



Supporting Information

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Catalytic Asymmetric Cross-Couplings of Racemic α -Bromoketones with Arylzinc Reagents

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Supporting Information

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I. General Information

All reactions were carried out in oven-dried glassware under an atmosphere of argon.

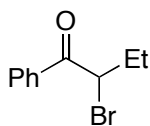
The following reagents were purchased and used without purification: ZnI_2 (Alfa), ZnPh_2 (Alfa), $\text{NiCl}_2 \cdot \text{glyme}$ (Strem), glyme (Fluka), THF (anhydrous; Aldrich), (1*S*,2*S*)-(+)-2-amino-3-methoxy-1-phenyl-1-propanol (Aldrich), and (1*R*,2*R*)-(+)-2-amino-1-phenyl-1,3-propanediol (TCI).

HPLC analyses were carried out on an Agilent 1100 series system with Daicel Chiralpak® columns.

II. Preparation of α -Bromoketones

General Procedure: Bromine (1.0 equiv) was added to a solution of the ketone in Et_2O . The solution was stirred for 30 min, and then the reaction was quenched with 10% aqueous potassium carbonate (10 mL). The organic layer was washed with sodium thiosulfate (10 mL) and brine (10 mL), dried over sodium sulfate, and concentrated. The α -bromoketone was purified by flash chromatography.

These procedures have not been optimized.



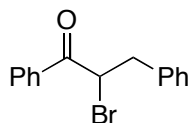
2-Bromo-1-phenylbutan-1-one [877-35-0]. Prepared from butyrophenone (1.49 g, 10 mmol) and bromine (0.51 mL, 10 mmol) in Et₂O (25 mL). Solvent system for chromatography: 3:1→2:1 hexanes:dichloromethane. The product was isolated as a yellow oil in 70% yield (1.6 g).

¹H NMR (400 MHz, CDCl₃): δ 8.04-8.02 (m, 2H), 7.62-7.59 (m, 1H), 7.52-7.48 (m, 2H), 5.09 (dd, *J* = 7.2, 7.6 Hz, 1H), 2.29-2.11 (m, 2H), 1.10 (t, *J* = 7.6 Hz, 3H);

¹³C NMR (100 MHz, CDCl₃): δ 193.4, 134.7, 133.9, 129.0, 128.0, 49.3, 27.1, 12.4;

IR (film): 1683, 1597, 1448, 1226, 1002, 899, 802, 703 cm⁻¹;

LRMS (EI) for C₁₀H₁₁O (M-Br): calcd 147, found 147.

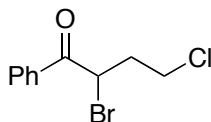


2-Bromo-1,3-diphenylpropan-1-one [51012-66-9]. Prepared from 3-phenylpropiophenone (2.3 g, 10 mmol) and bromine (0.51 mL, 10 mmol) in Et₂O (20 mL). Solvent system for chromatography: 4:1→2:1 hexanes:dichloromethane. The product was isolated as a white solid in 79% yield (2.3 g).

¹H NMR (400 MHz, CDCl₃): δ 8.00-7.97 (m, 2H), 7.61-7.57 (m, 1H), 7.49-7.45 (m, 2H), 7.33-7.24 (m, 5H), 5.34 (t, *J* = 7.2 Hz, 1H), 3.69 (dd, *J* = 7.6, 14 Hz, 1H), 3.38 (dd, *J* = 7.4, 14 Hz, 1H);

¹³C NMR (100 MHz, CDCl₃): δ 193.0, 137.7, 134.6, 134.0, 129.7, 129.04, 128.97, 128.8, 127.3, 46.8, 39.7;

LRMS (EI) for C₁₅H₁₃O (M-Br): calcd 209, found 209.



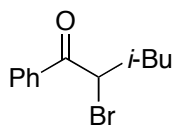
2-Bromo-4-chloro-1-phenylbutan-1-one [52868-15-2]. Prepared from 4-chlorobutyrophenone (1.81 g, 10 mmol) and bromine (0.51 mL, 10 mmol) in Et₂O (20 mL). Solvent system for chromatography: 3:1→2:1 hexanes:dichloromethane. The product was isolated as a yellow oil in 89% yield (1.8 g).

¹H NMR (400 MHz, CDCl₃): δ 8.14-8.07 (m, 2H), 7.68-7.64 (m, 1H), 7.58-7.54 (m, 2H), 5.55 (dd, *J* = 2.4, 7.6 Hz, 1H), 3.85-3.78 (m, 2H), 2.76-2.57 (m, 2H);

¹³C NMR (100 MHz, CDCl₃): δ 192.7, 134.20, 134.17, 129.2, 129.1, 43.9, 42.6, 35.9;

IR (film): 1685, 1596, 1449, 1257, 1178, 851, 707 cm⁻¹;

LRMS (EI) for C₁₀H₁₀BrO (M-Cl): calcd 225, found 225.



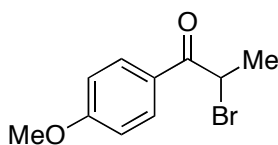
2-Bromo-4-methyl-1-phenylpentan-1-one [33809-96-0]. Prepared from 4-methylvalerophenone (2.3 g, 13.1 mmol), which was prepared according to a literature procedure,¹ and bromine (0.67 mL, 13.1 mmol) in Et₂O (30 mL). Solvent system for chromatography: 3:1 hexanes:dichloromethane. The product was isolated as a clear, colorless oil in 30% yield (1.0 g).

¹H NMR (400 MHz, CDCl₃): δ 8.05-8.02 (m, 2H), 7.63-7.59 (m, 1H), 7.53-7.49 (m, 2H), 5.23 (dd, *J* = 6.4, 8.0 Hz, 1H), 2.12-1.99 (m, 2H), 1.91-1.81 (m, 1H), 0.98 (dd, *J* = 3.6, 6.8 Hz, 6H);

¹³C NMR (100 MHz, CDCl₃): δ 193.5, 134.7, 133.9, 129.03, 129.00, 45.9, 42.2, 26.5, 22.9, 22.0;

IR (film): 1687, 1597, 1448, 1369, 1278, 705, 686 cm⁻¹;

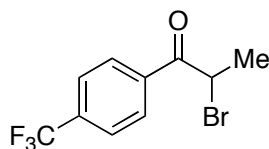
LRMS (EI) for C₁₂H₁₅O (M-Br): calcd 175, found 175.



2-Bromo-1-(4-methoxyphenyl)propan-1-one [21086-33-9]. Prepared from 4-methoxypropiophenone (1.64 g, 10 mmol) and bromine (0.51 mL, 10 mmol) in Et₂O (20 mL). Solvent system for chromatography: 1:1 hexanes:dichloromethane. The product was isolated as a white solid in 61% yield (1.5 g).

¹H NMR (400 MHz, CDCl₃): δ 8.02 (dd, *J* = 2.4, 8.8 Hz, 2H), 6.96 (dd, *J* = 2.4, 8.8 Hz, 2H), 5.27 (q, *J* = 6.8 Hz, 1H), 3.88 (s, 3H), 1.89 (d, *J* = 6.8 Hz, 3H);

¹³C NMR (100 MHz, CDCl₃): δ 192.2, 164.1, 131.5, 127.0, 114.1, 55.7, 41.7, 20.4.



2-Bromo-1-(4-(trifluoromethyl)phenyl)propan-1-one [95728-57-7]. Prepared from 4-(trifluoromethyl)propiophenone (2.02 g, 10 mmol) and bromine (0.51 mL, 10 mmol) in Et₂O (25 mL). Solvent system for chromatography: 3:1→2:1 hexanes:dichloromethane. The product was isolated as a white solid in 64% yield (1.8 g).

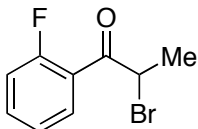
¹H NMR (400 MHz, CDCl₃): δ 8.14 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 5.27 (q, *J* = 6.4 Hz, 1H), 1.93 (d, *J* = 6.4 Hz, 3H);

(1) Cho, C. S. *J. Mol. Catal. A: Chem.* **2005**, *240*, 55–60.

^{13}C NMR (100 MHz, CDCl_3): δ 192.3, 136.8, 134.8 (q, $J = 132$ Hz), 129.3, 125.8 (t, $J = 16$ Hz), 123.5 (q, $J = 1088$ Hz), 41.4, 19.8;

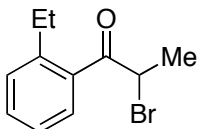
IR (film): 1694, 1446, 1410, 1154, 1119, 1056, 999, 861, 768, 701 cm^{-1} ;

LRMS (EI) for $\text{C}_{10}\text{H}_8\text{BrF}_3\text{O}$: calcd 280, found 280.



2-Bromo-1-(2-fluorophenyl)propan-1-one [186036-09-9]. Prepared from 2'-fluoropropiophenone (1.51 g, 10 mmol) and bromine (0.51 mL, 10 mmol) in Et_2O (20 mL). Solvent system for chromatography: 3:1 hexanes:dichloromethane. The product was isolated as a clear, colorless oil in 75% yield (1.7 g).

^1H NMR (400 MHz, CDCl_3): δ 7.91-7.87 (m, 1H), 7.55-7.53 (m, 1H), 7.27-7.24 (m, 1H), 7.12 (ddd, $J = 0.8, 8.0, 11.2$ Hz, 1H), 5.30 (dq, $J = 1.2, 6.8$ Hz, 1H), 1.89 (dd, $J = 0.8, 6.8$ Hz, 3H).



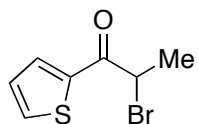
2-Bromo-1-(2-ethylphenyl)propan-1-one. Prepared from 2'-ethylpropiophenone (0.97 g, 6.3 mmol) and bromine (0.32 mL, 6.3 mmol) in Et_2O (12 mL). Solvent system for chromatography: 3:1→2:1 hexanes:dichloromethane. The product was isolated as a yellow oil in 75% yield (1.1 g).

^1H NMR (400 MHz, CDCl_3): δ 7.60-7.58 (m, 1H), 7.47-7.43 (m, 1H), 7.34 (d, $J = 7.6$ Hz, 1H), 7.30-7.26 (m, 1H), 5.20 (q, $J = 6.4$ Hz, 1H), 2.88-2.77 (m, 2H), 1.90 (d, $J = 6.4$ Hz, 3H), 1.27 (t, $J = 7.6$ Hz, 3H);

^{13}C NMR (100 MHz, CDCl_3): δ 197.4, 145.4, 135.8, 132.1, 130.7, 127.7, 125.8, 45.5, 27.1, 20.6, 16.1;

IR (film): 1688, 1444, 1331, 1222, 941, 754 cm^{-1} ;

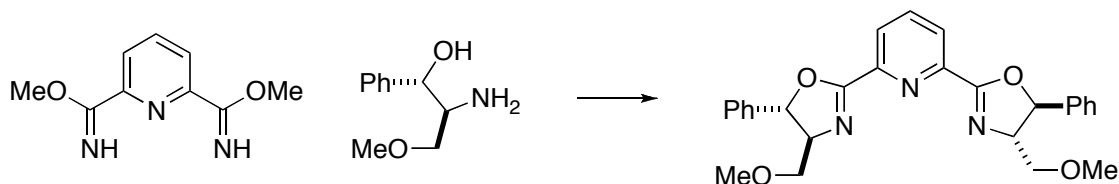
LRMS (EI) for $\text{C}_{11}\text{H}_{13}\text{O}$ (M-Br): calcd 161, found 161.



