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Supporting information

Catalytic Enantioselective Amadori-Heyns Rearrangement of Racemic α-Hydroxy Ketones with Arylamines: Synthesis of Optically Active α-Arylamino Ketones

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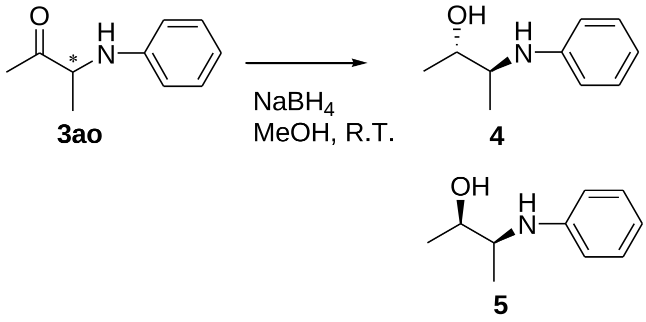
Absolute configuration determination of 3ao

Absolute configuration of **3ao** was assigned by its conversion to the corresponding β-amino alcohols (with either a 1,2-*syn* and 1,2-*anti* relationship) **4** and **5** and comparison of the specific rotation with reported value.



Comparison of $[\alpha]_D$ value obtained for compounds **4** ($[\alpha]_D^{27}$= +37.2 (*c* 0.43, CH_2Cl_2, ee 79%)) and **5** ($[\alpha]_D^{26}$= +18.1 (*c* 0.66, CH_2Cl_2, ee 79%)), to that presented in literature for *ent*-**4** (2*R*,3*R*)-3-(phenylamino)butan-2-ol ($[\alpha]_D^{20}$= -88.0 (c 1.07, CH_2Cl_2, ee 90%))[1] and *ent*-**5** (2*S*,3*R*)-3-(phenylamino)butan-2-ol ($[\alpha]_D^{20}$= -31.7 (c 1.04, $CHCl_3$, ee 96%))[2] allowed us to assign a *S* configuration at the 3 position.

Synthesis of 3-(phenylamino)butan-2-ol 4 and 5. To a solution of **3ao** (0.074g, 0.456 mmol) in MeOH (3 mL), $NaBH_4$ (0.022 g) was slowly added maintaining the pH = 5-6 by addition of glacial acetic acid. The reaction mixture was stirred at room temperature for 2h, then evaporated. The residue was disolved in NaOH (1mL) and the solution was extracted with $CHCl_3$. Evaporation of the organic layer gave an oil which was flash-chromatographed (silica gel, mixture of hexane/ether, 5:1→1:1) to give pure products **4** and **5** (0.03 g, 40% yield, diastereoisomeric ratio 40:60). The spectroscopic data are in accordance with those presented in literature.[1,2]

Experimental protocols

General Methods. ^{1}H NMR spectra were recorded at 500, 400 or 300 MHz at 27°C with $CDCl_3$ as solvent. Data are reported as follows: chemical shifts (δ), multiplicity, integration and coupling constants. ^{13}C NMR spectra were recorded operating respectively at 124, 100 or 75 MHz at 27°C with $CDCl_3$ as solvent. Infrared spectra were recorded on a FT-IR spectrophotometer. Low resolution mass spectral analyses were recorded in E.I. (70 eV) mode. Relative intensities are given in parentheses. Enantiomeric excesses of α-arylamino ketones were determined by HPLC, using a Chiralcel OJ, OD-H and Chiralpak AD-H analytical column with *i*-PrOH/hexane as eluent, using authentic racemic samples for reference comparison. Analytical thin layer chromatography was performed using 0.25 mm silica gel 60-F plates. Flash chromatography was performed using columns of 230-400 mesh silica gel 60 (0.040-0.063 mm). Yields refer to chromatographically pure materials. 3-hydroxy-2-butanon was purchased and used without further purification. 2-hydroxycyclohexanone was obtained by treating its dimer (purchased) with dilute (5%) HCl. The product was extracted with dichloromethane, dried, and stripped of solvent.[3] 3-hydroxy-4-phenylbutan-2-one and 2-hydroxypentan-3-one were synthesized by application of acetoacetate chemistry.[4]

General Procedure for α-Arylamination of α-Hydroxy Ketones.

In an ordinary vial equipped with a magnetic stir bar, β-isocupreidine (0.122 mmol) was suspended in toluene (0.5 mL) under argon atmosphere. After stirring at room temperature for 30 min, the α-hydroxy ketone **1** (4.06 mmol) was added, and the mixture was stirred for 30 min before the aniline **2** (0.406 mmol) was added. The mixture was allowed to stir at room temperature for 4-44 h. The crude reaction mixture was directly loaded on silica gel column without aqueous work-up and pure products were obtained by flash column chromatography (silica gel, mixture of hexane/ether). The racemates were synthesized using DMAP as catalyst at room temperature.

3-(4-methoxyphenylamino)butan-2-one 3aa: The spectroscopic data are in accordance with those presented in literature.[5] Yield 95% (74 mg); yellow oil. IR (neat): 3410, 2979, 1715, 1512, 1252 cm^{-1}. $[\alpha]_D^{22}$= +4.7 (*c* 2.11, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ: 1.37 (d, 3H, *J* = 7.0 Hz), 2.17 (s, 3H), 3.71 (s, 3H), 3.97 (q, 1H, *J* = 7.0 Hz), 6.51 (d, 2H, *J* = 9.0 Hz), 6.75 (2H, *J* = 9.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 18.0, 25.8, 55.7, 59.5, 114.4, 115.0, 140.7, 152.4, 210.6. MS *m/z*: 193 (M^+ (8)), 150 (100), 135 (14), 107 (10), 77 (5). Anal. Calcd. for $C_{11}H_{15}NO_2$; C, 68.37; H, 7.82; N, 7.25 Found: C, 68.35; H, 7.80; N, 7.29. The *ee* was determined to be 71% *ee* by HPLC (Chiralcel OD-H column, hexane/*i*-PrOH = 98:2, flow rate 1.0 mL/min, λ = 254 nm) t_R(major) = 18.53 min, t_R(minor) = 16.48 min.

3-(p-tolylamino)butan-2-one 3ab: The spectroscopic data are in accordance with those presented in literature.[5] Yield 68% (49 mg); orange oil. IR (neat): 3386, 2871, 1716, 1618, 1524 cm^{-1}. $[\alpha]_D^{24}$= +2.4 (*c* 4.82, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ: 1.31 (d, 3H, *J* = 7.0 Hz), 2.11 (s, 3H), 2.15 (s, 3H), 3.94 (q, 1H, *J* = 7.0 Hz), 6.40 (d, 2H, *J* = 8.0 Hz), 6.90 (d, 2H, *J* = 8.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 17.9, 20.3, 25.7, 58.9, 113.1, 127.1, 129.8, 144.2, 210.5. MS *m/z*: 177 (M^+ (10)), 134 (100), 119 (13), 91 (15), 65 (9), 43 (7). Anal. Calcd. for $C_{11}H_{15}NO$; C, 74.54; H, 8.53; N, 7.90 Found: C, 74.55; H, 8.50; N, 7.88. The *ee* was determined to be 74% *ee* by HPLC (Chiralcel OJ column, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) t_R(major) = 13.96 min, t_R(minor) = 9.80 min.

3-(4-ethylphenylamino)butan-2-one 3ac: Yield 58% (45 mg); yellow oil. IR (neat): 3399, 2968, 1720, 1622, 1528 cm^{-1}. $[\alpha]_D^{22}$= +2.2 (*c* 4.45, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ: 1.10 (t, 3H, *J* = 8.0 Hz), 1.31 (d, 3H, *J* = 7.0 Hz), 2.10 (s, 3H), 2.45 (q, 2H, *J* = 7.5 Hz), 3.94 (q, 1H, *J* = 7.0 Hz), 6.42 (d, 2H, *J* = 8.5 Hz), 6.92 (d, 2H, *J* = 8.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 15.7, 17.9, 25.6, 27.8, 58.8, 113.0, 128.6, 133.7, 144.4, 210.4. MS *m/z*: 191 (M^+ (19)), 148 (100), 119 (19), 77 (11), 43 (8). Anal. Calcd. for $C_{12}H_{17}NO$; C, 75.35; H, 8.96; N, 7.32 Found: C, 75.30; H, 9.00; N, 7.33.

The *ee* was determined to be 77% *ee* by HPLC (Chiralcel OJ column, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) t_R(major) = 11.66 min, t_R(minor) = 7.84 min.

3-(4-propylphenylamino)butan-2-one 3ad: Yield 60% (50 mg); yellow oil. IR (neat): 3386, 2964, 1712, 1614, 1524 cm^{-1}. $[\alpha]_D^{24}$= +2.0 (*c* 5.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.94 (t, 3H, *J* = 7.0 Hz), 1.42 (d, 3H, *J* = 7.0 Hz), 1.56-1.64 (m, 2H), 2.22 (s, 3H), 2.49 (t, 2H, *J* = 7.5 Hz), 4.05 (q, 1H, *J* = 7.0 Hz), 6.52 (d, 2H, *J* = 8.5 Hz), 7.01 (d, 2H, *J* = 8.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 13.7, 18.0, 24.7, 25.7, 37.0, 58.9, 113.0, 129.2, 132.2, 144.4, 210.5. MS *m/z*: 205 (M^+ (7)), 162 (100), 133 (13), 120 (13), 43 (6). Anal. Calcd. for $C_{13}H_{19}NO$; C, 76.06; H, 9.33; N, 6.82 Found: C, 76.09; H, 9.35; N, 6.79. The *ee* was determined to be 78% *ee* by HPLC (Chiralcel OJ column, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) t_R(major) = 10.25 min, t_R(minor) = 7.20 min.

3-(4-butylphenylamino)butan-2-one 3ae: Yield 54% (48 mg); yellow oil. IR (neat): 3395, 2930, 1720, 1622, 1520 cm^{-1}. $[\alpha]_D^{25}$= +2.2 (*c* 4,51 $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.93 (t, 3H, *J* = 7.5 Hz), 1.31-1.37 (m, 2H), 1.42 (d, 3H, *J* = 7.0 Hz), 1.52-1.59 (m, 2H), 2.21 (s, 3H), 2.51 (t, 2H, *J* = 8.0 Hz), 4.04 (q, 1H, *J* = 7.0 Hz), 6.51 (d, 2H, *J* = 8.5 Hz), 7.00 (d, 2H, *J* = 8.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 13.9, 18.0, 22.3, 25.7, 33.9, 34.6, 58.9, 113.0, 129.2, 132.4, 144.4, 210.5. MS *m/z*: 219 (M^+ (12)), 176 (100), 133 (19), 118 (12), 91 (7). Anal. Calcd. for $C_{14}H_{21}NO$; C, 76.67; H, 9.65; N, 6.39 Found: C, 76.70; H, 9.60; N, 6.41. The *ee* was determined to be 76% *ee* by HPLC (Chiralcel OJ column, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) t_R(major) = 8.34 min, t_R(minor) = 6.02 min.

3-(4-tert-butylphenylamino)butan-2-one 3af: Yield 61% (54 mg); yellow oil. IR (neat): 3399, 2968, 1716, 1618, 1520 cm^{-1}. $[\alpha]_D^{26}$= +2.5 (*c* 4.76, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.30 (s, 9H), 1.43 (d, 3H, *J* = 7.0 Hz), 2.23 (s, 3H), 4.05 (q, 1H, *J* = 7.0 Hz), 4.29 (brs, 1H), 6.54 (d, 2H, *J* = 6.5 Hz), 7.22 (d, 2H, *J* = 8.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 18.0, 25.7, 31.4, 33.8, 58.8, 112.6, 126.1, 140.7, 144.1, 210.4. MS *m/z*: 219 (M^+ (7)), 176 (100), 160 (16), 146 (7), 120 (10), 91

(4). Anal. Calcd. for $C_{14}H_{21}NO$; C, 76.67; H, 9.65; N, 6.39 Found: C, 76.63; H, 9.67; N, 6.38. The *ee* was determined to be 81% *ee* by HPLC (Chiralcel OJ column, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) t_R(major) = 16.18 min, t_R(minor) = 6.86 min.

3-(4-phenyl phenylamino)butan-2-one 3ag: Yield 65% (63 mg); yellow solid. M.p. 106-107 °C. IR (nujol): 3390, 3032, 1716, 1618, 1490 cm^{-1}. $[\alpha]_D^{25}$= +2.3 (*c* 1.73, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ: 1.33 (d, 3H, *J* = 7.0 Hz), 2.11 (s, 3H), 4.00 (q, 1H, *J* = 7.0 Hz), 4.36 (brs, 1H), 6.53 (d, 2H, *J* = 8.5 Hz), 7.25-7.41 (m, 7H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 17.9, 25.8, 58.5, 113.2, 126.1, 126.3, 128.0, 128.6, 130.9, 141.0, 145.8, 209.7. MS *m/z*: 239 (M^+ (10)), 196 (100), 169 (12), 152 (14), 115 (4). Anal. Calcd. for $C_{16}H_{17}NO$; C, 80.30; H, 7.16; N, 5.85 Found: C, 80.26; H, 7.19; N, 5.81. The *ee* was determined to be 67% *ee* by HPLC (Chiralcel OJ column, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) t_R(major) = 83.61 min, t_R(minor) = 38.36 min.

3-(4-phenoxyphenylamino)butan-2-one 3ah: Yield 67% (69 mg); yellow oil. IR (neat): 3386, 2981, 2359, 1720, 1494 cm^{-1}. $[\alpha]_D^{23}$= +1.0 (*c* 1.91, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ: 1.45 (d, 3H, *J* = 7.0 Hz), 2.24 (s, 3H), 4.07 (q, 1H, *J* = 7.0 Hz), 6.57-6.59 (m, 2H), 6.91-6.95 (m, 4H), 7.01-7.04 (m, 1H), 7.27-7.31 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 17.9, 25.8, 59.1, 114.1, 117.2, 121.2, 122.0, 129.4, 143.0, 148.2, 158.8, 209.8. MS *m/z*: 255 (M^+ (10)), 212 (100), 118 (20), 77 (8). Anal. Calcd. for $C_{16}H_{17}NO_2$; C, 75.27; H, 6.71; N, 5.49 Found: C, 75.31; H, 6.69; N, 5.48. The *ee* was determined to be 69% *ee* by HPLC (Chiralcel OJ column, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) t_R(major) = 28.37 min, t_R(minor) = 24.89 min.

3-(4-(methylthio)phenylamino)butan-2-one 3ai: Yield 73% (61 mg); yellow oil. IR (neat): 3377, 2986, 1712, 1605, 1499 cm^{-1}. $[\alpha]_D^{25}$= +5.6 (*c* 2.48, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ: 1.39 (d, 3H, *J* = 7.0 Hz), 2.18 (s, 3H), 2.38 (s, 3H), 4.03 (q, 1H, *J* = 7.0 Hz), 4.39 (brs, 1H), 6.49 (d, 2H, *J* = 8.5 Hz), 7.18 (d, 2H, *J* = 9.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 17.8, 18.9, 25.8, 58.5, 113.6, 125.1, 131.4, 145.2, 209.5. MS *m/z*: 209 (M^+ (18)), 166 (100), 151 (16), 119 (29), 43 (8). Anal. Calcd. for $C_{11}H_{15}NOS$; C, 63.12; H, 7.22; N, 6.69; S, 15.32 Found: C, 63.10; H, 7.20; N, 6.71; S, 15.35. The *ee* was determined to be 71% *ee* by HPLC (Chiralcel OJ column, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) t_R(major) = 27.80 min, t_R(minor) = 17.43 min.

3-(4-bromophenylamino)butan-2-one 3aj: Yield 44% (43 mg); yellow oil. IR (neat): 3386, 2981, 1716, 1597, 1494 cm^{-1}. $[\alpha]_D^{20}$= +5.5. (*c* 1.45, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ: 1.41 (d, 3H, *J* = 7.0 Hz), 2.21 (s, 3H), 4.03 (q, 1H, *J* = 7.0 Hz), 6.44 (d, 2H, *J* = 8.5 Hz), 7.25 (d, 2H, *J* = 9.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 17.6, 25.8, 58.4, 114.5, 116.6, 131.9, 132.0, 145.3, 209.2. MS *m/z*: 241 (M^+ (8)), 198 (100), 118 (100), 91 (23), 76 (20), 43 (37). Anal. Calcd. for $C_{10}H_{12}BrNO$; C, 49.61; H, 5.00; N, 5.79 Found: C, 49.66; H, 4.97; N, 5.83. The *ee* was determined to be 68% *ee* by HPLC (Chiralcel OD-H column, hexane/*i*-PrOH = 98:2, flow rate 1.0 mL/min, λ = 254 nm) t_R(major) = 14.67 min, t_R(minor) = 11.83 min.

3-(m-tolylamino)butan-2-one 3al: Yield 57% (41 mg); yellow oil. IR (neat): 3390, 2981, 1716, 1609, 1494 cm^{-1}. $[\alpha]_D^{23}$= +3.9 (*c* 4.09, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ: 1.43 (d, 3H, *J* = 7.0 Hz), 2.22 (s, 3H), 2.29 (s, 3H), 4.07 (q, 1H, *J* = 7.0 Hz), 6.38-6.41 (m, 2H), 6.57 (d, 1H, *J* = 7.5 Hz), 7.08 (t, 1H, *J* = 7.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 18.0, 21.5, 25.7, 58.6, 110.0, 113.7, 118.9, 129.2, 139.2, 146.5, 210.2. MS *m/z*: 177 (M^+ (6)), 134 (100), 119 (12), 91 (19), 65 (10), 43 (14). Anal. Calcd. for $C_{11}H_{15}NO$; C, 74.54; H, 8.53; N, 7.90 Found: C, 74.52; H, 8.51; N, 7.93. The *ee* was determined to be 73% *ee* by HPLC (Chiralcel OJ column, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) t_R(major) = 11.76 min, t_R(minor) = 8.38 min.

3-(3,4-dimethoxyphenylamino)butan-2-one 3am: Yield 74% (67 mg); yellow oil. IR (neat): 3382, 2832, 1716, 1524, 1235 cm^{-1}. $[\alpha]_D^{22}$= +7.9 (*c* 3.27, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ: 1.39 (d, 3H, *J* = 7.5 Hz), 2.19 (s, 3H), 3.78 (s, 3H), 3.82 (s, 3H), 4.00 (q, 1H, *J* = 7.0 Hz), 6.04-6.06 (m, 1H), 6.22 (d, 1H, *J* = 2.5 Hz), 6.71 (d, 1H, *J* = 8.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 17.9, 25.7, 55.6, 56.6, 59.4, 99.3, 103.5, 113.1, 141.2, 141.9, 150.0, 210.5. MS *m/z*: 223 (M^+ (14)), 180 (100), 164 (18), 149 (8), 79 (7), 43 (6). Anal. Calcd. for $C_{12}H_{17}NO_3$; C, 64.55; H, 7.67; N, 6.27 Found: C, 64.54; H, 7.70; N, 6.25. The *ee* was determined to be 65% *ee* by HPLC (Chiralcel OJ column, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) t_R(major) = 33.03 min, t_R(minor) = 27.16 min.

3-(o-tolylamino)butan-2-one 3an: The spectroscopic data are in accordance with those presented in literature.[5] Yield 26% (19 mg); yellow oil. IR (neat): 3416, 2981, 1716, 1609, 1511 cm^{-1}. $[\alpha]_D^{22}$= +17.8 (*c* 1.9, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.48 (d, 3H, *J* = 7.0 Hz); 2.23 (s, 3H), 2.24 (s, 3H), 4.13 (q, 1H, *J* = 7.0 Hz), 4.36 (brs, 1H), 6.47 (d, 1H, *J* = 8.0 Hz), 6.70 (t, 1H, *J* = 7.5 Hz), 7.09-7.11 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 17.4, 18.1, 25.6, 58.5, 109.7, 117.4, 122.3, 127.1, 130.4, 144.4, 209.9. MS *m/z*: 177 (M^+ (7)), 134 (100), 118 (17), 91 (19), 65 (11), 43 (13). Anal. Calcd. for $C_{11}H_{15}NO$; C, 74.54; H, 8.53; N, 7.90 Found: C, 74.55; H, 8.55; N, 7.91. The *ee* was determined to be 11% *ee* by HPLC (Chiralcel OJ column, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) t_R(major) = 9.11 min, t_R(minor) = 8.03 min.

3-(phenylamino)butan-2-one 3ao: The spectroscopic data are in accordance with those presented in literature.[6] Yield 37% (24 mg); yellow solid. M.p. 51-52°C. IR (nujol): 3390, 2368, 1716, 1605, 1511 cm^{-1}. $[\alpha]_D^{25}$= +4.1 (*c* 1.92, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.43 (d, 3H, *J* = 7.0 Hz), 2.22 (s, 3H), 4.08 (q, 1H, *J* = 7.0 Hz), 6.58 (d, 2H, *J* = 8.0 Hz), 6.74 (t, 1H, *J* = 7.5 Hz), 7.17-7.21 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 17.9, 25.7, 58.6, 113.0, 117.9, 129.4, 146.4, 210.0. MS *m/z*: 163 (M^+ (7)), 120 (100), 91 (6), 77 (19), 43 (9). Anal. Calcd. for $C_{10}H_{13}NO$; C, 73.59; H, 8.03; N, 8.58 Found: C, 73.53; H, 8.05; N, 8.57. The *ee* was determined to be 79% *ee* by HPLC (Chiralcel OJ column, hexane/*i*-PrOH = 90:10, flow rate 1.0 mL/min, λ = 254 nm) t_R(major) = 13.89 min, t_R(minor) = 10.34 min.

3-(4-methoxyphenylamino)-1-phenylbutan-2-one 3ba: The spectroscopic data are in accordance with those presented in literature.[7] Yield 82% (89 mg); white solid. M.p. 82-84°C. IR (nujol): 3390, 2832, 1720, 1516, 1239 cm^{-1}. $[\alpha]_D^{27}$= +2.2. (*c* 0.87, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.38 (d, 3H, *J* = 7.2 Hz), 3.73 (s, 3H), 3.81 (ABq, 2H, *J* = 15.6 Hz, *J* = 25.6 Hz), 4.11 (q, 1H, *J* = 6.8 Hz), 6.48 (d, 2H, *J* = 8.8 Hz), 6.74 (d, 2H, *J* = 8.8 Hz), 7.16 (d, 2H, *J* = 7.6 Hz), 7.24-7.33 (m, 3H). ^{13}C

NMR (100 MHz, $CDCl_3$) δ: 18.1, 45.6, 55.7, 58.6, 114.6, 114.9, 127.0, 128.6, 129.5, 133.6, 140.4, 152.5, 210.1. MS *m/z*: 269 (M^+ (6)), 150 (100), 135 (5), 91 (10). Anal. Calcd. for $C_{17}H_{19}NO_2$; C, 75.81; H, 7.11; N, 5.20 Found: C, 75.78; H, 7.13; N, 5.17. The *ee* was determined to be 61% *ee* by HPLC (Chiralpak AD-H column, hexane/*i*-PrOH = 90:10, flow rate 1.0 mL/min, λ = 254 nm) t_R(major) = 17.18 min, t_R(minor) = 14.61 min.

3-(4-methoxyphenylamino)pentan-2-one 3ca: Yield 73% (61 mg); yellow oil. IR (neat): 3382, 2973, 1716, 1520, 1239 cm^{-1}. $[\alpha]_D^{25}$= -1.3. (*c* 2.89, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ: 0.93 (t, 3H, *J* = 7.6 Hz), 1.67-1.74 (m, 1H), 1.85-1.92 (m, 1H), 2.15 (s, 3H), 3.72 (s, 3H), 3.88 (t, 1H, *J* = 6.0 Hz), 4.05 (brs, 1H), 6.53 (d, 2H, *J* = 8.4 Hz), 6.75 (d, 2H, *J* = 8.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 9.5, 24.8, 26.3, 55.7, 65.3, 114.4, 114.9, 141.0, 152.3, 210.5. MS *m/z*: 207 (M^+ (12)), 164 (100), 149 (12), 122 (20), 107 (10), 43 (27). Anal. Calcd. for $C_{12}H_{17}NO_2$; C, 69.54; H, 8.27; N, 6.76 Found: C, 69.50; H, 8.32; N, 6.71. The *ee* was determined to be 73% *ee* by HPLC (Chiralcel OJ column, hexane/*i*-PrOH = 70:30, flow rate 1.0 mL/min, λ = 254 nm) t_R(major) = 12.05 min, t_R(minor) = 10.19 min.

