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Iridium/Monodentate Phosphoramidite Catalyzed Asymmetric Hydrogenation of *N*-Aryl Imines

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Supporting Information

Contents:

General remarks.....	S2
Preparation of (<i>S</i>)-PipPhos.....	S2
General experimental procedure for the preparation of the imines.....	S2
General experimental procedure for hydrogenation.....	S3
General procedure for the deprotection of the hydrogenation products.....	S3
Characterizations.....	S3-S18
References.....	S18
Spectra.....	S20

General remarks

The catalyst was prepared *in situ*. Reaction was performed in stainless steel autoclave containing 7 glass vessels (8 mL volume). Vessels were closed with caps containing septa. Magnetic stirrers were placed inside of each vessel and needles were placed through the septa in order to enable entrance of hydrogen. Vessels were filled under air and then flushed with nitrogen before hydrogen pressure was applied. Solvents were distilled before use. NMR spectra were obtained on Varian AMX400 spectrometer. Chemical shifts are given in ppm relative to the residual solvent peak. GC analysis was carried out on an HP6890 using a flame ionization detector, while HPLC analysis was performed on a Shimadzu LC-10ADVP HPLC equipped with a Shimadzu SPD-M10AVP diode array detector. The enantiomeric excess was determined by HPLC with chiral columns (Chiralcel AD and OD-H) or by GC with Chiralsil DEX CB, in comparison with racemic products. High resolution mass spectra were recorded on an AEI-MS-902 mass spectrometer. Optical rotations were measured on a Schmidt + Haensch polarimeter (Polartronic MH8) with a 10 cm cell (c given in g/100 mL). Racemic amines were prepared by reduction of the imines with sodium borohydride in ethanol.

Preparation of (*S*)-1-(3,5-Dioxa-4-phospha-cyclohepta[2,1-a;3,4-a']dinaphthalen-4-yl)-piperidine ((*S*)-PipPhos)

1.5 g (5.24 mmol) of (*S*)-BINOL was refluxed overnight in neat PCl_3 (5 mL). Excess PCl_3 was removed by distillation; the chlorophosphite was stripped with dry toluene (3x5 mL) and then dissolved in 5 ml of dry toluene. This solution was added to a cooled (0 °C) solution of triethylamine (726 μL , 5.24 mmol) and piperidine (518 μL , 5.24 mmol) dissolved in 5 mL of dry toluene. The reaction mixture was stirred 2h at room temperature, ether was added (10 mL) and then the mixture was filtered over Celite. Solvents were removed *in vacuo* and the phosphoramidite was flushed over a short silica column (EtOAc/heptane = 1/4). After removal of the solvent, the product was isolated as a white solid in 80% yield (1.67 g). Spectral data were identical with those reported in the literature.¹

General experimental procedure for the preparation of the imines

A 100 mL round-bottom flask was filled with ketone (50 mmol) and amine (60 mmol) and molecular sieves (4Å, 20 g) in toluene (30 mL). The reaction mixture was stirred at room temperature overnight, filtered and evaporated. The crude product was purified by Kugelrohr distillation. Solid imines were recrystallized from dry pentane or ether.

General experimental procedure for hydrogenation

A mixture of $[\text{Ir}(\text{COD})_2]\text{BArF}$ (12.71 mg, 0.01 mmol), (*S*)-PipPhos (7.99 mg, 0.02 mmol), and substrate (1 mmol) was dissolved in 4 mL of dichloromethane, in a glass vial and provided with a stirring bar. The vial was placed in a stainless steel autoclave. Hydrogenation was performed at room temperature. After the reaction, hydrogen pressure was carefully released. Solvent was removed in vacuo and conversion was determined by ^1H NMR. Product was purified by chromatography column over silica gel. Absolute configurations were determined by measuring optical rotation and comparison with literature data.

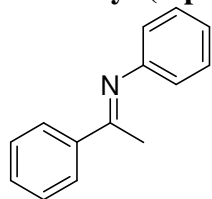
For the reproducibility of the results it was very important that both the imines and $[\text{Ir}(\text{COD})_2]\text{BArF}$ were highly pure.

General procedure for the deprotection of the hydrogenation products

0.50 mmol of secondary amine was dissolved in 10 mL of a mixture of acetonitrile and water (1/1). 500 μL of 1M sulfuric acid and 118 mg (0.50 mmol) of trichloroisocyanuric acid were added to the solution. The reaction was heated at 90 $^\circ\text{C}$ for 18h. The cooled reaction mixture was extracted with dichloromethane (3x100 mL). The resulting aqueous phase was subsequently brought to pH 10.5 through the addition of 2M aqueous KOH and extracted with ethyl acetate (3x100 mL). The organic layer was acidified with conc. HCl, dried and concentrated. Product was isolated as its hydrochloride salt.

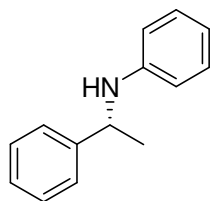
CHARACTERISATION:

N-Phenyl-(1-phenyl-ethylidene)-amine (1a)



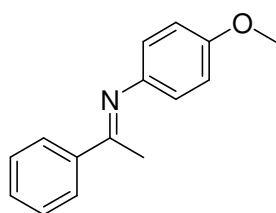
80% yield, light yellow solid, ^1H NMR (400 MHz, CDCl_3) 2.27 (s, 3H), 6.84 – 6.86 (m, 2H), 7.11 – 7.15 (m, 1H), 7.37 – 7.41 (m, 2H), 7.48 – 7.51 (m, 3H), 8.01 – 8.04 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) 18.3, 120.3, 124.2, 128.1, 129.3, 129.9, 131.4, 140.4, 152.7, 166.4 ppm; HRMS Calcd. for $\text{C}_{14}\text{H}_{13}\text{N}$ (M+1) 195.1048, found 195.1056. Mp = 40.1 – 40.5 $^\circ\text{C}$.

(R)-N-Phenyl-1-phenyl-ethylamine (1b)^{2,3}



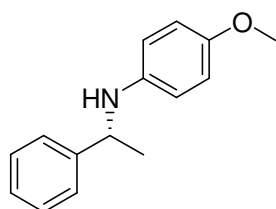
95% yield, 87% ee, yellow oil, $[\alpha]_D = -4.5$ (c 1.05, CHCl_3), lit. value⁴ 84% ee, $[\alpha]_D = -3.9$ (c 1.00, CHCl_3), the absolute configuration was determined by comparison of the optical rotation with literature^{2,5}; ^1H NMR (400 MHz, CDCl_3) 1.53 (d, $J = 6.7$ Hz, 3H), 3.98 (br, 1H), 4.50 (q, $J = 6.7$, 1H), 6.52 (d, $J = 7.6$ Hz, 2H), 6.66 (t, $J = 7.33$ Hz, 1H), 7.09 – 7.13 (m, 2H), 7.22 – 7.26 (m, 1H), 7.31 – 7.40 (m, 4H) ppm; ^{13}C NMR (100 MHz, CDCl_3) 25.9, 54.4, 114.2, 118.1, 126.8, 127.8, 129.6, 130.0, 146.2, 148.2 ppm; HRMS Calcd. for $\text{C}_{14}\text{H}_{15}\text{N}$ (M+1) 197.1204, found 197.1196, GC Chiralsil DEX CB, (initial temp. 100 °C for 5 min, then 5 °C/min to 160 °C, then 10 °C/min to 170 °C, then 10 °C/min to 100 °C), $t_1 = 31.5$ min, $t_2 = 34.3$ min.

N-(4-Methoxy-phenyl)-(1-phenyl-ethylidene)-amine (2a)



46% yield, yellow solid, ^1H NMR (400 MHz, CDCl_3) 2.26 (s, 3H), 3.82, (s, 3H), 6.75 – 6.78 (m, 2H), 6.90 – 6.93 (m, 2H), 7.44 – 7.46 (m, 3H), 7.95 – 7.99 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) 18.2, 56.4, 115.2, 121.7, 128.0, 129.3, 131.2, 140.7, 145.8, 156.9, 166.6 ppm; HRMS Calcd. for $\text{C}_{15}\text{H}_{15}\text{NO}$ (M+1) 225.1154, found 225.1143. Mp = 86.5 – 86.7 °C.

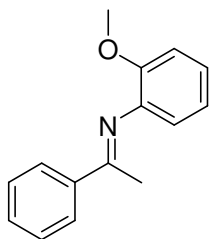
(R)-N-(4-Methoxy-phenyl)-1-phenyl-ethylamine (2b)⁶



92% yield, yellow solid, 71% ee, $[\alpha]_D = +1.4$ (c 1.00, CHCl_3), lit. value⁴ 88% ee, $[\alpha]_D = +1.3$ (c 1.00, CHCl_3); ^1H NMR (400 MHz, CDCl_3) 1.50 (d, $J = 6.7$ Hz, 3H), 3.86 (br, 1H), 3.70 (s, 3H), 4.42 (q, $J = 6.7$ Hz, 1H), 6.47 – 6.49 (m, 2H), 6.69 – 6.71 (m, 2H), 7.22 – 7.24 (m, 1H), 7.30 – 7.38 (m, 4H) ppm; ^{13}C NMR (100 MHz, CDCl_3) 26.0, 55.1, 56.6, 115.4, 115.6, 126.8, 127.7, 129.5, 142.5, 146.4, 152.8 ppm; HRMS Calcd. for $\text{C}_{15}\text{H}_{17}\text{NO}$ (M+1) 227.1310, found

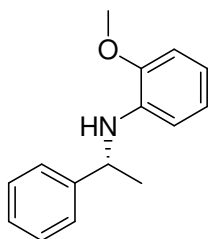
227.1300; Mp = 63.8 – 63.9 °C; HPLC (OD–H, eluent:heptane/*i*-PrOH = 99/1, detector: 215 nm, flow rate: 0.5 mL/min), $t_1 = 26.2$ min, $t_2 = 28.5$ min.

***N*-(2-Methoxy-phenyl)-(1-phenyl-ethylidene)-amine (3a)**



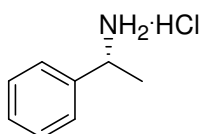
60% yield, yellow solid, $^1\text{H NMR}$ (400 MHz, CDCl_3) 2.20 (s, 3H), 3.80 (s, 3H), 6.78 – 6.82 (m, 1H), 6.93 – 7.10 (m, 3H), 7.44 – 7.50 (m, 3H), 8.01 – 8.06 (m, 2H) ppm; $^{13}\text{C NMR}$ (100 MHz, CDCl_3) 18.7, 56.6, 112.5, 121.5, 121.8, 125.1, 128.2, 129.2, 131.3, 140.4, 141.6, 149.9, 168.0 ppm; HRMS Calcd. for $\text{C}_{15}\text{H}_{15}\text{NO}$ ($\text{M}+1$) 225.1154, found 225.1145; Mp = 48 – 48.5 °C

***(R)*-*N*-(2-Methoxy-phenyl)-1-phenyl-ethylamine (3b)**



93% yield, light brown solid, 97% ee, $[\alpha]_{\text{D}} = -32.3$ (c 1.03, CHCl_3); absolute configuration determined by comparison of optical rotation with literature⁷; $^1\text{H NMR}$ (400 MHz, CDCl_3) 1.71 (d, $J = 6.7$ Hz, 3H), 4.02 (s, 3H), 4.65 (q, $J = 6.7$ Hz, 1H), 4.83 (br, 1H), 6.54 (d, $J = 7.8$ Hz, 1H), 6.78 – 6.81 (m, 1H), 6.87 – 6.94 (m, 2H), 7.36 – 7.40 (m, 1H), 7.46 – 7.50 (m, 2H), 7.54 – 7.56 (m, 2H) ppm; $^{13}\text{C NMR}$ (100 MHz, CDCl_3) 26.0, 54.1, 56.2, 110.1, 111.9, 117.2, 122.0, 126.7, 127.6, 129.4, 138.0, 146.3, 147.4 ppm; HRMS Calcd. for $\text{C}_{15}\text{H}_{17}\text{NO}$ ($\text{M}+1$) 227.1310, found 227.1302; Mp = 71.4 °C; HPLC (OD–H, eluent:heptane/*i*-PrOH = 99/1, detector: 215 nm, flow rate: 0.5 mL/min), $t_1 = 14.6$ min, $t_2 = 19.0$ min.

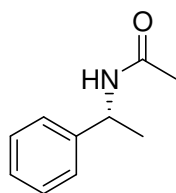
***(R)*-*N*-1-Phenyl-ethylamine hydrochloride (3c)**



70% yield, light brown solid, $^1\text{H NMR}$ (400 MHz, D_2O) 1.64 (d, $J = 6.91$ Hz, 3H), 4.53 (q, $J = 6.86$ Hz, 1H), 7.47 – 7.52 (m, 5H) ppm; $^{13}\text{C NMR}$ (100 MHz, D_2O) 19.5, 51.2, 126.7, 129.3, 129.4, 137.9 ppm; Mp = 142.5 – 142.7 °C; HRMS Calcd. for $\text{C}_8\text{H}_{12}\text{ClN}$ ($\text{M}+1-\text{HCl}$)

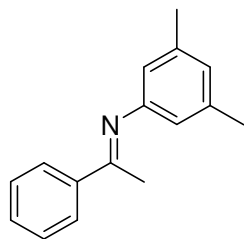
122.09643, found 122.09645; product was derivatized with acetic anhydride in the presence of triethylamine and enantioselectivity was determined by GC:

(R)-N-(1-Phenyl-ethyl)-acetamide (3d)⁸



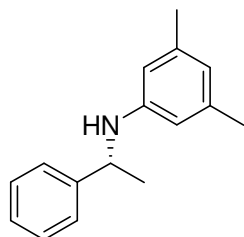
Light brown solid, 97% ee; ¹H NMR (400 MHz, CDCl₃) 1.47 (d, *J* = 6.91, 3H), 1.97 (s, 3H), 5.13 (q, *J* = 7.20 Hz, 1H), 5.88 (br, 1H), 7.26 – 7.34 (m, 5H) ppm; ¹³C NMR (100 MHz, CDCl₃) 22.6, 24.4, 49.7, 127.2, 128.3, 129.6, 144.1, 170.1 ppm; GC Chiralsil DEX CB, initial temp. 125 °C for 4 min, then 3 °C/min to 140 °C, then 10 °C/min to 180 °C, then 10 °C/min to 125 °C), *t*₁ = 13.0 min, *t*₂ = 13.25 min.

N-(3,5-Dimethyl-phenyl)-(1-phenyl-ethylidene)-amine (4a)



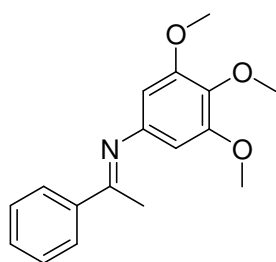
75% yield, yellow oil, ¹H NMR (400 MHz, CDCl₃) 2.25 (s, 3H), 2.34 (s, 6H), 6.44 (s, 2H), 6.75 (s, 1H), 7.44 – 7.48 (m, 3H), 7.96 – 8.00 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) 18.3, 22.3, 117.9, 125.8, 128.1, 129.3, 131.3, 139.5, 140.6, 152.7, 165.9 ppm; HRMS Calcd. for C₁₆H₁₇N (M+1) 223.1361, found 223.1359.

(R)-N-(3,5-Dimethyl-phenyl)-(1-phenyl-ethyl)-amine⁹ (4b)



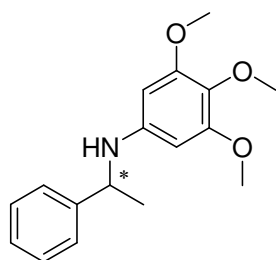
97% yield, yellow oil, >99% ee, [α]_D = +12.3 (*c* 1.02, CHCl₃), ¹H NMR (400 MHz, CDCl₃) 1.62 (d, *J* = 6.7 Hz, 3H), 2.32 (s, 6H), 4.02 (br, 1H), 4.61 (q, *J* = 6.7 Hz, 1H), 6.31 (s, 2H), 6.47 (s, 1H), 7.34 – 7.37 (m, 1H), 7.43 – 7.47 (m, 2H), 7.50 – 7.52 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) 22.4, 25.8, 54.2, 112.2, 120.2, 126.8, 127.7, 129.5, 139.6, 146.4, 148.3 ppm; HRMS Calcd. for C₁₆H₁₉N (M+1) 225.1517, found 225.1504. HPLC (OD-H, eluent:heptane/*i*-PrOH = 90/10, detector: 215 nm, flow rate: 0.5 mL/min), *t*₁ = 8.5 min, *t*₂ = 9.0 min.

***N*-(1-Phenyl-ethylidene)-(3,4,5-trimethoxy-phenyl)-amine (5a)**



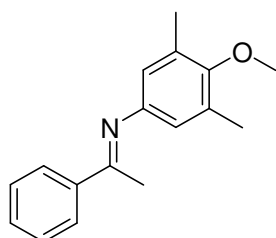
34% yield, light yellow solid, $^1\text{H NMR}$ (400 MHz, CDCl_3) 2.26 (s, 3H), 3.81 – 3.83 (m, 9H), 6.02 (s, 2H), 7.42 – 7.43 (m, 3H), 7.94 – 7.96 (m, 2H) ppm; $^{13}\text{C NMR}$ (100 MHz, CDCl_3) 18.3, 56.9, 61.8, 97.4, 128.0, 129.2, 131.4, 134.6, 140.1, 148.8, 154.4, 166.8 ppm, HRMS Calcd. for $\text{C}_{17}\text{H}_{19}\text{NO}_3$ (M+1) 285.1365, found 285.1421; Mp = 101.6 – 103 °C.

(-)-*N*-(1-Phenyl-ethyl)-3,4,5-trimethoxy-phenyl-amine (5b)



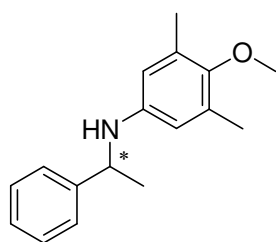
94% yield, yellow oil, 99% ee, $[\alpha]_{\text{D}} = -21.0$ (c 1.09, CHCl_3), $^1\text{H NMR}$ (400 MHz, CDCl_3) 1.51 (d, $J = 6.7$ Hz, 3H), 3.68 (s, 6H), 3.74 (s, 3H), 4.09 (br, 1H), 4.44 (q, $J = 6.7$ Hz, 1H), 5.77 (s, 2H), 7.21 – 7.25 (m, 1H), 7.31 – 7.35 (m, 2H), 7.38 – 7.40 (m, 2H) ppm; $^{13}\text{C NMR}$ (100 MHz, CDCl_3) 25.7, 54.8, 56.4, 61.7, 91.7, 126.5, 127.6, 129.4, 130.4, 144.9, 146.2, 154.4 ppm; HRMS Calcd. for $\text{C}_{17}\text{H}_{21}\text{NO}_3$ (M+1) 287.1521, found 287.1516; HPLC (AD, eluent:heptane/*i*-PrOH = 90/10, detector: 215 nm, flow rate: 0.5 mL/min), $t_1 = 11.1$ min, $t_2 = 23.8$ min.

***N*-(4-Methoxy-3,5-dimethyl-phenyl)-(1-phenyl-ethylidene)-amine (6a)**



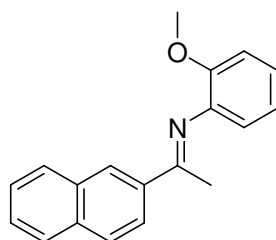
79% yield, light yellow solid, $^1\text{H NMR}$ (400 MHz, CDCl_3) 2.26 (s, 3H), 2.29 (s, 6H), 3.73 (s, 3H), 6.45 (s, 2H), 7.43 – 7.46 (m, 3H), 7.93 – 7.98 (m, 2H) ppm; $^{13}\text{C NMR}$ (100 MHz, CDCl_3) 16.4, 17.6, 60.1, 119.7, 127.3, 128.5, 130.5, 131.4, 139.9, 147.5, 153.2, 165.4 ppm; HRMS Calcd. for $\text{C}_{17}\text{H}_{19}\text{NO}$ (M+1) 253.1467, found 253.1457; Mp = 65.7 – 66.2 °C

(+)-*N*-(4-Methoxy-3,5-dimethyl-phenyl)-1-phenyl-ethylamine (6b)



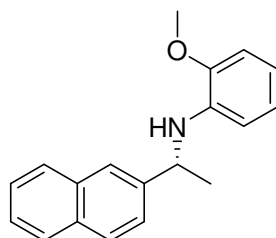
96% yield, light yellow solid, 99% ee, $[\alpha]_D = +9.0$ (*c* 1.02, CHCl₃), ¹H NMR (400 MHz, CDCl₃) 1.52 (d, *J* = 6.7 Hz, 3H), 2.20 (s, 6H), 3.66 (s, 3H), 3.81 (br, 1H), 4.46 (q, *J* = 6.7 Hz, 1H), 6.23 (s, 2H), 7.25 – 7.29 (m, 1H), 7.34 – 7.43 (m, 4H) ppm; ¹³C NMR (100 MHz, CDCl₃) 17.1, 25.8, 54.6, 60.7, 114.2, 126.7, 127.6, 129.4, 132.0, 144.3, 146.4, 149.6 ppm; HRMS Calcd. for C₁₇H₂₁NO (*M*+1) 255.1623, found 255.1630; Mp = 90.2 – 90.9 °C; HPLC (OD–H, eluent:heptane/*i*-PrOH = 80/20, detector: 215 nm, flow rate: 0.5 mL/min), *t*₁ = 9.2 min, *t*₂ = 9.9 min.

***N*-(2-Methoxy-phenyl)-(1-naphthalen-2-yl-ethylidene)-amine (7a)**



76% yield, light yellow solid, ¹H NMR (400 MHz, CDCl₃) 2.32 (s, 3H), 3.82 (s, 3H), 6.82 – 6.87 (m, 1H), 6.95 – 7.12 (m, 3H), 7.51 – 7.56 (m, 2H), 7.86 – 7.97 (m, 3H), 8.26 – 8.32 (m, 1H), 8.39 (s, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) 18.7, 56.6, 112.5, 121.6, 121.9, 125.2, 125.4, 127.2, 128.0, 128.6, 128.9, 129.9, 133.9, 135.4, 137.7, 141.6, 149.9, 167.8 ppm; HRMS Calcd. for C₁₉H₁₇NO (*M*+1) 275.1310, found 275.1309; Mp = 103.8 – 103.9 °C.

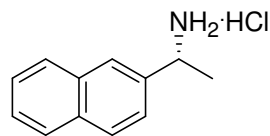
(*R*)-*N*-(2-Methoxy-phenyl)-1-naphthalen-2-yl-ethylamine (7b)



93% yield, white solid, 99% ee, $[\alpha]_D = -76.8$ (*c* 1.04, CHCl₃), absolute configuration determined by comparison of optical rotation of deprotected derivatized product **7d** with literature values⁸; ¹H NMR (400 MHz, CDCl₃) 1.70 (d, *J* = 6.7 Hz, 3H), 3.97 (s, 3H), 4.70 (q, *J* = 6.7 Hz, 1H), 4.82 (br, 1H), 6.45 – 6.50 (m, 1H), 6.64 – 6.88 (m, 3H), 7.48 – 7.61 (m, 3H), 7.89 – 7.91 (m, 4H) ppm; ¹³C NMR (100 MHz, CDCl₃) 26.1, 54.6, 56.4, 110.2, 112.1, 117.3,

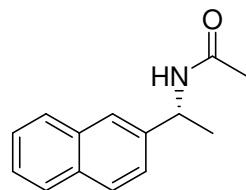
122.1, 125.2, 125.4, 126.4, 126.9, 128.6, 128.8, 129.4, 133.7, 134.5, 138.2, 143.9, 147.5 ppm; HRMS Calcd. for C₁₉H₁₉NO (M+1) 277.1467, found 277.1476. Mp = 110.5 – 111.2 °C; HPLC (OD-H, eluent:heptane/i-PrOH = 99/1, detector: 215 nm, flow rate: 0.5 mL/min), t₁ = 19.5 min, t₂ = 24.7 min.

(R)-1-Naphthalen-2-yl-ethylamine hydrochloride (7c)



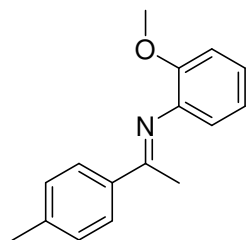
68% yield, light brown solid; ¹H NMR (400 MHz, D₂O) 1.47 (d, *J* = 6.49 Hz, 3H), 4.41 (q, *J* = 6.44 Hz, 1H), 7.28 – 7.30 (m, 3H), 7.57 – 7.65 (m, 4H) ppm; ¹³C NMR (100 MHz, D₂O) 19.4, 51.2, 123.9, 125.9, 127.0, 127.1, 127.8, 128.1, 129.2, 132.9, 133.1, 135.2 ppm; HRMS Calcd. for C₁₂H₁₄ClN (M+1-HCl) 172.11208, found 172.11195; Mp = 214.6 – 214.7 °C; product was derivatized with acetic anhydride in the presence of triethylamine and enantioselectivity was determined by GC:

(R)-N-(1-Naphthalen-2-yl-ethyl)-acetamide (7d)



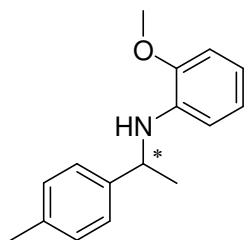
White solid, absolute configuration determined in comparison with literature⁸, 99% ee, [α]_D = +23.6 (*c* 1.00, CHCl₃); ¹H NMR (400 MHz, CDCl₃) 1.54 (d, *J* = 6.93 Hz, 3H), 1.97 (s, 3H), 5.26 (q, *J* = 7.24 Hz, 1H), 6.21 (br, 1H), 7.40 – 7.47 (m, 3H), 7.74 – 7.80 (m, 4H) ppm; ¹³C NMR (100 MHz, CDCl₃) 22.6, 24.4, 49.8, 125.5, 125.7, 126.8, 127.2, 128.6, 128.8, 129.4, 133.7, 134.3, 141.5, 170.1 ppm; HRMS Calcd. for C₁₄H₁₅NO (M+1) 214.12264, found 214.12283; Mp = 119.2 – 119.3 °C; GC Chiralsil DEX CB, initial temp. 125 °C for 4 min, then 3 °C/min to 140 °C, then 10 °C/min to 180 °C, then 10 °C/min to 125 °C, t₁ = 37.8 min, t₂ = 38.57 min.

N-(2-Methoxy-phenyl)-(1-p-tolyl-ethylidene)-amine (8a)



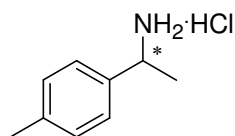
60% yield, yellow oil, ^1H NMR (400 MHz, CDCl_3) 2.17 (s, 3H), 2.42 (s, 3H), 3.79 (s, 3H), 6.78 – 6.80 (m, 1H), 6.93 – 7.10 (m, 3H), 7.25 – 7.27 (m, 2H), 7.92 – 7.94 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) 18.6, 22.3, 56.6, 112.6, 121.6, 121.8, 124.9, 128.2, 129.9, 137.7, 141.5, 141.7, 150.0, 167.7 ppm; HRMS Calcd. for $\text{C}_{19}\text{H}_{17}\text{NO}$ ($\text{M}+1$) 239.1310, found 239.1309.

(-)-*N*-(2-Methoxy-phenyl)-1-*p*-tolyl-ethylamine (8b)



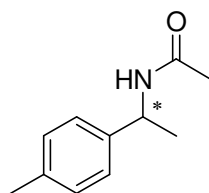
95% yield, light yellow solid, 98% ee, $[\alpha]_{\text{D}} = -19.1$ (c 1.00, CHCl_3), ^1H NMR (400 MHz, CDCl_3) 1.54 (d, $J = 6.7$ Hz, 3H), 2.32 (s, 3H), 3.88 (s, 3H), 4.45 (q, $J = 6.5$ Hz, 1H), 4.60 (br, 1H), 6.33 – 6.38 (m, 1H), 6.55 – 6.79 (m, 3H), 7.10 – 7.14 (m, 2H), 7.24 – 7.28 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) 22.0, 26.1, 53.9, 56.3, 110.1, 111.9, 117.1, 122.1, 126.7, 130.2, 137.2, 138.2, 143.4, 147.4 ppm; HRMS Calcd. for $\text{C}_{16}\text{H}_{19}\text{NO}$ ($\text{M}+1$) 241.1467, found 241.1458; $\text{Mp} = 88.6 - 88.8$ °C; HPLC (OD-H, eluent:heptane/*i*-PrOH = 99/1, detector: 215 nm, flow rate: 0.5 mL/min), $t_1 = 12.9$ min, $t_2 = 15.4$ min.

1-*p*-Tolyl-ethylamine hydrochloride (8c)



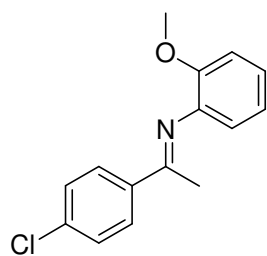
71% yield, light brown solid, ^1H NMR (400 MHz, D_2O) 1.47 (d, $J = 6.85$ Hz, 3H), 2.19 (s, 3H), 4.35 (q, $J = 6.74$, 1H), 7.15 – 7.22 (m, 4H) ppm; ^{13}C NMR (100 MHz, D_2O) 19.5, 20.4, 51.0, 126.7, 130.0, 134.9, 139.7 ppm; HRMS Calcd. for $\text{C}_9\text{H}_{14}\text{ClN}$ ($\text{M}+1-\text{HCl}$) 136.11208, found 136.11205; product was derivatized (in the GC vial) with acetic anhydride in the presence of triethylamine and enantioselectivity was determined by GC:

(1-*p*-Tolyl-ethyl)-acetamide (8d)



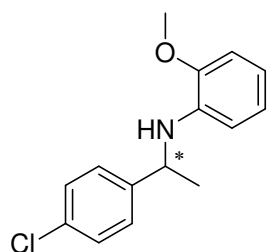
98% ee, GC Chiralsil DEX CB, initial temp. 125 °C for 4 min, then 3 °C/min to 140 °C, then 10 °C/min to 180 °C, then 10 °C/min to 125 °C, $t_1 = 14.7$ min, $t_2 = 15.0$ min.

***N*-[1-(4-Chloro-phenyl)-ethylidene]-(2-methoxy-phenyl)-amine (9a)**



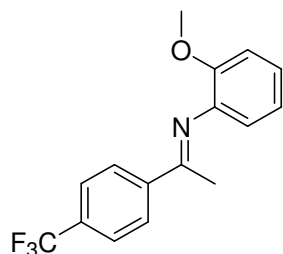
46% yield, light yellow solid, ^1H NMR (400 MHz, CDCl_3) 2.16 (s, 3H), 3.79 (s, 3H), 6.76 – 6.78, (m, 1H), 6.93 – 6.99 (m, 2H), 7.07 – 7.11 (m, 1H) 7.40 – 7.42 (m, 2H), 7.95 – 7.97 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) 18.6, 56.5, 112.5, 121.4, 121.8, 125.3, 129.4, 129.6, 137.4, 138.7, 141.2, 149.8, 166.8 ppm; HRMS Calcd. for $\text{C}_{15}\text{H}_{14}\text{ClNO}$ (M+1) 259.0764, found 259.0772. Mp = 62.8 – 62.9 °C.

(-)-*N*-[1-(4-Chloro-phenyl)-ethyl]-(2-methoxy-phenyl)-amine (9b)



95% yield, light brown solid, 97% ee, $[\alpha]_{\text{D}} = -34.8$ (c 1.01, CHCl_3), ^1H NMR (400 MHz, CDCl_3) 1.53 (d, $J = 6.7$ Hz, 3H), 3.89 (s, 3H), 4.45 (q, $J = 5.1$ Hz, 1H), 4.61 (br, 1H), 6.26 – 6.28 (m, 1H), 6.60 – 6.79 (m, 3H), 7.26 – 7.32 (m, 4H) ppm; ^{13}C NMR (100 MHz, CDCl_3) 25.4, 53.1, 55.6, 109.5, 111.2, 116.8, 121.3, 127.5, 129.0, 132.5, 137.2, 144.3, 146.8 ppm; HRMS Calcd. for $\text{C}_{15}\text{H}_{16}\text{ClNO}$ (M+1) 261.0920, found 261.0915; Mp = 113.3 – 114.1 °C; HPLC (OD–H, eluent:heptane/*i*-PrOH = 99/1, detector: 215 nm, flow rate: 0.5 mL/min), $t_1 = 16.4$ min, $t_2 = 22.7$ min.

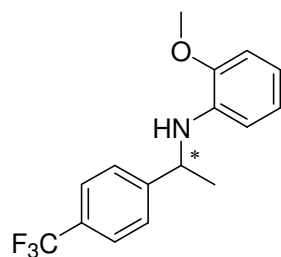
***N*-[1-(4-(trifluoromethyl)-phenyl)-ethylidene]-(2-methoxy-phenyl)-amine (10a)**



34% yield, light yellow solid, ^1H NMR (400 MHz, CDCl_3) 2.20 (s, 3H), 3.80 (s, 3H), 6.76 – 6.80 (m, 1H), 6.94 – 7.15 (m, 3H), 7.68 – 7.72 (m, 2H), 8.10 – 8.14 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) 18.8, 56.5, 112.5, 121.3, 121.9, 125.0 (q, $J = 272.2$ Hz), 125.5 (q, $J = 3.7$ Hz), 125.5, 128.6, 132.9 (q, $J = 32.6$ Hz), 141.0, 143.5, 149.6, 166.9 ppm; ^{19}F (376 MHz,

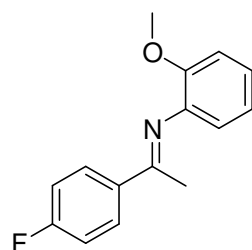
CDCl₃) –63.1 ppm HRMS Calcd. for C₁₆H₁₄F₃NO (M+1) 293.1028, found 293.1014; Mp = 87.1 – 87.3 °C.

(–)-N-(2-Methoxy-phenyl)-1-(4-trifluoromethyl-phenyl)-ethylamine (10b)



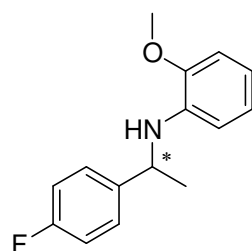
97% yield, white solid, 97% ee, [α]_D = –40.8 (c 1.01, CHCl₃), ¹H NMR (400 MHz, CDCl₃) 1.56 (d, *J* = 6.7 Hz, 3H), 3.91 (s, 3H), 4.53 (q, *J* = 6.2 Hz, 1H), 4.66 (br, 1H), 6.24 – 6.26 (m, 1H), 6.63 – 6.72 (m, 2H), 6.78 – 6.80 (m, 1H), 7.48–7.50 (m, 2H), 7.57 – 7.59 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) 26.0, 54.1, 56.3, 110.3, 111.9, 117.7, 122.0, 125.3 (q, *J* = 271.9 Hz), 126.5 (q, *J* = 3.8 Hz), 127.1, 130.0 (q, *J* = 32.2 Hz), 137.7, 147.5, 150.7 ppm; ¹⁹F (376 MHz, CDCl₃) –62.7 ppm; HRMS Calcd. for C₁₆H₁₆F₃NO (M+1) 295.1184, found 295.1171; Mp = 93.7 – 93.8 °C; HPLC (OD–H, eluent:heptane/*i*-PrOH = 99/1, detector: 215 nm, flow rate: 0.5 mL/min), *t*₁ = 16.2 min, *t*₂ = 24.2 min.

N-[1-(4-Fluoro-phenyl)-ethylidene]-(2-methoxy-phenyl)-amine (11a)



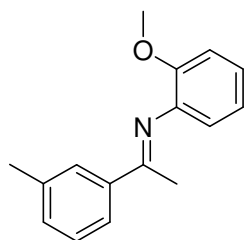
55% yield, light yellow solid, ¹H NMR (400 MHz, CDCl₃) 2.17 (s, 3H), 3.80 (s, 3H), 6.77 – 6.80 (m, 1H), 6.94 – 7.0 (m, 2H), 7.07 – 7.14 (m, 3H), 8.01 – 8.05 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) 17.9, 55.8, 111.8, 115.4 (d, *J* = 21.5 Hz), 120.8, 121.2, 124.5, 129.6, 129.7, 135.8, 140.6, 149.2, 164.5 (d, *J* = 250.36 Hz), 166.0 ppm; ¹⁹F (376 MHz, CDCl₃) –111.0 ppm; HRMS Calcd. for C₁₅H₁₄FNO (M+1) 243.1059, found 243.1048; Mp = 65.7 – 65.9 °C

(–)-N-[1-(4-Fluoro-phenyl)-ethyl]-(2-methoxy-phenyl)-amine (11b)



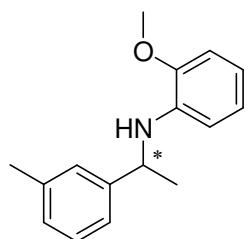
94% yield, white solid, 97% ee, $[\alpha]_D = -56.0$ (c 1.00, CHCl_3), $^1\text{H NMR}$ (400 MHz, CDCl_3) 1.68 (d, $J = 6.7$ Hz, 3H), 4.01 (s, 3H), 4.62 (q, $J = 6.7$ Hz, 1H), 4.82 (br, 1H), 6.50 – 6.52 (m, 1H), 6.79 – 6.84 (m, 1H), 6.88 – 6.95 (m, 2H), 7.13 – 7.17 (m, 2H), 7.47 – 7.50 (m, 2H) ppm; $^{13}\text{C NMR}$ (100 MHz, CDCl_3) 25.6, 53.0, 55.7, 109.5, 111.3, 115.6 (d, $J = 21.3$ Hz), 116.8, 121.4, 127.5 (d, $J = 7.9$ Hz), 137.3, 141.3 (d, $J = 3.0$ Hz), 146.8, 162.0 (d, $J = 244.1$ Hz) ppm; ^{19}F (376 MHz, CDCl_3) –116.9 ppm; HRMS Calcd. for $\text{C}_{15}\text{H}_{16}\text{FNO}$ ($M+1$) 243.1059, found 243.1048; Mp = 71.0 – 72.1 °C; HPLC (OD–H, eluent:heptane/*i*-PrOH = 99/1, detector: 215 nm, flow rate: 0.5 mL/min), $t_1 = 15.3$ min, $t_2 = 20.3$ min.

***N*-(2-Methoxy-phenyl)-(1-*m*-tolyl-ethylidene)-amine (12a)**



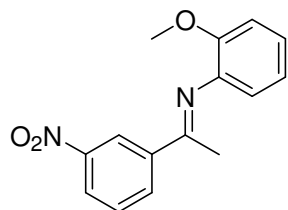
61% yield, light yellow solid, $^1\text{H NMR}$ (400 MHz, CDCl_3) 2.17 (s, 3H), 2.42 (s, 3H), 3.79 (s, 3H), 6.76 – 6.79 (m, 1H), 6.92 – 6.98 (m, 2H), 7.05 – 7.09 (m, 1H), 7.26 – 7.35 (m, 2H), 7.75 – 7.77 (m, 1H), 7.88 (s, 1H) ppm; $^{13}\text{C NMR}$ (100 MHz, CDCl_3) 18.8, 22.4, 56.5, 112.4, 121.5, 121.8, 125.0, 125.4, 128.7, 129.1, 132.1, 138.9, 140.3, 141.6, 149.8, 168.2 ppm; HRMS Calcd. for $\text{C}_{16}\text{H}_{17}\text{NO}$ ($M+1$) 239.1310, found 239.1297; Mp = 64.8 – 64.9 °C.

(–)-*N*-(2-Methoxy-phenyl)-1-*m*-tolyl-ethylamine (12b)



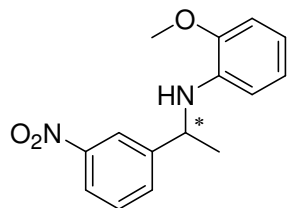
88% yield, colorless oil, 93% ee, $[\alpha]_D = -16.9$ (c 1.00, CHCl_3), $^1\text{H NMR}$ (400 MHz, CDCl_3) 1.54 (d, $J = 6.7$ Hz, 3H), 2.34 (s, 3H), 3.89 (s, 3H), 4.43 (q, $J = 6.7$ Hz, 1H), 4.61 (br, 1H), 6.34 – 6.39 (m, 1H), 6.57 – 6.80 (m, 3H), 7.02 – 7.05 (m, 1H), 7.18 – 7.26 (m, 3H) ppm; $^{13}\text{C NMR}$ (100 MHz, CDCl_3) 22.4, 26.1, 54.3, 56.2, 110.1, 111.9, 117.1, 122.1, 123.8, 127.4, 128.5, 129.4, 138.2, 139.0, 146.4, 147.4 ppm; HRMS Calcd. for $\text{C}_{16}\text{H}_{19}\text{NO}$ ($M+1$) 241.1467, found 241.1452; HPLC (OD–H, eluent:heptane/*i*-PrOH = 99/1, detector: 215 nm, flow rate: 0.5 mL/min), $t_1 = 12.8$ min, $t_2 = 15.8$ min.

***N*-(2-Methoxy-phenyl)-[1-(3-nitro-phenyl)-ethylidene]-amine (13a)**



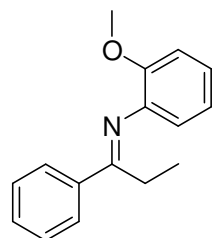
76% yield, yellow solid, ^1H NMR (400 MHz, CDCl_3) 2.23 (s, 3H), 3.80 (s, 3H), 6.77 – 6.80 (m, 1H), 6.95 – 7.00 (m, 2H), 7.09 – 7.12 (m, 1H), 7.59 – 7.64 (m, 1H), 8.28 – 8.31 (m, 1H), 8.36 – 8.39 (m, 1H), 8.81 – 8.83 (m, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3) 18.7, 56.5, 112.4, 121.3, 121.8, 123.2, 125.7, 125.8, 130.2, 134.1, 140.5, 141.9, 149.3, 149.5, 165.8 ppm; HRMS Calcd. for $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_3$ (M+1) 271.10772, found 271.10760; Mp = 89.7 – 90.1 °C

(-)-*N*-2-Methoxy-phenyl-1-(3-nitro-phenyl)-ethylamine (13b)



95% yield, 61% ee, yellow solid, $[\alpha]_{\text{D}} = -41.7$ (c 1.02, CHCl_3); ^1H NMR (400 MHz, CDCl_3) 1.61 (d, $J = 6.75$, 3H), 3.93 (s, 3H), 4.59 (q, $J = 6.70$ Hz, 1H), 4.76 (br, 1H), 6.25 – 6.28 (m, 1H), 6.65 – 6.75 (m, 2H), 6.81 – 6.84 (m, 1H), 7.49 (t, $J = 7.9$ Hz, 1H), 7.73 – 7.76 (m, 1H), 8.08 – 8.11 (m, 1H), 8.28 – 8.29 (m, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3) 26.0, 53.9, 56.3, 110.3, 111.7, 117.9, 121.8, 121.9, 122.9, 130.5, 133.0, 137.4, 147.5, 149.0, 149.5 ppm; HRMS Calcd. for $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_3$ (M+1) 273.12337, found 273.12329; Mp = 78.9 – 79.6 °C; HPLC (OD-H, eluent:heptane/*i*-PrOH = 80/20, detector: 215 nm, flow rate: 0.5 mL/min), $t_1 = 12.6$ min, $t_2 = 16.8$ min.

***N*-(2-Methoxy-phenyl)-(1-phenyl-propylidene)-amine (14a)**

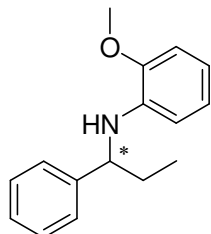


47% yield, light yellow solid, mixture of isomers (6.7/1),

^1H NMR (400 MHz, CDCl_3) 1.05 (major isomer, t, $J = 7.68$ Hz, 3H), 1.25 (minor isomer, t, $J = 7.42$ Hz, 3H), 2.60 (major isomer, q, $J = 7.67$ Hz, 2H), 2.84 (minor isomer, q, $J = 7.42$ Hz, 2H), 3.70 (minor isomer, s, 3H), 3.79 (major isomer, s, 3H), 6.75 – 6.77 (m, 1H), 6.93 – 6.98 (m, 2H), 7.05 – 7.09 (m, 1H), 7.44 – 7.46 (m, 3H), 7.95 – 7.98 (m, 2H) ppm; ^{13}C NMR (100

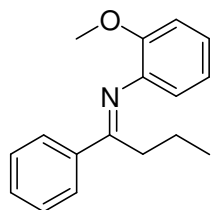
MHz, CDCl₃) 13.1, 25.1, 56.5, 112.4, 121.1, 121.8, 124.8, 128.7, 129.3, 131.2, 139.0, 141.6, 149.7, 173.1 ppm; HRMS Calcd. for C₁₆H₁₇NO (M+1) 239.1310, found 239.1314; Mp = 55.7–57.0 °C.

(-)-N-(2-Methoxy-phenyl)-1-phenyl-propylamine (14b)



96% yield, yellow oil, 94% ee, [α]_D = -13.7 (*c* 1.00, CHCl₃); ¹H NMR (400 MHz, CDCl₃) 1.06 (t, *J* = 7.44 Hz, 3H), 1.94 (quint, *J* = 7.05, 2H), 3.95 (s, 3H), 4.30 (br, 1H), 4.78 (br, 1H), 6.43–6.45 (m, 1H), 6.67 – 6.69 (m, 1H), 6.76 – 6.84 (m, 2H), 7.29 – 7.31 (m, 1H), 7.38 – 7.42 (m, 4H) ppm; ¹³C NMR (100 MHz, CDCl₃) 11.7, 32.6, 56.2, 60.4, 110.1, 111.7, 117.0, 122.0, 127.3, 127.6, 129.3, 138.3, 145.0, 147.5 ppm; HRMS Calcd. for C₁₆H₁₉NO (M+1) 241.1467, found 241.1469; HPLC (OD–H, eluent:heptane/*i*-PrOH = 99/1, detector: 215 nm, flow rate: 0.5 mL/min), *t*₁ = 13.0 min, *t*₂ = 15.1 min.

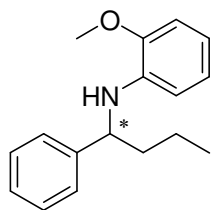
N-(2-Methoxy-phenyl)-(1-phenyl-butylidene)-amine (15a)



27% yield, yellow oil, 7% of enamine present, mixture of isomers 3.9:1

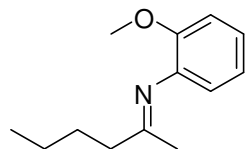
¹H NMR (400 MHz, CDCl₃) 0.81 (major isomer, t, *J* = 7.41 Hz, 3H), 1.06 (minor isomer, t, *J* = 7.39 Hz, 3H), 1.44 – 1.54 (major isomer, m, 2H), 1.66–1.72 (minor isomer, m, 2H), 2.22 (minor isomer, t, *J* = 7.35 Hz, 2H), 2.54 – 2.58 (major isomer, m, 2H), 3.78 (major isomer, s, 3H), 3.93 (minor isomer, s, 3H), 6.74 – 6.76 (m, 1H), 6.92 – 6.98 (m, 2H), 7.04 – 7.09 (m, 1H), 7.43 – 7.45 (m, 3H), 7.92 – 7.95 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) 14.6, 15.0, 20.9, 21.8, 33.8, 44.0, 56.5, 111.8, 112.3, 121.1, 121.4, 121.7, 122.1, 124.8, 127.1, 127.8, 128.6, 129.2, 131.1, 139.4, 141.5, 149.7, 172.1 ppm; HRMS Calcd. for C₁₇H₁₉NO (M+1) 254.15394, found 254.15384

(-)-*N*-(2-Methoxy-phenyl)-(1-phenyl-butyl)-amine (15b)



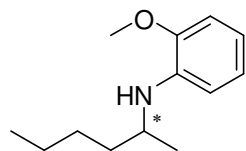
96% yield, colorless oil, 97% ee, $[\alpha]_D = -23.6$ (c 1.03, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3) 0.96 (t, $J = 7.35$ Hz, 3H), 1.35 – 1.53 (m, 2H), 1.78 – 1.88 (m, 2H), 3.90 (s, 3H), 4.31 (t, $J = 6.86$ Hz, 1H), 4.70 (br, 1H), 6.35 – 6.37 (m, 1H), 6.58 – 6.62 (m, 1H), 6.68 – 6.78 (m, 2H), 7.20 – 7.26 (m, 1H), 7.30 – 7.37 (m, 4H) ppm; $^{13}\text{C NMR}$ (100 MHz, CDCl_3) 15.0, 20.6, 42.2, 56.4, 58.8, 110.29, 111.8, 117.0, 122.1, 127.3, 127.7, 129.4, 138.4, 145.5, 147.5 ppm; HRMS Calcd. for $\text{C}_{17}\text{H}_{21}\text{NO}$ ($M+1$) 256.16959, found 256.16949; HPLC (OD–H, eluent:heptane/*i*-PrOH = 99/1, detector: 215 nm, flow rate: 0.5 mL/min), $t_1 = 12.1$ min, $t_2 = 17.9$ min.

