Supporting Information for

One-pot transformation of alkynes into alcohols and amines with formic acid

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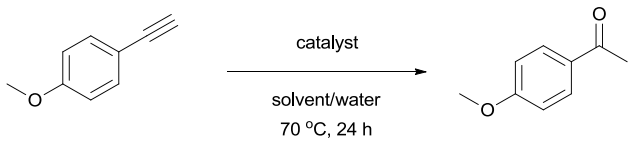
Contents

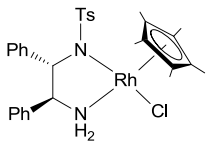
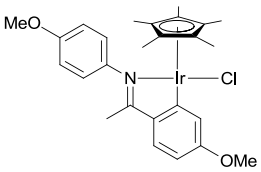
1. General information

Unless otherwise specified, all reagents were obtained commercially and used without further purification. MeOH was dried over magnesium and distilled prior to use. Dichloromethane (DCM) was dried over CaH_2 and distilled prior to use. NMR spectra were recorded on a Brucker 300 Hz or 400 Hz NMR spectrometer with TMS as the internal standard at ambient temperature. Imines were prepared according to the literature.[1] Complexes **1**[2,3] and **3**[4,5] were prepared according to the literature. pH was measured with a Sartorius PB-10 pH meter at 25 ^{o}C. Enantiomeric excess (ee) was determined using a SHIMADZU LC-2010A HT HPLC with a Chiralcel OD-H or AD-H column.

2. Transfer hydrogenation catalysts for alkyne hydration reaction

Table S1 Alkyne hydration catalysed by transfer hydrogenation catalysts[a]



Entry	Catalyst	Yield (%)[b]
1		NR
2		NR
3	$[RuCl_2(p\text{-cymene})]_2$	36
4	$[Cp^*RhCl_2]_2$	41
5	$[Cp^*IrCl_2]_2$	60
6[c]	$[Cp^*IrCl_2]_2$	75

[a] Reaction conditions: Alkyne (2 mmol), MeOH/H_2O (0.6/1.4 ml), catalyst (0.005 mmol), 70 ^{o}C, 24 h. [b] Isolated yield. [c] S/C = 200

3. Typical procedure for transforming alkynes to achiral alcohols

A tube was charged with a magnetic stir bar and phenylacetylene (3 mmol). HCOOH (99%) was introduced into the tube with a syringe (3 mL). The resulting mixture was bubbled with argon for 15 min. The tube was then sealed and the mixture was stirred at 100 ^{o}C for 0.5 h. Upon cooling to room temperature, the tube was opened and 5.6 mL of HCOONa solution (15.5 mol/L) was added to adjust the solution pH to 3.5. After addition of catalyst **1** (0.003 mmol), the resulting mixture was stirred at 80 ℃ for 6 h. After cooling to room temperature, the reaction mixture was transferred to a beaker containing 30 mL MeOH and the resulting mixture was basified with KOH (pH = 9~10) and stirred for 30 min to hydrolyse any formyl ester product. MeOH was then removed from the mixture under vacuum and the aqueous solution was extracted with ethyl acetate. The organic phase was washed with brine and dried over anhydrous Na_2SO_4. After removing ethyl acetate under vacuum, the residue was purified by flash chromatography [petroleum ether (m.p = 60~90 ^{o}C): ethyl acetate = 8:1] to afford 1-phenylethanol in 80% yield.

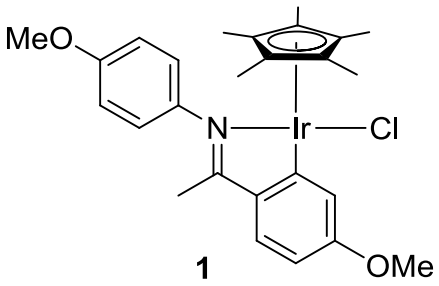
4. Typical procedure for transforming alkynes to chiral alcohols

A tube was charged with a magnetic stir bar and phenylacetylene (3 mmol). HCOOH (99%) was introduced into the tube with a syringe (3 mL). The resulting mixture was bubbled with argon for 15 min. The tube was then sealed and the mixture was stirred at 100 ^{o}C for 0.5 h. Upon cooling to room temperature, the tube was opened and NaOH solution (17 mol/L) was added to adjust the solution pH to 7. After addition of catalyst **3** (0.015 mmol), the resulting mixture was stirred at 40 ℃ for 3 h. After cooling to room temperature, the reaction mixture was extracted with ethyl acetate. The organic phase was washed with brine and dried over anhydrous Na_2SO_4. After removing ethyl acetate under vacuum, the residue was purified by flash chromatography [petroleum ether (m.p = 60~90 ^{o}C): ethyl acetate = 8:1] to afford 1-phenylethanol in 87% yield. The enantiomeric excess of product was determined by chiral HPLC analysis: Chiralcel OD-H (hexane/*i*PrOH = 97/3, flow rate: 0.5 mL/min), t_R (major) = 25.67 min, t_S (minor) = 35.55 min, 99% ee.

5. Typical procedure for transforming alkynes to amines

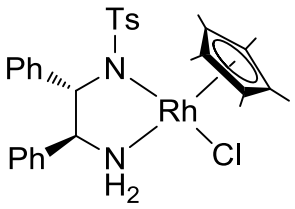
A tube was charged with a magnetic stir bar and phenylacetylene (3 mmol). HCOOH (99%) was introduced into the tube with a syringe (3 mL). The resulting mixture was bubbled with argon for 15 min. The tube was then sealed and the mixture was stirred at 100 ^{o}C for 0.5 h. Upon cooling to room temperature, the tube was opened and 4.7 mL of NaOH solution (17 mol/L) was added to adjust the solution pH to 4.8. After addition of catalyst **1** (0.006 mmol) and *p*-anisidine (6 mmol), the resulting mixture was stirred at 80 ℃ for 3.5 h. After cooling to room temperature, a HCl solution (3 mol/L) was added to adjust solution pH to around 2-3 and the mixture was stirred at room temperature for 10 min to hydrolysis any imines. The resulting mixture was then basified with NaOH solution (6 mol/L) to pH around 9-10 and extracted with ethyl acetate. The organic phase was washed with brine and dried over anhydrous Na_2SO_4. After removing ethyl acetate under vacuum, the residue was purified by flash chromatography [petroleum ether (m.p = 60~90 ^{o}C): ethyl acetate = 40:1] to afford 4-methoxy-*N*-(1-phenylethyl)aniline in 75% yield.

6. Characterization data for catalysts and products



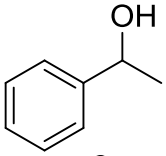
1

Catalyst 1:[2,3] Yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.45 (d, *J* = 8.8 Hz, 1H), 7.35 (d, *J* = 2.4 Hz, 1H), 6.94-6.92 (m, 2H), 6.58 (dd, *J* = 8.8 Hz, 2.4 Hz, 1H), 3.91 (s, 3H), 3.85 (s, 3H), 2.38 (s, 3H) ,1.44 (s, 15H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 180.1, 170.4, 162.1, 157.6, 144.3, 141.3, 130.0, 124.7, 119.2, 113.6, 107.8, 89.0, 55.5, 55.0, 16.8, 8.6; HRMS for $C_{26}H_{31}ClIrNO_2$ $[M\text{-}Cl]^+$: m/z calc.: 582.1984. Found: 582.1979.



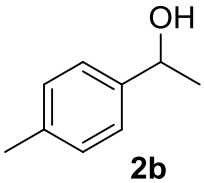
3

Catalyst 3:[4,5] Orange solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.43 (d, *J* = 8.0 Hz, 2H), 7.16-7.08 (m, 3H), 6.90-6.78 (m, 7H), 6.66 (d, *J* = 7.2 Hz, 2H), 3.98 (d, *J* = 10.4 Hz, 2H), 3.71 (t, *J* = 11.6 Hz, 1H), 3.32 (d, *J* = 8.4 Hz, 1H), 2.22 (s, 3H), 1.86 (s, 15H); ^{13}C NMR ($CDCl_3$,100 MHz) δ (ppm): 140.8, 139.8, 139.4, 139.3, 128.6, 128.5, 128.5, 128.4, 127.8, 127.1, 127.0, 126.5, 94.1, 71.9, 69.5, 21.2, 9.7.



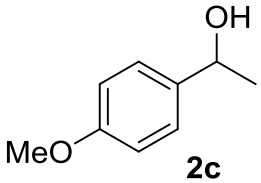
2a

1-Phenylethanol:[6] 80% yield, colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.33-7.22 (m, 5H), 4.82 (q, *J* = 6.4 Hz, 1H), 2.40 (brs, 1H), 1.44 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 145.9, 128.5, 127.5, 125.5, 70.4, 25.2; MS (CI) for $C_8H_{10}O$ $[M+H]^+$: m/z 123 (100%).



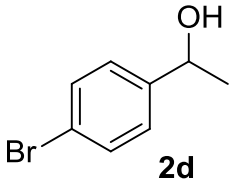
2b

1-(*p*-Tolyl)ethanol:[6] 85% yield, colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.26 (d, *J* = 6.0 Hz, 2H), 7.16 (d, *J* = 5.7 Hz, 2H), 4.86 (q, *J* = 4.8 Hz, 3H), 2.34 (s, 3H), 1.48 (d, *J* = 4.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 142.9, 137.1, 129.2, 125.4, 70.2, 25.1, 21.1; MS (CI) for $C_9H_{12}O$ $[M+H]^+$: m/z 137 (100%).



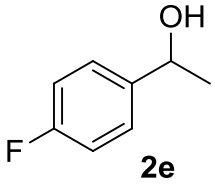
2c

1-(4-Methoxyphenyl)ethanol:[6] 60% yield, colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.26 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.79 (q, *J* = 6.4 Hz, 1H), , 3.77 (s, 3H), 1.44 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 159.0, 138.1, 126.7, 113.8, 69.9, 55.3, 25.0; MS (CI) for $C_9H_{12}O_2$ $[M+H]^+$: m/z 153 (100%).



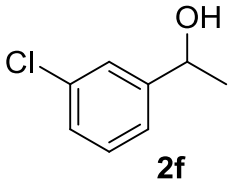
2d

1-(4-Bromophenyl)ethanol:[6] 87% yield, colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.45 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 2H), 4.83 (q, *J* = 5.7 Hz, 1H), 2.15 (brs, 1H), 1.44 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 144.8, 131.5, 127.2, 121.1, 69.7, 25.2; MS (CI) for C_8H_9BrO $[M+H]^+$: m/z 201 (100%).



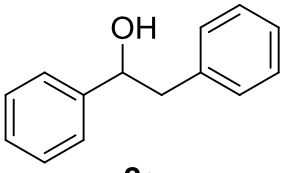
2e

1-(4-Fluorophenyl)ethanol:[6] 89% yield, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.29 (d, *J* = 19.5 Hz, 2H), 7.02 (t, J = 7.6 Hz, 2H), 4.87 (d, J = 6.0 Hz, 1H), 1.98 (s, 1H), 1.46 (d, J = 6.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 162.1 (d, $^{1}J_{C\text{-}F}$ = 182.6 Hz), 141.6 (d, $^{4}J_{C\text{-}F}$ = 2.3 Hz), 127.1 (d, $^{3}J_{C\text{-}F}$ = 6.0 Hz), 115.2 (d, $^{2}J_{C\text{-}F}$ = 15.9 Hz), 69.6 (d, $^{5}J_{C\text{-}F}$ = 2.1 Hz) 25.2; MS(EI) for C_8H_9FO $[M+H]^+$: m/z 141.



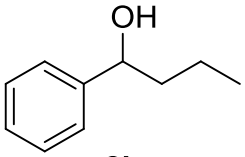
2f

1-(3-Chlorophenyl)ethanol:[7] 87% yield, colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.32 (s, 1H), 7.24-7.17 (m, 3H), 4.81 (q, *J* = 4.5 Hz, 1H), 2.39 (brs, 1H), 1.43 (d, *J* = 3.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 147.9, 134.4, 129.8, 127.5, 125.7, 123.5, 69.8, 25.2; MS (CI) for C_8H_9ClO $[M+H]^+$: m/z 157 (100%).



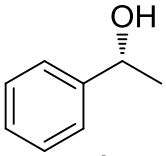
2g

1,2-Diphenylethanol: 79% yield, white solid; m.p. = 60-61 ^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.35-7.17 (m, 10H), 4.88 (s, 1H), 3.01 (q, *J* = 8.4 Hz, 2H), 1.98 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 143.8, 138.1, 129.5, 128.5, 128.4, 127.6, 126.6, 125.9, 75.3, 46.1; MS (CI) for $C_{14}H_{14}O$ $[M+H]^+$: m/z 199 (100%).



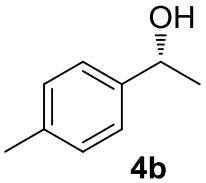
2h

1-Phenylbutan-1-ol:[8] 85% yield, yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.32-7.23 (m, 5H), 4.62 (q, *J* = 6.0 Hz, 1H), 2.16 (brs, 1H), 1.77-1.62 (m, 2H), 1.42-1.25 (m, 2H), 0.91 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 145.0, 128.4, 127.4, 126.0, 74.4, 41.2, 19.0, 14.0; MS (CI) for $C_{10}H_{14}O$ $[M+H]^+$: m/z 151 (100%).



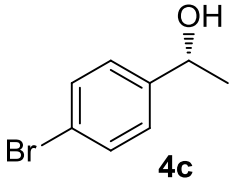
4a

(*R*)-1-Phenylethanol:[10] 87% yield, >99% ee, Colorless oil; HPLC analysis: Chiralcel OD-H (hexane/*i*-PrOH = 97/3, 0.5 mL/min), t_R (major) = 25.67 min, t_S (minor) = 35.55 min. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.33-7.22 (m, 5H), 4.82 (q, *J* = 6.4 Hz, 1H), 2.40 (brs, 1H), 1.44 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 145.8, 128.5, 127.4, 125.4, 70.4, 25.1; MS (CI) for $C_8H_{10}O$ $[M+H]^+$: m/z 123 (100%).



4b

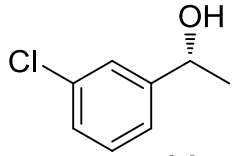
(*R*)-1-(*p*-Tolyl)ethanol:[10] 72% yield, 98% ee, Colorless oil; HPLC analysis: Chiralcel AD-H (hexane/*i*-PrOH = 98/2, 0.2 mL/min), t_S (minor) = 15.51 min, t_R (major) = 19.32 min. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.24 (d, *J* = 7.2 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 4.82 (q, *J* = 6.4 Hz, 1H), 2.33 (s, 3H), 1.45 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 142.9, 137.1, 129.2, 125.3, 70.2, 25.1, 21.1; MS (CI) for $C_9H_{12}O$ $[M+H]^+$: m/z 137 (100%).



4c

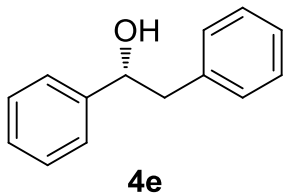
(*R*)-1-(4-Bromophenyl)ethanol:[10] 86% yield, 99% ee, Colorless oil; HPLC analysis: Chiralcel AD-H (hexane/*i*-PrOH = 98.7/1.3, 0.9 mL/min), t_R (major) = 33.08 min, t_S (minor) = 35.98min. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.45 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 2H), 4.83 (q, *J* = 7.8 Hz, 1H), 2.15 (brs, 1H), 1.44 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 144.8, 131.5, 127.2, 121.1, 69.7, 25.2; MS (CI) for C_8H_9BrO $[M+H]^+$: m/z

201 (100%).



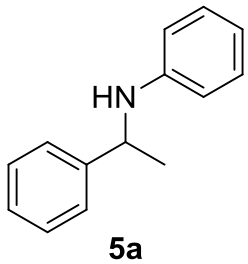
4d

(*R*)-1-(3-Chlorophenyl)ethanol:[10] 86% yield, 95% ee, Colorless oil; HPLC analysis: Chiralcel AD-H (hexane/*i*-PrOH = 98.5/1.5, 0.9 mL/min), t_S (minor) = 20.90 min, t_R (major) = 23.24 min. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.32 (s, 1H), 7.24-7.17 (m, 3H), 4.81 (q, *J* = 4.5 Hz, 1H), 2.39 (brs, 1H), 1.43 (d, *J* = 3.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 147.9, 134.4, 129.8, 127.5, 125.6, 123.5, 69.8, 25.2; MS (CI) for C_8H_9ClO $[M+H]^+$: m/z 157 (100%).



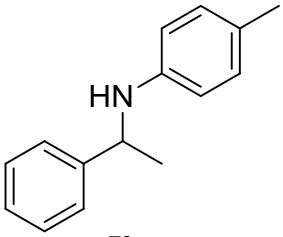
4e

(*R*)-1,2-Diphenylethanol:[11] 84% yield, 96% ee, white solid; m.p. = 60-61 ^{o}C; HPLC analysis: Chiralcel AD-H (hexane/*i*-PrOH = 98.8/1.2, 0.7 mL/min), t_S (minor) =56.16 min, t_R (major) =58.39 min. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.37-7.18 (m, 10H), 4.90 (q, *J* = 4.8 Hz, 1H), 3.07-2.96 (m, 2H); 1.91 (brs, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 143.8, 138.1, 129.5, 128.5, 128.4, 127.6, 126.6, 125.9, 75.3, 46.1; MS (CI) for $C_{14}H_{14}O$ $[M+H]^+$: m/z 199 (100%).



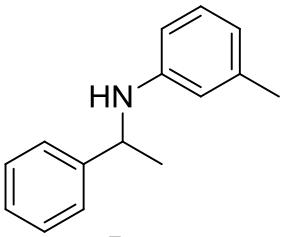
5a

***N*-(1-Phenylethyl)aniline**:[9] 52% yield, yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.34 (d, *J* = 7.2 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.19 (t, *J* = 4.8 Hz, 2H), 7.06 (t, *J* = 7.6 Hz, 2H), 6.61 (t, *J* = 7.2 Hz, 1H), 6.48 (d, *J* = 7.6 Hz, 2H), 4.46 (q, *J* = 6.8 Hz, 1H), 1.48 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 147.3, 145.3, 129.1, 128.6, 126.9, 125.9, 117.3, 113.4, 53.5, 25.0; HRMS for $C_{14}H_{15}N$ $[M+H]^+$: m/z calc.: 198.1283. Found: 198.1284.



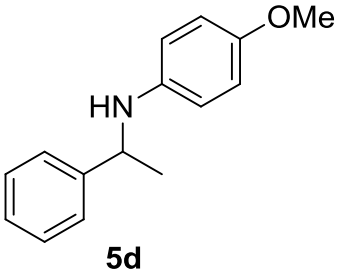
5b

4-Methyl-*N*-(1-phenylethyl)aniline:[9] 70% yield, white solid; m.p. = 69-71 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.32 (q, *J* = 7.2 Hz, 2H), 7.19 (t, J = 5.2 Hz, 3H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.41 (d, *J* = 8.4 Hz, 2H), 4.43 (q, *J* = 6.8 Hz, 1H), 3.87 (s, 1H), 2.17 (s, 3H), 1.48 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 145.5, 145.1, 129.6, 128.6, 126.8, 126.4, 126.0, 113.5, 53.7, 25.0, 20.4; HRMS for $C_{15}H_{17}N$ $[M+H]^+$: m/z calc.: 234.1259. Found: 234.1260.