2-Bromo-1-(thiophen-2-yl)propan-1-one [75815-46-2]. Prepared from 2-propionylthiophene (1.94 g, 13.9 mmol) and bromine (0.71 mL, 13.9 mmol) in Et_2O (20 mL). Solvent system for chromatography: 3:1 hexanes:dichloromethane. The product was isolated as an orange oil in 40% yield (0.88 g).

^1H NMR (400 MHz, CDCl_3): δ 7.85 (dd, $J = 1.0, 4.0$ Hz, 1H), 7.70 (dd, $J = 1.0, 5.2$ Hz, 1H), 7.17 (dd, $J = 4.0, 5.2$ Hz, 1H), 5.15 (q, $J = 6.8$ Hz, 1H), 1.90 (d, $J = 6.8$ Hz, 3H);
 ^{13}C NMR (100 MHz, CDCl_3): δ 187.1, 141.0, 135.2, 133.3, 128.6, 42.7, 20.6;
 IR (film): 1666, 1519, 1413, 1246, 1167, 1065, 855, 723, 648 cm^{-1} ;
 LRMS (EI) for $\text{C}_7\text{H}_8\text{BrOS}$ ($\text{M}+\text{H}$): calcd 219, found 219.

III. Preparation of Ligand 2



2,6-Bis((4S,5S)-4-(methoxymethyl)-5-phenyl-4,5-dihydrooxazol-2-yl)pyridine ((+)-2). A solution of (1S,2S)-(+)-2-amino-3-methoxy-1-phenyl-1-propanol (1.0 g, 5.5 mmol) and 2,6-pyridinedicarboximidic acid, dimethyl ester (531 mg, 2.75 mmol; 0.50 equiv) prepared according to a literature procedure²) in dichloromethane (10 mL) was heated to reflux in a Schlenk tube for two days. The solvent was then removed, and the residue was purified by flash chromatography (2% triethylamine in ethyl acetate), which afforded the product as a white solid in 60% yield (761 mg; not optimized).

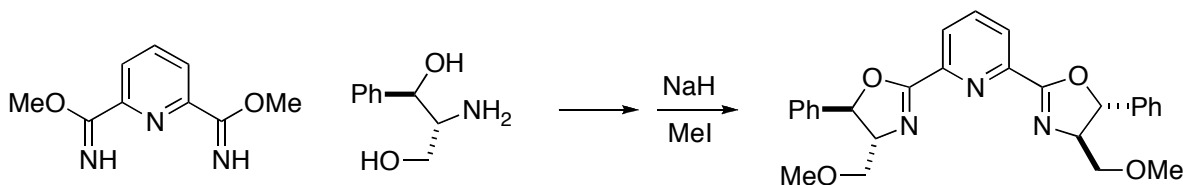
^1H NMR (400 MHz, CDCl_3): δ 8.24 (d, $J = 8.0$ Hz, 2H), 7.92 (t, $J = 8.0$ Hz, 1H), 7.33–7.26 (m, 10H), 5.58 (d, $J = 7.6$ Hz, 2H), 4.42–4.37 (m, 2H), 3.74–3.70 (m, 2H), 3.63–3.59 (m, 2H), 3.42 (s, 6H);

^{13}C NMR (100 MHz, CDCl_3): δ 163.1, 147.2, 140.5, 137.5, 128.9, 128.5, 126.4, 126.2, 84.9, 75.2, 74.3, 59.5;

IR (film): 1645, 1575, 1457, 1385, 1193, 1132, 964, 733, 699 cm^{-1} ;

HRMS (ESI) for $\text{C}_{27}\text{H}_{27}\text{N}_3\text{O}_4$ ($\text{M}+\text{H}$): calcd 458.2074, found 258.2063;

$[\alpha]_D^{22} +90$ (c 1.03, CDCl_3).



2,6-Bis((4R,5R)-4-(methoxymethyl)-5-phenyl-4,5-dihydrooxazol-2-yl)pyridine ((-)-2). A solution of (1R,2R)-2-amino-1-phenyl-1,3-propanediol (2.00 g, 12 mmol) and 2,6-pyridinedicarboximidic acid, dimethyl ester (1.16 g, 6.0 mmol; 0.5 equiv) in dichloromethane (30 mL) was heated to 80 °C in a Schlenk tube for 40 h. The solvent

(2) Müller, P.; Boléa, C. *Helv. Chim. Acta* **2001**, *84*, 1093–1111.

was then removed, and the residue was washed with ethyl acetate to give the pybox diol (1.8 g), which was dissolved in THF (45 mL) and cooled to 0 °C. NaH (351 mg, 14.7 mmol; 3.5 equiv) was added, and the solution was stirred for 1 h. Next, iodomethane (5.2 mL, 83.5 mmol; 20 equiv) was added. The reaction mixture was stirred overnight at room temperature, and then the reaction was quenched with saturated ammonium chloride (10 mL). The mixture was washed with brine (10 mL), dried over sodium sulfate, and concentrated. The resulting residue was passed through a column of silica gel (eluant: 2% triethylamine in ethyl acetate). The residue was recrystallized from ethyl acetate to give 400 mg of the product as a white solid (15% yield; not optimized).

¹H NMR (400 MHz, CDCl₃): δ 8.24 (d, *J* = 8.0 Hz, 2H), 7.92 (t, *J* = 8.0 Hz, 1H), 7.33-7.26 (m, 10H), 5.58 (d, *J* = 7.6 Hz, 2H), 4.42-4.37 (m, 2H), 3.74-3.70 (m, 2H), 3.63-3.59 (m, 2H), 3.42 (s, 6H);

[α]_D²² -95 (*c* 1.01, CDCl₃).

IV. Asymmetric α-Arylations of Ketones

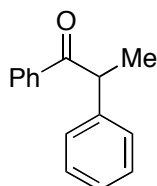
General Procedure A: Asymmetric α-arylation with ArZnI: A solution of the arylmagnesium bromide (1.6 mmol; 1.6 equiv) was added to a solution of ZnI₂ (510 mg, 1.6 mmol; 1.6 equiv) in THF (final concentration of ArZnI = 0.20 M) under argon. The mixture was stirred for 40 min at room temperature (a precipitate is immediately observed), and then it was cooled to -30 °C. NiCl₂·glyme (11.0 mg, 0.050 mmol; 0.050 equiv) and (+)-2 (29.9 mg, 0.065 mmol; 0.065 equiv) were added to an oven-dried 50-mL flask. The flask was purged with argon, and the α-bromoketone (1.0 mmol; 1.0 equiv) was added, followed by glyme (13.5 mL). This solution was allowed to stir at room temperature for 20 min, and then it was cooled to -30 °C. The suspension of ArZnI (6.5 mL, 1.3 mmol; 1.3 equiv) was added dropwise over 3 min, and the reaction mixture was stirred at -30 °C for 4 h. Then, the reaction was quenched with saturated ammonium chloride (10 mL). The reaction mixture was diluted with Et₂O (50 mL), washed with distilled water (10 mL) and brine (10 mL), dried over magnesium sulfate, and concentrated. The product was purified by flash chromatography.

The second run was conducted with (-)-2.

General Procedure B: Asymmetric α-arylation with Ar₂Zn: A solution of ZnCl₂ in Et₂O (1.0 M; 1.3 mL, 1.3 mmol; 1.3 equiv) under argon was diluted with THF (5.2 mL) to provide a solution that was 0.20 M in zinc. A solution of the arylmagnesium bromide (2.6 mmol; 2.6 equiv) was added (if a suspension formed, the mixture was filtered through an acrodisc), and the solution was stirred for 20 min at r.t. Then, the reaction mixture was cooled to -30 °C. NiCl₂·glyme (11.0 mg, 0.050 mmol; 0.050 equiv) and (+)-2 (29.9 mg, 0.065 mmol; 0.065 equiv) were added to an oven-dried 50-mL flask. The flask was purged with argon, and the α-bromoketone (1.00 mmol; 1.00 equiv) was added, followed by glyme (14.5 mL). This solution was allowed to stir at room temperature for

20 min, and then it was cooled to $-30\text{ }^{\circ}\text{C}$. The solution of Ar_2Zn (5.5 mL, 1.1 mmol; 1.1 equiv) was added dropwise over ~ 5 min, and the reaction mixture was stirred at $-30\text{ }^{\circ}\text{C}$ for 90 min. Then, the reaction was quenched with saturated ammonium chloride (10 mL). The reaction mixture was diluted with Et_2O (50 mL), washed with distilled water (10 mL) and brine (10 mL), dried over magnesium sulfate, and concentrated. The product was purified by flash chromatography.

The second run was conducted with (-)-2.



1,2-Diphenylpropan-1-one (Table 2, entry 1). 2-Bromopropiophenone (213 mg, 1.0 mmol) and an arylzinc reagent prepared from phenylmagnesium bromide were used. Solvent system for chromatography: 3:1 \rightarrow 2:1 hexanes:dichloromethane. The product was isolated as a clear, colorless oil.

PhZnI : Run 1, 172 mg (82% yield, 96% ee). Run 2, 189 mg (90% yield, 96% ee).

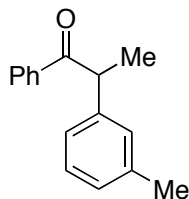
Ph_2Zn (in situ): Run 1, 170 mg (81% yield, 93% ee). Run 2, 178 mg (85% yield, 93% ee).

Ph_2Zn (solid): Run 1, 176 mg (84% yield, 95% ee). Run 2, 191 mg (91% yield, 95% ee).

The ee was determined on an OJ-H column (hexanes:isopropanol 99:1, flow 1.0 mL/min), with enantiomers eluting at 14.7 (minor) and 16.8 (major) min.

^1H NMR (400 MHz, CDCl_3): δ 7.98-7.96 (m, 2H), 7.51-7.47 (m, 1H), 7.41-7.37 (m, 2H), 7.31-7.26 (m, 4H), 7.24-7.20 (m, 1H), 4.71 (q, $J = 6.8$ Hz, 1H), 1.55 (d, $J = 6.8$ Hz, 3H);

$[\alpha]_{\text{D}}^{22} +190$ (c 1.08, CHCl_3); 96% ee, from (-)-2.



1-Phenyl-2-*m*-tolylpropan-1-one (Table 2, entry 3). 2-Bromopropiophenone (213 mg, 1.0 mmol) and an arylzinc iodide reagent prepared from *m*-tolylmagnesium bromide were used. Solvent system for chromatography: 3:1 \rightarrow 2:1 hexanes:dichloromethane. The product was isolated as a yellow oil.

Run 1, 197 mg (88% yield, 95% ee). Run 2, 195 mg (87% yield, 93% ee).

The ee was determined on an OJ-H column (hexanes:isopropanol 99:1, flow 1.0 mL/min), with enantiomers eluting at 12.6 (major) and 13.7 (minor) min.

