Electronic Supplementary Information

Iron(III)-salan complexes catalysed highly enantioselective fluorination and hydroxylation of β-keto esters and N-Boc oxindoles

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**General information**

All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon. Solvents were predried over activated 4 Å molecular sieves and were refluxed over magnesium (methanol), sodium (toluene, THF, Et₂O, benzene, dioxane, cyclohexane), or calcium hydride (DCM, DCE, EA, MeCN) under an argon atmosphere and collected by distillation. ¹H and ¹³C NMR spectra were recorded on a Varian Mercury 300 (300 MHz) or Bruker AM 400 (400 MHz) spectrometer. ¹H and ¹³C NMR spectra were referenced internally to residual protio-solvent (¹H) or solvent (¹³C) resonances and are reported relative to tetramethylsilane. HPLC analyses on an Agilent 1100 Series chromatograph. Infrared spectra were prepared as KBr pellets and were recorded on a Bio-Rad FTS-185 FT-IR spectrometer. Optical rotations were measured with a Perkin-Elmer 241 polarimeter in a 1 dm cuvette. Mass spectra were recorded by the mass spectrometry service of Shanghai Institute of Organic Chemistry. (R,R)-2,2'-Bipyridylidine¹,² was synthesized according to the literature procedures. All other reagents were commercially available and used as received.

**I. Preparation of the iron complexes**

![Chemical diagram](image-url)
Synthesis of salicylaldehyde $10^{3-4}$

At room temperature, tin(IV) tetrachloride (0.4 mL) was added to a solution of phenol (33.3 mmol) and 2,6-lutidine (23.4 mmol) in freshly distilled toluene (30 mL) under a argon atmosphere. After the addition was complete, the mixture was stirred at room temperature for a further 30 min. Paraformaldehyde (2.2 g) was then introduced and the resulting yellowish solution was heated to 100 °C for 10 h. The reaction mixture was allowed to cool down to room temperature, poured into water (100 mL) and acidified with 2 M HCl until pH = 2. The solution was extracted with DCM (3 × 30 mL). The organic layer was washed with brine (30 mL), dried over MgSO$_4$, concentrated, and purified by flash chromatography to generate the product 9.

To a stirred solution of the salicylaldehyde 9 (92.1 mmol) in HOAc (46 mL) was added a solution of Br$_2$ (5.18 mL, 102 mmol) in HOAc (20 mL) dropwise within 20 min. The reaction mixture was stirred for 3 h at room temperature and afterward diluted with DCM. The organic layer was washed with 39% sodium bisulfate solution, water, saturated aqueous NaHCO$_3$, and brine, and was dried with sodium sulfate. The solvent was removed in vacuum. The product was purified by column chromatography on silica gel.

Yield: 73% (4.30 g); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 11.80 (s, 1H), 9.88 (s, 1H), 7.54 (dd, $J = 1.2, 7.4$ Hz, 1H), 7.41 (dd, $J = 1.2, 7.8$ Hz, 1H), 6.95 (t, $J = 7.8$ Hz, 1H), 1.42 (s, 9H); MS (EI): $m/z$ 178 (M$^+$), 164 (14.82), 163 (100.00), 135 (60.44), 115 (14.18), 107 (22.30), 91 (16.47), 77 (12.92).

Yield: 65% (3.55 g); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 11.38 (s, 1H), 9.89 (s, 1H), 7.45 (d, $J = 7.2$ Hz, 1H), 7.40 (dd, $J = 2.1, 7.8$ Hz, 1H), 6.99 (t, $J = 7.2$ Hz, 1H), 3.35-3.41
(m, 1H), 1.25 (d, $J = 7.2$ Hz, 6H); MS (ESI): $m/z$ 165.0 [M+1]$^+$. 

Yield: 90% (21.3 g); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 11.74 (s, 1H), 9.82 (s, 1H), 7.58 (d, $J = 2.1$ Hz, 1H), 7.52 (t, $J = 2.1$ Hz, 1H), 1.40 (s, 9H); MS (EI): $m/z$ 256 (M$^+$), 243 (99.43), 241 (100.00), 215 (38.24), 213 (40.85), 134 (44.88), 115 (33.85).

Yield: 84% (18.8 g); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 11.31 (s, 1H), 9.83 (s, 1H), 7.53 (s, 2H), 3.37-3.32 (m, 1H), 1.24 (d, $J = 7.2$ Hz, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 195.57, 158.08, 139.71, 136.16, 132.83, 121.08, 111.26, 26.30, 21.90; MS (ESI): $m/z$ 241.0 [M-1]$^+${; IR (KBr): $\nu$max 3159, 2964, 2869, 1659, 1606, 1434, 1298, 1159, 1066, 1434, 1298, 1261, 1207, 973, 766, 720, 701 cm$^{-1}$.}

**Synthesis of ligand 11**$^{5,6}$

To a solution of the salicylaldehyde 10 (24.4 mmol) in MeOH (50 mL) was added NaBH$_4$ (1.84 g, 48.8 mmol) slowly. During addition, the mixture turned from pale yellow to colourless and stirring was continued for 1 h at room temperature. The volatiles were then removed using a rotary evaporator and the residue was mixed with water (50 mL). The mixture was neutralized with glacial acetic acid before being extracted with DCM (3 x 150 mL). The combined extracts were dried over anhydrous MgSO$_4$ and concentrated to give the crude 2-hydroxybenzyl alcohol.

To a solution of 2-hydroxybenzyl alcohol (23.4 mmol) in CHCl$_3$ (50 mL) was added PBr$_3$ (1.10 mL, 11.7 mmol). White fumes appeared immediately during addition and stirring was continued for 8 h at room temperature. Then cold water (30 mL) was added with vigorous stirring for 2 min. The organic layer was separated and the aqueous residue was extracted with CHCl$_3$ (2 x 50 mL). The combined extracts
were dried over anhydrous MgSO₄, concentrated, and dried in vacuo to give a pale-yellow liquid, which was used without further purification.

Et₃N (0.2 mL, 2 equiv) was added dropwise to a solution of (R,R)-bipyrrolidine (180 mg, 1.28 mmol) and 2-(bromomethyl)-phenol (2.56 mmol) in THF (50 mL). The mixture was stirred for 24 h at RT, producing a white precipitate of Et₃N·HBr, which was filtered off and extracted with cold THF. The filtrate was concentrated under reduced pressure and the resulting crude product was purified by column chromatography on silica-gel to give the ligand 11 as white solid.

Yield: 67% (494 mg); ¹H NMR (300 MHz, CDCl₃): δ 7.23 (d, J = 2.1 Hz, 2H), 6.81 (d, J = 2.1 Hz, 2H), 4.00 (d, J = 13.5 Hz, 2H), 3.38 (d, J = 13.5 Hz, 2H), 3.07-3.04 (m, 2H), 2.77-2.74 (m, 2H), 2.23-2.19 (m, 2H), 1.99 (m, 2H), 1.81-1.73 (m, 6H), 1.41 (s, 18H), 1.28 (s, 18H); MS (ESI): m/z 577.3 [M+1]⁺.

Yield: 55% (471 mg); m.p.(°C): 224-226; ¹H NMR (300 MHz, CDCl₃): δ 7.56 (d, J = 1.9 Hz, 2H), 7.06 (d, J = 1.9 Hz, 2H), 4.24 (d, J = 14.1 Hz, 2H), 3.37 (d, J = 14.1 Hz, 2H), 3.10-3.05 (m, 2H), 2.99-2.95 (m, 2H), 2.28-2.23 (m, 2H), 2.13-2.08 (m, 2H), 1.91-1.80 (m, 6H); ¹³C NMR (75 MHz, CDCl₃): δ153.67, 134.08, 129.72, 124.68, 110.69, 64.60, 57.46, 54.81, 25.20, 23.57; IR (KBr): νmax3445, 3065, 2962, 2875, 2842, 2533, 1592, 1447, 1385, 1283, 1257, 1151, 1110, 967, 924, 883, 820, 726, 684, 560, 511, 419 cm⁻¹; MS (ESI): m/z 669.0 [M+1]⁺; HRMS (MALDI): For [C₂₂H₂₅N₂O₂Br₄⁺] Calcd. 664.8644, Found: 664.8659; [α]D²⁵: +61.1 (c= 1.02, solv: 

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**11a**

**11b**
Yield: 70% (557 mg); m.p.(°C): 176-178; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 10.96 (br, 2H), 7.26 (s, 2H), 6.97 (s, 2H), 3.99 (d, \(J = 13.8\) Hz, 2H), 3.41 (d, \(J = 13.8\) Hz, 2H), 3.05-3.00 (m, 2H), 2.85-2.81 (m, 2H), 2.26-2.26 (m, 2H), 2.00 (m, 2H), 1.85-1.77 (m, 6H), 1.37 (s, 18H); \(^13\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 155.72, 138.78, 128.84, 128.44, 124.65, 110.50, 65.33, 58.25, 54.89, 34.86, 29.20, 25.53, 23.81; IR (KBr): \(\nu\) max 3418, 2959, 2872, 2823, 1467, 1426, 1393, 1360, 1238, 1161, 1110, 988, 931, 869, 761, 702 cm\(^{-1}\); MS (ESI): \(m/z\) 623.1 [M+1] \(^+\); HRMS (MALDI): For: \([\text{C}_{30}\text{H}_{43}\text{N}_2\text{O}_2\text{Br}_2]^+\) Calcl. 621.1686, Found: 621.1687; \([\alpha]^{D}_{25}\): +36.6 (c= 0.89, solv: CHCl\(_3\)).

Yield: 62% (472 mg); m.p.(°C): 170-172; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 10.92 (br, 2H), 7.20 (d, \(J = 2.1\) Hz, 2H), 6.95 (d, \(J = 2.1\) Hz, 2H), 4.16 (d, \(J = 13.8\) Hz, 2H), 3.33 (d, \(J = 13.8\) Hz, 2H), 3.32-3.24 (m, 2H) 3.07-3.01 (m, 2H), 2.94-2.89 (m, 2H), 2.26-2.22 (m, 2H), 2.06-2.02 (m, 2H), 1.88-1.79 (m, 6H), 1.20 (dd, \(J = 3.3, 7.1\) Hz, 12H); \(^13\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 153.78, 137.57, 128.15, 127.86, 123.69, 110.85, 64.81, 57.72, 54.82, 26.51, 25.33, 23.62, 22.55, 22.40; IR (KBr): \(\nu\) max 2961, 2869, 2826, 1604, 1466, 1436, 1337, 1276, 1212, 1110, 871, 730, 409 cm\(^{-1}\); MS (ESI): \(m/z\) 593.0 [M+1] \(^+\); HRMS (MALDI): For: \([\text{C}_{28}\text{H}_{39}\text{N}_2\text{O}_2\text{Br}_2]^+\) Calcl. 593.1373, Found: 593.1363; \([\alpha]^{D}_{20}\): +81.7 (c= 0.91, solv: CHCl\(_3\)).

Synthesis of iron complex 3
FeCl₃ (1.0 mmol, 162.2 mg) and ligand (1.1 equiv, 1.1 mmol) were dissolved in MeOH (6 mL). The reaction mixture was refluxed for 8 h and then cooled down to room temperature. Water and DCM were added and the organic layer was washed with water and dried over Na₂SO₄ and concentrated. The complex was obtained by recrystallization of the residue in DCM and hexane.

Yield: 75% (500 mg); IR (KBr): ν_max 3445, 2956, 2904, 2868, 1633, 1467, 1440, 1362, 1295, 1267, 1240, 1203, 1169, 841; MS (MALDI): m/z 630.4 [M-Cl]^+; HRMS (MALDI): For [C38H58N2O2\textsuperscript{54}Fe]\textsuperscript{+} (M-Cl)^+ Calcd. 628.3889, Found: 628.3881.

Yield: 71% (538 mg); IR (KBr): ν_max 3449, 2922, 2850, 1728, 1574, 1440, 1309, 1275, 1160, 1001, 889, 859, 717, 572; MS (MALDI): m/z 717.8 [M-Cl]^+.

Yield: 78% (555 mg); IR (KBr): ν_max 3445, 2955, 1732, 1463, 1430, 1408, 1389, 1357, 1293, 1250, 1167, 870, 814, 733, 569, 496; MS (MALDI): m/z 674.1 [M-Cl]^+; HRMS (MALDI): For [C30H40N2O2Br\textsuperscript{54}Fe]\textsuperscript{+} (M-Cl)^+ Calcd. 672.0847, Found: 672.0841.
Synthesis of β-keto esters

Synthesis of cyclic 4a-4g, 4l

Indanone (5 mmol) in dry THF (5 mL) was added to a suspension of NaH (400 mg, 10 mmol) in dry THF (20 mL) at RT. The solution was warmed to reflux and tert-butyl pyrrole-1-carboxylate (1.67 mL, 10 mmol) in dry THF (2.5 mL) was added dropwise and the solution was stirred at reflux until completion (3-6 h). Following cooling to 0 °C, the solution was acidified with 1 N HCl. The solution was extracted with EtOAc (25 mL) and the organic portion was washed with brine (25 mL), dried (Na₂SO₄) and concentrated. The residue was purified by flash silica gel chromatography.

Yield: 81% (940 mg); ¹H NMR (300 MHz, CDCl₃): δ 7.77 (d, J = 7.8 Hz, 1H), 7.64 (t, J = 6.3 Hz, 1H), 7.50 (d, J = 7.5 Hz, 1H), 7.39 (t, J = 7.5 Hz, 1H), 3.63 (dd, J = 3.9, 8.3 Hz, 1H), 3.48 (d, J = 2.7 Hz, 1H), 3.37 (d, J = 8.3 Hz, 1H), 1.49 (s, 9H); MS (EI): m/z 232 (M⁺), 176 (78.10), 159 (52.00), 158 (40.63), 131 (39.10), 130 (100.00), 103 (28.91), 77 (29.88), 57 (46.19).
Yield: 80% (985 mg); m.p.(°C): 59-61; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.56 (s, 1H), 7.45-7.36 (m, 2H), 3.61 (dd, \(J = 3.9, 8.0\) Hz, 1H), 3.41 (d, \(J = 3.9\) Hz, 1H), 3.31 (d, \(J = 8.0\) Hz, 1H), 2.40 (s, 3H), 1.49 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 197.57, 165.89, 148.54, 135.04, 133.93, 133.01, 123.59, 121,85, 79.35, 52.13, 27.39, 25.44, 25.39, 18.45; IR (KBr): \(v_{\text{max}}\) 2981, 2933, 1724, 1699, 1616, 1581, 1495, 1370, 1325, 1284, 1219, 1142, 1114, 1032, 989, 877, 849, 817, 755, 493; MS (EI): \(m/z\) 246 (M\(^+\)), 190 (49.11), 173 (38.92), 172 (14.14), 145 (37.33), 144 (100.00), 116 (13.75), 115 (40.45), 57 (28.19); HRMS (EI): For: \([\text{C}_{15}\text{H}_{18}\text{O}_3]\)^+ Calcl. 246.1256; Found: 246.1254.

Yield: 67% (838 mg); m.p.(°C): 65-67; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.47 (dd, \(J = 4.0, 8.2\) Hz, 1H), 7.39 (dd, \(J = 2.4, 7.4\) Hz, 1H), 7.33 (td, \(J = 2.8, 8.4\) Hz, 1H), 3.68 (dd, \(J = 3.6, 8.2\) Hz, 1H), 3.46 (dd, \(J = 3.6, 17.4\) Hz, 1H), 3.30 (dd, \(J = 8.0, 17.4\) Hz, 1H), 1.49 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 196.50 (d, \(J = 3.5\) Hz), 165.33, 159.83 (d, \(J = 247.4\) Hz), 146.52 (d, \(J = 2.3\) Hz), 125.35, 120.43 (d, \(J = 20.8\) Hz), 107.57 (d, \(J = 7.2\) Hz), 103.31, 79.70, 52.55, 27.17, 25.41, 25.36; \(^{19}\)F NMR (282 MHz, CDCl\(_3\)): \(\delta\) -114.11- -114.17 (m, 1F); IR (KBr): \(v_{\text{max}}\) 3071, 3012, 2978, 2934, 1644, 1609, 1575, 1472, 1454, 1403, 1371, 1362, 1312, 1255, 1204, 1161, 1141, 1116, 1086, 880, 845, 807, 783, 737, 700, 652, 557; MS (EI): \(m/z\) 250 (M\(^+\)), 194 (52.51), 177(41.00), 176 (23.86), 149 (30.15), 148 (100.00), 120 (21.62), 101 (25.27), 57 (41.73); HRMS (EI): For: \([\text{C}_{14}\text{H}_{15}\text{O}_3\text{F}]^+\) Calcl. 250.1005; Found: 250.1009.
Yield: 70% (933 mg); m.p.(°C): 88-90; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.72 (s, 1H), 7.57 (dd, \(J = 0.6, 9.2\) Hz, 1H), 7.44 (d, \(J = 8.4\) Hz, 1H), 3.66 (dd, \(J = 3.6, 8.3\) Hz, 1H), 3.44 (d, \(J = 3.6\) Hz, 1H), 3.33 (d, \(J = 8.3\) Hz, 1H), 1.49 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 196.12, 165.24, 149.18, 136.30, 134.33, 131.48, 121.63, 102.91, 79.76, 52.22, 27.32, 25.42, 25.37; IR (KBr): \(\nu_{\text{max}}\) 3289, 2980, 2931, 1664, 1623, 1593, 1563, 1479, 1454, 1402, 1393, 1363, 1306, 1280, 1256, 1224, 1162, 1129, 1105, 874, 849, 803, 776, 755, 653, 547, 520, 462; MS (EI): \(m/z\) 266 (M\(^{+}\)), 210 (60.10), 193 (46.43), 166 (34.12), 165 (30.20), 164 (100.00), 102 (28.58), 101 (29.27), 57 (60.95); HRMS (EI): For: \([\text{C14H15O3Cl}]^+\) Calcd. 266.0710; Found: 266.0713.

\[ \text{Yield: 75\% (1.00 g); \(^1\)H NMR (300 MHz, CDCl}_3\): \(\delta\) 7.69 (d, \(J = 7.8\) Hz, 1H), 7.50 (s, 1H), 7.37 (d, \(J = 8.1\) Hz, 1H), 3.64 (dd, \(J = 4.2, 8.1\) Hz, 1H), 3.46 (d, \(J = 4.2\) Hz, 1H), 3.34 (d, \(J = 8.3\) Hz, 1H), 1.48 (s, 9H); MS (EI): \(m/z\) 266 (M\(^{+}\)), 210 (76.18), 193 (83.70), 192 (39.09), 165 (50.36), 164 (84.33), 102 (52.58), 101 (47.18), 57 (100.00).}
Yield: 82% (1.20 g); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.17 (s, 1H), 6.91 (s, 1H), 3.98 (s, 3H), 3.91 (s, 3H), 3.61 (dd, \(J = 3.3, 7.8\) Hz, 1H), 3.36 (d, \(J = 3.3\) Hz, 1H), 3.26 (d, \(J = 7.8\) Hz, 1H), 1.49 (s, 9H); MS (EI): \(m/z\) 236 (43.14), 219 (41.88), 218 (53.12), 192 (47.62), 191 (51.75), 190 (100.00), 163 (15.84), 57 (28.42).

Yield: 55% (677 mg); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.78 (d, \(J = 8.1\) Hz, 1H), 7.34-7.23 (m, 2H), 7.15 (d, \(J = 6.0\) Hz, 1H), 3.50 (dd, \(J = 4.8, 9.6\) Hz, 1H), 2.81-2.76 (m, 2H), 2.54-2.45 (m, 2H), 1.55 (s, 9H); MS (EI): \(m/z\) 266 (M\(^+\)), 210 (76.18), 193 (83.70), 192 (39.09), 165 (50.36), 164 (84.33), 102 (52.58), 101 (47.18), 57 (100.00).