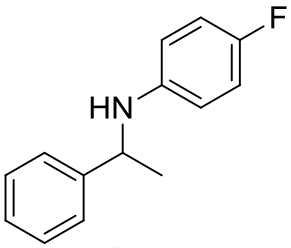
5c

3-Methyl-*N*-(1-phenylethyl)aniline:[9] 59% yield, yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.43 (d, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.29 (q, *J* = 7.2 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.63 (d, *J* = 7.6 Hz, 1H), 6.53 (s, 1H), 6.48 (d, *J* = 8.0 Hz, 1H), 4.55 (q, *J* = 6.8 Hz, 1H), 2.29 (s, 3H), 1.60 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 145.6, 144.0, 139.0, 129.1, 128.7, 127.2, 126.3, 119.9, 115.7, 111.9, 54.9, 24.1, 21.6; HRMS for $C_{15}H_{17}N$ $[M+H]^+$: m/z calc.: 258.1489. Found: 258.1492.



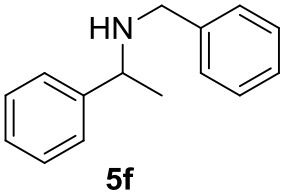
5d

4-Methoxy-*N*-(1-phenylethyl)aniline:[9] 75% yield, white solid; m.p. = 61-62 ^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.30 (d, *J* = 12.6 Hz, 2H), 7.18 (t, *J* = 6.6 Hz, 3H), 6.67 (d, *J* = 8.4 Hz, 2H), 6.44 (d, *J* = 8.4 Hz, 2H), 4.38 (d, *J* = 6.3 Hz, 1H), 3.65 (s, 3H), 1.46 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 152.0, 145.5, 141.6, 128.6, 126.8, 126.0, 114.8, 114.6, 55.8, 54.3, 25.1; MS (CI) for $C_{14}H_{23}NO$ $[M+H]^+$: m/z calc.: 228.1388. Found: 228.1382.



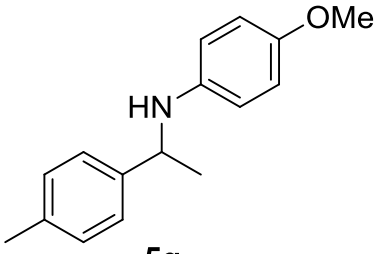
5e

4-Fluoro-*N*-(1-phenylethyl)aniline:[9] 63% yield, yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.45-7.39 (m, 2H), 7.33-7.28 (m, 3H), 6.88 (q, *J* = 6.4 Hz, 2H), 6.52-6.50 (m, 2H), 4.50 (d, *J* = 6.4 Hz, 1H), 3.96 (s, 1H), 1.58 (q, *J* = 1.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 155.6 (d, $^{1}J_{C\text{-}F}$ = 233.4 Hz), 145.0, 143.6, 128.6, 126.9, 125.8, 115.4 (d, $^{2}J_{C\text{-}F}$ = 22.1 Hz), 114.0 (d, $^{3}J_{C\text{-}F}$ = 7.3 Hz), 54.0, 24.0. HRMS for $C_{14}H_{14}FN$ $[M+H]^+$: m/z calc.: 216.1189. Found: 216.1189.



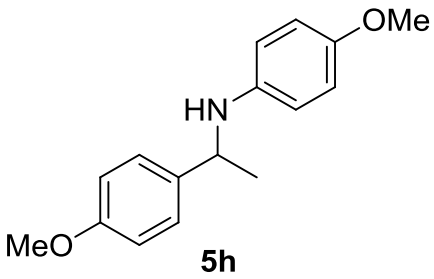
5f

***N*-Benzyl-1-phenylethanamine**:[9] 62% yield, yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.34-7.20 (m, 10H), 3.79 (q, *J* = 6.4 Hz, 1H), 3.61 (q, *J* = 12.8 Hz, 2H), , 1.68 (brs, 1H), 1.35 (d, *J* = 6.8 Hz 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 145.6, 140.7, 128.5, 128.4, 128.2, 126.8, 57.6, 51.7, 24.5; MS (CI) for $C_{14}H_{23}N$ $[M+H]^+$: m/z calc.: 212.1439. Found: 212.1437.



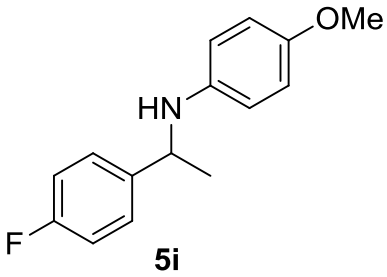
5g

4-Methoxy-*N*-(1-(4-methoxyphenyl)ethyl)aniline:[9] 75% yield, white solid; m.p. = 29-31 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.29 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 2H), 6.74 (d, *J* = 8.8 Hz, 2H), 6.52 (d, *J* = 8.8 Hz, 2H), 4.43 (q, *J* = 6.8 Hz, 1H), 3.73 (s, 3H), 2.36 (s, 3H), 1.52 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 152.0, 142.5, 141.7, 136.4, 129.3, 125.9, 114.8, 114.6, 55.8, 54.0, 25.1, 21.1; HRMS for $C_{16}H_{19}NO_2$ $[M+H]^+$: m/z calc.: 242.1545. Found: 242.1541.



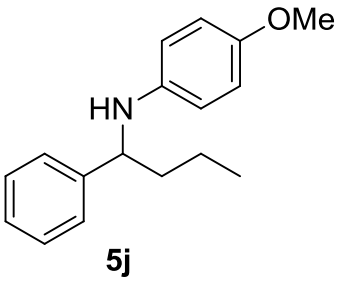
5h

4-Methoxy-*N*-(1-(4-methoxyphenyl)ethyl)aniline:[9] 64% yield, white solid; m.p. = 56-58 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.26 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.68 (d, *J* = 8.8 Hz, 2H), 6.46 (d, *J* = 9.2 Hz, 2H), 4.36 (q, *J* = 6.8 Hz, 1H), 3.76 (s, 3H), 3.68 (s, 3H), 1.46 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 158.5, 152.0, 141.7, 137.6, 127.0, 114.8, 114.7, 114.0, 55.8, 55.3, 53.7, 25.1; HRMS for $C_{16}H_{19}NO_2$ $[M+H]^+$: m/z calc.: 280.1313. Found: 280.1309.



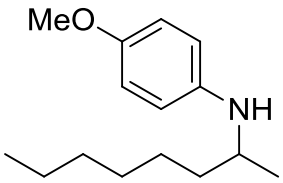
5i

***N*-(1-(4-Fluorophenyl)ethyl)-4-methoxyaniline**:[9] 86% yield, white solid; m.p. = 38-39 ^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.34 (t, *J* = 5.7 Hz, 2H), 7.01 (t, *J* = 8.4 Hz, 2H), 6.72 (d, *J* = 8.7 Hz, 2H), 6.47 (d, *J* = 8.7 Hz, 2H), 4.41 (q, *J* = 6.0 Hz, 1H), 3.71 (s, 3H), 1.49 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 161.8 (d, $^{1}J_{C\text{-}F}$ = 182.1 Hz), 152.1, 141.4, 141.2 (d, $^{4}J_{C\text{-}F}$ = 2.3 Hz), 127.4 (d, $^{3}J_{C\text{-}F}$ = 5.9 Hz), 115.4 (d, $^{2}J_{C\text{-}F}$ = 15.9 Hz), 114.8, 114.7, 55.7, 53.7, 25.2; HRMS for $C_{15}H_{16}FNO$ $[M+H]^+$: m/z calc.: 268.1114. Found: 268.1112.



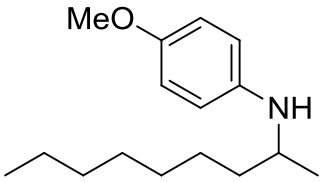
5j

4-Methoxy-*N*-(1-phenylbutyl)aniline:[9] 71% yield, yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.35-7.20 (m, 5H), 6.69 (d, *J* = 8.8 Hz, 2H), 6.48 (d, *J* = 8.8 Hz, 2H), 4.24 (t, *J* = 6.4 Hz, 1H), 3.69 (s, 3H),1.83-1.70 (m, 2H), 1.45-1.33 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 151.8, 144.6, 141.8, 128.5, 126.8, 126.4, 114.8, 114.4, 58.9, 55.8, 41.2, 19.5, 14.0; HRMS for $C_{17}H_{21}NO$ $[M+H]^+$: m/z calc.: 258.1489. Found: 258.1492.



5k

4-Methoxy-*N*-(octan-2-yl)aniline:[9] 78% yield, yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 6.79 (d, *J* = 8.8 Hz, 2H), 6.57 (d, *J* = 8.8 Hz, 2H), 3.76 (s, 3H), 3.37 (q, *J* = 6.0 Hz, 1H), 3.07 (s, 1H) 1.61-1.53 (m, 1H), 1.43-1.30 (m, 9H), 1.16 (d, *J* = 6.4 Hz, 3H) , 0.90 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 151.9, 142.0, 115.0, 114.7, 55.8, 49.6, 37.3, 31.9, 29.4, 26.1, 22.6, 20.8, 14.1;. MS (CI) for $C_{15}H_{25}NO$ $[M+H]^+$: m/z calc.: 236.2014. Found: 236.2015.



5l

4-Methoxy-*N*-(nonan-3-yl)aniline:[9] 79% yield, yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 6.76 (d, *J* = 8.7 Hz, 2H), 6.54 (d, *J* = 8.7 Hz, 2H), 3.73 (s, 3H), 3.34 (t, *J* = 5.3 Hz, 1H), 3.08 (brs, 1H), 1.56-1.27 (m, 12H), 1.14 (d, *J* = 6.3 Hz, 3H), 0.88-0.85 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 151.9, 142.0, 115.0, 114.8, 55.8, 50.4, 37.3, 31.8, 29.7, 29.3, 26.2, 22.7, 20.8, 14.1;. MS (CI) for $C_{16}H_{27}NO$ $[M+H]^+$: m/z calc.: 250.2171. Found: 250.2175.

7. References

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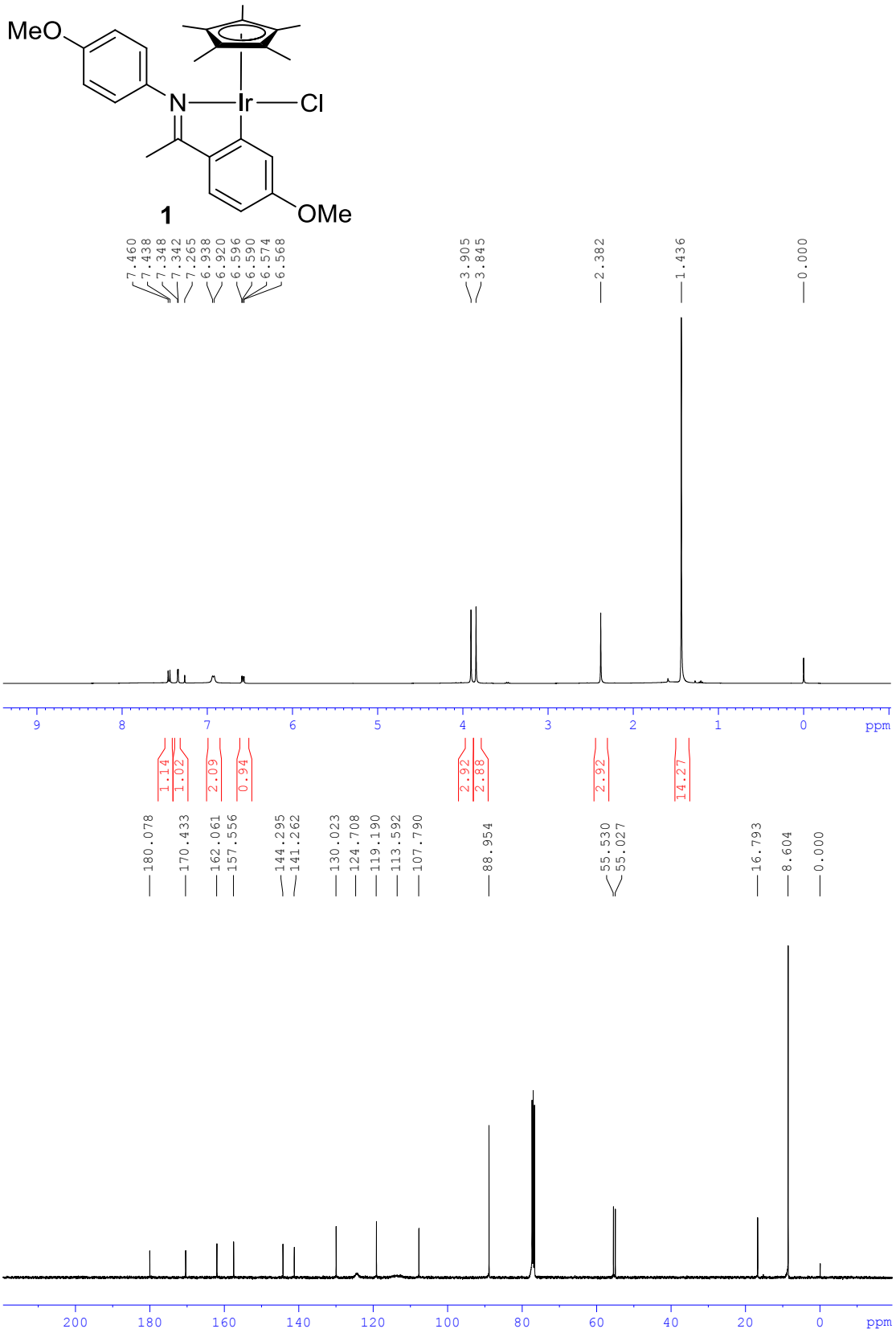
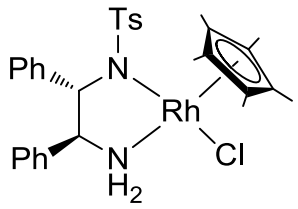
8. ^{1}H and ^{13}C NMR spectra of catalysts and products





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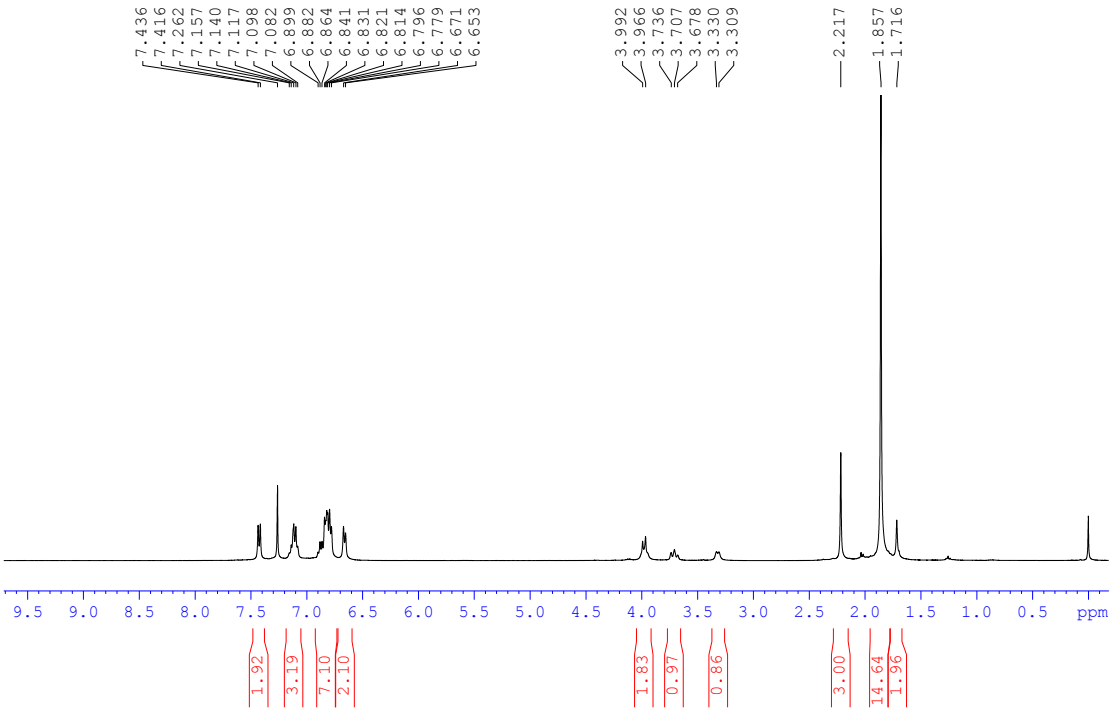
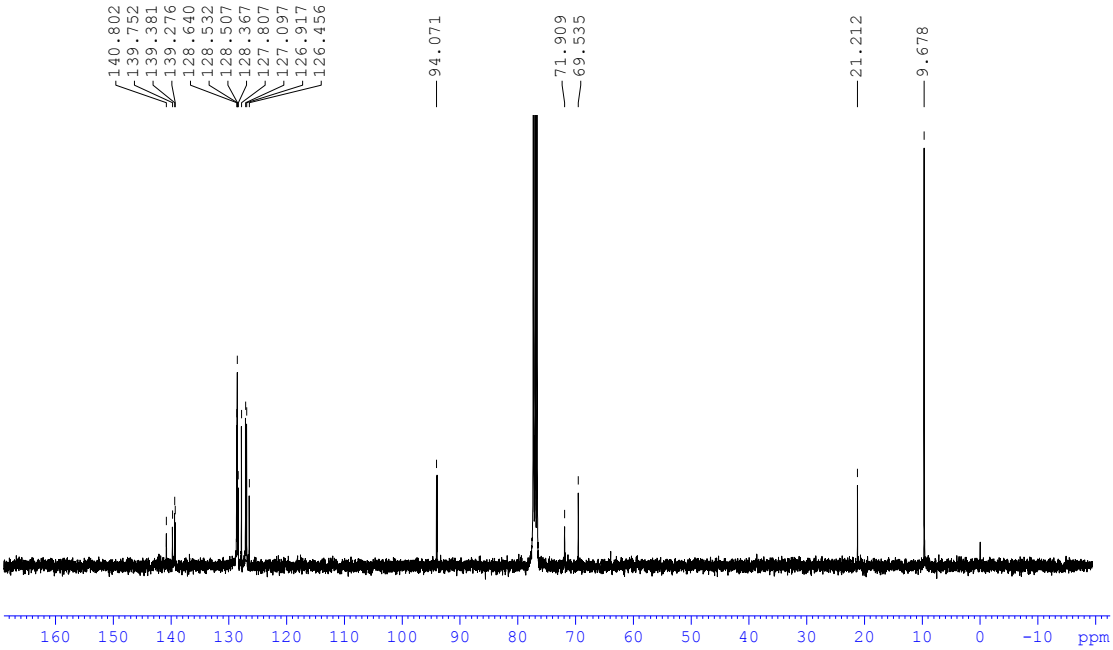
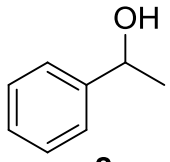
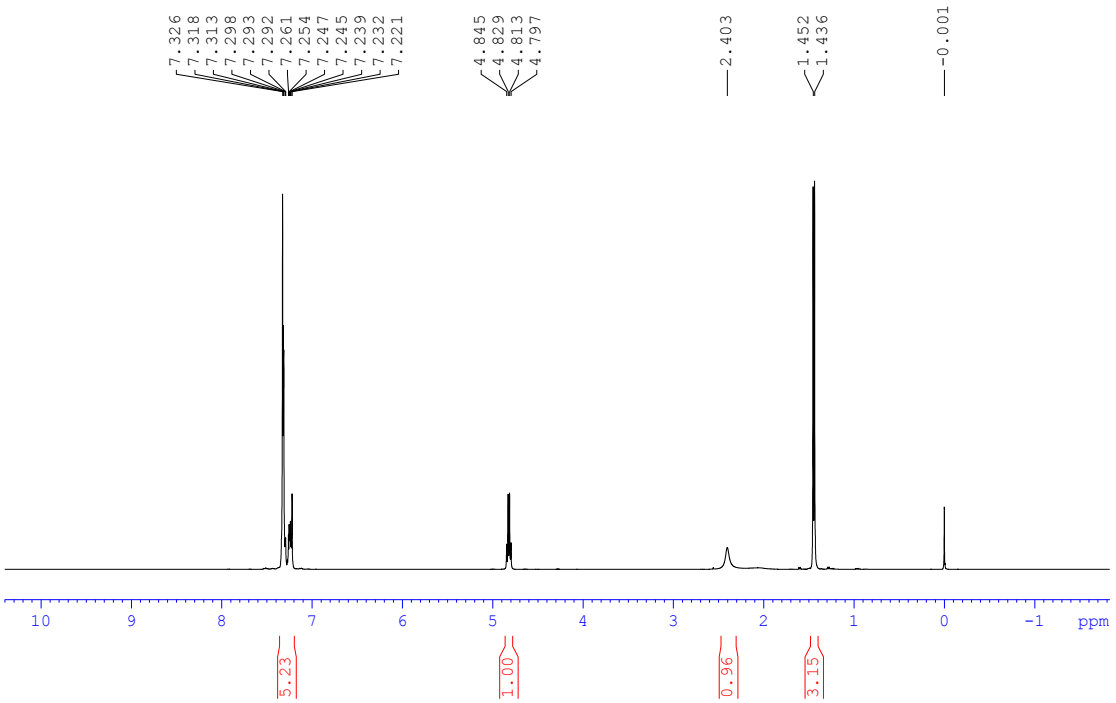





