Non-Enzymatic Dynamic Kinetic Resolution of Secondary Alcohols via Enantioselective Acylation: Synthetic and Mechanistic Studies

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Supporting Information

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I. General Information

The following reagents were purchased from Aldrich and used as received: KO*t*-Bu, *t*-amyl alcohol (anhydrous), toluene (anhydrous), and NEt_3 (anhydrous). **(C_5Ph_5)-DMAP***[1] and **Ru^{Cl_2}** were synthesized as previously described. 1-Phenylethanol, 1-phenyl-1-propanol, 2-methyl-1-phenyl-1-propanol, 1-(2-methylphenyl)ethanol, and Ac_2O were purchased (Aldrich or Alfa Aesar) and purified by vacuum distillation prior to use. 1-(1-Naphthyl)ethanol was purchased from Aldrich and purified by column chromatography prior to use. The other secondary alcohols have been reported previously and were synthesized either by the addition of a Grignard reagent to an aldehyde or by the reduction of a ketone (purification: column chromatography).

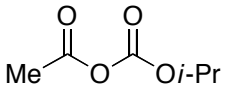
Unless otherwise specified, reactions were conducted with stirring in oven-dried glassware under an atmosphere of nitrogen.

HPLC analyses were carried out on an Agilent 1100 series system equipped with a Daicel CHIRALCEL OD column (internal diameter 4.6 mm, column length 250 mm, particle size 5 μ). GC analyses were obtained on an Agilent 6850 system equipped with a Varian CP-Chirasil-DEX CB column (internal diameter 0.25 mm, column length 25 m).

(1) Wurz, R. P.; Lee, E. C.; Ruble, J. C.; Fu, G. C. *Adv. Synth. Catal*. **2007**, *349*, 2345–2352.
(2) Martín-Matute, B.; Edin, M; Bogár, K.; Kaynak, F. B.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **2005**, *127*, 8817–8825.

II. Preparation of Acyl Carbonates

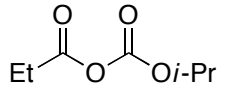
The procedures and yields have not been optimized.



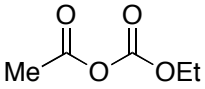
Acetyl isopropyl carbonate [60059-18-9]. Acetic acid (1.7 mL, 30 mmol) was added via syringe to a 250-mL round-bottom flask that contained anhydrous Et_2O (60 mL) and NEt_3 (4.2 mL, 30 mmol) at 0 °C. The reaction mixture was stirred for 5 min, and then isopropyl chloroformate (30 mL, 30 mmol; 1.0 M in toluene; Aldrich) was added dropwise via syringe over 10 min. The reaction mixture was stirred at 0 °C for 45 min. Next, an aqueous 10% citric acid solution (30 mL) was added. The organic layer was decanted and then washed with additional citric acid solution (20 mL), a saturated $NaHCO_3$ solution (30 mL), and brine (30 mL). The organic solvent was evaporated under reduced pressure, and the acyl carbonate was purified by vacuum distillation (30 °C at 500 mtorr), which provided a clear, colorless liquid (2.2 g, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.97 (septet, 1H, J = 6.4 Hz), 2.19 (s, 3H), 1.33 (d, 6H, J = 6.4 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 148.5, 74.5, 21.6, 21.2.



Propionyl isopropyl carbonate [176438-88-3]. Propionic acid (1.2 mL, 15 mmol) was added via syringe to a 250-mL round-bottom flask that contained anhydrous Et_2O (30 mL) and NEt_3 (2.1 mL, 15 mmol) at 0 °C. The reaction mixture was stirred for 5 min, and then isopropyl chloroformate (15 mL, 15 mmol; 1.0 M in toluene; Aldrich) was added dropwise via syringe over 10 min. The reaction mixture was stirred at 0 °C for 45 min. Next, an aqueous 10% citric acid solution (15 mL) was added. The organic layer was decanted and then washed with additional citric acid solution (10 mL), a saturated $NaHCO_3$ solution (15 mL), and brine (15 mL). The organic solvent was evaporated under reduced pressure, and the acyl carbonate was purified by vacuum distillation (27 °C at 450 mtorr), which provided a clear, colorless liquid (1.1 g, 46% yield).



Acetyl ethyl carbonate [15890-77-4]. Acetic acid (0.85 mL, 15 mmol) was added via syringe to a 250-mL round-bottom flask that contained anhydrous Et_2O (30 mL) and NEt_3 (2.1 mL, 15 mmol) at 0 °C. The reaction mixture was stirred for 5 min, and then ethyl chloroformate (1.4 mL, 15 mmol) was added dropwise via syringe over 10 min. The reaction mixture was stirred at 0 °C for 45 min. Next, an aqueous 10% citric acid solution (15 mL) was added. The organic layer was decanted and then washed with additional citric acid solution (10 mL), a saturated $NaHCO_3$ solution (15 mL), and brine (15 mL). The organic solvent was evaporated under reduced pressure, which provided a clear, colorless liquid (1.3 g, 66% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.30 (quartet, 2H, J = 6.9 Hz), 2.19 (s, 3H), 1.34 (t, 3H, J = 6.9 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 148.9, 65.6, 21.0, 13.9.

III. Dynamic Kinetic Resolutions of Secondary Alcohols

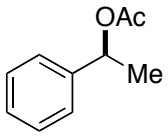
General procedure. In a nitrogen-filled glovebox (for a glovebox-free procedure, see below), **Ru^{Cl}** (16.6 mg, 0.026 mmol), KO*t*-Bu (2.5 mg, 0.022 mmol), toluene (100 μL), and *t*-amyl alcohol (150 μL) were combined in an oven-dried 4-mL vial equipped with a stir bar. The resulting mixture was stirred at r.t. for 6 min, and then the alcohol (0.50 mmol) and (+)-**(C$_5$Ph$_5$)-DMAP*** (3.3 mg in 50 μL toluene, 0.0050 mmol) were added to the vial. The vial was then capped with a septum-lined cap, removed from the glovebox, and cooled to 10 °C. After cooling the solution for 10 min, acetyl isopropyl carbonate (108 μL, 0.750 mmol) was added dropwise to the vial via syringe pump over 20 h (Notes: For optimal results, the tip of the needle should be aligned such that the acetyl isopropyl carbonate drips down the wall of the vial. Some grease was applied to the septum around the needle, to discourage moisture/air from entering the vial during the addition.). The reaction mixture was stirred at 10 °C for an additional 28 h. To remove the (+)-**(C$_5$Ph$_5$)-DMAP***, the mixture was then filtered through a plug of silica gel using Et_2O (10 mL) as the eluant, and the volatiles were removed under reduced pressure with minimal heat (to minimize evaporation of the products, since some are volatile). To remove a trace of a colored impurity, the residue was dissolved in CH_2Cl_2 (20 mL), H_2O (20 mL), and a 70% aqueous solution of *t*-BuOOH (2 mL). This mixture was stirred at r.t. for 2 h, and the product was isolated by extraction into CH_2Cl_2 (3 x 50 mL). The CH_2Cl_2 layers were combined and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The product was purified by column chromatography (hexanes → 20% Et_2O in hexanes).

Notes: For the sake of convenience, the DKRs were set up in a glovebox. However, this method does *not* require the use of a glovebox (see the next procedure).

For the alcohol illustrated in entry 1 of Table 1, the DKR proceeded in 81% ee and 88% yield when the acetyl isopropyl carbonate was added dropwise over 1 min, rather than by syringe pump over 20 h.

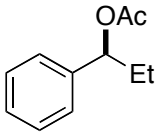
Glovebox-free procedure. **Ru^{Cl}** (16.6 mg, 0.026 mmol) and KO*t*-Bu (2.5 mg, 0.022 mmol) were added to an oven-dried 4-mL vial. The vial was capped, and then it was evacuated and backfilled with nitrogen (three cycles). Toluene (100 μL) and *t*-amyl alcohol (150 μL) were added via syringe, and the resulting solution was stirred at r.t. for 6 min. (+)-**(C$_5$Ph$_5$)-DMAP*** (3.3 mg, 0.0050 mmol) was added to another oven-dried 4-mL vial, and this vial was capped, and then it was evacuated and backfilled with nitrogen (three cycles); next, toluene (50 μL) was added. The alcohol (0.50 mmol) and the solution of (+)-**(C$_5$Ph$_5$)-DMAP*** were added in turn by syringe to the vial containing **Ru^{Cl}**. The resulting mixture was cooled to 10 °C. The remainder of the procedure (addition of acetyl isopropyl carbonate onward) follows the general procedure.

This procedure provided 86% ee and 95% yield for the DKR illustrated in entry 1 of Table 1, and it furnished 90% ee and 97% yield for the DKR depicted in entry 2 of Table 1.



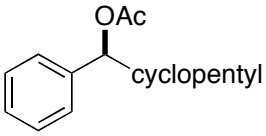
(*S*)-1-Phenylethyl acetate (Table 1, entry 1) [16197-93-6]. The title compound was prepared according to the general procedure, using 1-phenylethanol (61 mg, 0.50 mmol). After purification by column chromatography (hexanes → 20% Et_2O in hexanes), the title compound was isolated as a clear, colorless oil (70 mg, 85% yield; 95% calibrated GC yield) with 86% ee (GC analysis of the product: CP-Chirasil-DEX CB; heating program: 105 °C → 115 °C @ 1 °C/min, followed by 115 → 175 °C @ 5 °C/min; He flow rate: 1.0 ml/min; retention times: 6.5 min (major), 7.2 min (minor)).

The second run was performed with (–)-**(C_5Ph_5)-DMAP***. The product was isolated as a clear, colorless oil (69 mg, 84% yield; 95% calibrated GC yield) with 87% ee.



(*S*)-1-Phenylpropyl acetate (Table 1, entry 2) [83860-48-4]. The title compound was prepared according to the general procedure, using 1-phenylpropanol (68 mg, 0.50 mmol). After purification by column chromatography (hexanes → 20% Et_2O in hexanes), the title compound was isolated as a clear, colorless oil (82 mg, 92% yield; 95% calibrated GC yield) with 90% ee (GC analysis of the product: CP-Chirasil-DEX CB; heating program: 105 °C → 115 °C @ 0.5 °C/min, followed by 115 → 175 °C @ 5 °C/min; He flow rate: 1.0 ml/min; retention times: 9.3 min (major), 9.9 min (minor)).

The second run was performed with (–)-**(C_5Ph_5)-DMAP***. The product was isolated as a clear, colorless oil (86 mg, 97% yield; 97% calibrated GC yield) with 90% ee.



(*S*)-Cyclopentyl(phenyl) acetate (Table 1, entry 3). The title compound was prepared according to the general procedure, using cyclopentyl(phenyl)methanol (88 mg, 0.50 mmol). After purification by column chromatography (hexanes → 20% Et_2O in hexanes), the title compound was isolated as a clear, colorless oil (94 mg, 86% yield; 91% calibrated GC yield) with 82% ee (HPLC analysis of the product: Daicel CHIRALCEL OD-H column; solvent system: hexanes; 1.0 mL/min; retention times: 20.2 min (minor), 41.2 min (major)).

The second run was performed with (–)-**(C_5Ph_5)-DMAP***. The product was isolated as a clear, colorless oil (94 mg, 86% yield; 88% calibrated GC yield) with 81% ee.

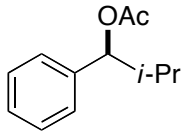
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.29 (m, 4H), 7.29–7.25 (m, 1H), 5.52 (d, 1H, J = 9.2 Hz), 2.34 (sextet, 1H, J = 8.4 Hz), 2.03 (s, 3H), 1.84–1.77 (m, 1H), 1.67–1.52 (m, 3H), 1.50–1.44 (m, 1H), 1.42–1.36 (m, 2H), 1.18–1.09 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 140.8, 128.4, 127.9, 127.2, 80.1, 45.6, 29.8, 29.3, 25.37, 25.35, 21.5.

IR (film) 3033, 2956, 2870, 1739, 1496, 1454, 1371, 1237, 1022, 965, 903, 761, 700 cm^{-1}.

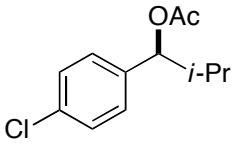
MS (EI) m/z (M^+) calcd for $C_{14}H_{18}O_2$: 218, found: 218.

$[\alpha]^{24}_{D} = -43°$ (c = 1.0, CH_2Cl_2; obtained with (+)-**(C_5Ph_5)-DMAP***).



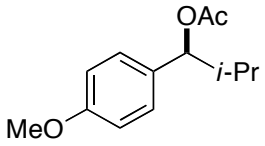
(*S*)-2-Methyl-1-phenylpropyl acetate (Table 1, entry 4) [84194-67-2]. The title compound was prepared according to the general procedure, using 2-methyl-1-phenylpropanol (75 mg, 0.50 mmol). After purification by column chromatography (hexanes → 20% Et_2O in hexanes), the title compound was isolated as a clear, colorless oil (91 mg, 95% yield; 98% calibrated GC yield) with 90% ee (GC analysis of the product: CP-Chirasil-DEX CB; heating program: 105 °C → 115 °C @ 0.5 °C/min, followed by 115 → 175 °C @ 5 °C/min; He flow rate: 1.0 ml/min; retention times: 10.7 min (major), 11.3 min (minor)).

The second run was performed with (–)-**(C_5Ph_5)-DMAP***. The product was isolated as a clear, colorless oil (90 mg, 94% yield; 97% calibrated GC yield) with 91% ee.



(*S*)-2-Methyl-1-(4-chlorophenyl)propyl acetate (Table 1, entry 5) [137408-30-01]. The title compound was prepared according to the general procedure, using 2-methyl-1-(4-chlorophenyl)propanol (92 mg, 0.50 mmol). After purification by column chromatography (hexanes → 20% Et_2O in hexanes), the title compound was isolated as a clear, colorless oil (100 mg, 88% yield; 87% calibrated GC yield) with 85% ee (GC analysis of the product: CP-Chirasil-DEX CB; heating program: 105 °C → 115 °C @ 1 °C/min, followed by 115 → 175 °C @ 5 °C/min; He flow rate: 1.0 ml/min; retention times: 17.2 min (major), 17.5 min (minor)).

The second run was performed with (–)-**(C_5Ph_5)-DMAP***. The product was isolated as a clear, colorless oil (100 mg, 88% yield; 90% calibrated GC yield) with 85% ee.



(*S*)-2-Methyl-1-(4-methoxyphenyl)propyl acetate (Table 1, entry 6). The title compound was prepared according to the general procedure, using 2-methyl-1-(4-methoxyphenyl)propanol (90 mg, 0.50 mmol). After purification by column chromatography (hexanes → 20% Et_2O in hexanes), the title compound was isolated as a white solid (103 mg, 93% yield; 95% calibrated GC yield) with 86% ee (GC analysis of the product: CP-Chirasil-DEX CB; heating program: 105 °C → 115 °C @ 0.5 °C/min, followed by 115 → 175 °C @ 5 °C/min; He flow rate: 1.0 ml/min; retention times: 27.5 min (major), 27.8 min (minor)).

The second run was performed with (–)-**(C_5Ph_5)-DMAP***. The product was isolated as a white solid (100 mg, 90% yield; 90% calibrated GC yield) with 89% ee.

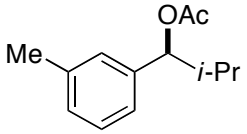
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, 2H, *J* = 8.8 Hz), 6.85 (d, 2H, *J* = 8.4 Hz), 5.39 (d, 1H, *J* = 8.0 Hz), 3.79 (s, 3H), 2.09–2.02 (m, 4H), 0.96 (d, 3H, *J* = 6.8 Hz), 0.76 (d, 3H, *J* = 6.8 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 159.2, 132.0, 128.5, 113.7, 80.9, 55.3, 33.5, 21.4, 19.4, 18.8.

IR (film) 2965, 2873, 1724, 1676, 1606, 1515, 1474, 1456, 1377, 1298, 1244, 1177, 1104, 1032, 1016, 975, 903, 832, 812 cm^{-1}.

MS (EI) *m*/*z* (M^+) calcd for $C_{13}H_{18}O_3$: 222, found: 222.

$[\alpha]^{24}_D$ = –43° (c = 1.0, CH_2Cl_2; obtained with (+)-**(C_5Ph_5)-DMAP***).



(*S*)-2-Methyl-1-(3-Methylphenyl)propyl acetate (Table 1, entry 7). The title compound was prepared according to the general procedure, using 2-methyl-1-(3-methyl)phenylpropanol (82 mg, 0.50 mmol). After purification by column chromatography (hexanes → 20% Et_2O in hexanes), the title compound was isolated as a clear, colorless oil (99 mg, 96% yield; 96% calibrated GC yield) with 90% ee (GC analysis of the product: CP-Chirasil-DEX CB; heating program: 105 °C → 115 °C @ 0.5 °C/min, followed by 115 → 175 °C @ 5 °C/min; He flow rate: 1.0 ml/min; retention times: 14.9 min (major), 15.8 min (minor)).

The second run was performed with (–)-**(C_5Ph_5)-DMAP***. The product was isolated as a clear, colorless oil (99 mg, 96% yield; 97% calibrated GC yield) with 91% ee.

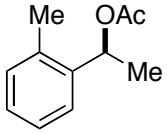
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.20 (m, 1H), 7.10–7.08 (m, 3H), 5.43 (d, 1H, *J* = 7.6 Hz), 2.35 (s, 3H), 2.13–2.05 (m, 4H), 0.97 (d, 3H, *J* = 6.8 Hz), 0.80 (d, 3H, *J* = 6.8 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 139.8, 137.8, 128.5, 128.1, 127.9, 124.2, 81.1, 33.6, 21.6, 21.3, 18.9, 18.6.

IR (film) 2964, 2875, 1736, 1686, 1610, 1450, 1371, 1237, 1160, 1023, 980, 908, 785, 705 cm^{-1}.

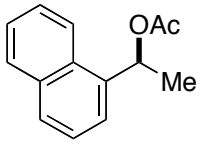
MS (EI) *m*/*z* (M^+) calcd for $C_{13}H_{18}O_2$: 206, found: 206.

$[\alpha]^{24}_D$ = –47° (c = 1.0, CH_2Cl_2; obtained with (+)-**(C_5Ph_5)-DMAP***).



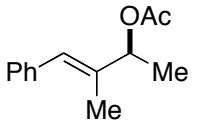
(*S*)-1-(2-Methylphenyl)ethyl acetate (Table 1, entry 8) [501659-37-6]. The title compound was prepared according to the general procedure, using 1-(2-methyl)phenylethanol (68 mg, 0.50 mmol). After purification by column chromatography (hexanes → 20% Et_2O in hexanes), the title compound was isolated as a clear, colorless oil (86 mg, 96% yield; 99% calibrated GC yield) with 93% ee (GC analysis of the product: CP-Chirasil-DEX CB; heating program: 90 °C → 115 °C @ 0.5 °C/min, followed by 115 → 175 °C @ 5 °C/min; He flow rate: 0.7 ml/min; retention times: 20.7 min (major), 21.5 min (minor)).

The second run was performed with (–)-**(C_5Ph_5)-DMAP***. The product was isolated as a clear, colorless oil (78 mg, 87% yield; 94% calibrated GC yield) with 92% ee.



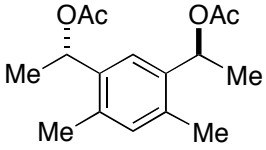
(*S*)-1-(1-naphthyl)ethyl acetate (Table 1, entry 9) [16197-95-8]. The title compound was prepared according to the general procedure, using 1-(1-naphthyl)ethanol (86 mg, 0.50 mmol). After purification by column chromatography (hexanes → 20% Et_2O in hexanes), the title compound was isolated as a clear, colorless oil (103 mg, 96% yield; 99% calibrated GC yield) with 89% ee (HPLC analysis of the product: Daicel CHIRALCEL OD-H column; solvent system: 1.0% *i*-PrOH in hexanes; 1.0 mL/min; retention times: 9.4 min (minor), 14.4 min (major)).

The second run was performed with (–)-**(C_5Ph_5)-DMAP***. The product was isolated as a clear, colorless oil (98 mg, 91% yield; 99% calibrated GC yield) with 91% ee.



(*S*,*E*)-3-Methyl-4-phenylbut-3-en-2-yl acetate (Table 1, entry 10) [187736-05-06]. The title compound was prepared according to the general procedure, using (*E*)-3-methyl-4-phenylbut-3-en-2-ol (81 mg, 0.50 mmol). After purification by column chromatography (hexanes → 20% Et_2O in hexanes), the title compound was isolated as a clear, colorless oil (98 mg, 96% yield; 95% calibrated GC yield) with 89% ee (HPLC analysis of the product: Daicel CHIRALCEL OD-H column; solvent system: 1.0% *i*-PrOH in hexanes; 1.0 mL/min; retention times: 5.9 min (major), 7.5 min (minor)).

The second run was performed with (–)-**(C_5Ph_5)-DMAP***. The product was isolated as a clear, colorless oil (85 mg, 83% yield; 99% calibrated GC yield) with 88% ee.



(1*S*,1'*S*)-1,1'-(4,6-Dimethyl-1,3-phenylene)bis(ethane-1,1-diyl) diacetate (eq 10) [205104-01-4 for the (1*R*,1'*R*) enantiomer]. In a nitrogen-filled glovebox, **Ru**^{Cl} (33.2 mg, 0.052 mmol), KO*t*-Bu (4.9 mg, 0.044 mmol), toluene (200 μL), and *t*-amyl alcohol (300 μL) were combined in an oven-dried 4-mL vial equipped with a stir bar. The resulting mixture was stirred at r.t. for 6 min, and then the alcohol (0.50 mmol) and (+)-**(C_5Ph_5)-DMAP*** (6.6 mg in 100 μL toluene, 0.010 mmol) were added to the vial. The vial was then capped with a septum-lined cap, removed from the glovebox, and cooled to 10 °C. After cooling the solution for 10 min, acetyl isopropyl carbonate (216 μL, 1.50 mmol) was added dropwise to the vial via syringe pump over 20 h (Notes: For optimal results, the tip of the needle should be aligned such that the acetyl isopropyl carbonate drips down the wall of the vial. Some grease was applied to the septum around the needle, to discourage moisture/air from entering the vial during the addition.). The reaction mixture was stirred at 10 °C for an additional 28 h. To remove the (+)-**(C_5Ph_5)-DMAP***, the mixture was then filtered through a plug of silica gel using Et_2O (15 mL) as the eluant, and the volatiles were removed under reduced pressure. To remove a trace of a colored impurity, the residue was dissolved in CH_2Cl_2 (40 mL), H_2O (40 mL), and a 70% aqueous

solution of *t*-BuOOH (4 mL). This mixture was stirred at r.t. for 2 h, and the product was isolated by extraction into CH_2Cl_2 (3 x 50 mL). The CH_2Cl_2 layers were combined and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The product was purified by column chromatography (hexanes → 20% Et_2O in hexanes), which furnished a mixture of the d,l and the meso diacetates (126 mg, 91% yield; dr: 7:1) as a clear, colorless oil. The diastereomers were separated by column chromatography (hexanes → 10% Et_2O in hexanes), which afforded the pure d,l diacetate (111 mg, 80% yield) with 99% ee.

The ee of the product was determined after deacetylation to the diol (HPLC analysis of the diol: Daicel CHIRALCEL OD-H column; solvent system: 5.0% *i*-PrOH in hexanes; 1.0 mL/min; retention times: 17.0 min (major), 28.0 min (minor)).

The second run was performed with (–)-**(C_5Ph_5)-DMAP***. The mixture of the d,l and the meso diacetates was isolated as a clear, colorless oil (128 mg, 92% yield; dr: 7:1). An additional column chromatography afforded the pure d,l diacetate (110 mg, 79% yield) with 99% ee.

The spectral data match those described in the literature.[3]

$[\alpha]^{24}_D = -94°$ (c = 1.0, CH_2Cl_2; obtained with (+)-**(C_5Ph_5)-DMAP***).

IV. Preparation of Ru^{OAc}

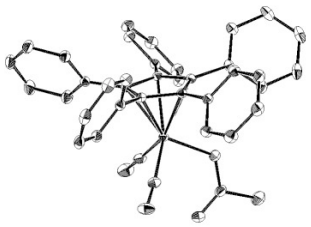
Synthesis of Ru^{OAc}. In a nitrogen-filled glovebox, Ru^{Cl} (100 mg, 0.157 mmol), KO*t*-Bu (17.6 mg, 0.157 mmol), and toluene (2.5 mL) were combined in an oven-dried 20-mL vial equipped with a stir bar. The mixture was stirred at r.t. for 6 min, and then Ac_2O (151 μL, 1.60 mmol) was added to the vial via syringe. The resulting solution was stirred at r.t. for 12 h. Next, the volatiles were removed under reduced pressure, and the residue was purified by column chromatography (20% Et_2O in hexanes → 50% Et_2O in hexanes), which furnished the title compound as a yellow solid (74 mg, 71% yield; not optimized).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21–7.17 (m, 5H), 7.10–7.06 (m, 10H), 6.99–6.97 (m, 10H), 2.00 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 177.5, 132.2, 130.0, 128.3, 127.9, 106.0, 23.1.

IR (film) 3060, 2039, 1989, 1623, 1601, 1503, 1445, 1361, 1309, 1183, 1075, 1028, 803, 785, 743, 699, 675, 561 cm^{-1}.

Structure determination of Ru^{OAc} by X-ray crystallography. X-ray quality crystals were obtained by slowly evaporating CH_2Cl_2 from a saturated solution of Ru^{OAc}.



The crystal contained ca. 5% (η^5-C_5Ph_5)$Ru(CO)_2Cl$, which is omitted for clarity.

(3) Ruble, J. C.; Tweddell, J.; Fu, G. C. *J. Org. Chem.* **1998**, *63*, 2794–2795.

Table 1. Crystal data and structure refinement for X11159.