**Synthesis of 4h and 4i**

Following the reported procedure, a 100 mL two-neck flask was charged with a suspension of NaH (3.32 g, 60% in mineral oil, 83 mmol, 2.2 equiv.) in dimethyl carbonate (10 mL). 1-Indanone (5.0 g, 37.75 mmol, 1 equiv.) in dimethyl carbonate (35 mL) was added dropwise and the resulting mixture was refluxed at 80 °C for 2 h. After cooling to RT, 100 mL of water was added. The aqueous layer was separated and extracted with DCM (3 x 25 mL). The combined organic extracts were dried over MgSO\(_4\), filtered, and concentrated under reduce pressure. The brown residual oil was purified by flash chromatography to afford the product.

Yield: 70% (5.03 g); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.78 (d, \(J = 8.1\) Hz, 1H), 7.64 (t, \(J 8.1\) Hz, 1H)
= 7.2 Hz, 1H), 7.51 (d, J = 7.8 Hz, 1H), 7.41 (t, J = 7.2 Hz, 1H), 3.80 (s, 3H), 3.75 (dd, 
J = 4.2, 8.3 Hz, 1H), 3.53 (d, J = 5.4 Hz, 1H), 3.42 (d, J = 8.4 Hz, 1H); MS (EI): m/z 
190 (M⁺), 159 (22.68), 131 (57.98), 130 (100.00), 103 (37.62), 102 (29.60), 77 
(34.05), 51 (15.22).

The reaction precedue was similar to that of 4h, except that diethyl carbonate was 
used instead of dimethyl carbonate.

Yield: 66% (5.09 g); ¹H NMR (300 MHz, CDCl₃): δ 7.77 (d, J = 7.8 Hz, 1H), 7.63 (t, 
J = 7.2 Hz, 1H), 7.51 (d, J = 7.8 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 4.25 (q, J = 7.2 Hz, 
2H), 3.72 (dd, J = 3.9, 8.3 Hz, 1H), 3.53 (d, J = 6.0 Hz, 1H), 3.40 (d, J = 8.4 Hz, 1H), 
1.31 (t, J = 6.9 Hz, 6H).

Synthesis of 4j, 4k

The methyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate with different 
substituent was prepared as 4h. A solution of methyl 
1-oxo-2,3-dihydro-1H-indene-2-carboxylate (1.0 mmol), dibutyltin oxide (0.10 mmol) 
and iso-propyl alcohol or 1-adamantanol (10 mmol) in toluene (10 mL) was 
refluxed for 8 h. Evaporation of the solvent and chromatography on silica gel afforded 
the product.

Yield: 61% (133 mg); ¹H NMR (300 MHz, CDCl₃): δ 7.77 (d, J = 7.2 Hz, 1H), 
7.65-7.60 (m, 1H), 7.51 (d, J = 7.5 Hz, 1H), 7.40 (t, J = 7.2 Hz, 1H), 5.12-5.07 (m, 
1H), 3.68 (dd, J = 4.2, 8.0 Hz, 1H), 3.52 (d, J = 4.2 Hz, 1H), 3.39 (d, J = 8.0 Hz, 1H), 
1.30 (dd, J = 3.3, 6.2 Hz, 6H); MS (EI): m/z 218 (M⁺), 176 (38.44), 159 (33.70), 158
Yield: 52% (162 mg); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.76 (d, \(J = 7.2\) Hz, 1H), 7.61 (t, \(J = 6.6\) Hz, 1H), 7.49 (d, \(J = 7.2\) Hz, 1H), 7.40 (t, \(J = 3.9\) Hz, 1H), 3.62 (dd, \(J = 3.9, 8.4\) Hz, 1H), 3.47 (d, \(J = 2.7\) Hz, 1H), 3.36 (d, \(J = 8.1\) Hz, 1H), 2.15 (s, 9H), 1.66 (s, 6H); MS (EI): \(m/z\) 310 (M\(^+\)), 152 (12.93), 136 (10.86), 135 (100.00), 95 (50.60), 93 (13.66), 92 (10.76), 79 (14.55), 77 (14.41).

Synthesis of 4m

A solution of adipoyl chloride (9.0 g) in Et\(_2\)O (10 mL) was added dropwise to a solution of \(^1\)BuOH (15 mL, 162 mmol) and \(N,N\)-dimethylaniline (20 mL, 157.0 mmol) in Et\(_2\)O (10 mL) at 0 \(^\circ\)C. The resultant mixture was allowed to warm slowly to RT and stirred for 24 h. The solution was diluted with H\(_2\)O (50 mL) and the aqueous phase was separated. The organic portion was washed sequentially with 1 M HCl (3 \(\times\) 50 mL), 2 M NaOH (aq, 2 \(\times\) 50 mL) and brine (80 mL), then dried and concentrated in vacuo to give di-\textit{tert}-butyl adipate (12) as a colourless oil.

NaH (60% suspension in mineral oil, 2.7 g, 112.5 mmol) was suspended in benzene (25 mL). A solution of di-\textit{tert}-butyl adipate (0.3 g) in \(^1\)BuOH (0.15 mL) and benzene (25 mL) was added. After refluxed for 30 min, more di-\textit{tert}-butyl adipate (8.0 g) as a solution in benzene (15 mL) was added dropwise over 45 min. The resultant mixture was heated to reflux for 10 h, then allowed to cool to RT before being cooled to 0 \(^\circ\)C prior to the sequential addition of AcOH (aq, 10%, 90 mL). The organic layer was separated, dried and concentrated in vacuo. Purification via vacuum distillation.
gave tertbutyl 2-oxocyclopentanecarboxylate as a colourless oil, bp 78-80 °C (2.0 mmHg).

![Structure 12](image)

Yield: 88% (11.2 g); \(^1\)H NMR (300 MHz, CDCl\(_3\)); \(\delta\) 2.26-2.20 (m, 4H), 1.65-1.58 (m, 4H), 1.44 (s, 18H); MS (EI): \(m/z\) 258 (M\(^+\)), 147 (17.64), 146 (28.10), 129 (94.67), 128 (14.98), 111 (18.99), 57 (100.00), 55 (18.76), 41 (23.54).

![Structure 4m](image)

Yield: 71% (4.20 g); \(^1\)H NMR (300 MHz, CDCl\(_3\)); \(\delta\) 3.05 (t, \(J = 9.0\) Hz, 1H), 2.32-2.22 (m, 4H), 2.16-2.09 (m, 1H), 1.89-1.82 (m, 1H), 1.47 (s, 9H); MS (EI): \(m/z\) 184 (M\(^+\)), 128 (53.65), 111 (100.00), 110 (28.49), 100 (60.84), 83 (23.86), 57 (100.00), 55 (49.94), 41 (36.10).

**Synthesis of 4n\(^{10}\)**

![Chemical Reaction](image)

To a solution of tert-butyl salicylate (400 mg, 2.06 mmol) and potassium carbonate (300 mg, 2.16 mmol) in 2-butanone (1 mL) was added tert-butyl bromoacetate (442 mg, 2.16 mmol) and the mixture was refluxed for 2 h. The reaction was quenched with water and the whole mixture was extracted with chloroform. The organic layer was washed with 5% NaOH (aq.) and brine successively and dried over Na\(_2\)SO\(_4\). Evaporation of the solvent and chromatography afforded the product as a white solid.

To a suspension of potassium tert-butoxide (218 mg, 1.95 mmol) in toluene (10 mL) was added tert-butyl 2-(2-tert-butoxy-2-oxoethyl) benzoate (300 mg, 0.974
mmol) and the mixture was stirred for 30 min at room temperature. The reaction was quenched with NH$_4$Cl (aq.) and the whole mixture was extracted with EA. The organic layer was washed with brine and dried over Na$_2$SO$_4$. Evaporation and chromatography afforded the product as a grey solid.

Yield: 86% (546 mg); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.74 (dd, $J = 0.6, 7.7$ Hz, 1H), 7.42-7.36 (m, 1H), 7.01 (t, $J = 7.7$ Hz, 1H), 6.85 (d, $J = 8.7$ Hz, 1H), 4.59 (s, 2H), 1.59 (s, 9H), 1.47 (s, 9H); MS (EI): m/z 308 (M$^+$), 196 (22.91), 179 (24.36), 152 (22.63), 151 (22.77), 123 (21.34), 121 (19.05), 57 (100.00), 41 (21.49).

Yield: 90% (205 mg); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.27 (br, 1H), 7.72 (d, $J = 7.8$ Hz, 1H), 7.47-7.45 (m, 1H), 7.31-7.25 (m, 2H), 1.67 (s, 9H); MS (EI): m/z 234 (M$^+$), 178 (67.11), 161 (30.09), 160 (100.00), 104 (37.91), 102 (22.67), 76 (20.98), 57 (50.29), 41 (17.04).

Synthesis of 4o$^{11}$

Aq. NaOH (33% w/v, 3.30 mL) was added to a solution of tert-butyl acetoacetate (10 mL, 74.6 mmol) in hexane (12 mL) and H$_2$O (25 mL) at 0 °C. Two dropping funnels were used to add aq. NaOH (33% w/v, 13.5 mL) and benzoyl chloride(10 mL, 86.1 mmol) simultaneously over 2 h, with vigorous stirring, maintaining the pH at about 11 and the temperature below 10 °C. The mixture was then warmed to 35 °C for 30 min, before transferring to a separating funnel. The aqueous layer was separated
and returned to the flask, to which NH₄Cl (4 g, 74.8 mmol) was added. After stirring at RT for a further 18 h the solution was diluted with brine (20 mL) and extracted to Et₂O (3 × 40 mL). The combined organic extracts were dried (MgSO₄) and concentrated in vacuo. The crude product was purified by flash chromatography to afford the product 14.

A mixture of 14 (11.6 mmol), MeI (1.45 mL, 23.2 mmol), K₂CO₃ (3.19 g, 23.2 mmol) and MeCN (40 mL) was refluxed for 18 h. The mixture was cooled, quenched with H₂O (100 mL), and extracted with Et₂O (2 × 80 mL). The combined organic extracts were dried (MgSO₄) and concentrated. The residue was purified by column chromatography to give the product 4o as a colourless oil.

Yield: 78% (12.8 g); ¹H NMR (300 MHz, CDCl₃): δ 7.59-7.43 (m, 5H), 3.90 (s, 2H), 1.43 (s, 9H); MS (EI): m/z 220 (M⁺), 165 (22.23), 164 (14.87), 147 (17.53), 105 (100.00), 77 (32.75), 57 (56.43), 51 (11.62), 41 (16.09).

Synthesis of 4p

NaH (60% suspension in mineral oil, 15.1 mmol, 1.25 equiv.) was suspended in THF (25 mL). A solution of tert-butyl acetoacetate (1.10 g, 12.1 mmol) in THF (15 mL) and benzyl bromide (1.75 mL, 15.1 mmol, 1.25 equiv.) was added and the reaction was stirred overnight. The mixture was quenched with H₂O (35 mL) and extracted with Et₂O (2 × 50 mL). The combined organic extracts were dried (MgSO₄)
and concentrated. The residue was purified by column chromatography to give the product 4p as a colourless oil.

Yield: 51% (1.52 g); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta \) 7.27-7.16 (m, 5H), 3.69 (t, \(J = 7.8\) Hz, 1H), 3.11 (dd, \(J = 2.7, 7.7\) Hz, 2H), 2.19 (s, 3H), 1.38 (s, 9H); MS (EI): \(m/z \) 248 (M\(^+\)), 192 (63.58), 149 (100.00), 147 (25.17), 131 (73.05), 91 (29.99), 57 (90.05), 43 (58.52), 41 (28.66).

Synthesis of 4q

Mono-tert-butyl malonate (1 g, 6.25 mmol) and NEt\(_3\) (0.871 mL, 6.25 mmol) were dissolved in THF (30 mL) and the solution cooled to 0 °C. After dropwise addition of methyl chloroformate, the mixture was stirred for 30 min and then filtered. The filtrate was concentrated in vacuo to give 15 as a yellow oil.

The preparation of 4q was similar to that of 4p, 15 was used instead of tert-butyl acetoacetate.

Yield: 74% (812 mg); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta \) 3.75 (s, 3H), 3.30 (s, 2H), 1.47 (s, 9H); MS (EI): \(m/z \) 159 ([M-CH\(_3\)]\(^+\)), 119 (29.94), 101 (99.20), 59 (32.00), 57 (100.00), 56 (15.46), 43 (16.01), 42 (16.38), 41 (31.62).

Yield: 57% (1.82 g); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta \) 7.28-7.19 (m, 5H), 3.70 (s, 3H),
3.58 (t, J = 8.0 Hz, 1H), 3.18 (dd, J = 1.2, 7.8 Hz, 2H), 1.39 (s, 9H); MS (EI): m/z 264 (M⁺), 208 (68.97), 162 (100.00), 159 (41.45), 148 (34.82), 131 (34.15), 103 (21.67), 91 (47.94), 57 (73.90).

III. Enatioselective fluoronation of β-keto esters

The β-ketoester (0.2 mmol or 0.267 mmol) was dissolved in the indicated solvent (1.0 mL). To this solution was added the iron complex (2 mol%, 0.004 mmol), and successively NFSI (75 mg, 0.24 mmol) was added at the given temperature (0 °C or -20 °C). The reaction mixture was stirred at the same temperature. After the completion of the reaction, the reaction mixture was filtered and the filtrate was concentrated, and the product was purified by flash column chromatography. The ee of the product was determined by chiral HPLC analysis.

Table S1 Catalyst screening for the fluorination reaction of 4a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Yield (%)</th>
<th>ee (%)</th>
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<td>58</td>
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<tr>
<td>2</td>
<td>1b</td>
<td>97</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>1c</td>
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<td>6</td>
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<tr>
<td>7</td>
<td>3c</td>
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<tr>
<td>9</td>
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<td>94</td>
<td>8</td>
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</table>

⁺ Reaction conditions: substrates (0.1 mmol), cat. (5 mol%) and NFSI (1.5 equiv.) were stirred in DCM with 4 Å MS at room temperature for 10 h under Aratmostphere.

Isolated yield. ‡ Determined by chiral HPLC. 10 mol% Co(acac)₂ and 10 mol% Jacobsen’s Salen ligand were used as catalyst.
Yield: 96% (64.1 mg); ¹H NMR (300 MHz, CDCl₃): δ 7.84 (d, J = 7.8 Hz, 1H), 7.70 (t, J = 7.5 Hz, 1H), 7.52-7.44 (m, 2H), 3.74 (dd, J = 11.1, 17.7 Hz, 1H), 3.41 (dd, J = 17.7, 23.1 Hz, 1H), 1.44 (s, 9H); ¹³F NMR(282 MHz, CDCl₃) δ -164.43 (dd, J = 10.7, 23.5 Hz, 1F); MS (EI): m/z 250 (M⁺), 194 (62.99), 174 (30.93), 150 (21.34), 149 (99.01), 130 (17.63), 101 (44.43), 57 (100.00), 41 (31.33); HPLC: Daicel Chiralpak AD-H, Hexane/PrOH=99/1, 1.0 mL/min, 254 nm, tR(major)= 11.7 min, tR(minor)= 14.0 min (94% ee); [α]D²⁰: -1.2 (c= 1.04, solv: CHCl₃, 94% ee).

Yield: 97% (68.2 mg); ¹H NMR (300 MHz, CDCl₃): δ 7.62 (s, 1H), 7.50 (dd, J = 1.2, 8.0 Hz, 1H), 7.37 (d, J = 7.5 Hz, 1H), 3.68 (dd, J = 10.8, 17.4 Hz, 1H), 3.34 (dd, J = 17.4, 22.5 Hz, 1H), 2.43 (s, 1H), 1.44 (s, 9H); ¹³C NMR (75 MHz, CDCl₃): δ195.81 (d, J = 18.0 Hz), 166.13, 148.37 (d, J = 4.1 Hz), 138.52, 137.71, 133.59 (d, J = 1.3 Hz), 126.08 (d, J = 1.5 Hz), 125.18 (d, J = 1.4 Hz), 94.65 (d, J = 199.9 Hz), 83.95, 37.94 (d, J = 23.7 Hz). 27.74, 21.02; ¹⁹F NMR (282 MHz, CDCl₃) δ -164.16 (dd, J = 11.0, 23.4 Hz, 1F); IR (KBr): νmax 2981, 2932, 1761, 1729, 1616, 1584, 1495, 1371, 1284, 1225, 1206, 1156, 1106, 1074, 959, 841, 802, 692, 504 cm⁻¹; MS (EI): m/z 249 ([M-CH₃]⁺), 208 (39.35), 188 (40.07), 163 (87.47), 135 (26.25), 133 (37.01), 115 (36.95), 57 (100.00), 41 (30.99); HRMS (EI): For [C₁₄H₁₄O₃F⁺] ([M-CH₃⁺]) Calcl. 249.0927, Found: 249.0933; HPLC: Daicel Chiralpak AD-H, Hexane/PrOH=99/1, 1.0 mL/min, 254 nm, tR(major)= 11.9 min, tR(minor)= 20.2 min (97% ee); [α]D²⁰: +5.0 (c= 1.05, solv: CHCl₃, 97% ee).
Yield: 95% (68.0 mg); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.48-7.40 (m, 3H), 3.70 (dd, $J$ = 10.5, 17.1 Hz, 1H), 3.34 (dd, $J$ = 17.1, 21.8 Hz, 1H), 1.44 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 194.82 (dd, $J = 3.1$, 18.6 Hz), 165.66 (d, $J = 27.7$ Hz), 162.47 (d, $J = 248.6$ Hz), 146.30 (dd, $J = 2.3$, 4.2 Hz), 135.06 (d, $J = 7.6$ Hz), 127.91 (d, $J = 8.8$ Hz), 124.06 (d, $J = 23.1$ Hz), 110.92 (d, $J = 22.4$ Hz), 94.62 (dd, $J = 1.2$, 201.6 Hz), 84.21, 37.61 (d, $J = 24.3$ Hz), 27.60; $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -112.65 -112.72 (m, 1F), -163.80 (dd, $J = 10.5$, 21.8 Hz, 1F); IR (KBr): $\nu_{\text{max}}$ 2982, 2936, 1763, 1733, 1615, 1489, 1441, 1396, 1372, 1286, 1228, 1210, 1156, 1077, 975, 865, 839, 805, 768 cm$^{-1}$; MS (El): $m/z$ 253 ([M-CH$_3$]+), 212 (26.75), 192 (20.53), 168 (11.18), 167 (46.62), 147 (11.03), 119 (30.11), 57 (100.00), 41 (25.21); HRMS (El): For [C13H11O3F2]$^+$ ([M-CH$_3$]$^+$) Calcd. 253.0676, Found: 253.0682; HPLC: Phenomenex PC-2, Hexane/iPrOH=95/5, 0.7 mL/min, 214 nm, tR(minor)= 15.0 min, tR(major)= 16.1 min (95% ee); [$\alpha$]$_{D}^{20}$: -4.9 (c= 1.21, solv: CHCl$_3$, 95% ee).

