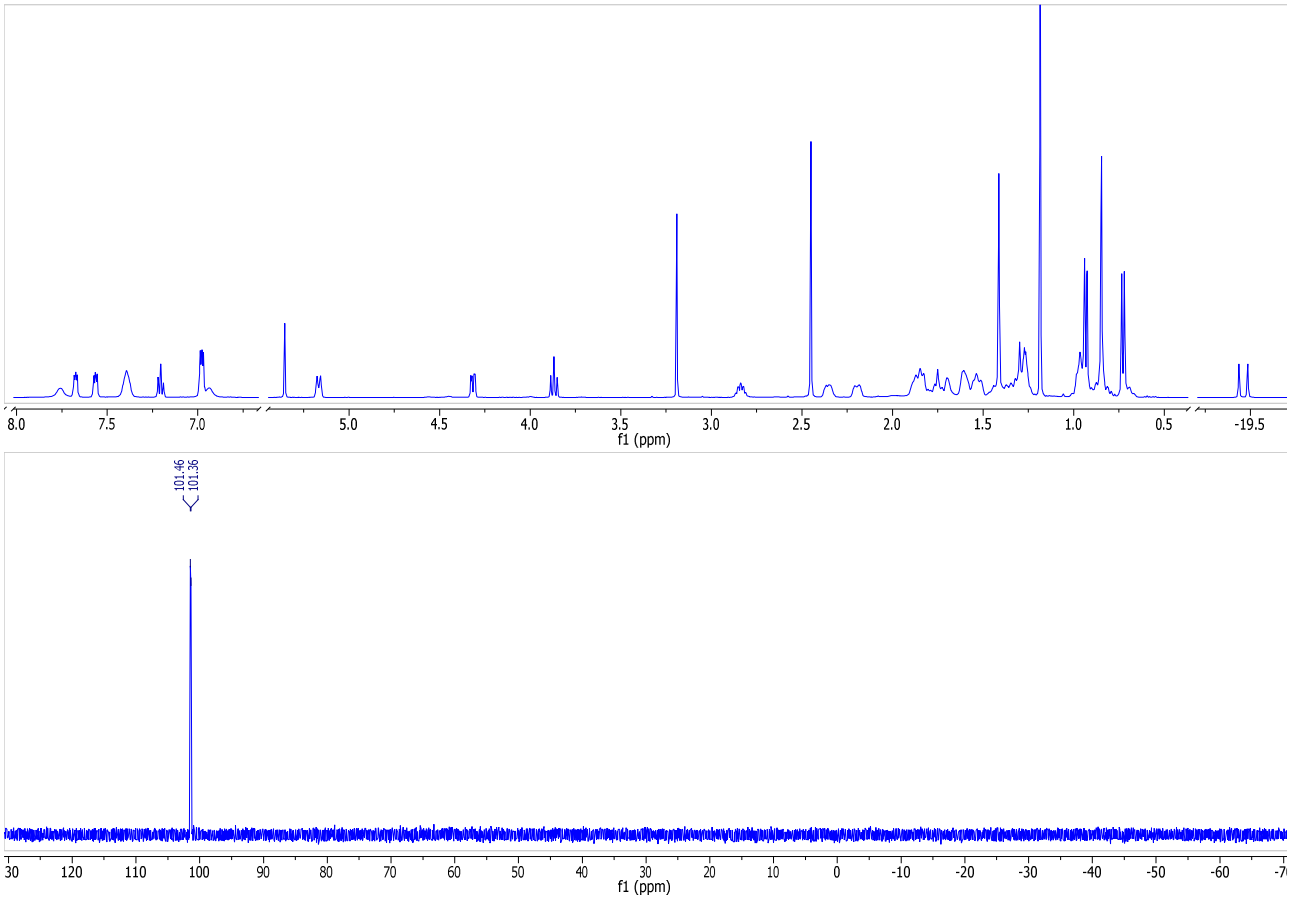


[Ir((S)-iPr-SimplePHOX)(I1)(H)(Cl)] (7)

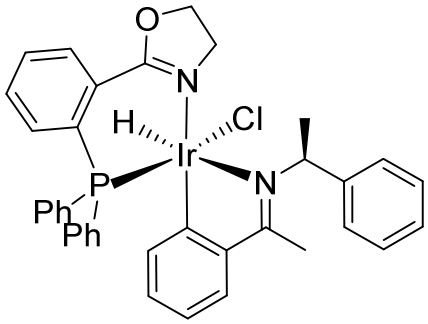


By general method [Ir(((*S*)-^{i}Pr-SimplePHOX)(COD)]BAr_F (50 mg, 0.03 mmol, 1.0 eq.) and **I1** (13 mg, 0.06 mmol, 2.0 eq.) afforded 18 mg (0.03 mmol, 76%) of **7** as a yellow solid.
X-Ray quality crystals were obtained by redissolving the precipitate in CH_2Cl_2 and layering with pentane. After evaporation of solvents an oil was observed which solidified into a crystalline material in the course of a few weeks.
$C_{35}H_{51}ClIrN_2O_2P$ (790.44 g/mol):

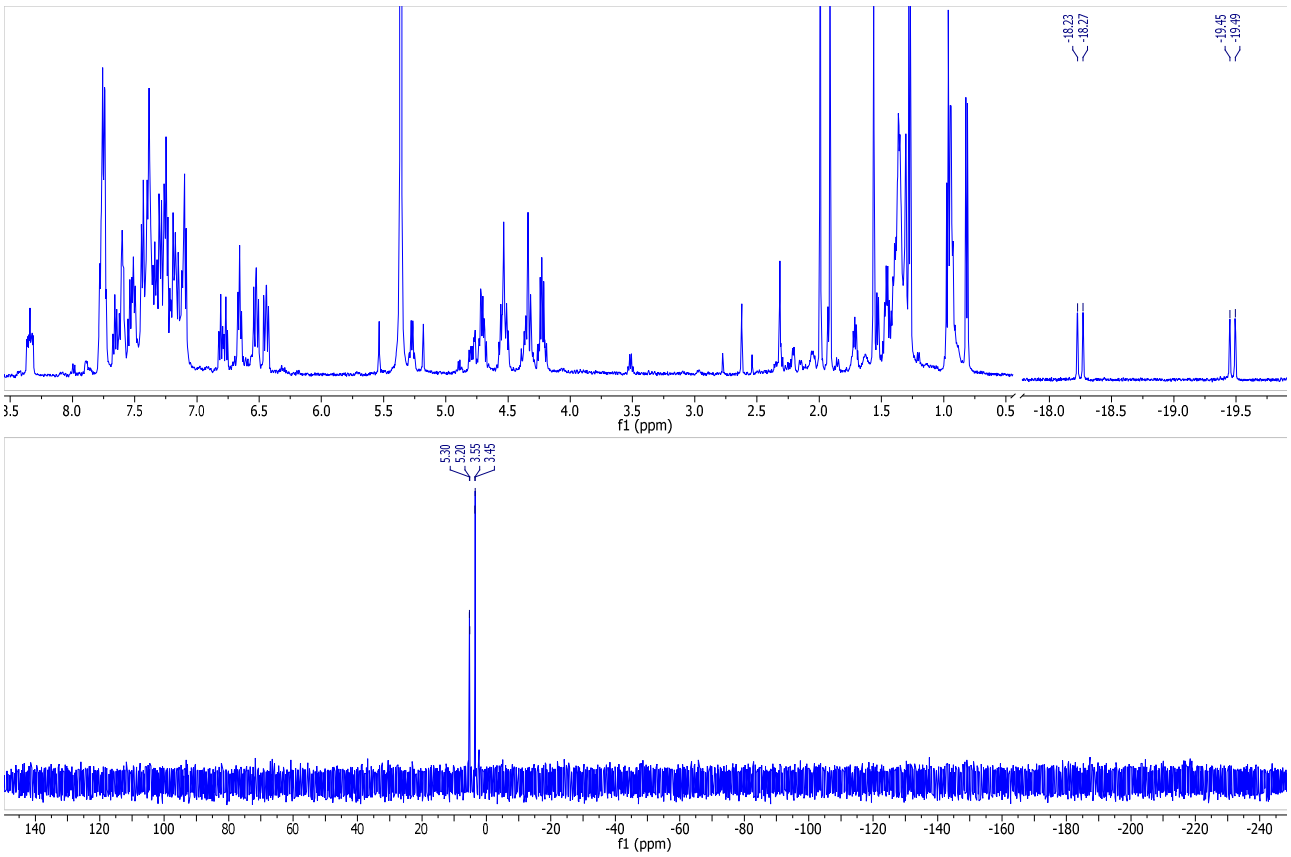
^{1}H-NMR (500 MHz, CD_2Cl_2) δ 7.72 (s, 1H), 7.68 – 7.61 (m, 1H), 7.56 – 7.49 (m, 1H), 7.36 (s, 2H), 7.17 (t, J = 7.4 Hz, 1H), 6.94 (dd, J = 8.3, 4.4 Hz, 2H), 6.90 (s, 1H), 5.13 (d, J = 9.3 Hz, 1H), 4.28 (dd, J = 8.7, 3.1 Hz, 1H), 3.83 (t, J = 9.1 Hz, 1H), 2.90 – 2.69 (m, 1H), 2.42 (s, 3H), 2.32 (d, J = 7.7 Hz, 1H), 2.16 (d, J = 12.1 Hz, 1H), 1.91 – 1.45 (m, 10H), 1.35 – 1.18 (m, 6H), 1.15 (s, 6H), 0.90 (d, J = 7.1 Hz, 3H), 0.69 (d, J = 6.9 Hz, 3H), -19.50 (d, J = 24.3 Hz, 1H); **^{31}P{^{1}H}-NMR** (202 MHz, CD_2Cl_2) δ 101.41 (d, J = 21.9 Hz).



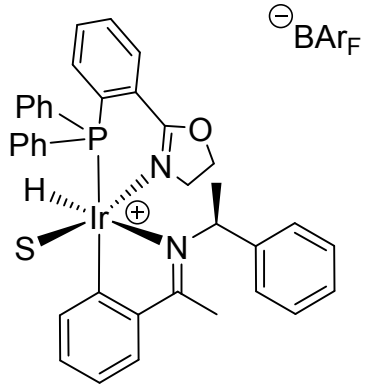
[Ir(PHOX)((*S*)-9)(H)(Cl)] (10)



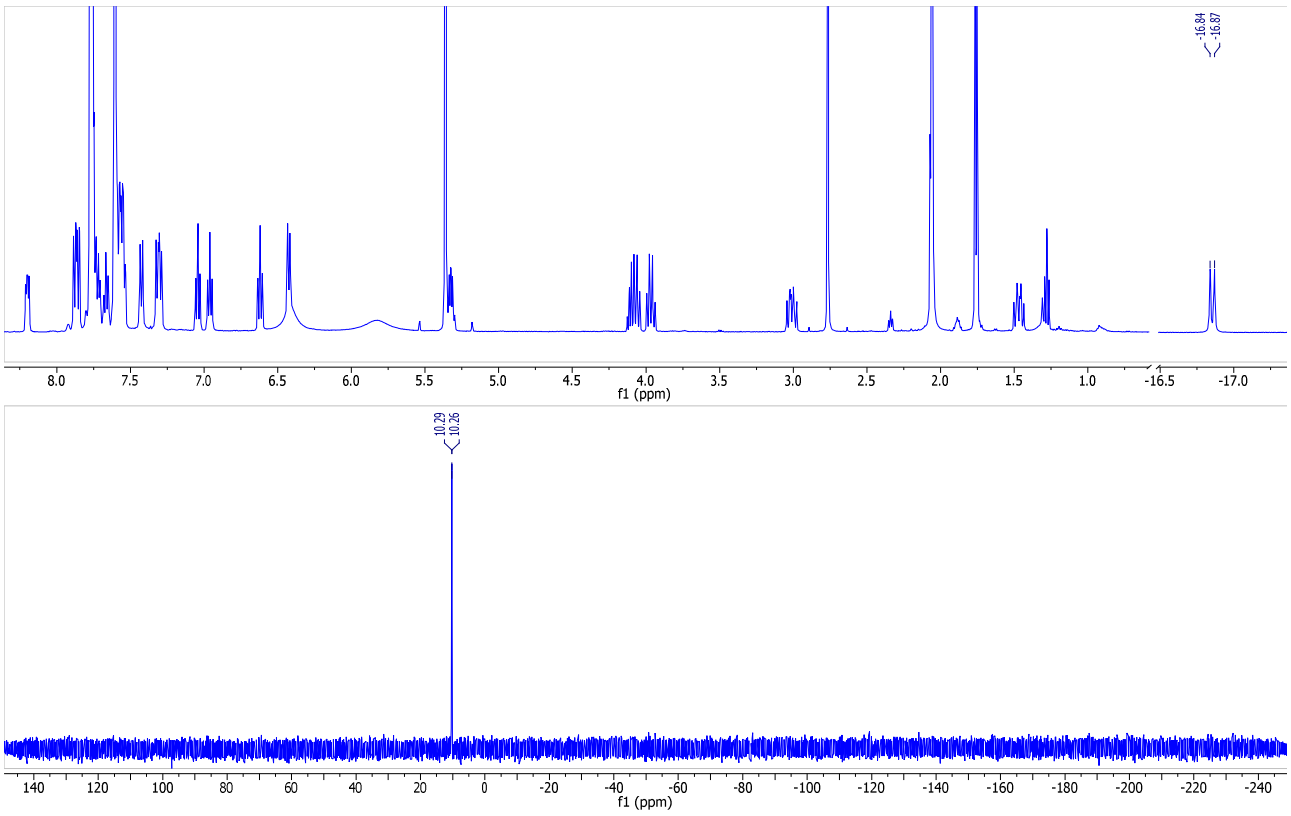
By general method [Ir(PHOX)(COD)]BAr_F (75 mg, 0.05 mmol, 1.0 eq.) and (*S*)**-9** (22.3 mg, 0.1 mmol, 2.0 eq.) afforded 33 mg (0.042 mmol, 83%) of **10** as a yellow solid.
$C_{38}H_{38}ClIrN_2OP$ (797.2 g/mol):
^{1}H-NMR (500 MHz, CD_2Cl_2) δ -18.25 (d, *J* = 22.7 Hz, 1H), -19.47 (d, *J* = 21.7 Hz, 1H); **^{31}P{^{1}H}-NMR** (202 MHz, CD_2Cl_2) δ 5.25 (d, *J* = 20.2 Hz), 3.50 (d, *J* = 19.8 Hz).



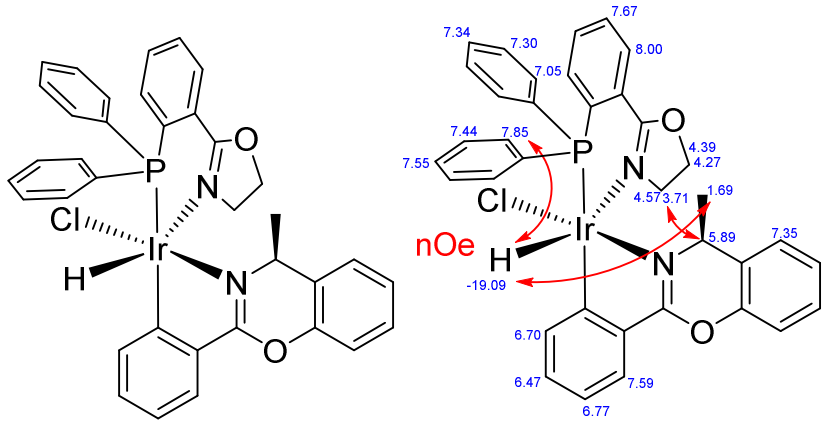
[Ir(PHOX)((*S*)-9)(H)(CH_2Cl_2)]BAr_F (11)



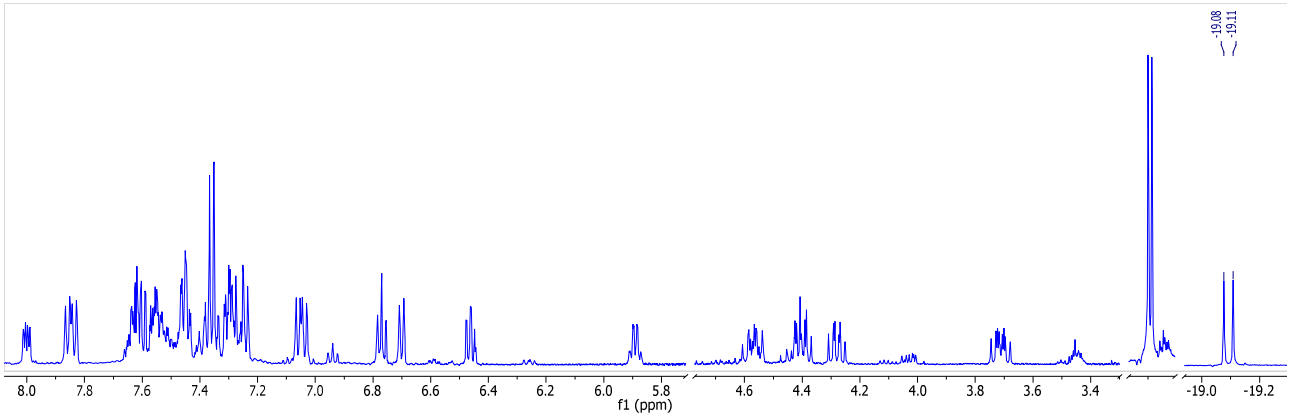
In the glove box, **10** (5 mg, 0.0063 mmol, 1.0 eq.) and $NaBAr_F$ (6 mg, 0.0068 mmol, 1.08 eq.) were added to a young's NMR tube and dissolved in CD_2Cl_2 (0.4 mL) at room temperature.The mixture was shaken until it turned homogenous and NMR spectra of **11** were recorded.
$C_{70}H_{49}BCl_2F_{24}IrN_2OP$ (1694.23 g/mol):
^{1}H-NMR (500 MHz, CD_2Cl_2) δ 8.23 – 8.17 (m, 1H), 7.87 (dd, *J* = 12.1, 7.7 Hz, 2H), 7.77 (dt, *J* = 5.1, 2.3 Hz, 13H), 7.75 – 7.69 (m, 2H), 7.67 (dd, *J* = 8.4, 6.4 Hz, 1H), 7.61 (s, 6H), 7.56 (ddt, *J* = 10.5, 7.8, 3.8 Hz, 4H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.35 – 7.27 (m, 2H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.62 (t, *J* = 7.6 Hz, 1H), 6.42 (d, *J* = 8.1 Hz, 1H), 5.35 – 5.29 (m, 1H), 4.14 – 4.03 (m, 1H), 3.97 (dt, *J* = 10.8, 8.6 Hz, 1H), 3.01 (ddd, *J* = 13.6, 11.0, 8.6 Hz, 1H), 2.77 (s, 3H), 1.76 (d, *J* = 6.6 Hz, 3H), 1.47 (dt, *J* = 13.6, 10.3 Hz, 1H), -16.85 (d, *J* = 14.6 Hz, 1H); **^{31}P{^{1}H}-NMR** (202 MHz, CD_2Cl_2) δ 10.28 (d, *J* = 5.7 Hz).



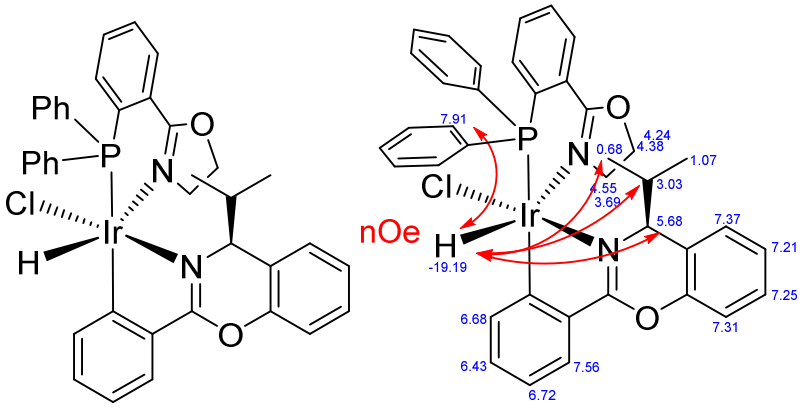
[Ir(PHOX)((*S*)-26)(H)(Cl)] (12)



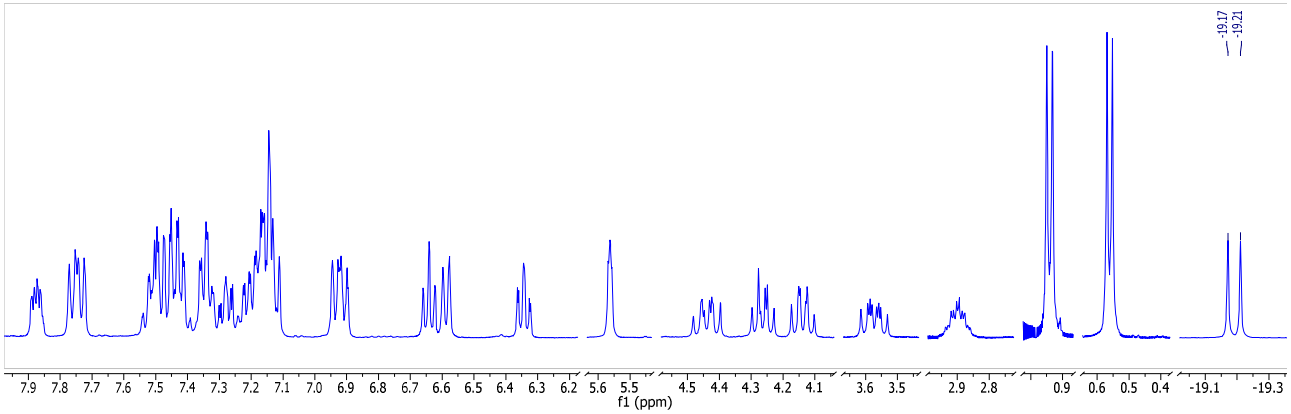
By general method [Ir(PHOX)(COD)]BAr_F (25 mg, 0.017 mmol, 1.0 eq.) and (*S*)-**26** (3 mg, 0.013 mmol, 0.8 eq.) afforded 6 mg (0.008 mmol, 59%) of **12** as a yellow solid.
$C_{36}H_{31}ClIrN_2O_2P$ (782.29 g/mol):
^{1}H-NMR (400 MHz, CD_2Cl_2) δ 7.89 (dd, *J* = 7.7, 3.2 Hz, 1H), 7.73 (dd, *J* = 11.4, 7.3 Hz, 2H), 7.57 – 7.08 (m, 21H), 6.93 (dd, *J* = 11.1, 6.9 Hz, 2H), 6.66 (t, *J* = 7.4 Hz, 1H), 6.59 (d, *J* = 7.9 Hz, 1H), 6.38 – 6.30 (m, 1H), 5.77 (dd, *J* = 12.4, 5.9 Hz, 1H), 4.52 – 4.39 (m, 2H), 4.29 (ddd, *J* = 16.4, 12.9, 10.0 Hz, 2H), 4.17 (dt, *J* = 17.7, 8.9 Hz, 1H), 3.60 (ddd, *J* = 13.6, 11.1, 8.5 Hz, 2H), 1.58 (d, *J* = 6.6 Hz, 3H), -19.09 (d, *J* = 15.9 Hz, 1H); **^{31}P{^{1}H}-NMR** (162 MHz, CD_2Cl_2) δ 12.44 (s_{br}).

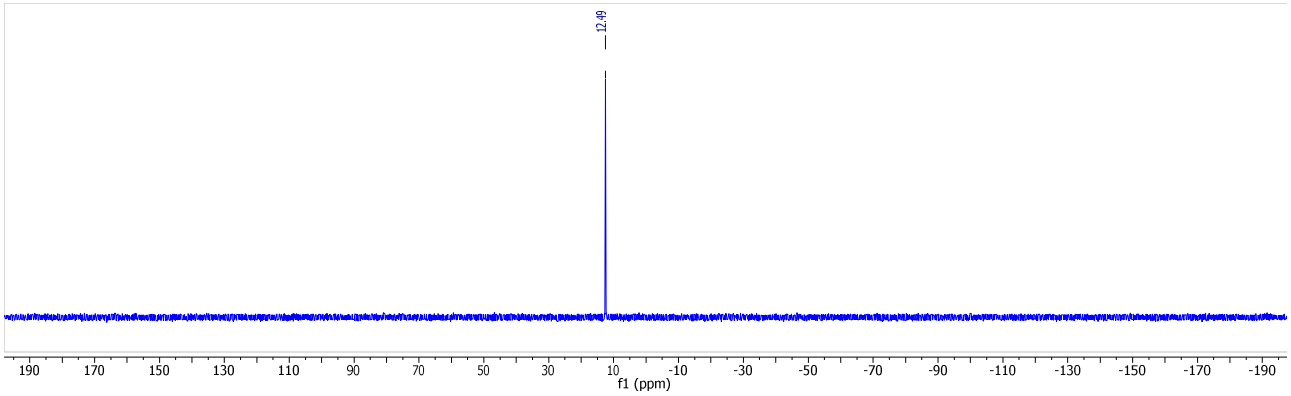


[Ir(PHOX)((*S*)-29)(H)(Cl)] (13)

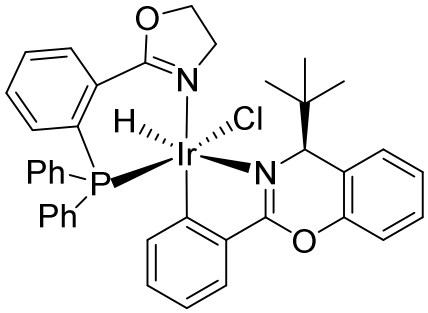


By general method [Ir(PHOX)(COD)]BAr_F (25 mg, 0.017 mmol, 1.0 eq.) and (*S*)-**29** (10.5 mg, 0.042 mmol, 2.5 eq.) afforded 10.4 mg (0.013 mmol, 75%) of **13** as a yellow solid.
$C_{38}H_{35}ClIrN_2O_2P$ (810.34 g/mol):
^{1}H-NMR (400 MHz, CD_2Cl_2) δ 7.88 (dd, *J* = 6.9, 3.5 Hz, 1H), 7.75 (dd, *J* = 11.4, 7.4 Hz, 2H), 7.55 – 7.38 (m, 5H), 7.34 (td, *J* = 7.6, 2.0 Hz, 2H), 7.31 – 7.25 (m, 1H), 7.25 – 7.09 (m, 5H), 6.98 – 6.86 (m, 2H), 6.64 (t, *J* = 7.3 Hz, 1H), 6.59 (d, *J* = 7.9 Hz, 1H), 6.34 (td, *J* = 7.7, 1.6 Hz, 1H), 5.59 – 5.51 (m, 1H), 4.44 (ddd, *J* = 13.6, 10.9, 9.4 Hz, 1H), 4.31 – 4.22 (m, 1H), 4.14 (dt, *J* = 10.9, 9.0 Hz, 1H), 3.57 (ddd, *J* = 13.6, 11.1, 8.3 Hz, 1H), 2.96 – 2.84 (m, 1H), 0.94 (d, *J* = 7.1 Hz, 3H), 0.56 (d, *J* = 6.9 Hz, 3H), -19.19 (d, *J* = 15.9 Hz, 1H); **^{31}P{^{1}H}-NMR** (162 MHz, CD_2Cl_2) δ 12.49 (s).

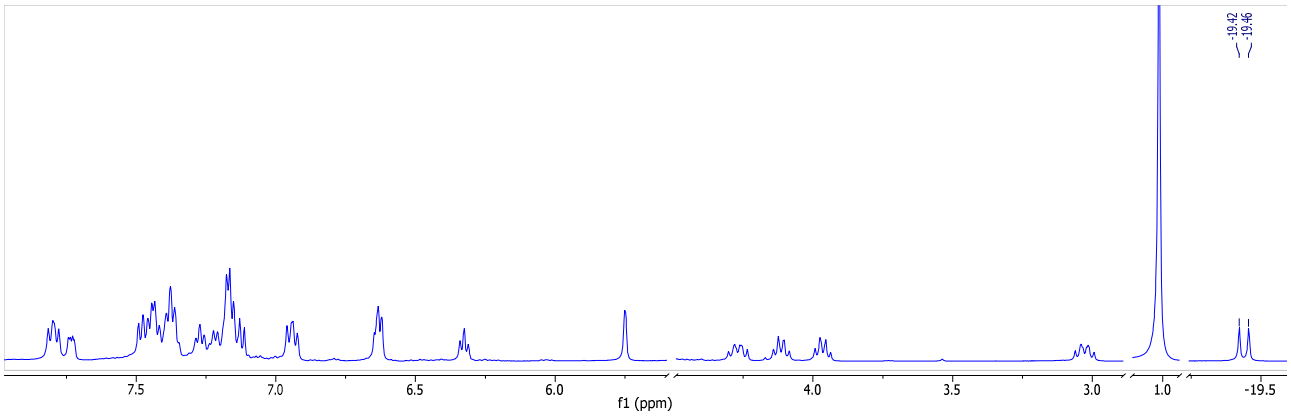


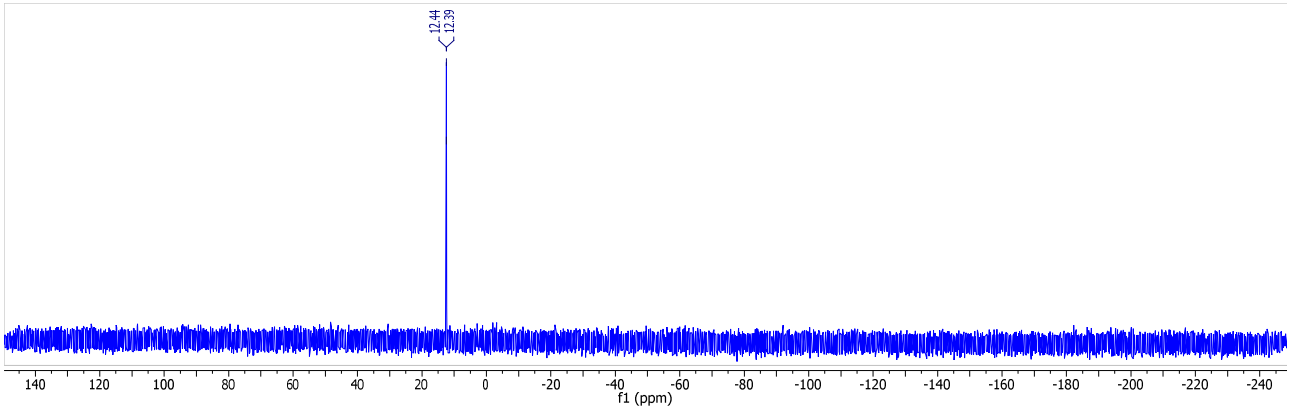


[Ir(PHOX)((*S*)-35)(H)(Cl)] (14)



By general method [Ir(PHOX)(COD)]BAr_F (50 mg, 0.0334 mmol, 1.0 eq.) and (*S*)**-35** (17.2 mg, 0.067 mmol, 2.0 eq.) afforded 15.1 mg (0.018 mmol, 55%) of **14** as a yellow solid.
$C_{39}H_{37}ClIrN_2O_2P$ (824.37 g/mol):
^{1}H-NMR (500 MHz, CD_2Cl_2) δ 7.80 (dd, *J* = 11.6, 7.6 Hz, 2H), 7.73 (dd, *J* = 8.0, 3.7 Hz, 1H), 7.55 – 7.33 (m, 8H), 7.33 – 7.10 (m, 8H), 6.94 (dd, *J* = 11.2, 7.5 Hz, 2H), 6.63 (dd, *J* = 8.1, 5.3 Hz, 2H), 6.33 (t, *J* = 7.5 Hz, 1H), 5.75 (d, *J* = 2.5 Hz, 1H), 4.27 (ddd, *J* = 13.8, 11.0, 8.7 Hz, 1H), 4.17 – 4.06 (m, 1H), 3.96 (dt, *J* = 11.1, 8.5 Hz, 1H), 3.03 (ddd, *J* = 13.7, 10.9, 8.6 Hz, 1H), 1.01 (s, 9H), -19.44 (d, *J* = 16.7 Hz, 1H); **^{31}P{1H}-NMR** (202 MHz, CD_2Cl_2) δ 12.41 (d, *J* = 10.9 Hz).



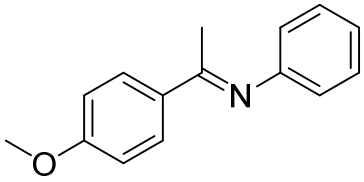


Synthesis of Imines

General Method:
A 25mL oven-dried two-neck round-bottom flask equipped with a stirrer, reflux condenser and a stopper was evacuated and purged with Argon gas three times. Freshly activated 4Å mol sieves were added under an argon counterflow. The stopper was replaced with a septum and ketone, aniline and solvent were added. A spatula tip of *p*-toluenesulfonic acid was added. The septum was replaced by a stopper and the solution was heated to reflux for 24 to 48 hours. After cooling to room temperature under argon the solution was filtered through a paper filter and rinsed with toluene. The solvent was removed under reduced pressure and the product was purified by Kugelrohr distillation.

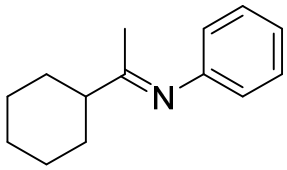
Compounds **I1**[11], **I19**[12], **I20**[13], **I21**[12] had been prepared previously in our laboratories.

N-(1-(4-methoxyphenyl)ethylidene)aniline (I2)[14]



By general method 4-methoxyacetophenone (2.7 g, 18 mmol, 1.0 eq.) and aniline (2 g, 21.9 mmol, 1.21 eq.) were dissolved in dry benzene (7.5 mL). Purification by Kugelrohr distillation (110-180 °C at 0.07 mbar) afforded 3.4 g (15.1 mmol, 83%) of **I2** as a yellow solid.
$C_{15}H_{15}NO$ (225.29 g/mol):
m.p.: 91-92 °C (Lit. 92-94°C); **^{1}H-NMR** (500 MHz, $CDCl_3$): 7.85 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}C_{Ar}C$=N), 7.25 (t, *J* = 7.7 Hz, 2H, $CH_{Ar}CH_{Ar}C_{Ar}$-N), 6.98 (t, *J* = 7.4 Hz, 1H, $CH_{Ar}CH_{Ar}CH_{Ar}C_{Ar}$-N), 6.86 (d, *J* = 8.6 Hz, 2H, $CH_{Ar}C_{Ar}$OMe), 6.70 (d, *J* = 7.7 Hz, 2H, $CH_{Ar}C_{Ar}$-N), 3.77 (s, 3H, OCH_3), 2.11 (s, 3H, CH_3C=N); **^{13}C{^{1}H}-NMR** (126 MHz, $CDCl_3$) δ 164.65 (*C*=N), 161.62 (C_{Ar}OMe), 151.99 (C_{Ar}-N), 132.30 ($C_{Ar}C$=N), 129.02 ($CH_{Ar}CH_{Ar}C_{Ar}$-N), 128.94 ($CH_{Ar}C_{Ar}C$=N), 123.12 ($CH_{Ar}CH_{Ar}CH_{Ar}C_{Ar}$-N), 119.71 ($CH_{Ar}C_{Ar}$-N), 113.70 ($CH_{Ar}C_{Ar}$OMe), 55.51 ($OCH_3$), 17.30 ($CH_3C$=N).

N-(1-cyclohexylethylidene)aniline (I3)[15]



By general method 1-Cyclohexylethan-1-one (1.83 g, 14.53 mmol, 1.0 eq.) and aniline (1.49 g, 15.98 mmol, 1.1 eq.) were dissolved in dry toluene (10 mL). Purification by Kugelrohr distillation (130 °C at 0.15 mbar) afforded 1.30 g (6.44 mmol, 44%) of **I3** as a colourless oil.
$C_{14}H_{19}N$ (201.31 g/mol):
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.22 (m, 2H), 7.05 – 6.98 (m, 1H), 6.71 – 6.63 (m, 2H), 2.30 (tt, J = 11.5, 3.2 Hz, 1H), 1.93 (dd, J = 6.7, 5.5 Hz, 2H), 1.89 – 1.80 (m, 2H), 1.74 – 1.70 (m, 3H), 1.49 – 1.16 (m, 6H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 175.75, 151.94, 128.96, 122.91, 119.52,

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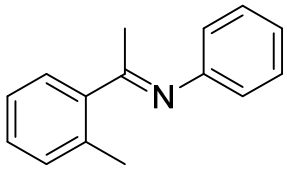
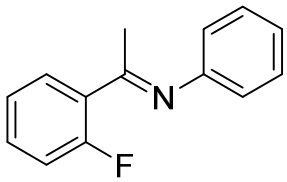
49.53, 30.39, 26.30, 26.28, 17.81; **GC** (Machary-Nagel Optima-5-Amin (0.50 µm x 0.25 µm x 30 m), 60 kPa H_2, 100 °C/2 min, 10 °C/min, 250 °C/7 min): t_R = 18.5 min; **HRMS**: calculated: 201.1512; found: 201.1512

***N*-(1-(o-tolyl)ethylidene)aniline (I4)**[16]



By general method acetophenone (2.29 g, 17 mmol, 1.0 eq.) and aniline (2 g, 22 mmol, 1.3 eq.) were dissolved in dry benzene (20 mL). Purification by Kugelrohr distillation (100-160 °C at 0.1 mbar) afforded 2.74 g (13.1 mmol, 77%) of **I4** as a yellow oil.
$C_{15}H_{15}N$ (209.29 g/mol):
major: **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 7.419 (m, 1H, CH_{Ar}C$_{Ar}$C=N), 7.392 (m, 2H, CH_{Ar}CH$_{Ar}$C$_{Ar}$-N), 7.297 (m, 1H, CH_{Ar}CH$_{Ar}$C$_{Ar}$CH$_3$), 7.280 (m, 1H, CH_{Ar}C$_{Ar}$CH$_3$), 7.278 (m, 1H, CH_{Ar}CH$_{Ar}$C$_{Ar}$C=N), 7.127 (m, 1H, CH_{Ar}CH$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 6.876 (m, 2H, CH_{Ar}C$_{Ar}$-N), 2.543 (s, 3H, C$_{Ar}$CH_3), 2.18 (s, 3H CH_3C=N); **^{13}C{^{1}H}-NMR** (126 MHz, $CDCl_3$) δ 170.036 (*C*=N), 151.291 (*C*$_{Ar}$-N), 141.571 (*C*$_{Ar}$C=N), 135.04 (*C*$_{Ar}$CH$_3$), 131.111 (*C*H$_{Ar}$C$_{Ar}$CH$_3$), 129.103 (*C*H$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 128.683 (*C*H$_{Ar}$CH$_{Ar}$C$_{Ar}$CH$_3$), 127.183 (*C*H$_{Ar}$C$_{Ar}$C=N), 125.849 (*C*H$_{Ar}$CH$_{Ar}$C$_{Ar}$C=N), 123.459 (*C*H$_{Ar}$CH$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 119.303 (*C*H$_{Ar}$C$_{Ar}$-N), 21.23 (*C*H$_3$C=N), 20.51 (C$_{Ar}$*C*H$_3$).
minor: **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 7.122 (m, 1H, CH_{Ar}CH$_{Ar}$C$_{Ar}$CH$_3$), 7.115 (m, 1H, CH_{Ar}CH$_{Ar}$C$_{Ar}$C=N), 7.107 (m, 2H, CH_{Ar}CH$_{Ar}$C$_{Ar}$-N), 7.052 (m, 1H, CH_{Ar}C$_{Ar}$C=N), 7.036 (m, 1H, CH_{Ar}C$_{Ar}$CH$_3$), 6.906 (m, 1H, CH_{Ar}CH$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 6.687 (m, 2H, CH_{Ar}C$_{Ar}$-N), 2.493 (s, 3H CH_3C=N), 2.133 (s, 3H, C$_{Ar}$CH_3); **^{13}C{^{1}H}-NMR** (126 MHz, $CDCl_3$) δ 171.106 (*C*=N), 150.290 (*C*$_{Ar}$-N), 139.050 (*C*$_{Ar}$C=N), 133.01 (*C*$_{Ar}$CH$_3$), 130.208 (*C*H$_{Ar}$C$_{Ar}$CH$_3$), 128.251 (*C*H$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 128.162 (*C*H$_{Ar}$CH$_{Ar}$C$_{Ar}$CH$_3$), 127.069 (*C*H$_{Ar}$C$_{Ar}$C=N), 125.379 (*C*H$_{Ar}$CH$_{Ar}$C$_{Ar}$C=N), 123.498 (*C*H$_{Ar}$CH$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 120.841 (*C*H$_{Ar}$C$_{Ar}$-N), 29.32 (*C*H$_3$C=N), 21.33 (C$_{Ar}$*C*H$_3$).
GC-MS: (Optima-5-Amine, 100.2/10.270/10): t_R = 14.6 min, *m/z* = 209 ([M]$^+$), 194 ([M-CH$_3$]$^+$), 118 (([M-NPh]$^+$).

