Catalytic Asymmetric Synthesis of Tertiary Alkyl Fluorides: Negishi Cross-Couplings of Racemic α,α-Dihaloketones

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Supporting Information

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I. General Information

Anhydrous THF and CH_2Cl_2 were purified and dried using a solvent-purification system that contained activated alumina. The following reagents were purchased and used as received: $NiCl_2$·glyme (Aldrich), $ZnCl_2$ (Aldrich; reagent grade, ≥98%), diglyme (Aldrich; anhydrous), *n*-BuLi (Aldrich; ~2.5 M in hexanes; titrated using diphenylacetic acid according to Kofron's method[1]), diisopropylamine (Aldrich; ≥99.5%), *N*-fluorobenzenesulfonimide (Oakwood), trimethylsilyl trifluoromethanesulfonate (Oakwood), triethylamine (Aldrich; ≥99.5%), butyrophenone (Aldrich), 3-phenylpropiophenone (Alfa Aesar), 4-chlorobutyrophenone (Alfa Aesar), 3-methyl-1-phenyl-1-butanone (Aldrich), 4'-*tert*-butyl-4-chlorobutyrophenone (Alfa Aesar), 4-chloro-4'-fluorobutyrophenone (Alfa Aesar), allylmagnesium chloride (Aldrich; 2.0 M in THF), 3-chloroperbenzoic acid (Aldrich; ≤77%), and 1,1,1,3,3,3-hexafluoro-2-propanol (Oakwood). *N*-Bromosuccinimide (Aldrich) and *N*-chlorosuccinimide (Aldrich) were recrystallized prior to use. Ligand (4*R*,5*S*)-**L*** was purchased from Aldrich. Ligand (4*S*,5*R*)-**L***

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(1) Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879–1880.

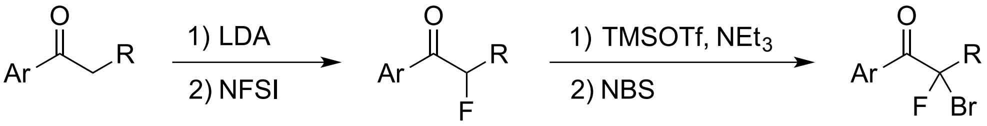
was synthesized according to a literature procedure (it is commercially available from Sh-Icon Inc.)[2] All aryl bromides were purchased (Aldrich, Alfa Aesar, TCI, and Oakwood) and used as received.

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

HPLC analyses were carried out on an Agilent 1100 Series system, using Daicel CHIRALCEL® columns or Daicel CHIRALPAK® columns (internal diameter 4.6 mm, column length 250 mm, particle size 5 μm).

II. Preparation of Electrophiles

The yields have not been optimized.



General Procedure A: This was based on published procedures.[3]

Fluorination. *n*-BuLi in hexane (2.30 M; 12.0 mL, 27.5 mmol; 1.10 equiv) was added over 5 min to a solution of diisopropylamine (4.24 mL, 30.3 mmol; 1.21 equiv) in THF (20 mL) at −78 °C. The mixture was allowed to stir for 10 min at −78 °C, and then it was warmed to r.t. and stirred for another 10 min. The clear solution was cooled to −78 °C, and a solution of the ketone (25.0 mmol) in THF (15 mL) was added over 5 min to the freshly prepared solution of LDA. The mixture was stirred at −78 °C for 1.5 h, and then a solution of *N*-fluorobenzenesulfonimide (NFSI; 9.46 g, 30.0 mmol; 1.20 equiv) in THF (30 mL) was added over 5 min to the solution of the enolate at −78 °C. The mixture was allowed to stir at −78 °C for 5 min, and then it was allowed to warm to r.t. (white or light-yellow suspension) and stirred for 6–12 h. Next, aqueous solutions of NH_4Cl (saturated; 20 mL) and of HCl (1 N; 50 mL) were added in turn. The mixture was extracted with CH_2Cl_2 (3 × 70 mL), and the organic layers were combined, dried over Na_2SO_4, and concentrated. The desired product was purified by flash chromatography on silica gel (10:1 hexane/diethyl ether, unless otherwise noted).

Bromination. Et_3N (3.07 mL, 22.0 mmol; 1.10 equiv) and trimethylsilyl trifluoromethanesulfonate (TMSOTf; 3.62 mL, 20.0 mmol; 1.00 equiv) were added to a solution of the α-fluoroketone (20.0 mmol) in CH_2Cl_2 (20 mL) at 0 °C. The reaction mixture was allowed to warm to r.t., and then it was stirred for 2.5 h. Next, *N*-bromosuccinimide (NBS; 4.63 g, 26.0 mmol; 1.30 equiv) was added in one portion to the reaction mixture, followed by CH_2Cl_2 (20 mL). The orange or red solution was allowed to stir at r.t. for 16 h, during which it became dark red. Then, the reaction was quenched with water (30 mL), and the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated.

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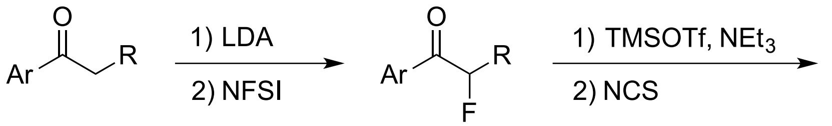
(2) Masamune, S.; Lowenthal, R. E. Cu Complexes of Bis-Oxazolines and Their Use. U.S. Patent 5,298,623, March 29, 1994.

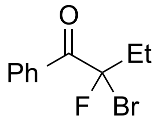
(3) (a) Shibatomi, K.; Yamamoto, H. *Angew. Chem. Int. Ed.* **2008**, *47*, 5796–5798. (b) Mohanta, P. K.; Davis, T. A.; Gooch, J. R.; Flowers, R. A., II. *J. Am. Chem. Soc.* **2005**, *127*, 11896–11897.

The desired product was purified by flash chromatography on silica gel (100:1 hexane/dichloromethane, unless otherwise noted).



General Procedure B: The first step is the same as for General Procedure A.

Chlorination. Et_3N (3.07 mL, 22.0 mmol; 1.10 equiv) and trimethylsilyl trifluoromethanesulfonate (TMSOTf; 3.62 mL, 20.0 mmol; 1.00 equiv) were added to a solution of the α-fluoroketone (20.0 mmol) in CH_2Cl_2 (20 mL) at 0 °C. The reaction mixture was allowed to warm to r.t., and then it was stirred for 2.5 h. Next, *N*-chlorosuccinimide (NCS; 3.47 g, 26.0 mmol; 1.30 equiv) was added in one batch to the reaction mixture, followed by the addition of CH_2Cl_2 (20 mL). The orange or red solution was allowed to stir at r.t. for 16 h, during which it became dark red. Then, the reaction was quenched with water (30 mL), and the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated. The desired product was purified by flash chromatography on silica gel (100:1 hexane/dichloromethane, unless otherwise noted).



2-Bromo-2-fluoro-1-phenylbutan-1-one [76650-11-8]. The title compound was synthesized according to General Procedure A from butyrophenone. The overall yield (2 steps) was 64%. The title compound was isolated as a colorless oil.

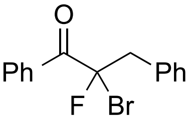
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 – 8.16 (m, 2H), 7.63 – 7.59 (m, 1H), 7.50 – 7.47 (m, 2H), 2.66 – 2.50 (m, 2H), 1.17 (t, 3H, *J* = 7.3 Hz);

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.1 (d, *J* = 28.5 Hz), 133.8, 132.1 (d, *J* = 3.6 Hz), 130.6 (d, *J* = 5.8 Hz), 128.4, 106.0 (d, *J* = 272.2 Hz), 34.2 (d, *J* = 21.1 Hz), 8.6 (d, *J* = 3.8 Hz);

^{19}F NMR (282 MHz, $CDCl_3$) δ −118.1 (t, 1F, *J* = 21.8 Hz);

FT-IR (film) 2982, 2944, 1690, 1598, 1448, 1262, 1152, 887, 828 cm^{-1};

GC-MS (EI) *m*/*z* (M^+–Br) calcd for $C_{10}H_{10}FO$: 165, found: 165.



2-Bromo-2-fluoro-1,3-diphenylpropan-1-one. The title compound was synthesized according to General Procedure A from 3-phenylpropiophenone. The overall yield (2 steps) was 43%. The title compound was isolated as a white solid.

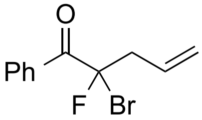
^{1}H NMR (500 MHz, CDCl$_3$) δ 8.09 – 8.06 (m, 2H), 7.60 – 7.57 (m, 1H), 7.46 – 7.43 (m, 2H), 7.36 – 7.30 (m, 5H), 3.99 (dd, 1H, *J* = 14.7, 25.6 Hz), 3.86 (dd, 1H, *J* = 14.7, 20.8 Hz);

^{13}C NMR (126 MHz, CDCl$_3$) δ 190.4 (d, *J* = 28.3 Hz), 133.8, 133.3, 132.2 (d, *J* = 3.7 Hz), 131.1, 130.4 (d, *J* = 5.7 Hz), 128.4, 128.3, 127.6, 103.7 (d, *J* = 274.1 Hz), 46.4 (d, *J* = 19.8 Hz);

^{19}F NMR (282 MHz, CDCl$_3$) δ −116.5 (dd, 1F, *J* = 20.7, 25.7 Hz);

FT-IR (film) 3063, 3032, 1690, 1597, 1448, 1262, 1135, 1087, 955, 885, 846, 743 cm^{-1};

GC-MS (EI) *m/z* (M$^+$−Br) calcd for $C_{15}H_{12}FO$: 227, found: 227.



2-Bromo-2-fluoro-1-phenylpent-4-en-1-one. The title compound was synthesized according to General Procedure A from 1-phenylpent-4-en-1-one. The overall yield (2 steps) was 38%. The title compound was isolated as a colorless oil (it should be stored in a refrigerator (~5 °C)).

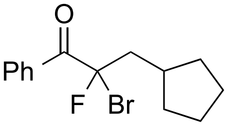
^{1}H NMR (500 MHz, CDCl$_3$) δ 8.18 – 8.16 (m, 2H), 7.63 – 7.60 (m, 1H), 7.50 – 7.47 (m, 2H), 5.94 – 5.86 (m, 1H), 5.33 – 5.29 (m, 2H), 3.36 – 3.29 (m, 2H);

^{13}C NMR (126 MHz, CDCl$_3$) δ 189.8 (d, *J* = 27.9 Hz), 133.9, 132.0 (d, *J* = 3.9 Hz), 130.6 (d, *J* = 5.8 Hz), 129.8 (d, *J* = 2.8 Hz), 128.4, 121.4, 103.5 (d, *J* = 273.0 Hz), 45.0 (d, *J* = 20.9 Hz);

^{19}F NMR (282 MHz, CDCl$_3$) δ −116.7 (tt, 1F, *J* = 1.9, 22.1 Hz);

FT-IR (film) 3077, 1694, 1598, 1448, 1263, 1137, 932, 870, 711 cm^{-1};

GC-MS (EI) *m/z* (M$^+$) calcd for $C_{11}H_{10}{}^{79}BrFO$: 256, found: 256, 258 (M$^+$+2).



2-Bromo-3-cyclopentyl-2-fluoro-1-phenylpropan-1-one. The title compound was synthesized according to General Procedure A from 3-cyclopentyl-1-phenylpropan-1-one. The overall yield (2 steps) was 50%. The title compound was isolated as a yellow oil.

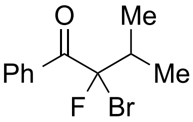
^{1}H NMR (500 MHz, CDCl$_3$) δ 8.17 – 8.14 (m, 2H), 7.63 – 7.59 (m, 1H), 7.50 – 7.46 (m, 2H), 2.70 (d, 1H, *J* = 6.6 Hz), 2.66 (dd, 1H, *J* = 1.1, 6.5 Hz), 2.15 – 2.06 (m, 1H), 1.91 – 1.82 (m, 2H), 1.67 – 1.60 (m, 2H), 1.56 – 1.48 (m, 2H), 1.30 – 1.12 (m, 2H);

^{13}C NMR (126 MHz, CDCl$_3$) δ 190.7 (d, *J* = 28.2 Hz), 133.7, 132.3 (d, *J* = 3.3 Hz), 130.6 (d, *J* = 5.6 Hz), 128.4, 105.5 (d, *J* = 273.7 Hz), 46.2 (d, *J* = 19.7 Hz), 37.0, 33.3 (dd, *J* = 1.5, 21.5 Hz), 24.7 (d, *J* = 23.1 Hz);

^{19}F NMR (282 MHz, CDCl$_3$) δ −114.6 (t, 1F, *J* = 23.6 Hz);

FT-IR (film) 2953, 2869, 1693, 1598, 1448, 1258, 1144, 915, 704 cm^{-1};

GC-MS (EI) *m/z* (M$^+$−Br) calcd for $C_{14}H_{16}FO$: 219, found: 219.



2-Bromo-2-fluoro-3-methyl-1-phenylbutan-1-one. The title compound was synthesized according to General Procedure A from 3-methyl-1-phenyl-1-butanone. The overall yield (2 steps) was 49%. The title compound was isolated as a light-yellow oil.

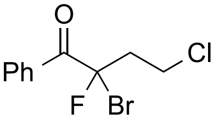
^{1}H NMR (500 MHz, CDCl$_3$) δ 8.13 – 8.11 (m, 2H), 7.62 – 7.59 (m, 1H), 7.50 – 7.46 (m, 2H), 2.91 – 2.81 (m, 1H), 1.35 (d, 3H, *J* = 6.8 Hz), 1.07 (dd, 3H, *J* = 0.8, 6.7 Hz);

^{13}C NMR (126 MHz, CDCl$_3$) δ 191.2 (d, *J* = 27.6 Hz), 133.6, 132.9 (d, *J* = 3.4 Hz), 130.3 (d, *J* = 6.2 Hz), 128.4, 109.9 (d, *J* = 275.6 Hz), 37.5 (d, *J* = 20.6 Hz), 17.6 (d, *J* = 2.9 Hz), 17.0 (d, *J* = 3.3 Hz);

^{19}F NMR (282 MHz, CDCl$_3$) δ −127.1 (d, 1F, *J* = 26.8 Hz);

FT-IR (film) 2980, 2940, 1692, 1598, 1448, 1263, 1026, 913, 843, 817 cm^{-1};

GC-MS (EI) *m*/*z* (M^{+}−Br) calcd for $C_{11}H_{12}FO$: 179, found: 179.



2-Bromo-4-chloro-2-fluoro-1-phenylbutan-1-one. The title compound was synthesized according to General Procedure A from 4-chlorobutyrophenone. The overall yield (2 steps) was 26%. The title compound was isolated as a light-yellow oil.

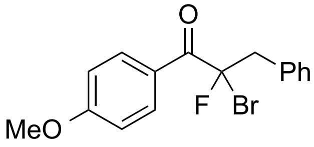
^{1}H NMR (500 MHz, CDCl$_3$) δ 8.18 – 8.16 (m, 2H), 7.65 – 7.62 (m, 1H), 7.52 – 7.48 (m, 2H), 3.83 (ddd, 1H, *J* = 5.5, 9.6, 10.9 Hz), 3.74 (ddd, 1H, *J* = 6.2, 9.7, 10.9 Hz), 3.13 – 2.98 (m, 2H);

^{13}C NMR (126 MHz, CDCl$_3$) δ 189.1 (d, *J* = 27.4 Hz), 134.2, 131.3 (d, *J* = 3.9 Hz), 130.7 (d, *J* = 5.5 Hz), 128.5, 102.4 (d, *J* = 272.7 Hz), 43.3 (d, *J* = 20.2 Hz), 38.4 (d, *J* = 4.1 Hz);

^{19}F NMR (282 MHz, CDCl$_3$) δ −117.1 (t, 1F, *J* = 19.9 Hz);

FT-IR (film) 3063, 2970, 1691, 1597, 1448, 1269, 1249, 1175, 1139, 1086, 898, 822 cm^{-1};

GC-MS (EI) *m*/*z* (M^{+}−Cl) calcd for $C_{10}H_{9}{}^{79}BrFO$: 243, found: 243, 245 (M^{+}−Cl+2).



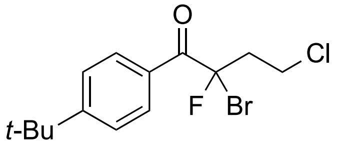
2-Bromo-2-fluoro-1-(4-methoxyphenyl)-3-phenylpropan-1-one. The title compound was synthesized according to General Procedure A from 1-(4-methoxyphenyl)-3-phenylpropan-1-one. The overall yield (2 steps) was 45%. The title compound was isolated as a light-yellow oil.

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.13 – 8.09 (m, 2H), 7.35 – 7.28 (m, 5H), 6.93 – 6.90 (m, 2H), 3.96 (dd, 1H, *J* = 14.7, 24.9 Hz), 3.88 – 3.79 (m, 4H);

^{13}C NMR (126 MHz, CDCl$_3$) δ 188.5 (d, *J* = 27.1 Hz), 164.0, 133.5, 133.0 (d, *J* = 6.4 Hz), 131.1, 128.2, 127.5, 124.7 (d, *J* = 4.0 Hz), 113.7 (d, *J* = 1.2 Hz), 104.2 (d, *J* = 274.4 Hz), 55.5, 46.4 (d, *J* = 19.8 Hz);

^{19}F NMR (282 MHz, CDCl$_3$) δ −115.3 (dd, 1F, *J* = 21.7, 24.7 Hz);

FT-IR (film) 3032, 2935, 2840, 1680, 1601, 1511, 1263, 1177, 1134, 1029, 853, 725 cm^{-1};
GC-MS (EI) *m*/*z* (M^+−Br) calcd for $C_{16}H_{14}FO_2$: 257, found: 257.



2-Bromo-1-(4-(*tert*-butyl)phenyl)-4-chloro-2-fluorobutan-1-one. The title compound was synthesized according to General Procedure A from 4'-*tert*-butyl-4-chlorobutyrophenone. The overall yield (2 steps) was 34%. The title compound was isolated as a light-yellow oil.

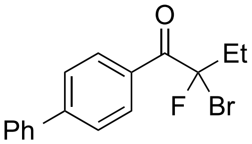
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 – 8.11 (m, 2H), 7.53 – 7.50 (m, 2H), 3.82 (ddd, 1H, *J* = 5.6, 9.7, 10.8 Hz), 3.73 (ddd, 1H, *J* = 6.1, 9.8, 10.8 Hz), 3.12 – 2.97 (m, 2H), 1.36 (s, 9H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 188.6 (d, *J* = 27.3 Hz), 158.3, 130.7 (d, *J* = 5.7 Hz), 128.5 (d, *J* = 3.7 Hz), 125.6 (d, *J* = 0.7 Hz), 102.6 (d, *J* = 273.0 Hz), 43.4 (d, *J* = 20.2 Hz), 38.5 (d, *J* = 4.0 Hz), 35.3, 31.0;

^{19}F NMR (282 MHz, $CDCl_3$) δ −116.6 (t, 1F, *J* = 19.9 Hz);

FT-IR (film) 2965, 2905, 2869, 1687, 1604, 1272, 1136, 1112, 899, 853 cm^{-1};

GC-MS (EI) *m*/*z* (M^+−Cl) calcd for $C_{14}H_{17}{}^{79}BrFO$: 299, found: 299, 301 (M^+−Cl+2).



1-([1,1'-Biphenyl]-4-yl)-2-bromo-2-fluorobutan-1-one. The title compound was synthesized according to General Procedure A from 1-([1,1'-biphenyl]-4-yl)butan-1-one. The overall yield (2 steps) was 59%. The title compound was isolated as a light-yellow solid.

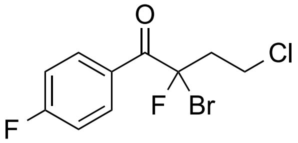
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 – 8.27 (m, 2H), 7.73 – 7.70 (m, 2H), 7.67 – 7.64 (m, 2H), 7.51 – 7.48 (m, 2H), 7.45 – 7.41 (m, 1H), 2.70 – 2.53 (m, 2H), 1.20 (t, 3H, *J* = 7.3 Hz);

^{13}C NMR (126 MHz, $CDCl_3$) δ 189.6 (d, *J* = 27.9 Hz), 146.5, 139.6, 131.2 (d, *J* = 5.9 Hz), 130.7 (d, *J* = 3.8 Hz), 129.0, 128.4, 127.3, 127.0, 106.2 (d, *J* = 272.2 Hz), 34.2 (d, *J* = 21.1 Hz), 8.6 (d, *J* = 3.7 Hz);

^{19}F NMR (282 MHz, $CDCl_3$) δ −117.9 (t, 1F, *J* = 21.8 Hz);

FT-IR (film) 2981, 1687, 1604, 1264, 1152, 885, 856, 745, 723 cm^{-1};

GC-MS (EI) *m*/*z* (M^+−HBr) calcd for $C_{16}H_{13}FO$: 240, found: 240.



2-Bromo-4-chloro-2-fluoro-1-(4-fluorophenyl)butan-1-one. The title compound was synthesized according to General Procedure A from 4-chloro-4'-fluorobutyrophenone. The overall yield (2 steps) was 42%. The title compound was isolated as a light-yellow oil.

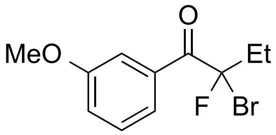
^{1}H NMR (500 MHz, CDCl$_3$) δ 8.23 – 8.20 (m, 2H), 7.19 – 7.14 (m, 2H), 3.82 (ddd, 1H, *J* = 5.5, 9.5, 10.9 Hz), 3.73 (ddd, 1H, *J* = 6.2, 9.6, 10.9 Hz), 3.11 – 2.96 (m, 2H);

^{13}C NMR (126 MHz, CDCl$_3$) δ 187.5 (d, *J* = 27.5 Hz), 166.2 (d, *J* = 258.0 Hz), 133.6 (dd, *J* = 5.9, 9.5 Hz), 127.5, 115.9 (d, *J* = 22.2 Hz), 102.4 (d, *J* = 272.5 Hz), 43.2 (d, *J* = 20.1 Hz), 38.4 (d, *J* = 4.1 Hz);

^{19}F NMR (282 MHz, CDCl$_3$) δ −102.2 (m, 1F), −117.0 (t, 1F, *J* = 20.0 Hz);

FT-IR (film) 2971, 1695, 1599, 1506, 1412, 1277, 1241, 1162, 1139, 899, 854, 710 cm^{-1};

GC-MS (EI) *m/z* (M$^+$−Cl) calcd for $C_{10}H_8{}^{79}BrF_2O$: 261, found: 261, 263 (M$^+$−Cl+2).



2-Bromo-2-fluoro-1-(3-methoxyphenyl)butan-1-one. The title compound was synthesized according to General Procedure A from 1-(3-methoxyphenyl)butan-1-one. The overall yield (2 steps) was 52%. The title compound was isolated as a light-yellow oil.

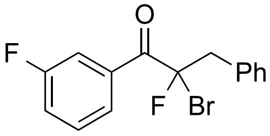
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.80 (dddd, 1H, *J* = 0.9, 1.6, 2.2, 7.7 Hz), 7.66 (dt, 1H, *J* = 1.5, 2.8 Hz), 7.39 (t, 1H, *J* = 8.0 Hz), 7.15 (ddd, 1H, *J* = 0.9, 2.7, 8.3 Hz), 3.86 (s, 3H), 2.65 – 2.49 (m, 2H), 1.16 (t, 3H, *J* = 7.3 Hz);

^{13}C NMR (126 MHz, CDCl$_3$) δ 189.9 (d, *J* = 28.0 Hz), 159.4, 133.3 (d, *J* = 3.4 Hz), 129.4 (d, *J* = 1.2 Hz), 123.2 (d, *J* = 7.4 Hz), 120.3, 114.9 (d, *J* = 4.6 Hz), 106.0 (d, *J* = 272.5 Hz), 55.4, 34.3 (d, *J* = 21.2 Hz), 8.6 (d, *J* = 3.7 Hz);

^{19}F NMR (282 MHz, CDCl$_3$) δ −117.9 (t, 1F, *J* = 21.7 Hz);

FT-IR (film) 2979, 2943, 1694, 1598, 1580, 1489, 1463, 1428, 1271, 1226, 1152, 1039, 719 cm^{-1};

GC-MS (EI) *m/z* (M$^+$) calcd for $C_{11}H_{12}{}^{79}BrFO_2$: 274, found: 274, 276 (M$^+$+2).



2-Bromo-2-fluoro-1-(3-fluorophenyl)-3-phenylpropan-1-one. The title compound was synthesized according to General Procedure A from 1-(3-fluorophenyl)-3-phenylpropan-1-one. The overall yield (2 steps) was 31%. The title compound was isolated as a light-yellow oil.

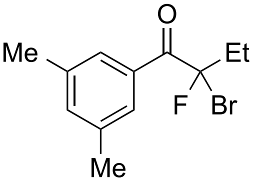
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.86 (dtd, 1H, *J* = 1.0, 1.7, 7.9 Hz), 7.73 (ddt, 1H, *J* = 1.6, 2.9, 9.6 Hz), 7.42 (td, 1H, *J* = 5.6, 8.1 Hz), 7.33 – 7.28 (m, 6H), 3.96 (dd, 1H, *J* = 14.7, 25.9 Hz), 3.84 (dd, 1H, *J* = 14.7, 20.6 Hz);

^{13}C NMR (126 MHz, CDCl$_3$) δ 189.2 (dd, *J* = 2.3, 28.4 Hz), 162.3 (d, *J* = 247.9 Hz), 134.0 (dd, *J* = 3.7, 4.8 Hz), 133.1, 131.1 (d, *J* = 1.0 Hz), 130.1 (dd, *J* = 0.8, 7.7 Hz), 128.4, 127.7, 126.2 (dd, *J* = 3.1, 6.4 Hz), 120.9 (d, *J* = 21.4 Hz), 117.3 (dd, *J* = 5.7, 23.4 Hz), 103.5 (d, *J* = 273.5 Hz), 46.4 (d, *J* = 19.7 Hz);

^{19}F NMR (282 MHz, CDCl$_3$) δ −111.5 (m, 1F), −117.1 (dd, 1F, *J* = 20.6, 25.6 Hz);

FT-IR (film) 3067, 3034, 1694, 1587, 1440, 1270, 1124, 894, 721 cm^{-1};

GC-MS (EI) *m*/*z* (M^+–Br) calcd for $C_{15}H_{11}F_2O$: 245, found: 245.



2-Bromo-1-(3,5-dimethylphenyl)-2-fluorobutan-1-one. The title compound was synthesized according to General Procedure A from 1-(3,5-dimethylphenyl)butan-1-one. The overall yield (2 steps) was 61%. The title compound was isolated as a colorless oil.

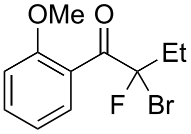
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.77 (m, 2H), 7.25 – 7.24 (m, 1H), 2.63 – 2.50 (m, 2H), 2.39 (s, 6H), 1.15 (t, 3H, *J* = 7.3 Hz);

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.6 (d, *J* = 27.9 Hz), 138.0, 135.5, 132.3 (d, *J* = 3.6 Hz), 128.2 (d, *J* = 5.7 Hz), 106.1 (d, *J* = 272.7 Hz), 34.3 (d, *J* = 21.2 Hz), 21.3, 8.6 (d, *J* = 3.7 Hz);

^{19}F NMR (282 MHz, $CDCl_3$) δ −117.7 (t, 1F, *J* = 21.8 Hz);

FT-IR (film) 2980, 2944, 2919, 1690, 1604, 1459, 1301, 1215, 1152, 1060, 922, 869 cm^{-1};

GC-MS (EI) *m*/*z* (M^+) calcd for $C_{12}H_{14}{}^{79}BrFO$: 272, found: 272, 274 (M^++2).



2-Bromo-2-fluoro-1-(2-methoxyphenyl)butan-1-one. The title compound was synthesized according to General Procedure A from 1-(2-methoxyphenyl)butan-1-one. The overall yield (2 steps) was 60%. The title compound was isolated as a light-yellow oil.

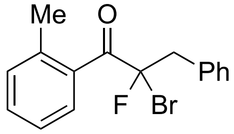
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (dt, 1H, *J* = 1.4, 7.6 Hz), 7.46 (ddd, 1H, *J* = 1.7, 7.5, 8.3 Hz), 7.01 (td, 1H, *J* = 0.9, 7.5 Hz), 6.97 (dd, 1H, *J* = 0.9, 8.4 Hz), 3.84 (s, 3H), 2.59 – 2.47 (m, 2H), 1.16 (t, 3H, *J* = 7.3 Hz);

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.2 (d, *J* = 31.8 Hz), 157.5 (d, *J* = 0.8 Hz), 132.7, 129.6 (d, *J* = 2.8 Hz), 125.2 (d, *J* = 2.4 Hz), 120.3, 111.4, 106.0 (d, *J* = 272.0 Hz), 55.7, 34.0 (d, *J* = 21.0 Hz), 8.6 (d, *J* = 3.0 Hz);

^{19}F NMR (282 MHz, $CDCl_3$) δ −119.8 (t, 1F, *J* = 20.9 Hz);

FT-IR (film) 2982, 2943, 2839, 1719, 1599, 1488, 1462, 1435, 1291, 1256, 1162, 1021, 893, 753 cm^{-1};

GC-MS (EI) *m*/*z* (M^+–Br) calcd for $C_{11}H_{12}FO_2$: 195, found: 195.



2-Bromo-2-fluoro-3-phenyl-1-(*o*-tolyl)propan-1-one. The title compound was synthesized according to General Procedure A from 3-phenyl-1-(*o*-tolyl)propan-1-one. The overall yield (2 steps) was 22%. The title compound was isolated as a light-yellow oil.

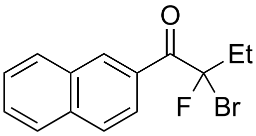
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.44 (ddd, 1H, *J* = 1.3, 3.9, 8.0 Hz), 7.35 – 7.29 (m, 6H), 7.20 (dt, 1H, *J* = 0.7, 7.8 Hz), 7.14 (tdd, 1H, *J* = 0.6, 1.3, 7.4 Hz), 4.04 (dd, 1H, *J* = 14.4, 30.7 Hz), 3.85 (dd, 1H, *J* = 14.4, 15.7 Hz), 2.18 (s, 3H);

^{13}C NMR (126 MHz, CDCl$_3$) δ 195.4 (d, *J* = 29.9 Hz), 138.4, 133.5 (d, *J* = 2.8 Hz), 133.2, 131.4, 131.3, 131.1 (d, *J* = 1.3 Hz), 128.8 (d, *J* = 8.1 Hz), 128.5, 127.8, 124.9, 103.2 (d, *J* = 274.9 Hz), 47.0 (d, *J* = 19.5 Hz), 19.9;

^{19}F NMR (282 MHz, CDCl$_3$) δ −115.6 (ddd, 1F, *J* = 4.0, 15.8, 30.7 Hz);

FT-IR (film) 3064, 3033, 2930, 1700, 1496, 1455, 1264, 1226, 1122, 940, 886, 724 cm^{-1};

GC-MS (EI) *m/z* (M$^+$–Br) calcd for $C_{16}H_{14}FO$: 241, found: 241.



2-Bromo-2-fluoro-1-(naphthalen-2-yl)butan-1-one. The title compound was synthesized according to General Procedure A from 1-(naphthalen-2-yl)butan-1-one. The overall yield (2 steps) was 41%. The title compound was isolated as a light-yellow oil.

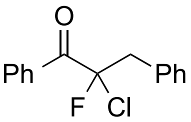
^{1}H NMR (500 MHz, CDCl$_3$) δ 8.81 – 8.80 (m, 1H), 8.17 (dt, 1H, *J* = 1.7, 8.7 Hz), 7.99 (dd, 1H, *J* = 0.7, 8.2 Hz), 7.92 – 7.87 (m, 2H), 7.65 – 7.61 (m, 1H), 7.58 – 7.55 (m, 1H), 2.73 – 2.56 (m, 2H), 1.22 (t, 3H, *J* = 7.3 Hz);

^{13}C NMR (126 MHz, CDCl$_3$) δ 190.0 (d, *J* = 27.9 Hz), 135.7, 132.9 (d, *J* = 7.8 Hz), 132.2 (d, *J* = 0.7 Hz), 130.0, 129.3 (d, *J* = 3.6 Hz), 129.1, 128.2 (d, *J* = 0.8 Hz), 127.7, 126.8, 125.6 (d, *J* = 4.0 Hz), 106.3 (d, *J* = 272.2 Hz), 34.3 (d, *J* = 21.2 Hz), 8.6 (d, *J* = 3.7 Hz);

^{19}F NMR (282 MHz, CDCl$_3$) δ −117.4 (t, 1F, *J* = 21.6 Hz);

FT-IR (film) 3060, 2981, 2942, 1686, 1627, 1462, 1280, 1230, 1151, 1123, 1108, 979, 910, 868, 741 cm^{-1};

GC-MS (EI) *m/z* (M$^+$) calcd for $C_{14}H_{12}{}^{79}BrFO$: 294, found: 294, 296 (M$^+$+2).



2-Chloro-2-fluoro-1,3-diphenylpropan-1-one [1062229-21-3]. The title compound was synthesized according to General Procedure B from 3-phenylpropiophenone. The overall yield (2 steps) was 40%. The title compound was isolated as a light-yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 – 8.07 (m, 2H), 7.61 – 7.58 (m, 1H), 7.47 – 7.44 (m, 2H), 7.36 – 7.29 (m, 5H), 3.86 (dd, 1H, *J* = 14.5, 22.5 Hz), 3.70 (dd, 1H, *J* = 14.6, 22.2 Hz);

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.0 (d, *J* = 29.8 Hz), 133.9, 132.6, 132.1 (d, *J* = 3.8 Hz), 131.2, 130.4 (d, *J* = 5.5 Hz), 128.4 (d, *J* = 0.6 Hz), 128.3, 127.6, 109.0 (d, *J* = 262.1 Hz), 45.1 (d, *J* = 20.8 Hz);

^{19}F NMR (282 MHz, $CDCl_3$) δ −114.9 (t, 1F, *J* = 22.4 Hz);

FT-IR (film) 3065, 3033, 1694, 1598, 1497, 1455, 1448, 1264, 1135, 893, 853, 749 cm^{-1};

GC-MS (EI) *m*/*z* (M^+−Cl) calcd for $C_{15}H_{12}FO$: 227, found: 227.

III. Asymmetric Negishi Cross-Couplings

General procedure for the preparation of solutions of the arylzinc reagent (0.30 M): In the air, $ZnCl_2$ (Aldrich; reagent grade, ≥98%; dried with a heat gun under high vacuum for 20 min before the reaction; 2.04 g, 15.0 mmol; 1.50 equiv) was added quickly to an oven-dried 20 mL vial equipped with a stir bar. The vial was closed with a PTFE septum cap and then evacuated and back-filled with nitrogen (three cycles). THF (8.5 mL) was added to this vial, and the resulting mixture was stirred vigorously until the $ZnCl_2$ had completely dissolved. THF was then added to provide a 1.50 M solution of $ZnCl_2$. Next, an oven-dried 40 mL vial equipped with a stir bar was charged with the aryl bromide (9.00 mmol) and then closed with a PTFE septum cap. The vial was evacuated and back-filled with nitrogen (three cycles), and then THF (6.5 mL) was added to this vial.

A solution of *n*-BuLi (2.61 M; 3.45 mL, 9.00 mmol; 1.00 equiv) was added over ~5 min to the vial that contained the solution of the aryl bromide, which had been cooled to –78 °C. The mixture was allowed to stir at –78 °C for another 5 min, and then the solution of $ZnCl_2$ (1.50 M; 9.00 mL, 13.5 mmol; 1.50 equiv) was added to the vial. The mixture was allowed to warm to r.t., and then it was stirred for 40 min at r.t.

The arylzinc solution was titrated using I_2 according to Knochel's method[4] (concentration ~0.4 M). This solution was then diluted with THF to generate a 0.30 M solution in an oven-dried 40 mL vial.

General procedure for asymmetric Negishi cross-couplings: In the air, $NiCl_2$·glyme (33.0 mg, 0.150 mmol) and (4*R*,5*S*)-**L*** (the enantiomer illustrated in eq 2; 73.4 mg, 0.160 mmol) were added to an oven-dried 40 mL vial equipped with a stir bar. The vial was closed with a PTFE septum cap and then evacuated and back-filled with nitrogen (three cycles). Diglyme (2.5 mL) was added to the vial, and the mixture was vigorously stirred at r.t. for 45 min. In the air, an oven-dried 4 mL vial was charged with the α-bromo-α-fluoroketone (1.00 mmol), and then the vial was sparged with nitrogen for 10 min. Diglyme (0.9 mL) was added, and the resulting solution was transferred via syringe to the 40 mL reaction vial. The 4 mL vial was rinsed with diglyme (0.8 mL × 2), and the washings were transferred to the reaction vial. The reaction vial was wrapped with electrical tape and then cooled to –25 °C for 15 min; at the same time, an oven-dried 40 mL vial that contained the arylzinc solution (0.30 M) was also cooled to –25 °C for 15 min (a nitrogen-filled balloon was attached to each vial). To the vigorously stirred solution of catalyst and electrophile was added the solution of the arylzinc reagent (0.30 M; 6.67 mL, 2.00 mmol; 2.00 equiv) over 3 min, during which the reaction mixture turned to orange. The balloon

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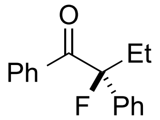
(4) Krasovskiy, A.; Knochel, P. *Synthesis* **2006**, 890–891.

was removed, and the septum cap was sealed with grease. The mixture was stirred vigorously at –25 °C for 36 h. Then, the reaction was quenched by the addition of EtOH (2 mL), and the mixture was allowed to warm to r.t. and then diluted with Et_2O (100 mL) and washed with deionized water (25 mL × 4). The organic layer was dried over Na_2SO_4 and then concentrated, and the residue was purified by flash chromatography.