Yield: 98% (74.5 mg); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.79 (d, $J = 2.1$ Hz, 1H), 7.64 (dd, $J = 2.1$, 8.1 Hz, 1H), 7.44 (d, $J = 8.1$ Hz, 1H), 3.70 (dd, $J = 10.5$, 17.7 Hz, 1H), 3.36 (dd, $J = 17.7$, 22.2 Hz, 1H), 1.44 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 194.59 (d, $J = 18.5$ Hz), 165.72 (d, $J = 26.9$ Hz), 148.98 (d, $J = 4.1$ Hz), 136.40, 134.89 (d, $J = 1.3$ Hz), 134.81, 127.67 (d, $J = 0.9$ Hz), 124.97 (d, $J = 1.1$ Hz), 94.42 (d, $J = 201.3$ Hz), 84.43, 37.84 (d, $J = 24.3$ Hz), 27.73; $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -163.86 (dd, $J = 10.5$, 22.2 Hz, 1F); IR (KBr): $\nu_{\text{max}}$ 2981, 2935, 1763, 1732, 1602, 1471, 1428, 1371, 1293, 1258, 1204, 1187, 1155, 1118, 1075, 949, 839, 802, 731, 598, 515 cm$^{-1}$; MS (El): $m/z$ 269 ([M-CH$_3$]$^+$), 228 (15.58), 208 (13.38), 183 (28.39), 135 (12.44), 120 (13.93), 57 (100.00), 43 (21.19), 41 (27.78); HRMS (El): For [C13H11O3FCI]$^+$
([M-CH$_3$]$^+$) Calcd. 269.0381, Found: 269.0382; HPLC: Daicel Chiralpak IC, Hexane/iPrOH=95/5, 0.7 mL/min, 254 nm, tR(major)= 18.6 min, tR(minor)= 23.3 min (94% ee); [$\alpha$]$^D_{20}$: -16.9 (c= 1.10, solv: CHCl$_3$, 94% ee).

Yield: 93% (70.7 mg); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.77 (d, $J = 8.1$ Hz, 1H), 7.50 (s, 1H), 7.44 (d, $J = 8.1$ Hz, 1H), 3.71 (dd, $J = 10.5$, 17.9 Hz, 1H), 3.38 (dd, $J = 17.9$, 22.4 Hz, 1H), 1.44 (s, 9H); $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -163.76 (dd, $J = 10.5$, 22.4 Hz, 1F); MS (EI): m/z 284 (M$^+$), 228 (34.42), 185 (22.46), 184 (23.02), 183 (64.13), 135 (22.66), 120 (29.99), 57 (100.00), 41 (25.56); HPLC: Daicel Chiralpak AD-H, Hexane/iPrOH=99/1, 1.0 mL/min, 254 nm, tR(major)= 29.3 min, tR(minor)= 40.1 min (94% ee); [$\alpha$]$^D_{20}$: +36.8 (c= 1.08, solv: CHCl$_3$, 95% ee).

Yield: 99% (74.1 mg); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.38 (d, $J = 8.4$ Hz, 1H), 7.29-7.24 (m, 2H), 3.86 (s, 3H), 3.65 (dd, $J = 10.2$, 17.3 Hz, 1H), 3.32 (dd, $J = 17.3$, 22.8 Hz, 1H), 1.44 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 195.78 (d, $J = 18.6$ Hz), 166.24 (d, $J = 27.7$ Hz), 159.93, 143.91 (d, $J = 4.3$ Hz), 134.62 (d, $J = 1.2$ Hz), 127.14 (d, $J = 1.5$ Hz), 125.87, 106.21 (d, $J = 0.8$ Hz), 94.93 (d, $J = 200.4$ Hz), 84.02, 55.60, 37.63 (d, $J = 24.5$ Hz), 27.7; $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -163.96 (dd, $J = 10.2$, 22.8 Hz, 1F); IR (KBr): $\nu_{max}$ 2980, 2936, 1760, 1723, 1616, 1494, 1458, 1435, 1396, 1371, 1309, 1281, 1235, 1156, 1075, 1026, 966, 858, 839, 804, 768, 546 cm$^{-1}$; MS (EI): m/z 280 (M$^+$), 224 (42.05), 204 (100.00), 180 (20.74), 179 (94.28), 178 (26.94), 107 (24.87), 57 (86.16), 41 (21.70); HRMS (EI): For [C15H17O4F]+ Calcd. 280.1111, Found: 280.1108; HPLC: Daicel Chiralpak AD-H, Hexane/iPrOH=99/1, 1.0 mL/min, 254 nm, tR(major)= 16.6 min, tR(minor)= 18.7 min (95% ee); [$\alpha$]$^D_{20}$: -11.1 (c= 0.94, 94% ee).
solv: CHCl₃, 95% ee).

Yield: 99% (82.0 mg); ¹H NMR (300 MHz, CDCl₃): δ 7.22 (s, 1H), 6.90 (s, 1H), 4.01 (s, 1H), 3.93 (s, 3H), 3.64 (dd, J = 10.5, 17.3 Hz, 1H), 3.30 (dd, J = 17.3, 22.1 Hz, 1H), 1.47 (s, 9H); ¹⁹F NMR (282 MHz, CDCl₃) δ -163.60 (dd, J = 10.5, 22.1 Hz, 1F); MS (EI): m/z 310 (M⁺), 254 (58.93), 234 (100.00), 226 (14.96), 210 (36.35), 209 (92.16), 208 (24.29), 57 (63.77), 41 (19.75); HPLC: Daicel Chiralpak AD-H, Hexane/iPrOH=85/15, 0.7 mL/min, 254 nm, tR(minor)= 10.8 min, tR(major)= 11.9 min (96% ee); [α]D²⁰: +59.9 (c= 1.09, solv: CHCl₃, 96% ee).

Yield: 99% (55.0 mg); ¹H NMR (300 MHz, CDCl₃): δ 7.85 (d, J = 8.7 Hz, 1H), 7.72 (t, J = 7.2 Hz, 1H), 7.49 (dd, J = 7.5, 14.7 Hz, 2H), 3.81 (dd, J = 11.7, 17.7 Hz, 1H), 3.82 (s, 3H), 3.45 (dd, J = 17.7, 23.4 Hz, 1H); ¹⁹F NMR (282 MHz, CDCl₃) δ -164.96 (dd, J = 11.7, 23.4 Hz, 1F); MS (EI): m/z 208 (M⁺), 188 (64.52), 157 (25.50), 149 (100.00), 148 (23.88), 137 (24.18), 129 (34.32), 101 (66.20), 75 (26.06); HPLC: Daicel Chiralpak IC, Hexane/iPrOH=85/15, 0.7 mL/min, 254 nm, tR(major)= 30.8 min, tR(minor)= 35.8 min (46% ee).

Yield: 99% (58.7 mg); ¹H NMR (300 MHz, CDCl₃): δ 7.85 (d, J = 7.8 Hz, 1H), 7.71 (dt, J = 1.5, 7.7 Hz, 1H), 7.48 (dd, J = 7.8, 14.9 Hz, 2H), 4.29 (q, J = 7.5 Hz, 2H), 3.80 (dd, J = 11.7, 17.6 Hz, 1H), 3.43 (dd, J = 17.6, 23.2 Hz, 1H), 1.27 (t, J = 7.5 Hz, 6H); ¹⁹F NMR (282 MHz, CDCl₃) δ -164.87 (dd, J = 11.7, 23.2 Hz, 1F); MS (EI): m/z
Yield: 98% (61.8 mg); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.84 (d, $J = 7.8$ Hz, 1H), 7.70 (t, $J = 7.8$ Hz, 1H), 7.48 (dd, $J = 8.1$, 15.2 Hz, 2H), 5.17-5.12 (m, 1H), 3.77 (dd, $J = 11.7$, 17.4 Hz, 1H), 3.43 (dd, $J = 17.4$, 23.1 Hz, 1H), 1.25 (t, $J = 6.6$ Hz, 6H); $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -164.77 (dd, $J = 11.7$, 23.1 Hz, 1F); MS (EI): $m/\ell$ 236 (M$^+$), 194 (32.68), 174 (29.94), 149 (100.00), 148 (26.26), 130 (32.53), 118 (28.21), 101 (59.52), 43 (71.30); HPLC: Daicel Chiralpak IC, Hexane/$i$PrOH=95/5, 0.7 mL/min, 254 nm, tR(major)= 36.7 min, tR(minor)= 45.0 min (79% ee); $[\alpha]_D^20$: -10.8 (c= 0.55, solv: CHCl$_3$, 79% ee).

Yield: 99% (65.0 mg); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.83 (d, $J = 7.8$ Hz, 1H), 7.68 (t, $J = 7.8$ Hz, 1H), 7.46 (q, $J = 7.8$ Hz, 2H), 3.73 (dd, $J = 10.5$, 17.4 Hz, 1H), 3.32 (dd, $J = 17.4$, 22.8 Hz, 1H), 2.05 (s, 9H), 1.62 (s, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 195.83 (d, $J = 17.8$ Hz), 165.72 (d, $J = 28.3$ Hz), 150.95 (d, $J = 3.8$ Hz), 136.39, 133.51 (d, $J = 1.2$ Hz), 128.37, 126.42 (d, $J = 1.8$ Hz), 125.28 (d, $J = 17.8$ Hz), 94.22 (d, $J = 200.4$ Hz), 84.04, 40.93, 38.34 (d, $J = 23.6$ Hz), 35.78, 30.76; $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -164.55 (dd, $J = 10.5$, 22.8 Hz, 1F); IR (KBr): $\nu$$_{max}$ 2913, 2854, 1760, 1728, 1608, 1588, 1466, 1457, 1323, 1287, 1216, 1195, 1103, 1073, 1050, 965, 923, 836, 755, 695, 668 cm$^{-1}$; MS (EI): $m/\ell$ 328 (M$^+$), 136 (11.39), 135 (100.00), 107 (5.93), 101 (9.04), 93 (12.38), 91 (5.28), 79 (12.94), 67 (5.48); HRMS (EI): For [C20H21O3F]$^+$ Calcl. 328.1475, Found: 328.1473; HPLC: AD-H,
Hexane/iPrOH=99/1, 0.7 mL/min, 254 nm, tR(major)= 29.6 min, tR(minor)= 39.5 min (92% ee); [α]D20: -0.7 (c= 0.90, solv: CHCl3, 92% ee).

Yield: 96% (67.7 mg); 1H NMR (300 MHz, CDCl3): δ 8.07 (d, J = 8.1 Hz, 1H), 7.54 (td, J = 1.8, 7.5 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.27 (d, J = 7.5 Hz, 1H), 3.17-3.08 (m, 1H), 2.72-2.64 (m, 1H), 2.55-2.49 (m, 1H), 1.44 (s, 9H); 19F NMR (282 MHz, CDCl3) δ -163.72 (dd, J = 11.0, 20.6 Hz, 1F); HPLC: Daicel Chiralpak AD-H, Hexane/iPrOH=99/1, 1.0 mL/min, 254 nm, tR(minor)= 10.8 min, tR(major)= 12.2 min (69% ee); [α]D20: -6.1 (c= 0.88, solv: CHCl3, 69% ee).

Yield: 88% (47.5 mg); 1H NMR (300 MHz, CDCl3): δ 2.52-2.44 (m, 3H), 2.43-2.14 (m, 1H), 2.14-2.09 (m, 2H), 1.50 (s, 9H); 19F NMR (282 MHz, CDCl3) δ -163.19 (dd, J = 16.6, 21.4 Hz, 1F); MS (EI): m/z 202 (M+), 146 (41.59), 129 (19.22), 118 (32.81), 101 (37.26), 73 (33.17), 59 (24.20), 57 (100.00), 41 (28.12); HPLC: REGIS (S, S)-Whelk-O1, Hexane/iPrOH=98/2, 0.5 mL/min, 214 nm, tR(major)= 14.9 min, tR(minor)= 17.1 min (95% ee); [α]D20: -56.7 (c= 1.01, solv: CHCl3, 95% ee).

Yield: 91% (61.3 mg); 1H NMR (300 MHz, CDCl3): δ 7.76-7.70 (m, 2H), 7.28-7.21 (m, 2H), 1.50 (s, 9H); 19F NMR (282 MHz, CDCl3) δ -127.99 (s, 1F); MS (EI): m/z 252 (M+), 152 (27.43), 151 (41.78), 123 (9.65), 95 (13.96), 57 (100.00), 76 (14.36), 75 (6.84), 41 (19.54); HPLC: Phenomenex PC-2, Hexane/iPrOH=90/10, 0.5 mL/min, 214 nm, tR(minor)= 8.9 min, tR(major)= 9.7 min (83% ee); [α]D20: -47.6 (c= 1.02,
Yield: 87% (43.9 mg); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.06-8.02 (m, 2H), 7.62-7.55 (m, 1H), 7.49-7.26 (m, 2H), 1.82 (d, $J = 22.5$ Hz, 3H), 1.38 (s, 9H); $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -151.27 (q, $J = 22.5$ Hz, 1F); MS (EI): $m/z$ 196 ([M-C$_4$H$_8$]+), 151 (13.16), 123 (9.26), 106 (9.59), 105 (100.00), 77 (36.71), 57 (36.36), 41 (11.30); HPLC: Phenomenex PA-2, Hexane/iPrOH=95/5, 0.7 mL/min, 254 nm, tR(minor)= 6.3 min, tR(major)= 7.9 min (94% ee); $[\alpha]^{D}_{20}$: +62.6 (c= 0.60, solv: CHCl$_3$, 94% ee).

Yield: 96% (51.1 mg); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.30-7.22 (m, 5H), 3.44-3.27 (m, 2H), 2.13 (d, $J = 5.2$ Hz, 3H), 1.41 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 202.52 (d, $J = 29.0$ Hz), 164.61 (d, $J = 24.9$ Hz), 133.43, 130.77 (d, $J = 1.1$ Hz), 128.30, 127.27, 99.94 (d, $J = 198.2$ Hz), 84.03, 39.34 (d, $J = 20.1$ Hz), 27.65, 26.02; $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -163.04 (qt, $J = 4.9$, 25.6 Hz, 1F); IR (KBr): $\nu_{max}$ 3066, 3034, 2981, 2934, 1751, 1497, 1456, 1424, 1396, 1371, 1357, 1286, 1251, 1198, 1156, 1086, 1068, 839, 742, 701, 527 cm$^{-1}$; MS (EI): $m/z$ 266 (M$^+$), 210 (36.01), 193 (18.27), 190 (21.09), 150 (28.89), 78 (16.41), 57 (100.00), 43 (56.14), 41 (18.91); HRMS (EI): For [C15H19O3F]$^+$ Calcd. 266.1318, Found: 266.1314; HPLC: Phenomenex PC-3, Hexane/iPrOH=90/10, 0.7 mL/min, 214 nm, tR(major)= 8.5 min, tR(minor)= 10.4 min (87% ee); $[\alpha]^{D}_{20}$: +53.5 (c= 1.01, solv: CHCl$_3$, 87% ee).

Yield: 72% (40.7 mg); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.27 (s, 5H), 3.79 (s, 3H), 3.44
(d, J = 25.8 Hz, 2H), 1.42 (s, 9H); $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -163.77 (t, J = 25.8 Hz, 1F); MS (EI): m/z 282 (M$^+$), 226 (12.44), 209 (21.82), 206 (29.65), 174 (30.92), 91 (22.08), 84 (18.82), 57 (100.00), 41 (18.19); HPLC: Phenomenex PC-2, Hexane/iPrOH=95/5, 0.5 mL/min, 214 nm, tR(major)= 10.7 min, tR(minor)= 13.6 min (51% ee).

IV. Optimization of reaction conditions for enantioselective fluoronation of oxindoles

1. Optimization of the reaction conditions for 3-phenyl oxindole

**Table S2** Fluorination of 3-phenyl oxindole 6i catalysed by iron-salan complexes 3$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Cat.</th>
<th>Additives (5 mol%)</th>
<th>Temp. (°C)</th>
<th>Time (h)</th>
<th>Yield (%)</th>
<th>ee (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DCM</td>
<td>3c</td>
<td>-</td>
<td>25</td>
<td>3</td>
<td>86</td>
<td>78</td>
</tr>
<tr>
<td>2</td>
<td>MeCN</td>
<td>3c</td>
<td>-</td>
<td>25</td>
<td>1.5</td>
<td>90</td>
<td>64</td>
</tr>
<tr>
<td>3</td>
<td>toluene</td>
<td>3c</td>
<td>-</td>
<td>25</td>
<td>3</td>
<td>85</td>
<td>81</td>
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<tr>
<td>4</td>
<td>Et$_2$O</td>
<td>3c</td>
<td>-</td>
<td>25</td>
<td>1.5</td>
<td>91</td>
<td>80</td>
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<tr>
<td>5</td>
<td>THF</td>
<td>3c</td>
<td>-</td>
<td>25</td>
<td>3</td>
<td>92</td>
<td>70</td>
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<tr>
<td>6</td>
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<td>75</td>
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<td>8</td>
<td>Dioxane</td>
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<td>-</td>
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<td>79</td>
<td>77</td>
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<tr>
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<td>25</td>
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<td>92</td>
<td>80</td>
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<tr>
<td>10</td>
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<td>1.5</td>
<td>86</td>
<td>70</td>
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<tr>
<td>12</td>
<td>EA</td>
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<td>-</td>
<td>25</td>
<td>2</td>
<td>94</td>
<td>76</td>
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<tr>
<td>13</td>
<td>Et$_2$O</td>
<td>3b</td>
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<td>25</td>
<td>1.5</td>
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<td>75</td>
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<td>3a</td>
<td>-</td>
<td>25</td>
<td>4</td>
<td>63</td>
<td>79</td>
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</tbody>
</table>
2. Optimization of the reaction conditions for 3-methyl oxindole

Table S3 Fluorination of 3-methyl oxindole 6a catalysed by iron-salan complex 3c

<table>
<thead>
<tr>
<th>Entry</th>
<th>Additives</th>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>Time (h)</th>
<th>Yield (%)</th>
<th>ee (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>DCM</td>
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<td>20</td>
<td>78</td>
<td>91</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>Et₂O</td>
<td>25</td>
<td>6</td>
<td>93</td>
<td>93</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>Et₂O</td>
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<td>36</td>
<td>90</td>
<td>95</td>
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<tr>
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<td>AgClO₄</td>
<td>Et₂O</td>
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<td>0.5</td>
<td>96</td>
<td>94</td>
</tr>
<tr>
<td>5</td>
<td>AgClO₄</td>
<td>Et₂O</td>
<td>0</td>
<td>3</td>
<td>94</td>
<td>96</td>
</tr>
</tbody>
</table>

*aReaction conditions: substrate (0.2 mmol), cat. (5 mol%), NFSI (1.2 equiv.) and solvent (1.5 mL) and corresponding additive (5 mol%) were stirred under Ar atmosphere.

V. Synthesis of 3-alkyl or 3-aryl oxindoles

Synthesis of 16¹²

A solution of R¹MgBr (13.6 mmol) was added to a stirred cold (-40 °C) suspension of isatin (6.8 mmol) in THF (30 mL) under an atmosphere of argon. The mixture was allowed to warm to room temperature and was stirred until isatin was
consumed. The reaction mixture was diluted with ether, cooled in an ice-bath, and then quenched with 1N HCl. The aqueous layer was extracted with ether, and the combined organic layers were washed with water and brine and then dried over Na₂SO₄. After the removal of solvent, the crude product can be obtained without further purification.

The crude product of last step (0.132 mmol) was dissolved in DCM (1.3 mL). To this solution were added DMAP (1.6 mg, 0.0132 mmol) and (Boc)₂O (33 mg, 0.153 mmol) at room temperature, and then the mixture was stirred for 3 h. The reaction mixture was diluted with ethyl acetate, and then quenched with saturated aqueous NH₄Cl. The aqueous layer was extracted with ethyl acetate, and the combined organic layers were washed with water and brine and then dried over Na₂SO₄. After the removal of solvent, purification by flash column chromatography was carried out to give the product.

Yield: 65%; ¹H NMR (300 MHz, CDCl₃): δ 7.88 (d, J = 8.4 Hz, 1H), 7.40-7.32 (m, 2H), 7.18 (t, J = 7.2 Hz, 1H), 1.66 (s, 12H), 1.35 (s, 9H); MS (EI): m/z 363 (M⁺), 175 (54.42), 146 (35.34), 145 (15.15), 133 (89.11), 132 (31.59), 117(15.61), 57 (100.0), 41 (26.13).