***N*-(1-(2-fluorophenyl)ethylidene)aniline (I5)**

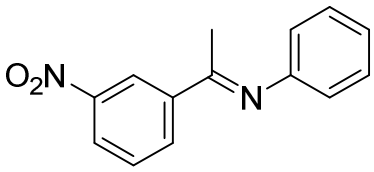


By general method 2-fluoroacetophenone (2.5 g, 18.1 mmol, 1.0 eq.) and aniline (2 g, 22 mmol, 1.2 eq.) were dissolved in dry benzene (20 mL). Purification by Kugelrohr distillation (110-160 °C at 0.1 mbar) afforded 3.08 g (14.5 mmol, 80%) of **I5** as a yellow oil.
$C_{14}H_{12}FN$ (213.25 g/mol):
E/Z mixture 7:1, signals overlapping, only *major* isomer characterised: **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 7.85 (td, *J* = 7.7, 1.9 Hz, 1H, CH_{Ar}C$_{Ar}$C=N), 7.41 (dddd, 1H, *J* = 8.2, 7.1, 5.1, 1.8 Hz, CH_{Ar}CHArC$_{Ar}$F), 7.37 (t, *J* = 7.7 Hz, 2H, CH_{Ar}CH$_{Ar}$C$_{Ar}$-N), 7.22 (t, *J* = 7.5 Hz, 1H, CH_{Ar}CH$_{Ar}$CH$_{Ar}$C$_{Ar}$C-N), 7.15 (m, 1H, CH_{Ar}C$_{Ar}$-F), 7.12 (m, 1H, CH_{Ar}CH$_{Ar}$C$_{Ar}$C=N), 6.83 (d, *J* = 7.7 Hz, 2H, CH_{Ar}C$_{Ar}$-N), 2.25 (d, *J* = 3.5 Hz, 3H, CH_3C=N); **^{13}C{^{1}H}-NMR** (126 MHz, $CDCl_3$): 165.37 (*C*=N), 161.22 (d, *J* = 250.6 Hz, *C*$_{Ar}$-F), 150.85 (*C*$_{Ar}$-N), 131.70 (d, *J* = 8.6 Hz,

[16] M. C. Hansen, S. L. Buchwald, *Org. Lett.* **2000**, *2*, 713-715

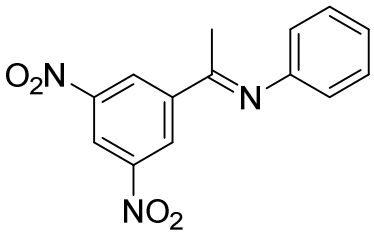
$CH_{Ar}CHArC_{Ar}F$), 130.18 (d, J = 3.5 Hz, $CH_{Ar}C_{Ar}C{=}N$), 129.15 ($CH_{Ar}CH_{Ar}C_{Ar}$-N) , 124.42 ($CH_{Ar}CH_{Ar}CH_{Ar}C_{Ar}C$-N), 123.69 ($CH_{Ar}CH_{Ar}C_{Ar}C{=}N$), 119.43 ($CH_{Ar}C_{Ar}$-N), 116.37 (d, J = 22.9 Hz, $CH_{Ar}C_{Ar}$-F), 20.80 (d, J = 6.8 Hz, $CH_3C{=}N$); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.34 (major), -113.43 (minor); **IR** (neat, ATR) ν/cm^{-1} = 3060 (w), 3031 (w), 2997 (w), 1634 (s), 1610 (m), 1593 (s), 1576 (m), 1485 (s), 1450 (m), 1368 (m), 1293 (m), 1211 (s), 1169 (w), 1113 (m), 1072 (m). 801 (m), 759 (s), 716 (m), 696 (s); **MS** (EI, 70 eV): 213.1 (55.7%), 198.1 (100%), 118.1 (8.1%); **EA**: calc. C, 78.85; H, 5.67; N, 6.57, found C, 78.68; H, 5.86; N, 6.47

***N*-(1-(3-nitrophenyl)ethylidene)aniline (I6)**



By general method 3-nitroacetophenone (0.5 g, 3 mmol, 1.0 eq.) and aniline (0.33 g, 3.6 mmol, 1.2 eq.) were dissolved in dry toluene (10 mL). Purification by Kugelrohr distillation (170 °C at 0.1 mbar) afforded 0.357 g (1.49 mmol, 49%) of **I6** as a yellow solid.
$C_{14}H_{12}N_2O_2$ (240.26 g/mol):
m.p.: 96 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.89 – 8.70 (m, 1H, $CH_{Ar}C_{Ar}NO_2$), 8.44 – 8.22 (m, 2H, $CH_{Ar}C_{Ar}NO_2$&$CH_{Ar}C_{Ar}C{=}N$), 7.64 (t, J = 8.0 Hz, 1H, $CH_{Ar}CH_{Ar}C_{Ar}C{=}N$), 7.38 (t, J = 7.8 Hz, 2H, $CH_{Ar}CH_{Ar}C_{Ar}$-N), 7.13 (t, J = 7.4 Hz, 1H, $CH_{Ar}CH_{Ar}CH_{Ar}C_{Ar}$-N), 6.80 (d, J = 7.3 Hz, 2H, $CH_{Ar}C_{Ar}$-N), 2.30 (s, 3H, $CH_3C{=}N$); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 163.33 ($C{=}N$), 150.91 (C_{Ar}-N), 141.21 ($C_{Ar}C{=}N$), 133.10 ($CH_{Ar}C_{Ar}C{=}N$), 129.51 ($C_{Ar}C{=}NCH_{Ar}C_{Ar}NO_2$), 129.24 ($CH_{Ar}CH_{Ar}C_{Ar}$-N), 125.12 ($CH_{Ar}CH_{Ar}CH_{Ar}C_{Ar}$-N), 124.01 ($CH_{Ar}C_{Ar}NO_2$), 122.38 ($CH_{Ar}CH_{Ar}C_{Ar}C{=}N$), 119.31 ($CH_{Ar}C_{Ar}$-N), 17.50 ($CH_3C{=}N$); **IR** (neat, ATR) ν/cm^{-1} = 3114 (w), 3099 (w), 3076 (w), 3070 (w), 3017 (w), 1623 (m), 1593 (m), 1576 (m), 1521 (s), 1483 (s), 1473 (s), 1432 (m), 1368 (m), 1345 (s), 1317 (m), 1286 (m), 1258 (m), 1213 (m), 1170 (w), 1111 (m), 1060 (m), 1024 (w), 900 (m), 818 (m), 744 (s), 735 (s), 693 (s); **MS** (EI, 70 eV): 240.1 (84.2%), 225.1 (100%), 179.1 (42.5%); **HRMS**: calculated: 240.0894; found: 240.0900; **EA**: calc. C, 69.99; H, 5.03; N, 11.66; found: C, 69.81; H, 5.14; N, 11.56

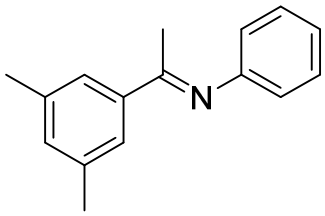
***N*-(1-(3,5-dinitrophenyl)ethylidene)aniline (I7)**



By general method 3,5-dinitroacetophenone (0.5 g, 2.38 mmol, 1.0 eq.) and aniline (0.26 g, 2.85 mmol, 1.2 eq.) were dissolved in dry toluene (10 mL). Purification by recrystallisation from ethanol afforded 0.291 g (1.02 mmol, 43%) of **I7** as an orange solid.
$C_{14}H_{11}N_3O_4$ (285.25 g/mol):
m.p.: 132-133 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 9.19 – 9.08 (m, 3H, CH_{ArNO2}), 7.48 – 7.34 (m, 2H, $CH_{Ar}CH_{Ar}C_{Ar}$-N), 7.22 – 7.13 (m, 1H, $CH_{Ar}CH_{Ar}CH_{Ar}C_{Ar}$-N), 6.82 (dd, J = 8.3, 1.0 Hz, 2H, $CH_{Ar}C_{Ar}$-N), 2.38 (s, 3H, $CH_3C{=}N$); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 161.25 ($C{=}N$), 150.01 (C_{Ar}-N), 148.83 (C_{Ar}-NO_2), 143.01 ($C_{Ar}C{=}N$), 129.37 ($CH_{Ar}CH_{Ar}C_{Ar}$-N), 127.24 ($CH_{Ar}C_{Ar}C{=}N$), 124.68 ($CH_{Ar}CH_{Ar}CH_{Ar}C_{Ar}$-N), 120.02 ($C_{Ar\text{-}NO2}CH_{Ar}C_{Ar\text{-}NO2}$), 119.22 ($CH_{Ar}C_{Ar}$-N), 17.48 ($CH_3C{=}N$); **IR** (neat, ATR) ν/cm^{-1} = 3117 (w), 3101 (w), 3059 (w), 3050 (w), 1646 (m), 1625 (m), 1590 (m), 1535 (s), 1481 (w) 1461 (w), 1438 (w), 1367 (m), 1345 (s), 1334 (s), 1285 (m), 1237 (w),

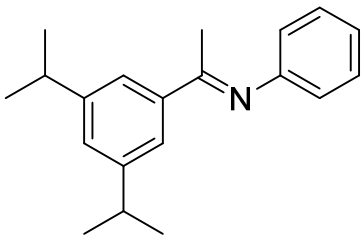
1209 (m), 1169 (w), 1144 (m), 1100 (w), 1073 (m), 910 (m), 903 (m), 810 (m), 795 (m), 753 (s), 728 (s), 654 (s); **MS** (EI, 70 eV): 285.1 (100%), 270.1 (82.8%), 224.1 (18.1%), 178.1 (24.1%); **HRMS**: calculated: 285.0744; found: 285.0740; **EA**: calc. C, 58.95; H, 3.89; N, 14.73; found: C, 58.93; H, 3.99; N, 14.64

***N*-(1-(3,5-dimethylphenyl)ethylidene)aniline (I8)**



By general method 3,5-dimethylacetophenone (0.3 g, 2 mmol, 1.0 eq.) and aniline (0.2 g, 2.2 mmol, 1.1 eq.) were dissolved in dry toluene (7.5 mL). Purification by Kugelrohr distillation (137 °C at 0.08 mbar) afforded 0.165 g (0.74 mmol, 37%) of **I8** as an off-yellow solid.
$C_{16}H_{17}N$ (223.31 g/mol):
b.p.: 137 °C at 0.08 mbar; **m.p.**: 44 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.58 (s, 2H, C$H_{Ar}C_{Ar}$C=N)), 7.40 – 7.29 (m, 2H, CH_{Ar}CH_{Ar}C$_{Ar}$-N), 7.11 (s, 1H, C$_{Ar}$CH$_3$CH_{Ar}C$_{Ar}$CH$_3$), 7.10 – 7.05 (m, 1H, CH_{Ar}CH_{Ar}CH_{Ar}C$_{Ar}$-N), 6.79 (dt, *J* = 8.3, 1.6 Hz, 2H, CH_{Ar}C$_{Ar}$-N), 2.38 (s, 6H, C$_{Ar}$CH_3), 2.21 (s, 3H, CH_3C=N); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 166.10 (*C*=N), 151.95 (*C*-N), 139.68 (*C*$_{Ar}$C=N), 138.05 (*C*$_{Ar}$CH$_3$), 132.25 (C$_{Ar}$CH$_3$CH_{Ar}C$_{Ar}$CH$_3$), 129.07 (CH_{Ar}CH_{Ar}C$_{Ar}$-N), 125.14 (CH_{Ar}C$_{Ar}$C=N), 123.27 (CH_{Ar}CH_{Ar}CH_{Ar}C$_{Ar}$-N), 119.54 (CH_{Ar}C$_{Ar}$-N), 21.49 (C$_{Ar}$CH_3), 17.70 (CH_3C=N); **IR** (neat, ATR) ν/cm^{-1} = 3027 (w), 3010 (w), 2959 (w), 2917 (w), 1628 (s), 1600 (m), 1590 (s), 1576 (m), 1480 (m), 1447 (m), 1438 (m), 1376 (w), 1363 (m), 1321 (m), 1272 (w), 1208 (s), 1167 (m), 1155 (m), 1071 (m), 1026 (m), 906 (m), 852 (s), 800 (s), 761 (s), 694 (s); **MS** (EI, 70 eV): 223.1 (43.9%), 208.1 (100%); **GC-MS**: (Rtx-5MS, 100.2/10.270/10): t_R = 19.1 min, *m*/*z* = 223 ([M]$^{+}$); **EA**: calc. C, 86.06; H, 7.67; N, 6.27, found C, 86.19; H, 7.65; N, 6.28

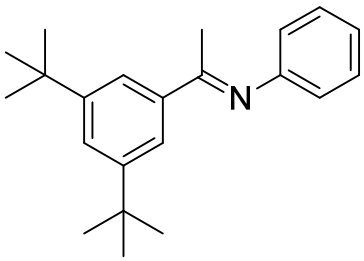
***N*-(1-(3,5-diisopropylphenyl)ethylidene)aniline (I9)**



By general method **13** (0.5 g, 2.45 mmol, 1.0 eq.) and aniline (0.29 g, 3.18 mmol, 1.3 eq.) were dissolved in dry toluene (10 mL). Purification by Kugelrohr distillation (160 °C at 0.08 mbar) afforded 0.310 g (1.11 mmol, 45%) of **I9** as a yellow oil.
$C_{20}H_{25}N$ (279.42 g/mol):
E/Z mixture 8:1, signals overlapping; *major*: **^{1}H-NMR** (500 MHz, $CDCl_3$) δ: 7.65 (d, *J* = 4.0 Hz, 2H, C$H_{Ar}C_{Ar}$C=N), 7.35 (t, *J* = 7.7 Hz, 2H, CH_{Ar}CH_{Ar}C$_{Ar}$-N), 7.20 (s, 1H, C$_{Ar}$CH(CH$_3$)$_2$CH_{Ar}C$_{Ar}$CH(CH$_3$)$_2$), 7.08 (t, *J* = 7.4 Hz, 1H, CH_{Ar}CH_{Ar}CH_{Ar}C$_{Ar}$-N), 6.80 (d, *J* = 7.7 Hz, 2H, CH_{Ar}C$_{Ar}$-N), 2.97 (hept, *J* = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 2.23 (d, *J* = 7.0 Hz, 3H, CH_3C=N), 1.30 (d, *J* = 7.1 Hz, 12H, CH(CH_3)$_2$); **^{13}C{^{1}H}-NMR** (125 MHz, $CDCl_3$) δ:166.23 (*C*=N), 152.10 (*C*$_{Ar}$-N), 149.18 (*C*$_{Ar}$CH(CH$_3$)$_2$), 139.68 (*C*$_{Ar}$C=N), 129.07 (CH_{Ar}CH_{Ar}C$_{Ar}$-N), 127.05 (CH_{Ar}CH_{Ar}CH_{Ar}C$_{Ar}$-N), 123.19 (C$_{Ar}$CH(CH$_3$)$_2$C*H*ArC$_{Ar}$CH(CH$_3$)$_2$), 123.07 (C$_{Ar}$CH(CH$_3$)$_2$CH_{Ar}C$_{Ar}$C=N), 119.54 (CH_{Ar}C$_{Ar}$-N), 34.48 (C*H*(CH$_3$)$_2$), 24.23 (CH(CH_3)$_2$), 17.84 (CH_3C=N); **IR** (neat, ATR) ν/cm^{-1} = 3058 (w), 2960 (s), 2927 (m), 2869 (m), 1634 (s), 1595 (s), 1485 (m), 1465 (m), 1440 (w), 1364 (m), 1255 (w), 1209 (s), 875 (w), 802 (w), 759 (w), 699 (m);

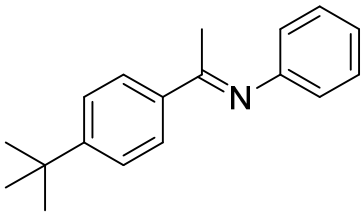
MS (EI, 70 eV): 279.2 (40.79%), 264.2 (100%), 248.1 (9.7%); **HRMS**: calculated: 279.1982; found: 279.1983; **EA**: calc. C, 85.97; H, 9.02; N, 5.01; found: C, 85.71; H, 8.91; N, 5.01.

***N*-(1-(3,5-di-tert-butylphenyl)ethylidene)aniline (I10)**



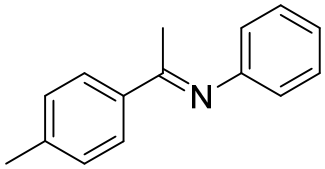
By general method **15** (0.5 g, 2.15 mmol, 1.0 eq.) and aniline (0.25 g, 2.8 mmol, 1.3 eq.) were dissolved in dry toluene (10 mL). Purification by Kugelrohr distillation (170 °C at 0.1 mbar) afforded 0.368 g (1.2 mmol, 56%) of **I10** as a yellow-white solid.
$C_{22}H_{29}N$ (307.47 g/mol):
m.p.: 86-90 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ:7.84 (s, 2H, CH_{Ar}C$_{Ar}$C=N)), 7.58 (s, 1H, C$_{Ar}$C(CH$_3$)$_3$CH_{Ar}C$_{Ar}$C(CH$_3$)$_3$), 7.36 (t, *J* = 7.7 Hz, 2H, CH_{Ar}CH$_{Ar}$C$_{Ar}$-N), 7.09 (t, *J* = 7.5 Hz, 1H, CH_{Ar}CH$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 6.82 (d, *J* = 7.7 Hz, 2H, CH_{Ar}C$_{Ar}$-N), 1.40 (s, 18H, C(CH_3)$_3$); **^{13}C{^{1}H}-NMR** (125 MHz, $CDCl_3$) δ: 166.42 (*C*=N), 152.23 (*C*$_{Ar}$-N), 150.93 (*C*$_{Ar}$C(CH$_3$)$_3$), 139.13 (*C*$_{Ar}$C=N), 129.07 (*C*H$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 124.88 (C$_{Ar}$C(CH$_3$)$_3$CH_{Ar}C$_{Ar}$C(CH$_3$)$_3$), 123.12 (*C*H$_{Ar}$CH$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 121.54 (*C*H$_{Ar}$C$_{Ar}$C=N), 119.52 (*C*H$_{Ar}$C$_{Ar}$-N), 35.14 (*C*(CH$_3$)$_3$), 31.63 (C(*C*H$_3$)$_3$), 17.92 (*C*H$_3$C=N); **IR** (neat, ATR) ν/cm^{-1} = 3061 (w), 2961 (m), 2934 (w), 2905 (w), 2865 (w), 1685 (w), 1636 (m), 1590 (m), 1477 (m), 1447 (m), 1393 (w), 1362 (m), 1323 (m), 1247 (m), 1212 (s), 1168 (m), 1068 (m), 1024 (m), 903 (m), 879 (m), 798 (m), 755 (s), 701 (s); **MS** (EI, 70 eV): 307.2 (52.7%), 292.2 (100%), 276.2 (12.6%); **HRMS**: calculated: 307.2295; found: 307.2294; **EA**: calc. C, 85.94; H, 9.51; N, 4.56; found: C, 85.93; H, 9.49; N, 4.44.

***N*-(1-(4-(tert-butyl)phenyl)ethylidene)aniline (I11)**



By general method 4-*tert*-butyl acetophenone (0.48 g, 2.72 mmol, 1.0 eq.) and aniline (0.35 g, 3.93 mmol, 1.44 eq.) were dissolved in dry toluene (10 mL). Purification by Kugelrohr distillation (125 °C at 0.08 mbar) afforded 0.28 g (1.11 mmol, 41%) of **I11** as yellow-white solid.
$C_{18}H_{21}N$ (251.37 g/mol):
b.p.: 125 °C at 0.08 mbar; **m.p.**: 63-64 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.5 Hz, 2H, CH_{Ar}C$_{Ar}$C=N), 7.48 (d, *J* = 8.5 Hz, 2H, CH_{Ar}C$_{Ar}$C(CH$_3$)$_3$), 7.35 (t, *J* = 7.8 Hz, 2H, CH_{Ar}CH$_{Ar}$C$_{Ar}$-N), 7.08 (t, *J* = 7.4 Hz, 1H, CH_{Ar}CH$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 6.79 (t, *J* = 7.4 Hz, 2H, CH_{Ar}C$_{Ar}$-N), 2.22 (s, 3H, CH_3C=N), 1.36 (s, 9H, C(CH_3)$_3$); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 165.31 (*C*=N), 154.01 (*C*$_{Ar}$C(CH$_3$)$_3$), 152.01 (*C*$_{Ar}$-N), 136.88 (*C*$_{Ar}$C=N), 129.06 (*C*H$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 127.12 (*C*H$_{Ar}$C$_{Ar}$C=N), 125.44 (*C*H$_{Ar}$C$_{Ar}$C(CH$_3$)$_3$), 123.21 (*C*H$_{Ar}$CH$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 119.58 (*C*H$_{Ar}$C$_{Ar}$-N), 34.97 (*C*(CH$_3$)$_3$), 31.38 (C(*C*H$_3$)$_3$), 17.40 (*C*H$_3$C=N); **IR** (neat, ATR) ν/cm^{-1} = 3053 (w), 2971 (w), 2952 (m), 2902 (w), 2864 (w), 1623 (m), 1601 (m), 1589 (m), 1560 (m), 1509 (w), 1478 (m), 1434 (m), 1360 (m), 1312 (w), 1290 (m), 1216 (m), 1199 (m), 1126 (m), 1024 (m), 1011 (m), 852 (m), 824 (s), 699 (s); **MS** (EI, 70 eV): 251.2 (46.7%), 236.1 (100%); **HRMS**: calculated: 251.1669; found: 251.1670; **EA**: calc. C, 86.01; H, 8.42; N, 5.57; found: C, 85.83; H, 8.49; N, 5.59.

***N*-(1-(p-tolyl)ethylidene)aniline (I12)**[17]

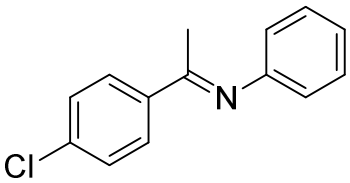


By general method 4-methyl acetophenone (1.3 mL, 10 mmol, 1 eq.) and aniline (1.1 ml, 12 mmol, 1.2 eq.) were dissolved in dry benzene (5 mL). Purification by Kugelrohr distillation (130 °C at 0.08 mbar) afforded 1.67 g (7.98 mmol, 79 %) of **I12** as a yellow oil.

$C_{15}H_{15}N$ (209.29 g/mol):

^{1}H-NMR (400 MHz, CD_2Cl_2): 7.90 (d, *J* = 8.0 Hz, 2H,C$H_{Ar}C_{Ar}$C=N); 7.37 (t, *J* = 7.25 Hz, 2H, CH_{Ar}C$H_{Ar}C_{Ar}$-N); 7.28 (d, *J* = 7.75 Hz, 2H, C$H_{Ar}C_{Ar}$CH_3); 7.10 (t, *J* = 7.5 Hz, 1H, CH_{Ar}CH_{Ar}C$H_{Ar}C_{Ar}$-N); 6.81 (d, *J* = 7.75 Hz, 2H, C$H_{Ar}C_{Ar}$-N); 2.43 (s, 3H, $C_{Ar}CH_3$); 2.21 (s, 3H, CH_3C=N); **^{13}C{^{1}H}-NMR** (100 MHz, CD_2Cl_2): 164.9 (*C*=N); 152.0 (C_{Ar}-N); 140.7 ($C_{Ar}CH_3$); 136.8 (C_{Ar}C=N); 128.9 (*C*H$_{Ar}C_{Ar}$CH_3); 128.8 (*C*H$_{Ar}$C$H_{Ar}C_{Ar}$-N); 127.0 (*C*H$_{Ar}C_{Ar}$C=N); 122.9 (*C*H$_{Ar}$CH_{Ar}C$H_{Ar}C_{Ar}$-N); 119.3 (*C*H$_{Ar}C_{Ar}$-N); 21.1 ($C_{Ar}CH_3$); 16.9 (*C*H$_3$C=N).

***N*-(1-(4-chlorophenyl)ethylidene)aniline (I13)**[18]

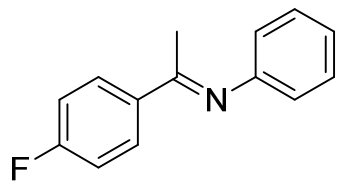


By general method 1-(4-chlorophenyl)ethanone (1.3 mL, 10 mmol, 1 eq.) and aniline (1.1 mL, 12 mmol, 1.2 eq.) were dissolved in dry benzene (5 mL). Purification by Kugelrohr distillation (145 °C at 0.08 mbar) afforded 1.87 g (8.1 mmol, 81 %) of **I13** as a yellow solid.

$C_{14}H_{12}ClN$ (229.70 g/mol):

m.p.: 93 °C (Lit. 93-95°C); **^{1}H-NMR** (600 MHz, CD_2Cl_2): 7.95 (d, *J* = 8.0 Hz, 2H, C$H_{Ar}C_{Ar}$C=N); 7.45 (d, *J* = 8.0 Hz, 2H, C$H_{Ar}C_{Ar}$Cl); 7.38 (t, *J* = 7.75 Hz, 2H, CH_{Ar}C$H_{Ar}C_{Ar}$-N); 7.12 (t, *J* = 7.25 Hz, 1H, CH_{Ar}CH_{Ar}C$H_{Ar}C_{Ar}$-N); 6.79 (d, *J* = 7.75 Hz, 2H, C$H_{Ar}C_{Ar}$-N); 2.21 (s, 3H, CH_3C=N); **^{13}C{^{1}H}-NMR** (100 MHz, CD_2Cl_2): 163.88 (C=N); 151.40 (C_{Ar}-N); 137.87 (C_{Ar}C=N); 136.21 (C_{Ar}Cl); 128.81 (CH_{Ar}C$H_{Ar}C_{Ar}$-N); 128.45 (C$H_{Ar}C_{Ar}$C=N); 128.27 (C$H_{Ar}C_{Ar}$Cl); 123.11 (*C*H$_{Ar}$CH_{Ar}C$H_{Ar}C_{Ar}$-N); 119.08 (*C*H$_{Ar}C_{Ar}$-N); 16.81 (*C*H$_3$C=N).

***N*-(1-(4-fluorophenyl)ethylidene)aniline (I14)**[15]



By general method 1-(4-fluorophenyl)ethanone (2.517 g, 18.22 mmol, 1.0 eq.) and aniline (2 g, 21.9 mmol, 1.2 eq.) were dissolved in dry benzene (7 mL). Purification by Kugelrohr distillation (120-160° C at 0.1 mbar) afforded 3.21 g (15 mmol, 82 %) of **I14** as a off-white solid.

$C_{14}H_{12}FN$ (213.25 g/mol):

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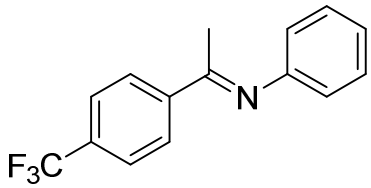
[17] Z. Wang, M. Cheng, P. Wu, S. Wei, J. Sun, *Org. Lett.* **2006**, *8*, 3045-3048

[18] Z. Han, Z. Wang, X. Zhang, K. Ding, *Angew. Chem. Int. Ed.* **2009**, *48*, 5345-5349

m.p.: 81 °C (Lit. 86-87°C); **^{1}H-NMR** (500 MHz, CD_2Cl_2) δ 8.03 – 7.81 (m, 2H, CH_{Ar}C$_{Ar}$C=N), 7.27 (t, *J* = 7.2 Hz, 2H, CH_{Ar}CH$_{Ar}$C$_{Ar}$-N), 7.03 (m, 3H, CH_{Ar}C$_{Ar}$F&CH_{Ar}CH$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 6.69 (d, *J* = 7.4 Hz, 2H, CH_{Ar}C$_{Ar}$-N), 2.12 (s, 3H, CH_3C=N); **^{13}C{^{1}H}-NMR** (126 MHz, CD_2Cl_2) δ 164.64 (d, *J* = 249.7 Hz, *C*$_{Ar}$-F), 164.33 (*C*=N), 152.07 (*C*$_{Ar}$-N), 136.22 (*C*$_{Ar}$C=N), 129.69 (d, *J* = 8.6 Hz, *C*H$_{Ar}$C$_{Ar}$C=N), 129.34 (*C*H$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 123.56 (*C*H$_{Ar}$CH$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 119.68 (C*H*$_{Ar}$C$_{Ar}$-N), 115.50 (d, *J* = 21.6 Hz, C*H*$_{Ar}$C$_{Ar}$F), 17.41 (*C*H$_3$C=N).

***N*-(1-(4-(trifluoromethyl)phenyl)ethylidene)aniline (I15)[18]**

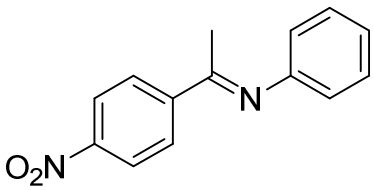


By general method 1-(4-trifluoromethylphenyl)ethanone (1.135 g, 6.03 mmol, 1.0 eq.) and aniline (0.67 g, 7.2 mmol, 1.2 eq.) were dissolved in dry benzene (7 mL). Purification by Kugelrohr distillation (100-150 °C at 0.07 mbar) afforded 1.23 g (4.7 mmol, 78 %) of **I15** as a yellow white solid.

$C_{15}H_{12}F_3N$ (263.26 g/mol):

m.p.: 72-74 °C (Lit. 75-77°C); **^{1}H-NMR** (400 MHz, CD_2Cl_2) δ 8.13 (d, *J* = 8.0 Hz, 2H, CH_{Ar}C$_{Ar}$C=N), 7.73 (d, *J* = 8.0 Hz, 2H, CH_{Ar}C$_{Ar}$-CF$_3$), 7.39 (t, *J* = 7.5 Hz, 2H, CH_{Ar}CH$_{Ar}$C$_{Ar}$-N), 7.13 (t, *J* = 7.2 Hz, 1H, CH_{Ar}CH$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 6.82 (t, *J* = 7.0, 2H, CH_{Ar}C$_{Ar}$-N), 2.27 (s, 3H, CH_3=N); **^{13}C{^{1}H}-NMR** (126 MHz, CD_2Cl_2) δ 164.61 (*C*=N), 151.72 (*C*$_{Ar}$-N), 143.24 (*C*$_{Ar}$C=N), 131.98 (q, *J* = 32.5 Hz, *C*$_{Ar}$-CF$_3$), 129.41 (*C*H$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 127.98 (*C*H$_{Ar}$C$_{Ar}$C=N), 125.62 (q, *J* = 3.8 Hz, *C*H$_{Ar}$C$_{Ar}$-CF$_3$), 123.90 (*C*H$_{Ar}$CH$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 119.52 (*C*H$_{Ar}$C$_{Ar}$-N), 17.57 (*C*H$_3$C=N); **^{19}F{^{1}H}-NMR** (376 MHz, CD_2Cl_2) δ -64.16.

***N*-(1-(4-nitrophenyl)ethylidene)aniline (I16)[14]**

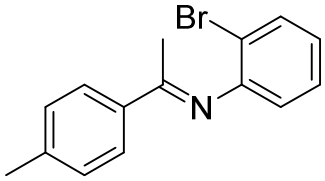


By general method 4-nitroacetophenone (0.5 g, 3.03 mmol, 1.0 eq.) and aniline (0.33 g, 3.55 mmol, 1.2 eq.) were dissolved in dry toluene (10 mL). Purification by recrystallisation from ethanol and pentane-washing afforded 0.456 g (1.89 mmol, 63 %) of **I16** as an orange solid.

$C_{14}H_{12}N_2O_2$ (240.26 g/mol):

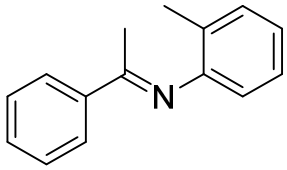
m.p.: 110-114 °C (Lit. 113-115°C); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.8 Hz, 2H, CH_{Ar}C$_{Ar}$-NO$_2$), 8.14 (d, *J* = 8.8 Hz, 2H, CH_{Ar}C$_{Ar}$C=N), 7.38 (t, *J* = 7.7 Hz, 2H, CH_{Ar}CH$_{Ar}$C$_{Ar}$-N), 7.14 (t, *J* = 7.4 Hz, 1H, CH_{Ar}CH$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 6.80 (d, *J* = 7.5 Hz, 2H, CH_{Ar}C$_{Ar}$-N), 2.29 (s, 3H, CH_3C=N); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 163.77 (*C*=N), 150.93 (*C*$_{Ar}$-N), 149.12 (*C*$_{Ar}$-NO$_2$), 145.10 (*C*$_{Ar}$C=N), 129.25 (*C*H$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 128.29 (*C*H$_{Ar}$C$_{Ar}$C=N), 124.10 (*C*H$_{Ar}$CH$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 123.70 (*C*H$_{Ar}$C$_{Ar}$-NO$_2$), 119.21 (*C*H$_{Ar}$C$_{Ar}$-N), 17.67 (*C*H$_3$C=N).

_N_-(2-bromophenyl)-1-(p-tolyl)ethan-1-imine (I17)



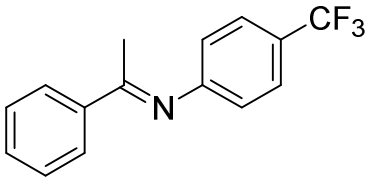
By general method 4-Me-acetophenone (1.0 g, 0.745 mmol, 1.0 eq.) and 2-bromoaniline (1.28 g, 0.745 mmol, 1.0 eq.) were dissolved in dry toluene (10 mL). Purification by Kugelrohr distillation (190 °C at 0.1 mbar) afforded 0.215 g (0.75 mmol, 10 %) of **I17** as yellow oil.
$C_{15}H_{14}BrN$ (287.03 g/mol):
b.p.: 190 °C at 0.1 mbar; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 7.92 (d, J = 8.1 Hz, 2H, CH_{Ar}C$_{Ar}$C=N), 7.59 (d, J = 8.0 Hz, 1H, CH_{Ar}C$_{Ar}$-Br), 7.28 (m, 1H, CH_{Ar}CH$_{Ar}$C$_{Ar}$-N), 7.26 (d, J = 8.0 Hz, CH_{Ar}C$_{Ar}$-CH$_3$), 6.94 (t, J = 7.7 Hz, 1H, CH_{Ar}CH$_{Ar}$C$_{Ar}$-Br), 6.79 (d, J = 7.8 Hz, 1H, CH_{Ar}C$_{Ar}$-N), 2.42 (s, 3H, CH_3); **^{13}C{^{1}H}-NMR** (126 MHz, $CDCl_3$) δ 167.29 (C=N), 150.27 (C_{Ar}-N), 141.31 (C_{Ar}-CH$_3$), 136.32 (C_{Ar}C=N), 132.97 (CH$_{Ar}$C$_{Ar}$-Br), 129.27 (CH$_{Ar}$C$_{Ar}$-CH$_3$), 128.09 (CH$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 127.54 (CH$_{Ar}$C$_{Ar}$C=N), 124.44 (CH$_{Ar}$CH$_{Ar}$C$_{Ar}$-Br), 120.64 (CH$_{Ar}$C$_{Ar}$-N), 114.01 (C_{Ar}-Br), 21.58 (C$_{Ar}C$H$_3$), 18.16 (CH$_3$C=N); **GC-MS**: (EI, 70 eV, PhMeSi, 100.2/10.270/10): t_R = 17.8 min, m/z = 287 ([M]$^+$), 274, 155.

2-Methyl-_N_-(1-phenylethylidene)aniline (I18)[20]



By general method acetophenone (0.515 g, 4.29 mmol, 1.15 eq.) and *o*-toluidine (0.4 g, 3.74 mmol, 1.0 eq.) were dissolved in dry toluene (10 mL). Purification by Kugelrohr distillation (125 °C at 0.08 mbar) afforded 0.678 g (3.24 mmol, 76 %) of **I18** as yellow oil.
$C_{15}H_{15}N$ (209.29 g/mol):
b.p.: 125°C at 0.08 mbar; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.09 – 7.91 (m, 2H, CH_{Ar}CC=N), 7.45 (m, 3H, CH_{Ar}&CH_{Ar}CHCC=N), 7.19 (m, 2H, C$_{Ar}$(CH$_3$)CH_{Ar}&CH$_{Ar}$CH_{Ar}CH$_{Ar}$), 7.00 (t, J = 7.4 Hz, 1H, C$_{Ar}$(CH$_3$)CH$_{Ar}$CH_{Ar}), 6.65 (d, J = 7.7 Hz, 1H, CH_{Ar}C-N), 2.16 (s, 3H, C$_{Ar}$CH_3), 2.10 (s, 3H, C=NCH_3).

_N_-(1-phenylethylidene)-4-(trifluoromethyl)aniline (I22)[19]

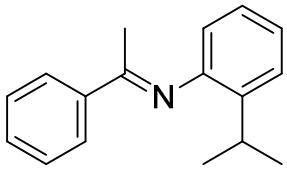


By general method acetophenone (0.373 g, 3.1 mmol, 1.0 eq.) and 4-(trifluoromethyl)aniline (0.5 g, 3.1 mmol, 1.0 eq.) were dissolved in dry toluene (10 mL). Purification by Kugelrohr distillation (150 °C at 0.2 mbar) afforded 0.056 g (0.21 mmol, 6 %) of **I22** as yellow-orange solid.
$C_{15}H_{12}F_3N$ (263.26 g/mol):
^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H, CH_{Ar}CC=N), 7.61 (d, J = 8.3 Hz, 2H, CH_{Ar}C(CF$_3$)), 7.54 – 7.42 (m, 3H, CH_{Ar}&CH_{Ar}CH$_{Ar}$C$_{Ar}$C=N), 6.88 (d, J = 8.2 Hz, 2H, CH_{Ar}C-N), 2.24 (s, 3H, CH_3C=N); **^{13}C{^{1}H}-NMR** (126 MHz, $CDCl_3$) δ 166.34 (s, C=N), 154.98 (s, C_{Ar}-N), 138.98 (s, C_{Ar}C=N), 131.06 (s, 1CH$_{Ar}$), 128.62 (s, 2CH$_{Ar}$), 127.40 (s, 2CH$_{Ar}$CC=N), 126.42 (d, J =

[19] T. Imamoto, N. Iwadate, K. Yoshida, *Org. Lett.* **2006**, *8*, 2289-2292

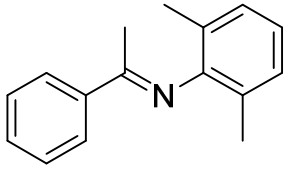
3.7 Hz, CH_{Ar}C(CF$_3$)), 125.66 (d, *J* = 13.5 Hz, *C*C(CF$_3$)), 124.45 (q, J = 225.2 Hz, *C*F$_3$), 119.54 (s, CH_{Ar}C-N), 17.75 (s, *C*H$_3$C=N); **GC-MS**: (Rtx-5MS, 100.2/10.270/10): t_R = 21.2 min, *m/z* = 263 ([M]$^+$); **m.p.**: 51-52 °C (Lit. 80-81°C)

2--Isopropyl-*N*-(1-phenylethylidene)aniline (I23)



By general method acetophenone (0.515 g, 4.29 mmol, 1.4 eq.) and 2-isopropylaniline (0.418 g, 3.1 mmol, 1.0 eq.) were dissolved in dry toluene (10 mL). Purification by Kugelrohr distillation (138 °C at 0.1 mbar) afforded 0.654 g (2.76 mmol, 89%) of **I23** as yellow oil.
$C_{17}H_{19}N$ (237.34 g/mol):
b.p.: 138 °C at 0.1 mbar; **^{1}H-NMR** (400 MHz, CDCl$_3$) δ: 8.08 – 7.96 (m, 2H CH_{Ar}CC=N), 7.56 – 7.42 (m, 3H, CH_{Ar}&CH_{Ar}CHCC=N), 7.32 (dd, *J* = 7.6, 1.2 Hz, 1H, C$_{Ar}$(CH(CH$_3$)$_2$)CH_{Ar}), 7.18 (td, *J* = 7.5, 1.5 Hz, 1H, C$_{Ar}$(CH(CH$_3$)$_2$)CH$_{Ar}$ CH_{Ar}), 7.10 (td, *J* = 7.5, 1.3 Hz, 1H, C$_{Ar}$(CH(CH$_3$)$_2$)CH$_{Ar}$ CH$_{Ar}$CH_{Ar}), 6.61 (dd, *J* = 7.7, 1.3 Hz, 1H, C$_{Ar}$-NCH_{Ar}), 3.09 – 2.92 (m, 1H, C$_{Ar}$C*H*(CH$_3$)$_2$), 2.23 (s, 3H, C=NC*H*$_3$), 1.19 (d, *J* = 6.9 Hz, 6H, C$_{Ar}$C*H*$_3$); **^{13}C{^{1}H}-NMR** (101 MHz, CDCl$_3$) δ 164.66 (*C*=N), 149.16 (*C*$_{Ar}$-N), 139.66 (*C*$_{Ar}$C=N), 138.27 (*C*$_{Ar}$CH(CH$_3$)$_2$), 130.50 (*C*H$_{Ar}$CH$_{Ar}$CH$_{Ar}$C$_{Ar}$C=N), 128.51 (*C*H$_{Ar}$CH$_{Ar}$C$_{Ar}$C=N), 127.28 (*C*H$_{Ar}$C$_{Ar}$C=N), 126.19 (*C*H$_{Ar}$CH$_{Ar}$CH$_{Ar}$C$_{Ar}$CH(CH$_3$)$_2$), 125.76 (*C*H$_{Ar}$CH$_{Ar}$C$_{Ar}$CH(CH$_3$)$_2$), 123.78 (*C*H$_{Ar}$C$_{Ar}$CH(CH$_3$)$_2$), 118.78 (*C*H$_{Ar}$C$_{Ar}$-N), 28.48 (C$_{Ar}$*C*H(CH$_3$)$_2$), 22.97 (C$_{Ar}$CH(*C*H$_3$)$_2$), 17.71 (*C*H$_3$C=N); **IR** (neat, ATR) ν/cm^{-1} = 3060 (w), 3021 (w), 2959 (m), 2925 (w), 2866 (w), 1645 (m), 1633 (s), 1594 (m), 1578 (m), 1480 (m), 1447 (m), 1365 (m), 1287 (m), 1220 (m), 1192 (w), 1084 (w), 1033 (w), 753 (m), 692 (m); **MS** (EI, 70 eV): 237.1 (16.5%), 222.1 (100%), 207.1 (15.1%); **HRMS**: calculated: 237.1512; found: 237.1515; **EA**: calc. C, 86.40; H, 7.68; N, 5.93; found: C, 85.90; H, 8.11; N, 5.9

2,6-Dimethyl-*N*-(1-phenylethylidene)aniline (I24)[20]



By general method acetophenone (0.98 g, 8.1 mmol, 1.0 eq.) and 2,6-dimethylaniline (0.98 g, 8.1 mmol, 1.0 eq.) were dissolved in dry toluene (10 mL). Purification by Kugelrohr distillation (137.5 °C at 0.1 mbar) afforded 0.4 g (1.8 mmol, 21 %) of **I24** as yellow-white solid.
$C_{16}H_{17}N$ (223.31 g/mol):
^{1}H-NMR (500 MHz, CDCl$_3$) δ 8.08 – 7.99 (m, 2H, CH_{Ar}CC=N), 7.54 – 7.42 (m, 3H, CH_{Ar}&CH_{Ar}CH$_{Ar}$C$_{Ar}$C=N), 7.06 (d, *J* = 7.5 Hz, 2H, CH_{Ar}C$_{Ar}$(CH$_3$)), 6.92 (t, *J* = 7.5 Hz, 1H, C$_{Ar}$(CH$_3$)CHArCH_{Ar}), 2.07 (s, 3H, C=NC*H*$_3$), 2.03 (s, 6H, C$_{Ar}$(*C*H$_3$)); **^{13}C{^{1}H}-NMR** (126 MHz, CDCl$_3$) δ 165.39 (*C*=N), 149.13 (*C*$_{Ar}$-N), 139.27 (*C*$_{Ar}$C=N), 130.60 (CH_{Ar}), 128.54 (CH_{Ar}), 127.96 (CH_{Ar}), 127.22 (CH_{Ar}), 125.88 (CH_{Ar}), 122.88 (CH_{Ar}), 18.11 (C$_{Ar}$(CH$_3$)), 17.63(*C*H$_3$C=N); **m.p.**: 61-62 °C (Lit. 59-60°C)