A second run was performed with the (4*S*,5*R*)-**L***.



(*S*)-2-Fluoro-1,2-diphenylbutan-1-one (Table 2, Entry 1) [1355165-74-0]. 2-Bromo-2-fluoro-1-phenylbutan-1-one (245 mg, 1.00 mmol) and the arylzinc chloride reagent prepared from bromobenzene were used. Solvent system for chromatography: (1) normal-phase silica, 5%→7.5%→10%→12.5% dichloromethane in hexane; (2) reverse-phase silica (C-18), 40%→50% MeCN in water. The title compound was isolated as a colorless oil.

Run 1, 151 mg (62% yield, 97% ee); Run 2, 150 mg (62% yield, 97% ee).

The ee was determined on an AD-H column (0.25% *i*-PrOH/hexane, flow rate 0.8 mL/min); retention times for compound obtained using (4*R*,5*S*)-**L***: 8.4 min (minor), 14.1 min (major).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 – 7.87 (m, 2H), 7.52 – 7.47 (m, 3H), 7.41 – 7.30 (m, 5H), 2.51 – 2.39 (m, 1H), 2.26 – 2.14 (m, 1H), 0.93 (t, 3H, *J* = 7.4 Hz);

^{13}C NMR (126 MHz, $CDCl_3$) δ 198.5 (d, *J* = 28.2 Hz), 138.8 (d, *J* = 22.1 Hz), 135.1 (d, *J* = 3.5 Hz), 132.9, 129.9 (d, *J* = 6.4 Hz), 128.7 (d, *J* = 1.8 Hz), 128.1, 124.1 (d, *J* = 9.3 Hz), 103.7 (d, *J* = 189.5 Hz), 32.8 (d, *J* = 23.7 Hz), 7.5 (d, *J* = 4.2 Hz);

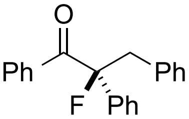
^{19}F NMR (282 MHz, $CDCl_3$) δ −165.2 (t, 1F, *J* = 24.6 Hz);

FT-IR (film) 3061, 2978, 2940, 1683, 1447, 1259, 974, 858, 842, 754, 709 cm^{-1};

MS (ESI) *m*/*z* (M+Na$^+$) calcd for $C_{16}H_{15}FNaO$: 265, found: 265;

$[\alpha]^{25}_{D} = -176°$ (*c* = 1.00, $CHCl_3$); 97% ee, from (4*R*,5*S*)-**L***.

The spectral data are in agreement with literature data.[5]



(*S*)-2-Fluoro-1,2,3-triphenylpropan-1-one (Table 2, Entry 2). 2-Bromo-2-fluoro-1,3-diphenylpropan-1-one (307 mg, 1.00 mmol) and the arylzinc chloride reagent prepared from bromobenzene were used. Solvent system for chromatography: 20:1→10:1 hexane/dichloromethane. The title compound was isolated as a white solid.

Run 1, 224 mg (74% yield, 98% ee); Run 2, 218 mg (72% yield, 97% ee).

This compound was also prepared on a 7.00 mmol scale, using 2-bromo-2-fluoro-1,3-diphenylpropan-1-one (2.15 g, 7.00 mmol) and the arylzinc chloride reagent prepared from

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(5) Guo, C.; Wang, R.-W.; Guo, Y.; Qing, F.-L. *J. Fluorine Chem.* **2012**, *133*, 86–96.

bromobenzene (0.30 M, 46.7 mL, 14.0 mmol; 2.00 equiv). Following the general procedure, the title compound was isolated in 66% yield (1.41 g) and 97% ee.

The ee was determined on an AD-H column (2% *i*-PrOH/hexane, flow rate 0.6 mL/min); retention times for compound obtained using (4*R*,5*S*)-**L***: 12.4 min (minor), 14.3 min (major).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.79 – 7.76 (m, 2H), 7.46 – 7.42 (m, 3H), 7.37 – 7.29 (m, 5H), 7.20 – 7.17 (m, 3H), 7.09 – 7.07 (m, 2H), 3.74 (dd, 1H, *J* = 14.4, 24.7 Hz), 3.47 (dd, 1H, *J* = 14.4, 26.1 Hz);

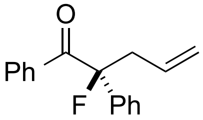
^{13}C NMR (126 MHz, CDCl$_3$) δ 198.1 (d, *J* = 28.1 Hz), 138.3 (d, *J* = 22.1 Hz), 135.0 (d, *J* = 3.5 Hz), 134.6, 132.9, 130.9, 129.9 (d, *J* = 6.2 Hz), 128.6 (d, *J* = 2.1 Hz), 128.3 (d, *J* = 0.7 Hz), 128.1, 127.8, 126.7, 124.2 (d, *J* = 9.0 Hz), 102.7 (d, *J* = 191.7 Hz), 45.5 (d, *J* = 22.5 Hz);

^{19}F NMR (282 MHz, CDCl$_3$) δ −160.9 (t, 1F, *J* = 25.4 Hz);

FT-IR (film) 3062, 3031, 1686, 1598, 1496, 1447, 1261, 1075, 1029, 942, 763 cm^{-1};

MS (ESI) *m*/*z* (M+Na^{+}) calcd for $C_{21}H_{17}FNaO$: 327, found: 327;

$[\alpha]^{25}_{D}$ = −215° (*c* = 1.03, CHCl$_3$); 98% ee, from (4*R*,5*S*)-**L***.



(*S*)-2-Fluoro-1,2-diphenylpent-4-en-1-one (Table 2, Entry 3). 2-Bromo-2-fluoro-1-phenylpent-4-en-1-one (257 mg, 1.00 mmol) and the arylzinc chloride reagent prepared from bromobenzene were used. Solvent system for chromatography: 25:1→10:1 hexane/dichloromethane. The title compound was isolated as a colorless oil.

Run 1, 104 mg (41% yield, 97% ee); Run 2, 115 mg (45% yield, 96% ee).

The ee was determined on an AD-H column (0.25% *i*-PrOH/hexane, flow rate 0.6 mL/min); retention times for compound obtained using (4*R*,5*S*)-**L***: 12.5 min (minor), 19.5 min (major).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.89 – 7.87 (m, 2H), 7.51 – 7.46 (m, 3H), 7.41 – 7.31 (m, 5H), 5.73 (ddt, 1H, *J* = 7.0, 10.2, 17.2 Hz), 5.15 – 5.08 (m, 2H), 3.18 (dddt, 1H, *J* = 1.2, 7.0, 14.8, 25.7 Hz), 2.94 (dddt, 1H, *J* = 1.3, 7.0, 14.8, 24.3 Hz);

^{13}C NMR (126 MHz, CDCl$_3$) δ 197.8 (d, *J* = 27.9 Hz), 138.4 (d, *J* = 22.2 Hz), 134.8 (d, *J* = 3.6 Hz), 133.0, 131.1 (d, *J* = 3.4 Hz), 130.0 (d, *J* = 6.3 Hz), 128.7 (d, *J* = 1.9 Hz), 128.3, 128.1, 124.1 (d, *J* = 9.2 Hz), 119.7, 102.5 (d, *J* = 190.4 Hz), 44.0 (d, *J* = 22.8 Hz);

^{19}F NMR (282 MHz, CDCl$_3$) δ −161.8 (t, 1F, *J* = 24.9 Hz);

FT-IR (film) 3074, 3028, 1687, 1598, 1448, 1259, 1239, 923, 759, 723 cm^{-1};

MS (ESI) *m*/*z* (M+Na^{+}) calcd for $C_{17}H_{15}FNaO$: 277, found: 277;

$[\alpha]^{25}_{D}$ = −208° (*c* = 1.00, CHCl$_3$); 97% ee, from (4*R*,5*S*)-**L***.

(*S*)-3-Cyclopentyl-2-fluoro-1,2-diphenylpropan-1-one (Table 2, Entry 4). 2-Bromo-3-cyclopentyl-2-fluoro-1-phenylpropan-1-one (299 mg, 1.00 mmol) and the arylzinc chloride reagent prepared from bromobenzene were used. Solvent system for chromatography: (1)

normal-phase silica, 5%→10% dichloromethane in hexane; (2) reverse-phase silica (C-18), 70% MeCN in water. The title compound was isolated as a colorless oil.

Run 1, 174 mg (59% yield, 91% ee); Run 2, 175 mg (59% yield, 90% ee).

The ee was determined on an AD-H column (0.25% *i*-PrOH/hexane, flow rate 0.8 mL/min); retention times for compound obtained using (4*R*,5*S*)-**L***: 11.5 min (minor), 14.8 min (major).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.89 – 7.87 (m, 2H), 7.54 – 7.42 (m, 2H), 7.50 – 7.46 (m, 1H), 7.41 – 7.30 (m, 5H), 2.48 (ddd, 1H, *J* = 6.2, 14.8, 25.8 Hz), 2.31 (ddd, 1H, *J* = 5.6, 14.8, 26.7 Hz), 1.84 – 1.77 (m, 2H), 1.64 – 1.51 (m, 3H), 1.47 – 1.36 (m, 2H), 1.19 – 1.03 (m, 2H);

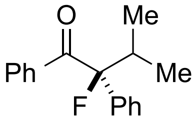
^{13}C NMR (126 MHz, CDCl$_3$) δ 198.9 (d, *J* = 28.4 Hz), 139.3 (d, *J* = 22.6 Hz), 135.1 (d, *J* = 3.4 Hz), 132.8, 129.9 (d, *J* = 6.3 Hz), 128.7 (d, *J* = 1.9 Hz), 128.1, 128.0, 124.1 (d, *J* = 9.2 Hz), 104.0 (d, *J* = 190.3 Hz), 45.2 (d, *J* = 22.1 Hz), 35.7, 33.7 (dd, *J* = 1.4, 9.7 Hz), 24.8 (d, *J* = 17.0 Hz).

^{19}F NMR (282 MHz, CDCl$_3$) δ −162.3 (t, 1F, *J* = 26.2 Hz);

FT-IR (film) 3061, 2952, 2868, 1687, 1683, 1598, 1447, 1259, 757, 712 cm^{-1};

MS (ESI) *m*/*z* (M+Na$^+$) calcd for $C_{20}H_{21}FNaO$: 319, found: 319;

$[\alpha]^{25}_{D}$ = −154° (*c* = 1.02, CHCl$_3$); 91% ee, from (4*R*,5*S*)-**L***.



(*S*)-2-Fluoro-3-methyl-1,2-diphenylbutan-1-one (Table 2, Entry 5). 2-Bromo-2-fluoro-3-methyl-1-phenylbutan-1-one (259 mg, 1.00 mmol) and the arylzinc chloride reagent prepared from bromobenzene were used. Solvent system for chromatography: 25:1 hexane/dichloromethane. The title compound was isolated as a colorless oil.

Run 1, 142 mg (55% yield, 83% ee); Run 2, 140 mg (55% yield, 81% ee).

The ee was determined on an AD-H column (0.25% *i*-PrOH/hexane, flow rate 0.6 mL/min); retention times for compound obtained using (4*R*,5*S*)-**L***: 10.6 min (minor), 17.0 min (major).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.89 – 7.86 (m, 2H), 7.57 – 7.54 (m, 2H), 7.50 – 7.46 (m, 1H), 7.41 – 7.35 (m, 4H), 7.32 – 7.29 (m, 1H), 2.87 (ddq, 1H, *J* = 6.8, 13.7, 32.1 Hz), 1.09 (d, 3H, *J* = 6.7 Hz), 0.74 (d, 3H, *J* = 7.0 Hz);

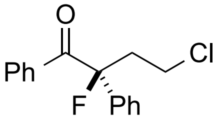
^{13}C NMR (126 MHz, CDCl$_3$) δ 200.1 (d, *J* = 29.3 Hz), 138.2 (d, *J* = 22.5 Hz), 136.0 (d, *J* = 3.4 Hz), 132.7, 129.6 (d, *J* = 6.3 Hz), 128.6 (d, *J* = 2.2 Hz), 128.1 (d, *J* = 0.8 Hz), 128.0, 124.4 (d, *J* = 10.1 Hz), 106.0 (d, *J* = 194.8 Hz), 36.6 (d, *J* = 22.6 Hz), 17.2 (d, *J* = 4.6 Hz), 15.8 (d, *J* = 3.1 Hz);

^{19}F NMR (282 MHz, CDCl$_3$) δ −180.3 (d, 1F, *J* = 32.1 Hz);

FT-IR (film) 2973, 1685, 1598, 1447, 1259, 1012, 836, 749 cm^{-1};

MS (ESI) *m*/*z* (M+Na$^+$) calcd for $C_{17}H_{17}FNaO$: 279, found: 279;

$[\alpha]^{25}_{D}$ = −94.0° (*c* = 1.00, CHCl$_3$); 83% ee, from (4*R*,5*S*)-**L***.



(*S*)-4-Chloro-2-fluoro-1,2-diphenylbutan-1-one (Table 2, Entry 6). 2-Bromo-4-chloro-2-fluoro-1-phenylbutan-1-one (280 mg, 1.00 mmol) and the arylzinc chloride reagent prepared from bromobenzene were used. Solvent system for chromatography: 25:1 hexane/dichloromethane. The title compound was isolated as a colorless oil.

Run 1, 171 mg (62% yield, 98% ee); Run 2, 168 mg (61% yield, 98% ee).

The ee was determined on an AD-H column (0.25% *i*-PrOH/hexane, flow rate 0.6 mL/min); retention times for compound obtained using (4*R*,5*S*)-**L***: 15.9 min (minor), 24.0 min (major).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 – 7.87 (m, 2H), 7.51 – 7.48 (m, 3H), 7.43 – 7.40 (m, 2H), 7.38 – 7.33 (m, 3H), 3.60 (td, 1H, *J* = 5.6, 10.8 Hz), 3.45 (td, 1H, *J* = 4.9, 10.7 Hz), 2.91 (dddd, 1H, *J* = 5.6, 10.8, 14.5, 23.5 Hz), 2.70 (dddd, 1H, *J* = 4.9, 10.9, 14.5, 22.9 Hz);

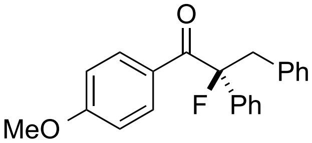
^{13}C NMR (126 MHz, $CDCl_3$) δ 196.6 (d, *J* = 27.4 Hz), 137.6 (d, *J* = 21.8 Hz), 134.1 (d, *J* = 3.5 Hz), 133.0, 130.1 (d, *J* = 5.7 Hz), 129.1 (d, *J* = 2.1 Hz), 128.7, 128.3 (d, *J* = 0.6 Hz), 123.8 (d, *J* = 9.1 Hz), 102.1 (d, *J* = 190.5 Hz), 42.6 (d, *J* = 22.6 Hz), 38.6 (d, *J* = 5.0 Hz);

^{19}F NMR (282 MHz, $CDCl_3$) δ −163.2 (t, 1F, *J* = 23.2 Hz);

FT-IR (film) 3061, 2971, 1686, 1597, 1448, 1265, 1065, 758, 709 cm^{-1};

MS (ESI) *m*/*z* (M+Na$^+$) calcd for $C_{16}H_{14}ClFNaO$: 299, found: 299;

$[\alpha]^{25}_{D} = -201°$ (*c* = 0.99, $CHCl_3$); 98% ee, from (4*R*,5*S*)-**L***.



(*S*)-2-Fluoro-1-(4-methoxyphenyl)-2,3-diphenylpropan-1-one (Table 2, Entry 7). 2-Bromo-2-fluoro-1-(4-methoxyphenyl)-3-phenylpropan-1-one (337 mg, 1.00 mmol) and the arylzinc chloride reagent prepared from bromobenzene were used. Solvent system for chromatography: 8:1→3:1 hexane/dichloromethane. The title compound was isolated as a white solid.

Run 1, 205 mg (61% yield, 97% ee); Run 2, 212 mg (63% yield, 95% ee).

The ee was determined on an AD-H column (2% *i*-PrOH/hexane, flow rate 0.8 mL/min); retention times for compound obtained using (4*R*,5*S*)-**L***: 23.7 min (minor), 25.1 min (major).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.83 (m, 2H), 7.40 – 7.38 (m, 2H), 7.34 – 7.27 (m, 3H), 7.18 – 7.15 (m, 3H), 7.07 – 7.04 (m, 2H), 6.80 – 6.77 (m, 2H), 3.79 (s, 3H), 3.71 (dd, 1H, *J* = 14.4, 23.8 Hz), 3.45 (dd, 1H, *J* = 14.4, 27.0 Hz);

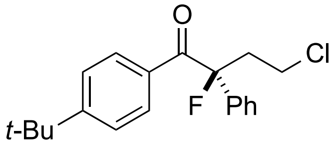
^{13}C NMR (126 MHz, $CDCl_3$) δ 195.9 (d, *J* = 26.8 Hz), 163.3, 138.7 (d, *J* = 22.2 Hz), 134.8, 132.6 (d, *J* = 6.7 Hz), 130.9, 128.5 (d, *J* = 2.0 Hz), 128.1, 127.8, 127.5 (d, *J* = 3.6 Hz), 126.6, 124.2 (d, *J* = 8.9 Hz), 113.4 (d, *J* = 1.2 Hz), 102.8 (d, *J* = 191.7 Hz), 55.3, 45.4 (d, *J* = 22.6 Hz);

^{19}F NMR (282 MHz, $CDCl_3$) δ −160.1 (t, 1F, *J* = 25.2 Hz);

FT-IR (film) 3031, 1676, 1600, 1259, 1175, 1030, 839, 751 cm^{-1};

MS (ESI) *m*/*z* (M+Na$^+$) calcd for $C_{22}H_{19}FNaO_2$: 357, found: 357;

$[\alpha]^{25}_{D} = -157°$ (*c* = 0.98, $CHCl_3$); 97% ee, from (4*R*,5*S*)-**L***.



(*S*)-1-(4-(*tert*-Butyl)phenyl)-4-chloro-2-fluoro-2-phenylbutan-1-one (Table 2, Entry 8). 2-Bromo-1-(4-(*tert*-butyl)phenyl)-4-chloro-2-fluorobutan-1-one (336 mg, 1.00 mmol) and the arylzinc chloride reagent prepared from bromobenzene were used. Solvent system for chromatography: 25:1 hexane/dichloromethane. The title compound was isolated as a colorless oil.

Run 1, 245 mg (74% yield, 98% ee); Run 2, 257 mg (77% yield, 98% ee).

The ee was determined on an AD-H column (0.25% *i*-PrOH/hexane, flow rate 0.6 mL/min); retention times for compound obtained using (4*R*,5*S*)-**L***: 17.1 min (minor), 23.2 min (major).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.85 – 7.83 (m, 2H), 7.50 – 7.47 (m, 2H), 7.42 – 7.32 (m, 5H), 3.59 (td, 1H, *J* = 5.5, 10.8 Hz), 3.45 (td, 1H, *J* = 4.9, 10.8 Hz), 2.90 (dddd, 1H, *J* = 5.5, 10.9, 14.5, 23.8 Hz), 2.68 (dddd, 1H, *J* = 4.9, 11.0, 14.4, 22.6 Hz), 1.28 (s, 9H);

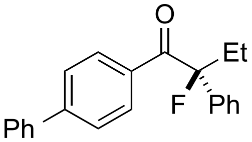
^{13}C NMR (126 MHz, CDCl$_3$) δ 196.0 (d, *J* = 26.8 Hz), 157.2, 137.8 (d, *J* = 22.0 Hz), 131.4 (d, *J* = 3.5 Hz), 130.2 (d, *J* = 6.0 Hz), 129.0 (d, *J* = 1.8 Hz), 128.6, 125.3, 123.8 (d, *J* = 9.1 Hz), 102.2 (d, *J* = 190.5 Hz), 42.6 (d, *J* = 22.6 Hz), 38.7 (d, *J* = 5.0 Hz), 35.1, 30.9;

^{19}F NMR (282 MHz, CDCl$_3$) δ −162.9 (t, 1F, *J* = 23.3 Hz);

FT-IR (film) 2965, 1681, 1605, 1449, 1269, 1106, 707 cm^{-1};

MS (ESI) *m/z* (M+Na$^+$) calcd for $C_{20}H_{22}ClFNaO$: 355, found: 355;

$[\alpha]^{25}_D$ = +124° (*c* = 1.02, CHCl$_3$); 98% ee, from (4*S*,5*R*)-**L***.



(*S*)-1-([1,1'-Biphenyl]-4-yl)-2-fluoro-2-phenylbutan-1-one (Table 2, Entry 9). 1-([1,1'-Biphenyl]-4-yl)-2-bromo-2-fluorobutan-1-one (321 mg, 1.00 mmol) and the arylzinc chloride reagent prepared from bromobenzene were used. Solvent system for chromatography: 20:1→10:1 hexane/dichloromethane. The title compound was isolated as a colorless oil.

Run 1, 161 mg (51% yield, 96% ee); Run 2, 181 mg (57% yield, 95% ee).

The ee was determined on an AD-H column (2% *i*-PrOH/hexane, flow rate 0.8 mL/min); retention times for compound obtained using (4*R*,5*S*)-**L***: 13.9 min (minor), 17.6 min (major).

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.01 – 7.99 (m, 2H), 7.60 – 7.53 (m, 6H), 7.46 – 7.32 (m, 6H), 2.48 (ddq, 1H, *J* = 7.3, 14.6, 24.9 Hz), 2.23 (ddq, 1H, *J* = 7.4, 14.8, 24.4 Hz), 0.95 (t, 3H, *J* = 7.3 Hz);

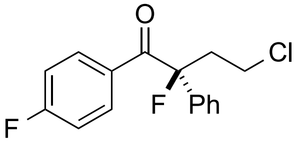
^{13}C NMR (126 MHz, CDCl$_3$) δ 197.8 (d, *J* = 27.9 Hz), 145.6, 139.9, 138.8 (d, *J* = 22.2 Hz), 133.7 (d, *J* = 3.8 Hz), 130.6 (d, *J* = 6.7 Hz), 128.9, 128.7 (d, *J* = 1.8 Hz), 128.2, 128.1, 127.2, 126.8 (d, *J* = 0.9 Hz), 124.1 (d, *J* = 8.8 Hz), 103.8 (d, *J* = 189.5 Hz), 32.8 (d, *J* = 23.8 Hz), 7.5 (d, *J* = 4.6 Hz).

^{19}F NMR (282 MHz, CDCl$_3$) δ −165.0 (t, 1F, *J* = 24.7 Hz);

FT-IR (film) 3059, 3030, 2978, 2939, 2882, 1681, 1604, 1448, 1259, 1008, 857, 760, 748, 738 cm^{-1};

MS (ESI) *m/z* (M+Na$^+$) calcd for $C_{22}H_{19}FNaO$: 341, found: 341;

$[\alpha]^{25}_D$ = −46.2° (*c* = 1.02, CHCl$_3$); 96% ee, from (4*R*,5*S*)-**L***.



(*S*)-4-Chloro-2-fluoro-1-(4-fluorophenyl)-2-phenylbutan-1-one (Table 2, Entry 10). 2-Bromo-4-chloro-2-fluoro-1-(4-fluorophenyl)butan-1-one (298 mg, 1.00 mmol) and the arylzinc chloride reagent prepared from bromobenzene were used. Solvent system for chromatography: 25:1 hexane/dichloromethane. The title compound was isolated as a colorless oil.

Run 1, 181 mg (61% yield, 97% ee); Run 2, 192 mg (65% yield, 97% ee).

The ee was determined on an AD-H column (0.25% *i*-PrOH/hexane, flow rate 0.6 mL/min); retention times for compound obtained using (4*R*,5*S*)-**L***: 17.5 min (minor), 20.9 min (major).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.94 (ddd, 2H, *J* = 1.7, 5.4, 9.0 Hz), 7.47 – 7.34 (m, 5H), 7.04 – 7.01 (m, 2H), 3.59 (td, 1H, *J* = 5.6, 10.7 Hz), 3.44 (td, 1H, *J* = 4.9, 10.7 Hz), 2.90 (dddd, 1H, *J* = 5.6, 10.7, 14.5, 23.4 Hz), 2.70 (dddd, 1H, *J* = 4.9, 10.8, 14.5, 23.2 Hz);

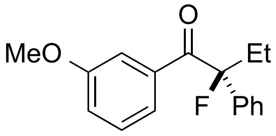
^{13}C NMR (126 MHz, CDCl$_3$) δ 194.8 (d, *J* = 27.1 Hz), 165.7 (d, *J* = 256.6 Hz), 137.4 (d, *J* = 22.0 Hz), 133.0 (dd, *J* = 6.6, 9.5 Hz), 130.3 (t, *J* = 3.4 Hz), 129.1 (d, *J* = 2.0 Hz), 128.8 (d, *J* = 0.9 Hz), 123.7 (d, *J* = 9.1 Hz), 115.5 (d, *J* = 21.5 Hz), 102.2 (d, *J* = 190.3 Hz), 42.4 (d, *J* = 22.6), 38.5 (d, *J* = 5.1 Hz);

^{19}F NMR (282 MHz, CDCl$_3$) δ −103.9 (m, 1F), −163.0 (t, 1F, *J* = 23.3 Hz);

FT-IR (film) 1685, 1599, 1506, 1449, 1263, 1239, 1160, 845, 743 cm^{-1};

MS (ESI) *m*/*z* (M+Na$^+$) calcd for $C_{16}H_{13}ClF_2NaO$: 317, found: 317;

$[\alpha]^{25}_D$ = +174° (*c* = 1.06, CHCl$_3$); 97% ee, from (4*S*,5*R*)-**L***.



(*S*)-2-Fluoro-1-(3-methoxyphenyl)-2-phenylbutan-1-one (Table 2, Entry 11). 2-Bromo-2-fluoro-1-(3-methoxyphenyl)butan-1-one (275 mg, 1.00 mmol) and the arylzinc chloride reagent prepared from bromobenzene were used. Solvent system for chromatography: 10:1→5:1 hexane/dichloromethane. The title compound was isolated as a white solid.

Run 1, 154 mg (57% yield, 97% ee); Run 2, 140 mg (51% yield, 97% ee).

The ee was determined on an AD-H column (2% *i*-PrOH/hexane, flow rate 0.6 mL/min); retention times for compound obtained using (4*R*,5*S*)-**L***: 9.9 min (minor), 11.6 min (major).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.51 – 7.48 (m, 3H), 7.42 – 7.37 (m, 3H), 7.33 – 7.30 (m, 1H), 7.27 – 7.24 (m, 1H), 7.03 (ddd, 1H, *J* = 1.0, 2.7, 8.2 Hz), 3.78 (s, 3H), 2.45 (ddq, 1H, *J* = 7.3, 14.6, 24.6 Hz), 2.20 (ddq, 1H, *J* = 7.4, 14.7, 24.5 Hz), 0.93 (t, 3H, *J* = 7.3 Hz);

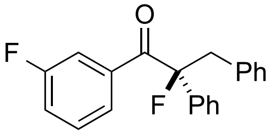
^{13}C NMR (126 MHz, CDCl$_3$) δ 198.1 (d, *J* = 28.6 Hz), 159.2, 138.8 (d, *J* = 22.1 Hz), 136.2 (d, *J* = 3.5 Hz), 129.1 (d, *J* = 1.5 Hz), 128.7 (d, *J* = 1.8 Hz), 128.1, 124.0 (d, *J* = 9.0 Hz), 122.6 (d, *J* = 7.6 Hz), 119.4, 114.2 (d, *J* = 5.0 Hz), 103.6 (d, *J* = 190.0 Hz), 55.3, 32.7 (d, *J* = 23.7 Hz), 7.4 (d, *J* = 4.5 Hz);

^{19}F NMR (282 MHz, CDCl$_3$) δ −165.2 (t, 1F, *J* = 24.6 Hz);

FT-IR (film) 2975, 2942, 1686, 1579, 1446, 1431, 1270, 1218, 763, 734 cm^{-1};

MS (ESI) *m*/*z* (M+Na$^+$) calcd for $C_{17}H_{17}FNaO_2$: 295, found: 295;

$[\alpha]^{25}_D$ = −158° (*c* = 1.03, CHCl$_3$); 97% ee, from (4*R*,5*S*)-**L***.



(*S*)-2-Fluoro-1-(3-fluorophenyl)-2,3-diphenylpropan-1-one (Table 2, Entry 12). 2-Bromo-2-fluoro-1-(3-fluorophenyl)-3-phenylpropan-1-one (325 mg, 1.00 mmol) and the arylzinc chloride reagent prepared from bromobenzene were used. Solvent system for chromatography: 7.5%→10%→12.5% dichloromethane in hexane. The title compound was isolated as a white solid.

Run 1, 197 mg (61% yield, 97% ee); Run 2, 185 mg (57% yield, 97% ee).

The ee was determined on an AD-H column (0.25% *i*-PrOH/hexane, flow rate 0.8 mL/min); retention times for compound obtained using (4*R*,5*S*)-**L***: 12.4 min (minor), 14.0 min (major).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.56 (dtd, 1H, *J* = 1.0, 1.7, 7.8 Hz), 7.46 (ddt, 1H, *J* = 1.5, 2.8, 9.7 Hz), 7.43 – 7.41 (m, 2H), 7.38 – 7.26 (m, 4H), 7.21 – 7.18 (m, 3H), 7.15 (tdd, 1H, *J* = 1.0, 2.7, 8.3 Hz), 7.10 – 7.07 (m, 2H), 3.73 (dd, 1H, *J* = 14.4, 25.3 Hz), 3.45 (dd, 1H, *J* = 14.4, 25.7 Hz);

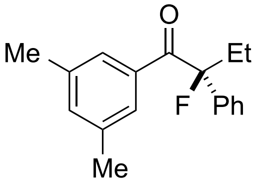
^{13}C NMR (126 MHz, CDCl$_3$) δ 196.8 (dd, *J* = 2.3, 28.4 Hz), 162.1 (d, *J* = 247.2 Hz), 137.9 (d, *J* = 22.1 Hz), 136.7 (dd, *J* = 3.5, 6.6 Hz), 134.4, 130.9 (d, *J* = 0.7 Hz), 129.7 (d, *J* = 7.9 Hz), 128.7 (d, *J* = 1.9 Hz), 128.5, 127.9, 126.8, 125.7 (dd, *J* = 3.2, 6.7 Hz), 124.2 (d, *J* = 8.9 Hz), 119.9 (d, *J* = 21.4 Hz), 116.7 (dd, *J* = 6.3, 23.1 Hz), 102.8 (d, *J* = 191.8 Hz), 45.5 (d, *J* = 22.2 Hz).

^{19}F NMR (282 MHz, CDCl$_3$) δ −112.2 (m, 1F), −161.3 (t, 1F, *J* = 25.5 Hz);

FT-IR (film) 1687, 1643, 1586, 1438, 1269, 770, 733 cm^{-1};

MS (ESI) *m*/*z* (M+Na$^+$) calcd for $C_{21}H_{16}F_2NaO$: 345, found: 345;

$[\alpha]^{25}_D$ = +192° (*c* = 0.98, CHCl$_3$); 97% ee, from (4*S*,5*R*)-**L***.



(*S*)-1-(3,5-Dimethylphenyl)-2-fluoro-2-phenylbutan-1-one (Table 2, Entry 13). 2-Bromo-1-(3,5-dimethylphenyl)-2-fluorobutan-1-one (273 mg, 1.00 mmol) and the arylzinc chloride reagent prepared from bromobenzene were used. Solvent system for chromatography: 20:1 hexane/dichloromethane. The title compound was isolated as a colorless oil.

Run 1, 166 mg (61% yield, 97% ee); Run 2, 187 mg (69% yield, 96% ee).

The ee was determined on an AD-H column (0.05% *i*-PrOH/hexane, flow rate 0.3 mL/min); retention times for compound obtained using (4*R*,5*S*)-**L***: 21.2 min (minor), 22.3 min (major).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.53 – 7.49 (m, 4H), 7.41 – 7.38 (m, 2H), 7.34 – 7.30 (m, 1H), 7.13 – 7.12 (m, 1H), 2.44 (ddq, 1H, *J* = 7.3, 14.7, 25.4 Hz), 2.29 (s, 6H), 2.19 (ddq, 1H, *J* = 7.4, 14.7, 23.8 Hz), 0.93 (t, 3H, *J* = 7.4 Hz);

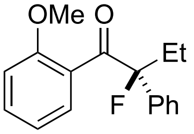
^{13}C NMR (126 MHz, CDCl$_3$) δ 199.0 (d, *J* = 28.2 Hz), 138.9 (d, *J* = 22.1 Hz), 137.7, 135.2 (d, *J* = 3.4 Hz), 134.6, 128.6 (d, *J* = 1.8 Hz), 128.0 (d, *J* = 1.0 Hz), 127.6 (d, *J* = 6.3 Hz), 124.1 (d, *J* = 9.2 Hz), 103.7 (d, *J* = 189.9 Hz), 32.9 (d, *J* = 23.7 Hz), 21.2, 7.5 (d, *J* = 4.4 Hz);

^{19}F NMR (282 MHz, CDCl$_3$) δ −165.0 (t, 1F, *J* = 24.6 Hz);

FT-IR (film) 2977, 2923, 1682, 1604, 1448, 1303, 1207, 1060, 975, 762, 733 cm^{-1};

MS (ESI) *m*/*z* (M+Na$^+$) calcd for $C_{18}H_{19}FNaO$: 293, found: 293;

[α]$^{25}_{D}$ = −132° (*c* = 1.02, $CHCl_3$); 97% ee, from (4*R*,5*S*)-**L***.



(*S*)-2-Fluoro-1-(2-methoxyphenyl)-2-phenylbutan-1-one (Table 2, Entry 14). 2-Bromo-2-fluoro-1-(2-methoxyphenyl)butan-1-one (275 mg, 1.00 mmol) and the arylzinc chloride reagent prepared from bromobenzene were used. Solvent system for chromatography: 10:1→5:1 hexane/dichloromethane. The title compound was isolated as a light-yellow oil.

Run 1, 174 mg (64% yield, 92% ee); Run 2, 160 mg (59% yield, 92% ee).

The ee was determined on an AD-H column (2% *i*-PrOH/hexane, flow rate 0.6 mL/min); retention times for compound obtained using (4*R*,5*S*)-**L***: 11.4 min (minor), 26.7 min (major).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.50 (m, 2H), 7.41 – 7.36 (m, 3H), 7.34 – 7.31 (m, 1H), 7.06 (ddd, 1H, *J* = 0.8, 1.7, 7.7 Hz), 6.91 – 6.88 (m, 2H), 3.67 (s, 3H), 2.46 (ddq, 1H, *J* = 7.3, 14.6, 24.3 Hz), 2.20 (ddq, 1H, *J* = 7.4, 14.7, 24.0 Hz), 0.94 (t, 3H, *J* = 7.4 Hz);

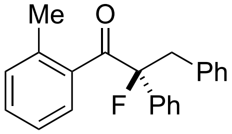
^{13}C NMR (126 MHz, $CDCl_3$) δ 204.4 (d, *J* = 33.4 Hz), 157.2 (d, *J* = 1.5 Hz), 138.6 (d, *J* = 22.8 Hz), 131.9, 128.4 (d, *J* = 3.1 Hz), 128.2 (d, *J* = 2.0 Hz), 128.0 (d, *J* = 2.2 Hz), 127.7, 124.5 (d, *J* = 9.6 Hz), 120.0, 111.2, 103.0 (d, *J* = 190.4 Hz), 55.3, 33.0 (d, *J* = 23.1 Hz), 7.5 (d, *J* = 4.0 Hz);

^{19}F NMR (282 MHz, $CDCl_3$) δ −169.3 (t, 1F, *J* = 24.1 Hz);

FT-IR (film) 2976, 2940, 1708, 1598, 1488, 1462, 1290, 1256, 1024, 754 cm^{-1};

MS (ESI) *m*/*z* (M+Na$^+$) calcd for $C_{17}H_{17}FNaO_2$: 295, found: 295;

[α]$^{25}_{D}$ = −96.5° (*c* = 1.03, $CHCl_3$); 92% ee, from (4*R*,5*S*)-**L***.