Yield: 70%; ¹H NMR (300 MHz, CDCl₃): δ 7.74 (d, J = 8.1 Hz, 1H), 7.16 (d, J = 8.1 Hz, 1H), 7.13 (s, 1H), 2.35 (s, 3H), 1.65 (s, 9H), 1.63 (s, 3H), 1.35 (s, 9H); ¹³C NMR (75 MHz, CDCl₃): δ 173.28, 150.59, 148.93, 136.57, 134.37, 130.24, 128.15, 122.38, 115.09, 84.25, 83.60, 77.89, 27.97, 27.38, 24.32, 20.87; IR (KBr): νmax 2985, 2937,
1783, 1751, 1721, 1495, 1485, 1372, 1337, 1292, 1252, 1148, 1102, 1061, 1006, 832, 758, 501 cm\(^{-1}\); MS (EI): \(m/z\) 377 (M\(^+\)), 221 (56.55), 171 (11.64), 160 (50.98), 159(94.18), 131 (17.22), 130 (22.09), 57 (100.00), 41 (26.68); HRMS (EI): For [C20H27NO6]\(^+\) Calcl. 377.1838, Found: 377.1841.

![Image 16c](image16c)

Yield: 61%; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.79 (d, \(J = 9.9\) Hz, 1H), 6.89 (s, 1H), 6.88 (d, \(J = 7.5\) Hz, 1H), 3.81 (s, 3H), 1.65 (s, 12H), 1.36 (s, 9H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 173.12, 156.94, 150.55, 148.90, 132.15, 129.46, 116.33, 114.35, 107.97, 84.18, 83.66, 77.89, 55.48, 27.94, 27.35, 24.29; IR (KBr): \(\nu_{\text{max}}\) 3016, 2985, 2938, 1782, 1747, 1721, 1600, 1488, 1444, 1396, 1373, 1349, 1286, 1250, 1147, 1127, 1103, 1060, 1043, 1001, 850, 837, 792, 758, 726 cm\(^{-1}\); MS (EI): \(m/z\) 393 (M\(^+\)), 238 (7.96), 237 (61.92), 176 (43.94), 175 (100.00), 165 (7.65), 132 (10.15), 57 (72.39), 41 (19.37); HRMS (EI): For [C20H27NO7]\(^+\) Calcl. 393.1788, Found: 393.1786.

![Image 16d](image16d)

Yield: 73%; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.90-7.85 (m, 1H), 7.09-7.03 (m, 2H), 1.65 (s, 12H), 1.37 (s, 9H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 172.59, 159.83 (d, \(J = 242.9\) Hz), 150.59, 148.78, 134.91 (d, \(J = 2.3\) Hz), 129.98 (d, \(J = 7.4\) Hz), 116.81 (d, \(J = 7.4\) Hz), 116.17 (d, \(J = 22.8\) Hz), 109.37 (d, \(J = 24.5\) Hz), 84.52, 83.85, 77.44, 27.87, 27.30, 24.03; \(^{19}\)F NMR(282 MHz, CDCl\(_3\))\(\delta\) -117.48--117.55 (m, 1F); IR (KBr): \(\nu_{\text{max}}\) 2985, 2939, 1790, 1754, 1721, 1482, 1374, 1346, 1284, 1142, 1100, 1057, 1008, 889, 850, 834, 796, 778, 757 cm\(^{-1}\); MS (EI): \(m/z\) 381 (M\(^+\)), 225 (51.04), 181 (9.50), 164 (30.91), 163 (50.54), 135 (18.19), 57 (100.00), 43 (8.06), 41 (18.28); HRMS (EI): For [C19H24NO6F]\(^+\) Calcl. 381.1588, Found: 381.1584.
Yield: 74%; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.87 (d, $J = 8.1$ Hz, 1H), 7.37 (t, $J = 8.1$ Hz, 1H), 7.31-7.26 (m, 1H), 7.18 (t, $J = 7.5$ Hz, 1H), 2.05 (t, $J = 3.3$ Hz, 2H), 1.65 (s, 9H), 1.34 (s, 9H), 0.82 (t, $J = 7.5$ Hz, 3H); MS (EI): $m/z$ 377 (M$^+$), 221 (33.70), 175 (21.55), 159 (37.01), 146 (17.44), 133 (35.74), 57 (100.00), 43 (29.85), 41 (26.38).

Yield: 68%; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.87 (d, $J = 8.1$ Hz, 1H), 7.36 (td, $J = 1.5$, 8.1 Hz, 1H), 7.31-7.26 (m, 1H), 7.18 (t, $J = 7.5$ Hz, 1H), 2.00-1.94 (m, 2H), 1.65 (s, 9H), 1.34 (s, 9H), 1.35-1.18 (m, 2H), 0.85 (t, $J = 7.5$ Hz, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 172.94, 150.72, 148.86, 139.64, 129.73, 127.14, 124.53, 122.29, 115.15, 84.31, 83.50, 80.58, 39.71, 28.00, 27.39, 15.52, 13.75; IR (KBr): $\nu_{\text{max}}$ 3003, 2984, 2972, 1799, 1748, 1720, 1610, 1481, 1471, 1399, 1373, 1344, 1293, 1276, 1244, 1152, 1098, 1079, 963, 916, 867, 845, 772, 677 cm$^{-1}$; MS (EI): $m/z$ 381 (M$^+$), 235 (31.99), 209 (71.34), 181 (14.90), 180 (100.00), 173 (48.35), 146 (17.16), 57 (62.17), 41 (15.19); HRMS (EI): For [C21H29NO6]$^+$ Calcd. 391.1995, Found: 391.1996.

Yield: 60%; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.87 (d, $J = 8.1$ Hz, 1H), 7.39 (t, $J = 1.5$ Hz, 1H), 7.35-7.26 (m, 1H), 7.18 (t, $J = 7.5$ Hz, 1H), 2.05-1.94 (m, 2H), 1.64 (s, 9H), 1.64-1.51 (m, 1H), 1.33 (s, 9H), 0.85 (d, $J = 6.9$ Hz, 3H), 0.73 (d, $J = 6.9$ Hz, 3H); MS (EI): $m/z$ 405 (M$^+$), 193 (29.57), 187 (53.56), 180 (29.85), 149 (22.15), 146
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Yield: 74%; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta 7.60 (d, J = 8.1 \text{ Hz, 1H}), 7.31-7.25 (m, 1H), 7.16-7.05 (m, 5H), 6.84 (d, J = 6.9 \text{ Hz, 2H}), 3.30 (q, J = 15.6 \text{ Hz, 2H}), 1.55 (s, 9H), 1.35 (s, 9H); MS (EI): \(m/z\) 439 (M\(^+\)), 222 (16.96), 221 (50.44), 148 (41.35), 91 (28.35), 85 (43.47), 83 (66.78), 57 (100.00), 41 (21.71).

Yield: 82%; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta 7.97 (d, J = 8.4 \text{ Hz, 1H}), 7.43 (t, J = 6.9 \text{ Hz, 1H}), 7.33-7.24 (m, 8H), 1.58 (s, 9H), 1.38 (s, 9H); MS (EI): \(m/z\) 425 (M\(^+\)), 225 (13.13), 209 (22.54), 208 (27.92), 207 (72.53), 180 (22.50), 179 (20.92), 57 (100.0), 41 (21.65).

Yield: 77%; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta 7.98 (d, J = 8.1 \text{ Hz, 1H}), 7.45 (td, J = 1.5, 8.1 \text{ Hz, 1H}), 7.32-7.19 (m, 4H), 7.12 (d, J = 8.1 \text{ Hz, 2H}), 2.31 (s, 3H), 1.60 (s, 9H), 1.38 (s, 9H); MS (EI): \(m/z\) 439 (M\(^+\)), 225 (19.57), 222 (16.86), 221 (44.66), 180 (20.67), 173 (16.37), 146 (14.24), 57 (100.00), 41 (22.83).
Yield: 73%; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.98 (d, $J = 8.4$ Hz, 1H), 7.47 (td, $J = 1.8$, 7.2 Hz, 1H), 7.34-7.25 (m, 4H), 7.00 (t, $J = 8.4$ Hz, 2H), 1.61 (s, 9H), 1.38 (s, 9H); $^{19}$F NMR(282 MHz, CDCl$_3$): $\delta$ -112.68- -112.77 (m, 1F); MS (EI): $m/z$ 443 (M$^+$), 287 (15.59), 243 (10.02), 226 (32.05), 225 (79.98), 197 (15.11), 123 (9.75), 57 (100.00), 41 (17.20).

Synthesis of 6$^{12}$

The product of last step (16, 0.116 mmol) was dissolved in methanol (2 mL). Pd/C (20 mg) was added to this solution, and the resulting mixture was stirred under hydrogen atmosphere (balloon) for 3 h at room temperature. The reaction mixture was passed through celite to remove Pd/C, and the residue was washed with ether. After the removal of solvent, the crude product was purified by flash column chromatography to give the product.

Yield: 84%; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.81 (d, $J = 8.1$ Hz, 1H), 7.33-7.14 (m, 3H), 3.56 (q, $J = 7.8$ Hz, 1H), 1.65 (s, 9H), 1.53 (d, $J = 7.8$ Hz, 3H); MS (EI): $m/z$ 247 (M$^+$), 148 (10.41), 147 (100.00), 146 (16.67), 128 (13.78), 119 (42.87), 118 (14.12), 57 (67.29), 41 (16.26).
Yield: 79%; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.68 (d, $J = 8.4$ Hz, 1H), 7.09 (d, $J = 8.4$ Hz, 1H), 7.05 (s, 1H), 3.52 (q, $J = 7.5$ Hz, 1H), 2.35 (s, 3H), 1.64 (s, 9H), 1.50 (d, $J = 7.5$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 176.90, 149.21, 137.13, 133.79, 129.19, 128.35, 123.94, 114.59, 83.85, 40.94, 27.95, 20.87, 15.84; IR (KBr): $\nu_{\text{max}}$ 2980, 2934, 1793, 1771, 1728, 1489, 1456, 1370, 1341, 1304, 1285, 1252, 1158, 1116, 1043, 1029, 845, 818, 773, 447 cm$^{-1}$; MS (EI): $m/z$ 261 (M$^+$), 162 (11.50), 161 (100.00), 160 (13.84), 146 (16.65), 133 (38.68), 132 (16.78), 57 (57.53), 41 (17.28); HRMS (EI): For [C15H19NO3]$^+$ Calcl. 261.1365, Found: 261.1369.

Yield: 83%; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.73 (d, $J = 9.6$ Hz, 1H), 6.83-6.80 (m, 2H), 3.81 (s, 3H), 3.54 (q, $J = 7.5$ Hz, 1H), 1.64 (s, 9H), 1.51 (d, $J = 7.5$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 176.65, 156.63, 149.15, 132.81, 130.52, 115.63, 112.37, 109.68, 83.73, 55.37, 41.15, 27.90, 15.78; IR (KBr): $\nu_{\text{max}}$ 2980, 2936, 2837, 1770, 1725, 1599, 1490, 1394, 1370, 1341, 1303, 1283, 1253, 1153, 1116, 1037, 994, 950, 845, 811, 773, 720, 670 cm$^{-1}$; MS (EI): $m/z$ 277 (M$^+$), 178 (14.65), 177 (100.00), 162 (32.47), 134 (25.08), 111 (26.33), 57 (79.51), 55 (19.70), 41 (31.96); HRMS (EI): For [C15H19NO4]$^+$ Calcl. 277.1314, Found: 277.1313.

Yield: 81%; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.80 (dd, $J = 4.8$, 8.7 Hz, 1H), 7.03-6.95 (m, 2H), 3.56 (q, $J = 7.2$ Hz, 1H), 1.64 (s, 9H), 1.52 (d, $J = 7.2$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 176.50, 156.60, 149.13, 132.83, 130.52, 115.63, 112.37, 109.68, 83.72, 55.37, 41.12, 27.90, 15.78; IR (KBr): $\nu_{\text{max}}$ 2980, 2936, 2837, 1770, 1725, 1599, 1490, 1394, 1370, 1341, 1303, 1283, 1253, 1153, 1116, 1037, 994, 950, 845, 811, 773, 720, 670 cm$^{-1}$; MS (EI): $m/z$ 277 (M$^+$), 178 (14.65), 177 (100.00), 162 (32.47), 134 (25.08), 111 (26.33), 57 (79.51), 55 (19.70), 41 (31.96); HRMS (EI): For [C15H19NO4]$^+$ Calcl. 277.1314, Found: 277.1313.
MHz, CDCl$_3$): $\delta$ 176.04, 159.70 (d, $J = 241.8$ Hz), 149.07, 135.45 (d, $J = 2.3$ Hz), 131.00 (d, $J = 8.0$ Hz), 116.05 (d, $J = 7.4$ Hz), 114.28 (d, $J = 22.3$ Hz), 110.80 (d, $J = 22.3$ Hz), 84.14, 41.01 (d, $J = 1.7$ Hz), 27.85, 15.58; $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -118.57, -118.64 (m, 1F); IR (KBr): $\nu_{\text{max}}$ 2984, 2936, 1770, 1732, 1611, 1487, 1367, 1348, 1304, 1277, 1253, 1149, 1105, 997, 915, 866, 840, 820, 773, 721, 598, 572 cm$^{-1}$; MS (EI): $m/z$ 265 (M$^+$), 165 (100.00), 164 (16.43), 146 (14.46), 137 (40.73), 136 (14.73), 109 (11.21), 57 (79.99), 41 (17.92); HRMS (EI): For [C14H16FNO3]$^+$ Calcd. 265.1114, Found: 265.1117.

![Image of compound 6e](image)

Yield: 78%; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.81 (d, $J = 8.1$ Hz, 1H), 7.30-7.23 (m, 2H), 7.17 (d, $J = 7.5$ Hz, 1H), 3.54 (t, $J = 5.7$ Hz, 1H), 2.09-2.02 (m, 1H), 1.65 (s, 9H), 0.91 (t, $J = 7.5$ Hz, 3H); MS (EI): $m/z$ 261 (M$^+$), 161 (84.51), 160 (14.27), 133 (83.24), 132 (28.87), 118 (12.16), 117 (14.02), 57 (100.00), 41 (25.58).

![Image of compound 6f](image)

Yield: 75%; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.81 (d, $J = 8.1$ Hz, 1H), 7.32-7.23 (m, 2H), 7.18-7.12 (m, 1H), 3.56 (t, $J = 5.7$ Hz, 1H), 2.00-1.92 (m, 2H), 1.65 (s, 9H), 1.44-1.34 (m, 2H), 0.92 (t, $J = 7.5$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 176.25, 149.25, 140.07, 128.03, 127.90, 124.15, 123.62, 114.84, 84.07, 45.80, 33.33, 28.04, 18.95, 13.94; IR (KBr): $\nu_{\text{max}}$ 2962, 2934, 2874, 1770, 1731, 1609, 1480, 1465, 1370, 1351, 1294, 1253, 1150, 1087, 845, 753 cm$^{-1}$; MS (EI): $m/z$ 275 (M$^+$), 176 (10.24), 175 (77.21), 146 (31.22), 133 (100.00), 132 (33.74), 117 (10.93), 57 (75.57), 41 (16.71); HRMS (EI): For [C16H21NO3]$^+$ Calcd. 275.1521, Found: 275.1519.
Yield: 70%; \[^1\text{H} \text{NMR (300 MHz, CDCl}_3\text{): \delta 7.21 (d, J = 8.1 Hz, 1H), 7.32-7.23 (m, 2H), 7.17-7.14 (m, 1H), 3.56 (t, J = 6.9 Hz, 1H), 2.08-2.03 (m, 1H), 1.90-1.83 (m, 1H), 1.75-1.64 (m, 1H), 1.64 (s, 9H), 0.97 (t, J = 6.6 Hz, 6H).}

Yield: 73%; \[^1\text{H} \text{NMR (300 MHz, CDCl}_3\text{): \delta 7.73 (d, J = 8.1 Hz, 1H), 7.27-7.22 (m, 4H), 7.17-7.14 (m, 2H), 7.00 (t, J = 7.5 Hz, 1H), 6.73 (d, J = 7.5 Hz, 1H), 3.82 (dd, J = 4.2, 9.3 Hz, 1H), 3.51 (dd, J = 4.2, 13.8 Hz, 1H), 2.95 (dd, J = 9.3, 13.8 Hz, 1H), 1.63 (s, 9H); MS (EI): m/z 323 (M\(^+\)), 223 (22.44), 175 (41.27), 146 (29.52), 133 (76.24), 132 (31.79), 91 (49.31), 57 (100.00), 41 (31.51).}

Yield: 84%; \[^1\text{H} \text{NMR (300 MHz, CDCl}_3\text{): \delta 7.93 (d, J = 8.1 Hz, 1H), 7.38-7.29 (m, 4H), 7.21-7.16 (m, 4H), 4.73 (s, 1H), 1.63 (s, 9H); MS (EI): m/z 309 (M\(^+\)), 210 (15.46), 209 (100.00), 208 (13.07), 180 (55.04), 165 (12.62), 57 (62.20), 43 (9.49), 41 (15.23).}
Yield: 81%; \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta\) 7.92 (d, \(J = 8.1\) Hz, 1H), 7.38-7.32 (m, 1H), 7.17-7.13 (m, 4H), 7.07 (d, \(J = 8.1\) Hz, 2H), 4.69 (s, 1H), 2.33 (s, 3H), 1.62 (s, 9H); MS (EI): \(m/z\) 323 (M\textsuperscript{+}), 224 (16.96), 223 (100.00), 222 (13.86), 208 (11.26), 194 (24.70), 180 (31.79), 57 (79.57), 41 (18.20).

![Image of compound 6k](image)

Yield: 80%; \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta\) 7.93 (d, \(J = 7.8\) Hz, 1H), 7.40-7.34 (m, 1H), 7.21-7.14 (m, 4H), 7.03 (t, \(J = 8.4\) Hz, 2H), 4.71 (s, 1H), 1.63 (s, 9H); \textsuperscript{19}F NMR (282 MHz, CDCl\textsubscript{3}): \(\delta\) -114.74 -114.83 (m, 1F); MS (EI): \(m/z\) 327 (M\textsuperscript{+}), 228 (14.00), 227 (92.16), 226 (17.11), 223 (15.35), 198 (48.09), 180 (16.44), 57 (100.00), 41 (21.14).

**VI. Enantioselective fluoronation of oxindoles**

The oxindole (0.2 mmol) was dissolved in the indicated solvent (2.0 mL). To this solution was added the iron complex (5 mol\%, 0.01 mmol), and successively NFSI (75 mg, 0.24 mmol) was added at the given temperature (0 °C). The reaction mixture was stirred at the same temperature. After the completion of the reaction, the reaction mixture was filtered through silica gel with DCM and the filtrate was concentrated, and the product was purified by flash column chromatography. The ee of the product was determined by chiral HPLC analysis.
Yield: 94% (49.9 mg); $^1H$ NMR (300 MHz, CDCl$_3$): $\delta$ 7.90 (d, $J = 8.1$ Hz, 1H), 7.49-7.41 (m, 2H), 7.27-7.21 (m, 1H), 1.79 (d, $J = 21.6$ Hz, 3H), 1.65 (s, 9H); $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -144.40 (q, $J = 22.8$ Hz, 1F); MS (EI): m/z 265 (M$^+$), 166 (7.50), 165 (74.12), 164 (16.18), 137 (29.78), 117 (12.73), 116 (15.28), 57 (100.00), 41 (20.36); HPLC: Daicel Chiralcel OD-H, Hexane/iPrOH=99/1, 0.4 mL/min, 214 nm, $t_R$(minor)= 14.0 min, $t_R$(major)= 15.5 min (96% ee); $[\alpha]^{D}_{20}$: +2.1 (c= 0.94, solv: CHCl$_3$, 96% ee).