OH

2a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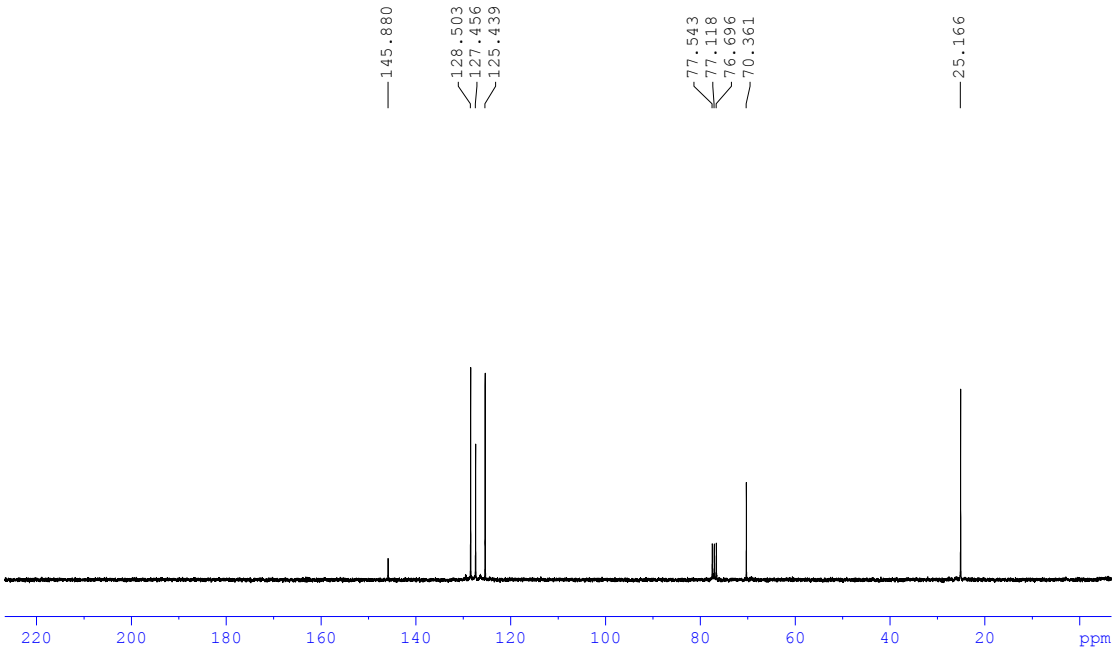
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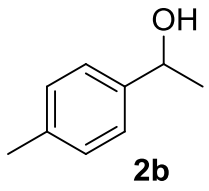

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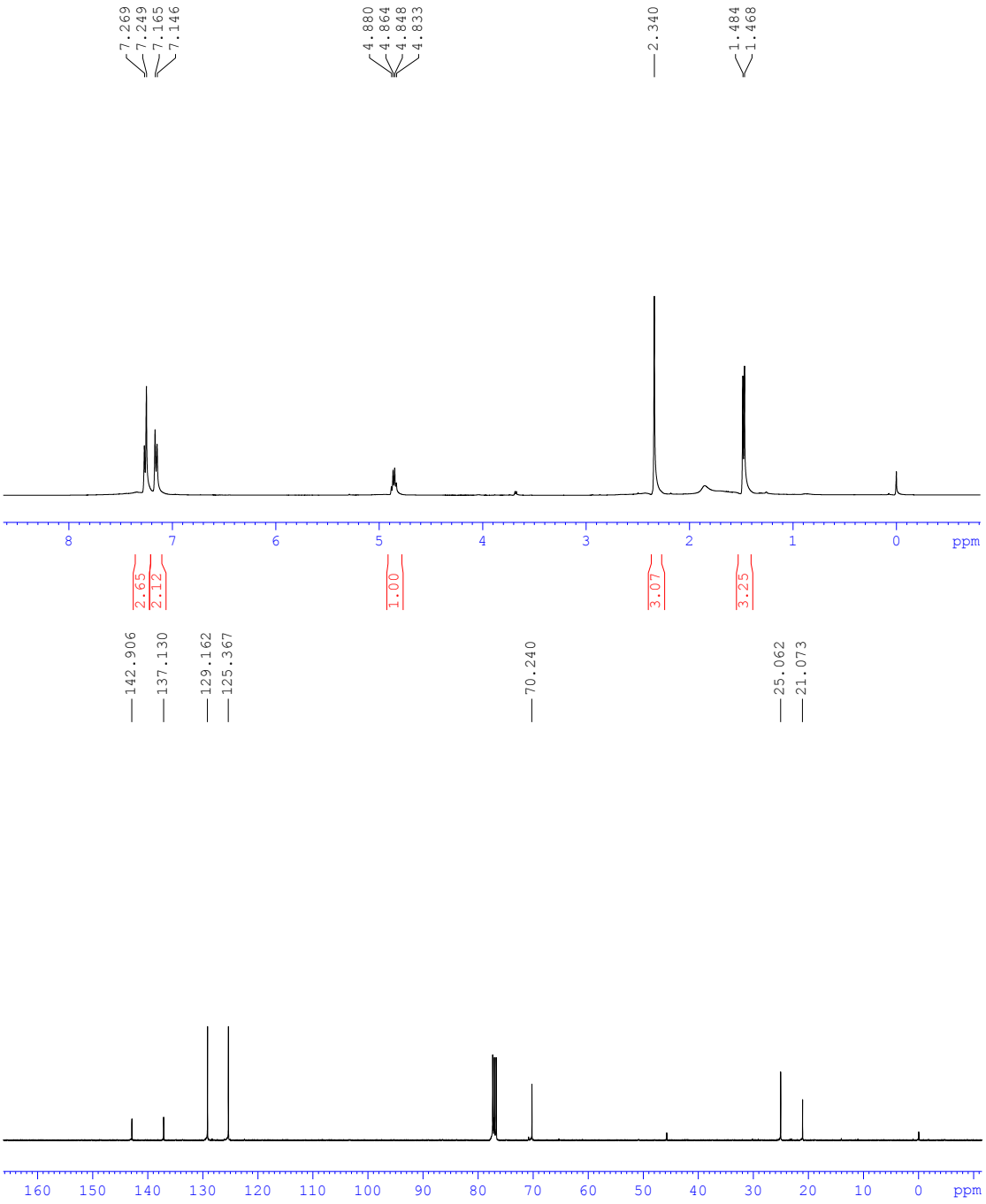

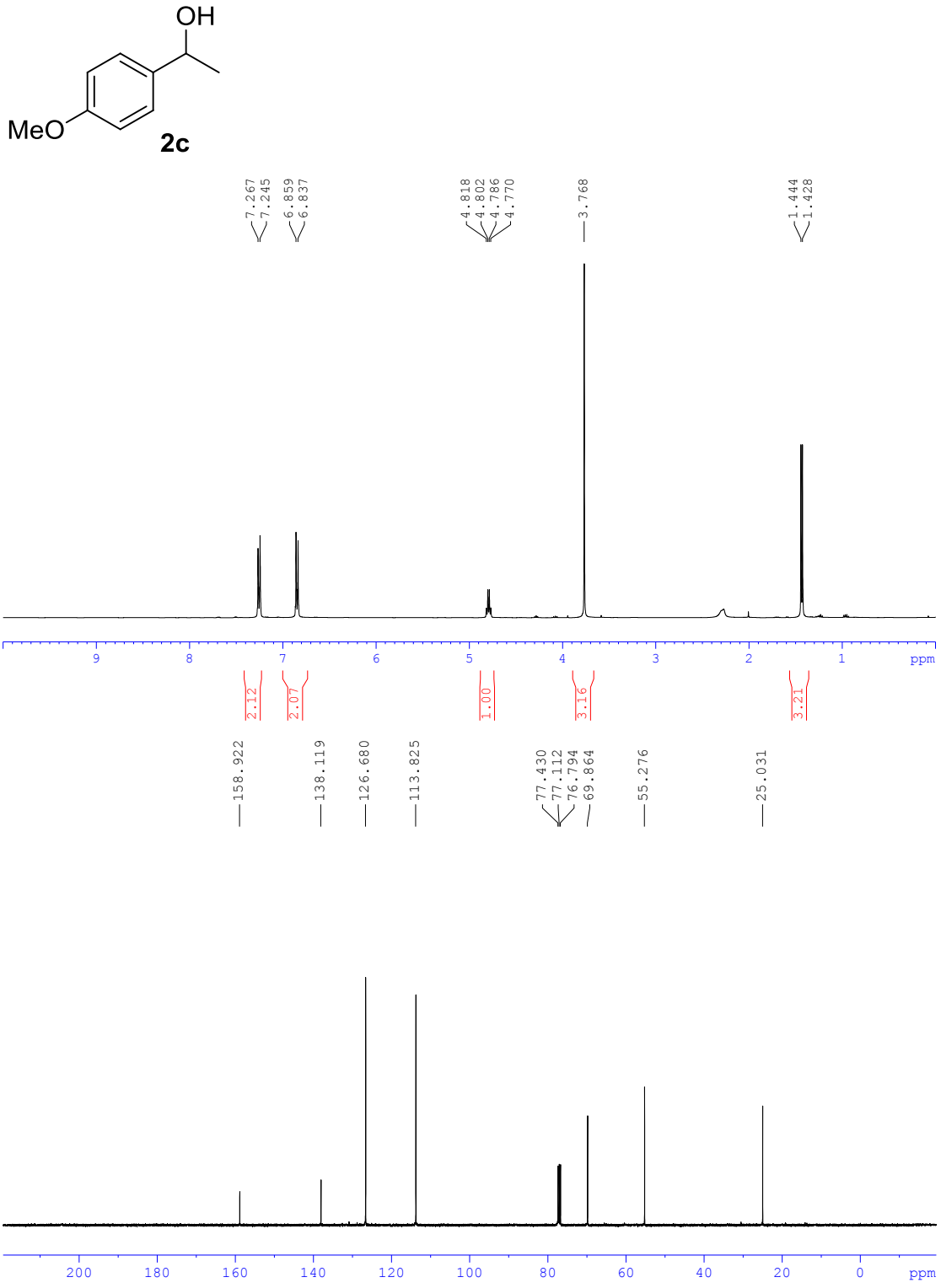

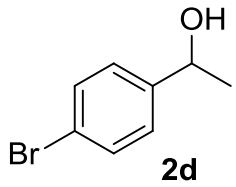

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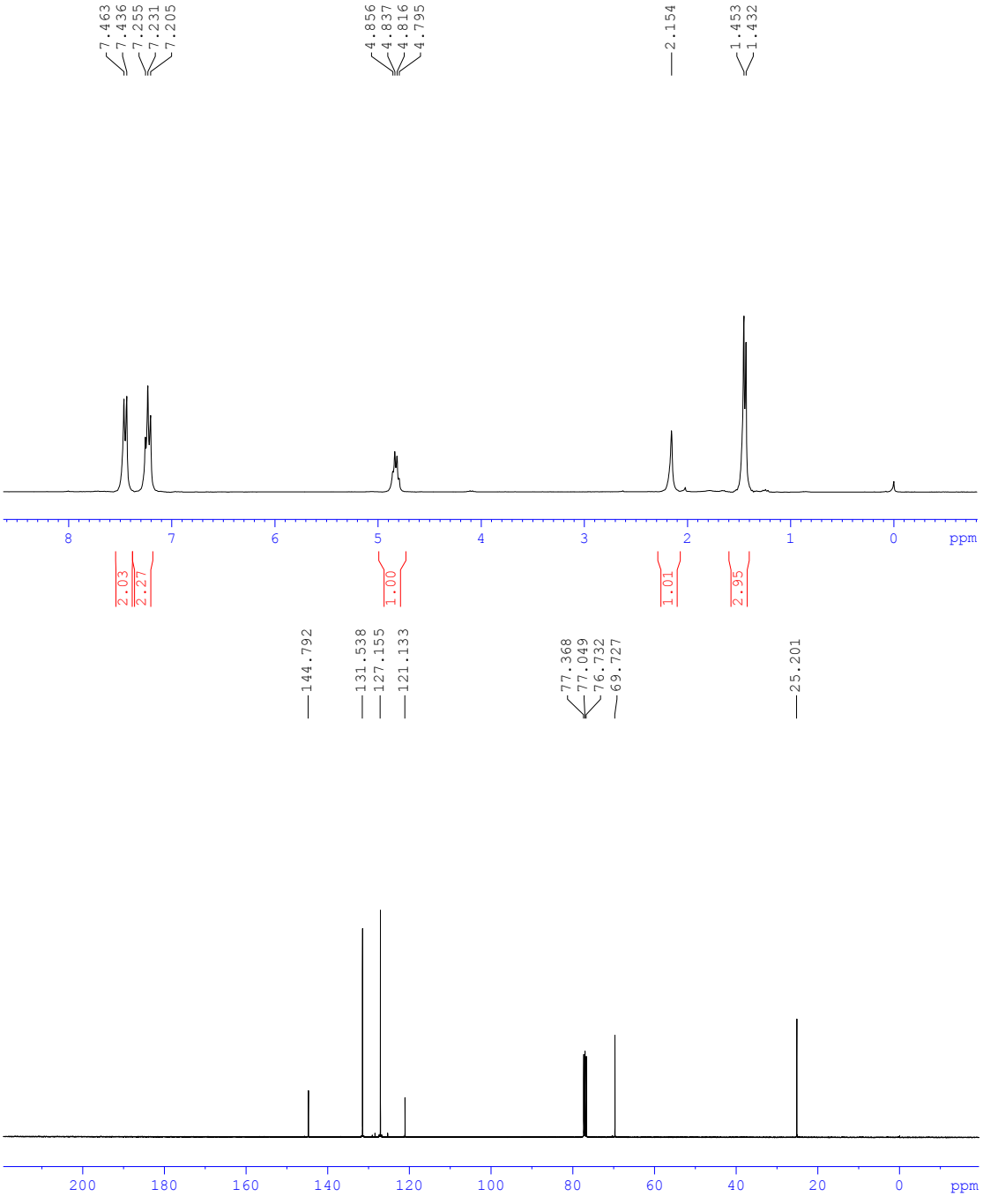

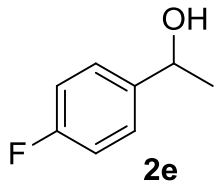

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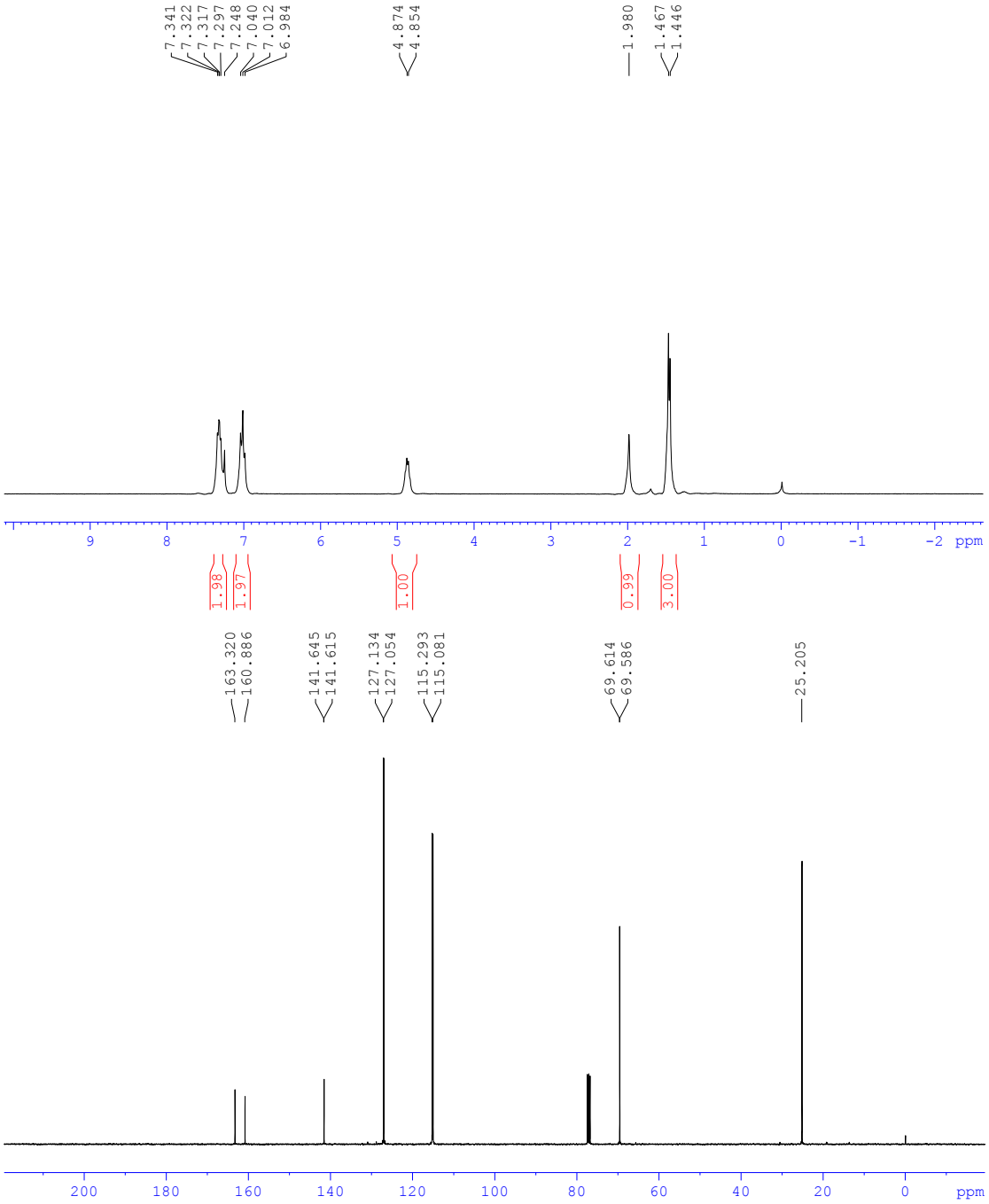