Identification code	x11159	
Empirical formula	C38.91 H27.86 Cl0.05 O3.91 Ru	
Formula weight	660.56	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 19.5003(10) Å	a= 90°.
	b = 10.5810(5) Å	b= 104.8110(10)°.
	c = 14.9192(8) Å	g = 90°.
Volume	2976.0(3) $Å^3$	
Z	4	
Density (calculated)	1.474 Mg/m^3	
Absorption coefficient	0.573 mm^{-1}	
F(000)	1349	
Crystal size	0.45 x 0.20 x 0.08 mm^3	
Theta range for data collection	2.16 to 29.94°.	
Index ranges	-27<=h<=27, -14<=k<=14, -20<=l<=20	
Reflections collected	116985	
Independent reflections	8640 [R(int) = 0.0289]	
Completeness to theta = 29.94°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9556 and 0.7825	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8640 / 110 / 426	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I)]	R1 = 0.0212, wR2 = 0.0548	
R indices (all data)	R1 = 0.0234, wR2 = 0.0564	
Largest diff. peak and hole	0.455 and -0.642 e. $Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for X11159. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	2599(1)	6419(1)	4071(1)	12(1)
C(1)	2032(1)	6959(1)	5182(1)	13(1)
C(11)	1295(1)	6702(1)	5227(1)	14(1)

C(12)	1184(1)	6442(1)	6096(1)	18(1)
C(13)	498(1)	6319(1)	6203(1)	23(1)
C(14)	-79(1)	6446(1)	5441(1)	24(1)
C(15)	27(1)	6702(1)	4574(1)	22(1)
C(16)	711(1)	6835(1)	4462(1)	18(1)
C(2)	2637(1)	6192(1)	5573(1)	12(1)
C(21)	2624(1)	4928(1)	5997(1)	13(1)
C(22)	3065(1)	4642(1)	6872(1)	16(1)
C(23)	3045(1)	3444(1)	7254(1)	18(1)
C(24)	2590(1)	2525(1)	6774(1)	19(1)
C(25)	2148(1)	2801(1)	5904(1)	19(1)
C(26)	2166(1)	3992(1)	5520(1)	16(1)
C(3)	3266(1)	6879(1)	5477(1)	13(1)
C(31)	4013(1)	6568(1)	5960(1)	14(1)
C(32)	4391(1)	7425(1)	6614(1)	18(1)
C(33)	5066(1)	7131(1)	7154(1)	23(1)
C(34)	5375(1)	5981(2)	7044(1)	25(1)
C(35)	5013(1)	5133(1)	6382(1)	25(1)
C(36)	4333(1)	5422(1)	5845(1)	20(1)
C(4)	3026(1)	8042(1)	5007(1)	13(1)
C(41)	3462(1)	9143(1)	4874(1)	14(1)
C(42)	3363(1)	10269(1)	5316(1)	18(1)
C(43)	3737(1)	11353(1)	5205(1)	22(1)
C(44)	4208(1)	11324(1)	4646(1)	22(1)
C(45)	4311(1)	10208(1)	4210(1)	20(1)
C(46)	3944(1)	9115(1)	4328(1)	17(1)
C(5)	2260(1)	8081(1)	4794(1)	13(1)
C(51)	1809(1)	9156(1)	4354(1)	14(1)
C(52)	1898(1)	9718(1)	3544(1)	18(1)
C(53)	1474(1)	10728(1)	3139(1)	22(1)
C(54)	954(1)	11184(1)	3538(1)	22(1)
C(55)	868(1)	10645(1)	4352(1)	20(1)
C(56)	1296(1)	9642(1)	4763(1)	16(1)
C(8)	3019(1)	4851(1)	3902(1)	19(1)
O(3)	3271(1)	3900(1)	3830(1)	29(1)
O(1)	1638(1)	5699(1)	3315(1)	22(1)
C(6)	1556(1)	5270(1)	2481(1)	20(1)
O(2)	2007(1)	5300(1)	2041(1)	23(1)
C(7)	839(1)	4676(2)	2083(1)	40(1)

C(9A)	1735(14)	6050(30)	3110(20)	22(5)
O(4A)	1230(11)	5740(30)	2537(16)	42(6)
C(9)	2849(1)	7030(1)	3004(1)	18(1)
O(4)	3046(1)	7430(1)	2409(1)	27(1)
Cl(1A)	3017(5)	7011(10)	2694(7)	26(2)

Table 3. Bond lengths [Å] and angles [°] for X11159.

Ru(1)-C(9)	1.894(2)
Ru(1)-C(8)	1.8955(13)
Ru(1)-C(9A)	1.953(14)
Ru(1)-O(1)	2.0689(11)
Ru(1)-C(3)	2.2213(11)
Ru(1)-C(4)	2.2360(11)
Ru(1)-C(2)	2.2363(11)
Ru(1)-C(5)	2.2487(11)
Ru(1)-C(1)	2.2880(11)
Ru(1)-Cl(1A)	2.477(11)
C(1)-C(2)	1.4290(15)
C(1)-C(5)	1.4403(16)
C(1)-C(11)	1.4802(15)
C(11)-C(12)	1.3950(17)
C(11)-C(16)	1.3984(16)
C(12)-C(13)	1.3932(17)
C(12)-H(12)	0.9500
C(13)-C(14)	1.387(2)
C(13)-H(13)	0.9500
C(14)-C(15)	1.387(2)
C(14)-H(14)	0.9500
C(15)-C(16)	1.3919(17)
C(15)-H(15)	0.9500
C(16)-H(16)	0.9500
C(2)-C(3)	1.4630(15)
C(2)-C(21)	1.4830(16)
C(21)-C(22)	1.3992(16)
C(21)-C(26)	1.4002(16)
C(22)-C(23)	1.3945(16)
C(22)-H(22)	0.9500
C(23)-C(24)	1.3864(18)

C(23)-H(23)	0.9500
C(24)-C(25)	1.3925(17)
C(24)-H(24)	0.9500
C(25)-C(26)	1.3882(17)
C(25)-H(25)	0.9500
C(26)-H(26)	0.9500
C(3)-C(4)	1.4342(16)
C(3)-C(31)	1.4882(16)
C(31)-C(36)	1.3941(17)
C(31)-C(32)	1.3968(17)
C(32)-C(33)	1.3922(17)
C(32)-H(32)	0.9500
C(33)-C(34)	1.387(2)
C(33)-H(33)	0.9500
C(34)-C(35)	1.387(2)
C(34)-H(34)	0.9500
C(35)-C(36)	1.3965(18)
C(35)-H(35)	0.9500
C(36)-H(36)	0.9500
C(4)-C(5)	1.4459(15)
C(4)-C(41)	1.4841(16)
C(41)-C(46)	1.3939(16)
C(41)-C(42)	1.3984(17)
C(42)-C(43)	1.3912(17)
C(42)-H(42)	0.9500
C(43)-C(44)	1.389(2)
C(43)-H(43)	0.9500
C(44)-C(45)	1.387(2)
C(44)-H(44)	0.9500
C(45)-C(46)	1.3936(17)
C(45)-H(45)	0.9500
C(46)-H(46)	0.9500
C(5)-C(51)	1.4839(16)
C(51)-C(52)	1.3953(16)
C(51)-C(56)	1.3977(16)
C(52)-C(53)	1.3910(17)
C(52)-H(52)	0.9500
C(53)-C(54)	1.3871(19)
C(53)-H(53)	0.9500

C(54)-C(55)	1.3900(19)
C(54)-H(54)	0.9500
C(55)-C(56)	1.3913(17)
C(55)-H(55)	0.9500
C(56)-H(56)	0.9500
C(8)-O(3)	1.1362(16)
O(1)-C(6)	1.2951(17)
C(6)-O(2)	1.2237(18)
C(6)-C(7)	1.510(2)
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(9A)-O(4A)	1.171(15)
C(9)-O(4)	1.134(3)

C(9)-Ru(1)-C(8)	88.49(6)
C(9)-Ru(1)-C(9A)	79.0(12)
C(8)-Ru(1)-C(9A)	92.8(12)
C(9)-Ru(1)-O(1)	93.43(6)
C(8)-Ru(1)-O(1)	88.15(5)
C(9A)-Ru(1)-O(1)	15.3(11)
C(9)-Ru(1)-C(3)	120.25(5)
C(8)-Ru(1)-C(3)	98.56(5)
C(9A)-Ru(1)-C(3)	157.6(13)
O(1)-Ru(1)-C(3)	145.65(5)
C(9)-Ru(1)-C(4)	97.30(5)
C(8)-Ru(1)-C(4)	130.58(5)
C(9A)-Ru(1)-C(4)	136.5(11)
O(1)-Ru(1)-C(4)	139.83(5)
C(3)-Ru(1)-C(4)	37.54(4)
C(9)-Ru(1)-C(2)	158.26(5)
C(8)-Ru(1)-C(2)	97.74(5)
C(9A)-Ru(1)-C(2)	121.2(12)
O(1)-Ru(1)-C(2)	107.52(5)
C(3)-Ru(1)-C(2)	38.32(4)
C(4)-Ru(1)-C(2)	62.92(4)
C(9)-Ru(1)-C(5)	107.84(5)
C(8)-Ru(1)-C(5)	159.77(5)
C(9A)-Ru(1)-C(5)	101.8(12)

O(1)-Ru(1)-C(5)	102.32(5)
C(3)-Ru(1)-C(5)	63.15(4)
C(4)-Ru(1)-C(5)	37.61(4)
C(2)-Ru(1)-C(5)	62.74(4)
C(9)-Ru(1)-C(1)	143.10(5)
C(8)-Ru(1)-C(1)	128.38(5)
C(9A)-Ru(1)-C(1)	95.6(13)
O(1)-Ru(1)-C(1)	87.10(4)
C(3)-Ru(1)-C(1)	62.33(4)
C(4)-Ru(1)-C(1)	61.80(4)
C(2)-Ru(1)-C(1)	36.80(4)
C(5)-Ru(1)-C(1)	37.01(4)
C(9)-Ru(1)-Cl(1A)	6.4(3)
C(8)-Ru(1)-Cl(1A)	82.3(3)
C(9A)-Ru(1)-Cl(1A)	81.1(12)
O(1)-Ru(1)-Cl(1A)	94.9(2)
C(3)-Ru(1)-Cl(1A)	119.4(2)
C(4)-Ru(1)-Cl(1A)	100.0(2)
C(2)-Ru(1)-Cl(1A)	157.6(2)
C(5)-Ru(1)-Cl(1A)	113.5(3)
C(1)-Ru(1)-Cl(1A)	149.4(3)
C(2)-C(1)-C(5)	108.92(10)
C(2)-C(1)-C(11)	125.99(10)
C(5)-C(1)-C(11)	124.95(10)
C(2)-C(1)-Ru(1)	69.63(6)
C(5)-C(1)-Ru(1)	70.01(6)
C(11)-C(1)-Ru(1)	129.88(8)
C(12)-C(11)-C(16)	119.35(11)
C(12)-C(11)-C(1)	117.45(11)
C(16)-C(11)-C(1)	122.88(11)
C(13)-C(12)-C(11)	120.40(12)
C(13)-C(12)-H(12)	119.8
C(11)-C(12)-H(12)	119.8
C(14)-C(13)-C(12)	119.93(13)
C(14)-C(13)-H(13)	120.0
C(12)-C(13)-H(13)	120.0
C(13)-C(14)-C(15)	120.03(12)
C(13)-C(14)-H(14)	120.0
C(15)-C(14)-H(14)	120.0

C(14)-C(15)-C(16)	120.42(12)
C(14)-C(15)-H(15)	119.8
C(16)-C(15)-H(15)	119.8
C(15)-C(16)-C(11)	119.88(12)
C(15)-C(16)-H(16)	120.1
C(11)-C(16)-H(16)	120.1
C(1)-C(2)-C(3)	107.63(10)
C(1)-C(2)-C(21)	125.73(10)
C(3)-C(2)-C(21)	126.64(10)
C(1)-C(2)-Ru(1)	73.57(6)
C(3)-C(2)-Ru(1)	70.28(6)
C(21)-C(2)-Ru(1)	121.64(8)
C(22)-C(21)-C(26)	118.79(11)
C(22)-C(21)-C(2)	121.26(10)
C(26)-C(21)-C(2)	119.95(10)
C(23)-C(22)-C(21)	120.18(11)
C(23)-C(22)-H(22)	119.9
C(21)-C(22)-H(22)	119.9
C(24)-C(23)-C(22)	120.52(11)
C(24)-C(23)-H(23)	119.7
C(22)-C(23)-H(23)	119.7
C(23)-C(24)-C(25)	119.68(11)
C(23)-C(24)-H(24)	120.2
C(25)-C(24)-H(24)	120.2
C(26)-C(25)-C(24)	120.08(11)
C(26)-C(25)-H(25)	120.0
C(24)-C(25)-H(25)	120.0
C(25)-C(26)-C(21)	120.75(11)
C(25)-C(26)-H(26)	119.6
C(21)-C(26)-H(26)	119.6
C(4)-C(3)-C(2)	107.35(9)
C(4)-C(3)-C(31)	125.67(10)
C(2)-C(3)-C(31)	125.69(10)
C(4)-C(3)-Ru(1)	71.79(6)
C(2)-C(3)-Ru(1)	71.40(6)
C(31)-C(3)-Ru(1)	132.30(8)
C(36)-C(31)-C(32)	118.56(11)
C(36)-C(31)-C(3)	123.13(11)
C(32)-C(31)-C(3)	118.10(11)

C(33)-C(32)-C(31)	120.80(12)
C(33)-C(32)-H(32)	119.6
C(31)-C(32)-H(32)	119.6
C(34)-C(33)-C(32)	120.17(13)
C(34)-C(33)-H(33)	119.9
C(32)-C(33)-H(33)	119.9
C(33)-C(34)-C(35)	119.63(12)
C(33)-C(34)-H(34)	120.2
C(35)-C(34)-H(34)	120.2
C(34)-C(35)-C(36)	120.26(13)
C(34)-C(35)-H(35)	119.9
C(36)-C(35)-H(35)	119.9
C(31)-C(36)-C(35)	120.56(12)
C(31)-C(36)-H(36)	119.7
C(35)-C(36)-H(36)	119.7
C(3)-C(4)-C(5)	108.72(10)
C(3)-C(4)-C(41)	127.75(10)
C(5)-C(4)-C(41)	122.87(10)
C(3)-C(4)-Ru(1)	70.67(6)
C(5)-C(4)-Ru(1)	71.67(6)
C(41)-C(4)-Ru(1)	130.88(8)
C(46)-C(41)-C(42)	119.20(11)
C(46)-C(41)-C(4)	123.78(11)
C(42)-C(41)-C(4)	117.00(10)
C(43)-C(42)-C(41)	120.46(12)
C(43)-C(42)-H(42)	119.8
C(41)-C(42)-H(42)	119.8
C(44)-C(43)-C(42)	120.01(12)
C(44)-C(43)-H(43)	120.0
C(42)-C(43)-H(43)	120.0
C(45)-C(44)-C(43)	119.83(12)
C(45)-C(44)-H(44)	120.1
C(43)-C(44)-H(44)	120.1
C(44)-C(45)-C(46)	120.43(12)
C(44)-C(45)-H(45)	119.8
C(46)-C(45)-H(45)	119.8
C(45)-C(46)-C(41)	120.06(12)
C(45)-C(46)-H(46)	120.0
C(41)-C(46)-H(46)	120.0

C(1)-C(5)-C(4)	107.24(10)
C(1)-C(5)-C(51)	126.91(10)
C(4)-C(5)-C(51)	125.50(10)
C(1)-C(5)-Ru(1)	72.98(6)
C(4)-C(5)-Ru(1)	70.72(6)
C(51)-C(5)-Ru(1)	126.90(8)
C(52)-C(51)-C(56)	118.79(11)
C(52)-C(51)-C(5)	121.30(10)
C(56)-C(51)-C(5)	119.90(10)
C(53)-C(52)-C(51)	120.86(12)
C(53)-C(52)-H(52)	119.6
C(51)-C(52)-H(52)	119.6
C(54)-C(53)-C(52)	119.89(12)
C(54)-C(53)-H(53)	120.1
C(52)-C(53)-H(53)	120.1
C(53)-C(54)-C(55)	119.83(12)
C(53)-C(54)-H(54)	120.1
C(55)-C(54)-H(54)	120.1
C(54)-C(55)-C(56)	120.31(12)
C(54)-C(55)-H(55)	119.8
C(56)-C(55)-H(55)	119.8
C(55)-C(56)-C(51)	120.30(11)
C(55)-C(56)-H(56)	119.8
C(51)-C(56)-H(56)	119.8
O(3)-C(8)-Ru(1)	177.64(11)
C(6)-O(1)-Ru(1)	121.65(10)
O(2)-C(6)-O(1)	125.23(14)
O(2)-C(6)-C(7)	121.31(13)
O(1)-C(6)-C(7)	113.45(14)
O(4A)-C(9A)-Ru(1)	175(3)
O(4)-C(9)-Ru(1)	174.81(14)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for X11159. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

$U^{11}U^{22}$	U^{33}	U^{23}	U^{13}	U^{12}		
Ru(1)	13(1)	12(1)	10(1)	1(1)	4(1)	1(1)
C(1)13(1)	14(1)	12(1)	0(1)	4(1)	1(1)	
C(11)13(1)	12(1)	18(1)	0(1)	5(1)	1(1)	
C(12)18(1)	18(1)	21(1)	2(1)	8(1)	1(1)	
C(13)22(1)	20(1)	32(1)	1(1)	16(1)	1(1)	
C(14)16(1)	17(1)	43(1)	-3(1)	13(1)	0(1)	
C(15)13(1)	16(1)	34(1)	-4(1)	2(1)	2(1)	
C(16)16(1)	15(1)	21(1)	-1(1)	2(1)	2(1)	
C(2)13(1)	13(1)	10(1)	1(1)	3(1)	0(1)	
C(21)13(1)	12(1)	13(1)	1(1)	4(1)	1(1)	
C(22)17(1)	14(1)	15(1)	0(1)	2(1)	-1(1)	
C(23)21(1)	17(1)	16(1)	4(1)	2(1)	1(1)	
C(24)23(1)	14(1)	21(1)	3(1)	7(1)	0(1)	
C(25)20(1)	15(1)	21(1)	-1(1)	4(1)	-4(1)	
C(26)16(1)	17(1)	15(1)	1(1)	2(1)	-1(1)	
C(3)13(1)	13(1)	12(1)	0(1)	3(1)	0(1)	
C(31)12(1)	17(1)	13(1)	2(1)	4(1)	1(1)	
C(32)16(1)	20(1)	18(1)	0(1)	4(1)	-1(1)	
C(33)17(1)	30(1)	20(1)	0(1)	0(1)	-4(1)	
C(34)14(1)	36(1)	23(1)	7(1)	2(1)	3(1)	
C(35)19(1)	27(1)	27(1)	4(1)	4(1)	8(1)	
C(36)18(1)	20(1)	22(1)	-1(1)	2(1)	3(1)	
C(4)14(1)	13(1)	11(1)	0(1)	4(1)	0(1)	
C(41)14(1)	14(1)	14(1)	3(1)	2(1)	-1(1)	
C(42)20(1)	16(1)	19(1)	0(1)	4(1)	-1(1)	
C(43)22(1)	15(1)	26(1)	1(1)	1(1)	-2(1)	
C(44)18(1)	19(1)	27(1)	8(1)	-1(1)	-4(1)	
C(45)14(1)	25(1)	21(1)	7(1)	2(1)	-2(1)	
C(46)14(1)	19(1)	17(1)	2(1)	3(1)	0(1)	
C(5)14(1)	12(1)	12(1)	0(1)	4(1)	1(1)	
C(51)14(1)	12(1)	14(1)	0(1)	2(1)	1(1)	
C(52)20(1)	19(1)	17(1)	3(1)	6(1)	4(1)	
C(53)26(1)	20(1)	20(1)	7(1)	6(1)	5(1)	
C(54)24(1)	17(1)	24(1)	4(1)	2(1)	7(1)	

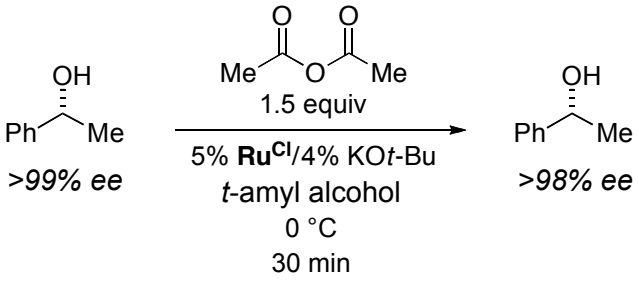
C(55)19(1)	17(1)	22(1)	-1(1)	4(1)	5(1)	
C(56)18(1)	14(1)	16(1)	-1(1)	4(1)	1(1)	
C(8)23(1)	20(1)	12(1)	0(1)	4(1)	2(1)	
O(3)39(1)	22(1)	24(1)	-3(1)	4(1)	12(1)	
O(1)16(1)	33(1)	18(1)	-8(1)	4(1)	-4(1)	
C(6)19(1)	21(1)	16(1)	-4(1)	0(1)	0(1)	
O(2)24(1)	28(1)	17(1)	-6(1)	6(1)	-1(1)	
C(7)25(1)	66(1)	27(1)	-18(1)	2(1)	-15(1)	
C(9A)	22(7)	14(11)	28(12)	1(9)	2(5)	-6(8)
O(4A)	16(9)	62(14)	41(11)	4(11)	-4(6)	-6(10)
C(9)23(1)	14(1)	16(1)	-2(1)	4(1)	0(1)	
O(4)39(1)	26(1)	20(1)	0(1)	14(1)	-7(1)	
Cl(1A)	42(5)	25(5)	17(4)	3(3)	20(3)	-7(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for X11159.

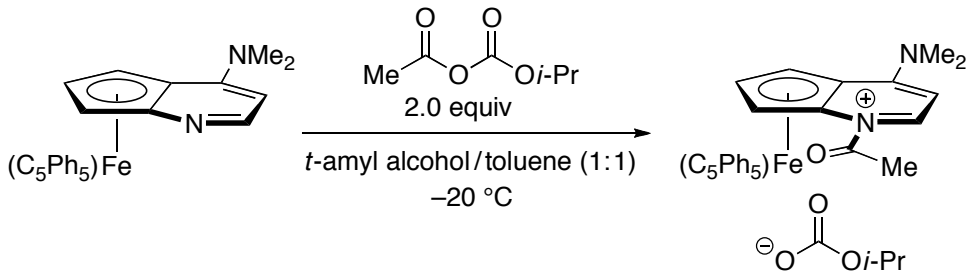
x	y	z	U(eq)	
H(12)	1579	6347	6618	22
H(13)	426	6147	6797	28
H(14)	-547	6359	5512	29
H(15)	-370	6787	4053	27
H(16)	780	7015	3868	21
H(22)	3378	5266	7206	19
H(23)	3345	3257	7848	22
H(24)	2580	1709	7037	23
H(25)	1835	2175	5574	23
H(26)	1864	4174	4926	19
H(32)	4185	8218	6691	22
H(33)	5316	7720	7600	28
H(34)	5833	5775	7419	29
H(35)	5227	4352	6294	30
H(36)	4086	4832	5397	24
H(42)	3039	10295	5695	22
H(43)	3671	12113	5511	26
H(44)	4458	12066	4563	27
H(45)	4633	10188	3829	25

H(46)	4023	8351	4036	20
H(52)	2251	9406	3267	22
H(53)	1541	11105	2590	27
H(54)	658	11863	3256	27
H(55)	516	10964	4630	24
H(56)	1239	9287	5324	19
H(7A)	616	5068	1484	60
H(7B)	538	4808	2510	60
H(7C)	897	3768	1996	60

V. Mechanistic/Reactivity Studies



Eq 5. In a nitrogen-filled glovebox, a solution of **Ru**^{Cl} (6.4 mg, 0.010 mmol) and KO*t*-Bu (0.90 mg, 0.0080 mmol) in *t*-amyl alcohol (400 μL) in an oven-dried 5-mL vial equipped with a stir bar was stirred at room temperature for 6 min. The vial was then capped with a septum-lined cap, removed from the glovebox, and cooled to 0 °C. Next, Ac_2O (28 μL, 0.30 mmol) was added dropwise to the reaction vial over 1 min. Then, (*R*)-1-phenylethanol (24 μL, 0.20 mmol) was added, and the reaction mixture was stirred at 0 °C. After 30 min, an aliquot (40 μL) of the reaction mixture was removed and diluted with Et_2O (1.0 mL). The ee of 1-phenylethanol was determined by chiral GC analysis.



Eq 11. In a nitrogen-filled glovebox, **C_5Ph_5-DMAP***** (20 mg, 0.030 mmol), toluene-d_8 (0.25 mL), and *t*-amyl alcohol (0.25 mL) were combined in a dry NMR tube. The NMR tube was then capped with a screw-cap and removed from the glovebox. The NMR tube was cooled to –20 °C, and then acetyl isopropyl carbonate (8.6 μL, 0.60 mmol) was added to the NMR tube via syringe. The reaction was monitored by ^{1}H NMR as a function of time. After 1.5 h at –20 °C, the acylpyridinium salt had

formed almost quantitatively. The ^{1}H and ^{13}C NMR spectra of the acylpyridinium salt are included in Section VI.

Determination of the rate law: DKR of 1-phenylethanol. In a nitrogen-filled glovebox, **Ru^{Cl}**, KO*t*-Bu, tetradecane, toluene (250 μL), and *t*-amyl alcohol (250 μL) were combined in an oven-dried 4-mL vial equipped with a stir bar. The mixture was stirred at room temperature for 6 min, and then 1-phenylethanol and **(C$_5$Ph$_5$)-DMAP*** were added to the vial. The vial was then capped with a septum-lined cap, removed from the glovebox, and cooled to 10 °C. After cooling the solution for 10 min, acetyl isopropyl carbonate was added dropwise to the vial via syringe over 1 min. An aliquot (40 μL) of the reaction mixture was removed after 10 min, 30 min, 50 min, 80 min, and 120 min, and then filtered through a short pad of silica. The amount of the product was determined by GC analysis (calibrated with tetradecane as the internal standard).

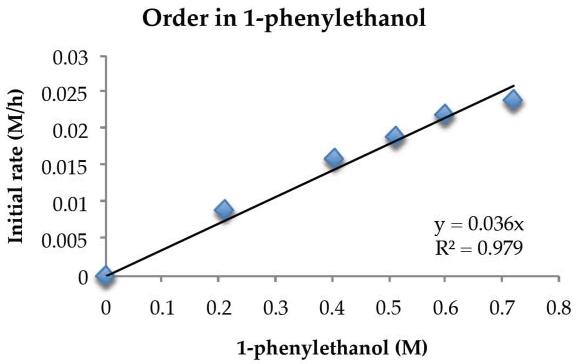
Order in 1-phenylethanol:

Table S1. Observed Initial Rates

$[\text{1-phenylethanol}]_{initial}$ (M)[a]	k_{obs} (M/h)
0.00	0.00
0.21	0.0092
0.40	0.016
0.51	0.019
0.60	0.022
0.72	0.024

[a] Reaction conditions: $[\text{acetyl isopropyl carbonate}]_{initial}$ = 0.75 M, $[\textbf{(C}_5\textbf{Ph}_5\textbf{)-DMAP*}]_{initial}$ = 5.0 mM, $[\textbf{Ru}^{Cl}]_{initial}$ = 0.026 M, and $[\text{KO}t\text{-Bu}]_{initial}$ = 0.022 M.

Figure S1.



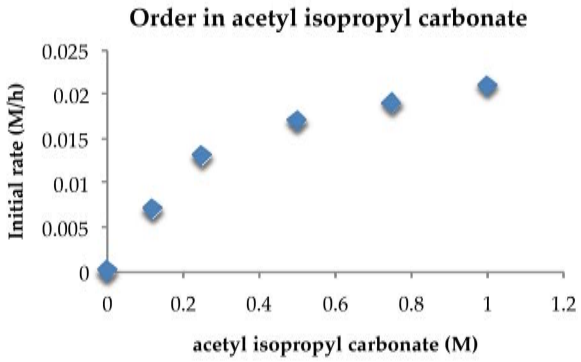
Order in acetyl isopropyl carbonate:

Table S2. Observed Initial Rates

[acetyl isopropyl carbonate]$_{initial}$ (M)[a]	k_{obs} (M/h)
0.00	0.00
0.12	0.0071
0.25	0.013
0.50	0.017
0.75	0.019
1.00	0.021

[a] Reaction conditions: [1-phenylethanol]$_{initial}$ = 0.50 M, [**(C$_5$Ph$_5$)-DMAP***]$_{initial}$ = 5.0 mM, [**Ru^{Cl}**]$_{initial}$ = 0.026 M, and [KO*t*-Bu] $_{initial}$ = 0.022 M.

Figure S2.