Yield: 89% (49.7 mg); $^1H$ NMR (300 MHz, CDCl$_3$): $\delta$ 7.78-7.75 (m, 1H), 7.27-7.26 (m, 1H), 7.24-7.21 (m, 1H), 2.37 (s, 3H), 1.77 (d, $J = 16.5$ Hz, 3H), 1.64 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 171.36 (d, $J = 21.6$ Hz), 148.77 (d, $J = 0.7$ Hz), 137.19 (d, $J = 4.9$ Hz), 134.81 (d, $J = 2.6$ Hz), 131.77 (d, $J = 2.9$ Hz), 126.01 (d, $J = 18.6$ Hz), 124.49 (d, $J = 0.7$ Hz), 115.29 (d, $J = 1.5$ Hz), 90.37 (d, $J = 182.9$ Hz), 84.69, 27.95, 21.75 (d, $J = 29.7$ Hz), 20.84; $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -144.75 (q, $J = 21.4$ Hz, 1F); IR (KBr): $\nu_{max}$ 2983, 2932, 2872, 1786, 1735, 1622, 1600, 1492, 1456, 1395, 1371, 1334, 1307, 1282, 1250, 1148, 1105, 1077, 1009, 963, 929, 889, 843, 823, 767, 564, 474 cm$^{-1}$; MS (EI): m/z 279 (M$^+$), 179 (100.00), 178 (17.77), 151 (47.91), 131 (14.53), 130 (30.28), 83 (16.27), 57(97.42), 41 (21.57); HRMS (EI): For [C15H18NO3F]$^+$ Calcd. 279.1271, Found: 279.1266; HPLC: Phenomenex PC-3, Hexane/iPrOH=80/20, 0.7 mL/min, 214 nm, $t_R$(minor)= 5.4 min, $t_R$(major)= 5.9 min (94% ee); $[\alpha]^{D}_{20}$: +0.9 (c= 0.96, solv: CHCl$_3$, 94% ee).
Yield: 82% (48.4 mg); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.81 (dd, $J = 1.2$, 9.2 Hz, 1H), 7.01 (t, $J = 2.4$ Hz, 1H), 6.95 (td, $J = 2.0$, 9.2 Hz, 1H), 3.83 (s, 3H), 1.78 (d, $J = 21.6$ Hz, 3H), 1.64 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 171.22 (dd, $J = 0.8$, 21.6 Hz), 157.11 (dd, $J = 3.1$, 244.4 Hz), 148.73 (d, $J = 0.7$ Hz), 132.67 (d, $J = 5.3$ Hz), 127.14 (d, $J = 18.3$ Hz), 116.58 (d, $J = 1.5$ Hz), 116.32 (d, $J = 2.6$ Hz), 109.64 (d, $J = 0.8$ Hz), 90.39 (d, $J = 184.1$ Hz), 84.63, 55.59, 27.90, 21.81 (d, $J = 29.6$ Hz); $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -145.48 (q, $J = 20.3$ Hz, 1F); IR (KBr): $\nu_{\text{max}}$ 3010, 2987, 2937, 1790, 1716, 1599, 1487, 1450, 1397, 1376, 1337, 1315, 1296, 1251, 1186, 1139, 1105, 1071, 1033, 966, 923, 890, 878, 836, 784, 765, 618, 588 cm$^{-1}$; MS (EI): $m/z$ 295 (M$^+$), 196 (11.70), 195 (100.00), 194 (13.12), 179 (16.59), 167 (28.16), 152 (30.27), 57 (98.42), 41 (27.40); HRMS (EI): For [C15H18NO4F]$^+$ Calcd. 295.1220, Found: 295.1224; HPLC: Phenomenex PC-3, Hexane/iPrOH=80/20, 0.7 mL/min, 214 nm, tR(minor)= 6.8 min, tR(major)= 8.4 min (88% ee); [$\alpha]^D_{20}$: +1.7 (c= 0.96, solv: CHCl$_3$, 88% ee).

Yield: 84% (47.6 mg); $^1$H NMR (300 MHz, CDCl$_3$): 7.93-7.89 (m, 1H), 7.20-7.11 (m, 2H), 1.78 (d, $J = 21.6$ Hz, 3H), 1.64 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 170.66 (dd, $J = 0.8$, 21.6 Hz), 159.92 (dd, $J = 3.1$, 244.4 Hz), 148.62, 135.45 (dd, $J = 2.7$, 4.9 Hz), 127.63 (dd, $J = 8.0$, 18.6 Hz), 117.86 (dd, $J = 2.7$, 22.7 Hz), 117.11 (dd, $J = 1.2$, 7.6 Hz), 111.46 (d, $J = 25.1$ Hz), 89.90 (dd, $J = 1.9$, 184.9 Hz), 85.06, 27.87, 21.70 (d, $J = 29.6$ Hz); $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -116.47/-116.53 (m, 1F), -146.10 (q, $J = 21.1$ Hz, 1F); IR (KBr): $\nu_{\text{max}}$ 2985, 2935, 1789, 1736, 1612, 1489, 1372, 1341, 1297, 1274, 1198, 1143, 1109, 1062, 1010, 897, 827, 772, 736, 610, 569 cm$^{-1}$; MS (EI): $m/z$ 283 (M$^+$), 183 (57.81), 182 (13.26), 155 (21.83), 134 (12.68), 135 (9.92), 107 (6.78), 57 (100.00), 41 (19.07); HRMS (EI): For [C14H15NO3F2]$^+$ Calcd. 283.1020, Found:
Yield: 94% (52.5 mg); 1H NMR (300 MHz, CDCl₃): δ 7.95 (d, J = 8.4 Hz, 1H), 7.47-7.27 (m, 2H), 7.24 (t, J = 7.8 Hz, 1H), 2.26-2.16 (m, 1H), 1.65 (s, 9H), 0.85 (t, J = 7.8 Hz, 1H); 19F NMR (282 MHz, CDCl₃) δ -149.31 (t, J = 13.5 Hz, 1F); MS (EI): m/z 279 (M⁺), 179 (55.83), 178 (13.05), 151 (34.49), 150 (13.96), 130 (25.24), 57 (100.00), 43 (38.54), 41 (19.79); HPLC: Daicel Chiralcel OD-H, Hexane/iPrOH=99/1, 0.5 mL/min, 214 nm, tR(minor)= 12.5 min, tR(major)= 16.3 min (93% ee); [α]D₂₀: +12.2 (c= 1.05, solv: CHCl₃, 93% ee).

Yield: 84% (49.3 mg); 1H NMR (300 MHz, CDCl₃): δ 7.89 (d, J = 8.7 Hz, 1H), 7.46-7.40 (m, 2H), 7.23 (t, J = 7.5 Hz, 1H), 2.18-2.08 (m, 2H), 1.65 (s, 9H), 1.35-1.09 (m, 2H), 0.90 (t, J = 7.5 Hz, 1H); 13C NMR (100 MHz, CDCl₃): δ 171.26 (d, J = 21.3 Hz), 148.69 (d, J = 0.7 Hz), 140.64 (d, J = 4.9 Hz), 131.17 (d, J = 3.0 Hz), 125.07 (d, J = 18.6 Hz), 124.86 (d, J = 2.7 Hz), 124.33 (d, J = 0.7 Hz), 115.40 (d, J = 1.1 Hz), 92.73 (d, J = 185.6 Hz), 84.81, 37.58 (d, J = 26.9 Hz), 27.94, 16.03 (d, J = 6.8 Hz), 13.86; 19F NMR (282 MHz, CDCl₃) δ -148.30 (t, J = 13.5 Hz, 1F); IR (KBr): νmax 3380, 2963, 2934, 2874, 1767, 1728, 1609, 1480, 1466, 1370, 1351, 1293, 1253, 1154, 1087, 1004, 845, 754, 734 cm⁻¹; MS (EI): m/z 293 (M⁺), 193 (52.66), 164 (18.95), 151 (73.12), 150 (15.83), 130 (10.25), 57 (100.00), 43 (29.14), 41 (20.48); HRMS (EI): For [C16H20NO3F]⁺ Calcd. 293.1427, Found: 293.1423; HPLC: Phenomenex PC-3, Hexane/iPrOH=98/2, 0.4 mL/min, 214 nm, tR(minor)= 11.8 min, tR(major)= 12.8
Yield: 87% (53.5 mg); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.90 (d, $J$ = 8.7 Hz, 1H), 7.46-7.43 (m, 2H), 7.26 (t, $J$ = 7.2 Hz, 1H), 2.16-2.10 (m, 2H), 2.22-2.03 (m, 1H), 1.64 (s, 9H), 0.84 (dd, $J$ = 6.9, 11.3 Hz, 1H); $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -143.91 (t, $J$ = 16.6 Hz, 1F); MS (EI): m/z 307 (M$^+$), 207 (34.23), 164 (12.41), 152 (9.46), 151 (90.68), 135 (9.66), 57 (100.00), 43 (17.30), 41 (23.52); HPLC: Daicel Chiralpak AD-H, Hexane/iPrOH=99.5/0.5, 0.5 mL/min, 214 nm, tR(minor)= 11.1 min, tR(major)= 11.7 min (85% ee); [$\alpha$]$^D_{20}$: +13.6 (c= 0.98, solv: CHCl$_3$, 85% ee).

Yield: 88% (60.1 mg); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.74 (d, $J$ = 8.1 Hz, 1H), 7.36 (t, $J$ = 7.8 Hz, 1H), 7.23-6.99 (m, 7H), 3.57 (dd, $J$ = 9.6, 13.2 Hz, 1H), 3.24 (dd, $J$ = 13.2, 22.2 Hz, 1H), 1.60 (s, 9H); $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -150.73 (dd, $J$ = 9.3, 22.2 Hz, 1F); MS (EI): m/z 341 (M$^+$), 245 (44.42), 244 (19.38), 241 (34.18), 216 (31.92), 91 (56.57), 57 (100.00), 43 (19.55); HPLC: Daicel Chiralcel OJ-H, Hexane/iPrOH=99/1, 0.7 mL/min, 214 nm, tR(minor)= 12.2 min, tR(major)= 15.9 min (96% ee); [$\alpha$]$^D_{20}$: +43.5 (c= 1.02, solv: CHCl$_3$, 96% ee).

Yield: 93% (60.9 mg); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.01 (d, $J$ = 8.1 Hz, 1H), 7.49 (t, $J$ = 8.1 Hz, 1H), 7.41-7.37 (m, 6H), 7.30-7.26 (m, 1H), 1.62 (s, 9H); $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -145.79 (s, 1F); MS (EI): m/z 327 (M$^+$), 228 (14.27), 227 (89.04), 226

min (91% ee); [$\alpha$]$^D_{20}$: +12.9 (c= 1.09, solv: CHCl$_3$, 91% ee).
(25.95), 199 (7.79), 198 (53.98), 197 (11.18), 57 (100.00), 41 (19.92); HPLC: Daicel
Chiralcel OD-H, Hexane/PrOH=99/1, 0.25 mL/min, 254 nm, tR(major)= 23.4 min,
tR(minor)= 26.2 min (85% ee); [α]^D_20: -73.7 (c= 0.99, solv: CHCl₃, 85% ee).

Yield: 88% (60.1 mg); ¹H NMR (300 MHz, CDCl₃): δ 8.00 (d, J = 8.1 Hz, 1H), 7.50
(t, J = 8.1 Hz, 1H), 7.37 (d, J = 6.0 Hz, 1H), 7.29-6.17 (m, 5H), 2.35 (s, 3H), 1.61 (s,
9H); ¹⁹F NMR (282 MHz, CDCl₃) δ -144.95 (s, 1F); MS (EI): m/z 341 (M⁺), 241
(86.75), 240 (25.84), 226 (21.62), 212 (26.30), 198 (22.17), 57 (100.00), 43 (23.07),
41 (21.95); HPLC: Daicel Chiralcel OD-H, Hexane/PrOH=99/1, 0.7 mL/min, 214 nm,
tR(major)= 6.8 min, tR(minor)= 8.0 min (82% ee); [α]^D_20: -73.4 (c= 0.99, solv: CHCl₃,
82% ee).

Yield: 86% (60.9 mg); ¹H NMR (300 MHz, CDCl₃): δ 8.01 (d, J = 8.1 Hz, 1H),
7.56-7.51 (m, 1H), 7.39-7.26 (m, 4H), 7.08 (t, J = 8.1 Hz, 2H), 1.62 (s, 9H); ¹⁹F NMR
(282 MHz, CDCl₃) δδ -111.92- -111.99 (m, 1F), -143.36 (s, 1F); MS (EI): m/z 345
(M⁺), 245 (47.89), 244 (19.97), 241 (18.05), 216 (32.11), 83 (8.85), 57 (100.00), 43
(30.16), 41 (19.14); HPLC: Daicel Chiralcel OD-H, Hexane/PrOH=99/1, 0.7 mL/min,
214 nm, tR(major)= 6.7 min, tR(minor)= 8.3 min (83% ee); [α]^D_20: -91.6 (c= 1.05,
solv: CHCl₃, 83% ee).
VII. Optimization of reaction conditions for enatioselective hydroxylation of \( \beta \)-keto ester

Table S4 Hydroxylation of \( \beta \)-keto ester 4a catalysed by iron-salan complexes 3

<table>
<thead>
<tr>
<th>Entry</th>
<th>Oxidant</th>
<th>Cat.</th>
<th>Additives (x mol%)</th>
<th>Solvent</th>
<th>Temp. (°C)</th>
<th>Time (h)</th>
<th>Yield (%)</th>
<th>ee (%)</th>
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<td>DCM</td>
<td>RT</td>
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<td>3c</td>
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<td>DCM</td>
<td>RT</td>
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<tr>
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<td>20</td>
<td>3c</td>
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VIII. Synthesis of oxidants

![Synthesis Diagram]

Synthesis of 22, 23, 24<sup>13</sup>

In a 250 mL, three-necked, round-bottom flask equipped with a water knockout trap and a condenser were placed benzenesulfonamide (10 mmol), benzaldehyde (10 mmol), 5 Å powdered molecular sieves (7.50 g), and Amberlyst 15 ion-exchange resin (61.5 mg) in 150 mL of toluene in argon atmosphere. The reaction mixture was heated at reflux for 24 h, diluted with DCM (100 mL), and filtered. The residue was washed with an additional DCM (100 mL) and the filtrates were combined. The solvent was removed on the rotatory evaporator to give the crude product. Crystallization from ethyl acetate gave the pure benzenesulfonamide.
Yield: 55%; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 9.07 (s, 1H), 8.02 (dd, \(J = 1.2, 8.4\) Hz, 2H), 7.94 (d, \(J = 7.2\) Hz, 2H), 7.65-7.47 (m, 6H); MS (EI): \(m/z\) 245 (M\(^+\)), 157 (32.85), 141 (24.03), 94 (16.15), 93 (35.98), 77 (100.00), 78 (7.93), 51 (32.08), 50 (13.39).

Yield: 64%; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 9.15 (s, 1H), 8.35 (d, \(J = 8.7\) Hz, 2H), 8.13 (d, \(J = 9.0\) Hz, 2H), 8.04 (dd, \(J = 1.5, 7.7\) Hz, 2H), 7.70 (t, \(J = 7.5\) Hz, 1H), 7.63-7.57 (m, 2H); MS (EI): \(m/z\) 290 (M\(^+\)), 179 (10.61), 141 (57.71), 78 (8.81), 77 (100.00), 76 (22.74), 51 (20.46), 50 (15.11).

Yield: 63%; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 9.11 (s, 1H), 8.36 (d, \(J = 9.0\) Hz, 2H), 8.12 (d, \(J = 9.0\) Hz, 2H), 7.91 (d, \(J = 8.1\) Hz, 2H), 7.39 (d, \(J = 8.1\) Hz, 2H), 2.46 (s, 3H).

Synthesis of 17, 18, 19\(^{14}\)

In a 250-mL three-necked flask, equipped with an addition funnel, were placed the appropriate sulfonimines (9.6 mmol) in toluene (94 mL) and K\(_2\)CO\(_3\) (11.1 g) in water (58 mL). The reaction was stirred vigorously and a solution of Oxone (7.0 g) in water (58 mL) was added dropwise over 15 min. When the reaction was complete, the organic layer was separated and the aqueous layer was extracted with toluene (3×70 mL). The organic layer was combined and dried over anhydrous MgSO\(_4\), and the solvent was evaporated on a rotary evaporator to afford the pure product.
Yield: 84%; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.06 (dd, $J = 1.2$, 8.1 Hz, 1H), 7.77 (t, $J = 7.2$ Hz, 1H), 7.64 (d, $J = 8.1$ Hz, 1H), 7.48-7.40 (m, 5H), 5.50 (s, 1H); MS (EI): $m/z$ 245 ([M-O]$^+$), 141 (32.54), 125 (22.95), 105 (10.76), 94 (7.64), 77 (100.00), 78 (11.09), 65 (9.65), 51 (22.89).

Yield: 87%; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.28 (d, $J = 8.7$ Hz, 2H), 8.06 (d, $J = 7.8$ Hz, 2H), 7.81 (t, $J = 7.2$ Hz, 1H), 7.71-7.63 (m, 4H), 5.61 (s, 1H); MS (EI): $m/z$ 290 ([M-O]$^+$), 150 (7.66), 141 (63.01), 94 (10.43), 78 (8.44), 77 (100.00), 76 (11.10), 51 (21.74), 50 (11.00).

Yield: 84%; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.27 (d, $J = 8.4$ Hz, 2H), 7.93 (d, $J = 8.1$ Hz, 2H), 7.64 (d, $J = 8.7$ Hz, 2H), 7.46 (d, $J = 8.4$ Hz, 2H), 5.56 (s, 1H), 2.51 (s, 3H); MS (EI): $m/z$ 304 ([M-O]$^+$), 155 (81.70), 108 (11.92), 92 (11.27), 91 (100.00), 77 (8.29), 76 (7.79), 65 (21.86), 63 (8.13).

Synthesis of 25, 26$^{15}$

To a 250 mL Schlenck flask equipped with a condenser, septum and magnetic stirring bar was placed saccharin (1.83 g, 10.0 mmol) in THF (100 mL). The flask was cooled to –78 °C in a dry ice-acetone bath, and methyl lithium or phenyl lithium (21 mmol) was carefully added by syringe. The reaction was stirred at –78 °C for an additional 4 h; H$_2$O (50 mL) was added, and the reaction mixture was warmed to room temperature. The solution was transferred to a 1 L separator funnel where ether
(100 mL) was added and the aqueous layer was separated. The organic layer was washed successively with 10% HCl (2×50 mL), 10% NaHCO₃ (2×60 mL), and H₂O (100 mL) and dried over anhydrous MgSO₄. Removal of the solvent in vacuo gave a white solid, which was crystallized from absolute ethanol to give the product.

Yield: 71%; ¹H NMR (300 MHz, CDCl₃): δ 7.93-7.90 (m, 1H), 7.78-7.69 (m, 3H), 2.68 (s, 3H); MS (EI): m/z 243 (M⁺), 179 (25.05), 141 (23.79), 105 (16.35), 94 (15.11), 77 (100.00), 76 (15.73), 51 (37.35), 50 (17.88).

Yield: 76%; ¹H NMR (300 MHz, CDCl₃): δ 8.04-8.01 (m, 1H), 7.99-7.96 (m, 2H), 7.80-7.75 (m, 2H), 7.73-7.68 (m, 1H), 7.61 (t, J = 8.1 Hz, 2H); MS (EI): m/z 181 (M⁺), 141 (22.40), 133 (18.61), 77 (100.00), 76 (48.31), 75 (16.85), 51 (30.68), 50 (32.93).