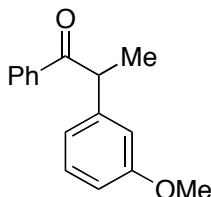
^1H NMR (400 MHz, CDCl_3): δ 7.99-7.97 (m, 2H), 7.49-7.47 (m, 1H), 7.41-7.37 (m, 2H), 7.22-7.18 (m, 1H), 7.12 (br s, 2H), 7.04-7.02 (m, 1H), 4.67 (q, $J = 6.8$ Hz, 1H), 2.32 (s, 3H), 1.54 (d, $J = 6.8$ Hz, 3H);

^{13}C NMR (100 MHz, CDCl_3): δ 200.6, 141.6, 138.9, 136.7, 133.0, 129.04, 129.98, 128.7, 128.5, 127.9, 125.1, 48.0, 21.6, 19.8;

IR (film): 1682, 1597, 1449, 1208, 95.7, 734, 693 cm^{-1} ;

LRMS (EI) for $\text{C}_{16}\text{H}_{17}\text{O}$ ($\text{M}+\text{H}$): calcd 225, found 225;

$[\alpha]_{\text{D}}^{22} +182$ (c 1.13, CHCl_3); 93% ee, from (-)-2.



2-(3-Methoxyphenyl)-1-phenylpropan-1-one (Table 2, entry 4). 2-

Bromopropiophenone (213 mg, 1.0 mmol) and a diarylzinc reagent prepared from 3-methoxyphenylmagnesium bromide were used. Solvent system for chromatography: 1:1 hexanes:dichloromethane. The product was isolated as a clear, colorless oil.

Ar_2Zn (in situ): Run 1, 206 mg (86% yield, 96% ee). Run 2, 211 mg (88% yield, 93% ee).

The ee was determined on an OD-H column (hexanes:isopropanol 99:1, flow 1.0 mL/min), with enantiomers eluting at 7.3 (minor) and 8.8 (major) min.

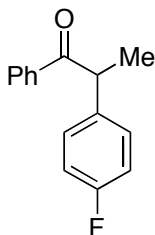
^1H NMR (400 MHz, CDCl_3): δ 7.95-7.93 (m, 2H), 7.46-7.42 (m, 1H), 7.37-7.33 (m, 2H), 7.21-7.17 (m, 1H), 6.87-6.85 (m, 1H), 6.82-6.81 (m, 1H), 6.73-6.71 (m, 1H), 4.64 (q, $J = 6.8$ Hz, 1H), 3.73 (s, 3H), 1.51 (d, $J = 6.8$ Hz, 3H);

^{13}C NMR (100 MHz, CDCl_3): δ 200.3, 160.2, 143.2, 136.7, 133.0, 130.2, 129.0, 128.7, 120.4, 113.7, 112.3, 55.4, 48.1, 19.7;

IR (film): 1682, 1598, 1485, 1448, 1264, 1045, 957, 693 cm^{-1} ;

LRMS (EI) for $\text{C}_{16}\text{H}_{17}\text{O}_2$ ($\text{M}+\text{H}$): calcd 241, found 241;

$[\alpha]_{\text{D}}^{22} +166$ (c 1.04, CHCl_3); 93% ee, from (-)-2.



2-(4-Fluorophenyl)-1-phenylpropan-1-one (Table 2, entry 5). 2-

Bromopropiophenone (213 mg, 1.0 mmol) and an arylzinc iodide reagent prepared from *p*-fluorophenylmagnesium bromide were used. Solvent system for chromatography: 3:1→2:1 hexanes:dichloromethane. The product was isolated as a yellow oil.

Run 1, 162 mg (71% yield, 96% ee). Run 2, 173 mg (76% yield, 96% ee).

The ee was determined on an OJ-H column (hexanes:isopropanol 99:1, flow 1.0 mL/min), with enantiomers eluting at 12.5 (major) and 14.2 (minor) min.

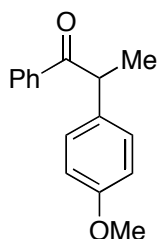
^1H NMR (400 MHz, CDCl_3): δ 7.96-7.94 (m, 2H), 7.53-7.48 (m, 1H), 7.42-7.39 (m, 2H), 7.28-7.25 (m, 2H), 7.02-6.97 (m, 2H), 4.71 (q, $J = 6.8$ Hz, 1H), 1.54 (d, $J = 6.8$ Hz, 3H);

^{13}C NMR (100 MHz, CDCl_3): δ 200.4, 162.0, 137.3, 136.4, 133.1, 129.5, 128.9, 128.8, 116.0, 47.1, 19.8;

IR (film): 1684, 1507, 1448, 1223, 840, 738 cm^{-1} ;

LRMS (EI) for $\text{C}_{15}\text{H}_{14}\text{FO}$ (M+H): calcd 229, found 229;

$[\alpha]_D^{22} +159$ (c 1.02, CHCl_3); 96% ee, from (-)-2.



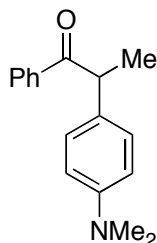
2-(4-Methoxyphenyl)-1-phenylpropan-1-one (Table 2, entry 6) [(S) enantiomer: 35572-39-5]. 2-Bromopropiophenone (213 mg, 1.0 mmol) and an arylzinc iodide reagent prepared from 4-methoxyphenylmagnesium bromide were used. Solvent system for chromatography: 1:1 hexanes:dichloromethane. The product was isolated as a yellow oil.

Run 1, 230 mg (96% yield, 96% ee). Run 2, 214 mg (89% yield, 95% ee).

The ee was determined on an AD-H column (hexanes:isopropanol 99:1, flow 1.0 mL/min), with enantiomers eluting at 11.2 (minor) and 14.4 (major) min.

^1H NMR (400 MHz, CDCl_3): δ 7.94-7.91 (m, 2H), 7.47-7.43 (m, 1H), 7.37-7.33 (m, 2H), 7.24-7.15 (m, 2H), 6.83-6.79 (m, 2H), 4.65 (q, $J = 6.8$ Hz, 1H), 3.76 (s, 3H), 1.51 (d, $J = 6.8$ Hz, 3H);

$[\alpha]_D^{22} +161$ (c 1.00, CHCl_3); 95% ee, from (-)-2.



2-(4-(Dimethylamino)phenyl)-1-phenylpropan-1-one (Table 2, entry 7) [740843-43-0]. 2-Bromopropiophenone (213 mg, 1.0 mmol) and an arylzinc iodide reagent prepared from *p*-(*N,N*-dimethylamino)phenylmagnesium bromide were used. Solvent system for chromatography: 49:49:2 hexanes:dichloromethane:triethylamine. The product was isolated as a white solid.

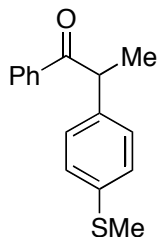
Run 1, 218 mg (86% yield, 93% ee). Run 2, 213 mg (84% yield, 92% ee).

The ee was determined on an AD-H column (hexanes:isopropanol 95:5, flow 1.0 mL/min), with enantiomers eluting at 7.5 (minor) and 10.9 (major) min.

^1H NMR (400 MHz, CDCl_3): δ 8.03-8.01 (m, 2H), 7.47-7.46 (m, 1H), 7.41-7.37 (m, 2H), 7.21-7.19 (m, 2H), 6.71-6.69 (m, 2H), 4.65 (q, $J = 6.8$ Hz, 1H), 2.91 (s, 6H), 1.55 (d, $J = 6.8$ Hz, 3H);

IR (film): 1684, 1653, 1559, 1521, 1507, 1228 cm^{-1} ;

$[\alpha]_{\text{D}}^{22} -162$ (c 0.98, CHCl_3); 93% ee, from (+)-2.



2-(4-(Methylthio)phenyl)-1-phenylpropan-1-one (Table 2, entry 8). 2-

Bromopropiophenone (213 mg, 1.0 mmol) and an arylzinc iodide reagent prepared from 4-(methylthio)phenylmagnesium bromide were used. Solvent system for chromatography: 1:1 hexanes:dichloromethane. The product was isolated as a white solid.

Run 1, 182 mg (71% yield, 96% ee). Run 2, 182 mg (71% yield, 95% ee).

The ee was determined on an AS-H column (hexanes:isopropanol 99:1, flow 1.0 mL/min), with enantiomers eluting at 7.7 (minor) and 8.9 (major) min.

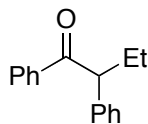
^1H NMR (400 MHz, CDCl_3): δ 7.96-7.94 (m, 2H), 7.51-7.47 (m, 1H), 7.41-7.37 (m, 2H), 7.23-7.17 (m, 4H), 4.66 (q, $J = 6.8$ Hz, 1H), 2.44 (s, 3H), 1.52 (d, $J = 6.8$ Hz, 3H);

^{13}C NMR (100 MHz, CDCl_3): δ 200.4, 138.4, 137.1, 136.6, 133.1, 128.9, 128.7, 128.5, 127.3, 47.5, 19.6, 16.0;

IR (film): 2927, 2361, 1653, 1457, 1131, 971, 699 cm^{-1} ;

LRMS (EI) for $\text{C}_{16}\text{H}_{17}\text{OS}$ ($\text{M}+\text{H}$): calcd 257, found 257;

$[\alpha]_{\text{D}}^{22} +125$ (c 1.00, CHCl_3); 95% ee, from (-)-2.



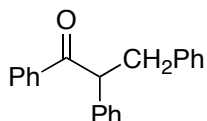
1,2-Diphenylbutan-1-one (Table 3, entry 1) [(S) enantiomer: 175274-19-8; (R) enantiomer: 175274-18-7]. 2-Bromo-1-phenylbutan-1-one (227 mg, 1.0 mmol) and an arylzinc reagent prepared from phenylmagnesium bromide were used. Solvent system for chromatography: 3:1→2:1 hexanes:dichloromethane. The product was isolated as a white solid.

Run 1, 186 mg (83% yield, 94% ee). Run 2, 197 mg (88% yield, 93% ee).

The ee was determined on an OD-H column (hexanes:isopropanol 99:1, flow 1.0 mL/min), with enantiomers eluting at 5.2 (minor) and 5.8 (major) min.

^1H NMR (400 MHz, CDCl_3): δ 8.00-7.98 (m, 2H), 7.50-7.47 (m, 1H), 7.42-7.38 (m, 2H), 7.35-7.30 (m, 4H), 7.24-7.22 (m, 1H), 4.47 (t, $J = 7.0$ Hz, 1H), 2.26-2.19 (m, 1H), 1.92-1.85 (m, 1H), 0.93 (t, $J = 7.4$ Hz, 3H);

$[\alpha]_{\text{D}}^{22} +155$ (c 1.01, CHCl_3); 88% ee, from (-)-2.



1,2,3-Triphenylpropan-1-one (Table 3, entry 2). 2-Bromo-1,3-diphenylpropan-1-one (289 mg, 1.0 mmol) and an arylzinc iodide reagent prepared from phenylmagnesium bromide were used. Solvent system for chromatography: 3:1→2:1 hexanes:dichloromethane. The product was isolated as a white solid.

Run 1, 206 mg (72% yield, 95% ee). Run 2, 229 mg (80% yield, 94% ee).

The ee was determined on an OJ-H column (hexanes:isopropanol 99:1, flow 1.0 mL/min), with enantiomers eluting at 17.2 (major) and 20.0 (minor) min.