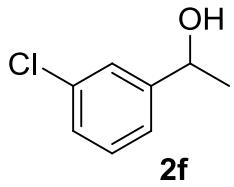
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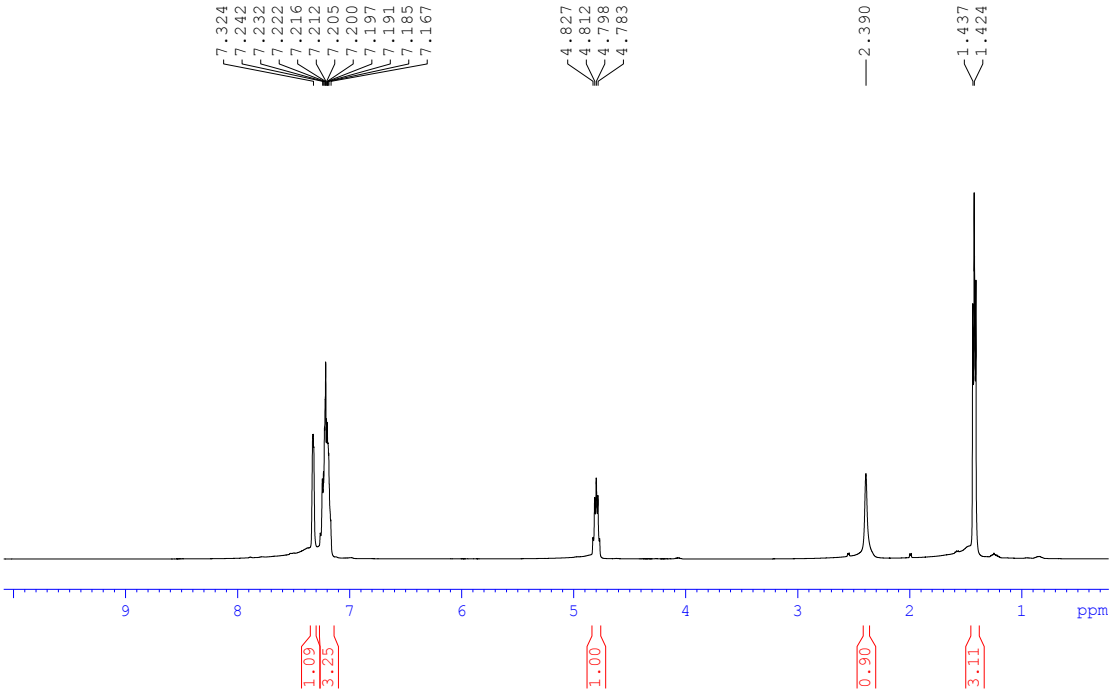
2f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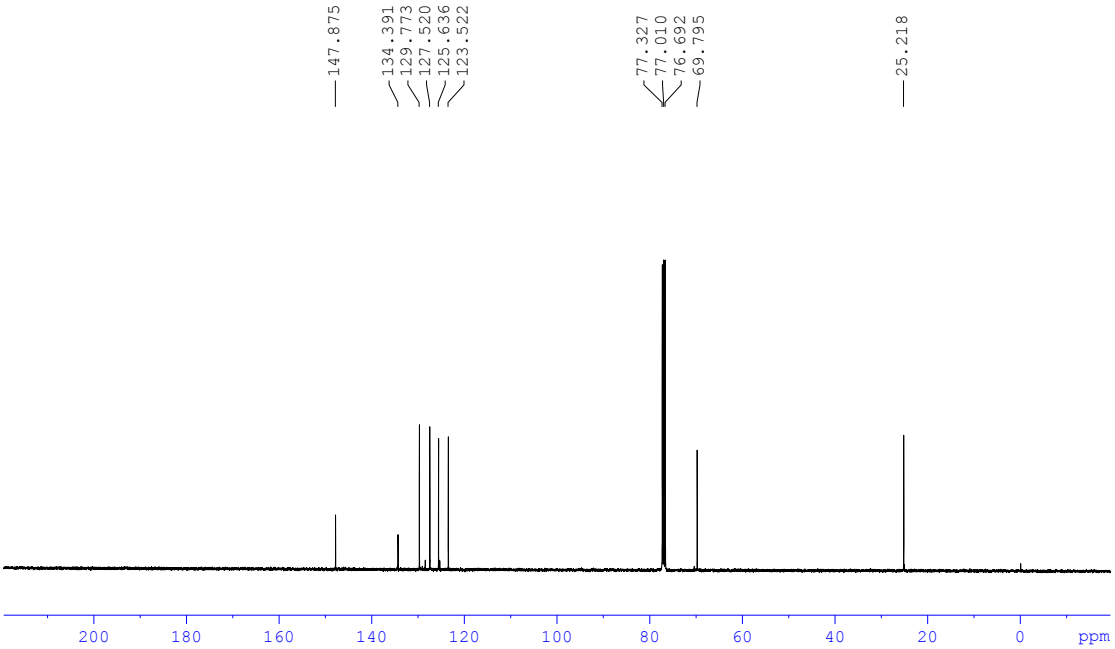
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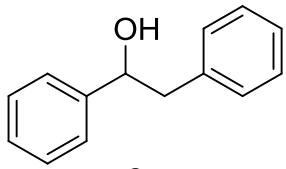

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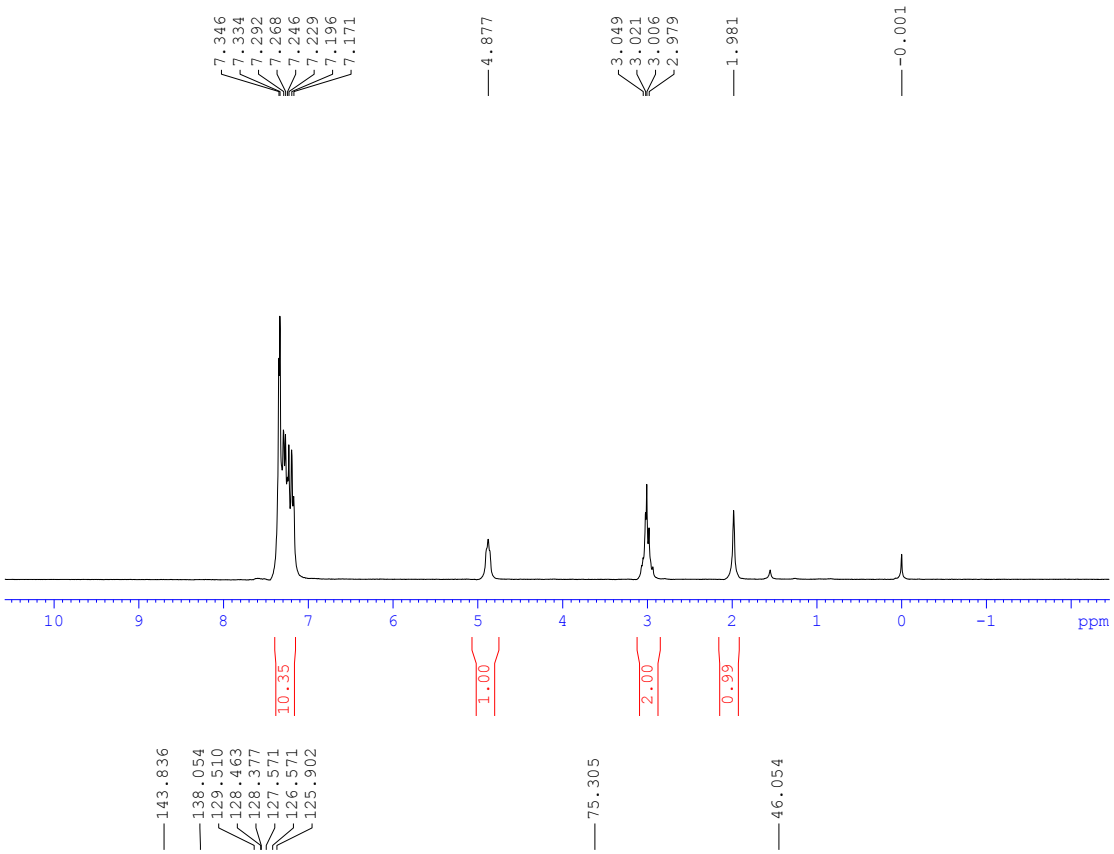

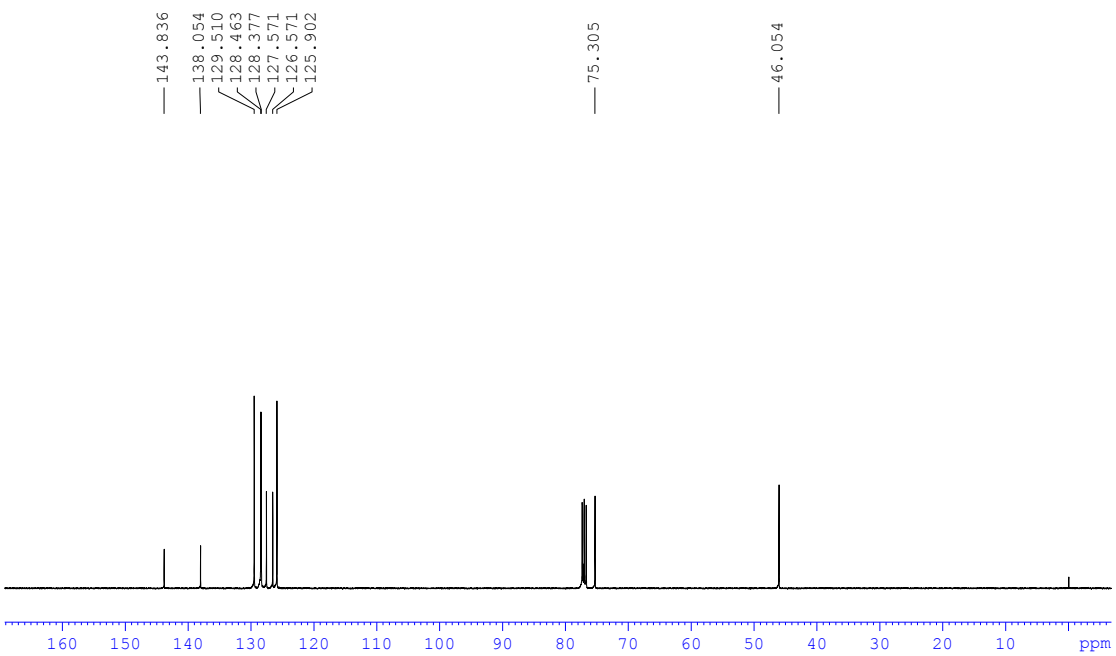

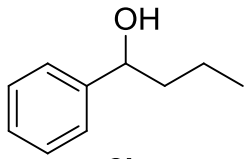

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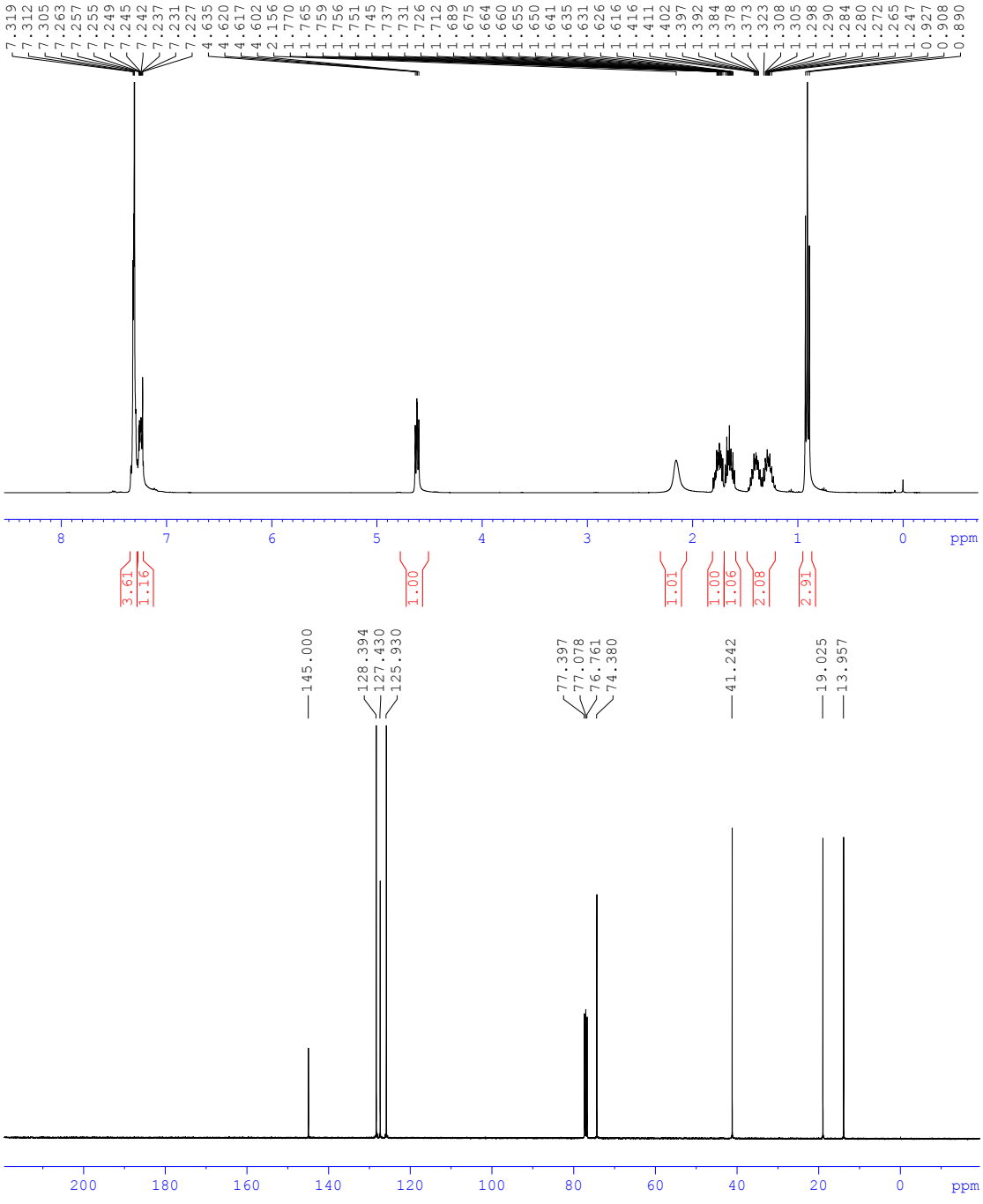
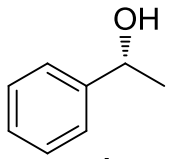
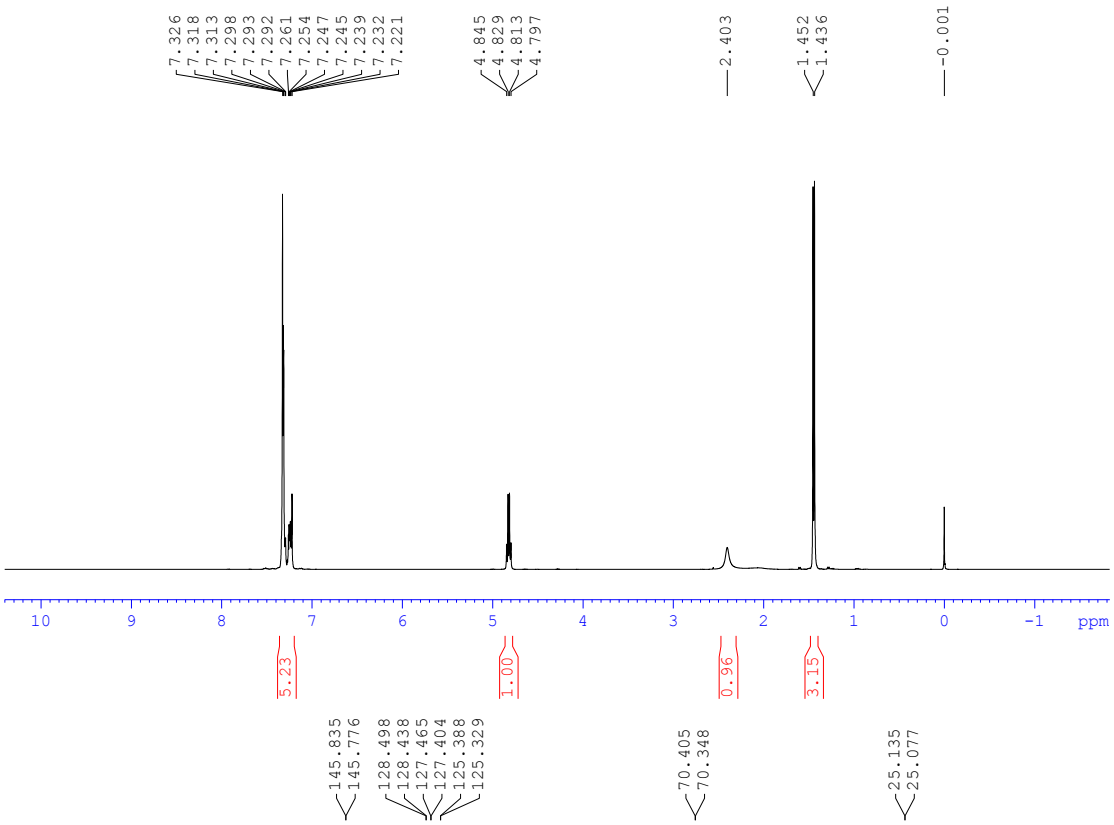