Synthesis of 20, 21¹⁶

In a 100 mL three-necked flask, equipped with an addition funnel, were placed the appropriate 1,2-benzisothiazole-1,1-dioxide (2.0 mmol) in DCM (30 mL) and 30 mL of saturated solution of potassium carbonate. The reaction was stirred vigorously and a solution of mCPBA (0.56 g) in DCM (20 mL) was added dropwise over 10 min. The reaction was stirred for an additional 2 h. When the reaction was complete, the organic layer was separated and the aqueous layer was extracted with DCM. The organic layer was combined, washed successively with saturated solution of sodium bisulfate, sodium bicarbonate, sodium chloride and dried over anhydrous MgSO₄, and the solvent was evaporated on a rotary evaporator to afford the crude product, which
was crystallized from absolute ethanol to give the product as white solid.

\[ \text{Yield: 72%; } ^1\text{H NMR (300 MHz, CDCl}_3\text{): } \delta 7.79-7.74 (m, 4H), 2.14 (s, 3H); MS (EI): m/z 197 (M}^+\text{), 167 (100.00), 103 (47.46), 77 (92.03), 76 (73.64), 64 (48.01), 63 (46.12), 50 (66.33), 43 (63.73).} \]

Yield: 77%; \(^1\text{H NMR (300 MHz, CDCl}_3\text{)}: \delta 7.88 (d, J = 0.6, 6.6 Hz, 1H), 7.81-7.71 (m, 2H), 7.65-7.50 (m, 6H); MS (EI): m/z 259 (M}^+\text{), 229 (40.92), 184 (69.51), 179 (59.39), 105 (55.09), 77 (100.00), 76 (46.64), 51 (43.12), 50 (34.54).}

**IX. Enatioselective hydroxylation of β-keto esters**

The β-ketoester (0.15 mmol) was dissolved in the indicated solvent (2.0 mL). To this solution was added the iron complex (5 mol%, 0.0075 mmol), and successively 3-(4-nitrophenyl)-2-(phenylsulfonyl)-1,2-oxaziridine (55.2 mg, 0.18 mmol) was added at the given temperature (-10 °C). The reaction mixture was stirred at the same temperature. After the completion of the reaction, the reaction mixture was filtered and the filtrate was concentrated, and the product was purified by flash column chromatography. The ee of the product was determined by chiral HPLC analysis.

Yield: 95% (35.0 mg); \(^1\text{H NMR (300 MHz, CDCl}_3\text{): } \delta 7.80 (d, J = 7.5 Hz, 1H), 7.66
(t, J = 7.5 Hz, 1H), 7.50-7.39 (m, 2H), 4.01 (s, 1H), 3.66 (d, J = 17.1 Hz, 1H), 3.23 (d, J = 17.1 Hz, 1H), 1.36 (s, 9H); MS (EI): m/z 248 (M+), 192 (78.33), 147 (75.60), 136 (25.54), 118 (35.10), 91 (34.35), 90 (28.86), 89 (30.49), 57 (100.00); HPLC: Daicel Chiralcel OJ-H, Hexane/iPrOH=90/10, 1.0 mL/min, 254 nm, tR(major)= 8.1 min, tR(minor)= 13.7 min (83% ee); [α]D: +36.9 (c= 1.03, solv: CHCl3, 83% ee).

Yield: 95% (39.7 mg); 1H NMR (300 MHz, CDCl3): δ 7.37 (d, J = 8.1 Hz, 1H), 7.27-7.21 (m, 2H), 4.03 (s, 1H), 3.85 (s, 3H), 3.57 (d, J = 16.8 Hz, 1H), 3.14 (d, J = 16.8 Hz, 1H), 1.37 (s, 9H); 13C NMR (100 MHz, CDCl3): δδ 201.32, 170.54, 159.55, 145.25, 134.92, 126.92, 125.19, 105.94, 83.82, 81.06, 55.52, 38.76, 27.60; IR (KBr): νmax 3413, 2921, 2851, 1739, 1720, 1615, 1494, 1456, 1430, 1397, 1369, 1311, 1284, 1266, 1224, 1157, 1130, 1027, 975, 829, 769, 552, 520 cm⁻¹; MS (EI): m/z 278 (M+), 222 (37.67), 204 (65.85), 177 (60.11), 166 (22.57), 160 (23.91), 121 (22.03), 57 (100.00), 41 (30.88); HRMS (EI): For [C15H18O5]+ Calcd. 278.1154, Found: 278.1151; HPLC: Daicel Chiralpak IC, Hexane/iPrOH=90/10, 1.0 mL/min, 254 nm, tR(major)= 22.1 min, tR(minor)= 28.2 min (80% ee); [α]D: +22.8 (c= 1.04, solv: CHCl3, 80% ee).

Yield: 97% (47.5 mg); 1H NMR (300 MHz, CDCl3): δ 7.79 (d, J = 6.0 Hz, 1H), 7.65 (dt, J = 0.9, 5.7 Hz, 1H), 7.48 (d, J = 6.0 Hz, 1H), 7.42 (dt, J = 0.6, 5.7 Hz, 1H), 4.02 (s, 1H), 3.66 (d, J = 12.9 Hz, 1H), 3.22 (d, J = 12.9 Hz, 1H), 2.12 (s, 3H), 1.97-1.95 (m, 6H), 1.61-1.59 (m, 6H); MS (EI): m/z 326 (M+), 136 (11.70), 135 (100.00), 107 (5.74), 93 (11.05), 91 (9.06), 79 (11.42), 55 (6.52), 41 (6.17); HPLC: Daicel Chiralpak AD-H, Hexane/iPrOH=90/10, 1.0 mL/min, 254 nm, tR(major)= 16.7 min, tR(minor)=
26.4 min (87% ee); $\left[\alpha\right]_{D}^{20} +29.8$ (c= 1.07, solv: CHCl$_3$, 87% ee).

Yield: 97% (49.5 mg); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.58 (s, 1H), 7.46 (d, $J = 8.1$ Hz, 1H), 7.35 (d, $J = 8.1$ Hz, 1H), 3.99 (s, 1H), 3.61 (d, $J = 17.1$ Hz, 1H), 3.16 (d, $J = 17.1$ Hz, 1H), 2.12 (s, 3H), 1.98-1.96 (m, 6H), 1.60-1.59 (m, 6H); MS (EI): $m/z$ 340 (M$^+$), 136 (11.76), 135 (100.00), 93 (10.79), 79 (12.30), 77 (8.25), 43 (5.85), 40 (34.92); HPLC: Daicel Chiralpak AD-H, Hexane/iPrOH=85/15, 1.0 mL/min, 254 nm, tR(major)= 11.1 min, tR(minor)= 19.7 min (84% ee); $\left[\alpha\right]_{D}^{20} +17.7$ (c= 1.06, solv: CHCl$_3$, 84% ee).

Yield: 92% (49.8 mg); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.72 (d, $J = 8.4$ Hz, 1H), 7.48 (s, 1H), 7.40 (d, $J = 8.1$ Hz, 1H), 4.08 (s, 1H), 3.63 (d, $J = 17.4$ Hz, 1H), 3.20 (d, $J = 17.4$ Hz, 1H), 2.13 (s, 3H), 1.98-1.96 (m, 6H), 1.60-1.59 (m, 6H); MS (ESI): $m/z$ 383.0 ([M+Na$^+$]), 743.0 ([2M+Na$^+$]); HPLC: Daicel Chiralpak AD-H, Hexane/iPrOH=70/30, 0.7 mL/min, 214 nm, tR(major)= 13.9 min, tR(minor)= 23.1 min (63% ee); $\left[\alpha\right]_{D}^{20} +44.5$ (c= 1.02, solv: CHCl$_3$, 63% ee).

Yield: 89% (31.3 mg); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.80 (d, $J = 7.5$ Hz, 1H), 7.67 (t, $J = 7.5$ Hz, 1H), 7.51-7.41, (m, 2H), 5.14-5.01 (m, 1H), 4.03 (s, 1H), 3.70 (d, $J = 17.1$ Hz, 1H), 3.24 (d, $J = 17.1$ Hz, 1H), 1.17 (dd, $J = 6.3$, 20.7 Hz, 6H); MS (EI): $m/z$ 234 (M$^+$), 192 (87.67), 147 (100.00), 136 (37.37), 118 (83.81), 91 (48.34), 90 (39.43), 89 (34.60), 43 (48.80); HPLC: Daicel Chiralpak AD-H, Hexane/iPrOH=90/10, 0.7
mL/min, 254 nm, tR(major)= 26.5 min, tR(minor)= 29.7 min (69% ee); \([\alpha]_{D}^{20}: +38.6 (c= 0.84, \text{solv: CHCl}_3, 69% \text{ ee}).

Yield: 95% (39.7 mg); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 3.70 (s, 1H), 2.47-2.40 (m, 3H), 2.18-2.05 (m, 12H), 1.65-1.67 (m, 6H); MS (EI): \(m/z\) 278 (M\(^+\)), 136 (11.07), 135 (100.00), 107 (6.53), 93 (13.13), 91 (4.95), 79 (12.77), 77 (5.31), 67 (4.99); HPLC: Phenomenex PC-4, Hexane/PrOH=95/5, 0.7 mL/min, 214 nm, tR(major)= 28.9 min, tR(minor)= 34.0 min (89% ee); \([\alpha]_{D}^{20}: -7.4 (c= 0.97, \text{solv: CHCl}_3, 89% \text{ ee}).

Yield: 88% (26.4 mg); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 3.68 (s, 1H), 2.45-2.40 (m, 3H), 2.10-2.06 (m, 3H), 1.48 (s, 9H); MS (EI): \(m/z\) 200 (M\(^+\)), 144 (32.30), 99 (17.68), 88 (31.20), 59 (33.94), 57 (100.00), 43 (11.75), 42 (11.92), 41 (25.57); HPLC: Daicel Chiralpak IC, Hexane/PrOH=80/20, 0.7 mL/min, 214 nm, tR(major)= 12.7 min, tR(minor)= 14.0 min (84% ee); \([\alpha]_{D}^{20}: -7.2 (c= 0.96, \text{solv: CHCl}_3, 84% \text{ ee}).

Yield: 92% (36.2 mg); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.04 (d, \(J = 7.5\) Hz, 1H), 7.52 (t, \(J = 6.9\) Hz, 1H), 7.34 (t, \(J = 7.5\) Hz, 1H), 7.28-7.25 (m, 1H), 4.24 (s, 1H), 3.14-3.12 (m, 2H), 2.68-2.61 (m, 1H), 2.28-2.20 (m, 1H), 1.39 (s, 9H); MS (ESI): \(m/z\) 285.0 ([M+Na]\(^+\)), 547.1 ([2M+Na]\(^+\)); HPLC: Daicel Chiralpak AD-H, Hexane/PrOH=90/10, 0.7 mL/min, 254 nm, tR(major)= 20.8 min, tR(minor)= 23.5 min (46% ee); \([\alpha]_{D}^{20}: -2.9 (c= 0.85, \text{solv: CHCl}_3, 46% \text{ ee}).
X. Mass spectrometry analysis

Positive-ion electrospray ionization (ESI) mass spectrum was obtained on a Waters Micromass Q-Tof Premier quadrupole time-of-flight tandem mass spectrometer. A mixture of the Fe(III) complex ($5 \times 10^{-4}$ M) and the substrate (10 equiv.) in acetonitrile was reacted at room temperature for 5 min. After dilution in acetonitrile to $1 \times 10^{-5}$ M, the reaction mixture was introduced into the ESI source by using a syringe pump (flow rate: 5 μL min$^{-1}$). The mass resolution was fixed at about 8000 (full width at half-height).
References

Fig. S1 Upper: Simulated isotopic distribution pattern for the adduct formed between the deprotonated form of substrate 4e with catalyst 3c (with ClO$_4^-$ as counter anion). Lower: Observed isotopic distribution pattern for the peak at m/z 941.4 detected by high-resolution ESI-MS analysis of a reaction mixture of 4e and 3c in acetonitrile.
HPLC of 5a

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**Chromatogram**

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S54
HPLC of 5b

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色谱分析报告

样品名称：
样品批号：
分析日期：2011-09-21

样品文件名：Gx-6-74---PC-29550.7214.che
分析者：
分析时间：12:27

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<th>保留时间</th>
<th>峰面积</th>
<th>峰面积百分比（%）</th>
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<td>143565.1</td>
<td>2699796.1</td>
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色谱分析报告

样品名称：
样品编号：
分析日期：2011-09-22

样品名称：gx-6-90, che
分析者：
分析日期：09:27

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</table>

S57
HPLC of 5d

Data File C: \ HPCHMEM \ DATA \ SIG16598.D

IC, 95/5, 0.7 ml/min 254 nm

Injection Date : 9/28/11 8:46:47 PM
Sample Name : gx-6-86
Acq. Operator : gx
Method : C:\HPCHMEM\METHODS\EXAMINE.M
Last changed : 9/28/11 8:23:16 PM by gx
(modified after loading)

Area Percent Report

Sorted By : Signal
Multiplier : 1.00000
Dilution : 1.00000

Signal 1: WWD1 A, Wavelength=254 nm

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret Time</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU * s]</th>
<th>Height [mAU]</th>
<th>Area [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>PB</td>
<td>0.34225</td>
<td>4624.59326</td>
<td>208.11803</td>
<td>50.1494</td>
</tr>
<tr>
<td>2</td>
<td>22.594</td>
<td>BB</td>
<td>0.41680</td>
<td>4597.03125</td>
<td>171.09820</td>
<td>49.8506</td>
</tr>
</tbody>
</table>

Totals : 9221.62451 379.21631

Results obtained with enhanced integrator!

*** End of Report ***

Instrument 1 9/28/11 9:22:06 PM gx
Data File: C:\HPChem\DATA\SIG16599.D

IC, 95/5, 0.7 ml/min 254 nm

Injection Date: 9/28/11 9:29:59 PM  
Sample Name: gx-6-96  
Acq. Operator: gx  
Method: C:\HPChem\METHODS\EXAMINE.M  
Last changed: 9/28/11 9:29:52 PM by gx
(modified after loading)

VWD1 A, Wavelength=254 nm (SIG16599.D)

Area Percent Report

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000

Signal 1: VWD1 A, Wavelength=254 nm

<table>
<thead>
<tr>
<th>Peak RetTime</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU *s]</th>
<th>Height [mAU]</th>
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<td>BB</td>
<td>0.4220</td>
<td>1176.69836</td>
<td>42.89130</td>
<td>3.0088</td>
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</table>

Totals: 3.91080e4 1478.02068

Results obtained with enhanced integrator!

*** End of Report ***

Instrument 1 9/28/11 10:08:05 PM gx

Page 1 of 1
HPLC of Se

Integration Results

<table>
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<tr>
<th>No</th>
<th>Peak Name</th>
<th>Retention Time [min]</th>
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<th>Height [mAUL]</th>
<th>Relative Area [%]</th>
<th>Relative Height [%]</th>
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</table>

S60
HPLC of 5f
HPLC of 5g

Data File C:\HPCHM\DATA\SIG16594.D

Sample Name: gx-6-93
Location: Vial 1

Injection Date: 9/27/11 8:22:33 PM
Sample Name: gx-6-93
Method: C:\HPCHM\METHODS\IXAMINE.M
Last changed: 9/27/11 8:55:02 PM by gx
(modified after loading)

Area Percent Report

Signal 1: VWD1 A, Wavelength=254 nm

Signal 1: VWD1 A, Wavelength=254 nm

Sorted By: Signal
Multiplier: 1.00000
Dilution: 1.00000

Peak RetTime Type Width Area Height Area
# [min] [min] mAU *s [mAU] %
---|-----|--|---------|--------|---|-----|
1 11.686 VB 0.3008 2666.55103 129.83043 50.0119
2 13.013 BB 0.3377 2665.28418 116.75018 49.9881

Totals: 5331.83521 246.58061

Results obtained with enhanced integrator!

*** End of Report ***

Instrument 1 9/27/11 8:55:07 PM gx
Data File C:\HPCHEM\DATA\SIG16597.D

AD-H, 85/15, 0.7 ml/min 254 nm

Injection Date : 9/28/11 7:54:10 PM
Sample Name : gx-6-98
Acq. Operator : gx
Method : C:\HPCHEM\METHODS\ZIAMEX.M
Last changed : 9/28/11 8:10:54 PM by gx
(modified after loading)

VWD1 A, Wavelength=254 nm (8016597.D)

--- Area Percent Report ---

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type Width Area Height Area %
--------- ------- ------- ------ -------- -------
1 10.830 VB 0.2704 110.68613 6.08534 2.1845
2 11.926 FN 0.3051 4956.20850 238.42421 97.8155

Totals : 5066.89463 244.50955

Results obtained with enhanced integrator!

*** End of Report ***

Instrument 1 9/28/11 8:10:58 PM gx
### HPLC of 5h

**Data File** C:\HPCHEM1\DATA\SIG16619.D

- **IC**: 85/15, 0.7 mL/min 254 nm

---

**Injection Date**: 10/20/11 8:44:55 AM  
**Sample Name**: gx-7-14  
**Location**: Vial 1  
**Acq. Operator**: gx  
**Method**: C:\HPCHEM1\METHODS\EXAMINE.M  
**Last changed**: 10/20/11 9:28:07 AM by gx  
(modified after loading)

---

#### Area Percent Report

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<tr>
<td>Dilution</td>
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</tr>
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</table>

**Signal 1**: WVD1 A, Wavelength=254 nm

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<th>Peak RetTime</th>
<th>Type Width</th>
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<tbody>
<tr>
<td>#</td>
<td>[min] [min] mAU *s [mAU]</td>
<td>%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>29.219</td>
<td>0.5020</td>
<td>5216.41016</td>
<td>161.52530</td>
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<td>2</td>
<td>33.679</td>
<td>0.5761</td>
<td>5202.62158</td>
<td>138.19668</td>
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</table>

**Totals**: 1.04190e4 299.72218

Results obtained with enhanced integrator!

---

*** End of Report ***

---

**Instrument 1**: 10/20/11 9:34:39 AM gx

---

S64
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type Width Area Height Area
# [min] [min] mAU *m [mAU] %
1 30.748 RV 0.5402 3.17215e4 337.85455 73.0247
2 35.773 BB 0.6159 4329.93164 108.07890 26.9753
Totals : 1.60514e4 445.93345

Results obtained with enhanced integrator!

*** End of Report ***

Instrument 1 10/20/11 10:29:41 PM gx
HPLC of Si

Data File C:\HPChem\DATA\SIG16618.D

IC, 90/10, 0.7 ml/min 254 nm

<table>
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<th>10/19/11 10:58:36 PM</th>
<th>Location</th>
<th>Vial 1</th>
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<tr>
<td>Sample Name</td>
<td>gx-7-16</td>
<td>Acq. Operator</td>
<td>gx</td>
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<tr>
<td>Acq. Method</td>
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<td>10/19/11 10:41:13 PM by gx (modified after loading)</td>
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<tr>
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<td>Last changed</td>
<td>10/19/11 11:49:47 PM by gx (modified after loading)</td>
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</table>

VWD1 A, Wavelength=254 nm (SIG16618.D)

Area Percent Report

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000

Signal 1: VWD1 A, Wavelength=254 nm

<table>
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<tr>
<th>Peak RetTime Type</th>
<th>Width [min]</th>
<th>Area [mAU]</th>
<th>Height [mAU]</th>
<th>Area [%]</th>
</tr>
</thead>
<tbody>
<tr>
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<td>34.491</td>
<td>5984.5393</td>
<td>626299</td>
<td>199.8973</td>
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<td>40.416</td>
<td>6942.5389</td>
<td>99316</td>
<td>120.7057</td>
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Totals: 1.0783e+4 260.56357

Results obtained with enhanced integrator!