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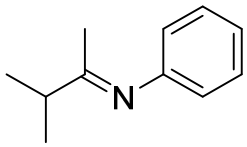
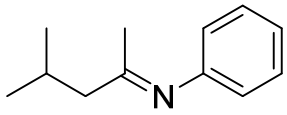
[20] C. R. V. Reddy, S. Urgaonkar, J. G. Verkade, *Org. Lett.* **2005**, *7*, 4427-4430

***N*-(3-methylbutan-2-ylidene)aniline (I25)**[14]



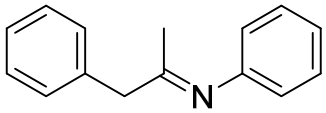
By general method 3-methyl-2-butanone (2.11 g, 24.5 mmol, 1.14 eq.) and aniline (2.0 g, 21.5 mmol, 1.0 eq.) were dissolved in dry benzene (6 mL). Purification by Kugelrohr distillation (75° C at 0.15 mbar) afforded 2.01 g (12.47 mmol, 58%) of **I25** as a colourless oil.
$C_{11}H_{15}N$ (161.24 g/mol):
E/Z mixture 6:1, *major*:**^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.05 – 6.98 (m, 1H), 6.70 – 6.64 (m, 2H), 2.62 (hept, J = 6.9 Hz, 1H), 1.73 (s, 3H), 1.20 (d, J = 6.9 Hz, 6H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 176.31, 151.88, 128.98, 122.95, 119.47, 119.32, 39.32, 20.02, 17.14.
minor: **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.18 – 7.12 (m, 2H), 6.75 (tt, J = 7.5, 1.1 Hz, 1H), 6.71 – 6.64 (m, 2H), 2.72 (dt, J = 13.7, 6.9 Hz, 1H), 2.07 (s, 3H), 1.02 (d, J = 6.9 Hz, 6H); **GC** (Machary-Nagel Optima-5-Amin (0.50 µm x 0.25 µm x 30 m), 60 kPa H_2, 100 °C/2 min, 10°C/min, 250 °C/7 min): t_R = 12.0 min; **GC-MS** (EI, 70 eV, PhMeSi, 80.2/10.270/10): t_R = 9.2 min, *m/z* = 161 ($[M]^+$), 146, 118 ($[M-(C(CH_3)_3)]^+$); **HRMS**: calculated: 161.1199; found: 161.1200

***N*-(4-methylpentan-2-ylidene)aniline (I26)**



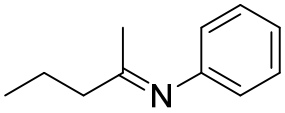
By general method 4-Methyl-2-pentanone (3.0 g, 30 mmol, 1.0 eq.) and aniline (2.79 g, 30 mmol, 1.0 eq.) were dissolved in dry toluene (10 mL). Purification by Kugelrohr distillation (95° C at 0.1 mbar) afforded 1.14 g (6.5 mmol, 21%) of **I26** as a colourless oil.
$C_{12}H_{17}N$ (175.27 g/mol):
E/Z 3.2:1, *major*: **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 7.30 (t, J = 7.8 Hz, 2H), 7.05 (t, J = 7.3 Hz, 1H), 6.71 (dd, J = 8.3, 1.0 Hz, 2H), 2.31 (d, J = 7.3 Hz, 2H), 2.20 – 2.11 (sept, J = 7.0 Hz, 1H), 1.78 (s, 3H), 1.03 (d, J = 6.6 Hz, 6H); **^{13}C{^{1}H}-NMR** (101 MHz, CDCl3) δ 171.75 (*C*=N), 151.73 (C_{Ar}-N), 128.99 ($CH_{Ar}CH_{Ar}C_{Ar}$-N), 123.08 ($CH_{Ar}CH_{Ar}CH_{Ar}C_{Ar}$-N), 119.64 ($CH_{Ar}C_{Ar}$-N), 50.85 ($CH_2CH(CH_3)_2$), 26.39 ($CH(CH_3)_2$), 22.66 ($CH(CH_3)_2$), 19.90 ($CH_3C$=N); minor: **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 7.28 (m, 2H, $CH_{Ar}CH_{Ar}C_{Ar}$-N), 7.03 (m, 1H, $CH_{Ar}CH_{Ar}CH_{Ar}C_{Ar}$-N), 6.68 (dd, *J* = 8.3, 1.0 Hz, 2H, $CH_{Ar}C_{Ar}$-N), 2.17 (s, 3H, CH_3C=N), 2.08 (d, *J* = 7.2 Hz, 2H, $CH_2C(CH_3)C$=N), 2.00 (sept, *J* = 6.5 Hz, 1H, $(CH_3)_2CHCH_2$), 0.84 (d, *J* = 6.5 Hz, 6H, $(CH_3)_2CHCH_2$); **^{13}C{^{1}H}-NMR** (101 MHz, CDCl3) δ 171.99 (*C*=N), 151.13 (C_{Ar}-N), 128.88 ($CH_{Ar}CH_{Ar}C_{Ar}$-N), 122.86 ($CH_{Ar}CH_{Ar}CH_{Ar}C_{Ar}$-N), 119.75 ($CH_{Ar}C_{Ar}$-N), 43.07 ($CH_2CH(CH_3)_2$), 26.37 ($CH(CH_3)_2$), 26.16 ($CH_3C$=N), 22.64 ($CH(CH_3)_2$); **IR** (neat, ATR) ν/cm^{-1} = 3075 (w), 3028 (w), 2955 (m), 2869 (w), 1656 (s), 1593 (s), 1483 (m), 1464 (w), 1366 (m), 1252 (w), 1188 (w), 1168 (w), 1103 (w), 1070 (w), 900 (w), 794 (m), 744 (s), 696 (s); **GC** (Machary-Nagel Optima-5-Amin (0.50 µm x 0.25 µm x 30 m), 60 kPa H_2, 100 °C/2 min, 10 °C/min, 250 °C/7 min): t_R = 13.6 min; **GC-MS**: (Rtx-5MS, 100.2/10.270/10): t_R = 8.8 min, *m/z* = 175 ($[M]^+$), 160, 132, 118, 104, 92; **EA**: calc. C, 82.23; H, 9.78; N, 7.99; found: C, 81.84; H, 9.60; N, 8.32

***N*-(1-phenylpropan-2-ylidene)aniline (I27)**[21]



By general method Phenylacetone (2.7 g, 20 mmol, 1.0 eq.) and aniline (2 g, 22 mmol, 1.1 eq.) were dissolved in dry benzene (7 mL). Purification by Kugelrohr distillation (125° C at 0.1 mbar) afforded 1.58 g (7.55 mmol, 38%) of **I27** as a yellow-orange clear oil.
$C_{15}H_{15}N$ (209.29 g/mol):
E/Z mixture 3:1, major: **^{1}H-NMR** (400 MHz, CD_2Cl_2) δ 7.42 – 7.28 (m, 7H), 7.10 – 7.04 (m, 1H), 6.73 (d, J = 7.7 Hz, 2H), 3.74 (s, 2H), 1.74 (s, 3H); **^{13}C{^{1}H}-NMR** (126 MHz, CD_2Cl_2) δ 170.63, 151.93, 137.74, 129.63, 129.23, 128.93, 127.02, 123.34, 119.70, 48.73, 19.02; *minor*: **^{1}H-NMR** (400 MHz, CD_2Cl_2) δ 7.14 (d, J = 7.5 Hz, 1H), 6.81 (d, J = 7.7 Hz, 1H), 3.51 (s, 1H), 2.07 (s, 2H). *other signals overlayed by major isomer*; **^{13}C{^{1}H}-NMR** (126 MHz, CD_2Cl_2) δ 169.58, 151.60, 137.27, 129.41, 129.38, 129.02, 126.87, 119.82, 115.15, 40.65, 25.99; **GC** (Machary-Nagel Optima-5-Amin (0.50 µm x 0.25 µm x 30 m), 60 kPa H_2, 100 °C/2 min, 10°C/min, 250 °C/10 min): t_R = 20.2 min; **GC-MS** (Rtx-5MS, 50.2/30.250/5): t_R = 8.9 min, *m/z* = 209 ($[M]^+$), 193, 167, 118, 91, 77.

***N*-(pentan-2-ylidene)aniline (I28):**



By general method 2-pentanone (1.62 g, 18.8 mmol, 1.0 eq.) and aniline (2 g, 21.5 mmol, 1.14 eq.) were dissolved in dry toluene (10 mL). Purification by Kugelrohr distillation (75° C at 0.1 mbar) afforded 1.16 g (7.2 mmol, 38%) of **I28** as a colourless oil.
$C_{11}H_{15}N$ (161.24 g/mol):
3:1 E/Z mixture, *major*: **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.30 (m, 2H, CH_{Ar}CH_{Ar}C$_{Ar}$-N), 7.03 (t, *J* = 7.4 Hz, 1H, CH_{Ar}CH_{Ar}CH_{Ar}C$_{Ar}$-N), 6.68 (d, *J* = 7.3, 2H, CH_{Ar}C$_{Ar}$-N), 2.41 (t, *J* = 7.5 Hz, 2H, CH_2C=N), 1.77 (s, 3H, CH_3C=N), 1.70 (tq (m), 2H, CH_2CH_2C=N), 1.02 (t, *J* = 7.4 Hz, 3H, CH_3CH_2CH_2C=N); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 172.12 (*C*=N), 151.75 (*C*$_{Ar}$-N), 128.96 (*C*H_{Ar}CH_{Ar}C$_{Ar}$-N), 123.05 (*C*H_{Ar}CH_{Ar}CH_{Ar}C$_{Ar}$-N), 119.64 (*C*H_{Ar}C$_{Ar}$-N), 43.74 (*C*H_2C=N), 19.83 (*C*H_3C=N), 19.52 (*C*H_2CH_2C=N), 13.91 (*C*H_3CH_2CH_2C=N); *minor*: **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.30 (m, 2H, CH_{Ar}CH_{Ar}C$_{Ar}$-N), 7.03 (t, *J* = 7.4 Hz, 1H, CH_{Ar}CH_{Ar}CH_{Ar}C$_{Ar}$-N), 6.66 (d, *J* = 7.2 Hz, 2H, CH_{Ar}C$_{Ar}$-N), 2.15 (s, 3H, *C*H$_3$C=N), 2.11 (dd, *J* = 8.7, 6.9 Hz, 2H, CH_2C=N), 1.52 (qt (m), 2H, *C*H$_2$CH_2C=N), 0.83 (t, *J* = 7.4 Hz, 3H, *C*H$_3$CH_2CH_2C=N); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 173.64 (*C*=N), 151.21 (*C*$_{Ar}$-N), 129.39 (*C*H_{Ar}CH_{Ar}C$_{Ar}$-N), 122.94 (*C*H_{Ar}CH_{Ar}CH_{Ar}C$_{Ar}$-N), 115.20 (*C*H_{Ar}C$_{Ar}$-N), 36.12 (*C*H_2C=N), 25.97 (*C*H_3C=N), 20.39 (*C*H_2CH_2C=N), 14.14 (*C*H_3CH_2CH_2C=N); **IR** (neat, ATR) ν/cm^{-1} = 3075 (w), 3060 (w), 3028 (w), 3018 (w), 2959 (m), 2931 (w), 2872 (w), 1658 (s), 1594 (s), 1483 (m), 1366 (m), 1252 (m), 1225 (w), 1186 (m), 1168 (w), 1093 (w), 1071 (m), 900 (w), 797 (m), 746 (m), 698 (s); **GC** (Machary-Nagel Optima-5-Amin (0.50 µm x 0.25 µm x 30 m), 60 kPa H_2, 100 °C/2 min, 10 °C/min, 250 °C/7 min): t_R = 12.7 min; **GC-MS** (EI, 70 eV, PhMeSi, 100.2/10.270/10): t_R = 7.1 min, *m/z* = 161 ($[M]^+$); **EA**: calc. C, 81.94; H, 9.38; N, 8.69; found: C, 81.72; H, 9.33; N, 8.65.

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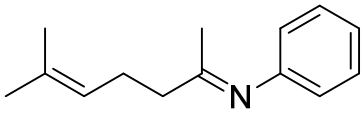
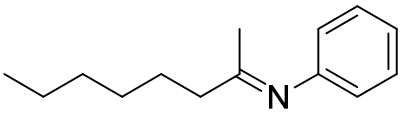
[21] L. L. Anderson, J. Arnold, R. G. Bergman, *Org. Lett.* **2004**, *6*, 2519-2522

N-(6-methylhept-5-en-2-ylidene)aniline (I29)

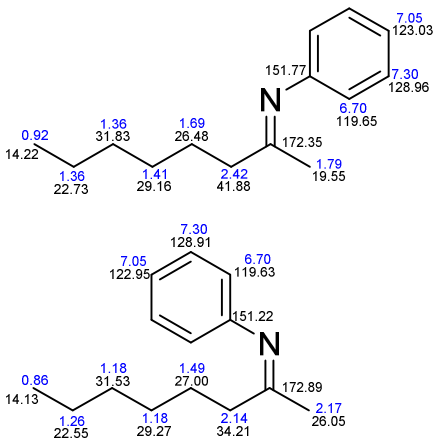


By general method 6-methylhept-5-en-2-one (1.71 g, 13.55 mmol, 1.0 eq.) and aniline (1.26 g, 13.55 mmol, 1.0 eq.) were dissolved in dry toluene (10 mL). Purification by Kugelrohr distillation (112.5° C at 0.1 mbar) afforded 600 mg (3.0 mmol, 22%) of **I29** as a yellow clear oil.
$C_{14}H_{19}N$ (201.31 g/mol):
E/Z mixture 3:1, *major*: **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.05 (tt, J = 7.5, 1.2 Hz, 1H), 6.70 (dd, J = 8.4, 1.1 Hz, 2H), 5.22 (dddt, J = 6.8, 5.3, 2.8, 1.4 Hz, 1H), 2.48 – 2.43 (m, 2H), 2.42 – 2.37 (m, 2H), 1.79 (s, 3H), 1.74 (d, J = 1.2 Hz, 3H), 1.68 (d, J = 1.2 Hz, 3H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 171.71, 151.63, 132.37, 128.86, 123.28, 122.95, 119.51, 41.59, 25.77, 25.04, 19.66, 17.79; *minor*: **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 7.06 – 7.02 (m, 1H), 6.72 – 6.68 (m, 2H), 4.97 (dddt, J = 7.0, 5.5, 3.0, 1.5 Hz, 1H), 2.47 – 2.45 (m, 2H), 2.39 – 2.36 (m, 2H), 2.18 (s, 3H), 1.67 (d, J = 1.1 Hz, 3H), 1.53 (d, J = 1.2 Hz, 3H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 172.26, 151.09, 132.91, 128.79, 122.85, 122.66, 119.51, 34.02, 26.04, 25.64, 25.43, 17.56; **GC** (Machary-Nagel Optima-5-Amin (0.50 µm x 0.25 µm x 30 m), 60 kPa H_2, 100 °C/2 min, 10°C/min, 250 °C/10 min): t_R = 17.2 min; **GC-MS** (Rtx-5MS, 50.2/30.250/5): t_R = 8.1 min, *m/z* = 201 ($[M]^+$), 186, 158, 144, 132, 118, 109, 93, 77; **IR** (neat, ATR) ν/cm^{-1} = 3072 (w), 3057 (w), 3022 (w), 2966 (m), 2914 (m), 2854 (m), 1663 (s), 1593 (m), 1483 (m), 1443 (w), 1367 (w), 1246 (w), 1169 (w); **EA**: calculated: C, 83.53; H, 9.51; N, 6.96, found: C, 83.45; H, 9.31; N, 6.87.

N-(octan-2-ylidene)aniline (I30)[22]



By general method 2-Octanone (1.64 g, 12.8 mmol, 1.0 eq.) and aniline (1.19 g, 12.8 mmol, 1.0 eq.) were dissolved in dry toluene (10 mL). Purification by Kugelrohr distillation (125° C at 0.1 mbar) afforded 847 mg (4.17 mmol, 32%) of **I30** as a slighty yellowish clear oil.
$C_{14}H_{21}N$ (203.32 g/mol):
E/Z mixture 3:1, *major*: **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.30 (m, 2H), 7.05 (m, 1H), 6.70 (m, 2H), 2.42 (m, 2H), 1.79 (s, 3H), 1.69 (m, 2H), 1.41 (m, 2H), 1.36 (m, 4H), 0.92 (m, 3H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 172.35, 151.77, 128.96, 123.03, 119.65, 41.88, 31.83, 29.16, 26.48, 22.73, 19.55, 14.22; *minor*: **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.30 (m, 2H), 7.05 (m, 1H), 6.70 (m, 2H), 2.17 (s, 3H), 2.14 (m, 2H), 1.49 (m, 2H), 1.18 (m, 4H), 1.26 (m, 2H), 0.86 (m, 3H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 172.89, 151.22, 128.91, 122.95, 119.63, 34.21, 31.52, 29.27, 27.00, 26.05, 22.55, 14.13; **GC** (Machary-Nagel Optima-5-Amin (0.50 µm x 0.25 µm x 30 m), 60 kPa H_2, 100 °C/2 min, 10°C/min, 250 °C/10 min): t_R = 17.3 min; **GC-MS** (Rtx-5MS, 100.2/10.270/10): t_R = 13.3 min, *m/z* = 203 ($[M]^+$), 188, 174, 160, 146, 132, 118, 92, 77.



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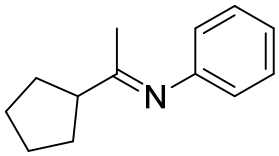
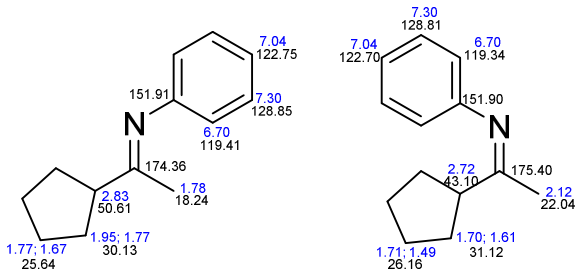
[22] C. G. Hartung, A. Tillack, H. Trauthwein, M. Beller, *J. Org. Chem.* **2001**, *66*, 6339-6343

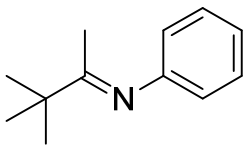
N-(1-cyclopentylethylidene)aniline (I31)



By general method **8** (0.34 g, 3.125 mmol, 1.0 eq.) and aniline (0.32 g, 3.43 mmol, 1.1 eq.) were dissolved in dry toluene (10 mL). Purification by Kugelrohr distillation (100° C at 0.15 mbar) afforded 0.25 g (1.33 mmol, 42%) of **I31** as a colourless oil.
$C_{13}H_{17}N$ (187.28 g/mol):
6:1 E/Z mixture, *major*: **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 7.27 (m, 2H, C*H*$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 7.02 (d, *J* = 7.4 Hz, 1H, C*H*$_{Ar}$CH$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 6.67 (dd, *J* = 8.3, 1.1 Hz, 2H, C*H*$_{Ar}$C$_{Ar}$-N), 2.81 (pent, *J* = 8.1 Hz, 1H, C*H*C=N), 1.95 (m, 2H, C*H*HCHC=N), 1.77 (m, 4H, C*H*HC*H*HCHC=N), 1.76 (s, 3H, C*H*$_3$), 1.67 (m, 2H, C*H*HCHHCHC=N); **^{13}C{^{1}H}-NMR** (126 MHz, $CDCl_3$) δ 174.36 (*C*=N), 151.90 (*C*$_{Ar}$-N), 128.85 (*C*H$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 122.75 (*C*H$_{Ar}$CH$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 119.41 (*C*H$_{Ar}$C$_{Ar}$-N), 50.61 (*C*HC=N), 30.13 (*C*H$_2$CHC=N), 25.64 (*C*H$_2$CH$_2$CHC=N), 18.24 (*C*H$_3$); *minor*: **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 7.27 (m, 2H, C*H*$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 7.02 (d, *J* = 7.4 Hz, 1H, C*H*$_{Ar}$CH$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 6.67 (dd, *J* = 8.3, 1.1 Hz, 2H, C*H*$_{Ar}$C$_{Ar}$-N), 2.70 (pent, *J* = 8.0 Hz, 1H, C*H*C=N), 2.10 (s, 3H, *C*H$_3$), 1.71 (m, 2H, C*H*HCHHCHC=N), 1.70 (m, 2H, C*H*HCHC=N), 1.61 (m, 2H, C*H*HCHC=N), 1.49 (m, 2H, C*H*HCHHCHC=N); **^{13}C{^{1}H}-NMR** (126 MHz, $CDCl_3$) δ 175.40 (*C*=N), 151.90 (*C*$_{Ar}$-N), 128.81 (*C*H$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 122.71 (*C*H$_{Ar}$CH$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 119.34 (*C*H$_{Ar}$C$_{Ar}$-N), 43.12 (*C*HC=N), 31.12 (*C*H$_2$CHC=N), 26.16 (*C*H$_2$CH$_2$CHC=N), 22.04 (*C*H$_3$); **GC** (Machary-Nagel Optima-5-Amin (0.50 µm x 0.25 µm x 30 m), 60 kPa H_2, 100 °C/2 min, 10 °C/min, 250 °C/7 min): t_R = 16.8 min; **GC-MS**: (Rtx-5MS, 100.2/10.270/10): t_R = 12.7 min, *m/z* = 187 ([M]$^+$), 146, 118; **IR** (neat, ATR) ν/cm^{-1} = 3060 (w), 3018 (w), 2950 (m), 2866 (m), 1567 (s), 1594 (s), 1578 (w), 1483 (m), 1447 (w), 1364 (m), 1192 (m), 1166 (m), 1070 (w), 1025 (w), 899 (w), 798 (w), 697 (s); **EA**: calc. C, 83.37; H, 9.15; N, 7.48; found: C, 82.26; H, 8.96; N, 7.88.



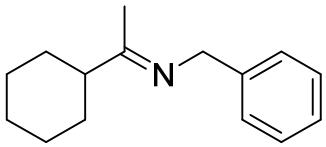
N-(3,3-dimethylbutan-2-ylidene)aniline (I32)[23]



By general method Pinacolone (2.15 g, 21.4 mmol, 1.0 eq.) and aniline (2.0 g, 21.5 mmol, 1.0 eq.) were dissolved in dry benzene (6 mL). Purification by Kugelrohr distillation (100-150° C at 0.07 mbar) afforded 1.5 g (8.56 mmol, 40%) of **I32** as a colourless oil.
$C_{12}H_{17}N$ (175.27 g/mol):
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.27 (m, 2H, C*H*$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 7.00 (m, 1H, C*H*$_{Ar}$CH$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 6.63 (m, 2H, C*H*$_{Ar}$C$_{Ar}$-N), 1.74 (s, 3H, C*H*$_3$), 1.22 (s, 9H, C(C*H*$_3$)$_3$); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 177.60 (*C*=N), 152.34 (*C*$_{Ar}$-N), 129.00 (*C*H$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 122.69 (*C*H$_{Ar}$CH$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 119.15 (*C*H$_{Ar}$C$_{Ar}$-N), 40.35 (*C*(CH$_3$)$_3$), 27.95 (*C*H$_3$C=N), 15.38 (C(*C*H$_3$)$_3$); **GC** (Machary-Nagel Optima-5-Amin (0.50 µm x 0.25 µm x 30 m), 60 kPa H_2, 100 °C/2 min, 10°C/min, 250 °C/10 min): t_R = 12.7 min; **GC-MS** (EI, 70 eV, PhMeSi, 100.2/10.270/10): t_R = 7.9 min, *m/z* = 175 ([M]$^+$), 118; **HRMS**: calculated: 175.1356; found: 175.1357.

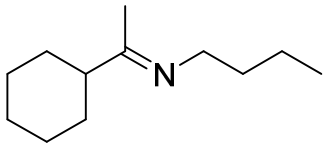
[23] A. H. Vetter, A. Berkessel, *Synthesis* **1995**, *4*, 419-423

N-(1-cyclohexylethylidene)-1-phenylmethanamine (I33)[24]

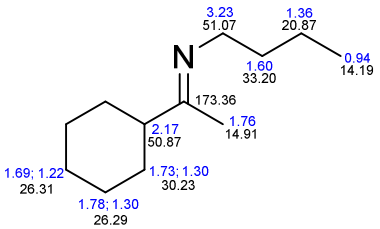


By general method cyclohexylmethylketone (1.09 g, 8.6 mmol, 1.0 eq.) and benzylamine (1.02 g, 9.5 mmol, 1.1 eq.) were dissolved in dry toluene (10 mL). Purification by Kugelrohr distillation (125° C at 0.1 mbar) afforded 0.84 g (3.9 mmol, 45%) of **I33** as a colourless clear oil.
$C_{15}H_{21}N$ (215.33 g/mol):
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.31 (m, 5H, CH_{Ar}), 4.49 (s, 2H, CH_2), 2.25 (tt, J = 11.6, 3.3 Hz, 1H, C*H*C=N), 1.84 (s, 3H, CH_3), 1.77 (m, 4H, CH_{Aliph}), 1.32 (m, 6H, CH_{Aliph}); **GC** (Machary-Nagel Optima-5-Amin (0.50 µm x 0.25 µm x 30 m), 60 kPa H_2, 100 °C/2 min, 10°C/min, 250 °C/7 min): t_R = 20.6 min (I34); **GC-MS** (Rtx-5MS, 100.2/10.270/10): t_R = 16.8 min, m/z = 215 ([M]$^+$), 200, 186, 174, 160, 147, 124, 91.

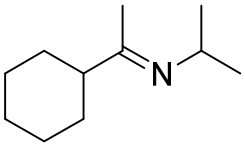
N-(1-cyclohexylethylidene)butan-1-amine (I34)



By general method cyclohexylmethylketone (0.92 g, 7.27 mmol, 1.0 eq.) and *n*-butylamine (1.6 g, 21.8 mmol, 3.0 eq.) were dissolved in dry toluene (10 mL). Purification by Kugelrohr distillation (87° C at 0.15 mbar) afforded 0.75 g (4.11 mmol, 56%) of **I34** as a colourless clear oil.
$C_{12}H_{23}N$ (181.32 g/mol):
^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.23 (t, *J* = 7.3 Hz, 2H), 2.17 (ddt, *J* = 11.3, 6.6, 3.3 Hz, 1H), 1.83 – 1.73 (m, 4H), 1.76 (s, 3H), 1.72 – 1.66 (m, 1H), 1.60 (p, J = 7.4 Hz, 2H), 1.39 – 1.34 (m, 2H), 1.30 (ddd, J = 12.2, 8.5, 3.0 Hz, 4H), 1.19 (dddd, J = 15.9, 12.3, 7.4, 3.4 Hz, 1H), 0.94 (t, J = 7.3 Hz, 3H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 173.36, 51.07, 50.87, 33.20, 30.32, 26.31, 26.29, 20.87, 14.91, 14.19; **GC** (Machary-Nagel Optima-5-Amin (0.50 µm x 0.25 µm x 30 m), 60 kPa H_2, 100 °C/2 min, 10°C/min, 250 °C/10 min): t_R = 13.8 min (I35); **GC-MS** (Rtx-5MS, 50.2/30.250/5): t_R = 7.0 min, m/z = 181 ([M]$^+$), 166, 152, 126, 98; **IR** (neat, ATR) ν/cm^{-1} = 2955 (s), 2924 (s), 2851 (s), 1663 (m), 1643 (w), 1447 (m), 1369 (w), 1248 (w), 1198 (w); **EA**: calculated: C, 79.49; H, 12.79; N, 7.72, found: C, 79.61; H, 12.63; N, 7.76.



N-(1-cyclohexylethylidene)propan-2-amine (I35)

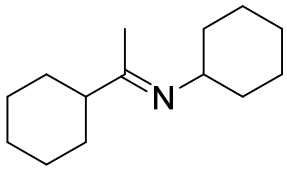


By general method cyclohexylmethylketone (0.92 g, 7.27 mmol, 1.0 eq.) and isoproylamine (2.15 g, 36.33 mmol, 5.0 eq.) were dissolved in dry toluene (10 mL) and stirred at room temperature for four days. Purification by Kugelrohr distillation (100° C at 0.15 mbar) afforded 0.52 g (3.1 mmol, 43%) of **I35** as a colourless clear oil.
$C_{11}H_{21}N$ (167.29 g/mol):
E/Z mixture 16:1, *major*: **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 3.60 (hept, J = 6.3 Hz, 1H), 2.16 (td, J = 9.6, 8.9, 4.8 Hz, 1H), 1.75 (s, 3H), 1.81 – 1.65 (m, 6H), 1.36 – 1.25 (m, 4H), 1.10 (s, 3H), 1.09 (s,

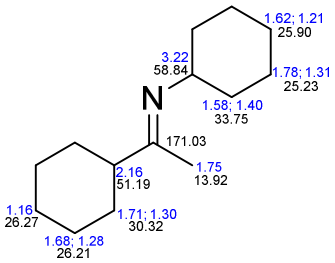
[24] F. Chen, Z. Ding, Y. He, J. Qin, T. Wang, Q.-H. Fan, Tetrahedron **2012**, 68, 5248-5257

3H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 170.70, 51.16, 49.81, 30.25, 26.26, 26.20, 23.63, 13.78; **GC** (Machary-Nagel Optima-5-Amin (0.50 µm x 0.25 µm x 30 m), 60 kPa H_2, 100 °C/2 min, 10°C/min, 250 °C/10 min): t_R = 10.8 min; **GC-MS** (Rtx-5MS, 50.2/30.250/5): t_R = 6.0 min, *m/z* = 167 ([M]$^+$), 152, 126, 112, 99, 84; **IR** (neat, ATR) ν/cm^{-1} = 2964 (m), 1924 (s), 1853 (m), 1663 (m), 1643 (m), 1448 (m), 1373 (w), 1364 (w), 1246 (w), 1202 (w), 1159 (w), 808 (w); **EA**: calculated: C, 78.97; H, 12.65; N, 8.37, found: C, 78.44; H, 12.50; N, 8.34.

***N*-(1-cyclohexylethylidene)cyclohexanamine (I36)**



By general method cyclohexylmethylketone (1.834 g, 14.53 mmol, 1.0 eq.) and cyclohexylamine (1.439 g, 14.53 mmol, 1.0 eq.) were dissolved in dry toluene (10 mL). Purification by Kugelrohr distillation (100° C at 0.1 mbar) afforded 1.153 g (5.56 mmol, 38%) of **I36** as a colourless clear oil. $C_{14}H_{25N}$ (207.35 g/mol):



^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.22 (m, 1H, C*H*C-N), 2.19 – 2.12 (m, 1H, C*H*C=N), 1.82 – 1.61 (m, 11H), 1.61 – 1.54 (m, 2H), 1.45 – 1.13 (m, 10H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 171.13, 58.93, 51.29, 33.85, 30.41, 26.36, 26.30, 25.99, 25.33, 14.01; **GC** (Machary-Nagel Optima-5-Amin (0.50 µm x 0.25 µm x 30 m), 60 kPa H_2, 100 °C/2 min, 10°C/min, 250 °C/10 min): t_R = 17.4 min; **GC-MS** (Rtx-5MS, 100.2/10.270/10): t_R = 13.2 min, *m/z* = 207 ([M]$^+$), 192, 178, 166, 152, 126, 124, 83; **IR** (neat, ATR) ν/cm^{-1} = 2922 (s), 2851 (s), 1657 (m), 1447 (m), 1369 (w), 1358 (w), 1240 (w), 1196 (w), 1028 (w), 889 (w), 843 (w); **EA**: calculated: C, 81.09; H, 12.15; N, 6.75, found: C, 80.69; H, 12.04; N, 6.94.

Hydrogenations

All hydrogenation reactions were carried out in anhydrous crown-cap dichloromethane, which was used without further purification.

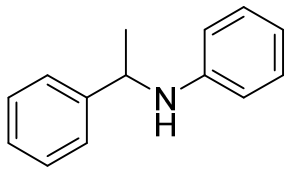
Procedure for the hydrogenation at elevated pressure:
Imine (0.1 mmol), catalyst (2 µmol), addtive (2 µmol), and a stir bar were added to an oven-dried glass vial that had been placed in an autoclave (60 mL) and purged with argon for 5 min. Anhydrous CH_2Cl_2 (1 mL) was added by syringe under a stream of argon and the autoclave was closed. For reactions at low temperature the autoclave was immersed in a cooling bath for 60 min before starting the reaction. The autoclave was pressurized with hydrogen gas, hydrogen was released and the autoclave pressurized again. It was then placed on a stirring plate for the time indicated. After pressure release the solvent was evaporated under a stream of nitrogen.

Procedure for the hydrogenation at atmospheric pressure:
Same procedure as above, but the vials were placed in a flask equipped with 24/40 joint which was closed with a rubber septum. The flask was evacuated and purged with hydrogen gas via H_2-filled balloon (Dräger 1.5 L) three times. The solvent (1 mL) was added via syringe and the flask placed on a stirring plate for the time indicated.

The residue was suspended in pentane/ether (5:1) and filtered through a short elution plug (cotton bottom, 40x5 mm silica gel). The crude filtrate was analysed by GC for conversion before being purified by flash chromatography (SiO_2, pentane/ether 20:1, 15x2 cm) and analysed by HPLC on a chiral stationary phase for determination of the enantiomeric excess.

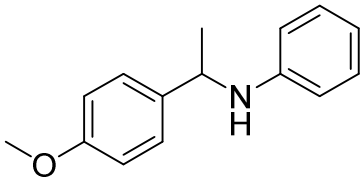
Derivatization for the determination of enantiomeric excess:
A35 was dissolved in CH_2Cl_2 (1 mL) before acetic anhydride and triethylamine (4 drops each) were added. The solution was stirred for 30 minutes at room temperature and solvents evaporated by a stream of nitrogen. The residue was suspended in pentane/ether (5:1) and filtered through a CHROMAPHIL HPLC filter prior to GC analysis.
A33 and **A36** was dissolved in CH_2Cl_2 (1 mL) before 1-naphtoyl chloride and triethylamine (4 drops each) were added. The solution was stirred for 30 minutes at room temperature. The product was purified by flash chromatography prior to HPLC analysis.

***N*-(1-phenylethyl)aniline (A1)[11]**



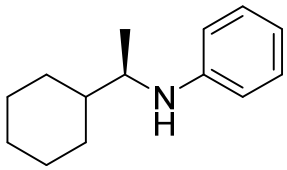
$C_{14}H_{15}N$ (197.28 g/mol):
GC (Machary-Nagel Optima-5-Amin (0.50 µm x 0.25 µm x 30 m), 60 kPa He, 150 °C min, 7°C/min, 250 °C/10 min): t_R = 12.8 min; **HPLC** (Daicel Chiracel OD-H (2.6 x 250 mm), *n*-heptane/iso-propanol 99:1, 0.5 mL/min, 20 °C, 210 nm): t_R = 24.6 min ((*S*)-A1), t_R = 33.0 min ((*R*)-A1).

_N_-(1-(4-methoxyphenyl)ethyl)aniline (A2)[11]



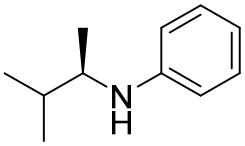
$C_{15}H_{17}NO$ (227.31 g/mol):
GC (Machary-Nagel Optima-5-Amin (0.50 µm x 0.25 µm x 30 m), 60 kPa He, 150 °C min, 7°C/min, 250 °C/10 min): t_R = 19.6 min.

(_R_)-(-)-_N_-(1-cyclohexylethyl)aniline (A3)[23]



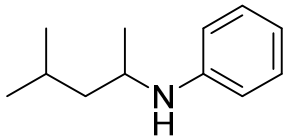
$C_{14}H_{21}N$ (203.32 g/mol):
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.10 (m, 2H), 6.64 (t, *J* = 7.3 Hz, 1H), 6.57 (d, *J* = 7.7 Hz, 2H), 3.48 (s, 1H), 3.39 – 3.25 (m, 1H), 1.88 – 1.61 (m, 5H), 1.51 – 1.39 (m, 1H), 1.32 – 1.15 (m, 3H), 1.12 (d, *J* = 6.5 Hz, 3H), 1.10 – 0.99 (m, 2H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 148.10, 129.40, 116.63, 113.07, 53.10, 43.10, 29.93, 28.54, 26.79, 26.63, 26.49, 17.55; **GC** (Machary-Nagel Optima-5-Amin (0.50 µm x 0.25 µm x 30 m), 60 kPa H_2, 100 °C/2 min, 10°C/min, 250 °C/10 min): t_R = 19.6 min; **GC-MS**: (Rtx-5MS, 100.2/10.270/10): t_R = 15.7 min, *m/z* = 203 ($[M]^+$), 120; **HPLC** (Daicel Chiracel OJ-H, *n*-heptane/iso-propanol 99:1, 0.5 mL/min, 25 °C, 247/297 nm): t_R = 21.0 min ((*R*)-(-)-A3), t_R = 24.0 min ((*S*)-(+)-A3); **Optical Rotation**: $[\alpha]_D^{20}$ = - 19.0 (c 1.0 in $CHCl_3$, 0.75% EtOH).

(_R_)-(-)-_N_-(3-methylbutan-2-yl)aniline (A25)[15]



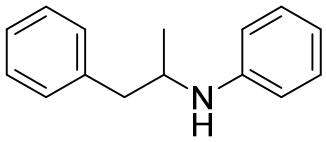
$C_{11}H_{17}N$ (163.26 g/mol):
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.16 (t, *J* = 7.9 Hz, 2H), 6.65 (t, *J* = 7.3 Hz, 1H), 6.58 (d, *J* = 7.8 Hz, 2H), 3.48 (s, 1H), 3.42 – 3.27 (m, 1H), 1.93 – 1.77 (m, 1H), 1.10 (d, *J* = 6.4 Hz, 3H), 0.98 (d, *J* = 6.9 Hz, 3H), 0.92 (d, *J* = 6.8 Hz, 3H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 147.98, 129.41, 116.75, 113.18, 53.55, 32.35, 19.34, 17.65, 16.71; **GC-MS** (EI, 70 eV, PhMeSi, 80.2/10.270/10): tR = 10.4 min, *m/z* = 163 ($[M]^+$), 120 ($[M-(C(CH_3)_3)]^+$); **GC** (Machary-Nagel Optima-5-Amin (0.50 µm x 0.25 µm x 30 m), 60 kPa H_2, 100 °C/2 min, 10°C/min, 250 °C/7 min): t_R = 13.3 min; **HPLC** (Daicel Chiracel OJ, *n*-heptane/iso-propanol 100:0, 0.5 mL/min, 25 °C, 247/297 nm): t_R = 31.2 min ((*R*)-(-)-A25), t_R = 36.1 min ((*S*)-(+)-A25); **Optical Rotation**: $[\alpha]_D^{20}$ = - 49.4 (c 1.0 in $CHCl_3$, 0.75% EtOH).

(-)-*N*-(4-methylpentan-2-yl)aniline (A26)[25]



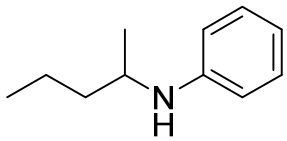
$C_{12}H_{19}N$ (177.29 g/mol):
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.16 (t, *J* = 7.9 Hz, 2H), 6.66 (t, *J* = 7.3 Hz, 1H), 6.58 (d, *J* = 7.8 Hz, 2H), 3.60 – 3.47 (m, 1H), 3.36 (s, 1H), 1.84 – 1.68 (m, 1H), 1.48 (dt, *J* = 14.0, 7.1 Hz, 1H), 1.26 (dt, *J* = 13.7, 6.9 Hz, 1H), 1.16 (d, *J* = 6.2 Hz, 3H), 0.95 (d, *J* = 6.6 Hz, 3H), 0.91 (d, *J* = 6.6 Hz, 3H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 147.85, 129.42, 116.86, 113.15, 47.07, 46.58, 25.23, 23.10, 22.72, 21.21; **GC-MS**: (Rtx-5MS, 100.2/10.270/10): t_R = 9.8 min, *m/z* = 177 ($[M]^+$), 162, 120; **GC** (Machary-Nagel Optima-5-Amin (0.50 µm x 0.25 µm x 30 m), 60 kPa H_2, 100 °C/2 min, 10°C/min, 250 °C/7 min): t_R = 14.4 min; **HPLC** (Daicel Chiracel OJ-H, *n*-heptane/iso-propanol 99:1, 0.5 mL/min, 25 °C, 247/297 nm): t_R = 19.6 min ((+)-A26), t_R = 22.5 min ((-)-A26); **Optical Rotation**: $[\alpha]_D^{20}$ = - 24.6 (c 1.10 in $CHCl_3$ 0.75% EtOH), 69% ee.

***N*-(1-phenylpropan-2-yl)aniline (A27)**[23]



$C_{15}H_{17}N$ (211.30 g/mol):
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.30 (m, 2H, C*H*$_{Ar}$), 7.20 (m, 5H, C*H*$_{Ar}$), 6.69 (t, *J* = 7.3 Hz, 1H, C*H*$_{Ar}$CH$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 6.63 (dd, *J* = 8.5, 0.9 Hz, 2H, C*H*$_{Ar}$C$_{Ar}$-N)), 3.77 (qdd (m), 1H, C*H*NH), 3.53 (s_{br}, 1H, N*H*), 2.95 (dd, *J* = 13.4, 4.7 Hz, 1H, C*H*$_2$Ph), 2.70 (dd, *J* = 13.4, 7.3 Hz, 1H, C*H*$_2$Ph), 1.16 (d, *J* = 6.4 Hz, 3H, C*H*$_3$CHNH); **GC-MS**: (Rtx-5MS, 100.2/10.270/10): t_R = 17.3 min, *m/z* = 211 ($[M]^+$), 120, 103, 91; **GC** (Machary-Nagel Optima-5-Amin (0.50 µm x 0.25 µm x 30 m), 60 kPa H_2, 100 °C/2 min, 10°C/min, 250 °C/7 min): t_R = 21.1 min; **HPLC** (Daicel Chiracel OJ-H, *n*-heptane/iso-propanol 97:3, 0.5 mL/min, 25 °C, 208/243 nm): t_R = 21.2 min ((+)-A27), t_R = 23.2 min ((-)-A27); **Optical Rotation**: $[\alpha]_D^{20}$ = +1.3 (c 0.65 in $CHCl_3$ 0.75% EtOH), 72% ee.