(*S*)-2-Fluoro-2,3-diphenyl-1-(*o*-tolyl)propan-1-one (Table 2, Entry 15). 2-Bromo-2-fluoro-3-phenyl-1-(*o*-tolyl)propan-1-one (321 mg, 1.00 mmol) and the arylzinc chloride reagent prepared from bromobenzene were used. Solvent system for chromatography: 7.5%→10%→12.5% dichloromethane in hexane. The title compound was isolated as a colorless oil.

Run 1, 219 mg (69% yield, 94% ee); Run 2, 224 mg (70% yield, 94% ee).

The ee was determined on an AD-H column (2% *i*-PrOH/hexane, flow rate 0.8 mL/min); retention times for compound obtained using (4*R*,5*S*)-**L***: 6.9 min (minor), 9.0 min (major).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.57 (m, 2H), 7.45 – 7.41 (m, 2H), 7.40 – 7.36 (m, 1H), 7.27 – 7.23 (m, 6H), 7.13 (dt, 1H, *J* = 0.7, 7.7 Hz), 7.03 – 6.99 (m, 1H), 6.88 (ddd, 1H, *J* = 1.3, 3.2, 7.8 Hz), 3.82 (dd, 1H, *J* = 14.3, 31.1 Hz), 3.44 (dd, 1H, *J* = 14.3, 19.8 Hz), 2.00 (s, 3H);

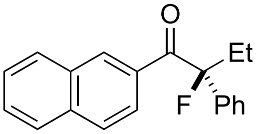
^{13}C NMR (126 MHz, CDCl$_3$) δ 203.5 (d, *J* = 31.8 Hz), 138.3 (d, *J* = 22.6 Hz), 137.2, 136.4 (d, *J* = 2.5 Hz), 134.7, 131.1 (d, *J* = 1.1 Hz), 131.0, 130.5, 128.6 (d, *J* = 1.7 Hz), 128.4, 128.0, 127.8 (d, *J* = 7.1 Hz), 126.9, 124.5, 124.4 (d, *J* = 9.5 Hz), 102.6 (d, *J* = 192.8 Hz), 45.8 (d, *J* = 21.7 Hz), 19.5.

^{19}F NMR (282 MHz, CDCl$_3$) δ −161.4 (ddd, 1F, *J* = 3.1, 19.8, 31.1 Hz);

FT-IR (film) 3063, 3031, 2927, 1694, 1496, 1455, 1448, 1253, 934, 761, 746, 732 cm^{-1};

MS (ESI) *m*/*z* (M+Na$^+$) calcd for $C_{22}H_{19}FNaO$: 341, found: 341;

$[\alpha]^{25}_D$ = −138° (*c* = 1.03, CHCl$_3$); 94% ee, from (4*R*,5*S*)-**L***.



(*S*)-2-Fluoro-1-(naphthalen-2-yl)-2-phenylbutan-1-one (Table 2, Entry 16). 2-Bromo-2-fluoro-1-(naphthalen-2-yl)butan-1-one (295 mg, 1.00 mmol) and the arylzinc chloride reagent prepared from bromobenzene were used. Solvent system for chromatography: 25:1→20:1 hexane/dichloromethane. The title compound was isolated as a colorless oil.

Run 1, 145 mg (50% yield, 97% ee); Run 2, 151 mg (52% yield, 96% ee).

The ee was determined on an AD-H column (0.5% *i*-PrOH/hexane, flow rate 0.6 mL/min); retention times for compound obtained using (4*R*,5*S*)-**L***: 16.0 min (minor), 23.7 min (major).

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.51 (s, 1H), 7.95 (dt, 1H, *J* = 1.7, 8.7 Hz), 7.88 (dd, 1H, *J* = 1.2, 8.2 Hz), 7.82 – 7.79 (m, 2H), 7.59 – 7.54 (m, 3H), 7.51 – 7.48 (m, 1H), 7.43 – 7.40 (m, 2H), 7.35 – 7.31 (m, 1H), 2.53 (ddq, 1H, *J* = 7.3, 14.6, 24.8 Hz), 2.27 (ddq, 1H, *J* = 7.4, 14.7, 24.5 Hz), 0.98 (t, 3H, *J* = 7.3 Hz);

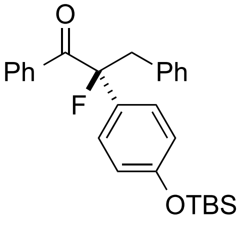
^{13}C NMR (126 MHz, CDCl$_3$) δ 198.2 (d, *J* = 27.7 Hz), 138.9 (d, *J* = 22.2 Hz), 135.3, 132.24 (d, *J* = 3.5 Hz), 132.18 (d, *J* = 1.2 Hz), 132.13 (d, *J* = 8.6 Hz), 129.8, 128.7 (d, *J* = 1.8 Hz), 128.5, 128.1, 127.8, 127.6, 126.5, 125.4 (d, *J* = 4.5 Hz), 124.1 (d, *J* = 8.9 Hz), 103.9 (d, *J* = 189.6 Hz), 32.8 (d, *J* = 23.6 Hz), 7.5 (d, *J* = 4.5 Hz).

^{19}F NMR (282 MHz, CDCl$_3$) δ −164.6 (t, 1F, *J* = 24.6 Hz);

FT-IR (film) 3060, 2978, 2940, 1681, 1627, 1448, 1278, 775, 762, 749 cm^{-1};

MS (ESI) *m*/*z* (M+Na$^+$) calcd for $C_{20}H_{17}FNaO$: 315, found: 315;

$[\alpha]^{25}_D$ = −10.2° (*c* = 1.05, CHCl$_3$); 97% ee, from (4*R*,5*S*)-**L***.



(*S*)-2-(4-((*tert*-Butyldimethylsilyl)oxy)phenyl)-2-fluoro-1,3-diphenylpropan-1-one (Table 3, Entry 1). 2-Bromo-2-fluoro-1,3-diphenylpropan-1-one (307 mg, 1.00 mmol) and the arylzinc chloride reagent prepared from (4-bromophenoxy)(*tert*-butyl)dimethylsilane were used.

Solvent system for chromatography: 20:1→10:1 hexane/dichloromethane. The title compound was isolated as a colorless oil.

Run 1, 300 mg (69% yield, 97% ee); Run 2, 277 mg (64% yield, 97% ee).

The ee was determined of 2-fluoro-2-(4-hydroxyphenyl)-1,3-diphenylpropan-1-one (obtained by deprotection of the TBS group with TBAF) on an AD-H column (10% *i*-PrOH/hexane, flow rate 1.0 mL/min); retention times for compound obtained using (4*R*,5*S*)-**L***: 16.0 min (minor), 18.4 min (major).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.76 (m, 2H), 7.46 – 7.43 (m, 1H), 7.33 – 7.29 (m, 2H), 7.28 – 7.25 (m, 2H), 7.19 – 7.17 (m, 3H), 7.07 – 7.05 (m, 2H), 6.83 – 6.80 (m, 2H), 3.68 (dd, 1H, *J* = 14.3, 24.0 Hz), 3.45 (dd, 1H, *J* = 14.4, 26.7 Hz), 0.98 (s, 9H), 0.19 (s, 6H);

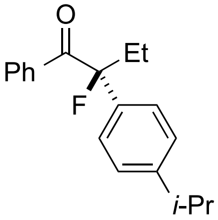
^{13}C NMR (126 MHz, $CDCl_3$) δ 198.3 (d, *J* = 28.1 Hz), 155.7, 135.0 (d, *J* = 3.2 Hz), 134.7, 132.8, 130.94 (d, *J* = 22.4 Hz), 130.94, 129.9 (d, *J* = 5.9 Hz), 128.0, 127.8, 126.6, 125.6 (d, *J* = 8.5 Hz), 120.2 (d, *J* = 1.5 Hz), 102.6 (d, *J* = 190.7 Hz), 45.4 (d, *J* = 22.7 Hz), 25.6, 18.2, −4.4 (d, *J* = 2.6 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ −159.6 (t, 1F, *J* = 25.4 Hz);

FT-IR (film) 2955, 2929, 2857, 1686, 1606, 1508, 1260, 913, 839, 782, 698 cm^{-1};

MS (ESI) *m*/*z* (M+Na$^+$) calcd for $C_{27}H_{31}FNaO_2Si$: 457, found: 457;

$[\alpha]^{25}_D = -156°$ (*c* = 1.05, $CHCl_3$); 97% ee, from (4*R*,5*S*)-**L***.



(*S*)-2-Fluoro-2-(4-isopropylphenyl)-1-phenylbutan-1-one (Table 3, Entry 2). 2-Bromo-2-fluoro-1-phenylbutan-1-one (245 mg, 1.00 mmol) and the arylzinc chloride reagent prepared from 1-bromo-4-isopropylbenzene were used. Solvent system for chromatography: 20:1 hexane/dichloromethane. The title compound was isolated as a light-yellow oil.

Run 1, 205 mg (72% yield, 97% ee); Run 2, 198 mg (70% yield, 97% ee).

The ee was determined on an AD-H column (0.25% *i*-PrOH/hexane, flow rate 0.7 mL/min); retention times for compound obtained using (4*R*,5*S*)-**L***: 8.4 min (minor), 12.5 min (major).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 – 7.90 (m, 2H), 7.50 – 7.46 (m, 1H), 7.44 – 7.41 (m, 2H), 7.38 – 7.35 (m, 2H), 7.26 – 7.24 (m, 2H), 2.93 – 2.88 (m, 1H), 2.45 (ddq, 1H, *J* = 7.3, 14.6, 25.6 Hz), 2.19 (ddq, 1H, *J* = 7.4, 14.7, 23.6 Hz), 1.24 (dd, 6H, *J* = 1.4, 6.9 Hz), 0.94 (t, 3H, *J* = 7.3 Hz);

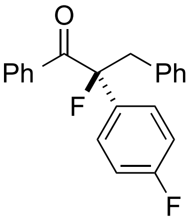
^{13}C NMR (126 MHz, $CDCl_3$) δ 198.7 (d, *J* = 28.4 Hz), 148.7, 136.1 (d, *J* = 22.1 Hz), 135.2 (d, *J* = 3.4 Hz), 132.8, 130.0 (d, *J* = 6.3 Hz), 128.1, 126.7 (d, *J* = 1.8 Hz), 124.1 (d, *J* = 9.0 Hz), 103.8 (d, *J* = 189.0 Hz), 33.7, 32.8 (d, *J* = 23.6 Hz), 23.9 (d, *J* = 2.7 Hz), 7.5 (d, *J* = 4.6 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ −164.6 (t, 1F, *J* = 24.6 Hz);

FT-IR (film) 2961, 2871, 1671, 1448, 1260, 1219, 826 cm^{-1};

MS (ESI) *m*/*z* (M+Na$^+$) calcd for $C_{19}H_{21}FNaO$: 307, found: 307;

$[\alpha]^{25}_D = +38.4°$ (*c* = 0.97, $CHCl_3$); 97% ee, from (4*S*,5*R*)-**L***.



(*S*)-2-Fluoro-2-(4-fluorophenyl)-1,3-diphenylpropan-1-one (Table 3, Entry 3). 2-Bromo-2-fluoro-1,3-diphenylpropan-1-one (307 mg, 1.00 mmol) and the arylzinc chloride reagent prepared from 1-bromo-4-fluorobenzene were used. The reaction was run at −20 °C for 36 h. Solvent system for chromatography: 20:1→10:1 hexane/dichloromethane. The title compound was isolated as a colorless oil.

Run 1, 210 mg (65% yield, 94% ee); Run 2, 211 mg (65% yield, 93% ee).

The ee was determined on an AD-H column (1% *i*-PrOH/hexane, flow rate 0.8 mL/min); retention times for compound obtained using (4*R*,5*S*)-**L***: 12.1 min (minor), 14.4 min (major).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 – 7.74 (m, 2H), 7.48 – 7.45 (m, 1H), 7.41 – 7.37 (m, 2H), 7.34 – 7.31 (m, 2H), 7.21 – 7.18 (m, 3H), 7.07 – 7.02 (m, 4H), 3.71 (dd, 1H, *J* = 14.4, 23.8 Hz), 3.45 (dd, 1H, *J* = 14.4, 27.2 Hz);

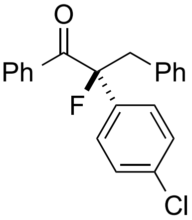
^{13}C NMR (126 MHz, $CDCl_3$) δ 198.1 (d, *J* = 27.8 Hz), 162.6 (d, *J* = 246.7 Hz), 134.8 (d, *J* = 3.3 Hz), 134.3, 134.1 (dd, *J* = 3.1, 22.7 Hz), 133.0, 130.9, 129.9 (d, *J* = 6.2 Hz), 128.1, 127.9, 126.8, 126.2 (t, *J* = 8.7 Hz), 115.6 (dd, *J* = 1.7, 21.8 Hz), 102.5 (d, *J* = 192.3 Hz), 45.5 (d, *J* = 22.6 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ −113.7 (m, 1F), −159.8 (t, 1F, *J* = 25.4 Hz);

FT-IR (film) 3064, 3031, 2927, 1686, 1508, 1260, 1236, 1162, 837 cm^{-1};

MS (ESI) *m*/*z* (M+Na$^+$) calcd for $C_{21}H_{16}F_2NaO$: 345, found: 345;

$[\alpha]^{25}_{D}$ = +191° (*c* = 1.06, $CHCl_3$); 93% ee, from (4*S*,5*R*)-**L***.



(*S*)-2-(4-Chlorophenyl)-2-fluoro-1,3-diphenylpropan-1-one (Table 3, Entry 4). 2-Bromo-2-fluoro-1,3-diphenylpropan-1-one (307 mg, 1.00 mmol) and the arylzinc chloride reagent prepared from 1-bromo-4-chlorobenzene were used. The reaction was run at −20 °C for 36 h. Solvent system for chromatography: 20:1→10:1 hexane/dichloromethane. The title compound was isolated as a colorless oil.

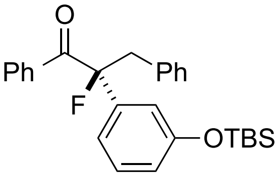
Run 1, 232 mg (68% yield, 93% ee); Run 2, 243 mg (72% yield, 93% ee).

The ee was determined on an AD-H column (1% *i*-PrOH/hexane, flow rate 0.8 mL/min); retention times for compound obtained using (4*R*,5*S*)-**L***: 13.3 min (minor), 18.2 min (major).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 – 7.73 (m, 2H), 7.48 – 7.45 (m, 1H), 7.36 – 7.30 (m, 6H), 7.20 – 7.18 (m, 3H), 7.07 – 7.05 (m, 2H), 3.70 (dd, 1H, *J* = 14.4, 23.7 Hz), 3.44 (dd, 1H, *J* = 14.4, 27.2 Hz);

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.9 (d, *J* = 27.7 Hz), 136.8 (d, *J* = 22.8 Hz), 134.7 (d, *J* = 3.5 Hz), 134.4, 134.2, 133.1, 130.9 (d, *J* = 1.0 Hz), 129.8 (d, *J* = 6.1 Hz), 128.8 (d, *J* = 1.8 Hz), 128.2, 127.9, 126.9, 125.8 (d, *J* = 9.0 Hz), 102.4 (d, *J* = 192.6 Hz), 45.4 (d, *J* = 22.4 Hz).

^{19}F NMR (282 MHz, CDCl$_3$) δ −160.6 (t, 1F, *J* = 25.6 Hz);
FT-IR (film) 3063, 3031, 1684, 1490, 1260, 1094, 1083, 733, 698 cm^{-1};
MS (ESI) *m*/*z* (M+Na$^+$) calcd for $C_{21}H_{16}ClFNaO$: 361, found: 361;
[α]$^{25}_{D}$ = −195° (*c* = 1.00, CHCl$_3$); 93% ee, from (4*R*,5*S*)-**L***.



(*S*)-2-(3-((*tert*-Butyldimethylsilyl)oxy)phenyl)-2-fluoro-1,3-diphenylpropan-1-one (Table 3, Entry 5). 2-Bromo-2-fluoro-1,3-diphenylpropan-1-one (307 mg, 1.00 mmol) and the arylzinc chloride reagent prepared from (3-bromophenoxy)(*tert*-butyl)dimethylsilane were used. Solvent system for chromatography: 15:1→10:1 hexane/dichloromethane. The title compound was isolated as a colorless oil.

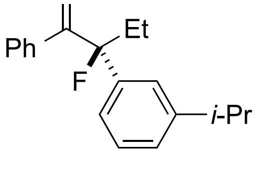
Run 1, 338 mg (78% yield, 99% ee); Run 2, 334 mg (77% yield, 99% ee).

The ee was determined of 2-fluoro-2-(3-hydroxyphenyl)-1,3-diphenylpropan-1-one (obtained by deprotection of the TBS group with TBAF) on an AD-H column (10% *i*-PrOH/hexane, flow rate 1.0 mL/min); retention times for compound obtained using (4*R*,5*S*)-**L***: 13.5 min (minor), 18.9 min (major).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.80 – 7.78 (m, 2H), 7.47 – 7.43 (m, 1H), 7.33 – 7.29 (m, 2H), 7.21 – 7.16 (m, 4H), 7.08 – 7.06 (m, 2H), 7.00 – 6.97 (m, 1H), 6.89 – 6.88 (m, 1H), 6.76 (ddd, 1H, *J* = 1.0, 2.4, 8.1 Hz), 3.68 (dd, 1H, *J* = 14.4, 22.9 Hz), 3.47 (dd, 1H, *J* = 14.4, 28.2 Hz), 0.95 (s, 9H), 0.12 (d, 6H, *J* = 1.0 Hz);

^{13}C NMR (126 MHz, CDCl$_3$) δ 197.7 (d, *J* = 28.0 Hz), 155.9 (d, *J* = 2.3 Hz), 139.7 (d, *J* = 22.2 Hz), 134.8 (d, *J* = 3.4 Hz), 134.6, 132.9, 130.9, 129.9 (d, *J* = 5.8 Hz), 129.7 (d, *J* = 1.7 Hz), 128.1, 127.8, 126.7, 120.0, 117.2 (d, *J* = 8.4 Hz), 116.1 (d, *J* = 9.6 Hz), 102.4 (d, *J* = 191.7 Hz), 45.2 (d, *J* = 22.4 Hz), 25.7, 18.2, −4.5 (d, *J* = 4.5 Hz).

^{19}F NMR (282 MHz, CDCl$_3$) δ −160.5 (dd, 1F, *J* = 22.9, 28.1 Hz);
FT-IR (film) 2956, 2929, 2858, 1685, 1599, 1484, 1280, 1258, 946, 830, 783, 696 cm^{-1};
MS (ESI) *m*/*z* (M+Na$^+$) calcd for $C_{27}H_{31}FNaO_2Si$: 457, found: 457;
[α]$^{25}_{D}$ = +180° (*c* = 1.05, CHCl$_3$); 99% ee, from (4*S*,5*R*)-**L***.



(*S*)-2-Fluoro-2-(3-isopropylphenyl)-1-phenylbutan-1-one (Table 3, Entry 6). 2-Bromo-2-fluoro-1-phenylbutan-1-one (245 mg, 1.00 mmol) and the arylzinc chloride reagent prepared from 1-bromo-3-isopropylbenzene were used. Solvent system for chromatography: 20:1 hexane/dichloromethane. The title compound was isolated as a light-yellow oil.

Run 1, 202 mg (71% yield, 98% ee); Run 2, 213 mg (75% yield, 96% ee).

The ee was determined on an AD-H column (100% hexane, flow rate 0.4 mL/min); retention times for compound obtained using (4*R*,5*S*)-**L***: 16.0 min (minor), 17.5 min (major).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.88 (m, 2H), 7.50 – 7.46 (m, 1H), 7.38 – 7.30 (m, 5H), 7.20 – 7.18 (m, 1H), 2.95 – 2.89 (m, 1H), 2.46 (ddq, 1H, *J* = 7.3, 14.6, 25.6 Hz), 2.20 (ddq, 1H, *J* = 7.4, 14.7, 23.6 Hz), 1.25 (dd, 6H, *J* = 0.7, 6.9 Hz), 0.94 (t, 3H, *J* = 7.3 Hz);

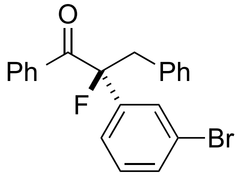
^{13}C NMR (126 MHz, $CDCl_3$) δ 198.6 (d, *J* = 28.8 Hz), 149.4 (d, *J* = 1.8 Hz), 138.7 (d, *J* = 22.3 Hz), 135.3 (d, *J* = 3.0 Hz), 132.8, 129.9 (d, *J* = 5.8 Hz), 128.6 (d, *J* = 1.6 Hz), 128.1, 126.1, 122.3 (d, *J* = 8.9 Hz), 121.6 (d, *J* = 9.3 Hz), 103.9 (d, *J* = 188.9 Hz), 34.2, 32.9 (d, *J* = 23.7 Hz), 23.9 (d, *J* = 11.0), 7.5 (d, *J* = 4.6 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ −164.6 (m, 1F);

FT-IR (film) 2962, 2882, 1682, 1598, 1447, 1258, 795, 703 cm^{-1};

MS (ESI) *m*/*z* (M+Na$^+$) calcd for $C_{19}H_{21}FNaO$: 307, found: 307;

$[\alpha]^{25}_D = -121°$ (*c* = 1.00, $CHCl_3$); 98% ee, from (4*R*,5*S*)-**L***.



(*S*)-2-(3-Bromophenyl)-2-fluoro-1,3-diphenylpropan-1-one (Table 3, Entry 7). 2-Bromo-2-fluoro-1,3-diphenylpropan-1-one (307 mg, 1.00 mmol) and the arylzinc chloride reagent prepared from 1,3-dibromobenzene were used. The reaction was run at −20 °C for 36 h. Solvent system for chromatography: 15:1 hexane/dichloromethane. The title compound was isolated as a colorless oil.

Run 1, 224 mg (58% yield, 92% ee); Run 2, 221 mg (58% yield, 90% ee).

The ee was determined on an AS-H column (0.05% *i*-PrOH/hexane, flow rate 0.6 mL/min); retention times for compound obtained using (4*R*,5*S*)-**L***: 18.0 min (major), 22.2 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 – 7.73 (m, 2H), 7.59 (t, 1H, *J* = 1.9 Hz), 7.49 – 7.43 (m, 2H), 7.37 – 7.31 (m, 3H), 7.24 – 7.18 (m, 4H), 7.09 – 7.07 (m, 2H), 3.71 (dd, 1H, *J* = 14.4, 25.3 Hz), 3.42 (dd, 1H, *J* = 14.4, 25.6 Hz);

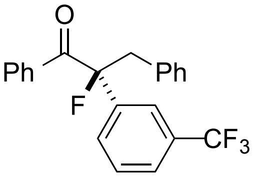
^{13}C NMR (126 MHz, $CDCl_3$) δ 197.7 (d, *J* = 27.9 Hz), 140.6 (d, *J* = 22.5 Hz), 134.7 (d, *J* = 3.6 Hz), 134.1, 133.1, 131.5, 130.9 (d, *J* = 1.2 Hz), 130.2 (d, *J* = 1.9 Hz), 129.8 (d, *J* = 6.2 Hz), 128.2, 128.0, 127.4 (d, *J* = 9.7 Hz), 126.9, 123.0 (d, *J* = 8.9 Hz), 122.9 (d, *J* = 2.3 Hz), 102.2 (d, *J* = 193.8 Hz), 45.6 (d, *J* = 22.3 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ −160.5 (t, 1F, *J* = 25.4 Hz);

FT-IR (film) 3063, 3031, 1685, 1596, 1567, 1260, 1076, 781, 715, 692 cm^{-1};

MS (ESI) *m*/*z* (M+Na$^+$) calcd for $C_{21}H_{16}{}^{79}BrFNaO$: 405, found: 405, 407 (M+Na$^+$+2);

$[\alpha]^{25}_D = -180°$ (*c* = 1.00, $CHCl_3$); 92% ee, from (4*R*,5*S*)-**L***.



(*S*)-2-Fluoro-1,3-diphenyl-2-(3-(trifluoromethyl)phenyl)propan-1-one (Table 3, Entry 8). 2-Bromo-2-fluoro-1,3-diphenylpropan-1-one (307 mg, 1.00 mmol) and the arylzinc chloride reagent prepared from 1-bromo-3-(trifluoromethyl)benzene were used. The reaction was run at −20 °C for 36 h. Solvent system for chromatography: 20:1→15:1 hexane/dichloromethane. The title compound was isolated as a colorless oil.

Run 1, 237 mg (64% yield, 90% ee); Run 2, 247 mg (66% yield, 90% ee).

The ee was determined on an OJ-H column (0.5% *i*-PrOH/hexane, flow rate 0.5 mL/min); retention times for compound obtained using (4*R*,5*S*)-**L***: 21.6 min (minor), 25.9 min (major).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.76 – 7.74 (m, 2H), 7.71 – 7.70 (m, 1H), 7.65 – 7.63 (m, 1H), 7.60 – 7.57 (m, 1H), 7.50 – 7.46 (m, 2H), 7.35 – 7.32 (m, 2H), 7.21 – 7.18 (m, 3H), 7.08 – 7.06 (m, 2H), 3.76 (dd, 1H, *J* = 14.4, 24.9 Hz), 3.46 (dd, 1H, *J* = 14.4, 26.2 Hz);

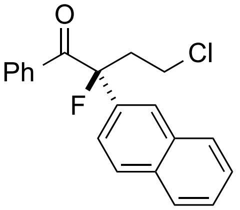
^{13}C NMR (126 MHz, CDCl$_3$) δ 197.8 (d, *J* = 27.9 Hz), 139.4 (d, *J* = 22.7 Hz), 134.7 (d, *J* = 3.6 Hz), 133.9, 133.2, 130.8 (d, *J* = 1.1 Hz), 129.8 (d, *J* = 6.4 Hz), 129.1 (d, *J* = 2.0 Hz), 128.2, 128.0, 127.7 (m), 127.0, 125.2 (m), 124.9, 122.7, 121.3 (m), 102.4 (d, *J* = 193.9), 45.7 (d, *J* = 22.3 Hz).

^{19}F NMR (282 MHz, CDCl$_3$) δ −62.7 (s, 3F), −160.7 (t, 1F, *J* = 25.6 Hz);

FT-IR (film) 3065, 3032, 1685, 1448, 1332, 1169, 1129, 1078, 699 cm^{-1};

MS (ESI) *m*/*z* (M+Na$^+$) calcd for $C_{22}H_{16}F_4NaO$: 395, found: 395;

$[\alpha]^{25}_{D}$ = −151° (*c* = 1.00, CHCl$_3$); 90% ee, from (4*R*,5*S*)-**L***.



(*S*)-4-Chloro-2-fluoro-2-(naphthalen-2-yl)-1-phenylbutan-1-one (Table 3, Entry 9). 2-Bromo-4-chloro-2-fluoro-1-phenylbutan-1-one (280 mg, 1.00 mmol) and the arylzinc chloride reagent prepared from 2-bromonaphthalene were used. Solvent system for chromatography: 20:1→15:1 hexane/dichloromethane. The title compound was isolated as a colorless oil.

Run 1, 190 mg (58% yield, 98% ee); Run 2, 190 mg (58% yield, 97% ee).

The ee was determined on an AD-H column (1% *i*-PrOH/hexane, flow rate 0.8 mL/min); retention times for compound obtained using (4*R*,5*S*)-**L***: 15.5 min (minor), 22.0 min (major).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.97 (d, 1H, *J* = 1.9 Hz), 7.93 – 7.83 (m, 5H), 7.58 (dd, 1H, *J* = 1.9, 8.6 Hz), 7.55 – 7.50 (m, 2H), 7.48 (ddt, 1H, *J* = 1.3, 7.2, 8.7 Hz), 7.36 – 7.33 (m, 2H), 3.64 (td, 1H, *J* = 5.5, 10.8 Hz), 3.48 (td, 1H, *J* = 4.9, 10.7 Hz), 3.00 (dddd, 1H, *J* = 5.5, 10.7, 14.5, 23.1 Hz), 2.81 (dddd, 1H, *J* = 4.9, 10.9, 14.5, 23.3 Hz);

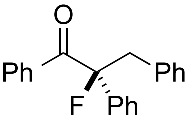
^{13}C NMR (126 MHz, CDCl$_3$) δ 196.6 (d, *J* = 27.0 Hz), 134.9 (d, *J* = 22.0 Hz), 134.1 (d, *J* = 3.5 Hz), 133.03 (d, *J* = 0.8 Hz), 132.99 (d, *J* = 1.8 Hz), 133.0, 130.2 (d, *J* = 6.3 Hz), 129.2 (d, *J* = 2.0 Hz), 128.29, 128.26, 128.25, 127.7, 126.8 (d, *J* = 3.9 Hz), 123.1 (d, *J* = 9.6 Hz), 121.2 (d, *J* = 8.6 Hz), 102.3 (d, *J* = 190.6 Hz), 42.5 (d, *J* = 22.5 Hz), 38.7 (d, *J* = 4.9 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ −162.6 (t, 1F, *J* = 23.2 Hz);

FT-IR (film) 3059, 2968, 1684, 1597, 1448, 1264, 1244, 819, 748, 708 cm^{-1};

MS (ESI) *m*/*z* (M+Na$^+$) calcd for $C_{20}H_{16}ClFNaO$: 349, found: 349;

$[\alpha]^{25}_D$ = +202° (*c* = 0.60, $CHCl_3$); 97% ee, from (4*S*,5*R*)-**L***.



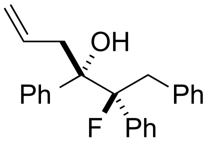
(*S*)-2-Fluoro-1,2,3-triphenylpropan-1-one (eq 3). 2-Chloro-2-fluoro-1,3-diphenylpropan-1-one (263 mg, 1.00 mmol) and the arylzinc chloride reagent prepared from bromobenzene were used. The reaction was run at −20 °C for 36 h. Solvent system for chromatography: 20:1→10:1 hexane/dichloromethane. The title compound was isolated as a white solid.

Run 1, 205 mg (67% yield, 98% ee); Run 2, 206 mg (68% yield, 98% ee).

The ee was determined on an AD-H column (2% *i*-PrOH/hexane, flow rate 0.6 mL/min); retention times for compound obtained using (4*R*,5*S*)-**L***: 12.4 min (minor), 14.3 min (major).

For the characterization data, see Table 2, Entry 2 (above).

IV. Derivatization of the Cross-Coupling Products



(2*S*,3*S*)-2-Fluoro-1,2,3-triphenylhex-5-en-3-ol (eq 4). A solution of allylmagnesium chloride (2.0 M in THF; 0.21 mL, 0.42 mmol; 1.2 equiv) was added over 1 min to a solution of (*S*)-2-fluoro-1,2,3-triphenylpropan-1-one (107 mg, 0.350 mmol; 98% ee; Table 2, entry 2; from a Negishi cross-coupling reaction using (4*R*,5*S*)-**L***) in THF (1.0 mL) at −78 °C. The mixture was allowed to stir at −78 °C for 10 min, and then it was stirred at r.t. for 60 min. Next, the reaction mixture was cooled to 0 °C, and aqueous NH_4Cl (saturated; 2 mL) was added to quench the reaction. The mixture was washed with brine and extracted with Et_2O (3 × 20 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated. The product was purified by flash chromatography on silica gel. Solvent system for chromatography: 50%→75% dichloromethane in hexane. The title compound was isolated as a white solid.

Run 1, 121 mg (100% yield, >20:1 dr, 97% ee); Run 2, 119 mg (98% yield, >20:1 dr, 97% ee).

The ee was determined on an AS-H column (1% *i*-PrOH/hexane, flow rate 1.0 mL/min); retention time: 7.5 min (major), 9.9 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 – 7.21 (m, 5H), 7.14 – 7.08 (m, 3H), 7.06 – 7.03 (m, 3H), 6.98 – 6.93 (m, 4H), 5.54 – 5.45 (m, 1H), 5.19 (d, 1H, *J* = 17.1 Hz), 5.09 (d, 1H, *J* = 10.2, Hz), 3.87 (dd, 1H, *J* = 10.3, 14.6 Hz), 3.20 (dd, 1H, *J* = 14.6, 41.7 Hz), 2.94-2.83 (m, 2H), 2.64 (s, 1H);

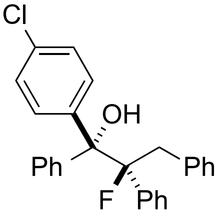
^{13}C NMR (126 MHz, CDCl$_3$) δ 140.0 (d, *J* = 2.4 Hz), 137.9 (d, *J* = 22.1 Hz), 136.0, 133.4, 130.7 (d, *J* = 1.8 Hz), 128.0 (d, *J* = 1.6 Hz), 127.5, 127.3, 127.23, 127.19, 127.0, 126.8, 126.0, 120.0, 102.6 (d, *J* = 185.9 Hz), 79.5 (d, *J* = 24.7 Hz), 40.3 (d, *J* = 3.9 Hz), 39.5 (d, *J* = 20.9 Hz);

^{19}F NMR (282 MHz, CDCl$_3$) δ −165.2 (dd, 1F, *J* = 10.3, 41.7 Hz);

FT-IR (film) 3552, 3060, 3029, 1497, 1446, 1032, 1000, 977, 722, 700 cm^{-1};

MS (ESI) *m*/*z* (M+Na$^+$) calcd for $C_{24}H_{23}FNaO$: 369, found: 369;

$[\alpha]^{25}_{D}$ = −73.3° (*c* = 0.97, CHCl$_3$).



(1*R*,2*S*)-1-(4-Chlorophenyl)-2-fluoro-1,2,3-triphenylpropan-1-ol (eq 5). A solution of *n*-BuLi in hexane (2.61 M; 0.17 mL, 0.46 mmol; 1.3 equiv) was added over 1 min to a solution of 1-chloro-4-bromobenzene (95.8 mg, 0.500 mmol; 1.43 equiv) in THF (0.7 mL) at −78 °C. The mixture was stirred at −78 °C for 10 min, and then a solution of (*S*)-2-fluoro-1,2,3-triphenylpropan-1-one (107 mg, 0.350 mmol; 98% ee; Table 2, entry 2; from a Negishi cross-coupling reaction using (4*R*,5*S*)-**L***) in THF (1.0 mL) was added to the aryllithium solution at −78 °C. The mixture was allowed to stir at −78 °C for 60 min, and then the reaction was quenched with aqueous NH$_4$Cl (saturated; 2 mL). The mixture was washed with brine and extracted with Et$_2$O (3 × 20 mL). The organic layers were combined, dried over Na$_2$SO$_4$, and concentrated. The product was purified by flash chromatography on silica gel. Solvent system for chromatography: 15%→50% dichloromethane in hexane. The title compound was isolated as a white solid.

Run 1, 137 mg (94% yield, >20:1 dr, 98% ee); Run 2, 143 mg (98% yield, >20:1 dr, 98% ee).

The ee was determined on an AS-H column (2% *i*-PrOH/hexane, flow rate 1.0 mL/min); retention times: 12.1 min (major), 15.6 min (minor).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.83 – 7.81 (m, 2H), 7.39 – 7.36 (m, 2H), 7.33 – 7.31 (m, 2H), 7.22 – 7.20 (m, 2H), 7.15 – 7.11 (m, 6H), 7.06 – 7.04 (m, 3H), 6.91 – 6.89 (m, 2H), 3.62 – 3.45 (m, 2H), 2.83 (s, 1H);

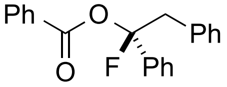
^{13}C NMR (126 MHz, CDCl$_3$) δ 142.9 (d, *J* = 1.3 Hz), 142.0 (d, *J* = 2.2 Hz), 138.4 (d, *J* = 22.3 Hz), 135.6 (d, *J* = 1.5 Hz), 133.2, 130.6 (d, *J* = 1.3 Hz), 129.3 (d, *J* = 5.2 Hz), 128.1, 127.57, 127.56, 127.4 (d, *J* = 1.2 Hz), 127.3 (d, *J* = 2.1 Hz), 127.2 (d, *J* = 2.2 Hz), 127.1 (m), 126.1, 102.6 (d, *J* = 190.6 Hz), 81.0 (d, *J* = 25.6 Hz), 41.4 (d, *J* = 20.3 Hz);

^{19}F NMR (282 MHz, CDCl$_3$) δ −161.3 (dd, 1F, *J* = 11.4, 37.6 Hz);

FT-IR (film) 3568, 3069, 3031, 1491, 1446, 1013, 746, 699 cm^{-1};

MS (ESI) *m*/*z* (M+Na$^+$) calcd for $C_{27}H_{22}ClFNaO$: 439, found: 439;

$[\alpha]^{25}_{D}$ = +65.6° (*c* = 0.99, CHCl$_3$).