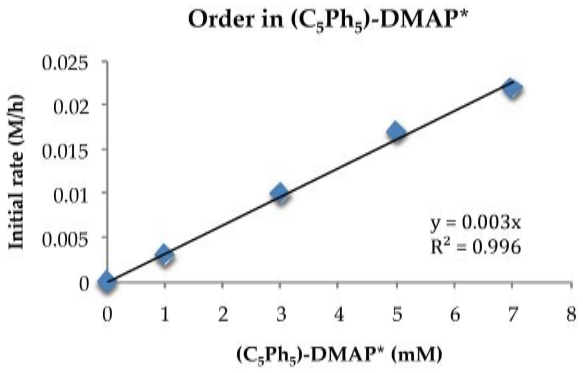
Order in (C$_5$Ph$_5$)-DMAP*:

Table S3. Observed Initial Rates

[**(C$_5$Ph$_5$)-DMAP***]$_{initial}$ (mM)[a]	k_{obs} (M/h)
0.0	0.00
1.0	0.0034
3.0	0.010
5.0	0.017
7.0	0.022

[a] Reaction conditions: [1-phenylethanol]$_{initial}$ = 0.50 M, [acetyl isopropyl carbonate]$_{initial}$ = 0.75 M, [**Ru^{Cl}**]$_{initial}$ = 0.026 M, and [KO*t*-Bu] $_{initial}$ = 0.022 M.

Figure S3.



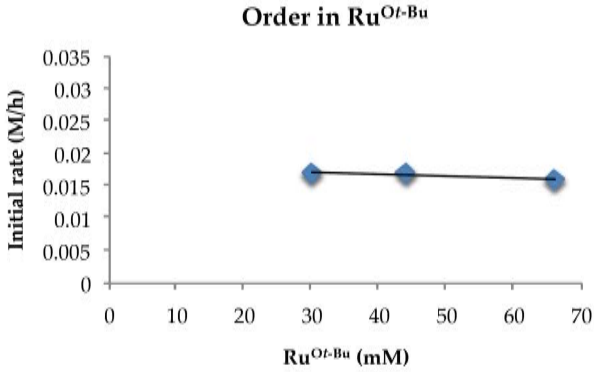
Order in $Ru^{O\text{-}tBu}$

Table S4. Observed Initial Rates

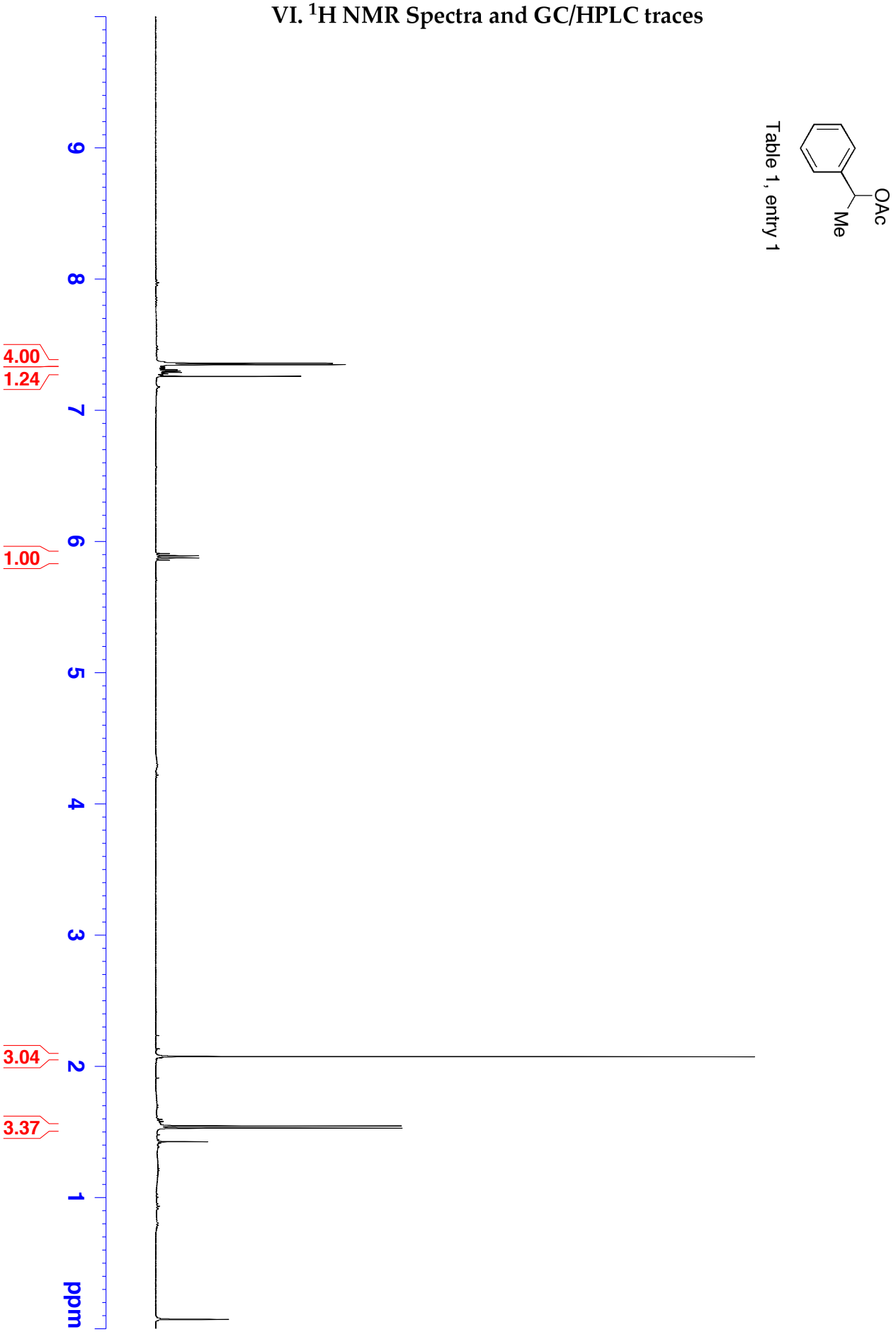
$[\mathbf{Ru}^{\mathbf{O\text{-}tBu}}]_{initial}$ (M)[a]	k_{obs} (M/h)
0.030	0.017
0.044	0.017
0.066	0.016

[a] Reaction conditions: $[\text{1-phenylethanol}]_{initial}$ = 0.50 M, $[\text{acetyl isopropyl carbonate}]_{initial}$ = 0.75 M, and $[\mathbf{(C_5Ph_5)\text{-}DMAP^*}]_{initial}$ = 5.0 mM.

Figure S4.



VI. ^{1}H NMR Spectra and GC/HPLC traces



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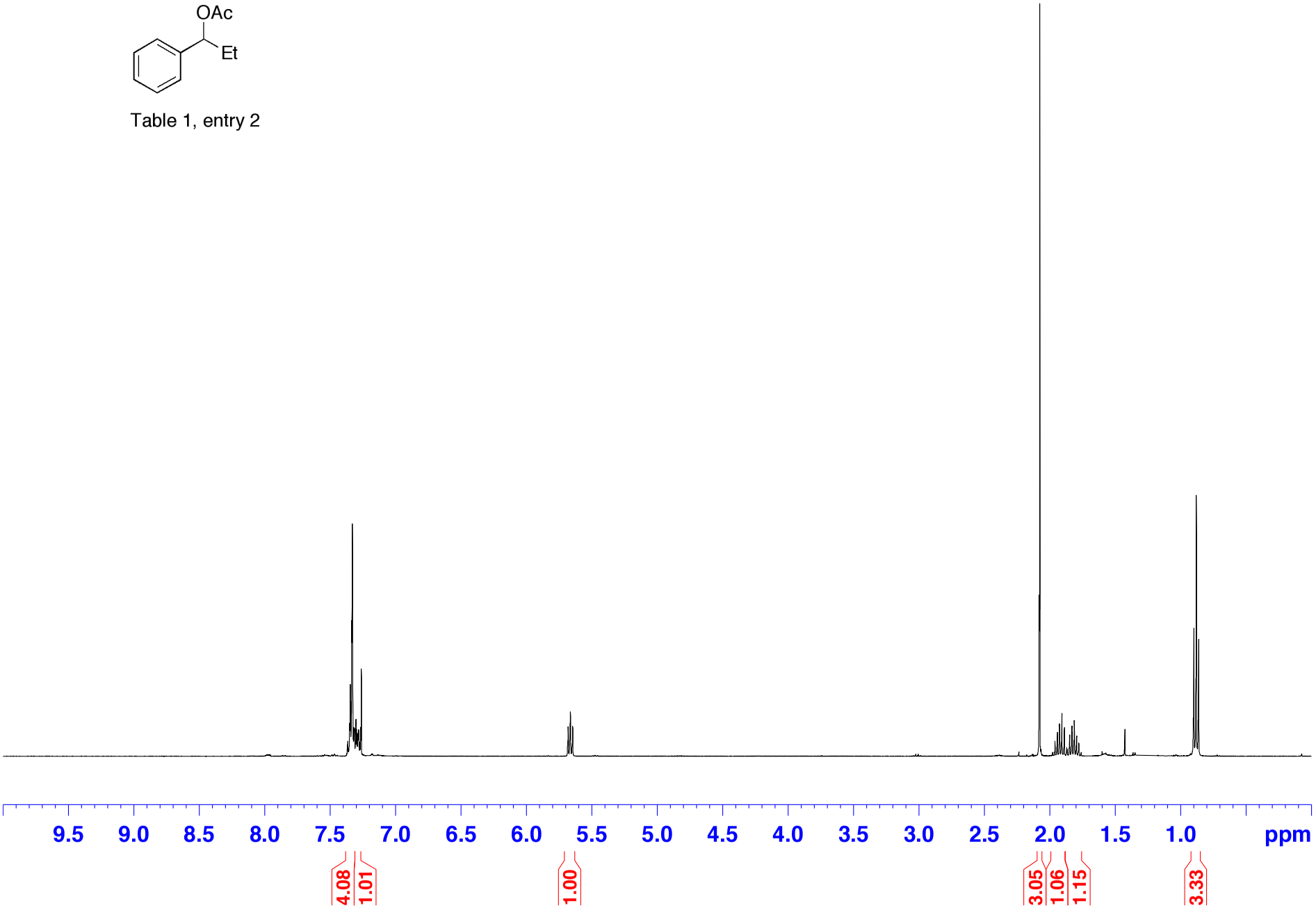

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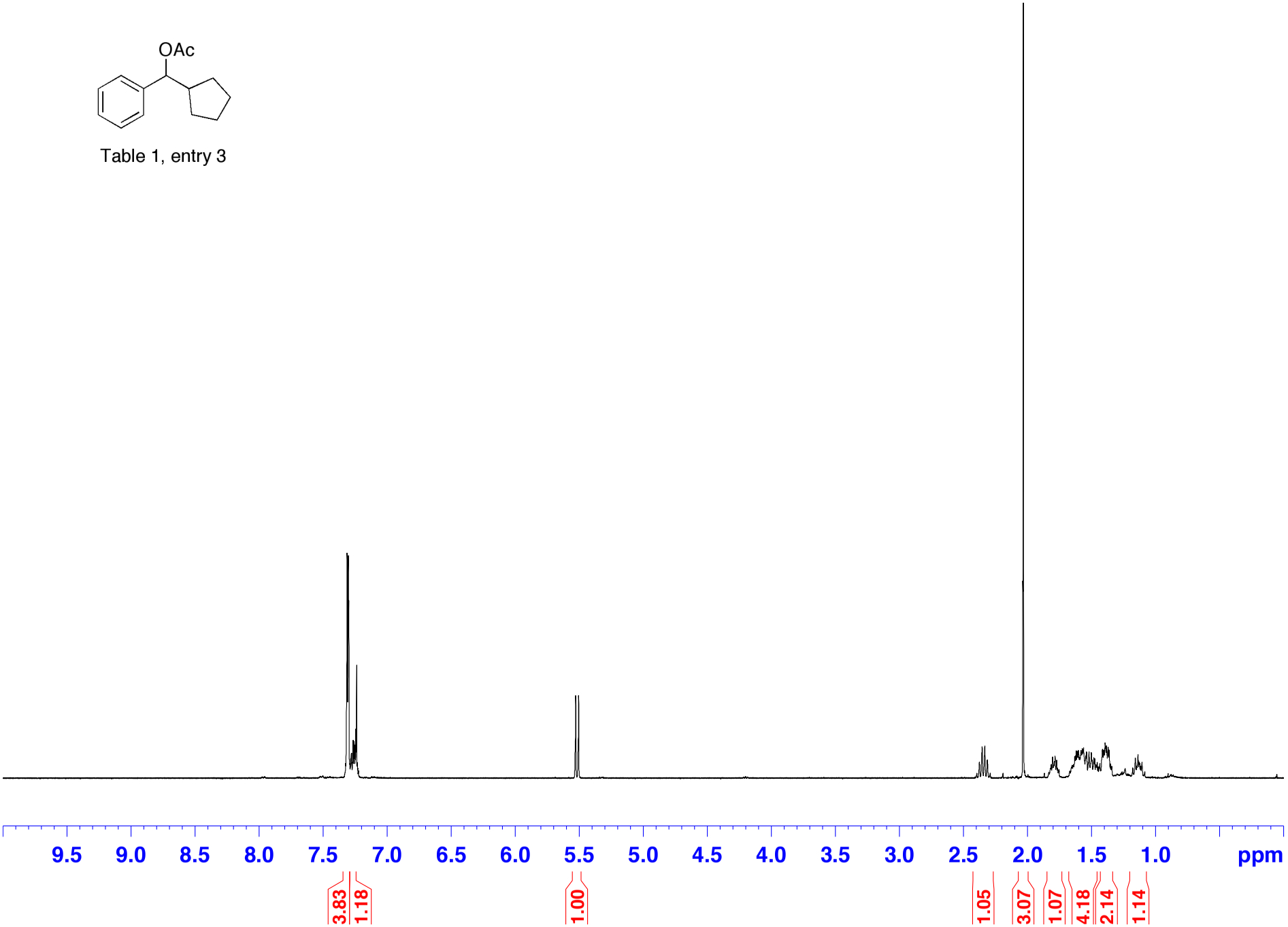

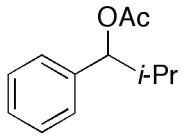

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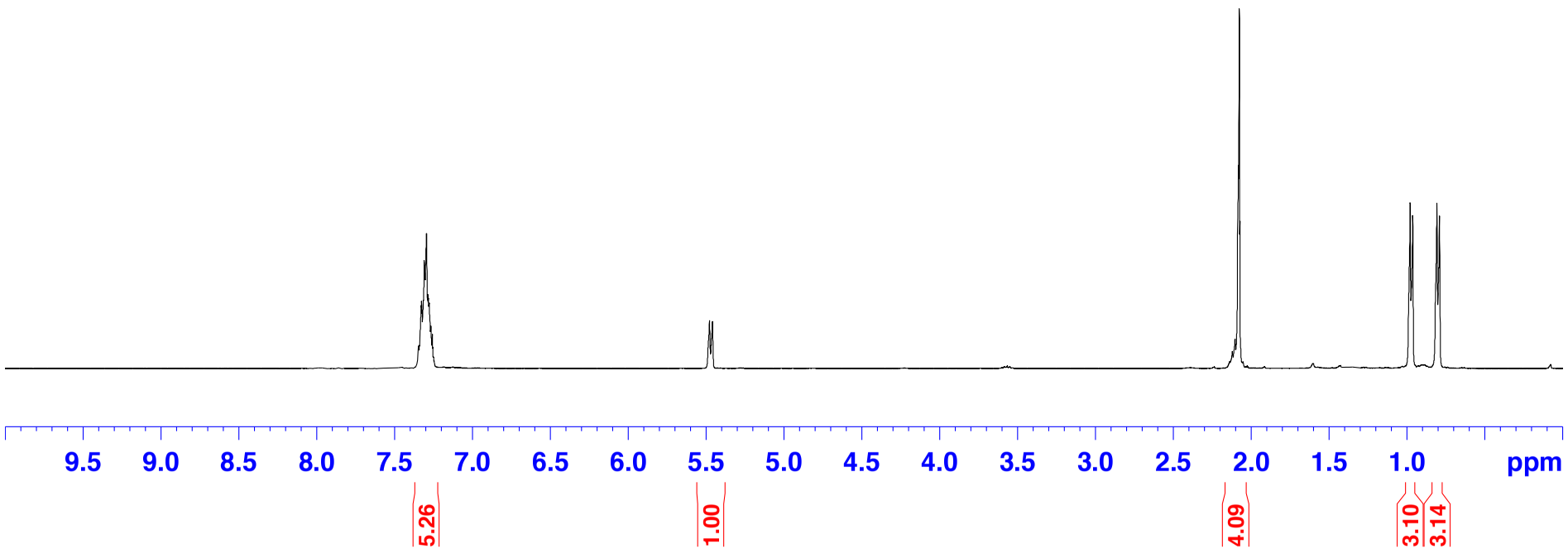

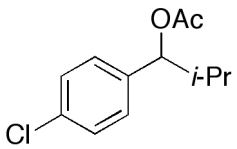

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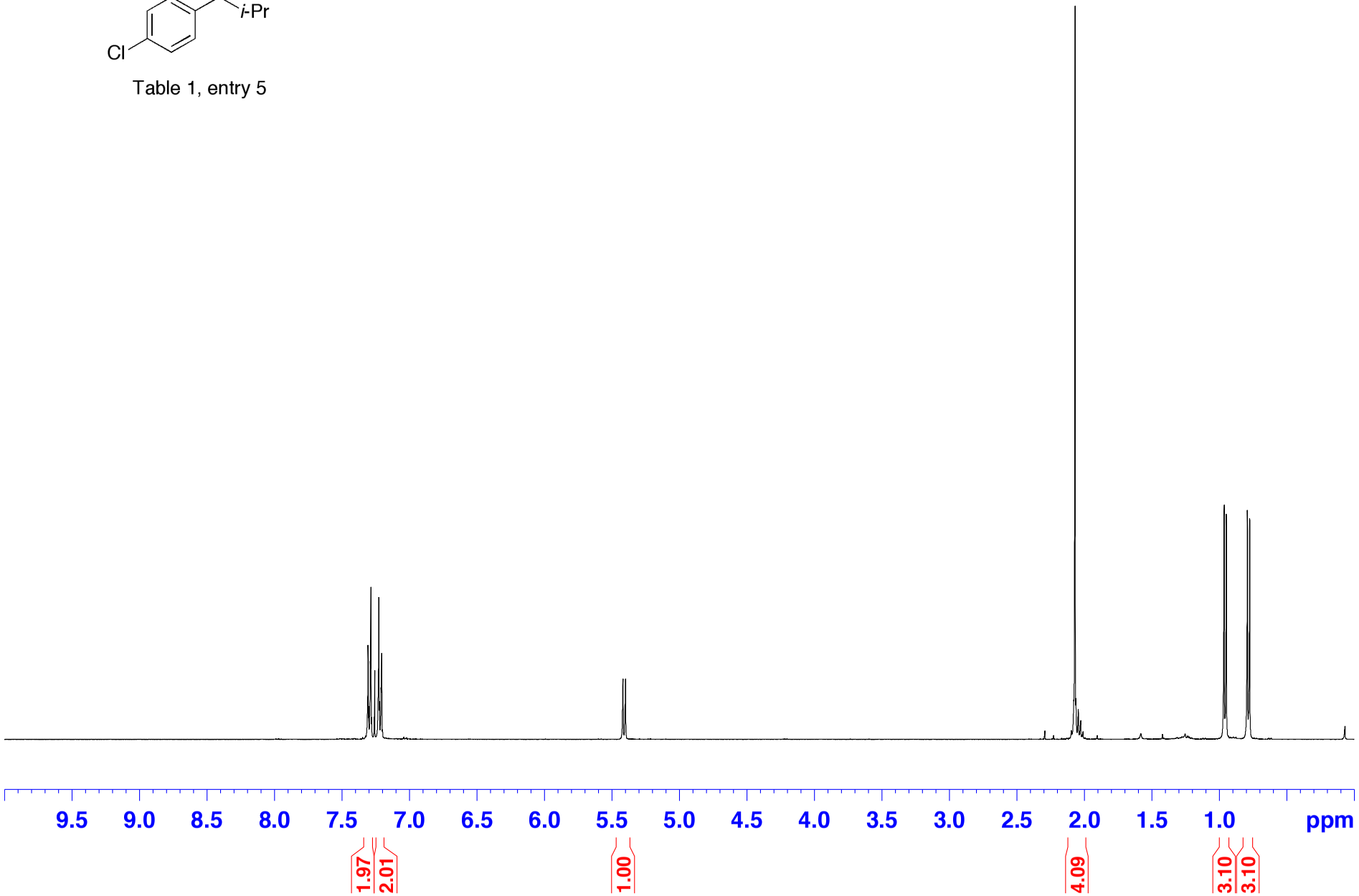

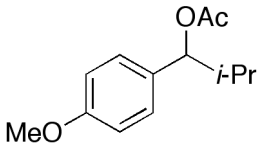

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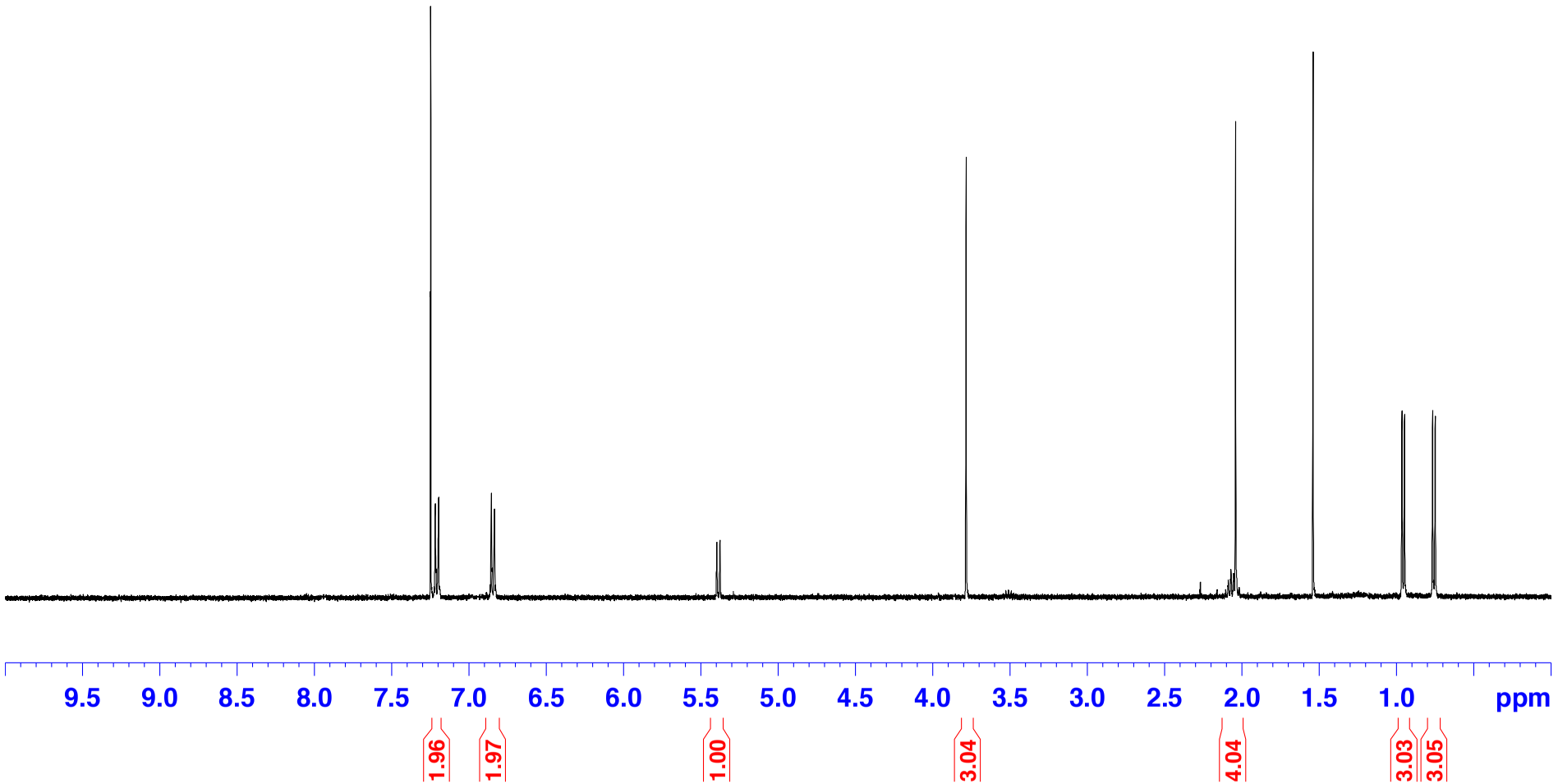

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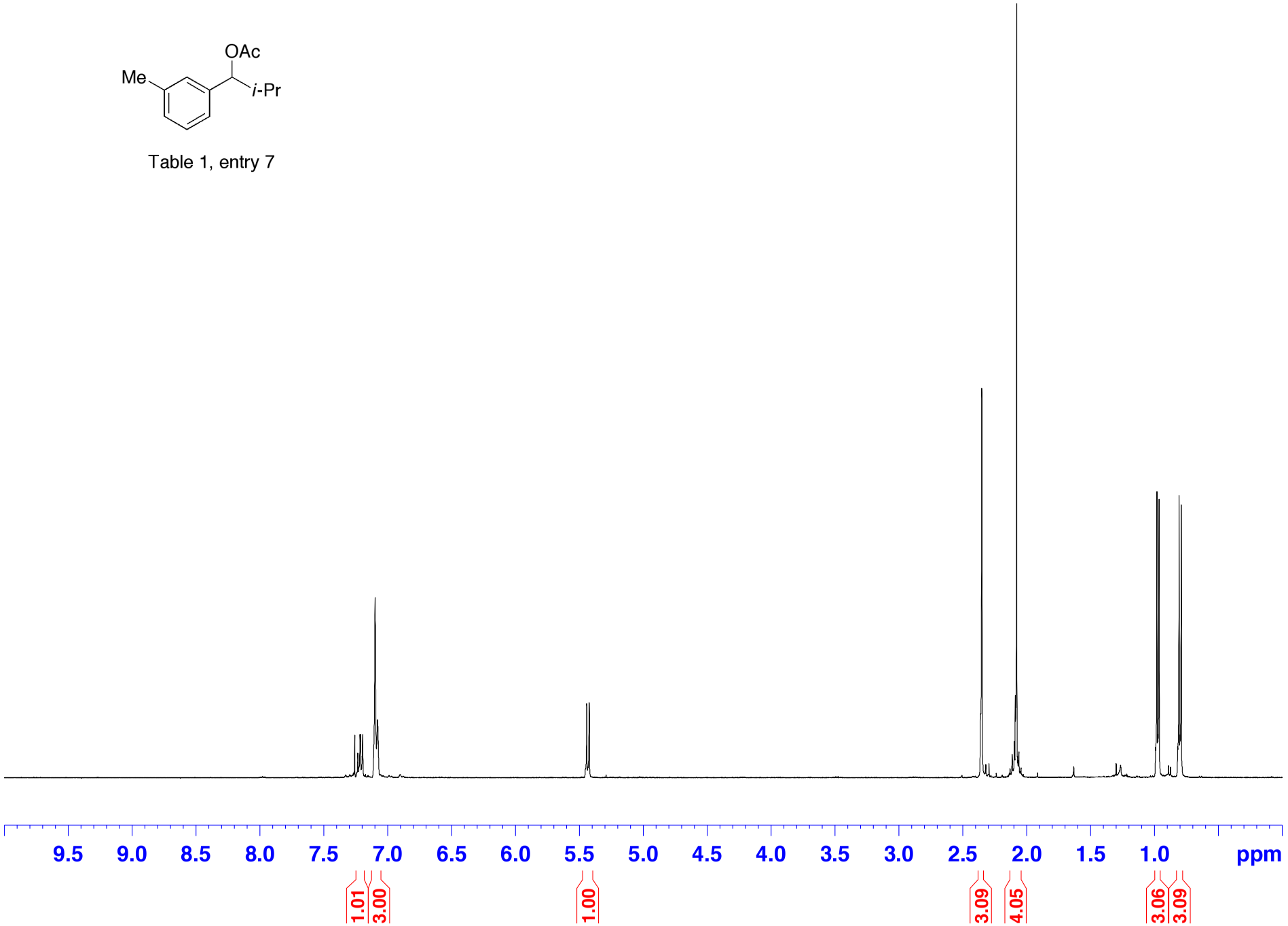