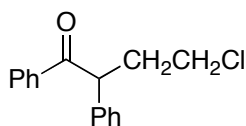
^1H NMR (400 MHz, CDCl_3): δ 7.93-7.89 (m, 2H), 7.48-7.44 (m, 1H), 7.38-7.34 (m, 2H), 7.30-7.19 (m, 7H), 7.17-7.13 (m, 1H), 7.11-7.08 (m, 2H), 4.83 (t, $J = 7.2$ Hz, 1H), 3.58 (dd, $J = 7.2, 13.6$ Hz, 1H), 3.08 (dd, $J = 7.2, 13.6$ Hz, 1H);

^{13}C NMR (100 MHz, CDCl_3): δ 199.4, 140.0, 139.3, 136.9, 133.1, 129.3, 129.1, 128.9, 128.7, 128.5, 128.4, 127.4, 126.3, 56.1, 40.3;

IR (film): 1675, 1596, 1447, 1244, 950, 757, 736, 695 cm^{-1} ;

LRMS (EI) for $\text{C}_{21}\text{H}_{18}\text{O}$: calcd 286, found 286;

$[\alpha]_{\text{D}}^{22} +215$ (c 1.00, CHCl_3); 94% ee, from (-)-2.



4-Chloro-1,2-diphenylbutan-1-one (Table 3, entry 3). 2-Bromo-4-chloro-1-phenylbutan-1-one (262 mg, 1.0 mmol) and an arylzinc reagent prepared from phenylmagnesium bromide were used. The reaction was run at -20 °C. Solvent system for chromatography: 3:1→2:1 hexanes:dichloromethane. The product was isolated as a yellow oil.

Run 1, 225 mg (87% yield, 93% ee). Run 2, 240 mg (93% yield, 91% ee).

The ee was determined on an OJ-H column (hexanes:isopropanol 99:1, flow 1.0 mL/min), with enantiomers eluting at 16.0 (minor) and 16.9 (major) min.

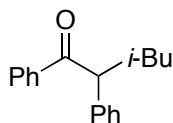
^1H NMR (400 MHz, CDCl_3): δ 8.00-7.97 (m, 2H), 7.52-7.49 (m, 1H), 7.42-7.38 (m, 2H), 7.34-7.31 (m, 4H), 7.26-7.22 (m, 1H), 4.47 (dd, $J = 6.8, 7.6$ Hz, 1H), 3.63-3.58 (m, 1H), 3.47-3.41 (m, 1H), 2.64-2.56 (m, 1H), 2.35-2.27 (m, 1H);

^{13}C NMR (100 MHz, CDCl_3): δ 199.2, 138.3, 136.5, 133.3, 129.4, 129.0, 128.8, 128.5, 127.7, 50.3, 43.3, 36.2;

IR (film): 1684, 1653, 1559, 1540, 1507, 1448, 756, 698 cm^{-1} ;

LRMS (EI) for $\text{C}_{16}\text{H}_{15}\text{ClO}$: calcd 258, found 258;

$[\alpha]_{\text{D}}^{22} +233$ (c 1.02, CHCl_3); 91% ee, from (-)-2.



4-Methyl-1,2-diphenylpentan-1-one (Table 3, entry 4). 2-Bromo-4-methyl-1-phenylpentan-1-one (191 mg, 0.75 mmol) and an arylzinc reagent prepared from phenylmagnesium bromide were used. Solvent system for chromatography: 3:1→2:1 hexanes:dichloromethane. The product was isolated as a white solid.

Ph_2Zn (in situ): Run 1, 168 mg (89% yield, 94% ee). Run 2, 166 mg (88% yield, 95% ee).

The ee was determined on an IA-H column (hexanes:isopropanol 99:1, flow 1.0 mL/min), with enantiomers eluting at 5.2 (minor) and 6.2 (major) min.

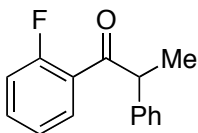
^1H NMR (400 MHz, CDCl_3): δ 7.99 (d, $J = 7.2$ Hz, 2H), 7.50 (t, $J = 7.2$ Hz, 1H), 7.43-7.39 (m, 2H), 7.34-7.27 (m, 4H), 7.23-7.19 (m, 1H), 4.69 (t, $J = 7.2$ Hz, 1H), 2.13-2.069 (m, 1H), 1.75 (q, $J = 6.8$ Hz, 1H), 1.51 (s, $J = 6.8$ Hz, 1H), 0.96 (d, $J = 6.8$ Hz, 3H), 0.91 (d, $J = 6.8$ Hz, 3H);

^{13}C NMR (100 MHz, CDCl_3): δ 200.4, 140.0, 137.1, 133.0, 129.1, 128.8, 128.7, 128.4, 127.1, 51.5, 43.2, 26.0, 23.1, 22.7;

IR (film): 1682, 1597, 1448, 1208, 757, 698 cm^{-1} ;

LRMS (EI) for $\text{C}_{18}\text{H}_{21}\text{O}$ (M+H): calcd 253, found 253;

$[\alpha]_{\text{D}}^{22} +144$ (c 0.98, CHCl_3); 95% ee, from (-)-2.



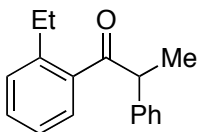
1-(2-Fluorophenyl)-2-phenylpropan-1-one (Table 3, entry 6). 2-Bromo-1-(2-fluorophenyl)propan-1-one (231 mg, 1.0 mmol) and an arylzinc reagent prepared from phenylmagnesium bromide were used. Solvent system for chromatography: 3:1 hexanes:dichloromethane. The product was isolated as a yellow oil.

Run 1, 182 mg (80% yield, 73% ee). Run 2, 180 mg (79% yield, 70% ee).

The ee was determined on an OJ-H column (hexanes:isopropanol 99:1, flow 1.0 mL/min), with enantiomers eluting at 12.5 (minor) and 16.3 (major) min.

^1H NMR (400 MHz, CDCl_3): δ 7.75 (td, $J = 2.0, 7.6$ Hz, 1H), 7.43-7.37 (m, 1H), 7.29-7.27 (m, 4H), 7.22-7.18 (m, 1H), 7.14 (td, $J = 1.2, 7.6$ Hz, 1H), 7.03 (ddd, $J = 1.2, 8.4, 11.2$ Hz, 1H), 4.65 (m, 1H), 1.56 (dd, $J = 0.8, 6.8$ Hz, 3H);

^{13}C NMR (100 MHz, CDCl_3): δ 199.8 (d, $J = 16$ Hz), 161.1 (d, $J = 1000$ Hz), 140.7, 134.2 (d, $J = 36$ Hz), 131.2 (d, $J = 12$ Hz), 128.9, 128.4, 127.2, 126.3 (d, $J = 52$ Hz), 124.6 (d, $J = 16$ Hz), 116.7 (d, $J = 96$ Hz), 52.1 (d, $J = 28$ Hz), 19.1;
IR (film): 1687, 1609, 1480, 1450, 1273, 1212, 762, 700 cm^{-1} ;
LRMS (EI) for $\text{C}_{15}\text{H}_{13}\text{FO}$: calcd 228, found 228;
 $[\alpha]_{\text{D}}^{22} +175$ (c 1.04, CHCl_3); 70% ee, from (-)-2.



1-(2-Ethylphenyl)-2-phenylpropan-1-one (Table 3, entry 7). 2-Bromo-1-(2-ethylphenyl)propan-1-one (241 mg, 1.0 mmol) and an arylzinc iodide reagent prepared from phenylmagnesium bromide were used. The reaction was run at -20 $^{\circ}\text{C}$, with a large stir bar. Solvent system for chromatography: 3:1 \rightarrow 2:1 hexanes:dichloromethane. The product was isolated as a yellow oil.

Run 1, 195 mg (82% yield, 75% ee). Run 2, 181 mg (76% yield, 70% ee).

The ee was determined on an OJ-H column (hexanes:isopropanol 99:1, flow 1.0 mL/min), with enantiomers eluting at 11.6 (major) and 20.1 (minor) min.

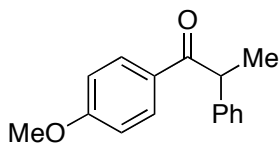
^1H NMR (400 MHz, CDCl_3): δ 7.54 (dd, $J = 1.2, 7.6$ Hz, 1H), 7.34-7.21 (m, 8H), 4.58 (q, $J = 6.8$ Hz, 1H), 2.69-2.59 (m, 2H), 1.63 (d, $J = 7.2$ Hz, 3H), 1.17 (t, $J = 7.6$ Hz, 3H);

^{13}C NMR (100 MHz, CDCl_3): δ 205.3, 144.0, 140.5, 138.9, 131.0, 130.3, 129.0, 128.3, 127.8, 127.2, 125.5, 51.3, 26.9, 18.7, 16.2;

IR (film): 1687, 1600, 1453, 1250, 943, 756, 700 cm^{-1} ;

LRMS (EI) for $\text{C}_{17}\text{H}_{18}\text{O}$: calcd 238, found 238;

$[\alpha]_{\text{D}}^{22} -79$ (c 1.03, CHCl_3); 71% ee, from (+)-2.



1-(4-Methoxyphenyl)-2-phenylpropan-1-one (Table 3, entry 8) [(S) enantiomer: 36065-28-8 ; (R) enantiomer: 28968-16-3]. 2-Bromo-1-(4-methoxyphenyl)propan-1-one (243 mg, 1.0 mmol) and an arylzinc iodide reagent prepared from phenylmagnesium bromide were used. Solvent system for chromatography: 1:1 dichloromethane:hexanes. The product was isolated as a white solid.

Run 1, 206 mg (86% yield, 97% ee). Run 2, 223 mg (93% yield, 95% ee).

The ee was determined on an AS-H column (hexanes:isopropanol 99:1, flow 1.0 mL/min), with enantiomers eluting at 9.8 (minor) and 11.1 (major) min.

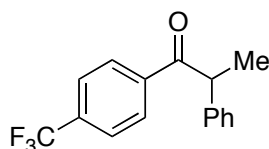
^1H NMR (400 MHz, CDCl_3): δ 7.95-7.91 (m, 2H), 7.27-7.26 (m, 4H), 7.19-7.16 (m, 1H), 6.86 (d, $J = 8.8$ Hz, 2H), 4.67 (q, $J = 6.8$ Hz, 1H), 3.80 (s, 3H), 1.54 (d, $J = 6.8$ Hz, 3H);

^{13}C NMR (100 MHz, CDCl_3): δ 199.1, 163.4, 142.1, 131.3, 129.6, 129.1, 127.9, 127.0, 113.9, 55.6, 47.7, 19.8;

IR (film): 1674, 1600, 1510, 1251, 1170, 1029, 701 cm^{-1} ;

LRMS (EI) for $\text{C}_{16}\text{H}_{17}\text{O}_2$ (M+H): calcd 241, found 241;

$[\alpha]_{\text{D}}^{22} +117$ (c 1.03, CHCl_3); 95% ee, from (-)-2.



2-Phenyl-1-(4-(trifluoromethyl)phenyl)propan-1-one (Table 3, entry 9). 2-Bromo-1-(4-(trifluoromethyl)phenyl)propan-1-one (281 mg, 1.0 mmol) and an arylzinc reagent prepared from phenylmagnesium bromide were used. Solvent system for chromatography: 3:1→2:1 hexanes:dichloromethane. The product was isolated as a white solid.

PhZnI: Run 1, 203 mg (73% yield, 87% ee). Run 2, 217 mg (78% yield, 86% ee).

Ph_2Zn (in situ): Run 1, 220 mg (79% yield, 89% ee). Run 2, 234 mg (84% yield, 88% ee).

The ee was determined on an OJ-H column (hexanes:isopropanol 99:1, flow 1.0 mL/min), with enantiomers eluting at 7.1 (minor) and 8.3 (major) min.