(*S*)-1-Fluoro-1,2-diphenylethyl benzoate (eq 6). This procedure is based on a published procedure.[6] To a solution of (*S*)-2-fluoro-1,2,3-triphenylpropan-1-one (122 mg, 0.400 mmol; 98% ee; Table 2, entry 2; from a Negishi cross-coupling reaction using (4*R*,5*S*)-**L***) and 3-chloroperbenzoic acid (MCPBA, ≤77% purity; 448 mg, 2.00 mmol; 5.00 equiv) in CH_2Cl_2 (1.0 mL) was added 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP; 1.0 mL) and phosphate buffer solution (pH 7; 0.4 mL). The mixture was stirred vigorously at r.t. for 36 h. The reaction was then quenched with aqueous $Na_2S_2O_3$ (saturated; 7 mL). The mixture was washed with aqueous $NaHCO_3$ (saturated; 15 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated. The product was purified by flash chromatography on silica gel. Solvent system for chromatography: (1) flash chromatography on silica, 15%→30% dichloromethane in hexane; (2) preparative TLC on silica, 15% ethyl acetate in hexane. The title compound was isolated as a white solid.

Run 1, 104 mg (81% yield, 98% ee); Run 2, 104 mg (81% yield, 98% ee).

The ee was determined on an AD-H column (5% *i*-PrOH/hexane, flow rate 1.0 mL/min); retention times: 8.3 min (major), 10.6 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 8.02 (m, 2H), 7.61 – 7.58 (m, 1H), 7.48 – 7.44 (m, 2H), 7.35 – 7.33 (m, 5H), 7.28 – 7.25 (m, 3H), 7.15 – 7.13 (m, 2H), 3.63 – 3.51 (m, 2H);

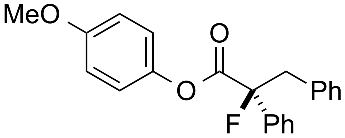
^{13}C NMR (126 MHz, $CDCl_3$) δ 163.1, 138.7 (d, *J* = 26.2 Hz), 133.5, 133.3 (d, *J* = 3.5 Hz), 130.9, 129.9, 129.8, 128.7 (d, *J* = 1.2 Hz), 128.5, 128.2, 128.0, 127.1, 124.7 (d, *J* = 6.9 Hz), 113.8 (d, *J* = 236.4 Hz), 47.4 (d, *J* = 26.4 Hz);

^{19}F NMR (282 MHz, $CDCl_3$) δ −113.5 (t, 1F, *J* = 17.5 Hz);

FT-IR (film) 3063, 3032, 2929, 1740, 1451, 1265, 1135, 1084, 1066, 1024, 1008, 999, 707, 701, 603 cm^{-1};

MS (ESI) *m*/*z* (M+Na$^+$) calcd for $C_{21}H_{17}FNaO_2$: 343, found: 343;

$[\alpha]^{25}_D = -74.2°$ (*c* = 0.97, $CHCl_3$).



4-Methoxyphenyl (*S*)-2-fluoro-2,3-diphenylpropanoate (eq 7). This procedure is based on a published procedure.[6] To a solution of (*S*)-2-fluoro-1-(4-methoxyphenyl)-2,3-diphenylpropan-1-one (117 mg, 0.350 mmol; 97% ee; Table 2, entry 7; from a Negishi cross-coupling reaction using (4*R*,5*S*)-**L***) and 3-chloroperbenzoic acid (MCPBA, 77% purity; 392 mg, 1.75 mmol; 5.00 equiv) in CH_2Cl_2 (1.0 mL) was added 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP; 1.0 mL) and phosphate buffer solution (pH 7; 0.4 mL). The mixture was stirred vigorously at r.t. for 36 h. The reaction was quenched with aqueous $Na_2S_2O_3$ (saturated; 7 mL). The mixture was washed with aqueous $NaHCO_3$ (saturated; 15 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The organic layers were

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(6) Kobayashi, S.; Tanaka, H.; Amii, H.; Uneyama, K. *Tetrahedron* **2003**, *59*, 1547−1552.

combined, dried over Na$_2$SO$_4$, and concentrated. The product was purified by flash chromatography on silica gel. Solvent system for chromatography: (1) flash chromatography on silica, 20%→50% dichloromethane in hexane; (2) preparative TLC on silica, 20% ethyl acetate in hexane. The title compound was isolated as a white solid.

Run 1, 104 mg (85% yield, 97% ee); Run 2, 100 mg (82% yield, 97% ee).

The ee was determined on an AD-H column (5% *i*-PrOH/hexane, flow rate 1.0 mL/min); retention times: 15.6 min (minor), 20.7 min (major).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.70 – 7.68 (m, 2H), 7.47 – 7.39 (m, 3H), 7.36 – 7.29 (m, 5H), 6.83 – 6.80 (m, 2H), 6.74 – 6.70 (m, 2H), 3.78 (dd, 1H, J = 14.5, 32.9 Hz), 3.76 (s, 3H), 3.51 (dd, 1H, J = 14.5, 18.4 Hz);

^{13}C NMR (126 MHz, CDCl$_3$) δ 168.8 (d, J = 27.1 Hz), 157.5, 143.5, 137.7 (d, J = 22.6 Hz), 134.1, 130.7 (d, J = 1.5 Hz), 128.8 (d, J = 1.3 Hz), 128.6 (d, J = 1.5 Hz), 128.3, 127.3, 124.8 (d, J = 9.3 Hz), 121.9, 114.4, 96.8 (d, J = 194.2 Hz), 55.5, 44.9 (d, J = 21.4 Hz);

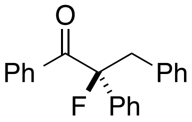
^{19}F NMR (282 MHz, CDCl$_3$) δ −161.8 (dd, 1F, J = 18.5, 32.8 Hz);

FT-IR (film) 3062, 3032, 2931, 2836, 1774, 1753, 1503, 1248, 1189, 1031, 696 cm^{-1};

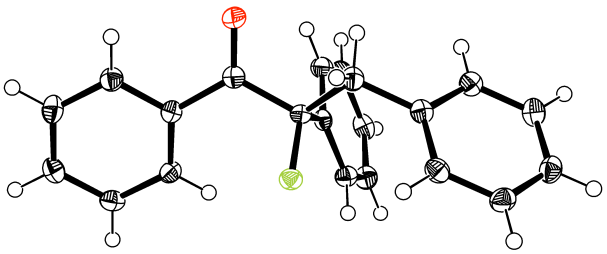
MS (ESI) *m*/*z* (M+H$^+$) calcd for C$_{22}$H$_{20}$FO$_3$: 351, found: 351;

$[\alpha]^{25}_{D}$ = +9.7° (*c* = 1.02, CHCl$_3$).

V. Assignment of the Absolute Stereochemistry of the Cross-Coupling Products



Absolute stereochemistry of product from Entry 2 of Table 2 (run with (4*R*,5*S*)-L*). (*S*)-2-Fluoro-1,2,3-triphenylpropan-1-one.



A crystal of C$_{21}$H$_{17}$F$_1$O$_1$ was selected and mounted in a nylon loop in immersion oil. All measurements were made on a Rigkau Saturn944+ with filtered Cu-Kα radiation at a temperature of 93 K. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Cryst. (2009). 42, 339–341.
2. SHELXS, G.M. Sheldrick, Acta Cryst. (2008). A64, 112–122
3. SHELXL, G.M. Sheldrick, Acta Cryst. (2008). A64, 112–122

Table S–1. Crystal data and structure refinement for crystal_001.

Identification code	crystal_001	
Empirical formula	$C_{21} H_{17} F_1 O_1$	
Formula weight	304.36	
Temperature	93 K	
Wavelength	1.54187 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 5.89490(10) Å	α= 90°.
	b = 15.2807(3) Å	β= 90 °.
	c = 17.2167(12) Å	γ = 90 °.
Volume	1550.85(12) Å^3	
Z	4	
Density (calculated)	1.303 Mg/m^3	
Absorption coefficient	0.697 mm^{-1}	
F(000)	640	
Crystal size	0.2 x 0.05 x 0.05 mm^3	
Theta range for data collection	3.868 to 68.146°.	
Index ranges	-7<=h<=7, -18<=k<=18, -20<=l<=20	
Reflections collected	53111	
Independent reflections	2831 [R(int) = 0.0685]	
Completeness to theta = 67.687°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.902	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2831 / 0 / 208	
Goodness-of-fit on F^2	1.063	
Final R indices [I>2sigma(I)]	R1 = 0.0252, wR2 = 0.0621	
R indices (all data)	R1 = 0.0258, wR2 = 0.0626	
Absolute structure parameter	0.06(4)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.102 and -0.154 e/Å^{-3}	

Table S–2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3)
for crystal_001. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1)	1126(2)	6163(1)	7538(1)	21(1)
O(1)	-3721(2)	5645(1)	6546(1)	27(1)
C(1)	-392(3)	6179(1)	5945(1)	19(1)
C(2)	-1906(3)	6014(1)	6624(1)	20(1)
C(3)	-1220(3)	6315(1)	7451(1)	18(1)
C(4)	-2440(3)	5754(1)	8058(1)	21(1)
C(5)	1456(3)	6748(1)	5966(1)	21(1)
C(6)	2811(3)	6861(1)	5316(1)	23(1)
C(7)	2325(3)	6410(1)	4638(1)	24(1)
C(8)	465(3)	5855(1)	4608(1)	26(1)
C(9)	-891(3)	5737(1)	5257(1)	23(1)
C(10)	-1677(3)	7287(1)	7554(1)	18(1)
C(11)	-3756(3)	7631(1)	7329(1)	23(1)
C(12)	-4232(3)	8511(1)	7445(1)	25(1)
C(13)	-2646(3)	9056(1)	7786(1)	25(1)
C(14)	-574(3)	8713(1)	8014(1)	25(1)
C(15)	-82(3)	7833(1)	7900(1)	22(1)
C(16)	-1913(3)	5999(1)	8888(1)	20(1)
C(17)	-3448(3)	6488(1)	9323(1)	22(1)
C(18)	-2990(3)	6698(1)	10091(1)	25(1)
C(19)	-997(3)	6417(1)	10435(1)	25(1)
C(20)	550(3)	5933(1)	10009(1)	25(1)
C(21)	97(3)	5726(1)	9239(1)	23(1)

Table S–3. Bond lengths [Å] and angles [°] for crystal_001.

F(1)-C(3)	1.4103(17)
O(1)-C(2)	1.216(2)
C(1)-C(2)	1.492(2)
C(1)-C(5)	1.394(2)
C(1)-C(9)	1.396(2)
C(2)-C(3)	1.551(2)
C(3)-C(4)	1.529(2)
C(3)-C(10)	1.520(2)
C(4)-C(16)	1.510(2)
C(5)-C(6)	1.385(2)
C(6)-C(7)	1.386(3)
C(7)-C(8)	1.388(3)
C(8)-C(9)	1.385(2)
C(10)-C(11)	1.388(2)
C(10)-C(15)	1.392(2)
C(11)-C(12)	1.388(2)
C(12)-C(13)	1.383(3)
C(13)-C(14)	1.385(3)
C(14)-C(15)	1.390(2)
C(16)-C(17)	1.392(2)
C(16)-C(21)	1.394(2)
C(17)-C(18)	1.388(2)
C(18)-C(19)	1.384(3)
C(19)-C(20)	1.384(3)
C(20)-C(21)	1.390(2)
C(5)-C(1)-C(2)	123.58(14)
C(5)-C(1)-C(9)	119.24(15)
C(9)-C(1)-C(2)	117.18(15)
O(1)-C(2)-C(1)	121.19(15)
O(1)-C(2)-C(3)	117.93(14)
C(1)-C(2)-C(3)	120.87(14)
F(1)-C(3)-C(2)	107.73(12)
F(1)-C(3)-C(4)	107.24(12)
F(1)-C(3)-C(10)	108.79(12)
C(4)-C(3)-C(2)	109.77(13)
C(10)-C(3)-C(2)	110.49(13)
C(10)-C(3)-C(4)	112.64(13)
C(16)-C(4)-C(3)	114.25(14)
C(6)-C(5)-C(1)	120.48(15)
C(5)-C(6)-C(7)	119.99(16)
C(6)-C(7)-C(8)	119.84(17)
C(9)-C(8)-C(7)	120.45(17)

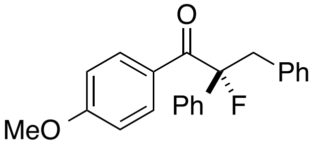
C(8)-C(9)-C(1)	119.98(16)
C(11)-C(10)-C(3)	119.62(14)
C(11)-C(10)-C(15)	119.22(15)
C(15)-C(10)-C(3)	121.09(15)
C(10)-C(11)-C(12)	120.36(16)
C(13)-C(12)-C(11)	120.50(16)
C(12)-C(13)-C(14)	119.28(16)
C(13)-C(14)-C(15)	120.61(17)
C(14)-C(15)-C(10)	120.03(16)
C(17)-C(16)-C(4)	120.56(16)
C(17)-C(16)-C(21)	118.68(16)
C(21)-C(16)-C(4)	120.74(15)
C(18)-C(17)-C(16)	120.72(17)
C(19)-C(18)-C(17)	120.01(17)
C(18)-C(19)-C(20)	119.98(16)
C(19)-C(20)-C(21)	119.99(17)
C(20)-C(21)-C(16)	120.61(17)

Table S–4. Anisotropic displacement parameters ($Å^2 x 10^3$) for crystal_001. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

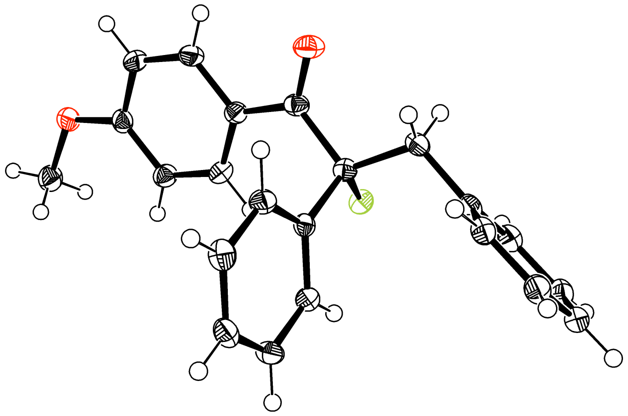
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	18(1)	21(1)	22(1)	0(1)	-2(1)	3(1)
O(1)	24(1)	34(1)	24(1)	-4(1)	1(1)	-10(1)
C(1)	21(1)	17(1)	18(1)	2(1)	-1(1)	2(1)
C(2)	21(1)	17(1)	22(1)	0(1)	0(1)	1(1)
C(3)	15(1)	20(1)	19(1)	0(1)	-1(1)	0(1)
C(4)	24(1)	19(1)	21(1)	0(1)	1(1)	-2(1)
C(5)	22(1)	22(1)	19(1)	0(1)	-3(1)	-2(1)
C(6)	19(1)	25(1)	26(1)	5(1)	-1(1)	-2(1)
C(7)	26(1)	25(1)	22(1)	3(1)	5(1)	3(1)
C(8)	35(1)	22(1)	21(1)	-4(1)	3(1)	0(1)
C(9)	26(1)	20(1)	23(1)	-1(1)	1(1)	-3(1)
C(10)	20(1)	17(1)	15(1)	1(1)	2(1)	-1(1)
C(11)	21(1)	24(1)	23(1)	2(1)	-1(1)	-1(1)
C(12)	24(1)	26(1)	27(1)	5(1)	4(1)	6(1)
C(13)	32(1)	17(1)	26(1)	4(1)	8(1)	2(1)
C(14)	30(1)	20(1)	26(1)	-3(1)	2(1)	-4(1)
C(15)	21(1)	21(1)	23(1)	1(1)	-2(1)	-1(1)
C(16)	24(1)	14(1)	21(1)	3(1)	2(1)	-2(1)
C(17)	24(1)	21(1)	23(1)	3(1)	0(1)	1(1)
C(18)	32(1)	21(1)	23(1)	0(1)	3(1)	3(1)
C(19)	33(1)	23(1)	20(1)	1(1)	-1(1)	-5(1)
C(20)	24(1)	27(1)	24(1)	6(1)	-4(1)	-3(1)
C(21)	23(1)	22(1)	25(1)	3(1)	3(1)	0(1)

Table S–5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for crystal_001.

	x	y	z	U(eq)
H(4A)	-4063	5805	7976	25
H(4B)	-2027	5147	7977	25
H(5)	1780	7055	6419	26
H(6)	4046	7239	5335	28
H(7)	3244	6480	4203	29
H(8)	125	5561	4150	32
H(9)	-2134	5362	5233	27
H(11)	-4835	7269	7100	27
H(12)	-5628	8736	7291	30
H(13)	-2967	9645	7862	30
H(14)	498	9076	8246	30
H(15)	1313	7609	8056	26
H(17)	-4796	6675	9096	27
H(18)	-4024	7028	10376	30
H(19)	-696	6554	10951	30
H(20)	1893	5746	10239	30
H(21)	1144	5402	8955	28



Absolute stereochemistry of product from Entry 7 of Table 2 (run with (4*S*,5*R*)-L*). (*R*)-2-Fluoro-1-(4-methoxyphenyl)-2,3-diphenylpropan-1-one.



A crystal of $C_{22}H_{19}F_1O_2$ was selected and mounted in a nylon loop in immersion oil. All measurements were made on a Rigkau Saturn944+ with filtered Cu-Kα radiation at a temperature of 93 K. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Cryst. (2009). 42, 339–341.
2. SHELXS, G.M. Sheldrick, Acta Cryst. (2008). A64, 112–122
3. SHELXL, G.M. Sheldrick, Acta Cryst. (2008). A64, 112–122

Table S–6. Crystal data and structure refinement for crystal_002.

Identification code	crystal_002	
Empirical formula	$C_{22} H_{19} F_1 O_2$	
Formula weight	334.37	
Temperature	93 K	
Wavelength	1.54187 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 5.86120(10) Å	α= 90°.
	b = 15.7648(3) Å	β= 90 °.

	c = 18.3237(13) Å	γ = 90 °.
Volume	1693.12(13) Å^3	
Z	4	
Density (calculated)	1.312 Mg/m^3	
Absorption coefficient	0.731 mm^{-1}	
F(000)	704	
Crystal size	0.15 x 0.05 x 0.05 mm^3	
Theta range for data collection	3.699 to 68.208°.	
Index ranges	-7<=h<=7, -18<=k<=18, -21<=l<=22	
Reflections collected	58234	
Independent reflections	3085 [R(int) = 0.0587]	
Completeness to theta = 67.687°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.912	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3085 / 0 / 227	
Goodness-of-fit on F^2	1.058	
Final R indices [I>2sigma(I)]	R1 = 0.0237, wR2 = 0.0599	
R indices (all data)	R1 = 0.0238, wR2 = 0.0600	
Absolute structure parameter	-0.01(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.109 and -0.166 e.Å^{-3}	

Table S–7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for crystal_002. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1)	-1506(2)	-9122(1)	-7196(1)	21(1)
O(1)	3412(2)	-9778(1)	-8002(1)	28(1)
O(2)	-2372(2)	-8682(1)	-10727(1)	27(1)
C(1)	1652(3)	-9363(1)	-7999(1)	20(1)
C(2)	862(2)	-8975(1)	-7264(1)	19(1)
C(3)	2025(3)	-9430(1)	-6627(1)	22(1)
C(4)	404(3)	-9191(1)	-8689(1)	19(1)
C(5)	-1648(3)	-8745(1)	-8735(1)	22(1)
C(6)	-2659(3)	-8565(1)	-9401(1)	23(1)
C(7)	-1597(3)	-8832(1)	-10040(1)	22(1)
C(8)	435(3)	-9294(1)	-10001(1)	24(1)
C(9)	1410(3)	-9473(1)	-9339(1)	23(1)
C(10)	1425(3)	-9081(1)	-5884(1)	20(1)
C(11)	2943(3)	-8551(1)	-5519(1)	22(1)
C(12)	2455(3)	-8252(1)	-4822(1)	25(1)
C(13)	434(3)	-8480(1)	-4484(1)	24(1)
C(14)	-1107(3)	-9001(1)	-4844(1)	25(1)
C(15)	-619(3)	-9299(1)	-5541(1)	23(1)
C(16)	1281(3)	-8024(1)	-7265(1)	17(1)
C(17)	3364(3)	-7707(1)	-7509(1)	22(1)
C(18)	3794(3)	-6842(1)	-7503(1)	25(1)
C(19)	2163(3)	-6281(1)	-7243(1)	24(1)
C(20)	96(3)	-6593(1)	-6993(1)	25(1)
C(21)	-349(3)	-7461(1)	-7003(1)	21(1)
C(22)	-4298(3)	-8134(1)	-10802(1)	29(1)

Table S–8. Bond lengths [Å] and angles [°] for crystal_002.

F(1)-C(2)	1.4127(17)
O(1)-C(1)	1.222(2)
O(2)-C(7)	1.3585(18)
O(2)-C(22)	1.429(2)
C(1)-C(2)	1.549(2)
C(1)-C(4)	1.487(2)
C(2)-C(3)	1.531(2)
C(2)-C(16)	1.520(2)
C(3)-C(10)	1.511(2)
C(4)-C(5)	1.395(2)
C(4)-C(9)	1.402(2)
C(5)-C(6)	1.386(2)
C(6)-C(7)	1.392(2)
C(7)-C(8)	1.398(2)
C(8)-C(9)	1.371(2)
C(10)-C(11)	1.391(2)
C(10)-C(15)	1.396(2)
C(11)-C(12)	1.391(2)
C(12)-C(13)	1.385(2)
C(13)-C(14)	1.387(2)
C(14)-C(15)	1.391(2)
C(16)-C(17)	1.393(2)
C(16)-C(21)	1.390(2)
C(17)-C(18)	1.387(2)
C(18)-C(19)	1.387(2)
C(19)-C(20)	1.385(2)
C(20)-C(21)	1.393(2)
C(7)-O(2)-C(22)	117.34(12)
O(1)-C(1)-C(2)	117.93(13)
O(1)-C(1)-C(4)	120.60(14)
C(4)-C(1)-C(2)	121.35(13)
F(1)-C(2)-C(1)	107.80(11)
F(1)-C(2)-C(3)	107.06(12)
F(1)-C(2)-C(16)	108.70(11)
C(3)-C(2)-C(1)	110.19(12)
C(16)-C(2)-C(1)	109.88(12)
C(16)-C(2)-C(3)	113.03(12)
C(10)-C(3)-C(2)	114.42(12)
C(5)-C(4)-C(1)	124.58(13)
C(5)-C(4)-C(9)	118.12(14)
C(9)-C(4)-C(1)	117.26(14)
C(6)-C(5)-C(4)	121.65(14)

C(5)-C(6)-C(7)	119.18(14)
O(2)-C(7)-C(6)	125.24(15)
O(2)-C(7)-C(8)	115.02(14)
C(6)-C(7)-C(8)	119.74(14)
C(9)-C(8)-C(7)	120.50(15)
C(8)-C(9)-C(4)	120.78(15)
C(11)-C(10)-C(3)	120.15(14)
C(11)-C(10)-C(15)	118.75(14)
C(15)-C(10)-C(3)	121.07(14)
C(12)-C(11)-C(10)	120.84(15)
C(13)-C(12)-C(11)	119.92(15)
C(12)-C(13)-C(14)	119.86(15)
C(13)-C(14)-C(15)	120.19(15)
C(14)-C(15)-C(10)	120.42(15)
C(17)-C(16)-C(2)	119.69(13)
C(21)-C(16)-C(2)	121.25(13)
C(21)-C(16)-C(17)	119.02(14)
C(18)-C(17)-C(16)	120.59(15)
C(19)-C(18)-C(17)	120.29(15)
C(20)-C(19)-C(18)	119.39(14)
C(19)-C(20)-C(21)	120.51(15)
C(16)-C(21)-C(20)	120.19(15)

Symmetry transformations used to generate equivalent atoms:

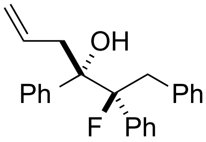
Table S–9. Anisotropic displacement parameters ($Å^2 x 10^3$) for crystal_002. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	18(1)	23(1)	22(1)	-1(1)	2(1)	-3(1)
O(1)	24(1)	30(1)	29(1)	-6(1)	-2(1)	8(1)
O(2)	38(1)	25(1)	18(1)	0(1)	-2(1)	7(1)
C(1)	20(1)	16(1)	24(1)	-2(1)	1(1)	-1(1)
C(2)	16(1)	20(1)	21(1)	0(1)	0(1)	0(1)
C(3)	24(1)	18(1)	23(1)	2(1)	-1(1)	4(1)
C(4)	22(1)	16(1)	21(1)	-2(1)	2(1)	-2(1)
C(5)	22(1)	26(1)	20(1)	-3(1)	4(1)	1(1)
C(6)	21(1)	25(1)	23(1)	-1(1)	2(1)	1(1)
C(7)	29(1)	17(1)	19(1)	1(1)	0(1)	-3(1)
C(8)	32(1)	21(1)	21(1)	-3(1)	6(1)	2(1)
C(9)	25(1)	18(1)	26(1)	-2(1)	3(1)	3(1)
C(10)	22(1)	16(1)	21(1)	4(1)	-2(1)	3(1)
C(11)	22(1)	22(1)	22(1)	4(1)	0(1)	0(1)
C(12)	30(1)	21(1)	23(1)	1(1)	-4(1)	-2(1)
C(13)	31(1)	22(1)	20(1)	1(1)	1(1)	5(1)
C(14)	23(1)	27(1)	25(1)	6(1)	2(1)	2(1)
C(15)	24(1)	20(1)	25(1)	3(1)	-3(1)	-2(1)
C(16)	19(1)	18(1)	15(1)	0(1)	-3(1)	1(1)
C(17)	19(1)	24(1)	24(1)	0(1)	1(1)	2(1)
C(18)	22(1)	26(1)	27(1)	3(1)	-1(1)	-5(1)
C(19)	32(1)	18(1)	23(1)	2(1)	-5(1)	-2(1)
C(20)	28(1)	20(1)	26(1)	-2(1)	0(1)	6(1)
C(21)	21(1)	22(1)	21(1)	1(1)	3(1)	2(1)
C(22)	29(1)	34(1)	24(1)	3(1)	-2(1)	4(1)

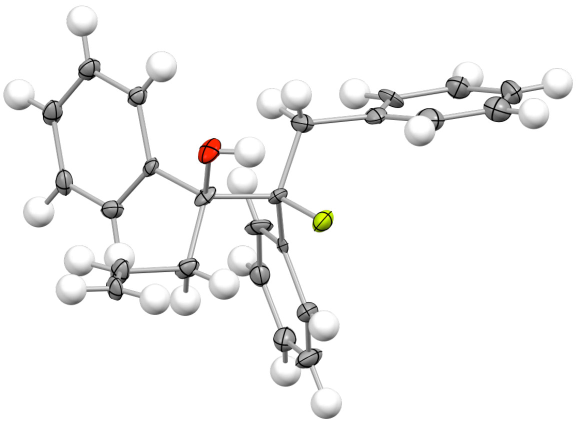
Table S–10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for crystal_002.

	x	y	z	U(eq)
H(3A)	1611	-10026	-6642	26
H(3B)	3665	-9394	-6692	26
H(5)	-2355	-8564	-8308	27
H(6)	-4030	-8269	-9421	28
H(8)	1130	-9482	-10428	29
H(9)	2754	-9786	-9321	28
H(11)	4302	-8395	-5744	27
H(12)	3486	-7899	-4584	30
H(13)	111	-8285	-4016	29
H(14)	-2470	-9150	-4618	30
H(15)	-1662	-9646	-5780	27
H(17)	4476	-8079	-7678	27
H(18)	5182	-6637	-7674	30
H(19)	2454	-5702	-7236	29
H(20)	-1004	-6220	-6818	30
H(21)	-1741	-7664	-6833	26
H(22A)	-3947	-7590	-10595	44
H(22B)	-5582	-8375	-10553	44
H(22C)	-4657	-8067	-11310	44

VI. Assignment of the Stereochemistry of the Derivatization Products



Relative stereochemistry of product from eq 4 (run with the product of a cross-coupling conducted with (4*R*,5*S*)-L*). (2*S*,3*S*)-2-Fluoro-1,2,3-triphenylhex-5-en-3-ol.



A crystal of $C_{24}H_{23}F_1O_1$ was selected and mounted in a nylon loop in immersion oil. All measurements were made on a Bruker Smart with filtered Mo-Kα radiation at a temperature of 100 K. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimization. The absolute stereochemistry could not be determined on the basis of the absolute structure parameter, but was instead assigned by reference to the tertiary stereocenter in the starting material ((*S*)-2-fluoro-1,2,3-triphenylpropan-1-one).

1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Cryst. (2009). 42, 339–341.
2. SHELXS, G.M. Sheldrick, Acta Cryst. (2008). A64, 112–122
3. SHELXL, G.M. Sheldrick, Acta Cryst. (2008). A64, 112–122

Table S–11. Crystal data and structure refinement for crystal_004.

Identification code	crystal_004
Empirical formula	$C_{24}H_{23}FO$

Formula weight	346.42	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C_2	
Unit cell dimensions	a = 16.777(6) Å	α= 90°.
	b = 15.082(5) Å	β= 110.639(6) °.
	c = 15.600(6) Å	γ = 90 °.
Volume	3694(2) Å^3	
Z	8	
Density (calculated)	1.246 Mg/m^3	
Absorption coefficient	0.081 mm^{-1}	
F(000)	1472	
Crystal size	0.27 x 0.21 x 0.17 mm^3	
Theta range for data collection	1.395 to 26.357°.	
Index ranges	-20<=h<=20, -18<=k<=18, -19<=l<=19	
Reflections collected	25299	
Independent reflections	7544 [R(int) = 0.1056]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7544 / 1 / 471	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I)]	R1 = 0.0797, wR2 = 0.1624	
R indices (all data)	R1 = 0.1120, wR2 = 0.1746	
Absolute structure parameter	-0.5(5)	
Largest diff. peak and hole	0.334 and -0.379 e/Å^{-3}	

Table S–12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for crystal_004. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1)	1016(2)	1283(2)	191(2)	23(1)
O(1)	459(3)	-295(3)	-636(3)	22(1)
C(1)	1455(4)	912(4)	-357(4)	16(1)
C(2)	1352(4)	-117(4)	-277(4)	16(1)
C(3)	1762(4)	-618(4)	-873(4)	14(1)
C(4)	2605(5)	-914(4)	-521(4)	20(2)
C(5)	2962(5)	-1357(4)	-1074(4)	20(1)
C(6)	2495(5)	-1518(4)	-1975(4)	24(2)
C(7)	1667(5)	-1233(4)	-2346(4)	21(2)
C(8)	1294(5)	-801(4)	-1793(4)	16(1)
C(9)	1698(5)	-412(4)	728(4)	20(2)
C(10)	1571(4)	-1379(4)	866(4)	21(2)
C(11)	1105(4)	-1680(4)	1319(4)	18(1)
C(12)	979(5)	1245(4)	-1329(4)	26(2)
C(13)	926(4)	2236(4)	-1457(4)	22(2)
C(14)	355(5)	2730(5)	-1188(5)	34(2)
C(15)	250(5)	3644(5)	-1350(5)	32(2)
C(16)	713(5)	4059(5)	-1813(5)	32(2)
C(17)	1290(5)	3585(5)	-2094(4)	29(2)
C(18)	1380(5)	2673(4)	-1921(4)	28(2)
C(19)	2370(4)	1211(4)	60(4)	16(1)
C(20)	2704(5)	1510(4)	962(4)	22(2)
C(21)	3555(5)	1745(5)	1350(4)	30(2)
C(22)	4088(5)	1683(4)	848(5)	28(2)
C(23)	3764(4)	1384(4)	-43(4)	22(2)
C(24)	2919(5)	1156(4)	-439(4)	24(2)
F(1B)	-1077(2)	-1387(2)	-5179(2)	21(1)
O(1B)	-359(3)	-2912(3)	-4322(3)	22(1)
C(1B)	-1411(4)	-1774(4)	-4552(4)	15(1)
C(2B)	-1270(4)	-2804(4)	-4616(4)	17(1)
C(3B)	-1590(4)	-3340(4)	-3988(4)	15(1)
C(4B)	-2425(4)	-3634(4)	-4252(4)	19(1)
C(5B)	-2708(5)	-4135(4)	-3680(4)	23(2)
C(6B)	-2166(5)	-4346(4)	-2807(5)	28(2)
C(7B)	-1331(5)	-4069(4)	-2522(4)	22(2)
C(8B)	-1034(4)	-3573(4)	-3096(4)	18(1)
C(9B)	-1665(4)	-3114(4)	-5627(4)	17(1)
C(10B)	-1501(4)	-4077(4)	-5750(4)	21(2)
C(11B)	-1125(6)	-4372(5)	-6301(6)	47(3)

C(12B)	-884(5)	-1389(4)	-3617(4)	24(2)
C(13B)	-857(5)	-392(4)	-3562(4)	22(2)
C(14B)	-328(5)	97(5)	-3902(4)	25(2)
C(15B)	-299(5)	1010(5)	-3825(5)	31(2)
C(16B)	-765(5)	1464(4)	-3402(4)	27(2)
C(17B)	-1292(5)	992(4)	-3069(4)	24(2)
C(18B)	-1342(5)	67(4)	-3149(4)	24(2)
C(19B)	-2339(4)	-1537(4)	-4850(4)	12(1)
C(20B)	-2771(4)	-1204(4)	-5730(4)	15(1)
C(21B)	-3633(4)	-1034(4)	-6025(4)	20(2)
C(22B)	-4087(5)	-1199(4)	-5467(5)	29(2)
C(23B)	-3672(5)	-1520(4)	-4597(5)	27(2)
C(24B)	-2806(5)	-1678(4)	-4290(4)	19(2)

Table S–13. Bond lengths [Å] and angles [°] for crystal_004.