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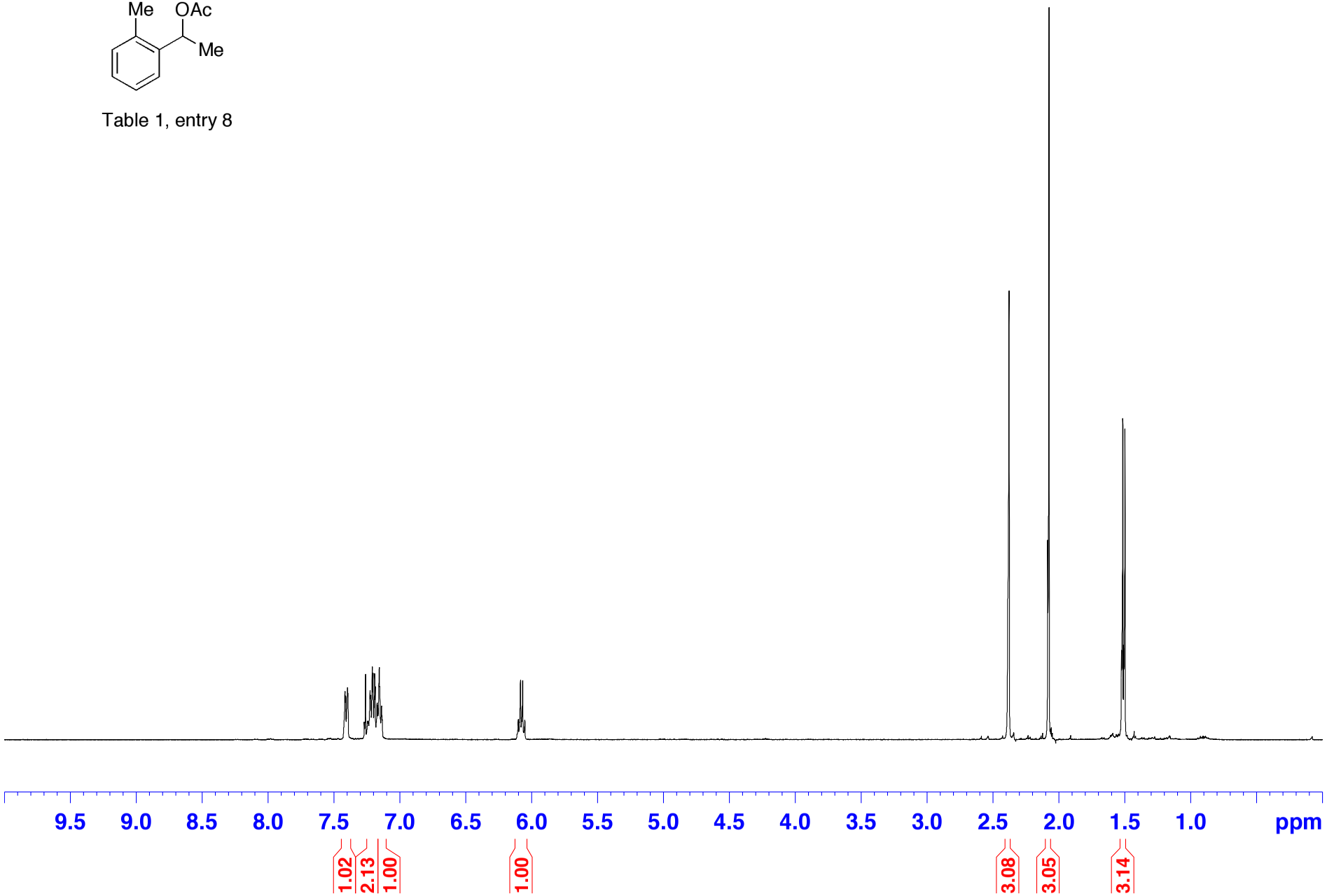

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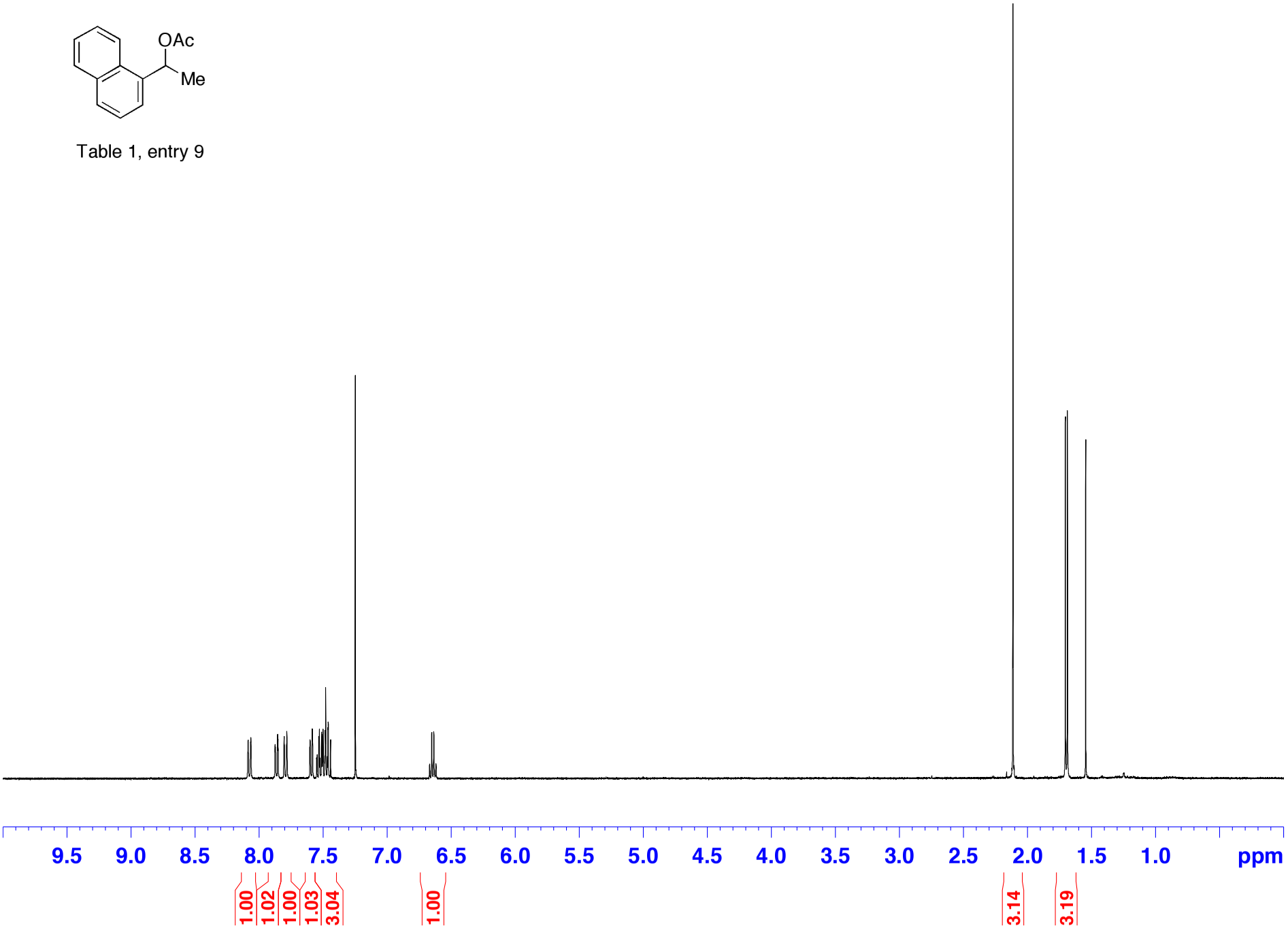

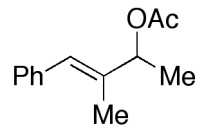

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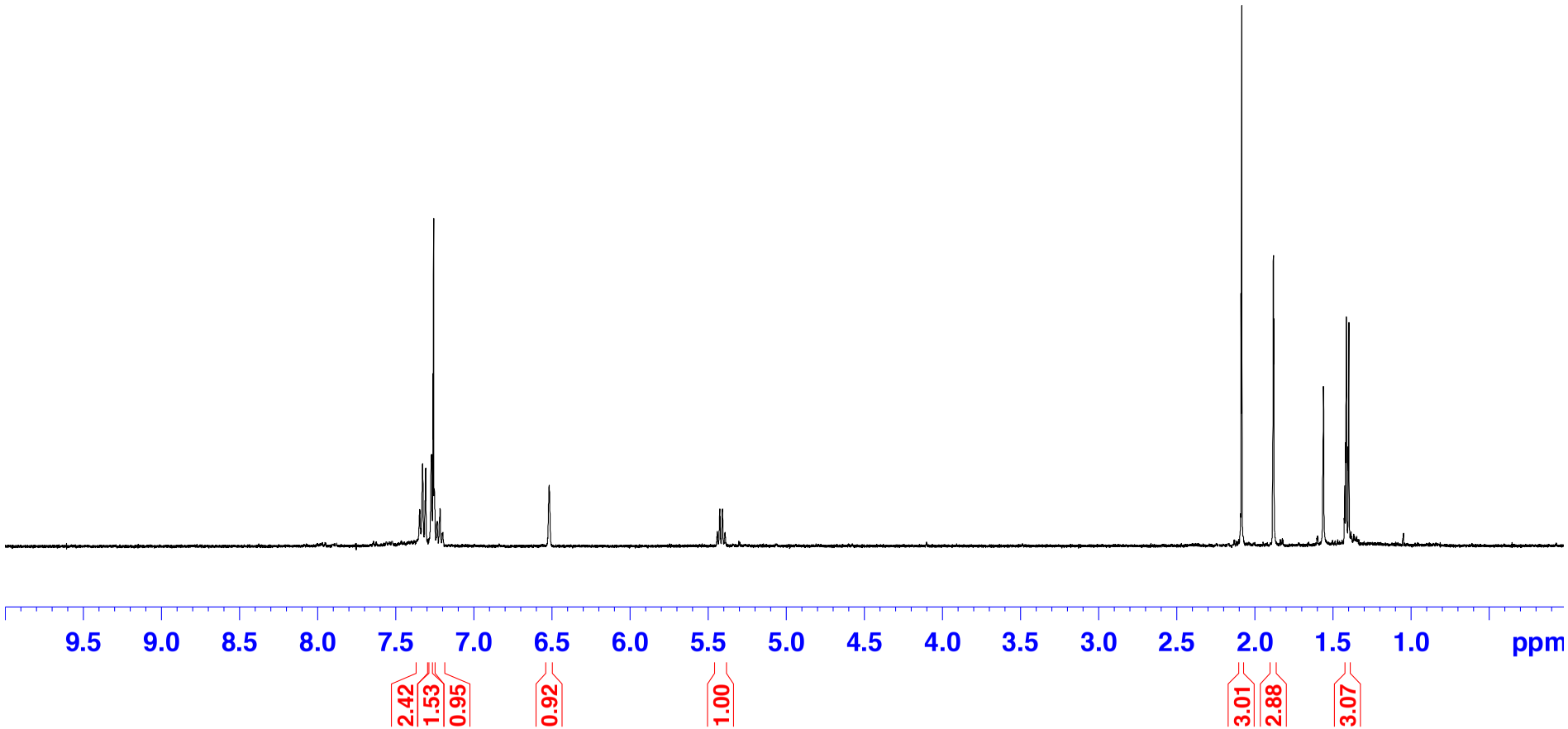

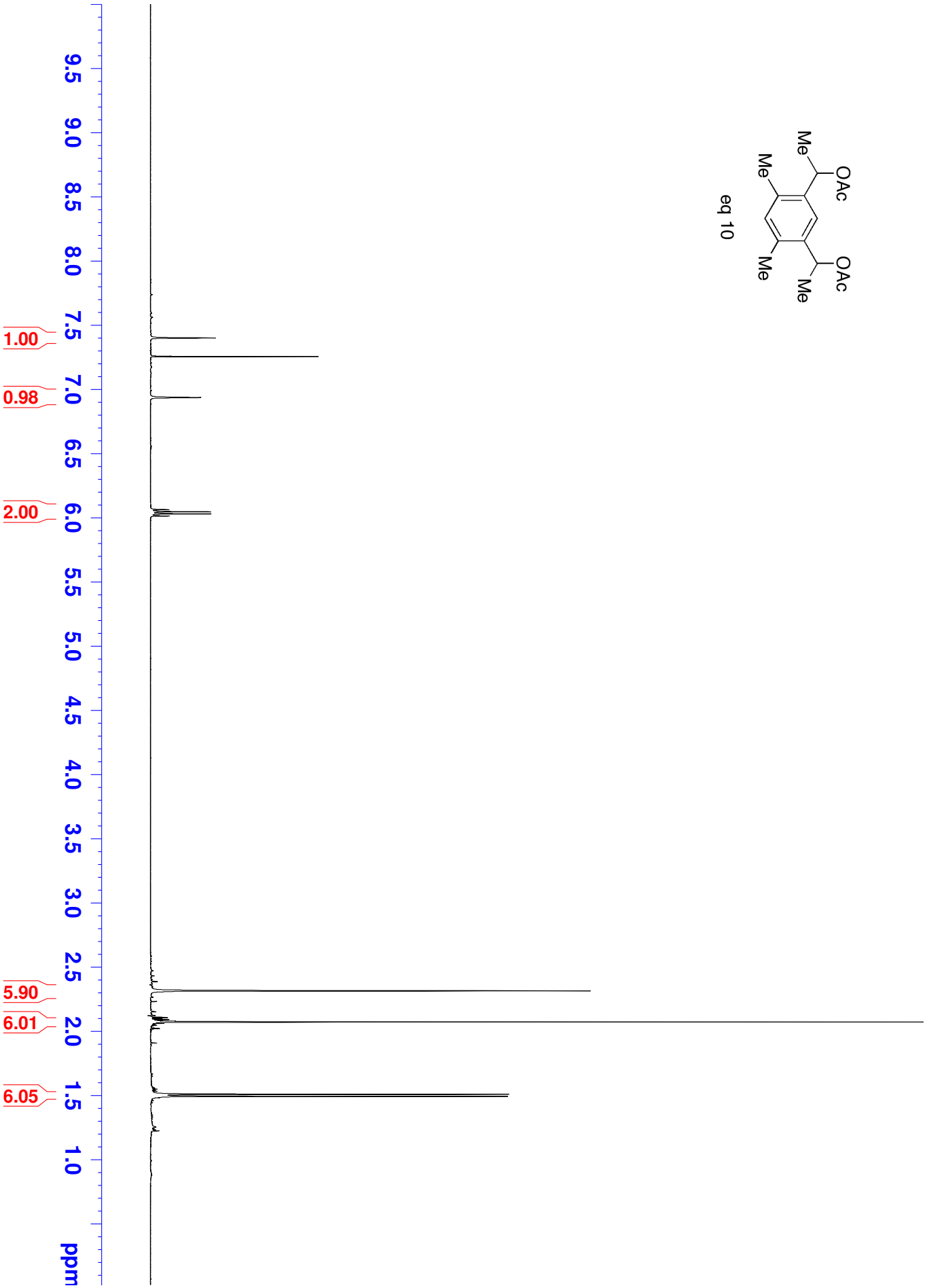
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2.0
1.5
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ppm
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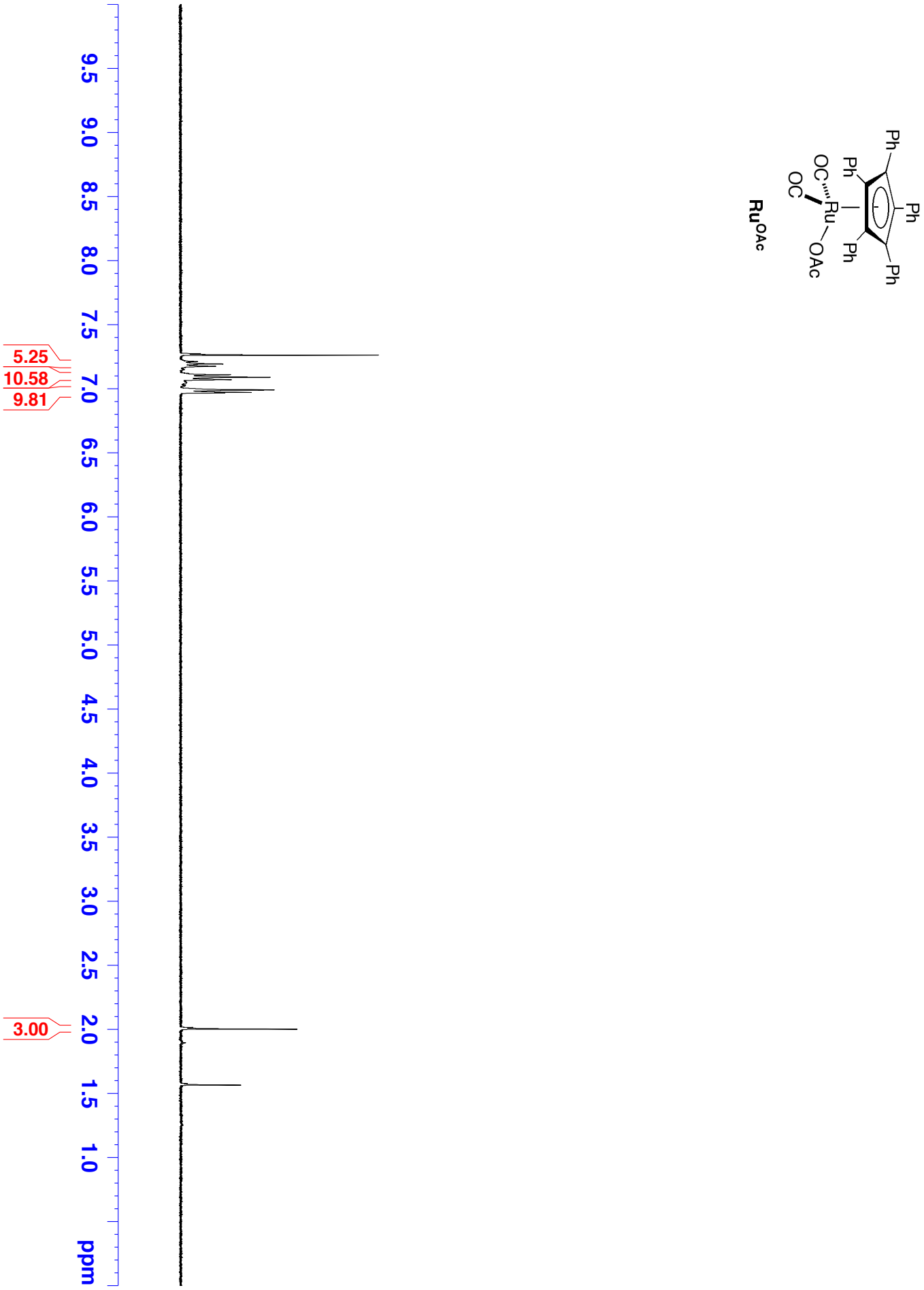
6.05
Me
OAc
Me
Me
OAc
Me

eq 10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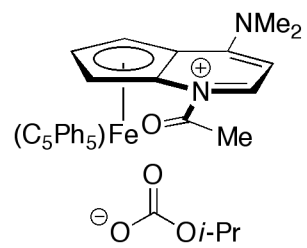

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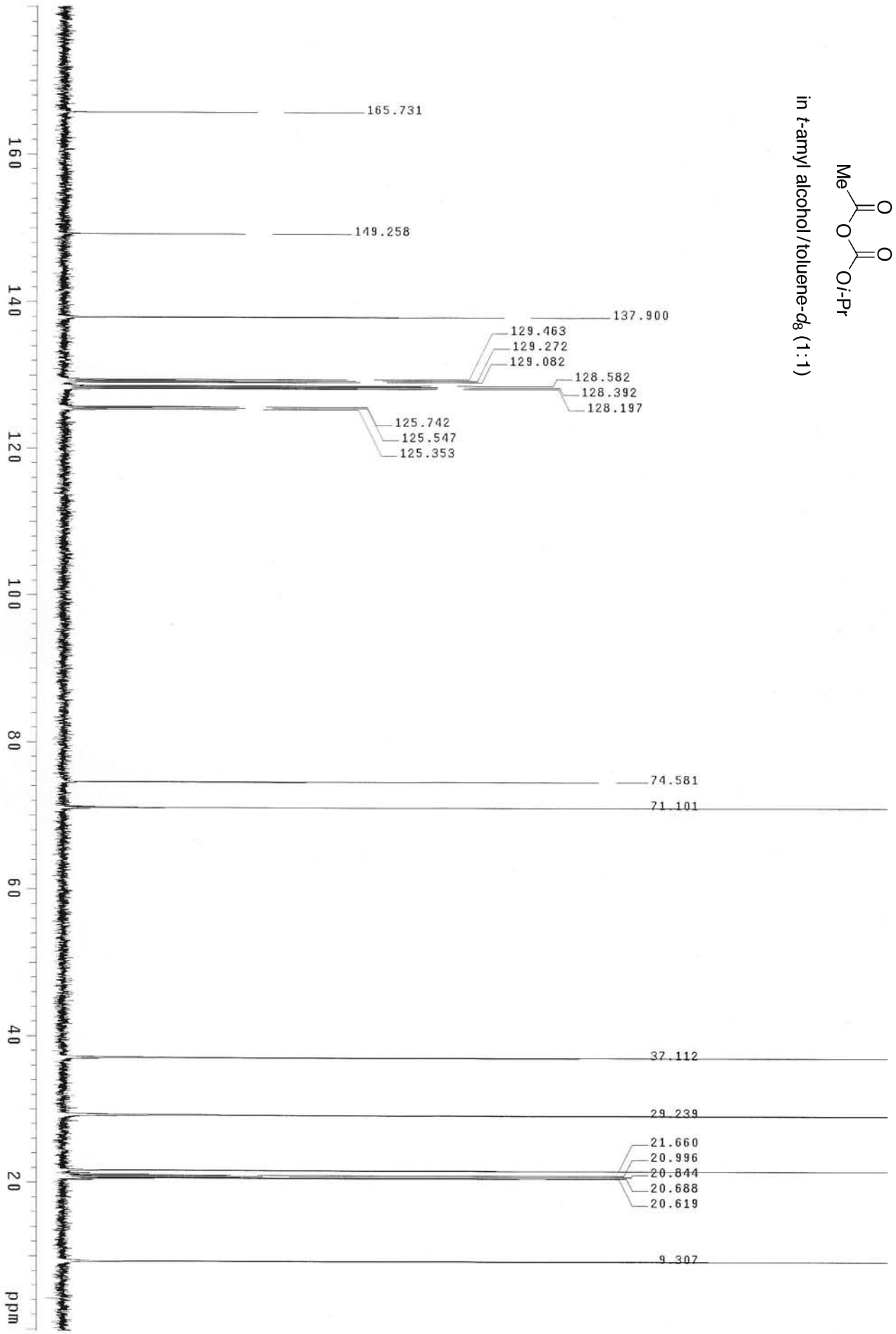
eq 11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O
O
O-i-Pr
in t-amyl alcohol/toluene-d8 (1:1)
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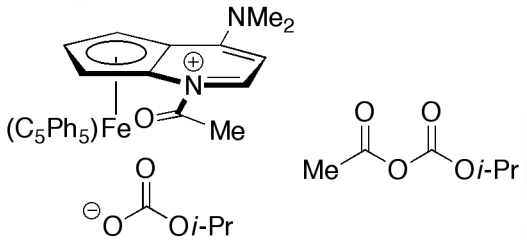
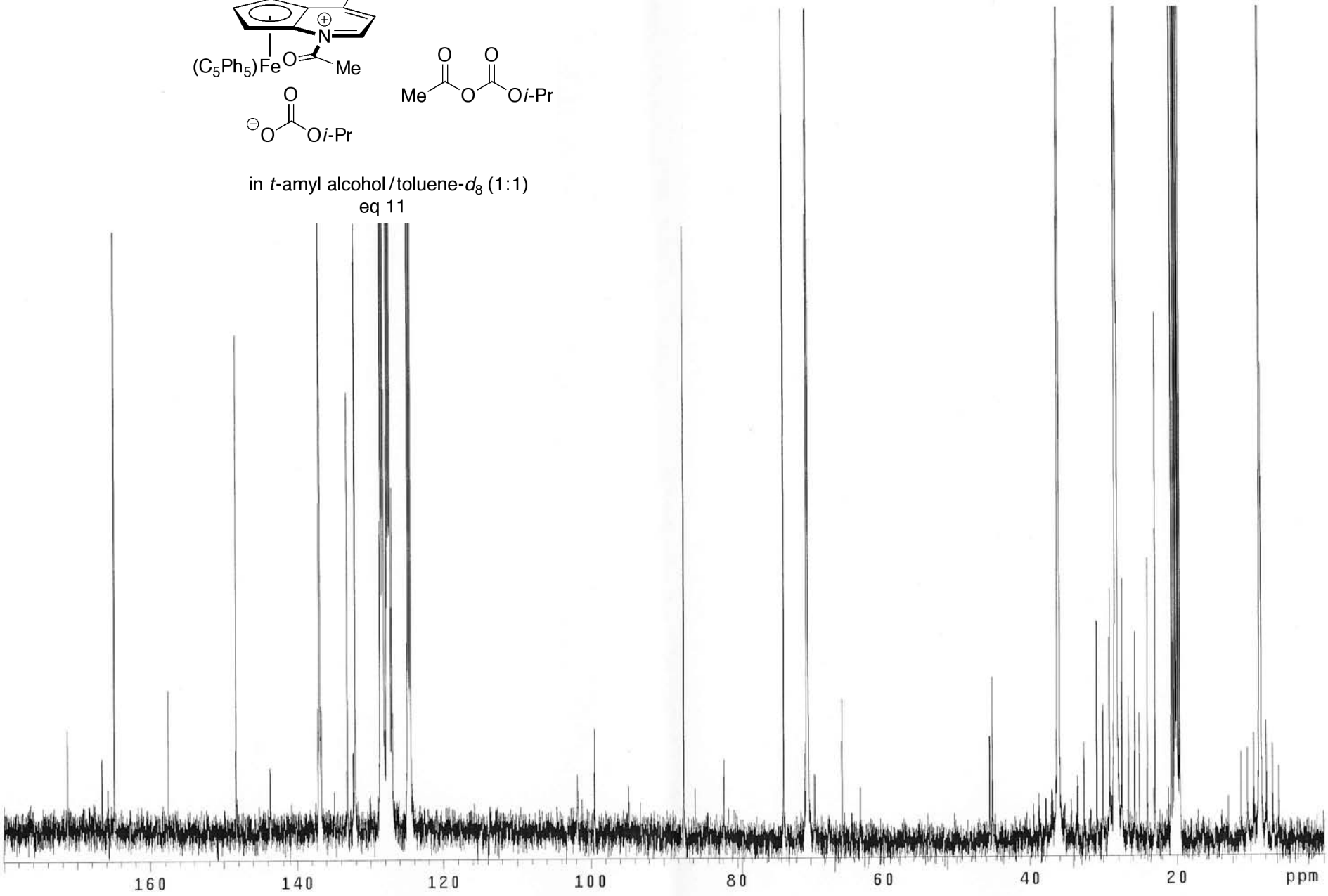
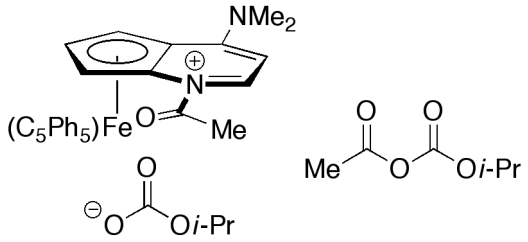
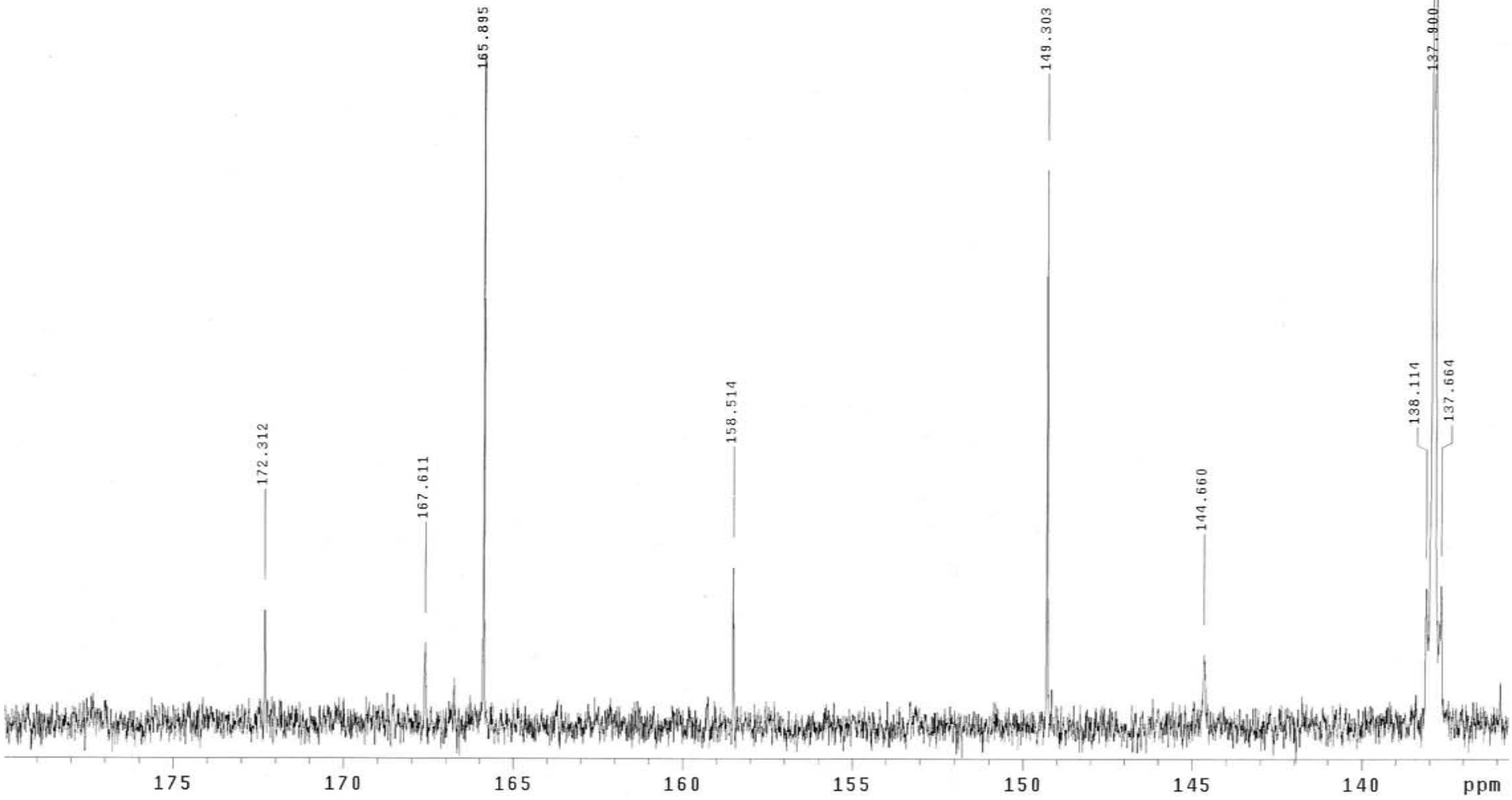