OH

4a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7.293
7.292
7.261
7.254
7.247
7.245
7.239
7.232
7.221
4.845
4.829
4.813
4.797
2.403
1.452
1.436
-0.001
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
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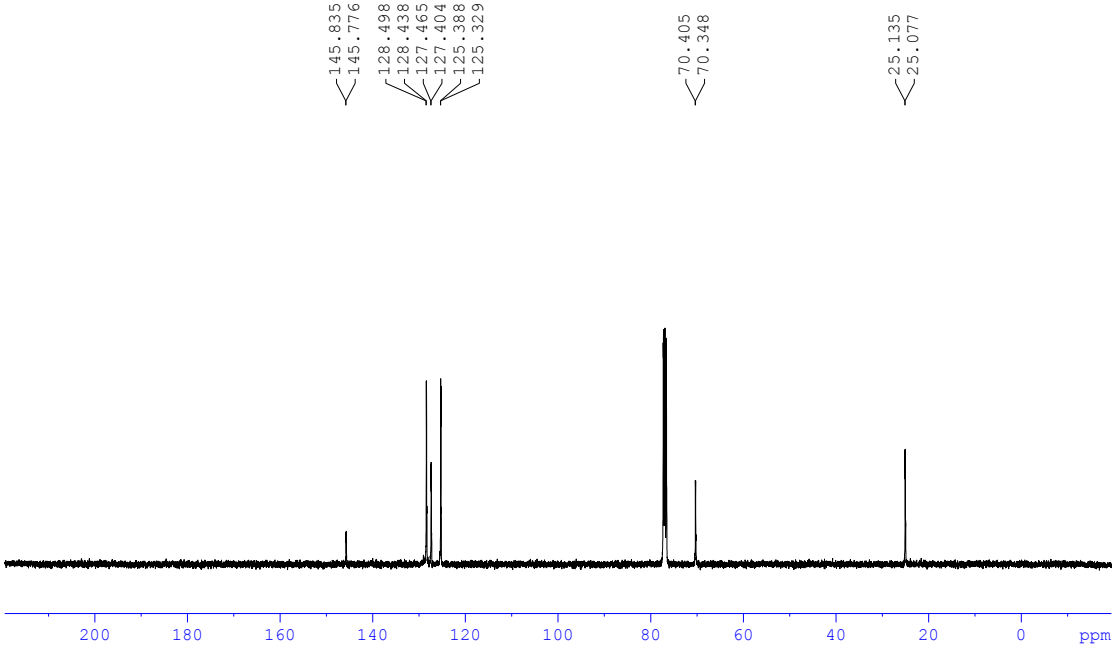
1.00
0.96
3.15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145.776
128.498
128.438
127.465
127.404
125.388
125.329
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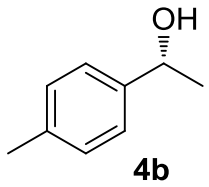
70.348
25.135
25.077
200
180
160
140
120
100
80
60
40
20
0
ppm



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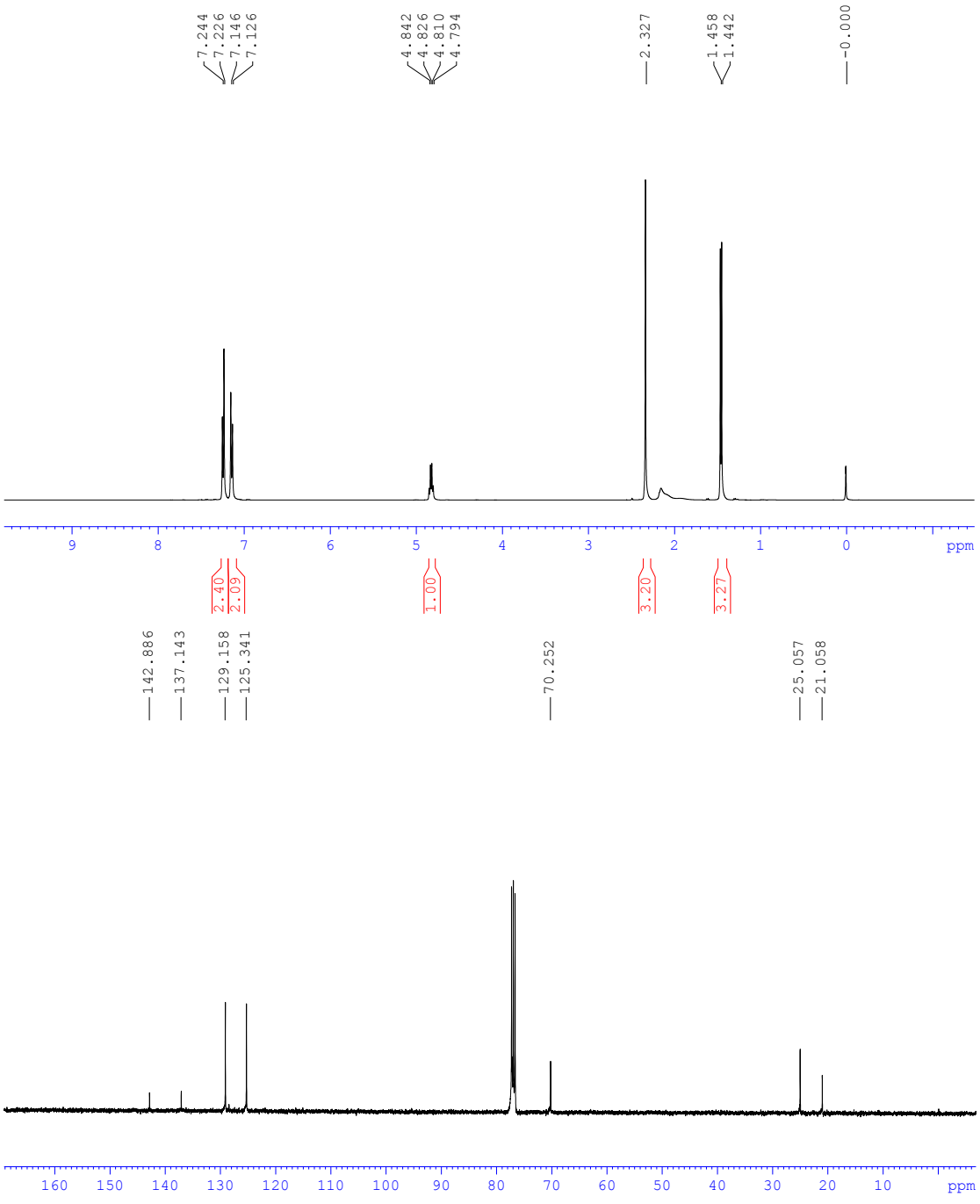

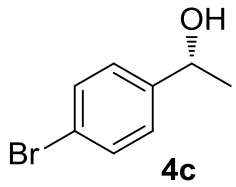

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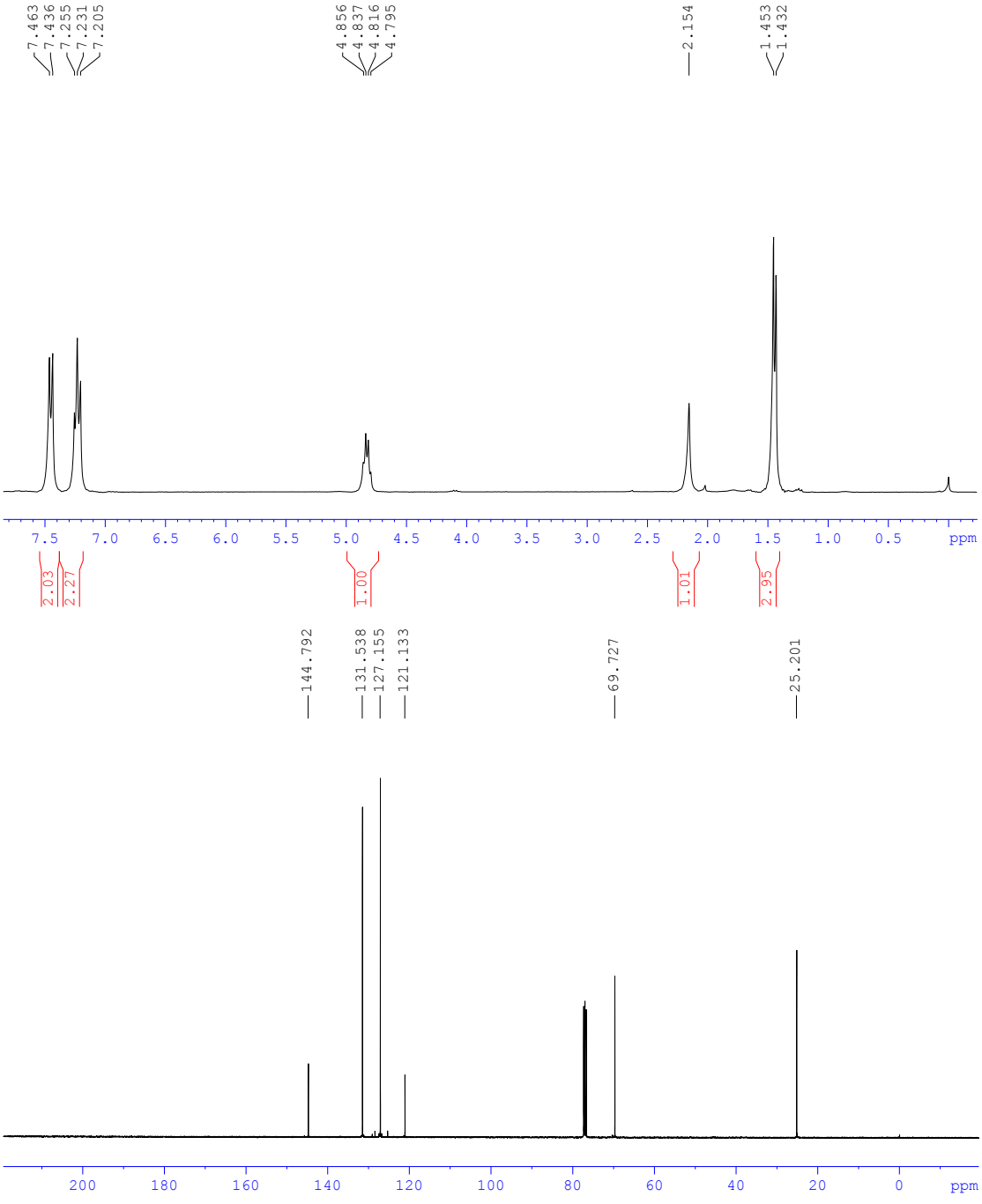

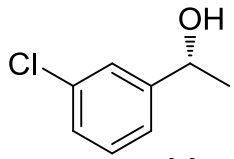

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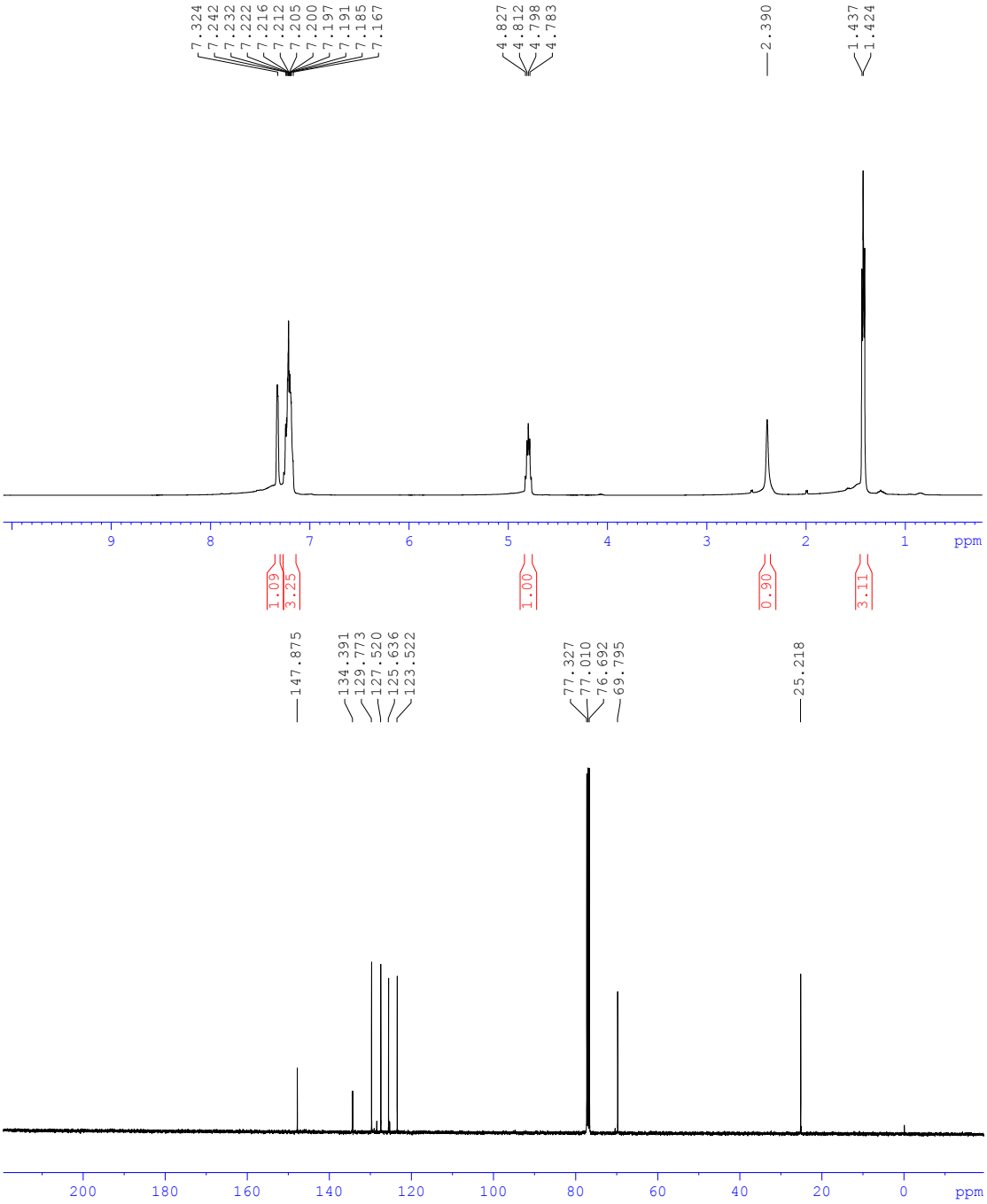
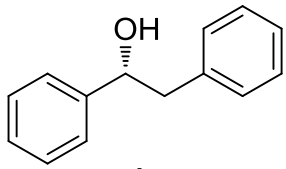
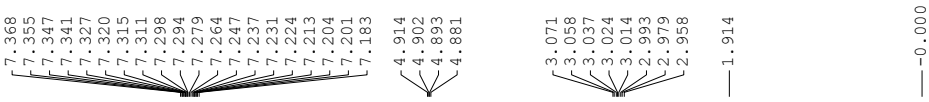



OH

4e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7.311
7.298
7.294
7.279
7.264
7.247
7.237
7.231
7.224
7.213
7.204
7.201
7.183
4.914
4.902
4.893
4.881
3.071
3.058
3.037
3.024
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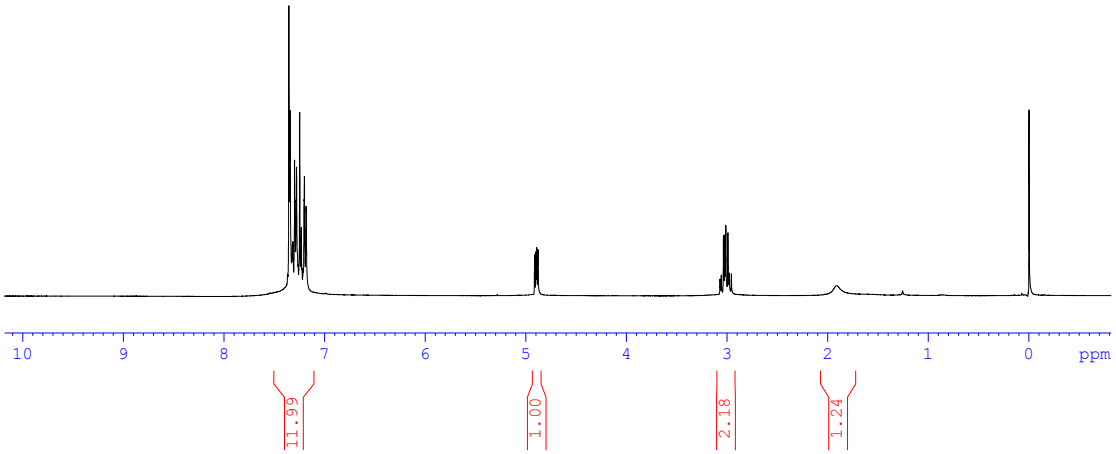
2.993
2.979
2.958
1.914
0.000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7
6
5
4
3
2
1
0
ppm
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1.00
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1.24


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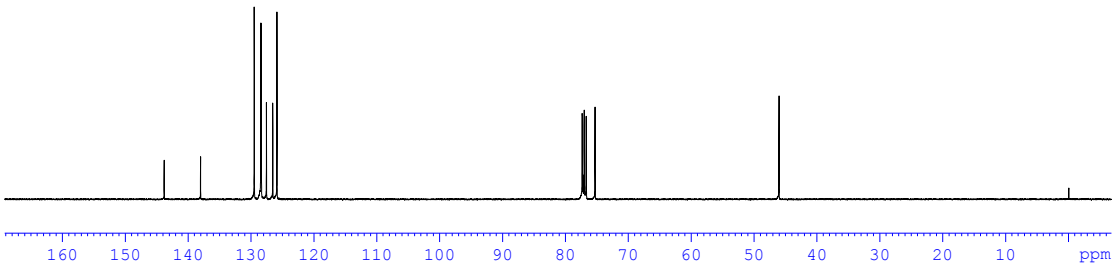
129.510
128.463
128.377
127.571
126.571
125.902
75.305
46.054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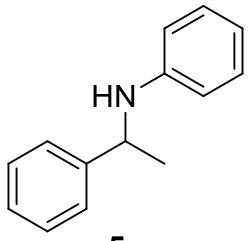
10
ppm



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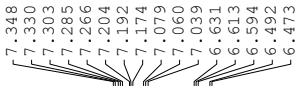