(-)-*N*-(pentan-2-yl)aniline (A28)[25]



$C_{11}H_{17}N$ (163.26 g/mol):
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.21 - 7.11 (m, 2H), 6.69 - 6.63 (m, 1H), 6.61 - 6.55 (m, 2H), 3.48 (dq, J = 21.1, 5.9 Hz, H), 3.42 (s, 1H), 1.60 - 1.51 (m, 1H), 1.48 - 1.36 (m, 3H), 1.18 (d, *J* = 6.3 Hz, 3H), 0.94 (ddd, *J* = 7.1, 4.1, 3.2 Hz, 3H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 147.87 (*C*$_{Ar}$-N), 129.41 (*C*H$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 116.86 (*C*H$_{Ar}$CH$_{Ar}$CH$_{Ar}$C$_{Ar}$-N), 113.18 (*C*H$_{Ar}$C$_{Ar}$-N), 48.30 (*C*HNH), 39.60 (*C*H$_2$CHNH), 20.92 (*C*H$_2$CH$_2$CHNH), 19.47 (*C*H$_3$CHNH), 14.27 (*C*H$_3$CH$_2$); **GC-MS** (EI, 70 eV, PhMeSi, 100.2/10.270/10): t_R = 7.9 min, *m/z* = 163 ($[M]^+$), 148, 132, 120; **GC** (Machary-Nagel Optima-5-Amin (0.50 µm x 0.25 µm x 30 m), 60 kPa H_2, 100 °C/2 min, 10°C/min, 250 °C/7 min): t_R = 13.6 min; **HPLC** (Daicel Chiracel OJ-H, *n*-heptane/iso-propanol 99:1, 0.5 mL/min, 25 °C, 247/297 nm): t_R = 19.1 min ((+)-A28), t_R = 21.6 min ((-)-A28); **Optical Rotation**: $[\alpha]_D^{20}$ = -14.5 (c 2.565 in $CHCl_3$ 0.75% EtOH), 40% ee.

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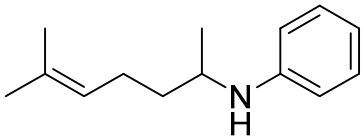
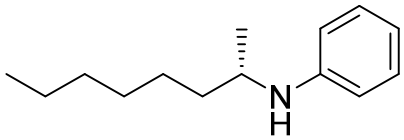
[25] L. Rubio-Pérez, F. J. Pérez-Flores, P. Sharma, L. Velasco, A. Cabrera, *Org. Lett.* **2009**, *11*, 265–268

_N_-(6-methylhept-5-en-2-yl)aniline (A29)[26]



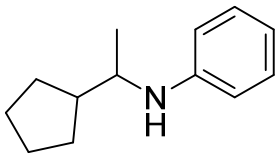
$C_{14}H_{21}N$ (203.32 g/mol):
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.16 (t, *J* = 7.7 Hz, 2H, $CH_{Ar}CH_{Ar}C_{Ar}$-N), 6.66 (t, *J* = 7.3 Hz, 1H, $CH_{Ar}CH_{Ar}CH_{Ar}C_{Ar}$-N), 6.57 (d, *J* = 7.9 Hz, 2H, $CH_{Ar}C_{Ar}$-N), 5.13 (t, *J* = 7.3 Hz, 1H, $(CH_3)_2C{=}CHCH_2$), 3.47 (qd, *J* = 12.8, 6.4 Hz, 1H, CHNH), 3.42 (s_{br}, 1H, NH), 2.09 (dd, *J* = 14.7, 7.5 Hz, 2H, $(CH_3)_2C{=}CHCH_2CH_2$), 1.70 (s, 3H, $(CH_3)_2C{=}CH$), 1.60 (m, 1H, CH_2CH_2CHNH), 1.59 (s, 3H, $(CH_3)_2C{=}CH$), 1.48 (dt, *J* = 13.9, 7.1 Hz, 1H, CH_2CH_2CHNH), 1.19 (d, *J* = 6.2 Hz, 3H, CH_3CHNH); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 147.86 (C_{Ar}-N), 132.14 ($(CH_3)_2C{=}CH$), 129.39 ($CH_{Ar}CH_{Ar}C_{Ar}$-N), 124.14 ($(CH_3)_2C{=}CH$), 116.91 ($CH_{Ar}CH_{Ar}CH_{Ar}C_{Ar}$-N), 113.25 ($CH_{Ar}C_{Ar}$-N), 48.23 (CHNH), 37.34 (CH_2CHNH), 25.86 ($(CH_3)_2C{=}CH$), 24.87 ($C{=}CHCH_2$), 20.93 (CH_3CHNH), 17.82 ($(CH_3)_2C{=}CH$); **GC-MS**: (Rtx-5MS, 100.2/10.270/10): t_R = 14.2 min, *m/z* = 203 ($[M]^+$), 188, 160, 1446, 133, 120; **GC** (Machary-Nagel Optima-5-Amin (0.50 µm x 0.25 µm x 30 m), 60 kPa H_2, 100 °C/2 min, 10°C/min, 250 °C/7 min): t_R = 17.9 min; **HPLC** (Daicel Chiracel OJ-H, *n*-heptane/iso-propanol 99:1, 0.5 mL/min, 25 °C, 247/297 nm): t_R = 16.1 min ((+)-A29), t_R = 18.6 min ((-)-A29); **Optical Rotation**: $[\alpha]_D^{20}$ = -0.8 (c 1.0 in $CHCl_3$ 0.75% EtOH), 50% ee.

(*S*)-(+)-*N*-(octan-2-yl)aniline (A30)[27]



$C_{14}H_{23}N$ (205.34 g/mol):
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.13 (m, 2H), 6.68 – 6.63 (m, 1H), 6.60 – 6.55 (m, 2H), 3.46 (dt, *J* = 12.6, 6.2 Hz, 1H), 3.43 – 3.37 (m, 1H), 1.62 – 1.52 (m, 1H), 1.47 – 1.34 (m, 3H), 1.34 – 1.24 (m, 6H), 1.17 (d, *J* = 6.2 Hz, 3H), 0.92 – 0.85 (m, 3H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 147.85, 129.40, 116.85, 113.19, 48.59, 37.38, 32.00, 29.52, 26.29, 22.78, 20.93, 14.25; **GC-MS**: (Rtx-5MS, 100.2/10.270/10): t_R = 14.2 min, *m/z* = 205 ($[M]^+$), 190, 132, 120; **GC** (Machary-Nagel Optima-5-Amin (0.50 µm x 0.25 µm x 30 m), 60 kPa H_2, 100 °C/2 min, 10°C/min, 250 °C/7 min): t_R = 18.07 min; **HPLC** (Daicel Chiracel OB-H, *n*-heptane/iso-propanol 99:1, 0.5 mL/min, 40 °C, 247/297 nm): t_R = 9.97 min ((*R*)-(-)-A30), t_R = 10.71 min ((*S*)-(+)-A30); **Optical Rotation**: $[\alpha]_D^{20}$ = +14.8 (c 1.0 in $CHCl_3$, 0.75% EtOH).

(-)-*N*-(1-cyclopentylethyl)aniline (A31)

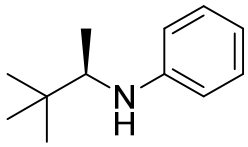


$C_{13}H_{19}N$ (189.30 g/mol):
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.15 (t, *J* = 7.9 Hz, 2H), 6.64 (t, *J* = 7.3 Hz, 1H), 6.58 (d, *J* = 7.7 Hz, 2H), 3.47 (s, 1H), 3.32 (s, 1H), 1.92 (dq, *J* = 16.3, 8.0 Hz, 1H), 1.86 – 1.70 (m, 2H), 1.69 – 1.48 (m, 4H), 1.37 – 1.23 (m, 2H), 1.16 (d, *J* = 6.2 Hz, 3H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 148.10, 129.39, 116.73, 113.14, 53.07, 46.80, 29.91, 29.62, 25.84, 25.65, 19.49; **IR** (neat, ATR) ν/cm^{-1} =

[26] C. Li, B. Villa-Marcos, J. Xiao, *J. Am. Chem. Soc.* **2009**, *131*, 6967-6969
[27] P. Yin and T.-P. Loh, *Org. Lett.* **2009**, *11*, 3791-3793

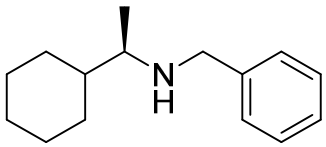
3401 (w_{br}), 3050 (w), 3017 (w), 2950 (m), 2864 (m), 1600 (s), 1502 (s), 1450 (w), 1426 (w), 1318 (m), 1250 (w), 1178 (w), 1144 (m), 1074 (w), 993 (w), 745 (s), 692 (m); **GC-MS**: (Rtx-5MS, 100.2/10.270/10): t_R = 13.8 min, *m/z* = 189 ($[M]^+$), 120; **GC** (Machary-Nagel Optima-5-Amin (0.50 µm x 0.25 µm x 30 m), 60 kPa H_2, 100 °C/2 min, 10°C/min, 250 °C/7 min): t_R = 17.8 min; **HPLC** (Daicel Chiracel OJ-H, *n*-heptane/iso-propanol 99:1, 0.5 mL/min, 25 °C, 247/297 nm): t_R = 23.1 min ((+)-A31), t_R = 26.1 min ((-)-A31): **EA**: calc. C, 82.48; H, 10.12; N, 7.40; found: C, 82.19; H, 9.95; N, 7.58; **Optical Rotation**: $[\alpha]_D^{20}$ = - 0.5 (c 0.05 in $CHCl_3$ 0.75% EtOH), 76% ee.

(*R*)-(-)-*N*-(3,3-dimethylbutan-2-yl)aniline (A32)[23]



$C_{12}H_{19}N$ (177.29 g/mol):
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.15 (t, *J* = 7.9 Hz, 2H, $CH_{Ar}CH_{Ar}C_{Ar}$-N), 6.63 (t, *J* = 7.4 Hz, 1H, $CH_{Ar}CH_{Ar}CH_{Ar}C_{Ar}$-N), 6.59 (d, *J* = 8.5 Hz, 2H, $CH_{Ar}C_{Ar}$-N), 3.39 (s_{br}, 1H, NH), 3.24 (q, *J* = 6.5 Hz, 1H, CH_3CH), 1.09 (d, *J* = 6.4 Hz, 3H, CH_3CHNH), 0.96 (s, 9H, $C(CH_3)_3$); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 148.63 (C_{Ar}-N), 129.40 ($CH_{Ar}CH_{Ar}C_{Ar}$-N), 116.65 ($CH_{Ar}CH_{Ar}CH_{Ar}C_{Ar}$-N), 113.13 ($CH_{Ar}C_{Ar}$-N), 57.32 (*C*HNH), 34.92 ($C(CH_3)_3$), 26.68 ($C(CH_3)_3$), 15.98 (CH_3CHNH); **GC-MS**: (Rtx-5MS, 100.2/10.270/10): t_R = 9.3 min, *m/z* = 177 ($[M]^+$), 120; **GC** (Machary-Nagel Optima-5-Amin (0.50 µm x 0.25 µm x 30 m), 60 kPa H_2, 100 °C/2 min, 10°C/min, 250 °C/10 min): t_R = 14.1 min; **HPLC** (Daicel Chiracel OJ-H, *n*-heptane/iso-propanol 99:1, 0.5 mL/min, 25 °C, 247/297 nm): t_R = 15.1 min ((*R*)-(-)-A32), t_R = 18.4 min ((*S*)-(+)-A32); **Optical Rotation**: $[\alpha]_D^{20}$ = - 65.6 (c 1.0 in $CHCl_3$, 0.75% EtOH).

(*R*)-N-benzyl-1-cyclohexylethanamine (A33)[28]



$C_{15}H_{23}N$ (217.35 g/mol):
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 4H), 7.26 – 7.21 (m, 1H), 3.84 (d, J = 13.1 Hz, 1H), 3.71 (d, J = 13.1 Hz, 1H), 2.50 (p, J = 6.3 Hz, 1H), 1.80 – 1.62 (m, 5H), 1.36 (tdt, J = 11.5, 5.6, 3.1 Hz, 1H), 1.30 – 1.19 (m, 2H), 1.19 – 1.10 (m, 2H), 1.03 (m, 2H), 1.03 (d, J = 6.5 Hz, 3H); **GC** (Machary-Nagel Optima-5-Amin (0.50 µm x 0.25 µm x 30 m), 60 kPa H_2, 100 °C/2 min, 10°C/min, 250 °C/7 min): t_R = 20.0 min (A34); **GC-MS**: (Rtx-5MS, 100.2/10.270/10): t_R = 16.2 min, m/z = 202 ($[M\text{-}CH_3]^+$), 134 ($[M\text{-}C_6H_{11}]^+$), 91; **HPLC** (Daicel Chiracel OD-H, *n*-heptane/iso-propanol 95:5, 0.8 mL/min, 25 °C, 225/287 nm): t_R = 15.9 min ((*R*)-A33-1-naphtamide), t_R = 19.9 min ((*S*)-A33-1-naphtamide); **Optical Rotation**: $[\alpha]_D^{20}$ = - 23.7° (c 1.0 in $CHCl_3$ 0.75% EtOH)

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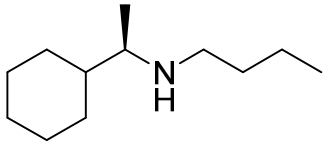
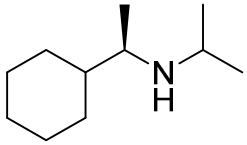
[28] C. A. Willoughby , S. L. Buchwald, *J. Am. Chem. Soc.* **1994**, *116*, 8952-8965

(*R*)-N-(1-cyclohexylethyl)butan-1-amine (A34)



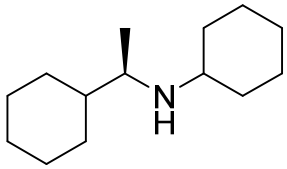
$C_{12}H_{25}N$ (183.33 g/mol):
^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.63 (dt, J = 13.9, 7.3 Hz, 1H), 2.50 (dt, J = 11.3, 7.2 Hz, 1H), 2.42 (p, J = 6.2 Hz, 1H), 1.75 (dt, J = 12.4, 3.4 Hz, 2H), 1.71 – 1.61 (m, 3H), 1.45 (p, J = 7.1 Hz, 2H), 1.34 (h, J = 7.5 Hz, 3H), 1.27 – 0.98 (m, 5H), 0.97 (d, J = 6.6 Hz, 3H), 0.91 (t, J = 7.1 Hz, 3H), 0.81 (s, 1H, NH); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 58.03, 47.54, 43.06, 32.79, 30.18, 28.10, 26.96, 26.85, 26.69, 20.76, 16.98, 14.19; **IR** (neat, ATR) ν/cm^{-1} = 2956 (m), 2920 (s), 2851 (s), 2809 (w), 1463 (w), 1447 (m), 1370 (m), 1154 (w), 1124 (w), 890 (w), 834 (w); **GC** (Machary-Nagel Optima-5-Amin (0.50 µm x 0.25 µm x 30 m), 60 kPa H_2, 100 °C/2 min, 10°C/min, 250 °C/7 min): t_R = 13.7 min (A35); **GC-MS**: (Rtx-5MS, 100.2/10.270/10): t_R = 9.0 min m/z = 168 ([M-CH_3]$^+$), 140, 100 ([M-C_6H_{11}]$^+$); **GC** (MEGA Diethyl-terbutylsilyl-b-086 (0.25 µm x 0.25 mm x 25 m), 60 kPa H_2, 90 °C/10 min, 1°C/min to 120°C, 10°C/min to 180°C, 10 min): t_R = 21.7 min ((*S*)-A34), t_R = 22.1 min ((*R*)-A34); **HRMS:** calc. 183.1987, found: 184.2062 (M+H); **Optical Rotation**: $[\alpha]_D^{20}$ = - 12.2° (c 1.0 in $CHCl_3$ 0.75% EtOH)

(*R*)-*N*-(1-cyclohexylethyl)propan-2-amine (A35)



$C_{11}H_{23}N$ (169.31 g/mol):
^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.84 (hept, *J* = 6.3 Hz, 1H), 2.48 (p, *J* = 6.3 Hz, 1H), 1.73 (dt, *J* = 11.8, 3.5 Hz, 2H), 1.64 (q, *J* = 11.4 Hz, 3H), 1.28 (tq, *J* = 11.3, 3.4 Hz, 1H), 1.20 (dddd, J = 15.9, 9.7, 5.1, 3.3 Hz, 2H), 1.16 – 1.08 (m, 1H), 1.02 (d, *J* = 6.3 Hz, 3H), 0.99 (d, *J* = 6.2 Hz, 3H), 0.97 (m, 1H), 0.96 (m, H), 0.94 (d, J = 6.5 Hz, 3H), 0.63 (s, 1H, NH); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 54.64, 45.69, 43.23, 30.33, 27.93, 26.97, 26.86, 26.67, 23.99, 23.27, 17.54; **GC-MS**: (Rtx-5MS, 100.2/10.270/10): t_R = 6.1 min, *m/z* = 154 ([M-CH_3]$^+$), 86; **GC** (Machary-Nagel Optima-5-Amin (0.50 µm x 0.25 µm x 30 m), 60 kPa H_2, 100 °C/2 min, 10°C/min, 250 °C/7 min): t_R = 11.1 min; **GC** (MEGA Diethyl-terbutylsilyl-b-086 (0.25 µm x 0.25 mm x 25 m), 60 kPa H_2, 100 °C/2 min, 1°C/min to 135°C, 10°C/min to 180°C, 10 min): t_R = 32.1 min ((*R*)-A35-acetamide), t_R = 32.4 min ((*S*)-A35-acetamide); **IR** (neat, ATR) ν/cm^{-1} = 2959 (m), 2921 (s), 2851 (s), 1465 (m), 1448 (m), 1377 (m), 1336 (w), 1168 (m), 1134 (w), 890 (w), 834 (w), 713 (m); **HRMS:** calc. 169.1830, found: 170.1901 (M+H); **Optical Rotation**: $[\alpha]_D^{20}$ = - 13.6 (c 1.0 in $CHCl_3$ 0.75% EtOH).

(*R*)-*N*-(1-cyclohexylethyl)cyclohexanamine (A36)



$C_{14}H_{27}N$ (209.37 g/mol):
^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.59 – 2.49 (m, 1H), 2.49 – 2.38 (m, 1H), 1.83 (t, *J* = 14.5 Hz, 2H), 1.77 – 1.55 (m, 8H), 1.33 – 0.96 (m, 11H), 0.95 (d, *J* = 6.5 Hz, 3H), 0.66 (s, 1H); **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ 54.23, 54.09, 43.36, 34.79, 34.05, 30.32, 28.10, 26.96, 26.84, 26.67, 26.40, 25.51, 25.35, 17.85; **GC-MS** (Rtx-5MS, 50.2/30.250/5): t_R = 8.2 min, *m/z* = 209 ([M]$^+$), 194, 166,

127, 126, 44; **GC** (Machary-Nagel Optima-5-Amin (0.50 µm x 0.25 µm x 30 m), 60 kPa H_2, 100 °C/2 min, 10°C/min, 250 °C/7 min): t_R = 17.6 min; **HPLC** (Daicel Chiracel OD-H, *n*-heptane/iso-propanol 97:3, 0.5 mL/min, 40 °C, 225/284 nm): t_R = 19.2 min ((*S*)-A36-1-naphtamide), t_R = 21.3 min ((*R*)-A36-1-naphtamide); **IR** (neat, ATR) ν/cm^{-1} = 2919 (s), 2848 (s), 1463 (m), 1447 (m), 1371 (m), 1155 (w), 1115 (w), 888 (w), 843 (w); **HRMS:** calc. 209.2143, found: 210.2217 (M+H); **Optical Rotation**: $[\alpha]_D^{20}$ = - 17.3 (c 1.0 in $CHCl_3$ 0.75% EtOH).

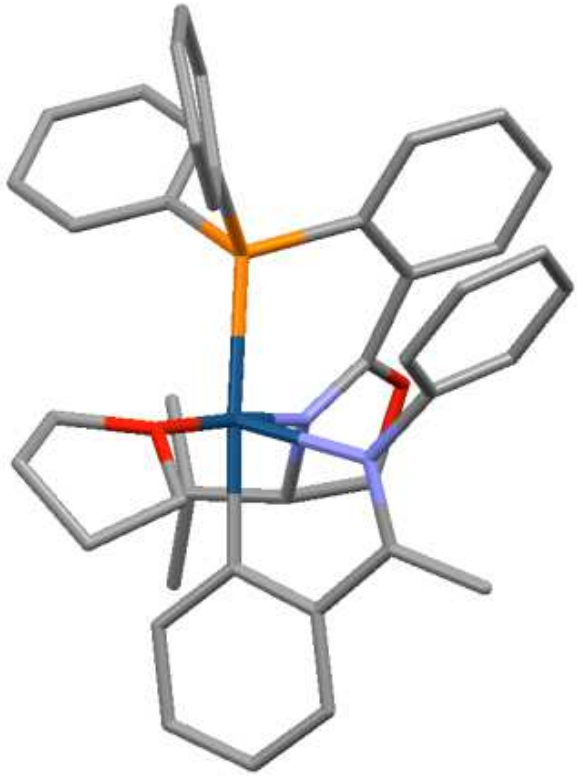
Crystal Structures

Single crystals were obtained by layering a solution of **5** in THF with diethylether and **7** in CH_2Cl_2 with pentane. The crystals were mounted with an oil drop on a glass fiber and frozen in the cold gas stream of a CRYOstream cooler. Data collection was carried out at 173 K using the "Collect" data collection software (Nonius BV, 2002). The structure were solved with SIR92 or SIR97 and refined with *CRYSTALS*. The plots have been created using the program *Mercury*.

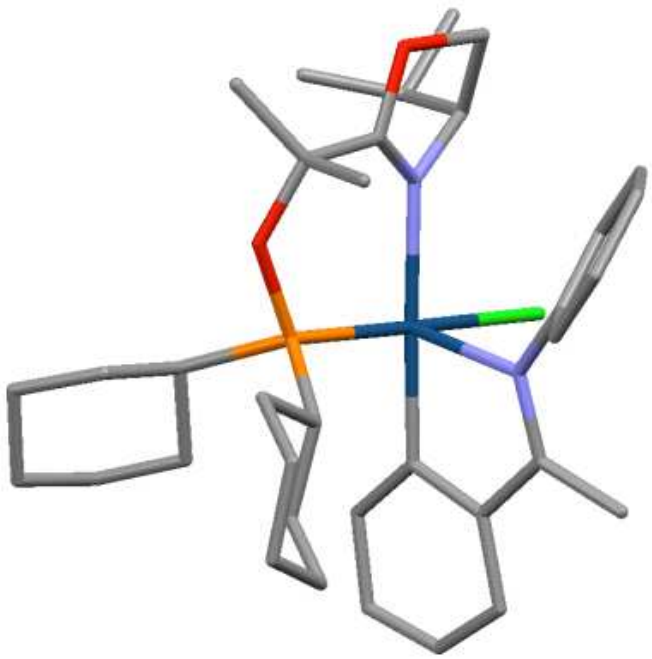
The structure of **7** presented very big problems on various levels. The best crystals that could be obtained after numerous crystallization experiments were far from optimal for a structure determination. Apart from the fact that diffraction stopped to be observable at quite low Theta values it also seems that they were multiply twinned. The triclinic unit cell did not permit transformation to higher symmetry, even if the structure vaguely suggested the presence of a 3_1 axes as a symmetry element. Attempts to use alternative methods to determine the unit cell, for instance the program "cell_now", always confirmed the strange unit cell with two axes a and b of approximately the same dimension and the angle γ of about 120 degrees, but angles α and β far away from 90 degrees which makes transformation to a higher symmetry impossible.

The Z value of the structure is 12. The data quality did not permit to locate all atoms, and like that the refinement finished at some intermediate state. Nevertheless the structure seems to demonstrate that all 12 complex molecules have the same configuration. While all peripheral groups are fuzzy the coordination sphere seems to be determined well enough to identify the compound and confirm its main geometrical features.

Nevertheless the refinement could, even with big efforts, not be brought to a level that would permit the deposition with the CCDC. For this reason the structure is mentioned here as unfinished work.



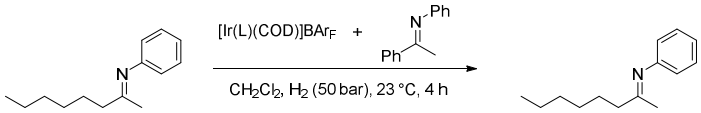
5



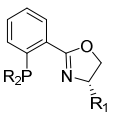
7

Compound	**5**	**7**
Molecular Formula	$C_{42}H_{44}F_6Ir_1N_2O_2P_2$	$C_{36}H_{53}Cl_3IrN_2O_2P$
Formula Weight [g*mol^{-1}]	976.98	874.25
Shape	plate	-
Colour	Yellow	Yellow
Temperature [K]	173K	173K
Crystal size	0.04 · 0.06 · 0.40 mm^3	-
Crystal system	hexagonal	triclinic
Space group	P 6_3	P 1
a [Å]	19.4370(2) Å	20.3432(8) Å
b [Å]	19.4370(2) Å	20.3463(8) Å
c [Å]	18.1371(2) Å	32.2232(19) Å
α [°]	90°	91.006(3)°
β [°]	90°	99.548(3)°
γ [°]	120°	119.941(2)°
Volume [Å^3]	5934.13(11) Å^3	11318.5(10) Å^3
Z	6	12
Density (calc.) [g*cm^{-1}]	1.640 Mg · m^{-3}	1.234 Mg · m^{-3}
μ (Mo Kα) [mm^{-1}]	3.523 mm^{-1}	3.781 mm^{-1}
Transmission (min/max)	0.81 / 0.87	-
Radiation type	Mo K_α (λ = 0.71073 Å)	Mo K_α (λ = 0.71073 Å)
F(000)	2922	3945.800
Reflections measured	47359	149545
Reflections independent	9429 (merging r = 0.065)	87895 (merging r = 0.049)
Reflections used	5400 (I>3.0σ(I))	52759 (I>2.0σ(I))
Number of parameters	497	1914
R (observed data)	0.0216	0.1174
R_W (all data)	0.0234	0.2026
goodness-of-fit on F	0.7012	0.4068

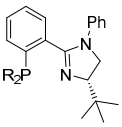
Ligand Screening



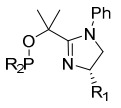
Entry	Ligand	Conv. [%]	*ee* [%]
1	**L1**	>99	24 (R)
2	**L2**	>99	18 (R)
3	**L3**	>99	18 (R)
4	**L4**	>99	14 (R)
5	**L5**	97	7
6	**L6**	>99	8
7	**L7**	39	nd
8	**L8**	51	nd
9	**L9**	>99	14
10	**L10**	13	nd
11	**L11**	95	10
12	**L12**	33	nd
13	**L13**	43	nd
14	**L14**	>99	3
15	**L15**	>99	13
16	**L16**	31	rac.
17	**L17**	97	11
18	**L18**	>99	21
19	**L19**	>99	18
20	**L20**	>99	17
21	**L21**	>99	11
22	**L22**	>99	10
23	**L23**	>99	2
24	**L24**	>99	4
25	**L25**	30	nd
26	**L26**	>99	3
27	**L27**	>99	2
28	**L28**	>99	12
29	**L29**	>99	3
30	**L30**	>99	15



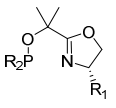
L1: R$_1$=^{t}Bu, R$_2$=Ph
L2: R$_1$=^{i}Pr, R$_2$=Ph
L3: R$_1$=^{t}Bu, R$_2$=Cy
L4: R$_1$=^{i}Pr, R$_2$=Cy



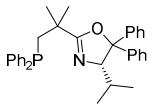
L5: R$_2$=*o*-Tol
L6: R$_2$=Cy



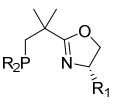
L7: R$_1$=^{t}Bu, R$_2$=*o*-Tol
L8: R$_1$=^{t}Bu, R$_2$=Ph
L9: R$_1$=^{i}Pr, R$_2$=Ph
L10: R$_1$=^{t}Bu, R$_2$=Cy
L11: R$_1$=^{i}Pr, R$_2$=Cy
L12: R$_1$=^{t}Bu, R$_2$=^{t}Bu
L13: R$_1$=^{i}Pr, R$_2$=^{t}Bu



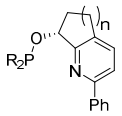
L14: R$_1$=^{t}Bu, R$_2$=*o*-Tol
L15: R$_1$=^{i}Pr, R$_2$=Ph
L16: R$_1$=^{t}Bu, R$_2$=^{t}Bu
L17: R$_1$=^{t}Bu, R$_2$=Cy
L18: R$_1$=^{i}Pr, R$_2$=Cy



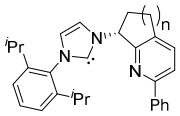
L19



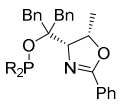
L20: R$_1$=^{t}Bu, R$_2$=*o*-Tol
L21: R$_1$=^{t}Bu, R$_2$=Ph
L22: R$_1$=^{i}Pr, R$_2$=Ph



L23: n=1, R=^{t}Bu
L24: n=1, R=Ph
L26: n=2, R=*o*-Tol
L27: n=2, R=Ph



L25: n=1
L28: n=2

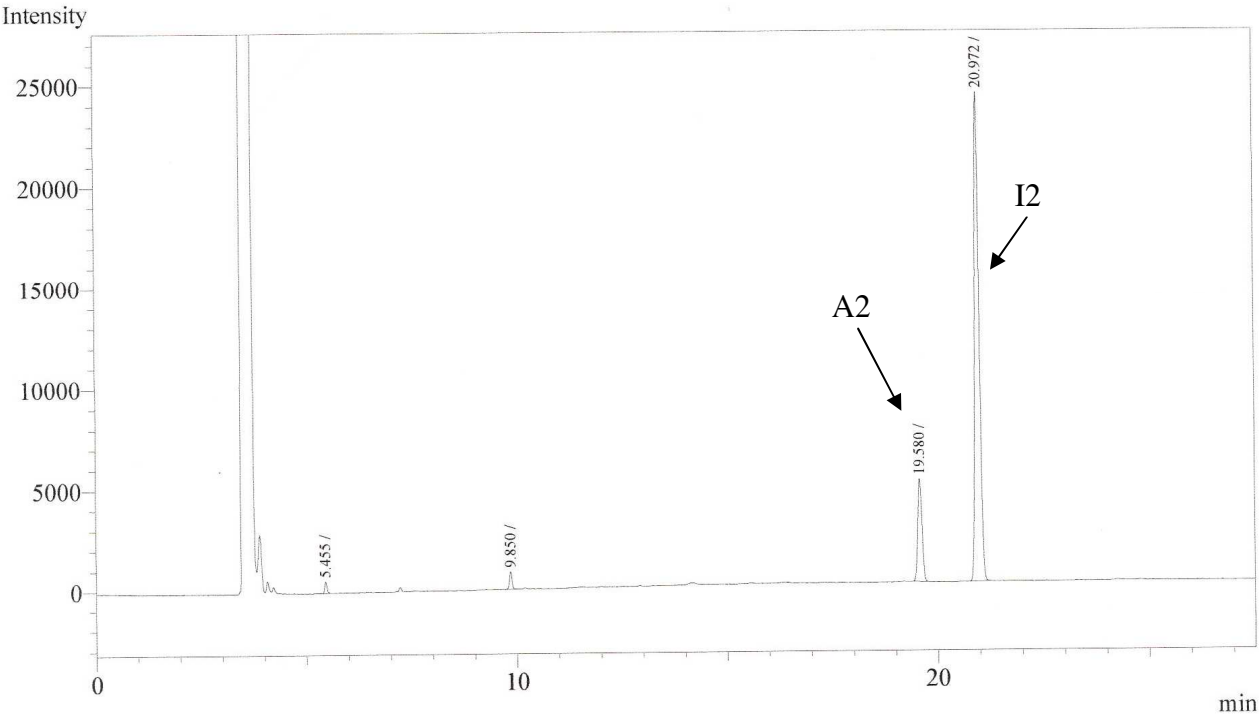


L29: R=Cy
L30: R=Ph

Competition experiment

Throughout the catalytic reaction, neither imine **I1** nor amine **A1** can be observed by GC analysis. However, once the substrated is fully reduced, a new peak at t_R = 23 min appears and rises at the end of the reaction to about 2%. This decomposition product has not been identified or further investigated.

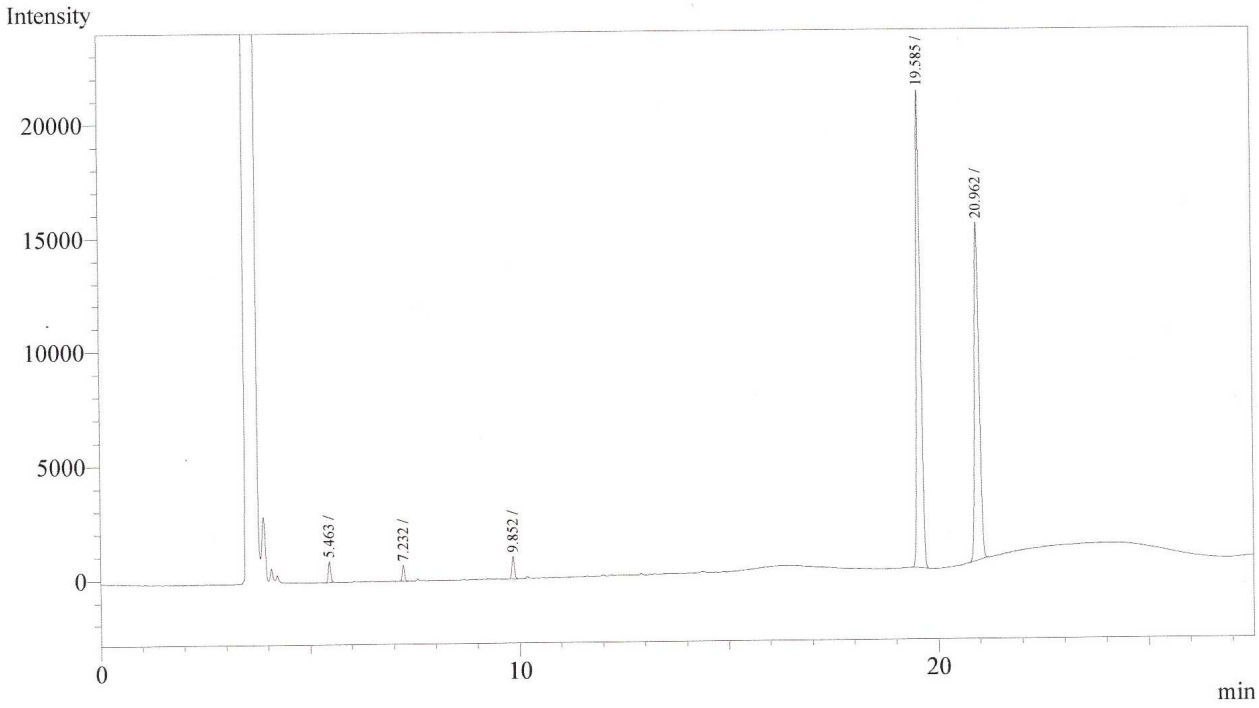
Analysis Date & Time	: 6/20/2011 9:49:20 PM
User Name	: Admin
Vial#	: 42
Sample Name	: YSII467_a
Sample ID	: YSII467_a
Sample Type	: Unknown
Injection Volume	: 1.00
ISTD Amount	:
Data Name	: D:\DATA\York\YSII467_a.gcd
Method Name	: D:\DATA\York\Methode Line 2 amine_mittellang_methoxyimin.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	5.455	2276	577	1.011				
2	9.850	3617	867	1.607				
3	19.580	35285	5084	15.675				
4	20.972	183923	24210	81.707				
Total		225101	30738					

Analysis Date & Time : 6/20/2011 10:52:36 PM
User Name : Admin
Vial# : 44
Sample Name : YSII467_c
Sample ID : YSII467_c
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

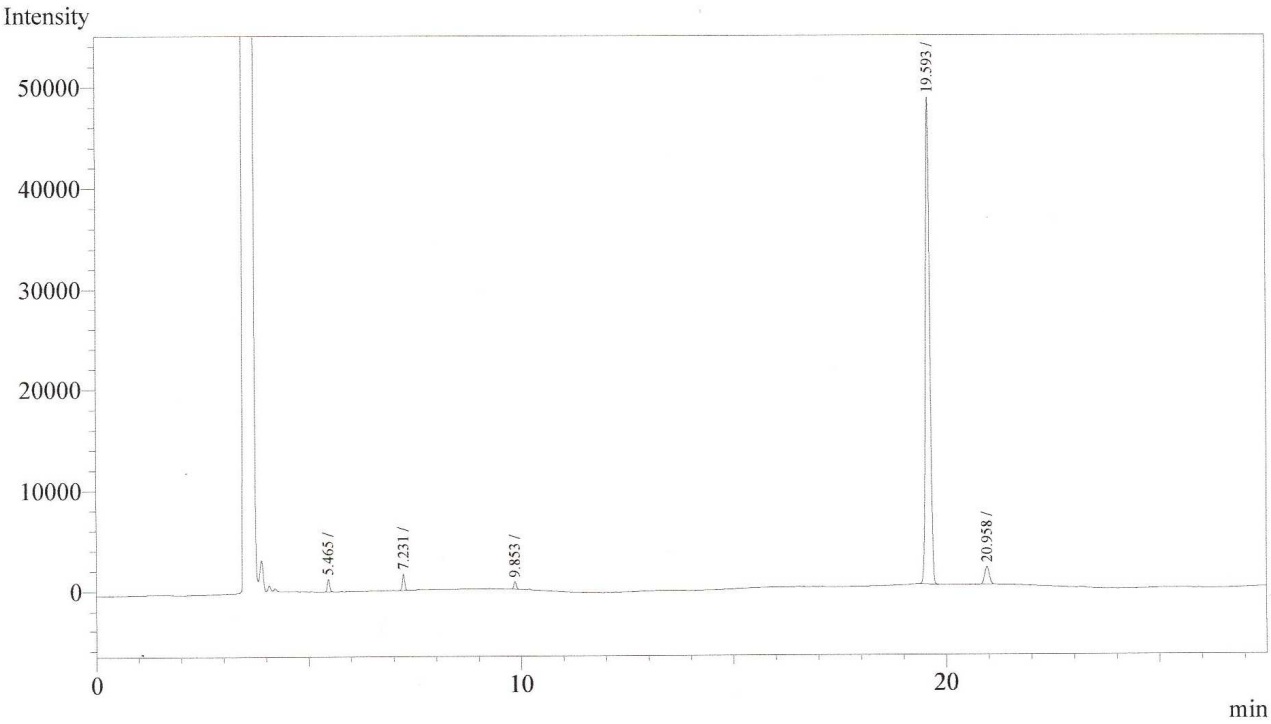
Data Name : D:\DATA\York\YSII467_c.gcd
Method Name : D:\DATA\York\Methode Line 2 amine_mittellang_methoxyimin.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	5.463	3556	912	1.324				
2	7.232	2599	703	0.968				
3	9.852	4010	966	1.493				
4	19.585	142757	20993	53.160				
5	20.962	115617	14850	43.054		V		
Total		268539	38424					

Analysis Date & Time : 6/20/2011 11:55:50 PM
User Name : Admin
Vial# : 46
Sample Name : YSII467_e
Sample ID : YSII467_e
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

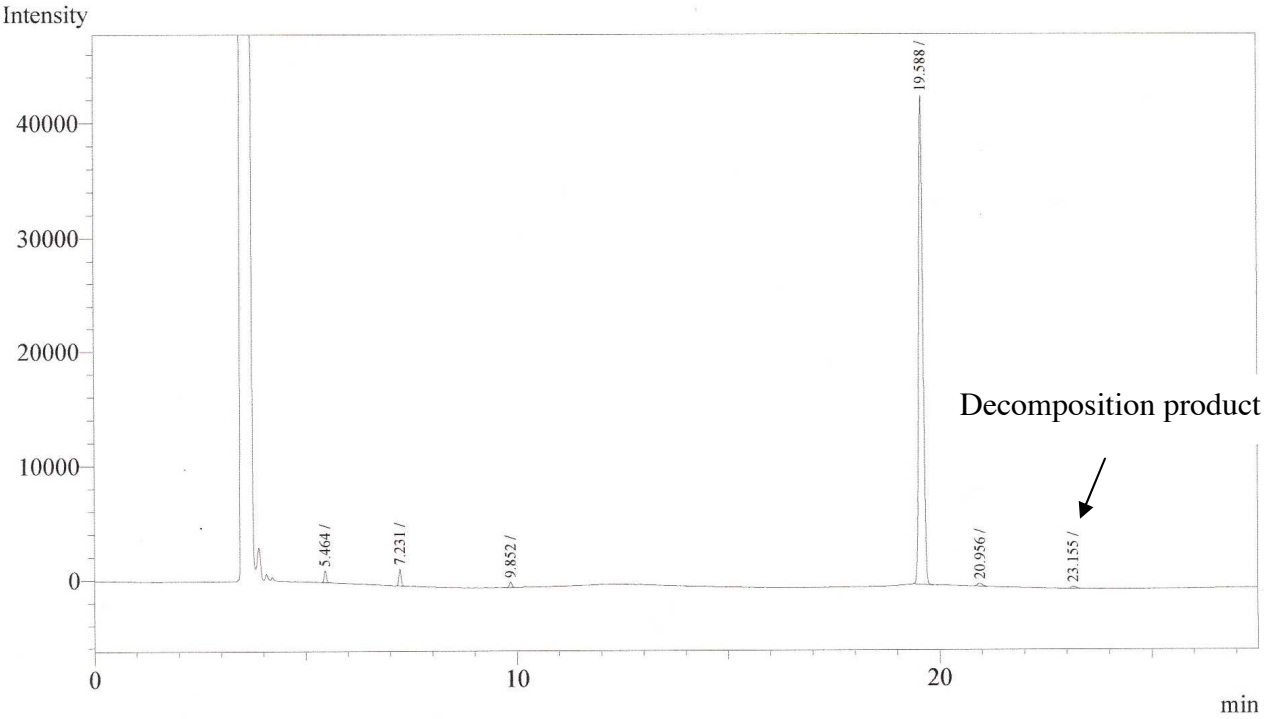
Data Name : D:\DATA\York\YSII467_e.gcd
Method Name : D:\DATA\York\Methode Line 2 amine_mittellang_methoxyimin.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	5.465	4749	1237	1.329				
2	7.231	6013	1607	1.683				
3	9.853	3137	758	0.878				
4	19.593	329985	48319	92.383				
5	20.958	13307	1746	3.725				
Total		357191	53667					