in *t*-amyl alcohol / toluene-d_8 (1:1)
eq 11





in *t*-amyl alcohol / toluene-d_8 (1:1)
eq 11



Data File C:\HPCHEM\3\DATA\HD\SY4-030A.D

```
==============================================================================
Injection Date  : 11/7/2011 9:41:11 PM          Seq. Line :   1
Sample Name     :                               Location : Vial 2
Acq. Operator   : HD                               Inj :   1
Acq. Instrument : Instrument 3                  Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3 µl
Acq. Method     : C:\HPCHEM\3\METHODS\AU105115.M
Last changed    : 6/10/2008 10:06:18 AM by BJ
Analysis Method : C:\HPCHEM\3\METHODS\SY90115.M
Last changed    : 12/27/2011 5:54:50 PM by HD
                  (modified after loading)
```

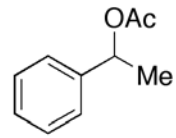
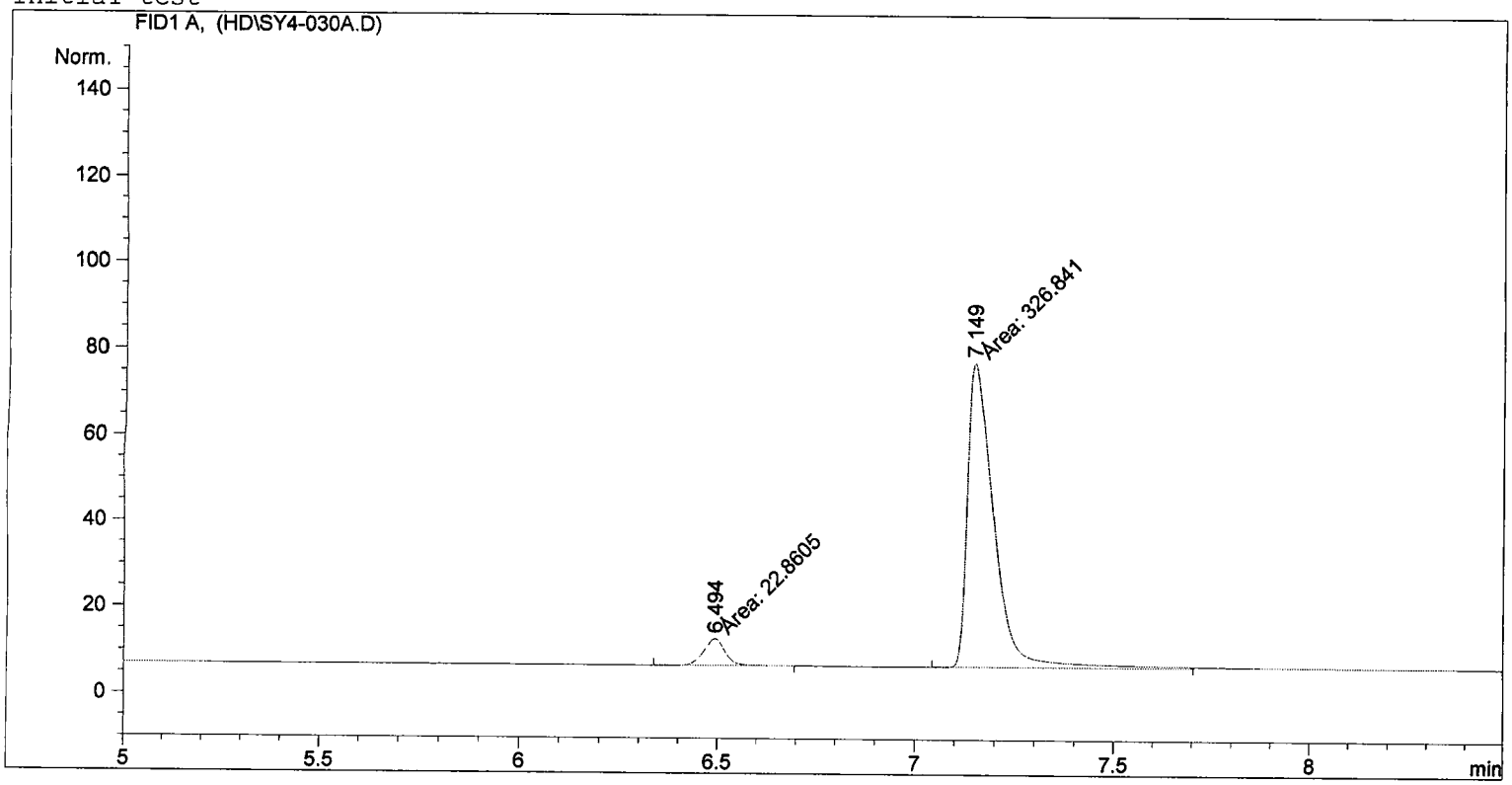


Table 1, entry 1
with (–)-C_5Ph_5-DMAP*

Initial test




```
==============================================================================
                          Area Percent Report
==============================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1   6.494 MM    0.0623   22.86055    6.11847  6.53716
   2   7.149 MM    0.0771  326.84085   70.63768 93.46284

Totals :                   349.70140   76.75615

 Results obtained with enhanced integrator!
==============================================================================
                          *** End of Report ***
```

Data File C:\HPCHEM\3\DATA\SN\SY4-054B.D

```
Injection Date  : 11/25/2011 7:08:08 PM          Seq. Line :   3
Sample Name     :                                 Location : Vial 3
Acq. Operator   : SN                                  Inj :   1
Acq. Instrument : Instrument 3                  Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3 µl
Acq. Method     : C:\HPCHEM\3\METHODS\AU105115.M
Last changed    : 6/10/2008 10:06:18 AM by BJ
Analysis Method : C:\HPCHEM\3\METHODS\SY90115.M
Last changed    : 12/27/2011 5:51:06 PM by HD
                  (modified after loading)
```

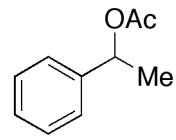
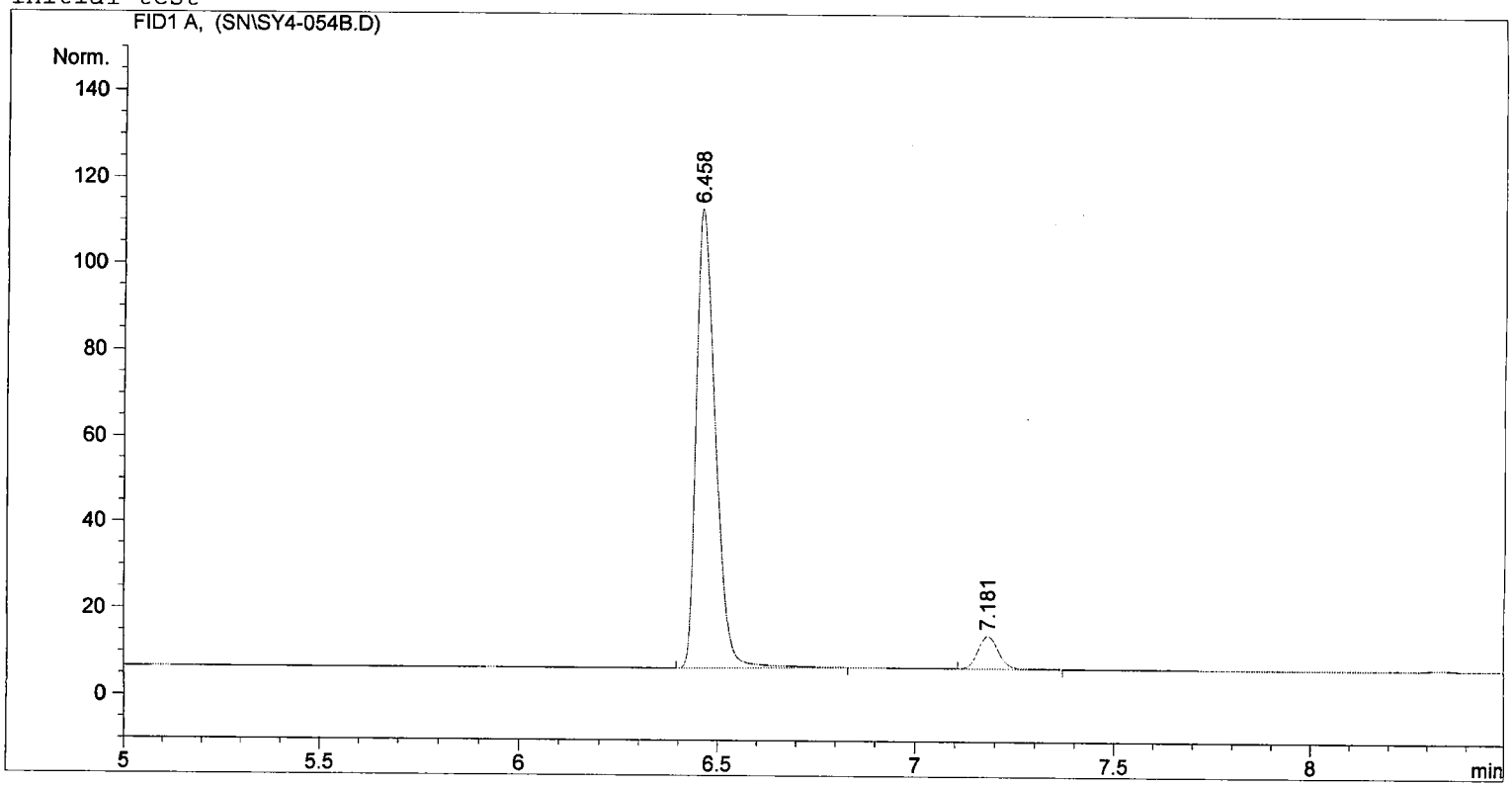


Table 1, entry 1
with (+)-C_5Ph_5-DMAP*

Initial test



Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1   6.458 PB    0.0513  363.56866  106.53935 93.02377
   2   7.181 BB    0.0570   27.26548    7.49099  6.97623

Totals :                   390.83414  114.03034

 Results obtained with enhanced integrator!
```

*** End of Report ***

Data File C:\HPCHEM\3\DATA\HD\SY4026B.D

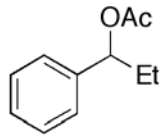
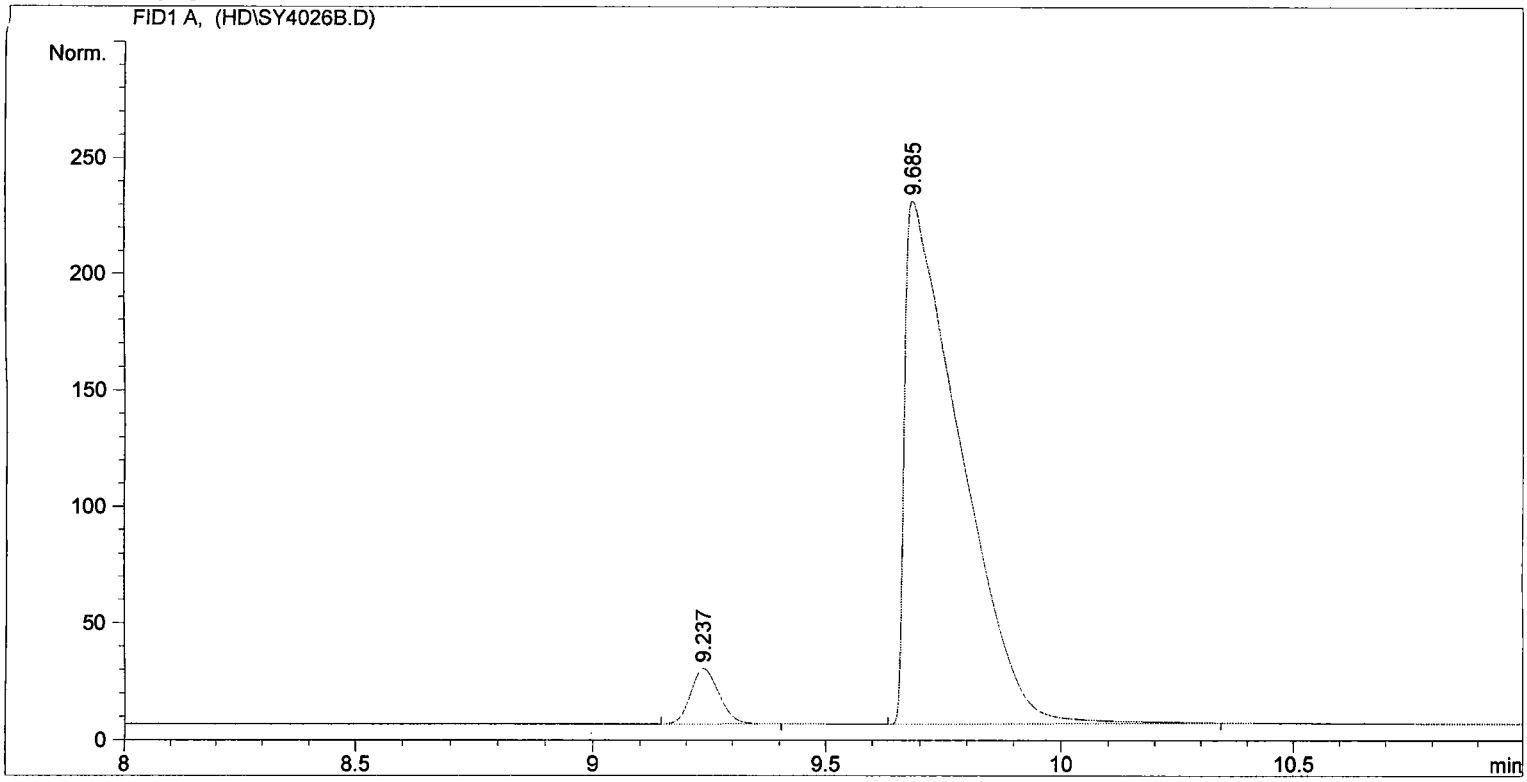


Table 1, entry 2
with (–)-C_5Ph_5-DMAP*

```
Injection Date  : 12/28/2011 12:09:26 AM         Seq. Line :   7
Sample Name     :                                Location : Vial 4
Acq. Operator   : HD                                 Inj :   1
Acq. Instrument : Instrument 3                  Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 2 µl
Acq. Method     : C:\HPCHEM\3\METHODS\SY105115.M
Last changed    : 12/27/2011 7:22:35 PM by HD
Analysis Method : C:\HPCHEM\3\METHODS\SY100ISA.M
Last changed    : 12/28/2011 1:37:54 PM by HD
                  (modified after loading)
Initial test
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1   9.237 BP    0.0667  100.69203   23.61509  5.23181
   2   9.685 PB    0.1042 1823.91992  224.75095 94.76819

Totals :                   1924.61195  248.36604

 Results obtained with enhanced integrator!
=====================================================================
                        *** End of Report ***
```

Data File C:\HPCHEM\3\DATA\HD\SY4-2.D

```
Injection Date  : 11/24/2011 3:48:47 PM          Seq. Line :   8
Sample Name     :                                Location : Vial 1
Acq. Operator   : HD                                 Inj :   1
Acq. Instrument : Instrument 3                  Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3 µl
Acq. Method     : C:\HPCHEM\3\METHODS\SY105115.M
Last changed    : 11/24/2011 12:17:48 PM by jc
Analysis Method : C:\HPCHEM\3\METHODS\SY90115.M
Last changed    : 12/27/2011 5:47:31 PM by HD
                  (modified after loading)
```

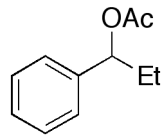
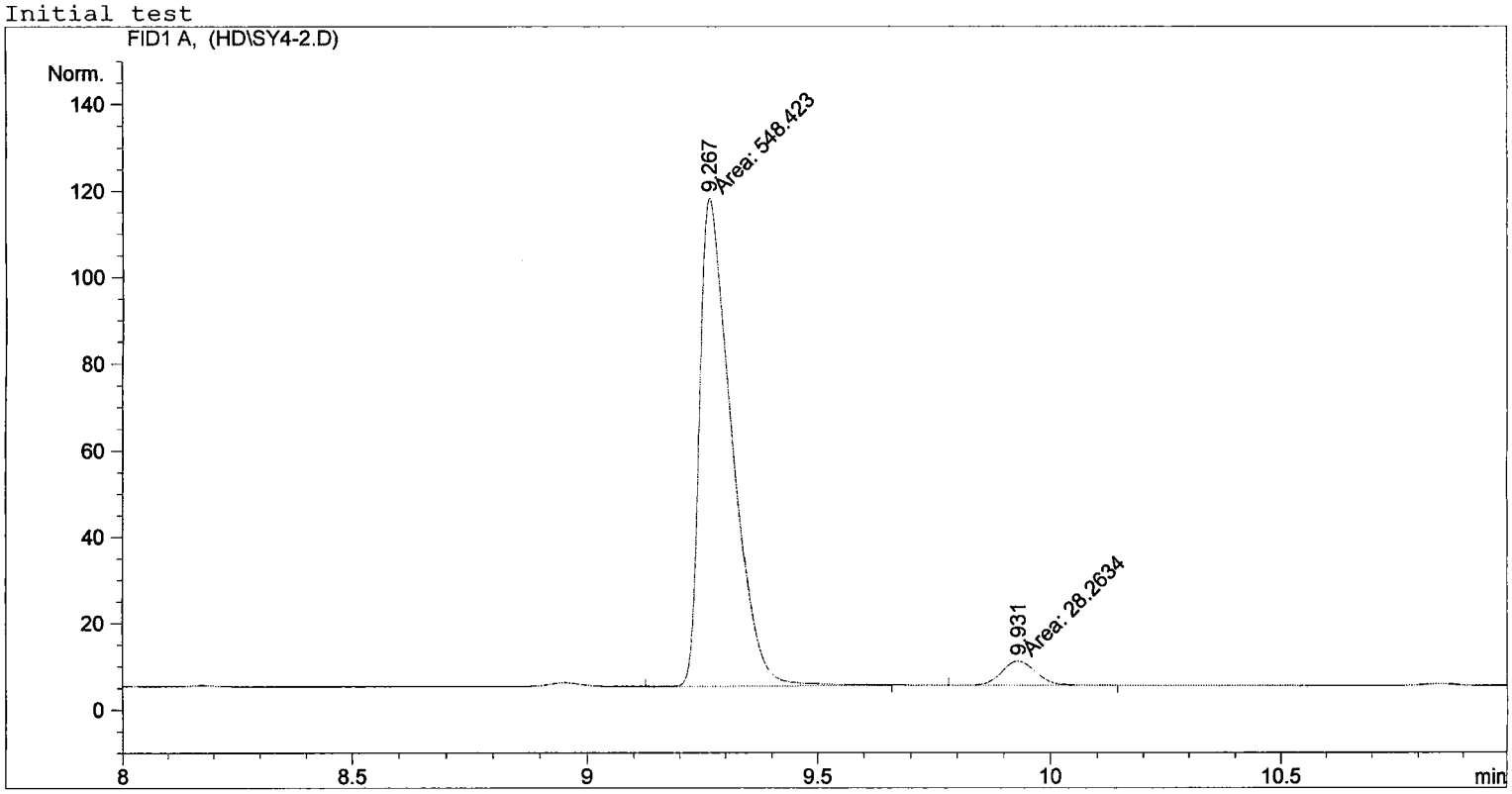


Table 1, entry 2
with (+)-C_5Ph_5-DMAP*

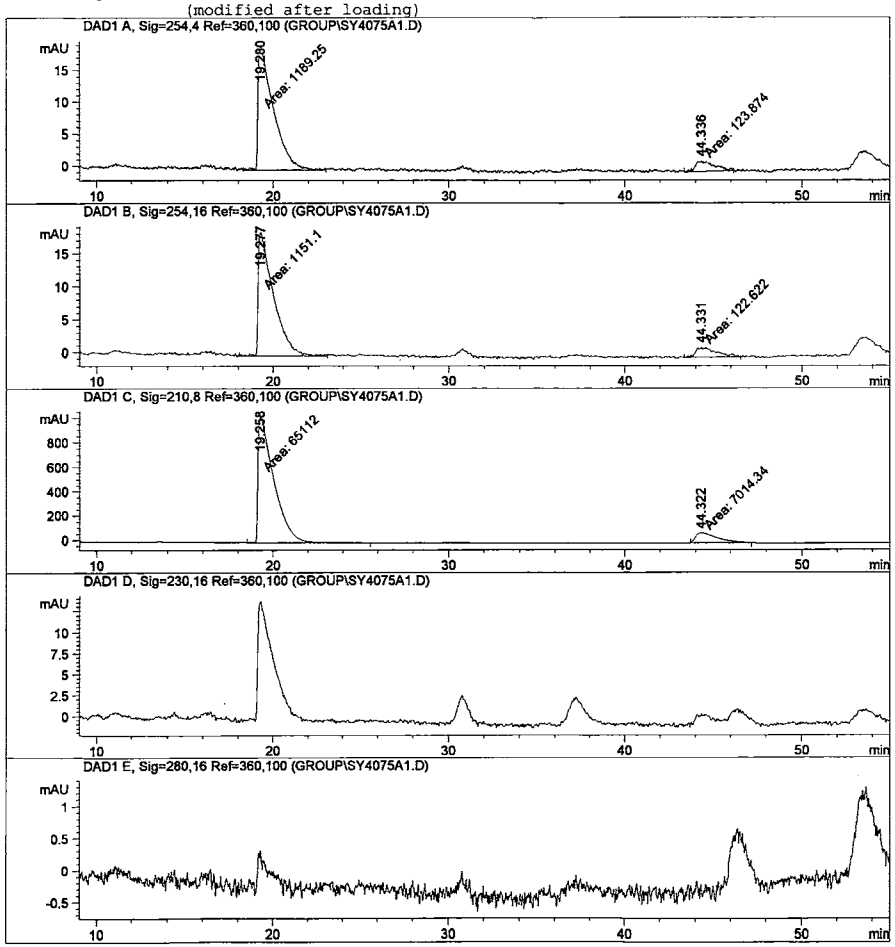
Initial test




```
                        Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1   9.267 MM    0.0809  548.42279  112.92822 95.09900
   2   9.931 MM    0.0841   28.26339    5.60311  4.90100

Totals :                   576.68618  118.53133

 Results obtained with enhanced integrator!