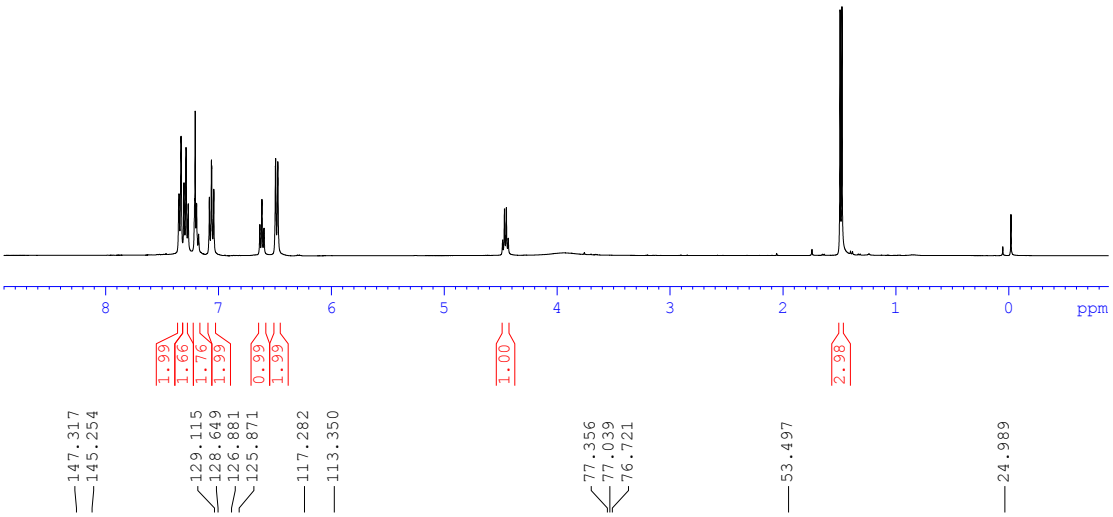

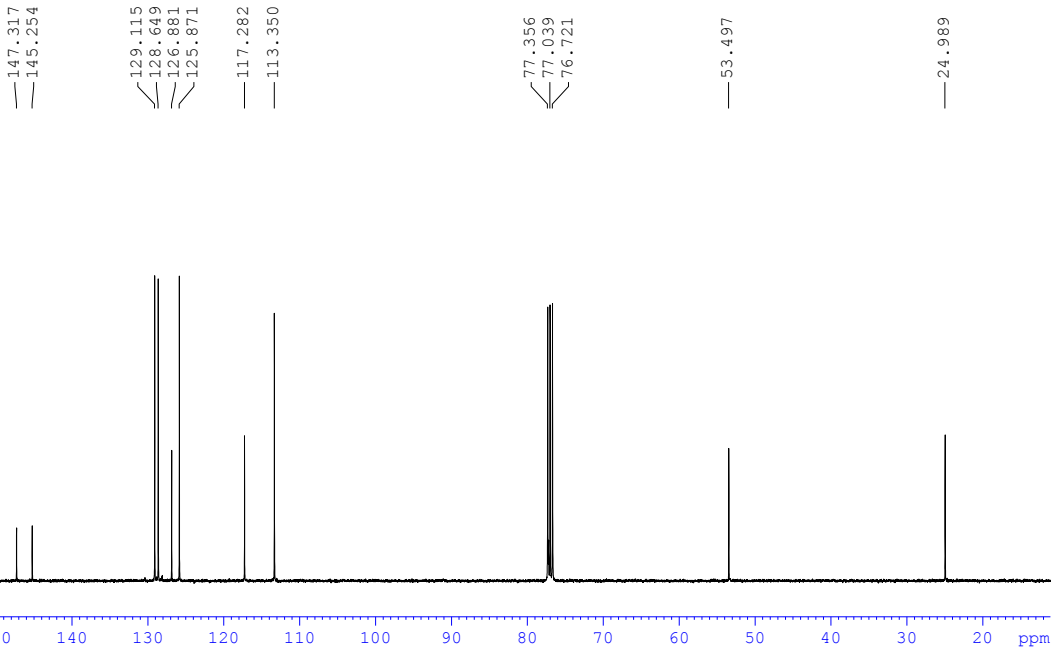

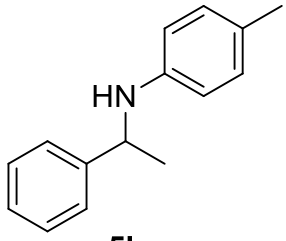

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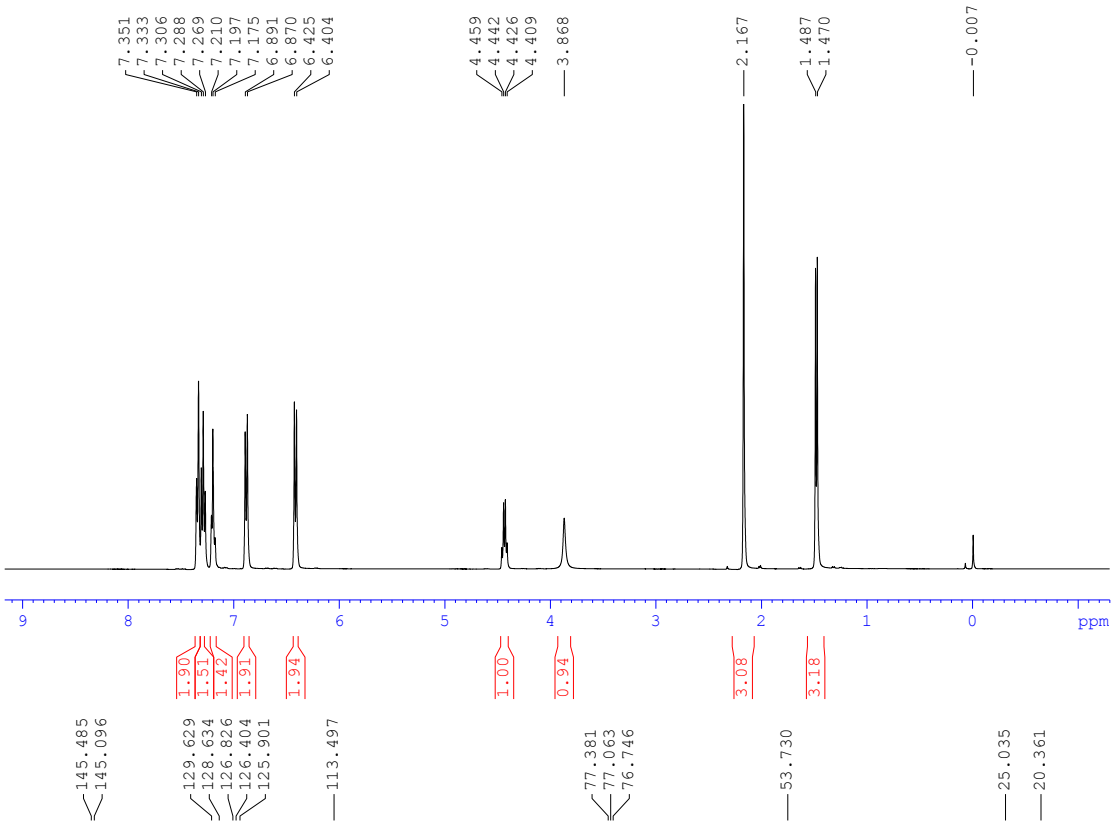
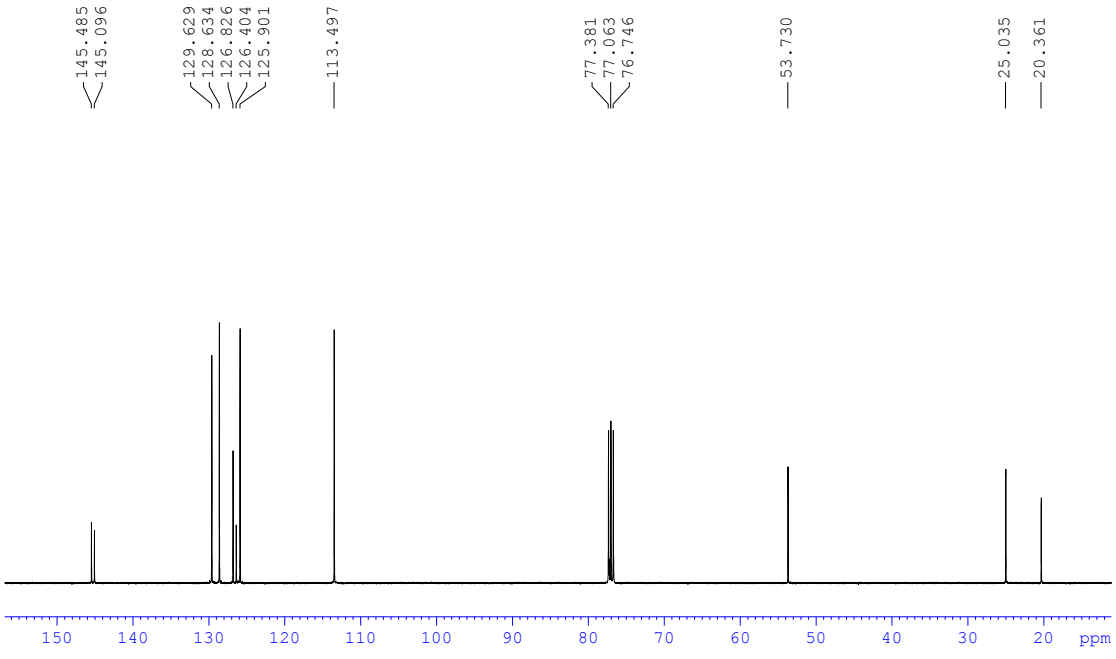
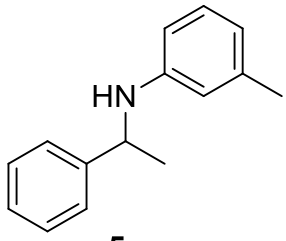
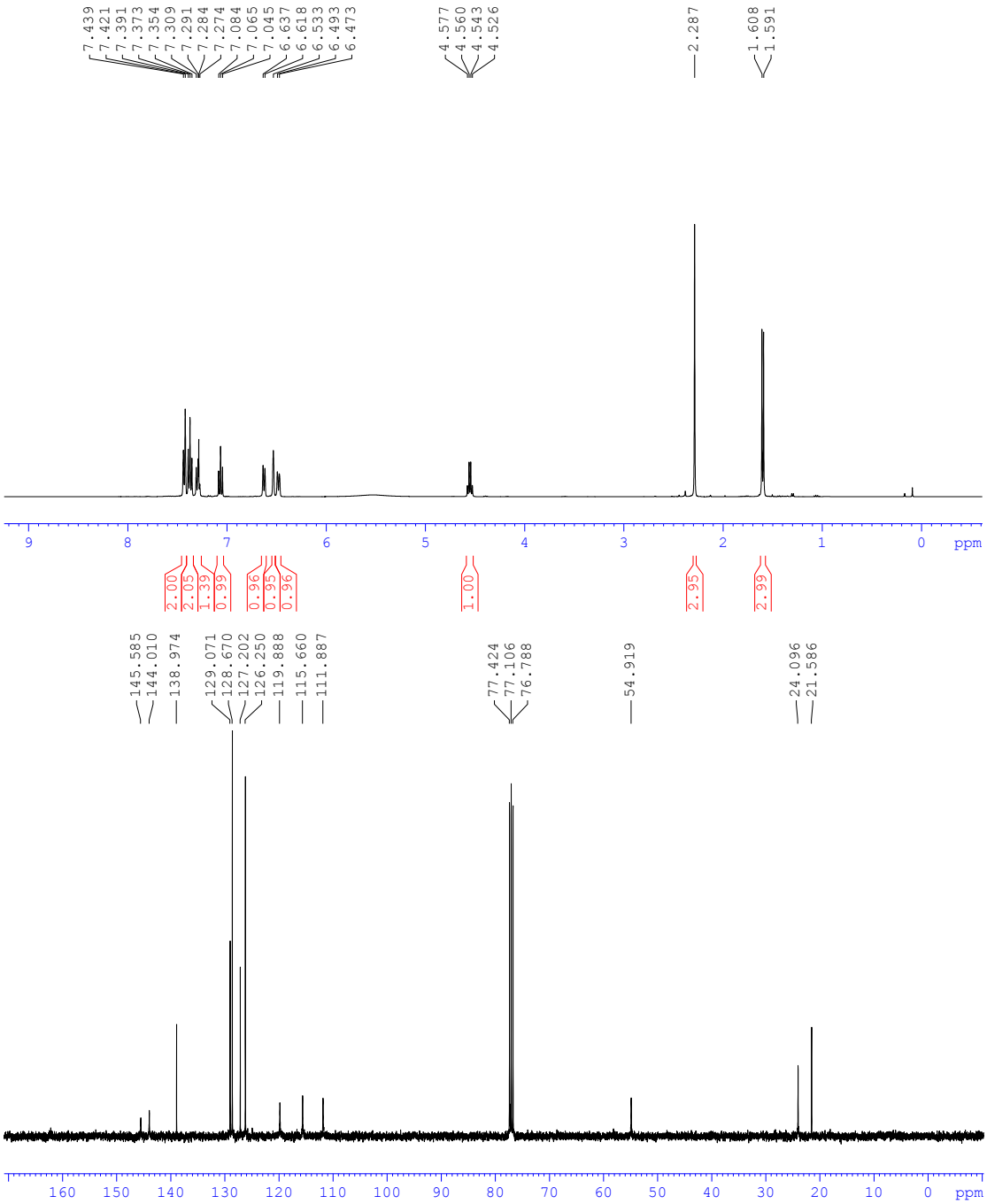





HN

5c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7.045
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6.618
6.533
6.493
6.473
4.577
4.560
4.543
4.526
2.287
1.608
1.591
9
8
7
6
5
4
3
2
1
0
ppm
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2.05
1.39
0.99
0.96
0.95
0.96
1.00
2.95
2.99
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144.010
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129.071
128.670
127.202
126.250
119.888
115.660
111.887
77.424
77.106
76.788
54.919
24.096
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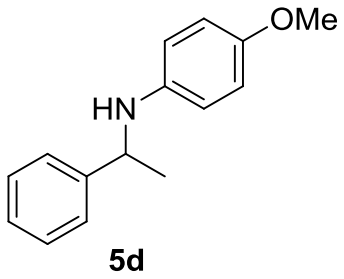
ppm



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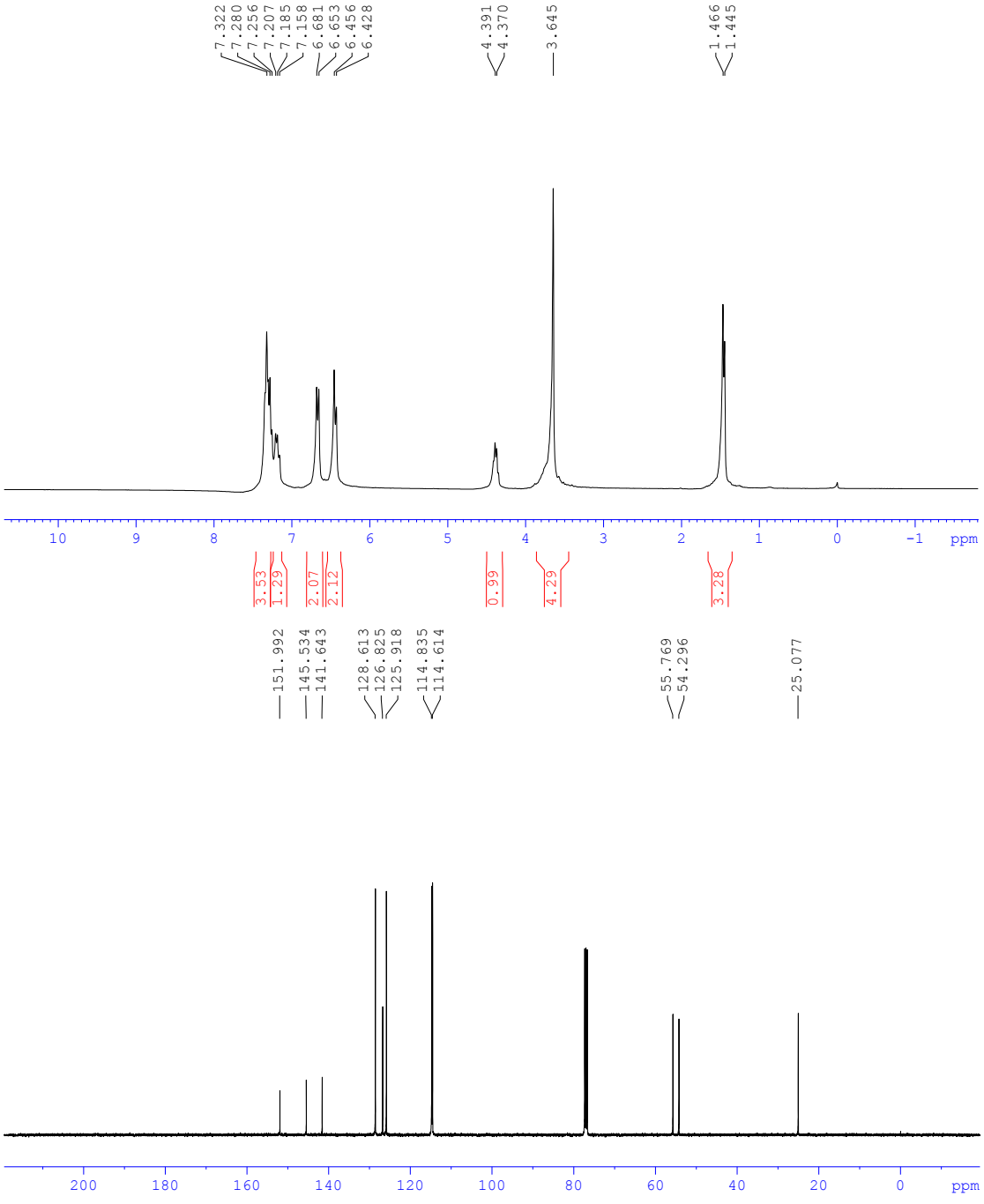

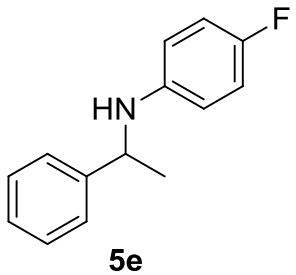

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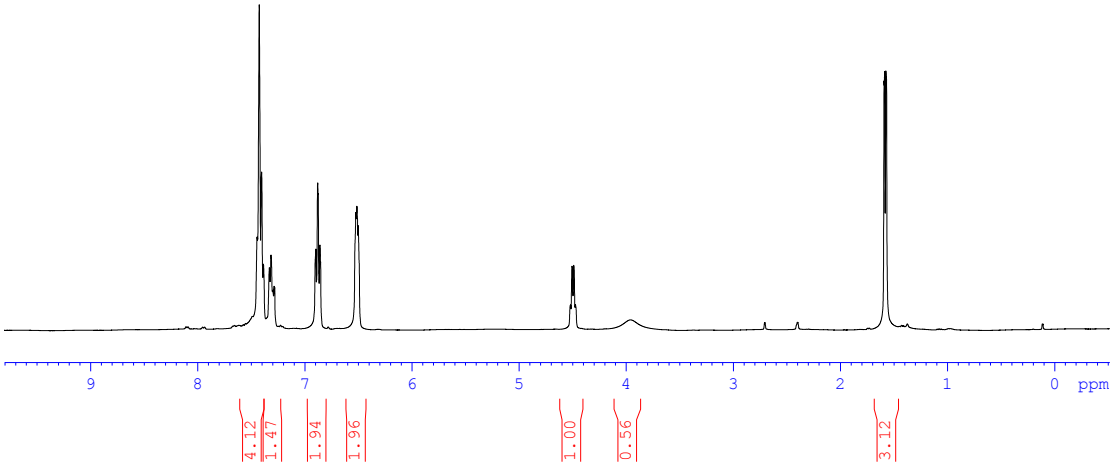