Analysis Date & Time : 6/21/2011 12:27:29 AM
User Name : Admin
Vial# : 47
Sample Name : YSII467_f
Sample ID : YSII467_f
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

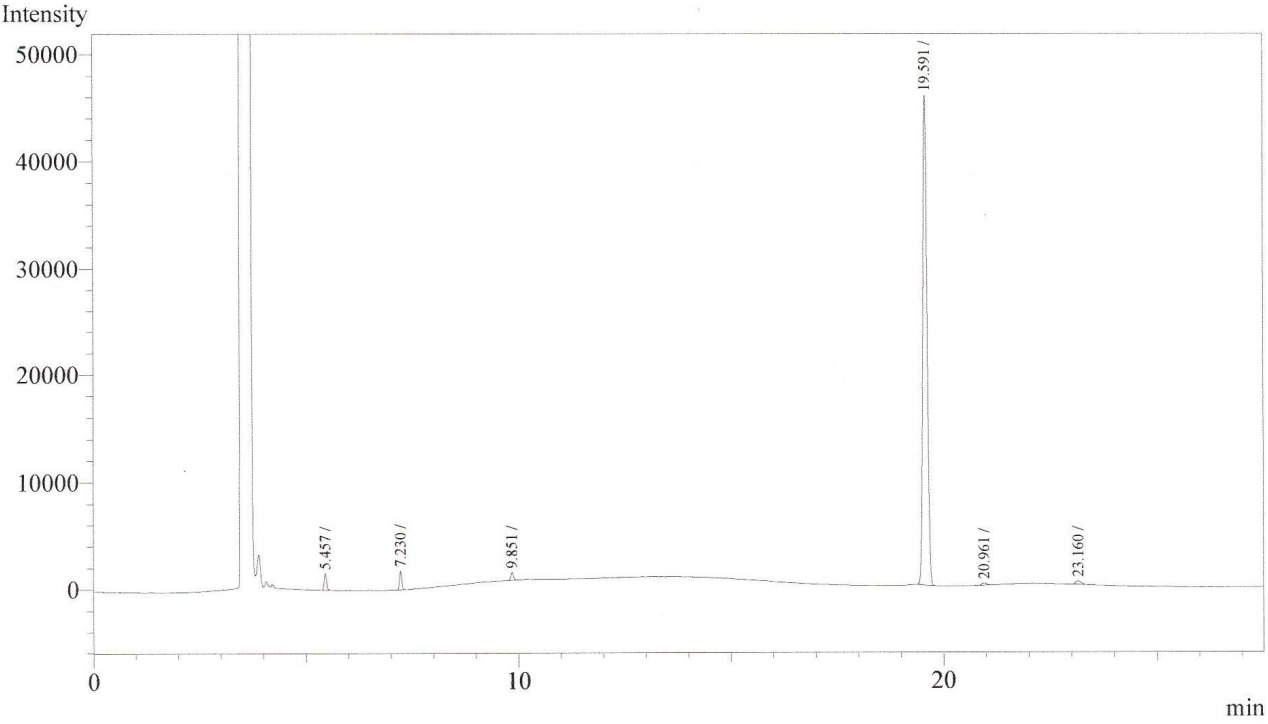
Data Name : D:\DATA\York\YSII467_f.gcd
Method Name : D:\DATA\York\Methode Line 2 amine_mittellang_methoxyimin.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	5.464	3967	1037	1.291				
2	7.231	5448	1462	1.773				
3	9.852	1907	463	0.621				
4	19.588	292437	42798	95.182				
5	20.956	1984	262	0.646				
6	23.155	1496	167	0.487				
Total		307239	46189					

Analysis Date & Time : 6/21/2011 12:59:07 AM
User Name : Admin
Vial# : 48
Sample Name : YSII467_g
Sample ID : YSII467_g
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

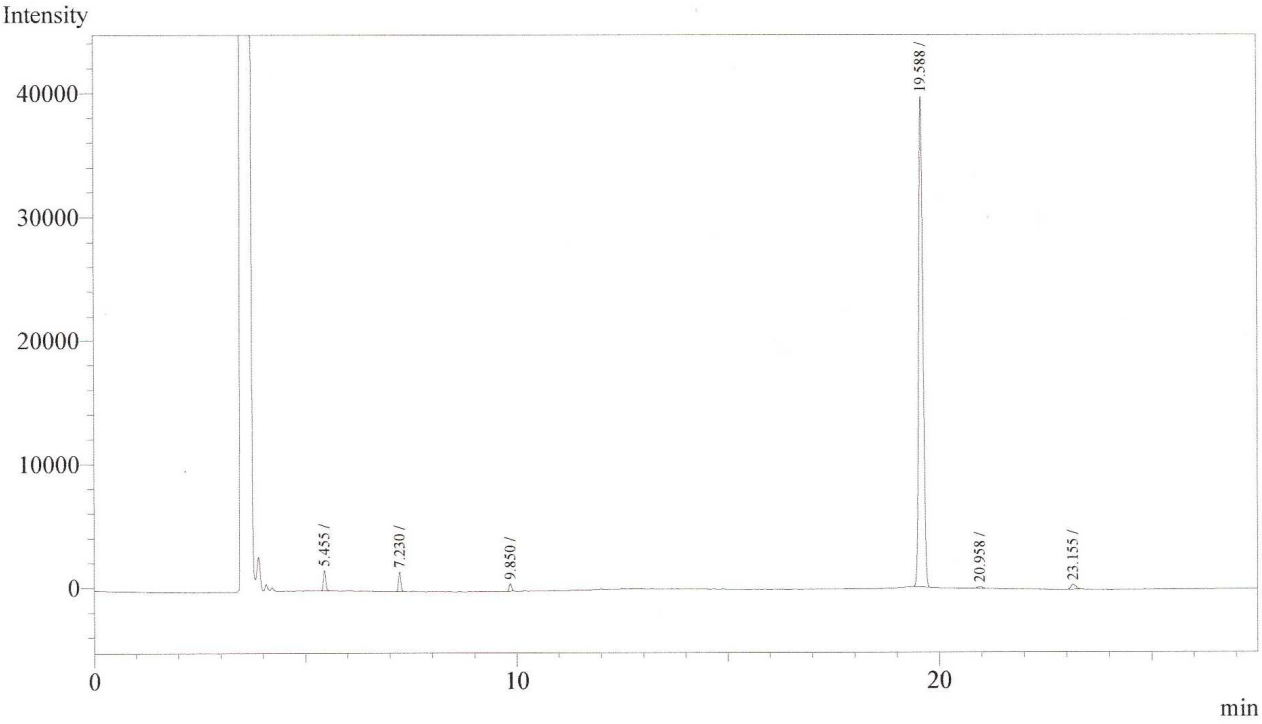
Data Name : D:\DATA\York\YSII467_g.gcd
Method Name : D:\DATA\York\Methode Line 2 amine_mittellang_methoxyimin.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	5.457	6135	1550	1.821				
2	7.230	6564	1741	1.948				
3	9.851	2996	719	0.889				
4	19.591	317029	45740	94.087				
5	20.961	1482	197	0.440				
6	23.160	2748	324	0.815				
Total		336954	50271					

Analysis Date & Time : 6/21/2011 1:30:43 AM
User Name : Admin
Vial# : 49
Sample Name : YSII467_h
Sample ID : YSII467_h
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

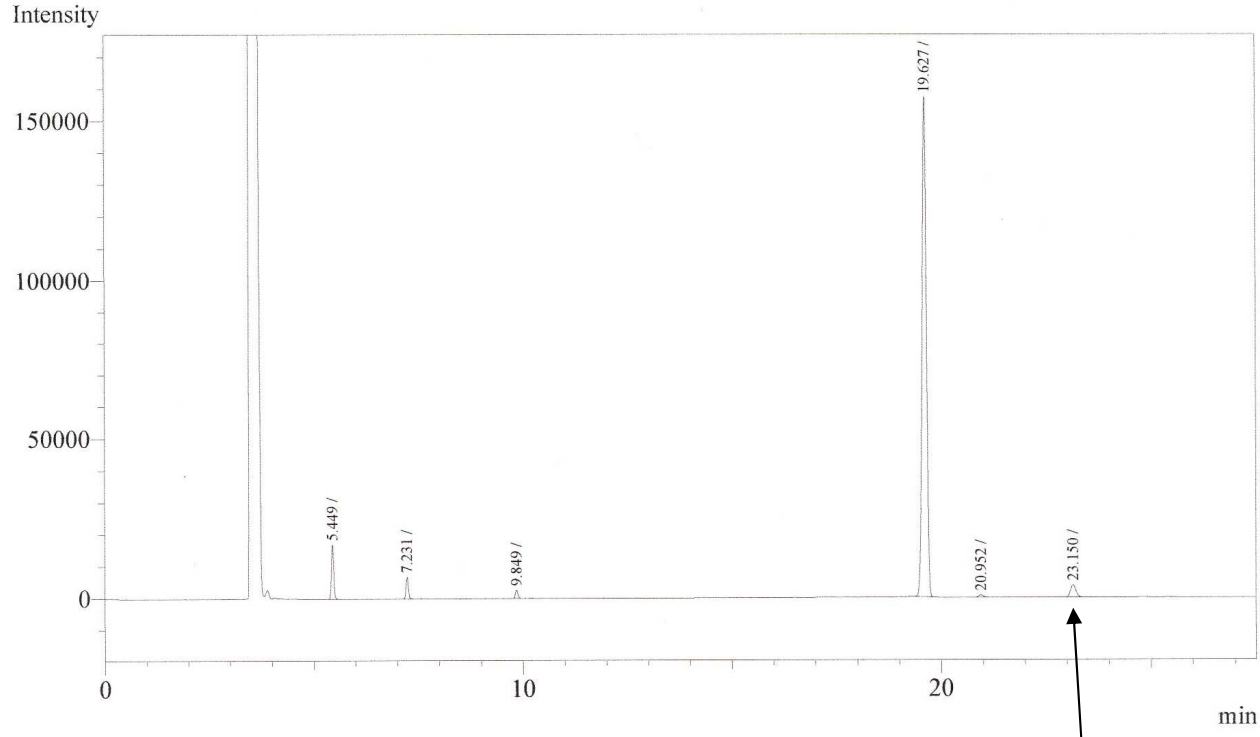
Data Name : D:\DATA\York\YSII467_h.gcd
Method Name : D:\DATA\York\Methode Line 2 amine_mittellang_methoxyimin.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	5.455	6355	1625	2.161				
2	7.230	5896	1559	2.005				
3	9.850	2505	620	0.852				
4	19.588	275008	39665	93.509				
5	20.958	1028	138	0.349				
6	23.155	3305	397	1.124				
Total		294097	44004					

Analysis Date & Time : 6/21/2011 2:02:20 AM
User Name : Admin
Vial# : 28
Sample Name : YSII467_end
Sample ID : YSII467_end
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

Data Name : D:\DATA\York\YSII467_end.gcd
Method Name : D:\DATA\York\Methode Line 2 amine_mittellang_methoxyimin.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	5.449	64961	16980	5.149				
2	7.231	26338	6789	2.088				
3	9.849	10702	2625	0.848				
4	19.627	1119979	157087	88.775				
5	20.952	5553	713	0.440				
6	23.150	34062	3807	2.700				
Total		1261595	188001					

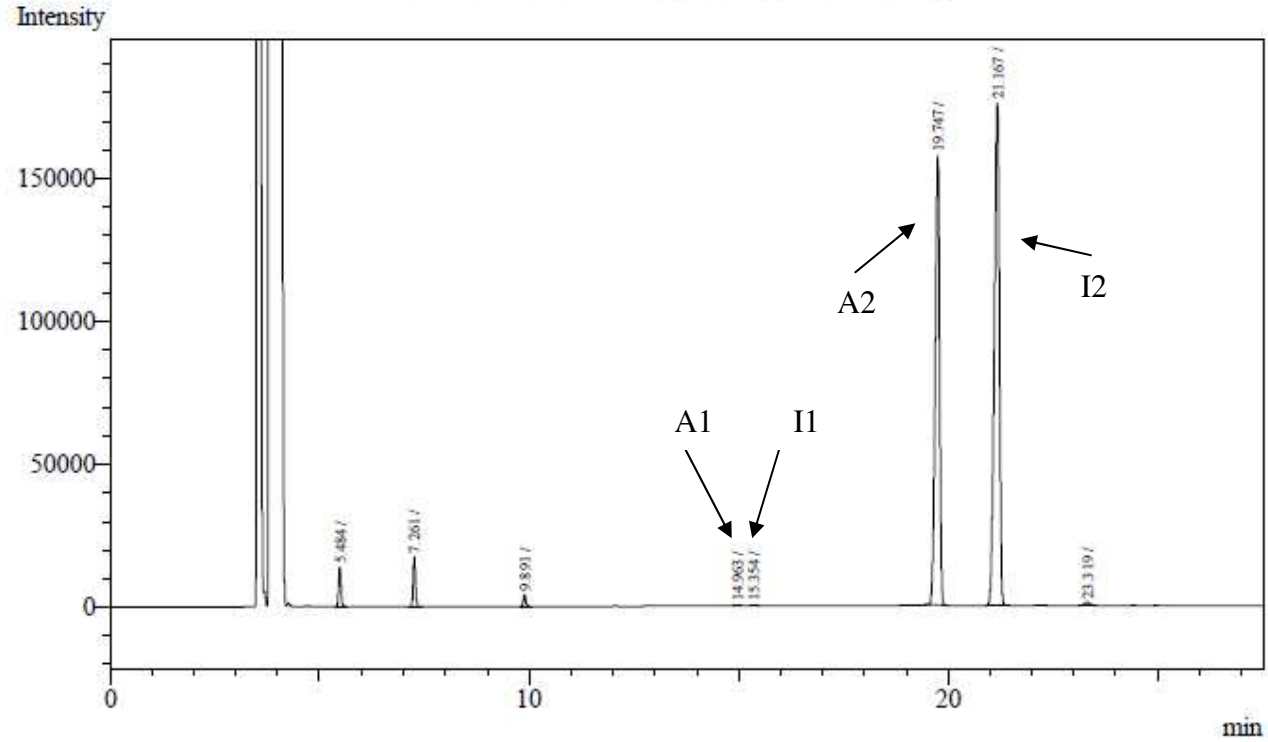
Decomposition product (ca. 2%)

Concentration series

To an equimolar mixture of **I2** and **A2** was added **I1** and **A1** in different concentrations to detect the minimal threshold in GC analysis of these substrates. They can already be detected at concentrations as low as 0.1 mol%.

0.1 mol%

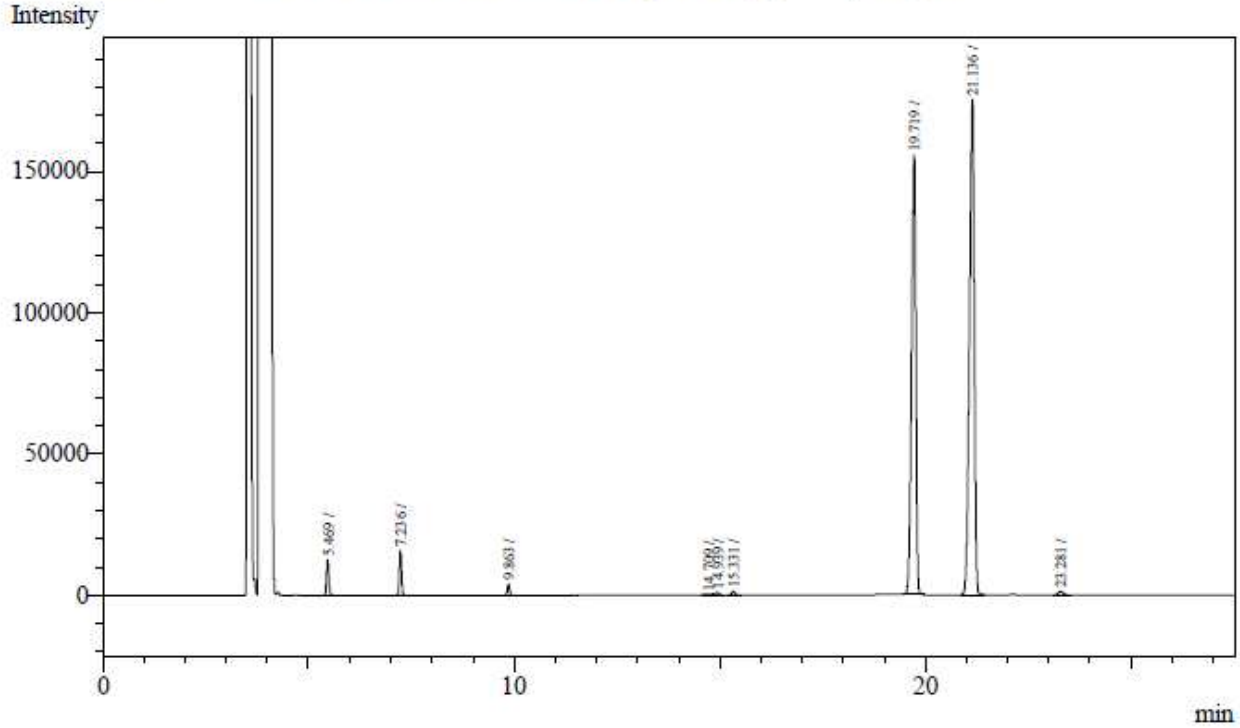
Analysis Date & Time	: 12/26/2012 8:46:14 AM
User Name	: User
Vial#	: 26
Sample Name	: YSIV743_0.1mol%
Sample ID	:
Sample Type	: Unknown
Injection Volume	: 1.00
ISTD Amount	:
Data Name	: D:\DATA\York\YSIV743_01mol%.gcd
Method Name	: D:\DATA\York\Methode Line 2 amine_mittellang_methoxyimin.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	5.484	52412	13612	1.913				
2	7.261	64747	17394	2.364				
3	9.891	16708	4060	0.610				
4	14.963	1062	209	0.039				
5	15.354	1417	278	0.052				
6	19.747	1144954	157198	41.800				
7	21.167	1447577	175813	52.848				
8	23.319	10268	1160	0.375				
Total		2739145	369724					

0.5 mol%:

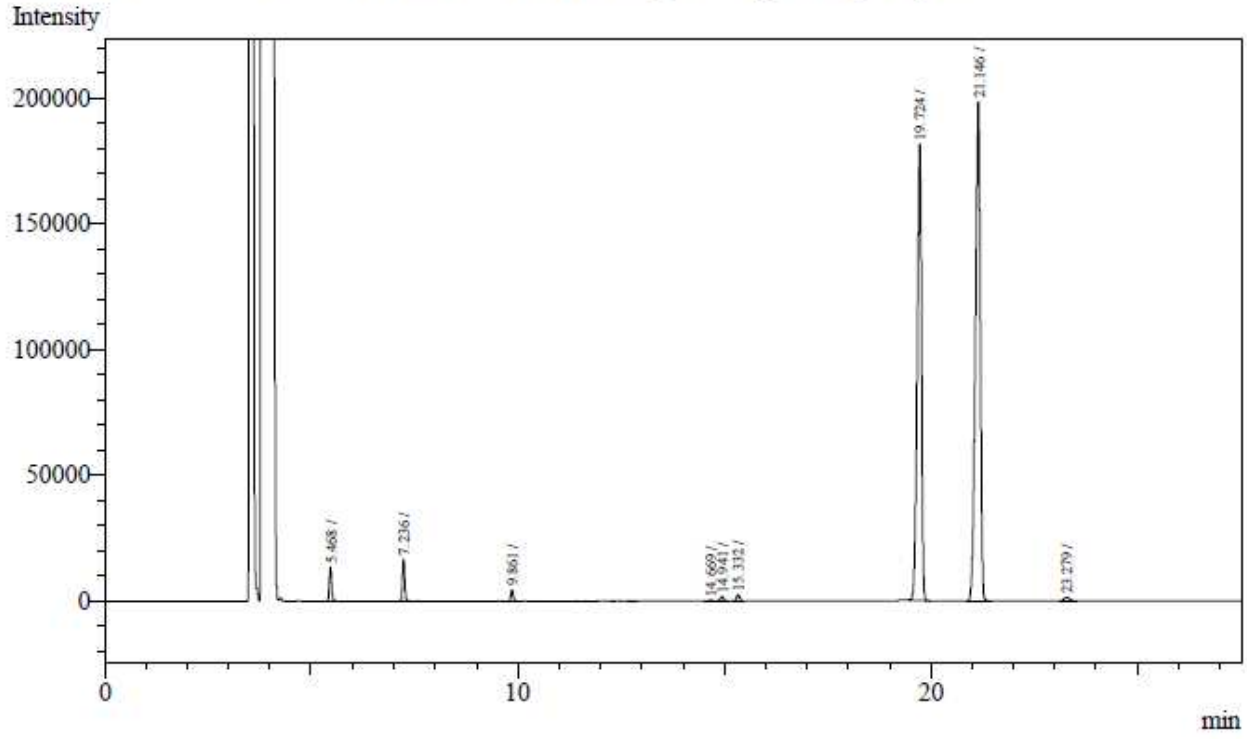
Analysis Date & Time	: 12/26/2012 9:17:46 AM
User Name	: User
Vial#	: 27
Sample Name	: YSIV743_0.5mol%
Sample ID	:
Sample Type	: Unknown
Injection Volume	: 1.00
ISTD Amount	:
Data Name	: D:\DATA\York\YSIV743_05mol%.gcd
Method Name	: D:\DATA\York\Methode Line 2 amine_mittellang_methoxyimin.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	5.469	48404	12556	1.802				
2	7.236	59247	15985	2.206				
3	9.863	16275	3952	0.606				
4	14.709	2641	232	0.098				
5	14.939	4526	855	0.168		V		
6	15.331	6555	1245	0.244				
7	19.719	1128764	155499	42.020				
8	21.136	1409568	175177	52.473				
9	23.281	10272	1149	0.382				
Total		2686252	366650					

1.0 mol%:

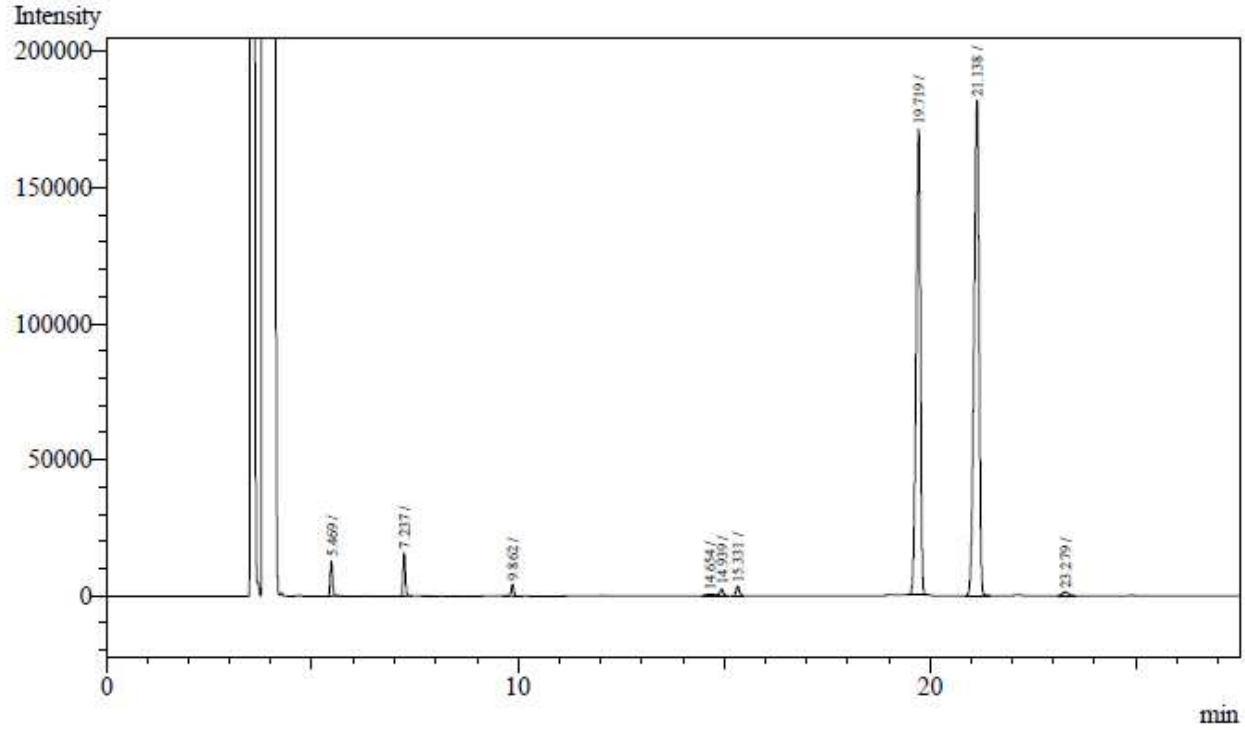
Analysis Date & Time	: 12/26/2012 9:49:18 AM
User Name	: User
Vial#	: 28
Sample Name	: YSIV743_1mol%
Sample ID	:
Sample Type	: Unknown
Injection Volume	: 1.00
ISTD Amount	:
Data Name	: D:\DATA\York\YSIV743_1mol%.gcd
Method Name	: D:\DATA\York\Methode Line 2 amine_mittellang_methoxyimin.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	5.468	51756	13411	1.663				
2	7.236	62239	16797	2.000				
3	9.861	18850	4590	0.606				
4	14.669	2313	207	0.074				
5	14.941	8909	1731	0.286		V		
6	15.332	13392	2536	0.430				
7	19.724	1315954	181241	42.285				
8	21.146	1626919	198259	52.277				
9	23.279	11808	1295	0.379				
Total		3112140	420067					

2.0 mol%:

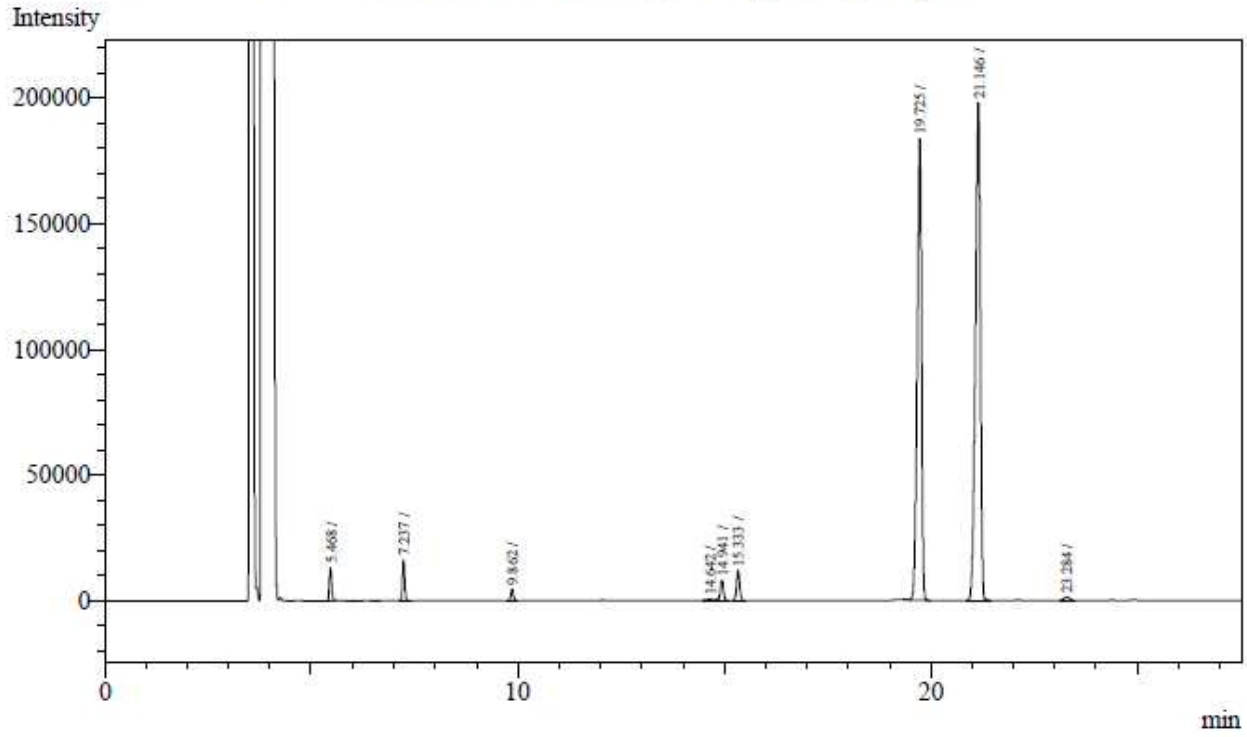
Analysis Date & Time	: 12/26/2012 10:20:49 AM
User Name	: User
Vial#	: 29
Sample Name	: YSIV743_2mol%
Sample ID	:
Sample Type	: Unknown
Injection Volume	: 1.00
ISTD Amount	:
Data Name	: D:\DATA\York\YSIV743_2mol%.gcd
Method Name	: D:\DATA\York\Methode Line 2 amine_mittellang_methoxyimin.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	5.469	49373	12788	1.689				
2	7.237	59466	16019	2.035				
3	9.862	17622	4270	0.603				
4	14.654	6086	480	0.208				
5	14.939	12142	2322	0.415		V		
6	15.331	17951	3435	0.614				
7	19.719	1229163	171178	42.054				
8	21.138	1519626	181891	51.992				
9	23.279	11403	1283	0.390				
Total		2922832	393666					

5.0 mol%:

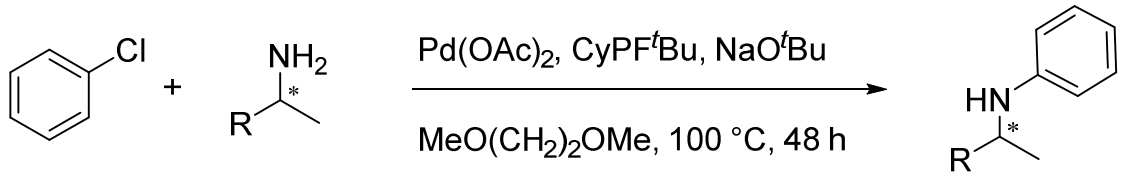
Analysis Date & Time	: 12/26/2012 10:52:22 AM
User Name	: User
Vial#	: 30
Sample Name	: YSIV743_5mol%
Sample ID	:
Sample Type	: Unknown
Injection Volume	: 1.00
ISTD Amount	:
Data Name	: D:\DATA\York\YSIV743_5mol%.gcd
Method Name	: D:\DATA\York\Methode Line 2 amine_mittellang_methoxyimin.gcm



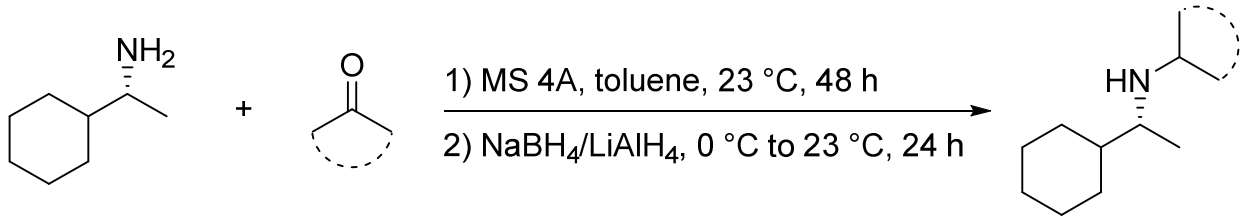
Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	5.468	50287	13049	1.558				
2	7.237	59722	16237	1.850				
3	9.862	18934	4611	0.586				
4	14.642	4852	391	0.150				
5	14.941	40982	8036	1.269		V		
6	15.333	63591	11973	1.970				
7	19.725	1337816	183595	41.439				
8	21.146	1640861	197917	50.826				
9	23.284	11352	1287	0.352				
Total		3228397	437096					

Assignment of the absolute configuration:

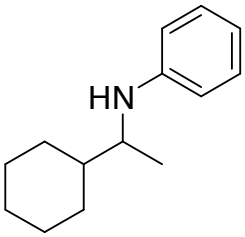
The absolute configuration of **A3**, **A28**, **A30** and **A32** was assigned by comparison of the chiral staionary phase GC or HPLC data obtained after conducting a Buchwald-Hartwig amination.[29]

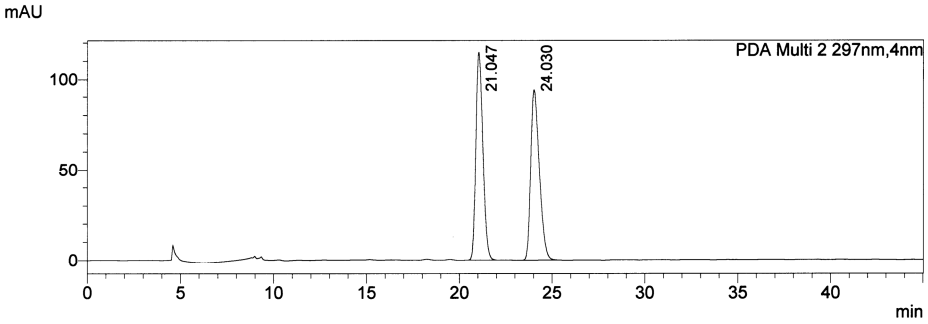


The absolute configuration of **A33** to **A36** was assigned by comparison of the chiral staionary phase GC or HPLC data obtained after condensation of (*R*)-cyclohexylethylamine with the corresonding aldehyde and subsequent reduction with $NaBH_4$ or $LiAlH_4$.



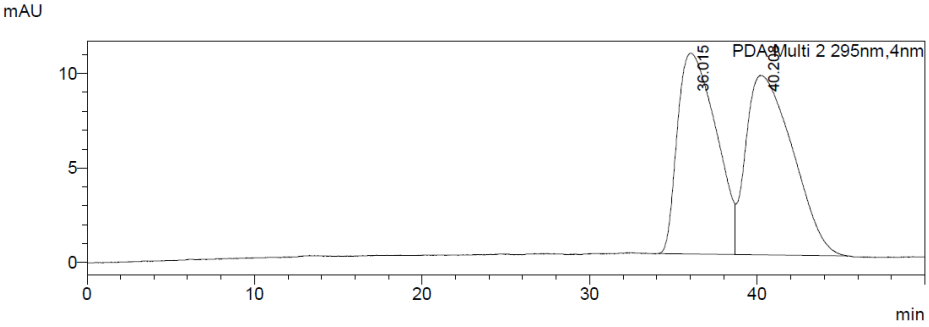
[29] Q. Shen, S. Shekhar, J. P. Stambuli, J. F. Hartwig, *Angew. Chem. Int. Ed.* **2005**, *44*, 1371-1375





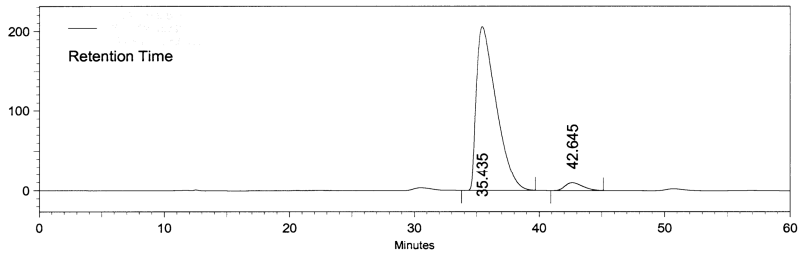
PDA Ch2 297nm

Peak#	Ret. Time	Height	Area	Area%
1	21.047	114588	3024054	49.941
2	24.030	93622	3031200	50.059
Total		208210	6055254	100.000



PDA Ch2 295nm

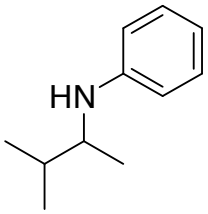
Peak#	Ret. Time	Height	Area	Area%
1	36.015	10650	1710001	48.094
2	40.208	9515	1845518	51.906
Total		20165	3555519	100.000

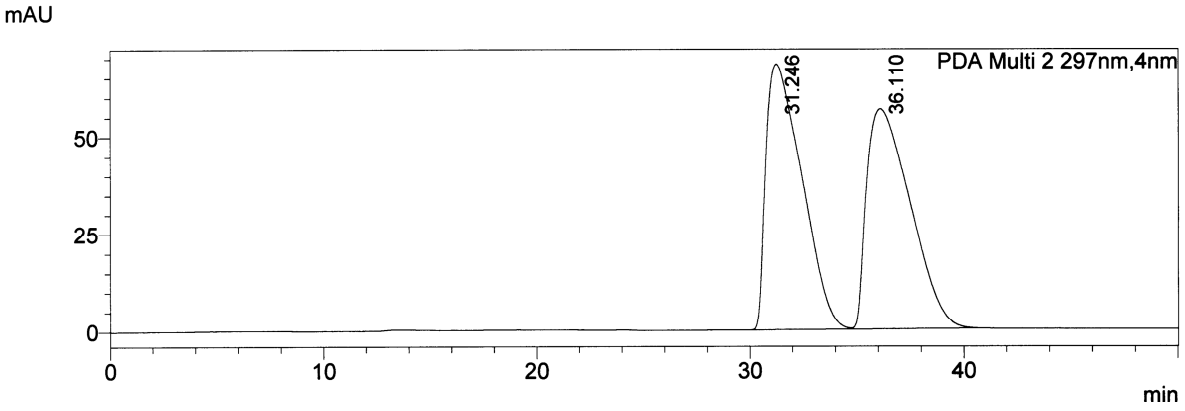


2: 297 nm, 8 nm

Retention Time	Area	Area Percent
35.435	22615329	96.04
42.645	931978	3.96

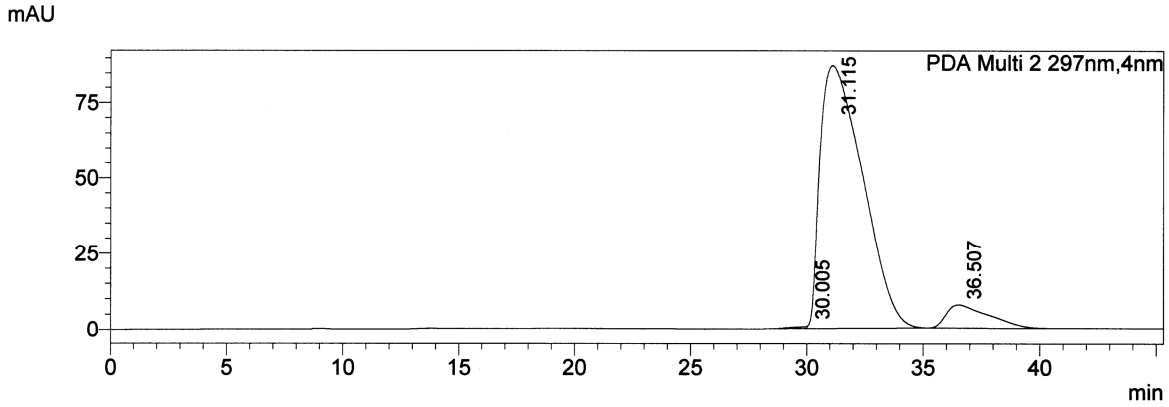
Totals		
	23547307	100.00





PDA Ch2 297nm

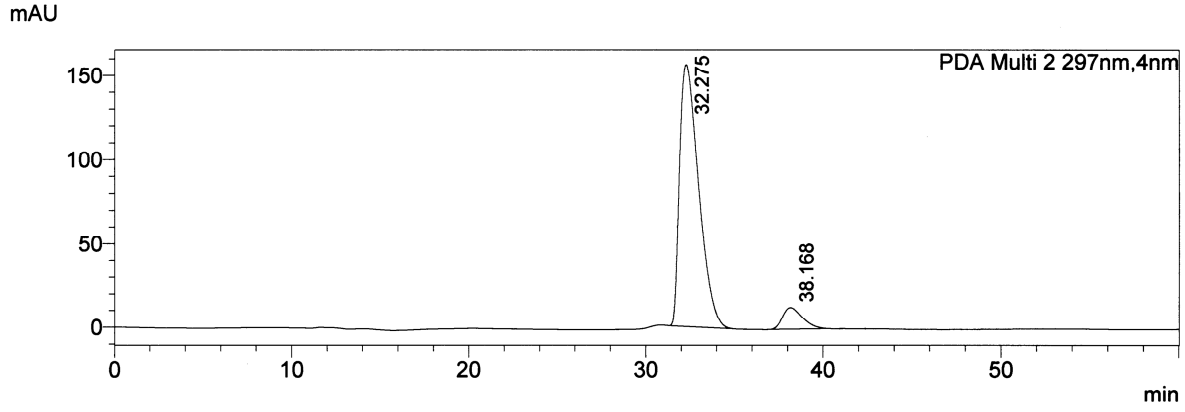
Peak#	Ret. Time	Height	Area	Area%
1	31.246	68088	7994697	49.963
2	36.110	56439	8006492	50.037
Total		124527	16001189	100.000



PDA Ch2 297nm

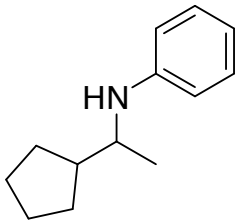
Peak#	Ret. Time	Height	Area	Area%
1	30.005	725	34796	0.289
2	31.115	87082	11055434	91.786
3	36.507	7557	954612	7.925
Total		95365	12044842	100.000