                        *** End of Report ***
```

Data File C:\HPCHEM\1\DATA\GROUP\SY4075A1.D

Injection Date : 3/1/2012 1:22:20 AM Seq. Line : 23
Sample Name : Location : Vial 73
Acq. Operator : JTM Inj : 1
Acq. Instrument : Instrument 1 Inj Volume : 5 µl
Acq. Method : C:\HPCHEM\1\METHODS\ODH-0060.M
Last changed : 1/19/2012 5:01:32 PM by SN
Analysis Method : C:\HPCHEM\1\METHODS\YL-AD02.M
Last changed : 3/1/2012 11:00:43 AM by JTM
(modified after loading)



Data File C:\HPCHEM\1\DATA\GROUP\SY4075A1.D

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.280	MM	1.0234	1189.24658	19.36803	90.5665
2	44.336	MM	1.2010	123.87383	1.71897	9.4335
Totals :				1313.12041	21.08699	

Results obtained with enhanced integrator!

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.277	MM	1.0216	1151.10132	18.77863	90.3730
2	44.331	MM	1.2736	122.62193	1.60466	9.6270
Totals :				1273.72325	20.38329	

Results obtained with enhanced integrator!

Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.258	MM	1.0545	6.51120e4	1029.08911	90.2749
2	44.322	MM	1.3988	7014.33838	83.57714	9.7251
Totals :				7.21264e4	1112.66625	

Results obtained with enhanced integrator!

Signal 4: DAD1 D, Sig=230,16 Ref=360,100

Signal 5: DAD1 E, Sig=280,16 Ref=360,100

*** End of Report ***

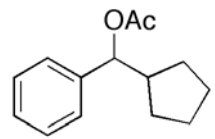
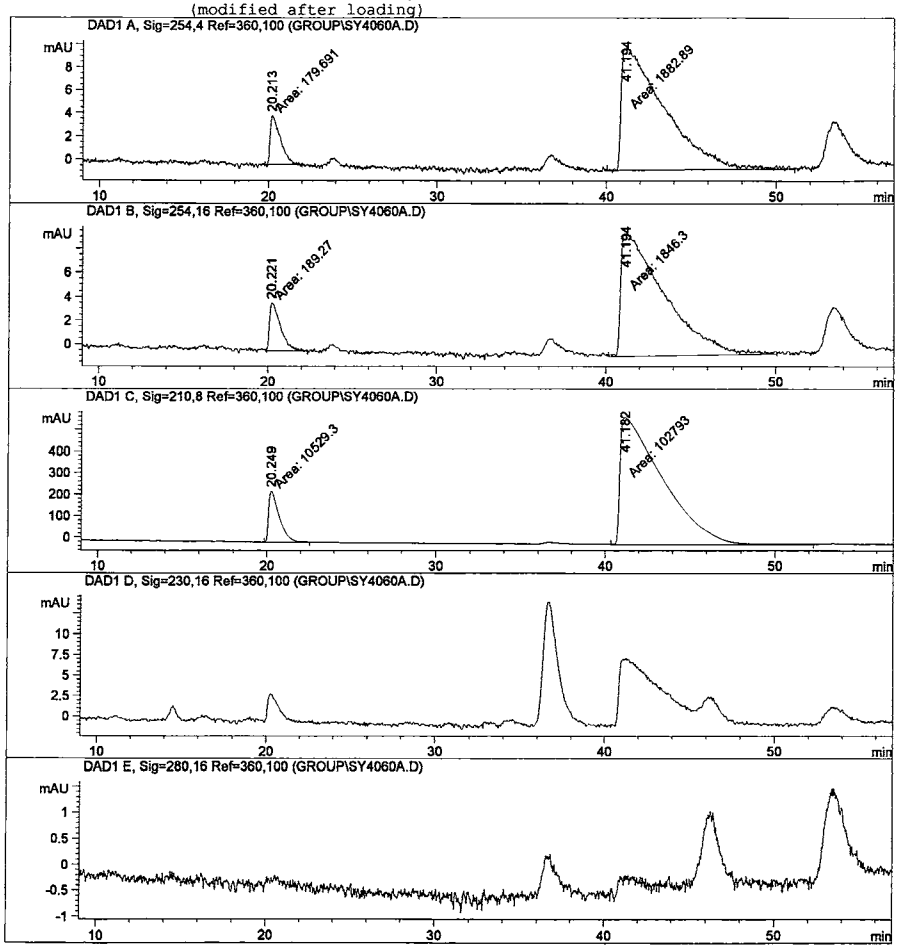


Table 1, entry 3 with (–)-C_5Ph_5-DMAP*

Data File C:\HPCHEM\1\DATA\GROUP\SY4060A.D

Injection Date	: 2/28/2012 7:45:00 PM	Seq. Line	: 6
Sample Name	:	Location	: Vial 71
Acq. Operator	: JTM	Inj	: 1
Acq. Instrument	: Instrument 1	Inj Volume	: 5 µl
Acq. Method	: C:\HPCHEM\1\METHODS\ODH-0060.M		
Last changed	: 1/19/2012 5:01:32 PM by SN		
Analysis Method	: C:\HPCHEM\1\METHODS\YL-AD02.M		
Last changed	: 2/28/2012 8:45:25 PM by JTM (modified after loading)		



Data File C:\HPCHEM\1\DATA\GROUP\SY4060A.D

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.213	MM	0.7092	179.69051	4.22263	8.7119
2	41.194	MM	2.9283	1882.89258	10.71659	91.2881
Totals :				2062.58308	14.93922	

Results obtained with enhanced integrator!

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.221	MM	0.7715	189.27020	4.08862	9.2981
2	41.194	MM	2.9698	1846.30212	10.36168	90.7019
Totals :				2035.57233	14.45030	

Results obtained with enhanced integrator!

Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.249	MM	0.7388	1.05293e4	237.52646	9.2915
2	41.182	MM	2.9146	1.02793e5	587.81067	90.7085
Totals :				1.13322e5	825.33713	

Results obtained with enhanced integrator!

Signal 4: DAD1 D, Sig=230,16 Ref=360,100

Signal 5: DAD1 E, Sig=280,16 Ref=360,100

*** End of Report ***

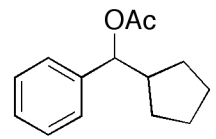


Table 1, entry 3
with (+)-C_5Ph_5-DMAP*

Data File C:\HPCHEM\3\DATA\HD\SY4026C.D

```
Injection Date  : 12/28/2011 12:45:56 AM        Seq. Line :   8
Sample Name     :                               Location : Vial 5
Acq. Operator   : HD                               Inj :   1
Acq. Instrument : Instrument 3                 Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 2 µl
Acq. Method     : C:\HPCHEM\3\METHODS\SY105115.M
Last changed    : 12/27/2011 7:22:35 PM by HD
Analysis Method : C:\HPCHEM\3\METHODS\SY100ISA.M
Last changed    : 12/28/2011 1:39:13 PM by HD
                  (modified after loading)
```

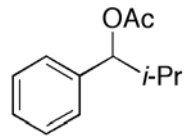
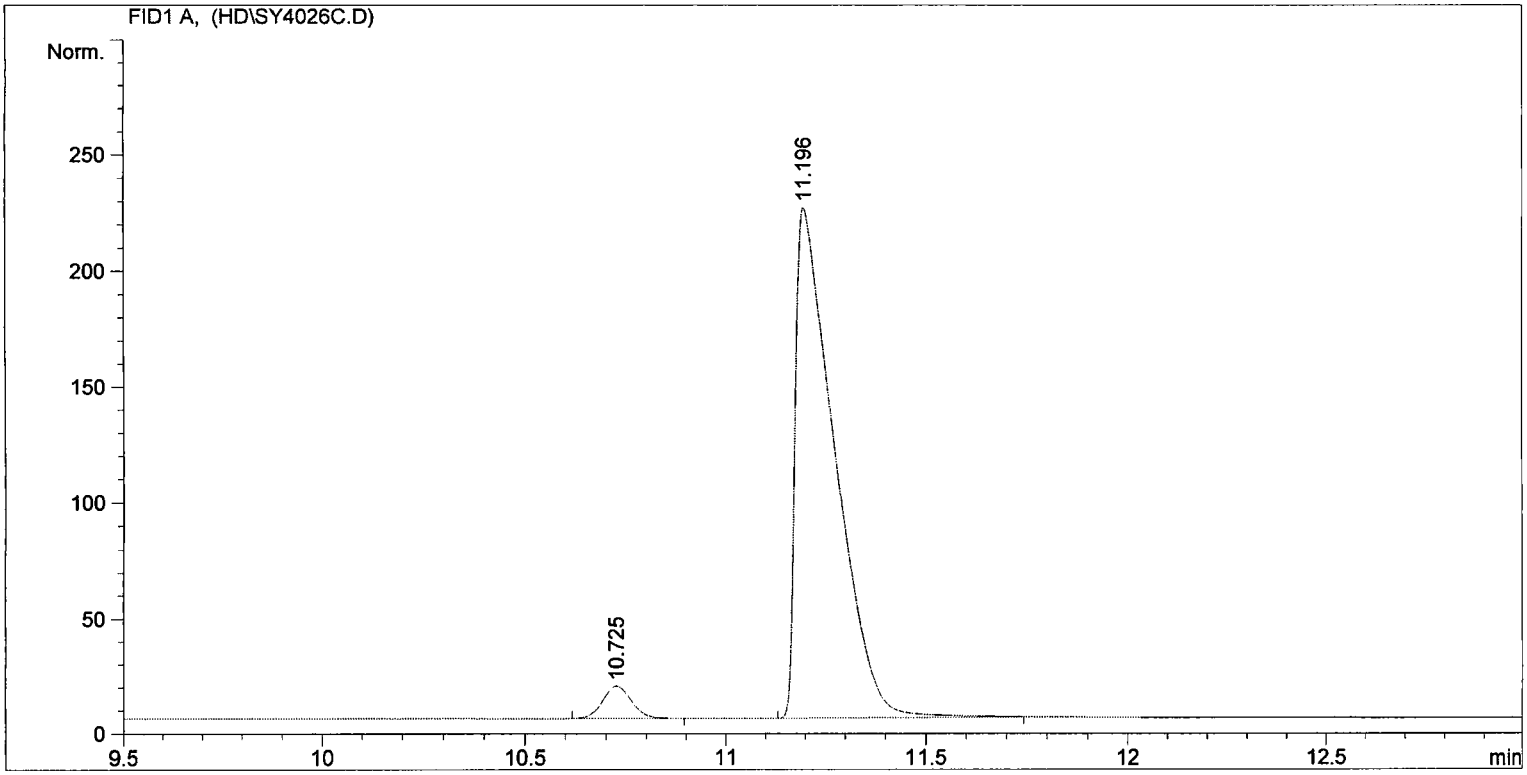


Table 1, entry 4
with (–)-C_5Ph_5-DMAP*

Initial test




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1  10.725 BB    0.0768   69.37827   14.00787  4.39299
   2  11.196 PB    0.0933 1509.91589  220.63409 95.60701

Totals :                  1579.29417  234.64197

 Results obtained with enhanced integrator!

                          *** End of Report ***
```

Data File C:\HPCHEM\3\DATA\HD\SY4068A.D

```
Injection Date  : 12/10/2011 7:18:42 PM          Seq. Line :  11
Sample Name     :                                Location : Vial 2
Acq. Operator   : hd                                Inj :   1
Acq. Instrument : Instrument 3                  Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3 µl
Acq. Method     : C:\HPCHEM\3\METHODS\SY105115.M
Last changed    : 11/24/2011 12:17:48 PM by jc
Analysis Method : C:\HPCHEM\3\METHODS\SY90115.M
Last changed    : 12/27/2011 6:04:59 PM by HD
                  (modified after loading)
```

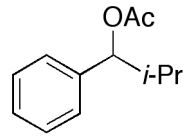
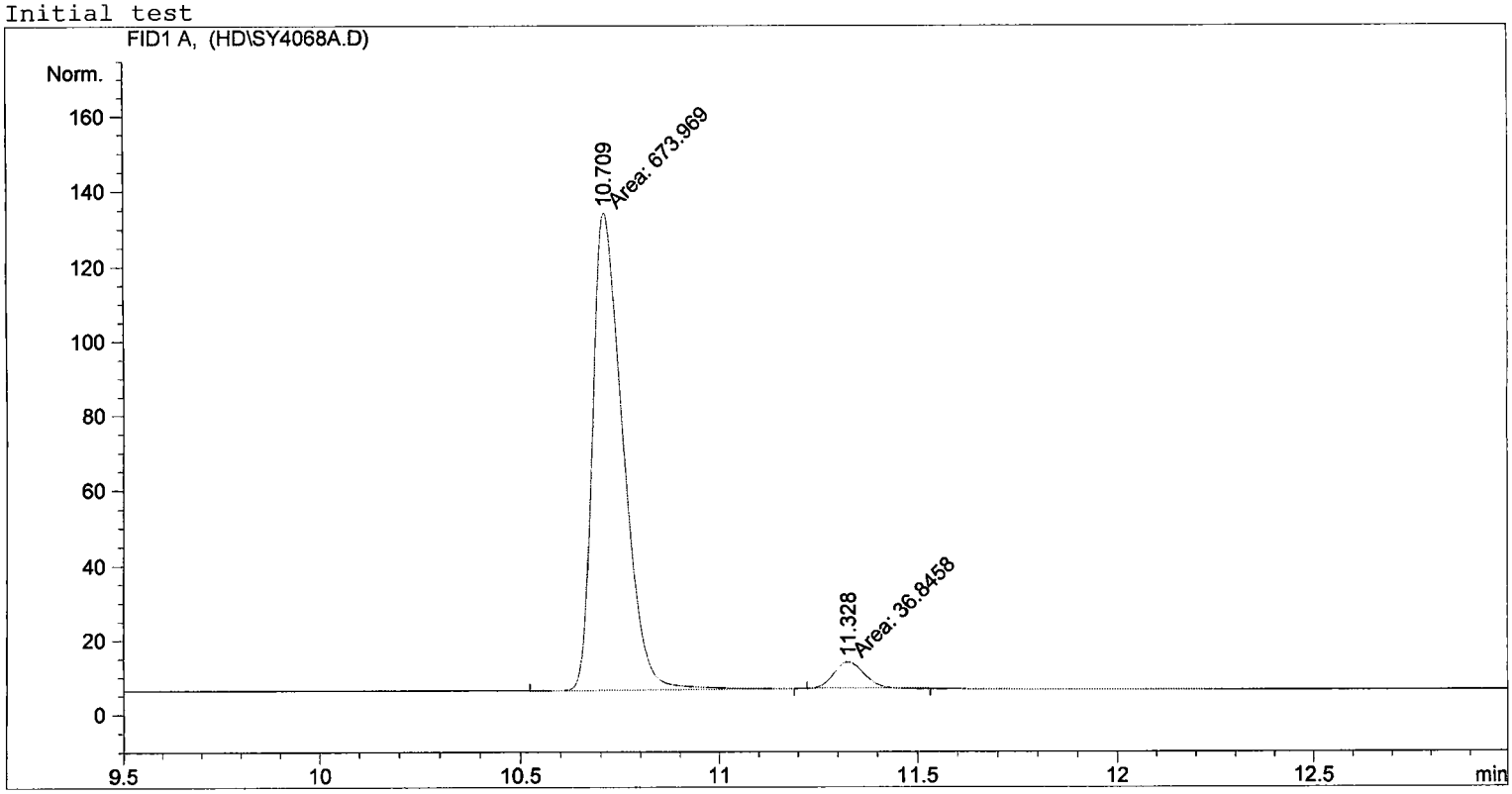


Table 1, entry 4
with (+)-C_5Ph_5-DMAP*

Initial test



Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1  10.709 MM    0.0879  673.96893  127.77182 94.81639
   2  11.328 MM    0.0871   36.84584    7.04818  5.18361

Totals :                   710.81477  134.82000

 Results obtained with enhanced integrator!
```

*** End of Report ***

Data File C:\HPCHEM\3\DATA\HD\SY4030B.D

```
Injection Date  : 12/28/2011 4:09:40 PM          Seq. Line :  11
Sample Name     :                                Location : Vial 3
Acq. Operator   : HD                                 Inj :   1
Acq. Instrument : Instrument 3                   Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 2 µl
Acq. Method     : C:\HPCHEM\3\METHODS\AU105115.M
Last changed    : 6/10/2008 10:06:18 AM by BJ
Analysis Method : C:\HPCHEM\3\METHODS\SY100ISA.M
Last changed    : 12/28/2011 6:10:33 PM by HD
                  (modified after loading)
Initial test
```

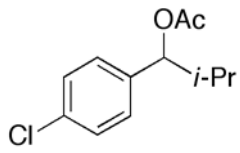
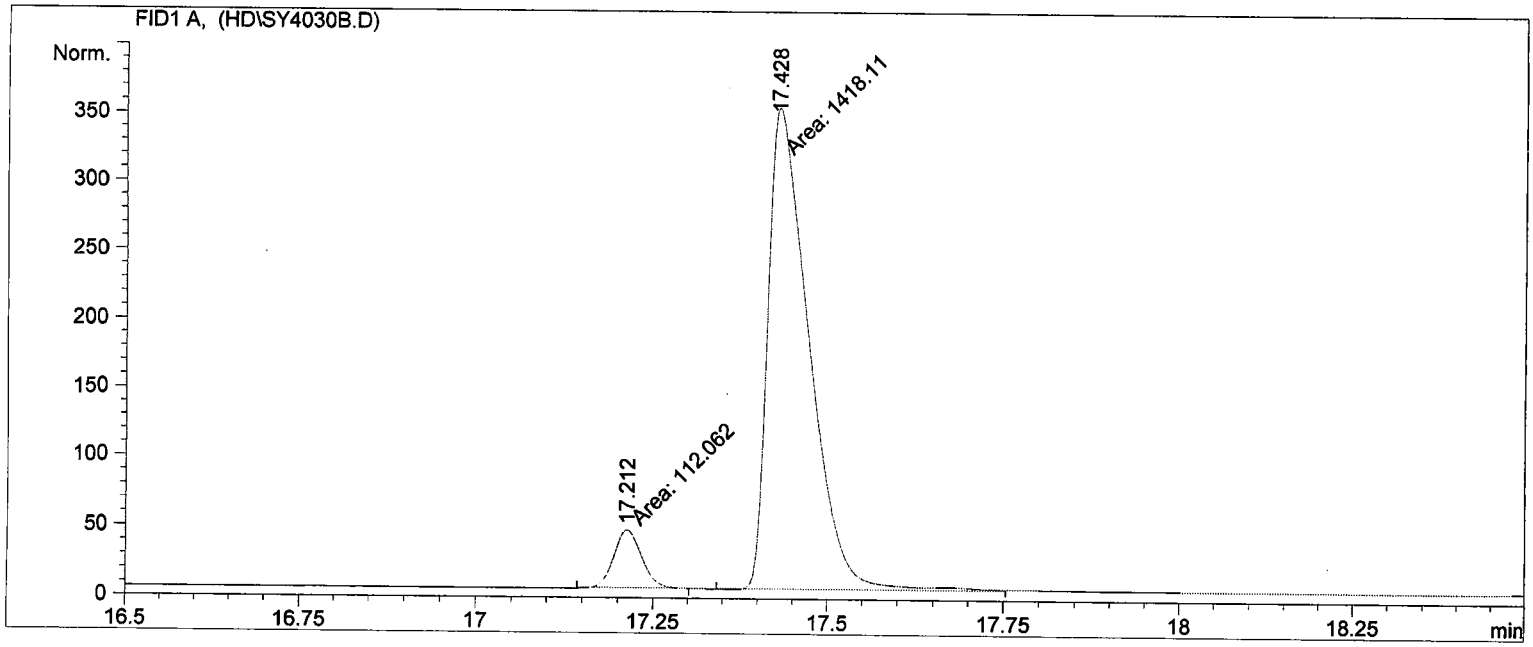


Table 1, entry 5
with (–)-**C_5Ph_5-DMAP***



Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  17.212 MM    0.0453  112.06217   41.26473  7.32348
   2  17.428 MM    0.0678 1418.11487  348.77933 92.67652

Totals :                  1530.17704  390.04406

 Results obtained with enhanced integrator!
```

Summed Peaks Report

```
Signal 1: FID1 A,
```

Final Summed Peaks Report

```
Signal 1: FID1 A,
```

Data File C:\HPCHEM\3\DATA\CC\SY4-060C.D

```
Injection Date  : 12/2/2011 2:16:51 PM          Seq. Line :   4
Sample Name     :                               Location : Vial 2
Acq. Operator   : CC                               Inj :   1
Acq. Instrument : Instrument 3                 Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3 µl
Acq. Method     : C:\HPCHEM\3\METHODS\AU105115.M
Last changed    : 6/10/2008 10:06:18 AM by BJ
Analysis Method : C:\HPCHEM\3\METHODS\SY90115.M
Last changed    : 12/27/2011 6:15:42 PM by HD
                  (modified after loading)
```

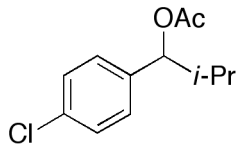
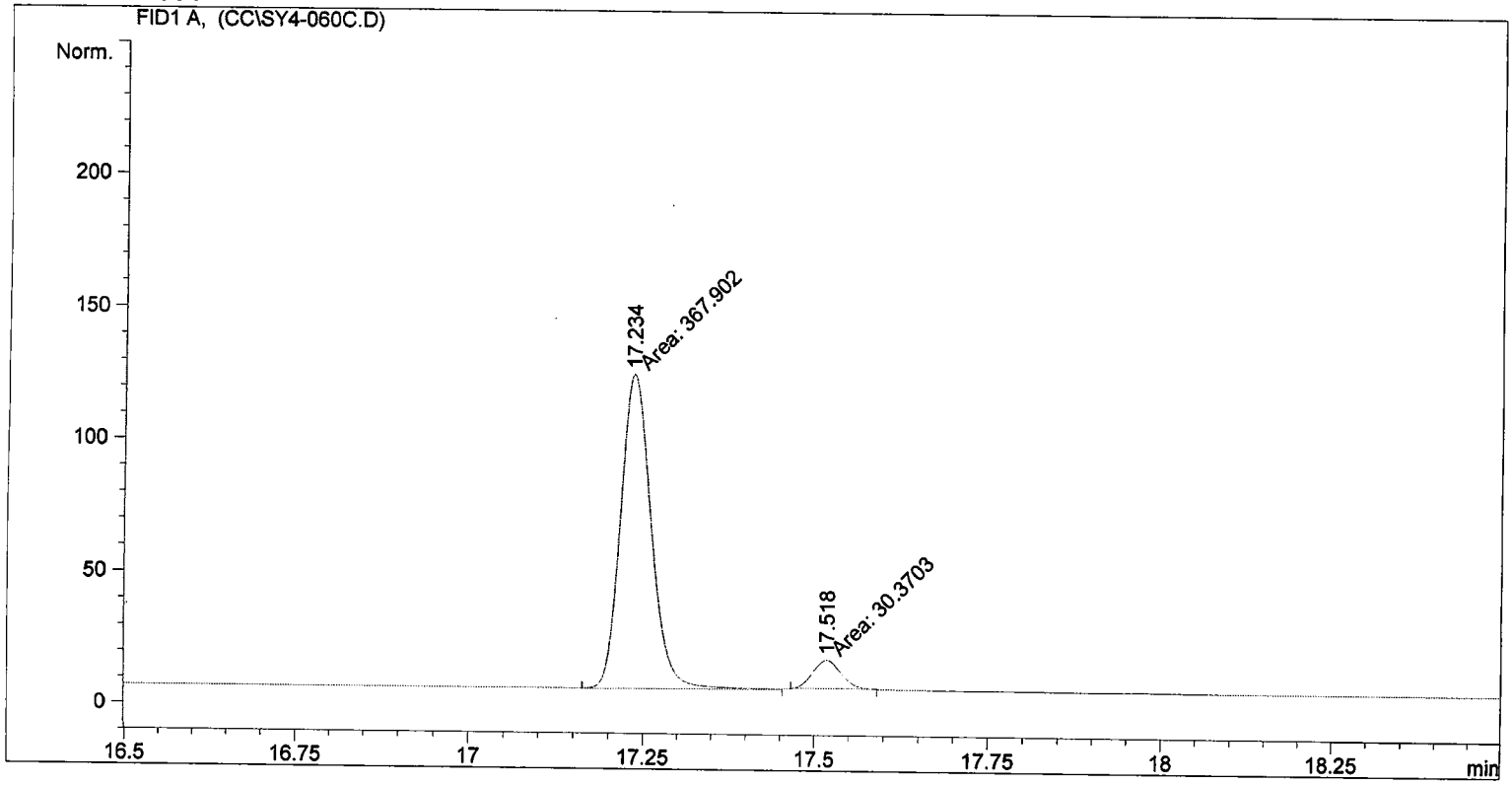


Table 1, entry 5
with (+)-C_5Ph_5-DMAP*

Initial test



Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  17.234 MM    0.0516  367.90179  118.76257 92.37450
   2  17.518 MM    0.0468   30.37025   10.82276  7.62550

Totals :                   398.27205  129.58533

 Results obtained with enhanced integrator!
```

*** End of Report ***

Data File C:\HPCHEM\3\DATA\SN\SY4054A.D