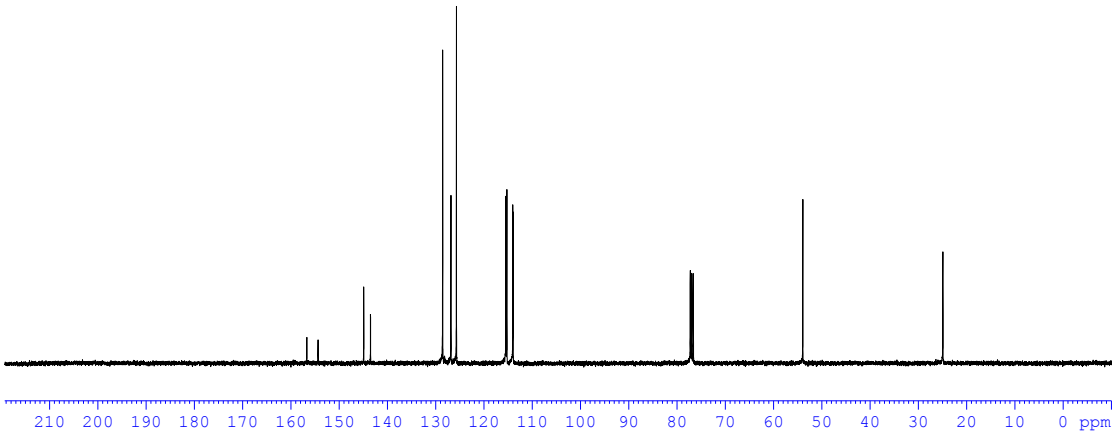

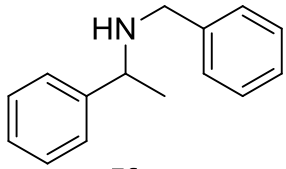
HN

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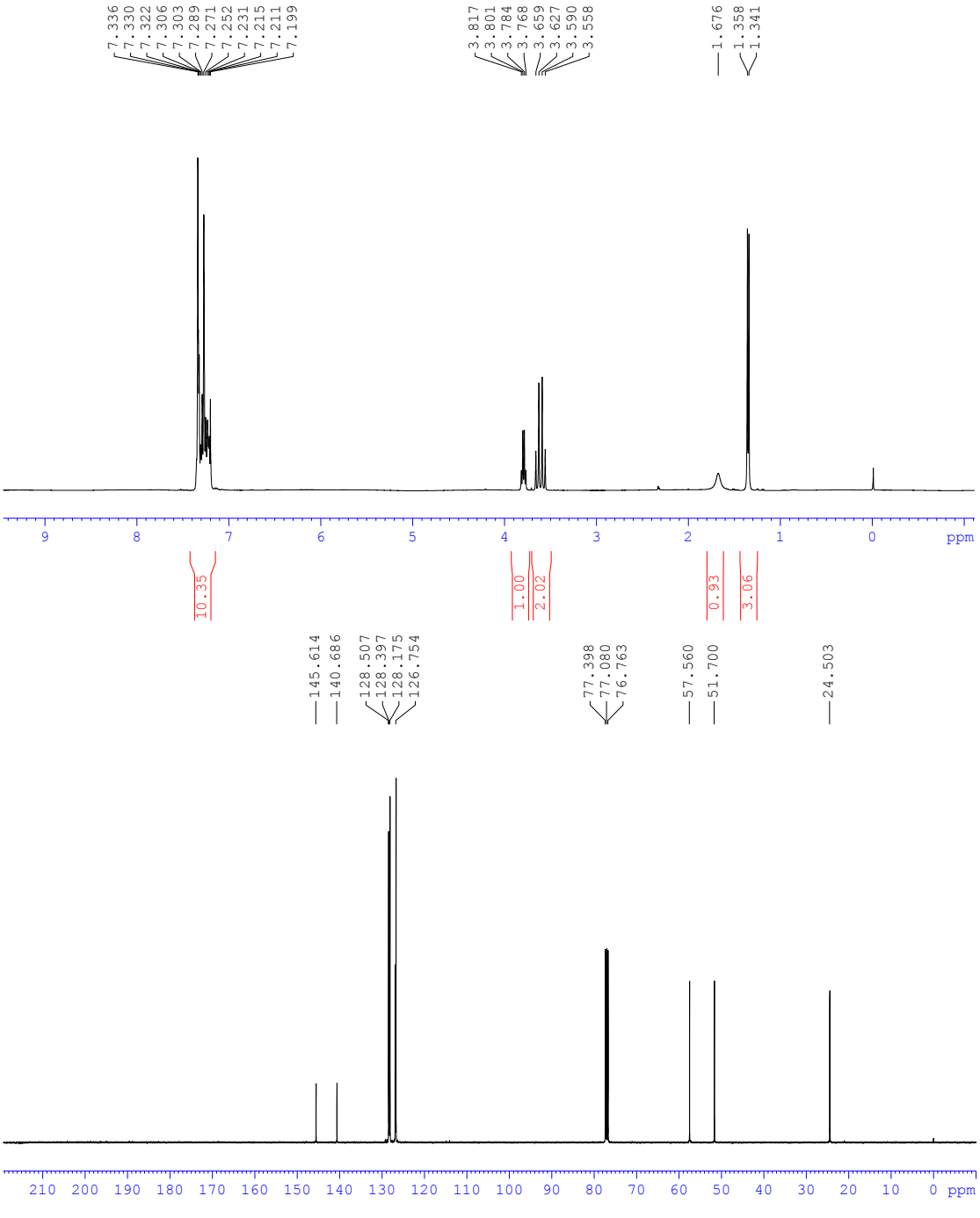
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3.768
3.659
3.627
3.590
3.558
1.676
1.358
1.341
9
8
7
6
5
4
3
2
1
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ppm
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1.00
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0.93
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128.175
126.754
77.398
77.080
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24.503
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200
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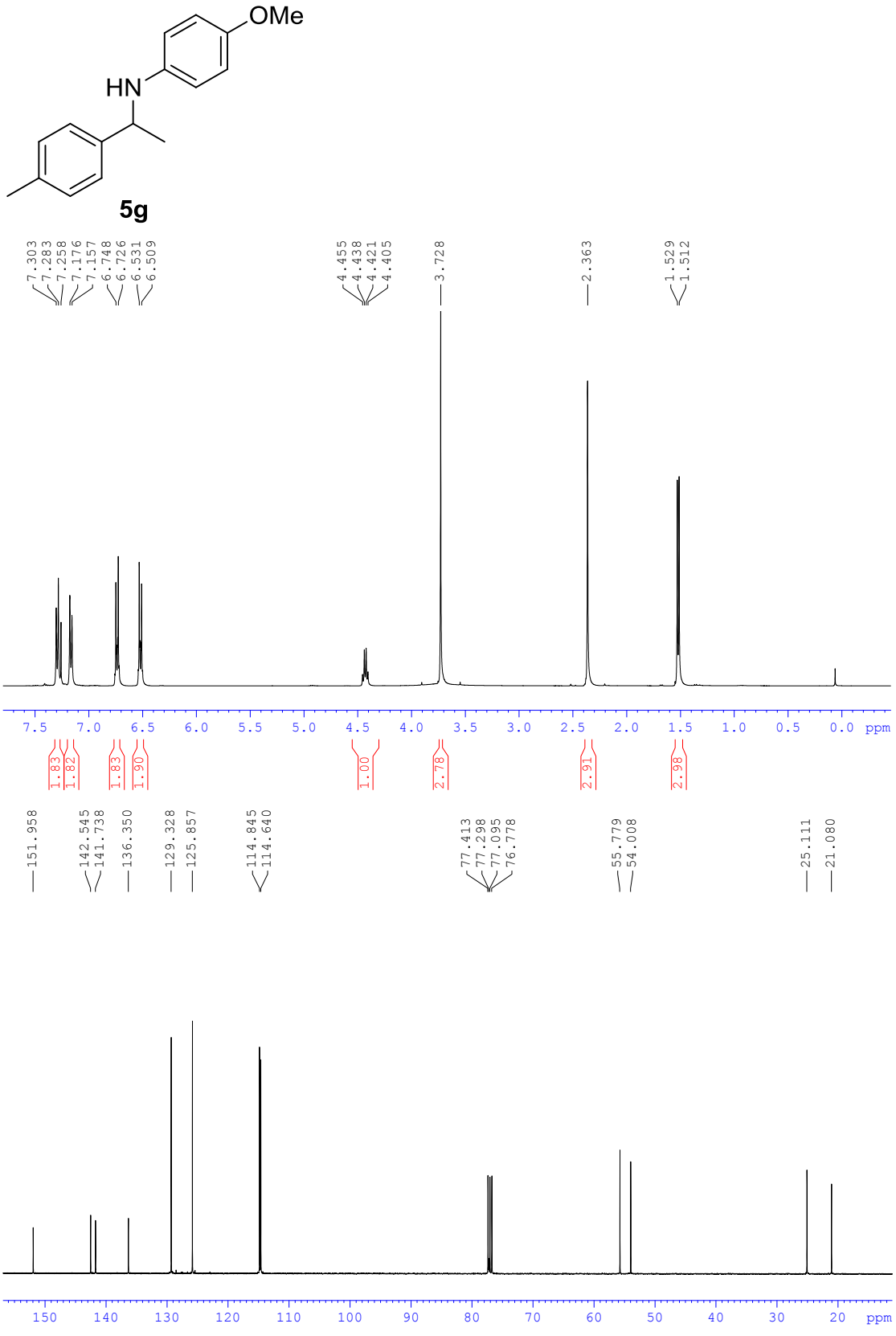
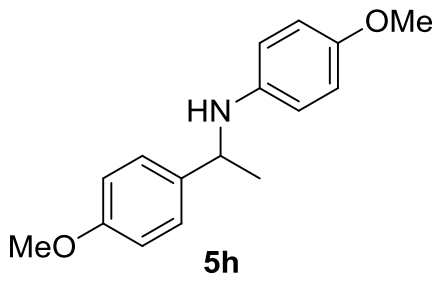
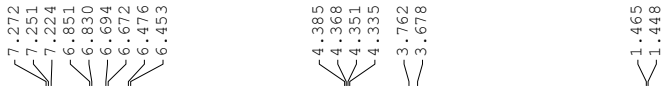
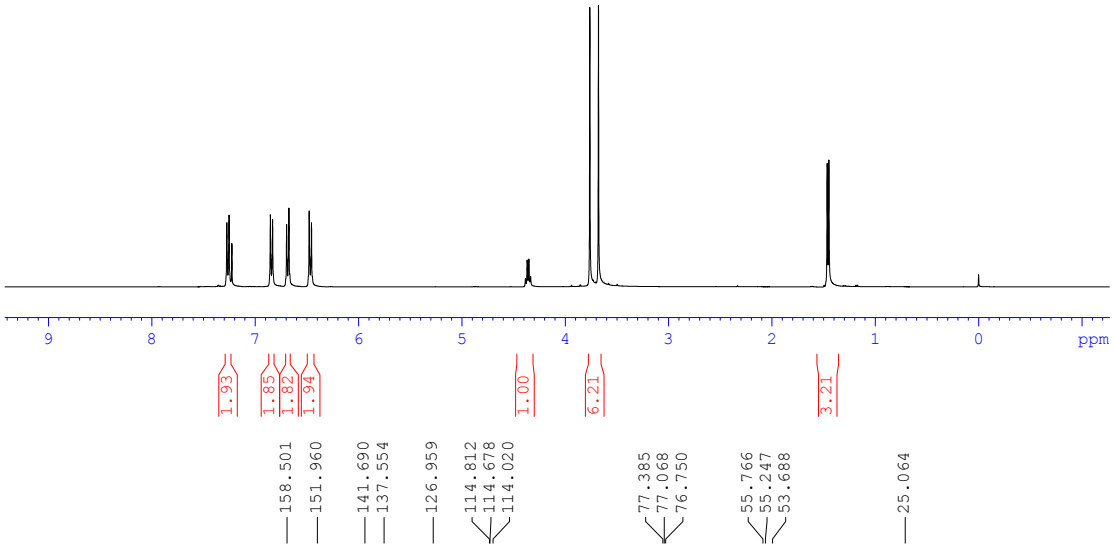
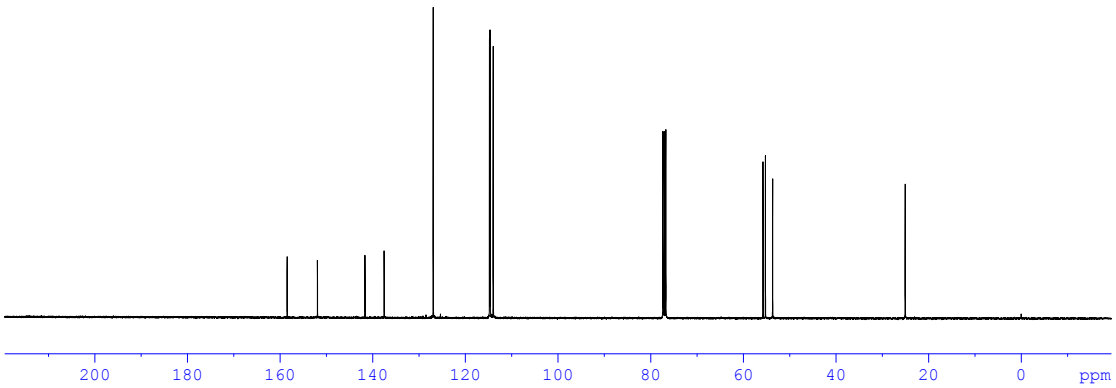


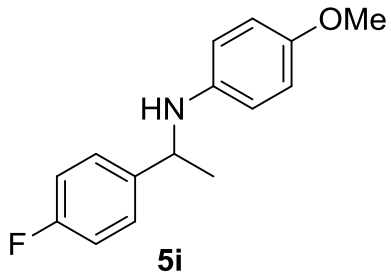


5h

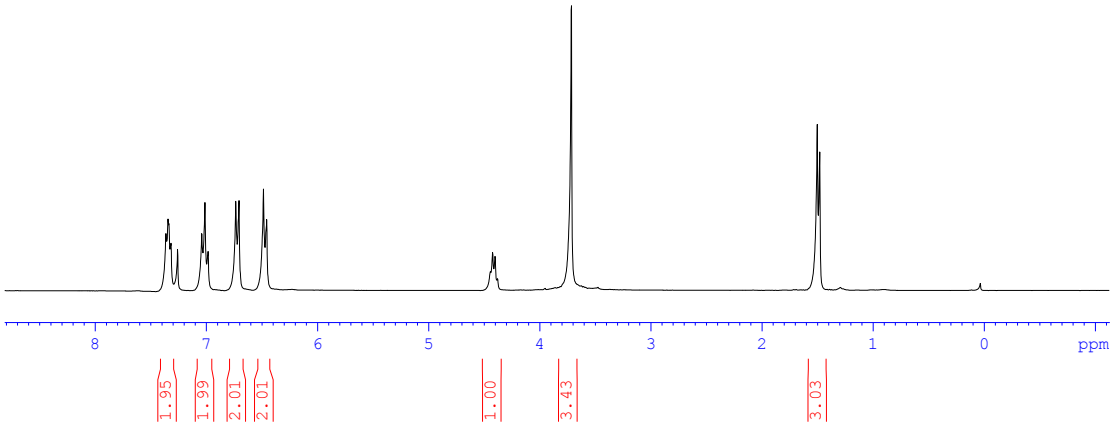


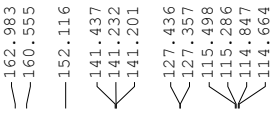


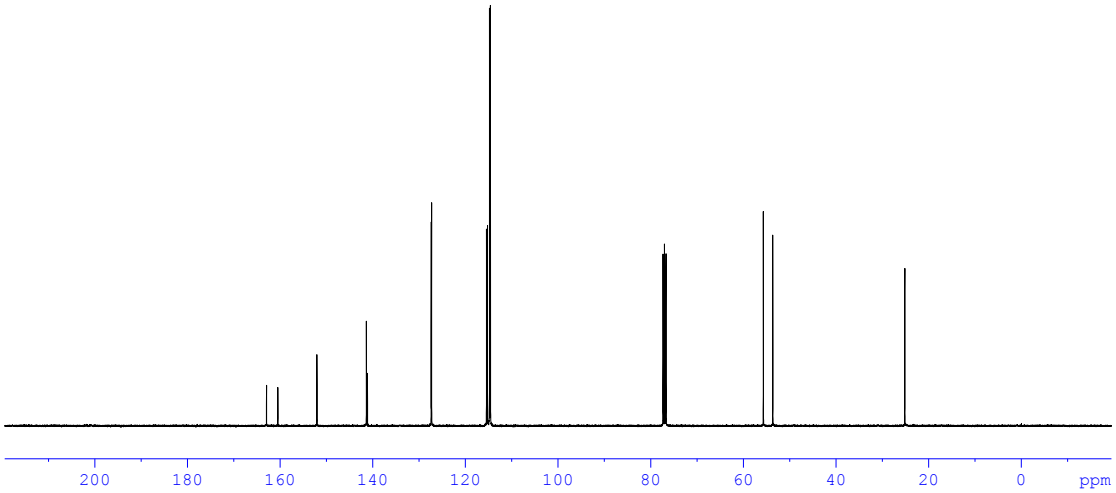


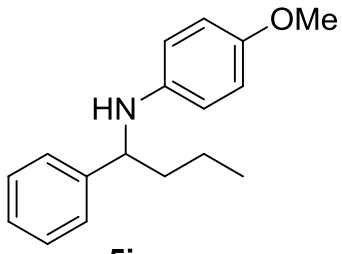


5i









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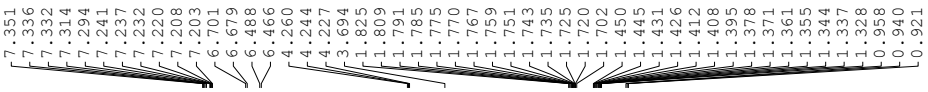