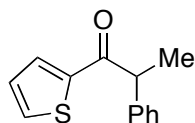
^1H NMR (400 MHz, CDCl_3): δ 8.04 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H), 7.28-7.21 (m, 5H), 4.67 (q, J = 6.8 Hz, 1H), 1.56 (d, J = 6.8 Hz, 3H);

^{13}C NMR (100 MHz, CDCl_3): δ 199.4, 141.0, 139.4, 134.2 (q, J = 128 Hz), 129.4, 129.3, 127.9, 127.4, 125.7 (q, J = 16 Hz), 123.8 (q, J = 1084 Hz), 48.7, 19.6;

IR (film): 1690, 1409, 1323, 1170, 1130, 1067, 700 cm^{-1} ;

LRMS (EI) for $\text{C}_{16}\text{H}_{13}\text{F}_3\text{O}$: calcd 278, found 278;

$[\alpha]_{\text{D}}^{22} +145$ (c 1.05, CHCl_3); 86% ee, from (-)-2.



2-Phenyl-1-(thiophen-2-yl)propan-1-one (Table 3, entry 10). 2-Bromo-1-(thiophen-2-yl)propan-1-one (219 mg, 1.0 mmol) and an arylzinc reagent prepared from phenylmagnesium bromide were used. The reaction was run for six hours. Solvent system for chromatography: 3:1→2:1 hexanes:dichloromethane. The product was isolated as a white solid.

Run 1, 171 mg (79% yield, 95% ee). Run 2, 179 mg (83% yield, 96% ee).

The ee was determined on an OJ-H column (hexanes:isopropanol 99:1, flow 1.0 mL/min), with enantiomers eluting at 24.5 (minor) and 37.0 (major) min.

^1H NMR (400 MHz, CDCl_3): δ 7.68 (d, $J = 3.6$ Hz, 1H), 7.57 (dd, $J = 0.8, 4.8$ Hz, 1H), 7.35-7.30 (m, 4H), 7.27-7.22 (m, 1H), 7.05 (dd, $J = 4.0, 4.4$ Hz, 1H), 4.52 (s, $J = 6.8$ Hz, 1H), 1.55 (d, $J = 6.8$ Hz, 3H);

^{13}C NMR (100 MHz, CDCl_3): δ 193.5, 143.9, 141.5, 133.8, 132.6, 129.1, 128.2, 127.9, 127.3, 49.5, 19.4;

IR (film): 1661, 1414, 1323, 1235, 856, 699 cm^{-1} ;

LRMS (EI) for $\text{C}_{13}\text{H}_{13}\text{OS}$ (M+H): calcd 217, found 217;

$[\alpha]_{\text{D}}^{22} +161$ (c 1.00, CHCl_3); 96% ee, from (-)-2.

Gram-scale asymmetric α -arylation of ketones: Negishi reaction of 2-bromopropiophenone with phenylzinc iodide. Because the reaction mixture is heterogeneous, we decided to determine if General Procedure A can be applied without modification to a cross-coupling that is carried out on a larger scale. In a gram-scale experiment, we found that the ee remains the same, but that the reaction is much slower. However, if the cross-coupling is conducted at -10 $^\circ\text{C}$, the desired product is obtained in 93% ee and 81% yield.

V. Assignment of Absolute Configuration

The optical rotations were measured of the products generated in the presence of (-)-2.

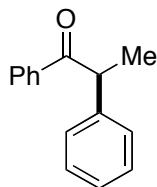


Table 2, entry 1.

$[\alpha]_{\text{D}}^{22} +190$ (c 1.08, CHCl_3); 96% ee, from (-)-2. Lit.³ $[\alpha]_{\text{D}}^{19} +196$ (c 1.10, CHCl_3).

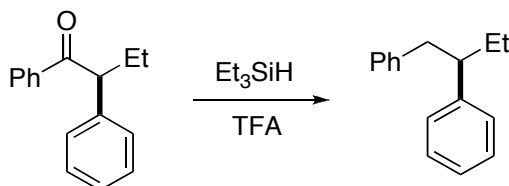


Table 3, entry 1.

(3) Shionhara, T.; Suzuki, K. *Synthesis* **2003**, 141–146.

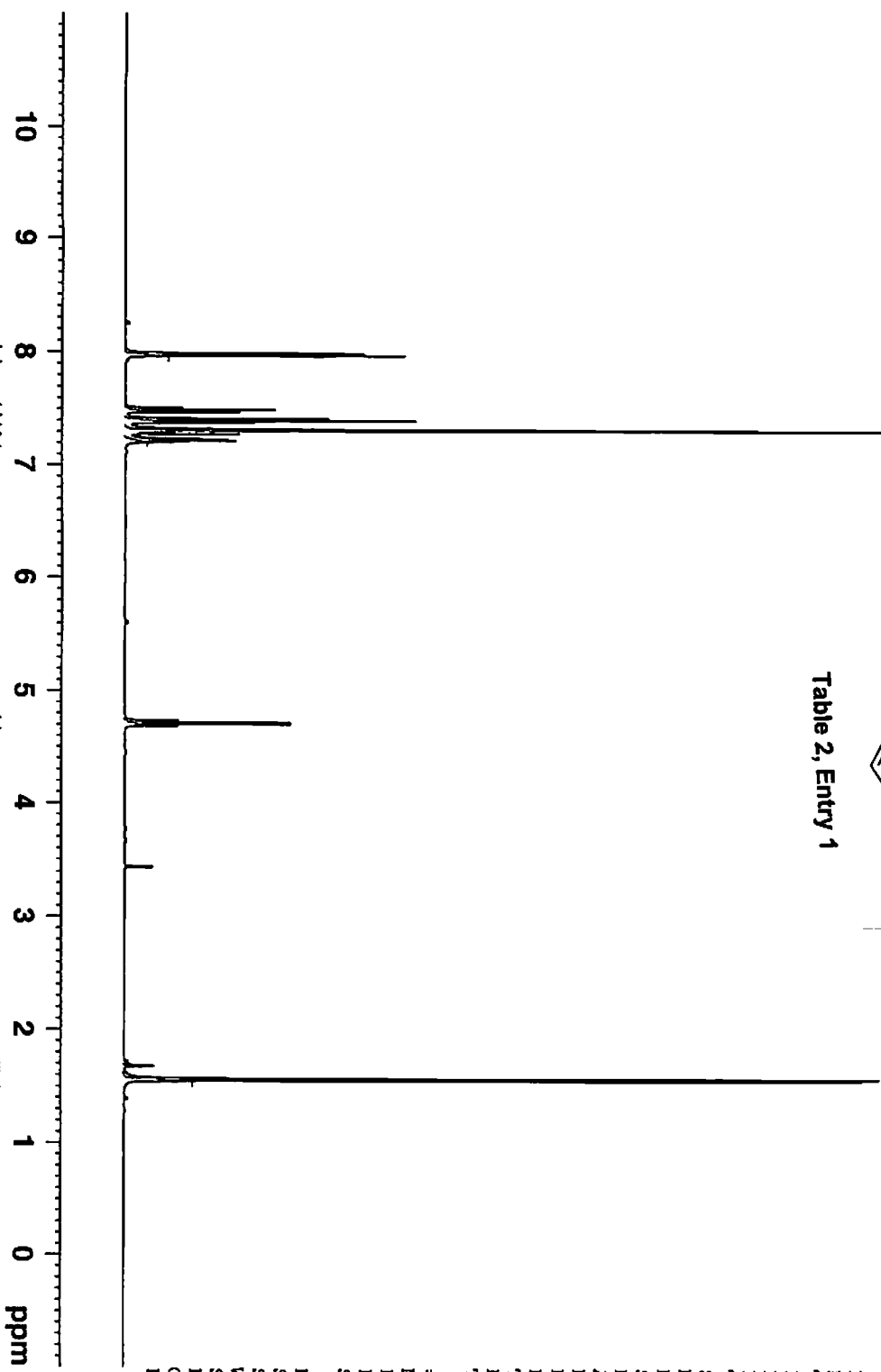
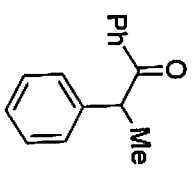
$[\alpha]_{\text{D}}^{22} -75$ (*c* 1.01, CHCl_3); 94% ee, from (-)-**2**. Lit.⁴ $[\alpha]_{\text{D}}^{20} -102$ (*c* 1, CHCl_3).

(4) Ruano, J. L. G.; Aranda, M. T.; Puente, M. *Tetrahedron* **2005**, *61*, 10099–10104.



Current Data Parameters
NAME II-297
EXPNO 1
PROCNO 1

Table 2, Entry 1



F2 - Acquisition Parameters
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Time 16.35
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SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 228.1
DW 60.400 usec
DE 6.00 usec
TE 293.2 K
D1 1.00000000 sec
TD0 1

==== CHANNEL f1 =====
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 65536
SF 400.1300053 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1.00
0.50
1.04
2.02
0.52

0.50

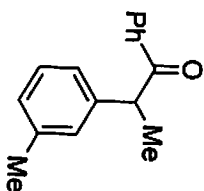
0.09
1.57

10
9
8
7
6
5
4
3
2
1
0 ppm



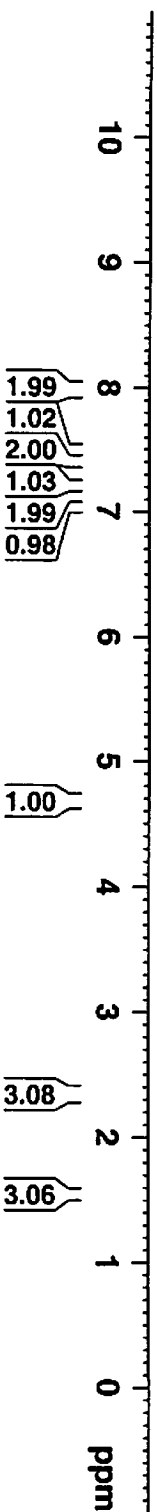
Current Data Parameters
NAME II-289
EXPNO 1
PROCNO 1

Table 2, Entry 3



F2 - Acquisition Parameters
Date_ 20070619
Time 20.07
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 143.7
DW 60.400 usec
DE 6.00 usec
TE 293.2 K
D1 1.00000000 sec
TD0 1

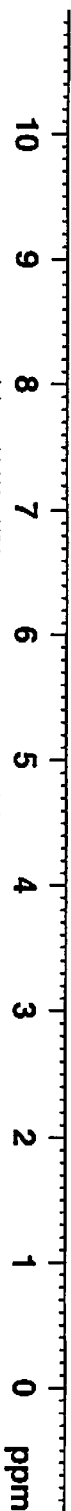
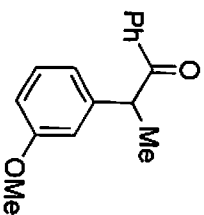
==== CHANNEL f1 =====
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 65536
SF 400.1300659 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00





Current Data Parameters
NAME II-284
EXPNO 3
PROCNO 1

Table 2, Entry 4



F2 - Acquisition Parameters
Date_ 20070615
Time 12.54
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 45.3
DW 60.400 usec
DE 6.00 usec
TE 293.2 K
D1 1.0000000 sec
TDO 1