```
==========================================================================
Injection Date  : 11/25/2011 8:01:16 PM          Seq. Line :   5
Sample Name     :                                 Location : Vial 2
Acq. Operator   : SN                                 Inj :   1
Acq. Instrument : Instrument 3                   Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3 µl
Acq. Method     : C:\HPCHEM\3\METHODS\SY105115.M
Last changed    : 11/24/2011 12:17:48 PM by jc
Analysis Method : C:\HPCHEM\3\METHODS\COOLDOWN.M
Last changed    : 4/19/2012 3:17:34 PM by hc
                  (modified after loading)
standby
```

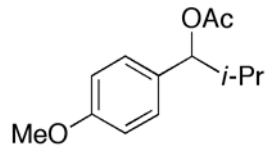
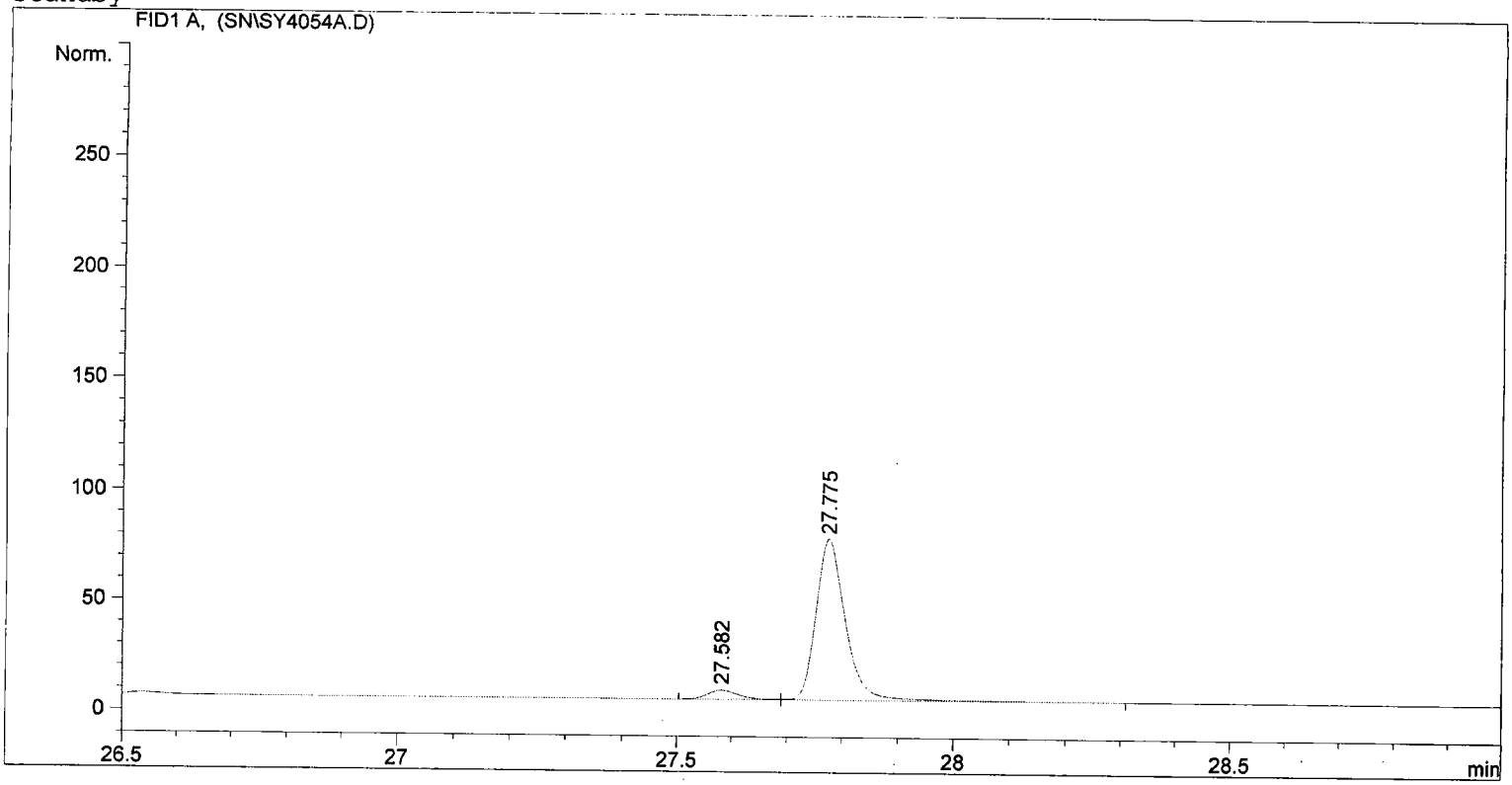


Table 1, entry 6
with (–)-**C_5Ph_5-DMAP***




```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]       %
----|-------|----|------|----------|----------|--------|
   1  27.582 PV    0.0603   16.20505    4.08384  5.61661
   2  27.775 VB    0.0557  272.31488   72.77936 94.38339

Totals :                   288.51993   76.86319

 Results obtained with enhanced integrator!
==========================================================================
                          Summed Peaks Report
==========================================================================

Signal 1: FID1 A,
```

```
==========================================================================
Injection Date  : 12/3/2011 12:36:06 PM          Seq. Line :   9
Sample Name     :                                 Location : Vial 2
Acq. Operator   : CC                                  Inj :   1
Acq. Instrument : Instrument 3                   Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3 µl
Acq. Method     : C:\HPCHEM\3\METHODS\SY105115.M
Last changed    : 11/24/2011 12:17:48 PM by jc
Analysis Method : C:\HPCHEM\3\METHODS\SY90115.M
Last changed    : 12/27/2011 6:23:02 PM by HD
                  (modified after loading)
```

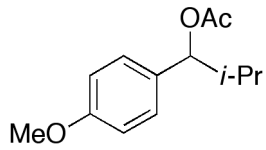
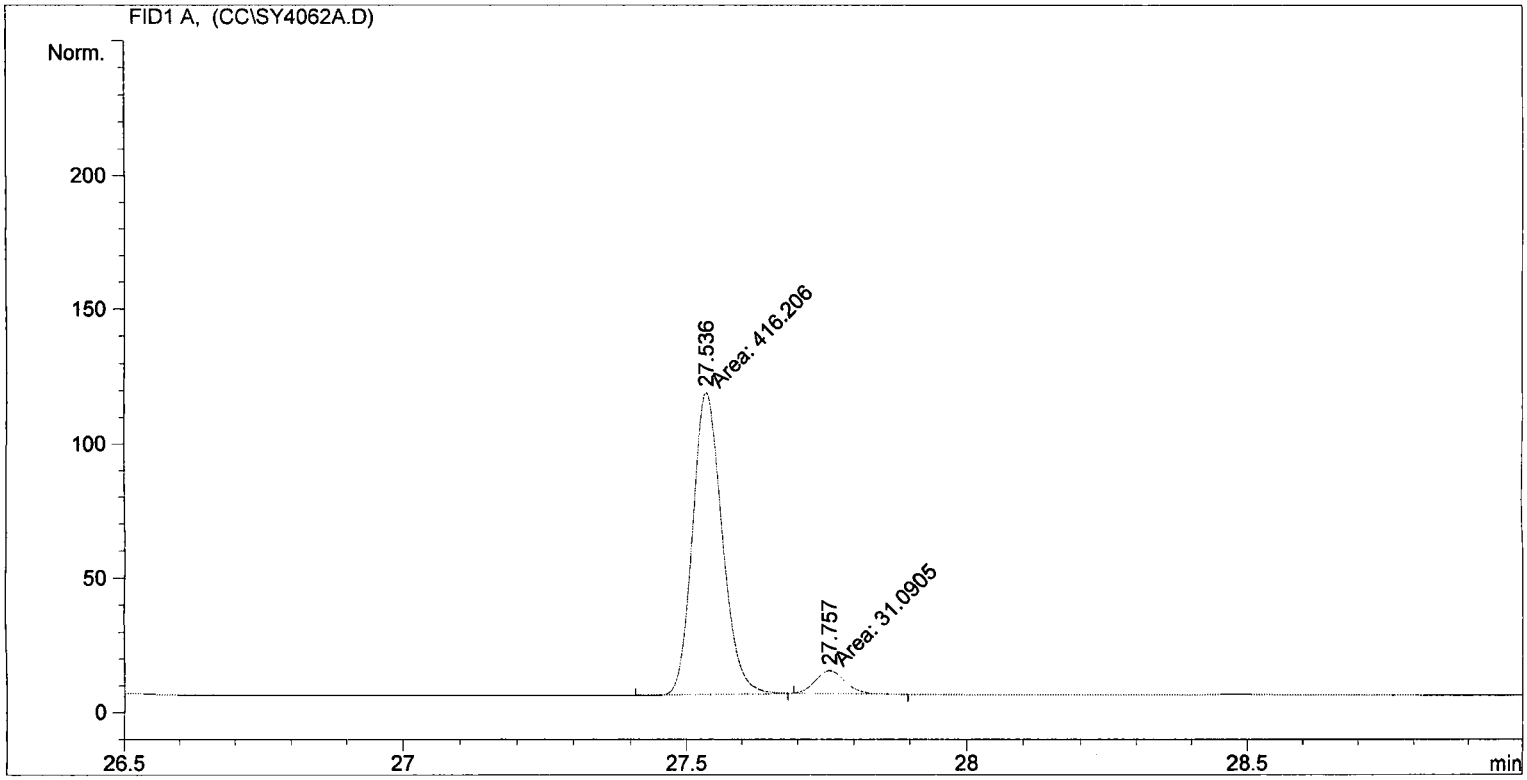


Table 1, entry 6
with (+)-**C_5Ph_5-DMAP***

Initial test




```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  27.536 MM    0.0617  416.20593  112.49719 93.04924
   2  27.757 MM    0.0609   31.09052    8.51014  6.95076

Totals :                   447.29645  121.00733

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

Data File C:\HPCHEM\3\DATA\HD\SY4028A.D

```
Injection Date  : 12/28/2011 4:36:13 PM          Seq. Line :  12
Sample Name     :                                Location : Vial 4
Acq. Operator   : HD                                 Inj :   1
Acq. Instrument : Instrument 3                  Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 2 µl
Acq. Method     : C:\HPCHEM\3\METHODS\SY105115.M
Last changed    : 12/27/2011 7:22:35 PM by HD
Analysis Method : C:\HPCHEM\3\METHODS\SY100ISA.M
Last changed    : 12/28/2011 6:12:44 PM by HD
                  (modified after loading)
```

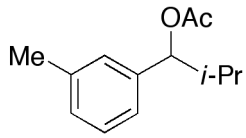
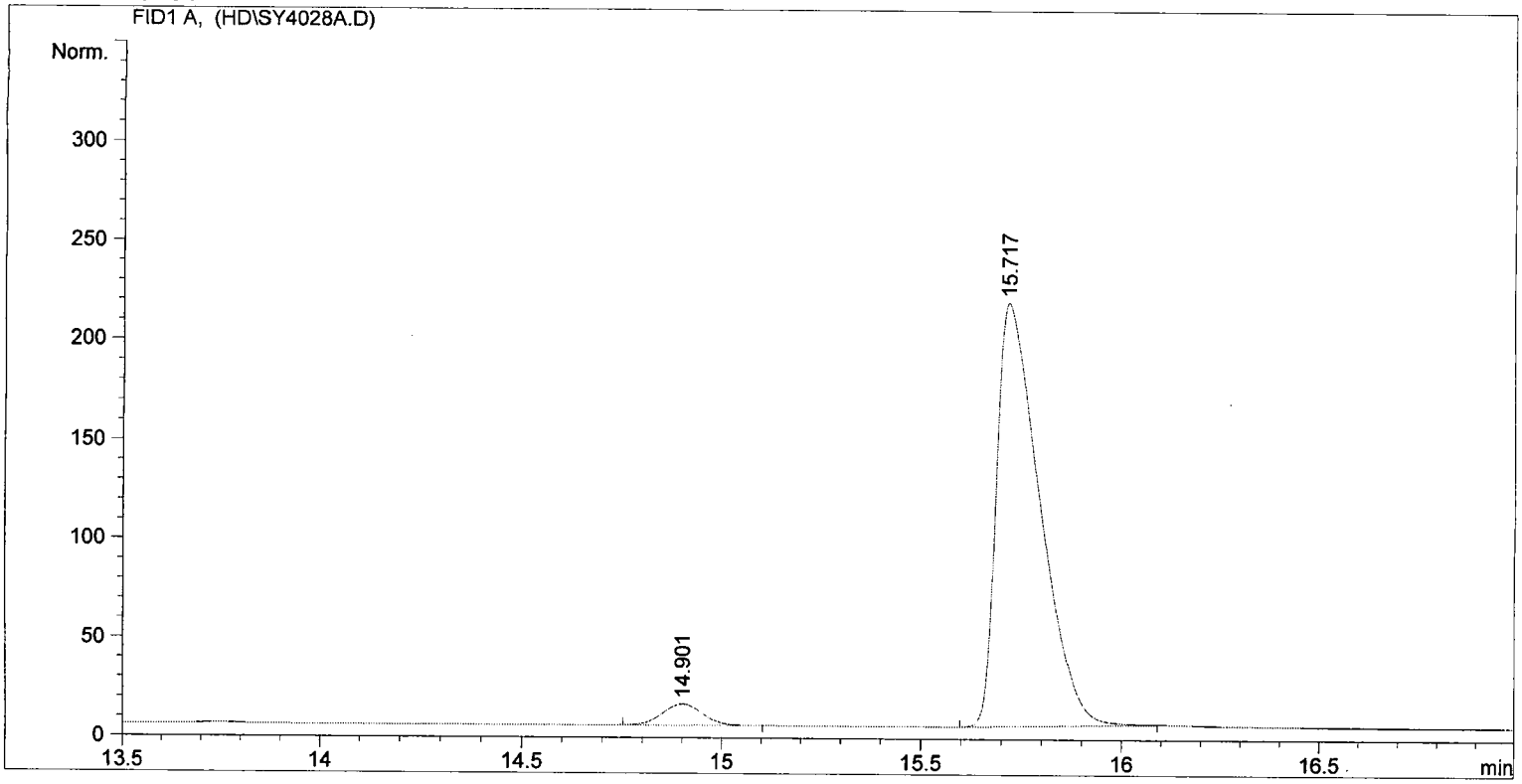


Table 1, entry 7
with (–)-**C_5Ph_5-DMAP***

Initial test



Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  14.901 BB    0.1087   75.04472   10.64902  4.48550
   2  15.717 PB    0.1104 1598.00769  213.32225 95.51450

Totals :                  1673.05241  223.97127

 Results obtained with enhanced integrator!
```

*** End of Report ***

Data File C:\HPCHEM\3\DATA\HD\SY4058B.D

```
Injection Date  : 12/28/2011 5:12:40 PM          Seq. Line :  13
Sample Name     :                                Location : Vial 5
Acq. Operator   : HD                                 Inj :   1
Acq. Instrument : Instrument 3                  Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 2 µl
Acq. Method     : C:\HPCHEM\3\METHODS\SY105115.M
Last changed    : 12/27/2011 7:22:35 PM by HD
Analysis Method : C:\HPCHEM\3\METHODS\SY100ISA.M
Last changed    : 12/28/2011 6:15:38 PM by HD
                  (modified after loading)
```

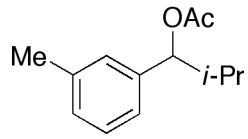
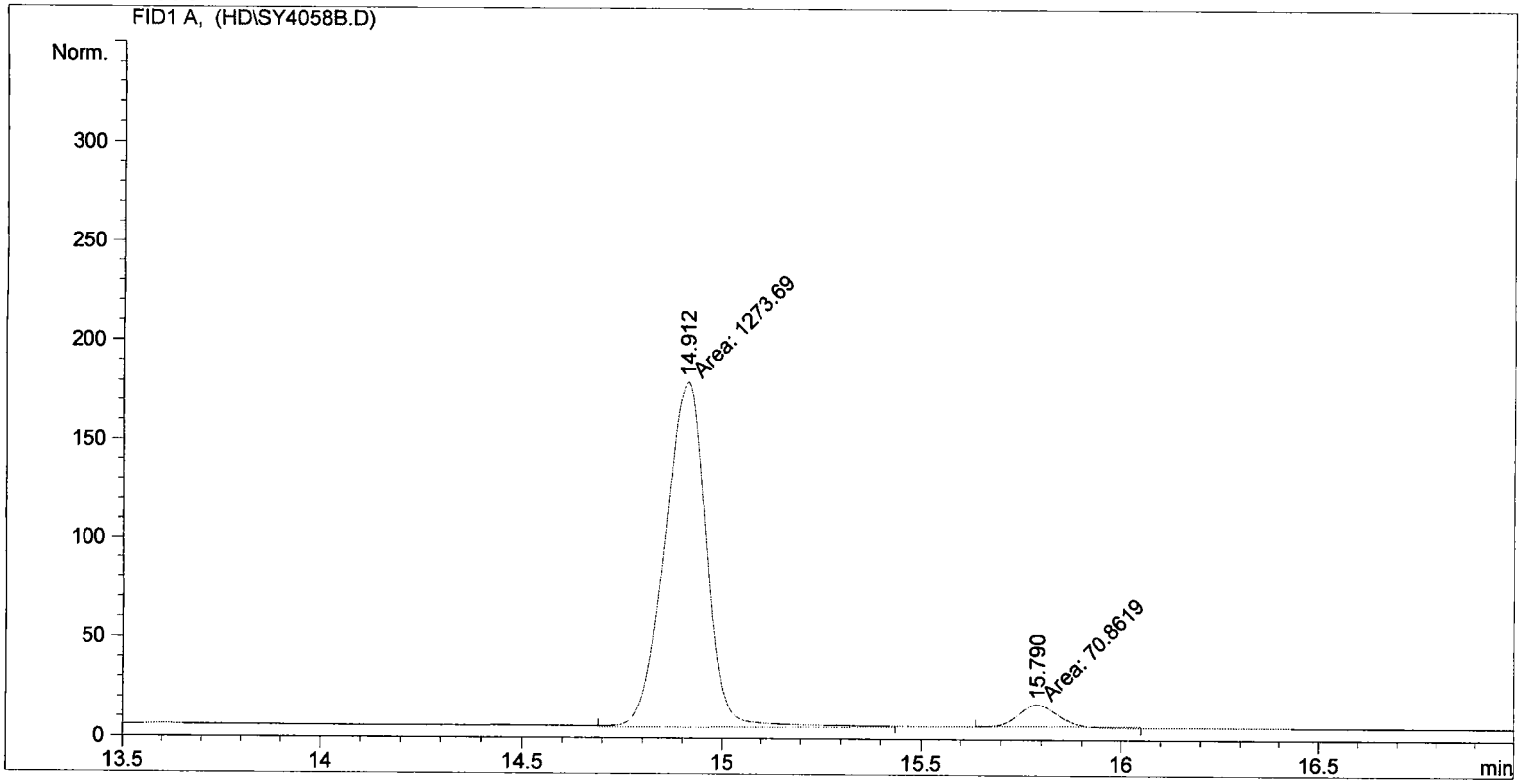


Table 1, entry 7
with (+)-**C_5Ph_5-DMAP***

Initial test



Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  14.912 MM    0.1215 1273.69214  174.75676 94.72971
   2  15.790 MM    0.1074   70.86195   10.99810  5.27029

Totals :                  1344.55408  185.75486

 Results obtained with enhanced integrator!
```

*** End of Report ***

```
==========================================================================
Injection Date  : 12/27/2011 6:22:37 PM          Seq. Line :   3
Sample Name     :                                 Location : Vial 5
Acq. Operator   : HD                                 Inj :   1
Acq. Instrument : Instrument 3                   Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3 µl
Acq. Method     : C:\HPCHEM\3\METHODS\SY90115.M
Last changed    : 12/27/2011 3:02:56 PM by HD
Analysis Method : C:\HPCHEM\3\METHODS\SY105130.M
Last changed    : 12/27/2011 7:18:21 PM by HD
                  (modified after loading)
Initial test
```

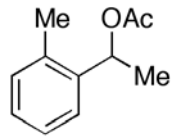
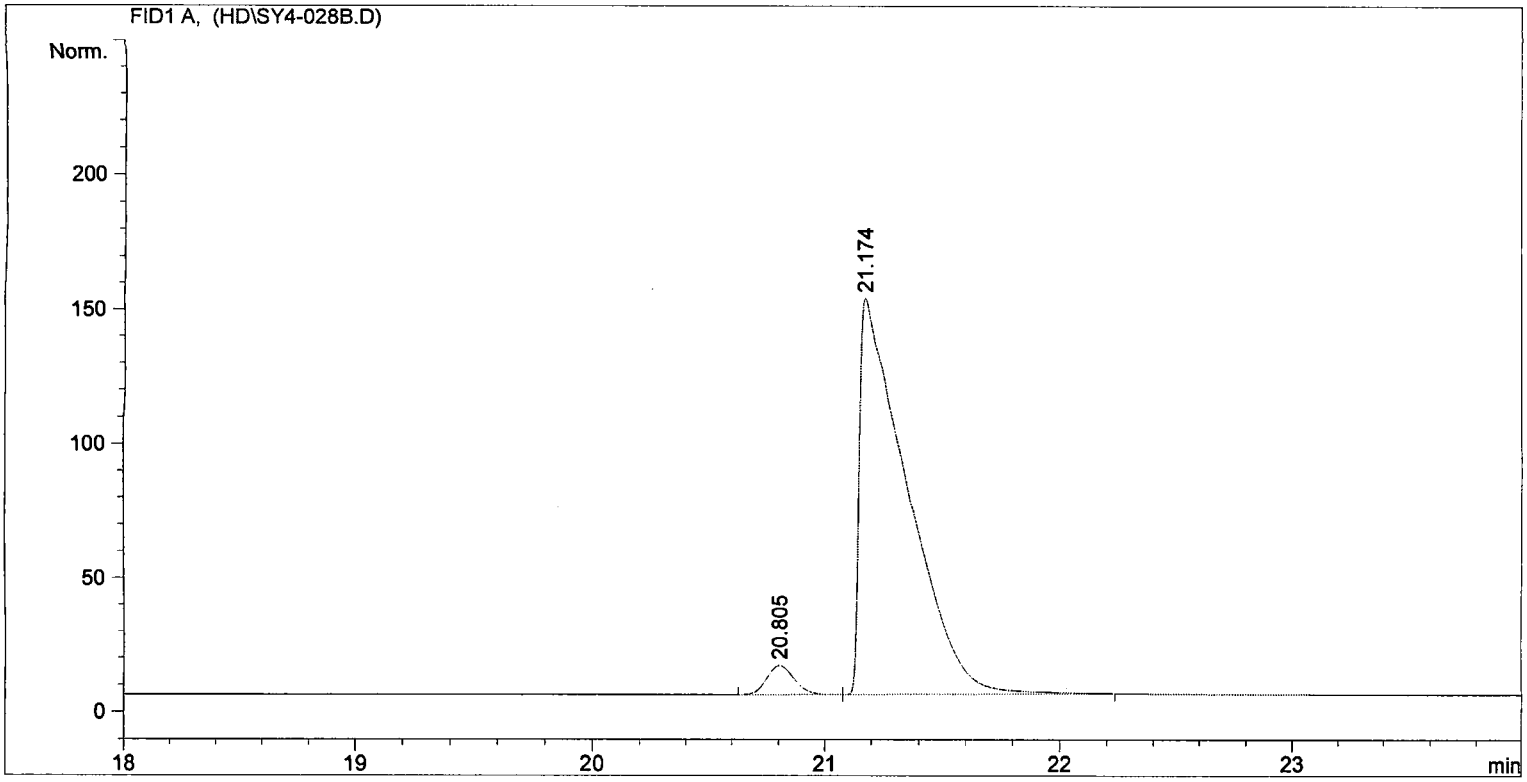


Table 1, entry 8
with (–)-C_5Ph_5-DMAP*




```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1  20.805 PP    0.1294   88.95095   10.76215  4.09658
   2  21.174 VB    0.1783 2082.39575  147.86237 95.90342

Totals :                  2171.34670  158.62451

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

Data File C:\HPCHEM\3\DATA\HD\SY4-062B.D

```
Injection Date  : 12/27/2011 8:26:19 PM          Seq. Line :   1
Sample Name     :                                Location : Vial 3
Acq. Operator   : HD                                 Inj :   1
Acq. Instrument : Instrument 3                   Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3 µl
Acq. Method     : C:\HPCHEM\3\METHODS\SY90115.M
Last changed    : 12/27/2011 3:02:56 PM by HD
Analysis Method : C:\HPCHEM\3\METHODS\SY100ISA.M
Last changed    : 12/28/2011 1:42:35 PM by HD
                  (modified after loading)
```

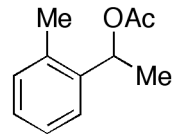
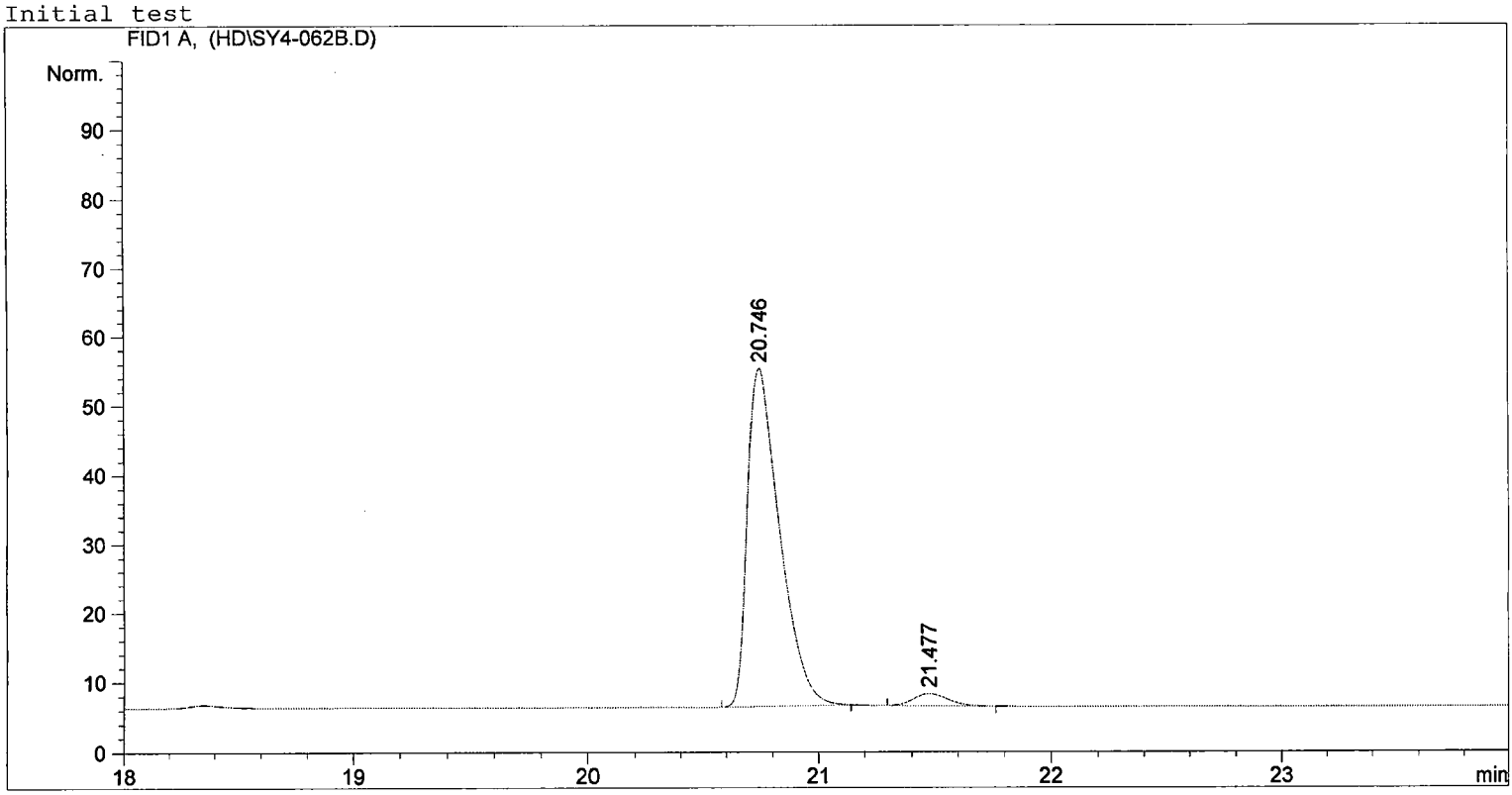


Table 1, entry 8
with (+)-**C_5Ph_5-DMAP***

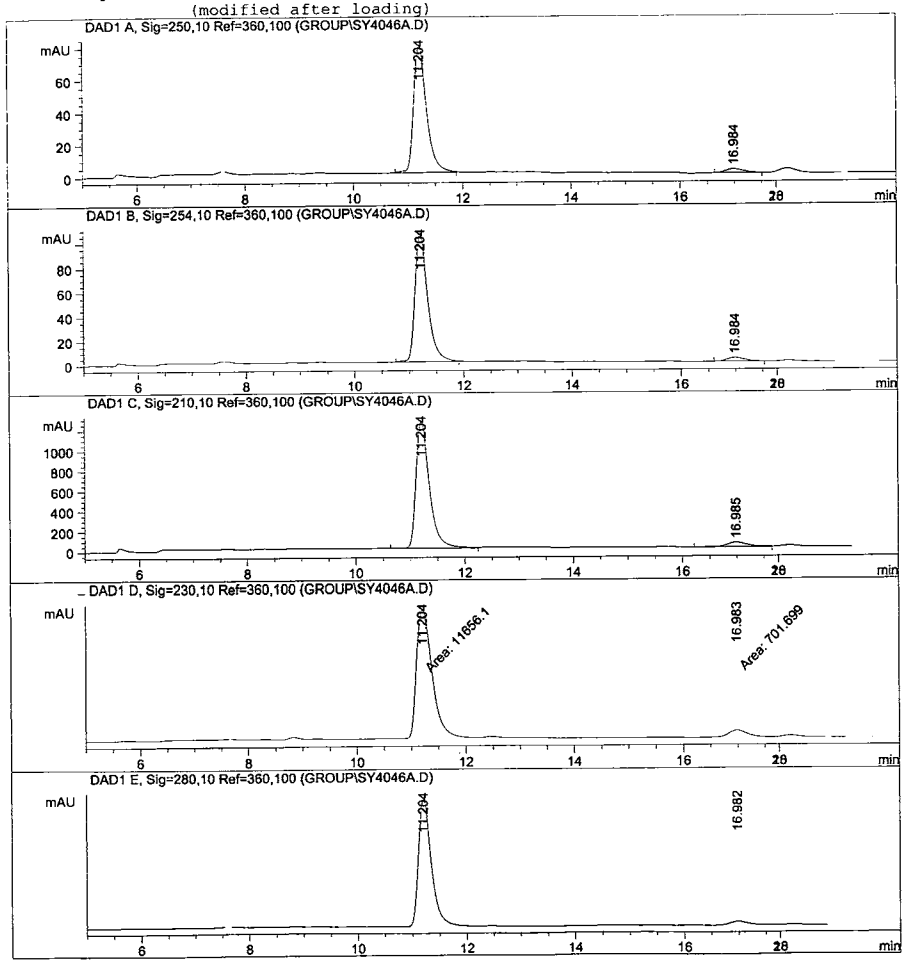
Initial test




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1  20.746 PB    0.1371  471.79797   48.86399 96.36722
   2  21.477 BP    0.1221   17.78549    1.73504  3.63278

Totals :                   489.58346   50.59904

 Results obtained with enhanced integrator!

                        *** End of Report ***
```

Data File C:\HPCHEM\1\DATA\GROUP\SY4046A.D

```
Injection Date  : 11/25/2011 7:03:54 PM          Seq. Line :   5
Sample Name     :                                 Location : Vial 2
Acq. Operator   : JTM                                 Inj :   1
Acq. Instrument : Instrument 1                Inj Volume : 15 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 1 µl
Acq. Method     : C:\HPCHEM\1\METHODS\OD-01-60.M
Last changed    : 11/25/2011 4:57:32 PM by NB
Analysis Method : C:\HPCHEM\1\METHODS\YL-AD08.M
Last changed    : 12/27/2011 7:49:48 PM by JTM
                  (modified after loading)
```



Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.204	BB	0.2482	1293.14844	78.50520	95.8974
2	16.984	PB	0.3429	55.32301	2.41821	4.1026
Totals :				1348.47145	80.92342	

Results obtained with enhanced integrator!