*** End of Report ***

Instrument 1 10/19/11 11:50:00 PM gx
Data File C:\HPCHEM1\DATA\SIG16622.D

IC, 90/10, 0.7 ml/min 254 nm

Injection Date : 10/20/11 8:23:30 PM
Sample Name : gx-7-19
Acq. Operator : gx
Method : C:\HPCHEM1\METHODS\EXAMINE.M
Last changed : 10/20/11 9:07:26 PM by gx
(modified after loading)

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: VWD1 A, Wavelength=254 nm

<table>
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<tr>
<th>Peak RetTime Type</th>
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<tbody>
<tr>
<td>#</td>
<td>[min]</td>
<td>[min]</td>
<td>[mAU]</td>
<td>[mAU]</td>
</tr>
<tr>
<td>1</td>
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<tr>
<td>2</td>
<td>42.034</td>
<td>VB</td>
<td>0.7355</td>
<td>4202.13184</td>
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Totals : 2.03259e4 486.7086

Results obtained with enhanced integrator!

*** End of Report ***
HPLC of 5j

Data File C:\HPCHEM\DATA\SIG16617.D

IC, 95/5, 0.7 ml/min 254 nm

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: Wavelength=254 nm

<table>
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<tr>
<th>Peak RetTime</th>
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<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
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</thead>
<tbody>
<tr>
<td>1 35.273</td>
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<td>0.7405</td>
<td>1.0130e4</td>
<td>211.04936</td>
<td>50.0447</td>
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Totals : 2.0242e4 467.06557

Results obtained with enhanced integrator!

*** End of Report ***
Data File C:\HPCHEM\DATA\SIG16625.D

IC, 95/5, 0.7 ml/min 254 nm

Injection Date: 10/22/11 11:12:49 AM
Sample Name: gx-7-23
Location: Vial 1
Acq. Operator: gx
Method: C:\HPCHEM\METHODS\L5AMINE.M
Last changed: 10/22/11 12:01:15 PM by gx
(modified after loading)

VWD1 A, Wavelength=254 nm (SIG16625.D)

Area Percent Report

Signal 1: VWD1 A, Wavelength=254 nm

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000

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<th>Peak RetTime Type</th>
<th>Width [min]</th>
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<th>Area mAU s</th>
<th>[mAU]</th>
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<tbody>
<tr>
<td>1 36.759 VB</td>
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<td>3.322495e4</td>
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<td>2 45.024 BB</td>
<td>0.7855</td>
<td>3791.12085</td>
<td>75.10535</td>
<td>10.5190</td>
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Totals: 3.60406e4 816.34803

Results obtained with enhanced integrator!

*** End of Report ***

Instrument 1 10/22/11 12:01:21 PM gx
HPLC of 5k

Data File C:\RPCHEM\DATA\SIG16611.D

AD-N, 99/1, 0.7 mL/min 254 nm

Injection Date : 10/19/11 3:33:31 PM
Sample Name : gx-7-17
Acq. Operator : gx
Method : C:\RPCHEM\METHODS\EXAMINE.M
Last changed : 10/19/11 4:19:14 PM by gx
(modified after loading)

Area Percent Report

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<th>Signal</th>
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</thead>
<tbody>
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<td>Multiplier: 1.0000</td>
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</tr>
<tr>
<td>Dilution : 1.0000</td>
<td></td>
</tr>
</tbody>
</table>

Signal 1: WVD1 A, Wavelength=254 nm

<p>| Peak RetTime Type Width Area Height Area |
|---------|-----|---|-----|-----|</p>
<table>
<thead>
<tr>
<th># [min]</th>
<th>[min]</th>
<th>mAU</th>
<th>s [mAU]</th>
<th>[mAU]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 31.181 BB 0.7693 1.03615e4</td>
<td>204.31961 50.0937</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>2 40.980 BB 1.0381 1.03227e4</td>
<td>149.03740 49.9063</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Totals : 2.06841e4 353.35701

Results obtained with enhanced integrator!

*** End of Report ***
Data File C:\HPChem\DATA\SIG16624.D

AD-M, 99/1, 0.7 ml/min 254 nm

Injection Date: 10/21/11 9:06:12 PM
Sample Name: gx-7-22
Acq. Operator: gx
Method: C:\HPChem\METHODS\EXAMINE.M
Last changed: 10/21/11 9:46:48 PM by gx
(modified after loading)

Area Percent Report

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000

Signal: WVD1 A, Wavelength=254 nm

Peak RetTime Type Width Area Height Area %
--- --- --- --- --- --- --- --- --- --- --- --- ---
1 29.637 BB 0.7773 4.40646e4 845.02240 96.0269
2 39.455 BB 0.9223 1826.05176 27.58408 3.9791

Totals: 4.58906e4 872.60648

Results obtained with enhanced integrator!

*** End of Report ***

Instrument 1 10/21/11 9:56:17 PM gx
HPLC of SI

Data File C:\HPChem1\DATA\SIG16584.D

AD-N, 99/1, 1 ml/min 254 nm

Injection Date : 9/22/11 1:29:21 PM  Location : Vial 1
Sample Name : gx-9-98
Acq. Operator : gx
Method : C:\HPChem1\METHODS\EXAMINE.M
Last changed : 9/22/11 1:54:24 PM by gx
(modified after loading)

Area Percent Report

<table>
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<th>Peak RetTime</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU *s]</th>
<th>Height [mAU]</th>
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</tr>
</thead>
<tbody>
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<td>51.1074</td>
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<tr>
<td>12.882</td>
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<td>0.371</td>
<td>1.33688</td>
<td>544.34467</td>
<td>49.8926</td>
</tr>
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</table>

Totals : 2.67951e4 1162.80762

Results obtained with enhanced integrator!

*** End of Report ***

Instrument 1 9/22/11 1:54:45 PM gx
Injection Date: 9/22/11 11:54:23 PM
Sample Name: ga-6-92
Anal. Operator: gx
Method: C:\HPCHEM1\METHODS\ZKAMINE.M
Last changed: 9/23/11 12:09:29 AM by gx
(modified after loading)

---

Area Percent Report
---

Sorted By: Signal
Multiplier: 1.00000
Dilution: 1.00000

Signal 1: WVD1 A, Wavelength=254 nm

<table>
<thead>
<tr>
<th>Peak RetTime Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 10.800 s</td>
<td>0.315 s</td>
<td>2.42756e4</td>
<td>1158.21375</td>
<td>84.3408</td>
</tr>
<tr>
<td>2 12.238 s</td>
<td>0.334 s</td>
<td>4507.18848</td>
<td>198.87408</td>
<td>15.6592</td>
</tr>
</tbody>
</table>

Totals: 2.87830e4 1357.08783
Results obtained with enhanced integrator!

---

**End of Report**
---

Page 1 of 1
HPLC REPORT

Sample Name: gx-7-25-rac.che
Time: 11:53
Column:
Wave Length:

Date: 2011-10-31
Method:
Flow Rate:
Mobile Phase:

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</tr>
<tr>
<td>2</td>
<td>2</td>
<td>Unknown</td>
<td>15.645</td>
<td>26568.5</td>
<td>1149158.9</td>
<td>50.3185</td>
</tr>
</tbody>
</table>

Total | 70325.0 | 2275822.4 | 100.0000 |
HPLC REPORT

Sample Name: gx-7-65.che  Date: 2011-12-05
Time: 08:58  Method:
Column:  Flow Rate:
Wavelength:  Mobile Phase:

![Graph]

<table>
<thead>
<tr>
<th>No.</th>
<th>PeakNo</th>
<th>ID. Name</th>
<th>R. Time</th>
<th>PeakHeight</th>
<th>PeakArea</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>Unknown</td>
<td>14.873</td>
<td>33170.9</td>
<td>1150166.4</td>
<td>97.2868</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>Unknown</td>
<td>17.127</td>
<td>1360.2</td>
<td>32097.0</td>
<td>2.7132</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td>33431.1</td>
<td>1182241.4</td>
<td>100.0000</td>
</tr>
</tbody>
</table>

S75
HPLC Report

Sample Name:  
Operator:  
Time: 09:17

Data File: GX-7-94(RAC)PC-2910.5214.cho  
Date: 2012-06-08

<table>
<thead>
<tr>
<th>No.</th>
<th>PeakNo</th>
<th>ID Name</th>
<th>R Time</th>
<th>PeakHeight</th>
<th>PeakArea</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>8.945</td>
<td>51817.6</td>
<td>735415.1</td>
<td>9.0291</td>
<td>49.4709</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>9.723</td>
<td>459403.8</td>
<td>7392542.7</td>
<td>50.4709</td>
<td>50.4709</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>977521.4</td>
<td>14564157.8</td>
<td>100.0000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

HPLC of 5n
HPLC Report

Sample Name:  Data File: GX-9-69.cho
Operator:  Date: 2012-06-08
Time: 09:50

![HPLC Graph]

<table>
<thead>
<tr>
<th>No.</th>
<th>Peak No.</th>
<th>ID Name</th>
<th>R.Time</th>
<th>Peak Height</th>
<th>Peak Area</th>
<th>Per Cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td></td>
<td>8.927</td>
<td>71419.4</td>
<td>1108978.1</td>
<td>8.6569</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td></td>
<td>9.727</td>
<td>59064.1</td>
<td>11643856.4</td>
<td>91.3041</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>665083.5</td>
<td>12752834.5</td>
<td>100.0000</td>
<td></td>
</tr>
</tbody>
</table>

S77
HPLC of 5o

HPLC Report

Sample Name:  
Operator:  
Time: 10:58

Data File: GX-10-60--.che  
Date: 2012-09-27

<table>
<thead>
<tr>
<th>No.</th>
<th>PeakNo</th>
<th>ID Name</th>
<th>R. Time</th>
<th>PeakHeight</th>
<th>PeakArea</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>6.388</td>
<td>61974.5</td>
<td>512200.4</td>
<td>53.3600</td>
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</tr>
<tr>
<td>2</td>
<td>2</td>
<td>7.856</td>
<td>49441.9</td>
<td>438115.8</td>
<td>45.5420</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>11.377</td>
<td>344.2</td>
<td>5613.7</td>
<td>0.5223</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>13.377</td>
<td>278.9</td>
<td>4865.9</td>
<td>0.4757</td>
<td></td>
</tr>
</tbody>
</table>

Total 108539.6  969896.8  100.0000
# HPLC Report

**Sample Name:**

**Operator:**

**Time:** 10:06

**Data File:** GX-10-75.che

**Date:** 2012-09-27

<table>
<thead>
<tr>
<th>No.</th>
<th>PeakNo</th>
<th>ID Name</th>
<th>R. Time</th>
<th>Peak Weight</th>
<th>Peak Area</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td></td>
<td>6.293</td>
<td>32416.7</td>
<td>235865.1</td>
<td>3.1594</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td></td>
<td>7.927</td>
<td>732298.1</td>
<td>7301244.0</td>
<td>96.8706</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td>764874.8</td>
<td>7537110.1</td>
<td>100.0000</td>
<td></td>
</tr>
</tbody>
</table>

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S79
# HPLC Report

Sample Name:  
Operator:  
Time: 08:47  
Data File: Gr-10-84+PC-3910.7214.che  
Date: 2012-10-19

## Chromatogram

![Chromatogram Image]

## Table: HPLC Analysis

<table>
<thead>
<tr>
<th>No.</th>
<th>PeakNo</th>
<th>ID Name</th>
<th>R.Time</th>
<th>PeakHeight</th>
<th>PeakArea</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td></td>
<td>8.400</td>
<td>1696693.4</td>
<td>2348697.1</td>
<td>46.8652</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td></td>
<td>10.232</td>
<td>1520680.8</td>
<td>23558761.0</td>
<td>51.1348</td>
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<td></td>
<td></td>
<td>3217874.1</td>
<td>46045758.1</td>
<td>100.0000</td>
<td></td>
</tr>
</tbody>
</table>

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S80
HPLC Report

Sample Name:  
Operator:  
Time: 09:09  
Data File: GX-10-93.che  
Date: 2012-10-19

<table>
<thead>
<tr>
<th>No.</th>
<th>PeakNo</th>
<th>ID. Name</th>
<th>R. Time</th>
<th>PeakHeight</th>
<th>PeakArea</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td></td>
<td>8.487</td>
<td>53174.6</td>
<td>564931.8</td>
<td>93.5189</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td></td>
<td>10.363</td>
<td>3222.5</td>
<td>39131.5</td>
<td>6.4811</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td>56397.2</td>
<td>604083.3</td>
<td>100.000</td>
</tr>
</tbody>
</table>

S81
**HPLC Report**

Sample Name:  | Data File:GX-11-33+-PC-29550.5214.che  
Operator:    | Date:2012-11-07  
Time:10:41   |  

![HPLC Graph](S82)

<table>
<thead>
<tr>
<th>No.</th>
<th>PeakNo</th>
<th>ID. Name</th>
<th>R.Time</th>
<th>PeakHeight</th>
<th>PeakArea</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td></td>
<td>10.777</td>
<td>87899.1</td>
<td>379373.6</td>
<td>42.4520</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td></td>
<td>11.557</td>
<td>21332.8</td>
<td>646131.1</td>
<td>72.557</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td></td>
<td>12.777</td>
<td>14344.6</td>
<td>361889.5</td>
<td>4.0638</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td></td>
<td>13.677</td>
<td>130039.5</td>
<td>4113158.4</td>
<td>46.1885</td>
</tr>
<tr>
<td>-----</td>
<td>--------</td>
<td>----------</td>
<td>--------</td>
<td>------------</td>
<td>----------</td>
<td>---------</td>
</tr>
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<td></td>
<td>363907.0</td>
<td>8965152.6</td>
<td>100.0000</td>
<td></td>
</tr>
</tbody>
</table>
HPLC Report

Sample Name:  
Operator:  
Time: 11:38  

Data File: G0-11-44.che  
Date: 2012-11-07

<table>
<thead>
<tr>
<th>No.</th>
<th>Peak No.</th>
<th>ID. Name</th>
<th>R. Time</th>
<th>Peak Height</th>
<th>Peak Area</th>
<th>PerCent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td></td>
<td>10.677</td>
<td>343350.0</td>
<td>7115988.4</td>
<td>53.6153</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td></td>
<td>11.427</td>
<td>36925.5</td>
<td>1039827.2</td>
<td>7.7884</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td></td>
<td>12.527</td>
<td>114871.0</td>
<td>2790354.8</td>
<td>21.0280</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td></td>
<td>13.077</td>
<td>64928.0</td>
<td>1326966.3</td>
<td>17.5582</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>559778.1</td>
<td>1326966.3</td>
<td>100.0000</td>
<td></td>
</tr>
</tbody>
</table>

S83
== Shimadzu LCsolution Analysis Report ==

Acquired by: Admin
Sample Name: gx-6-30
Method: OD-H, 0.99, 1.0, 4.214
Injection Volume: 10 µL
Data File Name: gx-6-30.lcd
Report File Name: 1.txt
Data Acquired: 2012-4-20 14:22:44
Data Processed: 2012-4-20 14:40:28

<Chromatogram>

Detector A Ch 1 214nm

Peak Table

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret Time</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.900</td>
<td>79324150</td>
<td>3041483</td>
<td>48.955</td>
</tr>
<tr>
<td>2</td>
<td>15.760</td>
<td>82625968</td>
<td>3082210</td>
<td>51.045</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>161868118</td>
<td>6123793</td>
<td>100.000</td>
</tr>
</tbody>
</table>

C:\LabSolutions\Data\Project1\guxin\gx-9-30.lcd
## HPLC Report

Sample Name:  
Operator:  
Time: 10:16  
Data File: GX-10-G-PC-3820.7214.cde  
Date: 2012-07-10

### Chromatogram

![Chromatogram Image]

### Table

<table>
<thead>
<tr>
<th>No.</th>
<th>PeakNo</th>
<th>ID. Name</th>
<th>R. Time</th>
<th>PeakHeight</th>
<th>PeakArea</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>5.442</td>
<td>166670.0</td>
<td>1141748.0</td>
<td>50.1585</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>5.895</td>
<td>157199.3</td>
<td>1134735.3</td>
<td>49.8415</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>3268369.3</td>
<td>22764965.2</td>
<td>100.0000</td>
<td></td>
</tr>
</tbody>
</table>

---

S86
### HPLC Report

**Sample Name:**

**Operator:**

**Time:** 10:31

**Data File:** GX-10-7.che

**Date:** 2012-07-10

#### Chromatogram

![Chromatogram Image]

#### Table

<table>
<thead>
<tr>
<th>No.</th>
<th>PeakNo</th>
<th>ID. Name</th>
<th>Ret. Time</th>
<th>Peak Height</th>
<th>Peak Area</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>5.427</td>
<td>56625.7</td>
<td>417313.3</td>
<td>3.026</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>5.890</td>
<td>1852568.2</td>
<td>13340465.5</td>
<td>96.974</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>1879263.9</td>
<td>13757678.8</td>
<td>100.000</td>
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</tr>
</tbody>
</table>
HPLC Report

Sample Name: HPLC of 7c
Operator: 
Time: 09:44

Data File: Gr-10-8-PC-3820.7214.che
Date: 2012-07-10

<table>
<thead>
<tr>
<th>No.</th>
<th>PeakNo</th>
<th>ID. Name</th>
<th>R.Time</th>
<th>PeakHeight</th>
<th>PeakArea</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td></td>
<td>6.795</td>
<td>1176611.7</td>
<td>10186968.1</td>
<td>50.0012</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td></td>
<td>8.365</td>
<td>82097.0</td>
<td>10185430.5</td>
<td>49.9988</td>
</tr>
</tbody>
</table>

Total 1997008.7 20371338.7 100.0000
## HPLC Report

**Sample Name:**

**Operator:**

**Time:** 10:02

**Data File:** Ox-10-9.che

**Date:** 2012-07-10

### Graph

![HPLC Graph](image)

### Table

<table>
<thead>
<tr>
<th>No.</th>
<th>PeakNo</th>
<th>ID_Name</th>
<th>R.Time</th>
<th>PeakHeight</th>
<th>PeakArea</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td></td>
<td>6.827</td>
<td>18061.3</td>
<td>184280.3</td>
<td>5.5217</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td></td>
<td>8.377</td>
<td>243361.2</td>
<td>2907641.7</td>
<td>94.0783</td>
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<td></td>
<td></td>
<td></td>
<td>261422.5</td>
<td>3111925.0</td>
<td>100.0000</td>
</tr>
</tbody>
</table>

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S89
### HPLC Report

Sample Name: [Name]
Operator: [Name]
Time: 10:38
Date: 2012-07-11

![HPLC Graph]

<table>
<thead>
<tr>
<th>No.</th>
<th>PeakNo</th>
<th>ID. Name</th>
<th>R. Time</th>
<th>PeakHeight</th>
<th>PeakArea</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>6.077</td>
<td>831682.6</td>
<td>778951.4</td>
<td>50.1265</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>7.127</td>
<td>796004.5</td>
<td>764175.8</td>
<td>49.8735</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100.0000</td>
</tr>
</tbody>
</table>

Total: 1570765.1, 1421886.9, 100.0000
# HPLC Report

**Sample Name:**

**Operator:**

**Time:** 10:53

**Data File:** GX-10-11.che

**Date:** 2012-07-11

<table>
<thead>
<tr>
<th>No.</th>
<th>Peak No</th>
<th>ID Name</th>
<th>R Time</th>
<th>Peak Height</th>
<th>Peak Area</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td></td>
<td>6.077</td>
<td>96421.8</td>
<td>342600.7</td>
<td>3.4071</td>
</tr>
<tr>
<td>2</td>
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<td>7.087</td>
<td>1048461.8</td>
<td>9713068.1</td>
<td>96.5929</td>
</tr>
</tbody>
</table>