2-(4-methoxyphenylamino)cyclohexanone 3da: The spectroscopic data are in accordance with those presented in literature.[8] Yield 62% (55 mg); yellow solid. M.p. 100-102 °C. IR (nujol): 2947, 2368, 1716, 1516, 1239 cm^{-1}. $[\alpha]_D^{28}$= +19.7 (*c* 1.92, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ: 1.34-1.42 (m, 1H), 1.58-1.78 (m, 2H), 1.84-1.88 (m, 1H), 2.05-2.10 (m, 1H), 2.30-2.37 (m, 1H), 2.48-2.58 (m, 2H), 3.66 (s, 3H), 3.83-3.86 (m, 1H), 6.51 (d, 2H, *J* = 5.4 Hz), 6.70 (d, 2H, *J* = 5.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 24.1, 28.0, 35.9, 41.1, 55.8, 62.9, 114.5, 114.9, 140.7, 152.3, 208.7. MS *m/z*: 219 (M^+ (80)), 191 (44), 176 (15), 162 (100), 149 (56), 134 (32). Anal. Calcd. for $C_{13}H_{17}NO_2$; C, 71.21; H, 7.81; N, 6.39 Found: C, 71.24; H, 7.78; N, 6.37. The *ee* was determined to be 73% *ee* by HPLC (Chiralcel OD-H column, hexane/*i*-PrOH = 98:2, flow rate 1.0 mL/min, λ = 254 nm) t_R(major) = 19.15 min, t_R(minor) = 16.56 min.

References

(1) K. Arai, S. Lucarini, M. M. Salter, K. Ohta, Y. Yasuhiro, S. Kobayashi, *J. Am. Chem. Soc*. 2007, **129**, 8103.

(2) J.-H. Xie, S. Liu, W.-L. Kong, W.-J. Bai, X.-C. Wang, L.-X. Wang, Q.-L. Zhou, *J. Am. Chem. Soc*. 2009, **131**, 4222.

(3) S. Gatling, J. E. Jackson, *J. Am. Chem. Soc*. 1999, **121**, 8655.

(4) G. Scheid, W. Kuit, E. Ruijter, R. V. A. Orru, E. Henke, U. Bornscheuer, L. A. Wessjohann, *Eur. J. Org. Chem.* 2004, 1063.

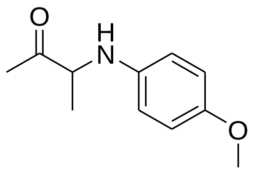
(5) B. Alcaide, O. Arjona, R. F. de la Pradilla, J. Plumet, I. M. Rodriguez-Campos, M. J. Santesmases, *J. Chem. Res. Miniprint* 1988, **3**, 932.

(6) A. Fürstner, M. Alcarazo, V. César, C. W. Lehmann, *Chem. Commun.*, 2006, 2176.

(7) T. Satoh, Y. Kaneko, K. Sakata, K. Yamakawa, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 457.

(8) S. Liu, J.-H. Xie, W. Li, W.-L. Kong, L.-X. Wang, Q.-L. Zhou, *Org. Lett.* 2009, **11**, 4994.

Copies of NMR spectra



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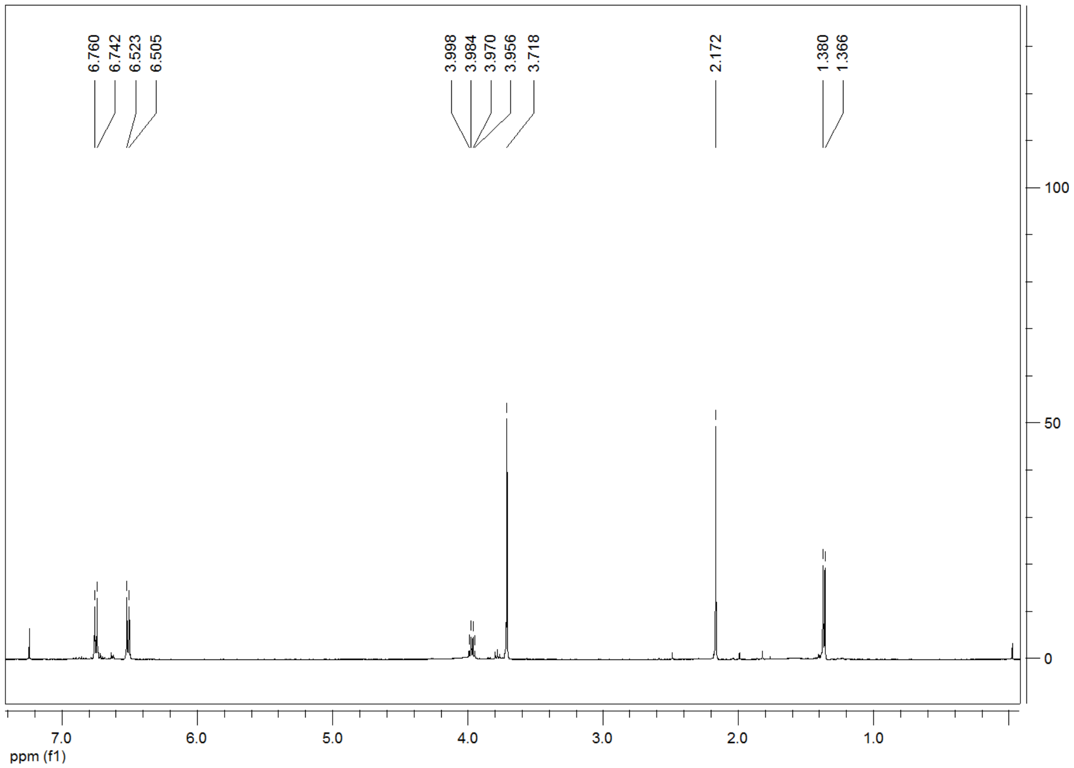

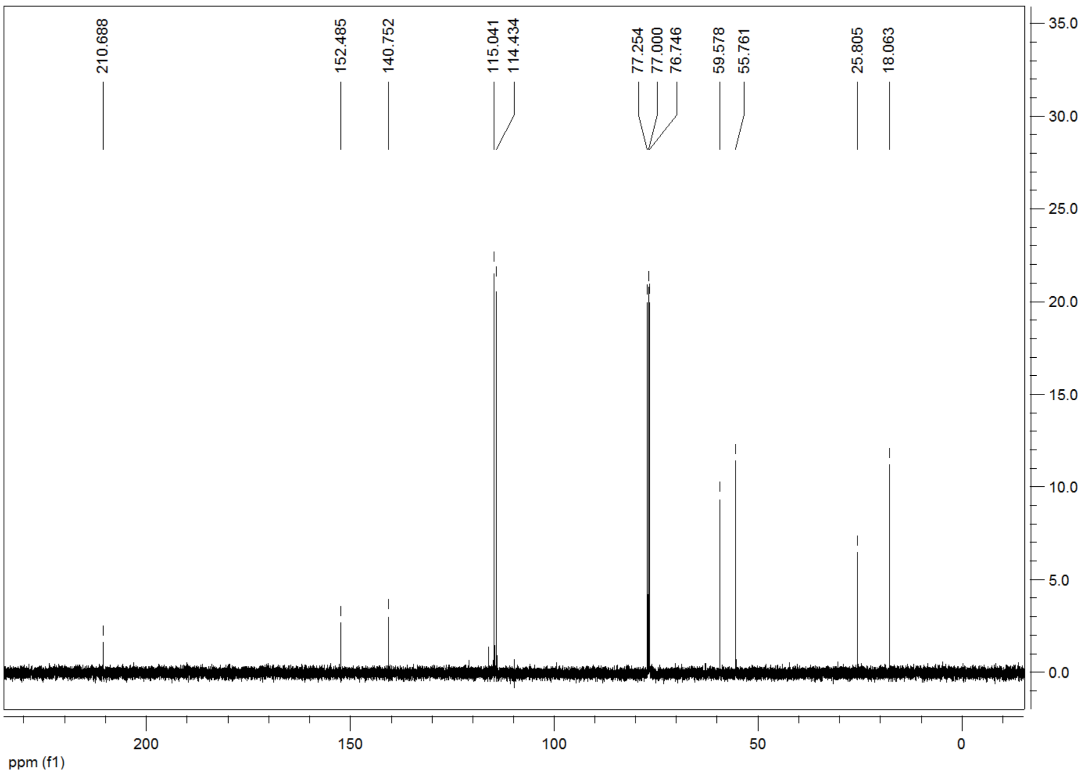

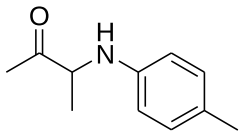

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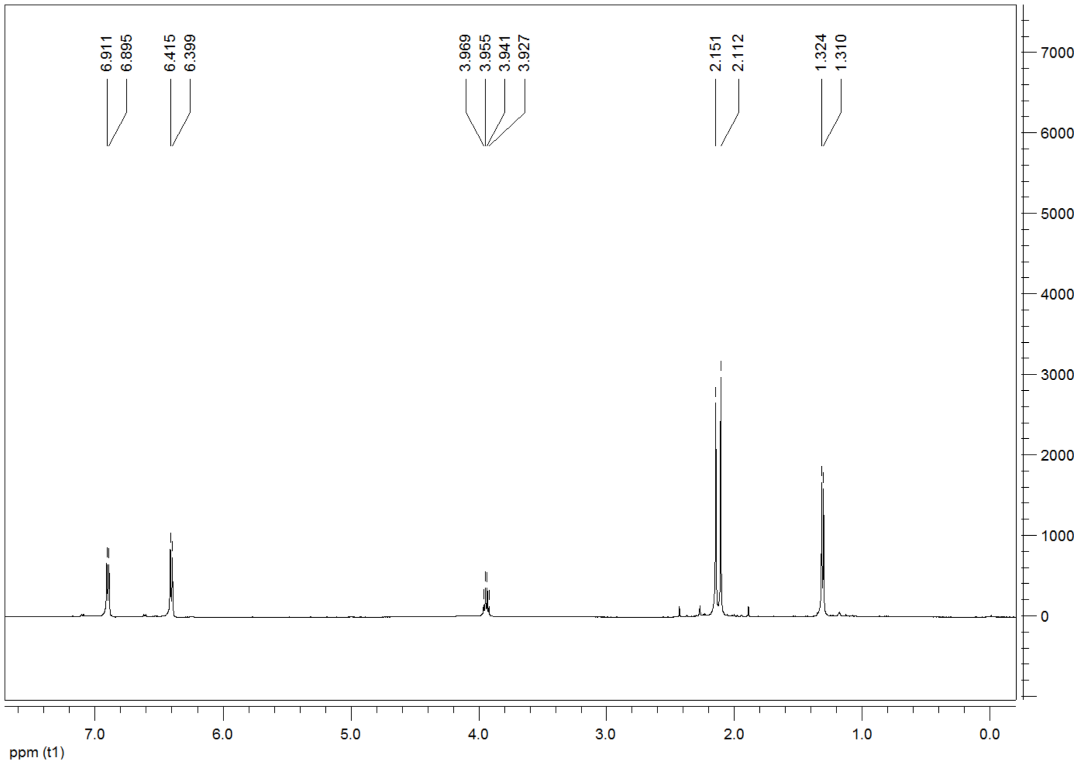
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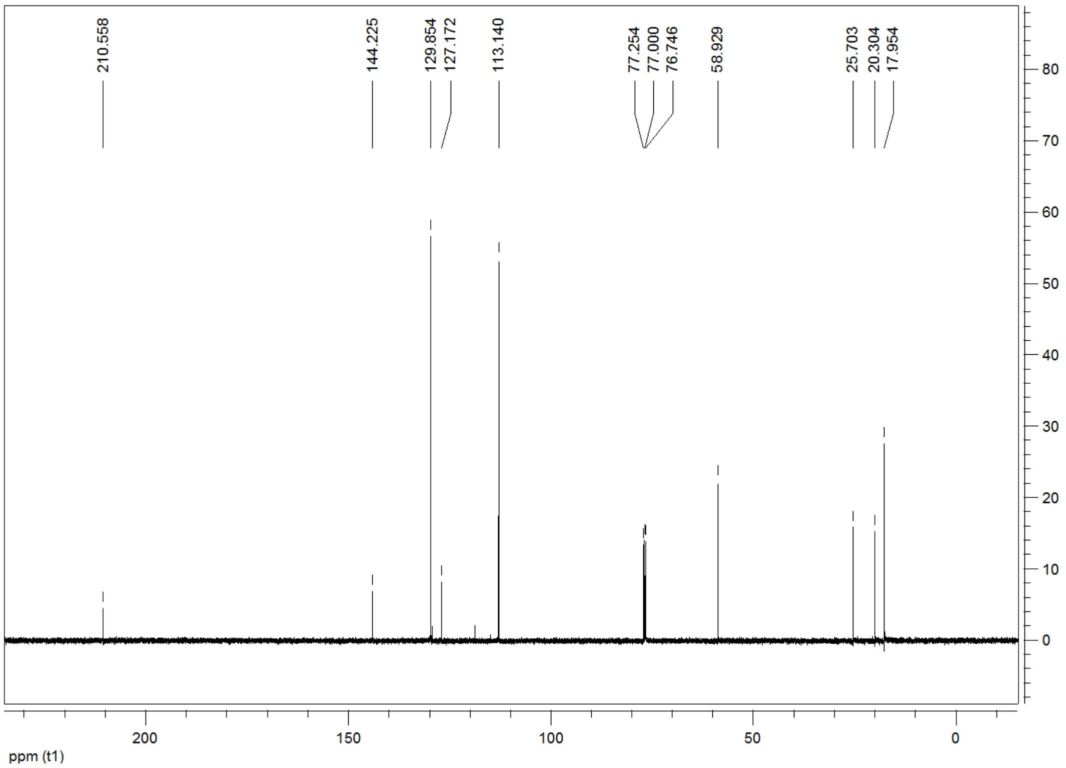
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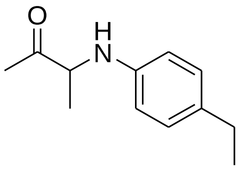

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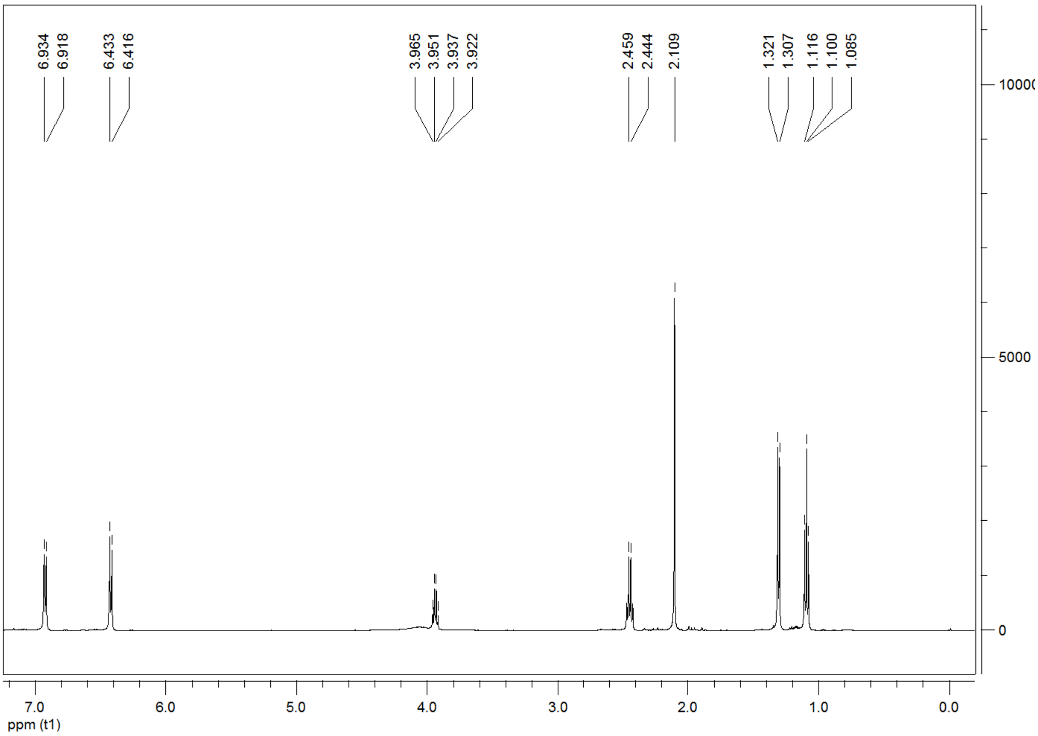
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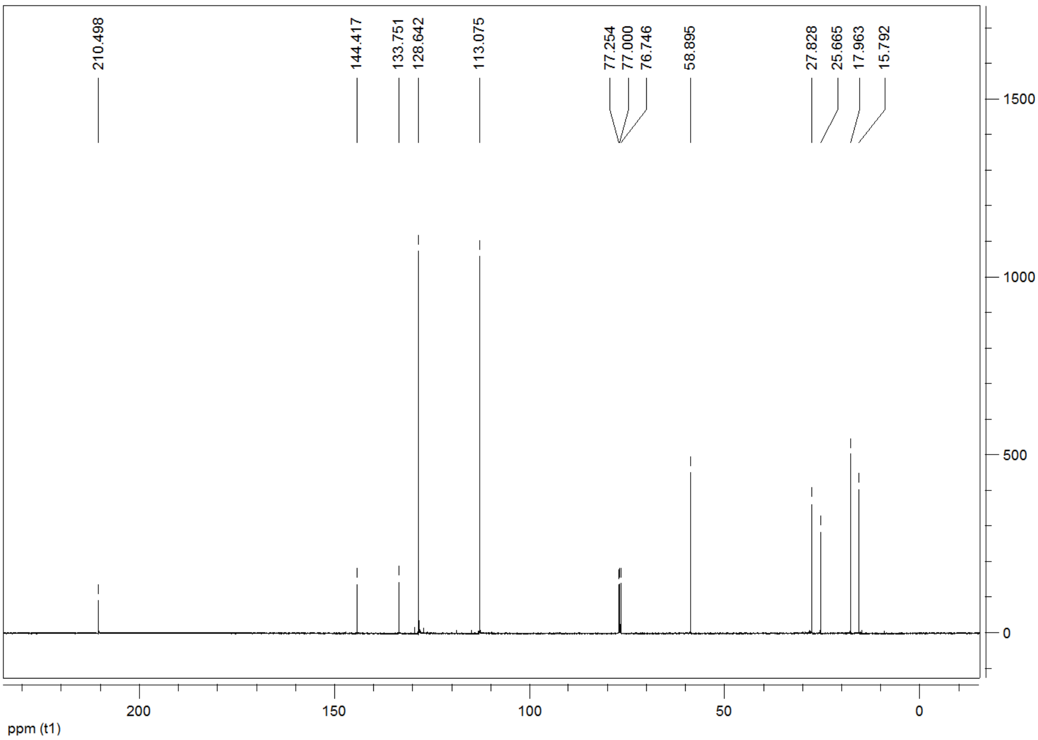
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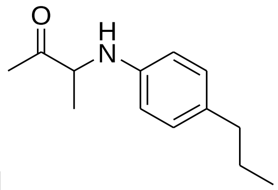
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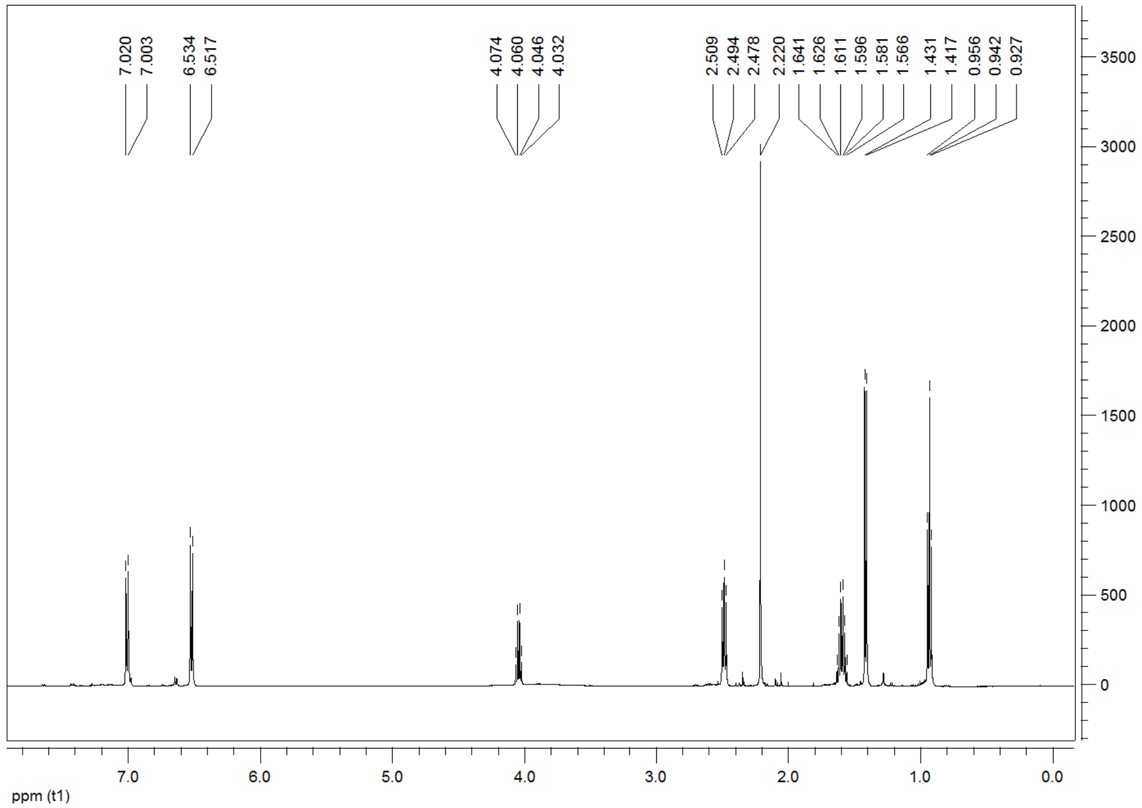
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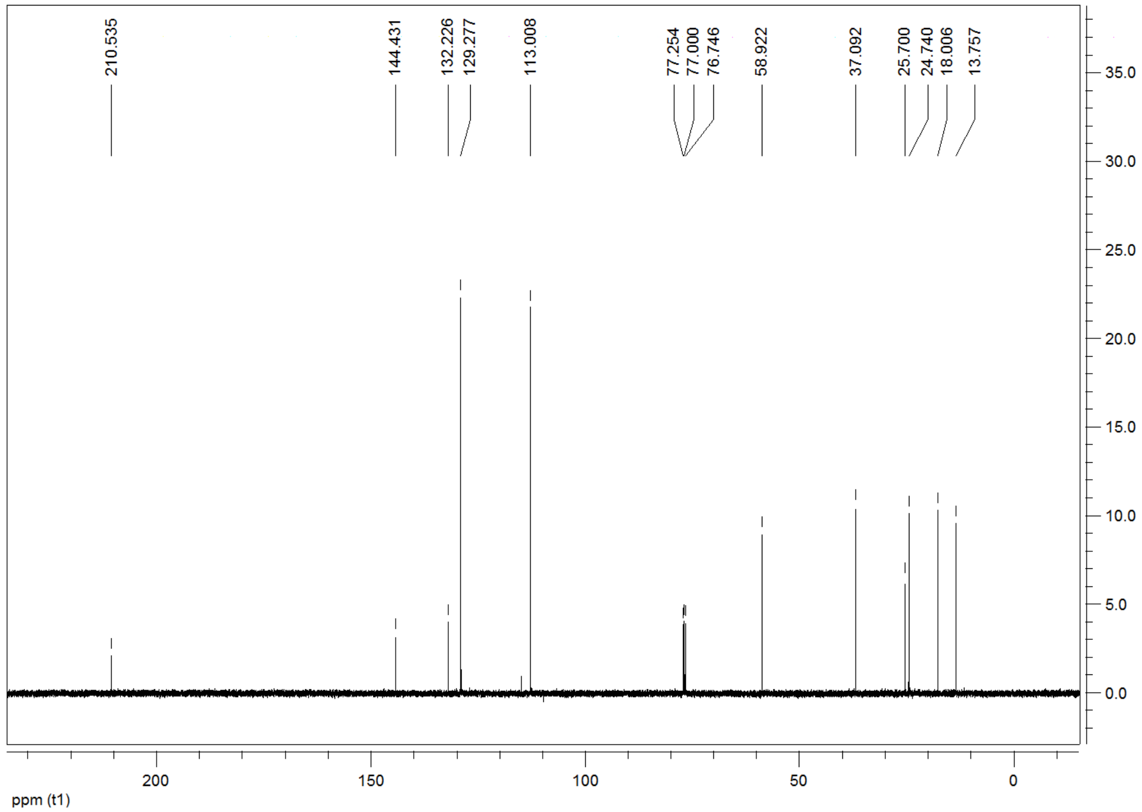
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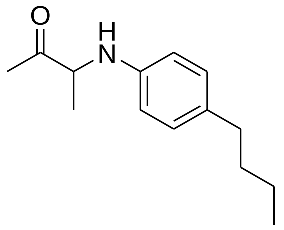