***N*-(hexan-2-ylidene)-2-methoxyaniline (16a)**



35% yield, yellow liquid, mixture of isomers 3.9:1; $^1\text{H NMR}$ (400 MHz, CDCl_3) 0.79 (minor isomer, t, $J = 7.24$ Hz, 3H), 0.96 (major isomer, t, $J = 7.21$ Hz, 3H), 1.19 (minor isomer, sextet, $J = 7.20$ Hz, 2H), 1.43 (major isomer, sextet, $J = 7.37$ Hz, 2H), 1.67 (major isomer, quintet, $J = 7.37$ Hz, 2H), 1.72 (major isomer, s, 3H), 2.06 (minor isomer, t, $J = 8.09$ Hz, 2H), 2.19 (minor isomer, s, 3H), 2.45 (major isomer, t, $J = 7.30$ Hz, 2H), 3.76 (s, 3H), 6.61 – 6.67 (m, 1H), 6.84 – 7.05 (m, 3H) ppm; $^{13}\text{C NMR}$ (100 MHz, CDCl_3) 14.7, 14.9, 20.6, 23.3, 23.5, 26.8, 29.6, 35.3, 42.4, 56.3, 56.4, 111.9, 112.3, 121.5, 121.6, 121.7, 124.7, 140.9, 141.4, 150.1, 174.8, 175.2 ppm; HRMS Calcd. for $\text{C}_{13}\text{H}_{19}\text{NO}$ ($M+1$) 205.1467, found 205.1464.

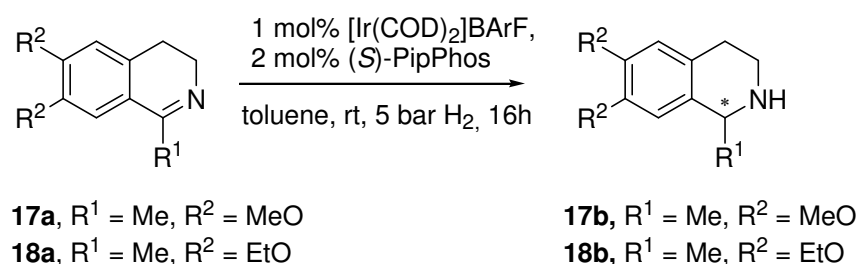
***N*-(hexan-2-yl)-2-methoxyaniline (16b)**



96% yield, light yellow liquid, 16% ee; $^1\text{H NMR}$ (400 MHz, CDCl_3) 0.93 (t, $J = 6.72$ Hz, 3H), 1.20 – 1.70 (m, 9H), 3.48 (q, $J = 6.03$ Hz, 1H), 3.86 (s, 3H), 4.06 (br, 1H), 6.60 – 6.68 (m, 2H), 6.77 – 6.89 (m, 2H) ppm; $^{13}\text{C NMR}$ (100 MHz, CDCl_3) 15.1, 21.8, 23.8, 29.4, 37.9, 49.0, 56.3, 110.4, 110.9, 116.5, 122.2, 138.6, 147.6 ppm; HRMS Calcd. for $\text{C}_{13}\text{H}_{21}\text{NO}$ ($M+1$) 207.1623, found 207.1620.

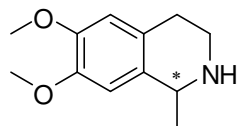
CYCLIC IMINES:

Table 1. Asymmetric hydrogenation of dihydroisoquinolines



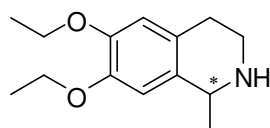
R ¹ /R ²	Ir precursor	Solvent	Conversion (%)	ee (%)
Me/MeO	[Ir(COD) ₂]BArF	toluene	62	62
Me/EtO	[Ir(COD) ₂]BArF	Toluene	100	51

6,7-dimethoxy-1-methyl-1,2,3,4-tetrahydroisoquinoline (**17b**)



98% yield, white solid; ¹H NMR (400 MHz, CDCl₃) 1.41 (d, *J* = 6.28 Hz, 3H), 2.61 – 2.65 (m, 1H), 2.75 – 2.80 (m, 2H), 2.94 – 2.99 (m, 1H), 3.21 – 3.24 (m, 1H), 3.81 (s, 6H), 4.03 (br, 1H), 6.53 (s, 1H), 6.58 (s, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) 23.6, 30.2, 42.5, 52.0, 56.7, 56.9, 109.9, 112.6, 127.5, 133.0, 148.2, 148.3 ppm; HPLC (OD–H, eluent:heptane/*i*-PrOH = 88/12, detector: 215 nm, flow rate: 0.5 mL/min), *t*₁ = 23.5 min, *t*₂ = 28.3 min; Mp = 97.3 – 97.9 °C.

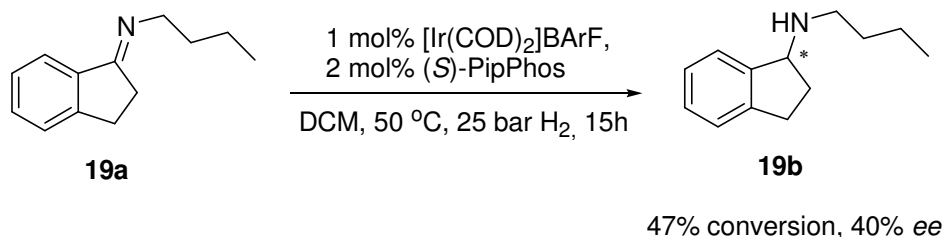
6,7-diethoxy-1-methyl-1,2,3,4-tetrahydroisoquinoline (**18b**)



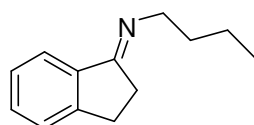
97% yield, light yellow solid; ¹H NMR (400 MHz, CDCl₃) 1.38 – 1.44 (m, 9H), 1.68 (br, 1H), 2.58 – 2.65 (m, 1H), 2.72 – 2.80 (m, 1H), 2.95 – 3.01 (m, 1H), 3.20 – 3.26 (m, 1H), 4.05 (q, *J* = 6.99 Hz, 5H), 6.57 (s, 1H), 6.64 (s, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) 15.4, 15.5, 23.3, 30.0, 42.5, 51.7, 65.0, 65.4, 112.4, 114.6, 127.7, 133.2, 147.4, 147.8 ppm; HPLC (OD–H, eluent:heptane/*i*-PrOH = 88/12, detector: 215 nm, flow rate: 0.5 mL/min), *t*₁ = 18.0 min, *t*₂ = 25.4 min; Mp = 63.9 – 64.0 °C.

N-BUTYL IMINE

Scheme 1. Asymmetric hydrogenation of *N*-(2,3-dihydro-1*H*-inden-1-ylidene)butan-1-amine (**19a**)

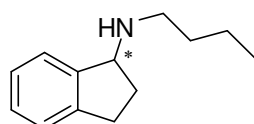


N-(2,3-dihydro-1*H*-inden-1-ylidene)butan-1-amine (**19a**)



31% yield, colorless oil, ¹H NMR (400 MHz, CDCl₃) 0.97 (t, *J* = 7.35 Hz, 3H), 1.44 (sextet, *J* = 6.44 Hz, 2H), 1.72 (quintet, *J* = 7.20 Hz, 2H), 2.69 (t, *J* = 6.45 Hz, 2H), 3.06 (t, *J* = 6.07 Hz, 2H), 3.46 (t, *J* = 7.24 Hz, 2H), 7.25 – 7.38 (m, 3H), 7.82 (d, *J* = 7.56 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) 15.0, 21.8, 28.8, 29.0, 54.6, 123.1, 126.4, 127.7, 131.7, 140.8, 150.3, 174.5 ppm; HRMS Calcd. for C₁₃H₁₇N (M+1) 188.14338, found 188.14279.

N-butyl-2,3-dihydro-1*H*-inden-1-amine (**19b**)



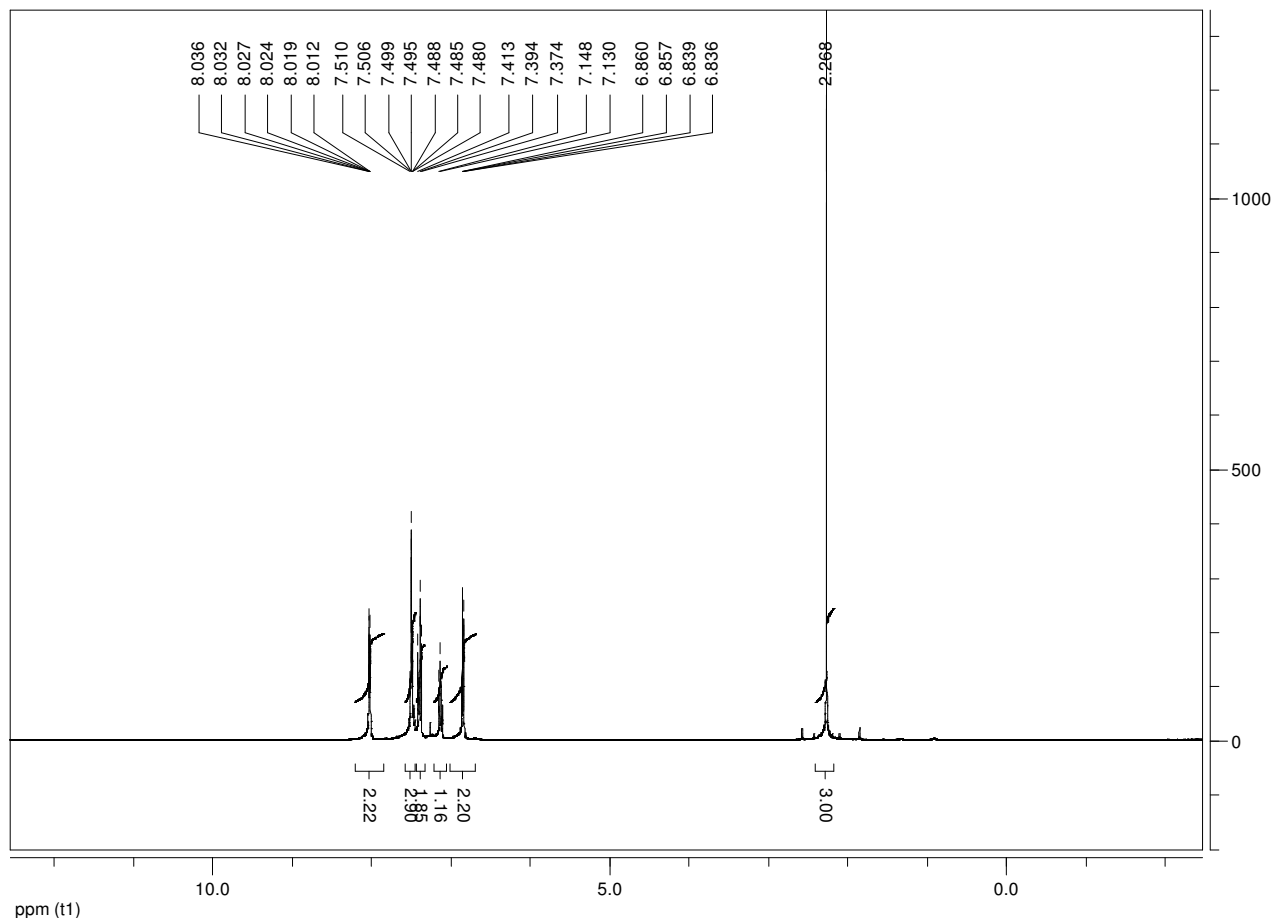
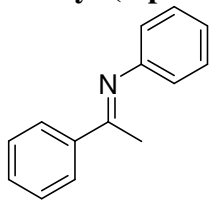
orange oil; ¹H NMR (400 MHz, CDCl₃) 0.98 (t, *J* = 7.37 Hz, 3H), 1.39 (sextet, *J* = 7.37 Hz, 2H), 1.52 (quintet, *J* = 6.95 Hz, 2H), 1.80 – 1.89 (m, 1H), 2.38 – 2.46 (m, 1H), 2.74 (t, *J* = 7.37 Hz, 2H), 2.78 – 2.86 (m, 1H), 2.98 – 3.05 (m, 1H), 4.26 (t, *J* = 6.57 Hz, 1H), 7.19 – 7.26 (m, 3H), 7.35 – 7.37 (m, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) 15.0, 21.5, 31.3, 33.6, 34.6, 48.1, 64.3, 125.0, 125.7, 127.1, 128.2, 144.5, 146.4 ppm; HRMS Calcd. for C₁₃H₁₉N (M+1) 190.15903, found 190.15839; HPLC (AS–H, eluent:heptane/*i*-PrOH = 99.7/0.3, detector: 210 nm, flow rate: 0.5 mL/min), *t*₁ = 8.7 min, *t*₂ = 9.7 min.

References:

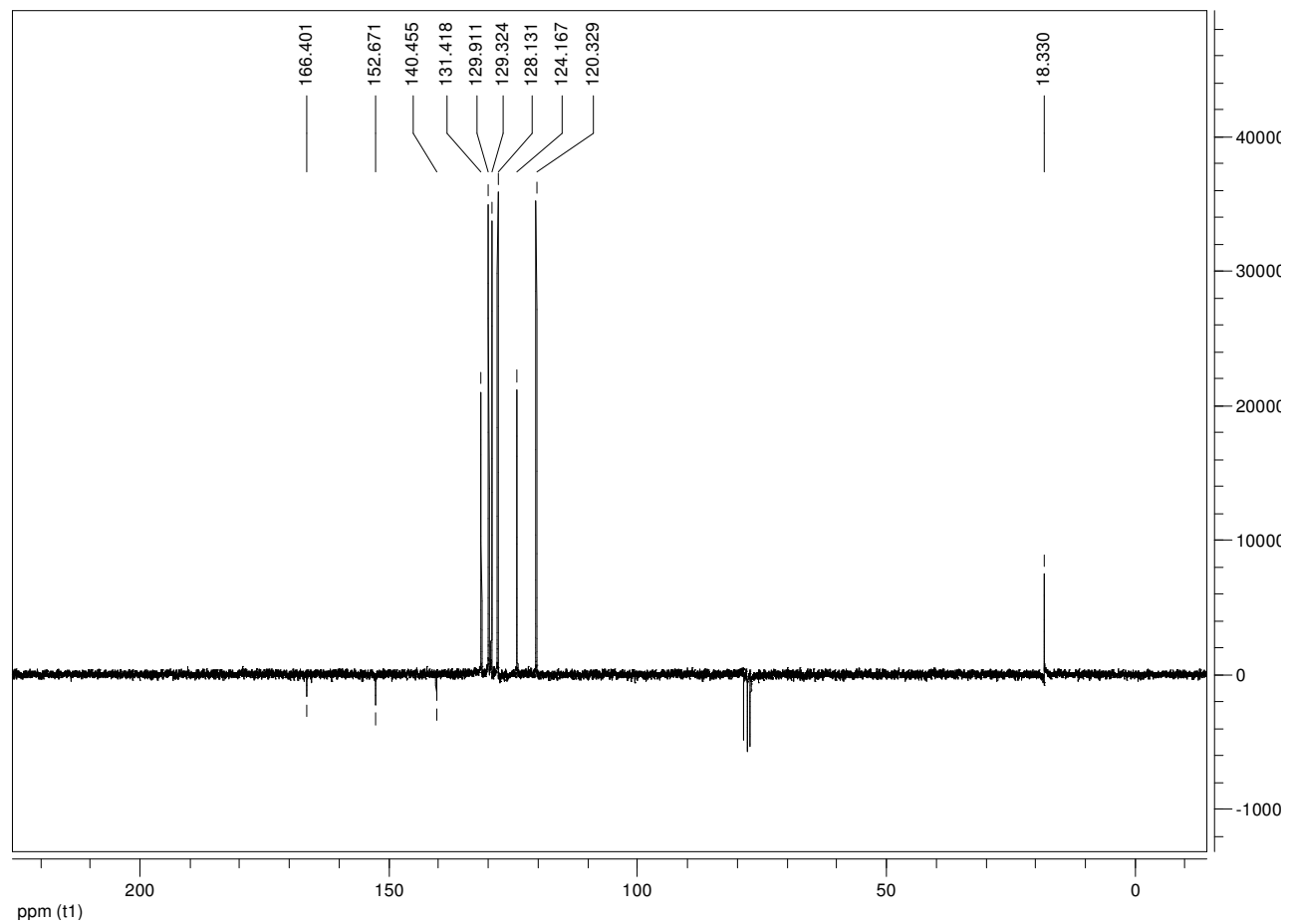
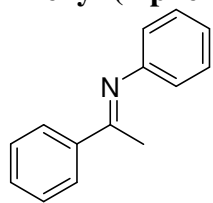
- (1) Arnold, L. A.; Imbos, R.; Mandoli, A.; de Vries, A. H. M.; Naasz, R.; Feringa, B. L. *Tetrahedron* **2000**, *56*, 2865-2878.
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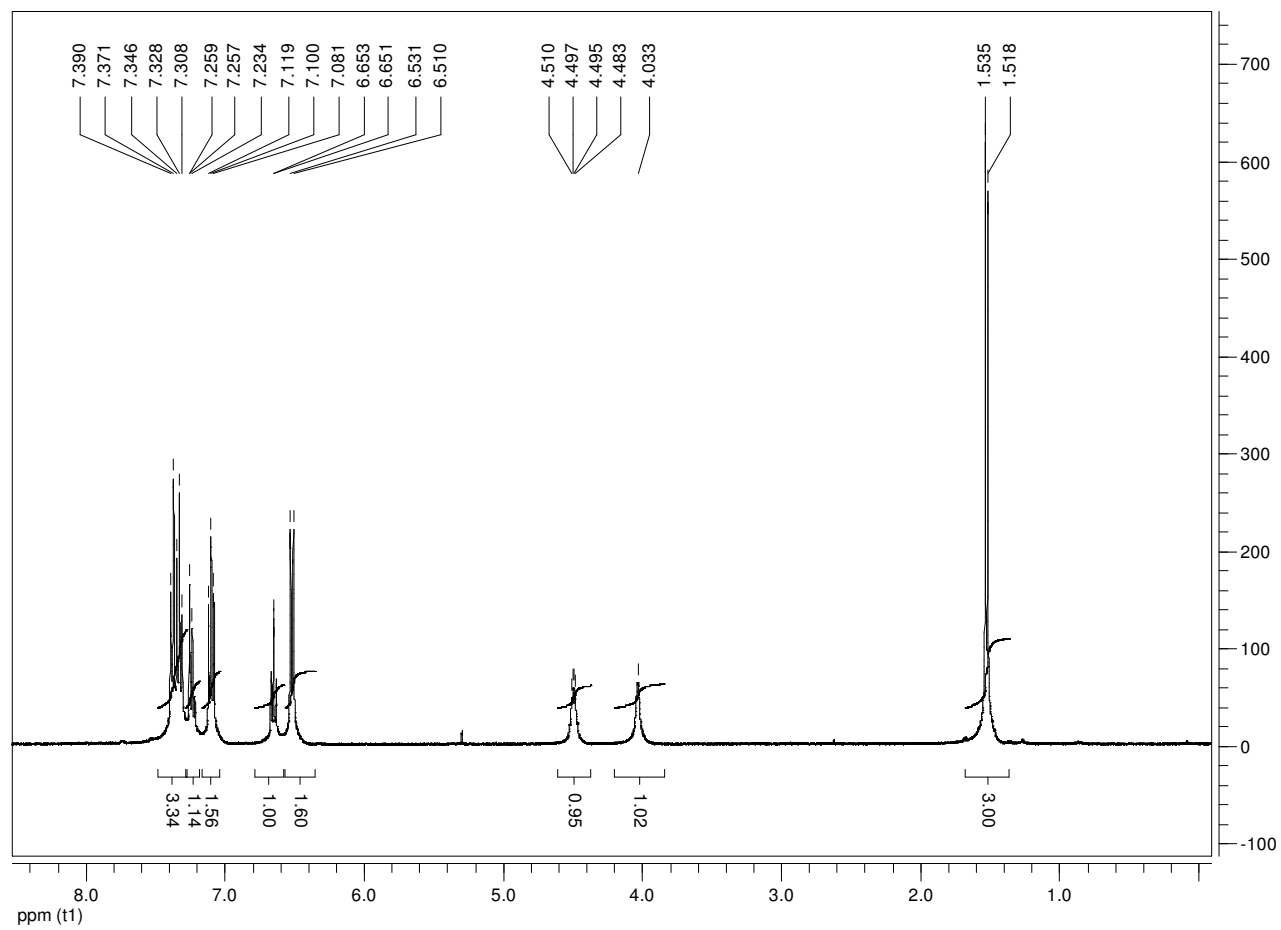
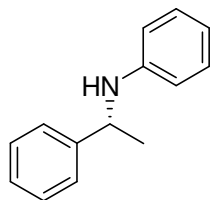
Phenyl-(1-phenyl-ethylidene)-amine (1a), ¹H



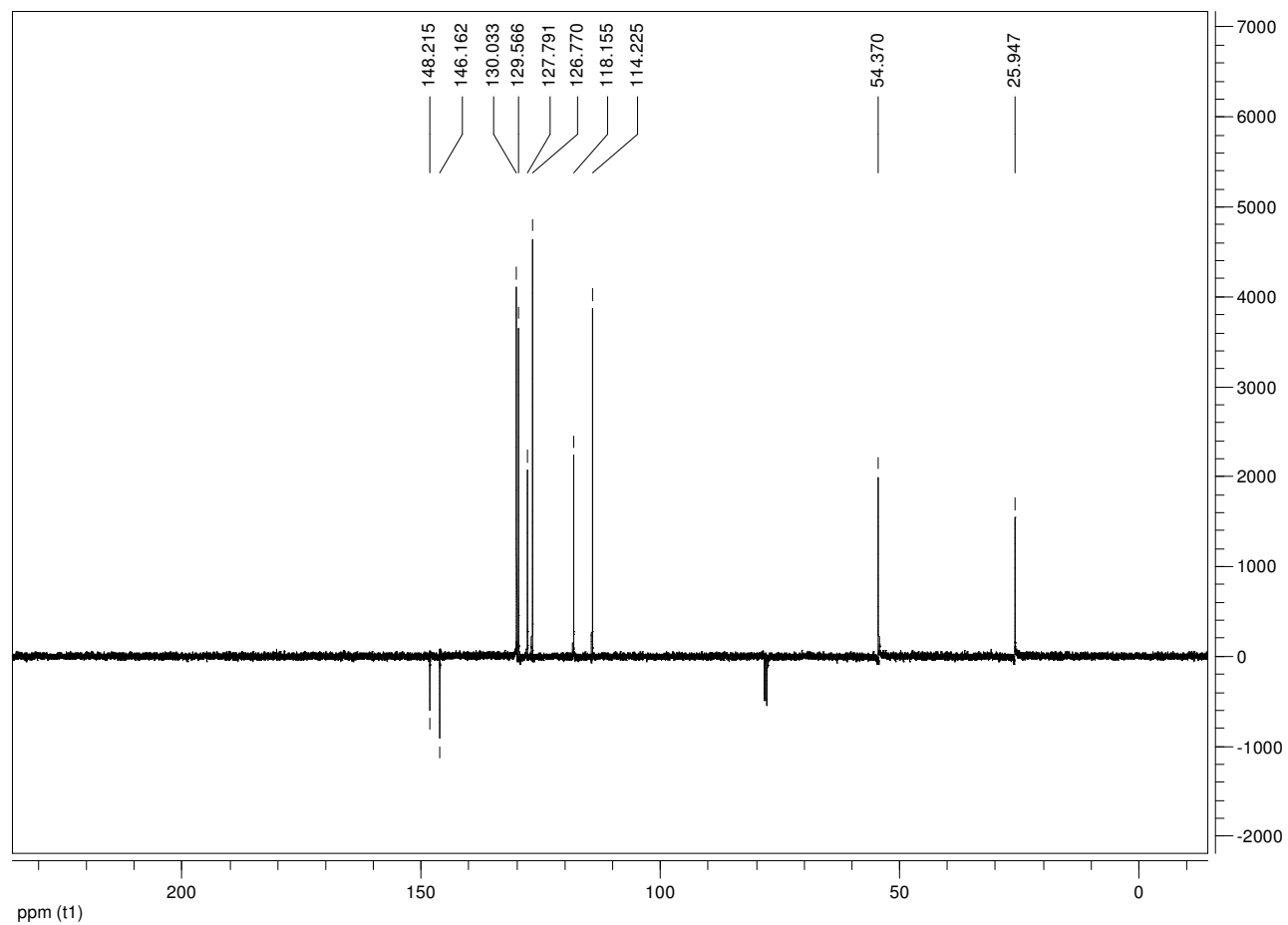
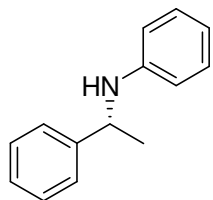
Phenyl-(1-phenyl-ethylidene)-amine (1a), ¹³C



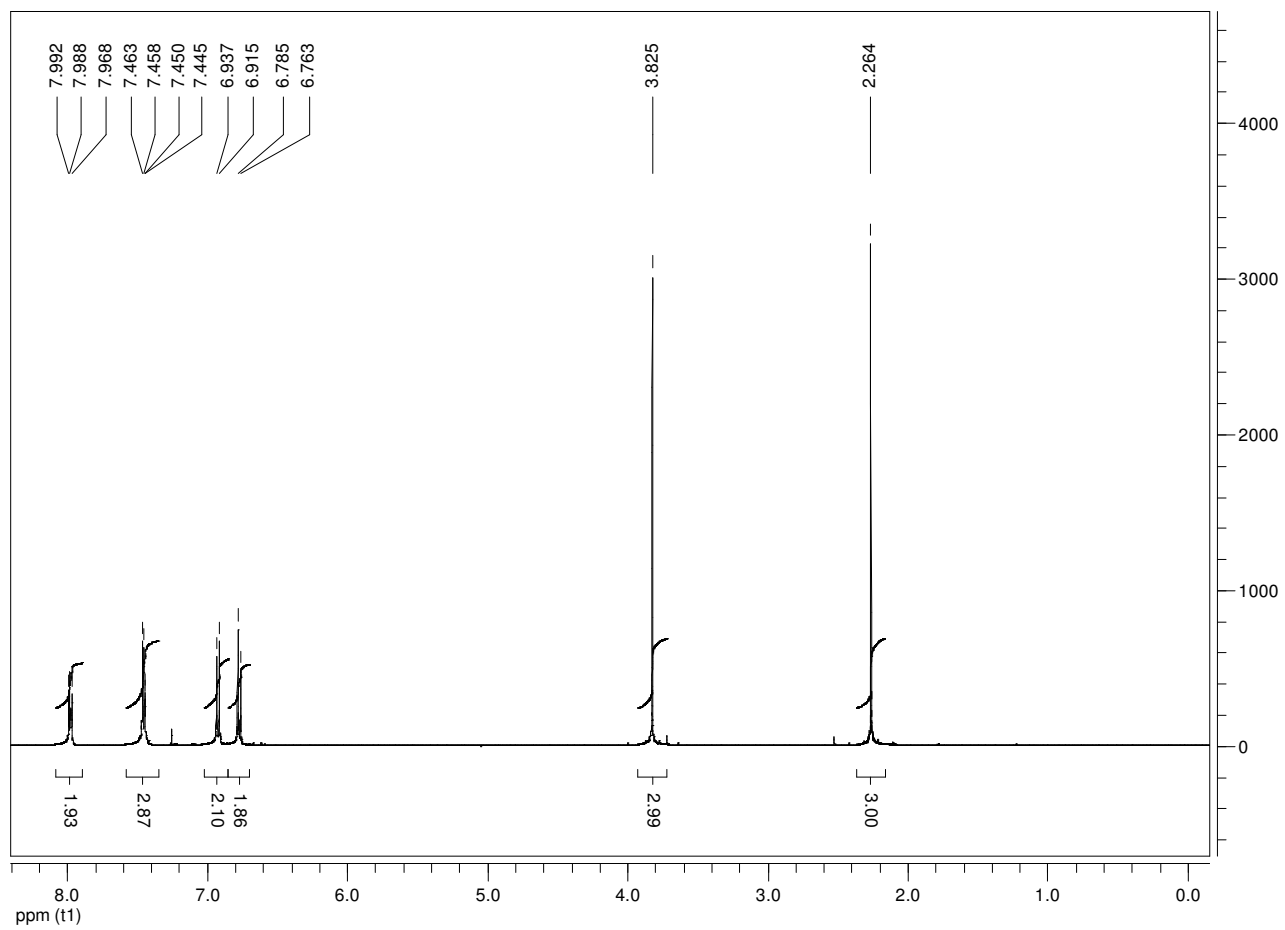
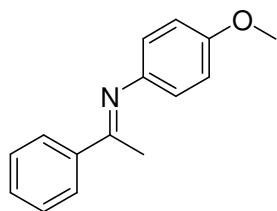
(R)-Phenyl-(1-phenyl-ethyl)-amine (1b), ¹H



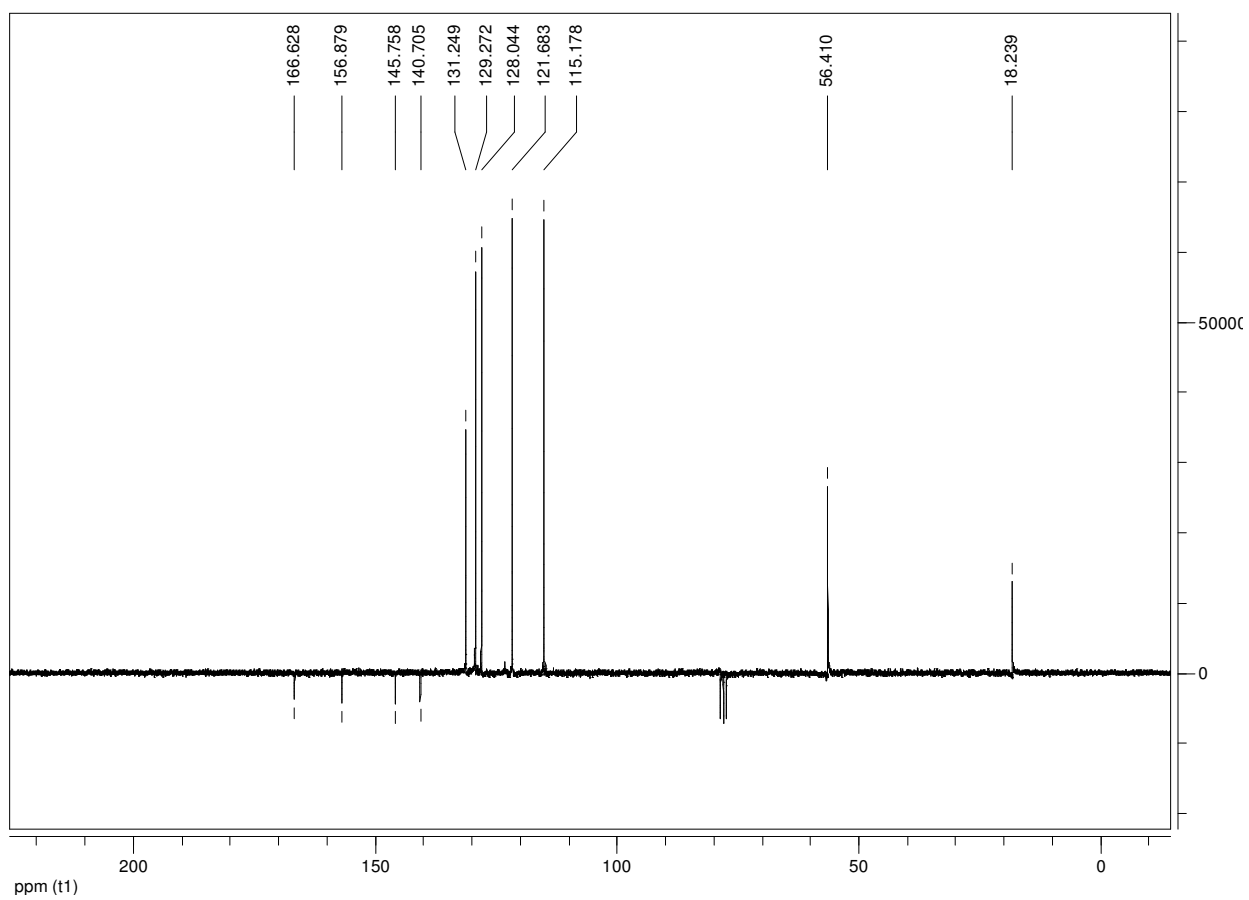
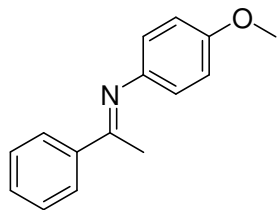
(R)-Phenyl-(1-phenyl-ethyl)-amine (1b), ^{13}C



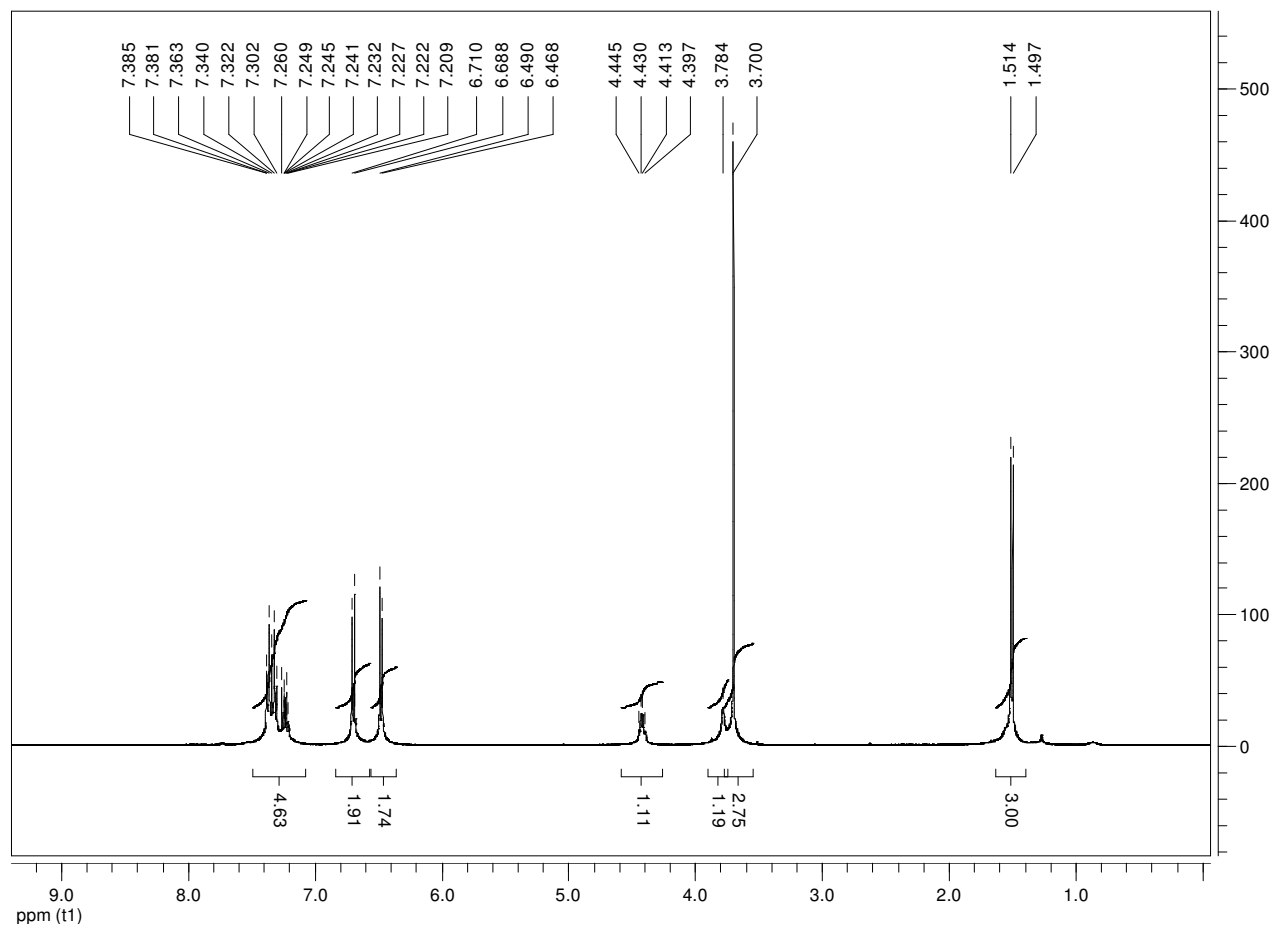
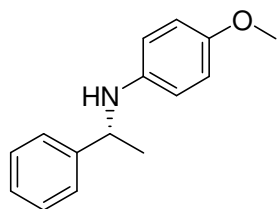
(4-Methoxy-phenyl)-(1-phenyl-ethylidene)-amine (2a), ¹H



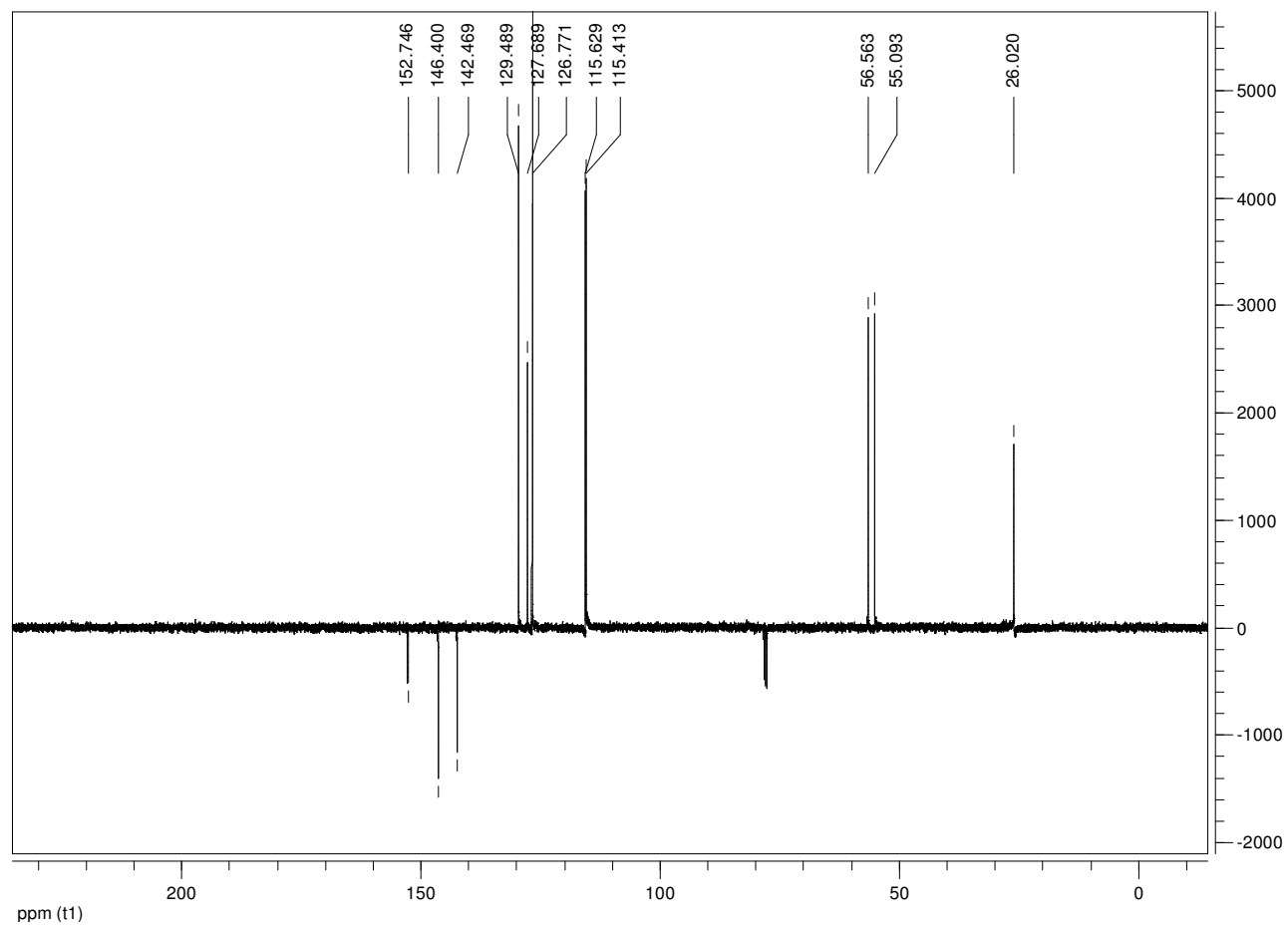
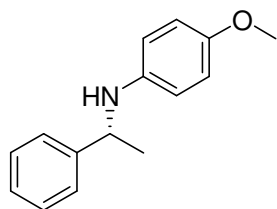
(4-Methoxy-phenyl)-(1-phenyl-ethylidene)-amine (2a), ^{13}C



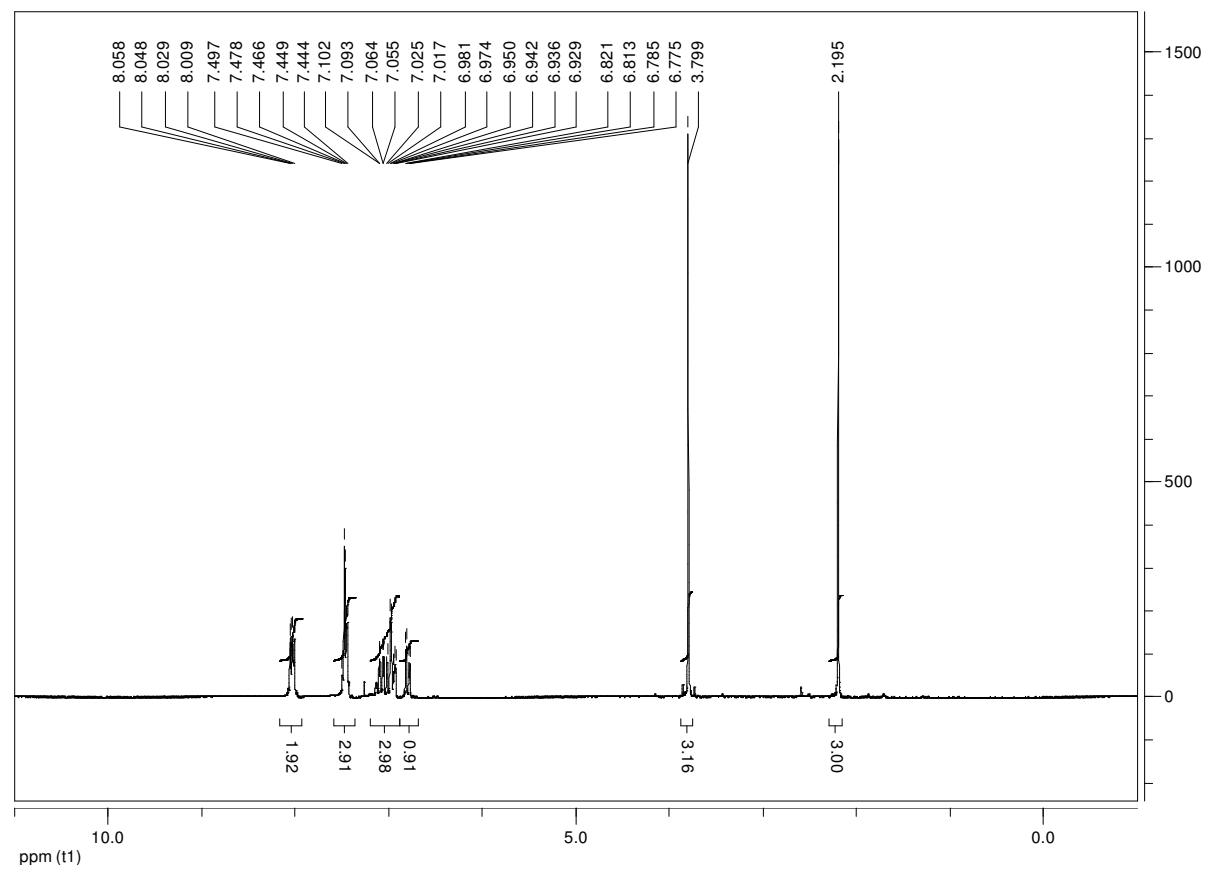
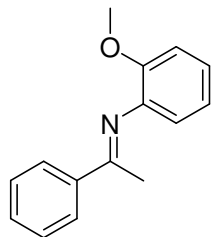
(R)-(4-Methoxy-phenyl)-(1-phenyl-ethyl)-amine (2b), ¹H



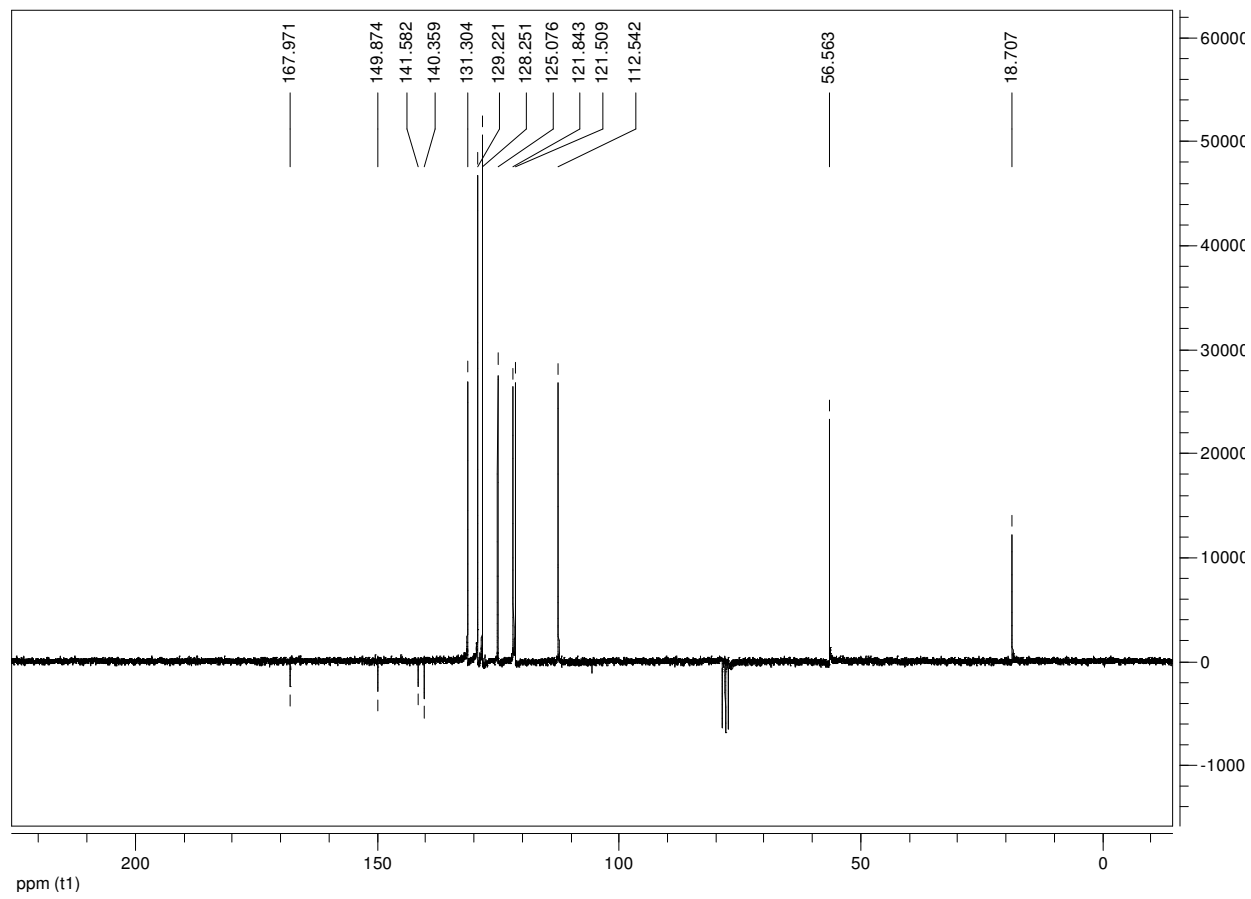
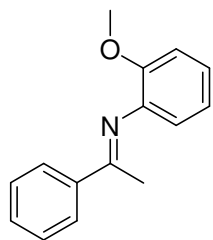
(R)-(4-Methoxy-phenyl)-(1-phenyl-ethyl)-amine (2b), ^{13}C