F(1)-C(1)	1.426(7)
O(1)-C(2)	1.428(8)
C(1)-C(2)	1.572(8)
C(1)-C(12)	1.527(8)
C(1)-C(19)	1.509(9)
C(2)-C(3)	1.534(8)
C(2)-C(9)	1.534(8)
C(3)-C(4)	1.398(9)
C(3)-C(8)	1.400(8)
C(4)-C(5)	1.383(9)
C(5)-C(6)	1.368(9)
C(6)-C(7)	1.372(10)
C(7)-C(8)	1.393(9)
C(9)-C(10)	1.500(8)
C(10)-C(11)	1.307(9)
C(12)-C(13)	1.507(9)
C(13)-C(14)	1.390(11)
C(13)-C(18)	1.389(10)
C(14)-C(15)	1.402(10)
C(15)-C(16)	1.384(11)
C(16)-C(17)	1.393(10)
C(17)-C(18)	1.399(9)
C(19)-C(20)	1.393(8)
C(19)-C(24)	1.403(9)
C(20)-C(21)	1.386(10)
C(21)-C(22)	1.384(11)
C(22)-C(23)	1.378(9)
C(23)-C(24)	1.374(10)
F(1B)-C(1B)	1.414(6)
O(1B)-C(2B)	1.440(8)
C(1B)-C(2B)	1.579(9)
C(1B)-C(12B)	1.529(8)
C(1B)-C(19B)	1.502(9)
C(2B)-C(3B)	1.508(8)
C(2B)-C(9B)	1.553(8)
C(3B)-C(4B)	1.386(9)
C(3B)-C(8B)	1.419(8)
C(4B)-C(5B)	1.374(8)
C(5B)-C(6B)	1.383(10)
C(6B)-C(7B)	1.377(10)
C(7B)-C(8B)	1.388(8)
C(9B)-C(10B)	1.503(8)
C(10B)-C(11B)	1.311(10)

C(12B)-C(13B)	1.507(9)
C(13B)-C(14B)	1.396(9)
C(13B)-C(18B)	1.387(10)
C(14B)-C(15B)	1.380(10)
C(15B)-C(16B)	1.371(10)
C(16B)-C(17B)	1.373(10)
C(17B)-C(18B)	1.400(9)
C(19B)-C(20B)	1.400(8)
C(19B)-C(24B)	1.380(8)
C(20B)-C(21B)	1.378(9)
C(21B)-C(22B)	1.367(10)
C(22B)-C(23B)	1.377(10)
C(23B)-C(24B)	1.381(10)

F(1)-C(1)-C(2)	104.2(5)
F(1)-C(1)-C(12)	105.4(5)
F(1)-C(1)-C(19)	106.7(4)
C(12)-C(1)-C(2)	111.7(5)
C(19)-C(1)-C(2)	112.6(5)
C(19)-C(1)-C(12)	115.2(5)
O(1)-C(2)-C(1)	106.5(5)
O(1)-C(2)-C(3)	107.5(5)
O(1)-C(2)-C(9)	108.3(5)
C(3)-C(2)-C(1)	110.6(5)
C(9)-C(2)-C(1)	110.8(4)
C(9)-C(2)-C(3)	112.8(5)
C(4)-C(3)-C(2)	121.8(5)
C(4)-C(3)-C(8)	117.6(6)
C(8)-C(3)-C(2)	120.6(6)
C(5)-C(4)-C(3)	120.7(6)
C(6)-C(5)-C(4)	120.6(7)
C(5)-C(6)-C(7)	120.4(6)
C(6)-C(7)-C(8)	119.6(6)
C(7)-C(8)-C(3)	121.0(6)
C(10)-C(9)-C(2)	114.0(5)
C(11)-C(10)-C(9)	123.9(6)
C(13)-C(12)-C(1)	116.3(5)
C(14)-C(13)-C(12)	120.4(7)
C(18)-C(13)-C(12)	121.5(6)
C(18)-C(13)-C(14)	117.8(6)
C(13)-C(14)-C(15)	121.9(7)
C(16)-C(15)-C(14)	118.8(7)
C(15)-C(16)-C(17)	120.8(7)
C(16)-C(17)-C(18)	118.9(7)
C(13)-C(18)-C(17)	121.7(7)

C(20)-C(19)-C(1)	121.2(6)
C(20)-C(19)-C(24)	118.1(6)
C(24)-C(19)-C(1)	120.7(5)
C(21)-C(20)-C(19)	120.6(7)
C(22)-C(21)-C(20)	120.4(6)
C(23)-C(22)-C(21)	119.3(7)
C(24)-C(23)-C(22)	120.9(7)
C(23)-C(24)-C(19)	120.7(6)
F(1B)-C(1B)-C(2B)	105.0(5)
F(1B)-C(1B)-C(12B)	105.4(5)
F(1B)-C(1B)-C(19B)	107.9(5)
C(12B)-C(1B)-C(2B)	112.6(5)
C(19B)-C(1B)-C(2B)	112.2(5)
C(19B)-C(1B)-C(12B)	113.1(5)
O(1B)-C(2B)-C(1B)	104.9(5)
O(1B)-C(2B)-C(3B)	108.3(5)
O(1B)-C(2B)-C(9B)	108.3(5)
C(3B)-C(2B)-C(1B)	113.0(5)
C(3B)-C(2B)-C(9B)	112.1(5)
C(9B)-C(2B)-C(1B)	109.9(4)
C(4B)-C(3B)-C(2B)	122.2(5)
C(4B)-C(3B)-C(8B)	117.3(5)
C(8B)-C(3B)-C(2B)	120.5(6)
C(5B)-C(4B)-C(3B)	121.8(6)
C(4B)-C(5B)-C(6B)	120.5(7)
C(7B)-C(6B)-C(5B)	119.3(6)
C(6B)-C(7B)-C(8B)	120.7(6)
C(7B)-C(8B)-C(3B)	120.3(6)
C(10B)-C(9B)-C(2B)	112.8(5)
C(11B)-C(10B)-C(9B)	124.3(6)
C(13B)-C(12B)-C(1B)	115.4(5)
C(14B)-C(13B)-C(12B)	121.1(7)
C(18B)-C(13B)-C(12B)	120.9(6)
C(18B)-C(13B)-C(14B)	118.0(6)
C(15B)-C(14B)-C(13B)	120.1(7)
C(16B)-C(15B)-C(14B)	122.1(7)
C(15B)-C(16B)-C(17B)	118.4(6)
C(16B)-C(17B)-C(18B)	120.6(7)
C(13B)-C(18B)-C(17B)	120.8(7)
C(20B)-C(19B)-C(1B)	120.7(5)
C(24B)-C(19B)-C(1B)	121.7(5)
C(24B)-C(19B)-C(20B)	117.6(6)
C(21B)-C(20B)-C(19B)	121.0(6)
C(22B)-C(21B)-C(20B)	120.5(6)
C(21B)-C(22B)-C(23B)	119.4(7)

C(22B)-C(23B)-C(24B)	120.4(6)
C(19B)-C(24B)-C(23B)	121.1(6)

Table S–14. Anisotropic displacement parameters ($Å^2 x 10^3$) for crystal_004. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

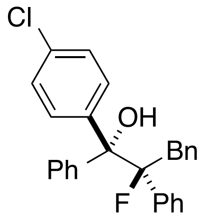
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	31(2)	19(2)	18(2)	-7(2)	7(2)	-2(2)
O(1)	17(3)	20(2)	30(3)	-9(2)	8(2)	-7(2)
C(1)	20(4)	17(3)	10(3)	-7(2)	3(3)	2(3)
C(2)	15(4)	14(3)	18(3)	-7(2)	6(3)	-8(3)
C(3)	23(4)	7(3)	12(3)	-3(2)	6(3)	-3(3)
C(4)	28(4)	15(3)	14(3)	-1(2)	3(3)	-1(3)
C(5)	28(4)	12(3)	22(3)	2(3)	12(3)	4(3)
C(6)	44(5)	18(3)	16(3)	2(3)	17(3)	5(3)
C(7)	32(4)	18(3)	12(3)	-2(2)	8(3)	-2(3)
C(8)	25(4)	12(3)	12(3)	-1(2)	7(3)	-3(3)
C(9)	30(4)	16(3)	14(3)	-1(2)	8(3)	-8(3)
C(10)	37(4)	10(3)	19(3)	0(2)	13(3)	-3(3)
C(11)	31(4)	9(3)	18(3)	2(2)	12(3)	-2(3)
C(12)	33(5)	19(3)	16(3)	0(3)	-6(3)	1(3)
C(13)	22(4)	19(3)	15(3)	-4(3)	-5(3)	-3(3)
C(14)	38(5)	34(4)	22(4)	1(3)	-1(3)	-3(4)
C(15)	33(5)	31(4)	26(4)	0(3)	4(3)	7(3)
C(16)	46(5)	17(3)	22(3)	5(3)	-3(4)	4(3)
C(17)	41(5)	26(4)	17(3)	4(3)	7(3)	3(3)
C(18)	35(5)	24(4)	15(3)	8(3)	-1(3)	7(3)
C(19)	27(4)	5(3)	8(3)	3(2)	-1(3)	1(3)
C(20)	26(4)	19(3)	17(3)	-2(2)	2(3)	3(3)
C(21)	29(5)	37(4)	19(3)	-14(3)	1(3)	5(3)
C(22)	26(4)	23(4)	29(4)	-5(3)	3(3)	3(3)
C(23)	26(4)	16(3)	25(3)	1(3)	10(3)	5(3)
C(24)	37(5)	25(4)	8(3)	1(2)	4(3)	-8(3)
F(1B)	20(2)	31(2)	14(2)	7(2)	8(2)	-6(2)
O(1B)	13(3)	34(3)	17(2)	11(2)	3(2)	1(2)
C(1B)	18(4)	19(3)	8(3)	1(2)	5(3)	-9(3)
C(2B)	13(4)	26(3)	11(3)	6(2)	5(3)	-1(3)
C(3B)	15(3)	17(3)	15(3)	2(2)	8(3)	0(3)
C(4B)	23(4)	20(3)	19(3)	1(3)	14(3)	-1(3)
C(5B)	37(4)	15(3)	29(4)	-13(3)	24(3)	-9(3)
C(6B)	45(5)	19(3)	26(4)	-4(3)	20(4)	-12(3)
C(7B)	38(5)	17(3)	13(3)	4(3)	10(3)	3(3)
C(8B)	27(4)	17(3)	13(3)	-2(2)	11(3)	-3(3)
C(9B)	20(4)	20(3)	11(3)	3(2)	6(3)	0(3)
C(10B)	28(4)	22(3)	12(3)	4(3)	7(3)	-1(3)
C(11B)	73(7)	30(4)	64(5)	-31(4)	55(5)	-32(4)
C(12B)	28(4)	26(4)	14(3)	9(3)	3(3)	-8(3)

C(13B)	31(4)	22(3)	9(3)	5(2)	1(3)	-9(3)
C(14B)	21(4)	29(4)	19(3)	10(3)	0(3)	-7(3)
C(15B)	30(5)	32(4)	23(4)	9(3)	-2(3)	-14(3)
C(16B)	35(4)	17(3)	22(3)	8(3)	1(3)	1(3)
C(17B)	28(4)	22(3)	18(3)	3(3)	2(3)	5(3)
C(18B)	33(4)	20(3)	15(3)	5(3)	4(3)	-4(3)
C(19B)	16(3)	11(3)	11(3)	-1(2)	6(2)	-4(2)
C(20B)	23(4)	12(3)	10(3)	1(2)	5(3)	2(3)
C(21B)	20(4)	12(3)	20(3)	4(2)	-1(3)	3(3)
C(22B)	23(4)	19(3)	45(4)	6(3)	12(4)	7(3)
C(23B)	27(4)	20(4)	43(4)	3(3)	24(4)	6(3)
C(24B)	33(4)	12(3)	15(3)	-4(2)	10(3)	0(3)

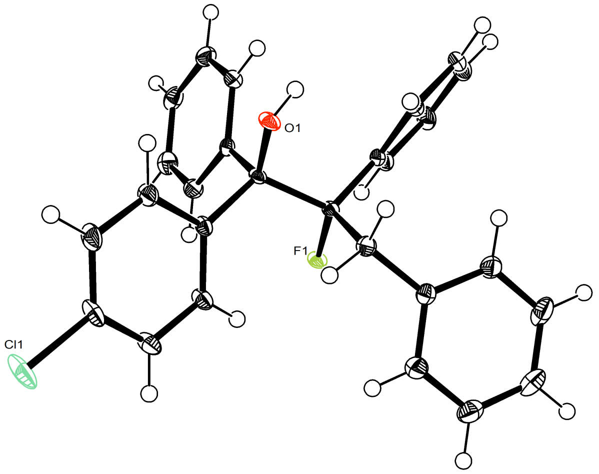
Table S–15. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for crystal_004.

	x	y	z	U(eq)
H(1)	195	129	-511	33
H(4)	2936	-809	104	24
H(5)	3537	-1551	-826	24
H(6)	2745	-1829	-2346	29
H(7)	1349	-1331	-2976	25
H(8)	713	-628	-2045	19
H(9A)	2315	-278	987	24
H(9B)	1414	-61	1075	24
H(10)	1846	-1797	608	25
H(11A)	823	-1278	1585	22
H(11B)	1049	-2301	1383	22
H(12A)	1259	994	-1737	32
H(12B)	392	1006	-1532	32
H(14)	26	2439	-886	41
H(15)	-133	3972	-1146	38
H(16)	636	4676	-1941	39
H(17)	1617	3876	-2399	35
H(18)	1762	2345	-2127	33
H(20)	2345	1553	1314	27
H(21)	3774	1950	1965	36
H(22)	4671	1845	1114	33
H(23)	4128	1333	-388	26
H(24)	2705	960	-1057	29
H(1B)	-163	-2568	-4622	33
H(4B)	-2812	-3486	-4844	22
H(5B)	-3281	-4337	-3887	28
H(6B)	-2367	-4680	-2408	34
H(7B)	-954	-4218	-1925	27
H(8B)	-455	-3388	-2891	22
H(9BA)	-2287	-3010	-5848	21
H(9BB)	-1426	-2751	-6008	21
H(10B)	-1681	-4499	-5404	25
H(11C)	-937	-3967	-6656	57
H(11D)	-1041	-4991	-6346	57
H(12C)	-1117	-1617	-3157	28
H(12D)	-293	-1612	-3445	28
H(14B)	14	-198	-4187	30
H(15B)	55	1333	-4074	38
H(16B)	-724	2091	-3342	32

H(17B)	-1625	1295	-2780	29
H(18B)	-1713	-249	-2919	29
H(20B)	-2466	-1094	-6129	18
H(21B)	-3913	-800	-6622	23
H(22B)	-4683	-1093	-5678	34
H(23B)	-3984	-1633	-4204	32
H(24B)	-2527	-1887	-3683	23



Relative and absolute stereochemistry of product from eq 5 (run with the product of a cross-coupling conducted with (4*R*,5*S*)-L*). (1*R*,2*S*)-1-(4-Chlorophenyl)-2-fluoro-1,2,3-triphenylpropan-1-ol (for the sake of simplicity, disordered solvent molecules (CH_2Cl_2) have been omitted)**.**



A crystal of a solvate of $C_{27}H_{22}Cl_1F_1O_1$ was selected and mounted in a nylon loop in immersion oil. All measurements were made on a Bruker Apex-II with filtered Mo-Kα radiation at a temperature of 100 K. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimization. The disordered and partially occupied dichloromethane solvent was refined with similarity restraints placed on the appropriate atom bond lengths and displacement parameters. The occupancy of the dichloromethane was also refined. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Cryst. (2009). 42, 339–341.
2. SHELXS, G.M. Sheldrick, Acta Cryst. (2008). A64, 112–122
3. SHELXL, G.M. Sheldrick, Acta Cryst. (2008). A64, 112–122

Table S–16. Crystal data and structure refinement for crystal_005.

Identification code	crystal_005
Empirical formula	C_{27} H_{22} Cl_1 F O · (0.58 CH_2Cl_2)
Formula weight	466.24

Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 11.4485(6) Å	α = 90°.
	b = 5.9142(3) Å	β = 91.076(3) °.
	c = 17.0352(8) Å	γ = 90 °.
Volume	1153.23(10) Å^3	
Z	2	
Density (calculated)	1.343 Mg/m^3	
Absorption coefficient	0.326 mm^{-1}	
F(000)	484.8	
Crystal size	0.3 x 0.1 x 0.05 mm^3	
Theta range for data collection	1.779 to 37.564°.	
Index ranges	-19<=h<=19, -9<=k<=10, -28<=l<=28	
Reflections collected	62094	
Independent reflections	11432 [R(int) = 0.0601]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11432 / 68 / 321	
Goodness-of-fit on F^2	0.957	
Final R indices [I>2sigma(I)]	R1 = 0.0499, wR2 = 0.1202	
R indices (all data)	R1 = 0.0773, wR2 = 0.1290	
Absolute structure parameter	-0.005(18)	
Largest diff. peak and hole	0.818 and -0.637 e/Å^{-3}	

Table S–17. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3)
for crystal_005. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)	Occ
Cl(1)	-3149(1)	-8113(1)	-3825(1)	33(1)	
F(1)	-3173(1)	-9003(2)	-7865(1)	14(1)	
O(1)	-3390(1)	-3198(2)	-7234(1)	16(1)	
C(1)	-2872(2)	-6682(3)	-7856(1)	11(1)	
C(2)	-3704(2)	-5518(3)	-7253(1)	12(1)	
C(3)	-3090(2)	-5802(3)	-8686(1)	12(1)	
C(4)	-2652(2)	-3711(3)	-8930(1)	16(1)	
C(5)	-2846(2)	-2956(4)	-9698(1)	18(1)	
C(6)	-3464(2)	-4295(4)	-10232(1)	21(1)	
C(7)	-3910(2)	-6353(4)	-9993(1)	20(1)	
C(8)	-3730(2)	-7103(3)	-9224(1)	15(1)	
C(9)	-1579(2)	-6523(3)	-7607(1)	14(1)	
C(10)	-804(2)	-8115(4)	-8052(1)	15(1)	
C(11)	-491(2)	-7697(4)	-8830(1)	20(1)	
C(12)	216(2)	-9199(5)	-9226(1)	27(1)	
C(13)	629(2)	-11144(4)	-8862(1)	25(1)	
C(14)	347(2)	-11570(4)	-8090(1)	24(1)	
C(15)	-371(2)	-10072(4)	-7688(1)	21(1)	
C(16)	-3531(2)	-6300(3)	-6398(1)	13(1)	
C(17)	-3843(2)	-4760(3)	-5813(1)	18(1)	
C(18)	-3740(2)	-5302(4)	-5022(1)	22(1)	
C(19)	-3313(2)	-7411(4)	-4810(1)	20(1)	
C(20)	-3022(2)	-8995(4)	-5373(1)	19(1)	
C(21)	-3140(2)	-8431(3)	-6168(1)	17(1)	
C(22)	-4982(2)	-5871(3)	-7507(1)	13(1)	
C(23)	-5592(2)	-4212(3)	-7925(1)	17(1)	
C(24)	-6762(2)	-4514(4)	-8141(1)	21(1)	
C(25)	-7343(2)	-6478(4)	-7942(1)	21(1)	
C(26)	-6739(2)	-8158(4)	-7531(1)	20(1)	
C(27)	-5575(2)	-7861(3)	-7317(1)	16(1)	
Cl(2)	762(3)	-18036(7)	-5767(2)	136(1)	0.581(3)
Cl(3A)	-738(8)	-13650(20)	-5696(6)	156(2)	0.235(3)
C(28)	381(9)	-15326(17)	-5956(7)	141(2)	0.581(3)
Cl(3B)	144(19)	-12920(40)	-5390(13)	158(3)	0.106(3)
Cl(3C)	-295(9)	-15040(20)	-5084(6)	169(3)	0.240(3)

Table S–18. Bond lengths [Å] and angles [°] for crystal_005.

Cl(1)-C(19)	1.7347(19)
F(1)-C(1)	1.416(2)
O(1)-C(2)	1.419(2)
C(1)-C(2)	1.573(2)
C(1)-C(3)	1.522(2)
C(1)-C(9)	1.535(2)
C(2)-C(16)	1.537(2)
C(2)-C(22)	1.533(3)
C(3)-C(4)	1.400(3)
C(3)-C(8)	1.394(3)
C(4)-C(5)	1.397(3)
C(5)-C(6)	1.389(3)
C(6)-C(7)	1.384(3)
C(7)-C(8)	1.394(3)
C(9)-C(10)	1.508(3)
C(10)-C(11)	1.402(3)
C(10)-C(15)	1.399(3)
C(11)-C(12)	1.386(3)
C(12)-C(13)	1.386(4)
C(13)-C(14)	1.383(3)
C(14)-C(15)	1.397(3)
C(16)-C(17)	1.402(3)
C(16)-C(21)	1.392(3)
C(17)-C(18)	1.387(3)
C(18)-C(19)	1.386(3)
C(19)-C(20)	1.386(3)
C(20)-C(21)	1.399(3)
C(22)-C(23)	1.393(3)
C(22)-C(27)	1.399(3)
C(23)-C(24)	1.393(3)
C(24)-C(25)	1.384(3)
C(25)-C(26)	1.392(3)
C(26)-C(27)	1.386(3)
Cl(2)-C(28)	1.691(10)
Cl(3A)-C(28)	1.687(11)
F(1)-C(1)-C(2)	106.29(13)
F(1)-C(1)-C(3)	106.66(14)
F(1)-C(1)-C(9)	107.18(14)
C(3)-C(1)-C(2)	111.50(14)
C(3)-C(1)-C(9)	112.15(14)
C(9)-C(1)-C(2)	112.61(14)
O(1)-C(2)-C(1)	106.35(14)

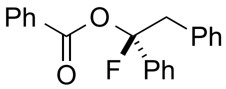
O(1)-C(2)-C(16)	104.00(14)
O(1)-C(2)-C(22)	112.20(15)
C(16)-C(2)-C(1)	114.78(14)
C(22)-C(2)-C(1)	110.06(14)
C(22)-C(2)-C(16)	109.34(14)
C(4)-C(3)-C(1)	121.57(16)
C(8)-C(3)-C(1)	119.78(16)
C(8)-C(3)-C(4)	118.64(16)
C(5)-C(4)-C(3)	120.55(18)
C(6)-C(5)-C(4)	120.1(2)
C(7)-C(6)-C(5)	119.63(18)
C(6)-C(7)-C(8)	120.50(19)
C(3)-C(8)-C(7)	120.55(19)
C(10)-C(9)-C(1)	113.33(15)
C(11)-C(10)-C(9)	121.90(18)
C(15)-C(10)-C(9)	120.05(16)
C(15)-C(10)-C(11)	118.05(18)
C(12)-C(11)-C(10)	120.6(2)
C(11)-C(12)-C(13)	120.8(2)
C(14)-C(13)-C(12)	119.5(2)
C(13)-C(14)-C(15)	120.1(2)
C(14)-C(15)-C(10)	120.9(2)
C(17)-C(16)-C(2)	116.65(16)
C(21)-C(16)-C(2)	125.05(16)
C(21)-C(16)-C(17)	118.23(17)
C(18)-C(17)-C(16)	121.49(19)
C(19)-C(18)-C(17)	119.00(19)
C(18)-C(19)-Cl(1)	119.94(16)
C(18)-C(19)-C(20)	121.06(18)
C(20)-C(19)-Cl(1)	119.00(17)
C(19)-C(20)-C(21)	119.28(19)
C(16)-C(21)-C(20)	120.90(17)
C(23)-C(22)-C(2)	121.02(17)
C(23)-C(22)-C(27)	118.07(18)
C(27)-C(22)-C(2)	120.91(16)
C(22)-C(23)-C(24)	121.01(19)
C(25)-C(24)-C(23)	120.45(19)
C(24)-C(25)-C(26)	119.03(19)
C(27)-C(26)-C(25)	120.6(2)
C(26)-C(27)-C(22)	120.89(19)
Cl(3A)-C(28)-Cl(2)	134.6(11)

Table S–19. Anisotropic displacement parameters ($Å^2$x 10^3) for crystal_005. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

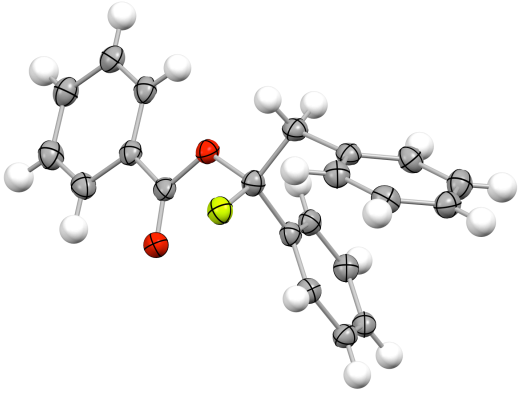
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	60(1)	29(1)	9(1)	4(1)	0(1)	-10(1)
F(1)	21(1)	7(1)	14(1)	0(1)	1(1)	-1(1)
O(1)	28(1)	7(1)	13(1)	0(1)	3(1)	-1(1)
C(1)	16(1)	7(1)	11(1)	0(1)	1(1)	0(1)
C(2)	19(1)	7(1)	9(1)	0(1)	1(1)	0(1)
C(3)	15(1)	11(1)	10(1)	1(1)	4(1)	2(1)
C(4)	18(1)	14(1)	15(1)	2(1)	3(1)	0(1)
C(5)	21(1)	18(1)	16(1)	6(1)	6(1)	3(1)
C(6)	22(1)	29(1)	12(1)	6(1)	3(1)	5(1)
C(7)	22(1)	27(1)	11(1)	0(1)	1(1)	0(1)
C(8)	18(1)	16(1)	12(1)	0(1)	2(1)	-1(1)
C(9)	17(1)	14(1)	12(1)	-1(1)	0(1)	0(1)
C(10)	13(1)	17(1)	15(1)	-1(1)	0(1)	-1(1)
C(11)	17(1)	26(1)	17(1)	2(1)	0(1)	4(1)
C(12)	19(1)	43(1)	18(1)	-5(1)	2(1)	10(1)
C(13)	16(1)	29(1)	31(1)	-9(1)	-1(1)	5(1)
C(14)	19(1)	18(1)	36(1)	0(1)	2(1)	2(1)
C(15)	19(1)	20(1)	23(1)	3(1)	2(1)	1(1)
C(16)	18(1)	11(1)	10(1)	0(1)	2(1)	-2(1)
C(17)	27(1)	14(1)	13(1)	-2(1)	3(1)	1(1)
C(18)	34(1)	20(1)	12(1)	-3(1)	5(1)	-1(1)
C(19)	30(1)	20(1)	10(1)	3(1)	0(1)	-7(1)
C(20)	31(1)	14(1)	13(1)	3(1)	-1(1)	-2(1)
C(21)	27(1)	12(1)	11(1)	0(1)	1(1)	-1(1)
C(22)	17(1)	13(1)	8(1)	-1(1)	3(1)	2(1)
C(23)	22(1)	16(1)	14(1)	3(1)	4(1)	4(1)
C(24)	22(1)	24(1)	16(1)	1(1)	1(1)	9(1)
C(25)	19(1)	27(1)	16(1)	-6(1)	1(1)	4(1)
C(26)	21(1)	21(1)	18(1)	-3(1)	1(1)	-2(1)
C(27)	21(1)	14(1)	15(1)	0(1)	1(1)	1(1)
Cl(2)	132(2)	156(3)	116(2)	-63(2)	-62(2)	26(2)
Cl(3A)	136(4)	181(4)	150(4)	-49(4)	-42(3)	3(4)
C(28)	105(4)	181(5)	134(4)	-52(5)	-65(4)	2(4)
Cl(3B)	139(5)	183(5)	151(5)	-41(5)	-49(4)	10(5)
Cl(3C)	140(4)	189(5)	176(5)	-36(5)	-37(4)	2(4)

Table S–20. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for crystal_005.

	x	y	z	U(eq)	Occ
H(1)	-3514	-2623	-7679	24	
H(4)	-2218	-2799	-8569	19	
H(5)	-2556	-1525	-9856	22	
H(6)	-3580	-3801	-10758	25	
H(7)	-4342	-7261	-10355	24	
H(8)	-4045	-8513	-9066	18	
H(9A)	-1306	-4954	-7689	17	
H(9B)	-1504	-6860	-7039	17	
H(11)	-765	-6370	-9088	24	
H(12)	418	-8893	-9754	32	
H(13)	1103	-12177	-9141	30	
H(14)	642	-12882	-7833	29	
H(15)	-568	-10386	-7160	25	
H(17)	-4133	-3313	-5961	22	
H(18)	-3958	-4242	-4633	26	
H(20)	-2745	-10447	-5221	23	
H(21)	-2951	-9518	-6556	20	
H(23)	-5205	-2853	-8064	21	
H(24)	-7162	-3364	-8428	25	
H(25)	-8143	-6676	-8084	25	
H(26)	-7127	-9519	-7396	24	
H(27)	-5174	-9025	-7038	20	
H(28A)	1081	-14455	-5790	169	0.581
H(28B)	363	-15250	-6537	169	0.581



Absolute stereochemistry of product from eq 6 (run with the product of a cross-coupling conducted with (4*R*,5*S*)-L*). (*S*)-1-Fluoro-1,2-diphenylethyl benzoate.



A crystal of $C_{21}H_{17}F_1O_2$ was selected and mounted in a nylon loop in immersion oil. All measurements were made on a Rigkau Saturn944+ with filtered Cu-Kα radiation at a temperature of 93 K. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Cryst. (2009). 42, 339–341.
2. SHELXS, G.M. Sheldrick, Acta Cryst. (2008). A64, 112–122
3. SHELXL, G.M. Sheldrick, Acta Cryst. (2008). A64, 112–122

Table S–21. Crystal data and structure refinement for crystal_003.

Identification code	crystal_003	
Empirical formula	C_{21} H_{17} F_1 O_2	
Formula weight	320.36	
Temperature	93 K	
Wavelength	1.54187 Å	
Crystal system	Monoclinic	
Space group	C 1 2 1	
Unit cell dimensions	a = 23.9583(4) Å	α= 90°.
	b = 5.74320(10) Å	β= 98.352(7) °.
	c = 11.8825(8) Å	γ = 90 °.
Volume	1617.66(12) Å^3	
Z	4	

Density (calculated)	1.315 Mg/m^3
Absorption coefficient	0.743 mm^{-1}
F(000)	672
Crystal size	0.3 x 0.15 x 0.1 mm^3
Theta range for data collection	3.730 to 68.193°.
Index ranges	-28<=h<=28, -6<=k<=6, -14<=l<=14
Reflections collected	17522
Independent reflections	2923 [R(int) = 0.0897]
Completeness to theta = 67.687°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.742
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2923 / 1 / 217
Goodness-of-fit on F^2	1.138
Final R indices [I>2sigma(I)]	R1 = 0.0427, wR2 = 0.1153
R indices (all data)	R1 = 0.0440, wR2 = 0.1173
Absolute structure parameter	0.1(2)
Extinction coefficient	n/a
Largest diff. peak and hole	0.172 and -0.227 e/Å^{-3}

Table S–22. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for crystal_003. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1)	946(1)	3233(3)	6557(1)	32(1)
O(1)	1179(1)	3964(3)	4361(2)	32(1)
O(2)	827(1)	6566(3)	5507(2)	28(1)
C(1)	928(1)	5744(5)	4476(2)	28(1)
C(2)	1132(1)	5518(5)	6505(2)	27(1)
C(3)	944(1)	6845(5)	7497(2)	29(1)
C(4)	1242(1)	6041(5)	8638(2)	27(1)
C(5)	1090(1)	3966(5)	9131(2)	31(1)
C(6)	1386(1)	3197(5)	10155(2)	34(1)
C(7)	1834(1)	4486(6)	10705(2)	34(1)
C(8)	1985(1)	6552(6)	10225(2)	35(1)
C(9)	1693(1)	7309(5)	9200(2)	31(1)
C(10)	1762(1)	5559(5)	6497(2)	25(1)
C(11)	2102(1)	3735(5)	6945(2)	28(1)
C(12)	2684(1)	3855(5)	6969(2)	29(1)
C(13)	2927(1)	5805(5)	6552(2)	29(1)
C(14)	2589(1)	7632(5)	6101(2)	30(1)
C(15)	2008(1)	7532(5)	6079(2)	28(1)
C(16)	695(1)	7307(5)	3528(2)	26(1)
C(17)	754(1)	6595(5)	2424(2)	32(1)
C(18)	556(1)	8001(6)	1505(2)	34(1)
C(19)	303(1)	10121(5)	1687(2)	34(1)
C(20)	244(1)	10830(5)	2775(2)	32(1)
C(21)	444(1)	9419(5)	3702(2)	29(1)

Table S–23. Bond lengths [Å] and angles [°] for crystal_003.

F(1)-C(2)	1.390(3)
O(1)-C(1)	1.204(3)
O(2)-C(1)	1.367(3)
O(2)-C(2)	1.432(3)
C(1)-C(16)	1.484(4)
C(2)-C(3)	1.526(4)
C(2)-C(10)	1.512(3)
C(3)-C(4)	1.511(4)
C(4)-C(5)	1.399(4)
C(4)-C(9)	1.391(4)
C(5)-C(6)	1.389(4)
C(6)-C(7)	1.387(4)
C(7)-C(8)	1.387(5)
C(8)-C(9)	1.384(4)
C(10)-C(11)	1.385(4)
C(10)-C(15)	1.401(4)
C(11)-C(12)	1.391(4)
C(12)-C(13)	1.387(4)
C(13)-C(14)	1.385(4)
C(14)-C(15)	1.390(4)
C(16)-C(17)	1.401(4)
C(16)-C(21)	1.382(4)
C(17)-C(18)	1.384(4)
C(18)-C(19)	1.390(5)
C(19)-C(20)	1.383(4)
C(20)-C(21)	1.395(4)
C(1)-O(2)-C(2)	117.5(2)
O(1)-C(1)-O(2)	123.4(2)
O(1)-C(1)-C(16)	124.6(2)
O(2)-C(1)-C(16)	112.0(2)
F(1)-C(2)-O(2)	107.8(2)
F(1)-C(2)-C(3)	107.7(2)
F(1)-C(2)-C(10)	109.9(2)
O(2)-C(2)-C(3)	104.9(2)
O(2)-C(2)-C(10)	112.3(2)
C(10)-C(2)-C(3)	113.9(2)
C(4)-C(3)-C(2)	112.7(2)
C(5)-C(4)-C(3)	121.2(2)
C(9)-C(4)-C(3)	120.3(3)
C(9)-C(4)-C(5)	118.5(2)
C(6)-C(5)-C(4)	120.5(3)
C(7)-C(6)-C(5)	120.3(3)

C(8)-C(7)-C(6)	119.6(3)
C(9)-C(8)-C(7)	120.1(3)
C(8)-C(9)-C(4)	121.1(3)
C(11)-C(10)-C(2)	121.2(2)
C(11)-C(10)-C(15)	119.7(2)
C(15)-C(10)-C(2)	119.0(2)
C(10)-C(11)-C(12)	120.1(2)
C(13)-C(12)-C(11)	120.2(2)
C(14)-C(13)-C(12)	119.8(2)
C(13)-C(14)-C(15)	120.3(3)
C(14)-C(15)-C(10)	119.8(2)
C(17)-C(16)-C(1)	117.1(2)
C(21)-C(16)-C(1)	122.8(2)
C(21)-C(16)-C(17)	120.1(3)
C(18)-C(17)-C(16)	119.9(3)
C(17)-C(18)-C(19)	119.7(3)
C(20)-C(19)-C(18)	120.6(3)
C(19)-C(20)-C(21)	119.8(3)
C(16)-C(21)-C(20)	119.9(3)

Table S–24. Anisotropic displacement parameters ($Å^2 x 10^3$) for crystal_003. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	30(1)	31(1)	34(1)	-1(1)	5(1)	-5(1)
O(1)	32(1)	33(1)	31(1)	-4(1)	1(1)	4(1)
O(2)	26(1)	36(1)	22(1)	-1(1)	3(1)	4(1)
C(1)	22(1)	34(1)	28(1)	-5(1)	3(1)	-1(1)
C(2)	28(1)	28(1)	25(1)	2(1)	2(1)	-1(1)
C(3)	27(1)	35(2)	26(1)	-1(1)	6(1)	4(1)
C(4)	25(1)	31(1)	25(1)	-1(1)	7(1)	3(1)
C(5)	30(1)	36(2)	29(1)	0(1)	8(1)	-3(1)
C(6)	40(2)	32(2)	31(1)	3(1)	10(1)	0(1)
C(7)	35(2)	41(2)	25(1)	2(1)	4(1)	6(1)
C(8)	34(1)	43(2)	28(1)	0(1)	4(1)	-3(1)
C(9)	37(1)	31(1)	27(1)	-1(1)	7(1)	-2(1)
C(10)	27(1)	29(1)	20(1)	-2(1)	3(1)	-1(1)
C(11)	29(1)	29(1)	26(1)	2(1)	6(1)	0(1)
C(12)	28(1)	34(2)	26(1)	1(1)	3(1)	4(1)
C(13)	26(1)	33(1)	27(1)	-4(1)	4(1)	-2(1)
C(14)	30(1)	33(2)	27(1)	0(1)	5(1)	-4(1)
C(15)	32(1)	30(1)	23(1)	1(1)	1(1)	1(1)
C(16)	21(1)	33(1)	26(1)	-1(1)	4(1)	-3(1)
C(17)	29(1)	36(2)	31(1)	-6(1)	7(1)	-4(1)
C(18)	36(1)	43(2)	24(1)	0(1)	6(1)	-2(1)
C(19)	32(1)	39(2)	30(2)	5(1)	2(1)	-3(1)
C(20)	26(1)	35(2)	33(2)	2(1)	3(1)	-2(1)
C(21)	23(1)	39(2)	26(1)	-2(1)	4(1)	-5(1)

Table S–25. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for crystal_003.

	x	y	z	U(eq)
H(3A)	1018	8526	7407	35
H(3B)	532	6641	7475	35
H(5)	782	3077	8762	38
H(6)	1281	1781	10481	41
H(7)	2036	3958	11406	41
H(8)	2290	7447	10601	42
H(9)	1803	8719	8875	38
H(11)	1938	2399	7236	33
H(12)	2916	2596	7273	35
H(13)	3325	5887	6575	34
H(14)	2755	8959	5806	36
H(15)	1777	8799	5781	34
H(17)	929	5150	2305	38
H(18)	592	7519	755	41
H(19)	170	11091	1057	41
H(20)	68	12275	2892	38
H(21)	408	9908	4451	35

VII. ^{1}H NMR Spectra

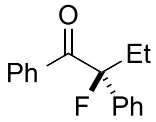
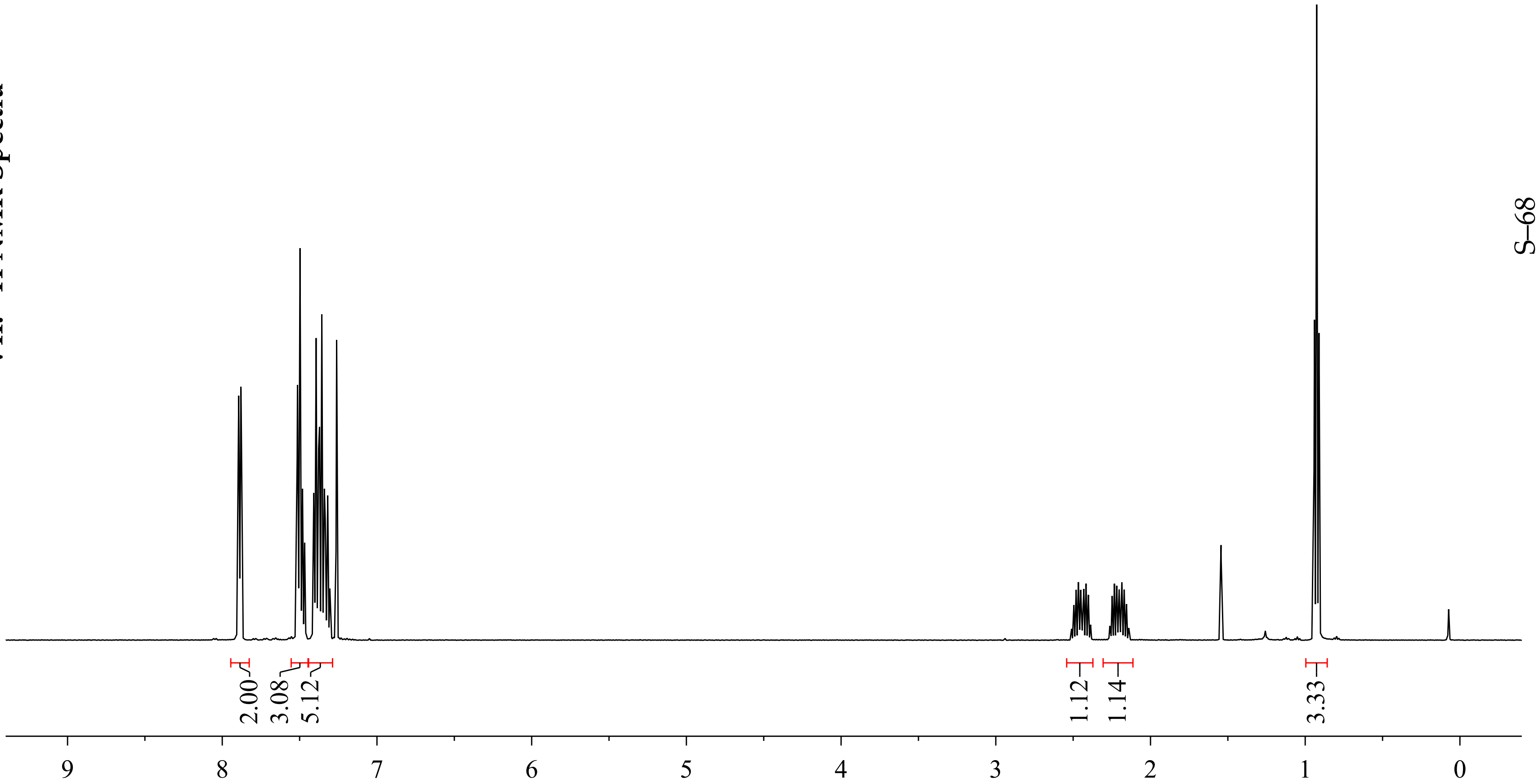