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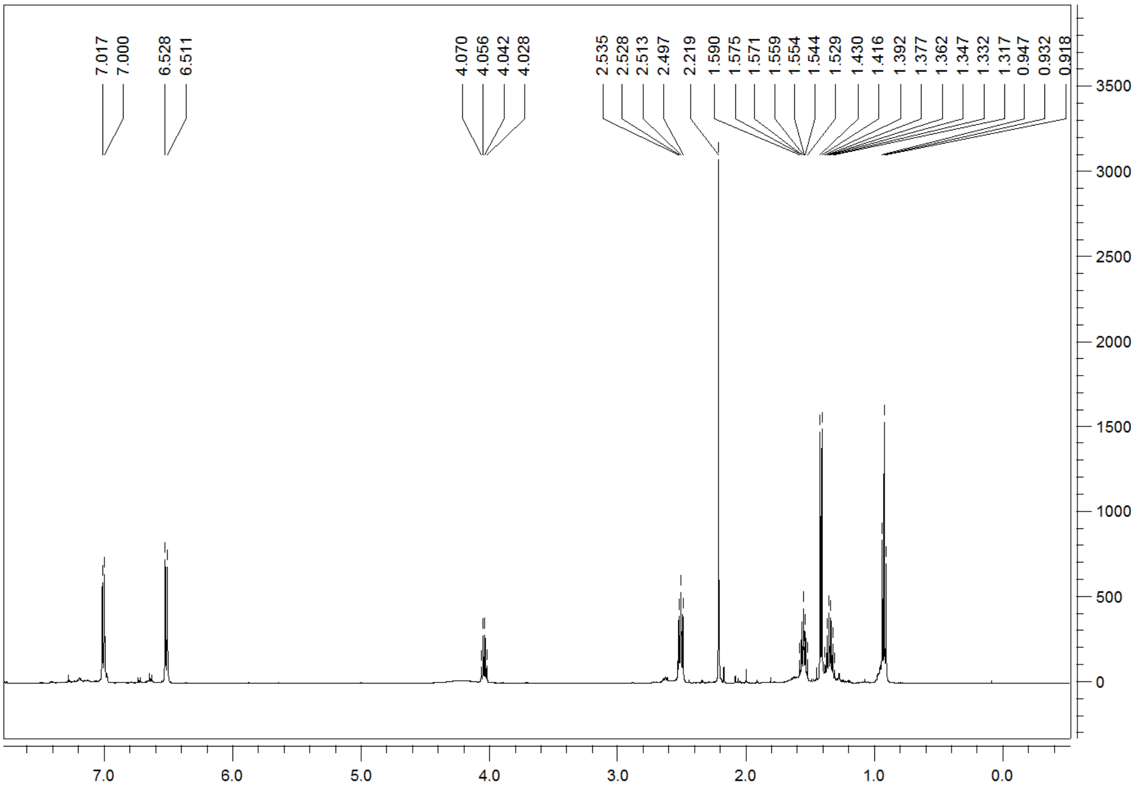
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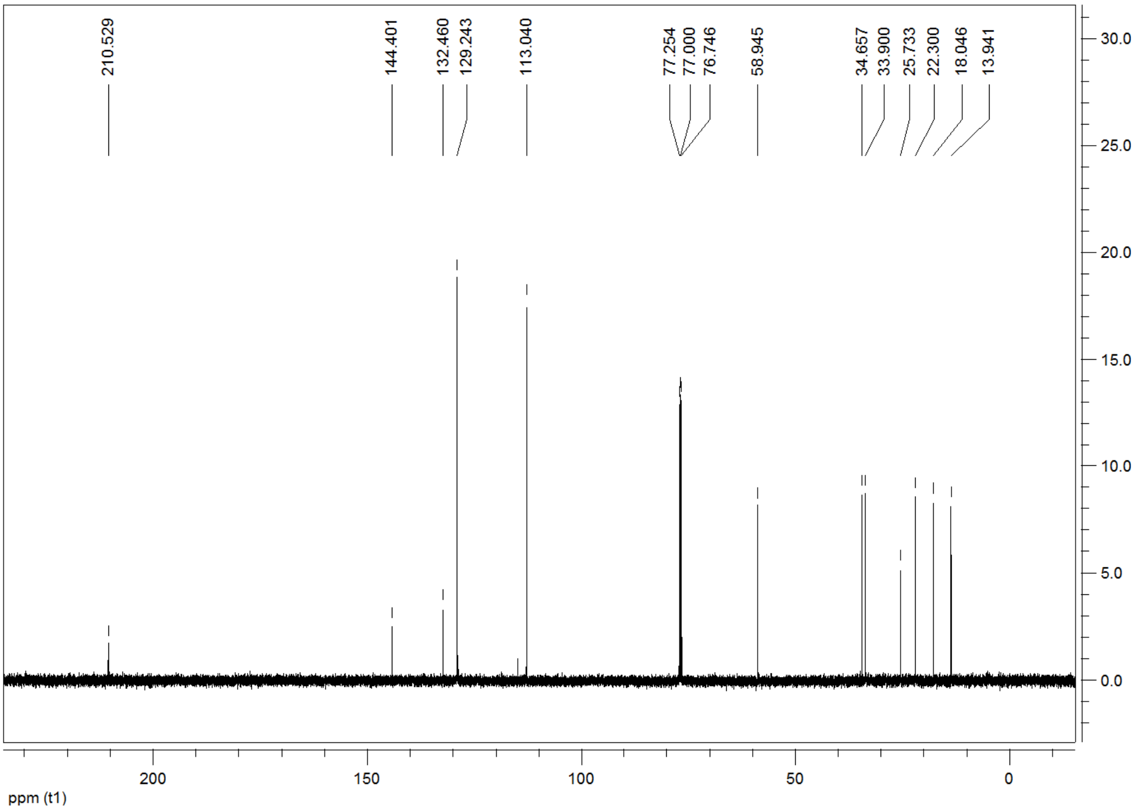
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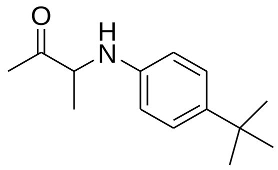
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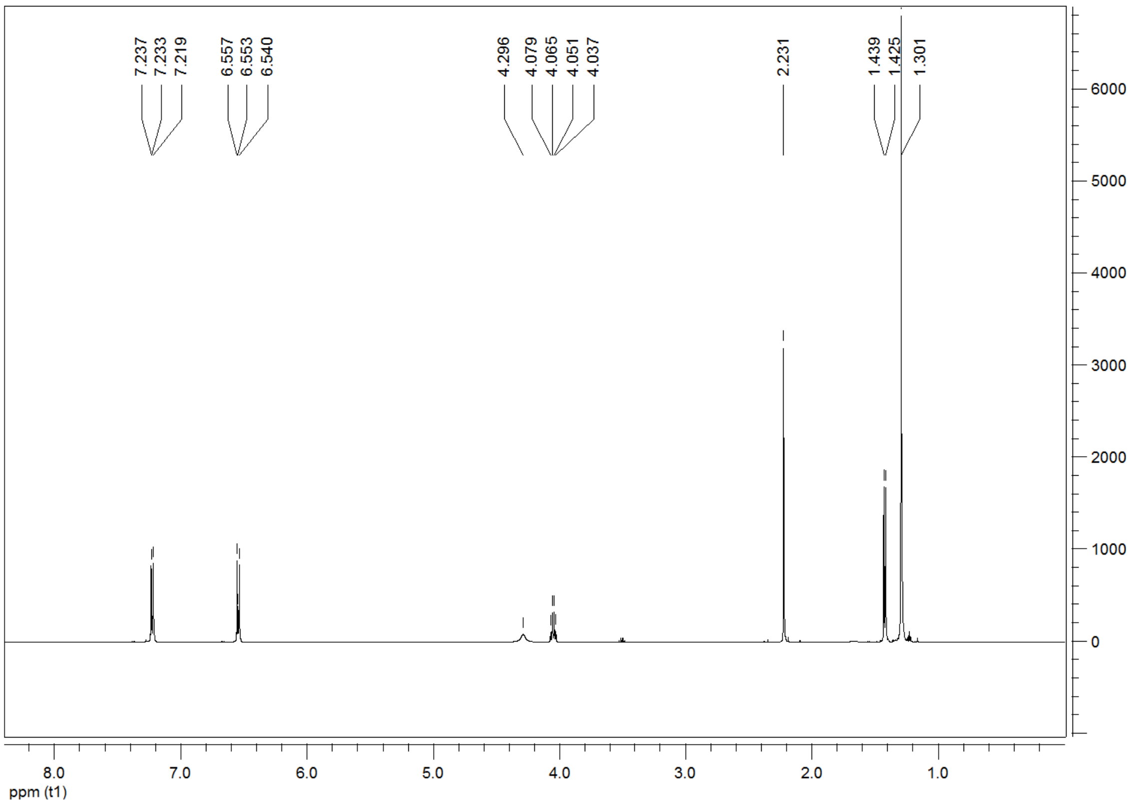
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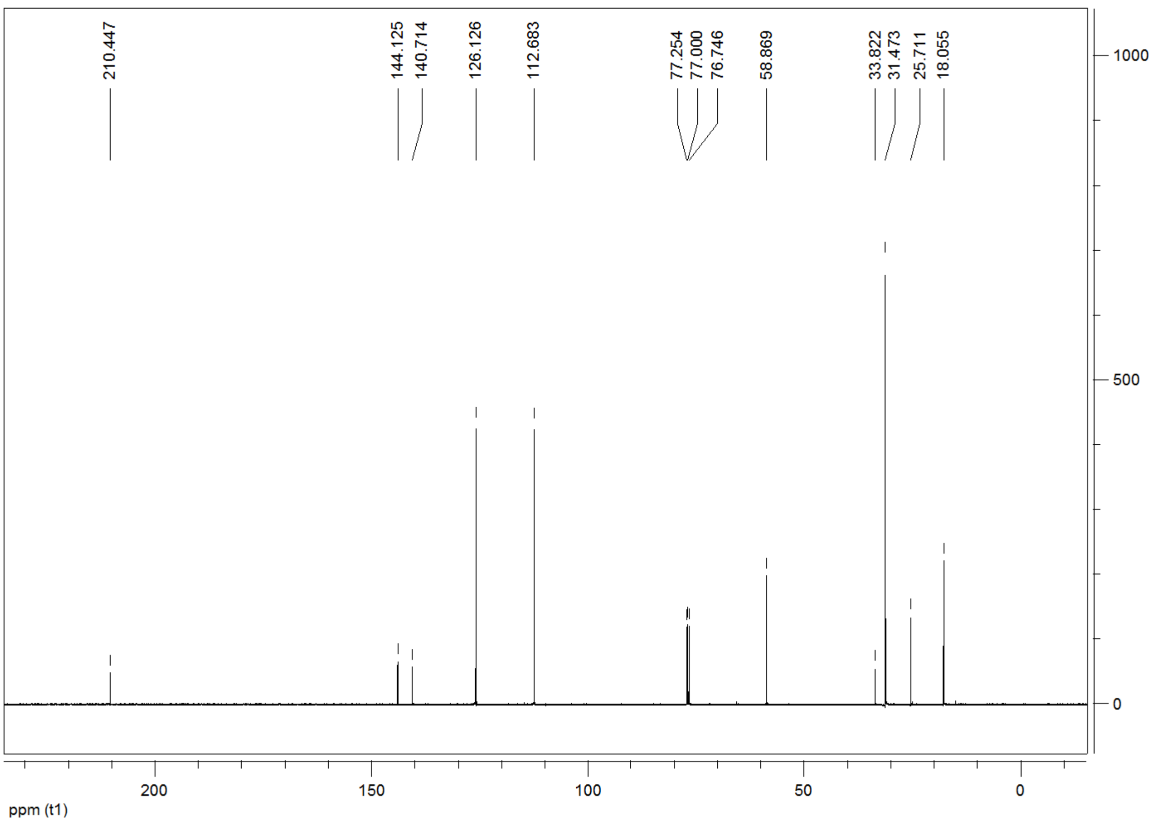
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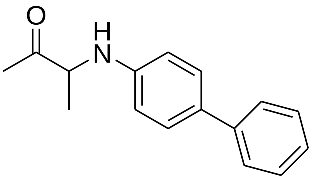

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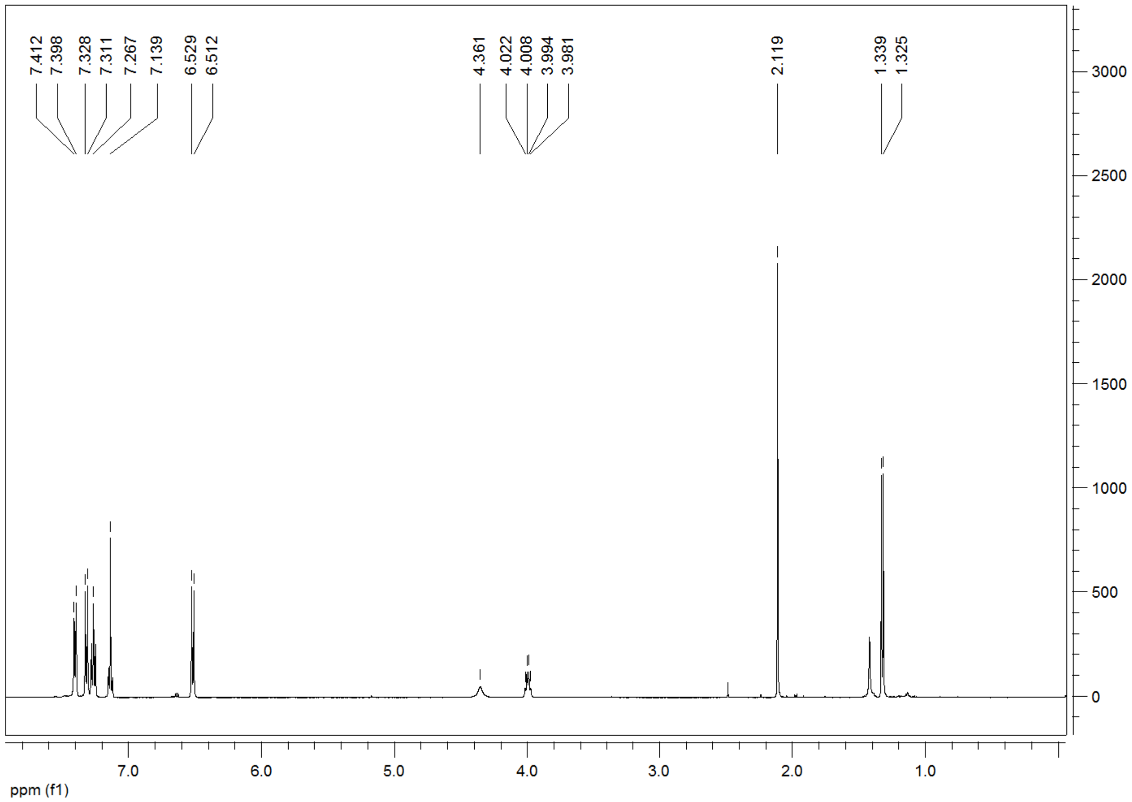
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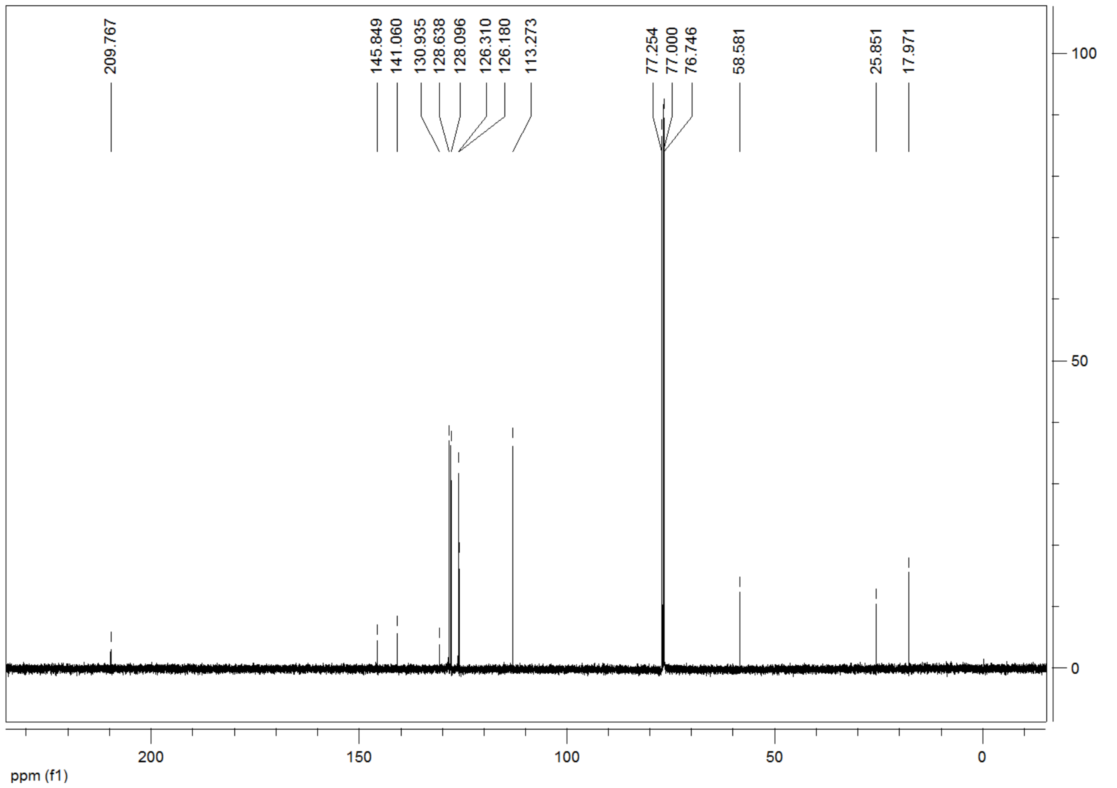
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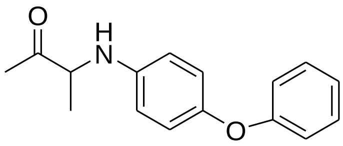