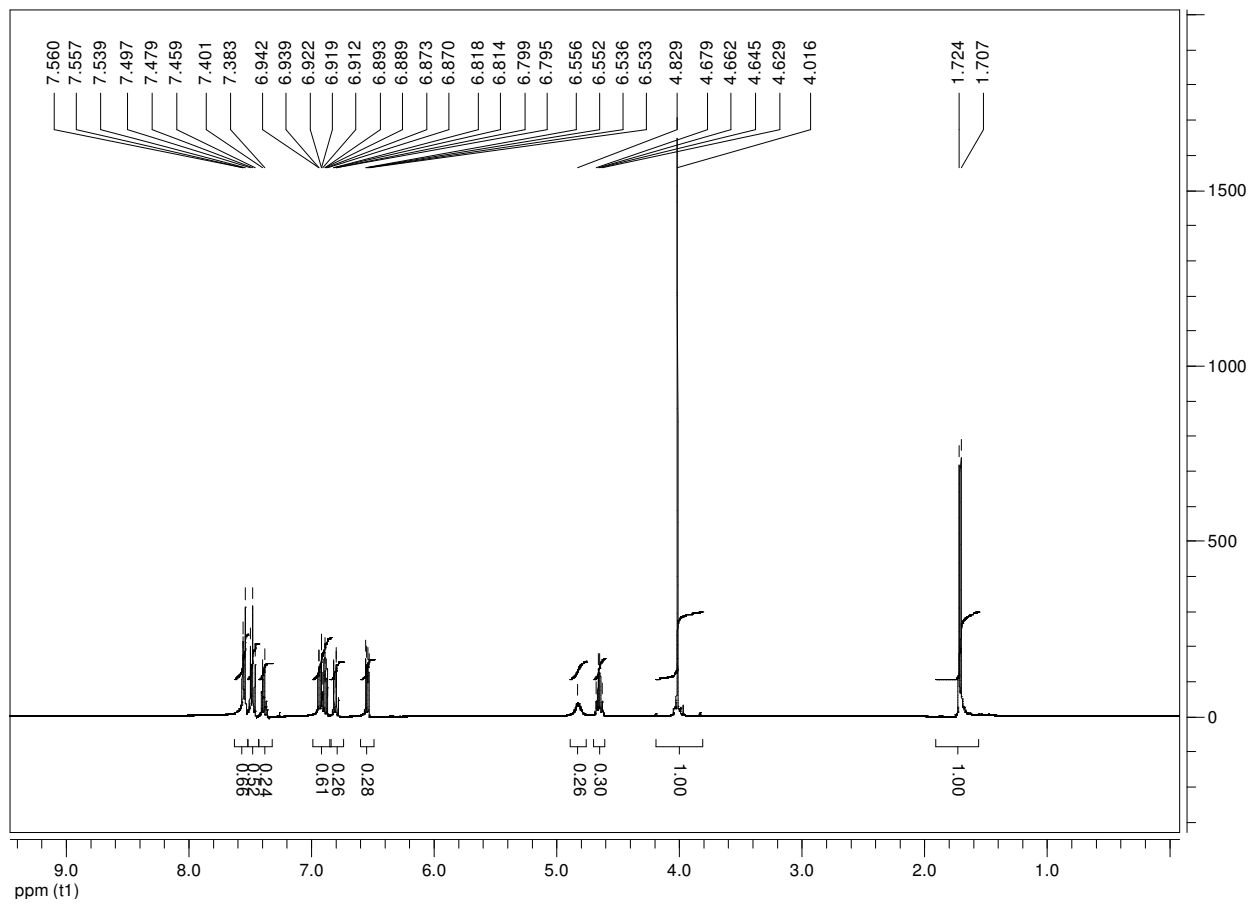
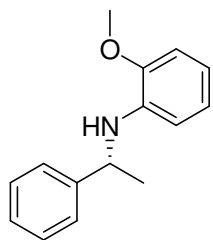
(2-Methoxy-phenyl)-(1-phenyl-ethylidene)-amine (3a), ^1H



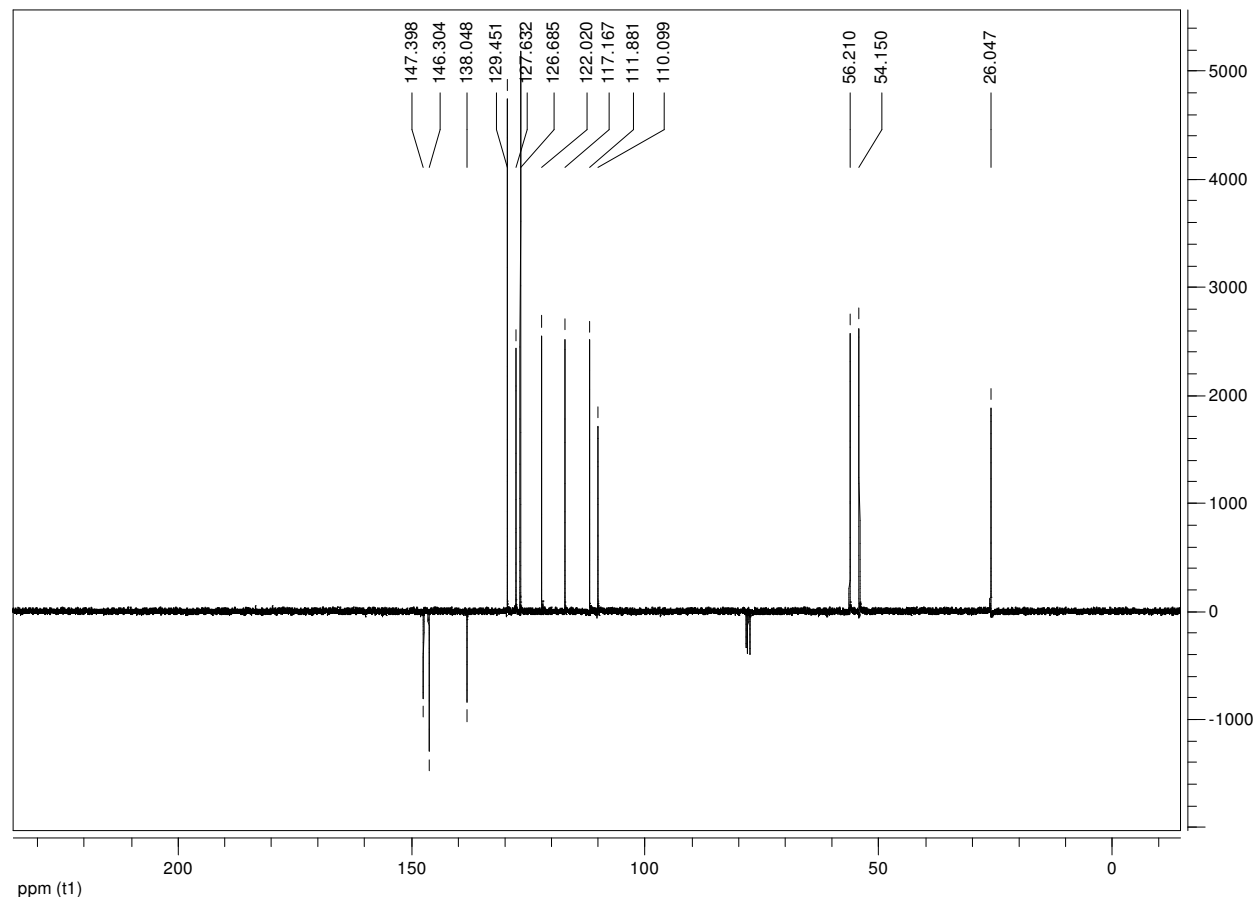
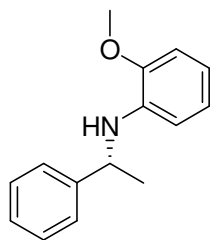
(2-Methoxy-phenyl)-(1-phenyl-ethylidene)-amine (3a), ^{13}C



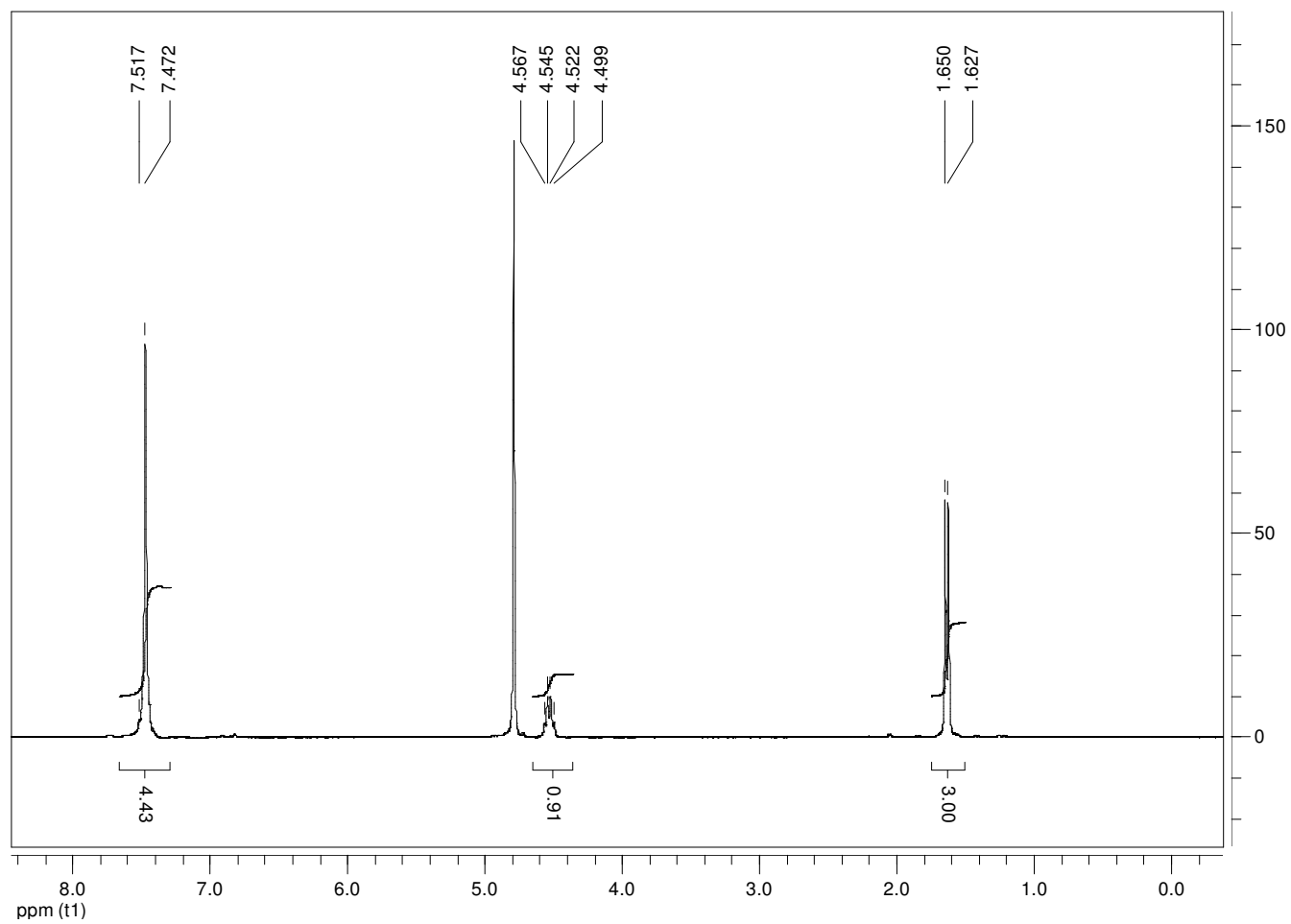
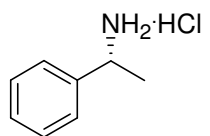
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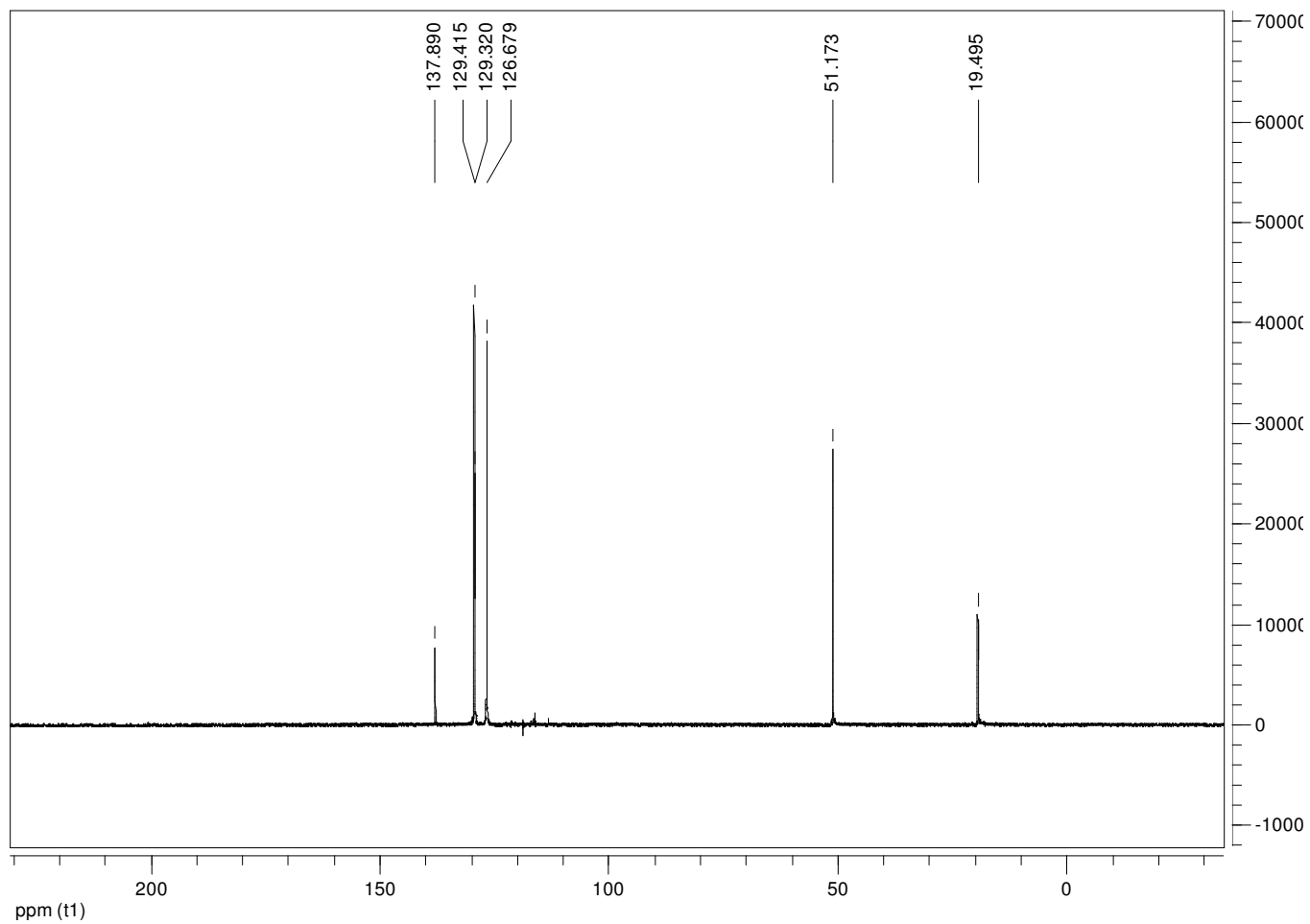
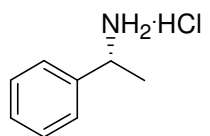
(R)-(2-Methoxy-phenyl)-(1-phenyl-ethyl)-amine (3b), ¹³C



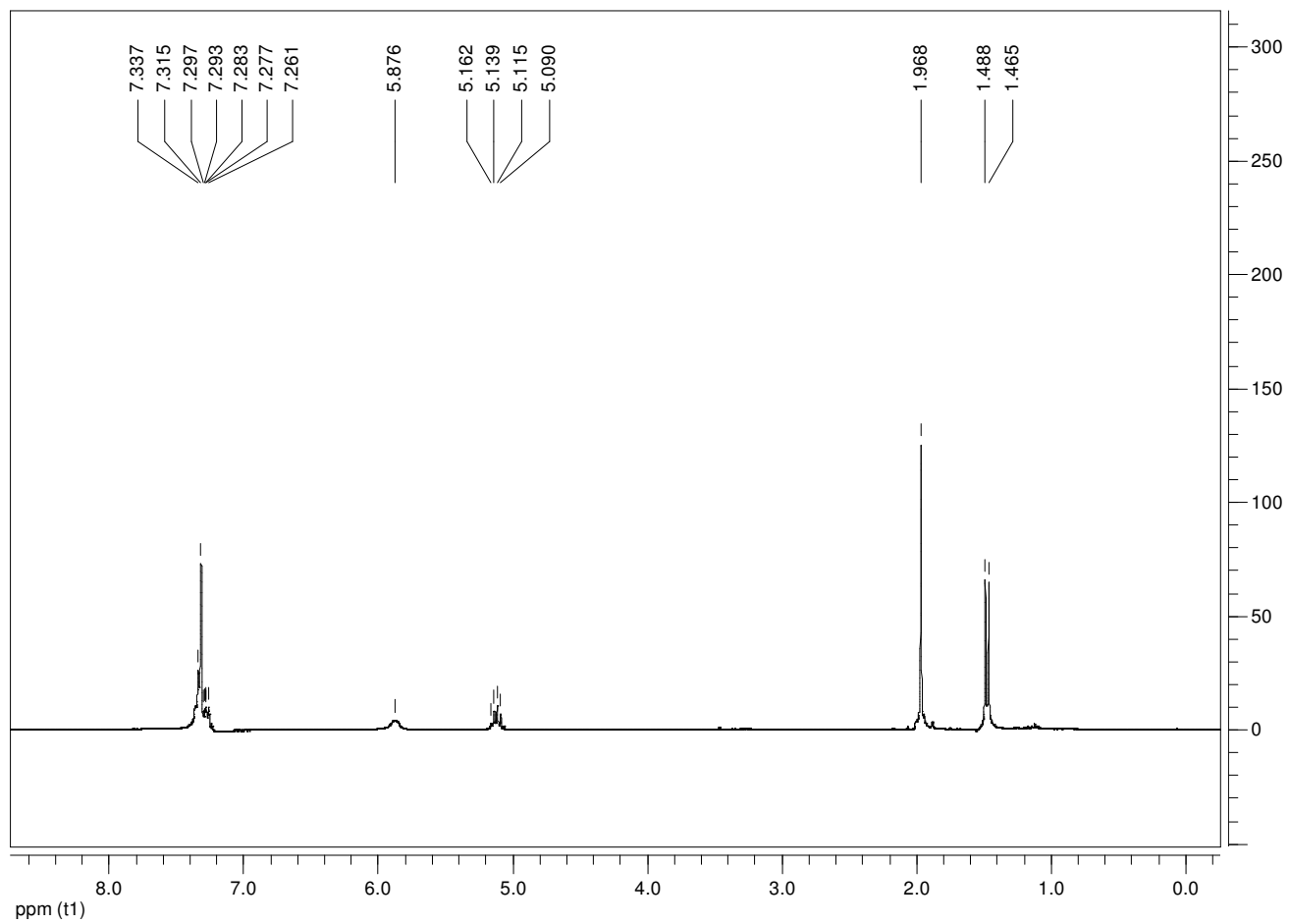
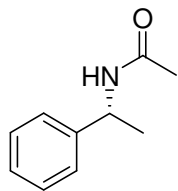
(R)-1-Phenyl-ethylamine hydrochloride (3c), ¹H



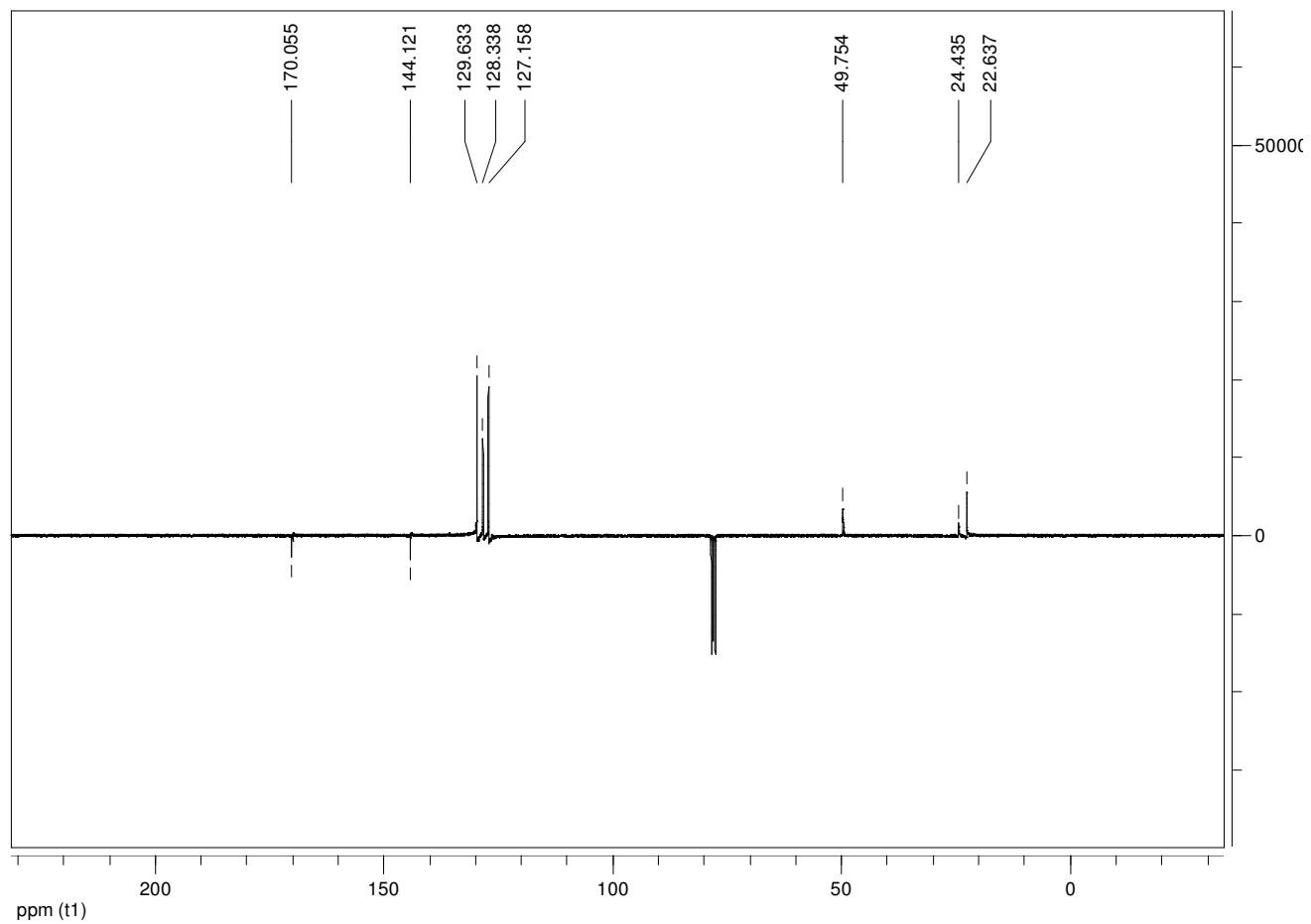
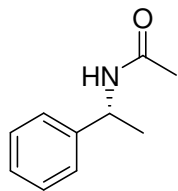
(R)-1-Phenyl-ethylamine hydrochloride (3c), ¹³C



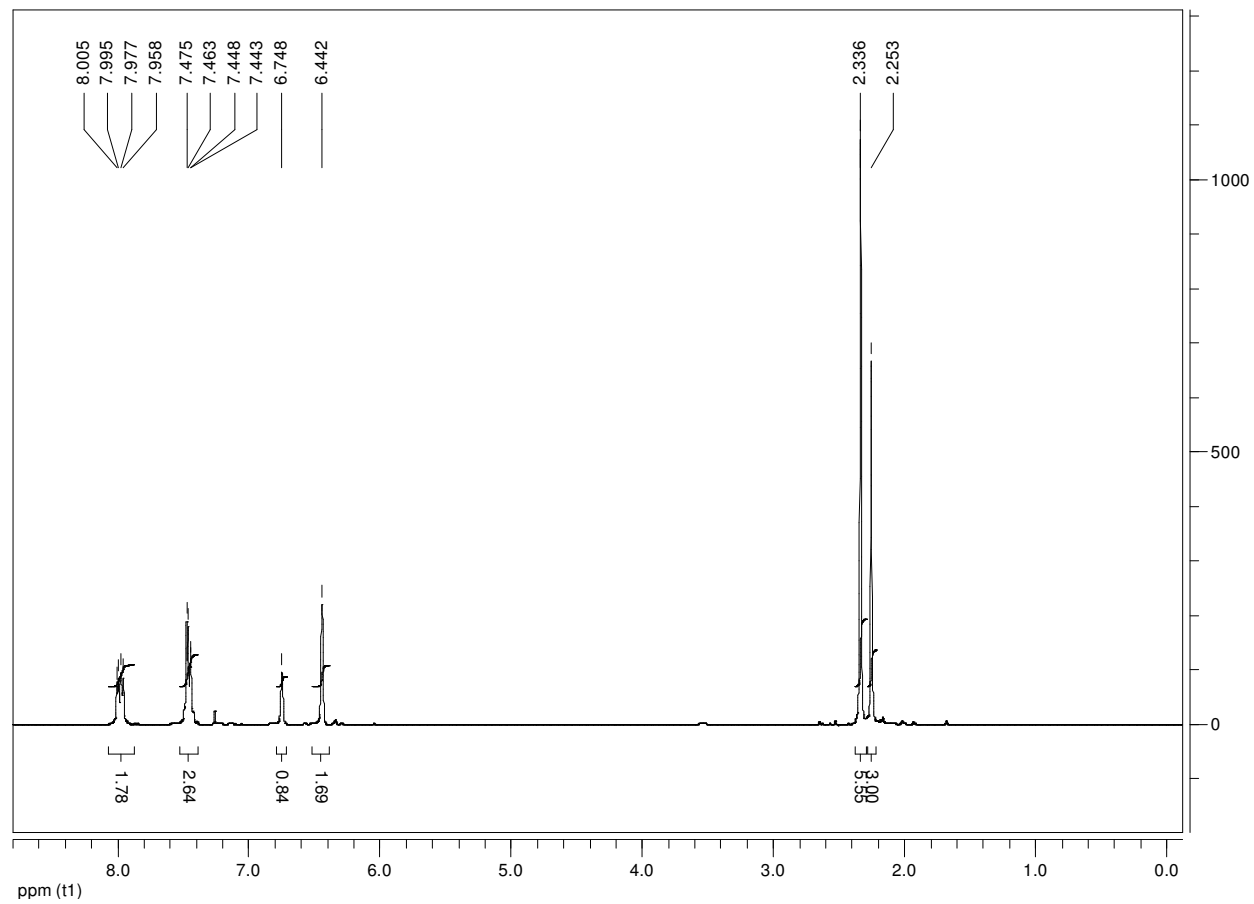
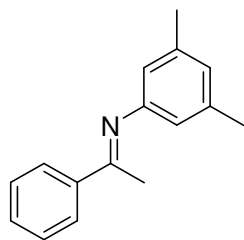
(R)-N-(1-Phenyl-ethyl)-acetamide (3d), ¹H



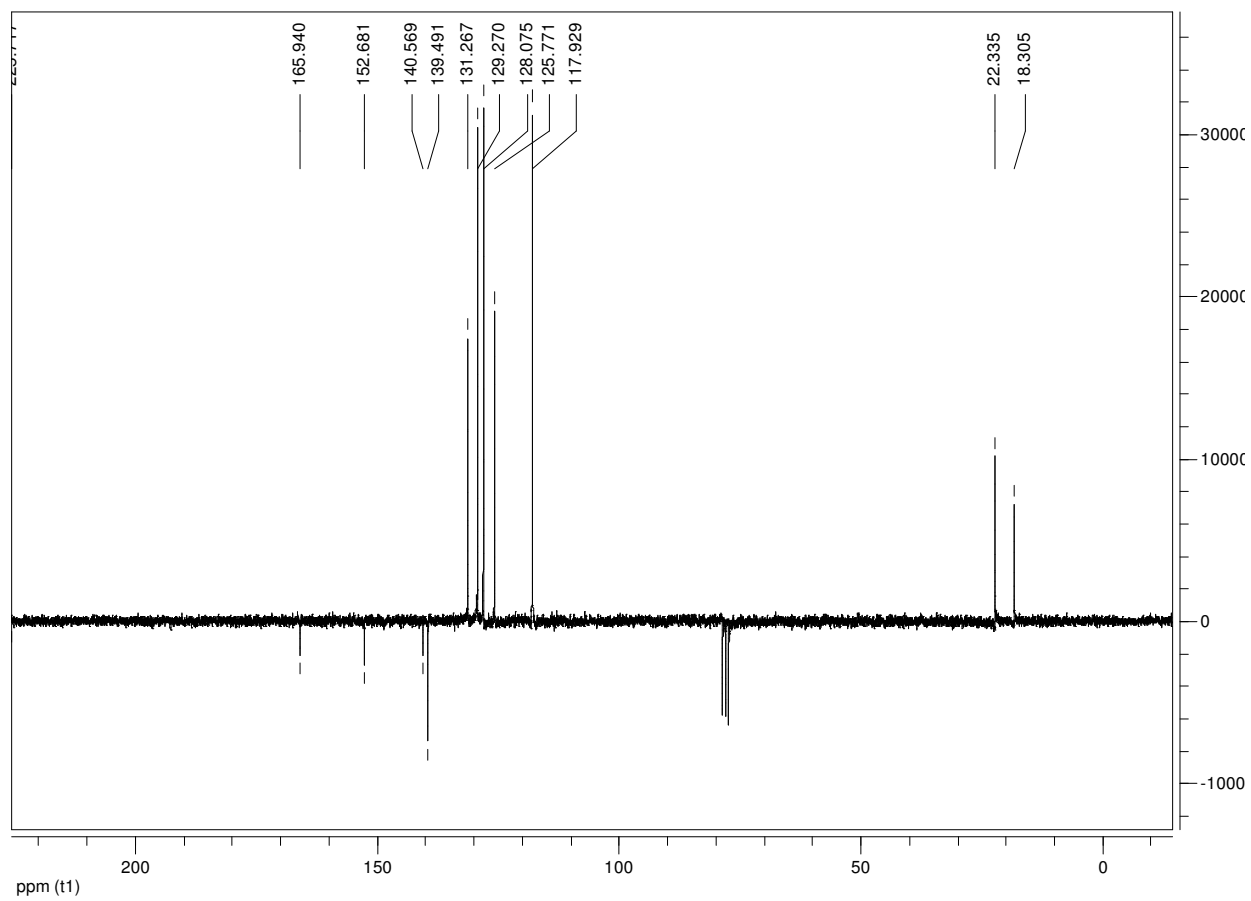
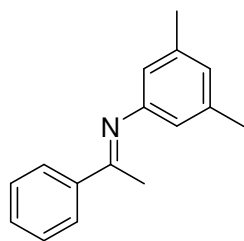
(R)-N-(1-Phenyl-ethyl)-acetamide (3d), ¹³C



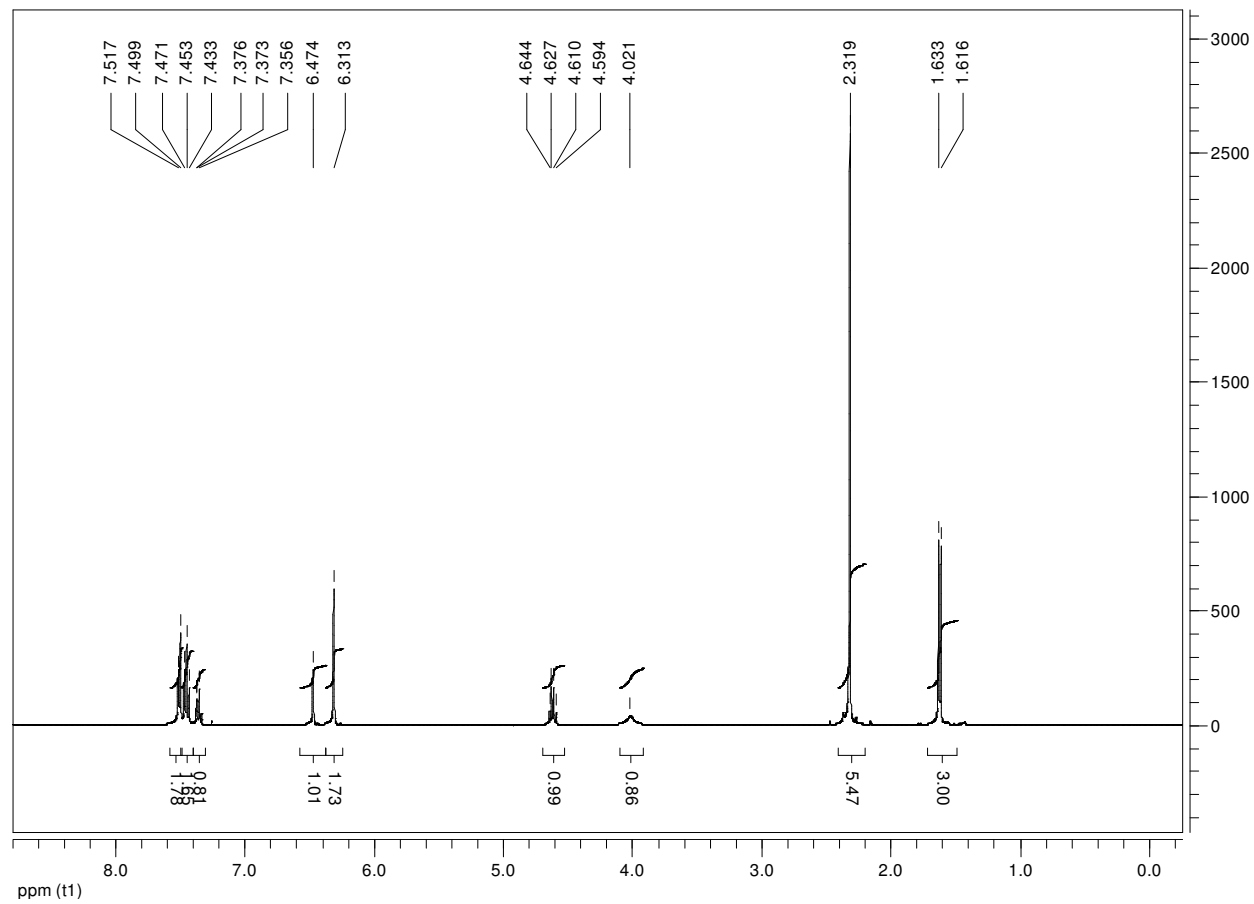
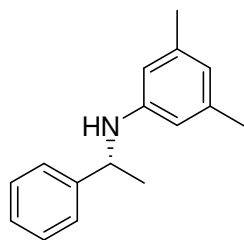
(3,5-Dimethyl-phenyl)-(1-phenyl-ethylidene)-amine (4a), ¹H



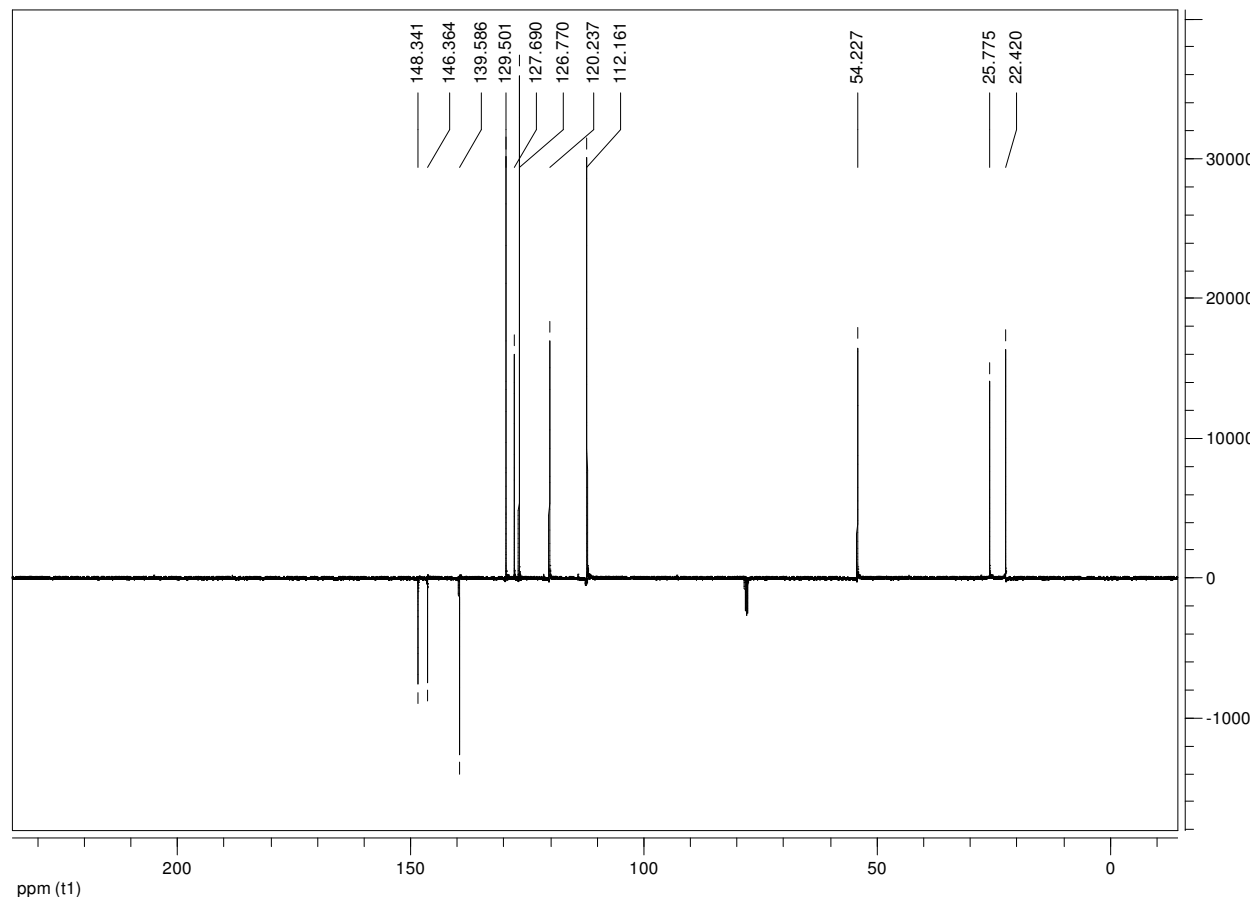
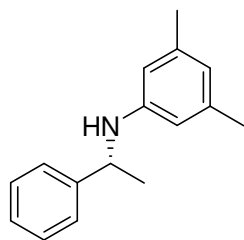
(3,5-Dimethyl-phenyl)-(1-phenyl-ethylidene)-amine (4a), ^{13}C



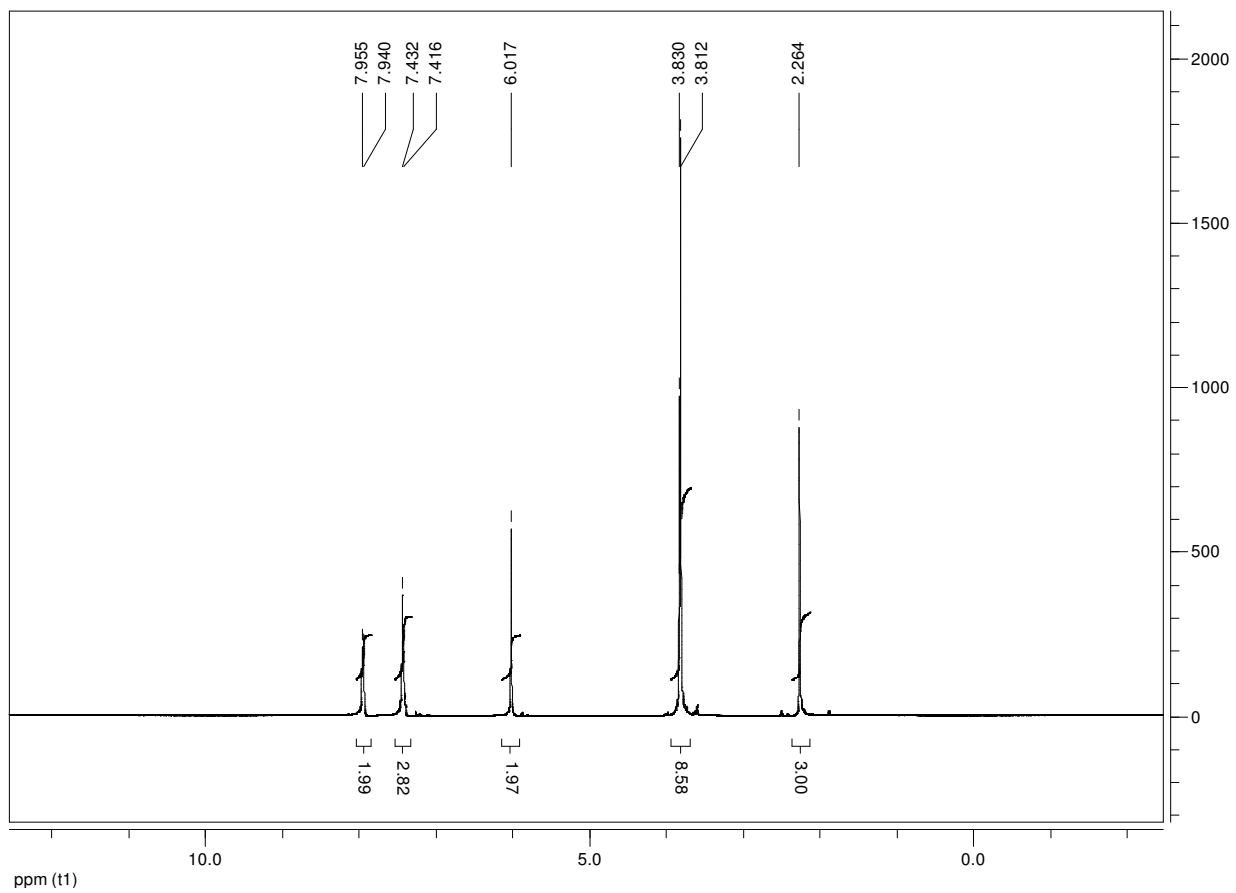
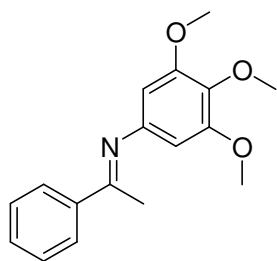
(R)-(3,5-Dimethyl-phenyl)-(1-phenyl-ethyl)-amine (4b), ¹H



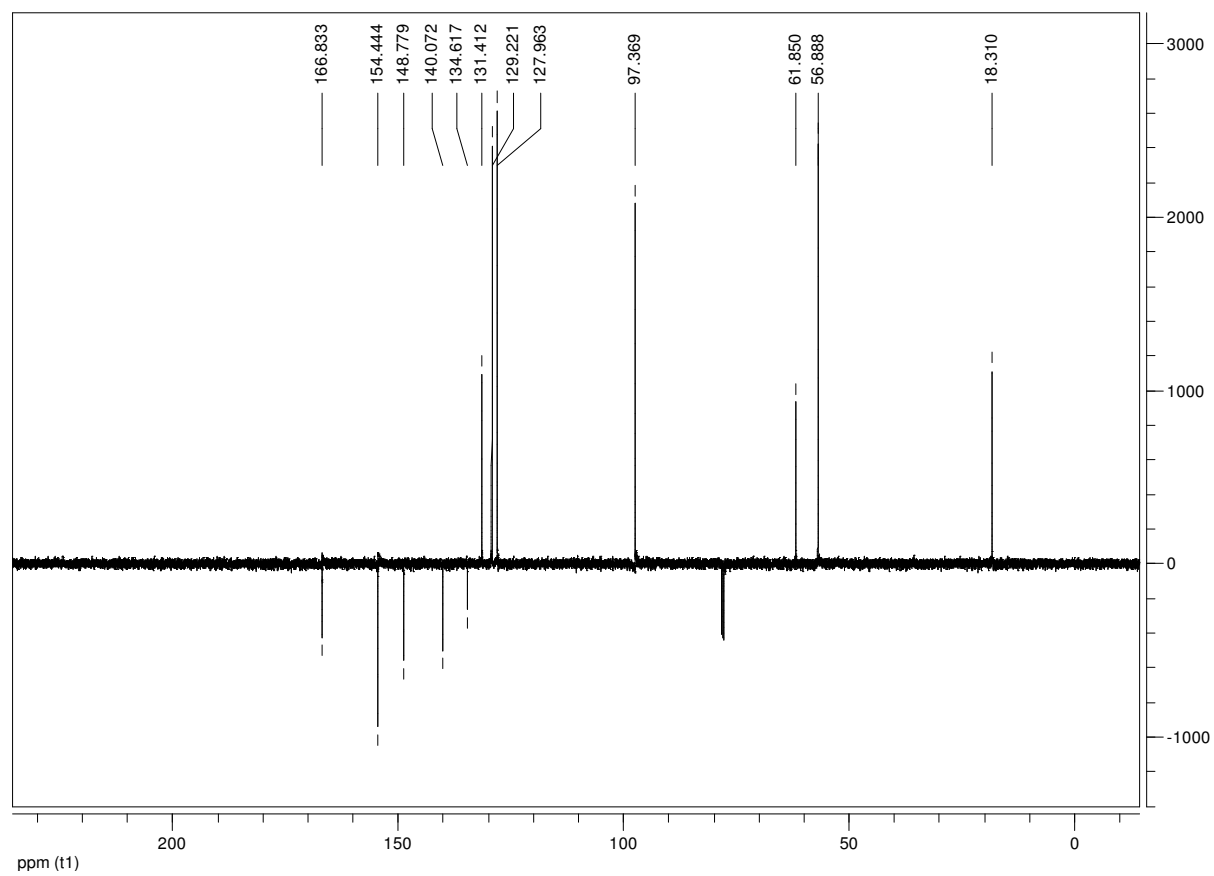
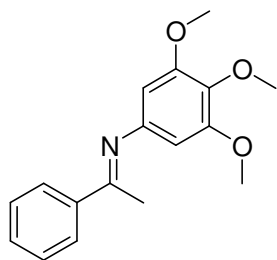
(R)-(3,5-Dimethyl-phenyl)-(1-phenyl-ethyl)-amine (4b), ¹³C



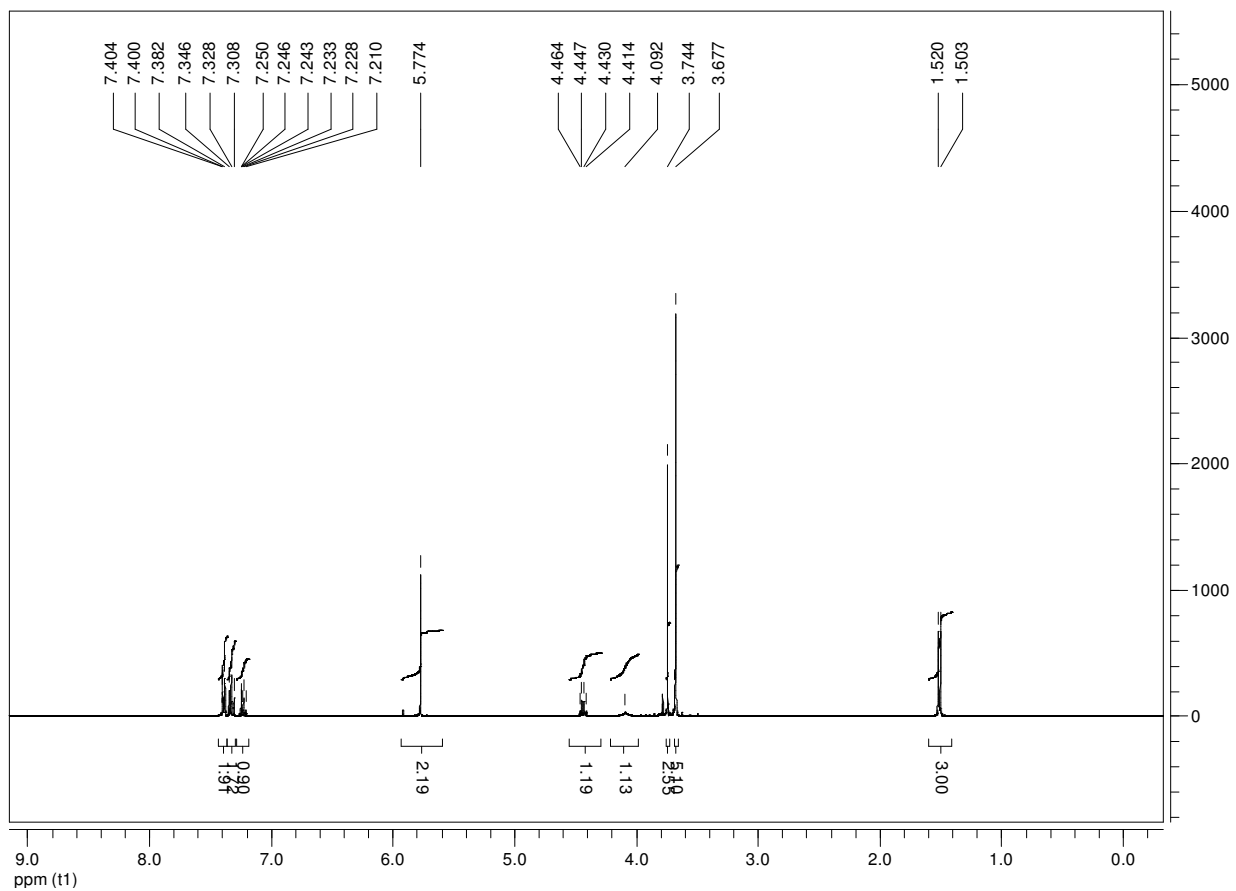
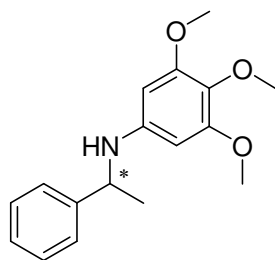
(1-Phenyl-ethylidene)-(3,4,5-trimethoxy-phenyl)-amine (5a), ¹H