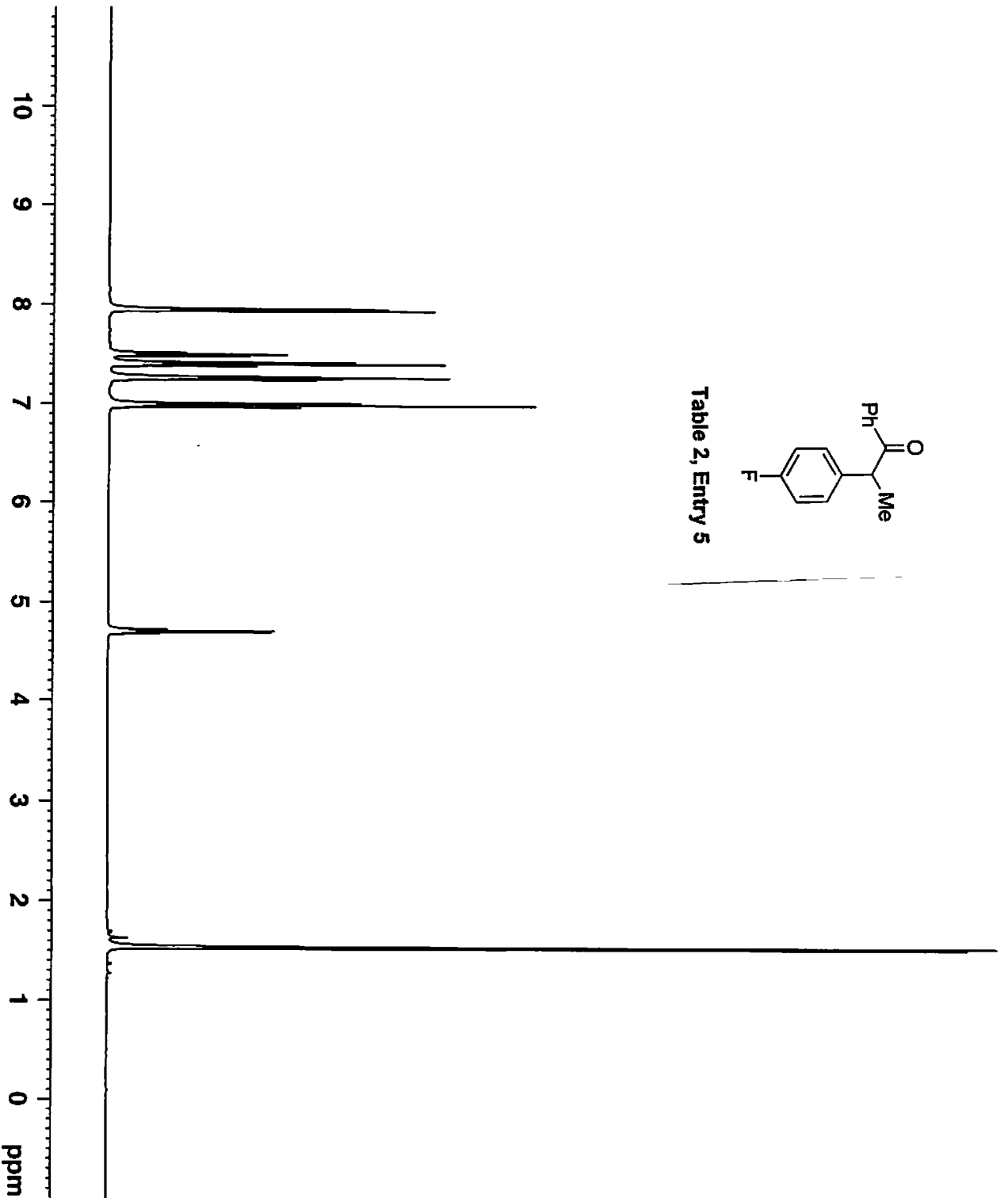
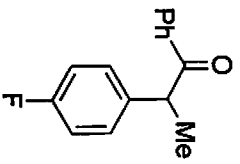
==== CHANNEL f1 =====
NUC1 1H
P1 15.07 usec
PL1 0.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 65536
SF 400.1300212 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
NAME III-017
EXPNO 1
PROCNO 1

Table 2, Entry 5



F2 - Acquisition Parameters
Date_ 20070706
Time 13.34
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 228.1
DW 60.400 usec
DE 6.00 usec
TE 294.2 K
D1 1.00000000 sec
TD0 1

==== CHANNEL f1 =====
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 65536
SF 400.1300057 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

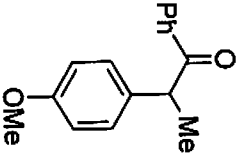
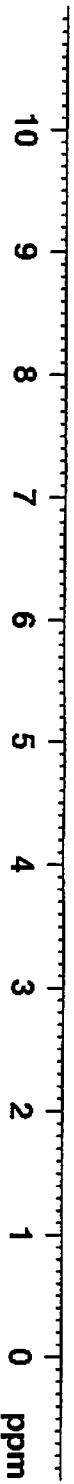


Table 2, Entry 6



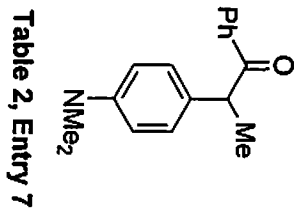
Current Data Parameters
NAME III-072
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070905
Time 9.51
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 11
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 128
DW 60.400 usec
DE 6.00 usec
TE 293.2 K
D1 1.00000000 sec
TD0 1

==== CHANNEL f1 =====
NUC1 1H
P1 15.07 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 65536
SF 400.1300059 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
NAME II-276
EXPNO 4
PROCNO 1

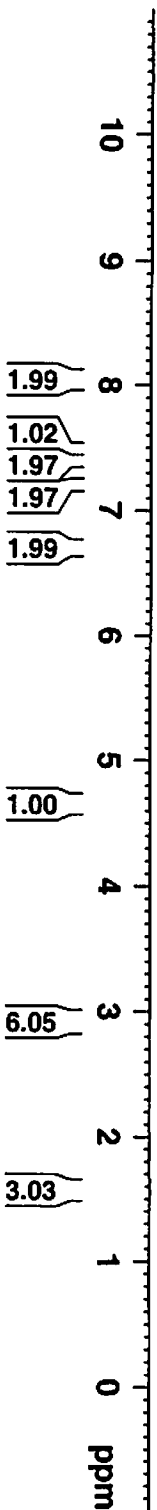


F2 - Acquisition Parameters
Date_ 20070607
Time 16.41

INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl₃
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 35.9
DW 60.400 usec
DE 6.00 usec
TE 294.2 K
D1 1.00000000 sec
TD0 1

==== CHANNEL f1 =====
NUC1 1H
P1 15.07 usec
PL1 0.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 65536
SF 400.1300065 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00





Current Data Parameters
NAME II-280
EXPNO 3
PROCNO 1

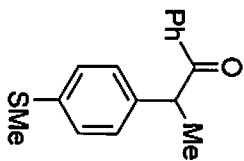
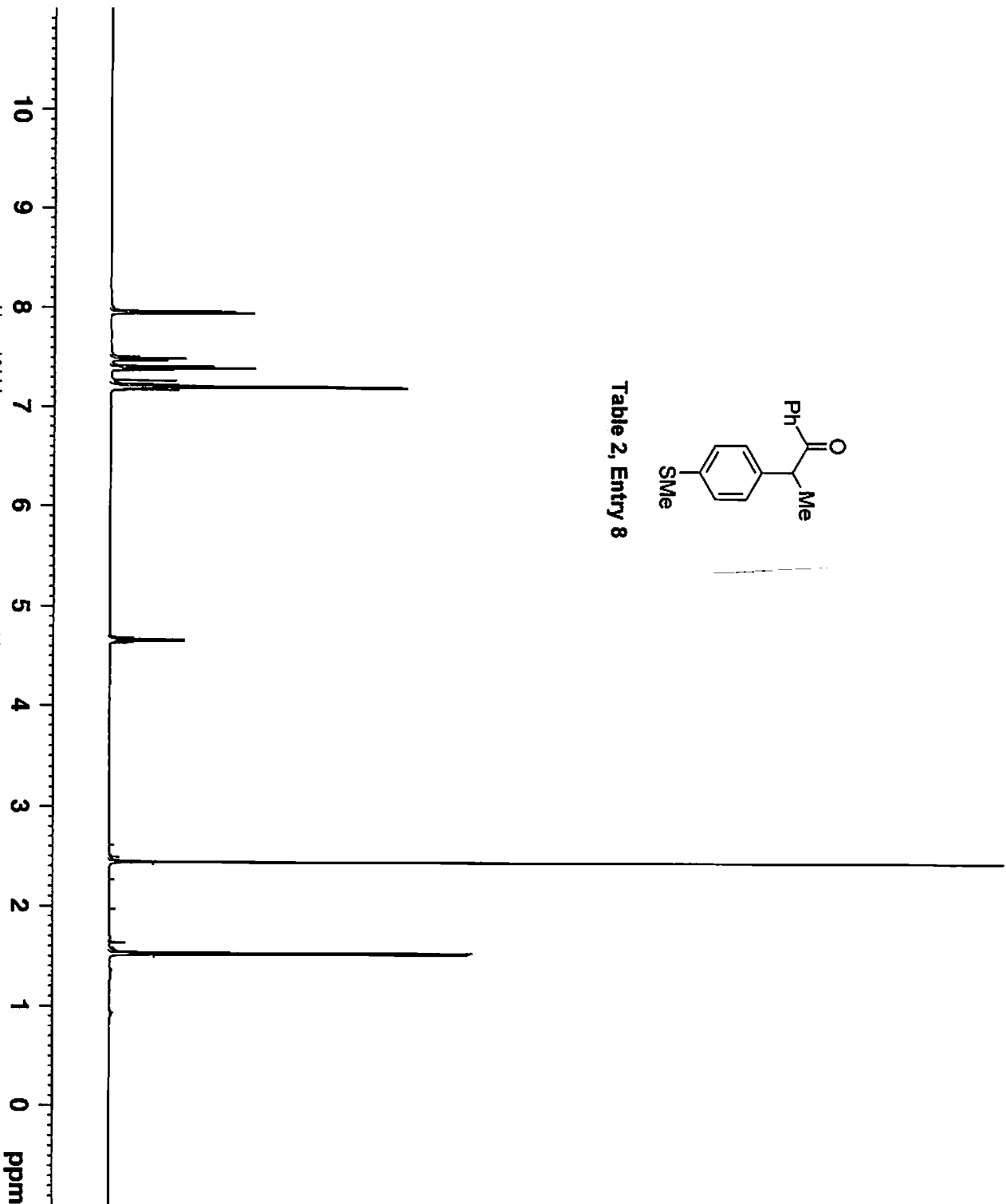


Table 2, Entry 8



F2 - Acquisition Parameters
Date_ 20070606
Time 11.17
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 128
DW 60.400 usec
DE 6.00 usec
TE 293.2 K
D1 1.0000000 sec
TD0 1

==== CHANNEL f1 =====
NUC1 1H
P1 15.07 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 65536
SF 400.1300060 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