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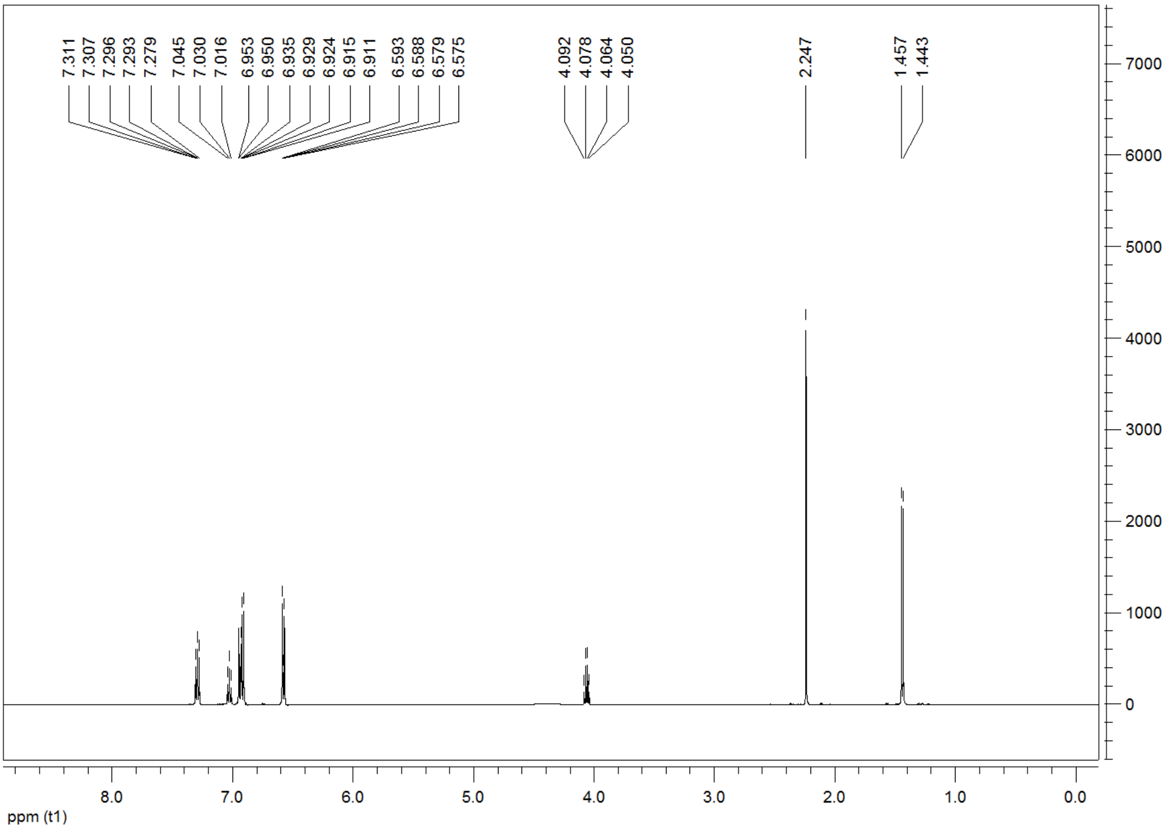
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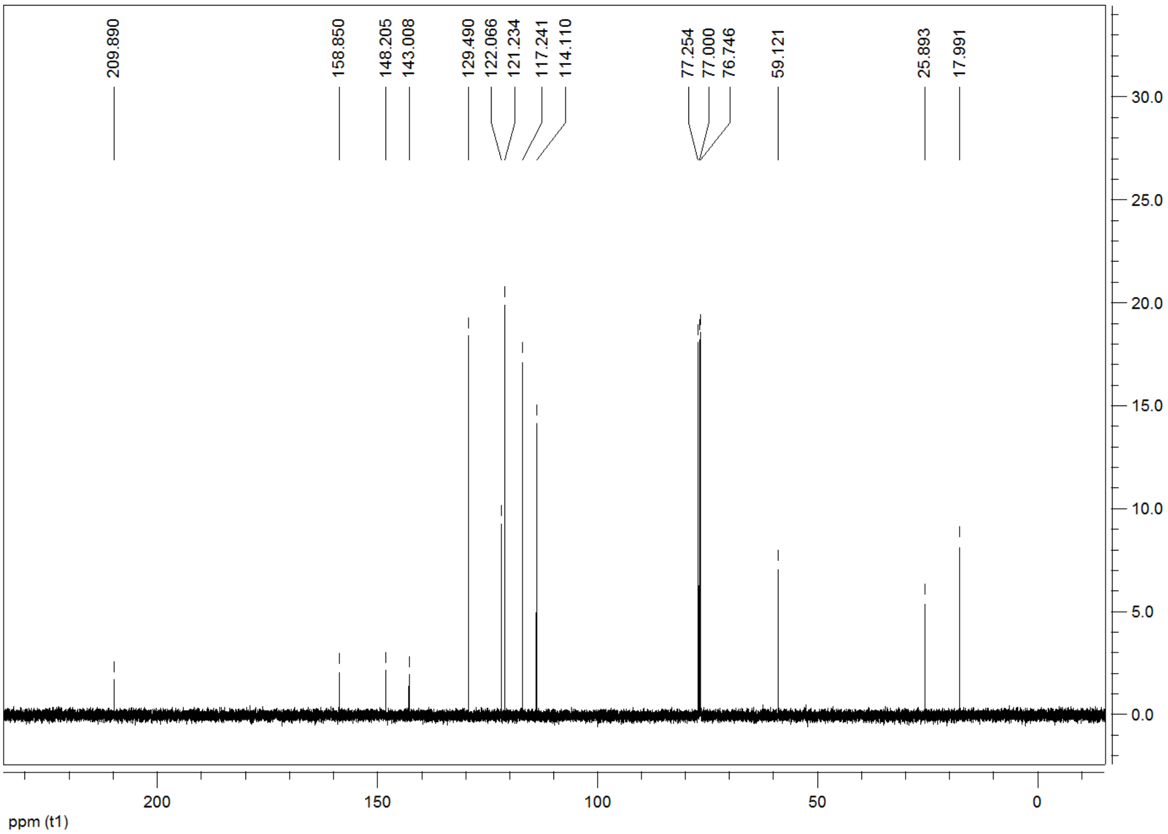
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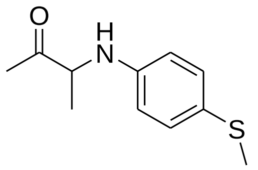
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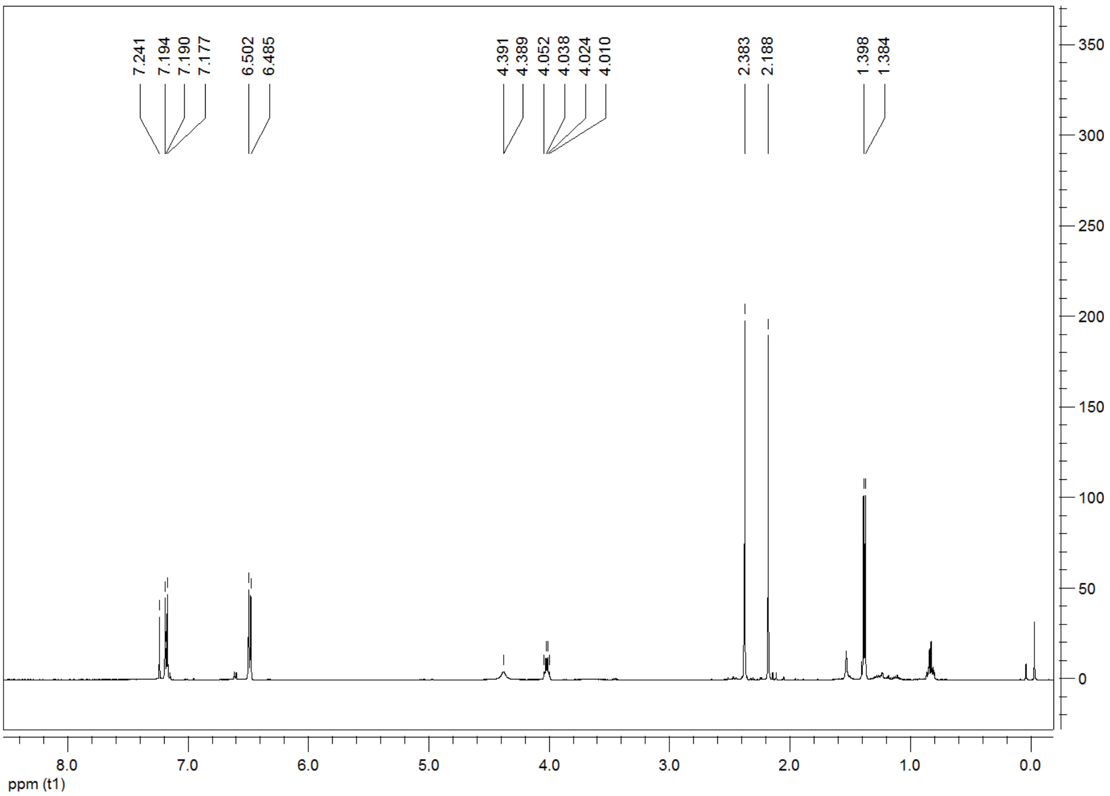
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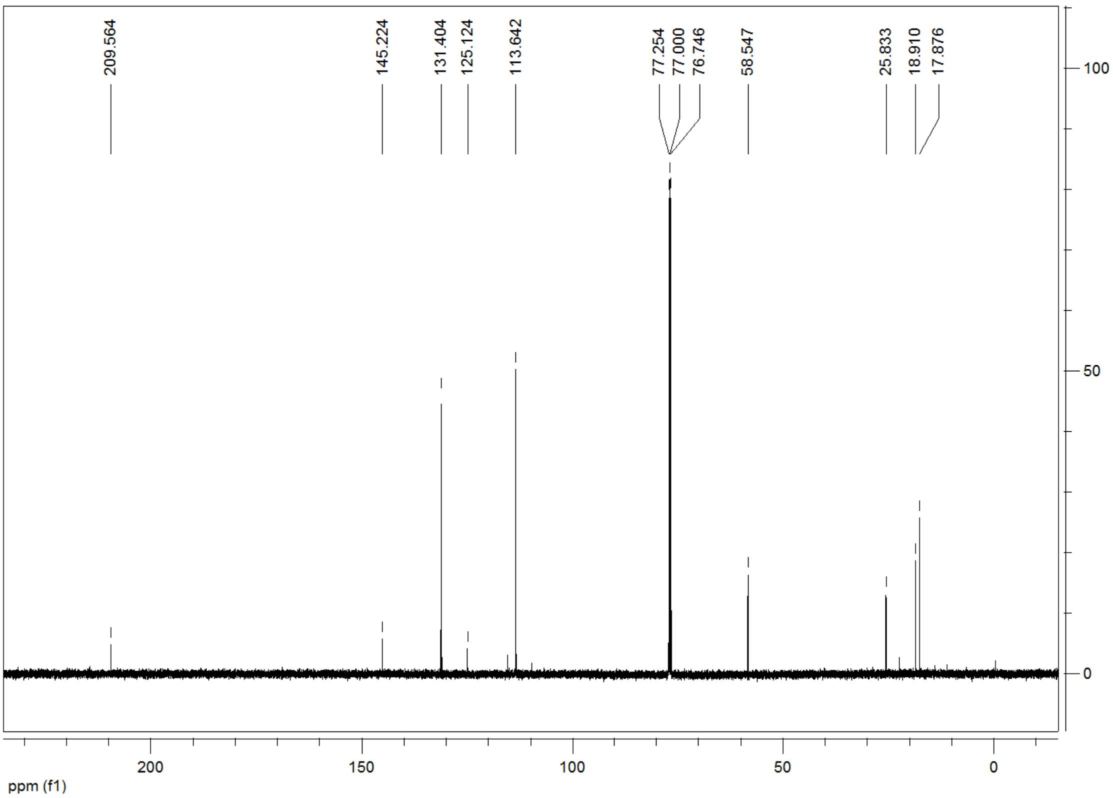
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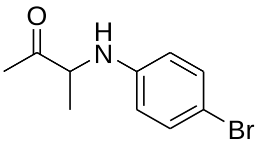
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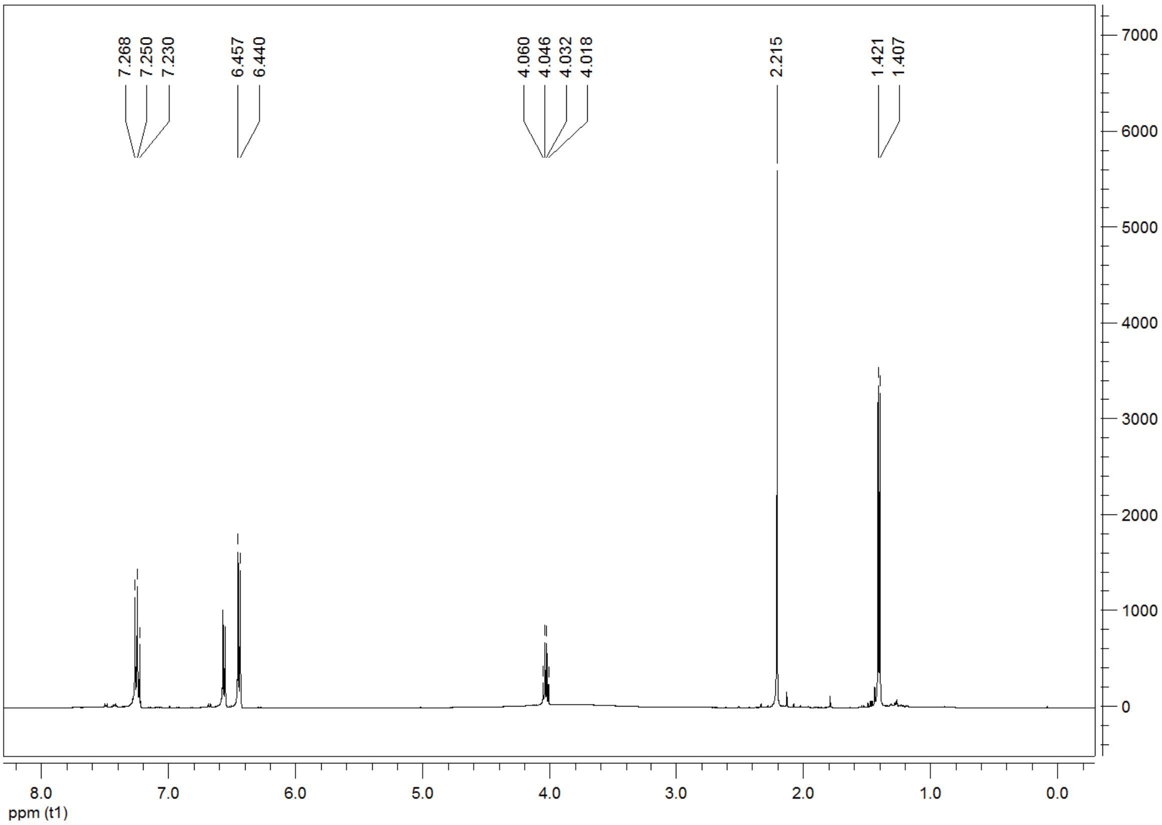
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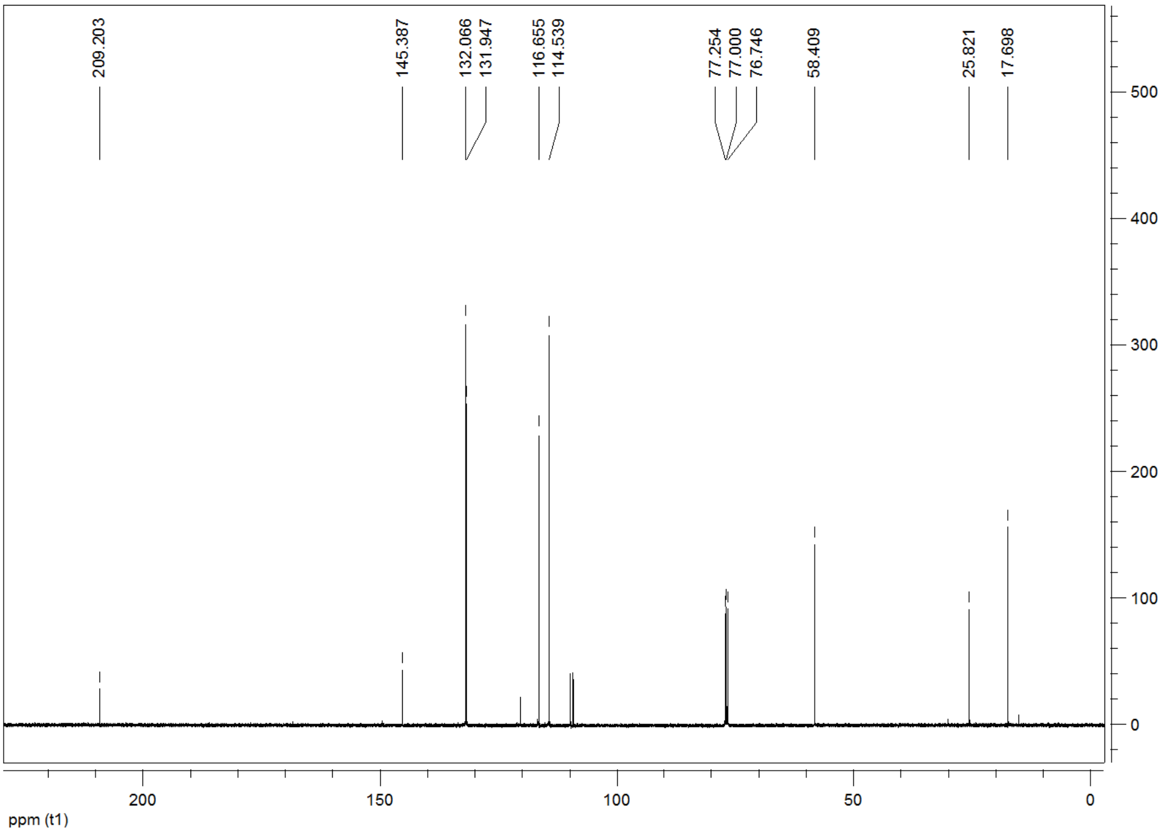
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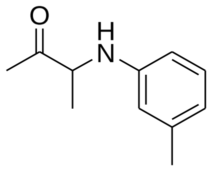
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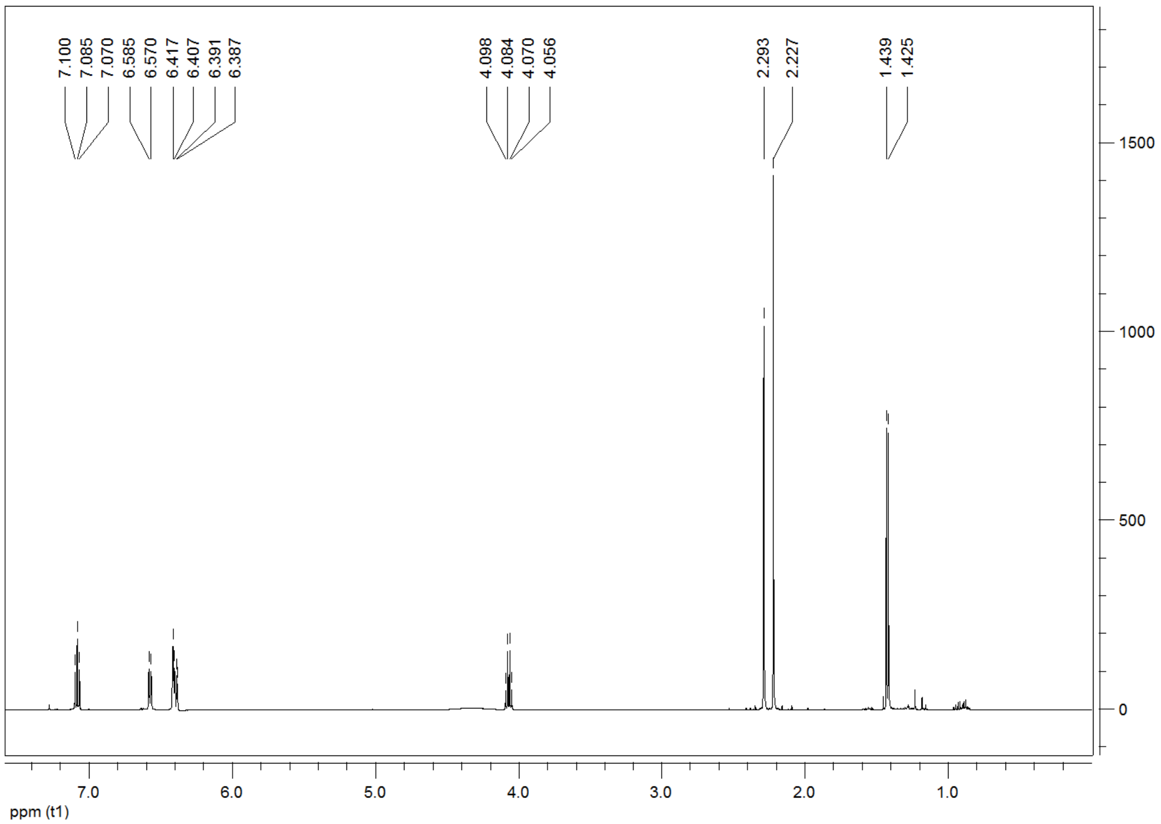
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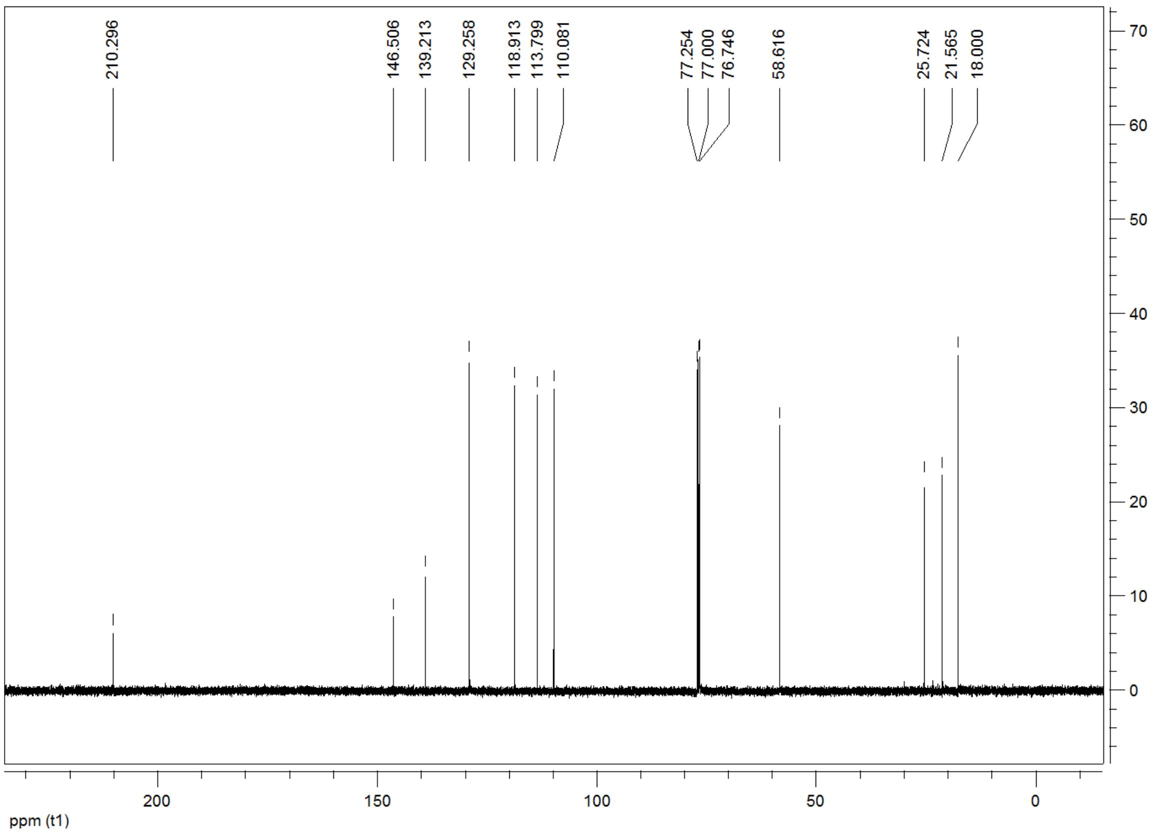
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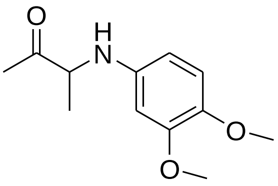

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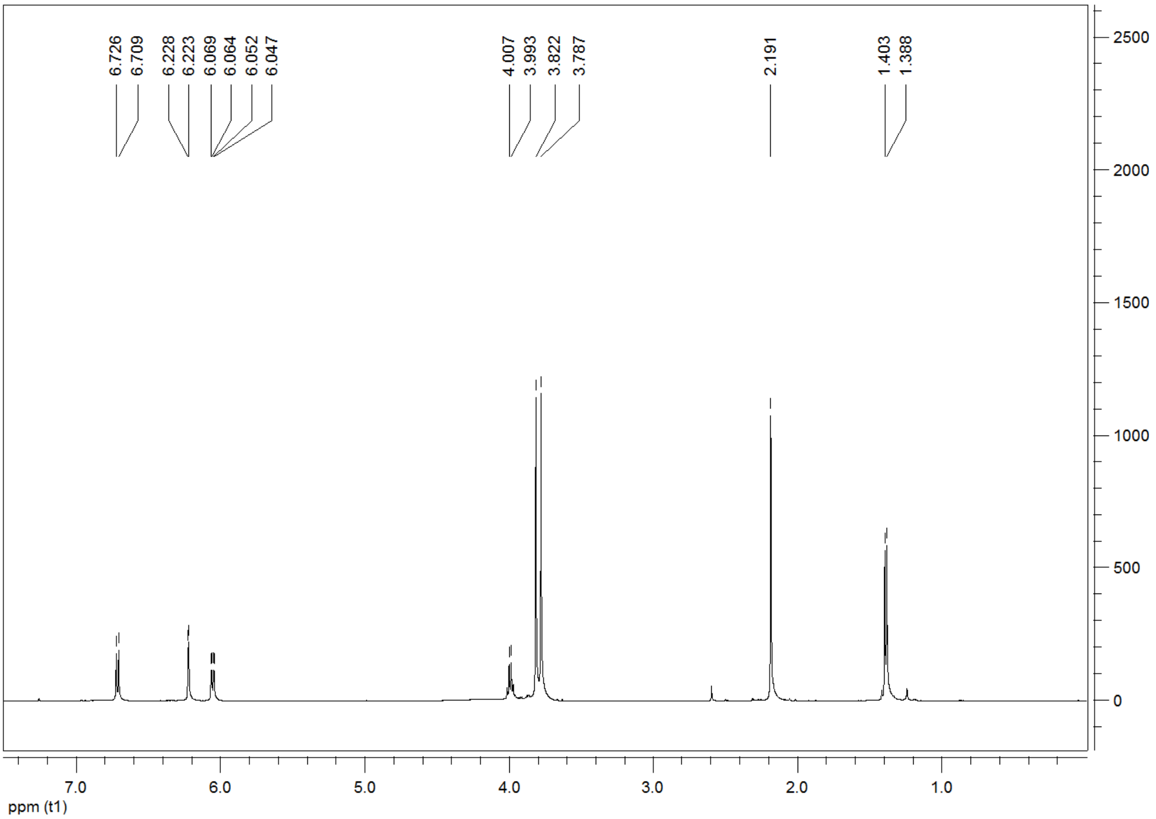
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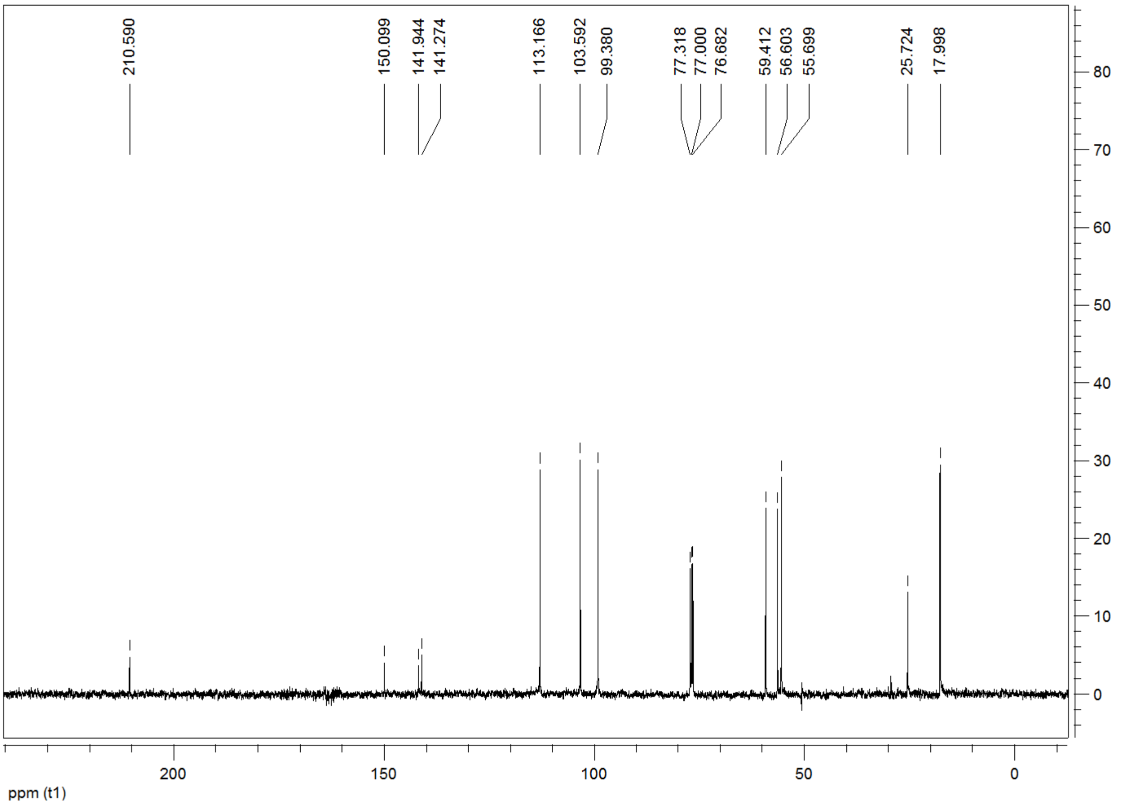
3.0
2.0
1.0
ppm (t1)