Table 2, Entry 1
($CDCl_3$, 500 MHz)



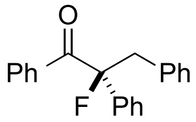
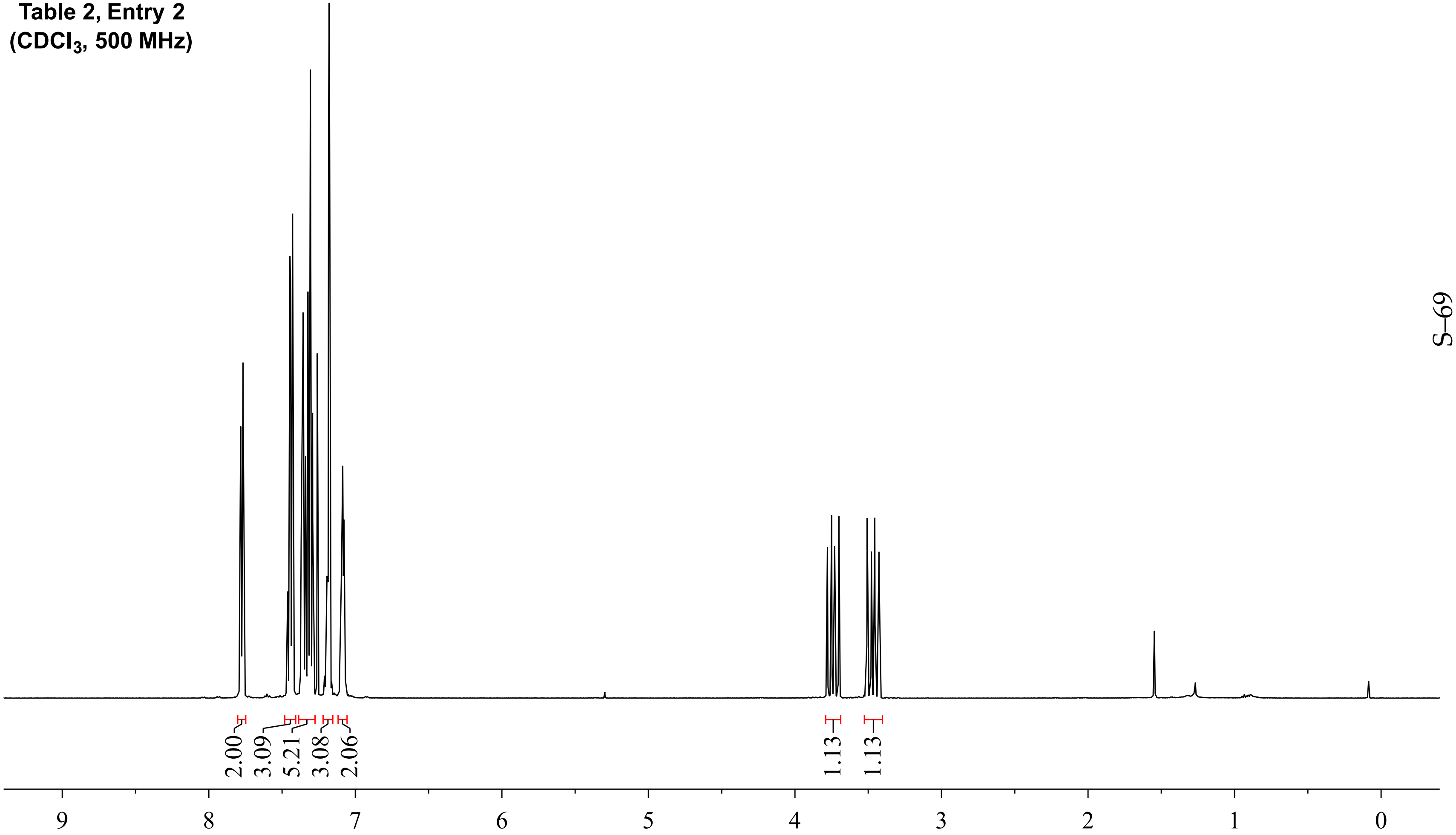


Table 2, Entry 2
(CDCl$_3$, 500 MHz)



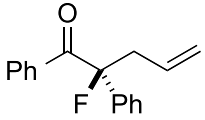
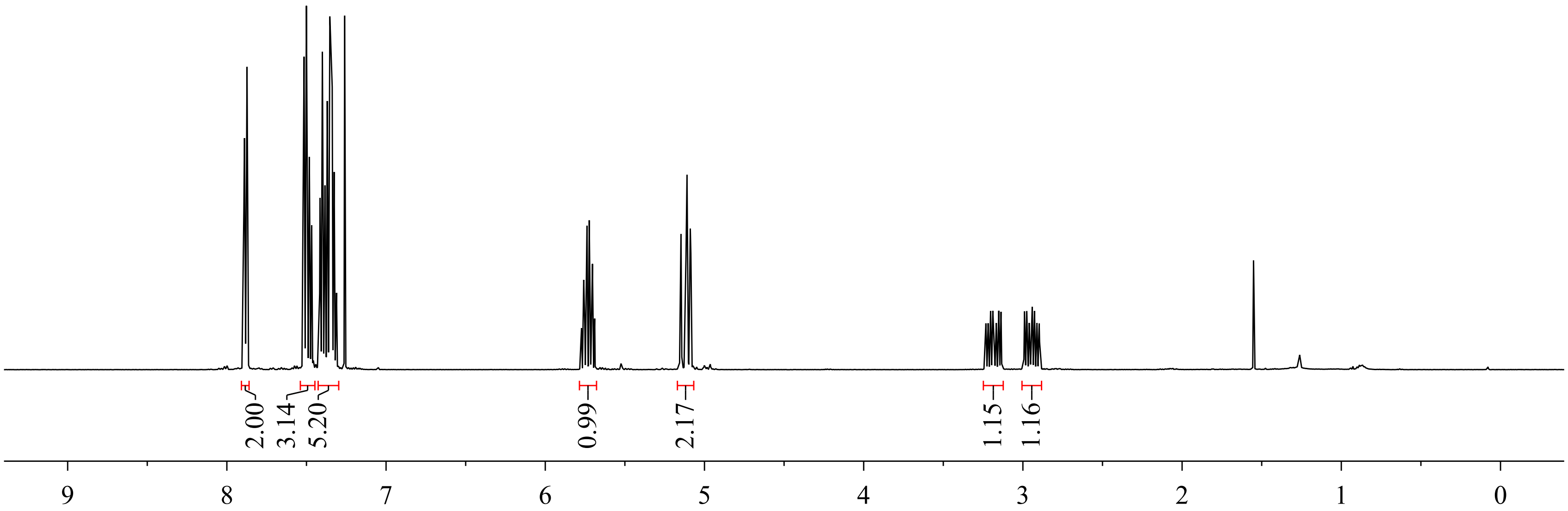


Table 2, Entry 3
(CDCl$_3$, 500 MHz)



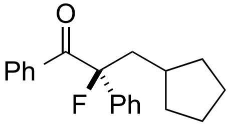
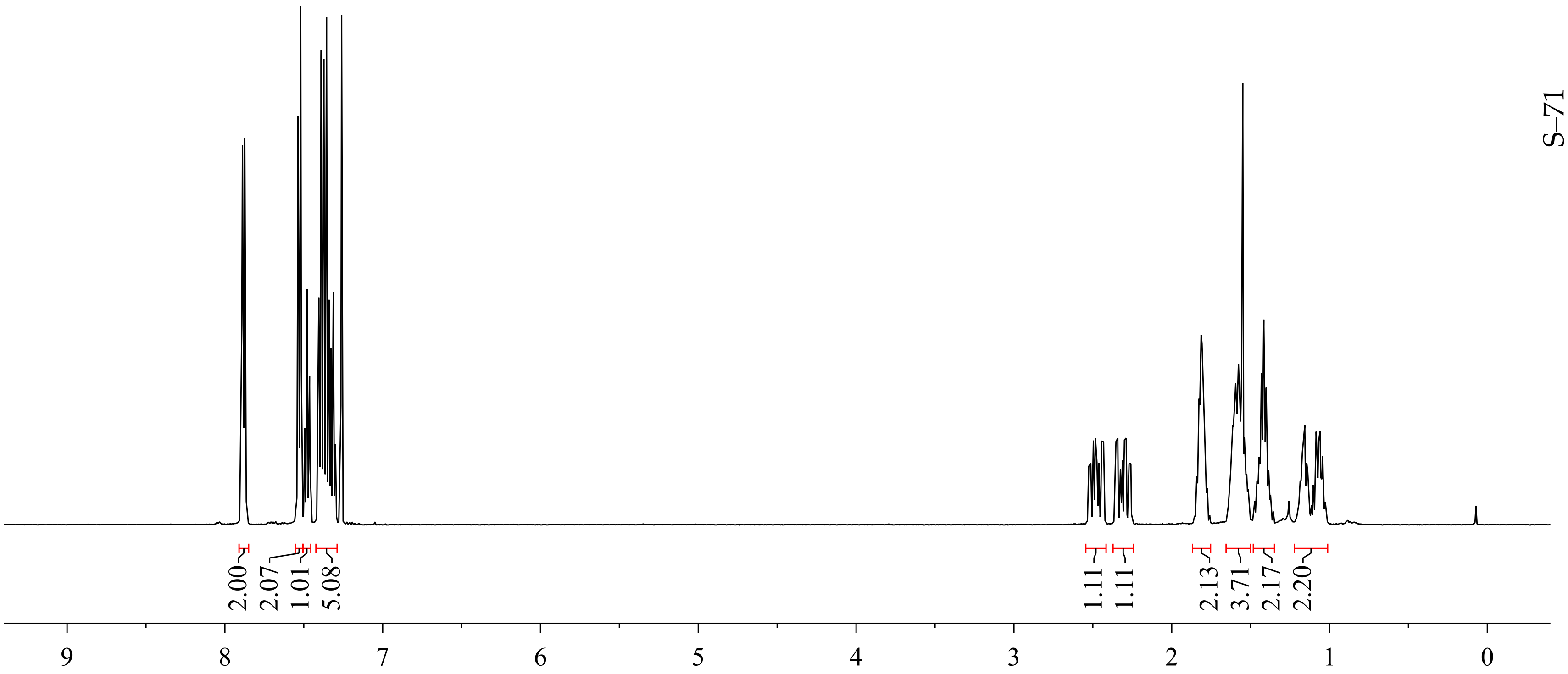


Table 2, Entry 4
($CDCl_3$, 500 MHz)



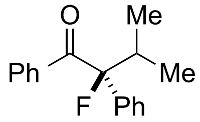
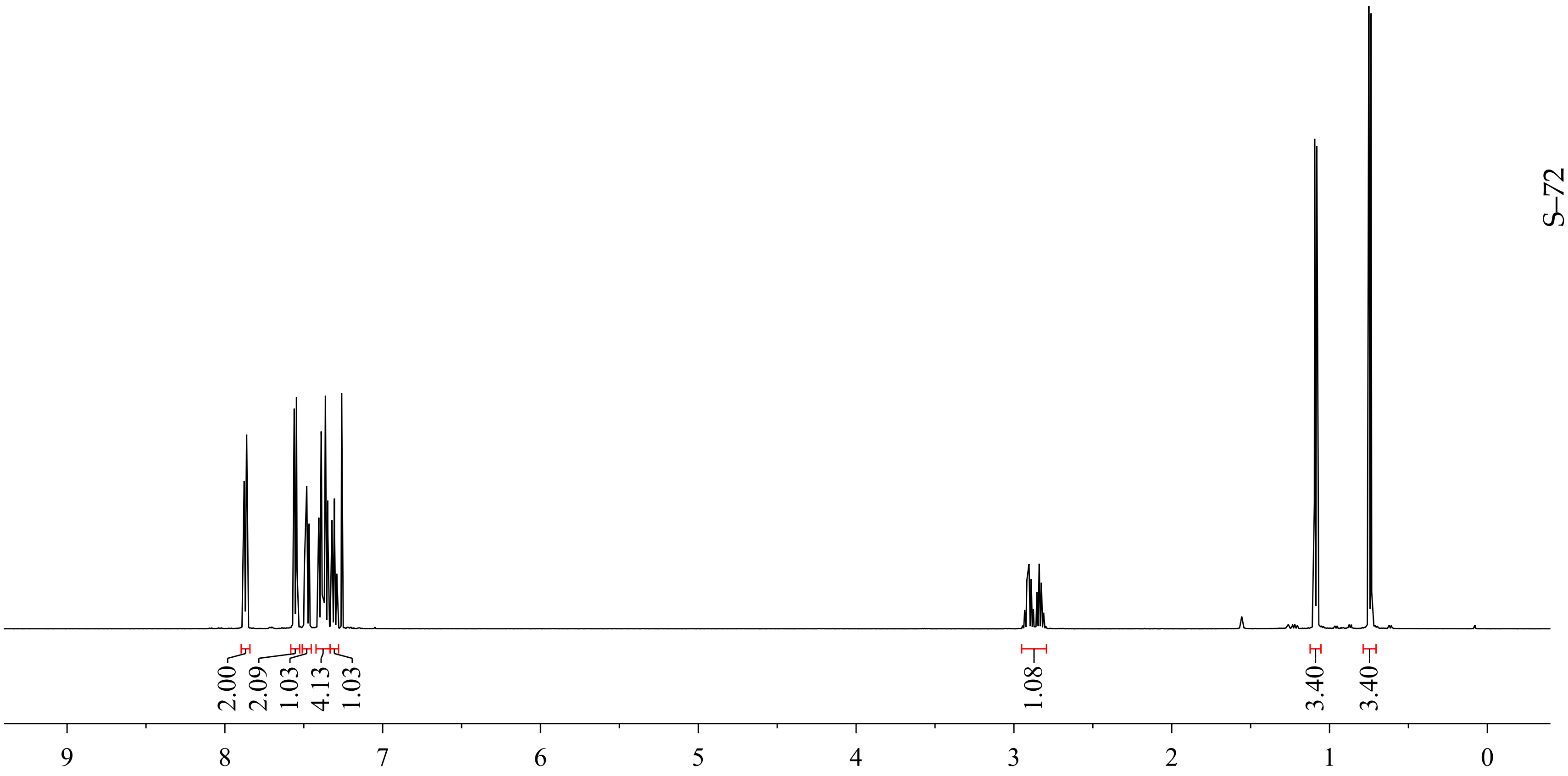


Table 2, Entry 5
($CDCl_3$, 500 MHz)



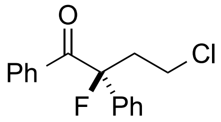


Table 2, Entry 6
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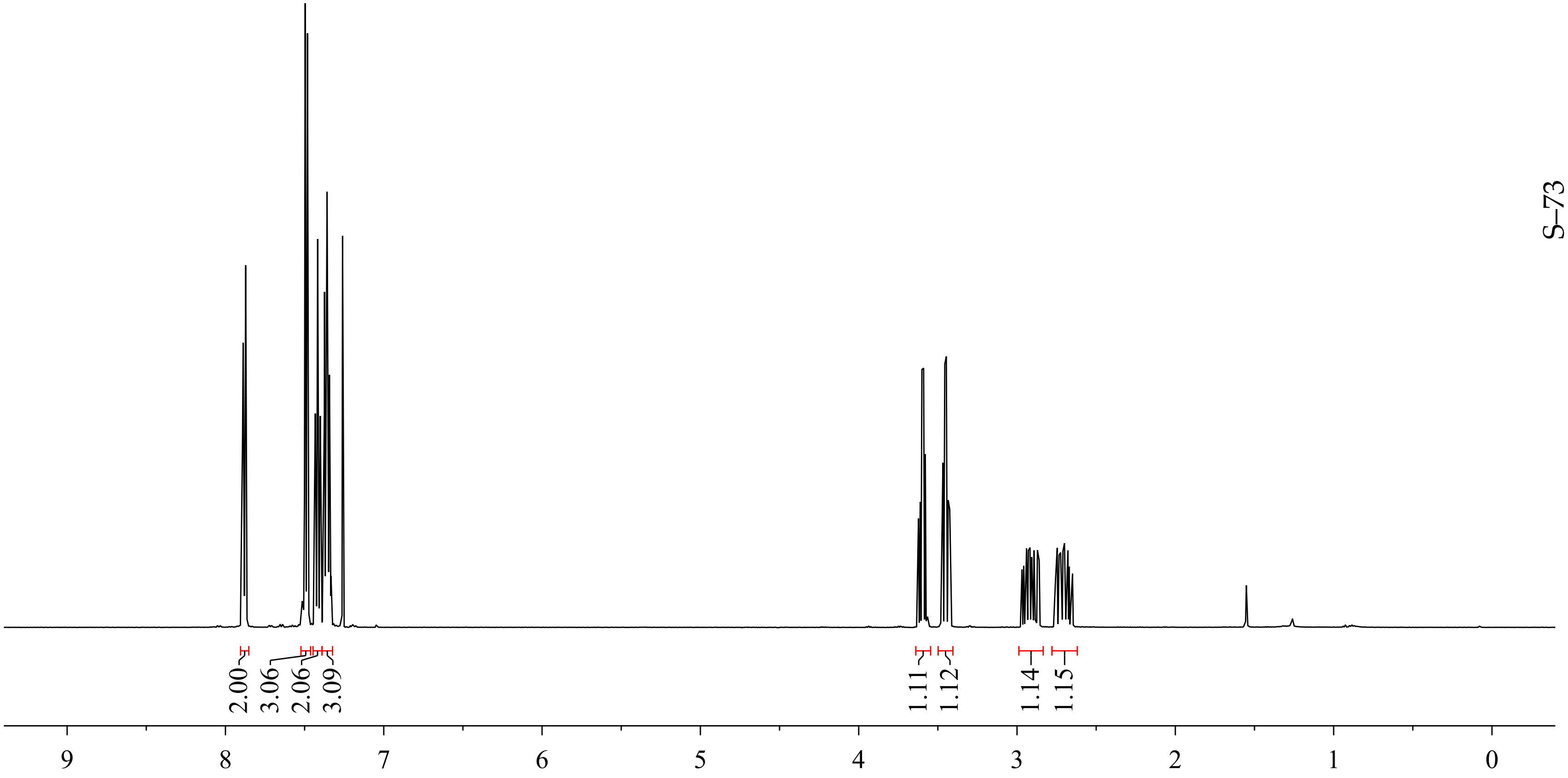

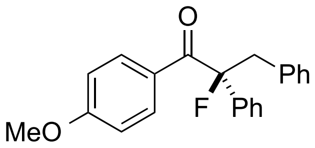

Table 2, Entry 7
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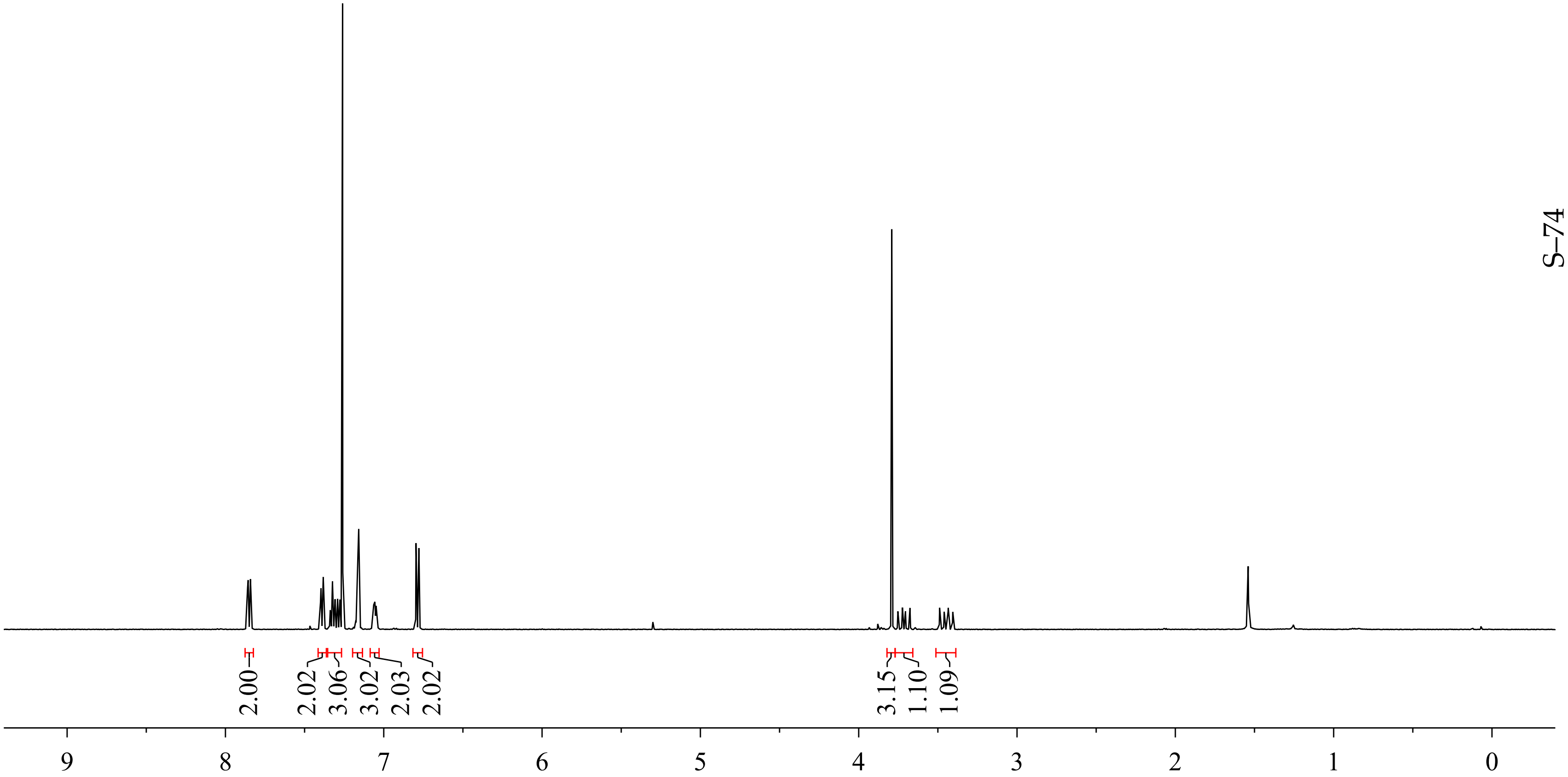

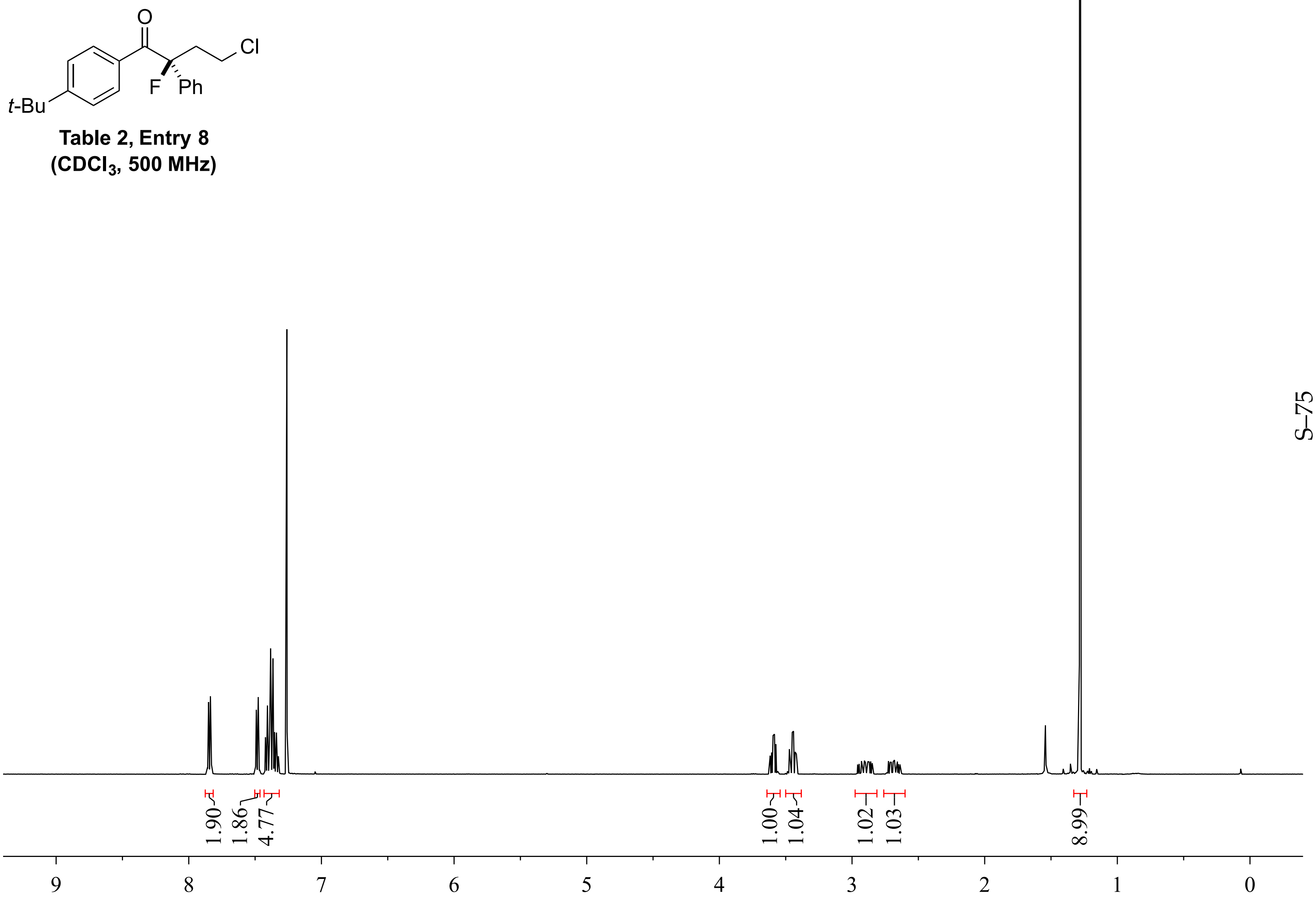

Table 2, Entry 8
($CDCl_3$, 500 MHz)

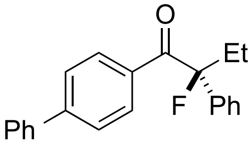

Table 2, Entry 9
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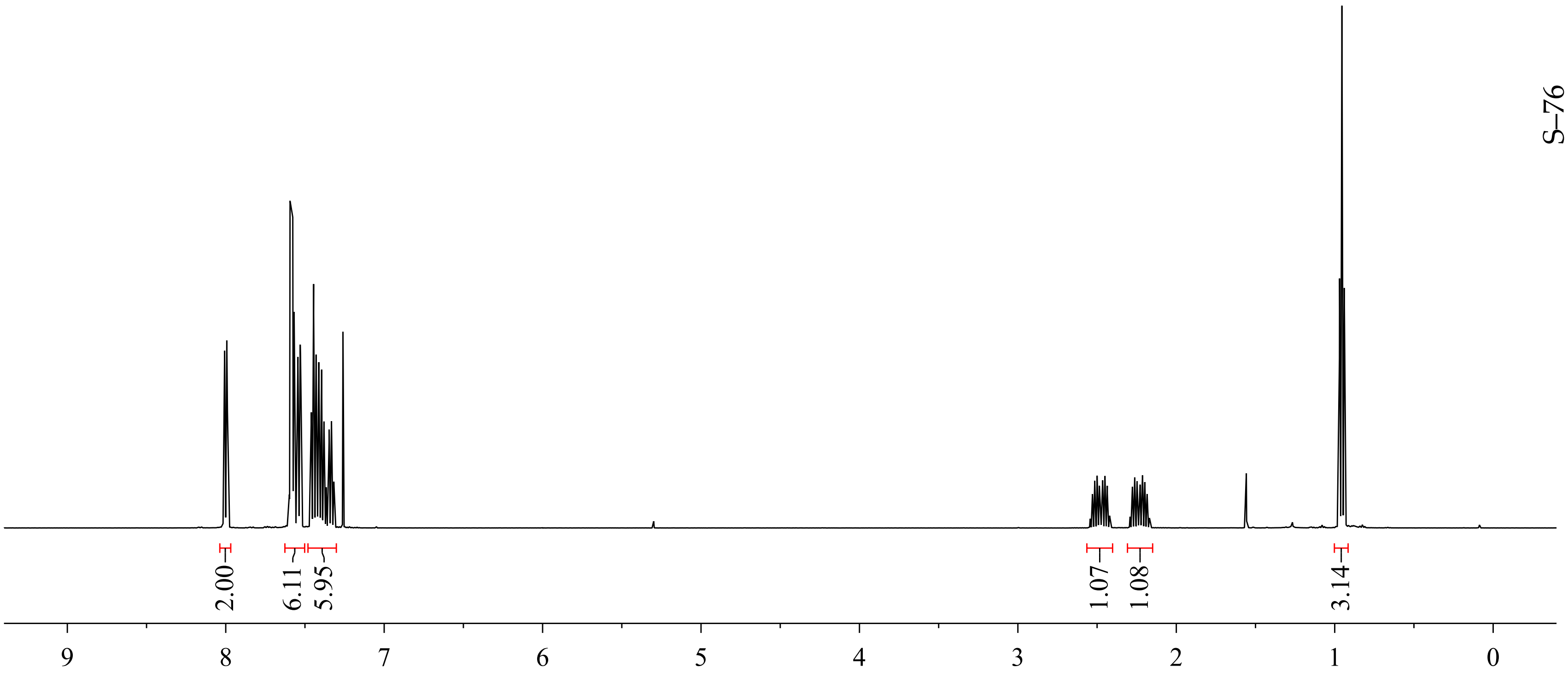

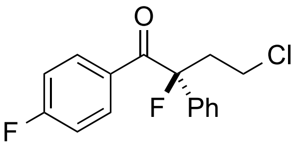

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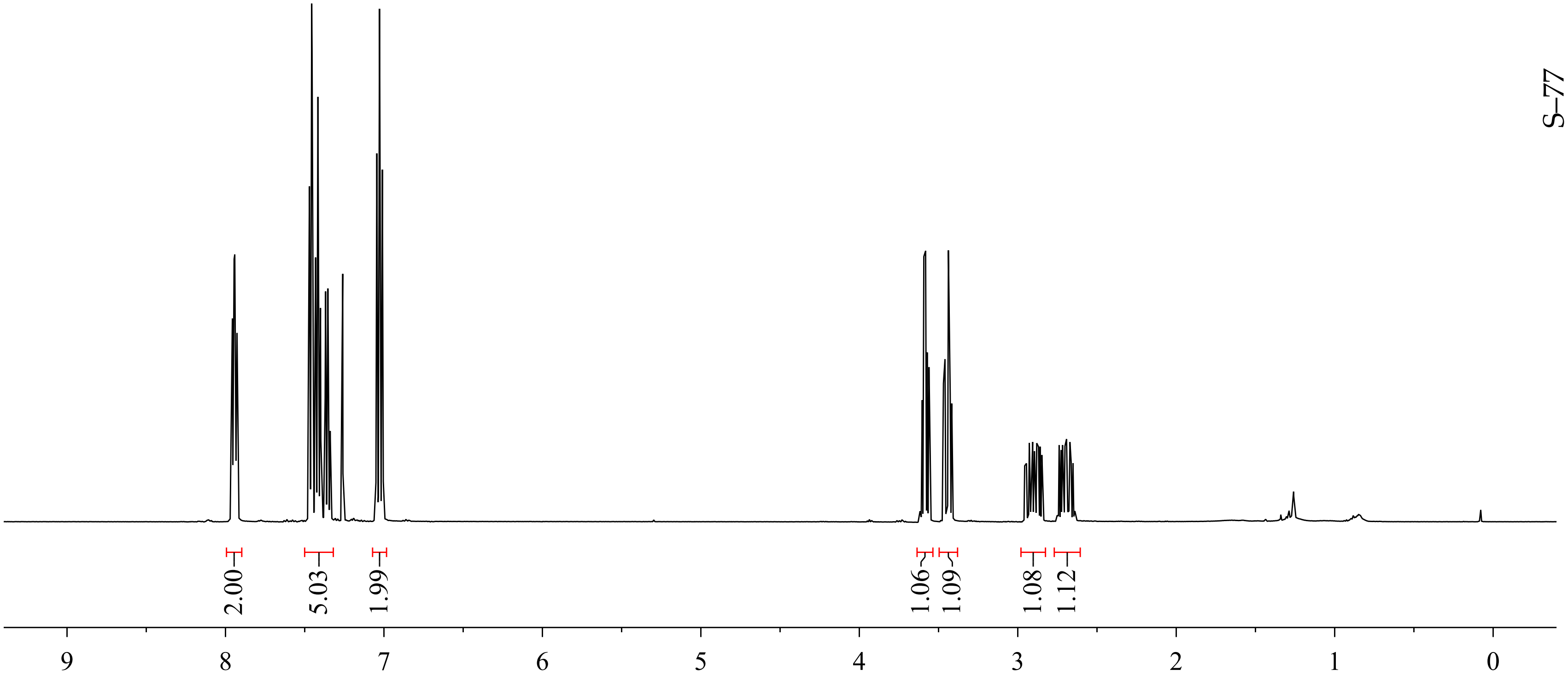

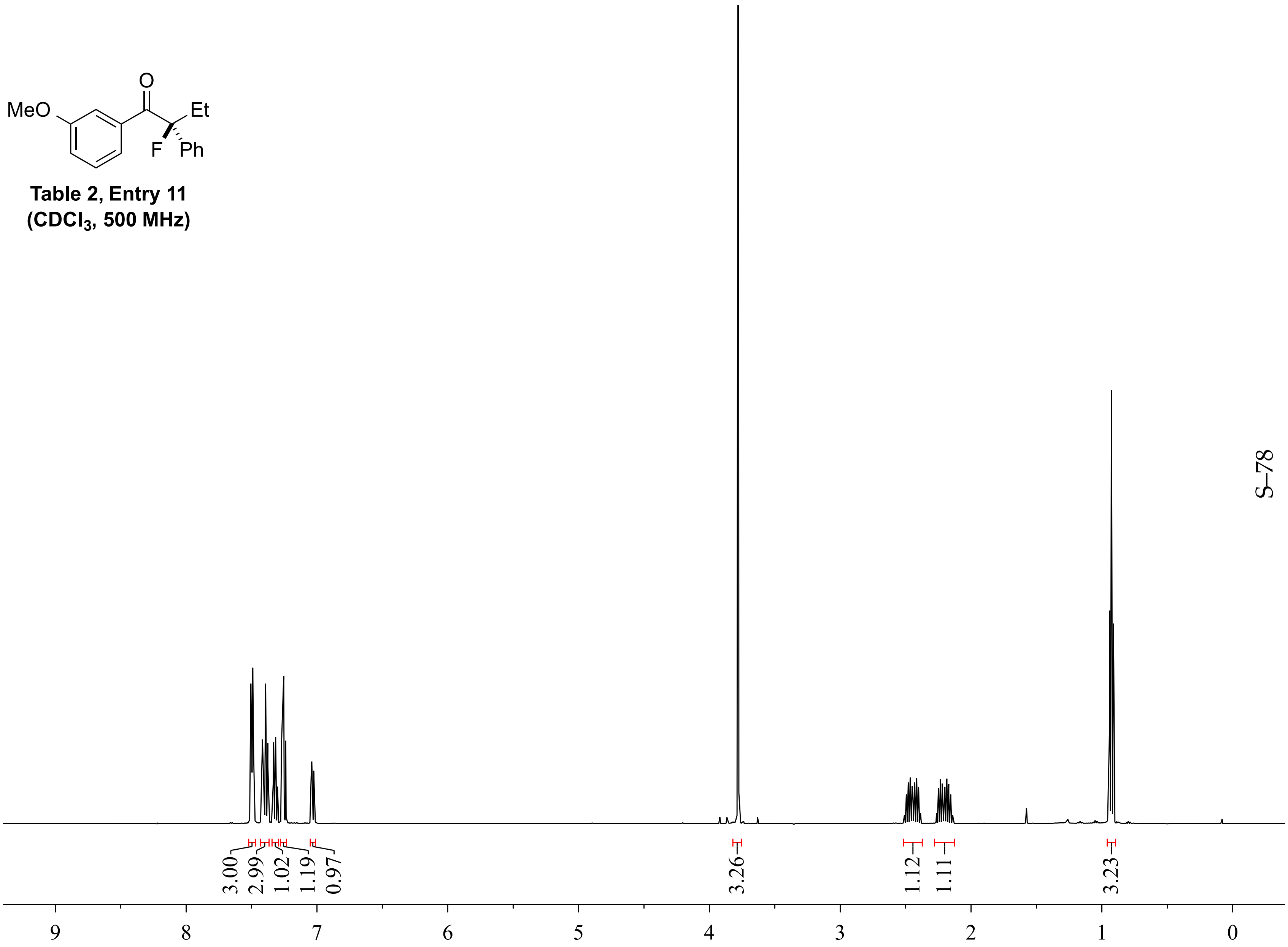

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($CDCl_3$, 500 MHz)