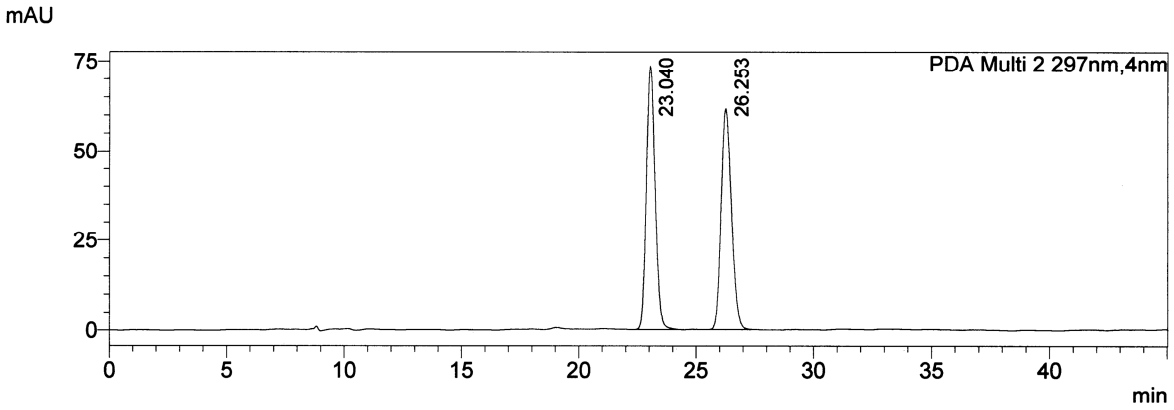
} 84%



PDA Ch2 297nm

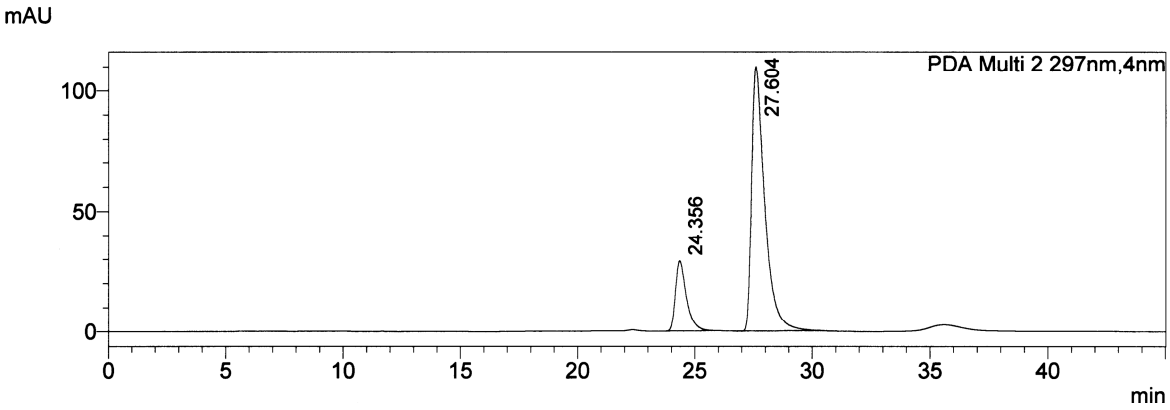
Peak#	Ret. Time	Height	Area	Area%
1	32.275	156101	11741060	91.997
2	38.168	13037	1021403	8.003
Total		169139	12762464	100.000





PDA Ch2 297nm

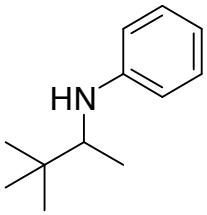
Peak#	Ret. Time	Height	Area	Area%
1	23.040	73324	1911766	50.234
2	26.253	61664	1893984	49.766
Total		134988	3805750	100.000

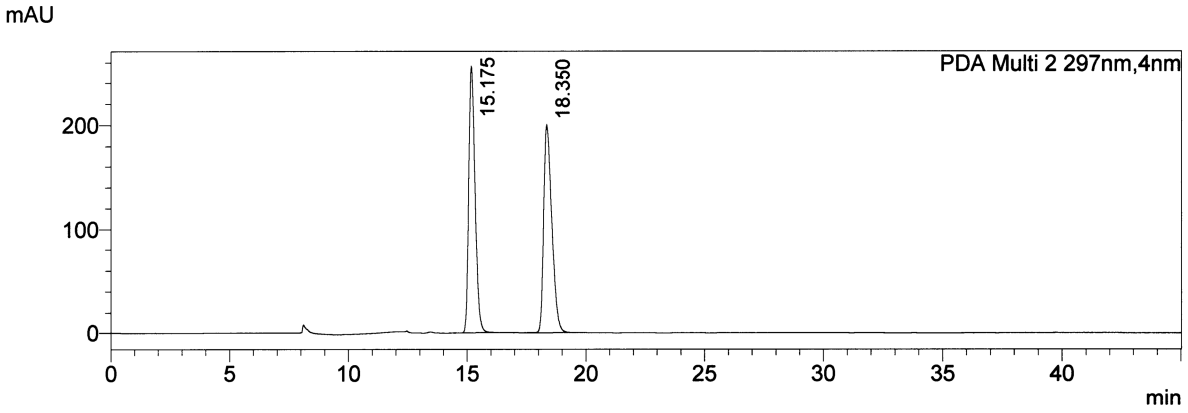


PDA Ch2 297nm

Peak#	Ret. Time	Height	Area	Area%
1	24.356	29165	954064	18.201
2	27.604	109881	4287784	81.799
Total		139046	5241848	100.000

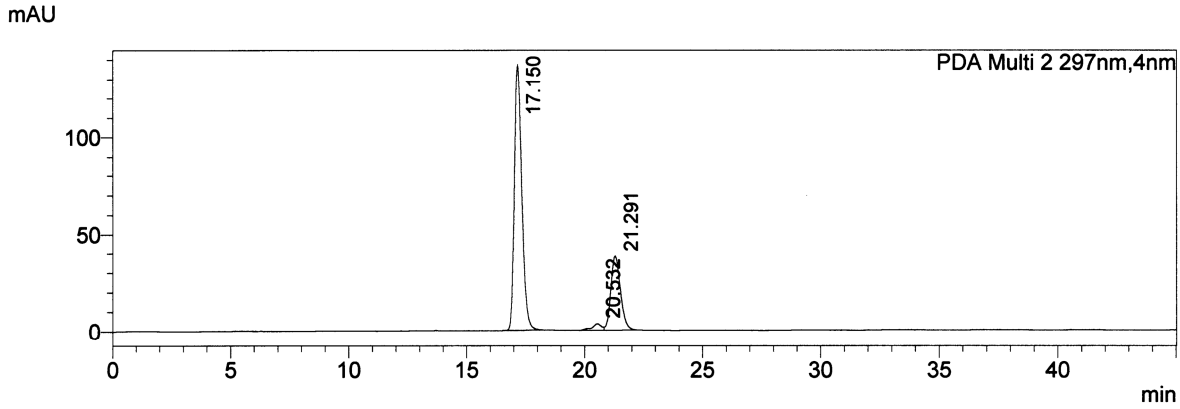
63,558





PDA Ch2 297nm

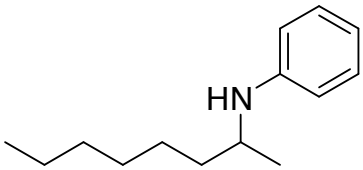
Peak#	Ret. Time	Height	Area	Area%
1	15.175	256078	4782576	49.961
2	18.350	200273	4790128	50.039
Total		456350	9572704	100.000

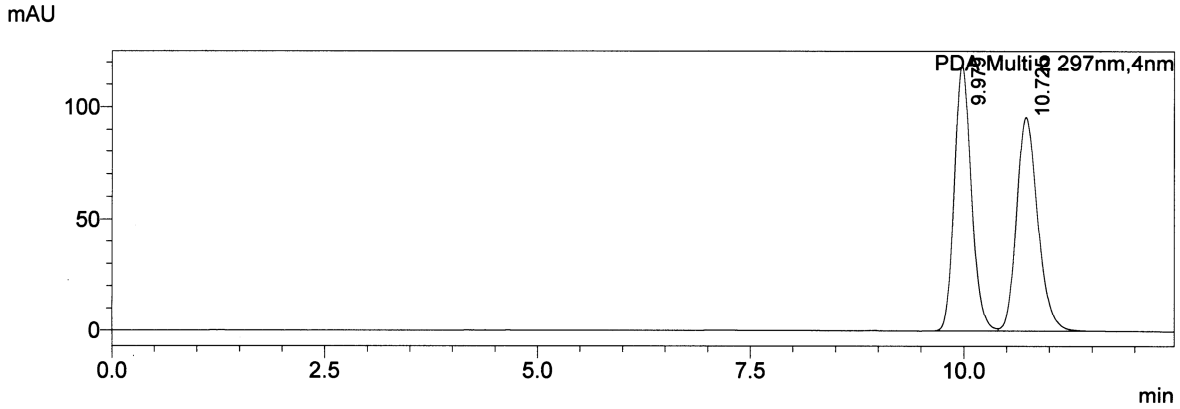


PDA Ch2 297nm

Peak#	Ret. Time	Height	Area	Area%
1	17.150	136557	2992392	71.911
2	20.532	3243	91804	2.206
3	21.291	37948	1077050	25.883
Total		177747	4161246	100.000

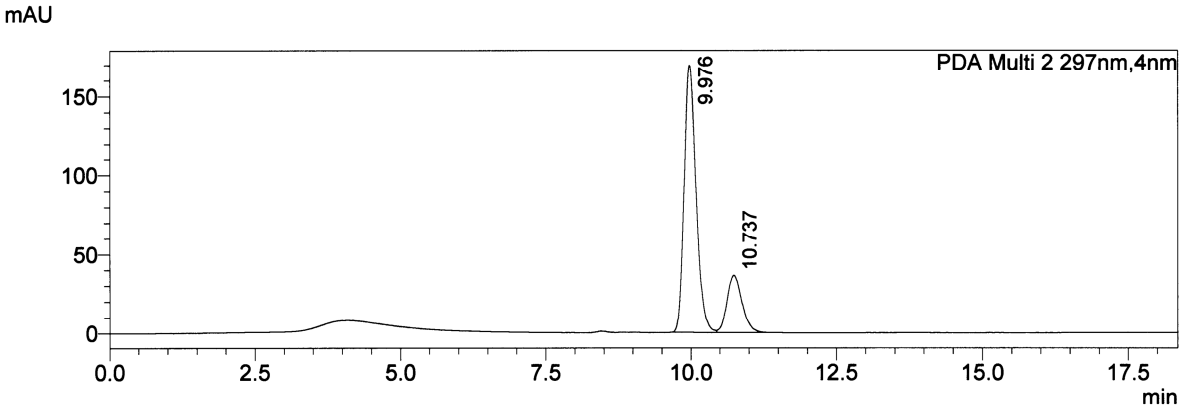
41'068'442 47,07 7.





PDA Ch2 297nm

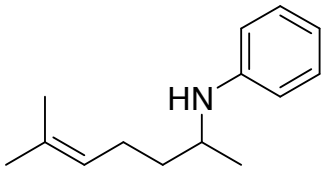
Peak#	Ret. Time	Height	Area	Area%
1	9.979	118511	1654369	49.948
2	10.725	95686	1657784	50.052
Total		214197	3312152	100.000

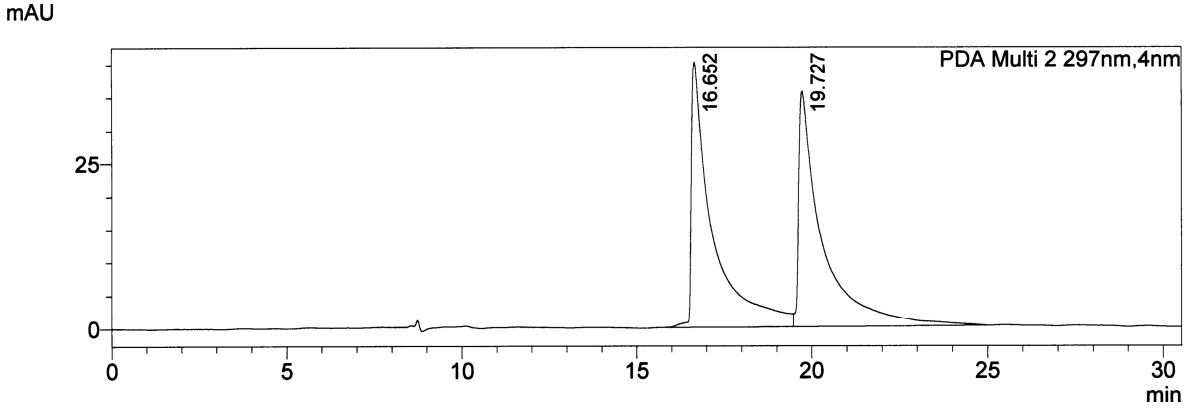


PDA Ch2 297nm

Peak#	Ret. Time	Height	Area	Area%
1	9.976	169269	2418559	78.794
2	10.737	36191	650908	21.206
Total		205461	3069467	100.000

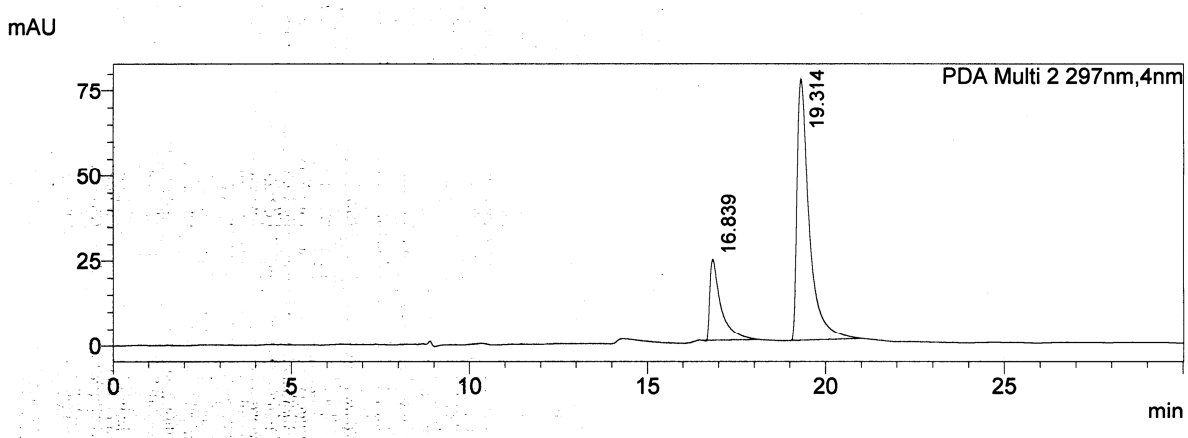
57,588





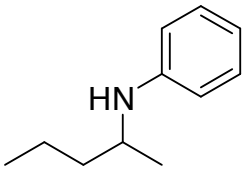
PDA Ch2 297nm

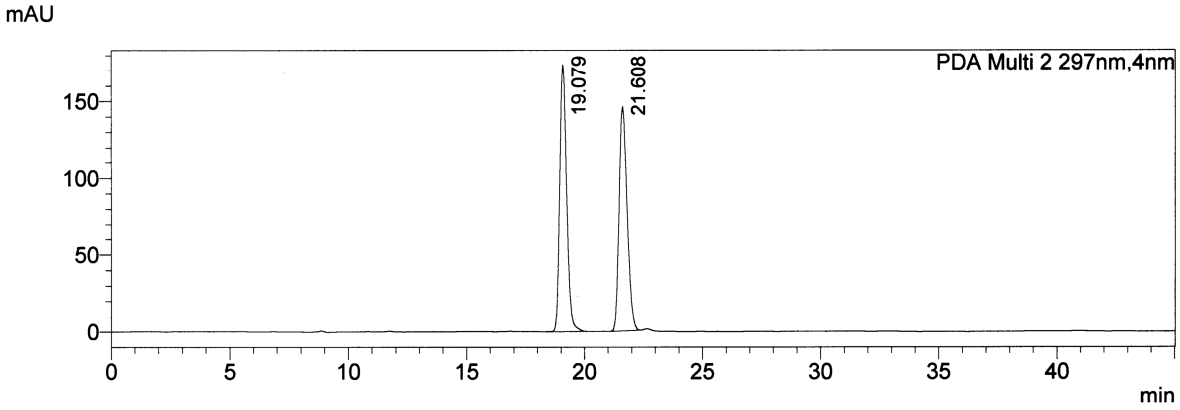
Peak#	Ret. Time	Height	Area	Area%
1	16.652	40190	1685856	50.330
2	19.727	35639	1663753	49.670
Total		75829	3349609	100.000



PDA Ch2 297nm

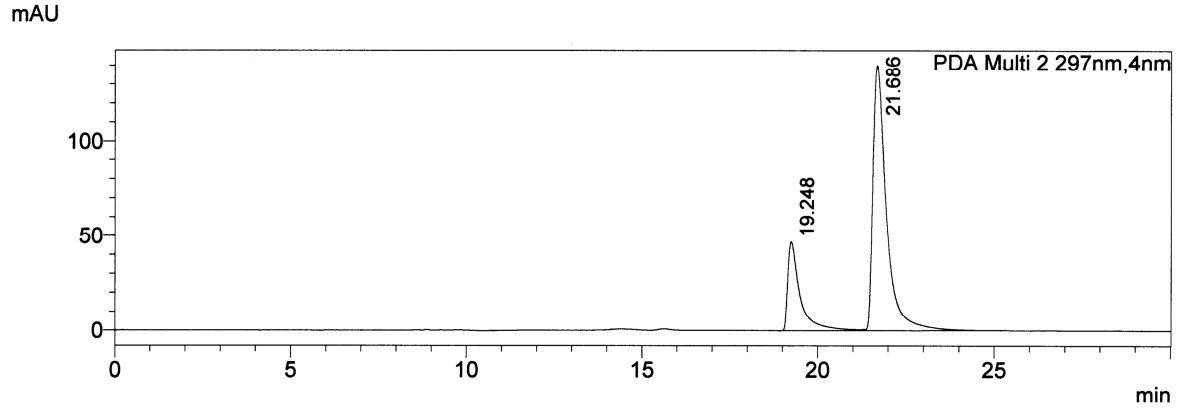
Peak#	Ret. Time	Height	Area	Area%
1	16.839	23802	520325	22.074
2	19.314	76989	1836837	77.926
Total		100792	2357162	100.000





PDA Ch2 297nm

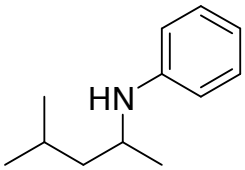
Peak#	Ret. Time	Height	Area	Area%
1	19.079	173496	3550850	50.591
2	21.608	145939	3467845	49.409
Total		319435	7018695	100.000

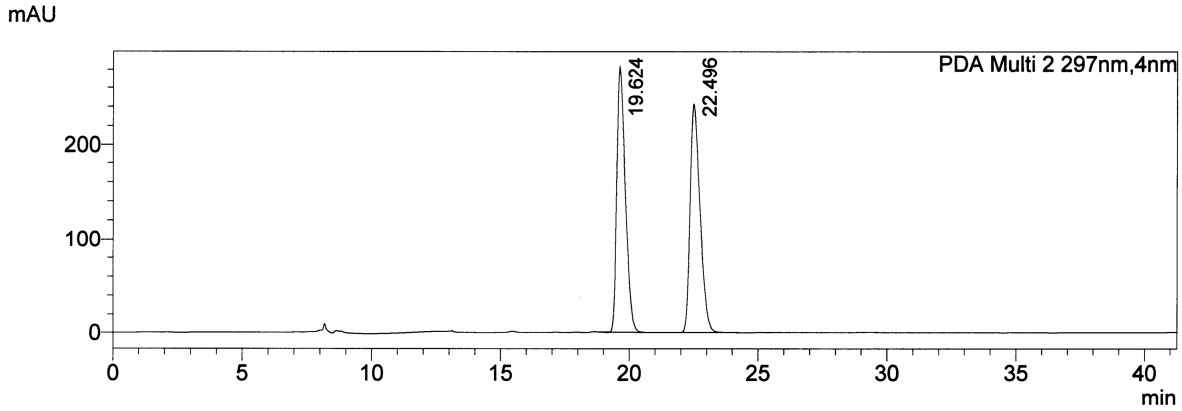


PDA Ch2 297nm

Peak#	Ret. Time	Height	Area	Area%
1	19.248	47004	1157581	23.582
2	21.686	140120	3751066	76.418
Total		187124	4908646	100.000

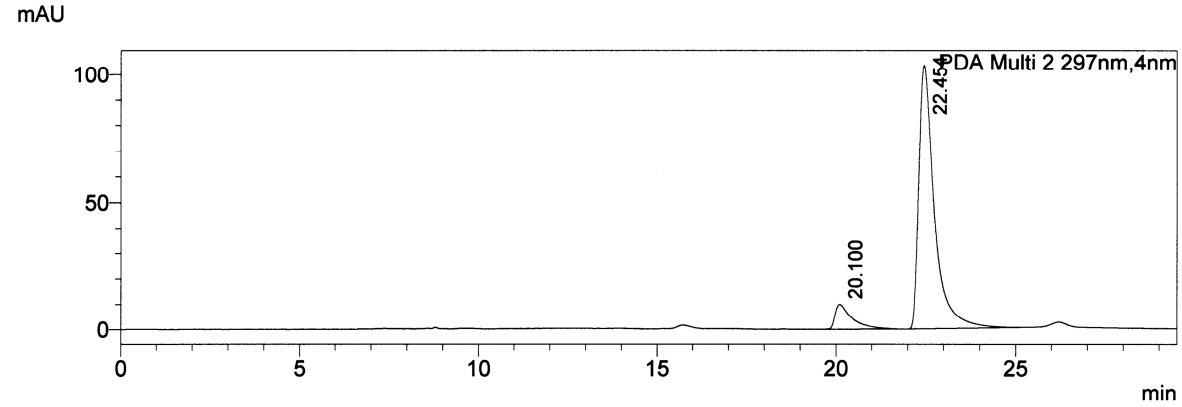
} 52,84





PDA Ch2 297nm

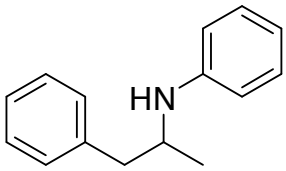
Peak#	Ret. Time	Height	Area	Area%
1	19.624	282804	6518241	49.828
2	22.496	242837	6563228	50.172
Total		525641	13081469	100.000

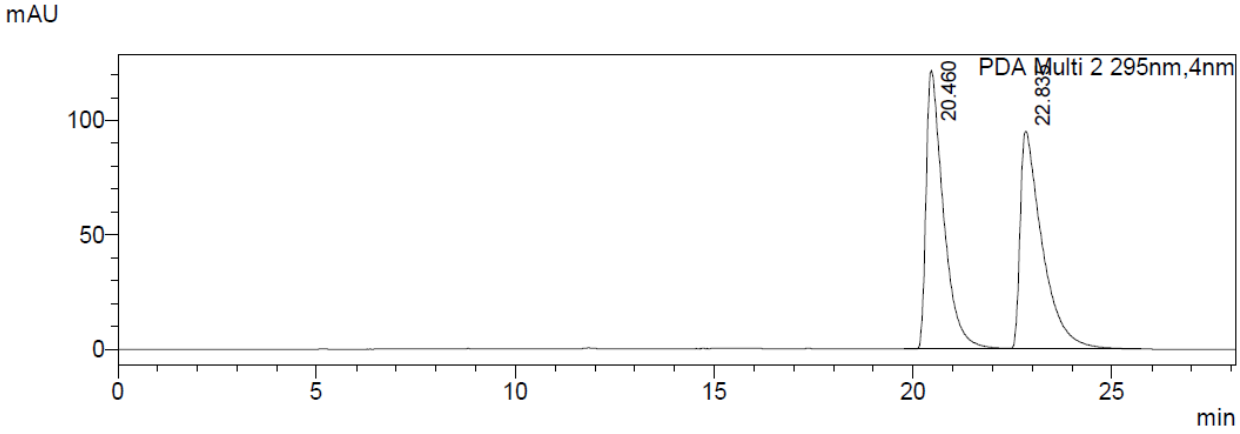


PDA Ch2 297nm

Peak#	Ret. Time	Height	Area	Area%
1	20.100	9899	330362	9.550
2	22.454	103484	3128783	90.450
Total		113383	3459145	100.000

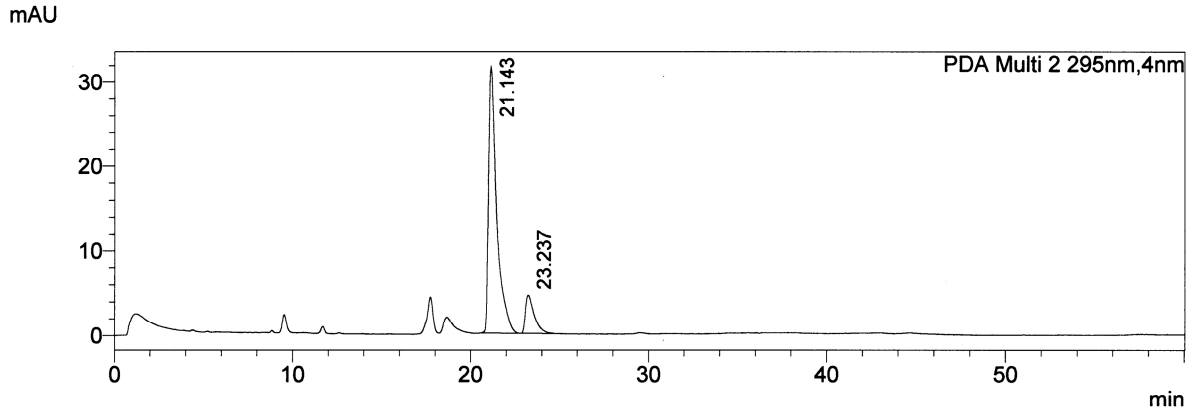
} 86.9





PDA Ch2 295nm

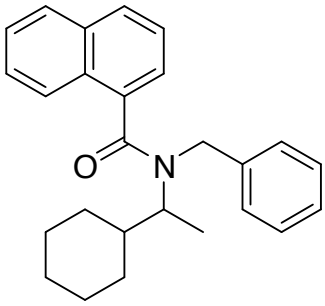
Peak#	Ret. Time	Height	Area	Area%
1	20.460	121696	3702809	50.106
2	22.835	95110	3687109	49.894
Total		216806	7389918	100.000

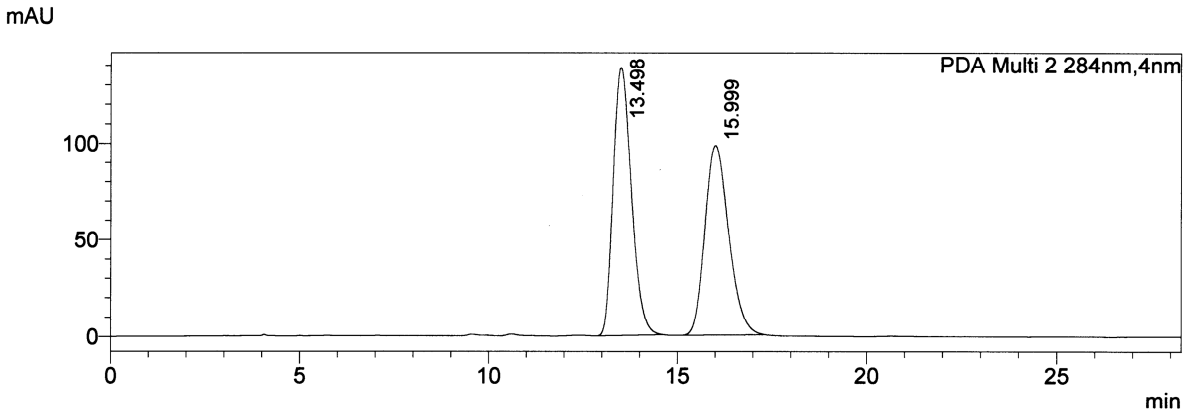


PDA Ch2 295nm

Peak#	Ret. Time	Height	Area	Area%
1	21.143	31581	1007597	86.345
2	23.237	4575	159349	13.655
Total		36156	1166946	100.000

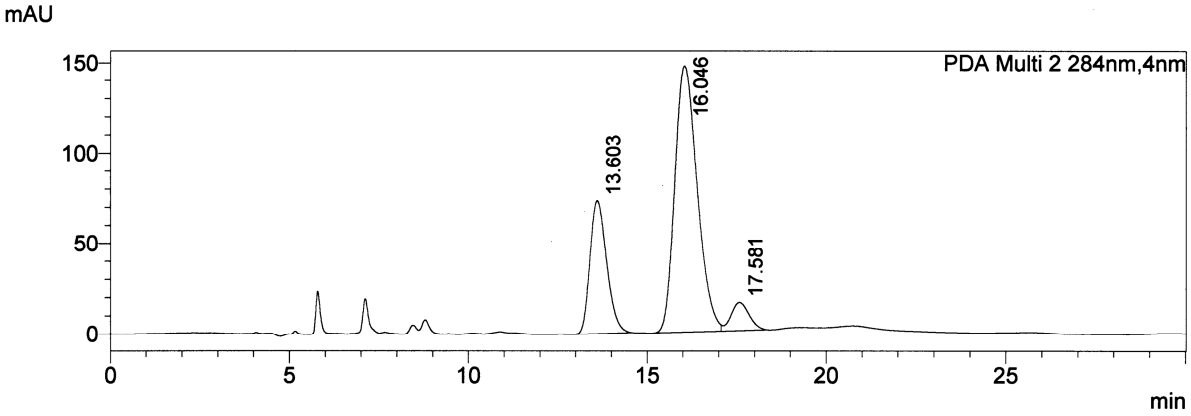
72.65





PDA Ch2 284nm

Peak#	Ret. Time	Height	Area	Area%
1	13.498	138286	4661850	51.934
2	15.999	98278	4314656	48.066
Total		236565	8976506	100.000

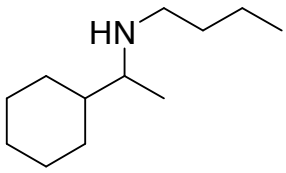


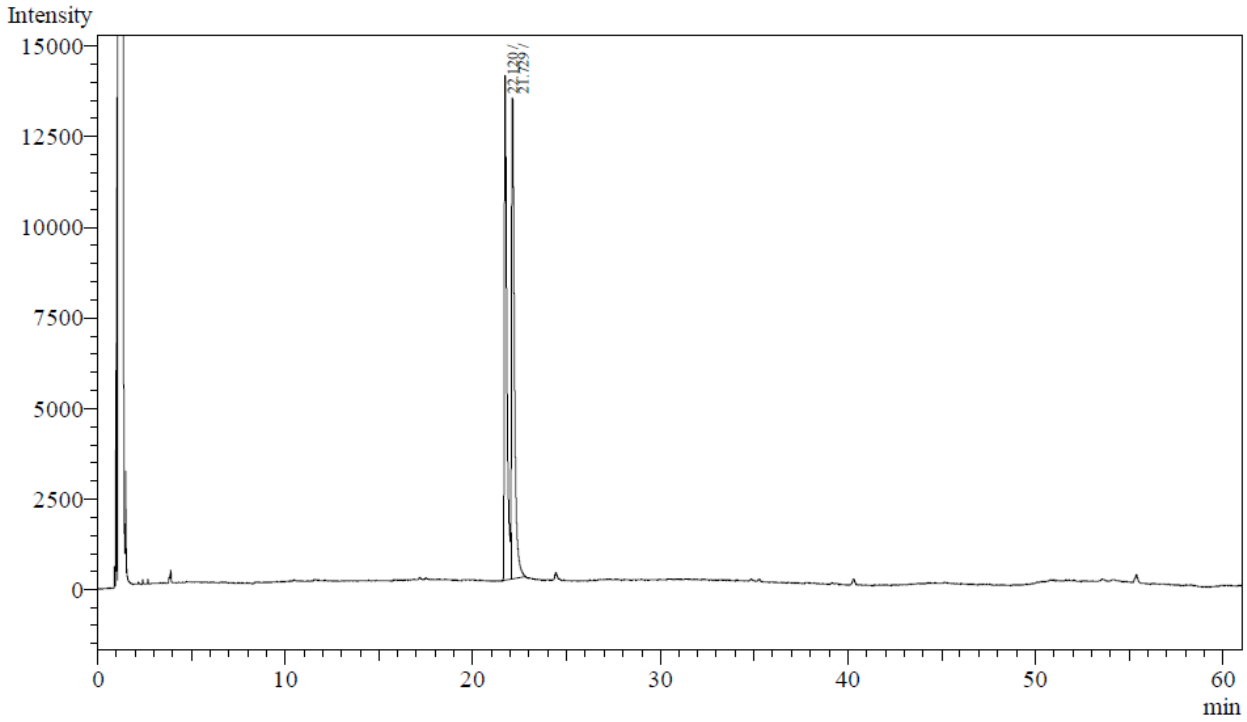
PDA Ch2 284nm

Peak#	Ret. Time	Height	Area	Area%
1	13.603	73430	2388471	25.510
2	16.046	147103	6420273	68.573
3	17.581	15464	553996	5.917
Total		235997	9362740	100.000

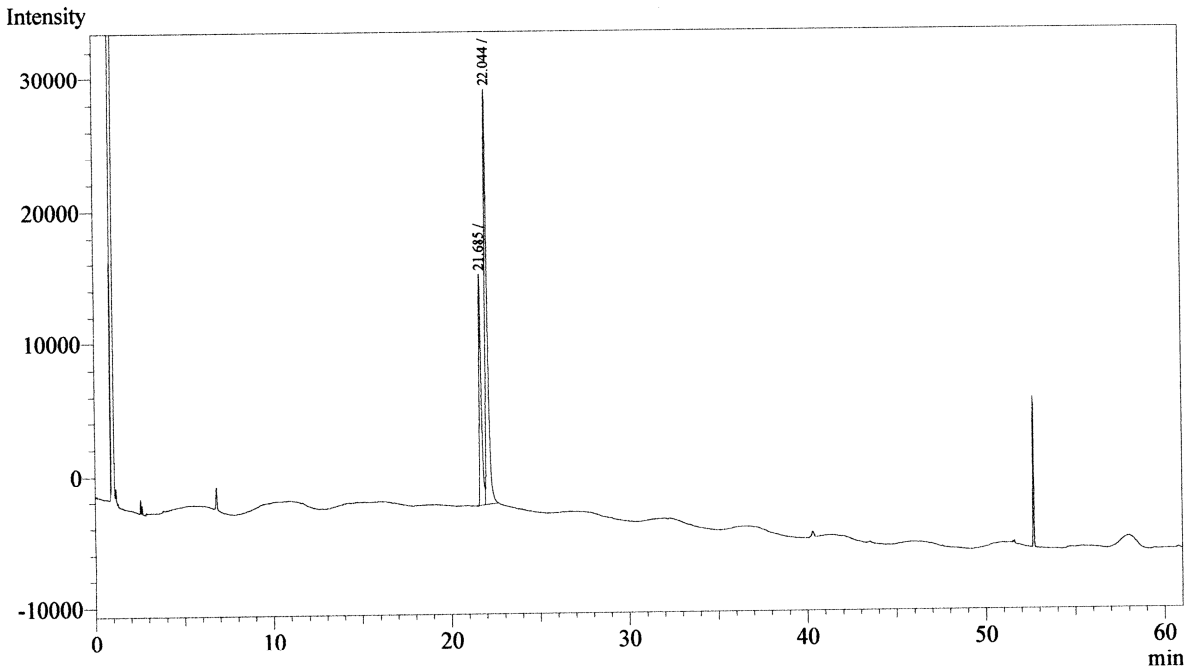
94,083

45,8% ee

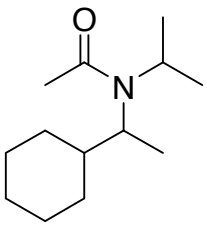


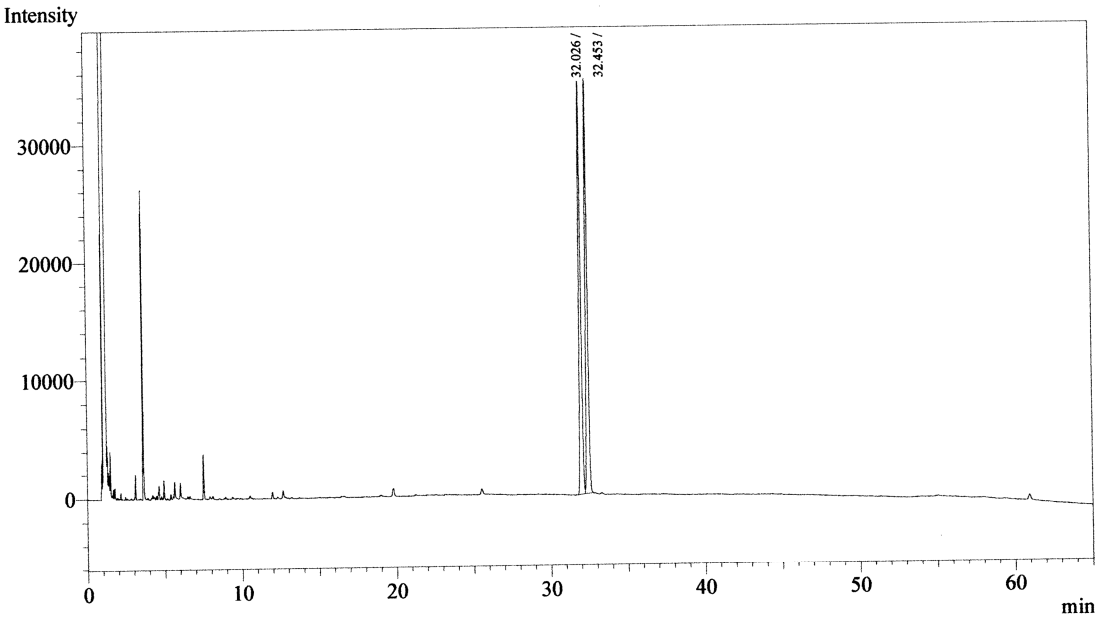


Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	21.729	130707	13907	49.629				
2	22.120	132661	13274	50.371		V		
Total		263368	27181					

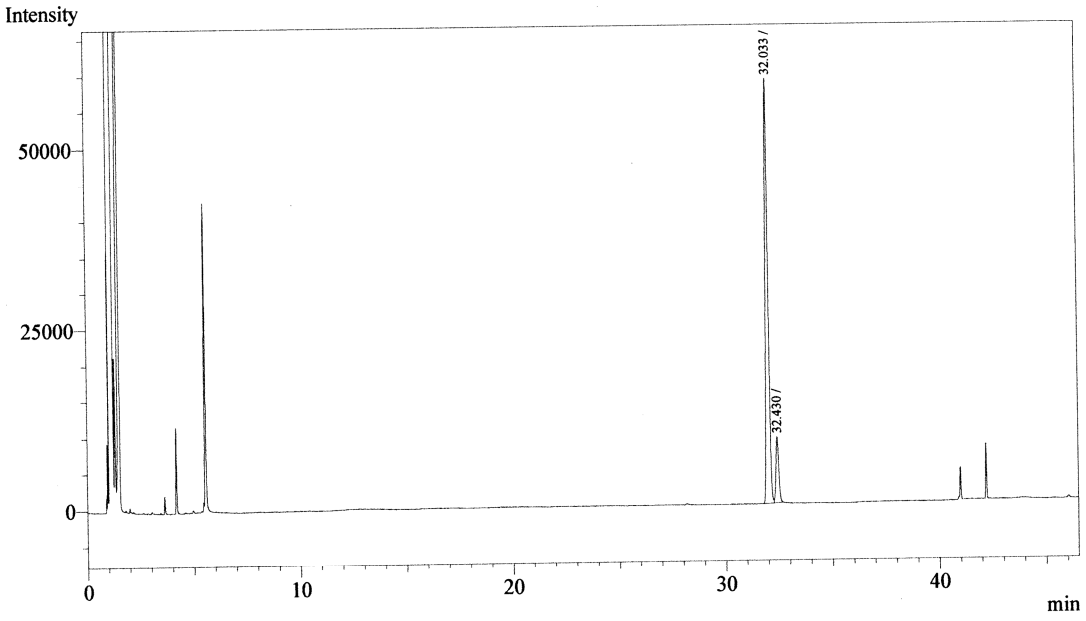


Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	21.685	145797	17468	33.538				
2	22.044	288919	31362	66.462		V		
Total		434716	48830					

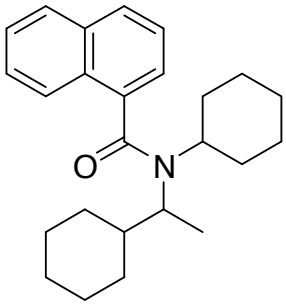


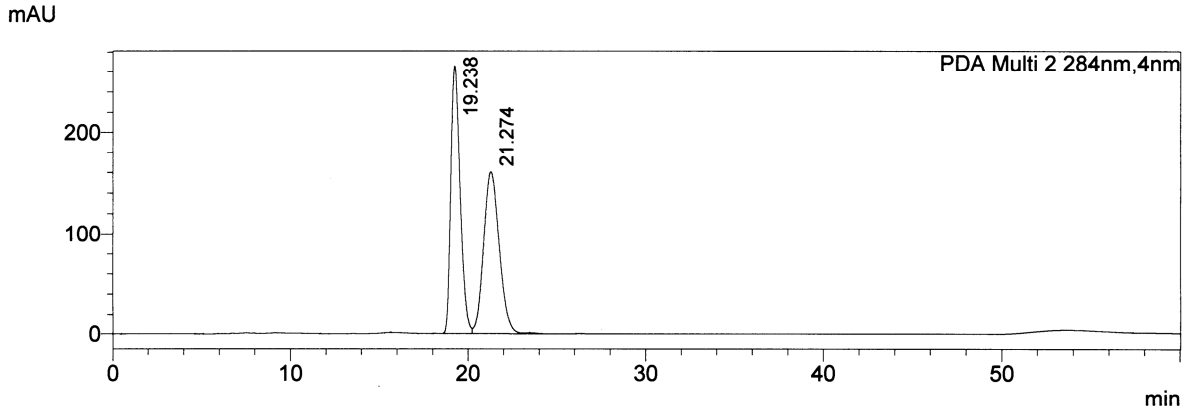


Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	32.026	313719	35135	49.927				
2	32.453	314638	35275	50.073		V		
Total		628357	70410					