210.590
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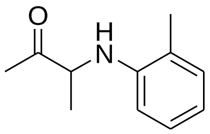
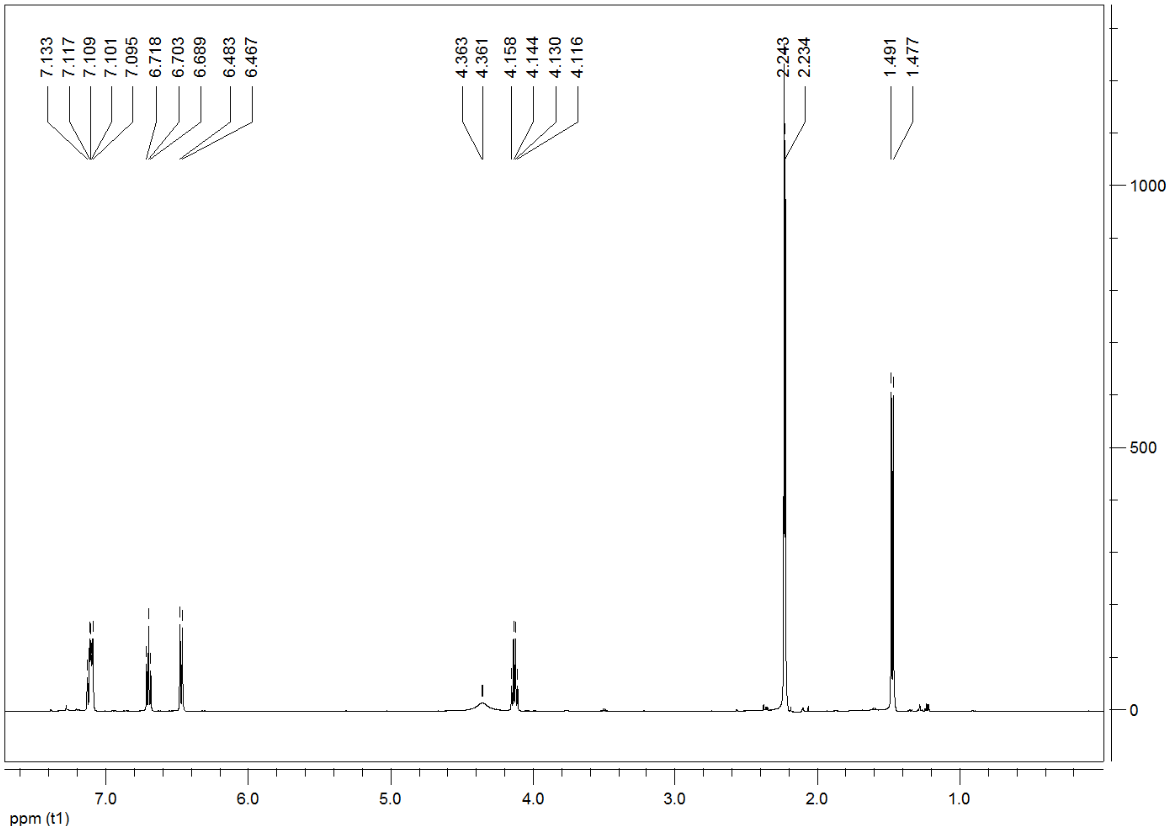
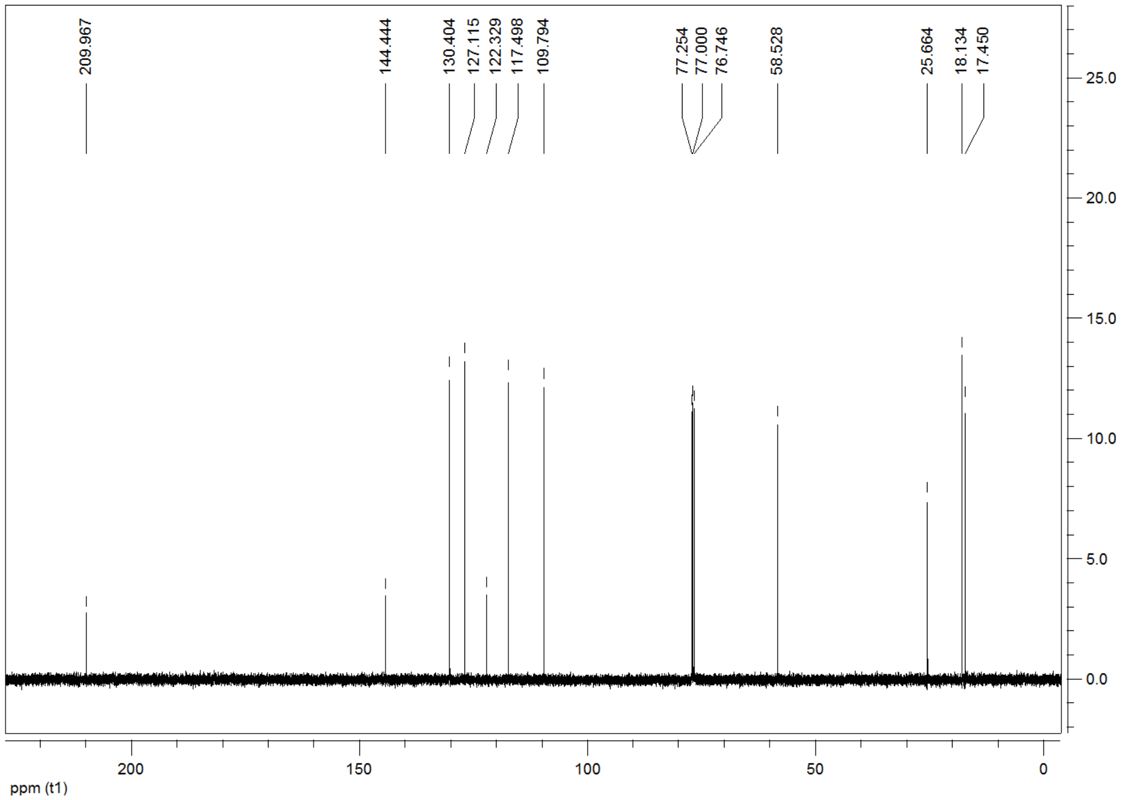
141.944
141.274
113.166
103.592
99.380
77.318
77.000
76.682
59.412
56.603
55.699
25.724
17.998
80
70
60
50
40
30
20
10
0
200
150
100
50
0
ppm (t1)



3an


7.133
7.117
7.109
7.101
7.095
6.718
6.703
6.689
6.483
6.467
4.363
4.361
4.158
4.144
4.130
4.116
2.243
2.234
1.491
1.477
1000
500
0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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130.404
127.115
122.329
117.498
109.794
77.254
77.000
76.746
58.528
25.664
18.134
17.450
25.0
20.0
15.0
10.0
5.0
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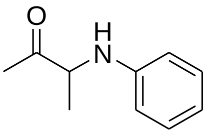
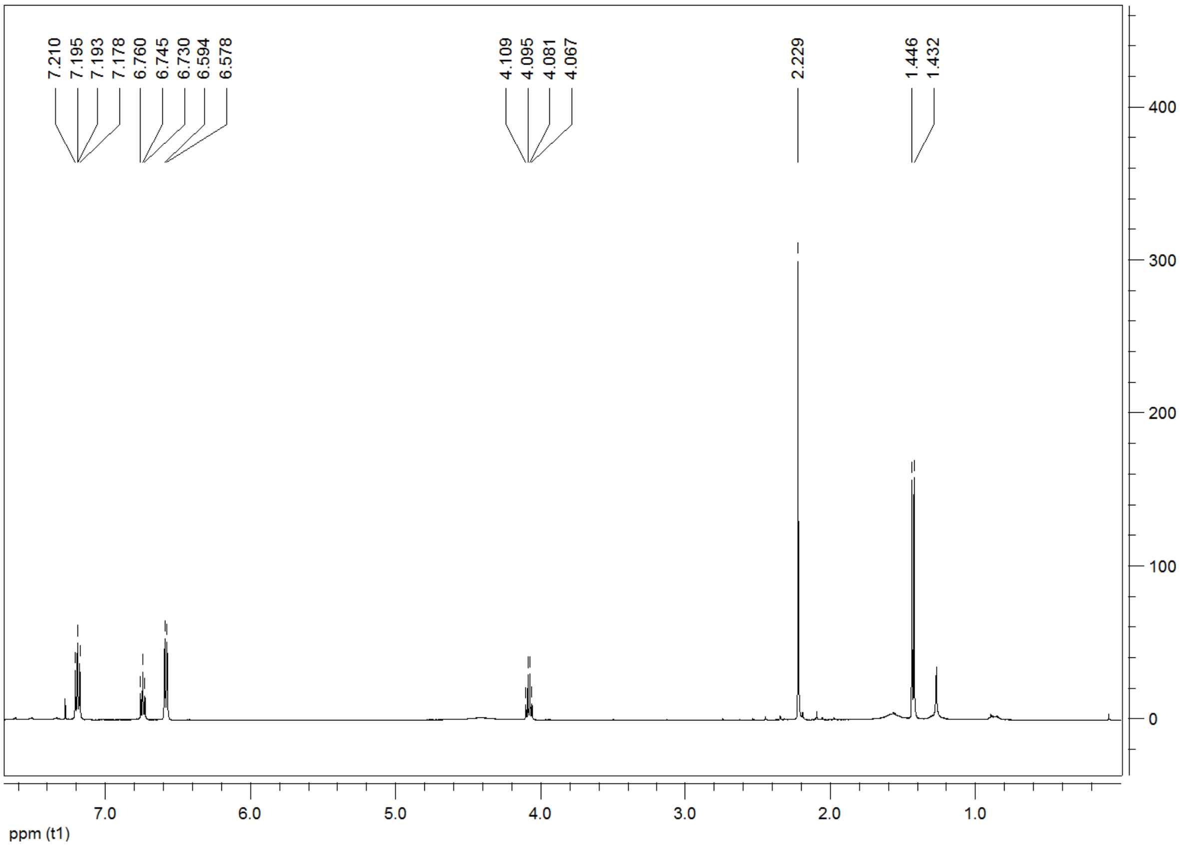
200
150
100
50
0
ppm (t1)



3ao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7.193
7.178
6.760
6.745
6.730
6.594
6.578
4.109
4.095
4.081
4.067
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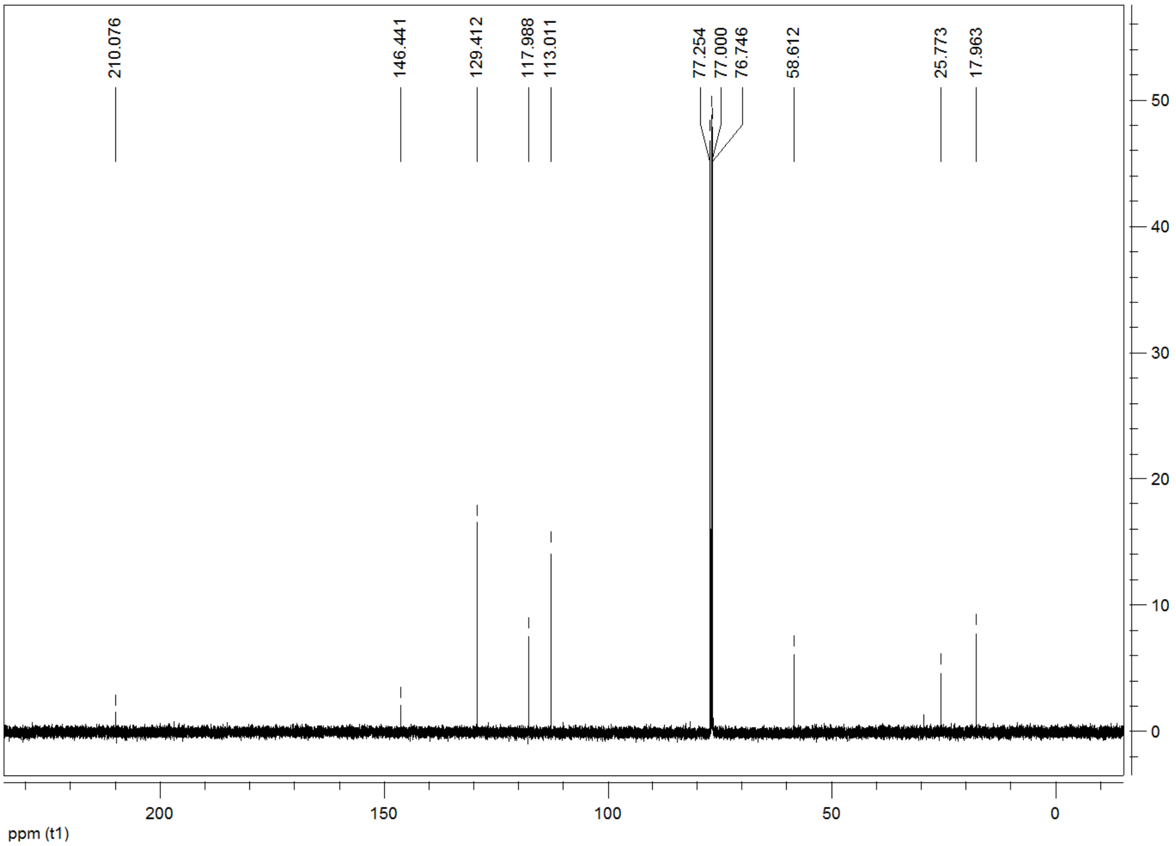
1.446
1.432
ppm (t1)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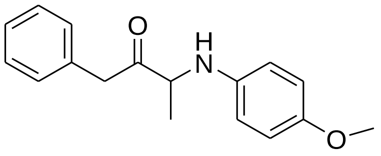
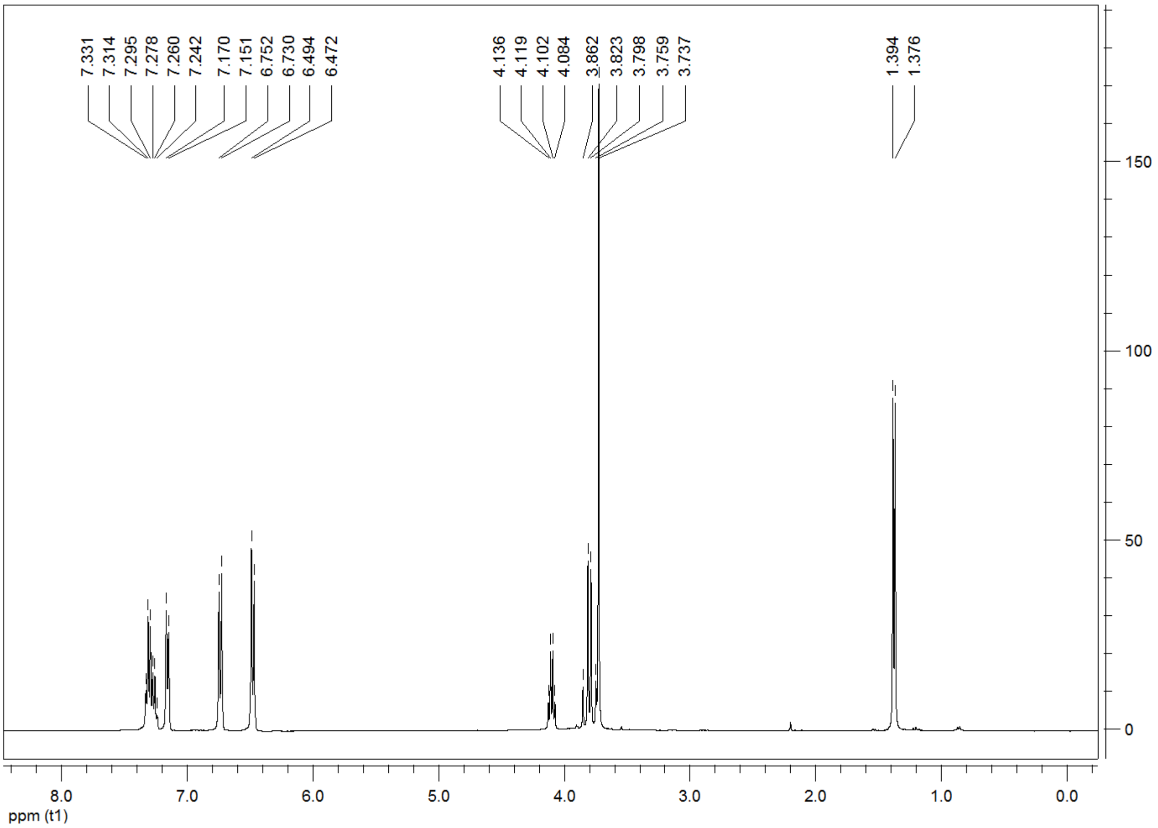
117.988
113.011
77.254
77.000
76.746
58.612
25.773
17.963
ppm (t1)


O
H
N
O

3ba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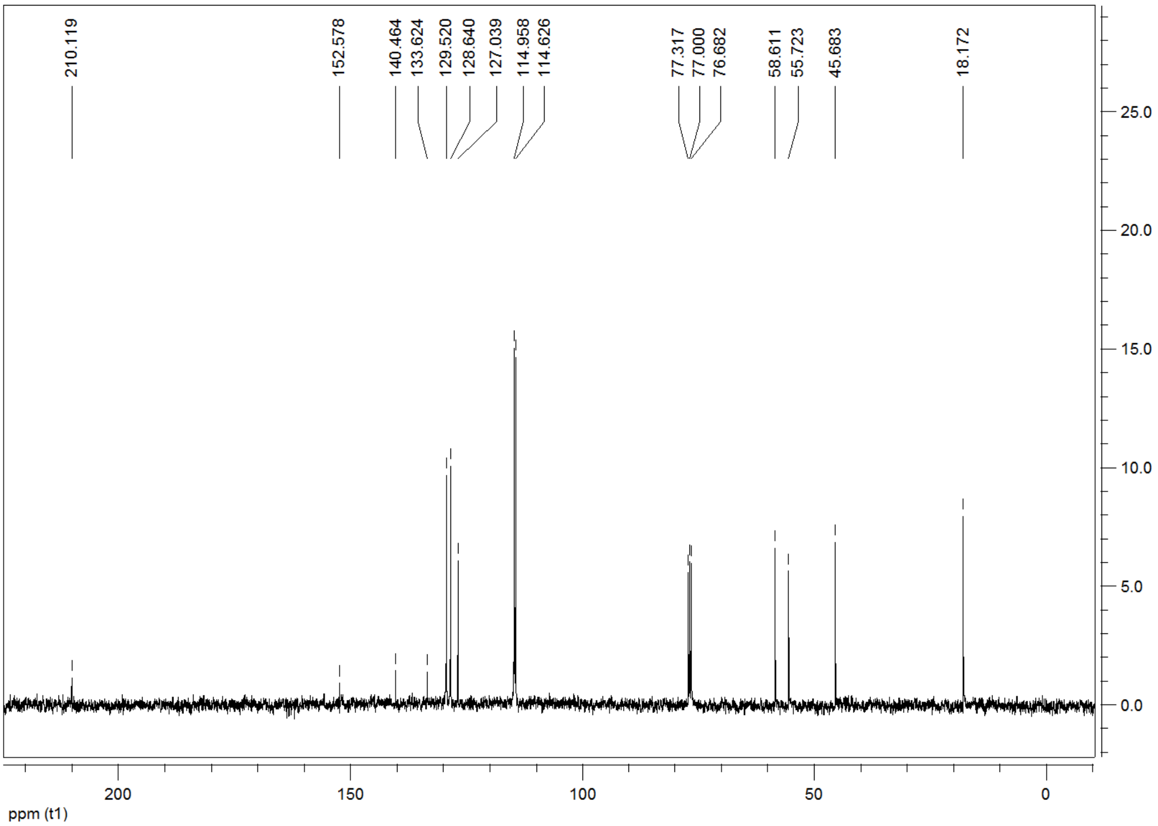
7.260
7.242
7.170
7.151
6.752
6.730
6.494
6.472
4.136
4.119
4.102
4.084
3.862
3.823
3.798
3.759
3.737
1.394
1.376
150
100
50
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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114.958
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77.317
77.000
76.682
58.611
55.723
45.683
18.172
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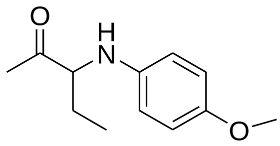
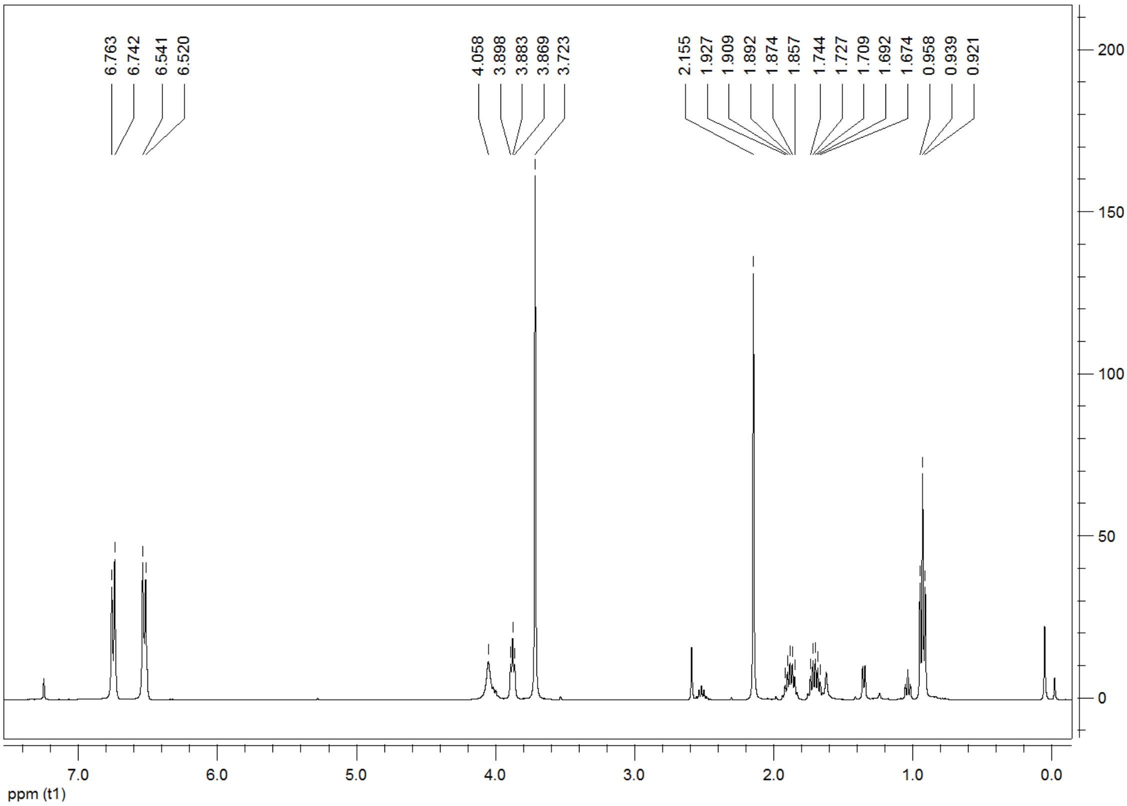
20.0
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)



3ca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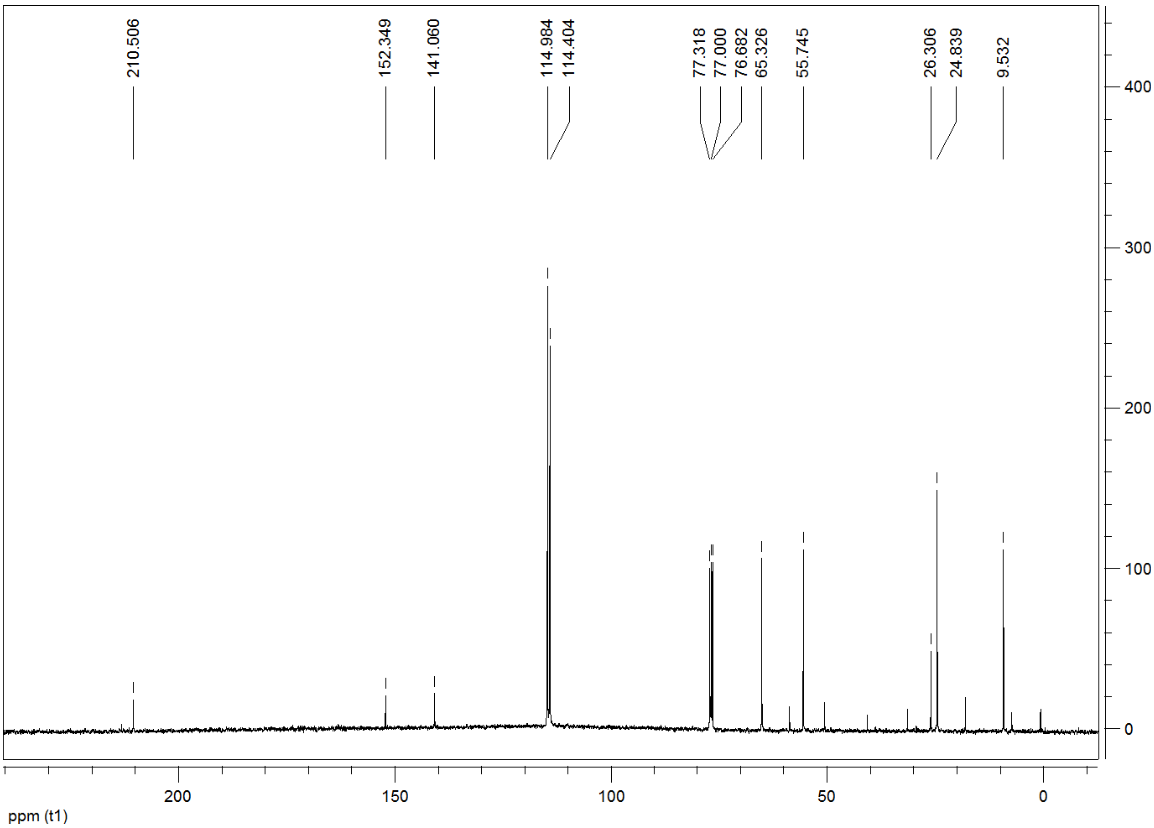
6.541
6.520
4.058
3.898
3.883
3.869
3.723
2.155
1.927
1.909
1.892
1.874
1.857
1.744
1.727
1.709
1.692
1.674
0.958
0.939
0.921
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
200
150
100
50
0