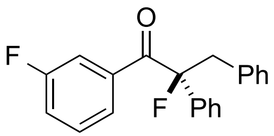

Table 2, Entry 12
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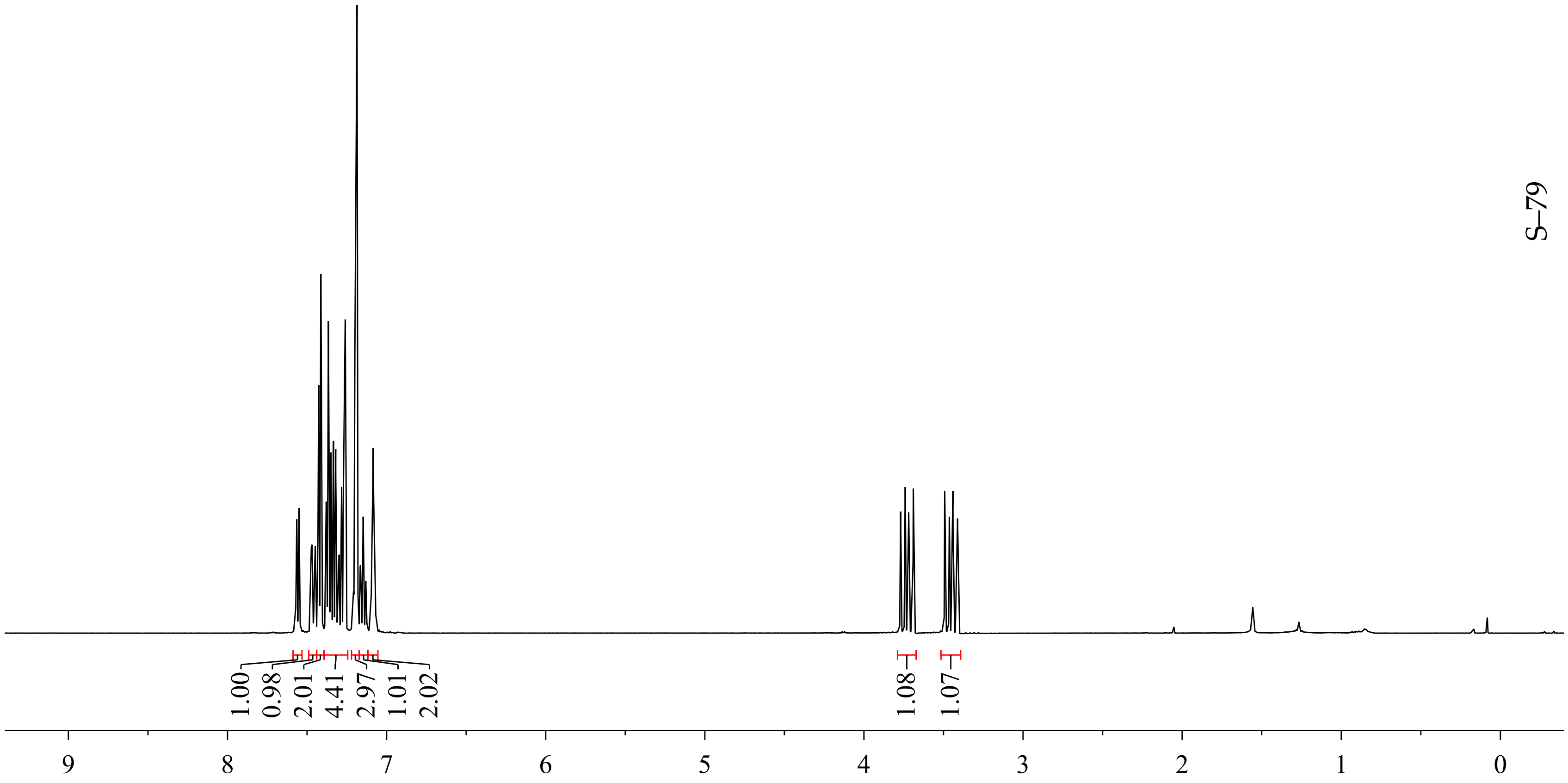

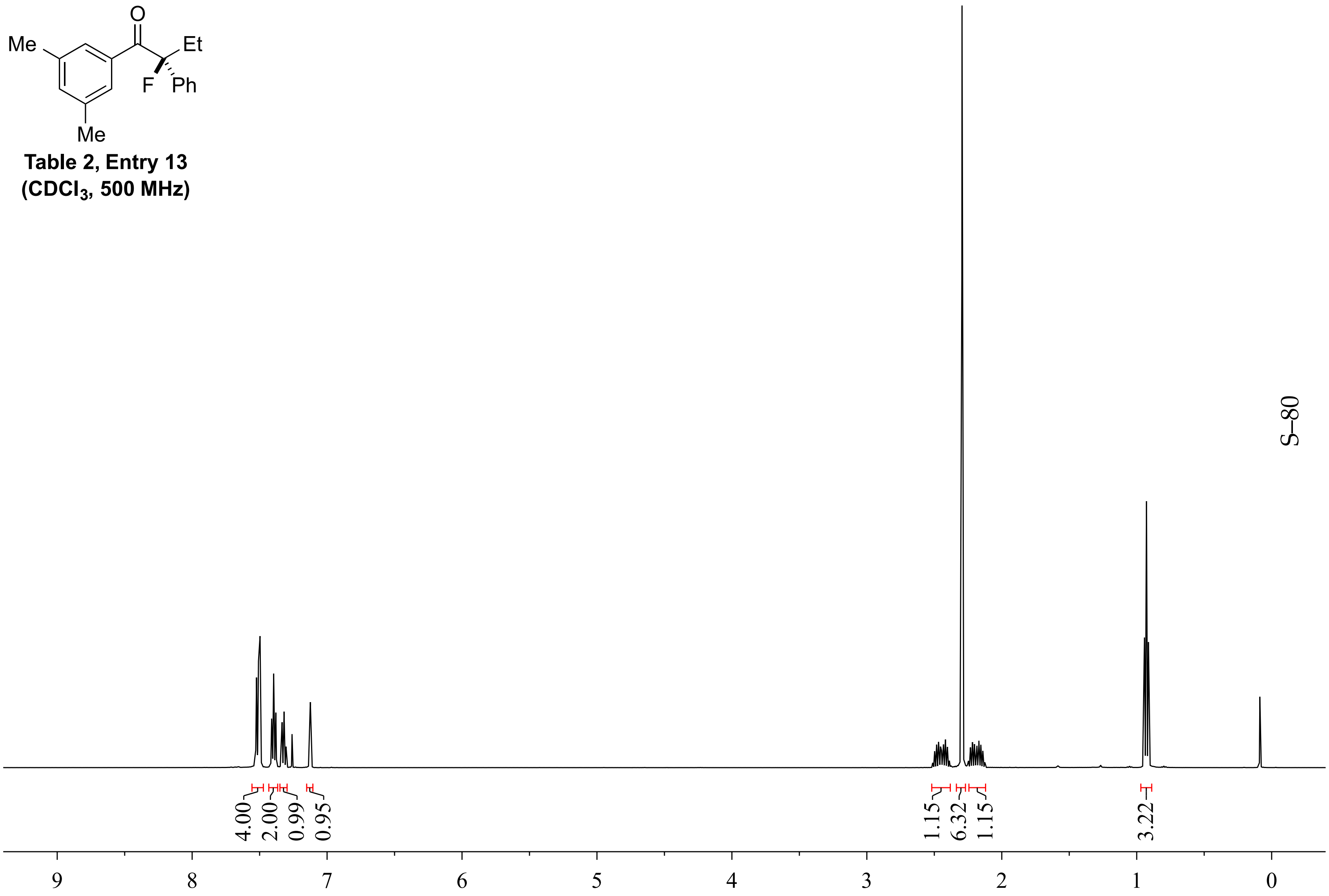

Table 2, Entry 13
($CDCl_3$, 500 MHz)

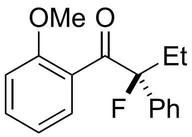

Table 2, Entry 14
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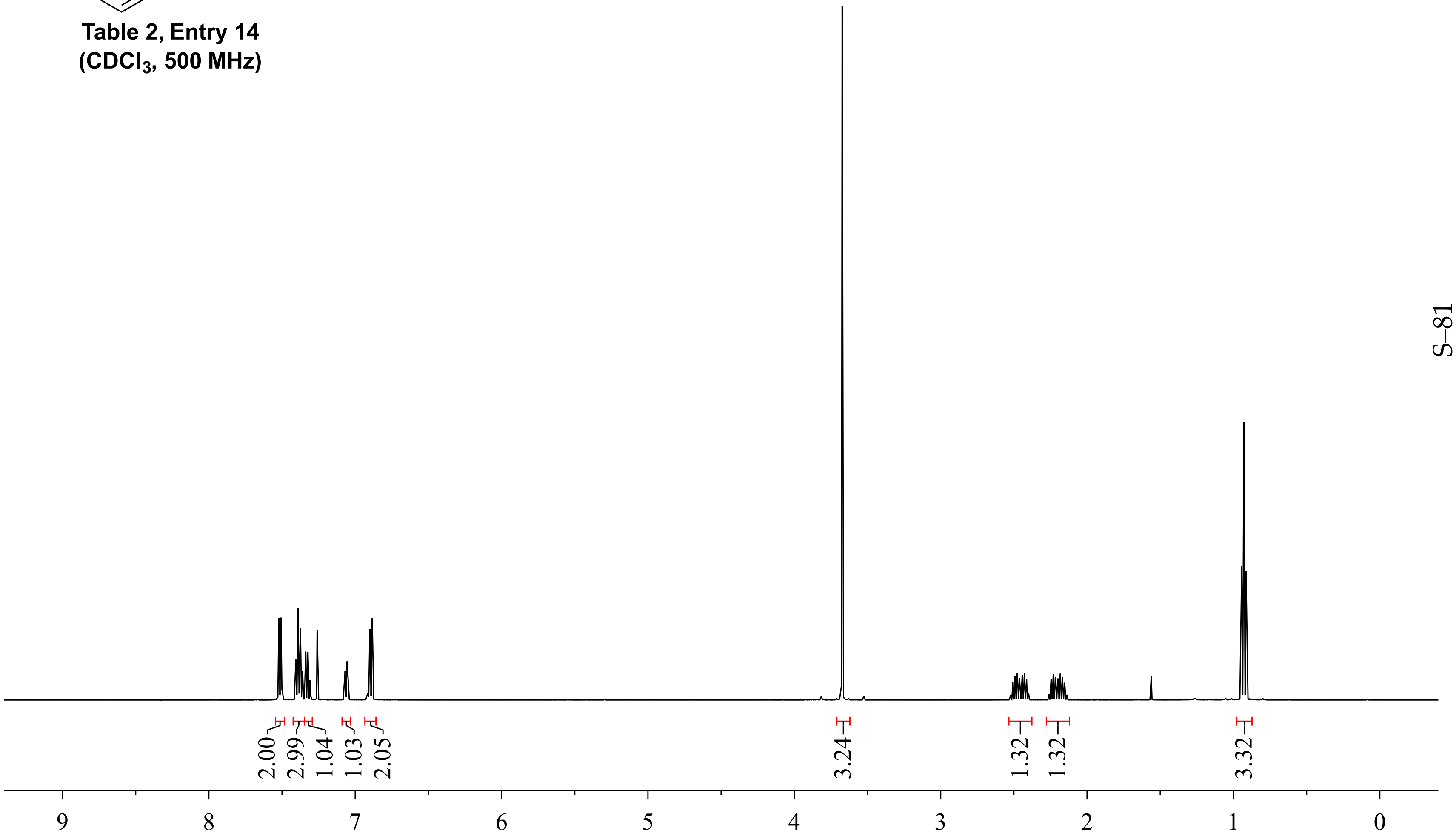

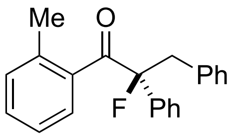

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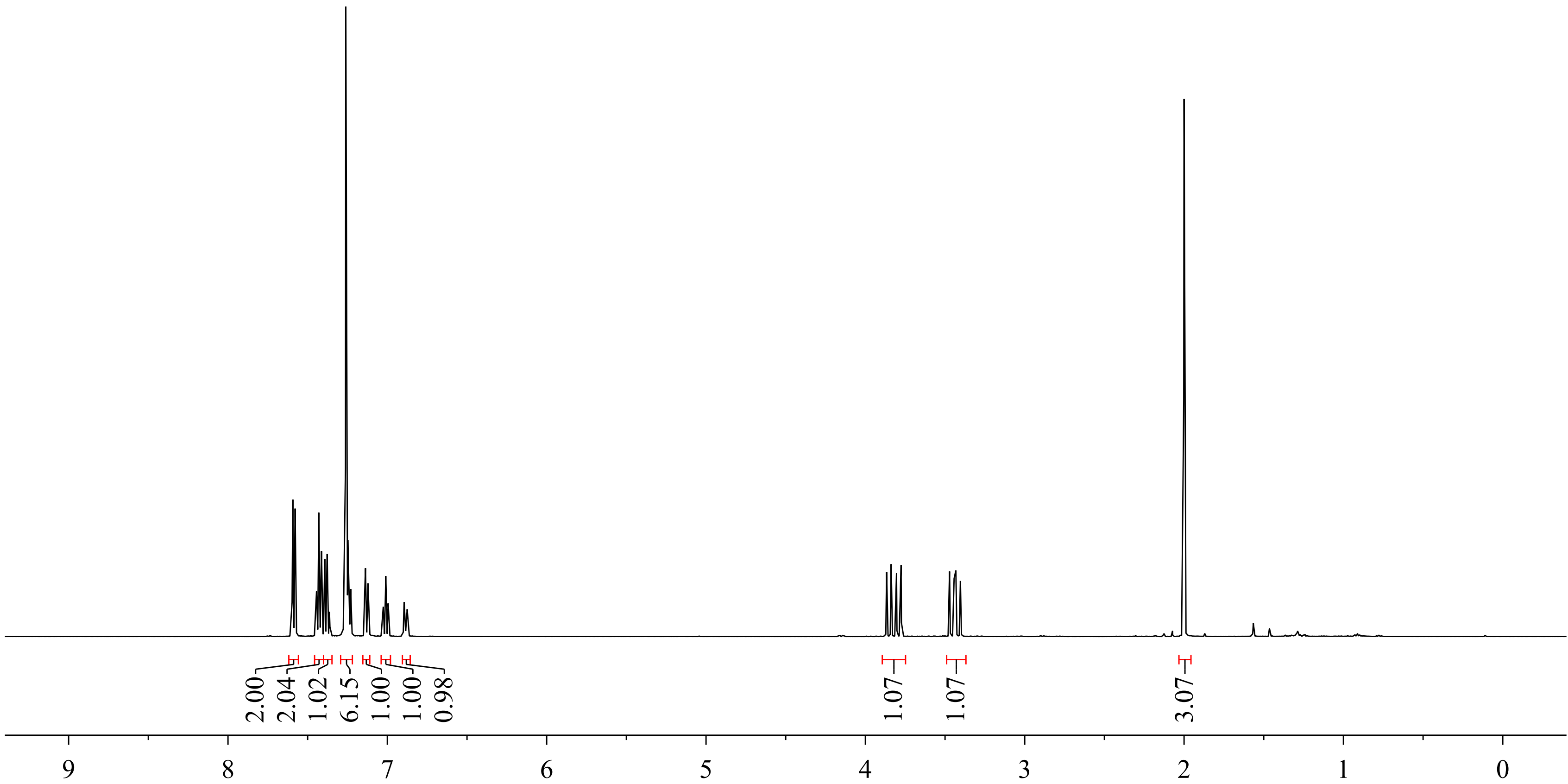


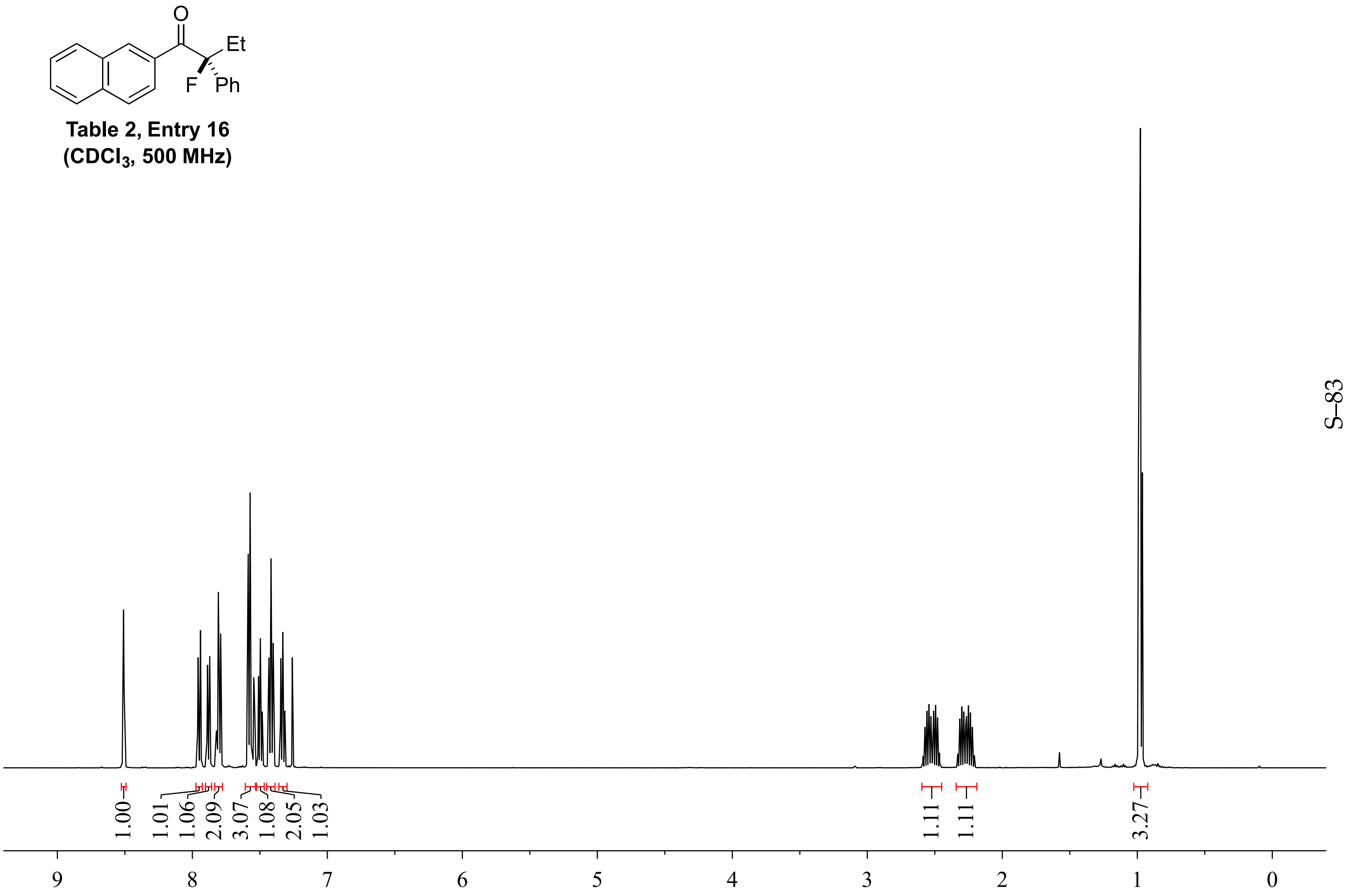


Table 2, Entry 16
($CDCl_3$, 500 MHz)

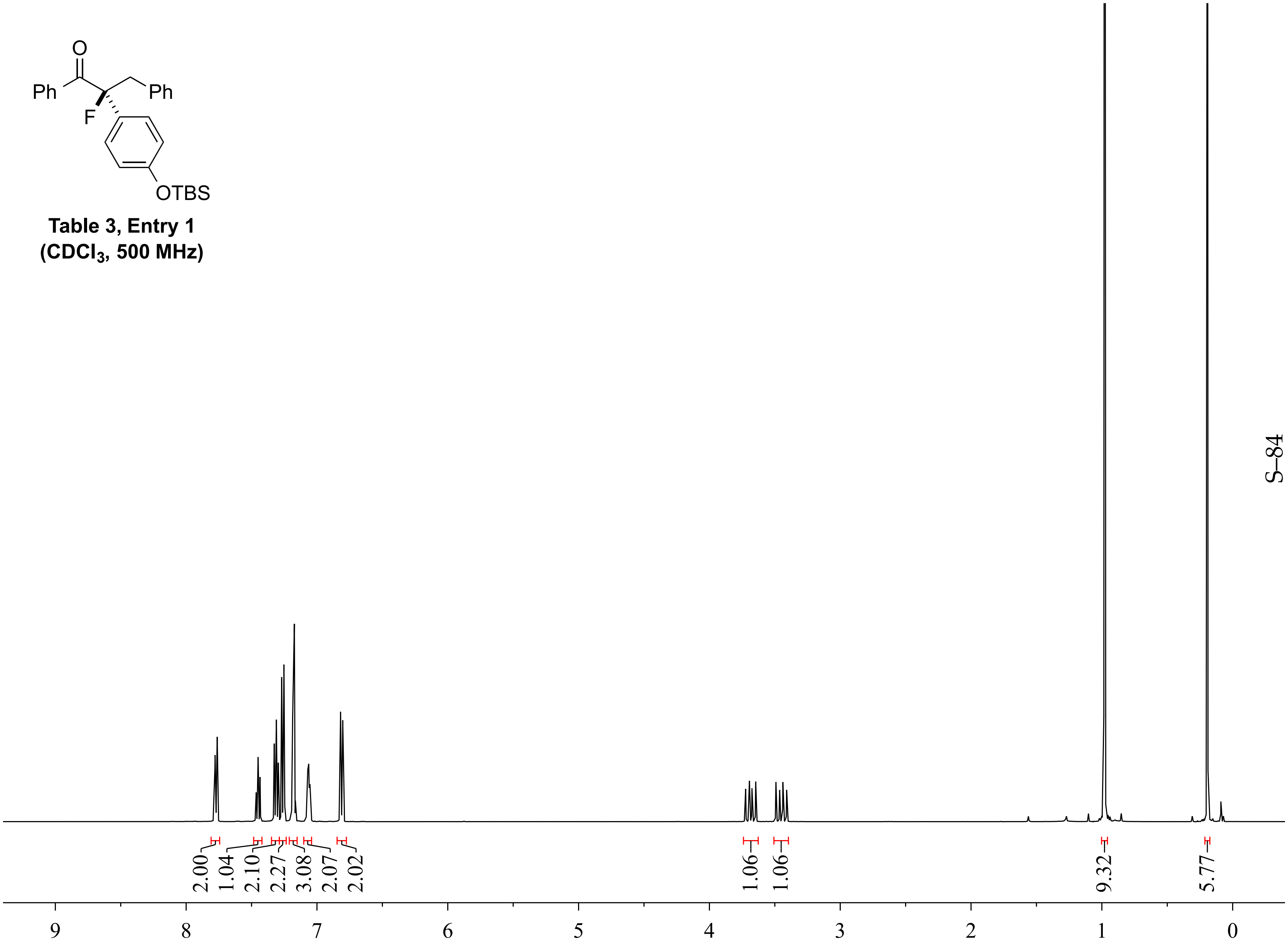
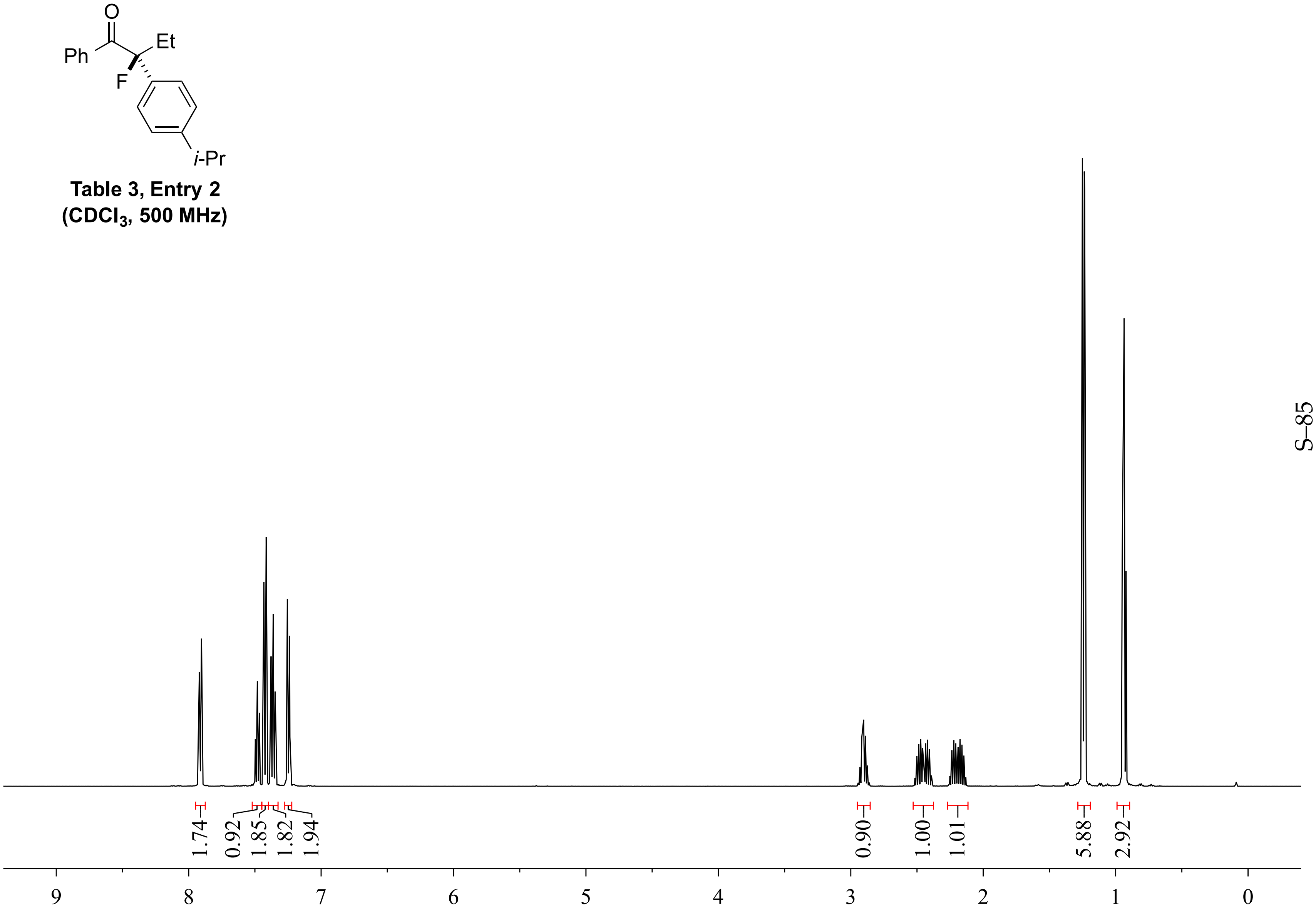


Table 3, Entry 1
($CDCl_3$, 500 MHz)



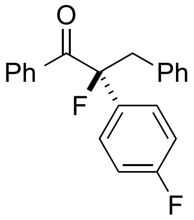


Table 3, Entry 3
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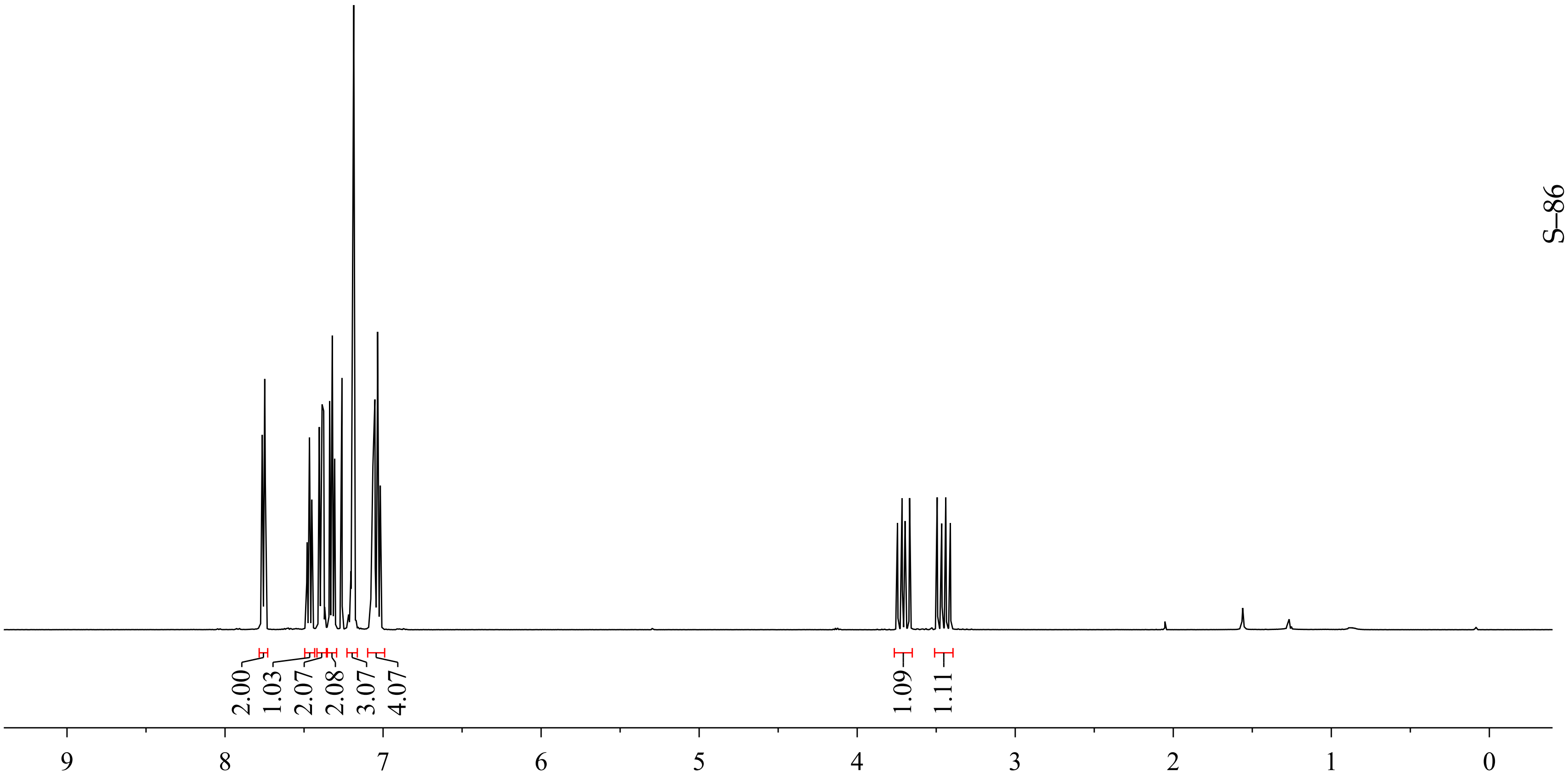

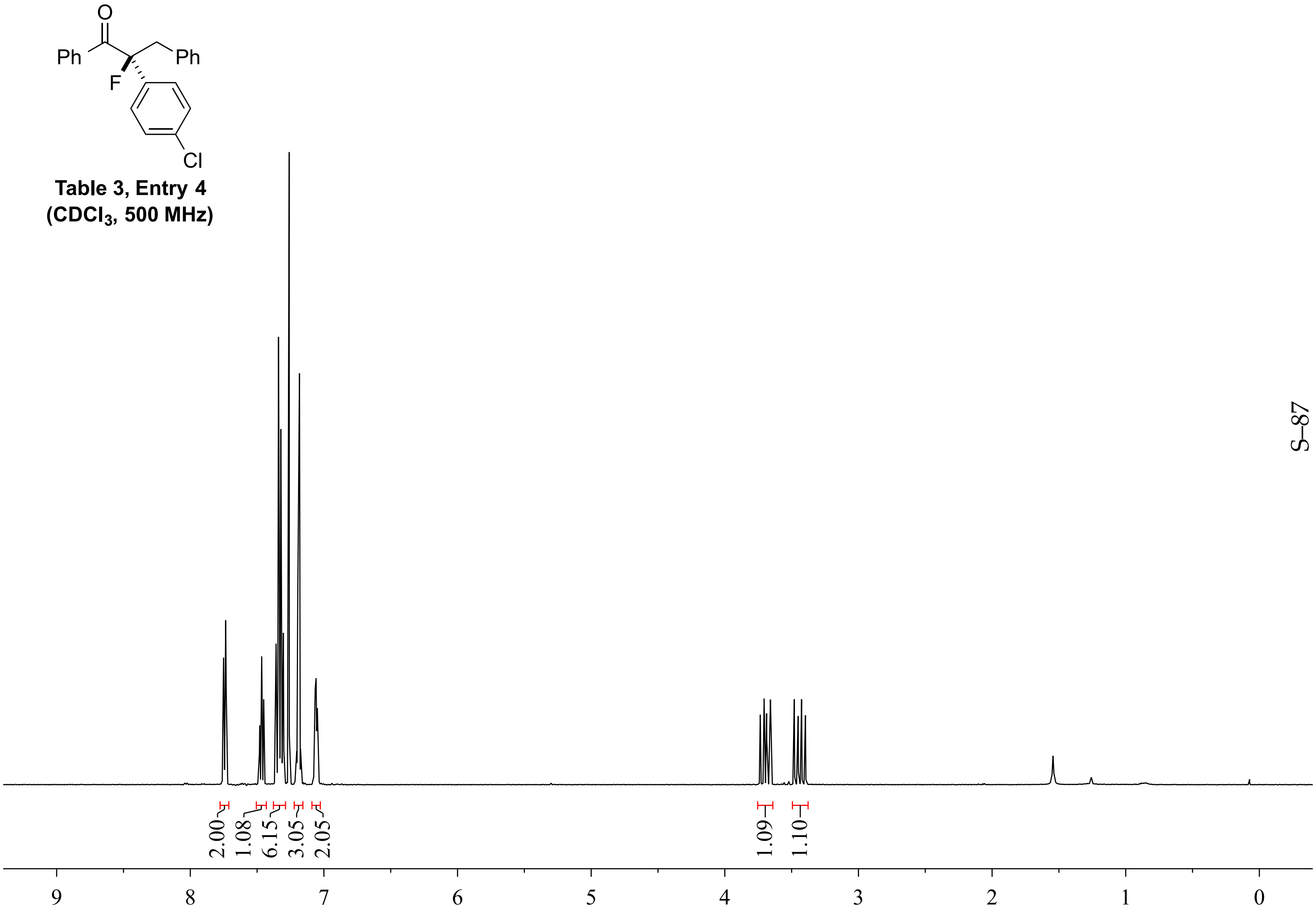

Table 3, Entry 4
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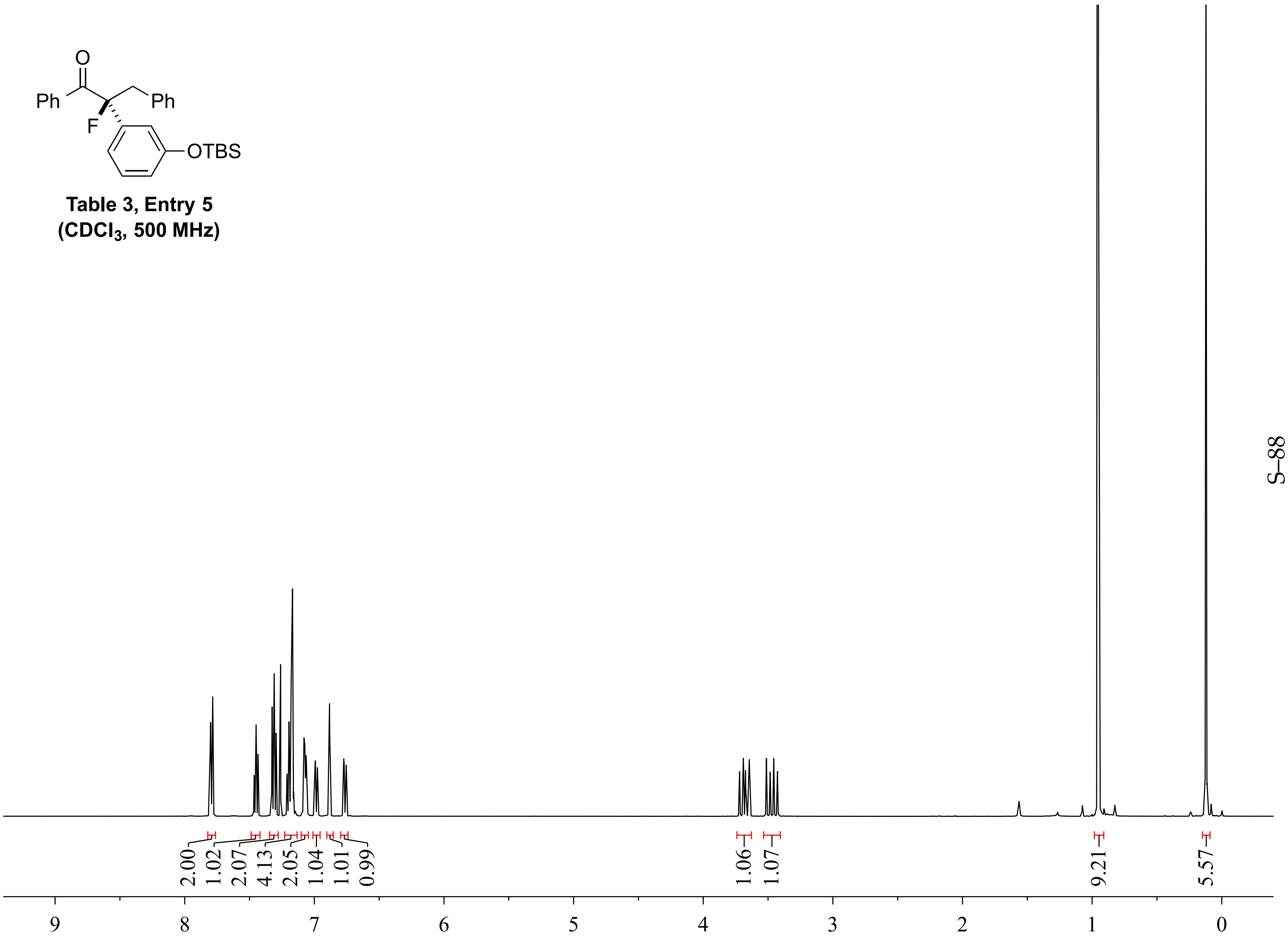