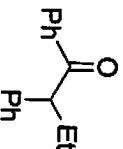
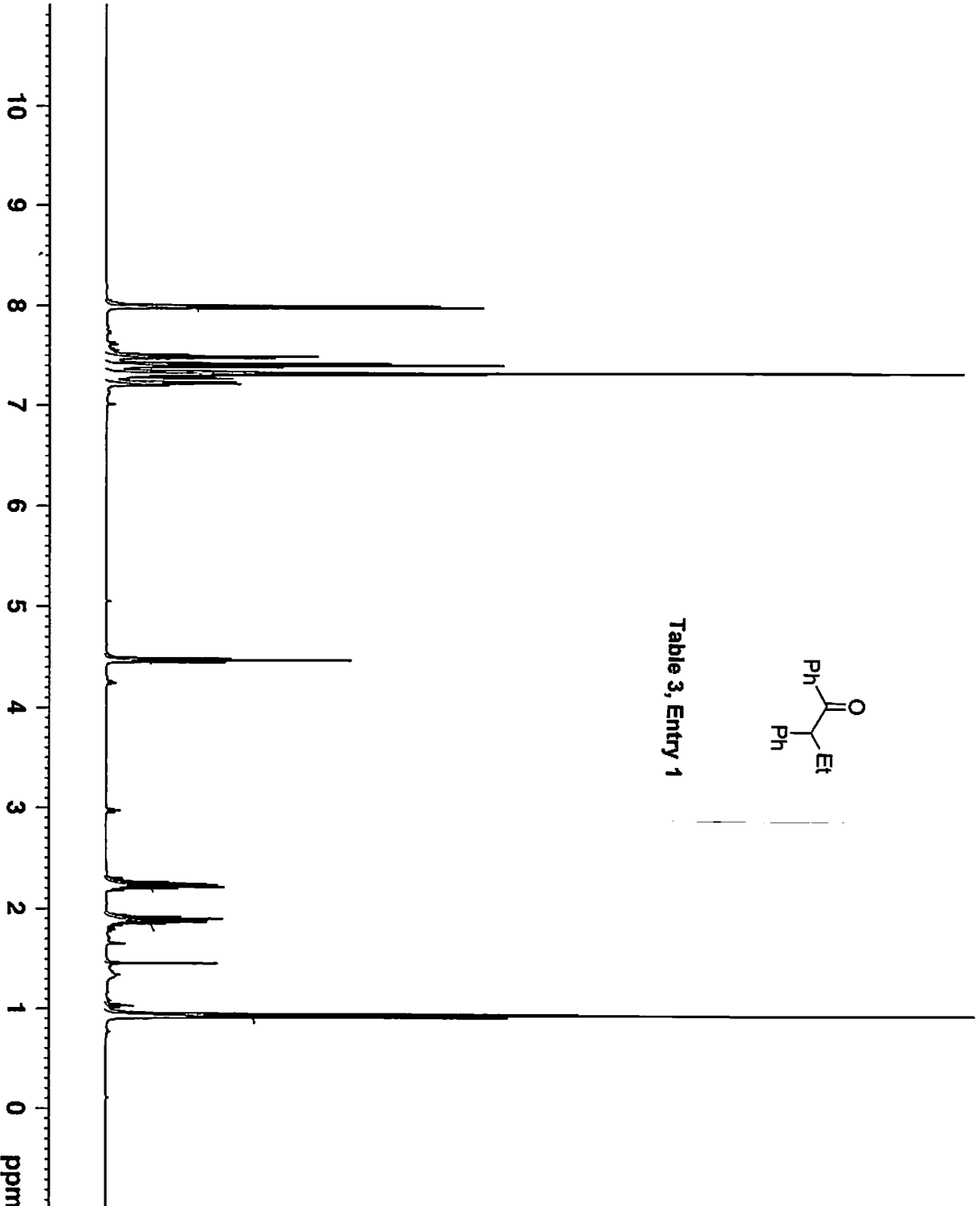


Table 3, Entry 1



Current Data Parameters
NAME 11-287
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070617
Time 8.24

INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2

SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 80.6
DW 60.400 usec
DE 6.00 usec
TE 293.2 K
D1 1.0000000 sec
TD0 1

==== CHANNEL f1 =====
NUC1 1H
P1 15.07 usec
PL1 0.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 65536
SF 400.1300053 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

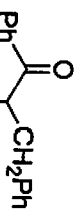
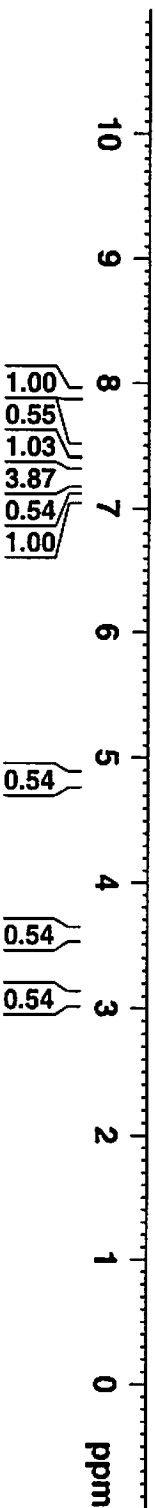


Table 3, Entry 2

Current Data Parameters
NAME II-299
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070627
Time 18.26
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 15
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 181
DW 60.400 usec
DE 6.00 usec
TE 294.2 K
D1 1.0000000 sec
TD0 1

==== CHANNEL f1 =====
NUC1 1H
P1 15.07 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 65536
SF 400.1300059 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00





Current Data Parameters
 NAME TI-290
 EXPNO 3
 PROCNO 1

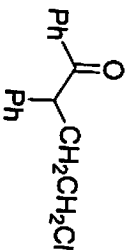
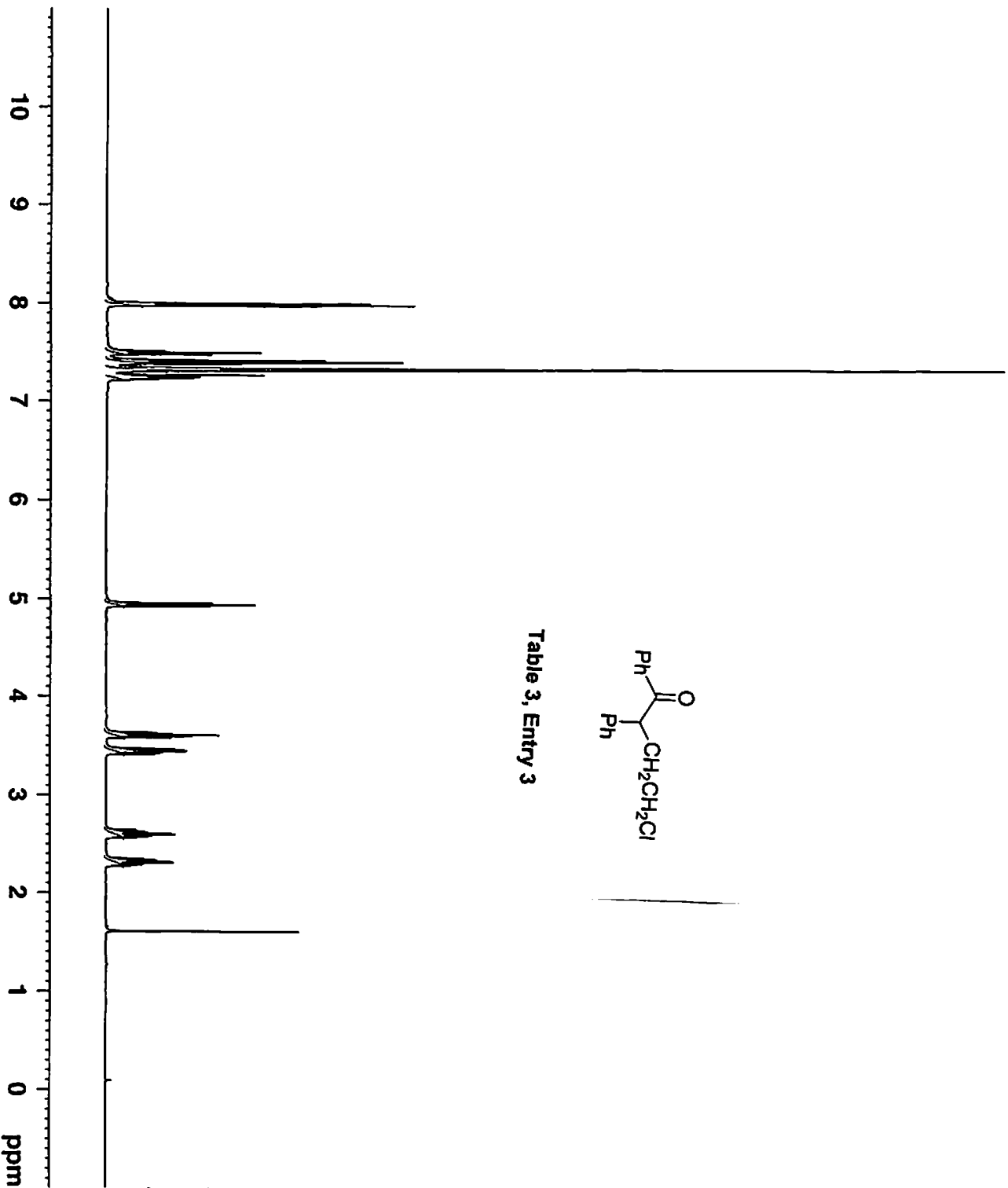


Table 3, Entry 3



F2 - Acquisition Parameters
 Date_ 20070622
 Time 9.06
 INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SMH 8278.146 Hz
 FIDRES 0.126314 Hz
 AQ 3.9584243 sec
 RG 128
 DW 60.400 usec
 DE 6.00 usec
 TE 293.2 K
 D1 1.00000000 sec
 TD0 1

==== CHANNEL f1 =====
 NUC1 1H
 P1 15.07 usec
 PL1 0.00 dB
 SFO1 400.1324710 MHz

F2 - Processing parameters
 SI 65536
 SF 400.1300058 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

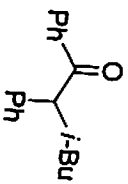
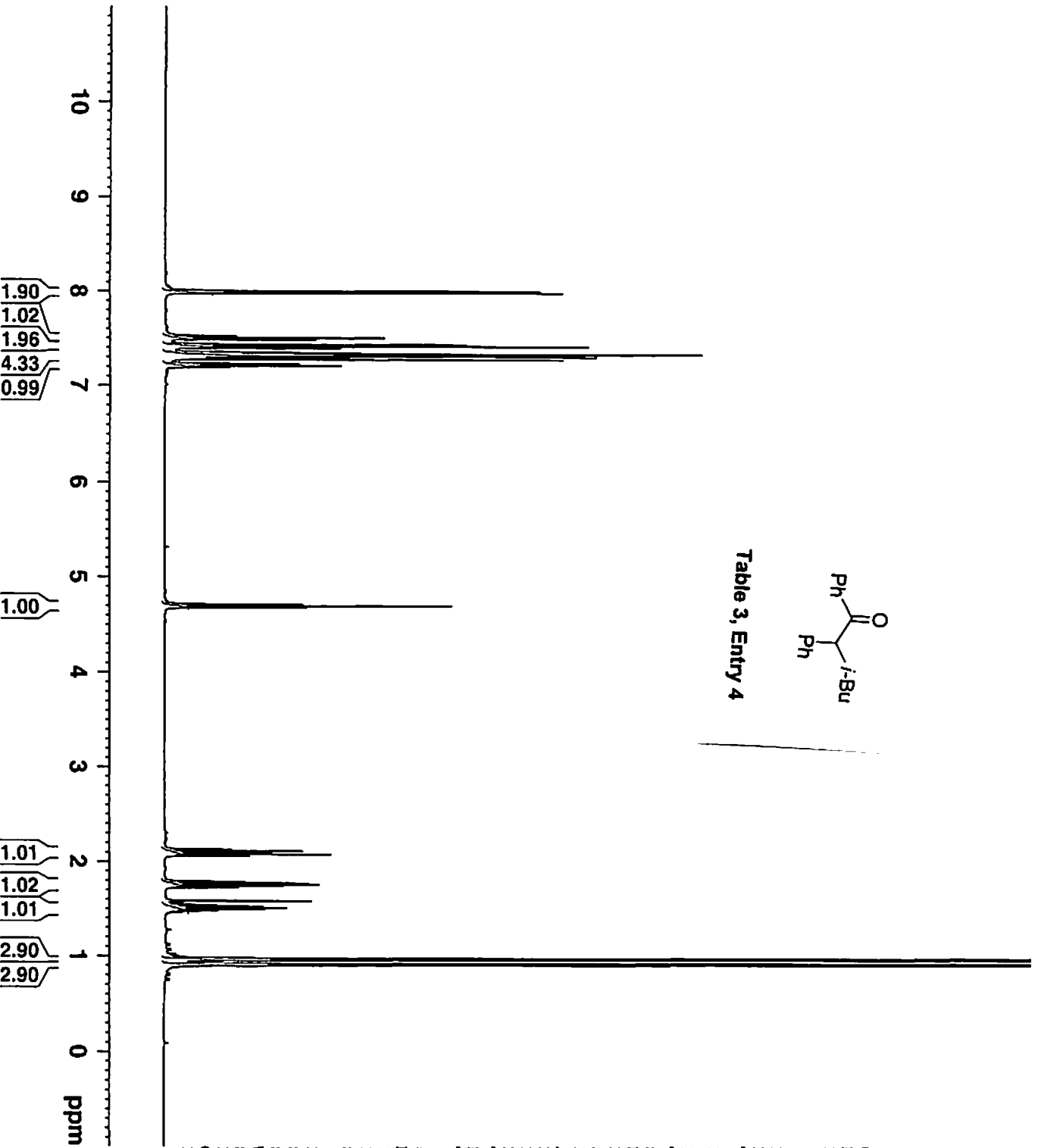