Signal 2: DAD1 B, Sig=254,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.204	BB	0.2474	1709.65356	104.23670	95.7928
2	16.984	PB	0.3439	75.08683	3.19879	4.2072
Totals :				1784.74039	107.43549	

Results obtained with enhanced integrator!

Signal 3: DAD1 C, Sig=210,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.204	VB	0.2630	2.14601e4	1245.90479	94.7669
2	16.985	VB	0.3941	1185.03430	45.16370	5.2331
Totals :				2.26451e4	1291.06848	

Results obtained with enhanced integrator!

Signal 4: DAD1 D, Sig=230,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.204	MM	0.3314	1.16561e4	586.18079	94.3218
2	16.983	MM	0.3784	701.69916	30.90495	5.6782
Totals :				1.23578e4	617.08573	

Results obtained with enhanced integrator!

Signal 5: DAD1 E, Sig=280,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.204	BB	0.2462	4694.26367	287.88928	95.8319
2	16.982	BB	0.3586	204.17297	8.73924	4.1681
Totals :				4898.43665	296.62852	

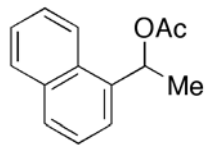
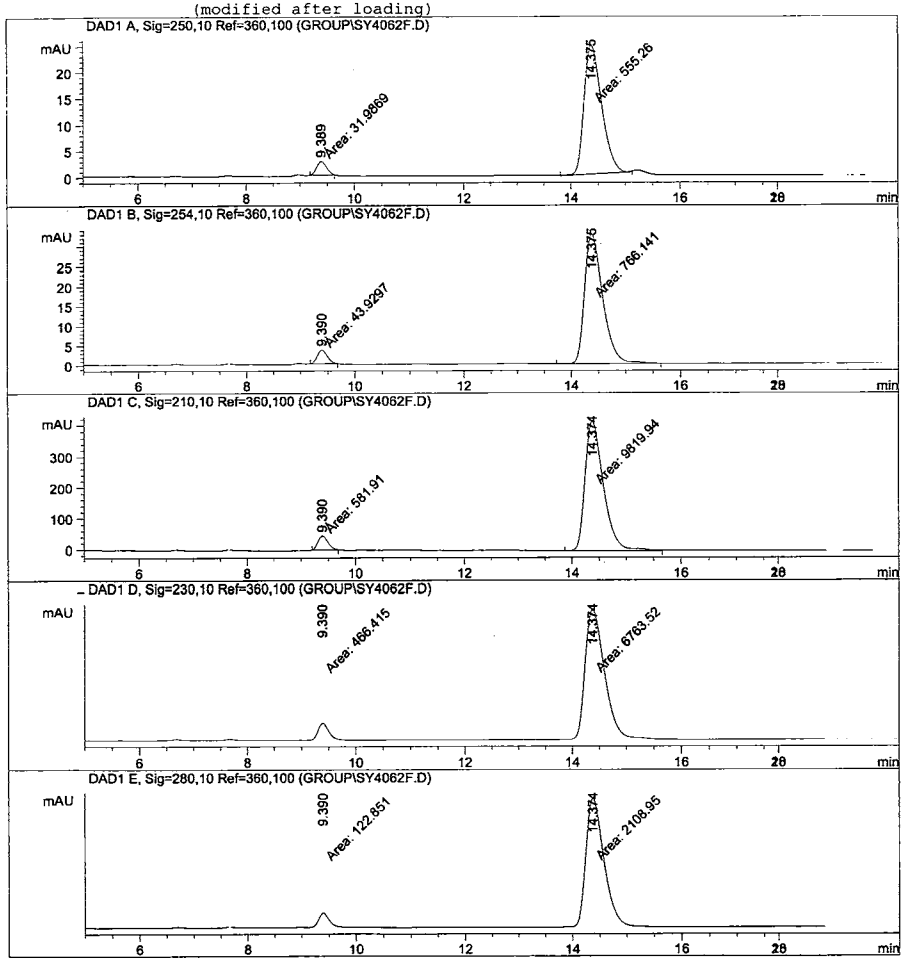


Table 1, entry 9
with (–)-C_5Ph_5-DMAP*

Data File C:\HPCHEM\1\DATA\GROUP\SY4062F.D

```
Injection Date  : 1/13/2012 2:31:26 PM          Seq. Line :   2
Sample Name     :                               Location : Vial 1
Acq. Operator   : JTM                              Inj :   1
Acq. Instrument : Instrument 1                 Inj Volume : 15 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 1 µl
Acq. Method     : C:\HPCHEM\1\METHODS\OD-01-40.M
Last changed    : 8/17/2010 4:39:48 PM by JTM
Analysis Method : C:\HPCHEM\1\METHODS\OD-10-40.M
Last changed    : 4/16/2012 1:52:26 PM by CE
                  (modified after loading)
```



Data File C:\HPCHEM\1\DATA\GROUP\SY4062F.D

Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.389	MM	0.2057	31.98688	2.59194	5.4469
2	14.375	MM	0.3774	555.26025	24.52152	94.5531
Totals :				587.24713	27.11346	

Results obtained with enhanced integrator!

Signal 2: DAD1 B, Sig=254,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.390	MM	0.2120	43.92972	3.45371	5.4229
2	14.375	MM	0.3905	766.14087	32.69531	94.5771
Totals :				810.07059	36.14901	

Results obtained with enhanced integrator!

Signal 3: DAD1 C, Sig=210,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.390	MM	0.2145	581.91028	45.20829	5.5943
2	14.374	MM	0.3936	9819.93750	415.82935	94.4057
Totals :				1.04018e4	461.03764	

Results obtained with enhanced integrator!

Signal 4: DAD1 D, Sig=230,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.390	MM	0.2201	466.41537	35.31659	6.4512
2	14.374	MM	0.4124	6763.52100	273.33804	93.5488
Totals :				7229.93637	308.65463	

Results obtained with enhanced integrator!

Signal 5: DAD1 E, Sig=280,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.390	MM	0.2165	122.85142	9.45909	5.5046
2	14.374	MM	0.3907	2108.95215	89.95865	94.4954
Totals :				2231.80357	99.41774	

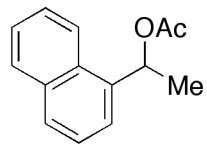
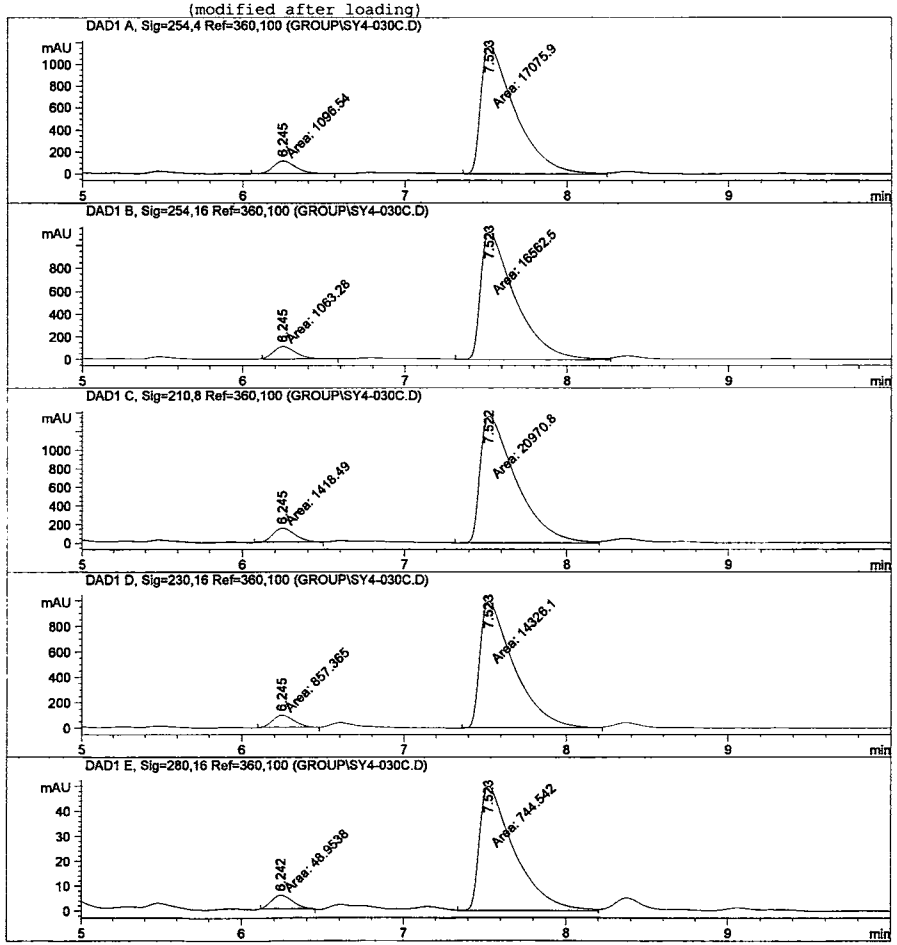


Table 1, entry 9
with (+)-C_5Ph_5-DMAP*

Data File C:\HPCHEM\1\DATA\GROUP\SY4-030C.D

```
Injection Date  : 11/12/2011 12:04:53 PM        Seq. Line :   2
Sample Name     :                                Location : Vial 63
Acq. Operator   : SN                                Inj :   1
Acq. Instrument : Instrument 1                  Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3 µl
Acq. Method     : C:\HPCHEM\1\METHODS\ODH-0130.M
Last changed    : 8/3/2011 6:13:51 PM by JTM
Analysis Method : C:\HPCHEM\1\METHODS\SNIA0125.M
Last changed    : 12/27/2011 7:59:40 PM by SN
                  (modified after loading)
```



Data File C:\HPCHEM\1\DATA\GROUP\SY4-030C.D

Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.245	MM	0.1581	1096.53711	115.62602	6.0341
2	7.523	MF	0.2445	1.70759e4	1163.97253	93.9659
Totals :				1.81725e4	1279.59856	

Results obtained with enhanced integrator!

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.245	MM	0.1584	1063.28137	111.85748	6.0325
2	7.523	MF	0.2465	1.65625e4	1120.00134	93.9675
Totals :				1.76258e4	1231.85883	

Results obtained with enhanced integrator!

Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.245	MM	0.1560	1418.48560	151.57990	6.3356
2	7.522	MF	0.2575	2.09708e4	1357.52087	93.6644
Totals :				2.23893e4	1509.10077	

Results obtained with enhanced integrator!

Signal 4: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.245	MM	0.1504	857.36493	95.02280	5.6467
2	7.523	MF	0.2408	1.43261e4	991.72699	94.3533
Totals :				1.51835e4	1086.74979	

Results obtained with enhanced integrator!

Signal 5: DAD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.242	MM	0.1497	48.95375	5.44952	6.1694
2	7.523	MF	0.2476	744.54169	50.11868	93.8306
Totals :				793.49544	55.56819	

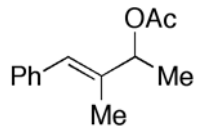
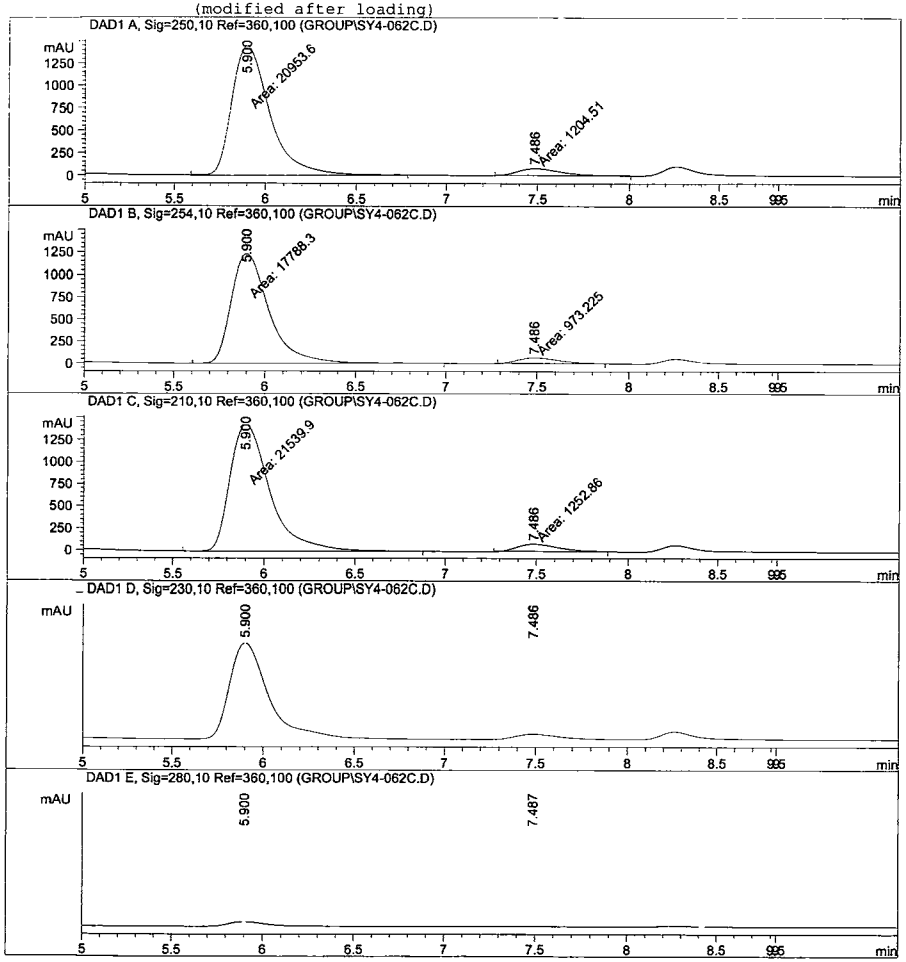


Table 1, entry 10 with (–)-**C_5Ph_5-DMAP***

Data File C:\HPCHEM\1\DATA\GROUP\SY4-062C.D

```
Injection Date  : 12/8/2011 12:22:44 AM          Seq. Line :   8
Sample Name     :                                 Location : Vial 1
Acq. Operator   : JTM                                Inj :   1
Acq. Instrument : Instrument 1                 Inj Volume : 15 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3 µl
Acq. Method     : C:\HPCHEM\1\METHODS\OD-01-30.M
Last changed    : 4/7/2011 2:40:51 AM by CC
Analysis Method : C:\HPCHEM\1\METHODS\YL-AD07.M
Last changed    : 12/27/2011 8:21:33 PM by JTM
                  (modified after loading)
```



Data File C:\HPCHEM\1\DATA\GROUP\SY4-062C.D

Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.900	MM	0.2418	2.09536e4	1444.29919	94.5640
2	7.486	MM	0.2629	1204.50964	76.36211	5.4360
Totals :				2.21581e4	1520.66131	

Results obtained with enhanced integrator!

Signal 2: DAD1 B, Sig=254,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.900	MM	0.2407	1.77883e4	1231.64832	94.8127
2	7.486	MM	0.2537	973.22461	63.92531	5.1873
Totals :				1.87616e4	1295.57362	

Results obtained with enhanced integrator!

Signal 3: DAD1 C, Sig=210,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.900	MM	0.2526	2.15399e4	1420.97913	94.5033
2	7.486	MM	0.2553	1252.85693	81.78120	5.4967
Totals :				2.27927e4	1502.76032	

Results obtained with enhanced integrator!

Signal 4: DAD1 D, Sig=230,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.900	BB	0.2265	1.59096e4	1076.05347	94.1519
2	7.486	PP	0.2571	988.19049	59.09837	5.8481
Totals :				1.68978e4	1135.15183	

Results obtained with enhanced integrator!

Signal 5: DAD1 E, Sig=280,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.900	BB	0.2255	767.51825	52.22518	94.1434
2	7.487	BP	0.2459	47.74647	3.02838	5.8566
Totals :				815.26472	55.25356	

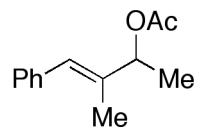
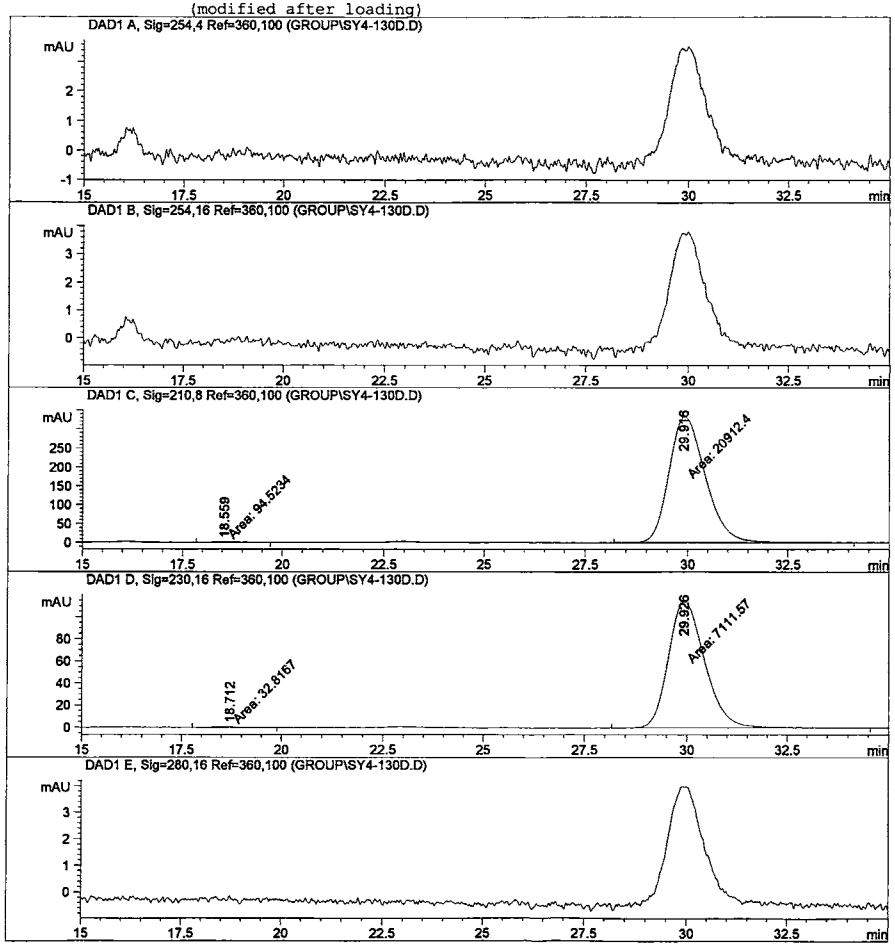


Table 1, entry 10
with (+)-C_5Ph_5-DMAP*

Data File C:\HPCHEM\1\DATA\GROUP\SY4-130D.D

```
Injection Date  : 1/22/2012 7:29:46 PM          Seq. Line :   1
Sample Name     :                               Location : Vial 11
Acq. Operator   : JTM                              Inj :   1
Acq. Instrument : Instrument 1                 Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3 µl
Acq. Method     : C:\HPCHEM\1\METHODS\ODH-0540.M
Last changed    : 9/7/2011 9:23:44 AM by SN
Analysis Method : C:\HPCHEM\1\METHODS\YL-AD08.M
Last changed    : 4/19/2012 1:41:14 PM by JTM
                  (modified after loading)
```

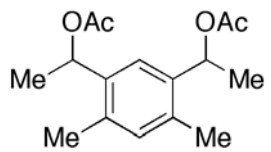


Data File C:\HPCHEM\1\DATA\GROUP\SY4-130D.D

Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100


Signal 2: DAD1 B, Sig=254,16 Ref=360,100


Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  18.559 MM    0.8222   94.52335    1.91597   0.4500
   2  29.916 MM    1.0443 2.09124e4   333.75858  99.5500

Totals :                  2.10069e4   335.67454

 Results obtained with enhanced integrator!

Signal 4: DAD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  18.712 MM    0.8052   32.81665 6.79271e-1   0.4593
   2  29.926 MM    1.0365 7111.57129  114.34914  99.5407

Totals :                  7144.38794  115.02841

 Results obtained with enhanced integrator!

Signal 5: DAD1 E, Sig=280,16 Ref=360,100
```

*** End of Report ***

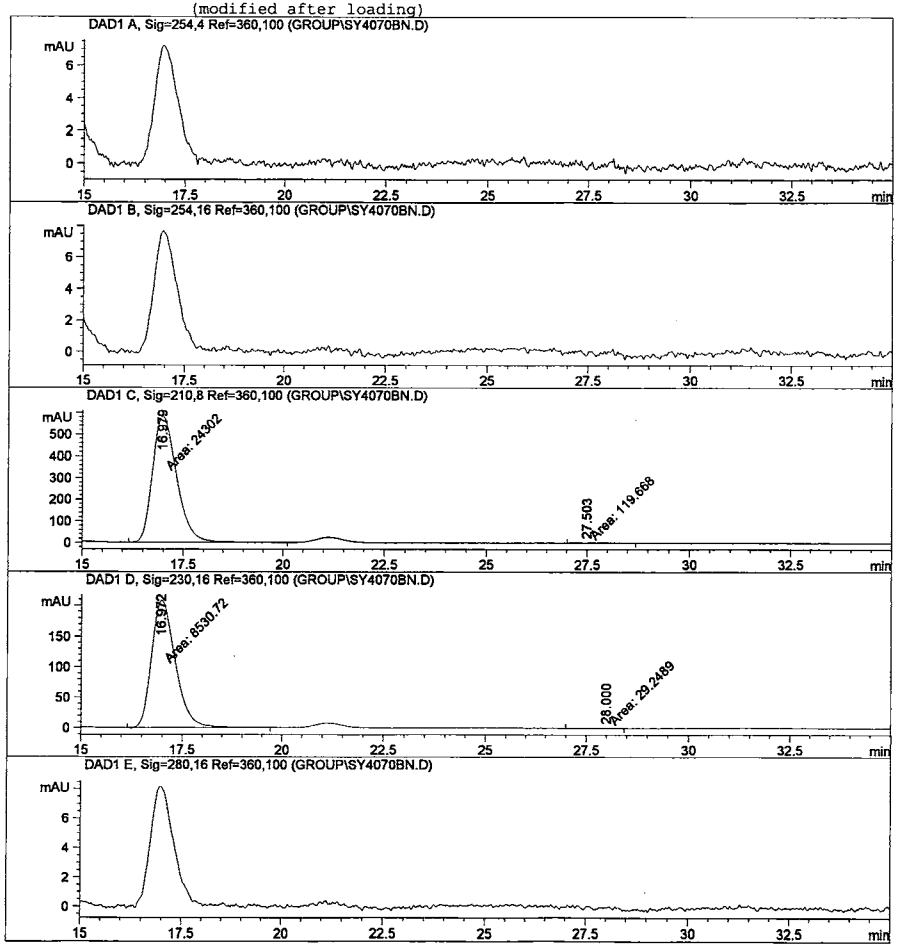


eq 10

with (–)-C_5Ph_5-DMAP*

Data File C:\HPCHEM\1\DATA\GROUP\SY4070BN.D

Injection Date	: 4/19/2012 10:40:12 AM	Seq. Line	: 46
Sample Name	:	Location	: Vial 22
Acq. Operator	: JTM	Inj	: 1
Acq. Instrument	: Instrument 1	Inj Volume	: 5 µl
Acq. Method	: C:\HPCHEM\1\METHODS\ODH-0540.M		
Last changed	: 9/7/2011 9:23:44 AM by SN		
Analysis Method	: C:\HPCHEM\1\METHODS\YL-AD08.M		
Last changed	: 4/19/2012 1:40:50 PM by JTM		
	(modified after loading)		



Data File C:\HPCHEM\1\DATA\GROUP\SY4070BN.D

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.979	MM	0.6942	2.43020e4	583.45728	99.5100
2	27.503	MM	0.9062	119.66791	2.20082	0.4900
Totals :				2.44217e4	585.65809	

Results obtained with enhanced integrator!

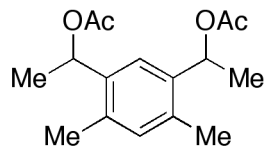
Signal 4: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.972	MM	0.6832	8530.72363	208.09496	99.6583
2	28.000	MM	0.8272	29.24886	5.89296e-1	0.3417
Totals :				8559.97249	208.68425	

Results obtained with enhanced integrator!

Signal 5: DAD1 E, Sig=280,16 Ref=360,100

*** End of Report ***



eq 10

with (+)-C_5Ph_5-DMAP*