Table 3, Entry 5
(CDCl$_3$, 500 MHz)

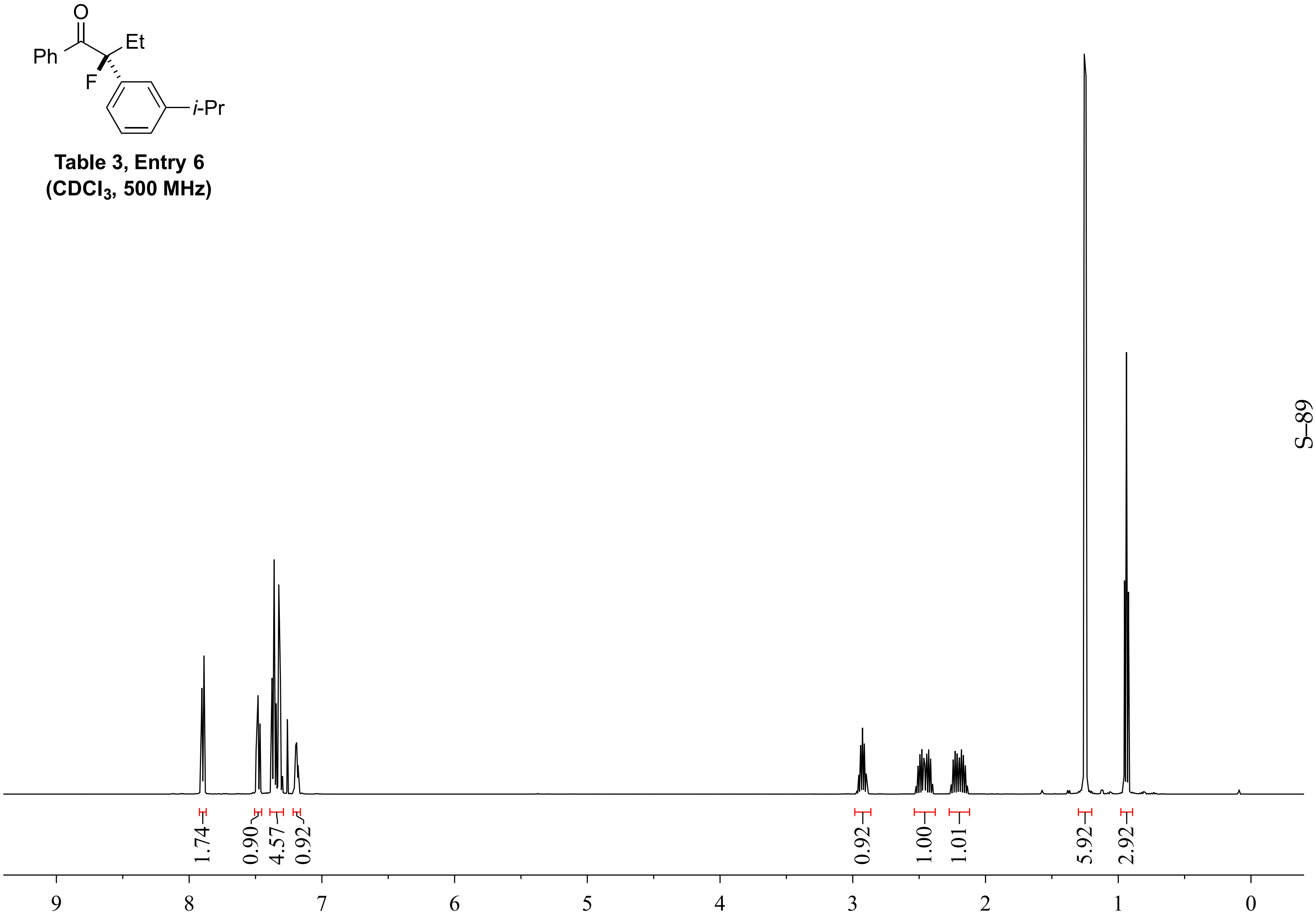


Table 3, Entry 6
(CDCl$_3$, 500 MHz)

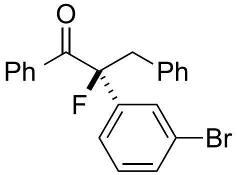
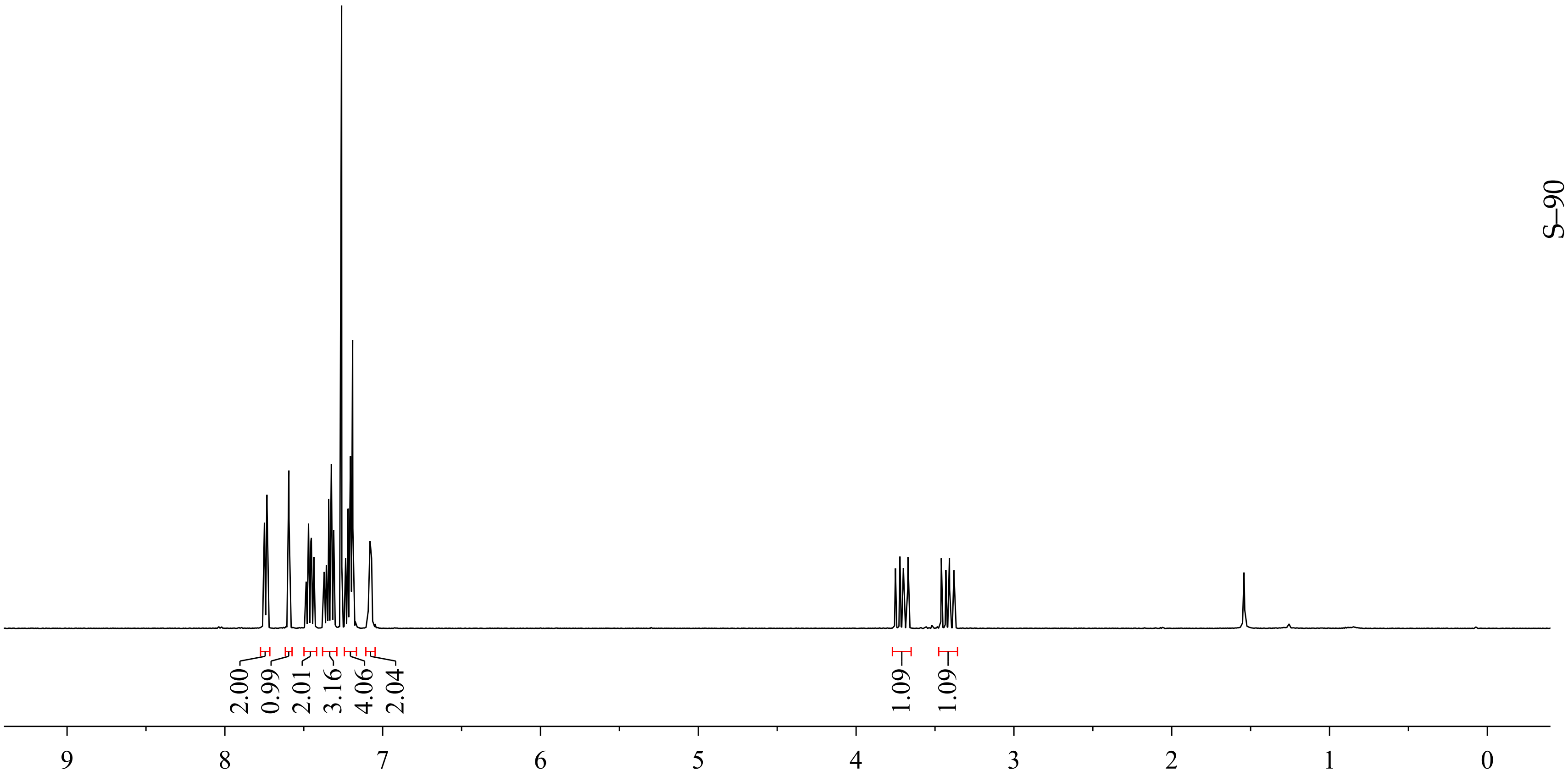


Table 3, Entry 7
(CDCl$_3$, 500 MHz)



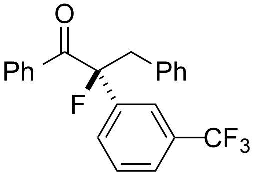
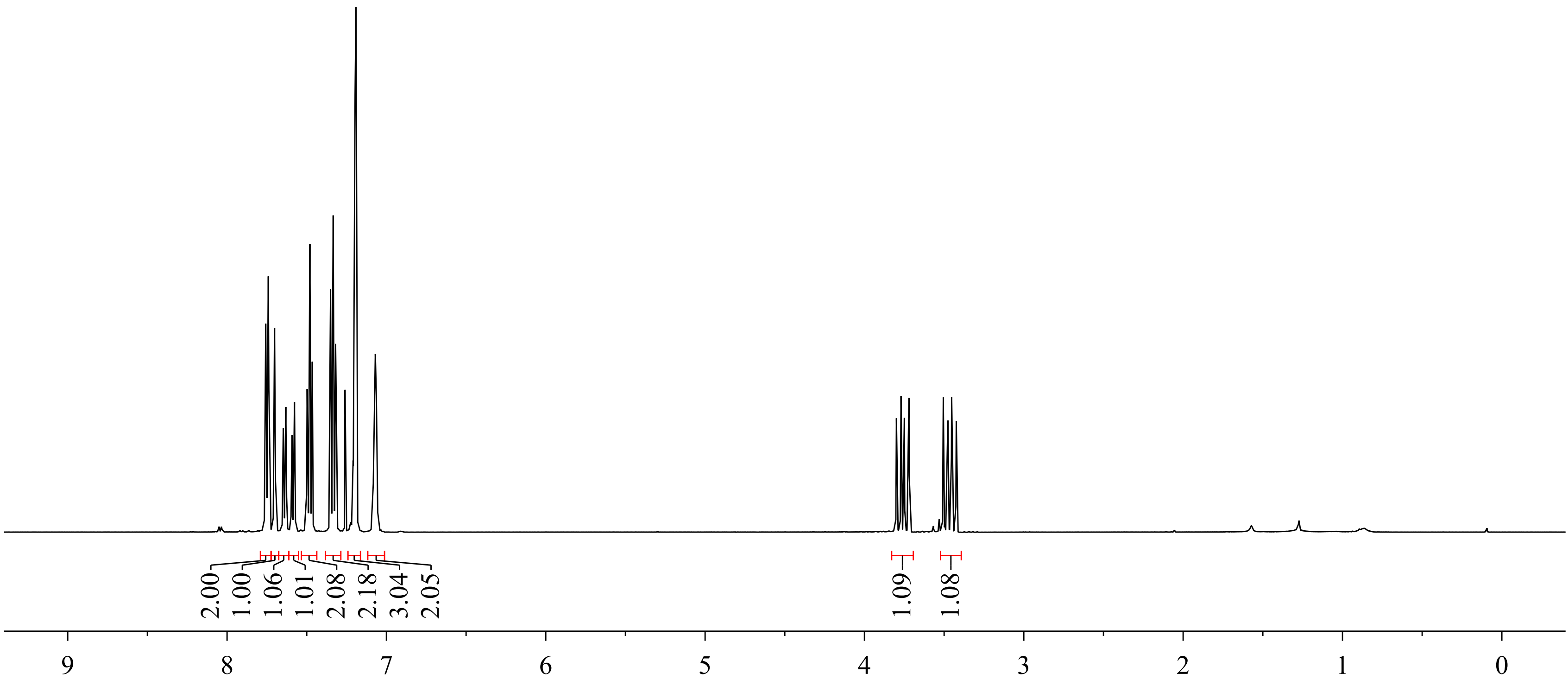


Table 3, Entry 8
($CDCl_3$, 500 MHz)



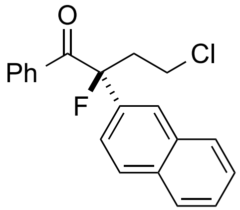


Table 3, Entry 9
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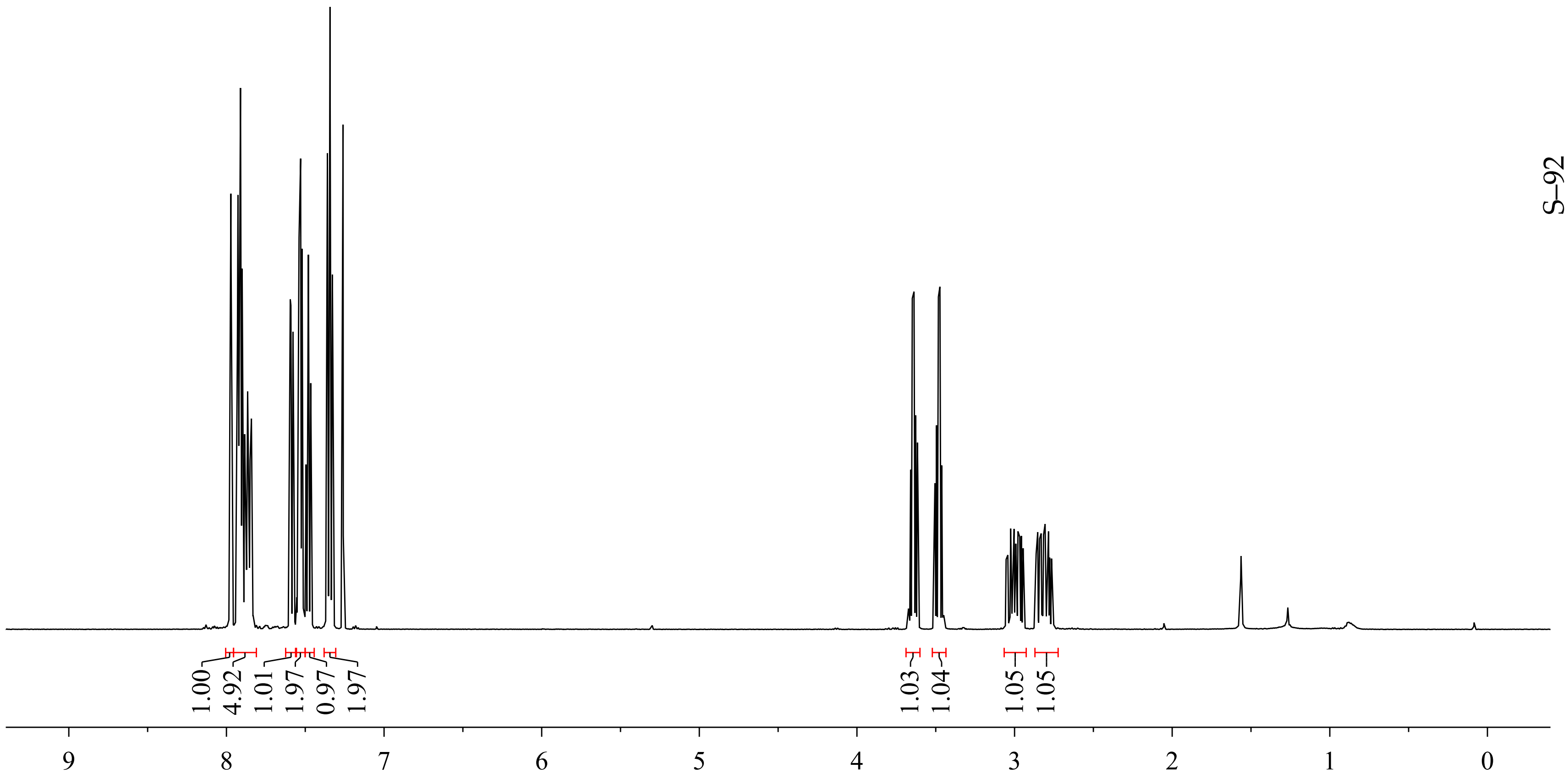
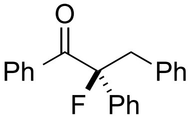
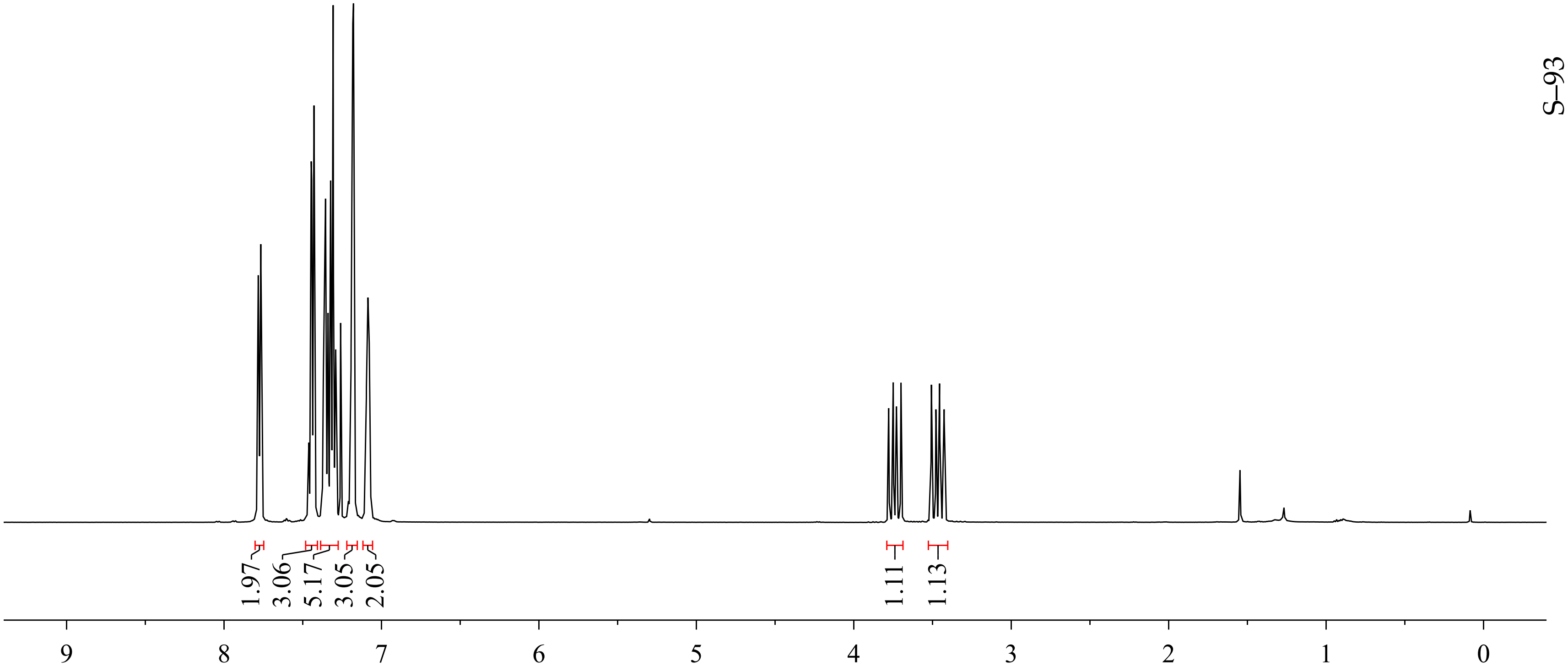
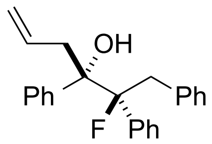




Eq 3
($CDCl_3$, 500 MHz)





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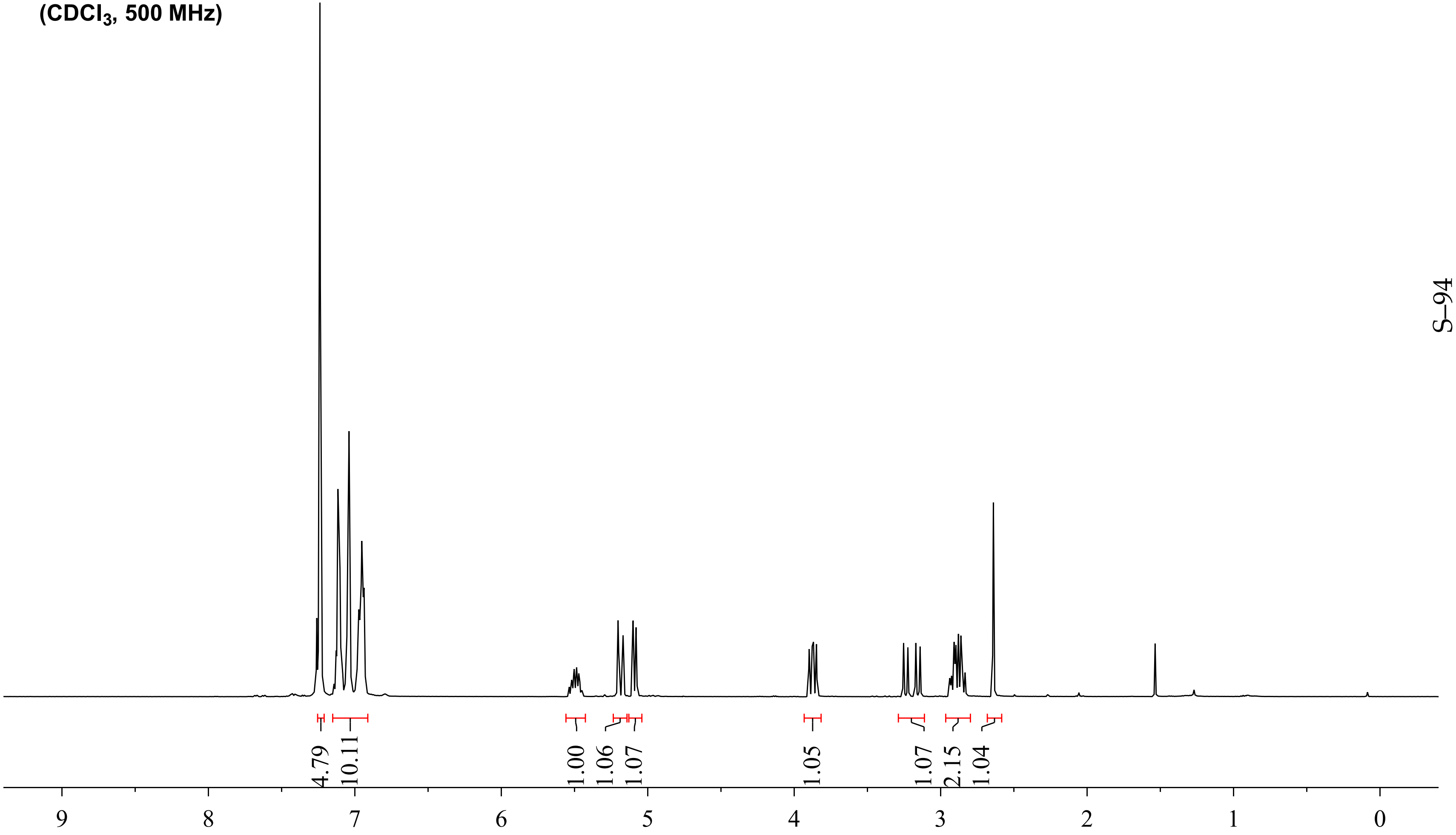
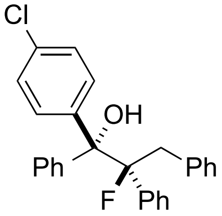
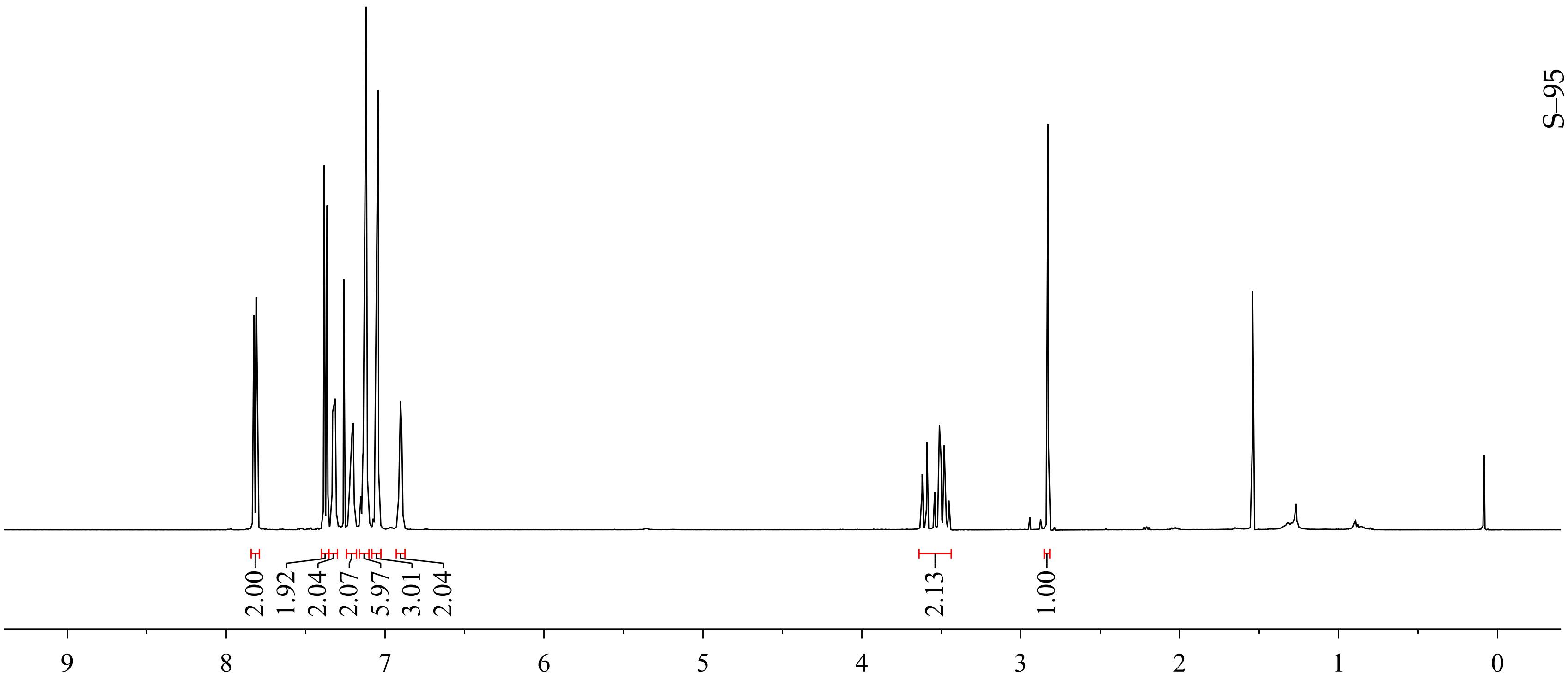
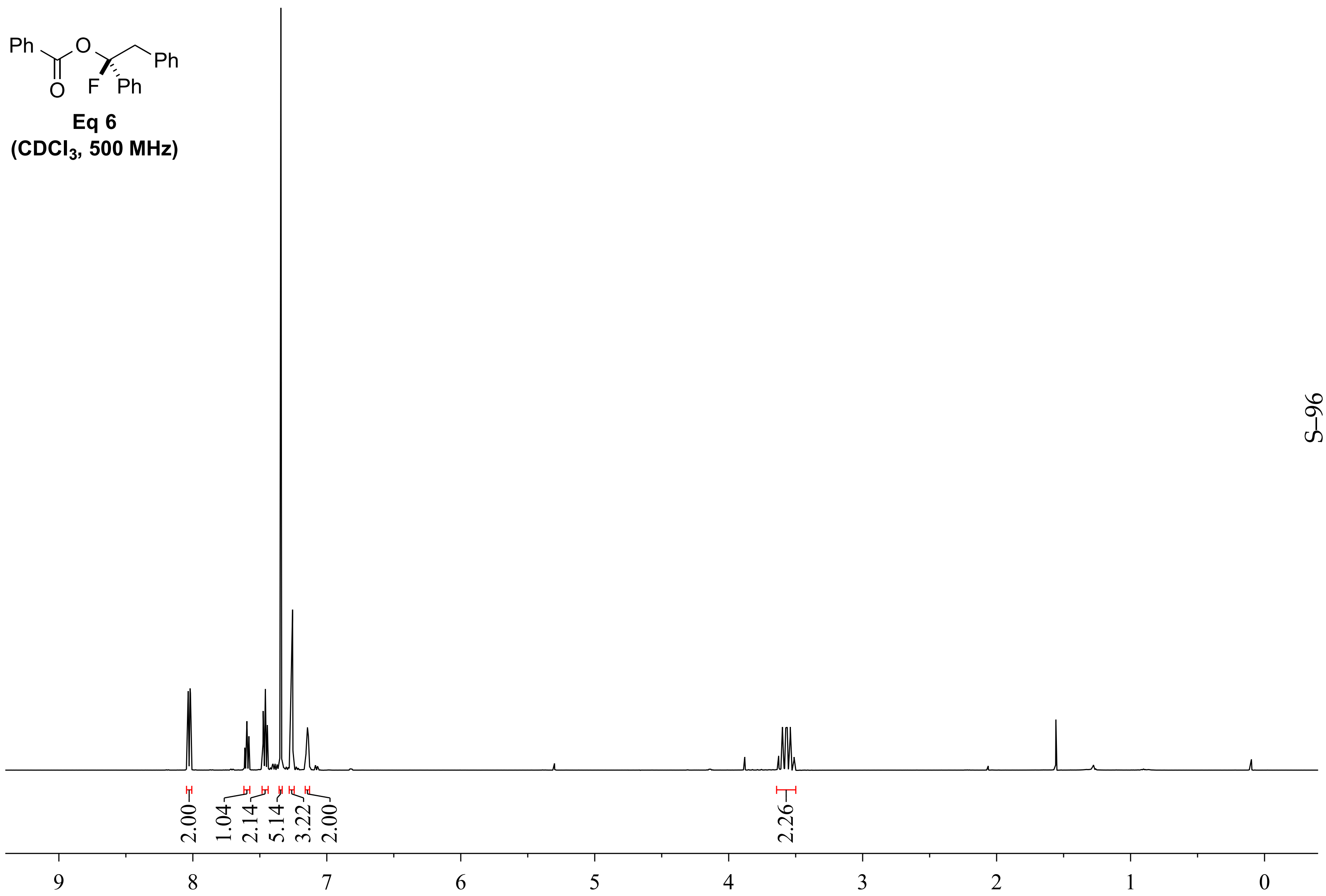
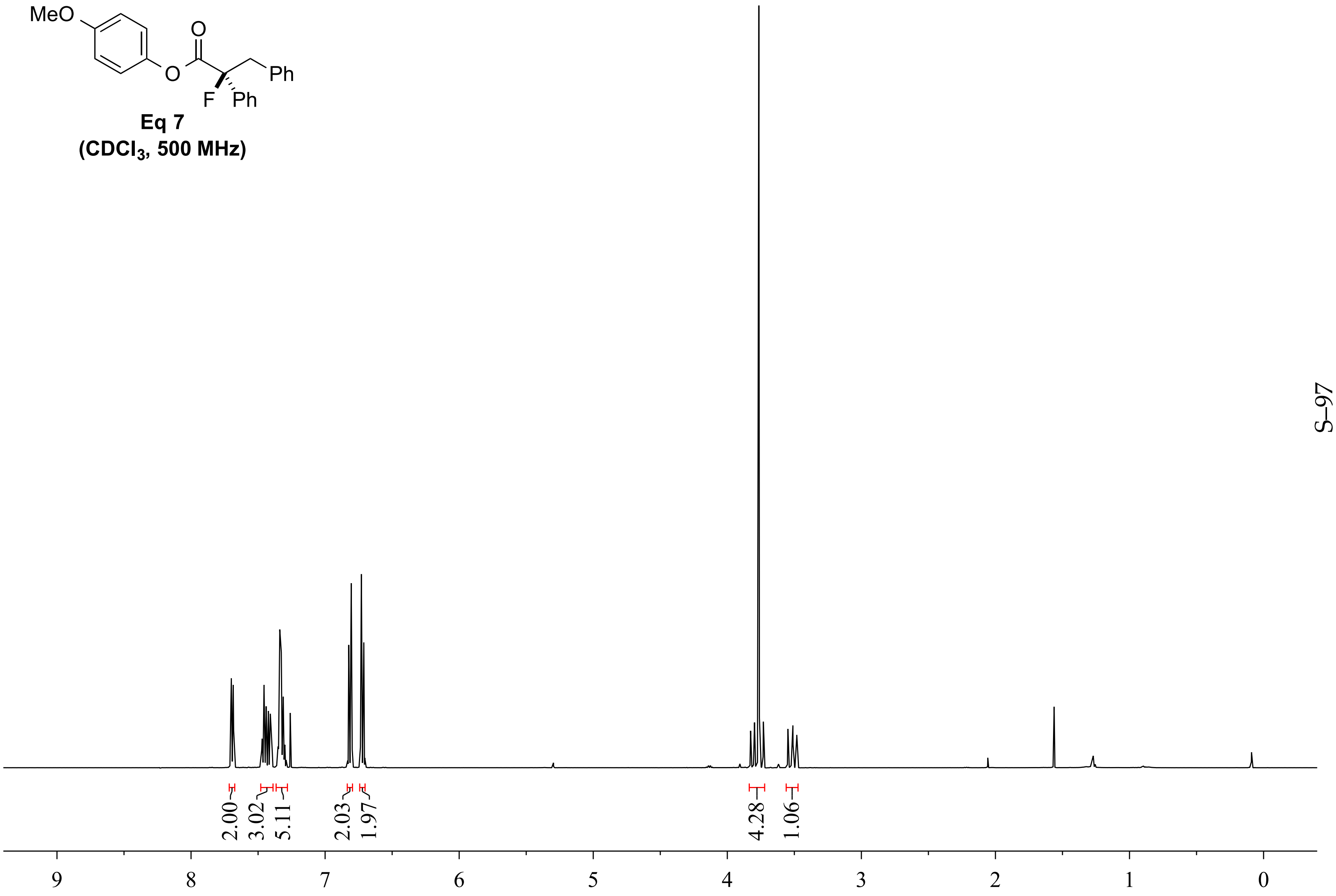




Eq 5
(CDCl$_3$, 500 MHz)




Eq 6
($CDCl_3$, 500 MHz)



Eq 7

(CDCl$_3$, 500 MHz)