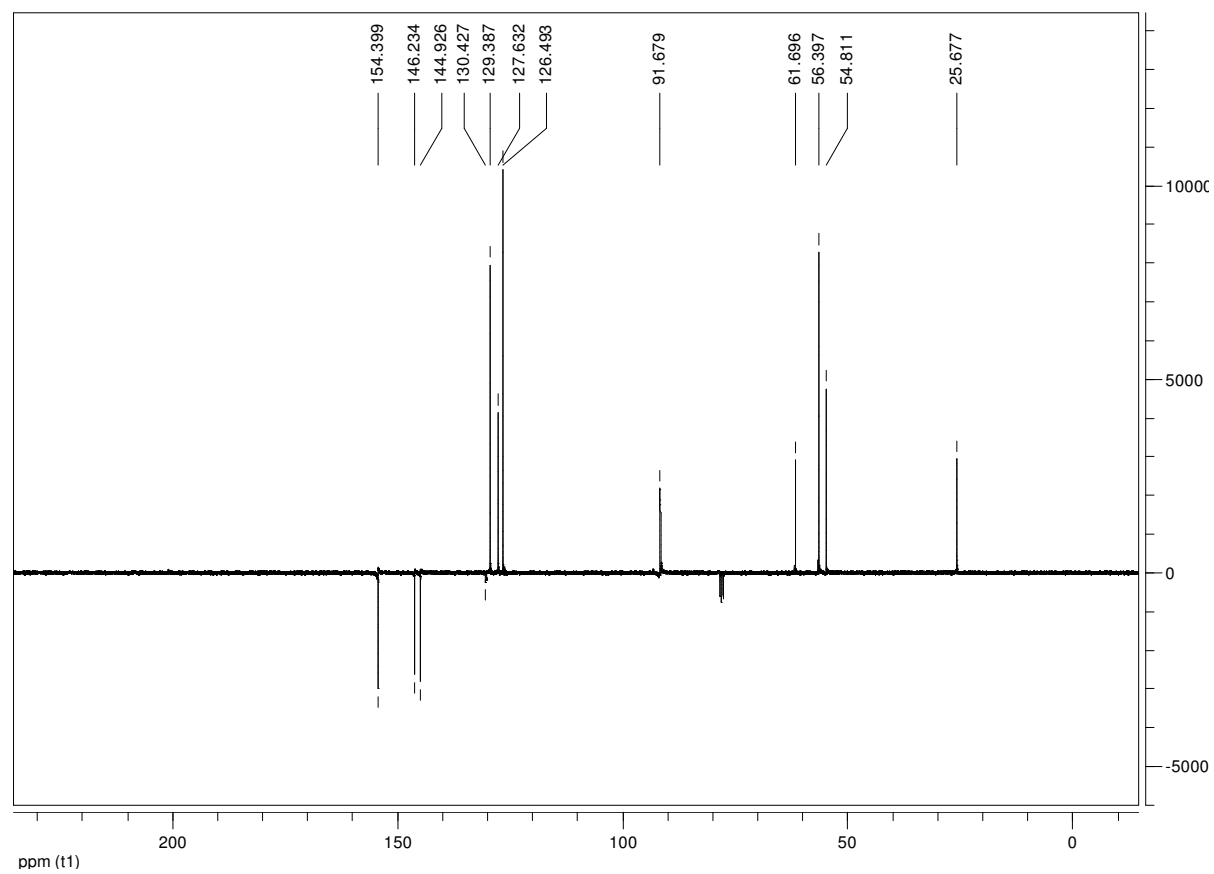
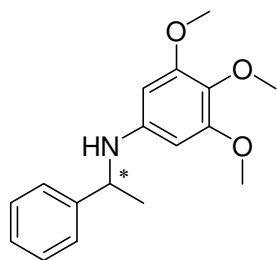
(1-Phenyl-ethylidene)-(3,4,5-trimethoxy-phenyl)-amine (5a), ^{13}C



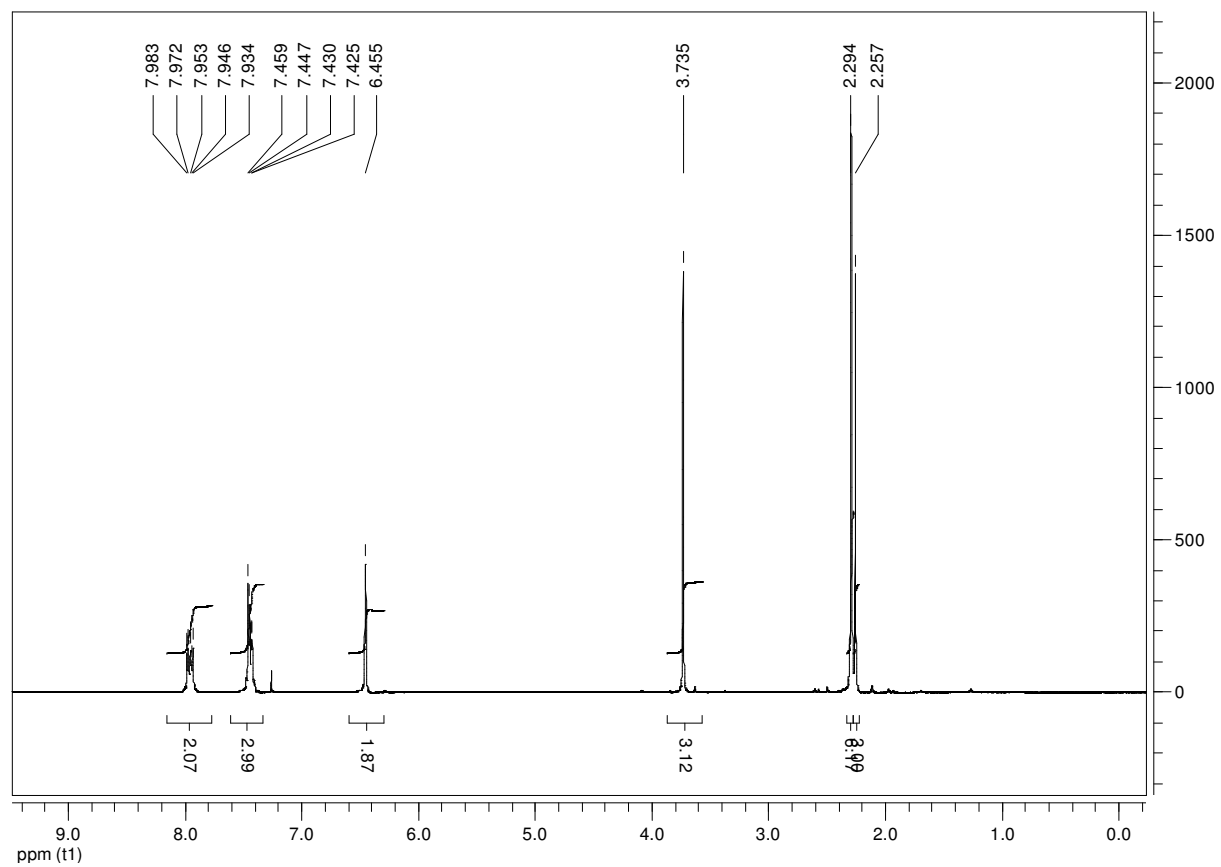
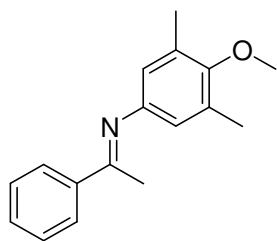
(-)-(1-Phenyl-ethyl)-(3,4,5-trimethoxy-phenyl)-amine (5b), ¹H



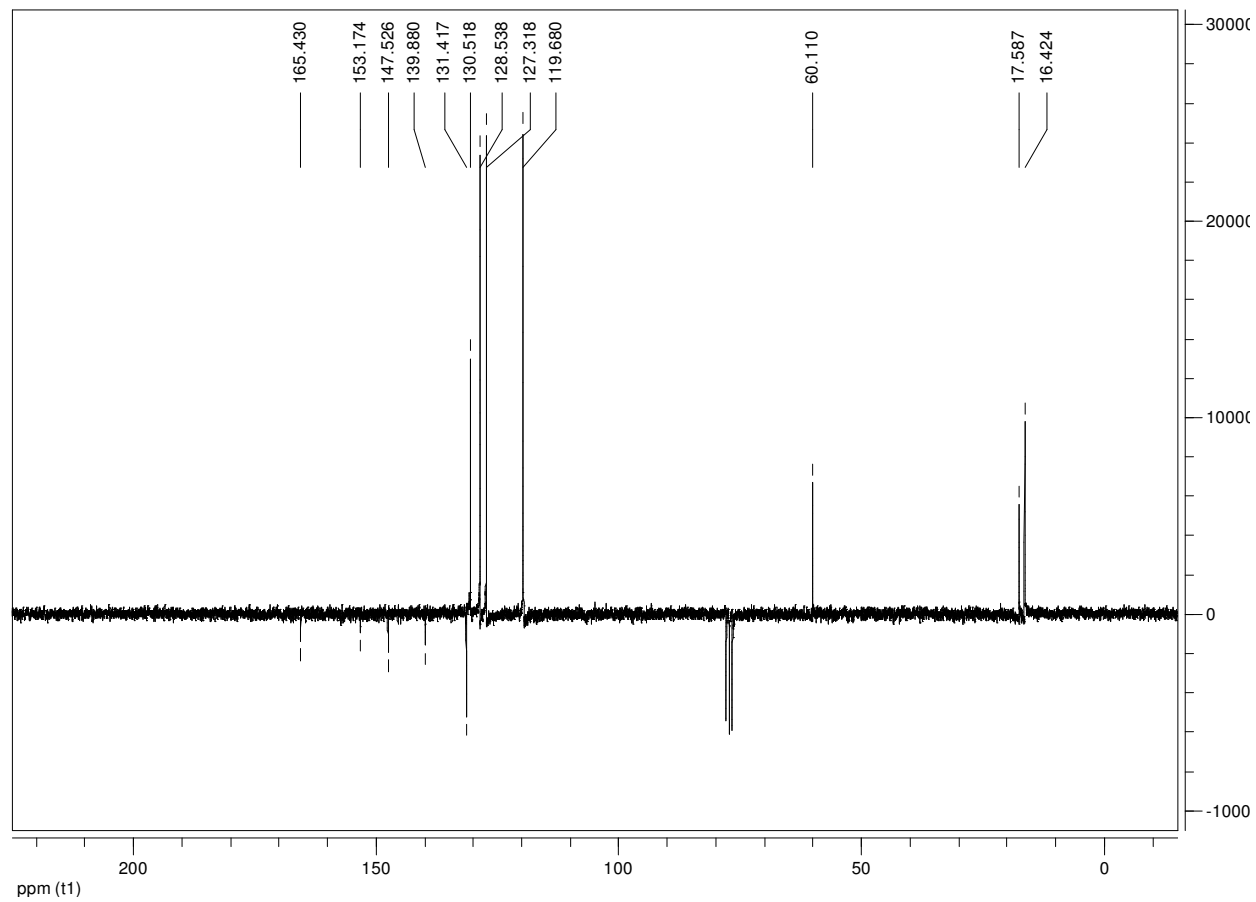
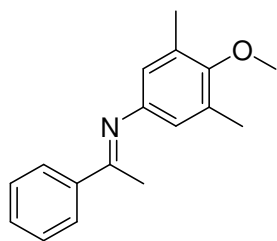
(-)-(1-Phenyl-ethyl)-(3,4,5-trimethoxy-phenyl)-amine (5b), ¹³C



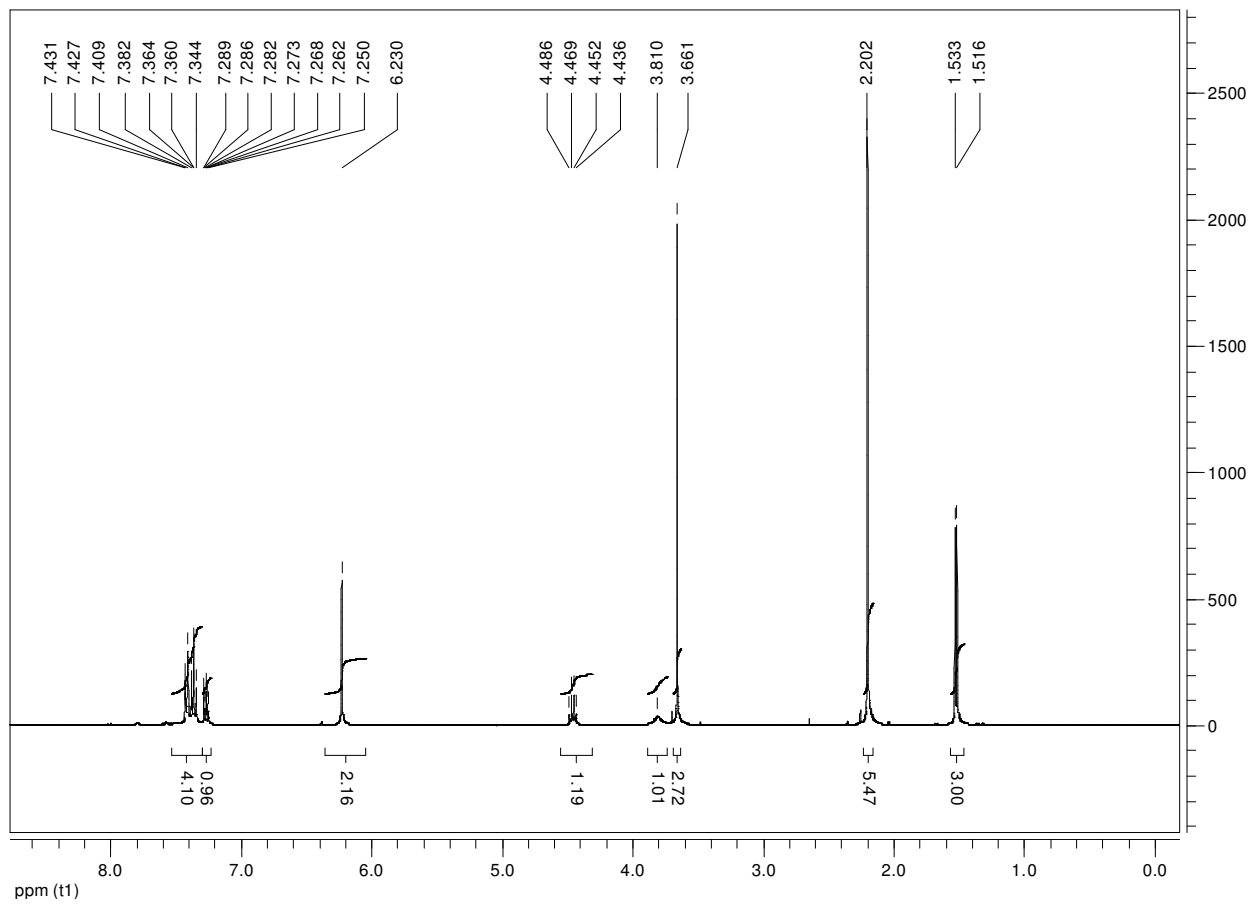
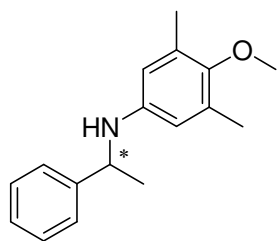
(4-Methoxy-3,5-dimethyl-phenyl)-(1-phenyl-ethylidene)-amine (6a), ¹H



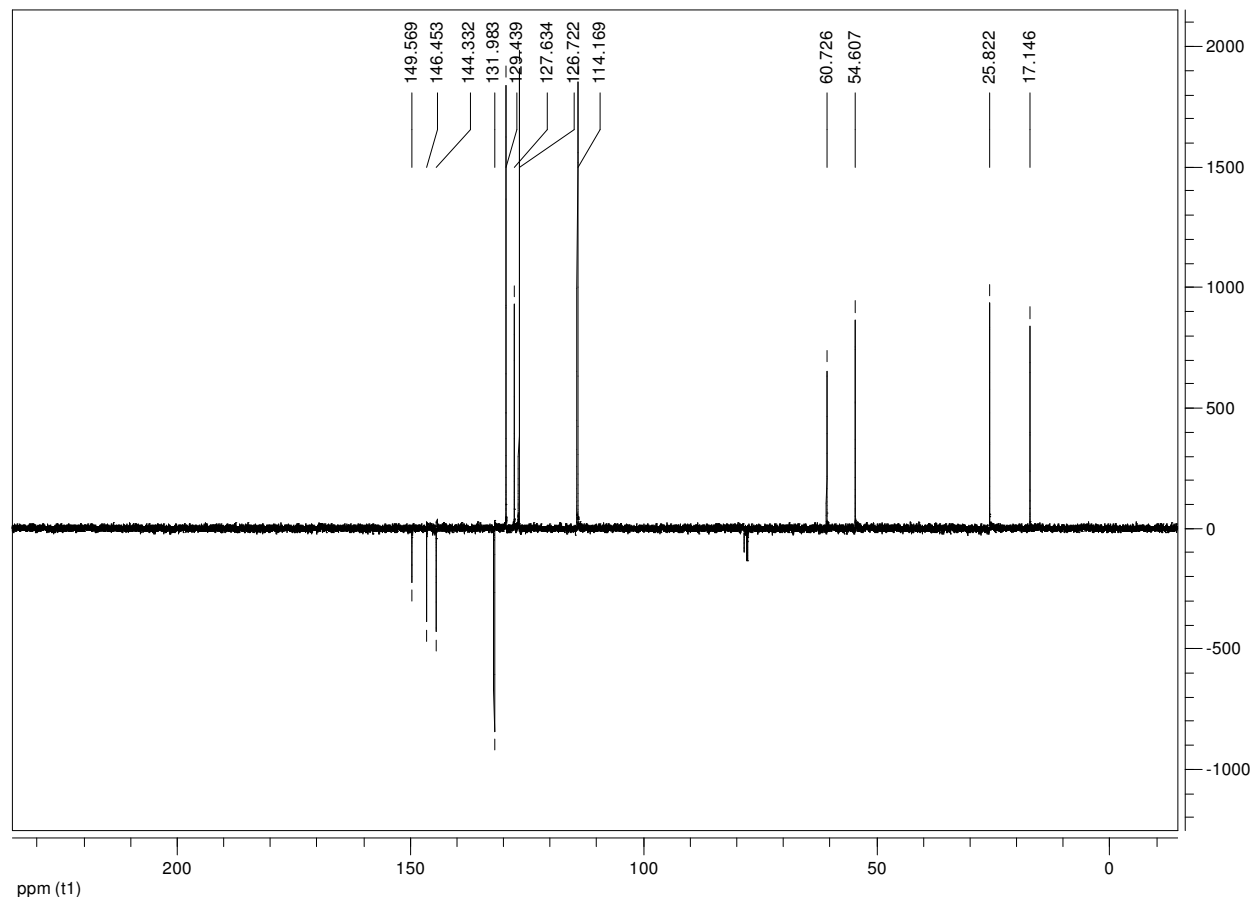
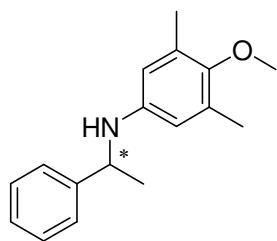
(4-Methoxy-3,5-dimethyl-phenyl)-(1-phenyl-ethylidene)-amine (6a), ^{13}C



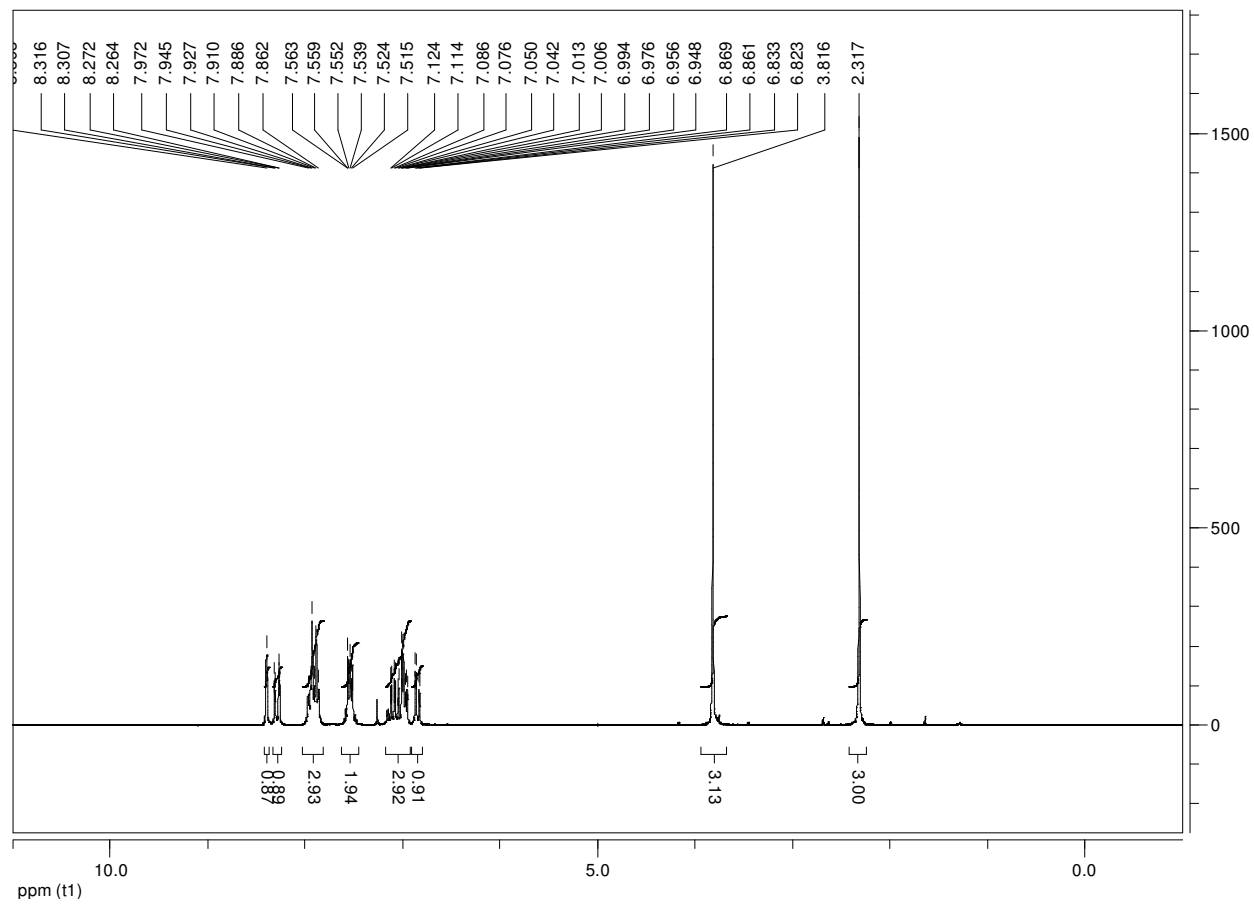
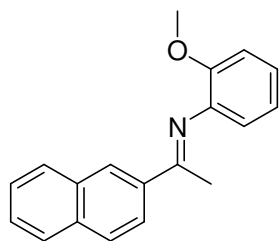
(+)-(4-Methoxy-3,5-dimethyl-phenyl)-(1-phenyl-ethyl)-amine (6b), ^1H



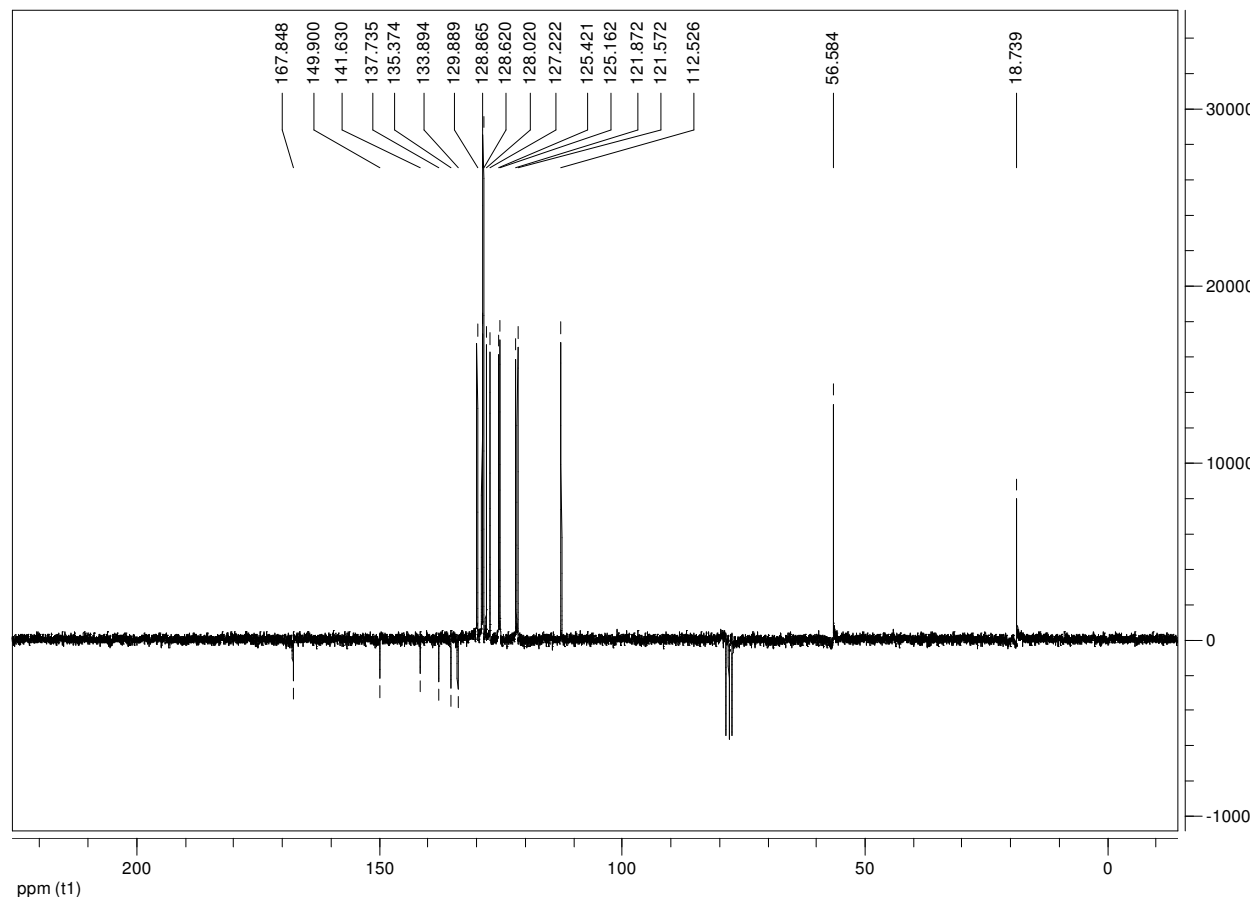
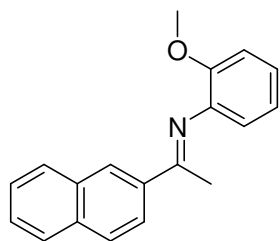
(+)-(4-Methoxy-3,5-dimethyl-phenyl)-(1-phenyl-ethyl)-amine (6b), ¹³C



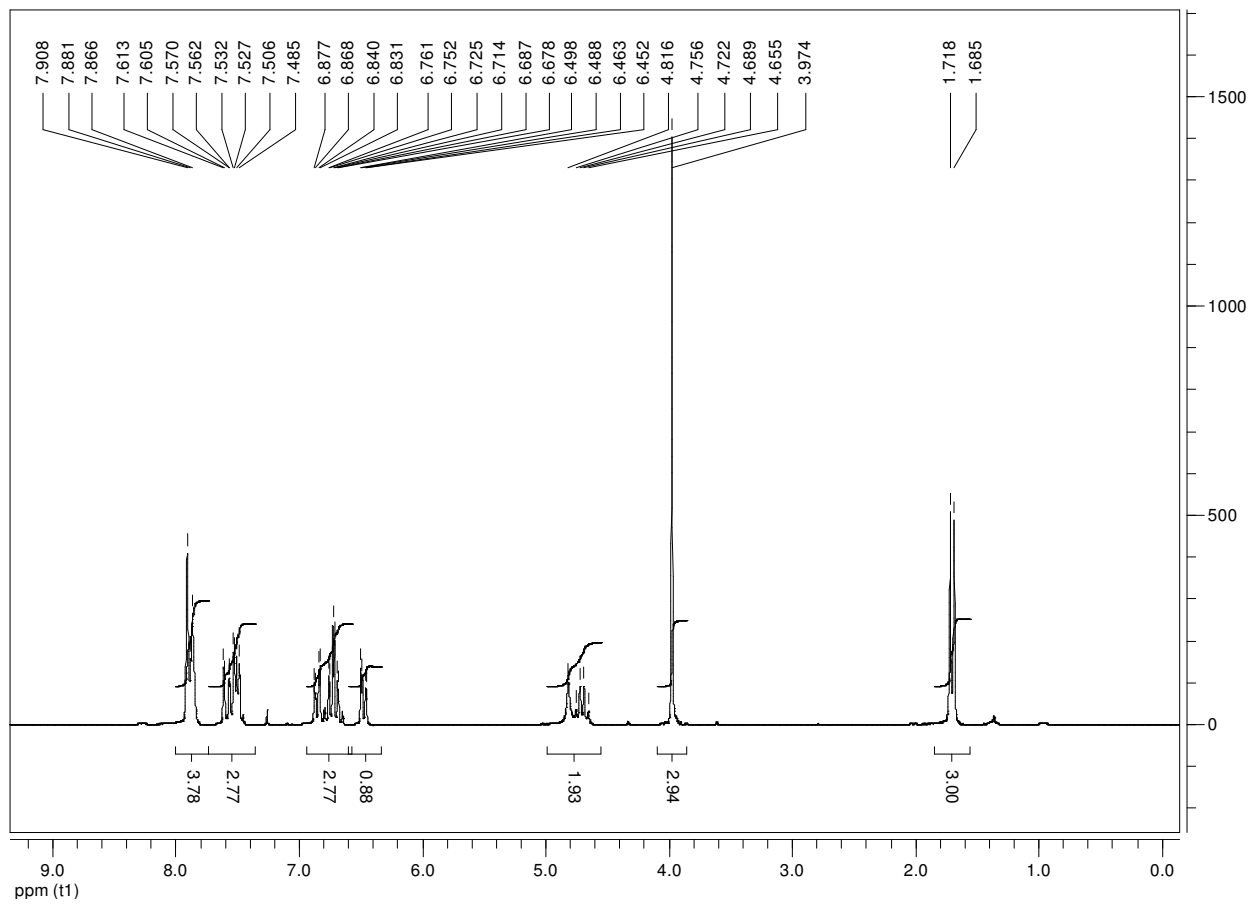
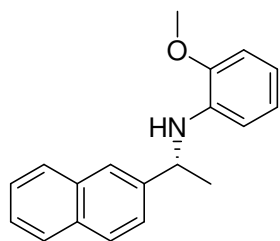
(2-Methoxy-phenyl)-(1-naphthalen-2-yl-ethylidene)-amine (7a), ¹H



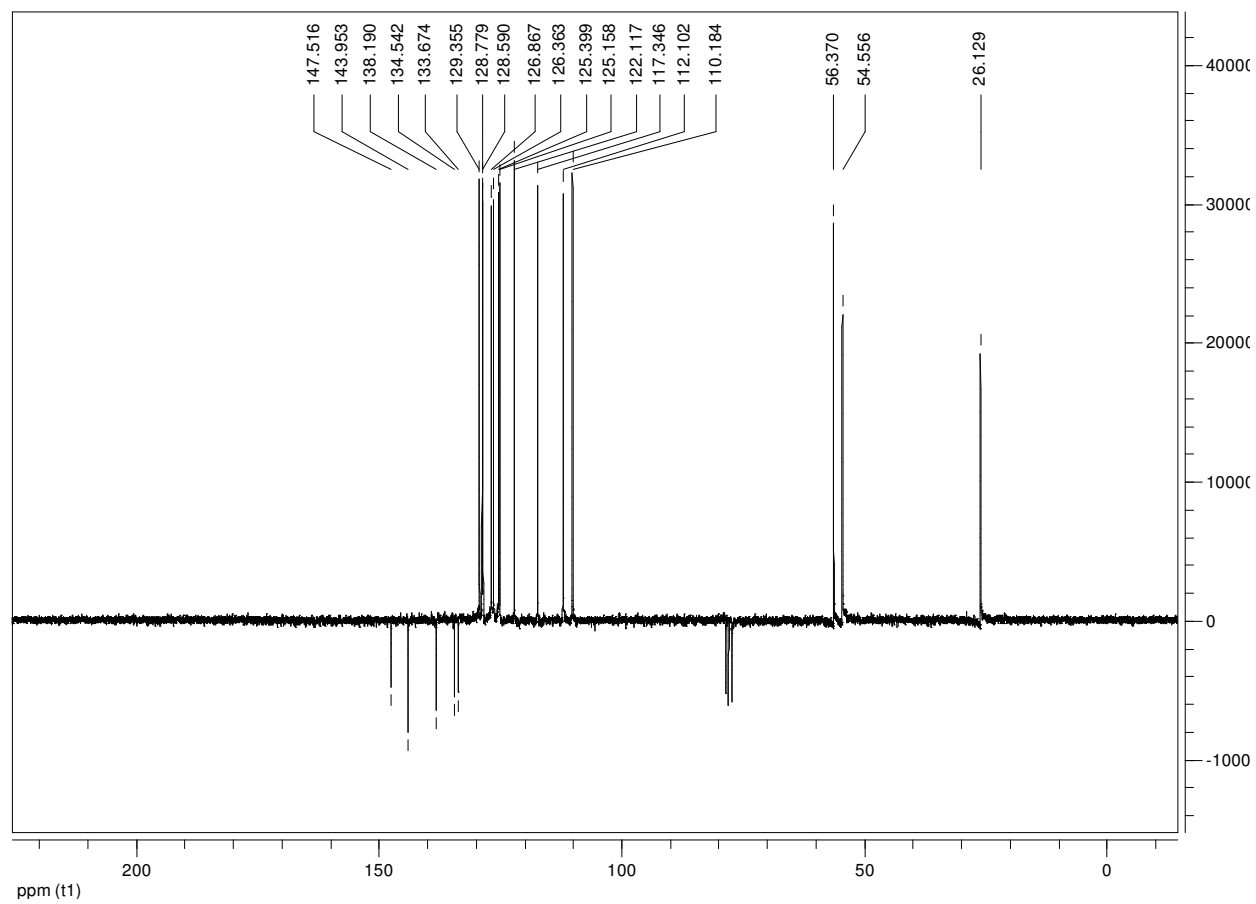
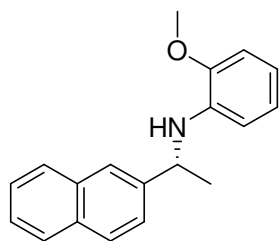
(2-Methoxy-phenyl)-(1-naphthalen-2-yl-ethylidene)-amine (7a), ^{13}C



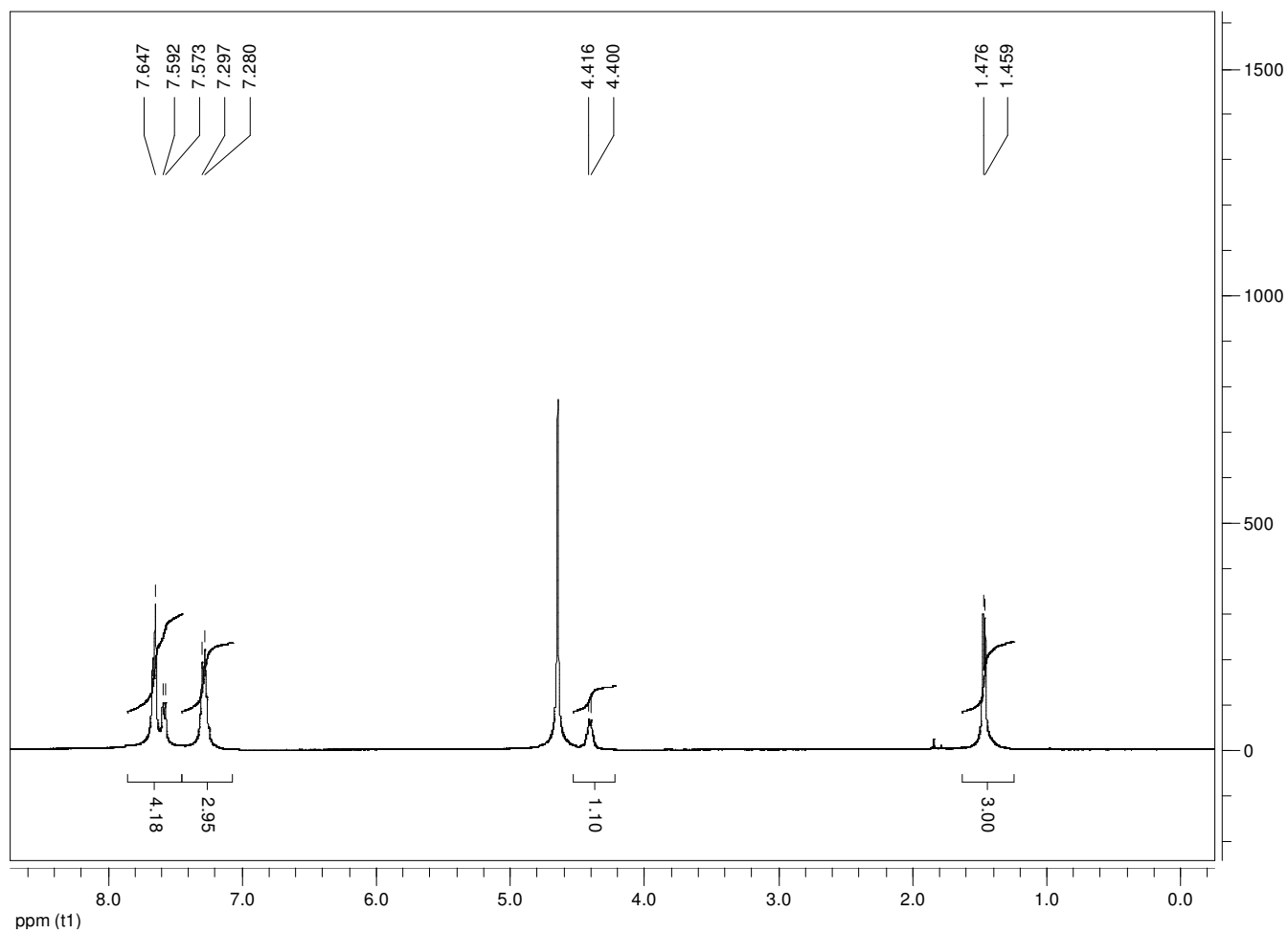
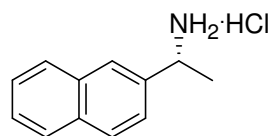
(R)-(2-Methoxy-phenyl)-(1-naphthalen-2-yl-ethyl)-amine (7b), ¹H



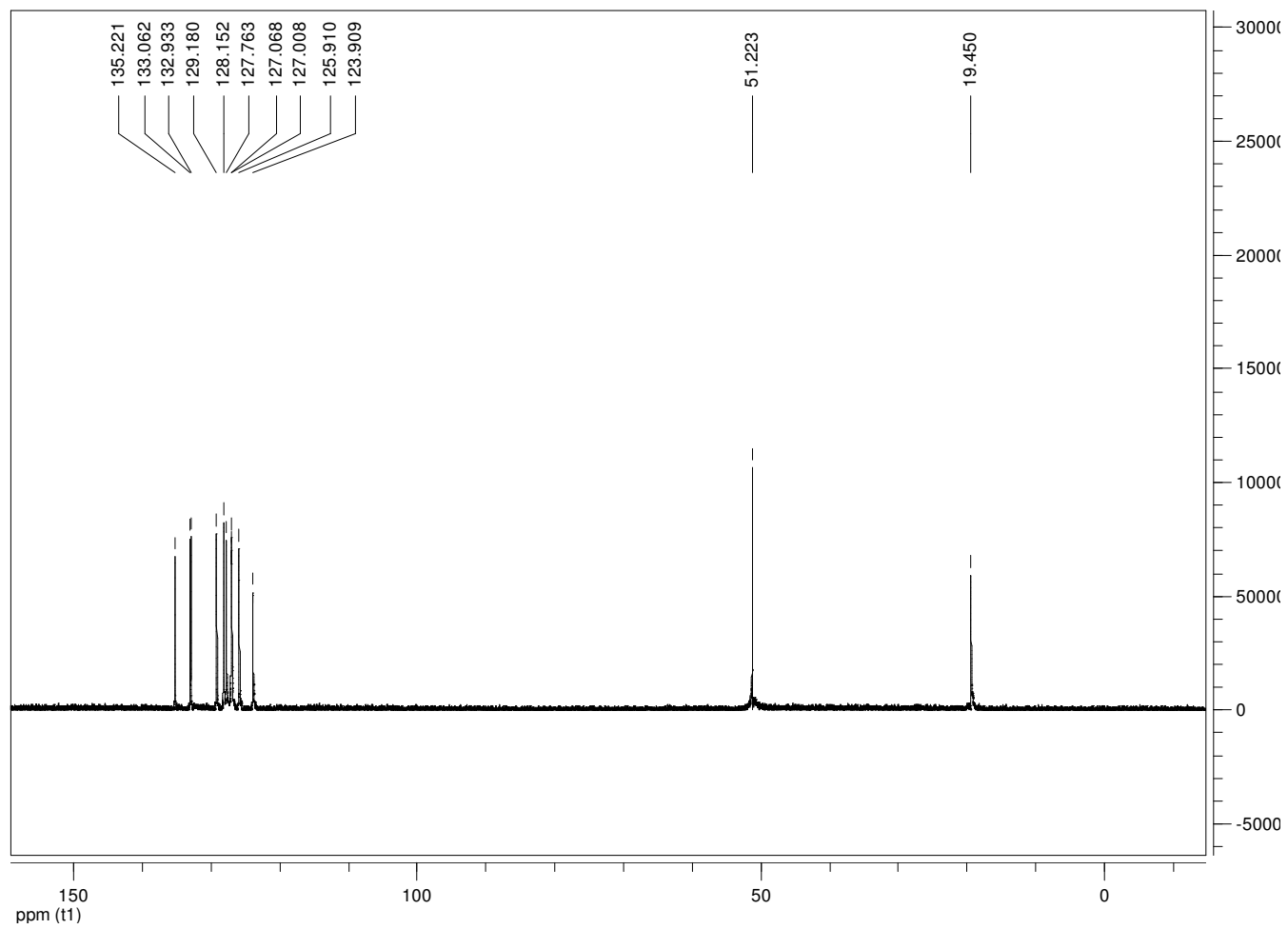
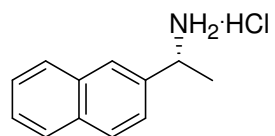
(R)-(2-Methoxy-phenyl)-(1-naphthalen-2-yl-ethyl)-amine (7b), ¹³C



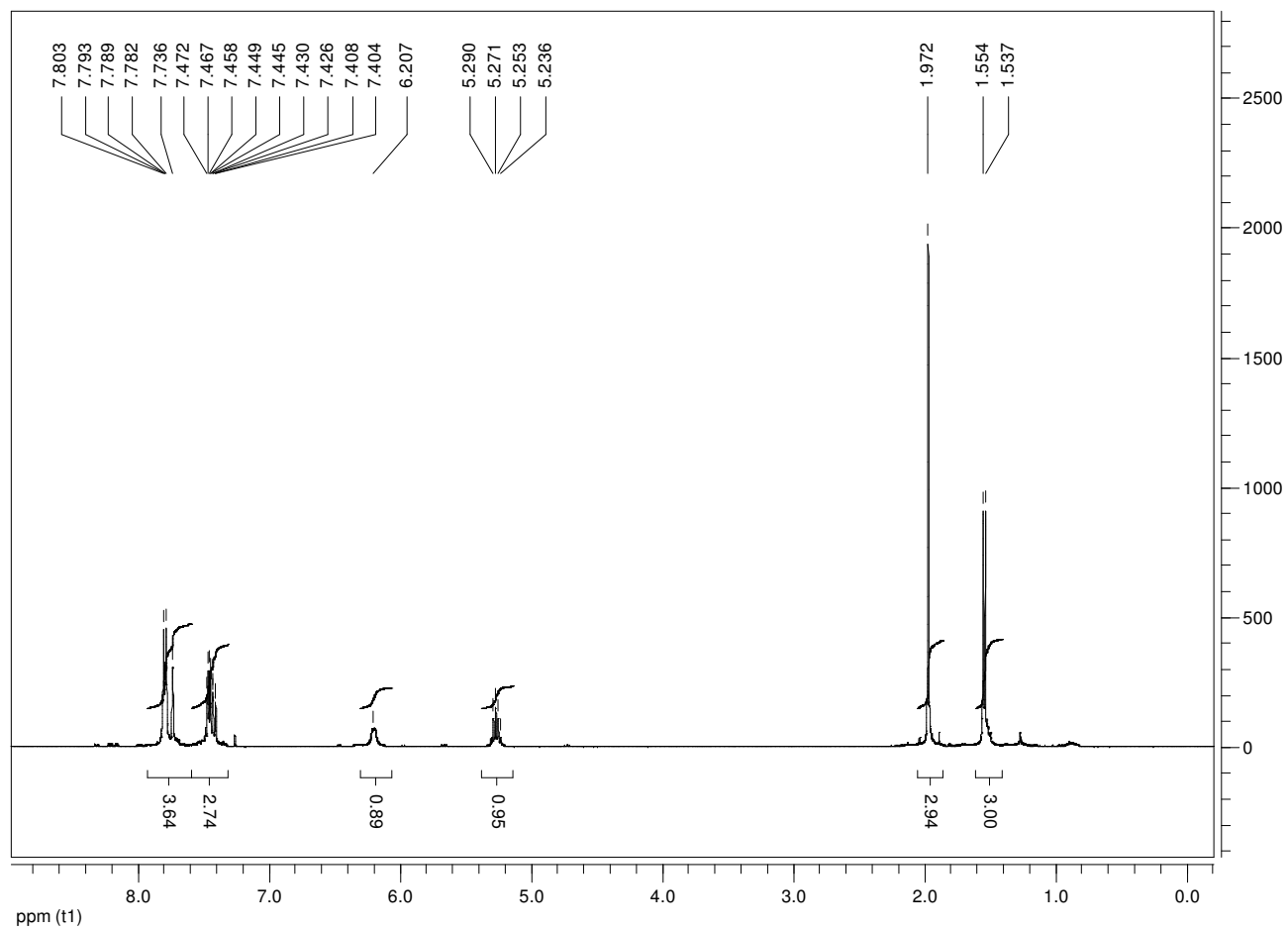
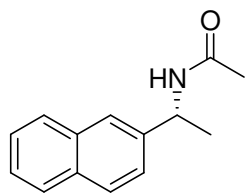
(R)-1-Naphthalen-2-yl-ethylamine hydrochloride (7c)