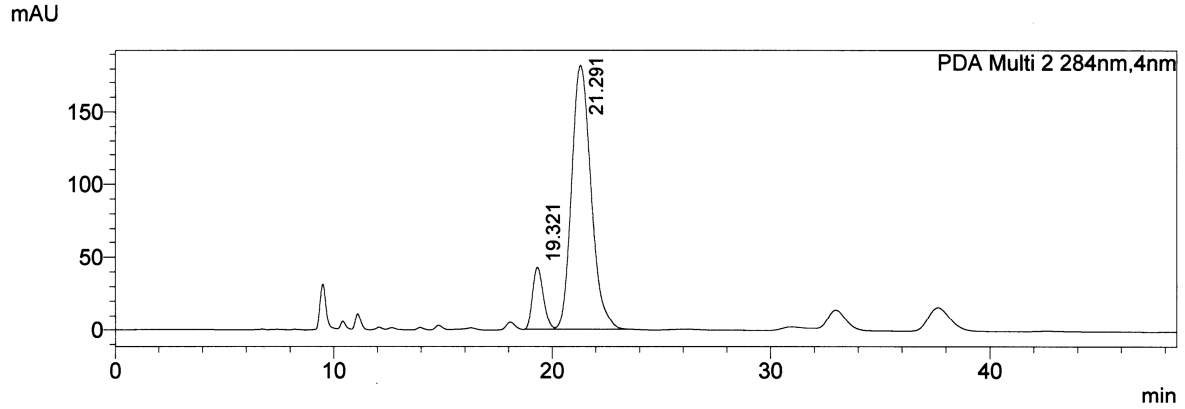
Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	32.033	526515	58948	86.326				
2	32.430	83398	9189	13.674		V		
Total		609913	68137					





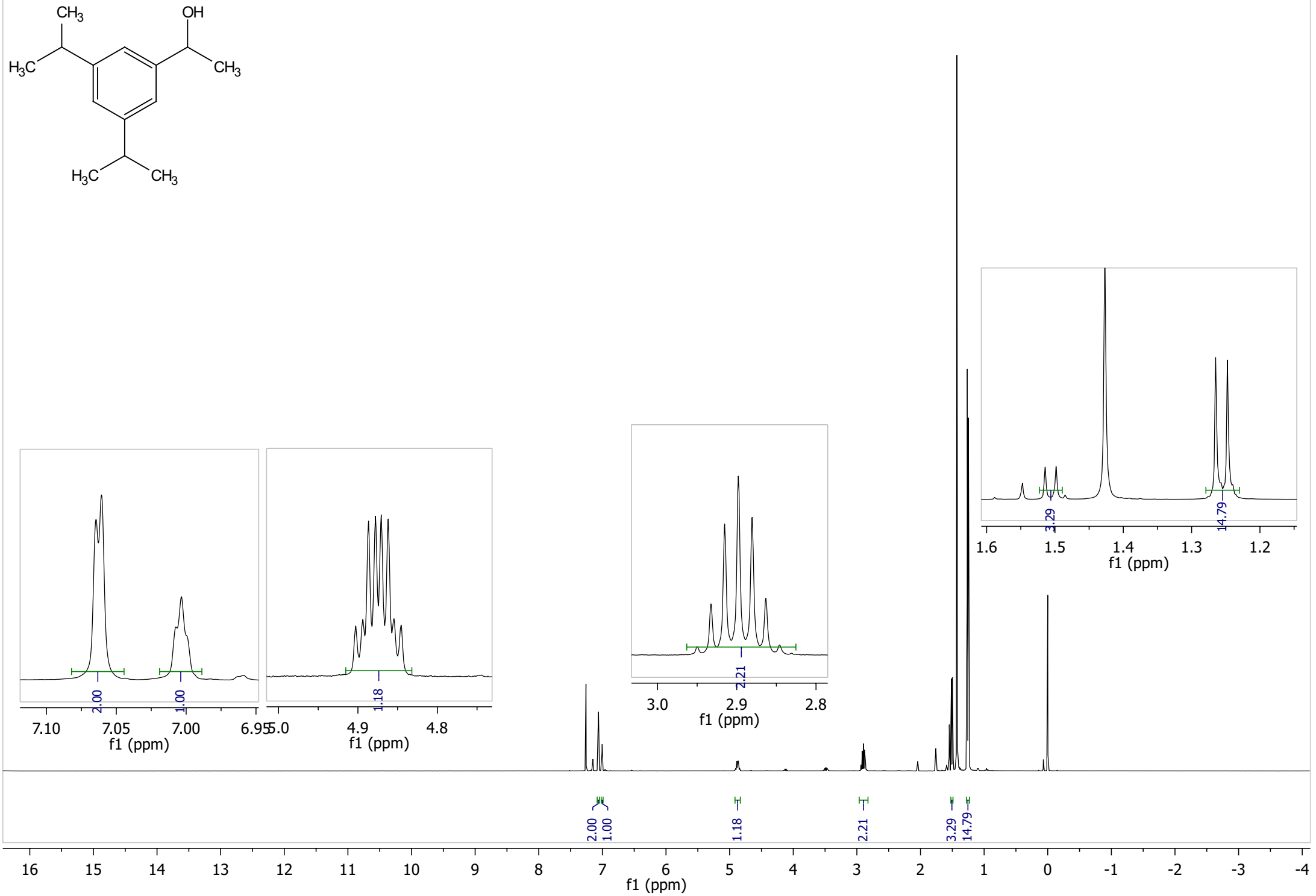
PDA Ch2 284nm

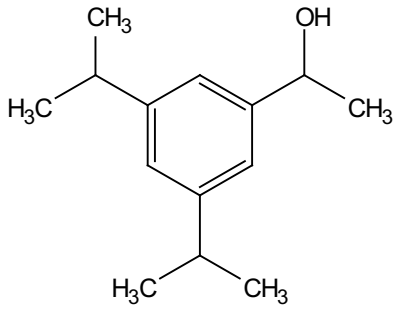
Peak#	Ret. Time	Height	Area	Area%
1	19.238	265837	9745832	49.511
2	21.274	160475	9938165	50.489
Total		426312	19683997	100.000

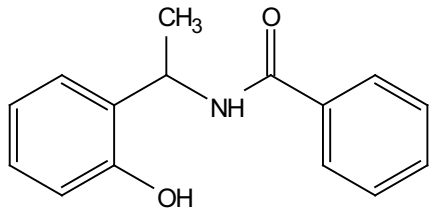


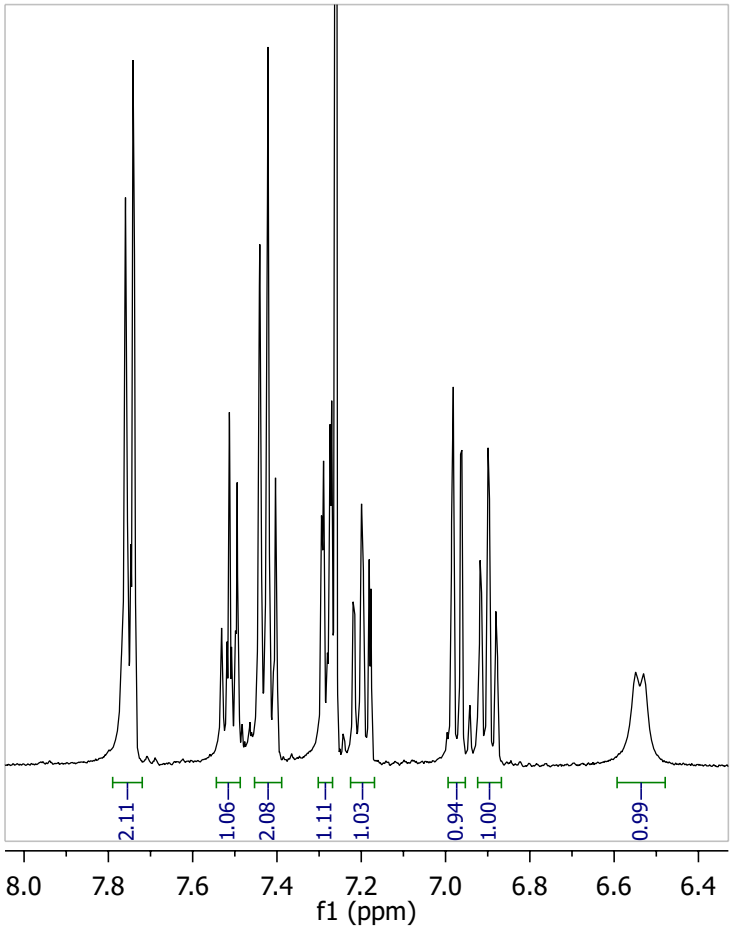
PDA Ch2 284nm

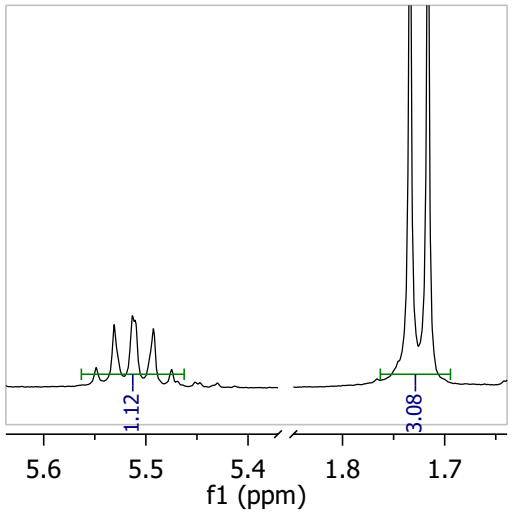
Peak#	Ret. Time	Height	Area	Area%
1	19.321	42688	1474299	11.553
2	21.291	181961	11287356	88.447
Total		224650	12761655	100.000

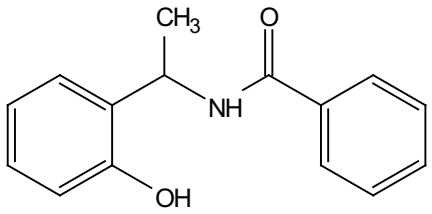


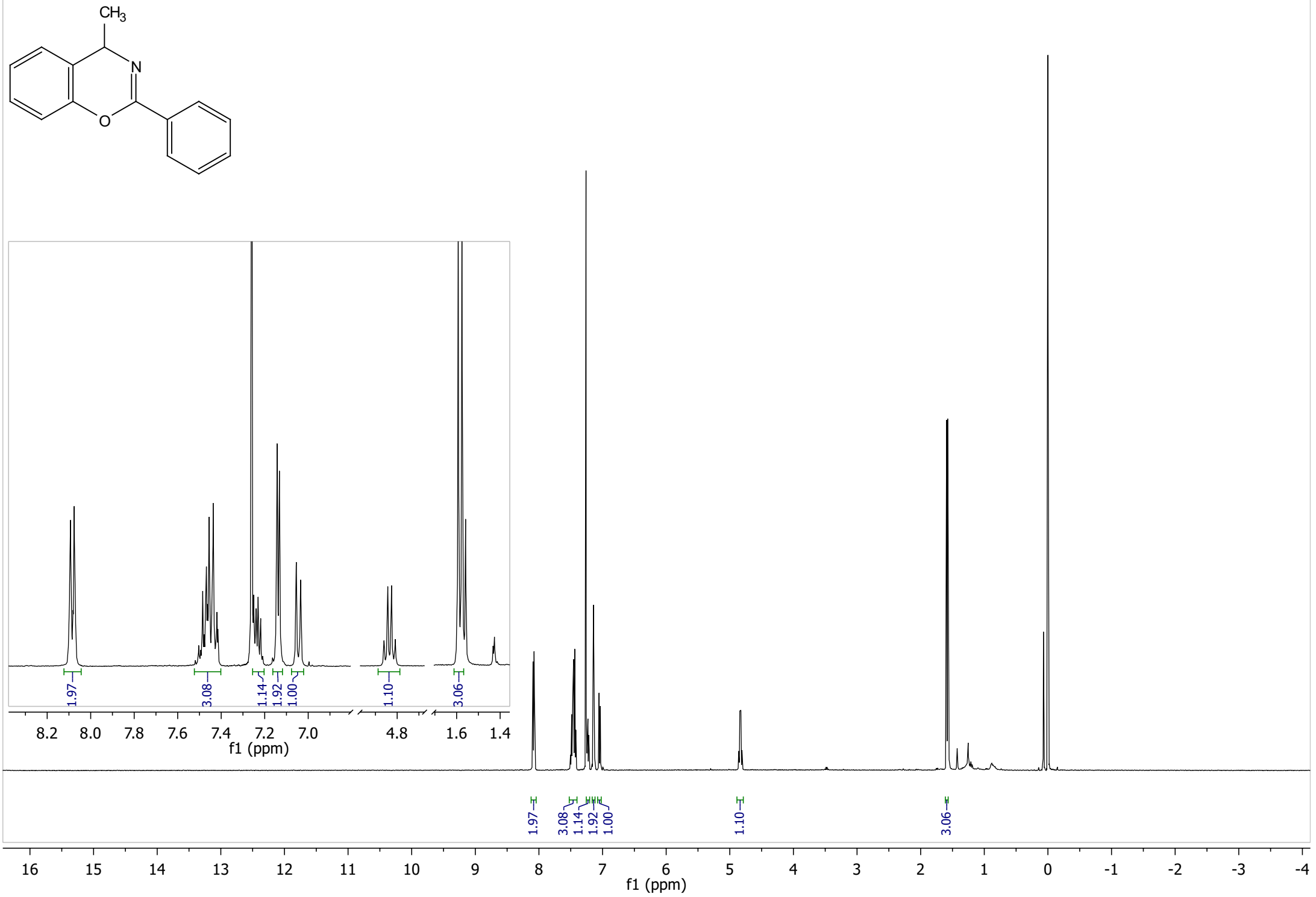


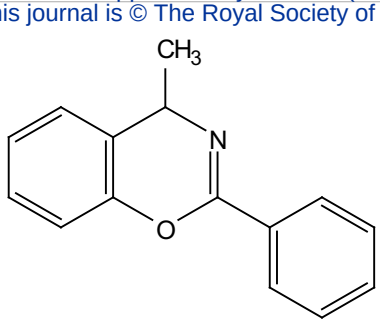








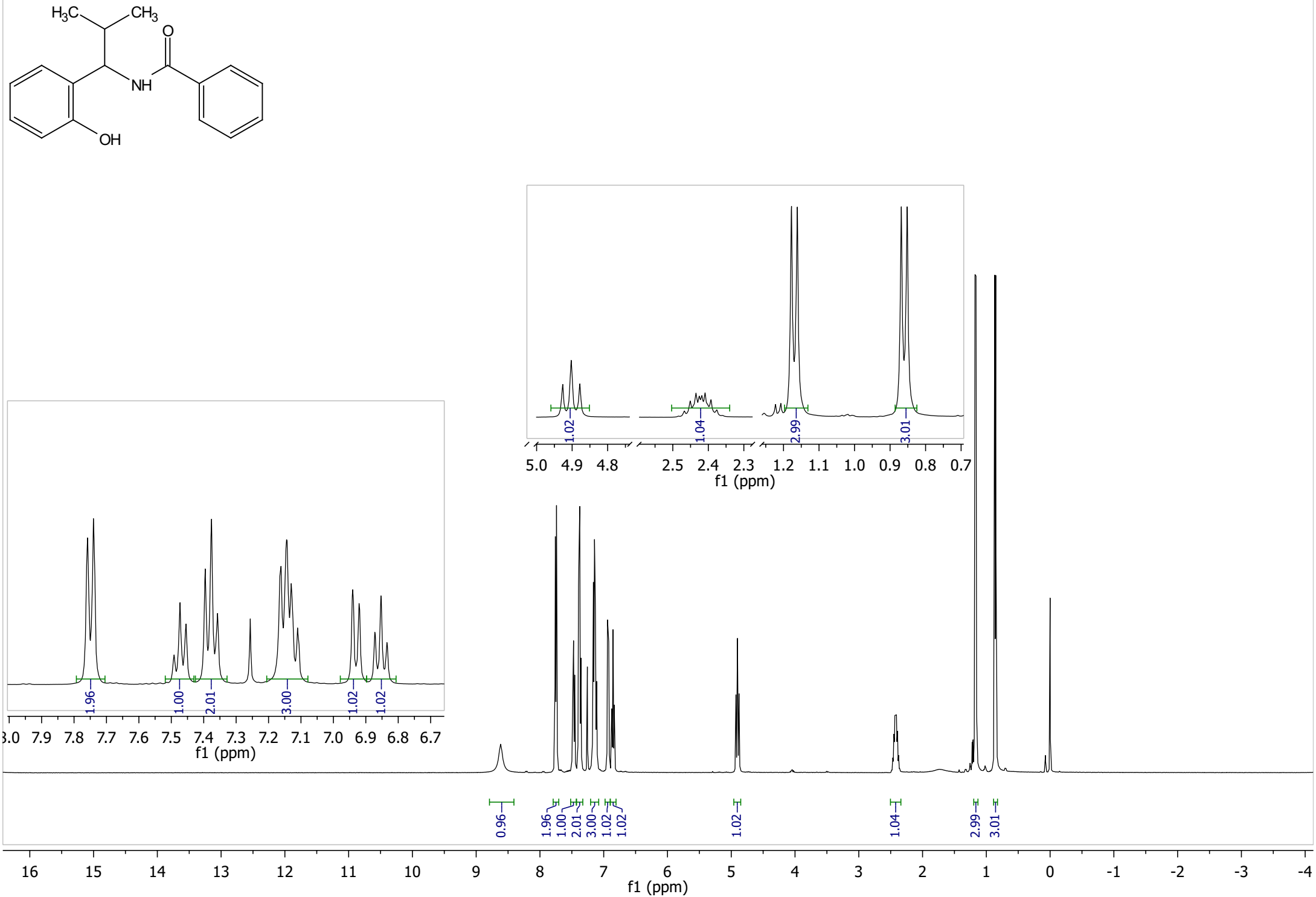


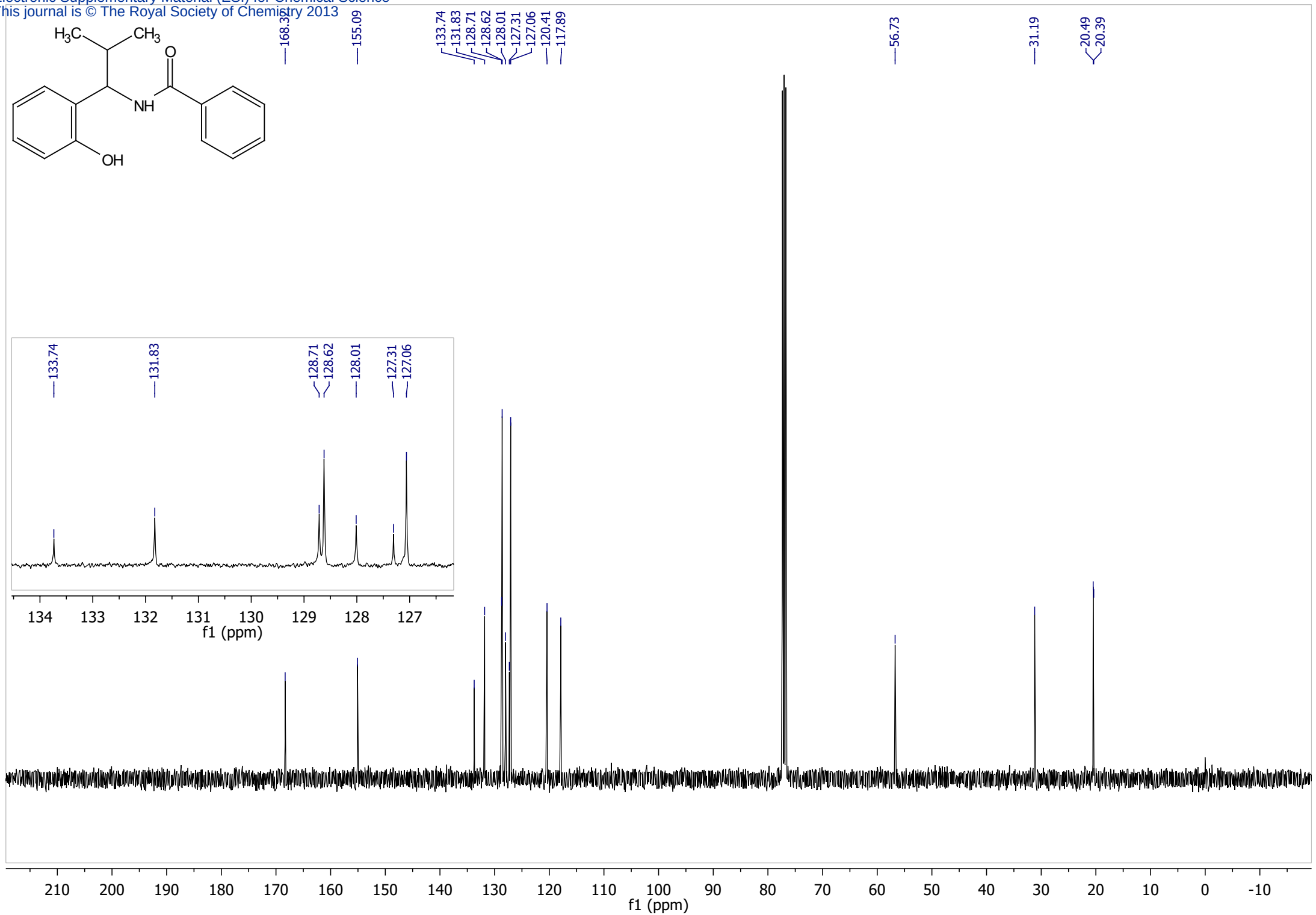


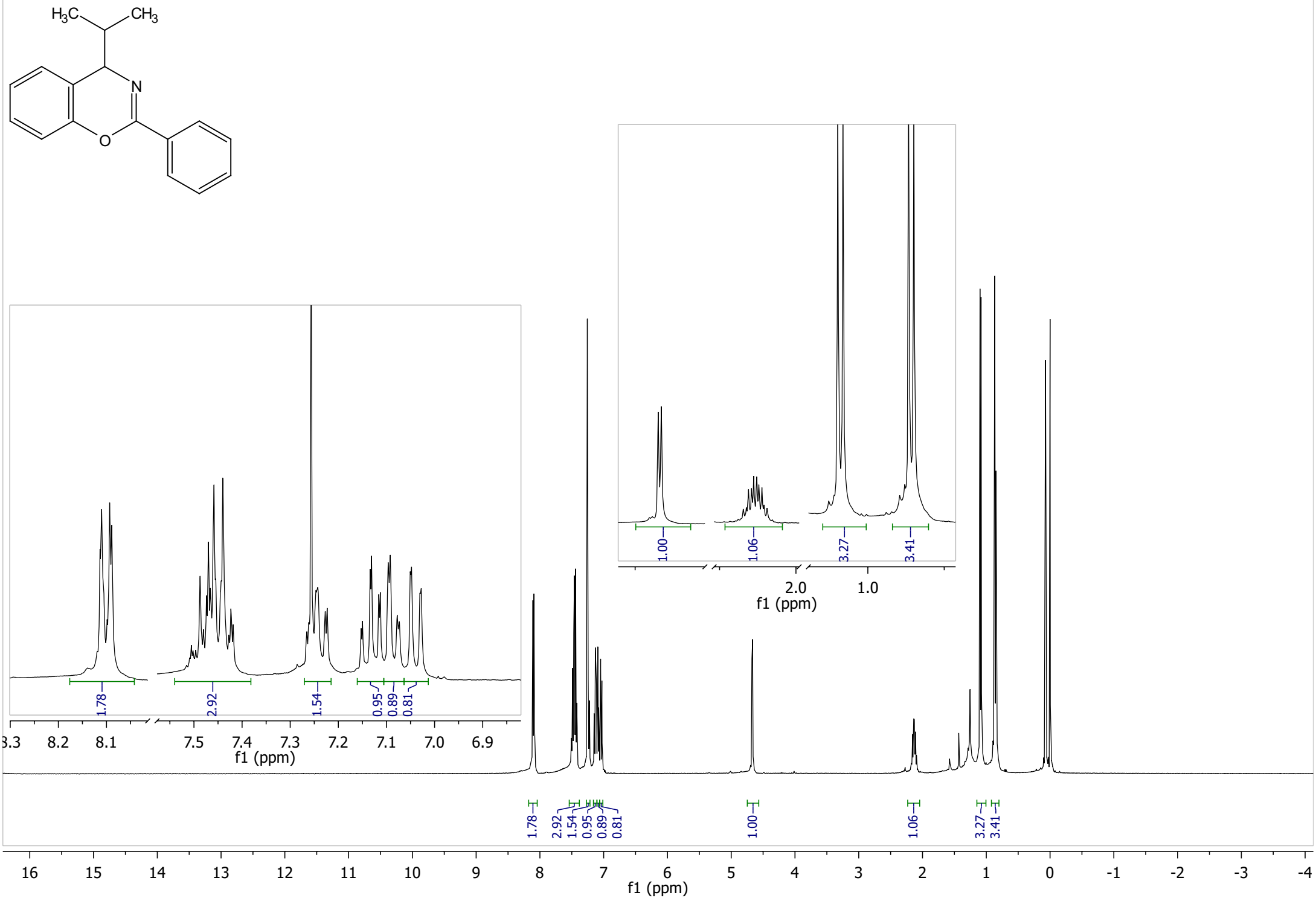
148.82
132.39
130.91
128.22
127.89
127.40
125.98
124.74
115.48
50.02
25.37

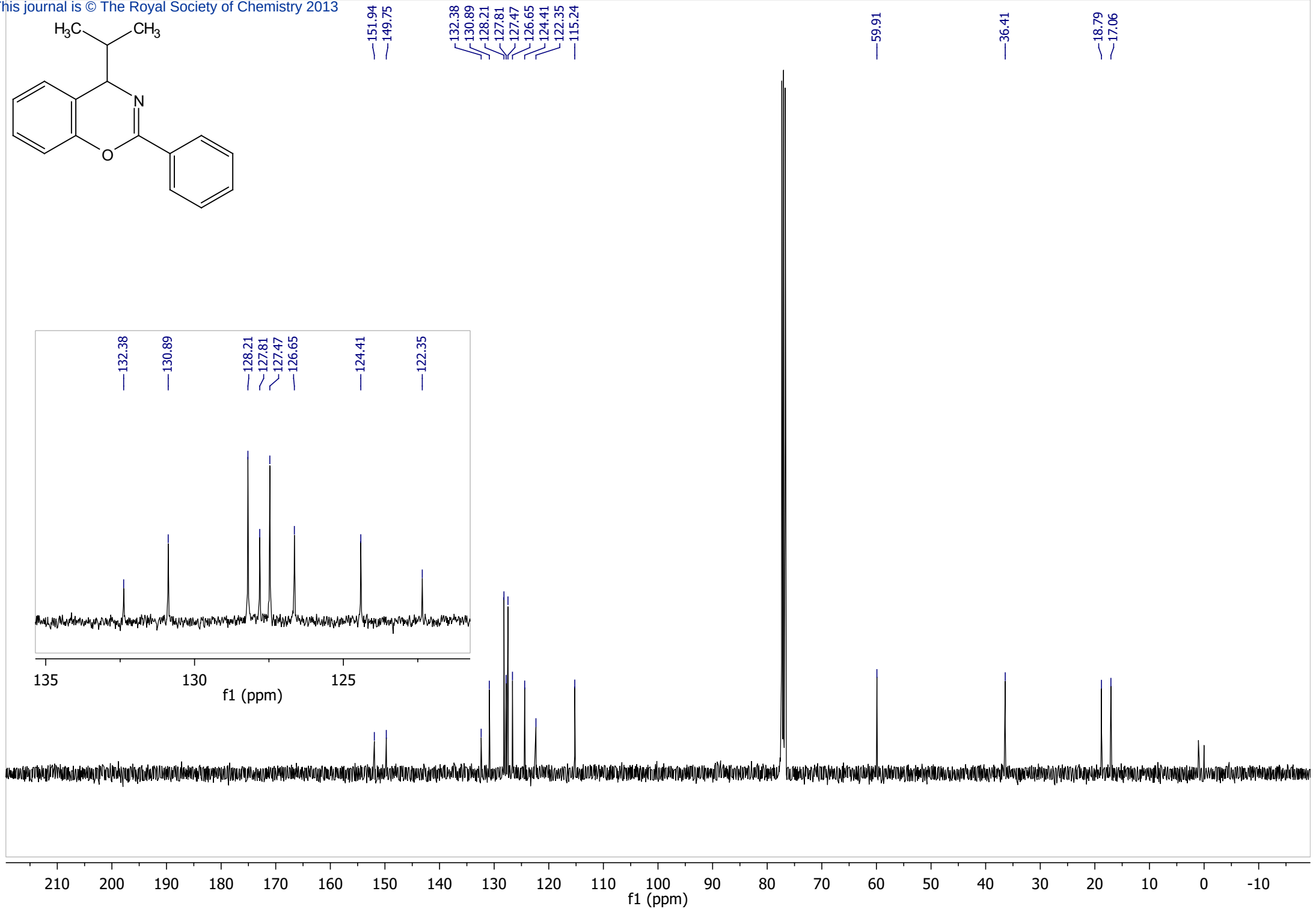
f1 (ppm)

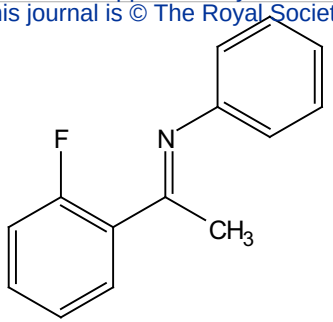
f1 (ppm)