210.506
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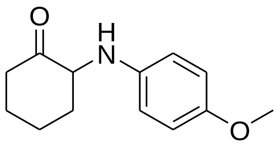
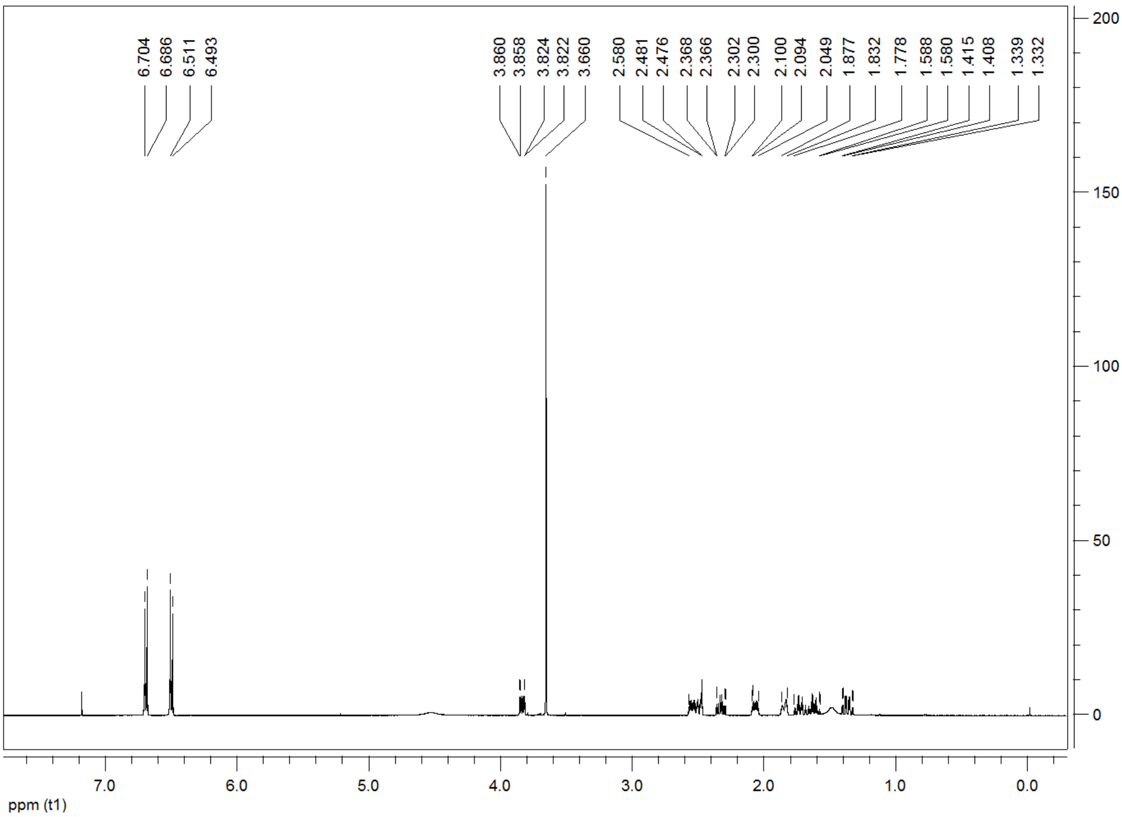
141.060
114.984
114.404
77.318
77.000
76.682
65.326
55.745
26.306
24.839
9.532
200
150
100
50
0
ppm (t1)
400
300
200
100
0



3da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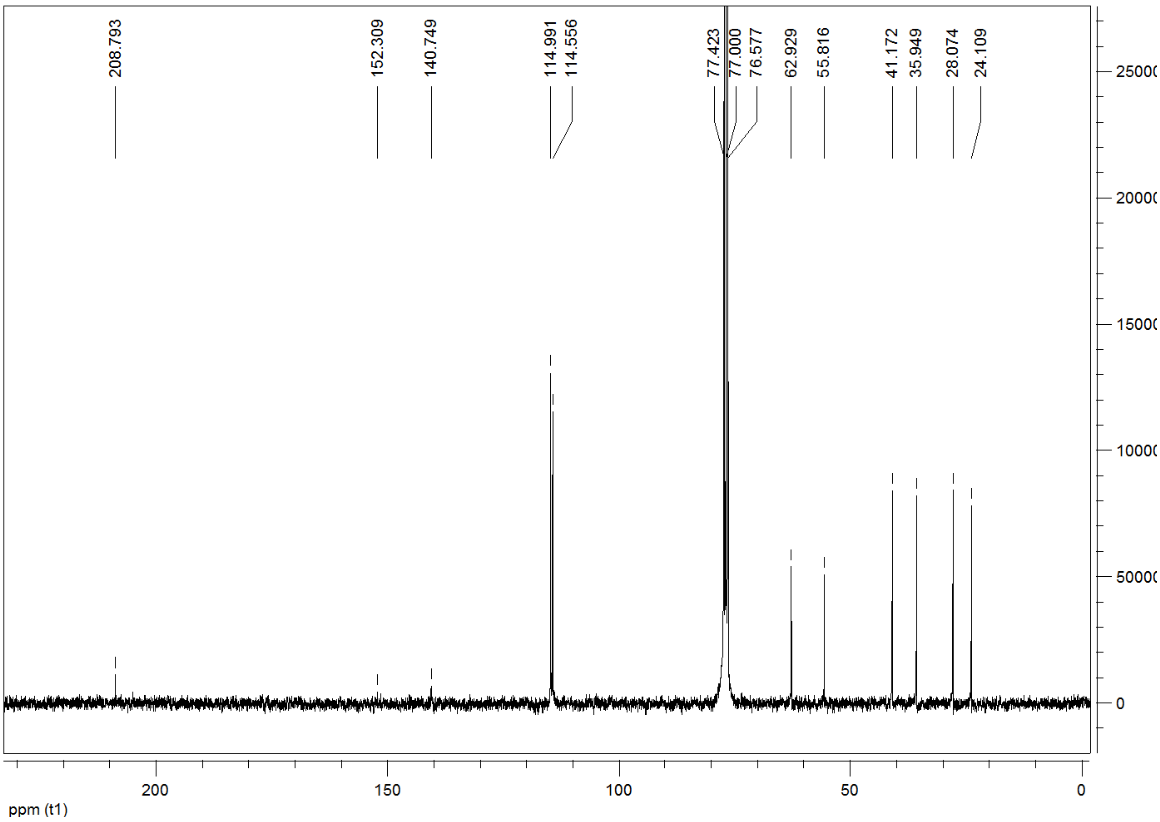
6.686
6.511
6.493
3.860
3.858
3.824
3.822
3.660
2.580
2.481
2.476
2.368
2.366
2.302
2.300
2.100
2.094
2.049
1.877
1.832
1.778
1.588
1.580
1.415
1.408
1.339
1.332
200
150
100
50
0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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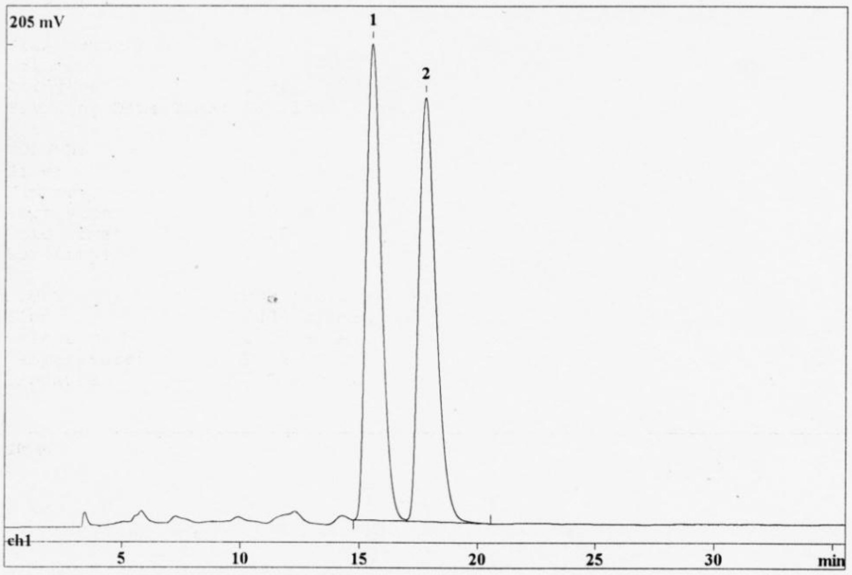
140.749
114.991
114.556
77.423
77.000
76.577
62.929
55.816
41.172
35.949
28.074
24.109
200
150
100
50
0
ppm (t1)

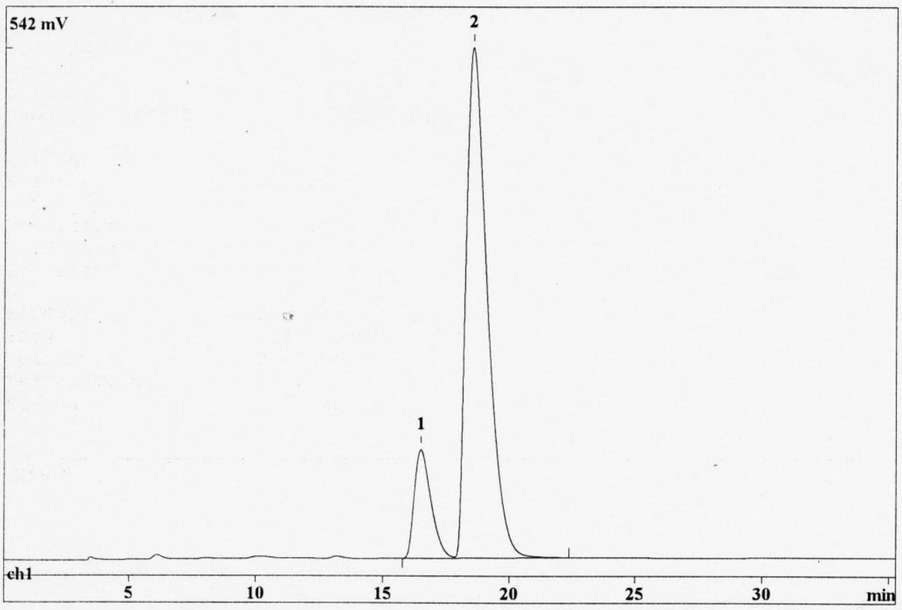
Copies of HPLC chromatograms of racemic/enantioenriched products

3aa: Chiralcel OD-H column, hexane/i-PrOH = 98:2, flow rate 1.0 mL/min, λ = 254 nm



Quantitation method: Absolute concentration
Standard component: No
Normalization: 100.00

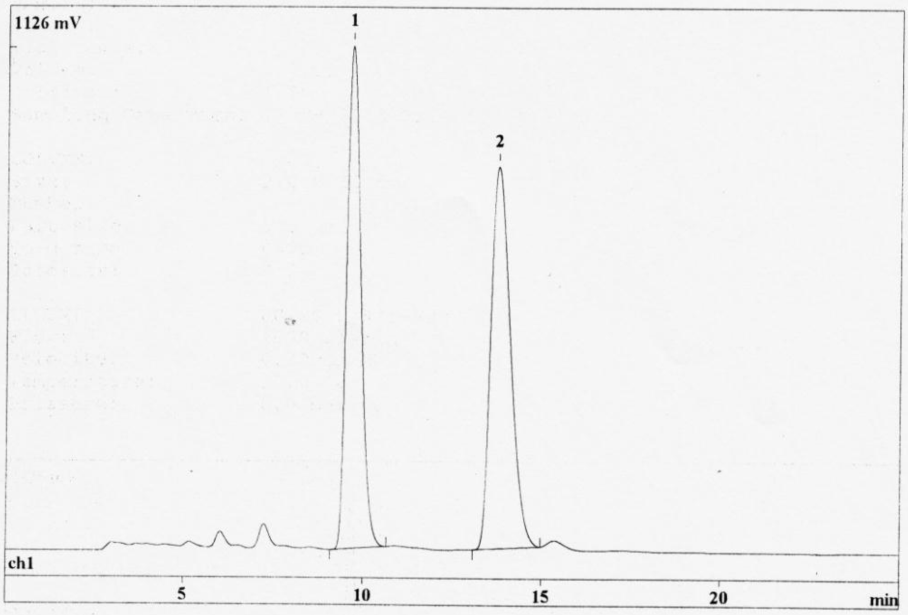
No	Retention min	Area mV*sec	Area %	Name
1	15.51	8756.278	49.66	
2	17.76	8876.574	50.34	
2	35.56	17632.851	100.00	



Quantitation method: Absolute concentration
Standard component: No
Normalization: 100.00

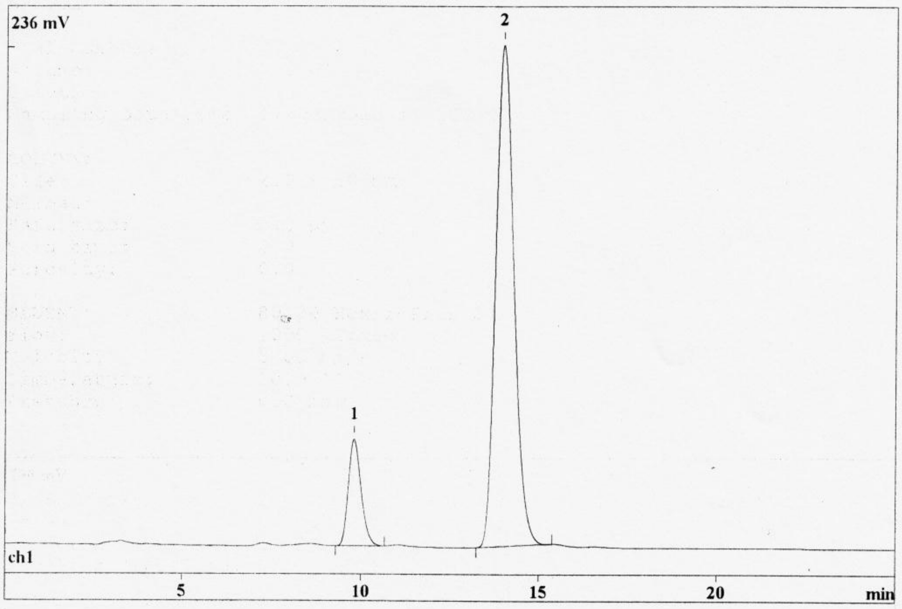
No	Retention min	Area mV*sec	Area %	Name
1	16.48	5145.537	14.37	
2	18.53	30666.723	85.63	
2	35.28	35812.260	100.00	

3ab: Chiralcel OJ column, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm



Quantitation method: Absolute concentration
Standard component: No
Normalization: 100.00

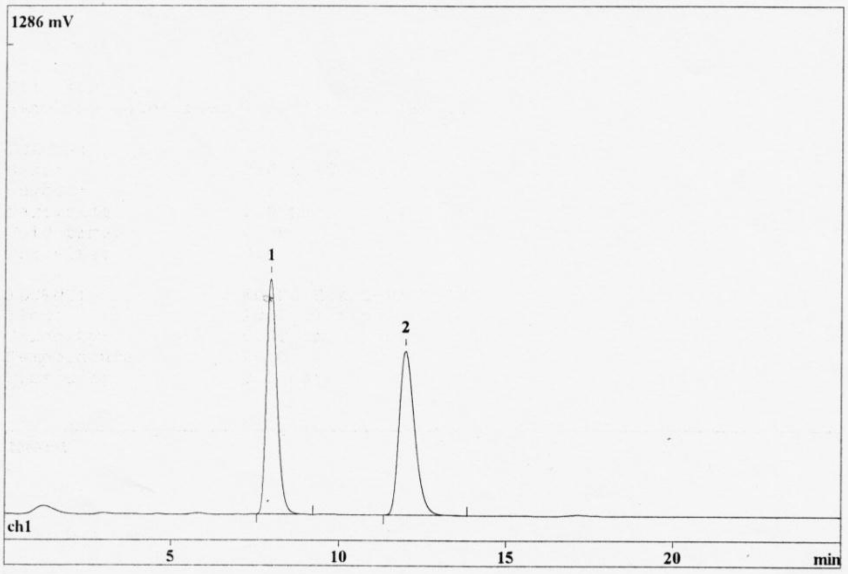
No	Retention min	Area mV*sec	Area %	Name
1	9.64	29299.901	48.50	
2	13.74	31108.701	51.50	
2	25.00	60408.601	100.00	



Quantitation method: Absolute concentration
Standard component: No
Normalization: 100.00

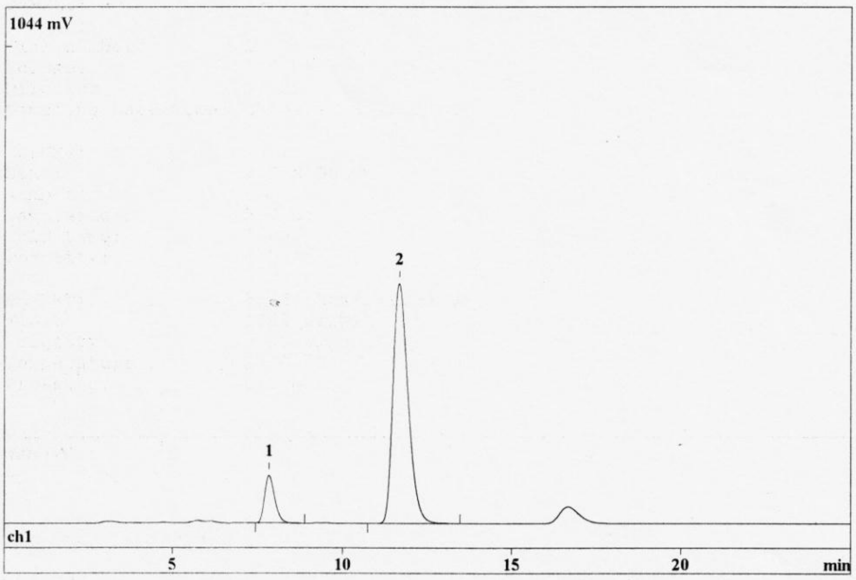
No	Retention min	Area mV*sec	Area %	Name
1	9.80	1198.179	12.97	
2	13.96	8039.490	87.03	
2	25.00	9237.668	100.00	

3ac: Chiralcel OJ column, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm



Quantitation method: Absolute concentration
Standard component: No
Normalization: 100.00

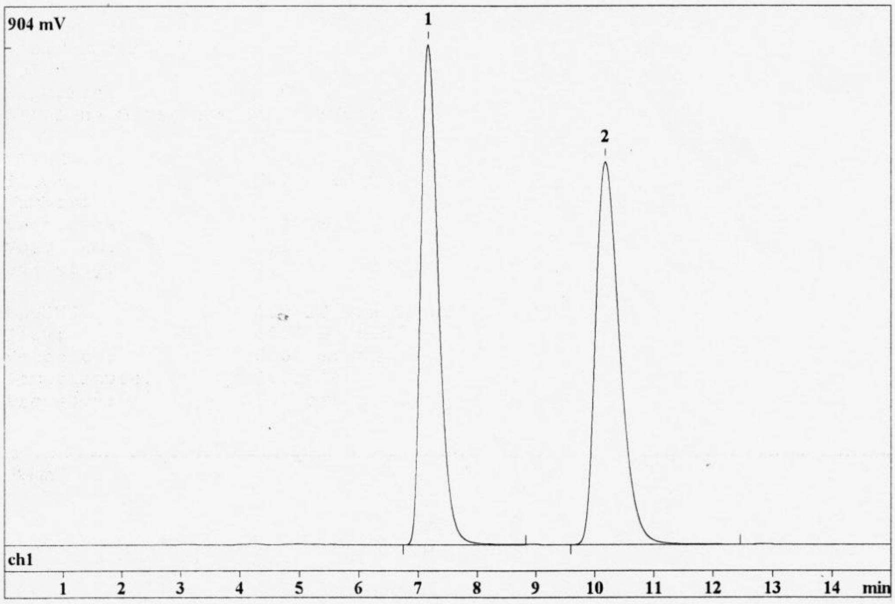
No	Retention min	Area mV*sec	Area %	Name
1	7.96	13290.762	49.22	
2	11.97	13710.224	50.78	
2	25.00	27000.986	100.00	



Quantitation method: Absolute concentration
Standard component: No
Normalization: 100.00

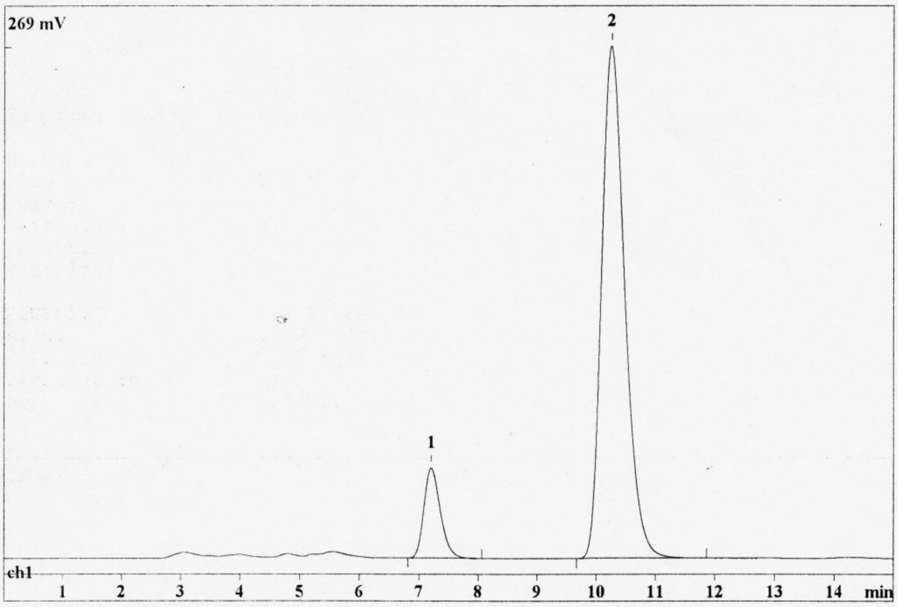
No	Retention min	Area mV*sec	Area %	Name
1	7.84	2059.309	11.73	
2	11.66	15490.933	88.27	
2	25.00	17550.243	100.00	

3ad: Chiralcel OJ column, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm



Quantitation method: Absolute concentration
Standard component: No
Normalization: 100.00

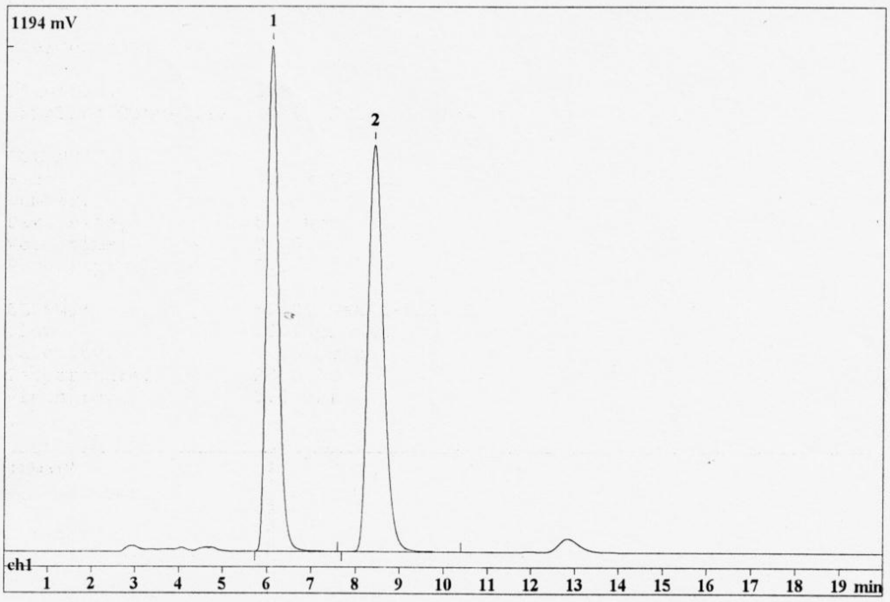
No	Retention min	Area mV*sec	Area %	Name
1	7.16	17769.997	48.67	
2	10.18	18742.692	51.33	
2	15.00	36512.689	100.00	



Quantitation method: Absolute concentration
Standard component: No
Normalization: 100.00

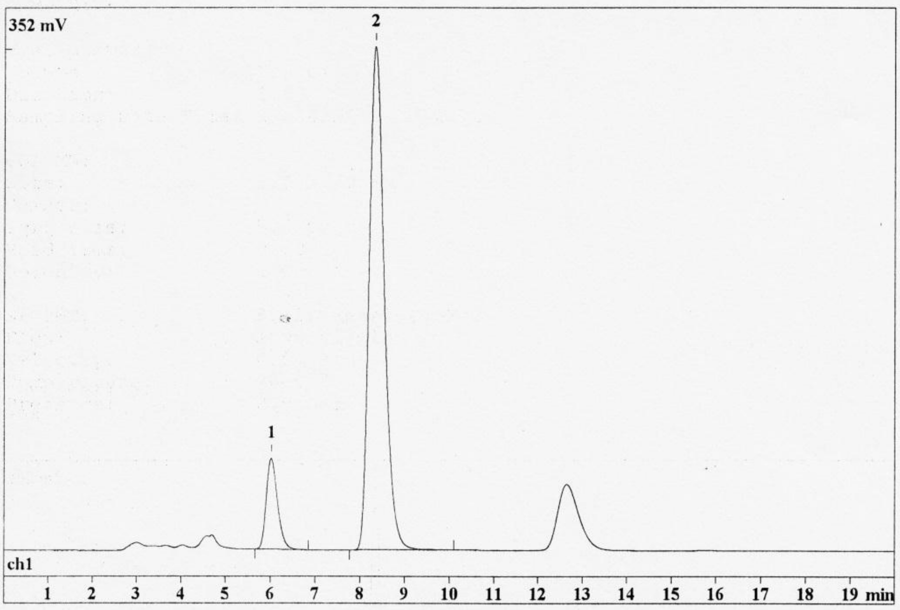
No	Retention min	Area mV*sec	Area %	Name
1	7.20	889.873	11.15	
2	10.25	7092.299	88.85	
2	15.00	7982.172	100.00	