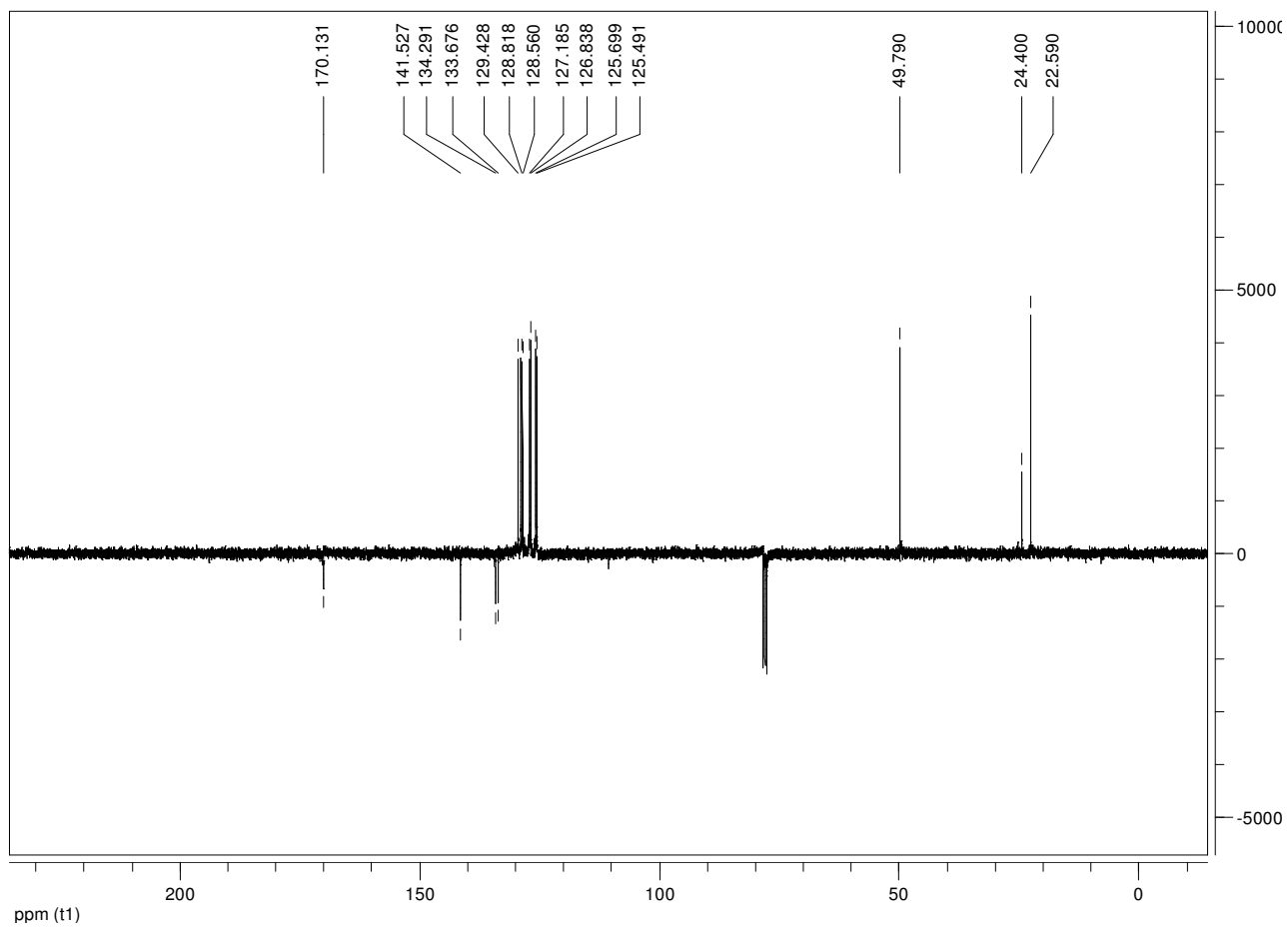
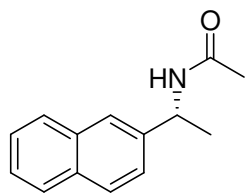
(R)-1-Naphthalen-2-yl-ethylamine hydrochloride (7c)



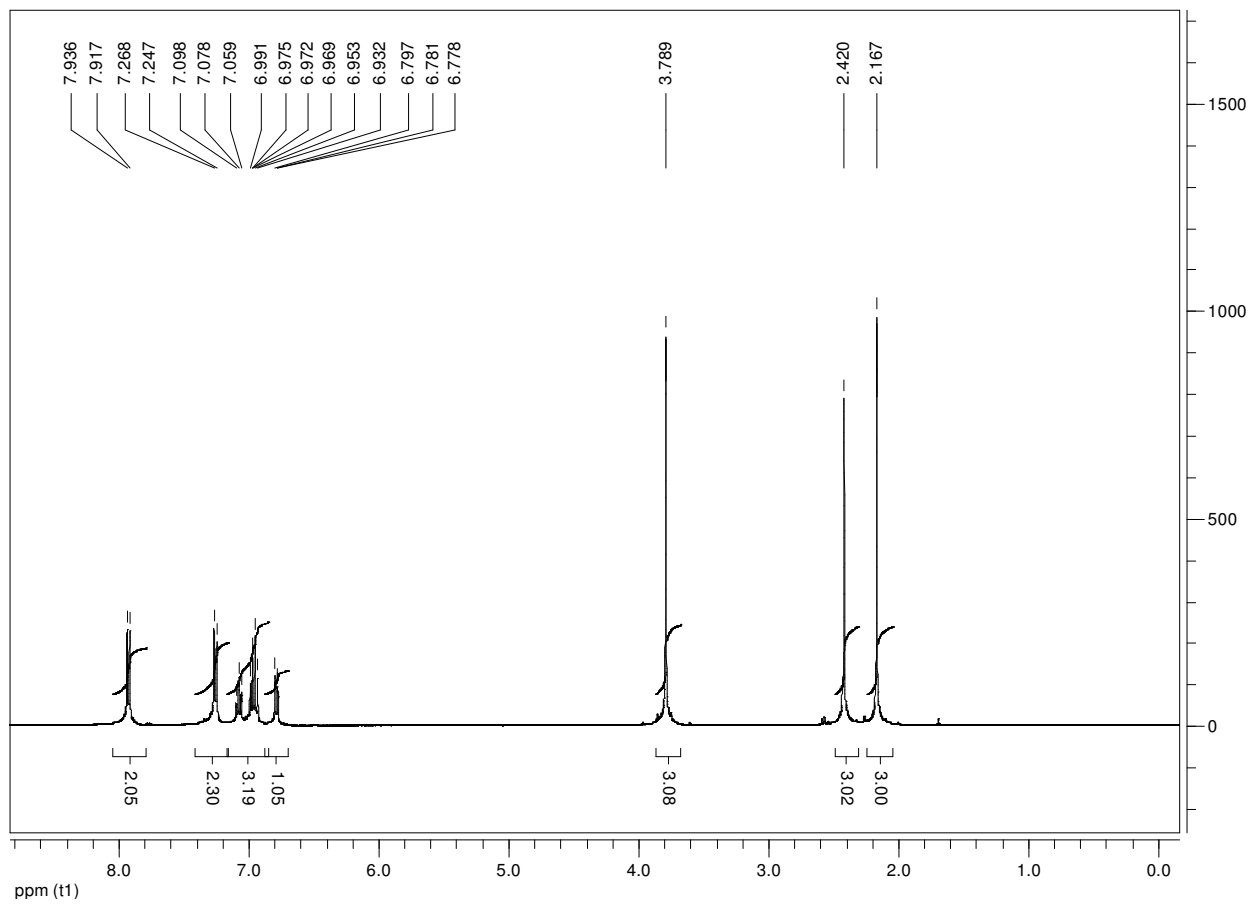
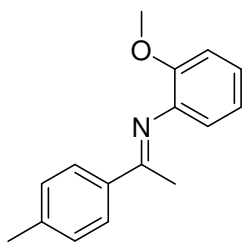
(R)-N-(1-Naphthalen-2-yl-ethyl)-acetamide (7d), ¹H



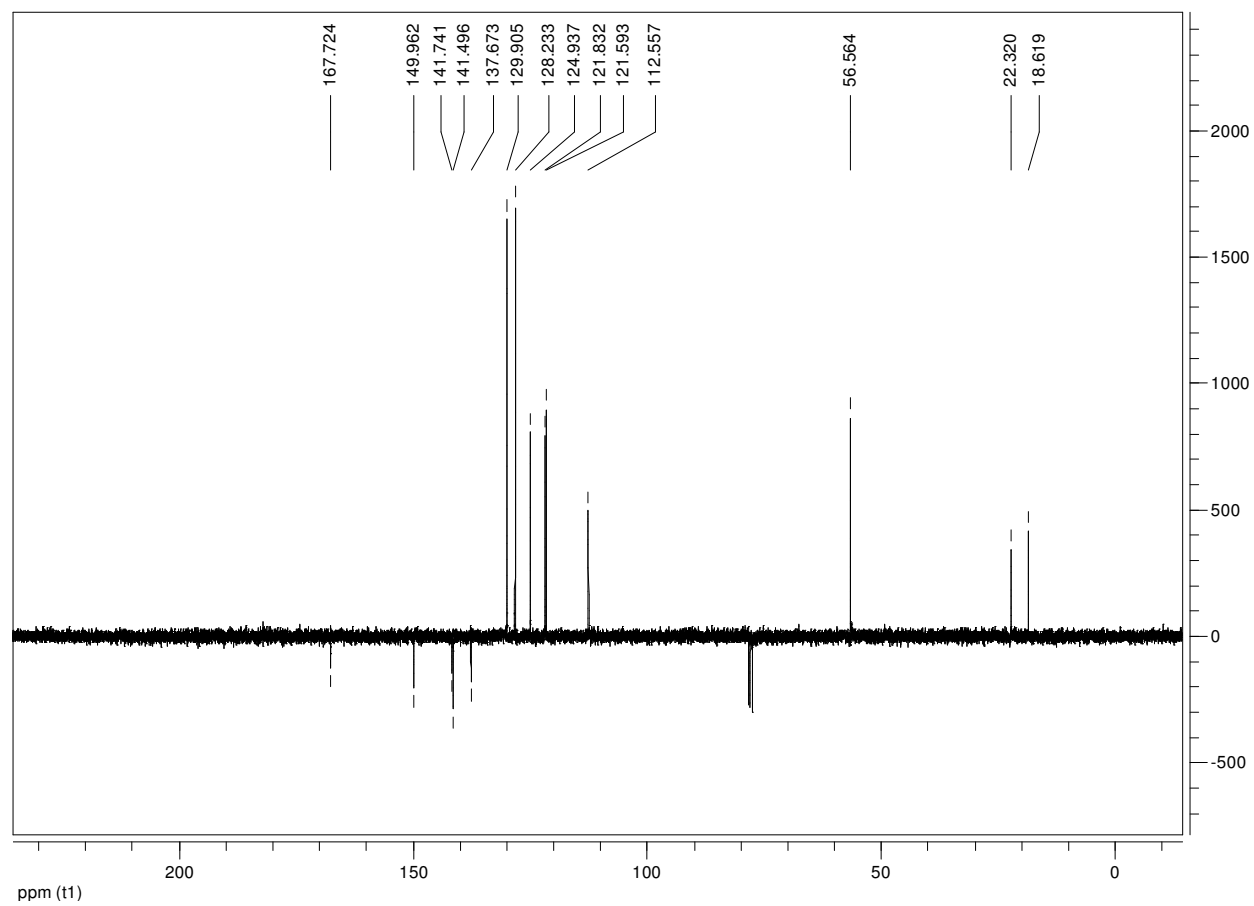
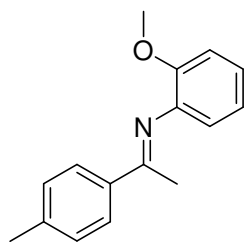
(R)-N-(1-Naphthalen-2-yl-ethyl)-acetamide (7d), ¹³C



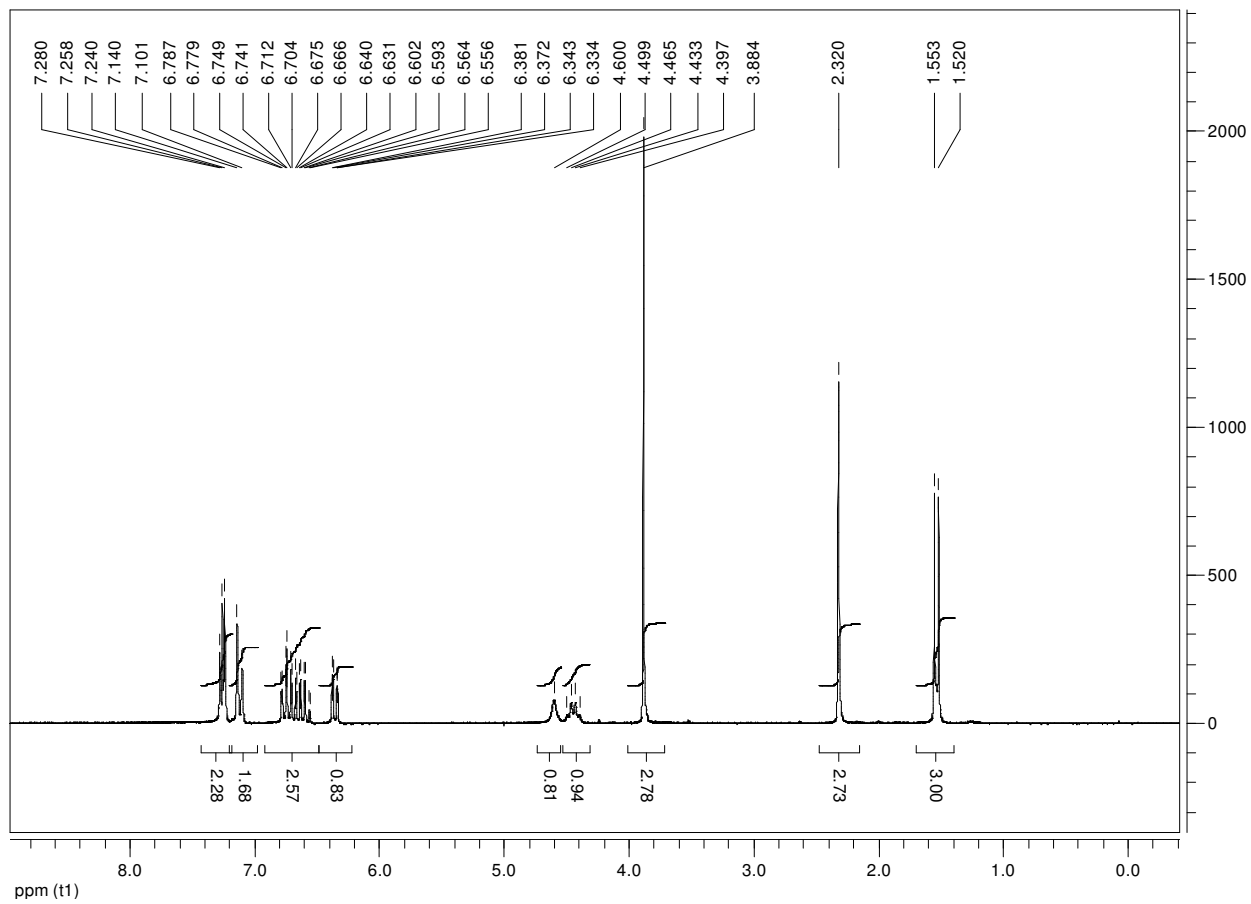
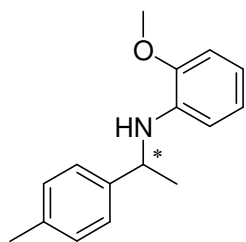
(2-Methoxy-phenyl)-(1-p-tolyl-ethylidene)-amine (8a), ¹H



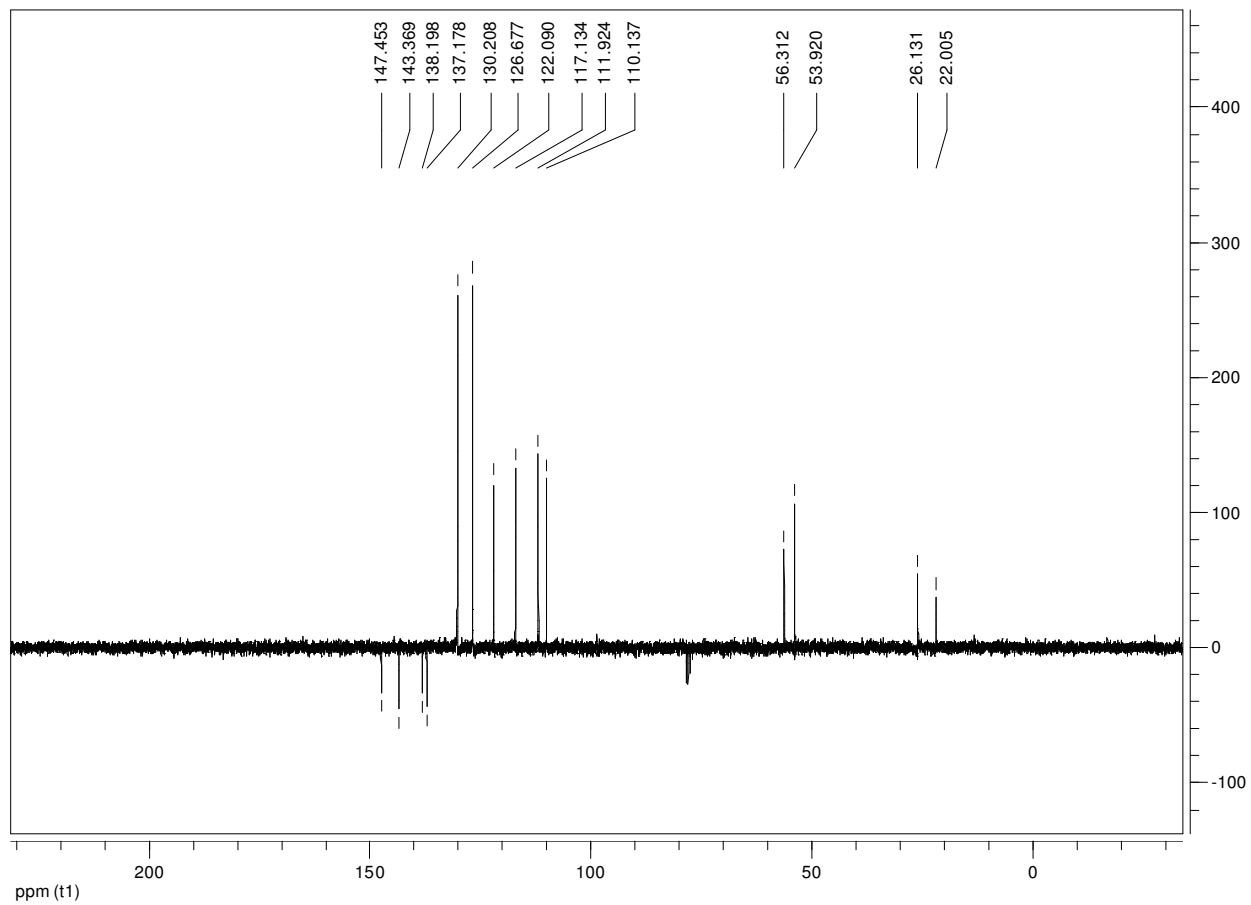
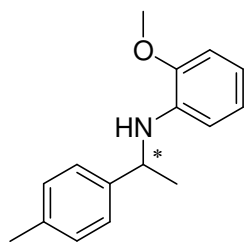
(2-Methoxy-phenyl)-(1-p-tolyl-ethylidene)-amine (8a), ^{13}C



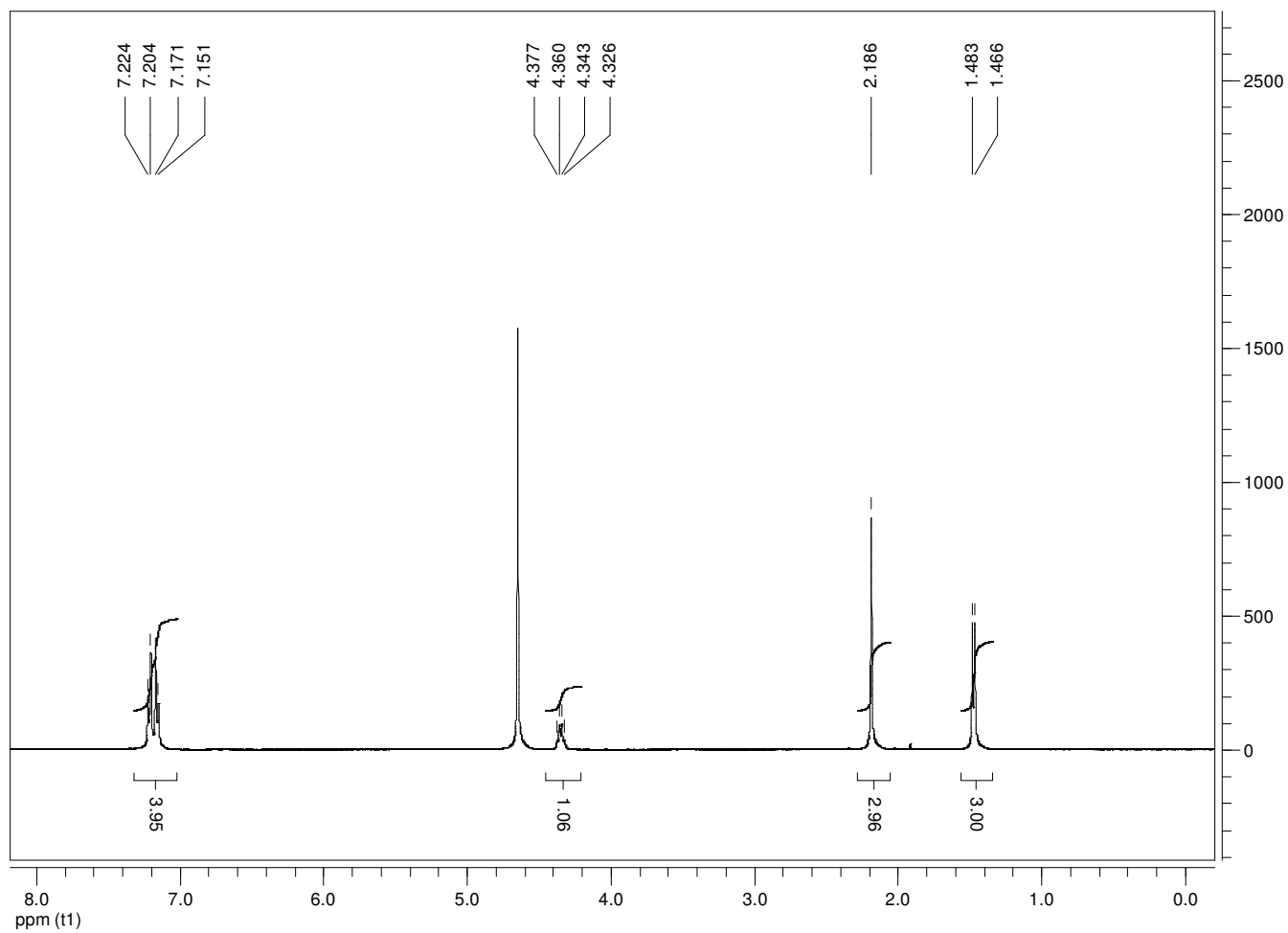
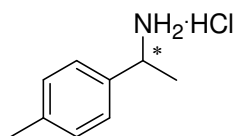
(-)-(2-Methoxy-phenyl)-(1-p-tolyl-ethyl)-amine (8b), ¹H



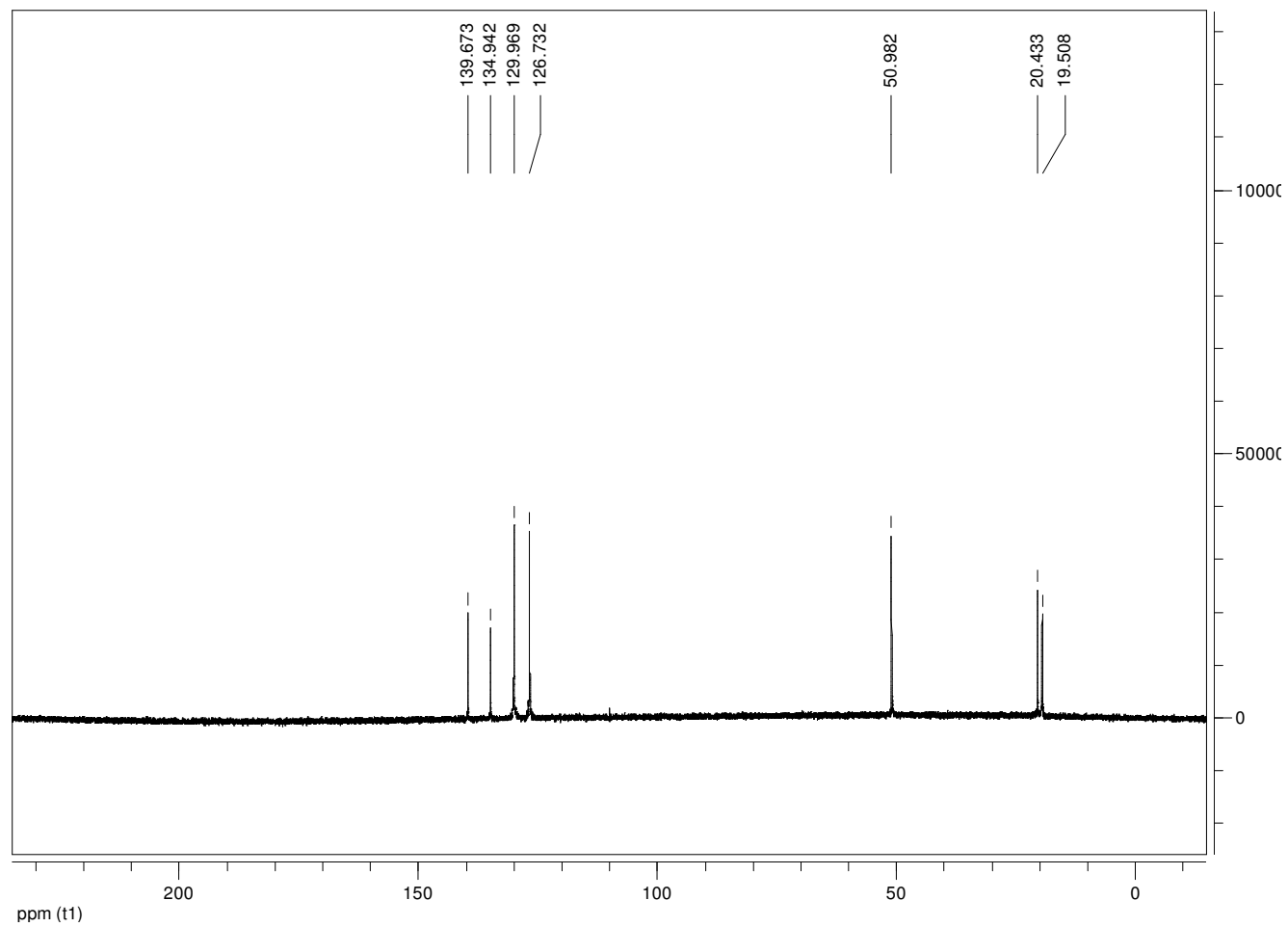
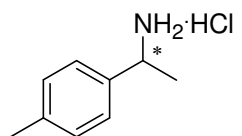
(-)-(2-Methoxy-phenyl)-(1-p-tolyl-ethyl)-amine (8b), ^{13}C



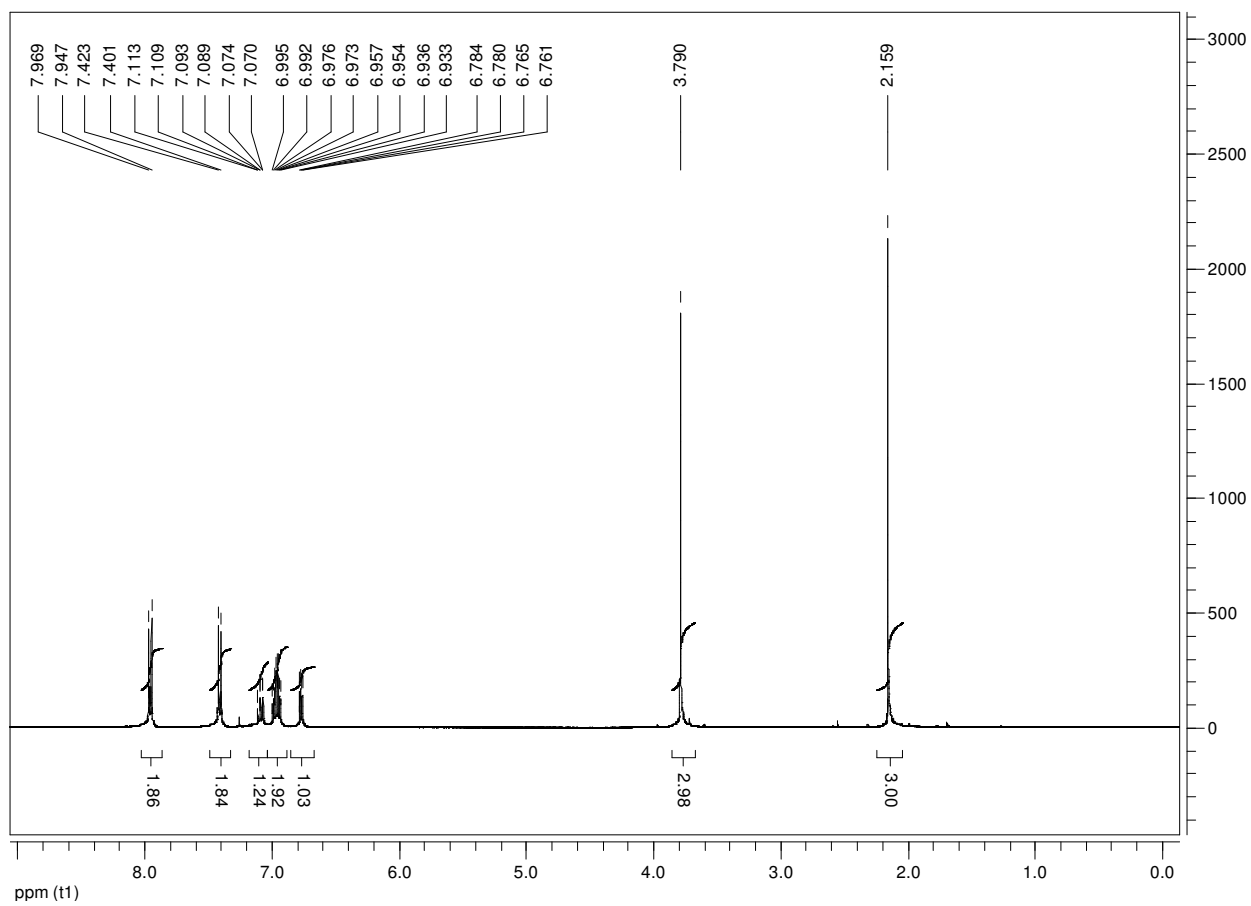
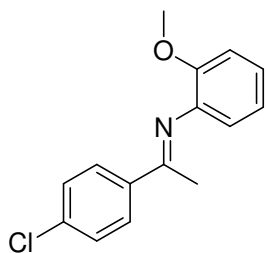
1-p-Tolyl-ethylamine hydrochloride (8c)



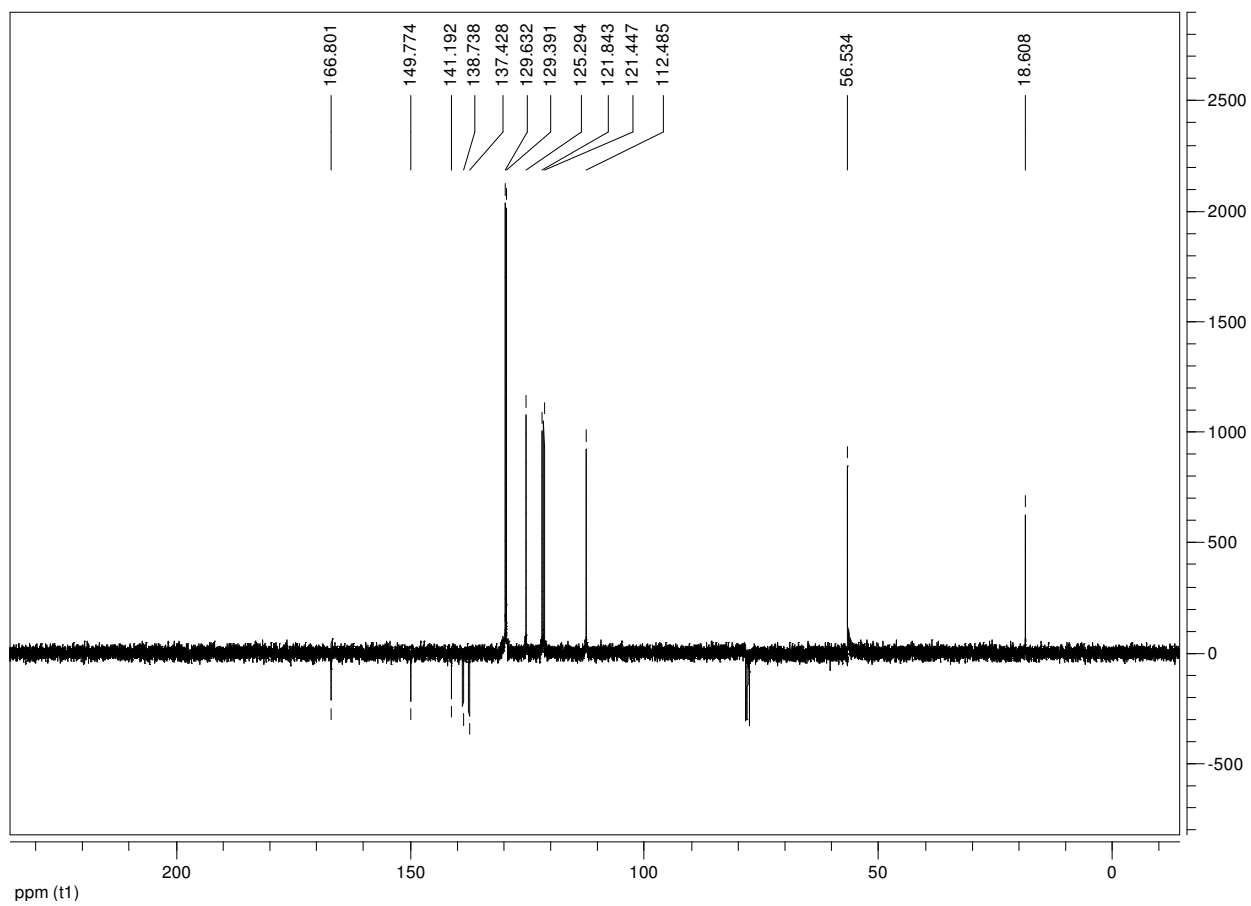
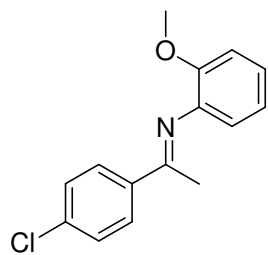
1-p-Tolyl-ethylamine hydrochloride (8c)



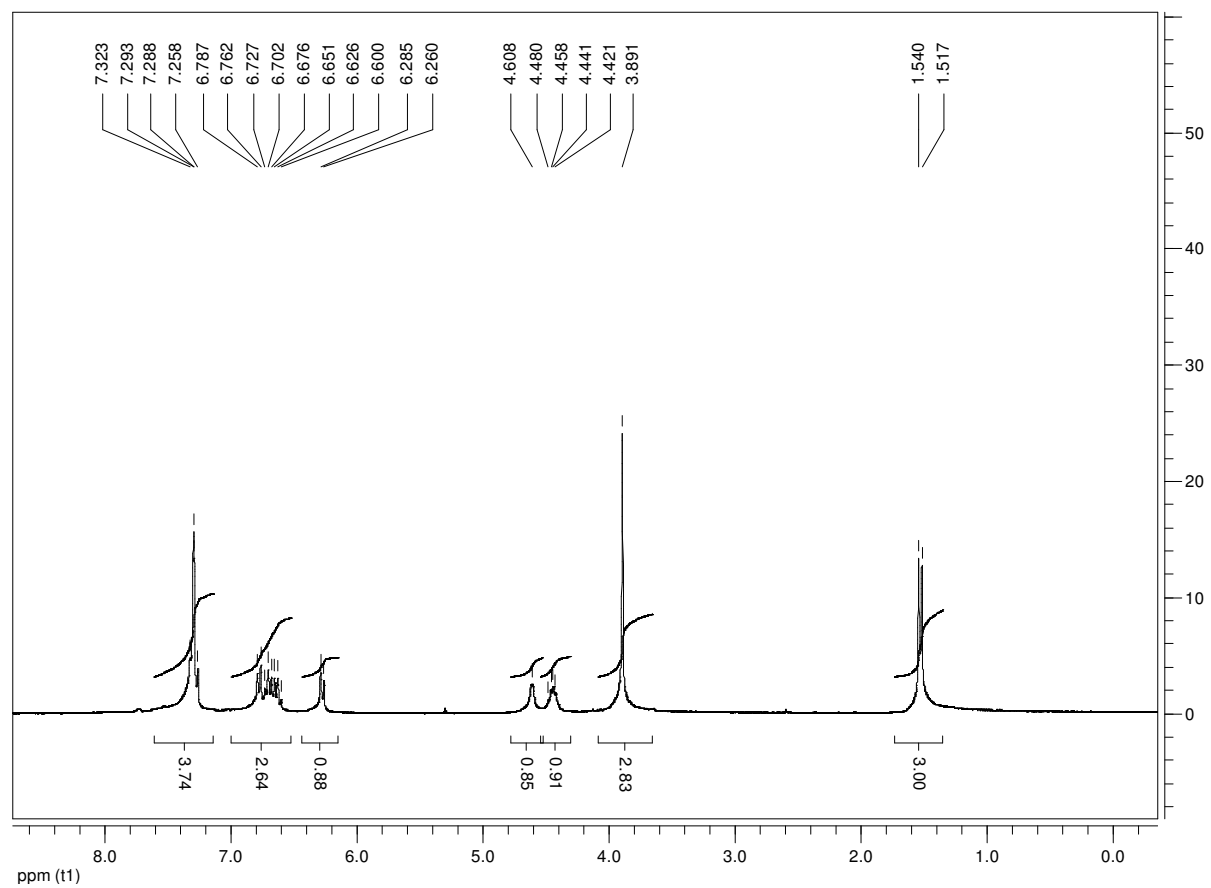
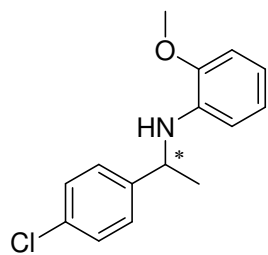
[1-(4-Chloro-phenyl)-ethylidene]-(2-methoxy-phenyl)-amine (9a), ¹H



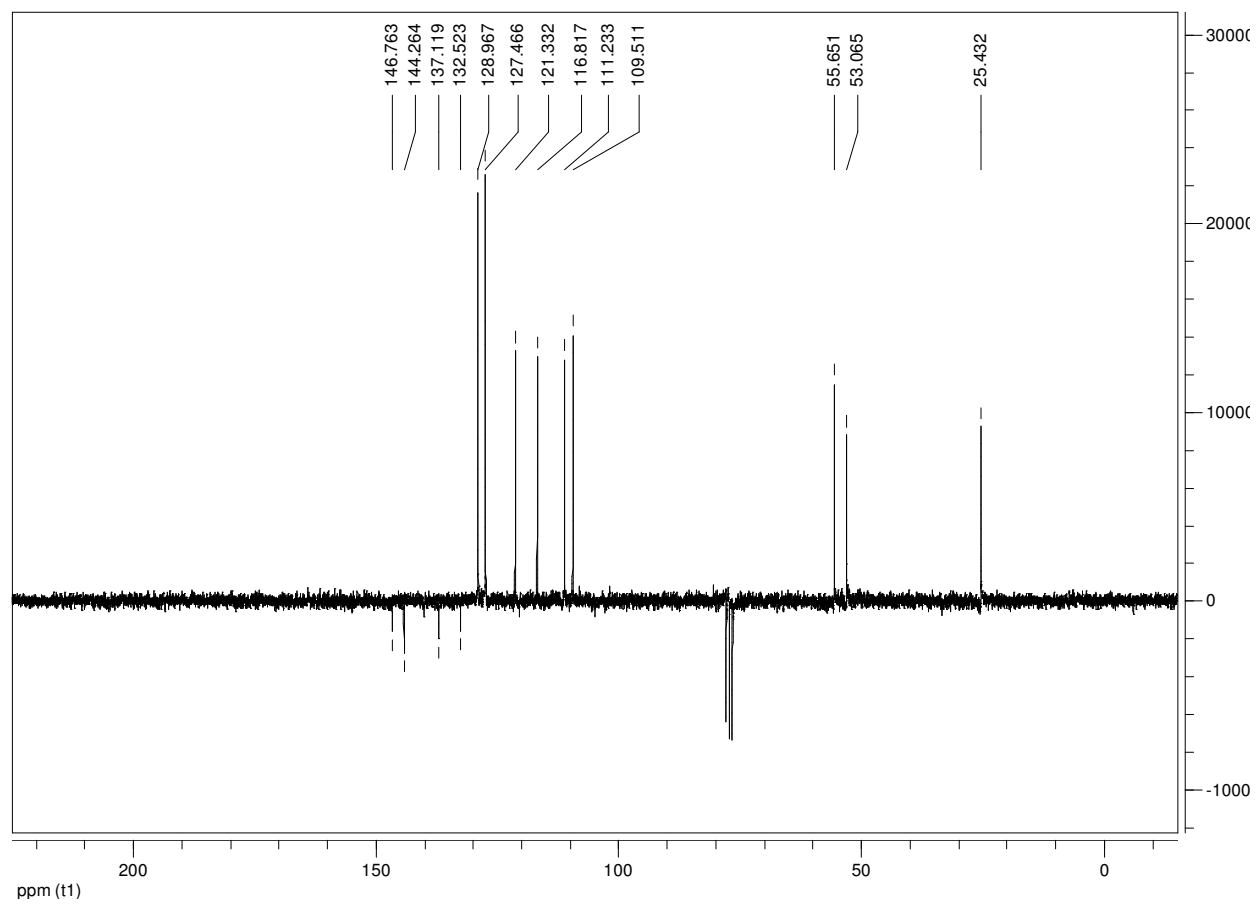
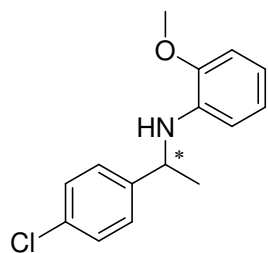
[1-(4-Chloro-phenyl)-ethylidene]-(2-methoxy-phenyl)-amine (9a), ^{13}C



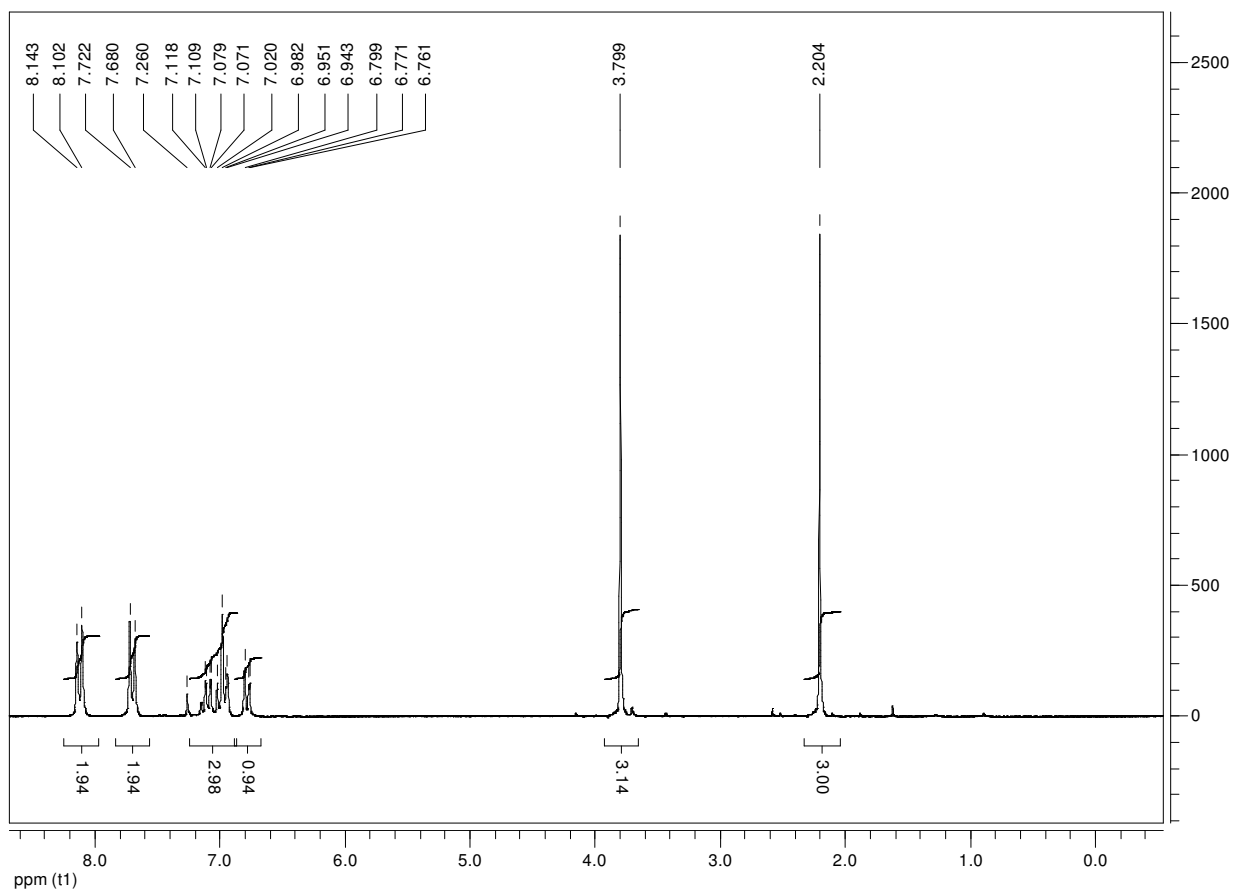
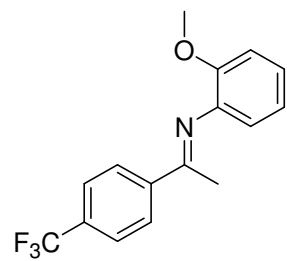
(-)-[1-(4-Chloro-phenyl)-ethyl]-(2-methoxy-phenyl)-amine (9b), ^1H



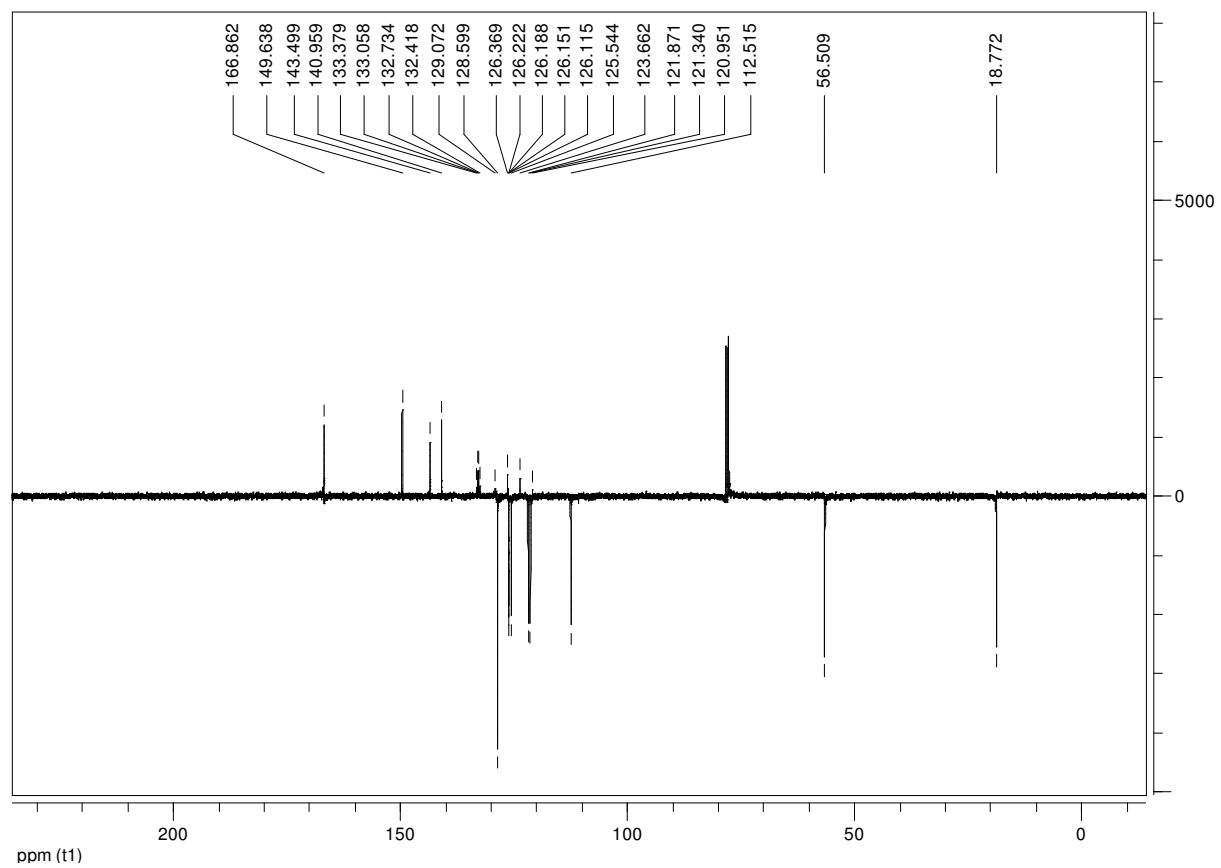
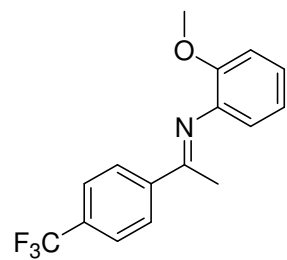
(-)-[1-(4-Chloro-phenyl)-ethyl]-(2-methoxy-phenyl)-amine (9b), ^{13}C