Table 3, Entry 4



Current Data Parameters
NAME III-041
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070801
Time 8.21

INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3

NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 181
DW 60.400 usec
DE 6.00 usec
TE 293.2 K
DI 1.00000000 sec
TDO 1

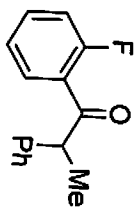
==== CHANNEL f1 =====
NUC1 1H
P1 15.07 usec
PL1 0.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 65536
SF 400.1300052 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
 NAME IIT-109
 EXPNO 4
 PROCNO 1

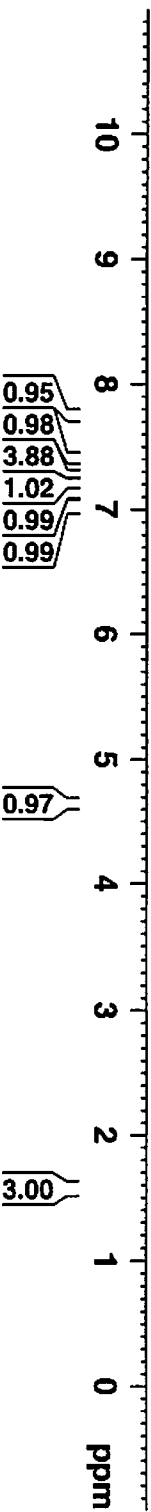
Table 3, Entry 6



F2 - Acquisition Parameters
 Date_ 20071113
 Time 16.16
 INSTRUM spect
 PROBHD 5 mm QNP 1H/13
 PULPROG zg30
 TTD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8278.146 Hz
 FIDRES 0.126314 Hz
 AQ 3.9584243 sec
 RG 57
 DW 60.400 usec
 DE 6.00 usec
 TE 292.2 K
 D1 1.0000000 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 14.00 usec
 PL1 0.00 dB
 SFO1 400.1324710 MHz

F2 - Processing parameters
 SI 65536
 SF 400.1300667 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



0.95
 0.98
 3.88
 1.02
 0.99
 0.99

0.97

3.00

10
9
8
7
6
5
4
3
2
1
0 ppm

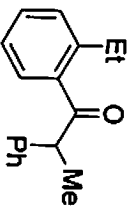


Table 3, Entry 7

Current Data Parameters
NAME III-011
EXPNO 2
PROCNO 1

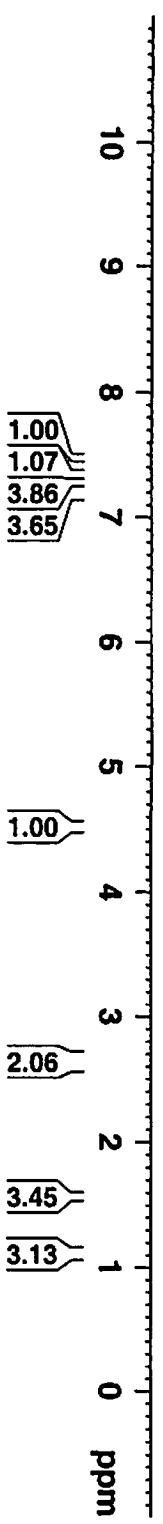
F2 - Acquisition Parameters
Date_ 20070702
Time 9.43

INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2

SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 322.5
DW 60.400 usec
DE 6.00 usec
TE 293.2 K
D1 1.00000000 sec
TD0 1

==== CHANNEL f1 =====
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 65536
SF 400.1300061 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



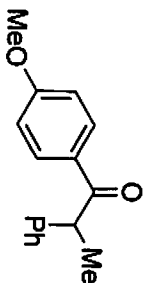
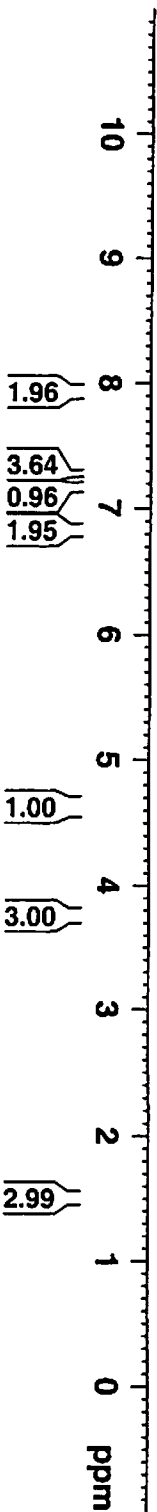


Table 3, Entry 8

Current Data Parameters
NAME I1-300
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070627
Time 18.19
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 12
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 45.3
DM 60.400 usec
DE 6.00 usec
TE 293.2 K
D1 1.0000000 sec
TD0 1

==== CHANNEL f1 =====
NUC1 1H
P1 15.07 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 65536
SF 400.1300212 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



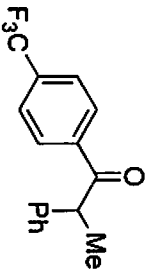
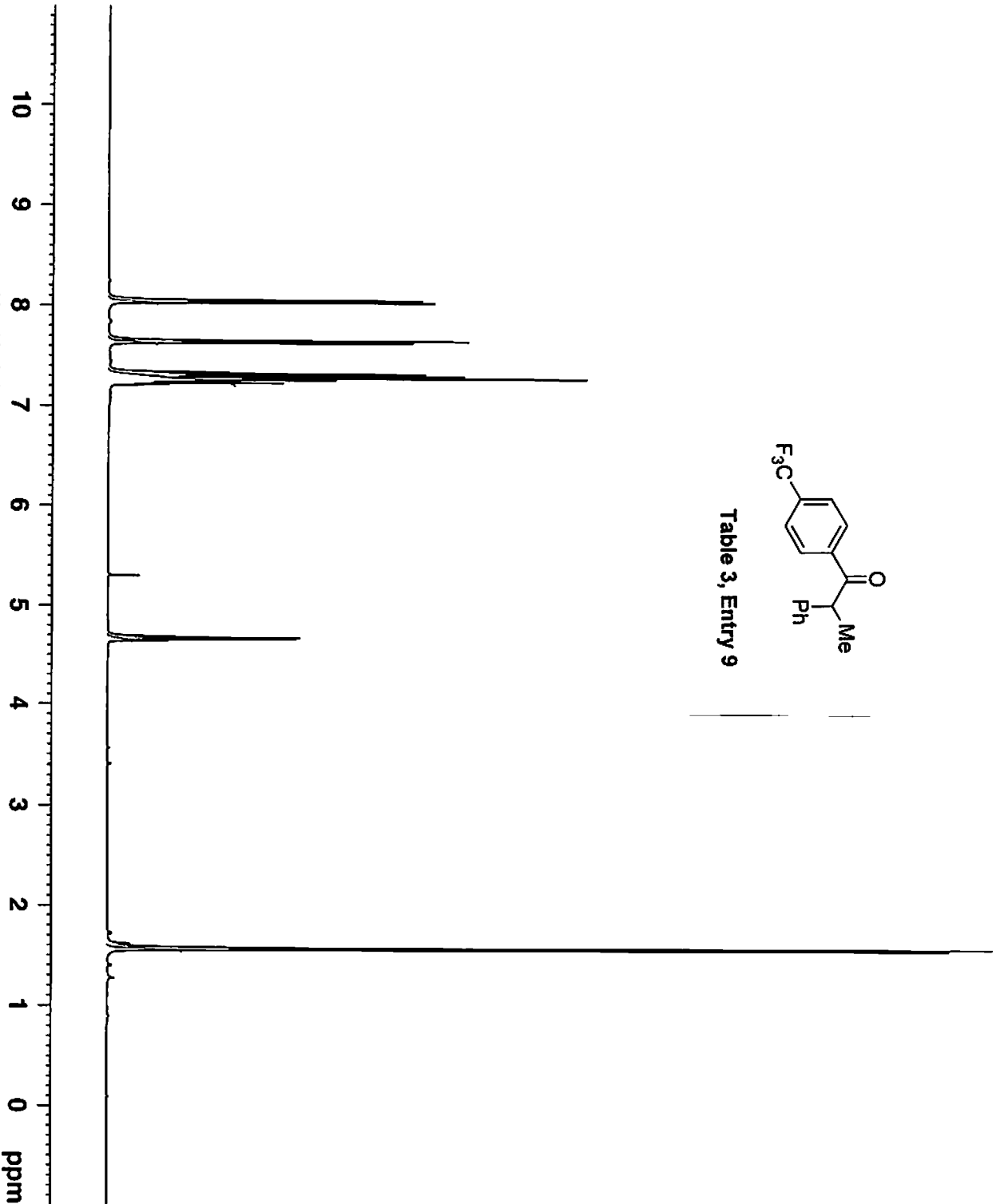


Table 3, Entry 9



Current Data Parameters
NAME III-028
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070716
Time 17.57

INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30

TD 65536
SOLVENT CDCl3
NS 16
DS 2

SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec

RG 57
DW 60.400 usec
DE 6.00 usec
TE 293.2 K

D1 1.00000000 sec
TD0 1

==== CHANNEL f1 =====
NUC1 1H
P1 14.00 usec
PL1 0.00 dB

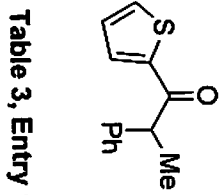
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 65536
SF 400.1300071 MHz

WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
NAME III-027
EXPNO 2
PROCNO 1



F2 - Acquisition Parameters
Date_ 20070716
Time 17.50
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 14
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 362
DW 60.400 usec
DE 6.00 usec
TE 293.2 K
D1 1.00000000 sec
TD0 1

==== CHANNEL f1 =====
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 65536
SF 400.1300067 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