**Total**

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>R Time</td>
<td>10.8834</td>
<td>Peak Area</td>
<td>10655668.9</td>
</tr>
<tr>
<td>Percent</td>
<td>100.0000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
HPLC of 7e

==== Shimadzu LC solution Analysis Report ====

Acquired by: Admin
Sample Name: gx-9-41
Method: C2-H, 99/1, 0.5, 214
Injection Volume: 10 μL
Data File Name: gx-9-41.lcd
Method File Name: 1.lcm
Report File Name: 1.lcr
Data Acquired: 2012-5-19 17:01:57
Data Processed: 2012-5-19 17:21:06

<Chromatogram>

Detector A Ch1 214nm

PeakTable

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret. Time</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.457</td>
<td>6971277</td>
<td>310358</td>
<td>49.909</td>
</tr>
<tr>
<td>2</td>
<td>16.350</td>
<td>6999722</td>
<td>264807</td>
<td>50.091</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>13970999</td>
<td>515165</td>
<td>100.000</td>
</tr>
</tbody>
</table>

C:\LabSolutions\Data\Project1\guxin\gx-9-41.lcd
**** Shimadzu LCsolution Analysis Report ****

Acquired by : Admin
Sample Name : gx-9-42
method : C6-H, 99/1, 0.5, 214
Injection Volume : 10 ul.
Data File Name : gx-9-42.lcd
Method File Name : 1.lcm
Report File Name : 1.fc
Data Acquired : 2012-5-19 17:25:37
Data Processed : 2012-5-19 17:43:49

<C chromatogram>

Detector A Ch1/214nm

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret. Time</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.492</td>
<td>964524</td>
<td>4130</td>
<td>3.427</td>
</tr>
<tr>
<td>2</td>
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<td>2717681</td>
<td>77427</td>
<td>95.373</td>
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<tr>
<td>Total</td>
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<td>28140605</td>
<td>816038</td>
<td>100.00</td>
</tr>
</tbody>
</table>

C:\LabSolutions\Data\Project1\guxin\gx-9-42.lcd

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HPLC of 7f

HPLC Report

Sample Name: 
Operator: 
Time: 13:51

Data File: GX-9-68 (RAC) PC-39820. 4214. che
Date: 2012-06-08

<table>
<thead>
<tr>
<th>No</th>
<th>PeakNo</th>
<th>ID Name</th>
<th>R Time</th>
<th>PeakHeight</th>
<th>PeakArea</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>11.777</td>
<td>1.052711</td>
<td>21543994.1</td>
<td>50.0997</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>13.777</td>
<td>0.97550</td>
<td>2165945.3</td>
<td>99.9003</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>1.069622</td>
<td>2599638.1</td>
<td>100.0000</td>
<td></td>
</tr>
</tbody>
</table>

S94
HPLC Report

Sample Name:  
Operator:  
Time: 14:13

Data File: Ox-9-72.che  
Date: 2012-06-06

<table>
<thead>
<tr>
<th>No</th>
<th>Peak No</th>
<th>ID Name</th>
<th>R Time</th>
<th>Peak Height</th>
<th>Peak Area</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>11.827</td>
<td>10319.2</td>
<td>198941.0</td>
<td>4.6099</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>12.827</td>
<td>178451.8</td>
<td>4019200.6</td>
<td>95.3991</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td></td>
<td>185771.0</td>
<td>4213081.7</td>
<td>100.0000</td>
<td></td>
</tr>
</tbody>
</table>

S95
HPLC of 7g

### Shimadzu LCsolution Analysis Report ###

Acquired by: Admin
Sample Name: gx-9-55
Method: AD-H, 99:5/0.5, 0.5, 214
Injection Volume: 10 ul
Data File Name: gx-9-55.lcd
Method File Name: 1.lcm
Report File Name: 1.lcr
Data Acquired: 2012-5-29 10:18:08
Data Processed: 2012-5-29 10:32:44

<Chromatogram>

```
<Peak Table>
Peaks | Ret. Time | Area  | Height | Area % |
-----|-----------|-------|--------|-------|
1    | 11.151    | 455110| 388661 | 49.888|
2    | 11.744    | 4545529| 368245 | 50.112|
Total| 5076699   | 769805| 100.000|
```

C:\LabSolutions\Data\Project1\guxin\gx-9-55.lcd
Shimadzu LCsolution Analysis Report

Acquired by: Admin
Sample Name: gx-9-57
Method: AO-H, 99.6/0.5, 0.5, 214
Injection Volume: 10 ul
Data File Name: gx-9-57.lcd
Method File Name: 1.tom
Report File Name: 1.lcr
Data Acquired: 2012-5-29 10:33:41
Data Processed: 2012-5-29 10:48:47

<Chromatogram>

Detected Area @ 214nm

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret. Time</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.154</td>
<td>297588</td>
<td>25326</td>
<td>7.753</td>
</tr>
<tr>
<td>2</td>
<td>11.745</td>
<td>354560</td>
<td>279023</td>
<td>92.247</td>
</tr>
<tr>
<td>Total</td>
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<td>3841187</td>
<td>364149</td>
<td>100.000</td>
</tr>
</tbody>
</table>

C:\LabSolutions\Data\Project1\guxin\gx-9-57.lcd
HPLC of 7h

=== Shimadzu LCsolution Analysis Report ===

Acquired by: Admin
Sample Name: gx-6-77
Method: qj-1,991.0,70.2,14
Injection Volume: 10 μL
Data File Name: gx-6-77.lcd
Method File Name: 21.lcm
Report File Name: 1.lcr
Data Acquired: 2012-6-9 10:32:32
Data Processed: 2012-6-9 10:50:51

<Chromatogram>

C:\LabSolutions\Data\Project1guxin\gx-9-77.lcd

Peak Table

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret. Time</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.301</td>
<td>5045074</td>
<td>184141</td>
<td>52.700</td>
</tr>
<tr>
<td>2</td>
<td>16.685</td>
<td>5067180</td>
<td>87069</td>
<td>47.300</td>
</tr>
<tr>
<td>Total</td>
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<td>10712853</td>
<td>271210</td>
<td>100.000</td>
</tr>
</tbody>
</table>

C:\LabSolutions\Data\Project1guxin\gx-9-77.lcd
HPLC of 7i

Data File C:\HPCHEM\1\DATA\SIG16653.D

OD=H, 99/1, 0.25 ml/min 254 nm

Injection Date : 11/4/11 9:57:40 AM
Sample Name : qx-7-35
Aqc. Operator : qx
Method : C:\HPCHEM\1\METHOD\EXAMINE.M
Last changed : 11/4/11 9:26:59 AM by qx
(modified after loading)

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: WVD1 A, Wavelength=254 nm

Peak RetTime Type Width Area Height Area
# [min] [min] mAU s [mAU] %
--- --- --- --- --- --- --- --- --- --- --- --- --- ---
1 21.874 BB 0.6782 4409.16211 96.05463 50.2630
2 24.866 BB 0.6590 4303.02197 99.42214 49.7370

Totals : 8772.18408 195.47677

Results obtained with enhanced integrator!

*** End of Report ***
HPLC of 7j

2012-7-3 12:06:16 1/1

Shimadzu LCsolution Analysis Report

Acquired by: Admin
Sample Name: gx-9-100
Method: GC-H,001, O.7, 214
Injection Volume: 10 uL
Data File Name: gx-9-100.lcd
Method File Name: 211cm
Report File Name: 1.icr
Data Acquired: 2012-7-3 11:55:15
Data Processed: 2012-7-3 12:05:21

C:\LabSolutions\Data\Project1\guixin\gx-9-100.lcd

<Chromatogram>

mV

750

500

250

0

0.0 2.5 5.0 7.5 min

Det A Ch1/214nm

Peak Table

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret. Time</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.796</td>
<td>9166436</td>
<td>517833</td>
<td>49.35</td>
</tr>
<tr>
<td>2</td>
<td>8.074</td>
<td>9346903</td>
<td>656605</td>
<td>50.65</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>18453739</td>
<td>1274440</td>
<td>100.00</td>
</tr>
</tbody>
</table>

C:\LabSolutions\Data\Project1\guixin\gx-9-100.lcd

S102
Chromatogram

Detector A Ch1 254nm

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret. Time</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.761</td>
<td>7477552</td>
<td>24319</td>
<td>91.100</td>
</tr>
<tr>
<td>2</td>
<td>7.999</td>
<td>730528</td>
<td>55838</td>
<td>8.900</td>
</tr>
<tr>
<td>Total</td>
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<td>82088081</td>
<td>489577</td>
<td>100.000</td>
</tr>
</tbody>
</table>

C:\LabSolutions\Data\Project1\gxuxin\gx-10-3.lcd
### Shimadzu LC solution Analysis Report

**Acquired by:** Admin  
**Sample Name:** gx-8-90  
**method:** OD-H, 0.9 ml, 0.7, 214  
**Injection Volume:** 10 µl  
**Data File Name:** gx-8-90.lcd  
**Method File Name:** 21.1cm  
**Report File Name:** 1.lcr  
**Data Acquired:** 2012-7-3 12:24:54  
**Data Processed:** 2012-7-3 12:34:51

### Chromatogram

![Chromatogram Image]

---

**Detector A Ch1 214 nm**

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret. Time</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.743</td>
<td>1151065</td>
<td>737712</td>
<td>47.984</td>
</tr>
<tr>
<td>2</td>
<td>8.320</td>
<td>12486963</td>
<td>961191</td>
<td>52.016</td>
</tr>
<tr>
<td>Total</td>
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<td>24006028</td>
<td>1698900</td>
<td>100.000</td>
</tr>
</tbody>
</table>

---

C:\LabSolutions\Data\Project1\gxinxs-9-90.lcd
Shimadzu LC solution Analysis Report

Acquired by: Admin
Sample Name: gx-10-4
Method: C6H5O6/1, 0.7, 214
Injection Volume: 10 µl
Data File Name: gx-10-4.lcd
Method File Name: 21 loc
Report File Name: 1.loc
Date Acquired: 2012-7-3 12:39:45
Date Processed: 2012-7-3 12:49:04

<Chromatogram>

Detector A Ch1 254nm

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret Time</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.683</td>
<td>8570596</td>
<td>491601</td>
<td>91.427</td>
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<tr>
<td>2</td>
<td>8.345</td>
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<tr>
<td>Total</td>
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<td>9377222</td>
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<td>100.000</td>
</tr>
</tbody>
</table>

C:\LabSolutions\Data\Project1\guxir\gx-10-4.lcd
HPLC of 8a

== Shimadzu LCsolution Analysis Report ==

Acquired by: Admin
Sample Name: gx-7-99
Injection Volume: 10 µL
Data File Name: gx-7-99.lcd
Method File Name: 1.lcm
Report File Name: 1.lcr
Data Acquired: 2011-12-17 23:01:45
Data Processed: 2011-12-17 23:19:15

<Chromatogram>

Det. A Ch1

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret. Time</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.229</td>
<td>173098</td>
<td>126608</td>
<td>49.801</td>
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<tr>
<td>2</td>
<td>14.815</td>
<td>176951</td>
<td>72576</td>
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<tr>
<td>Total</td>
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<td>348048</td>
<td>199084</td>
<td>100.000</td>
</tr>
</tbody>
</table>

C:/LabSolutions/Data/Project1/guxin/gx-7-99.lcd
HPLC of 8b

2012-11-29 23:09:50 1 / 1

==== Shimadzu LCsolution Analysis Report ====

Acquired by : Admin
Sample Name : D2-11-89+-
method IC, 9/1, 1.0, 254
Injection Volume : 5 µL
Data File Name : d1-11-89+-.l0d
Method File Name : D.ich
Report File Name : D.ich
Data Acquired : 2012-11-29 22:31:50
Data Processed : 2012-11-29 23:02:39

<Chromatogram>

C:\LabSolutions\Data\Project1\guxi\guxi-11-89+-.l0d

1 Det A Ch1/254nm

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret. Time</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>22.166</td>
<td>3900233</td>
<td>121155</td>
<td>89.992</td>
</tr>
<tr>
<td>2</td>
<td>28.053</td>
<td>3601489</td>
<td>97748</td>
<td>80.008</td>
</tr>
<tr>
<td>Total</td>
<td>7801772</td>
<td>221602</td>
<td>100.000</td>
<td></td>
</tr>
</tbody>
</table>

C:\LabSolutions\Data\Project1\guxi\guxi-11-89+-.l0d
Shimadzu LCsolution Analysis Report

Acquired by: Admin
Sample Name: 1QX-11-89-3
method: IC, Wf, 1, 0, 20, 25
Injection Volume: 5 uL
Data File Name: gx-11-89-3.lcd
Method File Name: 1.1cm
Report File Name: 1.lcr
Data Acquired: 2012-11-29 23:07:04
Data Processed: 2012-11-29 23:37:18

<Chromatogram>

Detector A Ch 254nm

<table>
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<tr>
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<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
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<td>19866641</td>
<td>33341</td>
<td>10.128</td>
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</table>

C:\LabSolutions\Data\Project1\guxin\gx-11-89-3.lcd
HPLC of 8c

--- Shimadzu LCsolution Analysis Report ---

Acquired by: Admin
Sample Name: gx-11-53
Method: AD-H, 80/10, 1.0, 254
Injection Volume: 5 uL
Data File Name: gx-11-53.lcd
Method File Name: 1.lcm
Report File Name: 1.lcr
Data Acquired: 2012-11-9 17:57:16
Data Processed: 2012-11-9 18:28:09

--- Chromatogram ---

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret. Time</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16.806</td>
<td>4679667</td>
<td>197313</td>
<td>48.110</td>
</tr>
<tr>
<td>2</td>
<td>26.472</td>
<td>3847213</td>
<td>125395</td>
<td>51.890</td>
</tr>
<tr>
<td>Total</td>
<td>5526860</td>
<td>332769</td>
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</tr>
</tbody>
</table>

C:\LabSolutions\Data\Project1\guxirngx-11-53.lcd
Shimadzu LCsolution Analysis Report

Acquired by: Admin
Sample Name: gx-11-52
Method: AUH-20010, 1.0, 254
Injection Volume: 5 μL
Data File Name: gx-11-52.lcd
Method File Name: 1 lcm
Report File Name: 1 lcr
Data Acquired: 2012-11-9 16:28:59
Data Processed: 2012-11-9 19:01:30

<Chromatogram>

mV

0 100 200 300

Det.A Ch1

C:\LabSolutions\Data\Project1\guxingx-11-52.lcd

1 Dot.A Ch1/254nm

Detector A Ch1 254nm

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret. Time</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16.746</td>
<td>8660030</td>
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<td>93.576</td>
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<tr>
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</tr>
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</table>

C:\LabSolutions\Data\Project1\guxingx-11-52.lcd
HPLC of 8d

### Shimadzu LCsolution Analysis Report

- **Acquired by**: Admin
- **Sample Name**: gx-11-67-2
- **Injection Volume**: 1 mL
- **Data File Name**: gx-11-67-2.lcd
- **Method File Name**: gc.lcm
- **Date Acquired**: 2012-11-20 14:38:48
- **Date Processed**: 2012-11-20 15:08:20

### Chromatogram

![Chromatogram Graph]

### Peak Table

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret. Time</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.475</td>
<td>2016846</td>
<td>139912</td>
<td>50.080</td>
</tr>
<tr>
<td>2</td>
<td>20.107</td>
<td>2030344</td>
<td>71866</td>
<td>49.920</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>4047190</td>
<td>201979</td>
<td>100.000</td>
</tr>
</tbody>
</table>

C:\LabSolutions\Data\Project1\guxin\gx-11-67-2.lcd
Shimadzu LCsolution Analysis Report

Acquired by: Admin
Sample Name: gx-11-70
Method: ad-h, 85/15, 1, 254
Injection Volume: 5 µL
Data File Name: gx-11-70.lcd
Method File Name: 1.icol
Report File Name: 1.lcr
Data Acquired: 2012-11-20 15:10:47
Data Processed: 2012-11-20 15:32:16

<Chromatogram>

![Chromatogram Image]

Detector A Ch1 254nm

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret. Time</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.129</td>
<td>5752485</td>
<td>48921</td>
<td>92.144</td>
</tr>
<tr>
<td>2</td>
<td>19.626</td>
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<td>23580</td>
<td>7.856</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>8218104</td>
<td>505562</td>
<td>100.000</td>
</tr>
</tbody>
</table>

S113
HPLD of 8e

HPLC Report

Sample Name:  
Operator:  
Time: 13:28

Data File: GX-11-61RADH730.7214.chc  
Date: 2012-11-26

<table>
<thead>
<tr>
<th>No.</th>
<th>PeakNo</th>
<th>ID Name</th>
<th>R.Time</th>
<th>PeakHeight</th>
<th>PeakArea</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>13.677</td>
<td>133772.4</td>
<td>2617061.2</td>
<td>56.0524</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>23.177</td>
<td>77693.4</td>
<td>2613020.1</td>
<td>49.9476</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>211466.7</td>
<td>5296632.1</td>
<td>100.0000</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

S114
## HPLC Report

Sample Name:  Data File: GX-11-81.che  
Operator:  Date: 2012-11-26  
Time: 14:04

<table>
<thead>
<tr>
<th>No.</th>
<th>PeakNo</th>
<th>ID. Name</th>
<th>R.Time</th>
<th>PeakHeight</th>
<th>PeakArea</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td></td>
<td>13.827</td>
<td>236988.0</td>
<td>461965.2</td>
<td>81.4694</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td></td>
<td>23.127</td>
<td>30328.7</td>
<td>1021717.7</td>
<td>18.5306</td>
</tr>
</tbody>
</table>

Total  | 269916.6 | 5513682.9 | 100.0000 |
## HPLC Report

**Sample Name:**

**Operator:**

**Time:** 08:27

**Data File:** GX-11-78RACD-H910.7254.che

**Date:** 2012-11-23

### Chromatogram

![Chromatogram](image)

### Table

<table>
<thead>
<tr>
<th>No.</th>
<th>PeakNo</th>
<th>ID Name</th>
<th>R Time</th>
<th>PeakHeight</th>
<th>PeakArea</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>37.237</td>
<td>297166.9</td>
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S116
HPLC Report

Sample Name: 
Operator: 
Time: 09:07

Data File: GX-11-78.che
Date: 2012-11-23

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<th>Percent</th>
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S117
HPLC Report

Sample Name: 8g
Operator: Data File:GX-11-66-PC-49552140.7.che
Time: 09:58 Date: 2012-11-20

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Total 119199.6 580318.0
HPLC Report

Sample Name:  
Operator:  
Time: 09:15  

Data File: GX-11-68.che  
Date: 2012-11-20

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Total 191665.4 10335128.0 100.0000
## 色谱分析报告

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<th>峰面积</th>
<th>面积百分比 (%)</th>
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色谱分析报告

样品名称：
样品批号：
分析日期：2012-12-05

样品文件名：CX-11-91-2.che
分析者：
分析时间：10:06

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合计：105881.5 2010031.2 100.0000
HPLC Report

Sample Name: 
Operator: 
Time: 09:49

Data File: GX-11-77RA-AD-H910.7254.cho
Date: 2012-11-23

![HPLC Graph]

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<th>PeakArea</th>
<th>Percent</th>
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Total   |          |          | 81955.6 | 2296576.5 | 100.0000 |
### HPLC Report

**Sample Name:**

**Operator:**

**Time:** 10:24

**Data File:** GX-11-77-2.cbe

**Date:** 2012-11-23

![HPLC Chromatogram]

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S123