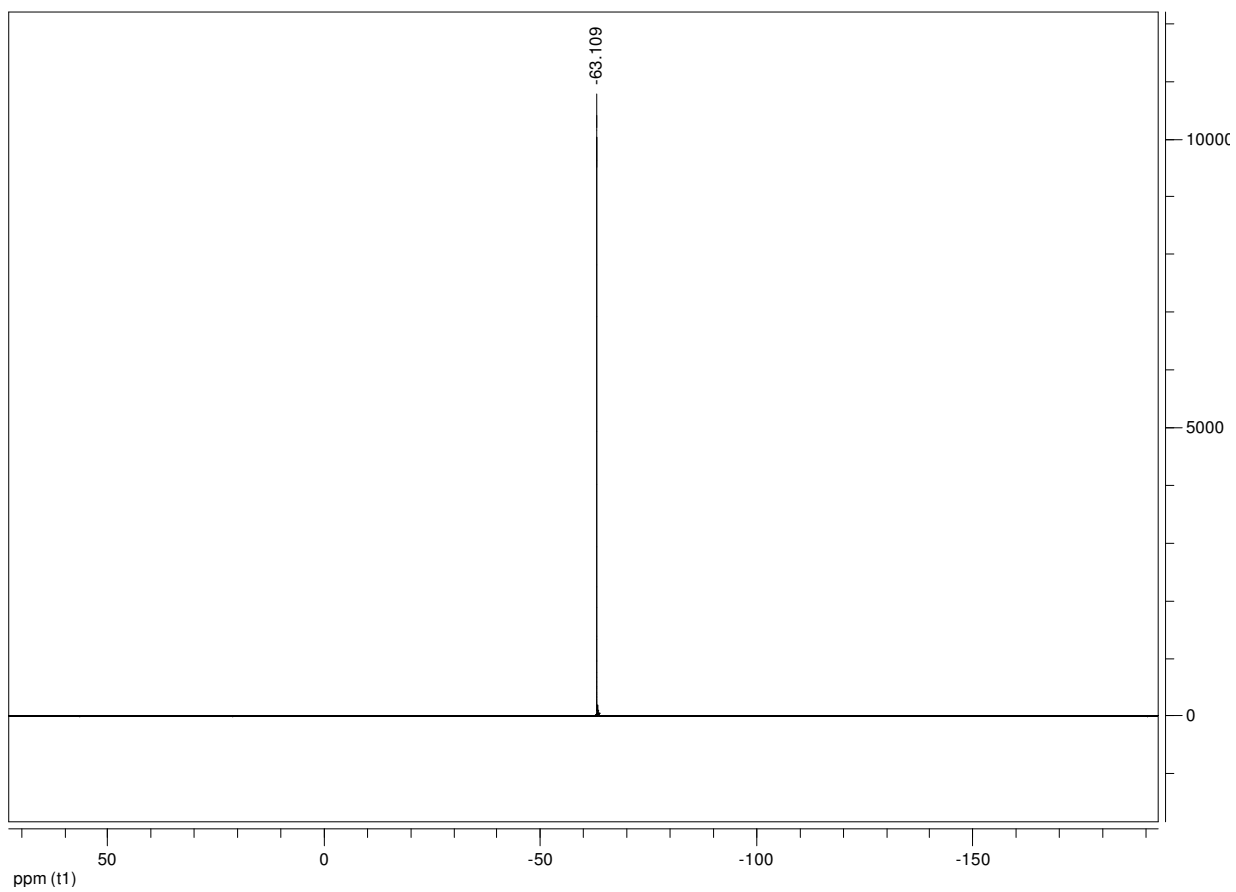
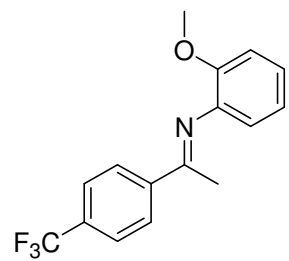
(2-Methoxy-phenyl)-[1-(4-trifluoromethyl-phenyl)-ethylidene]-amine (10a), ¹H



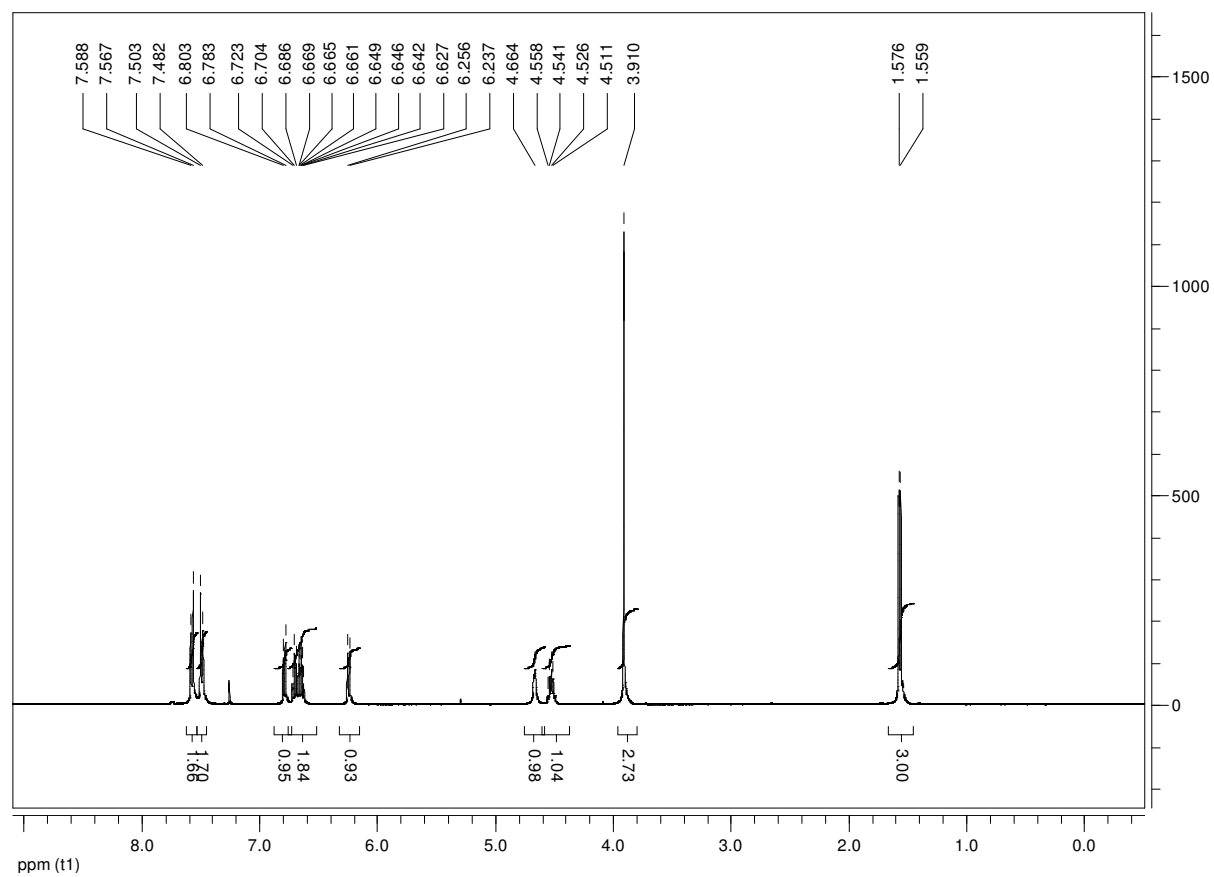
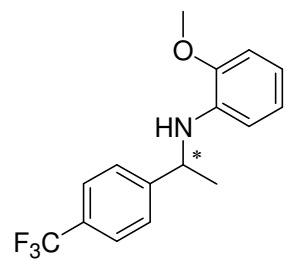
(2-Methoxy-phenyl)-[1-(4-trifluoromethyl-phenyl)-ethylidene]-amine (10a), ^{13}C



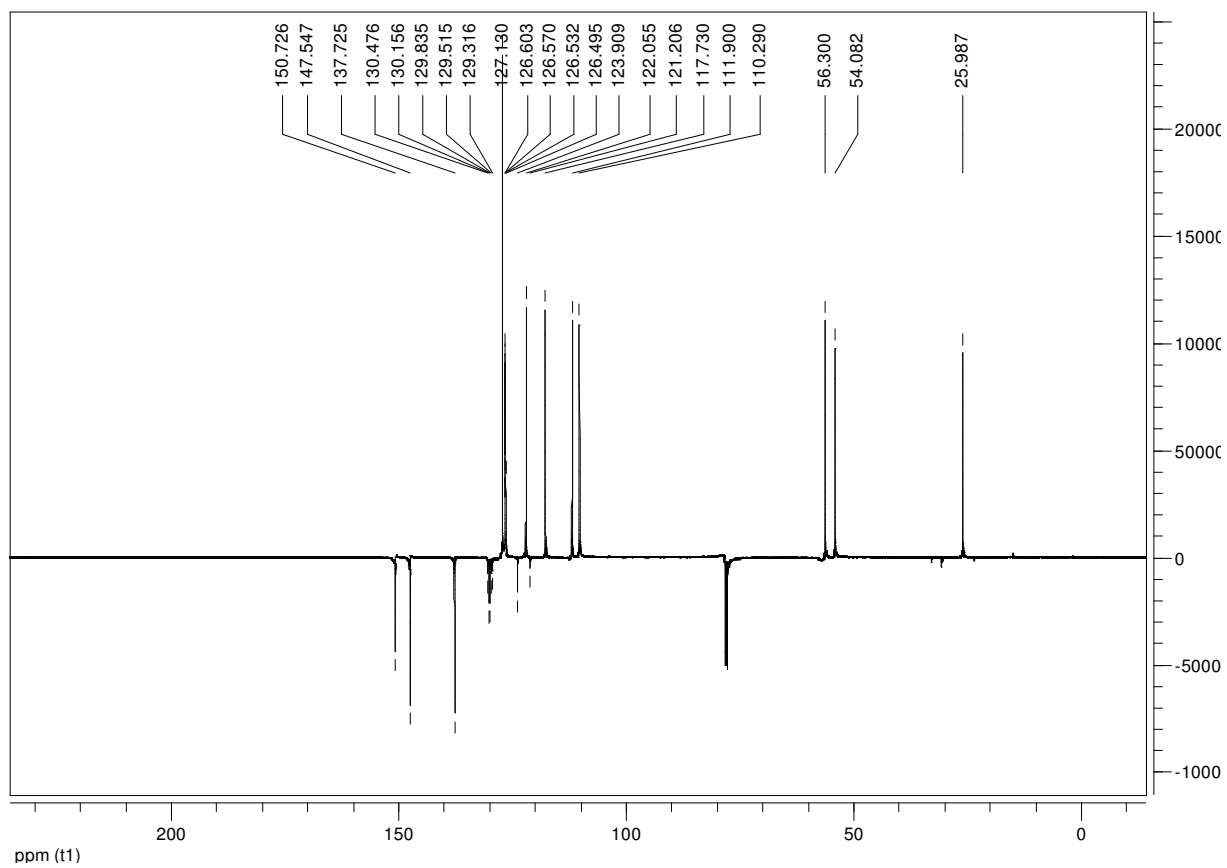
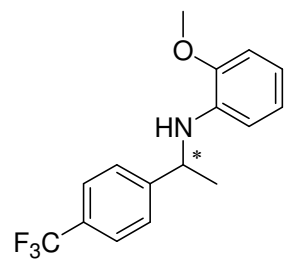
(2-Methoxy-phenyl)-[1-(4-trifluoromethyl-phenyl)-ethylidene]-amine (10a), ¹⁹F



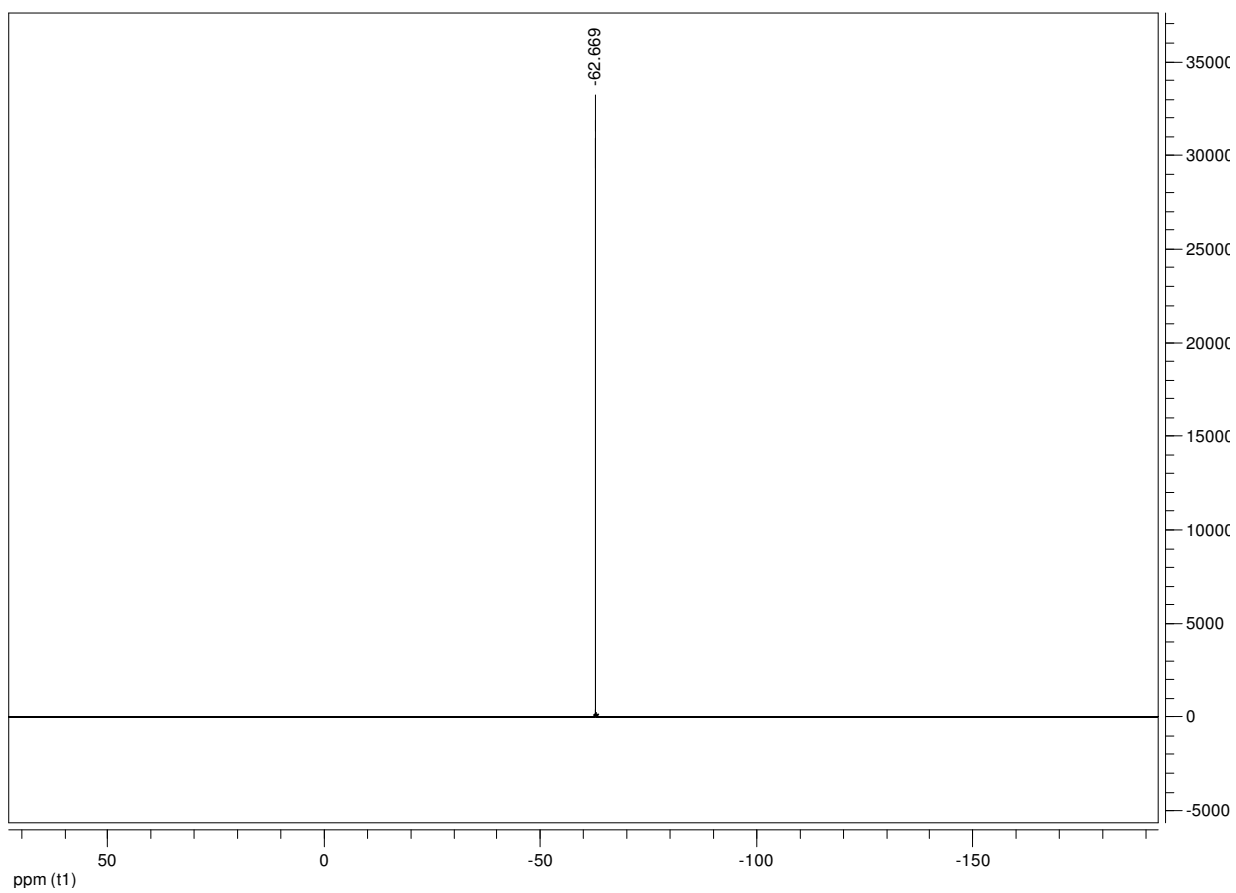
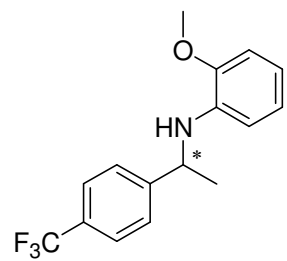
(-)-(2-Methoxy-phenyl)-[1-(4-trifluoromethyl-phenyl)-ethyl]-amine (10b), ^1H



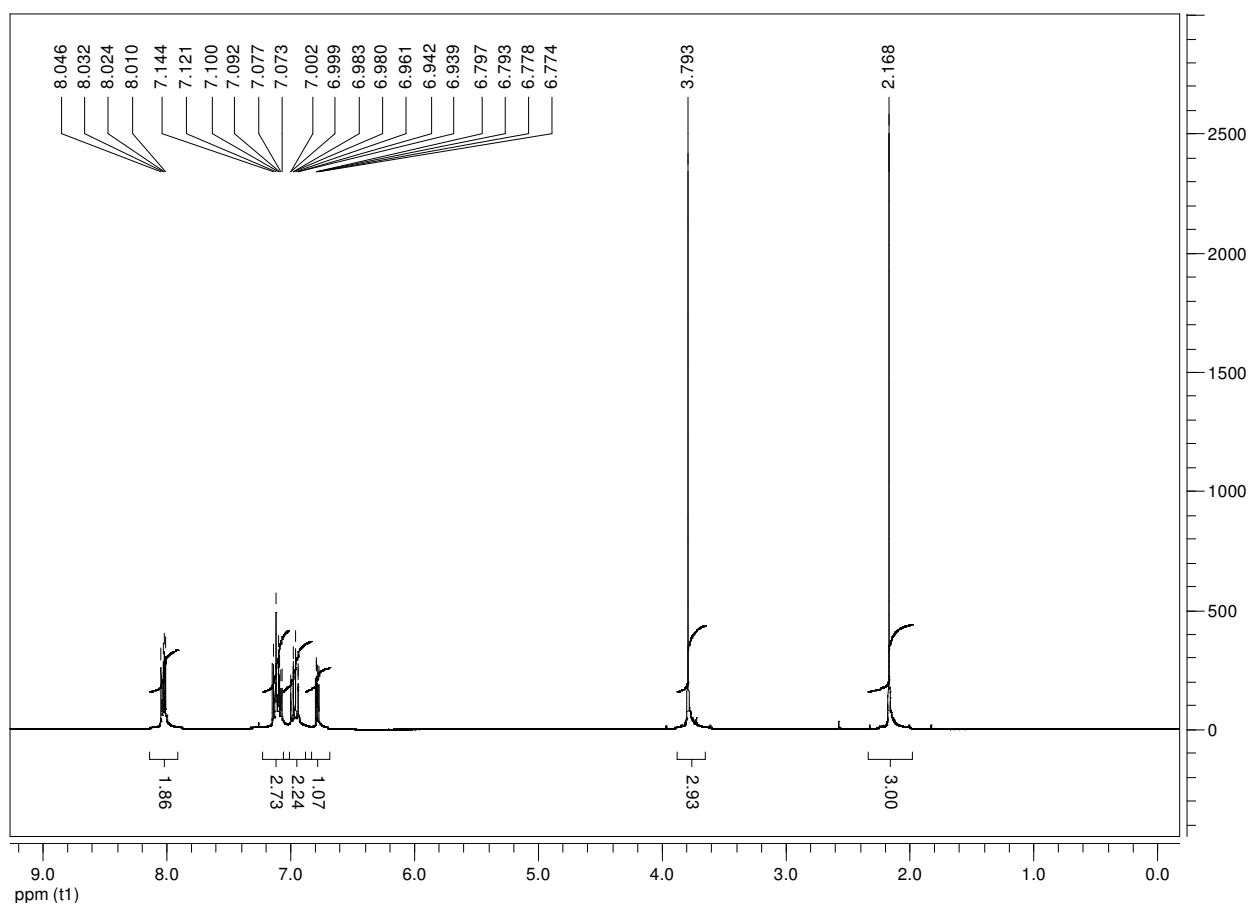
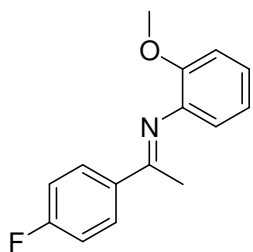
(-)-(2-Methoxy-phenyl)-[1-(4-trifluoromethyl-phenyl)-ethyl]-amine (10b), ¹³C



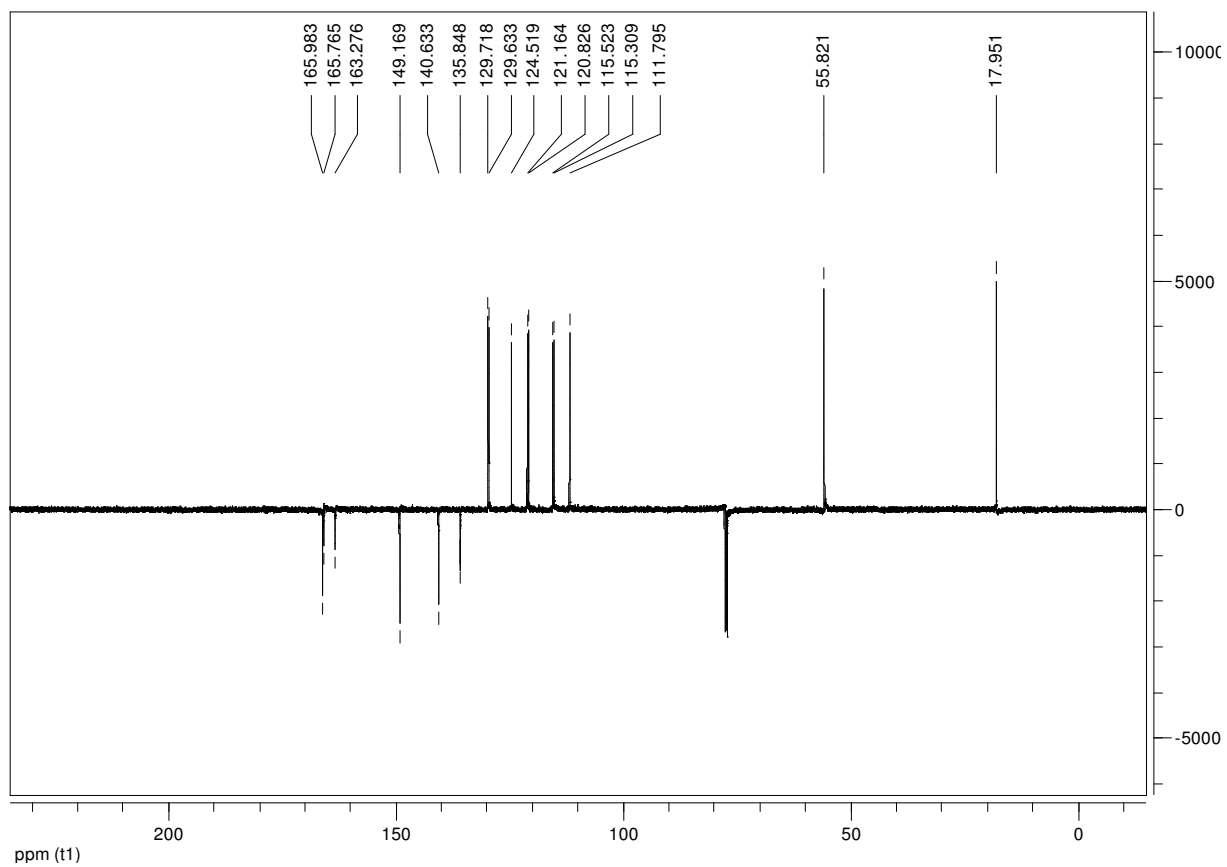
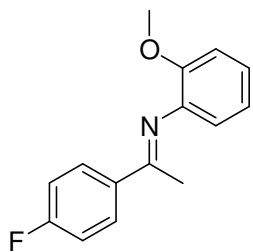
(-)-(2-Methoxy-phenyl)-[1-(4-trifluoromethyl-phenyl)-ethyl]-amine (10b), ¹⁹F



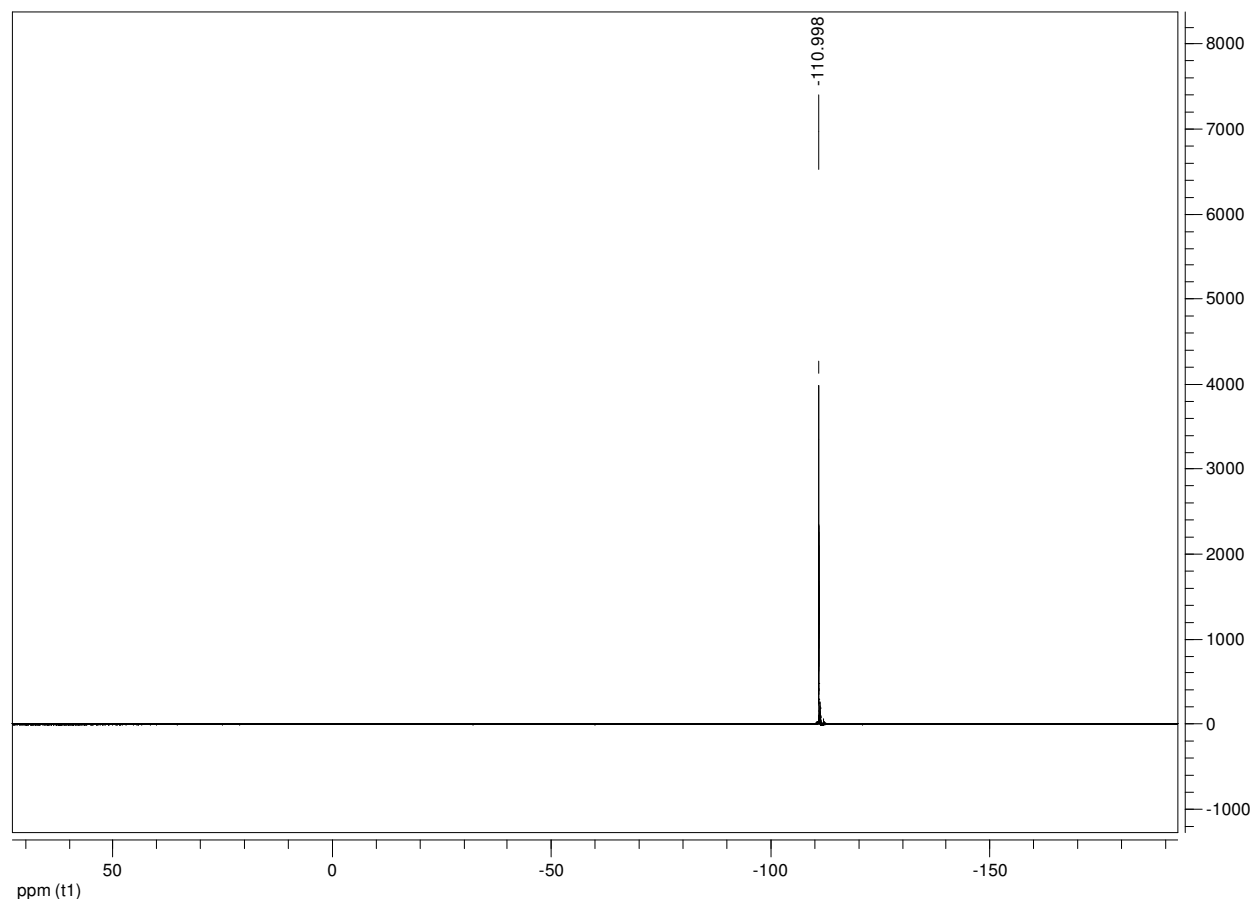
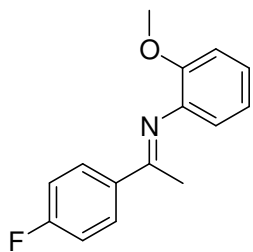
[1-(4-Fluoro-phenyl)-ethylidene]-(2-methoxy-phenyl)-amine (11a), ¹H



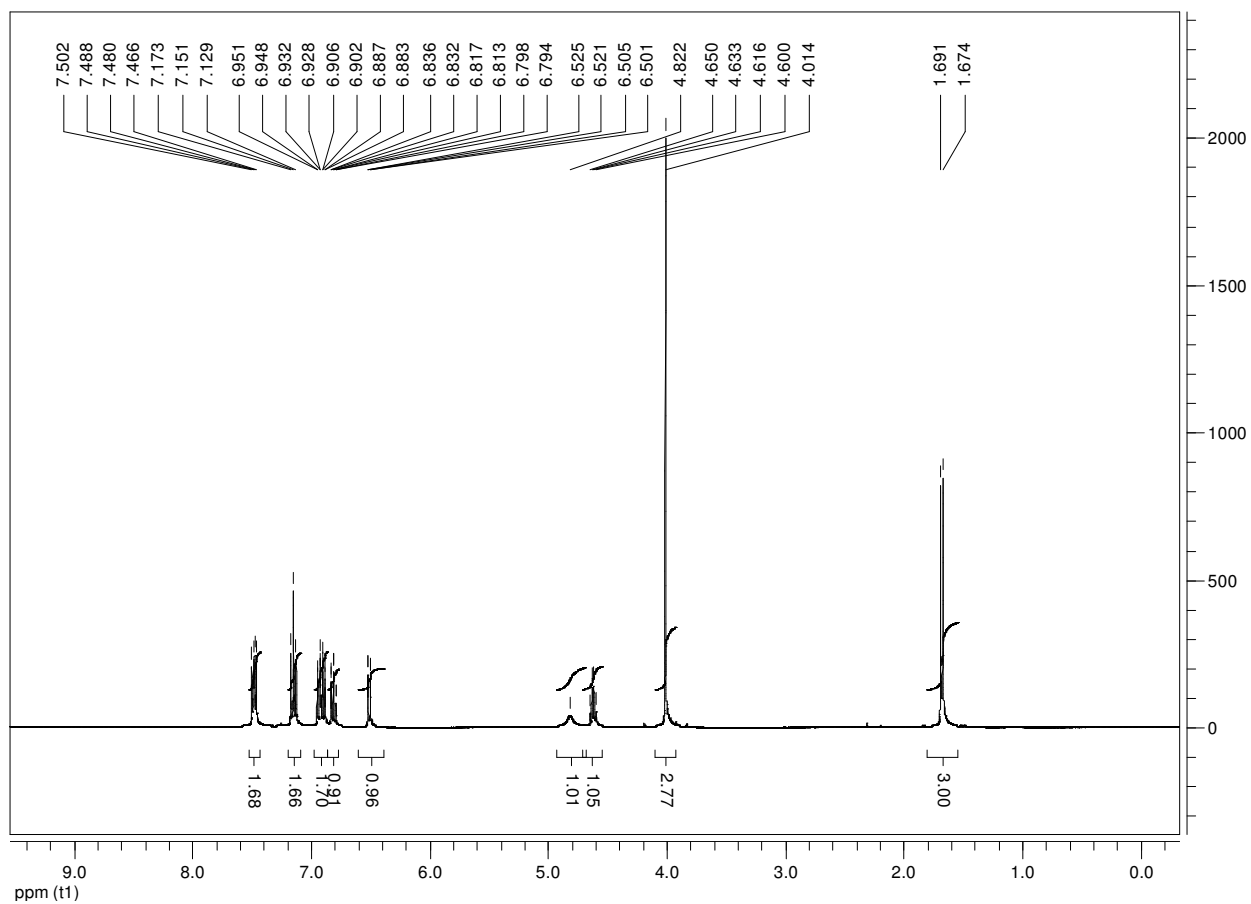
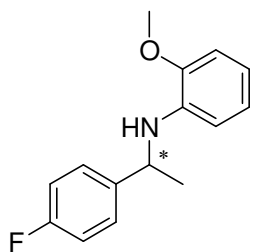
[1-(4-Fluoro-phenyl)-ethylidene]-(2-methoxy-phenyl)-amine (11a), ¹³C



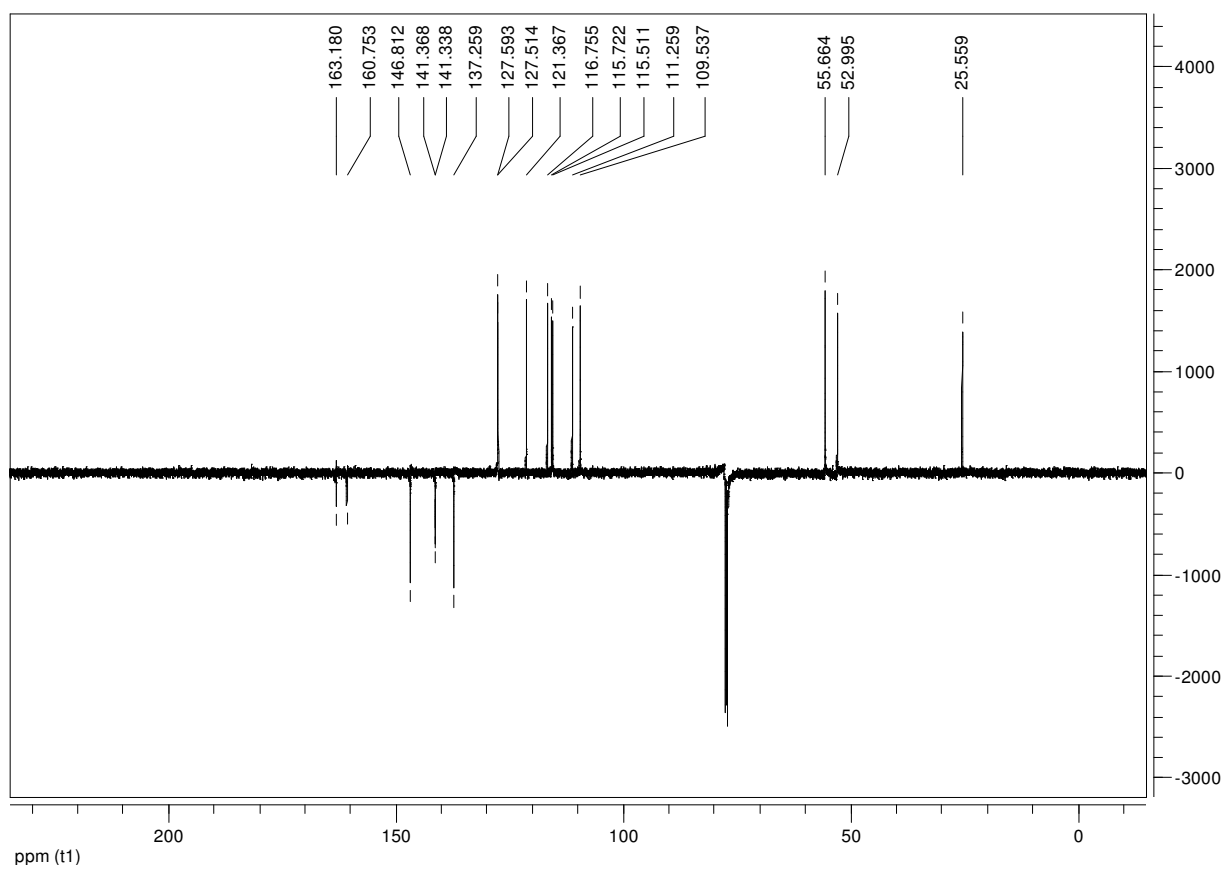
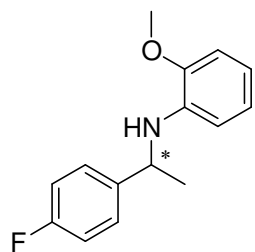
[1-(4-Fluoro-phenyl)-ethylidene]-(2-methoxy-phenyl)-amine (11a), ¹⁹F



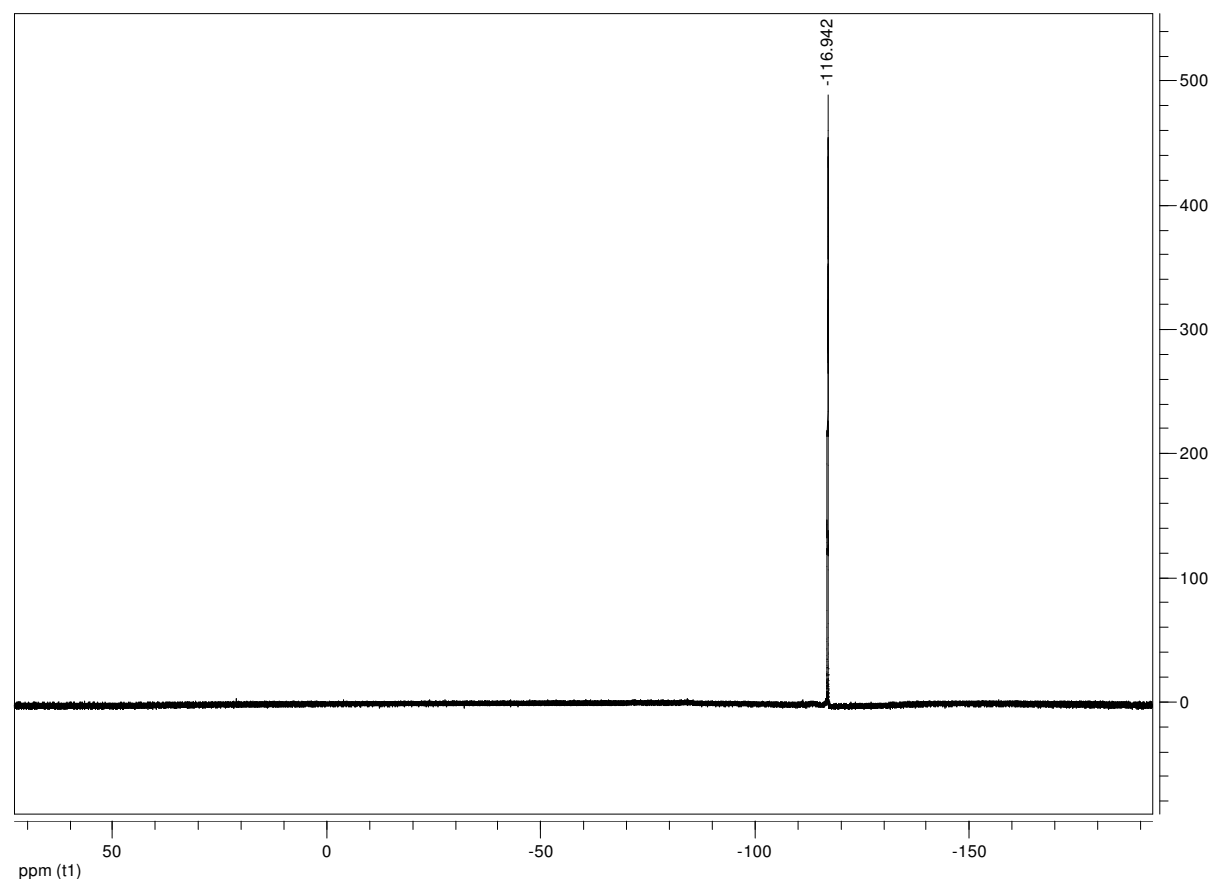
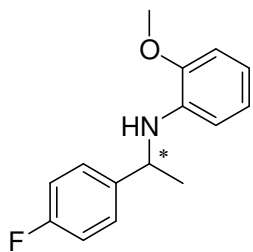
(-)-[1-(4-Fluoro-phenyl)-ethyl]-(2-methoxy-phenyl)-amine (11b), ^1H



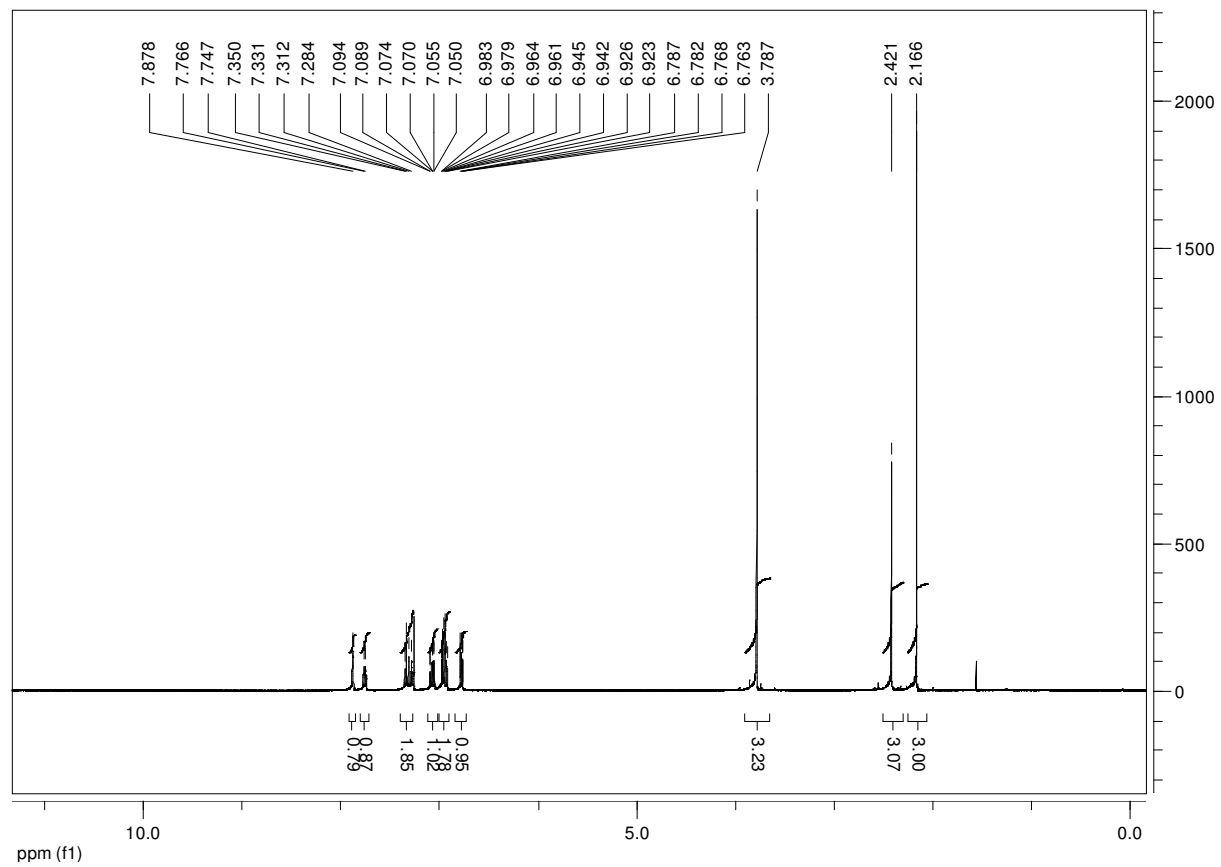
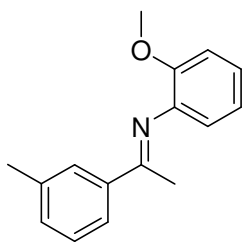
(-)-[1-(4-Fluoro-phenyl)-ethyl]-(2-methoxy-phenyl)-amine (11b), ^{13}C



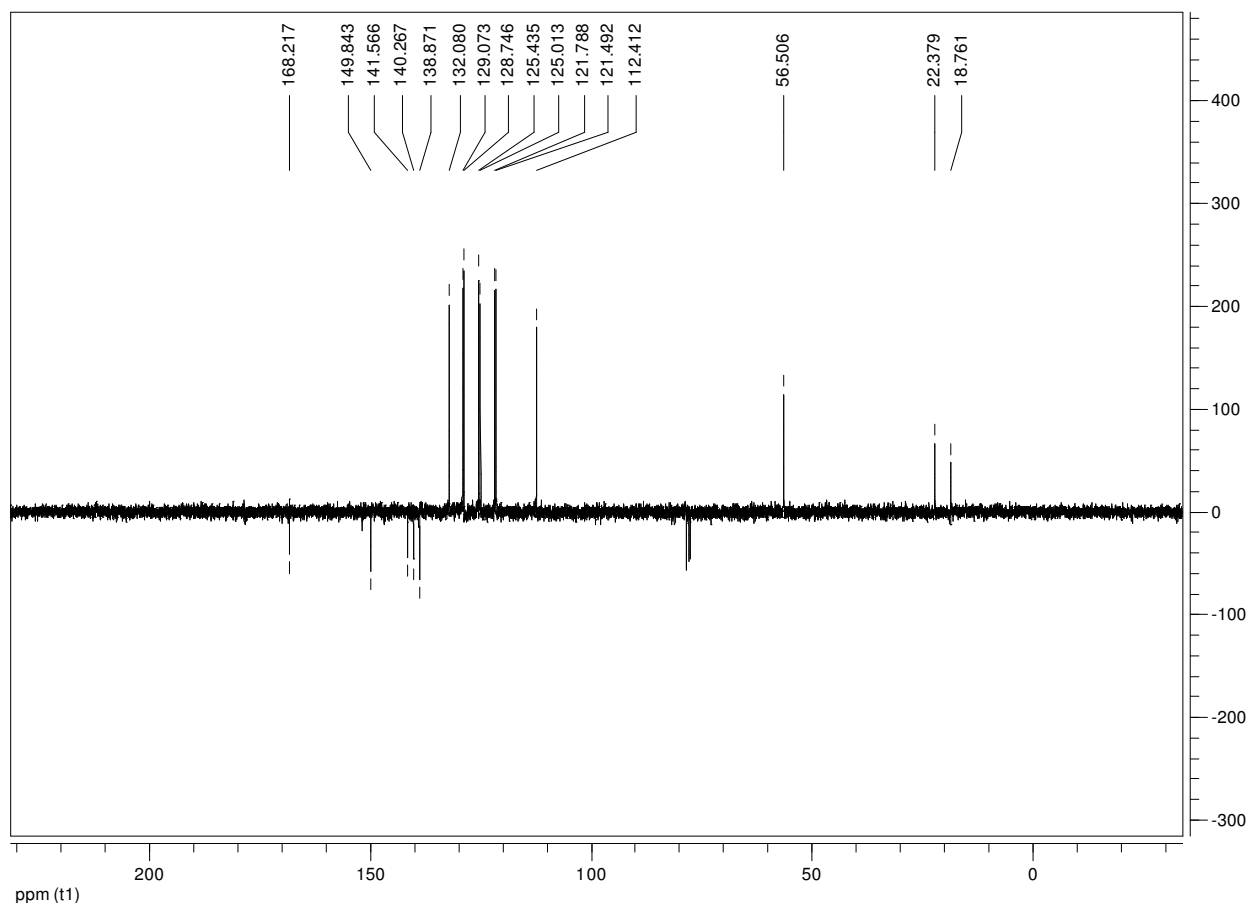
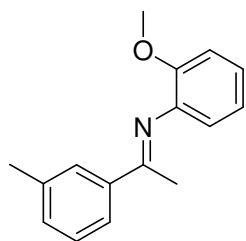
(-)-[1-(4-Fluoro-phenyl)-ethyl]-(2-methoxy-phenyl)-amine (11b), ^{19}F