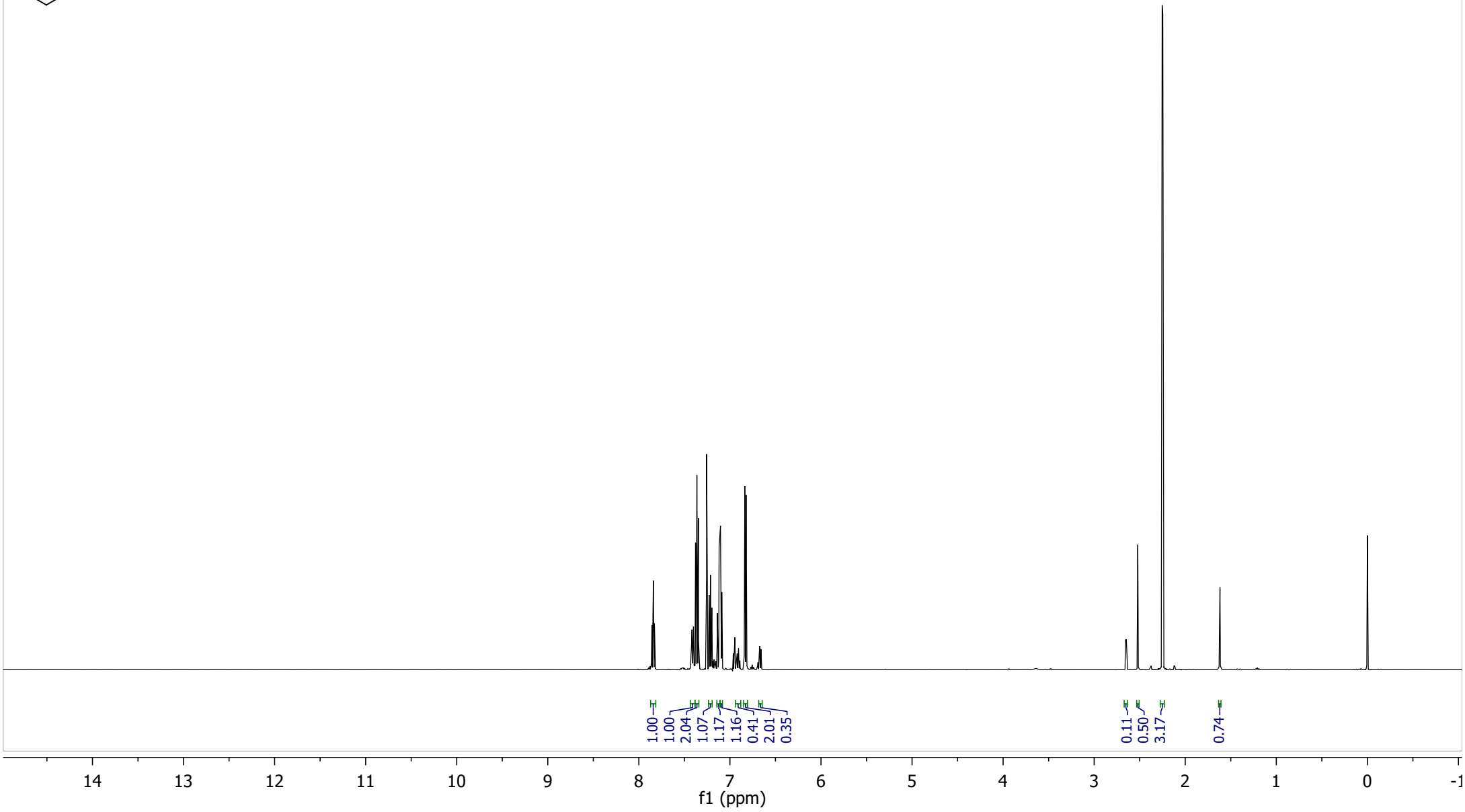


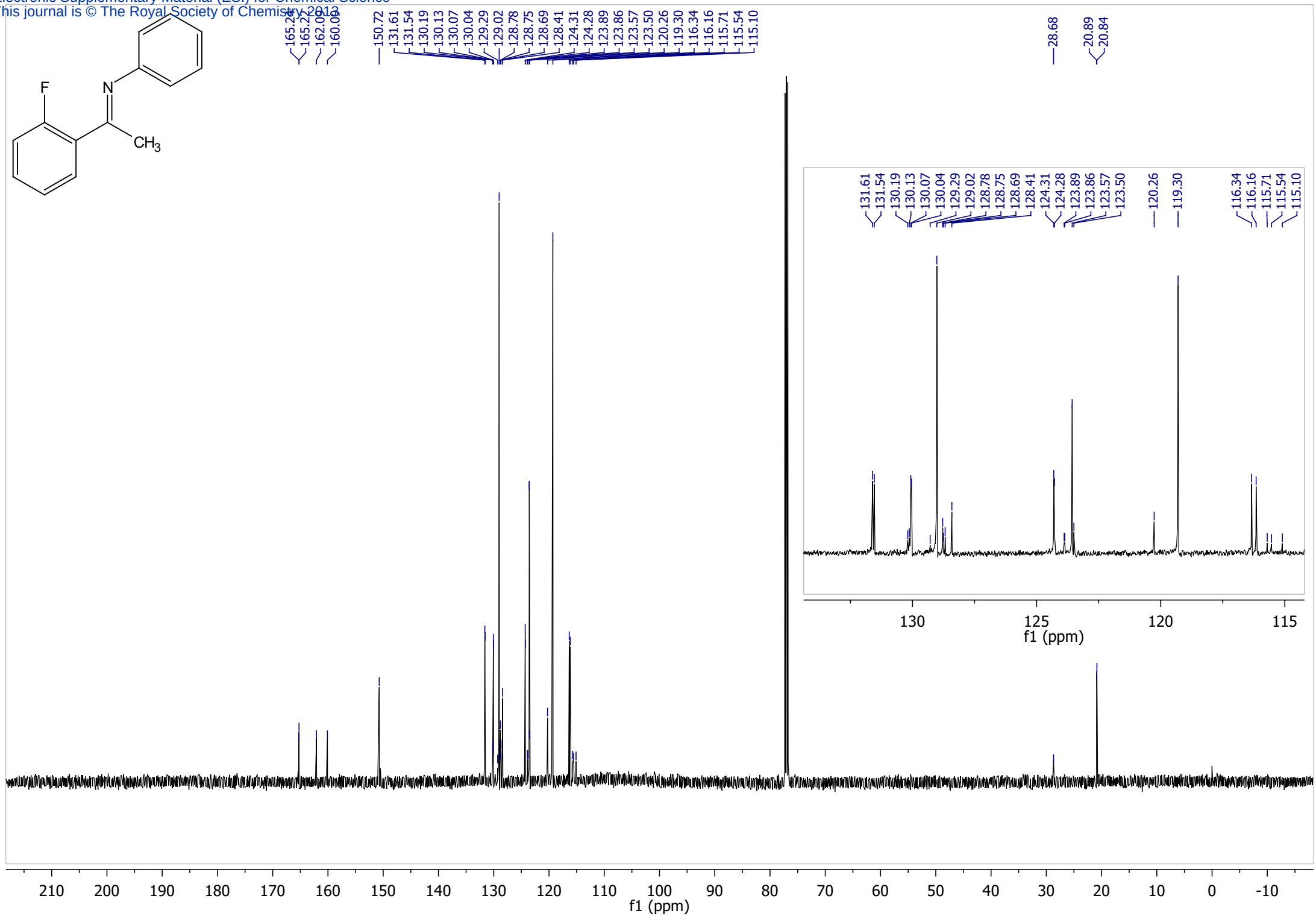


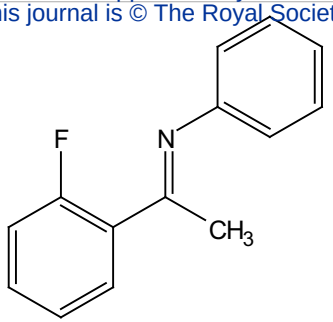


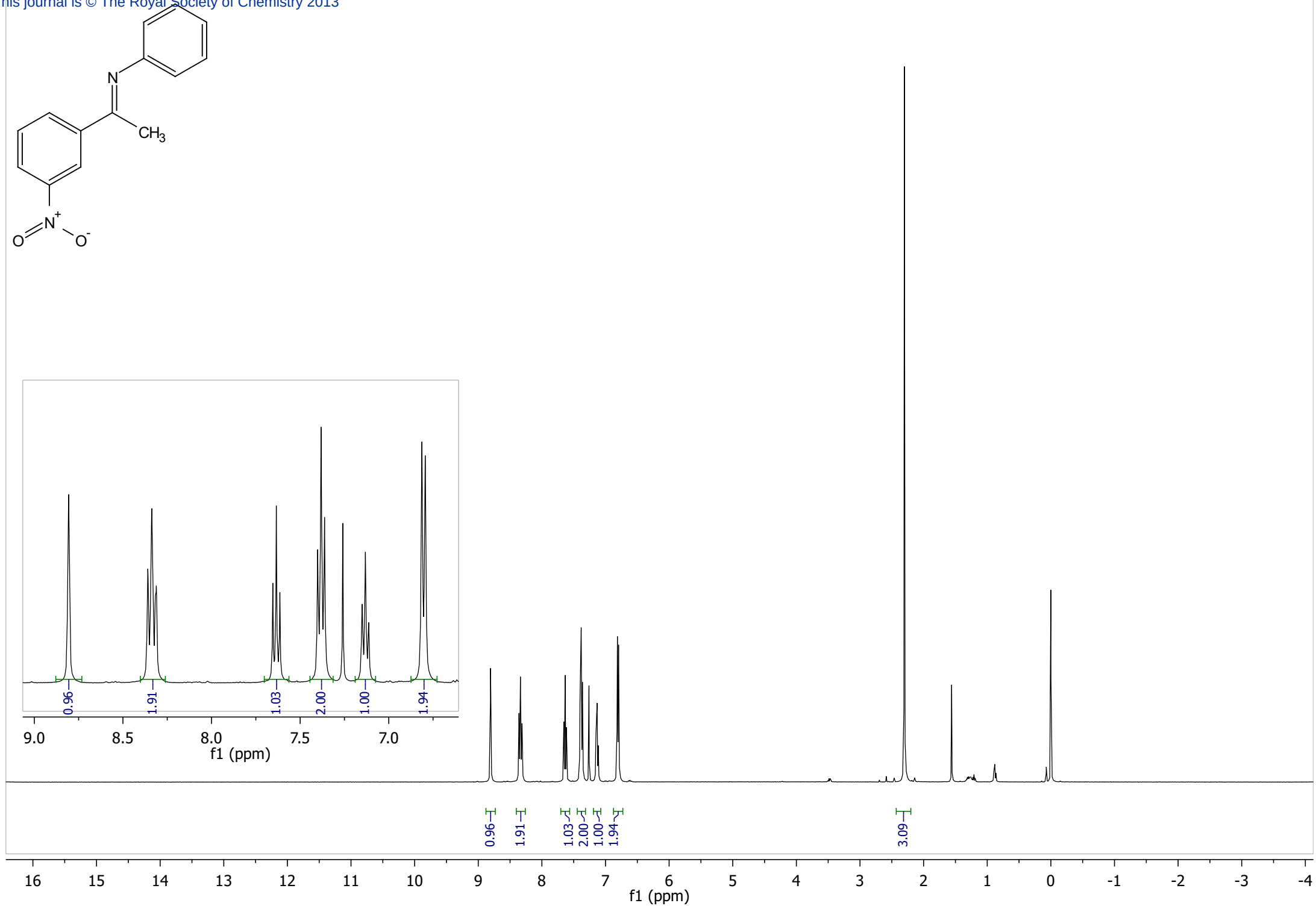


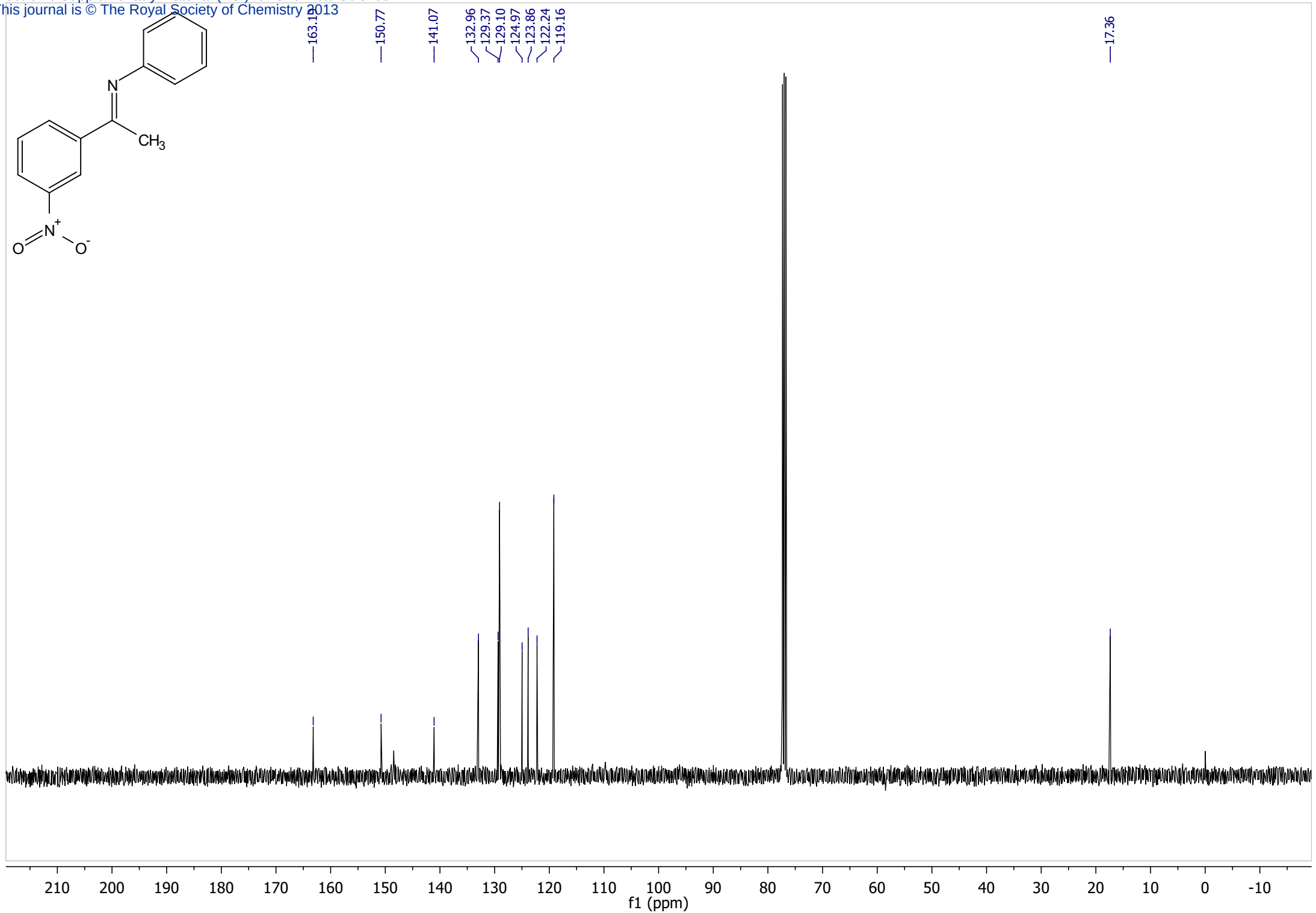


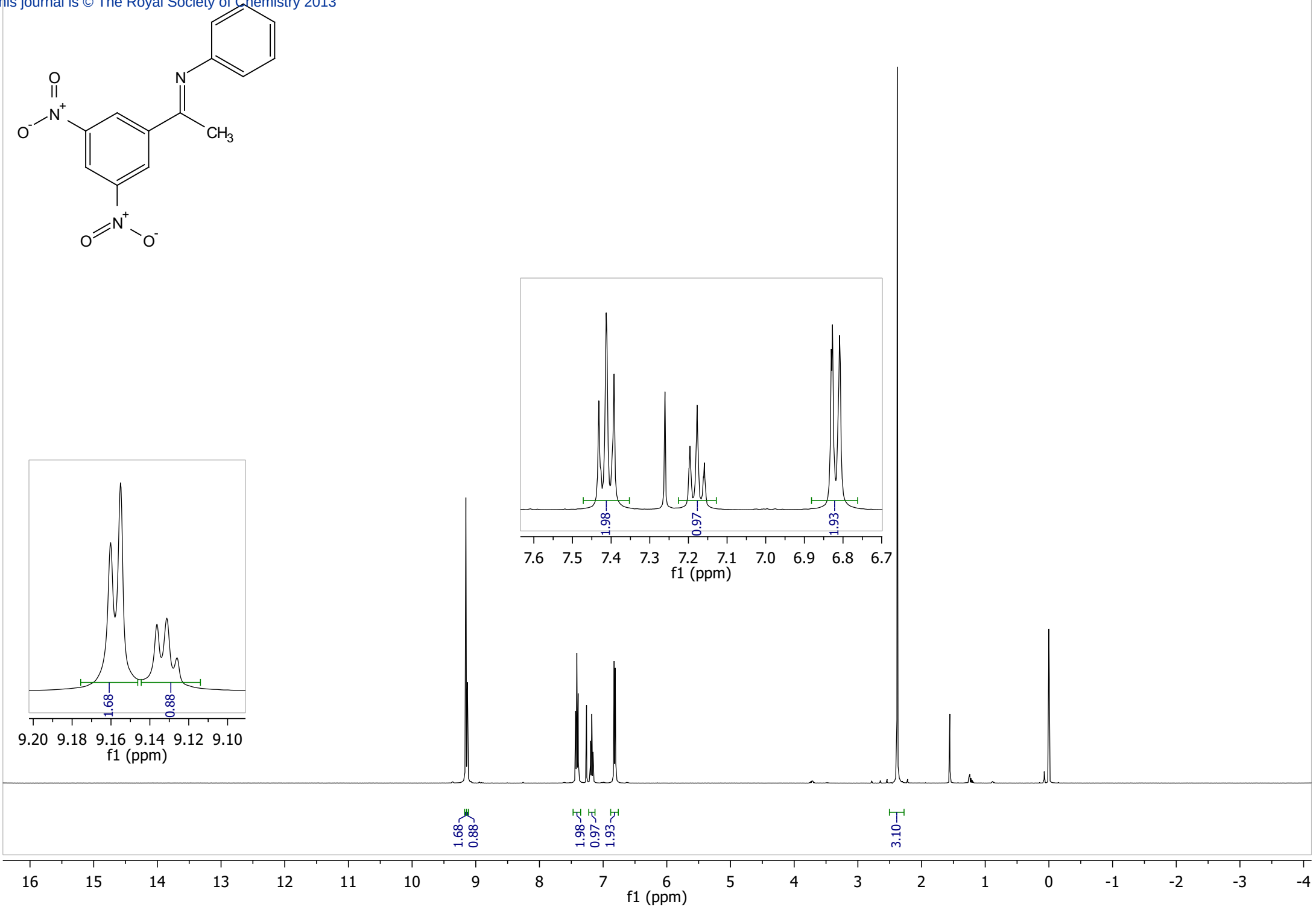


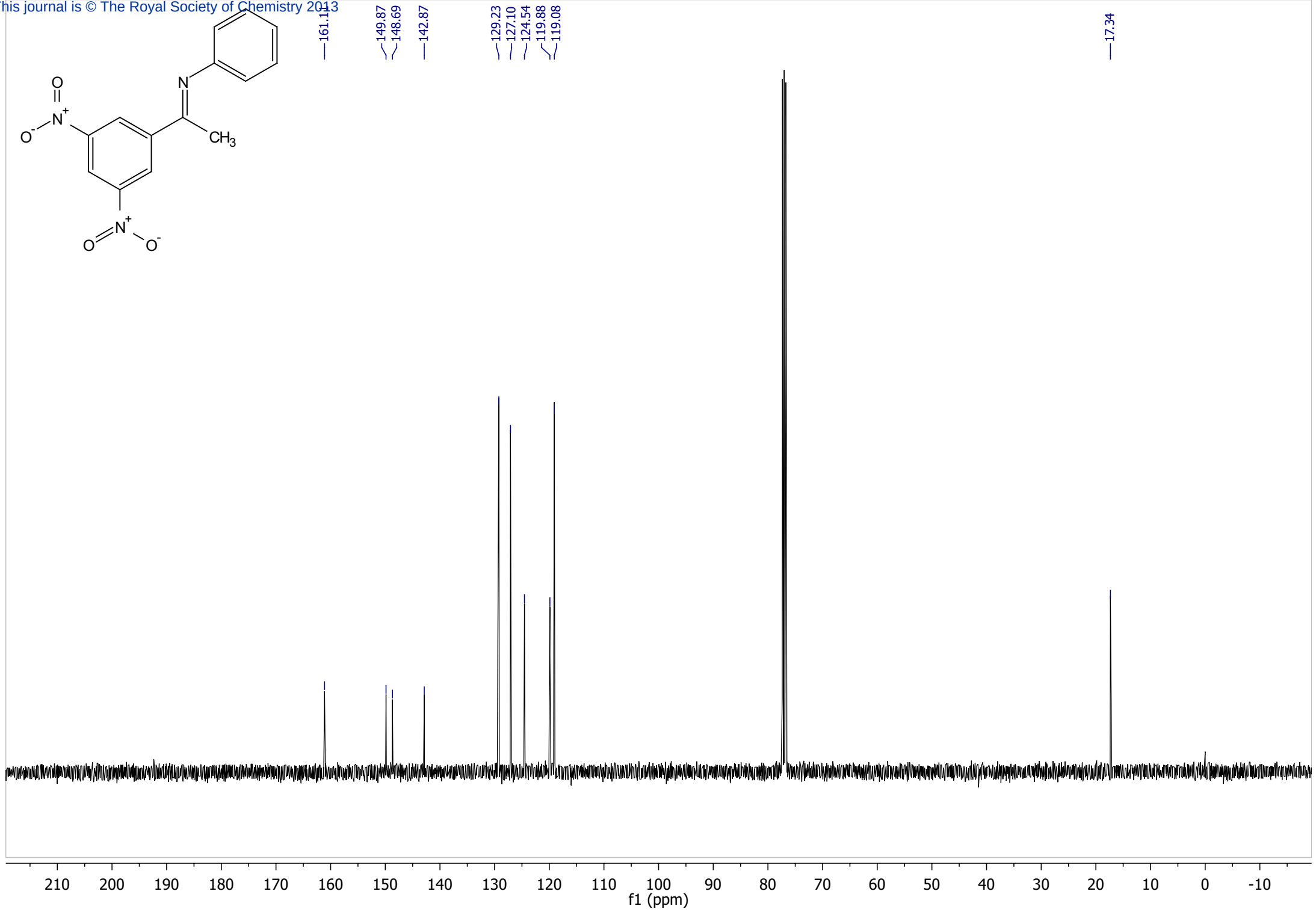


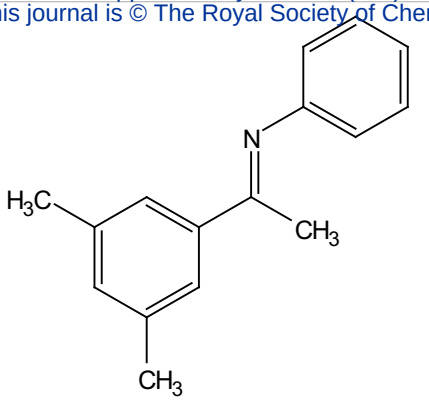


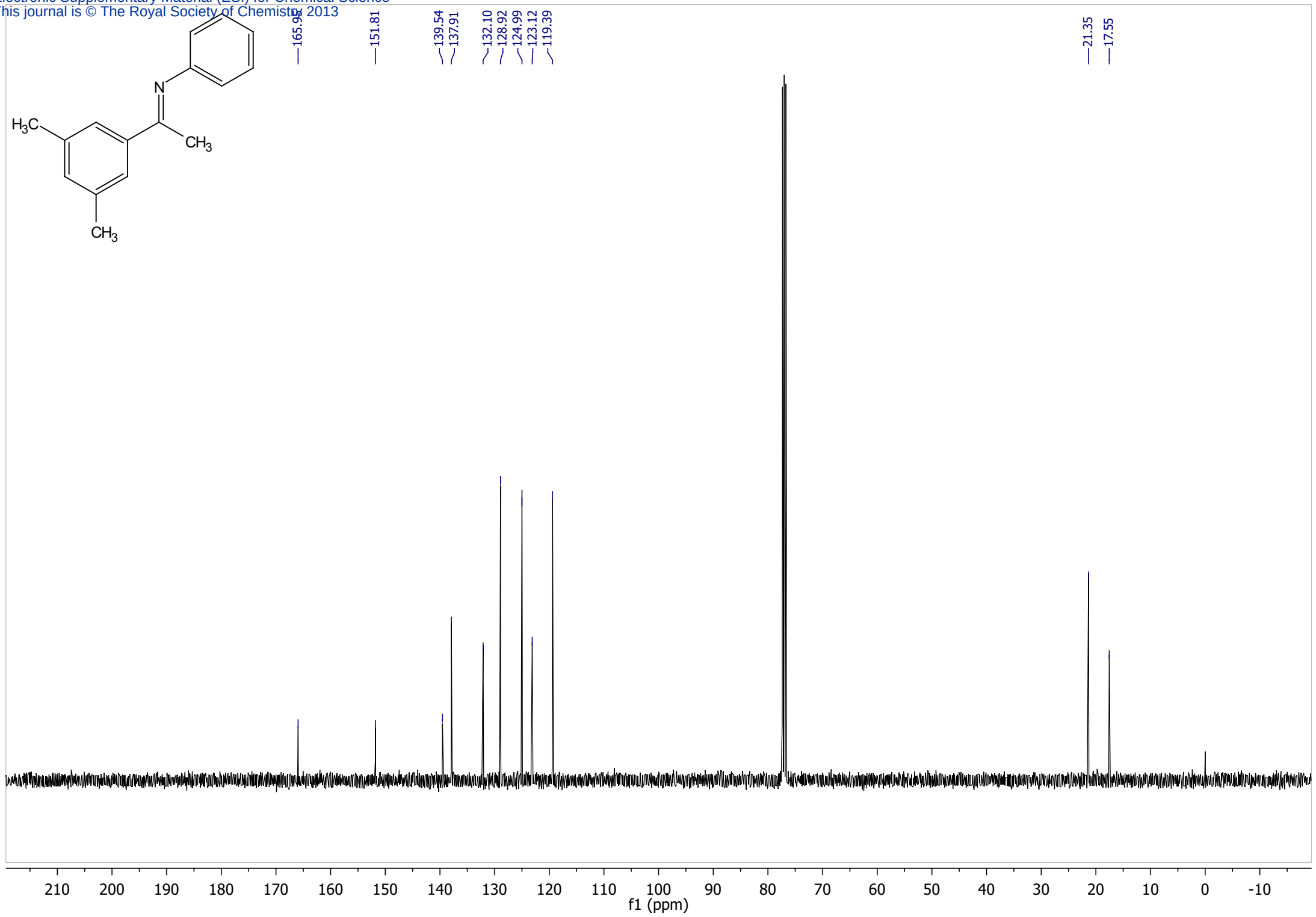


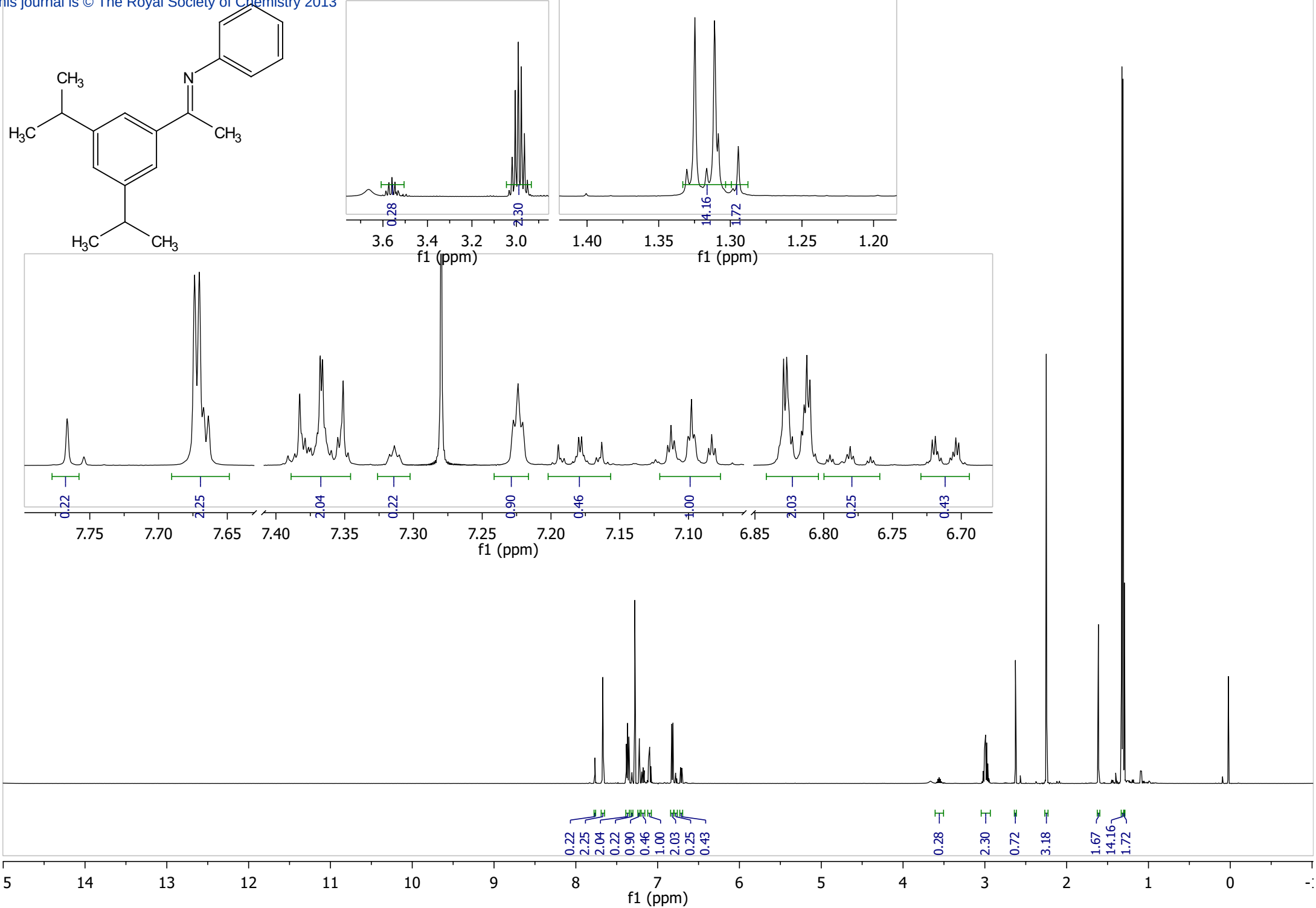


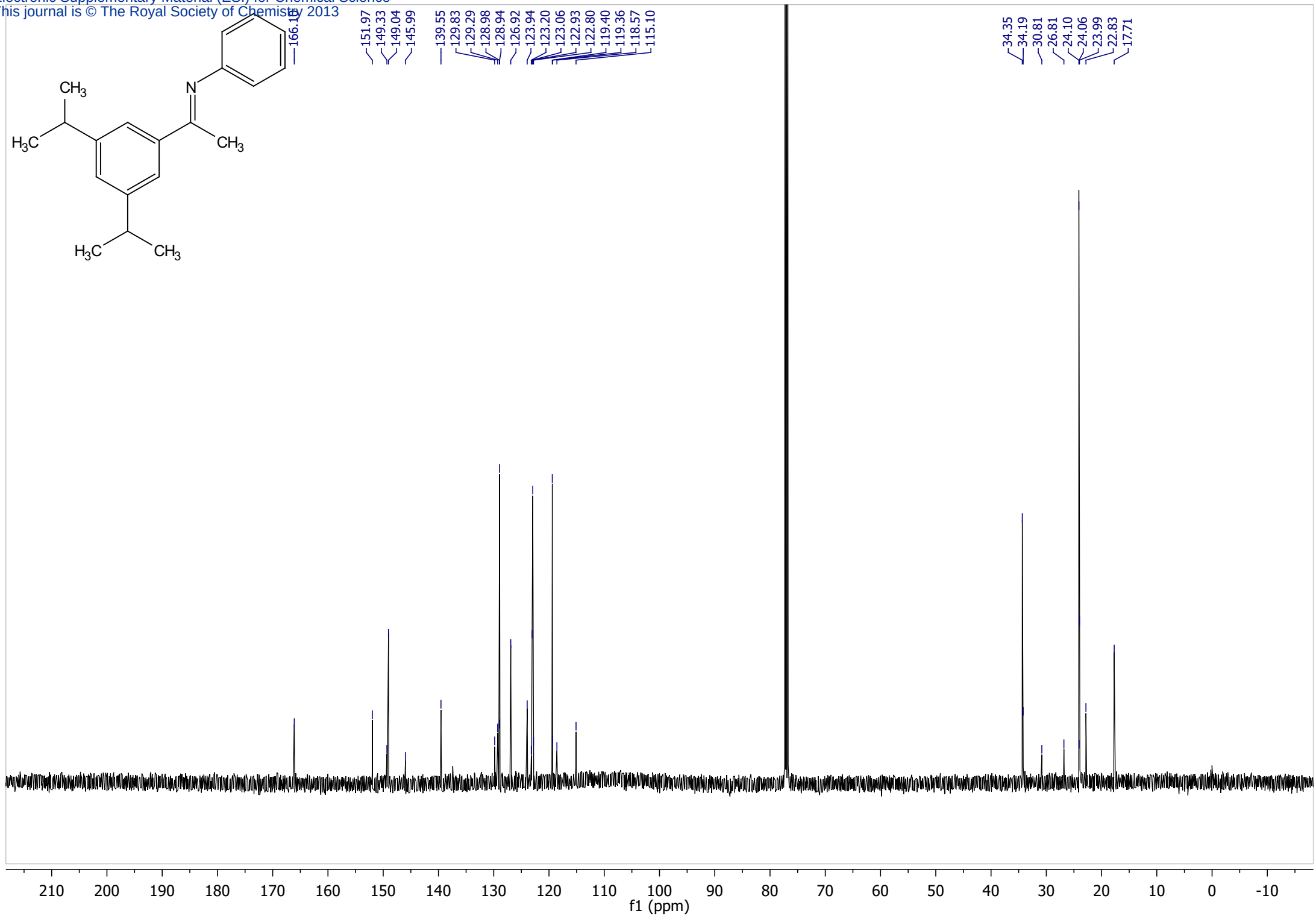


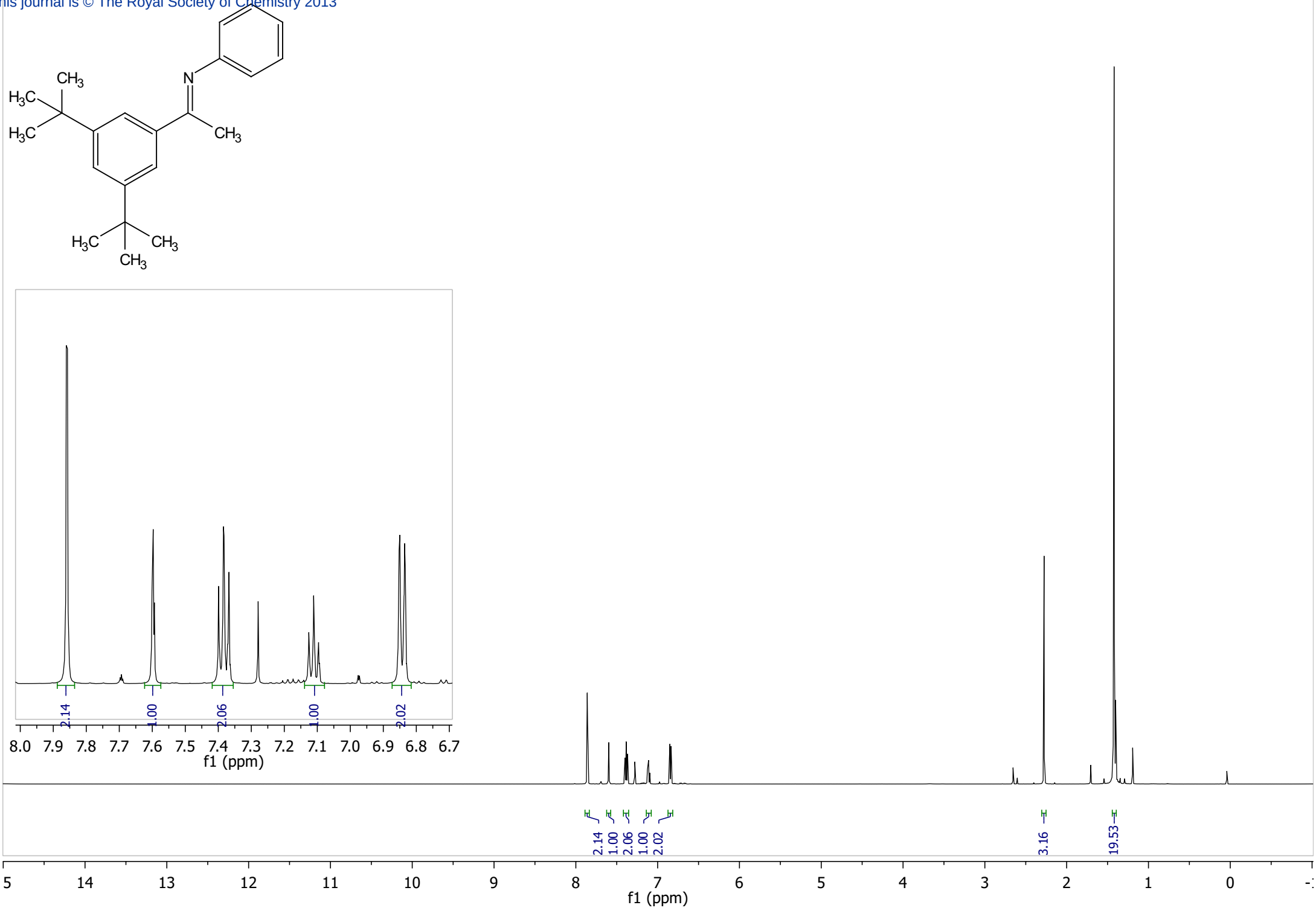


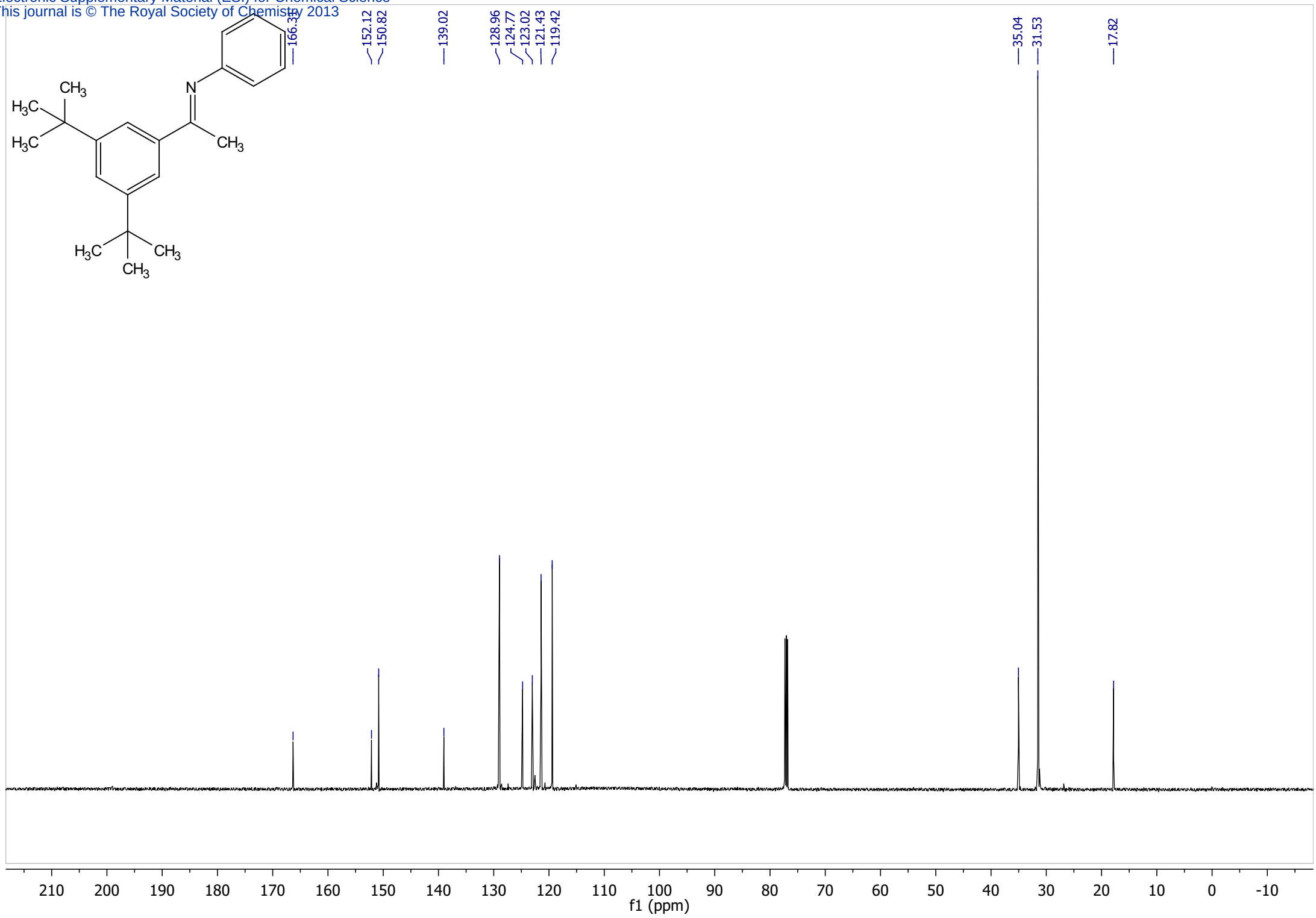


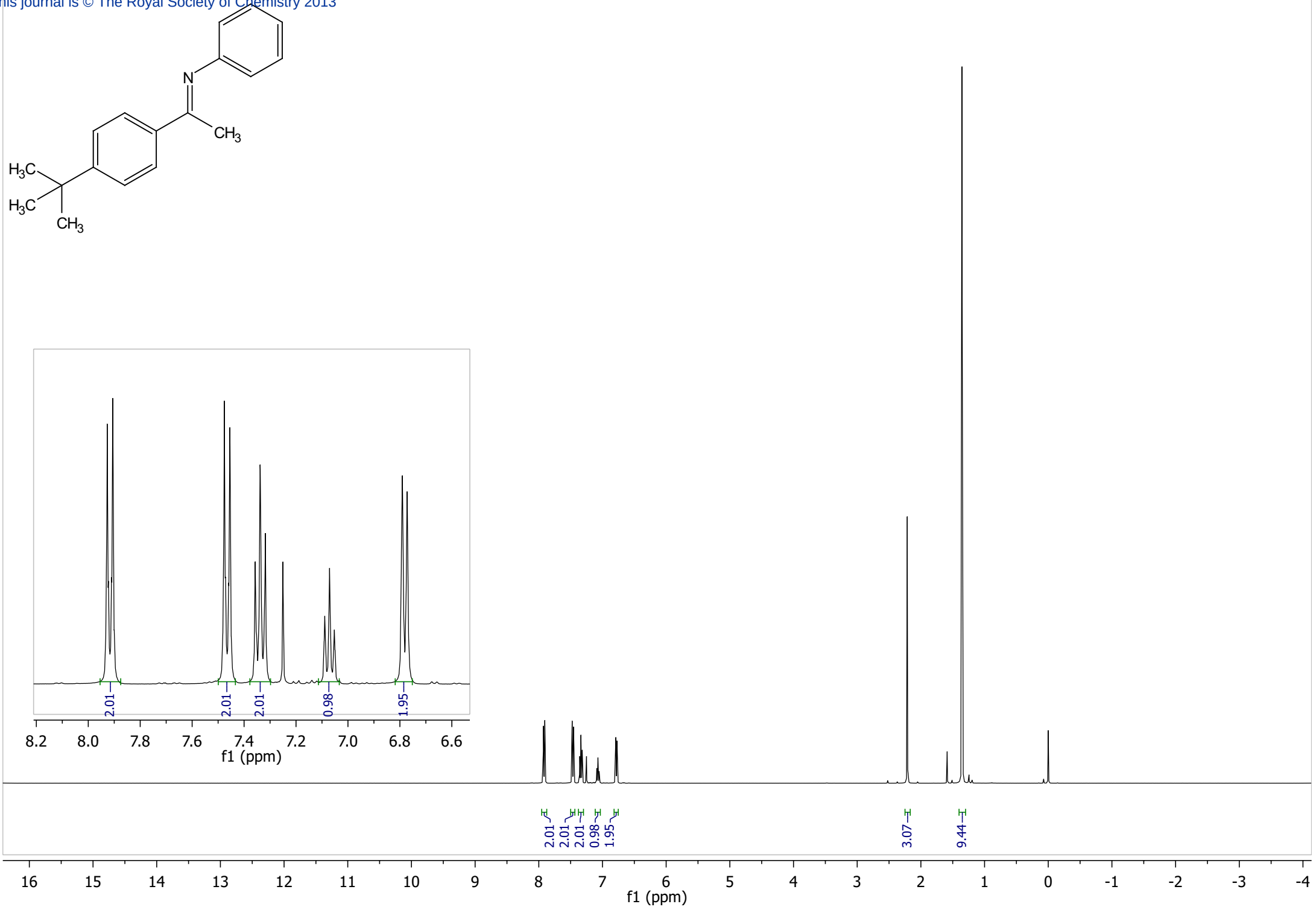


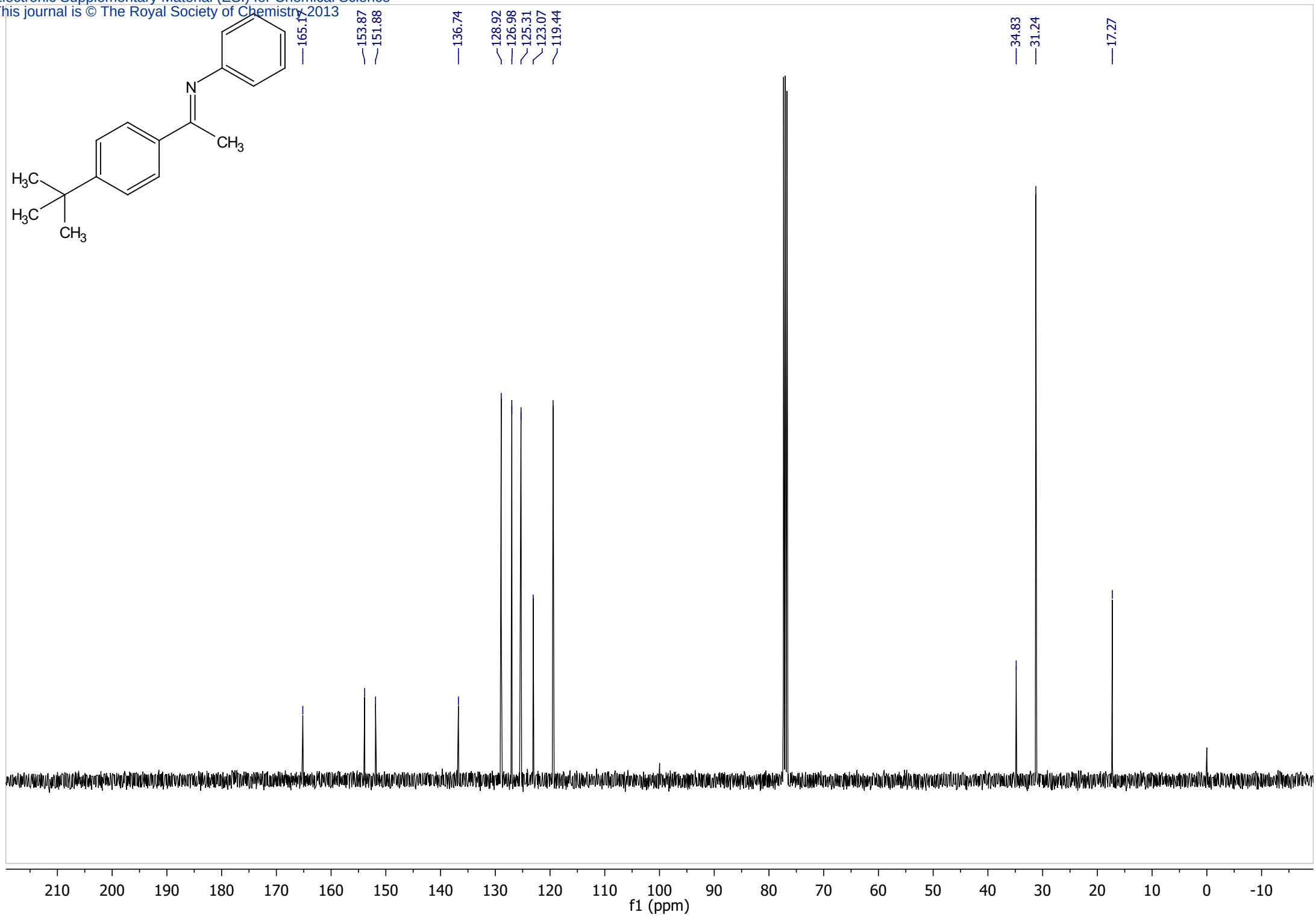


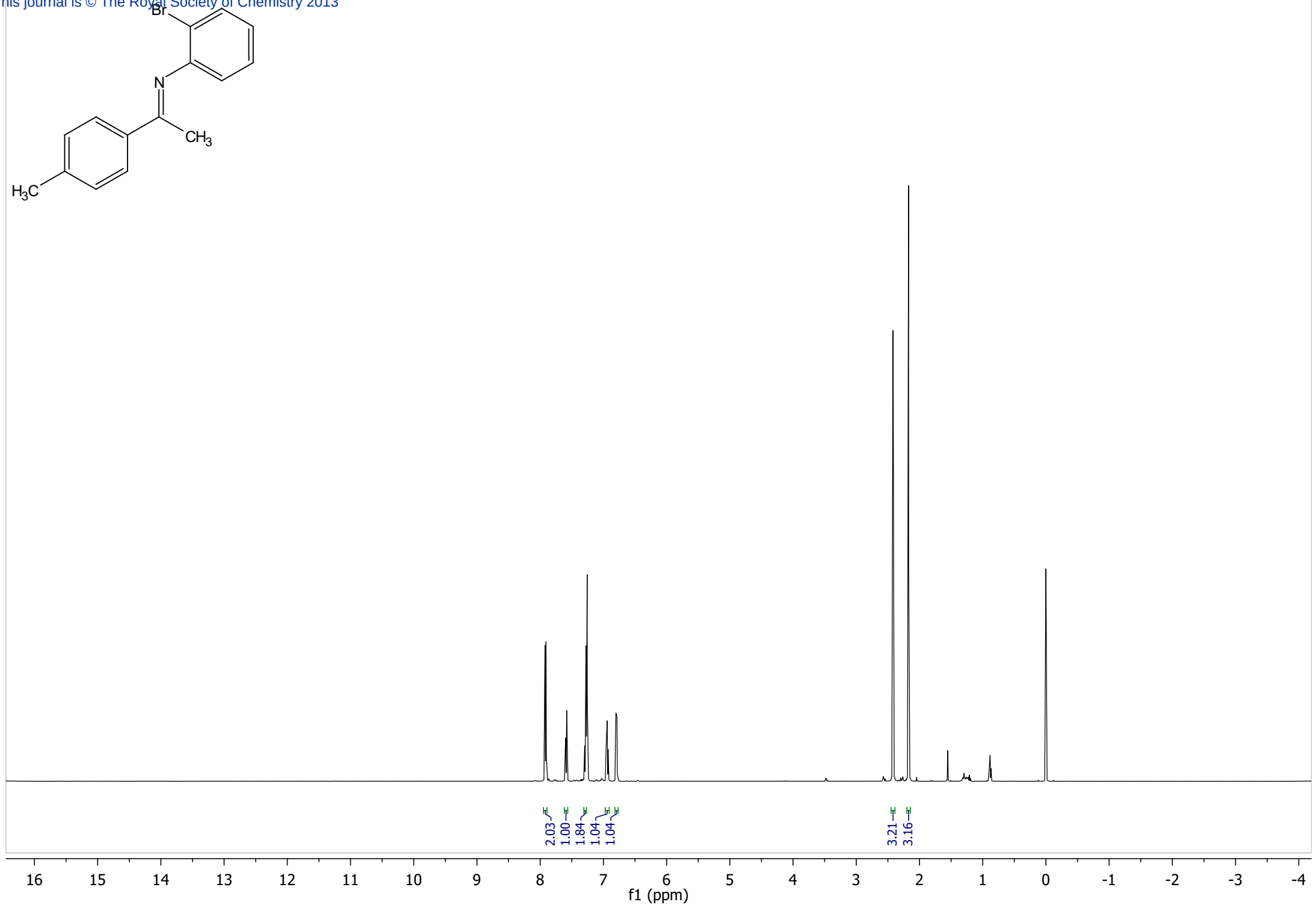


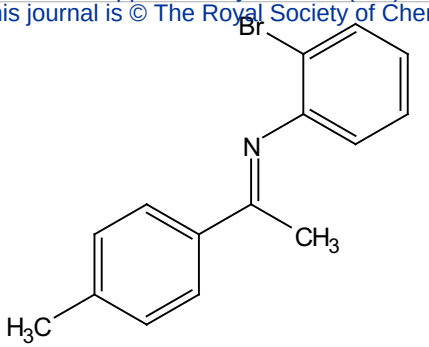




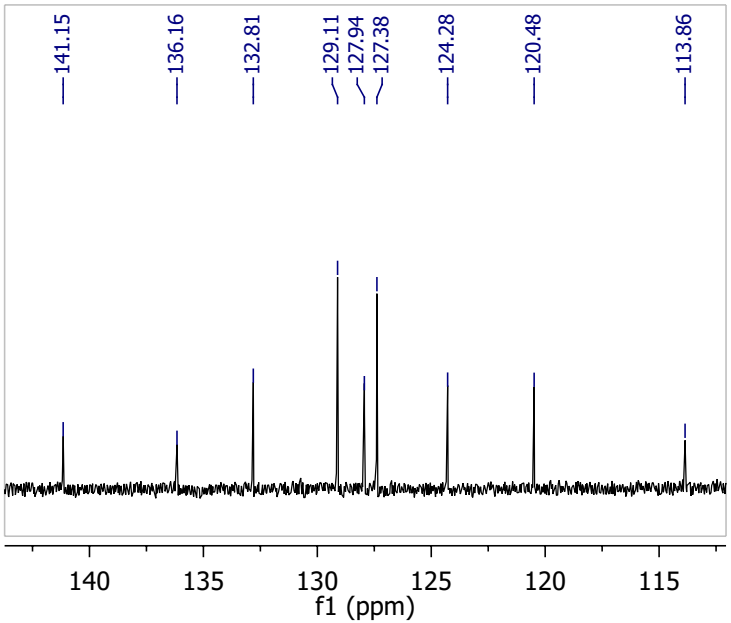








167.13
150.12
141.15
136.16
132.81
129.11
127.94
127.38
124.28
120.48
113.86
21.43
18.01



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)