3ae: Chiralcel OJ column, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm



Quantitation method: Absolute concentration
Standard component: No
Normalization: 100.00

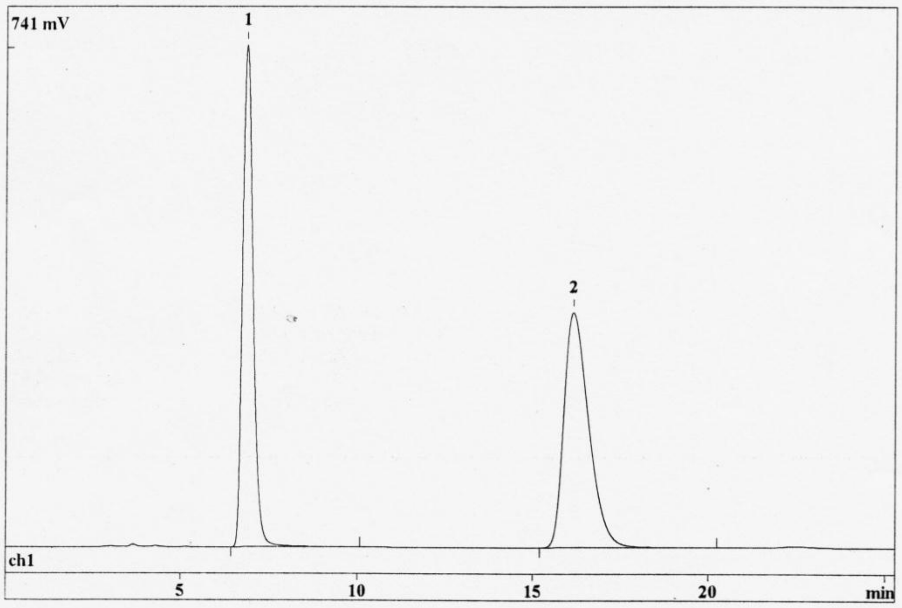
No	Retention min	Area mV*sec	Area %	Name
1	6.07	21420.826	48.58	
2	8.40	22675.592	51.42	
2	20.00	44096.418	100.00	



Quantitation method: Absolute concentration
Standard component: No
Normalization: 100.00

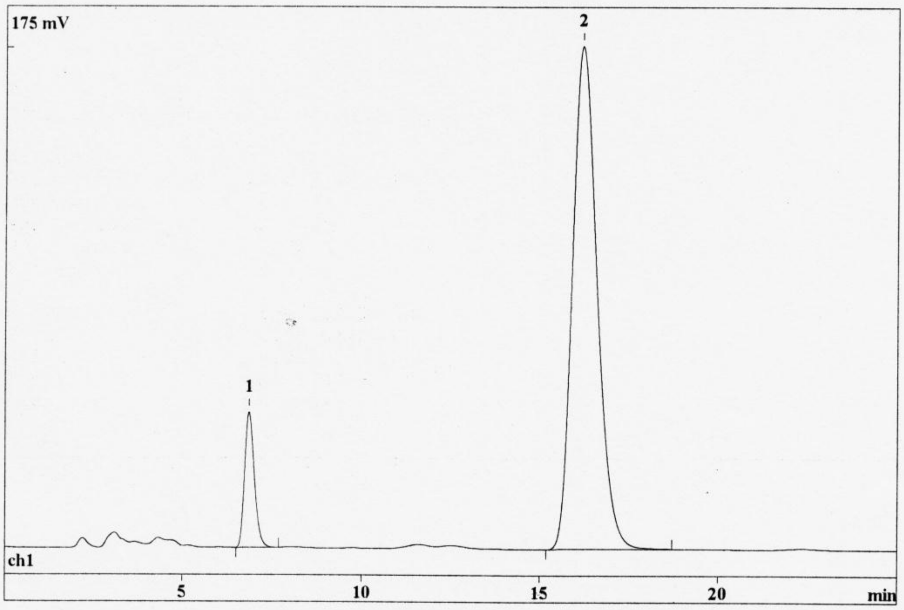
No	Retention min	Area mV*sec	Area %	Name
1	6.02	1053.710	11.87	
2	8.34	7825.231	88.13	
2	20.00	8878.941	100.00	

3af: Chiralcel OJ column, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm



Quantitation method: Absolute concentration
Standard component: No
Normalization: 100.00

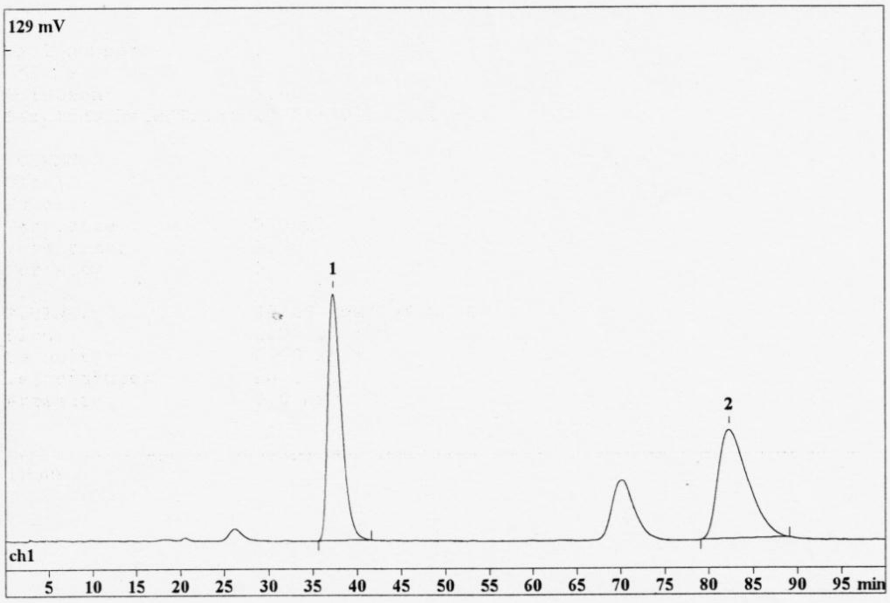
No	Retention min	Area mV*sec	Area %	Name
1	6.87	14613.930	47.17	
2	16.16	16370.219	52.83	
2	25.30	30984.149	100.00	



Quantitation method: Absolute concentration
Standard component: No
Normalization: 100.00

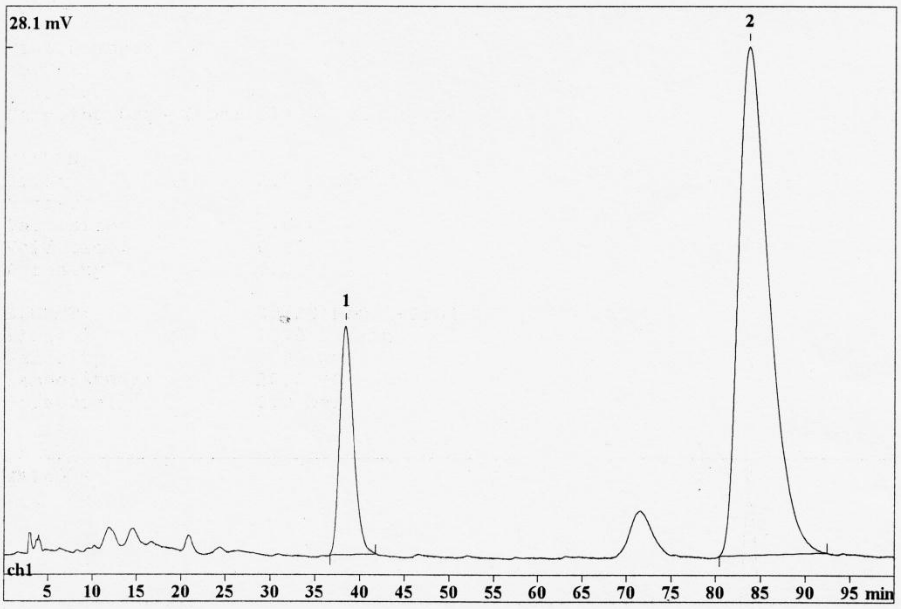
No	Retention min	Area mV*sec	Area %	Name
1	6.86	848.985	9.55	
2	16.18	8043.271	90.45	
2	25.00	8892.256	100.00	

3ag: Chiralcel OJ column, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm



Quantitation method: Absolute concentration
Standard component: No
Normalization: 100.00

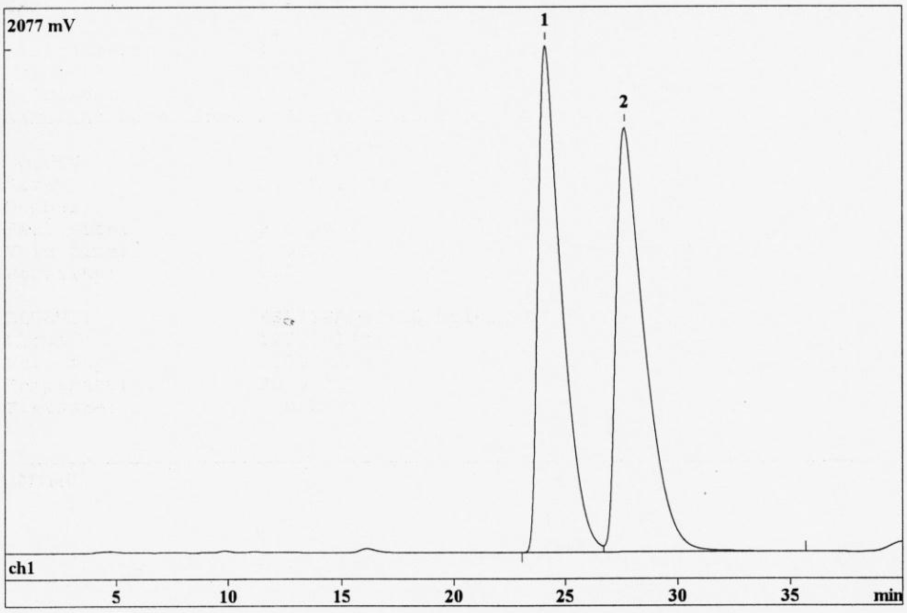
No	Retention min	Area mV*sec	Area %	Name
1	37.27	6574.525	50.74	
2	82.27	6383.009	49.26	
2	100.00	12957.533	100.00	



Quantitation method: Absolute concentration
Standard component: No
Normalization: 100.00

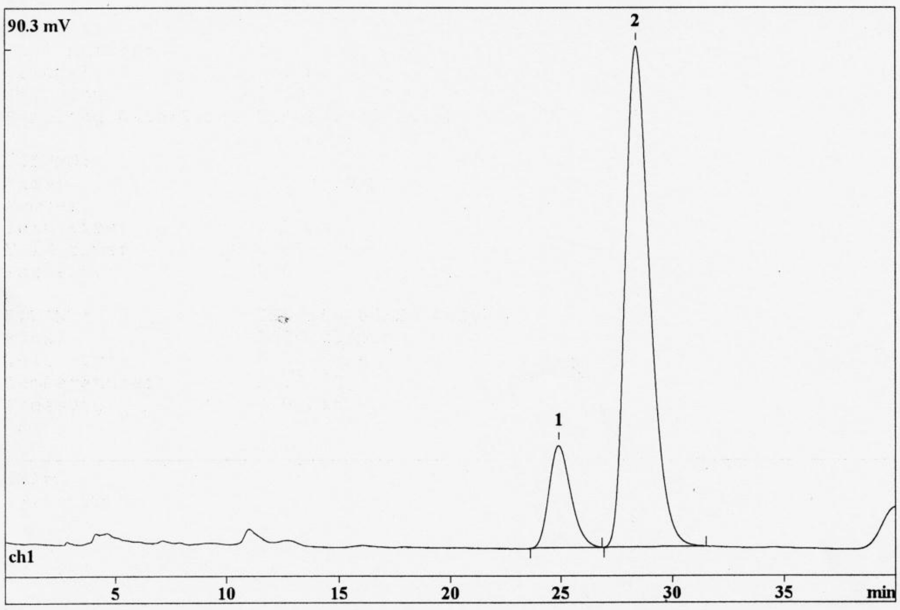
No	Retention min	Area mV*sec	Area %	Name
1	38.36	1301.335	16.74	
2	83.61	6473.609	83.26	
2	100.00	7774.944	100.00	

3ah: Chiralcel OJ column, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm



Quantitation method: Absolute concentration
Standard component: No
Normalization: 100.00

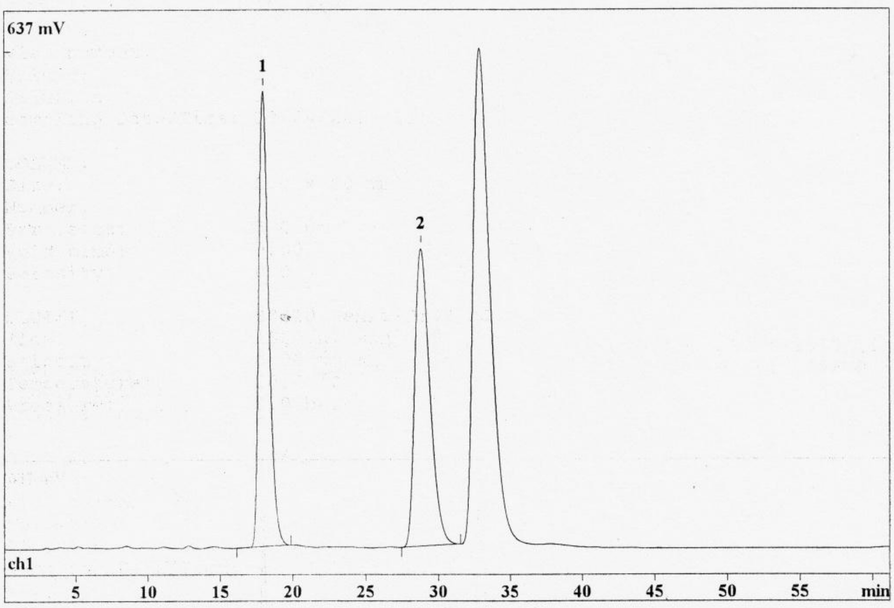
No	Retention min	Area mV*sec	Area %	Name
1	24.10	145869.107	49.97	
2	27.63	146051.640	50.03	
2	40.00	291920.747	100.00	



Quantitation method: Absolute concentration
Standard component: No
Normalization: 100.00

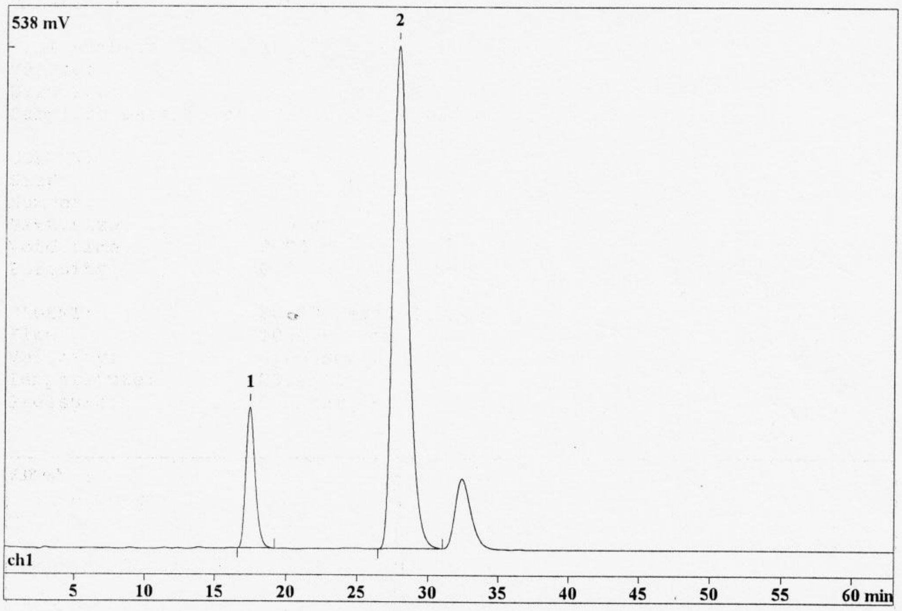
No	Retention min	Area mV*sec	Area %	Name
1	24.89	1206.355	15.42	
2	28.37	6614.764	84.58	
2	40.00	7821.118	100.00	

3ai: Chiralcel OJ column, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm



Quantitation method: Absolute concentration
Standard component: No
Normalization: 100.00

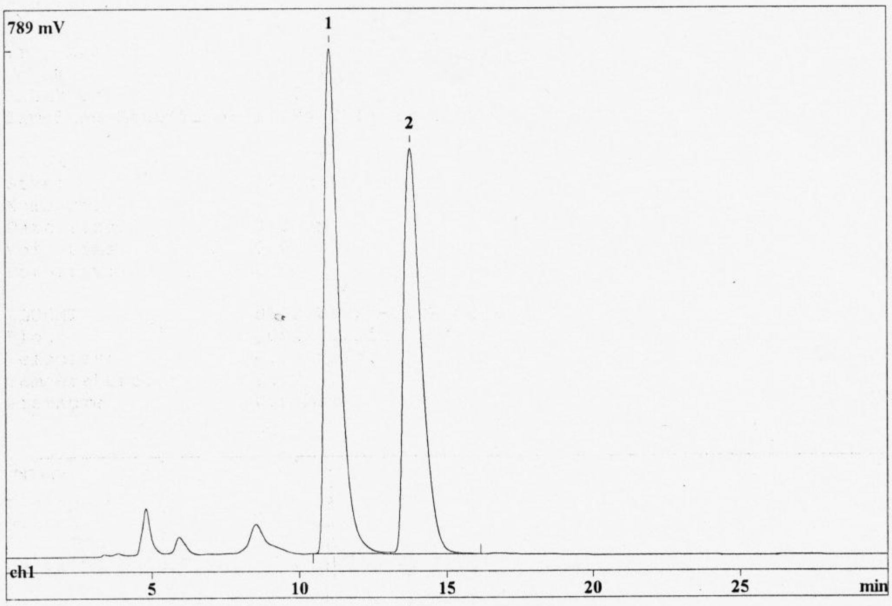
No	Retention min	Area mV*sec	Area %	Name
1	17.93	26342.073	50.02	
2	28.78	26325.063	49.98	
2	61.20	52667.136	100.00	



Quantitation method: Absolute concentration
Standard component: No
Normalization: 100.00

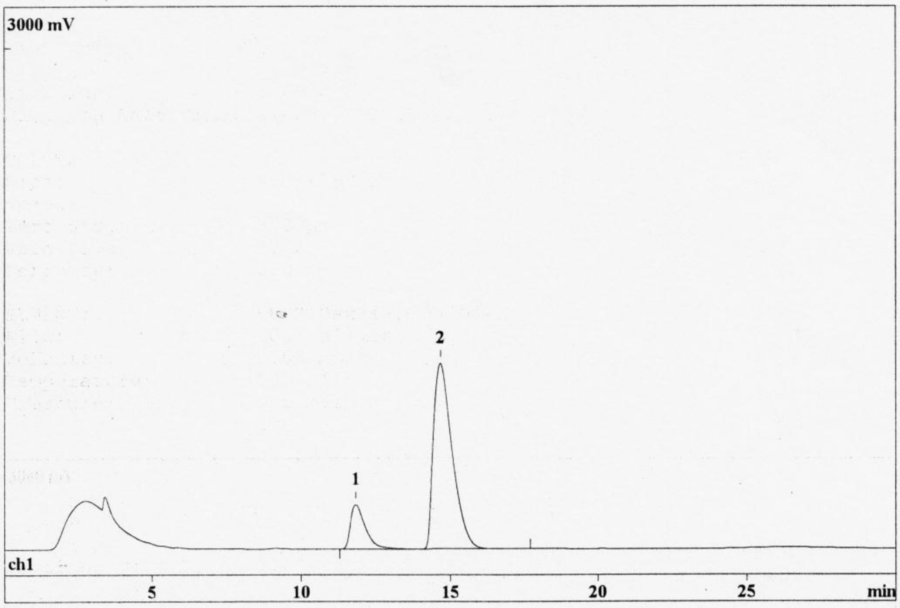
No	Retention min	Area mV*sec	Area %	Name
1	17.43	6504.526	14.28	
2	27.80	39037.099	85.72	
2	63.00	45541.626	100.00	

3aj: Chiralcel OD-H column, hexane/*i*-PrOH = 98:2, flow rate 1.0 mL/min, λ = 254 nm



Quantitation method: Absolute concentration
Standard component: No
Normalization: 100.00

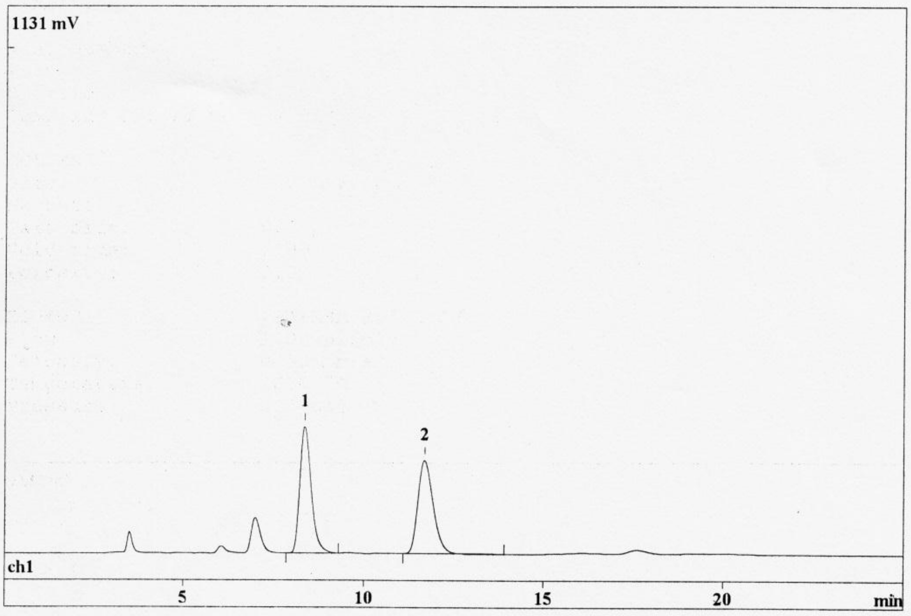
No	Retention min	Area mV*sec	Area %	Name
1	11.04	26501.310	51.09	
2	13.77	25370.361	48.91	
2	30.00	51871.670	100.00	



Quantitation method: Absolute concentration
Standard component: No
Normalization: 100.00

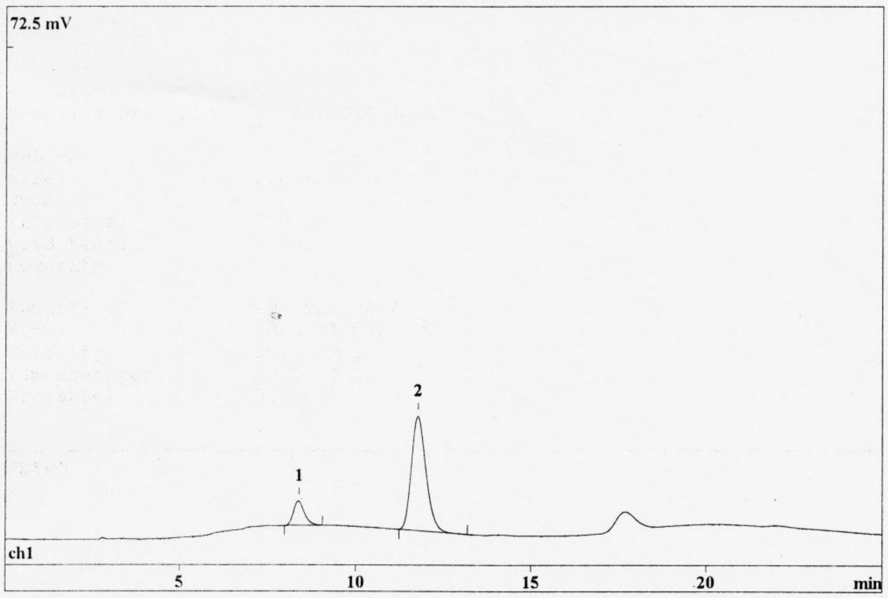
No	Retention min	Area mV*sec	Area %	Name
1	11.83	8847.744	15.99	
2	14.67	46495.990	84.01	
2	30.00	55343.734	100.00	