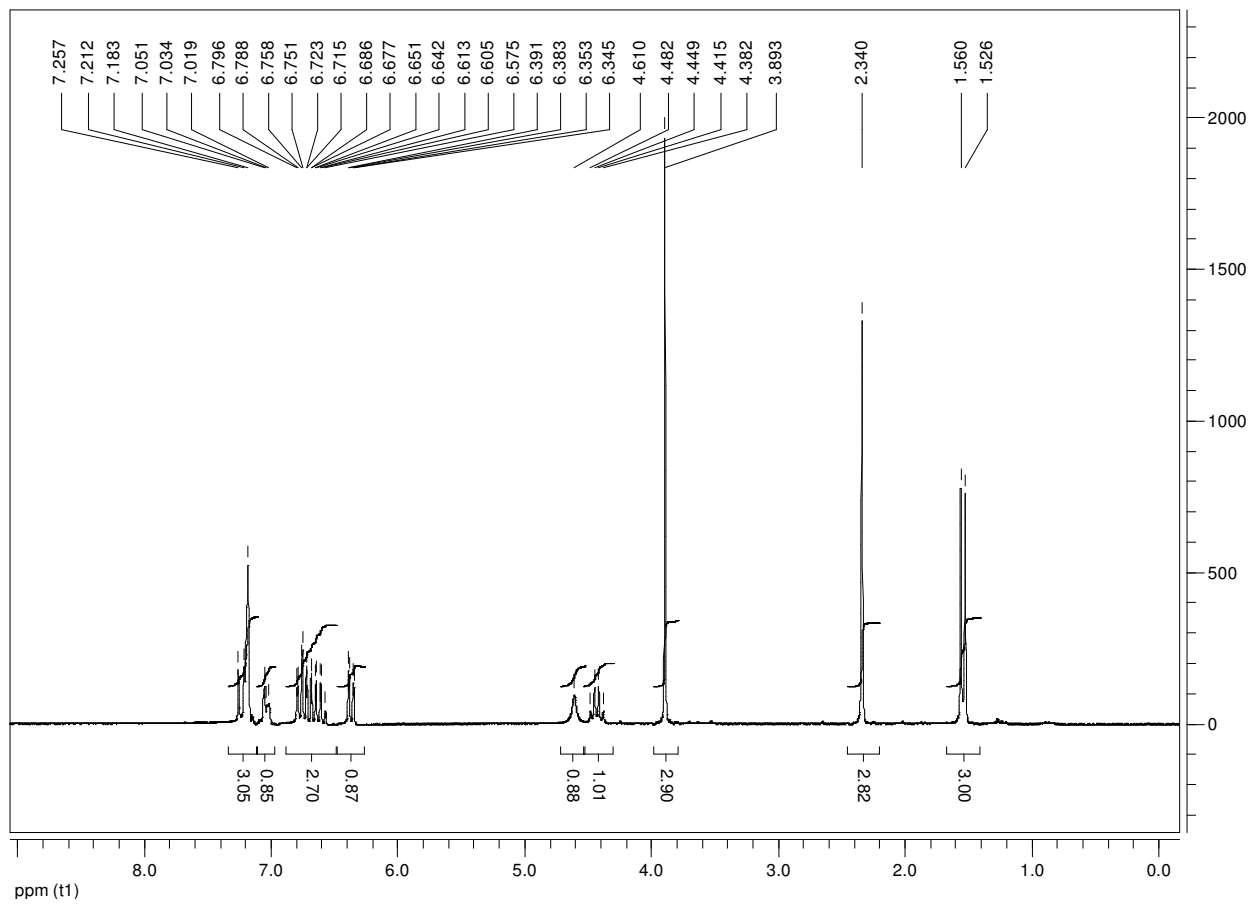
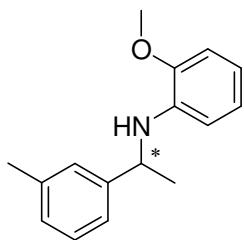
(2-Methoxy-phenyl)-(1-m-tolyl-ethylidene)-amine (12a), ¹H



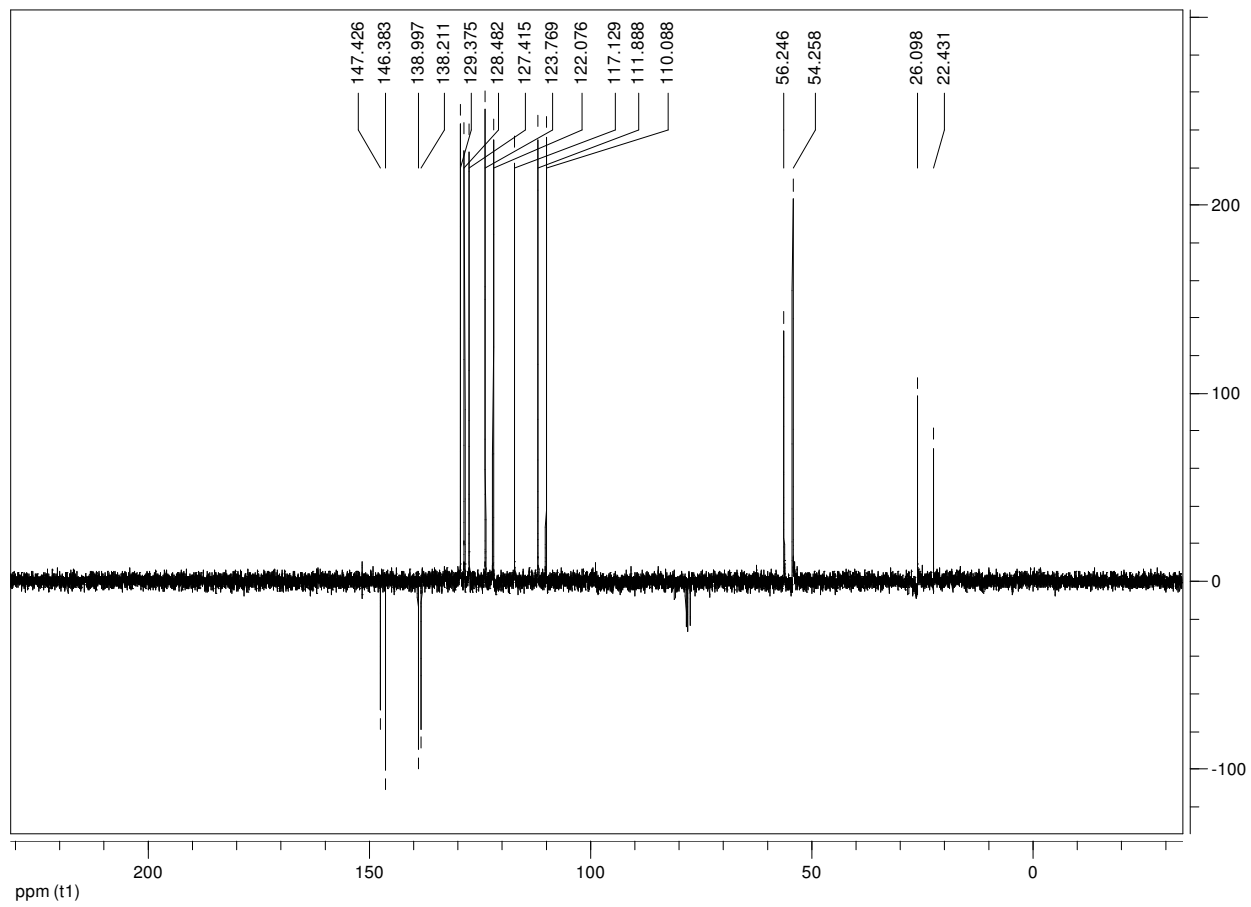
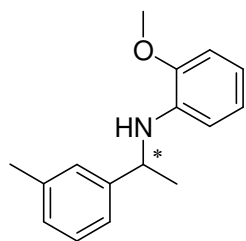
(2-Methoxy-phenyl)-(1-m-tolyl-ethylidene)-amine (12a), ^{13}C



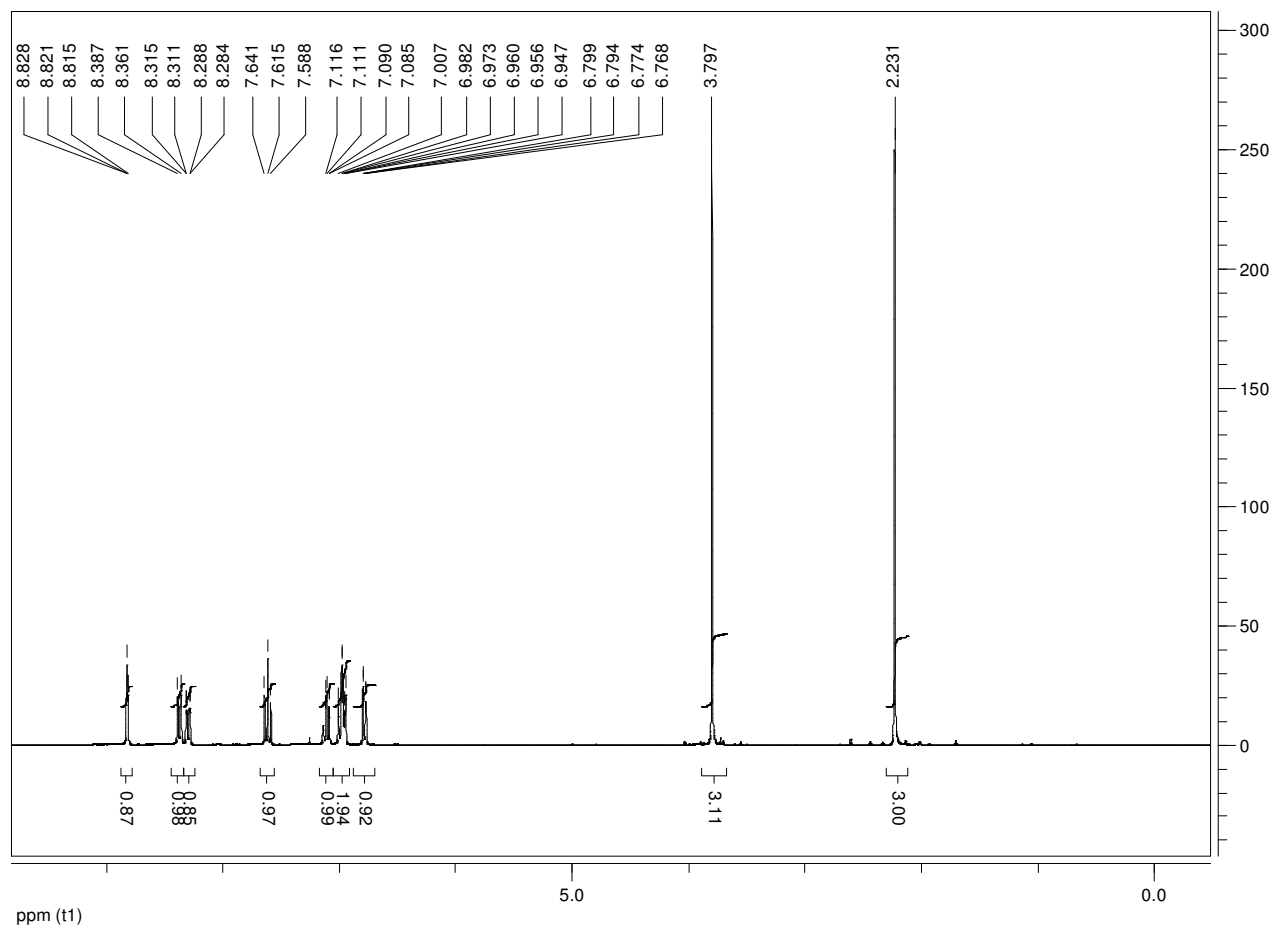
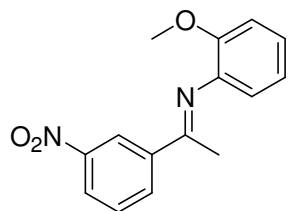
(-)-(2-Methoxy-phenyl)-(1-m-tolyl-ethyl)-amine (12b), ¹H



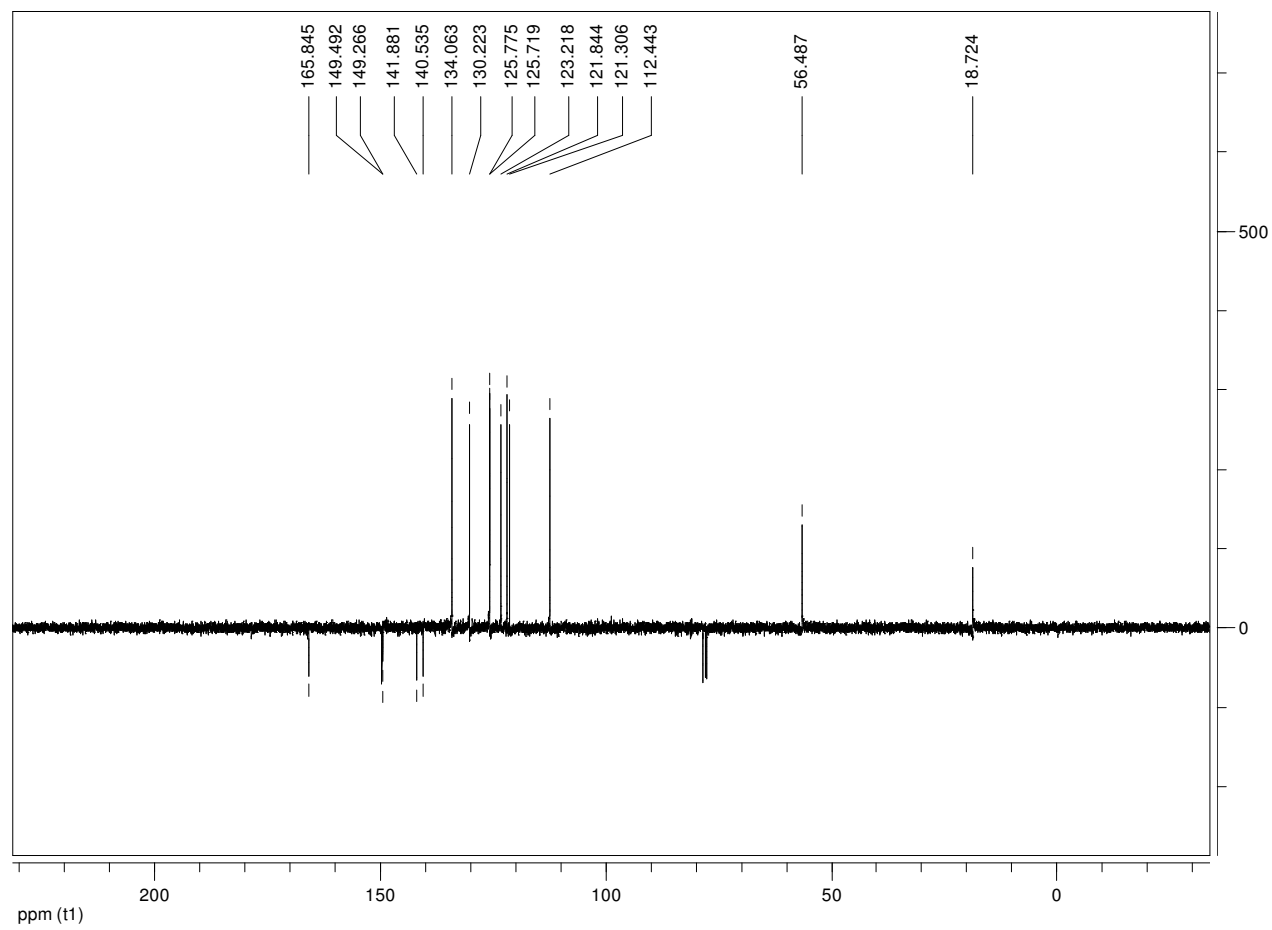
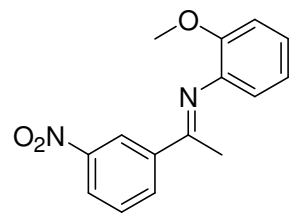
(-)-(2-Methoxy-phenyl)-(1-m-tolyl-ethyl)-amine (12b), ^{13}C



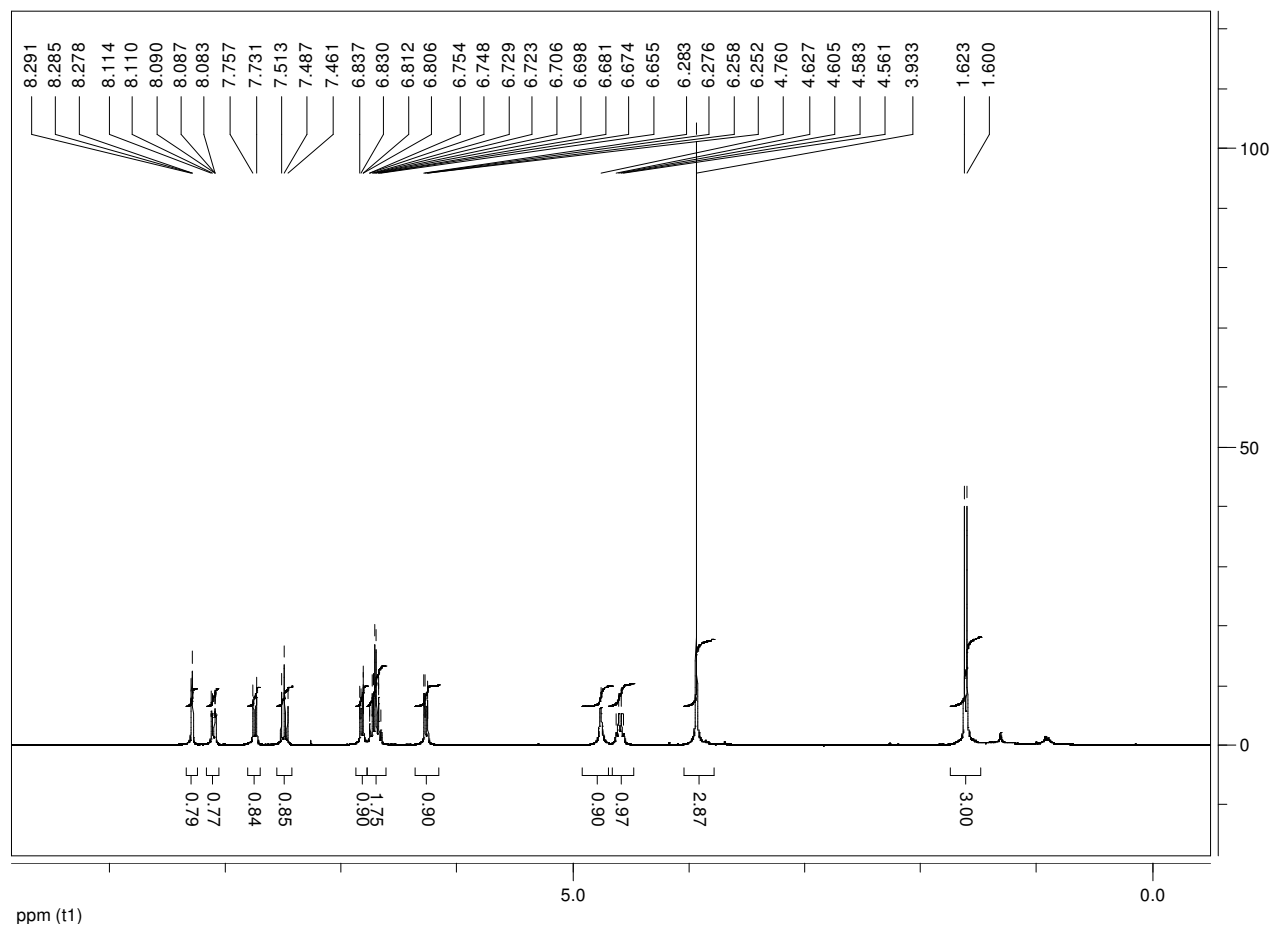
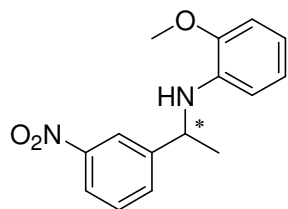
(2-Methoxy-phenyl)-[1-(3-nitro-phenyl)-ethylidene]-amine (13a), ¹H



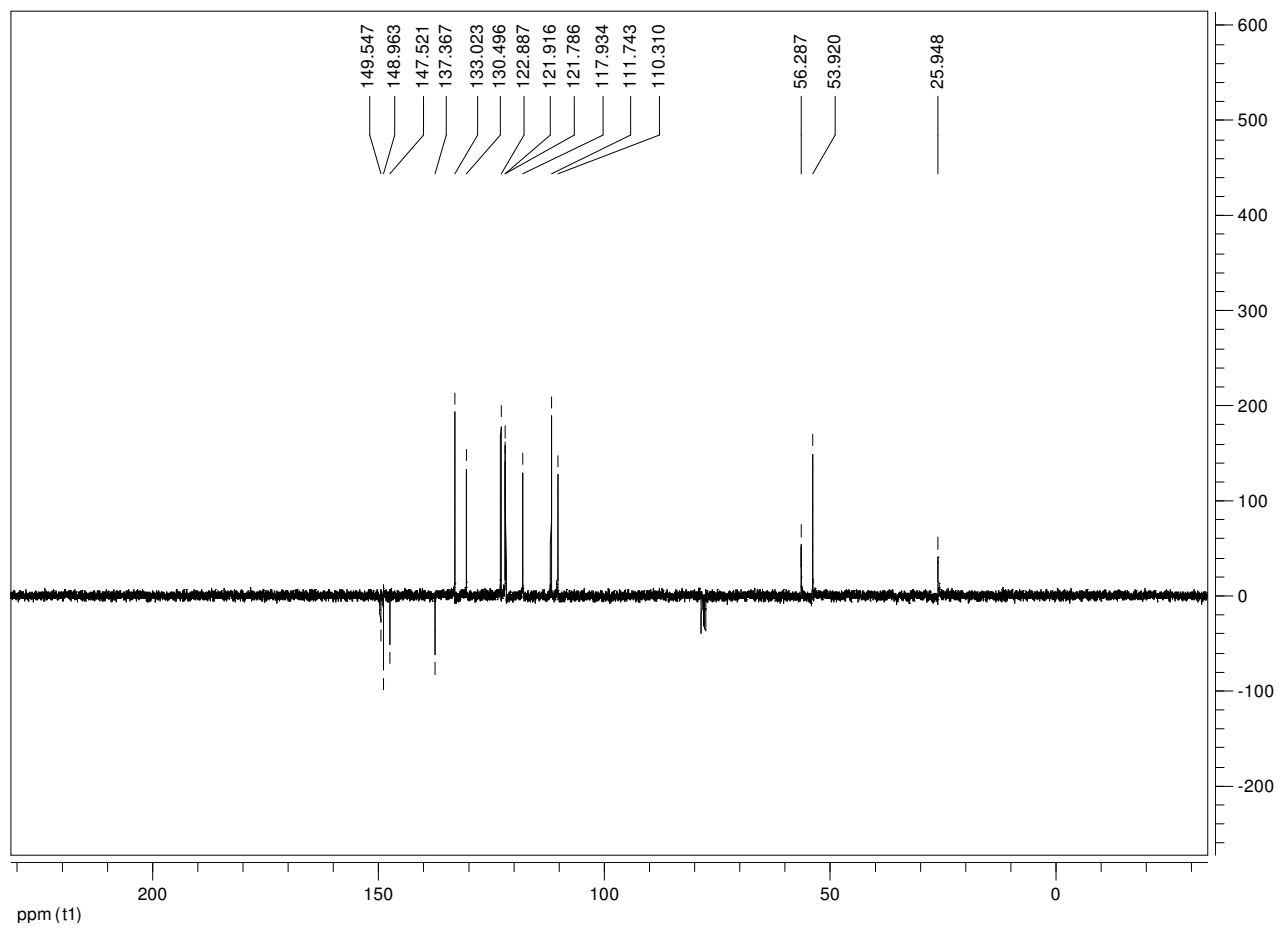
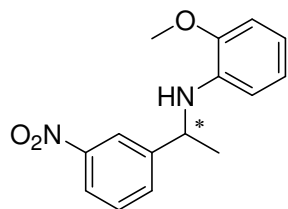
(2-Methoxy-phenyl)-[1-(3-nitro-phenyl)-ethylidene]-amine (13a), ^{13}C



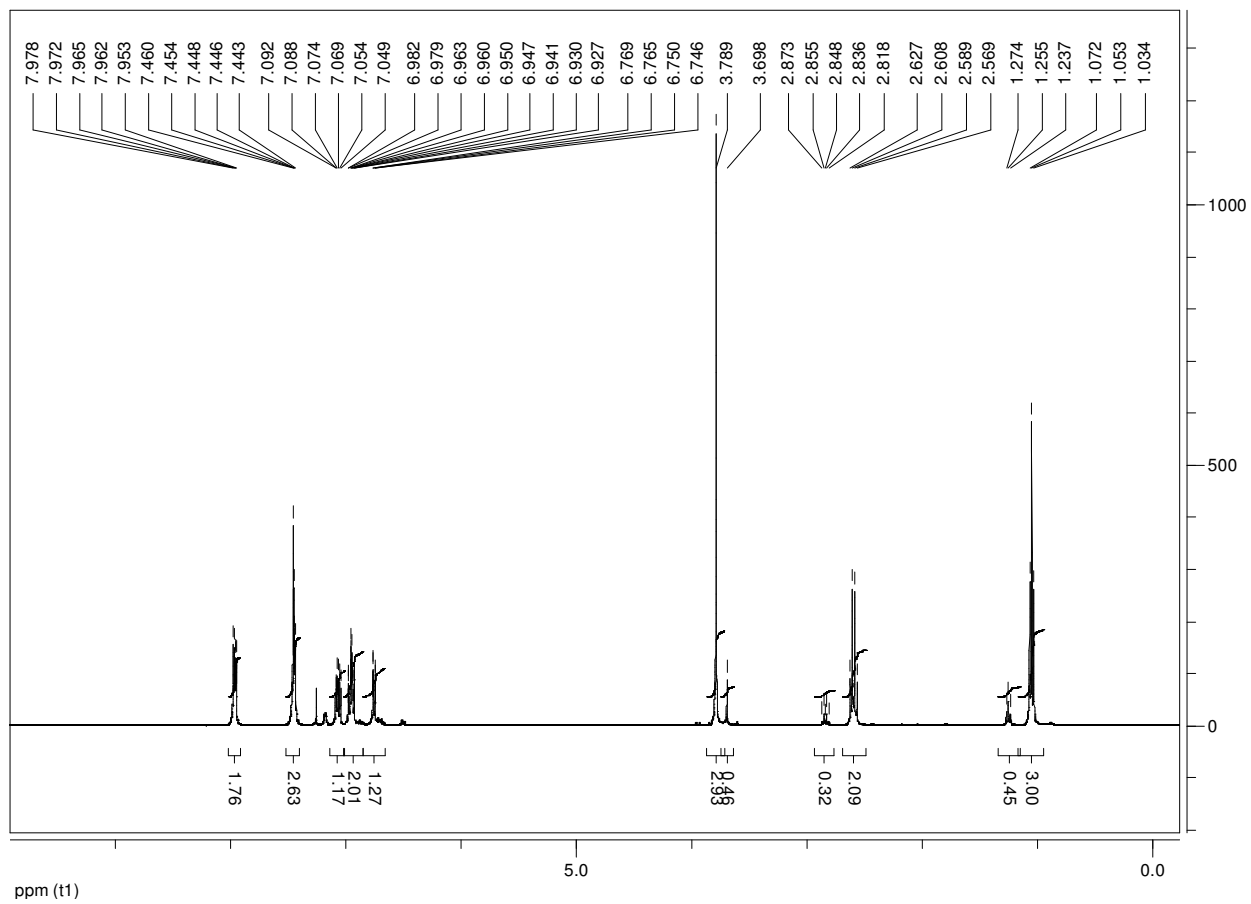
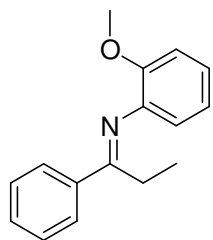
(-)-(2-Methoxy-phenyl)-[1-(3-nitro-phenyl)-ethyl]-amine (13b), ¹H



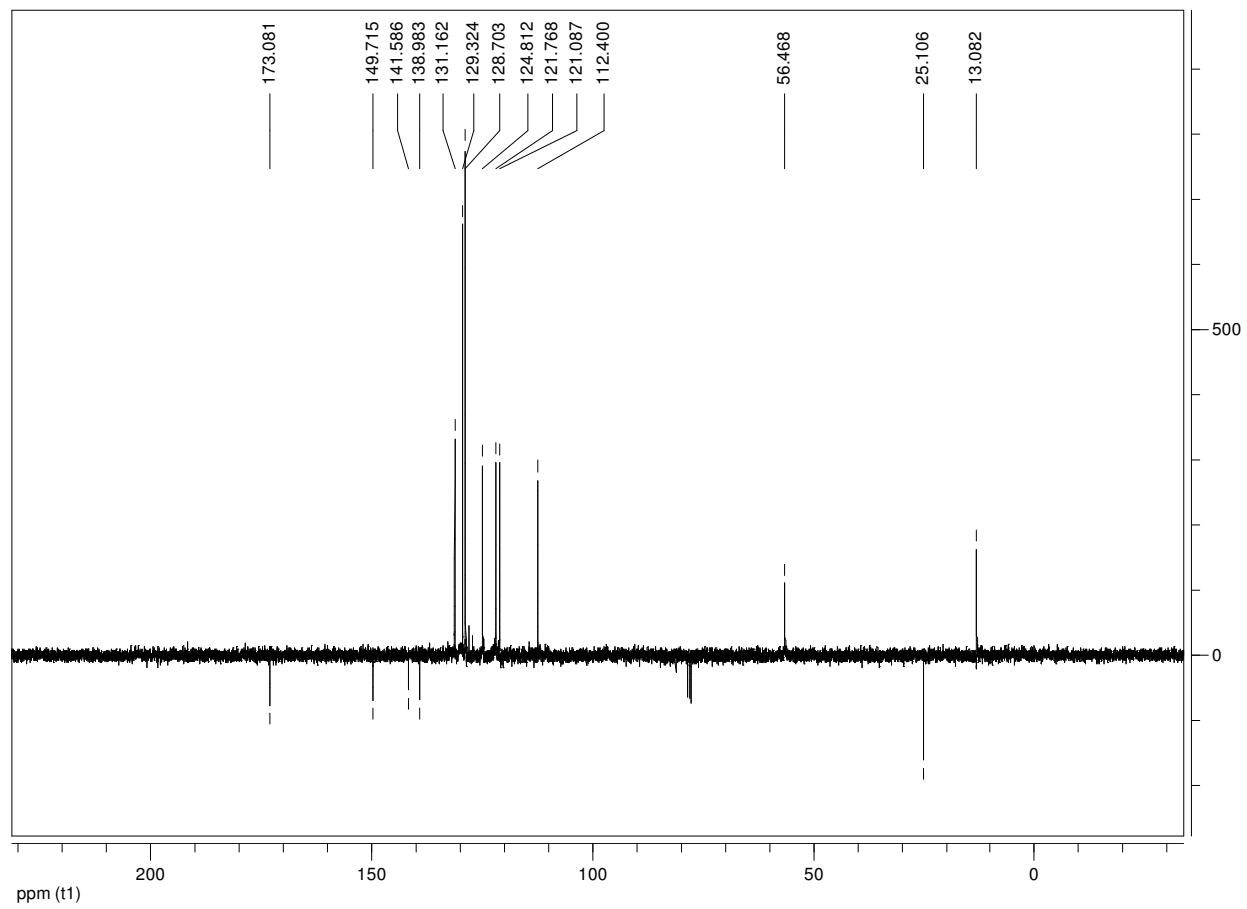
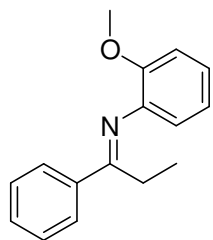
(-)-(2-Methoxy-phenyl)-[1-(3-nitro-phenyl)-ethyl]-amine (13b), ^{13}C



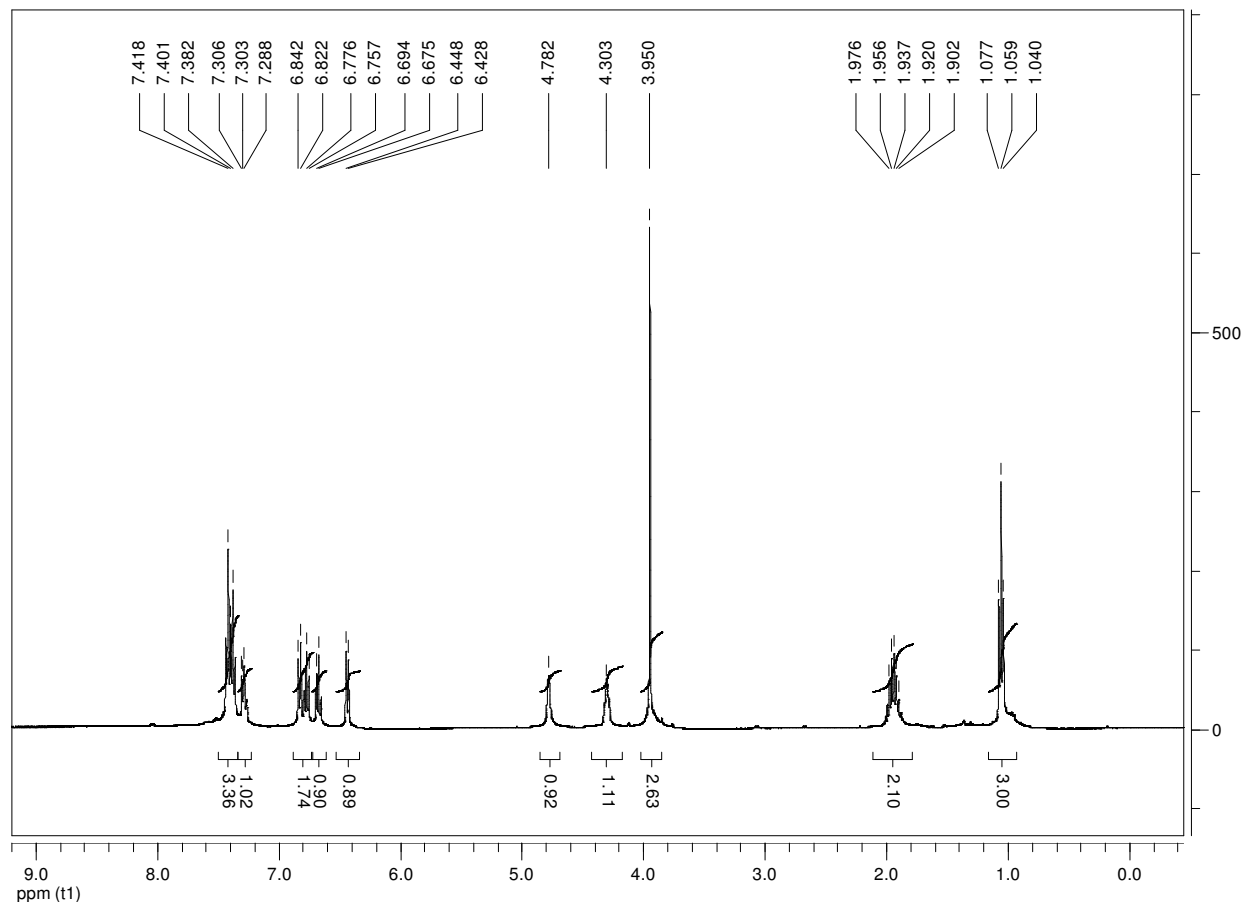
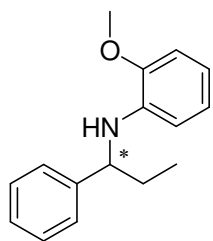
(2-Methoxy-phenyl)-(1-phenyl-propylidene)-amine (14a), ¹H



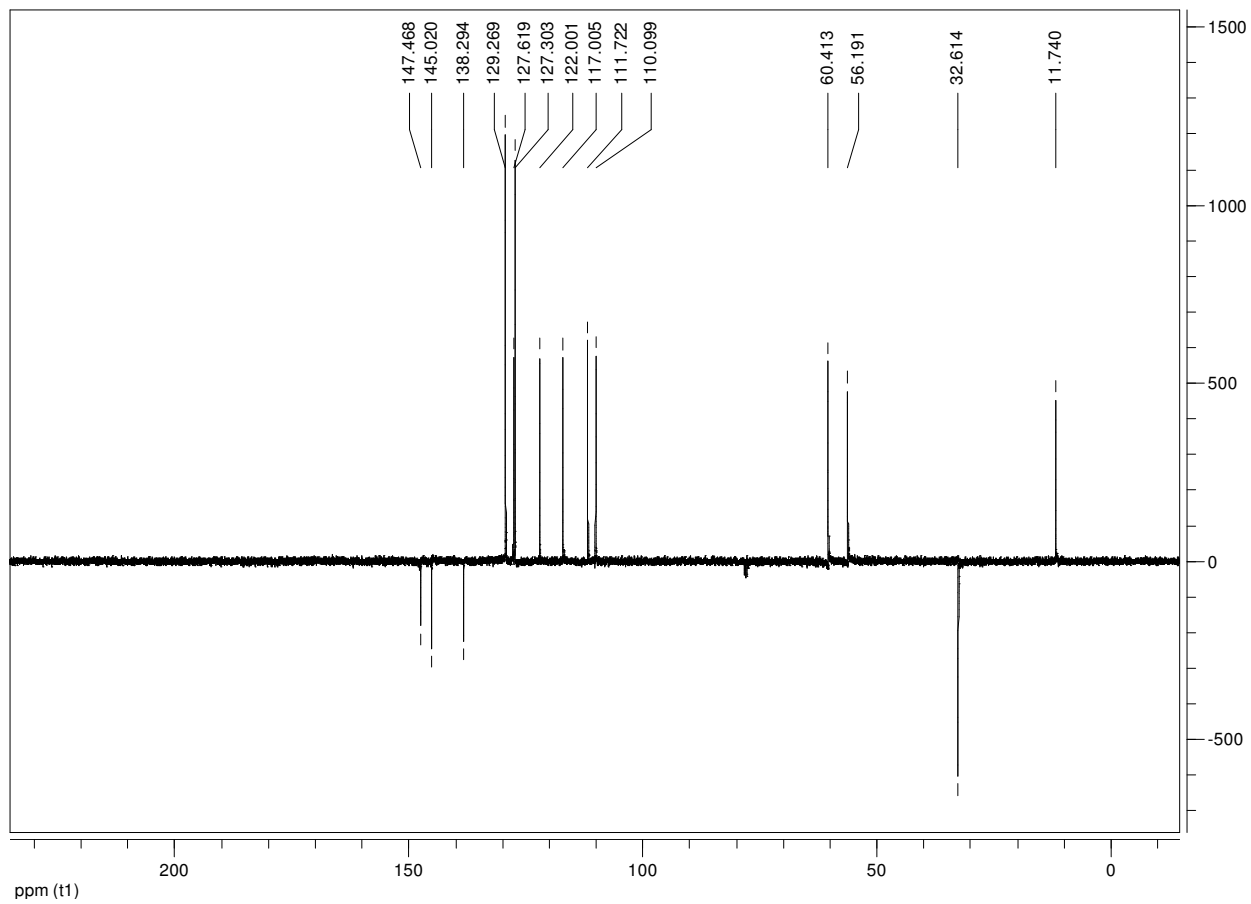
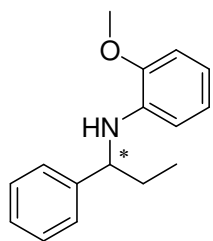
(2-Methoxy-phenyl)-(1-phenyl-propylidene)-amine (14a), ¹³C



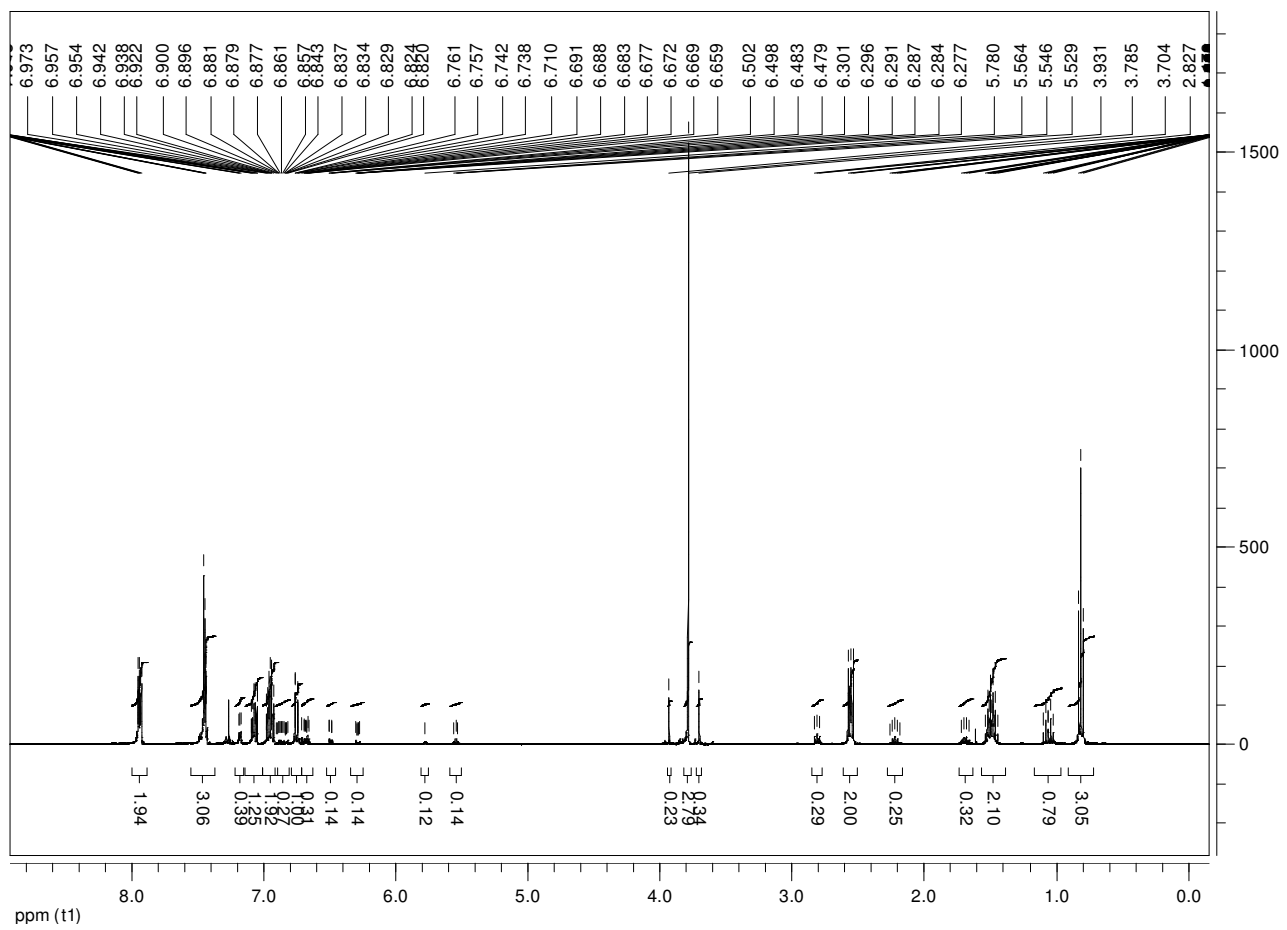
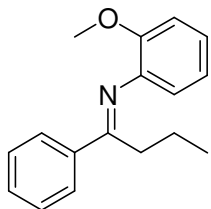
(-)-(2-Methoxy-phenyl)-(1-phenyl-propyl)-amine (14b), ¹H



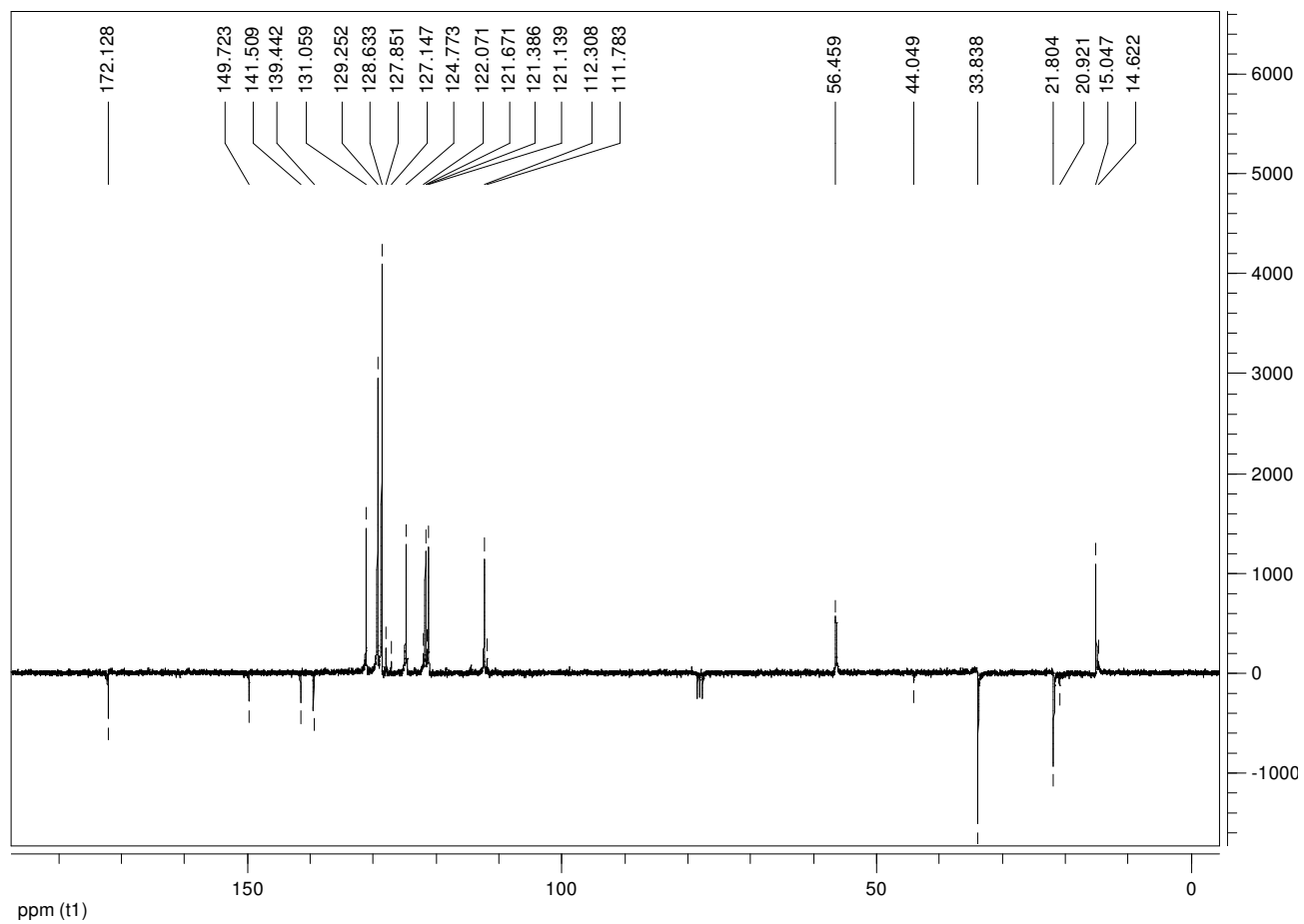
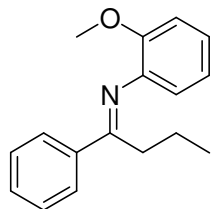
(-)-(2-Methoxy-phenyl)-(1-phenyl-propyl)-amine (14b), ¹³C



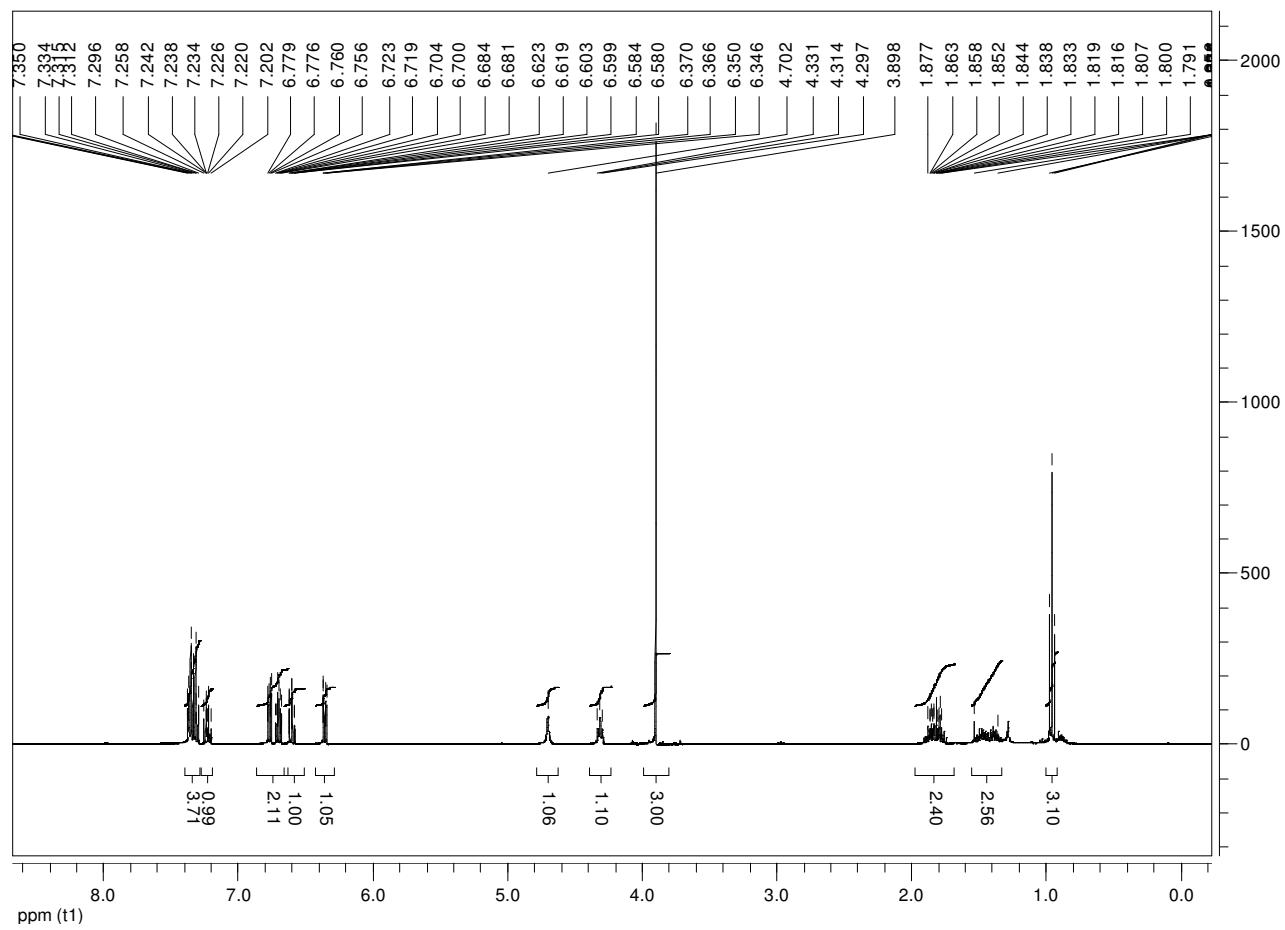
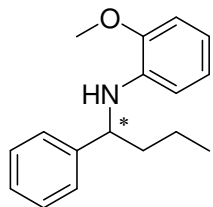
(2-Methoxy-phenyl)-(1-phenyl-butylidene)-amine (15a), ¹H