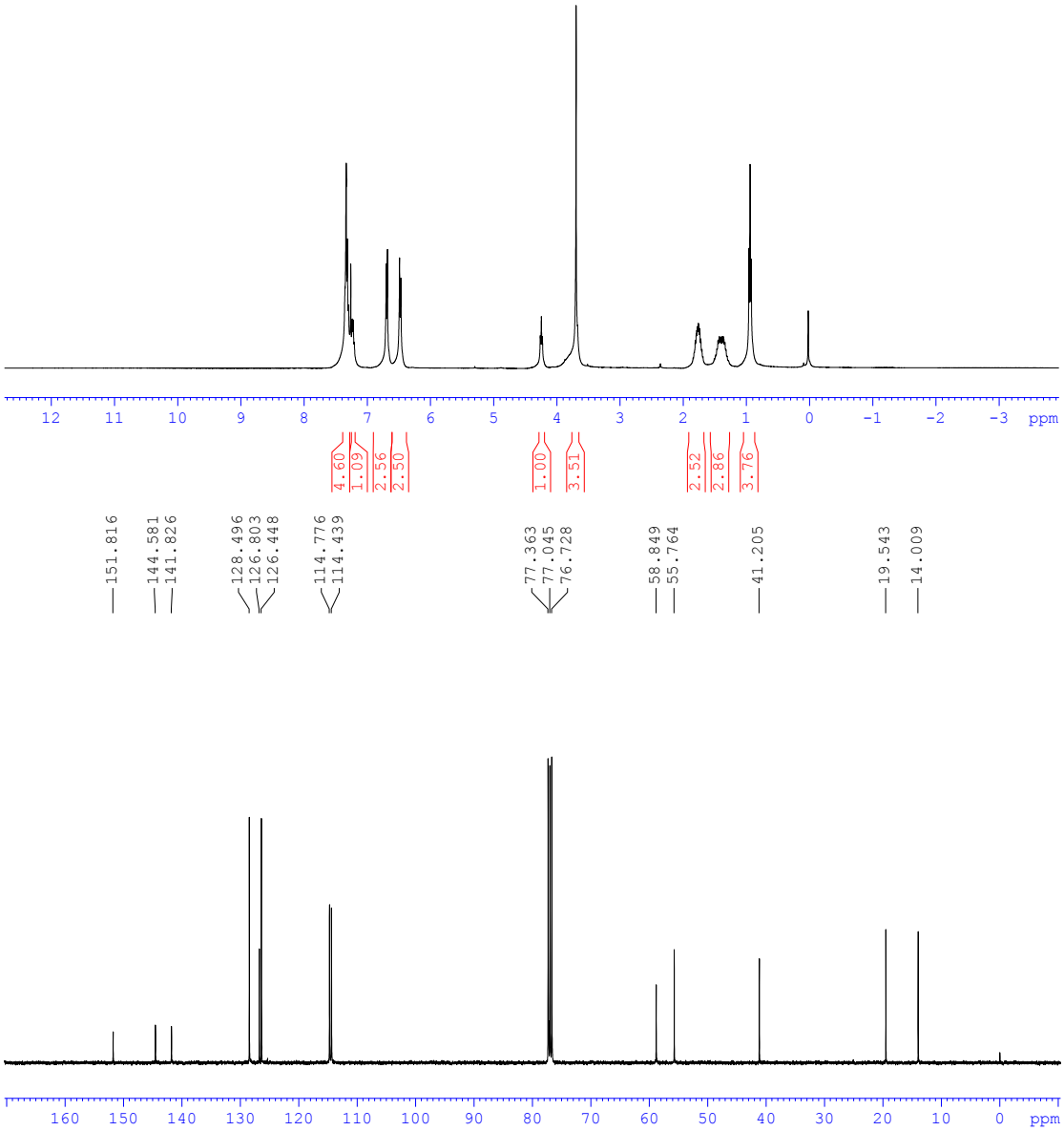

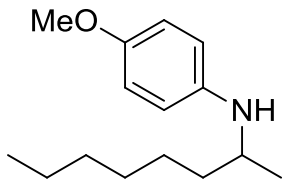

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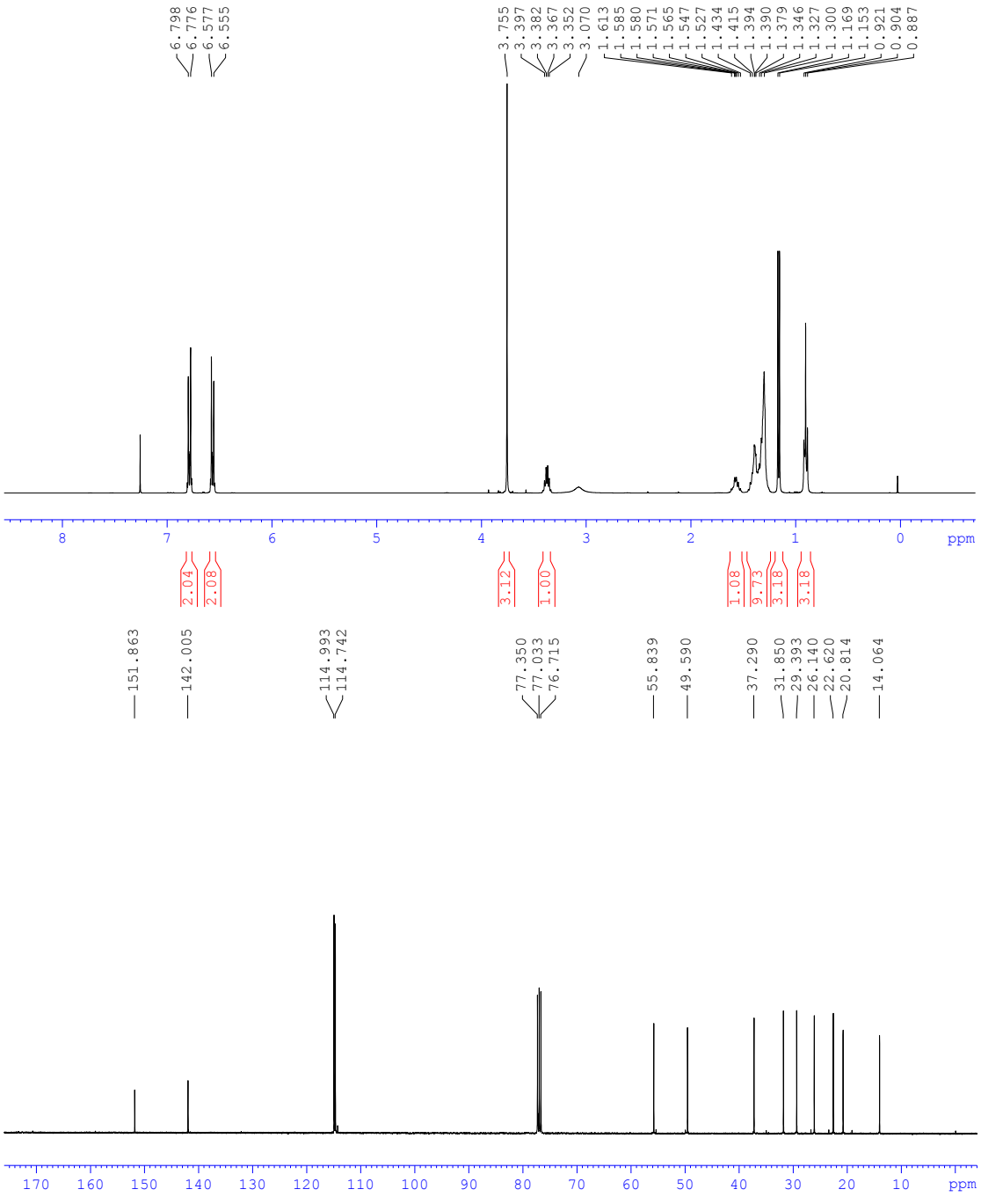
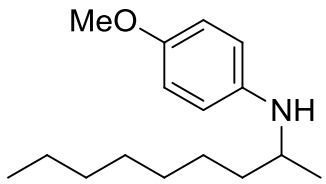
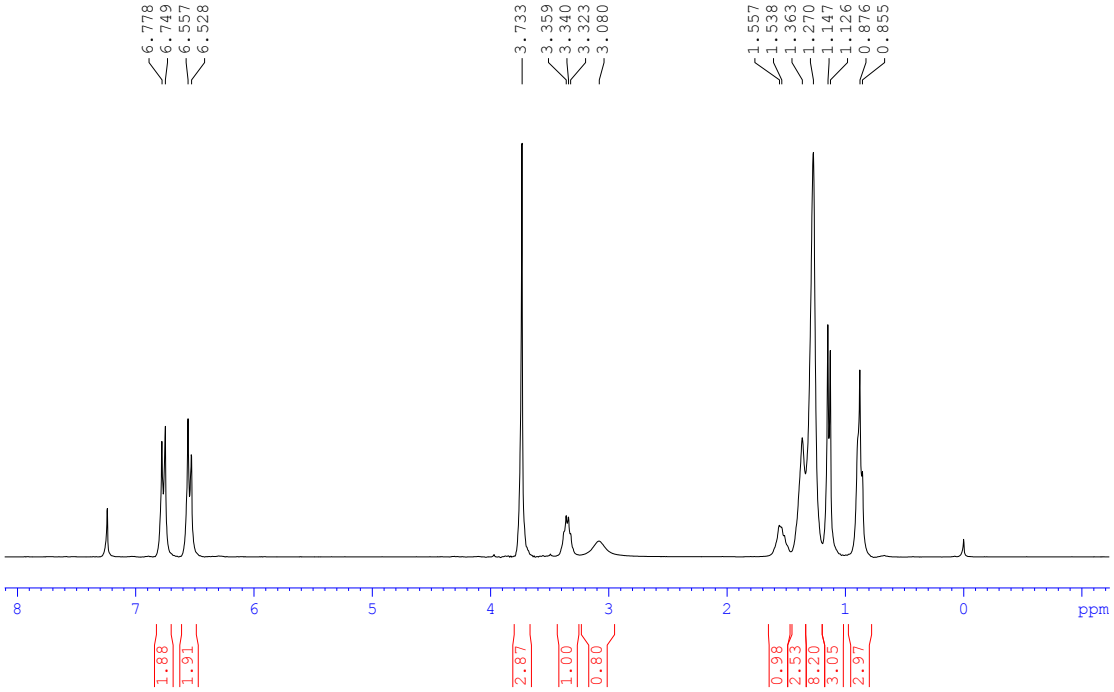
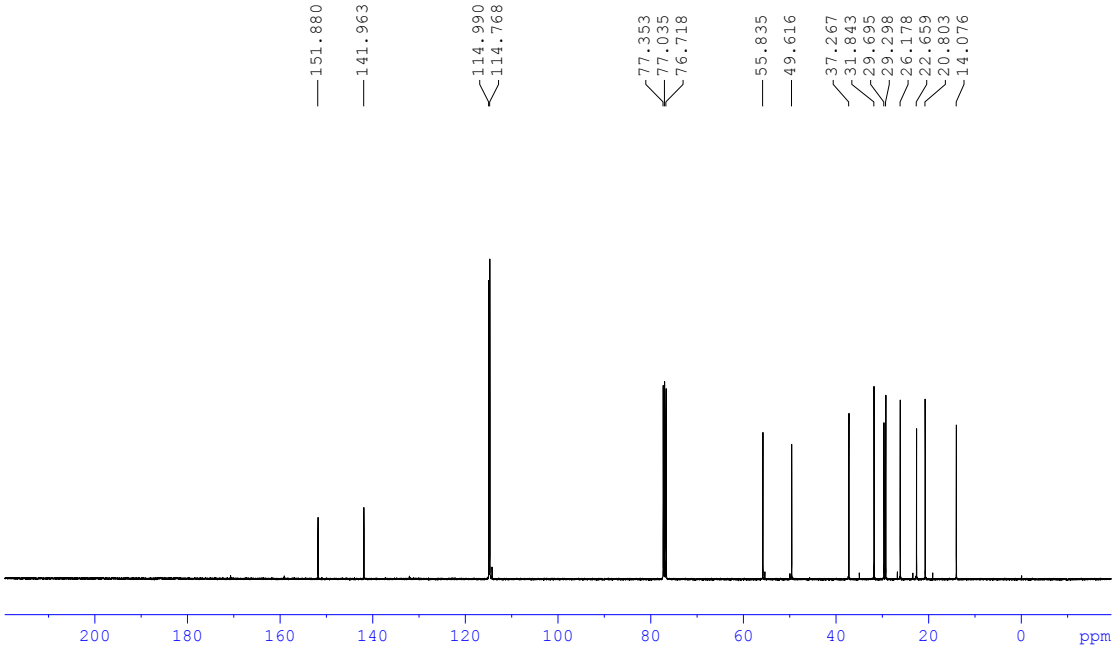


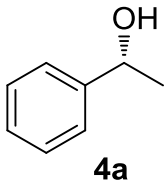


5l

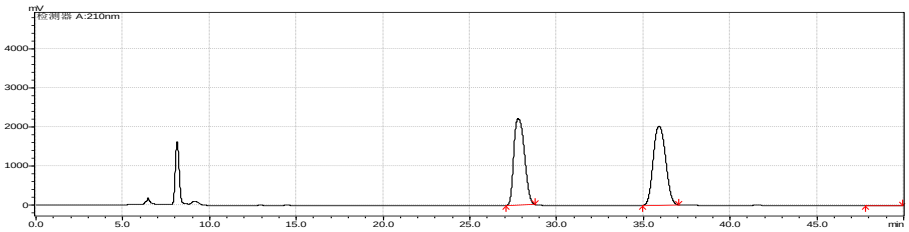


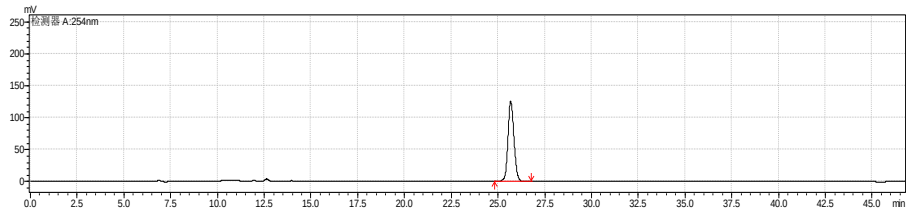


9. HPLC traces of chiral alcohols



4a

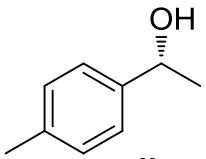




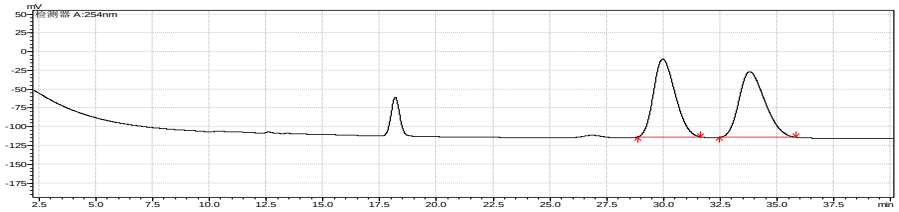
Peak results

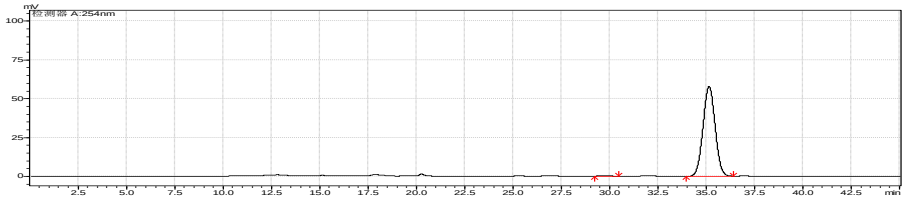
	Time	Area	Height	Area%
1	27.784	94615684	2216613	48.4104
2	35.899	94615672	2028015	51.5896
Total				100

	Time	Area	Height	Area%
1	25.673	2821638	125952	99.9758
2	34.689	684	22	0.0242
Total				100



4b

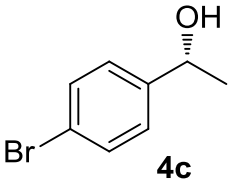




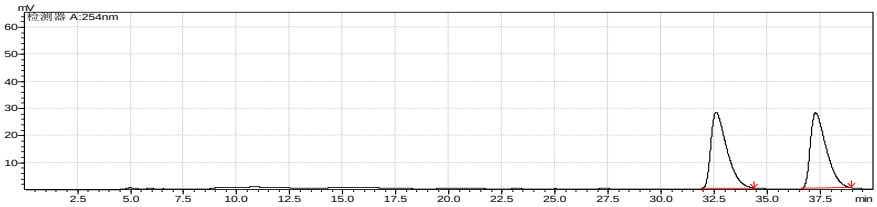
Peak results

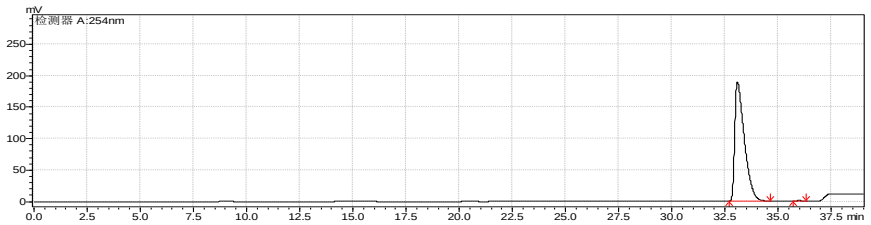
	Time	Area	Height	Area%
1	29.957	6896757	103863	49.9084
2	33.788	6922071	87559	50.0916
Total				100

	Time	Area	Height	Area%
1	29.731	17513	496	0.6899
2	35.142	2520926	57937	99.3101
Total				100



4c

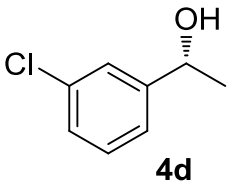




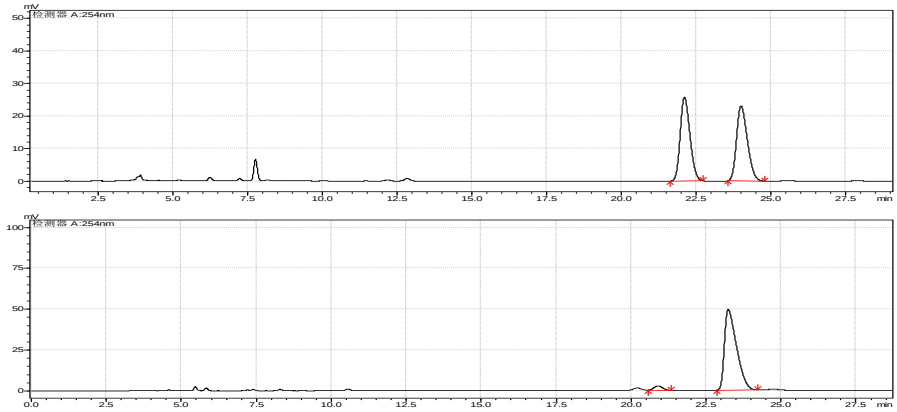
Peak results

	Time	Area	Height	Area%
1	32.588	1463940	28087	50.1584
2	37.277	1454692	27832	49.8416
Total				100

	Time	Area	Height	Area%
1	33.083	5978312	189601	99.7621
2	35.978	14257	718	0.2379
Total				100



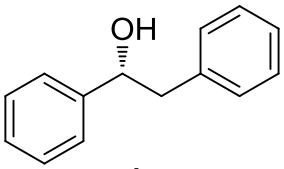
4d



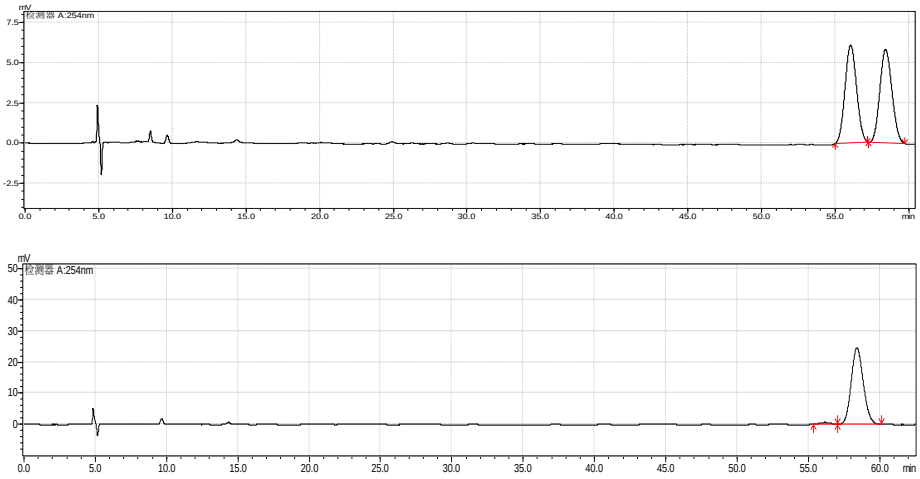
Peak results

	Time	Area	Height	Area%
1	22.103	585874	25840	50.008
2	23.996	585686	23106	49.992
Total				100

	Time	Area	Height	Area%
1	20.897	52430	2603	3.6419
2	23.237	1387195	49396	96.3581
Total				100



4e



Peak results

	Time	Area	Height	Area%
1	56.046	331030	6075	49.8192
2	58.418	333433	5810	50.1808
Total				100

	Time	Area	Height	Area%
1	56.159	30422	605	2.0514
2	58.394	1452552	24575	97.9486
Total				100