3al: Chiralcel OJ column, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm



Quantitation method: Absolute concentration
Standard component: No
Normalization: 100.00

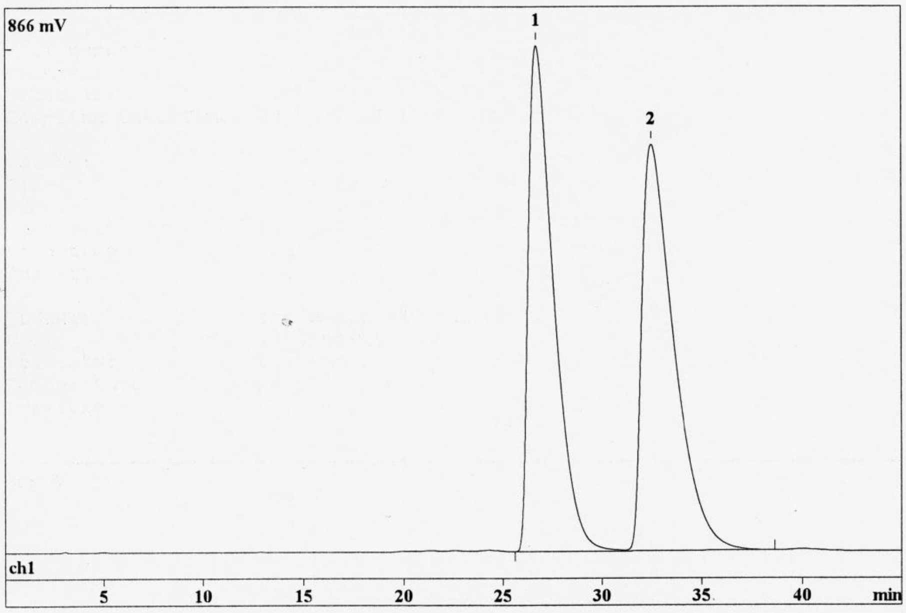
No	Retention min	Area mV*sec	Area %	Name
1	8.36	5856.876	50.05	
2	11.67	5844.443	49.95	
2	25.00	11701.318	100.00	



Quantitation method: Absolute concentration
Standard component: No
Normalization: 100.00

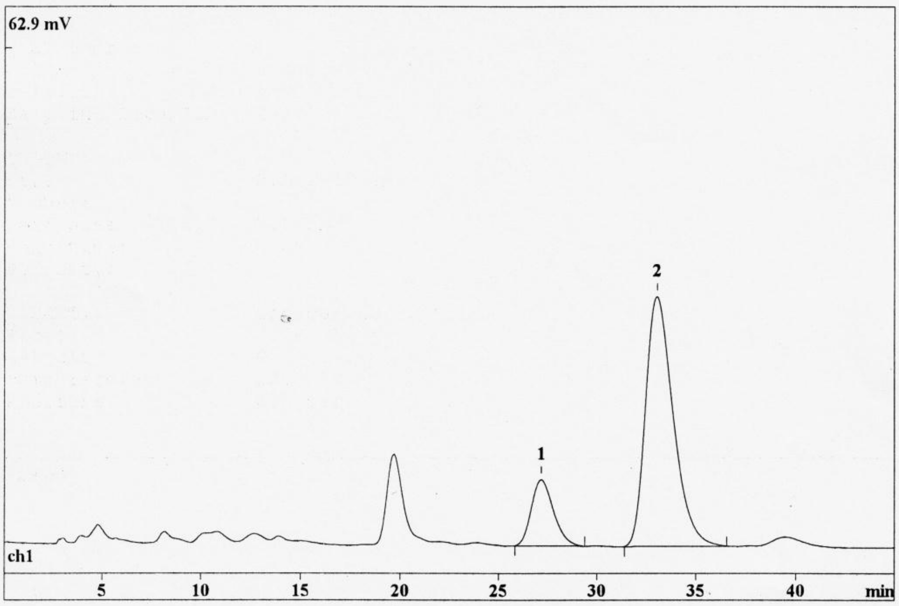
No	Retention min	Area mV*sec	Area %	Name
1	8.38	73.381	13.61	
2	11.76	465.624	86.39	
2	25.00	539.005	100.00	

3am: Chiralcel OJ column, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm



Quantitation method: Absolute concentration
Standard component: No
Normalization: 100.00

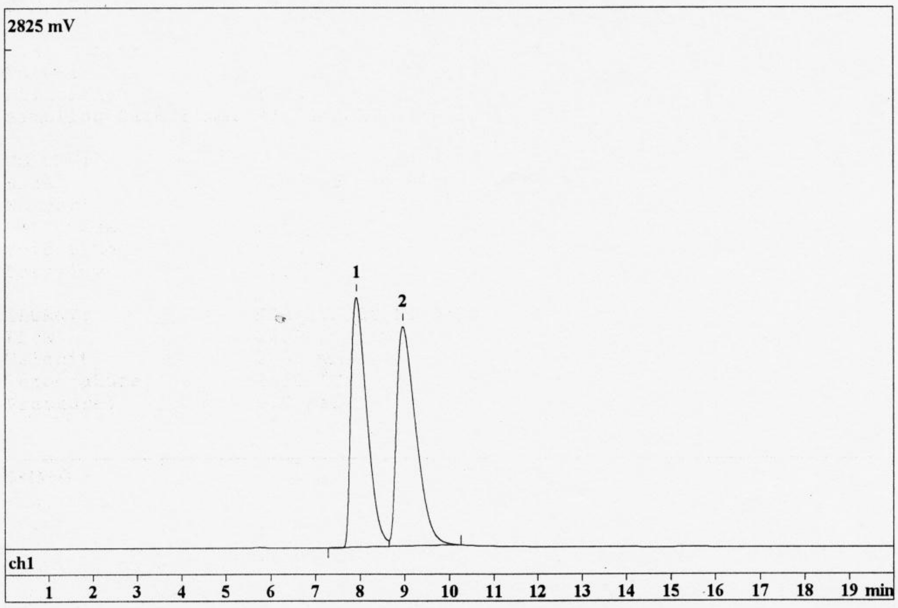
No	Retention min	Area mV*sec	Area %	Name
1	26.69	73154.639	49.61	
2	32.48	74297.902	50.39	
2	45.00	147452.542	100.00	



Quantitation method: Absolute concentration
Standard component: No
Normalization: 100.00

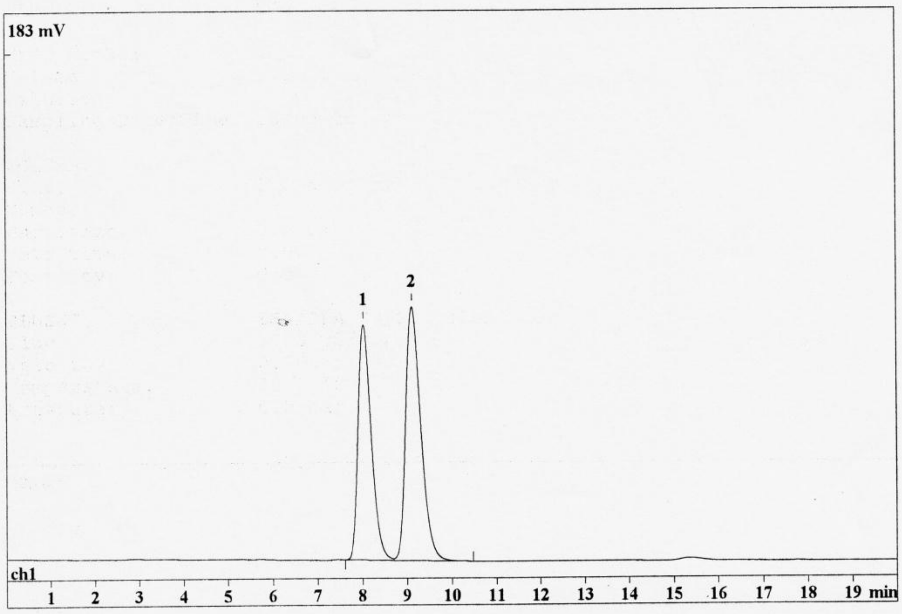
No	Retention min	Area mV*sec	Area %	Name
1	27.16	623.330	17.67	
2	33.03	2903.454	82.33	
2	45.00	3526.784	100.00	

3an: Chiralcel OJ column, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm



Quantitation method: Absolute concentration
Standard component: No
Normalization: 100.00

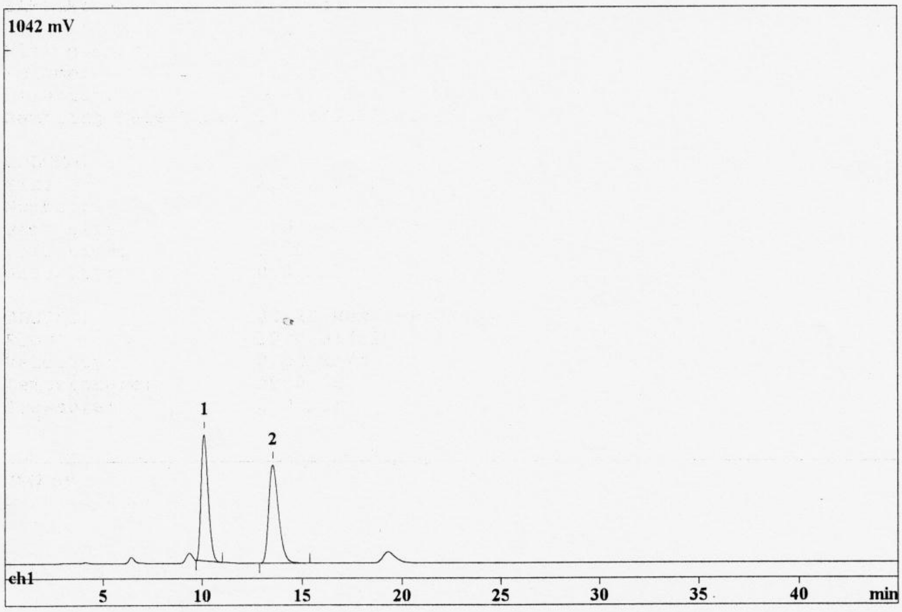
No	Retention min	Area mV*sec	Area %	Name
1	7.91	33443.255	48.44	
2	8.96	35594.304	51.56	
2	20.00	69037.559	100.00	



Quantitation method: Absolute concentration
Standard component: No
Normalization: 100.00

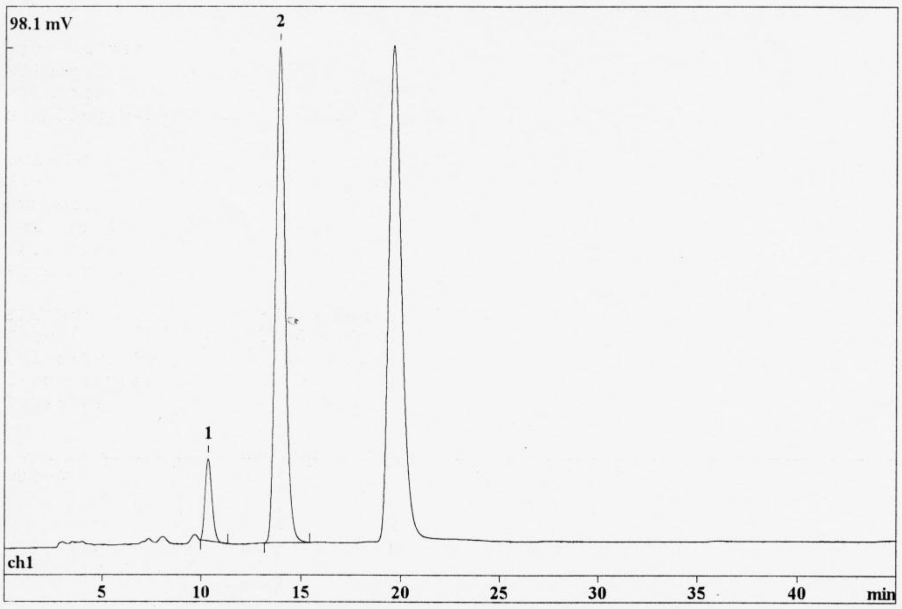
No	Retention min	Area mV*sec	Area %	Name
1	8.03	1677.718	44.64	
2	9.11	2080.911	55.36	
2	20.00	3758.629	100.00	

3ao: Chiralcel OJ column, hexane/*i*-PrOH = 90:10, flow rate 1.0 mL/min, λ = 254 nm



Quantitation method: Absolute concentration
Standard component: No
Normalization: 100.00

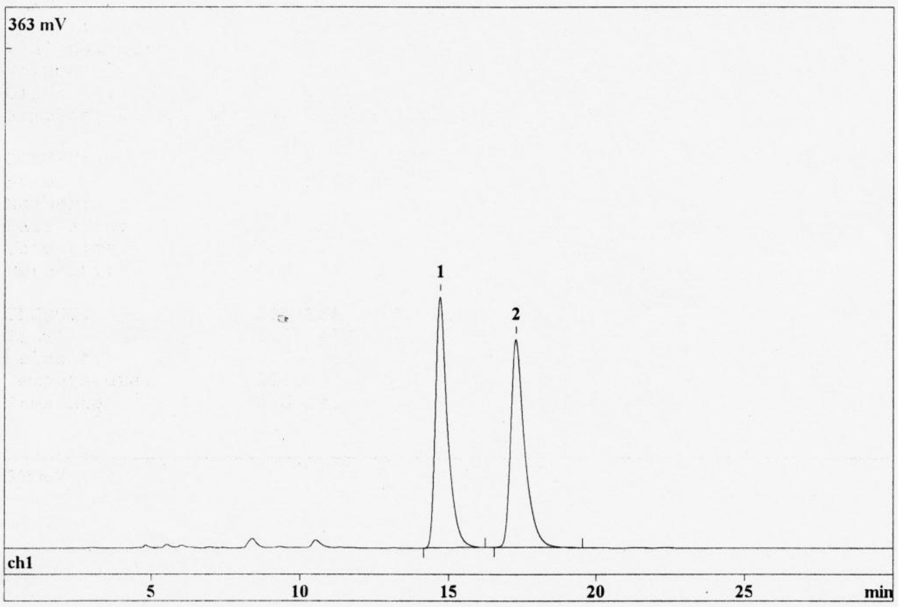
No	Retention min	Area mV*sec	Area %	Name
1	10.10	6187.008	48.41	
2	13.54	6594.227	51.59	
2	45.00	12781.235	100.00	



Quantitation method: Absolute concentration
Standard component: No
Normalization: 100.00

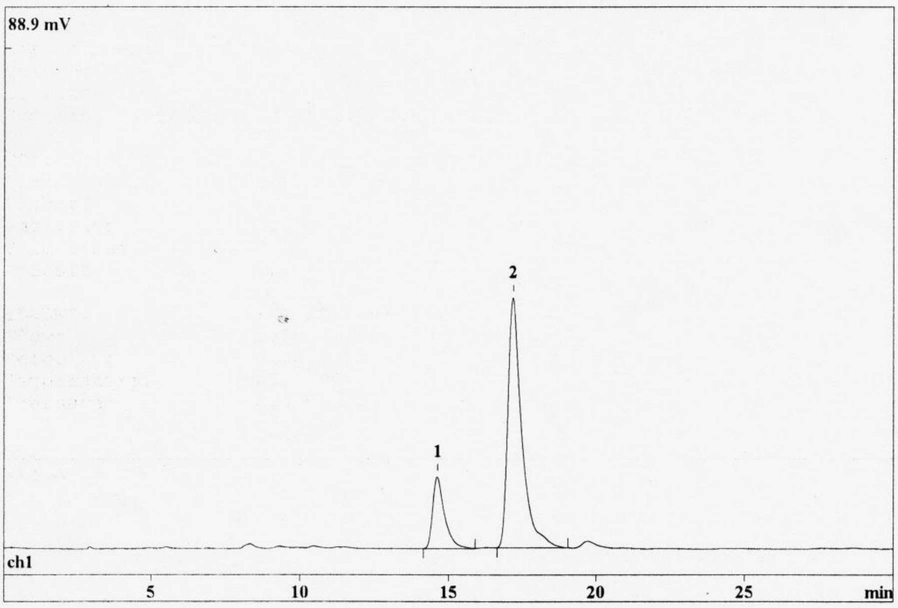
No	Retention min	Area mV*sec	Area %	Name
1	10.34	367.444	10.53	
2	13.89	3121.624	89.47	
2	45.00	3489.068	100.00	

3ba: Chiralpak AD-H column, hexane/*i*-PrOH = 90:10, flow rate 1.0 mL/min, λ = 254 nm



Quantitation method: Absolute concentration
Standard component: No
Normalization: 100.00

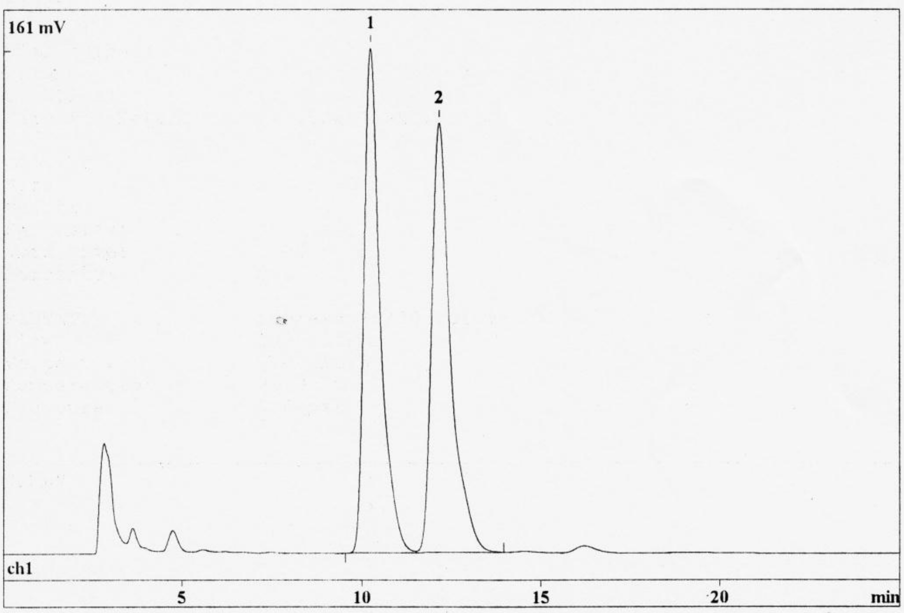
No	Retention min	Area mV*sec	Area %	Name
1	14.70	4887.685	50.44	
2	17.27	4802.681	49.56	
2	30.00	9690.366	100.00	



Quantitation method: Absolute concentration
Standard component: No
Normalization: 100.00

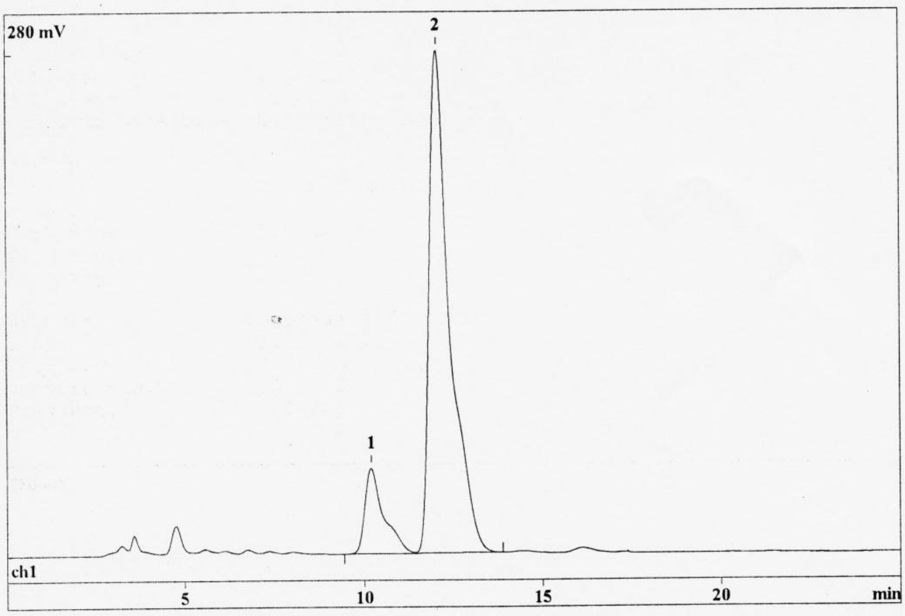
No	Retention min	Area mV*sec	Area %	Name
1	14.61	336.469	19.35	
2	17.18	1402.549	80.65	
2	30.00	1739.017	100.00	

3ca: Chiralcel OJ column, hexane/*i*-PrOH = 70:30, flow rate 1.0 mL/min, λ = 254 nm



Quantitation method: Absolute concentration
Standard component: No
Normalization: 100.00

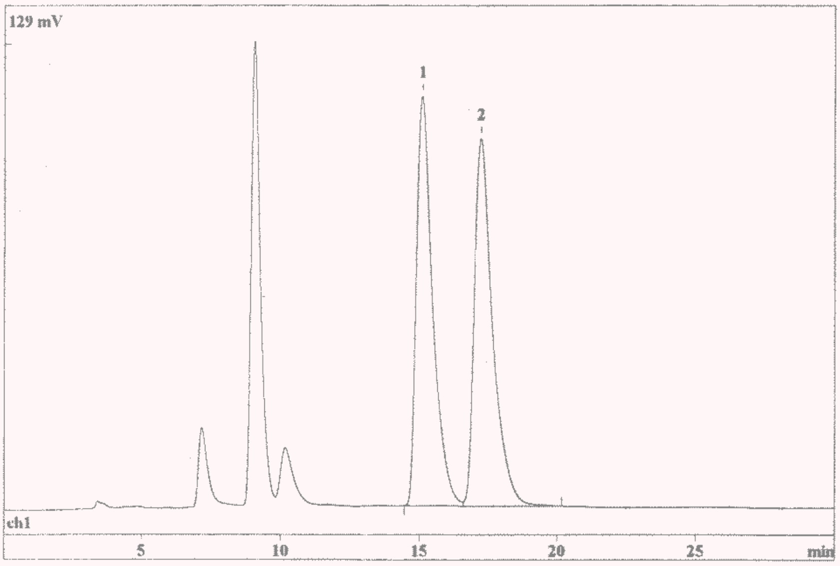
No	Retention min	Area mV*sec	Area %	Name
1	10.24	4803.255	49.84	
2	12.15	4833.952	50.16	
2	25.00	9637.207	100.00	



Quantitation method: Absolute concentration
Standard component: No
Normalization: 100.00

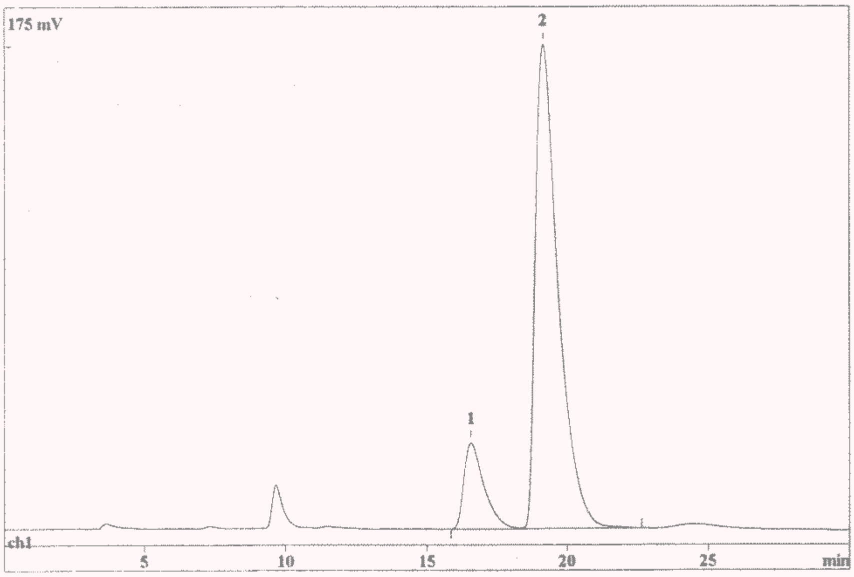
No	Retention min	Area mV*sec	Area %	Name
1	10.19	1677.323	13.62	
2	12.05	10633.536	86.38	
2	25.00	12310.859	100.00	

3da: Chiralcel OD-H column, hexane/i-PrOH = 98:2, flow rate 1.0 mL/min, λ = 254 nm



Quantitation method: Absolute concentration
Standard component: No
Normalization: 100.00

No	Retention min	Area mV*sec	Area %	Name
1	15.09	4416.716	49.54	
2	17.22	4498.710	50.46	
2	30.00	8915.426	100.00	



Quantitation method: Absolute concentration
Standard component: No
Normalization: 100.00

No	Retention min	Area mV*sec	Area %	Name
1	16.56	1530.094	13.73	
2	19.15	9616.804	86.27	
2	30.00	11146.898	100.00	