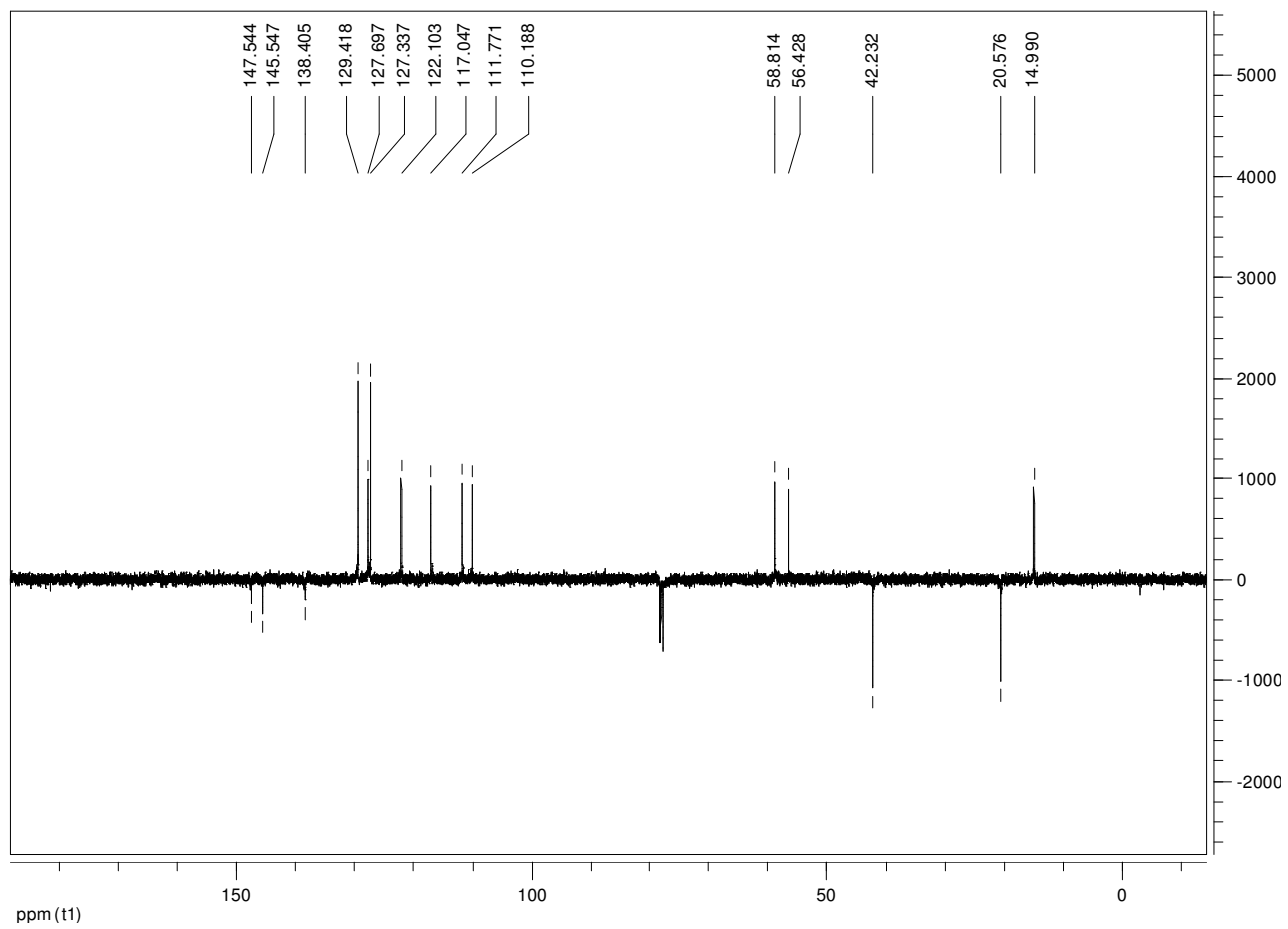
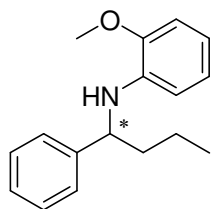
(2-Methoxy-phenyl)-(1-phenyl-butylidene)-amine (15a), ^{13}C



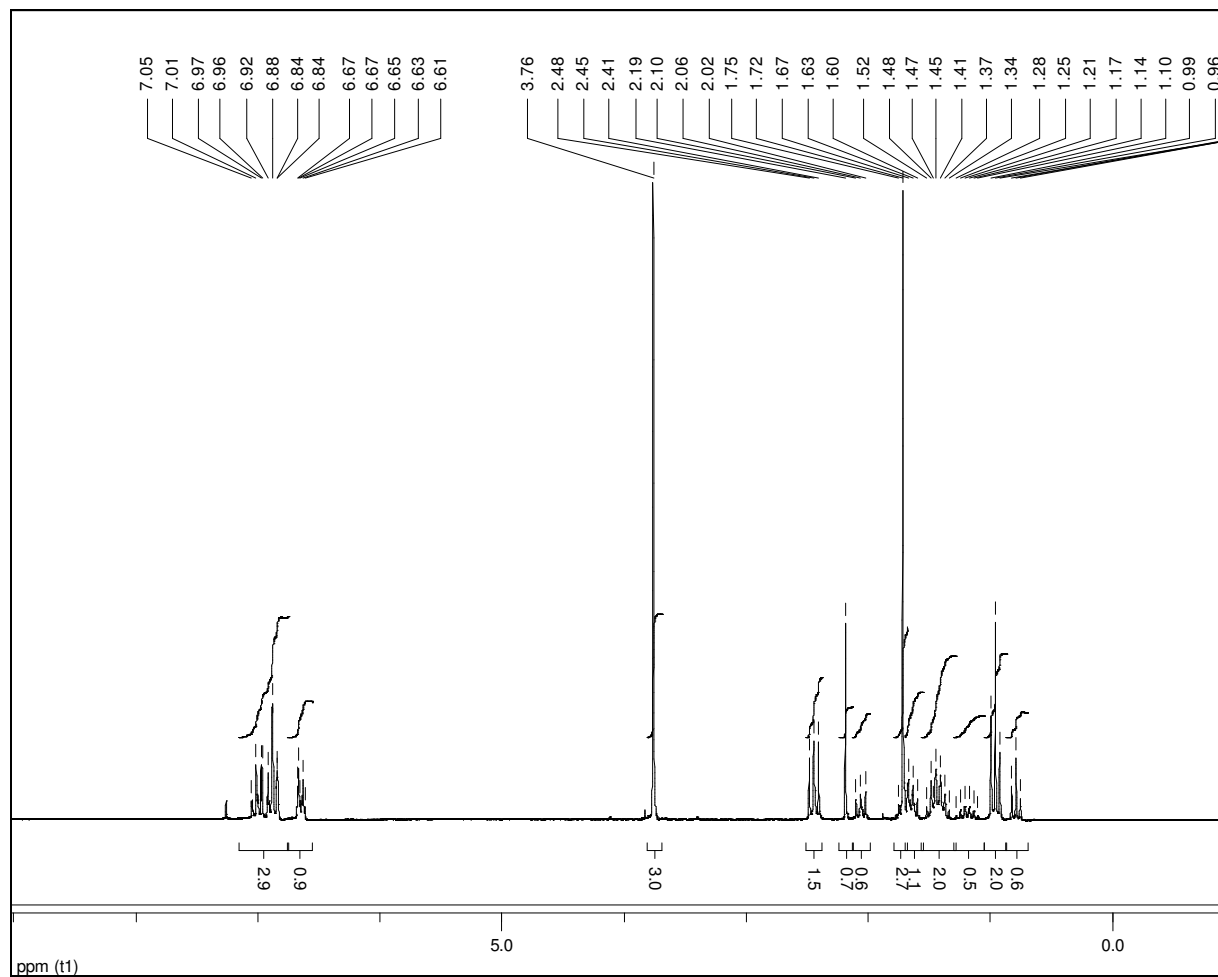
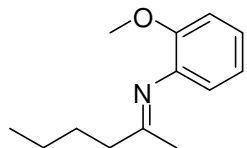
(-)-(2-Methoxy-phenyl)-(1-phenyl-butyl)-amine (15b), ¹H



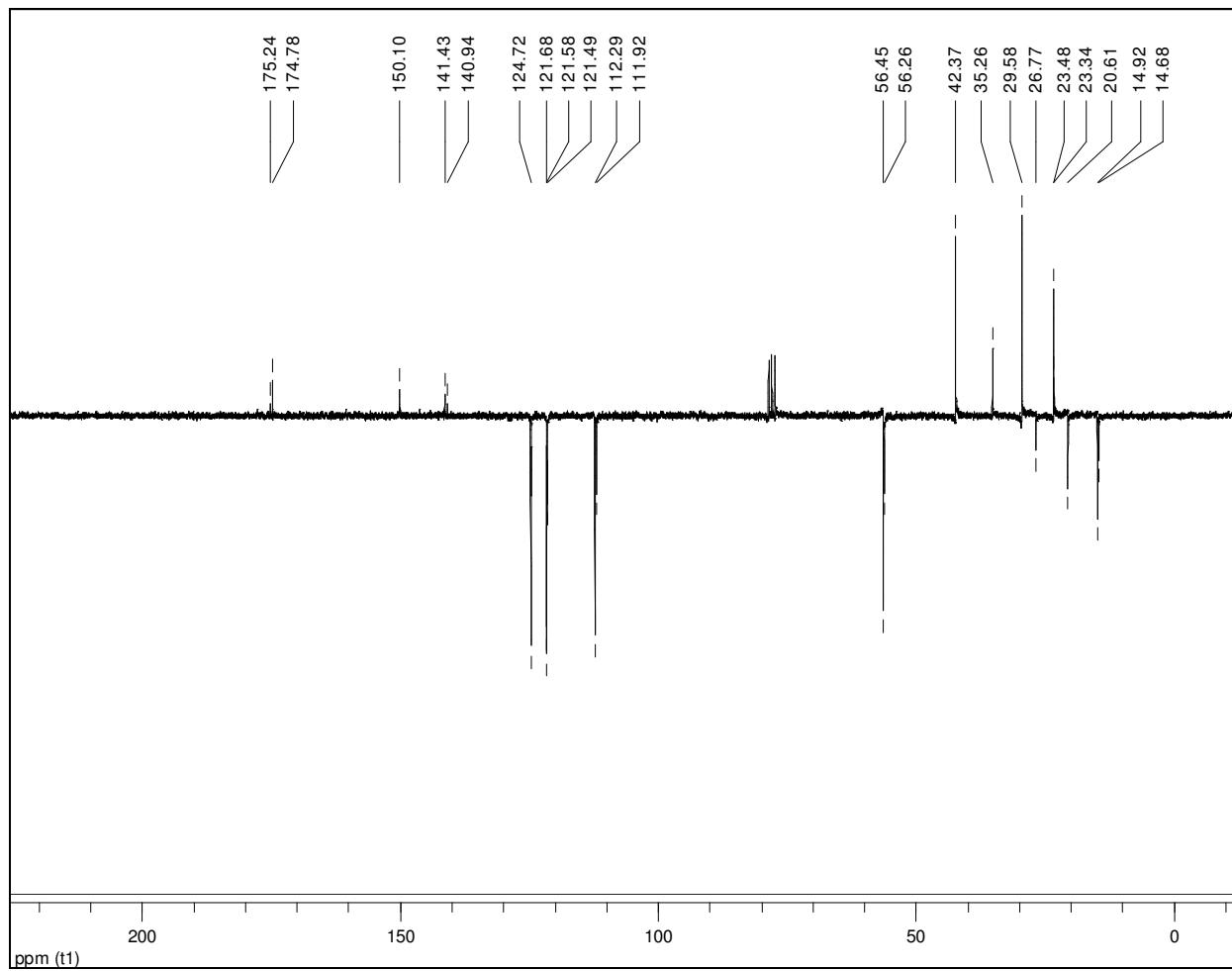
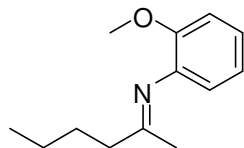
(-)-(2-Methoxy-phenyl)-(1-phenyl-butyl)-amine (15b), ¹³C



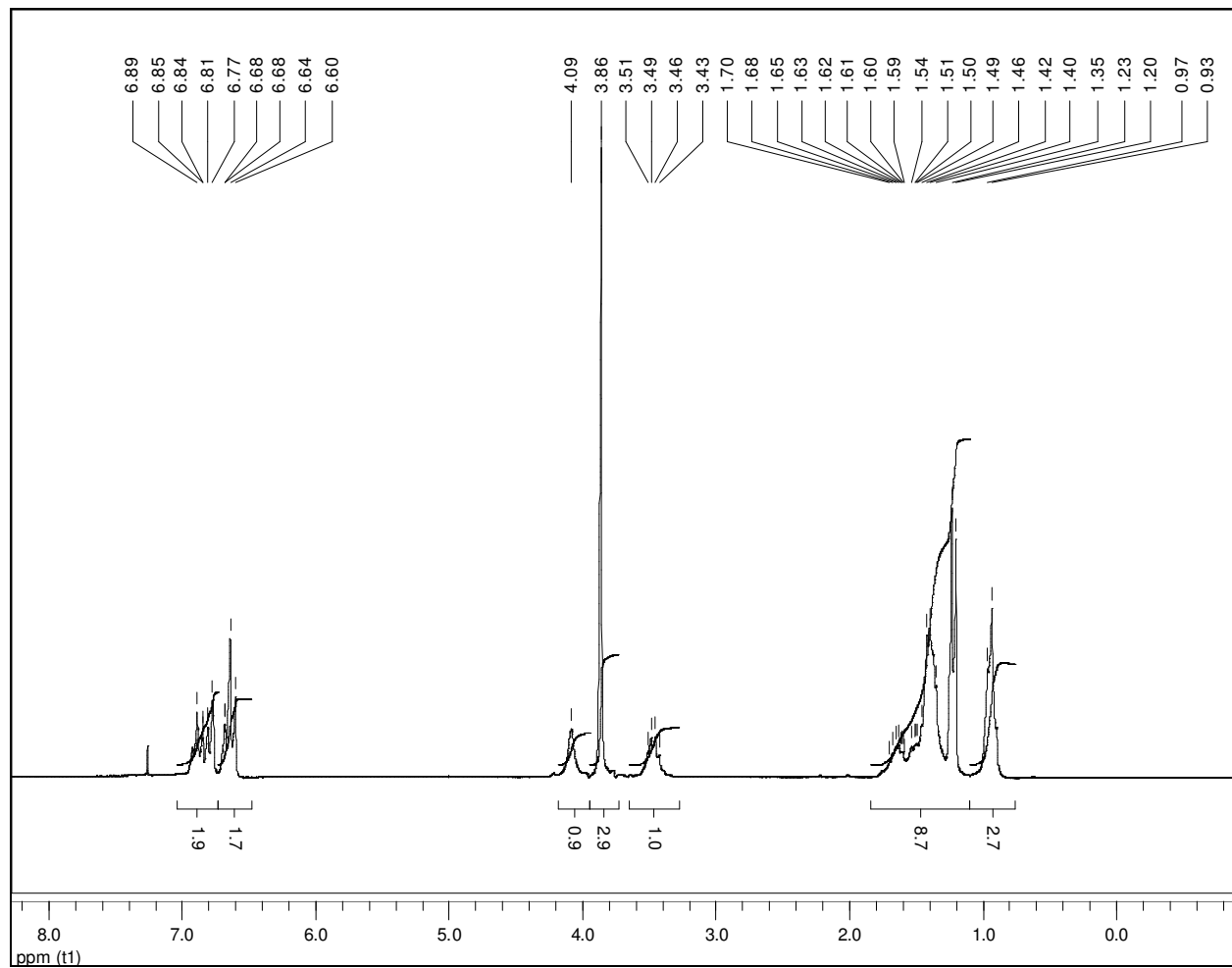
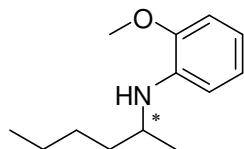
N-(hexan-2-ylidene)-2-methoxyaniline (16a), ¹H



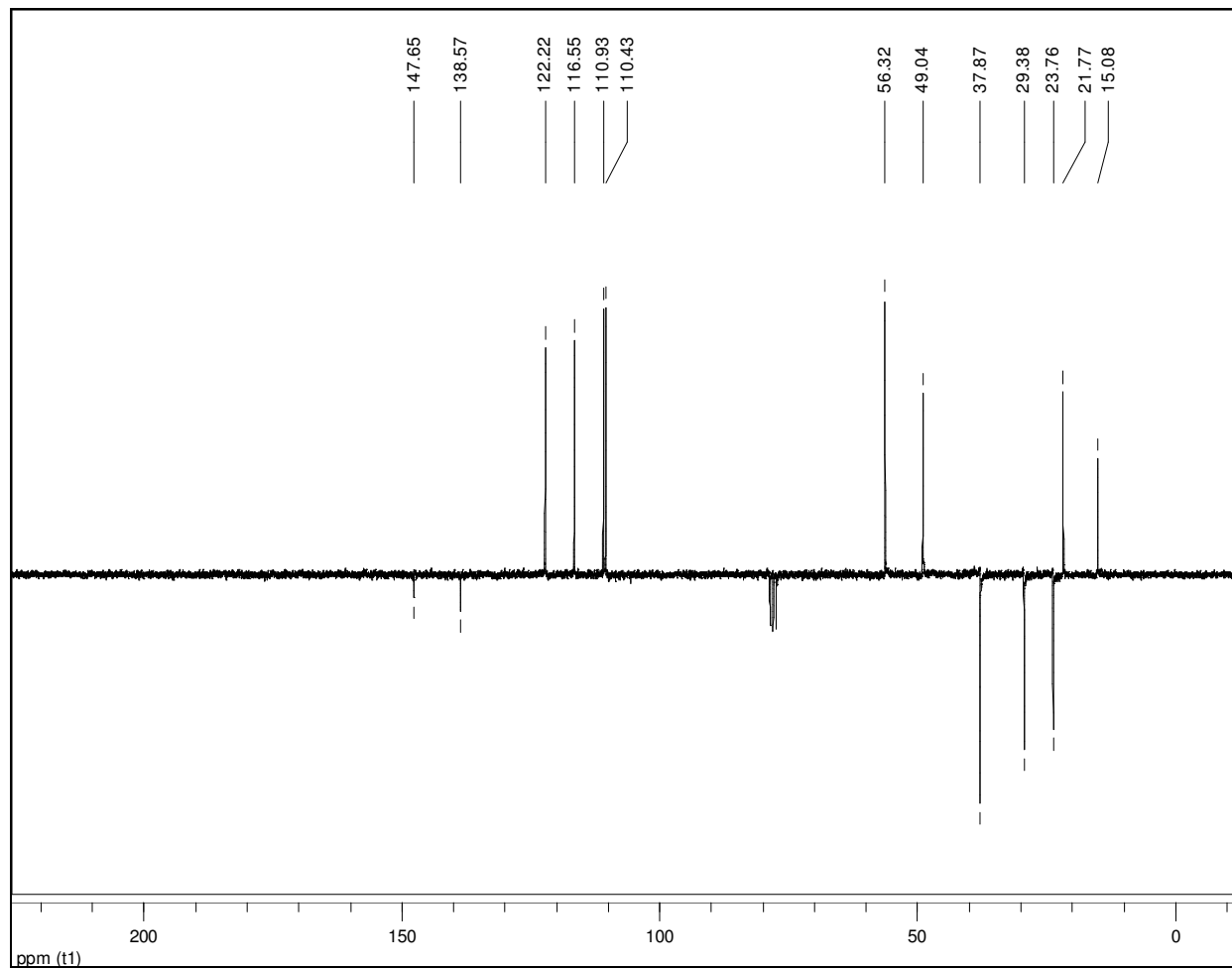
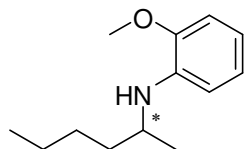
N-(hexan-2-ylidene)-2-methoxyaniline (16a), ¹³C



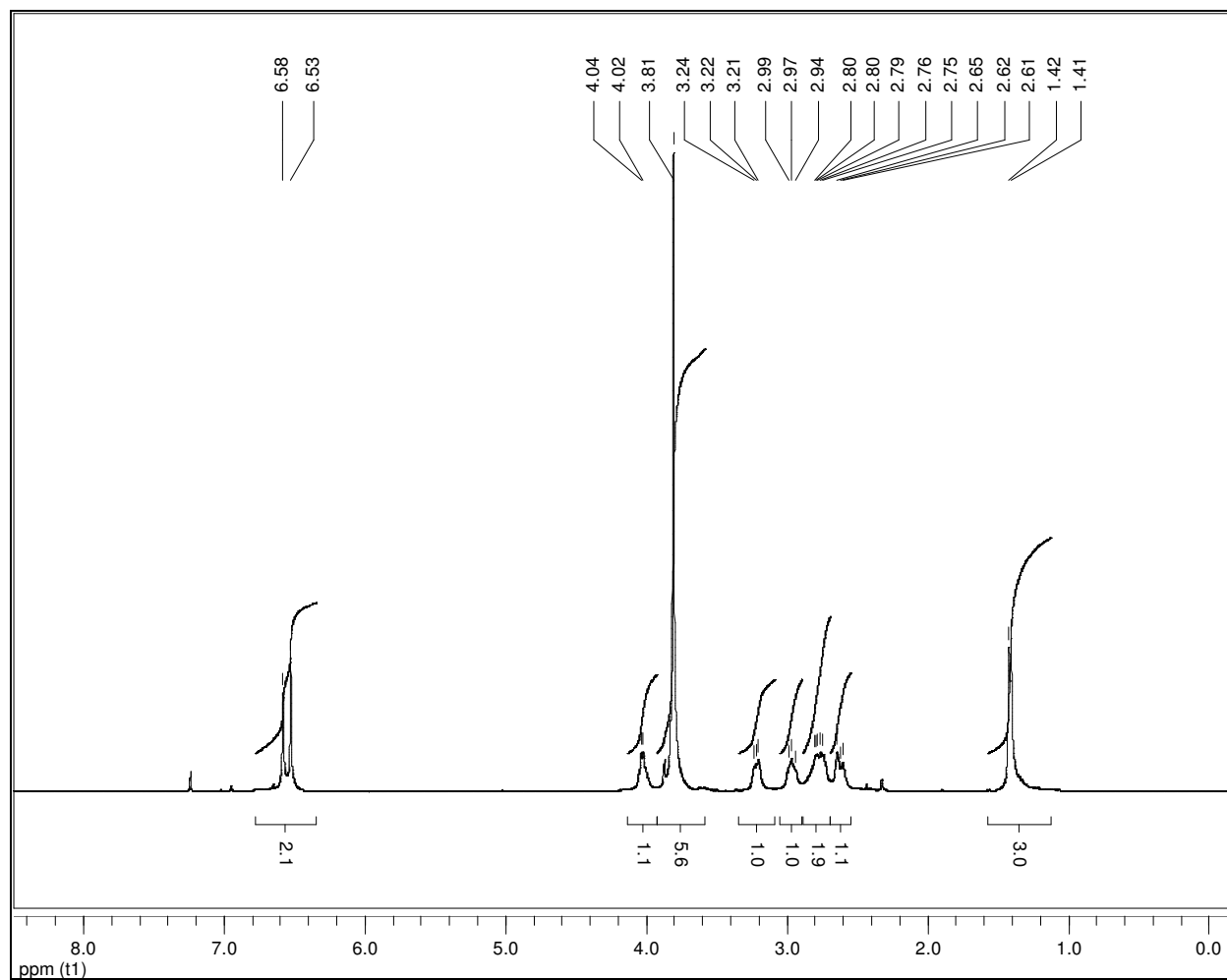
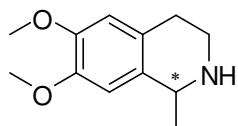
***N*-(hexan-2-yl)-2-methoxyaniline (16b), ¹H**



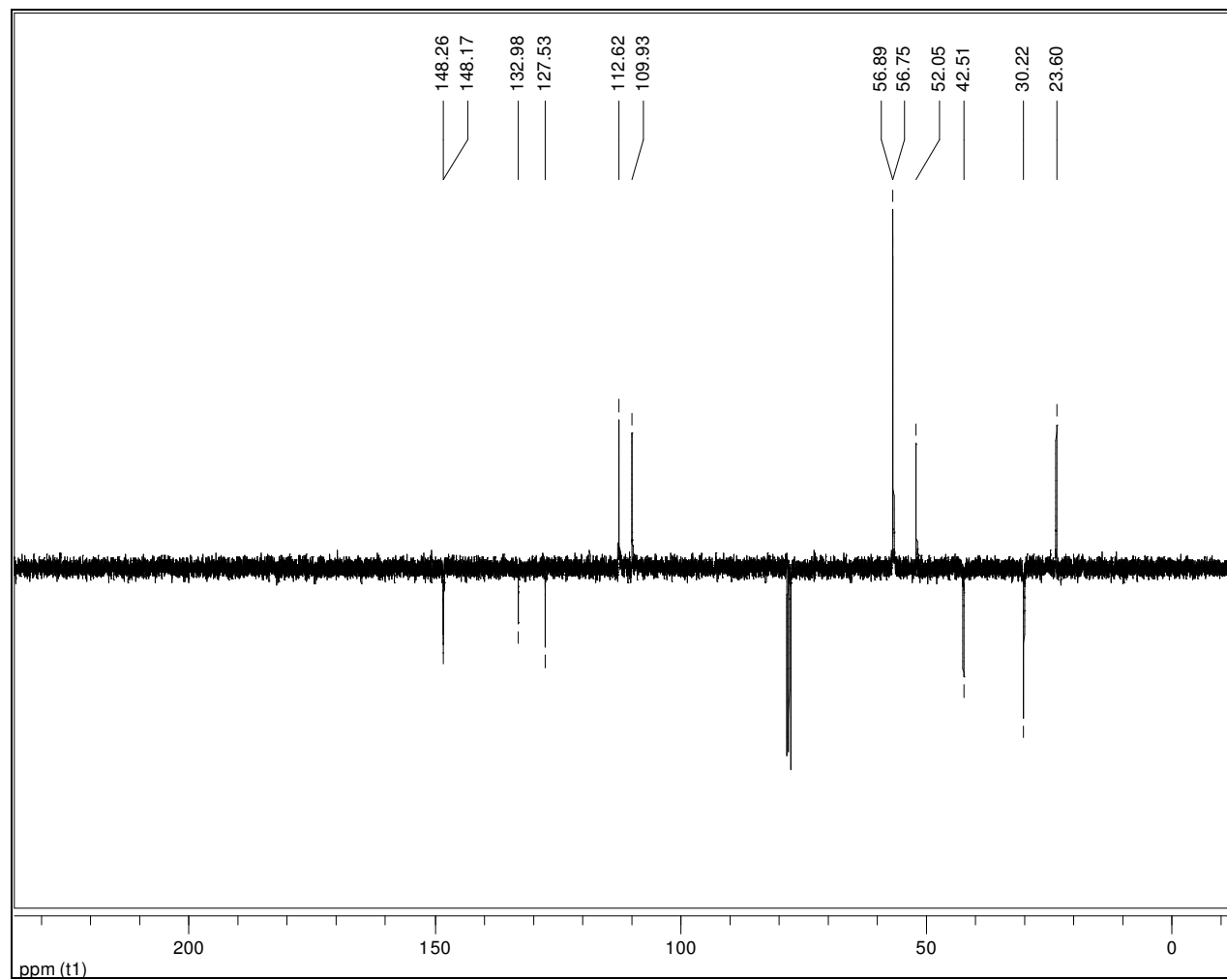
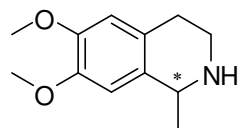
N-(hexan-2-yl)-2-methoxyaniline (16b), ¹³C



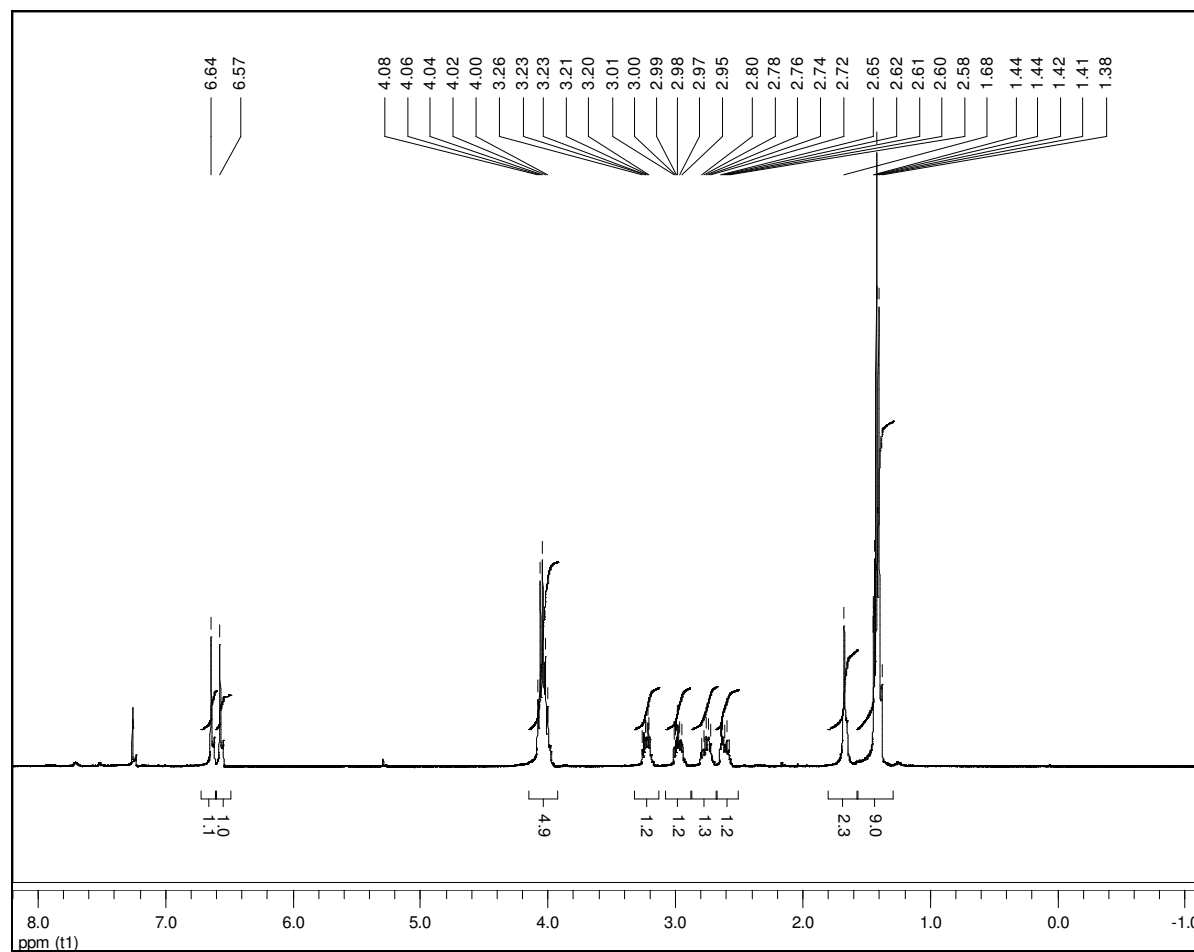
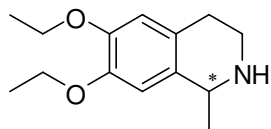
6,7-dimethoxy-1-methyl-1,2,3,4-tetrahydroisoquinoline (17b), ¹H



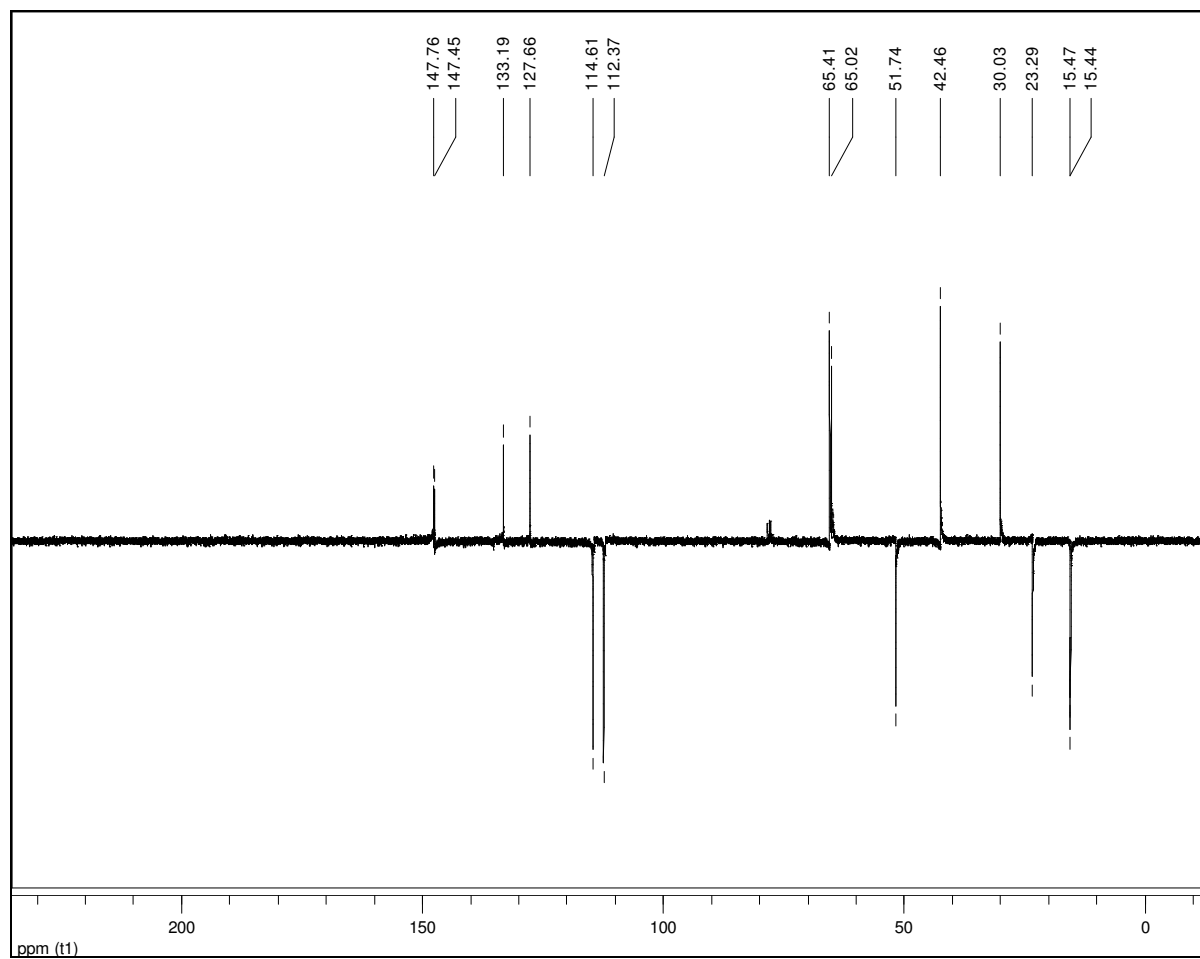
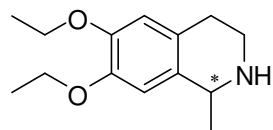
6,7-dimethoxy-1-methyl-1,2,3,4-tetrahydroisoquinoline (17b), ^{13}C



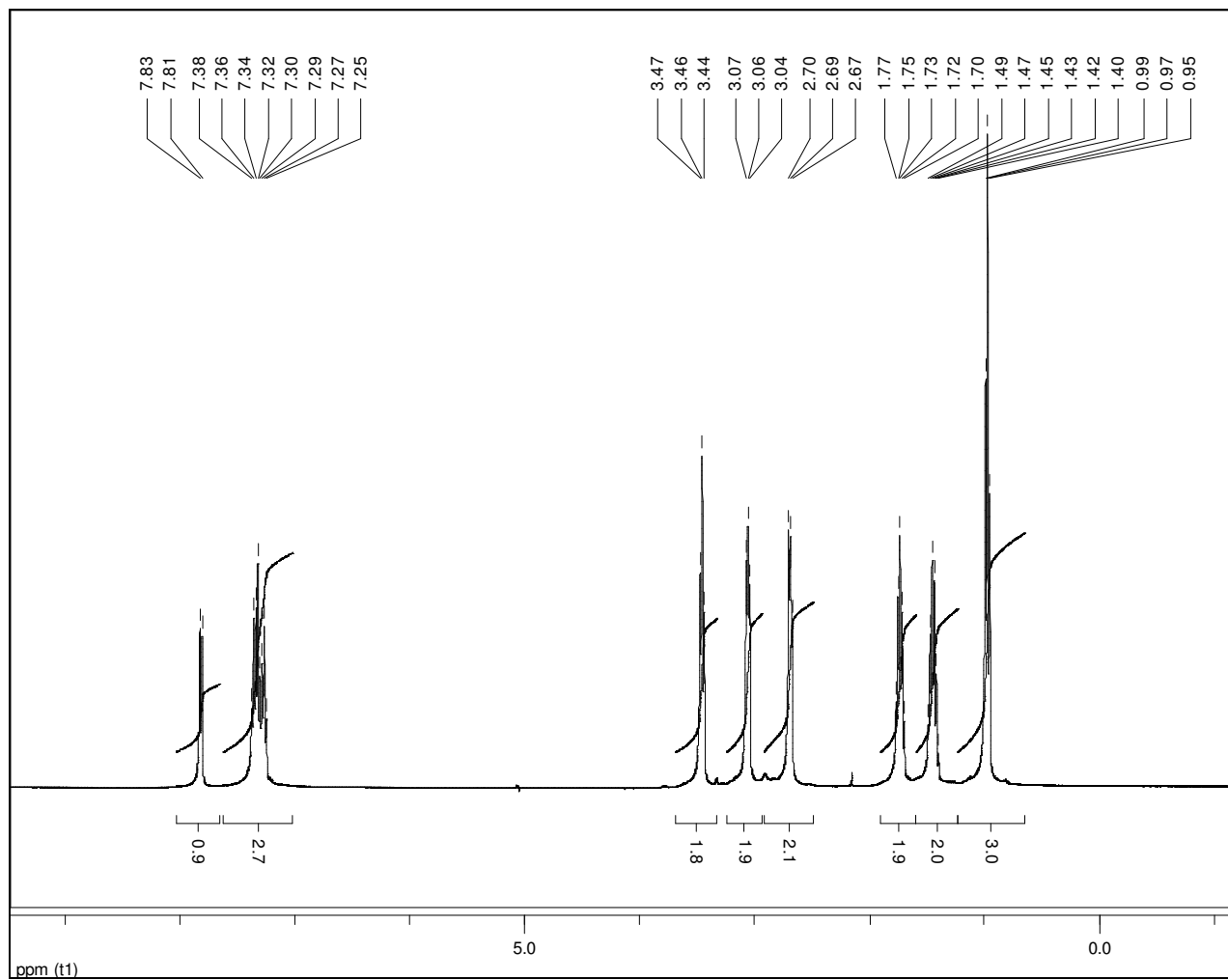
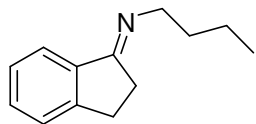
6,7-diethoxy-1-methyl-1,2,3,4-tetrahydroisoquinoline (18b), ^1H



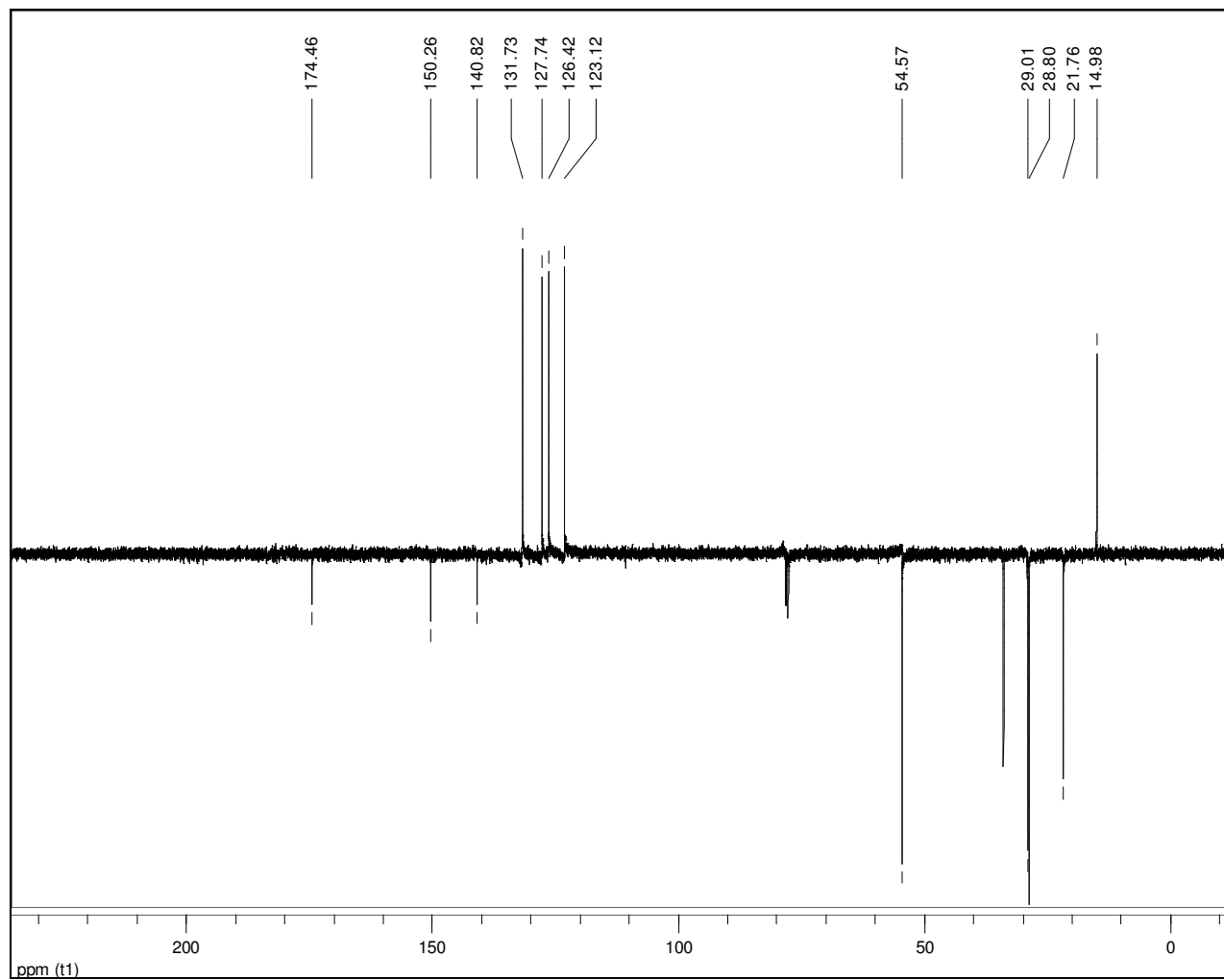
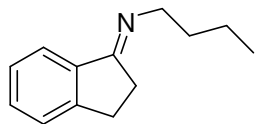
6,7-diethoxy-1-methyl-1,2,3,4-tetrahydroisoquinoline (18b), ^{13}C



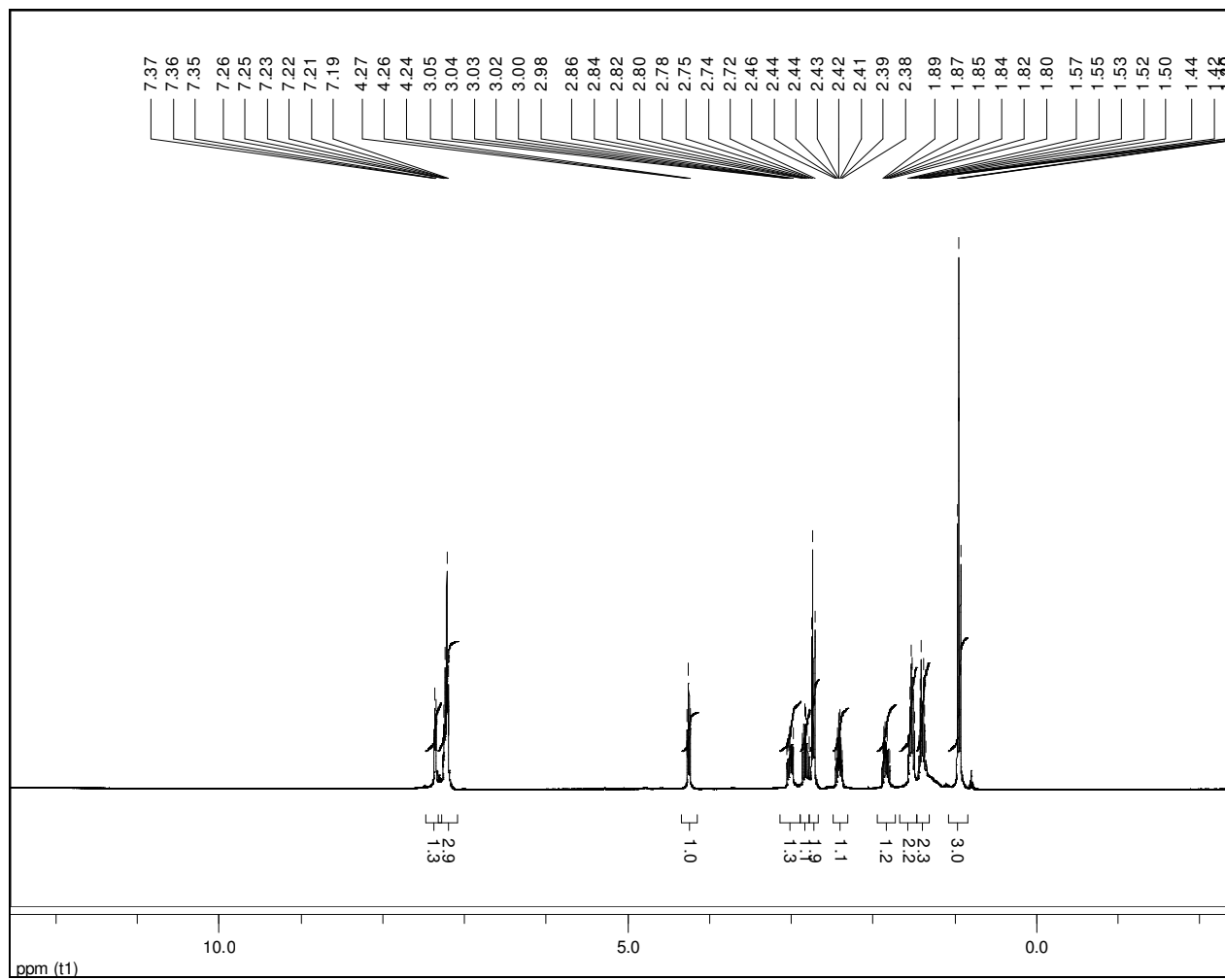
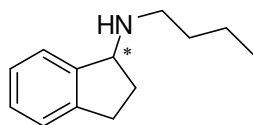
***N*-(2,3-dihydro-1*H*-inden-1-ylidene)butan-1-amine (19a), ¹H**



N-(2,3-dihydro-1*H*-inden-1-ylidene)butan-1-amine (19a), ¹³C



***N*-butyl-2,3-dihydro-1*H*-inden-1-amine (19b), ¹H**



N-butyl-2,3-dihydro-1*H*-inden-1-amine (19b), ¹³C

